PALLADIUM-CATALYZED FUNCTIONALIZATION OF C(sp)-H AND C(sp2)-H BONDS

CHOY PUI YING

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Department of Applied Biology and Chemical Technology

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CHOY Pui Ying

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degree of Doctor of Philosophy

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Declaration

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CHOY Pui Ying

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Abstract

Abstract of thesis entitled "Palladium-Catalyzed Functionalization of C(sp)-H and C(sp_2)-H Bonds"

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Functionalization of unreactive arene C-H bonds has recently received intensive attention. Mild and selective methods for the direct transformation of carbon-hydrogen bonds to carbon-oxygen/ carbon bonds are undoubtedly found widespread applications across the field of pharmaceuticals, agrochemicals, natural products and feedstock commodity chemicals. However, the C-H bond functionalization remains a critical challenge in organic chemistry. The foremost difficulty lies to achieve high levels of regioselectivity, chemoselectivity and the activation of inert nature of C-H bonds. One of the strategies to achieve the goal is transition metal-catalyzed C-H bond functionalization.

In the first half of this dissertation, we explore four studies on the palladium-catalyzed functionalization of $C_{(sp)}$-H and $C_{(sp2)}$-H bonds. Firstly, a general and simple method of palladium-catalyzed direct and selective oxidative C3-acetoxylation of 2,3-unsubstituted indoles has been developed. The first examples of selective carbon-hydrogen bond cleavage followed by carbon-oxygen bond formation sequence is achievable without any *ortho*-directing groups. This protocol requires 2 mol% Pd-loading under mild reaction conditions (70 °C and with weak base, KOAc) which tolerates a variety of functional groups. It is compatible to bromo-group which is a useful component for potential chemical transformations using coupling technology. Secondly, a palladium-catalyzed C-H bond oxygenation reaction of aromatic ketones is presented. This first example of carbon-hydrogen bond functionalization followed by carbon-oxygen bond formation sequence has been accomplished with ketone moiety as the *ortho*-directing group. This protocol provides a facile access to a wide range of *ortho*-acylphenol compounds from arylketones. Next, the first general palladium-catalyzed direct arylation of polyfluoroarenes with aryl sulfonates is described. This coupling protocol performs under relatively mild reaction conditions (90 °C with weak base, KOAc and without addition of acid additives) for successful coupling with both aryl tosylates and more challenging aryl mesylates. Last, the palladium-catalyzed Sonogashira coupling of aryl/ heteroaryl sulfonates is explored. A variety of functional groups are compatible such as nitrile, aldehyde, keto, and amide. This versatile coupling approach provides a facile access to 2-substituted isoquinoline by a one-pot cascade process.

In the second half of this dissertation, we engineer the syntheses for new family of monodentate phosphine ligands. The straightforward syntheses involve facile, high yielding conversion of Fischer Indolization into a broad scope of potentially and differentially substituted phosphine ligands. Besides, a modification of well-developed CM-phos with altering the *N*-substituted group is carried out. By expanding the size of the protecting group, both the steric and electronic properties of ligands are tuned. Furthermore, inspired by previously developed Andole-phos and Nadole-phos, a new family of ligands is designed with combined electronic (OR) and steric effect (naphthyl). The newly modified CM-phos-N*i*-Pr uncovered a facile approach for challenging tri-*ortho*-substituted biaryl synthesis with carbon-carbon bond formation. To our delights, it represents the first palladium-catalyzed Suzuki-Miyaura cross-coupling of sterically demanding aryl arenesulfonates that proceeded smoothly at low catalyst loading (0.2-1.5 mol% Pd) within 24 h to generate good to excellent product yields.

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2. Choy, P. Y.; Chow, W. K.; So, C. M.; Lau, C. P.; Kwong, F. Y. Palladium-Catalyzed Sonogashira Coupling of Aryl Mesylates and Tosylates, *Chem. Eur. J.* **2010**, *16*, 9982-9985.

3. Choy, P. Y.; Lau, C. P.; Kwong, F. Y. Palladium-Catalyzed Direct and Regioselective C-H Bond Functionalization/ Oxidative Acetoxylative of Indoles, *J. Org. Chem.* **2011**, *76,* 80-84.

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7. Choy, P. Y.; Kwong, F. Y. Palladium-Catalyzed *ortho*-CH-Bond Oxygenation of Aromatic Ketones, *Org. Lett.* **2013**, *15*, 270-273.

8. Yuen, O. Y.; Choy, P. Y.; Chow, W. K.; Wong, W. T.; Kwong, F. Y. Synthesis of 3-Cyanoindole Derivatives Mediated by Copper(I) Iodide Using Benzyl Cyanide, *J. Org. Chem.* **2013**, *78*, 3374-3378.

9. Chow, W. K.; Yuen, O. Y.; Choy, P. Y.; So, C. M.; Lau, C. P.; Wong, W. T.; Kwong, F. Y. A decade advancement of transition metal-catalyzed borylation of aryl halides and sulfonates, *RSC Advances* **2013**, *3*, 12518-12539.

10. Chan, T. L.; Wu, Y.; Choy, P. Y.; Kwong, F. Y. A Radical Process towards the Development of Transition-Metal-Free Aromatic Carbon-Carbon Bond-Forming Reactions, *Chem. Eur. J.* **2013**, *19*, 15802-15814.

11. Choy, P. Y.; So, C. M.; Lau, C. P.; Kwong, F. Y. Palladium-Catalyzed Suzuki-Miyaura Coupling for Tri-*ortho*-Substituted Biaryl compounds syntheses with Aryl Tosylates and Mesylates, *to be submitted.*

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Abbreviations

δ	Chemical shift (NMR)
η	Descriptor for hapticity
υ	Frequency
m/z	Mass-to-charge ratio
s	Singlet
d	Doublet
t	Triplet
q	Quartet
m	Multiplet
GC	Gas chromatography
HRMS	High resolution mass spectroscopy
MS	Mass spectrometry
IR	Infra-red
NMR	Nuclear magnetic resonance spectroscopy
equvi.	Equivalent
h	Hour
rt	Room temperature
L	Generalized ligand, in particular a $2e^-$ ligand
LnM	Generalized metal fragment with n ligands
THF	Tetrahydrofuran
MeOH	Methanol
EtOH	Ethanol
t-BuOH	*tert*-Butanol
t-AmOH	*tert*-Amyl alcohol
Et_2O	Diethyl ether
EtOAc	Ethyl acetate
DMF	Dimethyl formamide
DMA	Dimethylacetamide
DCE	1,2-Dichloroethane
DCM	Dichloromethane

TFA	Trifluoroacetic acid
AcOH	Acetic acid
$ClPPh_2$	Chlorodiphenylphosphine
$ClPCy_2$	Chlorodicyclohexylphosphine
$ClP\textit{i}\text{-}Pr_2$	Chlorodiisopropylphosphine
n-BuLi	*n*-Butyllithium
R	Generalized alkyl group
Me	Methyl
Et	Ethyl
n-Pr	*n*-Propyl
i-Pr	*iso*-propyl
n-Bu	*n*-Butyl
i-Bu	*iso*-Butyl
t-Bu	*tert*-Butyl
s-Bu	*sec*-Butyl
Ar	Aryl
Ph	Phenyl
Bn	Benzyl
Cy	Cyclohexyl
OTf	Trifluoromethanesulfonate
OTs	*p*-Toluenesulfonate
OMs	Methanesulfonate
PPh_3	Triphenylphosphine
PCy_3	Tricyclohexylphosphine
JohnPhos	(2-Biphenyl)di-*tert*-butylphosphine
CyJohnPhos	(2-Biphenyl)dicyclohexylphosphine
XPhos	2-Dicyclohexylphosphino-2′,4′,6′-tri*iso*propylbiphenyl
SPhos	2-Dicyclohexylphosphino-2',6'-dimethoxybiphenyl
BrettPhos	2-(Dicyclohexylphosphino)3,6-dimethoxy-2′,4′,6′-tri*iso*propyl-1,1′-biphenyl
RuPhos	2-Dicyclohexylphosphino-2′,6′-diisopropoxybiphenyl
CyPF-*t*-Bu	(R)-(–)-1-[(S)-2-(diphenylphosphino)ferrocenyl]ethyldi-*tert*-butyl phosphine
MePhos	2-Dicyclohexylphosphino-2′-methylbiphenyl

Chapter 1 Introduction

1.1 Introduction to Palladium-Catalyzed C−H Functionalization

1.1.1 Background and Challenges of C−H Functionalization

Unactivated carbon−hydrogen (C−H) bonds are the simplest chemical moieties found in Nature. They are typically inert in chemical transformations, however, they are highly desirable from the perspective of organic synthesis that such selective transformation is undoubtedly find widespread application in the synthesis of pharmaceuticals, natural products, polymers, and agrochemicals.

C−H bonds are unreactive and robust that the low reactivity is mainly attributed to the fact that they are strong, localized and unpolarized bonds.[1] The relatively higher bond strength of C-H bonds in arenes (Ar-H, 110 kcal mol^{-1}) than the C-X bonds (Ar-I, 65 kcal mol^{-1}) arises the difficulties in activation of C-H bond. The traditional approaches for the functionalization of them are mainly relied on (i) free radicals protocol of abstracting hydrogen atom to form reactive C• species for functionalization;[2] (ii) enzymatic approach to oxidize the C−H bonds;[3] (iii) transition metals mediated/ catalyzed C−H functionalization.[1,4,5] There were a number of examples of direct transformation of carbon−hydrogen (C−H) bonds into carbon−carbon (C−C) bond prior to our work.[6] However, the development of methods for direct transformation of carbon−hydrogen (C−H) bonds into carbon−heteroatom (C−O) bonds still remains a grand challenge in organic chemistry.[7] The major challenges are the inert nature of C−H bonds and the selective functionalization of a single C−H bond within a complex molecule.

Different strategies have been introduced to address these difficulties, the most commonly applied method is employing substrates with directing groups/-coordinating ligands, which bind to the metal center and direct the catalyst to the proximal C−H bond. Palladium complexes have been specifically developed to catalyze such transformation and it can be finely tailored through unique ligand design. The functionalization process can be performed under ambient air and moisture, which can be practically applied in organic synthesis. Unlike other transition metals, palladium participates in cyclometalation with many different types of directing groups, for promoting the activation of the C−H sites. Also, coordination of C−H to palladium metal center can be used to form a wide range of bonds especially carbon-carbon and carbon-oxygen linkages. Our goal was to develop a palladium-catalyzed mild, regio-, and chemoselective method to convert C-H bond to C-O bond, which is useful in petroleum and chemical industries.

1.2 Carbon-Oxygen Bond Formation

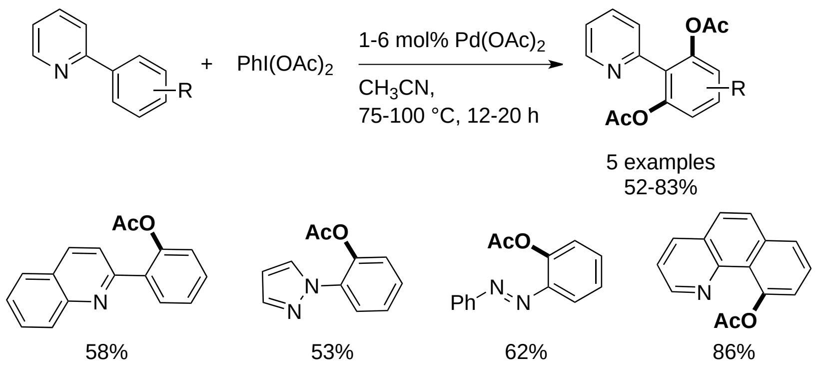
1.2.1 Transition Metal-Catalyzed Acetoxylation

A wide range of oxidants can facilitate palladium-catalyzed $C_{(sp2)}$−H bond oxygenation reactions. Iodine and oxygen are the most commonly used oxidants for C−H bond functionalizations.[8]

1.2.1.1 Background of Acetoxylation of Arenes with Directing Groups

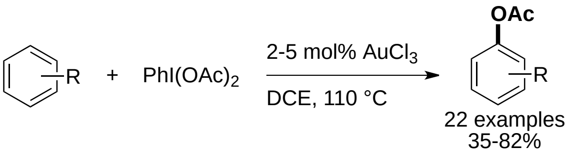
In 1996, Crabtree and co-workers demonstrated the first example of direct palladium-catalyzed acetoxylation of arenes with stoichiometric $PhI(OAc)_2$ which successfully transformed C-H bond to a C-OAc bond.[9] However, low to moderate yield were resulted and the regioselectivity of acetoxylation was not satisfactory. A mixture of *ortho-, meta-* and *para*-regioisomers of acetoxylated product were obtained. This report was indicated as a key demonstration that C-H bonds can be oxygenated with readily available catalyst with mild conditions.

Sanford showed examples of palladium-catalyzed $C_{(sp2)}$–H bond oxygenation using $PhI(OAc)_2$ as a stoichiometric oxidants in 2004 with high selectivity.[10] Acetoxylation was steered by excellent directing group of *ortho*-pyridyl moieties with product yields ranging from 54-88% (Scheme 1.1). Later, Sanford and co-workers further developed acetoxylation protocol using other nitrogen-containing directing groups such as imines, oxime ethers, pyrazoles, and other nitrogen heterocycles.[11] However, aldehyde and ketone are poor directing groups for acetoxylation, and thus rare examples were shown.[12] Detailed investigation of mechanism indicated that Pd(IV)/Pd(II) cycle is involved in the catalysis.



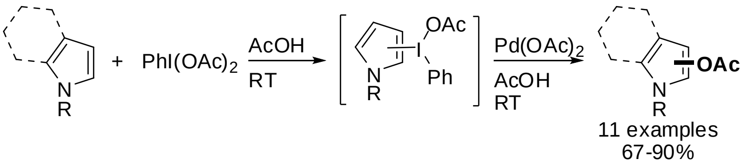
Scheme 1.1. Pd-catalyzed acetoxylation of arene with directing groups

Yu and co-workers reported a $Cu(OAc)_2$ catalyzed acetoxylation of 2-phenylpyridine with oxygen as the oxidant.[13] Mono- and di-acetoxylation products were given. In 2011, Wang's group developed an efficient $AuCl_3$-catalyzed direct acetoxylation of electron-rich arenes with $PhI(OAc)_2$ as the reagent.[14] Moderate-to-good yields of the corresponding acetoxylation products were resulted (Scheme 1.2).



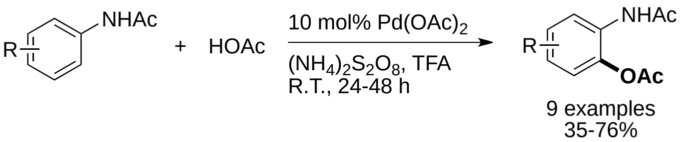
Scheme 1.2. Gold-catalyzed acetoxylation of electron-rich arenes with $PhI(OAc)_2$

In the meanwhile, Suna and co-workers introduced a mild-room temperature palladium-catalyzed acetoxylation of pyrroles with phenyliodonium acetates.[15] Pyrrolyl(phenyl)iodonium acetates were formed as intermediates, which acetoxylation was proceeded afterwards. Isolation of the intermediates could be neglected as a one-pot sequential procedure for the acetoxylation was shown (Scheme 1.3).



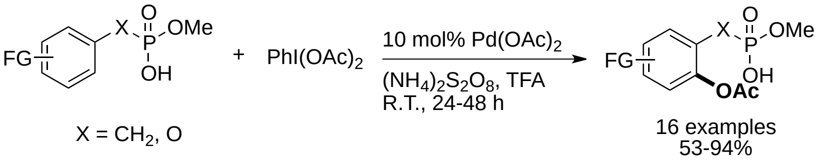
Scheme 1.3. Pd-catalyzed regioselective acetoxylation of pyyrole

In 2008, Wu group presented a room temperature *ortho*-acetoxylation of acetanilides[16] with $Pd(OAc)_2$. You and Song reported a similar acetoxylation approach in 2013 but anilides were used instead.[17]



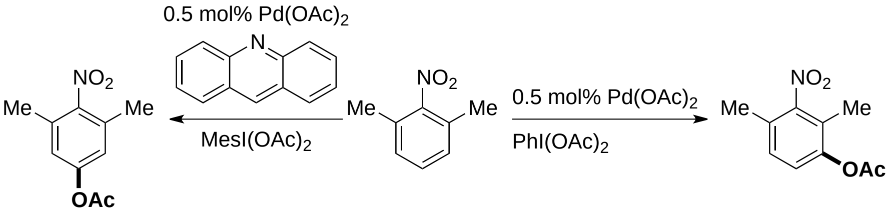
Scheme 1.4. Acetoxylation of anilides with palladium complex

Organophosphates can be used as the directing group such as benzylic phosphonic and aryl phosphoric monoacids. Kim and co-workers showed a simple and efficient method for acetoxylation of organophosphates and also provided an easy access to various acetoxy benzylic phopshonic acids along with catechol derivatives (Scheme 1.5).[18]



Scheme 1.5. Pd-catalyzed acetoxylation of organophosphates

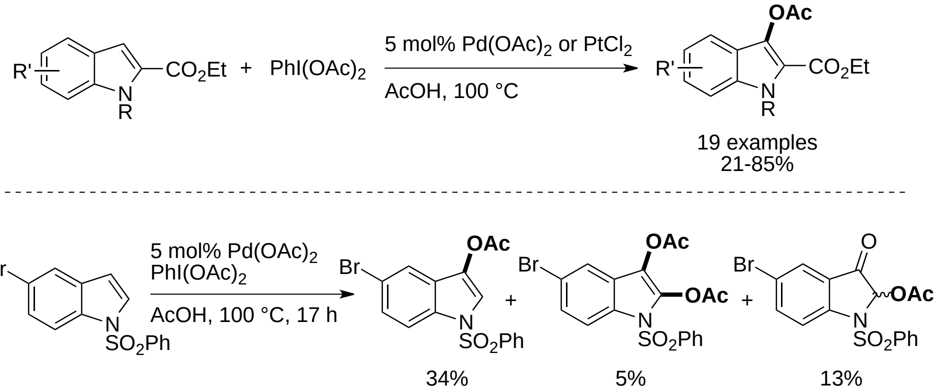
In 2013, Sanford continued her research in Pd-catalyzed acetoxylation of simple arenes.[19] The use of MesI(OAc)$_2$ as the terminal oxidant, and Pd(OAc)$_2$ with acridine catalytic system gave site selectivity to the sterically controlled manner. In contrast, when PhI(OAc)$_2$ was used as the oxidant, electronic effects dominate the selectivity of arene acetoxylation (Scheme 1.6).



Scheme 1.6. Steric control of site selectivity in Pd-catalyzed acetoxylation

1.2.1.2 Development of Acetoxylation of Indoles Derivatives

With similar catalytic systems, regioselective acetoxylation of indole derivatives were disclosed. 1,2-Disubstituted indoles could be acetoxylated together with 3,3'-biindolyl products using lead tetraacetate.[20] In 2009, Suna introduced an acetoxylation of 2,3-unsubstituted indole to give 3-acetoxyindole accompanying with a mixture of oxidized products (Scheme 1.7).[21]



Scheme 1.7. Pd-catalyzed acetoxylation of indole with directing group

In 2010, Zhang disclosed the 2,3'-biindole synthesis together with the C3-acetoxylated products using AgOAc under O_2.[22] Despite these remarkable developments, the direct and regioselective acetoxylation (*via* C-H bond activation/C-O bond coupling sequence) without the assistance from the *ortho*-directing group remained sporadically study. In 2011, Kwong developed a simple and general Pd-catalyzed direct and selective oxidative C-3 acetoxylation of 2,3-unsubstituted indole without directing group.[23] In the meanwhile, Lei explored a similar selective C-H acetoxylation of indole derivatives.[24] A kinetic study showed that the reaction was zero-order with respect to the oxidant and first-order with respect to the indole derivatives. Later, Taniguchi developed a new method for direct α-acetoxylation of 2,3-disubstituted indoles under mild conditions using iodine reagents.[25] These transformations are beneficial for organic synthesis since they tolerant ambient air and moisture, and many common functional groups are compatible under these reactions conditions.

1.2.2 Background of Hydroxylation of Arenes

A classical protocol for the synthesis of *ortho*-acylphenol scaffold is the Fries rearrangement of phenyl esters (Figure 1.1A).[26] Yet, this route suffers from a regioselective drawback, and thus an undesirable *para*-substituted product would be formed. Moreover, this anionic protocol is not compatible with enolizable ketones. Traditional Friedel-Crafts acylation[27] of phenols and direct hydroxylation of arylketones using a radical approach[28] show poor site-selectivity, and a possible *ortho*-, *meta*- and *para*-isomers of acylphenol are usually generated. These regio-mixtures are generally difficult to be purified. Palladium-catalyzed aromatic C-O bond formation has emerged as an alternative route for preparing site-selective phenolic compounds.[29] Successful hydroxylation of aryl halides have been reported recently (Figure 1.1B).[30]

Apart from these developments, we envisioned that the direct C-H bond functionalization would be even more attractive.[31] Hence, Pd-catalyzed direct $C_{(sp2)}$-H bond cleavage/$C_{(sp2)}$-O bond formation sequence is a desirable approach. In 2004, Sanford reported oxime as a directing group for *ortho*-acetoxylation of aromatic/aliphatic C-H bonds.[10b,32] Later, Yu disclosed a Pd-catalyzed *ortho*-hydroxylation of carboxylic acid salts at 115 °C (Figure 1.1B).[33] Apart from Pd catalysis, Rao and Lei groups recently showed that Ru and Cu complexes could be applied in hydroxylation of benzoate esters and electron-deficient arenes, respectively.[34,35] These establishments potentially provide synthetic method to access *ortho*-acylphenol moiety. Nevertheless, additional steps are necessary to retrieve the phenol or obtain the ketone moiety (Figure 1.1B). Therefore, it would be attractive to access *ortho*-acylphenols if ketone group could be directly employed as the directing group for direct $C_{(sp2)}$-H bond oxygenation.

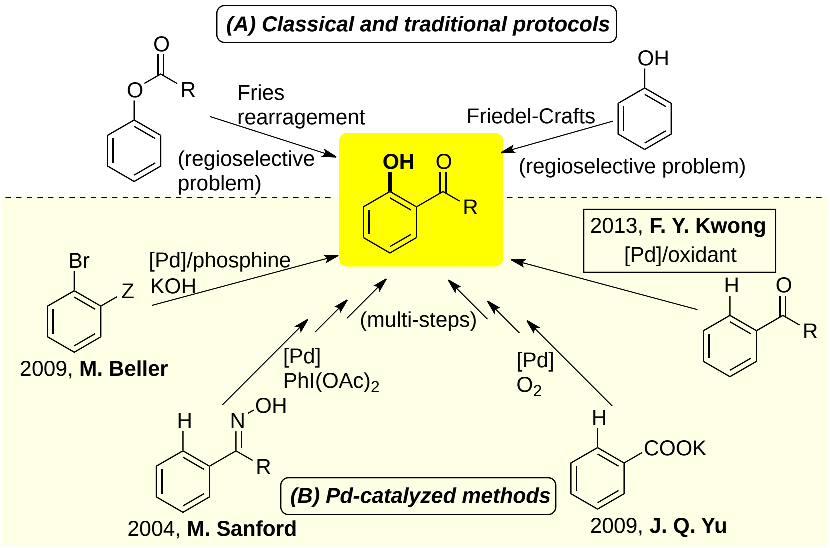
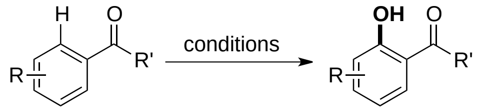


Figure 1.1. Synthetic pathways for *ortho*-acylphenol motifs

Ketone-directed C-H bond functionalization has been established since Murai's initial work on Ru-catalyzed olefin coupling.[36] Apart from the significant development of ketone-directed C-H bond cleavage/C-C bond-forming strategy,[37] there have been very limited examples on C-X bond formation. Until very recently, Liu[38] and Glorius[39] reported ketone-directed C-N and C-Br bond formation by employing Pd and Rh catalysts, respectively. Pal reported the hydroxylation of benzophenone under UV photoactivation conditions, leading to a mixture of regioisomers.[40] Yet, there has been no report on ketone-directed arene oxidation (C-O bond formation). Presumably the weaker coordinating ability (with respected to amides, oximes, carboxylic salts/esters and 2-phenylpyridine)[41] likely gives lower reactivity at the initial *ortho*-directed electrophilic palladation, and consequently more forcing conditions are needed, in which these conditions would lead to substrate decomposition or undesired product formation.

Direct transformation of readily available aryl ketones into valuable 2-hydroxylated products by palladium-catalyzed C-H functionalization is arguably a highly efficient and atom-economic method to access the compounds. Regio- and chemoselective oxygenation is a challenging reaction to obtain desirable phenol synthesis. In 2012, Rao, Dong, and Kwong's groups independently reported palladium-catalyzed ketone-directed hydroxylation of arenes. (Scheme 1.8).



Rao (2012)	5 mol% $Pd(OAc)_2$, TFA/TFAA oxidant, 50-90 °C	34 examples 11-88%
Dong (2012)	5 mol% $Pd(TFA)_2$, $PhI(OTFA)_2$, DCE 80 °C, 2 h	10 examples 21-83%
	5 mol% $Pd(OAc)_2$, $K_2S_2O_8$, TFA 50 °C, 1.5-12 h	7 examples 36-78%
Kwong (2012) [my work]	5 mol% $Pd(OAc)_2$, $PhI(OTFA)_2$, DCE 80 °C, 2 h	20 examples 50-88%
Ackermann (2013)	2.5 mol% [Ru]* $PhI(OAc)_2$, TFA/TFAA 120 °C, 22 h	12 examples 39-83%

* $[Ru(O_2CMes)_2(p\text{-cymene})]$

Scheme 1.8. Reaction conditions for hydroxylation of aromatic ketones

From Rao's group, a combination of Pd(II) catalysts, oxidants, and TFA/TFAA was applied for the unique regioselective oxygenation reaction.[42] For Dong's protocol, two methods were introduced for the oxygenation:

$Pd(TFA)_2$ and [bis(trifluoroacetoxyl)iodo]benzene were used as the catalytic system; and $Pd(OAc)_2$, $K_2S_2O_8$, and trifluoroacetic acids were applied. Mono- and di-hydroxylated products were afforded.[43] Kwong's group developed a catalytic system with $Pd(OAc)_2$ and $PhI(OTFA)_2$ to afford the desired hydroxylated products.[44] After these publications, Ackermann described a ruthenium complexes enabling the C-H oxygenation of aromatic ketons which tolerant excellent functional groups with high chemoselectivity and site selectivity.[45]

1.3 Carbon-Carbon Bond Formation

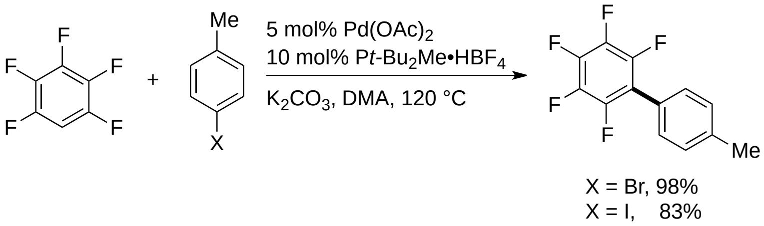
Palladium-catalyzed ligand-directed C-H functionalization to afford arylated, alkylated, and carbonylated products are widely studied in the recent years. These related early works have been extensively reviewed.[46]

1.3.1 C-H Direct Arylation of Polyfluoroarenes

Polyfluorinated biaryl scaffolds are important and interesting motifs in natural and materials science.[47] In particular, polyfluorinated compounds play an importance role as active materials in biological and electronic areas. In medicinal chemistry, the fluorine atoms are introduced into small molecules to give an advantage in drug effectiveness. For instance, the binding affinity and selectivity to target protein would be increased, and the lipophilicity can be fine tuned.[48,49] For material chemistry, organic light emitting diodes (OLEDs), field-effect transistors (FETs), liquid crystals and high mobility n-type semi-conductors are representative examples that make use of the component of polyfluorinated biaryls.[47d, 50] The strong electron-withdrawing fluorine group gives significant effect to minimize the chance of self-quenching, enhance the photoluminescence efficiency and lower the energy of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).[47d] Hence, numerous efficient reactions protocols were established to access these valuable compounds in these few years. The direct arylation with C-H bond functionalization is one of the effective methods to afford fluorinated biaryl compounds.[51]

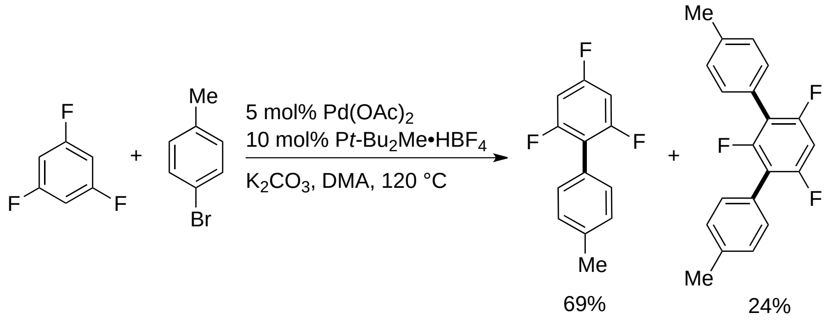
1.3.1.1 Development in Coupling Reactions of Aryl Halides with Polyfluoroarenes

Palladium-catalyzed arylation of aryl halides with perfluoroarenes has been well-developed for these ten years. The most representative paper of cross-coupling of aryl halides with perfluoroarenes appeared in 2006 by Fagnou and co-workers (Scheme 1.9).[52] Pentafluorobenzene was chosen as substrate since it would not react via electrophilic aromatic substitution.



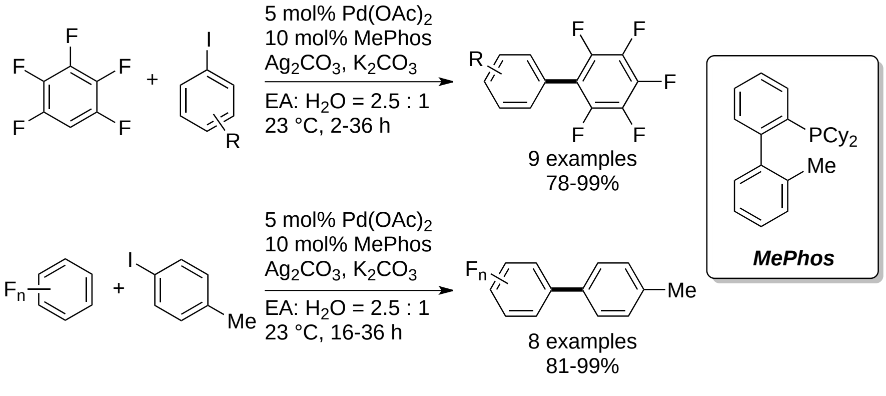
Scheme 1.9. Direct arylation of pentafluorobenzenes with iodo/bromotoluene

For some perfluoroarenes, there is more than one potential site for arylation. A mixture of products was formed including mono-, di- and triarylation products. Indeed, di-, and triarylation were inhibited by steric effect and lower percentage yield was afforded (Scheme 1.10). Only one example was shown for arylation of 4-chlorotoluene with pentafluorobenzene (57% yield).



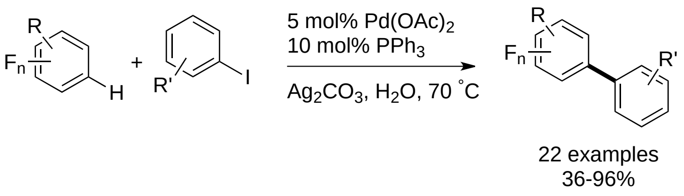
Scheme 1.10. Direct arylation of 1,3,5-trifluorobenzene with bromotoluene

Fagnou and co-workers continued their investigation in 2010.[53] They further improved the reaction conditions, which performed at room temperature and the product yields obtained up to 99% by using a new biphasic organic/ aqueous media. A series of phosphine ligands developed by Buchwald group (RuPhos, S-Phos, DavePhos, MePhos) were tested and MePhos gave the best performance in this perfluoro-coupling reaction.



Scheme 1.11. Direct arylation of perfluoroarenes with aryl iodides using MePhos

Recently, Zhang and co-workers developed a catalyst system for the palladium-catalyzed direct arylation of perfluoroarenes with aryl iodides.[54] This catalytic system provided good functional group compatibility with high reaction efficiency. Mild reaction conditions and the use of water as the sole solvent are the attractive features to the scientists.



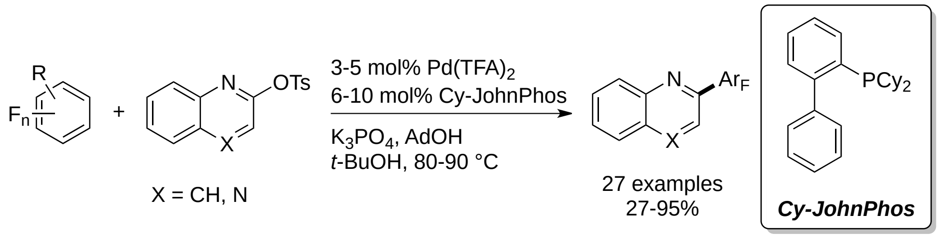
Scheme 1.12. Direct arylation of polyfluoroarenes with aryl iodides in water

1.3.1.2 Development of Coupling Reactions of Aryl Arenesulfonates with Polyfluoroarenes

Cross-coupling reaction of aryl halides and perfluoroarenes has been extensively established in these few years. In contrast, there were only a few reports about coupling of aryl arenesulfonates. Aryl triflates were seldom applied in such cross-coupling reaction, these constrains possibly due to the expensiveness of the triflating agent (e.g. Tf_2O),[55] and the low hydrolytic stability of aryl triflates under basic reaction conditions. It is worth to develop methods for phenolic compound derivatives to be used as electrophiles. In fact, they usually offer different or unique substituted groups in the aromatic ring, in which the corresponding aryl halides are not commonly available, or require additional synthetic steps to manipulate the pattern of complementary substitution. Thus, the exploration of less expensive, yet more stable aryl arenesulfonates in cross-coupling of perfluoroarenes is highly favourable. Nevertheless, the higher stability of aryl arenesulfonates (e.g. aryl tosylates) makes this less reactive to subject oxidative addition under palladium catalytic system. Thus, the successful of applying tosylates and mesylates as coupling partners in C-C bond forming reaction is seldom reported.

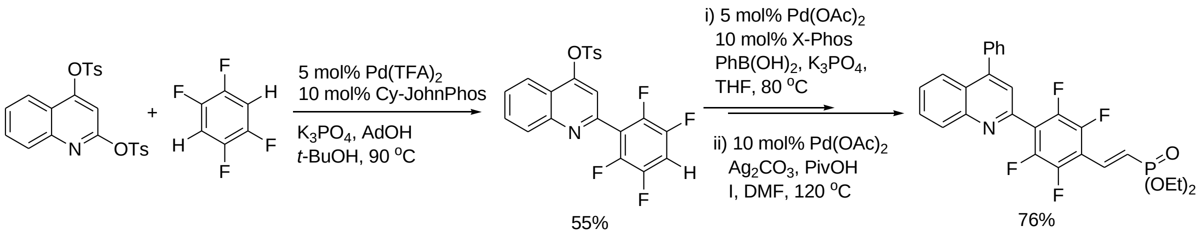
In 2006, the first example of phenyltriflates as coupling partner was reported by Fagnou and co-workers.[52] After this publication, no more discovery in coupling of aryl arenesulfonates with perfluoroarenes for 5 years.

Zhang group reported a palladium-catalyzed direct arylation of perfluoroarenes with heteroaryl tosylates in 2011 which is the first publication by using heteroaryl tosylates as coupling partners (Scheme 1.13).[56] The reaction conditions are mild with good reaction efficiency and chemoselectivity. Various polyfluoroarylated azine or diazine can be coupled smoothly with high to excellent isolated yields.



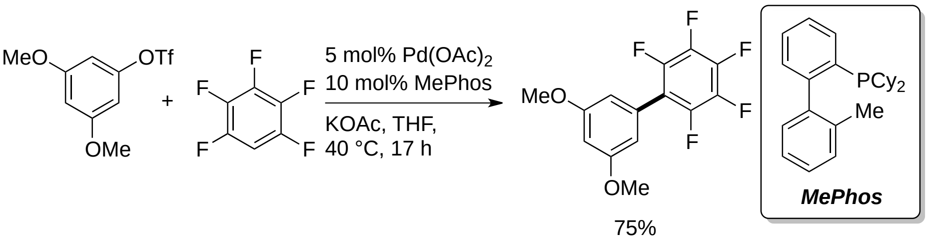
Scheme 1.13. Direct arylation of perfluoroarenes with various heteroaryl tosylates

This protocol is attractive by sequential C-H bond functionalization and C-O bond activation from inexpensive starting materials when comparing to aryl iodides/ bromides/ triflates. Zhang and co-workers demonstrated an example of chemoselective functionalization of quinoline-2,4-diyl bis(tosylate) to give monofluorinated compound and then react with phenylboronic acid to give a polyarylated product (Scheme 1.14). The product afforded is a semiconducting polyfluorophenylquinoline compound, which can be used in a wide range of functional materials.



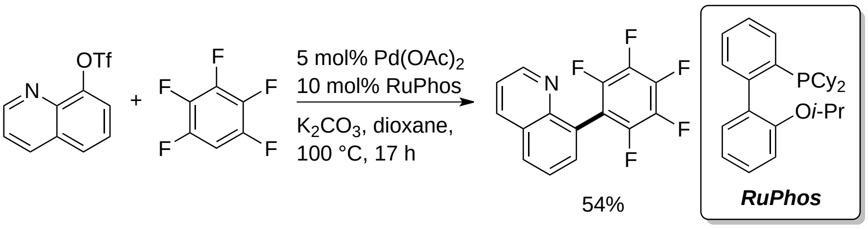
Scheme 1.14. Sequential coupling example of heteroaryl tosylate with tetrafluorobenzene

Recently, Seayad and co-workers released a publication about direct arylation of fluorinated aromatics compounds with aryl arenesulfonates (Scheme 1.15).[57] It is mainly focused on the coupling of aryl triflates by using catalytic system of $Pd(OAc)_2$/ MePhos. However, no deactivated aryl triflates example was shown in this report.



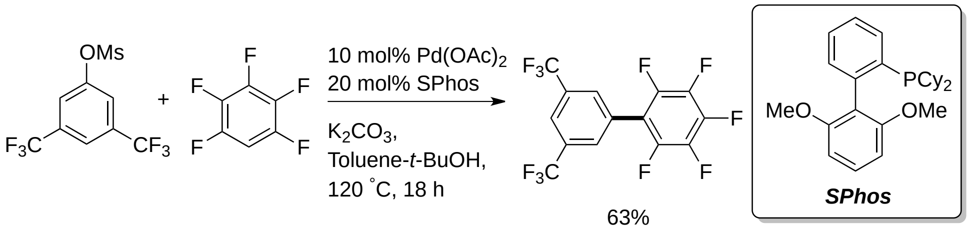
Scheme 1.15. Cross-coupling of 3,5-dimethoxyphenyl triflate with pentafluorobenzene

For high steric bulky substrates, RuPhos was used instead MePhos. The base was changed from KOAc to K_2CO_3 while the solvent was also changed to dioxane (Scheme 1.16).[57] Heteroaryl triflates were feasible coupling partners for this reaction and moderate yield was obtained.



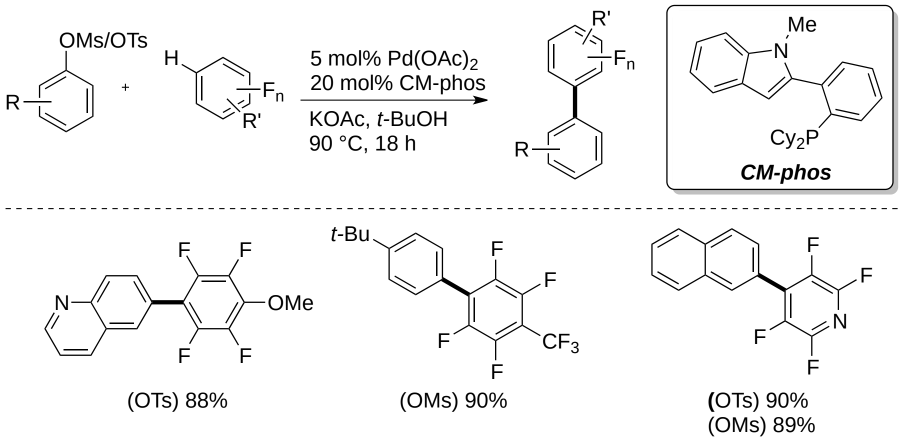
Scheme 1.16. Cross-coupling of steric hindered heteroaryl triflate with pentafluorobenzene

The first example of coupling of aryl mesylates and perfluoroarenes was introduced by Seayad in 2012.[57] 10 mol% of $Pd(OAc)_2$ was used together with SPhos. Mixed solvent of toluene/ *t*-BuOH were applied. Poor-to-moderate isolated yield was obtained and only activated aryl mesylates could serve as coupling partners. High reaction temperature (120 °C for 18 h) was required for the reactions.



Scheme 1.17. Cross-coupling of activated aryl mesylate with pentafluorobenzene

In 2012, Kwong and co-workers described the first general palladium-catalyzed direct arylation of polyfluoroarenes with aryl tosylates and aryl mesylates.[58] Relatively mild reaction conditions and only 5 mol% $Pd(OAc)_2$ was sufficient to catalyze the arylation. A wide range of polyfluoroarenes was applied for successful coupling with aryl tosylates and mesylates.



Scheme 1.18. Cross-coupling of aryl arenesulfonates with polyfluoroarenes by CM-phos

1.3.2 C-H Alkynylation of Sonogashira Cross-Coupling

The palladium-catalyzed cross-coupling of aryl, heteroaryl, and vinyl halides/ sulfonates (sp^2-hybridized carbon atoms – $C_{(sp2)}$) with terminal alkynes (sp-hybridized carbon atoms – $C_{(sp)}$) is named as, Sonogashira coupling.[59] This methodology features a modular approach to prepare an array of diversified aryl alkynes and conjugated enynes, which are important synthetic precursor and sub-unit for a range of pharmaceutically attractive and materially valuable organic compounds.[60]

1.3.2.1 Background of Alkynylation and Sonogashira Coupling

Over the past few decades, a number of protocols have been developed for the construction of $C_{(sp2)}$-$C_{(sp)}$ bond (alkynylation). The earliest studies on this topic was reported by Stephens and Castro who provided a palladium-free synthetic pathway for coupling of phenyl/ vinyl halides with copper acetylides in refluxing pyridine.[61] Concurrently, Cassar also investigated nickel and palladium-catalyzed coupling between aryl/ alkenyl halides with terminal alkynes and found that nickel catalyst system was failed in such coupling reaction.[62] Later, Sonogashira, Tohda, and Hagihara published a protocol which is generally considered to be superior to previously reported methodologies.[63] They observed that small quantities of copper(I) iodide added to the reaction can greatly increase the yield and also accelerate the reaction and hence allow the reactions to be conducted at room temperature.[63a] Due to its wide applicability, convenience, and overall excellence, the Sonogashira-Hagihara protocol thus become the most popular and reliable procedures for the synthesis of aryl/ alkenyl alkynes.

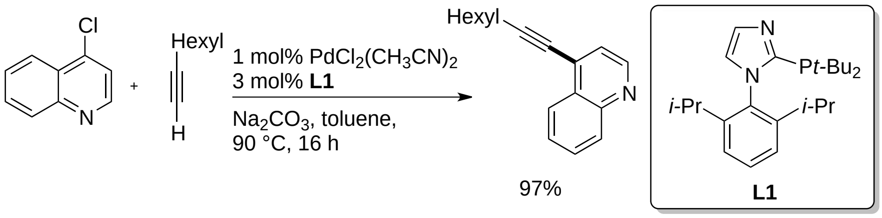
Although Sonogashira protocol seems to be the best among the other, there are some drawbacks for this coupling. The addition of copper co-catalysts could be a main limitation. The presence of copper would lead to the *in situ* formation of copper acetylides which induce the homo-coupling of terminal alkynes and thus the side products are formed. There are two common methods to avoid the unwanted homo-coupling products. Slow addition of terminal alkynes in the presence of phase-transfer reagent can only diminished the amount of side products obtained but they are still not completely avoided.[64] Ho group suggested that using an atmosphere of hydrogen gas diluted with nitrogen or argon to act as reducing agent to reduce the homo-coupling to happen.[65] Recently, Sonogashira coupling can be facilitated even without Cu(I) co-catalyst[66] and at room temperature[67] by using other metal co-catalysts,[68] or specially designed ligands.[69]

Until late 1990s, the most challenging topic for palladium-catalyzed Sonogashira cross coupling is the applicability of the reaction to different substrates/ coupling partners. Poor reactivity of aryl chlorides, tosylates and mesylates is the main limitation for the coupling when compared to the more reactive aryl iodides, bromides and triflates. If the reactivity problems of difficult substrates can be overcome, this would bring the cross coupling methodology to a new circumstance.

1.3.2.2 Development in Sonogashira Coupling of Aryl Halides and Arenesulfonates

Tremendous catalyst systems have been applied in the Sonogashira reactions.[70] Despite those impressive developments, only few reports deal with more functionalized substrates as well as heteroaryl halides were still be a challenge.

The most representative paper on Sonogashira cross-coupling reaction of aryl chlorides appeared in 2003 by Buchwald and co-workers.[64c] 1.0 mol% of $PdCl_2(CH_3CN)_2$ with 3 mol% XPhos was used to activate a wide range of aryl chlorides including sterically hindered substrates and various functional groups could be tolerated. After this publication, more papers were released in such investigation with different catalyst systems.[71] However, there is still much room for improvement that long reaction times and low substrate generality are some of the problem. Beller and coworker designed a new *N*-substituted heteroaryl phosphine ligand **L1** for Sonogashira couplings which can be applied in myriads of aryl/ heteroaryl chlorides and alkynes (Scheme 1.19).[72] Various functional groups for instance, amino, silyl and alkyl groups can be tolerated under the conditions while the procedures are cost effective without the addition of copper co-catalysts.

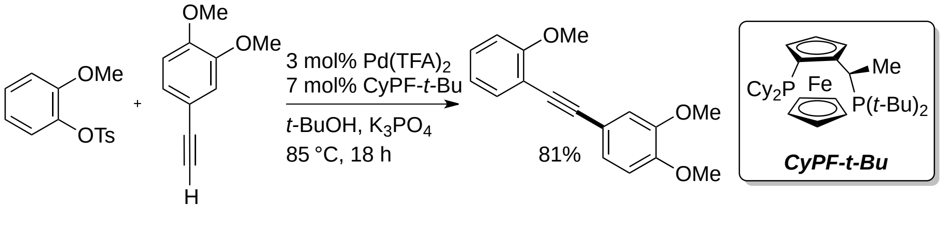


Scheme 1.19. Sonogashira reaction of heteroaryl chloride by heteroaryl phosphine

After the long development of Sonogashira cross-coupling reactions, the alkyne coupling procedure of aryl halides has been extensively established. In contrast, there are only very few reports about the coupling of aryl arenesulfonates. Aryl triflates and tosylates were seldom applied in Sonogashira coupling. Only vinyl tosylates were found successful in this transformation.[73]

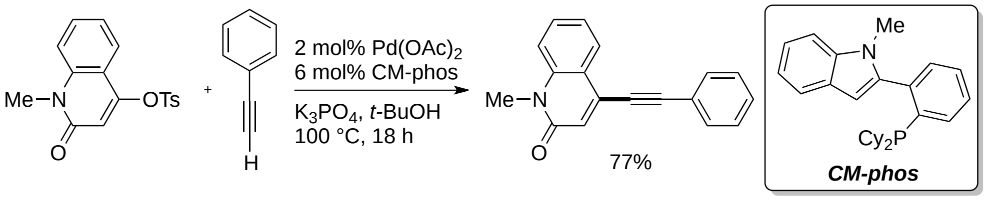
In 2003, the Sonogashira coupling of strongly activated and electron-deficient *para*- and *meta*-substituted aryl tosylates was disclosed by Buchwald group using the Pd/Xphos complex under the refluxing propionitrile solvent.[64c] This is the representative publication for coupling of aryl arenesulfonates. However, these pioneering examples required the slow addition of diluted alkyne substrates in 8 hours over the course of reaction. Moreover, a note was found that a high purity of the aryl tosylates was prerequisite for these successful couplings.

Recently, an operationally-simple and general procedures for Sonogashira coupling of non-activated aryl and heteroaryl tosylates were explored by Kwong[74] and Nazaré[75] independently. The latter authors from Sanofi Adventis published an European patent which described the application of $Pd(TFA)_2$/Josiphos-type ligand system for this reaction (Scheme 1.20).[76] In particular, *ortho*-substituted aryl tosylates were reacted with comparable efficiency and non-activated substrates or even deactivated aryl tosylates were found to be applicable under the reaction conditions.



Scheme 1.20. Sonogashira coupling with aryl tosylates by using ferrocene type ligand

Kwong and co-workers reported a general and efficient catalyst system for aryl tosylates.[74] Heterocyclic benzthiazolyl and quinolinyl tosylates furnished the corresponding coupling products smoothly. Alkenyl tosylate could also be coupled with phenylacetylene to afford good product yield (Scheme 1.21). In particular, Kwong group also uncovered the first examples of more difficult but more atom-economical aryl mesylates coupling with terminal alkynes.



Scheme 1.21. Sonogashira coupling with alkenyl tosylates by indolyl phosphine ligand

1.4 Ligand Development for Suzuki-Miyaura Cross-Coupling Reactions

Palladium-catalyzed Suzuki-Miyaura cross-coupling reaction has been developed for decades. Several approaches have been attempted to allow challenging aryl chlorides/ sulfonates as coupling partners in the palladium-catalyzed coupling reaction. A proper ligand design was critical for the success in coupling catalysis under mild reaction conditions and low catalyst loading. The most effective ligands can be grouped into two main categories: organophosphous ligands; and *N*-heterocyclic carbenes (NHCs). They are good σ-donors that increase the electron density of metal center which enhance the oxidative addition step, while appropriate steric bulkiness improves the reductive elimination step.

Phosphines are the most commonly used ligands in cross-coupling reactions. The traditional ligands employed for cross-coupling reactions are PPh_3, PCy_3, dppf, dppp, P*t*-Bu_3 and etc.[77] However, they are ineffective in the challenging Suzuki-coupling of aryl chlorides/ sulfonates. Only trace yield was obtained in most of these couplings.

The most efficient ligands developed recently that are known to be effective for Suzuki-Miyaura coupling reaction are phosphine possessing secondary or tertiary alkyl groups. They have been proved to be more superior to traditional triarylphosphines. Dialkylbiaryl phosphines have demonstrated outstanding performance in the Suzuki-Miyaura reactions. It is mainly due to the optimal cone angles and better σ-donation to palladium metal with inductive effects. Although many new ligands have been prepared (Figure 1.2), a simple, efficient and potentially tunable ligand design is still of great demand for tackling the existing challenges and problematic bond-construction processes.[78]

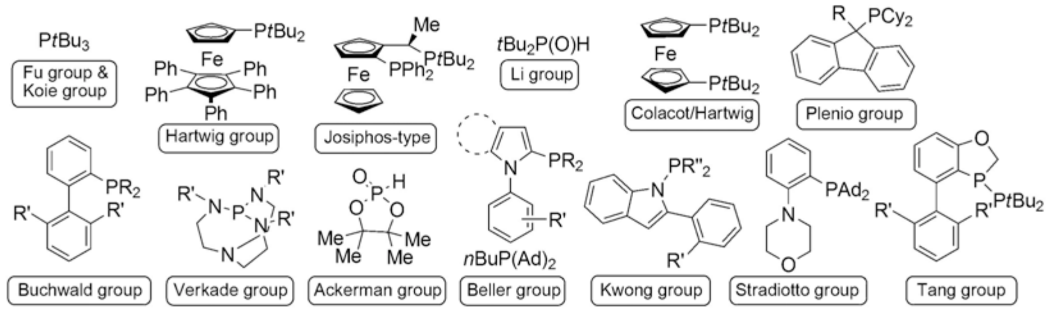


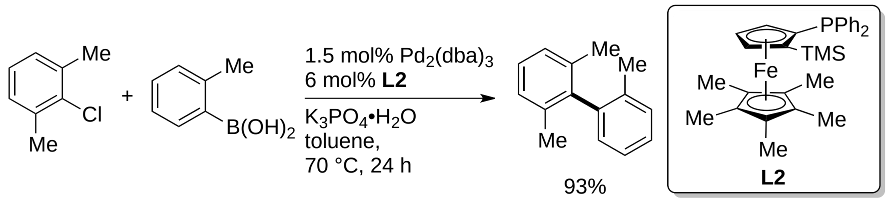
Figure 1.2. Selected examples of effective phosphines for Pd-catalyzed coupling

1.5 Palladium-Catalyzed Suzuki-Miyaura Cross-Coupling for Tri-*ortho*-substituted Biaryls Syntheses

Ortho-substituted biaryls are important structural motifs in myriad natural products from various origins and have a wide range of biological properties.[79] Kinpholone, can be extracted from African plants, which are used in folk medicine;[80] (*R*)-Gossypol can be used as an oral anti-fertility agent in men which also shows activity for potential treatment of HIV infections and cancer.[81] Natural products such as *vancomycin,* [82] $\alpha_{2/3}$-selective $GABA_A$ agonist candidate [83] and *steganacin* [84] are the *ortho*-substituted biaryl containing compounds. One of the most applied methods to obtain these valuable *ortho*-substituted biaryls compounds is the Suzuki-Miyaura cross-coupling reaction.

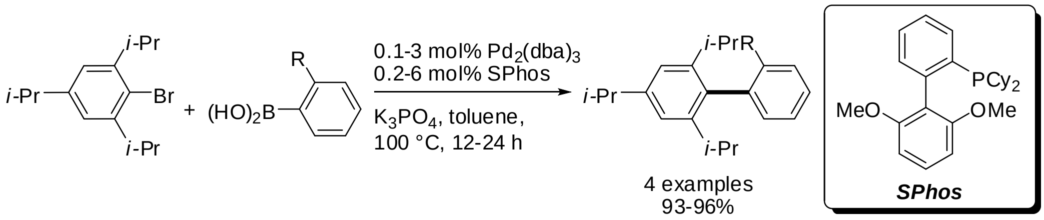
In the past few decades, sterically hindered biaryl synthesis is a highly challenging reaction. Considerable efforts have been undertaken by researchers in both academia and industry over the past decade to expand its feasibility. However, only a few publications were disclosed for successful examples and usually high catalyst loading with elevated reaction temperature were required.[85] To the best of our knowledge, general tri-*ortho*-substituted biaryl synthesis from aryl chlorides by Suzuiki-Miyaura coupling reactions remains sporadically reported to date.

The first successful examples of tri-*ortho*-substituted Suzuki coupling of aryl chlorides appeared in 2001 by Fu.[86] 2-Chloro-1,3-dimethylbenzene was successfully coupled with *o*-tolyboronic acids to afford desired products in 93% yield (Scheme 1.23).



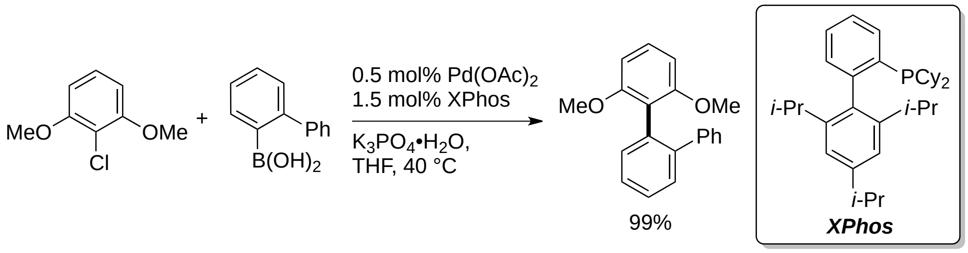
Scheme 1.23. First examples of tri-*ortho*-substituted Suzuki coupling by Fu

In 2004, Buchwald and co-workers developed a catalyst system that enabled the coupling of very hindered aryl bromides with hindered arylboronic acids at exceptionally low catalyst loading (Scheme 1.24).[87] Later, they further expanded the substrates scope to even more steric hindered 2-bromo-1,3,5-tri-*tert*-butylbenzene with isolated yield up to 99%.[88]



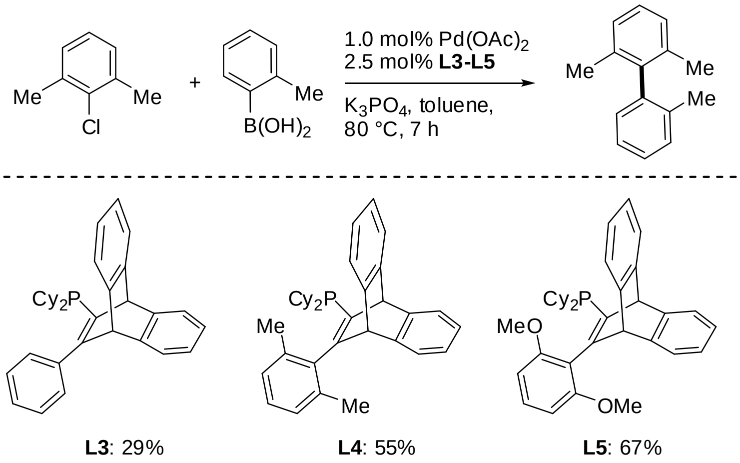
Scheme 1.24. Pd-catalyzed Suzuki coupling of very hindered aryl bromides

2-Chloro-1,3-dimethylbenzene was also successfully coupled with *o*-tolyboronic acids at 0.5 mol% catalyst loading with XPhos.[88] Also, the coupling reaction can be achieved at exceptional low temperature with 99% isolated yield (Scheme 1.25).



Scheme 1.25. Pd-catalyzed Suzuki coupling of hindered aryl chlorides by Buchwald

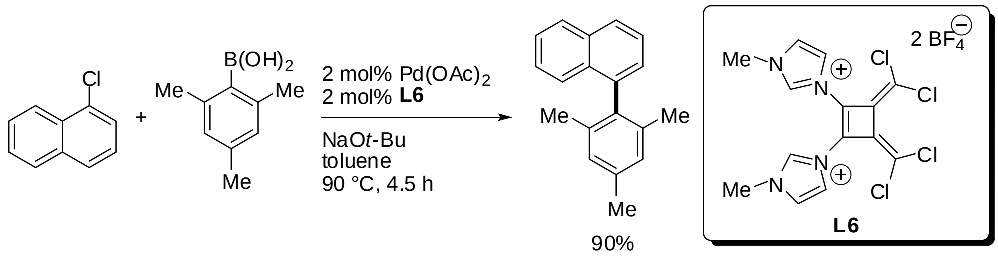
Tsuji and co-workers described a triarylphosphines with dendritically arranged tetraethylene glycol moieties for the palladium-catalyzed Suzuki-Miyaura coupling reaction.[89] One tri-*ortho*-substituted biaryl example was showed with 55% yield. KITPHOS catalyst was introduced by Doherty and Knight to allow *ortho*-substituted Suzuki coupling (Scheme 1.26).[90] Only 29-67% isolated yields were resulted.



Scheme 1.26. Application of KITPHOS in sterically hindered Suzuki coupling

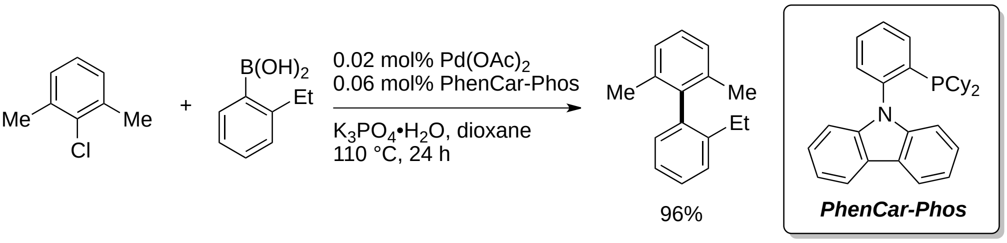
In 2010, Jin group discovered a highly active, easily recoverable, and practical heterogeneous catalyst for the coupling of 2-chloro-1,3-dimethylbenzene with *o*-tolyboronic acids.[91] One year later, they introduced another designed ligand β -diketiminatophosphine palladium complex for the coupling of a wide range of sterically hindered aryl chlorides at a low catalyst loading of 0.1 mol%.[92]

A specially designed ligand 3,3’-(3,4-bis(dichloro-methylene)-cyclobut-1-ene-1,2-diyl)bis(1-methyl-1H-imidazolium) bis(tetra-fluoroborate) was introduced by Schmidt (Scheme 1.27).[93] A wide range of very sterically hindered aryl bromides and chlorides can be coupled with different hindered arylboronic acids with 2 mol% of $Pd(OAc)_2$.



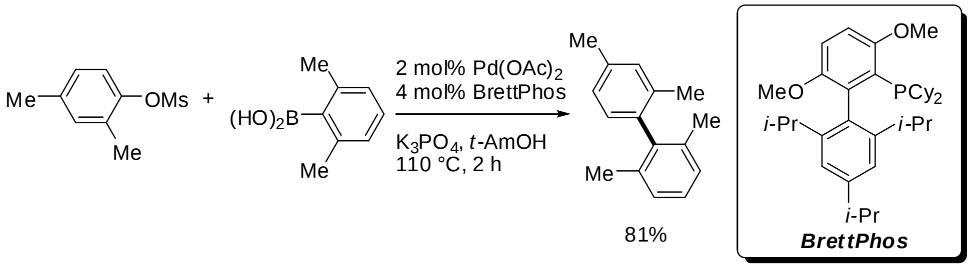
Scheme 1.27. Cyclobutene-1,2-bis(imidazolium)salt for Suzuki coupling by Schmidt

To continue the study of ligand application, Kwong developed another family of phosphine ligands – PhenCar-Phos bearing a bulky carbazolyl scaffold.[94] Difficult tri-*ortho*-substituted biaryl couplings are successfully achieved with the catalyst loading as low as 0.02 mol% of Pd. The result reflected that the coupling is highly sensitive to the ligand bulkiness which provide important note for future ligand design.



Scheme 1.28. Pd-catalyzed Suzuki coupling of di-*ortho*-substituted aryl chlorides

Particularly noteworthy is that aryl arenesulfonates are rarely applied in the preparation of tri-*ortho*-substituted biaryls by Suzuki-Miyaura cross-coupling reactions. Recent superb findings by the Buchwald group demonstrated only one example of 2,4-dimethylphenyl mesylate coupled with 2,6-dimethylphenylboronic acid by using a biarylphosphine ligand BrettPhos (Scheme 1.28).[95] Therefore, the development of efficient and general catalyst to address this limitation is still challenging.



Scheme 1.29. The only example of aryl mesylates coupled with hindered arylboronic acids

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Chapter 2 Palladium-Catalyzed Direct and Regioselective C-H Bond Functionalization/Oxidative Acetoxylation of Indoles

2.1 Introduction

Employing a modular approach for generating a new series of compounds has been one of the most important themes in modern convergent organic synthesis,[1] since it offers a direct and simple route to prepare an array of structurally similar, yet diversified pharmaceutically attractive molecules.[2] Certainly, the transition metal-catalyzed C-H bond activation/functionalization sequences have become a cutting-edge methodology in this area for the construction of carbon-carbon and carbon-heteroatom bonds.[3,4]

Among the field of $C_{(sp2)}$-heteroatom cross-couplings, the C-O bond-forming reaction (from ArX electrophile and ROH nucleophile) is the most problematic and difficult process.[5] Thus, it would be a considerable interest if this catalytic process is free of expensive tailor-made phosphine ligand and can be done by applying more atom-economical C-H activation/functionalization cascade protocol. Moreover, it would further add an advantage if it is in a regioselective manner, yet requiring no chelating-assisted groups.

In the repertoire of acetoxylation (C_{sp2}-O bond forming reaction), Sanford[6] and Yu[7] recently reported landmark explorations concerning the arene acetoxylation which directed by *ortho*-pyridyl or -iminyl moieties and catalyzed by palladium or copper complexes, respectively. More recently, regioselective acetoxylation of indole derivatives has been reported by Suna,[8] Zhang,[9] Kwong,[10] and Lei.[11]

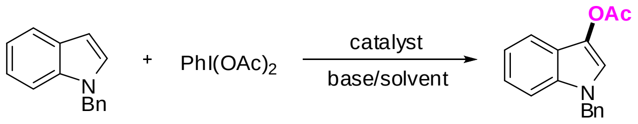
Indole is an important class of compound in pharmaceutical chemistry as it possesses unique biological activities.[12] In particular, 3-hydroxyindoles (and their alkoxy derivatives) are common scaffolds in medicinal chemistry. They have been used in the development of COX-2 inhibitors,[13] as well as have been applied as Mcl-1 inhibitors in the design of novel antitumor agents.[14] Moreover, they could serve as 5-HT$_6$ receptor ligand mimics.[15] Literature methods for accessing these 3-hydroxyl(-alkoxyl) indoles in moderate-to-good yields were mainly from the precursors of 3-bromoindoles[16,17] or 3-formylindoles.[18] Recently, Beller and co-workers reported the Ti- and Zn-mediated hydroamination of silyl-protected propargylic alcohol with arylhydrazine for accessing 3-silyloxy-2-methylindoles.[19] Despite these limited 3-oxyindole syntheses, an exploration of a facile protocol for the direct acetoxylation of indole, and thus hydroxy/alkoxyindoles, would be highly favorable. Herein, we disclose our efforts on direct palladium-catalyzed oxidative C3-acetoxylation of 2-unsubstituted indole in a highly regioselective manner *via* the C-H bond functionalization/C-O bond formation sequence.

2.2 Result and Discussion

2.2.1 Preliminary Evaluation of Palladium-Catalyzed Direct C3-Acetoxylation of Indoles

To examine the feasibility of the Pd-catalyzed acetoxylation of indole without directing groups, probing of reaction parameter screenings were deployed in the initial studies.

Table 2.1. Initial optimization of direct C3-acetoxylation of *N*-benzylindole[a]



entry	catalyst	solvent	base	% yield[b]
1	$Pd(OAc)_2$	CH_3CN	KOAc	70
2	$PdCl_2$	CH_3CN	KOAc	60
3	$Pd_2(dba)_3$	CH_3CN	KOAc	58
4	$Pd(TFA)_2$	CH_3CN	KOAc	59
5	-	CH_3CN	KOAc	Trace
6	$Pd(OAc)_2$	1,2-DCE	KOAc	55
7	$Pd(OAc)_2$	DMF	KOAc	50
8	$Pd(OAc)_2$	dioxane	KOAc	26
9	$Pd(OAc)_2$	toluene	KOAc	22
10	$Pd(OAc)_2$	CH_3CN	K_2CO_3	30
11	$Pd(OAc)_2$	CH_3CN	K_3PO_4	56
12	$Pd(OAc)_2$	CH_3CN	KOH	51
13	$Pd(OAc)_2$	CH_3CN	NaOH	56
14	$Pd(OAc)_2$	CH_3CN	NaOAc	53
15	$Pd(OAc)_2$	CH_3CN	Na_3PO_4	57
16	$Pd(OAc)_2$	CH_3CN	Et_3N	16
17	$Pd(OAc)_2$	CH_3CN	-	31

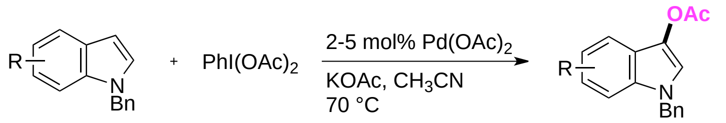
[a] Reaction conditions: Pd source (0.01 mmol, 2 mol%), *N*-benzyl indole (0.5 mmol), $PhI(OAc)_2$ (1.0 mmol), base (0.6 mmol), solvent (2.0 mL) were stirred at 70 °C under nitrogen for 2 hours. [b] Calibrated GC yields were reported, using dodecane as the internal standard.

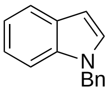
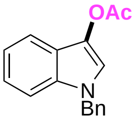
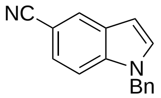
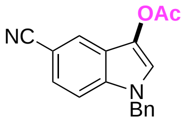
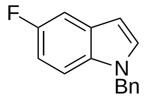
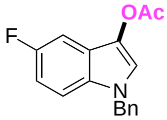
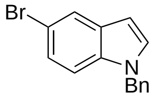
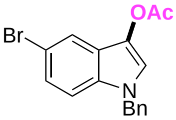
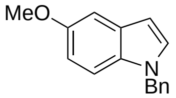
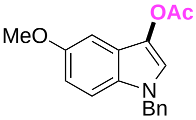
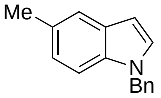
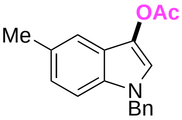
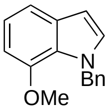
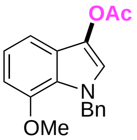
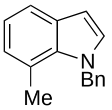
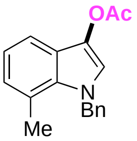
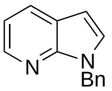
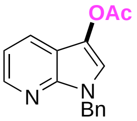
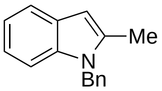
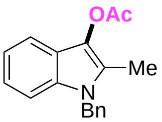
N-Benzyl protected indole substrate was chosen in the prototypical trials (Table 2.1). In the model catalysis, $PhI(OAc)_2$ was used as the oxidant to provide the acetoxy group to indole. An array of commonly used catalyst precursors for coupling reactions were surveyed (Table 2.1, entries 1-4). $Pd(OAc)_2$ gave the best conversion and yield of the product (entry 1). Control experiment revealed that no product was formed in the absence of palladium catalyst (entry 5). Among solvents screened, CH_3CN afforded the best results (entry 1 *vs* entries 6-9). KOAc base was found to be superior to the other inorganic bases (entry 1 *vs* entries 10-15). However, poorer yields were obtained when organic base or base-free conditions were used (entries 16-17).

2.2.2 Scope of Palladium-Catalyzed Direct C3-Acetoxylation of Substituted Indoles

With the preliminary optimized reaction conditions on hand, we next test the generality of the catalyst system for direct acetoxylation of substituted indoles (Table 2.2). In general, 2 mol% of $Pd(OAc)_2$ was sufficient to catalyze the reaction. Notably, this direct acetoxylation of indole could be performed at room temperature with 5 mol% $Pd(OAc)_2$ and prolonged reaction time (Table 2.2, entry 2). Functional groups such as cyano, bromo, fluoro and methoxy were compatible under these reaction conditions (entries 4-7). Notably, the bromo group remained intact throughout this palladium catalysis. This is of beneficial for further functionalization using other coupling protocols. Apart from various 5-substituted indoles, 7-substituted indoles furnished the desired product smoothly (entry 9-10). Azaindole was found to be a feasible substrate for this reaction (entry 11).

Table 2.2. Palladium-catalyzed direct C3-acetoxylation of *N*-benzylindoles[a]

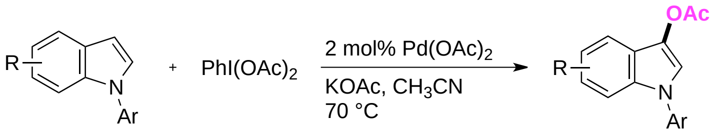


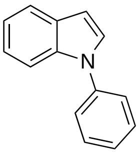
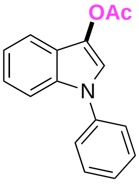
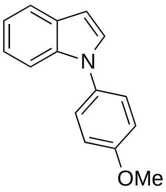
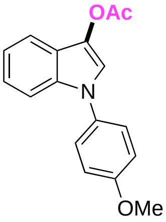
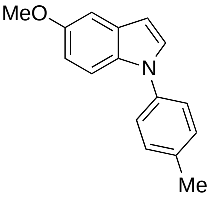
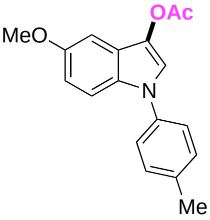
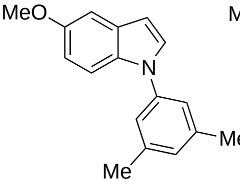
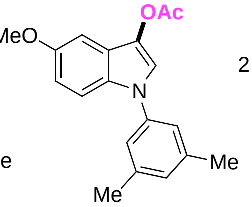
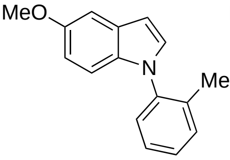
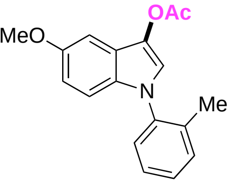
entry	indole	product	mol%Pd, time(h)	% yield[b]
1			2 mol%, 1 h	70
2			5 mol%, 60 h (RT.)	52
3			2 mol%, 1 h (air)	50
4			2 mol%, 18 h	48
5			2 mol%, 1 h	61
6			5 mol%, 1 h	66
7			2 mol%, 1 h	85
8			2 mol%, 1 h	70
9			2 mol%, 1 h	73
10			2 mol%, 1 h	69
11			2 mol%, 18 h	53
12			2 mol%, 1 h	63

[a]Reaction conditions: Pd(OAc)$_2$ (0.01 mmol, 2 mol%), *N*-benzyl indoles (0.5 mmol), PhI(OAc)$_2$ (1.0 mmol), KOAc (0.6 mmol), CH$_3$CN (1.0 mL) were stirred at 70 °C under nitrogen for 1-18 hours. [b]Isolated yields.

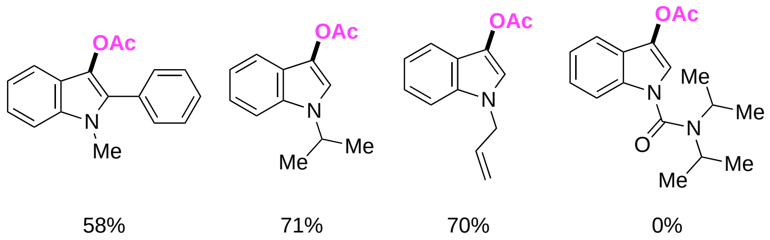
To further evaluate the catalytic system, we examined the acetoxylation of *N*-aryl indoles (Table 2.3). Moderate to good yields of the corresponding products were obtained (entries 1-5). This protocol was found to be compatible with *ortho*-, *meta*- and *para*-substituted aryl ring on the indolyl scaffold.

Table 2.3. Palladium-catalyzed direct C3-acetoxylation of *N*-arylindoles[a]



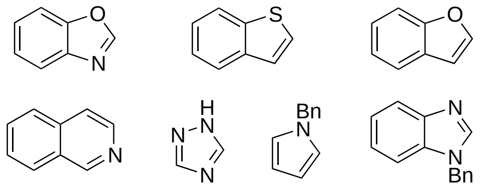
entry	indole	product	mol%Pd, time(h)	% yield^b
1			2 mol%, 2 h	68
2			2 mol%, 2 h	61
3			2 mol%, 1 h	65
4			2 mol%, 1 h	76
5			2 mol%, 1 h	63

[a]Reaction conditions: $Pd(OAc)_2$ (0.01 mmol, 2 mol%), *N*-aryl indoles (0.5 mmol), $PhI(OAc)_2$ (1.0 mmol), KOAc (0.6 mmol), CH_3CN (1.0 mL) were stirred at 70 °C under nitrogen for 1-2 hours. [b]Isolated yields.



Scheme 2.1. Palladium-catalyzed direct acetoxylation of *N*-alkylated indoles (reaction conditions were the same as in Table 2.2, entry 1)

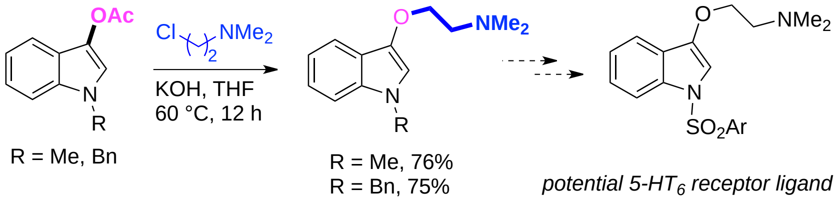
Apart from *N*-benzyl and *N*-arylindoles, *N*-alkylated indoles were feasible substrates for direct acetoxylation (Scheme 2.1). *N-iso*propyl and *N*-allylindoles were transformed to their corresponding product in good yields. Interestingly, no acetoxylation of olefin moiety was observed on allyl group under our reaction conditions.[20] Sterically congested 2-phenyl-*N*-methylindoles furnished the product in slightly lower yield presumably due to the steric hindrance of the *ortho*-phenyl ring. For 1-(1*H*-indol-1-yl)-2-isopropyl-3-methylbutan-1-one, it was not a suitable substrate for the acetoxylation. Besides, other heterocyclic compounds were tested but no desired products could be obtained (Scheme 2.2).



Scheme 2.2. Unsuccessful heterocyclic substrates in the acetoxylation protocol (reaction conditions were the same as in Table 2.2, entry 6)

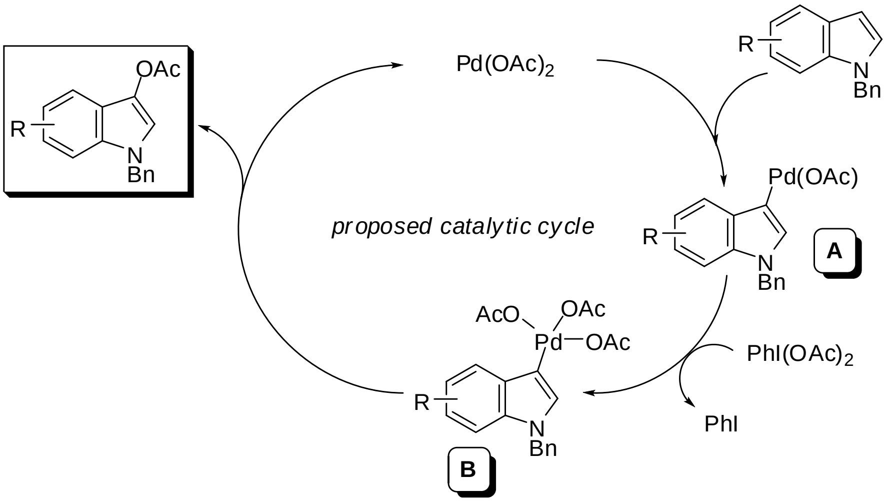
2.2.3 Application of Palladium-Catalyzed Direct C3-Acetoxylation of Substituted Indoles

3-Hydroxyindoles are slightly unstable and preferably to have silyl- or acetyl-protection for storage. Indeed, the direct acetoxylation of indole would be a useful way to prepare protected form of 3-oxyindoles, which can be further functionalized by an easy alkaline hydrolysis in achieving 3-hydroxyindoles *in situ*. In fact, this organic transformation offers a simple protocol to afford a series of potential 5-HT_6 receptor ligands.[15] Thus, the cascade deacetoxylation and subsequent alkylation processes provide a versatile pathway to access tryptamine-like 5-HT_6 receptor ligand scaffolds for further structural manipulation (Scheme 2.3).



Scheme 2.3. Cascade deacetoxylation-alkylation processes of acetoxyindoles

2.2.4 Proposed Mechanism of Palladium-Catalyzed Direct C3-Acetoxylation of Substituted Indoles



Scheme 2.4. Proposed mechanism of Pd-catalyzed direct C3 acetoxylation of indoles

For the mechanism of acetoxylation, the first step is the electrophilic palladation of indole to form the complex A. Then, subsequent oxidation of indolyl-Pd(II) species with the oxidant PhI()$Ac)_2$ would be undergo to form

Pd(IV) complex B. Finally, reductive elimination occurred to give the acetoxylated products and regenerate the Pd(II) species. The C3 position of indole is more electron-rich which is more favourable for palladation to occur under the catalytic system. That also explained the phenomena of prolonged reaction time when electron-deficient indole was used.

2.3 Conclusion

In summary, we have developed a general palladium-catalyzed direct and regioselective C3-acetoxylation of 2,3-unsubstituted indoles, which serves complementarily to current difficult C-O bond coupling processes using aryl halides as electrophiles. Moreover, this selective C-H functionalization/C-O bond-coupling sequence is achievable without the aid of *ortho*-directing groups. This protocol provides a facile and direct access to a variety of pharmaceutically useful 3-oxyindoles scaffolds under mild reaction conditions (weak base, KOAc; at 70 °C for 1-18 h), and is compatible to bromo-group which offers potential for further structural manipulation using other coupling technology.

2.4 Experimental Section

2.4.1 General Considerations

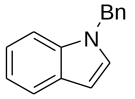
Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. All acetoxylation reactions were performed in resealable screw cap Schlenk flask (approx. 8 mL volume) in the presence of Teflon coated magnetic stirrer bar (3 mm × 10 mm). Acetonitrile was distilled from calcium hydride under nitrogen, *N*,*N*-dimethylformamide (DMF) was distilled with calcium hydride under reduced.[21] Toluene was distilled from sodium under nitrogen pressure and tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. KOH was purchased directly from commercial supplier and used with grinding. Thin layer chromatography was performed on precoated silica gel 60 F_{254} plates. Silica gel (70-230 and 230-400 mesh) was used for column chromatography. ^{1}H NMR spectra were recorded on a 400 MHz spectrometer. Spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.26 ppm), or with tetramethylsilane (TMS, δ 0.00 ppm) as the internal standard. Chemical shifts (δ) were reported as part per million (ppm) in δ scale downfield from TMS. ^{13}C NMR spectra were referenced to $CDCl_3$ (δ 77.0 ppm, the middle peak). Coupling constants (*J*) were reported in Hertz (Hz). Mass spectra (EI-MS and ES-MS) were recorded on a Mass Spectrometer. High-resolution mass spectra (HRMS) were obtained on a ESIMS mass spectrometer. GC-MS analysis was conducted on a GCD system using a column with dimension of 30 m × 0.25 mm. The products described in GC yield were accorded to the authentic samples/dodecane calibration standard from GC-FID system.

2.4.2 Preparation of Substituted Indole Substrates

General Procedure for the preparation of substituted benzyl indole substrates: Commercially available indole (10 mmol) was dissolved in a freshly distilled DMF (15 mL) at room temperature under nitrogen atmosphere. KOH

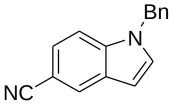
(0.67 g, 12 mmol) was then added into the reaction mixture and kept stirring at room temperature. After all the KOH were dissolved, benzyl bromide was added in dropwise and stirred overnight. 25 ml of water was added to the mixture and stirred for 30 min. The mixture was then extracted with dichloromethane and the organic layer was washed with water twice. The solvent was then removed by reduced pressure. The crude product was filtered through a short silica pad (3 × ~10 cm) and washed with corresponding solvent system indicated. The solution was evaporated to yield solid mixture. Small amount of cold hexane was used to further wash the product. The product was then dried under vacuum to afford desired products.

1-Benzyl-1*H*-indole (Table 2.2, entry 1)[22]



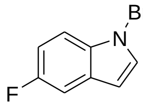
DCM: Hexane = 1:3, R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.36 (s, 2H), 6.59 (d, *J*=2.0 Hz, 1H), 7.13-7.22 (m, 5H), 7.31-7.34(m, 4H), 7.69 (dd, *J*=1.2, 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 50.0, 101.6, 109.6, 119.4, 120.9, 121.6, 126.7, 127.5, 128.2, 128.7, 136.2, 137.5; MS (EI): *m/z* (relative intensity) 207 (M^+, 72), 91 (100), 65 (18).

1-Benzyl-1H-indole-5-carbonitrile (Table 2.2, entry 4)[23]



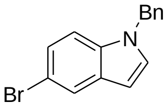
EA: Hexane = 1:9, R_f = 0.65; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.37 (s, 2H), 6.65 (dd, *J*=0.8, 2.4 Hz, 1H), 7.10-7.12 (m, 2H), 7.27-7.40 (m, 7H), 8.01 (t, *J*=0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 50.4, 102.7, 102.8, 110.5, 120.7, 124.6, 126.6, 126.7, 128.0, 128.4, 129.0, 130.6, 136.4, 137.7; MS (EI): *m/z* (relative intensity) 232 (M^+, 55), 91 (100), 65 (20).

1-Benzyl-5-fluoro-1*H*-indole (Table 2.2, entry 5)[24]



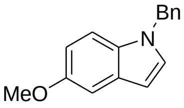
EA: Hexane = 1:9, R_f = 0.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.33 (s, 2H), 6.54 (dd, *J*=0.8, 2.4 Hz, 1H), 6.91-6.96 (m, 1H), 7.11-7.13 (d, *J*=6.4 Hz, 2H), 7.17-7.21 (m, 2H), 7.30-7.33 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 50.3, 101.5, 101.6, 105.5, 105.7, 109.9, 110.20, 110.25, 110.3, 126.6, 127.7, 128.8, 129.8, 137.2; MS (EI): *m/z* (relative intensity) 225 (M^+, 64), 91 (100), 65 (19).

1-Benzyl-5-bromo-1*H*-indole (Table 2.2, entry 6)[25]



EA: Hexane = 1:9, R_f = 0.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.32 (s, 2H), 6.51 (dd, *J*=0.4, 2.8 Hz, 1H), 7.09-7.17 (m, 2H), 7.25-7.33 (m, 5H), 7.79(s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 50.3, 101.2, 111.2, 112.9, 123.4, 124.5, 126.6, 127.8, 128.8, 129.5, 130.4, 134.9, 137.0; MS (EI): *m/z* (relative intensity) 285 (M^+, 36), 204 (5), 115 (7), 91 (100), 65 (14).

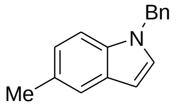
1-Benzyl-5-methoxy-1*H*-indole (Table 2.2, entry 7)[26]



EA: Hexane = 1:9, R_f = 0.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.88 (s, 3H), 5.32 (s, 2H), 6.51 (dd, *J*=0.8, 2.4 Hz, 1H), 6.85-6.88 (m, 1H), 7.12-7.20 (m, 5H), 7.28-

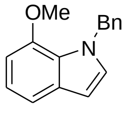
7.34 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 50.2, 55.8, 101.1, 192.6, 110.4, 111.9, 126.6, 127.5, 128.7, 128.8, 129.0, 131.6, 137.6, 154.0; MS (EI): *m/z* (relative intensity) 137 (M^+, 93), 222 (23), 146 (8), 91 (100), 65 (12).

1-Benzyl-5-methyl-1*H*-indole (Table 2.2, entry 8)[27]



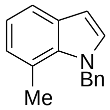
EA: Hexane = 1:9, R_f = 0.7; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.56 (s, 3H), 5.36 (s, 2H), 6.58 (dd, *J*=0.8, 2.8 Hz, 1H), 7.10 (dd, *J*=1.2, 2.8 Hz, 1H), 7.12-7.20 (m, 3H), 7.26 (d, *J*=8.4 Hz, 1H), 7.34-7.55 (m, 3H), 7.56 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 50.0, 101.0, 109.3, 120.5, 123.2, 126.6, 127.4, 128.2, 128.6, 128.9, 134.6, 137.6; MS (EI): *m/z* (relative intensity) 221 (M^+, 67), 91 (100), 65 (14).

1-Benzyl-7-methoxy-1*H*-indole (Table 2.2, entry 9)



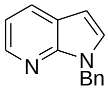
EA: Hexane = 1:4, R_f = 0.7; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86 (s, 3H), 5.67 (s, 2H), 6.54 (d, *J*=4.0 Hz, 1H), 6.66 (d, *J*=7.6 Hz, 1H), 7.02-7.07 (m, 2H), 7.14 (t, *J*=7.2 Hz, 2H), 7.25-7.33 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.4, 55.3, 102.0, 102.7, 113.7, 119.9, 126.6, 127.0, 128.4, 129.0, 130.9, 139.7, 147.6; MS (EI): *m/z* (relative intensity) 237 (M^+, 83), 222 (18), 91 (100), 65 (15); HRMS: calcd. for $C_{16}H_{16}NO^+$: 238.1232, found 238.1225.

1-Benzyl-7-methyl-1*H*-indole (Table 2.2, entry 10)[27]



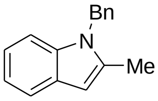
EA: Hexane = 1:9, R_f = 0.7; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.58 (s, 3H), 5.63 (s, 2H), 6.62 (d, *J*=3.2 Hz, 1H), 6.93-7.11 (m, 5H), 7.28-7.34 (m, 3H), 7.57 (t, *J*=7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.5, 52.2, 102.0, 119.1, 119.8, 121.0, 124.5, 125.4, 127.2, 128.7, 129.7, 130.1, 135.0, 139.6; MS (EI): *m/z* (relative intensity) 221 (M^+, 65), 91 (100), 65 (14).

1-Benzyl-7-azaindole (Table 2.2, entry 11)[28]



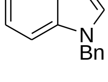
EA: Hexane = 1:9, R_f = 0.6; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.54 (s, 1H), 6.51(d, *J*=3.2 Hz, 1H), 7.09-7.12 (m, 1H), 7.20-7.34 (m, 6H), 7.95 (dd, *J*=1.6, 6.4 Hz, 1H), 8.37 (d, *J*=1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 47.7, 100.0, 115.8, 120.4, 127.4, 127.5, 127.8, 128.6, 128.7, 137.7, 142.9, 147.7; MS (EI): *m/z* (relative intensity) 207 (M^+, 100), 131 (27), 91 (68), 65 (23).

1-Benzyl-2-methyl-1*H*-indole (Table 2.2, entry 12)[22]



DCM: Hexane = 0.8:1, R_f = 0.7; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 5.33 (s, 2H), 6.38 (s, 1H), 7.02 (d, J=7.2 Hz, 2H), 7.13-7.14 (m, 2H), 7.26-7.31 (m, 5H), 7.60- 7.62 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.7,, 46.4, 100.4, 109.1, 119.4, 119.6, 120.7, 125.9, 127.2, 128.1, 128.7, 136.6, 137.1, 137.8; MS (EI): *m/z* (relative intensity) 221 (M^+, 40), 91 (100).

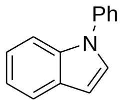
1-Benzyl-1*H*-benzoimidazole (Scheme 2.2)[29]



EA: Hexane = 1:9, R_f = 0.6; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.38 (s, 2H), 7.19-7.22 (m, 2H), 7.28-7.36 (m, 6H), 7.84-7.86 (m, 1H), 7.98 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 48.8, 109.9, 10.4, 122.2, 123.0, 127.0, 128.2, 129.0, 135.4, 143.1, 144.0; MS (EI): *m/z* (relative intensity) 208 (M^+, 57), 91 (100), 65 (14).

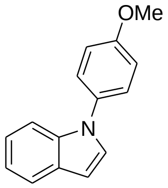
General Procedure for preparation of other substituted indole substrates (Table 2.3, entry 1-5): 1-phenyl-1*H*-indole,[22] 1-(4-methoxyphenyl)-1*H*-indole,[22] 5-methoxy-1-(4-methylphenyl)-1*H*-indole,[30] 1-(3,5-dimethylphenyl)-5-methoxy-1*H*-indole[31] and 5-methoxy-1-(*o*-tolyl)-1*H*-indole[32] were prepared from their corresponding indoles with corresponding substituted bromide/ iodide in the presence of copper iodide and ligand in dry toluene according to the literature method.[32]

1-Phenyl-1*H*-indole (Table 2.3, entry 1)[22]



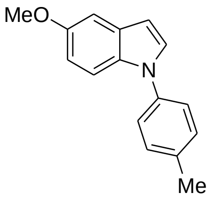
DCM: Hexane = 1:3, R_f = 0.6; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83-6.84 (m, 1H), 7.33-7.38 (m, 2H), 7.46 (d, *J*=4.0 Hz, 2H), 7.60-7.63 (m, 4H), 7.71-7.73(m, 1H), 7.84-7.86(m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 103.5, 110.5, 120.3, 121.0, 122.3, 124.2, 126.3, 127.8, 129.2, 192.5, 135.7, 139.7; MS (EI): *m/z* (relative intensity) 193 (M^+, 100), 165 (25), 89 (15).

1-(4-Methoxyphenyl)-1*H*-indole (Table 2.3, entry 2)[22]



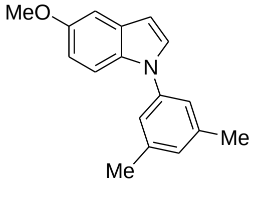
EA: Hexane = 1:4, R$_f$ = 0.4; ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.91 (s, 3H), 6.69 (dd, *J*=0.8, 1.2 Hz, 1H), 7.05-7.09 (m, 2H), 7.17-7.32 (m, 3H), 7.42-7.51 (m, 3H), 7.71 (d, *J*=0.8 Hz, 1H), 7.73 (d, *J*=0.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 55.5, 102.8, 110.3, 114.7, 120.0, 120.9, 122.1, 125.9, 128.2, 128.9, 132.8, 136.3, 158.2; MS (EI): *m/z* (relative intensity) 223 (M$^+$, 100), 206 (75), 180 (21), 152 (19).

5-Methoxy-1-(4-methylphenyl)-1*H*-indole (Table 2.3, entry 3)[30]



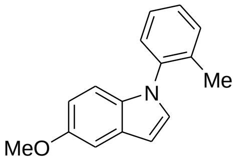
EA: Hexane = 1:4, R$_f$ = 0.5; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.45 (s, 3H), 3.89 (s, 3H), 6.61 (d, *J*=3.2 Hz, 1H), 6.9 (dd, *J*=2.4, 6.8 Hz, 1H), 7.16 (d, *J*=2.4 Hz, 1H), 7.31 (d, *J*=3.2 Hz, 1H), 7.33-7.46 (m, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 21.0, 55.8, 102.6, 102.8, 111.3, 112.3, 124.0, 128.4, 130.1, 131.3, 136.2, 137.5, 154.6; MS (EI): *m/z* (relative intensity) 237 (M$^+$, 100), 219 (79), 194 (43).

1-(3,5-Dimethylphenyl)-5-methoxy-1*H*-indole (Table 2.3, entry 4)[31]



EA: Hexane = 1:50, R$_f$ = 0.5; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.42 (s, 6H), 3.89 (s, 3H), 6.60 (d, *J*=2.8 Hz, 1H), 6.9 (dd, *J*=2.0, 6.4 Hz, 1H), 7.00 (s, 1H), 7.15 (t, *J*=8.4 Hz, 3H), 7.32 (d, *J*=3.2 Hz, 1H), 7.48 (d, *J*=9.2 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 21.2, 55.7, 102.6, 102.8, 111.4, 112.2, 121.7, 127.8, 128.3, 129.7, 131.0, 139.2, 139.7, 154.4; MS (EI): *m/z* (relative intensity) 251 (M^+, 100), 234 (81), 208 (33).

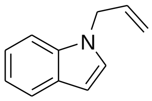
5-Methoxy-1-(*o*-tolyl)-1*H*-indole (Table 2.3, entry 5)[32]



DCM: Hexane = 1:3, R_f = 0.15; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.10 (s, 3H), 3.90 (s, 3H), 6.2 (d, *J*=3.2 Hz, 1H), 6.87 (d, *J*=2.4 Hz, 1H), 6.96 (d, *J*=8.8 Hz, 1H), 7.16-7.18 (m, 2H), 7.32-7.39 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.6, 55.8, 102.0, 102.4, 111.2, 112.2, 126.7, 128.0, 128.1, 128.6, 129.1, 131.1, 132.3, 135.7, 138.3, 154.3; MS (EI): *m/z* (relative intensity) 237 (M^+, 100), 222 (91), 194 (27).

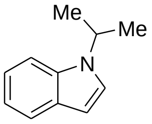
General Procedure for the preparation of substituted alkyl indole substrates (Scheme 2.1): Commercially available substituted indole (10 mmol) was dissolved in a freshly distilled DMF (15 mL) at room temperature under a nitrogen atmosphere. KOH (0.67 g, 12 mmol) was then added into the reaction mixture and kept stirring at room temperature. After all the KOH were dissolved, allyl bromide/ 2-bromopropane was added dropwisely for 1-allyl-1*H*-indole[33] and 1-isopropyl-1*H*-indole[34] respectively. The mixture was then stirred overnight. 25 ml of water was added to the mixture and stirred for 30 min. The mixture was then extracted with dichloromethane and the organic layer was washed with water twice. The solvent was then removed by reduced pressure. The crude product was filtered through a short silica pad (3 × ~10 cm) and washed with DCM/ hexane/ 0.2 ml triethylamine. The solution was evaporated and then dried under vacuum to afford desired products.

1-Allyl-1*H*-indole (Scheme 2.1)[33]



DCM: Hexane = 1:3, R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.80-4.82 (m, 2H), 5.20 (d, *J*=17.2 Hz, 1H), 5.30-5.33 (m, 1H), 6.05-6.15 (m, 1H), 6.66 (s, 1H), 7.21 (d, *J*=2.8 Hz, 1H), 7.24-7.46 (m, 3H), 7.77-7.80 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 48.7, 101.3, 109.5, 117.11, 119.3, 120.8, 121.4, 127.7, 128.6, 133.4, 136.0; MS (EI): *m/z* (relative intensity) 156 (M^+, 100), 130 (47), 116 (19), 89 (19).

1-Isopropyl-1*H*-indole (Scheme 2.1)[34]



DCM: Hexane = 1:3, R_f = 0.6; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.70 (dd, J=1.2, 5.2 Hz, 6H), 4.79-4.89 (m, 1H), 6.75 (s, 1H), 7.32-7.45 (m, 3H), 7.58-7.60 (m, 1H), 7.87-7.89 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.6, 46.8, 101.0, 119.1, 120.8, 121.0, 123.4, 128.5, 135.4; MS (EI): *m/z* (relative intensity) 159 (M^+, 51), 144 (100), 117 (40), 89 (19).

2.4.3 General Procedures for Initial Reaction Conditions Screening

General Procedure for reaction condition screenings: $Pd(OAc)_2$ (2.3 mg, 0.010 mmol), $PhI(OAc)_2$ (0.75 mmol), benzyl indoles (0.5 mmol) and base (0.6 mmol) were loaded into a Schlenk tube equipped with a Teflon-coated magnetic stir bar. The tubes were evacuated and backfilled with nitrogen (3 cycles). The solvent (1.0 mL) was added with stirring at room temperature for several minutes. The tube was then placed into a preheated oil bath (70 °C) and stirred for the time as indicated. After completion of reaction, the reaction tube was allowed to cool to room temperature. Ethyl acetate (~2 mL), dodecane (113 μL, internal standard) and water were added. The organic layer was subjected to GC analysis. The GC yield obtained was previously calibrated by authentic sample/dodecane calibration curve.

2.4.4 General Procedures for Acetoxylation of Substituted Indoles

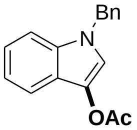
General procedures for acetoxylation of N-substituted indoles (the Pd catalysts loading range from 2-5 mol%): $Pd(OAc)_2$, $PhI(OAc)_2$ (1.0 mmol), *N*-substituted indoles (0.5 mmol) and KOAc (0.6 mmol)were loaded into a Schlenk tube equipped with a Teflon-coated magnetic stir bar. The tube was evacuated and flushed with nitrogen for three times. The solvent acetonitrile (1.0 mL) was then added with stirring at room temperature for several minutes. The tube was then placed into a preheated oil bath (70 °C/ 25 °C) and stirred for the time as indicated in Table 2.2 and 2.3. After completion of reaction as judged by GC analysis, the reaction tube was allowed to cool to room temperature and quenched with sodium bisulfate solution and water. Ethyl acetate was then added for dilution. The organic layer was separated and the aqueous layer was washed with ethyl acetate. The filtrate was concentrated under reduced pressure. The crude products were purified by flash column chromatography on silica gel (230-400 mesh) to afford the desired product.

2.4.5 General Procedures for the Reaction of Acetoxyindole with 2-Chloro-*N*,*N*-dimethylethylamine Hydrochloride

General procedures for the reaction of acetoxyindole with 2-chloro-N,N-dimethylethylamine hydrochloride: Acetoxyindole (0.5 mmol) was dissolved in a freshly distilled dry THF (4 ml) at room temperature under a nitrogen atmosphere. KOH (0.28 g, 5 mmol) and 2-chloro-*N*,*N*-dimethylethylamine hydrochloride (0.43 g, 3 mmol) were then added and the mixture was stirred at 60^{o}C overnight. After completion of reaction as judged by GC analysis, the reaction tube was allowed to cool to room temperature and 5 ml of water was added to the mixture. Chloroform ($CHCl_3$) was then added for dilution. The organic layer was separated and the aqueous layer was washed with $CHCl_3$. The filtrate was concentrated under reduced pressure. The crude products were purified by flash column chromatography on silica gel (230-400 mesh) to afford the desired product.

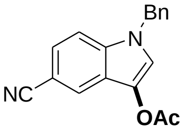
2.5 Characterization Data of Acetoxyindole and Related Products

1-Benzyl-1*H*-indol-3-yl acetate (Table 2.2, entry 1-3; Scheme 2.3)[35]



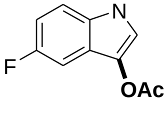
EA: Petroleum ether: Et_3N = 1:9: 0.1, R_f = 0.3; ^1H NMR (400 MHz, $CDCl_3$) δ 2.39 (s, 3H), 5.30 (s, 2H), 7.16-7.26 (m, 4H), 7.29-7.38 (m, 5H), 7.62-7.64 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 50.0, 109.6, 117.2, 117.6, 119.5, 120.3, 122.5, 126.7, 127.6, 128.7, 129.7, 133.3, 137.1, 168.4; MS (EI): *m/z* (relative intensity) 265 (M^+, 20), 223 (89), 91 (100).

1-Benzyl-5-cyano-1*H*-indol-3-yl acetate (Table 2.2, entry 4)



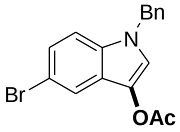
EA: Petroleum ether: Et_3N = 1: 2: 0.1, R_f = 0.5; ^1H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 5.29 (s, 2H), 7.13 (dd, *J*=1.2, 6.0 Hz, 2H), 7.30-7.41 (m, 5H), 7.50 (s, 1H), 7.96 (dd, *J*=0.4, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.7, 50.3, 102.6, 110.5, 119.4, 120.1, 123.5, 125.1, 126.7, 128.0, 128.8, 129.8, 134.2, 135.9; MS (EI): *m/z* (relative intensity) 290 (M^+, 9), 248 (57), 91 (100); HRMS: calcd. for $C_{18}H_{15}N_2O_2^+$: 291.1134, found 291.1140.

1-Benzyl-5-fluoro-1*H*-indol-3-yl acetate (Table 2.2, entry 5)



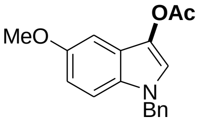
EA: Petroleum ether: Et_3N = 1: 9: 0.1, R_f = 0.4; ^1H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 5.26 (s, 2H), 6.95-7.00 (m, 1H), 7.14-7.21 (m, 3H), 7.26-7.36 (m, 4H), 7.42 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 50.3, 102.5, 102.7, 110.6, 110.7, 110.9, 111.2, 119.0, 120.4, 120.5, 126.7, 127.7, 128.7, 129.5, 129.9, 136.8, 156.5, 158.8, 168.3; MS (EI): *m/z* (relative intensity) 283 (M^+, 14), 241 (69), 91 (100); HRMS: calcd. for $C_{17}H_{15}NO_2F^+$: 284.1087, found 284.1048.

1-Benzyl-5-bromo-1*H*-indol-3-yl acetate (Table 2.2, entry 6)



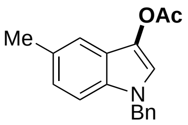
EA: Petroleum ether: Et_3N = 1: 9: 0.1, R_f = 0.3; ^1H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 5.24 (s, 2H), 7.12-7.26 (m, 3H), 7.28-7.33 (m, 4H), 7.38 (s, 1H), 7.76 (dd, *J*=0.4, 1.2Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 50.2, 111.2, 112.8, 118.4, 120.2, 121.9, 125.3, 126.6, 127.8, 128.7, 131.8, 136.6, 168.2; MS (EI): *m/z* (relative intensity) 343 (M^+, 8), 301 (43), 91 (100); HRMS: calcd. for $C_{17}H_{14}NO_2NaBr^+$: 366.0106, found 366.0117.

1-Benzyl-5-methoxy-1*H*-indol-3-yl acetate (Table 2.2, entry 7)



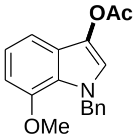
EA: Petroleum ether: Et_3N = 1: 4: 0.1, R_f = 0.5; ^1H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 3H), 3.90 (s, 3H), 5.24 (s, 2H), 6.89-6.92 (m, 1H), 7.05 (s, 1H), 7.14-7.19 (m, 3H), 7.28-7.36 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 50.1, 55.6, 98.7, 110.7, 113.2, 117.8, 120.4, 126.6, 127.5, 128.6, 129.3, 137.25, 154.0, 168.4; MS (EI): *m/z* (relative intensity) 295 (M^+, 25), 253 (100), 162 (26), 91 (90); HRMS: calcd. for $C_{18}H_{18}NO_3^+$: 296.1287, found 296.1290.

1-Benzyl-5-methyl-1*H*-indol-3-yl acetate (Table 2.2, entry 8)



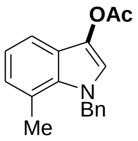
EA: Petroleum ether: Et_3N = 1: 6: 0.1, R_f = 0.5; ^1H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 3H), 2.51 (s, 3H), 5.27 (s, 2H), 7.06-7.18 (m, 4H), 7.28-7.36 (s, 4H), 7.42 (t, *J*=0.8Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 21.3, 50.0, 109.4, 117.1, 117.3, 120.5, 124.2, 126.7, 127.5, 128.6, 128.8, 129.2, 131.8, 137.3; MS (EI): *m/z* (relative intensity) 279 (M^+, 23), 257 (100), 146 (31), 91 (94); HRMS: calcd. for $C_{18}H_{18}NO_2^+$: 280.1338, found 280.1339.

1-Benzyl-7-methoxy-1*H*-indol-3-yl acetate (Table 2.2, entry 9)



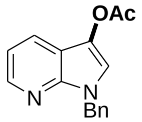
EA: Petroleum ether: Et_3N = 1: 6: 0.1, R_f = 0.45; ^1H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 3.88 (s, 3H), 5.63 (s, 2H), 6.7 (d, *J*=7.6Hz, 1H), 7.05-7.10 (m, 1H), 7.18-7.34 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 52.4, 55.2, 103.3, 110.2, 118.0, 120.0, 122.4, 123.1, 126.7, 127.1, 128.4, 129.8, 139.2, 147.4, 168.3; MS (EI): *m/z* (relative intensity) 295 (M^+, 33), 253 (100), 162 (16), 91 (64); HRMS: calcd. for $C_{18}H_{18}NO_3^+$: 296.1287, found 296.1293.

1-Benzyl-7-methyl-1*H*-indol-3-yl acetate (Table 2.2, entry 10)



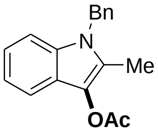
EA: Petroleum ether: Et_3N = 1: 9: 0.1, R_f = 0.45; ^1H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 2.54 (s, 3H), 5.55 (s, 2H), 6.92-6.98 (m, 3H), 7.04 (t, *J*=7.2Hz, 1H), 7.25-7.45 (m, 4H), 7.47 (d, *J*=0.4Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.5, 20.9, 52.2, 115.5, 118.9, 119.8, 121.2, 121.4, 125.4, 127.3, 128.8, 129.7, 132.2, 139.2, 168.4; MS (EI): *m/z* (relative intensity) 279 (M^+, 25), 237 (83), 146 (41), 91 (100); HRMS: calcd. for $C_{18}H_{17}NO_2Na^+$: 302.1157, found 302.1157.

1-Benzyl-1*H*-pyrrolo[2,3-b]pyridine-3-yl acetate (Table 2.2, entry 11)



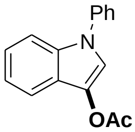
EA: Petroleum ether: Et_3N = 1: 6: 0.1, R_f = 0.5; ^1H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 5.50 (s, 2H), 7.10-7.14 (dd, *J*=0.8, 3.2 Hz, 1H), 7.24-7.35 (m, 6H), 7.89 (dd, *J*=1.6, 6.4 Hz, 1H), 7.10-8.40 (t, *J*=3.2Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.7, 47.5, 112.7, 115.7, 116.7, 126.2, 127.4, 127.6, 127.9, 128.6, 137.3, 143.8, 144.0; MS (EI): *m/z* (relative intensity) 266 (M^+, 16), 224 (92), 147 (18), 91 (100); HRMS: calcd. for $C_{16}H_{15}N_2O_2^+$: 267.1134, found 267.1130.

1-Benzyl-2-methyl-1*H*-indol-3-yl acetate (Table 2.2, entry 12)



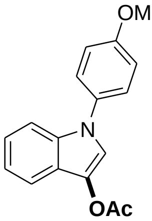
EA: Petroleum ether: Et_3N = 1: 4: 0.1, R_f = 0.7; ^1H NMR (400 MHz, $CDCl_3$) δ 2.28 (s, 3H), 2.44 (s, 3H), 5.31 (s, 2H), 7.04 (d, *J*=6.8 Hz, 2H), 7.14-7.20 (m, 2H), 7.25-7.34 (m, 4H), 7.45-7.47 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.0, 20.5, 46.4, 109.3, 116.7, 119.6, 120.7, 121.4, 125.6, 125.9, 126.5, 127.3, 128.7, 133.9, 137.5, 169.3; MS (EI): *m/z* (relative intensity) 279 (M^+, 23), 237 (100), 146 (35), 91 (91); HRMS: calcd. for $C_{18}H_{18}NO_2^+$: 280.1338, found 280.1341.

1-Phenyl-1*H*-indol-3-yl acetate (Table 2.3, entry 1)[36]



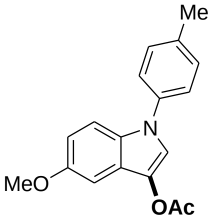
EA: Petroleum ether: Et_3N = 1: 9: 0.1, R_f = 0.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 3H), 7.25-7.33 (m, 2H), 7.37-7.41 (m, 1H), 7.54-7.70 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 110.5, 116.9, 117.7, 120.3, 121.1, 123.1, 124.3, 126.3, 129.5, 131.4, 132.7, 139.3, 168.3; MS (EI): *m/z* (relative intensity) 251 (M^+, 18), 209 (100), 180 (33), 77 (20).

1-(4-Methoxyphenyl)-1*H*-indol-3-yl acetate (Table 2.3, entry 2)[37]



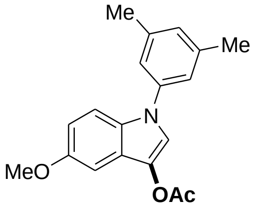
EA: Petroleum ether: Et_3N = 1: 4: 0.1, R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3H), 3.90 (s, 3H), 7.04-7.08 (m, 2H), 7.21-7.30 (m, 2H), 7.43-7.44 (m, 3H), 7.45 (s, 1H), 7.47-7.69 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 55.4, 110.3, 114.6, 117.3, 117.6, 120.0, 120.7, 122.9, 125.9, 130.9, 132.2, 133.2, 158.1, 168.3; MS (EI): *m/z* (relative intensity) 281 (M^+, 22), 239 (100), 210 (15), 77 (12).

5-Methoxy-1-(4-methylphenyl)-1*H*-indol-3-yl acetate (Table 2.3, entry 3)



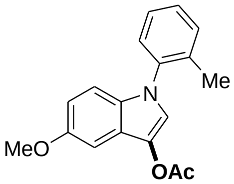
EA: Petroleum ether: Et_3N = 1: 4: 0.1, R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (d, *J*=6.8 Hz, 3H), 3.92 (s, 3H), 6.93 (dd, *J*=2.0, 6.8 Hz, 1H), 7.07 (d, *J*=2.8 Hz, 1H), 7.32 (d, *J*=4.0, 2H), 7.39-7.46 (m, 5H), 7.56 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 20.9, 55.7, 98.8, 111.6, 113.5, 117.5, 121.2, 123.9, 128.1, 130.0, 130.9, 136.0, 136.9, 154.4, 158.3; MS (EI): *m/z* (relative intensity) 295 (M^+, 22), 253 (100), 210 (15); HRMS: calcd. for $C_{18}H_{18}NO_3^+$: 296.1287, found 296.1295.

1-(3,5-Dimethylphenyl)-5-methoxy-1*H*-indol-3-yl acetate (Table 2.3, entry 4)



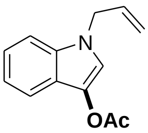
EA: Petroleum ether: Et_3N = 1: 4: 0.1, R_f = 0.5; ^1H NMR (400 MHz, $CDCl_3$) δ 2.43 (d, *J*=3.6 Hz, 9H), 3.93 (s, 3H), 6.95 (dd, *J*=2.8, 6.4 Hz, 1H), 7.00 (s, 1H), 7.07 (d, *J*=2.4 Hz, 1H), 7.14 (s, 2H), 7.50 (d, *J*=8.8 Hz, 1H), 7.58 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 21.2, 55.7, 98.7, 111.7, 113.5, 117.4, 121.3, 121.7, 127.8, 128.0, 131.0, 139.2, 139.3, 154.4, 158.3; MS (EI): *m/z* (relative intensity) 309 (M^+, 24), 267 (100), 251 (18); HRMS: calcd. for $C_{19}H_{20}NO_3^+$: 310.1443, found 310.1454.

5-Methoxy-1-*o*-tolyl-1*H*-indol-3-yl acetate (Table 2.3, entry 5)



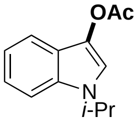
EA: Petroleum ether: Et_3N = 1: 4: 0.1, R_f = 0.7; ^1H NMR (400 MHz, $CDCl_3$) δ 2.13 (s, 3H), 2.43 (s, 3H), 3.92 (s, 3H), 6.88-6.97 (m, 2H), 7.09 (d, *J*=2.0 Hz, 1H), 7.33-7.43 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.5, 20.9, 55.7, 98.7, 111.6, 113.5, 118.3, 120.2, 126.6, 128.1, 128.1, 129.3, 130.4, 131.1, 135.7, 137.8, 154.3, 168.2; MS (EI): *m/z* (relative intensity) 295 (M^+, 23), 253 (100), 238 (20); HRMS: calcd. for $C_{18}H_{17}NO_3Na^+$: 318.1106, found 318.1093.

1-Allyl-1*H*-indol-3-yl acetate (Scheme 2.1)



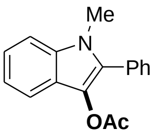
EA: Petroleum ether: Et_3N = 1: 9: 0.1, R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.39 (s, 3H), 4.70-4.72 (m, 2H), 5.12-5.14 (m, 1H), 5.17-5.18 (m, 1H), 5.22-5.26 (m, 1H), 5.96-6.06 (m, 1H), 7.14-7.18 (m, 1H), 7.24-7.28 (m, 1H), 7.31-7.33 (m, 2H), 7.58-7.61 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 48.7, 109.5, 116.8, 117.4, 117.5, 119.4, 120.3, 122.3, 129.5, 133.1, 133.1, 168.3; MS (EI): *m/z* (relative intensity) 215 (M^+, 28), 173 (100), 132 (76); HRMS: calcd. for $C_{13}H_{13}NO_2Na^+$: 238.084, found 238.0851.

1-Isopropyl-1*H*-indol-3-yl acetate (Scheme 2.1)



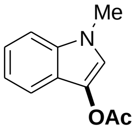
EA: Petroleum ether: Et_3N = 1: 9: 0.1, R_f = 0.45; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.56 (d, *J*=6.8 Hz, 6H), 2.41 (s, 3H), 4.68-4.75 (m, 1H), 7.16-7.20 (m, 1H), 7.27-7.31 (m, 1H), 7.41 (d, *J*=8.4 Hz, 1H), 7.47 (s, 1H), 7.63 (d, *J*=8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 22.5, 47.0, 109.3, 112.7, 117.5, 119.1, 120.1, 121.9, 129.5, 132.4, 168.5; MS (EI): *m/z* (relative intensity) 217 (M^+, 34), 175 (89), 160 (100), 132 (44); HRMS: calcd. for $C_{13}H_{15}NO_2Na^+$: 240.1000, found 240.1002.

1-Methyl-2-phenyl-1*H*-indol-3-yl acetate (Scheme 2.1)



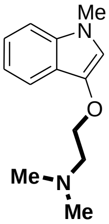
EA: Petroleum ether: Et_3N = 1: 9: 0.1, R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 3H), 3.72 (s, 3H), 7.21-7.25 (m, 1H), 7.31-7.35 (m, 1H), 7.41-7.57 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.4, 30.8, 109.7, 117.3, 119.9, 120.5, 122.4, 126.4, 128.2, 128.5, 129.4, 130.0, 134.9, 169.8; MS (EI): *m/z* (relative intensity) 265 (M^+, 13), 223 (100); HRMS: calcd. for $C_{17}H_{16}NO_2^+$: 266.1181, found 266.1173.

1-Methyl-1*H*-indol-3-yl acetate (Scheme 2.3)[38]



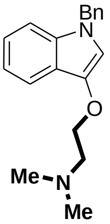
EA: Hexane: Et_3N = 1:4: 0.1, R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.39 (s, 3H), 3.77 (s, 3H), 7.14-7.18 (m, 1H), 7.26-7.34 (m, 3H), 7.57-7.60 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 32.7, 109.2, 117.4, 117.8, 119.2, 120.0, 122.2, 129.0, 133.6, 168.7; MS (EI): *m/z* (relative intensity) 189 (M^+, 21), 147 (100), 132 (11), 77 (13).

***N,N*-Dimethyl-2-(1-methyl-1*H*-indol-3-yloxy)ethanamine (Scheme 2.3)**



MeOH: $CHCl_3$ = 1: 9, R_f = 0.45; ^{1}H NMR (400 MHz, C_6D_6) δ 2.18 (s, 6H), 2.64 (t, *J*=6.0 Hz, 2H), 2.97 (s, 3H), 3.98 (t, *J*=6.0 Hz, 2H), 6.11 (s, 1H), 6.98 (d, *J*=8.0 Hz, 1H), 7.09-7.22 (m, 2H), 7.94 (d, *J*=8.0 Hz, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 31.9, 46.0, 58.7, 70.0, 109.2, 110.0, 118.5, 118.7, 120.6, 122.5, 135.3, 140.4; MS (EI): *m/z* (relative intensity) 218 (M^+, 8), 146 (10), 72 (100), 58 (33) ; HRMS: calcd. for $C_{13}H_{19}N_2O^+$: 219.1497, found 219.1506.

N,N-Dimethyl-2-(1-benzyl-1*H*-indol-3-yloxy)ethanamine (Scheme 2.3)



MeOH: $CHCl_3$ = 1: 9, R_f = 0.5; ^{1}H NMR (400 MHz, C_6D_6) δ 2.16 (s, 6H), 2.62 (t, *J*=6.0 Hz, 2H), 3.93 (t, *J*=8.0 Hz, 2H), 4.68 (s, 2H), 6.27 (s, 1H), 6.81-6.84 (m, 2H), 6.97-7.03 (m, 4H), 7.07-7.16 (m, 2H), 7.96-7.98 (m, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 46.6, 50.1, 59.2, 70.4, 109.6, 110.2, 119.4, 119.5, 121.5, 123.6, 127.4, 128.1, 128.3, 129.4, 135.7, 139.1, 141.6; MS (EI): *m/z* (relative intensity) 294 (M^+, 7), 91 (32), 72 (100), 58 (23) ; HRMS: calcd. for $C_{19}H_{23}N_2O^+$: 295.1810, found 295.1796.

2.6 References

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Chapter 3 Palladium-Catalyzed *ortho*-CH-Bond Oxygenation of Aromatic Ketones

3.1 Introduction

Phenols bearing an acyl group are important and commonly found sub-unit in a number of drug-relevant and bioactive molecules (Figure 3.1).[1] In particular, *ortho*-acylphenols are versatile synthetic building blocks for preparing various pharmaceuticals and natural products.[2] Thus, method development for accessing this structural motif is of high interest.

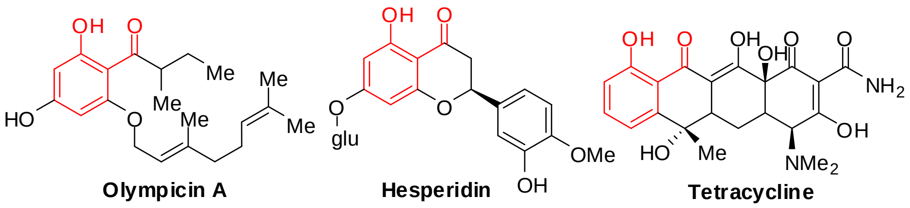


Figure 3.1. Pharmaceuticals and natural products bearing *ortho*-acylphenol skeleton

Transition metal-catalyzed directed $C_{(sp2)}$-H bond cleavage/$C_{(sp2)}$-O bond formation approach is a desirable protocol. Sanford, Yu, Rao and Lei groups recently showed that Ru, Cu, Pd complexes could be applied in hydroxylation of substituted arenes and carboxylic acid salts.[3] However, additional steps are necessary to directly obtain the phenol with ketone moiety. Therefore, it would be attractive to access *ortho*-acylphenols if ketone group could be directly employed as the directing group for direct $C_{(sp2)}$-H bond oxygenation.

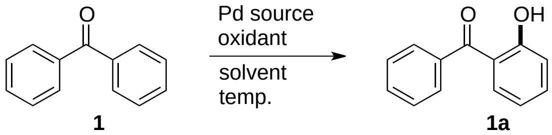
Inspired by the need for efficient synthesis of *ortho*-acylphenol motifs from arylketones, we started to embark this challenge by using a Pd-catalyzed arene oxygenation approach. In continuing our research program on Pd-catalyzed *ortho*-acylaniline synthesis[4] and direct C-H acetoxylation,[5] herein we report our investigation on the ketone-directed *ortho*-oxygenation of aromatic ketones. This protocol demonstrates a straightforward access of *ortho*-acylphenol frameworks and also allows enolizable ketones to react smoothly. In particular, halo groups are found to be compatible under these mild reaction conditions (80 °C). The hydroxylation of aryl ketone protocol is attractive as aryl ketones have rich available feedstock and can be prepared in one step through electrophilic aromatic acylation, benzylic oxidations or other related means.

3.2 Result and Discussion

3.2.1 Preliminary Evaluation of Palladium-Catalyzed Oxygenation of Aromatic Ketones

In order to test the feasibility of the palladium-catalyzed oxygenation of aromatic ketones, we initially started our investigation by using benzophenone as the model substrate (Table 3.1). Commonly used oxidants were examined (entries 1-4). A more electrophilic oxidants, $PhI(OTFA)_2$, was found significantly better than $PhI(OAc)_2$ (entry 3 vs 4). However, there was no essential difference between $Pd(OAc)_2$ and $Pd(OTFA)_2$ when they were used as the pre-catalysts (entry 10 vs 12). A screening of solvent revealed that DCE was the solvent of choice (entries 4-7). Lowering the catalyst loading to 5 mol % Pd was found capable (entries 8-10). Indeed, the initial product formed from this reaction was the 2-trifluoroacetoxylbenzophenone. Upon aqueous workup, the desired hydrolyzed phenolic product was obtained.

Table 3.1. A screening of Pd-catalyzed *ortho*-oxygenation reaction conditions[a]



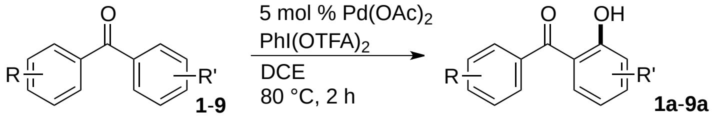
entry	Pd (mol %)	oxidant	solvent	temp/ °C	% yield[b]
1	$Pd(OAc)_2$ (10)	BQ	DCE	80	0
2	$Pd(OAc)_2$ (10)	$K_2S_2O_8$	DCE	80	0
3	$Pd(OAc)_2$ (10)	$PhI(OAc)_2$	DCE	80	0
4	$Pd(OAc)_2$ (10)	$PhI(OTFA)_2$	DCE	80	82
5	$Pd(OAc)_2$ (10)	$PhI(OTFA)_2$	toluene	110	0
6	$Pd(OAc)_2$ (10)	$PhI(OTFA)_2$	dioxane	80	4
7	$Pd(OAc)_2$ (10)	$PhI(OTFA)_2$	THF	80	6
8	$Pd(OAc)_2$ (1)	$PhI(OTFA)_2$	DCE	80	5
9	$Pd(OAc)_2$ (2)	$PhI(OTFA)_2$	DCE	80	45
10	$Pd(OAc)_2$ (5)	$PhI(OTFA)_2$	DCE	80	79 (71)
11	$Pd(OAc)_2$ (10)	$PhI(OTFA)_2$	DCE	50	10
12	$Pd(TFA)_2$ (5)	$PhI(OTFA)_2$	DCE	80	80
13	$Pd(TFA)_2$ (5)	$PhI(OAc)_2$	DCE	80	0
14[c]	$Pd(OAc)_2$ (10)	$PhI(OAc)_2$	CH_3CN	80	0

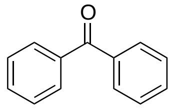
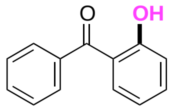
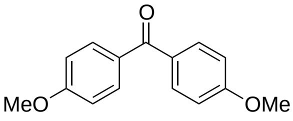
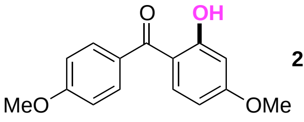
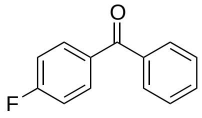
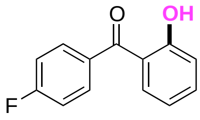
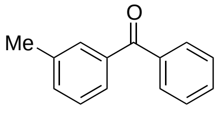
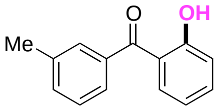
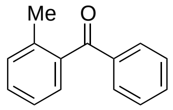
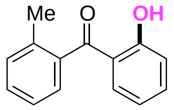
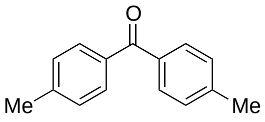
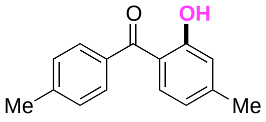
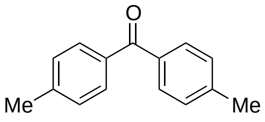
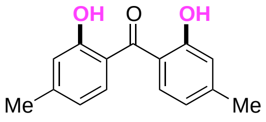
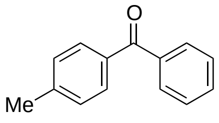
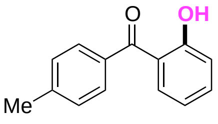
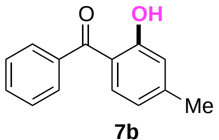
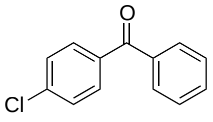
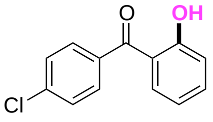
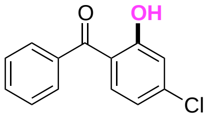
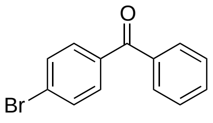
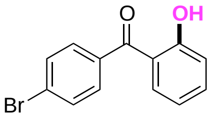
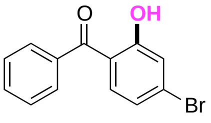
[a]Reaction conditions: Benzophenone (0.5 mmol), Pd source (mol % as indicated), oxidant (1.0 mmol) and solvent (2.0 mL) were stirred at specified reaction temperature for 2 h under air. [b]Calibrated GC yields were reported using dodecane as the internal standard. Isolated yield in parenthesis. [c]KOAc was added as base.

3.2.2 Scope of Palladium-Catalyzed Oxygenation of Aromatic Ketones

With our optimized reaction conditions in hand, we next tested the substrate scope of this oxgyenation reaction (Table 3.2).

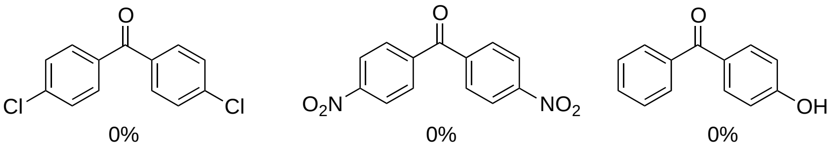
Table 3.2. Pd-catalyzed *ortho*-oxygenation of benzophenone derivatives[a]



entry	ArC(O)Ar'	product	% yield[b]
1	 **1**	 **1a**	81
2	 **2**	 **2a**	70
3	 **3**	 **3a**	88
4	 **4**	 **4a**	72
5	 **5**	 **5a**	71
6[c]	 **6**	 **6a**	86
7[d]	 **6**	 **6b**	68
8	 **7**	 **7a**  **7b** **7a**:**7b** = 1:1	86
9	 **8**	 **8a**  **8b** **8a**:**8b** = 20:1	73
10	 **9**	 **9a**  **9b** **9a**:**9b** = 20:1	85

[a] Reaction conditions: Substituted benzophenones **1-9** (0.5 mmol), Pd(OAc)$_2$ (5 mol %), PhI(OTFA)$_2$ (1.0 mmol) and DCE (2.0 mL) were stirred at 80 ℃ for 2 h under air. [b] Isolated yields were reported. [c] 0.75 mmol of PhI(OTFA)$_2$ was used. [d] 1.2 mmol of PhI(OTFA)$_2$ was used.

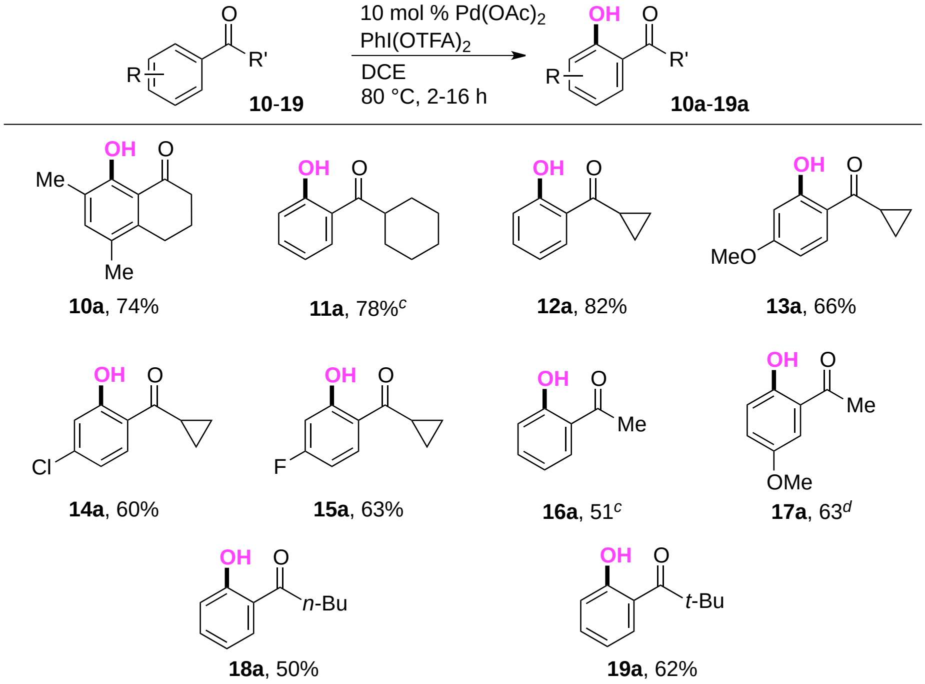
The aromatic ketones proceeded smoothly to give the corresponding product in good yields. Fluoro, chloro and bromo groups were compatible under these reaction conditions (entries 3, 9-10). This halo group tolerance is versatile for further modification of *ortho*-acylphenol using traditional cross-coupling technology.[6] Apart from the symmetrical diarylketones, we also probed the hydroxylation regioselectivity of the unsymmetrical diarylketones (entries 3-5, 8-10). Steric effect allowed regioselective hydroxylation of the unsubstituted phenyl ring (entries 4-5). The electron-withdrawing group on the unsymmetrical diarylketones offered a regioselective electrophilic palladation on other phenyl ring. Essentially complete regioselectivity was observed when 4-fluorobenzophenone was employed (entry 3). Less electron-withdrawing groups (e.g. –Cl & –Br) provided regioselectivity as high as 20 to 1 (entries 9-10). On contrary, no regioselective hydroxylation was observed when tolylphenylketone was used (entry 8). Addition of 2.4 equivalents of $PhI(OTFA)_2$ promoted dihydroxylation product (entry 7). When benzophenone substituted with electron-withdrawing group, the hydroxylation process was failed (Scheme 3.1).



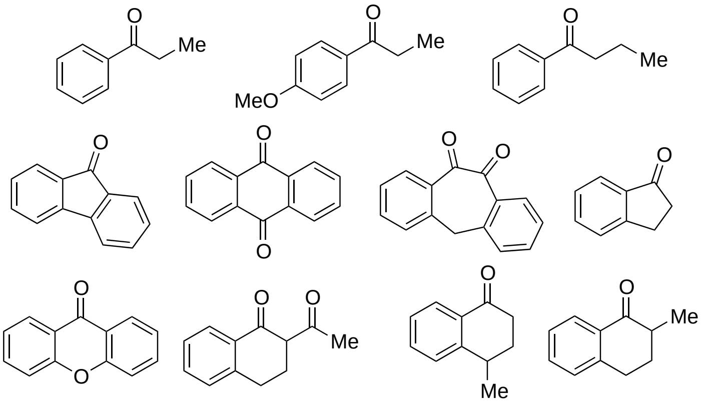
Scheme 3.1. Unsuccessful substrates in the hydroxylation protocol

3.2.3 Scope of Palladium-Catalyzed Oxygenation of Arylalkylketones

Enolizable arylalkylketones were also examined in this Pd-catalyzed *ortho*-oxygenation reaction (Scheme 3.2). Tetralone reacted smoothly to give corresponding product in good yield (**10a**). Cyclohexylphenylketone and cyclopropylarylketones furnished the hydroxylated products without being affected by the substituted groups at the *para*-position (**13a-15a**, with respected to the acyl group). Primary alkyl arylketone (e.g. acetophenone & *p*-OMe-acetophenone) proceeded to form the desired products **16a** and **17a**. In general, lower yield was obtained since the alpha-proton of primary alkylarylketones can be easily oxidized through Baeyer-Villiger-type oxidation to give side-products.



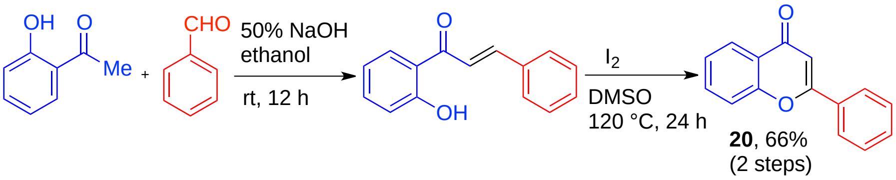
Scheme 3.2. Pd-catalyzed *ortho*-oxygenation of alkylarylketones (Reaction conditions: Substituted benzophenones **10-19** (0.5 mmol), $Pd(OAc)_2$ (10 mol %), $PhI(OTFA)_2$ (1.0 mmol) and DCE (2.0 mL) were stirred at 80 ℃ for 2 h under air. [b]Isolated yields were reported. [c]16 h were used. [d]5 mol% of $Pd(OAc)_2$ was used, and 0.2 mmol of $PhI(OTFA)_2$ was used.)



Scheme 3.3. Unsuccessful arylalkylketones in the hydroxylation protocol

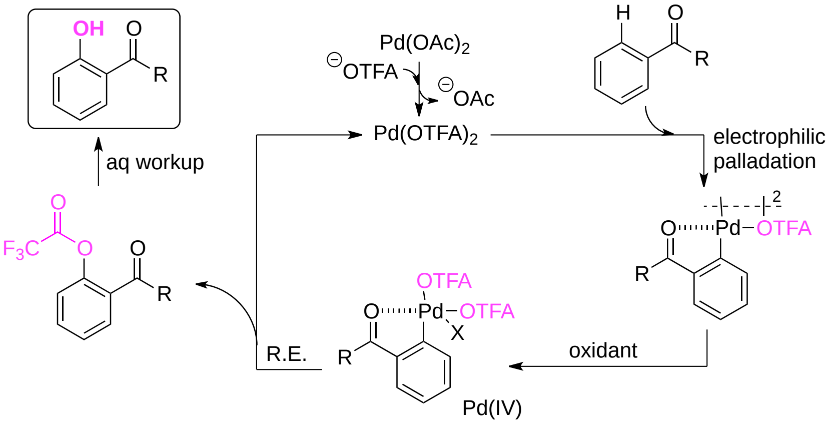
3.2.4 Application of Palladium-Catalyzed Oxygenation of Arylalkylketones

The hydroxylated arylalkyl ketone products are versatile materials for synthesizing various substituted flavones through a modular assembly with arylaldehydes (Scheme 3.4).[7] Importantly, the *t*-butylphenyl ketone was applicable in this reaction. This substrate was found to be problematic in Fries rearrangement.[8]



Scheme 3.4. Application of the hydroxylated product for the modular synthesis of flavones

3.2.5 Proposed Mechansim of Palladium-Catalyzed Oxygenation of Aromatic Ketone



Scheme 3.5. Proposed mechanism of Pd-catalyzed oxygenation of aryl ketones

For the mechanism of oxygenation, there is a ligand exchange for $Pd(OAc)_2$ to $Pd(OTFA)_2$ for the first step. After that, similar mechanism was carried out with that of acetoxylation. Electrophilic plladation of aryl ketones occurred that the Pd(II) coordinated to the ketone carbonyl oxygen and then undergo chelate-directed C-H activation to afford a cylcophalladium(II) dimeric intermediate. Then, subsequent oxidation occur from Pd(II) to Pd(IV) complexes. Reductive elimination was then followed to give the trifluoroacetated products and regenerate the Pd(II) species. Finally, the trifluoroacetated aryl ketones was converted into the hydroxylated ketone after aqueous workup.

3.3 Conclusion

In summary, we have reported the first ketone-directed Pd-catalyzed oxygenation of arenes. This protocol represents a direct and facile approach for accessing a variety of *ortho*-acylphenol compounds from arylketones. In view of the rich feedstock of arylketones in nature, we believe this method has a significant value in organic synthesis. In particular, the success of this research would inspire further explorations of simple ketone-directed C-H bond functionalizations.

3.4 Experimental Section

3.4.1 General Considerations

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. All oxygenation reactions were performed in reaction tube (approx. 10 mL volume) equipped with a septum in the presence of Teflon coated magnetic stirrer bar (3 mm × 10 mm). Dichloroethane (DCE) was distilled under calcium hydride under reduced pressure. Dioxane and tetrahydrofuran (THF) were distilled from sodium under nitrogen. Acetonitrile was distilled from calcium hydride under nitrogen prior to use. Thin layer chromatography was performed on Merck precoated silica gel 60 F_{254} plates. Silica gel (Merck, 70-230 and 230-400 mesh) was used for column chromatography. ^{1}H NMR spectra were recorded on a Bruker (400 MHz) or Varian (500 MHz) spectrometer. Spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.26 ppm), or with tetramethylsilane (TMS, δ 0.00 ppm) as the internal standard. Chemical shifts (δ) were reported as part per million (ppm) in δ scale downfield from TMS. ^{13}C NMR spectra were referenced to $CDCl_3$ (δ 77.0 ppm, the middle peak). Coupling constants (J) were reported in Hertz (Hz). Mass spectra (EI-MS and ES-MS) were recorded on a HP 5989B Mass Spectrometer. High-resolution mass spectra (HRMS) were obtained on a Brüker APEX 47e FT-ICR mass spectrometer (ESIMS). GC-MS analysis was conducted on a HP 5973 GCD system using a HP5MS column (30 m × 0.25 mm). The products described in GC yield were accorded to the authentic samples/dodecane calibration standard from HP 6890 GC-FID system.

3.4.2 General Procedures for Initial Reaction Conditions Screening

General Procedure for reaction condition screenings: $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), oxidant (1.0 mmol), benzophenone (0.5 mmol) and solvent (2.0 mL) were loaded into a reaction tube equipped with a septum in the presence of Teflon coated magnetic stirrer bar under air. The tube was then placed into a preheated oil bath (80 °C) and stirred for the time as indicated. After completion of reaction, the reaction tube was allowed to cool to room temperature. Ethyl acetate (~2 mL), dodecane (113 μL, internal standard) and water were added. The organic layer was subjected to GC analysis. The GC yield obtained was previously calibrated by authentic sample/dodecane calibration curve.

3.4.3 General Procedures for Oxygenation of Aromatic Ketones

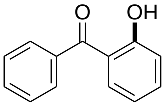
General procedures for oxygenation of aromatic ketones (the Pd catalysts loading range from 5-10 mol%): $Pd(OAc)_2$, $PhI(OTFA)_2$ (1.0 mmol), aromatic ketones (0.5 mmol) and DCE (2.0 mL) were loaded into a reaction tube equipped with a septum in the presence of Teflon coated magnetic stirrer bar under air. The tube was then placed into a preheated oil bath (80 °C) and stirred for the time as indicated. After completion of reaction as judged by GC analysis, the reaction tube was allowed to cool to room temperature and quenched with water. Ethyl acetate was then added for dilution. The organic layer was separated and the aqueous layer was washed with ethyl acetate. The filtrate was concentrated under reduced pressure. The crude products were purified by flash column chromatography on silica gel (230-400 mesh) to afford the desired product.

3.4.4 General Procedures for Further Synthesis of Flavones

General procedures for further synthesis of flavones from hydroxylated products: $Pd(OAc)_2$ (10.0 mol%), $PhI(OTFA)_2$ (4.0 mmol), acetophenone (2.0 mmol) and DCE (8.0 mL) were loaded into a reaction tube equipped with a septum in the presence of Teflon coated magnetic stirrer bar under air. The tube was then placed into a preheated oil bath (80 °C) and stirred for 2 h. After isolation of the desired hydroxylated product, benzaldehyde was added with 50% NaOH and ethanol and further reaction was carried out by adding I_2 in DMSO to form flavones according to the literature procedures.[9]

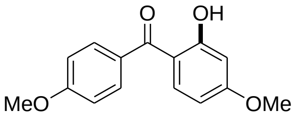
3.5 Characterization Data of Hydroxylated Products

(2-Hydroxyphenyl)phenylmethanone (Table 3.2, entry 1, product 1a)[10]



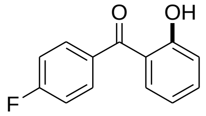
EA: Hexane = 1:9, R_f = 0.6, yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (t, *J* = 7.6 Hz, 1H), 7.09-7.12 (m, 1H), 7.53 (t, *J* = 7.6 Hz, 3H), 7.59-7.62 (m, 2H), 7.70 (d, *J* = 7.2 Hz, 1H), 12.07 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.4, 118.6, 118.7, 118.8, 119.1, 119.8, 128.3, 129.1, 131.9, 133.0, 133.6, 135.9, 136.3, 137.9, 163.2, 201.6.

(2-Hydroxy-4-methoxyphenyl)(4-methoxyphenyl)methanone (Table 3.2, entry 2, product 2a)[11]



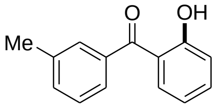
EA: Hexane = 1:9, R_f = 0.25, yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 (d, *J* = 10.8 Hz, 6H), 6.42-6.53 (m, 1H), 7.00 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 9.2 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 12.70 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.4, 55.5, 101.1, 107.1, 113.2, 113.6, 130.7, 131.3, 134.4, 134.9, 162.5, 165.88, 166.0, 198.7.

(4-Fluorophenyl)(2-hydroxyphenyl)methanone (Table 3.2, entry 3, product 3a)[12]



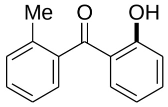
EA: Hexane = 1:9, R_f = 0.6, yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 7.20 (t, *J* = 8.8 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.73 (m, 2H), 11.91 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 115.4, 115.6, 118.5, 118.7, 119.0, 128.4, 129.0, 131.7, 131.8, 133.2, 134.0, 136.4, 163.1, 163.7, 166.2, 199.9.

(2-Hydroxyphenyl)(*m*-tolyl)methanone (Table 3.2, entry 4, product 4a)[13]



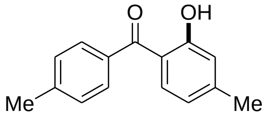
EA: Hexane = 1:9, R_f = 0.6, yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.27 (s, 3H), 7.00 (d, *J* = 8.4 Hz, 1H), 7.36 (t, *J* = 8.4 Hz, 2H), 7.53 (t, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 7.2 Hz, 2H) , 11.86 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.4, 118.1, 118.8, 127.7, 128.3, 129.1, 131.7, 133.2, 137.3, 138.1, 161.1, 201.6.

(2-Hydroxyphenyl)(*o*-tolyl)methanone (Table 3.2, entry 5, product 5a)[14]



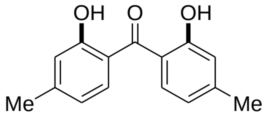
EA: Hexane = 1:9, R_f = 0.6, colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 3H), 6.83 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 1H), 7.29-7.33 (m, 4H), 7.41-7.45 (m, *1*H), 7.52 (t, *J* = 7.6 Hz, 2H) , 12.27 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.5, 118.3, 118.8, 119.9, 125.3, 127.4, 130.1, 130.8, 133.7, 135.5, 136.7, 137.8, 163.3, 204.4.

(2-Hydroxy-4-methylphenyl)(*p*-tolyl)methanone (Table 3.2, entry 6, product 6a)[15]



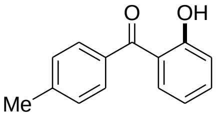
EA: Hexane = 1:9, R_f = 0.65, yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.39 (s, 3H), 2.47 (s, 3H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.90 (s, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 2H), 12.17 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 21.9, 117.9, 118.4, 119.8, 128.9, 129.3, 133.4, 135.3, 142.4, 147.7, 163.3, 200.8.

Bis(2-hydroxy-4-methylphenyl)methanone (Table 3.2, entry 7, product 6b)[16]

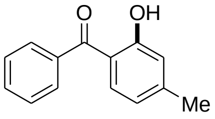


EA: Hexane = 1:9, R_f = 0.6, yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 6H), 6.76 (d, *J* = 8.0 Hz, 2H), 6.90 (s, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 10.78 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 117.5, 118.6, 120.0, 132.9, 147.3, 161.9, 201.4.

(2-Hydroxyphenyl)(*p*-tolyl)methanone (Table 3.2, entry 8, product 7a)[17] **(2-Hydroxy-4-methylphenyl)(phenyl)methanone (Table 3.2, entry 8, product 7b)**[17]



7a

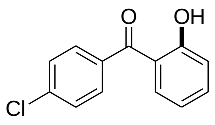


7b

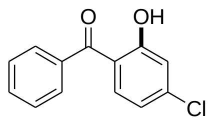
EA: Hexane = 1:9, R_f = 0.5, yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 3H), 2.47 (s,3H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 6.8 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.48-7.53 (m, 4H), 7.58-7.64 (m, 3H), 7.68 (d, *J* = 7.6 Hz, 3H), 12.05 (s, 1H), 12.14 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

21.6, 22.0, 116.9, 118.3, 118.4, 118.5, 119.3, 119.9, 128.3, 129.0, 129.4, 131.7, 133.5, 135.1, 136.0, 138.1, 142.7, 148.0, 163.1, 163.4, 201.1, 201.3.

(4-Chlorophenyl)(2-hydroxyphenyl)methanone (Table 3.2, entry 9, product 8a)[17] **(4-Chloro-2-hydroxyphenyl)(phenyl)methanone (Table 3.2, entry 9, product 8b)**[18]



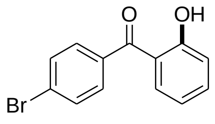
8a



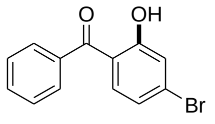
8b

EA: Hexane = 1:9, R_f = 0.5, yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (d, *J* = 7.2 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 7.47-7.57 (m, 4H), 7.67 (d, *J* = 7.2 Hz, 2H), 7.79 (d, *J* = 6.8 Hz, 1H), 11.9 (s, 1H), 12.21 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.5, 118.8, 118.9, 119.3, 128.4, 128.6, 128.7, 129.0, 129.9, 130.6, 131.4, 132.2, 133.2, 134.5, 136.1, 136.5, 138.4, 163.2, 200.1.

(4-Bromophenyl)(2-hydroxyphenyl)methanone (Table 3.2, entry 10, product 9a)[19] **(4-Bromo-2-hydroxyphenyl)(phenyl)methanone (Table 3.2, entry 10, product 9b)**[20]



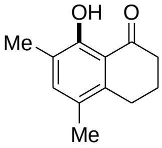
9a



9b

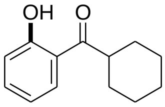
EA: Hexane = 1:9, R_f = 0.5, yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (t, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 7.51-7.58 (m, 4H), 7.67 (d, *J* = 8.4 Hz, 3H), 11.90 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.5, 118.8, 121.6, 122.2, 126.9, 128.4, 128.5, 129.1, 129.9, 130.7, 130.9, 131.5, 131.6, 132.2, 133.2, 134.4, 136.6, 163.2, 163.6, 200.3.

3,4-Dihydro-8-hydroxy-5,7-dimethylnaphthalen-1(2*H*)-one (Scheme 3.4, product 10a)[21]



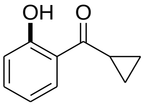
EA: Hexane = 1:9, R_f = 0.7, pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.08-2.14 (m, 2H), 2.20 (d, *J* = 10.0 Hz, 6H), 2.67 (d, *J* = 6.8 Hz, 2H), 2.82 (d, *J* = 6.4 Hz, 2H), 7.16 (s, 1H), 12.72 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.9, 18.6, 22.5, 26.6, 38.8, 116.3, 123.7, 124.8, 139.2, 139.9, 159.5, 205.6.

Cyclohexyl(2-hydroxyphenyl)methanone (Scheme 3.4, product 11a)[22]



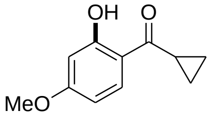
EA: Hexane = 1:9, R_f = 0.5, yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28-1.65 (m, 5H), 1.78 (d, *J* = 11.2 Hz, 1H), 1.90 (s, 4H), 3.32 (t, *J* = 11.2 Hz, 1H), 6.91 (t, *J* = 7.2 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 1H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.80 (d, *J* = 7.2 Hz, 1H), 12.60 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.7, 25.8, 29.5, 45.2, 118.2, 118.7, 129.7, 136.1, 163.1, 210.1.

Cyclopropyl(2-hydroxyphenyl)methanone (Scheme 3.4, product 12a)[23]



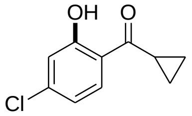
EA: Hexane = 1:9, R_f = 0.5, yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.1-1.14 (m, 2H), 1.30-1.34 (m, 2H), 2.69-2.76 (m, 1H), 6.93-7.01 (m, 2H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.99 (d, *J* = 7.6 Hz, 1H), 12.52 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.1, 16.4, 118.3, 118.8, 120.1, 130.0, 136.0, 162.1, 205.5.

Cyclopropyl(2-hydroxy-4-methoxyphenyl)methanone (Scheme 3.4, product 13a)



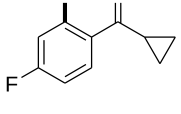
EA: Hexane = 1:9, R_f = 0.35, yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.06-1.09 (m, 2H), 1.26-1.30 (m, 2H), 2.57-2.63 (m, 1H), 3.86 (s, 3H), 6.44-6.51 (m, 2H), 7.88 (d, *J* = 9.2 Hz, 1H), 13.04 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.6, 16.0, 55.5, 100.9, 107.5, 114.2, 131.5, 165.0, 165.8, 203.6; HRMS: calcd. for $C_{11}H_{13}O_3^+$: 193.0864, found 193.00869.

Cyclopropyl(2-hydroxy-4-chlorophenyl)methanone (Scheme 3.4, product 14a)



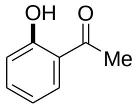
EA: Hexane = 1:9, R_f = 0.45, yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.12-1.17 (m, 2H), 1.31-1.35 (m, 2H), 1.59 (s, 1H), 2.61-2.68 (m, 1H), 6.93 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.02 (s, 1H), 7.91 (d, *J* = 8.4, 1H), 12.68 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.4, 16.6, 118.4, 118.6, 119.5, 130.9, 141.7, 162.8, 182.6, 204.8; HRMS: calcd. for $C_{10}H_{10}O_2Cl^+$: 197.0369, found 197.0366.

Cyclopropyl(2-hydroxy-4-fluorophenyl)methanone (Scheme 3.4, product 15a)[24]



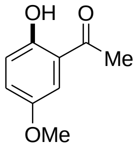
EA: Hexane = 1:9, R_f = 0.45, yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.12-1.15 (m, 2H), 1.31-1.63 (m, 2H), 2.60-2.66 (m, 1H), 6.64-6.69 (m, 2H), 7.99 (t, *J* = 6.8 Hz, 1H), 12.88 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.2, 16.5, 104.7, 105.0, 106.9, 107.1, 117.2, 132.2, 132.3, 164.6, 164.8, 166.1, 168.6, 204.4.

1-(2-Hydroxyphenyl)ethanone (Scheme 3.4, product 16a)[25]



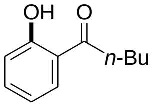
EA: Hexane = 1:9, R_f = 0.45, yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.66 (s, 3H), 6.92 (t, *J* = 7.6 Hz, 1H), 7.00 (t, *J* = 8.4 Hz, 1H), 7.49 (t, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 12.26 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.5, 118.4, 118.9, 119.7, 130.6, 136.4, 162.4, 204.4.

1-(2-Hydroxy-5-methoxyphenyl)ethanone (Scheme 3.4, product 17a)[26]



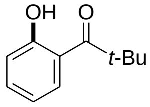
EA: Hexane = 1:9, R_f = 0.25, yellowish orange solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.65 (s, 3H), 3.92 (s, 3H), 6.86 (t, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 12.58 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.0, 56.2, 117.0, 118.2, 119.7, 121.8, 148.9, 152.8, 204.9.

1-(2-Hydroxyphenyl)pentan-1-one (Scheme 3.4, product 18a)[27]



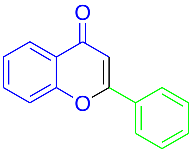
EA: Hexane = 1:9, R_f = 0.8, yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99 (t, *J* = 7.6 Hz, 3H), 1.40-1.50 (m, 2H), 1.72-1.79 (m, 2H), 2.97-3.03(m, 2H), 6.91 (t, *J* = 7.2 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 7.47(dd, *J* = 6.8, 1.2 Hz, 1H), 7.79 (d, *J* = 6.8 Hz, 1H), 12.42 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 22.4, 26.6, 38.0, 118.5, 118.8, 119.3, 128.0, 128.5, 130.0, 136.1, 162.5, 206.9.

1-(2-Hydroxyphenyl)-2,2-dimethylpropan-1-one (Scheme 3.4, product 19a)[14]



EA: Hexane = 1:9, R_f = 0.7, yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.47 (s, 9H), 6.86 (t, J = 8.4 Hz, 1H), 7.03 (d, J = 8.4 Hz, 1H), 7.43 (t, J = 8.0 Hz, 1H), 8.04 (d, J = 7.6 Hz, 1H), 12.71 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.7, 44.6, 117.5, 117.7, 119.3, 130.8, 135.3, 163.6, 212.1.

2-Phenyl-4*H*-chromen-4-one (Scheme 3.6, product 20)[28]



EA: Hexane = 1:4, R_f = 0.7, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (s, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.57 (m, 4H), 7.73 (t, J = 8.4 Hz, 1H), 7.96 (m, 2H), 8.26 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 107.5, 118.1, 123.9, 125.2, 125.7, 126.3, 129.0, 131.6, 131.8, 133.8, 156.2, 163.4, 178.4.

3.6 References

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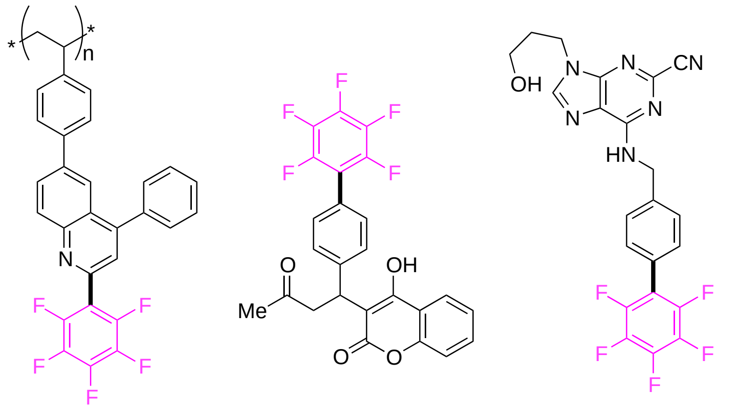
Chapter 4 Palladium-Catalyzed Direct Arylation of Polyfluoroarenes with Aryl Tosylates and Mesylates

4.1 Introduction

Polyfluorobiphenyl motifs are commonly found in numerous pharmaceutically attractive and materially valuable molecules.[1] For instance, the perfluorinated polyphenylene sub-unit in photovoltaic polymer (P5FQ),[2] perfluorosubstituted hydroxycoumarins (2*H*-1-benzopyran-2-one) in rodenticides,[3] and trypanosomal cathepsin TbcatB inhibitors (9*H*-purine-2-carbonitrile)[4] have aroused considerable focus in the polyfluorinated biaryl synthesis.



P5FQ **2-*H*-1-benzopyran-2-one** **9*H*-purine-2-carbonitrile (TBcatB inhibitor)**

Figure. 4.1. Examples of useful perfluoroarene containing molecules

Although the traditional cross-coupling repertoire has been successful for connecting two aromatic fragments, multi-step syntheses of organometallic nucleophiles are possibly the drawbacks. Indeed, in addition to the difficult preparation of highly electron-deficient nucleophiles (e.g. $C_6F_5B(OH)_2$), the application of electron-poor nucleophilic partners in aromatic bond-forming reactions remain problematic.[5] Recent notable findings showed a great achievement in cross-coupling by using direct arylation of C-H bond from electron-deficient polyfluoroarenes.[6] Aryl halides[7] and aryl organometallic reagents[8] such as arylboronic acids[9] can both act as efficient coupling partners with polyfluoroarenes. These new protocols are attractive when compared to conventional coupling methods. However, the substrates scope is mainly limited to aryl halides associating with particular reactivity. Apart from aryl halides, it is worth to establish method for phenolic electrophile (pseudo-halide) in these reactions. In fact, aryl sulfonates would have complementary advantage with respected to aryl halides. They potentially offer different or unique substituted pattern in the aromatic ring, in which the corresponding aryl halides may not be commonly available. Thus, the exploration of less expensive, yet more stable aryl arenesulfonates (when compared to aryl triflates) in coupling reaction is highly favourable. Precedence for palladium-catalyzed direct arylation of polyfluoroarenes using aryl sulfonates remains less explored. In 2006, Fagnou group reported one example of palladium-catalyzed direct arylation of pentafluorobenzene using phenyl triflate.[7b] Very recently, the coupling of aryl triflates was further improved by Seayad and co-workers employing Pd/MePhos catalyst system.[10] Additionally, steric encumbered aryl triflates could be coupled with pentafluorobenzene with Pd/RuPhos complex.[10] Apart from triflates, the coupling of aryl tosylates with polyfluoroarenes was only developed recently. In 2011, Zhang reported the palladium-catalyzed direct coupling of polyfluoroarenes with activated heteroaryl tosylates.[11] Yet, no examples of non-activated tosylates were shown.

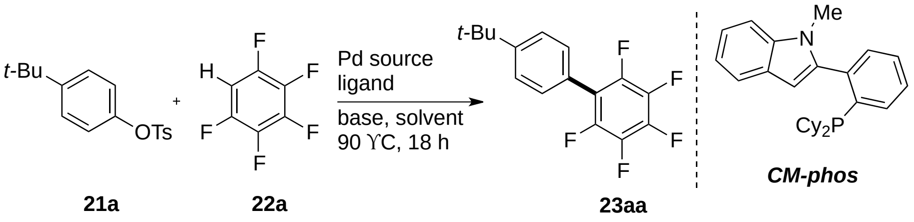
Aryl mesylates is more atom economical than corresponding aryl tosylates due to their significantly lower molecular weight. However, aryl mesylates are relatively more inactive and challenging to be applied in C-H bond functionalization under palladium catalysis. In 2012, Seayad showed the first palladium-catalyzed coupling of aryl mesylates with polyfluoroarenes.[10] However, only activated aryl mesylates were successfully applied in this transformation under the conditions of high Pd loading (10 mol%) and at high temperature (120 °C). To the best of our knowledge, a general procedure for non-activated (hetero)aryl mesylates and aryl tosylates has been sporadically reported to date. Herein, we report our effort in developing general and efficient catalyst system for handling aryl tosylates/mesylates in direct arylation of perfluoroarenes.

4.2 Result and Discussion

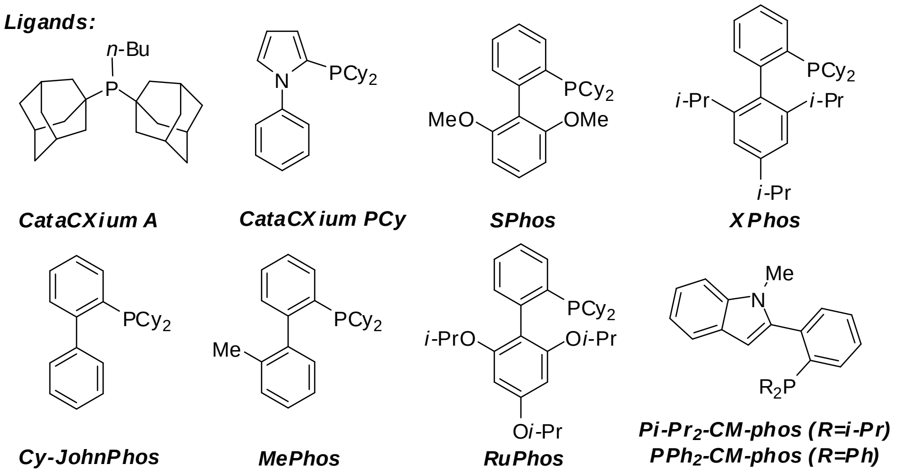
4.2.1 Preliminary Evaluation of Palladium-Catalyzed Direct Arylation of Aryl Arenesulfonates

We initially embarked the coupling of aryl tosylates with polyfluoroarenes by using non-activated 4-*tert*-butylphenyl tosylate and pentafluorobenzene as the benchmark substrates (Table 4.1). A series of reaction parameter screenings were then deployed.

Table 4.1. Initial catalyst screenings of Pd-catalyzed arylation of polyfluoroarenes with aryl tosylates[a]



entry	Pd source	ligand	Base	%yield[b]
1	$Pd(OAc)_2$	CataCXium® A	K_2CO_3	0
2	$Pd(OAc)_2$	CataCXium® PCy	K_2CO_3	0
3	$Pd(OAc)_2$	SPhos	K_2CO_3	47
4	$Pd(OAc)_2$	XPhos	K_2CO_3	37
5	$Pd(OAc)_2$	Cy-JohnPhos	K_2CO_3	4
6	$Pd(OAc)_2$	MePhos	K_2CO_3	12
7	$Pd(OAc)_2$	RuPhos	K_2CO_3	43
8	$Pd(OAc)_2$	CM-phos	K_2CO_3	76
9	$Pd(OAc)_2$	P*i*-Pr_2-CM-phos	K_2CO_3	33
10	$Pd(OAc)_2$	PPh_2-CM-phos	K_2CO_3	0
11[c]	$Pd(OAc)_2$	CM-phos	K_2CO_3	43
12	$Pd(TFA)_2$	CM-phos	K_2CO_3	26
13	$Pd_2(dba)_3$	CM-phos	K_2CO_3	0
14	$PdCl_2$	CM-phos	K_2CO_3	10



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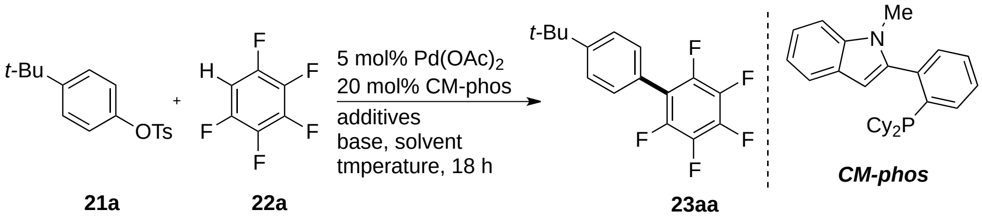
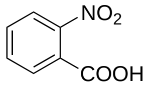
[a] Reaction conditions: ArOTs **21a** (0.3 mmol), C_6F_5H (0.6 mmol), $Pd(OAc)_2$ (5.0 mol%), (Pd:ligand = 1:4), base (0.45 mmol) and *t*-BuOH (1.0 mL) under N_2 at 90 °C for 18 h. [b] GC yields were reported. [c] 2.0 mol% of $Pd(OAc)_2$ was used.

Commercially available and well-recognized phosphine ligands[12] such as CataCXium®A, CataCXium®PCy, SPhos, Xphos, Cy-JohnPhos, MePhos and RuPhos were initially screened (entries 1-7). Moderate substrate conversions and fair product yields were afforded by using biaryl-type monodentate phosphines (entries 3-7). Catalyst system comprising $Pd(OAc)_2$ and CM-phos[13] was found superior for this tosylate coupling (entry 8).

Of commonly used organic solvents examined, alcoholic solvent *t*-BuOH was found to be the best solvent of choice whereas DMF and dioxane gave moderate and poor conversions, respectively (Table 4.2, entries 1, 8, 10). *t*-BuOH/ DMF solvent mixtures also afforded good yield for this direct arylation (entries 9). The addition of pivalic acid (to K_2CO_3 system) greatly improved the conversion (entries 1 *vs* 3) while other additives showed slightly improvement (entries 2-7). Surprisingly, weak base such as KOAc, Na_2HCO_3 or Na_2CO_3 were equally efficient to give excellent yield even without the employment of additional PivOH (entries 14, 15, 18). Lowering the reaction tempearture to 50 °C, the yield significantly dropped to 3% (entry 1 *vs* 11) while increasing the temperature to 110 °C, comparable result 72% was obtained (entry 1 *vs* 12).

Table 4.2. Initial reaction condition screenings of Pd-catalyzed arylation of polyfluoroarenes with aryl tosylate [a]



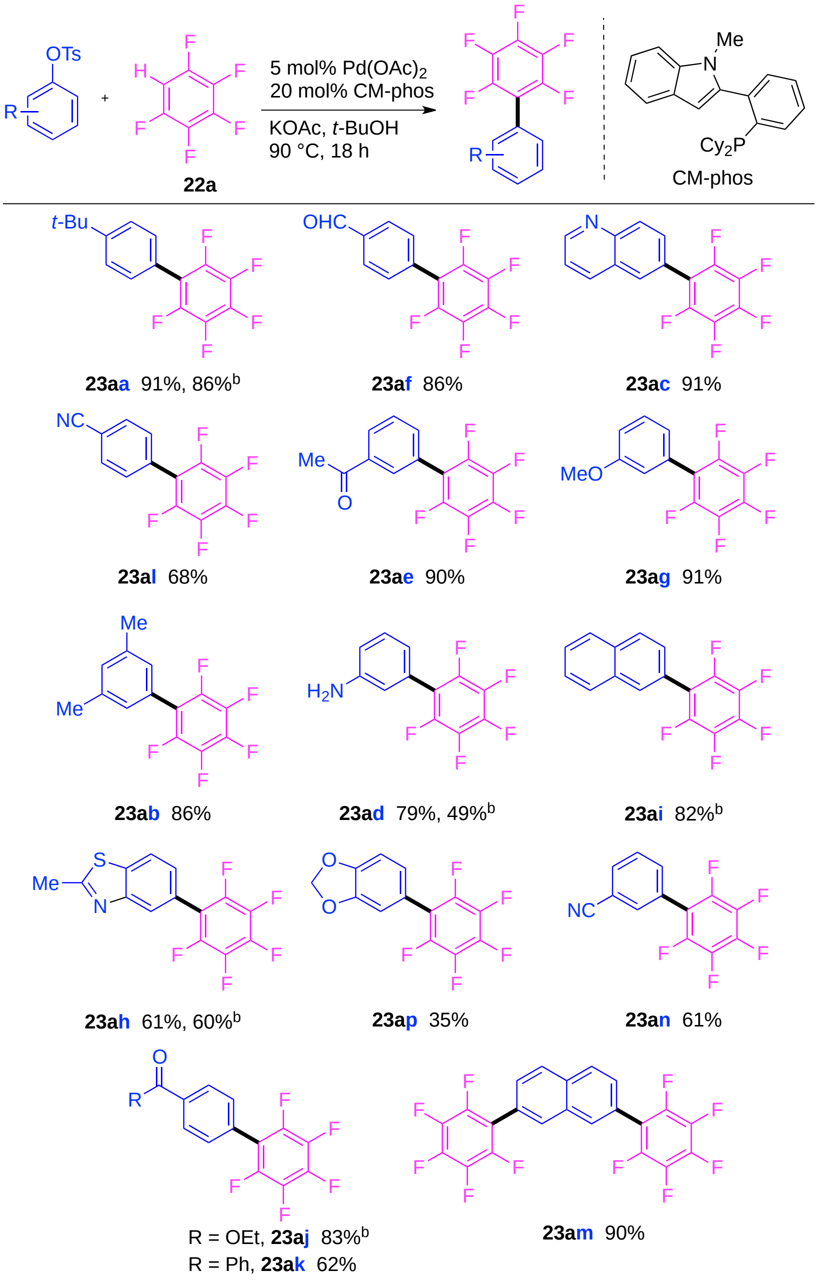
entry	Additives (mol%)	Solvent	Base	%yield[b]
1	--	t-BuOH	K_2CO_3	76
2	 (10)	t-BuOH	K_2CO_3	62
3	PivOH (10)	t-BuOH	K_2CO_3	87
4	TsCOOH•H_2O (10)	t-BuOH	K_2CO_3	75
5	PhCOOH(10)	t-BuOH	K_2CO_3	80
6	AcOH (10)	t-BuOH	K_2CO_3	82
7	CF_3COOH (10)	t-BuOH	K_2CO_3	70
8	--	DMF	K_2CO_3	51
9	--	t-BuOH/ DMF (1:1)	K_2CO_3	77
10	--	Dioxane	K_2CO_3	32
11[c]	--	t-BuOH	K_2CO_3	3
12[d]	--	t-BuOH	K_2CO_3	72
13	--	t-BuOH	Na_2HPO_4	17
14	--	t-BuOH	Na_2HCO_3	89
15	--	t-BuOH	Na_2CO_3	90
16	PivOH (10)	t-BuOH	Na_2CO_3	84
17	PivOH (20)	t-BuOH	Na_2CO_3	78
18	--	t-BuOH	KOAc	90
19	PivOH (10)	t-BuOH	KOAc	92
20	--	t-BuOH	NaOAc	73
21	--	t-BuOH	CF_3COONa	7

[a] Reaction conditions: ArOTs **21a** (0.3 mmol), C_6F_5H (0.6 mmol), $Pd(OAc)_2$ (5.0 mol%), (Pd:ligand = 1:4), base (0.45 mmol) and *t*-BuOH (1.0 mL) under N_2 at 90 °C for 18 h. [b] GC yields were reported. [c] 50 °C was used. [d] 110 °C was used.

4.2.2 Scope of Pd-Catalyzed Direct Arylation of Pentafluorobenzene with Aryl Tosylates and Mesylates

Having the preliminary optimized reaction conditions in hand, we examined a range of aryl tosylates in this reaction (Table 4.3).

Table 4.3. Palladium-catalyzed arylation of pentafluorobenzene with aryl and heteroaryl tosylates[a]



23aa 91%, 86%[b]

23af 86%

23ac 91%

23al 68%

23ae 90%

23ag 91%

23ab 86%

23ad 79%, 49%[b]

23ai 82%[b]

23ah 61%, 60%[b]

23ap 35%

23an 61%

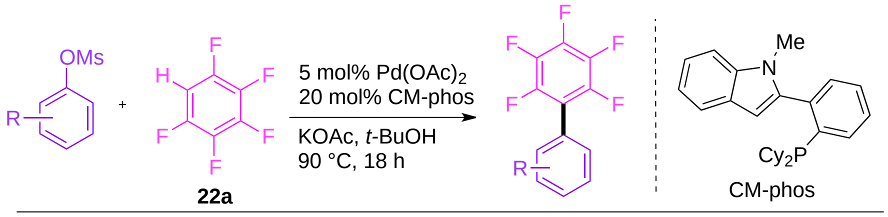
R = OEt, **23aj** 83%[b]
R = Ph, **23ak** 62%

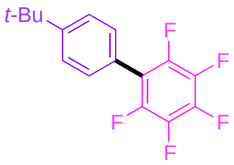
23am 90%

[a] Reaction conditions: ArOTs (0.3 mmol), C_6F_5H (0.6 mmol), $Pd(OAc)_2$ (5.0 mol%), (Pd:CM-phos = 1:4), KOAc (0.45 mmol) and t-BuOH (1.0 mL) under N_2 at 90 °C for 18 h (reaction time for each substrate was not optimized). Isolated yields were reported. [b] Na_2CO_3 was used as base.

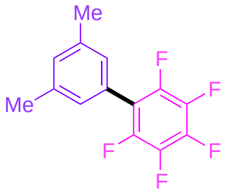
To the best of our knowledge, there has been no successful example of non-activated aryl tosylates reported to date in direct arylation of perfluoroarenes. Electronically neutral aryl tosylates were effective and gave the corresponding products in good to excellent yields. Functional groups such as methoxy, keto, cyano, ester and aldehyde were compatible under these reaction conditions. Heterocyclic benzothiazoyl and quinolinyl tosylates furnished the corresponding coupling products smoothly.

Table 4.4. Palladium-catalyzed arylation of pentafluorobenzene with neutral aryl mesylates[a]

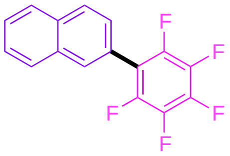




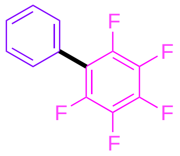
23aa 85%



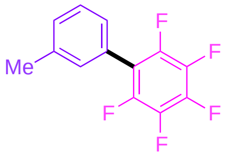
23ab 75%



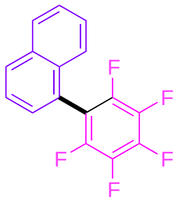
23ai 89%



23aq 63%



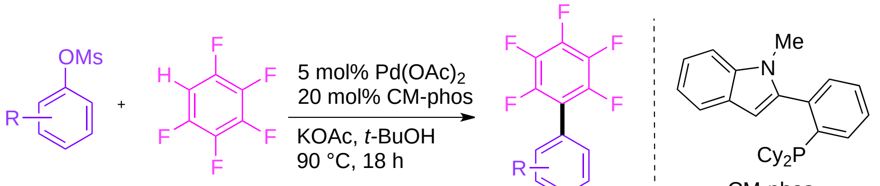
23ar 52%



23au 12%

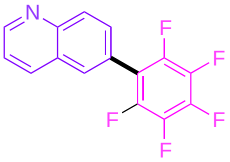
[a]Reaction conditions: ArOMs (0.3 mmol), C_6F_5H (0.6 mmol), $Pd(OAc)_2$ (5.0 mol%), (Pd:CM-phos = 1:4), KOAc (0.45 mmol) and *t*-BuOH (1.0 mL) under N_2 at 90 °C for 18 h (reaction time for each substrate was not optimized). Isolated yields were reported.

Table 4.5. Palladium-catalyzed arylation of pentafluorobenzene with aryl and hetreroaryl mesylates[a]

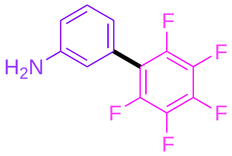


22a

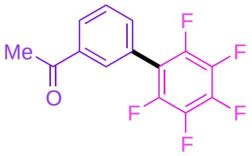
CM-phos



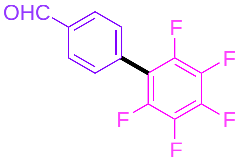
23ac 76%



23ad 60%



23ae 67%



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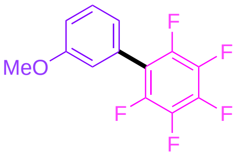
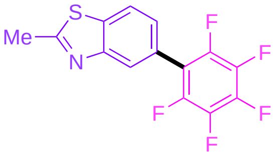


23ag 78%



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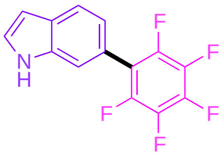

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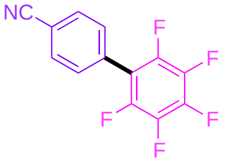
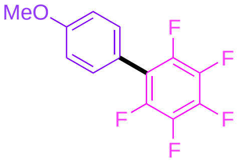
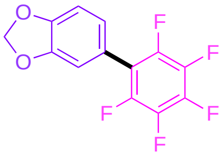


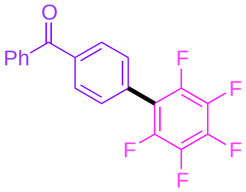
23al 44%



23aw 54%



23ap 35%



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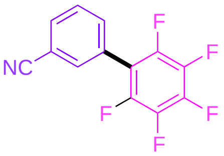
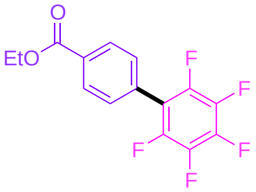
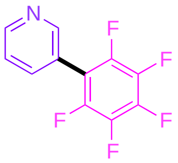


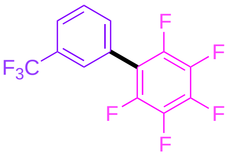
23an 24%



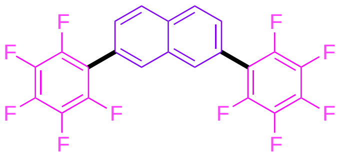
23aj 83%



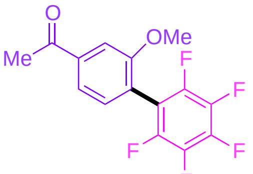
23ao 33%



23as 48%



23am 47%



23at 35%

[a]Reaction conditions: ArOMs (0.3 mmol), C_6F_5H (0.6 mmol), $Pd(OAc)_2$ (5.0 mol%), (Pd:CM-phos = 1:4), KOAc (0.45 mmol) and *t*-BuOH (1.0 mL) under N_2 at 90 °C for 18 h (reaction time for each substrate was not optimized). Isolated yields were reported.

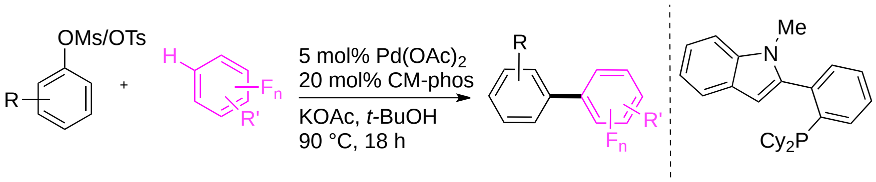
In view of commonly used arenesulfonate leaving groups, the mesylate can be regarded as the most inert group since the pK_a of the corresponding conjugate acid is the highest among the others. Nevertheless, mesylate provides the best atom efficiency when compared with tosylate and triflate. Inspired by its intrinsic attractiveness, we turned to examine the possibility of using more difficult, yet more beneficial aryl mesylate as the electrophilic partner in the direct arylation of polyfluoroarenes. The Pd/CM-phos catalytic system was also found to be effective in promoting the coupling of aryl mesylates (Table 4.4 and 4.5). An array of aryl mesylates were tested in this coupling reaction. Sterically hindered aryl mesylates resulted in a lower product yield. Heteroaryl mesylates were found applicable in this system.

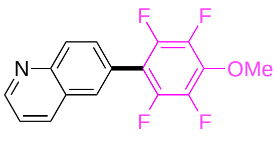
4.2.3 Scope of Pd-Catalyzed Direct Arylation of Polyfluoroarenes with Aryl Tosylates and Mesylates

To further expand the substrate scope, we next investigated the feasibility of using other polyfluoroarenes as the coupling partners (Table 4.6). In general, a slightly higher amount of polyfluoroarenes (3 equivalent) was needed when compared to that of pentafluorobenzenes (2 equivalent). Moderate to excellent yields were resulted.

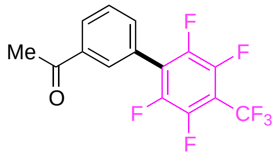
When 1,2,4,5-tetrafluorobenzene was coupled with 3-methoxytosylates, mixture of products was resulted with mono-arylation and di-arylation (Scheme 4.1). High temperature favours di-arylation from the experimental result. 1,3,5-Trifluorobenzene and 1,2,3,4- were attempted but no desired product was formed.

Table 4.6. Palladium-catalyzed arylation of polyfluoroarenes with (hetero)aryl tosylates and aryl mesylates[a]

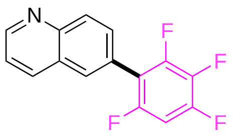




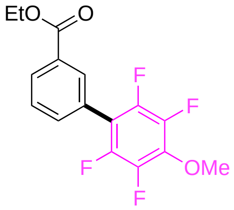
23bc (OTs) 88%



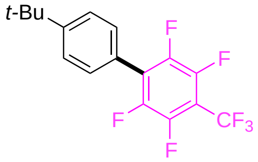
23ce (OTs) 97%



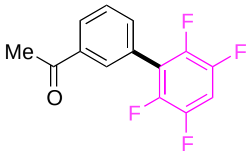
23dc (OTs) 61%



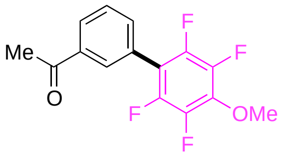
23bj (OMs) 78%



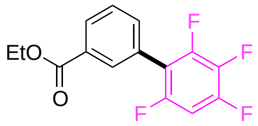
23ca (OMs) 90%



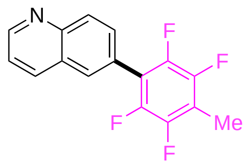
23ee (OTs) 64%[b]



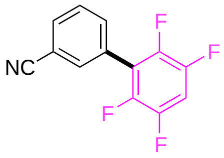
23be (OTs) 67%[c]



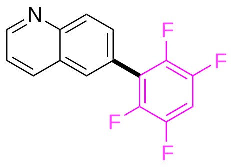
23dj (OMs) 45%



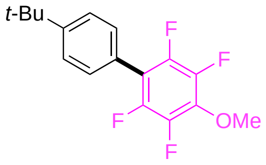
23gc (OTs) 56%



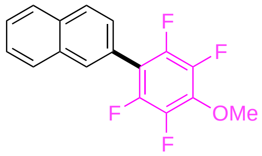
23en (OTs) 35%



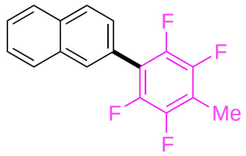
23ec (OTs) 56%



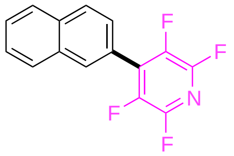
23ba (OTs) 51%



23bi (OMs) 58%

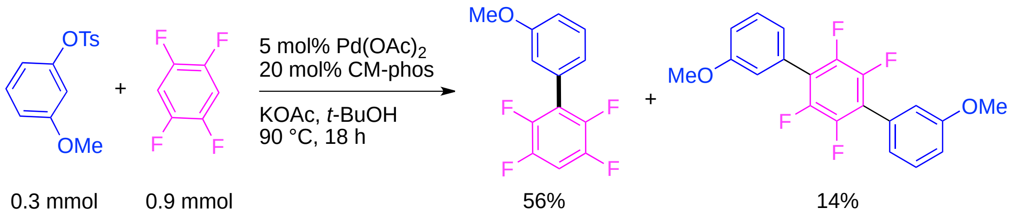


23gi (OMs) 47%



23fi (OTs) 90%[d]
(OMs) 89%[d]

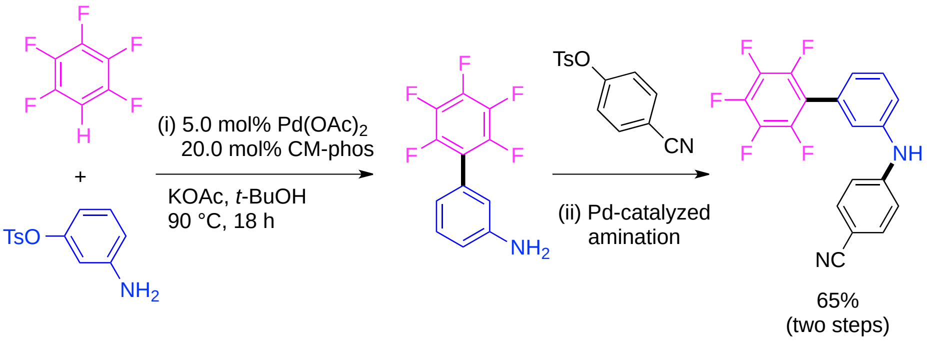
[a] Reaction conditions: ArOTs/OMs (0.3 mmol), polyfluoroarene (0.9 mmol), Pd(OAc)$_2$ (5.0 mol%), (Pd:CM-phos = 1:4), KOAc (0.45 mmol) and t-BuOH (1.0 mL) under N$_2$ at 90 °C for 18 h (reaction time for each substrate was not optimized). Isolated yields were reported. [b] 1.2 mmol of polyfluoroarene was used. [c] 0.6 mmol of polyfluoroarene was used. [d] 24 h was used.



Scheme 4.1. Palladium-catalyzed coupling of 3-methoxytosylate with 1,2,4,5-tetrafluorobenzene (Reaction conditions: ArOTs (0.3 mmol), 1,2,4,5-tetrafluorobenzene (0.9 mmol), $Pd(OAc)_2$ (5.0 mol%), (Pd:CM-phos = 1:4), KOAc (0.45 mmol), and t-BuOH (1.0 mL) under N_2 at 90 °C for 18 h.)

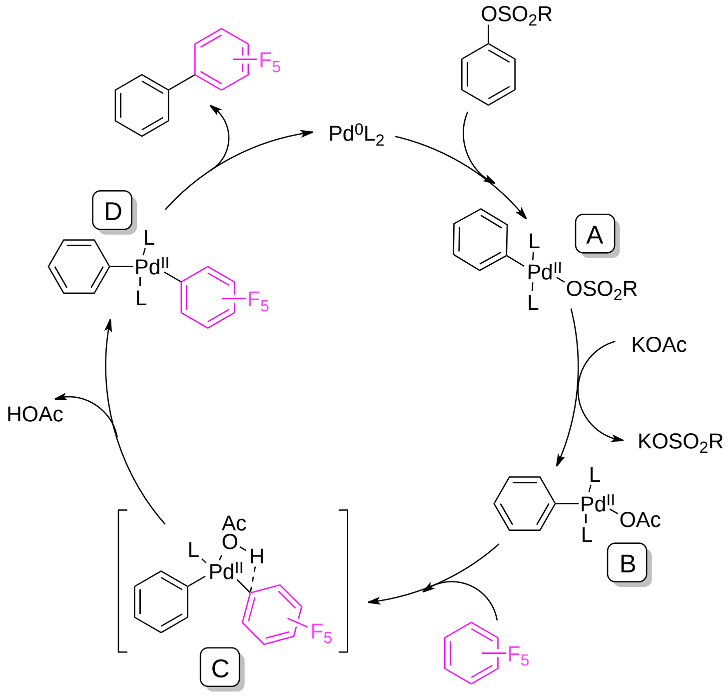
4.2.4 Application of Pd-Catalyzed Direct Arylation of Polyfluoroarenes with Aryl Tosylates and Mesylates

To further show the potential application of this coupling process in synthesizing related cathepsin TbcatB inhibitors (consist of $–C_6F_5$, *N*-Ar and –CN moieties),[4] a tandem reaction was attempted. To our delight, the one-pot synthesis of an *N*-aryl aminobenzonitrile (65% yield in two steps) was successful from direct coupling of aryl tosylate with pentafluorobenzene and subsequent *N*-arylation of the amino moiety (Scheme 4.2).



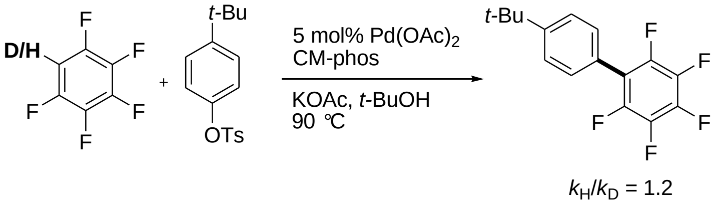
Scheme 4.2. One pot sequential reaction (Reaction conditions: i. ArOTs (0.3 mmol), pentafluorobenzene (0.6 mmol), $Pd(OAc)_2$ (5.0 mol%), (Pd:CM-phos = 1:4), KOAc (0.45 mmol), and *t*-BuOH (1.0 mL) under N_2 at 90 °C for 18 h. ii. Ar'OTs (0.158 mmol), K_2CO_3 (0.395 mmol), and *t*-BuOH (1.0 mL) under N_2 at 110 °C for 24 h.)

4.2.5 Proposed Mechanism of Pd-Catalyzed Direct Arylation of Polyfluoroarenes with Aryl Tosylates and Mesylates



Scheme 4.3. Proposed mechanism for Pd-catalyzed direct arylation of polyfluoroarenes

Initially, oxidative addition of aryl sulfonates to the Pd(0) complex leads to Pd(II)(aryl)sulfonate intermediate complex A. After that, there is an exchange of the sulfonate with the base (i.e. acetate or carbonate depend on the substrate applied). The Pd(II) complex B activated the polyfluoroarenes by the cyclometallation deprotonation (CMD) pathway assisted by acetate or carbonate anion to form complex C. Reductive elimination was then followed from Pd(II) diaryl intermediate D to regenerate the Pd(0) species.



Scheme 4.4. Kinetic isotope effect experiment for C-H bond cleavage determination

In order to further investigate the mechanism for dependence of the C-H bond cleavage, a kinetic isotope effect (KIE) experiment was carried out. A KIE of 1.2 was observed from the competitive experiment of deuteropentafluorobenzene and pentafluorobenzene (Scheme 4.3). This result indicated that the C-H bond cleavage is likely to be not the kinetically rate-determining step in this catalysis.

4.3 Conclusion

In summary, we showed the first general palladium-catalyzed direct arylation of polyfluoroarenes with aryl tosylates and mesylates. This protocol offers a convenient access to polyfluorobiaryl scaffold from phenolic derivatives. Particularly noteworthy is that the reaction conditions are relatively mild (weak base, KOAc; at 90 °C, without acid additives). Moreover, the cascade direct arylation/C-N bond-coupling sequence could be carried out by using one Pd/CM-phos catalyst system. We believe this direct arylation protocol using sulfonate coupling partners is versatile for diversified functional materials and pharmaceuticals.

4.4 Experimental Section

4.4.1 General Considerations

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. All arylation reactions were performed in Rotaflo® (England) resealable screw cap Schlenk flask (approx. 8 mL volume) in the presence of Teflon coated magnetic stirrer bar (3 mm × 10 mm). Toluene and dioxane were distilled from sodium under nitrogen. *N*,*N*-Dimethylformamide (DMF) was distilled from calcium hydride under reduced pressure. *tert*-Butanol was distilled from sodium under nitrogen and stored with calcium hydride.[14] K_2CO_3 was purchased from Fluka. KOAc and Na_2CO_3 were purchased from Aldrich. CM-phos ligand was developed and prepared by our group.[15] All aryl/heteroaryl tosylates and mesylates used were generated from the corresponding phenols according to the literature.[16] Thin layer chromatography was performed on Merck precoated silica gel 60 F_{254} plates. Silica gel (Merck, 70-230 and 230-400 mesh) was used for column chromatography. ^{1}H NMR spectra were recorded on a Brüker (400 MHz) or Varian (500 MHz) spectrometer. Spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.26 ppm), or with tetramethylsilane (TMS, δ 0.00 ppm) as the internal standard. Chemical shifts (δ) were reported as part per million (ppm) in δ scale downfield from TMS. ^{13}C NMR spectra were referenced to $CDCl_3$ (δ 77.0 ppm, the middle peak). Coupling constants (*J*) were reported in Hertz (Hz). Mass spectra (EI-MS and ES-MS) were recorded on a HP 5989B Mass Spectrometer. High-resolution mass spectra (HRMS) were obtained on a Brüker APEX 47e FT-ICR mass spectrometer (ESIMS). GC-MS analysis was conducted on a HP 5973 GCD system using a HP5MS column (30 m × 0.25 mm). The products described in GC yield were accorded to the authentic samples/dodecane calibration standard from HP 6890 GC-FID system.

4.4.2 General Procedures for Initial Ligand and Reaction Conditions Screening

General Procedure for reaction condition screenings: Pd(OAc)$_2$ (3.4 mg, 0.015 mmol) and ligand (Pd:L = 1:4) were loaded into a Schlenk tube equipped with a Teflon-coated magnetic stir bar. The tubes were evacuated and backfilled with nitrogen (3 cycles). Precomplexation was applied by adding freshly distilled dichloromethane (1.0 mL) and Et$_3$N (0.05 mL) into the tube. The palladium complex stock solution was stirred and warmed using a hair drier for 1 to 2 minutes until the solvent started boiling. The solvent was then evaporated under high vacuum. 4-*tert*-Butylphenyl tosylate (0.3 mmol) and base (0.45 mmol) were loaded into the tube, and the system was further evacuated and flushed with nitrogen for three times. The solvent (1.0 mL) was then added with stirring at room temperature for several minutes and pentafluorobenzene (0.6 mmol) was then loaded into the tube. The tube was then placed into a preheated oil bath (90 °C) and stirred for 18 hours. After completion of reaction, the reaction tube was allowed to cool to room temperature and quenched with water and diluted with ethyl acetate. Dodecane (68 μL, internal standard) was then added. The organic layer was subjected to GC analysis. The GC yield obtained was previously calibrated by authentic sample/dodecane calibration curve.

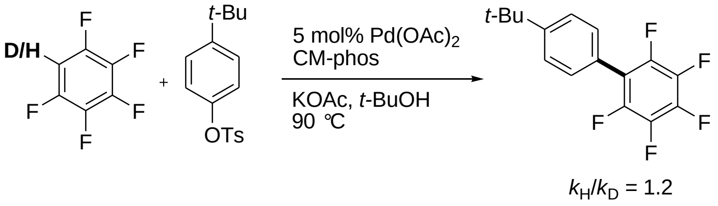
4.4.3 General Procedures for Direct Arylation of Polyfluoroarenes with Aryl Arenesulfonates

General procedures for direct arylation of polyfluoroarenes with aryl sulfonates: Pd(OAc)$_2$ (3.4 mg, 0.015 mmol) and ligand (Pd:L = 1:4) were loaded into a Schlenk tube equipped with a Teflon-coated magnetic stir bar. The tubes were evacuated and backfilled with nitrogen (3 cycles). Precomplexation was applied by adding freshly distilled dichloromethane (1.0 mL) and Et_3N (0.05 mL) into the tube. The palladium complex stock solution was stirred and warmed using a hair drier for 1 to 2 minutes until the solvent started boiling. The solvent was then evaporated under high vacuum. Aryl tosylates/ mesylates (0.3 mmol) and base (0.45 mmol) were loaded into the tube, and the system was further evacuated and flushed with nitrogen for three times. The solvent (1.0 mL) was then added with stirring at room temperature for several minutes and polyfluoroarenes (0.6 mmol) was then loaded into the tube. The tube was then placed into a preheated oil bath (90 °C) and stirred for the time as indicated. After completion of reaction, the reaction tube was allowed to cool to room temperature and quenched with water and diluted with ethyl acetate (EA). The organic layer was separated and the aqueous layer was washed with EA. The filtrate was concentrated under reduced pressure. The crude products were purified by flash column chromatography on silica gel (230-400 mesh) to afford the desired product.

4.4.4 General Procedures for Sequential Arylation of Aryl Tosylates

General procedures for one-pot stepwise sequential arylation of aryl tosylates: $Pd(OAc)_2$ (3.4 mg, 0.015 mmol) and ligand (Pd:L = 1:4) were loaded into a Schlenk tube equipped with a Teflon-coated magnetic stir bar. The tubes were evacuated and backfilled with nitrogen (3 cycles). Precomplexation was applied by adding freshly distilled dichloromethane (1.0 mL) and Et_3N (0.05 mL) into the tube. The palladium complex stock solution was stirred and warmed using a hair drier for 1 to 2 minutes until the solvent started boiling. The solvent was then evaporated under high vacuum. 3-Aminophenyl tosylate (0.3 mmol) and KOAc (0.45 mmol) were loaded into the tube, and the system was further evacuated and flushed with nitrogen for three times. The solvent *tert*-butanol (1.0 mL) was then added with stirring at room temperature for several minutes and pentafluorobenzene (0.6 mmol) was then loaded into the tube. The tube was then placed into a preheated oil bath (90 °C) and stirred for 18 hours. After completion of reaction, the reaction tube was allowed to cool to room temperature. The system was flushed with nitrogen while 4-cyanophenyl tosylate (0.158 mmol) and K_2CO_3 (0.395 mmol) were loaded into the tube. Another 1.0 mL solvent of *tert*-butanol was then added to the system. The tube was then placed into a preheated oil bath (110 °C) and stirred for another 24 hours. After the completion of reaction, the tube was allowed to cool to room temperature. The reaction was then quenched with water and diluted with EA and judged as GC. The organic layer was separated and the aqueous layer was washed with EA. The filtrate was concentrated under reduced pressure. The crude products were purified by flash column chromatography on silica gel (230-400 mesh) to afford the desired product.

4.4.5 Kinetic Isotope Experiment

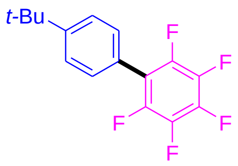


Deuteropentafluorobenzene used was synthesized from bromopentafluorobenzene. Bromopentafluorobenzene was refluxed with Mg in anhydrous diethyl ether for 1 h and was quenched by deuterium oxide according to the literature.[17,18]

$Pd(OAc)_2$ (3.4 mg, 0.015 mmol) and ligand (Pd:L = 1:4) were loaded into a Schlenk tube equipped with a Teflon-coated magnetic stir bar. The tubes were evacuated and backfilled with nitrogen (3 cycles). Precomplexation was applied by adding freshly distilled dichloromethane (1.0 mL) and Et_3N (0.05 mL) into the tube. The palladium complex stock solution was stirred and warmed using a hair drier for 1 to 2 minutes until the solvent started boiling. The solvent was then evaporated under high vacuum. 4-*tert*-Butylphenyl tosylate (0.3 mmol) and KOAc (0.45 mmol) were loaded into the tube, and the system was further evacuated and flushed with nitrogen for three times. *tert*-Butanol (1.0 mL) was then added with stirring at room temperature for several minutes and pentafluorobenzene or deuteropentafluorobenzene (0.6 mmol) was then loaded into the tube. The tube was then placed into a preheated oil bath (90 °C) and stirred for assigned time intervals. The reaction tube was allowed to cool to room temperature and quenched with water and diluted with ethyl acetate (EtOAc). Dodecane (68 μL, internal standard) was then added. The organic layer was subjected to GC analysis. The GC yield obtained was previously calibrated by authentic sample/dodecane calibration curve.

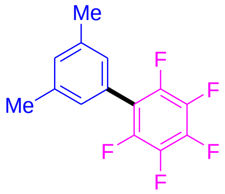
4.5 Characterization Data of Coupling Products

2,3,4,5,6-Pentafluoro-4'-*tert*-butylbiphenyl (Table 4.3, 4.4; Product 23aa)[19]



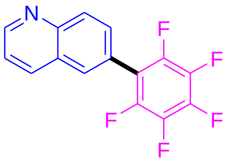
Pure Hexane, $R_f = 0.4$; m.p. 81-83.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41 (s, 9H), 7.39-7.42 (m, 2H), 7.53-7.57 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 31.2, 34.7, 115.9 (m), 123.4, 125.7, 129.8, 136.6 (m), 139.1 (m), 141.4 (m), 143.12 (m) 145.4 (m), 152.4; ^{19}F NMR (400 MHz, $CDCl_3$) δ -162.5 (m, 2F), -156.2 (t, 1F), -143.3 (dd, 2F).

2,3,4,5,6-Pentafluoro-3',5'-dimethyl-1,1'-biphenyl (Table 4.3, 4.4; Product 23ab)[24]



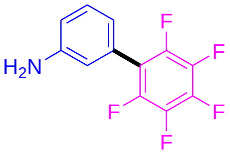
Pure Hexane, $R_f = 0.7$; m. p. 83-84.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.42 (s, 3H), 7.06 (s, 2H), 7.14 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 21.2, 116.3 (m), 126.1, 127.8, 130.9, 136.5 (m), 138.3, 139.0 (m), 141.4 (m), 142.9 (m), 145.4 (m); ^{19}F NMR (400 MHz, $CDCl_3$) δ -162.6 (m, 2F), -156.2 (t, 1F), -143.0 (dd, 2F).

6'-(2,3,4,5,6-Pentafluorophenyl)quinoline (Table 4.3, 4.5; Product 23ac)



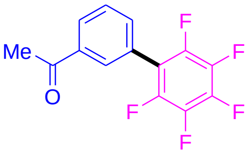
Hexane: EA = 4:1, $R_f = 0.45$; m. p. 172-173.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (q, *J*=4.4Hz, 1H), 7.75 (dd, *J*=7.2, 1.6Hz, 1H), 7.93 (s, 1H), 8.21-8.25 (m, 2H), 9.01 (d, *J*=2.8Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 121.8, 124.6, 127.9, 129.9, 130.0, 130.6, 136.3, 147.9, 151.6, 192.2; ^{19}F NMR (400 MHz, $CDCl_3$) δ -161.7 (m, 2F), -154.5 (t, 1F), -142.9 (dd, 2F); HRMS: calcd. for $C_{15}H_7NF_5^+$: 296.0499, found 296.0495.

2,3,4,5,6-Pentafluoro-3'-aminobiphenyl (Table 4.3, 4.5; Product 23ad)[20]



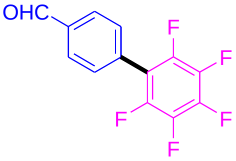
Hexane: EA = 10:1, R$_f$ = 0.2; m. p. 100-101.2 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.81 (s, 2H), 6.73 (s, 1H), 6.78-6.82 (m, 2H), 7.29 (dd, *J*=5.2, 2.8Hz, 1H); ^{13}C NMR (100MHz, CDCl$_3$) δ 115.9, 116.2, 116.5, 120.3, 127.2, 129.6, 136.4 (m), 139.0 (m), 141.5 (m), 142.9 (m), 145.3 (m), 146.6; ^{19}F NMR (400 MHz, CDCl$_3$) δ -162.5 (m, 2F), -156.0 (t, 1F), -142.7 (dd, 2F).

3'-(2,3,4,5,6-Pentafluorophenyl)acetophenone (Table 4.3, 4.5; Product 23ae)



Hexane: EA = 9:1, R$_f$ = 0.4; m. p. 106-108 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.65 (s, 3H), 7.62 (d, *J*=3.6Hz, 2H), 8.03-8.07 (m, 2H); ^{13}C NMR (100MHz, CDCl$_3$) δ 26.5, 114.9 (m), 126.9, 129.0, 130.0, 134.4, 136.6 (m), 137.5, 139.1 (m), 142.8 (m), 145.3 (m), 197.0; ^{19}F NMR (400 MHz, CDCl$_3$) δ -161.8 (m, 2F), -154.5 (t, 1F), -143.1 (dd, 2F); HRMS: calcd. for $C_{14}H_8OF_5^+$: 287.0495, found 287.0485.

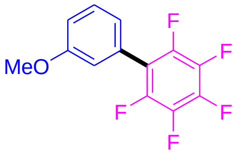
2',3',4',5',6'-Pentafluoro-[1,1'-biphenyl]-4-carboxaldehyde (Table 4.3, 4.5; Product 23af)[21]



Hexane: EA = 9:1, R$_f$ = 0.4; m. p. 75.8-78.2 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.63 (q, *J*=6.8, 1.2Hz, 2H), 8.01-8.04 (m, 2H), 10.1 (s, 1H); ^{13}C NMR (100MHz, CDCl$_3$) δ 129.7, 130.9, 132.3, 134.3 (m), 136.8 (d), 139.5 (d), 141.4 (m), 142.8

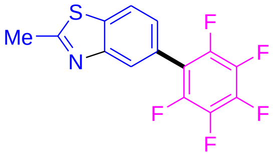
(m), 145.3 (m), 191.4; ^{19}F NMR (400 MHz, $CDCl_3$) δ -161.4 (m, 2F), -153.6 (t, 1F), -142.7 (dd, 2F).

2,3,4,5,6-Pentafluoro-3'-methoxybiphenyl (Table 4.3, 4.5; Product 23ag)[24]



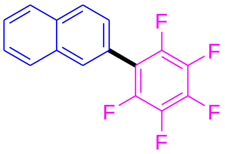
Hexane: EA = 20:1, R_f = 0.45; m. p. 33.8-34.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 (s, 3H), 6.97 (s, 1H), 7.02-7.05 (m, 2H), 7.43 (t, *J*=7.6Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 55.3, 114.8, 115.8, 122.4, 127.4, 129.7,134.1 (m), 136.5 (m), 139.0 (m), 141.6 (m), 142.8 (m), 145.5 (m), 159.6; ^{19}F NMR (400 MHz, $CDCl_3$) δ -162.3 (m, 2F), -155.6 (t, 1F), -142.8 (dd, 2F).

2-Methyl-5-(pentafluorophenyl)benzo[*d*]thiazole (Table 4.3, 4.5; Product 23ah)



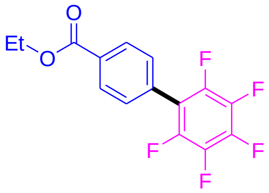
Hexane: EA = 20:1, R_f = 0.25; m. p. 152.6-154.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.88 (s, 3H), 7.39 (dd, *J*=6.8, 1.6, 1H), 7.94 (d, *J*=8.4Hz, 1H), 8.03 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 20.1, 121.7, 124.0, 124.1, 126.2, 136.8, 153.5, 168.3; ^{19}F NMR (400 MHz, $CDCl_3$) δ -161.9 (m, 2F), -155.1 (t, 1F), -143.0 (dd, 2F); HRMS: calcd. for $C_{14}H_7NSF_5^+$: 316.0219, found 316.0207.

2-(2,3,4,5,6-Pentafluorophenyl)naphthalene (Table 4.3, 4.4; Product 23ai)[22]



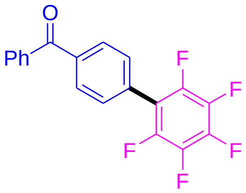
Hexane: EA = 9:1, R_f = 0.7; m. p. 168-169.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.62 (m, 3H), 7.91-7.99 (m, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ 123.7, 126.6, 127.0, 127.1, 127.7, 128.2, 128.4, 130.1, 133.0, 133.2; ^{19}F NMR (400 MHz, $CDCl_3$) δ -162.1 (m, 2F), -155.4 (t, 1F), -142.9 (dd, 2F).

[1,1'-Biphenyl]-4-carboxylic acid, 2',3',4',5',6'-pentafluoro-, ethyl ester (Table 4.3, 4.5; Product 23aj)



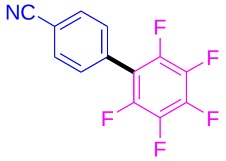
Hexane: EA = 20:1, R_f = 0.25; m. p. 147-149.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.43 (t, *J*=7.2Hz, 3H), 4.43 (q, *J*=7.2Hz, 2H), 7.51-7.54 (m, 2H), 8.16-8.19 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 14.2, 61.2, 115.0, 129.8, 130.1, 130.7, 131.2, 136.6 (m), 139.2 (m), 139.6 (m), 142.0 (m), 142.8 (m), 145.3 (m), 165.8; ^{19}F NMR (400 MHz, $CDCl_3$) δ -161.7 (m, 2F), -154.3 (t, 1F), -142.8 (dd, 2F); HRMS: calcd. for $C_{15}H_9O_2F_5^+$: 316.0523, found 316.0533.

(2',3',4',5',6'-Pentafluoro[1,1'-biphenyl]-4-yl)phenylmethanone (Table 4.3, 4.5; Product 23ak)[23]



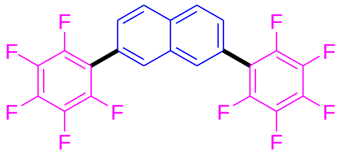
Hexane: EA = 9:1, R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.66 (m, 5H), 7.85-7.93 (m, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ 128.2, 128.3, 130.0, 130.1, 130.3, 132.3, 132.7, 136.6 (m), 137.1, 138.1, 138.1 (m), 138.9 (m), 139.6 (m), 142.8, 145.4 (m), 195.8; ^{19}F NMR (400 MHz, $CDCl_3$) δ -161.5 (m, 2F), -154.1 (t, 1F), -142.7 (dd, 2F).

2,3,4,5,6-Pentafluoro-4'-cyanobiphenyl (Table 4.3, 4.5; Product 23al)[24]



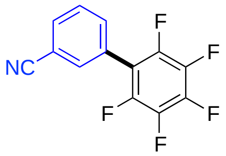
Hexane: EA = 10:1, R_f = 0.4; m. p. 126-128.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J*=8.4Hz, 2H), 7.80-7.83 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 113.3, 118.0, 130.9, 131.1, 132.4, 136.7 (m), 139.1 (m), 142.7 (m), 145.2 (m); ^{19}F NMR (400 MHz, $CDCl_3$) δ -161.0 (m, 2F) , -152.9 (t, 1F), -142.8 (dd, 2F).

2,7-Bis(pentafluorophenyl)naphthalene (Table 4.3; Product 23am)



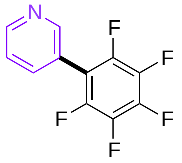
Hexane: EA = 9:1, R_f = 0.8; m. p. 140.7-143.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J*=1.2, 7.6Hz, 2H), 8.03 (t, *J*=8.8, 10Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 124.7, 128.3, 130.4, 132.7, 133.0; ^{19}F NMR (400 MHz, $CDCl_3$) δ -161.8 (m, 4F), -154.8 (t, 2F), -142.9 (dd, 4F); HRMS: calcd. for $C_{22}H_6F_{10}^+$: 460.0310, found 460.0313.

2,3,4,5,6-Pentafluoro-3'-cyanobiphenyl (Table 4.3, 4.5; Product 23an)[23]



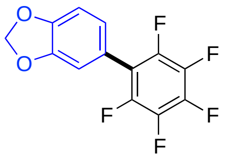
Hexane: EA = 20:1, R_f = 0.25; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J*=8.0Hz, 1H), δ 7.70 (d, *J*=8.0Hz, 1H), δ 7.76 (s, 1H), δ 7.78-7.80 (dt, *J*=6.0, 1.2, 1.6Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 113.3, 113.6, 117.9, 127.8, 129.7, 132.8, 133.6, 134.4, 139.2, 142.8, 145.3; ^{19}F NMR (400 MHz, $CDCl_3$) δ -161.0 (m, 2F) , -153.0 (t, 1F), -143.0 (dd, 2F).

3-(Perfluorophenyl)pyridine (Table 4.5; Product 23ao)[23]



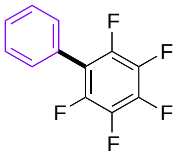
Hexane: EA = 10:1, $R_f = 0.2$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.48 (m, 1H), δ 7.79 (d, *J*=8.0Hz, 1H), δ 8.71-8.72 (dd, *J*=3.6, 1.2Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 123.0, 123.5, 137.4, 150.3, 150.4; ^{19}F NMR (400 MHz, $CDCl_3$) δ -161.2 (m, 2F) , -153.4 (t, 1F), -142.9 (dd, 2F).

5-(Perfluorophenyl)benzo[*d*][1,3]dioxole (Table 4.3, 4.5; Product 23ap)[23]



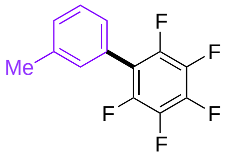
Hexane: EA = 20:1, $R_f = 0.5$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.06 (s, 2H), δ 6.90-6.96 (m, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 101.5, 108.6, 110.3, 119.4, 124.2, 147.9, 148.4; ^{19}F NMR (400 MHz, $CDCl_3$) δ -162.4 (m, 2F) , -156.0 (t, 1F), -143.1 (dd, 2F).

2,3,4,5,6-Pentafluoro-1,1'-biphenyl (Table 4.4; Product 23aq)[23]



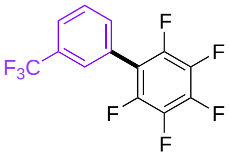
Hexane: EA = 20:1, $R_f = 0.6$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 3H), 7.51 (s, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 126.4, 128.7, 129.3, 130.1, 139.1; ^{19}F NMR (400 MHz, $CDCl_3$) δ -162.3 (m, 2F) , -155.6 (t, 1F), -143.3 (dd, 2F).

2,3,4,5,6-Pentafluoro-3'-methyl-1,1'-biphenyl (Table 4.4; Product 23ar)[21]



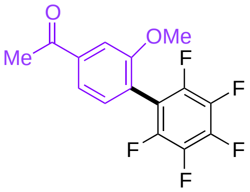
Hexane: EA = 20:1, R_f = 0.7; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.45 (s, 3H), 7.23-7.31 (m, 3H), 7.41 (t, *J*=7.6Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 21.3, 126.2, 127.1, 128.5, 130.0, 130.7, 138.5; ^{19}F NMR (400 MHz, $CDCl_3$) δ -162.4 (m, 2F) , -155.9 (t, 1F), -143.1 (dd, 2F).

2,3,4,5,6-Pentafluoro-3'-(trifluoromethyl)-1,1'-biphenyl (Table 4.5; Product 23as)[24]



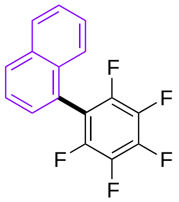
Hexane: EA = 20:1, R_f = 0.6; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.68 (m, 2H), δ 7.72 (s, 1H), δ 7.76 (d, *J*=5.2Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 125.0, 126.1 (m), 127.0, 127.2, 129.3, 131.2, 131.5, 133.4; ^{19}F NMR (400 MHz, $CDCl_3$) δ -161.4 (m, 2F) , -153.9 (t, 1F), -143.0 (dd, 2F), -62.8 (s, 3F).

1-(2',3',4',5',6'-Pentafluoro-2-methoxy-[1,1'-biphenyl]-4-yl)ethanone (Table 4.5; Product 23at)



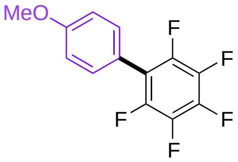
Hexane: EA = 20:1, R_f = 0.15; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.67 (s, 3H), δ 3.90 (s, 3H), 7.36 (d, *J*=8.4Hz, 1H), 7.64-7.66 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 26.6, 55.9, 110.0, 120.2, 121.1, 131.9, 139.6, 157.4, 197.3; ^{19}F NMR (400 MHz, $CDCl_3$) δ -162.5 (m, 2F) , -154.8 (t, 1F), -139.9 (dd, 2F).

1-(Perfluorophenyl)naphthalene (Table 4.4; Product 23au)[23]



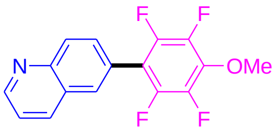
Hexane: EA = 20:1, R_f = 0.6; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.63 (m, 5H), 7.96-8.03 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 123.7, 124.5, 125.2, 126.4, 127.0, 128.6, 128.9, 130.1, 131.5, 133.6; ^{19}F NMR (400 MHz, $CDCl_3$) δ -161.8 (m, 2F) , -154.6 (t, 1F), -139.4 (dd, 2F).

2,3,4,5,6-Pentafluoro-4'-methoxy-1,1'-biphenyl (Table 4.5; Product 23av)[23]



Hexane: EA = 20:1, R_f = 0.6; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.89 (s, 3H), δ 7.05 (d, *J*=6.8Hz, 2H), δ 7.38 (d, *J*=8.8Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 55.3, 114.2, 131.4, 160.2; ^{19}F NMR (400 MHz, $CDCl_3$) δ -162.6 (m, 2F) , -156.5 (t, 1F), -143.6 (dd, 2F).

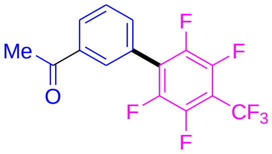
6'-(2,3,5,6-Tetrafluoro-4-methoxyphenyl)quinoline (Table 4.6; Product 23bc)



Hexane: EA = 9:1, R_f = 0.15; m. p. 162.8-165.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.13 (s, 3H), 7.42 (dd, *J*=4.4, 4.0Hz, 1H), 7.75 (d, *J*=8.8Hz, 1H), 7.90 (s, 1H), 8.18 (dd, *J*=9.2, 2.0Hz, 2H), 8.96 (d, *J*=3.2Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 62.07, 113.2, 121.6, 125.4, 127.9, 129.7, 130.8, 136.2, 137.8 (m), 139.9 (m), 142.4 (m), 143.0 (m), 145.6 (m), 147.7, 151.2; ^{19}F NMR (400 MHz, $CDCl_3$) δ -

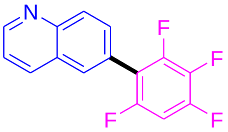
157.8 (dd, 2F), -144.7 (m, 2F); HRMS: calcd. for $C_{16}H_{10}NOF_4^+$: 308.0699, found 308.0706.

3'-(2,3,5,6-Tetrafluoro-4-(trifluoromethyl)phenyl)acetophenone (Table 4.6; Product 23ce)



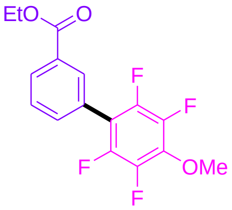
Hexane: EA = 9:1, R_f = 0.25; m. p. 86.3-88.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.661 (s, 3H), 7.66 (d, *J*=7.2Hz, 2H), 8.10 (dd, 4.4, 4.8Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 26.4, 119.3, 123.8, 126.5, 129.2, 129.6, 129.7, 134.1, 137.6, 142.9 (m), 145.4 (m), 196.8; ^{19}F NMR (400 MHz, $CDCl_3$) δ -141.3 (m, 2F), -140.3 (m, 3F), -56.4 (t, 2F); HRMS: calcd. for $C_{15}H_7OF_7^+$: 336.0385, found 336.0375.

6-(2,3,4,6-Tetrafluorophenyl)quinoline (Table 4.6; Product 23dc)



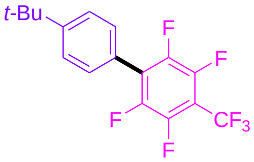
Hexane: EA = 4:1, R_f = 0.25; m. p. 130-132.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90-6.97 (m, 1H), 7.46 (dd, *J* = 4.4, 4.0 Hz, 1H), 7.76 (dd, *J* = 1.2, 7.6 Hz, 1H), 7.92 (s, 1H), 8.21 (t, *J* = 8.8 Hz, 2H), 8.98 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 101.0 (m), 121.6, 125.7, 127.9, 129.6, 129.7, 130.9, 136.3, 147.7, 151.2; ^{19}F NMR (400 MHz, $CDCl_3$) δ -164.3 (m, 1F), -135.2 (dd, 1F), -132.3 (dd, 1F), -117.8 (d, 1F); HRMS: calcd. for $C_{15}H_8NF_4^+$: 278.0593, found 278.0605.

[1,1'-Biphenyl]-3-carboxylic acid, 2',3',5',6'-tetrafluoro-4'-methoxy-, ethyl ester (Table 4.6; Product 23bj)



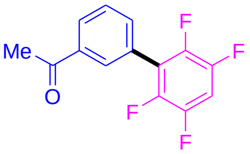
Hexane: EA = 9:1, R$_f$ = 0.5; m. p. 87.3-88.8 ^{o}C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.42 (t, *J* = 7.2 Hz, 3H), 4.14 (s, 3H), 4.42 (dd, *J* = 7.2, 6.8 Hz, 2H), 7.54-7.63 (m, 2H), 8.13 (d, *J* = 7.6 Hz, 2H),; ^{13}C NMR (100MHz, CDCl$_3$) δ 14.2, 61.2, 62.1, 113.1, 127.5, 128.6, 129.9, 131.0, 131.2, 134.3, 139.8 (m), 142.4 (m), 143.0 (m), 145.5 (m), 165.9; ^{19}F NMR (400 MHz, CDCl$_3$) δ -157.9 (dd, 2F), -145.1 (dd, 2F); HRMS: calcd. for $C_{16}H_{12}O_3F_4^+$: 328.0723, found 328.0722.

2,3,5,6-Tetrafluoro-4'-*tert*-butyl-4-(trifluoromethyl)-1,1'-biphenyl (Table 4.6; Product 23ca)



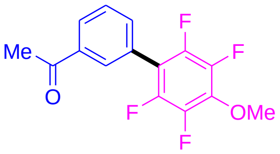
Pure hexane, R$_f$ = 0.7; m. p. 67-68.8 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.42 (s, 9H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.8 Hz, 2H),; ^{13}C NMR (100MHz, CDCl$_3$) δ 31.1, 34.8, 123.1, 124.9 (m), 125.8, 129.6, 143.0 (m), 145.6 (m), 153.3; ^{19}F NMR (400 MHz, CDCl$_3$) δ -141.7 (m, 3F), -141.0 (m, 2F), -56.2 (t, 2F); HRMS: calcd. for $C_{17}H_{13}F_7^+$: 350.0905, found 350.0906.

3'-(2,3,5,6-Tetrafluorophenyl)acetophenone (Table 4.6; Product 23ee)



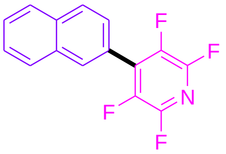
Hexane: EA = 9:1, R$_f$ = 0.48; m. p. 104.9-107 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.66 (s, 3H), 7.08-7.17 (m, 1H), 7.60-7.68 (m, 2H), 8.06-8.07 (t, *J*=5.2, 1.6Hz, 2H); ^{13}C NMR (100MHz, CDCl$_3$) δ 26.5, 105.4 (t), 120.6, 127.9, 128.9, 130.0, 134.5, 137.4, 142.5, 144.9, 147.5 (m), 150.9 (m), 197.2; ^{19}F NMR (400 MHz, CDCl$_3$) δ -143.7 (dd, 2F), -138.6 (dd, 2F); HRMS: calcd. for $C_{14}H_9OF_4^+$: 269.0590, found 269.0582.

3'-(2,3,5,6-Tetrafluoro-4-methoxyphenyl)acetophenone (Table 4.6; Product 23be)



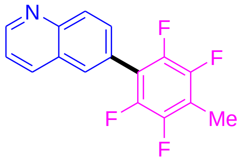
Hexane: EA = 9:1, R$_f$ = 0.35; m. p. 97.8-99.9 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.65 (s, 3H), 4.14 (s, 3H), 7.58-7.65 (m, 2H), 8.03 (t, *J*=4.8, 1.6Hz, 2H); ^{13}C NMR (100MHz, CDCl$_3$) δ 26.6, 62.1, 113.1, 127.8, 128.6 (d), 130.1, 134.6, 137.4 (m), 139.9 (d), 142.3 (m), 142.4 (m), 143.0 (m), 145.5 (m), 197.3; ^{19}F NMR (400 MHz, CDCl$_3$) δ -157.8 (dd, 2F), -145.1 (dd, 2F).

2,3,5,6-Tetrafluoro-4-(naphthalene-2-yl)pyridine (Table 4.6; Product 23fi)



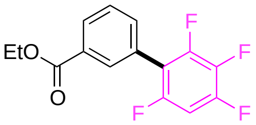
Hexane: EA = 9:1, R$_f$ = 0.65; m. p. 139.8-141.9 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.59-7.66 (m, 3H), 7.94-8.08 (m, 4H); ^{13}C NMR (100MHz, CDCl$_3$) δ 125.9, 127.0, 127.8, 127.0, 128.6, 128.7, 1303., 132.8, 133.7, 201.2; ^{19}F NMR (400 MHz, CDCl$_3$) δ -144.9 (dd, 2F), -90.7 (dd, 2F); HRMS: calcd. for $C_{15}H_{17}NF_4^+$: 277.0515, found 277.0514.

6-(2,3,5,6-Tetrafluoro-4-methylphenyl)quinoline (Table 4.6; Product 23gc)



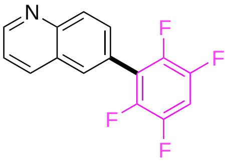
Hexane: EA = 4:1, R_f = 0.3; m. p. 197-198.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36 (s, 3H), 7.46 (dd, *J* = 4.4, 4.0 Hz, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.95 (s, 1H), 8.22 (t, *J* = 4.8, 4.0 Hz, 2H), 8.99 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 7.6, 121.6, 127.9, 129.7, 130.9, 136.3, 147.9, 151.3; ^{19}F NMR (400 MHz, $CDCl_3$) δ -145.4 (dd, 2F), -143.6 (dd, 2F); HRMS: calcd. for $C_{16}H_{10}NF_4^+$: 292.0749, found 292.0737.

Ethyl 2',3',4',6'-tetrafluoro-[1,1'-biphenyl]-3-carboxylate (Table 4.6; Product 23dj)



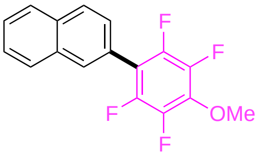
Hexane: EA = 4:1, R_f = 0.3; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41-1.44 (m, 3H), δ 4.40-4.45 (q, *J*=7.2Hz, 2H), δ 6.88-6.95 (m, 1H), δ 7.55-7.63 (m, 2H), δ 8.13-8.15 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 14.2, 61.2, 100.8, 101.0, 101.3, 127.7, 128.6, 129.9, 131.0, 131.2, 134.4, 165.9; ^{19}F NMR (400 MHz, $CDCl_3$) δ -164.4 (dd, 1F), -135.0 (m, 1F), -132.5 (d, 1F), -118.0 (d, 1F); HRMS: calcd. for $C_{15}H_{10}NO_2F_4^+$: 298.0617, found 298.0615.

6-(2,3,5,6-Tetrafluorophenyl)quinolone (Table 4.6; Product 23ec)



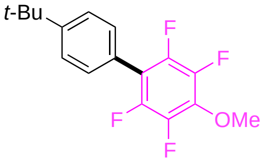
Hexane: EA = 9:1, R_f = 0.2; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10-7.18 (m, 1H), 7.46-7.50 (q, 1H), 7.79-7.81 (dd, *J*=7.2, 1.6Hz, 1H), 7.97 (s, 1H), 8.23 (t, *J*=8.4, 7.2Hz, 2H), 9.00-9.01 (dd, *J*=2.4, 1.6Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 105.1, 105.3, 105.6, 120.7, 121.7, 125.7, 129.9, 130.7, 136.4, 142.5, 145.1, 147.5, 148.0, 151.5; ^{19}F NMR (400 MHz, $CDCl_3$) δ -143.6 (dd, 2F), -138.6 (dd, 2F); HRMS: calcd. for $C_{15}H_8NF_4^+$: 278.0593, found 278.0588.

2-(2,3,5,6-Tetrafluoro-4-methoxyphenyl)naphthalene (Table 4.6; Product 23bi)



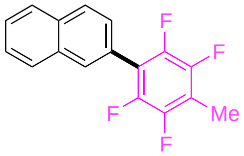
Hexane: EA = 4:1, R_f = 0.3; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.17 (s, 3H), 7.54-7.59 (m, 3H), 7.91-7.93 (m, 2H), 7.96-7.98 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 62.2, 114.2, 124.6, 126.5, 126.9, 127.3, 127.7, 128.2 (m), 130.0 , 133.1 (m), 142.5; ^{19}F NMR (400 MHz, $CDCl_3$) δ -158.1 (dd, 2F), -144.9 (dd, 2F).

4'-(*tert*-Butyl)-2,3,5,6-tetrafluoro-4-methoxy-1,1'-biphenyl (Table 4.6; Product 23ba)



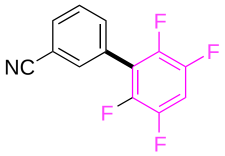
Hexane: EA = 9:1, R_f = 0.8; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40 (s, 9H), 4.14 (s, 3H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 31.2, 34.7, 62.1, 114.2, 124.2, 125.5, 129.8, 137.2, 139.8, 142.3, 142.5, 145.5, 151.9; ^{19}F NMR (400 MHz, $CDCl_3$) δ -158.4 (dd, 2F), -145.2 (dd, 2F); HRMS: calcd. for $C_{17}H_{16}OF_4^+$: 312.1137, found 312.1147.

2-(2,3,5,6-Tetrafluoro-4-methylphenyl)naphthalene (Table 4.6; Product 23gi)



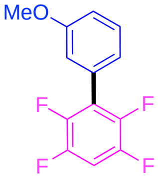
Hexane: EA = 9:1, R_f = 0.6; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.38 (s, 3H), 7.56-7.60 (m, 3H), 7.91-7.99 (m, 4H); ^{13}C NMR (100MHz, CDCl$_3$) δ 7.5, 115.1, 125.1, 126.4, 126.9, 127.2, 127.7, 128.1, 128.2, 129.9, 133.0, 133.1; ^{19}F NMR (400 MHz, CDCl$_3$) δ -145.4 (dd, 2F), -144.0 (dd, 2F); HRMS: calcd. for $C_{17}H_{10}F_4^+$: 290.0719, found 290.0714.

2',3',5',6'-Tetrafluoro-[1,1'-biphenyl]-3-carbonitrile (Table 4.6; Product 23en)



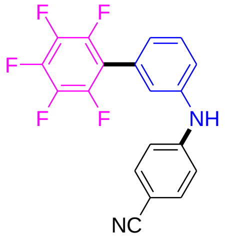
Hexane: EA = 9:1, R_f = 0.5; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.13-7.21 (m, 1H), 7.63-7.79 (m, 4H); ^{13}C NMR (100MHz, CDCl$_3$) δ 105.8, 106.1, 106.3, 113.2, 118.0, 128.8, 129.5, 132.6, 133.6, 134.4, 144.8, 147.5; ^{19}F NMR (400 MHz, CDCl$_3$) δ -143.7 (dd, 2F), -137.9 (dd, 2F); HRMS: calcd. for $C_{13}H_5NF_4^+$: 251.0358, found 251.0365.

2,3,5,6-Tetrafluoro-3'-methoxy-1,1'-biphenyl (Scheme 4.1)



Hexane: EA = 20:1, R_f = 0.4; ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.87 (s, 3H), 7.01-7.13 (m, 4H), 7.43 (t, J = 8.0 Hz, 1H); ^{13}C NMR (100MHz, CDCl$_3$) δ 55.3, 104.6, 104.8, 105.1, 114.8, 115.7, 122.4, 128.5, 129.6, 159.6; ^{19}F NMR (400 MHz, $CDCl_3$) δ -143.4 (dd, 2F), -139.1; HRMS: calcd. for $C_{13}H_8OF_4^+$: 256.0511, found 256.0514.

4-((3-(Pentafluorophenyl)phenyl)amino)benzonitrile (Scheme 4.1)



Hexane: EA = 9:1, R_f = 0.15; m. p. 127-128.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.37 (s, 1H), 7.06 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 2.8 Hz, 2H), 7.49 (dd, *J* = 8.0, 6.4 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 14.1, 102.2, 115.3, 115.4, 119.7, 121.4, 122.2, 125.3, 127.7, 130.0, 133.8, 140.7, 147.4; ^{19}F NMR (400 MHz, $CDCl_3$) δ -162.4 (M, 2F), -156.0 (t, 2F), -142.7 (dd, 1F); HRMS: calcd. for $C_{19}H_{10}N_2F_5^+$: 361.0764, found 361.0762.

4.6 References

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Chapter 5 Palladium-Catalyzed Sonogashira Coupling of Aryl Mesylates and Tosylates

5.1 Introduction

Aryl alkynes are important synthetic precursor and sub-unit for a range of pharmaceutically attractive and material science valuable organic compounds.[1] One of the most straightforward and versatile protocols for the construction of C(sp$_2$)-C(sp) bond is the palladium-catalyzed cross-coupling of aryl halides/sulfonates and terminal alkynes, namely Sonogashira coupling.[2] This methodology features a modular approach to assemble an array of diversified compounds from commonly available electrophilic and nucleophilic partners.[3]

A number of palladium catalyst systems have been developed for facilitating the Sonogashira coupling to proceed even without Cu(I) co-catalyst and at room temperature,[4,5] as well as showing the applicability of aryl chloride substrates.[6] Although the alkyne coupling of aryl halides has been extensively established, the popularity of aryl triflates has been limited. These constrain possibly due to the expensiveness of the triflating agent (e.g. Tf_2O),[7] and the low hydrolytic stability of aryl triflates under basic coupling reaction conditions. In fact, it is worth to develop methods for phenolic compound derivatives to be used as electrophiles. Since they usually offer different or unique substituted groups in the aromatic ring, in which the corresponding aryl halides are not commonly available, or require additional synthetic steps to manipulate the pattern of complementary substitution. Thus, the exploration of less expensive, yet more stable aryl arenesulfonates in Sonogashira coupling is highly favourable. Nevertheless, the higher stability of aryl arenesulfonate (e.g. aryl tosylate) makes this less reactive to subject oxidative addition under palladium catalytic system. Thus, the use of C(sp_2)-tosylates as coupling partners in C(sp_2)-C(sp) bond forming reaction has seldom been reported. Only vinyl tosylates were successful in this transformation.[8] Recently, the Sonogashira coupling of strongly activated and electron-deficient *para*- and *meta*-substituted aryl tosylates was disclosed using the Pd/X-Phos complex under the refluxing propionitrile solvent.[9] These pioneering examples required the slow addition of diluted alkyne substrates in 8 hours over the course of reaction. Moreover, a note was found that a high purity of the aryl tosylates was prerequisite for these successful couplings. An operationally-simple and general protocol for Sonogashira coupling of non-activated aryl and heteroaryl tosylate was reported by Kwong's group in 2010. In the meanwhile, Lindernschmidt and Nazaré described the application of $Pd(TFA)_2$/Josiphos-type ligand system for this reaction.[10] A wide variety of functionalized aryl and heteroaryl alkynes was used for further transformation to indoles and isoquinolines in high yields. In 2013, Quan and Wang reported a coupling reaction of pyrimidin-2-yl sulfonates with terminal alkynes using $Pd(OAc)_2$/CuI/DPE-Phos as the catalytic system. The pyrimidine scaffolds are useful for subunit for compounds having biological activities.[11]

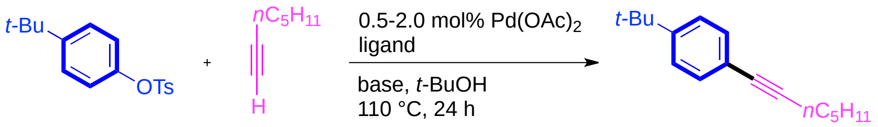
Recently, metal-free Sonogashira cross-coupling reactions become a popular topic to investigate.[12] Up to now, a variety of modifications of the Sonogashira-coupling have been developed with palladium complex, ligands, and additives. Herein, we report a general and efficient catalyst system for aryl tosylates in C(sp_2)-C(sp) coupling. In particular, we also uncover the first examples of more difficult but more atom-economical aryl mesylates coupling with alkynes.

5.2 Result and Discussion

5.2.1 Preliminary Evaluation of Palladium-Catalyzed Sonogashira Coupling of Aryl Sulfonates

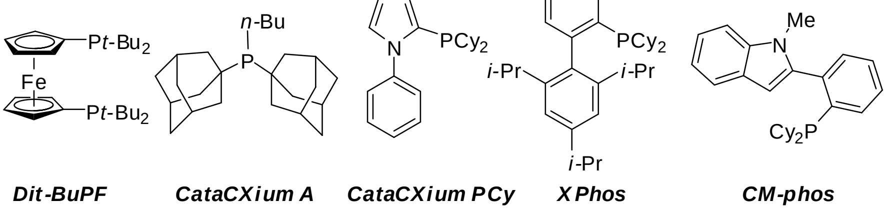
We started to embark investigation of Sonogashira coupling of aryl tosylate by using an unactivated 4-*tert*-butylphenyl tosylate and 1-heptyne as the model substrates (Table 5.1). Alcoholic solvent *t*-BuOH was our preference of choice instead of nitrile solvents. A survey of often-used inorganic bases revealed that K_3PO_4 and $K_3PO_4 \bullet H_2O$ were equally efficient (entries 1-4). The best Pd:CM-phos ratio was found to be 1:3 (entries 4, 7-8). Commonly well-recognized and commercially available phosphine ligands[13] such as Di*t*-BuPF, CataCXium®A, CataCXium®PCy and XPhos were tested for the feasibility of aryl tosylate-alkyne coupling (entries 9-12). Moderate substrate conversions and fair product yields were afforded by using biaryl-type monodentate phosphines as the supporting ligands (entries 11-12). A combination of $Pd(OAc)_2$ with CM-phos[14] was found to be the best catalyst system for this tosylate coupling (entry 7). Effect of solvent concentration was tested that 2 ml of *t*-BuOH gave the best product yield (entry 7 *vs* 13).

Table 5.1. Initial screenings of palladium-catalyzed Sonogashira coupling of aryl tosylates[a]



entry	Pd :L	ligand	base	%yield[b]
1	1:4	CM-phos	$K_3PO_4 \bullet H_2O$	89
2	1:4	CM-phos	Cs_2CO_3	59
3	1:4	CM-phos	K_2CO_3	Trace
4	1:4	CM-phos	K_3PO_4	90
5[c]	1:4	CM-phos	K_3PO_4	32
6[d]	1:4	CM-phos	K_3PO_4	59
7	1:3	CM-phos	K_3PO_4	93
8	1:2	CM-phos	K_3PO_4	62
9	1:3	Di*t*-BuPF	K_3PO_4	4
10	1:3	CataCXium® A	K_3PO_4	0
11	1:3	CataCXium® PCy	K_3PO_4	30
12	1:3	XPhos	K_3PO_4	39
13[e]	1:3	CM-phos	K_3PO_4	69

Ligands:

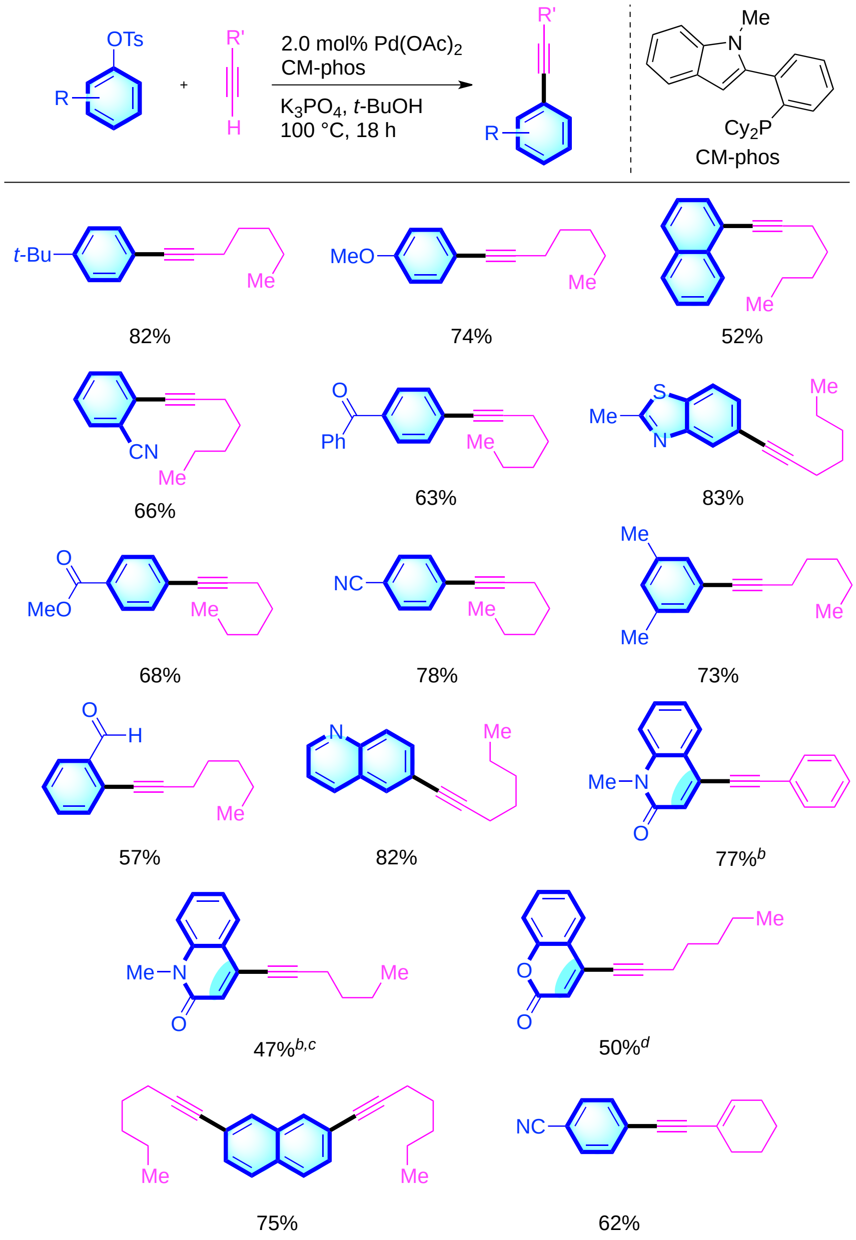


[a] Reaction conditions: ArOTs (0.5 mmol), alkyne (1.0 mmol), $Pd(OAc)_2$ (2.0 mol%), base (1.5 mmol) and *t*-BuOH (2.0 mL) under N_2 at 110 °C for 24 h (reaction time was not optimized). [b] Calibrated GC yields were reported, using dodecane as the internal standard. [c] 0.5 mol% of $Pd(OAc)_2$ was used. [d] 0.6 mmol of the corresponding alkyne was used. [e] 4 mL of *t*-BuOH was used.

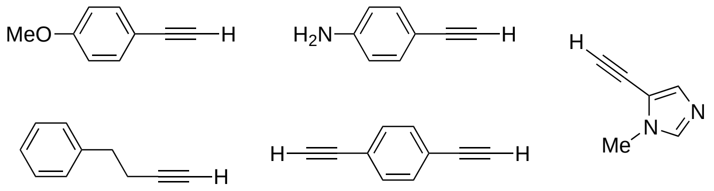
5.2.2 Scope of Palladium-Catalyzed Sonogashira Coupling of Aryl/alkenyl Tosylates

The preliminary results revealed that the Pd(OAc)$_2$/CM-phos catalytic system was effective towards the Sonogashira coupling reaction of aryl tosylates. To further evaluate the scope of this catalytic system, a variety of aryl tosylates coupling partners were examined with 1-heptyne under the optimized reaction conditions. (Table 5.2). In general, complete conversions were observed within 18 hours when 2 mol% of palladium was applied. Common functional groups such as cyano, keto, ester and aldehyde were compatible under the stated reaction conditions. Aryl tosylates bearing *ortho*-substituted groups were also effective substrates towards the coupling reaction. The electron-rich (deactivated) *p*-anisyl tosylate was also demonstrated to be a feasible coupling partner. Apart from functionalized aryl tosylates, heterocyclic benzthiazolyl and quinolinyl tosylates furnished the corresponding coupling products smoothly. Alkenyl tosylates were successfully coupled with terminal alkynes to afford moderate to good product yield with lower temperature or even at room temperature. 1-Ethynylcyclohex-1-ene could serve as an effective nucleophile for tosylate coupling (Table 5.2). However, except phenylacetylene, other aryl alkynes were not effective coupling partner for the coupling of aryl tosylates using the Pd(OAc)$_2$/CM-phos catalytic system. Homo-coupling product of aryl alkynes was resulted instead of Sonogashira coupling product (Scheme 5.1).

Table 5.2. Palladium-catalyzed Sonogashira coupling of aryl and heteroaryl tosylates[a]



[a] Reaction conditions: ArOTs (1.0 mmol), alkyne (2.0 mmol), $Pd(OAc)_2$ (2.0 mol%), (Pd:CM-phos = 1:3), K_3PO_4 (3.0 mmol) and *t*-BuOH (2.0 mL) under N_2 at 100 °C for 18 h (reaction time for each substrate was not optimized). Isolated yields were reported. [b] 50 °C was used. [c] 2 h was used. [d] Room temperature was used.

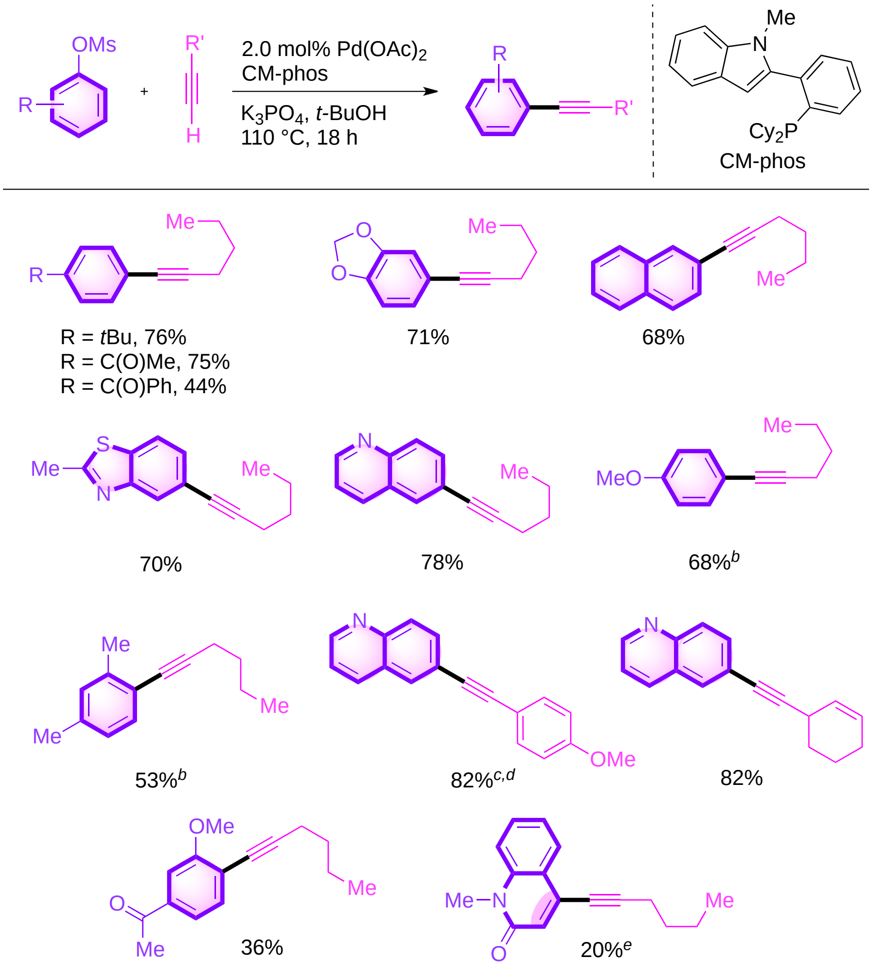


Scheme 5.1. Unsuccessful alkynes for Sonogashira coupling of aryl tosylate

5.2.3 Scope of Palladium-Catalyzed Sonogashira Coupling of Aryl/alkenyl Mesylates

Aryl mesylates are more attractive than the corresponding aryl tosylates as coupling substrates due to the atom economy of lower molecular weight. However, the application of aryl mesylates in Sonogashira coupling remains highly challenging. Gratifyingly, the Pd/CM-phos catalytic system was found to be effective in promoting the Sonogashira coupling of aryl mesylates (Table 5.3).

Table 5.3. Palladium-catalyzed Sonogashira coupling of aryl and heteroaryl mesylates[a]

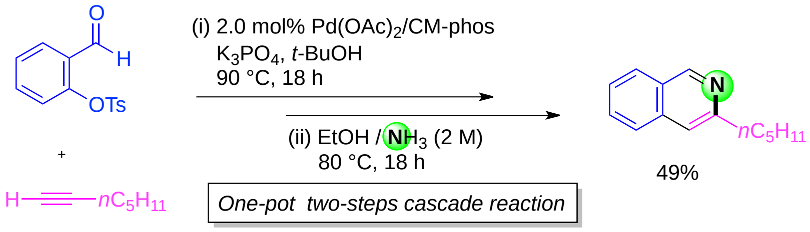


[a]Reaction conditions: ArOMs (1.0 mmol), alkyne (2.0 mmol), $Pd(OAc)_2$ (2.0 mol%), (Pd:CM-phos = 1:3), K_3PO_4 (3.0 mmol) and *t*-BuOH (2.0 mL) under N_2 at 110 °C for 18 h (reaction time for each substrate was not optimized). Isolated yields were reported. [b]5 mol% of $Pd(OAc)_2$ was used. [c]3.0 mmol of alkyne was used. [d]K_2CO_3 was used instead of K_3PO_4. [e]Room temperature was used.

An array of aryl mesylates were examined in this coupling reaction using 1-hexyne as the nucleophile. Heteroaryl mesylates were also compatible in this system. Aromatic alkyne and conjugated alkyne were found to be capable coupling partners (Table 5.3). These examples represent the first aryl mesylate-alkyne coupling reaction.

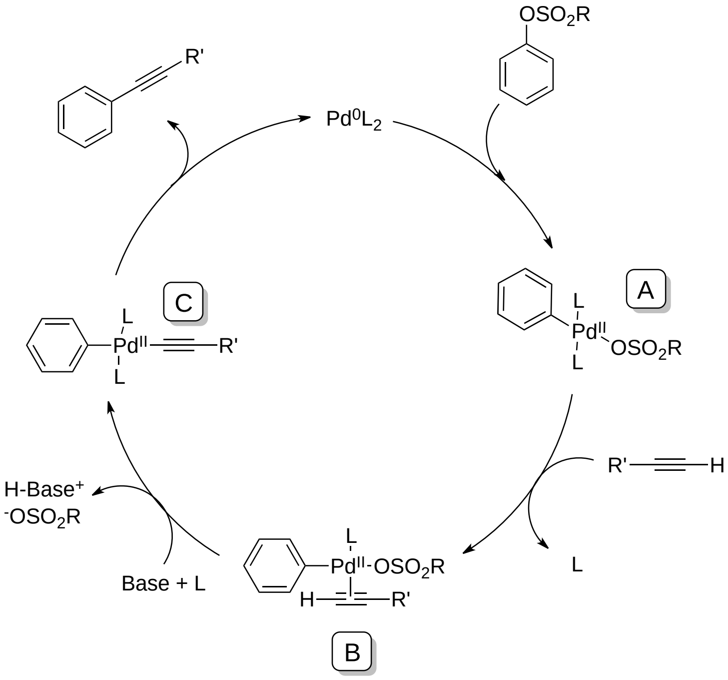
5.2.4 Application of Palladium-Catalyzed Sonogashira Coupling of Aryl Tosylates

In order to further show the application of this coupling process, a tandem reaction was investigated. The tosylate Sonogashira approach provided a facile access to nitrogen heterocycle, such as isoqinoline scaffold. To our best knowledge, this is the first example to target isoquinoline using a phenolic derivative (tosylate) precursor. The formylphenyl tosylate and 1-heptyne was directly transformed to 2-substituted isoquinoline effectively by an operationally simple one-pot two-steps cascade process (Scheme 5.2).



Scheme 5.2. One pot synthesis of substituted isoquinoline from aryl tosylate. (Reaction conditions: i. ArOTs (2.0 mmol), alkyne (4.0 mmol), $Pd(OAc)_2$ (2.0 mol%), (Pd:CM-phos = 1:3), K_3PO_4 (6.0 mmol) and t-BuOH (4.0 mL) under N_2 at 110 °C for 18 h; ii. Without purification/isolation processes, ethanolic ammonia was directly added to the reaction mixture and stirred at 80 °C for 18 h. Isolated yield in two steps.)

5.2.5 Proposed Mechanism of Palladium-Catalyzed Sonogashira Coupling of Aryl Sulfonates



Scheme 5.3. Proposed mechanism of Pd-catalyzed Sonogashira cross-coupling

For the general mechanism of Sonogashira coupling, the catalytic cycle is initiated by oxidative addition of aryl sulfonates to complex A with Pd(II) species. Then, coordination of terminal alkyne to the complex A, which produced an alkyne-Pd(II) complex B. After that, deprotonation was underwent which the base removed the proton from coordinated alkynes to form square planar Pd(II)-acetylide complex C. Finally, reductive elimination was carried out the expelled the desired products and regenerated the Pd(0) species.

5.3 Conclusion

In summary, we have established a general Sonogashira coupling of aryl and heteroaryl tosylates. This finding is of high significance as this procedure enables difficult phenolic derivative as the electrophilic partners, which usually offer different substitution patterns with respect to aryl halides, for aromatic alkyne synthesis. Notably, we have also succeeded in showing the first examples of even more difficult, yet more atom-economical aryl mesylate couplings under Sonogashira methodology. Indeed, the inertness of the mesylate group would feature aryl mesylate as a protecting group during multi-step synthesis and allow a number of orthogonal organic transformations and perform modular $C_{(sp2)}$-$C_{(sp)}$ bond construction at appropriate stage in the whole synthetic sequence. Particularly noteworthy is that this versatile alkyne-tosylate/mesylate coupling also provides a facile access to 2-substituted isoquinoline by a one-pot cascade process.

5.4 Experimental Section

5.4.1 General Considerations

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. All Sonogashira reactions were performed in Rotaflo® (England) resealable screw cap Schlenk flask (approx. 8 mL volume) in the presence of Teflon coated magnetic stirrer bar (3 mm × 10 mm). *tert*-Butanol was distilled from sodium under nitrogen. Commercially available alkynes were used as received. K_3PO_4 was purchased from Fluka. Thin layer chromatography was performed on Merck precoated silica gel 60 F_{254} plates. Silica gel (Merck, 70-230 and 230-400 mesh) was used for column chromatography. ^{1}H NMR spectra were recorded on a Bruker (400 MHz) or Varian (500 MHz) spectrometer. Spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.26 ppm), or with tetramethylsilane (TMS, δ 0.00 ppm) as the internal standard. Chemical shifts (δ) were reported as part per million (ppm) in δ scale downfield from TMS. ^{13}C NMR spectra were referenced to $CDCl_3$ (δ 77.0 ppm, the middle peak). Coupling constants (J) were reported in Hertz (Hz). Mass spectra (EI-MS and ES-MS) were recorded on a HP 5989B Mass Spectrometer. High-resolution mass spectra (HRMS) were obtained on a Brüker APEX 47e FT-ICR mass spectrometer (ESIMS). GC-MS analysis was conducted on a HP 5973 GCD system using a HP5MS column (30 m × 0.25 mm). The products described in GC yield were accorded to the authentic samples/dodecane calibration standard from HP 6890 GC-FID system.

5.4.2. General Procedures for Sonogashira Couplings of Aryl Tosylates and Mesylates

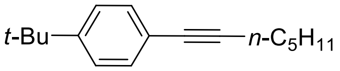
General procedures for Sonogashira couplings of aryl tosylates and mesylates (the Pd catalysts loading range from 0.5-5 mol%): $Pd(OAc)_2$ and CM-phos (Pd:L = 1:3) were loaded into a Schlenk tube equipped with a Teflon-coated magnetic stir bar. The tube was evacuated and flushed with nitrogen for three times. Precomplexation was applied by adding freshly distilled dichloromethane and Et_3N into the tube. The palladium complex stock solution was stirred and warmed using hair drier for 1 to 2 minutes until the solvent started boiling. The solvent was then evaporated under high vacuum. Aryl tosylate/ mesylate (0.5 mmol) and K_3PO_4 (1.5 mmol) were loaded into the tube, and the system was further evacuated and flushed with nitrogen for three times. The solvent *tert*-butanol (2.0 mL) was then added. The tube was stirred at room temperature for several minutes and alkyne (1.0 mmol) was then loaded into the tube. The tube was then placed into a preheated oil bath (110/ 100 °C) and stirred for 18 hours. After completion of reaction as judged by GC analysis, the reaction tube was allowed to cool to room temperature and quenched with water and diluted with ethyl acetate. The organic layer was separated and the aqueous layer was washed with ethyl acetate. The filtrate was concentrated under reduced pressure. The crude products were purified by flash column chromatography on silica gel (230-400 mesh) to afford the desired product.

5.4.3. General Procedures for Sequential Cyclization of Aryl Tosylates

General procedures for cyclization of aryl tosylates: Pd(OAc)$_2$ and ligand (Pd:L = 1:3) were loaded into a Schlenk tube (100 mL) equipped with a Teflon-coated magnetic stir bar. The tube was evacuated and flushed with nitrogen for three times. Precomplexation was applied by adding freshly distilled dichloromethane and Et$_3$N into the tube. The palladium complex stock solution was stirred and warmed using hair drier for 1 to 2 minutes until the solvent started boiling. The solvent was then evaporated under high vacuum. Aryl tosylate (2 mmol) and K$_3$PO$_4$ (7.5 mmol) were loaded into the tube, and the system was further evacuated and flushed with nitrogen for three times. The solvent *tert*-butanol (8.0 mL) was then added. The tube was stirred at room temperature for several minutes and alkyne (4.0 mmol) was then loaded into the tube. The tube was then placed into a preheated oil bath (110 °C) and stirred for 18 hours. After completion of reaction, the reaction tube was allowed to cool to room temperature. The system was flushed with nitrogen and ammonia in ethanol (2 M, 10 mL) was added. The tube was then placed into a preheated oil bath (80 °C) and stirred for another 18 hours. After the completion of reaction, the tube was allowed to cool to room temperature and the solvent was removed under vacuum. The reaction was then quenched with water and diluted with ethyl acetate and judged as GC. The organic layer was separated and the aqueous layer was washed with ethyl acetate. The filtrate was concentrated under reduced pressure. The crude products were purified by flash column chromatography on silica gel (230-400 mesh) to afford the desired product.

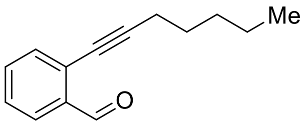
5.5. Characterization data of coupling products

1-*tert*-Butyl-4-(hept-1-ynyl)benzene (Table 5.2)[15]



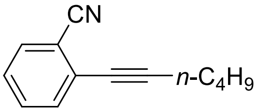
Pure Hexane, $R_f = 0.4$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, *J*=7.2Hz, 3H), 1.32 (s, 9H), 1.375-1.48 (m, 4H), 1.63 (q, *J*=7.2Hz, 2H), 2.41 (t, *J*=7.0Hz, 2H), 7.30-7.37 (q, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ 13.9, 19.3, 22.2, 28.5, 31.1, 31.2, 34.6, 80.5, 89.6, 121.1, 125.1, 131.2, 150.5; MS (EI): *m/z* (relative intensity) 228 (M^+, 20), 213 (100), 199 (5).

2-(Hept-1-ynyl)benzaldehyde (Table 5.2)[16]



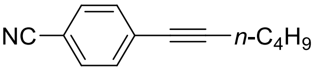
EA: Hexane = 1:9, $R_f = 0.6$; ^{1}H NMR (400 MHz, C_6D_6) δ 0.81 (t, *J*=7.2Hz, 3H), 1.52-1.37 (m, 6H), 2.11 (t, *J*=7.2Hz, 2H), 6.81-6.90 (m, 2H), 7.29 (dd, *J*=6.8, 0.8Hz, 1H), 7.88-7.90 (m, 1H), 10.76 (d, *J*=0.8Hz, 1H); ^{13}C NMR (100MHz, C_6D_6) δ 13.7, 19.2, 22.0, 28.0, 30.9, 76.6, 97.8, 126.8, 127.5, 127.7, 132.9, 133.0, 136.4, 190.5; MS (EI): *m/z* (relative intensity) 200 (M^+, 13), 157 (41), 144 (100), 128 (33), 115 (90).

2-(Hex-1-ynyl)benzonitrile (Table 5.2)[17]



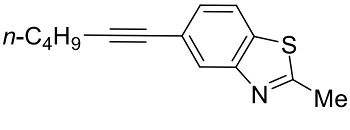
EA: Hexane=1:20, R_f = 0.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (t, *J*=7.4Hz, 3H), 1.50-1.58 (m, 2H), 1.62-1.67 (m, 2H), 2.50 (t, *J*=7.0Hz, 2H), 7.33-7.37 (m, 1H), 7.50-7.61 (m, 2H), 7.627 (d, *J*=0.8Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 13.5, 19.2, 21.9, 30.3, 97.9, 115.2, 117.7, 127.4, 128.0, 132.1, 132.2, 132.4; MS (EI): *m/z* (relative intensity) 182 (M^+, 82), 168 (100), 140 (90), 127 (39).

4-(Hex-1-ynyl)benzonitrile (Table 5.2)[18]



EA: Hexane= 1:20, R_f = 0.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, *J*=7.4Hz, 3H), 1.44-1.50 (m, 2H), 1.56-1.61 (m, 2H), 2.43 (t, *J*=7.0Hz, 2H), 7.43 (d, *J*=8.4Hz, 2H), 7.54 (d, *J*=8.4Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 13.4, 19.0, 21.8, 30.3, 79.3, 95.5, 110.6, 118.4, 129.0, 131.7, 131.9; MS (EI): *m/z* (relative intensity) 183 (M^+, 38), 168 (100), 154 (46), 140 (74), 127 (79).

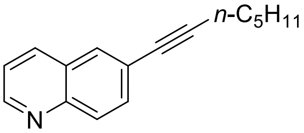
5-(Hex-1-ynyl)-2-methylbenzothiazole (Table 5.2, Table 5.3)



EA: Hexane= 1:9, R_f = 0.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 (t, *J*=7.2Hz, 3H), 1.46-1.55 (m, 2H), 1.58-1.66 (m, 2H), 2.44 (t, *J*=6.8Hz, 2H), 2.81 (s, 3H), 7.36

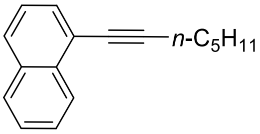
(dd, *J*=1.6, 6.8Hz, 1H), 7.70 (d, *J*=8.0Hz, 1H), 7.97 (bs, *J*=8.0Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 13.5, 19.0, 20.4, 21.9, 30.7, 80.1, 90.5, 120.9, 121.8, 125.2, 127.9, 134.8, 153.2, 167.5; MS (EI): *m/z* (relative intensity) 229 (M^+, 68), 214 (66), 200 (62), 186 (100); HRMS: calcd. for $C_{14}H_{16}NS^+$: 230.0992, found 230.1003.

6-(Hept-1-ynyl)quinoline (Table 5.2)



EA: Hexane= 1:4, R_f = 0.3; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, *J*=7.4Hz, 3H), 1.33-1.48 (m, 4H), 1.59-1.66 (m, 2H), 2.43 (t, *J*=7.2Hz, 2H), 7.31-7.34 (q, *J*=4.4Hz, 1H), 7.66 (dd, *J*=2.0, 1.6Hz, 1H), 7.83 (d, *J*=2.0Hz, 1H), 7.99-8.03 (t, *J*=8.4Hz), 8.83 (d, *J*=3.2Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 13.8, 19.3, 22.1, 28.2, 31.0, 80.1, 91.9, 121.3, 122.3, 127.8, 129.2, 130.5, 132.3, 135.3, 147.2, 150.3; MS (EI): *m/z* (relative intensity) 223 (M^+, 51), 194 (100), 180 (71), 168 (89), 139 (36); HRMS: calcd. for $C_{16}H_{18}N^+$: 224.1429, found 224.1439.

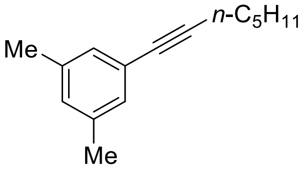
1-(Hept-1-ynyl)naphthalene (Table 5.2)15



Pure hexane, R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00 (t, *J*=7.2Hz, 3H), 1.44-1.59 (m, 4H), 1.75-1.78 (m, 2H), 2.61 (t, *J*=7.2Hz, 2H), 7.43 (t, *J*=7.6Hz, 1H), 7.53-7.60 (m, 1H), 7.60 (d, *J*=1.6Hz, 1H), 7.86 (dd, *J*=8.0, 0.4Hz, 2H), 8.39 (d, 8.4Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 14.0, 19.7, 22.2, 28.6, 31.2, 78.5, 95.6, 121.8, 125.2, 126.2, 126.3, 126.4, 127.8, 128.2, 129.9, 133.2, 133.5; MS

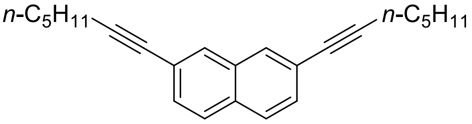
(EI): *m/z* (relative intensity) 222 (M^+, 44), 193 (27), 179 (35), 165 (100), 152 (23).

1-(Hept-1-ynyl)-3,5-dimethylbenzene (Table 5.2)



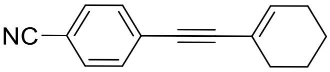
Pure hexane, R_f = 0.6; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 (t, *J*=7.2Hz, 3H), 1.36-1.60 (m, 4H), 1.62-1.65 (m, 2H), 2.30 (s, 6H), 2.42 (t, *J*=7.0Hz, 2H), 6.93 (s, 1H), 7.06 (s, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 13.9, 19.3, 21.0, 22.2, 28.5, 31.1, 80.7, 89.6, 123.7, 129.2, 129.3, 137.6; MS (EI): *m/z* (relative intensity) 200 (M^+, 44), 171 (41), 156 (35), 143 (100), 128 (44), 115 (27).

2,7-Di(hept-1-ynyl)naphthalene (Table 5.2)



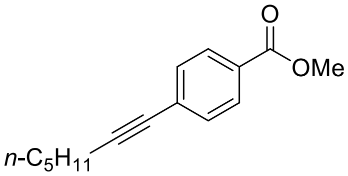
Pure hexane, R_f = 0.3; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (t, *J*=7.2Hz, 6H), 1.39-1.54 (m, 8H), 1.64-1.72 (m, 4H), 2.48 (t, *J*=7.2Hz, 4H), 7.45 (dd, *J*=1.2, 7.2Hz, 2H), 7.73 (d, *J*=8.4Hz, 2H), 7.85 (s, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 14.0, 19.5, 22.2, 28.5, 31.2, 80.7, 91.2, 122.0, 127.5, 129.1, 130.5, 131.4, 132.7; MS (EI): *m/z* (relative intensity) 316 (M^+, 100), 259 (31), 215 (38), 202 (62), 179 (37).

4-(Cyclohexenylethynyl)benzonitrile (Table 5.2)[19]



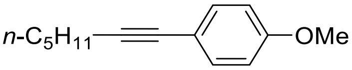
EA: Hexane=1:9, R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.63-1.72 (m, 4H), 2.18-2.24 (m, 4H), 6.29-6.31 (m, 1H), 7.50 (t, *J*=6.4Hz, 2H), 7.58-7.60 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 21.2, 22.1, 25.7, 28.8, 95.8, 110.7, 118.5, 120.1, 128.7, 131.7, 131.8, 137.1; MS (EI): *m/z* (relative intensity) 207 (M^+, 100), 192 (56), 179 (55), 165 (29), 151 (29), 140 (29).

4-Hept-1-ynyl-benzoic acid methyl ester (Table 5.2)15



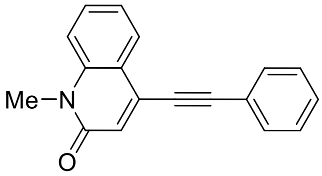
EA: Hexane=1:9, R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, *J*=7.2Hz, 3H), 1.36-1.46 (m, 4H), 1.60-1.64 (m, 2H), 2.42 (t, *J*=7.2Hz, 2H), 3.90 (s, 3H), 7.44 (d, *J*=8.4Hz, 2H),7.94 (d, *J*=8.4Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 13.8, 19.4, 22.1, 28.2, 31.0, 52.0, 80.0, 93.9, 128.7, 128.9, 129.3, 131.3, 166.5; MS (EI): *m/z* (relative intensity) 230 (M^+, 35), 201 (58), 142 (55), 129 (100), 115 (42).

1-(Hept-1-ynyl)-4-methoxybenzene (Table 5.2)15



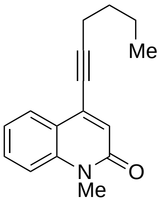
EA: Hexane= 1:50, R_f = 0.25; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, *J*=7.2Hz, 3H), 1.47-1.60 (m, 4H), 2.39 (t, *J*=7.0Hz, 2H), 3.79 (s, 3H), 6.80 (d, *J*=8.8Hz, 2H), 7.32 (d, *J*=8.8Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 13.6, 19.0, 30.9, 55.2, 80.2, 88.7, 113.7, 116.2, 132.8, 158.9; MS (EI): *m/z* (relative intensity) 188 (M^+, 50), 173 (32), 159 (32), 145 (100).

1-Methyl-4-(phenylethynyl)quinolin-2(1*H*)-one (Table 5.2)[20]



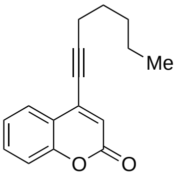
EA: Hexane= 1:4, R_f = 0.2; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.68 (s, 3H), 6.92 (s, 1H), 7.27-7.33 (m, 2H), 7.39-7.41 (m, 3H), 7.56-7.62 (m, 3H), 8.08 (dd, *J*=1.2, 4Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 29.2, 83.8, 114.1, 119.8, 121.6, 122.1, 124.2, 127.2, 128.3, 129.3, 130.9, 131.8, 132.2, 139.6,161.2; MS (EI): *m/z* (relative intensity) 259 (M^+, 100), 230 (54).

4-(Hex-1-yn-1-yl)-1-methylquinolin-2(1*H*)-one (Table 5.2, 5.3)



EA: Hexane= 1:4, R_f = 0.3; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, *J* = 7.2 Hz, 3H), 1.38-1.51 (m, 4H), 1.66-1.73 (m, 2H), 2.54 (t, *J* = 7.2 Hz, 2H), 3.69 (s, 3H), 6.81 (s, 1H), 7.24-7.34 (m, 2H), 7.54-7.59 (m, 1H), 8.01 (dd, *J* = 6.4, 1.2 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 13.8, 19.6, 22.0, 28.0, 29.2, 31.0, 75.6, 100.9, 114.0, 120.4, 122.0, 124.1, 127.4, 130.7, 133.2, 139.6, 161.5.

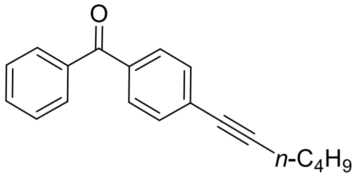
4-(Hept-1-yn-1-yl)-2*H*-chromen-2-one (Table 5.2)



EA: Hexane= 1:6, R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, *J*=7.2 Hz, *3H*), 1.39-1.50 (m, 4H), 1.67-1.75 (m, 2H), 2.57 (t, *J*=7.2 Hz, 2H), 6.49 (s, 1H), 7.28-7.33 (m, 2H), 7.52-7.56 (m, 1H), 7.83-7.86 (dd, *J*=1.6, 6.4Hz, 1H); ^{13}C NMR

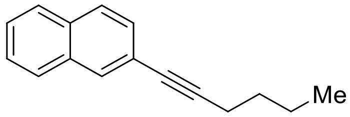
(100MHz, $CDCl_3$) δ 13.8, 19.7, 22.0, 27.8, 31.0, 74.7, 105.1, 116.8, 118.1, 118.7, 124.2, 126.6, 132.0, 138.0, 153.4, 160.3

(4-(Hex-1-ynyl)phenyl)(phenyl)methanone (Table 5.2)[21]



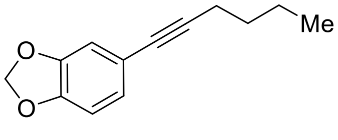
EA: Hexane= 1:9, R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (t, *J*=7.2Hz, 3H), 1.48-1.56 (m, 2H), 1.59-1.65 (m, 2H), 2.46 (t, *J*=7.2Hz, 2H), 7.47-7.51 (m, 4H), 7.57-7.61 (m, 1H), 7.74-7.80 (m, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ 13.5, 19.1,21.9, 30.6, 80.0, 94.0, 128.2, 128.5, 129.8, 129.9, 131.3, 132.3, 136.0, 137.4, 195.9; MS (EI): *m/z* (relative intensity) 262 (M^+, 50), 185 (57), 105 (100), 77 (40).

2-(Hex-1-ynyl)naphthalene (Table 5.3)[22]



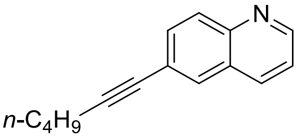
Pure Hexane, R_f = 0.45; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.03 (t, *J*=7.2Hz, 3H), 1.55-1.61 (m, 2H), 1.66-1.71 (m, 2H), 2.52 (t, *J*=7.2Hz, 2H), 7.49-7.53 (m, 3H), 7.78-7.85 (m, 3H), 7.97 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 13.6; 19.1, 22.0, 30.8, 80.9, 90.8, 121.4, 126.1, 126.3, 127.5, 127.6, 127.7, 128.7, 130.9, 132.4, 133.0; MS (EI): *m/z* (relative intensity) 208 (M^+, 60), 193 (36), 179 (66), 165 (100).

4-(1-Hexyn-1-yl)-1,2-(methylenedioxy)benzene (Table 5.3)[23]



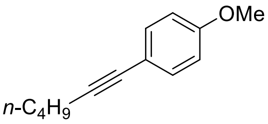
EA: Hexane= 1:40, R_f = 0.25; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (t, *J*=7.2Hz, 3H), 1.46-1.52 (m, 2H), 1.56-1.62 (m, 2H), 2.40 (t, *J*=7.2Hz, 2H), 5.96 (s, 2H), 6.74 (d, *J*=8Hz, 1H), 6.88 (d, *J*=1.6Hz, 1H), 6.93 (dd, *J*=6.4, 1.6Hz, 1H),; ^{13}C NMR (100MHz, $CDCl_3$) δ 13.5, 19.0, 20.0, 21.9, 30.7, 80.2, 90.5, 120.9, 121.8, 125.2, 128.0, 134.8, 153.3, 167.6; MS (EI): *m/z* (relative intensity) 229 (M^+, 70), 214 (64), 200 (61), 186(100).

6-(Hex-1-ynyl)quinoline (Table 5.3)



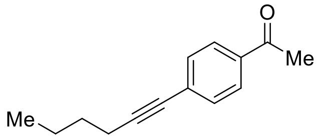
EA: Hexane= 1:4, R_f = 0.3; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, *J*=7.2Hz, 3H), 1.46-1.52 (m, 2H), 1.57-1.63 (m, 2H), 2.44 (t, *J*=7.2Hz, 2H), 7.33 (dd, *J*=4.4, 3.6Hz, 1H), 7.67 (dd, *J*=6.8, 2.0Hz, 1H), 7.83 (d, *J*=1.6Hz, 1H), 8.08 (t, *J*=8.8Hz, 2H), 8.84 (t, *J*=1.6Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 13.5, 19.0, 21.9, 30.6, 80.1, 91.8, 121.4, 122.3, 127.8, 129.1, 130.5, 132.3, 135.4, 147.2, 150.3; MS (EI): *m/z* (relative intensity) 209 (M^+, 55), 194 (73), 180 (100), 166 (68); HRMS: calcd. for $C_{15}H_{15}N^+$: 210.1285, found 210.1283.

1-(Hex-1-ynyl)-4-methoxybenzene (Table 5.3)[24]



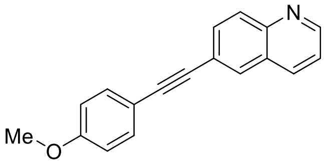
EA: Hexane= 1:50, R_f = 0.25; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (t, *J*=7.2Hz, 3H), 1.48-1.54 (m, 2H), 1.60-1.63 (m, 2H), 2.42 (t, *J*=7.2Hz, 2H), 3.81 (s, 3H), 6.82 (d, *J*=8.8Hz, 2H), 7.35 (d, *J*=8.8Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 13.6, 19.0, 21.9, 30.9, 55.1, 80.1, 88.6, 113.7, 116.2, 132.8, 158.9; MS (EI): *m/z* (relative intensity) 188 (M^+, 55), 173 (34), 159 (33), 145 (100).

1-(4-(Hex-1-ynyl)phenyl)ethanone (Table 5.3)[25]



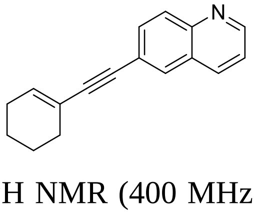
EA: Hexane= 1:4, R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (t, *J*=7.2Hz, 3H), 1.48-1.52 (m, 2H), 1.60-1.63 (m, 2H), 2.45 (t, *J*=7.2Hz, 2H), 2.59 (s, 3H), 7.46 (d, *J*=8.8Hz, 2H), 7.87 (t, *J*=6.8Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 13.6, 19.0, 21.9, 30.9, 55.1, 80.1, 88.6, 113.7, 116.2, 132.8, 158.913.5, 19.1, 21.9, 26.4, 30.5, 80.0, 94.3, 128.0, 129.1, 131.5, 135.5, 197.3; MS (EI): *m/z* (relative intensity) 200 (M^+, 23), 185 (100), 129 (26).

6-((4-Methoxyphenyl)ethynyl)quinoline (Table 5.3)[26]



EA: Hexane= 1:3, R_f = 0.25; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (s, 3H), 6.86 (d, *J*=8.8Hz, 2H), 7.32-7.36 (m, 1H), 7.50 (d, *J*=8.8Hz, 2H), 7.78 (dd, *J*=6.8, 1.6Hz 1H), 7.94 (d, *J*=1.6Hz, 1H), 8.03-8.06 (m, 2H), 8.86-8.87 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 55.1, 87.6, 90.6, 113.9, 114.8, 121.5, 121.7, 127.8, 129.3, 130.5, 131.9, 133.0, 135.4, 147.3, 150.5, 159.6; MS (EI): *m/z* (relative intensity) 259 (M^+,100), 244 (47), 216 (24).

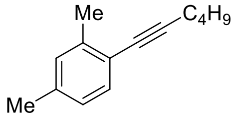
6-(Cyclohex-1-enylethynyl)quinoline (Table 5.3)



EA: Hexane= 1:6, R_f = 0.35; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.60-1.69 (m, 4H), 2.14-2.26 (m, 4H), 6.25-6.27 (m, 1H), 7.32-7.35 (m, 1H), 7.70 (q, *J*=6.8, 2.0Hz

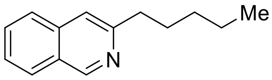
1H), 7.86 (d, *J*=1.6Hz, 1H), 7.99-8.04 (m, 2H), 8.84-8.86 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 21.3, 22.1, 25.6, 29.0, 86.3, 92.5, 120.4, 121.4, 122.0, 127.8, 129.2, 130.4, 132.1, 135.4, 135.8, 147.3, 150.4; MS (EI): *m/z* (relative intensity) 233 (M^+, 100), 218 (42), 204 (42). HRMS: calcd. for $C_{12}H_{16}N^+$: 234.1287, found 234.1283.

1-(Hex-1-ynyl)-2,4-dimethylbenzene (Table 5.3)[19]



Hexane, R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97-1.02 (m, 3H), 1.53-1.58 (m, 2H), 1.62-1.66 (m, 2H), 2.33-2.34 (d, *J*=2.0Hz, 3H), 2.42 (d, *J*=3.2, 3H), 2.46-2.51 (m, 2H), 6.94-6.96 (d, *J*=7.6, 1H), 7.03 (s, 1H), 7.28-7.31(m, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 13.6, 19.2, 20.5, 21.2, 21.9, 31.0, 79.4, 93.4, 120.8, 126.1, 130.0, 131.6, 137.2, 139.6; MS (EI): *m/z* (relative intensity) 186 (M^+, 71), 171 (57), 143 (93), 128 (100).

3-Pentylisoquinoline (Scheme 5.2)[27]



EA: Hexane= 1:4, R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, *J*=7.2Hz, 3H), 1.37-1.41 (m, 4H), 1.79-1.86 (m, 2H), 2.93 (t, *J*=7.6Hz, 2H), 7.45 (s, 2H), 7.50 (t, *J*=7.2Hz 1H), 2.62 (t, *J*=8.8Hz, 1H), 7.72 (d, *J*=8.8Hz, 1H), 7.89 (d, *J*=7.2Hz, 1H), 9.20 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 13.9, 22.5, 29.6, 31.5, 38.0, 117.8, 125.9, 126.1, 126.9, 127.3, 130.0, 136.4, 151.9, 155.7; MS (EI): *m/z* (relative intensity) 199 (M^+, 3), 170 (14), 156 (20), 143(100), 115(14).

5.6. Reference

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(2) For a Highlight and reviews, see: (a) Plenio, H. *Angew. Chem., Int. Ed.* **2008**, *47*, 6954. (b) Doucet, H.; Hierso, J.-C. *Angew. Chem., Int. Ed.* **2007**, *46*, 834. (c) Chinchilla, R.; Najera, C. *Chem. Rev.* **2007**, *107*, 874; d) Viciu, M. S.; Nolan, S. P. *Arylation Reactions of Alkynes: The Sonogashira Reaction*, In *Modern Arylation Methods*, L. Ackermann, Ed., Wiley-VCH: Weinheim, **2009**, pp. 183-220. (e) So, C. M.; Kwong, F. Y. *Chem. Soc. Rev.* **2011**, *40*, 4963. (f) Chinchilla, R.; Najera, C. *Chem. Soc. Rev.* **2011**, *40*, 5084. (g) Chinchilla, R.; Najera, C. *Chem. Rev.* **2013**, DOI: 10.1021/cr400133p.

(3) For a review describing modular/coupling approaches in total synthesis, see: Nicolaou, K. C.; Bulger, P. G.; Sarlah, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 4442.

(4) For examples of Sonogashira coupling without Cu co-catalyst, see: (a) Tougerti, A.; Negri, S.; Jutand, A. *Chem. Eur. J.* **2007**, *13*, 666. (b) Ahlquist, M.; Norrby, P. O. *Organometallics* **2007**, *26*, 550. (c) Liang, Y.; Xie, Y.-X.; Li, J.-H. *J. Org. Chem.* **2006**, *71*, 379. (d) Yi, C.; Hua, R. *J. Org. Chem.* **2006**, *71*, 2535. (e) Liang, B.; Dai, M.; Chen, J.; Yang, Z. *J. Org. Chem.* **2005**, *70*, 391. (f) Urgaonkar, S.; Verkade, J. G. *J. Org. Chem.* **2004**, *69*, 5752.

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(7) The prices of the sulfonating agent are: TsCl, approx. 0.05 USD/gram; Tf_2O, approx. 5 USD/gram, from commercial suppliers in 2005-2006. Note: TsCl is a solid form and sold in ordinary reagent bottle, while Tf_2O is a highly moisture sensitive liquid and usually sold in an ampule.

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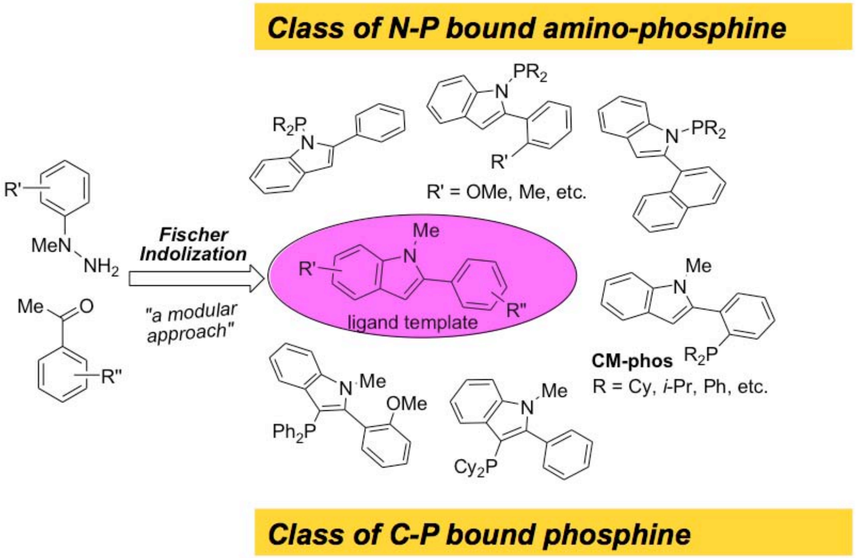
Chapter 6 Designs and syntheses of New Classes of Indolyl Phosphine Ligands

6.1 Introduction

Phosphine ligands have emerged as one of the most important parts in transition metal-catalyzed catalysis. The steric and electronic properties of the phosphine ligands may be varied by fine tuning of the ligand skeleton. Various supporting ligands have been designed by several research groups, such as biaryl monophosphines, [1] alkyl monophosphines, [2] and *N*-heterocyclic carbenes. [3] Although scientists have made intense contributions to cross-coupling by introducing specially designed catalyst, there is still limitations for instance, the complicated/ expensive synthetic methods of ligands.

Inspired by the previous fruitful works, our group focused on the development and exploration of simple and efficient ligands, which have a great potential of diversification to deal with particular challenge in coupling methodology. With the development of new series of indolyl phosphine ligands (Scheme 6.1), various palladium-catalyzed cross-coupling reactions were successfully achieved.[4] Notably, CM-phos facilitates the Suzuki cross-couplings and amination even for the unexplored aryl sulfonates in good-to-excellent yields with low catalyst loadings.[5]

In light of the performance of the catalyst, a modification of CM-phos was carried out to demonstrate the importance of altering the steric hinderance and electron density on *N*-substituted group. Moreover, as an extension of our continuous interest in the ligand, new classes of indolyl phosphine ligands were developed to tackle the problematic and difficult substrates in aromatic bond-construction processes.

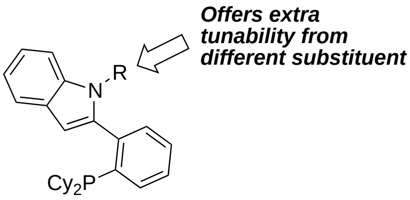


Scheme 6.1. N-P type and C-P type indolyl phosphine ligands developed by Kwong

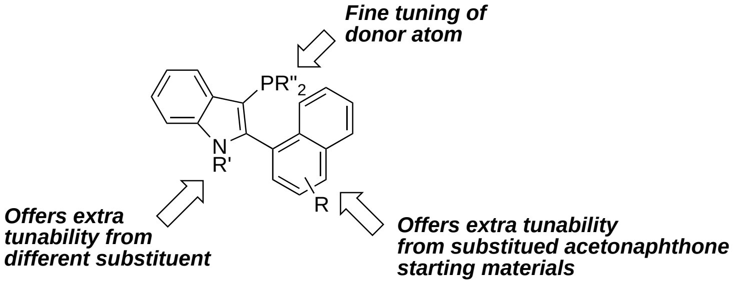
6.2 Strategic Design of New Classes of Ligands

The design of ligand is possibly a key to succeed of challenging cross-coupling. With our previous experiences in dealing with indolyl phosphines, we plan to the following considerations for the ligand skeleton fine-tuning:

1) To modify the well-developed CM-phos by incorporating groups at the *N*-position to expand the ligand diversification;



2) To develop a family of easily accessible C3-indolyl phosphine ligands which can be synthesized from phenylhydrazine and different substituted 1-acetonaphthone;

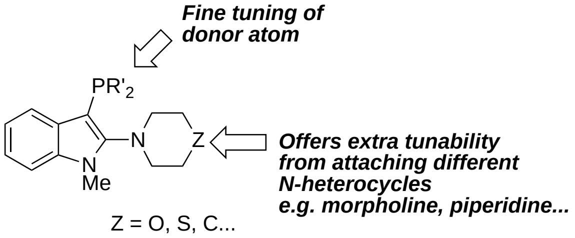


Fine tuning of donor atom

Offers extra tunability from different substituent

Offers extra tunability from substitued acetonaphthone starting materials

3) To develop a family of easily accessible indolyl morpholine phosphine ligands with the original phenyl ring is replaced by morpholine or related heterocycles.



Fine tuning of donor atom

Offers extra tunability from attaching different N-heterocycles e.g. morpholine, piperidine...

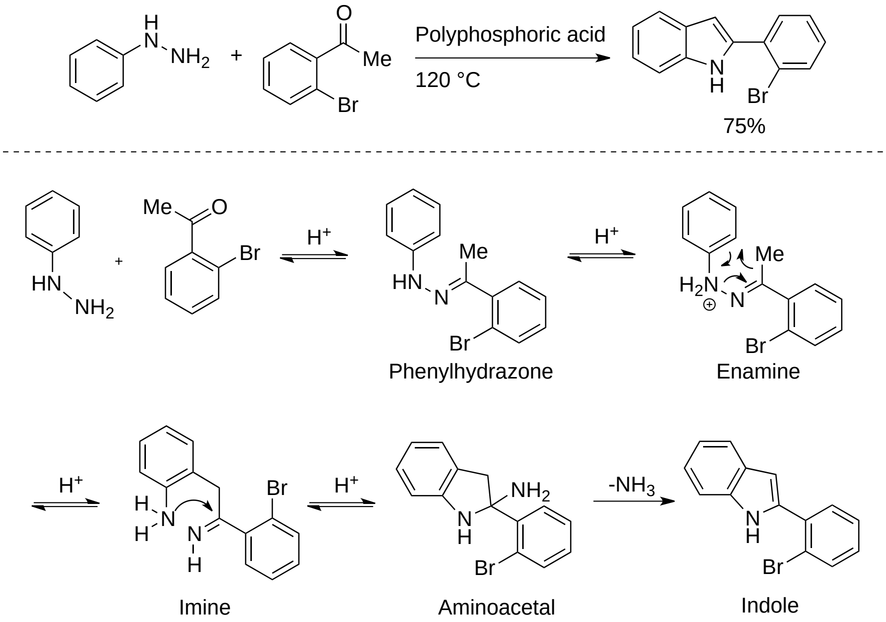
Z = O, S, C...

6.3 Result and Discussion

6.3.1 Modification of Well-Developed CM-phos Skeleton

With our previous experiences in dealing with CM-phos, the modified Fischer indolization was successful in synthesizing sterically hindered 2’-substituted 2-arylindoles.

Inexpensive phenylhydrazines and 2’-bromoacetophenone were used to synthesize the ligand precursors 2-(2-bromophenyl)-1*H*-indole. Initially, phenylhydrazone was formed when the starting materials were mixed together under acidic condition. Then, it would undergo isomerization to yield enamine. After protonation, a cyclic [3,3]-sigmatropic rearrangement occurred to produce an imine. The imine was then transformed into a cyclic aminoacetal and yielding the indole ligand precursor by elimination of NH_3. This approach benefits in a large-scale synthesis (Scheme 6.2).

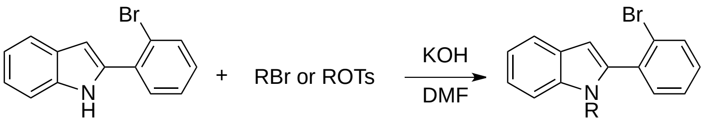


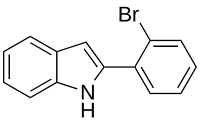
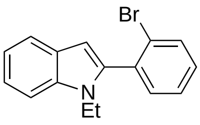
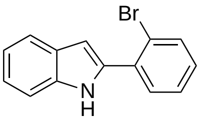
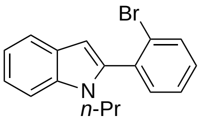
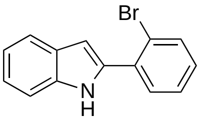
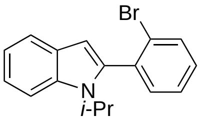
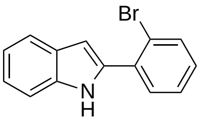
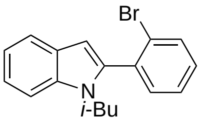
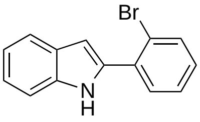
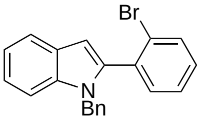
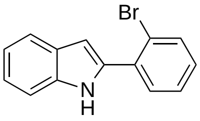
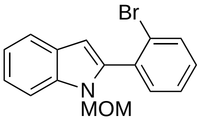
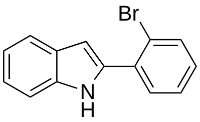
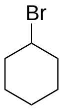
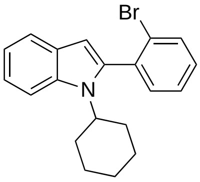
Scheme 6.2. Synthesis of 2-(2-bromophenyl)-1*H*-indole by Fischer Indolization

The acidic proton on the nitrogen atom was protected before the phosphination, otherwise, it would be firstly reacted under basic condition. The selection of the protecting group is the target tunable part of our ligand design, in which the substituent is attached to the nitrogen atom an thus offers extra steric and electronic tuning. For CM-phos, methyl group was chosen as the substituent in order to rapidly synthesize and examine the catalytic activity. After the well development of CM-phos, further substitution of the *N*-H group of the ligand was then continued.

N-Methylated 2-arylindole was obtained in excellent yield by using sodium hydride to abstract the acidic proton of 2-arylindoles and then quenching with dimethylsulfate. For other substituted groups, the corresponding alkyl bromides or tosylates were used with KOH in DMF (Table 6.1). However, substitution also occurred at the C-3 position of indole ring under strong basic condition. By tuning the basicity, the corresponding *N*-substituted ligand precursors could be afforded in moderate to good yields. However, there was no reaction while cyclohexyl bromide was applied. No target substitutions were resulted when cyclopropyl, cyclobutyl, cyclopentyl bromides, and 2-bromo-2-methylpropane were employed as the starting materials. This may due to the high steric effect.

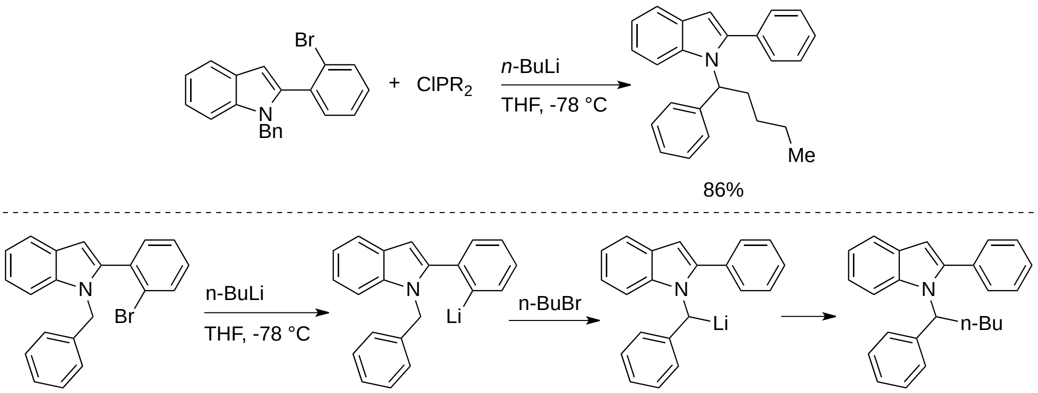
Table 6.1. Protection of indoles at the *N*-position with different substituents[a]



entry	ligand precurosr	RBr/OTs	product	% yield[b]
1[c]		EtBr		60%
2		*n*-PrOTs		69%
3		*i*-PrBr		71%
4		*i*-BuBr		52%
5		BnBr		74%
6[c]		MOMBr		33%
7				NR

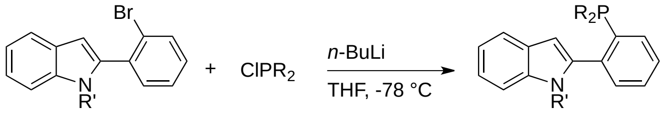
[a]Reaction conditions: 2-(2-bromophenyl)-1*H*-indole: R'Br/OTs: KOH = 1:3:5, stirred at room temperature overnight. [b]Isolated yields were reported. [c]NaH was used instead of KOH (indole: NaH: R'Br = 1: 2: 1.5).

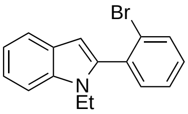
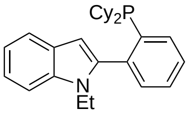
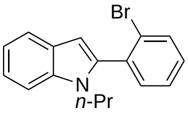
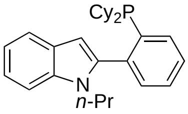
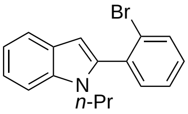
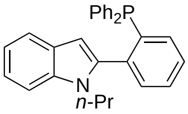
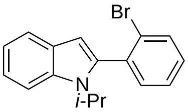
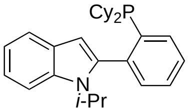
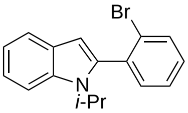
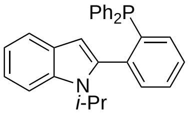
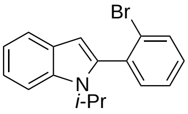
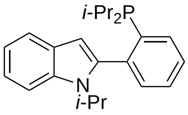
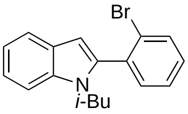
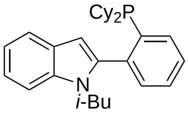
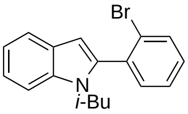
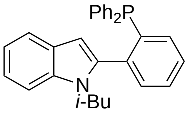
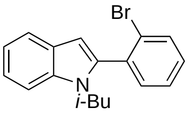
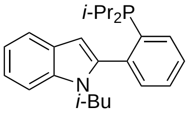
The straightforward deprotonation of 2-arylindole by *n*-BuLi and trapping by $ClPR_2$ afforded the corresponding phosphine ligands in moderate-to-good yields (Table 6.2). For 1-benzyl-2-(2-bromophenyl)-1*H*-indole, there is no desired product was obtained. After the lithiation by *n*-BuLi, the bromo-group was abstracted and replaced by lithium and yielding *n*-butyl bromides. However, the proton at the benzyl group ($-CH_2$) was very reactive that it is easy to undergo metal-hydrogen exchange. The lithium is then exchanged to the benzylic position. When chlorodiphenyl- or chlorodicyclohexylphosphine are added into the mixture, both *n*-BuBr and R_2PCl exist and they compete with each other to attack the lithium. Due to the steric effect, smaller *n*-BuBr is therefore finally attached to the indole and give to the unwanted side product (Scheme 6.3).



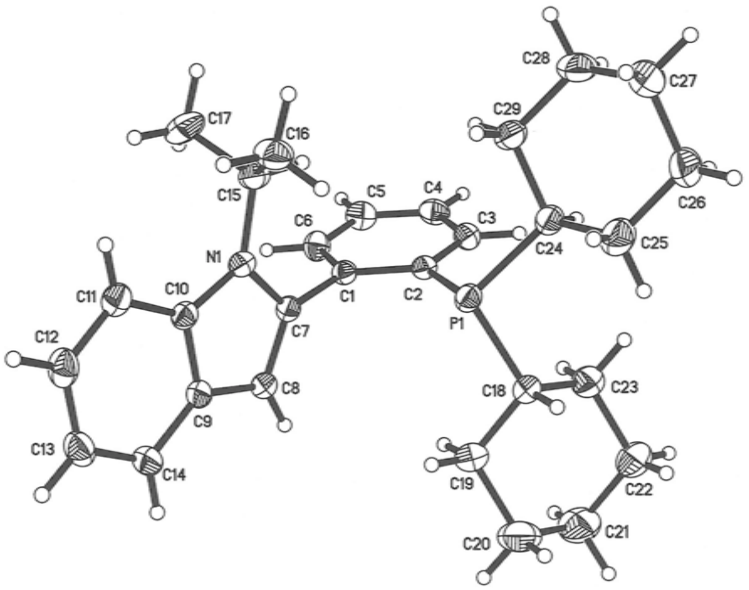
Scheme 6.3. Side product formation from phosphination of 1-benzyl-2-(2-bromophenyl)-1*H*-indole

Table 6.2. Phosphination of the *N*-substituted 2-(2’-bromophenyl)indoles[a]



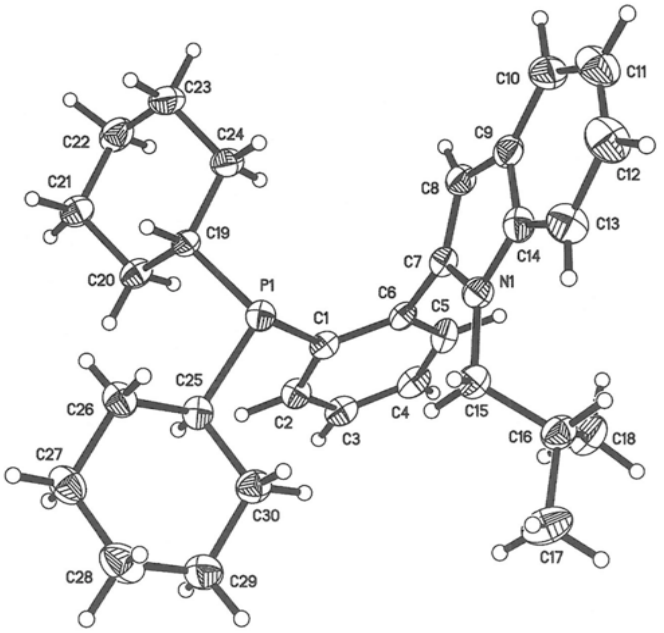
entry	ligand precurosr	$ClPR_2$	product	% yield[b]
1		$ClPCy_2$		80%
2		$ClPCy_2$		61%
3		$ClPPh_2$		57%
4		$ClPCy_2$		88%
5		$ClPPh_2$		69%
6		ClP*i*-Pr_2		53%
7		$ClPCy_2$		28%
8		$ClPPh_2$		60%
9		ClP*i*-Pr_2		58%

[a]Reaction conditions: 2-arylindole: $ClPR_2$: *n*-BuLi = 1: 1.1: 1.1, THF, -78 °C. [b]Isolated yields were reported.



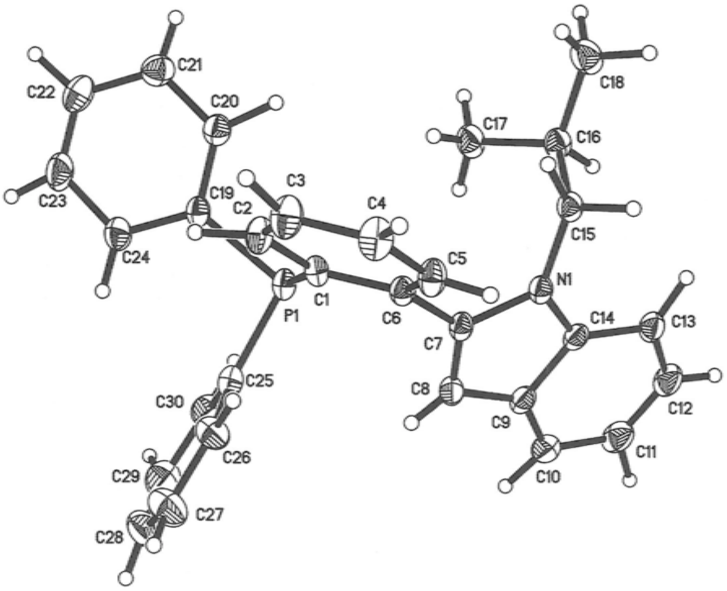
Bond distance (Å)		Bond angle (°)	
P(1)-C(2)	1.849 (2)	C(2)-P(1)-C(24)	100.54 (11)
P(1)-C(18)	1.858 (3)	C(2)-P(1)-C(18)	104.07 (11)
P(1)-C(24)	1.856 (3)	C(18)-P(1)-C(24)	102.50 (12)

Figure 6.1. X-ray crystal structure ORTEP representation of CM-phos-*N*-*i*Pr



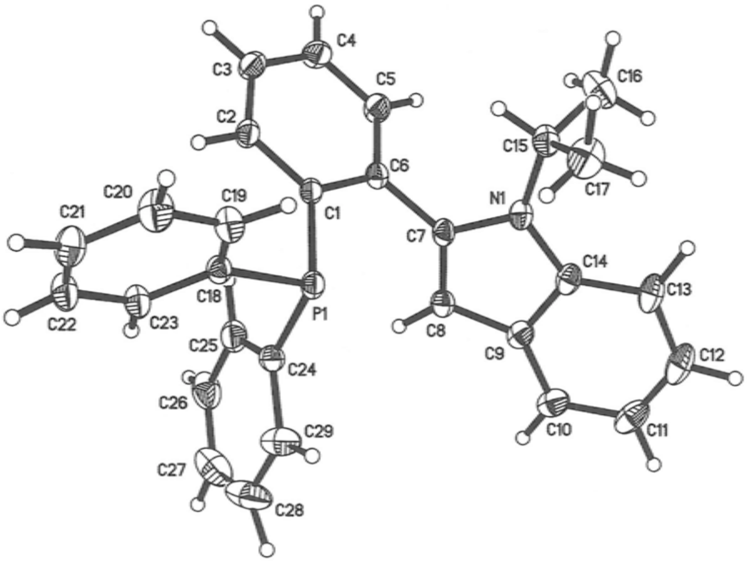
Bond distance (Å)		Bond angle (°)	
P(1)-C(1)	1.861 (4)	C(1)-P(1)-C(25)	102.21 (19)
P(1)-C(19)	1.860 (4)	C(1)-P(1)-C(19)	102.68 (12)
P(1)-C(25)	1.847 (5)	C(19)-P(1)-C(25)	103.00 (2)

Figure 6.2. X-ray crystal structure ORTEP representation of CM-phos-*N*-*i*Bu



Bond distance (Å)		Bond angle (°)	
P(1)-C(1)	1.833 (3)	C(1)-P(1)-C(25)	102.38(12)
P(1)-C(19)	1.842 (3)	C(1)-P(1)-C(19)	100.83 (12)
P(1)-C(25)	1.819 (3)	C(19)-P(1)-C(25)	101.32 (12)

Figure 6.3. X-ray crystal structure ORTEP representation of PPh_2-CM-phos-*N*-*i*Bu



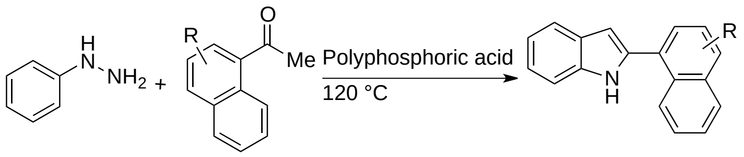
Bond distance (Å)		Bond angle (°)	
P(1)-C(1)	1.8389 (16)	C(1)-P(1)-C(24)	101.56 (8)
P(1)-C(18)	1.8385 (14)	C(1)-P(1)-C(18)	101.89 (7)
P(1)-C(24)	1.825 (2)	C(18)-P(1)-C(24)	100.76 (7)

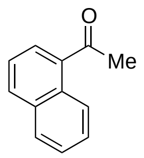
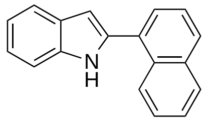
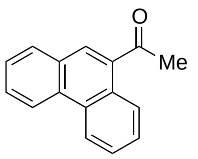
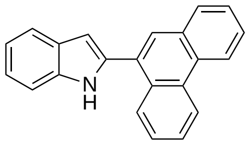
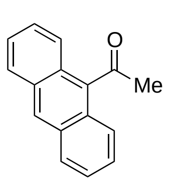
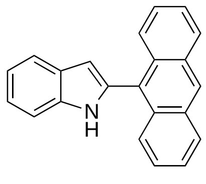
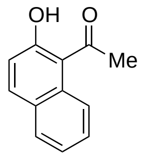
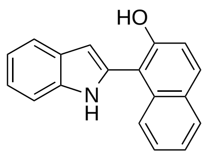
Figure 6.4. X-ray crystal structure ORTEP representation of PPh_2-CM-phos-*N*-*n*Bu

6.3.2 Development of New Class C-3 Naphdole Phosphine Ligands

By our previous work on new series of indolyl phosphine ligands,[4] C-3 indolyl phosphine category was developed. They were successfully applied in the Suzuki-cross coupling of aryl chlorides. In order to further improve this ligand skeleton, different substituted acetonaphthone was attempted to use as the starting material for Fischer indolization. The naphthyl scaffold would give extra steric effect to the catalytic system. Disappointingly, the steric effect retarded the Fischer indolization (Table 6.3). Acetonaphthone was the only one successful starting material to afford our target naphdole precursor.

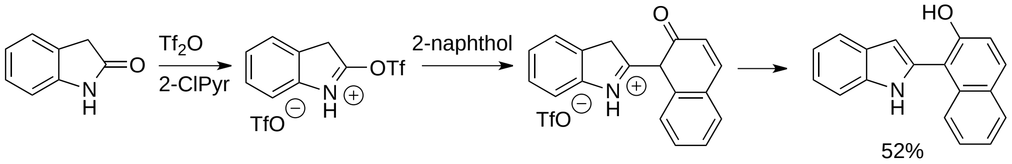
Table 6.3. Synthesis of Naphdole ligand precursors by Fischer Indolization[a]



entry	acetophenone	product	% yield[b]
1			58%
2			NR
3			NR
4			NR

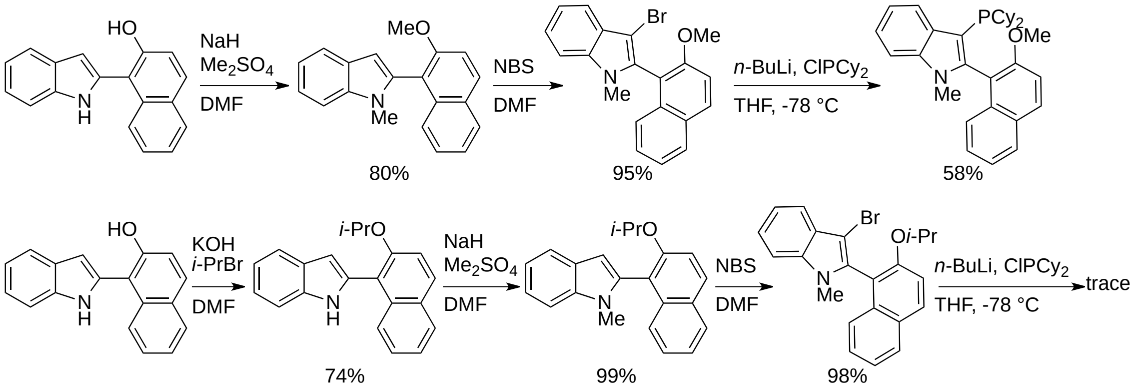
[a]Reaction conditions: Phenylhydrazine: acetonaphthone = 1.1:1, stirred at 120 °C for 2 h. [b]Isolated yield were reported.

In order to synthesize our proposed ligand skeleton, an alternative synthetic pathway was carried out (Scheme 6.4).[6] Oxindole was activated by a combination of trifluoromethanesulfonic anhydride (Tf_2O) and pyridine to afford the *O*-triflyliminium trifate. 2-Naphthol was then added to the reaction mixture to afford 1-(1*H*-indol-2-yl)naphthalen-2-ol which cannot be synthesized through traditional Fischer indolization.



Scheme 6.4. Synthesis of 1-(1*H*-indol-2-yl)naphthalen-2-ol

1-(1*H*-Indol-2-yl)naphthalen-2-ol can further transform into a wide range of ligand precursors by alkylation process (Scheme 6.5). By similar alkylation process, methylation can be simply done by using NaH and Me_2SO_4 while others can be afforded by KOH and corresponding alkyl bromides. Bromination step was then performed by addition of *N*-bromosuccinimide to undergo electrophilic substitution at the C-3 position of the indole. Lithium/bromide exchange of 3-bromo-2-arylindole and subsequently trapping with $ClPR_2$ was done to afford the desired naphdolyl phosphine ligand in moderate yields.



Scheme 6.5. Methylation, alkylation, bromination and phosphination of 1-(1*H*-indol-2-yl)naphthalen-2-ol

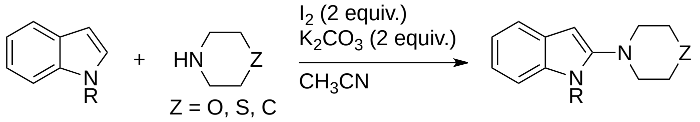
Unfortunately, although an alternative pathway can be applied to synthesize the desired ligand precursor, the yield of target naphdolyl phosphine ligands was fair. Only trace amount of 3-(dicyclohexylphosphino)-2-(2-*iso*propoxynaphthalen-1-yl)-1-methyl-1*H*-indole can be obtained while only debromination side reaction was resulted. The main reason for this failure is due to the bulky isopropyl group exerting a high steric hindrance to avoid the phosphination step to occur.

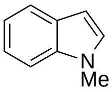
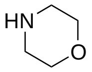
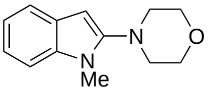
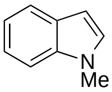
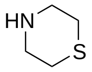
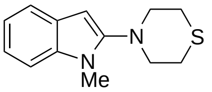
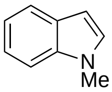
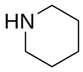
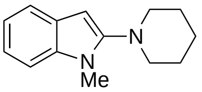
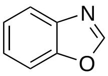
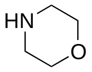
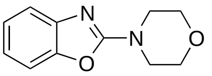
6.3.3 Development of New Class Indolyl Morpholine Phosphine Ligands

To further develop our indolyl phosphine ligands, we designed a new scaffold which keeping the original indole ring but replacing the 2-phenyl ring with *N*-heterocycles such as morpholine, piperidine etc. This would provide further modification with lone pair electrons from N or O atom, which can possibly affect the coordination.

Electrophile-promoted tandem reaction is a common method for the synthesis of heterocyclic compounds. According to Liang's report,[9] iodine-induced regioselective C-N bond formation of *N*-protected indole derivatives was applied to obtain the 4-(1-methyl-1*H*-indol-2-yl)morpholine.[7] With this method, other heterocycles were also applied to synthesize the new ligand precursors (Table 6.4). Thiomorpholine and piperidine could be coupled at C-2 position of *N*-protected indole under reflux conditions, yet in low yields (entries 3 and 4).

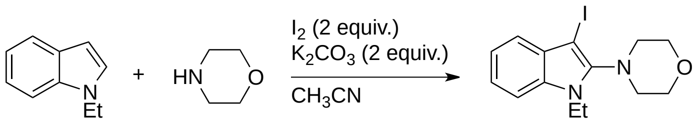
Table 6.4. Synthesis of indolyl morpholine ligand precursor[a]



entry	Indole	*N*-heterocycles	product	% yield[b]
1				66%
2				20%
3[c]				18%
4				30%

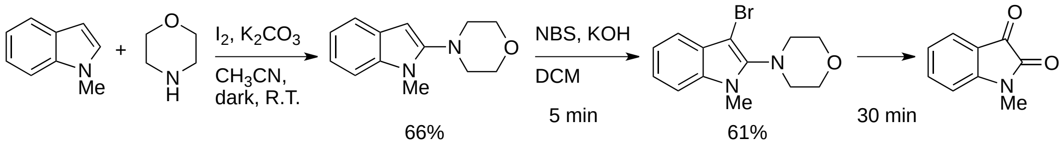
[a]Reaction conditions: *N*-protected indole (10 mmol), *N*-heterocycles (25-30 mmol), I_2 (20 mmol), K_2CO_3 (20 mmol), CH_3CN (20 ml), stirred at room temperature in dark overnight. [b]Isolated yields were reported.

After the reaction completed, saturated sodium bisulfite solution was used to wash the mixture to remove the excessive iodine. It should be noted that there is not enough washing of iodine, 4-(*N*-alkyl-3-iodo-1*H*-indol-2-yl)morpholine was given as the main product (Scheme 6.6). Nevertheless, this side product would be useful for further phosphination which can skip the bromination step. However, this compound is highly unstable under light that should be stored in dark.



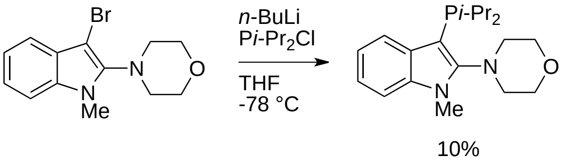
Scheme 6.6. Synthesis of 4-(1-ethyl-3-iodo-1*H*-indol-2-yl)morpholine

Bromination step was carried out as before by adding NBS in THF to the reaction. However, the reaction must be quenched in 5 minutes, otherwise, 1-methylisatin was resulted instead of the desired product (Scheme 6.7). The brominated product was found air- and light-sensitive which the solid turned from white to grey in 24 hours.



Scheme 6.7. Synthesis of 4-(3-bromo-1-methyl-1*H*-indol-2-yl)morpholine

In the phosphination step, high instability of the brominated ligand precursor becomes a concern. Chlorodi*iso*propylphosphine was used and only 10% isolated product was obtained (Scheme 6.8).



Scheme 6.8. Synthesis of 4-(3-(di*iso*propylphosphino)-1-methyl-1*H*-indol-2-yl)morpholine

Interestingly, during the characterization process, 4 morpholyl proton signals were broadened in the ^{1}H-NMR and one CH_2 peak was missing in C-NMR (DEPT). Further VT-NMR was then attempted. The missing proton signal and carbon peak were appeared when higher temperature (348K) of NMR analysis was applied (Figure 6.5). Crystallization was therefore successfully proved the structure of desirable ligand (Figure 6.6).

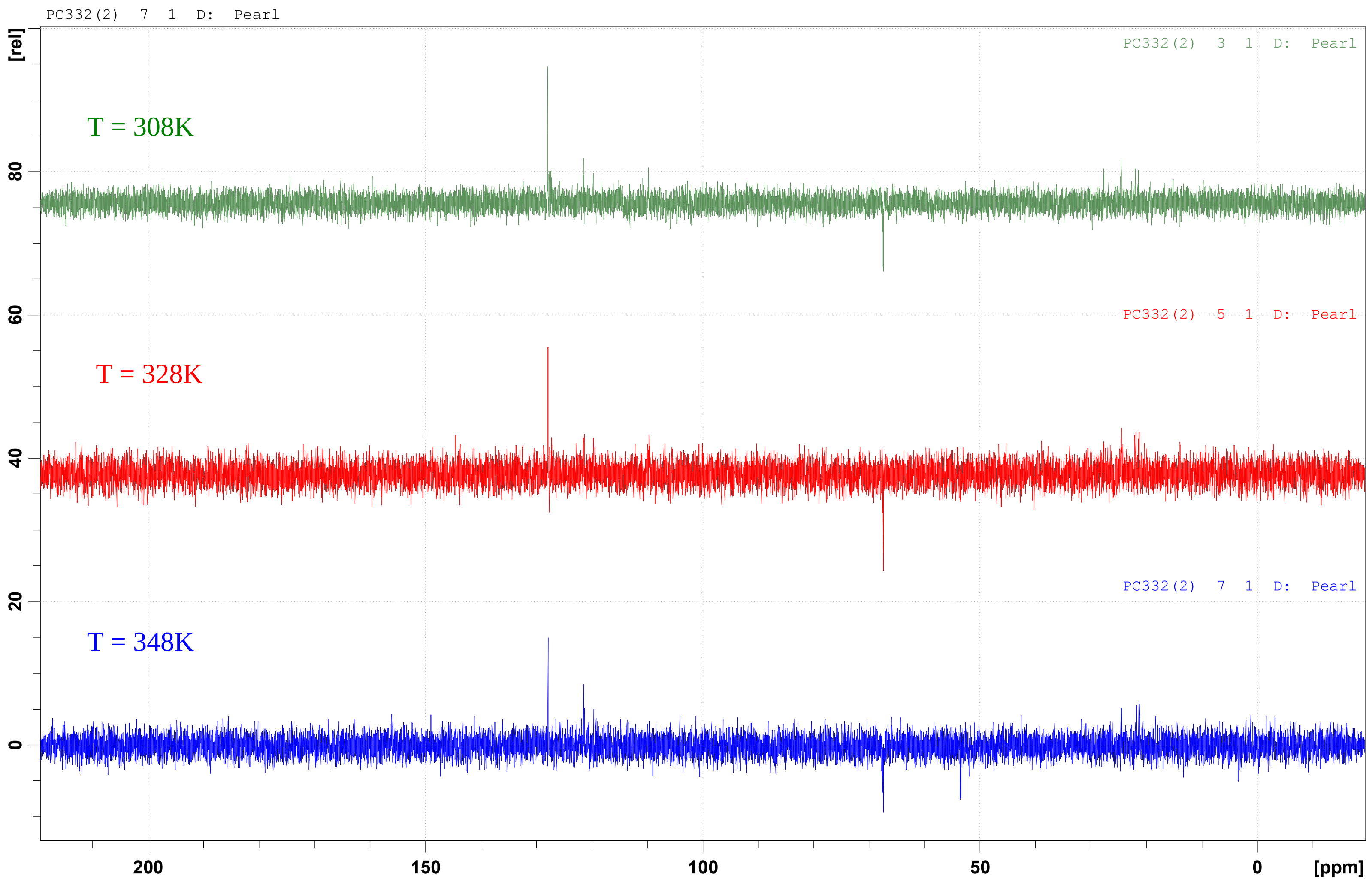
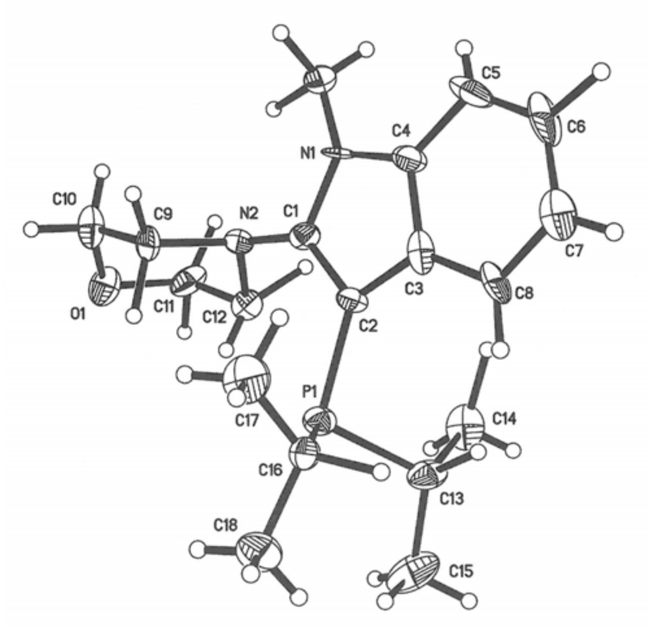


Figure 6.5. VT-NMR spectrum for analysis of 4-(3-(di*iso*propylphosphino)-1-methyl-1*H*-indol-2-yl)morpholine



Bond distance (Å)		Bond angle (°)	
P(1)-C(16)	1.839 (4)	C(16)-P(1)-C(2)	102.48 (16)
P(1)-C(2)	1.881 (3)	C(16)-P(1)-C(13)	102.64 (18)
P(1)-C(13)	1.889 (4)	C(2)-P(1)-C(13)	102.10 (16)

Figure 6.6. X-ray crystal structure of 4-(3-(diisopropylphosphino)-1-methyl-1*H*-indol-2-yl)morpholine

6.4 Conclusion

In conclusion, we have modified the *N*-substituted group with the existing CM-phos scaffold. Moreover, we designed simple approaches to potentially synthesize the proposed new ligands: C-3 naphdole phosphine ligands and C-3 indolyl morpholine phosphine ligands. These three ligand templates have advantages over other phosphine ligands: 1) inexpensive and can be prepared from well-developed synthetic pathway; 2) readily available from commercially accessible starting materials; 3) high potential for diversification and fine-tuning.

6.5 Experimental Section

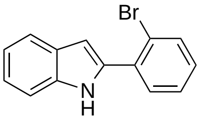
6.5.1 General considerations

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. Tetrahydrofuran (THF) was distilled from sodium under nitrogen.[8] *N*,*N*-Dimethylformamide (DMF) was distilled with calcium hydride under reduced pressure. Chlorodiphenylphosphane was distilled under vacuum prior to use. . New bottle of *n*-butyllithium was used (*Note*: since the concentration of *n*-BuLi from old bottle may vary, we recommend performing a titration prior to use). Thin layer chromatography was performed on Merck precoated silica gel 60 F_{254} plates. Silica gel (Merck, 70-230 and 230-400 mesh) was used for column chromatography. Melting points were recorded on an uncorrected Büchi Melting Point B-545 instrument. ^{1}H NMR spectra were recorded on a Bruker (400 MHz). Spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.26 ppm), or with tetramethylsilane (TMS, δ 0.00 ppm) as the internal standard. Chemical shifts (δ) were reported as part per million (ppm) in δ scale downfield from TMS. ^{13}C NMR spectra were referenced to $CDCl_3$ (δ 77.0 ppm, the middle peak). ^{31}P NMR spectra were referenced to 85% H_3PO_4 externally. Coupling constants (*J*) were reported in Hertz (Hz). Mass spectra (EI-MS and ES-MS) were recorded on a HP 5989B Mass Spectrometer. High-resolution mass spectra (HRMS) were obtained on a Brüker APEX 47e FT-ICR mass spectrometer (ESIMS). GC-MS analysis was conducted on a HP 5973 GCD system using a HP5MS column (30 m × 0.25 mm). All yields reported refer to the isolated yield of compounds.

6.5.2 General Procedures and Characterization Data

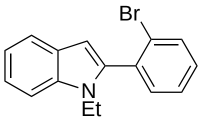
6.5.2.1 Preparation of Phosphine Ligand with Modified CM-phos Skeleton

2-(2'-Bromophenyl)-1*H*-indole (Scheme 6.2)[9]



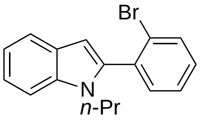
2'-Bromoacetophenone (2.70 mL, 20 mmol) was mixed with phenylhydrazine (1.97 mL, 20 mmol) in ethanol (10 mL), with 10 drops of glacial acetic acid. The reaction was heated to 80 °C and stirred for 1 hour. Solvent was evaporated to yield the phenylhydrazone intermediate, which was added to polyphosphoric acid (40 g). Exothermic reaction was observed and the reaction mixture was slowly heated to 120 °C (keep for 1 hour). The mixtures were poured into crashed ice cube and then neutralized with 2 M NaOH and extracted with CH_2Cl_2. The combined organic extracts were washed with water, dried over anhydrous Na_2SO_4, and concentrated to give the desired 2-(2'-Bromo)-1*H*-indole (4.07 g, 75%) as offwhite solid, which was then dried under reduced pressure. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 (s, 1H), 7.15-7.28 (m, 3H), 7.39-47 (m, 2H), 7.63-7.73 (m, 3H), 8.65 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 103.6, 111.0, 115.2, 120.1, 120.8, 121.2, 122.5, 127.6, 128.1, 129.1, 131.4, 133.4, 133.9, 136.2; MS (EI): *m/z* (relative intensity) 271 (M^+, 100), 191 (19), 165 (49), 95 (13).

2-(2-Bromophenyl)-1-ethyl-1*H*-indole (Table 6.1, entry 1)



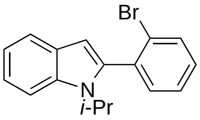
2-(2’-Bromophenyl)-1*H*-indole (2.17 g, 8 mmol) was dissolved in a freshly distilled DMF (15 mL) at room temperature under a nitrogen atmosphere. The solution was cooled to 0 °C in ice/water bath. NaH (0.34 g, 16 mmol) was then added into the reaction mixture and kept stirring at 0 °C until no bubbles were released. Bromoethane (0.90 mL, 12 mmol) was added dropwise and stirred overnight. 25 ml of water was added to the mixture and then extracted with dichloromethane (50 mL). The organic layer was washed with water (5 × 100 mL) and the solvent was then removed by reduced pressure. The crude product was filtered through a short silica pad (3 × ~10 cm) and washed with hexane then DCM/ hexane (1:3). The solution was evaporated and the residue was crystallized under hexane. Small amount of cold hexane was used to further wash the product. The product was then dried under vacuum to afford the desired 2-(2-bromophenyl)-1-ethyl-1*H*-indole (1.44 g, 60%) as offwhite solid. Melting point 79.6-82.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (t, *J* = 7.2 Hz, 3H), 4.05 (d, *J* = 7.2 Hz, 2H), 6.51 (bs, 1H), 7.15-7.19 (m, 1H), 7.26-7.36 (m, 2H), 7.41-7.44 (m, 3H), 7.68-7.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.2, 38.7, 102.5, 109.7, 119.6,120.8, 121.6, 125.1, 127.1, 128.0, 130.1, 132.7, 132.8, 134.4, 135.9, 138.8; IR (cm^{-1}): 3422.28, 3052.57, 2978.88, 1565.17, 1536.68, 1450.47, 1431.82, 1393.09, 1384.26, 1350.15, 1308.64, 1194.72, 1163.06, 1058.58, 1014.11, 782.39, 759.18, 750.15, 732.40, 672.30, 643.80, 583.64, 545.65, 422.16; MS (EI): *m/z* (relative intensity) 299 (M^+, 75), 284 (16), 205 (100), 190 (16); HRMS: calcd. for $C_{16}H_{15}BrN^+$: 300.0388, found 300.0384.

2-(2-Bromophenyl)-1-propyl-1*H*-indole (Table 6.1, entry 2)



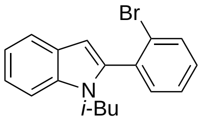
2-(2’-Bromophenyl)-1*H*-indole (1.36 g, 5 mmol) was dissolved in a freshly distilled DMF (15 mL) at room temperature under a nitrogen atmosphere. KOH (2.0 g, 50 mmol) was then added into the reaction mixture and kept stirring at room temperature. After all the KOH were dissolved, propyl tosylate (1.1 mL, 5.5 mmol) was added dropwise and stirred overnight. 25 ml of water was added to the mixture and then extracted with dichloromethane (100 mL). The organic layer was washed with water (5 × 100 mL) and the solvent was then removed by reduced pressure. The crude product was filtered through a short silica pad (3 × ~10 cm) and washed with hexane then DCM/ hexane (1:3, $R_f = 0.25$). The solution was evaporated and the residue was crystallized under hexane. Small amount of cold hexane was used to further wash the product. The product was then dried under vacuum to afford the desired 2-(2’-bromophenyl)-1-propyl-1*H*-indole (1.08 g, 69%) as offwhite solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.78-0.85 (m, 3H), 1.69-1.75 (q, *J* = 7.2, 7.6 Hz, 2H), 4.04 (s, 2H), 6.58 (s, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.31-7.39 (m, 2H), 7.44-7.51 (m, 3H), 7.74-7.79 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ11.3, 23.1, 45.6, 102.4, 109.7, 110.0, 118.7, 119.5, 120.7, 121.5, 127.0, 130.0 (overlapped) 132.7, 132.9, 133.3, 134.4, 136.4, 139.1; MS (EI): *m/z* (relative intensity) 419 (M^+, 63), 376 (100), 342 (8), 298 (12), 222 (28); HRMS: calcd. for $C_{17}H_{17}NBr^+$: 314.0544, found 314.0530.

2-(2-Bromophenyl)-1-isopropyl-1*H*-indole (Table 6.1, entry 3)



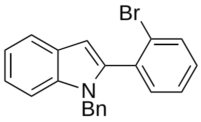
2-(2’-Bromophenyl)-1*H*-indole (0.68 g, 2.5 mmol) was dissolved in a freshly distilled DMF (15 mL) at room temperature under a nitrogen atmosphere. KOH (1.40 g, 25 mmol) was then added into the reaction mixture and kept stirring at room temperature. After all the KOH were dissolved, 2-bromopropane (1.41 mL, 15 mmol) was added dropwise and stirred overnight. 25 ml of water was added to the mixture and then extracted with dichloromethane (100 mL). The organic layer was washed with water (5 × 100 mL) and the solvent was then removed by reduced pressure. The crude product was filtered through a short silica pad (3 × ~10 cm) and washed with hexane then DCM/ hexane (1:3). The solution was evaporated and the residue was crystallized under hexane. Small amount of cold hexane was used to further wash the product. The product was then dried under vacuum to afford the desired 2-(2’-bromophenyl)-1-isopropyl-1*H*-indole (0.56 g, 71%) as offwhite solid. Melting point 103.0-105.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.50 (d, *J* = 7.2 Hz, 3H), 1.73 (d, *J* = 7.2 Hz, 3H), 4.21-4.28 (m, 1H), 6.44 (bs, 1H), 7.12-7.24 (m, 2H), 7.31-7.35 (m, 3H), 7.38-7.41 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5 (overlapped), 48.4, 102.3, 112.0, 119.3, 121.0, 121.1, 125.4, 127.0, 128.8, 130.0, 132.6, 132.7, 134.5, 135.1, 139.2; IR (cm^{-1}): 3060.95, 2970.35, 2931.00, 1450.32, 1433.42, 1405.58, 1385.52, 1361.98, 1346.20, 1303.22, 1176.28, 1156.23, 1139.60, 1113.42, 1101.18, 1049.08, 1016.68, 1001.40, 798.80, 760.57, 750.26, 741.34, 670.56, 608.97, 443.65, 427.11; MS (EI): *m/z* (relative intensity) 313 (M^+, 100), 298 (45), 271 (57), 219 (27), 204 (33), 191 (27), 165 (33); HRMS: calcd. for $C_{17}H_{17}NBr^+$: 314.0544, found 314.0559.

2-(2-Bromophenyl)-1-isobutyl-1*H*-indole (Table 6.1, entry 4)



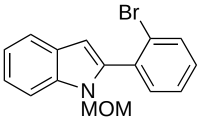
2-(2'-Bromophenyl)-1*H*-indole (1.36 g, 5 mmol) was dissolved in a freshly distilled DMF (15 mL) at room temperature under a nitrogen atmosphere. KOH (1.40 g, 25 mmol) was then added into the reaction mixture and kept stirring at room temperature. After all the KOH were dissolved, 1-bromo-2-methylpropane (1.70 mL, 15 mmol) was added dropwise and stirred overnight. 25 ml of water was added to the mixture and then extracted with dichloromethane (100 mL). The organic layer was washed with water (5 × 100 mL) and the solvent was then removed by reduced pressure. The crude product was filtered through a short silica pad (3 × ~10 cm) and washed with hexane then DCM/ hexane (1:3, Rf = 0.6). The solution was evaporated and the residue was crystallized under hexane. Small amount of cold hexane was used to further wash the product. The product was then dried under vacuum to afford the desired 2-(2'-bromophenyl)-1-isobutyl-1*H*-indole (0.61 g, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.70 (s, 6H), 2.01-2.12 (m, 1H), 3.84 (bs, 2H), 6.51 (s, 1H), 7.14-7.26 (m, 1H), 7.30-7.34 (m, 2H), 7.40-7.47 (m, 3H), 7.67-7.73 (q, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.1, 28.8, 51.6, 102.6, 110.3, 119.5, 120.7, 121.4, 125.0, 127.0, 127.7, 129.8, 132.7, 133.1, 134.5, 136.7, 139.4; HRMS: calcd. for $C_{18}H_{19}NBr^+$: 328.0701, found 328.0694.

1-Benzyl-2-(2-bromophenyl)-1*H*-indole (Table 6.1, entry 5)



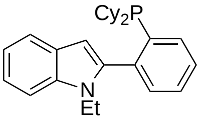
2-(2’-Bromophenyl)-1*H*-indole (1.36 g, 5 mmol) was dissolved in a freshly distilled DMF (15 mL) at room temperature under a nitrogen atmosphere. KOH (0.84 g, 15 mmol) was then added into the reaction mixture and kept stirring at room temperature. After all the KOH were dissolved, benzyl bromide (0.71 mL, 6 mmol) was added dropwise and stirred overnight. 25 ml of water was added to the mixture and then extracted with dichloromethane (100 mL). The organic layer was washed with water (5 × 100 mL) and the solvent was then removed by reduced pressure. The crude product was filtered through a short silica pad (3 × ~10 cm) and washed with hexane then DCM/ hexane (1:3, Rf = 0.55). The solution was evaporated and the residue was crystallized under hexane. Small amount of cold hexane was used to further wash the product. The product was then dried under vacuum to afford the desired 1-benzyl-2-(2-bromophenyl)-1*H*-indole (1.34 g, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.23 (s, 2H), 6.62 (s, 1H), 6.91 (t, *J* = 3.2, 4.8 Hz), 7.15-7.23 (m, 5H), 7.27-7.35 (m, 4H), 7.70-7.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 47.7, 103.2, 110.5, 119.9, 120.8, 121.9, 125.1, 126.3, 127.1, 128.0, 128.4, 130.1, 132.8, 132.9, 134.0, 136.8, 137.8, 139.4; MS (EI): *m/z* (relative intensity) 361 (M^+, 49), 280 (7), 204 (10), 191 (10), 91 (100), 65 (8).

2-(2-Bromophenyl)-1-(methoxymethyl)-1*H*-indole (Table 6.1, entry 5)



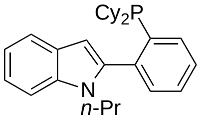
2-(2’-Bromophenyl)-1*H*-indole (2.71 g, 10 mmol) was dissolved in a freshly distilled DMF (15 mL) at room temperature under a nitrogen atmosphere. The solution was cooled to 0 °C in ice/water bath. NaH (0.34 g, 16 mmol) was then added into the reaction mixture and kept stirring at 0 °C until no bubbles were released. Chloromethyl methyl ether (1.14 mL, 15 mmol) was added dropwise and stirred overnight. 25 ml of water was added to the mixture and then extracted with dichloromethane (50 mL). The organic layer was washed with water (5 × 100 mL) and the solvent was then removed by reduced pressure. The crude product was filtered through a short silica pad (3 × ~10 cm) and washed with hexane then EA/ hexane (1:9, Rf = 0.5). The solution was evaporated and the residue was crystallized under hexane. Small amount of cold hexane was used to further wash the product. The product was then dried under vacuum to afford the desired 2-(2-bromophenyl)-1-(methoxymethyl)-1*H*-indole (1.04 g, 33%) as offwhite solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.16 (s, 3H), 5.43 (s, 2H), 6.68 (s, 1H), 7.32 (t, *J* = 8, 6.8 Hz, 1H), 7.37-7.43 (m, 2H), 7.49 (t, *J* = 7.6, 7.2 Hz, 1H), 7.58 (dd, *J* = 6.4, 1.2 Hz, 1H), 7.67 (d, *J* = 8 Hz), 7.79 (t, *J* = 8, 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 74.8, 104.2, 110.4, 120.5, 120.7, 122.3, 124.9, 127.1, 128.0, 130.1, 132.7, 133.0, 133.5, 136.9, 139.1; MS (EI): *m/z* (relative intensity) 315 (M^+, 100), 284 (41), 205 (84), 190 (41), 165 (31), 102 (19), 63 (15).

N-Ethyl-2-(2’-dicyclohexylphosphinophenyl)indole (Table 6.2, entry 1)



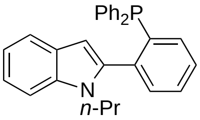
2-(2’-Bromophenyl)-1-ethyl-1*H*-indole (1.50 g, 5 mmol) was dissolved in freshly distilled THF (15 mL) at room temperature under a nitrogen atmosphere. The solution was cooled to -78 °C in dry ice/acetone bath. Titrated *n*-BuLi (5.5 mmol) was added dropwise by syringe. After the reaction mixture was stirred for 30 min at -78 °C, chlorodicyclohexylphosphine (1.21 mL, 5.5 mmol) in THF (5 mL) was added. The reaction was allowed to warm to room temperature and stirred overnight. Solvent was removed under reduced pressure. After the solvent was removed under vacuum, the product was successively washed with cold MeOH/EtOH mixture. The product was then dried under vacuum. White solid of *N*-Ethyl-2-(2'-dicyclohexylphosphinophenyl)indole (3.45 g, 80%) were obtained. Melting point 121.3-123.0 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.08-1.22 (m, 14H), 1.65-1.74 (m, 12H), 3.91-4.06 (m, 2H), 6.39 (s, 1H), 7.10-7.24 (m, 2H), 7.37-7.48 (m, 4H), 7.65 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 15.2, 26.3, 27.3, 38.6, 103.8, 109.7, 119.2, 120.4, 120.9, 127.7, 127.9, 131.9, 132.0, 132.5, 135.4 (unresolved complex C-P splittings were observed); ^{31}P NMR (162 MHz, CDCl$_3$) δ -10.5; IR (cm^{-1}): 3448.70, 2892.66, 2923.71, 2843.98, 1446.90, 1384.70, 1340.37, 1308.71, 1264.38, 1191.56, 1163.06, 1134.56, 995.25, 887.60, 852.77, 779.54, 750.71, 729.29, 678.63, 520.32; MS (EI): *m/z* (relative intensity) 417 (M$^+$, 18), 388 (9), 334 (100), 252 (30), 222 (47); HRMS: calcd. for C$_{28}$H$_{35}$NP$^+$: 416.2507, found 416.2518.

_N_-Propyl-2-(2'-dicyclohexylphosphinophenyl)indole (Table 6.2, entry 2)



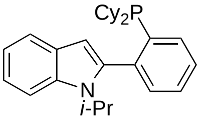
2-(2'-Bromophenyl)-1-propyl-1*H*-indole (1.57 g, 5 mmol), *n*-BuLi (5.5 mmol) and chlorodicyclohexylphosphine (1.21 mL, 5.5 mmol) were used to afford *N*-propyl-2-(2'-dicyclohexylphosphinophenyl)indole (1.31 g, 61%) as white solid. Melting point 92.7-93.7 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.73 (t, *J* = 7.6 Hz, 3H), 1.10 (bs, 11H), 7.70 (d, 14H), 2.10 (s, 1H), 3.80 (s, 1H), 3.98 (s, 1H), 6.38 (s, 1H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.36-7.47 (m, 4H), 7.63 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 11.4, 18.7, 23.1, 26.3, 27.4, 28.4, 30.2, 45.8, 103.8, 109.9, 119.2, 120.3, 121.0, 127.8, 129.2, 132.2, 132.3, 135.9, 140.8 (unresolved complex C-P splittings were observed); ^{31}P NMR (162 MHz, $CDCl_3$) δ -10.37; MS (EI): *m/z* (relative intensity) 431 (M^+, 17), 388 (6), 348 (100), 266 (21), 222 (33); HRMS: calcd. for $C_{29}H_{39}NP^+$: 432.2820, found 432.2821.

N-Propyl-2-(2’-diphenylphosphinophenyl)indole (Table 6.2, entry 3)



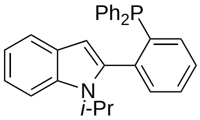
2-(2’-Bromophenyl)-1-propyl-1*H*-indole (1.57 g, 5 mmol), *n*-BuLi (5.5 mmol) and chlorodiphenylphosphine (1.02 mL, 5.5 mmol) were used to afford *N*-propyl-2-(2’-diphenylphosphinophenyl)indole (1.19 g, 57%) as white solid. Melting point 135.1-136.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.83 (t, *J* = 7.2 Hz, 3H), 1.72 (t, *J* = 7.2 Hz, 2H), 3.89 (s, 2H), 6.06 (s, 1H), 7.97-7.22 (m, 7H), 7.33-7.51 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.5, 23.4, 45.5, 104.7)ooverlapped), 109.9, 119.3, 120.6, 121.3, 127.7, 128.3, 128.4 (overlapped), 128.6, 131.4, 131.5, 133.7, 133.9 (overlapped), 136.4, 138.6, 138.8, 138.9 (overlapped) (unresolved complex C-P splittings were observed); ^{31}P NMR (162 MHz, $CDCl_3$) δ -13.73; HRMS: calcd. for $C_{29}H_{27}NP^+$: 420.1881, found 420.1878.

***N*-Isopropyl-2-(2’-dicyclohexylphosphinophenyl)indole (Table 6.2, entry 4)**



2-(2’-Bromophenyl)-1-isopropyl-1*H*-indole (1.57 g, 5 mmol), *n*-BuLi (5.5 mmol) and chlorodicyclohexylphosphine (1.21 mL, 5.5 mmol) were used to afford *N*-isopropyl-2-(2’-dicyclohexylphosphinophenyl)indole (1.90 g, 88%) as pale yellow solid. Melting point 155.2-159.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.03-1.24 (m, 10H), 1.29-1.77 (m, 17H), 1.80 (s, 1H), 4.14-4.18 (m, 1H), 6.32 (bs, 1H), 7.07-7.18 (m, 2H), 7.30-7.33 (m, 1H), 7.38-7.48 (m, 2H), 7.59-7.64 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.4, 26.93, 27.0 (overlapped), 27.1, 27.5 (overlapped), 27.6, 28.7, 28.8, 29.7, 29.8, 30.0, 30.2, 30.6, 30.8, 33.3, 33.4, 35.9, 36.1, 47.9, 103.9, 112.0, 118.8, 120.4, 120.6, 127.7, 127.9, 128.8, 131.6, 131.7, 132.5, 132.6, 134.0, 137.3, 140.5 (overlapped), 141.6, 141.9 (unresolved complex C-P splittings were observed); ^{31}P NMR (162 MHz, $CDCl_3$) δ -11.5; IR (cm^{-1}): 3415.82, 2978.67, 2920.09, 2843.42, 1453.79, 1431.01, 1404.94, 1384.93, 1349.81, 1306.47, 1264.38, 1174.80, 1128.80, 1001.59, 884.43, 849.60, 780.65, 769.14, 749.25, 730.29, 678.63, 615.30; MS (EI): *m/z* (relative intensity) 413 (M$^+$, 16), 388 (96), 348 (84), 266 (16), 222 (100), 207 (13), 55 (25); HRMS: calcd. for $C_{29}H_{39}NP^+$: 432.2820, found 432.2812.

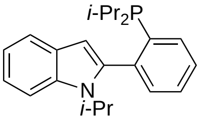
_N-Iso_propyl-2-(2'-diphenylphosphinophenyl)indole (Table 6.2, entry 5)



2-(2'-Bromophenyl)-1-isopropyl-1*H*-indole (0.94 g, 3 mmol), *n*-BuLi (3.3 mmol), chlorodiphenylphosphine (0.6 mL, 3.3 mmol) were used to afford *N-iso*propyl-2-(2'-diphenylphosphinophenyl)indole (0.87 g, 69%) as a white crystal. Melting point 174.2-179.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.55 (d, *J* = 6.8 Hz, 3H), 1.63 (d, *J* = 7.2 Hz, 3H), 4.33-4.40 (m, 1H), 6.02 (s, 1H), 7.07-7.39 (m, 17), 7.41-7.43 (dd, *J* = 1.6, 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4 (overlapped), 21.7, 104.6, 112.0, 118.9, 120.8 (overlapped), 128.3 (overlapped), 128.4, 128.6, 131.3, 133.5, 133.6, 133.7, 133.8, 134.0, 134.5, 138.9, 139.1, 139.3 (unresolved complex C-P splittings were observed); ^{31}P NMR (162 MHz, $CDCl_3$)

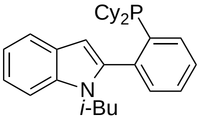
δ -14.7; IR (cm^{-1}): 3463.35, 3053.47, 2976.41, 2932.40, 1584.17, 1473.35, 1453.10, 1429.45, 1384.47, 1342.89, 1304.57, 1172.56, 1153.56, 1068.07, 1023.75, 998.42, 792.67, 768.05, 749.39, 737.68, 695.16, 615.30, 497.06; MS (EI): *m/z* (relative intensity) 419 (M^+, 12), 376 (100), 222 (33); HRMS: calcd. for $C_{29}H_{27}NP^+$: 420.1881, found 420.1897.

N-Isopropyl-2-(2'-diisopropylphosphinophenyl)indole (Table 6.2, entry 6)



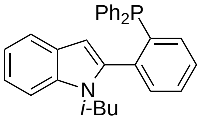
2-(2'-Bromophenyl)-1-isopropyl-1*H*-indole (1.56 g, 5 mmol), *n*-BuLi (3.3 mmol), chlorodiisopropylphosphine (0.88 mL, 5.5 mmol) were used to afford *N*-*iso*propyl-2-(2'-diisopropylphosphinophenyl)indole (0.96 g, 55%) as a white crystal. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92-1.15 (m, 12H), 1.50 (d, *J* = 6.8 Hz, 3H), 1.58 (s, 3H), 1.71 (d, *J* = 7.2 Hz, 3H), 1.92-1.93 (m, 1H), 2.26-2.67 (m, 1H), 4.17-4.20 (m, 1H), 6.33 (s, 1H), 7.11 (t, *J* = 6.8 Hz, 1H), 7.14-7.18 (td, *J* = 6.0, 1.6 Hz, 1H), 7.31-7.34 (m, 1H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.45-7.48 (td, *J* = 6.0, 1.6 Hz, 1H), 7.59-7.64 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.9 (overlapped), 19.9, 20.1, 20.2, 20.3, 20.5, 21.6, 21.8, 21.9, 23.1, 23.2, 26.1, 26.3, 27.6, 48.0, 103.9, 112.1, 118.9, 120.5, 120.7, 127.9, 128.1, 128.9, 131.7, 131.8, 132.3, 132.4, 134.1, 137.9, 138.1, 140.5 (overlapped), 141.4, 141.7 (unresolved complex C-P splittings were observed); ^{31}P NMR (162 MHz, $CDCl_3$) δ -3.32; MS (EI): *m/z* (relative intensity) 351 (M^+, 12), 308 (100), 266 (17), 222 (50).

***N*-Isobutyl-2-(2'-dicyclohexylphosphinophenyl)indole (Table 6.2, entry 7)**



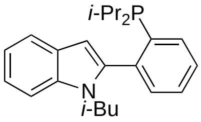
2-(2’-Bromophenyl)-1-isobutyl-1*H*-indole (0.63 g, 2 mmol), *n*-BuLi (2.2 mmol) and chlorodicyclohexylphosphine (0.49 mL, 2.2 mmol) were used to afford *N*-isobutyl-2-(2’-dicyclohexylphosphinophenyl)indole (0.25 g, 28%) as pale yellow solid. Melting point 124.1-125.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.58 (s, 3H), 0.78 (s, 3H), 0.98-1.32 (m, 9H), 1.5901.72 (m, 13H), 3.67 (s, 1H), 3.93 (s, 1H), 6.39 (s, 1H), 7.08-7.22 (m, 2H), 7.36-7.47 (m, 4H), 7.62 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.3, 26.4, 27.1, 27.5, 28.2, 28.8, 29.8, 30.4, 32.3, 35.8, 51.9 (overlapped), 103.8, 110.3, 119.1, 120.2, 120.9, 127.6, 127.8, 128.1, 132.4, 132.8 (overlapped), 136.4, 136.5, 136.7, 140.9, 141.2, (overlapped) (unresolved complex C-P splittings were observed); ^{31}P NMR (162 MHz, $CDCl_3$) δ -10.08; HRMS: calcd. for $C_{30}H_{39}NP^+$: 444.2820, found 444.2805.

N-Isobutyl-2-(2’-diphenylphosphinophenyl)indole (Table 6.2, entry 8)



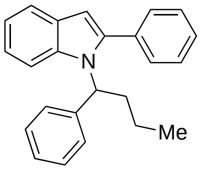
2-(2’-Bromophenyl)-1-isobutyl-1*H*-indole (0.65 g, 2 mmol), *n*-BuLi (2.2 mmol), chlorodiphenylphosphine (0.4 mL, 2.2 mmol) were used to afford *N*-*iso*butyl-2-(2’-diphenylphosphinophenyl)indole (0.52 g, 60%) as a white crystal. Melting point 134.0-134.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.79 (s, 6H), 2.05-2.15 (m, 1H), 3.82 (bs, 2H), 6.05 (s, 1H), 7.09 (t, J = 7.2 Hz, 1H), 7.11-7.26 (m, 6H), 7.33-7.50 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.4, 28.9, 51.4, 104.9 (overlapped), 110.1, 119.2, 120.5, 121.2, 127.5, 128.3 (overlapped), 128.4, 131.6, 131.7, 133.6, 133.8, 134.2, 136.8, 138.7, 138.9, 139.0 (unresolved complex C-P splittings were observed); ^{31}P NMR (162 MHz, $CDCl_3$) δ -13.82; HRMS: calcd. for $C_{30}H_{29}NP^+$: 434.2038, found 434.2036.

N-*Iso*butyl-2-(2’-diisopropylphosphinophenyl)indole (Table 6.2, entry 9)



2-(2’-Bromophenyl)-1-isobutyl-1*H*-indole (0.63 g, 2 mmol), *n*-BuLi (2.2 mmol) and chlorodiisopropylphosphine (0.49 mL, 2.2 mmol) were used to afford *N*-isobutyl-2-(2’-diisopropylphosphinophenyl)indole (0.25 g, 28%) as pale yellow solid. Melting point 124.1-125.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80-1.83 (m, 18H), 3.68 (bs, 1H), 3.97 (bs, 1H), 6.42 (s, 1H), 7.10-7.14 (m, 1H), 7.20-7.24 (m, 1H) 7.38-7.50 (m, 4H), 7.61-7.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.2, 28.7, 51.8, 51.9, 103.8, 110.3, 119.0, 120.1, 120.9, 127.7, 128.2, 132.1 (overlapped), 132.7, 132.8, 136.3, 140.7, 141.0, 141.1 (unresolved complex C-P splittings were observed); ^{31}P NMR (162 MHz, $CDCl_3$) δ -1.60; HRMS: calcd. for $C_{24}H_{33}NP^+$: 366.2351, found 366.2348.

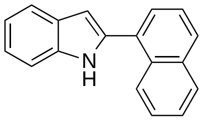
2-Phenyl-1-(1-phenylbutyl)-1*H*-indole (Scheme 6.3)



2-(2’-Bromophenyl)-1-benzyl-1*H*-indole (0.72 g, 2 mmol), *n*-BuLi (2.2 mmol), chlorodiphenylphosphine (0.4 mL, 2.2 mmol) were used to afford 2-phenyl-1-(1-phenylbutyl)-1*H*-indole (86%) as a white crystal. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.74 (*t*, 4H), 0.93-0.95 (m, 1H), 1.09-1.15 (m, 2H), 2.26-2.33 (m, 1H), 2.45-2.52 (m, 1H), 5.60-6.61 (m, 1H), 6.61 (s, 1H), 7.05-7.15 (m, 4H), 7.32-7.49 (m, 11H), 7.69 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 22.2, 28.1, 32.3, 58.3, 102.3, 113.1, 119.7, 120.6, 121.1, 126.3, 126.9, 127.9, 128.4, 128.6, 129.0, 129.4, 133.4, 135.8, 141.4, 143.2; MS (EI): *m/z* (relative intensity) 339 (M^+, 58), 282 (6), 193 (100), 165 (14), 91 (86).

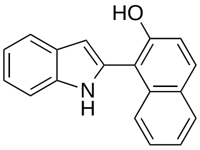
6.5.2.2 Preparation of C-3 Naphdole Phosphine Ligands

2-(Naphthalen-1-yl)-1*H*-indole (Table 6.3, entry 1)[10]



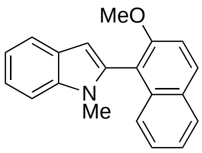
1-Acetonaphthone (7.6 ml, 50 mmol) was mixed with phenylhydrazine (4.9 ml, 50 mmol) in 10 ml phosphoric acid and stir at room temp for 30 min. About 50 g of PPA was added to the mixture and an exothermic reaction ensured whereupon the mixture was heated slowly to 120 °C and kept at this temperature for 1 h. The mixture was poured into ice water and then extract with Et_2O. The organic phase was combined and dried over Na_2SO_4. The concentrated organic phase was filtered over a pad of silica (5 × 2 inch) and washed with hexane then EA/hexane (1:9). The solution was evaporated to yield light yellow solid product. Pretty amount of cooled hexane was used to further purify of the product. The final product 2-(naphthalen-1-yl)-1*H*-indole was dried under vacuum (7.0 g, 58%) and formed a light yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 1H), 7.19-7.28 (m, 1H), 7.28-7.30 (m, 1H), 7.47-7.59 (m, 1H), 7.66-7.76 (m, 5H), 7.91-7.97 (m, 2H), 8.34-8.36 (m, 2H); MS (EI): *m/z* (relative intensity) 243 (M^+, 100), 207 (8), 120 (19).

1-(1*H*-Indol-2-yl)naphthalen-2-ol (Scheme 6.4)[6]



Oxindole (0.67g, 5 mmol) was mixed with 2-chloropyridine (0.57 ml, 6 mmol) in DCM (35 ml) under nitrogen. The mixture was then cooled to -78°C and Tf_2O (0.93 ml, 5.5 mmol) was added dropwisely via syringe. After 5 minutes, the reaction was warmed to 0 °C and 2-naphthol (0.721g, 5 mmol) was added. The mixture was allowed to warm to room temperature and stirred for 3 hours. After the completion of reaction by monitoring the TLC, saturated NaOH and $NaHCO_3$ solution were added to quench the reaction and neutralize the acidic salts. The organic phase was separated, washed with brine (20 ml), and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduce pressure and the residue purified by column chromatography (toluene: EA = 30:1, Rf = 0.45) to afford 1-(1*H*-indol-2-yl)naphthalen-2-ol as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (s, 1H), 7.23-7.49 (m, 6H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.86 (t, *J* = 8.4 Hz, 2H), 8.28 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 104.5, 111.1, 111.8, 117.3, 120.5, 120.8, 122.8, 123.7, 124.2, 127.2, 128.3, 128.7, 128.8, 130.2, 133.3, 137.0, 152.1.

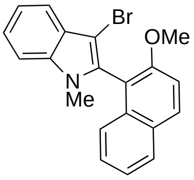
2-(2-Methoxynaphthalen-1-yl)-1-methyl-1*H*-indole (Scheme 6.5)



Sodium hydride (11 mmol) was stirred in THF (10 ml) under nitrogen. To a solution of 1-(1*H*-indol-2-yl)naphthalen-2-ol (0.73 g, 2.5 mmol) in anhydrous THF (10 ml) was added dropwise at room temperature. Afterward, Me_2SO_4 (1.04

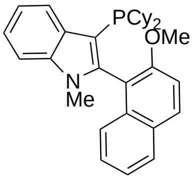
ml, 11 mmol) was added dropwise in the mixture. After stirring for 2 hours, the reaction mixture was extracted with CH_2C1_2/H_2O. The combined organic extracts were dried over anhydrous Na_2SO_4, and concentrated. The concentrated organic phase was filtered over a pad of silica (5 × 2 inch) and washed with EA/hexane (1:6, Rf = 0.5). The solution was evaporated to yield light yellow solid product. The product was washed with hexane to further purify of the product. The final product 2-(2-methoxynaphthalen-1-yl)-1-methyl-1*H*-indole was dried under vacuum (0.61 g, 85%) and formed a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.51 (s, 3H), 3.91 (s, 3H), 6.62 (s, 1H), 7.21 (t, J = 7.2 Hz, 1H), 7.31 (t, J = 8 Hz, 1H), 7.37-7.46 (m, 4H), 7.64 (t, J = 4.4 Hz, 1H), 7.65 (d, J = 7.6 Hz, 1H), 7.88 (t, J = 4 Hz, 1H), 8.02 (d, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.1, 56.5, 103.1, 109.3, 113.2, 115.4, 119.3, 120.5, 121.0, 123.8, 125.3, 126.9, 127.8, 128.1, 128.8, 130.7, 134.7, 134.9, 137.4, 155.7; MS (EI): *m/z* (relative intensity) 287 (M^+, 100), 270 (15), 254 (18), 228 (15), 202 (8), 169 (24), 144 (16), 127 (10).

3-Bromo-2-(2-methoxynaphthalen-1-yl)-1-methyl-1*H*-indole (Scheme 6.5)



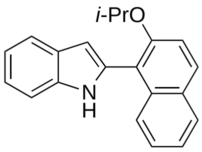
To a solution of 2-(2-methoxynaphthalen-1-yl)-1-methyl-1*H*-indole (0.3 g, 1.0 mmol) in anhydrous DMF (15 mL), a solution of *N*-bromosuccinimide (0.22 g, 1.2 mmol) in anhydrous DMF (10 mL) was added at room temperature. After stirring for 2 hours, the reaction mixture was poured onto crushed ice and DCM was added to the flask followed by water. The organic phase was washed with large amount of water, and was then concentrated. The concentrated solution was filtered over a pad of silica (6 × 2 inch) and washed with hexane then EA/hexane (1:6, Rf = 0.5). The solution was evaporated to give white solid product. The final product 3-bromo-2-(2-methoxynaphthalen-1-yl)-1-methyl-1*H*-indole was dried under vacuum (0.35 g, 93%) to give white solid as the desired compound. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.52 (s, 3H), 3.92 (s, 3H), 7.29-7.46 (m, 7H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.90-7.92 (m, 1H), 8.07 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.9, 56.6, 91.9, 109.6, 113.1, 113.4, 119.1, 120.0, 122.3, 124.0, 124.9, 127.2, 127.3, 128.1, 128.8, 131.6, 133.4, 133.8, 136.7, 156.4; MS (EI): *m/z* (relative intensity) 365 (M^+, 84), 286 (100), 271 (73), 255 (23), 241 (31), 227 (15), 143 (22), 120 (18); HRMS: calcd. for $C_{20}H_{17}NOBr^+$: 366.0494, found 366.0500.

3-(Dicyclohexylphosphino)-2-(2-methoxynaphthalen-1-yl)-1-methyl-1*H*-indole (Scheme 6.5)



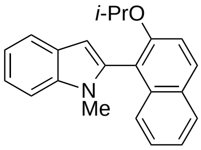
3-Bromo-2-(2-methoxynaphthalen-1-yl)-1-methyl-1*H*-indole (0.37 g, 1 mmol), *n*-BuLi (1.1 mmol), chlorodicyclohexylphosphine (0.25 mL, 1.1 mmol) were used to afford 3-(dicyclohexylphosphino)-2-(2-methoxynaphthalen-1-yl)-1-methyl-1*H*-indole as a white crystal. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.52 (s, 3H), 3.92 (s, 3H), 7.29-7.46 (m, 7H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.90-7.92 (m, 1H), 8.07 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.9, 56.6, 91.9, 109.6, 113.1, 113.4, 119.1, 120.0, 122.3, 124.0, 124.9, 127.2, 127.3, 128.1, 128.8, 131.6, 133.4, 133.8, 136.7, 156.4; (unresolved complex C-P splittings were observed); ^{31}P NMR (162 MHz, $CDCl_3$) δ -6.97; MS (EI): *m/z* (relative intensity) 483 (M^+, 22), 452 (100), 401 (15), 370 (11), 318 (84), 302 (21), 286 (31), 256 (10), 55 (21); HRMS: calcd. for $C_{32}H_{39}NOP^+$: 484.2769, found 484.2793.

2-(2-Isopropoxynaphthalen-1-yl)-1*H*-indole (Scheme 6.5)



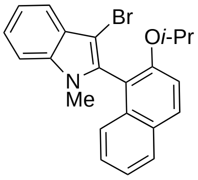
1-(1*H*-indol-2-yl)naphthalen-2-ol (1.09 g, 4.2 mmol) and K_2CO_3 (1.74 g, 12.6 mmol) were stirred in anhydrous DMF (20 ml) at room temperature for 30 min. 2-Bromopropane (1.2 ml, 12.6 mmol) was added dropwise at room temperature. After stirring for 2 hours, the reaction mixture was extracted with CH_2C1_2/H_2O. The combined organic extracts were dried over anhydrous Na_2SO_4, and concentrated. The concentrated organic phase was filtered over a pad of silica (5 × 2 inch) and washed with EA/hexane (1:4, Rf = 0.55). The solution was evaporated to yield light pink solid. The product was washed with hexane to further purify of the product. The final product 2-(2-isopropoxynaphthalen-1-yl)-1*H*-indole was dried under vacuum (0.93 g, 74%) and formed a light pink solid (EA: Hexane=1:4, Rf=0.55). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (d, *J* = 6 Hz, 6H), 4.47-4.53 (m, 1H), 6.79 (s, 1H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 9.2 Hz, 1H), 7.41-7.49 (m, 3H), 7.75 (d, *J* = 8 Hz, 1H), 7.87 (t, *J* = 7.6 Hz, 2H), 8.26 (d, *J* = 8.4 Hz, 1H), 8.74 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.35, 73.2, 104.9, 110.7, 118.3, 119.0, 119.6, 120.3, 121.7, 124.3, 125.6, 126.8, 128.0, 128.4, 129.9, 133.5, 136.1, 153.3; HRMS: calcd. for $C_{21}H_{20}NO^+$: 302.1545, found 302.1538.

2-(2-Isopropoxynaphthalen-1-yl)-1-methyl-1*H*-indole (Scheme 6.5)



Follow the General procedure for synthesis of the *N*-methyl-indole, 2-(2-isopropoxynaphthalen-1-yl)-1*H*-indole (1.03 g, 3.5 mmol), sodium hydride (7 mmol) and Me_2SO_4 (0.66 ml, 7 mmol) were given the desired product as light brown solution. The concentrated organic phase was filtered over a pad of silica (5 × 2 inch) and washed with EA/hexane (1:4, Rf = 0.65). The final product 2-(2-isopropoxynaphthalen-1-yl)-1-methyl-1*H*-indole was dried under vacuum (1.08 g, 98%) and formed light brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (d, *J* = 6 Hz, 3H), 1.34 (d, *J* = 6 Hz, 3H), 3.61 (s, 3H), 4.58-4.65 (m, 1H), 6.69 (s, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.38-7.54 (m, 5H), 7.75 (d, *J* = 2 Hz, 1H), 7.77-7.84 (m, 1H), 7.95 (d, *J* = 6.8 Hz, 1H), 8.01 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.3, 22.5, 30.4, 72.3, 103.4, 109.4, 117.5, 117.9, 119.3, 120.4, 120.9, 124.1, 125.6, 126.8, 127.8, 128.3, 130.5, 135.0, 135.4, 137.4, 154.5; HRMS: calcd. for $C_{22}H_{22}NO^+$: 316.1701, found 316.1714.

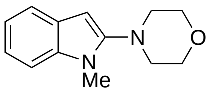
3-Bromo-2-(2-isopropoxynaphthalen-1-yl)-1-methyl-1*H*-indole (Scheme 6.5)



To a solution of 2-(2-isopropoxynaphthalen-1-yl)-1-methyl-1*H*-indole (0.3 g, 1 mmol) in anhydrous DMF (15 mL), a solution of *N*-bromosuccinimide (0.22 g, 1.2 mmol) in anhydrous DMF (10 mL) was added at room temperature. After stirring for 2 hours, the reaction mixture was poured onto crushed ice and DCM was added to the flask followed by water. The organic phase was washed with large amount of water, and was then concentrated. The concentrated solution was filtered over a pad of silica (6 × 2 inch) and washed with hexane then EA/hexane (1:6, Rf = 0.5). The final product 3-bromo-2-(2-isopropoxynaphthalen-1-yl)-1-methyl-1*H*-indole was dried under vacuum (0.35 g, 93%) to give pink solid as the desired compound. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.13 (d, J = 6 Hz, 3H), 1.26 (d, J = 6 Hz, 3H), 3.52 (s, 3H), 4.51-4.60 (m, 1H), 7.27-7.45 (m, 8H), 7.70 (d, J = 8 Hz, 1H), 7.88-7.90 (m, 1H), 8.00 (d, J = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.2, 22.5, 30.9, 72.5, 91.8, 109.5, 117.2, 119.0, 119.9, 122.1, 124.1, 125.1, 127.1, 127.2, 128.0, 129.1, 131. 2, 133.8, 133.9, 136.6, 155.1.

6.5.2.3 Preparation of C-3 Indolyl Morpholine Phosphine Ligands

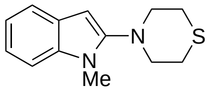
4-(1-Methyl-1*H*-indol-2-yl)morpholine (Table 6.4, entry 1)[7]



N-Methylindole (2.5 ml, 20 mmol), morpholine (4.37 ml, 50 mmol), K_2CO_3 (10 g, 40 mmol), I_2 (10 g, 40 mmol), and acetonitrile (80 ml) were stirred at room temperature under air overnight. The reaction mixture was washed with saturated $Na_2S_2O_3$. The combined organic phases were extracted with brine, dried over anhydrous sodium sulfate. The concentrated organic phases was purified by column chromatography with EA: hexane (1:4, Rf = 0.5) to afford the desired 4-(1-methyl-1*H*-indol-2-yl)morpholine (2.76 g, 64%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.07 (dd, J = 4.4, 2 Hz, 4H), 3.67 (s, 3H), 3.93 (dd, J = 2.8, 1.6 Hz, 4 H), 5.99 (s, 1H), 7.11-7.29 (m, 3H), 7.54-7.57 (m, 1H); ^{13}C

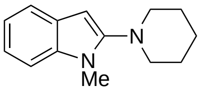
NMR (100 MHz, $CDCl_3$) δ 29.0, 52.7, 66.8, 86.8, 108.6, 119.3, 119.5, 120.2, 127.4, 135.2, 149.9.

4-(1-Methyl-1*H*-indol-2-yl)thiomorpholine (Table 6.4, entry 2)



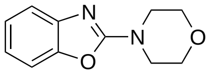
N-Methylindole (1.3 ml, 10 mmol), thiomorpholine (3 ml, 30 mmol), K_2CO_3 (5 g, 20 mmol), I_2 (5 g, 20 mmol), and acetonitrile (40 ml) were stirred at room temperature under air overnight. The concentrated organic phases was purified by column chromatography with EA: hexane (1:4, Rf = 0.55) to afford 4-(1-methyl-1*H*-indol-2-yl)thiomorpholine (2.33 g, 20%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.87 (t, *J* = 4.8 Hz, 4H), 3.31 (t, *J* = 4.4 Hz, 4H), 3.62 (s, 3H), 5.98 (s, 1H), 7.08-7.28 (m, 3H), 7.52 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.8, 28.6, 28.7, 28.9, 53.2, 96.2, 109.0, 119.0, 119.5, 121.3, 128.5, 134.2, 147.3.

1-Methyl-2-(piperidin-1-yl)-1*H*-indole (Table 6.4, entry 3)[11]



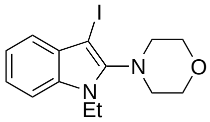
N-Methylindole (1.3 ml, 10 mmol), piperidine (2.6 ml, 25 mmol), Cs_2CO_3 (6.5 g, 20 mmol), I_2 (5 g, 20 mmol), and acetonitrile (20 ml) were stirred under reflux and air for 18 hours. The concentrated organic phases was purified by column chromatography with EA: hexane (1:15, Rf = 0.5) to afford 1-methyl-2-(piperidin-1-yl)-1*H*-indole (18%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.65-1.69 (m, 2H), 1.78-1.83 (m, 4H), 3.01 (t, *J* = 5.2 Hz, 4H), 3.65 (s, 3H), 5.93 (s, 1H), 7.09-7.28 (m, 3H), 7.52-7.54 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.2, 26.0, 29.0, 53.7, 86.1, 108.4, 119.0, 119.2, 119.7, 127.7, 135.2, 151.6.

2-Morpholinobenzo[*d*]oxazole (Table 6.4, entry 4)[12]



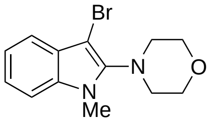
Benzoxazole (1.19 ml, 10 mmol), morpholine (2.2 ml, 25 mmol), Cs_2CO_3 (6.5 g, 20 mmol), I_2 (5 g, 20 mmol), and acetonitrile (40 ml) were stirred under reflux and air for 18 hours. The concentrated organic phases was purified by column chromatography with EA: hexane (1:3, Rf = 0.2) to afford 2-morpholinobenzo[*d*]oxazole (30%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.69-3.71 (m, 4H), 3.81-3.84 (m, 4H), 7.03-7.07 (m, 1H), 7.17-7.29 (m, 1H), 7.38 (d, 1H), 7.40 (d, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 45.6, 66.1, 108.7, 116.4, 120.9, 124.0, 142.7, 148.6, 162.0.

4-(1-Ethyl-3-iodo-1*H*-indol-2-yl)morpholine (Scheme 6.6)



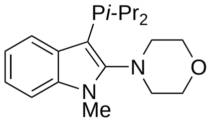
N-Ethylindole (1.41 ml, 20 mmol), morpholine (5.2 ml, 60 mmol), K_2CO_3 (2.76 g, 20 mmol), I_2 (5 g, 20 mmol), and acetonitrile (100 ml) were stirred at room temperature under air overnight. The reaction mixture was washed with saturated $Na_2S_2O_3$. The combined organic phases were extracted with brine, dried over anhydrous sodium sulfate. The concentrated organic phases was purified by column chromatography with EA: hexane (1:4, Rf = 0.45) to afford the desired 4-(1-ethyl-3-iodo-1*H*-indol-2-yl)morpholine (2.15 g, 63%) as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36 (t, *J* = 7.2 Hz, 3H), 3.37 (bs, 4H), 3.89 (s, 4H), 4.20-4.26 (m, 2H), 7.17-7.28 (m, 3H), 7.42 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.6, 37.1, 48.1, 51.0, 53.5, 67.7, 109.6, 120.2, 120.6, 122.4, 129.5, 133.3, 145.1.

4-(3-Bromo-1-methyl-1*H*-indol-2-yl)morpholine (Scheme 6.7)



To a solution of 4-(1-methyl-1*H*-indol-2-yl)morpholine (0.216 g, 1 mmol) in anhydrous DCM (5 mL), a solution of *N*-bromosuccinimide (0.178 g, 1.1 mmol) in anhydrous DCM (5 mL) was added at room temperature. After stirring for 5 minutes, the reaction mixture was poured into crushed ice and DCM was added to the flask followed by water. The organic phase was washed with large amount of water, and was then concentrated. The concentrated solution was filtered over a pad of silica (6 × 2 inch) and washed with hexane then EA/hexane (1:4, Rf = 0.35). The final product 4-(3-bromo-1-methyl-1*H*-indol-2-yl)morpholine was dried under vacuum (0.18 g, 61%) to give white solid as the desired compound. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.34 (bs, 4H), 3.68 (s, 3H), 3.88 (t, J = 4.4 Hz, 4H), 7.16-7.20 (m, 1H), 7.25-2.78 (m, 2H), 7.51 (d, J = 8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.6, 50.8, 67.6, 81.6, 109.3, 118.3, 120.1, 122.1, 126.4, 133.5.

4-(3-(Diisopropylphosphino)-1-methyl-1*H*-indol-2-yl)morpholine (Scheme 6.8)



4-(3-bromo-1-methyl-1*H*-indol-2-yl)morpholine (0.29 g, 1 mmol), *n*-BuLi (1.1 mmol), chlorodiisopropylphosphine (0.175 mL, 1.1 mmol) were used to afford 4-(3-(diisopropylphosphino)-1-methyl-1*H*-indol-2-yl)morpholine (33.2 mg, 10%) as a white crystal. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86-0.96 (m, 6H), 1.18-1.35 (m, 6H), 1.64 (bs, 4H), 2.54-2.63 (m, 2H), 3.67 (s, 3H), 3.85 (s, 4H), 7.06-7.10 (m, 1H), 7.20-7.28 (m, 2H), 7.70 (d, J = 8 Hz, 1H); ^{13}C NMR (100

MHz, $CDCl_3$) δ 21.5, 21.7, 22.0, 22.2, 24.4, 24.5, 28.4, 53.3, 53.4, 67.8, 98.8, 99.0, 109.6, 119.3, 121.2, 121.5, 129.2, 135.7, 154.4, 154.8 (unresolved complex C-P splittings were observed); ^{31}P NMR (162 MHz, $CDCl_3$) δ -11.97.

6.6 References

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Chapter 7 Palladium-Catalyzed Suzuki-Miyaura Coupling for Tri-*ortho*-Substituted Biaryl Compounds Synthesis with Aryl Tosylates and Mesylates

7.1 Introduction

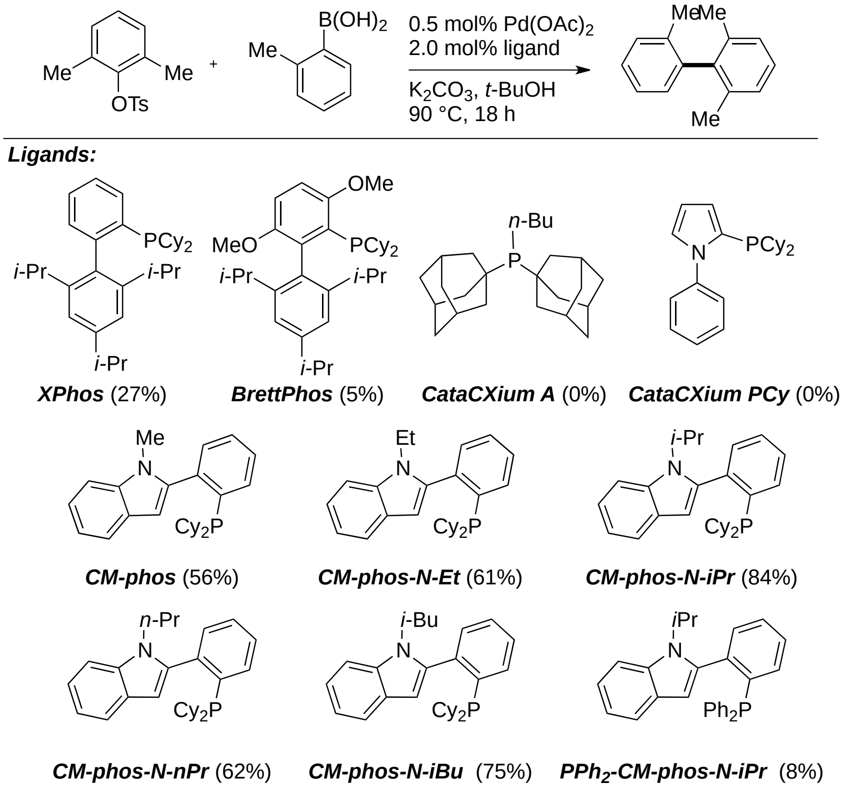
Over the past decade, palladium-catalyzed Suzuki-Miyaura coupling have been shown to be one of the most versatile synthetic tools in organic chemistry. The formation of carbon–carbon bonds has shown increasing utility in pharmaceutical, advanced materials, natural products and agricultural chemistry.[1] Huge efforts have been undertaken by researchers to aim at reaching a high degree of efficiency in such cross-coupling reaction toward the development of new ligands with the ability to achieve excellent catalytic generality and activity. Moreover, the activation of aryl iodides, bromides and even more challenging chlorides as electrophiles for the cross-coupling reactions is another research focus. A plethora of ligands have been developed to cater the catalysis with broad substrate scope, wide functional group tolerance, and at even low catalyst loadings.[2] Electron-rich and sterically demanding ligands such as biaryl monophosphines,[3] alkyl monophosphines,[4] *N*-heterocyclic carbenes,[5] and other ligands, have led to considerable progress in this area. In the past few years, Kwong's group has also reported specially designed ligands for palladium-catalyzed Suzuki-Miyaura coupling of aryl halides with arylboronic acids and other organoboron nucleophiles.[6] Notably, CM-phos facilitates the couplings even for the unexplored aryl arenesulfonates in good to excellent yields with low catalyst loadings.[7] In light of the performance of the catalyst, we focused on the less explored reactions of sterically hindered aryl arenesulfonates to afford tri-*ortho*-substituted biaryl compounds.

To the best of our knowledge, general tri-*ortho*-substituted biaryls synthesis from aryl chlorides by Suzuiki-Miyaura coupling reactions remains sporadically reported to date.[8] Particularly noteworthy is that aryl arenesulfonates are even rarely applied in the preparation of tri-*ortho*-substituted biaryls. Recent superb findings by the Buchwald group demonstrated only one example of 2,4-dimethylphenyl mesylate coupled with 2,6-dimethylphenylboronic acid by using a biarylphosphine ligand (BrettPhos).[3f] Therefore, the development of efficient and general catalyst to address this limitation is still a challenging area of research. We herein disclose exceptional capabilities of our newly designed ligand and the first general examples of sterically hindered Suzuki-Miyaura cross-coupling of *ortho*-substituted aryl tosylates/mesylates with arylboronic acids.

7.2 Result and Discussion

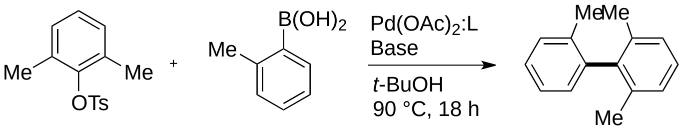
7.2.1 Preliminary Evaluation of Pd-Catalyzed Tri-*ortho*-Suzuki Cross-Coupling

With our newly developed ligands in hand, we evaluated their performance in the synthesis of tri-*ortho*-substituted biaryl compounds. Non-activated 2,6-dimethylphenyl tosylates and *o*-tolylboronic acid were initially used as model substrates in the prototypical reaction (Table 7.1). A series of commercially available ligands as well as our previously developed indolylphosphines were tested for their efficacy in this reaction (Scheme 7.1). Poor conversion of aryl tosylates was observed with the phosphine ligands XPhos,[9] and BrettPhos,[10] whereas the ligands CataCXium A[11] and CataCXium PCy[12] did not promote the coupling reaction. By expanding the alkyl group from methyl to *iso*propyl, CM-phos-*N*-*i*Pr gave the best product yield (84% yield) when compared to CM-phos-*N*-Et and CM-phos with 61% and 59% respectively. Not surprisingly, CM-phos-*N*-*n*Pr gave comparable result as CM-phos-*N*-Et with similar steric effect (62%). The product yield was slightly increased when CM-phos-*N*-*i*Bu (75%) was used when compared to CM-phos-*N*-Et and CM-phos-*N*-*n*Pr. These results indicated that more bulky group on the heterocyclic ring could improve the efficacy of the biaryl synthesis. PPh_2-CM-phos-*N*-*i*Pr (with a diphenylphosphino moiety) provided low conversion.



Scheme 7.1. Ligand screening for the palladium-catalyzed Suzuki-Miyaura cross-coupling of 2,6-dimethylphenyl tosylate. (Reaction conditions: aryl tosylates (0.5 mmol), arylboronic acid (1.0 mmol), $Pd(OAc)_2$ (0.0025 mmol, 0.5 mol%), ligand (2.0 mol%; Pd/L 1:4), K_2CO_3 (1.5 mmol), *t*-BuOH (1 mL), 90 °C, 18 h. Yields were determined by GC with dodecane as the internal standard. Cy=cyclohexyl. Ph=phenyl.)

Table 7.1. Initial screenings of Pd-catalyzed Suzuki coupling of aryl tosylates[a]



entry	Pd loding/ mol%	Pd:L	base	%yield[b]
1	1.0	1:4	K_2CO_3	78
2	1.0	1:4	K_3PO_4	69
3	1.0	1:4	$K_3PO_4{\bullet}H_2O$	60
4	1.0	1:4	Cs_2CO_3	20
5	1.0	1:4	Na_2CO_3	0
6	1.0	1:1	K_2CO_3	26
7	1.0	1:2	K_2CO_3	75
8	1.0	1:3	K_2CO_3	68
9	0.2	1:4	K_2CO_3	69
10[c]	0.5	1:4	K_2CO_3	84
11[d]	0.5	1:4	K_2CO_3	15
12[c]	1.0	1:4	K_2CO_3	87
13	2.0	1:4	K_2CO_3	90
14	0.5	1:4	K_3PO_4	68
15	2.0	1:4	K_3PO_4	66
16[e]	0.5	1:4	K_2CO_3	35
17[f]	0.5	1:4	K_2CO_3	71
18[g]	0.5	1:4	K_2CO_3	23
19[h]	0.5	1:4	K_2CO_3	76

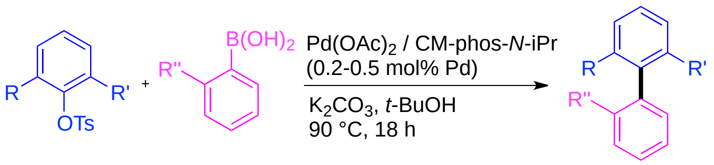
[a] Reaction conditions: ArOTs (0.5 mmol), Ar'B(OH)$_2$ (1.0 mmol), base (1.5 mmol), Pd/CM-phos-*N*-iPr = 1:4, *t*-BuOH (2.0 mL) were stirred for 18 h at 90 °C under nitrogen. [b] Calibrated GC yields were reported using dodecane as the internal standard. [c] 1 ml *t*-BuOH was used. [d] 4 ml *t*-BuOH was used. [e] Reaction was conducted at 50 °C. [f] Reaction was conducted at 70 °C. [g] Reaction was conducted at 140 °C with *t*-AmOH as solvent. [h] Reaction was conducted at 120 °C.

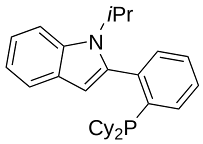
We carried out further experiments to optimize the reaction parameters. (Table 7.1). A survey of often-used inorganic bases revealed that K_2CO_3 afforded the best result (entry 1), whereas the reactions with K_3PO_4 and $K_3PO_4{\bullet}H_2O$ provided the product in moderate yield (entries 2-3). However, other carbonated bases gave poor conversion (entries 4-5). The best Pd/CM-phos-*N*-iPr ratio was found to be 1:4 (entries 1, 6-8). It is not surprisingly that higher palladium loading gave higher yield and 0.5 mol% of Pd(OAc)$_2$ gave 84% yield (entry 10 *vs* 12, entry 1 *vs* 13). Concentration effect altered the reaction that 1.0 ml of *t*-BuOH (0.5 M) gave the best conversion even lowering the Pd loading (entry 1 vs 10). 4.0 ml *t*-BuOH gave poor conversion (entry 11). The reaction could proceed when lower temperature was used (70 °C), yet gave slightly lower yield (entry 10 *vs* 17).

7.2.2 Scope of Pd-Catalyzed Tri-*ortho*-Suzuki Cross-Coupling of Aryl Tosylates and Mesylates

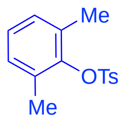
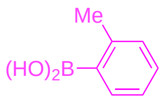
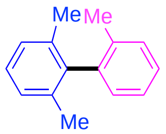
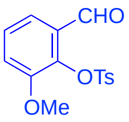
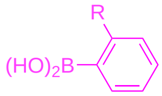
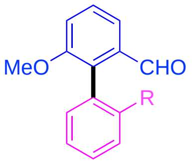
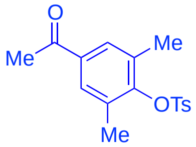
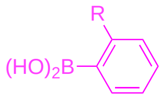
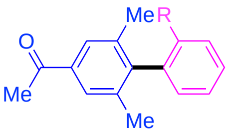
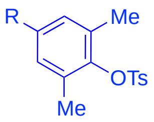
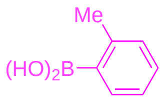
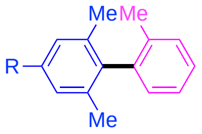
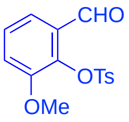
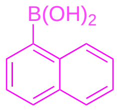
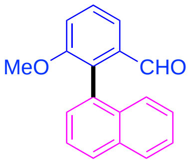
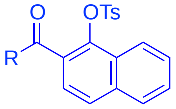
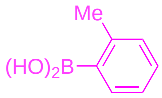
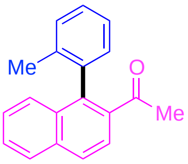
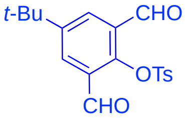
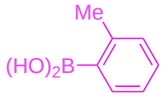
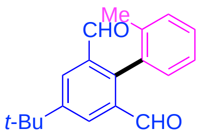
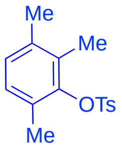
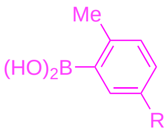
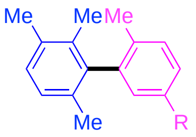
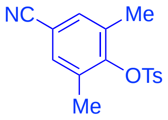
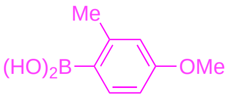
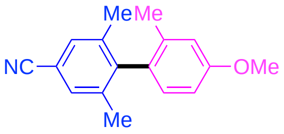
To test the effectiveness of Pd/ CM-phos-*N*-iPr catalytic system, a range of sterically congested aryl tosylates (prepared from substituted phenols with *p*-toluenesulfonyl chloride) and hindered arylboronic acids were examined using the preliminary optimized reaction conditions (Table 7.2). In general, the coupling of non-activated aryl tosylates was achieved with 0.5 mol% of Pd (Table 7.2, entries 1, 7, 9, 15-16). Catalyst loading for the aryl tosylates with functional group keto, aldehyde and methoxy group could be reduced to 0.2 mol% of Pd at 90 °C. This represents the lowest catalyst loading achieved so far for arenesulfonate coupling for tri-*ortho*-substituted biaryls (entries 5, 11, 12). Generally, aldehyde group is sensitive but they remain intact in our catalytic system (entries 2-4, 10, 11, 14). Cyano group containing substrate could furnish coupling products smoothly with good yield (entries 8, 17). *Ortho*-aldehyde-, ester- and keto-substituted aryl tosylates were feasible substrates for coupling with various arylboronic acids to afford corresponding biaryl products in moderate-to-excellent yield (entries 2-4, 11-14).

Table 7.2. Palladium-catalyzed Suzuki coupling of aryl tosylates[a]





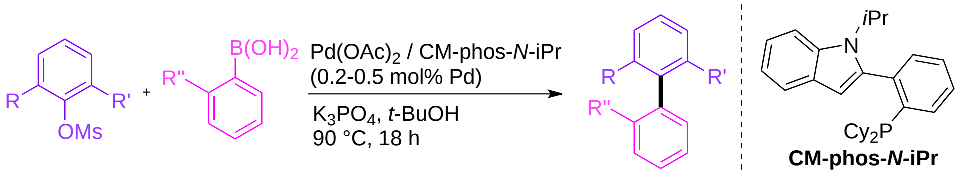
CM-phos-*N*-iPr

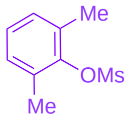
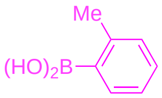
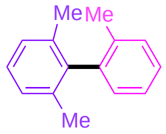
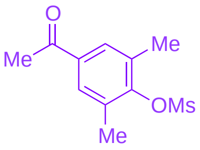
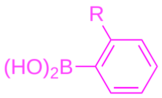
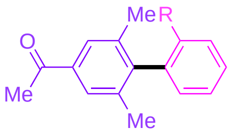
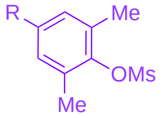
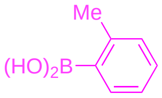
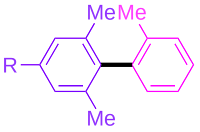
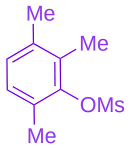
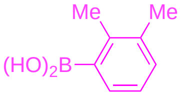
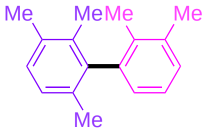
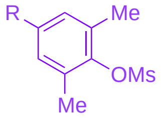
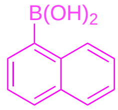
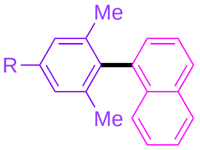
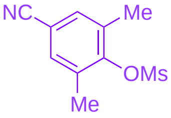
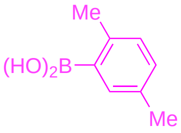
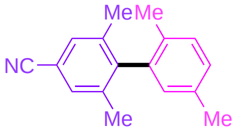
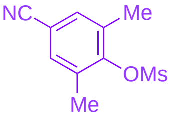
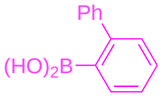
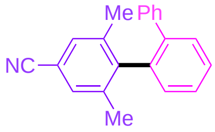
entry	ArOTs	Ar'B(OH)$_2$	product		mol% Pd	%yield[b]
1					0.5	83
2				R = Me	0.5	94
3				R = Ph	0.5	60
4[c]				R = OMe	0.5	87
5[d]				R = Me	0.2	94
6[d]				R = F	0.5	71
7[c]				R = Me	0.5	86
8				R = CN	0.5	83
9[c]				R = Ph	0.5	70
10				R = CHO	0.5	61
11					0.2	90
12				R = Me	0.2	77
13[c]				R = OMe	0.5	86
14					0.2	40
15				R = Me	0.5	87
16				R = H	0.5	71
17[c]					0.5	85

[a]Reaction conditions: ArOTs (0.5 mmol), Ar'B(OH)$_2$ (1.0 mmol), Pd:L = 1:4, K$_2$CO$_3$ (1.5 mmol) and *t*-BuOH (1.0 mL) under N$_2$ at 90 °C for 18 h (reaction time for each substrate was not optimized). [b]Isolated yields were reported. [c]K$_3$PO$_4$ was used instead of K$_2$CO$_3$. [d]110 °C was used.

In order to show the efficiency of the newly developed system, challenging electron-deficient[13] or sterically hindered arylboronic acids were used as the nucleophilic partners. Moderate product yields were obtained when 2-fluorophenylboronic acid and 2-biphenylboronic acid were used (entries 5, 12). These examples represent the first sterically hindered aryl tosylates – arylboronic acid coupling reaction for tri-*ortho*-substituted biaryls synthesis.

Table 7.3. Palladium-catalyzed Suzuki coupling of aryl mesylates[a]



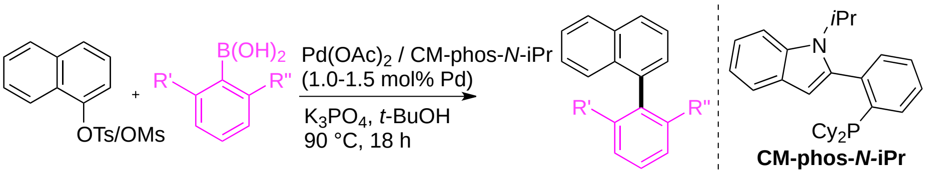
entry	ArOMs	Ar'B(OH)$_2$	product		mol% Pd	%yield[b]
1					0.5	81
2				R = Me	0.2	92
3				R = Et	0.2	87
4				R = OMe	0.5	82
5				R = F	0.5	86
6				R = Me	0.5	81
7				R = Ph	0.5	80
8					0.5	82
9				R = Me	0.5	66
10				R = Ph	0.5	90
11					0.5	78
12					0.5	32

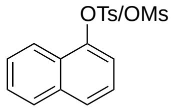
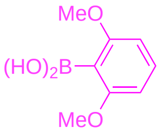
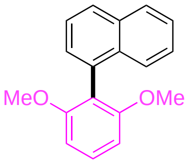
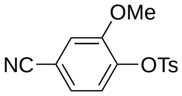
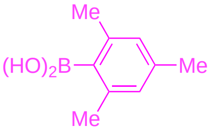
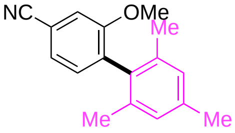
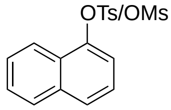
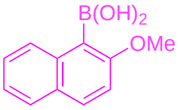
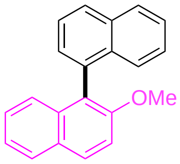
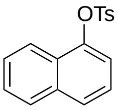
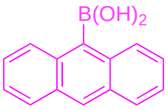
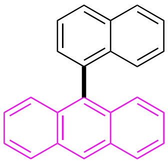
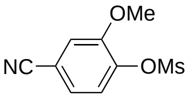
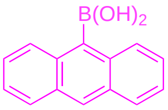
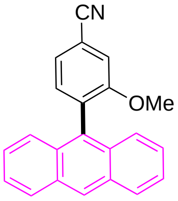
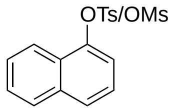
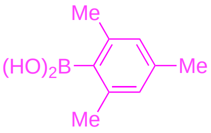
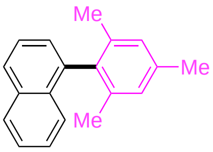
[a]Reaction conditions: ArOTs (0.5 mmol), Ar'B(OH)$_2$ (1.0 mmol), Pd:L = 1:4, K$_3$PO$_4$ (1.5 mmol) and *t*-BuOH (1.0 mL) under N$_2$ at 90 °C for 18 h (reaction time for each substrate was not optimized). [b]Isolated yields were reported.

Gratifyingly, the Pd/CM-phos-*N*-iPr catalyst system was found to be effective in promoting the tri-*ortho*-substituted biaryl coupling of aryl mesylates (Table 7.3). Aryl mesylate electrophiles are proposed to be less susceptible to oxidative addition than the corresponding aryl arenesulfonates.[14] *Ortho*-substitution on both aryl mesylates and arylboronic acids were tolerated to give moderate-to-excellent yield. For instance, the coupling of sterically more hindered 2-ethylphenylboronic acid with 4-acetyl-2,6-dimethylphenyl mesylate was successfully achieved with slightly lower yield than *o*-tolylboronic acid using 0.2 mol% of catalyst loading to give excellent yield (entries 2 and 3). Electronically neutral aryl mesylates could be coupled with hindered arylboronic acids to afford the corresponding desired biaryl products in good yields (entries 1, 6-10).

The newly developed catalyst system was further extended to test the feasibility of the coupling of 2,6-disubstituted arylboronic acids with various hindered aryl arenesulfonates to afford naphthalene derivatives which are useful scaffold in pharmaceutical and material chemistry.[15] Naphthalen-1-yl tosylates and naphthalen-1-yl mesylates coupled smoothly to give the desired product with good to excellent yield (Table 7.3). However, higher catalyst loading (1.0-1.5 mol%) and longer reaction time (24 h) were required that presumably the transmetallation of the bulky organoboron nucleophile is not efficient. When 9-anthracenylboronic acid was used as the coupling partner, the isolated yield dropped significantly. It is mainly due to the low solubility of the substrate, which got loss easily during purification of column chromatography. So far, these examples represent the lowest catalyst loading for coupling of di-*ortho*-arylboronic acid with *ortho*-aryl tosylates and mesylates.

Table 7.4. Palladium-catalyzed Suzuki coupling of aryl tosylates and mesylates with di-*ortho*-substituted arylboronic acids[a]



entry	ArOTs/ OMs	Ar'B(OH)$_2$	product	%yield[b]
1				88 (OTs) 87 (OMs)
2[c]				53
3				85 (OTs) 89 (OMs)
4[d]				58
5				23
6				86 (OTs) 89 (OMs)

[a]Reaction conditions: ArOTs/OMs (0.5 mmol), Ar'B(OH)$_2$ (1.0 mmol), Pd(OAc)$_2$ (1 mol%), Pd:L = 1:4, K$_3$PO$_4$ (1.5 mmol) and *t*-BuOH (1.0 mL) under N$_2$ at 90 °C for 18 h (reaction time for each substrate was not optimized). [b]Isolated yields were reported. [c]1.5 mol% Pd(OAc)$_2$ was used in 120 °C for 24 h. [d]110 °C was used with 24 h.

7.3 Conclusion

In conclusion, we have succeeded in achieving the first difficult palladium-catalyzed Suzuki-Miyaura tri-*ortho*-substituted biaryl synthesis of di-*ortho*-aryl tosylates/ mesylates with *ortho*-arylboronic acids using a newly developed phosphine ligand **CM-phos-*N*-*i*Pr**. We found that the highly challenging coupling is sensitive to the ligand bulkiness. Ligand bearing the more hindered *iso*-propyl group at the *N*-position in the heterocyclic ring favoured the catalysis. This experimental result may provide important information for the future ligand design to solve the difficult challenging coupling process. Moreover, this finding is of high significance as this procedure enables difficult phenolic derivative as the electrophilic partners, which usually offer different substitution patterns with respect to aryl halides, for tri-*ortho*-substituted biaryl synthesis. Notably, this system also allowed the cross-coupling with catalyst loading as low as 0.2 mol% Pd which is the lowest among other literature reports.

7.4 Experimental Section

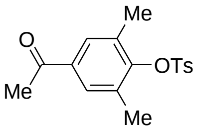
7.4.1 General considerations

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. All Suzuki-Miyaura reactions were performed in Rotaflo® (England) resealable screw-cap Schlenk flask (approx. 15 mL volume) in the presence of Teflon coated magnetic stirrer bar (4 mm × 10 mm). *tert*-Butanol was distilled from sodium under nitrogen and distilled calcium hydride. Most commercially available arylboronic acids were used as received. Some arylboronic acids may require further recrystallization depending on the received conditions. $Pd(OAc)_2$ was purchased from Strem Chemical. K_2CO_3 and K_3PO_4 were purchased from Fluka and used without grinding. Thin layer chromatography was performed on Merck precoated silica gel 60 F_{254} plates. Silica gel (Merck, 70-230 and 230-400 mesh) was used for column chromatography. Melting points were recorded on an uncorrected Büchi Melting Point B-545 instrument. ^1H NMR spectra were recorded on a Bruker (400 MHz). Spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.26 ppm), or with tetramethylsilane (TMS, δ 0.00 ppm) as the internal standard. Chemical shifts (δ) were reported as part per million (ppm) in δ scale downfield from TMS. ^{13}C NMR spectra were referenced to $CDCl_3$ (δ 77.0 ppm, the middle peak). ^{31}P NMR spectra were referenced to 85% H_3PO_4 externally. Coupling constants (J) were reported in Hertz (Hz). Mass spectra (EI-MS and ES-MS) were recorded on a HP 5989B Mass Spectrometer. High-resolution mass spectra (HRMS) were obtained on a Brüker APEX 47e FT-ICR mass spectrometer (ESIMS). GC-MS analysis was conducted on a HP 5973 GCD system using a HP5MS column (30 m × 0.25 mm). The products described in GC yield were accorded to the authentic samples/dodecane calibration standard from HP 6890 GC-FID system. All yields reported refer to the isolated yield of compounds. Compounds described in the literature were characterized by comparison of their ^1H, and/or ^{13}C NMR spectra to the previously reported data. The procedures in this section are representative, and thus the yields may differ from those reported in tables.

7.4.2 Preparation of Substrates for Coupling Reaction

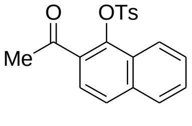
2,6-Dimethylphenyl tosylates,[16] 2,3,6-trimethylphenyl tosylates,[17] mesityl tosylates,[18] 2-formyl-6-methoxyphenyl tosylates,[19] 2,6-dimethylphenyl mesylates,[20] mesityl mesylates[21] were prepared from their corresponding phenols with TsCl and MsCl respectively in the presence of triethylamine in dry CH_2Cl_2 according to the literature methods.[22] Other aryl tosylates and mesylates were prepared according to the literature procedures.[22]

4-Acetyl-2,6-dimethylphenyl tosylate



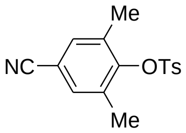
EA: Hexane = 1:4, R_f=0.25; 91% yield as white crystals; melting point 89.6-91.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.19 (s, 6H), 2.50 (s, 3H), 2.58 (s, 3H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.65 (s, 2H), 7.86 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.4, 21.7, 26.6, 128.0, 129.3, 129.9, 132.8, 134.0, 135.1, 145.5, 150.8, 197.2; MS (EI): *m/z* (relative intensity) 318 (M^+, 35), 155 (85), 135 (15), 91 (100), 65 (18); HRMS: calcd. for $C_{17}H_{19}O_4S^+$: 319.1004, found 319.0995.

2-Acetylnaphthalen-1-yl tosylate



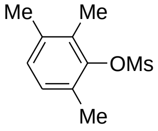
EA: Hexane = 1:4, R_f=0.2; 88% yield as white crystals; melting point 100.2-101.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 3H), 2.64 (s, 3H), 7.27 (d, *J* = 7.2 Hz, 2H), 7.37-7.42 (t, *J* = 5.6, 8.0 Hz, 1H), 7.51-7.55 (t, *J* = 0.8, 8.0 Hz, 1H), 7.66-7.13 (m, 3H), 7.81-7.89 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 30.1, 123.4, 124.8, 127.0, 127.2, 127.3, 127.7, 128.1, 128.6, 129.8, 131.3, 131.8, 135.9, 143.3, 145.9, 199.2; MS (EI): *m/z* (relative intensity) 340 (M^+, 100), 325 (39), 233 (25), 201 (30), 91 (32); HRMS: calcd. for $C_{19}H_{16}O_4NaS^+$: 363.0667, found 363.0663.

4-Cyano-2,6-dimethylphenyl tosylate



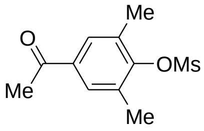
EA: Hexane = 1:4, R_f=0.4; 90% yield as white crystals; melting point 150.2-151.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.19 (s, 6H), 2.51 (s, 3H), 7.37 (s, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.88 (dd, *J* = 1.6, 4.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.2, 21.7, 110.6, 118.0, 128.0, 130.0, 132.8, 133.7, 134.2, 145.8, 150.5; MS (EI): *m/z* (relative intensity) 301 (M^+, 10), 151 (86), 91 (100), 65 (21); HRMS: calcd. for $C_{16}H_{16}NO_3S^+$: 302.0851, found 302.0861.

2,3,6-Trimethylphenyl mesylate



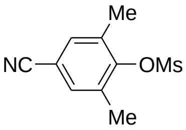
EA: Hexane = 1:4, R_f=0.4; 91% yield as white crystals; melting point 47.9-52.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (d, *J* = 5.2 Hz, 6H), 2.37 (s, 3H), 3.30 (s, 3H), 7.01 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 17.3, 19.8, 38.9, 128.2, 128.3, 129.0, 130.4, 136.3; MS (EI): *m/z* (relative intensity) 214 (M^+, 31), 135 (100), 91 (42), 79 (17); HRMS: calcd. for $C_{10}H_{15}O_3S^+$: 215.0742, found 215.0746.

4-Acetyl-2,6-dimethylphenyl mesylate

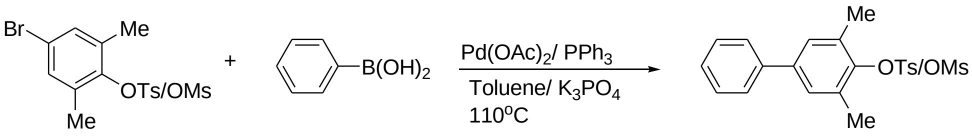


EA: Hexane = 1:2, R$_f$=0.4; 85% yield as white crystals; melting point 86.1-94.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 3H), 2.58 (s, 3H), 3.34 (s, 3H), 7.69 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.4, 39.5, 132.9, 134.1; MS (EI): *m/z* (relative intensity) 242 (M^+, 93), 227 (97), 163 (100), 149 (53), 135 (68), 120 (18), 91 (55); HRMS: calcd. for $C_{11}H_{15}O_4S^+$: 243.0691, found 243.0679.

4-Cyano-2,6-dimethylphenyl mesylate

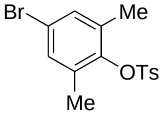


EA: Hexane = 1:4, R$_f$=0.4; 81% yield as white crystals; melting point 99.1-109.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 6H), 3.36 (d, *J* = 2.8 Hz, 3H), 7.41 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.3, 39.4, 132.8, 134; MS (EI): *m/z* (relative intensity) 225 (M^+, 43), 146 (100), 116 (25), 91 (26); HRMS: calcd. for $C_{10}H_{11}NO_3NaS^+$: 248.0357, found 248.0354.



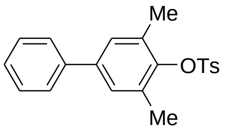
General procedure for the synthesis of ortho-substituted aryl tosylates/ mesylates were followed: $Pd(OAc)_2$ (22 mg, 0.10 mmol) and PPh_3 (26 mg, 0.10 mmol) were loaded into a 50 mL Schlenk tube equipped with a Teflon-coated magnetic stir bar. 4-Bromo-2,6-dimethylphenyl tosylate/ mesylate (10 mmol), phenylboronic acid (2.0 equiv.) and K_3PO_4 (3.0 equiv.) were then added to Schlenk tubes. The tube was evacuated and flushed with nitrogen for three cycles. The solvent toluene (10 mL) was then added. The tube was stirred at room temperature for several minutes and then placed into a preheated oil bath (110 ^{o}C) for 24 hours (reaction times and conditions were not optimized). After the completion of reaction as judged by GC analysis, the reaction tube was allowed to cool to room temperature and quenched with water and diluted with EtOAc. The organic layer was separated and the aqueous layer was further extracted with EtOAc (2 × 20 mL). The combined organic phases were concentrated under reduced pressure. The crude products were purified by flash column chromatography on silica gel (230-400 mesh). If necessary, the residue was recrystallized from minimal amount of hexane in fridge and wash with cool hexane to afford the corresponding aryl sulfonates.

4-Bromo-2,6-dimethylphenyl tosylate



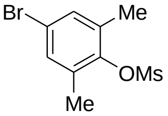
EA: Hexane = 1:4, R_f=0.5; 86% yield as white crystals; melting point 112.0-114.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.11 (s, 6H), 2.49 (s, 3H), 7.18 (s, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.0, 21.6, 119.7, 127.9, 129.8, 131.7, 134.3, 145.3; MS (EI): *m/z* (relative intensity) 356 (M^+, 26), 199 (77), 155 (65), 91 (100), 65 (28); HRMS: calcd. for $C_{15}H_{15}O_3NaSBr^+$: 376.9823, found 376.9831.

4-Phenyl-2,6-dimethylphenyl tosylate



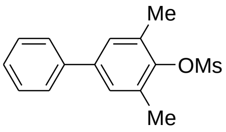
EA: Hexane = 1:9, R$_f$=0.5; 46% yield as white crystals; melting point 146.0-148.1 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.22 (s, 6H), 2.51 (s, 3H), 7.27 (s, 2H), 7.34-7.46 (m, 5H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.91 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 17.4, 21.6, 127.0, 127.3, 128.0, 128.6, 129.8, 132.4, 134.3, 139.5, 140.1, 145.1, 146.9; MS (EI): *m/z* (relative intensity) 352 (M$^+$, 12), 197 (100), 154 (7), 91 (11); HRMS: calcd. for $C_{21}H_{20}O_3NaS^+$: 375.1031, found 375.1020.

4-Bromo-2,6-dimethylphenyl mesylate



EA: Hexane = 1:4, R$_f$=0.4; 78% yield as white crystals; melting point 86.0-89.9 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.37 (s, 6H), 2.31 (s, 3H), 7.24 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 17.3, 39.1, 119.9, 131.9, 134.1, 145.8; MS (EI): *m/z* (relative intensity) 279 (M$^+$, 26), 199 (100), 91 (49); HRMS: calcd. for $C_9H_{12}O_3SBr^+$: 278.9691, found 278.9694.

4-Phenyl-2,6-dimethylphenyl mesylate



EA: Hexane = 1:4, R$_f$=0.3; 75% yield as white crystals; melting point 107.0-108.8 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.47 (s, 6H), 3.34 (s, 3H), 7.32-7.39 (m, 3H), 7.43-7.47 (m, 2H), 7.55-7.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.6, 39.1, 127.0, 127.4, 128.0, 128.7, 132.1; MS (EI): *m/z* (relative intensity) 276 (M^+, 22), 197 (100), 154 (13); HRMS: calcd. for $C_{15}H_{16}O_3NaS^+$: 299.0718, found 299.0731.

7.4.3. General Procedures for Initial Ligand and Reaction Conditions Screening

General procedure for reaction screening in Suzuki-Miyaura coupling of aryl sulfonates (Pd catalysts loading ranging from 1-2 mol %): $Pd(OAc)_2$ and ligand were loaded into a Schlenk tube equipped with a Teflon-coated magnetic stir bar (4 mm × 10 mm). The tube was evacuated and flushed with nitrogen for three cycles. Precomplexation was applied by adding freshly distilled dichloromethane and Et_3N into the tube. The palladium complex stock solution was stirred and warmed using hair drier for about 1 to 2 minutes until the solvent started boiling. The solvent was then evaporated under high vacuum. 2,6-Dimethylphenyl tosylates (0.5 mmol), *o-toly*-phenylboronic acid (1.0 mmol), base (1.5 mmol) were then added to Schlenk tubes. 1.0 mL of *t*-BuOH was added (to rinse the tube wall) with stirring at room temperature for several minutes. The tube was then placed into a preheated oil bath (90 °C) and stirred for the duration as indicated. After completion of reaction, the reaction tube was allowed to cool to room temperature. Ethyl acetate (~2mL), dodecane (113 µL, internal standard) and water were added. The organic layer was subjected to GC analysis. The GC yield obtained was previously calibrated by authentic sample/dodecane calibration curve.

General procedure for reaction screening in Suzuki-Miyaura coupling of aryl sulfonates (Pd catalysts loading lower than 0.5 mol %): A stock solution of $Pd(OAc)_2$ (5.6 mg) with ligand in freshly distilled dichloromethane was initially prepared with continuous stirring at room temperature. The Schlenk tube was equipped with a Teflon-coated magnetic stir bar (4 mm × 10 mm) and evacuated and flushed with nitrogen for three cycles. The stock solution of palladium complex were added to the Schlenk tube by syringe according to the Pd loading indicated. Precomplexation was then applied by adding distilled Et_3N into the tube. The palladium complex solution was stirred and warmed using hair drier for about 1 to 2 minutes until the solvent started boiling. The solvent was then evaporated under high vacuum. 2,6-Dimethylphenyl tosylates (0.5 mmol), *o-toly*-phenylboronic acid (1.0 mmol), base (1.5 mmol) were then added to Schlenk tubes. 1.0 mL of *t*-BuOH was added (to rinse the tube wall) with stirring at room temperature for several minutes. The tube was then placed into a preheated oil bath (90 °C) and stirred for the duration as indicated. After completion of reaction, the reaction tube was allowed to cool to room temperature. Ethyl acetate (~2mL), dodecane (113 μL, internal standard) and water were added. The organic layer was subjected to GC analysis. The GC yield obtained was previously calibrated by authentic sample/dodecane calibration curve.

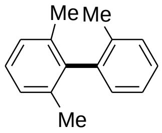
7.4.4. General Procedures for Suzuki-Miyaura Coupling of Aryl Arenesulfonates

General procedure for reaction screening in Suzuki-Miyaura coupling of aryl sulfonates (Pd catalysts loading ranging from 1-2 mol %): $Pd(OAc)_2$ and ligand were loaded into a Schlenk tube equipped with a Teflon-coated magnetic stir bar (4 mm × 10 mm). The tube was evacuated and flushed with nitrogen for three cycles. Precomplexation was applied by adding freshly distilled dichloromethane and Et_3N into the tube. The palladium complex stock solution was stirred and warmed using hair drier for about 1 to 2 minutes until the solvent started boiling. The solvent was then evaporated under high vacuum. Aryl sulfonates (0.5 mmol), aryl boronic acid (1.0 mmol), base (1.5 mmol) were then added to Schlenk tubes. 1.0 mL of *t*-BuOH was added (to rinse the tube wall) with stirring at room temperature for several minutes. The tube was then placed into a preheated oil bath (90 °C) and stirred for the duration as indicated. After the completion of reaction as judged by GC or TLC analysis, the reactions were allowed to reach room temperature and quenched with water and diluted with ethyl acetate. The filtrate was concentrated under reduced pressure. The crude products were purified by flash column chromatography on silica gel (230-400 mesh) to afford the desired product.

General procedure for reaction screening in Suzuki-Miyaura coupling of aryl sulfonates (Pd catalysts loading lower than 0.5 mol %): A stock solution of $Pd(OAc)_2$ (5.6 mg) with ligand in freshly distilled dichloromethane was initially prepared with continuous stirring at room temperature. The Schlenk tube was equipped with a Teflon-coated magnetic stir bar (4 mm × 10 mm) and evacuated and flushed with nitrogen for three cycles. The stock solution of palladium complex were added to the Schlenk tube by syringe according to the Pd loading indicated. Precomplexation was then applied by adding distilled Et_3N into the tube. The palladium complex solution was stirred and warmed using hair drier for about 1 to 2 minutes until the solvent started boiling. The solvent was then evaporated under high vacuum. Aryl sulfonates (0.5 mmol), aryl boronic acid (1.0 mmol), base (1.5 mmol) were then added to Schlenk tubes. 1.0 mL of *t*-BuOH was added (to rinse the tube wall) with stirring at room temperature for several minutes. The tube was then placed into a preheated oil bath (90 °C) and stirred for the duration as indicated. After the completion of reaction as judged by GC or TLC analysis, the reactions were allowed to reach room temperature and quenched with water and diluted with ethyl acetate. The filtrate was concentrated under reduced pressure. The crude products were purified by flash column chromatography on silica gel (230-400 mesh) to afford the desired product.

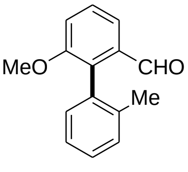
7.5 Characterization Data for Doupling Products

2,6,2'-Trimethylbiphenyl (Table 7.2, entry 1; Table 7.3, entry 1)[23]



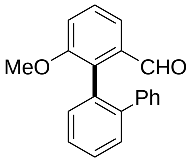
Pure hexane, R_f=0.6; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.06 (d, *J* = 8.0 Hz, 9H), 7.10-7.13 (m, 1H), 7.20-7.28 (m, 3H), 7.33-7.39 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.3, 20.2, 126.0, 126.8, 126.9, 127.2, 128.8, 129.9, 135.5, 135.8, 140.5, 141.0; MS (EI): *m/z* (relative intensity) 196 (M^+, 65), 181 (100), 165 (48).

6-Methoxy-2'-methyl-1,1'-biphenyl-2-carboxaldehyde (Table 7.2, entry 2)[24]



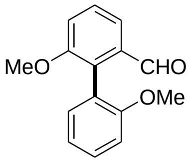
EA: Hexane = 1: 20, R$_f$=0.3; pale yellow solid; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.11 (s, 3H), 3.80 (s, 3H), 7.16-7.18 (m, 1H), 7.22-7.31 (m, 1H), 7.33-7.39 (m, 3H), 7.48-7.52 (m, 1H), 7.66-7.68 (m, 1H), 9.66 (s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 19.9, 55.8, 115.8, 118.7, 125.3, 127.9, 128.1, 128.7, 129.7, 130.7, 130.9, 133.0, 134.5, 135.0, 137.1, 156.9, 192.3; MS (EI): *m/z* (relative intensity) 226.1 (M$^+$, 100), 211 (46), 195 (25), 165 (64), 152 (38).

6-Methoxy-2'-phenyl-1,1'-biphenyl-2-carboxaldehyde (Table 7.2, entry 3)



EA: Hexane = 1: 6, R$_f$=0.45; pale yellow solid; ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.62 (s, 3H), 7.05 (d, *J* = 8.0 Hz, 1H), 7.10-7.12 (m, 2H), 7.17-7.23 (m, 3H), 7.34-7.39 (m, 2H), 7.46-7.56 (m, 4H), 9.79 (s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 55.6, 115.6, 118.8, 126.6, 126.9, 127.6, 128.4, 128.6, 128.7, 129.6, 131.7, 134.3, 134.9, 140.9, 142.6, 156.9, 192.0; MS (EI): *m/z* (relative intensity) 288 (M$^+$, 100), 257 (28), 239 (49), 226 (41), 215 (39); HRMS: calcd. for $C_{20}H_{16}O_2Na^+$: 311.1048, found 311.1046.

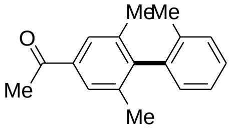
6-Methoxy-2'-methoxy-1,1'-biphenyl-2-carboxaldehyde (Table 7.2, entry 4)



EA: Hexane = 1: 6, R$_f$=0.35; colorless liquid; ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.75 (s, 3H), 3.79 (s, 3H), 7.02-7.11 (m, 2H), 7.23-7.28 (m, 2H), 7.42-7.50 (m, 2H), 7.65-7.67 (m, 1H), 9.73 (s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 55.3, 55.9, 110.6, 116.1, 118.5, 120.2, 121.7, 128.5, 129.6, 131.0, 132.3, 135.1, 157.0, 157.1, 192.6;

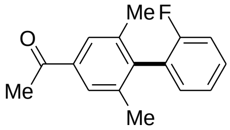
MS (EI): *m/z* (relative intensity) 242 (M^+, 66), 211 (100), 168 (21), 139 (20); HRMS: calcd. for $C_{15}H_{14}O_3Na^+$: 265.0841, found 265.0844.

1-(2,6-dimethyl-2’-methyl-[1,1'-biphenyl]-4-yl)-ethanone (Table 7.2, entry 5; Table 7.3, entry 2)



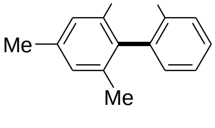
EA: Hexane = 1: 9, R_f=0.4; white solid; ^1H NMR (400 MHz, $CDCl_3$) δ 1.98 (s, 3H), 2.03 (s, 6H), 2.65 (s, 3H), 6.99 (t, *J* = 2.4, 5.6 Hz, 1H), 7.28-7.32 (m, 3H), 7.74 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.2, 20.3, 26.6, 126.1, 127.2, 127.4, 128.0, 130.1, 134.9, 135.8, 136.4, 139.5, 146.3, 198.3; MS (EI): *m/z* (relative intensity) 238 (M^+, 38), 223 (100), 180 (25), 165 (41); HRMS: calcd. for $C_{17}H_{19}O^+$: 239.1436, found 239.1438.

1-(2,6-dimethyl-2’-fluoro-[1,1'-biphenyl]-4-yl)-ethanone (Table 7.2, entry 6; Table 7.3, entry 5)



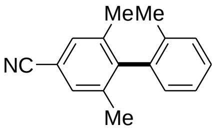
EA: Hexane = 1: 6, R_f=0.55; white solid; ^1H NMR (400 MHz, $CDCl_3$) δ 2.13 (s, 6H), 2.63 (s, 3H), 7.11-7.28 (m, 3H), 7.37-7.43 (m, 1H), 7.74 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.4, 26.5, 115.6, 115.9, 124.3 (overlapped), 126.9, 127.1, 129.4, 129.5, 130.5, 130.6, 136.3, 137.2, 140.3, 157.8, 160.2, 198.1; ^{19}F NMR (400 MHz, $CDCl_3$) δ -115.12; MS (EI): *m/z* (relative intensity) 242 (M^+, 38), 227 (100), 183 (37); HRMS: calcd. for $C_{16}H_{16}OF^+$: 243.1185, found 243.1195.

2,2',4,6-Tetramethyl-1,1'-biphenyl (Table 7.2, entry 7; Table 7.3, entry 6)[25]



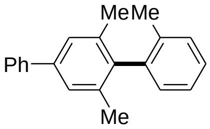
Pure hexane, R_f=0.4; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.02 (s, 6H), 2.07 (s, 3H), 2.43 (s, 3H), 7.04 (s, 2H), 7.11 (t, *J* = 1.2, 4.4 Hz, 1H), 7.32-7.36 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.4, 20.2, 21.0, 125.5, 125.9, 126.8, 127.1, 127.9, 129.1, 129.2, 129.7, 129.8, 135.6, 135.8, 136.3, 138.1, 140.5; MS (EI): *m/z* (relative intensity) 210 (M^+, 75), 195 (100), 180 (34), 165 (32).

4-Cyano-2,2',6-trimethyl-1,1'-biphenyl (Table 7.2, entry 8)



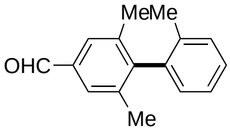
EA: Hexane = 1: 9, R_f=0.55; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.97 (s, 3H), 2.00 (s, 6H), 6.96-6.98 (m, 1H), 7.27-7.34 (m, 3H), 7.43 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.0, 20.0, 110.6, 119.0, 126.3, 127.6, 127.8, 130.2, 130.6, 134.6, 137.4, 138.5, 146.1; MS (EI): *m/z* (relative intensity) 221 (M^+, 58), 206 (100), 190 (40); HRMS: calcd. for $C_{16}H_{16}N^+$: 222.1283, found 222.1292.

4-Phenyl-2,2',6-trimethyl-1,1'-biphenyl (Table 7.2, entry 9; Table 7.3, entry 7)



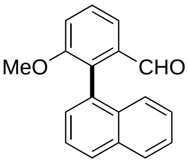
Pure hexane, R_f=0.3; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.16 (s, 9H), 7.20 (s, 1H), 7.39-7.58 (m, 8H), 7.77-7.79 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.4, 20.4, 126.0 (overlapped), 127.0 (overlapped), 128.6, 128.9, 129.9, 135.6, 136.2, 139.7, 140.2 (overlapped), 141.1; MS (EI): *m/z* (relative intensity) 272 (M^+, 100), 257 (51), 242 (27); HRMS: calcd. for $C_{21}H_{20}^+$: 272.1565, found 272.1561.

2,2',6-Trimethyl-[1,1'-biphenyl]-4-carbaldehyde (Table 7.2, entry 10)



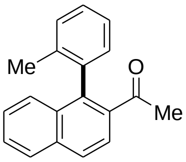
EA: Hexane = 1: 9, R_f=0.55; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.98 (s, 3H), 2.05 (s, 6H), 6.98-7.00 (m, 1H), 7.28-7.66 (m, 3H), 7.66 (s, 2H), 10.01 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.1, 20.2, 126.2, 127.5, 127.8, 128.6, 130.2, 134.7, 135.2, 137.1, 139.3, 147.8, 192.4.

3-Methoxy-2-(1-naphthalenyl)benzaldehyde (Table 7.2, entry 11)



EA: Hexane = 1: 9, R_f=0.3; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.70 (s, 3H), 7.30 (dd, *J* = 0.8, 7.2 Hz, 1H), 7.43-7.52 (m, 3H), 7.54-7.56 (m, 1H), 7.58-7.63 (m, 2H), 7.81 (dd, *J* = 1.2, 6.8 Hz, 1H), 7.96-8.00 (q, *J* = 4.0 Hz, 2H), 9.60 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.8, 115.9, 118.7, 124.9, 125.7, 125.8, 126.3, 128.2, 128.4, 128.6, 129.1, 131.2, 132.8, 133.0, 133.2, 136.0, 157.6, 192.0; MS (EI): *m/z* (relative intensity) 262 (M^+, 100), 247 (25), 231 (39), 218 (28), 202 (33), 189 (49); HRMS: calcd. for $C_{18}H_{14}O_2^+$: 262.0994, found 262.0982.

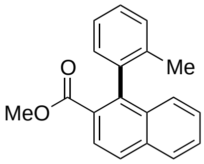
1-(1-*o*-Tolylnaphthalen-2-yl)ethanone (Table 7.2, entry 12)



EA: Hexane = 1: 6, R_f=0.6; yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.04 (s, 6H), 7.20 (dd, *J* = 0.8, 6.4 Hz, 1H), 7.32-7.40 (m, 1H), 7.42-7.49 (m, 4H), 7.55-7.59 (m, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.92-7.95 (m, 2H); ^{13}C NMR (100 MHz,

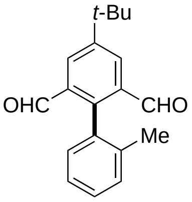
$CDCl_3$) δ 19.8, 30.1, 118.1, 124.3, 124.4, 124.8, 125.8, 126.7, 127.1, 127.2, 127.8, 127.9, 128.3, 130.0, 130.3, 131.7, 134.4, 136.9, 137.1, 137.8, 138.2, 203.3; MS (EI): *m/z* (relative intensity) 260 (M^+, 36), 245 (100), 215 (45), 202 (36); HRMS: calcd. for $C_{19}H_{16}ONa^+$: 283.1099, found 283.1111.

Methyl 1-(*o*-tolyl)-2-naphthoate (Table 7.2, entry 13)



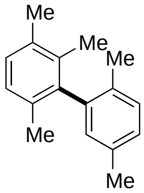
EA: Hexane = 1: 6, R_f=0.6; white solid; ^1H NMR (400 MHz, $CDCl_3$) δ 2.00 (s, 3H), 3.67 (s, 3H), 7.12 (d, *J* = 7.6 Hz, 1H), 7.28-7.44 (m, 5H), 7.56-7.60 (m, 1H), 7.93 (d, *J* = 8.8 Hz, 2H), 8.02 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.8, 51.9, 125.4, 125.6, 126.7, 127.5 (overlapped), 127.6 (overlapped), 127.9, 129.2, 129.4, 132.3, 134.8, 136.6, 138.6, 141.6, 168.1; HRMS: calcd. for $C_{19}H_{16}O_2Na^+$: 99.1048, found 299.1044.

4-(*tert*-Butyl)-2'-methyl-[1,1'-biphenyl]-2,6-dicarbaldehyde (Table 7.2, entry 14)



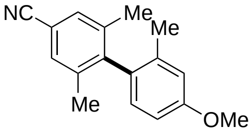
EA: Hexane = 1: 9, R_f=0.5; white solid; ^1H NMR (400 MHz, $CDCl_3$) δ 1.44 (s, 9H), 2.07 (s, 3H), 7.24 (dd, *J* = 6.4, 1.2 Hz, 1H), 7.30-7.35 (m, 2H), 7.37-7.42 (m, 1H), 8.31 (s, 2H), 9.71 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.4, 31.0, 35.0, 125.9, 129.1, 129.6, 130.2, 130.8, 132.2, 134.3, 137.0, 145.4, 151.8, 191.2; HRMS: calcd. for $C_{19}H_{20}O_2Na^+$: 303.1361, found 303.1353.

2,2',3,5',6-Pentamethyl-1,1'-biphenyl (Table 7.2, entry 15)



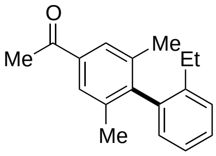
Pure hexane, R_f=0.4; colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.99 (s, 3H), 2.03 (s, 6H), 2.40 (s, 3H), 2.45 (s, 3H), 6.95 (s, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.5, 18.9, 20.3 (overlapped), 20.9, 126.7, 127.5, 128.2, 129.6, 129.7, 132.5, 133.2, 133.7, 134.1, 135.2, 141.0, 141.1; MS (EI): *m/z* (relative intensity) 224 (M^+, 71), 209 (100), 194 (41), 179 (35); HRMS: calcd. for $C_{17}H_{20}^+$: 224.1565, found 224.1560.

4-Cyano-4'-methoxy-2,2',6-trimethyl-1,1'-biphenyl (Table 7.2, entry 17)



EA: Hexane = 1: 9, R_f=0.5; colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.93 (s, 3H), 1.99 (s, 6H), 3.86 (s, 3H), 6.84-6.88 (m, 3H), 7.41 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.4, 20.1, 55.0, 110.5, 111.6, 115.6, 119.2, 128.8, 130.5, 130.9, 136.2, 138.0, 146.0, 158.9; MS (EI): *m/z* (relative intensity) 251 (M^+, 100), 236 (64), 221 (26), 190 (17); HRMS: calcd. for $C_{17}H_{18}NO^+$: 252.1388, found 252.1383.

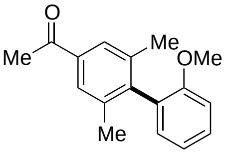
1-(2,6-Dimethyl-2'-ethyl-[1,1'-biphenyl]-4-yl)-ethanone (Table 7.3, entry 3)



EA: Hexane = 1: 9, R_f=0.4; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07 (t, *J* = 7.6 Hz, 3H), 2.05 (s, 6H), 2.29 (q, *J* = 7.6 Hz, 2H), 2.64 (s, 3H), 6.97 (d, *J* =

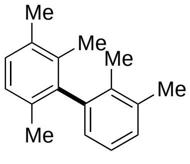
7.2 Hz, 1H), 7.28-7.38 (m, 3H), 7.74 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 14.4, 20.5, 25.6, 26.5, 126.0 (overlapped), 127.1, 127.5, 128.2, 128.3, 135.7, 136.6, 138.7, 140.8, 146.1, 198.2; MS (EI): *m/z* (relative intensity) 252 (M$^+$, 42), 237 (100), 179 (20); HRMS: calcd. for $C_{18}H_{20}O^+$: 252.1514, found 252.1520.

1-(2,6-Dimethyl-2'-methoxy-[1,1'-biphenyl]-4-yl)-ethanone (Table 7.3, entry 4)



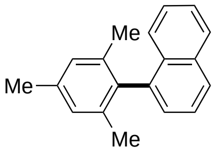
EA: Hexane = 1: 9, R$_f$=0.4; white solid; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.11 (s, 6H), 2.64 (s, 3H), 3.76 (s, 3H), 7.01-7.09 (m, 3H), 7.40 (t, *J* = 8.0, 7.6 Hz, 1H), 7.75 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 20.3, 26.4, 55.3, 110.8, 120.7, 126.9, 128.4, 128.8, 129.8, 135.7, 137.1, 143.5, 156.0, 198.2; MS (EI): *m/z* (relative intensity) 254 (M$^+$, 49), 239 (100), 196 (29); HRMS: calcd. for $C_{17}H_{19}O_2^+$: 255.1385, found 255.1376.

2,2',3,3',6-Pentamethyl-1,1'-biphenyl (Table 7.3, entry 8)



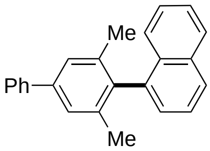
Pure hexane, R$_f$=0.3; white solid; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.00 (t, *J* = 6.8, 8.8 Hz, 9H), 2.40 (s, 3H), 2.45 (s, 3H), 6.96-6.99 (m, 1H), 7.12-7.19 (m, 2H), 7.23-7.26 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 15.7, 16.3, 16.6, 20.3, 20.4, 20.5, 125.0, 125.5, 126.6, 126.7, 127.2, 128.2 (overlapped), 133.4, 133.7, 134.2, 134.3, 136.7, 141.1, 141.6; MS (EI): *m/z* (relative intensity) 224 (M$^+$, 65), 209 (100), 194 (39), 179 (34); HRMS: calcd. for $C_{17}H_{20}^+$: 224.1565, found 224.1563.

1-Mesitylnaphthalene (Table 7.3, entry 9; Table 7.4, entry 6)[26]



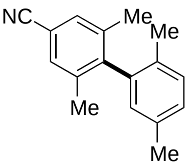
Pure hexane, R_f=0.5; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.00 (s, 6H), 2.50 (s, 3H), 7.13 (s, 2H), 7.37 (d, *J* = 6.8 Hz, 1H), 7.42-7.56 (m, 2H), 7.58 (t, *J* = 1.2, 5.6 Hz, 1H), 7.63 (t, *J* = 7.2, 8.0 Hz, 1H), 7.94-8.01 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.2, 21.1, 125.4, 125.6, 125.9, 126.6, 127.0, 128.0, 128.2, 131.9, 133.7, 136.7 (overlapped), 136.8 (overlapped); MS (EI): *m/z* (relative intensity) 246 (M^+, 100), 231 (67), 215 (52).

1-(4-Phenyl-2,6-Dimethylphenyl)naphthalene (Table 7.3, entry 10)



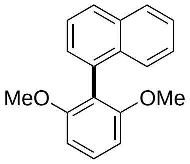
Pure hexane, R_f=0.25; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.11 (s, 6H), 7.43-7.84 (m, 10H), 7.83 (d, *J* = 7.2 Hz, 2H), 8.00 (q, *J* = 8.4, 7.6, 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 125.4, 125.6, 125.8, 126.0, 126.5, 127.1, 127.2, 128.3, 128.7, 131.7, 133.7, 137.4, 138.5, 138.7, 140.1, 141.1; MS (EI): *m/z* (relative intensity) 308 (M^+, 100), 293 (28); HRMS: calcd. for $C_{24}H_{20}^+$: 308.1565, found 308.1571.

4-Cyano-2,2',5',6-tetramethyl-1,1'-biphenyl (Table 7.3, entry 11)



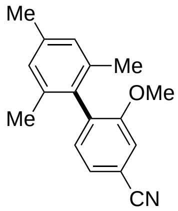
EA: Hexane = 1: 9, R_f=0.6; colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.92 (s, 3H), 2.00 (s, 6H), 2.36 (s, 3H), 6.79 (s, 1H), 7.12-7.22 (dd, *J* = 7.6, 7.2 Hz, 2H), 7.42 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.6, 20.0, 20.8, 110.5, 119.1, 128.3, 128.4, 130.1, 130.6, 131.5, 135.7, 137.4, 138.4, 146.3; MS (EI): *m/z* (relative intensity) 236 (M^+, 64), 220 (100), 190 (27); HRMS: calcd. for $C_{17}H_{18}N^+$: 236.1439, found 236.1429.

1-(2,6-Dimethoxyphenyl)naphthalene (Table 7.4, entry 1)[27]



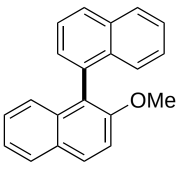
EA: Hexane = 1: 6, R_f=0.55; colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.73 (d, *J* = 3.6 Hz, 6H), 6.82-6.85 (m, 2H), 7.48-7.60 (m, 4H), 7.62-7.71 (m, 2H), 7.97-8.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.8, 104.1, 125.3 (overlapped), 125.9, 127.3, 127.9, 128.0, 129.0, 158.4; MS (EI): *m/z* (relative intensity) 264 (M^+, 100), 249 (25), 234 (22), 189 (19).

2-Methoxy-2',4',6'-trimethyl-[1,1'-biphenyl]-4-carbonitrile (Table 7.4, entry 2)



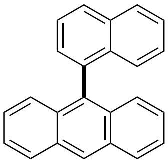
EA: Hexane = 1: 4, R_f=0.5; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.98 (s, 6H), 2.36 (s, 3H), 3.81 (s, 3H), 6.98 (s, 2H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.25 (s, 1H), 7.36-7.38 (dd, *J* = 6.4, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.2, 21.1, 55.8, 111.9, 113.9, 119.0, 124.9, 128.1, 131.9, 133.4, 135.3, 135.9, 137.4, 157.0; HRMS: calcd. for $C_{17}H_{17}NO^+$: 251.1310, found 251.1308.

2-Methoxy-1,1'-binaphthalene (Table 7.4, entry 3)[28]



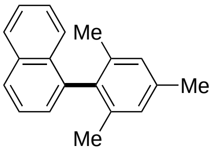
EA: Hexane = 1: 6, R_f=0.5; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.79 (s, 3H), 7.19-7.38 (m, 5H), 7.47-7.51 (m, 3H), 7.66 (t, *J* = 7.2, 8.0 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.97-8.01 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.8, 113.8, 123.6, 125.5 (overlapped), 125.6, 125.8, 126.1, 126.3, 127.7 (overlapped), 128.2, 128.4, 129.0, 129.4, 132.9, 133.7, 134.2, 134.5, 154.6; MS (EI): *m/z* (relative intensity) 284 (M^+, 100), 269 (25), 252 (25), 239 (44).

9-(Naphthalen-1-yl)anthracene (Table 7.4, entry 4)[3h]



Pure Hexane, R_f=0.8; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-7.33 (m, 4H), 7.51-7.56 (m, 5H), 7.62 (d, *J* = 6.8 Hz, 1H), 7.76 (t, *J* = 7.6 Hz, 1H), 8.07-8.17 (m, 4H), 8.66 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.2, 125.6 (overlapped), 126.0, 126.6, 127.0, 128.1, 128.3, 128.4, 129.2, 131.1, 131.5, 133.6, 133.7, 135.0, 136.6; MS (EI): *m/z* (relative intensity) 284 (M^+, 100), 269 (25), 252 (25), 239 (44).

1-Mesitylnaphthalene (Table 7, entry 6)[26]



Pure hexane, R_f=0.5; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.00 (s, 6H), 2.50 (s, 3H), 7.13 (s, 2H), 7.37 (d, *J* = 6.8 Hz, 1H), 7.42-7.56 (m, 2H), 7.58 (t, *J* = 1.2, 5.6 Hz, 1H), 7.63 (t, *J* = 7.2, 8.0 Hz, 1H), 7.94-8.01 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.2, 21.1, 125.4, 125.6, 125.9, 126.6, 127.0, 128.0, 128.2, 131.9, 133.7, 136.7 (overlapped), 136.8 (overlapped); MS (EI): *m/z* (relative intensity) 246 (M^+, 100), 231 (67), 215 (52).

7.6 References

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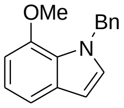
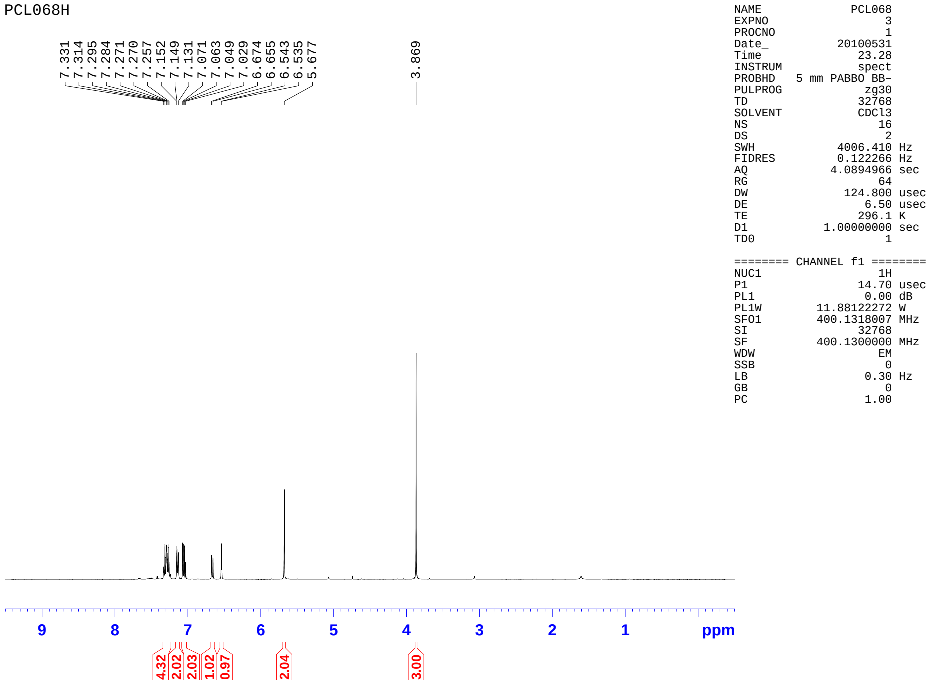
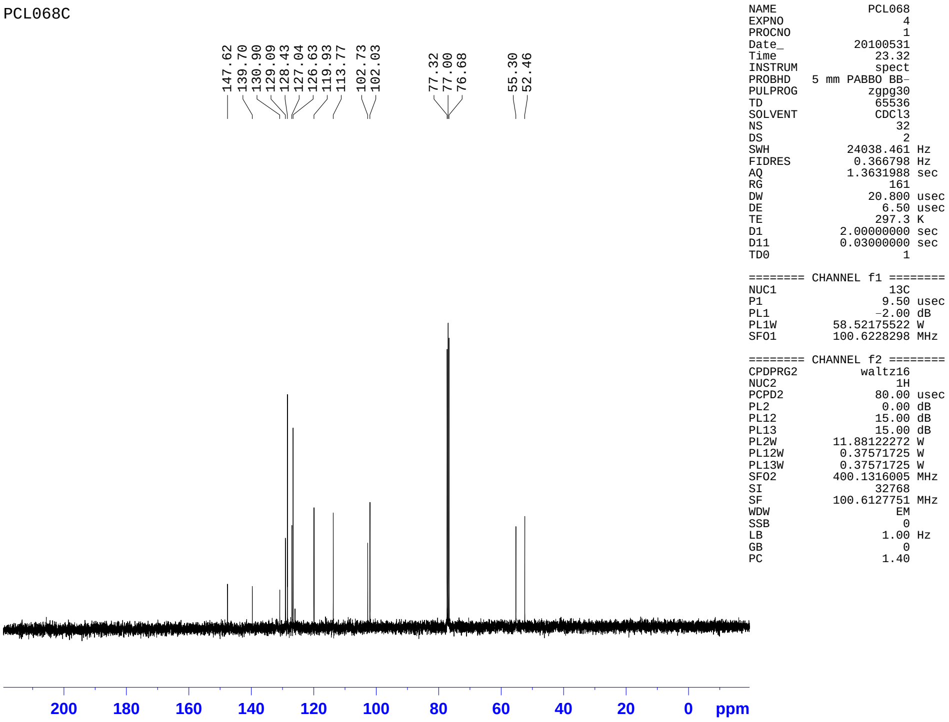
Appendix

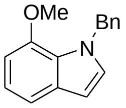
1-Benzyl-7-methoxy-1*H*-indole (Table 2.2, entry 9)

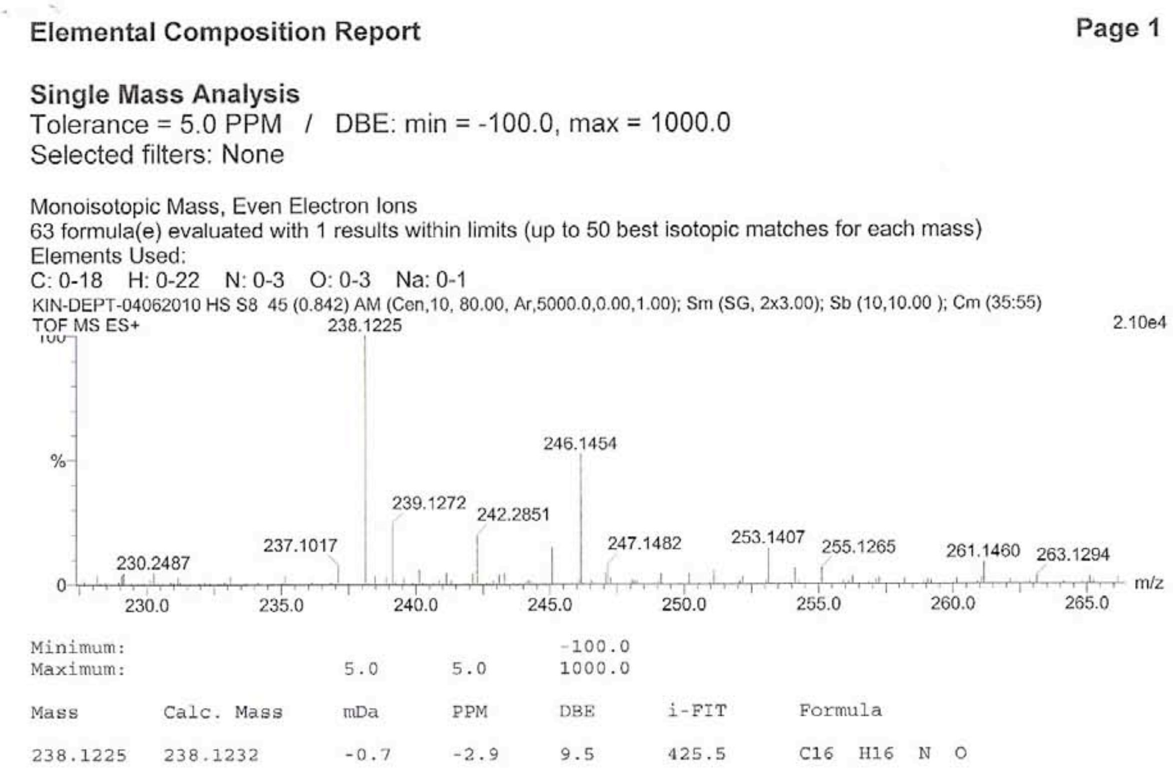






1-Benzyl-7-methoxy-1*H*-indole (Table 2.2, entry 9)





Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -100.0, max = 1000.0
Selected filters: None

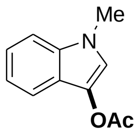
Monoisotopic Mass, Even Electron Ions
63 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-18 H: 0-22 N: 0-3 O: 0-3 Na: 0-1
KIN-DEPT-04062010 HS S8 45 (0.842) AM (Cen,10, 80.00, Ar,5000.0,0.00,1.00); Sm (SG, 2x3.00); Sb (10,10.00); Cm (35:55)
TOF MS ES+ 2.10e4

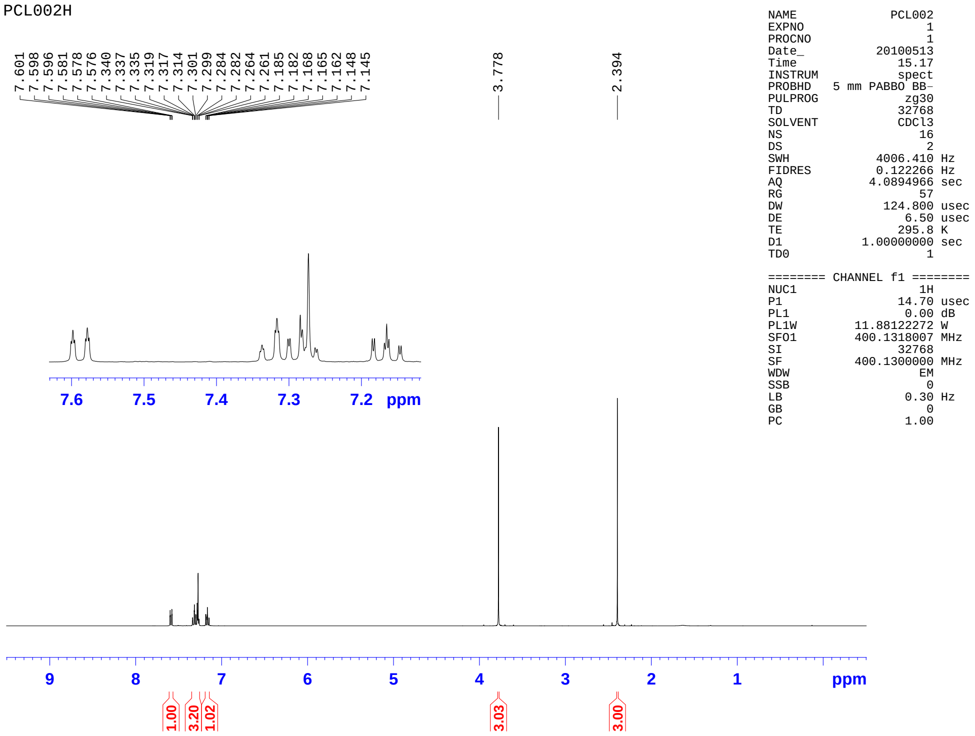
```
Minimum:                                        -100.0
Maximum:                      5.0       5.0     1000.0

Mass       Calc. Mass         mDa       PPM     DBE       i-FIT      Formula

238.1225   238.1232           -0.7      -2.9    9.5       425.5      C16  H16  N  O
```

1-Methyl-1*H*-indol-3-yl acetate (Scheme 2.3)





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TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              4006.410 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                     57
DW                124.800 usec
DE                   6.50 usec
TE                  295.8 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.70 usec
PL1                  0.00 dB
PL1W          11.88122272 W
SFO1          400.1318007 MHz
SI                  32768
SF            400.1300000 MHz
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PC                   1.00
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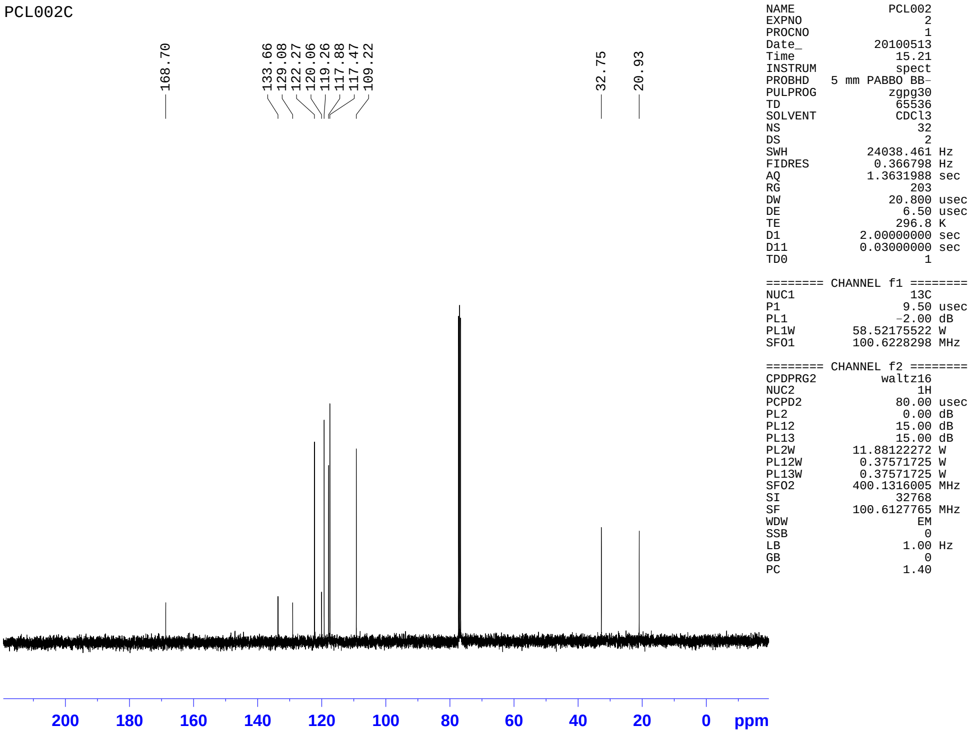

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TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      2
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                    203
DW                 20.800 usec
DE                   6.50 usec
TE                  296.8 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.50 usec
PL1                 -2.00 dB
PL1W          58.52175522 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                15.00 dB
PL13                15.00 dB
PL2W          11.88122272 W
PL12W          0.37571725 W
PL13W          0.37571725 W
SFO2          400.1316005 MHz
SI                  32768
SF            100.6127765 MHz
WDW                    EM
SSB                     0
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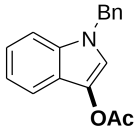
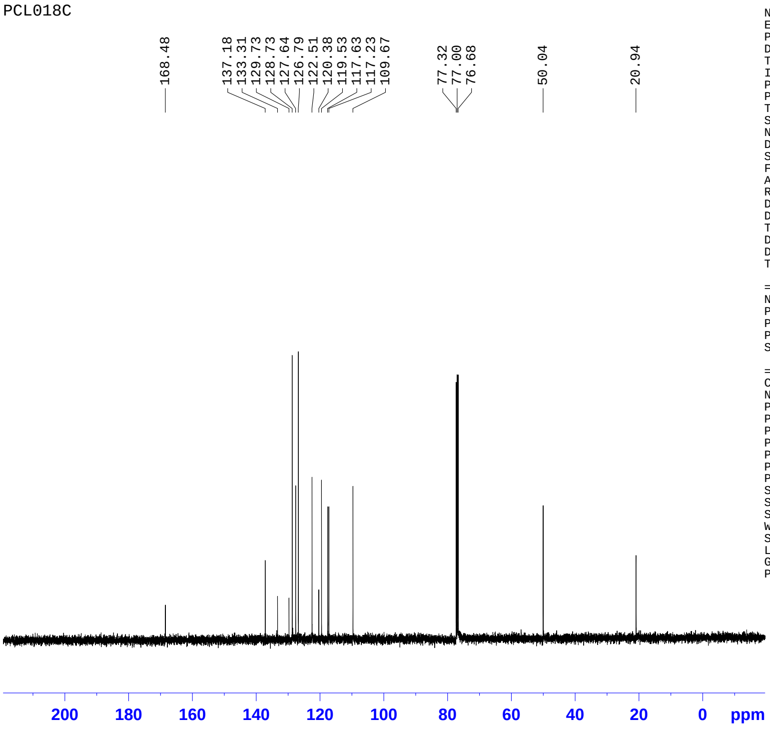
1-Benzyl-1*H*-indol-3-yl acetate (Table 2.2, entry 1-3; Scheme 2.3)





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SOLVENT            CDCl3
NS                    32
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   203
DW                20.800 usec
DE                  6.50 usec
TE                 297.3 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
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SF           100.6127780 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
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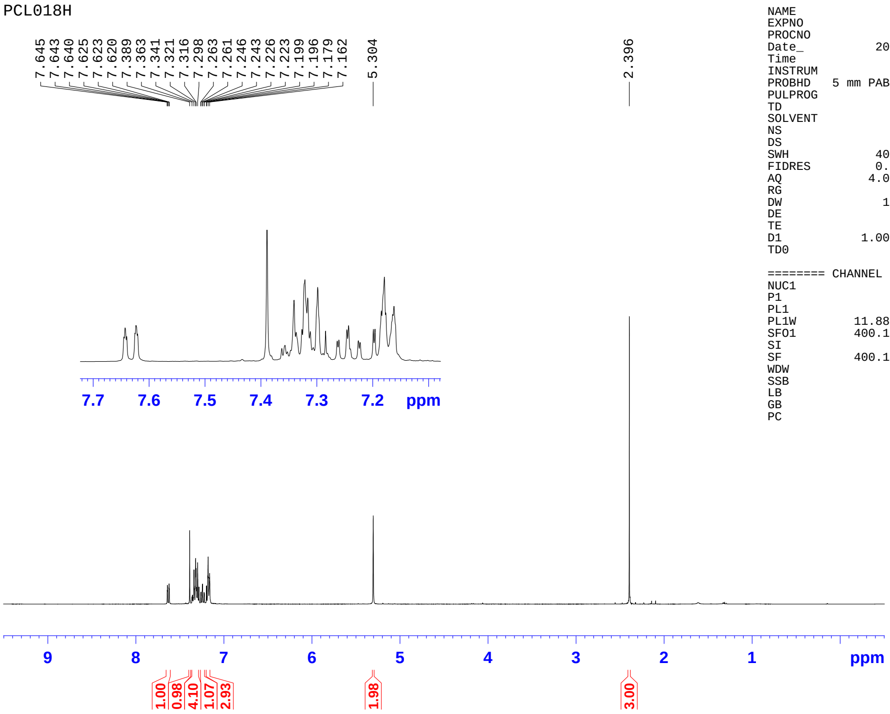

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TD                 32768
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NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  45.2
DW               124.800 usec
DE                  6.50 usec
TE                 296.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
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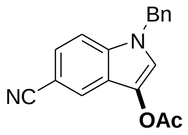
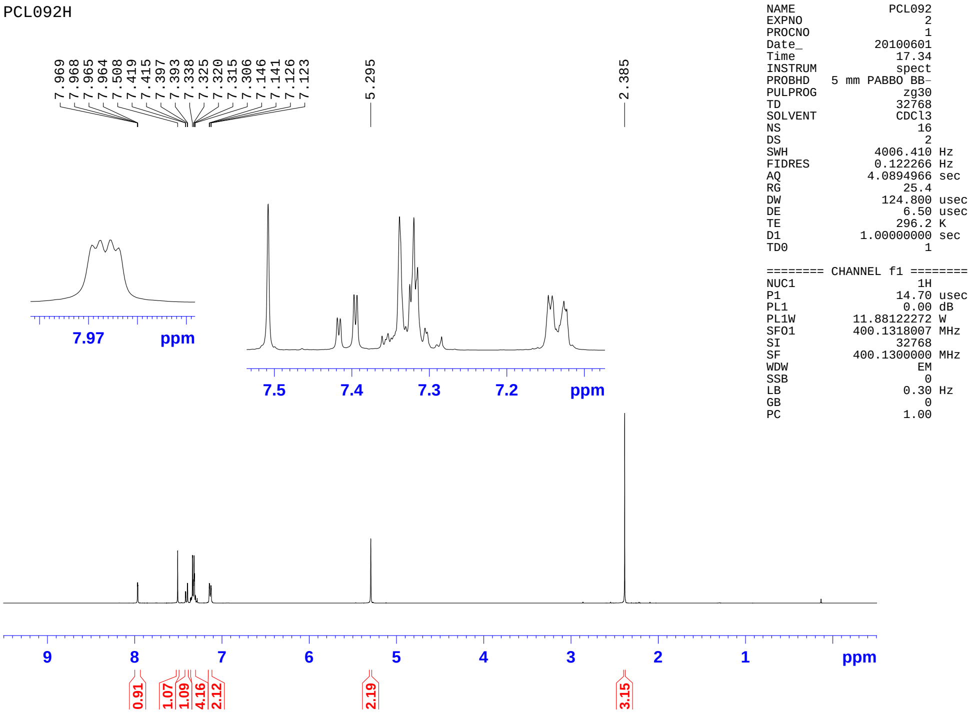
1-Benzyl-5-cyano-1*H*-indol-3-yl acetate (Table 2.2, entry 4)





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FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  25.4
DW               124.800 usec
DE                  6.50 usec
TE                 296.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
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LB                  0.30 Hz
GB                     0
PC                  1.00
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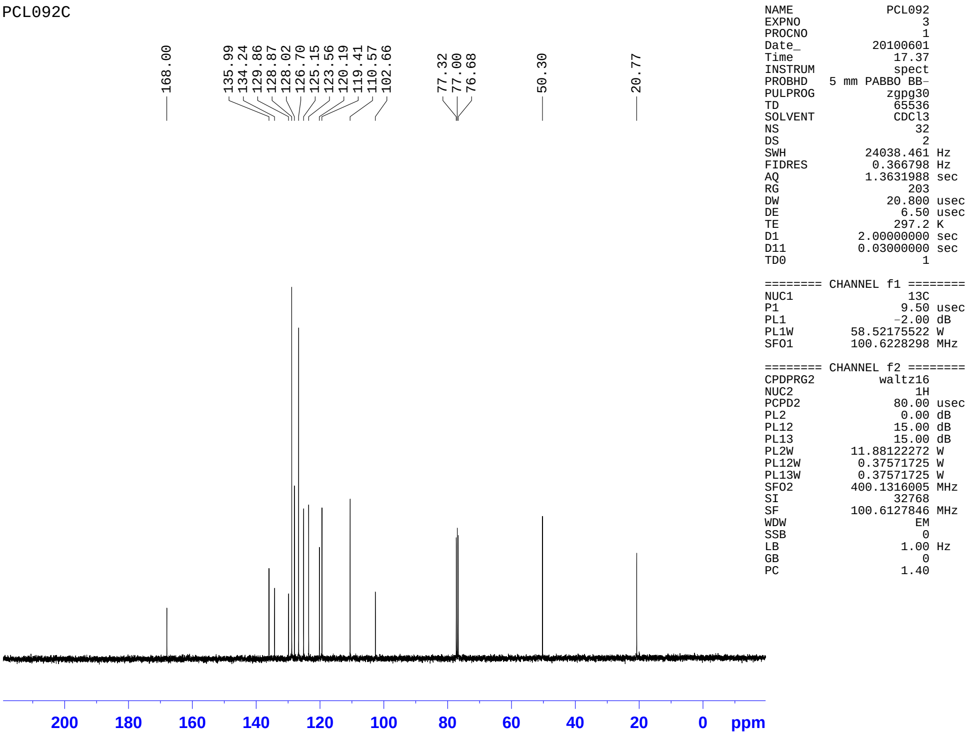

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NS                    32
DS                     2
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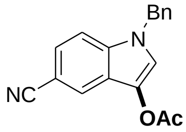
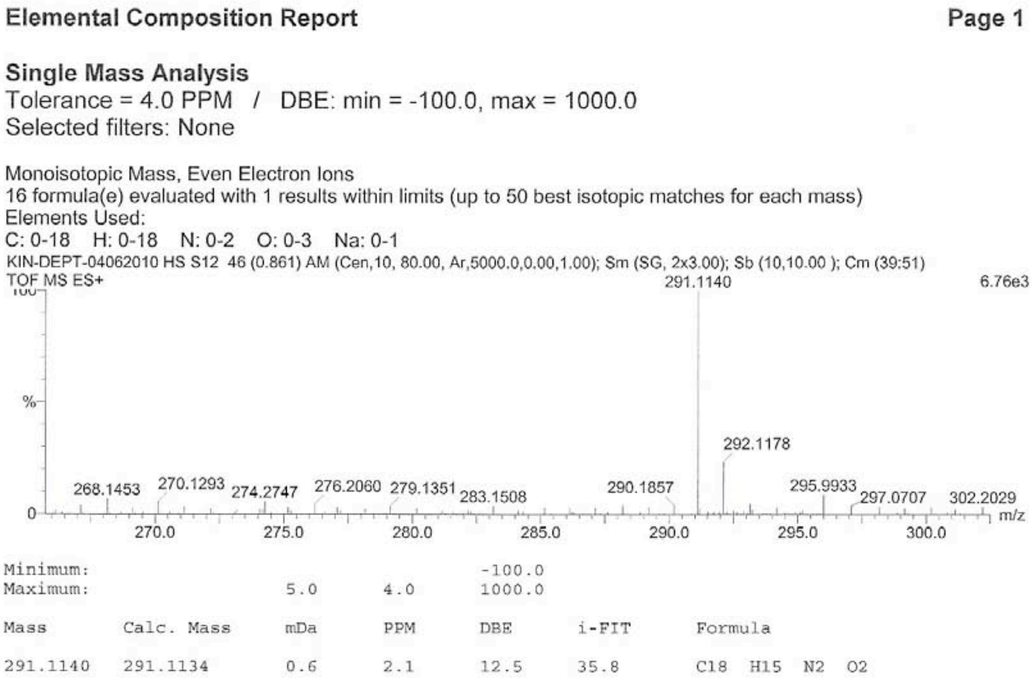
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   203
DW                20.800 usec
DE                  6.50 usec
TE                 297.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127846 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

1-Benzyl-5-cyano-1*H*-indol-3-yl acetate (Table 2.2, entry 4)





Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 4.0 PPM / DBE: min = -100.0, max = 1000.0
Selected filters: None

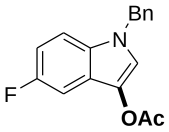
Monoisotopic Mass, Even Electron Ions
16 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-18 H: 0-18 N: 0-2 O: 0-3 Na: 0-1
KIN-DEPT-04062010 HS S12 46 (0.861) AM (Cen,10, 80.00, Ar,5000.0,0.00,1.00); Sm (SG, 2x3.00); Sb (10,10.00); Cm (39:51)
TOF MS ES+

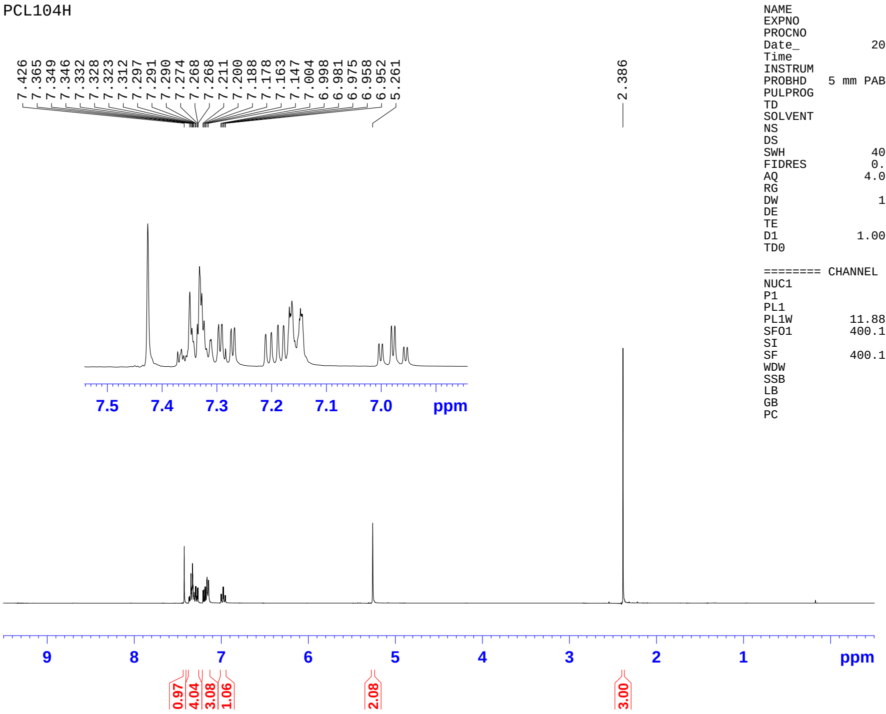
```
Minimum:                                   -100.0
Maximum:                 5.0       4.0     1000.0

Mass       Calc. Mass    mDa       PPM     DBE       i-FIT      Formula

291.1140   291.1134      0.6       2.1     12.5      35.8       C18  H15  N2  O2
```

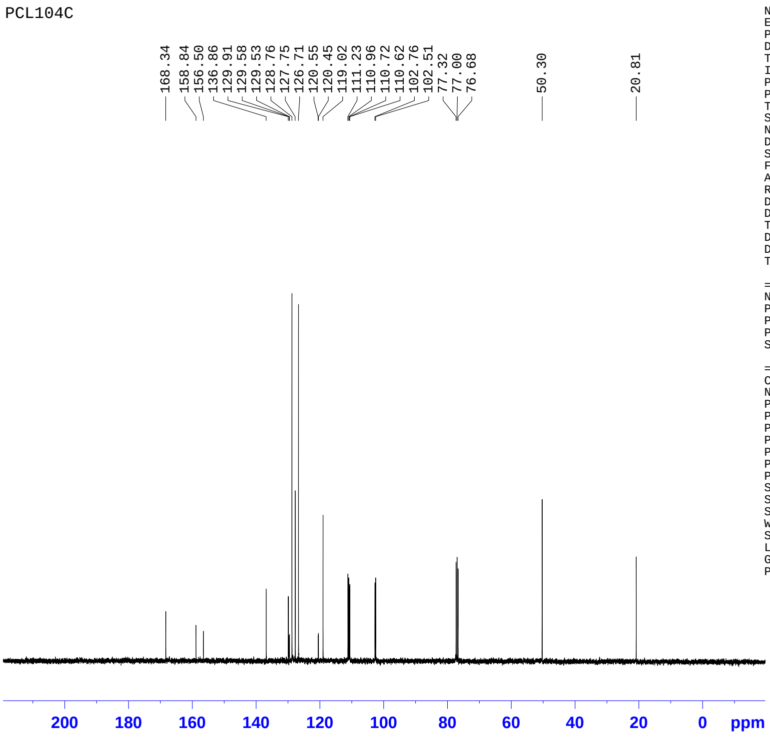
1-Benzyl-5-fluoro-1*H*-indol-3-yl acetate (Table 2.2, entry 5)





```
NAME             PCL104
EXPNO                 2
PROCNO                1
Date_          20100601
Time              17.43
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            4006.410 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                 25.4
DW              124.800 usec
DE                 6.50 usec
TE                296.2 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.70 usec
PL1                0.00 dB
PL1W        11.88122272 W
SFO1        400.1318007 MHz
SI                32768
SF          400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

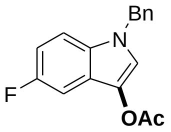


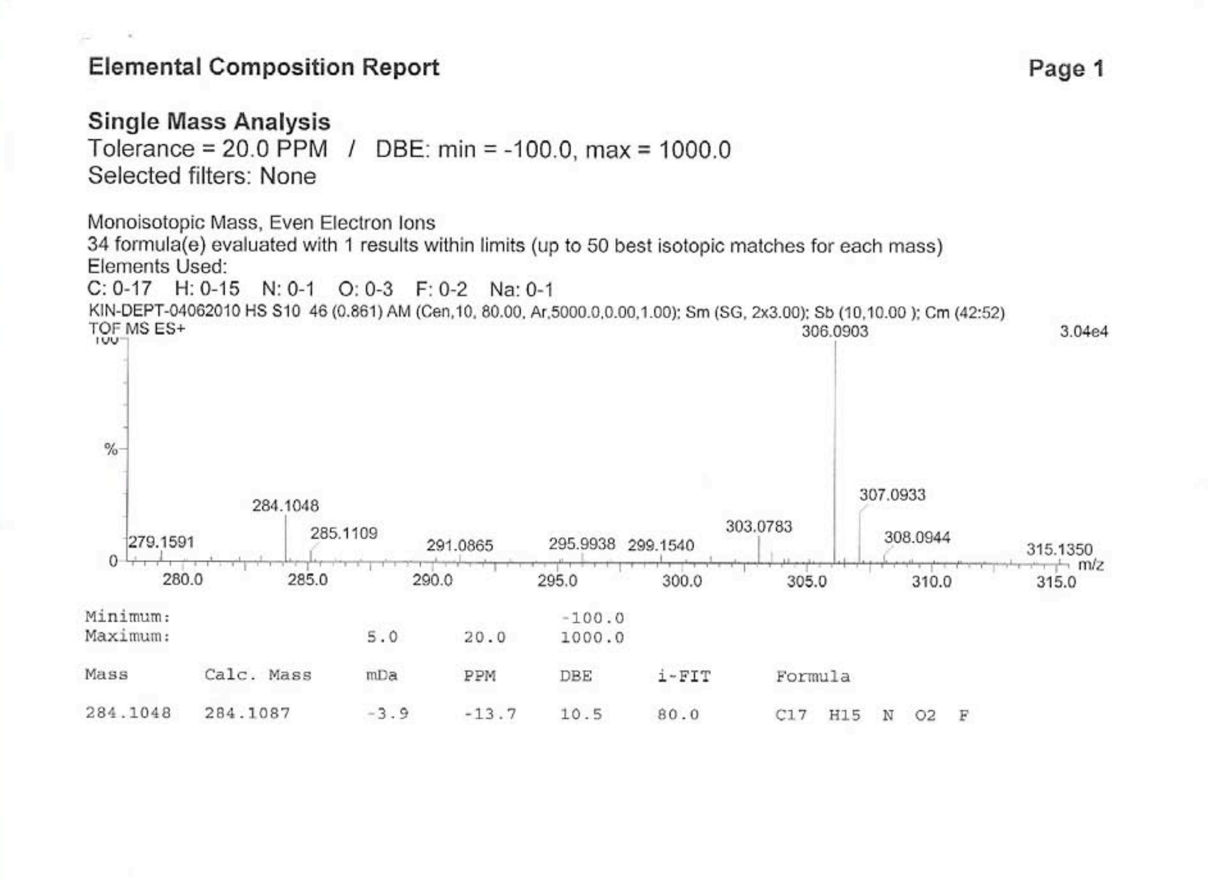
```
NAME             PCL104
EXPNO                 3
PROCNO                1
Date_          20100601
Time              17.46
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                  114
DW               20.800 usec
DE                 6.50 usec
TE                297.3 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.50 usec
PL1               -2.00 dB
PL1W        58.52175522 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL13              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
PL13W        0.37571725 W
SFO2        400.1316005 MHz
SI                32768
SF          100.6127816 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

1-Benzyl-5-fluoro-1*H*-indol-3-yl acetate (Table 2.2, entry 5)





Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -100.0, max = 1000.0
Selected filters: None

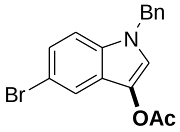
Monoisotopic Mass, Even Electron Ions
34 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-17 H: 0-15 N: 0-1 O: 0-3 F: 0-2 Na: 0-1
KIN-DEPT-04062010 HS S10 46 (0.861) AM (Cen,10, 80.00, Ar,5000.0,0.00,1.00); Sm (SG, 2x3.00); Sb (10,10.00); Cm (42:52)
TOF MS ES+

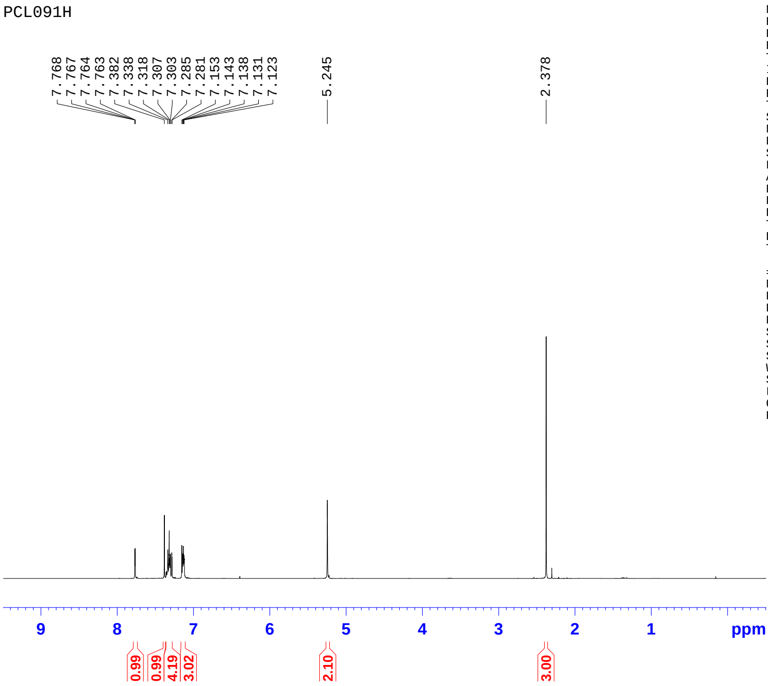
```
Minimum:                                  -100.0
Maximum:                  5.0      20.0   1000.0

Mass       Calc. Mass    mDa      PPM     DBE      i-FIT     Formula

284.1048   284.1087      -3.9     -13.7   10.5     80.0      C17  H15  N  O2  F
```

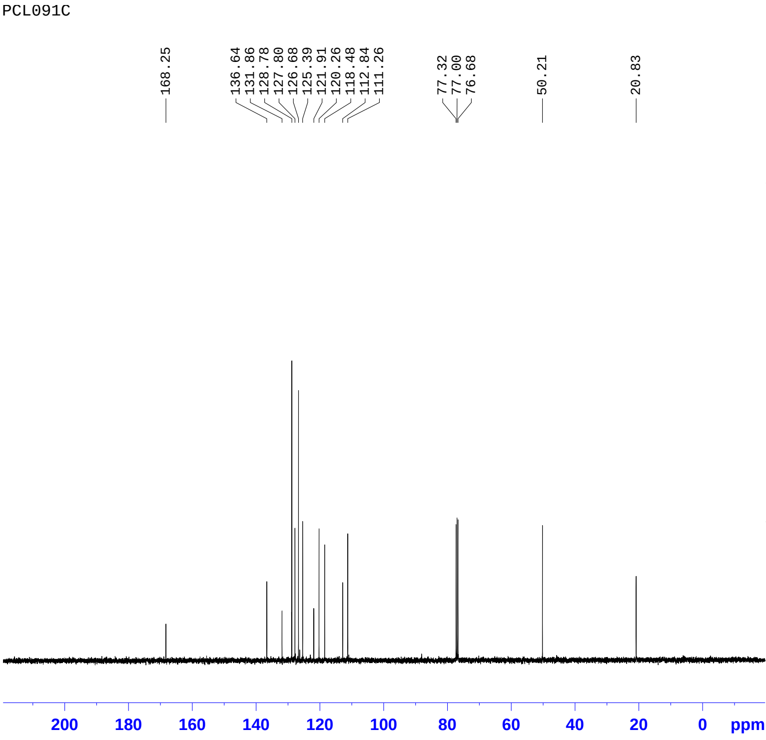
1-Benzyl-5-bromo-1*H*-indol-3-yl acetate (Table 2.2, entry 6)





```
NAME             PCL091
EXPNO                 1
PROCNO                1
Date_          20100530
Time              22.33
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            4006.410 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                 25.4
DW              124.800 usec
DE                 6.50 usec
TE                296.5 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.70 usec
PL1                0.00 dB
PL1W        11.88122272 W
SFO1        400.1318007 MHz
SI                32768
SF          400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

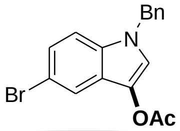


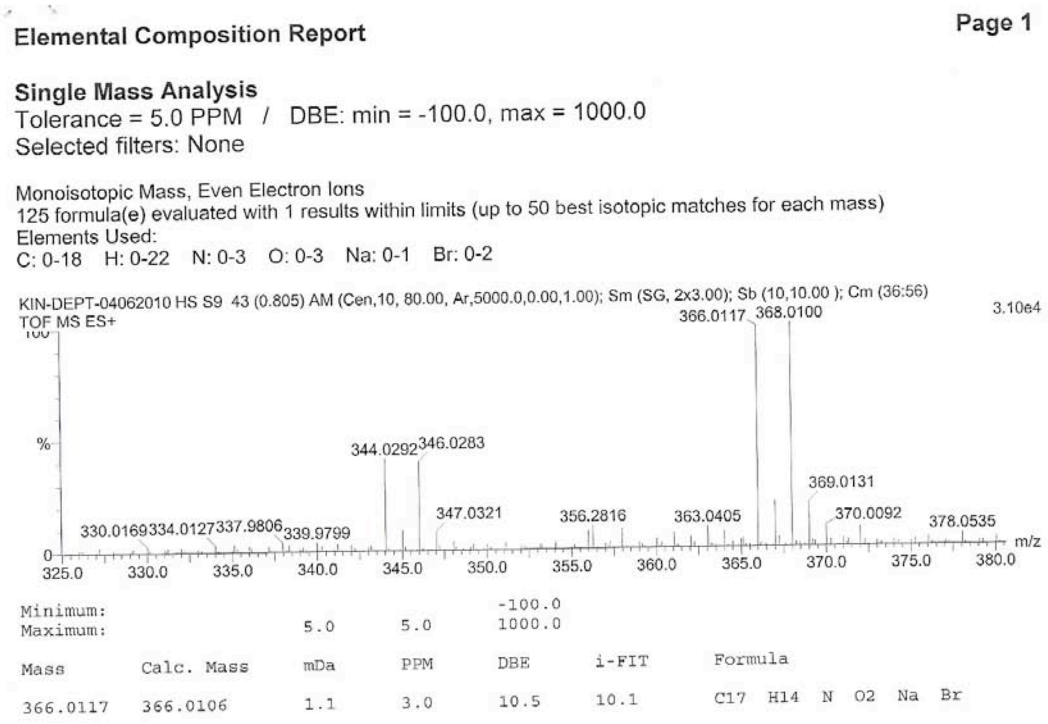
```
NAME             PCL091
EXPNO                 2
PROCNO                1
Date_          20100530
Time              22.38
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                  203
DW               20.800 usec
DE                 6.50 usec
TE                297.7 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.50 usec
PL1               -2.00 dB
PL1W        58.52175522 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL13              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
PL13W        0.37571725 W
SFO2        400.1316005 MHz
SI                32768
SF          100.6127817 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

1-Benzyl-5-bromo-1*H*-indol-3-yl acetate (Table 2.2, entry 6)





Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -100.0, max = 1000.0
Selected filters: None

Monoisotopic Mass, Even Electron Ions
125 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-18 H: 0-22 N: 0-3 O: 0-3 Na: 0-1 Br: 0-2

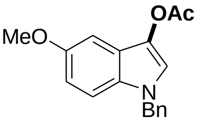
KIN-DEPT-04062010 HS S9 43 (0.805) AM (Cen,10, 80.00, Ar,5000.0,0.00,1.00); Sm (SG, 2x3.00); Sb (10,10.00); Cm (36:56)
TOF MS ES+ 3.10e4

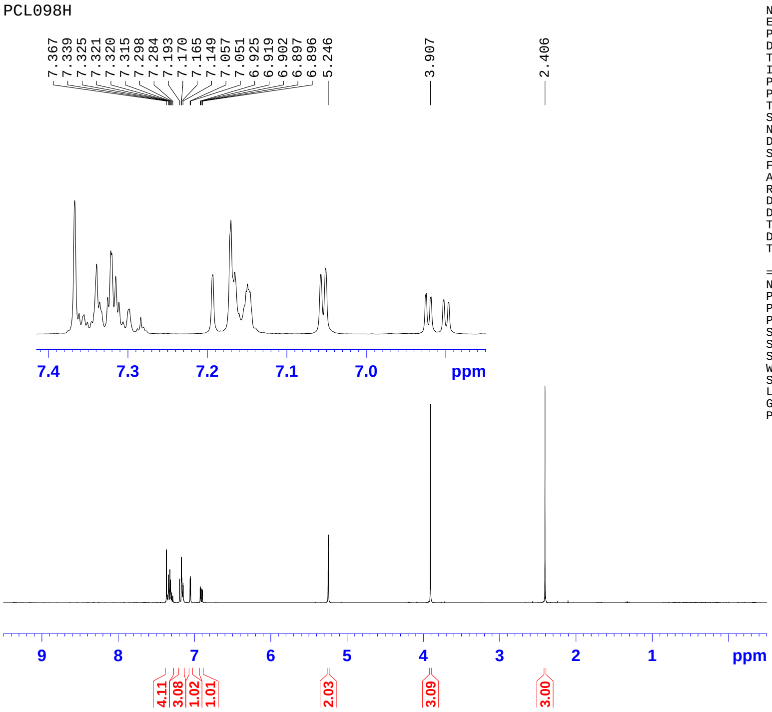
```
Minimum:                                    -100.0
Maximum:                    5.0       5.0   1000.0

Mass       Calc. Mass      mDa       PPM     DBE       i-FIT      Formula

366.0117   366.0106        1.1       3.0     10.5      10.1       C17  H14  N  O2  Na  Br
```

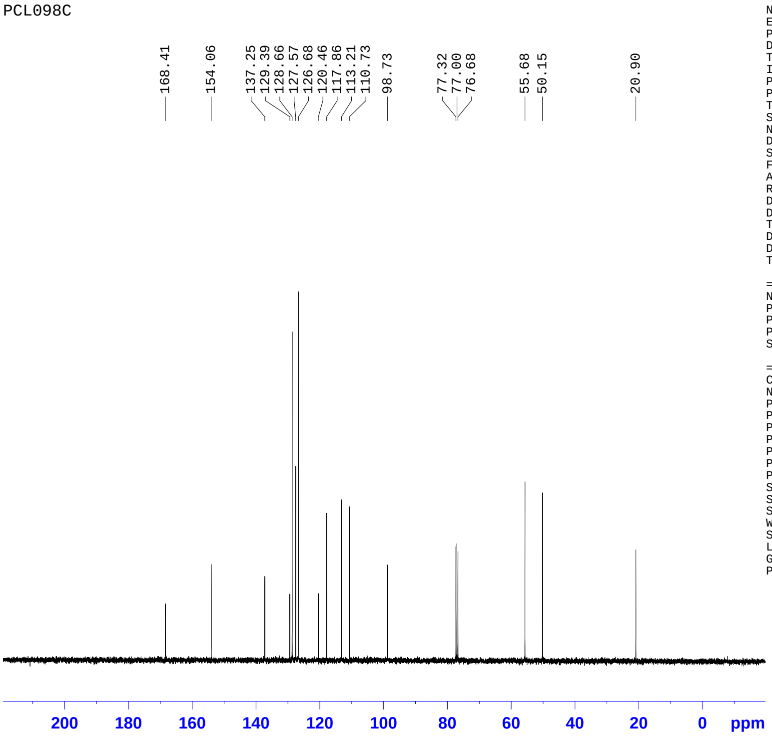
1-Benzyl-5-methoxy-1*H*-indol-3-yl acetate (Table 2.2, entry 7)





```
NAME             PCL098
EXPNO                 1
PROCNO                1
Date_          20100601
Time              17.51
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            4006.410 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                 25.4
DW              124.800 usec
DE                 6.50 usec
TE                296.3 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.70 usec
PL1                0.00 dB
PL1W        11.88122272 W
SFO1        400.1318007 MHz
SI                32768
SF          400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

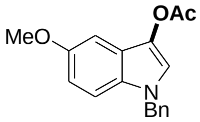


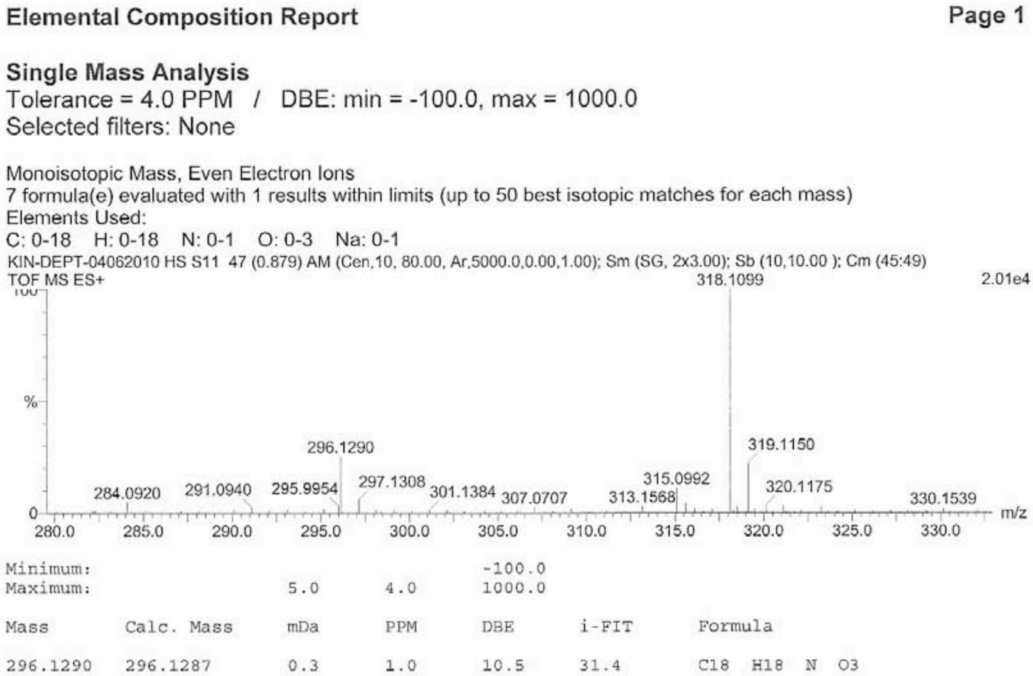
```
NAME             PCL098
EXPNO                 2
PROCNO                1
Date_          20100601
Time              17.54
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                  114
DW               20.800 usec
DE                 6.50 usec
TE                297.3 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.50 usec
PL1               -2.00 dB
PL1W        58.52175522 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL13              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
PL13W        0.37571725 W
SFO2        400.1316005 MHz
SI                32768
SF          100.6127839 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

1-Benzyl-5-methoxy-1*H*-indol-3-yl acetate (Table 2.2, entry 7)





Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 4.0 PPM / DBE: min = -100.0, max = 1000.0
Selected filters: None

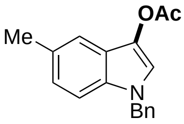
Monoisotopic Mass, Even Electron Ions
7 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-18 H: 0-18 N: 0-1 O: 0-3 Na: 0-1
KIN-DEPT-04062010 HS S11 47 (0.879) AM (Cen,10, 80.00, Ar,5000.0,0.00,1.00); Sm (SG, 2x3.00); Sb (10,10.00); Cm (45:49)
TOF MS ES+

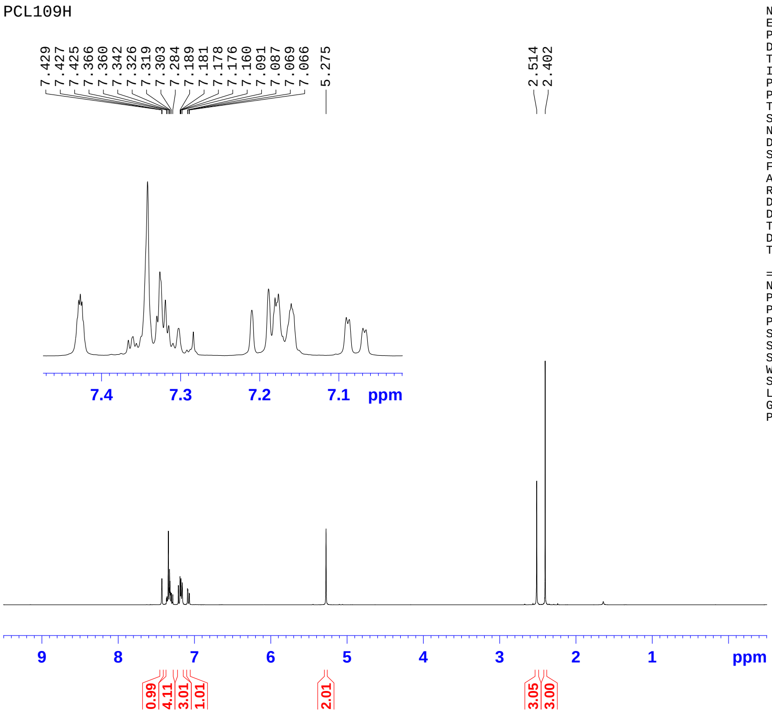
```
Minimum:                                 -100.0
Maximum:                5.0      4.0     1000.0

Mass       Calc. Mass   mDa      PPM     DBE      i-FIT     Formula

296.1290   296.1287     0.3      1.0     10.5     31.4      C18  H18  N  O3
```

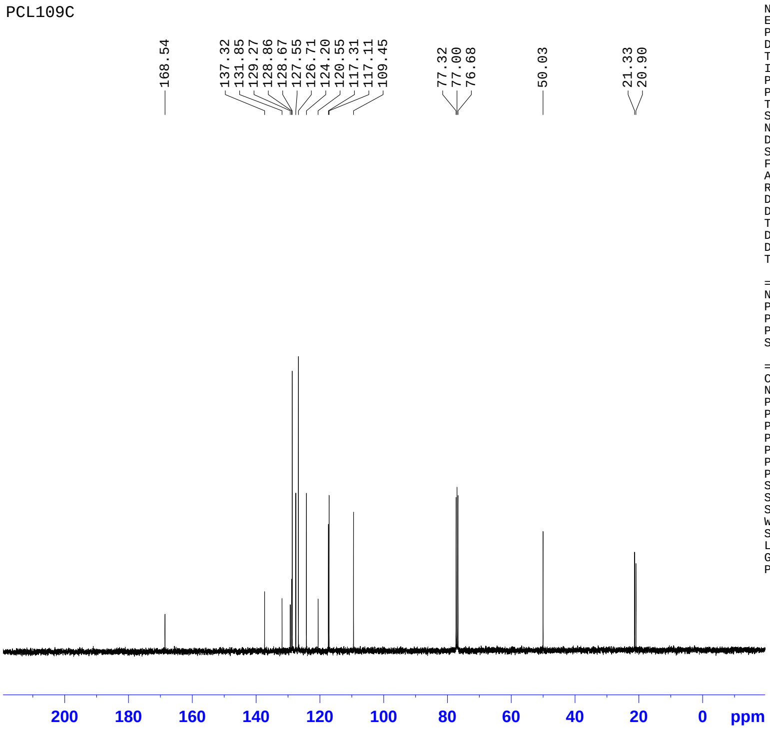
1-Benzyl-5-methyl-1*H*-indol-3-yl acetate (Table 2.2, entry 8)





```
NAME               PCL109
EXPNO                   1
PROCNO                  1
Date_            20100602
Time                21.56
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              4006.410 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                   25.4
DW                124.800 usec
DE                   6.50 usec
TE                  295.9 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.70 usec
PL1                  0.00 dB
PL1W          11.88122272 W
SFO1          400.1318007 MHz
SI                  32768
SF            400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

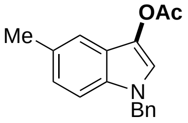


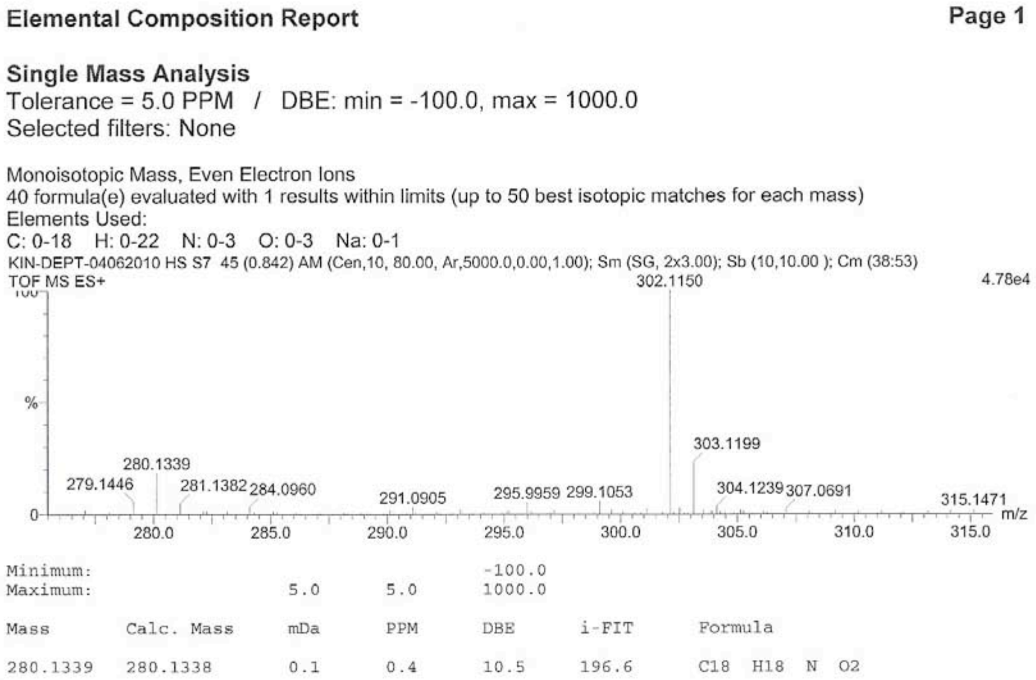
```
NAME               PCL109
EXPNO                   2
PROCNO                  1
Date_            20100602
Time                21.59
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      2
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                    203
DW                 20.800 usec
DE                   6.50 usec
TE                  297.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.50 usec
PL1                 -2.00 dB
PL1W          58.52175522 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                15.00 dB
PL13                15.00 dB
PL2W          11.88122272 W
PL12W          0.37571725 W
PL13W          0.37571725 W
SFO2          400.1316005 MHz
SI                  32768
SF            100.6127817 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

1-Benzyl-5-methyl-1*H*-indol-3-yl acetate (Table 2.2, entry 8)





Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -100.0, max = 1000.0
Selected filters: None

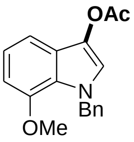
Monoisotopic Mass, Even Electron Ions
40 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-18 H: 0-22 N: 0-3 O: 0-3 Na: 0-1
KIN-DEPT-04062010 HS S7 45 (0.842) AM (Cen,10, 80.00, Ar,5000.0,0.00,1.00); Sm (SG, 2x3.00); Sb (10,10.00); Cm (38:53)
TOF MS ES+

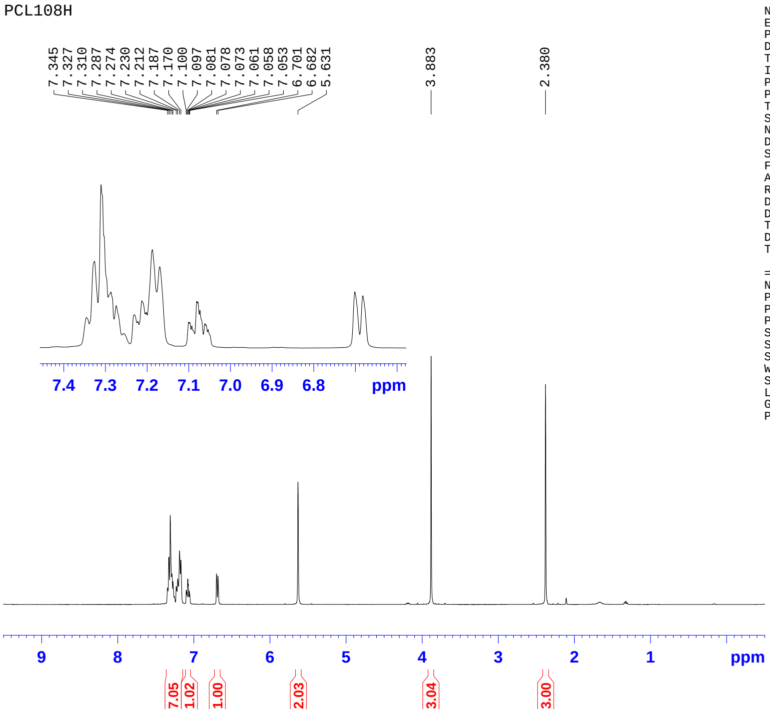
```
Minimum:                                 -100.0
Maximum:                5.0       5.0    1000.0

Mass       Calc. Mass   mDa       PPM    DBE       i-FIT     Formula

280.1339   280.1338     0.1       0.4    10.5      196.6     C18  H18  N  O2
```

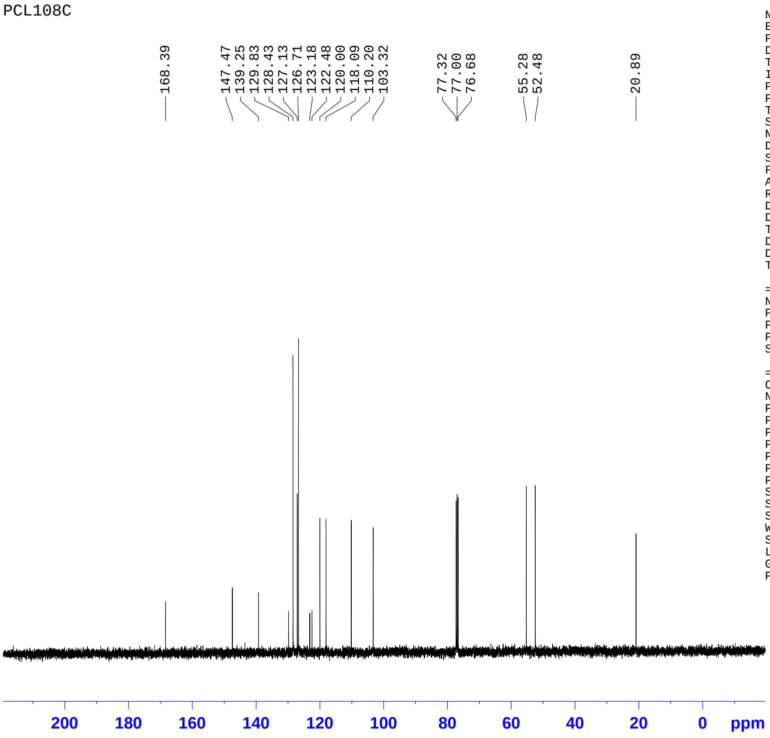
1-Benzyl-7-methoxy-1*H*-indol-3-yl acetate (Table 2.2, entry 9)





```
NAME              PCL108
EXPNO                  1
PROCNO                 1
Date_           20100602
Time               22.41
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  25.4
DW               124.800 usec
DE                  6.50 usec
TE                 295.9 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

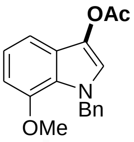


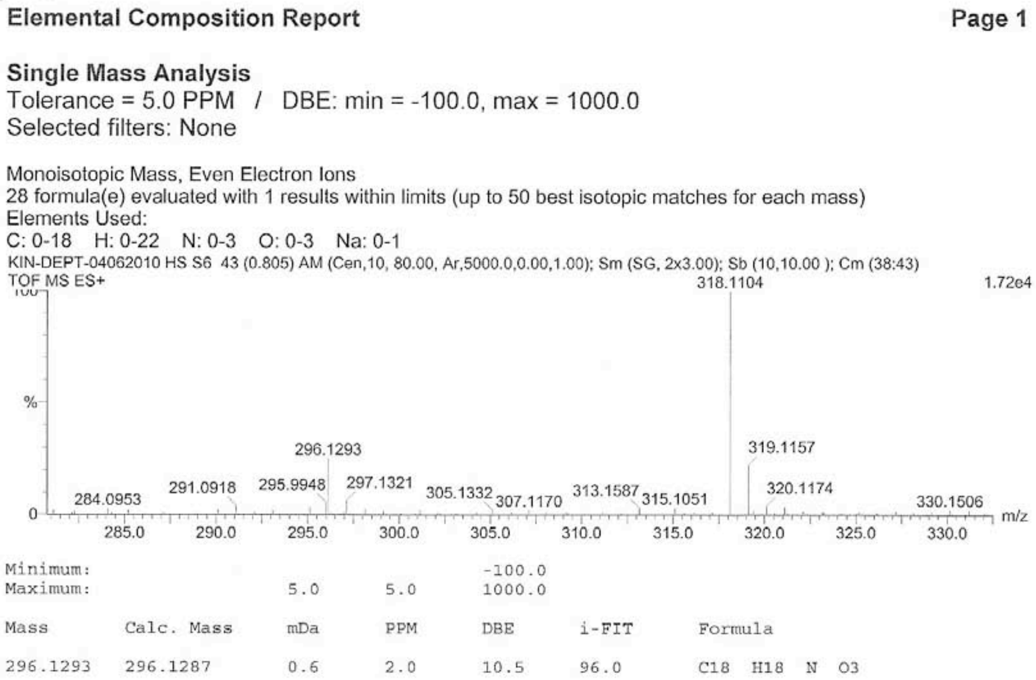
```
NAME              PCL108
EXPNO                  2
PROCNO                 1
Date_           20100602
Time               22.44
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   203
DW                20.800 usec
DE                  6.50 usec
TE                 297.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127815 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

1-Benzyl-7-methoxy-1*H*-indol-3-yl acetate (Table 2.2, entry 9)





Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -100.0, max = 1000.0
Selected filters: None

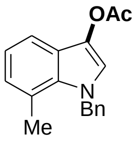
Monoisotopic Mass, Even Electron Ions
28 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-18 H: 0-22 N: 0-3 O: 0-3 Na: 0-1
KIN-DEPT-04062010 HS S6 43 (0.805) AM (Cen,10, 80.00, Ar,5000.0,0.00,1.00); Sm (SG, 2x3.00); Sb (10,10.00); Cm (38:43)
TOF MS ES+

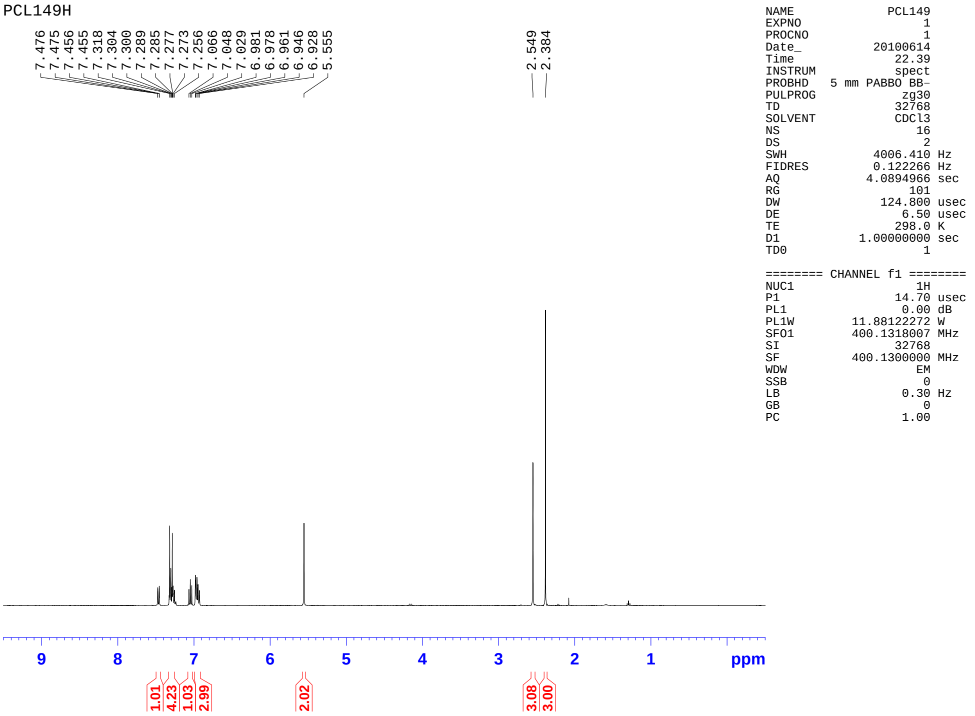
```
Minimum:                                        -100.0
Maximum:                      5.0       5.0     1000.0

Mass        Calc. Mass        mDa       PPM     DBE       i-FIT      Formula

296.1293    296.1287          0.6       2.0     10.5      96.0       C18  H18  N  O3
```

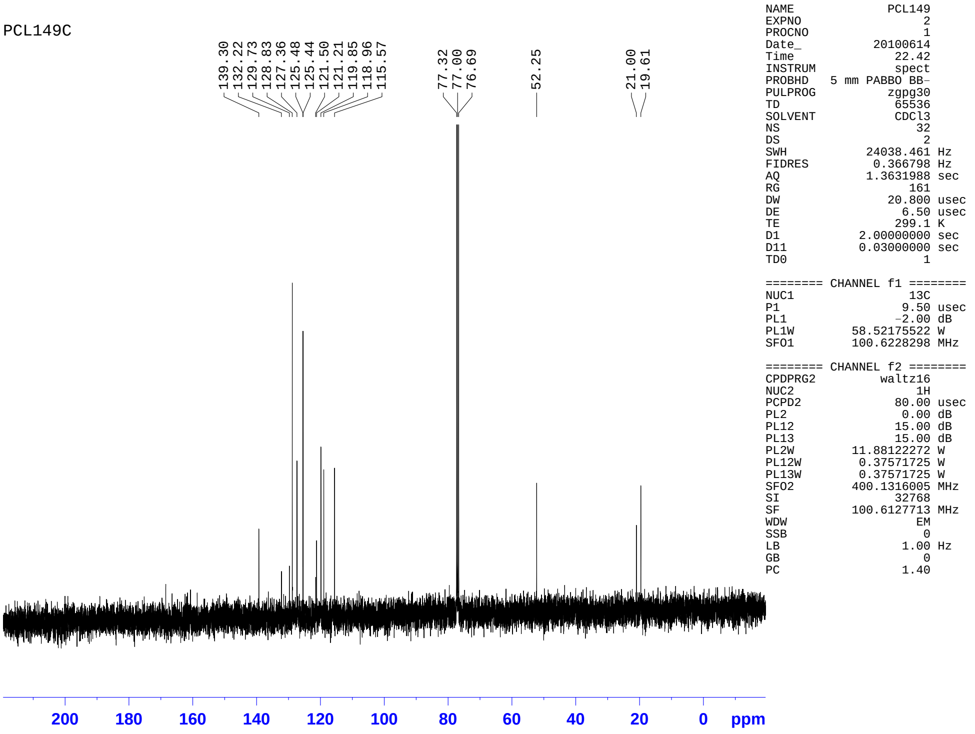
1-Benzyl-7-methyl-1*H*-indol-3-yl acetate (Table 2.2, entry 10)





```
NAME             PCL149
EXPNO                 1
PROCNO                1
Date_          20100614
Time              22.39
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            4006.410 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                  101
DW              124.800 usec
DE                 6.50 usec
TE                298.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.70 usec
PL1                0.00 dB
PL1W        11.88122272 W
SFO1        400.1318007 MHz
SI                32768
SF          400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

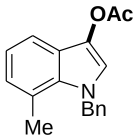


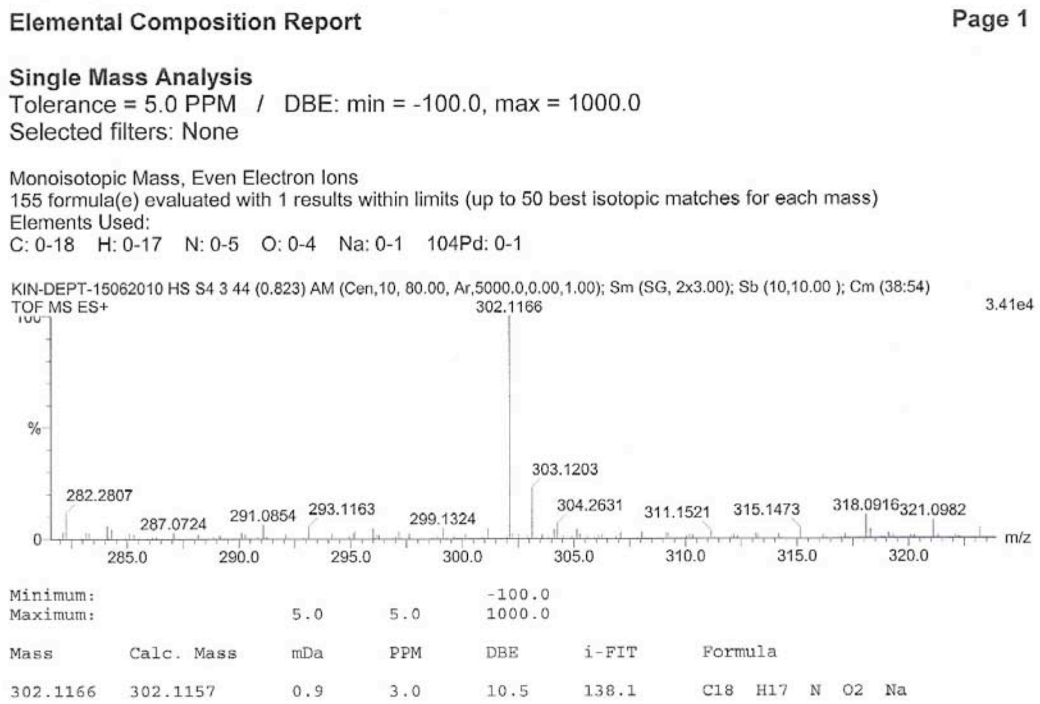
```
NAME             PCL149
EXPNO                 2
PROCNO                1
Date_          20100614
Time              22.42
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                  161
DW               20.800 usec
DE                 6.50 usec
TE                299.1 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.50 usec
PL1               -2.00 dB
PL1W        58.52175522 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL13              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
PL13W        0.37571725 W
SFO2        400.1316005 MHz
SI                32768
SF          100.6127713 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

1-Benzyl-7-methyl-1*H*-indol-3-yl acetate (Table 2.2, entry 10)





Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -100.0, max = 1000.0
Selected filters: None

Monoisotopic Mass, Even Electron Ions
155 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-18 H: 0-17 N: 0-5 O: 0-4 Na: 0-1 104Pd: 0-1

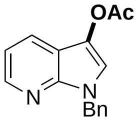
KIN-DEPT-15062010 HS S4 3 44 (0.823) AM (Cen,10, 80.00, Ar,5000.0,0.00,1.00); Sm (SG, 2x3.00); Sb (10,10.00); Cm (38:54)
TOF MS ES+

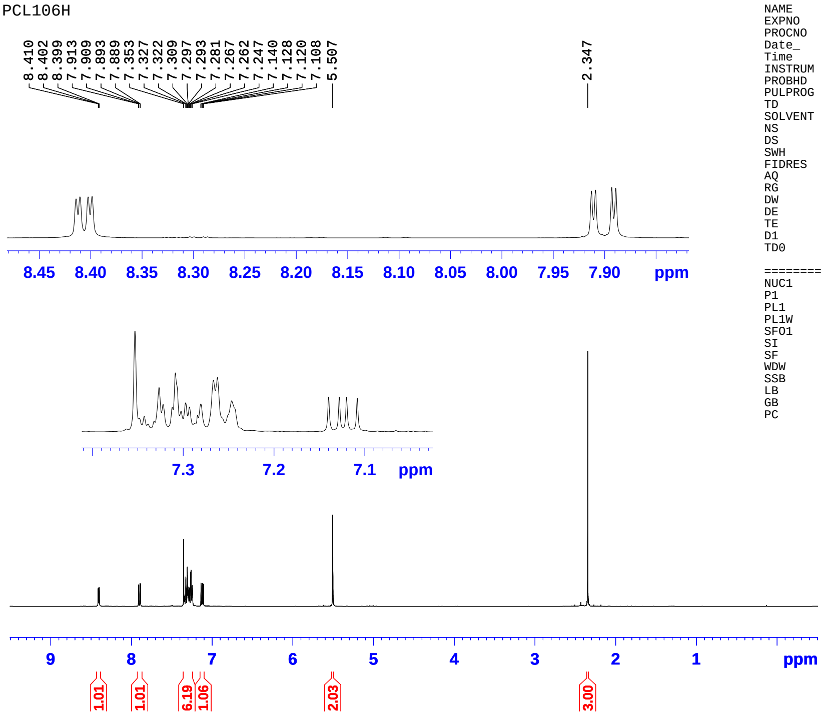
```
Minimum:                                  -100.0
Maximum:                 5.0      5.0     1000.0

Mass       Calc. Mass    mDa      PPM     DBE       i-FIT      Formula

302.1166   302.1157      0.9      3.0     10.5      138.1      C18  H17  N  O2  Na
```

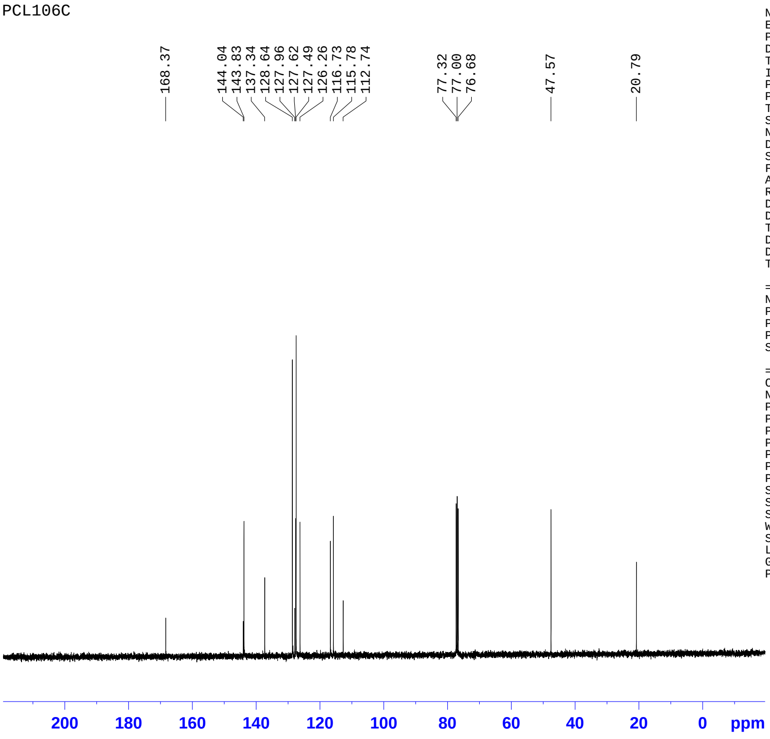
1-Benzyl-1*H*-pyrrolo[2,3-b]pyridine-3-yl acetate (Table 2.2, entry 11)





```
NAME                PCL106
EXPNO                    1
PROCNO                   1
Date_             20100602
Time                 15.50
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               4006.410 Hz
FIDRES            0.122266 Hz
AQ               4.0894966 sec
RG                    25.4
DW                 124.800 usec
DE                    6.50 usec
TE                   296.3 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   14.70 usec
PL1                   0.00 dB
PL1W           11.88122272 W
SFO1           400.1318007 MHz
SI                   32768
SF             400.1300000 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

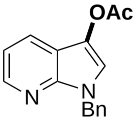


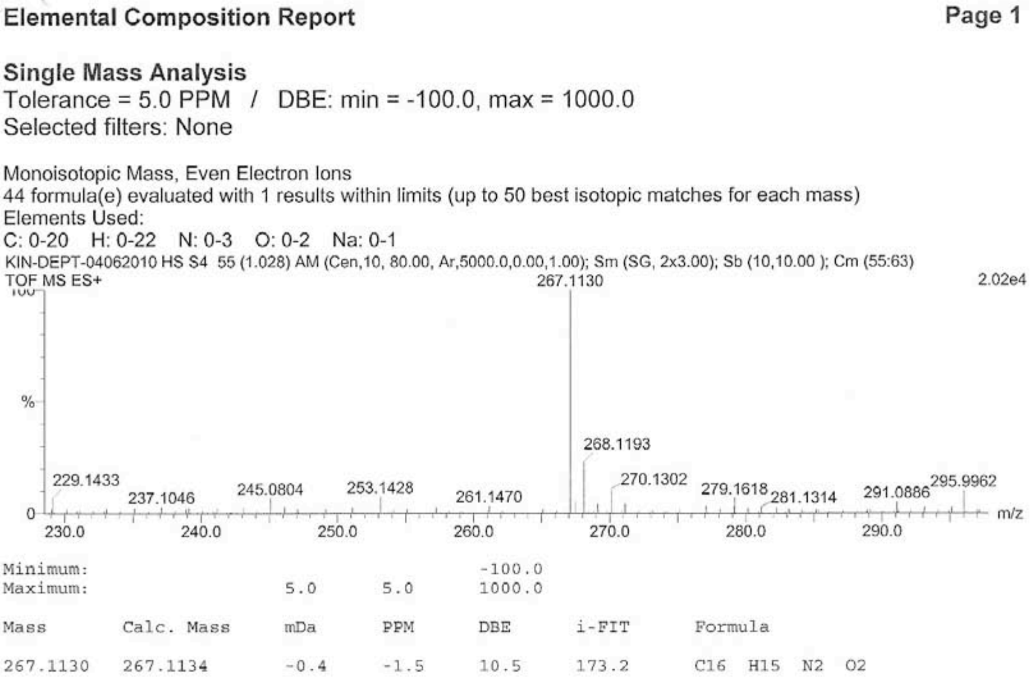
```
NAME                PCL106
EXPNO                    2
PROCNO                   1
Date_             20100602
Time                 15.53
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      32
DS                       2
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ               1.3631988 sec
RG                     144
DW                  20.800 usec
DE                    6.50 usec
TE                   297.4 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    9.50 usec
PL1                  -2.00 dB
PL1W           58.52175522 W
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   0.00 dB
PL12                 15.00 dB
PL13                 15.00 dB
PL2W           11.88122272 W
PL12W           0.37571725 W
PL13W           0.37571725 W
SFO2           400.1316005 MHz
SI                   32768
SF             100.6127795 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

1-Benzyl-1*H*-pyrrolo[2,3-b]pyridine-3-yl acetate (Table 2.2, entry 11)





Elemental Composition Report

Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -100.0, max = 1000.0
Selected filters: None

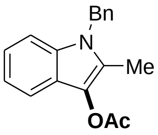
Monoisotopic Mass, Even Electron Ions
44 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-20 H: 0-22 N: 0-3 O: 0-2 Na: 0-1
KIN-DEPT-04062010 HS S4 55 (1.028) AM (Cen,10, 80.00, Ar,5000.0,0.00,1.00); Sm (SG, 2x3.00); Sb (10,10.00); Cm (55:63)
TOF MS ES+

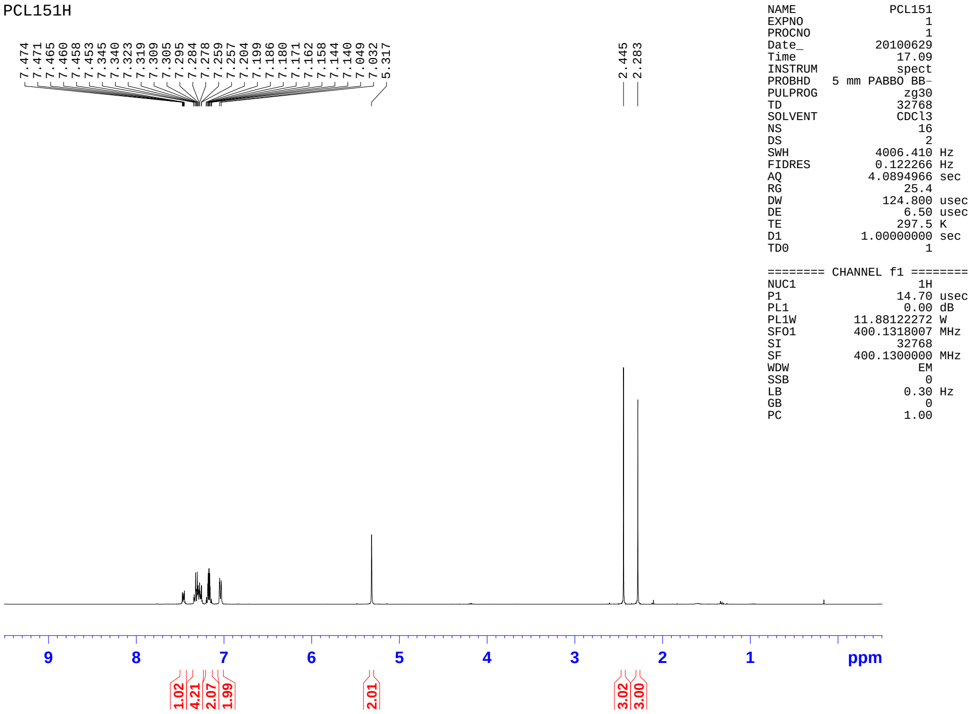
```
Minimum:                                  -100.0
Maximum:                 5.0       5.0    1000.0

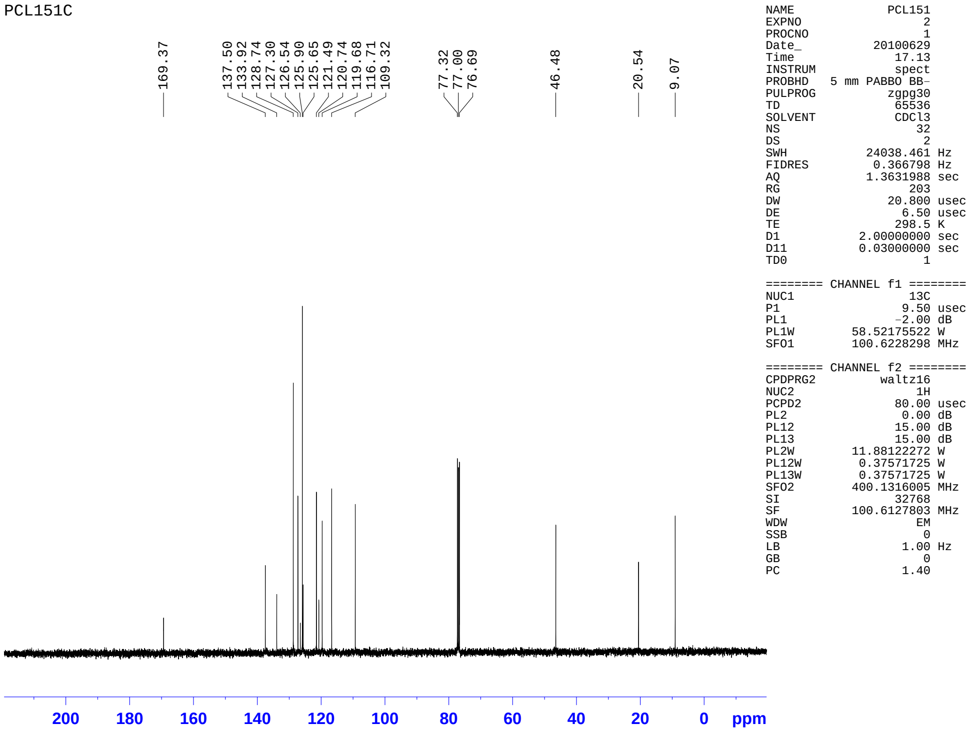
Mass       Calc. Mass    mDa       PPM    DBE       i-FIT     Formula

267.1130   267.1134      -0.4      -1.5   10.5      173.2     C16  H15  N2  O2
```

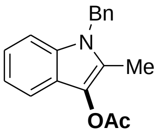
1-Benzyl-2-methyl-1*H*-indol-3-yl acetate (Table 2.2, entry 12)

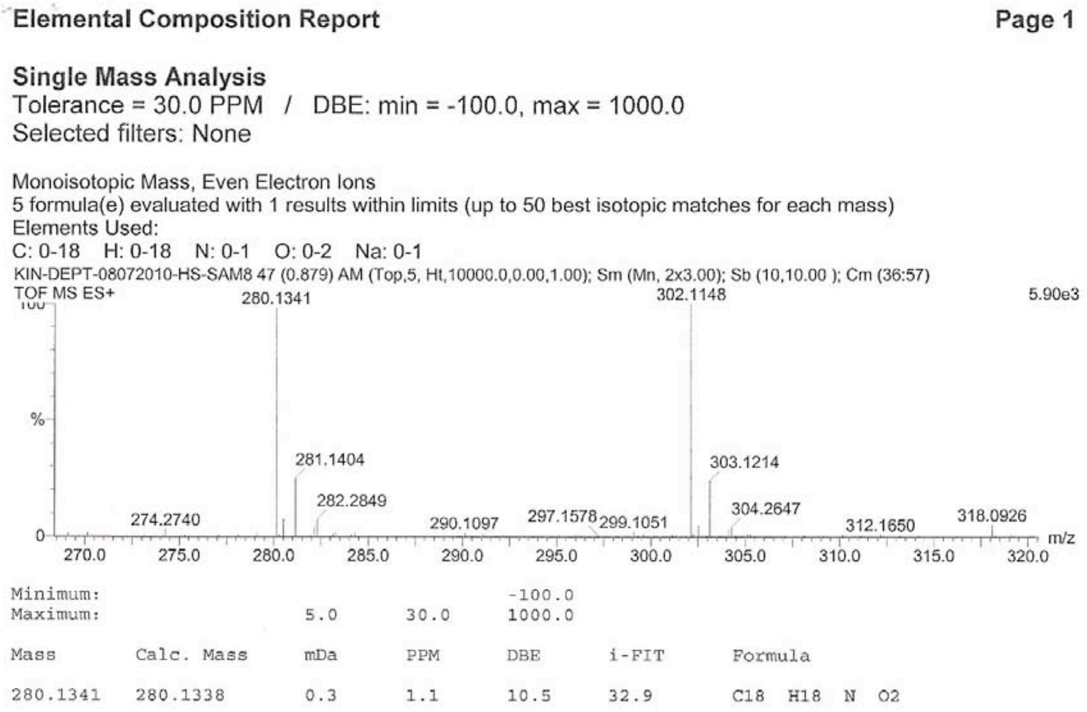






1-Benzyl-2-methyl-1*H*-indol-3-yl acetate (Table 2.2, entry 12)





Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 30.0 PPM / DBE: min = -100.0, max = 1000.0
Selected filters: None

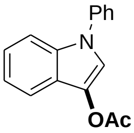
Monoisotopic Mass, Even Electron Ions
5 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-18 H: 0-18 N: 0-1 O: 0-2 Na: 0-1
KIN-DEPT-08072010-HS-SAM8 47 (0.879) AM (Top,5, Ht,10000.0,0.00,1.00); Sm (Mn, 2x3.00); Sb (10,10.00); Cm (36:57)
TOF MS ES+

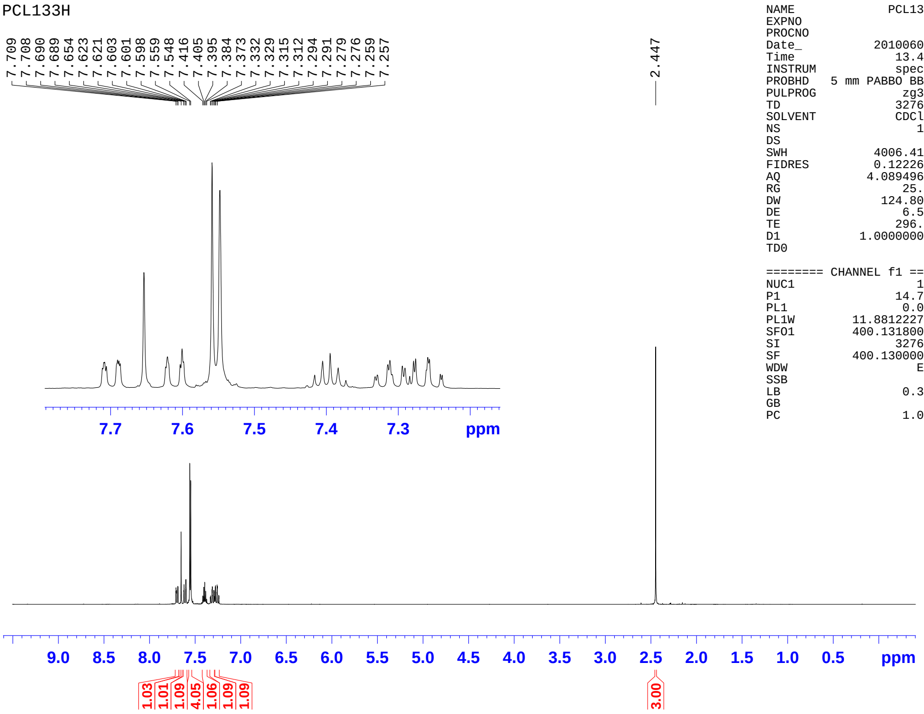
```
Minimum:                                          -100.0
Maximum:                        5.0      30.0     1000.0

Mass        Calc. Mass     mDa      PPM      DBE      i-FIT      Formula

280.1341    280.1338       0.3      1.1      10.5     32.9       C18  H18  N  O2
```

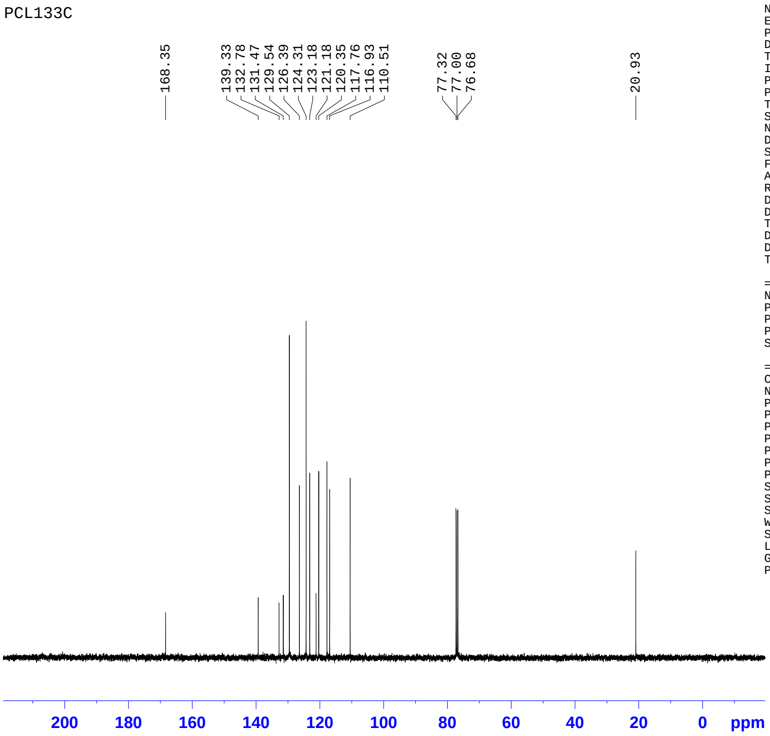
1-Phenyl-1*H*-indol-3-yl acetate (Table 2.3, entry 1)





```
NAME               PCL133
EXPNO                   1
PROCNO                  1
Date_            20100609
Time                13.47
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              4006.410 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                   25.4
DW                124.800 usec
DE                   6.50 usec
TE                  296.5 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.70 usec
PL1                  0.00 dB
PL1W          11.88122272 W
SFO1          400.1318007 MHz
SI                  32768
SF            400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

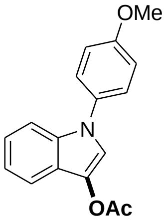


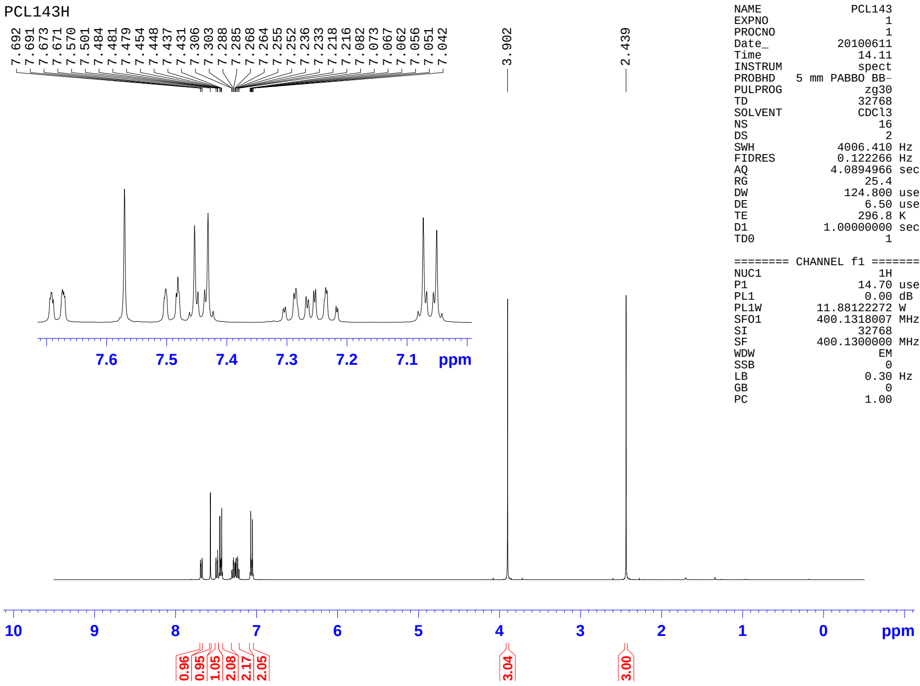
```
NAME               PCL133
EXPNO                   2
PROCNO                  1
Date_            20100609
Time                13.51
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      2
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                    203
DW                 20.800 usec
DE                   6.50 usec
TE                  297.7 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.50 usec
PL1                 -2.00 dB
PL1W          58.52175522 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                15.00 dB
PL13                15.00 dB
PL2W          11.88122272 W
PL12W          0.37571725 W
PL13W          0.37571725 W
SFO2          400.1316005 MHz
SI                  32768
SF            100.6127825 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

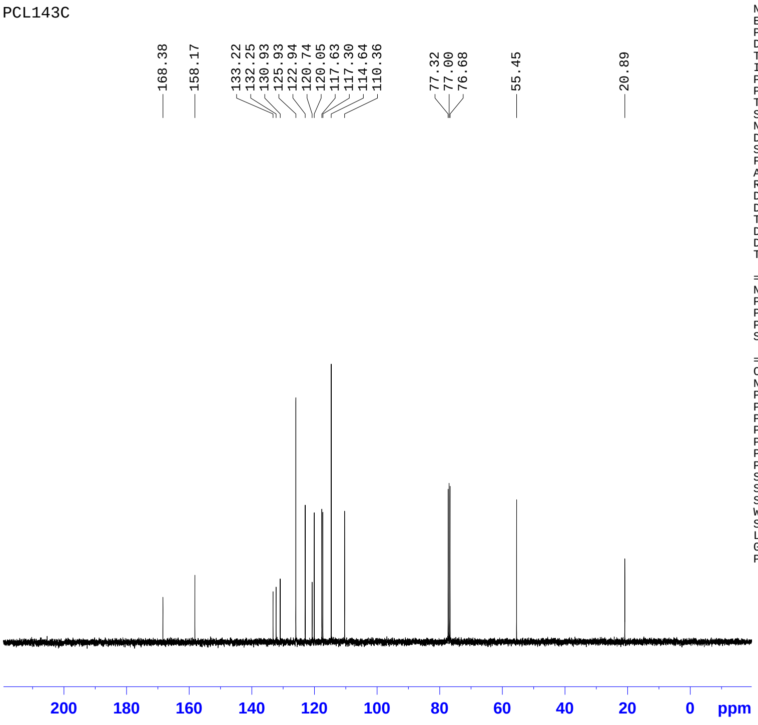
1-(4-Methoxyphenyl)-1*H*-indol-3-yl acetate (Table 2.3, entry 2)





```
NAME             PCL143
EXPNO                 1
PROCNO                1
Date_          20100611
Time              14.11
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            4006.410 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                 25.4
DW              124.800 usec
DE                 6.50 usec
TE                296.8 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.70 usec
PL1                0.00 dB
PL1W        11.88122272 W
SFO1        400.1318007 MHz
SI                32768
SF          400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

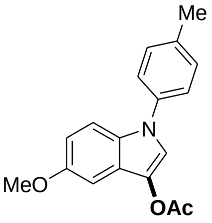


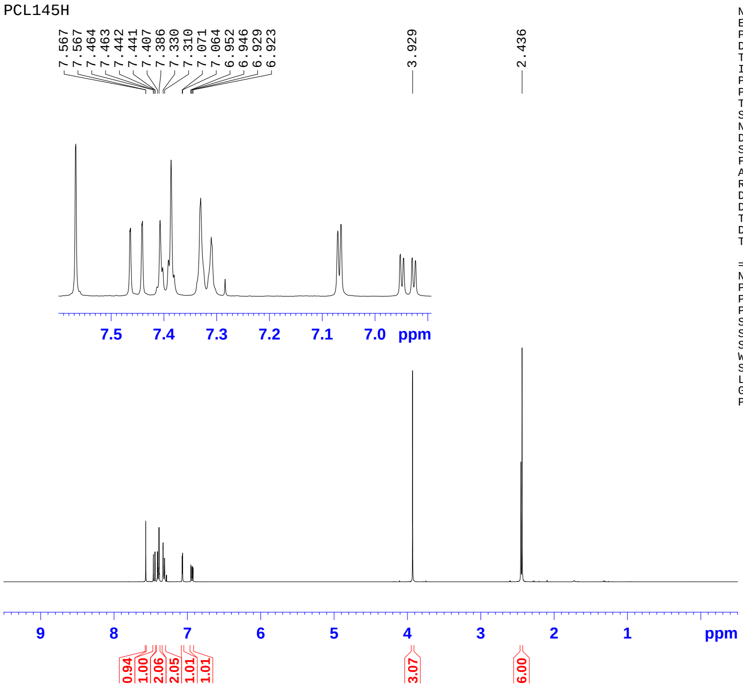
```
NAME             PCL143
EXPNO                 2
PROCNO                1
Date_          20100611
Time              14.14
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                  203
DW               20.800 usec
DE                 6.50 usec
TE                297.8 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.50 usec
PL1               -2.00 dB
PL1W        58.52175522 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL13              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
PL13W        0.37571725 W
SFO2        400.1316005 MHz
SI                32768
SF          100.6127838 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

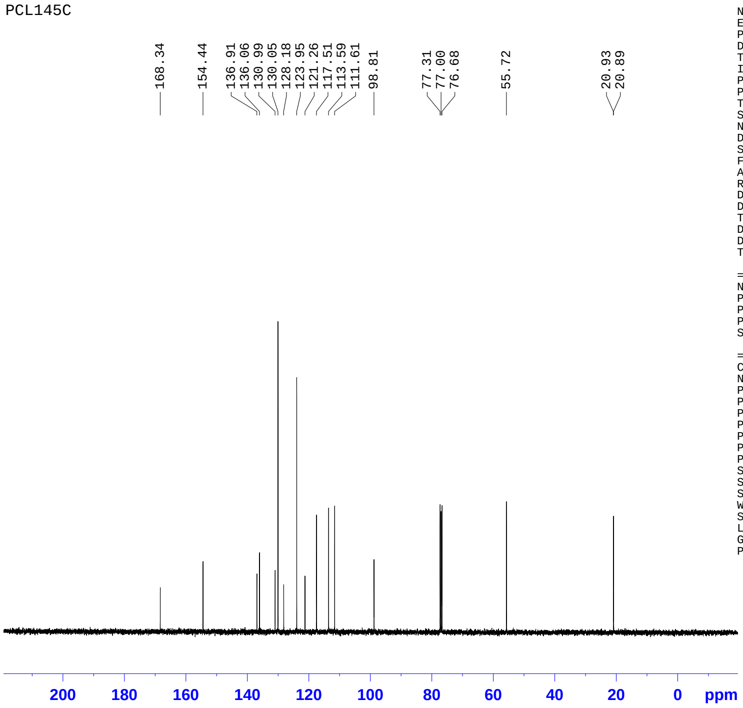
5-Methoxy-1-(4-methylphenyl)-1*H*-indol-3-yl acetate (Table 2.3, entry 3)





```
NAME             PCL145
EXPNO                 1
PROCNO                1
Date_          20100611
Time              21.35
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            4006.410 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                 25.4
DW              124.800 usec
DE                 6.50 usec
TE                297.2 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.70 usec
PL1                0.00 dB
PL1W        11.88122272 W
SFO1        400.1318007 MHz
SI                32768
SF          400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

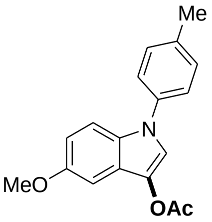


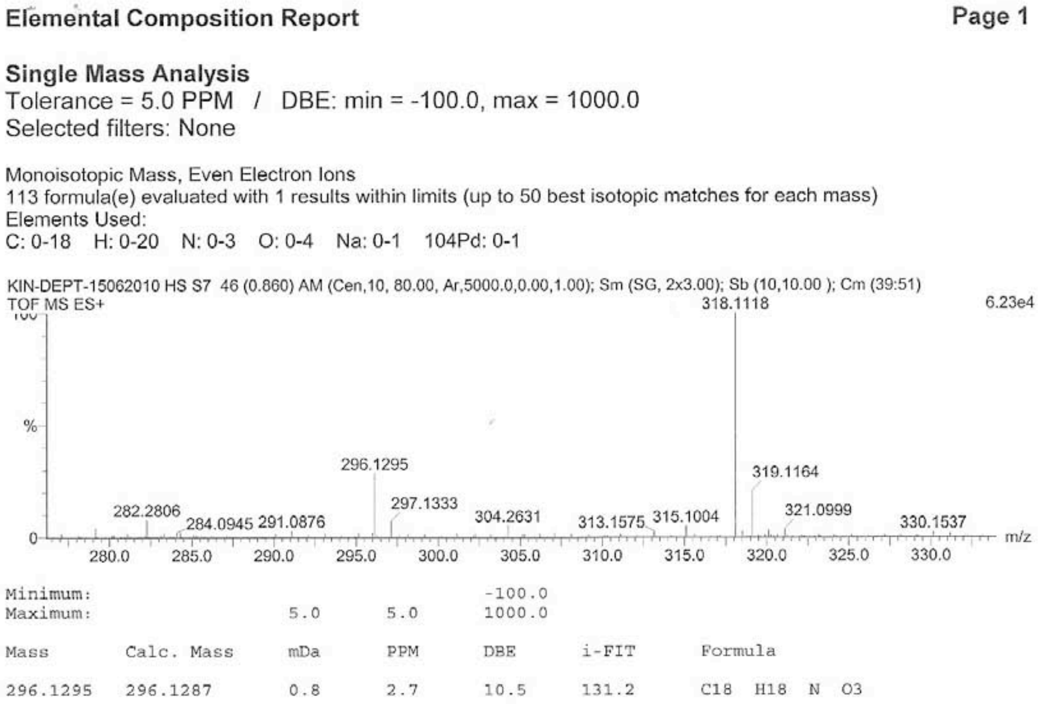
```
NAME             PCL145
EXPNO                 2
PROCNO                1
Date_          20100611
Time              21.39
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                  114
DW               20.800 usec
DE                 6.50 usec
TE                298.3 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.50 usec
PL1               -2.00 dB
PL1W        58.52175522 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL13              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
PL13W        0.37571725 W
SFO2        400.1316005 MHz
SI                32768
SF          100.6127817 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

5-Methoxy-1-(4-methylphenyl)-1*H*-indol-3-yl acetate (Table 2.3, entry 3)





Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -100.0, max = 1000.0
Selected filters: None

Monoisotopic Mass, Even Electron Ions
113 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-18 H: 0-20 N: 0-3 O: 0-4 Na: 0-1 104Pd: 0-1

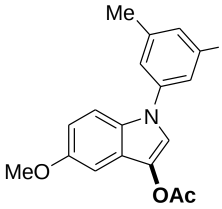
KIN-DEPT-15062010 HS S7 46 (0.860) AM (Cen,10, 80.00, Ar,5000.0,0.00,1.00); Sm (SG, 2x3.00); Sb (10,10.00); Cm (39:51)
TOF MS ES+

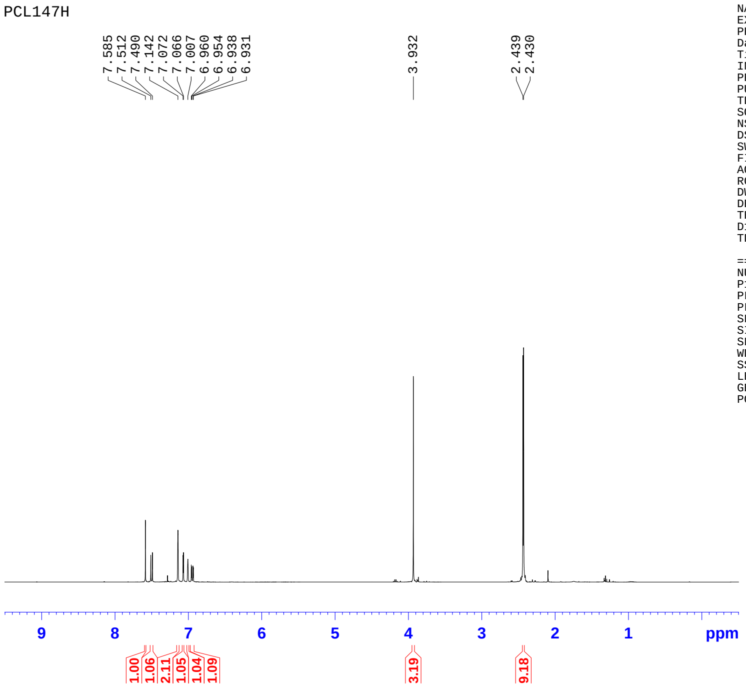
```
Minimum:                                  -100.0
Maximum:                  5.0      5.0    1000.0

Mass      Calc. Mass     mDa      PPM     DBE       i-FIT     Formula

296.1295  296.1287       0.8      2.7     10.5      131.2     C18  H18  N  O3
```

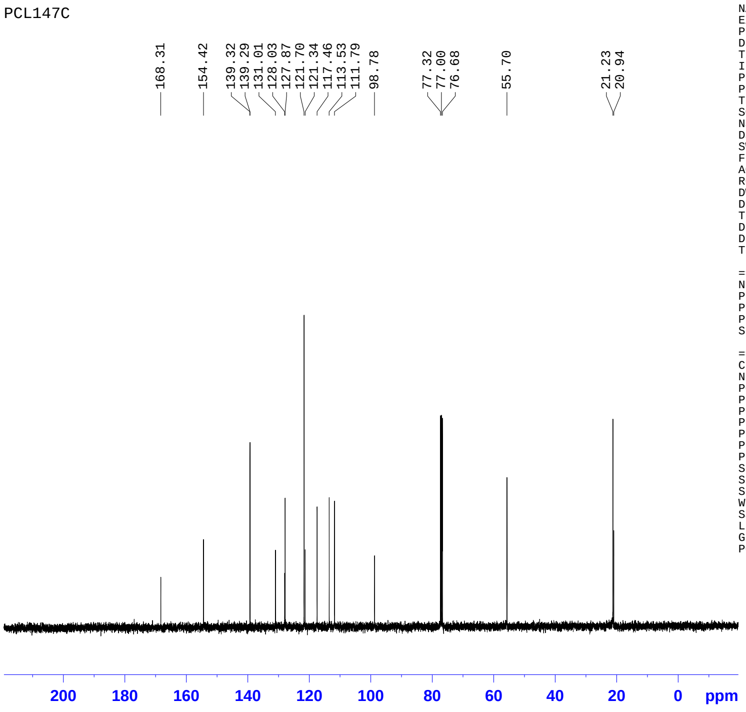
1-(3,5-Dimethylphenyl)-5-methoxy-1*H*-indol-3-yl acetate (Table 2.3, entry 4)





```
NAME              PCL147
EXPNO                  1
PROCNO                 1
Date_           20100611
Time               14.02
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  25.4
DW               124.800 usec
DE                  6.50 usec
TE                 296.7 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

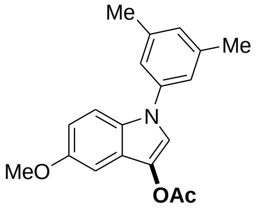


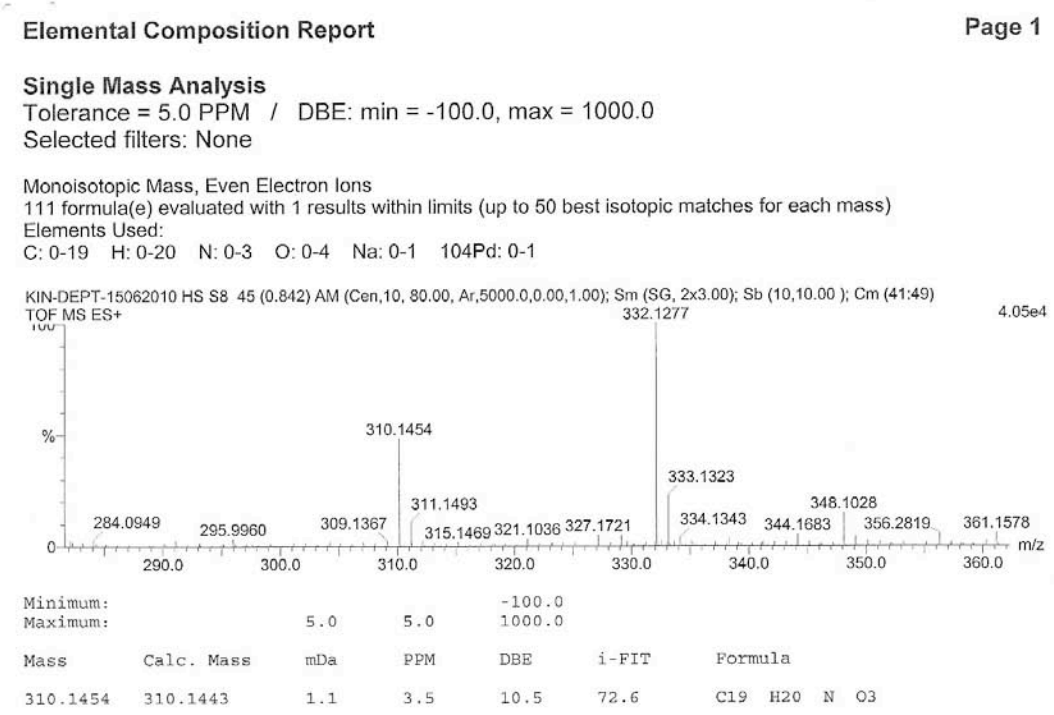
```
NAME              PCL147
EXPNO                  2
PROCNO                 1
Date_           20100611
Time               14.07
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   203
DW                20.800 usec
DE                  6.50 usec
TE                 297.8 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127816 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

1-(3,5-Dimethylphenyl)-5-methoxy-1*H*-indol-3-yl acetate (Table 2.3, entry 4)





Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -100.0, max = 1000.0
Selected filters: None

Monoisotopic Mass, Even Electron Ions
111 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-19 H: 0-20 N: 0-3 O: 0-4 Na: 0-1 104Pd: 0-1

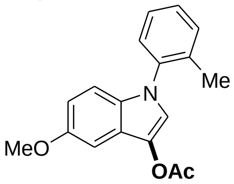
KIN-DEPT-15062010 HS S8 45 (0.842) AM (Cen,10, 80.00, Ar,5000.0,0.00,1.00); Sm (SG, 2x3.00); Sb (10,10.00); Cm (41:49)
TOF MS ES+

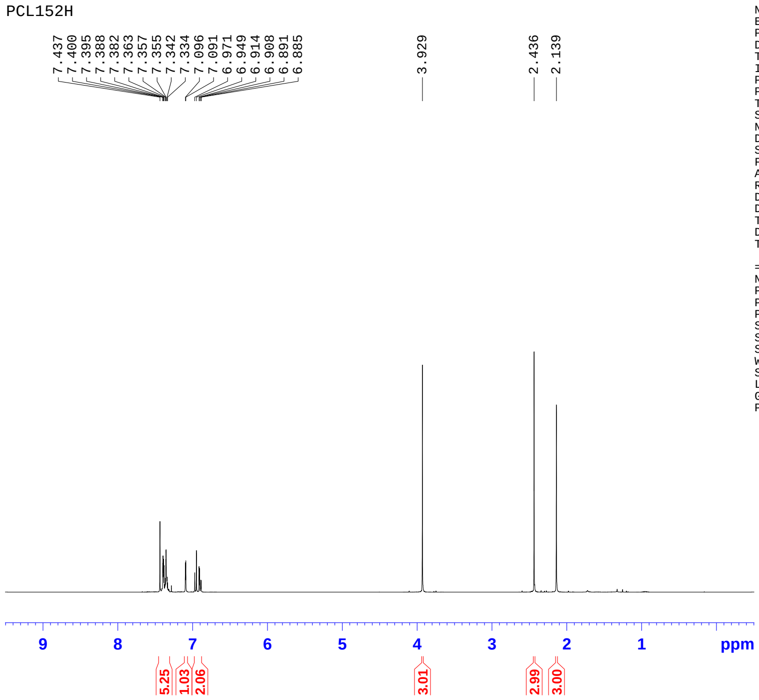
```
Minimum:                                   -100.0
Maximum:                5.0      5.0       1000.0

Mass      Calc. Mass    mDa      PPM       DBE      i-FIT      Formula

310.1454  310.1443      1.1      3.5       10.5     72.6       C19  H20  N  O3
```

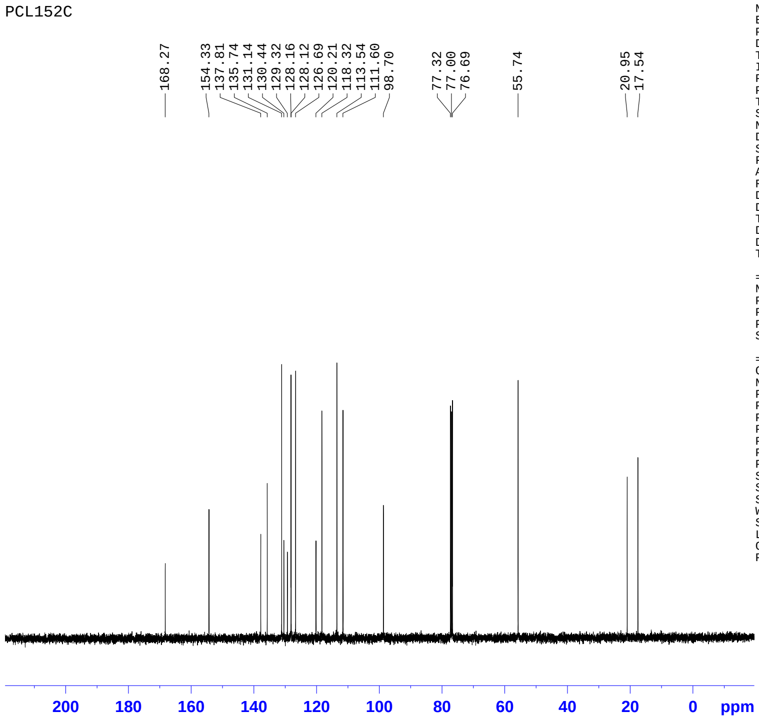
5-Methoxy-1-*o*-tolyl-1*H*-indol-3-yl acetate (Table 2.3, entry 5)





```
NAME              PCL152
EXPNO                  1
PROCNO                 1
Date_           20100629
Time               18.16
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  25.4
DW               124.800 usec
DE                  6.50 usec
TE                 297.4 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

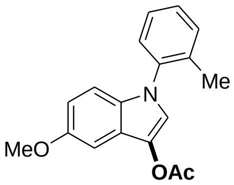


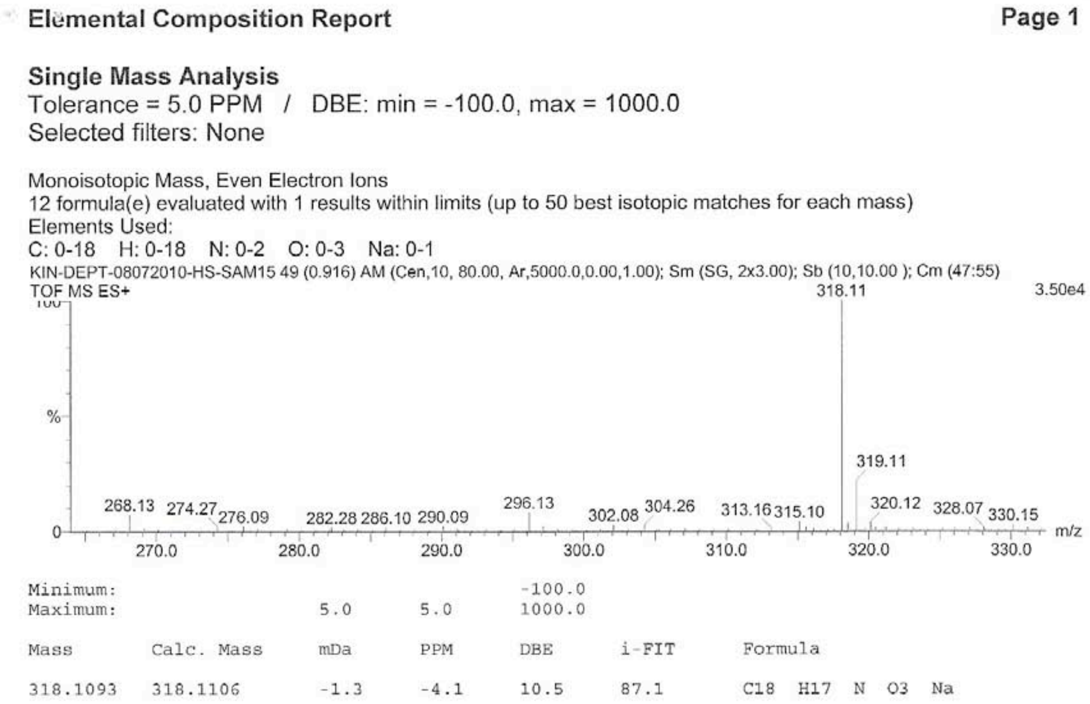
```
NAME              PCL152
EXPNO                  2
PROCNO                 1
Date_           20100629
Time               18.18
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   203
DW                20.800 usec
DE                  6.50 usec
TE                 298.5 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127810 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

5-Methoxy-1-*o*-tolyl-1*H*-indol-3-yl acetate (Table 2.3, entry 5)





Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -100.0, max = 1000.0
Selected filters: None

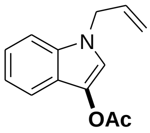
Monoisotopic Mass, Even Electron Ions
12 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-18 H: 0-18 N: 0-2 O: 0-3 Na: 0-1
KIN-DEPT-08072010-HS-SAM15 49 (0.916) AM (Cen,10, 80.00, Ar,5000.0,0.00,1.00); Sm (SG, 2x3.00); Sb (10,10.00); Cm (47:55)
TOF MS ES+

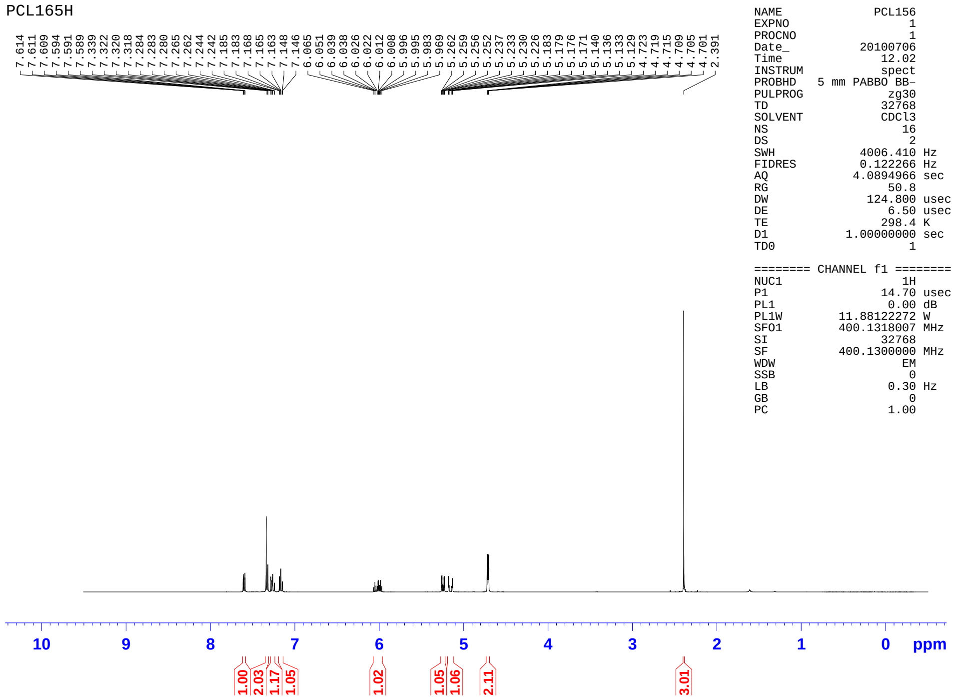
```
Minimum:                                   -100.0
Maximum:                 5.0      5.0      1000.0

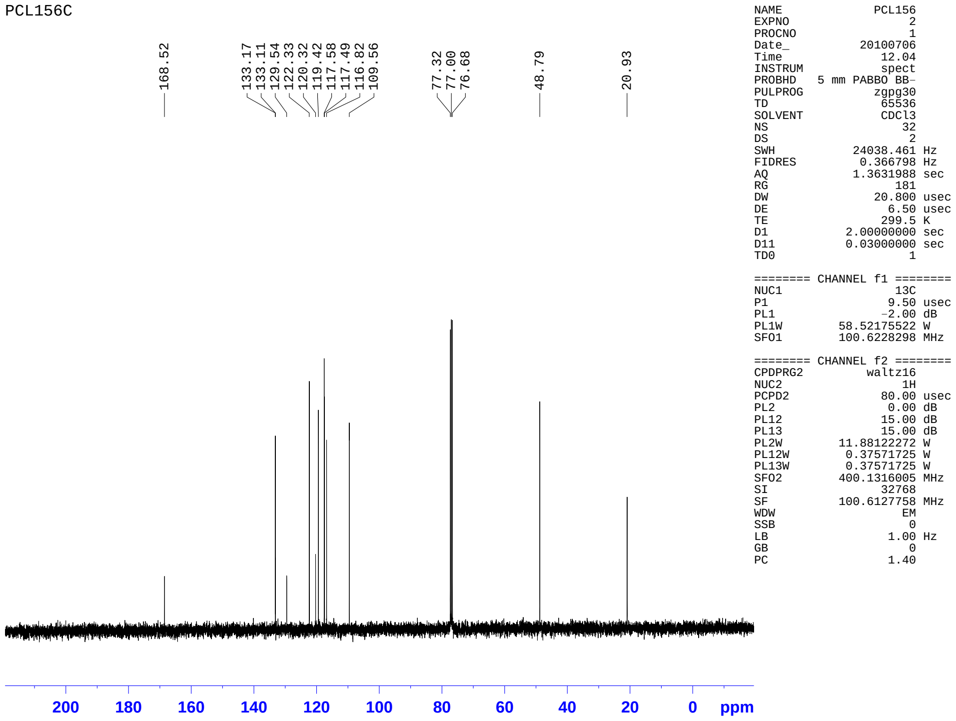
Mass      Calc. Mass     mDa      PPM      DBE      i-FIT      Formula

318.1093  318.1106       -1.3     -4.1     10.5     87.1       C18  H17  N  O3  Na
```

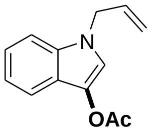
1-Allyl-1*H*-indol-3-yl acetate (Scheme 2.1)

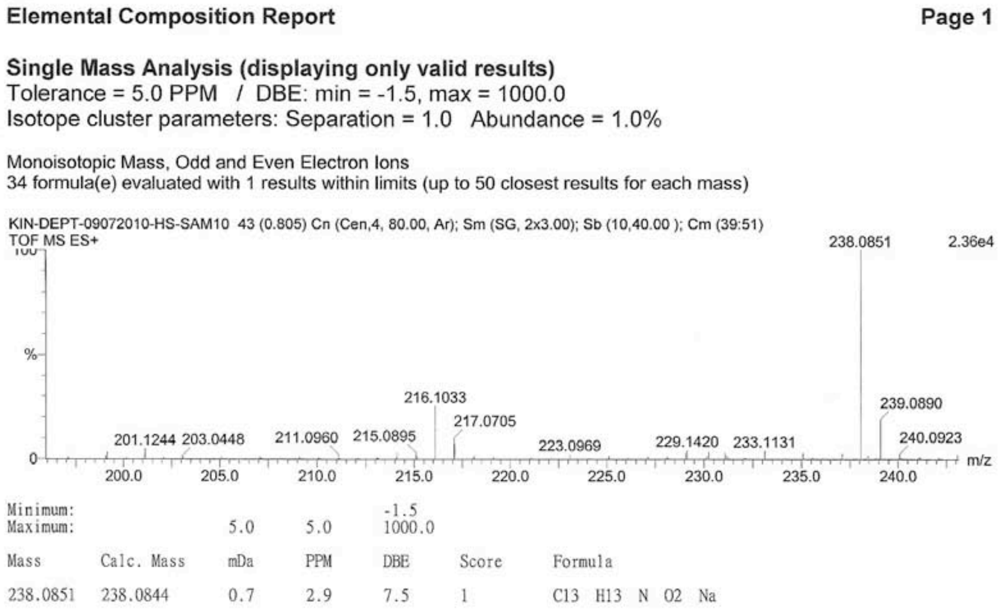






1-Allyl-1*H*-indol-3-yl acetate (Scheme 2.1)





Elemental Composition Report **Page 1**

Single Mass Analysis (displaying only valid results)
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 1000.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
34 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

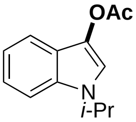
KIN-DEPT-09072010-HS-SAM10 43 (0.805) Cn (Cen,4, 80.00, Ar); Sm (SG, 2x3.00); Sb (10,40.00); Cm (39:51)
TOF MS ES+

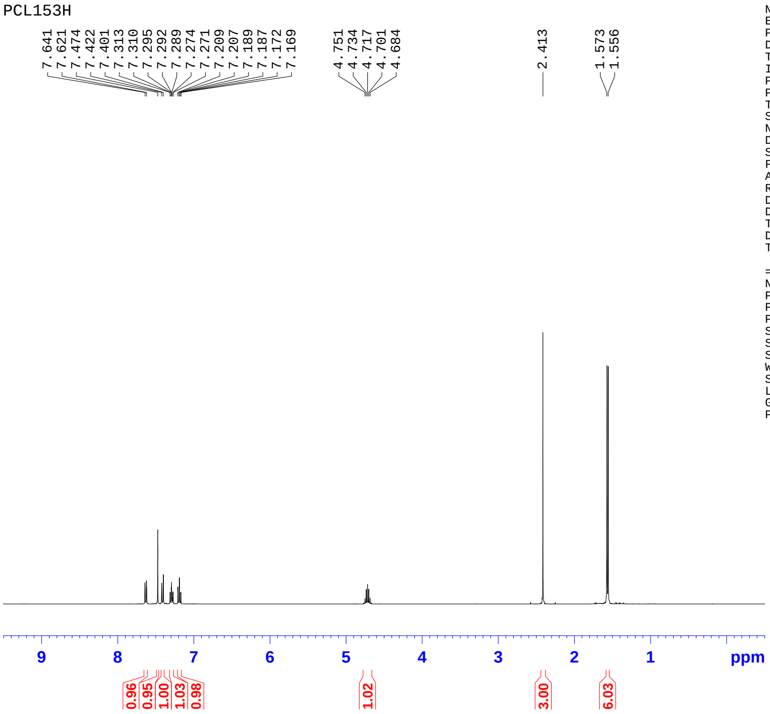
```
Minimum:                          -1.5
Maximum:            5.0     5.0   1000.0

Mass      Calc. Mass  mDa   PPM   DBE    Score   Formula

238.0851  238.0844    0.7   2.9   7.5    1       C13  H13  N  O2  Na
```

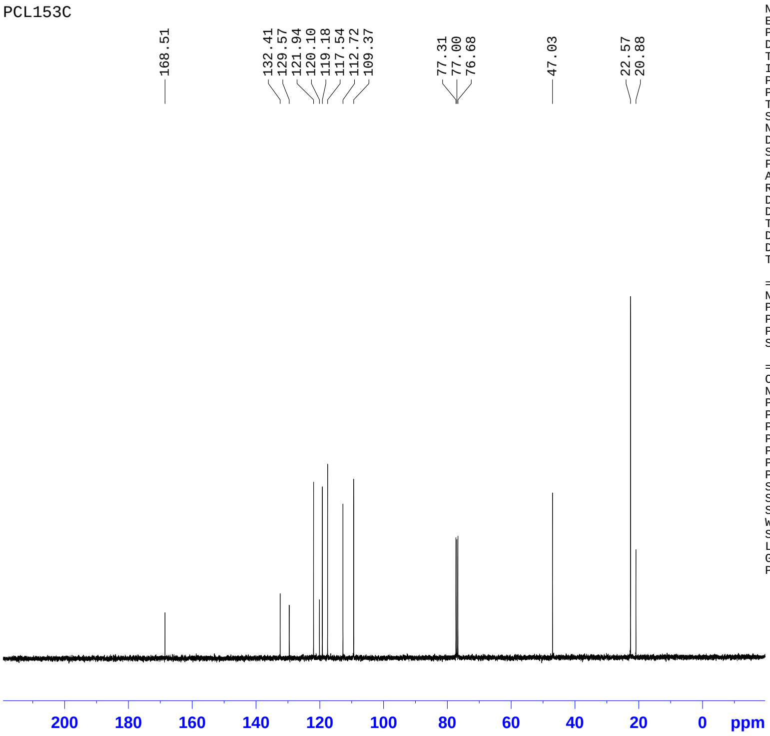
1-Isopropyl-1*H*-indol-3-yl acetate (Scheme 2.1)





```
NAME             PCL153
EXPNO                 1
PROCNO                1
Date_          20100705
Time              14.04
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            4006.410 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                 25.4
DW              124.800 usec
DE                 6.50 usec
TE                298.4 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.70 usec
PL1                0.00 dB
PL1W        11.88122272 W
SFO1        400.1318007 MHz
SI                32768
SF          400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

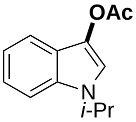


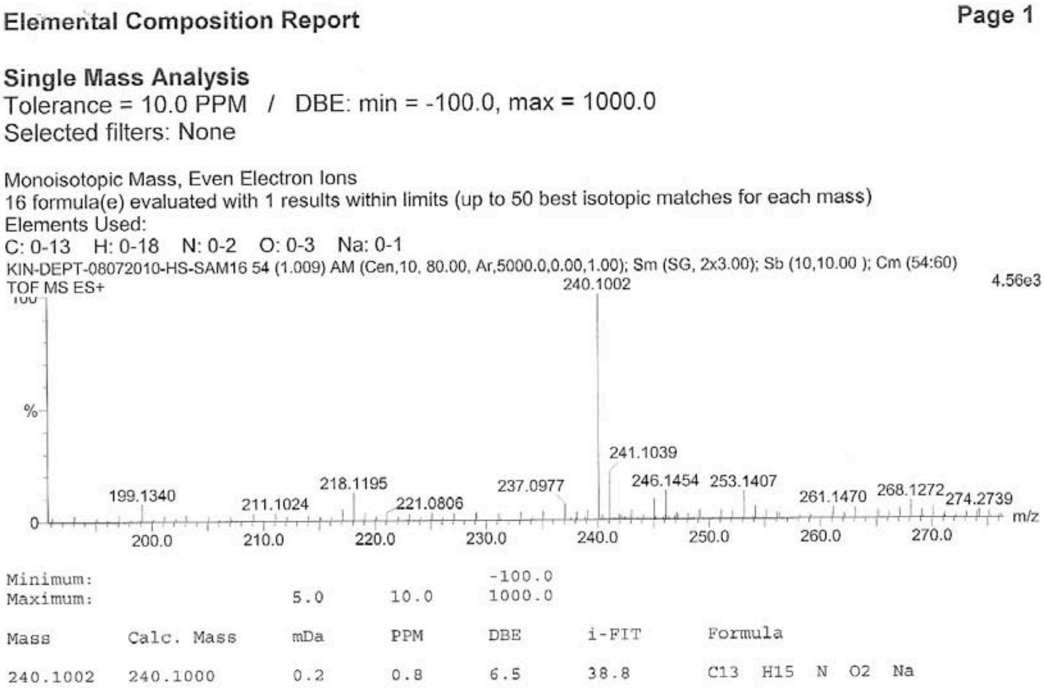
```
NAME             PCL153
EXPNO                 2
PROCNO                1
Date_          20100705
Time              14.07
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                  181
DW               20.800 usec
DE                 6.50 usec
TE                299.5 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.50 usec
PL1               -2.00 dB
PL1W        58.52175522 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL13              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
PL13W        0.37571725 W
SFO2        400.1316005 MHz
SI                32768
SF          100.6127847 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

1-Isopropyl-1*H*-indol-3-yl acetate (Scheme 2.1)





Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -100.0, max = 1000.0
Selected filters: None

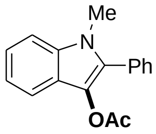
Monoisotopic Mass, Even Electron Ions
16 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-13 H: 0-18 N: 0-2 O: 0-3 Na: 0-1
KIN-DEPT-08072010-HS-SAM16 54 (1.009) AM (Cen,10, 80.00, Ar,5000.0,0.00,1.00); Sm (SG, 2x3.00); Sb (10,10.00); Cm (54:60)
TOF MS ES+

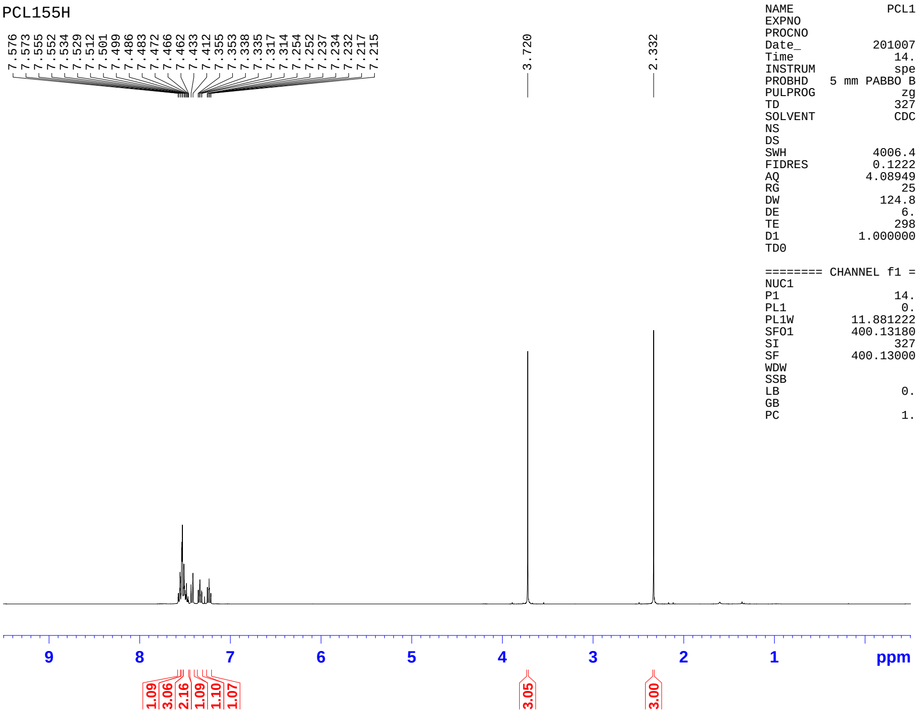
```
Minimum:                                  -100.0
Maximum:                    5.0    10.0   1000.0

Mass       Calc. Mass    mDa    PPM    DBE      i-FIT    Formula

240.1002   240.1000      0.2    0.8    6.5      38.8     C13  H15  N  O2  Na
```

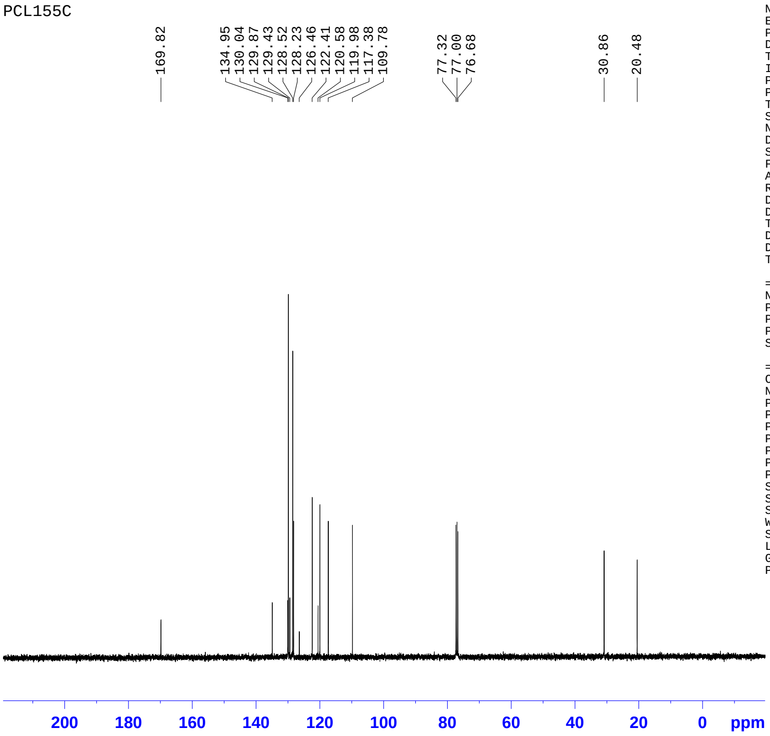
1-Methyl-2-phenyl-1*H*-indol-3-yl acetate (Scheme 2.1)





```
NAME            PCL155
EXPNO                1
PROCNO               1
Date_         20100705
Time             14.21
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG           zg30
TD               32768
SOLVENT          CDCl3
NS                  16
DS                   2
SWH           4006.410 Hz
FIDRES        0.122266 Hz
AQ           4.0894966 sec
RG                25.4
DW             124.800 usec
DE                6.50 usec
TE               298.5 K
D1          1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                1H
P1               14.70 usec
PL1               0.00 dB
PL1W       11.88122272 W
SFO1       400.1318007 MHz
SI               32768
SF         400.1300000 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.00
```

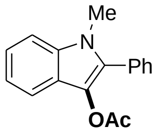


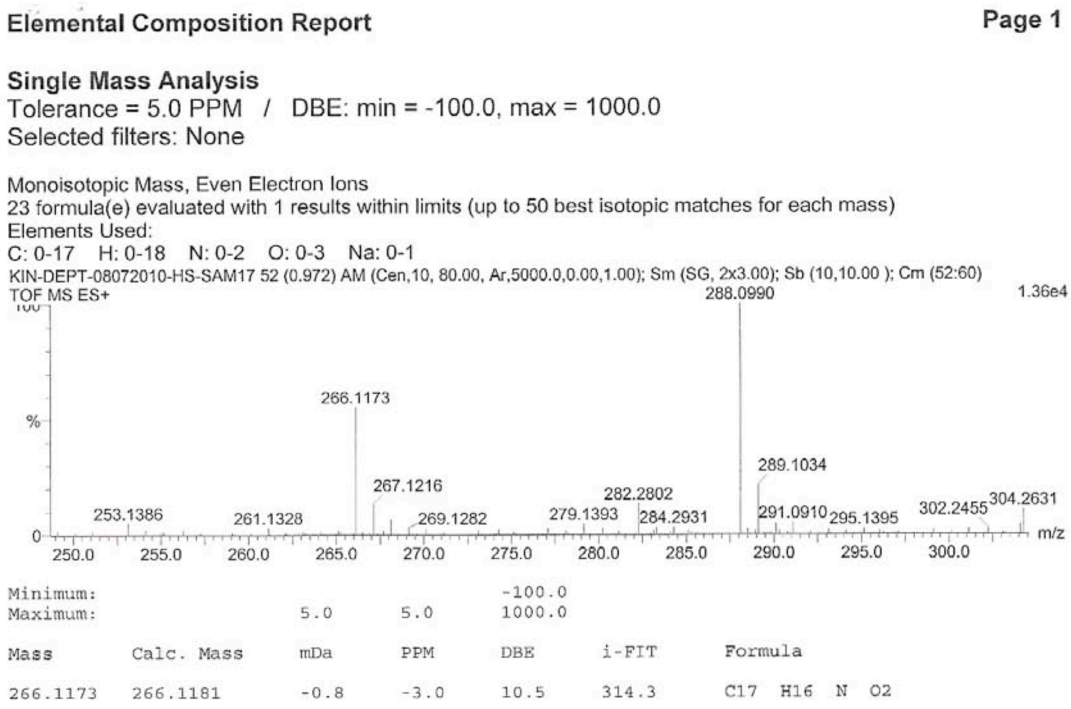
```
NAME            PCL155
EXPNO                2
PROCNO               1
Date_         20100705
Time             14.23
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                  32
DS                   2
SWH          24038.461 Hz
FIDRES        0.366798 Hz
AQ           1.3631988 sec
RG                 161
DW              20.800 usec
DE                6.50 usec
TE               299.5 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1                9.50 usec
PL1              -2.00 dB
PL1W       58.52175522 W
SFO1       100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2            80.00 usec
PL2               0.00 dB
PL12             15.00 dB
PL13             15.00 dB
PL2W       11.88122272 W
PL12W       0.37571725 W
PL13W       0.37571725 W
SFO2       400.1316005 MHz
SI               32768
SF         100.6127831 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```

1-Methyl-2-phenyl-1*H*-indol-3-yl acetate (Scheme 2.1)





Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -100.0, max = 1000.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

23 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 0-17 H: 0-18 N: 0-2 O: 0-3 Na: 0-1

KIN-DEPT-08072010-HS-SAM17 52 (0.972) AM (Cen,10, 80.00, Ar,5000.0,0.00,1.00); Sm (SG, 2x3.00); Sb (10,10.00); Cm (52:60)

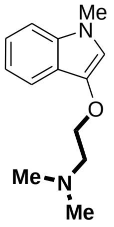
TOF MS ES+

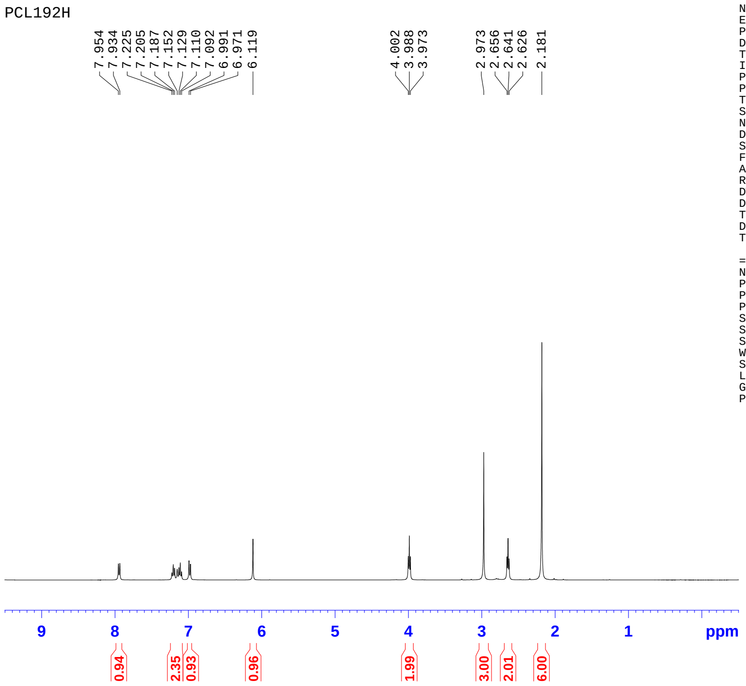
```
Minimum:                                -100.0
Maximum:                   5.0    5.0   1000.0

Mass      Calc. Mass      mDa    PPM    DBE     i-FIT     Formula

266.1173  266.1181        -0.8   -3.0   10.5    314.3     C17  H16  N  O2
```

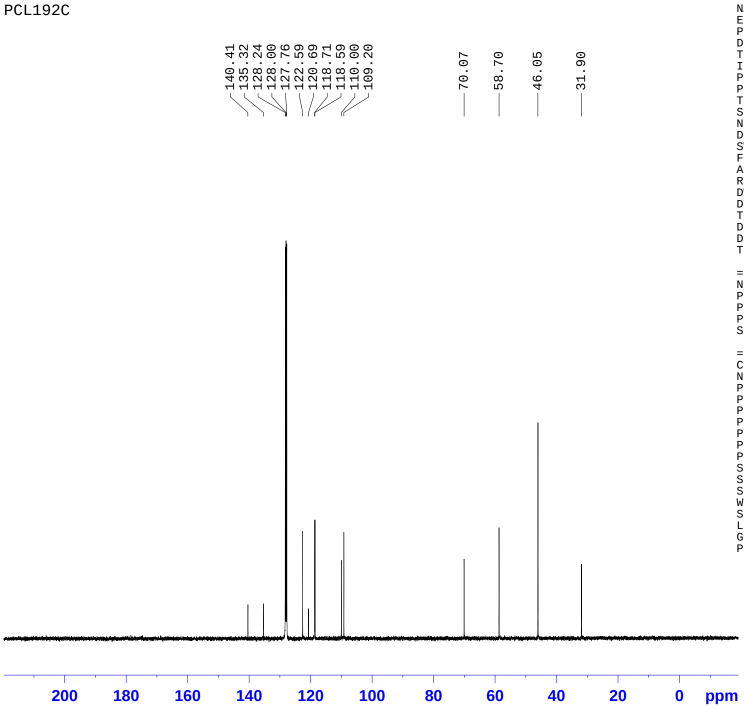
N,*N*-Dimethyl-2-(1-methyl-1*H*-indol-3-yloxy)ethanamine (Scheme 2.3)





```
NAME              PCL192
EXPNO                  1
PROCNO                 1
Date_           20100724
Time               22.40
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT             C6D6
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  12.7
DW               124.800 usec
DE                  6.50 usec
TE                 298.1 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

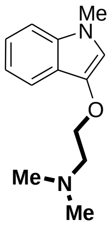


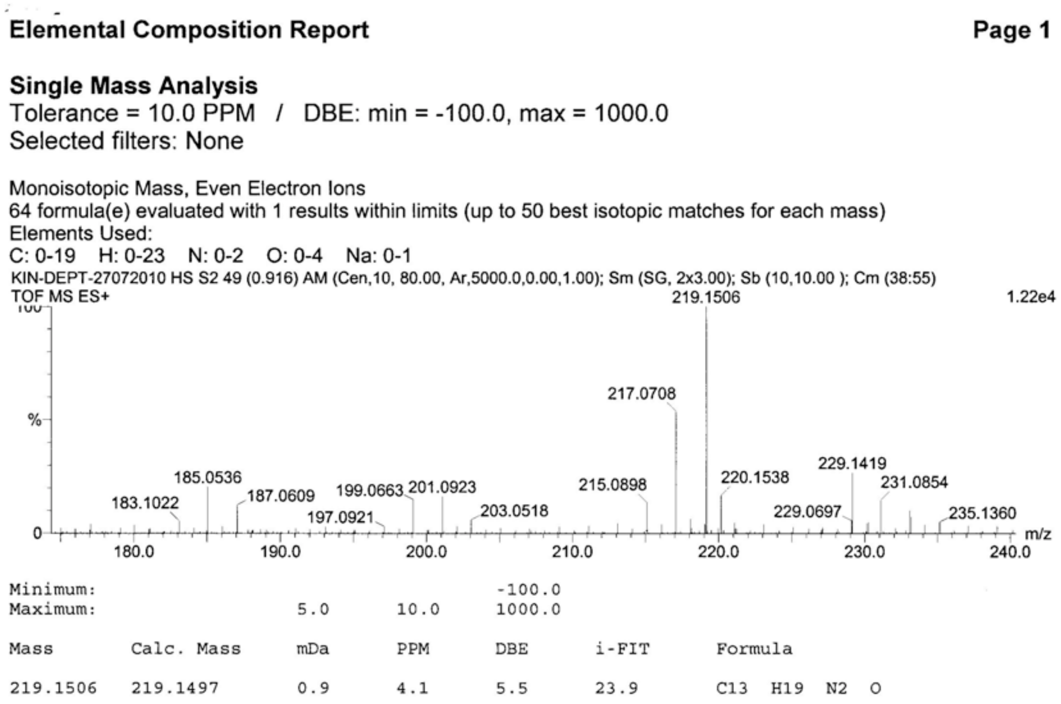
```
NAME              PCL192
EXPNO                  2
PROCNO                 1
Date_           20100724
Time               22.44
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT             C6D6
NS                    32
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   181
DW                20.800 usec
DE                  6.50 usec
TE                 299.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127381 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

N,N-Dimethyl-2-(1-methyl-1*H*-indol-3-yloxy)ethanamine (Scheme 2.3)





Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -100.0, max = 1000.0
Selected filters: None

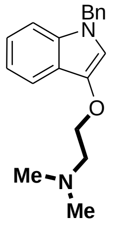
Monoisotopic Mass, Even Electron Ions
64 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-19 H: 0-23 N: 0-2 O: 0-4 Na: 0-1
KIN-DEPT-27072010 HS S2 49 (0.916) AM (Cen,10, 80.00, Ar,5000.0,0.00,1.00); Sm (SG, 2x3.00); Sb (10,10.00); Cm (38:55)
TOF MS ES+

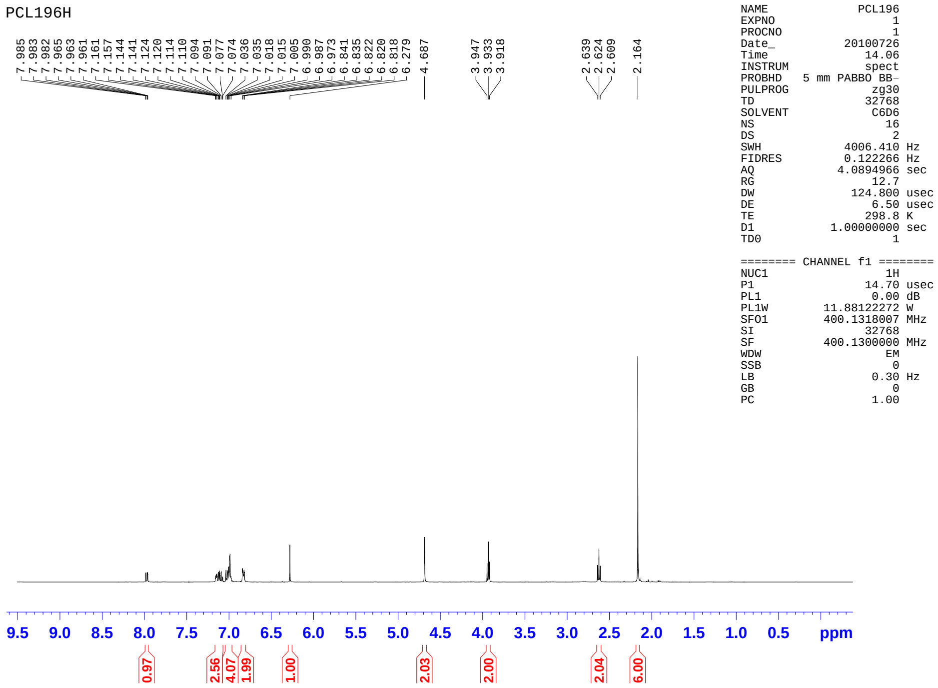
```
Minimum:                                      -100.0
Maximum:                   5.0       10.0     1000.0

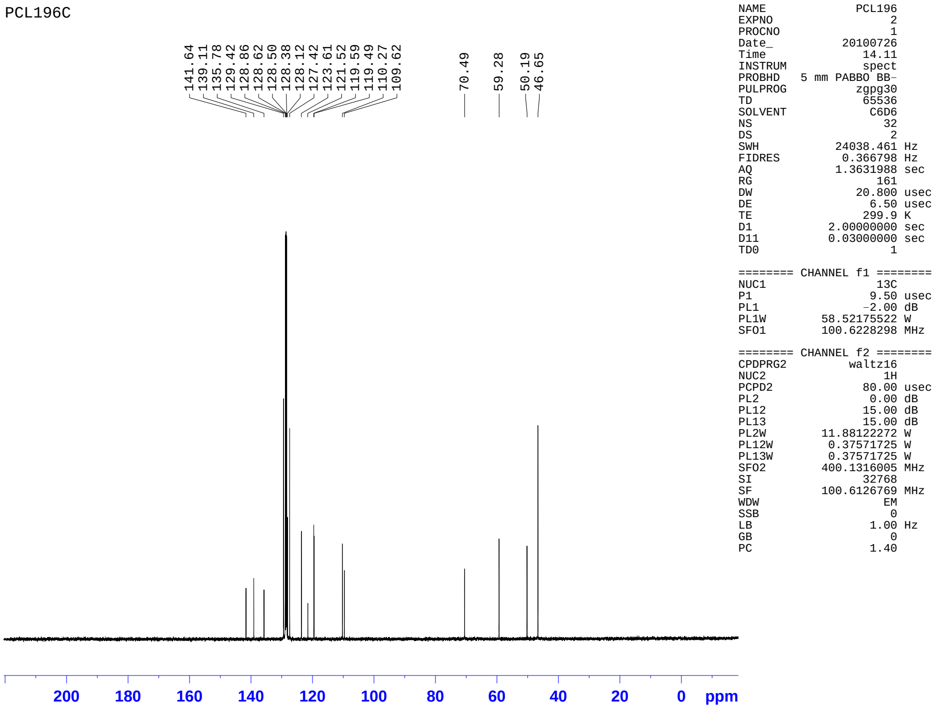
Mass       Calc. Mass      mDa       PPM      DBE        i-FIT       Formula

219.1506   219.1497        0.9       4.1      5.5        23.9        C13  H19  N2  O
```

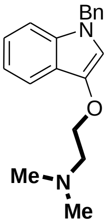
N,*N*-Dimethyl-2-(1-benzyl-1*H*-indol-3-yloxy)ethanamine (Scheme 2.3)

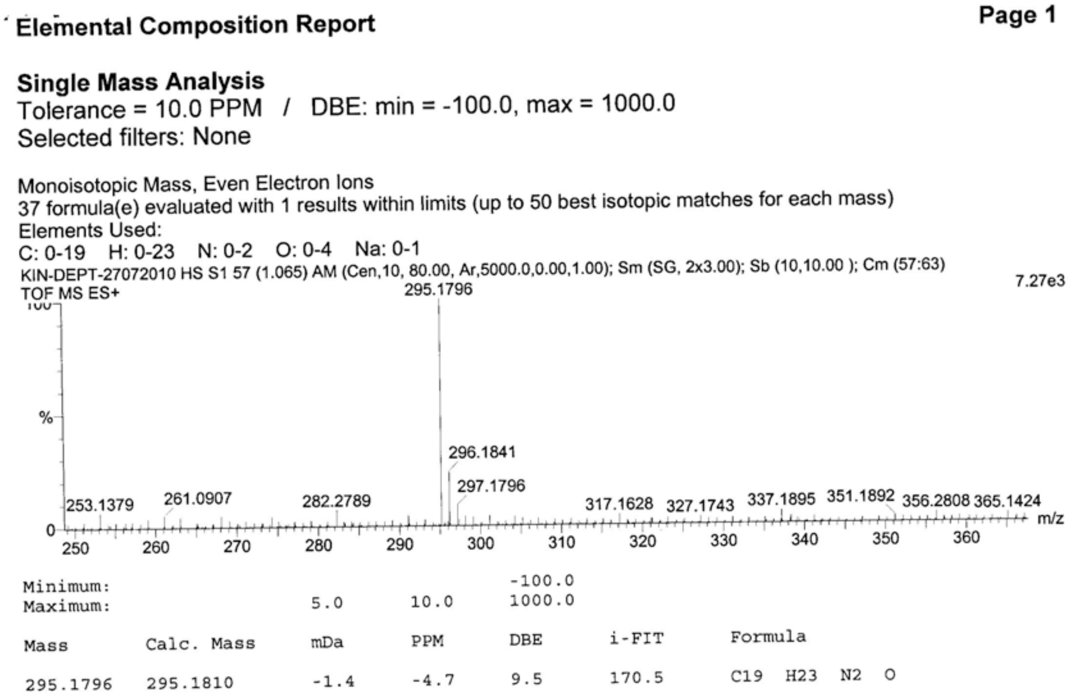






N,N-Dimethyl-2-(1-benzyl-1*H*-indol-3-yloxy)ethanamine (Scheme 2.3)





Elemental Composition Report

Page 1

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -100.0, max = 1000.0
Selected filters: None

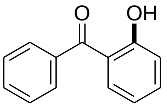
Monoisotopic Mass, Even Electron Ions
37 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-19 H: 0-23 N: 0-2 O: 0-4 Na: 0-1
KIN-DEPT-27072010 HS S1 57 (1.065) AM (Cen,10, 80.00, Ar,5000.0,0.00,1.00); Sm (SG, 2x3.00); Sb (10,10.00); Cm (57:63)
TOF MS ES+

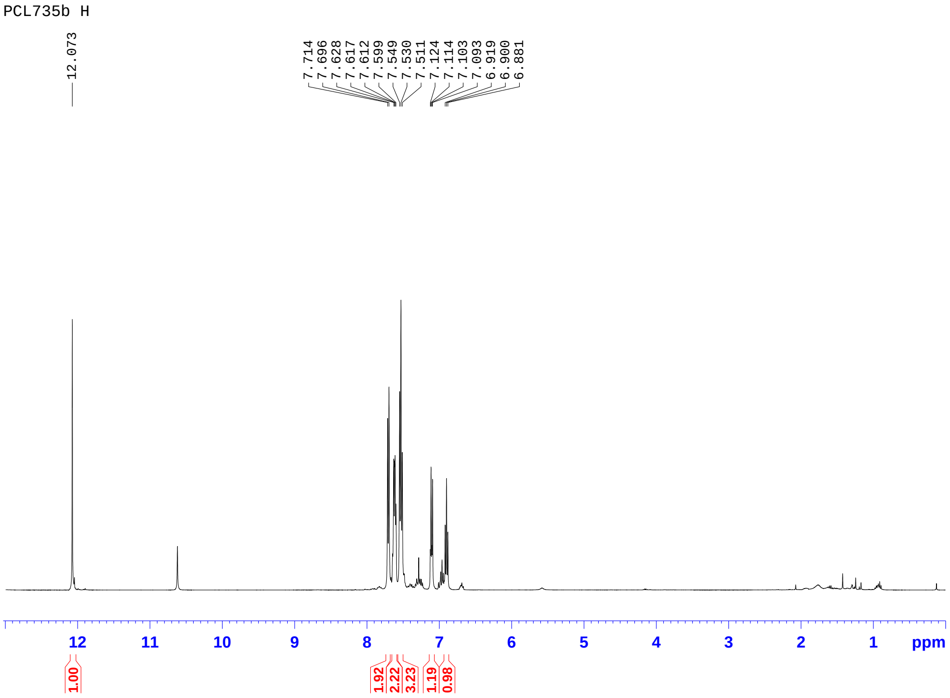
```
Minimum:                                   -100.0
Maximum:                  5.0      10.0    1000.0

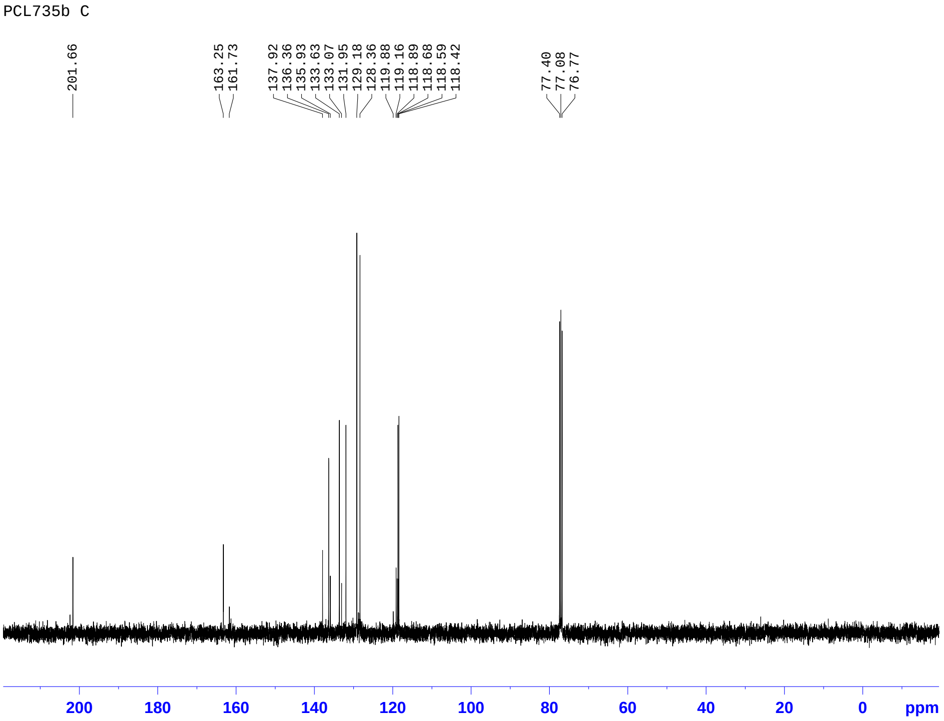
Mass       Calc. Mass     mDa      PPM     DBE      i-FIT      Formula

295.1796   295.1810       -1.4     -4.7    9.5      170.5      C19  H23  N2  O
```

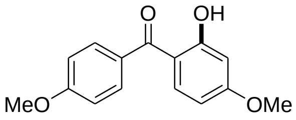
(2-Hydroxyphenyl)phenylmethanone (Table 3.2, entry 1, product 1a)

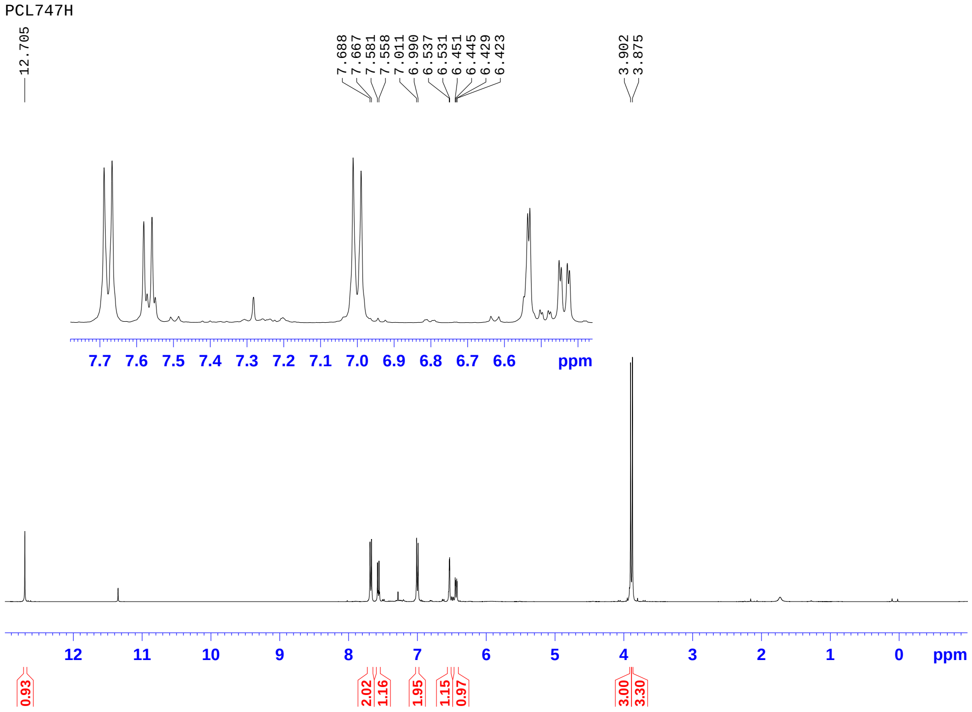


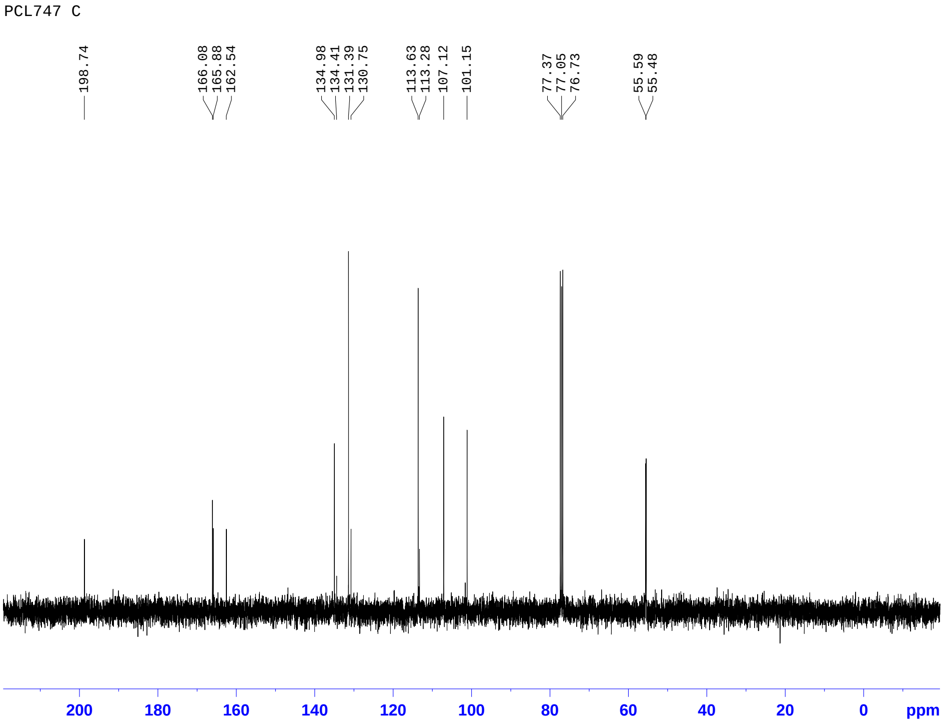




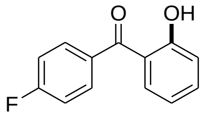
(2-Hydroxy-4-methoxyphenyl)(4-methoxyphenyl)methanone (Table 3.2, entry 2, product 2a)

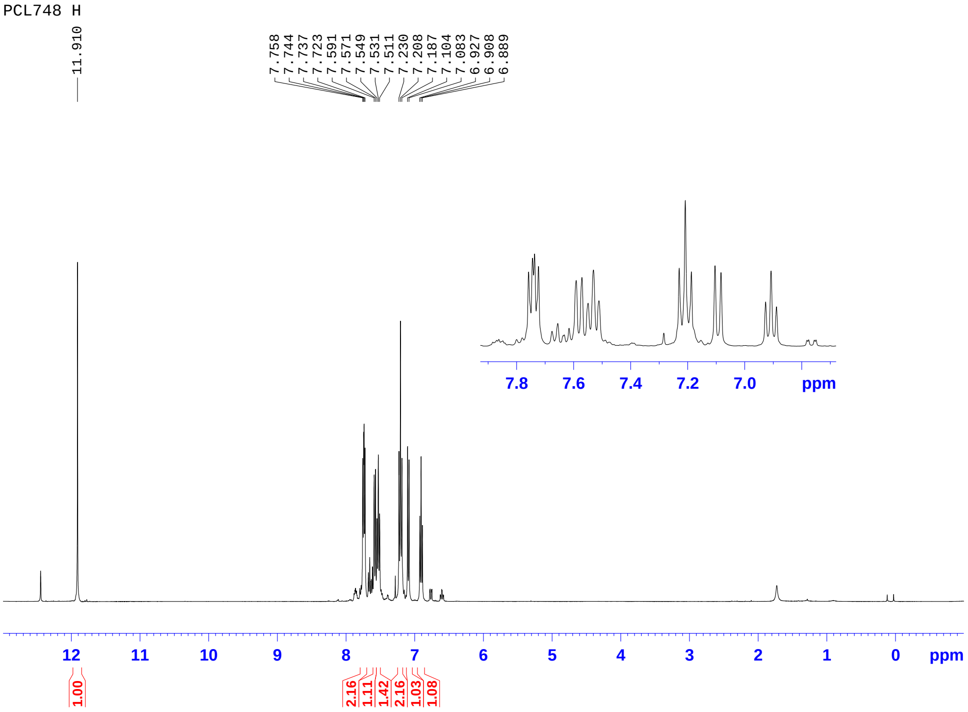


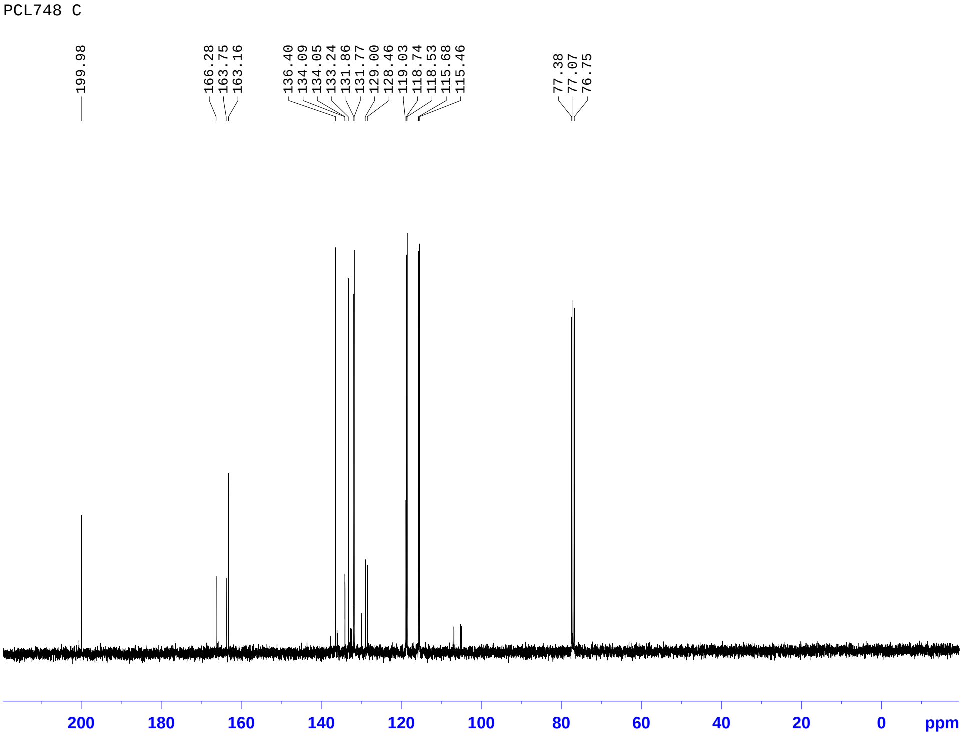




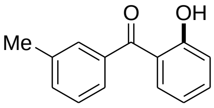
(4-Fluorophenyl)(2-hydroxyphenyl)methanone (Table 3.2, entry 3, product 3a)

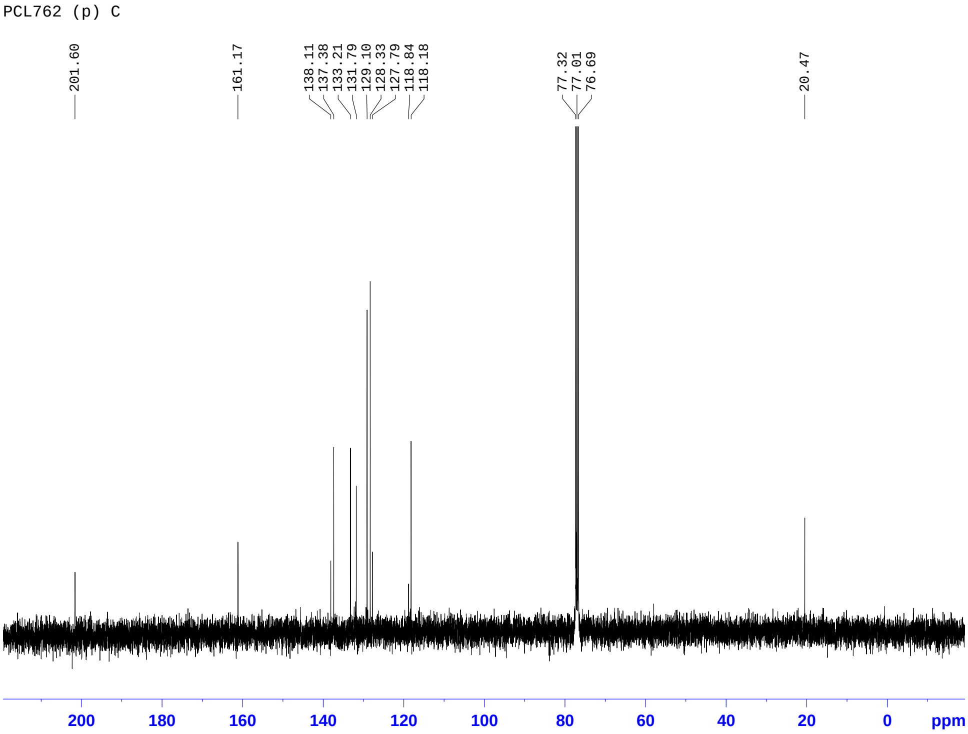


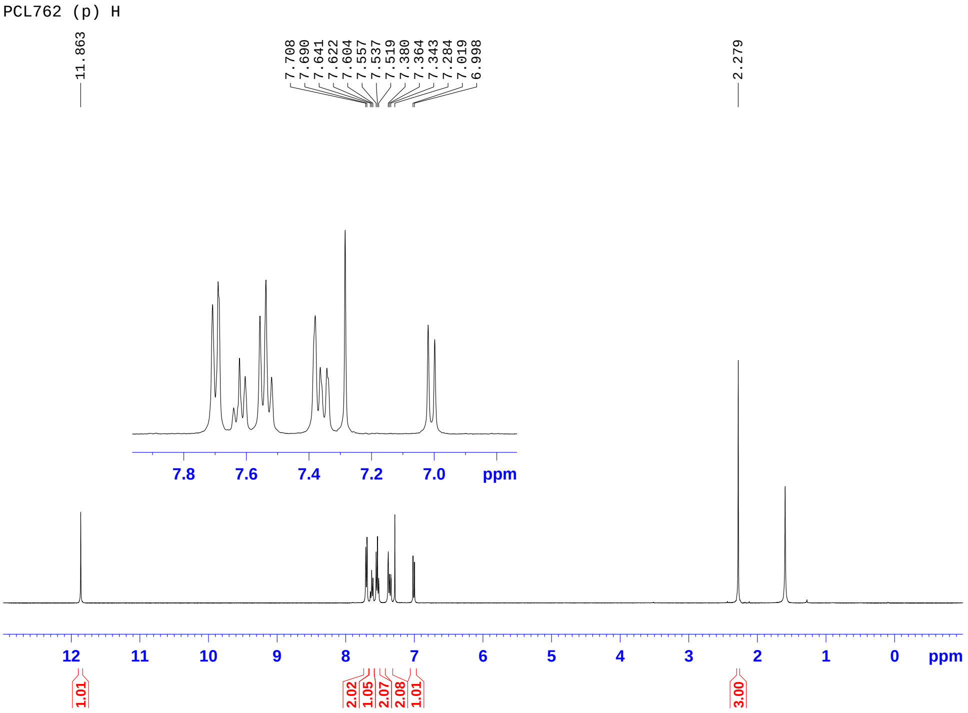




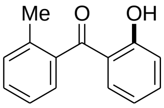
(2-Hydroxyphenyl)(*m*-tolyl)methanone (Table 3.2, entry 4, product 4a)

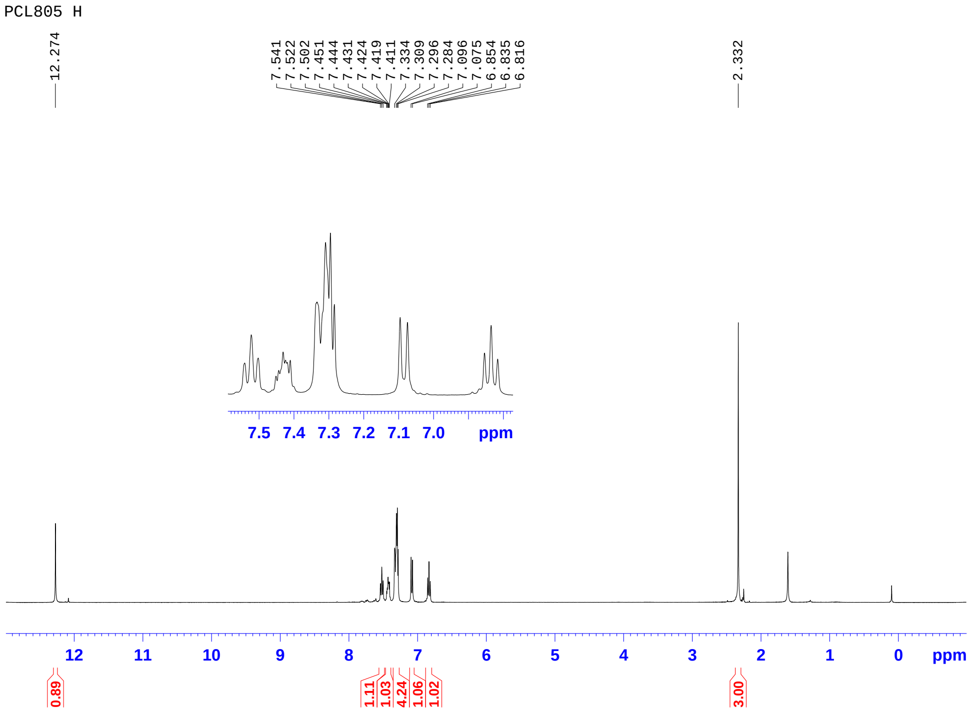


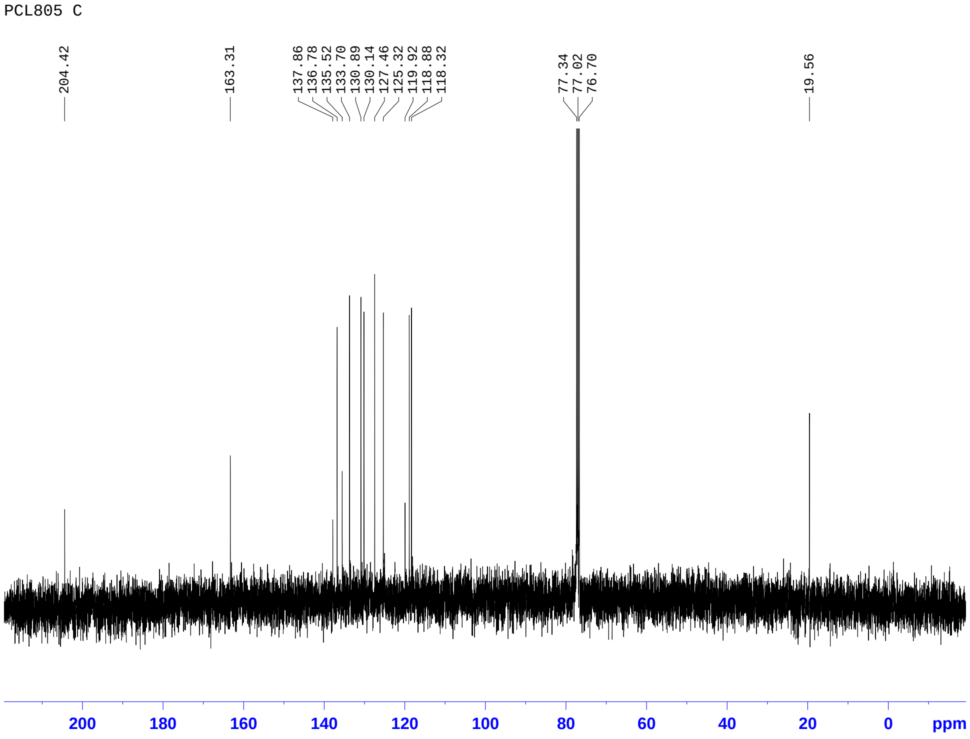




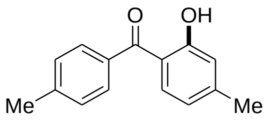
(2-Hydroxyphenyl)(*o*-tolyl)methanone (Table 3.2, entry 5, product 5a)

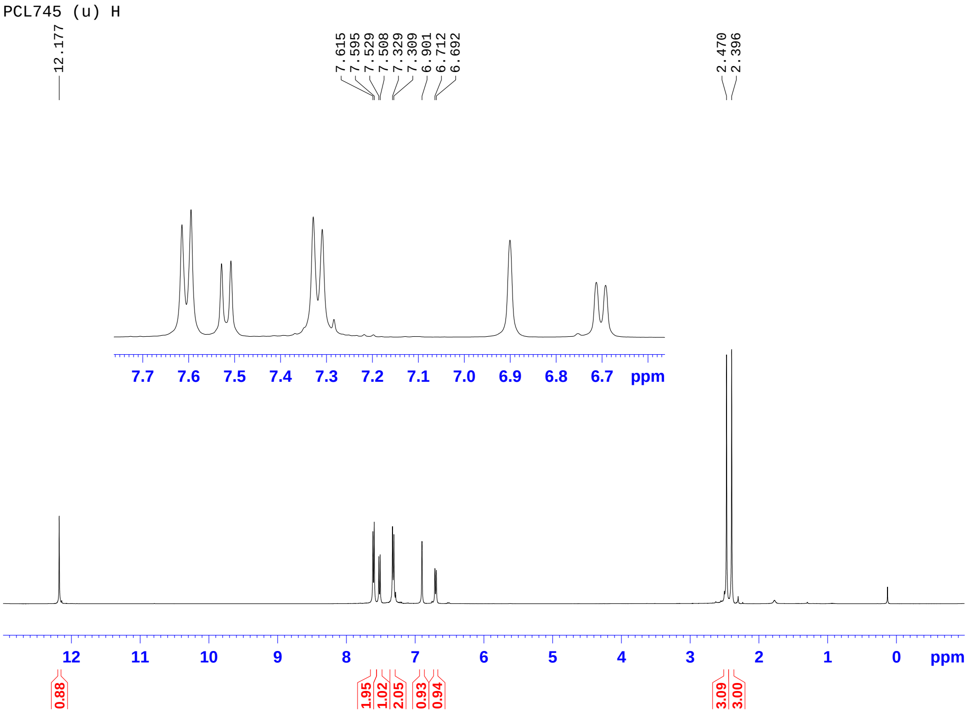


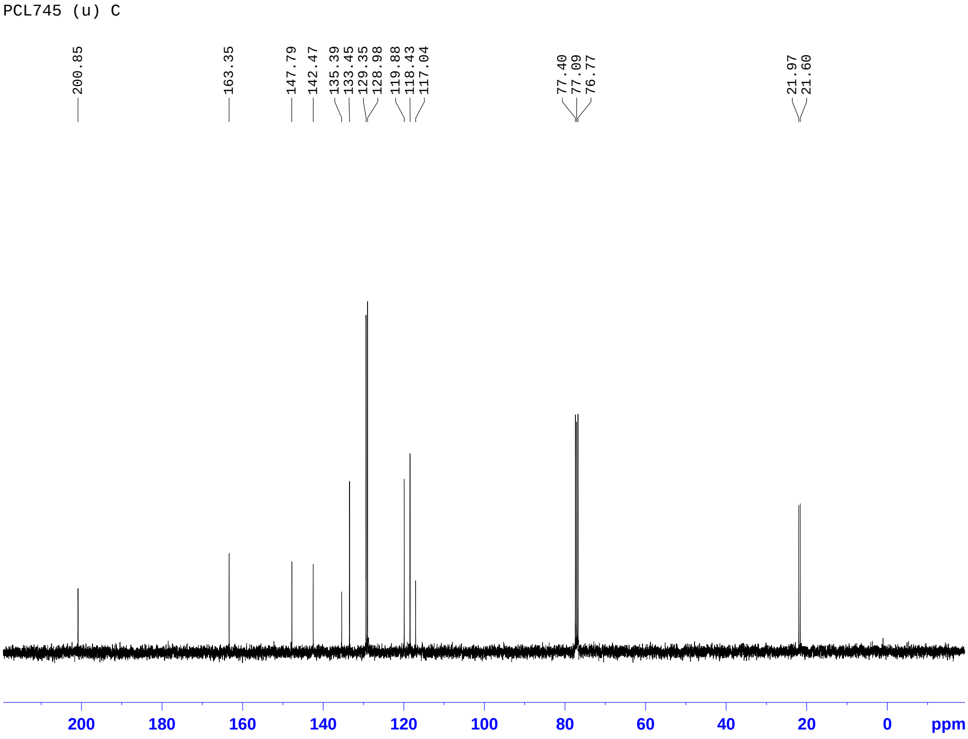




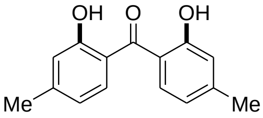
(2-Hydroxy-4-methylphenyl)(*p*-tolyl)methanone (Table 3.2, entry 6, product 6a)

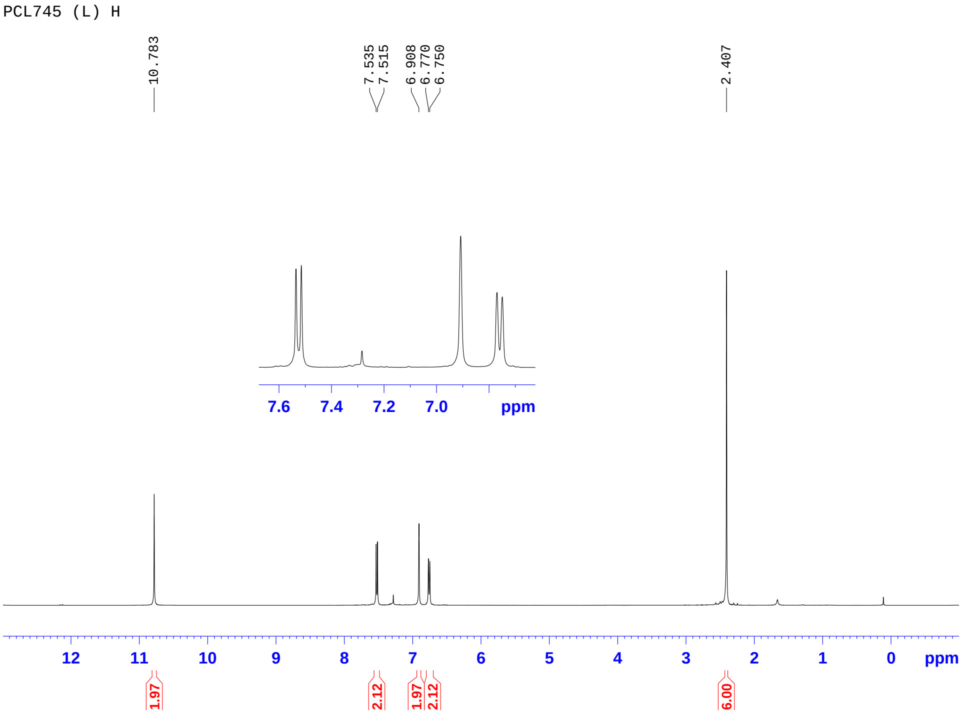


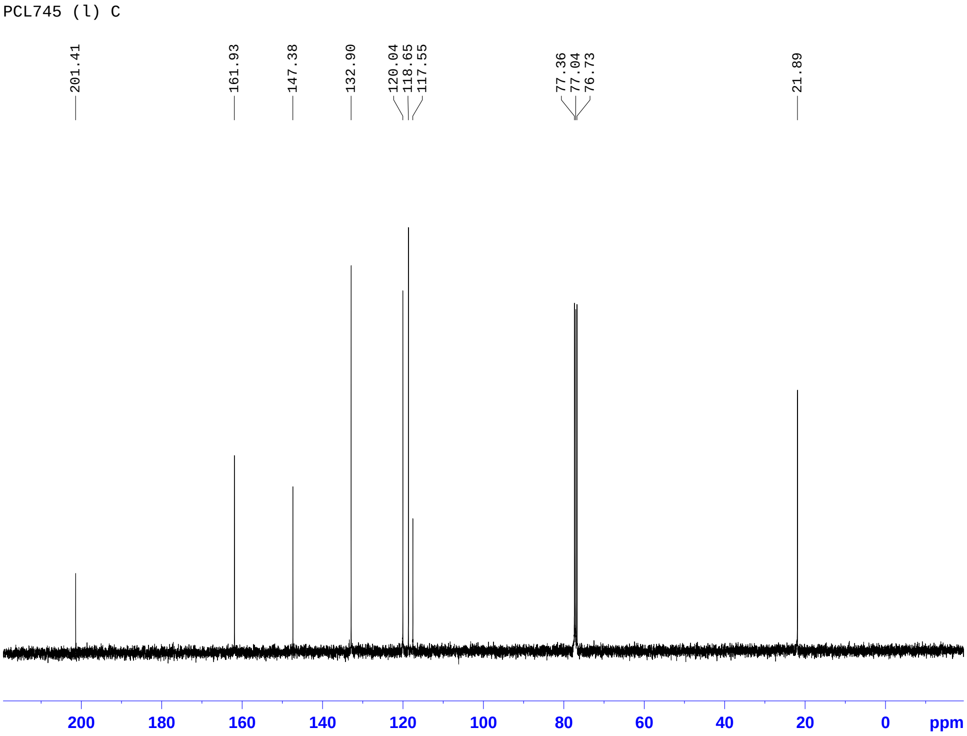




Bis(2-hydroxy-4-methylphenyl)methanone (Table 3.2, entry 7, product 6b)

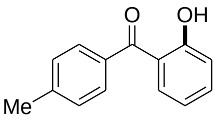




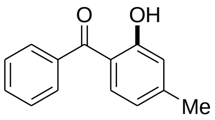


(2-Hydroxyphenyl)(*p*-tolyl)methanone (Table 3.2, entry 8, product 7a)

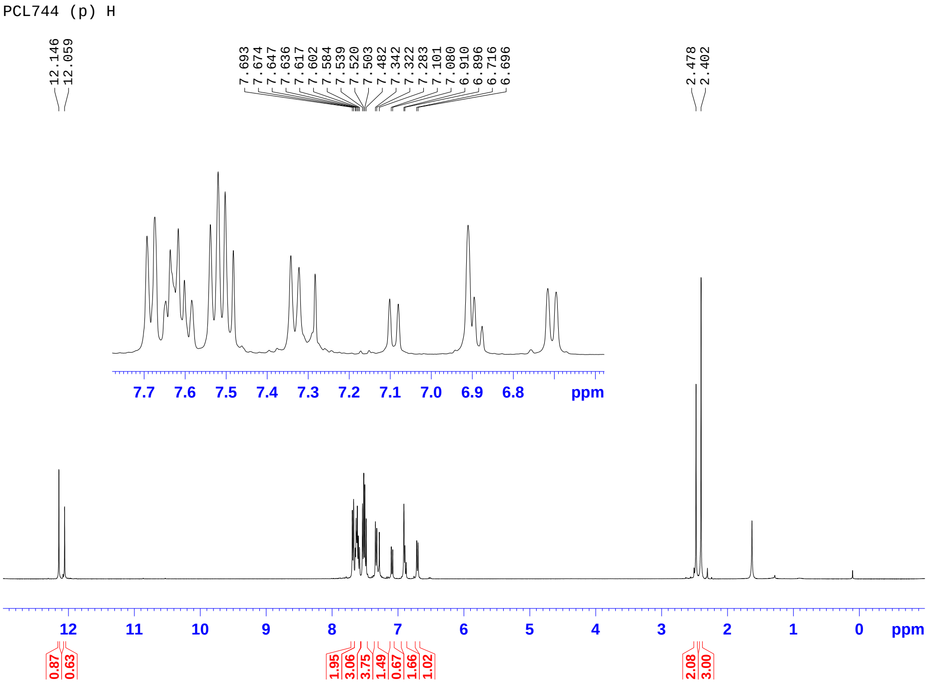
Hydroxy-4-methylphenyl)(phenyl)methanone (Table 3.2, entry 8, product 7b)

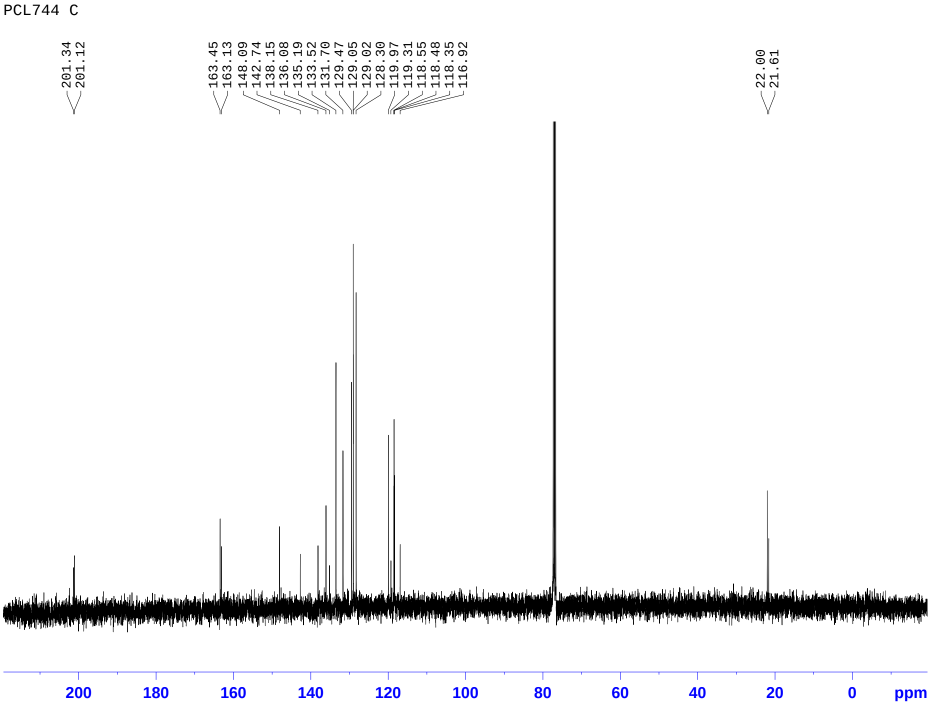


7a

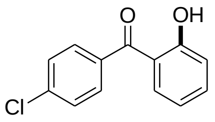


7b





(4-Chlorophenyl)(2-hydroxyphenyl)methanone (Table 3.2, entry 9, product 8a)
(4-Chloro-2-hydroxyphenyl)(phenyl)methanone (Table 3.2, entry 9, product 8b)



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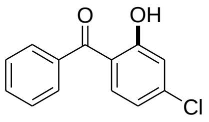

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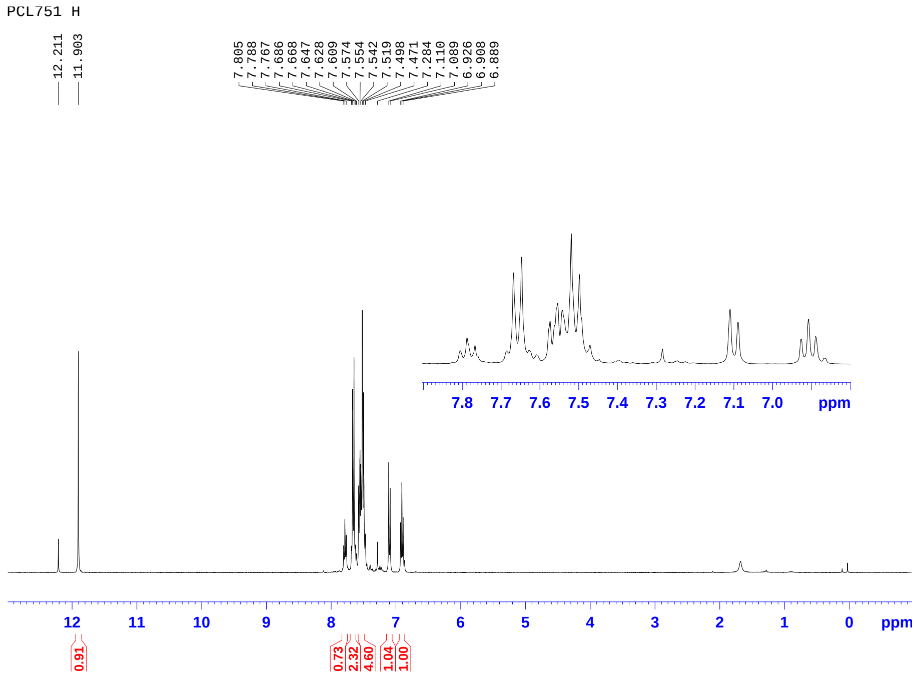
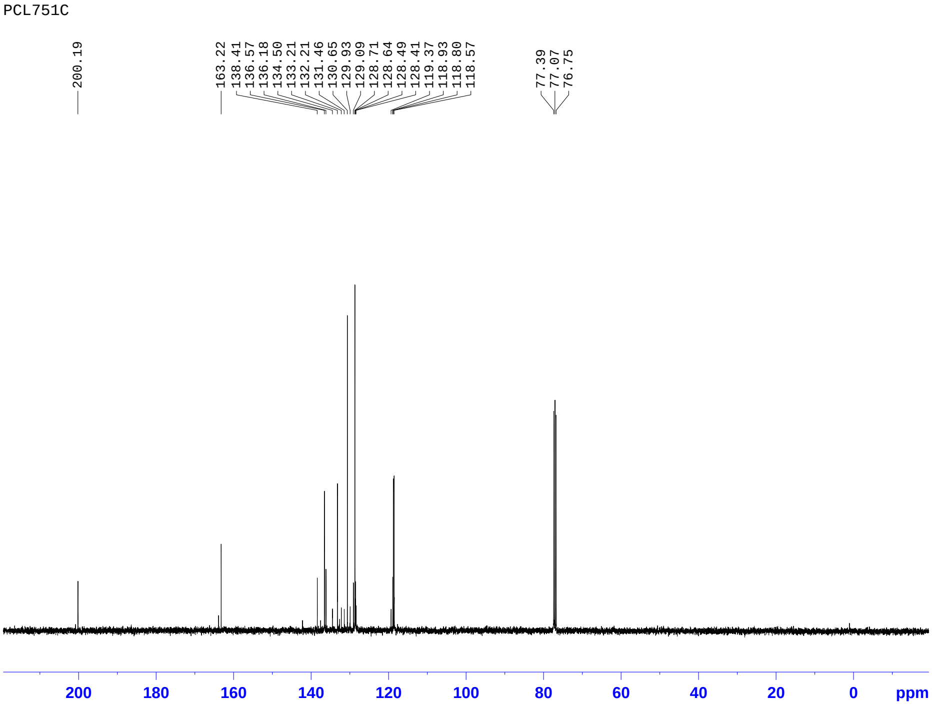
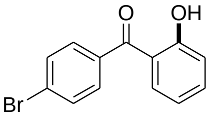




(4-Bromophenyl)(2-hydroxyphenyl)methanone (Table 3.2, entry 10, product 9a)
(4-Bromo-2-hydroxyphenyl)(phenyl)methanone (Table 3.2, entry 10, product 9b)



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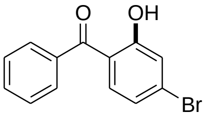

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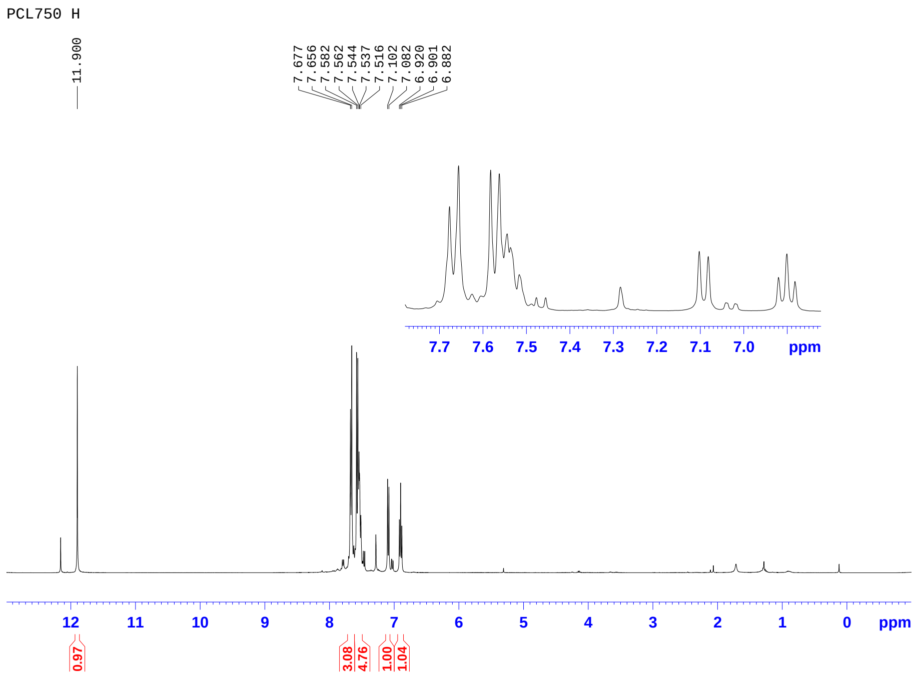
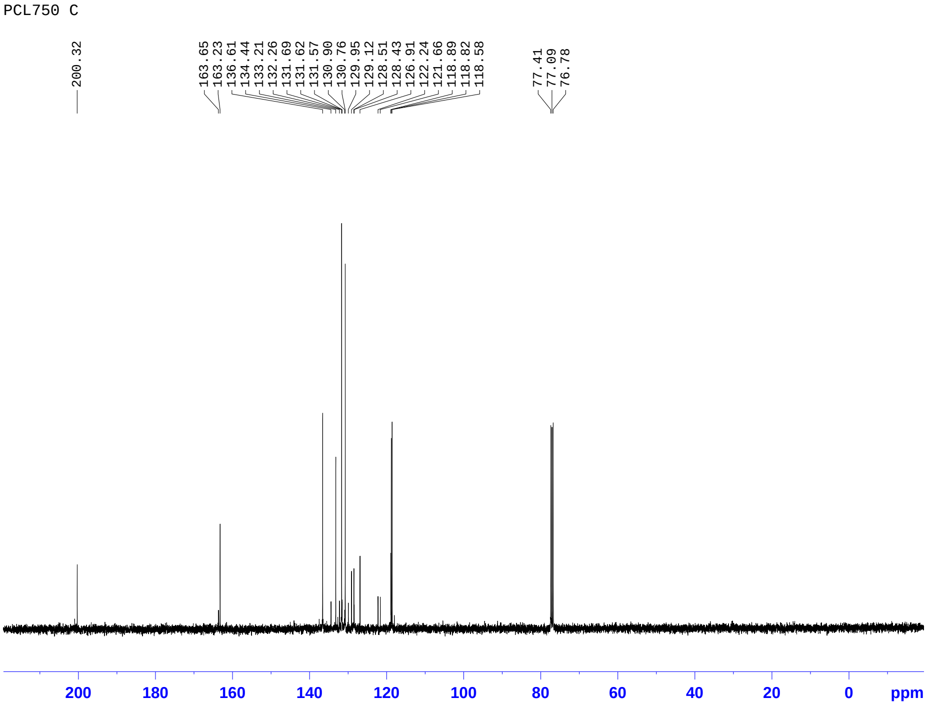
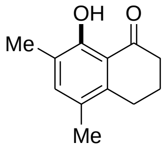
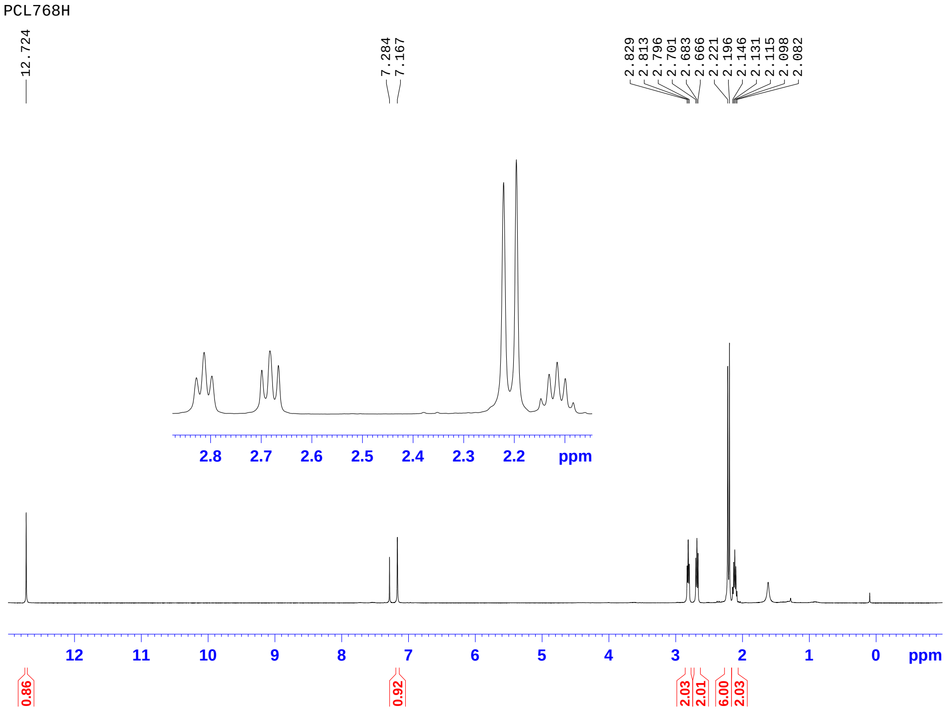
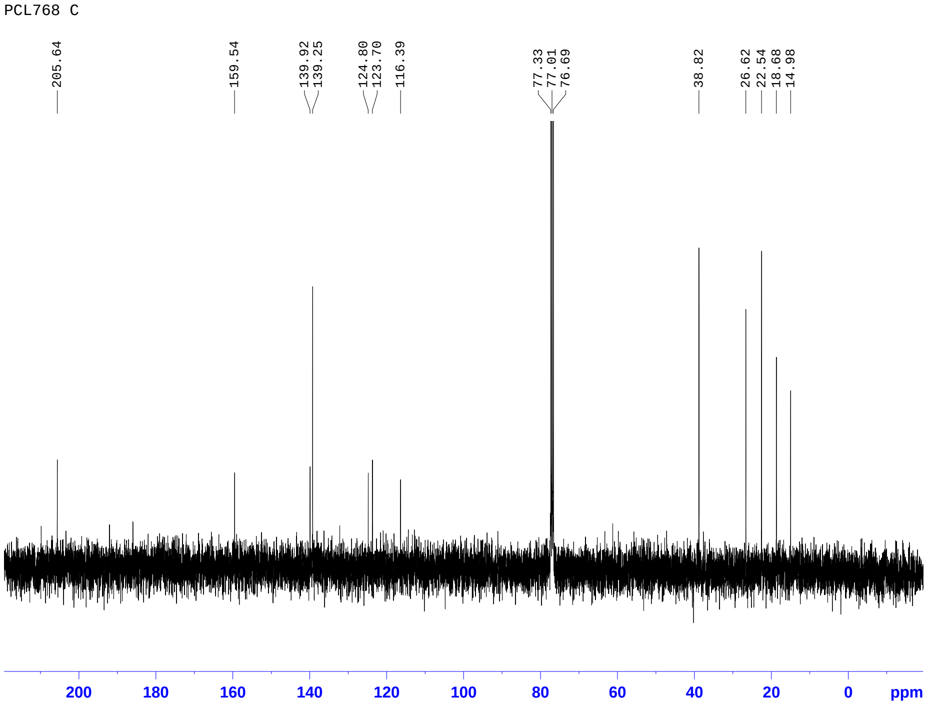




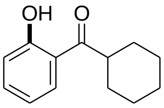
3,4-Dihydro-8-hydroxy-5,7-dimethylnaphthalen-1(2*H*)-one (Scheme 3.2, product 10a)

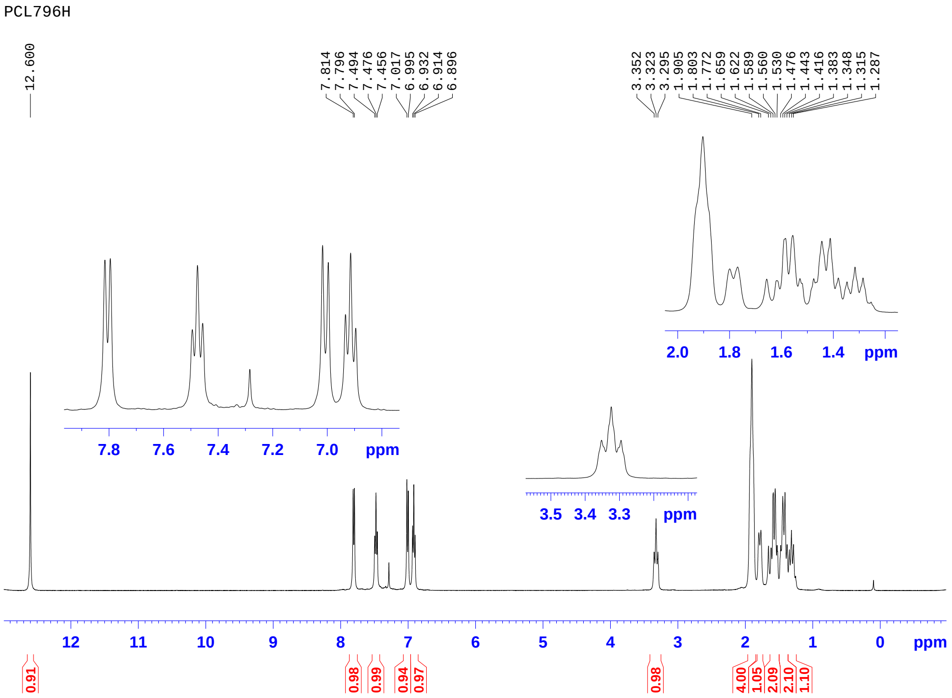


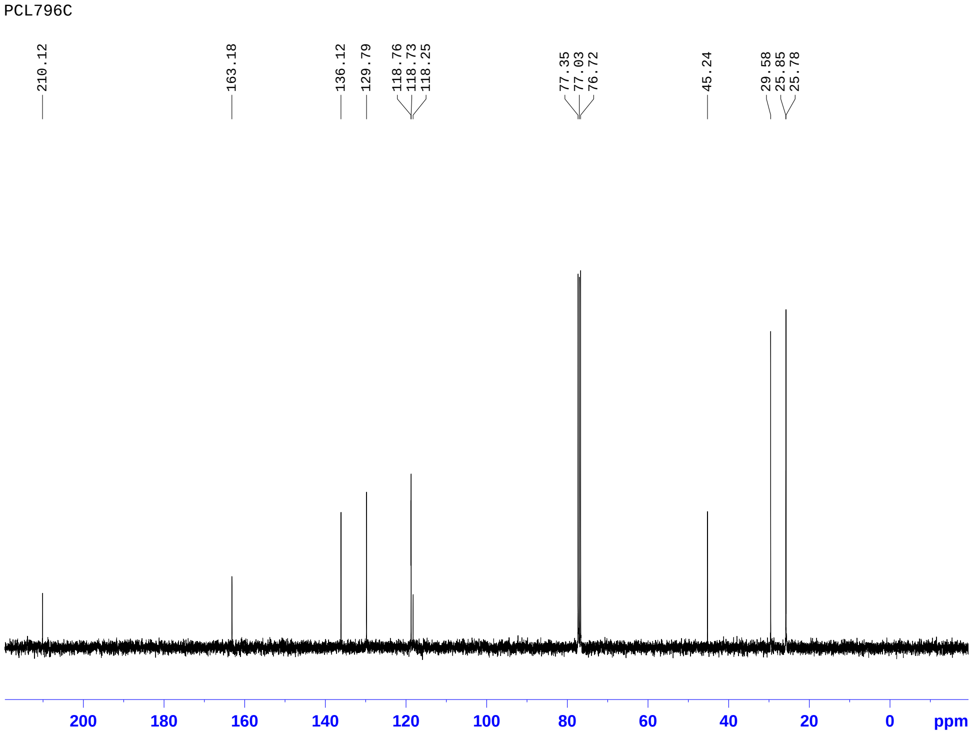




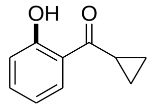
Cyclohexyl(2-hydroxyphenyl)methanone (Scheme 3.2, product 11a)

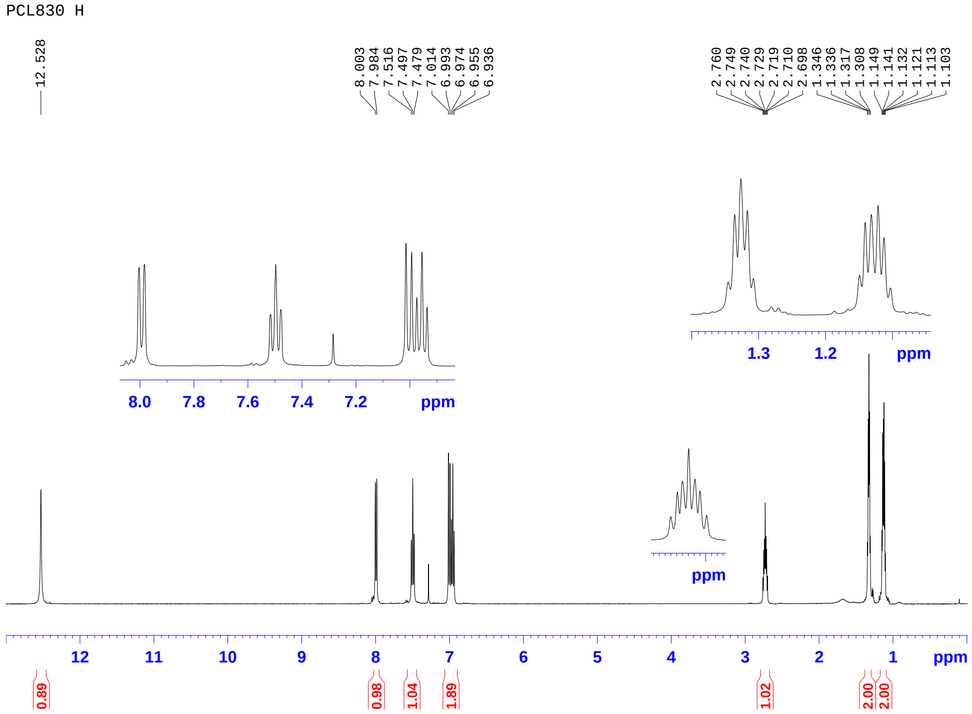


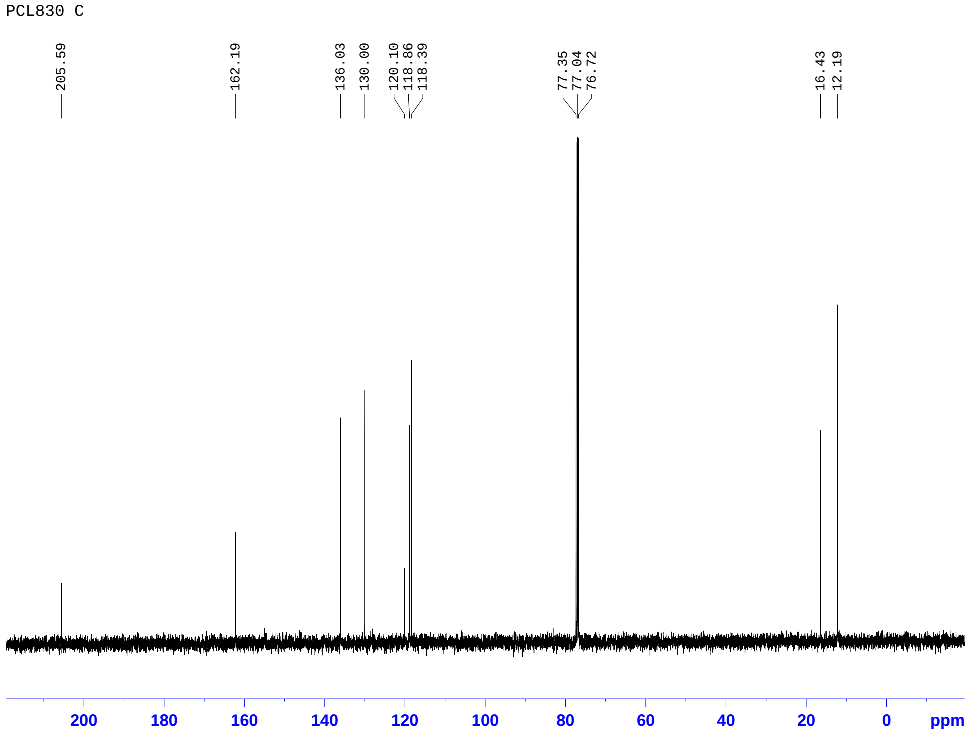




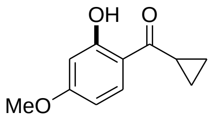
Cyclopropyl(2-hydroxyphenyl)methanone (Scheme 3.2, product 12a)

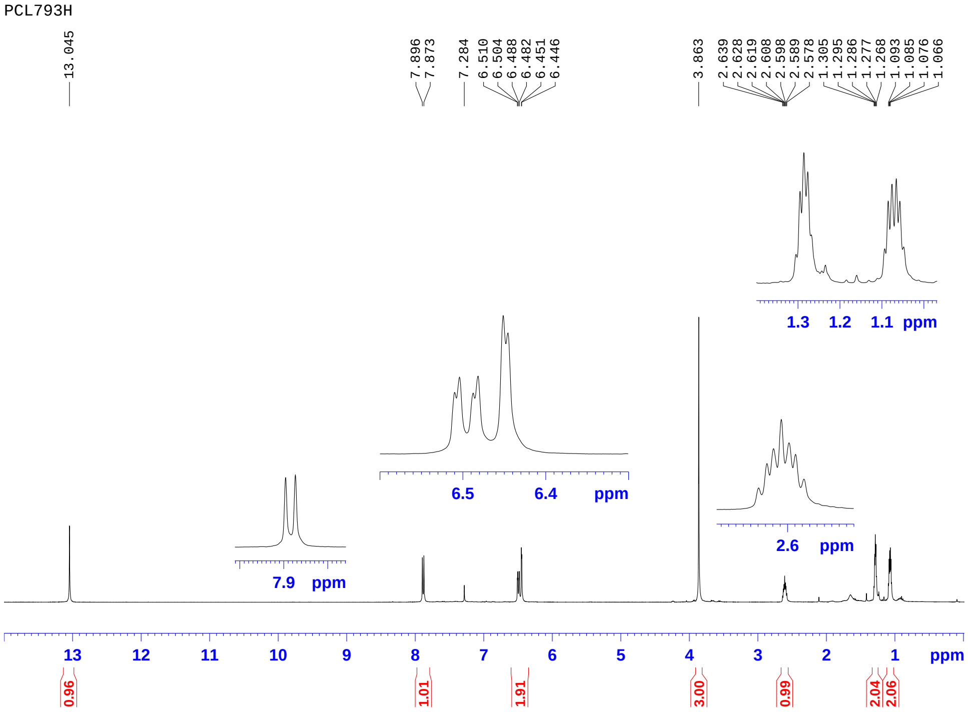


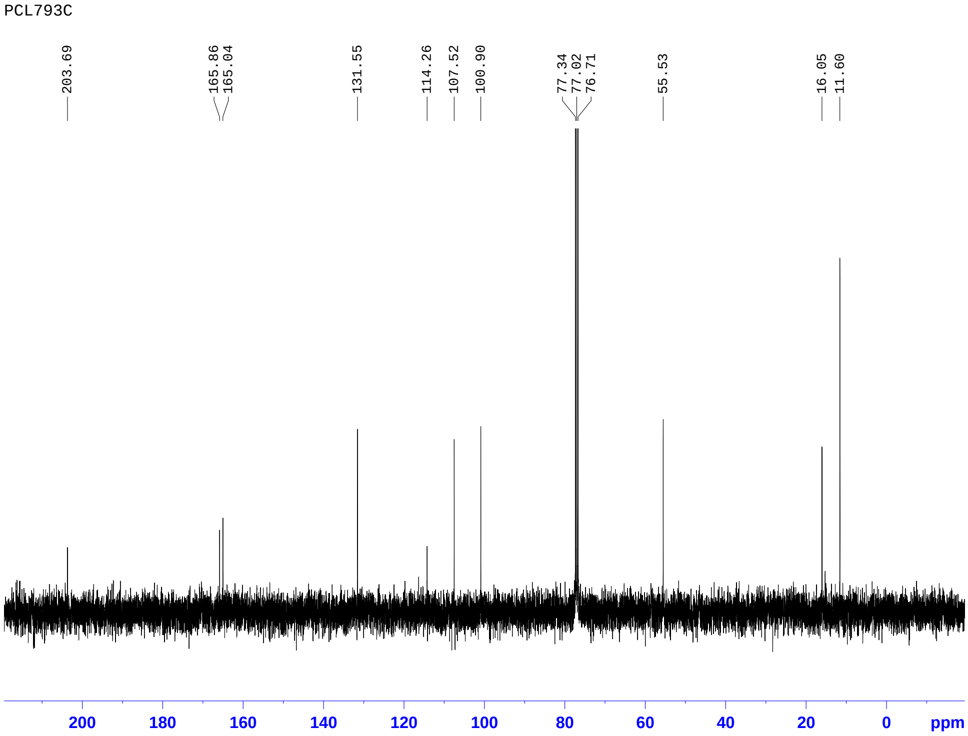




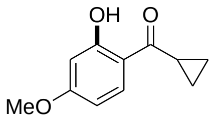
Cyclopropyl(2-hydroxy-4-methoxyphenyl)methanone (Scheme 3.2, product 13a)

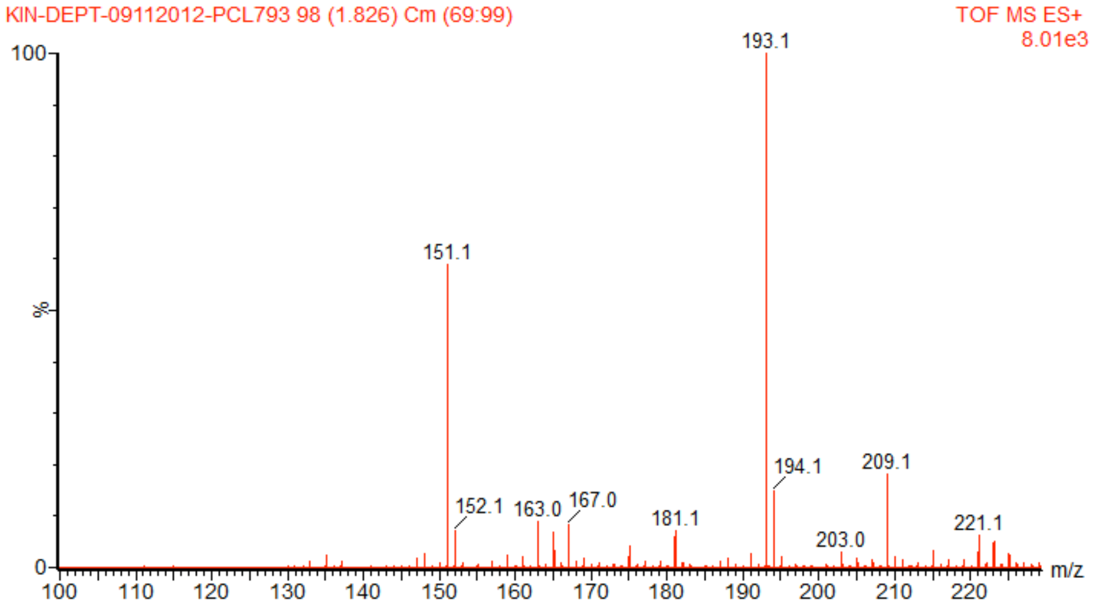


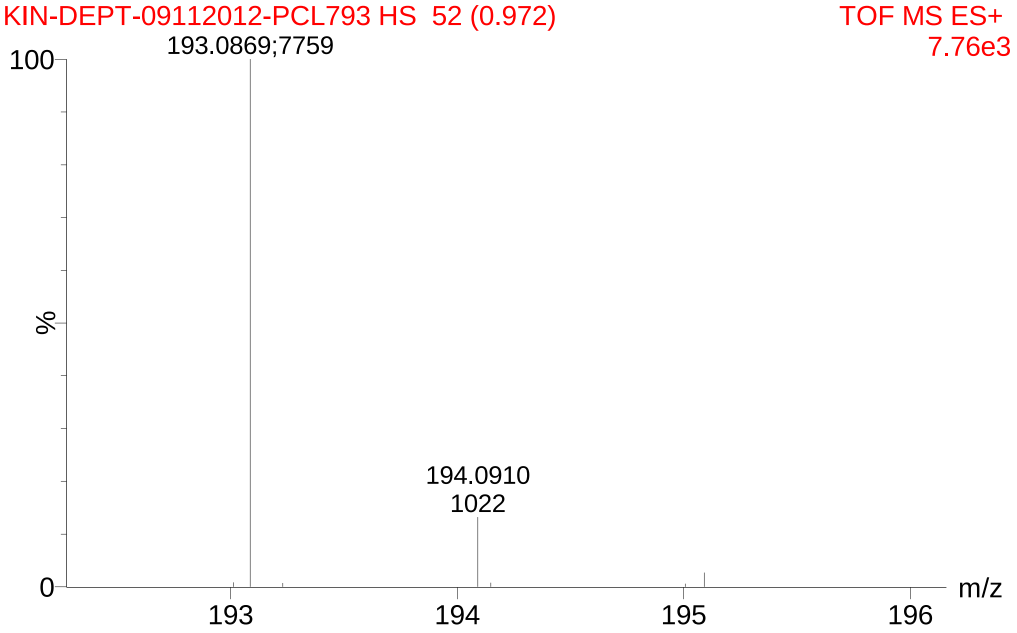




Cyclopropyl(2-hydroxy-4-methoxyphenyl)methanone (Scheme 3.2, product 13a)

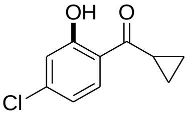


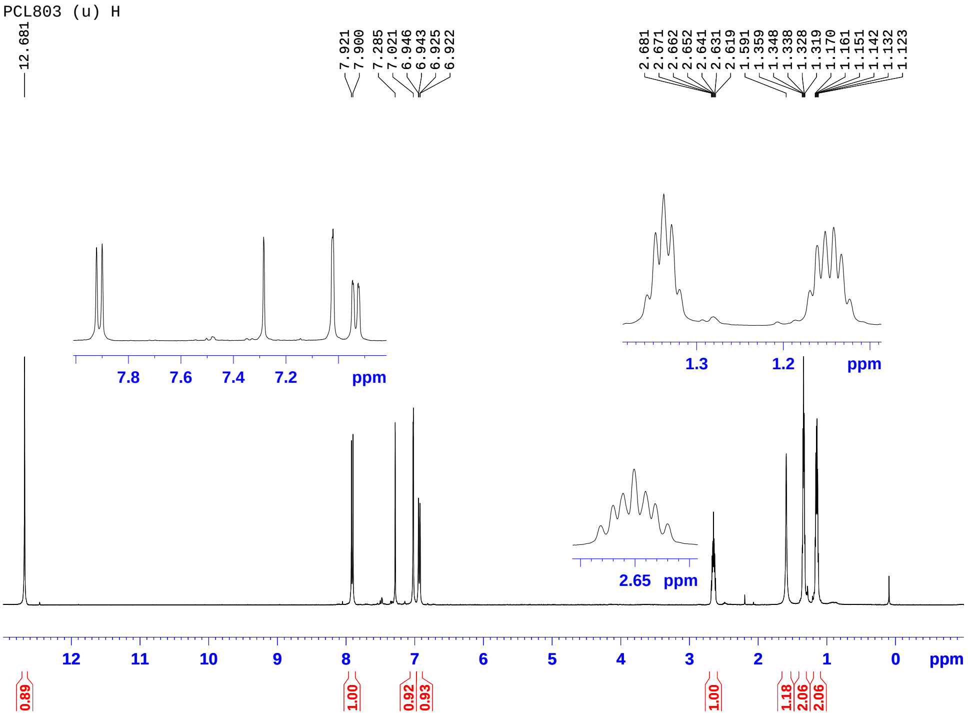


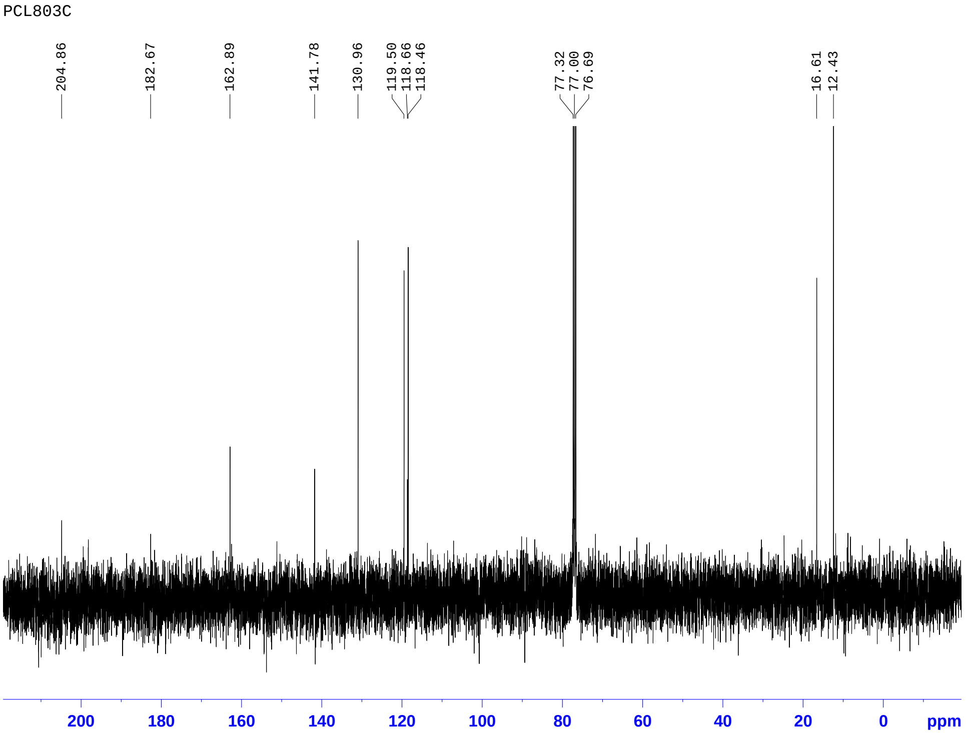


Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
193.0869	193.0865	0.4	2.1	5.5	27.3	C11 H13 O3

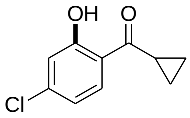
Cyclopropyl(2-hydroxy-4-chlorophenyl)methanone (Scheme 3.2, product 14a)

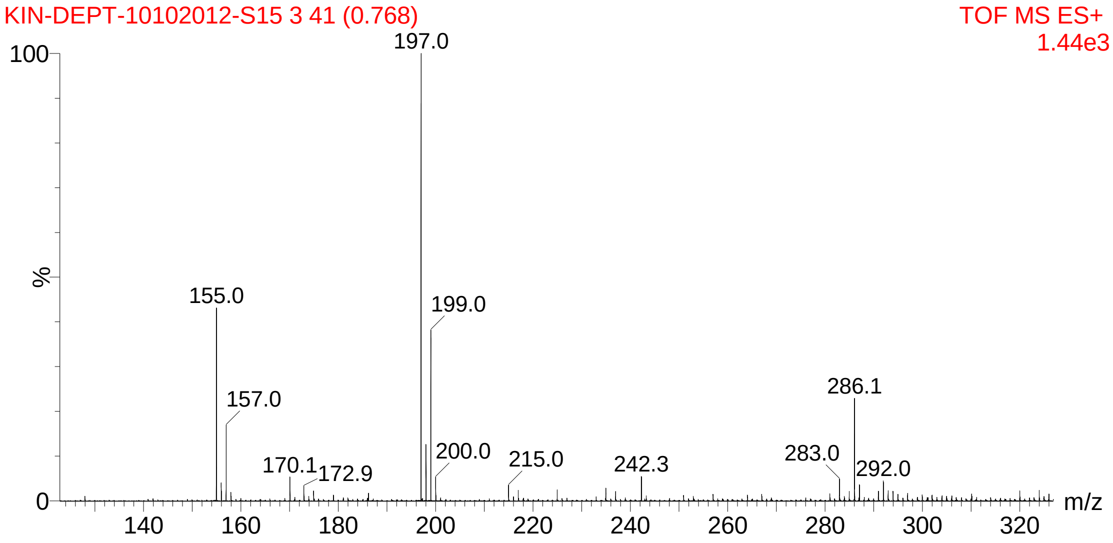


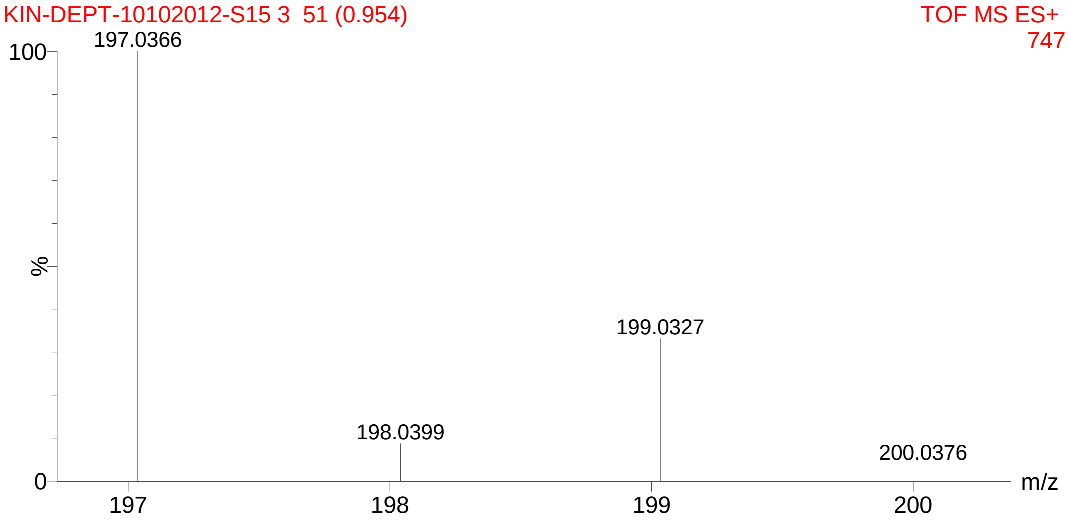




Cyclopropyl(2-hydroxy-4-chlorophenyl)methanone (Scheme 3.2, product 14a)







Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
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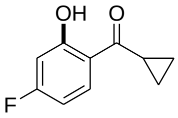
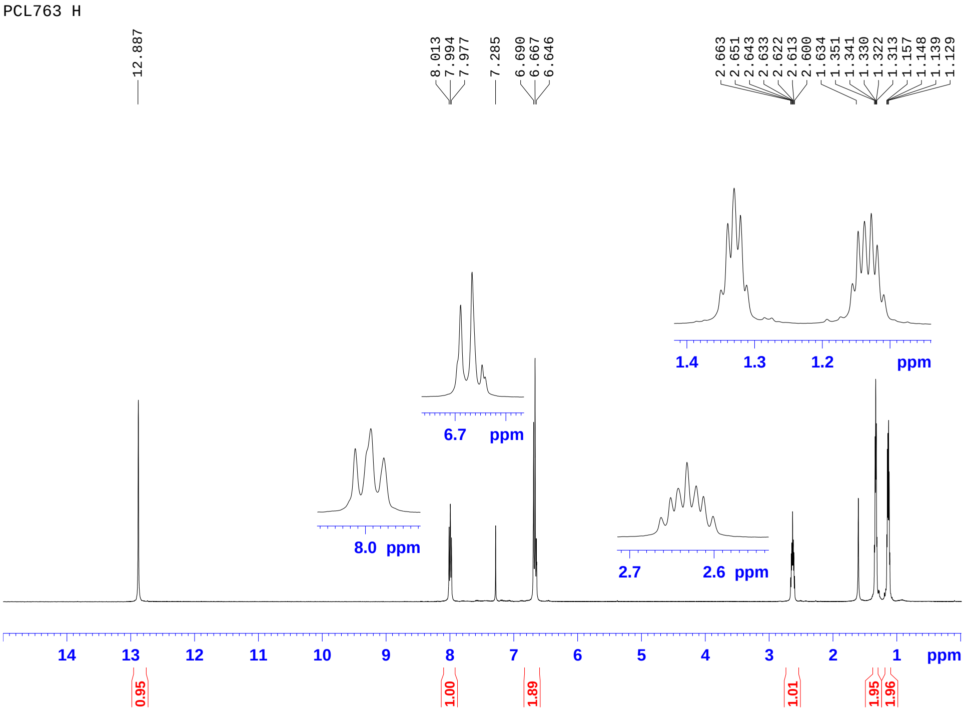
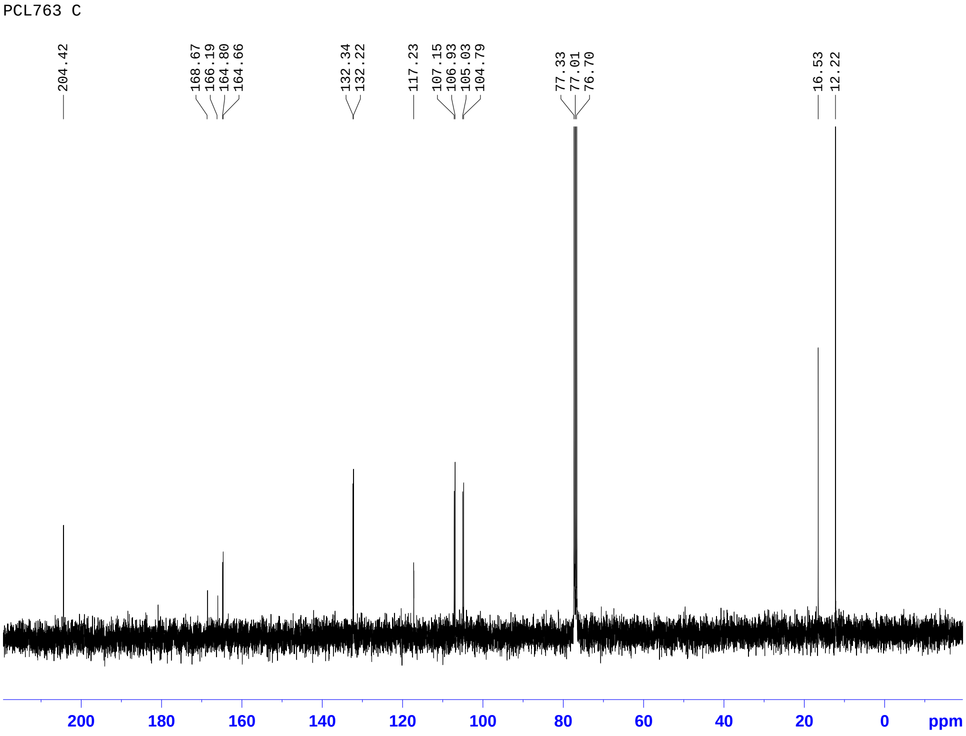
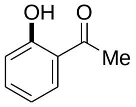
Cyclopropyl(2-hydroxy-4-fluorophenyl)methanone (Scheme 3.2, product 15a)

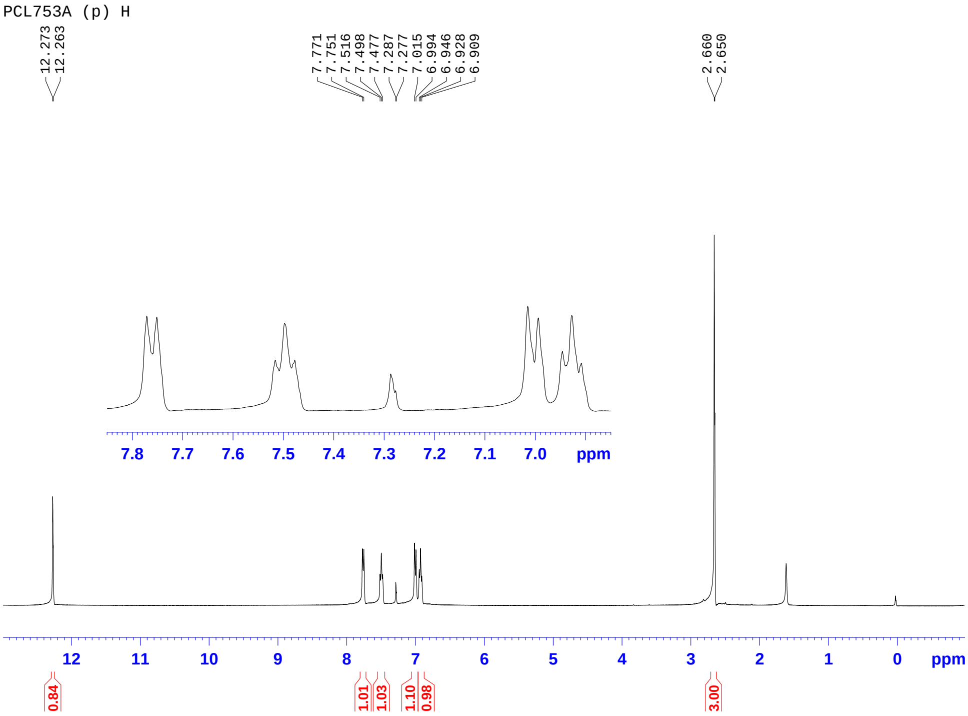


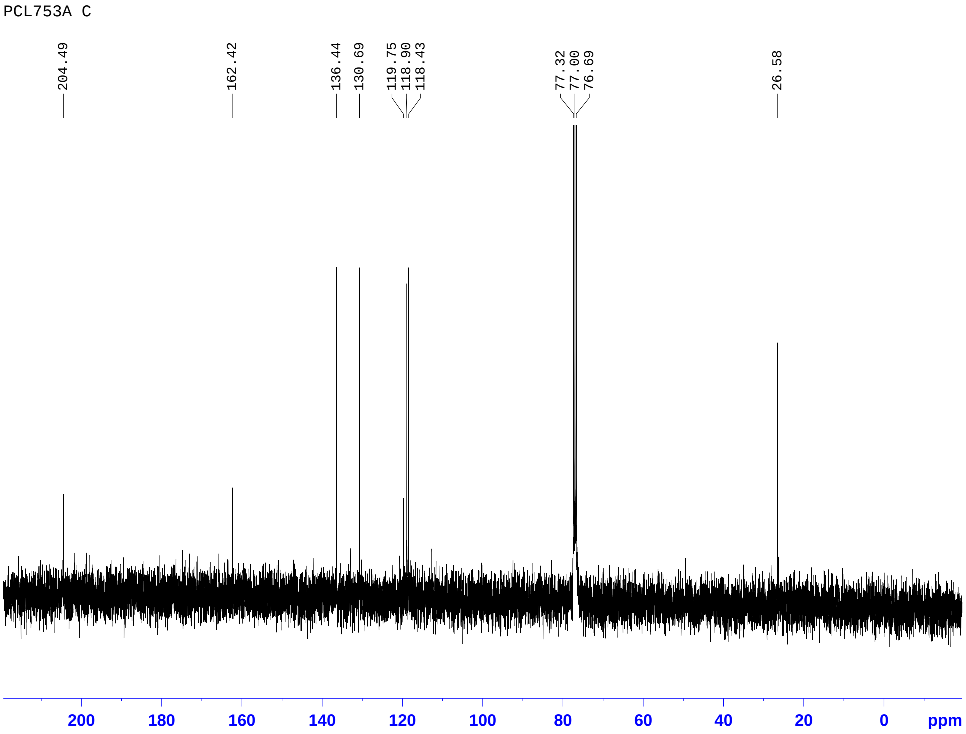




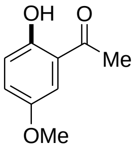
1-(2-Hydroxyphenyl)ethanone (Scheme 3.2, product 16a)

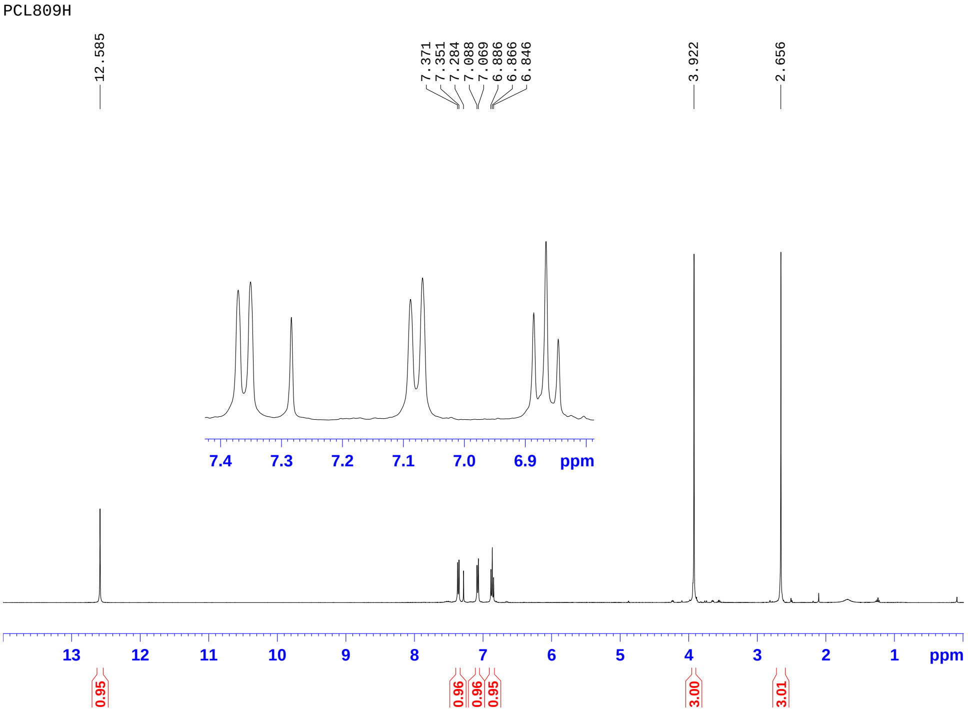


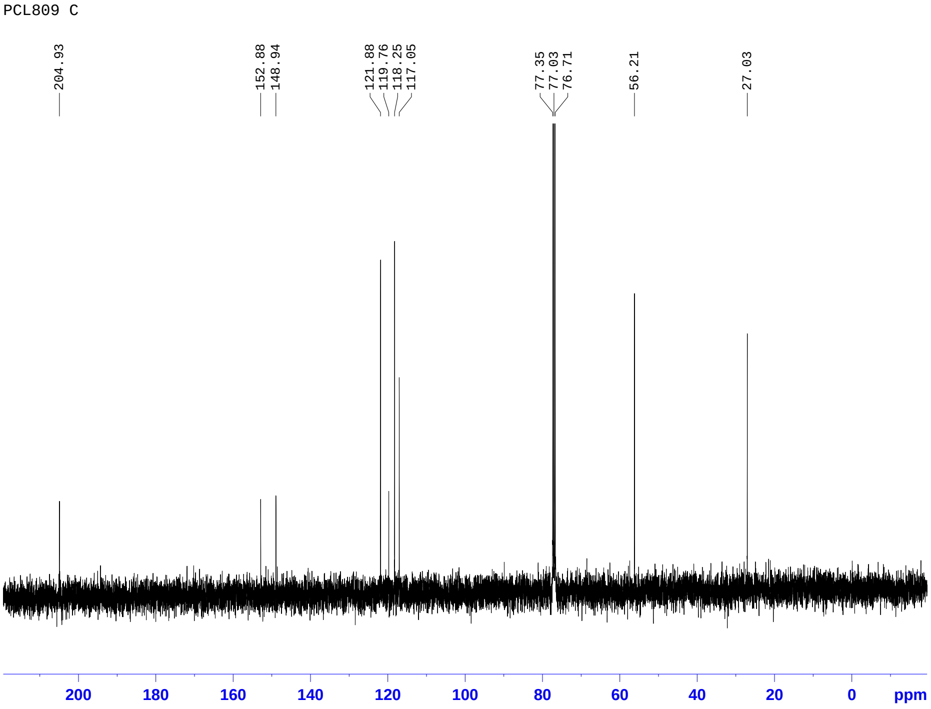




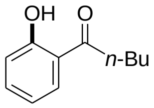
1-(2-Hydroxy-5-methoxyphenyl)ethanone (Scheme 3.2, product 17a)

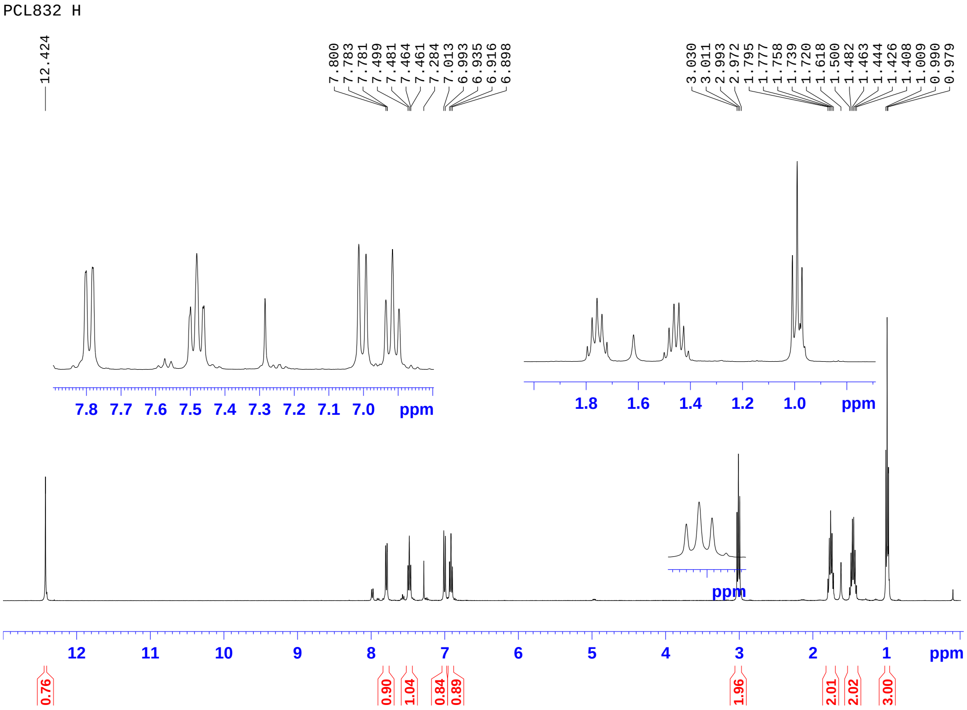


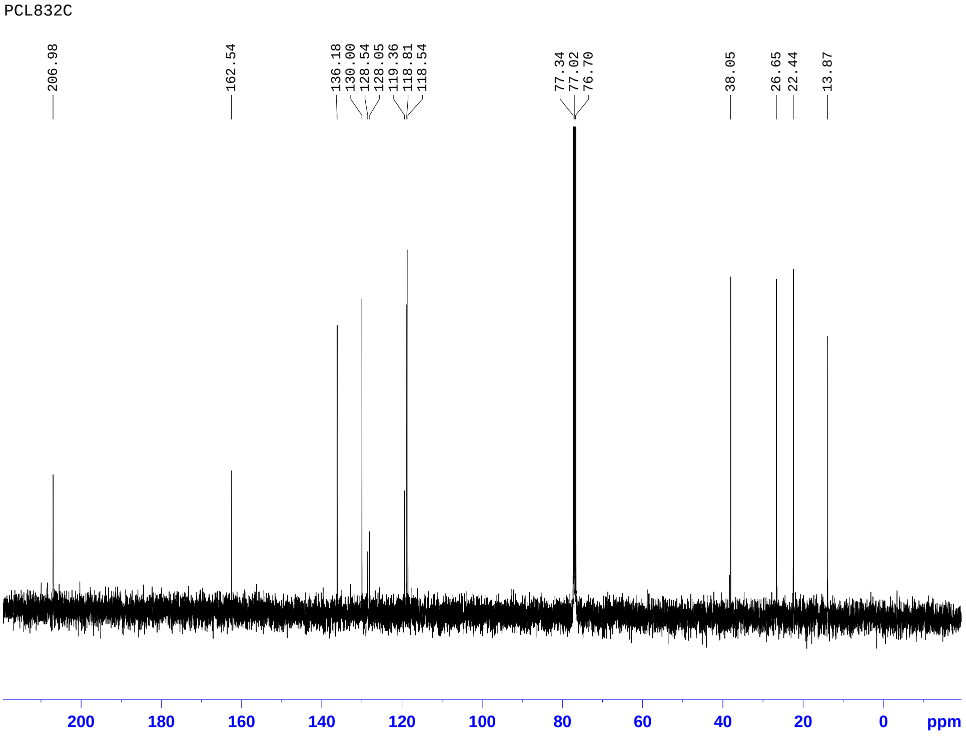




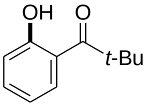
1-(2-Hydroxyphenyl)pentan-1-one (Scheme 3.2, product 18a)

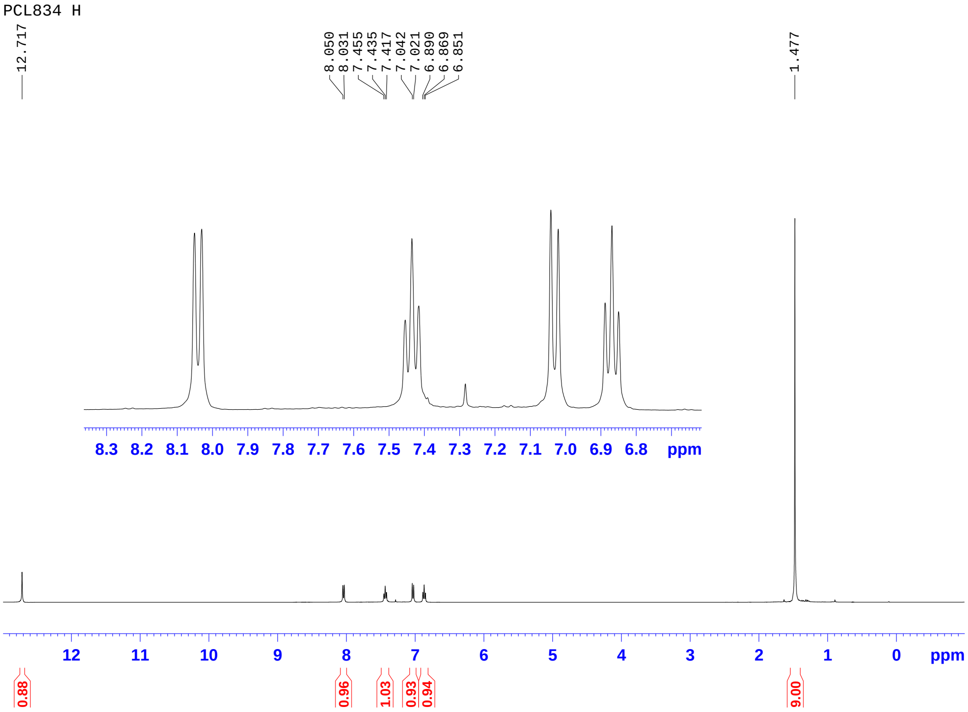


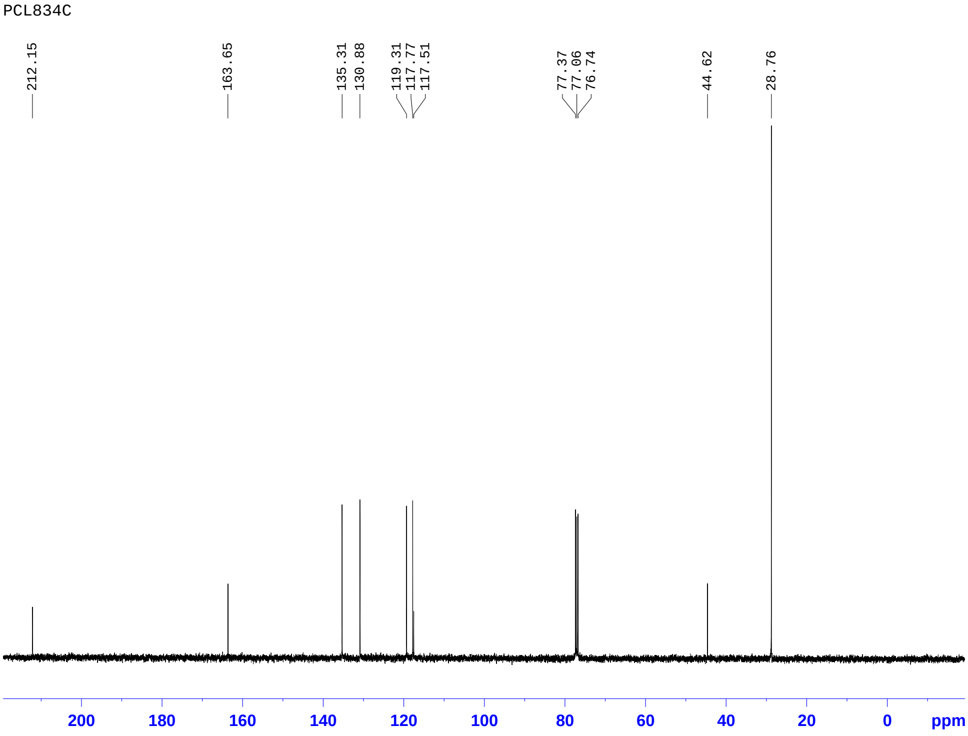




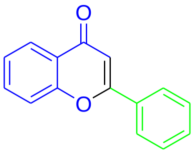
1-(2-Hydroxyphenyl)-2,2-dimethylpropan-1-one (Scheme 3.2, product 19a)

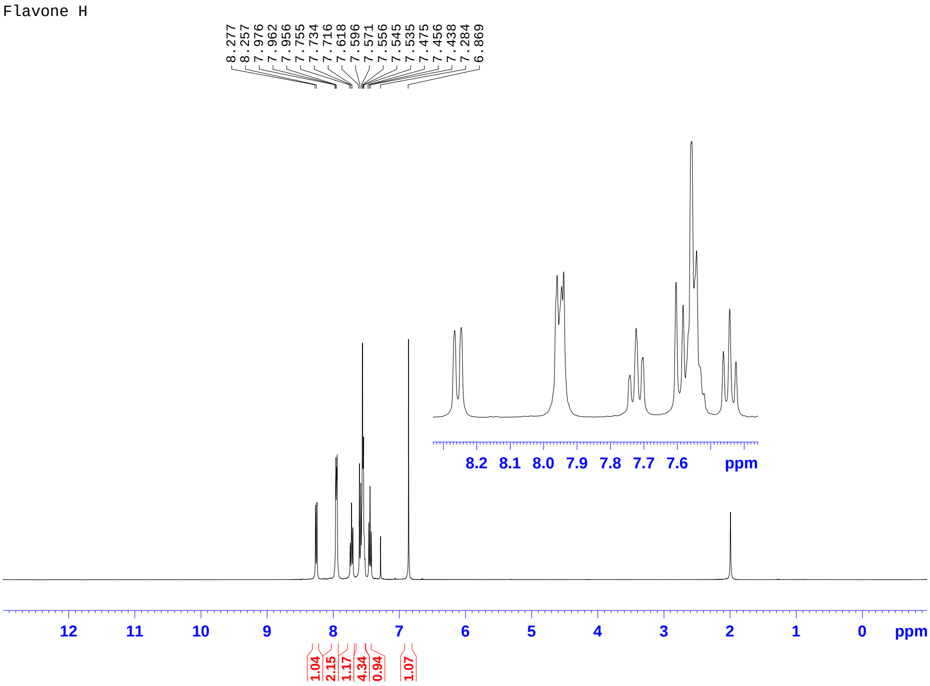


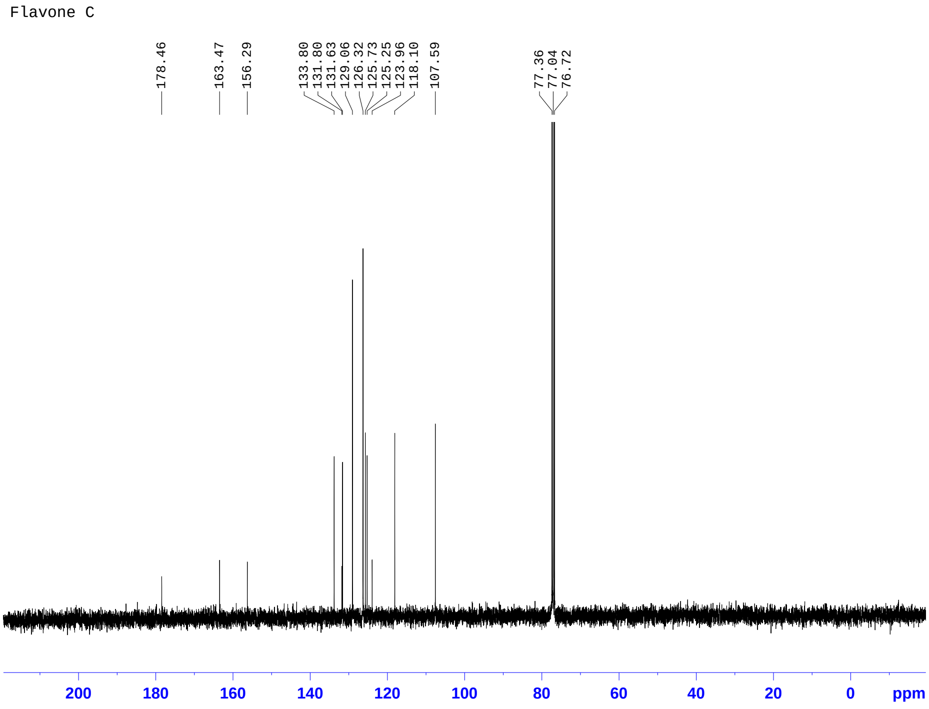




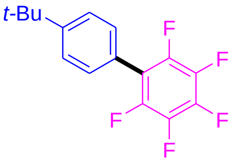
2-Phenyl-4*H*-chromen-4-one (Scheme 3.3, product 20)

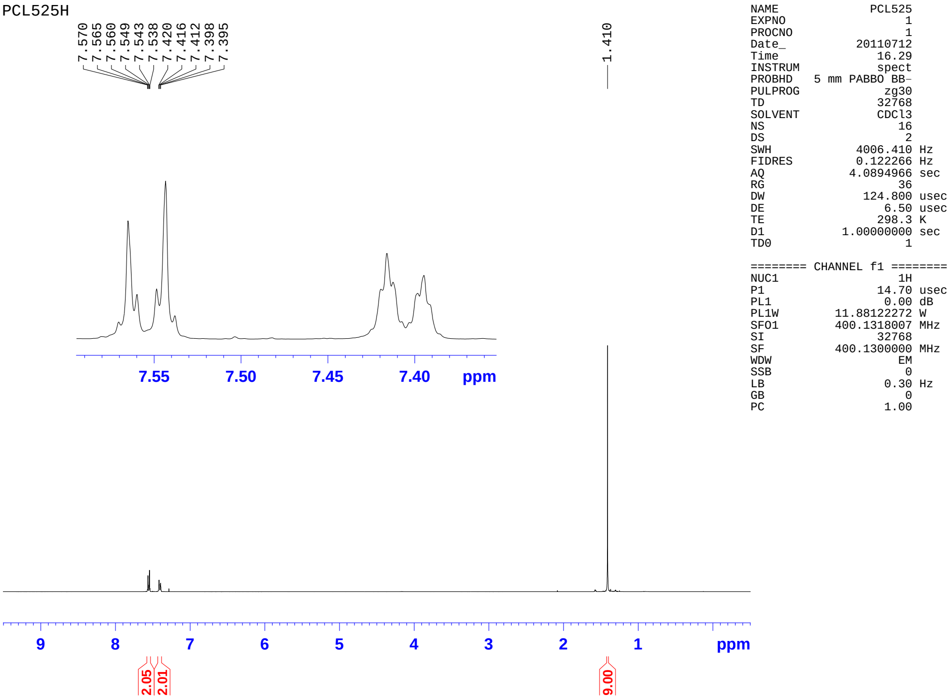






2,3,4,5,6-Pentafluoro-4'-*tert*-butylbiphenyl (Table 4.3, 4.4; Product 23aa)





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PROCNO                 1
Date_           20110712
Time               16.29
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                    36
DW               124.800 usec
DE                  6.50 usec
TE                 298.3 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
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LB                  0.30 Hz
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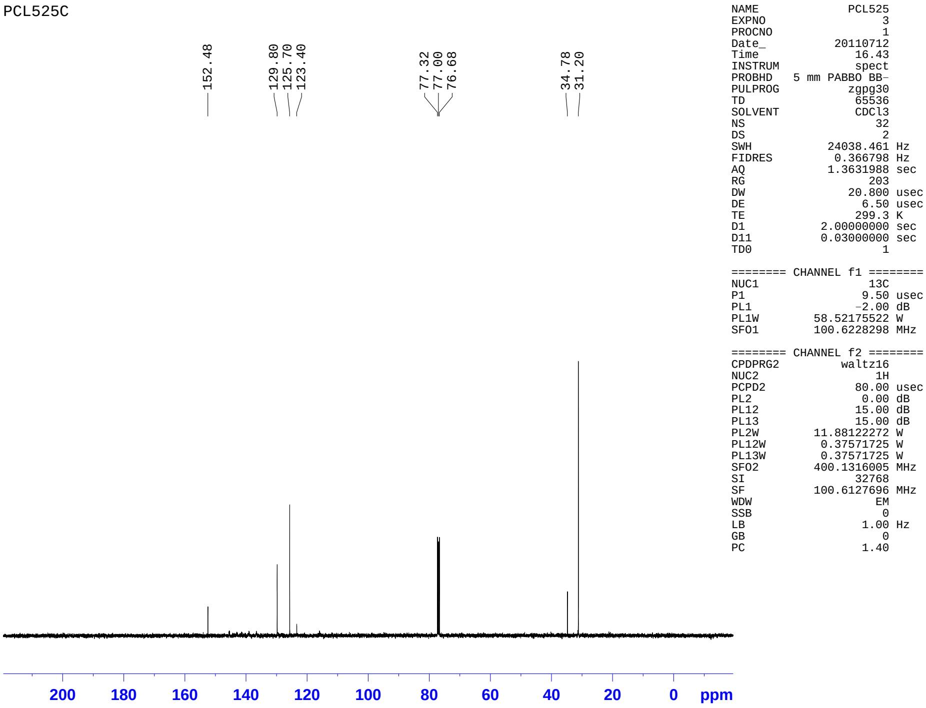
PC                  1.00
```



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TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   203
DW                20.800 usec
DE                  6.50 usec
TE                 299.3 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127696 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
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PC                  1.40
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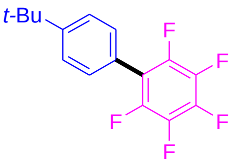
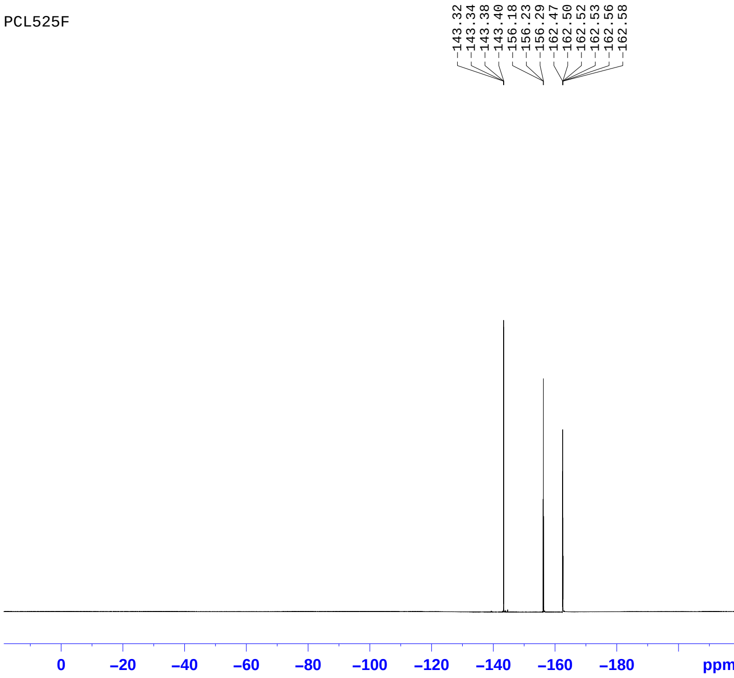
2,3,4,5,6-Pentafluoro-4'-*tert*-butylbiphenyl (Table 4.3, 4.4; Product 23aa)





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TD              131072
SOLVENT          CDCl3
NS                  16
DS                   4
SWH          89285.711 Hz
FIDRES        0.681196 Hz
AQ           0.7340532 sec
RG                 203
DW               5.600 usec
DE                6.50 usec
TE               298.5 K
D1          1.00000000 sec
D11         0.03000000 sec
D12         0.00002000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               19F
P1               14.20 usec
PL1              -3.00 dB
PL1W       18.69428444 W
SFO1       376.4607164 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2            80.00 usec
PL2               0.00 dB
PL12             15.00 dB
PL2W       11.88122272 W
PL12W       0.37571725 W
SFO2       400.1316005 MHz
SI               65536
SF         376.4983660 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.00
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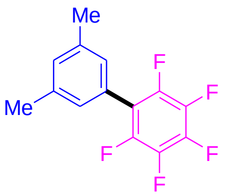
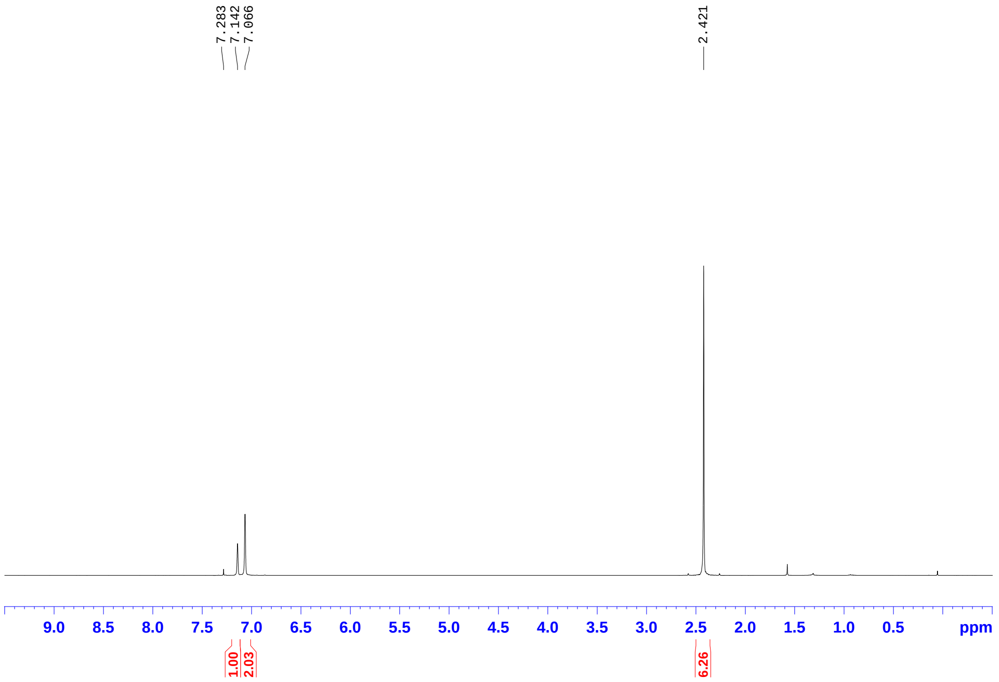
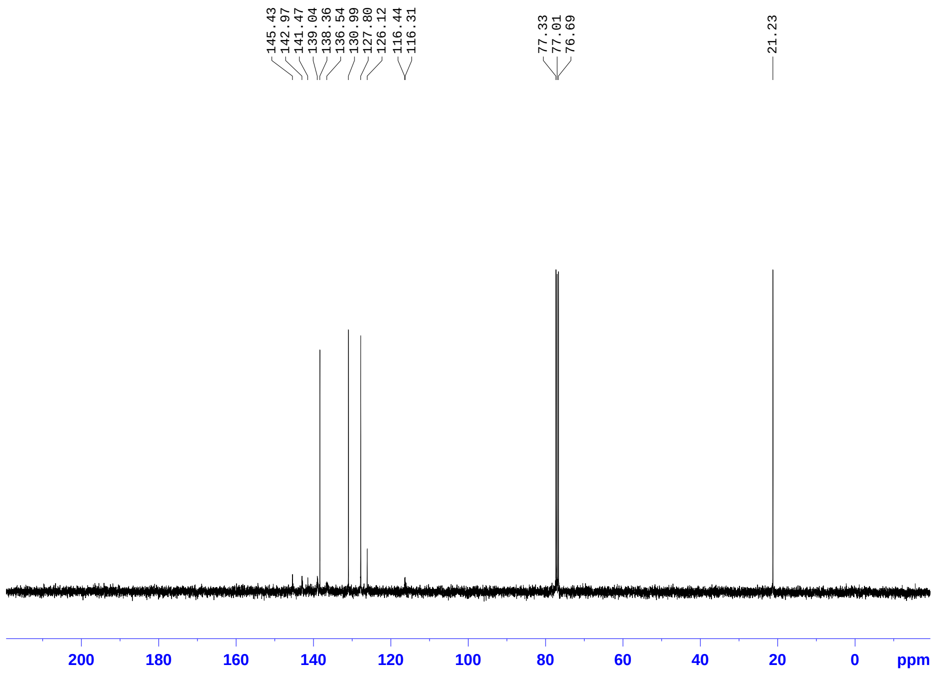
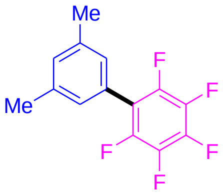
2,3,4,5,6-Pentafluoro-3',5'-dimethyl-1,1'-biphenyl (Table 4.3, 4.4; Product 23ab)

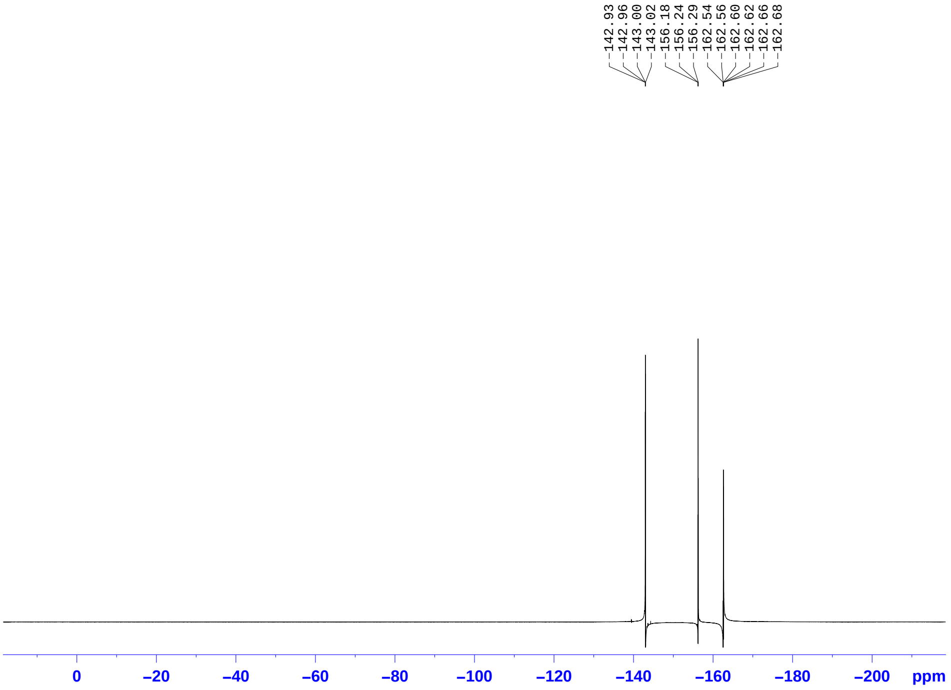




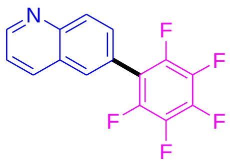


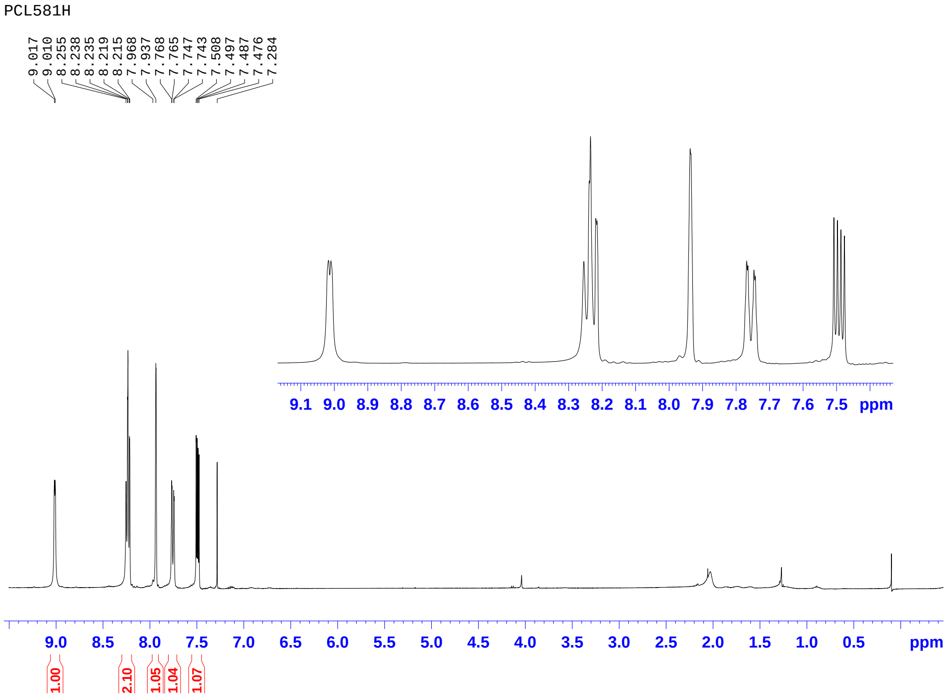
2,3,4,5,6-Pentafluoro-3',5’-dimethyl-1,1’-biphenyl (Table 4.3, 4.4; Product 23ab)

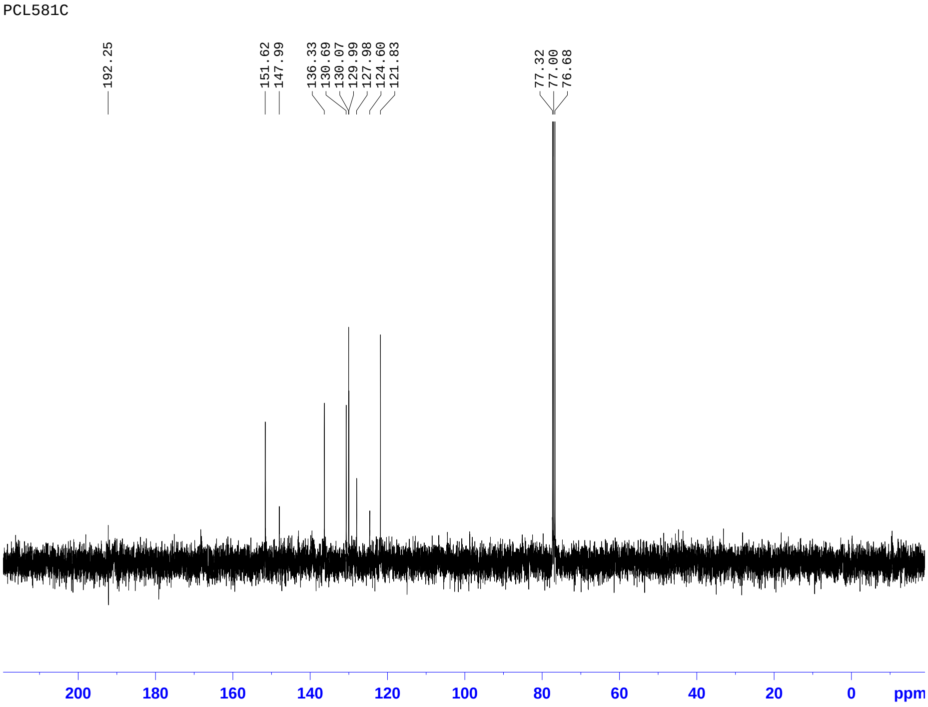




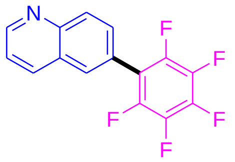
6'-(2,3,4,5,6-Pentafluorophenyl)quinoline (Table 4.3, 4.5; Product 23ac)

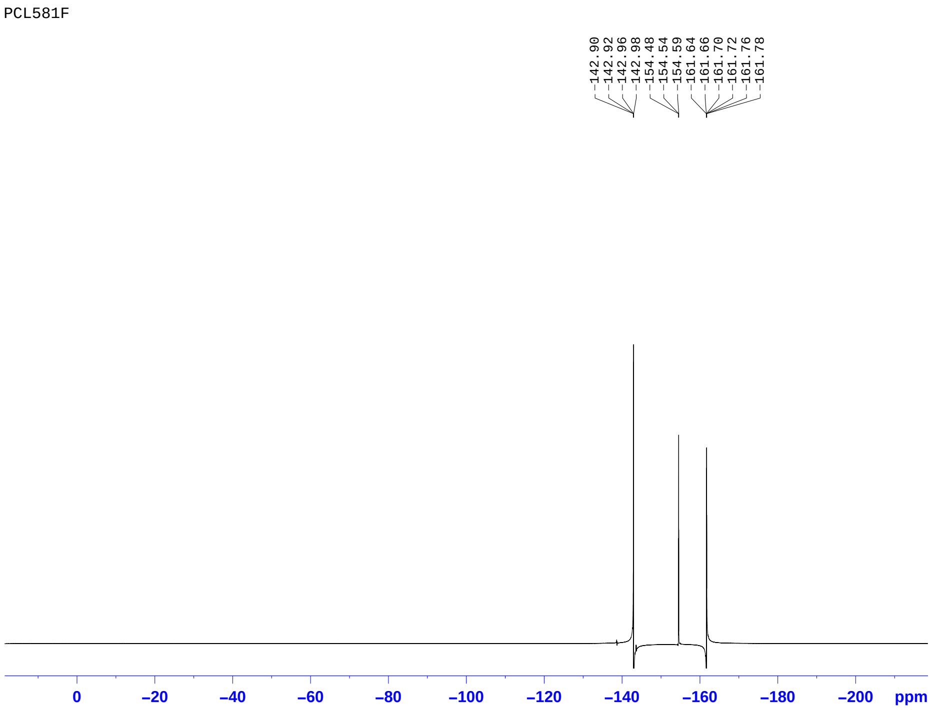


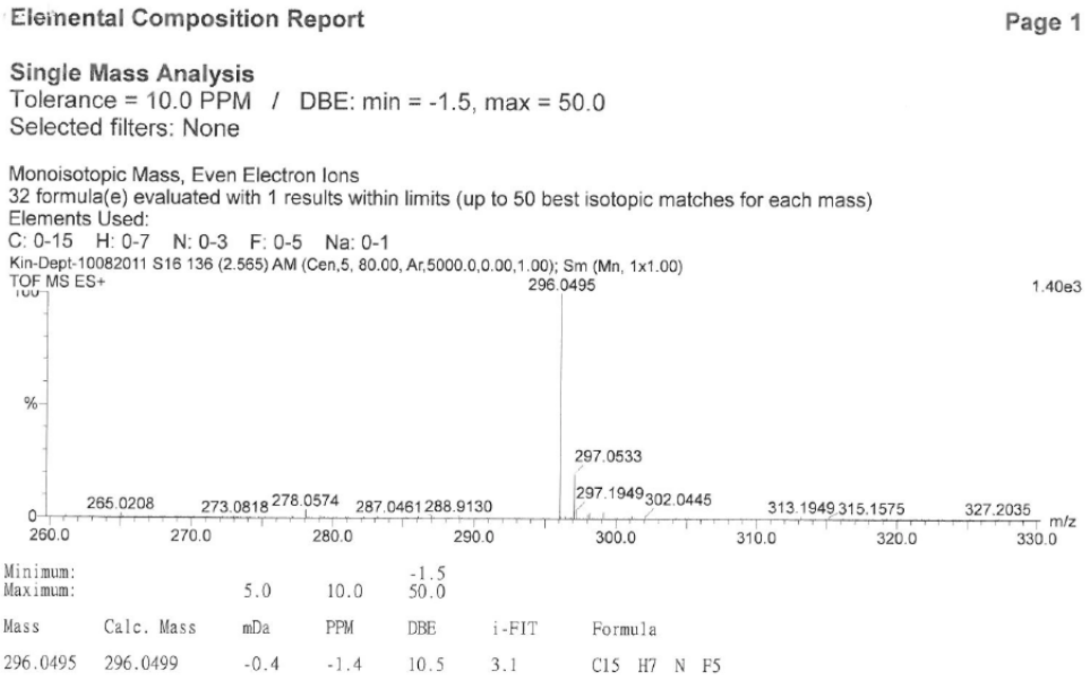




6'-(2,3,4,5,6-Pentafluorophenyl)quinoline (Table 4.3, 4.5; Product 23ac)







Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

32 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

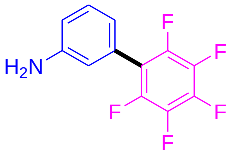
C: 0-15 H: 0-7 N: 0-3 F: 0-5 Na: 0-1

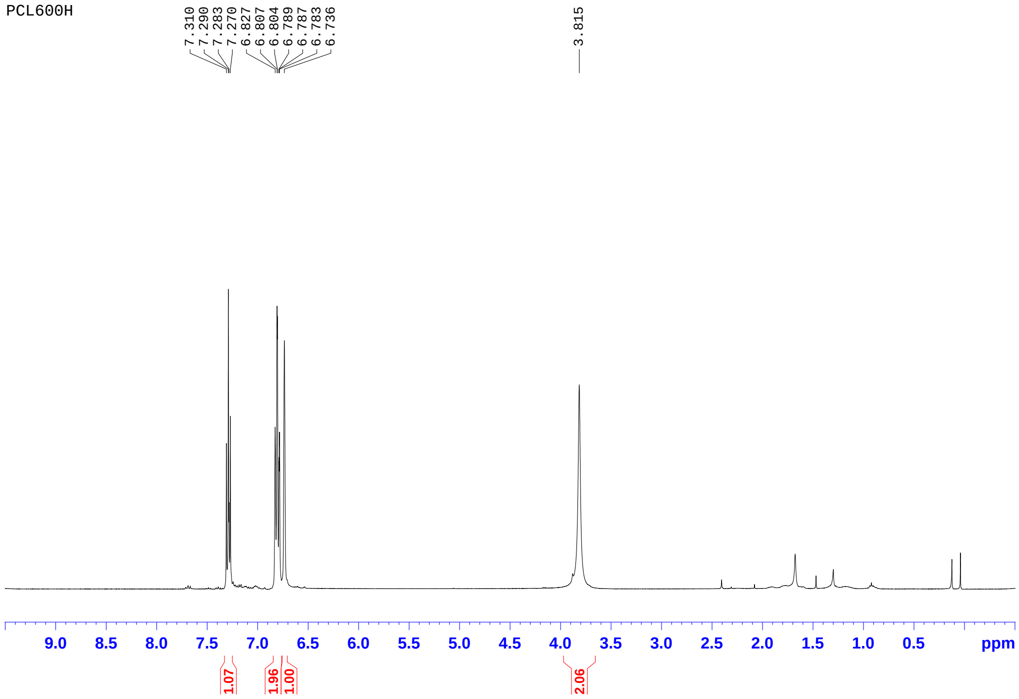
Kin-Dept-10082011 S16 136 (2.565) AM (Cen,5, 80.00, Ar,5000.0,0.00,1.00); Sm (Mn, 1x1.00)

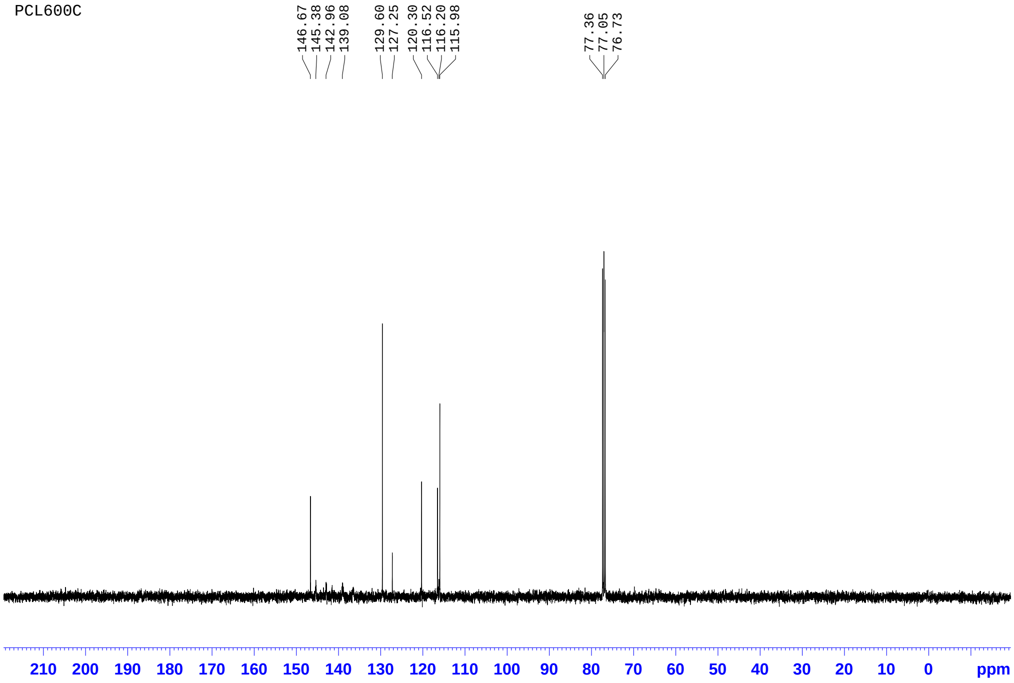
TOF MS ES+

Minimum:				-1.5		
Maximum:		5.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
296.0495	296.0499	-0.4	-1.4	10.5	3.1	C15 H7 N F5

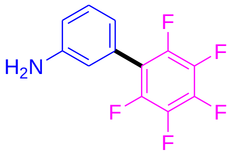
2,3,4,5,6-Pentafluoro-3'-aminobiphenyl (Table 4.3, 4.5; Product 23ad)

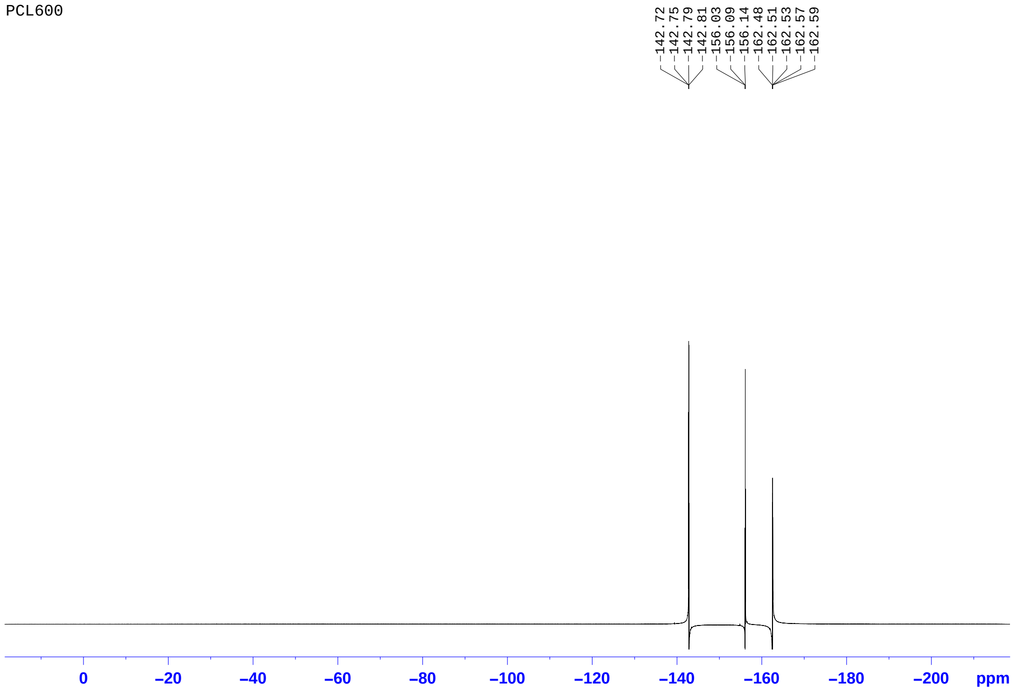




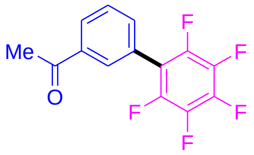


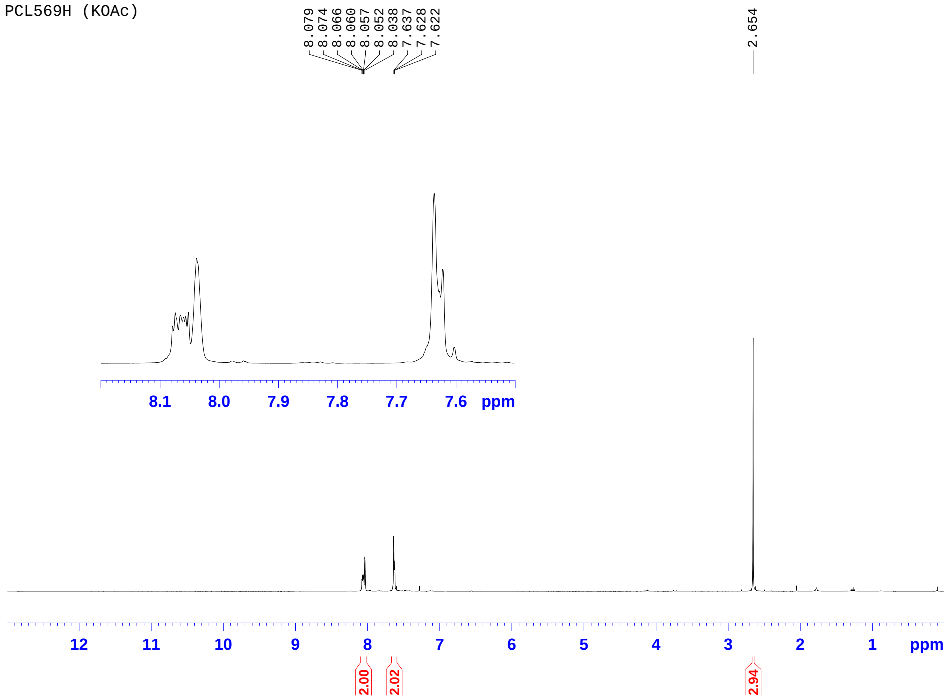
2,3,4,5,6-Pentafluoro-3'-aminobiphenyl (Table 4.3, 4.5; Product 23ad)

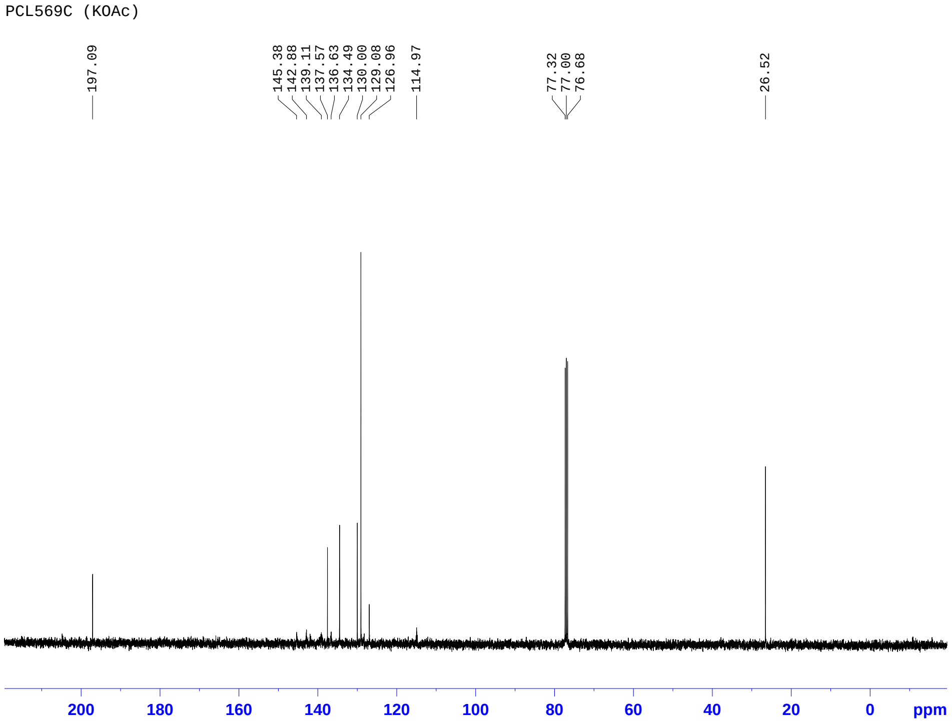




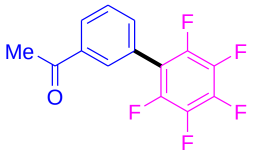
3'-(2,3,4,5,6-Pentafluorophenyl)acetophenone (Table 4.3, 4.5; Product 23ae)

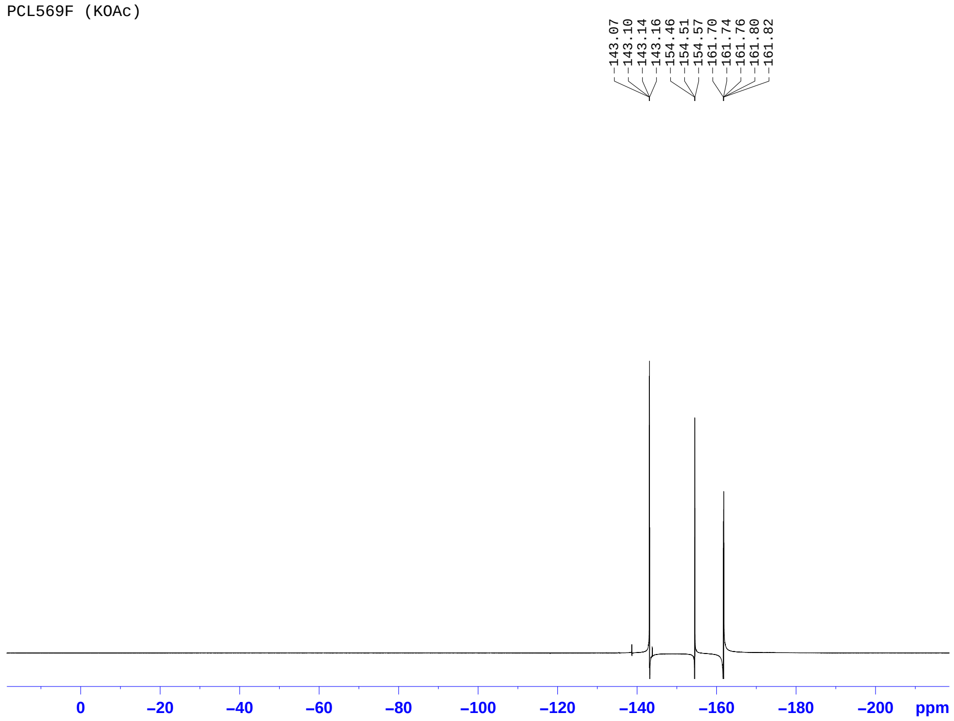




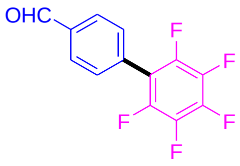


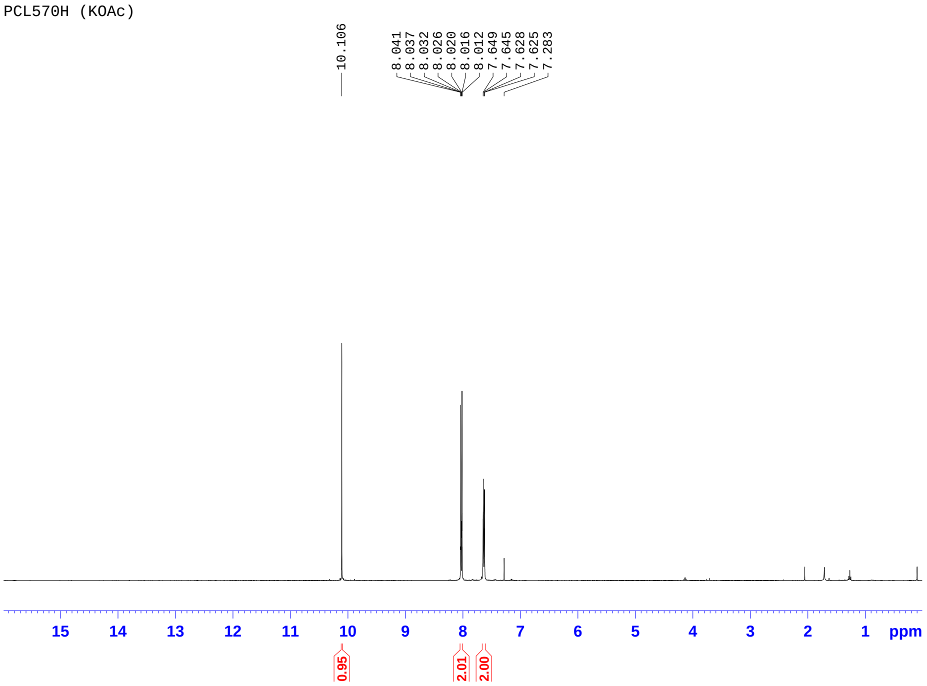
3'-(2,3,4,5,6-Pentafluorophenyl)acetophenone (Table 4.3, 4.5; Product 23ae)

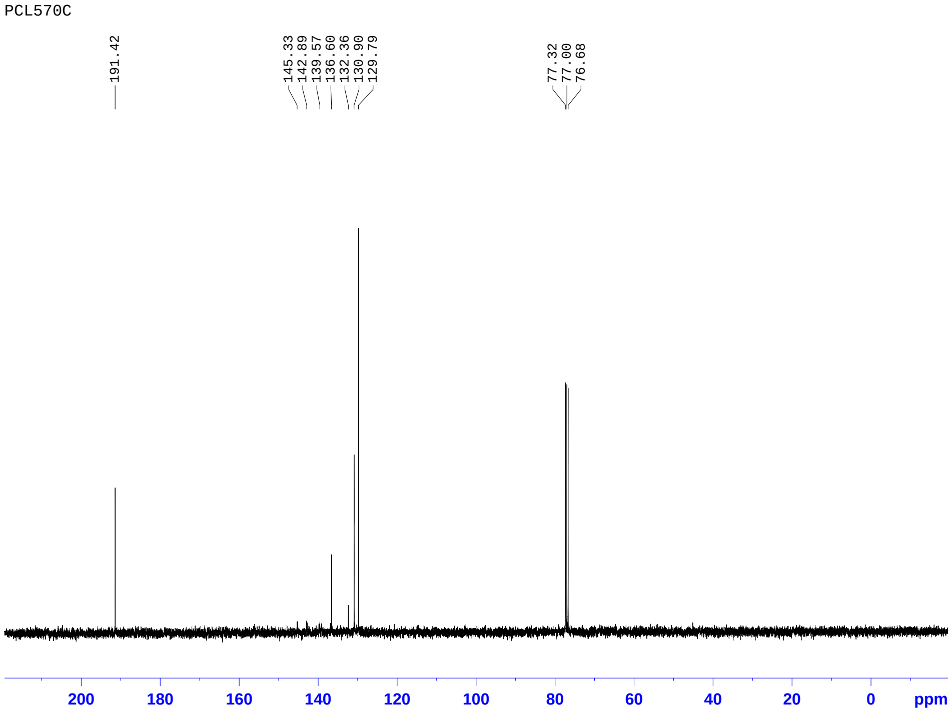




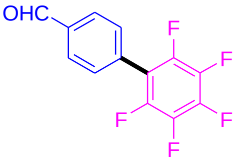
2',3',4',5',6'-Pentafluoro-[1,1'-biphenyl]-4-carboxaldehyde (Table 4.3, 4.5; Product 23af)

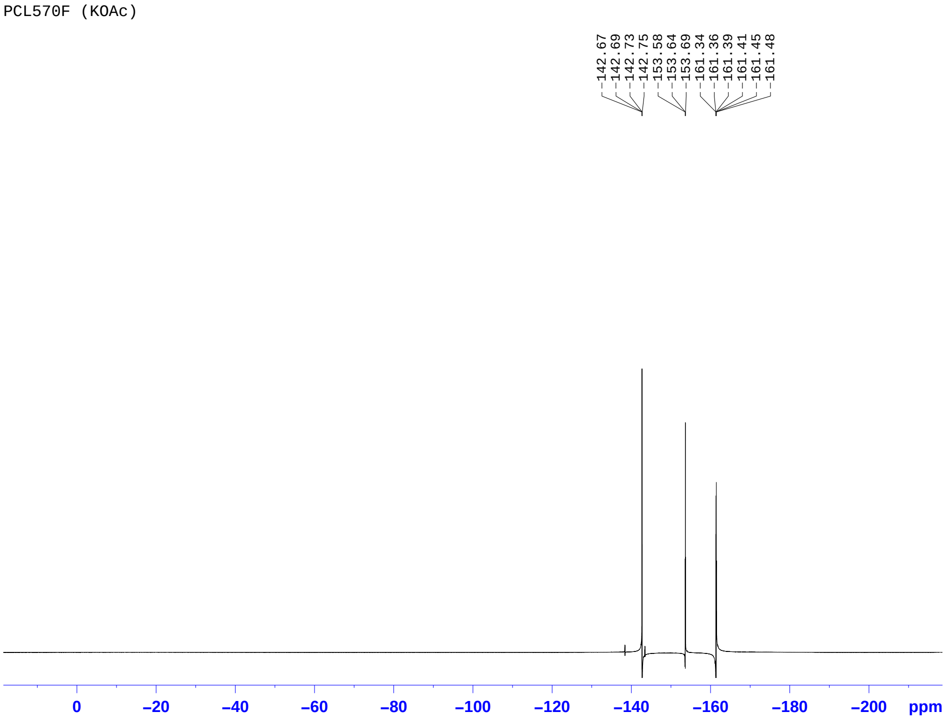




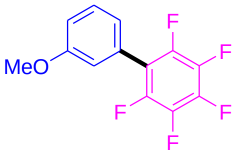


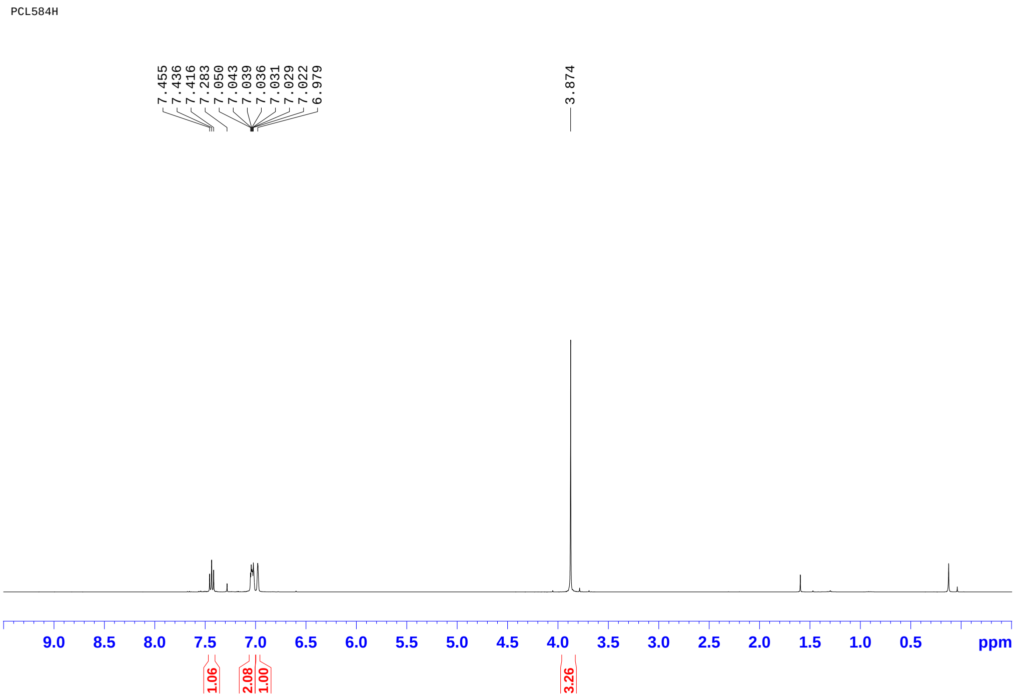
2',3',4',5',6'-Pentafluoro-[1,1'-biphenyl]-4-carboxaldehyde (Table 4.3, 4.5; Product 23af)

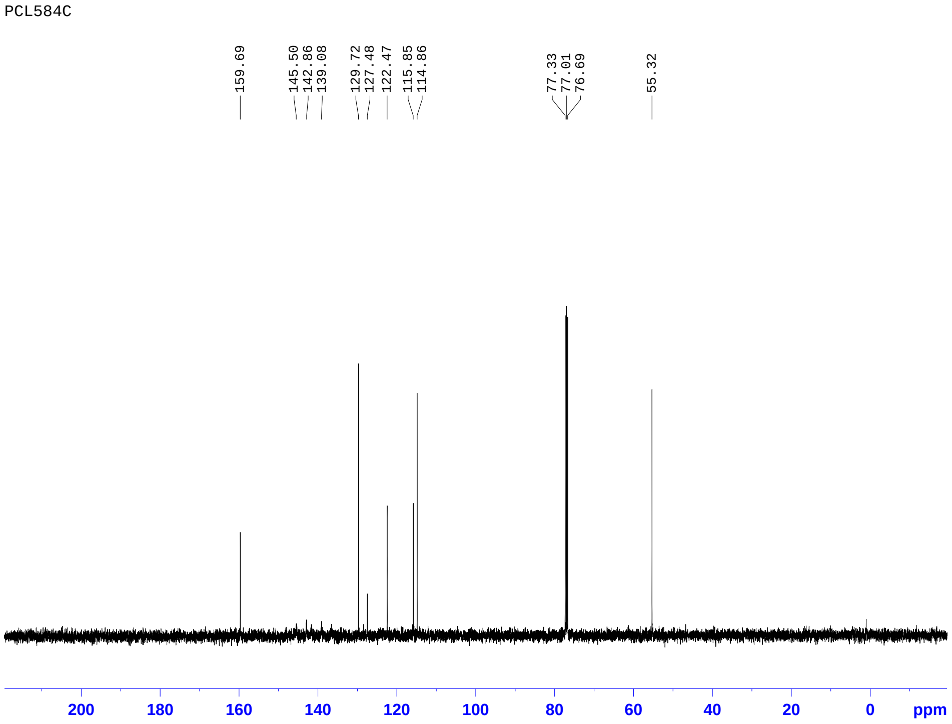




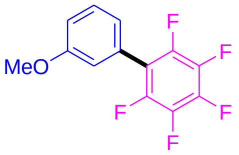
2,3,4,5,6-Pentafluoro-3'-methoxybiphenyl (Table 4.3, 4.5; Product 23ag)

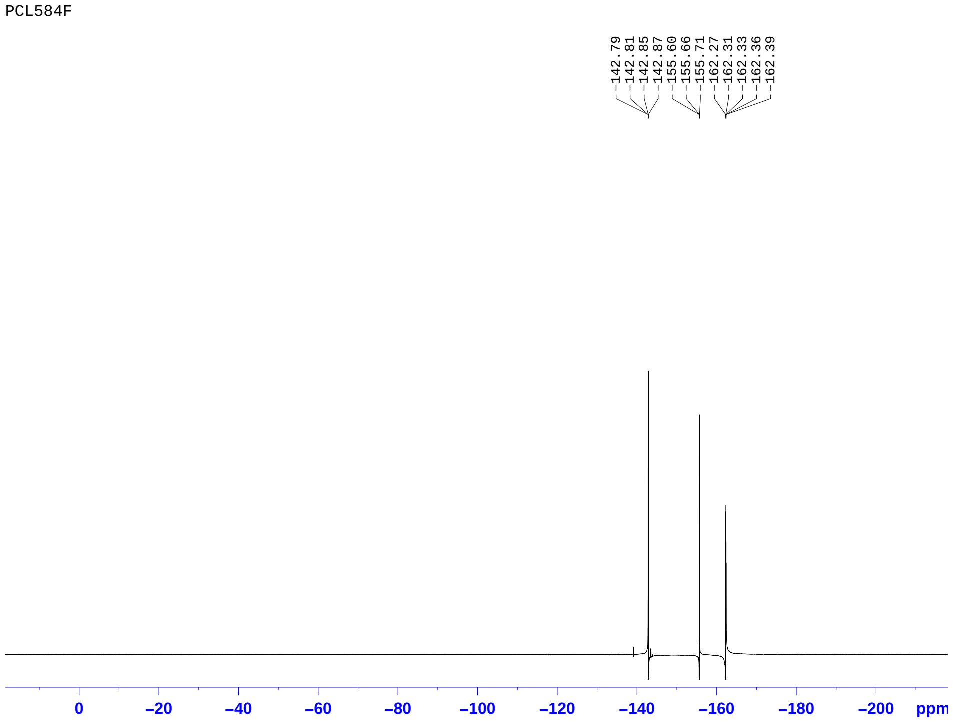




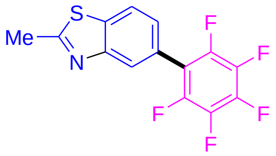


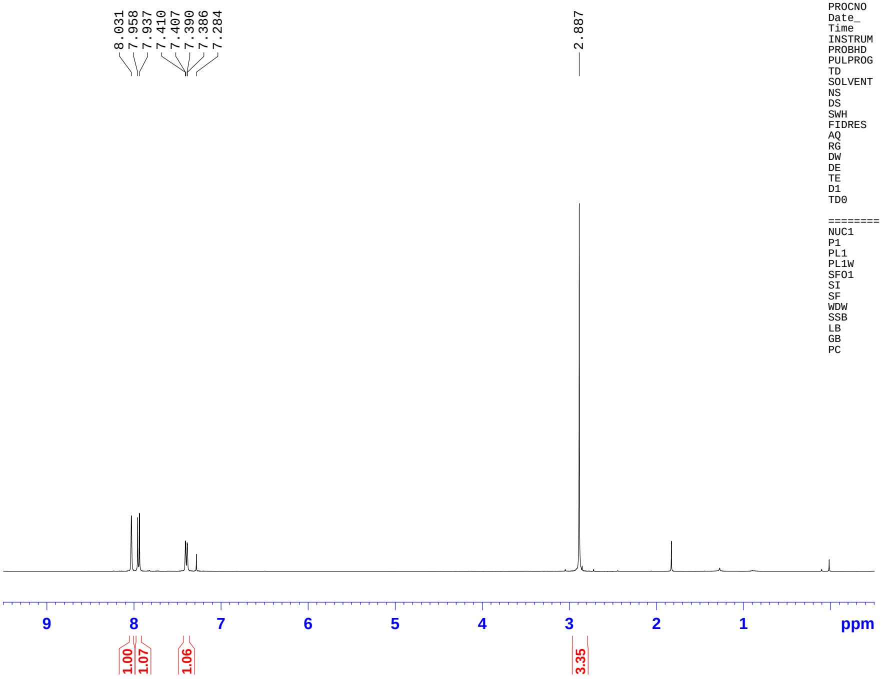
2,3,4,5,6-Pentafluoro-3'-methoxybiphenyl (Table 4.3, 4.5; Product 23ag)





2-Methyl-5-(pentafluorophenyl)benzo[*d*]thiazole (Table 4.3, 4.5; Product 23ah)





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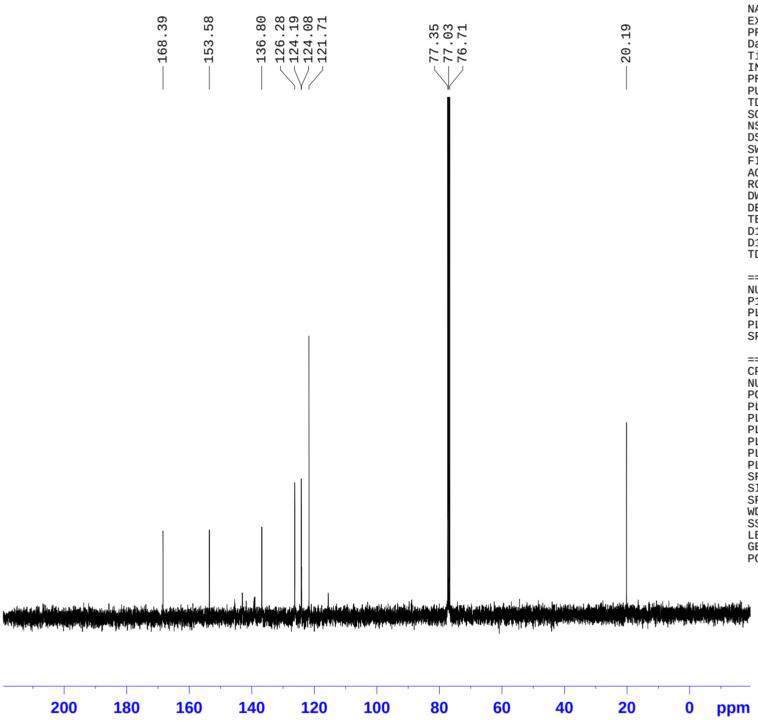
DS                      2
SWH              4006.410 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                     57
DW                124.800 usec
DE                   6.50 usec
TE                  298.2 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.70 usec
PL1                  0.00 dB
PL1W          11.88122272 W
SFO1          400.1318007 MHz
SI                  32768
SF            400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

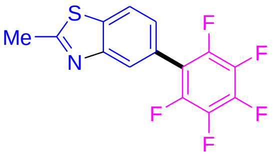


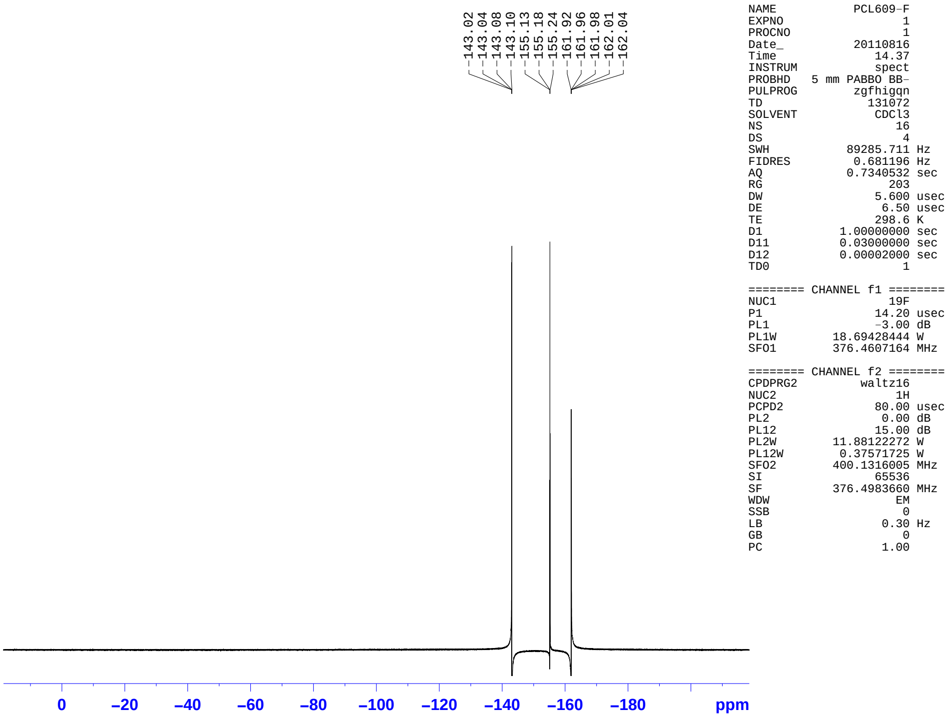
```
NAME             PCL609-C
EXPNO                   1
PROCNO                  1
Date_            20110816
Time                14.30
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      2
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                    203
DW                 20.800 usec
DE                   6.50 usec
TE                  299.1 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.50 usec
PL1                 -2.00 dB
PL1W          58.52175522 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                15.00 dB
PL13                15.00 dB
PL2W          11.88122272 W
PL12W          0.37571725 W
PL13W          0.37571725 W
SFO2          400.1316005 MHz
SI                  32768
SF            100.6127690 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

2-Methyl-5-(pentafluorophenyl)benzo[*d*]thiazole (Table 4.3, 4.5; Product 23ah)

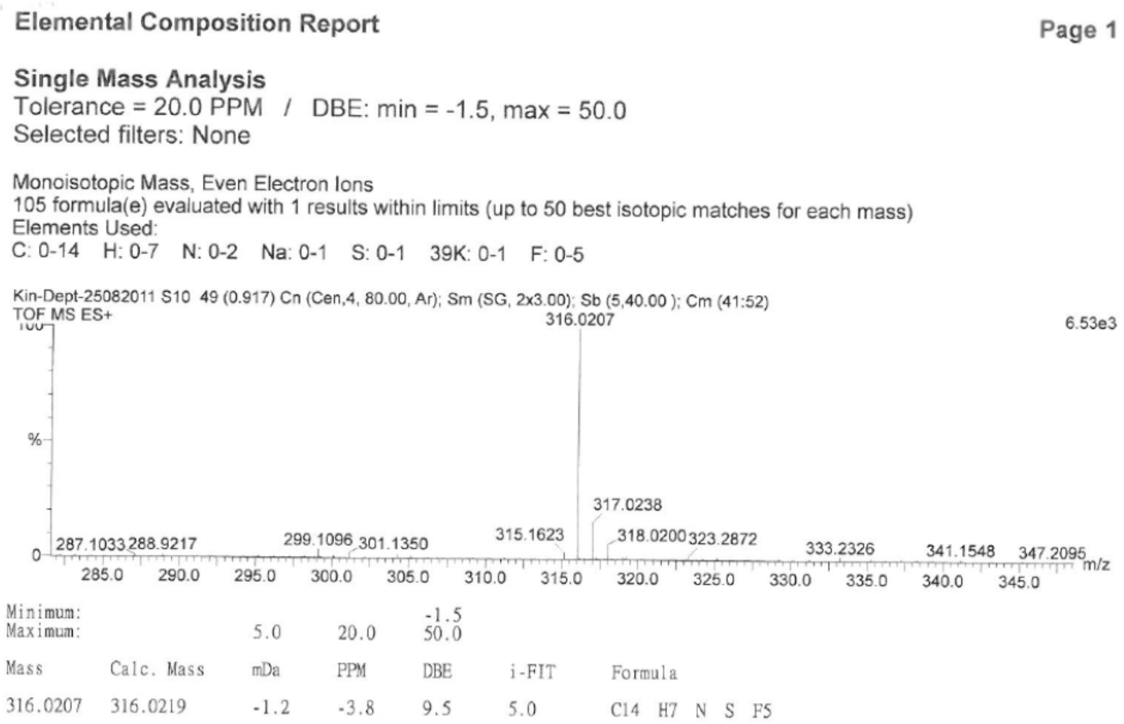




```
NAME            PCL609-F
EXPNO                  1
PROCNO                 1
Date_           20110816
Time               14.37
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG         zgfhigqn
TD                131072
SOLVENT            CDCl3
NS                    16
DS                     4
SWH           89285.711 Hz
FIDRES         0.681196 Hz
AQ            0.7340532 sec
RG                   203
DW                 5.600 usec
DE                  6.50 usec
TE                 298.6 K
D1            1.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 19F
P1                 14.20 usec
PL1                -3.00 dB
PL1W         18.69428444 W
SFO1         376.4607164 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
SFO2         400.1316005 MHz
SI                 65536
SF           376.4983660 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



Elemental Composition Report

Page 1

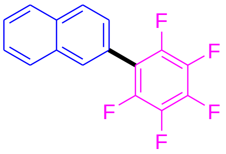
Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

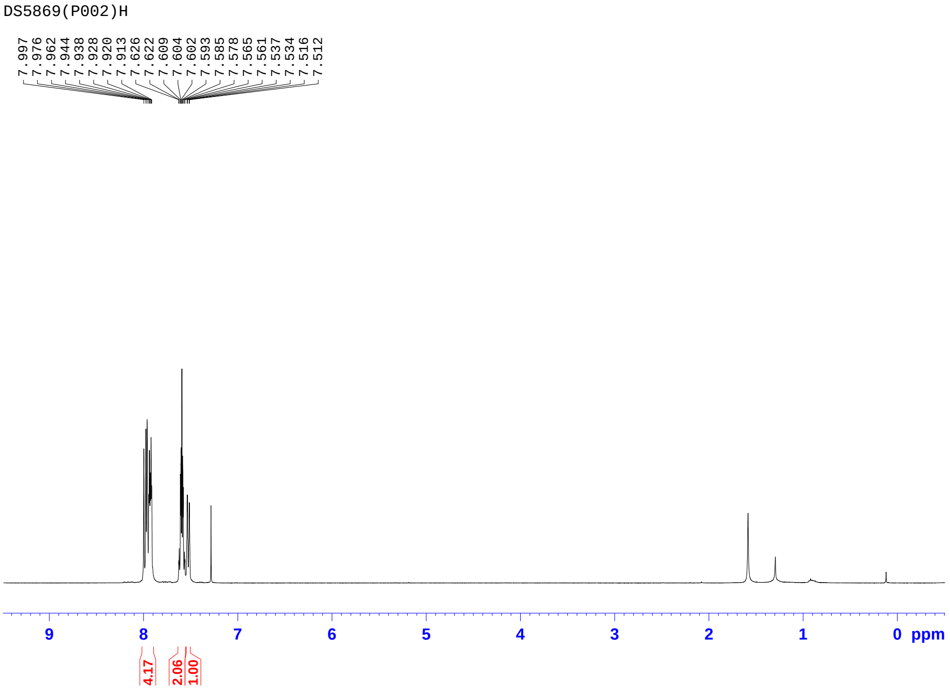
Monoisotopic Mass, Even Electron Ions
105 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-14 H: 0-7 N: 0-2 Na: 0-1 S: 0-1 39K: 0-1 F: 0-5

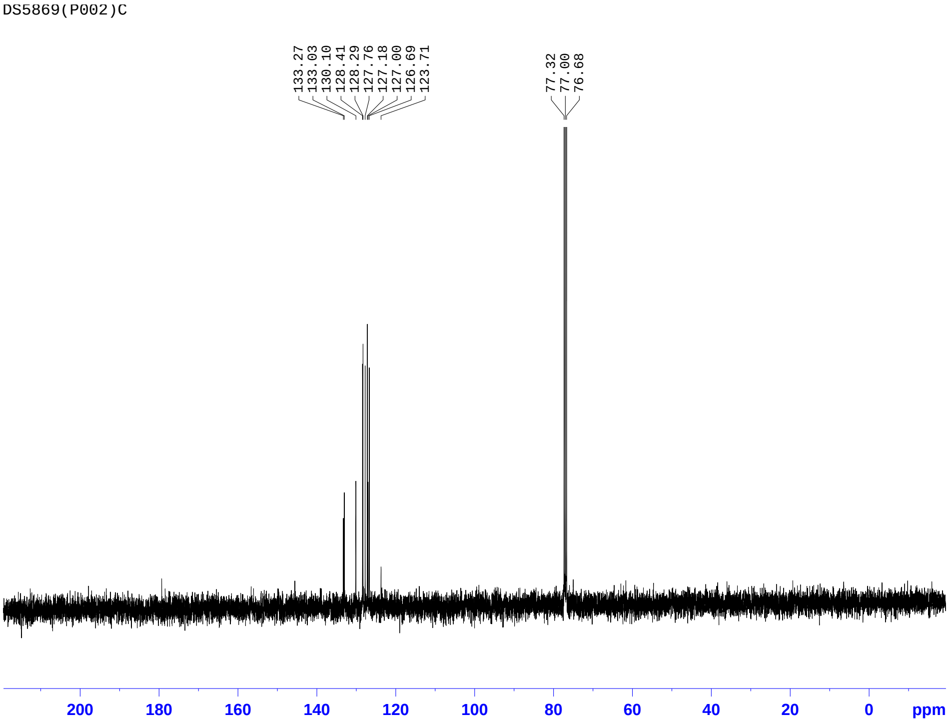
Kin-Dept-25082011 S10 49 (0.917) Cn (Cen,4, 80.00, Ar); Sm (SG, 2x3.00); Sb (5,40.00); Cm (41:52)
TOF MS ES+

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
Minimum:				-1.5		
Maximum:		5.0	20.0	50.0		
316.0207	316.0219	-1.2	-3.8	9.5	5.0	C14 H7 N S F5

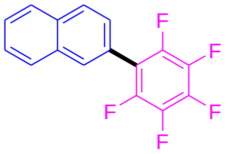
2-(2,3,4,5,6-Pentafluorophenyl)naphthalene (Table 4.3, 4.4; Product 23ai)

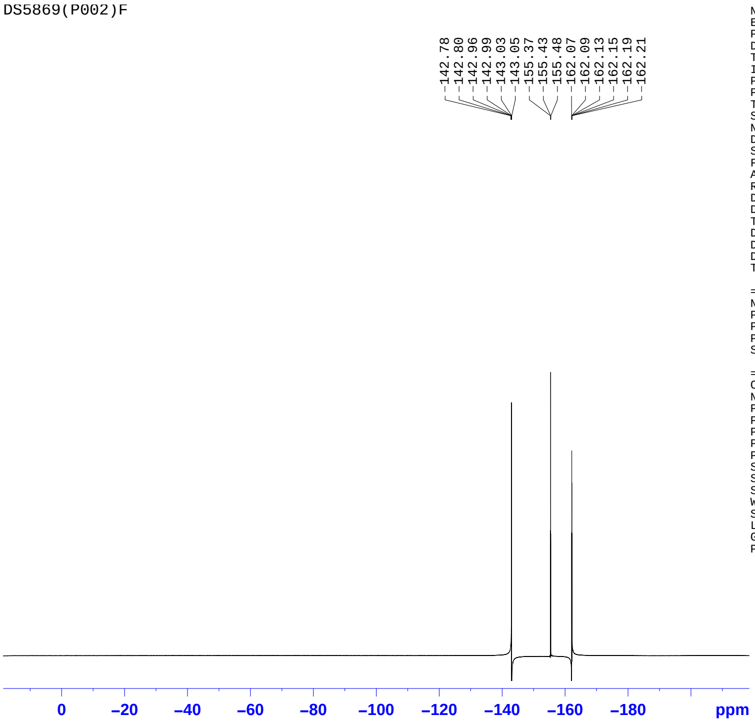






2-(2,3,4,5,6-Pentafluorophenyl)naphthalene (Table 4.3, 4.4; Product 23ai)



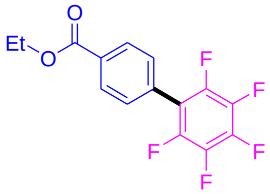


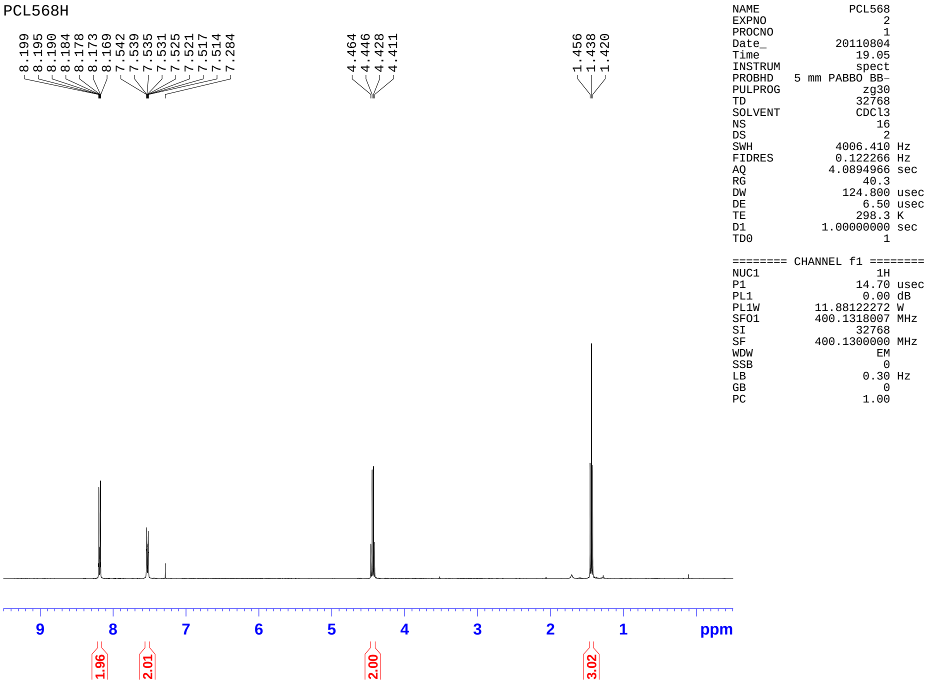
```
NAME        DS5869(P002)
EXPNO                  1
PROCNO                 1
Date_           20110804
Time               18.50
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgfhigqn
TD                131072
SOLVENT            CDCl3
NS                    16
DS                     4
SWH            89285.711 Hz
FIDRES          0.681196 Hz
AQ             0.7340532 sec
RG                   203
DW                 5.600 usec
DE                  6.50 usec
TE                 298.2 K
D1            1.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 19F
P1                 14.20 usec
PL1                -3.00 dB
PL1W         18.69428444 W
SFO1         376.4607164 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
SFO2         400.1316005 MHz
SI                 65536
SF           376.4983660 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

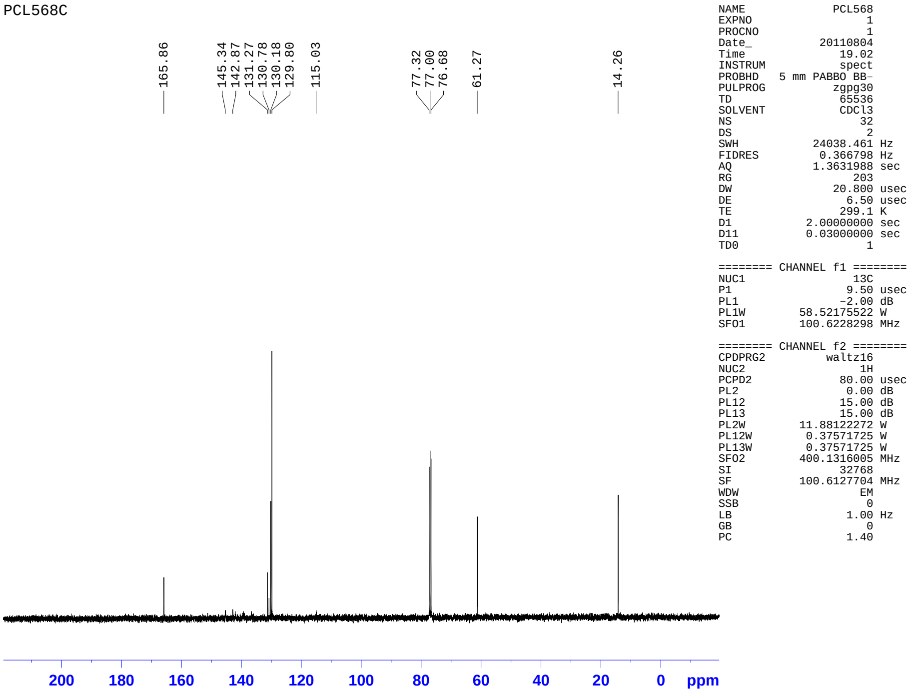
[1,1'-Biphenyl]-4-carboxylic acid, 2',3',4',5',6'-pentafluoro-, ethyl ester (Table 4.3, 4.5; Product 23aj)





```
NAME              PCL568
EXPNO                  2
PROCNO                 1
Date_           20110804
Time               19.05
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  40.3
DW               124.800 usec
DE                  6.50 usec
TE                 298.3 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

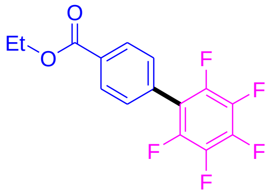


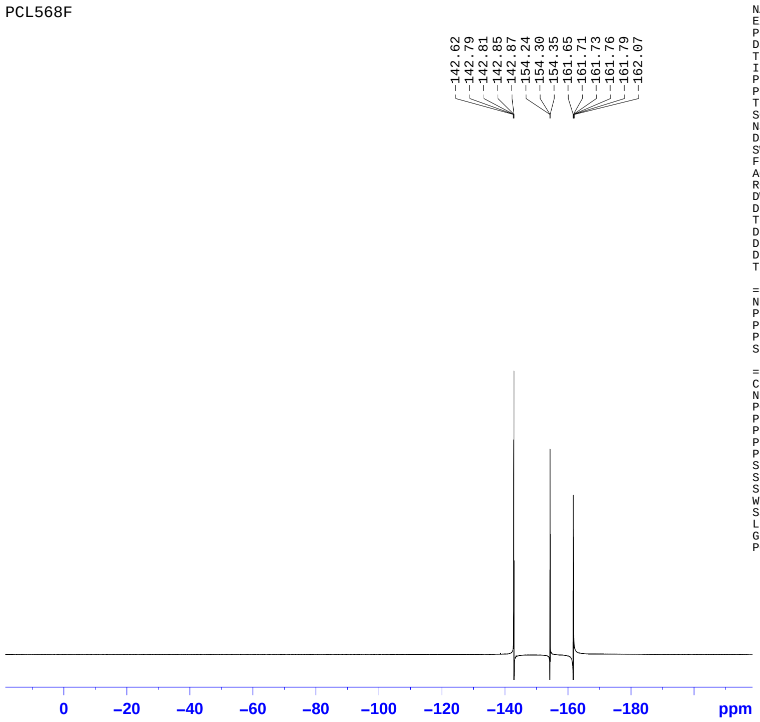
```
NAME              PCL568
EXPNO                  1
PROCNO                 1
Date_           20110804
Time               19.02
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   203
DW                20.800 usec
DE                  6.50 usec
TE                 299.1 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127704 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

[1,1'-Biphenyl]-4-carboxylic acid, 2',3',4',5',6'-pentafluoro-, ethyl ester (Table 4.3, 4.5; Product 23aj)

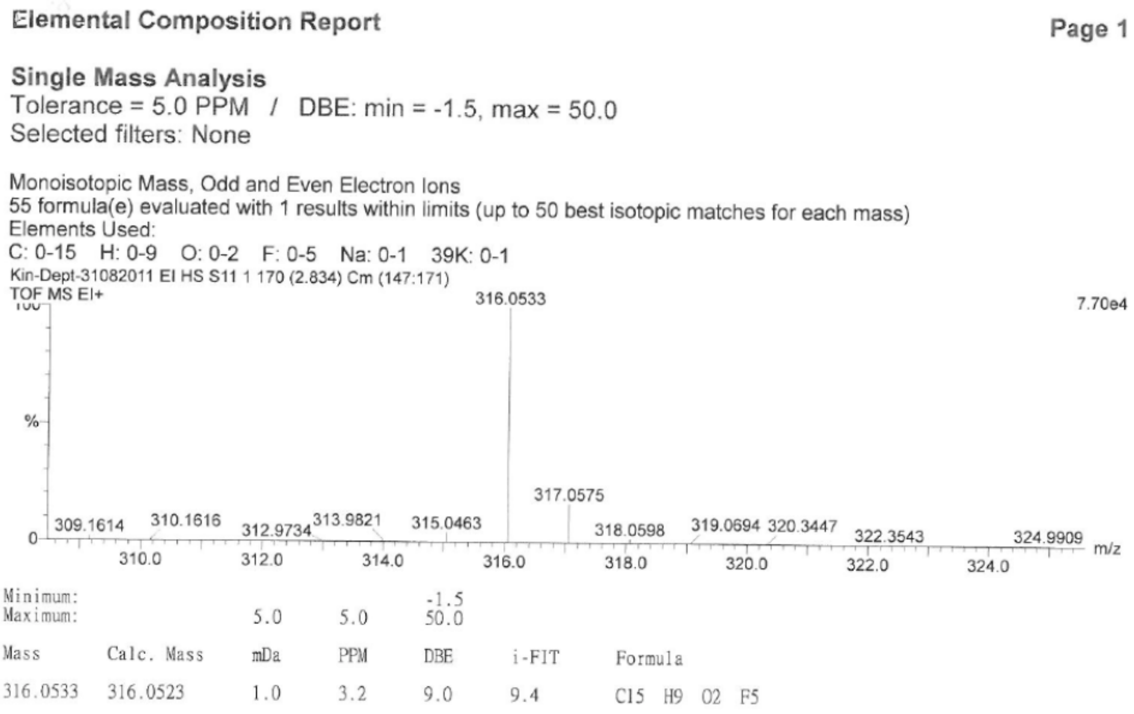




```
NAME              PCL568
EXPNO                  3
PROCNO                 1
Date_           20110804
Time               19.08
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG        zgfhigqn
TD                131072
SOLVENT            CDCl3
NS                    16
DS                     4
SWH           89285.711 Hz
FIDRES         0.681196 Hz
AQ            0.7340532 sec
RG                   203
DW                 5.600 usec
DE                  6.50 usec
TE                 298.3 K
D1            1.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 19F
P1                 14.20 usec
PL1                -3.00 dB
PL1W         18.69428444 W
SFO1         376.4607164 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
SFO2         400.1316005 MHz
SI                 65536
SF           376.4983660 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



Elemental Composition Report

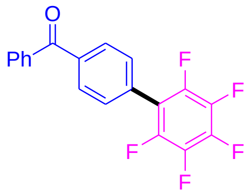
Page 1

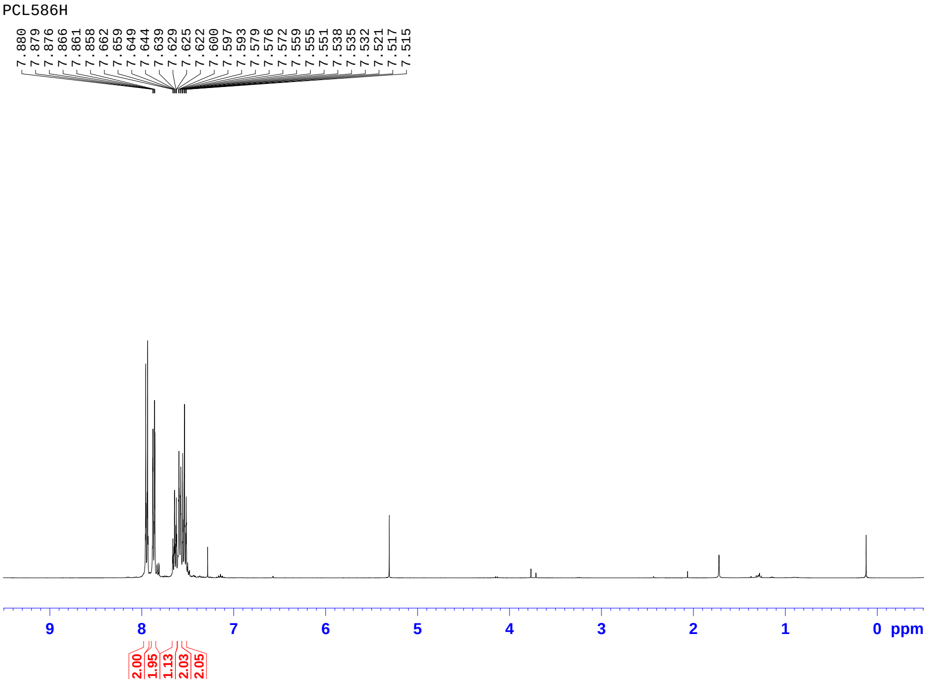
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

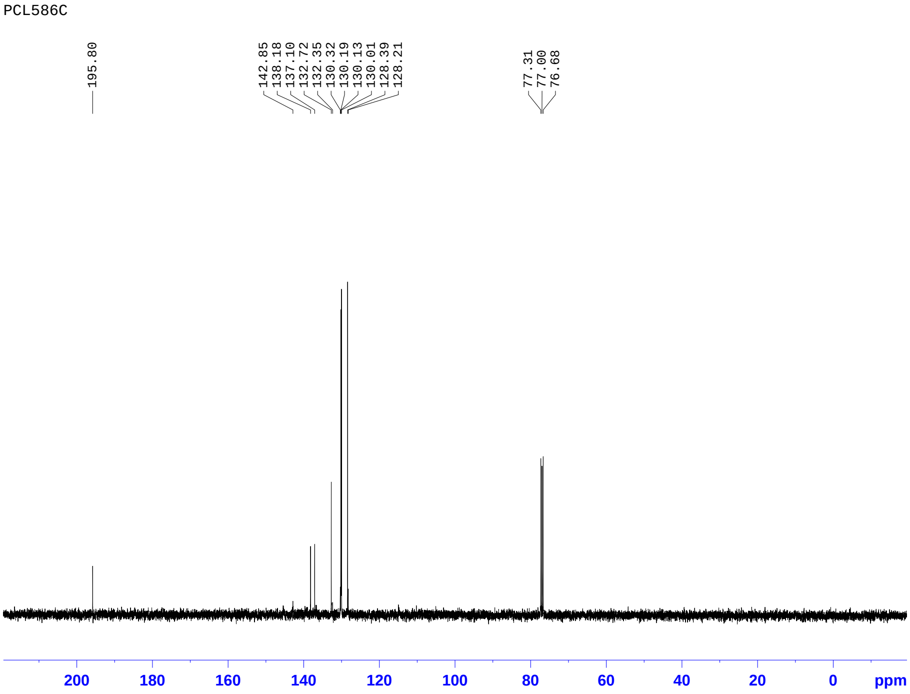
Monoisotopic Mass, Odd and Even Electron Ions
55 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-15 H: 0-9 O: 0-2 F: 0-5 Na: 0-1 39K: 0-1
Kin-Dept-31082011 EI HS S11 1 170 (2.834) Cm (147:171)
TOF MS EI+

Minimum:				-1.5		
Maximum:		5.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
316.0533	316.0523	1.0	3.2	9.0	9.4	C15 H9 O2 F5

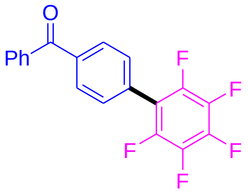
(2',3',4',5',6'-Pentafluoro[1,1'-biphenyl]-4-yl)phenylmethanone (Table 4.3, 4.5; Product 23ak)

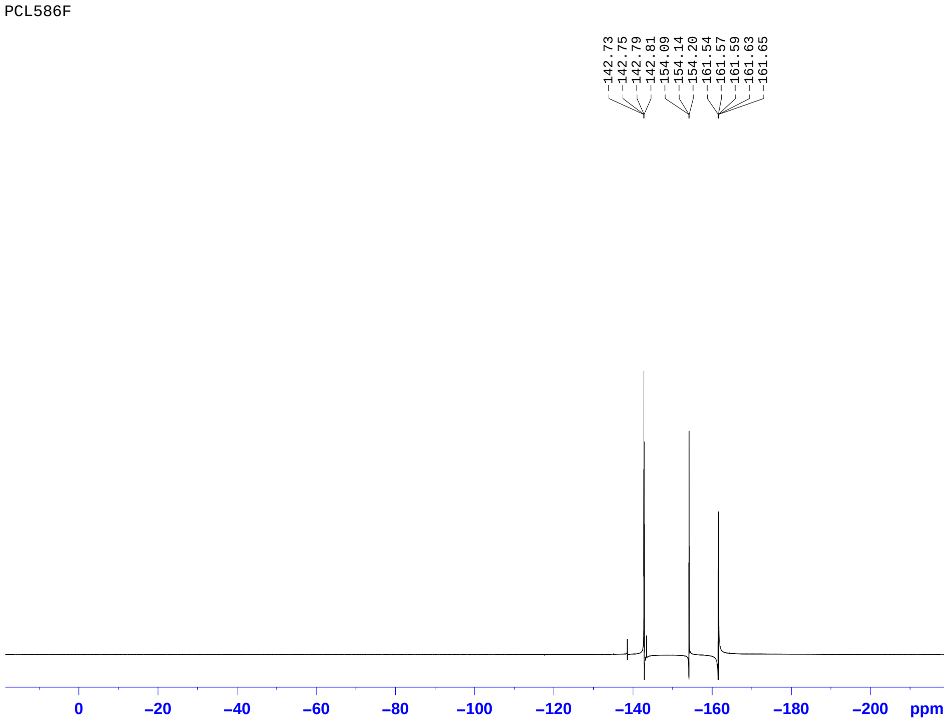




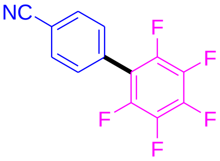


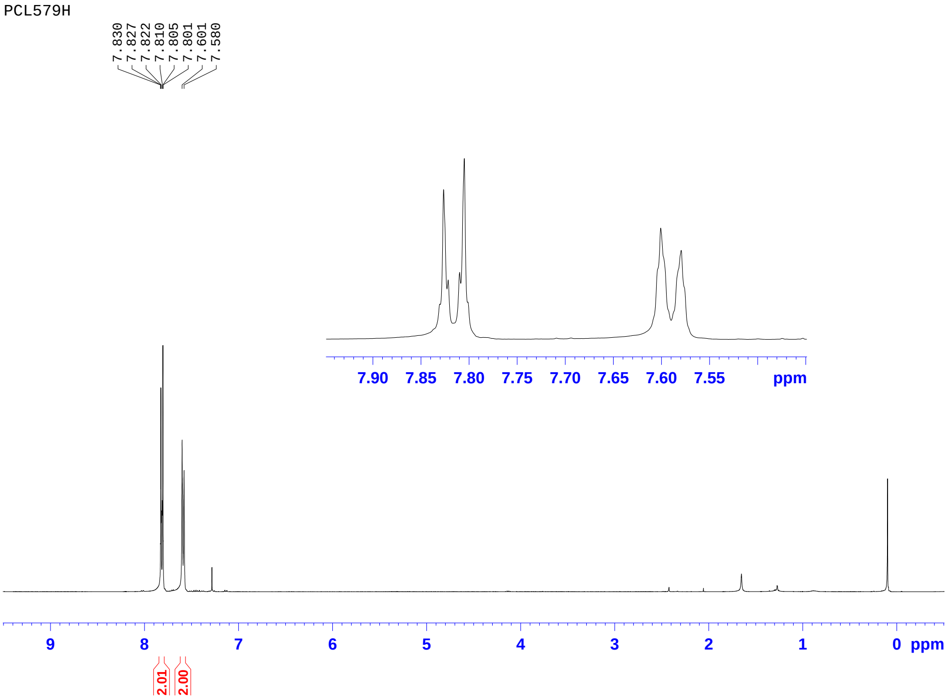
(2',3',4',5',6'-Pentafluoro[1,1'-biphenyl]-4-yl)phenylmethanone (Table 4.3, 4.5; Product 23ak)

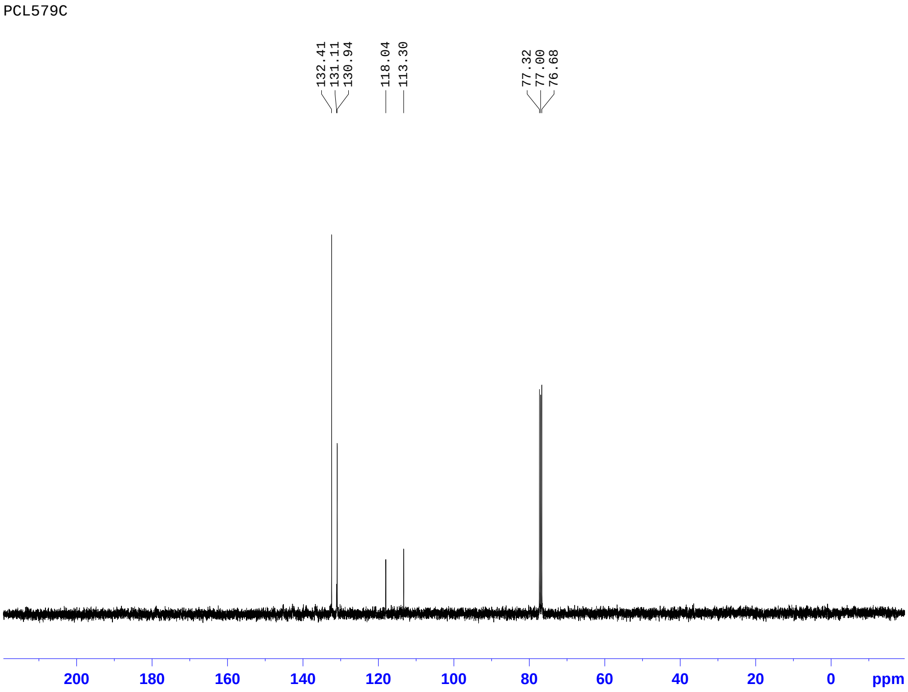




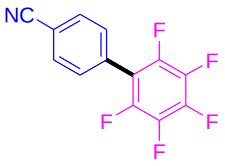
2,3,4,5,6-Pentafluoro-4'-cyanobiphenyl (Table 4.3, 4.5; Product 23al)

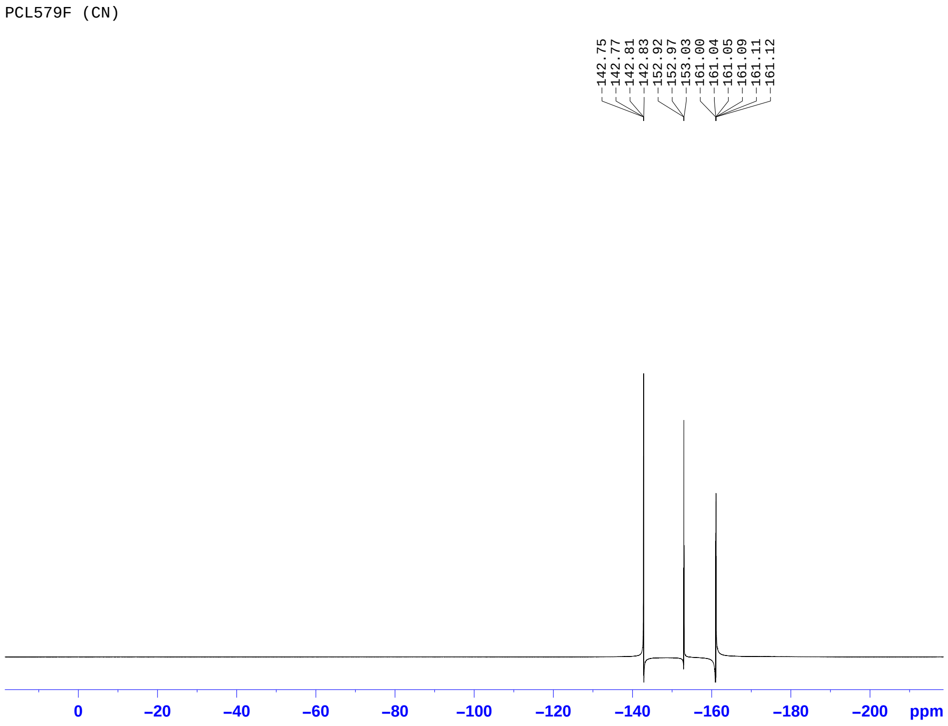




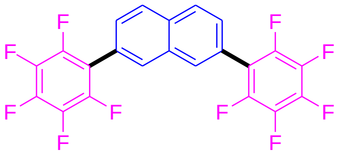


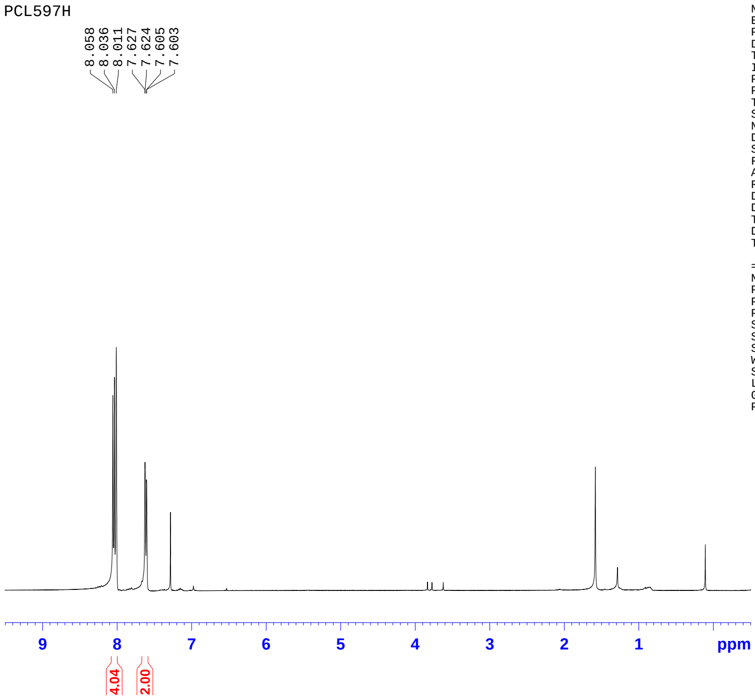
2,3,4,5,6-Pentafluoro-4'-cyanobiphenyl (Table 4.3, 4.5; Product 23al)





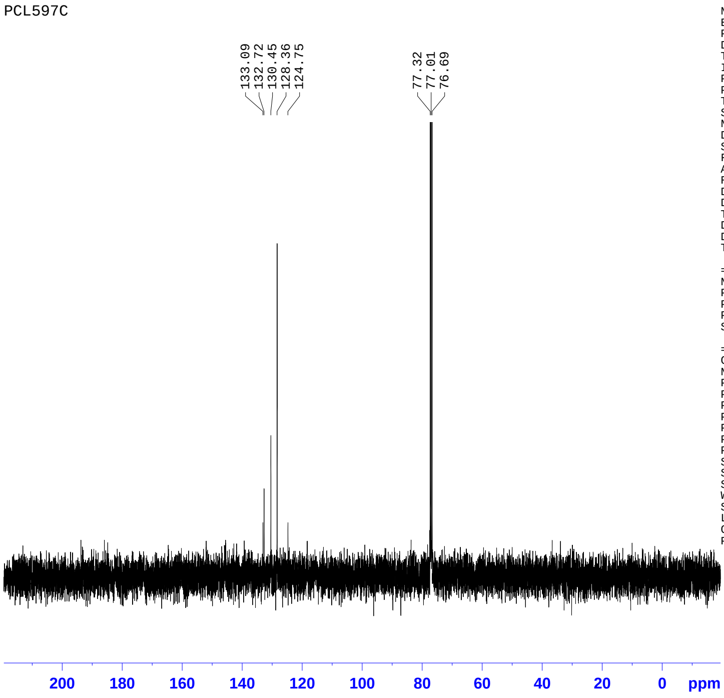
2,7-Bis(pentafluorophenyl)naphthalene (Table 4.3; Product 23am)





```
NAME              PCL597
EXPNO                  6
PROCNO                 1
Date_           20110818
Time               12.05
INSTRUM            spect
PROBHD    5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                   128
DW               124.800 usec
DE                  6.50 usec
TE                 297.8 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

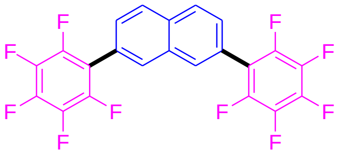


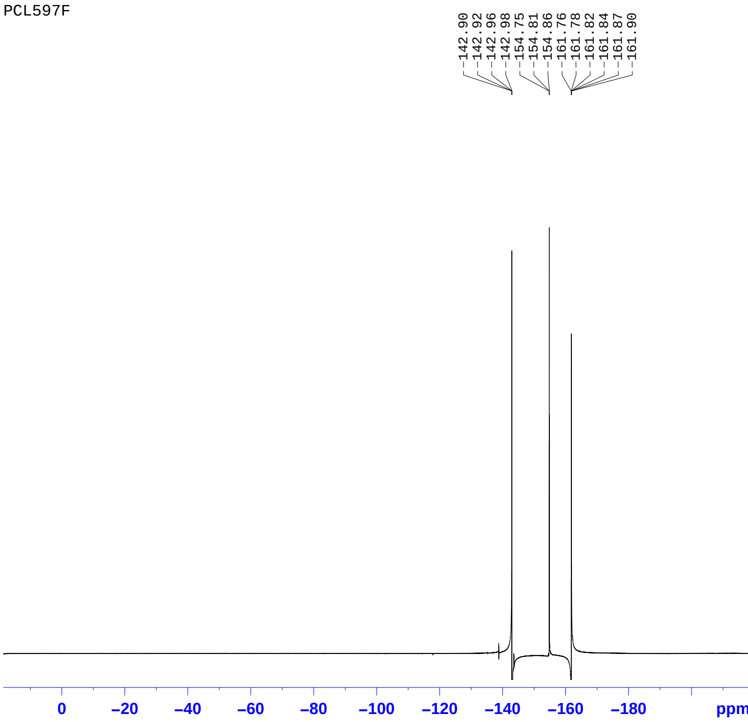
```
NAME              PCL597
EXPNO                  8
PROCNO                 1
Date_           20110818
Time               12.11
INSTRUM            spect
PROBHD    5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   101
DW                20.800 usec
DE                  6.50 usec
TE                 298.9 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127690 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

2,7-Bis(pentafluorophenyl)naphthalene (Table 4.3; Product 23am)





```
NAME               PCL597
EXPNO                   7
PROCNO                  1
Date_            20110818
Time                12.07
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG          zgfhigqn
TD                 131072
SOLVENT             CDCl3
NS                     16
DS                      4
SWH            89285.711 Hz
FIDRES          0.681196 Hz
AQ             0.7340532 sec
RG                    203
DW                  5.600 usec
DE                   6.50 usec
TE                  298.0 K
D1             1.00000000 sec
D11            0.03000000 sec
D12            0.00002000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  19F
P1                  14.20 usec
PL1                 -3.00 dB
PL1W          18.69428444 W
SFO1          376.4607164 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                15.00 dB
PL2W          11.88122272 W
PL12W          0.37571725 W
SFO2          400.1316005 MHz
SI                  65536
SF            376.4983660 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions

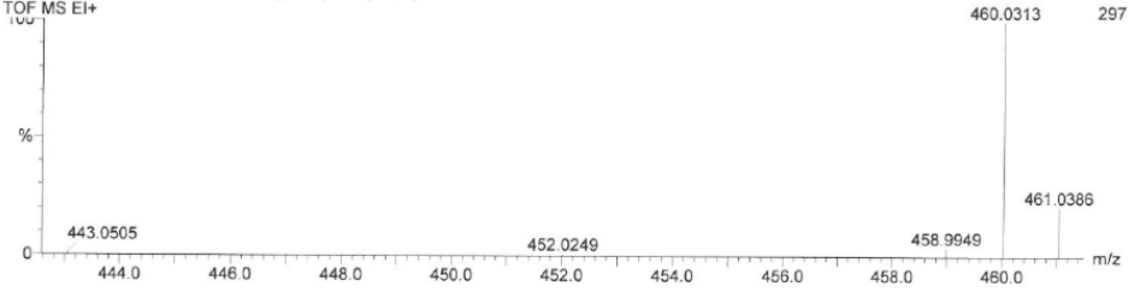
40 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 0-22 H: 0-15 F: 0-10 Na: 0-1 39K: 0-1

Kin-Dept-31082011 EI HS S14 1 54 (0.900) Cm (52:54)

TOF MS EI+

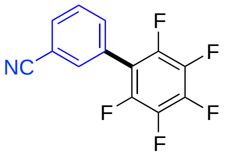


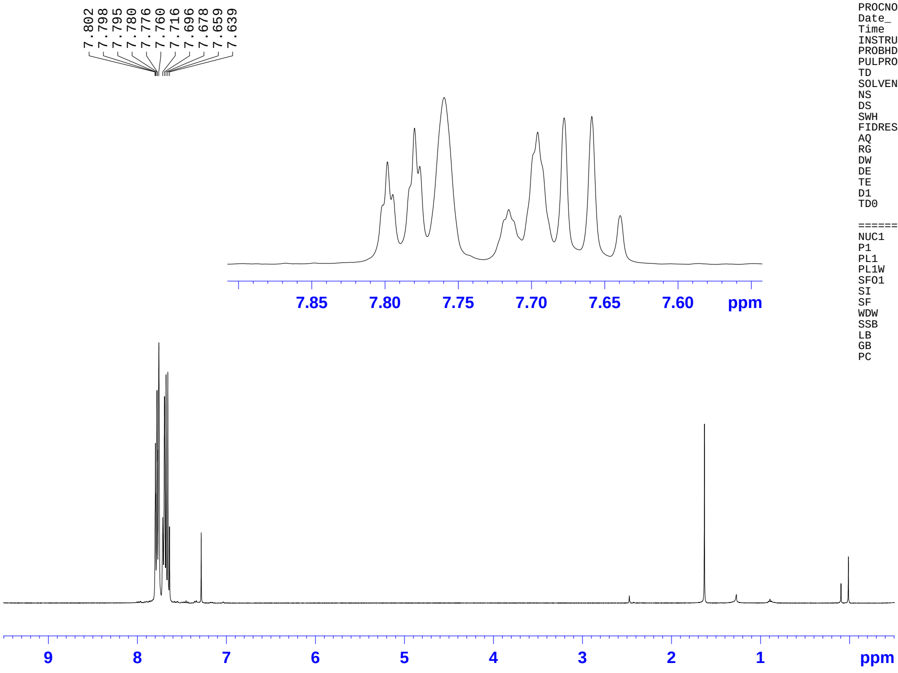
```
Minimum:                                      -1.5
Maximum:                  5.0        5.0      50.0

Mass       Calc. Mass     mDa        PPM      DBE       i-FIT         Formula

460.0313   460.0310       0.3        0.7      15.0      2773035.5     C22  H6  F10
```

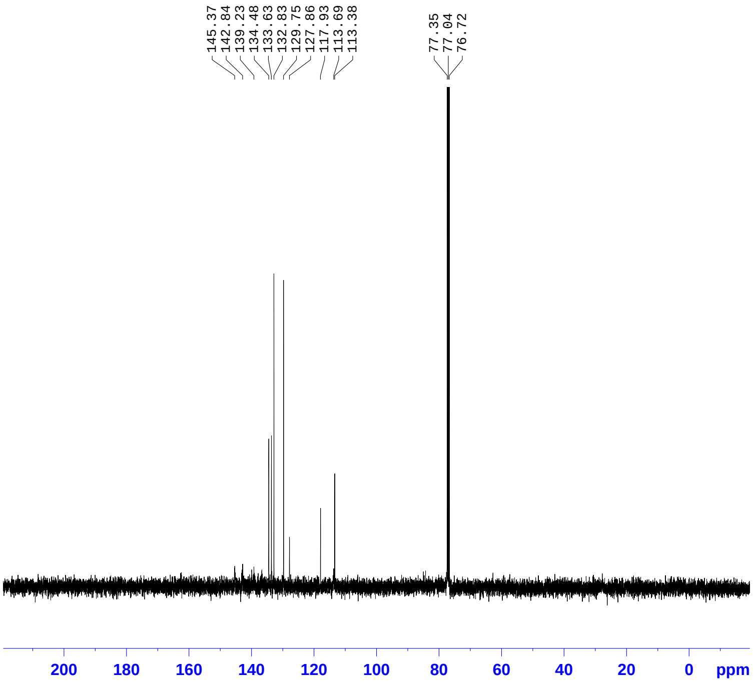
2,3,4,5,6-Pentafluoro-3'-cyanobiphenyl (Table 4.3, 4.5; Product 23an)





```
NAME             PCL599
EXPNO                 1
PROCNO                1
Date_          20110812
Time              13.55
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            4006.410 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 se
RG                 45.2
DW              124.800 us
DE                 6.50 us
TE                298.0 K
D1           1.00000000 se
TD0                   1

======== CHANNEL f1 =====
NUC1                 1H
P1                14.70 us
PL1                0.00 dB
PL1W        11.88122272 W
SFO1        400.1318007 MH
SI                32768
SF          400.1300000 MH
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

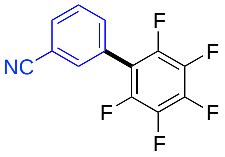


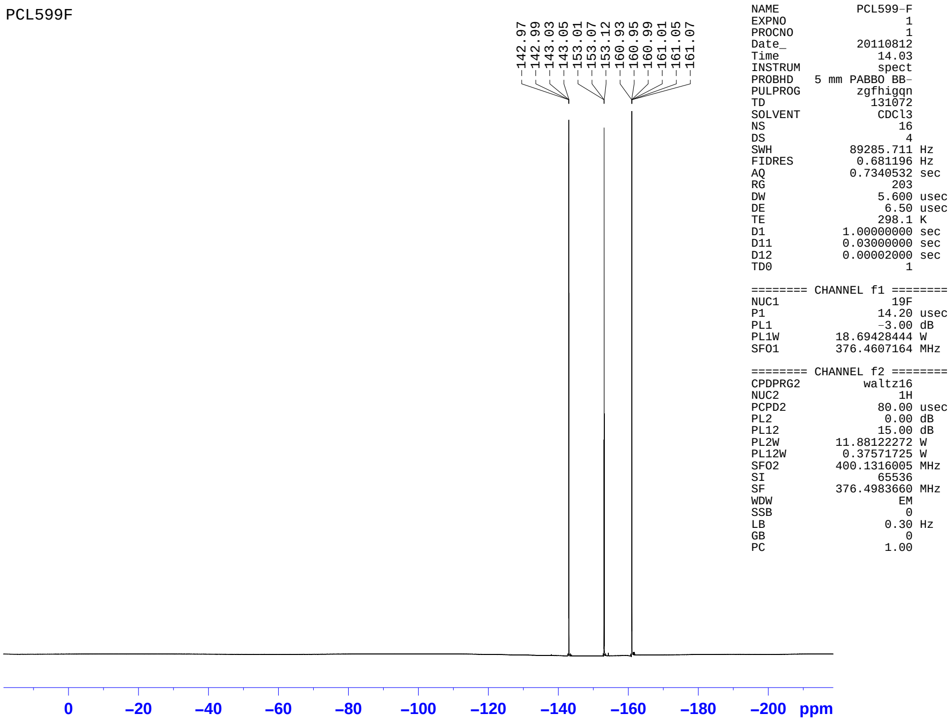
```
NAME           PCL599-C
EXPNO                 1
PROCNO                1
Date_          20110812
Time              13.59
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                  203
DW               20.800 usec
DE                 6.50 usec
TE                298.8 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.50 usec
PL1               -2.00 dB
PL1W        58.52175522 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL13              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
PL13W        0.37571725 W
SFO2        400.1316005 MHz
SI                32768
SF          100.6127690 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

2,3,4,5,6-Pentafluoro-3'-cyanobiphenyl (Table 4.3, 4.5; Product 23an)



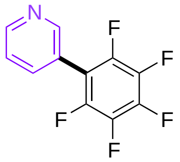


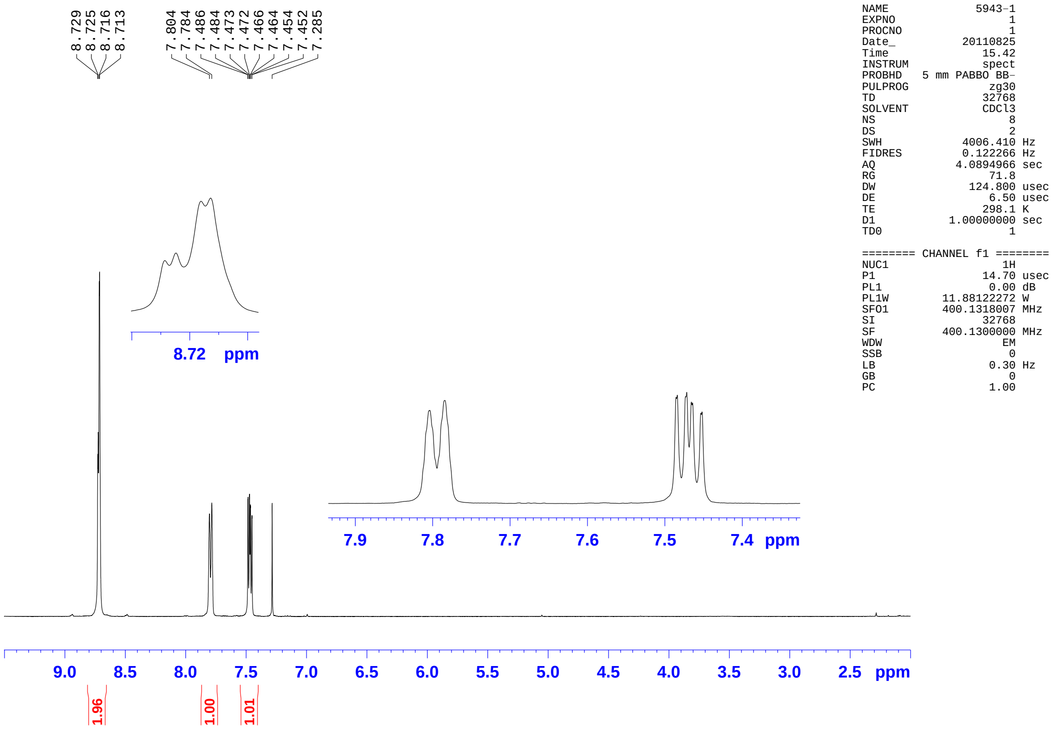
```
NAME          PCL599-F
EXPNO                1
PROCNO               1
Date_         20110812
Time             14.03
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG       zgfhigqn
TD              131072
SOLVENT          CDCl3
NS                  16
DS                   4
SWH          89285.711 Hz
FIDRES        0.681196 Hz
AQ           0.7340532 sec
RG                 203
DW               5.600 usec
DE                6.50 usec
TE               298.1 K
D1          1.00000000 sec
D11         0.03000000 sec
D12         0.00002000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               19F
P1               14.20 usec
PL1              -3.00 dB
PL1W       18.69428444 W
SFO1       376.4607164 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2            80.00 usec
PL2               0.00 dB
PL12             15.00 dB
PL2W       11.88122272 W
PL12W       0.37571725 W
SFO2       400.1316005 MHz
SI               65536
SF         376.4983660 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.00
```

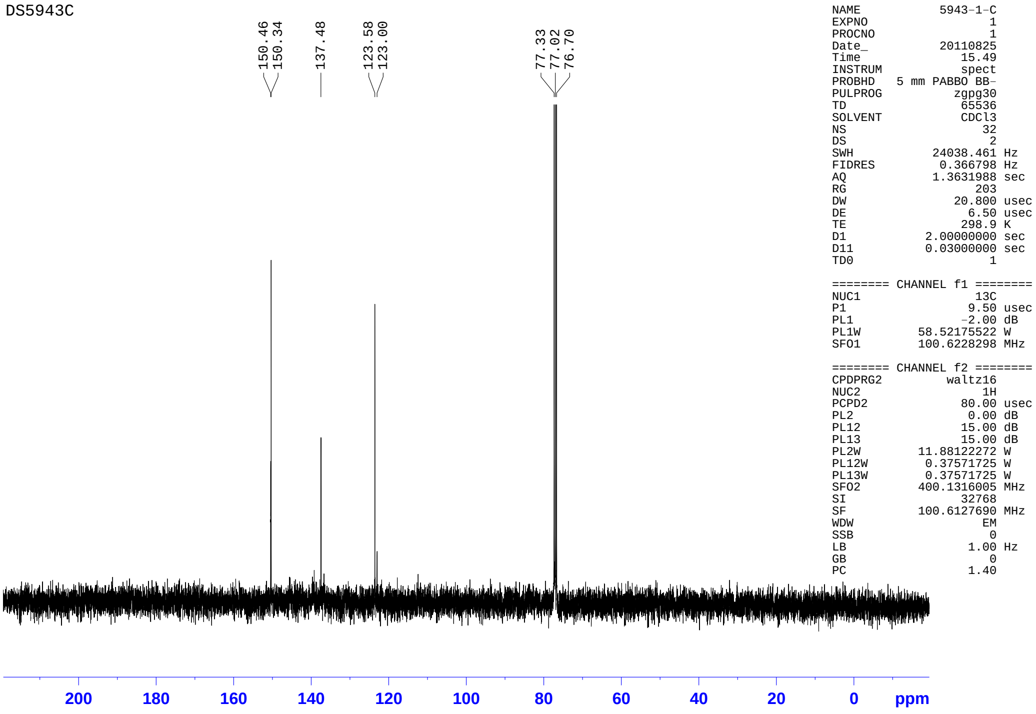
3-(Perfluorophenyl)pyridine (Table 4.5; Product 23ao)





```
NAME             5943-1
EXPNO                 1
PROCNO                1
Date_          20110825
Time              15.42
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            4006.410 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                 71.8
DW              124.800 usec
DE                 6.50 usec
TE                298.1 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.70 usec
PL1                0.00 dB
PL1W        11.88122272 W
SFO1        400.1318007 MHz
SI                32768
SF          400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

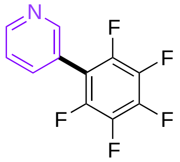


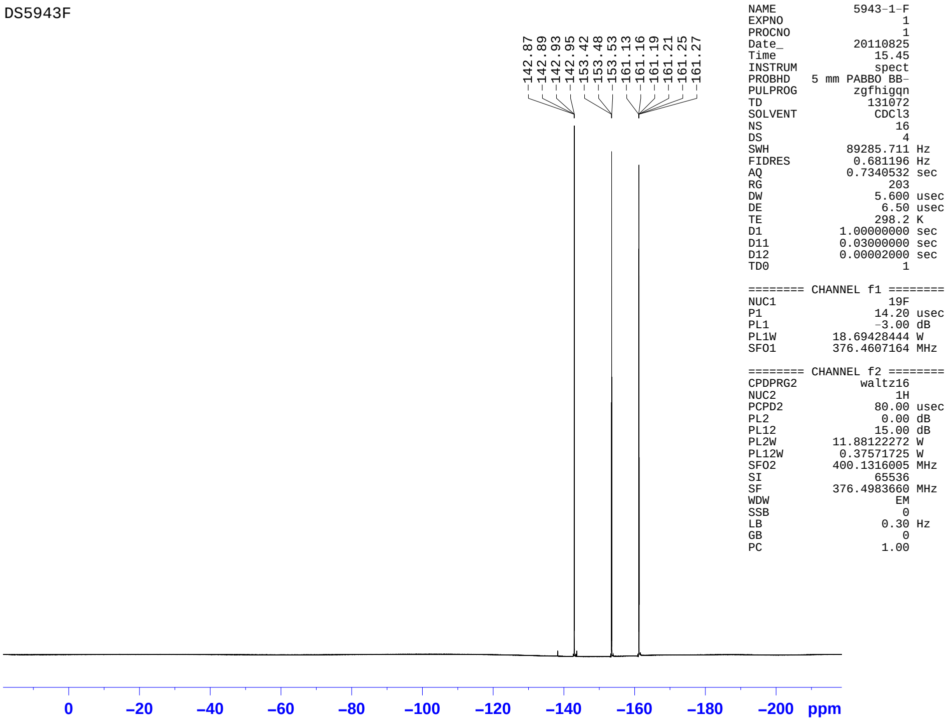
```
NAME           5943-1-C
EXPNO                 1
PROCNO                1
Date_          20110825
Time              15.49
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                  203
DW               20.800 usec
DE                 6.50 usec
TE                298.9 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.50 usec
PL1               -2.00 dB
PL1W        58.52175522 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL13              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
PL13W        0.37571725 W
SFO2        400.1316005 MHz
SI                32768
SF          100.6127690 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

3-(Perfluorophenyl)pyridine (Table 4.5; Product 23ao)



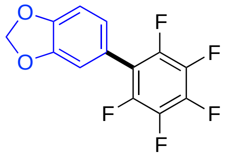


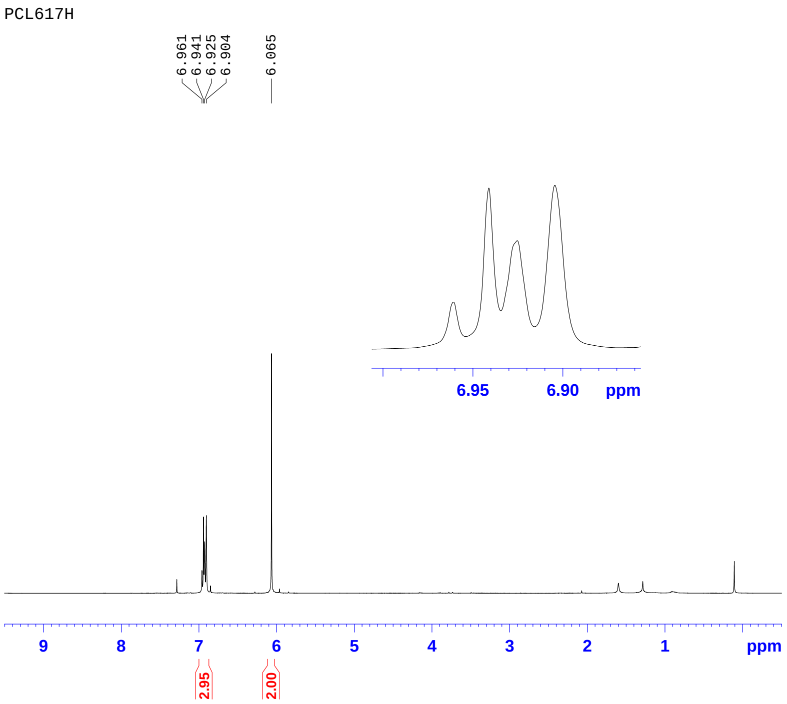
```
NAME           5943-1-F
EXPNO                 1
PROCNO                1
Date_          20110825
Time              15.45
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG        zgfhigqn
TD               131072
SOLVENT           CDCl3
NS                   16
DS                    4
SWH          89285.711 Hz
FIDRES        0.681196 Hz
AQ           0.7340532 sec
RG                  203
DW                5.600 usec
DE                 6.50 usec
TE                298.2 K
D1           1.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                19F
P1                14.20 usec
PL1               -3.00 dB
PL1W        18.69428444 W
SFO1        376.4607164 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
SFO2        400.1316005 MHz
SI                65536
SF          376.4983660 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

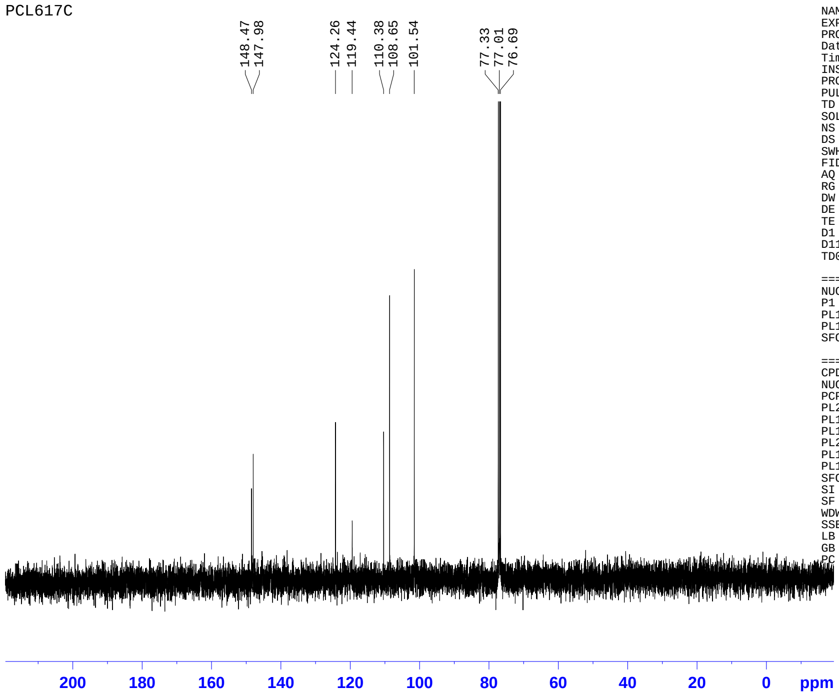
5-(Perfluorophenyl)benzo[*d*][1,3]dioxole (Table 4.3, 4.5; Product 23ap)





```
NAME               PCL617
EXPNO                   1
PROCNO                  1
Date_            20110824
Time                19.57
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              4006.410 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                   50.8
DW                124.800 usec
DE                   6.50 usec
TE                  297.9 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.70 usec
PL1                  0.00 dB
PL1W          11.88122272 W
SFO1          400.1318007 MHz
SI                  32768
SF            400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

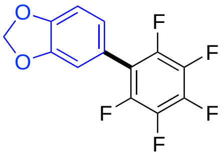


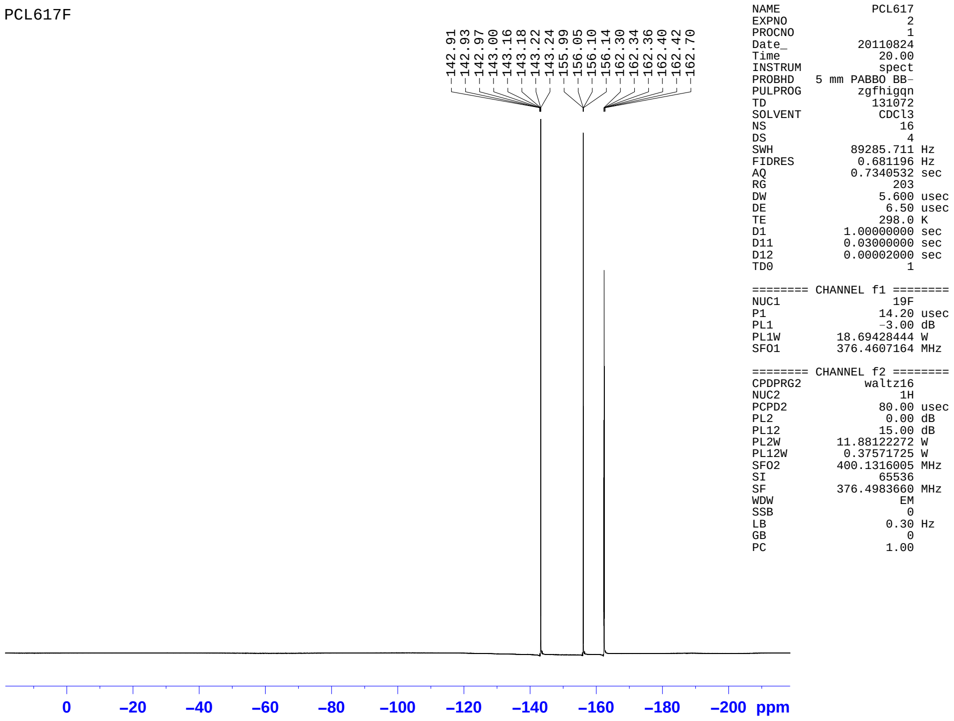
```
NAME               PCL617
EXPNO                   3
PROCNO                  1
Date_            20110824
Time                20.03
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                   80.6
DW                 20.800 usec
DE                   6.50 usec
TE                  298.6 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.50 usec
PL1                 -2.00 dB
PL1W          58.52175522 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                15.00 dB
PL13                15.00 dB
PL2W          11.88122272 W
PL12W          0.37571725 W
PL13W          0.37571725 W
SFO2          400.1316005 MHz
SI                  32768
SF            100.6127690 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

5-(Perfluorophenyl)benzo[*d*][1,3]dioxole (Table 4.3, 4.5; Product 23ap)



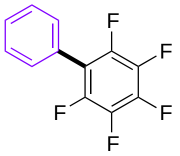


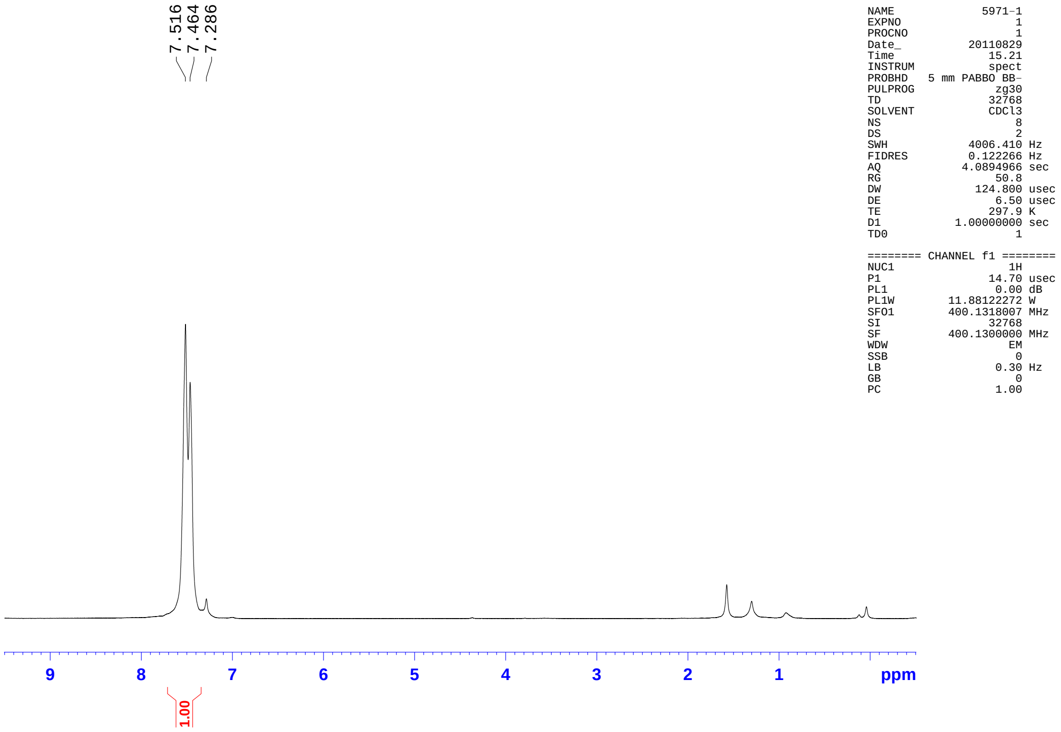
```
NAME              PCL617
EXPNO                  2
PROCNO                 1
Date_           20110824
Time               20.00
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG         zgfhigqn
TD                131072
SOLVENT            CDCl3
NS                    16
DS                     4
SWH            89285.711 Hz
FIDRES          0.681196 Hz
AQ             0.7340532 sec
RG                   203
DW                 5.600 usec
DE                  6.50 usec
TE                 298.0 K
D1            1.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 19F
P1                 14.20 usec
PL1                -3.00 dB
PL1W         18.69428444 W
SFO1         376.4607164 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
SFO2         400.1316005 MHz
SI                 65536
SF           376.4983660 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

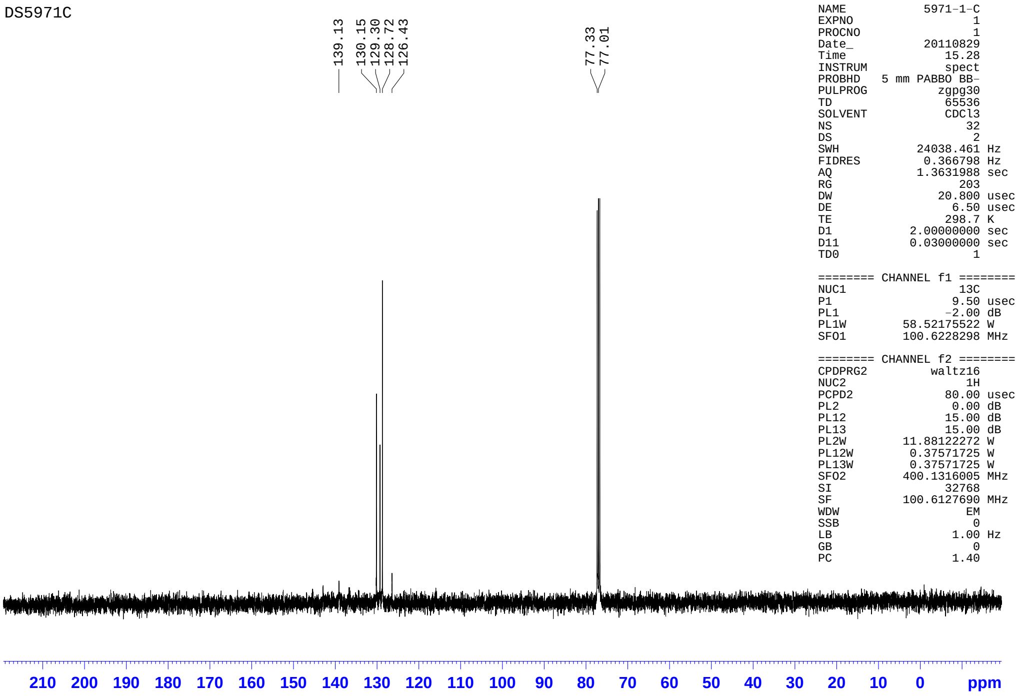
2,3,4,5,6-Pentafluoro-1,1'-biphenyl (Table 4.4; Product 23aq)





```
NAME             5971-1
EXPNO                 1
PROCNO                1
Date_          20110829
Time              15.21
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            4006.410 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                 50.8
DW              124.800 usec
DE                 6.50 usec
TE                297.9 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.70 usec
PL1                0.00 dB
PL1W        11.88122272 W
SFO1        400.1318007 MHz
SI                32768
SF          400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

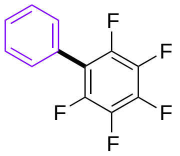


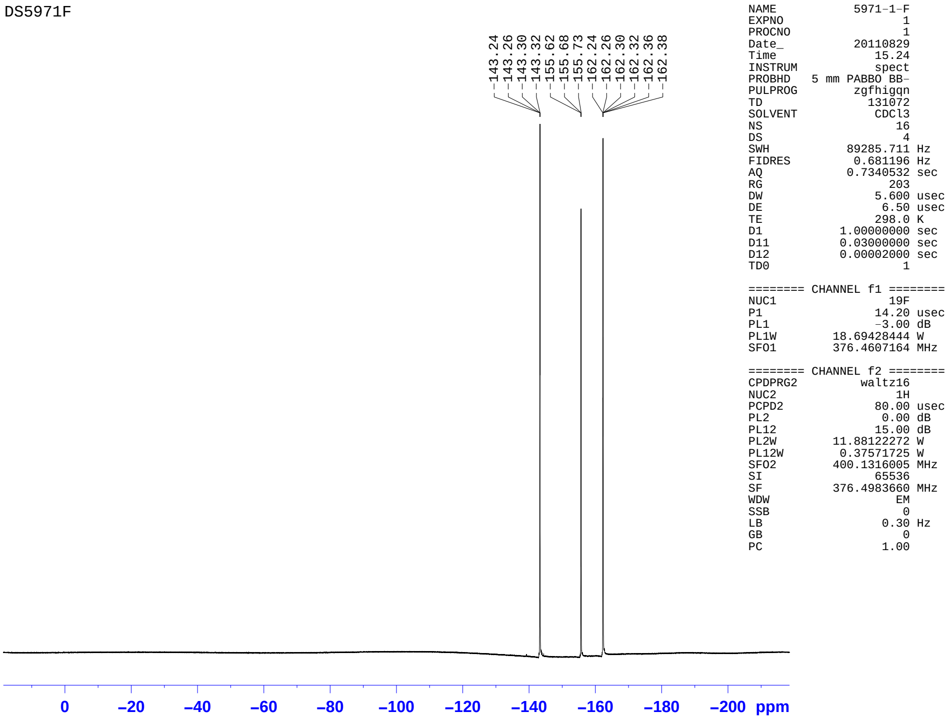
```
NAME           5971-1-C
EXPNO                 1
PROCNO                1
Date_          20110829
Time              15.28
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                  203
DW               20.800 usec
DE                 6.50 usec
TE                298.7 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.50 usec
PL1               -2.00 dB
PL1W        58.52175522 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL13              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
PL13W        0.37571725 W
SFO2        400.1316005 MHz
SI                32768
SF          100.6127690 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

2,3,4,5,6-Pentafluoro-1,1'-biphenyl (Table 4.4; Product 23aq)



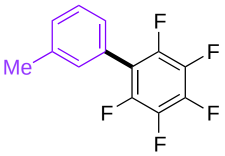


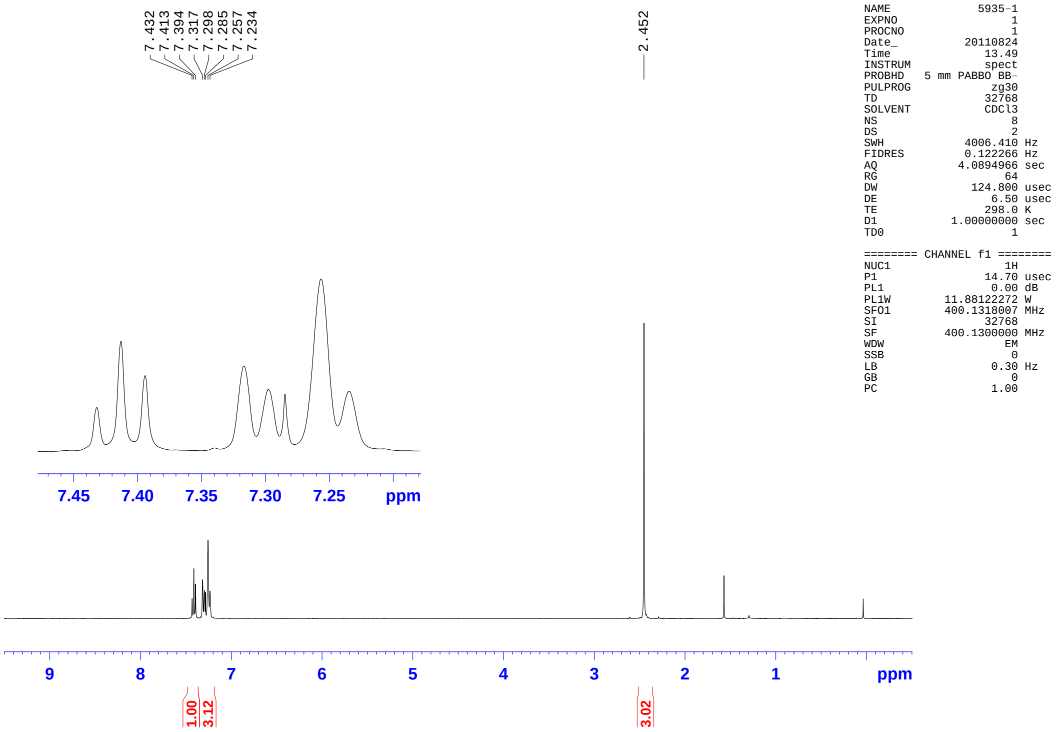
```
NAME            5971-1-F
EXPNO                  1
PROCNO                 1
Date_           20110829
Time               15.24
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG         zgfhigqn
TD                131072
SOLVENT            CDCl3
NS                    16
DS                     4
SWH           89285.711 Hz
FIDRES         0.681196 Hz
AQ            0.7340532 sec
RG                   203
DW                 5.600 usec
DE                  6.50 usec
TE                 298.0 K
D1            1.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 19F
P1                 14.20 usec
PL1                -3.00 dB
PL1W         18.69428444 W
SFO1         376.4607164 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
SFO2         400.1316005 MHz
SI                 65536
SF           376.4983660 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

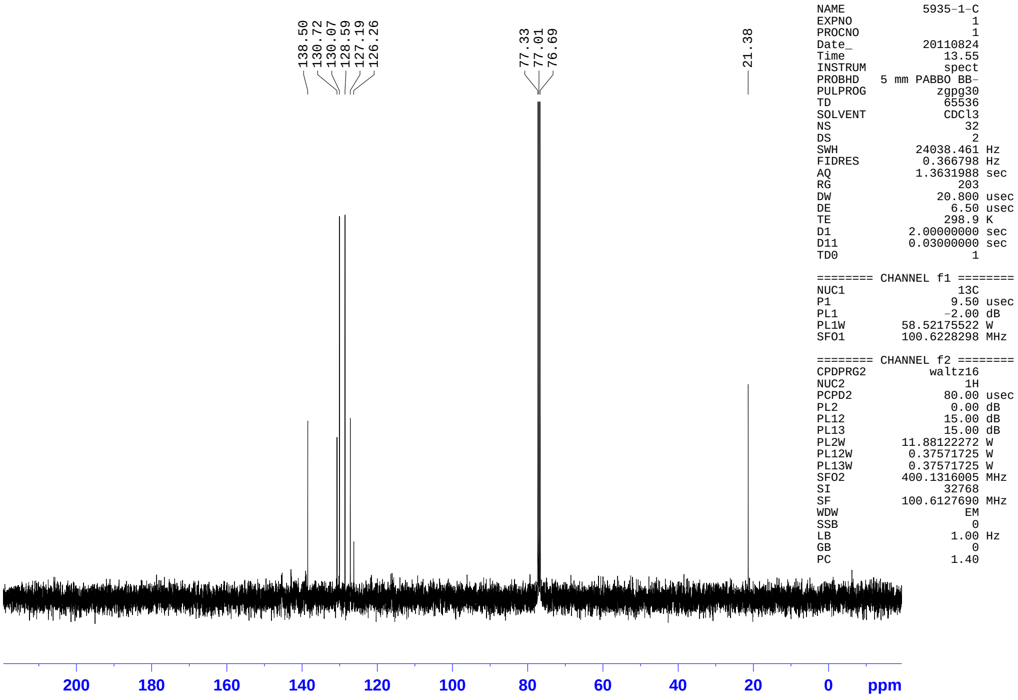
2,3,4,5,6-Pentafluoro-3'-methyl-1,1'-biphenyl (Table 4.4; Product 23ar)





```
NAME              5935-1
EXPNO                  1
PROCNO                 1
Date_           20110824
Time               13.49
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                    64
DW               124.800 usec
DE                  6.50 usec
TE                 298.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

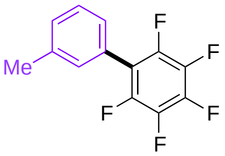


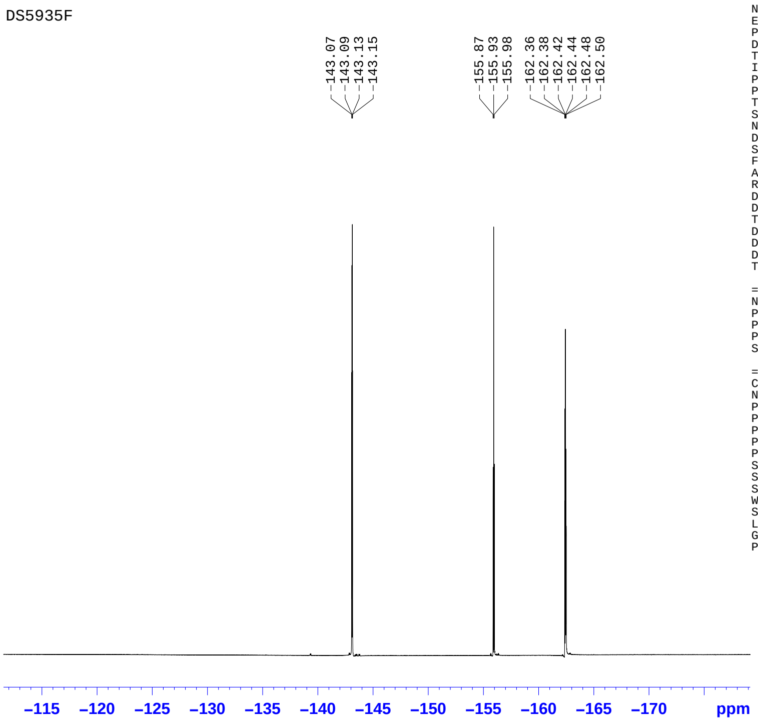
```
NAME            5935-1-C
EXPNO                  1
PROCNO                 1
Date_           20110824
Time               13.55
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   203
DW                20.800 usec
DE                  6.50 usec
TE                 298.9 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127690 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

2,3,4,5,6-Pentafluoro-3'-methyl-1,1'-biphenyl (Table 4.4; Product 23ar)



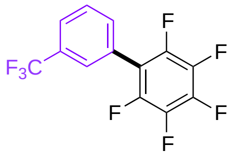


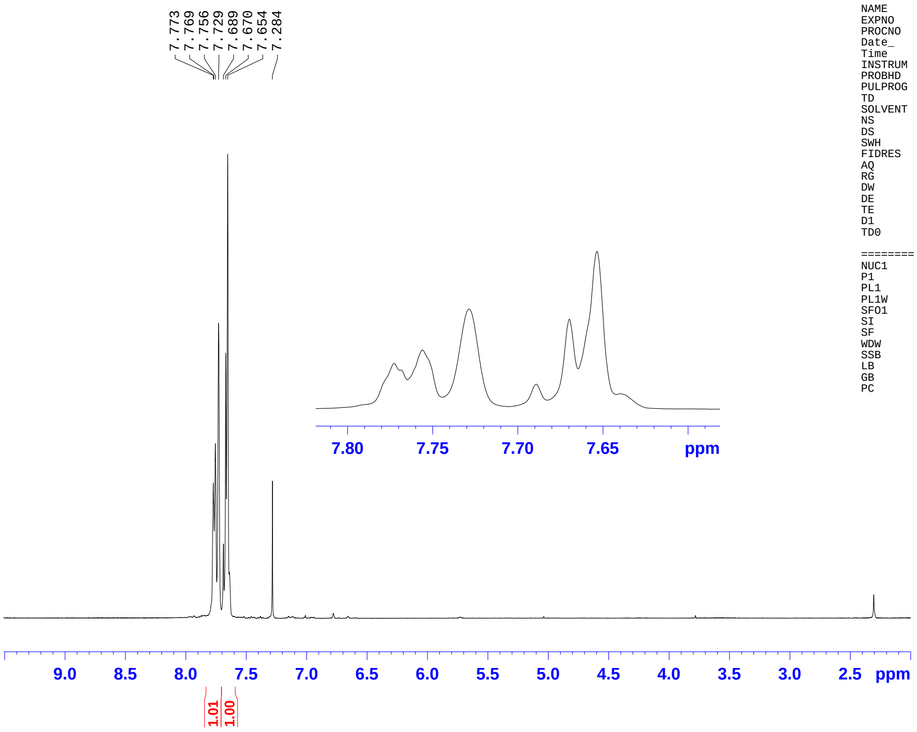
```
NAME           5935-1-F
EXPNO                 1
PROCNO                1
Date_          20110824
Time              13.52
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG        zgfhigqn
TD               131072
SOLVENT           CDCl3
NS                   16
DS                    4
SWH          89285.711 Hz
FIDRES        0.681196 Hz
AQ           0.7340532 sec
RG                  203
DW                5.600 usec
DE                 6.50 usec
TE                298.1 K
D1           1.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                19F
P1                14.20 usec
PL1               -3.00 dB
PL1W        18.69428444 W
SFO1        376.4607164 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
SFO2        400.1316005 MHz
SI                65536
SF          376.4983660 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

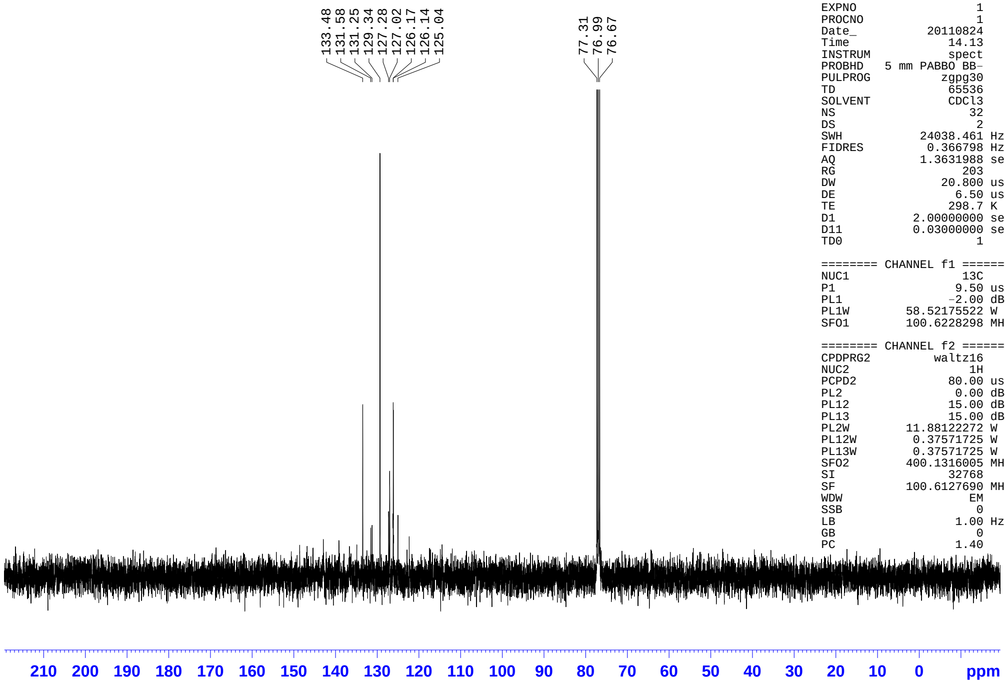
2,3,4,5,6-Pentafluoro-3'-(trifluoromethyl)-1,1'-biphenyl (Table 4.5; Product 23as)





```
NAME             5937-1
EXPNO                 1
PROCNO                1
Date_          20110824
Time              14.06
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            4006.410 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                 71.8
DW              124.800 usec
DE                 6.50 usec
TE                298.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.70 usec
PL1                0.00 dB
PL1W        11.88122272 W
SFO1        400.1318007 MHz
SI                32768
SF          400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

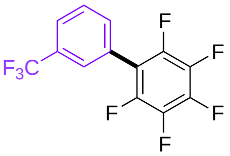


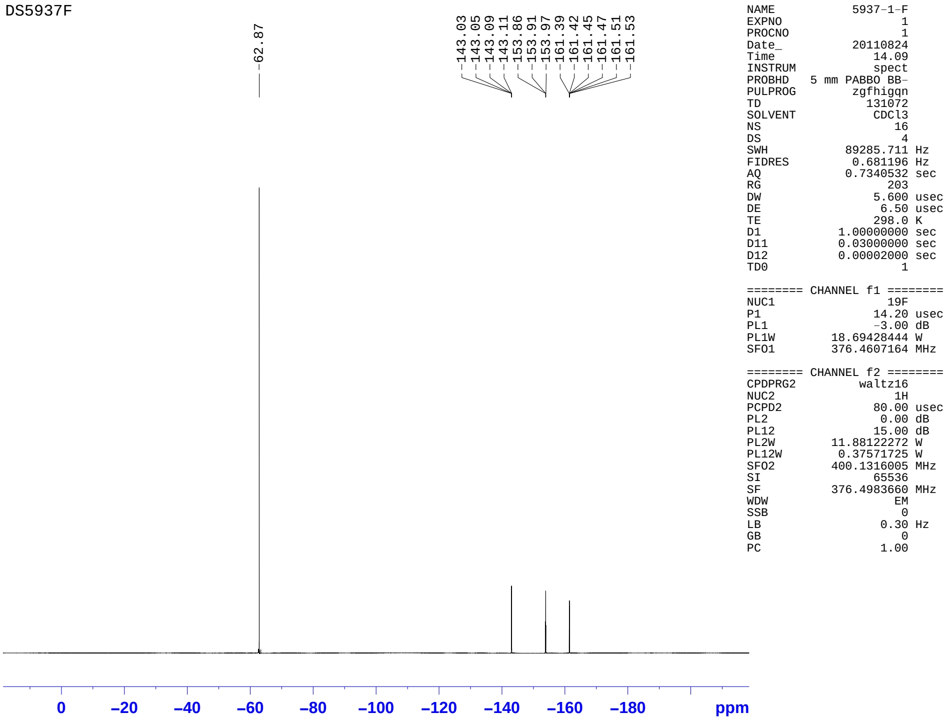
```
NAME           5937-1-C
EXPNO                 1
PROCNO                1
Date_          20110824
Time              14.13
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                  203
DW               20.800 usec
DE                 6.50 usec
TE                298.7 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.50 usec
PL1               -2.00 dB
PL1W        58.52175522 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL13              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
PL13W        0.37571725 W
SFO2        400.1316005 MHz
SI                32768
SF          100.6127690 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

2,3,4,5,6-Pentafluoro-3'-(trifluoromethyl)-1,1'-biphenyl (Table 4.5; Product 23as)



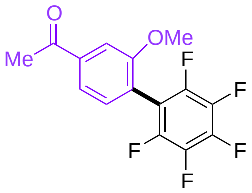


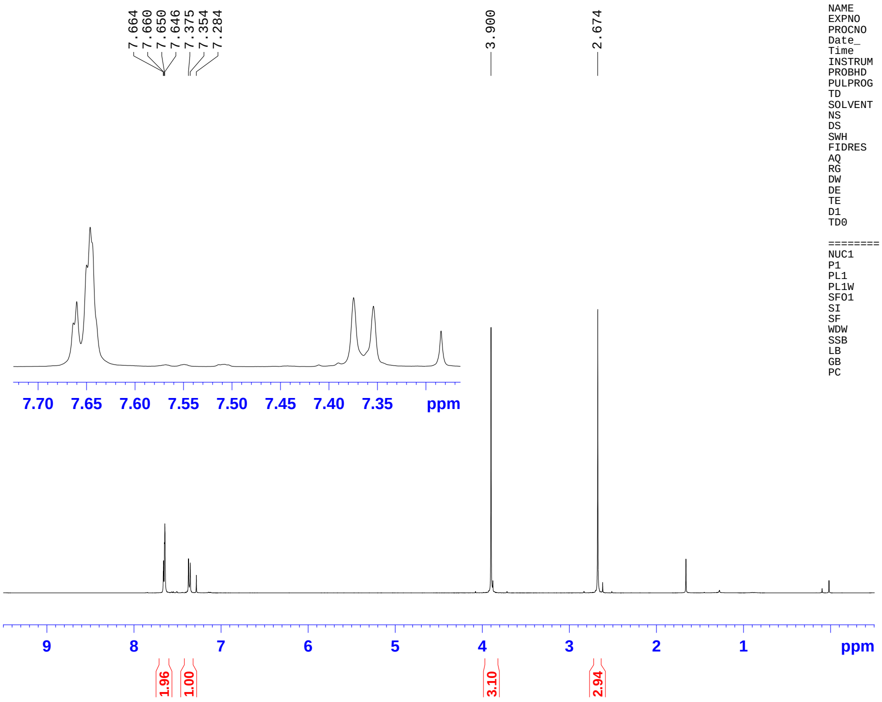
```
NAME            5937-1-F
EXPNO                  1
PROCNO                 1
Date_           20110824
Time               14.09
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG         zgfhigqn
TD                131072
SOLVENT            CDCl3
NS                    16
DS                     4
SWH           89285.711 Hz
FIDRES         0.681196 Hz
AQ            0.7340532 sec
RG                   203
DW                 5.600 usec
DE                  6.50 usec
TE                 298.0 K
D1            1.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 19F
P1                 14.20 usec
PL1                -3.00 dB
PL1W         18.69428444 W
SFO1         376.4607164 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
SFO2         400.1316005 MHz
SI                 65536
SF           376.4983660 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

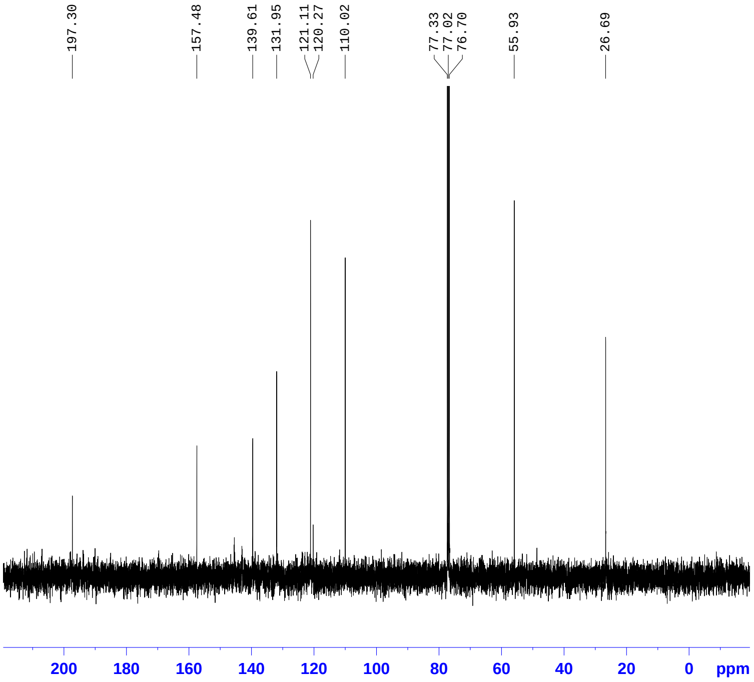
1-(2',3',4',5',6'-Pentafluoro-2-methoxy-[1,1'-biphenyl]-4-yl)ethanone (Table 4.5; Product 23at)





```
NAME              5959-1
EXPNO                  1
PROCNO                 1
Date_           20110828
Time               10.33
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                    57
DW               124.800 usec
DE                  6.50 usec
TE                 298.3 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

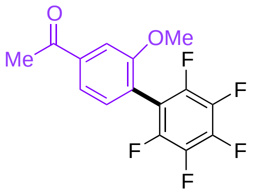


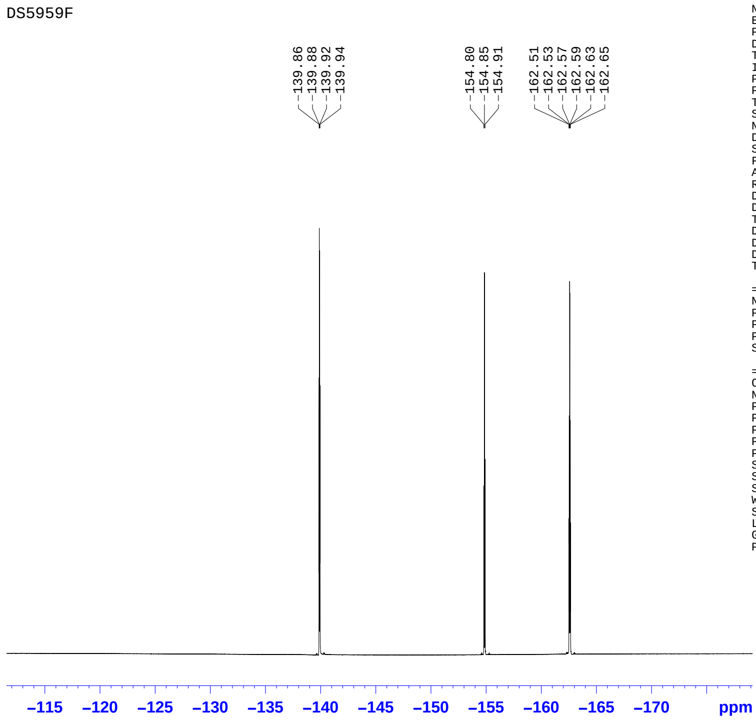
```
NAME            5959-1-C
EXPNO                  1
PROCNO                 1
Date_           20110828
Time               10.42
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   203
DW                20.800 usec
DE                  6.50 usec
TE                 299.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127690 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

1-(2',3',4',5',6'-Pentafluoro-2-methoxy-[1,1'-biphenyl]-4-yl)ethanone (Table 4.5; Product 23at)



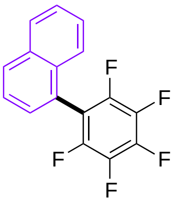


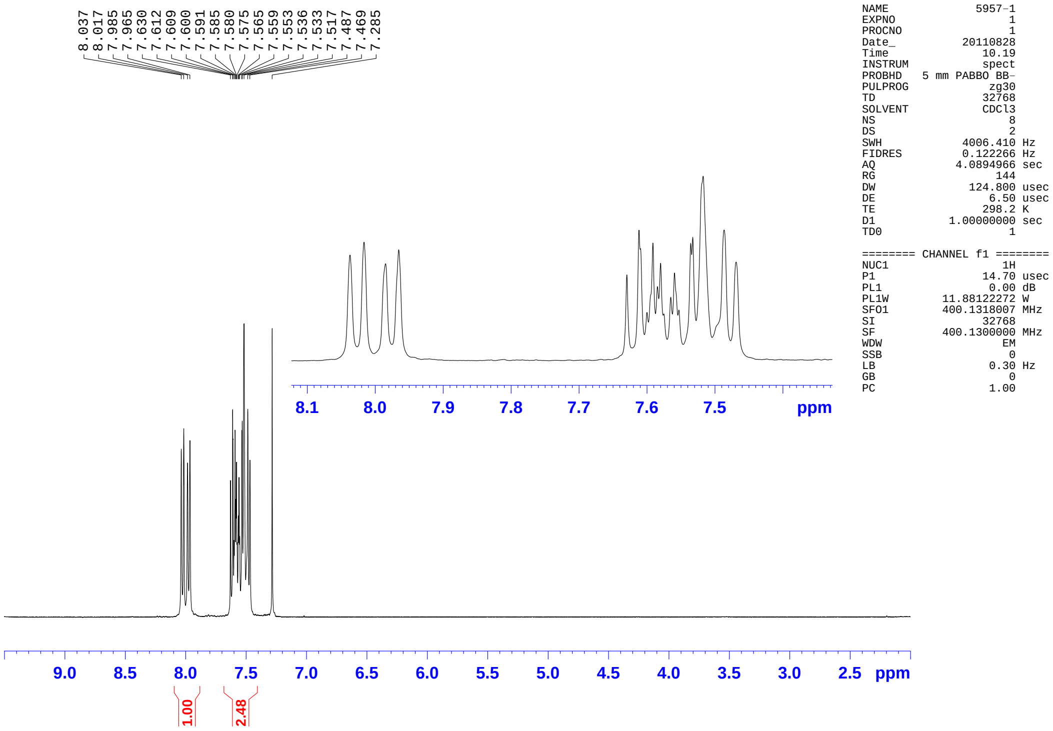
```
NAME           5959-1-F
EXPNO                 1
PROCNO                1
Date_          20110828
Time              10.37
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgfhigqn
TD               131072
SOLVENT           CDCl3
NS                   16
DS                    4
SWH          89285.711 Hz
FIDRES        0.681196 Hz
AQ           0.7340532 sec
RG                  203
DW                5.600 usec
DE                 6.50 usec
TE                298.4 K
D1           1.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                19F
P1                14.20 usec
PL1               -3.00 dB
PL1W        18.69428444 W
SFO1        376.4607164 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
SFO2        400.1316005 MHz
SI                65536
SF          376.4983660 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

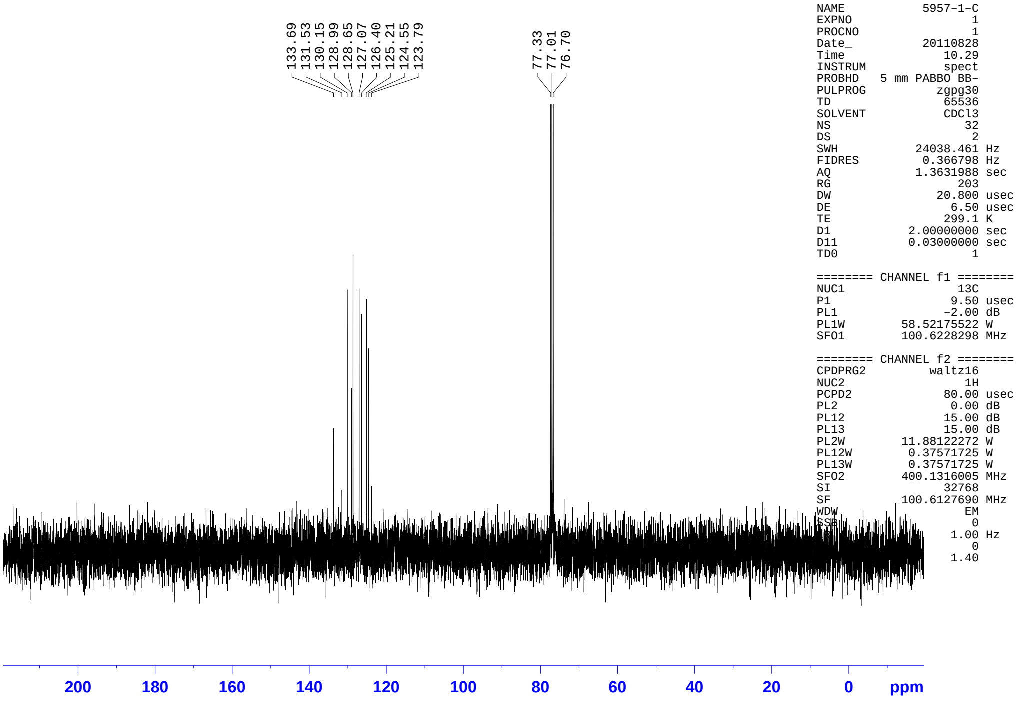
1-(Perfluorophenyl)naphthalene (Table 4.4; Product 23au)





```
NAME            5957-1
EXPNO                1
PROCNO               1
Date_         20110828
Time             10.19
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG           zg30
TD               32768
SOLVENT          CDCl3
NS                   8
DS                   2
SWH           4006.410 Hz
FIDRES        0.122266 Hz
AQ           4.0894966 sec
RG                 144
DW             124.800 usec
DE                6.50 usec
TE               298.2 K
D1          1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                1H
P1               14.70 usec
PL1               0.00 dB
PL1W       11.88122272 W
SFO1       400.1318007 MHz
SI               32768
SF         400.1300000 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.00
```

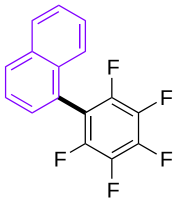


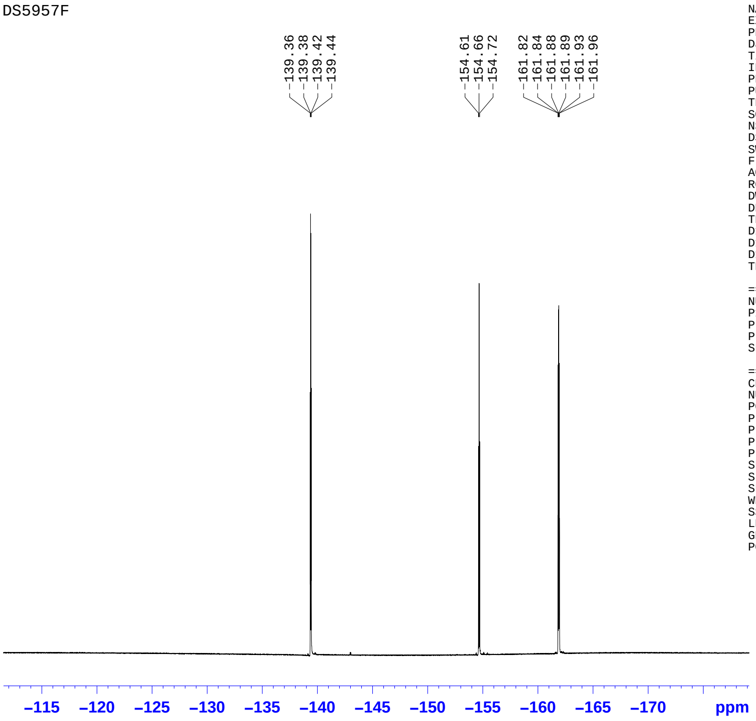
```
NAME          5957-1-C
EXPNO                1
PROCNO               1
Date_         20110828
Time             10.29
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG        zgpg30
TD               65536
SOLVENT          CDCl3
NS                  32
DS                   2
SWH          24038.461 Hz
FIDRES        0.366798 Hz
AQ           1.3631988 sec
RG                 203
DW              20.800 usec
DE                6.50 usec
TE               299.1 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1                9.50 usec
PL1              -2.00 dB
PL1W       58.52175522 W
SFO1       100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2            80.00 usec
PL2               0.00 dB
PL12             15.00 dB
PL13             15.00 dB
PL2W       11.88122272 W
PL12W       0.37571725 W
PL13W       0.37571725 W
SFO2       400.1316005 MHz
SI               32768
SF         100.6127690 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```

1-(Perfluorophenyl)naphthalene (Table 4.4; Product 23au)



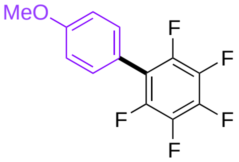


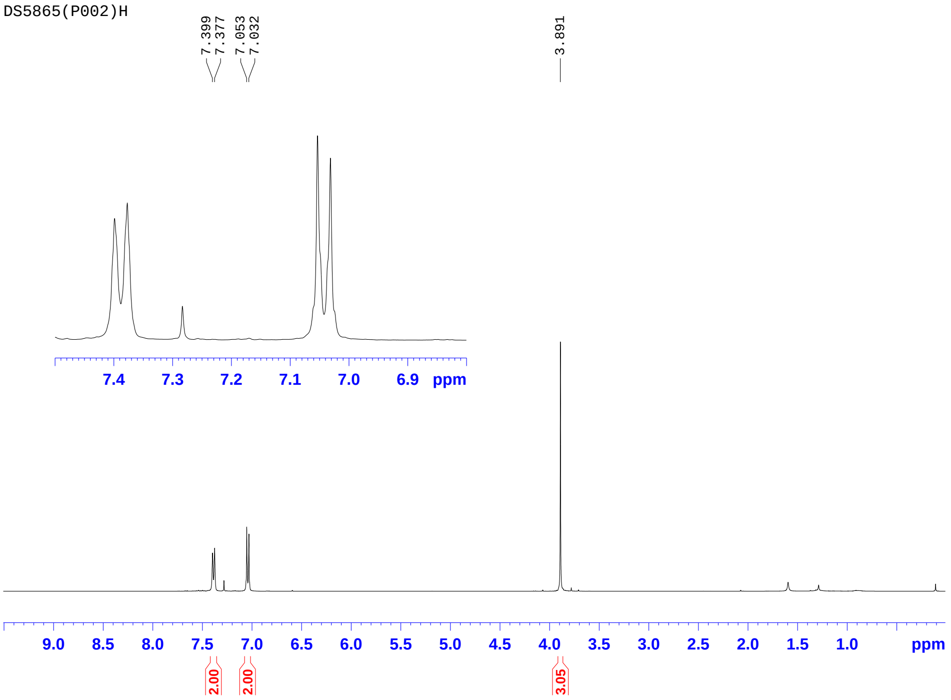
```
NAME            5957-1-F
EXPNO                  1
PROCNO                 1
Date_           20110828
Time               10.23
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG         zgfhigqn
TD                131072
SOLVENT            CDCl3
NS                    16
DS                     4
SWH           89285.711 Hz
FIDRES         0.681196 Hz
AQ            0.7340532 sec
RG                   203
DW                 5.600 usec
DE                  6.50 usec
TE                 298.3 K
D1            1.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
TD0                    1

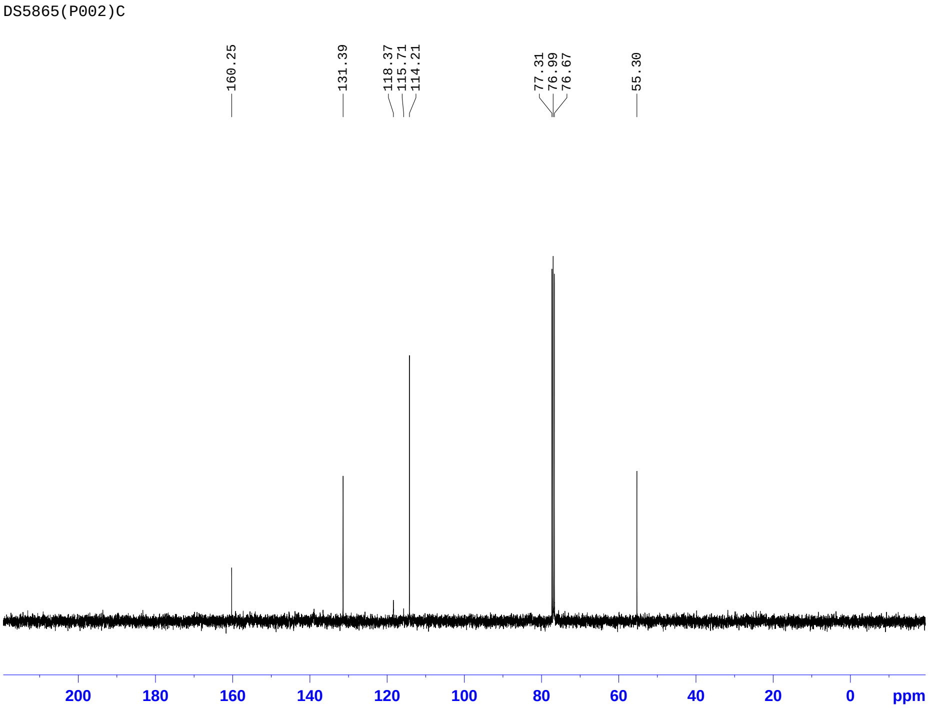
======== CHANNEL f1 ========
NUC1                 19F
P1                 14.20 usec
PL1                -3.00 dB
PL1W         18.69428444 W
SFO1         376.4607164 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
SFO2         400.1316005 MHz
SI                 65536
SF           376.4983660 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

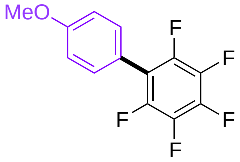
2,3,4,5,6-Pentafluoro-4'-methoxy-1,1'-biphenyl (Table 4.5; Product 23av)

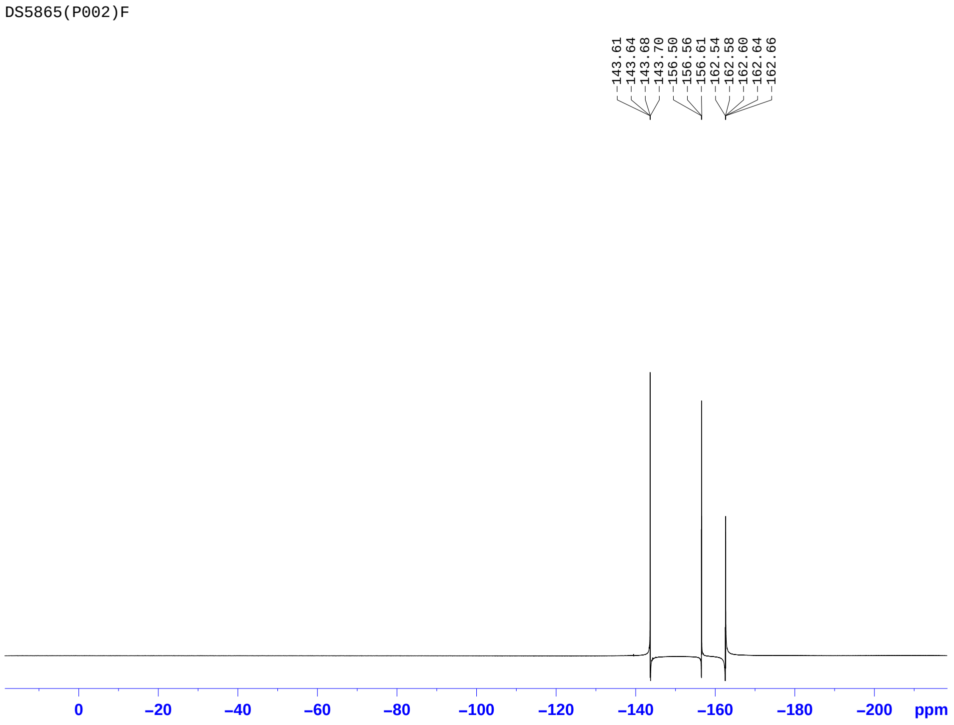




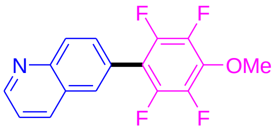


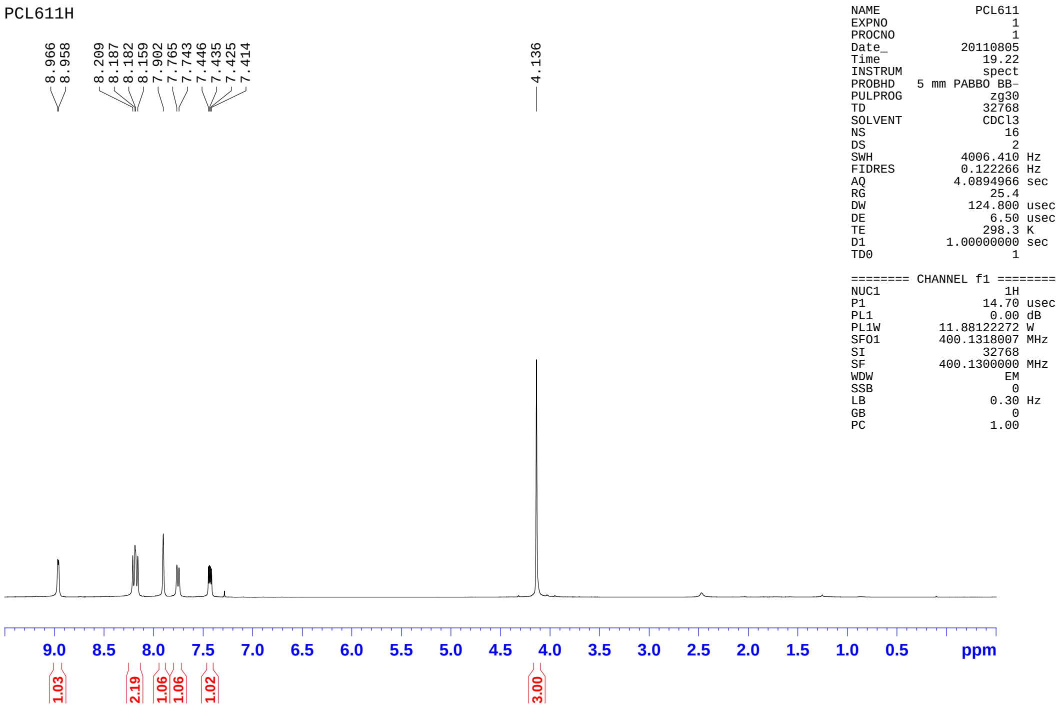
2,3,4,5,6-Pentafluoro-4'-methoxy-1,1'-biphenyl (Table 4.5; Product 23av)





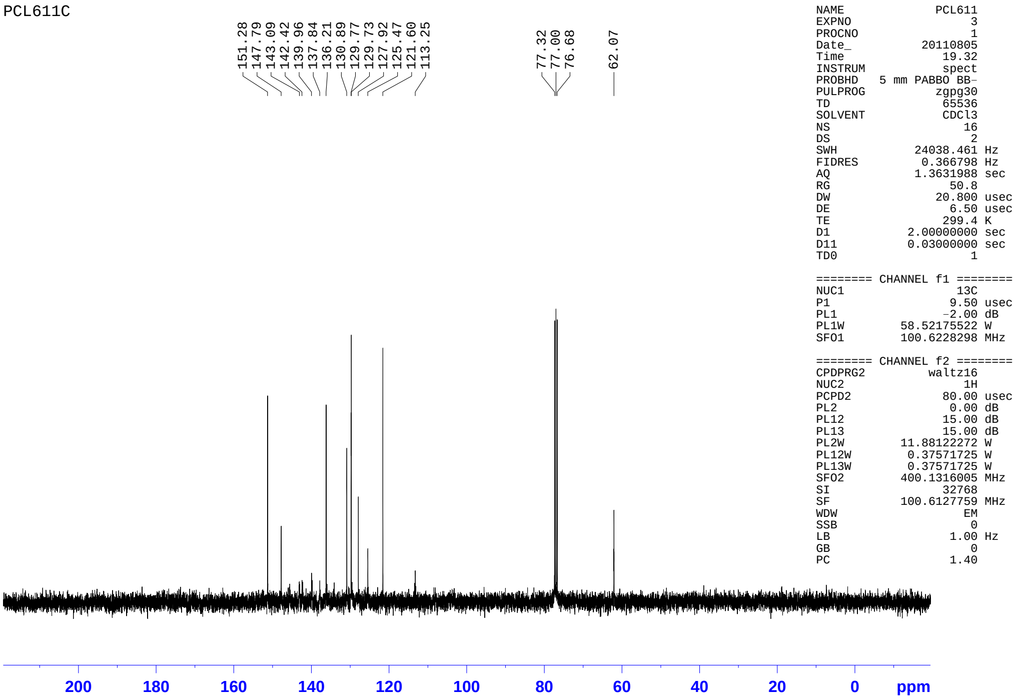
6'-(2,3,5,6-Tetrafluoro-4-methoxyphenyl)quinoline (Table 4.6; Product 23bc)





```
NAME              PCL611
EXPNO                  1
PROCNO                 1
Date_           20110805
Time               19.22
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  25.4
DW               124.800 usec
DE                  6.50 usec
TE                 298.3 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

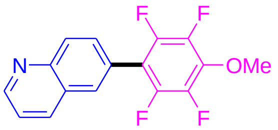


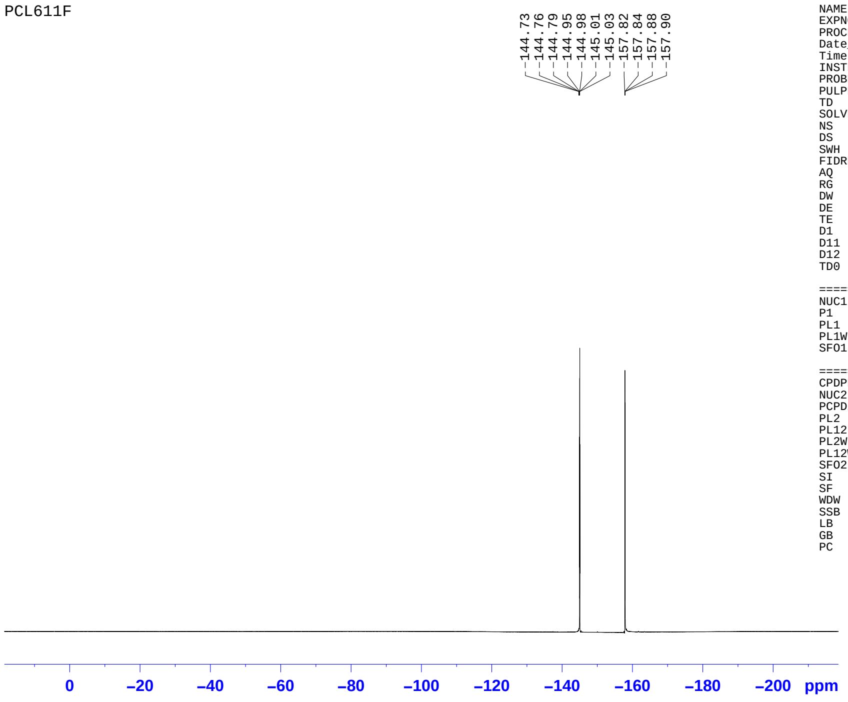
```
NAME              PCL611
EXPNO                  3
PROCNO                 1
Date_           20110805
Time               19.32
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                  50.8
DW                20.800 usec
DE                  6.50 usec
TE                 299.4 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127759 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

6'-(2,3,5,6-Tetrafluoro-4-methoxyphenyl)quinoline (Table 4.6; Product 23bc)

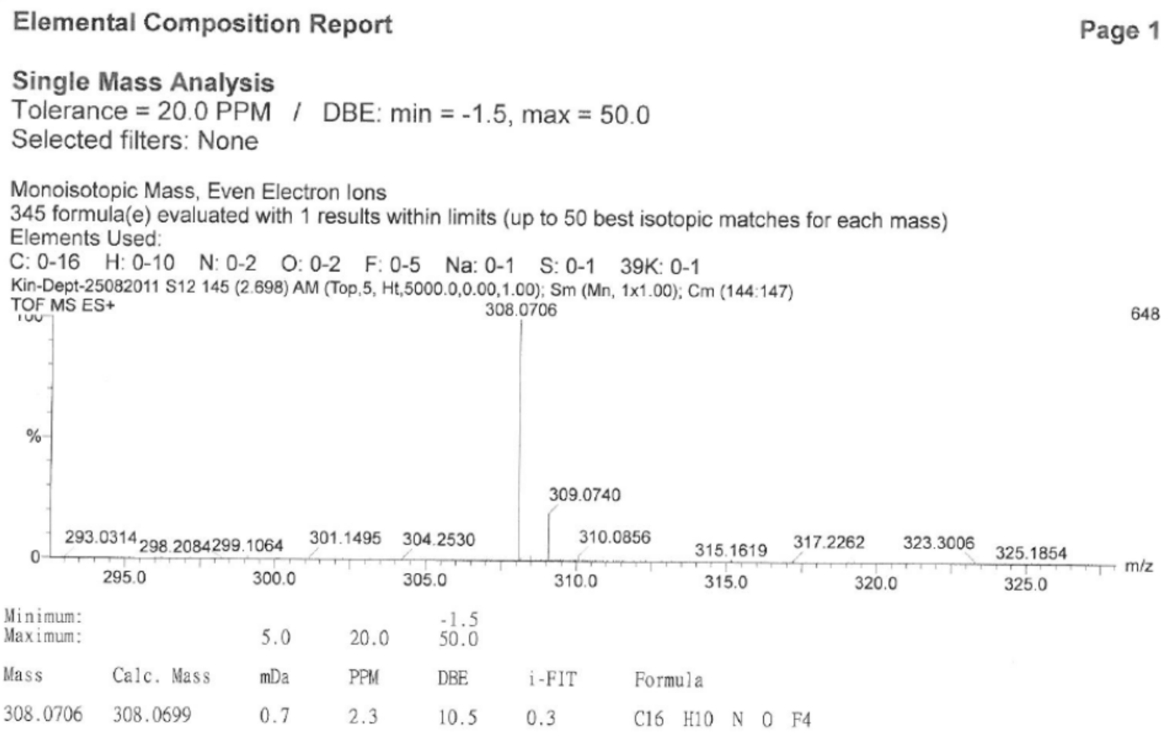




```
NAME              PCL611
EXPNO                  2
PROCNO                 1
Date_           20110805
Time               19.26
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG         zgfhigqn
TD                131072
SOLVENT            CDCl3
NS                    16
DS                     4
SWH            89285.711 Hz
FIDRES          0.681196 Hz
AQ             0.7340532 sec
RG                   203
DW                 5.600 usec
DE                  6.50 usec
TE                 298.5 K
D1            1.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 19F
P1                 14.20 usec
PL1                -3.00 dB
PL1W         18.69428444 W
SFO1         376.4607164 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
SFO2         400.1316005 MHz
SI                 65536
SF           376.4983660 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



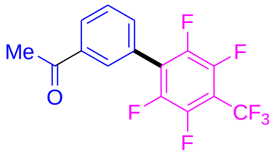
Elemental Composition Report Page 1

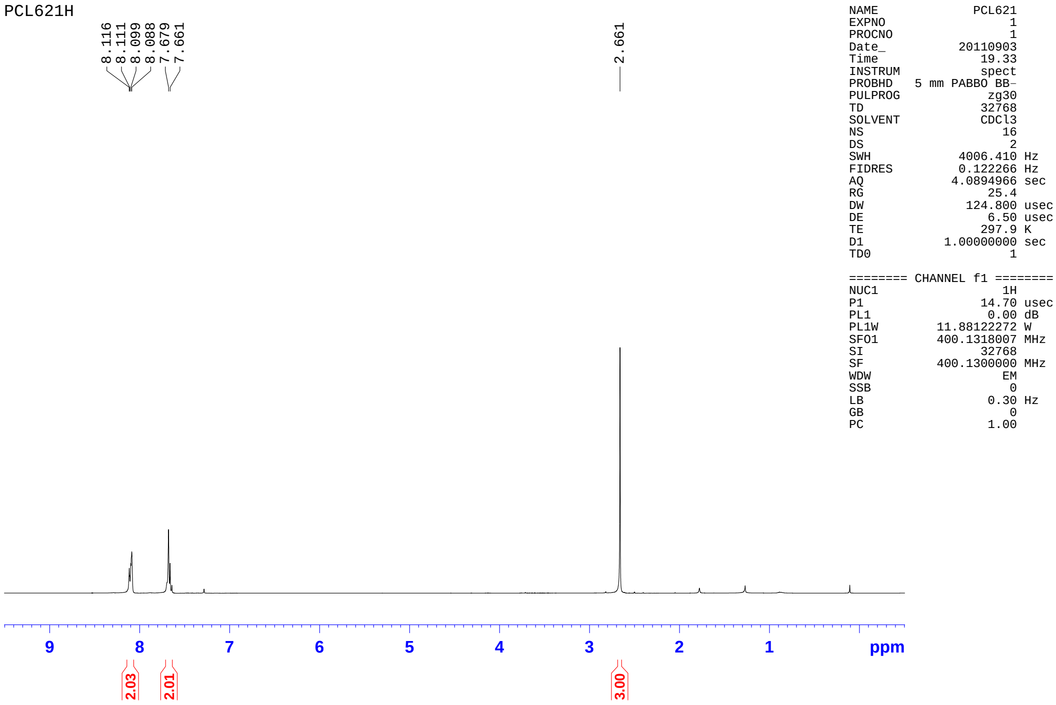
Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

Monoisotopic Mass, Even Electron Ions
345 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-16 H: 0-10 N: 0-2 O: 0-2 F: 0-5 Na: 0-1 S: 0-1 39K: 0-1
Kin-Dept-25082011 S12 145 (2.698) AM (Top,5, Ht,5000.0,0.00,1.00); Sm (Mn, 1x1.00); Cm (144:147)
TOF MS ES+

Minimum:				-1.5		
Maximum:		5.0	20.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
308.0706	308.0699	0.7	2.3	10.5	0.3	C16 H10 N O F4

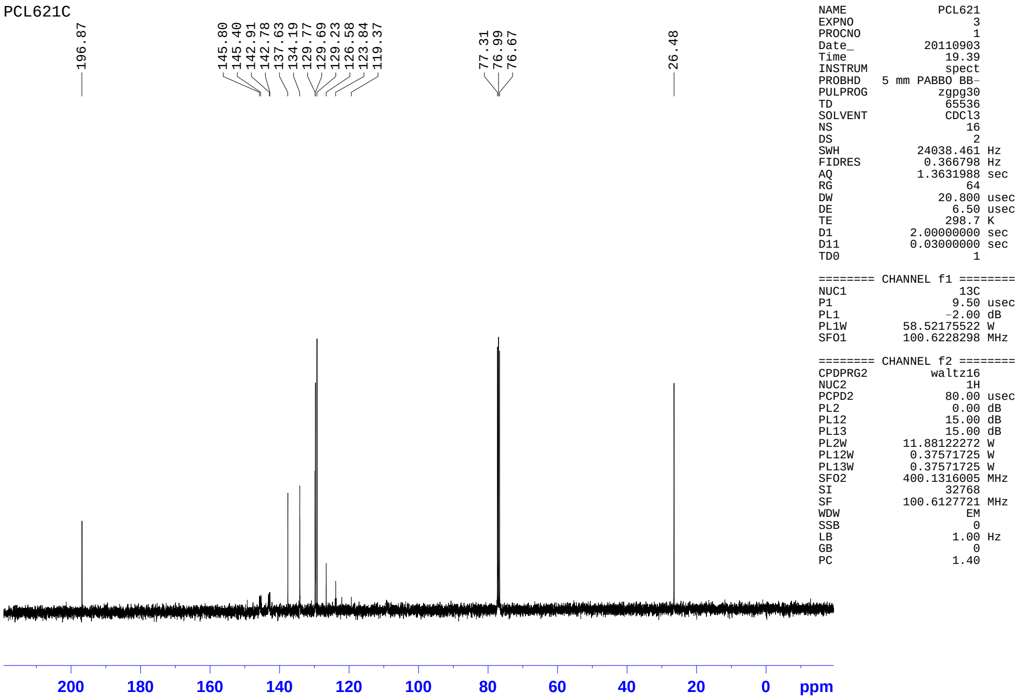
3'-(2,3,5,6-Tetrafluoro-4-(trifluoromethyl)phenyl)acetophenone (Table 4.6; Product 23ce)





```
NAME              PCL621
EXPNO                  1
PROCNO                 1
Date_           20110903
Time               19.33
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  25.4
DW               124.800 usec
DE                  6.50 usec
TE                 297.9 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

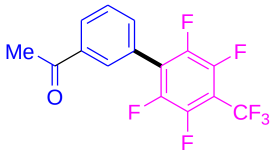


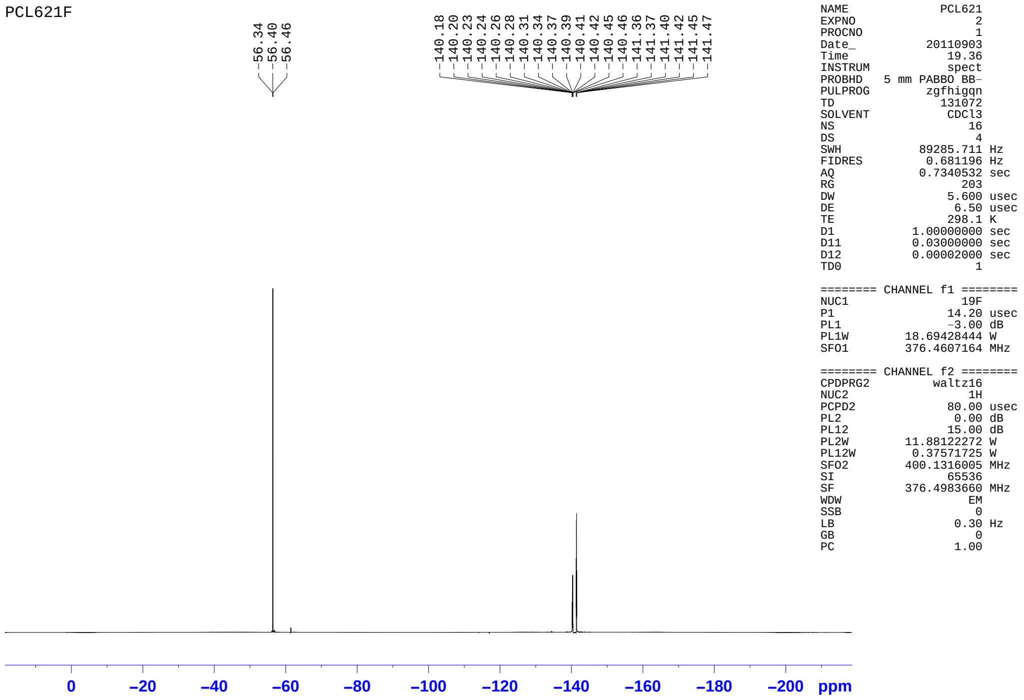
```
NAME              PCL621
EXPNO                  3
PROCNO                 1
Date_           20110903
Time               19.39
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                    64
DW                20.800 usec
DE                  6.50 usec
TE                 298.7 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127721 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

3'-(2,3,5,6-Tetrafluoro-4-(trifluoromethyl)phenyl)acetophenone (Table 4.6; Product 23ce)

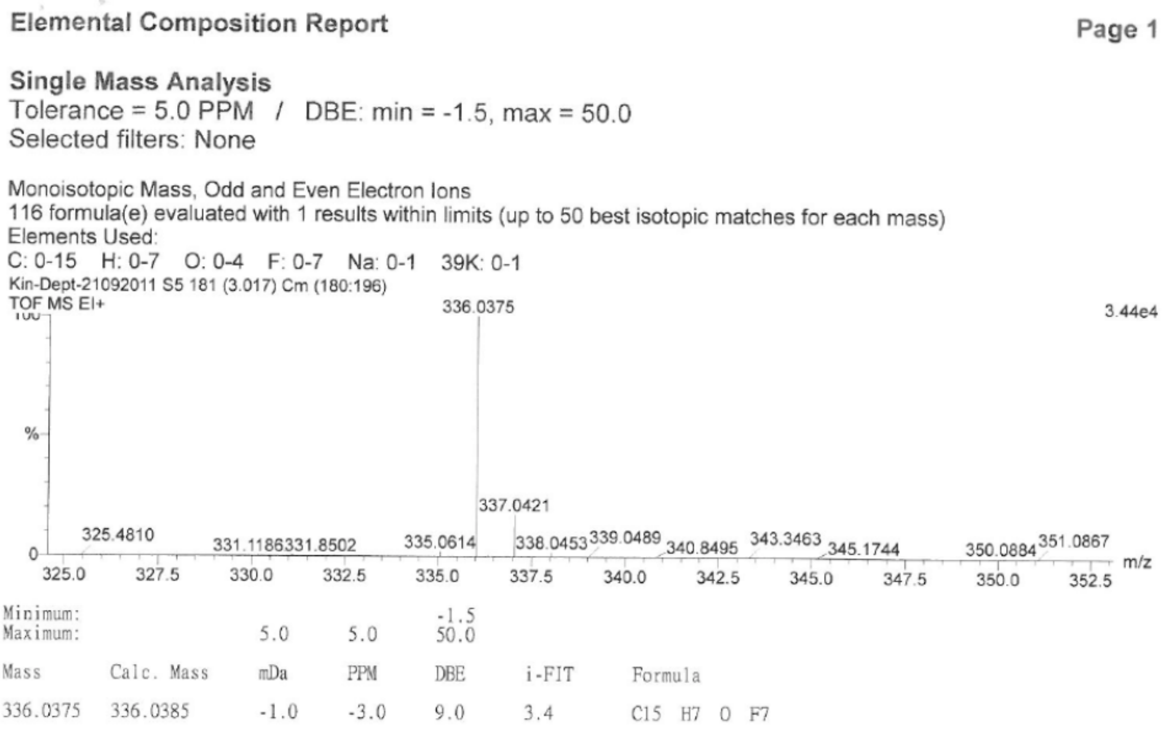




```
NAME              PCL621
EXPNO                  2
PROCNO                 1
Date_           20110903
Time               19.36
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG         zgfhigqn
TD                131072
SOLVENT            CDCl3
NS                    16
DS                     4
SWH            89285.711 Hz
FIDRES          0.681196 Hz
AQ             0.7340532 sec
RG                   203
DW                 5.600 usec
DE                  6.50 usec
TE                 298.1 K
D1            1.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 19F
P1                 14.20 usec
PL1                -3.00 dB
PL1W         18.69428444 W
SFO1         376.4607164 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
SFO2         400.1316005 MHz
SI                 65536
SF           376.4983660 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



Elemental Composition Report

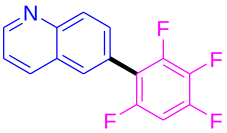
Page 1

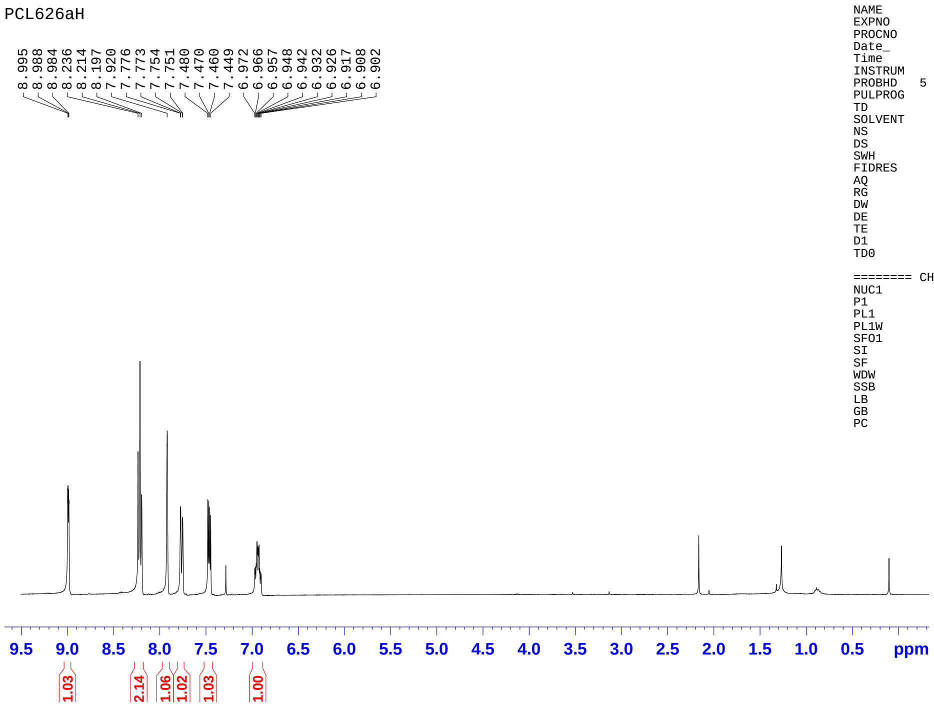
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
116 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-15 H: 0-7 O: 0-4 F: 0-7 Na: 0-1 39K: 0-1
Kin-Dept-21092011 S5 181 (3.017) Cm (180:196)
TOF MS EI+

Minimum:				-1.5		
Maximum:		5.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
336.0375	336.0385	-1.0	-3.0	9.0	3.4	C15 H7 O F7

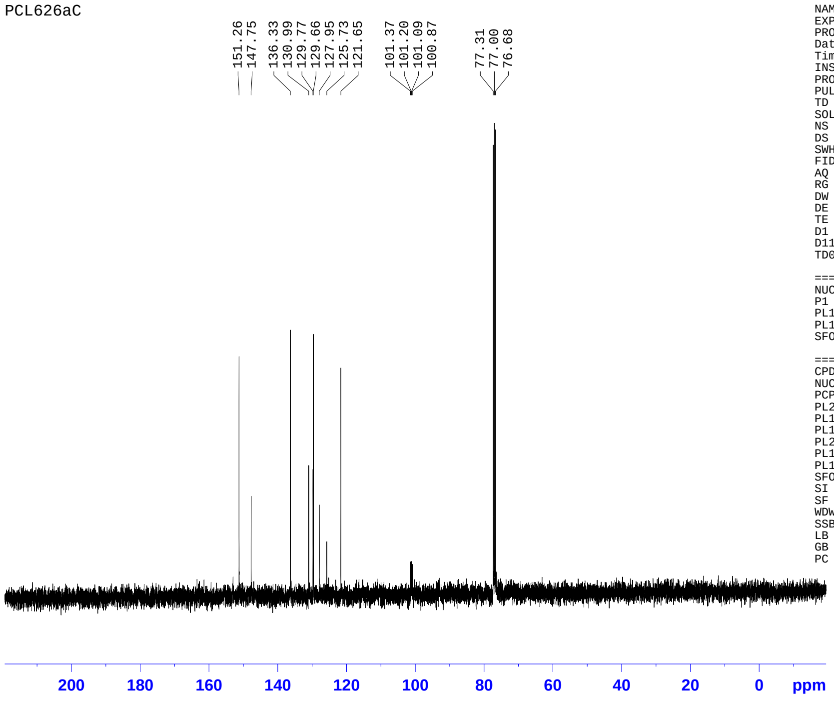
6-(2,3,4,6-Tetrafluorophenyl)quinoline (Table 4.6; Product 23dc)





```
NAME              PCL626a
EXPNO                   1
PROCNO                  1
Date_            20110904
Time                19.45
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              4006.410 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                   45.2
DW                124.800 usec
DE                   6.50 usec
TE                  298.1 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.70 usec
PL1                  0.00 dB
PL1W          11.88122272 W
SFO1          400.1318007 MHz
SI                  32768
SF            400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

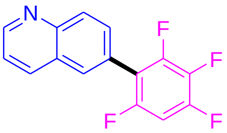


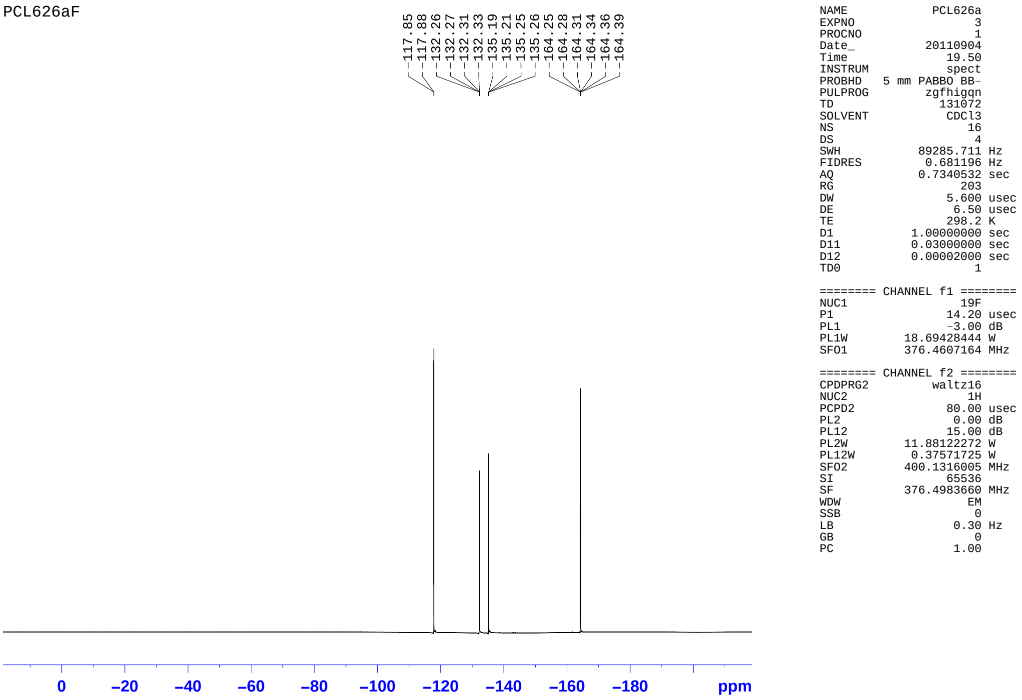
```
NAME              PCL626a
EXPNO                   2
PROCNO                  1
Date_            20110904
Time                19.47
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                    114
DW                 20.800 usec
DE                   6.50 usec
TE                  298.6 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.50 usec
PL1                 -2.00 dB
PL1W          58.52175522 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                15.00 dB
PL13                15.00 dB
PL2W          11.88122272 W
PL12W          0.37571725 W
PL13W          0.37571725 W
SFO2          400.1316005 MHz
SI                  32768
SF            100.6127738 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

6-(2,3,4,6-Tetrafluorophenyl)quinoline (Table 4.6; Product 23dc)





```
NAME             PCL626a
EXPNO                  3
PROCNO                 1
Date_           20110904
Time               19.50
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG        zgfhigqn
TD                131072
SOLVENT            CDCl3
NS                    16
DS                     4
SWH            89285.711 Hz
FIDRES          0.681196 Hz
AQ             0.7340532 sec
RG                   203
DW                 5.600 usec
DE                  6.50 usec
TE                 298.2 K
D1            1.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 19F
P1                 14.20 usec
PL1                -3.00 dB
PL1W         18.69428444 W
SFO1         376.4607164 MHz

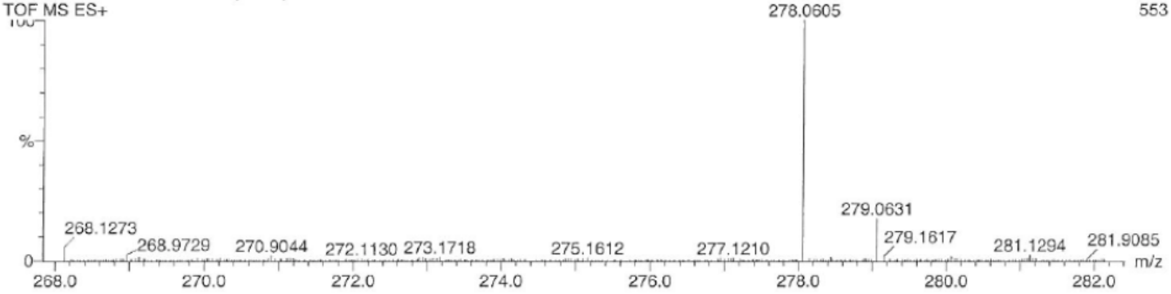
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
SFO2         400.1316005 MHz
SI                 65536
SF           376.4983660 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

Elemental Composition Report

Page 1

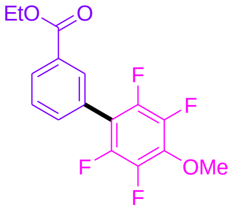
Single Mass Analysis (displaying only valid results)
Tolerance = 10.0 PPM / DBE: min = -100.0, max = 1000.0
Selected filters: None

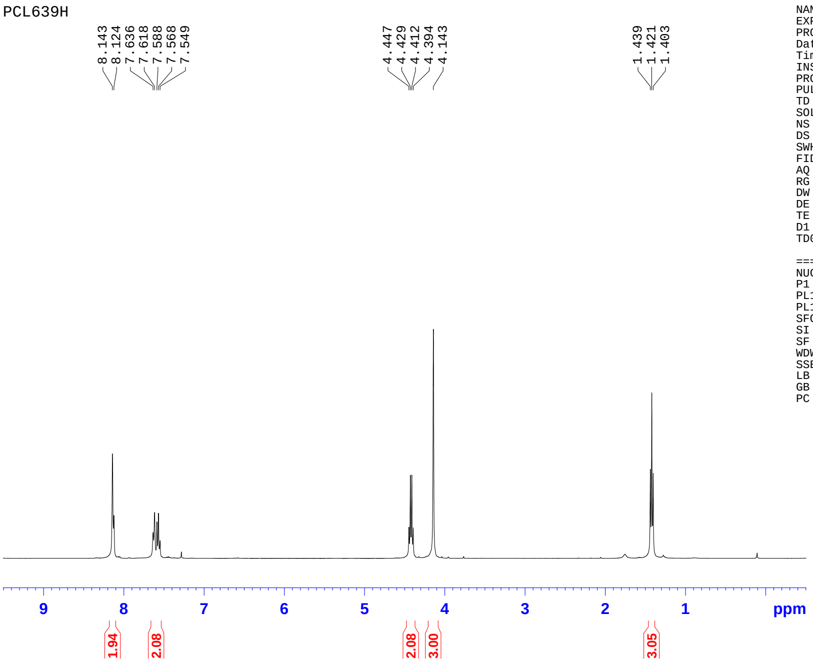
Monoisotopic Mass, Even Electron Ions
6 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-16 H: 5-10 N: 0-1 F: 0-4
KIN-DEPT-21092011 S7 179 (3.375)
TOF MS ES+



Minimum:				-100.0		
Maximum:		5.0	10.0	1000.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
278.0605	278.0593	1.2	4.3	10.5	0.3	C15 H8 N F4

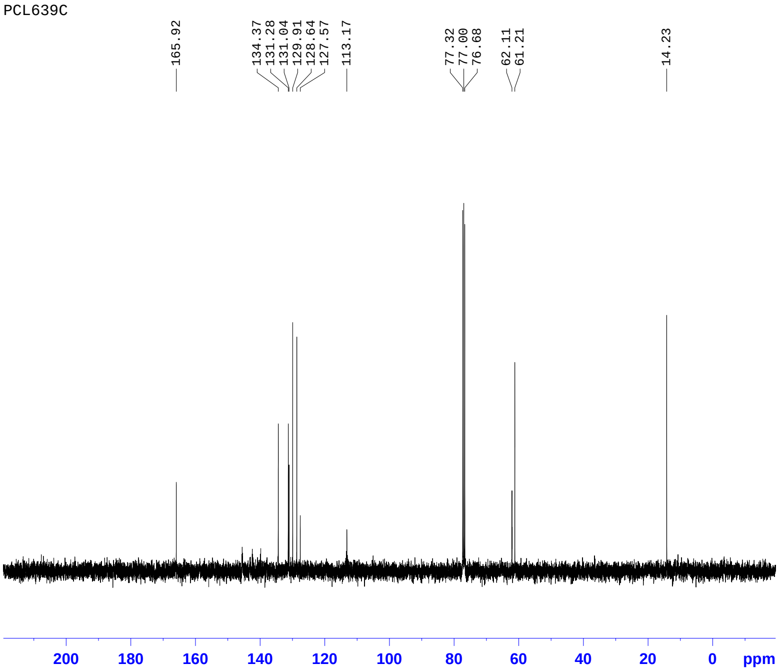
[1,1'-Biphenyl]-3-carboxylic acid, 2',3',5',6'-tetrafluoro-4'-methoxy-, ethyl ester (Table 4.6; Product 23bj)





```
NAME               PCL639
EXPNO                   1
PROCNO                  1
Date_            20110906
Time                22.57
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              4006.410 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                   25.4
DW                124.800 usec
DE                   6.50 usec
TE                  299.9 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.70 usec
PL1                  0.00 dB
PL1W          11.88122272 W
SFO1          400.1318007 MHz
SI                  32768
SF            400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

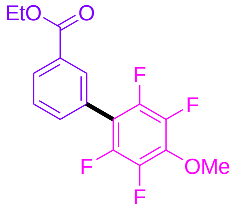


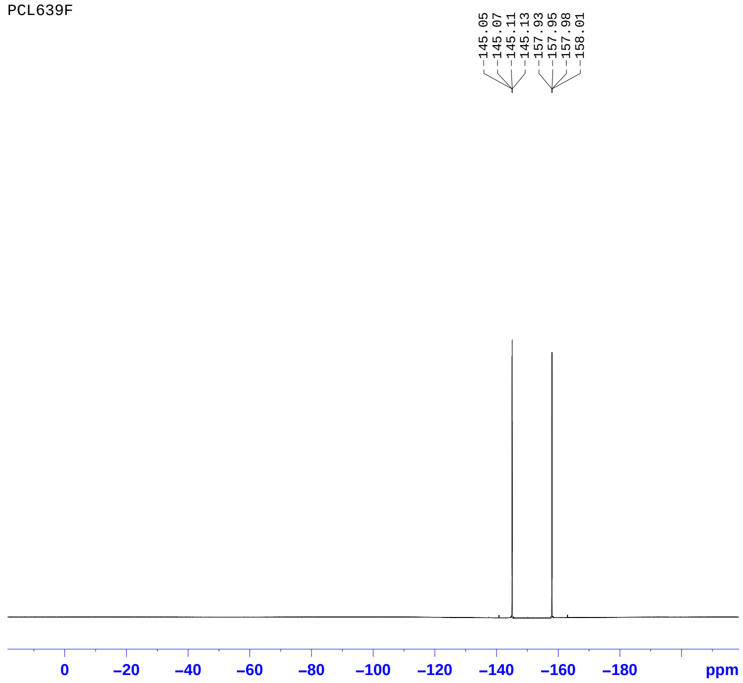
```
NAME               PCL639
EXPNO                   2
PROCNO                  1
Date_            20110906
Time                22.58
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                    203
DW                 20.800 usec
DE                   6.50 usec
TE                  300.4 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.50 usec
PL1                 -2.00 dB
PL1W          58.52175522 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                15.00 dB
PL13                15.00 dB
PL2W          11.88122272 W
PL12W          0.37571725 W
PL13W          0.37571725 W
SFO2          400.1316005 MHz
SI                  32768
SF            100.6127720 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

[1,1'-Biphenyl]-3-carboxylic acid, 2',3',5',6'-tetrafluoro-4'-methoxy-, ethyl ester (Table 4.6; Product 23bj)





```
NAME              PCL639
EXPNO                  3
PROCNO                 1
Date_           20110906
Time               23.01
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG         zgfhigqn
TD                131072
SOLVENT            CDCl3
NS                    16
DS                     4
SWH           89285.711 Hz
FIDRES         0.681196 Hz
AQ            0.7340532 sec
RG                   203
DW                 5.600 usec
DE                  6.50 usec
TE                 299.9 K
D1            1.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 19F
P1                 14.20 usec
PL1                -3.00 dB
PL1W         18.69428444 W
SFO1        376.4607164 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
SFO2        400.1316005 MHz
SI                 65536
SF          376.4983660 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

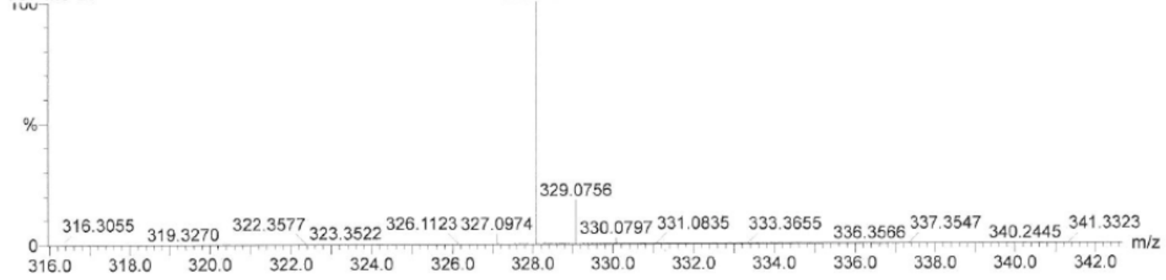
Elemental Composition Report

Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

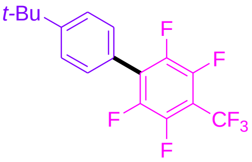
Monoisotopic Mass, Odd and Even Electron Ions
78 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-16 H: 0-12 O: 0-4 Na: 0-1 39K: 0-1 F: 0-4

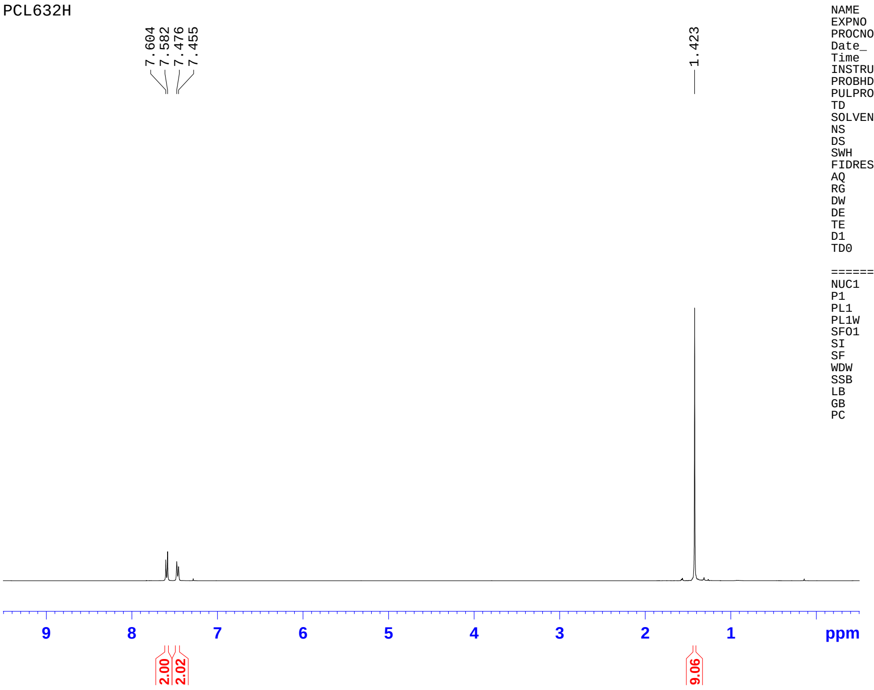
Kin-Dept-21092011 S1 124 (2.067) Cm (124:135)
TOF MS EI+



Minimum:				-1.5		
Maximum:		5.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
328.0722	328.0723	-0.1	-0.3	9.0	5.0	C16 H12 O3 F4

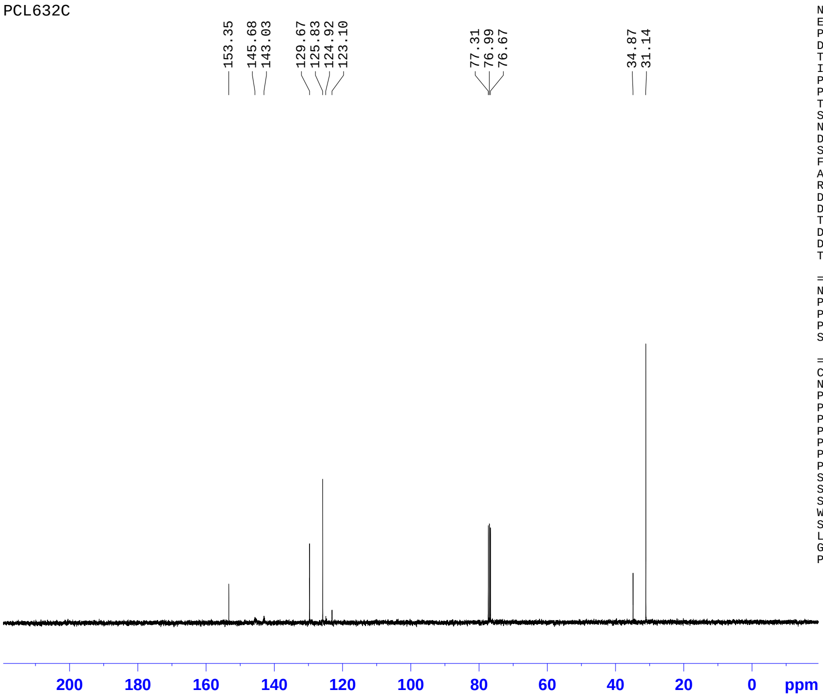
2,3,5,6-Tetrafluoro-4'-*tert*-butyl-4-(trifluoromethyl)-1,1'-biphenyl (Table 4.6; Product 23ca)





```
NAME              PCL632
EXPNO                  1
PROCNO                 1
Date_           20110904
Time               19.55
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  25.4
DW               124.800 usec
DE                  6.50 usec
TE                 297.9 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

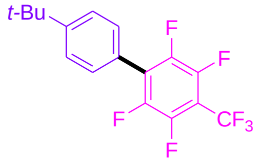


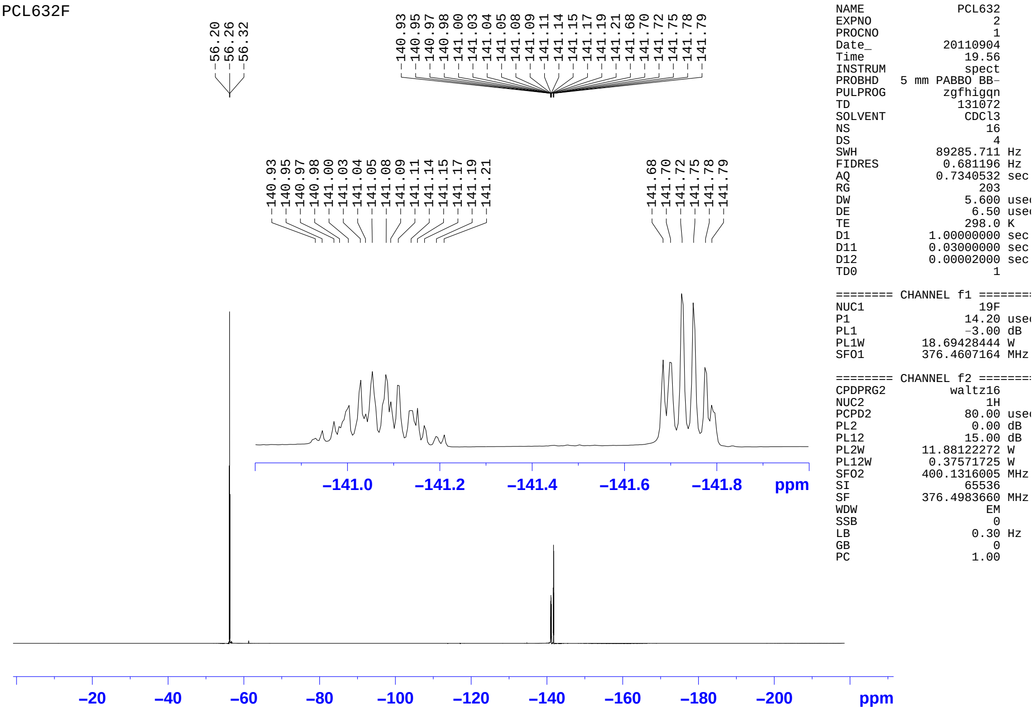
```
NAME              PCL632
EXPNO                  3
PROCNO                 1
Date_           20110904
Time               19.59
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                  71.8
DW                20.800 usec
DE                  6.50 usec
TE                 298.5 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127692 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

2,3,5,6-Tetrafluoro-4'-*tert*-butyl-4-(trifluoromethyl)-1,1'-biphenyl (Table 4.6; Product 23ca)

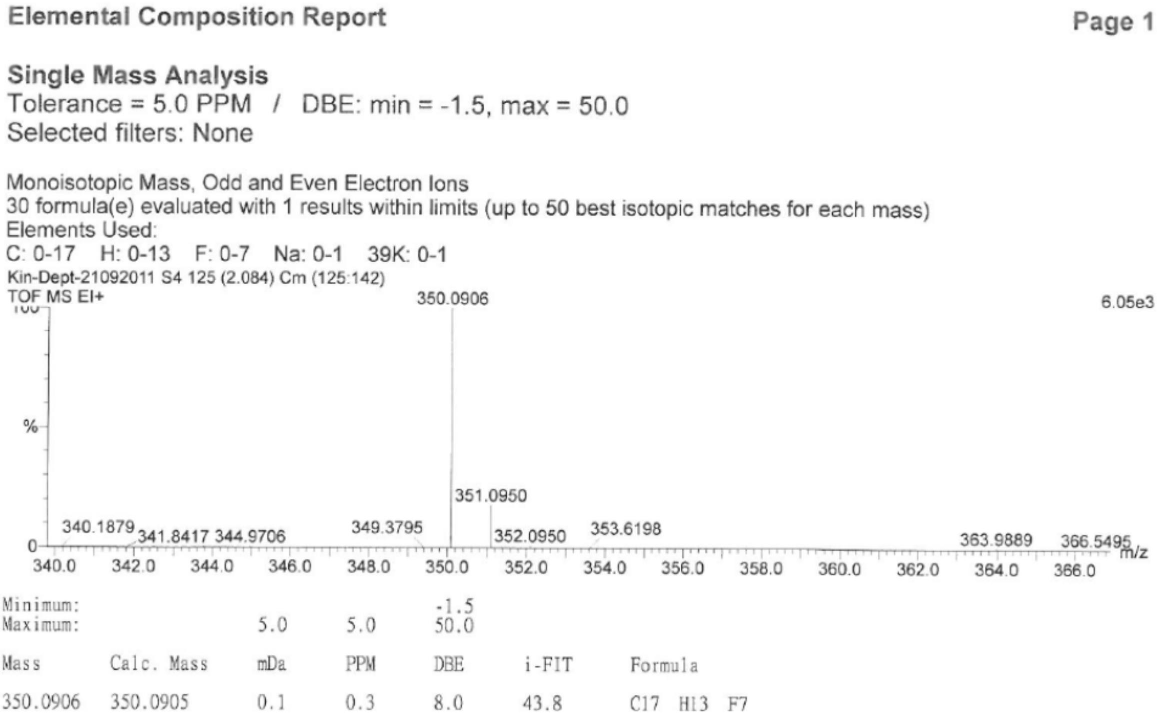




```
NAME            PCL632
EXPNO                2
PROCNO               1
Date_         20110904
Time             19.56
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG       zgfhigqn
TD              131072
SOLVENT          CDCl3
NS                  16
DS                   4
SWH         89285.711 Hz
FIDRES       0.681196 Hz
AQ          0.7340532 sec
RG                 203
DW               5.600 use
DE                6.50 use
TE               298.0 K
D1          1.00000000 sec
D11         0.03000000 sec
D12         0.00002000 sec
TD0                  1

======== CHANNEL f1 =======
NUC1               19F
P1               14.20 use
PL1              -3.00 dB
PL1W       18.69428444 W
SFO1       376.4607164 MHz

======== CHANNEL f2 =======
CPDPRG2        waltz16
NUC2                1H
PCPD2            80.00 use
PL2               0.00 dB
PL12             15.00 dB
PL2W       11.88122272 W
PL12W       0.37571725 W
SFO2       400.1316005 MHz
SI               65536
SF         376.4983660 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.00
```



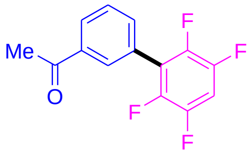
Elemental Composition Report Page 1

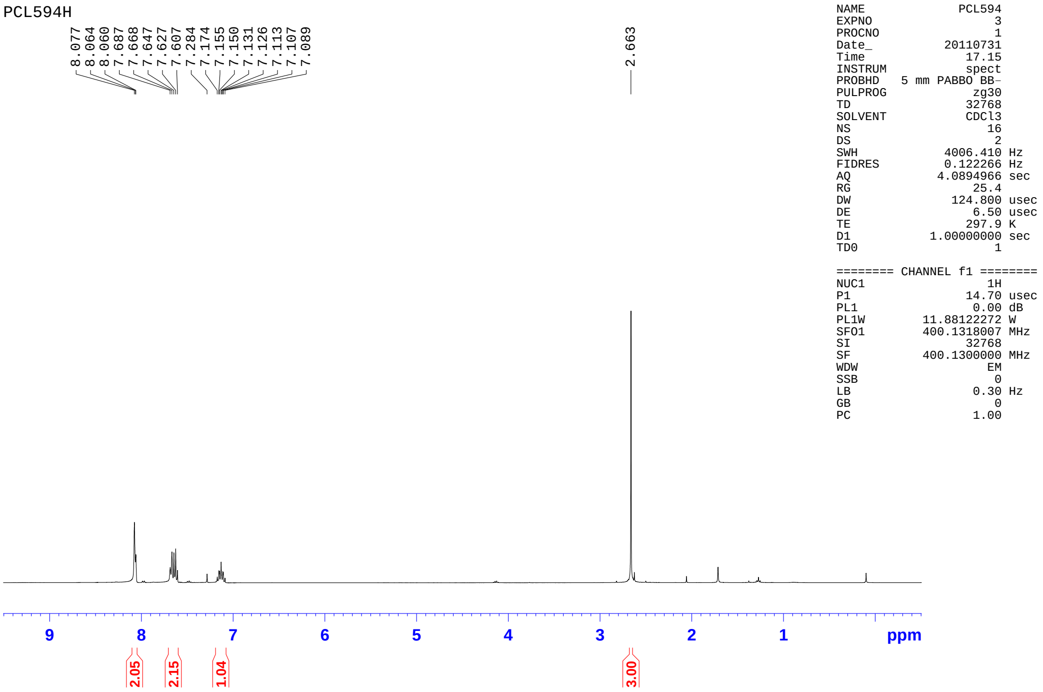
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
30 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-17 H: 0-13 F: 0-7 Na: 0-1 39K: 0-1
Kin-Dept-21092011 S4 125 (2.084) Cm (125:142)
TOF MS EI+

Minimum:				-1.5		
Maximum:		5.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
350.0906	350.0905	0.1	0.3	8.0	43.8	C17 H13 F7

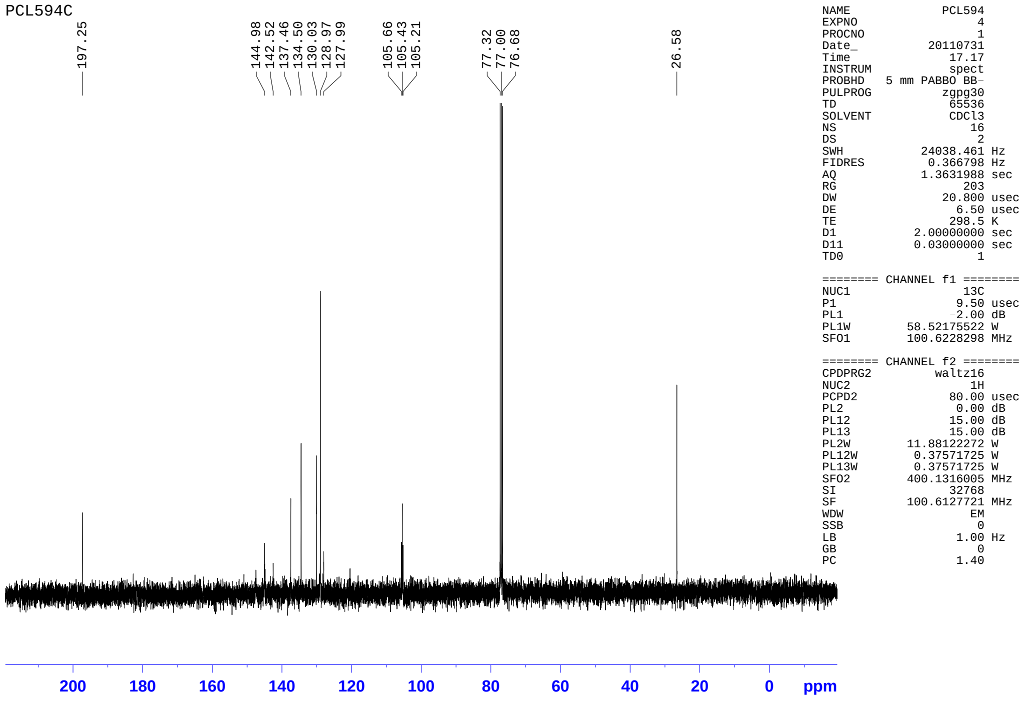
3'-(2,3,5,6-Tetrafluorophenyl)acetophenone (Table 4.6; Product 23ee)





```
NAME              PCL594
EXPNO                  3
PROCNO                 1
Date_           20110731
Time               17.15
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  25.4
DW               124.800 usec
DE                  6.50 usec
TE                 297.9 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

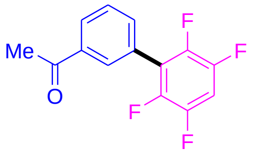


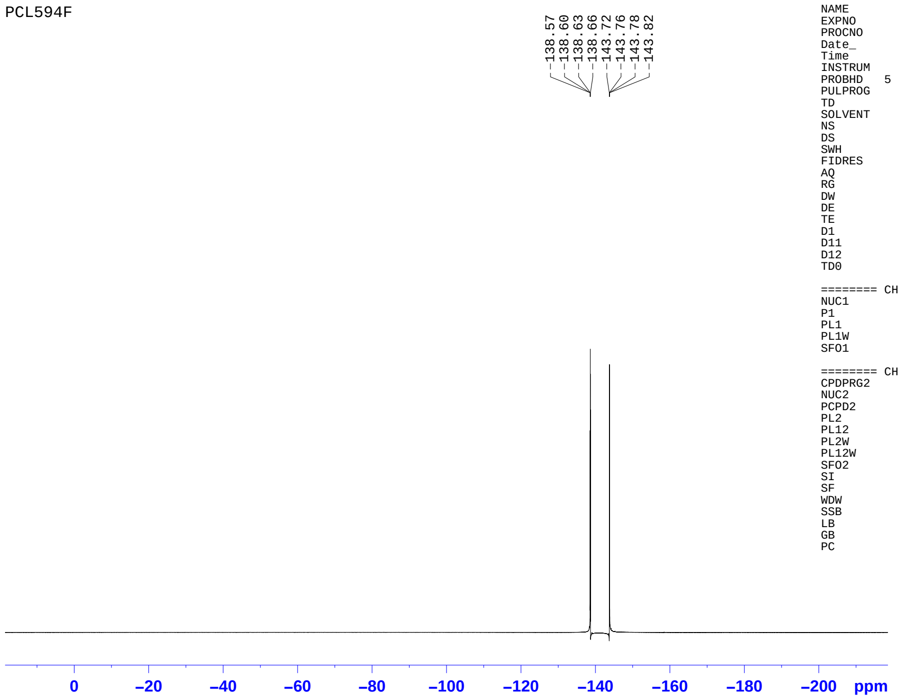
```
NAME              PCL594
EXPNO                  4
PROCNO                 1
Date_           20110731
Time               17.17
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   203
DW                20.800 usec
DE                  6.50 usec
TE                 298.5 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127721 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

3'-(2,3,5,6-Tetrafluorophenyl)acetophenone (Table 4.6; Product 23ee)

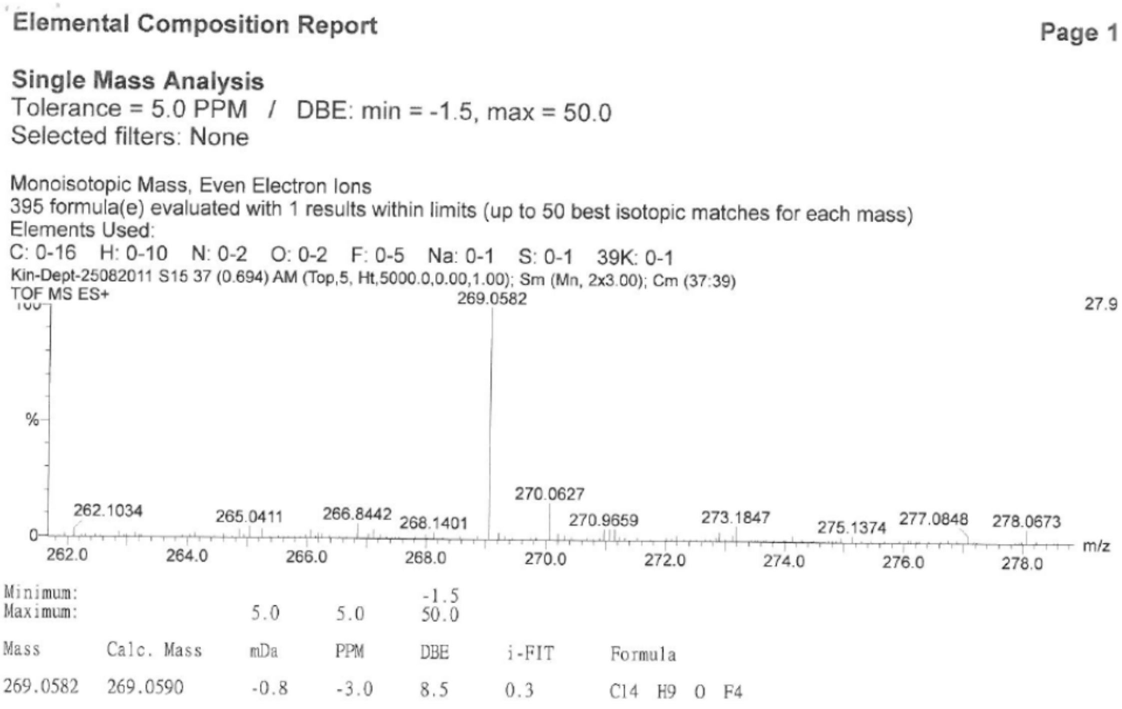




```
NAME             PCL594
EXPNO                 5
PROCNO                1
Date_          20110731
Time              17.20
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG        zgfhigqn
TD               131072
SOLVENT           CDCl3
NS                   16
DS                    4
SWH           89285.711 Hz
FIDRES         0.681196 Hz
AQ            0.7340532 sec
RG                  203
DW                5.600 usec
DE                 6.50 usec
TE                298.1 K
D1           1.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                19F
P1                14.20 usec
PL1               -3.00 dB
PL1W        18.69428444 W
SFO1        376.4607164 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
SFO2        400.1316005 MHz
SI                65536
SF          376.4983660 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```



Elemental Composition Report

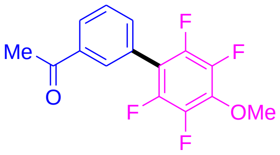
Page 1

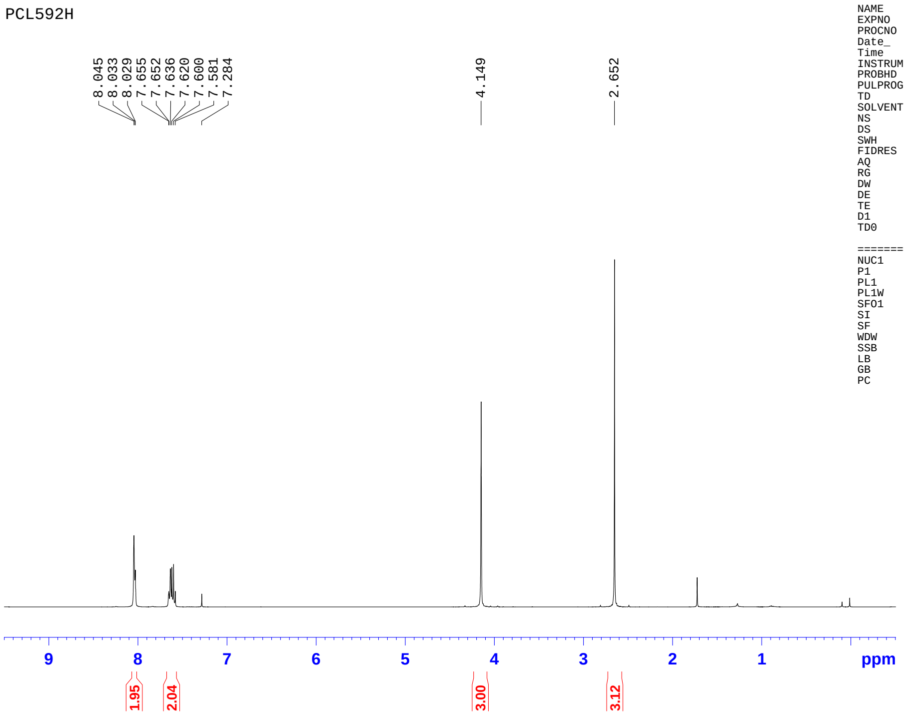
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

Monoisotopic Mass, Even Electron Ions
395 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-16 H: 0-10 N: 0-2 O: 0-2 F: 0-5 Na: 0-1 S: 0-1 39K: 0-1
Kin-Dept-25082011 S15 37 (0.694) AM (Top,5, Ht,5000.0,0.00,1.00); Sm (Mn, 2x3.00); Cm (37:39)
TOF MS ES+

Minimum:				-1.5		
Maximum:		5.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
269.0582	269.0590	-0.8	-3.0	8.5	0.3	C14 H9 O F4

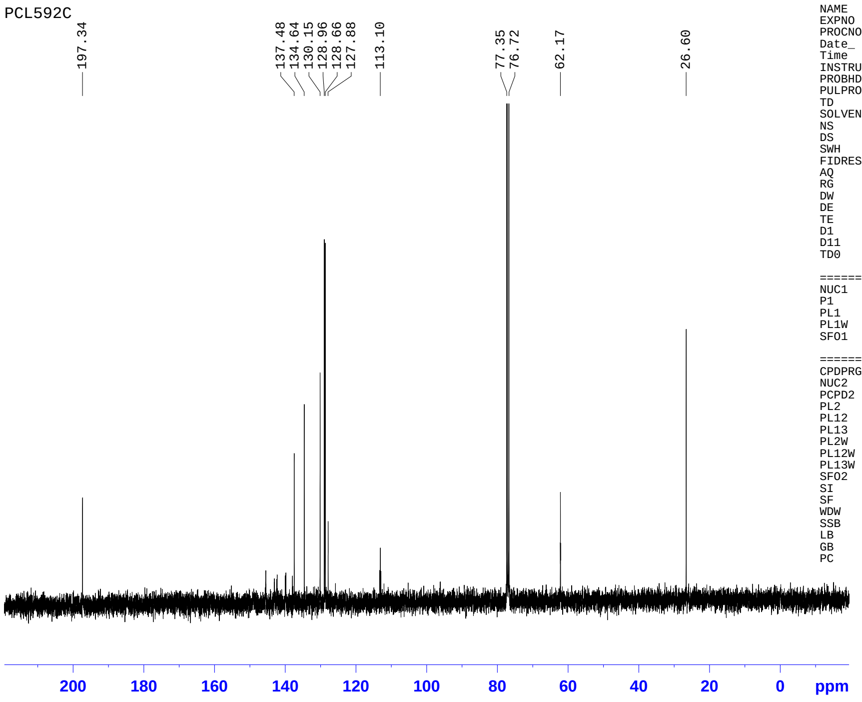
3'-(2,3,5,6-Tetrafluoro-4-methoxyphenyl)acetophenone (Table 4.6; Product 23be)





```
NAME               PCL592
EXPNO                   1
PROCNO                  1
Date_            20110716
Time                13.44
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              4006.410 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                   20.2
DW                124.800 use
DE                   6.50 use
TE                  297.9 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 =======
NUC1                   1H
P1                  14.70 use
PL1                  0.00 dB
PL1W          11.88122272 W
SFO1          400.1318007 MHz
SI                  32768
SF            400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

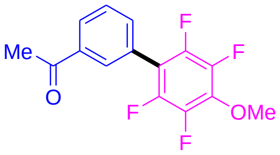


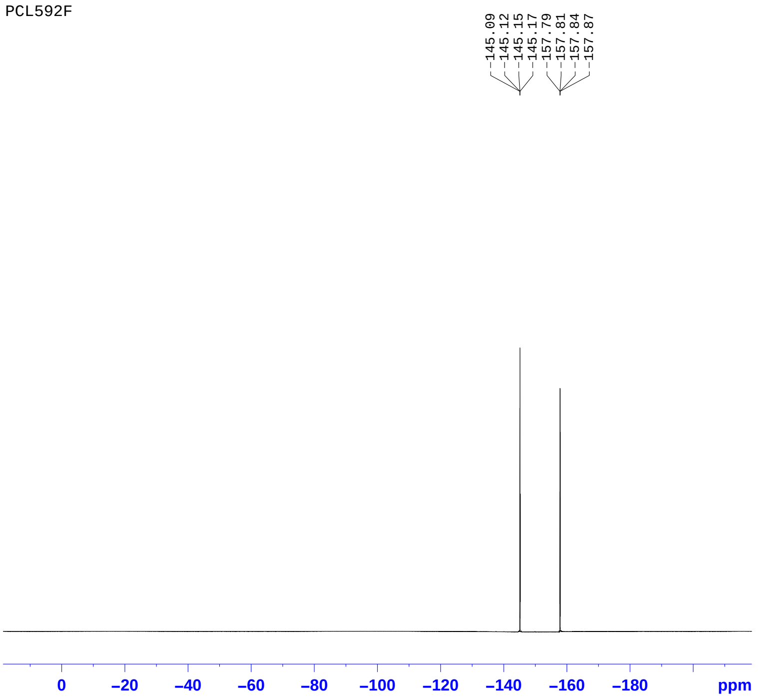
```
NAME             PCL592-C
EXPNO                   1
PROCNO                  1
Date_            20110716
Time                13.48
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      2
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                    203
DW                 20.800 usec
DE                   6.50 usec
TE                  298.9 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.50 usec
PL1                 -2.00 dB
PL1W          58.52175522 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                15.00 dB
PL13                15.00 dB
PL2W          11.88122272 W
PL12W          0.37571725 W
PL13W          0.37571725 W
SFO2          400.1316005 MHz
SI                  32768
SF            100.6127690 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

3'-(2,3,5,6-Tetrafluoro-4-methoxyphenyl)acetophenone (Table 4.6; Product 23be)



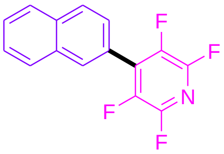


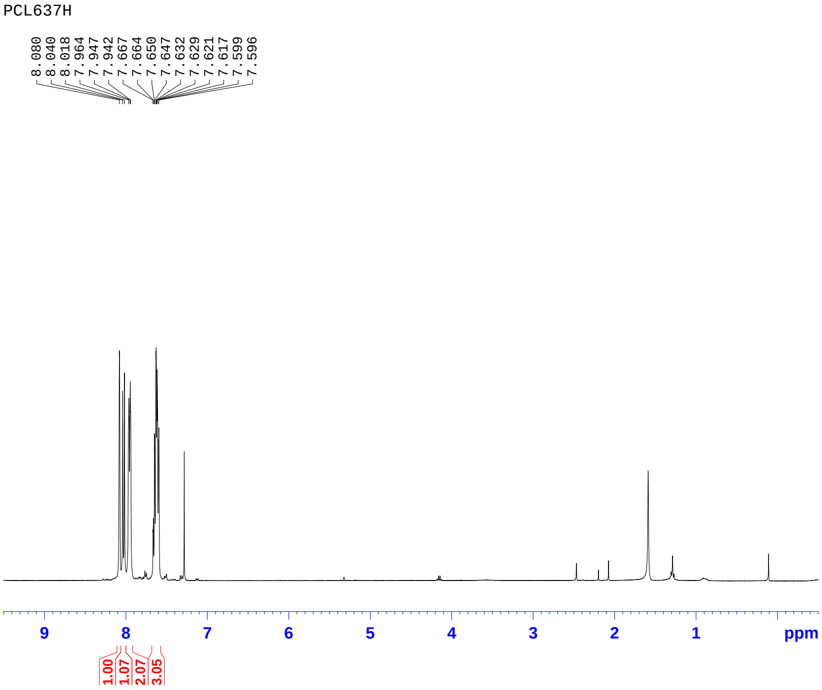
```
NAME            PCL592-F
EXPNO                  1
PROCNO                 1
Date_           20110716
Time               13.51
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG         zgfhigqn
TD                131072
SOLVENT            CDCl3
NS                    16
DS                     4
SWH            89285.711 Hz
FIDRES          0.681196 Hz
AQ             0.7340532 sec
RG                   203
DW                 5.600 usec
DE                  6.50 usec
TE                 298.3 K
D1            1.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 19F
P1                 14.20 usec
PL1                -3.00 dB
PL1W         18.69428444 W
SFO1        376.4607164 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
SFO2         400.1316005 MHz
SI                 65536
SF           376.4983660 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

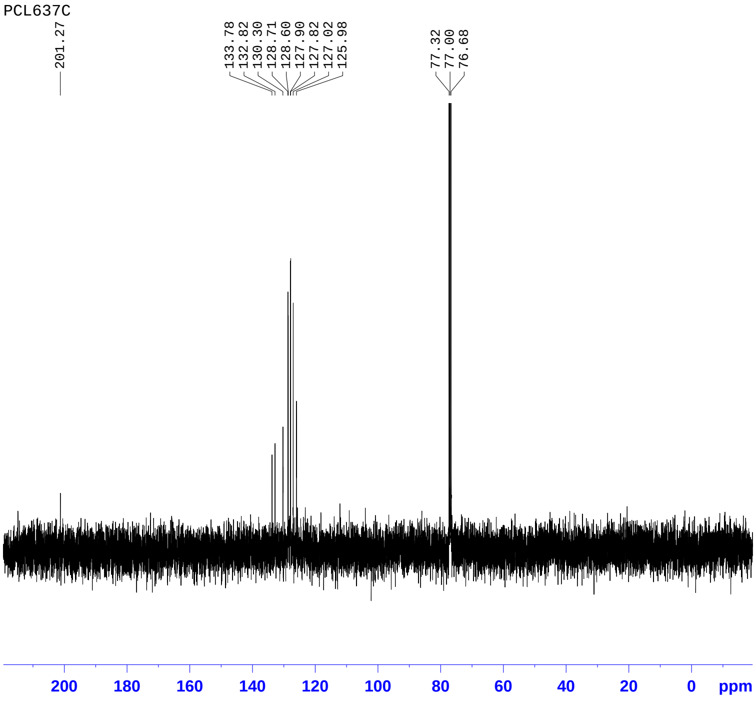
2,3,5,6-Tetrafluoro-4-(naphthalene-2-yl)pyridine (Table 4.6; Product 23fi)





```
NAME              PCL637
EXPNO                  1
PROCNO                 1
Date_           20110905
Time               11.44
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  90.5
DW               124.800 usec
DE                  6.50 usec
TE                 298.1 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

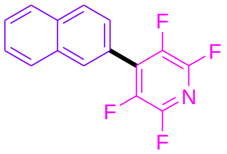


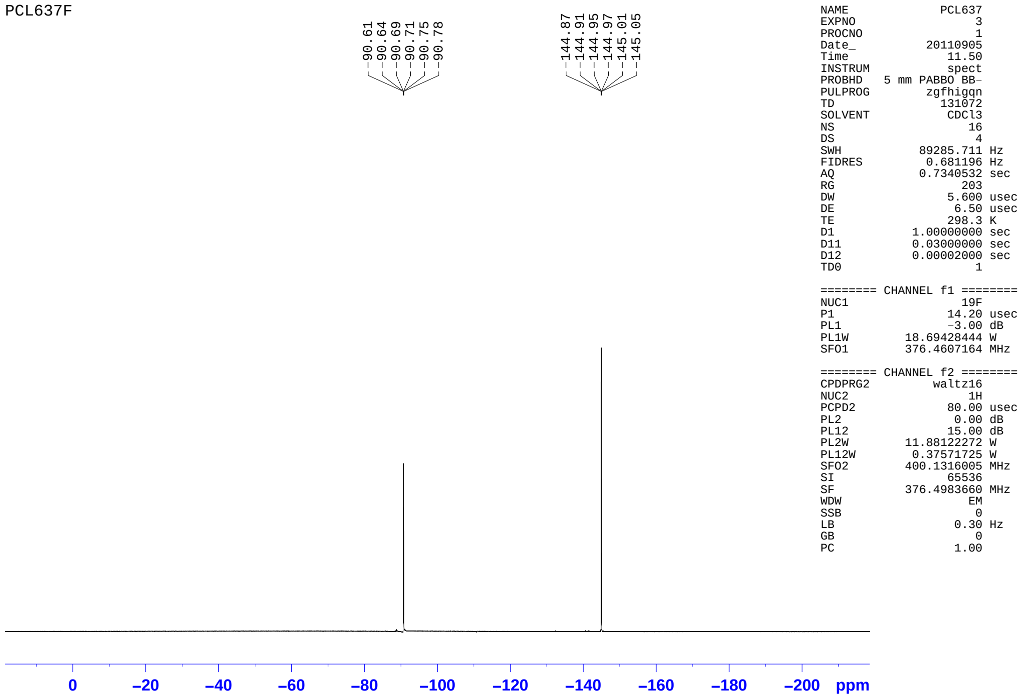
```
NAME              PCL637
EXPNO                  2
PROCNO                 1
Date_           20110905
Time               11.47
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   203
DW                20.800 usec
DE                  6.50 usec
TE                 298.7 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127713 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

2,3,5,6-Tetrafluoro-4-(naphthalene-2-yl)pyridine (Table 4.6; Product 23fi)

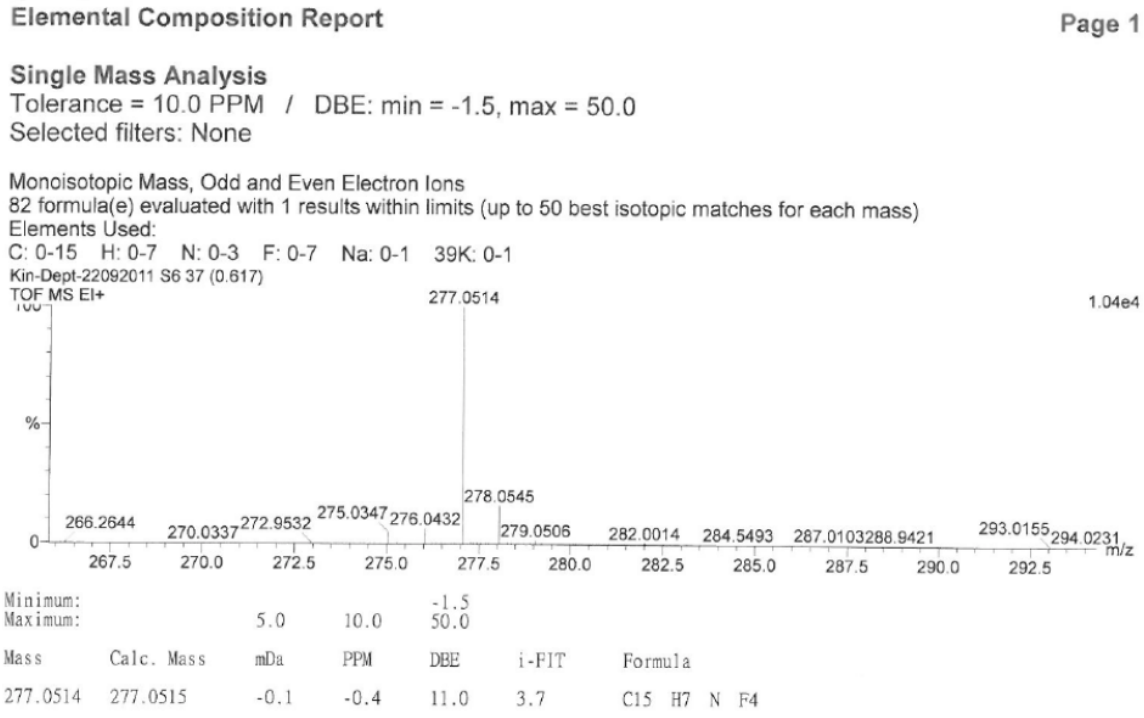




```
NAME            PCL637
EXPNO                3
PROCNO               1
Date_         20110905
Time             11.50
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG       zgfhigqn
TD              131072
SOLVENT          CDCl3
NS                  16
DS                   4
SWH         89285.711 Hz
FIDRES       0.681196 Hz
AQ          0.7340532 sec
RG                 203
DW               5.600 usec
DE                6.50 usec
TE               298.3 K
D1          1.00000000 sec
D11         0.03000000 sec
D12         0.00002000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               19F
P1               14.20 usec
PL1              -3.00 dB
PL1W       18.69428444 W
SFO1       376.4607164 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2            80.00 usec
PL2               0.00 dB
PL12             15.00 dB
PL2W       11.88122272 W
PL12W       0.37571725 W
SFO2       400.1316005 MHz
SI               65536
SF         376.4983660 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.00
```



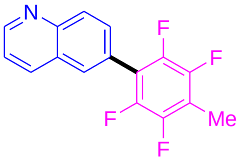
Elemental Composition Report Page 1

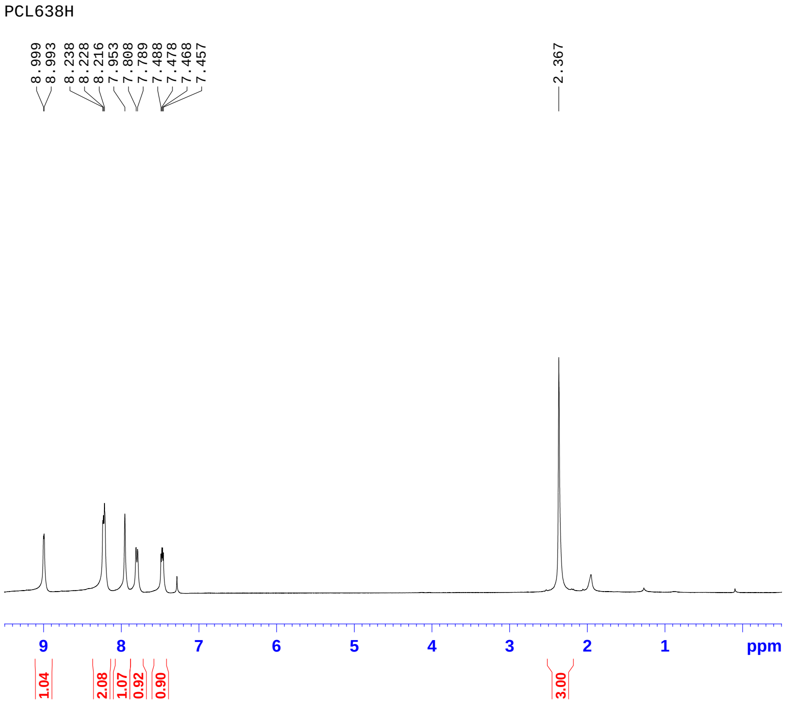
Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
82 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-15 H: 0-7 N: 0-3 F: 0-7 Na: 0-1 39K: 0-1
Kin-Dept-22092011 S6 37 (0.617)
TOF MS EI+

Minimum:				-1.5		
Maximum:		5.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
277.0514	277.0515	-0.1	-0.4	11.0	3.7	C15 H7 N F4

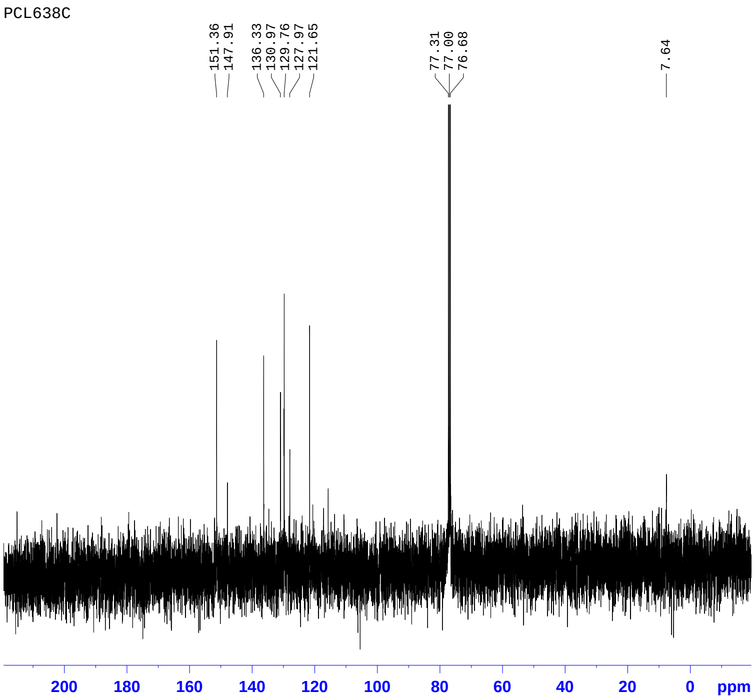
6-(2,3,5,6-Tetrafluoro-4-methylphenyl)quinoline (Table 4.6; Product 23gc)





```
NAME              PCL638
EXPNO                  1
PROCNO                 1
Date_           20110905
Time               23.07
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  45.2
DW               124.800 usec
DE                  6.50 usec
TE                 299.8 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

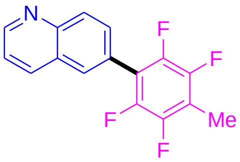


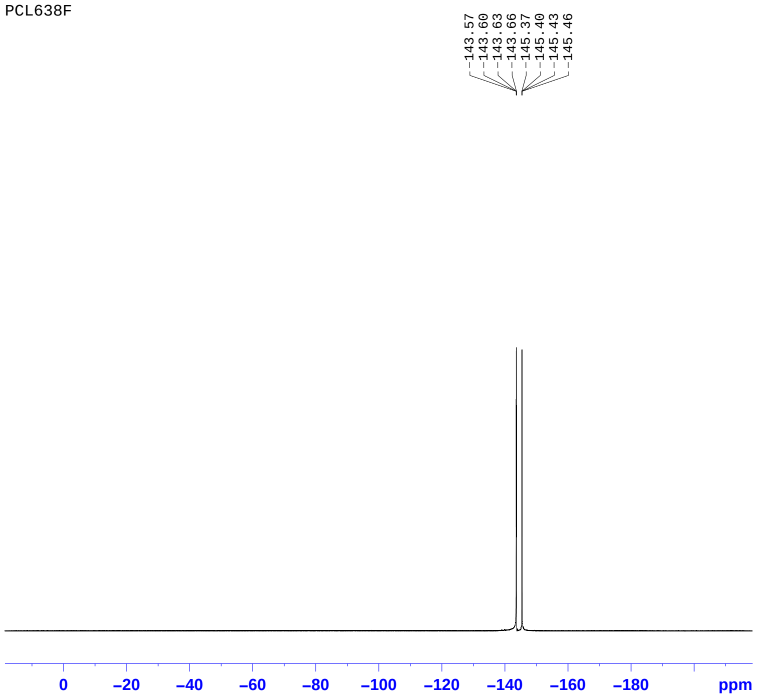
```
NAME              PCL638
EXPNO                  3
PROCNO                 1
Date_           20110905
Time               23.11
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   203
DW                20.800 usec
DE                  6.50 usec
TE                 301.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127714 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

6-(2,3,5,6-Tetrafluoro-4-methylphenyl)quinoline (Table 4.6; Product 23gc)

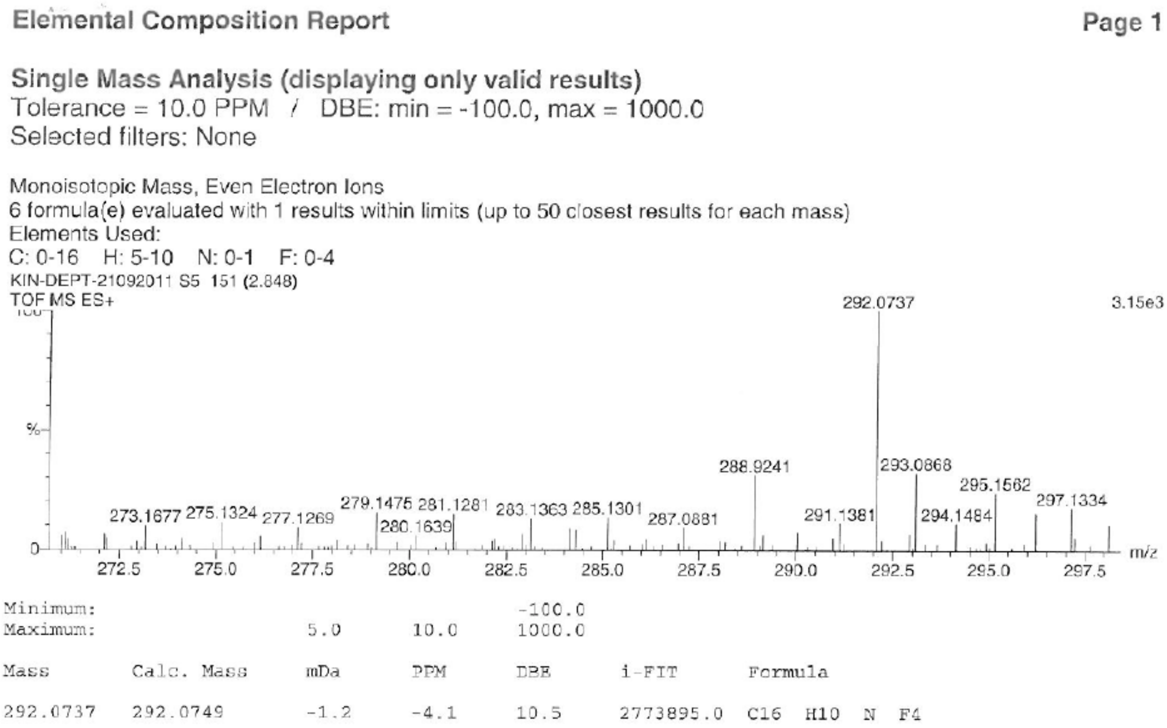




```
NAME              PCL638
EXPNO                  2
PROCNO                 1
Date_           20110905
Time               23.08
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgfhigqn
TD                131072
SOLVENT            CDCl3
NS                    16
DS                     4
SWH            89285.711 Hz
FIDRES          0.681196 Hz
AQ             0.7340532 sec
RG                   203
DW                 5.600 usec
DE                  6.50 usec
TE                 300.1 K
D1            1.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 19F
P1                 14.20 usec
PL1                -3.00 dB
PL1W         18.69428444 W
SFO1         376.4607164 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
SFO2         400.1316005 MHz
SI                 65536
SF           376.4983660 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



Elemental Composition Report

Page 1

Single Mass Analysis (displaying only valid results)
Tolerance = 10.0 PPM / DBE: min = -100.0, max = 1000.0
Selected filters: None

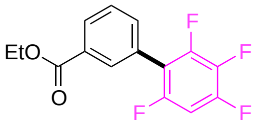
Monoisotopic Mass, Even Electron Ions
6 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-16 H: 5-10 N: 0-1 F: 0-4
KIN-DEPT-21092011 S5 151 (2.848)
TOF MS ES+

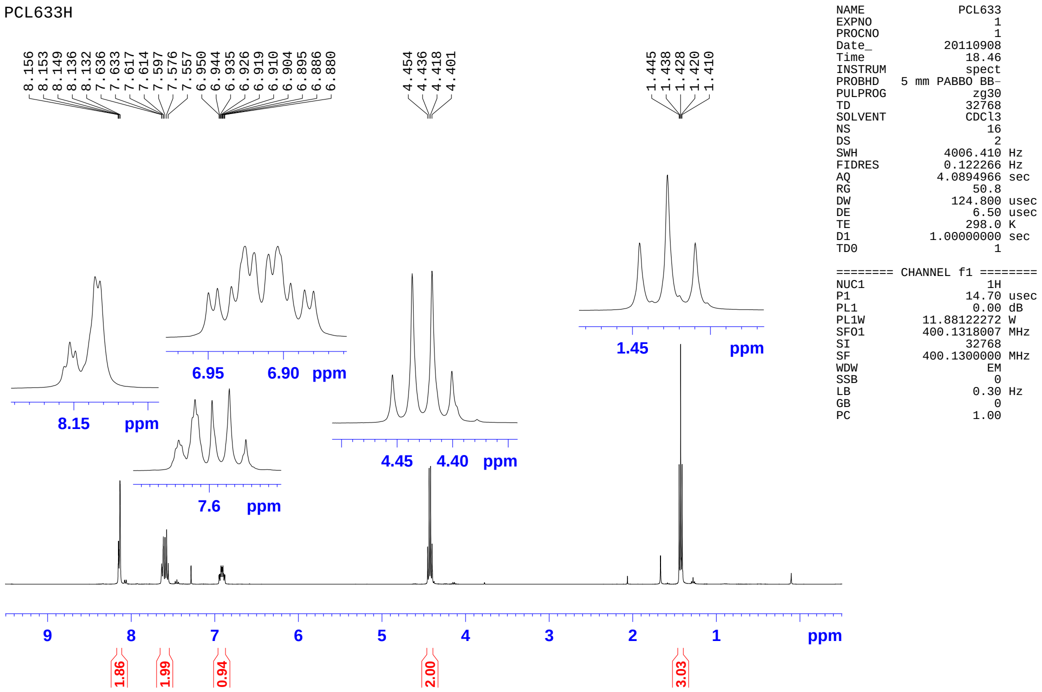
```
Minimum:                                         -100.0
Maximum:                        5.0      10.0    1000.0

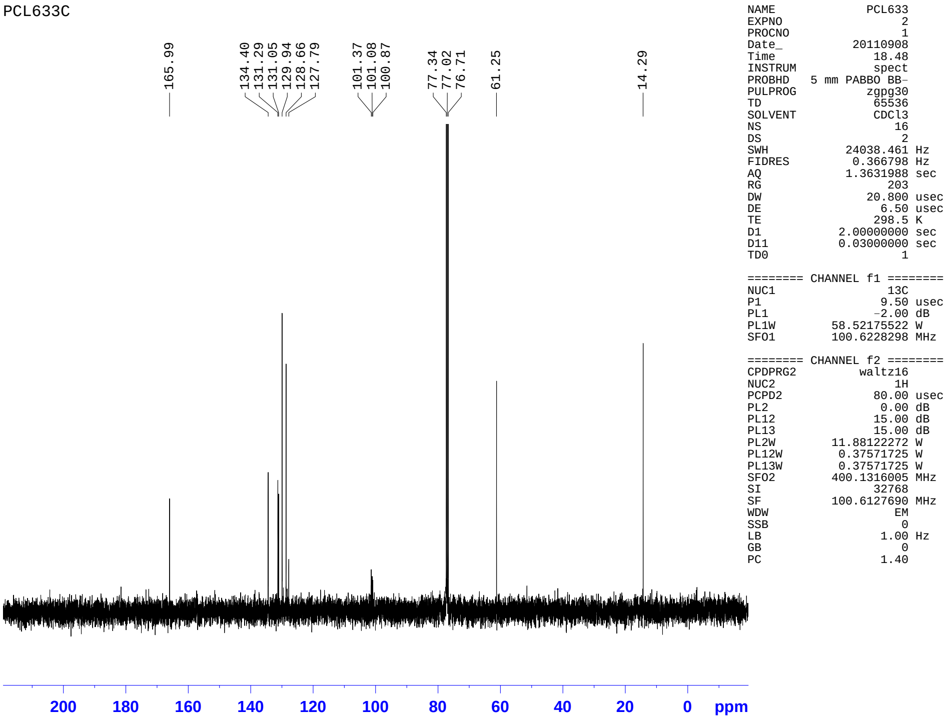
Mass       Calc. Mass     mDa     PPM     DBE     i-FIT        Formula

292.0737   292.0749       -1.2    -4.1    10.5    2773895.0    C16  H10  N  F4
```

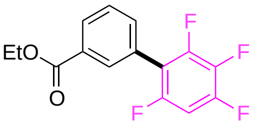
Ethyl 2',3',4',6'-tetrafluoro-[1,1'-biphenyl]-3-carboxylate (Table 4.6; Product 23dj)

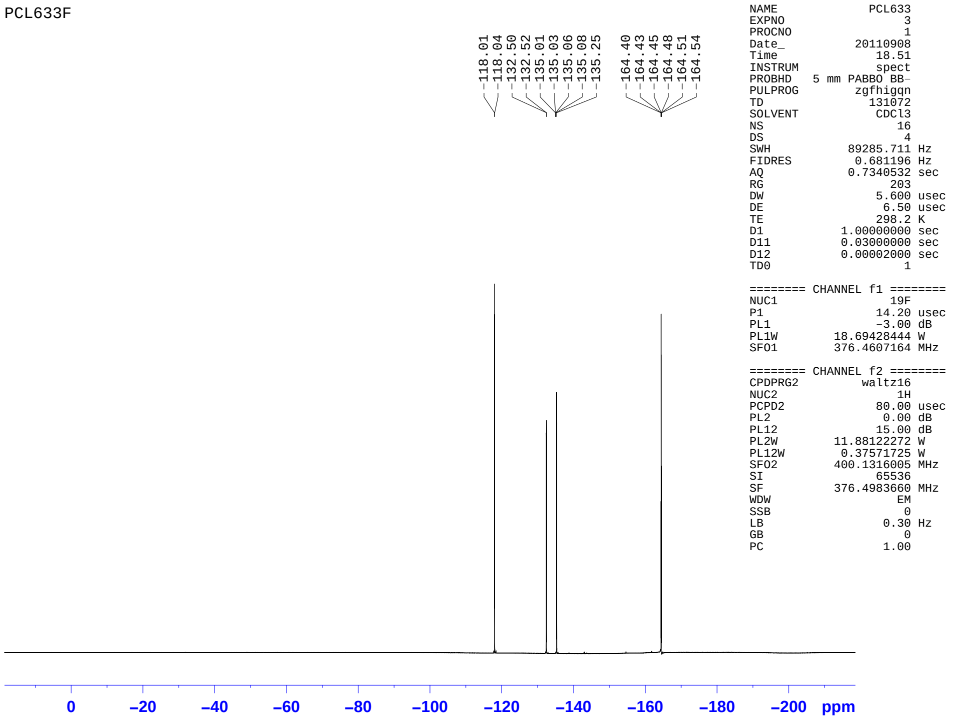






Ethyl 2',3',4',6'-tetrafluoro-[1,1'-biphenyl]-3-carboxylate (Table 4.6; Product 23dj)

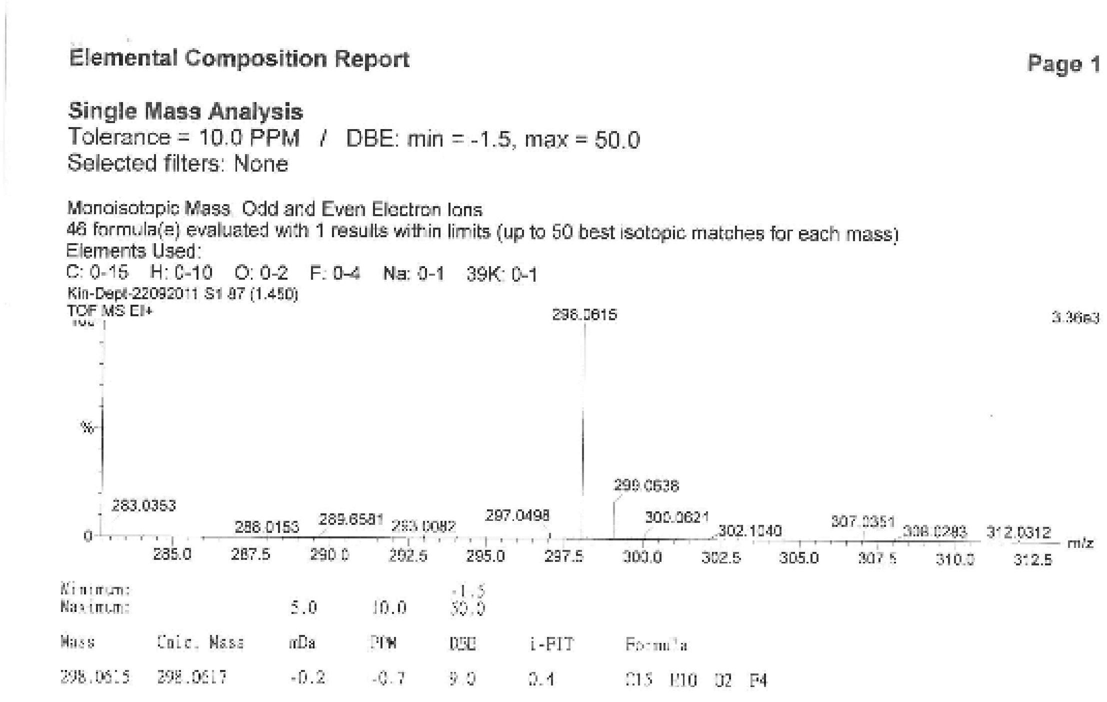




```
NAME                PCL633
EXPNO                    3
PROCNO                   1
Date_             20110908
Time                 18.51
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG           zgfhigqn
TD                  131072
SOLVENT              CDCl3
NS                      16
DS                       4
SWH             89285.711 Hz
FIDRES           0.681196 Hz
AQ              0.7340532 sec
RG                     203
DW                   5.600 usec
DE                    6.50 usec
TE                   298.2 K
D1              1.00000000 sec
D11             0.03000000 sec
D12             0.00002000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   19F
P1                   14.20 usec
PL1                  -3.00 dB
PL1W           18.69428444 W
SFO1           376.4607164 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   0.00 dB
PL12                 15.00 dB
PL2W           11.88122272 W
PL12W           0.37571725 W
SFO2           400.1316005 MHz
SI                   65536
SF             376.4983660 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



Elemental Composition Report

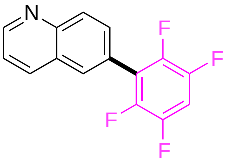
Page 1

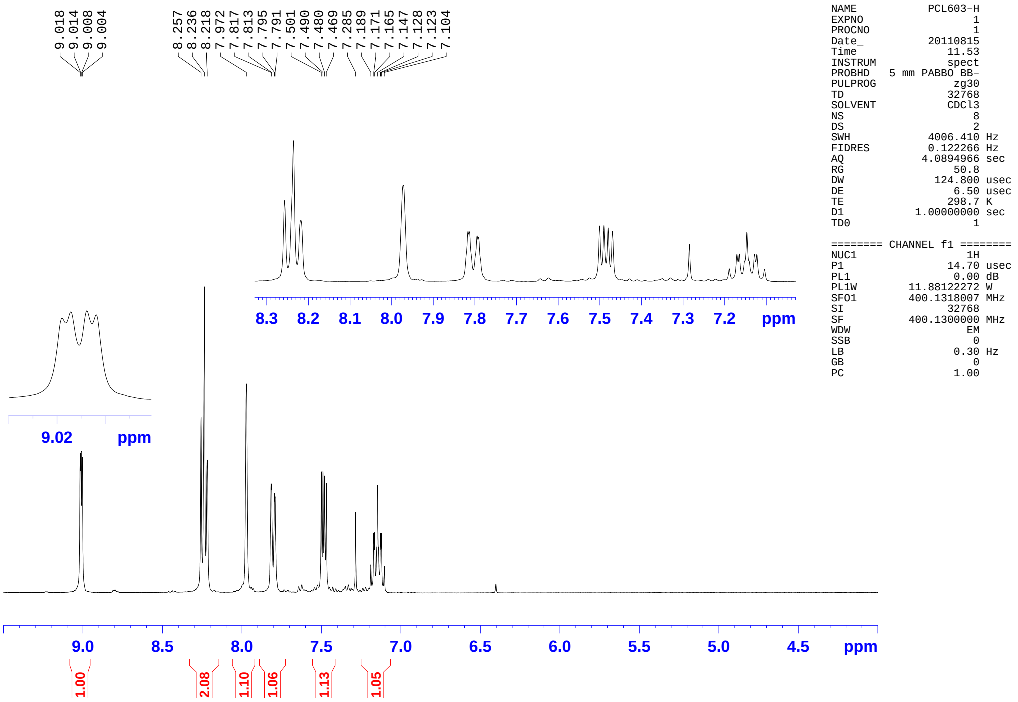
Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

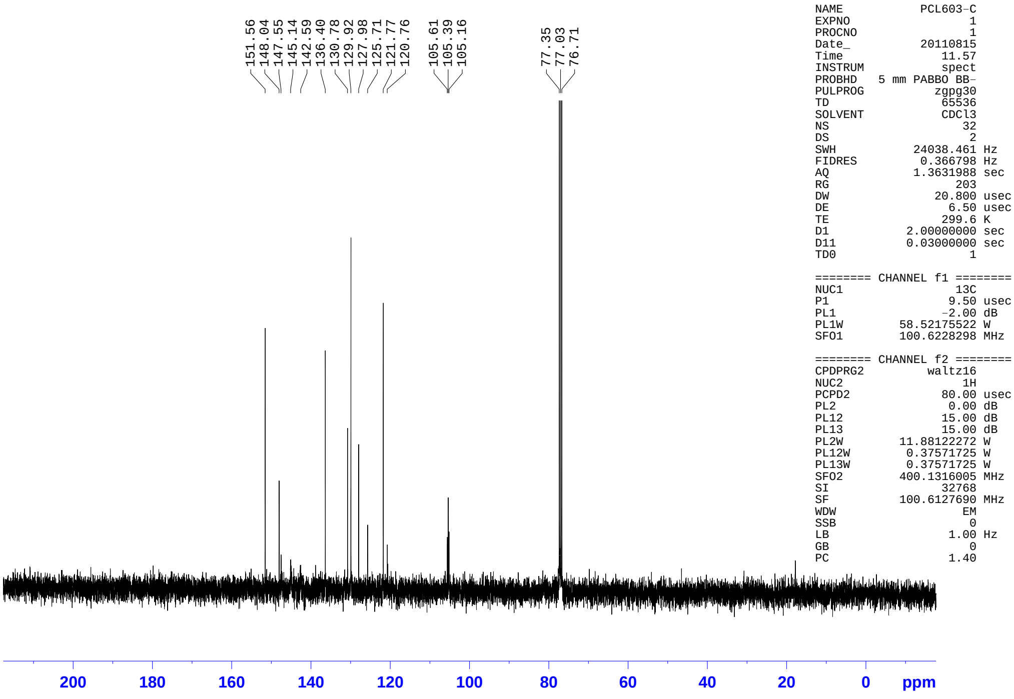
Monoisotopic Mass, Odd and Even Electron Ions
46 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-15 H: 0-10 O: 0-2 F: 0-4 Na: 0-1 39K: 0-1
Kin-Dept-22092011 S1 87 (1.450)
TOF MS EI+

Minimum:				-1.5		
Maximum:		5.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
298.0615	298.0617	-0.2	-0.7	9.0	0.4	C15 H10 O2 F4

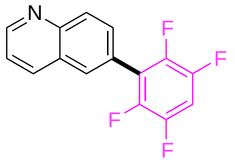
6-(2,3,5,6-Tetrafluorophenyl)quinolone (Table 4.6; Product 23ec)

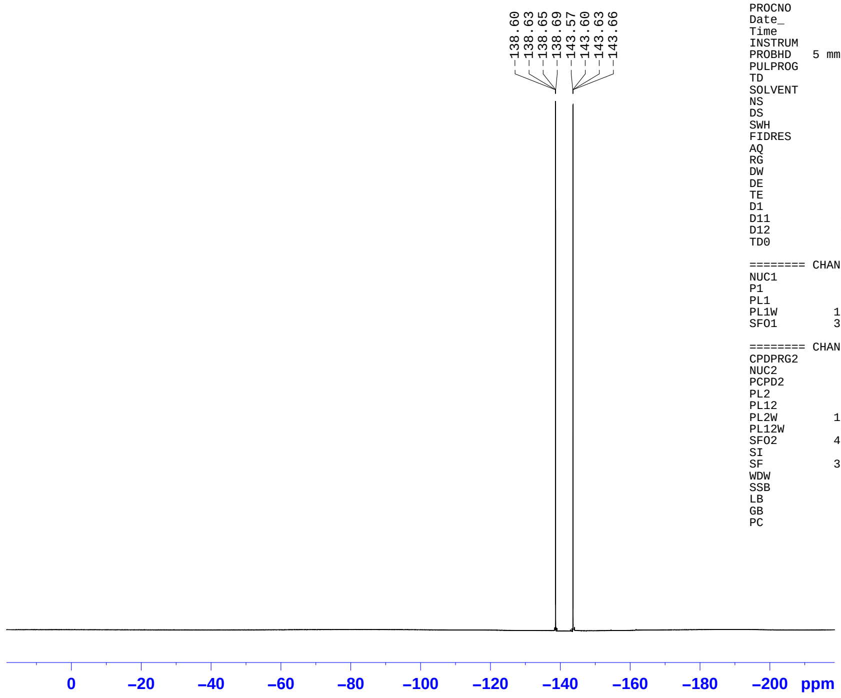






6-(2,3,5,6-Tetrafluorophenyl)quinolone (Table 4.6; Product 23ec)

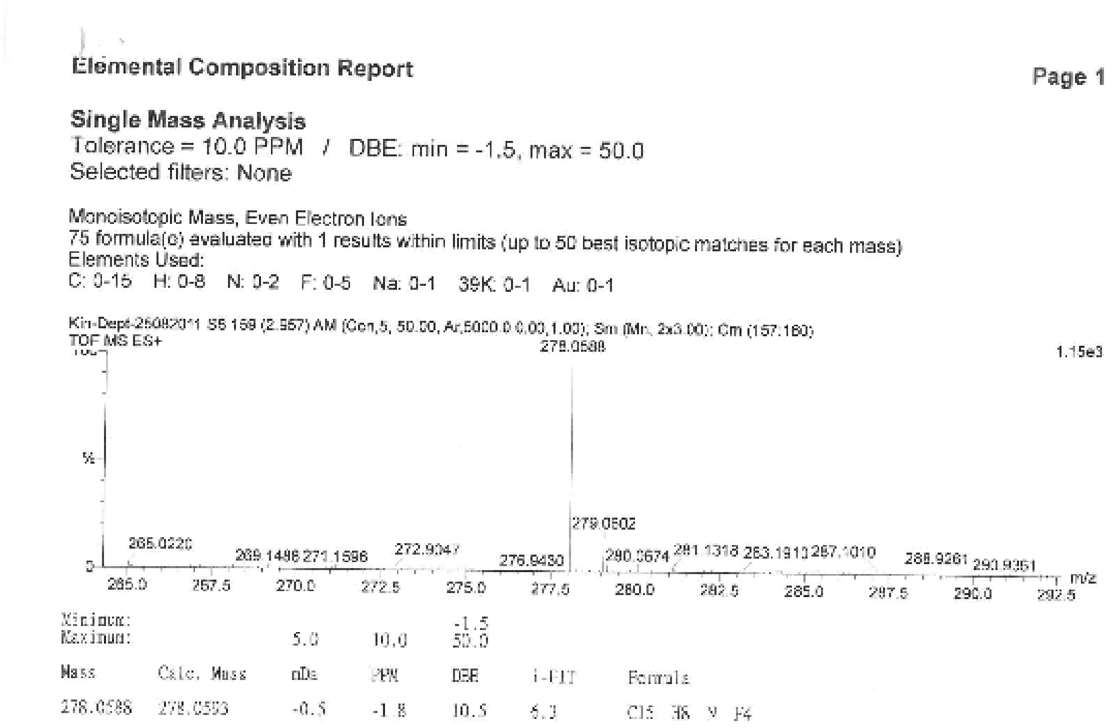




```
NAME           PCL603-F
EXPNO                 1
PROCNO                1
Date_          20110815
Time              12.04
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG        zgfhigqn
TD               131072
SOLVENT           CDCl3
NS                   16
DS                    4
SWH          89285.711 Hz
FIDRES        0.681196 Hz
AQ           0.7340532 sec
RG                  203
DW                5.600 usec
DE                 6.50 usec
TE                298.7 K
D1           1.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                19F
P1                14.20 usec
PL1               -3.00 dB
PL1W        18.69428444 W
SFO1        376.4607164 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
SFO2        400.1316005 MHz
SI                65536
SF          376.4983660 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```



Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

75 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

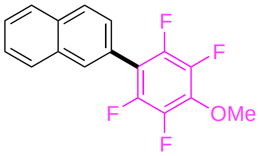
C: 0-15 H: 0-8 N: 0-2 F: 0-5 Na: 0-1 39K: 0-1 Au: 0-1

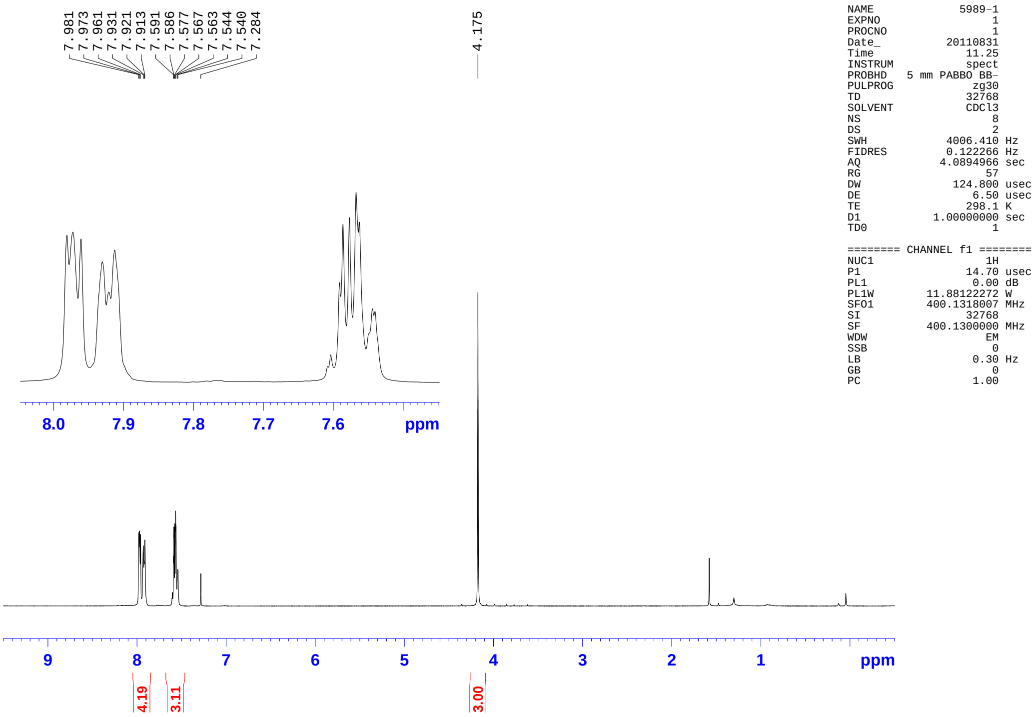
Kin-Dept-25082011 56 159 (2.957) AM (Cen,5, 50.00, Ar,5000.0,0.00,1.00); Sm (Mn, 2x3.00); Cm (157:160)

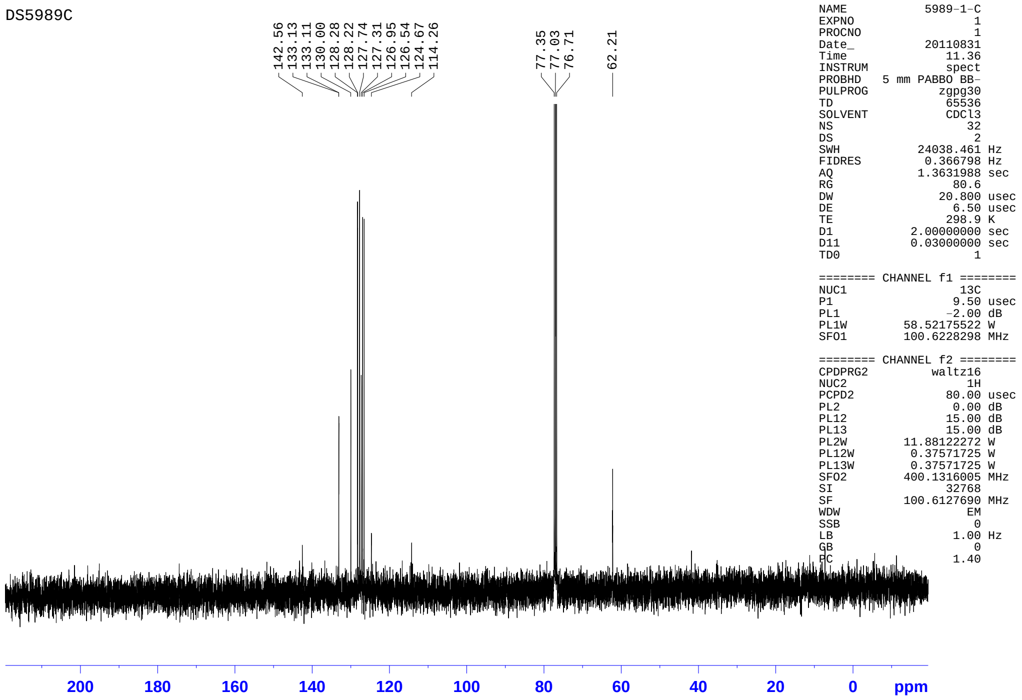
TOF MS ES+

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
Minimum:				-1.5		
Maximum:		5.0	10.0	50.0		
278.0588	278.0593	-0.5	-1.8	10.5	6.3	C15 H8 N F4

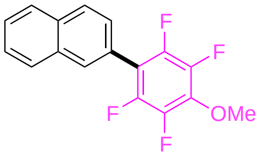
2-(2,3,5,6-Tetrafluoro-4-methoxyphenyl)naphthalene (Table 4.6; Product 23bi)

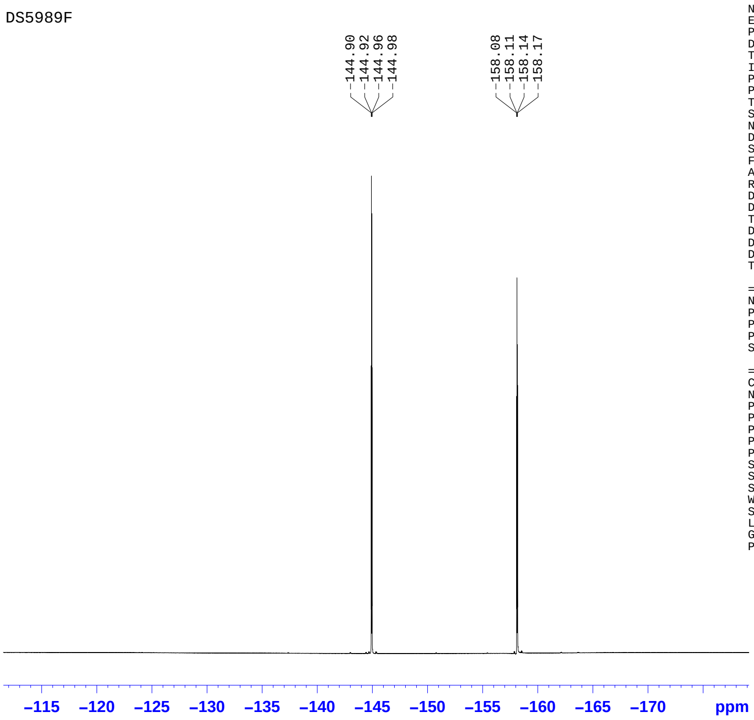






2-(2,3,5,6-Tetrafluoro-4-methoxyphenyl)naphthalene (Table 4.6; Product 23bi)



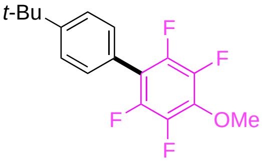


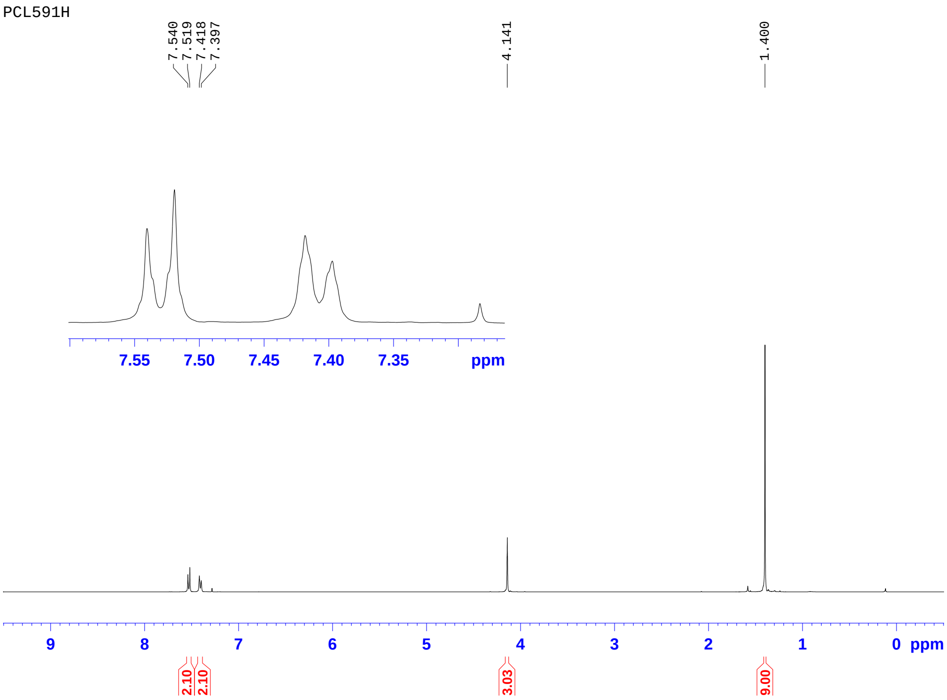
```
NAME             5989-1-F
EXPNO                   1
PROCNO                  1
Date_            20110831
Time                11.29
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG          zgfhigqn
TD                 131072
SOLVENT             CDCl3
NS                     16
DS                      4
SWH             89285.711 Hz
FIDRES           0.681196 Hz
AQ              0.7340532 sec
RG                    203
DW                  5.600 usec
DE                   6.50 usec
TE                  298.2 K
D1             1.00000000 sec
D11            0.03000000 sec
D12            0.00002000 sec
TD0                     1

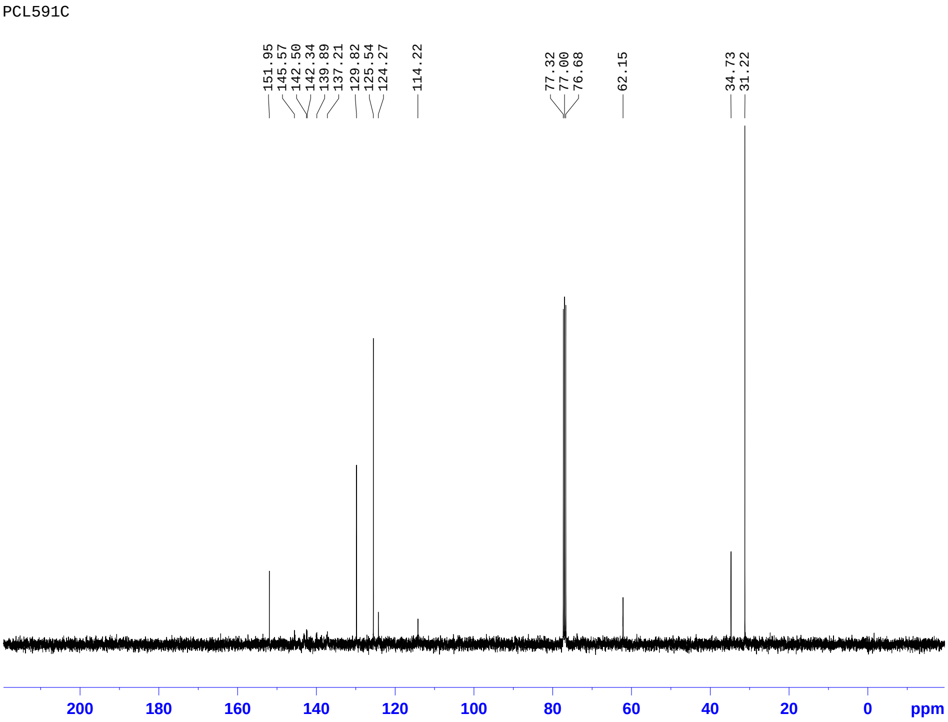
======== CHANNEL f1 ========
NUC1                  19F
P1                  14.20 usec
PL1                 -3.00 dB
PL1W          18.69428444 W
SFO1          376.4607164 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                15.00 dB
PL2W          11.88122272 W
PL12W          0.37571725 W
SFO2          400.1316005 MHz
SI                  65536
SF            376.4983660 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

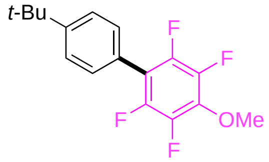
4'-(*tert*-Butyl)-2,3,5,6-tetrafluoro-4-methoxy-1,1'-biphenyl (Table 4.6; Product 23ba)



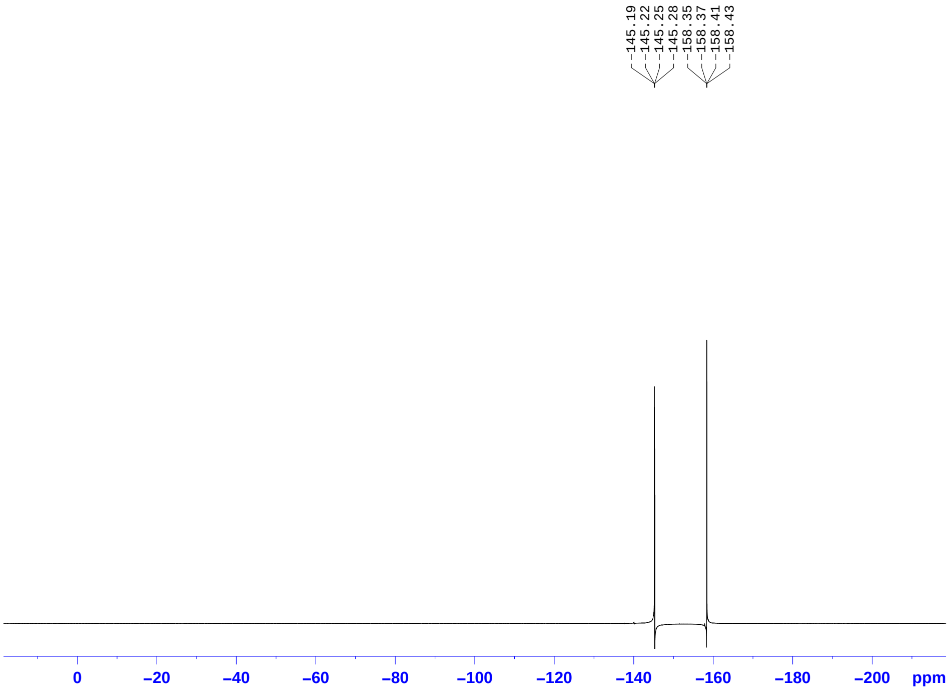


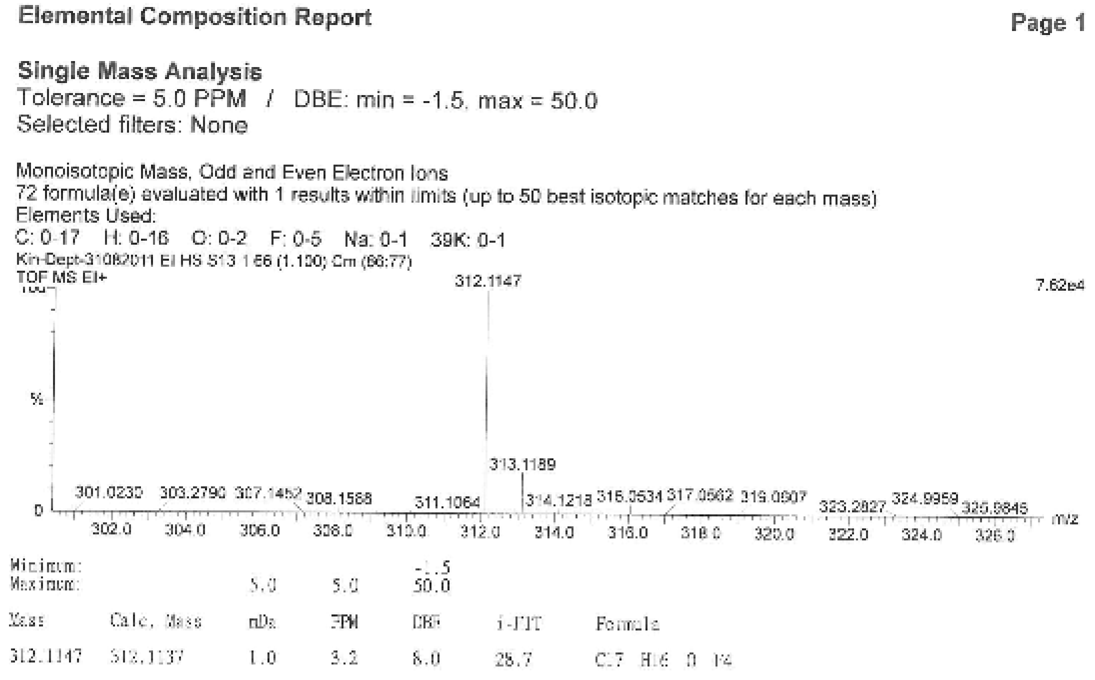


4'-(*tert*-Butyl)-2,3,5,6-tetrafluoro-4-methoxy-1,1'-biphenyl (Table 4.6; Product 23ba)



PCL591F





Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions

72 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

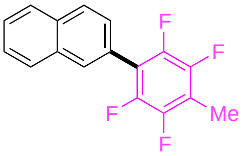
C: 0-17 H: 0-16 O: 0-2 F: 0-5 Na: 0-1 39K: 0-1

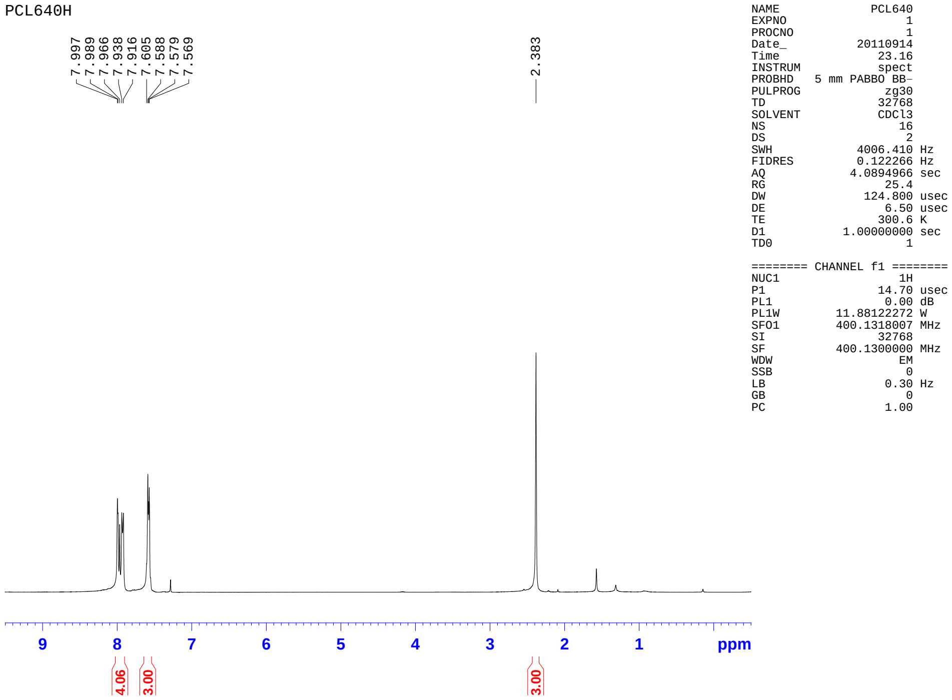
Kin-Dept-31082011 EI HS 513 1 66 (1.100) Cm (66:77)

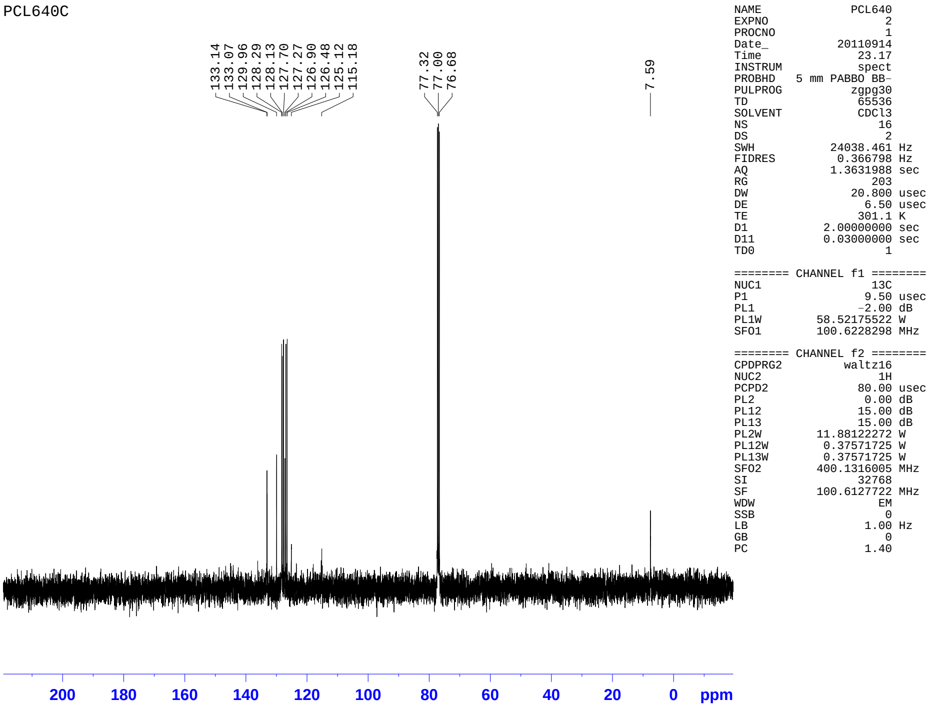
TOF MS EI+

Minimum:				-1.5		
Maximum:		5.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
312.1147	312.1137	1.0	3.2	8.0	25.7	C17 H16 O F4

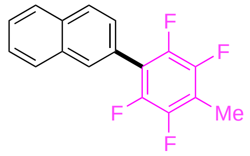
2-(2,3,5,6-Tetrafluoro-4-methylphenyl)naphthalene (Table 4.6; Product 23gi)

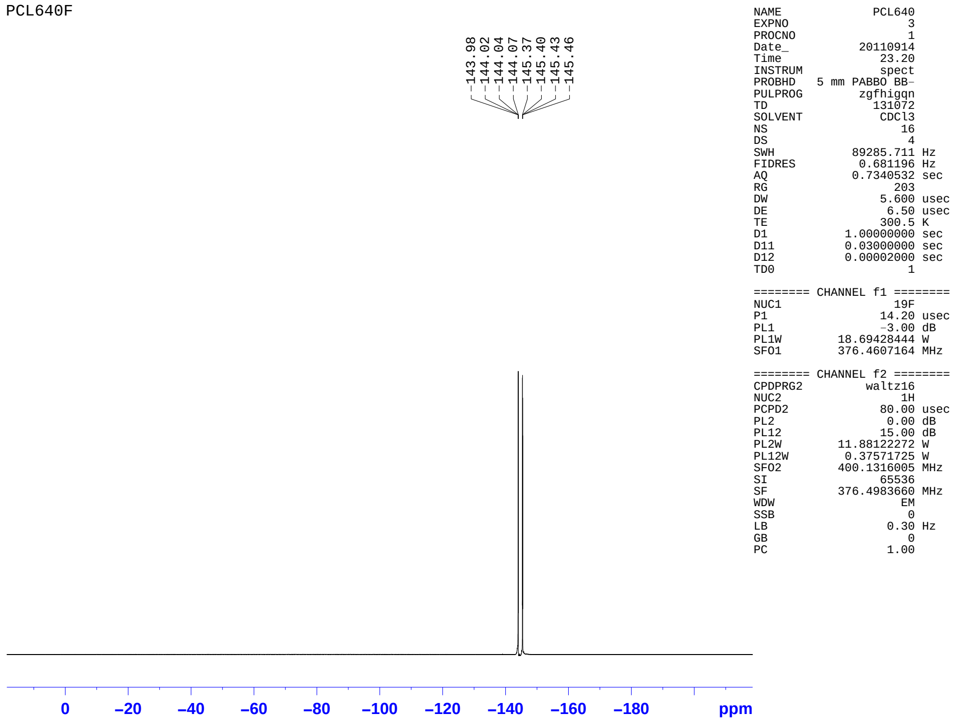






2-(2,3,5,6-Tetrafluoro-4-methylphenyl)naphthalene (Table 4.6; Product 23gi)

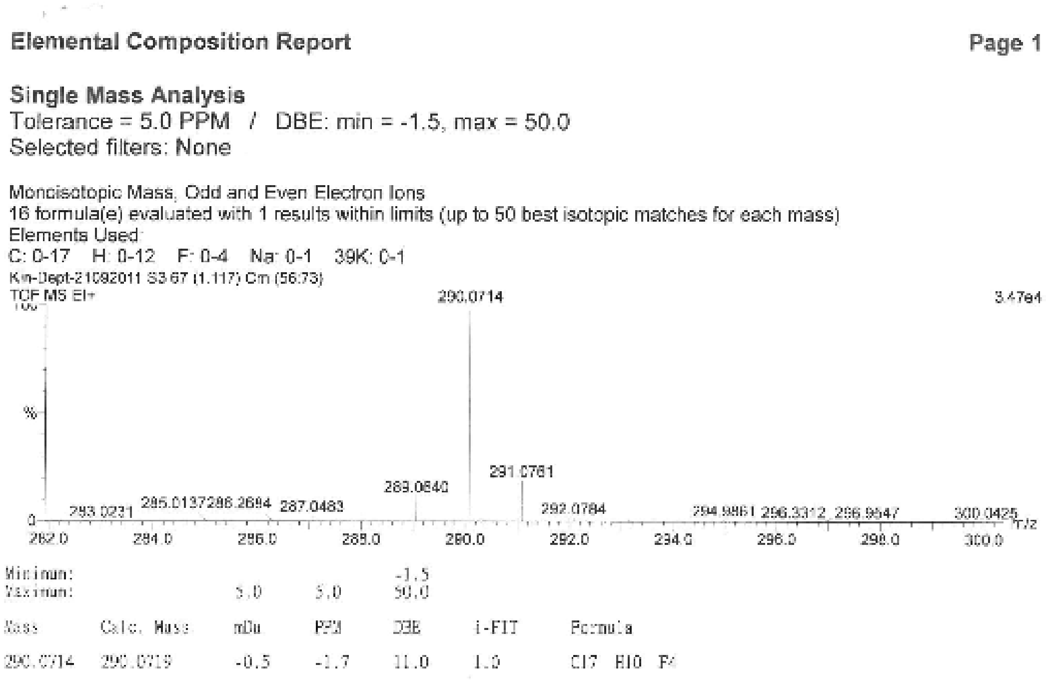



PCL640F

```
NAME              PCL640
EXPNO                  3
PROCNO                 1
Date_           20110914
Time               23.20
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG        zgfhigqn
TD                131072
SOLVENT            CDCl3
NS                    16
DS                     4
SWH            89285.711 Hz
FIDRES          0.681196 Hz
AQ             0.7340532 sec
RG                   203
DW                 5.600 usec
DE                  6.50 usec
TE                 300.5 K
D1            1.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 19F
P1                 14.20 usec
PL1                -3.00 dB
PL1W         18.69428444 W
SFO1         376.4607164 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
SFO2         400.1316005 MHz
SI                 65536
SF           376.4983660 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```


Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

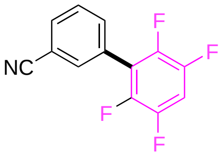
Monoisotopic Mass, Odd and Even Electron Ions
16 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-17 H: 0-12 F: 0-4 Na: 0-1 39K: 0-1
Kin-Dept-21092011 53 67 (1.117) Cm (56:73)
TOF MS EI+

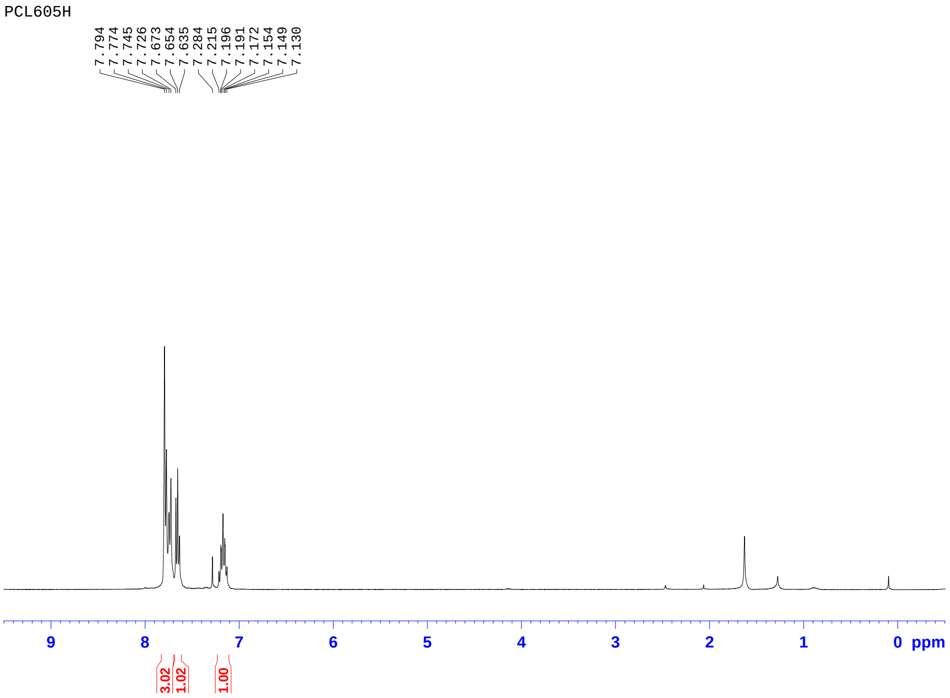
```
Minimum:                                 -1.5
Maximum:                  5.0      5.0   50.0

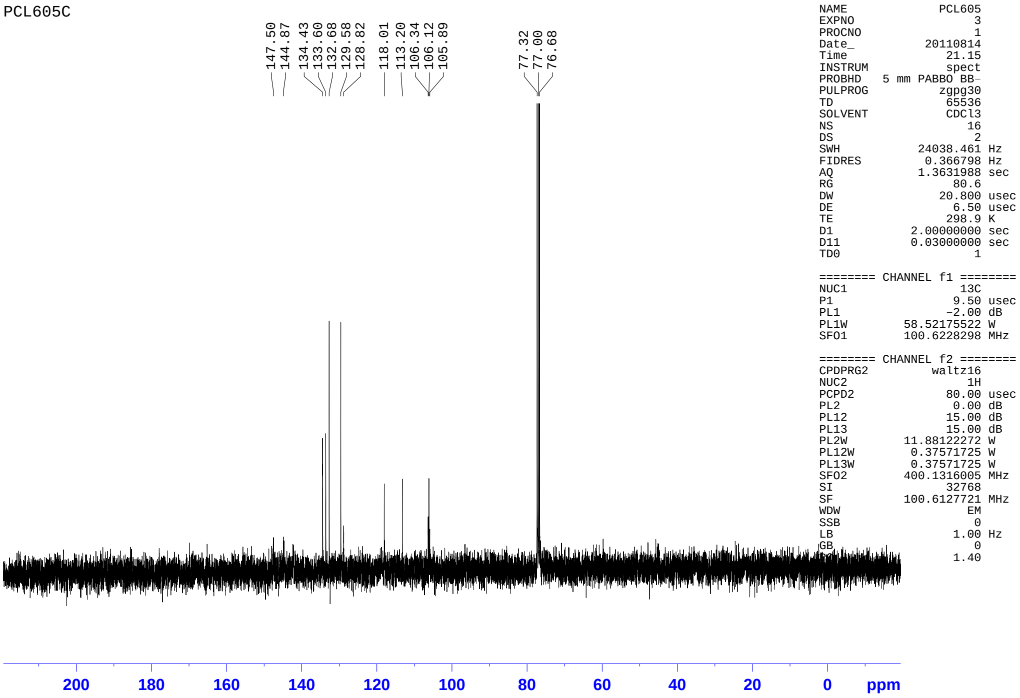
Mass      Calc. Mass      mDa      PPM   DBE    i-FIT    Formula

290.0714  290.0719        -0.5     -1.7  11.0   1.0      C17  H10  F4
```

2',3',5',6'-Tetrafluoro-[1,1'-biphenyl]-3-carbonitrile (Table 4.6; Product 23en)





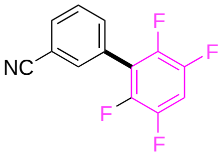


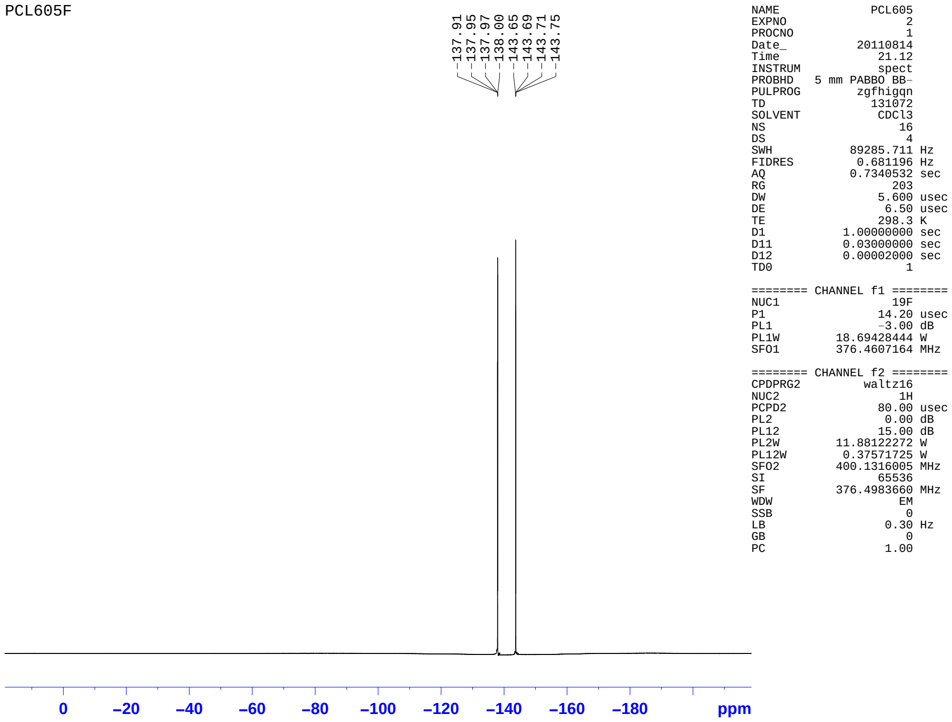
```
NAME                PCL605
EXPNO                    3
PROCNO                   1
Date_             20110814
Time                 21.15
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ               1.3631988 sec
RG                    80.6
DW                  20.800 usec
DE                    6.50 usec
TE                   298.9 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    9.50 usec
PL1                  -2.00 dB
PL1W           58.52175522 W
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   0.00 dB
PL12                 15.00 dB
PL13                 15.00 dB
PL2W           11.88122272 W
PL12W           0.37571725 W
PL13W           0.37571725 W
SFO2           400.1316005 MHz
SI                   32768
SF             100.6127721 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
                      1.40
```

2',3',5',6'-Tetrafluoro-[1,1'-biphenyl]-3-carbonitrile (Table 4.6; Product 23en)

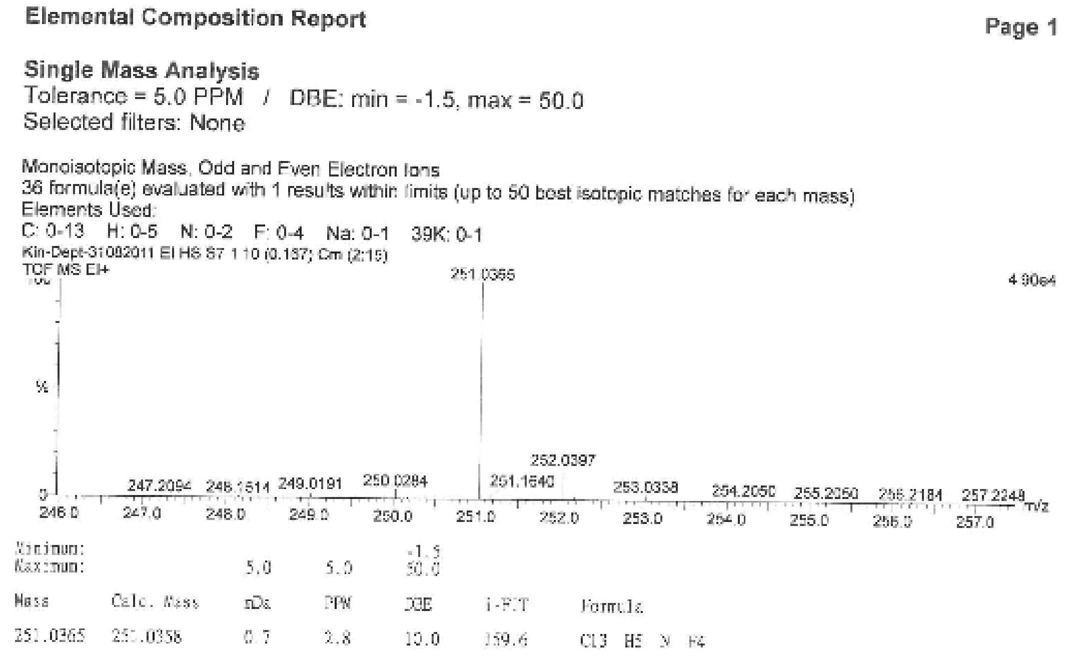




```
NAME             PCL605
EXPNO                 2
PROCNO                1
Date_          20110814
Time              21.12
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG        zgfhigqn
TD               131072
SOLVENT           CDCl3
NS                   16
DS                    4
SWH           89285.711 Hz
FIDRES         0.681196 Hz
AQ            0.7340532 sec
RG                  203
DW                5.600 usec
DE                 6.50 usec
TE                298.3 K
D1           1.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                19F
P1                14.20 usec
PL1               -3.00 dB
PL1W        18.69428444 W
SFO1        376.4607164 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
SFO2        400.1316005 MHz
SI                65536
SF          376.4983660 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```



Elemental Composition Report

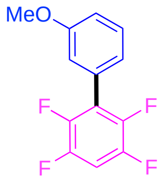
Page 1

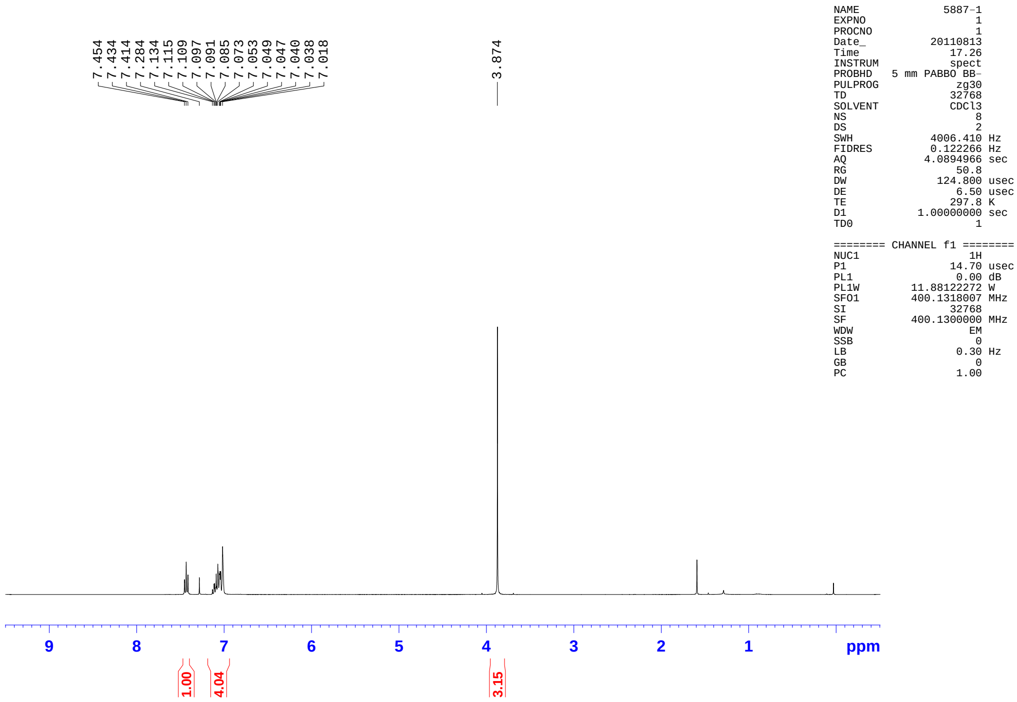
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
36 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-13 H: 0-5 N: 0-2 F: 0-4 Na: 0-1 39K: 0-1
Kin-Dept-31082011 EI HS 87 1 10 (0.137); Cm (2:15)
TOF MS EI+

Minimum:				-1.5		
Maximum:		5.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
251.0365	251.0358	0.7	2.8	10.0	159.6	C13 H5 N F4

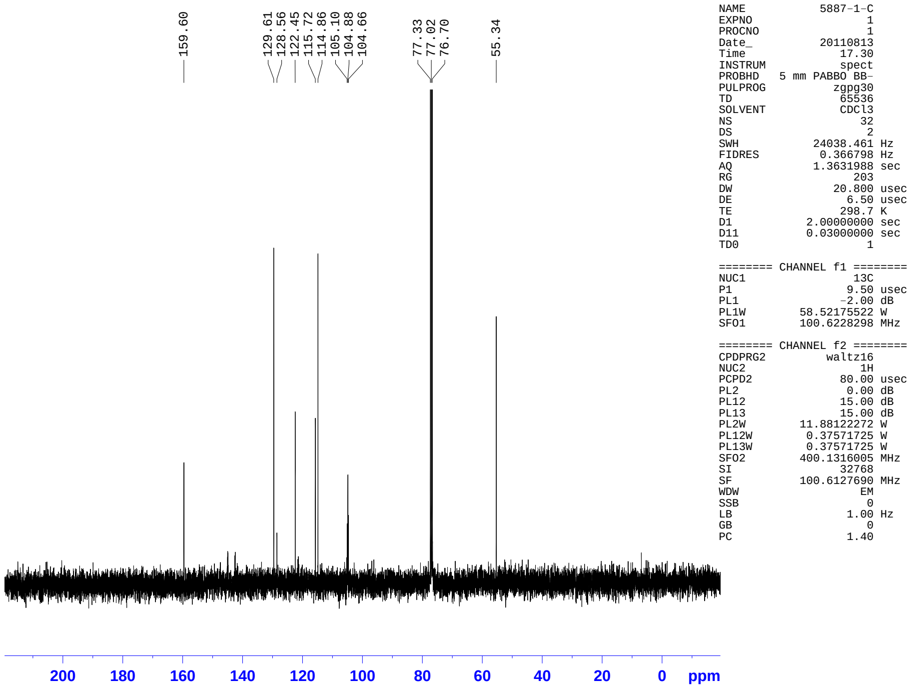
2,3,5,6-Tetrafluoro-3'-methoxy-1,1'-biphenyl (Scheme 4.1)





```
NAME             5887-1
EXPNO                 1
PROCNO                1
Date_          20110813
Time              17.26
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            4006.410 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                 50.8
DW              124.800 usec
DE                 6.50 usec
TE                297.8 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.70 usec
PL1                0.00 dB
PL1W        11.88122272 W
SFO1        400.1318007 MHz
SI                32768
SF          400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

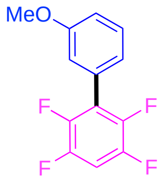


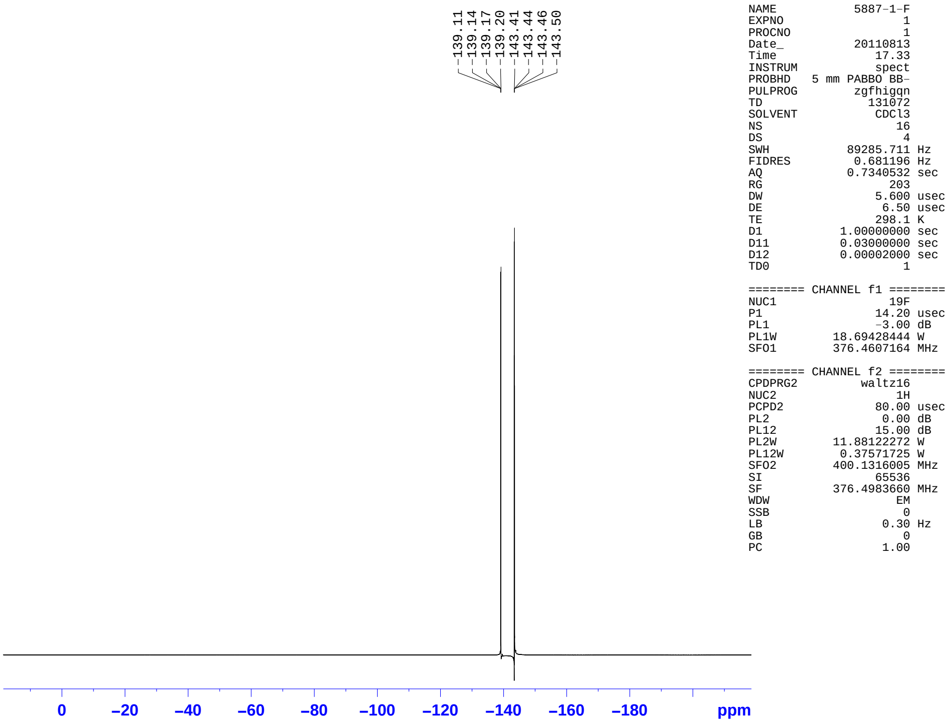
```
NAME           5887-1-C
EXPNO                 1
PROCNO                1
Date_          20110813
Time              17.30
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                  203
DW               20.800 usec
DE                 6.50 usec
TE                298.7 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.50 usec
PL1               -2.00 dB
PL1W        58.52175522 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL13              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
PL13W        0.37571725 W
SFO2        400.1316005 MHz
SI                32768
SF          100.6127690 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

2,3,5,6-Tetrafluoro-3'-methoxy-1,1'-biphenyl (Scheme 4.1)

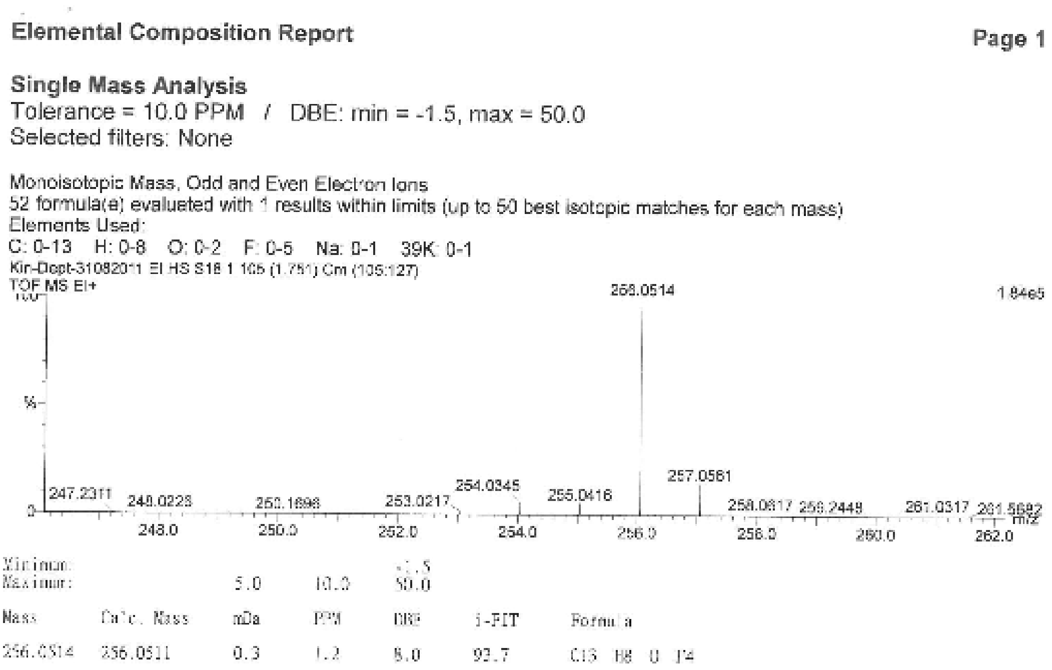




```
NAME             5887-1-F
EXPNO                   1
PROCNO                  1
Date_            20110813
Time                17.33
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgfhigqn
TD                 131072
SOLVENT             CDCl3
NS                     16
DS                      4
SWH             89285.711 Hz
FIDRES           0.681196 Hz
AQ              0.7340532 sec
RG                    203
DW                  5.600 usec
DE                   6.50 usec
TE                  298.1 K
D1             1.00000000 sec
D11            0.03000000 sec
D12            0.00002000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  19F
P1                  14.20 usec
PL1                 -3.00 dB
PL1W          18.69428444 W
SFO1          376.4607164 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                15.00 dB
PL2W          11.88122272 W
PL12W          0.37571725 W
SFO2          400.1316005 MHz
SI                  65536
SF            376.4983660 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



Elemental Composition Report

Page 1

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

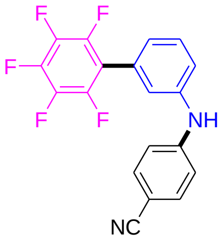
Monoisotopic Mass, Odd and Even Electron Ions
52 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-13 H: 0-8 O: 0-2 F: 0-5 Na: 0-1 39K: 0-1
Kir-Dept-31082011 EI HS S18 1 105 (1.751) Cm (105:127)
TOF MS EI+

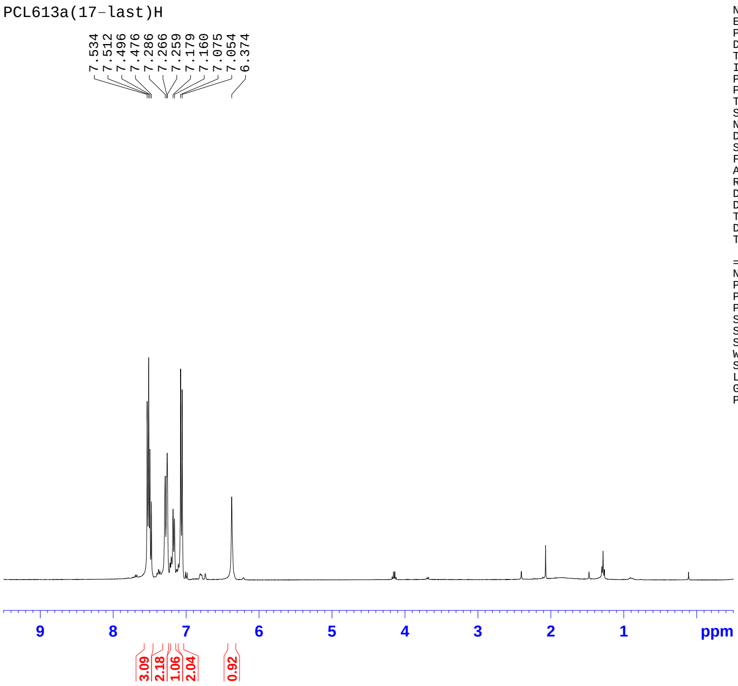
```
Minimum:                          -1.5
Maximum:            5.0    10.0   50.0

Mass      Calc. Mass   mDa   PPM   DBE   i-FIT   Formula

256.0514  256.0511     0.3   1.2   8.0   93.7    C13 H8 O F4
```

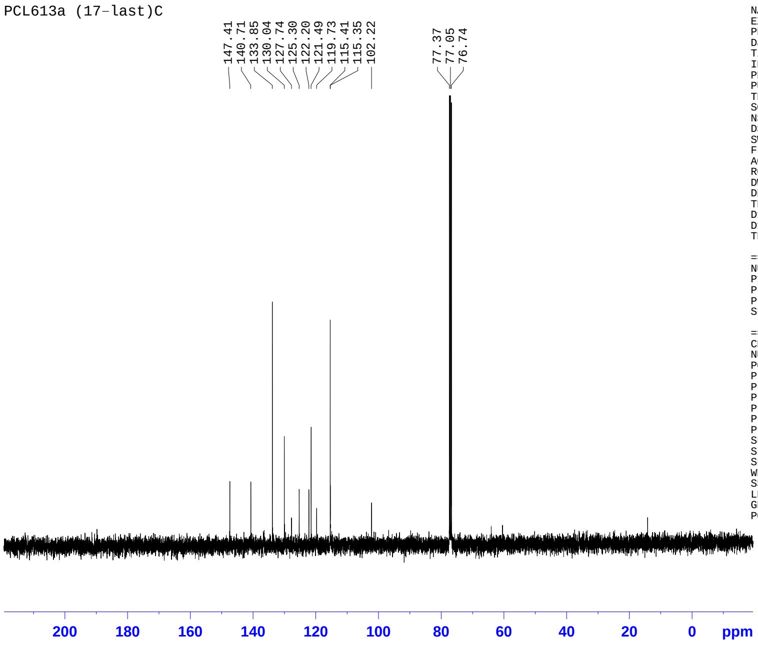
4-((3-(Pentafluorophenyl)phenyl)amino)benzonitrile (Scheme 4.2)





```
NAME             PCL613a
EXPNO                 11
PROCNO                 1
Date_           20110823
Time               20.59
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  45.2
DW               124.800 usec
DE                  6.50 usec
TE                 298.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

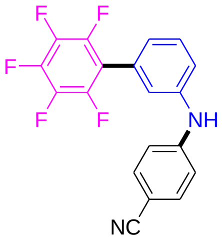


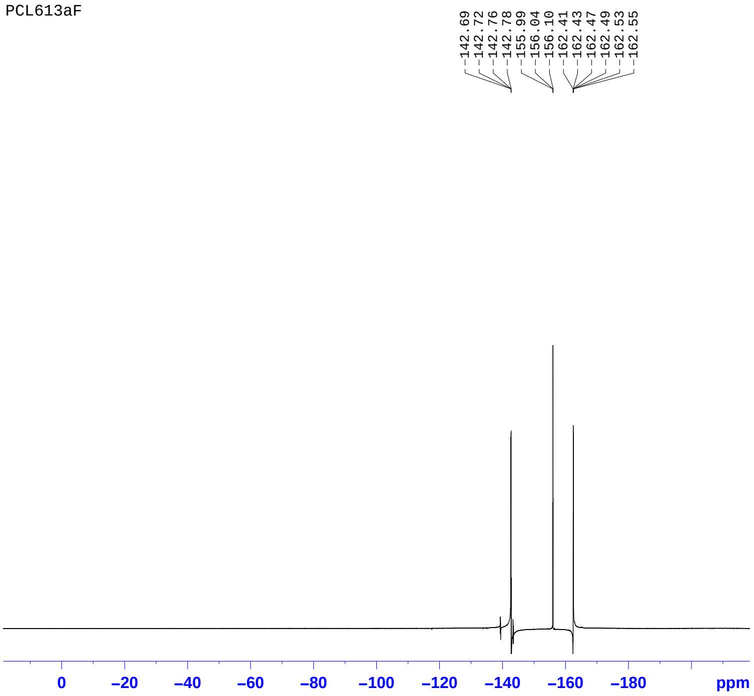
```
NAME             PCL613a
EXPNO                 10
PROCNO                 1
Date_           20110822
Time               20.52
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   114
DW                20.800 usec
DE                  6.50 usec
TE                 298.9 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127690 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

4-((3-(Pentafluorophenyl)phenyl)amino)benzonitrile (Scheme 4.2)



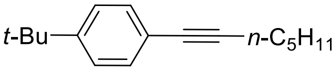


```
NAME             PCL613a
EXPNO                  2
PROCNO                 1
Date_           20110822
Time               11.52
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG         zgfhigqn
TD                131072
SOLVENT            CDCl3
NS                    16
DS                     4
SWH            89285.711 Hz
FIDRES          0.681196 Hz
AQ             0.7340532 sec
RG                   203
DW                 5.600 usec
DE                  6.50 usec
TE                 298.1 K
D1            1.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
TD0                    1

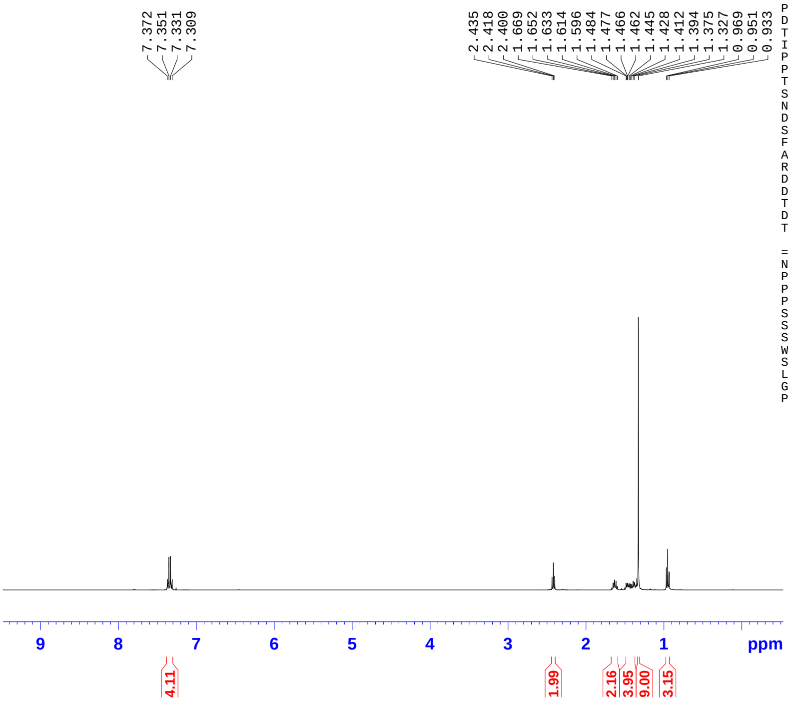
======== CHANNEL f1 ========
NUC1                 19F
P1                 14.20 usec
PL1                -3.00 dB
PL1W         18.69428444 W
SFO1         376.4607164 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
SFO2         400.1316005 MHz
SI                 65536
SF           376.4983660 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

1-*tert*-Butyl-4-(hept-1-ynyl)benzene (Table 5.2)



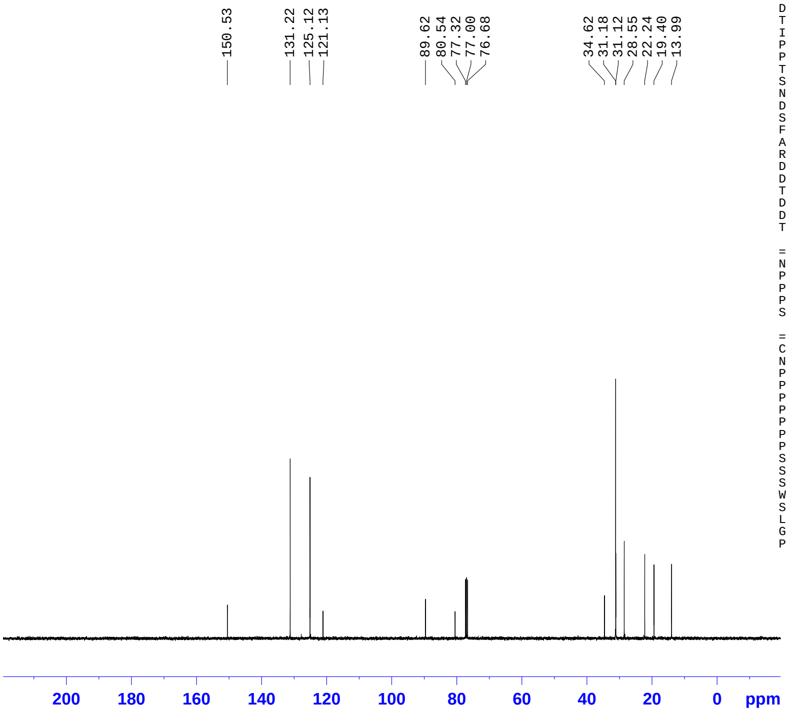
PC041-H



```
NAME              PC041
EXPNO                 1
PROCNO                1
Date_          20100304
Time              21.17
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            4006.410 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                 12.7
DW              124.800 usec
DE                 6.50 usec
TE                298.4 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.70 usec
PL1                0.00 dB
PL1W        11.88122272 W
SFO1        400.1318007 MHz
SI                32768
SF          400.1300101 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

PC041-C

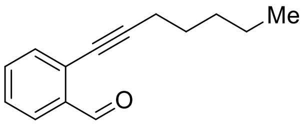


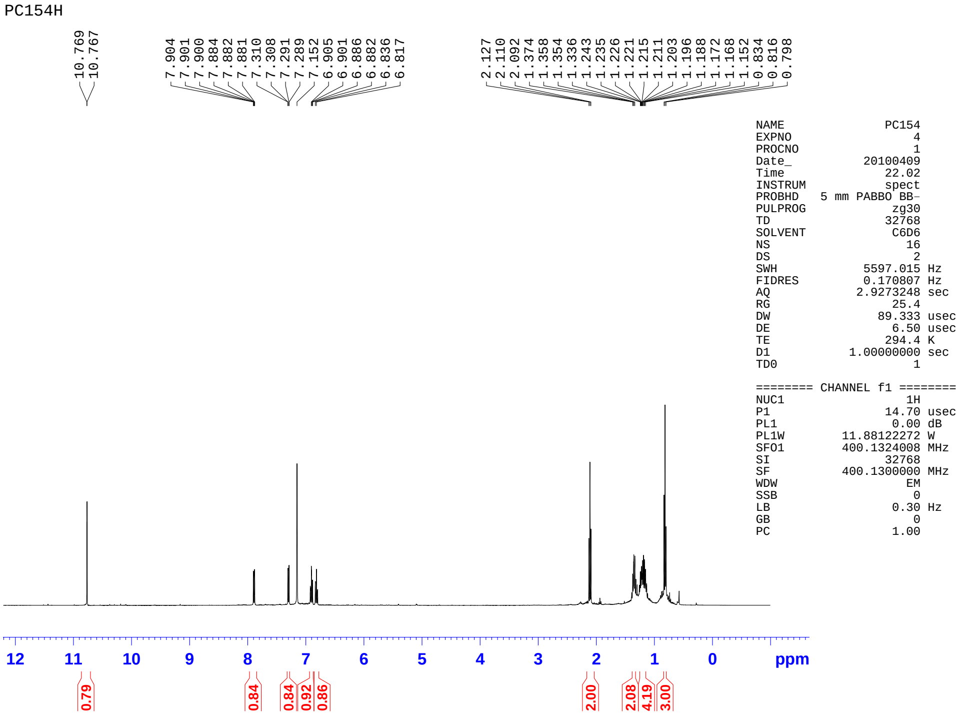
```
NAME              PC041
EXPNO                 2
PROCNO                1
Date_          20100304
Time              21.21
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                  114
DW               20.800 usec
DE                 6.50 usec
TE                299.6 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.50 usec
PL1               -2.00 dB
PL1W        58.52175522 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL13              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
PL13W        0.37571725 W
SFO2        400.1316005 MHz
SI                32768
SF          100.6127729 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

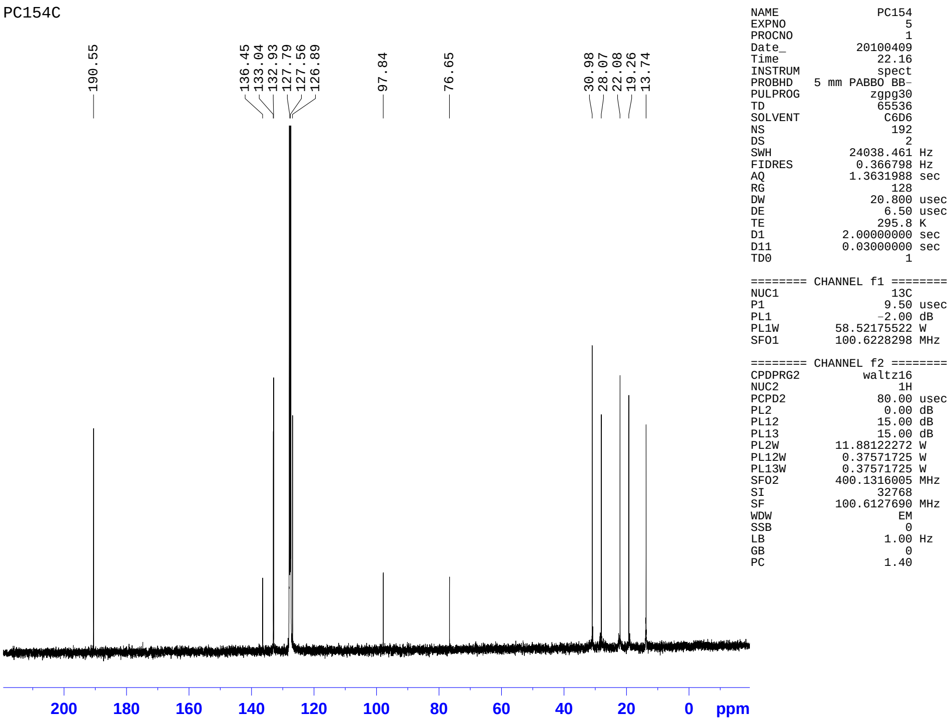
2-(Hept-1-ynyl)benzaldehyde (Table 5.2)





```
NAME             PC154
EXPNO                4
PROCNO               1
Date_         20100409
Time             22.02
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG           zg30
TD               32768
SOLVENT           C6D6
NS                  16
DS                   2
SWH           5597.015 Hz
FIDRES        0.170807 Hz
AQ           2.9273248 sec
RG                25.4
DW              89.333 usec
DE                6.50 usec
TE               294.4 K
D1          1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                1H
P1               14.70 usec
PL1               0.00 dB
PL1W       11.88122272 W
SFO1       400.1324008 MHz
SI               32768
SF         400.1300000 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.00
```

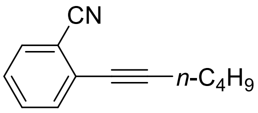


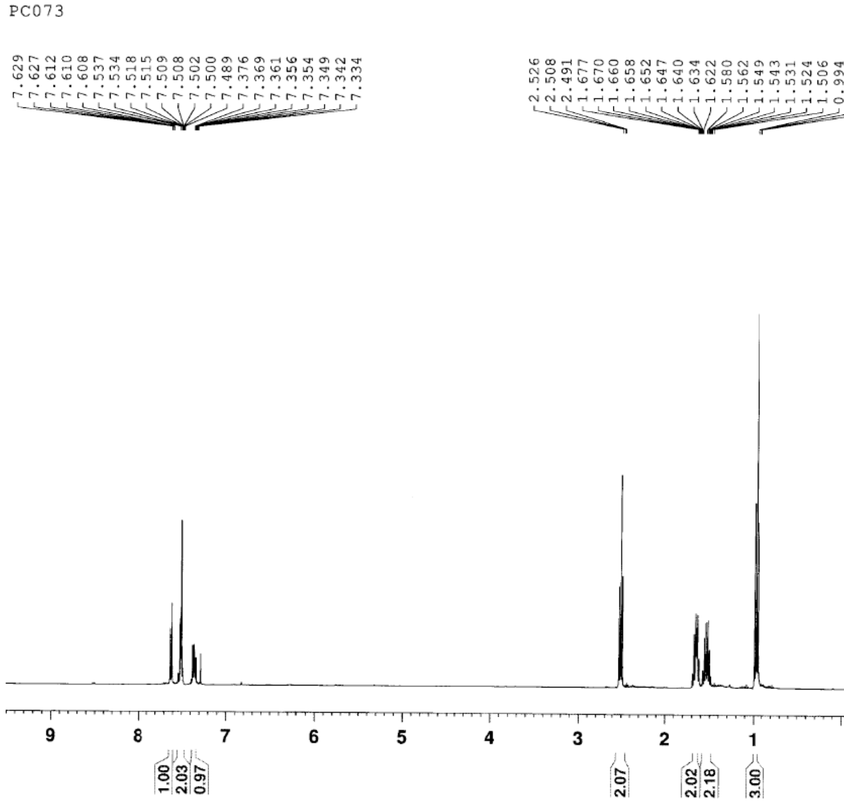
```
NAME             PC154
EXPNO                5
PROCNO               1
Date_         20100409
Time             22.16
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT           C6D6
NS                 192
DS                   2
SWH          24038.461 Hz
FIDRES        0.366798 Hz
AQ           1.3631988 sec
RG                 128
DW              20.800 usec
DE                6.50 usec
TE               295.8 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1                9.50 usec
PL1              -2.00 dB
PL1W       58.52175522 W
SFO1       100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2            80.00 usec
PL2               0.00 dB
PL12             15.00 dB
PL13             15.00 dB
PL2W       11.88122272 W
PL12W       0.37571725 W
PL13W       0.37571725 W
SFO2       400.1316005 MHz
SI               32768
SF         100.6127690 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```

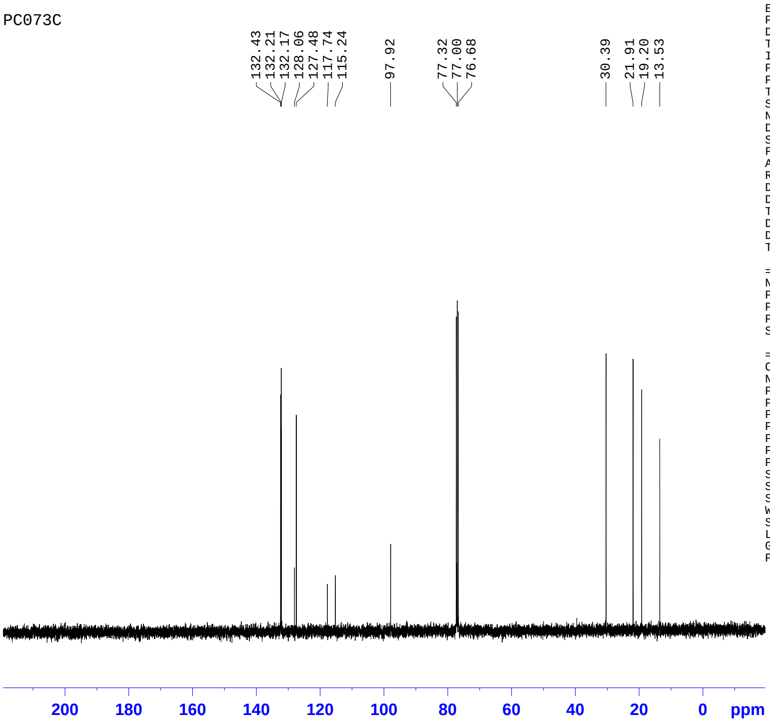
2-(Hex-1-ynyl)benzonitrile (Table 5.2)





```
NAME            PC073
EXPNO               1
PROCNO              1
Date_        20100324
Time            19.05
INSTRUM         spect
PROBHD   5 mm PABBO BB-
PULPROG          zg30
TD              32768
SOLVENT         CDCl3
NS                 16
DS                  2
SWH          4006.410 Hz
FIDRES       0.122266 Hz
AQ          4.0894966 sec
RG               45.2
DW            124.800 usec
DE               6.50 usec
TE              296.8 K
D1         1.00000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1               1H
P1              14.70 usec
PL1              0.00 dB
PL1W      11.88122272 W
SFO1      400.1318007 MHz
SI              32768
SF        400.1300000 MHz
WDW                EM
SSB                 0
LB               0.30 Hz
GB                  0
PC               1.00
```

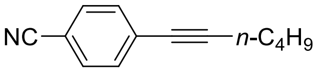


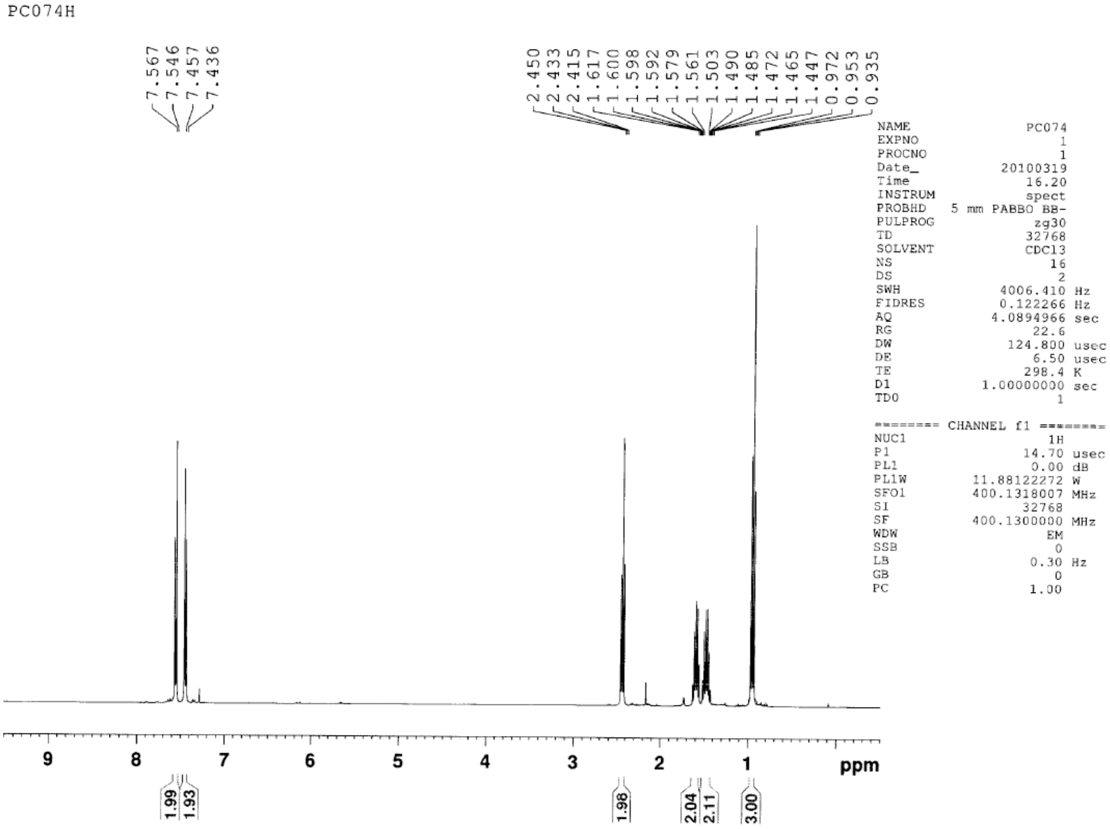
```
NAME            PC073
EXPNO               2
PROCNO              1
Date_        20100324
Time            19.07
INSTRUM         spect
PROBHD   5 mm PABBO BB-
PULPROG        zgpg30
TD              65536
SOLVENT         CDCl3
NS                 32
DS                  2
SWH         24038.461 Hz
FIDRES       0.366798 Hz
AQ          1.3631988 sec
RG                203
DW             20.800 usec
DE               6.50 usec
TE              297.9 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0                 1

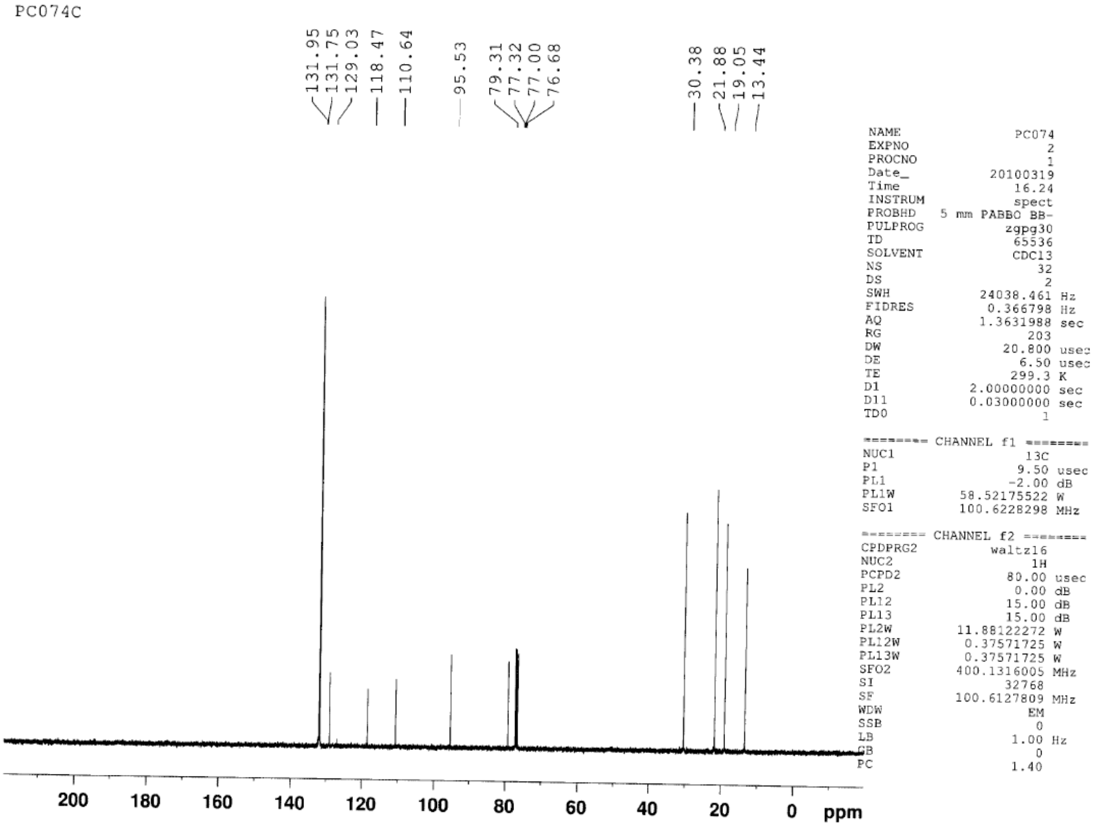
======== CHANNEL f1 ========
NUC1              13C
P1               9.50 usec
PL1             -2.00 dB
PL1W      58.52175522 W
SFO1      100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2       waltz16
NUC2               1H
PCPD2           80.00 usec
PL2              0.00 dB
PL12            15.00 dB
PL13            15.00 dB
PL2W      11.88122272 W
PL12W      0.37571725 W
PL13W      0.37571725 W
SFO2      400.1316005 MHz
SI              32768
SF        100.6127744 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```

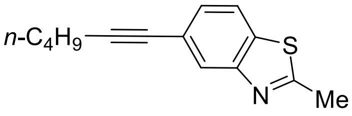
4-(Hex-1-ynyl)benzonitrile (Table 5.2)

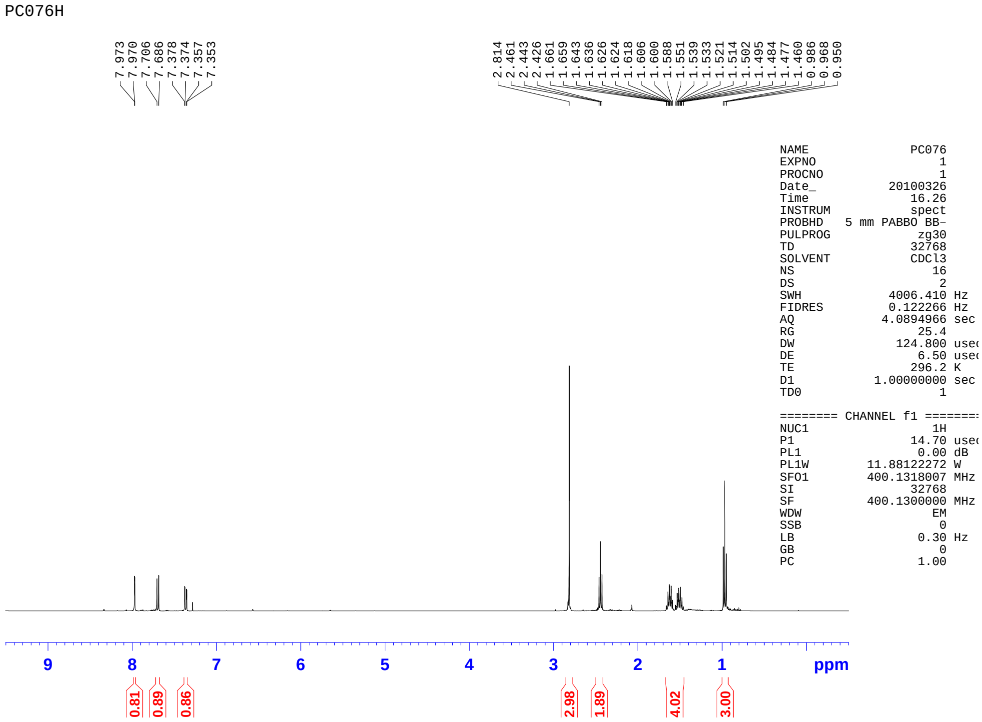






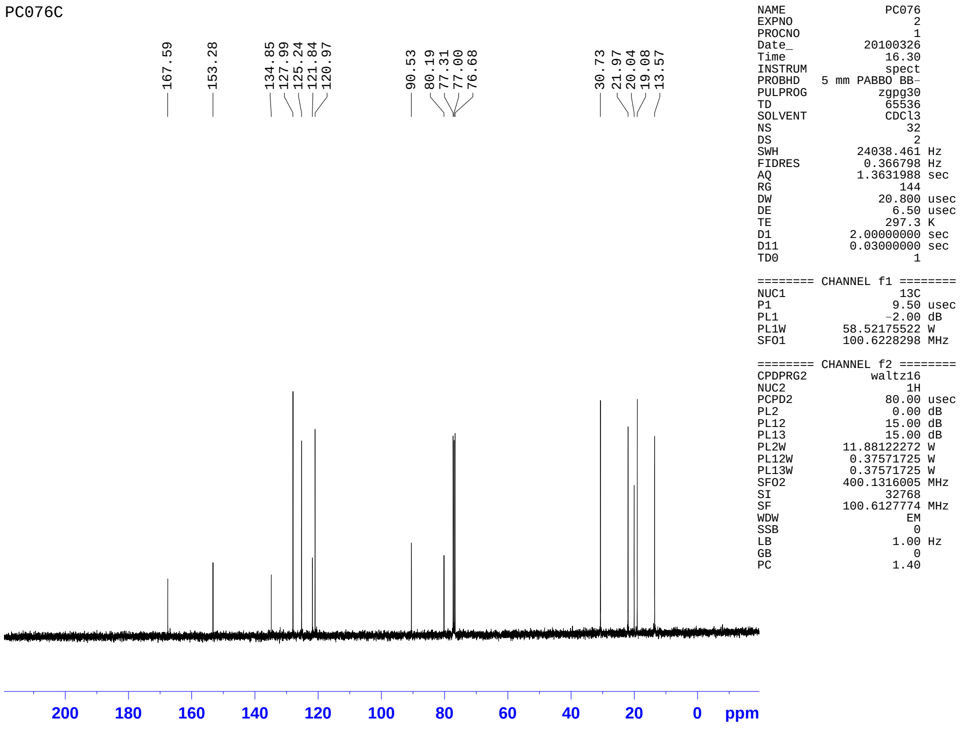
5-(Hex-1-ynyl)-2-methylbenzothiazole (Table 5.2, Table 5.3)





```
NAME               PC076
EXPNO                  1
PROCNO                 1
Date_           20100326
Time               16.26
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  25.4
DW               124.800 use
DE                  6.50 use
TE                 296.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 =======
NUC1                  1H
P1                 14.70 use
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

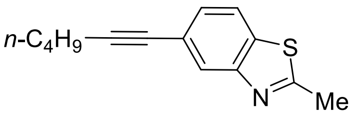


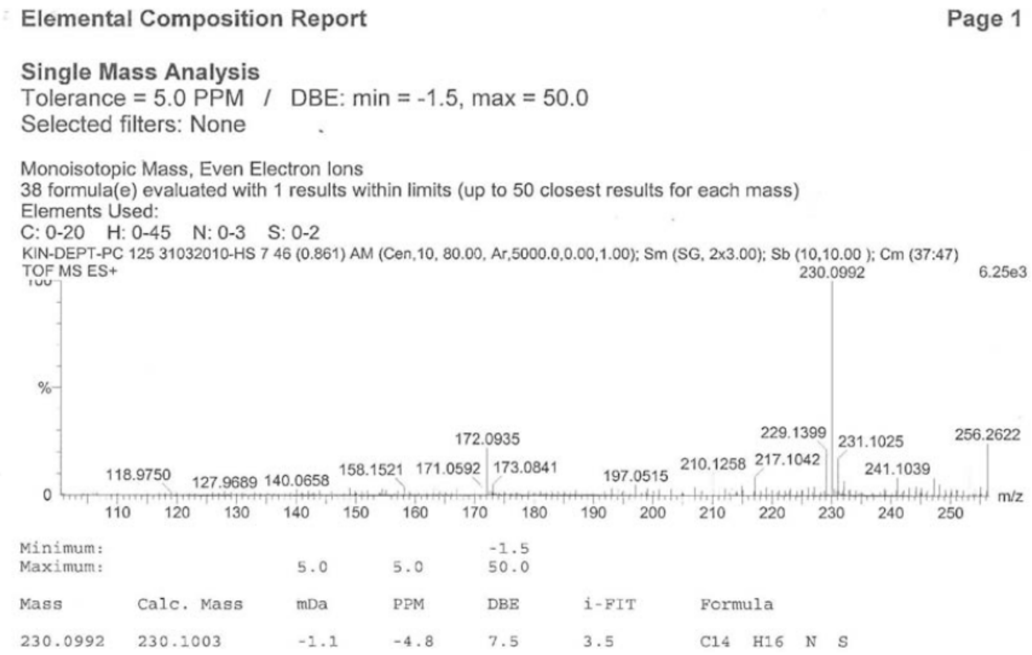
```
NAME               PC076
EXPNO                  2
PROCNO                 1
Date_           20100326
Time               16.30
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   144
DW                20.800 usec
DE                  6.50 usec
TE                 297.3 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127774 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

5-(Hex-1-ynyl)-2-methylbenzothiazole (Table 5.2, Table 5.3)





Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

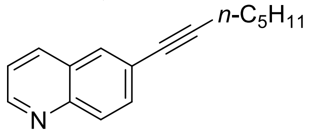
Monoisotopic Mass, Even Electron Ions
38 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-20 H: 0-45 N: 0-3 S: 0-2
KIN-DEPT-PC 125 31032010-HS 7 46 (0.861) AM (Cen,10, 80.00, Ar,5000.0,0.00,1.00); Sm (SG, 2x3.00); Sb (10,10.00); Cm (37:47)
TOF MS ES+

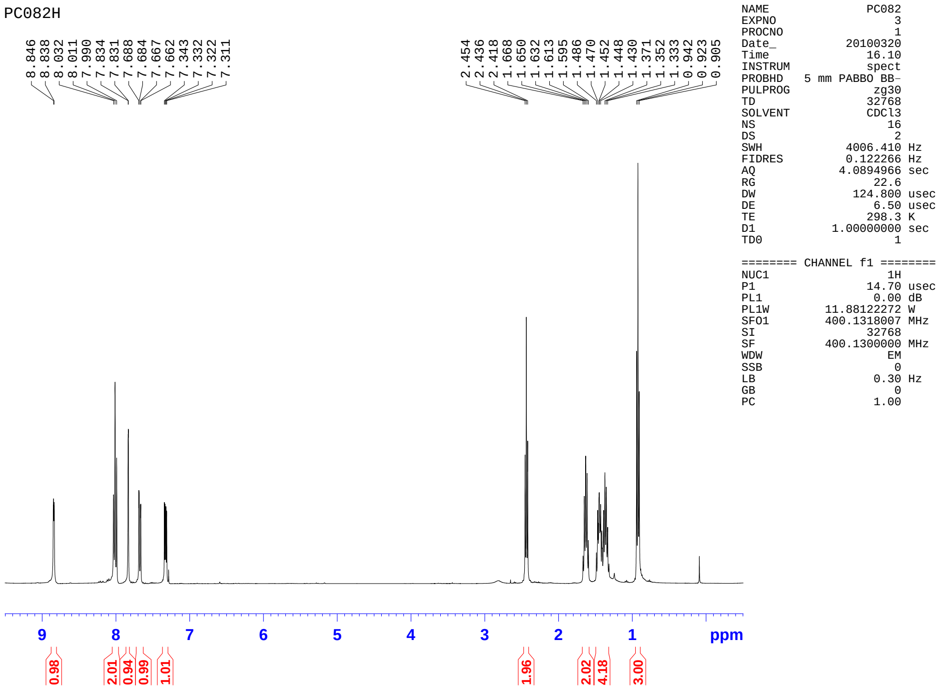
```
Minimum:                                      -1.5
Maximum:                   5.0       5.0      50.0

Mass        Calc. Mass     mDa       PPM      DBE       i-FIT       Formula

230.0992    230.1003       -1.1      -4.8     7.5       3.5         C14  H16  N  S
```

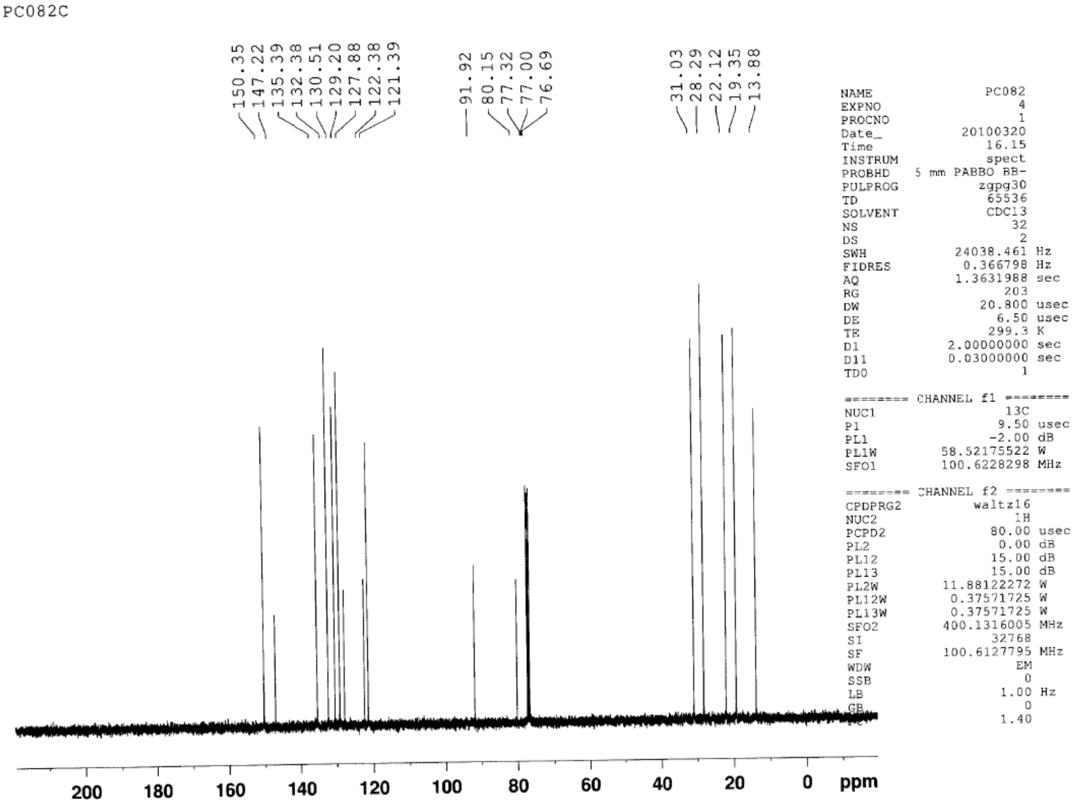
6-(Hept-1-ynyl)quinoline (Table 5.2)





```
NAME             PC082
EXPNO                3
PROCNO               1
Date_         20100320
Time             16.10
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG           zg30
TD               32768
SOLVENT          CDCl3
NS                  16
DS                   2
SWH           4006.410 Hz
FIDRES        0.122266 Hz
AQ           4.0894966 sec
RG                22.6
DW             124.800 usec
DE                6.50 usec
TE               298.3 K
D1          1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                1H
P1               14.70 usec
PL1               0.00 dB
PL1W       11.88122272 W
SFO1       400.1318007 MHz
SI               32768
SF         400.1300000 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.00
```

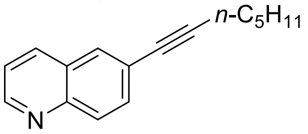


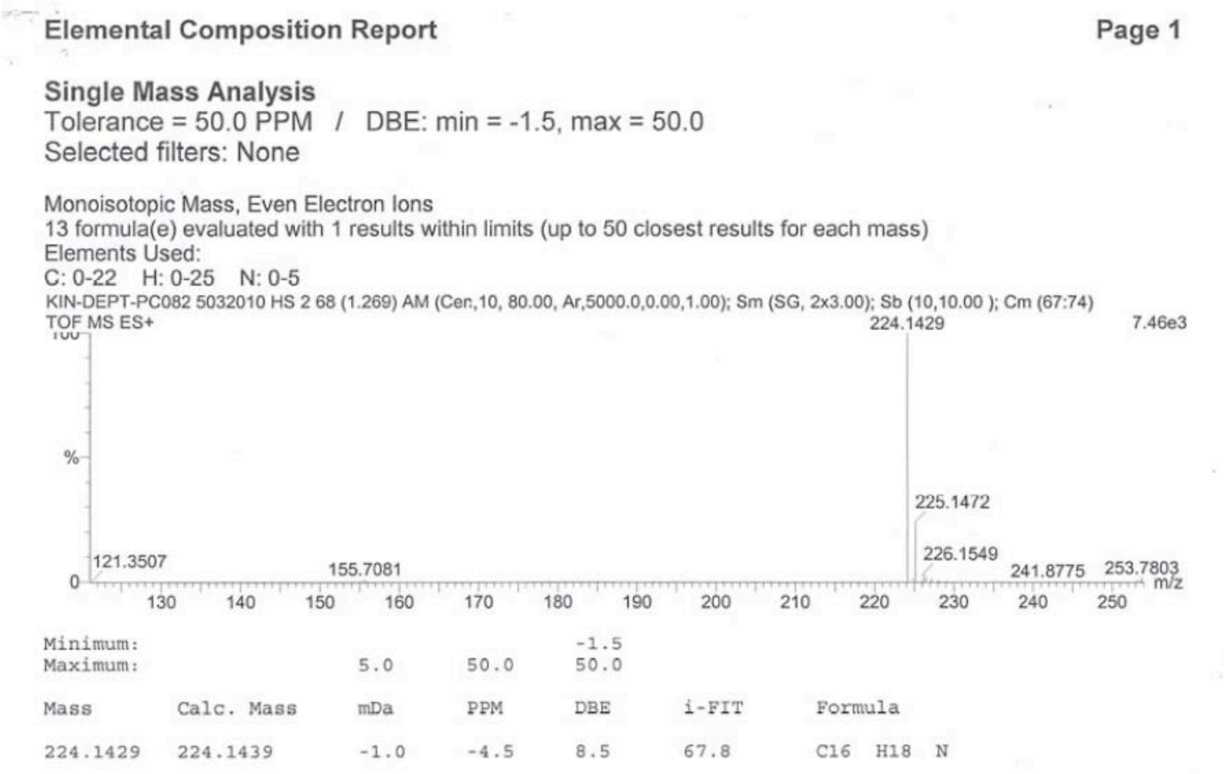
```
NAME             PC082
EXPNO                4
PROCNO               1
Date_         20100320
Time             16.15
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                  32
DS                   2
SWH          24038.461 Hz
FIDRES        0.366798 Hz
AQ           1.3631988 sec
RG                 203
DW              20.800 usec
DE                6.50 usec
TE               299.3 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1                9.50 usec
PL1              -2.00 dB
PL1W       58.52175522 W
SFO1       100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2            80.00 usec
PL2               0.00 dB
PL12             15.00 dB
PL13             15.00 dB
PL2W       11.88122272 W
PL12W       0.37571725 W
PL13W       0.37571725 W
SFO2       400.1316005 MHz
SI               32768
SF         100.6127795 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```

6-(Hept-1-ynyl)quinoline (Table 5.2)





Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

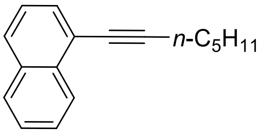
Monoisotopic Mass, Even Electron Ions
13 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-22 H: 0-25 N: 0-5
KIN-DEPT-PC082 5032010 HS 2 68 (1.269) AM (Cen,10, 80.00, Ar,5000.0,0.00,1.00); Sm (SG, 2x3.00); Sb (10,10.00); Cm (67:74)
TOF MS ES+

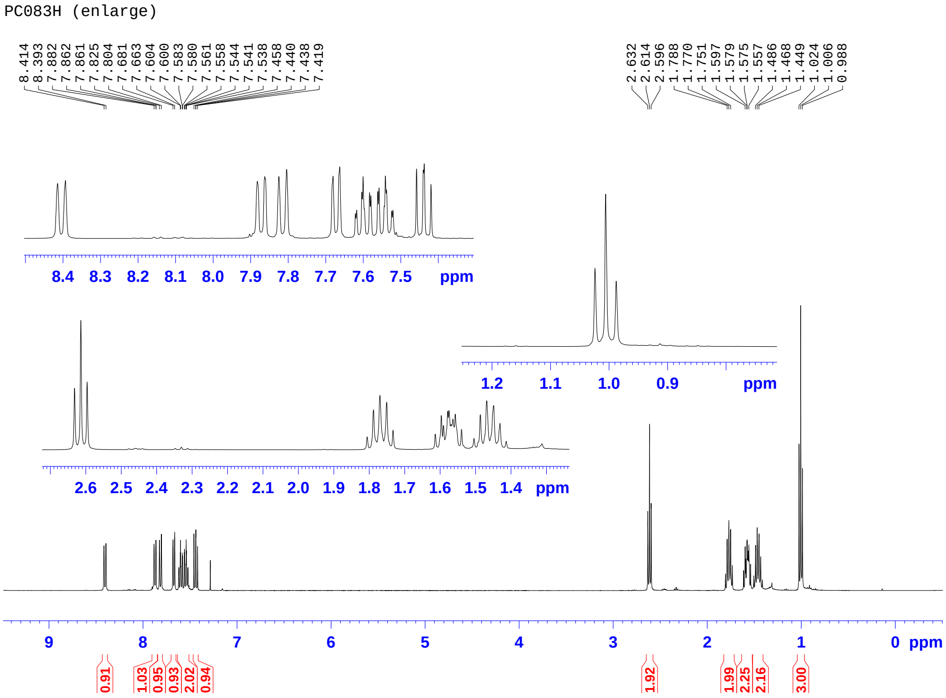
```
Minimum:                                    -1.5
Maximum:                   5.0      50.0    50.0

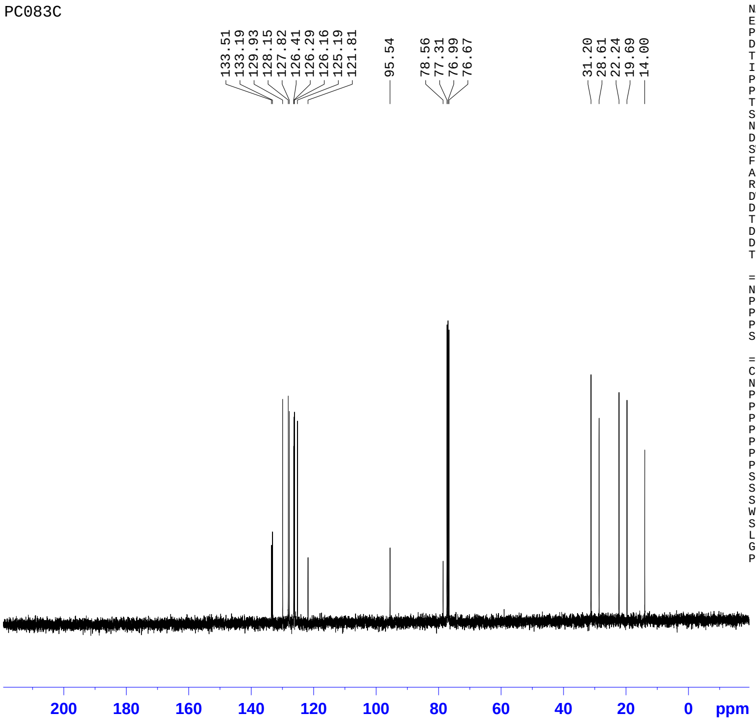
Mass       Calc. Mass     mDa      PPM      DBE      i-FIT      Formula

224.1429   224.1439       -1.0     -4.5     8.5      67.8       C16  H18  N
```

1-(Hept-1-ynyl)naphthalene (Table 5.2)





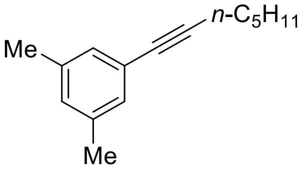


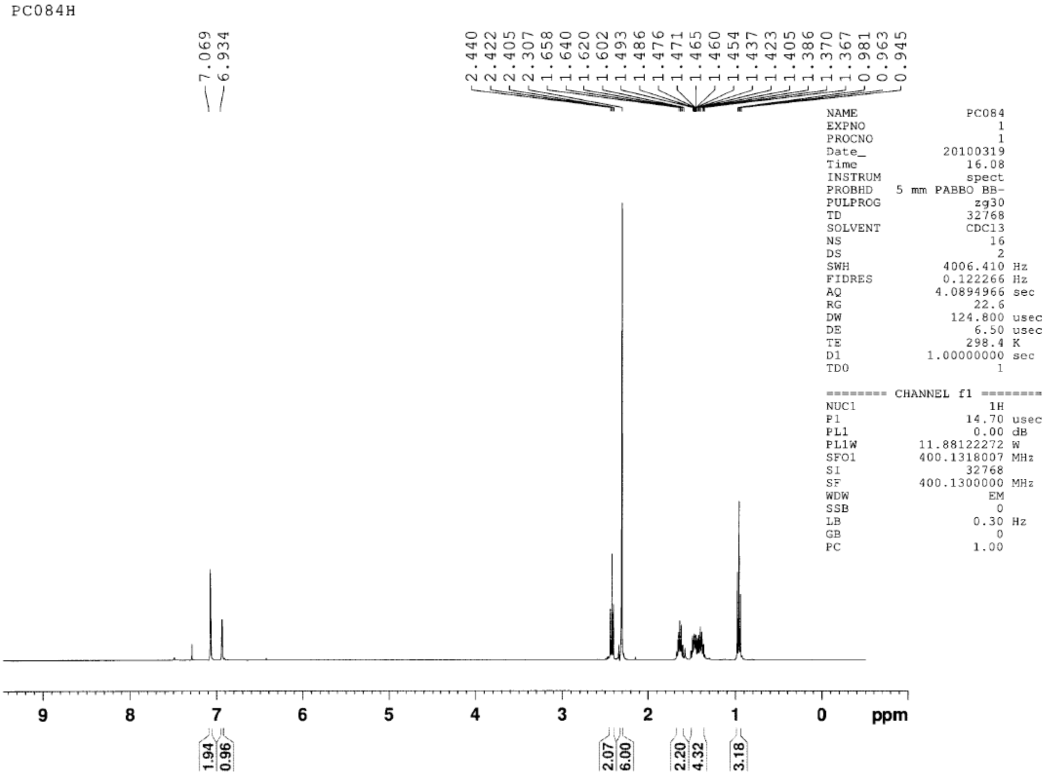
```
NAME              PC083
EXPNO                 2
PROCNO                1
Date_          20100322
Time              16.11
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                  161
DW               20.800 usec
DE                 6.50 usec
TE                299.6 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.50 usec
PL1               -2.00 dB
PL1W        58.52175522 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL13              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
PL13W        0.37571725 W
SFO2        400.1316005 MHz
SI                32768
SF          100.6127745 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

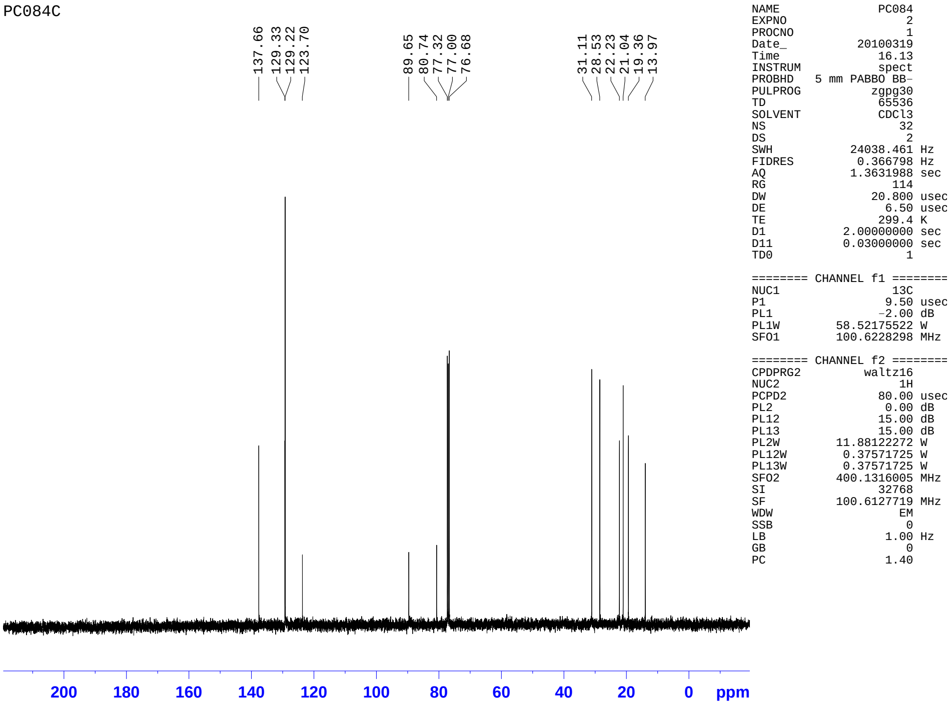
1-(Hept-1-ynyl)-3,5-dimethylbenzene (Table 5.2)





```
NAME              PC084
EXPNO                 1
PROCNO                1
Date_          20100319
Time              16.08
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            4006.410 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                 22.6
DW              124.800 usec
DE                 6.50 usec
TE                298.4 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.70 usec
PL1                0.00 dB
PL1W        11.88122272 W
SFO1        400.1318007 MHz
SI                32768
SF          400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

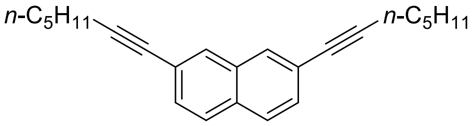


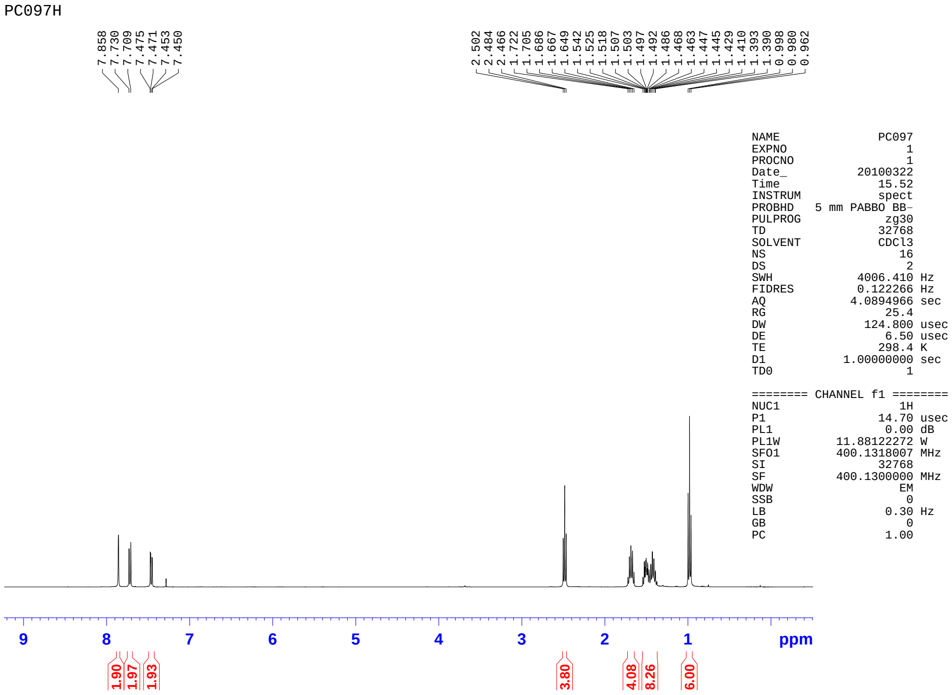
```
NAME              PC084
EXPNO                 2
PROCNO                1
Date_          20100319
Time              16.13
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                  114
DW               20.800 usec
DE                 6.50 usec
TE                299.4 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.50 usec
PL1               -2.00 dB
PL1W        58.52175522 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL13              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
PL13W        0.37571725 W
SFO2        400.1316005 MHz
SI                32768
SF          100.6127719 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

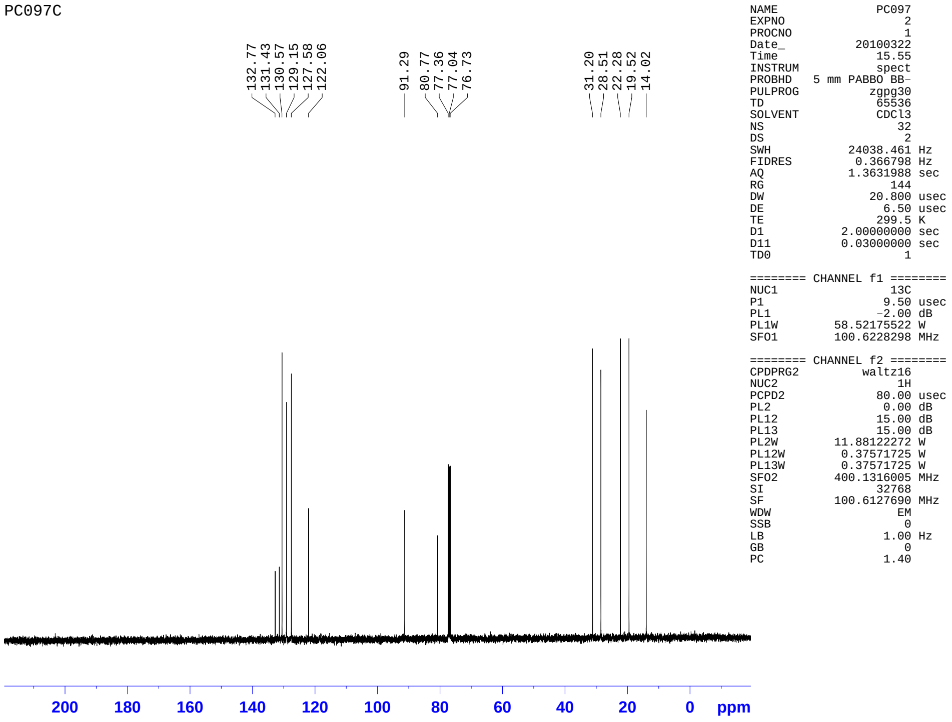
2,7-Di(hept-1-ynyl)naphthalene (Table 5.2)





```
NAME                PC097
EXPNO                   1
PROCNO                  1
Date_            20100322
Time                15.52
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              4006.410 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                   25.4
DW                124.800 usec
DE                   6.50 usec
TE                  298.4 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.70 usec
PL1                  0.00 dB
PL1W          11.88122272 W
SFO1          400.1318007 MHz
SI                  32768
SF            400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

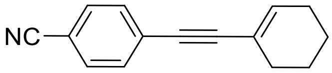


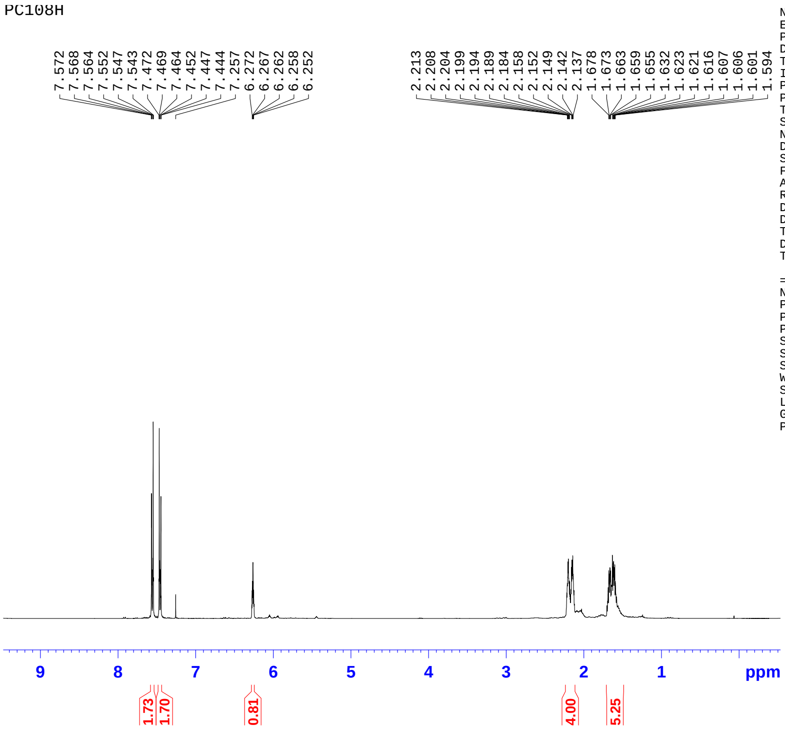
```
NAME                PC097
EXPNO                   2
PROCNO                  1
Date_            20100322
Time                15.55
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      2
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                    144
DW                 20.800 usec
DE                   6.50 usec
TE                  299.5 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.50 usec
PL1                 -2.00 dB
PL1W          58.52175522 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                15.00 dB
PL13                15.00 dB
PL2W          11.88122272 W
PL12W          0.37571725 W
PL13W          0.37571725 W
SFO2          400.1316005 MHz
SI                  32768
SF            100.6127690 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

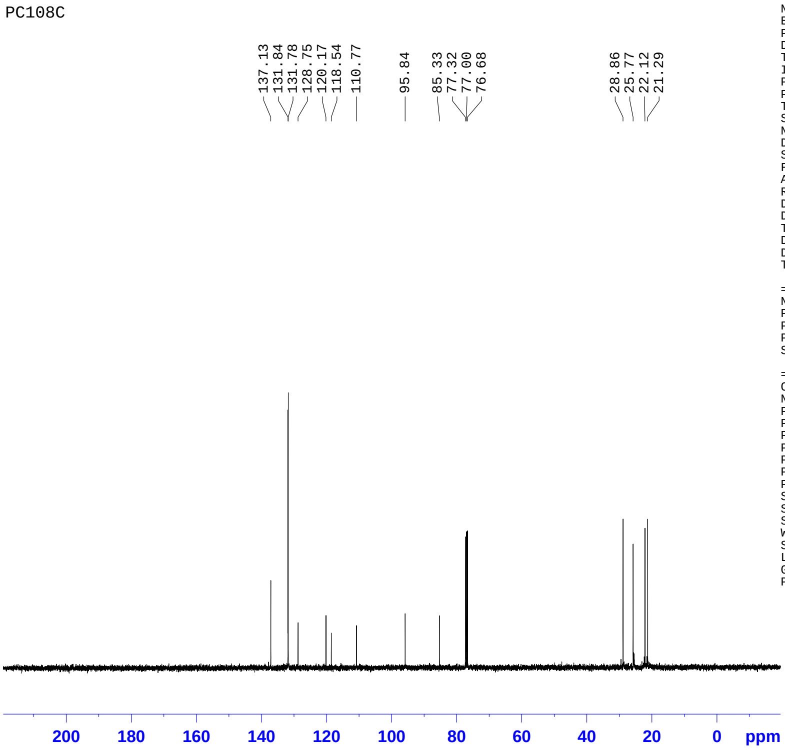
4-(Cyclohexenylethynyl)benzonitrile (Table 5.2)





```
NAME              PC108
EXPNO                 1
PROCNO                1
Date_          20100323
Time              23.26
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            4006.410 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                 25.4
DW              124.800 usec
DE                 6.50 usec
TE                297.5 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.70 usec
PL1                0.00 dB
PL1W        11.88122272 W
SFO1        400.1318007 MHz
SI                32768
SF          400.1300110 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

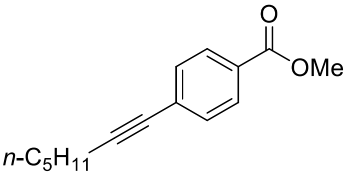


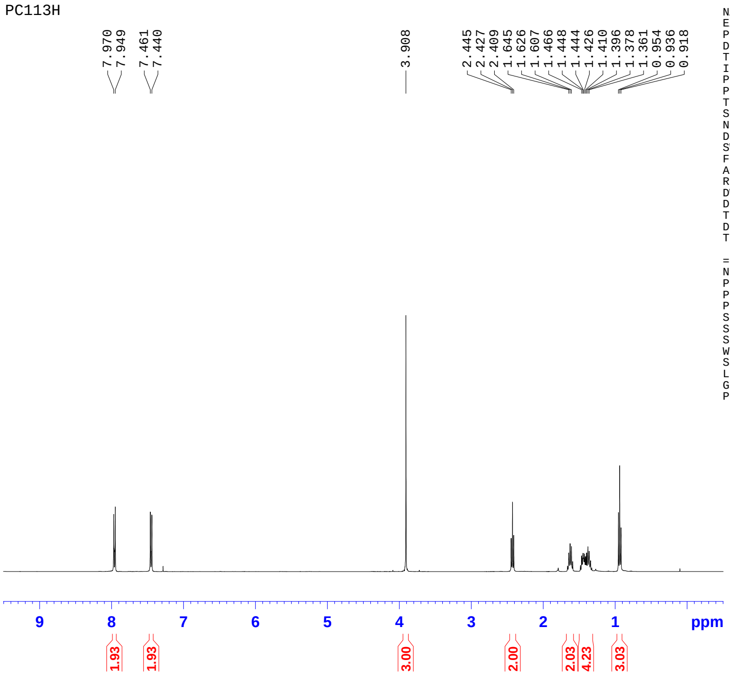
```
NAME              PC108
EXPNO                 2
PROCNO                1
Date_          20100323
Time              23.30
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                  203
DW               20.800 usec
DE                 6.50 usec
TE                298.6 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.50 usec
PL1               -2.00 dB
PL1W        58.52175522 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL13              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
PL13W        0.37571725 W
SFO2        400.1316005 MHz
SI                32768
SF          100.6127773 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

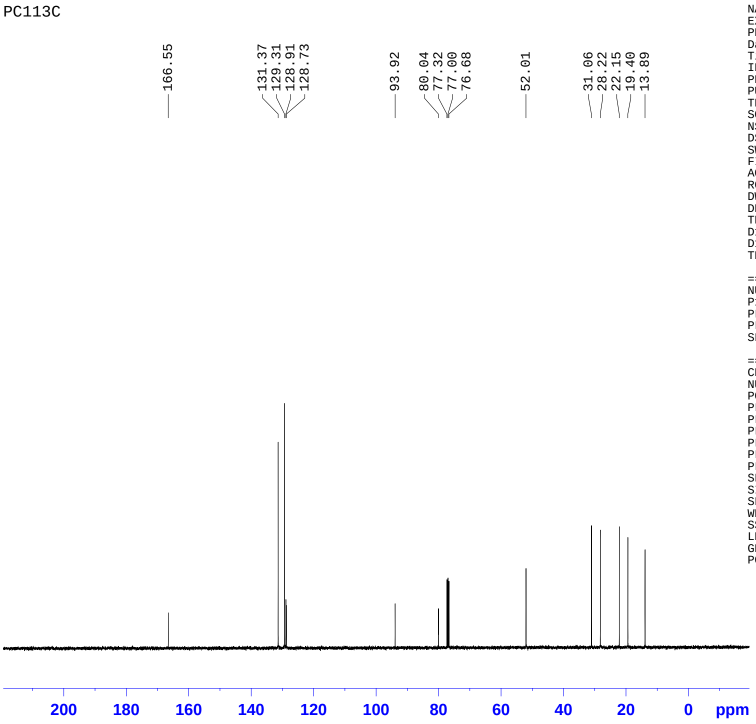
4-Hept-1-ynyl-benzoic acid methyl ester (Table 5.2)





```
NAME                PC113
EXPNO                   1
PROCNO                  1
Date_            20100322
Time                18.37
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              4006.410 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                   20.2
DW                124.800 usec
DE                   6.50 usec
TE                  297.4 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.70 usec
PL1                  0.00 dB
PL1W          11.88122272 W
SFO1          400.1318007 MHz
SI                  32768
SF            400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

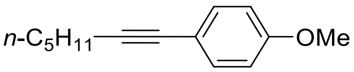


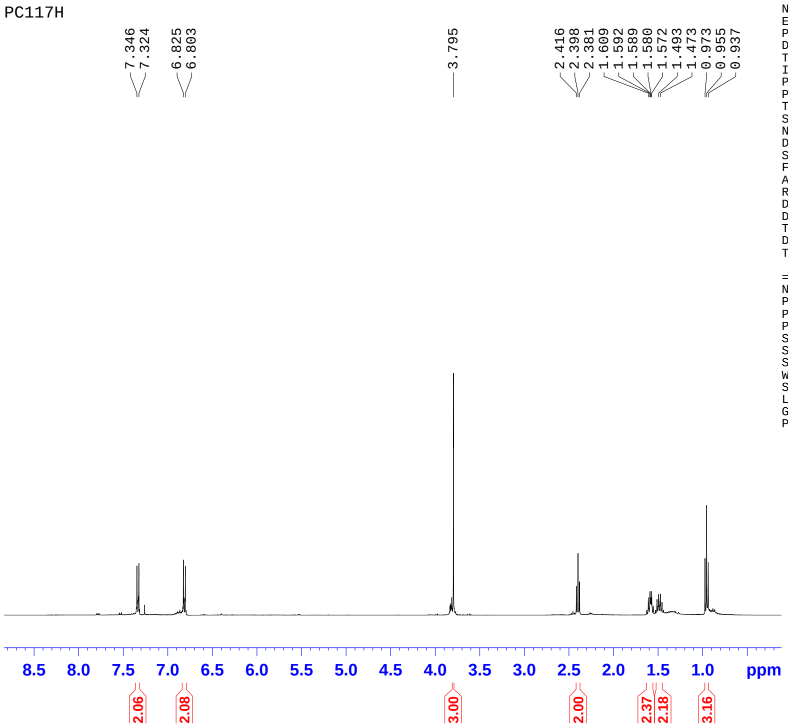
```
NAME                PC113
EXPNO                   2
PROCNO                  1
Date_            20100322
Time                18.41
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      2
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                    203
DW                 20.800 usec
DE                   6.50 usec
TE                  298.5 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.50 usec
PL1                 -2.00 dB
PL1W          58.52175522 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                15.00 dB
PL13                15.00 dB
PL2W          11.88122272 W
PL12W          0.37571725 W
PL13W          0.37571725 W
SFO2          400.1316005 MHz
SI                  32768
SF            100.6127750 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

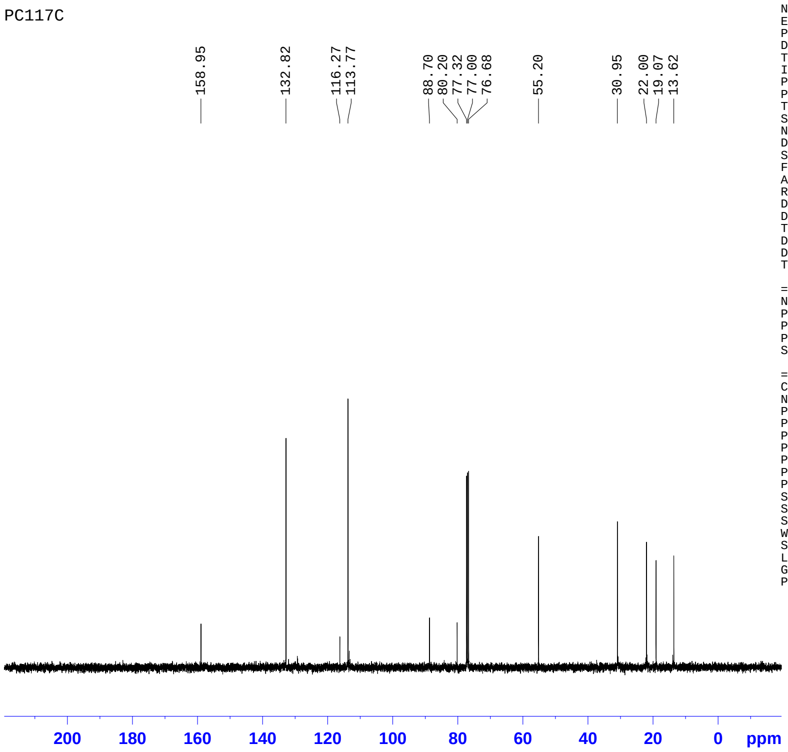
1-(Hept-1-ynyl)-4-methoxybenzene (Table 5.2)





```
NAME              PC117
EXPNO                 1
PROCNO                1
Date_          20100323
Time              15.58
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            4006.410 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                 25.4
DW              124.800 usec
DE                 6.50 usec
TE                297.5 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.70 usec
PL1                0.00 dB
PL1W        11.88122272 W
SFO1        400.1318007 MHz
SI                32768
SF          400.1300101 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

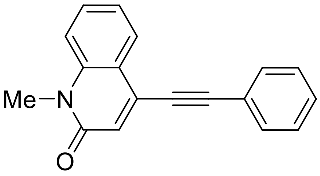


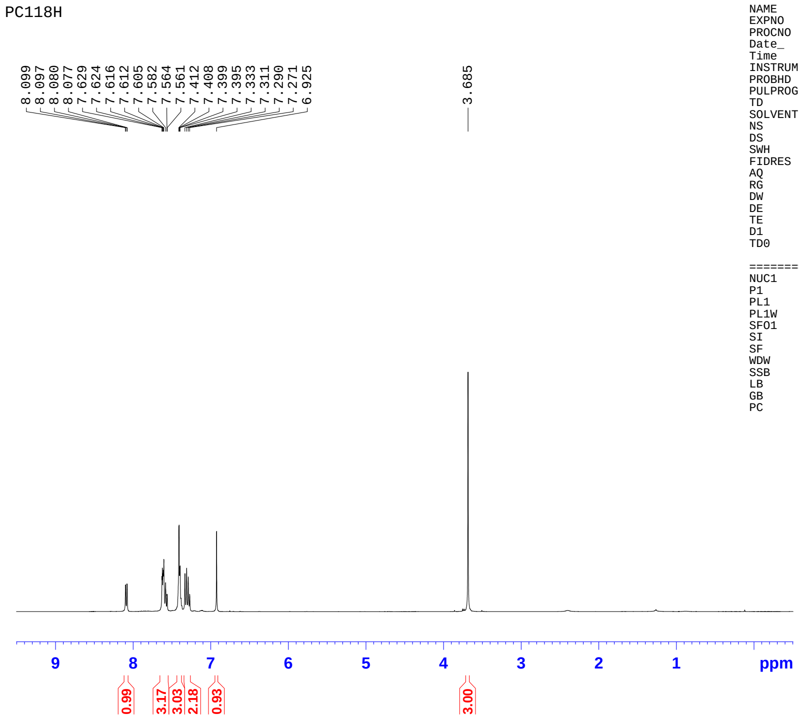
```
NAME              PC117
EXPNO                 2
PROCNO                1
Date_          20100323
Time              16.06
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                  128
DW               20.800 usec
DE                 6.50 usec
TE                298.5 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.50 usec
PL1               -2.00 dB
PL1W        58.52175522 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL13              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
PL13W        0.37571725 W
SFO2        400.1316005 MHz
SI                32768
SF          100.6127726 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

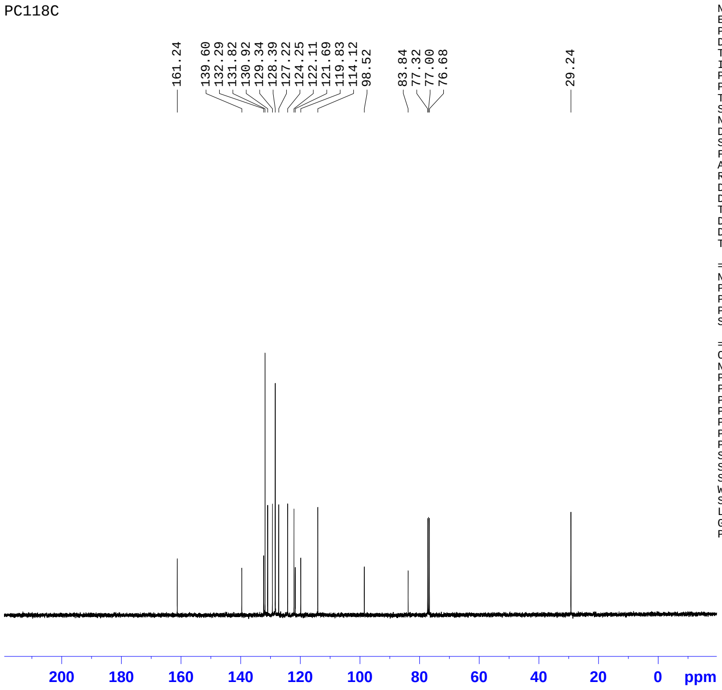
1-Methyl-4-(phenylethynyl)quinolin-2(1*H*)-one (Table 5.2)





```
NAME               PC118
EXPNO                  3
PROCNO                 1
Date_           20100326
Time               20.55
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  22.6
DW               124.800 usec
DE                  6.50 usec
TE                 296.7 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

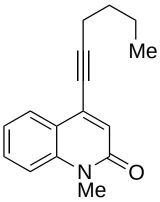


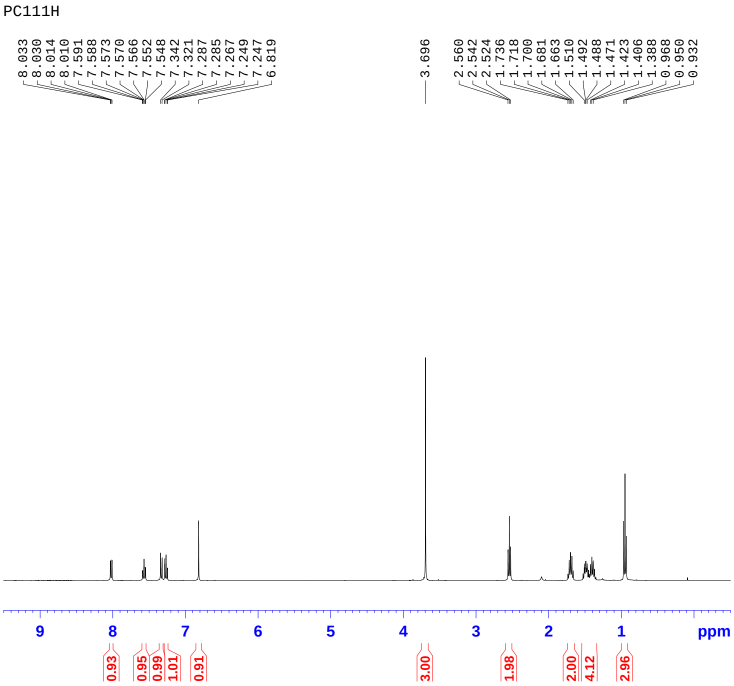
```
NAME               PC118
EXPNO                  4
PROCNO                 1
Date_           20100326
Time               20.57
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   203
DW                20.800 usec
DE                  6.50 usec
TE                 297.8 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127876 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

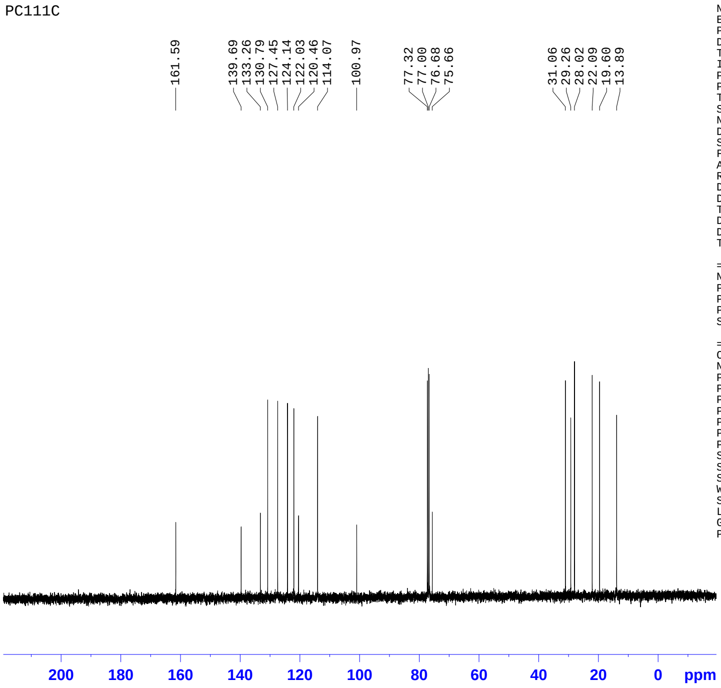
4-(Hex-1-yn-1-yl)-1-methylquinolin-2(1*H*)-one (Table 5.2, 5.3)





```
NAME                PC111
EXPNO                   1
PROCNO                  1
Date_            20100322
Time                23.34
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              4006.410 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                   25.4
DW                124.800 usec
DE                   6.50 usec
TE                  297.8 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.70 usec
PL1                  0.00 dB
PL1W          11.88122272 W
SFO1          400.1318007 MHz
SI                  32768
SF            400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

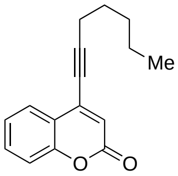


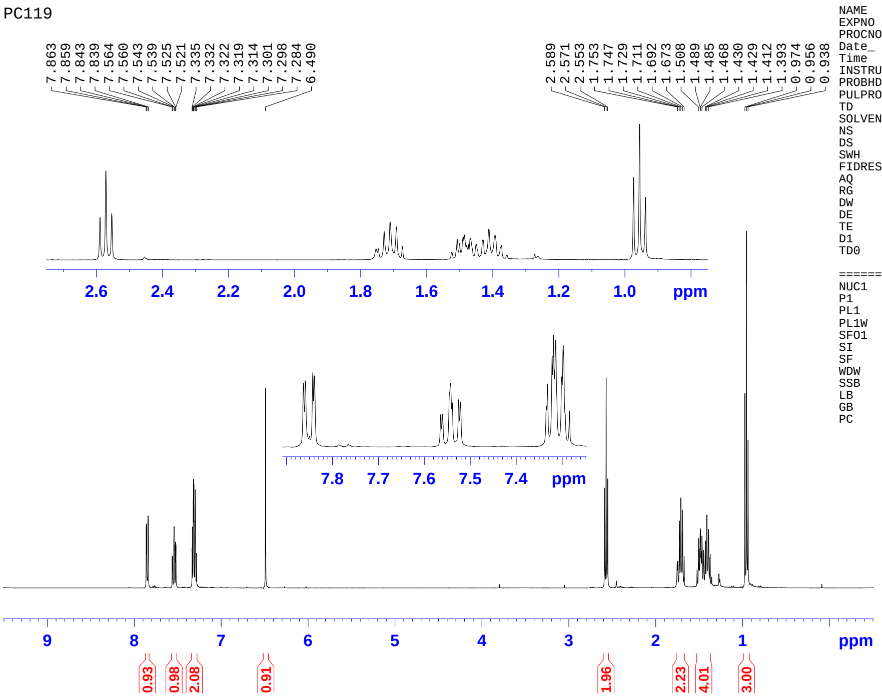
```
NAME                PC111
EXPNO                   2
PROCNO                  1
Date_            20100322
Time                23.36
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      2
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                    181
DW                 20.800 usec
DE                   6.50 usec
TE                  299.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.50 usec
PL1                 -2.00 dB
PL1W          58.52175522 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                15.00 dB
PL13                15.00 dB
PL2W          11.88122272 W
PL12W          0.37571725 W
PL13W          0.37571725 W
SFO2          400.1316005 MHz
SI                  32768
SF            100.6127772 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

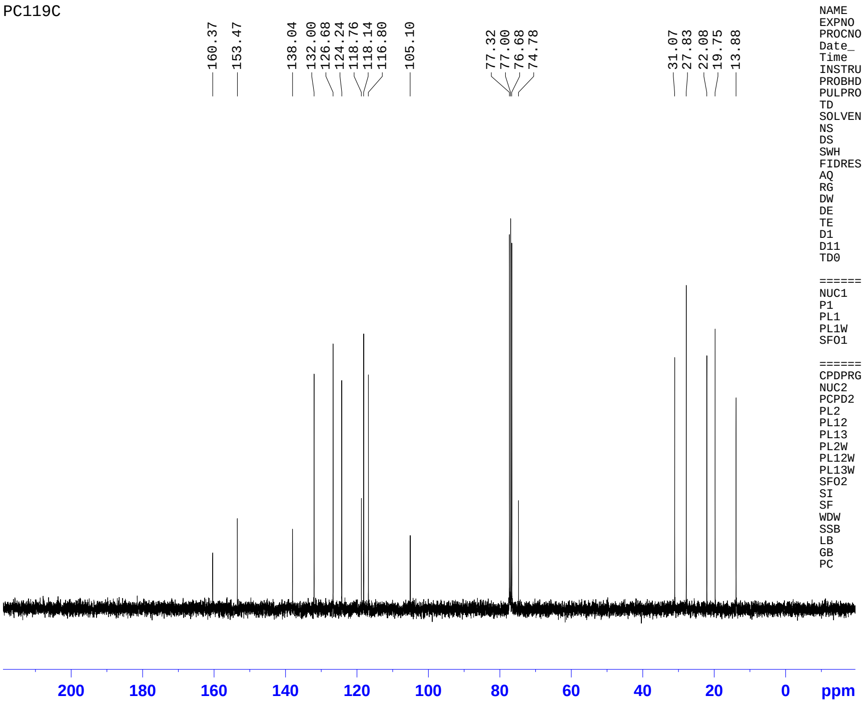
4-(Hept-1-yn-1-yl)-2*H*-chromen-2-one (Table 5.2)





```
NAME             PC119
EXPNO                1
PROCNO               1
Date_         20100324
Time             17.21
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG           zg30
TD               32768
SOLVENT          CDCl3
NS                  16
DS                   2
SWH           4006.410 Hz
FIDRES        0.122266 Hz
AQ           4.0894966 sec
RG                40.3
DW             124.800 usec
DE               6.50 usec
TE               297.2 K
D1          1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                1H
P1               14.70 usec
PL1               0.00 dB
PL1W       11.88122272 W
SFO1       400.1318007 MHz
SI               32768
SF         400.1300000 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.00
```

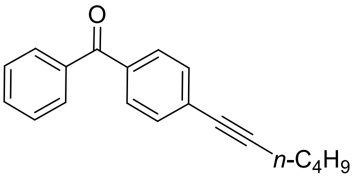


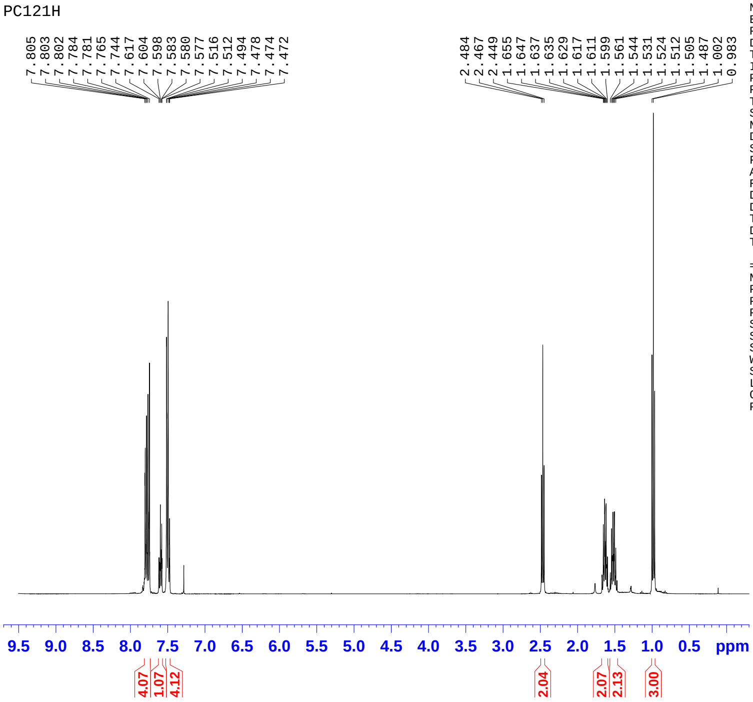
```
NAME             PC119
EXPNO                2
PROCNO               1
Date_         20100324
Time             17.25
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                  32
DS                   2
SWH          24038.461 Hz
FIDRES        0.366798 Hz
AQ           1.3631988 sec
RG                 203
DW              20.800 usec
DE               6.50 usec
TE               298.2 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1                9.50 usec
PL1              -2.00 dB
PL1W       58.52175522 W
SFO1       100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2            80.00 usec
PL2               0.00 dB
PL12             15.00 dB
PL13             15.00 dB
PL2W       11.88122272 W
PL12W       0.37571725 W
PL13W       0.37571725 W
SFO2       400.1316005 MHz
SI               32768
SF         100.6127751 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```

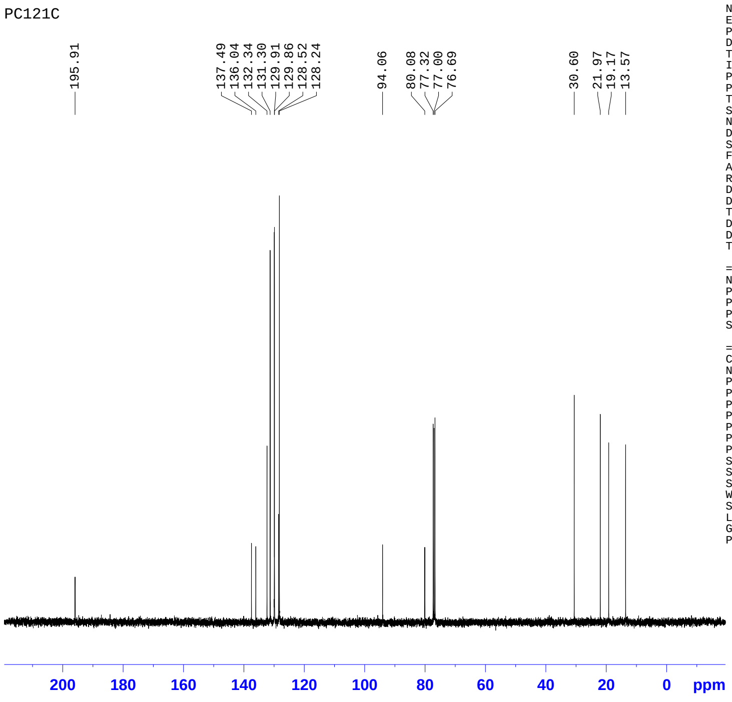
(4-(Hex-1-ynyl)phenyl)(phenyl)methanone (Table 5.2)





```
NAME                PC121
EXPNO                   1
PROCNO                  1
Date_            20100326
Time                18.14
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              4006.410 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                   22.6
DW                124.800 usec
DE                   6.50 usec
TE                  296.3 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.70 usec
PL1                  0.00 dB
PL1W          11.88122272 W
SFO1          400.1318007 MHz
SI                  32768
SF            400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

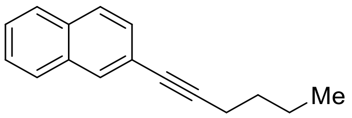


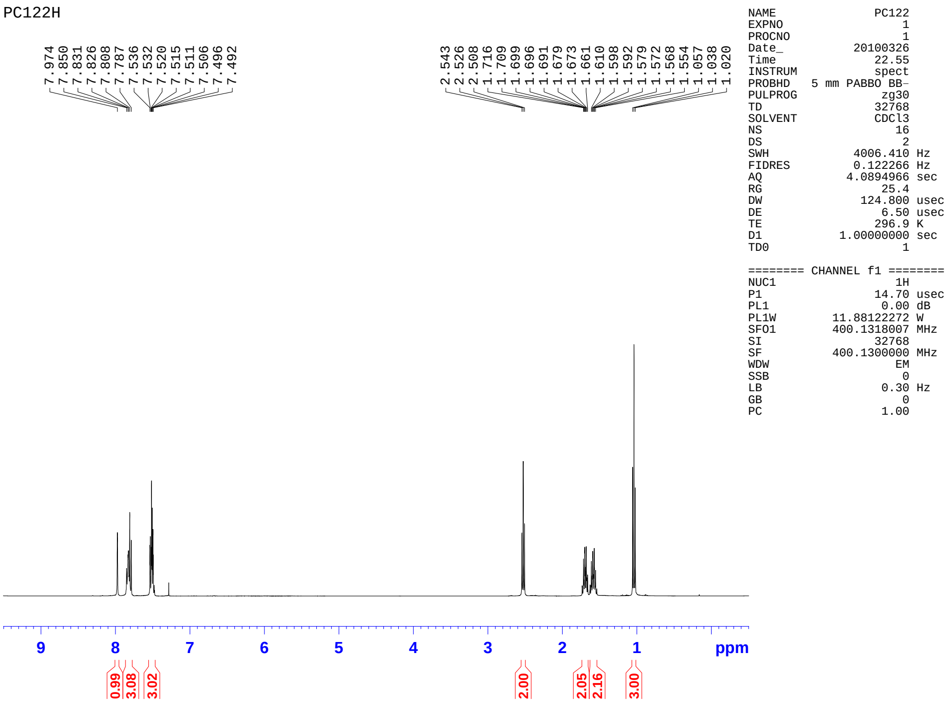
```
NAME                PC121
EXPNO                   2
PROCNO                  1
Date_            20100326
Time                18.16
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      2
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                    203
DW                 20.800 usec
DE                   6.50 usec
TE                  297.4 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

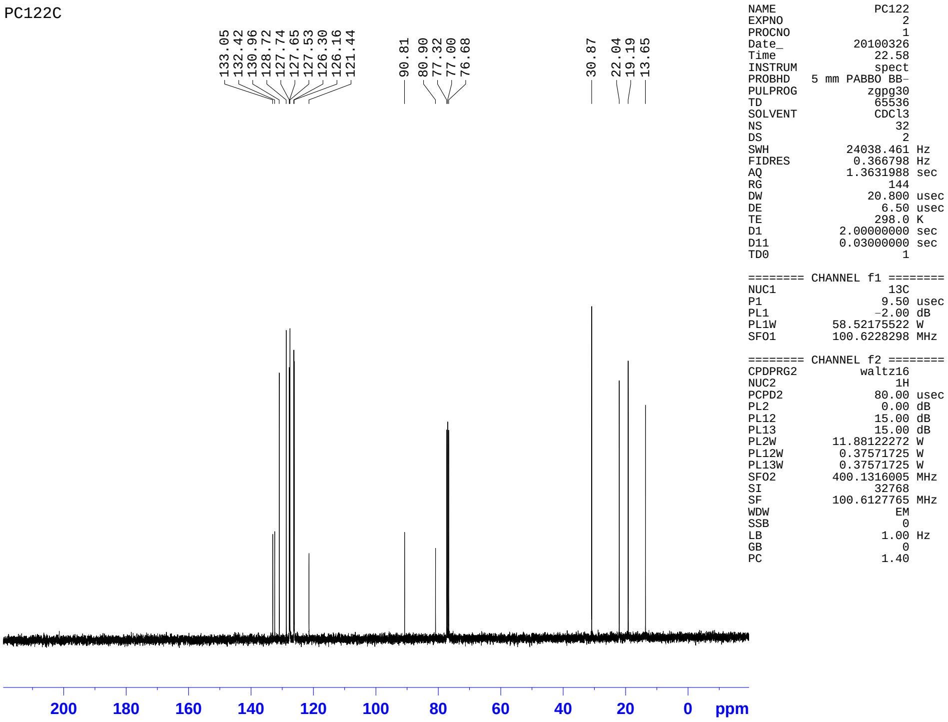
======== CHANNEL f1 ========
NUC1                  13C
P1                   9.50 usec
PL1                 -2.00 dB
PL1W          58.52175522 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                15.00 dB
PL13                15.00 dB
PL2W          11.88122272 W
PL12W          0.37571725 W
PL13W          0.37571725 W
SFO2          400.1316005 MHz
SI                  32768
SF            100.6127766 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

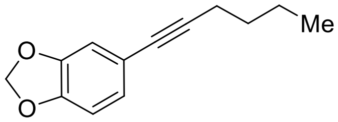
2-(Hex-1-ynyl)naphthalene (Table 5.3)

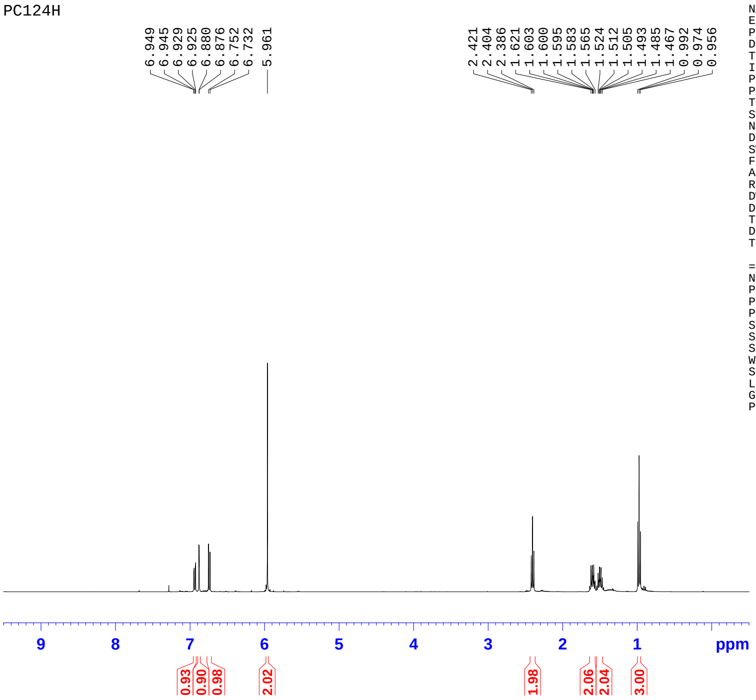






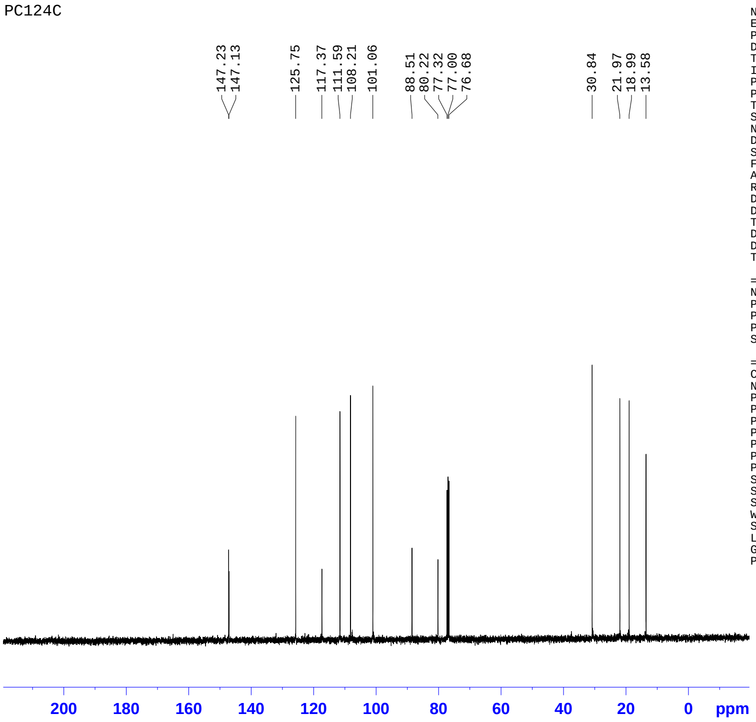
4-(1-Hexyn-1-yl)-1,2-(methylenedioxy)benzene (Table 5.3)





```
NAME              PC124
EXPNO                 1
PROCNO                1
Date_          20100327
Time              18.45
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            4006.410 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                 25.4
DW              124.800 usec
DE                 6.50 usec
TE                295.9 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.70 usec
PL1                0.00 dB
PL1W        11.88122272 W
SFO1        400.1318007 MHz
SI                32768
SF          400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

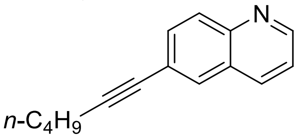


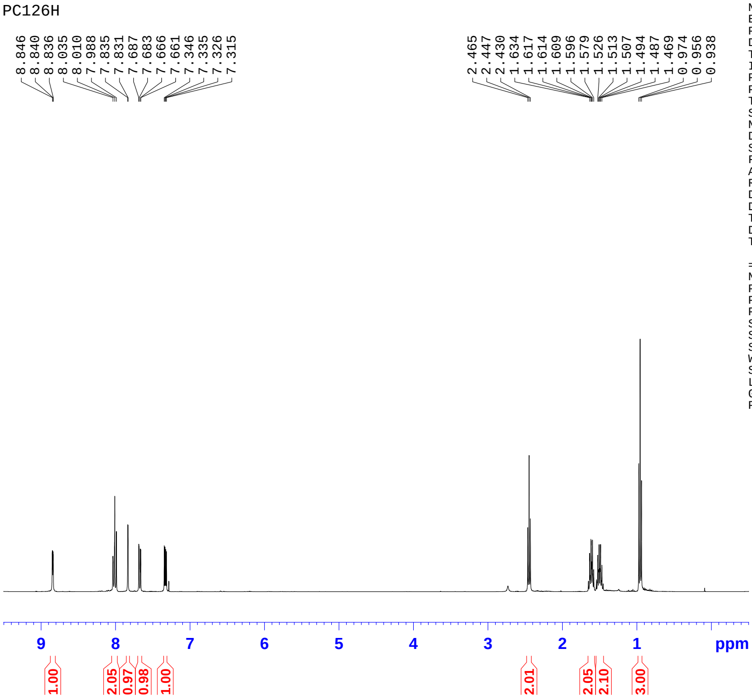
```
NAME              PC124
EXPNO                 2
PROCNO                1
Date_          20100327
Time              18.53
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                  144
DW               20.800 usec
DE                 6.50 usec
TE                297.1 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.50 usec
PL1               -2.00 dB
PL1W        58.52175522 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL13              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
PL13W        0.37571725 W
SFO2        400.1316005 MHz
SI                32768
SF          100.6127751 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

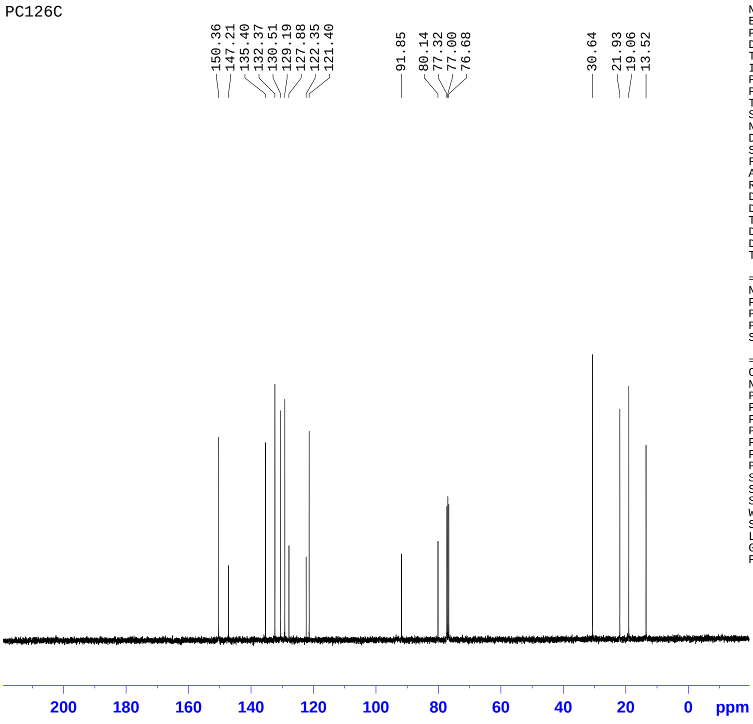
6-(Hex-1-ynyl)quinoline (Table 5.3)





```
NAME                PC126
EXPNO                   3
PROCNO                  1
Date_            20100328
Time                21.11
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              4006.410 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                   25.4
DW                124.800 usec
DE                   6.50 usec
TE                  295.3 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.70 usec
PL1                  0.00 dB
PL1W          11.88122272 W
SFO1          400.1318007 MHz
SI                  32768
SF            400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

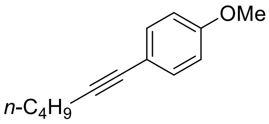


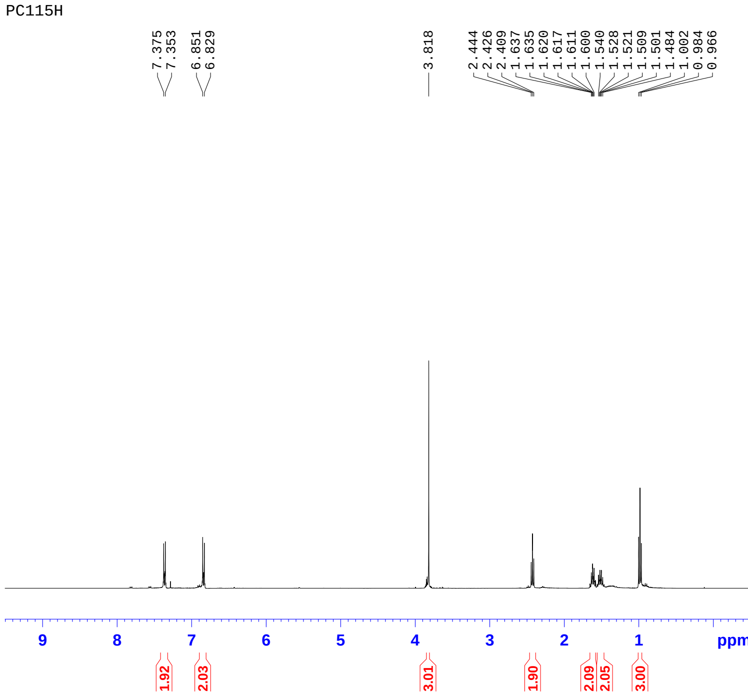
```
NAME                PC126
EXPNO                   4
PROCNO                  1
Date_            20100328
Time                21.15
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      2
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                    128
DW                 20.800 usec
DE                   6.50 usec
TE                  296.5 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.50 usec
PL1                 -2.00 dB
PL1W          58.52175522 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                15.00 dB
PL13                15.00 dB
PL2W          11.88122272 W
PL12W          0.37571725 W
PL13W          0.37571725 W
SFO2          400.1316005 MHz
SI                  32768
SF            100.6127803 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

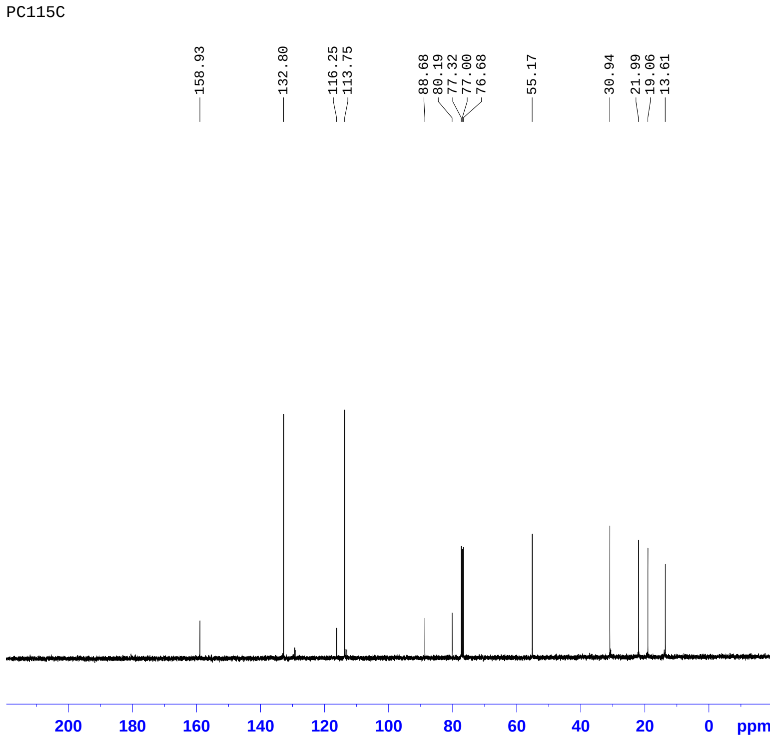
1-(Hex-1-ynyl)-4-methoxybenzene (Table 5.3)





```
NAME              PC115
EXPNO                 1
PROCNO                1
Date_          20100327
Time              18.57
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            4006.410 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                 25.4
DW              124.800 usec
DE                 6.50 usec
TE                296.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.70 usec
PL1                0.00 dB
PL1W        11.88122272 W
SFO1        400.1318007 MHz
SI                32768
SF          400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

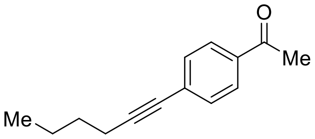


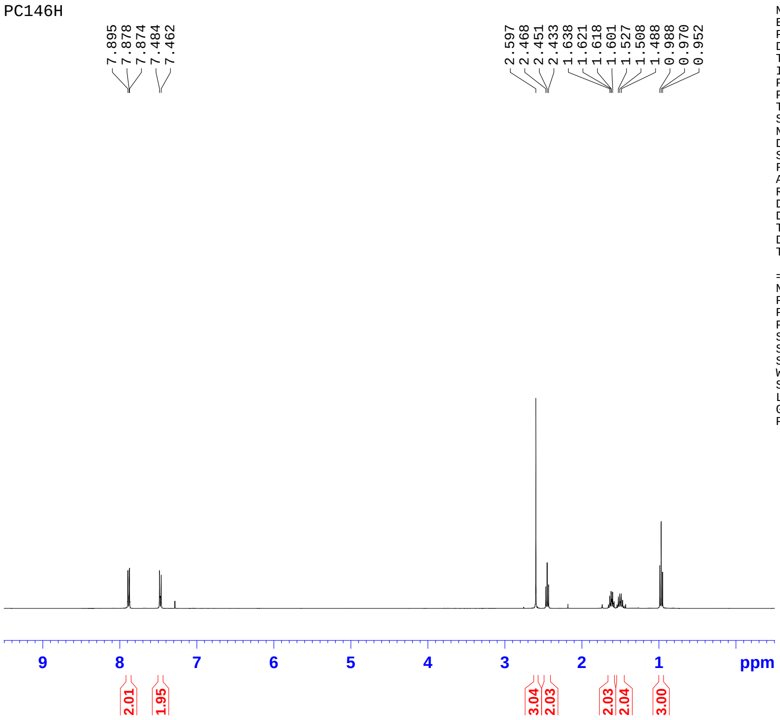
```
NAME              PC115
EXPNO                 2
PROCNO                1
Date_          20100327
Time              19.00
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                  128
DW               20.800 usec
DE                 6.50 usec
TE                297.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.50 usec
PL1               -2.00 dB
PL1W        58.52175522 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL13              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
PL13W        0.37571725 W
SFO2        400.1316005 MHz
SI                32768
SF          100.6127746 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

1-(4-(Hex-1-ynyl)phenyl)ethanone (Table 5.3)

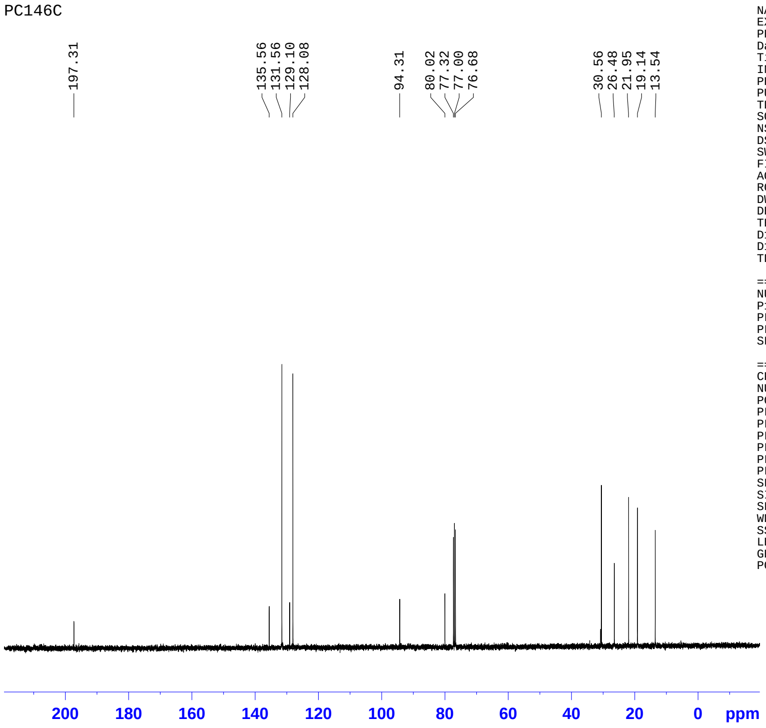




NAME	PC146
EXPNO	4
PROCNO	1
Date_	20100408
Time	23.39
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	4006.410 Hz
FIDRES	0.122266 Hz
AQ	4.0894966 sec
RG	40.3
DW	124.800 usec
DE	6.50 usec
TE	293.8 K
D1	1.00000000 sec
TD0	1

======== CHANNEL f1 ========

NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1318007 MHz
SI	32768
SF	400.1300000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



NAME	PC146
EXPNO	2
PROCNO	1
Date_	20100402
Time	19.13
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	32
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	161
DW	20.800 usec
DE	6.50 usec
TE	295.3 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1

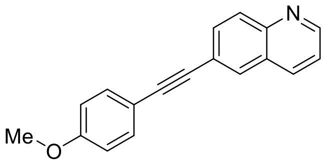
======== CHANNEL f1 ========

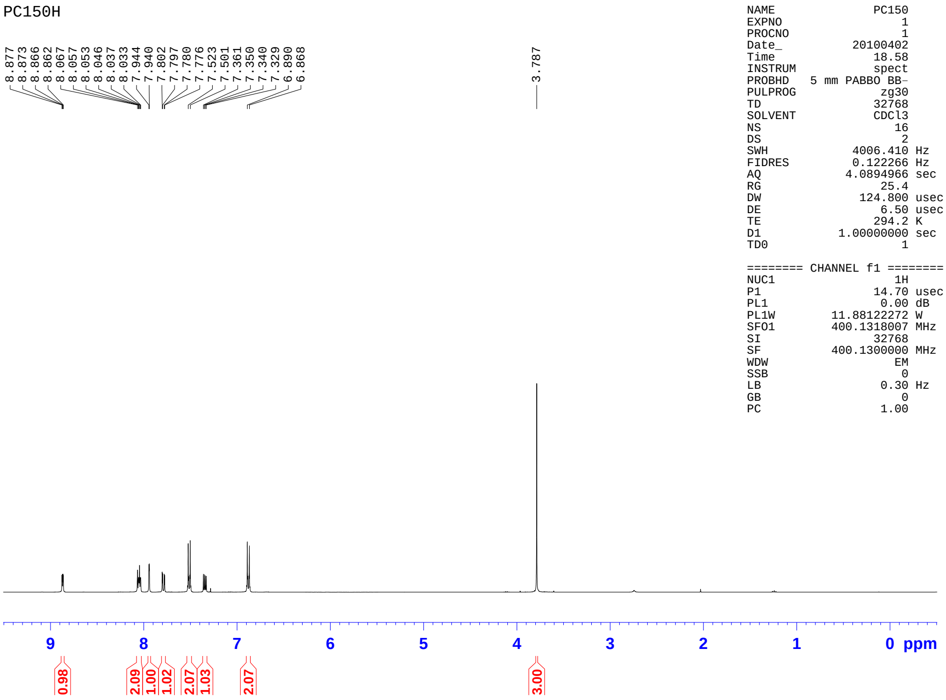
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz

======== CHANNEL f2 ========

CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	15.00 dB
PL2W	11.88122272 W
PL12W	0.37571725 W
PL13W	0.37571725 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127758 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

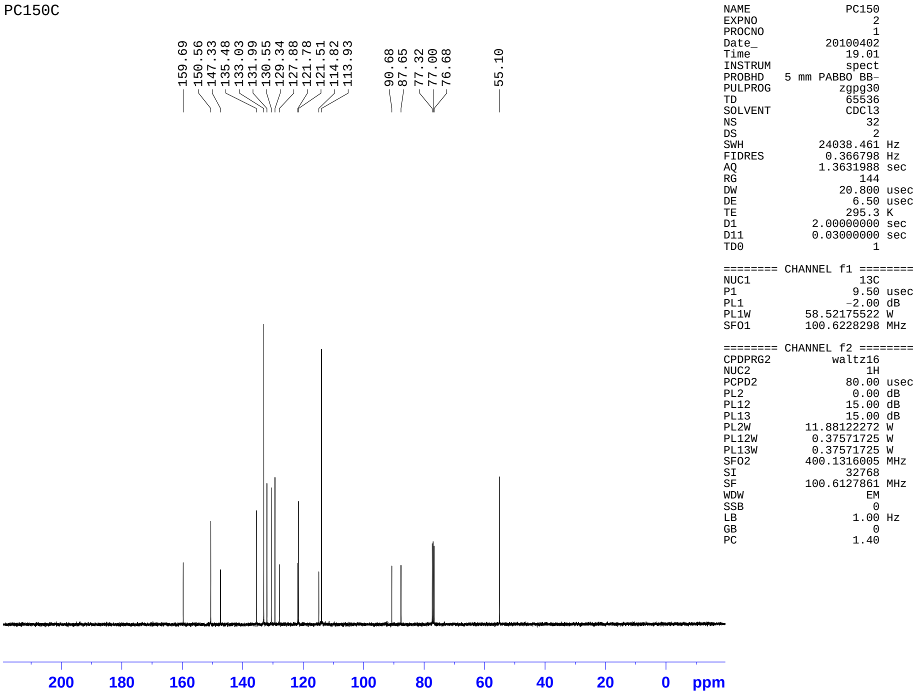
6-((4-Methoxyphenyl)ethynyl)quinoline (Table 5.3)





```
NAME              PC150
EXPNO                 1
PROCNO                1
Date_          20100402
Time              18.58
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            4006.410 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                 25.4
DW              124.800 usec
DE                 6.50 usec
TE                294.2 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.70 usec
PL1                0.00 dB
PL1W        11.88122272 W
SFO1        400.1318007 MHz
SI                32768
SF          400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

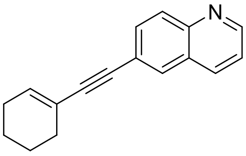


```
NAME              PC150
EXPNO                 2
PROCNO                1
Date_          20100402
Time              19.01
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                  144
DW               20.800 usec
DE                 6.50 usec
TE                295.3 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

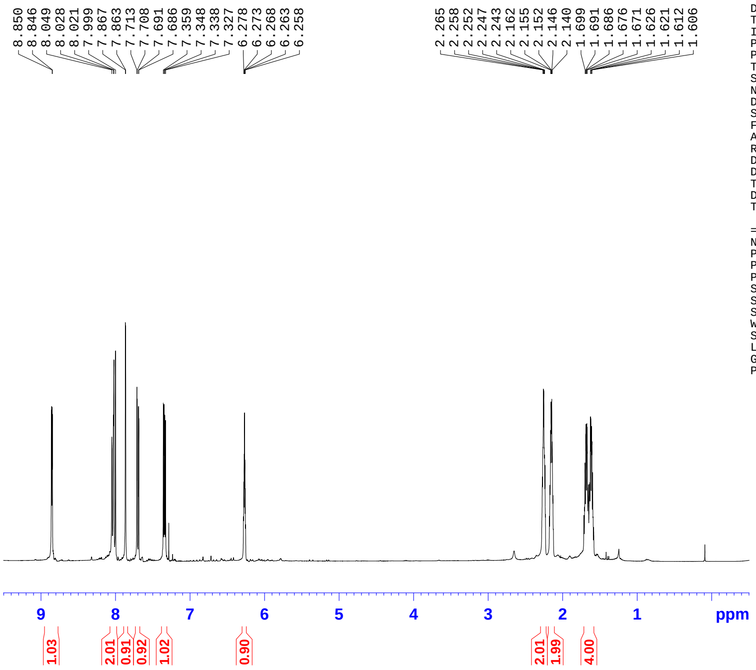
======== CHANNEL f1 ========
NUC1                13C
P1                 9.50 usec
PL1               -2.00 dB
PL1W        58.52175522 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL13              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
PL13W        0.37571725 W
SFO2        400.1316005 MHz
SI                32768
SF          100.6127861 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

6-(Cyclohex-1-enylethynyl)quinoline (Table 5.3)



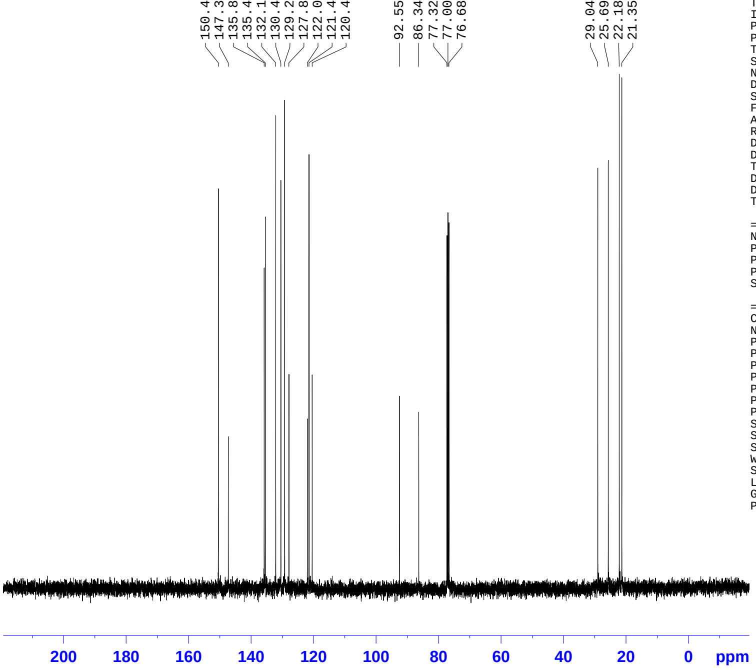
PC151H



```
NAME               PC151
EXPNO                  1
PROCNO                 1
Date_           20100331
Time               18.24
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  22.6
DW               124.800 usec
DE                  6.50 usec
TE                 294.9 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

PC151C

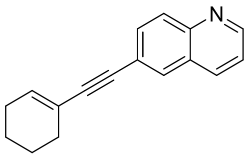


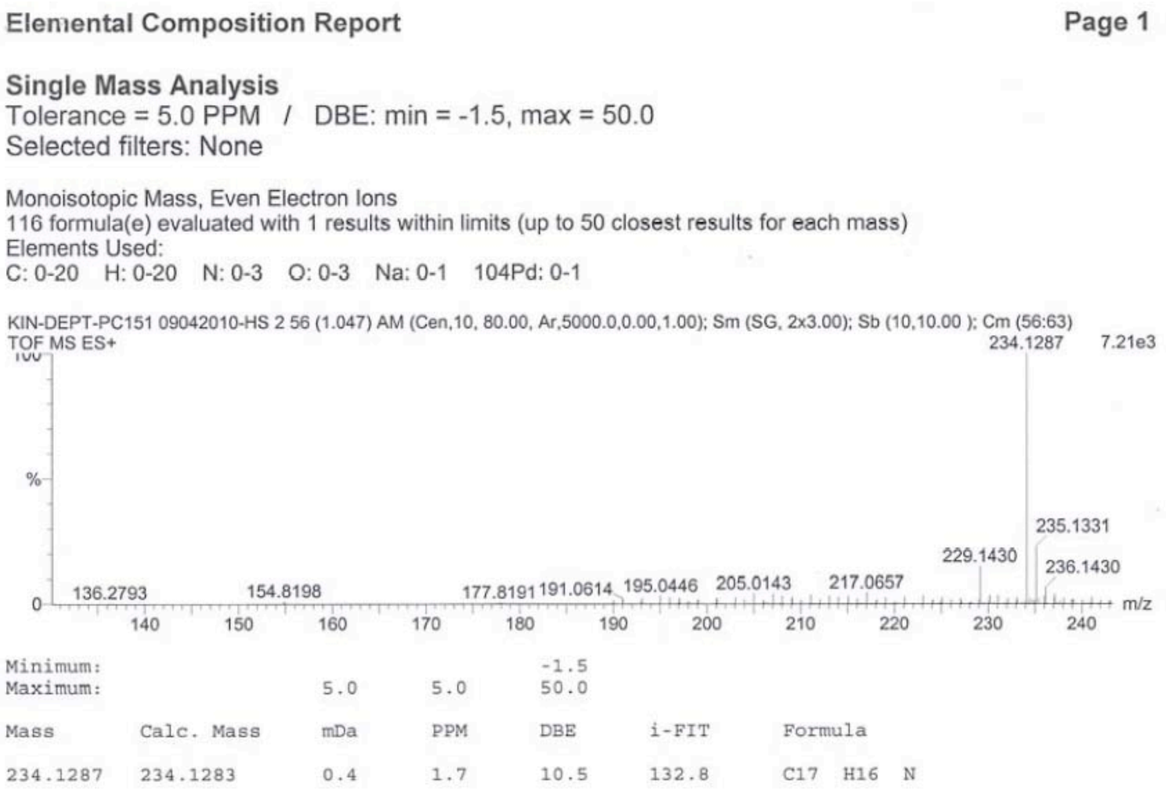
```
NAME               PC151
EXPNO                  2
PROCNO                 1
Date_           20100331
Time               18.27
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   114
DW                20.800 usec
DE                  6.50 usec
TE                 296.1 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127817 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

6-(Cyclohex-1-enylethynyl)quinoline (Table 5.3)





Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

Monoisotopic Mass, Even Electron Ions
116 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-20 H: 0-20 N: 0-3 O: 0-3 Na: 0-1 104Pd: 0-1

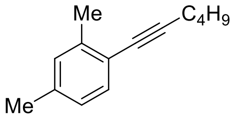
KIN-DEPT-PC151 09042010-HS 2 56 (1.047) AM (Cen,10, 80.00, Ar,5000.0,0.00,1.00); Sm (SG, 2x3.00); Sb (10,10.00); Cm (56:63)
TOF MS ES+

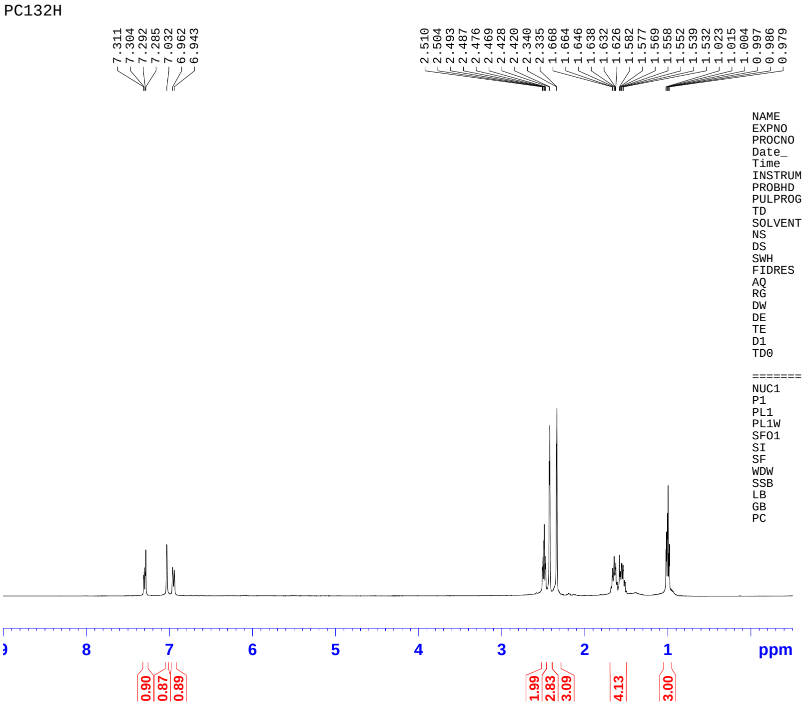
```
Minimum:                                    -1.5
Maximum:                  5.0       5.0     50.0

Mass       Calc. Mass     mDa       PPM     DBE       i-FIT       Formula

234.1287   234.1283       0.4       1.7     10.5      132.8       C17  H16  N
```

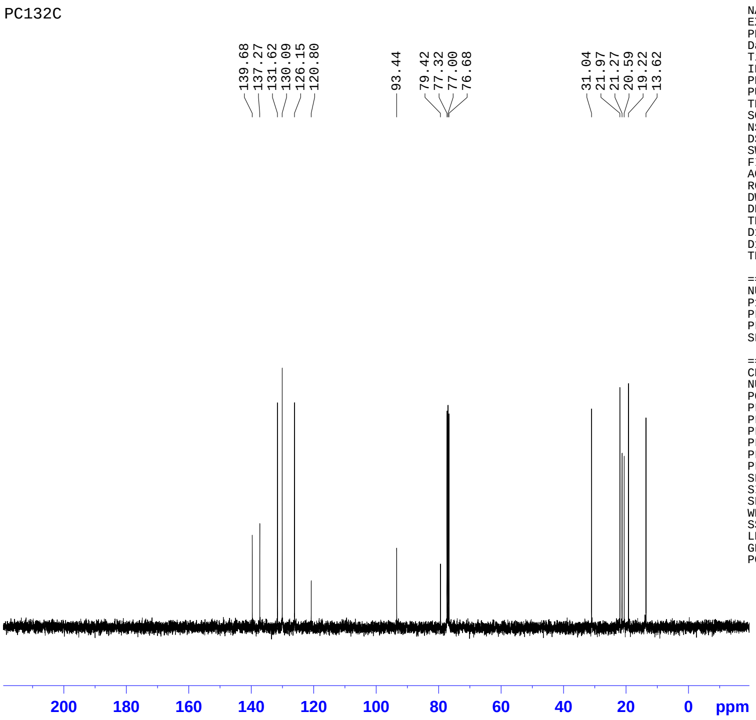
1-(Hex-1-ynyl)-2,4-dimethylbenzene (Table 5.3)





```
NAME                PC132
EXPNO                   1
PROCNO                  1
Date_            20100328
Time                21.20
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              4006.410 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                   25.4
DW                124.800 usec
DE                   6.50 usec
TE                  295.4 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.70 usec
PL1                  0.00 dB
PL1W          11.88122272 W
SFO1          400.1318007 MHz
SI                  32768
SF            400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

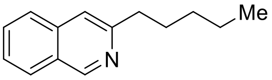


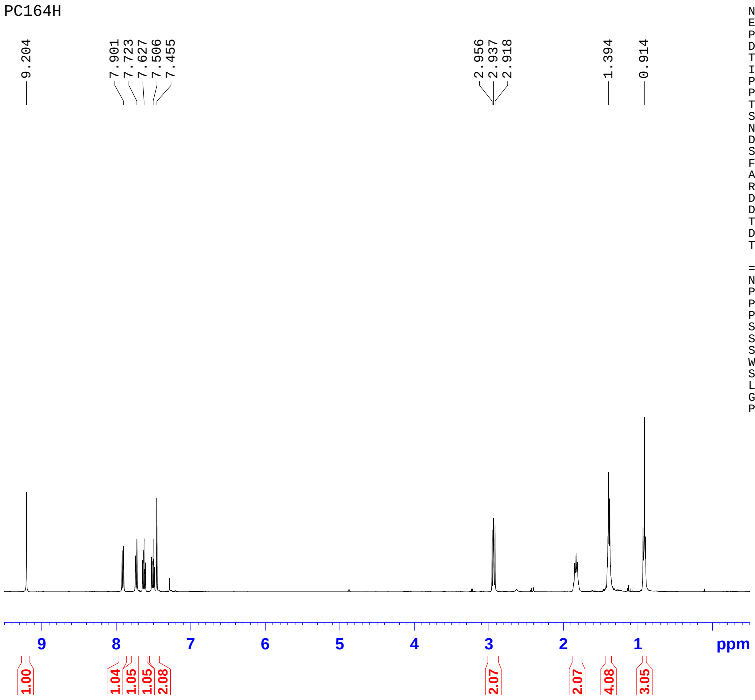
```
NAME                PC132
EXPNO                   2
PROCNO                  1
Date_            20100328
Time                21.23
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      2
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                    114
DW                 20.800 usec
DE                   6.50 usec
TE                  296.7 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.50 usec
PL1                 -2.00 dB
PL1W          58.52175522 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                15.00 dB
PL13                15.00 dB
PL2W          11.88122272 W
PL12W          0.37571725 W
PL13W          0.37571725 W
SFO2          400.1316005 MHz
SI                  32768
SF            100.6127736 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

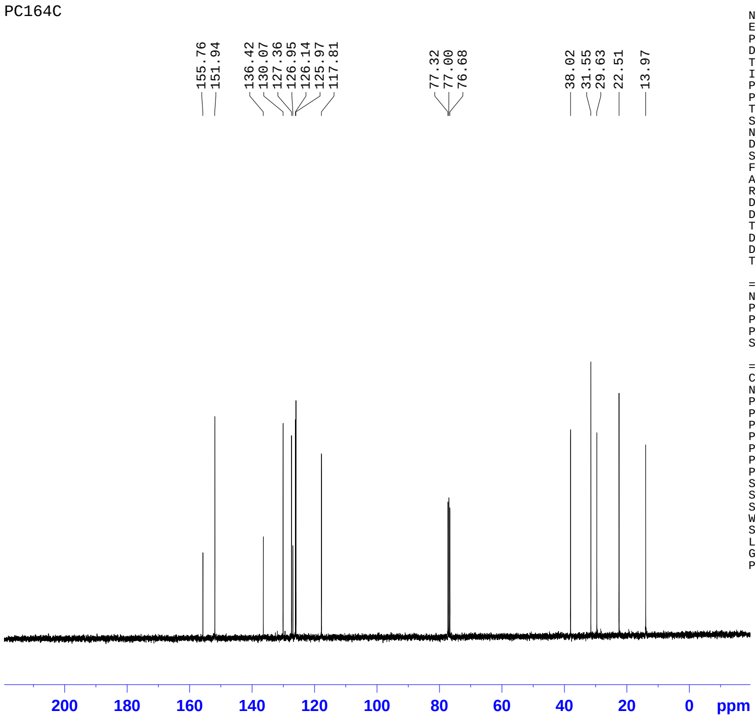
3-Pentylisoquinoline (Scheme 5.2)





```
NAME               PC164
EXPNO                  2
PROCNO                 1
Date_           20100408
Time               23.34
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  25.4
DW               124.800 usec
DE                  6.50 usec
TE                 293.9 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

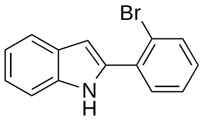


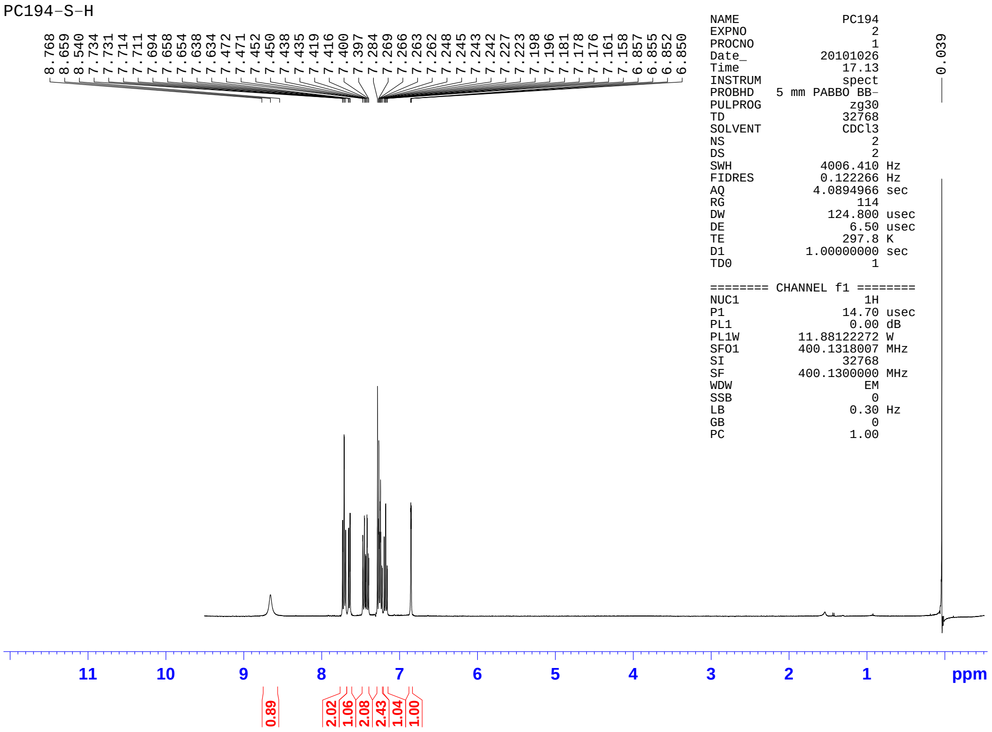
```
NAME              PC164B
EXPNO                  2
PROCNO                 1
Date_           20100409
Time               18.51
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   144
DW                20.800 usec
DE                  6.50 usec
TE                 295.9 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127787 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

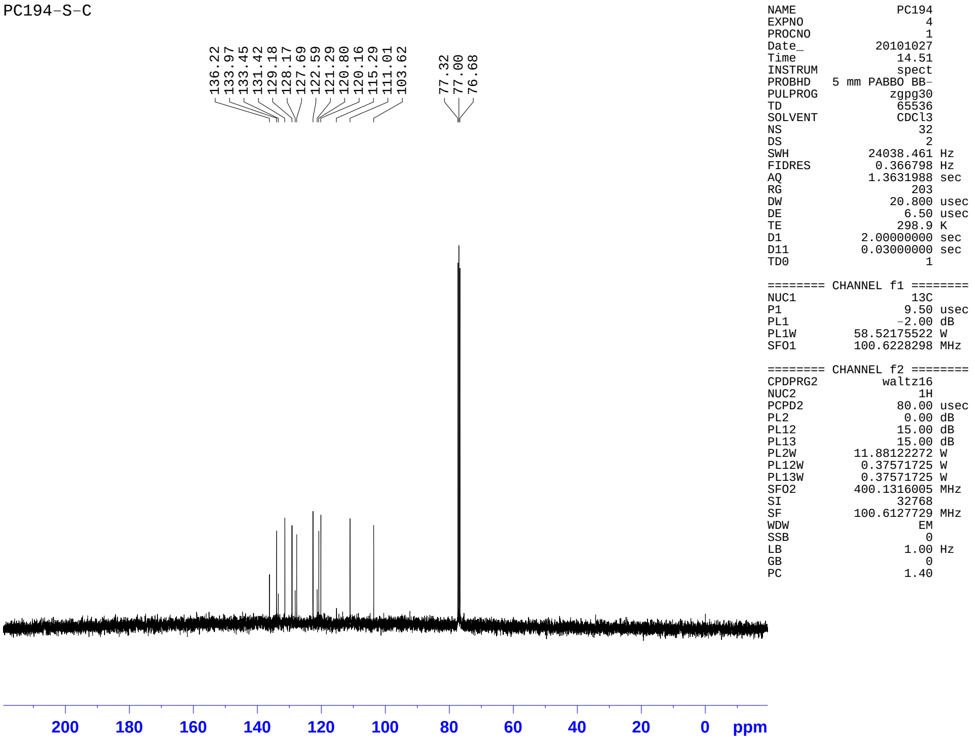
2-(2'-Bromophenyl)-1*H*-indole (Scheme 6.2)





```
NAME               PC194
EXPNO                  2
PROCNO                 1
Date_           20101026
Time               17.13
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                     2
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                   114
DW               124.800 usec
DE                  6.50 usec
TE                 297.8 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

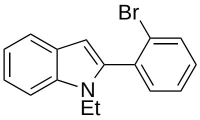


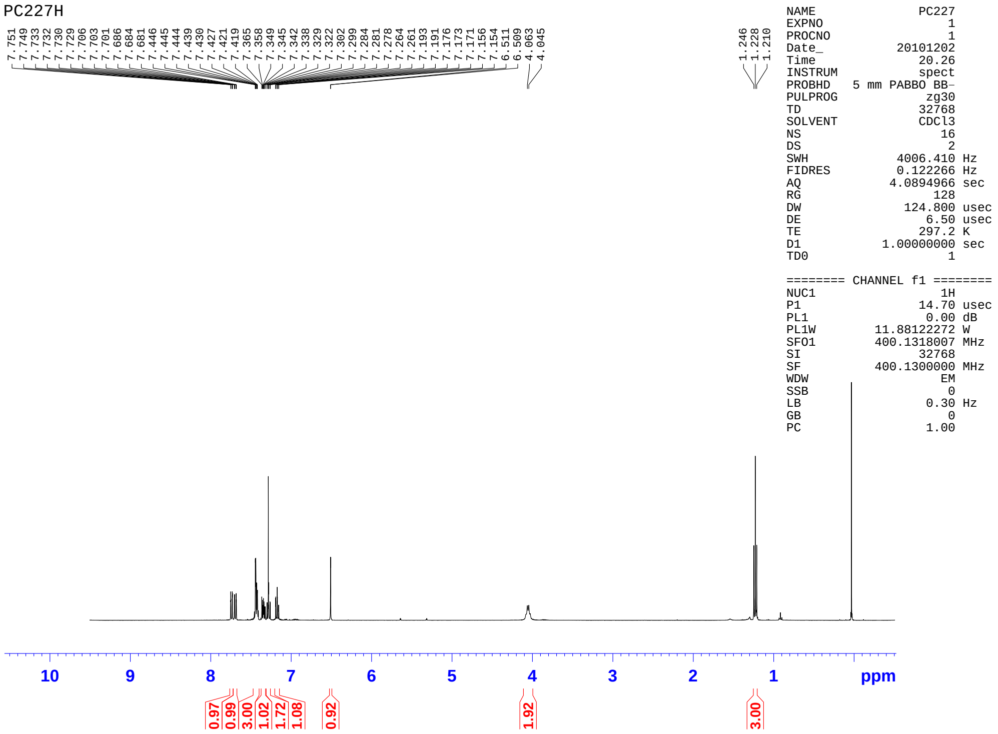
```
NAME               PC194
EXPNO                  4
PROCNO                 1
Date_           20101027
Time               14.51
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   203
DW                20.800 usec
DE                  6.50 usec
TE                 298.9 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

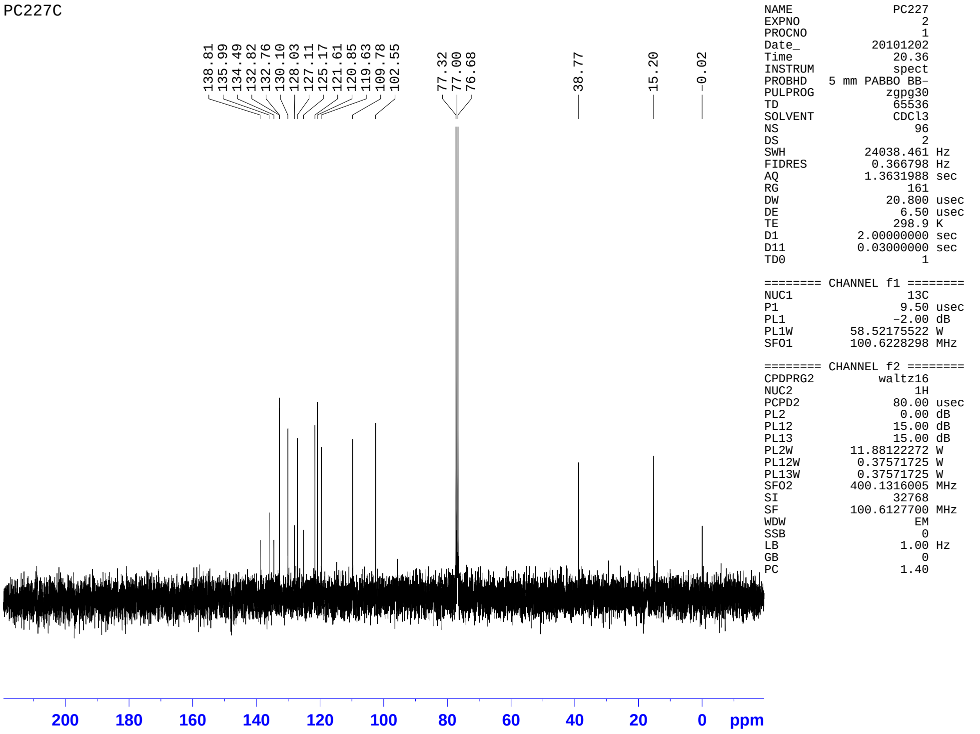
======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127729 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

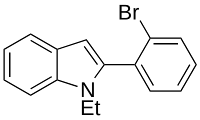
2-(2-Bromophenyl)-1-ethyl-1*H*-indole (Table 6.1, entry 1)

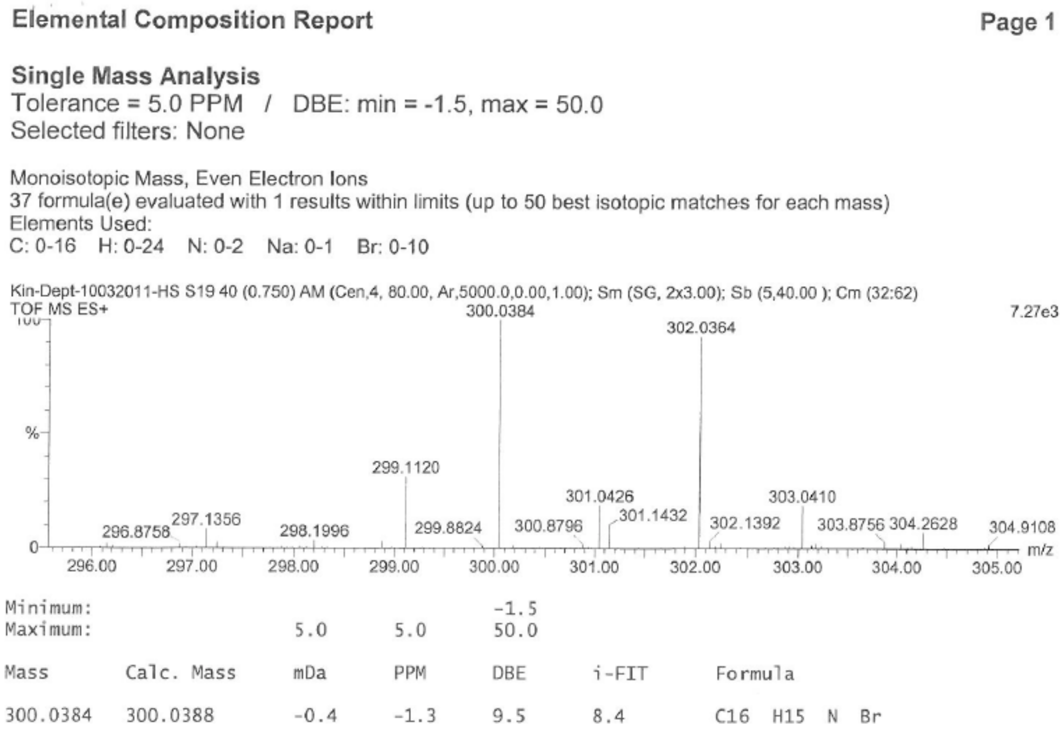






2-(2-Bromophenyl)-1-ethyl-1*H*-indole (Table 6.1, entry 1)





Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

Monoisotopic Mass, Even Electron Ions
37 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-16 H: 0-24 N: 0-2 Na: 0-1 Br: 0-10

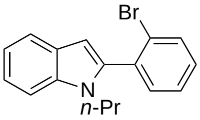
Kin-Dept-10032011-HS S19 40 (0.750) AM (Cen,4, 80.00, Ar,5000.0,0.00,1.00); Sm (SG, 2x3.00); Sb (5,40.00); Cm (32:62)
TOF MS ES+

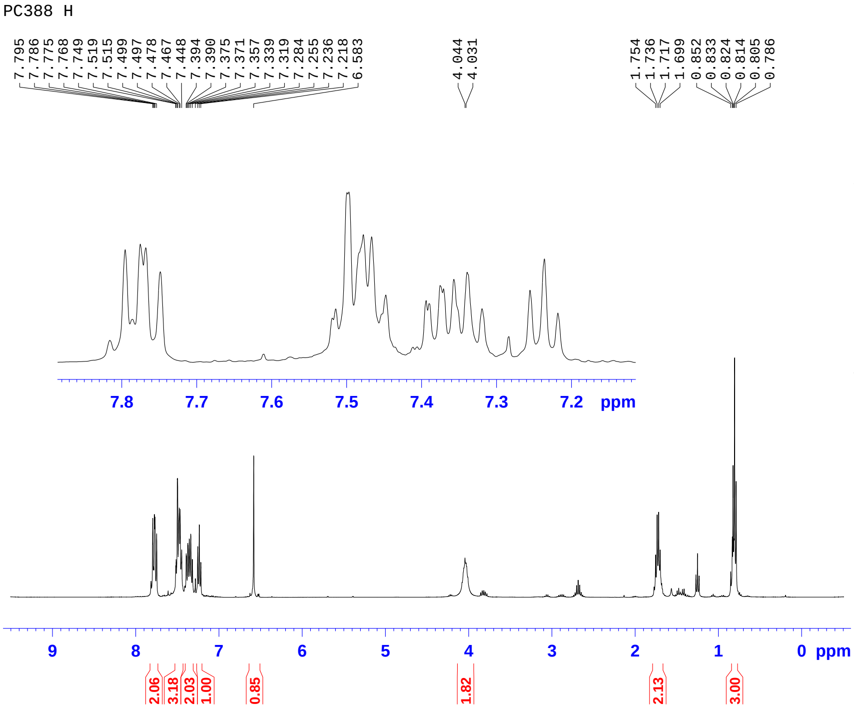
```
Minimum:                                          -1.5
Maximum:                   5.0        5.0         50.0

Mass        Calc. Mass     mDa        PPM         DBE        i-FIT       Formula

300.0384    300.0388       -0.4       -1.3        9.5        8.4         C16  H15  N  Br
```

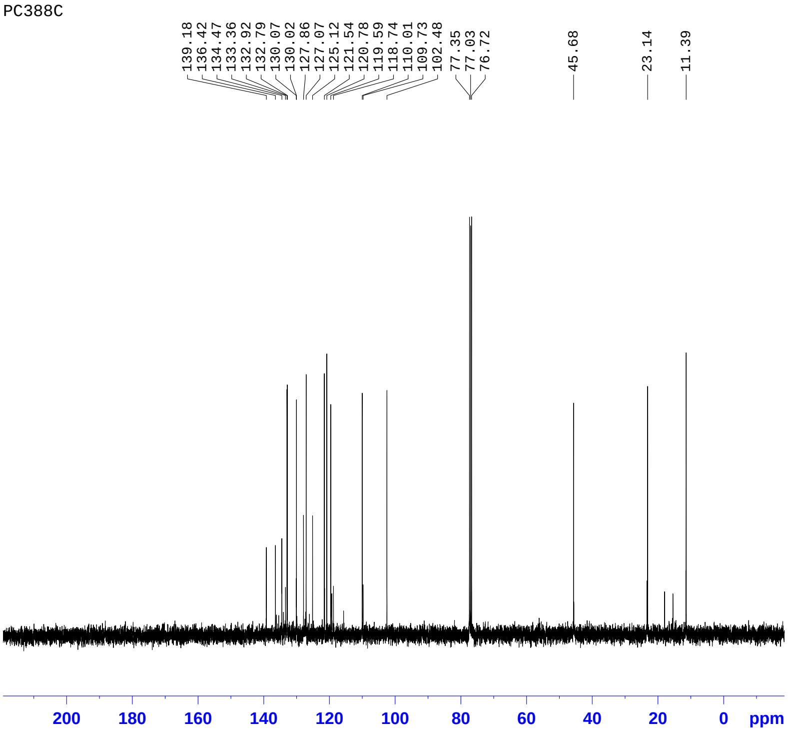
2-(2-Bromophenyl)-1-propyl-1*H*-indole (Table 6.1, entry 2)





```
NAME                PC388
EXPNO                   6
PROCNO                  1
Date_            20120211
Time                19.03
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              4006.410 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                     32
DW                124.800 usec
DE                   6.50 usec
TE                  296.1 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.70 usec
PL1                  0.00 dB
PL1W          11.88122272 W
SFO1          400.1318007 MHz
SI                  32768
SF            400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

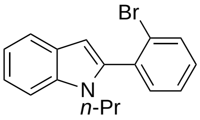


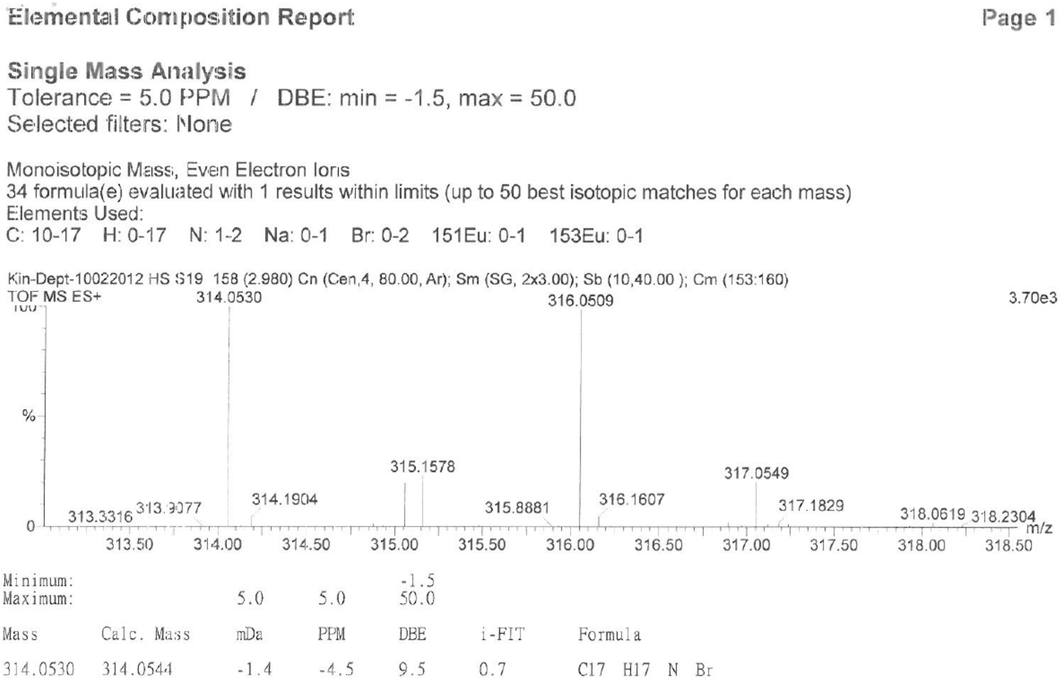
```
NAME                PC388
EXPNO                   7
PROCNO                  1
Date_            20120211
Time                19.05
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     19
DS                      2
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                    181
DW                 20.800 usec
DE                   6.50 usec
TE                  296.8 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.50 usec
PL1                 -2.00 dB
PL1W          58.52175522 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                15.00 dB
PL13                15.00 dB
PL2W          11.88122272 W
PL12W          0.37571725 W
PL13W          0.37571725 W
SFO2          400.1316005 MHz
SI                  32768
SF            100.6127794 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

2-(2-Bromophenyl)-1-propyl-1*H*-indole (Table 6.1, entry 2)





Elemental Composition Report Page 1

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

34 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 10-17 H: 0-17 N: 1-2 Na: 0-1 Br: 0-2 151Eu: 0-1 153Eu: 0-1

Kin-Dept-10022012 HS S19 158 (2.980) Cn (Cen,4, 80.00, Ar); Sm (SG, 2x3.00); Sb (10,40.00); Cm (153:160)

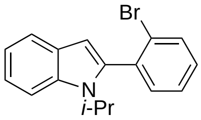
TOF MS ES+ 3.70e3

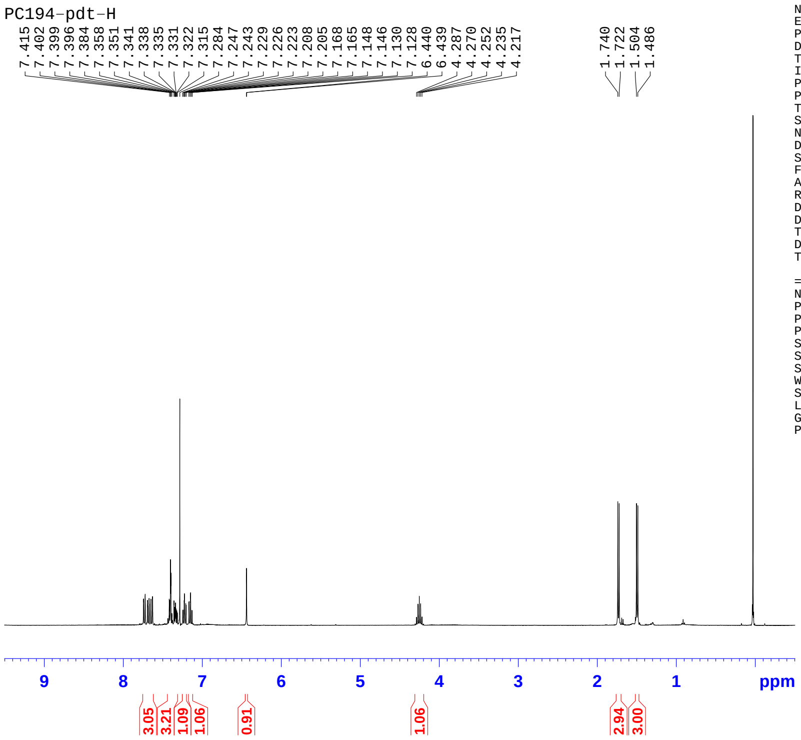
```
Minimum:                                   -1.5
Maximum:                  5.0      5.0     50.0

Mass       Calc. Mass     mDa      PPM     DBE      i-FIT     Formula

314.0530   314.0544       -1.4     -4.5    9.5      0.7       C17  H17  N  Br
```

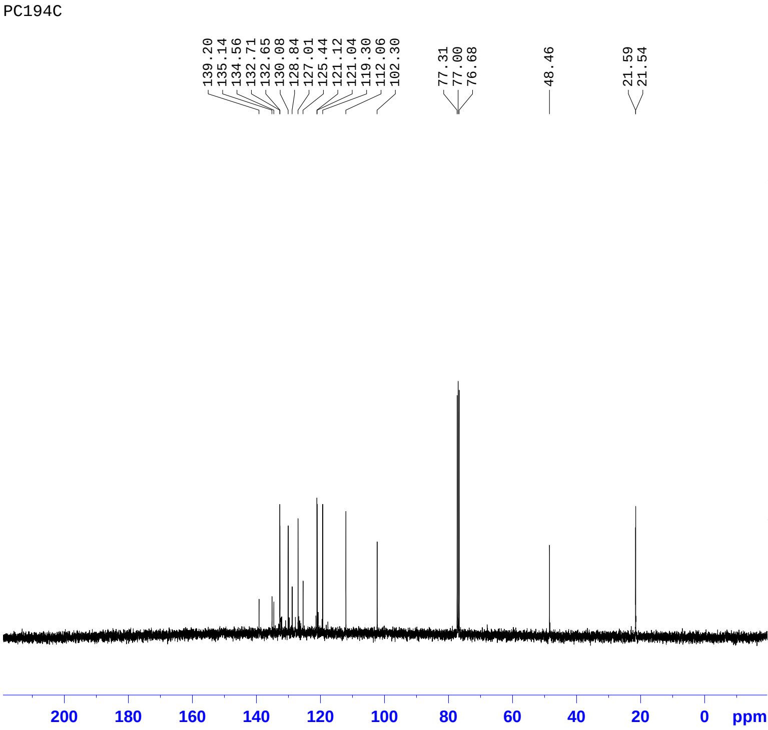
2-(2-Bromophenyl)-1-isopropyl-1*H*-indole (Table 6.1, entry 3)





```
NAME              PC194
EXPNO                 1
PROCNO                1
Date_          20101026
Time              17.09
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            4006.410 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                  203
DW              124.800 usec
DE                 6.50 usec
TE                297.8 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.70 usec
PL1                0.00 dB
PL1W        11.88122272 W
SFO1        400.1318007 MHz
SI                32768
SF          400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

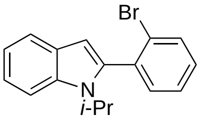


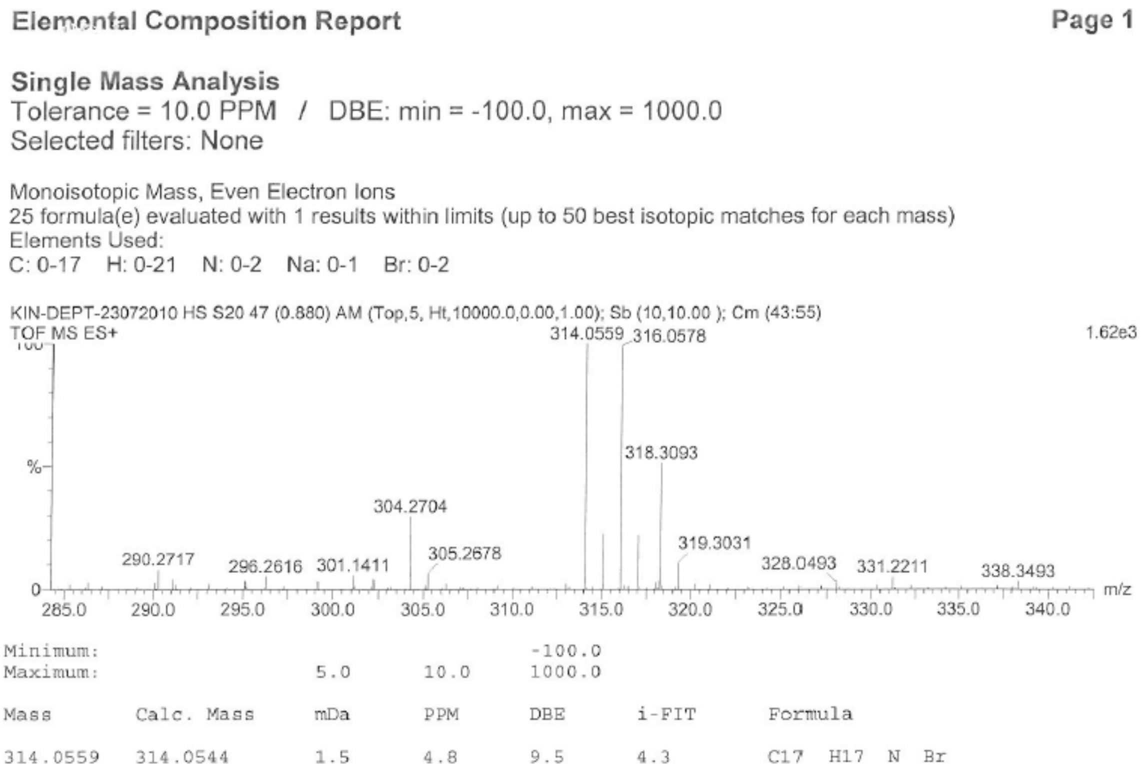
```
NAME              PC194
EXPNO                 3
PROCNO                1
Date_          20101027
Time              14.44
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                  203
DW               20.800 usec
DE                 6.50 usec
TE                298.9 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.50 usec
PL1               -2.00 dB
PL1W        58.52175522 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL13              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
PL13W        0.37571725 W
SFO2        400.1316005 MHz
SI                32768
SF          100.6127760 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

2-(2-Bromophenyl)-1-isopropyl-1*H*-indole (Table 6.1, entry 3)





Elemental Composition Report

Page 1

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -100.0, max = 1000.0
Selected filters: None

Monoisotopic Mass, Even Electron Ions
25 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-17 H: 0-21 N: 0-2 Na: 0-1 Br: 0-2

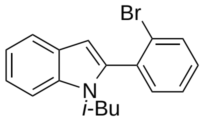
KIN-DEPT-23072010 HS S20 47 (0.880) AM (Top,5, Ht,10000.0,0.00,1.00); Sb (10,10.00); Cm (43:55)
TOF MS ES+

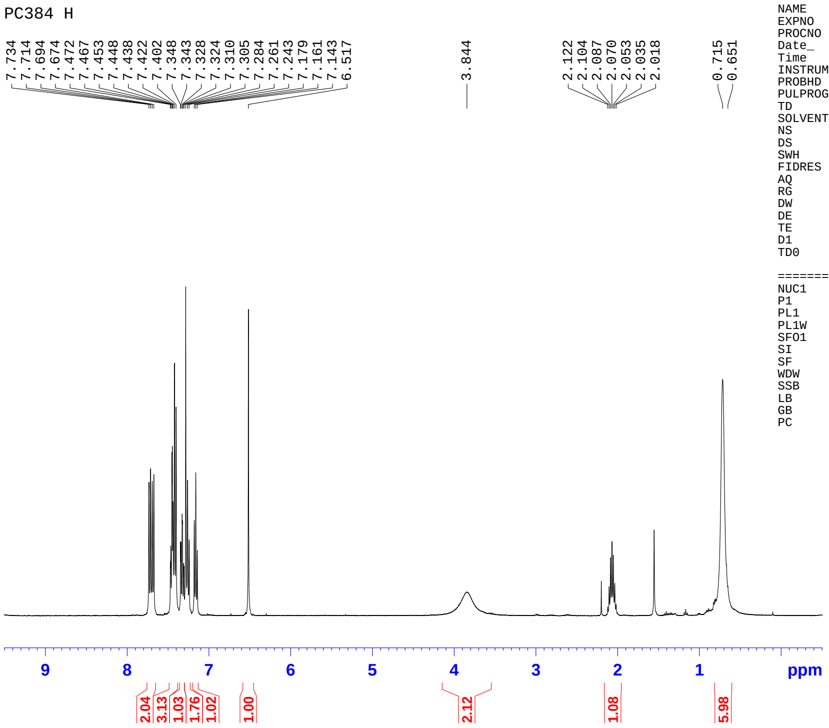
```
Minimum:                                     -100.0
Maximum:                  5.0       10.0     1000.0

Mass       Calc. Mass     mDa       PPM      DBE        i-FIT       Formula

314.0559   314.0544       1.5       4.8      9.5        4.3         C17  H17  N  Br
```

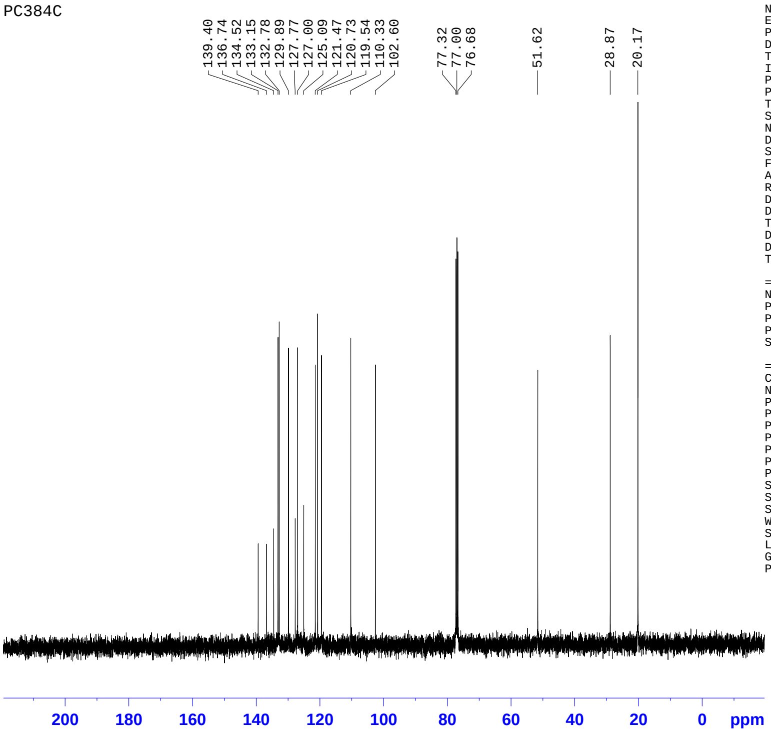
2-(2-Bromophenyl)-1-isobutyl-1*H*-indole (Table 6.1, entry 4)





```
NAME               PC384
EXPNO                  3
PROCNO                 1
Date_           20120201
Time               21.11
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                   203
DW               124.800 usec
DE                  6.50 usec
TE                 297.4 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

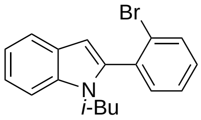


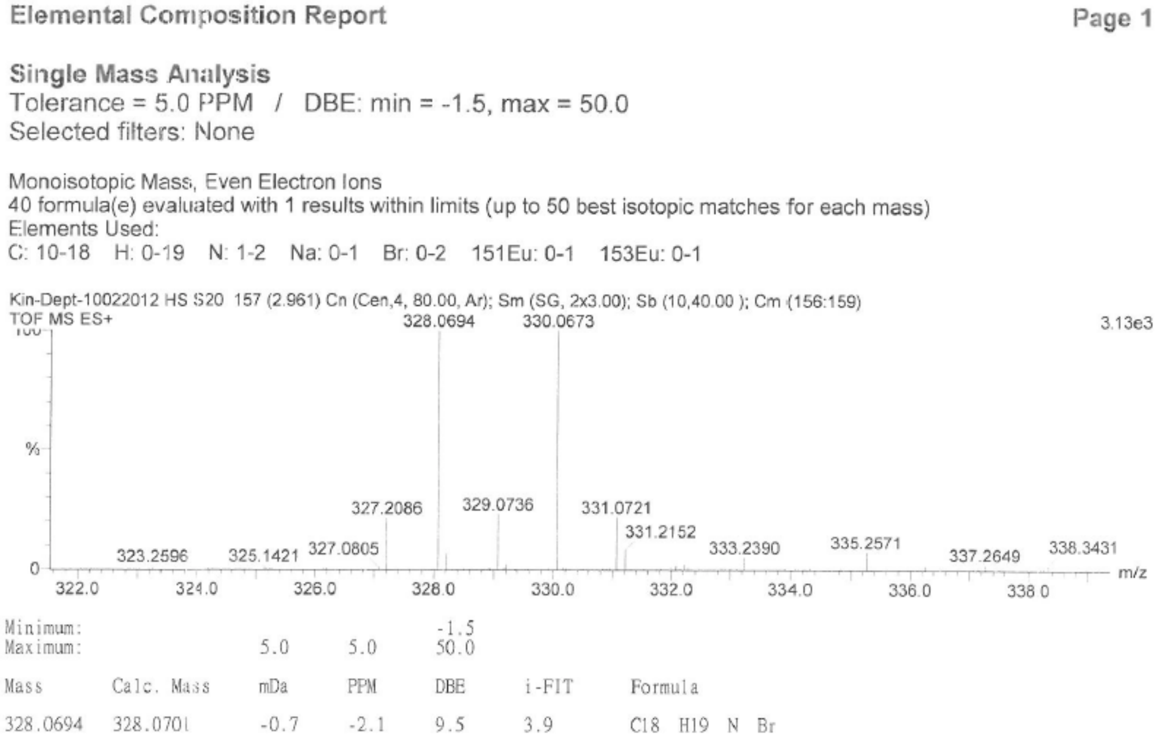
```
NAME               PC384
EXPNO                  5
PROCNO                 1
Date_           20120201
Time               21.57
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    37
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   181
DW                20.800 usec
DE                  6.50 usec
TE                 298.4 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127794 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

2-(2-Bromophenyl)-1-isobutyl-1*H*-indole (Table 6.1, entry 4)





Elemental Composition Report

Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

Monoisotopic Mass, Even Electron Ions
40 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 10-18 H: 0-19 N: 1-2 Na: 0-1 Br: 0-2 151Eu: 0-1 153Eu: 0-1

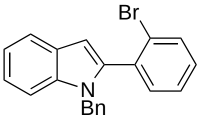
Kin-Dept-10022012 HS S20 157 (2.961) Cn (Cen,4, 80.00, Ar); Sm (SG, 2x3.00); Sb (10,40.00); Cm (156:159)
TOF MS ES+

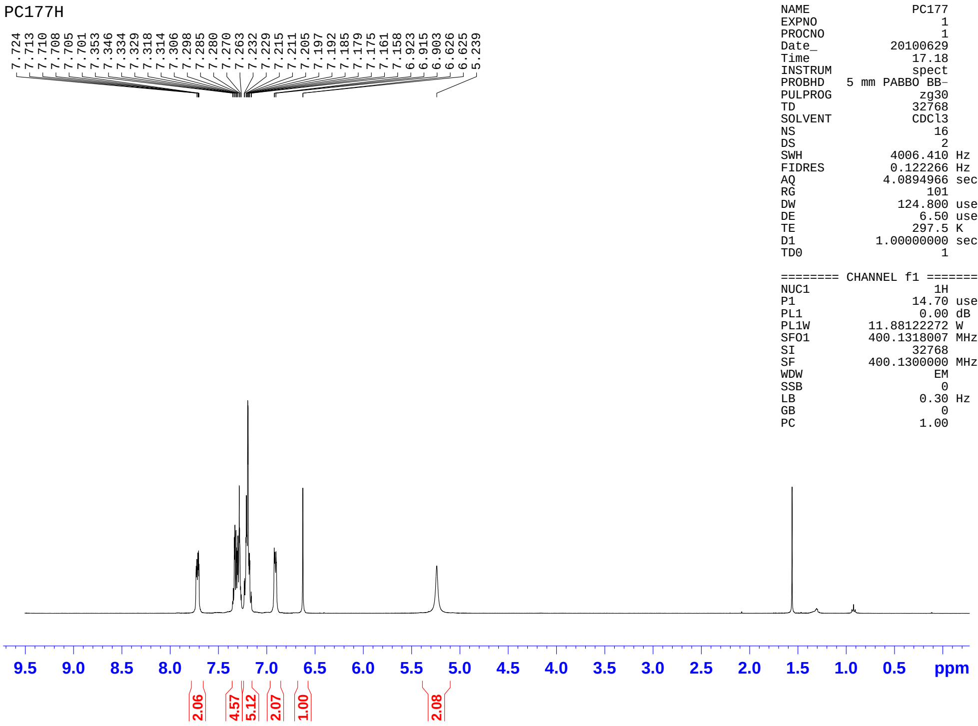
```
Minimum:                              -1.5
Maximum:             5.0      5.0     50.0

Mass      Calc. Mass  mDa     PPM     DBE     i-FIT    Formula

328.0694  328.0701    -0.7    -2.1    9.5     3.9      C18  H19  N  Br
```

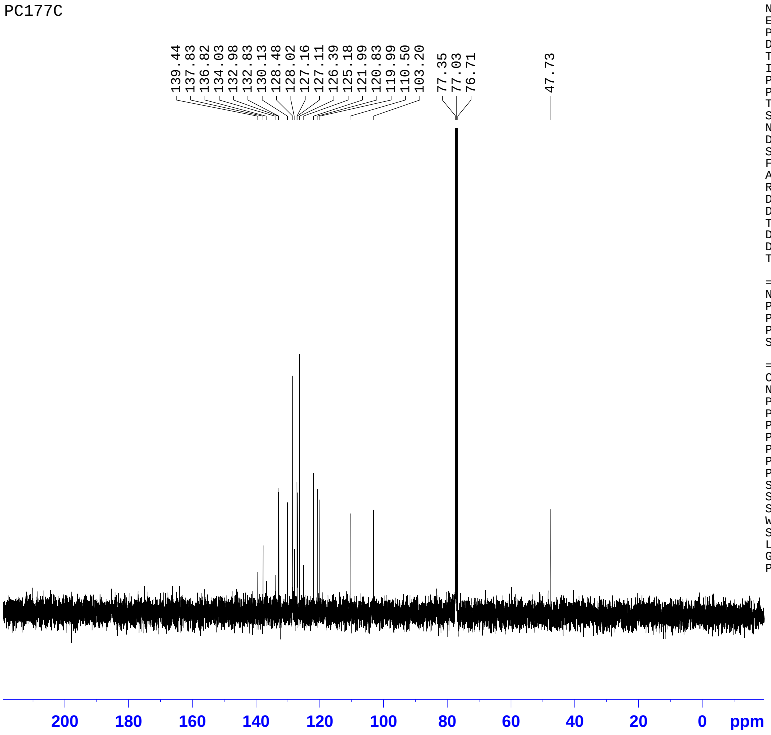
1-Benzyl-2-(2-bromophenyl)-1*H*-indole (Table 6.1, entry 5)





```
NAME                 PC177
EXPNO                    1
PROCNO                   1
Date_             20100629
Time                 17.18
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               4006.410 Hz
FIDRES            0.122266 Hz
AQ               4.0894966 sec
RG                     101
DW                 124.800 usec
DE                    6.50 usec
TE                   297.5 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   14.70 usec
PL1                   0.00 dB
PL1W           11.88122272 W
SFO1           400.1318007 MHz
SI                   32768
SF             400.1300000 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

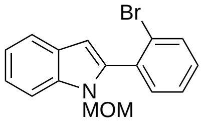


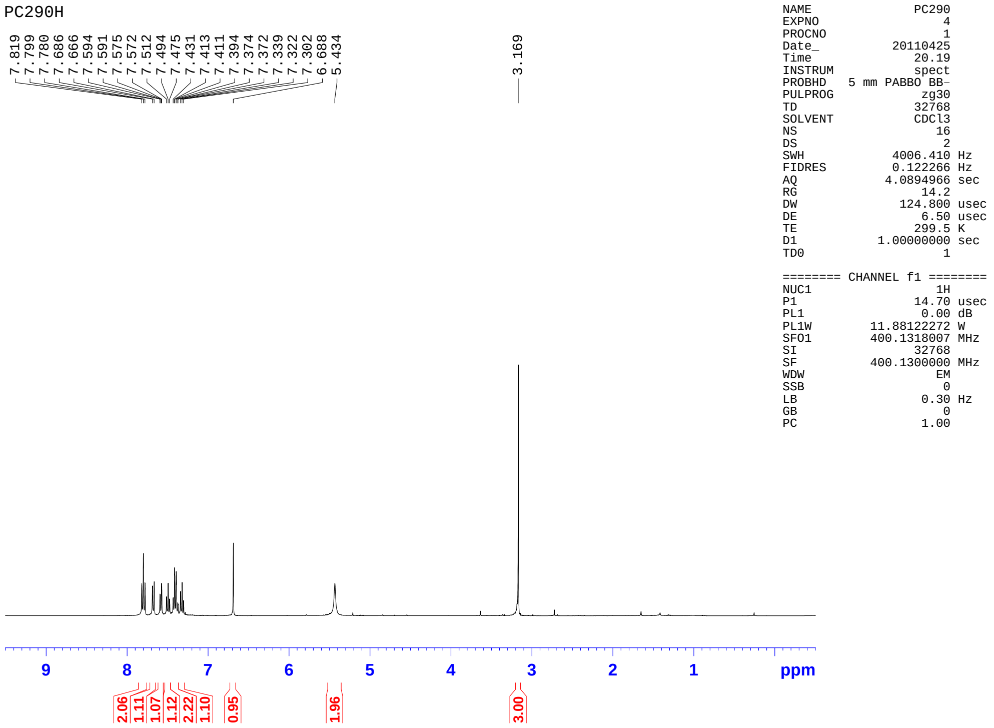
```
NAME                 PC177
EXPNO                    2
PROCNO                   1
Date_             20100629
Time                 17.21
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      32
DS                       2
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ               1.3631988 sec
RG                     203
DW                  20.800 usec
DE                    6.50 usec
TE                   298.5 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    9.50 usec
PL1                  -2.00 dB
PL1W           58.52175522 W
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   0.00 dB
PL12                 15.00 dB
PL13                 15.00 dB
PL2W           11.88122272 W
PL12W           0.37571725 W
PL13W           0.37571725 W
SFO2           400.1316005 MHz
SI                   32768
SF             100.6127690 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

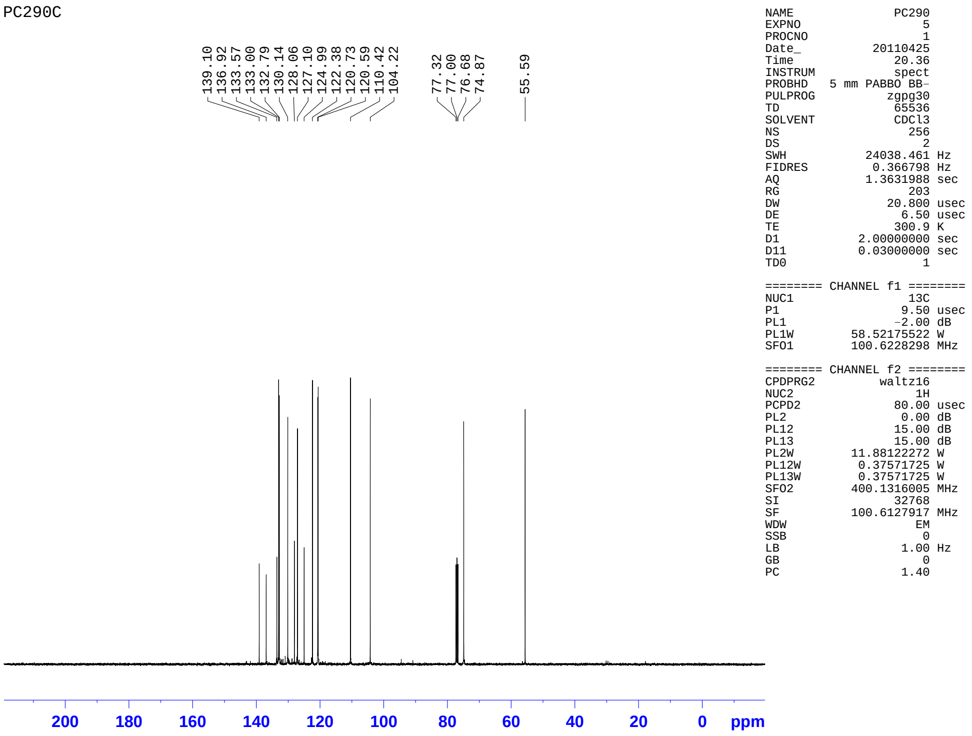
2-(2-Bromophenyl)-1-(methoxymethyl)-1*H*-indole (Table 6.1, entry 5)





```
NAME                PC290
EXPNO                   4
PROCNO                  1
Date_            20110425
Time                20.19
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              4006.410 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                   14.2
DW                124.800 usec
DE                   6.50 usec
TE                  299.5 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.70 usec
PL1                  0.00 dB
PL1W          11.88122272 W
SFO1          400.1318007 MHz
SI                  32768
SF            400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

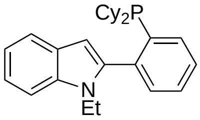


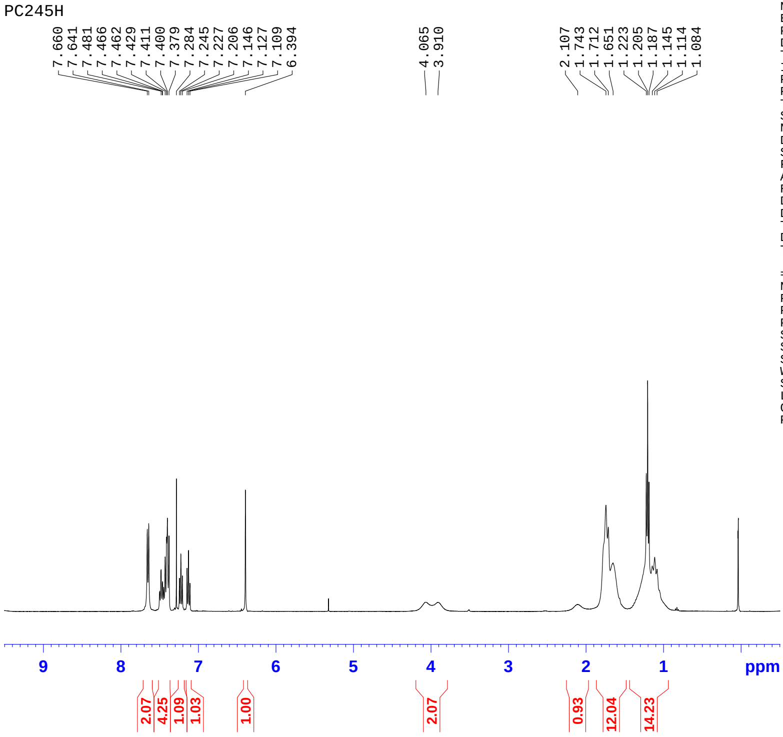
```
NAME                PC290
EXPNO                   5
PROCNO                  1
Date_            20110425
Time                20.36
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    256
DS                      2
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                    203
DW                 20.800 usec
DE                   6.50 usec
TE                  300.9 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.50 usec
PL1                 -2.00 dB
PL1W          58.52175522 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                15.00 dB
PL13                15.00 dB
PL2W          11.88122272 W
PL12W          0.37571725 W
PL13W          0.37571725 W
SFO2          400.1316005 MHz
SI                  32768
SF            100.6127917 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

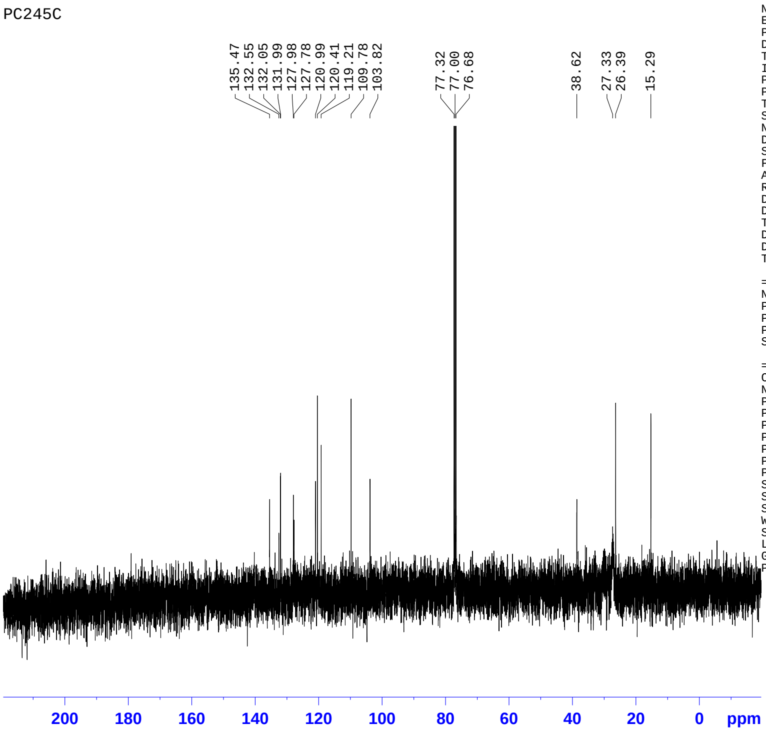
N-Ethyl-2-(2’-dicyclohexylphosphinophenyl)indole (Table 6.2, entry 1)





```
NAME               PC245
EXPNO                  1
PROCNO                 1
Date_           20110105
Time               17.49
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                    64
DW               124.800 usec
DE                  6.50 usec
TE                 295.5 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

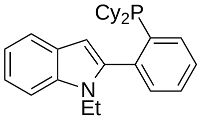


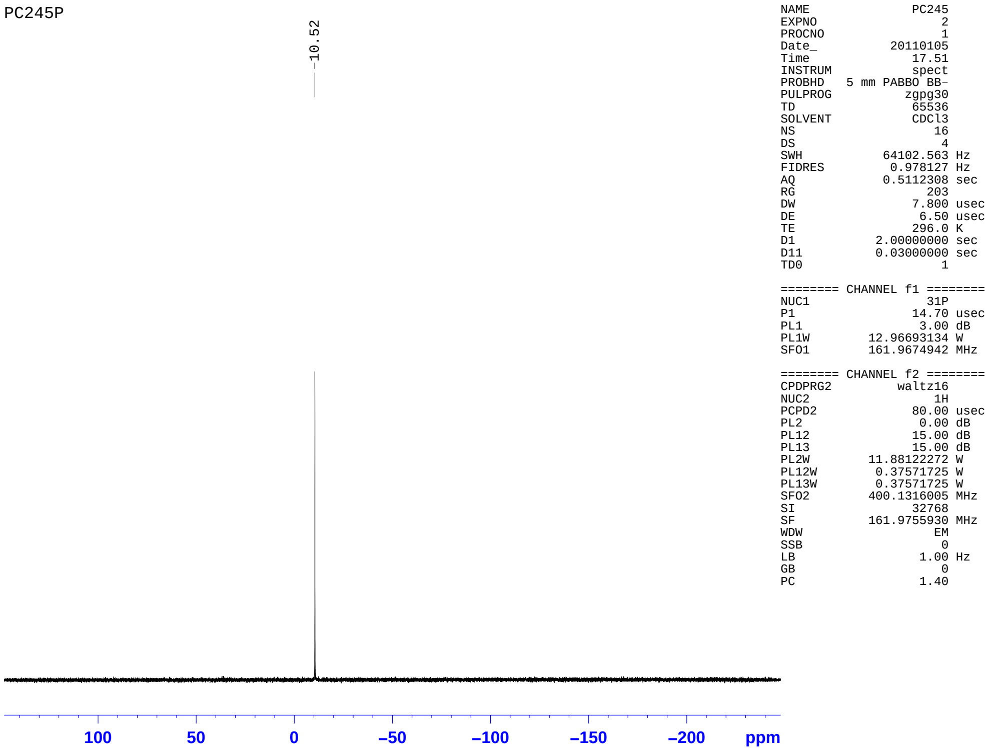
```
NAME               PC245
EXPNO                  3
PROCNO                 1
Date_           20110105
Time               17.55
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   114
DW                20.800 usec
DE                  6.50 usec
TE                 296.5 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127723 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

N-Ethyl-2-(2’-dicyclohexylphosphinophenyl)indole (Table 6.2, entry 1)

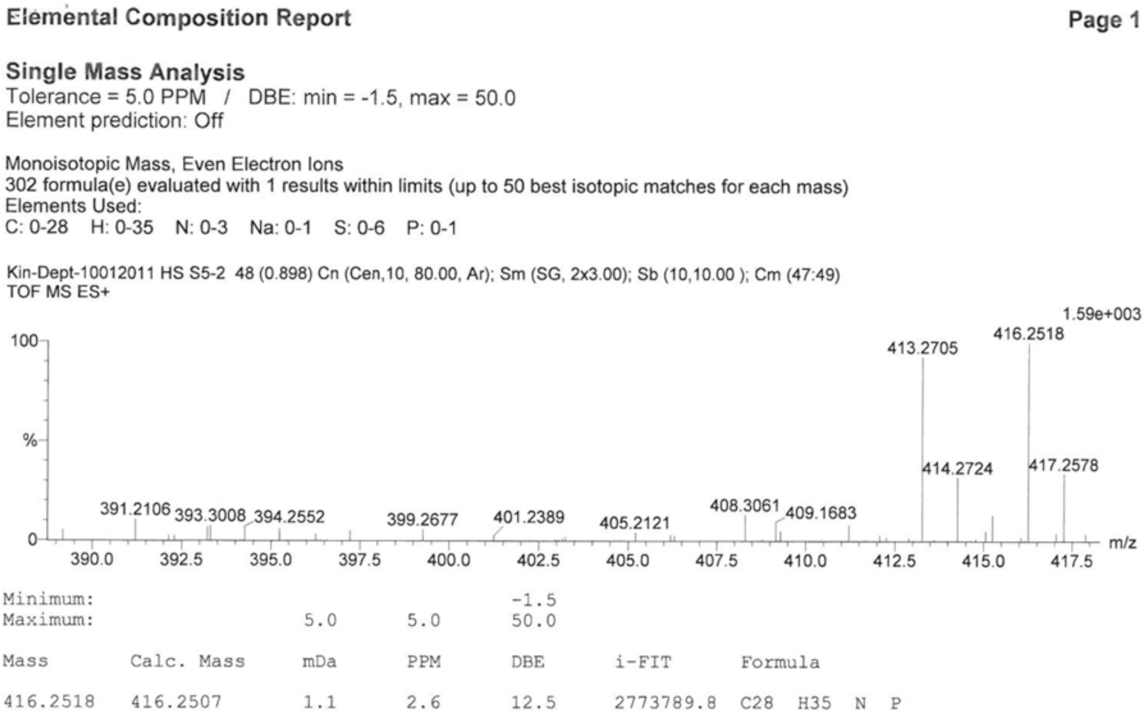




```
NAME              PC245
EXPNO                 2
PROCNO                1
Date_          20110105
Time              17.51
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    4
SWH           64102.563 Hz
FIDRES         0.978127 Hz
AQ            0.5112308 sec
RG                  203
DW                7.800 usec
DE                 6.50 usec
TE                296.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                31P
P1                14.70 usec
PL1                3.00 dB
PL1W        12.96693134 W
SFO1        161.9674942 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL13              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
PL13W        0.37571725 W
SFO2        400.1316005 MHz
SI                32768
SF          161.9755930 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```



Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Even Electron Ions
302 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-28 H: 0-35 N: 0-3 Na: 0-1 S: 0-6 P: 0-1

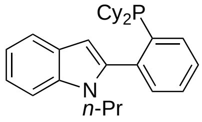
Kin-Dept-10012011 HS S5-2 48 (0.898) Cn (Cen,10, 80.00, Ar); Sm (SG, 2x3.00); Sb (10,10.00); Cm (47:49)
TOF MS ES+

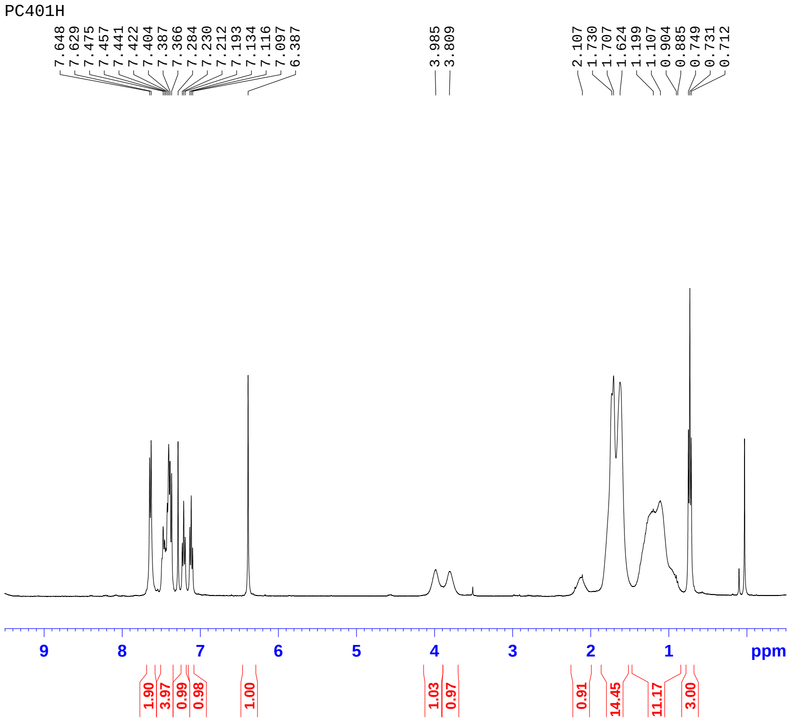
```
Minimum:                                  -1.5
Maximum:                 5.0      5.0     50.0

Mass       Calc. Mass    mDa      PPM     DBE     i-FIT       Formula

416.2518   416.2507      1.1      2.6     12.5    2773789.8   C28  H35  N  P
```

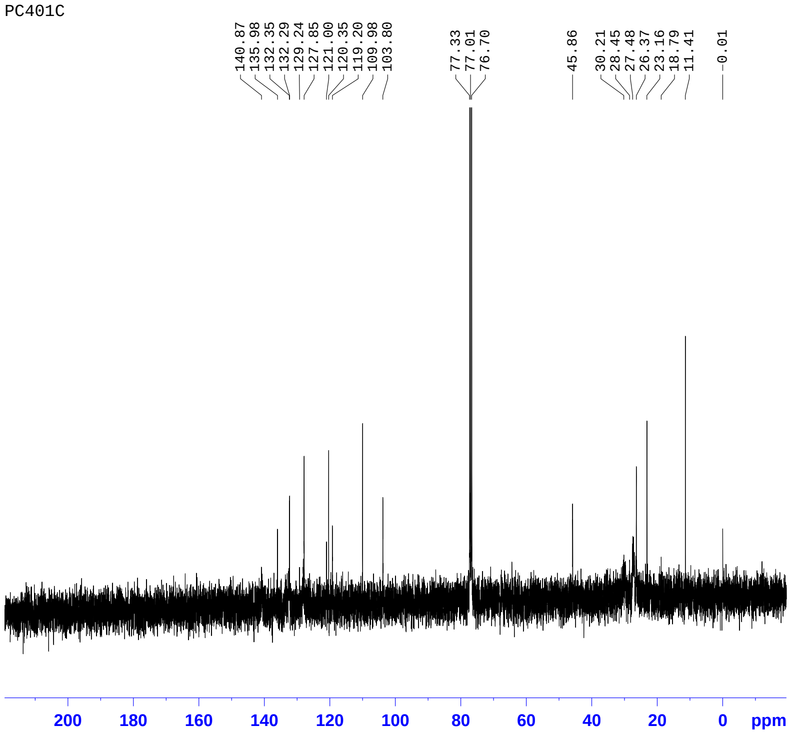
N-Propyl-2-(2’-dicyclohexylphosphinophenyl)indole (Table 6.2, entry 2)





```
NAME               PC401
EXPNO                  8
PROCNO                 1
Date_           20120227
Time               21.17
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  71.8
DW               124.800 usec
DE                  6.50 usec
TE                 294.6 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

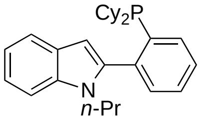


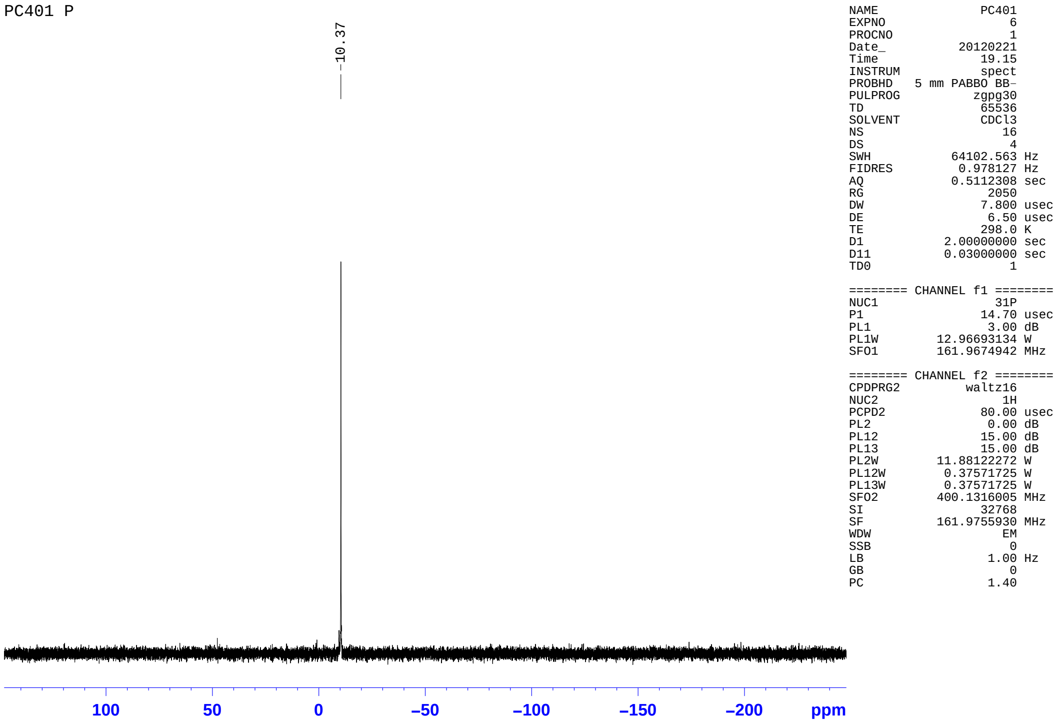
```
NAME               PC401
EXPNO                  3
PROCNO                 1
Date_           20120216
Time               20.55
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   265
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   181
DW                20.800 usec
DE                  6.50 usec
TE                 298.4 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127690 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

N-Propyl-2-(2’-dicyclohexylphosphinophenyl)indole (Table 6.2, entry 2)

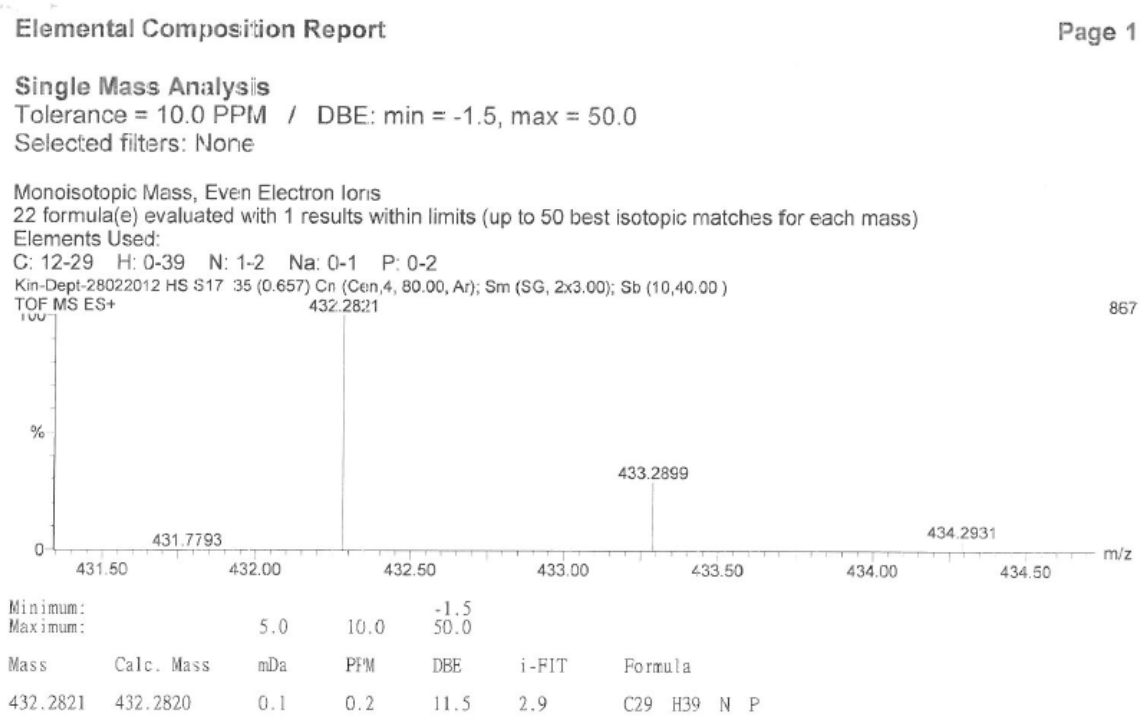




```
NAME               PC401
EXPNO                  6
PROCNO                 1
Date_           20120221
Time               19.15
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     4
SWH            64102.563 Hz
FIDRES          0.978127 Hz
AQ             0.5112308 sec
RG                  2050
DW                 7.800 usec
DE                  6.50 usec
TE                 298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 31P
P1                 14.70 usec
PL1                 3.00 dB
PL1W         12.96693134 W
SFO1         161.9674942 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           161.9755930 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



Elemental Composition Report

Page 1

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

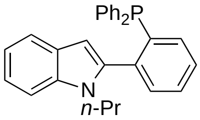
Monoisotopic Mass, Even Electron Ions
22 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 12-29 H: 0-39 N: 1-2 Na: 0-1 P: 0-2
Kin-Dept-28022012 HS S17 35 (0.657) Cn (Cen,4, 80.00, Ar); Sm (SG, 2x3.00); Sb (10,40.00)
TOF MS ES+

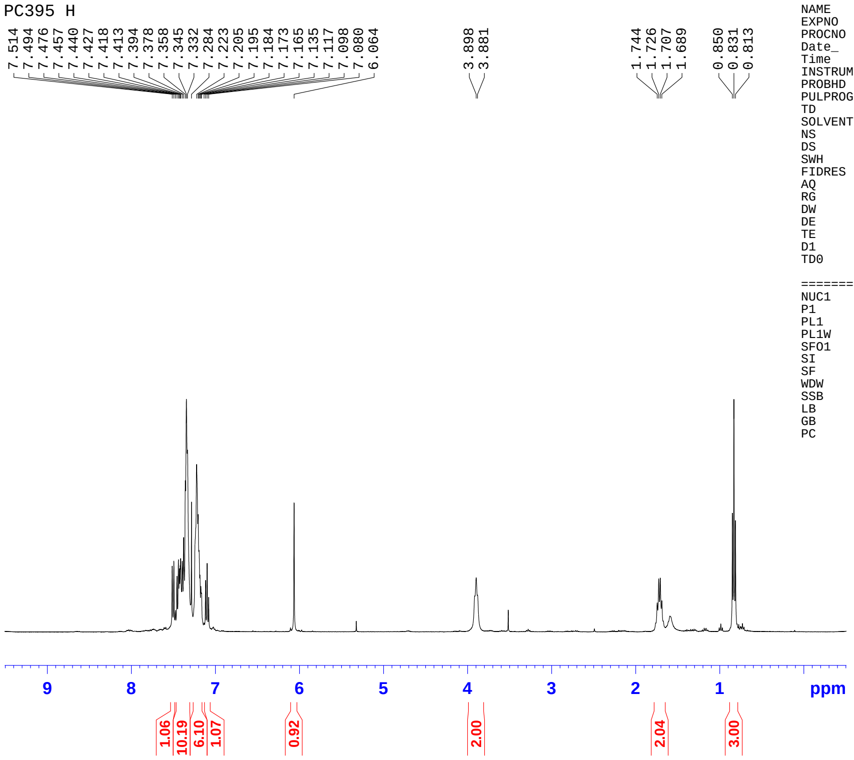
```
Minimum:                              -1.5
Maximum:                5.0    10.0   50.0

Mass      Calc. Mass    mDa    PPM    DBE    i-FIT    Formula

432.2821  432.2820      0.1    0.2    11.5   2.9      C29  H39  N  P
```

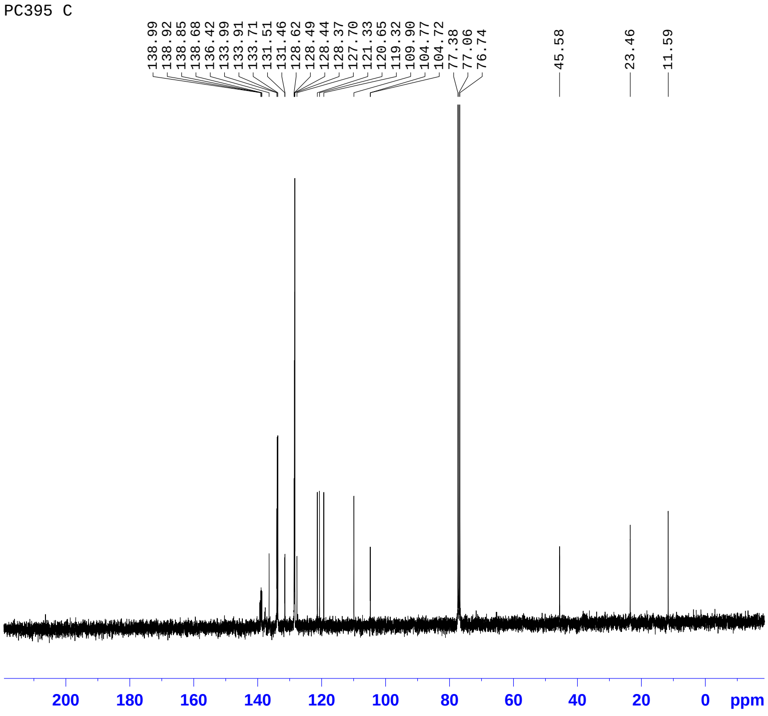
N-Propyl-2-(2’-diphenylphosphinophenyl)indole (Table 6.2, entry 3)





```
NAME              PC395
EXPNO                 1
PROCNO                1
Date_          20120208
Time              17.22
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            4006.410 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                  161
DW              124.800 usec
DE                 6.50 usec
TE                294.4 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.70 usec
PL1                0.00 dB
PL1W        11.88122272 W
SFO1        400.1318007 MHz
SI                32768
SF          400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

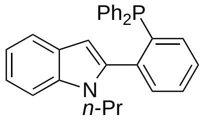


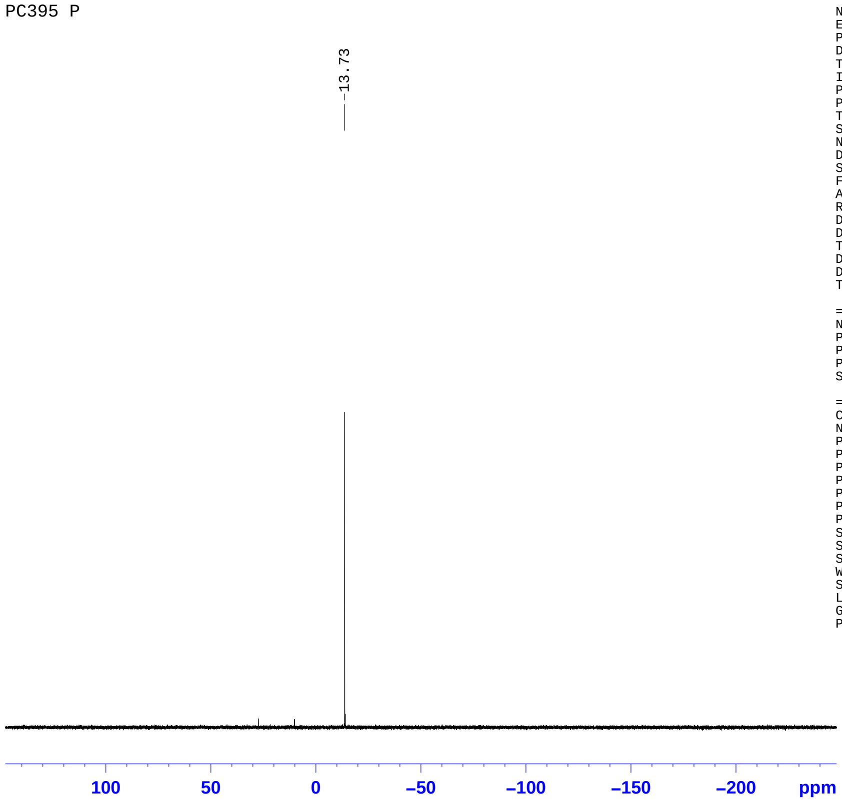
```
NAME              PC395
EXPNO                 4
PROCNO                1
Date_          20120209
Time              17.25
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  107
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                  203
DW               20.800 usec
DE                 6.50 usec
TE                295.3 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.50 usec
PL1               -2.00 dB
PL1W        58.52175522 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL13              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
PL13W        0.37571725 W
SFO2        400.1316005 MHz
SI                32768
SF          100.6127690 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

N-Propyl-2-(2’-diphenylphosphinophenyl)indole (Table 6.2, entry 3)

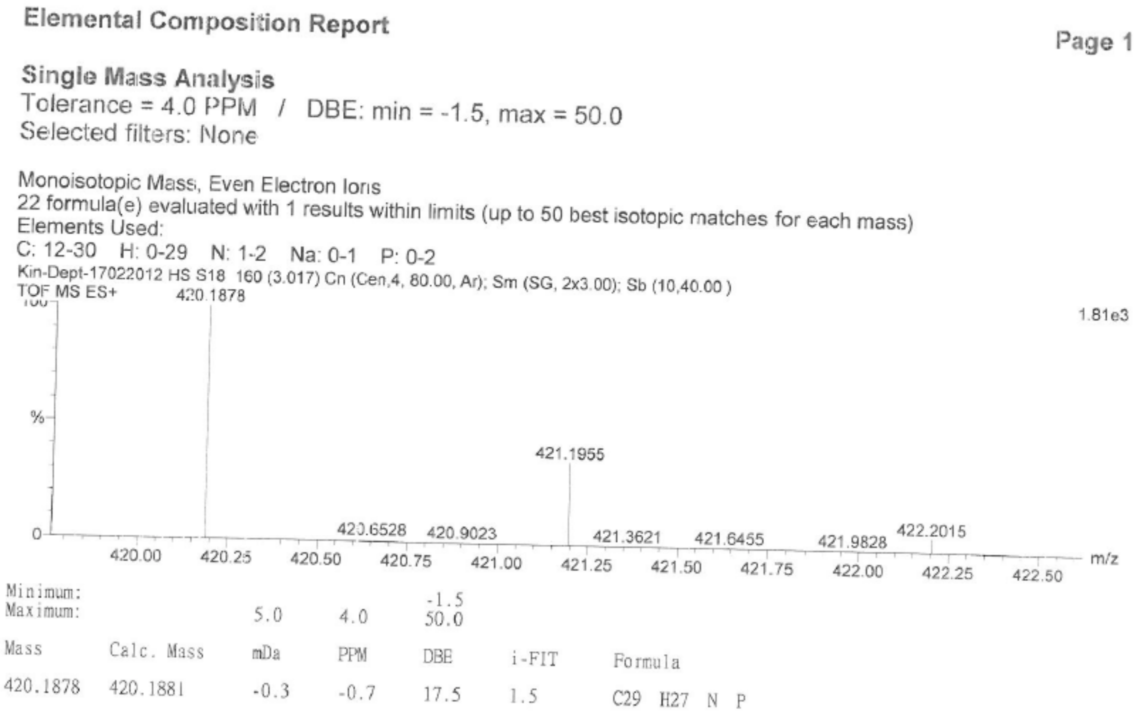




```
NAME             PC395
EXPNO                2
PROCNO               1
Date_         20120208
Time             17.26
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG        zgpg30
TD               65536
SOLVENT          CDCl3
NS                  16
DS                   4
SWH          64102.563 Hz
FIDRES        0.978127 Hz
AQ           0.5112308 sec
RG                2050
DW               7.800 usec
DE                6.50 usec
TE               294.9 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               31P
P1               14.70 usec
PL1               3.00 dB
PL1W       12.96693134 W
SFO1       161.9674942 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2            80.00 usec
PL2               0.00 dB
PL12             15.00 dB
PL13             15.00 dB
PL2W       11.88122272 W
PL12W       0.37571725 W
PL13W       0.37571725 W
SFO2       400.1316005 MHz
SI               32768
SF         161.9755930 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```



Elemental Composition Report

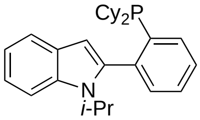
Page 1

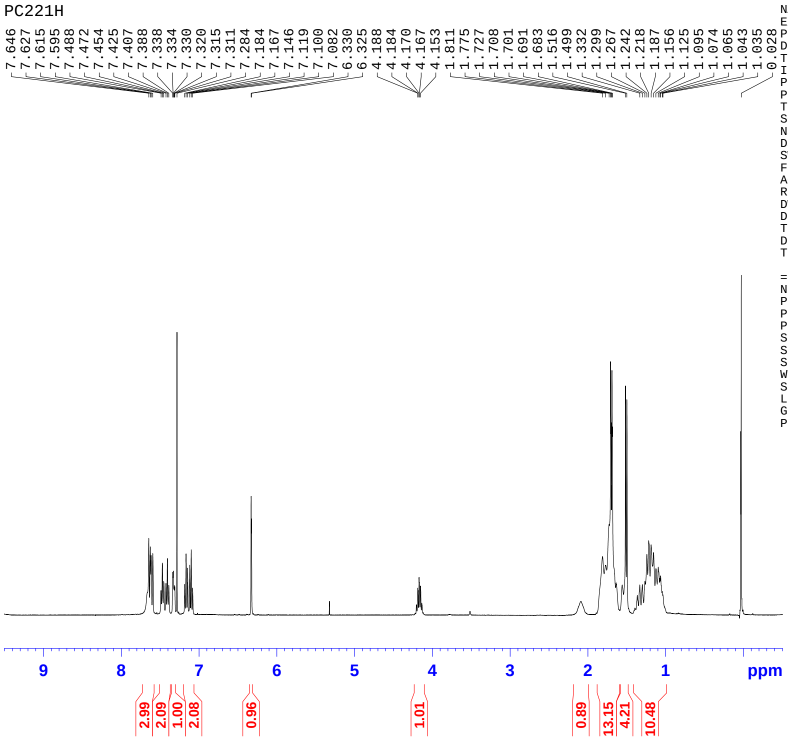
Single Mass Analysis
Tolerance = 4.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

Monoisotopic Mass, Even Electron Ions
22 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 12-30 H: 0-29 N: 1-2 Na: 0-1 P: 0-2
Kin-Dept-17022012 HS S18 160 (3.017) Cn (Cen,4, 80.00, Ar); Sm (SG, 2x3.00); Sb (10,40.00)
TOF MS ES+

Minimum:				-1.5		
Maximum:		5.0	4.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
420.1878	420.1881	-0.3	-0.7	17.5	1.5	C29 H27 N P

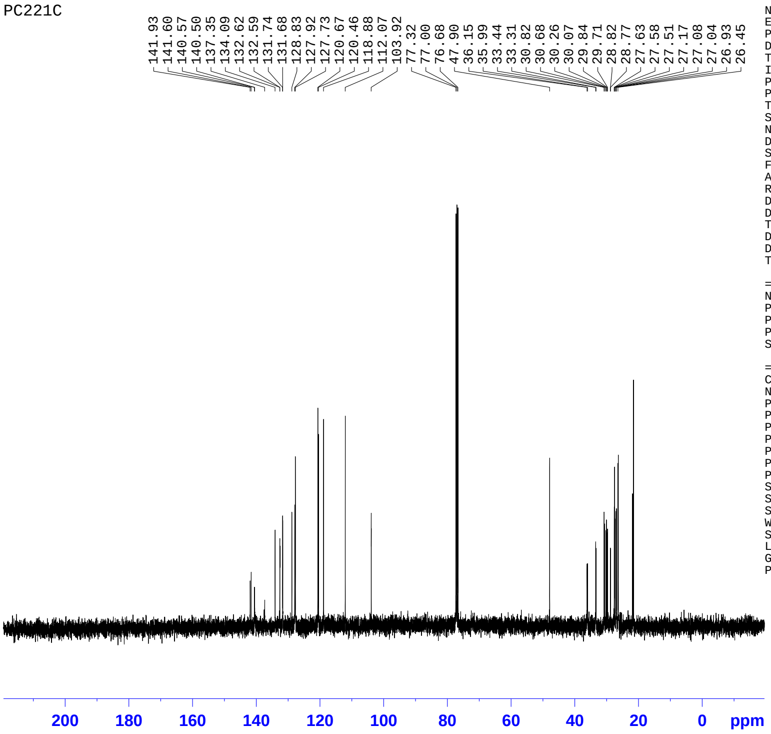
N-Isopropyl-2-(2'-dicyclohexylphosphinophenyl)indole (Table 6.2, entry 4)





```
NAME              PC221
EXPNO                 1
PROCNO                1
Date_          20101118
Time              18.58
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            4006.410 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                 90.5
DW              124.800 usec
DE                 6.50 usec
TE                297.4 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.70 usec
PL1                0.00 dB
PL1W        11.88122272 W
SFO1        400.1318007 MHz
SI                32768
SF          400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

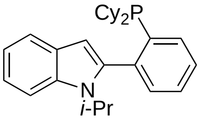


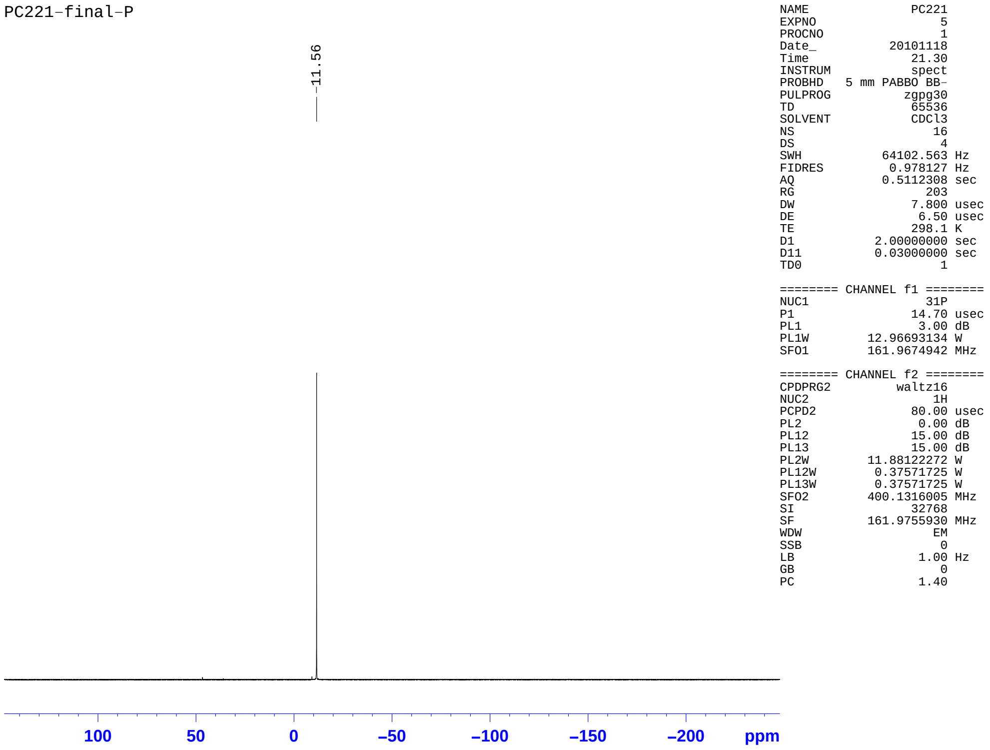
```
NAME              PC221
EXPNO                 4
PROCNO                1
Date_          20101118
Time              21.26
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                  161
DW               20.800 usec
DE                 6.50 usec
TE                298.5 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.50 usec
PL1               -2.00 dB
PL1W        58.52175522 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL13              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
PL13W        0.37571725 W
SFO2        400.1316005 MHz
SI                32768
SF          100.6127779 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

N-Isopropyl-2-(2’-dicyclohexylphosphinophenyl)indole (Table 6.2, entry 4)





```
NAME               PC221
EXPNO                  5
PROCNO                 1
Date_           20101118
Time               21.30
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     4
SWH            64102.563 Hz
FIDRES          0.978127 Hz
AQ             0.5112308 sec
RG                   203
DW                 7.800 usec
DE                  6.50 usec
TE                 298.1 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

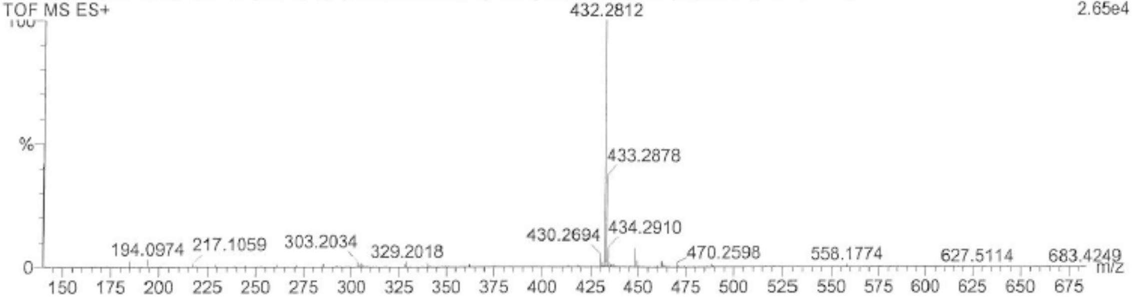
======== CHANNEL f1 ========
NUC1                 31P
P1                 14.70 usec
PL1                 3.00 dB
PL1W         12.96693134 W
SFO1         161.9674942 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           161.9755930 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -100.0, max = 1000.0
Selected filters: None

Monoisotopic Mass, Even Electron Ions
44 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-29 H: 0-39 N: 0-3 Na: 0-1 P: 0-2
Kin-dept-24112010-HS S4 33 (0.628) Cn (Cen,10, 80.00, Ar); Sm (SG, 2x3.00); Sb (10,10.00); Cm (23:47)
TOF MS ES+

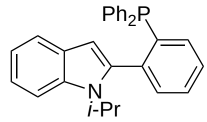


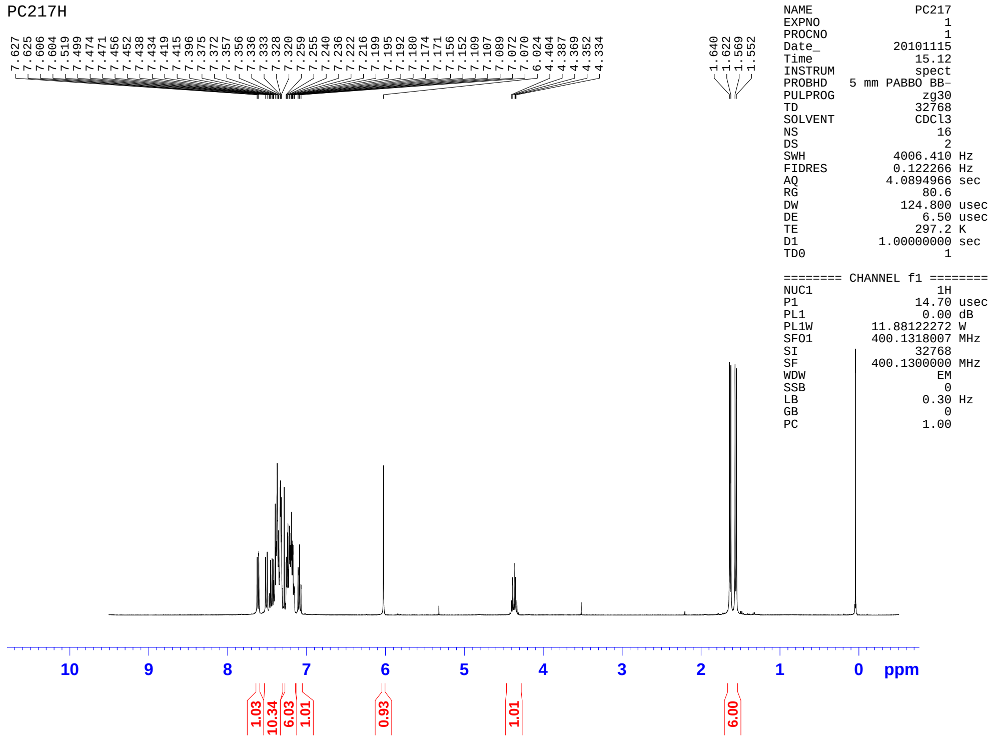
```
Minimum:                                         -100.0
Maximum:                    5.0        20.0      1000.0

Mass       Calc. Mass     mDa        PPM        DBE        i-FIT      Formula

432.2812   432.2820       -0.8       -1.9       11.5       136.8      C29  H39  N  P
```

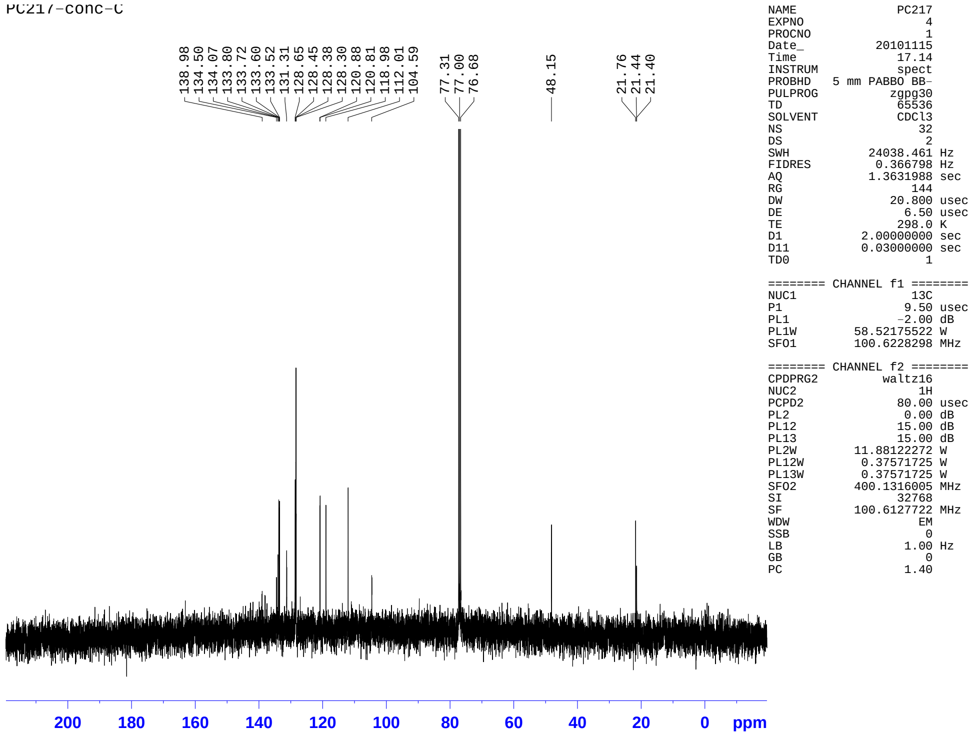
*N-Iso*propyl-2-(2’-diphenylphosphinophenyl)indole (Table 6.2, entry 5)





```
NAME               PC217
EXPNO                  1
PROCNO                 1
Date_           20101115
Time               15.12
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  80.6
DW               124.800 usec
DE                  6.50 usec
TE                 297.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

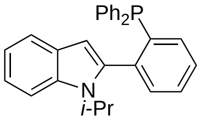


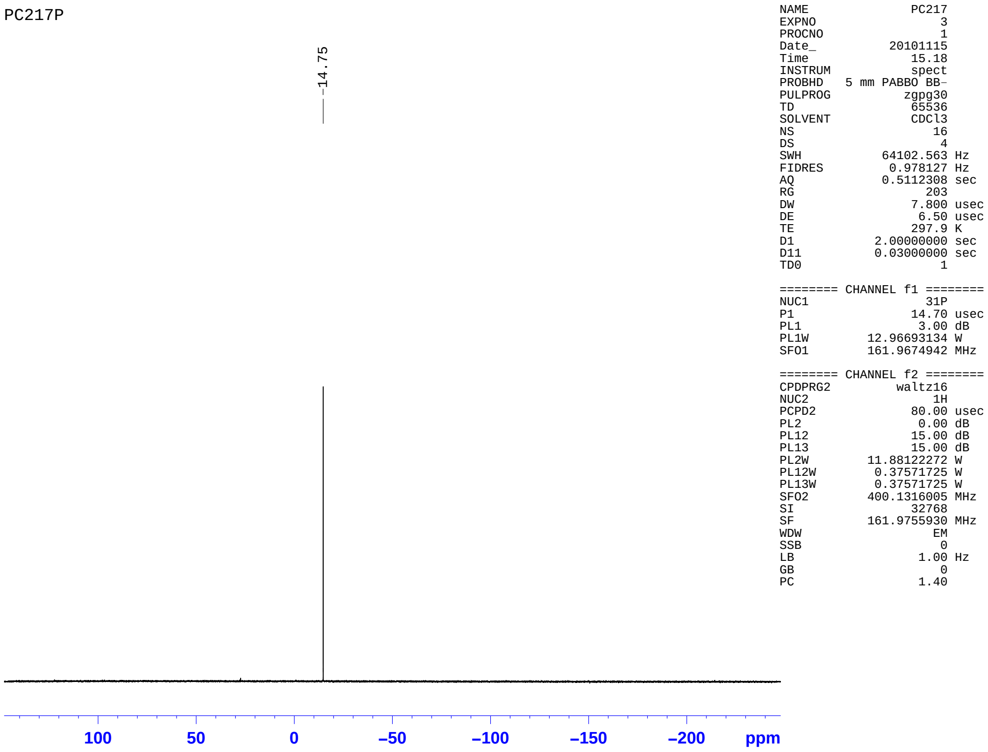
```
NAME               PC217
EXPNO                  4
PROCNO                 1
Date_           20101115
Time               17.14
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   144
DW                20.800 usec
DE                  6.50 usec
TE                 298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127722 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

*N-Iso*propyl-2-(2’-diphenylphosphinophenyl)indole (Table 6.2, entry 5)

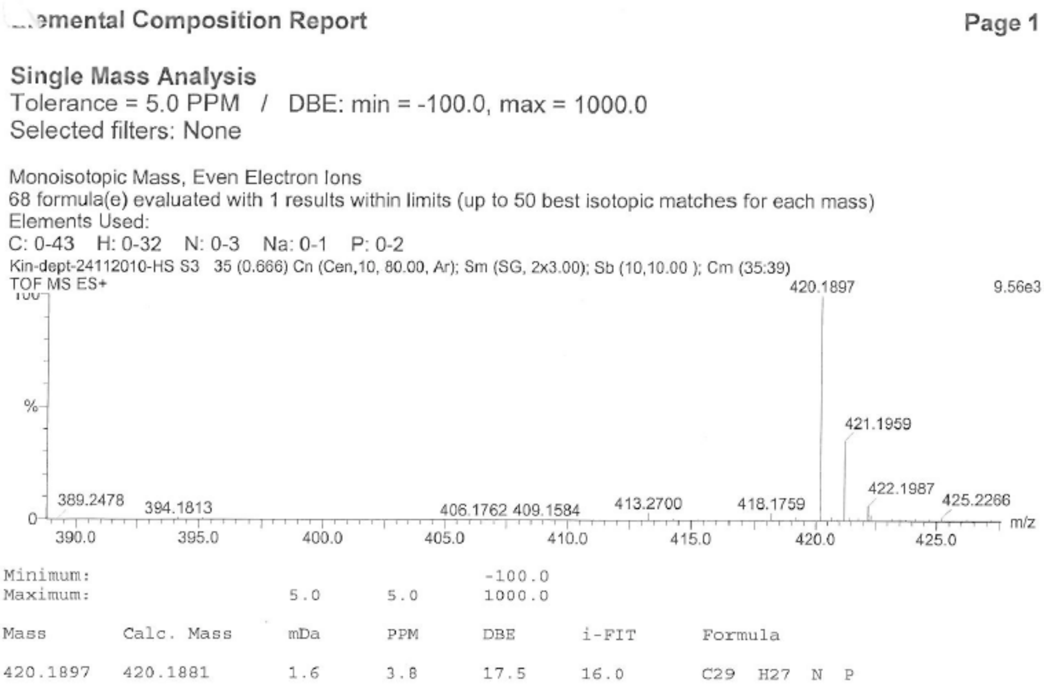




```
NAME                PC217
EXPNO                   3
PROCNO                  1
Date_            20101115
Time                15.18
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT             CDCl3
NS                     16
DS                      4
SWH             64102.563 Hz
FIDRES           0.978127 Hz
AQ              0.5112308 sec
RG                    203
DW                  7.800 usec
DE                   6.50 usec
TE                  297.9 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  31P
P1                  14.70 usec
PL1                  3.00 dB
PL1W          12.96693134 W
SFO1          161.9674942 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                15.00 dB
PL13                15.00 dB
PL2W          11.88122272 W
PL12W          0.37571725 W
PL13W          0.37571725 W
SFO2          400.1316005 MHz
SI                  32768
SF            161.9755930 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```



emental Composition Report

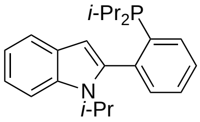
Page 1

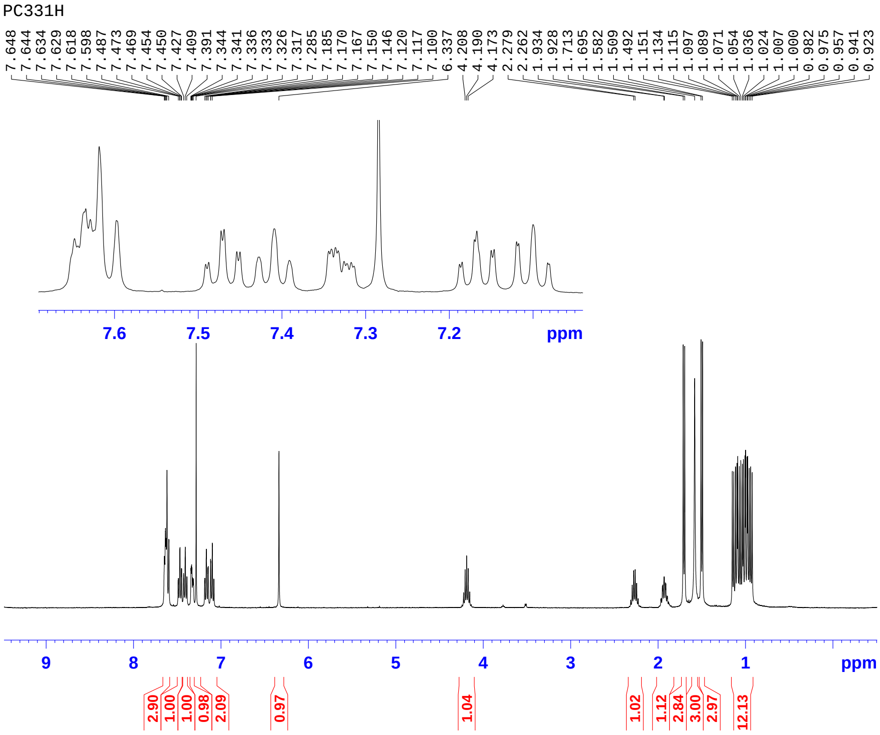
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -100.0, max = 1000.0
Selected filters: None

Monoisotopic Mass, Even Electron Ions
68 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-43 H: 0-32 N: 0-3 Na: 0-1 P: 0-2
Kin-dept-24112010-HS S3 35 (0.666) Cn (Cen,10, 80.00, Ar); Sm (SG, 2x3.00); Sb (10,10.00); Cm (35:39)
TOF MS ES+

Minimum:				-100.0		
Maximum:		5.0	5.0	1000.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
420.1897	420.1881	1.6	3.8	17.5	16.0	C29 H27 N P

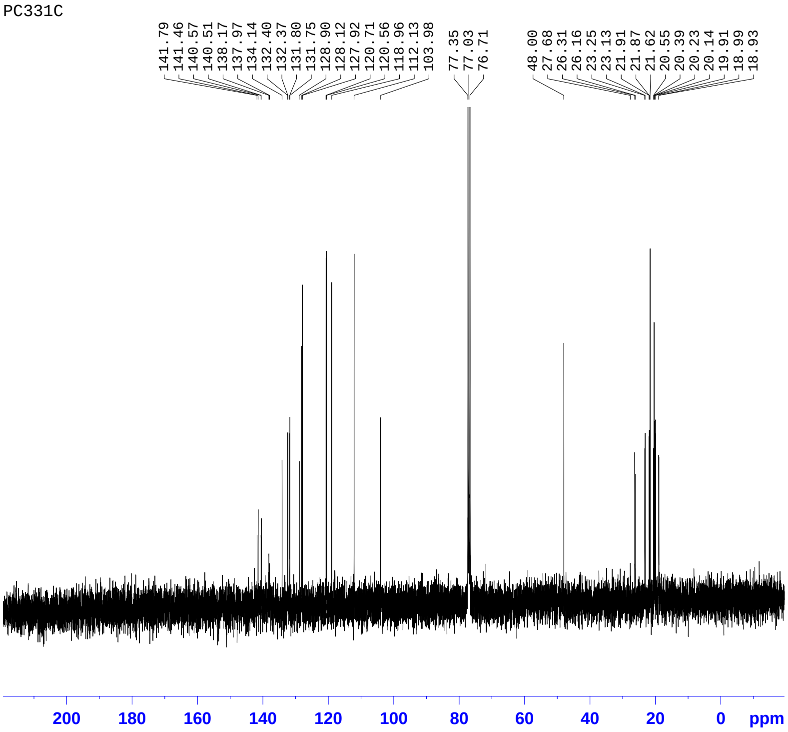
N-*Iso*propyl-2-(2’-diisopropylphosphinophenyl)indole (Table 6.2, entry 6)





```
NAME               PC331
EXPNO                  1
PROCNO                 1
Date_           20111017
Time               17.32
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                   128
DW               124.800 use
DE                  6.50 use
TE                 297.3 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 =======
NUC1                  1H
P1                 14.70 use
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

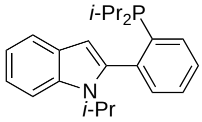


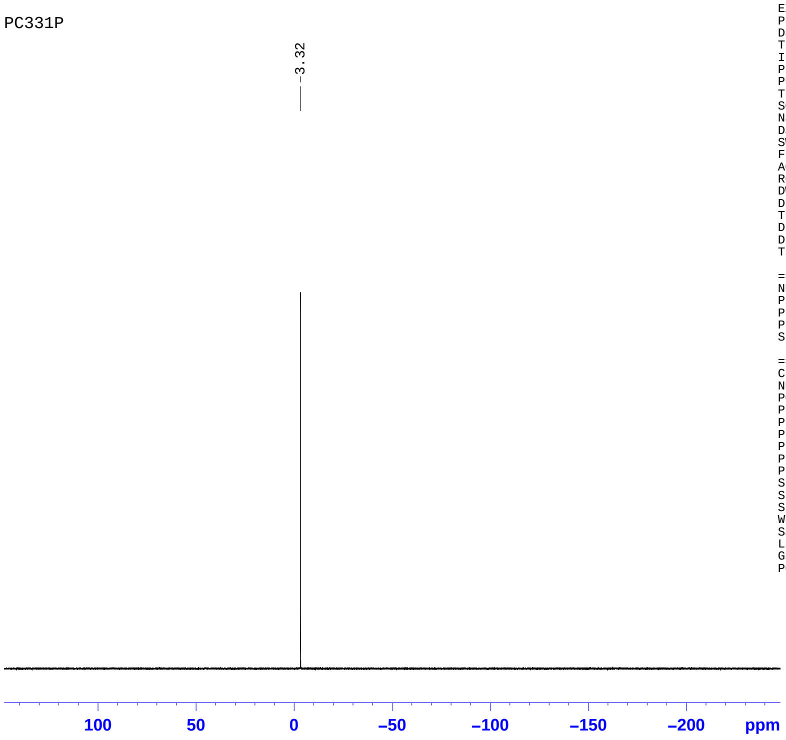
```
NAME               PC331
EXPNO                  2
PROCNO                 1
Date_           20111017
Time               19.09
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   111
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   203
DW                20.800 usec
DE                  6.50 usec
TE                 298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127690 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

*N-Iso*propyl-2-(2’-diisopropylphosphinophenyl)indole (Table 6.2, entry 6)



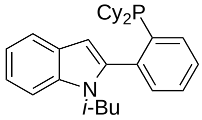


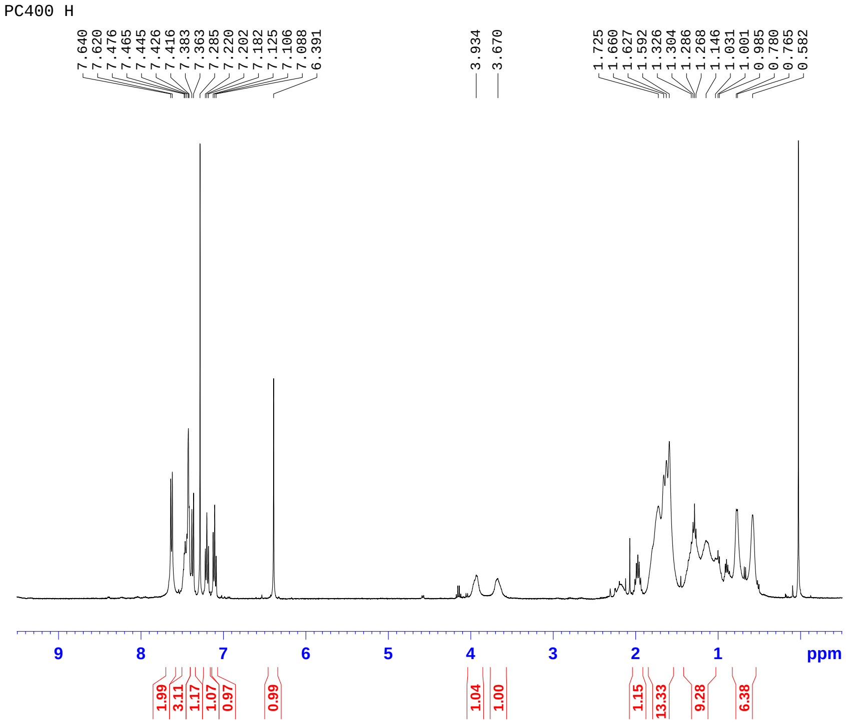
```
NAME              PC331
EXPNO                 3
PROCNO                1
Date_          20111017
Time              19.18
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    4
SWH           64102.563 Hz
FIDRES         0.978127 Hz
AQ            0.5112308 sec
RG                  203
DW                7.800 usec
DE                 6.50 usec
TE                298.1 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                31P
P1                14.70 usec
PL1                3.00 dB
PL1W        12.96693134 W
SFO1        161.9674942 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL13              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
PL13W        0.37571725 W
SFO2        400.1316005 MHz
SI                32768
SF          161.9755930 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

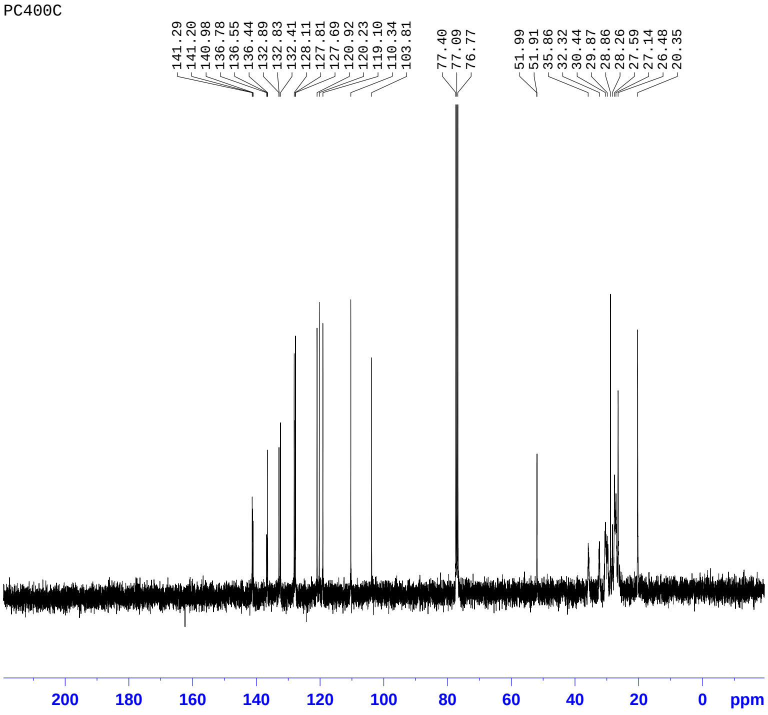
N-Isobutyl-2-(2’-dicyclohexylphosphinophenyl)indole (Table 6.2, entry 7)





```
NAME                PC400
EXPNO                   9
PROCNO                  1
Date_            20120221
Time                14.00
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              4006.410 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                    203
DW                124.800 usec
DE                   6.50 usec
TE                  297.5 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.70 usec
PL1                  0.00 dB
PL1W          11.88122272 W
SFO1          400.1318007 MHz
SI                  32768
SF            400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

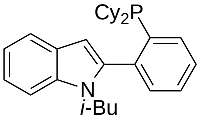


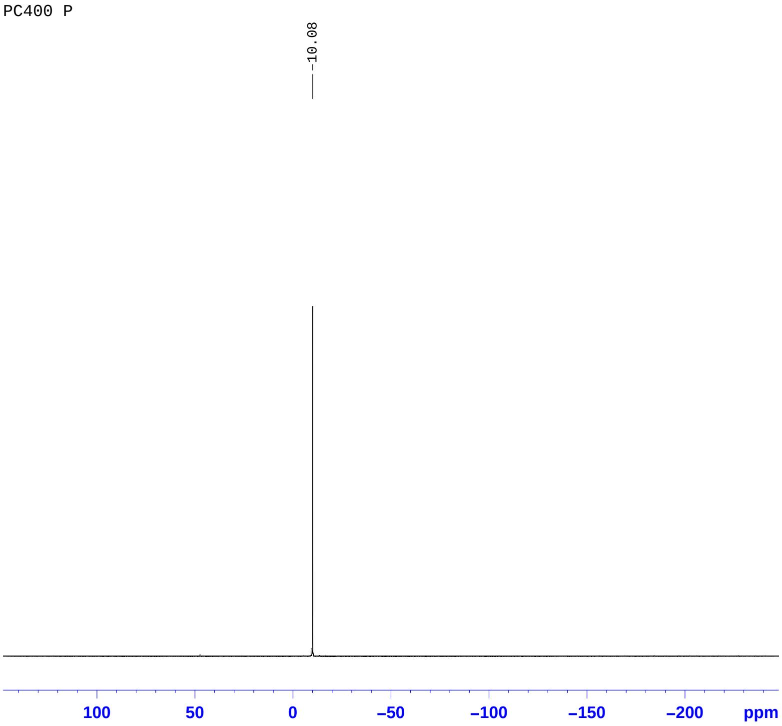
```
NAME                PC400
EXPNO                   8
PROCNO                  1
Date_            20120219
Time                15.54
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    102
DS                      2
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                    181
DW                 20.800 usec
DE                   6.50 usec
TE                  297.6 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.50 usec
PL1                 -2.00 dB
PL1W          58.52175522 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                15.00 dB
PL13                15.00 dB
PL2W          11.88122272 W
PL12W          0.37571725 W
PL13W          0.37571725 W
SFO2          400.1316005 MHz
SI                  32768
SF            100.6127690 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

N-Isobutyl-2-(2’-dicyclohexylphosphinophenyl)indole (Table 6.2, entry 7)





```
NAME               PC400
EXPNO                 12
PROCNO                 1
Date_           20120221
Time               19.44
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     4
SWH            64102.563 Hz
FIDRES          0.978127 Hz
AQ             0.5112308 sec
RG                  2050
DW                 7.800 usec
DE                  6.50 usec
TE                 298.1 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 31P
P1                 14.70 usec
PL1                 3.00 dB
PL1W         12.96693134 W
SFO1         161.9674942 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           161.9755930 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

Elemental Composition Report Page 1

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

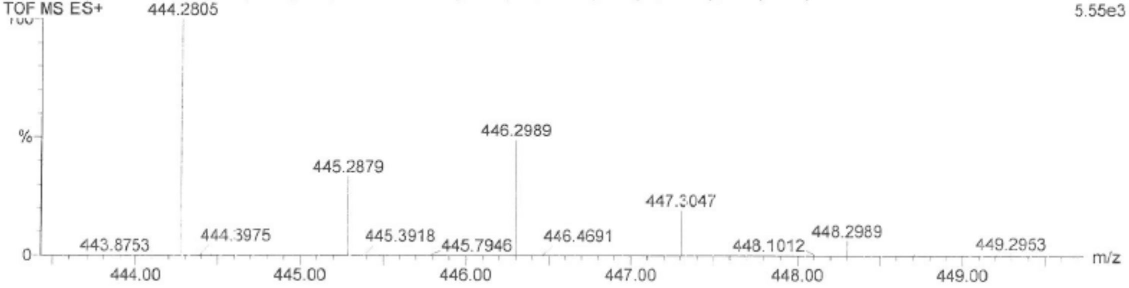
8 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 30-30 H: 0-42 N: 1-2 Na: 0-1 P: 0-2

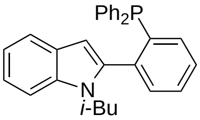
Kin-Dept-28022012 HS S18 91 (1.696) Cn (Cen,4, 80.00, Ar); Sm (SG, 2x3.00); Sb (10,40.00); Cm (87:92)

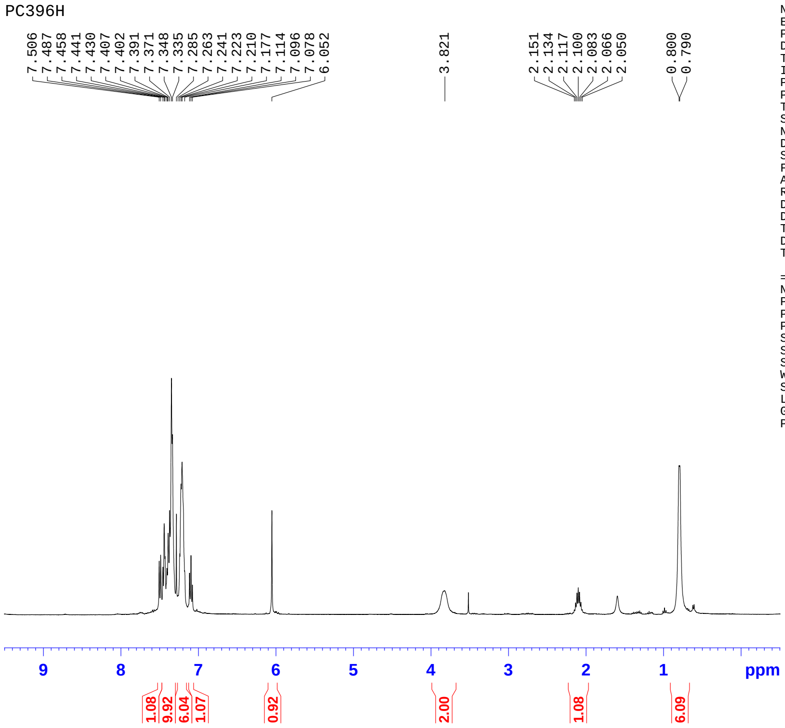
TOF MS ES+



Minimum:				-1.5		
Maximum:		5.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
446.2989	446.2977	1.2	2.7	11.5	55.7	C30 H41 N P

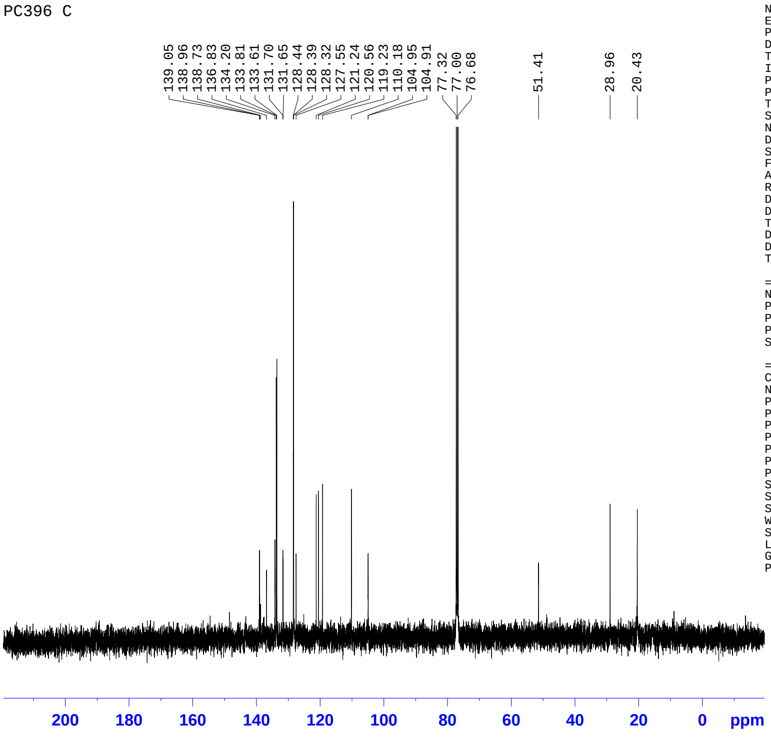
N-*Iso*butyl-2-(2’-diphenylphosphinophenyl)indole (Table 6.2, entry 8)





```
NAME              PC396
EXPNO                 1
PROCNO                1
Date_          20120208
Time              16.59
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            4006.410 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                  144
DW              124.800 usec
DE                 6.50 usec
TE                294.2 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.70 usec
PL1                0.00 dB
PL1W        11.88122272 W
SFO1        400.1318007 MHz
SI                32768
SF          400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

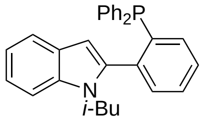


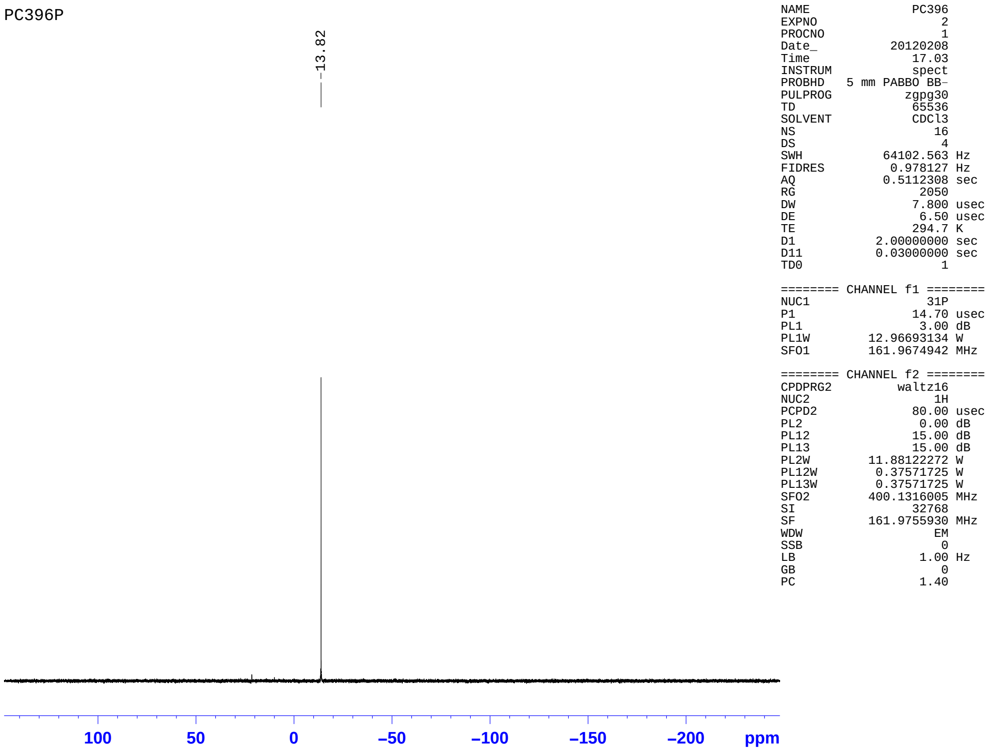
```
NAME              PC396
EXPNO                 3
PROCNO                1
Date_          20120208
Time              17.07
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  201
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                  203
DW               20.800 usec
DE                 6.50 usec
TE                295.1 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.50 usec
PL1               -2.00 dB
PL1W        58.52175522 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL13              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
PL13W        0.37571725 W
SFO2        400.1316005 MHz
SI                32768
SF          100.6127727 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

*N-Iso*butyl-2-(2’-diphenylphosphinophenyl)indole (Table 6.2, entry 8)

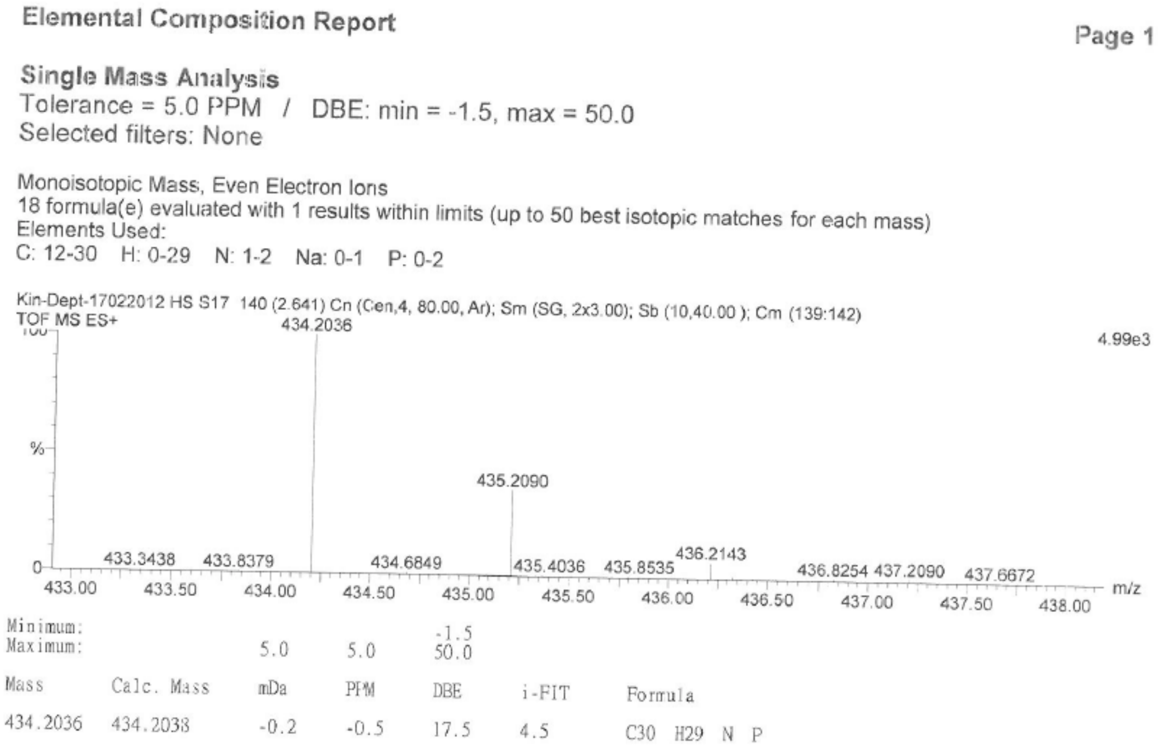




```
NAME              PC396
EXPNO                 2
PROCNO                1
Date_          20120208
Time              17.03
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    4
SWH           64102.563 Hz
FIDRES         0.978127 Hz
AQ            0.5112308 sec
RG                 2050
DW                7.800 usec
DE                 6.50 usec
TE                294.7 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                31P
P1                14.70 usec
PL1                3.00 dB
PL1W        12.96693134 W
SFO1        161.9674942 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL13              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
PL13W        0.37571725 W
SFO2        400.1316005 MHz
SI                32768
SF          161.9755930 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```



Elemental Composition Report

Page 1

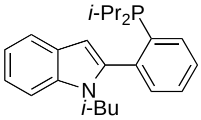
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

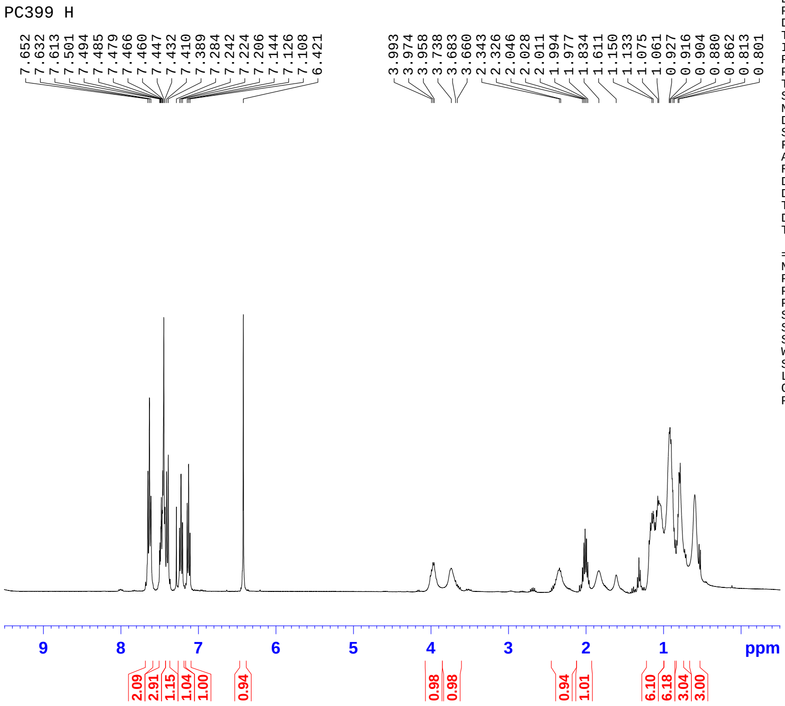
Monoisotopic Mass, Even Electron Ions
18 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 12-30 H: 0-29 N: 1-2 Na: 0-1 P: 0-2

Kin-Dept-17022012 HS S17 140 (2.641) Cn (Cen,4, 80.00, Ar); Sm (SG, 2x3.00); Sb (10,40.00); Cm (139:142)
TOF MS ES+

Minimum:				-1.5		
Maximum:		5.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
434.2036	434.2038	-0.2	-0.5	17.5	4.5	C30 H29 N P

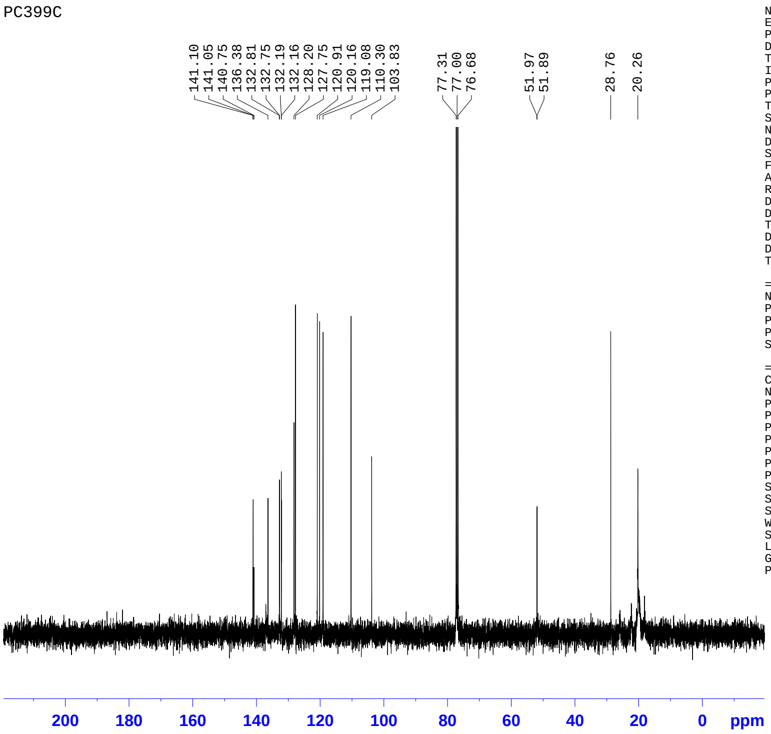
N-*Iso*butyl-2-(2’-diisopropylphosphinophenyl)indole (Table 6.2, entry 9)





```
NAME               PC399
EXPNO                  8
PROCNO                 1
Date_           20120221
Time               19.25
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  50.8
DW               124.800 usec
DE                  6.50 usec
TE                 297.6 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

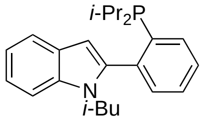


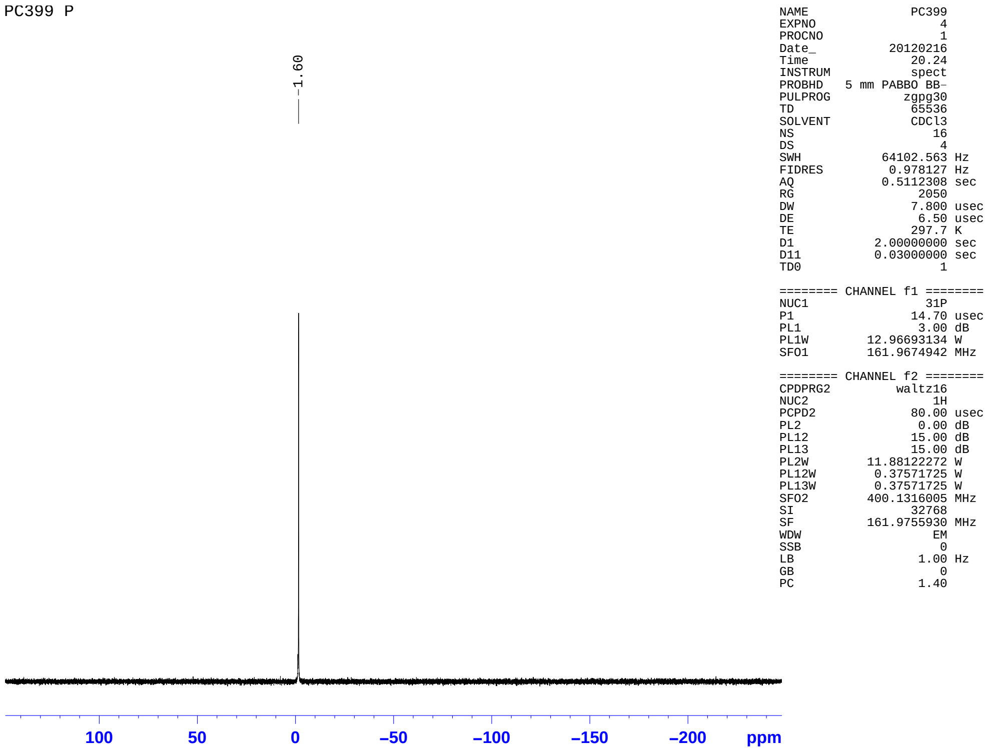
```
NAME               PC399
EXPNO                  6
PROCNO                 1
Date_           20120216
Time               20.28
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   161
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   203
DW                20.800 usec
DE                  6.50 usec
TE                 298.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127725 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

*N-Iso*butyl-2-(2’-diisopropylphosphinophenyl)indole (Table 6.2, entry 9)

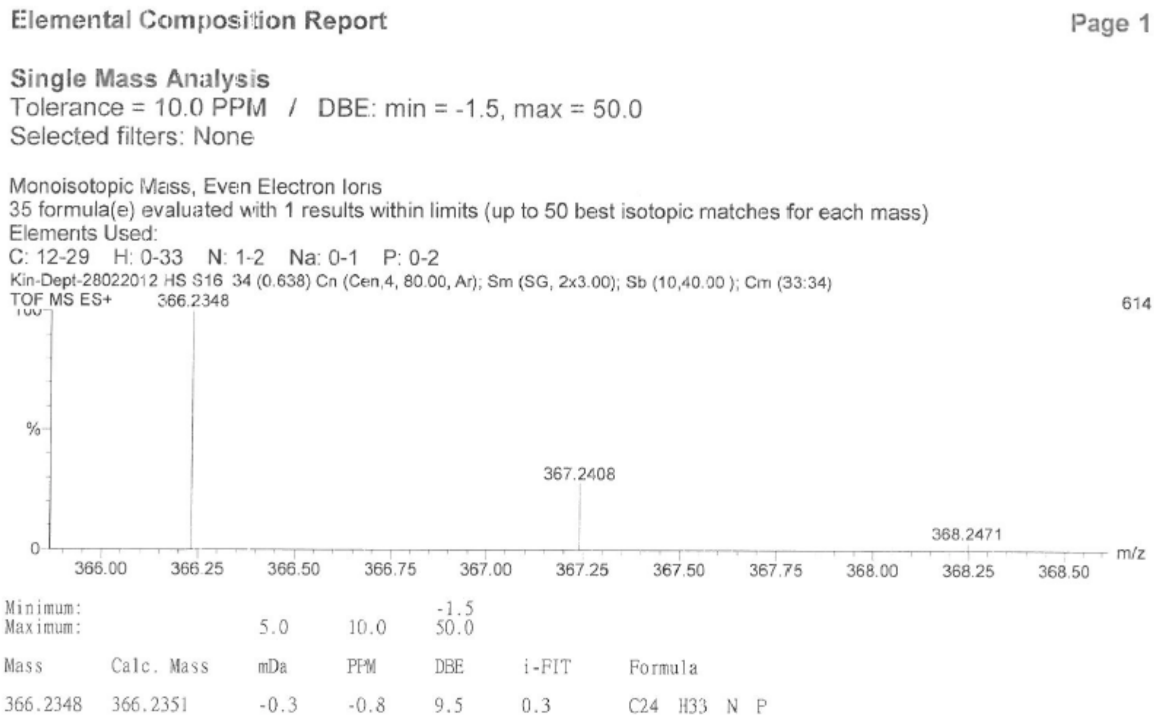




```
NAME                PC399
EXPNO                   4
PROCNO                  1
Date_            20120216
Time                20.24
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      4
SWH             64102.563 Hz
FIDRES           0.978127 Hz
AQ              0.5112308 sec
RG                   2050
DW                  7.800 usec
DE                   6.50 usec
TE                  297.7 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  31P
P1                  14.70 usec
PL1                  3.00 dB
PL1W          12.96693134 W
SFO1          161.9674942 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                15.00 dB
PL13                15.00 dB
PL2W          11.88122272 W
PL12W          0.37571725 W
PL13W          0.37571725 W
SFO2          400.1316005 MHz
SI                  32768
SF            161.9755930 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```



Elemental Composition Report

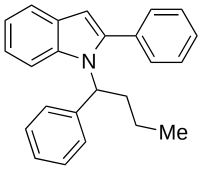
Page 1

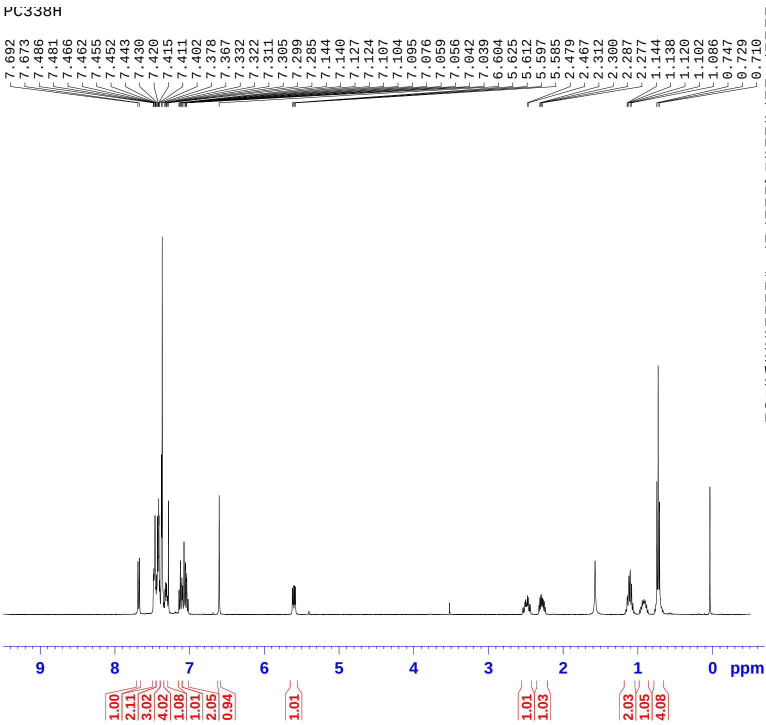
Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

Monoisotopic Mass, Even Electron Ions
35 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 12-29 H: 0-33 N: 1-2 Na: 0-1 P: 0-2
Kin-Dept-28022012 HS S16 34 (0.638) Cn (Cen,4, 80.00, Ar); Sm (SG, 2x3.00); Sb (10,40.00); Cm (33:34)
TOF MS ES+

Minimum:					-1.5		
Maximum:			5.0	10.0	50.0		
	Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
	366.2348	366.2351	-0.3	-0.8	9.5	0.3	C24 H33 N P

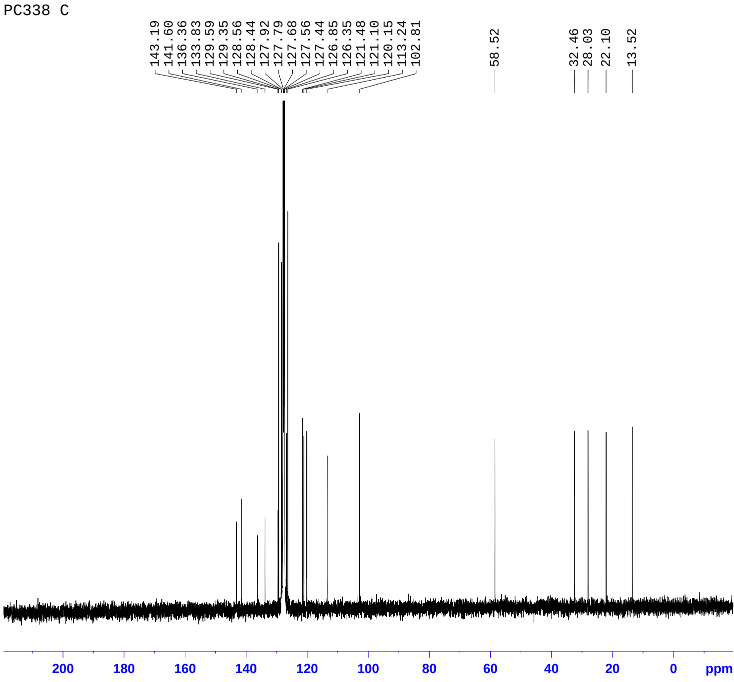
2-Phenyl-1-(1-phenylbutyl)-1*H*-indole (Scheme 6.3)





```
NAME                PC338
EXPNO                   1
PROCNO                  1
Date_            20111031
Time                15.07
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              4006.410 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                    161
DW                124.800 usec
DE                   6.50 usec
TE                  297.8 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.70 usec
PL1                  0.00 dB
PL1W          11.88122272 W
SFO1          400.1318007 MHz
SI                  32768
SF            400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

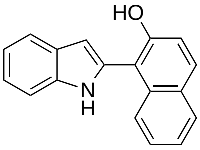


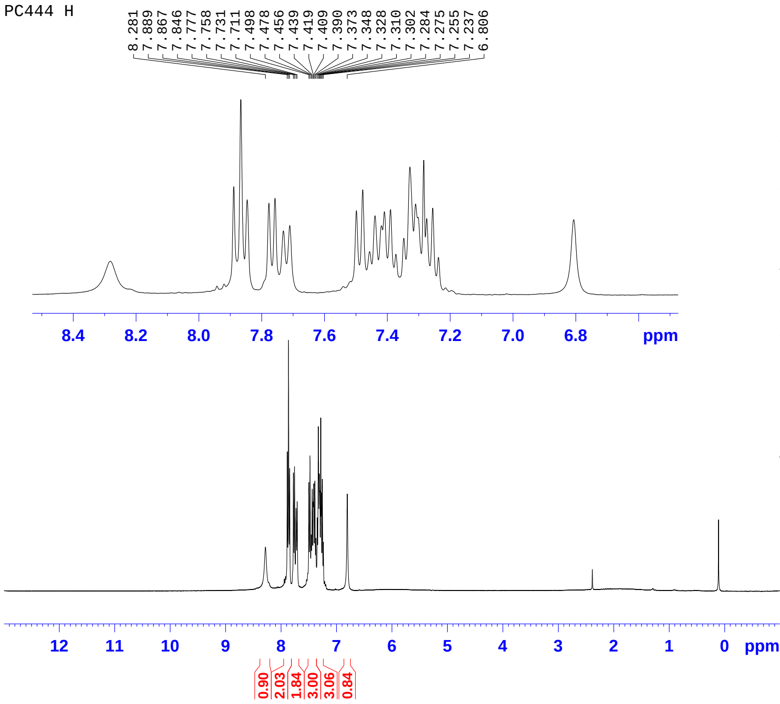
```
NAME                PC338
EXPNO                   6
PROCNO                  1
Date_            20111031
Time                19.14
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT              C6D6
NS                    210
DS                      2
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                    181
DW                 20.800 usec
DE                   6.50 usec
TE                  298.8 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.50 usec
PL1                 -2.00 dB
PL1W          58.52175522 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                15.00 dB
PL13                15.00 dB
PL2W          11.88122272 W
PL12W          0.37571725 W
PL13W          0.37571725 W
SFO2          400.1316005 MHz
SI                  32768
SF            100.6127690 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

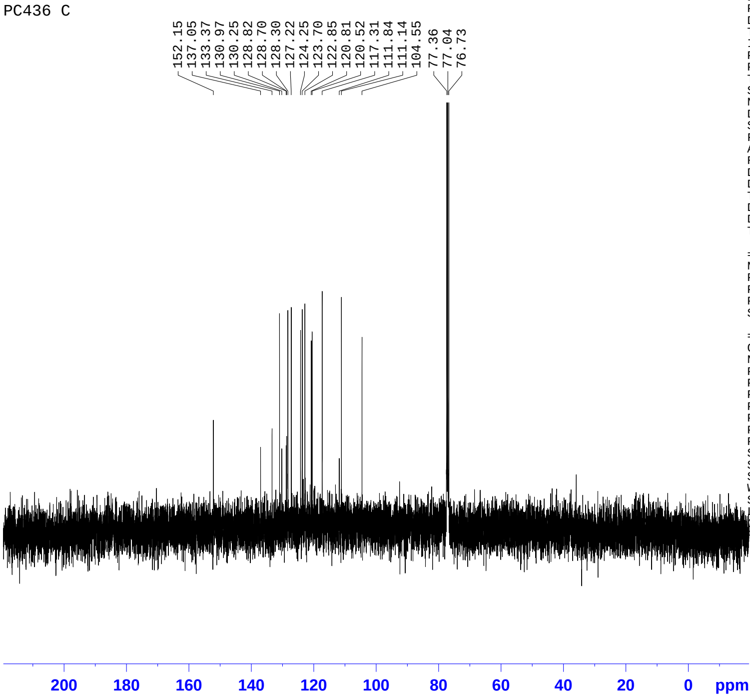
1-(1*H*-Indol-2-yl)naphthalen-2-ol (Scheme 6.4)





```
NAME                PC444
EXPNO                   1
PROCNO                  1
Date_            20121124
Time                19.40
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              5597.015 Hz
FIDRES           0.170807 Hz
AQ              2.9273248 sec
RG                    181
DW                 89.333 usec
DE                   6.50 usec
TE                  298.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.70 usec
PL1                  0.00 dB
PL1W          11.88122272 W
SFO1          400.1324008 MHz
SI                  32768
SF            400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

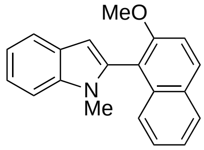


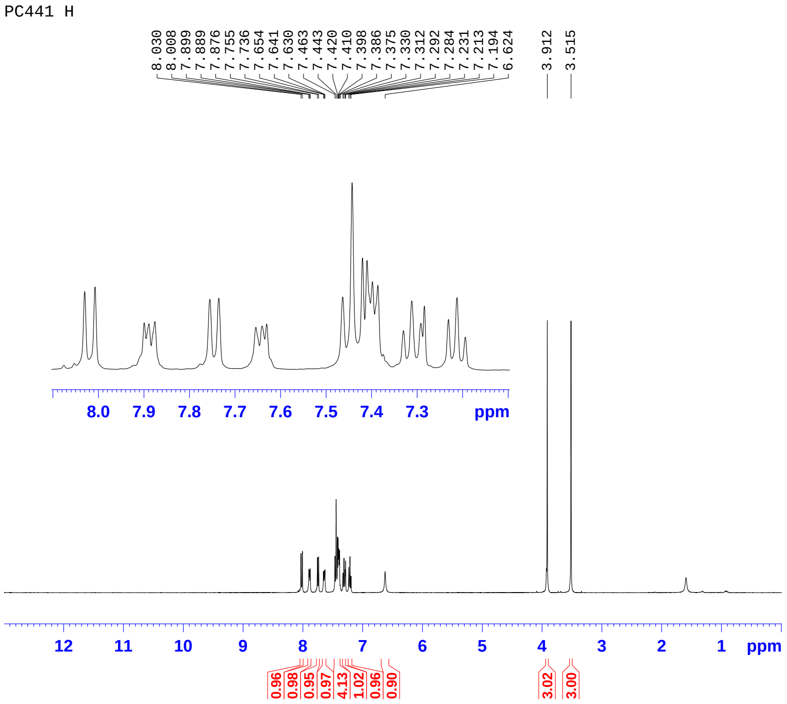
```
NAME                PC436
EXPNO                   2
PROCNO                  1
Date_            20121111
Time                19.27
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     25
DS                      2
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                    228
DW                 20.800 usec
DE                   6.50 usec
TE                  299.5 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.50 usec
PL1                 -2.00 dB
PL1W          58.52175522 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                15.00 dB
PL13                15.00 dB
PL2W          11.88122272 W
PL12W          0.37571725 W
PL13W          0.37571725 W
SFO2          400.1316005 MHz
SI                  32768
SF            100.6127690 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

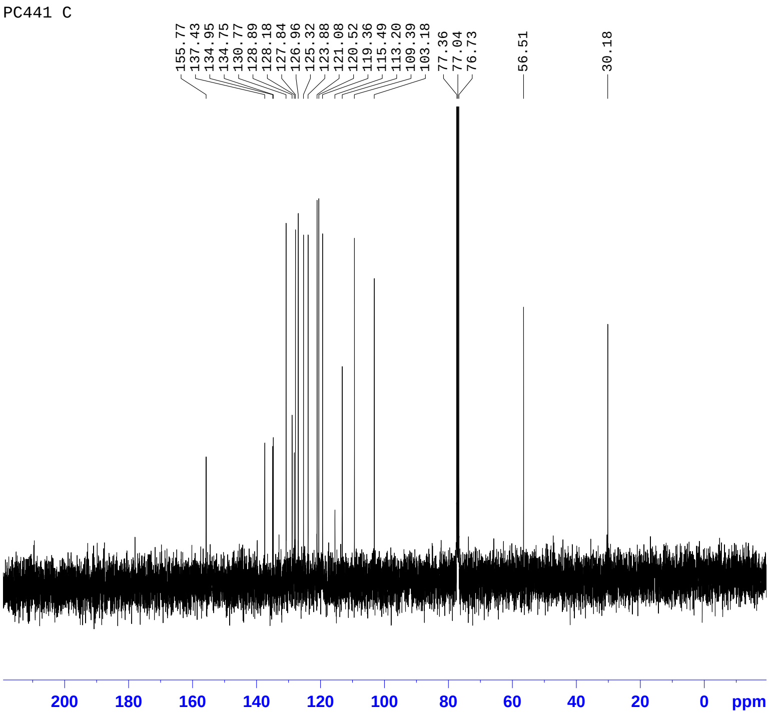
2-(2-Methoxynaphthalen-1-yl)-1-methyl-1*H*-indole (Scheme 6.5)





```
NAME                PC441
EXPNO                   3
PROCNO                  1
Date_            20121121
Time                21.10
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              5597.015 Hz
FIDRES           0.170807 Hz
AQ              2.9273248 sec
RG                    128
DW                 89.333 usec
DE                   6.50 usec
TE                  298.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.70 usec
PL1                  0.00 dB
PL1W          11.88122272 W
SFO1          400.1324008 MHz
SI                  32768
SF            400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

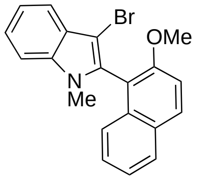


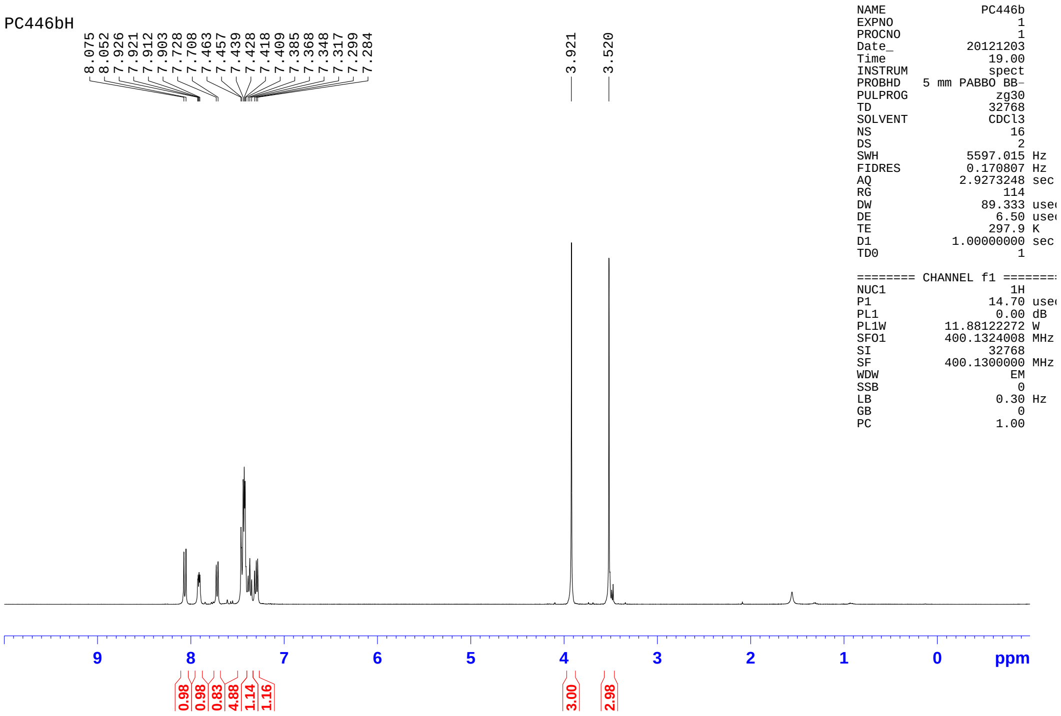
```
NAME                PC441
EXPNO                   4
PROCNO                  1
Date_            20121121
Time                21.14
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     56
DS                      2
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                    228
DW                 20.800 use
DE                   6.50 use
TE                  299.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 =======
NUC1                  13C
P1                   9.50 use
PL1                 -2.00 dB
PL1W          58.52175522 W
SFO1          100.6228298 MHz

======== CHANNEL f2 =======
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 use
PL2                  0.00 dB
PL12                15.00 dB
PL13                15.00 dB
PL2W          11.88122272 W
PL12W          0.37571725 W
PL13W          0.37571725 W
SFO2          400.1316005 MHz
SI                  32768
SF            100.6127690 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

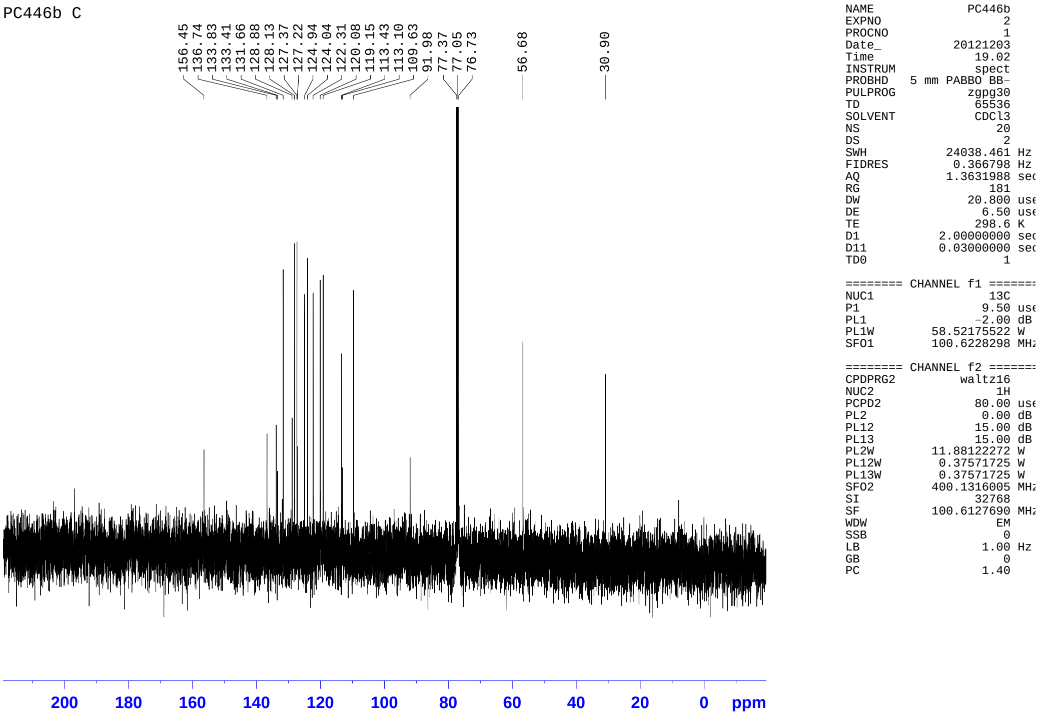
3-Bromo-2-(2-methoxynaphthalen-1-yl)-1-methyl-1*H*-indole (Scheme 6.5)





```
NAME              PC446b
EXPNO                  1
PROCNO                 1
Date_           20121203
Time               19.00
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             5597.015 Hz
FIDRES          0.170807 Hz
AQ             2.9273248 sec
RG                   114
DW                89.333 use
DE                  6.50 use
TE                 297.9 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 =======
NUC1                  1H
P1                 14.70 use
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1324008 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

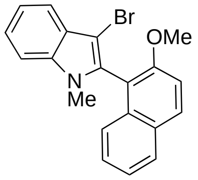


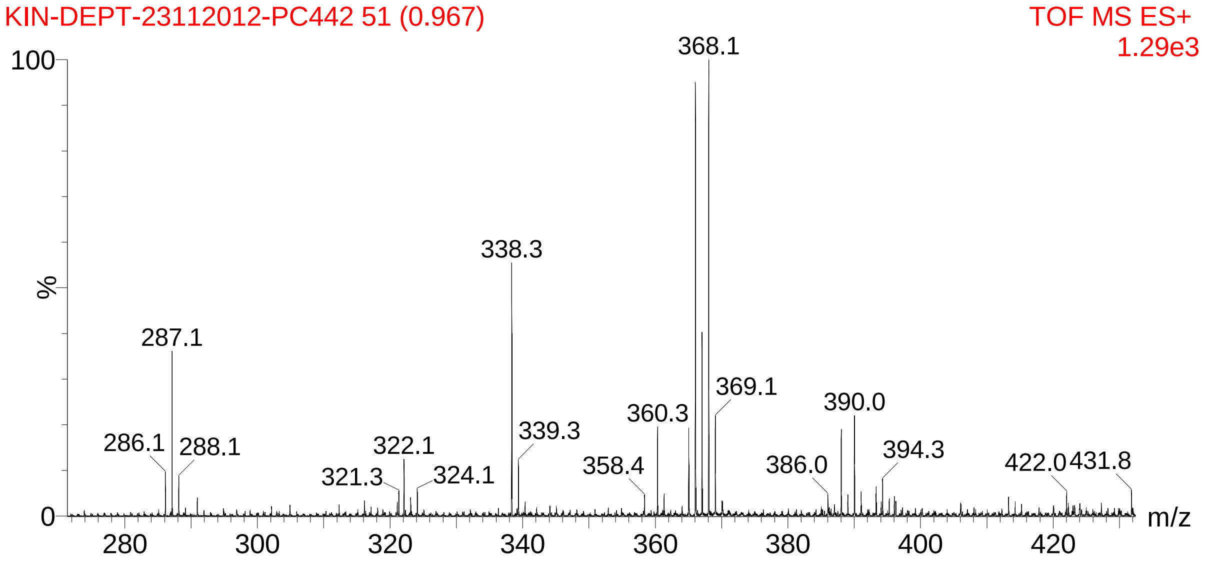
```
NAME              PC446b
EXPNO                  2
PROCNO                 1
Date_           20121203
Time               19.02
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    20
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 se
RG                   181
DW                20.800 us
DE                  6.50 us
TE                 298.6 K
D1            2.00000000 se
D11           0.03000000 se
TD0                    1

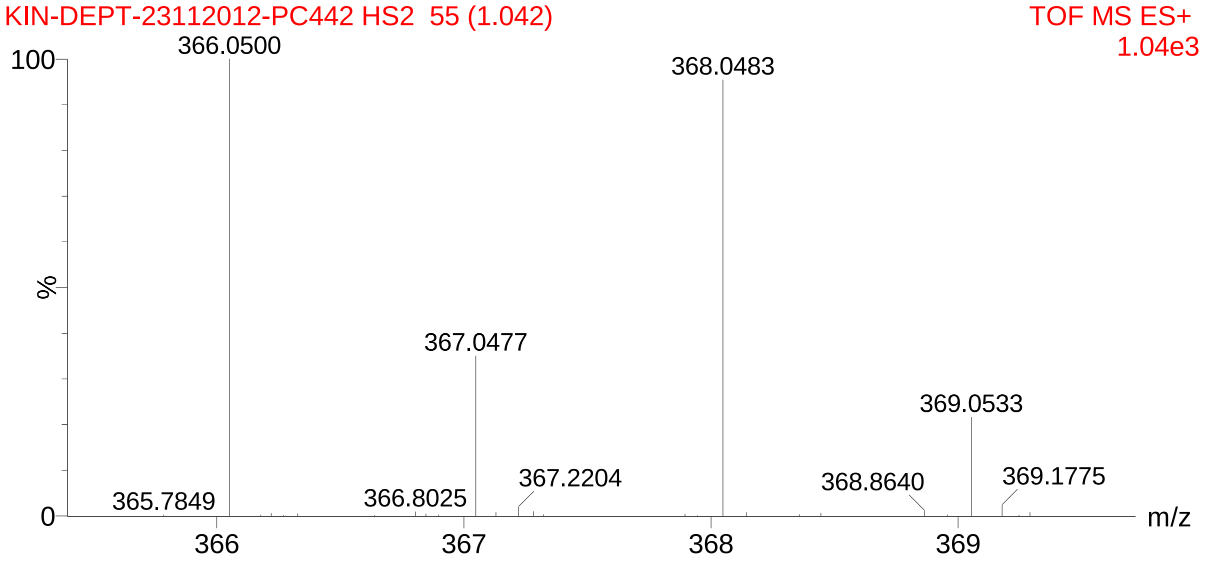
======== CHANNEL f1 ======
NUC1                 13C
P1                  9.50 us
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MH

======== CHANNEL f2 ======
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 us
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MH
SI                 32768
SF           100.6127690 MH
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

3-Bromo-2-(2-methoxynaphthalen-1-yl)-1-methyl-1*H*-indole (Scheme 6.5)

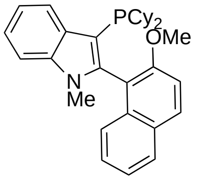


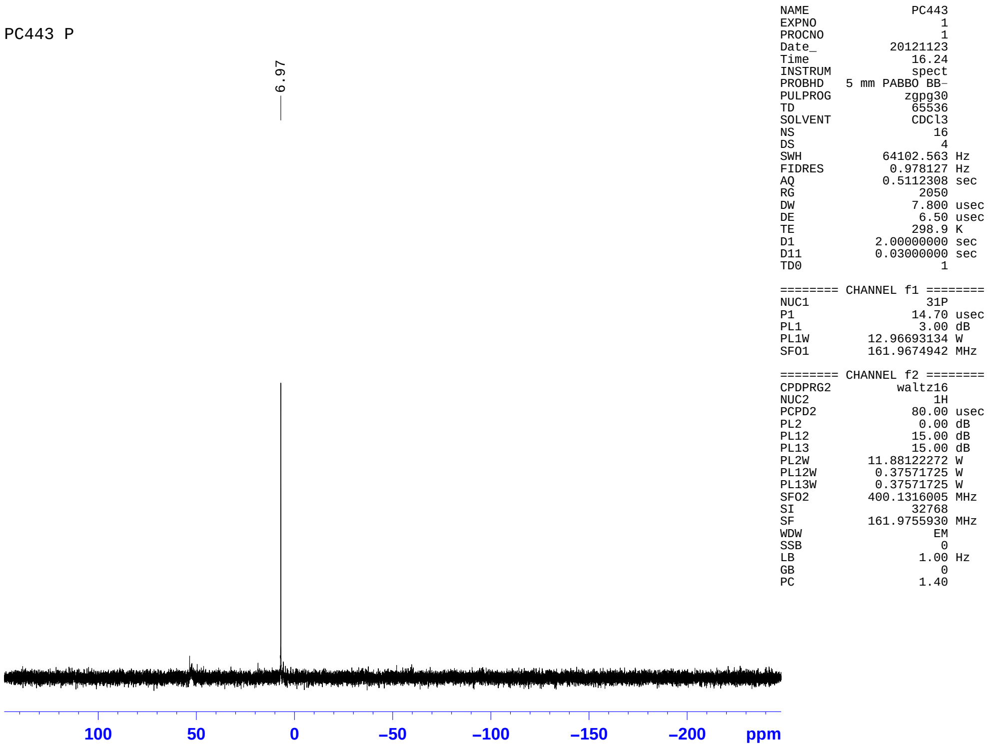




Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
366.0500	366.0494	0.6	1.6	12.5	23.0	C20 H17 N O Br

3-(Dicyclohexylphosphino)-2-(2-methoxynaphthalen-1-yl)-1-methyl-1*H*-indole (Scheme 6.5)

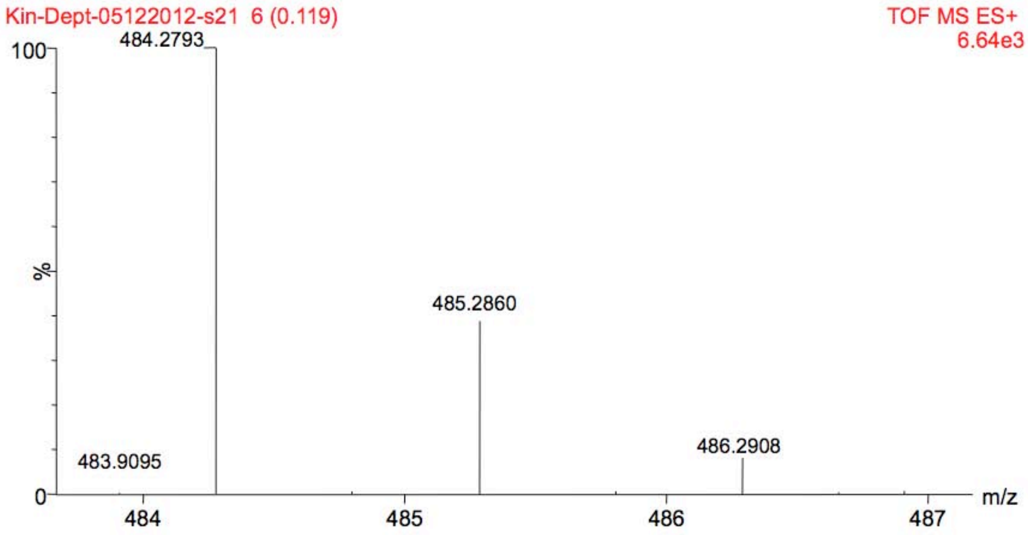




```
NAME               PC443
EXPNO                  1
PROCNO                 1
Date_           20121123
Time               16.24
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     4
SWH            64102.563 Hz
FIDRES          0.978127 Hz
AQ             0.5112308 sec
RG                  2050
DW                 7.800 usec
DE                  6.50 usec
TE                 298.9 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

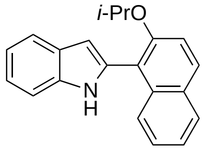
======== CHANNEL f1 ========
NUC1                 31P
P1                 14.70 usec
PL1                 3.00 dB
PL1W         12.96693134 W
SFO1         161.9674942 MHz

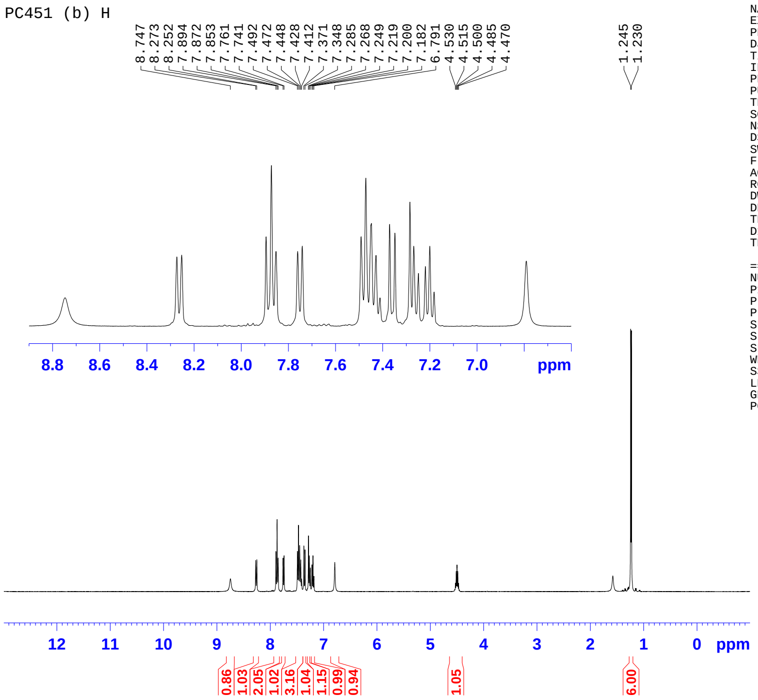
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           161.9755930 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
484.2793	484.2769	2.4	5.0	14.5	11.1	C32 H39 N O P

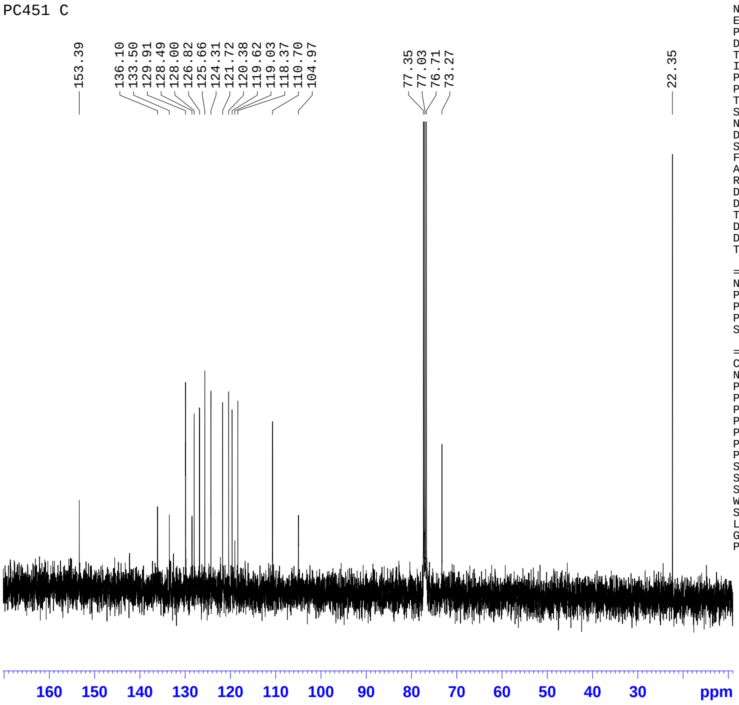
2-(2-Isopropoxynaphthalen-1-yl)-1*H*-indole (Scheme 6.5)





```
NAME               PC451
EXPNO                  1
PROCNO                 1
Date_           20130103
Time               14.14
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             5597.015 Hz
FIDRES          0.170807 Hz
AQ             2.9273248 sec
RG                   161
DW                89.333 usec
DE                  6.50 usec
TE                 298.3 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1324008 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

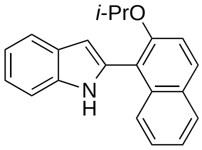


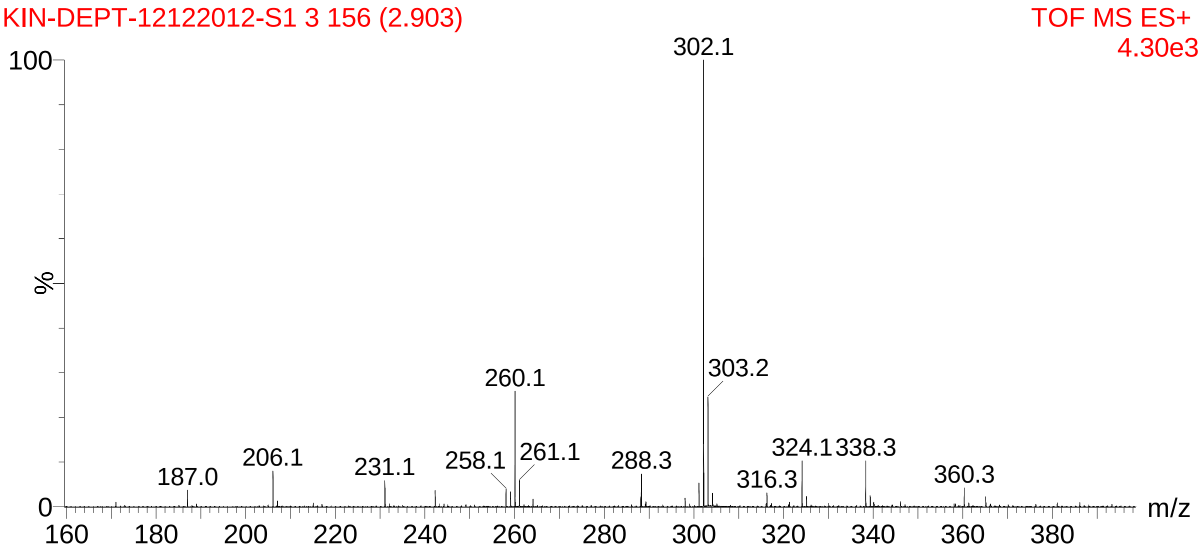
```
NAME               PC451
EXPNO                  2
PROCNO                 1
Date_           20130103
Time               14.16
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    71
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   228
DW                20.800 usec
DE                  6.50 usec
TE                 298.8 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

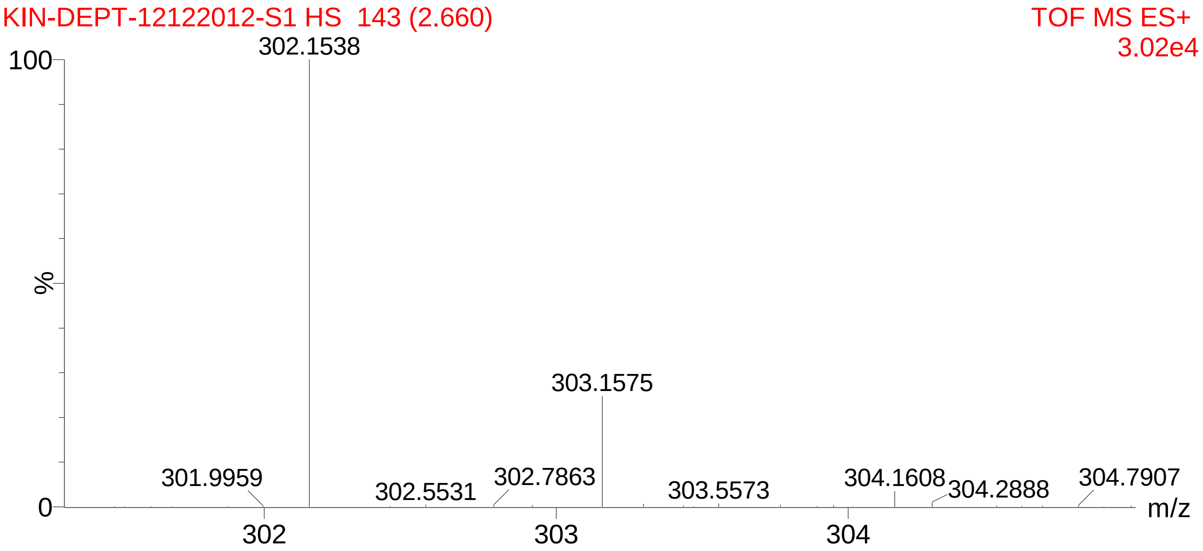
======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127690 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

2-(2-Isopropoxynaphthalen-1-yl)-1*H*-indole (Scheme 6.5)

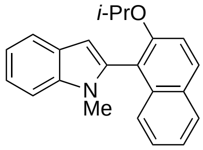


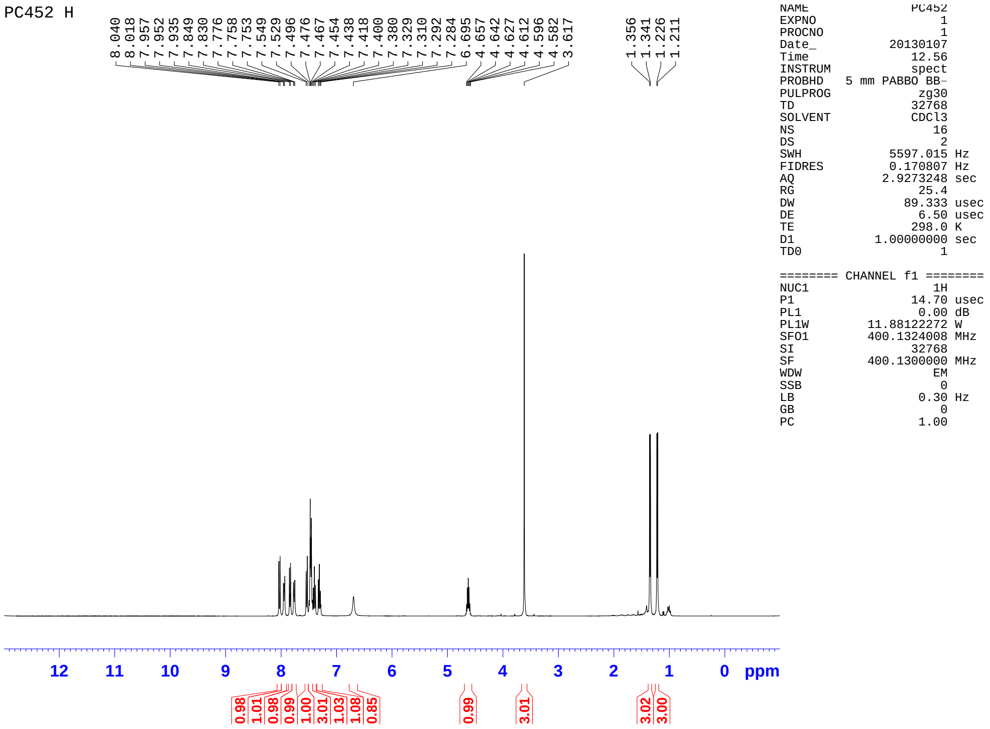




Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
302.1538	302.1545	-0.7	-2.3	12.5	12.1	C21 H20 N O

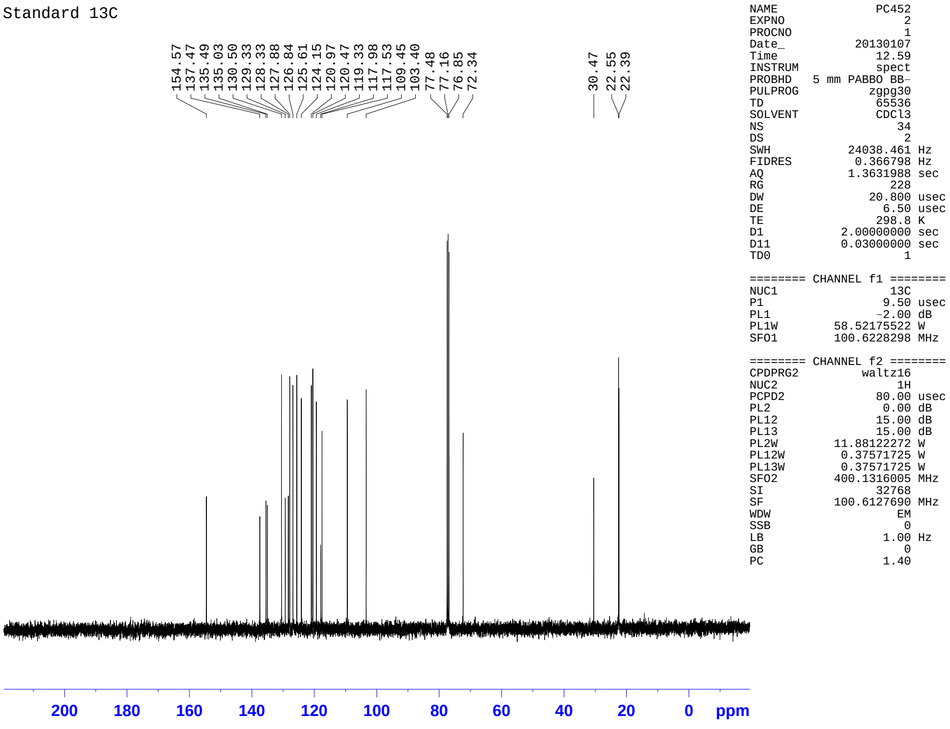
2-(2-Isopropoxynaphthalen-1-yl)-1-methyl-1*H*-indole (Scheme 6.5)





```
NAME                PC452
EXPNO                   1
PROCNO                  1
Date_            20130107
Time                12.56
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              5597.015 Hz
FIDRES           0.170807 Hz
AQ              2.9273248 sec
RG                   25.4
DW                 89.333 usec
DE                   6.50 usec
TE                  298.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.70 usec
PL1                  0.00 dB
PL1W          11.88122272 W
SFO1          400.1324008 MHz
SI                  32768
SF            400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

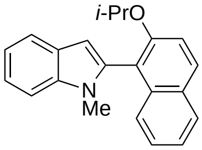


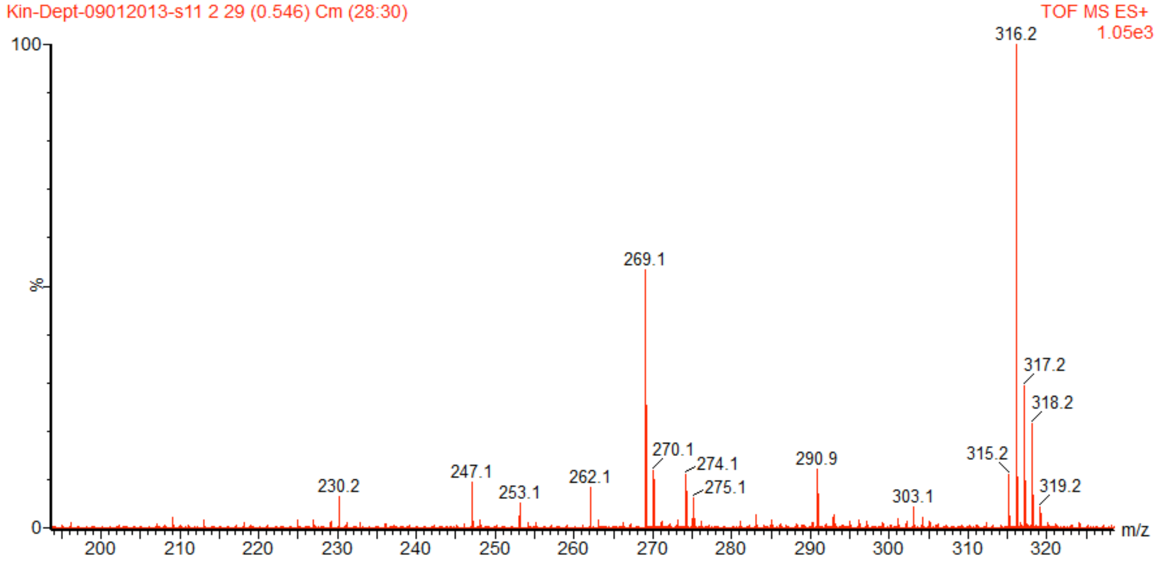
```
NAME                PC452
EXPNO                   2
PROCNO                  1
Date_            20130107
Time                12.59
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     34
DS                      2
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                    228
DW                 20.800 usec
DE                   6.50 usec
TE                  298.8 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

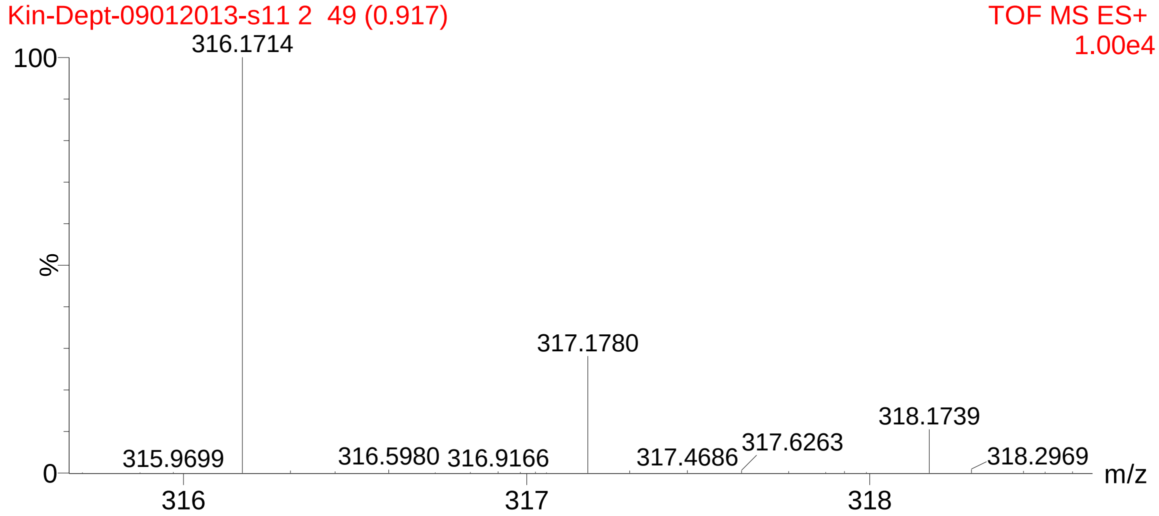
======== CHANNEL f1 ========
NUC1                  13C
P1                   9.50 usec
PL1                 -2.00 dB
PL1W          58.52175522 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                15.00 dB
PL13                15.00 dB
PL2W          11.88122272 W
PL12W          0.37571725 W
PL13W          0.37571725 W
SFO2          400.1316005 MHz
SI                  32768
SF            100.6127690 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

2-(2-Isopropoxynaphthalen-1-yl)-1-methyl-1*H*-indole (Scheme 6.5)

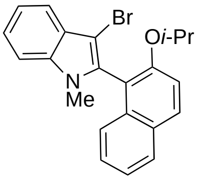


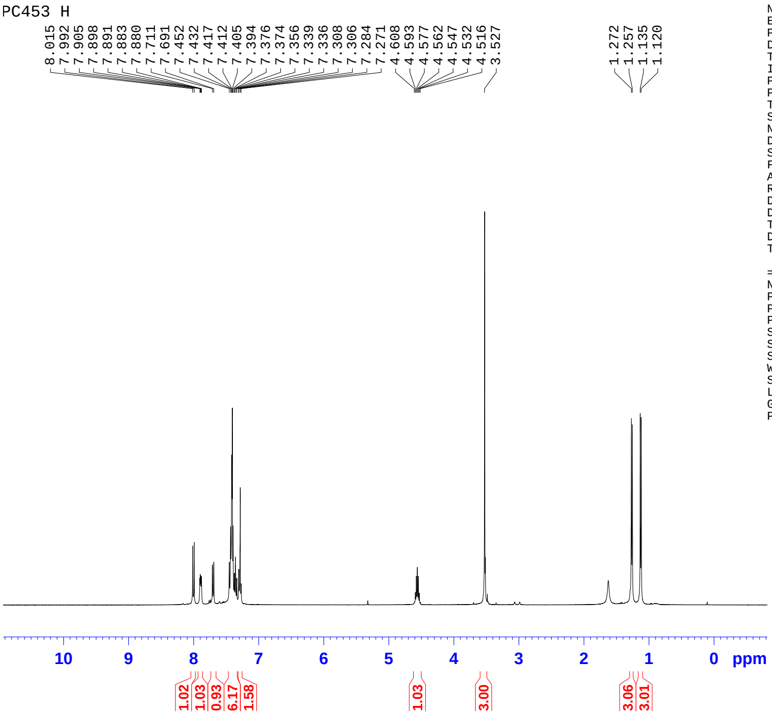




Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
316.1714	316.1701	1.3	4.1	12.5	257.3	C22 H22 N O

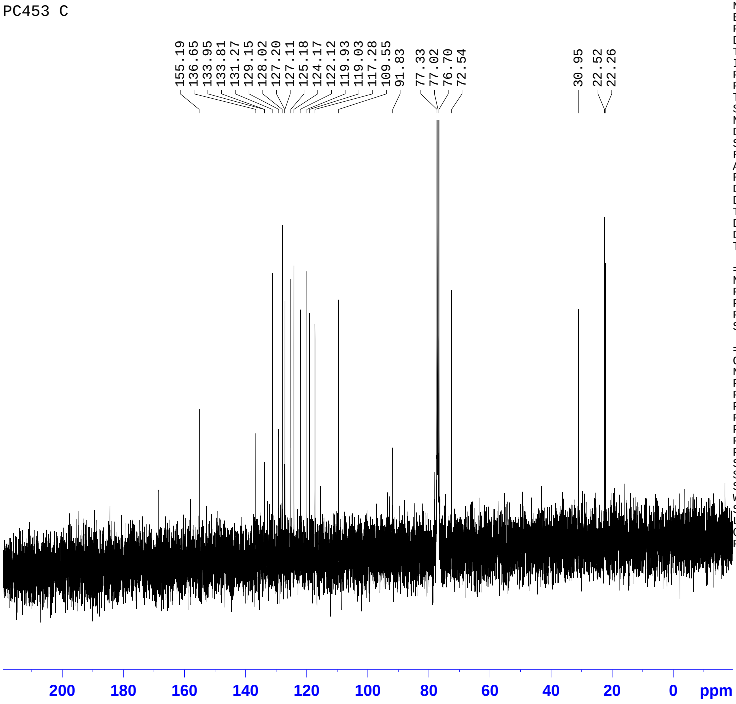
3-Bromo-2-(2-isopropoxynaphthalen-1-yl)-1-methyl-1*H*-indole (Scheme 6.5)





```
NAME              PC453
EXPNO                 1
PROCNO                1
Date_          20130108
Time              20.00
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            5597.015 Hz
FIDRES         0.170807 Hz
AQ            2.9273248 sec
RG                  203
DW               89.333 usec
DE                 6.50 usec
TE                298.3 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.70 usec
PL1                0.00 dB
PL1W        11.88122272 W
SFO1        400.1324008 MHz
SI                32768
SF          400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

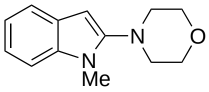


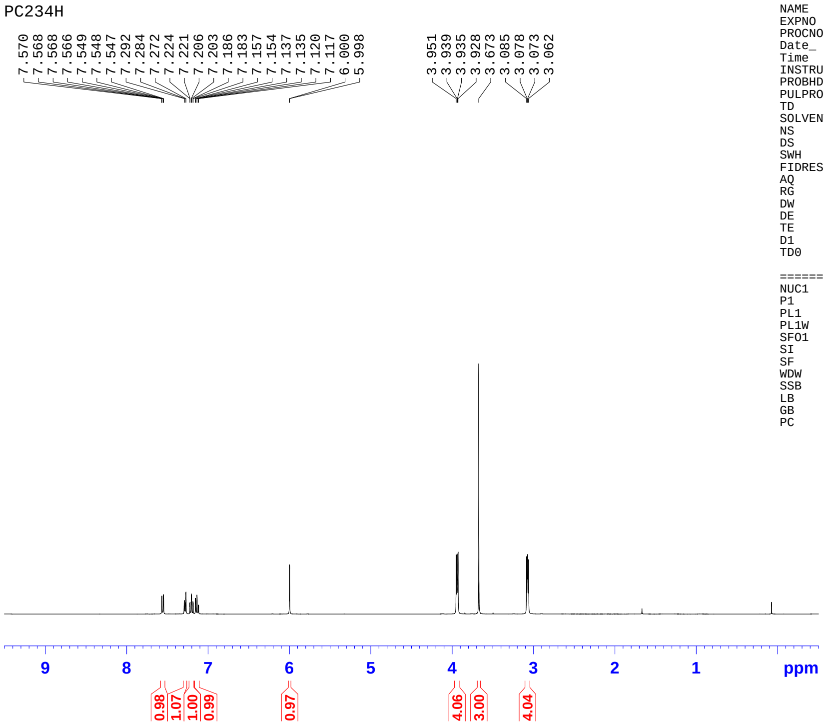
```
NAME              PC453
EXPNO                 2
PROCNO                1
Date_          20130108
Time              20.08
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  124
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                 90.5
DW               20.800 usec
DE                 6.50 usec
TE                299.6 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.50 usec
PL1               -2.00 dB
PL1W        58.52175522 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL13              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
PL13W        0.37571725 W
SFO2        400.1316005 MHz
SI                32768
SF          100.6127690 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

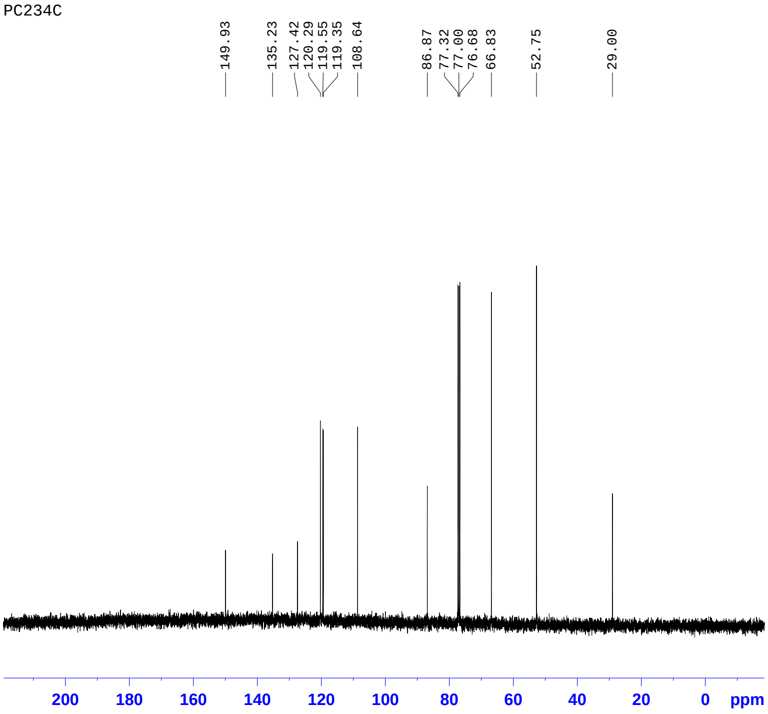
4-(1-Methyl-1*H*-indol-2-yl)morpholine (Table 6.4, entry 1)





```
NAME               PC234
EXPNO                  1
PROCNO                 1
Date_           20101227
Time               21.39
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  40.3
DW               124.800 usec
DE                  6.50 usec
TE                 295.5 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

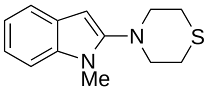


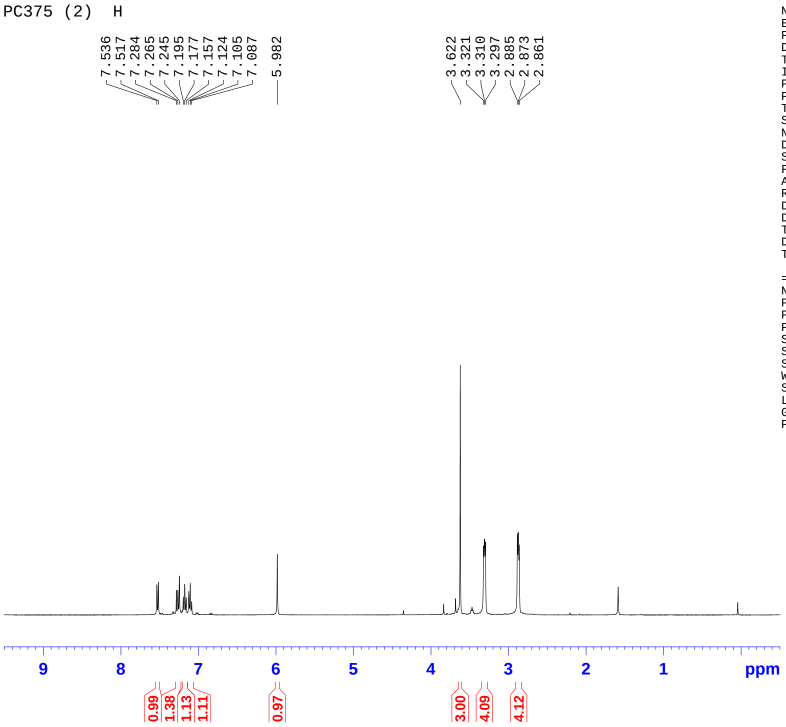
```
NAME               PC234
EXPNO                  2
PROCNO                 1
Date_           20101227
Time               21.43
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   203
DW                20.800 usec
DE                  6.50 usec
TE                 296.5 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127794 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

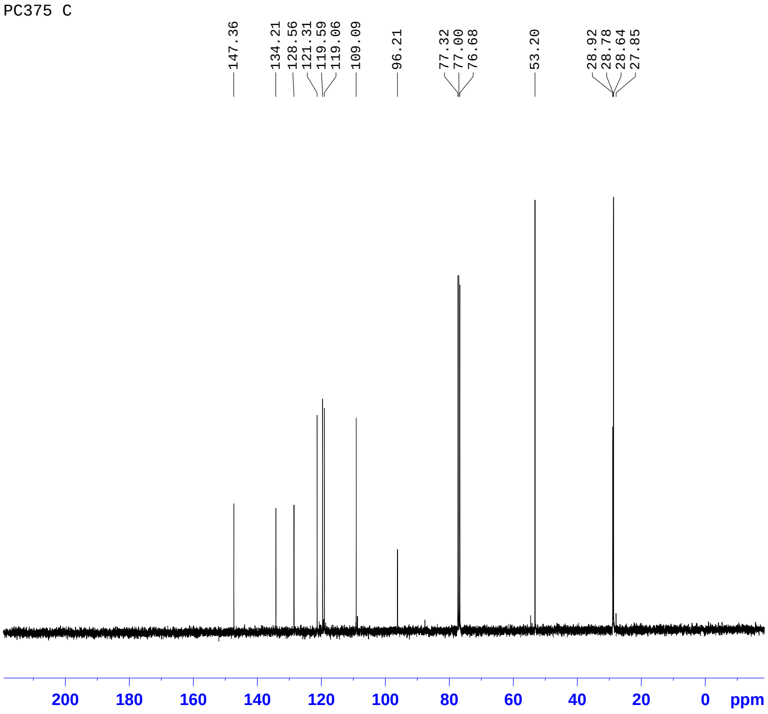
4-(1-Methyl-1*H*-indol-2-yl)thiomorpholine (Table 6.4, entry 2)





```
NAME               PC375
EXPNO                  3
PROCNO                 1
Date_           20120106
Time               15.27
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                   114
DW               124.800 usec
DE                  6.50 usec
TE                 296.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

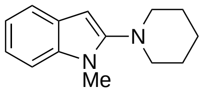


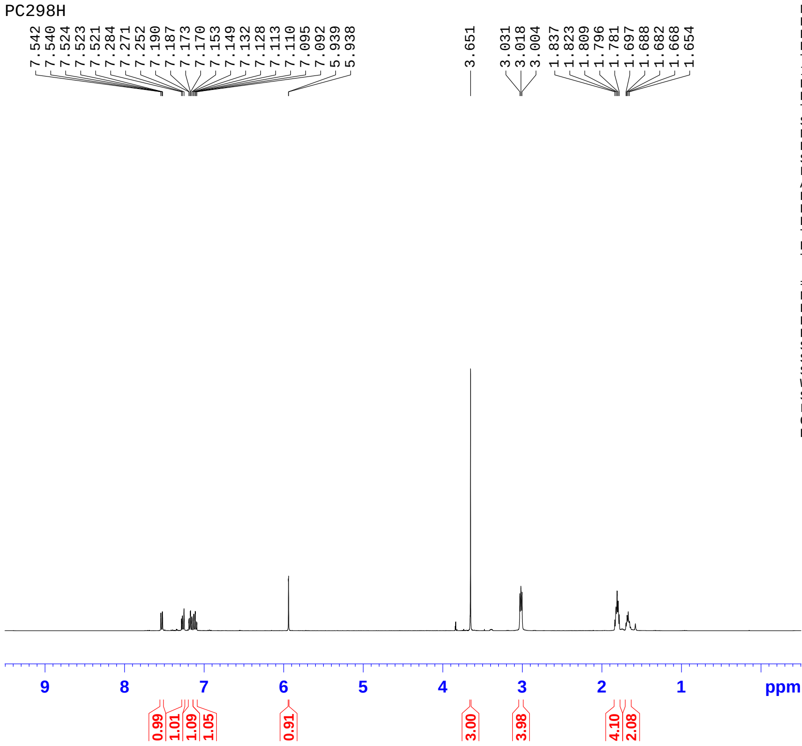
```
NAME               PC375
EXPNO                  2
PROCNO                 1
Date_           20120105
Time               10.56
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    59
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   181
DW                20.800 usec
DE                  6.50 usec
TE                 296.5 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127812 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

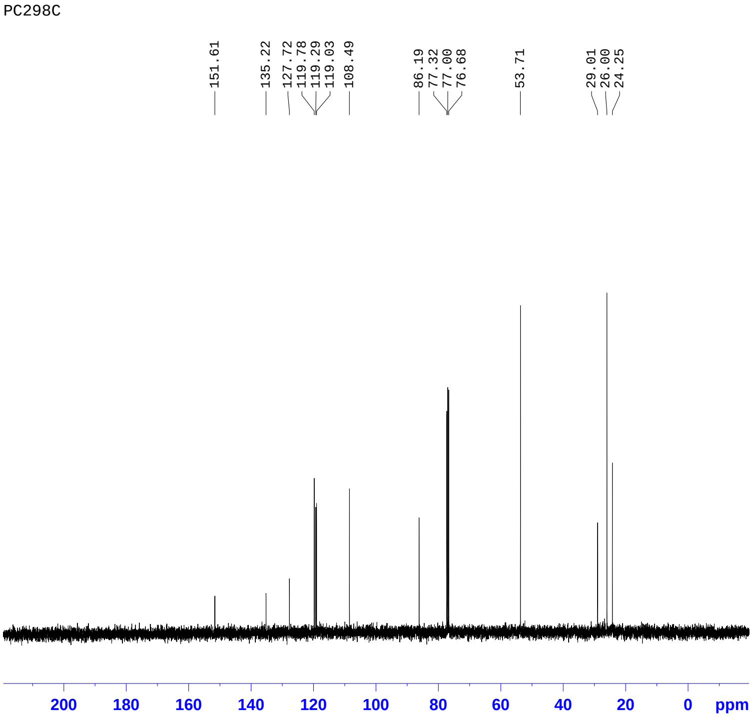
1-Methyl-2-(piperidin-1-yl)-1*H*-indole (Table 6.4, entry 3)





```
NAME                PC298
EXPNO                   3
PROCNO                  1
Date_            20110518
Time                15.28
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              4006.410 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                   25.4
DW                124.800 usec
DE                   6.50 usec
TE                  298.1 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.70 usec
PL1                  0.00 dB
PL1W          11.88122272 W
SFO1          400.1318007 MHz
SI                  32768
SF            400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

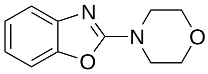


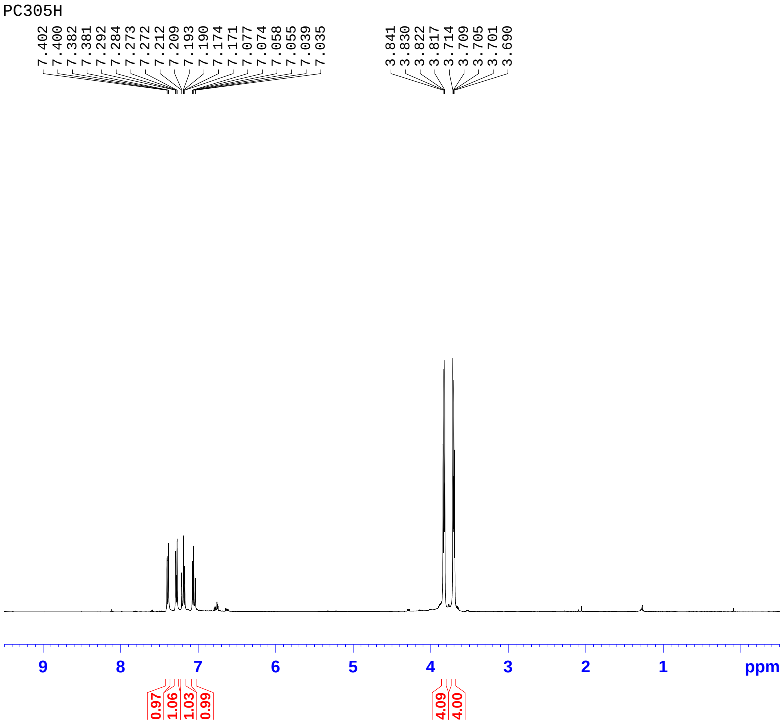
```
NAME                PC298
EXPNO                   4
PROCNO                  1
Date_            20110518
Time                15.32
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                    144
DW                 20.800 usec
DE                   6.50 usec
TE                  298.8 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.50 usec
PL1                 -2.00 dB
PL1W          58.52175522 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                15.00 dB
PL13                15.00 dB
PL2W          11.88122272 W
PL12W          0.37571725 W
PL13W          0.37571725 W
SFO2          400.1316005 MHz
SI                  32768
SF            100.6127767 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

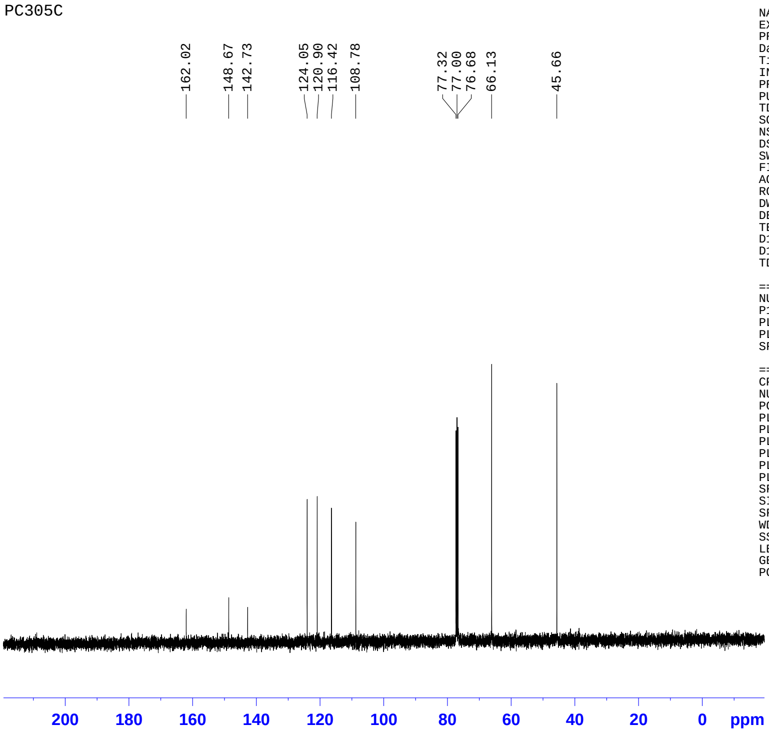
2-Morpholinobenzo[*d*]oxazole (Table 6.4, entry 4)





```
NAME               PC305
EXPNO                  1
PROCNO                 1
Date_           20110520
Time               20.12
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  25.4
DW               124.800 usec
DE                  6.50 usec
TE                 298.3 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

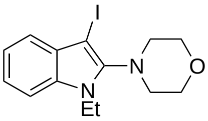


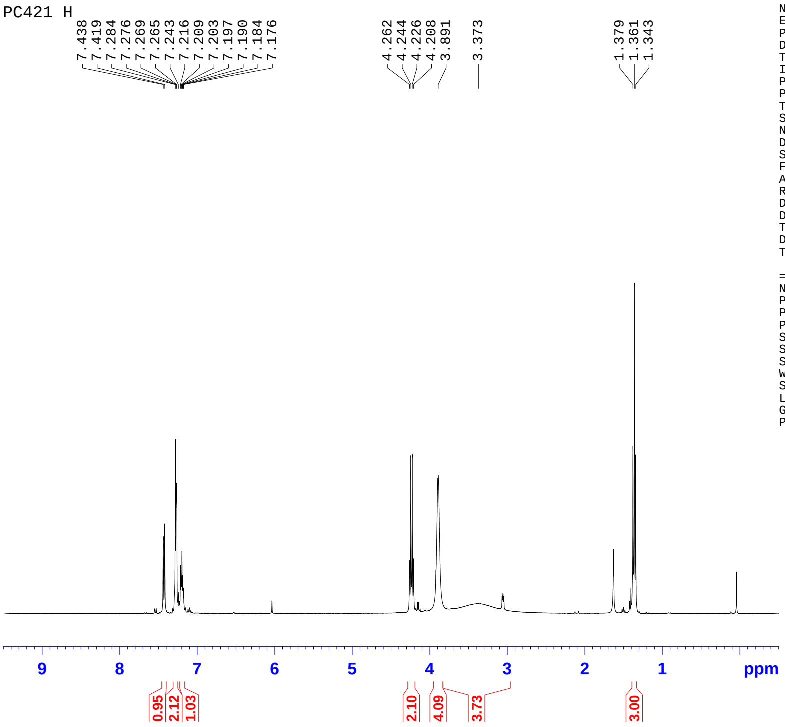
```
NAME               PC305
EXPNO                  2
PROCNO                 1
Date_           20110520
Time               20.15
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   101
DW                20.800 usec
DE                  6.50 usec
TE                 299.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127758 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

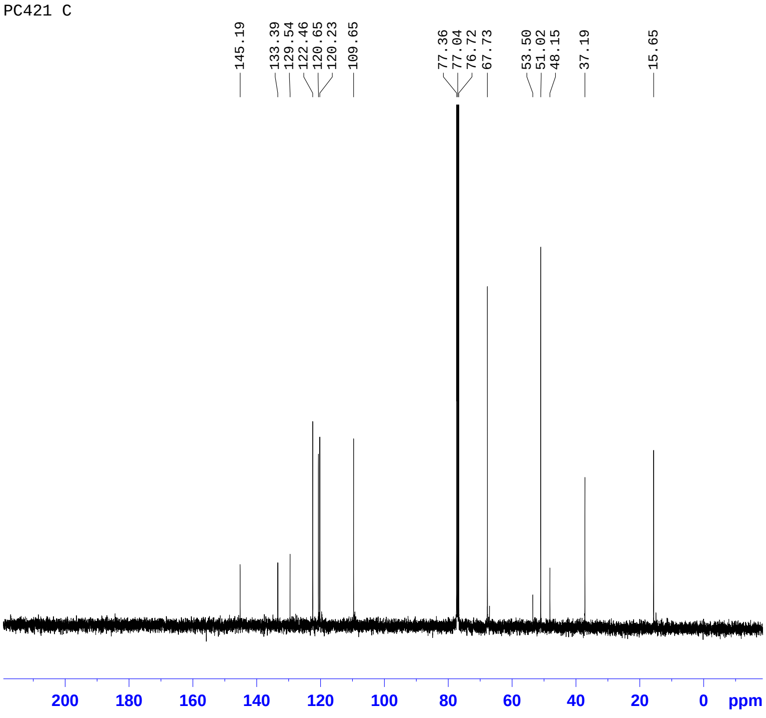
4-(1-Ethyl-3-iodo-1*H*-indol-2-yl)morpholine (Scheme 6.6)





```
NAME              PC421
EXPNO                 1
PROCNO                1
Date_          20120601
Time              18.23
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            4006.410 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                 90.5
DW              124.800 usec
DE                 6.50 usec
TE                299.1 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.70 usec
PL1                0.00 dB
PL1W        11.88122272 W
SFO1        400.1318007 MHz
SI                32768
SF          400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

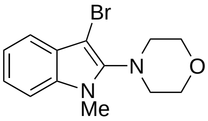


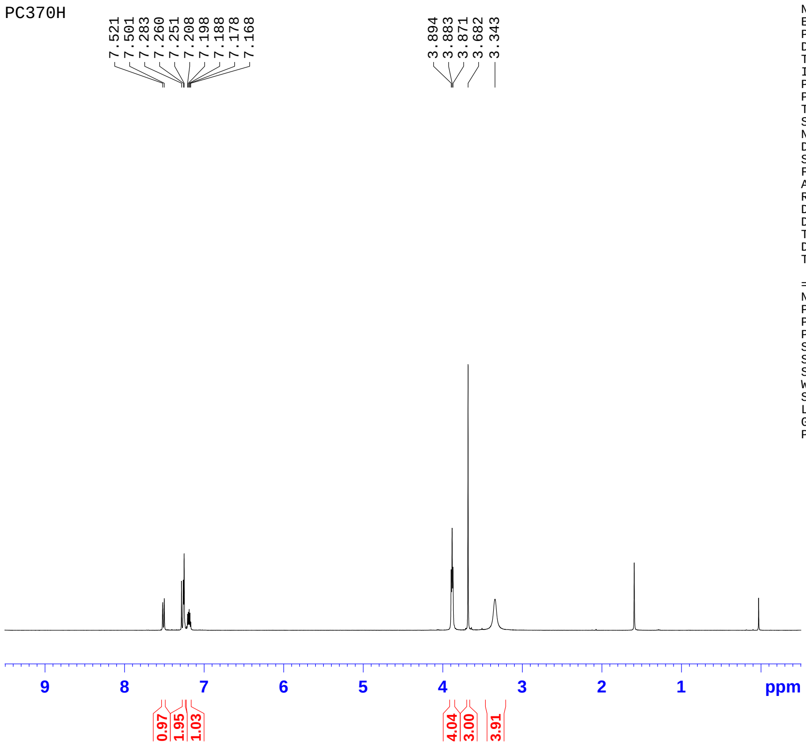
```
NAME              PC421
EXPNO                 2
PROCNO                1
Date_          20120601
Time              18.26
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                  120
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                  101
DW               20.800 usec
DE                 6.50 usec
TE                300.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.50 usec
PL1               -2.00 dB
PL1W        58.52175522 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL13              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
PL13W        0.37571725 W
SFO2        400.1316005 MHz
SI                32768
SF          100.6127690 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

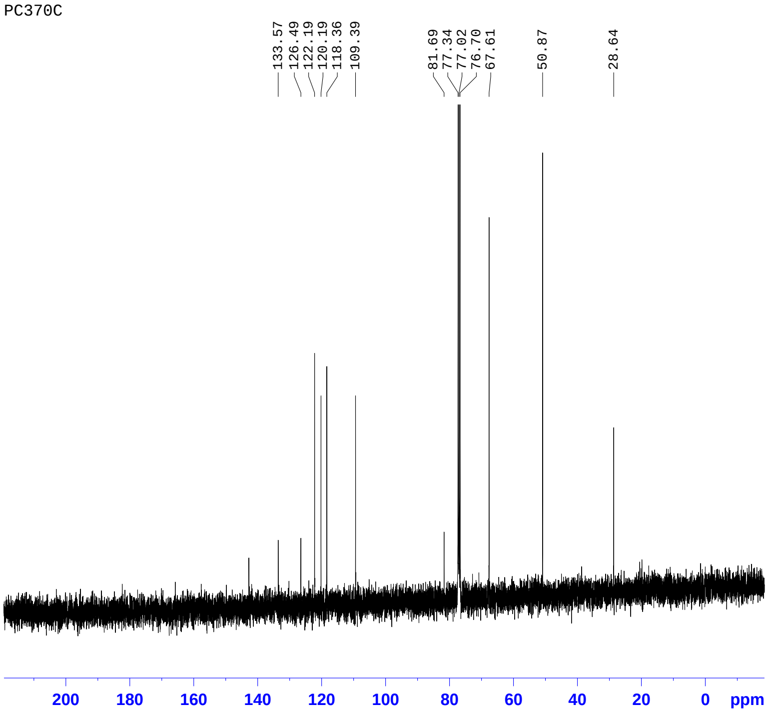
4-(3-Bromo-1-methyl-1*H*-indol-2-yl)morpholine (Scheme 6.7)





```
NAME                PC370
EXPNO                   1
PROCNO                  1
Date_            20111219
Time                19.30
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              4006.410 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                    203
DW                124.800 usec
DE                   6.50 usec
TE                  298.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.70 usec
PL1                  0.00 dB
PL1W          11.88122272 W
SFO1          400.1318007 MHz
SI                  32768
SF            400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

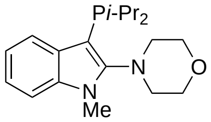


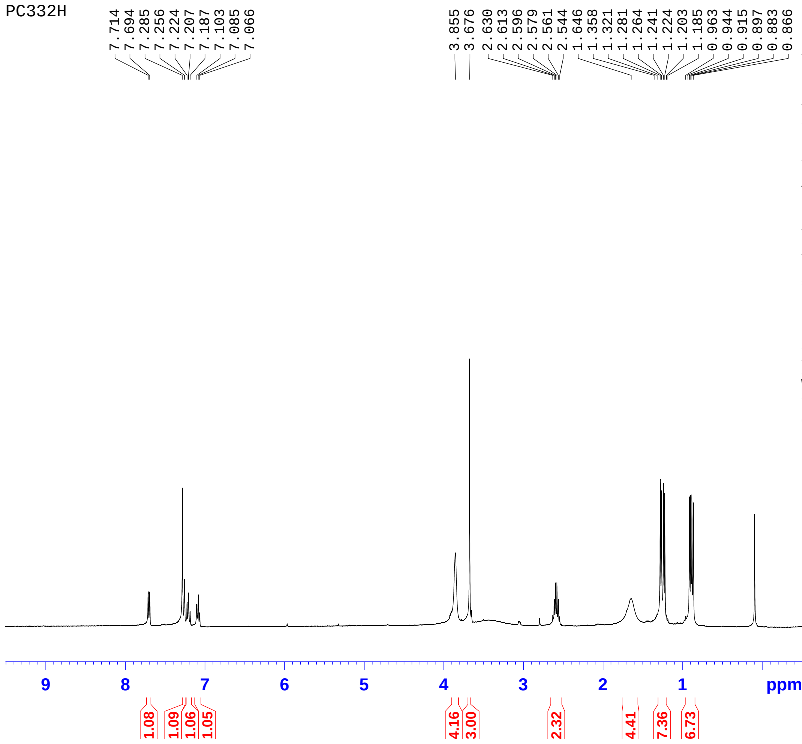
```
NAME                PC370
EXPNO                   2
PROCNO                  1
Date_            20111219
Time                19.38
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    167
DS                      2
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                    203
DW                 20.800 usec
DE                   6.50 usec
TE                  299.1 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.50 usec
PL1                 -2.00 dB
PL1W          58.52175522 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                15.00 dB
PL13                15.00 dB
PL2W          11.88122272 W
PL12W          0.37571725 W
PL13W          0.37571725 W
SFO2          400.1316005 MHz
SI                  32768
SF            100.6127690 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

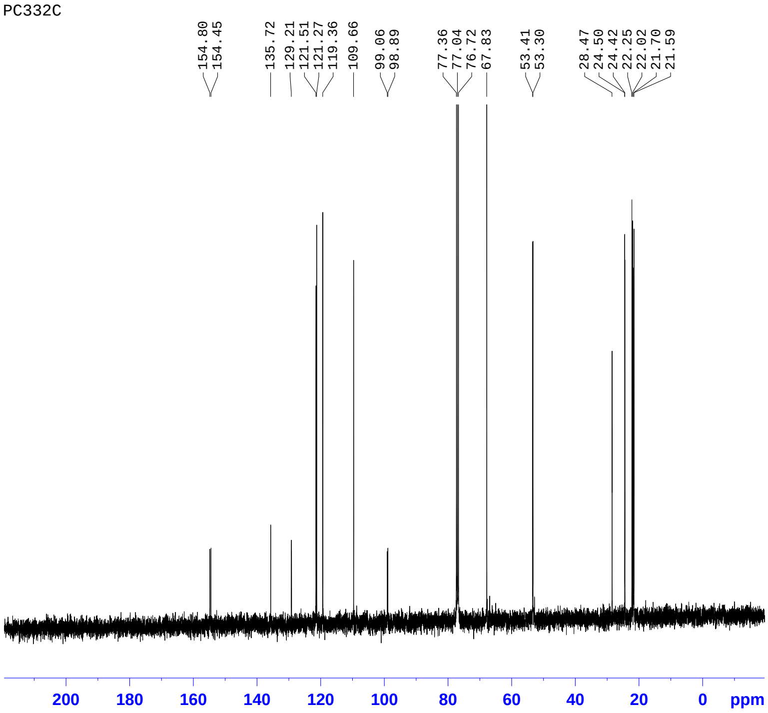
4-(3-(Diisopropylphosphino)-1-methyl-1*H*-indol-2-yl)morpholine (Scheme 6.8)





```
NAME                PC332
EXPNO                   1
PROCNO                  1
Date_            20111017
Time                17.18
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              4006.410 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                    144
DW                124.800 usec
DE                   6.50 usec
TE                  297.3 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.70 usec
PL1                  0.00 dB
PL1W          11.88122272 W
SFO1          400.1318007 MHz
SI                  32768
SF            400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

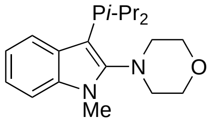


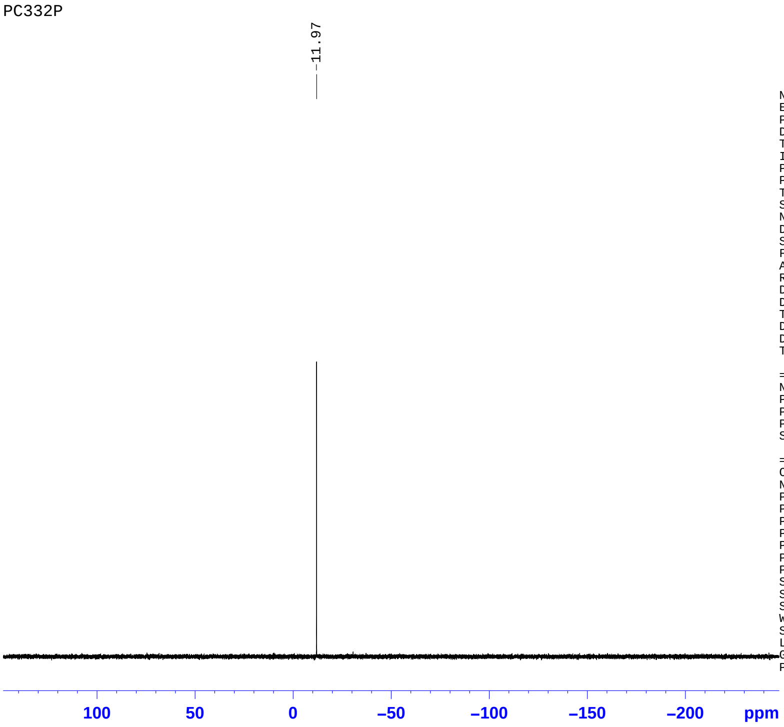
```
NAME                PC332
EXPNO                  10
PROCNO                  1
Date_            20111018
Time                15.20
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    194
DS                      2
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                    203
DW                 20.800 usec
DE                   6.50 usec
TE                  298.6 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.50 usec
PL1                 -2.00 dB
PL1W          58.52175522 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                15.00 dB
PL13                15.00 dB
PL2W          11.88122272 W
PL12W          0.37571725 W
PL13W          0.37571725 W
SFO2          400.1316005 MHz
SI                  32768
SF            100.6127690 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

4-(3-(Diisopropylphosphino)-1-methyl-1*H*-indol-2-yl)morpholine (Scheme 6.8)



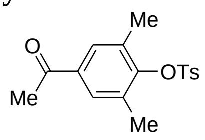


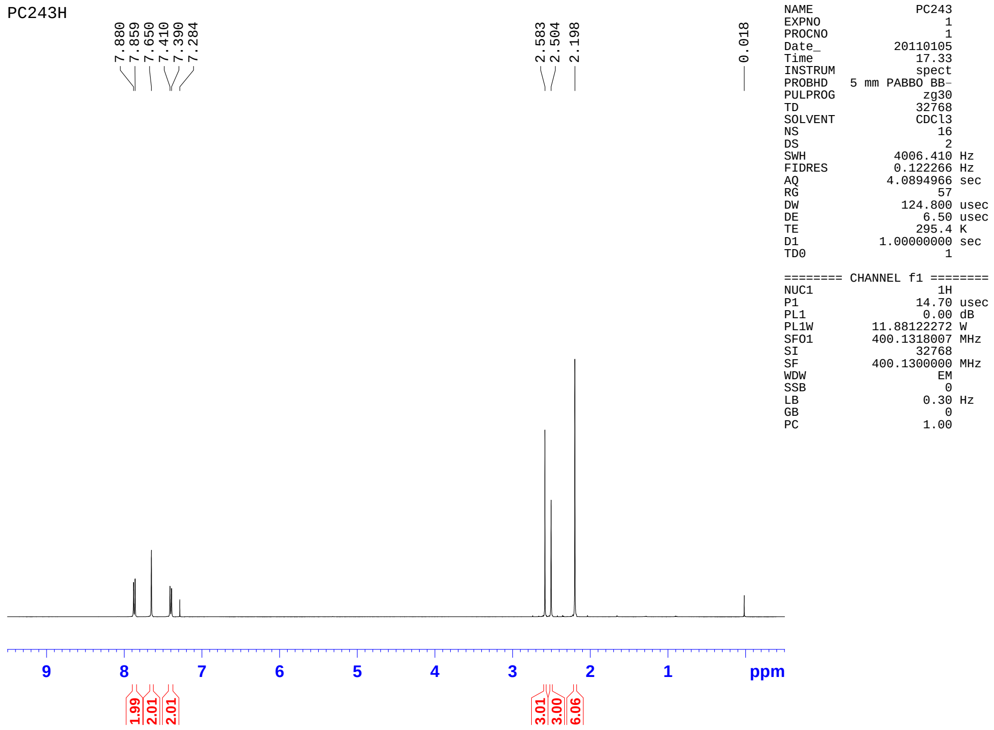
```
NAME            PC332
EXPNO               5
PROCNO              1
Date_        20111017
Time            18.49
INSTRUM         spect
PROBHD   5 mm PABBO BB-
PULPROG       zgpg30
TD              65536
SOLVENT         CDCl3
NS                 16
DS                  4
SWH         64102.563 Hz
FIDRES       0.978127 Hz
AQ          0.5112308 sec
RG                203
DW              7.800 usec
DE               6.50 usec
TE              297.4 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0                 1

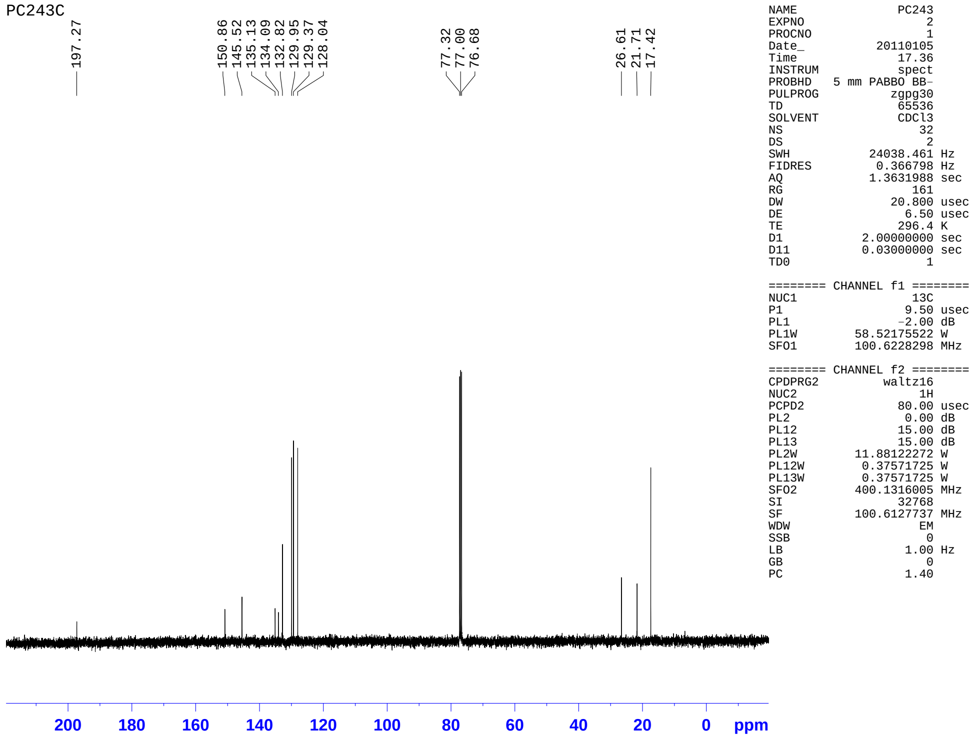
======== CHANNEL f1 ========
NUC1              31P
P1              14.70 usec
PL1              3.00 dB
PL1W      12.96693134 W
SFO1      161.9674942 MHz

======== CHANNEL f2 ========
CPDPRG2       waltz16
NUC2               1H
PCPD2           80.00 usec
PL2              0.00 dB
PL12            15.00 dB
PL13            15.00 dB
PL2W      11.88122272 W
PL12W      0.37571725 W
PL13W      0.37571725 W
SFO2      400.1316005 MHz
SI              32768
SF        161.9755930 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```

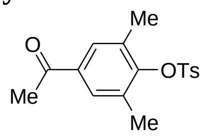
4-Acetyl-2,6-dimethylphenyl tosylate

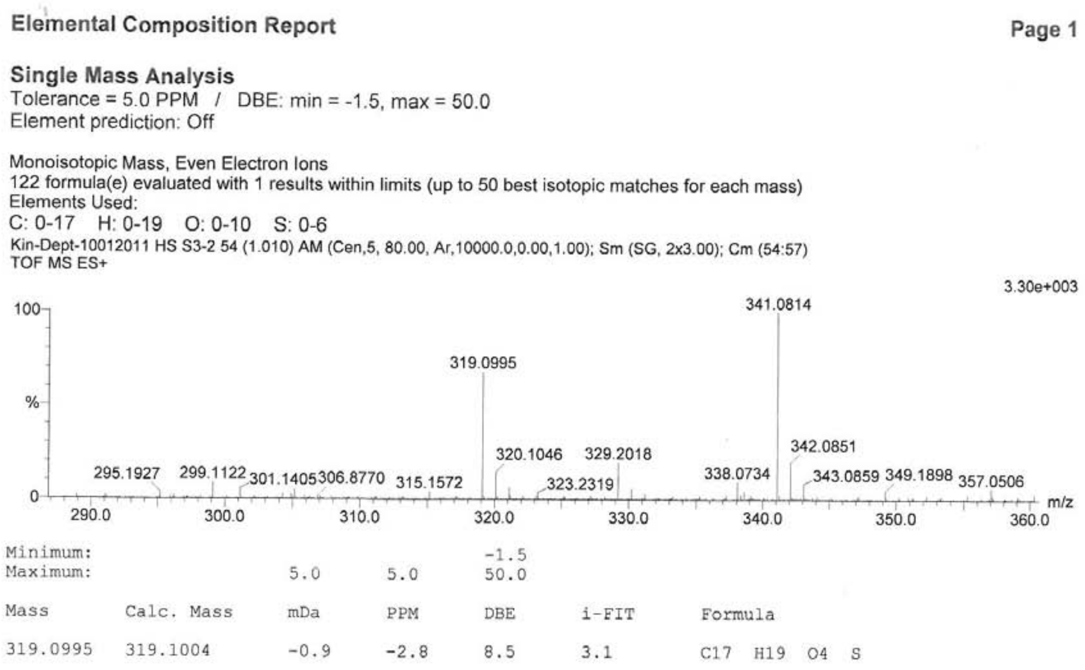






4-Acetyl-2,6-dimethylphenyl tosylate





Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

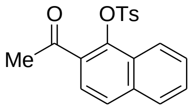
Monoisotopic Mass, Even Electron Ions
122 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-17 H: 0-19 O: 0-10 S: 0-6
Kin-Dept-10012011 HS S3-2 54 (1.010) AM (Cen,5, 80.00, Ar,10000.0,0.00,1.00); Sm (SG, 2x3.00); Cm (54:57)
TOF MS ES+

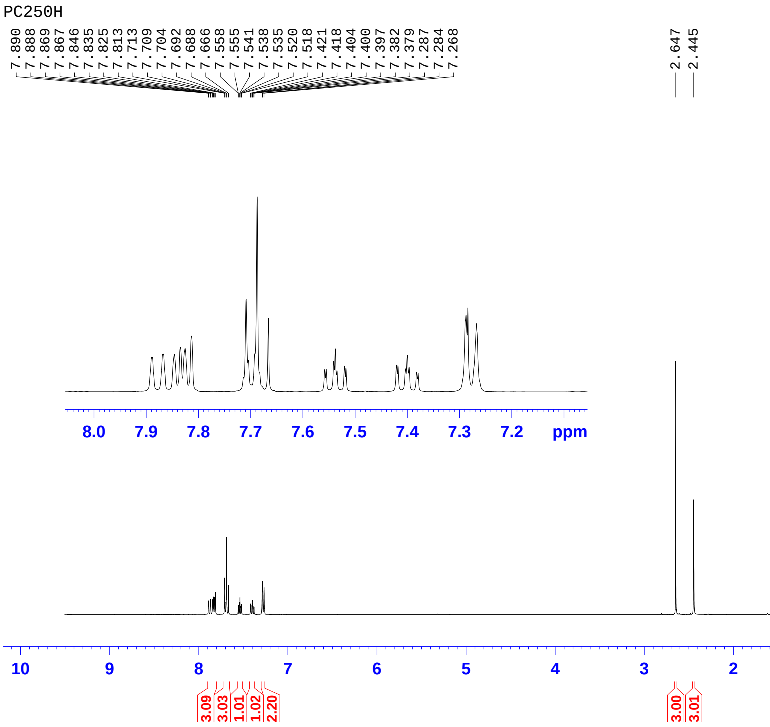
```
Minimum:                                     -1.5
Maximum:                5.0       5.0        50.0

Mass       Calc. Mass   mDa       PPM        DBE       i-FIT      Formula

319.0995   319.1004     -0.9      -2.8       8.5       3.1        C17  H19  O4  S
```

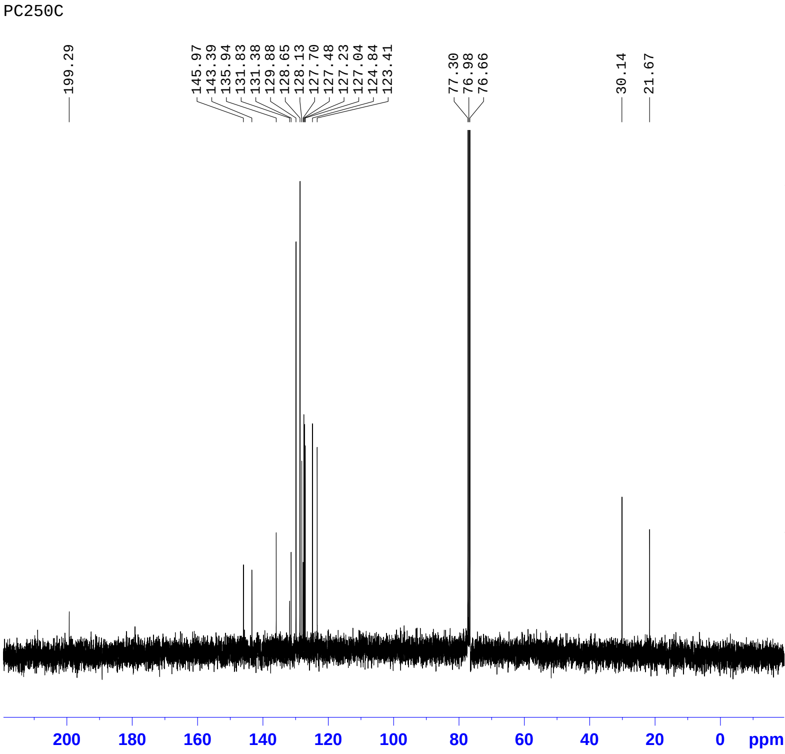
2-Acetylnaphthalen-1-yl tosylate





```
NAME              PC250
EXPNO                 1
PROCNO                1
Date_          20110119
Time              14.15
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            4006.410 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                 80.6
DW              124.800 usec
DE                 6.50 usec
TE                297.7 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.70 usec
PL1                0.00 dB
PL1W        11.88122272 W
SFO1        400.1318007 MHz
SI                32768
SF          400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

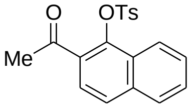


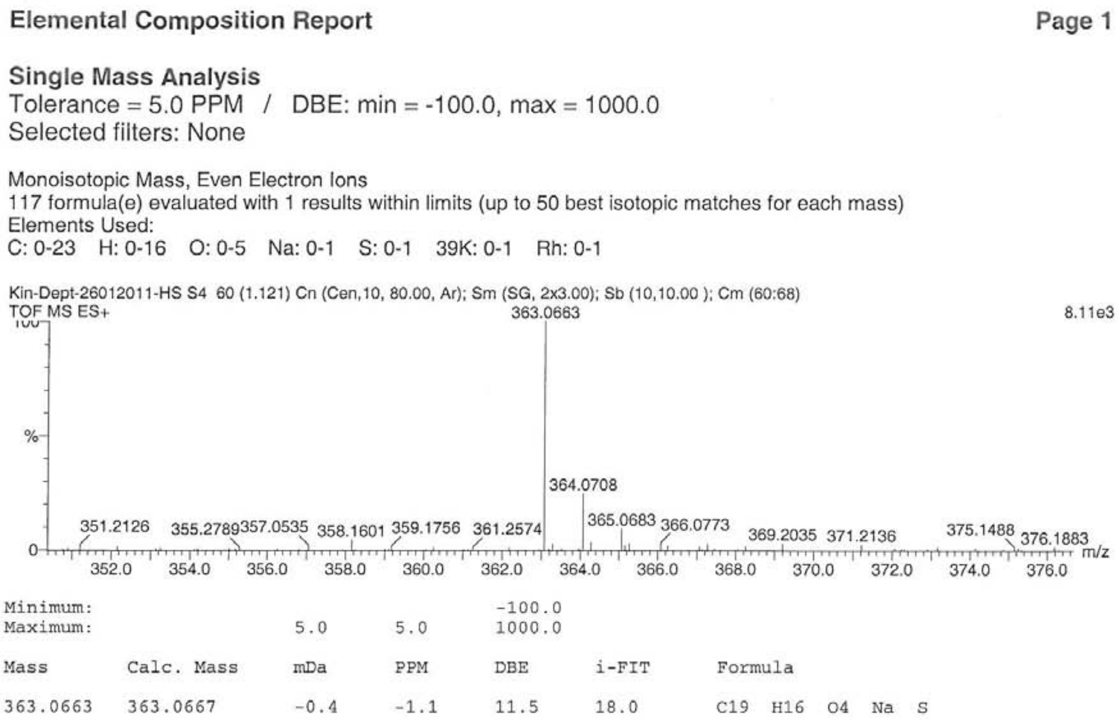
```
NAME              PC250
EXPNO                 2
PROCNO                1
Date_          20110119
Time              14.17
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                  161
DW               20.800 usec
DE                 6.50 usec
TE                298.6 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.50 usec
PL1               -2.00 dB
PL1W        58.52175522 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL13              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
PL13W        0.37571725 W
SFO2        400.1316005 MHz
SI                32768
SF          100.6127746 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

2-Acetylnaphthalen-1-yl tosylate





Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -100.0, max = 1000.0
Selected filters: None

Monoisotopic Mass, Even Electron Ions
117 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-23 H: 0-16 O: 0-5 Na: 0-1 S: 0-1 39K: 0-1 Rh: 0-1

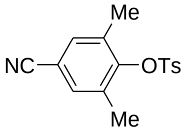
Kin-Dept-26012011-HS S4 60 (1.121) Cn (Cen,10, 80.00, Ar); Sm (SG, 2x3.00); Sb (10,10.00); Cm (60:68)
TOF MS ES+

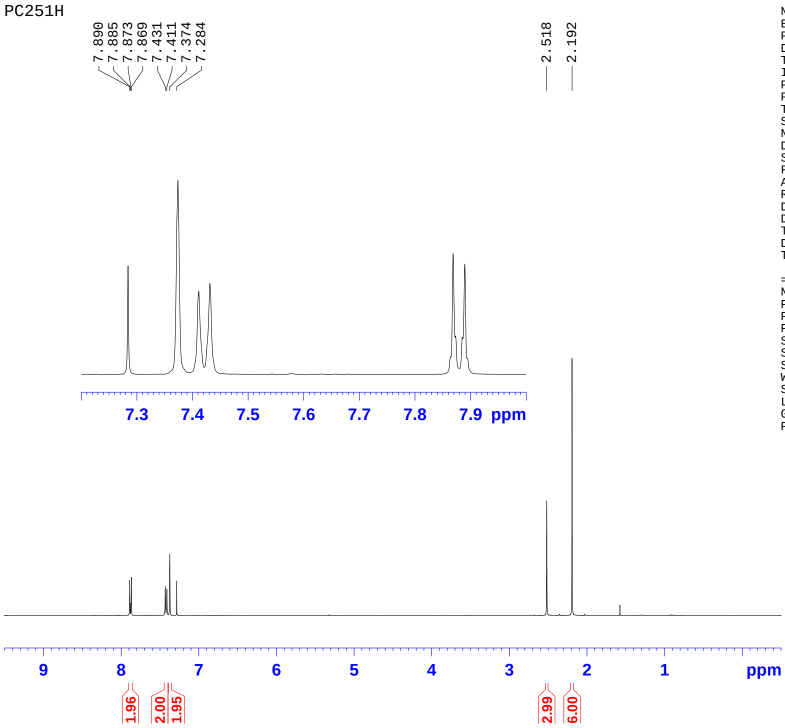
```
Minimum:                              -100.0
Maximum:                 5.0      5.0    1000.0

Mass       Calc. Mass    mDa      PPM      DBE      i-FIT      Formula

363.0663   363.0667      -0.4     -1.1     11.5     18.0       C19  H16  O4  Na  S
```

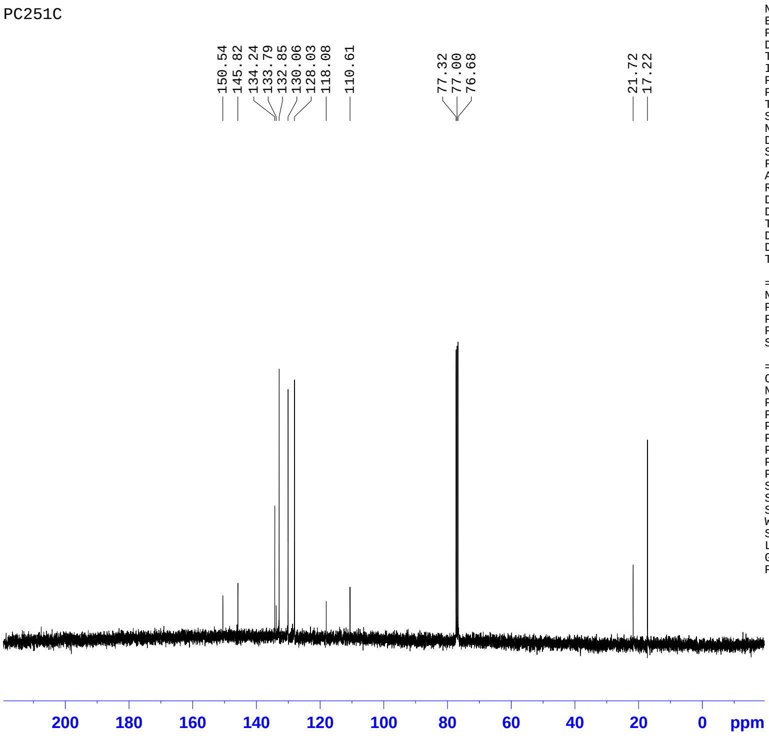
4-Cyano-2,6-dimethylphenyl tosylate





```
NAME                PC251
EXPNO                   1
PROCNO                  1
Date_            20110125
Time                18.05
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              4006.410 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                    144
DW                124.800 usec
DE                   6.50 usec
TE                  296.8 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.70 usec
PL1                  0.00 dB
PL1W          11.88122272 W
SFO1          400.1318007 MHz
SI                  32768
SF            400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

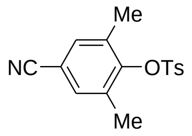


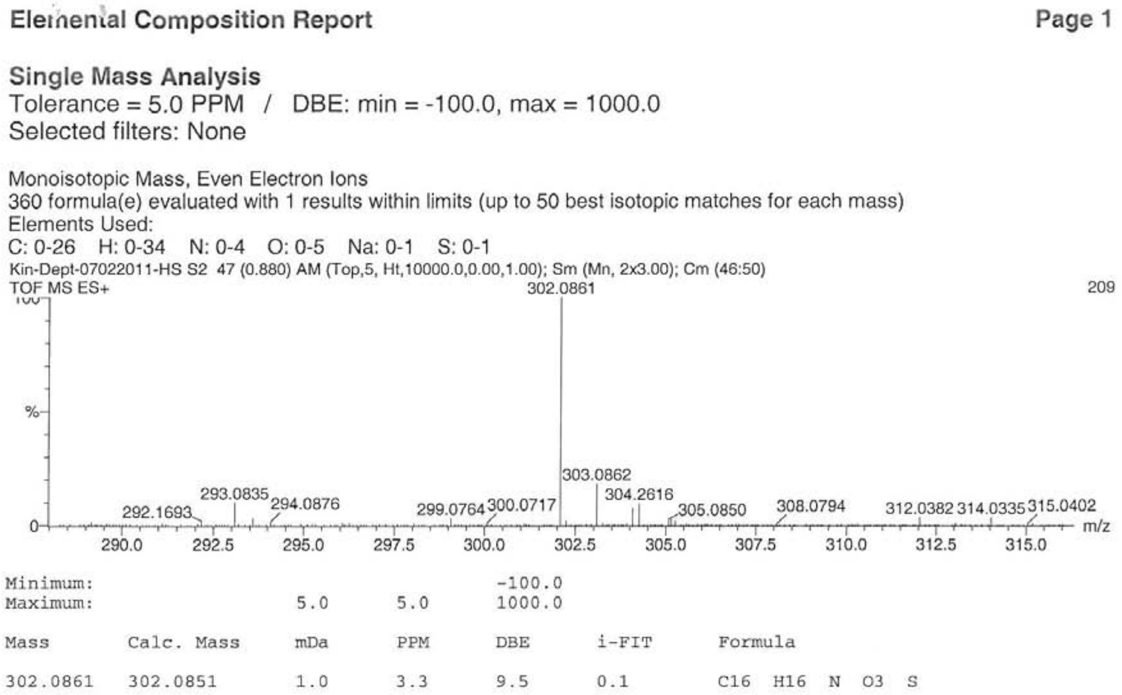
```
NAME                PC251
EXPNO                   3
PROCNO                  1
Date_            20110126
Time                22.02
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      2
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                    161
DW                 20.800 usec
DE                   6.50 usec
TE                  297.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.50 usec
PL1                 -2.00 dB
PL1W          58.52175522 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                15.00 dB
PL13                15.00 dB
PL2W          11.88122272 W
PL12W          0.37571725 W
PL13W          0.37571725 W
SFO2          400.1316005 MHz
SI                  32768
SF            100.6127740 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

4-Cyano-2,6-dimethylphenyl tosylate





Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -100.0, max = 1000.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

360 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 0-26 H: 0-34 N: 0-4 O: 0-5 Na: 0-1 S: 0-1

Kin-Dept-07022011-HS S2 47 (0.880) AM (Top,5, Ht,10000.0,0.00,1.00); Sm (Mn, 2x3.00); Cm (46:50)

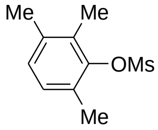
TOF MS ES+

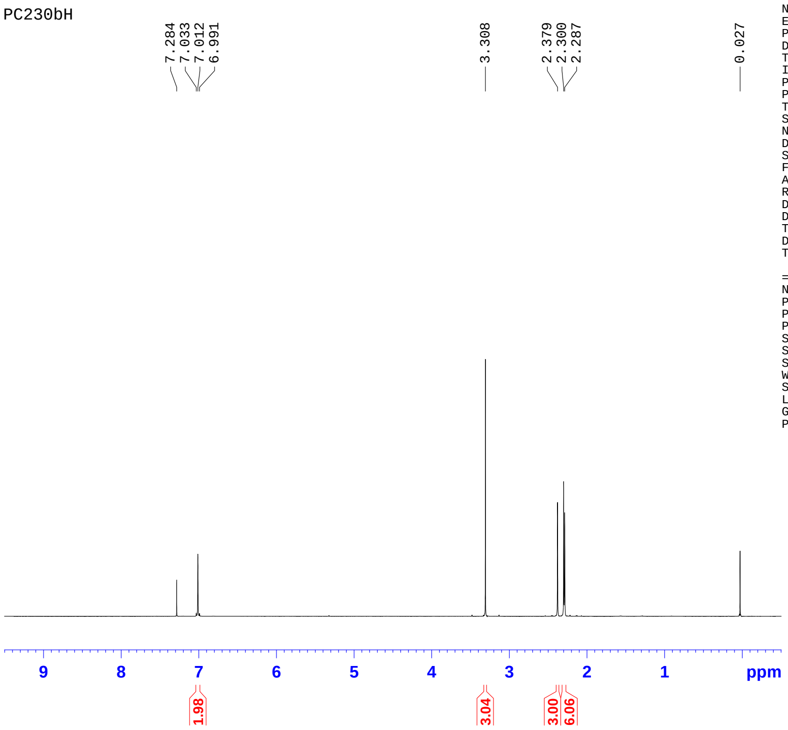
```
Minimum:                                       -100.0
Maximum:                  5.0       5.0        1000.0

Mass       Calc. Mass     mDa       PPM        DBE       i-FIT       Formula

302.0861   302.0851       1.0       3.3        9.5       0.1         C16  H16  N  O3  S
```

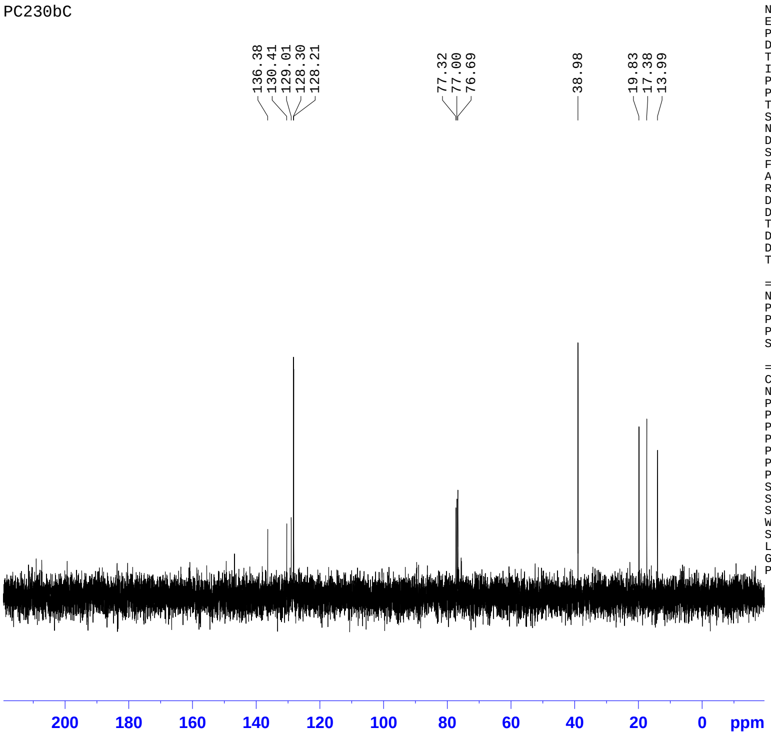
2,3,6-Trimethylphenyl mesylate





```
NAME             PC230b
EXPNO                 1
PROCNO                1
Date_          20101225
Time              21.06
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            4006.410 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                 90.5
DW              124.800 usec
DE                 6.50 usec
TE                295.1 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.70 usec
PL1                0.00 dB
PL1W        11.88122272 W
SFO1        400.1318007 MHz
SI                32768
SF          400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

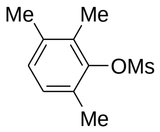


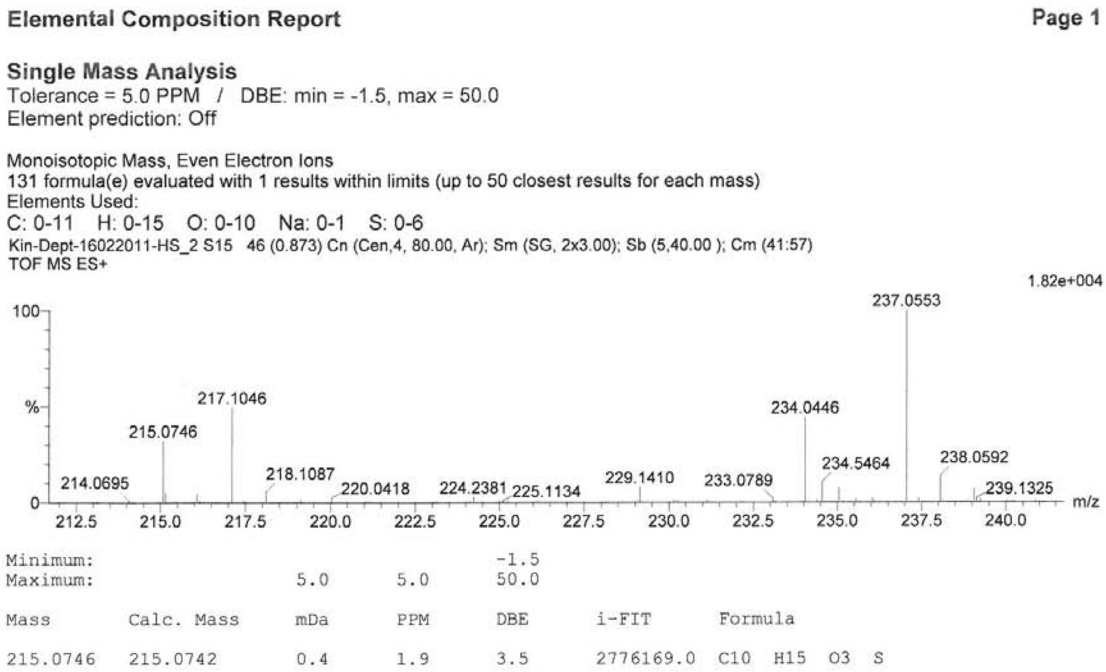
```
NAME             PC230b
EXPNO                 3
PROCNO                1
Date_          20110314
Time              15.16
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                    1
DW               20.800 usec
DE                 6.50 usec
TE                300.7 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.50 usec
PL1               -2.00 dB
PL1W        58.52175522 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL13              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
PL13W        0.37571725 W
SFO2        400.1316005 MHz
SI                32768
SF          100.6127803 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

2,3,6-Trimethylphenyl mesylate





Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

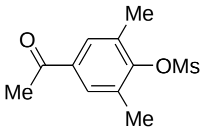
Monoisotopic Mass, Even Electron Ions
131 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-11 H: 0-15 O: 0-10 Na: 0-1 S: 0-6
Kin-Dept-16022011-HS_2 S15 46 (0.873) Cn (Cen,4, 80.00, Ar); Sm (SG, 2x3.00); Sb (5,40.00); Cm (41:57)
TOF MS ES+

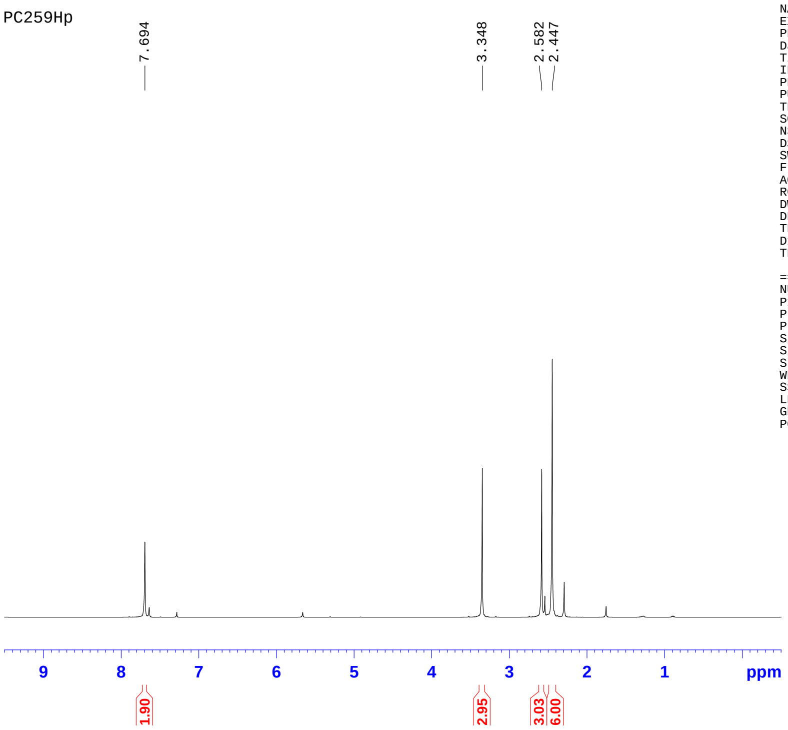
```
Minimum:                                        -1.5
Maximum:                      5.0      5.0      50.0

Mass       Calc. Mass    mDa      PPM      DBE      i-FIT       Formula

215.0746   215.0742      0.4      1.9      3.5      2776169.0   C10  H15  O3  S
```

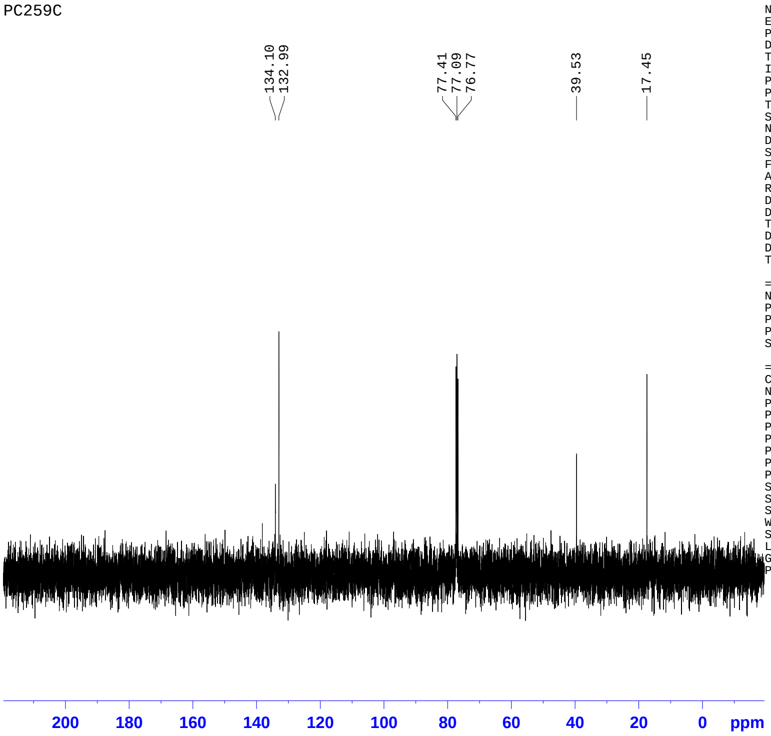
4-Acetyl-2,6-dimethylphenyl mesylate





```
NAME                PC259
EXPNO                   6
PROCNO                  1
Date_            20110218
Time                11.55
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              4006.410 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                     18
DW                124.800 usec
DE                   6.50 usec
TE                  296.5 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.70 usec
PL1                  0.00 dB
PL1W          11.88122272 W
SFO1          400.1318007 MHz
SI                  32768
SF            400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

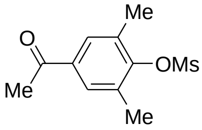


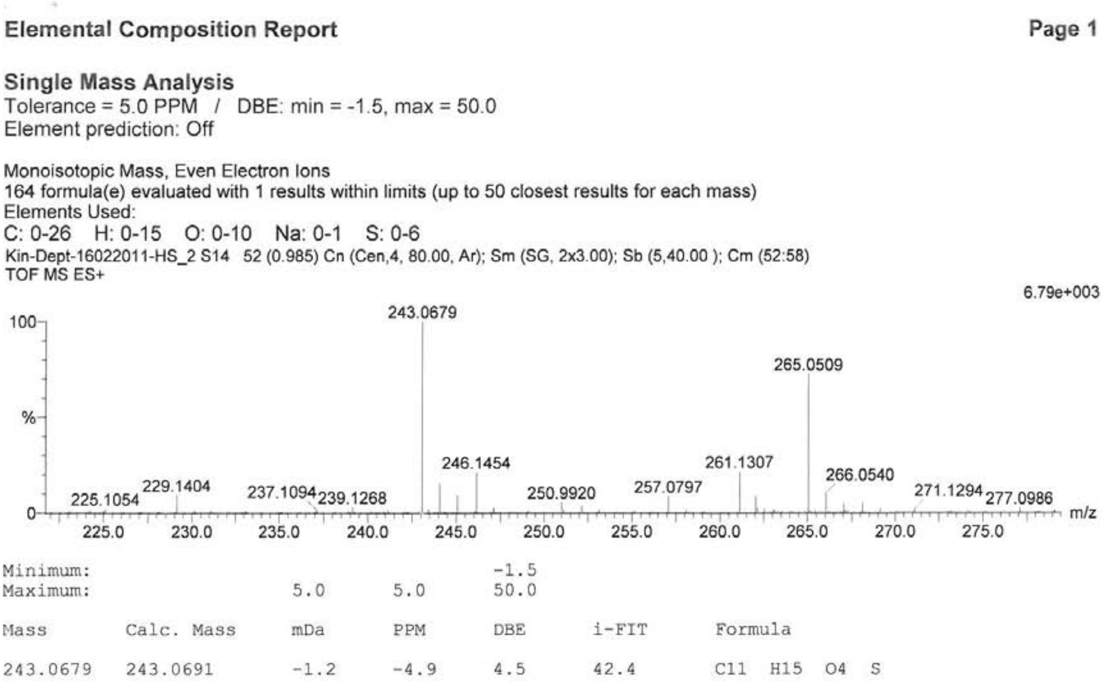
```
NAME                PC259
EXPNO                  10
PROCNO                  1
Date_            20110321
Time                15.25
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      2
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                      1
DW                 20.800 usec
DE                   6.50 usec
TE                  301.2 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.50 usec
PL1                 -2.00 dB
PL1W          58.52175522 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                15.00 dB
PL13                15.00 dB
PL2W          11.88122272 W
PL12W          0.37571725 W
PL13W          0.37571725 W
SFO2          400.1316005 MHz
SI                  32768
SF            100.6127690 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

4-Acetyl-2,6-dimethylphenyl mesylate





Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

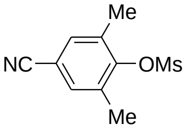
Monoisotopic Mass, Even Electron Ions
164 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-26 H: 0-15 O: 0-10 Na: 0-1 S: 0-6
Kin-Dept-16022011-HS_2 S14 52 (0.985) Cn (Cen,4, 80.00, Ar); Sm (SG, 2x3.00); Sb (5,40.00); Cm (52:58)
TOF MS ES+

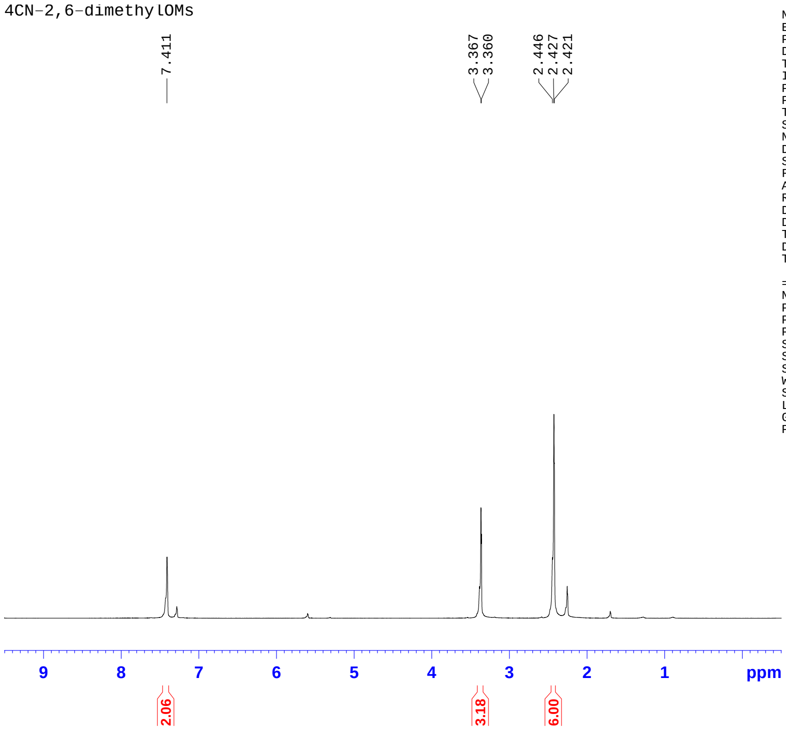
```
Minimum:                                          -1.5
Maximum:                          5.0      5.0    50.0

Mass        Calc. Mass    mDa      PPM      DBE      i-FIT      Formula

243.0679    243.0691      -1.2     -4.9     4.5      42.4       C11  H15  O4  S
```

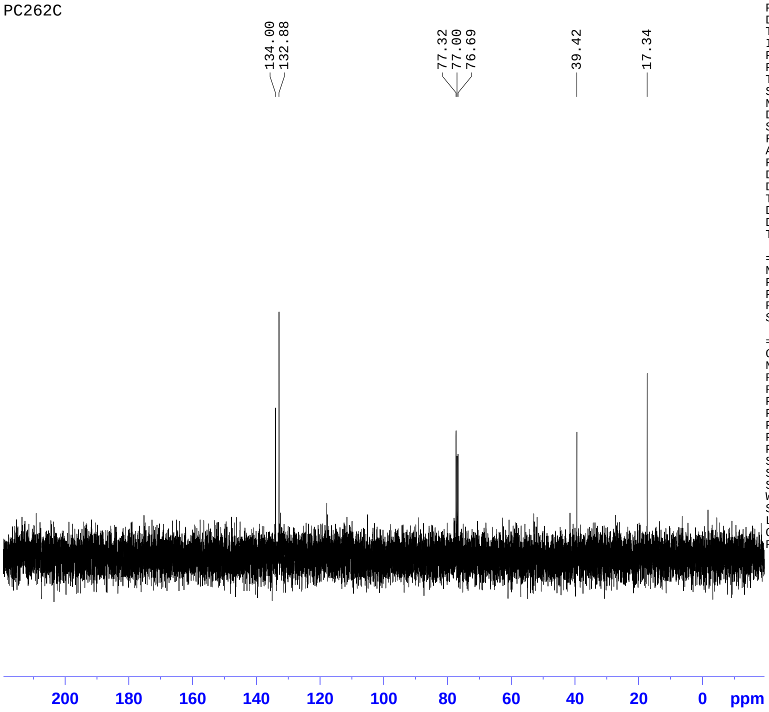
4-Cyano-2,6-dimethylphenyl mesylate





```
NAME              PC259
EXPNO                 9
PROCNO                1
Date_          20110321
Time              15.22
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            4006.410 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                    1
DW              124.800 usec
DE                 6.50 usec
TE                300.5 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.70 usec
PL1                0.00 dB
PL1W        11.88122272 W
SFO1        400.1318007 MHz
SI                32768
SF          400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

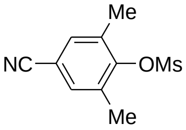


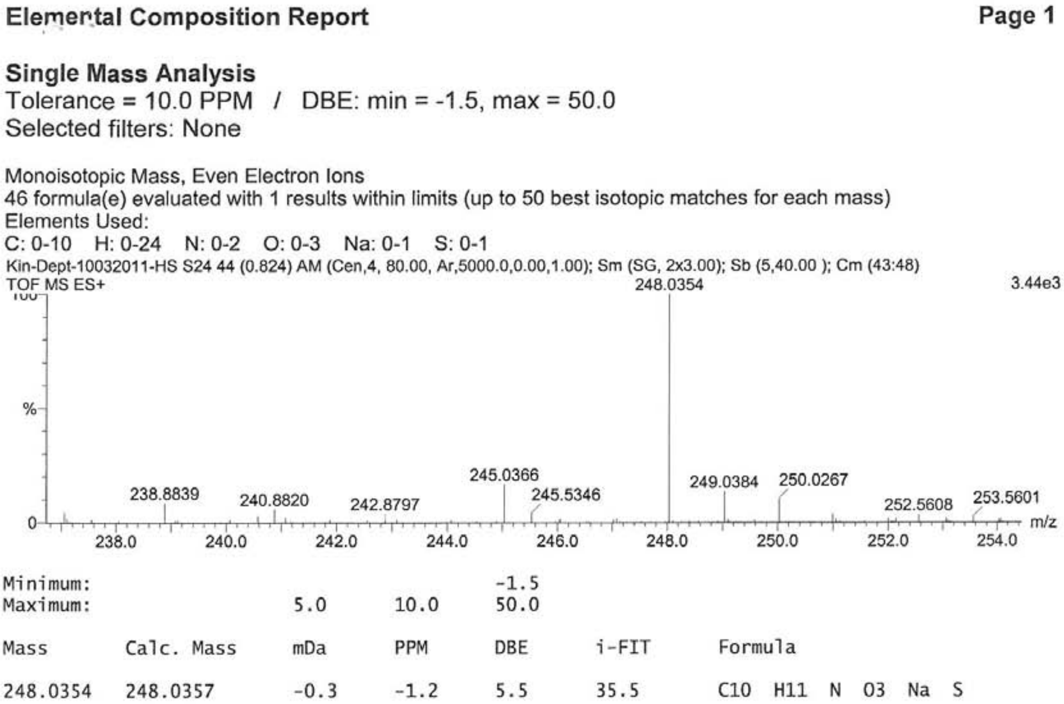
```
NAME              PC262
EXPNO                 4
PROCNO                1
Date_          20110302
Time              20.57
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                    1
DW               20.800 usec
DE                 6.50 usec
TE                300.7 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.50 usec
PL1               -2.00 dB
PL1W        58.52175522 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL13              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
PL13W        0.37571725 W
SFO2        400.1316005 MHz
SI                32768
SF          100.6127802 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

4-Cyano-2,6-dimethylphenyl mesylate





Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

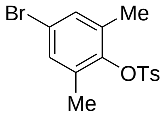
Monoisotopic Mass, Even Electron Ions
46 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-10 H: 0-24 N: 0-2 O: 0-3 Na: 0-1 S: 0-1
Kin-Dept-10032011-HS S24 44 (0.824) AM (Cen,4, 80.00, Ar,5000.0,0.00,1.00); Sm (SG, 2x3.00); Sb (5,40.00); Cm (43:48)
TOF MS ES+

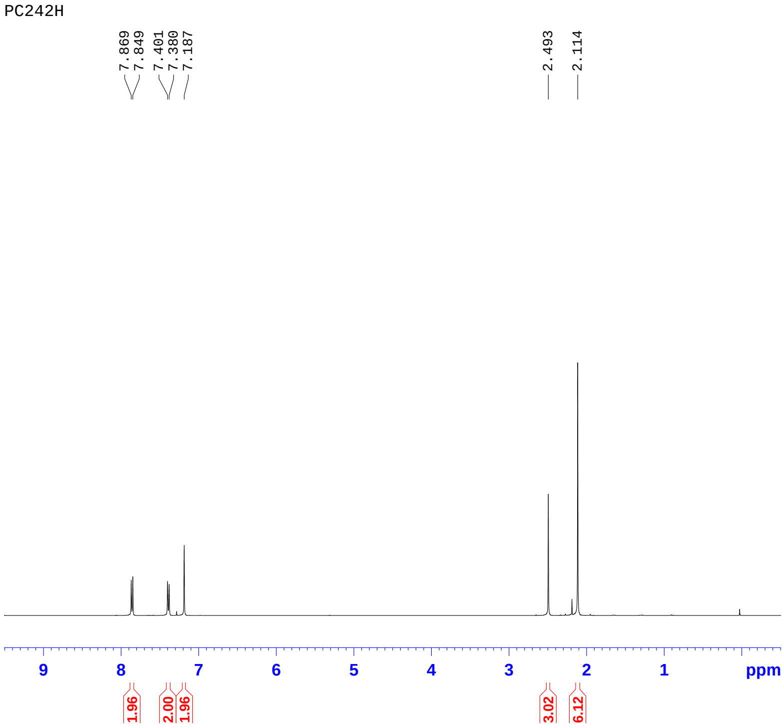
```
Minimum:                              -1.5
Maximum:                5.0    10.0   50.0

Mass       Calc. Mass   mDa    PPM    DBE    i-FIT    Formula

248.0354   248.0357     -0.3   -1.2   5.5    35.5     C10  H11  N  O3  Na  S
```

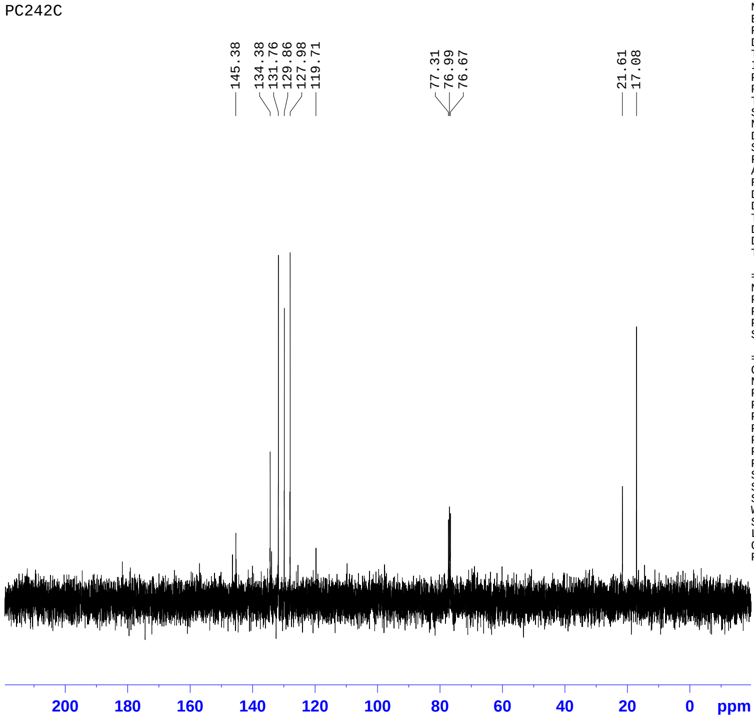
4-Bromo-2,6-dimethylphenyl tosylate





```
NAME                 PC242
EXPNO                    1
PROCNO                   1
Date_             20110103
Time                 12.34
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               4006.410 Hz
FIDRES            0.122266 Hz
AQ               4.0894966 sec
RG                    25.4
DW                 124.800 usec
DE                    6.50 usec
TE                   292.9 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   14.70 usec
PL1                   0.00 dB
PL1W           11.88122272 W
SFO1           400.1318007 MHz
SI                   32768
SF             400.1300000 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

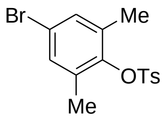


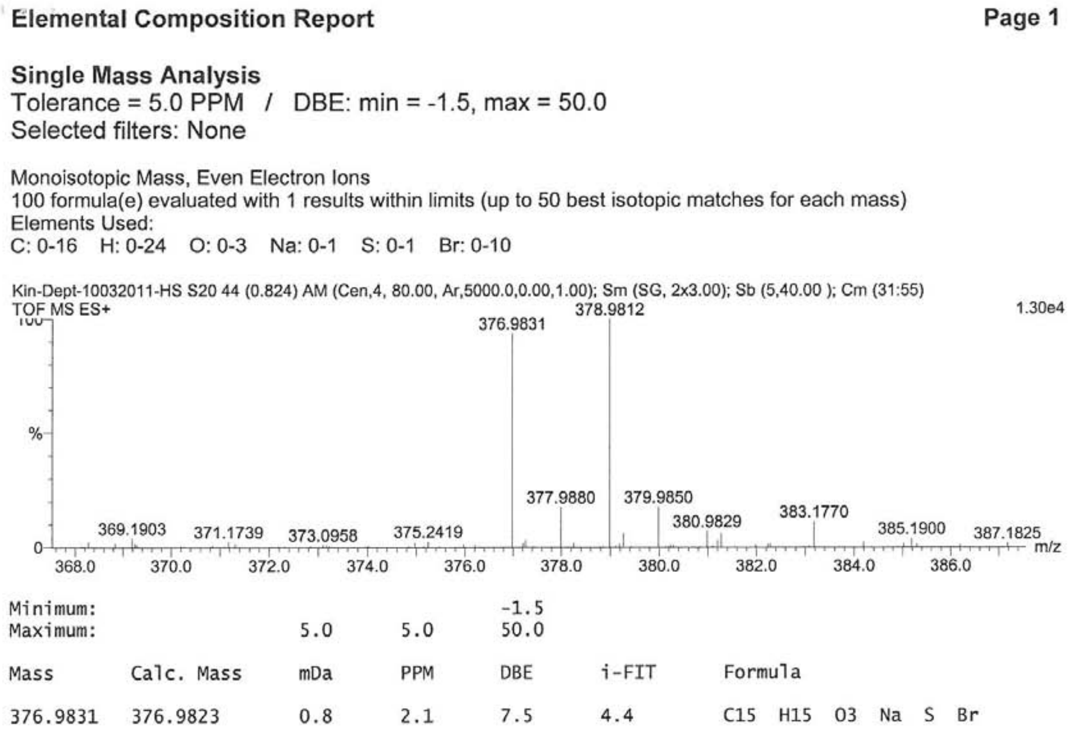
```
NAME                 PC242
EXPNO                    2
PROCNO                   1
Date_             20110314
Time                 15.29
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      32
DS                       2
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ               1.3631988 sec
RG                       1
DW                  20.800 usec
DE                    6.50 usec
TE                   300.7 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    9.50 usec
PL1                  -2.00 dB
PL1W           58.52175522 W
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   0.00 dB
PL12                 15.00 dB
PL13                 15.00 dB
PL2W           11.88122272 W
PL12W           0.37571725 W
PL13W           0.37571725 W
SFO2           400.1316005 MHz
SI                   32768
SF             100.6127813 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

4-Bromo-2,6-dimethylphenyl tosylate





Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

Monoisotopic Mass, Even Electron Ions
100 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-16 H: 0-24 O: 0-3 Na: 0-1 S: 0-1 Br: 0-10

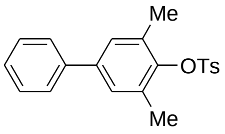
Kin-Dept-10032011-HS S20 44 (0.824) AM (Cen,4, 80.00, Ar,5000.0,0.00,1.00); Sm (SG, 2x3.00); Sb (5,40.00); Cm (31:55)
TOF MS ES+ 1.30e4

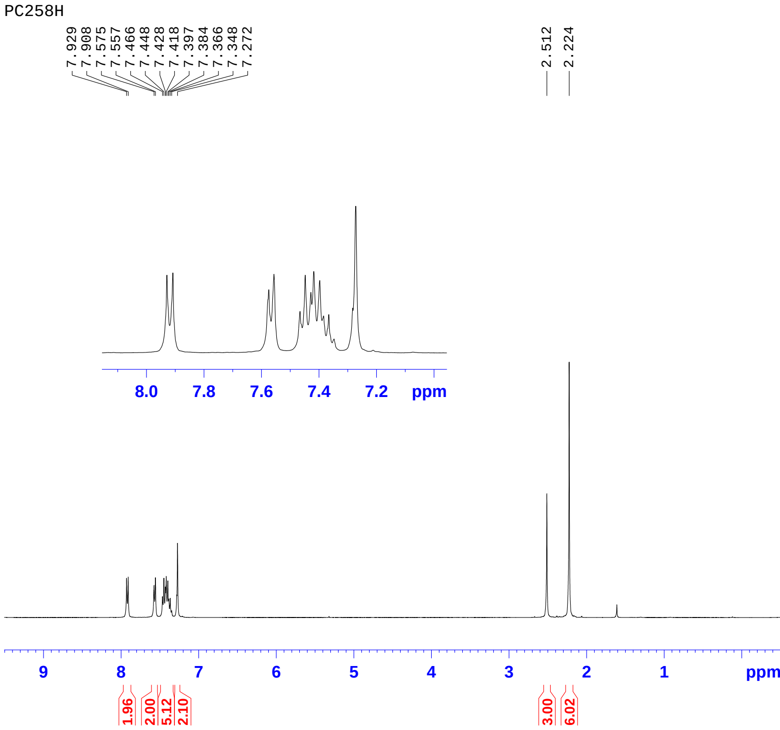
```
Minimum:                                      -1.5
Maximum:                  5.0        5.0      50.0

Mass         Calc. Mass    mDa        PPM      DBE       i-FIT       Formula

376.9831     376.9823      0.8        2.1      7.5       4.4         C15  H15  O3  Na  S  Br
```

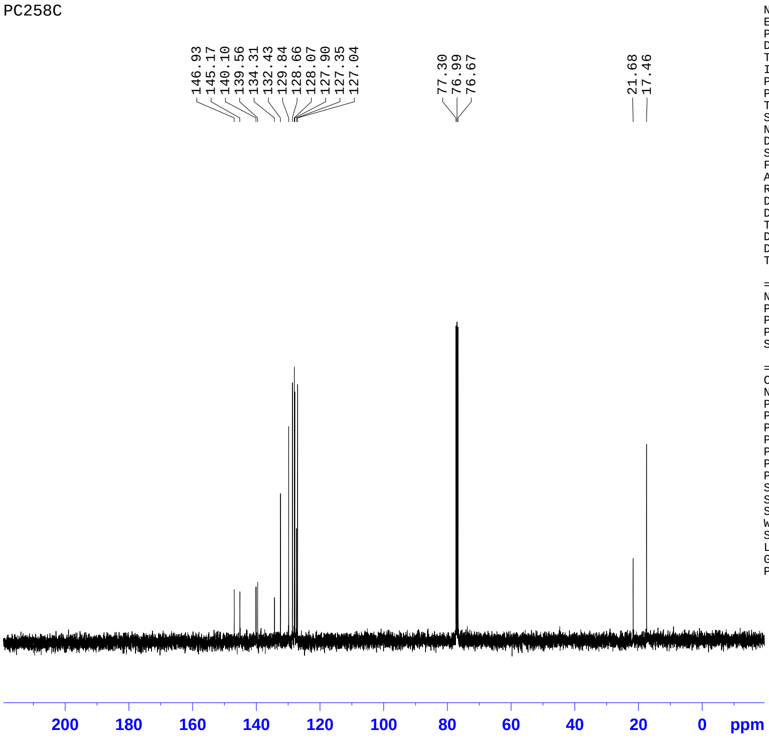
4-Phenyl-2,6-dimethylphenyl tosylate





```
NAME                PC258
EXPNO                   5
PROCNO                  1
Date_            20110215
Time                22.28
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              4006.410 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                   25.4
DW                124.800 usec
DE                   6.50 usec
TE                  294.2 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.70 usec
PL1                  0.00 dB
PL1W          11.88122272 W
SFO1          400.1318007 MHz
SI                  32768
SF            400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

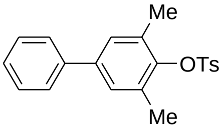


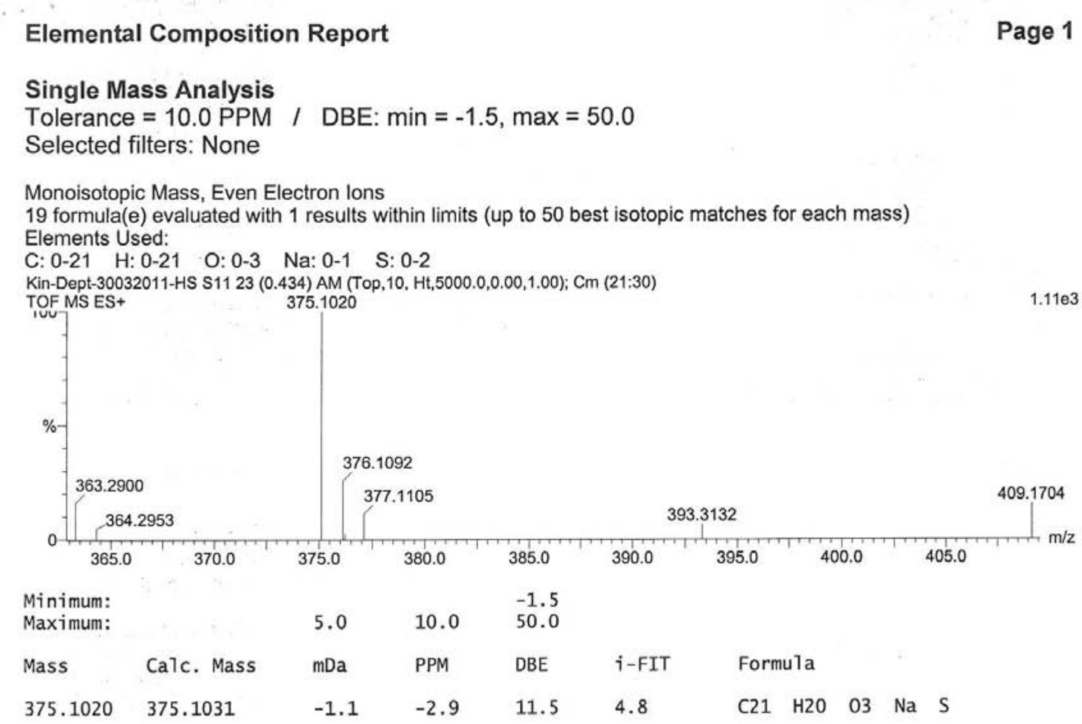
```
NAME                PC258
EXPNO                   4
PROCNO                  1
Date_            20110215
Time                22.26
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      2
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                   22.6
DW                 20.800 usec
DE                   6.50 usec
TE                  294.8 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.50 usec
PL1                 -2.00 dB
PL1W          58.52175522 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                15.00 dB
PL13                15.00 dB
PL2W          11.88122272 W
PL12W          0.37571725 W
PL13W          0.37571725 W
SFO2          400.1316005 MHz
SI                  32768
SF            100.6127774 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

4-Phenyl-2,6-dimethylphenyl tosylate





Elemental Composition Report **Page 1**

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

19 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 0-21 H: 0-21 O: 0-3 Na: 0-1 S: 0-2

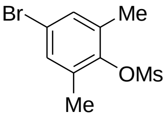
Kin-Dept-30032011-HS S11 23 (0.434) AM (Top,10, Ht,5000.0,0.00,1.00); Cm (21:30)

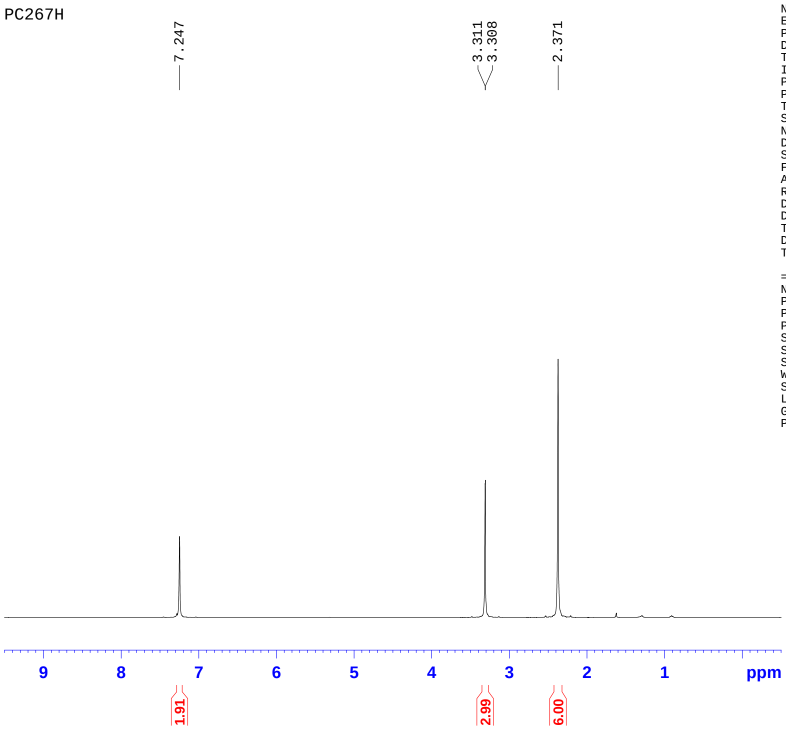
```
Minimum:                                    -1.5
Maximum:                  5.0      10.0     50.0

Mass       Calc. Mass     mDa      PPM      DBE      i-FIT      Formula

375.1020   375.1031       -1.1     -2.9     11.5     4.8        C21  H20  O3  Na  S
```

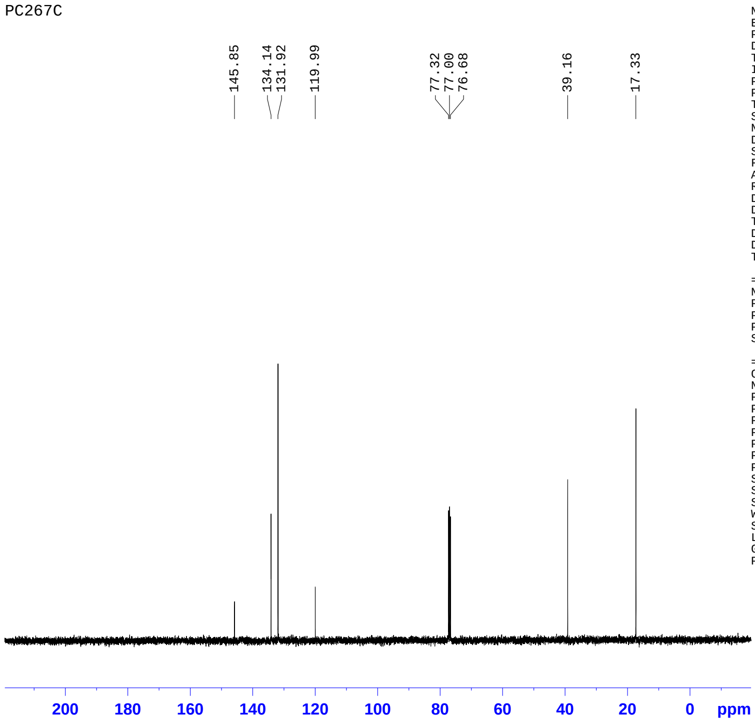
4-Bromo-2,6-dimethylphenyl mesylate





```
NAME               PC267
EXPNO                  1
PROCNO                 1
Date_           20110221
Time               21.31
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                     5
DW               124.800 usec
DE                  6.50 usec
TE                 297.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

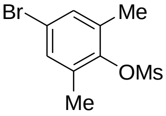


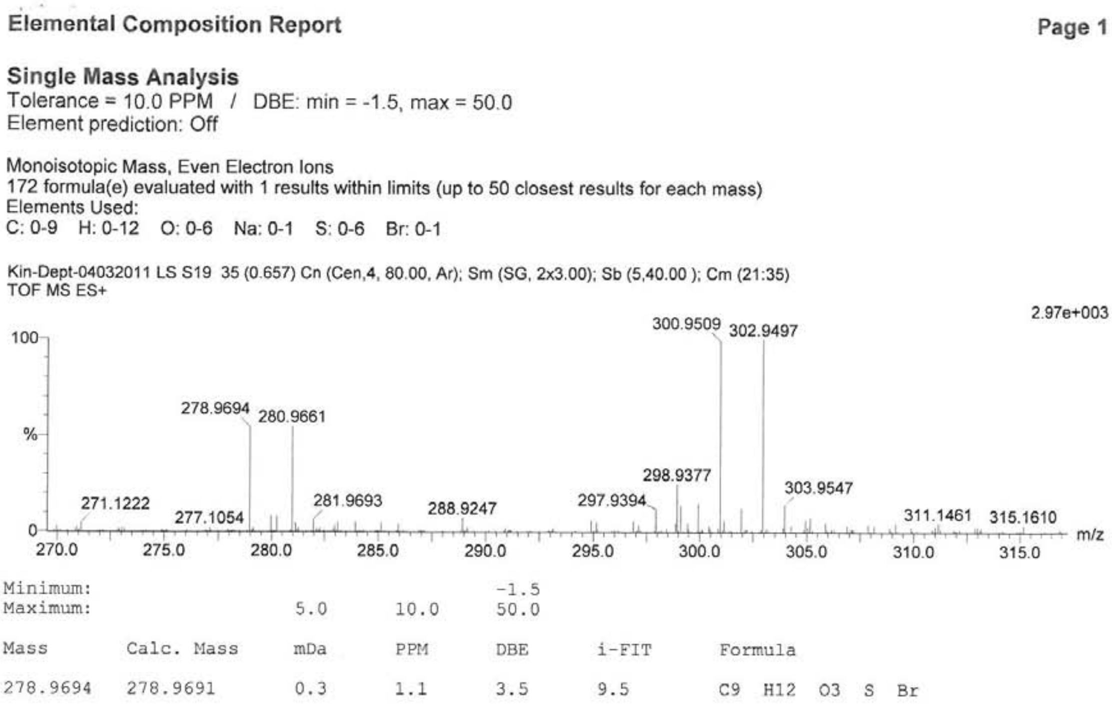
```
NAME               PC267
EXPNO                  2
PROCNO                 1
Date_           20110221
Time               21.34
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                    18
DW                20.800 usec
DE                  6.50 usec
TE                 298.1 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127774 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

4-Bromo-2,6-dimethylphenyl mesylate





Elemental Composition Report

Page 1

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Even Electron Ions
172 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-9 H: 0-12 O: 0-6 Na: 0-1 S: 0-6 Br: 0-1

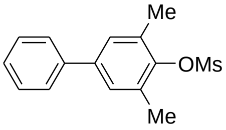
Kin-Dept-04032011 LS S19 35 (0.657) Cn (Cen,4, 80.00, Ar); Sm (SG, 2x3.00); Sb (5,40.00); Cm (21:35)
TOF MS ES+

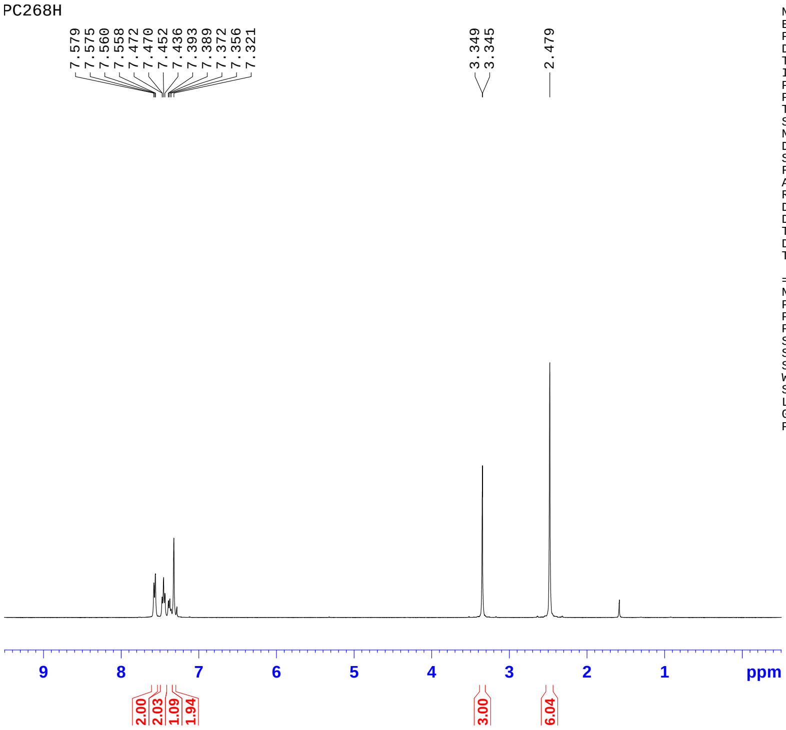
```
Minimum:                                     -1.5
Maximum:                 5.0       10.0      50.0

Mass        Calc. Mass   mDa       PPM       DBE       i-FIT      Formula

278.9694    278.9691     0.3       1.1       3.5       9.5        C9  H12  O3  S  Br
```

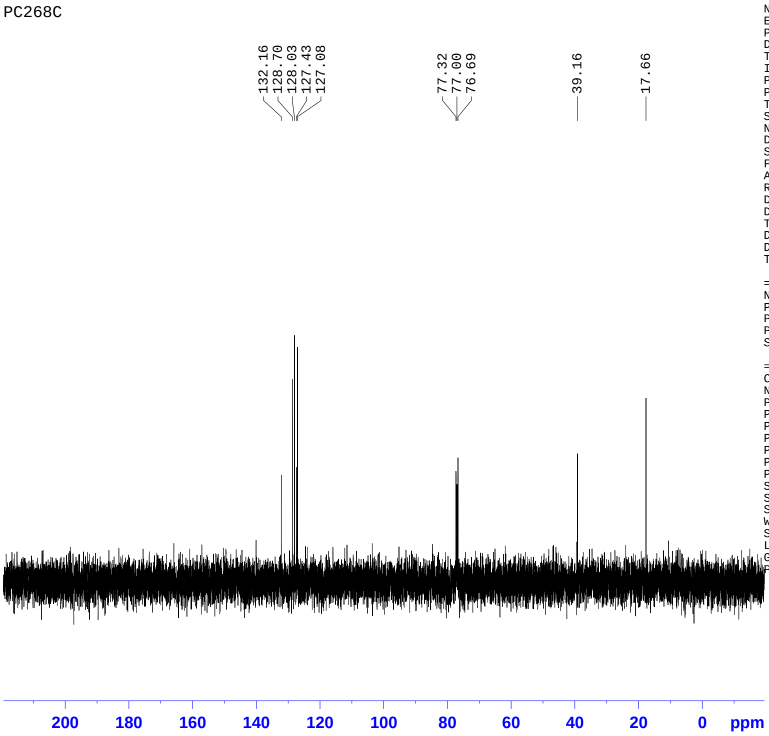
4-Phenyl-2,6-dimethylphenyl mesylate





```
NAME               PC268
EXPNO                  1
PROCNO                 1
Date_           20110227
Time               20.25
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                     1
DW               124.800 usec
DE                  6.50 usec
TE                 299.3 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

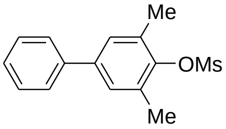


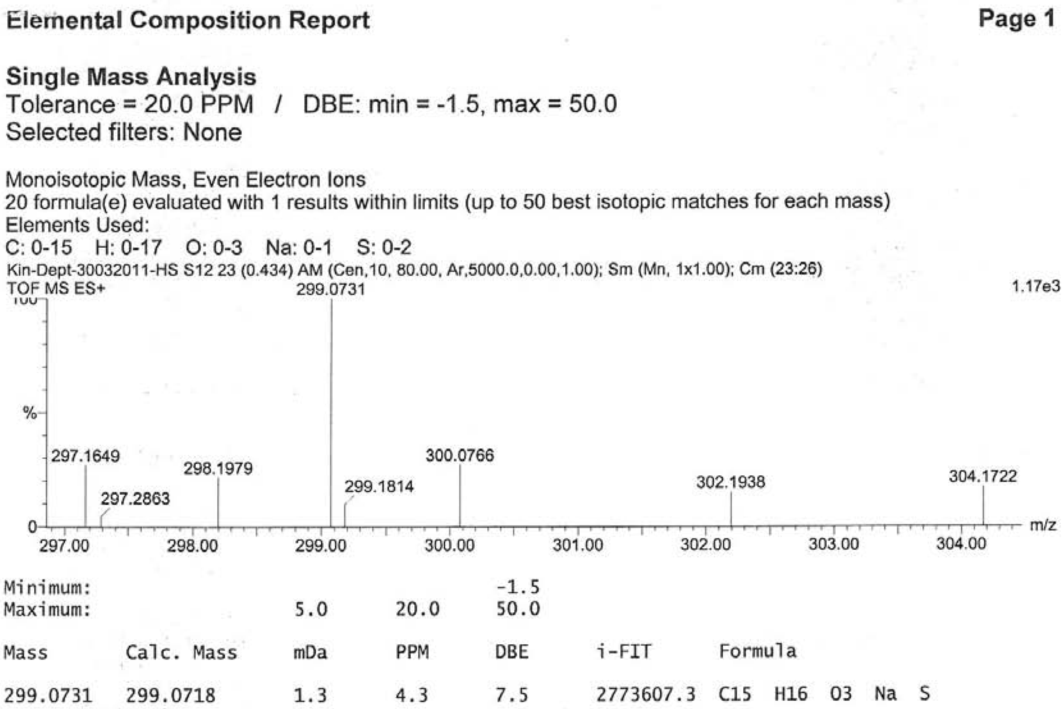
```
NAME               PC268
EXPNO                  4
PROCNO                 1
Date_           20110314
Time               15.33
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                     1
DW                20.800 usec
DE                  6.50 usec
TE                 300.5 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127766 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

4-Phenyl-2,6-dimethylphenyl mesylate





Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

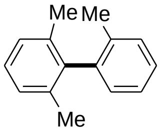
Monoisotopic Mass, Even Electron Ions
20 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-15 H: 0-17 O: 0-3 Na: 0-1 S: 0-2
Kin-Dept-30032011-HS S12 23 (0.434) AM (Cen,10, 80.00, Ar,5000.0,0.00,1.00); Sm (Mn, 1x1.00); Cm (23:26)
TOF MS ES+

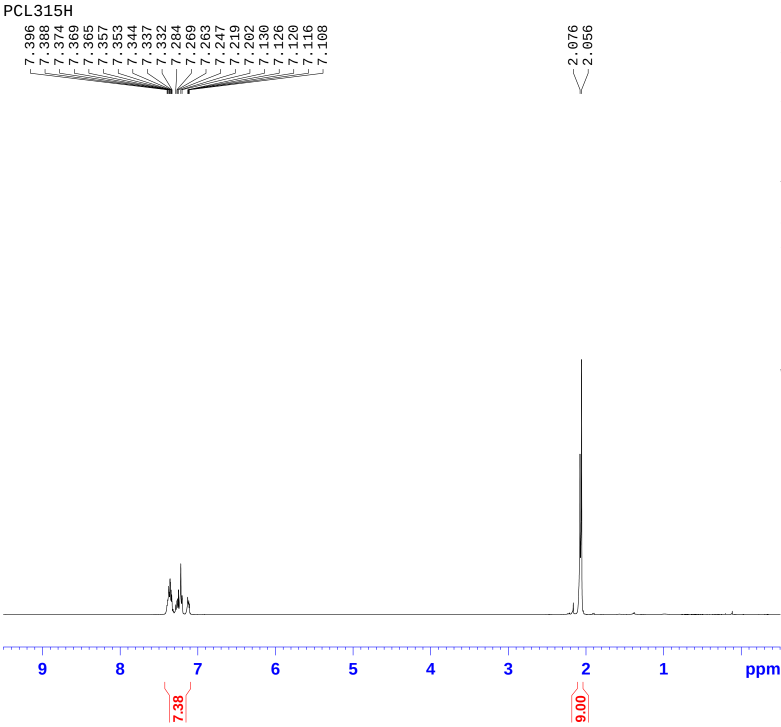
```
Minimum:                                       -1.5
Maximum:                       5.0     20.0    50.0

Mass        Calc. Mass        mDa     PPM     DBE      i-FIT       Formula

299.0731    299.0718          1.3     4.3     7.5      2773607.3   C15  H16  O3  Na  S
```

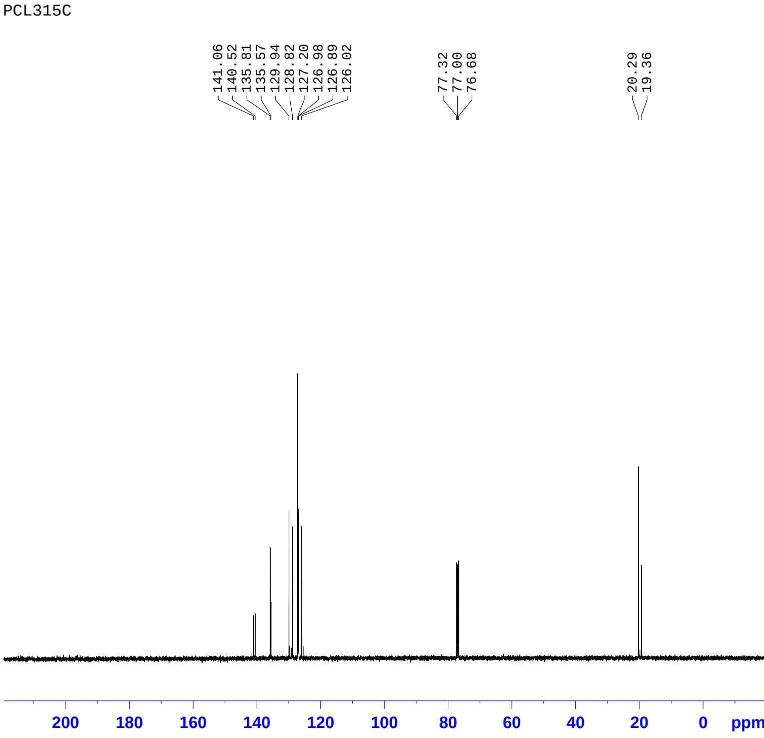
2,6,2'-Trimethylbiphenyl (Table 7.2, entry 1; Table 7.3, entry 1)





```
NAME              PCL315
EXPNO                  1
PROCNO                 1
Date_           20101207
Time               20.35
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  22.6
DW               124.800 usec
DE                  6.50 usec
TE                 297.5 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

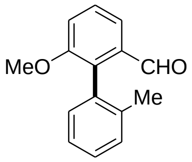


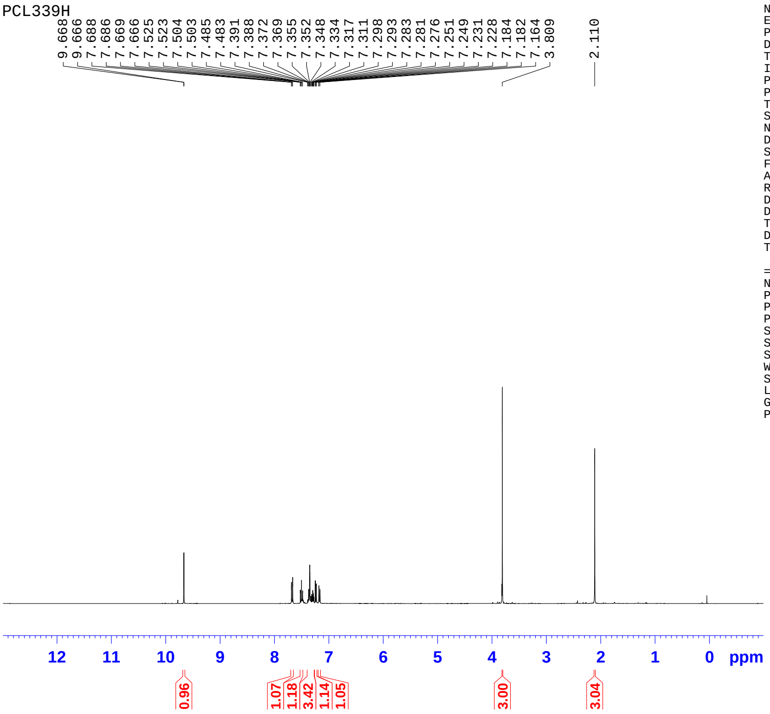
```
NAME              PCL315
EXPNO                  2
PROCNO                 1
Date_           20101207
Time               20.39
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   161
DW                20.800 usec
DE                  6.50 usec
TE                 298.4 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127802 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

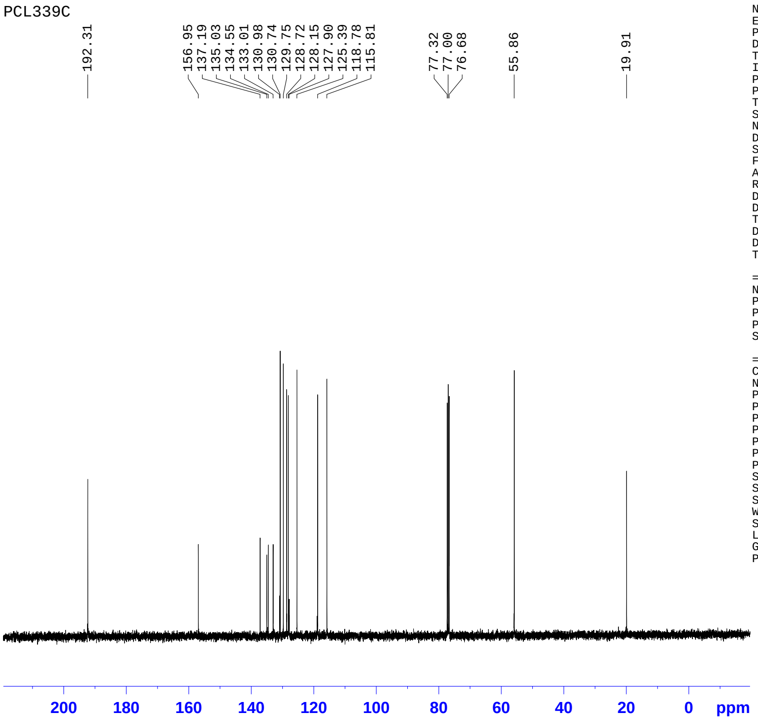
6-Methoxy-2'-methyl-1,1'-biphenyl-2-carboxaldehyde (Table 7.2, entry 2)





```
NAME              PCL339
EXPNO                  2
PROCNO                 1
Date_           20110103
Time               20.10
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             5597.015 Hz
FIDRES          0.170807 Hz
AQ             2.9273248 sec
RG                  25.4
DW                89.333 usec
DE                  6.50 usec
TE                 292.9 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1324008 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

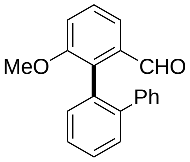


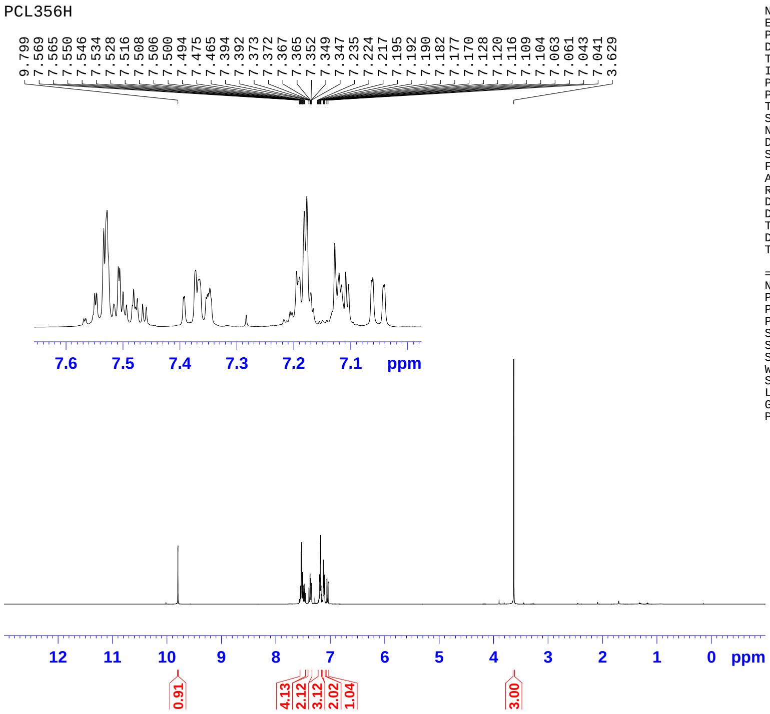
```
NAME              PCL339
EXPNO                  3
PROCNO                 1
Date_           20110103
Time               20.14
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   161
DW                20.800 usec
DE                  6.50 usec
TE                 293.9 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127817 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

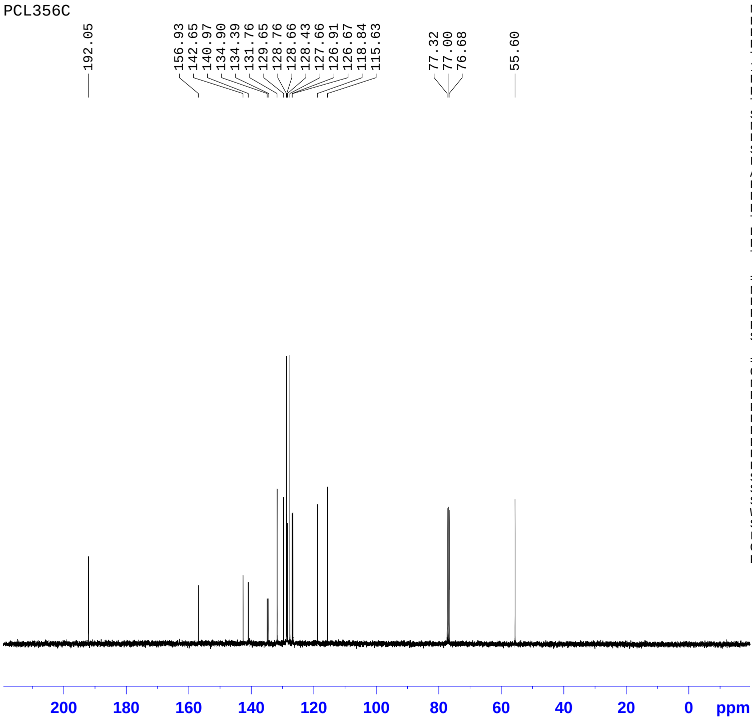
6-Methoxy-2'-phenyl-1,1'-biphenyl-2-carboxaldehyde (Table 7.2, entry 3)





```
NAME              PCL356
EXPNO                  1
PROCNO                 1
Date_           20110113
Time               21.36
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             5597.015 Hz
FIDRES          0.170807 Hz
AQ             2.9273248 sec
RG                  25.4
DW                89.333 usec
DE                  6.50 usec
TE                 295.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1324008 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

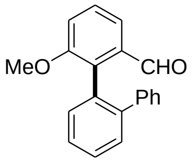


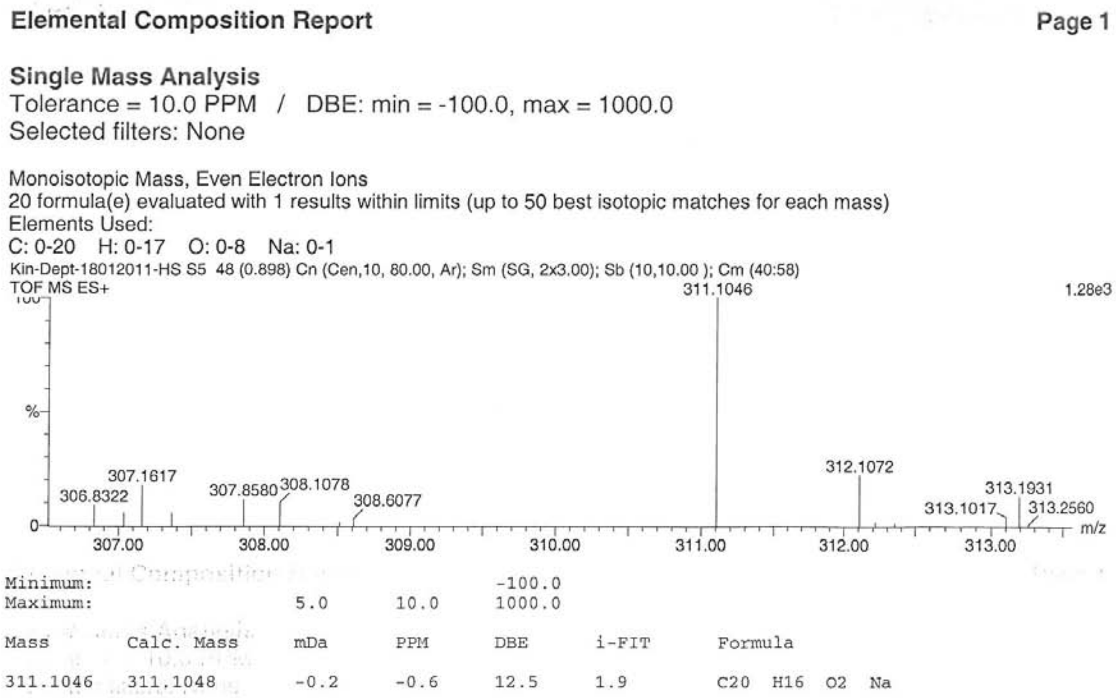
```
NAME              PCL356
EXPNO                  2
PROCNO                 1
Date_           20110113
Time               21.41
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   161
DW                20.800 usec
DE                  6.50 usec
TE                 296.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127817 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

6-Methoxy-2'-phenyl-1,1'-biphenyl-2-carboxaldehyde (Table 7.2, entry 3)





Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -100.0, max = 1000.0
Selected filters: None

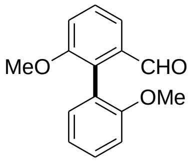
Monoisotopic Mass, Even Electron Ions
20 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-20 H: 0-17 O: 0-8 Na: 0-1
Kin-Dept-18012011-HS S5 48 (0.898) Cn (Cen,10, 80.00, Ar); Sm (SG, 2x3.00); Sb (10,10.00); Cm (40:58)
TOF MS ES+

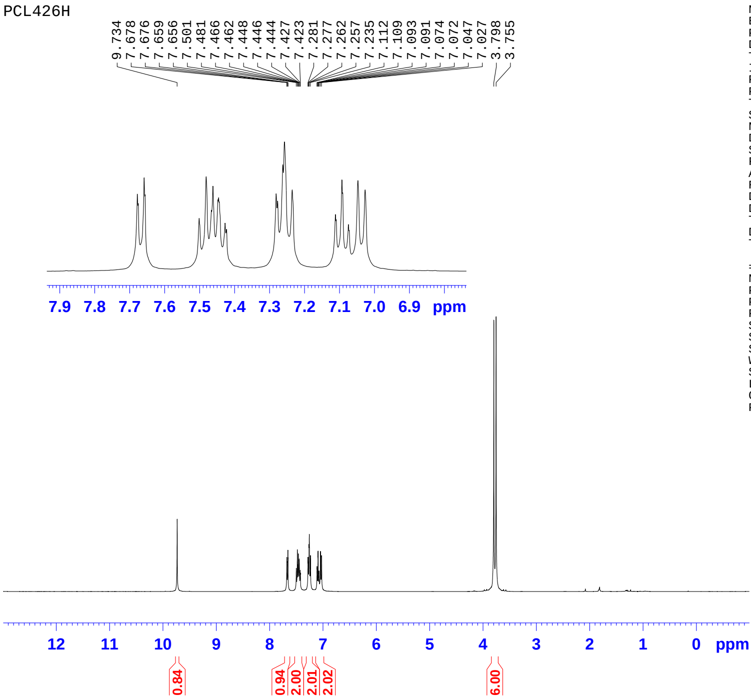
```
Minimum:                                   -100.0
Maximum:                5.0      10.0      1000.0

Mass       Calc. Mass   mDa      PPM       DBE       i-FIT      Formula

311.1046   311.1048     -0.2     -0.6      12.5      1.9        C20  H16  O2  Na
```

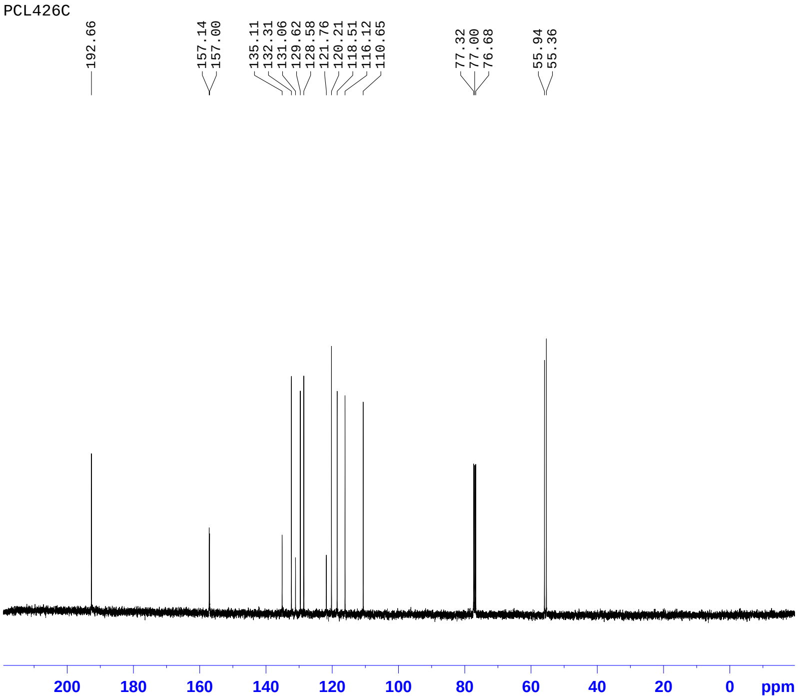
6-Methoxy-2'-methoxy-1,1'-biphenyl-2-carboxaldehyde (Table 7.2, entry 4)





```
NAME            PCL426
EXPNO                1
PROCNO               1
Date_         20110214
Time             21.52
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG           zg30
TD               32768
SOLVENT          CDCl3
NS                  16
DS                   2
SWH           5597.015 Hz
FIDRES        0.170807 Hz
AQ           2.9273248 sec
RG                   8
DW              89.333 usec
DE                6.50 usec
TE               292.4 K
D1          1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                1H
P1               14.70 usec
PL1               0.00 dB
PL1W       11.88122272 W
SFO1       400.1324008 MHz
SI               32768
SF         400.1300000 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.00
```

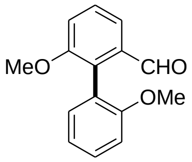


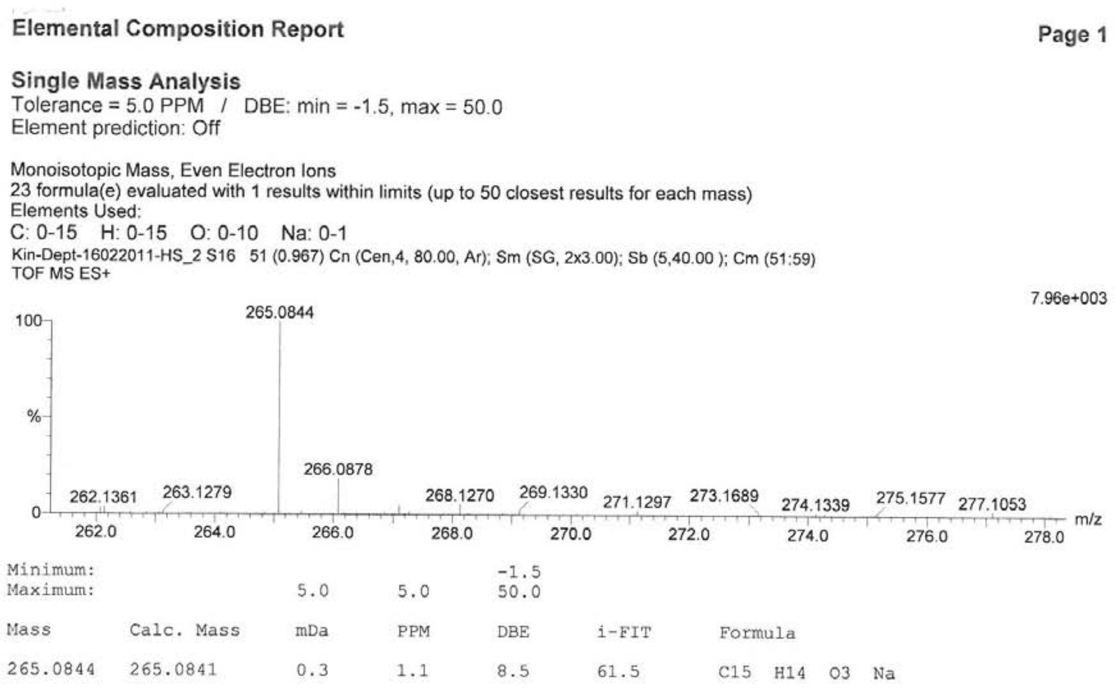
```
NAME            PCL426
EXPNO                2
PROCNO               1
Date_         20110214
Time             21.55
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                  32
DS                   2
SWH          24038.461 Hz
FIDRES        0.366798 Hz
AQ           1.3631988 sec
RG                 161
DW              20.800 usec
DE                6.50 usec
TE               293.2 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1                9.50 usec
PL1              -2.00 dB
PL1W       58.52175522 W
SFO1       100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2            80.00 usec
PL2               0.00 dB
PL12             15.00 dB
PL13             15.00 dB
PL2W       11.88122272 W
PL12W       0.37571725 W
PL13W       0.37571725 W
SFO2       400.1316005 MHz
SI               32768
SF         100.6127874 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```

6-Methoxy-2'-methoxy-1,1'-biphenyl-2-carboxaldehyde (Table 7.2, entry 4)





Elemental Composition Report

Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

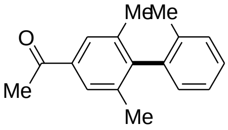
Monoisotopic Mass, Even Electron Ions
23 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-15 H: 0-15 O: 0-10 Na: 0-1
Kin-Dept-16022011-HS_2 S16 51 (0.967) Cn (Cen,4, 80.00, Ar); Sm (SG, 2x3.00); Sb (5,40.00); Cm (51:59)
TOF MS ES+

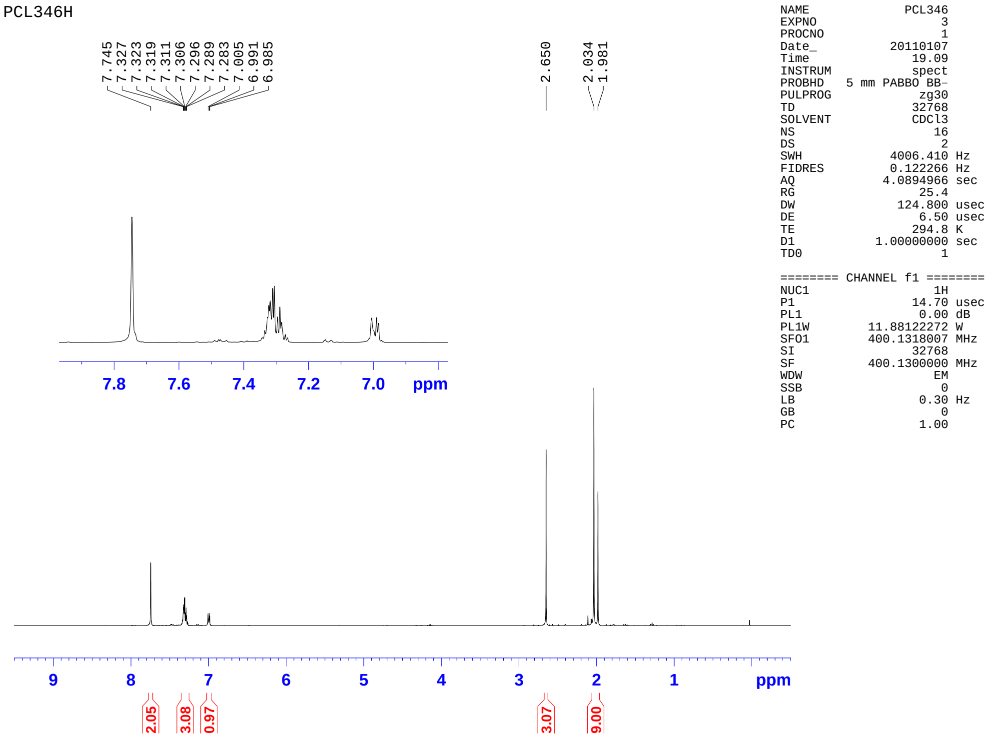
```
Minimum:                                      -1.5
Maximum:                      5.0      5.0    50.0

Mass       Calc. Mass     mDa      PPM      DBE      i-FIT     Formula

265.0844   265.0841       0.3      1.1      8.5      61.5      C15  H14  O3  Na
```

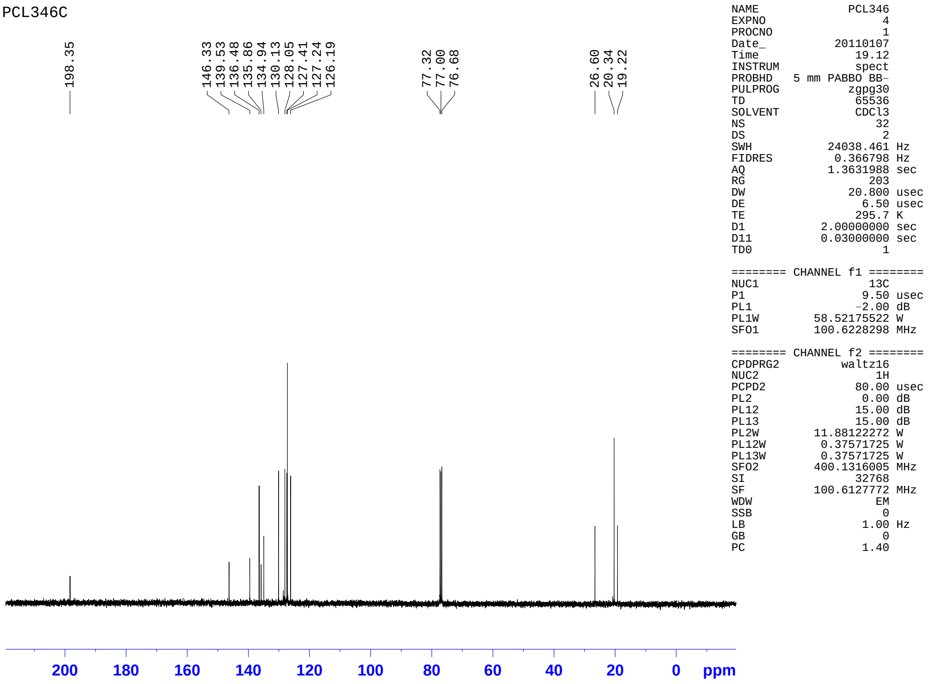
1-(2,6-Dimethyl-2’-methyl-[1,1'-biphenyl]-4-yl)-ethanone (Table 7.2, entry 5; Table 7.3, entry 2)





```
NAME             PCL346
EXPNO                 3
PROCNO                1
Date_          20110107
Time              19.09
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            4006.410 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                 25.4
DW              124.800 usec
DE                 6.50 usec
TE                294.8 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.70 usec
PL1                0.00 dB
PL1W        11.88122272 W
SFO1        400.1318007 MHz
SI                32768
SF          400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

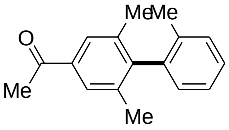


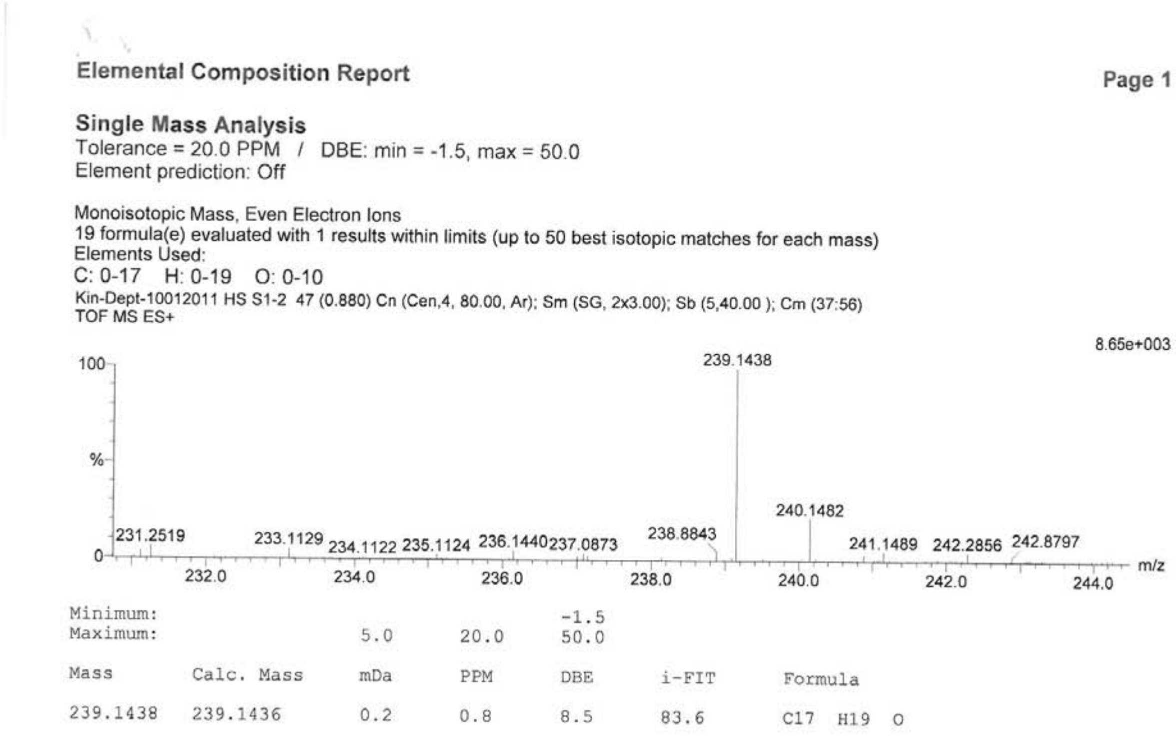
```
NAME             PCL346
EXPNO                 4
PROCNO                1
Date_          20110107
Time              19.12
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                  203
DW               20.800 usec
DE                 6.50 usec
TE                295.7 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.50 usec
PL1               -2.00 dB
PL1W        58.52175522 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL13              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
PL13W        0.37571725 W
SFO2        400.1316005 MHz
SI                32768
SF          100.6127772 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

1-(2,6-dimethyl-2’-methyl-[1,1'-biphenyl]-4-yl)-ethanone (Table 7.2, entry 5; Table 7.3, entry 2)





Elemental Composition Report

Page 1

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

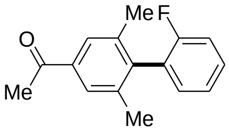
Monoisotopic Mass, Even Electron Ions
19 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-17 H: 0-19 O: 0-10
Kin-Dept-10012011 HS S1-2 47 (0.880) Cn (Cen,4, 80.00, Ar); Sm (SG, 2x3.00); Sb (5,40.00); Cm (37:56)
TOF MS ES+

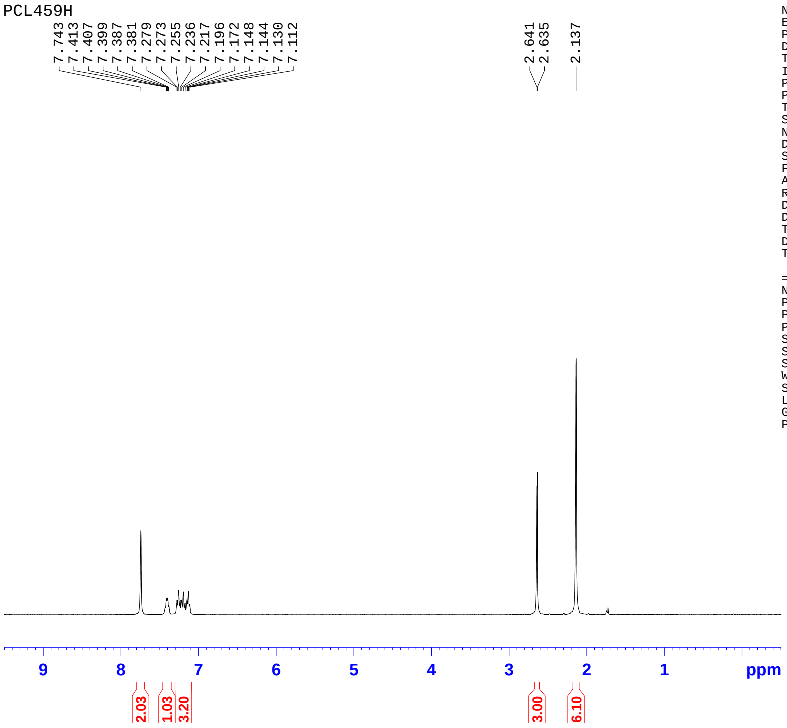
```
Minimum:                                        -1.5
Maximum:                      5.0      20.0     50.0

Mass        Calc. Mass        mDa      PPM      DBE      i-FIT      Formula

239.1438    239.1436          0.2      0.8      8.5      83.6       C17  H19  O
```

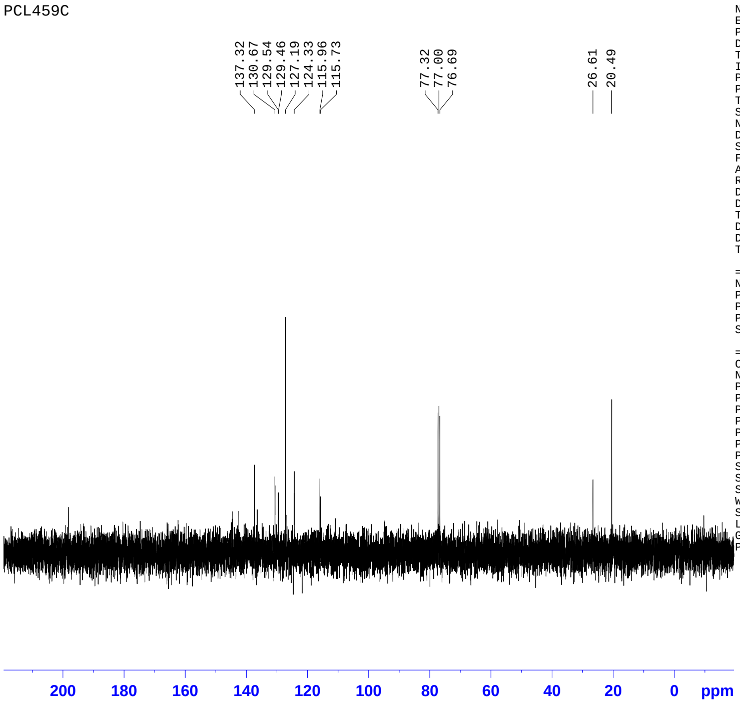
1-(2,6-dimethyl-2’-fluoro-[1,1'-biphenyl]-4-yl)-ethanone (Table 7.2, entry 6; Table 7.3, entry 5)





```
NAME              PCL459
EXPNO                  1
PROCNO                 1
Date_           20110305
Time               16.25
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                     1
DW               124.800 usec
DE                  6.50 usec
TE                 299.8 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

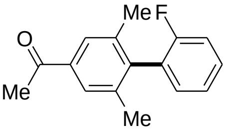


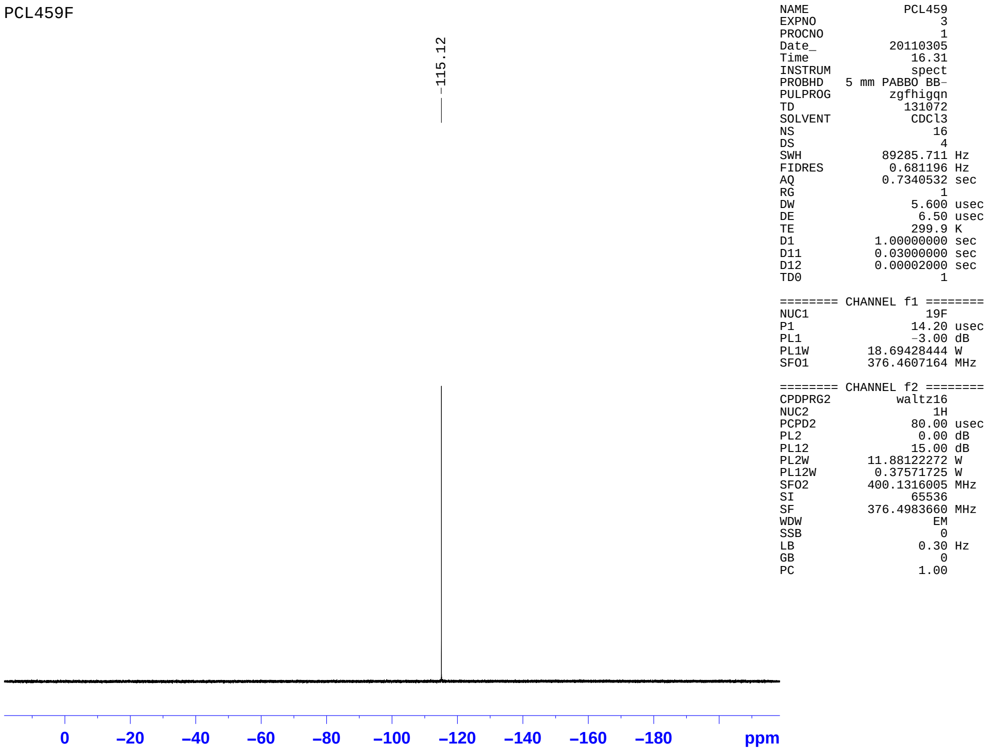
```
NAME              PCL459
EXPNO                  2
PROCNO                 1
Date_           20110305
Time               16.28
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                     1
DW                20.800 usec
DE                  6.50 usec
TE                 300.6 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127736 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

1-(2,6-dimethyl-2’-fluoro-[1,1'-biphenyl]-4-yl)-ethanone (Table 7.2, entry 6; Table 7.3, entry 5)

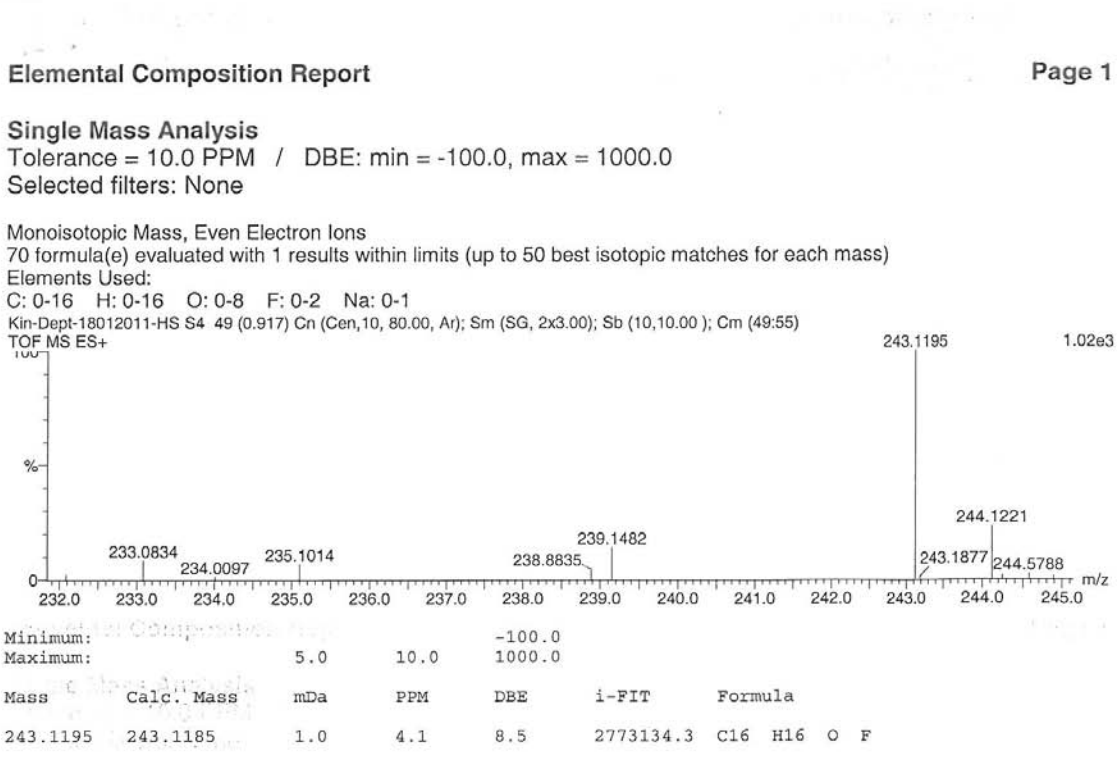




```
NAME            PCL459
EXPNO                3
PROCNO               1
Date_         20110305
Time             16.31
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG       zgfhigqn
TD              131072
SOLVENT          CDCl3
NS                  16
DS                   4
SWH          89285.711 Hz
FIDRES        0.681196 Hz
AQ           0.7340532 sec
RG                   1
DW               5.600 usec
DE                6.50 usec
TE               299.9 K
D1          1.00000000 sec
D11         0.03000000 sec
D12         0.00002000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               19F
P1               14.20 usec
PL1              -3.00 dB
PL1W       18.69428444 W
SFO1       376.4607164 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2            80.00 usec
PL2               0.00 dB
PL12             15.00 dB
PL2W       11.88122272 W
PL12W       0.37571725 W
SFO2       400.1316005 MHz
SI               65536
SF         376.4983660 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.00
```



Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -100.0, max = 1000.0
Selected filters: None

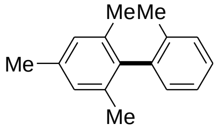
Monoisotopic Mass, Even Electron Ions
70 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-16 H: 0-16 O: 0-8 F: 0-2 Na: 0-1
Kin-Dept-18012011-HS S4 49 (0.917) Cn (Cen,10, 80.00, Ar); Sm (SG, 2x3.00); Sb (10,10.00); Cm (49:55)
TOF MS ES+

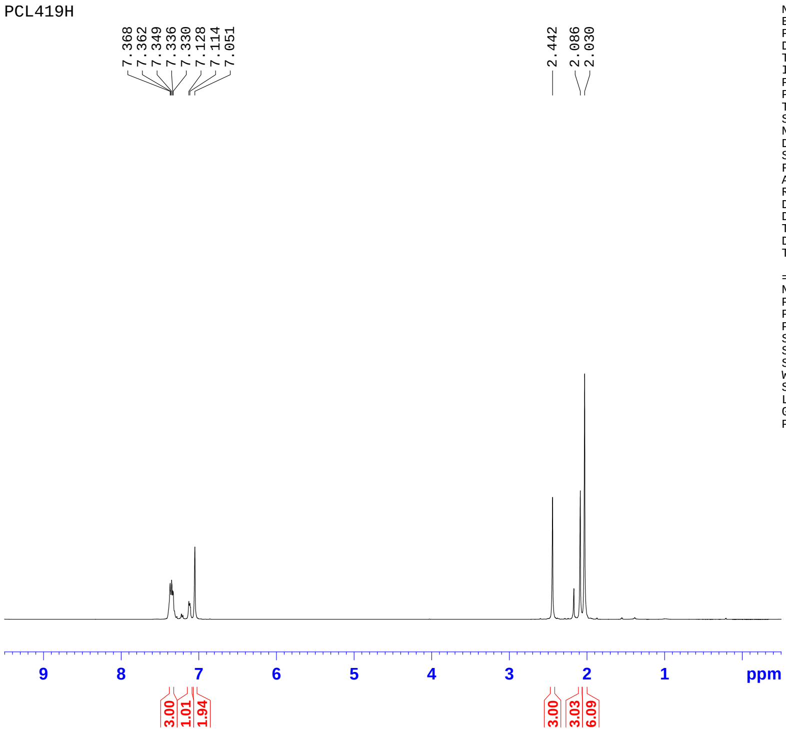
```
Minimum:                                        -100.0
Maximum:                        5.0      10.0   1000.0

Mass        Calc. Mass        mDa      PPM      DBE      i-FIT        Formula

243.1195    243.1185          1.0      4.1      8.5      2773134.3    C16  H16  O  F
```

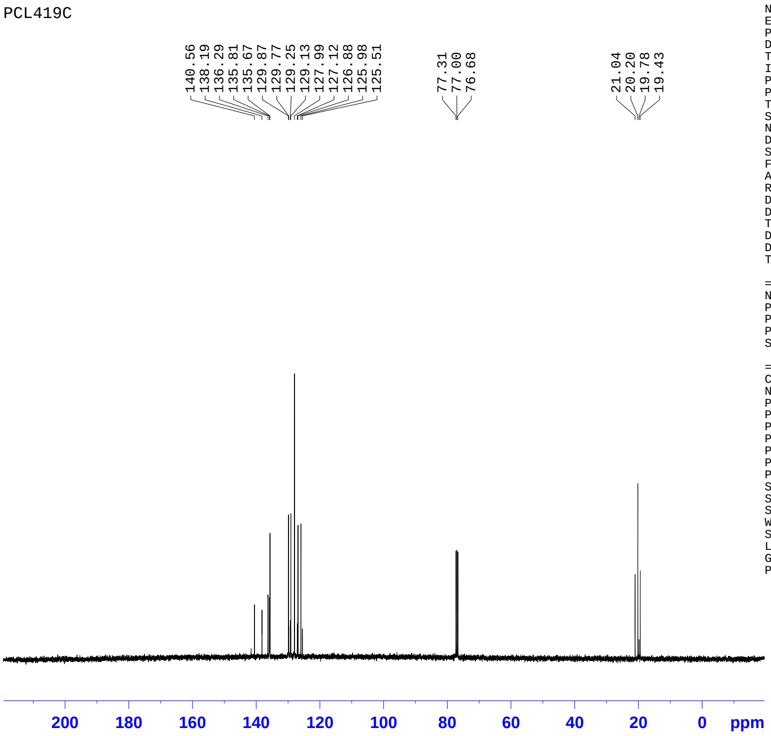
2,2',4,6-Tetramethyl-1,1'-biphenyl (Table 7.2, entry 7; Table 7.3, entry 6)





```
NAME              PCL419
EXPNO                  1
PROCNO                 1
Date_           20110211
Time               21.23
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  7.12
DW               124.800 usec
DE                  6.50 usec
TE                 296.9 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

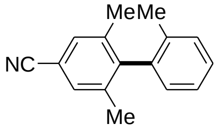


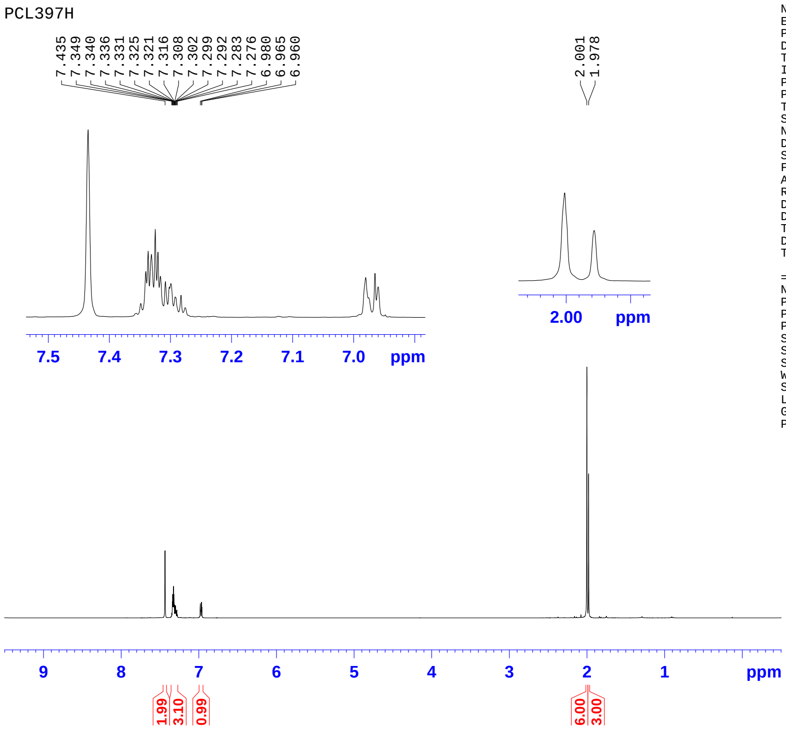
```
NAME              PCL419
EXPNO                  2
PROCNO                 1
Date_           20110211
Time               21.27
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                  40.3
DW                20.800 usec
DE                  6.50 usec
TE                 297.8 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127804 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

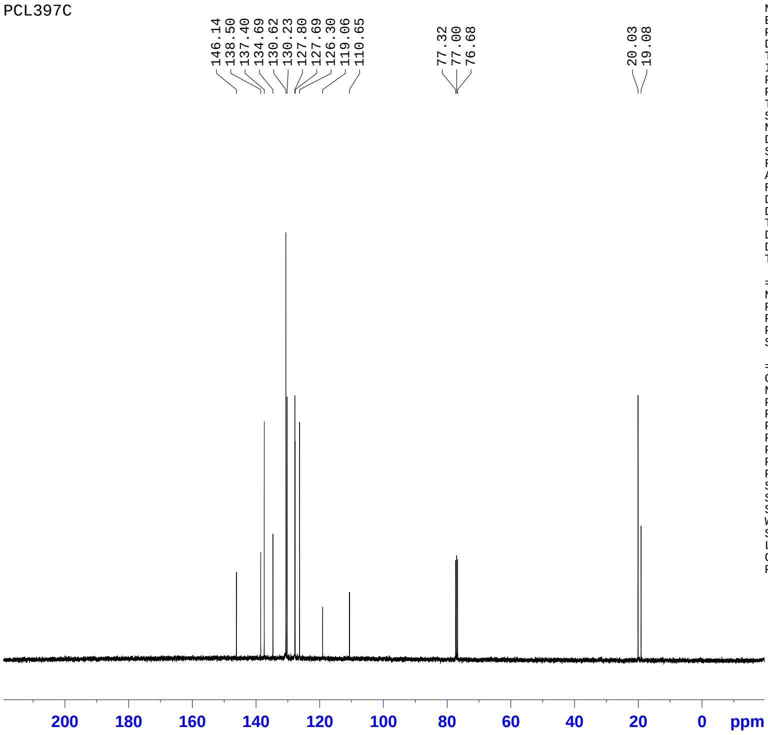
4-Cyano-2,2',6-trimethyl-1,1'-biphenyl (Table 7.2, entry 8)





```
NAME              PCL397
EXPNO                  1
PROCNO                 1
Date_           20110128
Time               13.31
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  11.3
DW               124.800 usec
DE                  6.50 usec
TE                 295.4 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

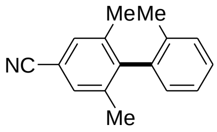


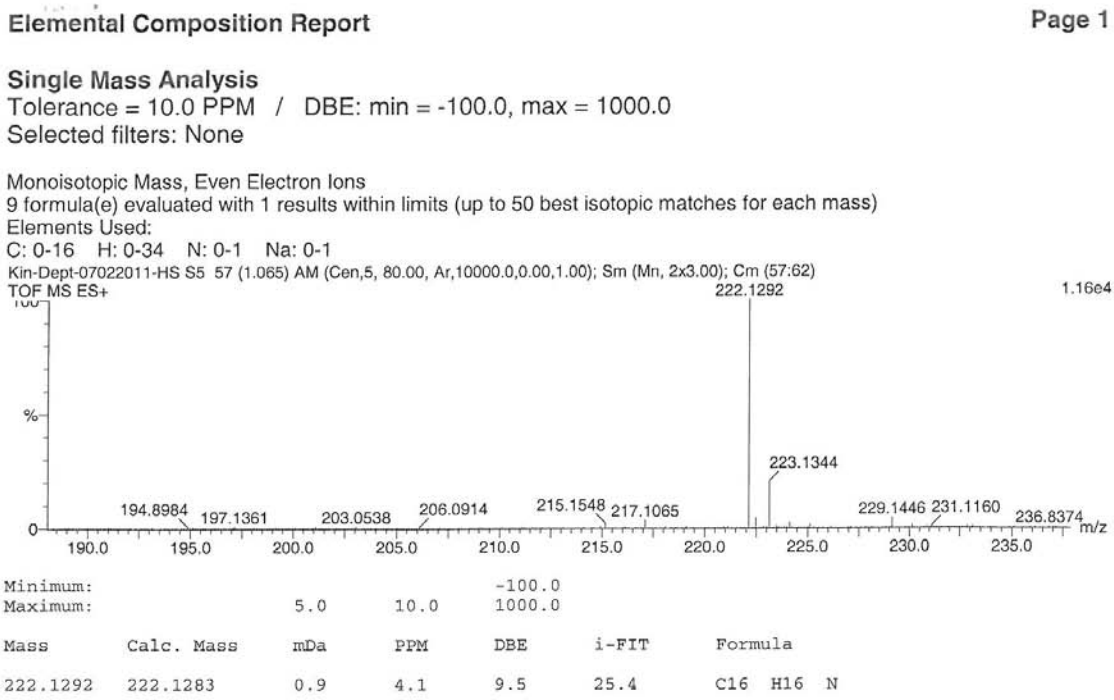
```
NAME              PCL397
EXPNO                  2
PROCNO                 1
Date_           20110128
Time               13.36
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   161
DW                20.800 usec
DE                  6.50 usec
TE                 296.3 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127862 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

4-Cyano-2,2',6-trimethyl-1,1'-biphenyl (Table 7.2, entry 8)





Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -100.0, max = 1000.0
Selected filters: None

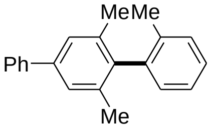
Monoisotopic Mass, Even Electron Ions
9 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-16 H: 0-34 N: 0-1 Na: 0-1
Kin-Dept-07022011-HS S5 57 (1.065) AM (Cen,5, 80.00, Ar,10000.0,0.00,1.00); Sm (Mn, 2x3.00); Cm (57:62)
TOF MS ES+

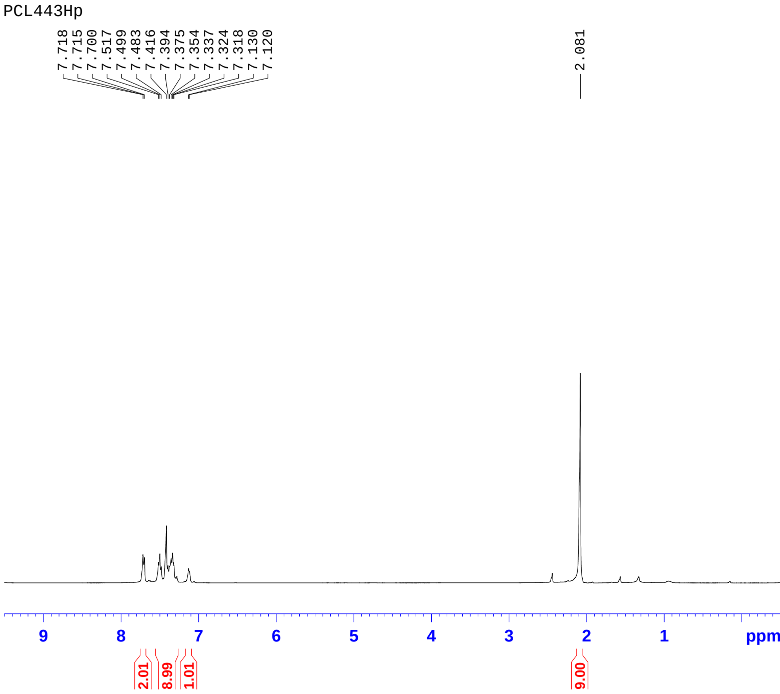
```
Minimum:                                       -100.0
Maximum:                        5.0     10.0   1000.0

Mass       Calc. Mass   mDa     PPM     DBE     i-FIT     Formula

222.1292   222.1283     0.9     4.1     9.5     25.4      C16  H16  N
```

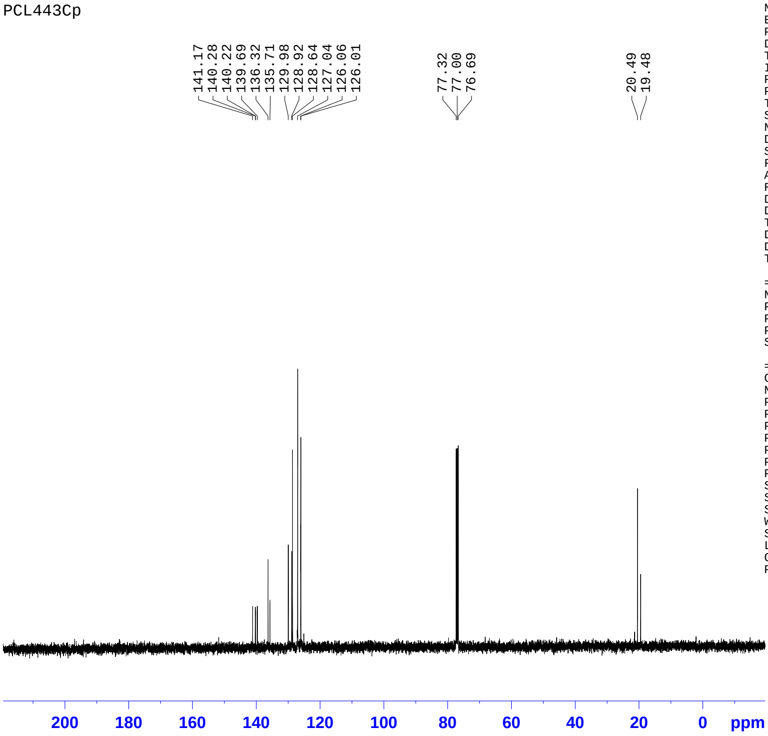
4-Phenyl-2,2',6-trimethyl-1,1'-biphenyl (Table 7.2, entry 9; Table 7.3, entry 7)





```
NAME              PCL443
EXPNO                  3
PROCNO                 1
Date_           20110218
Time               11.39
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                    16
DW               124.800 usec
DE                  6.50 usec
TE                 296.8 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

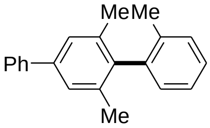


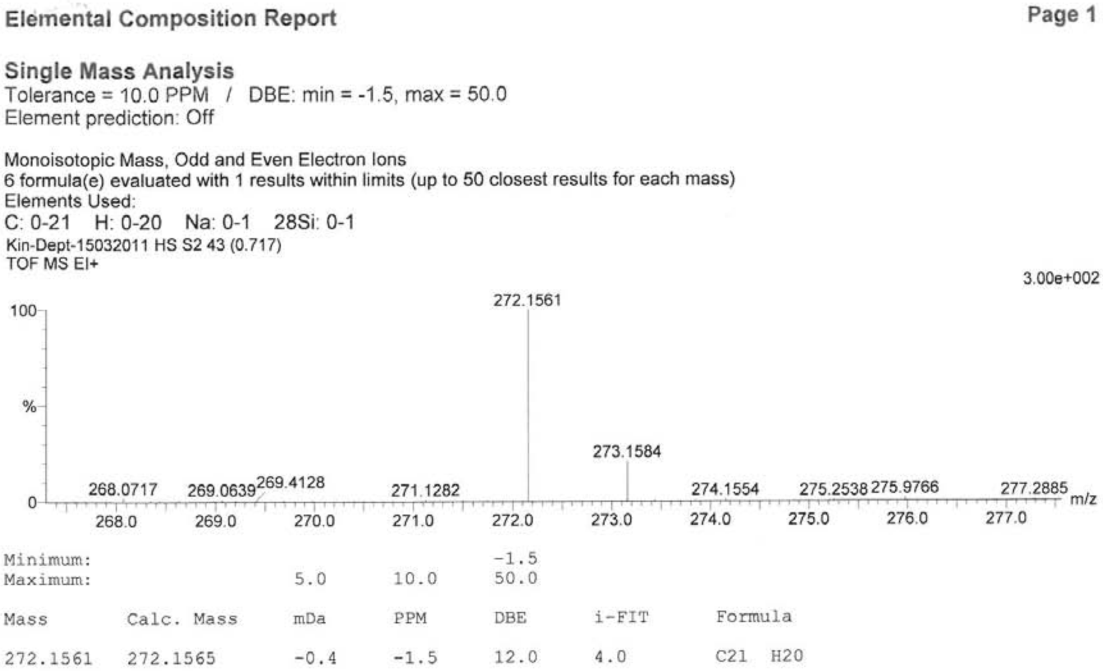
```
NAME              PCL443
EXPNO                  4
PROCNO                 1
Date_           20110218
Time               11.42
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   161
DW                20.800 usec
DE                  6.50 usec
TE                 297.6 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127759 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

4-Phenyl-2,2',6-trimethyl-1,1'-biphenyl (Table 7.2, entry 9; Table 7.3, entry 7)





Elemental Composition Report

Page 1

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

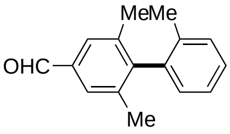
Monoisotopic Mass, Odd and Even Electron Ions
6 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-21 H: 0-20 Na: 0-1 28Si: 0-1
Kin-Dept-15032011 HS S2 43 (0.717)
TOF MS EI+

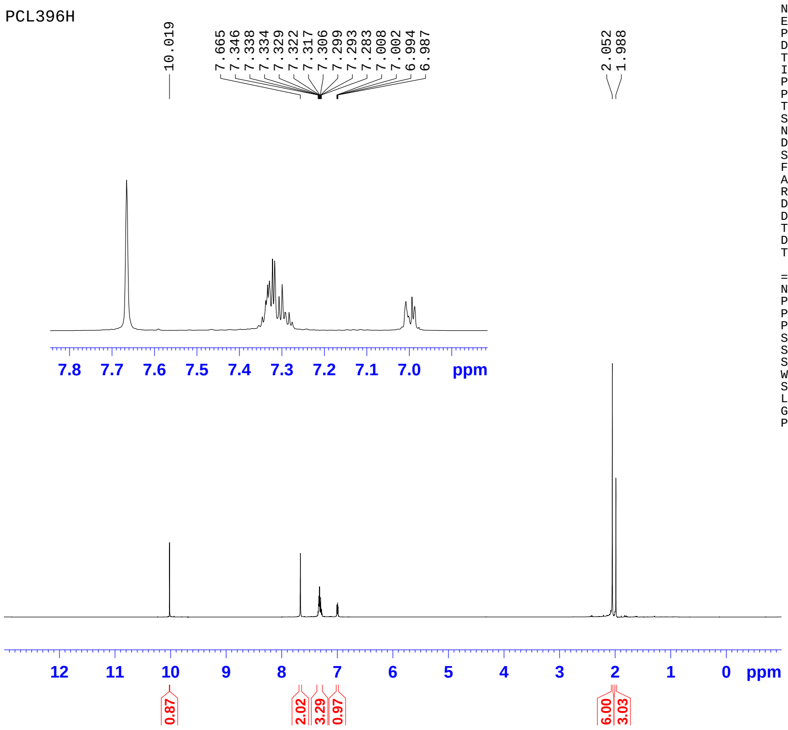
```
Minimum:                                      -1.5
Maximum:                    5.0       10.0    50.0

Mass       Calc. Mass       mDa       PPM     DBE      i-FIT      Formula

272.1561   272.1565         -0.4      -1.5    12.0     4.0        C21  H20
```

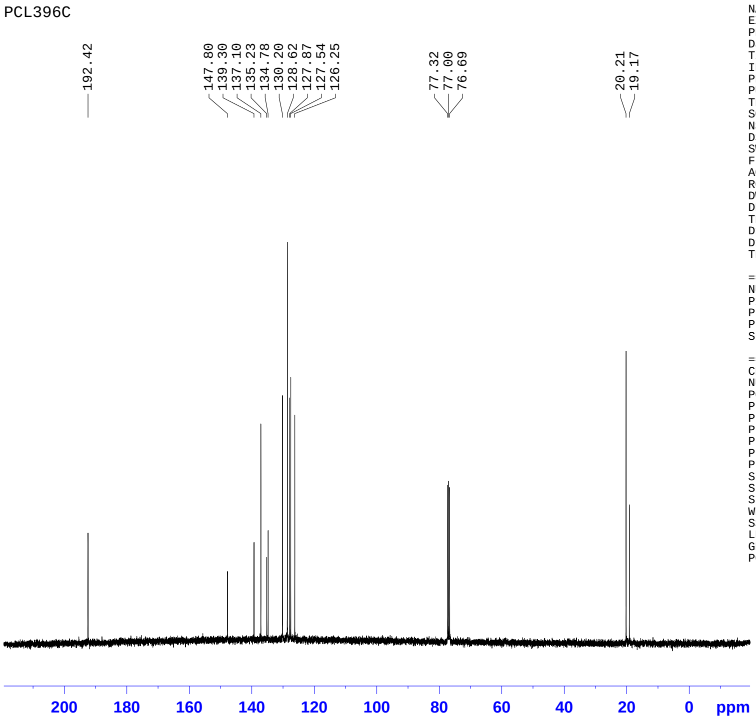
2,2',6-Trimethyl-[1,1'-biphenyl]-4-carbaldehyde (Table 7.2, entry 10)





```
NAME               PCL396
EXPNO                   1
PROCNO                  1
Date_            20110126
Time                21.52
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              5597.015 Hz
FIDRES           0.170807 Hz
AQ              2.9273248 sec
RG                     18
DW                 89.333 usec
DE                   6.50 usec
TE                  296.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.70 usec
PL1                  0.00 dB
PL1W          11.88122272 W
SFO1          400.1324008 MHz
SI                  32768
SF            400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

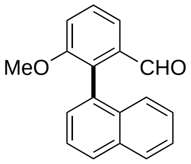


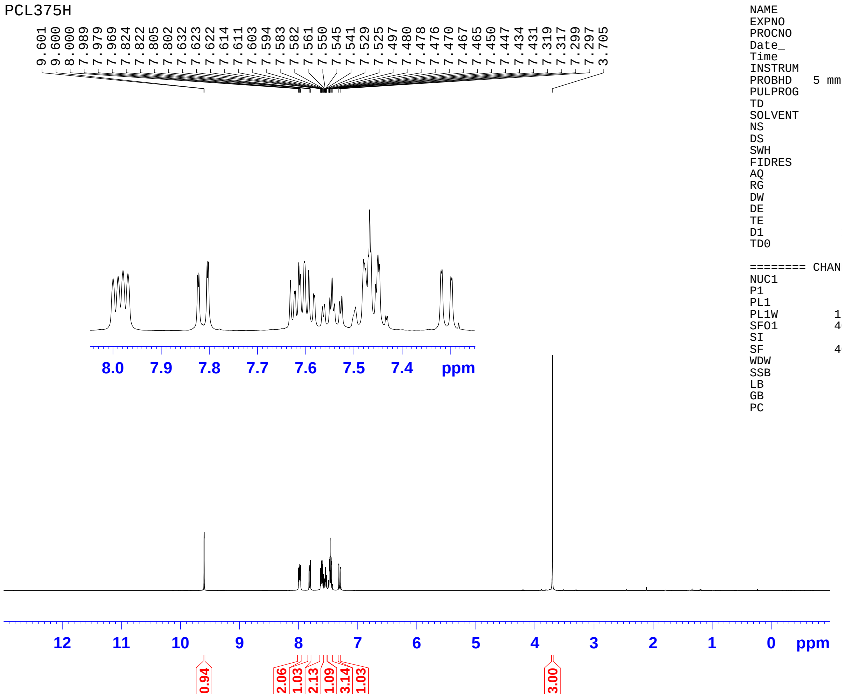
```
NAME               PCL396
EXPNO                   2
PROCNO                  1
Date_            20110126
Time                21.56
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      2
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                    161
DW                 20.800 usec
DE                   6.50 usec
TE                  296.9 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.50 usec
PL1                 -2.00 dB
PL1W          58.52175522 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                15.00 dB
PL13                15.00 dB
PL2W          11.88122272 W
PL12W          0.37571725 W
PL13W          0.37571725 W
SFO2          400.1316005 MHz
SI                  32768
SF            100.6127794 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

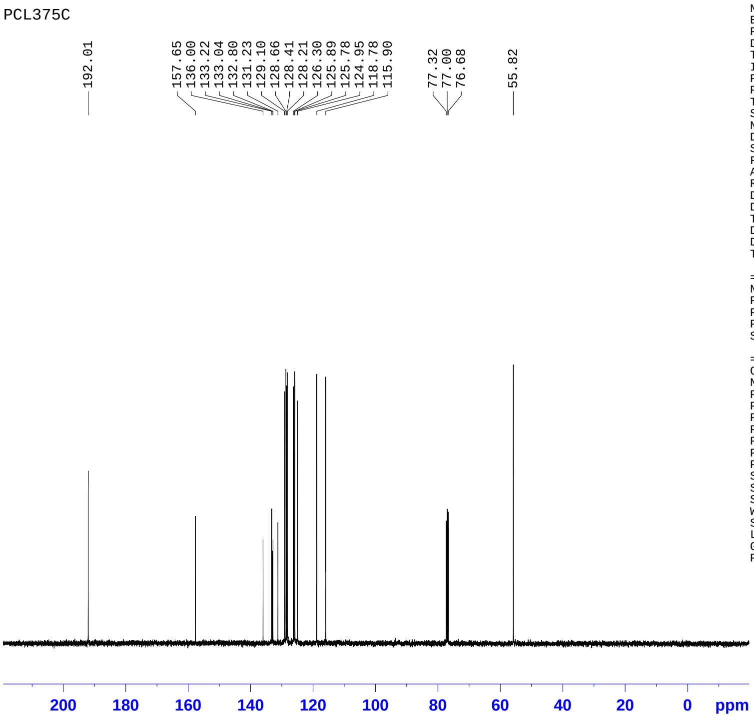
3-Methoxy-2-(1-naphthalenyl)benzaldehyde (Table 7.2, entry 11)





```
NAME            PCL375
EXPNO                1
PROCNO               1
Date_         20110115
Time             22.40
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG           zg30
TD               32768
SOLVENT          CDCl3
NS                  16
DS                   2
SWH           5597.015 Hz
FIDRES        0.170807 Hz
AQ           2.9273248 sec
RG                  16
DW              89.333 usec
DE                6.50 usec
TE               295.0 K
D1          1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                1H
P1               14.70 usec
PL1               0.00 dB
PL1W       11.88122272 W
SFO1       400.1324008 MHz
SI               32768
SF         400.1300000 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.00
```

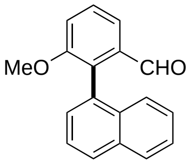


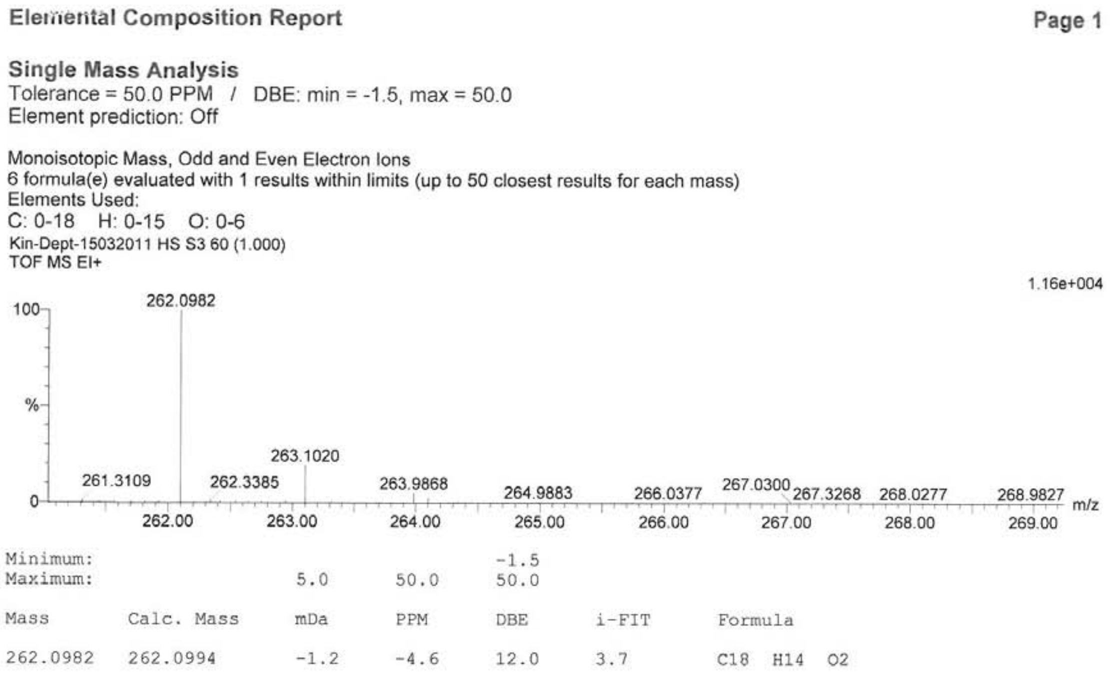
```
NAME            PCL375
EXPNO                2
PROCNO               1
Date_         20110115
Time             22.44
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG        zgpg30
TD               65536
SOLVENT          CDCl3
NS                  32
DS                   2
SWH          24038.461 Hz
FIDRES        0.366798 Hz
AQ           1.3631988 sec
RG                 161
DW              20.800 usec
DE                6.50 usec
TE               296.0 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1                9.50 usec
PL1              -2.00 dB
PL1W       58.52175522 W
SFO1       100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2            80.00 usec
PL2               0.00 dB
PL12             15.00 dB
PL13             15.00 dB
PL2W       11.88122272 W
PL12W       0.37571725 W
PL13W       0.37571725 W
SFO2       400.1316005 MHz
SI               32768
SF         100.6127929 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```

3-Methoxy-2-(1-naphthalenyl)benzaldehyde (Table 7.2, entry 11)





Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

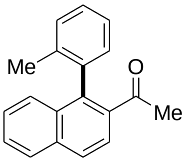
Monoisotopic Mass, Odd and Even Electron Ions
6 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-18 H: 0-15 O: 0-6
Kin-Dept-15032011 HS S3 60 (1.000)
TOF MS EI+

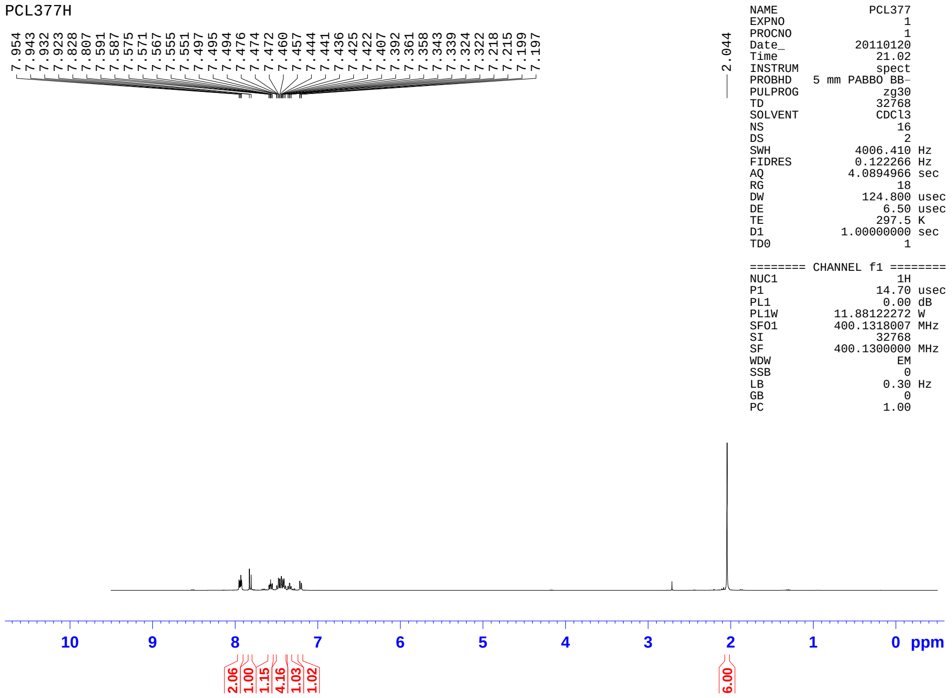
```
Minimum:                                      -1.5
Maximum:                     5.0      50.0    50.0

Mass      Calc. Mass         mDa      PPM     DBE      i-FIT      Formula

262.0982  262.0994           -1.2     -4.6    12.0     3.7        C18  H14  O2
```

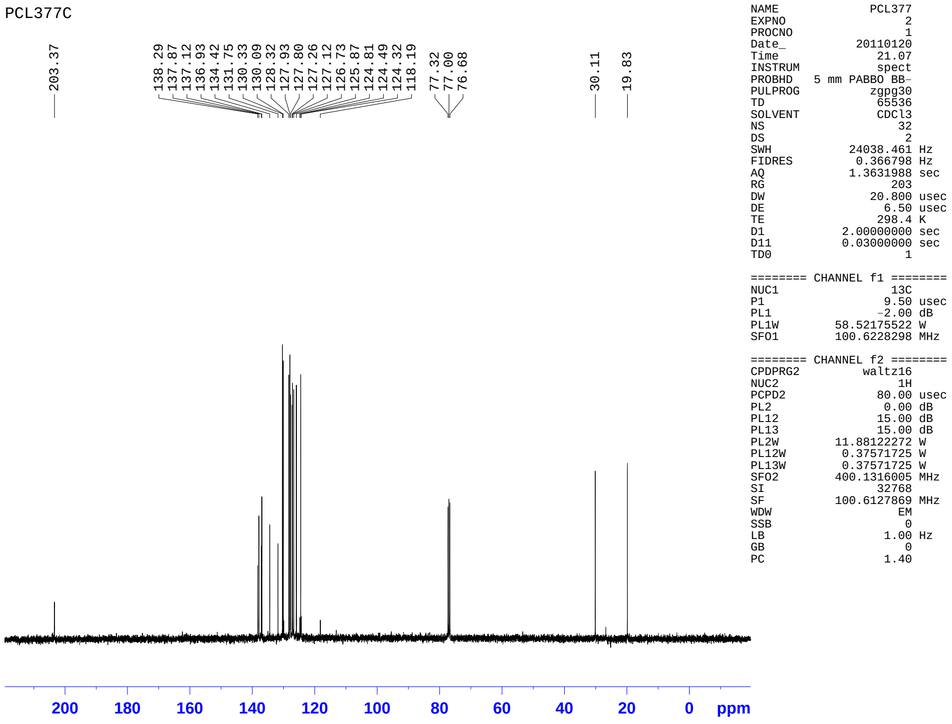
1-(1-*o*-Tolylnaphthalen-2-yl)ethanone (Table 7.2, entry 12)





```
NAME              PCL377
EXPNO                  1
PROCNO                 1
Date_           20110120
Time               21.02
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                    18
DW               124.800 usec
DE                  6.50 usec
TE                 297.5 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

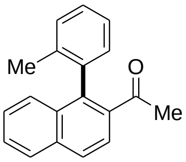


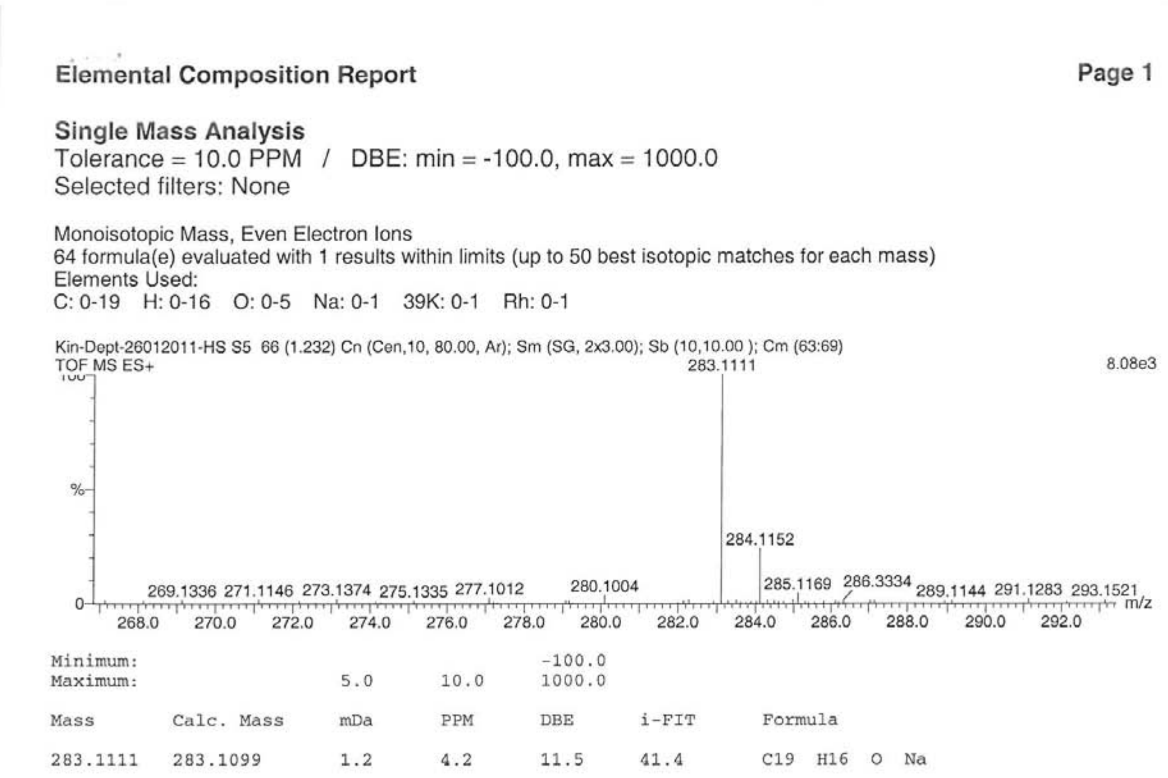
```
NAME              PCL377
EXPNO                  2
PROCNO                 1
Date_           20110120
Time               21.07
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   203
DW                20.800 usec
DE                  6.50 usec
TE                 298.4 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127869 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

1-(1-*o*-Tolylnaphthalen-2-yl)ethanone (Table 7.2, entry 12)





Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -100.0, max = 1000.0
Selected filters: None

Monoisotopic Mass, Even Electron Ions
64 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-19 H: 0-16 O: 0-5 Na: 0-1 39K: 0-1 Rh: 0-1

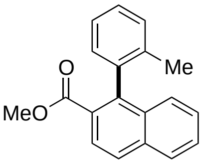
Kin-Dept-26012011-HS S5 66 (1.232) Cn (Cen,10, 80.00, Ar); Sm (SG, 2x3.00); Sb (10,10.00); Cm (63:69)
TOF MS ES+

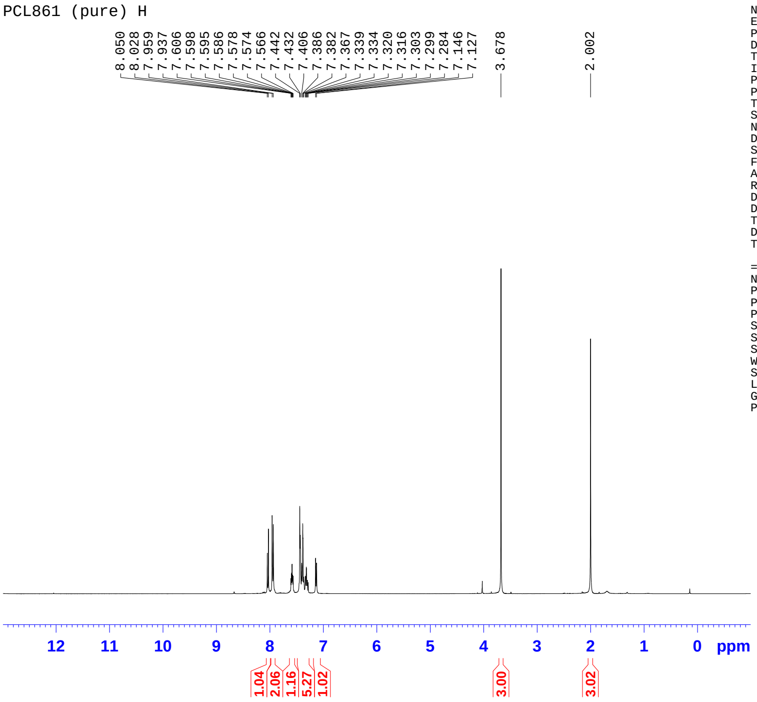
```
Minimum:                                      -100.0
Maximum:                    5.0       10.0    1000.0

Mass       Calc. Mass       mDa       PPM     DBE        i-FIT      Formula

283.1111   283.1099         1.2       4.2     11.5       41.4       C19  H16  O  Na
```

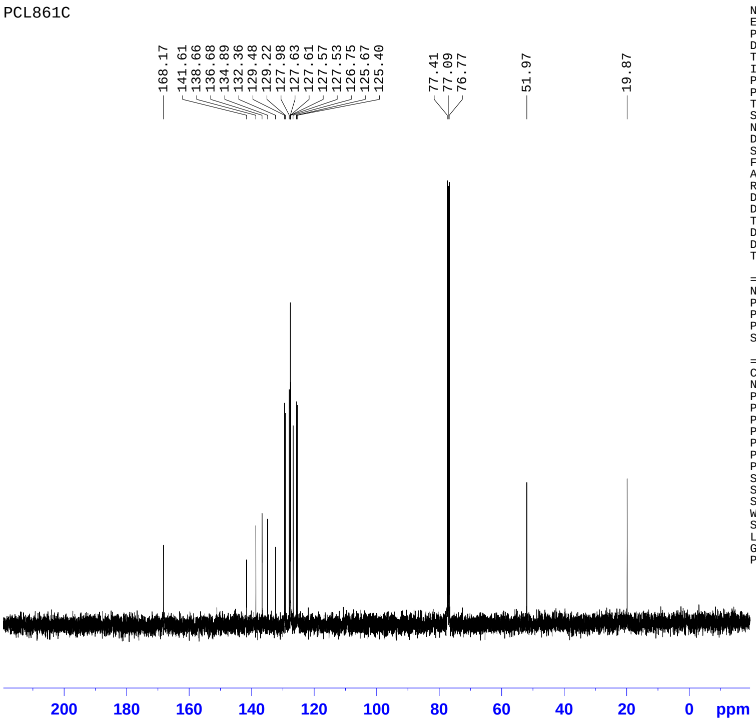
Methyl 1-(*o*-tolyl)-2-naphthoate (Table 7.2, entry 13)





```
NAME               PCL861
EXPNO                   1
PROCNO                  1
Date_            20130227
Time                23.39
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              5597.015 Hz
FIDRES           0.170807 Hz
AQ              2.9273248 sec
RG                   50.8
DW                 89.333 usec
DE                   6.50 usec
TE                  299.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.70 usec
PL1                  0.00 dB
PL1W          11.88122272 W
SFO1          400.1324008 MHz
SI                  32768
SF            400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

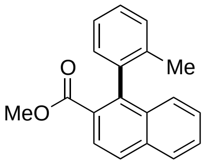


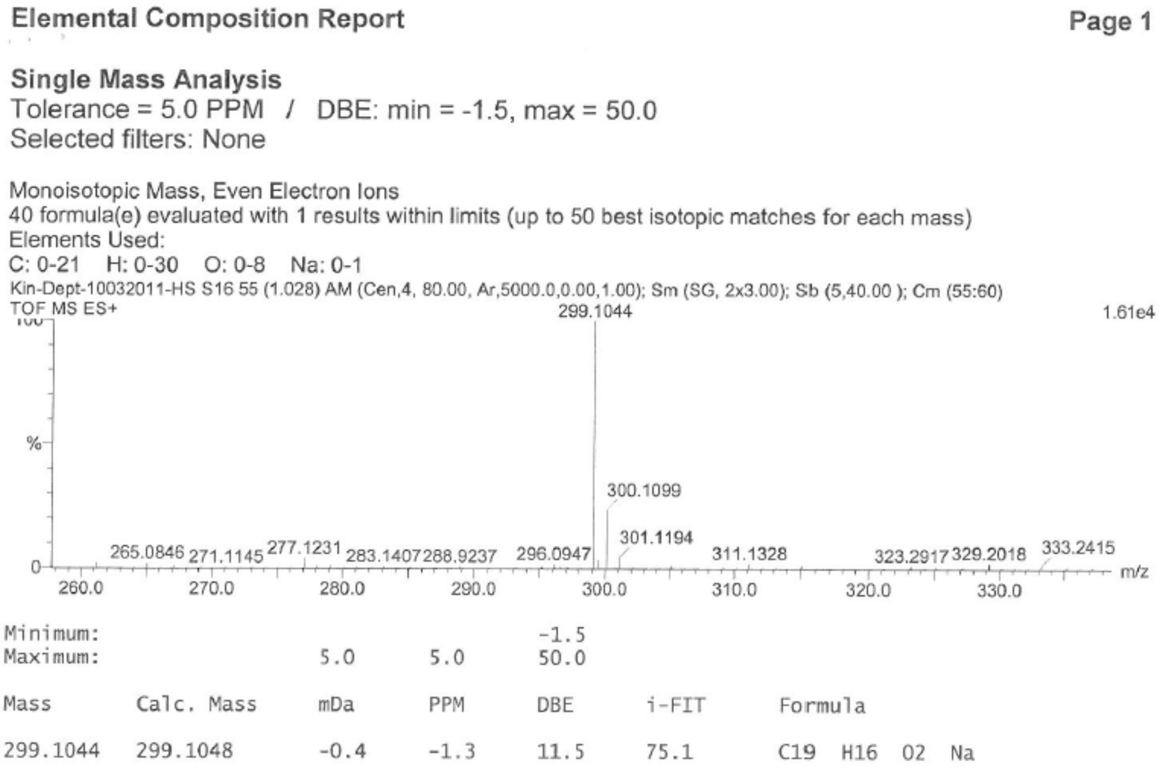
```
NAME               PCL861
EXPNO                   2
PROCNO                  1
Date_            20130227
Time                23.41
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     24
DS                      2
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                    228
DW                 20.800 usec
DE                   6.50 usec
TE                  299.5 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.50 usec
PL1                 -2.00 dB
PL1W          58.52175522 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                15.00 dB
PL13                15.00 dB
PL2W          11.88122272 W
PL12W          0.37571725 W
PL13W          0.37571725 W
SFO2          400.1316005 MHz
SI                  32768
SF            100.6127690 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

Methyl 1-(*o*-tolyl)-2-naphthoate (Table 7.2, entry 13)





Elemental Composition Report

Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

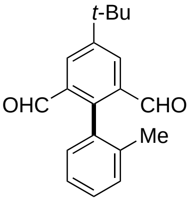
Monoisotopic Mass, Even Electron Ions
40 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-21 H: 0-30 O: 0-8 Na: 0-1
Kin-Dept-10032011-HS S16 55 (1.028) AM (Cen,4, 80.00, Ar,5000.0,0.00,1.00); Sm (SG, 2x3.00); Sb (5,40.00); Cm (55:60)
TOF MS ES+

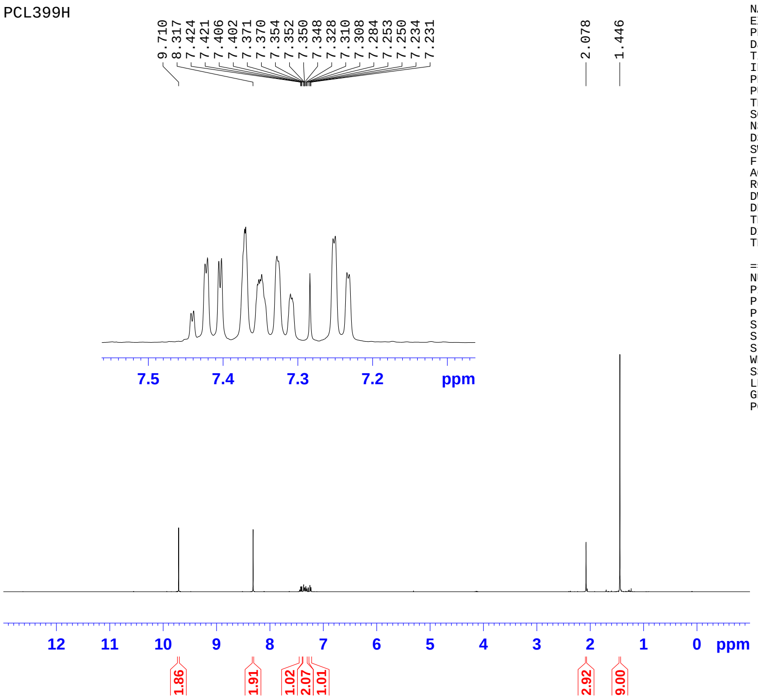
```
Minimum:                                  -1.5
Maximum:                  5.0     5.0     50.0

Mass      Calc. Mass      mDa     PPM     DBE     i-FIT     Formula

299.1044  299.1048        -0.4    -1.3    11.5    75.1      C19  H16  O2  Na
```

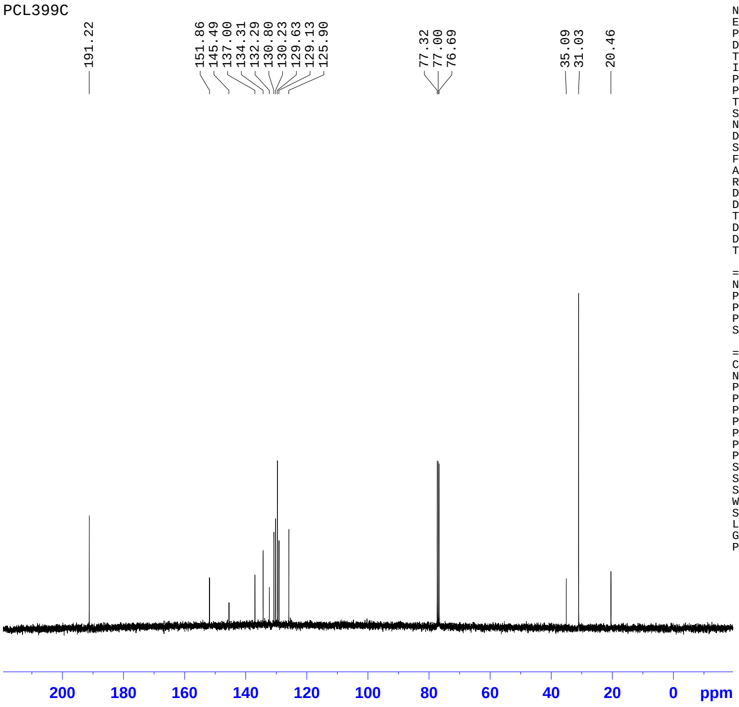
4-(*tert*-Butyl)-2'-methyl-[1,1'-biphenyl]-2,6-dicarbaldehyde (Table 7.2, entry 14)





```
NAME              PCL399
EXPNO                  1
PROCNO                 1
Date_           20110128
Time               21.53
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             5597.015 Hz
FIDRES          0.170807 Hz
AQ             2.9273248 sec
RG                  25.4
DW                89.333 usec
DE                  6.50 usec
TE                 296.3 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1324008 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

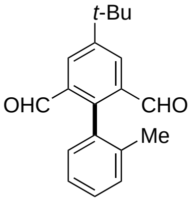


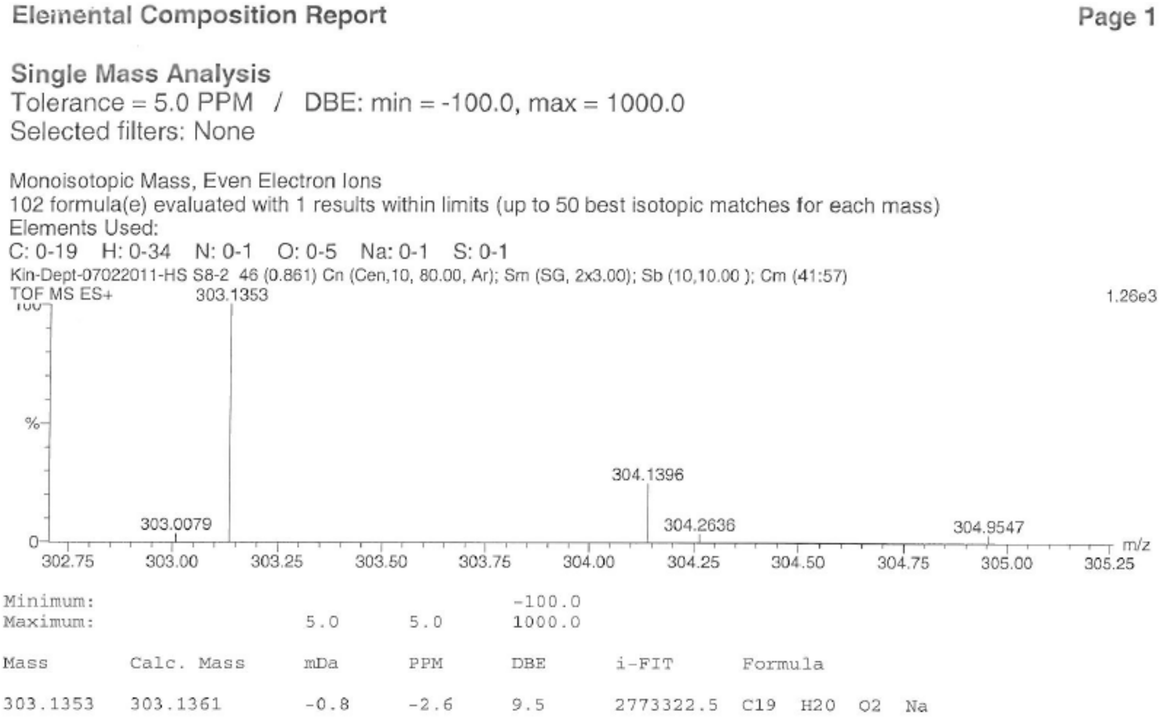
```
NAME              PCL399
EXPNO                  2
PROCNO                 1
Date_           20110128
Time               21.55
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                  25.4
DW                20.800 usec
DE                  6.50 usec
TE                 297.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127728 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

4-(*tert*-Butyl)-2'-methyl-[1,1'-biphenyl]-2,6-dicarbaldehyde (Table 7.2, entry 14)





Elemental Composition Report

Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -100.0, max = 1000.0
Selected filters: None

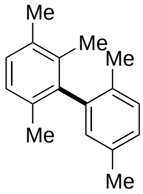
Monoisotopic Mass, Even Electron Ions
102 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-19 H: 0-34 N: 0-1 O: 0-5 Na: 0-1 S: 0-1
Kin-Dept-07022011-HS S8-2 46 (0.861) Cn (Cen,10, 80.00, Ar); Sm (SG, 2x3.00); Sb (10,10.00); Cm (41:57)
TOF MS ES+

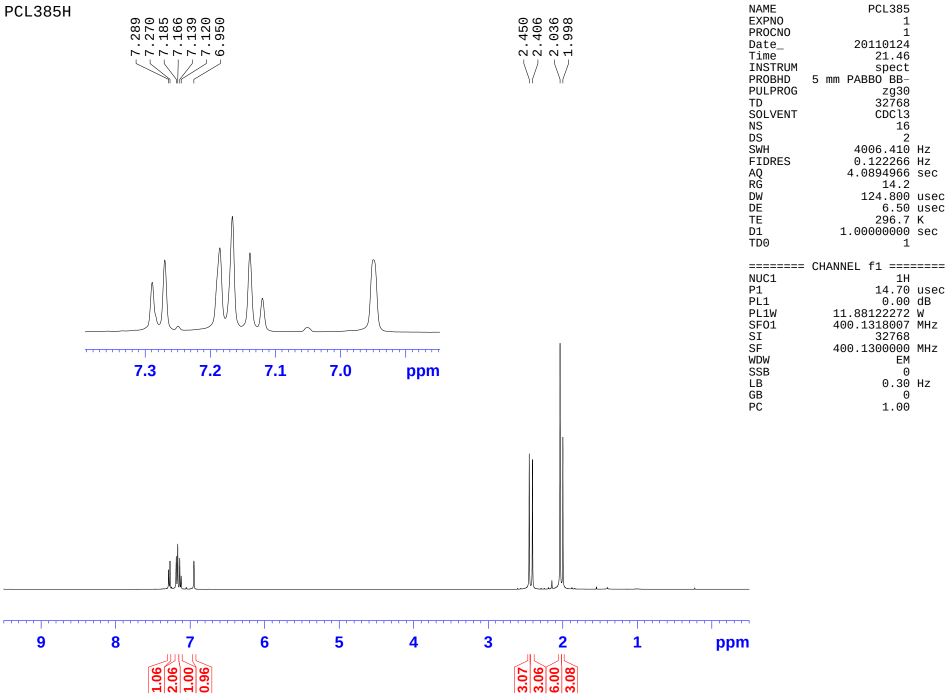
```
Minimum:                                        -100.0
Maximum:                    5.0       5.0       1000.0

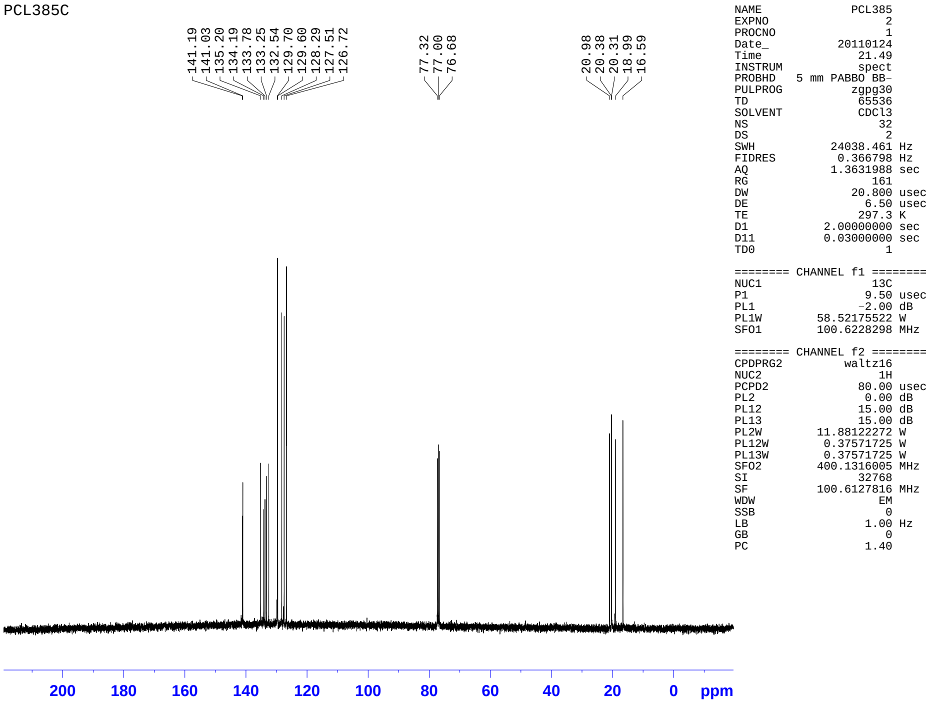
Mass        Calc. Mass      mDa       PPM       DBE        i-FIT       Formula

303.1353    303.1361        -0.8      -2.6      9.5        2773322.5   C19  H20  O2  Na
```

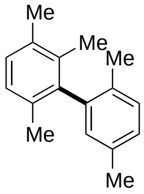
2,2',3,5’,6-Pentamethyl-1,1'-biphenyl (Table 7.2, entry 15)

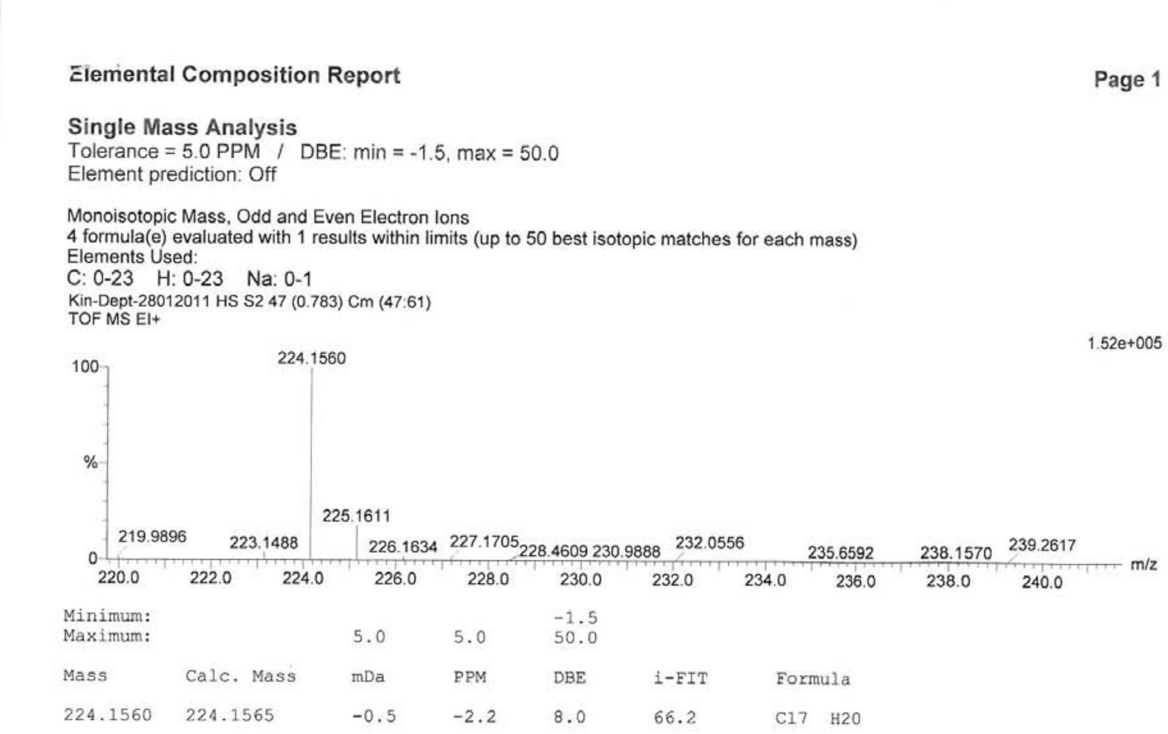






2,2',3,5',6-Pentamethyl-1,1'-biphenyl (Table 7.2, entry 15)





Elemental Composition Report

Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

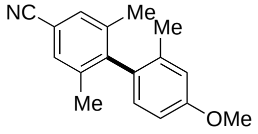
Monoisotopic Mass, Odd and Even Electron Ions
4 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-23 H: 0-23 Na: 0-1
Kin-Dept-28012011 HS S2 47 (0.783) Cm (47:61)
TOF MS EI+

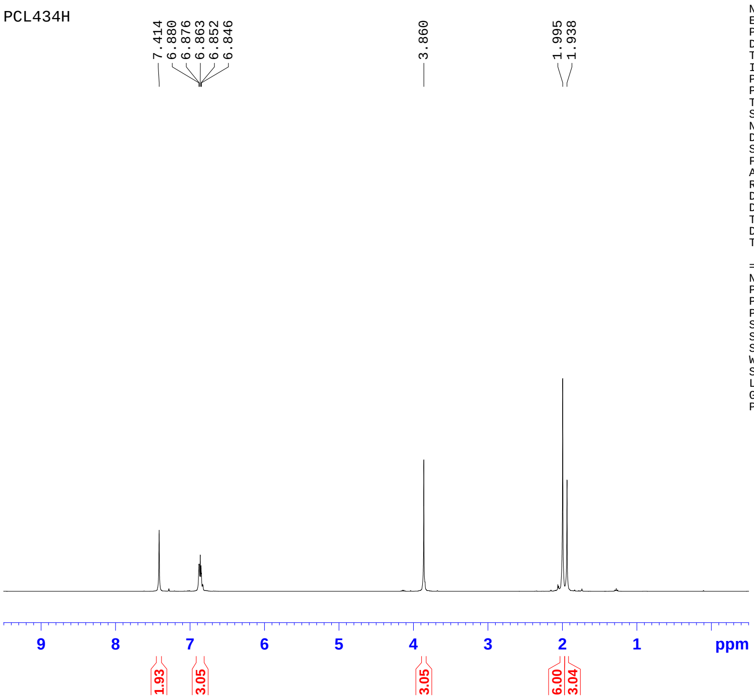
```
Minimum:                                      -1.5
Maximum:                  5.0       5.0       50.0

Mass       Calc. Mass     mDa       PPM       DBE        i-FIT      Formula

224.1560   224.1565       -0.5      -2.2      8.0        66.2       C17  H20
```

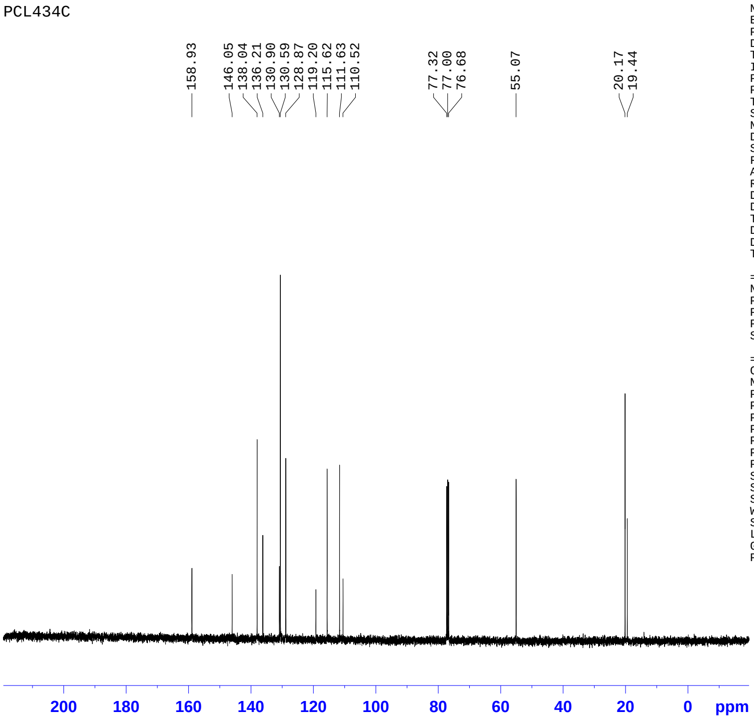
4-Cyano-4’-methoxy-2,2',6-trimethyl-1,1'-biphenyl (Table 7.2, entry 16)





```
NAME              PCL434
EXPNO                  1
PROCNO                 1
Date_           20110214
Time               21.37
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  7.12
DW               124.800 usec
DE                  6.50 usec
TE                 292.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

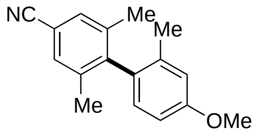


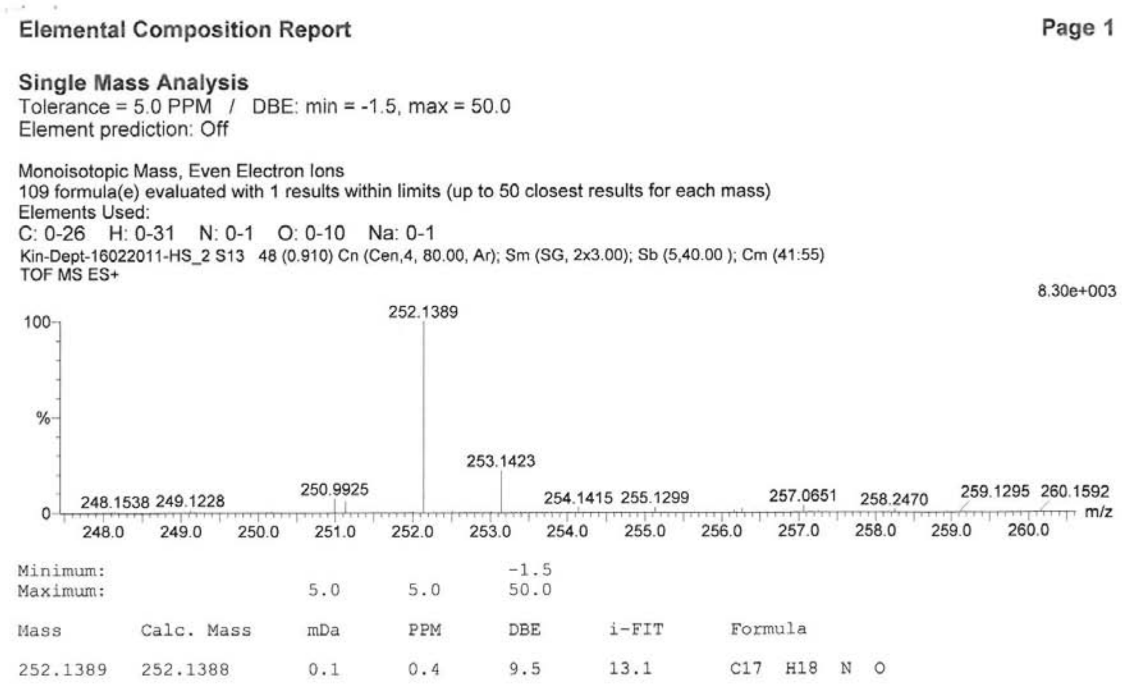
```
NAME              PCL434
EXPNO                  2
PROCNO                 1
Date_           20110214
Time               21.40
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                  25.4
DW                20.800 usec
DE                  6.50 usec
TE                 293.1 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127801 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

4-Cyano-4’-methoxy-2,2',6-trimethyl-1,1'-biphenyl (Table 7.2, entry 16)





Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

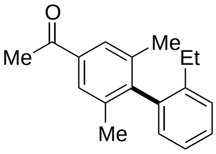
Monoisotopic Mass, Even Electron Ions
109 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-26 H: 0-31 N: 0-1 O: 0-10 Na: 0-1
Kin-Dept-16022011-HS_2 S13 48 (0.910) Cn (Cen,4, 80.00, Ar); Sm (SG, 2x3.00); Sb (5,40.00); Cm (41:55)
TOF MS ES+

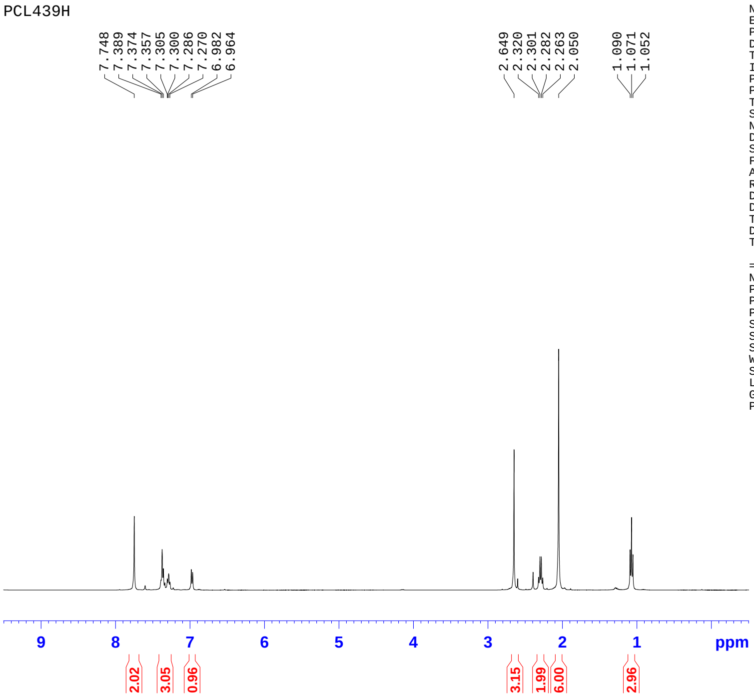
```
Minimum:                                      -1.5
Maximum:                    5.0       5.0     50.0

Mass        Calc. Mass      mDa       PPM     DBE       i-FIT      Formula

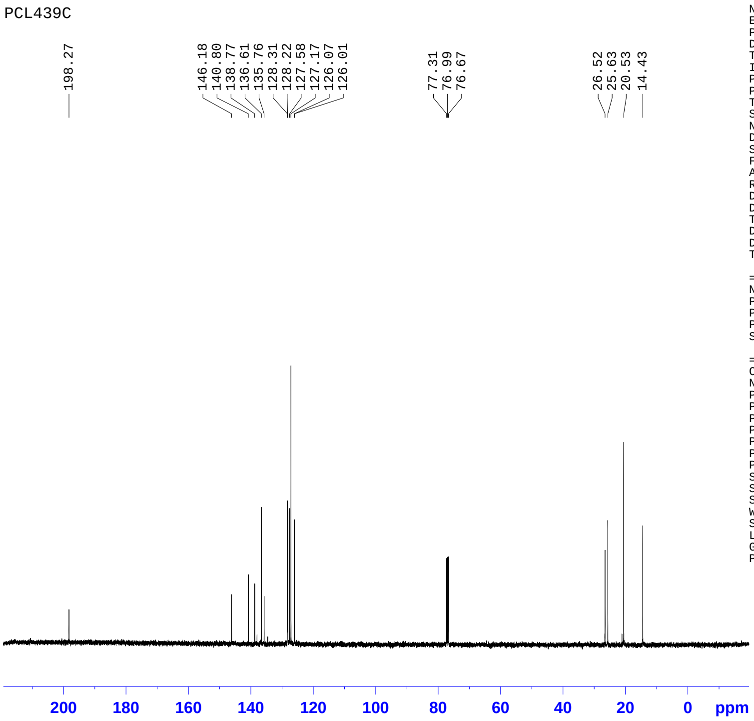
252.1389    252.1388        0.1       0.4     9.5       13.1       C17  H18  N  O
```

1-(2,6-Dimethyl-2’-ethyl-[1,1'-biphenyl]-4-yl)-ethanone (Table 7.3, entry 3)



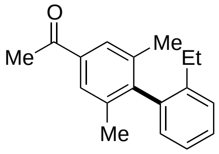


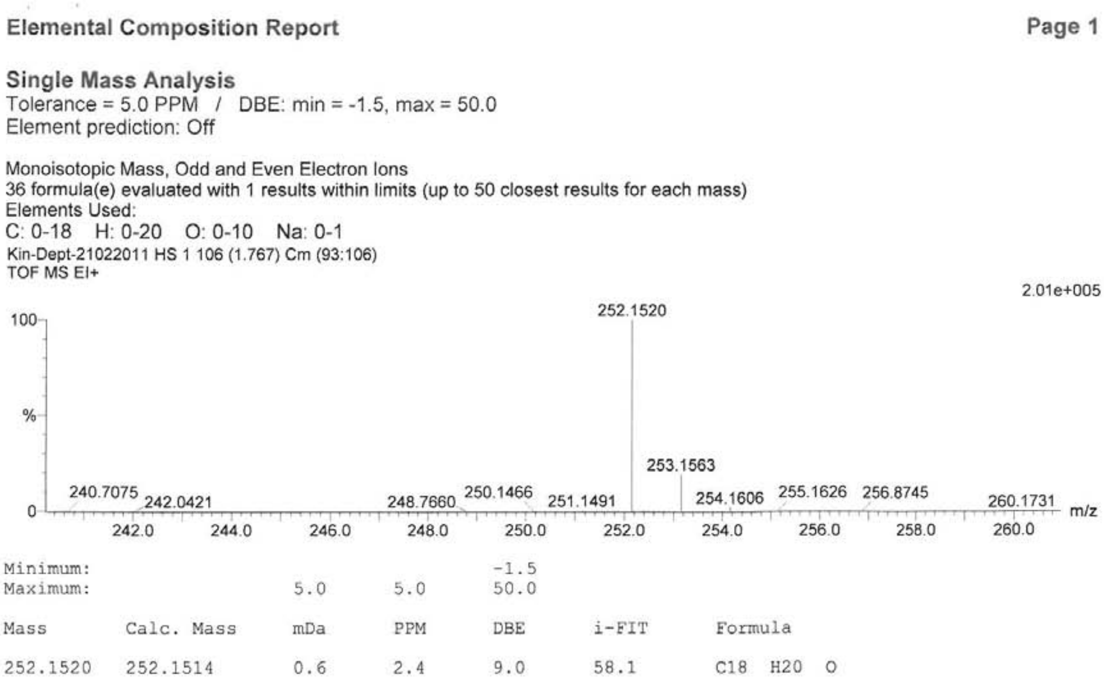
NAME	PCL439
EXPNO	1
PROCNO	1
Date_	20110214
Time	22.09
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	4006.410 Hz
FIDRES	0.122266 Hz
AQ	4.0894966 sec
RG	4.5
DW	124.800 usec
DE	6.50 usec
TE	292.8 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1318007 MHz
SI	32768
SF	400.1300000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



NAME	PCL439
EXPNO	2
PROCNO	1
Date_	20110214
Time	22.13
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	32
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	25.4
DW	20.800 usec
DE	6.50 usec
TE	293.6 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	15.00 dB
PL2W	11.88122272 W
PL12W	0.37571725 W
PL13W	0.37571725 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127841 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1-(2,6-Dimethyl-2’-ethyl-[1,1'-biphenyl]-4-yl)-ethanone (Table 7.3, entry 3)





Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

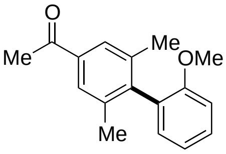
Monoisotopic Mass, Odd and Even Electron Ions
36 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-18 H: 0-20 O: 0-10 Na: 0-1
Kin-Dept-21022011 HS 1 106 (1.767) Cm (93:106)
TOF MS EI+

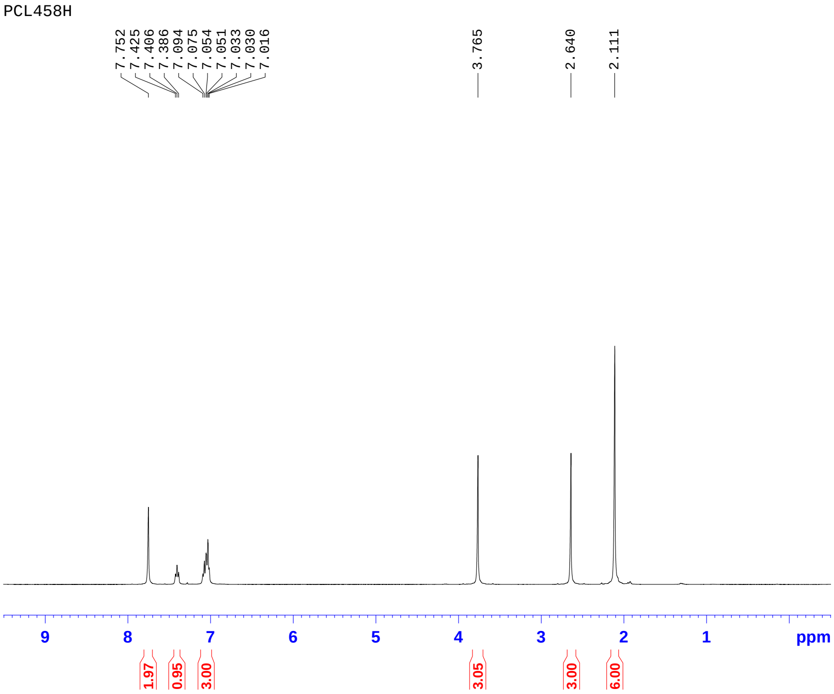
```
Minimum:                                       -1.5
Maximum:                    5.0       5.0      50.0

Mass        Calc. Mass      mDa       PPM      DBE        i-FIT      Formula

252.1520    252.1514        0.6       2.4      9.0        58.1       C18  H20  O
```

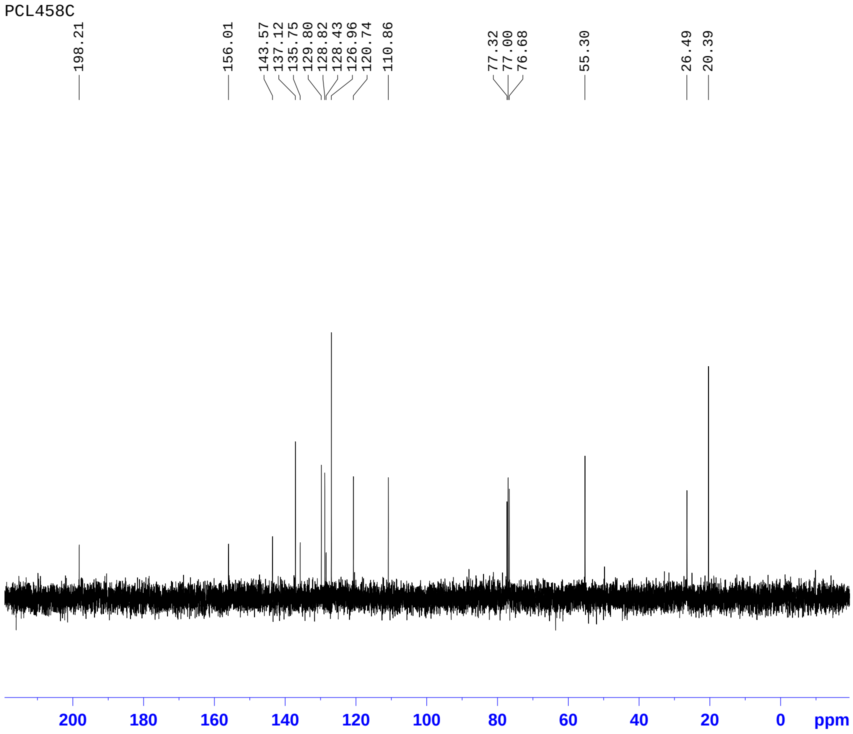
1-(2,6-Dimethyl-2’-methoxy-[1,1'-biphenyl]-4-yl)-ethanone (Table 7.3, entry 4)





```
NAME              PCL458
EXPNO                  1
PROCNO                 1
Date_           20110228
Time               13.58
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                     1
DW               124.800 usec
DE                  6.50 usec
TE                 299.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

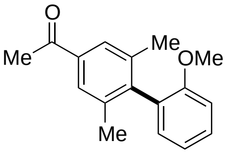


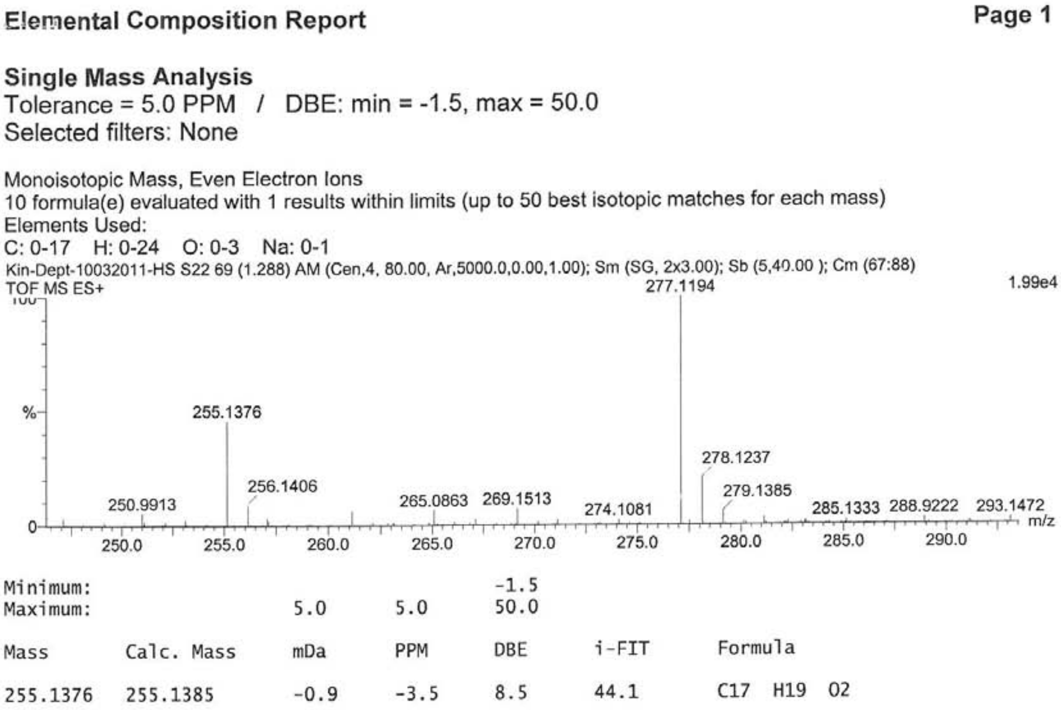
```
NAME              PCL458
EXPNO                  2
PROCNO                 1
Date_           20110228
Time               14.00
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                     1
DW                20.800 usec
DE                  6.50 usec
TE                 300.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127854 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

1-(2,6-Dimethyl-2’-methoxy-[1,1'-biphenyl]-4-yl)-ethanone (Table 7.3, entry 4)





Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

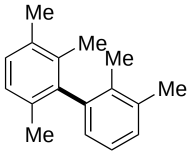
Monoisotopic Mass, Even Electron Ions
10 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-17 H: 0-24 O: 0-3 Na: 0-1
Kin-Dept-10032011-HS S22 69 (1.288) AM (Cen,4, 80.00, Ar,5000.0,0.00,1.00); Sm (SG, 2x3.00); Sb (5,40.00); Cm (67:88)
TOF MS ES+

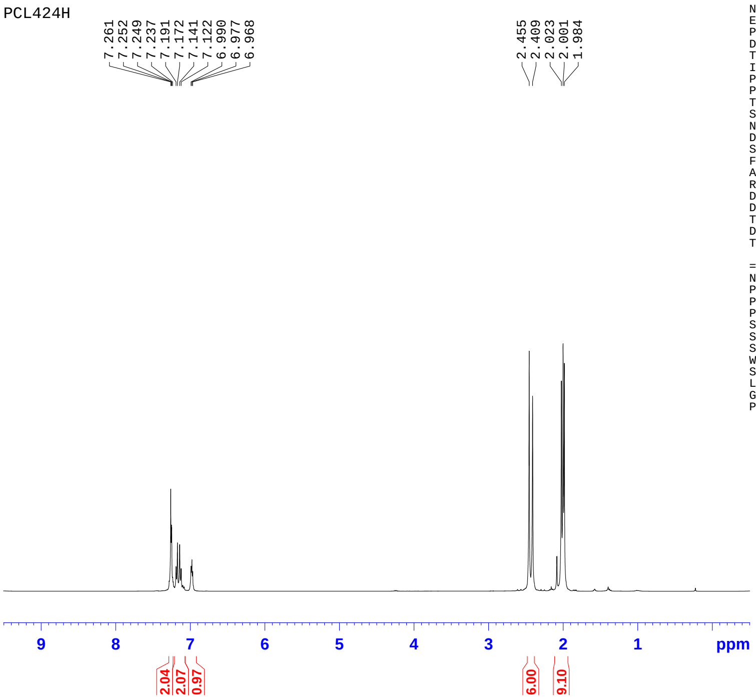
```
Minimum:                                        -1.5
Maximum:                        5.0      5.0    50.0

Mass        Calc. Mass          mDa      PPM    DBE      i-FIT      Formula

255.1376    255.1385            -0.9     -3.5   8.5      44.1       C17  H19  O2
```

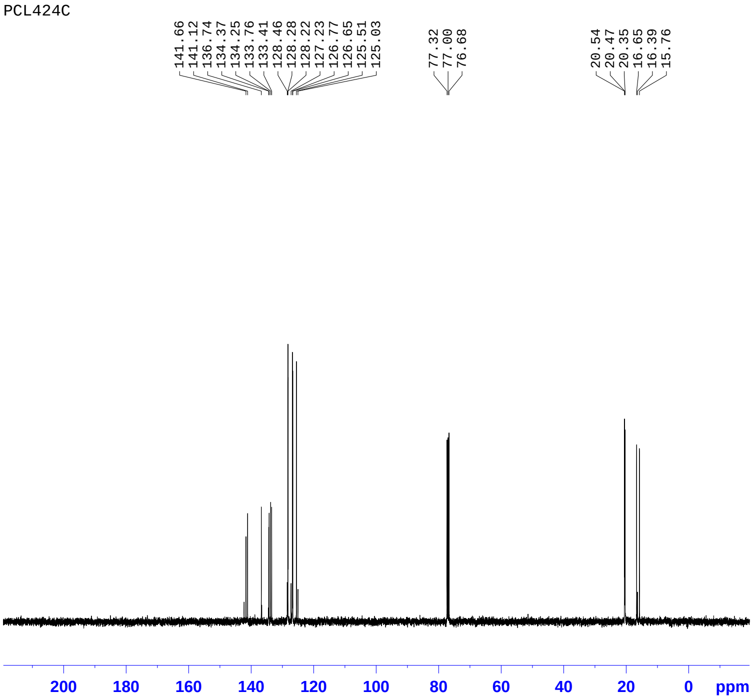
2,2',3,3’,6-Pentamethyl-1,1'-biphenyl (Table 7.3, entry 8)





```
NAME              PCL424
EXPNO                  1
PROCNO                 1
Date_           20110215
Time               22.10
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                     8
DW               124.800 usec
DE                  6.50 usec
TE                 293.8 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

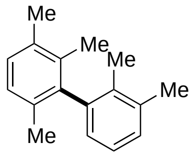


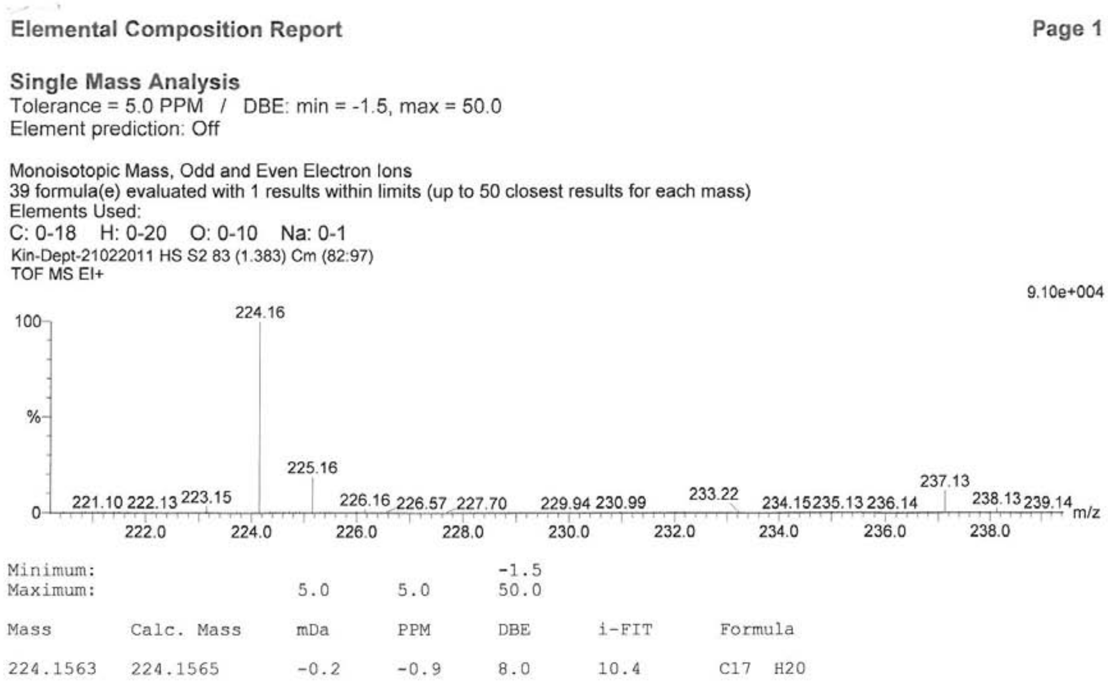
```
NAME              PCL424
EXPNO                  2
PROCNO                 1
Date_           20110215
Time               22.14
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   161
DW                20.800 usec
DE                  6.50 usec
TE                 294.7 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127837 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

2,2',3,3’,6-Pentamethyl-1,1'-biphenyl (Table 7.3, entry 8)





Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

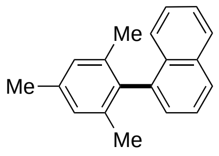
Monoisotopic Mass, Odd and Even Electron Ions
39 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-18 H: 0-20 O: 0-10 Na: 0-1
Kin-Dept-21022011 HS S2 83 (1.383) Cm (82:97)
TOF MS EI+

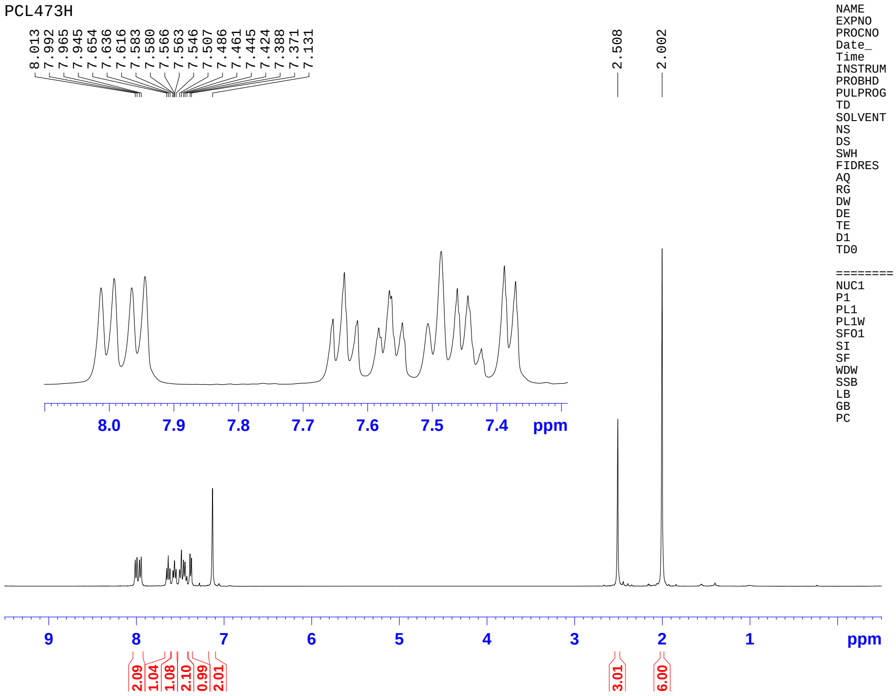
```
Minimum:                                    -1.5
Maximum:                   5.0      5.0     50.0

Mass       Calc. Mass     mDa      PPM      DBE      i-FIT      Formula

224.1563   224.1565       -0.2     -0.9     8.0      10.4       C17  H20
```

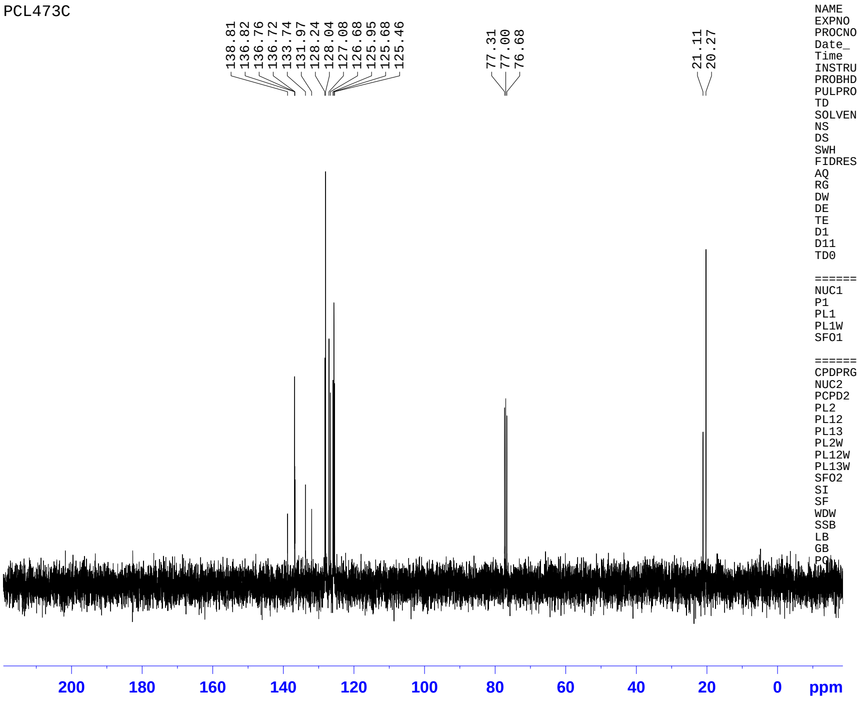
1-Mesitylnaphthalene (Table 7.3, entry 9; Table 7.4, entry 6)





```
NAME             PCL473
EXPNO                 1
PROCNO                1
Date_          20110305
Time              16.53
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            4006.410 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                    1
DW              124.800 usec
DE                 6.50 usec
TE                299.4 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.70 usec
PL1                0.00 dB
PL1W        11.88122272 W
SFO1        400.1318007 MHz
SI                32768
SF          400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

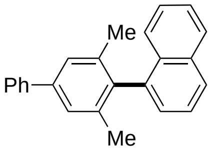


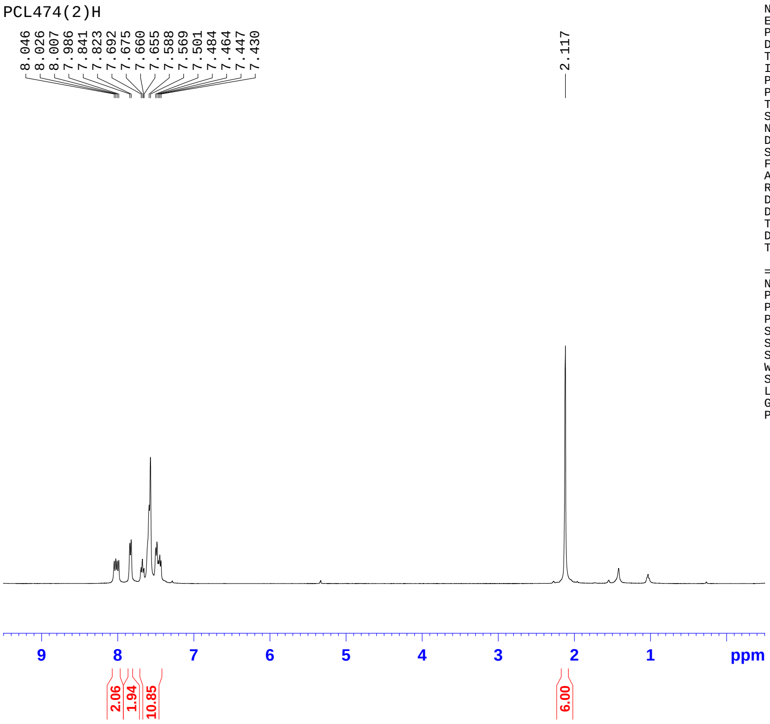
```
NAME             PCL473
EXPNO                 2
PROCNO                1
Date_          20110305
Time              16.57
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                    1
DW               20.800 usec
DE                 6.50 usec
TE                300.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.50 usec
PL1               -2.00 dB
PL1W        58.52175522 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL13              15.00 dB
PL2W        11.88122272 W
PL12W        0.37571725 W
PL13W        0.37571725 W
SFO2        400.1316005 MHz
SI                32768
SF          100.6127824 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

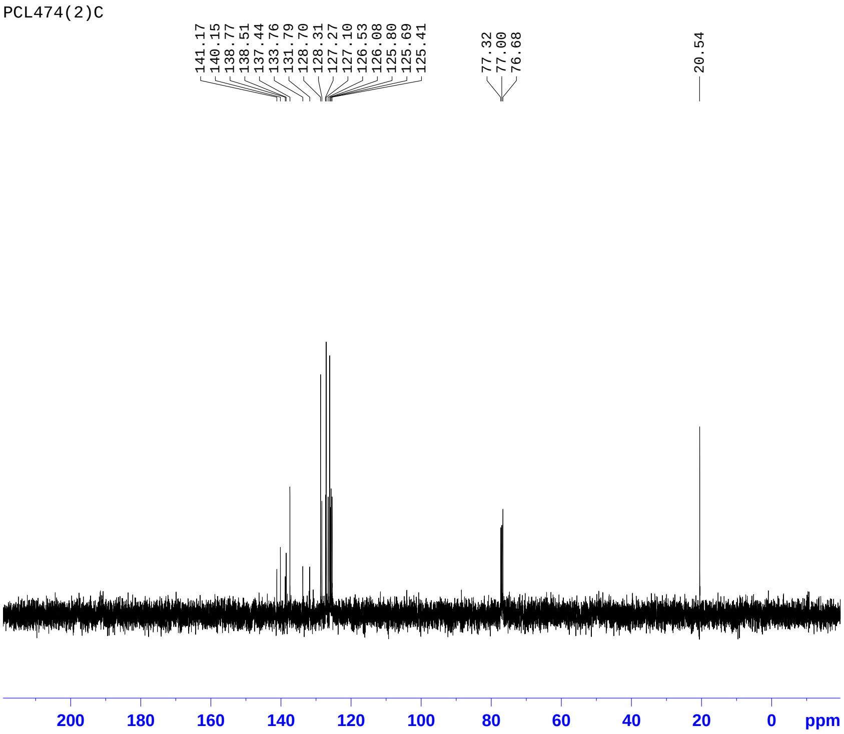
1-(4-Phenyl-2,6-Dimethylphenyl)naphthalene (Table 7.3, entry 10)





```
NAME           PCL474(2)
EXPNO                  1
PROCNO                 1
Date_           20110306
Time               19.24
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                     1
DW               124.800 usec
DE                  6.50 usec
TE                 299.5 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

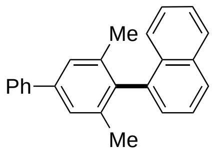


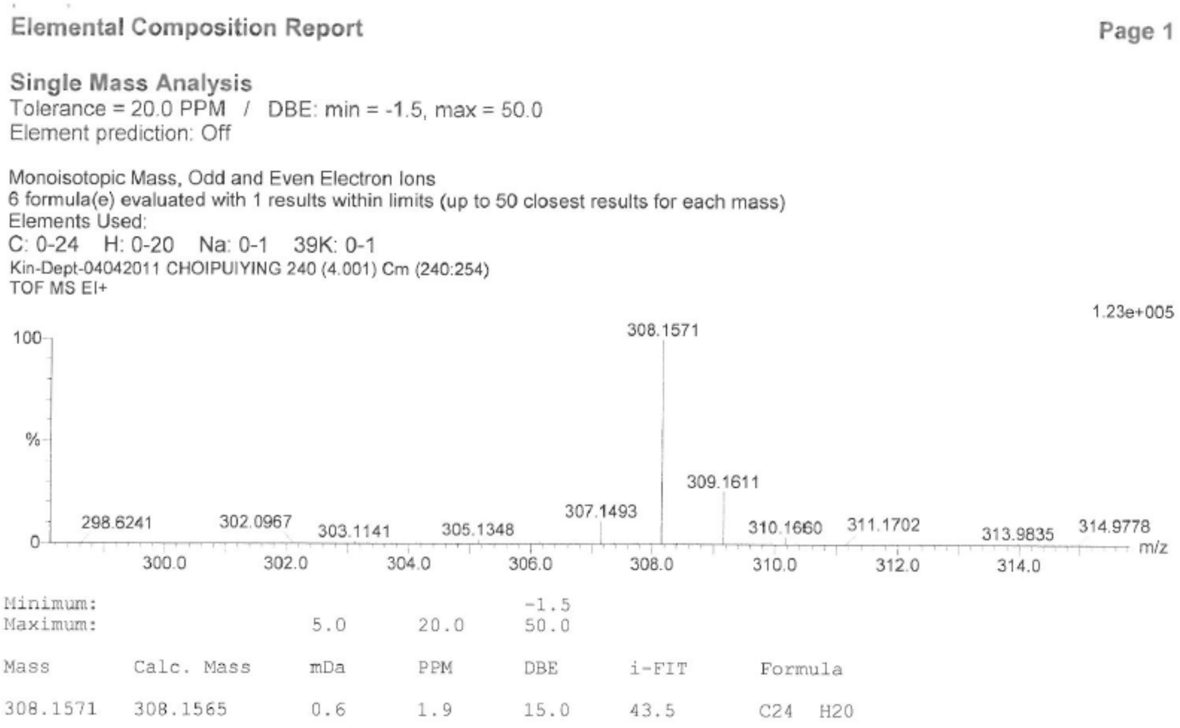
```
NAME           PCL474(2)
EXPNO                  2
PROCNO                 1
Date_           20110306
Time               19.27
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                     1
DW                20.800 usec
DE                  6.50 usec
TE                 300.3 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127849 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

1-(4-Phenyl-2,6-Dimethylphenyl)naphthalene (Table 7.3, entry 10)





Elemental Composition Report

Page 1

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

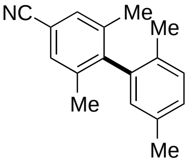
Monoisotopic Mass, Odd and Even Electron Ions
6 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-24 H: 0-20 Na: 0-1 39K: 0-1
Kin-Dept-04042011 CHOIPUIYING 240 (4.001) Cm (240:254)
TOF MS EI+

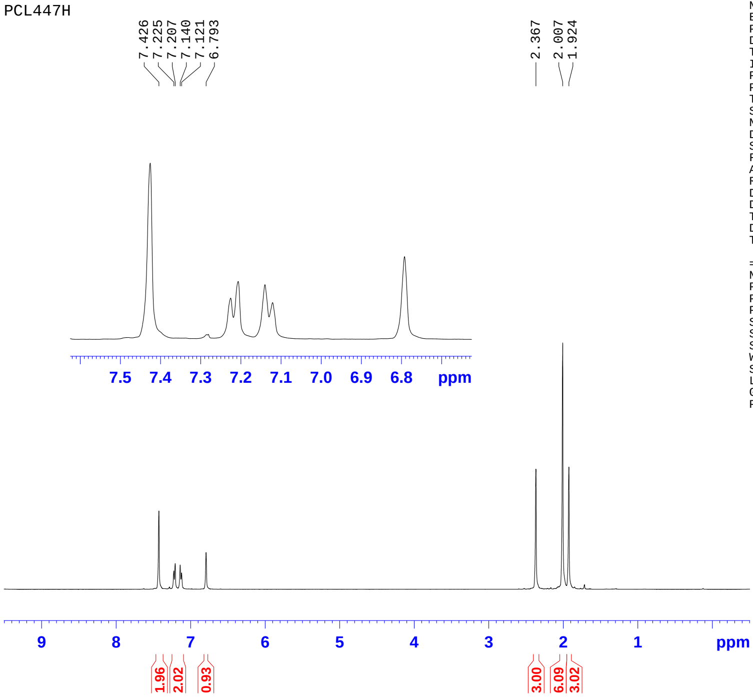
```
Minimum:                                   -1.5
Maximum:                5.0       20.0     50.0

Mass       Calc. Mass   mDa       PPM      DBE      i-FIT      Formula

308.1571   308.1565     0.6       1.9      15.0     43.5       C24  H20
```

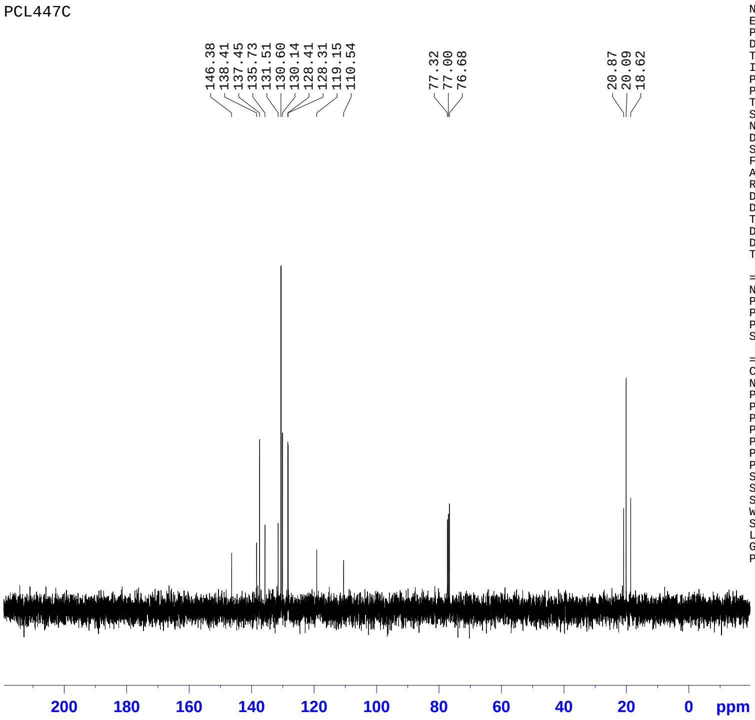
4-Cyano-2,2',5’,6-tetramethyl-1,1'-biphenyl (Table 7.3, entry 11)





```
NAME            PCL447
EXPNO                1
PROCNO               1
Date_         20110227
Time             19.53
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG           zg30
TD               32768
SOLVENT          CDCl3
NS                  16
DS                   2
SWH           4006.410 Hz
FIDRES        0.122266 Hz
AQ           4.0894966 sec
RG                   1
DW             124.800 usec
DE                6.50 usec
TE               299.1 K
D1          1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                1H
P1               14.70 usec
PL1               0.00 dB
PL1W       11.88122272 W
SFO1       400.1318007 MHz
SI               32768
SF         400.1300000 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.00
```

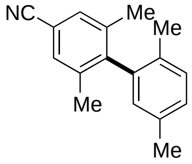


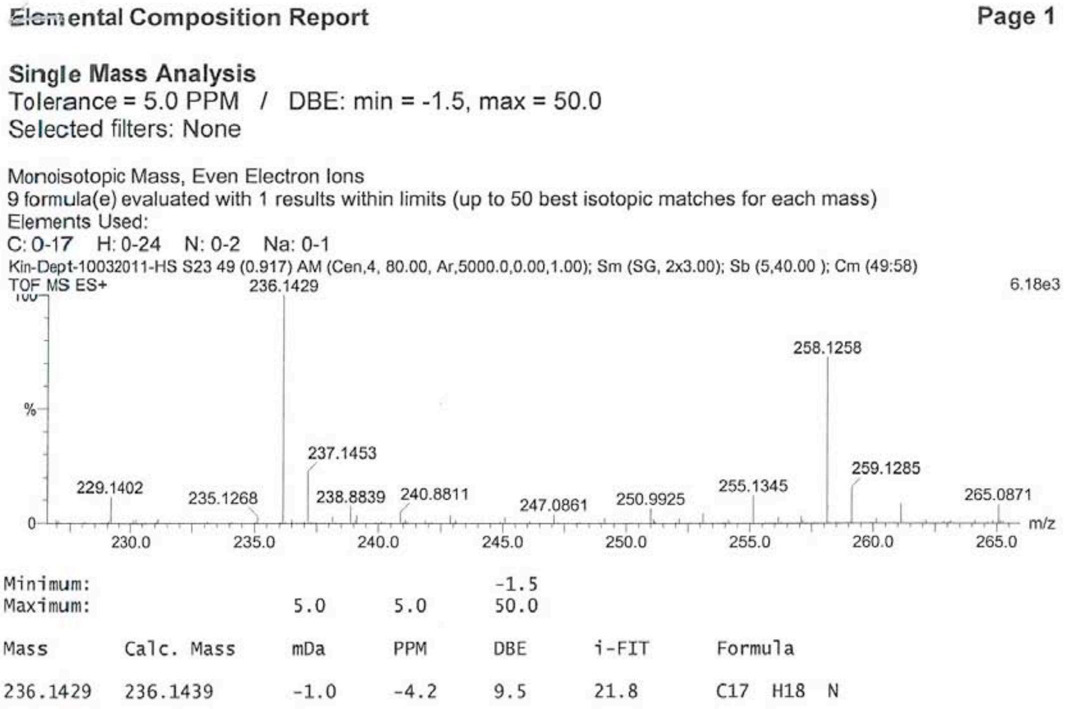
```
NAME            PCL447
EXPNO                2
PROCNO               1
Date_         20110227
Time             19.58
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                  32
DS                   2
SWH          24038.461 Hz
FIDRES        0.366798 Hz
AQ           1.3631988 sec
RG                   1
DW              20.800 usec
DE                6.50 usec
TE               299.8 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1                9.50 usec
PL1              -2.00 dB
PL1W       58.52175522 W
SFO1       100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2            80.00 usec
PL2               0.00 dB
PL12             15.00 dB
PL13             15.00 dB
PL2W       11.88122272 W
PL12W       0.37571725 W
PL13W       0.37571725 W
SFO2       400.1316005 MHz
SI               32768
SF         100.6127816 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```

4-Cyano-2,2',5’,6-tetramethyl-1,1'-biphenyl (Table 7.3, entry 11)





Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

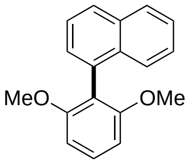
Monoisotopic Mass, Even Electron Ions
9 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-17 H: 0-24 N: 0-2 Na: 0-1
Kin-Dept-10032011-HS S23 49 (0.917) AM (Cen,4, 80.00, Ar,5000.0,0.00,1.00); Sm (SG, 2x3.00); Sb (5,40.00); Cm (49:58)
TOF MS ES+

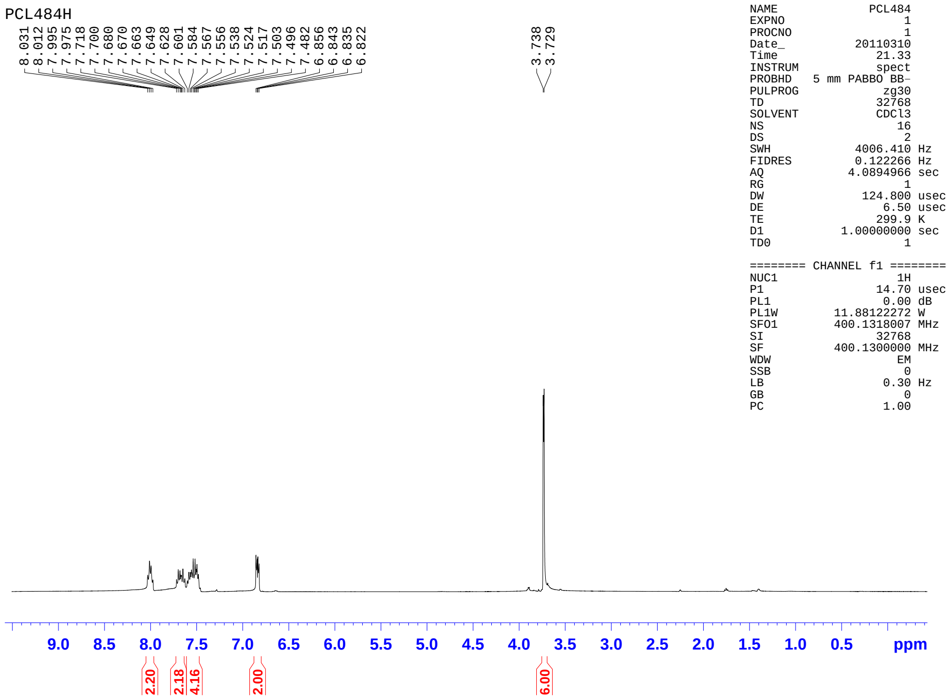
```
Minimum:                                  -1.5
Maximum:                 5.0       5.0     50.0

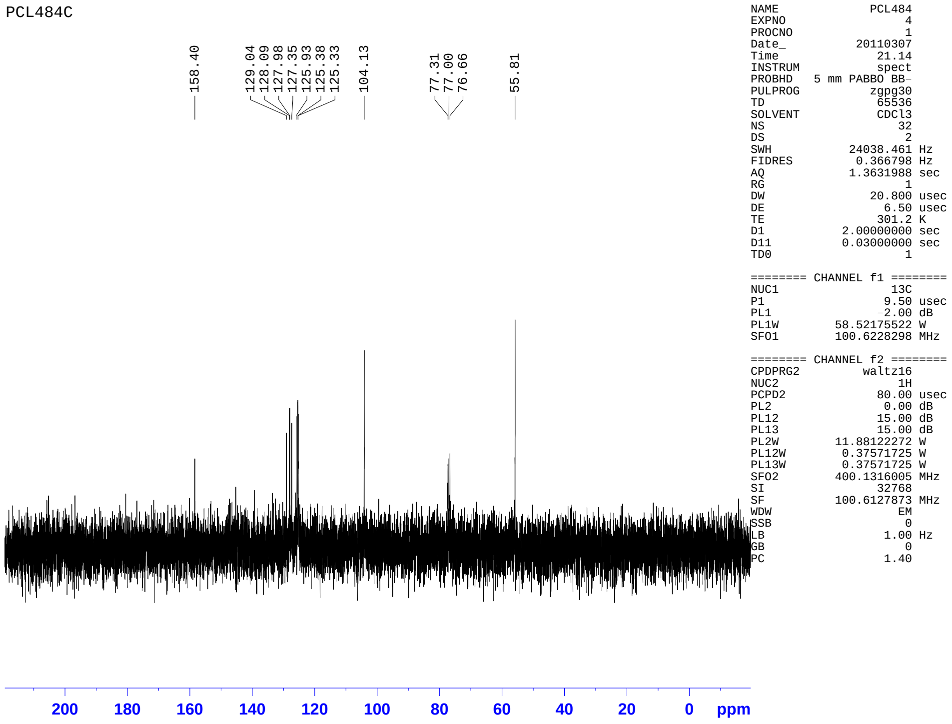
Mass       Calc. Mass    mDa       PPM     DBE       i-FIT      Formula

236.1429   236.1439      -1.0      -4.2    9.5       21.8       C17  H18  N
```

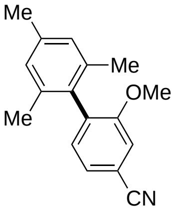
1-(2,6-Dimethoxyphenyl)naphthalene (Table 7.4, entry 1)

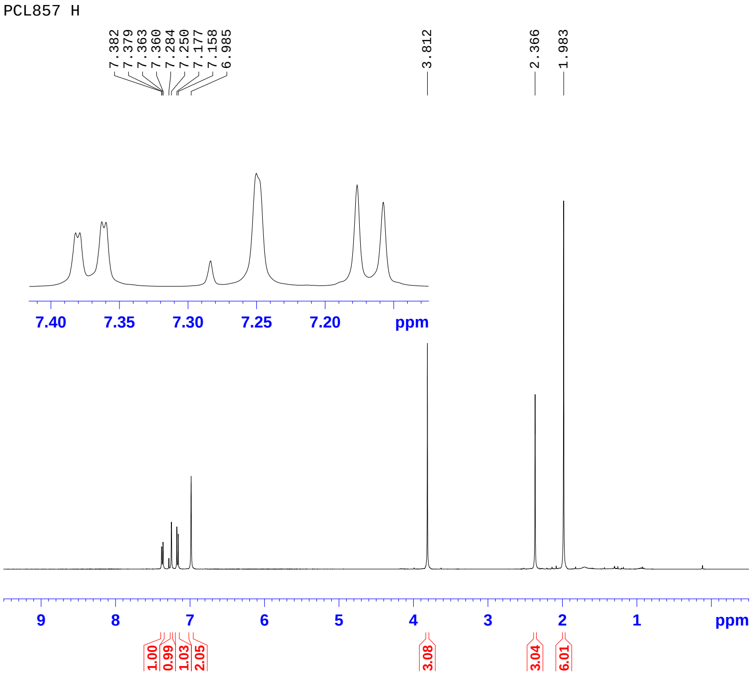






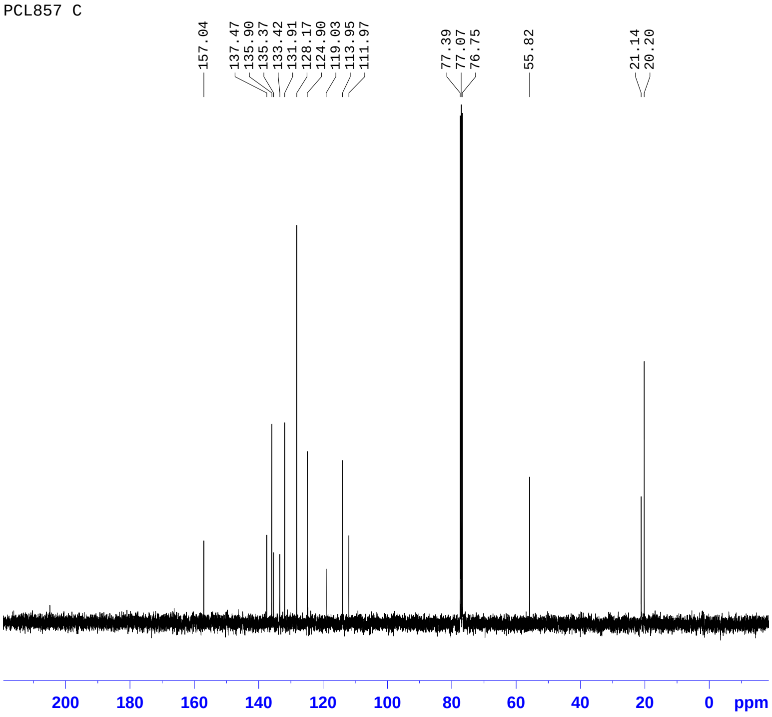
2-Methoxy-2',4',6'-trimethyl-[1,1'-biphenyl]-4-carbonitrile (Table 7.4, entry 2)





```
NAME              PCL857
EXPNO                  3
PROCNO                 1
Date_           20130225
Time               22.57
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH          5597.015 Hz
FIDRES       0.170807 Hz
AQ          2.9273248 sec
RG                  50.8
DW            89.333 usec
DE              6.50 usec
TE              298.6 K
D1         1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1             14.70 usec
PL1             0.00 dB
PL1W      11.88122272 W
SFO1      400.1324008 MHz
SI                 32768
SF        400.1300000 MHz
WDW                   EM
SSB                    0
LB               0.30 Hz
GB                     0
PC                  1.00
```

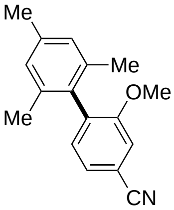


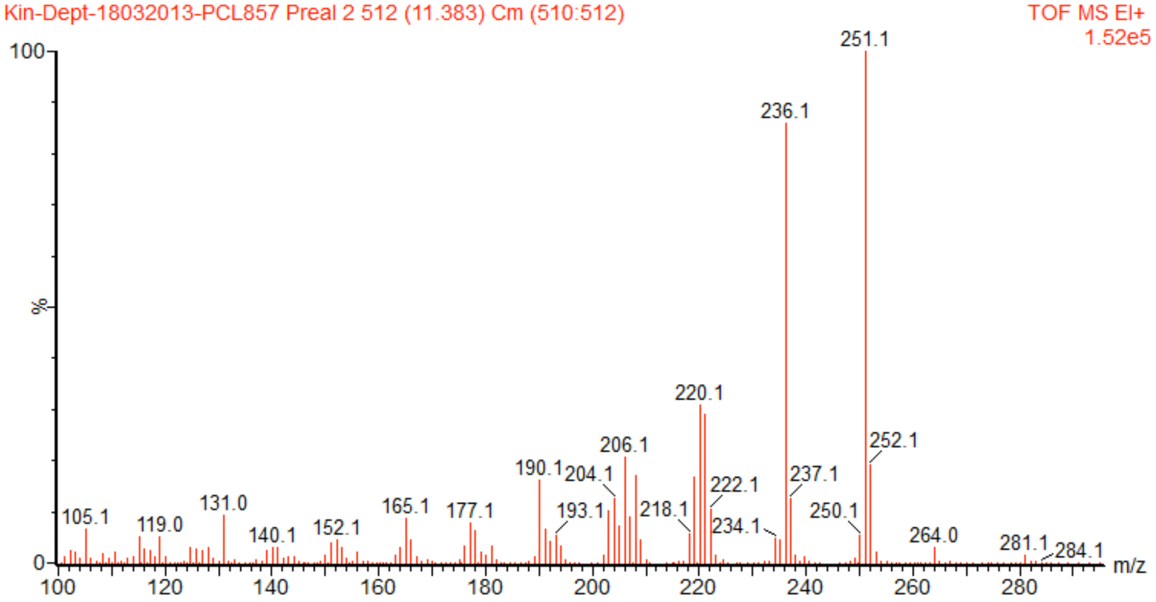
```
NAME              PCL857
EXPNO                  4
PROCNO                 1
Date_           20130225
Time               23.00
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    41
DS                     2
SWH         24038.461 Hz
FIDRES       0.366798 Hz
AQ          1.3631988 sec
RG                   228
DW            20.800 usec
DE              6.50 usec
TE              299.4 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0                    1

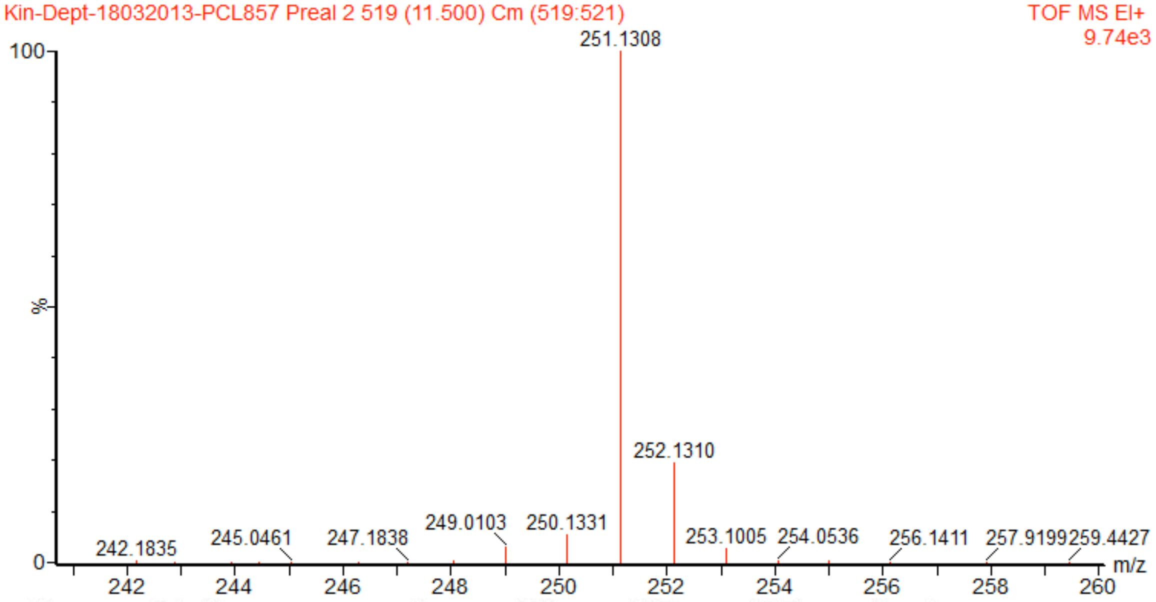
======== CHANNEL f1 ========
NUC1                 13C
P1              9.50 usec
PL1            -2.00 dB
PL1W      58.52175522 W
SFO1      100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2          80.00 usec
PL2             0.00 dB
PL12           15.00 dB
PL13           15.00 dB
PL2W      11.88122272 W
PL12W      0.37571725 W
PL13W      0.37571725 W
SFO2      400.1316005 MHz
SI                 32768
SF        100.6127690 MHz
WDW                   EM
SSB                    0
LB               1.00 Hz
GB                     0
PC                  1.40
```

2-Methoxy-2',4',6'-trimethyl-[1,1'-biphenyl]-4-carbonitrile (Table 7.4, entry 2)

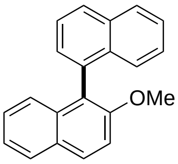




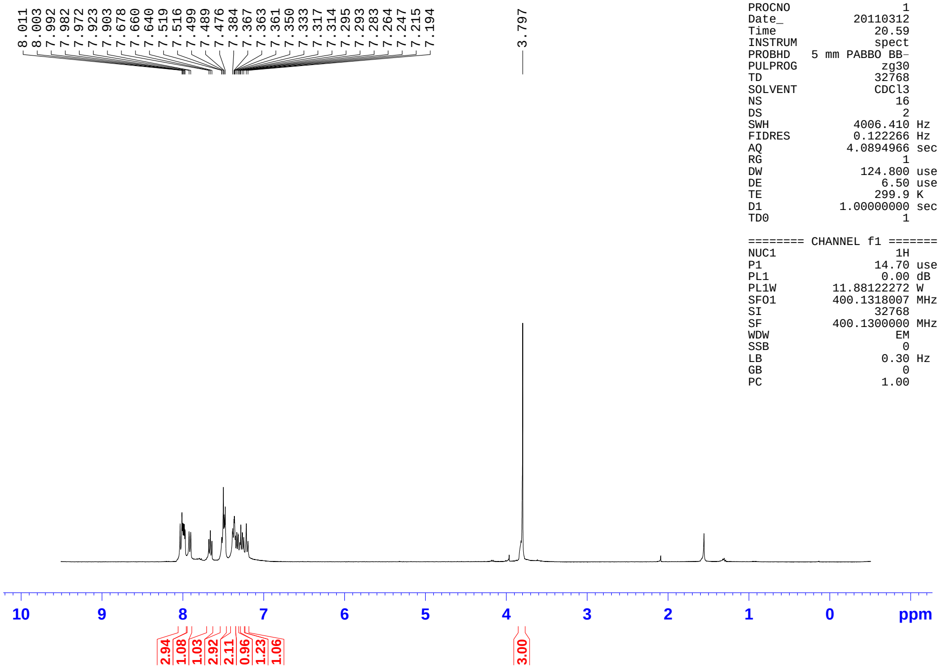


Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
251.1308	251.1310	-0.2	-0.8	10.0	2777427.5	C17 H17 N O

2-Methoxy-1,1'-binaphthalene (Table 7.4, entry 3)



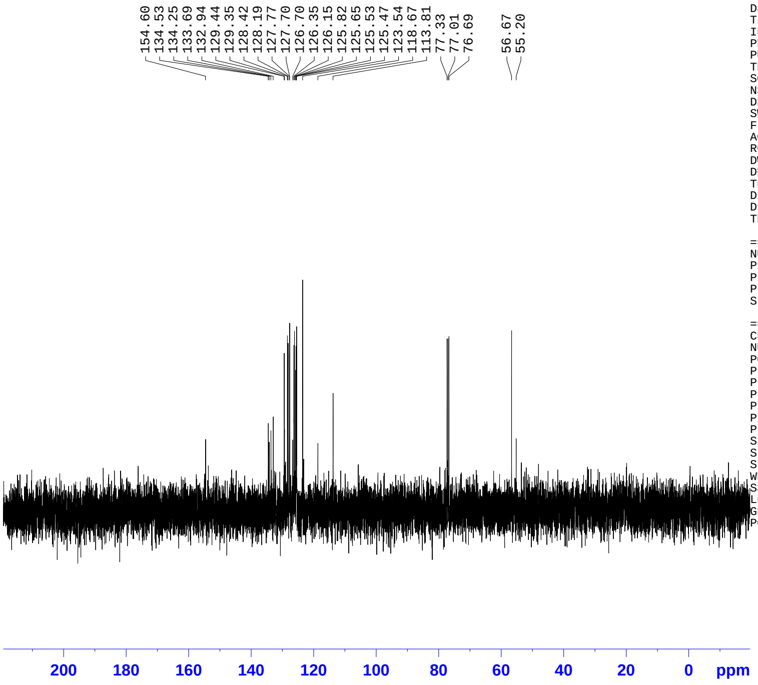
PCL491H



```
NAME              PCL491
EXPNO                  1
PROCNO                 1
Date_           20110312
Time               20.59
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                     1
DW               124.800 usec
DE                  6.50 usec
TE                 299.9 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

PCL491C

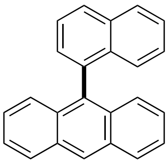


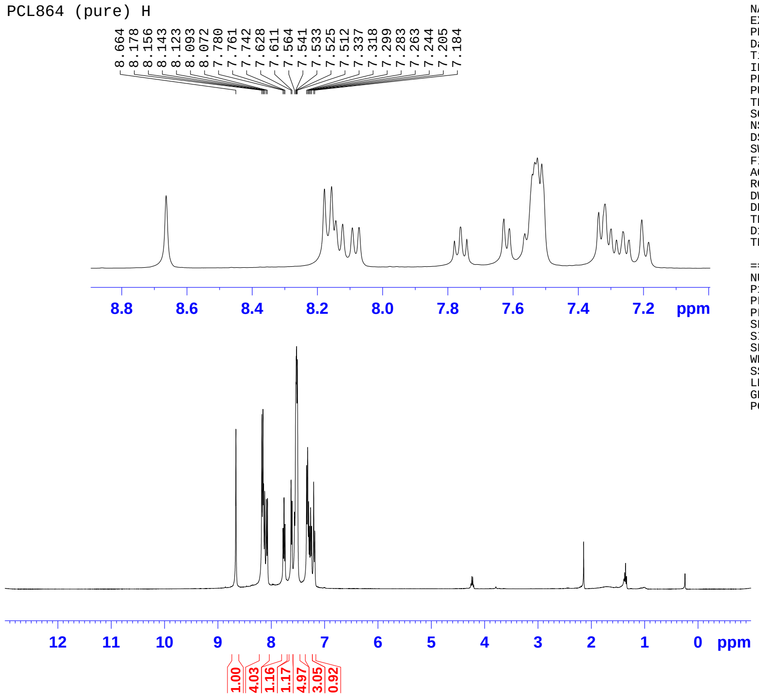
```
NAME              PCL491
EXPNO                  4
PROCNO                 1
Date_           20110312
Time               21.17
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                     1
DW                20.800 usec
DE                  6.50 usec
TE                 301.5 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127849 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

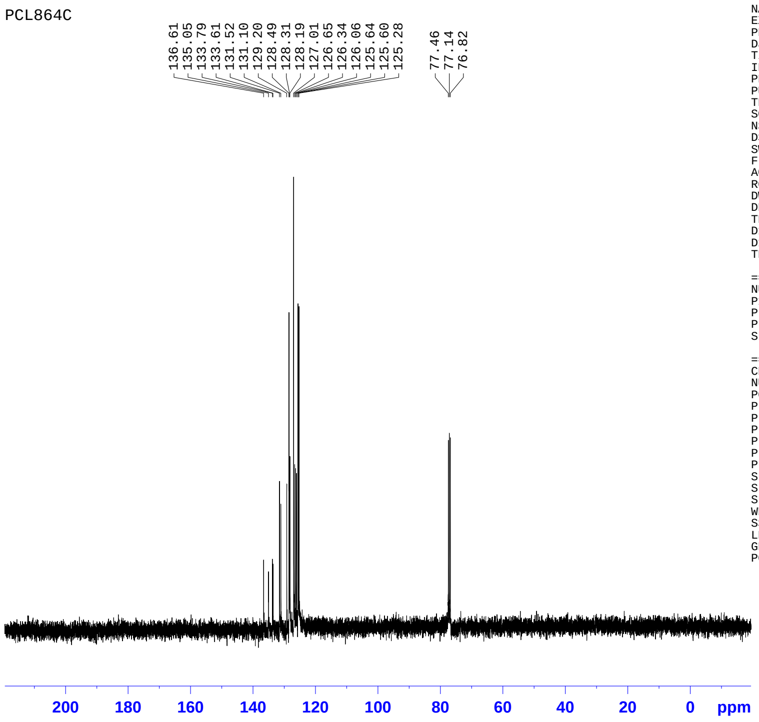
9-(Naphthalen-1-yl)anthracene (Table 7.4, entry 4)





```
NAME              PCL864
EXPNO                  2
PROCNO                 1
Date_           20130228
Time               19.19
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             5597.015 Hz
FIDRES          0.170807 Hz
AQ             2.9273248 sec
RG                    36
DW                89.333 usec
DE                  6.50 usec
TE                 298.9 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1324008 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

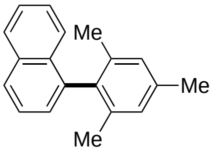


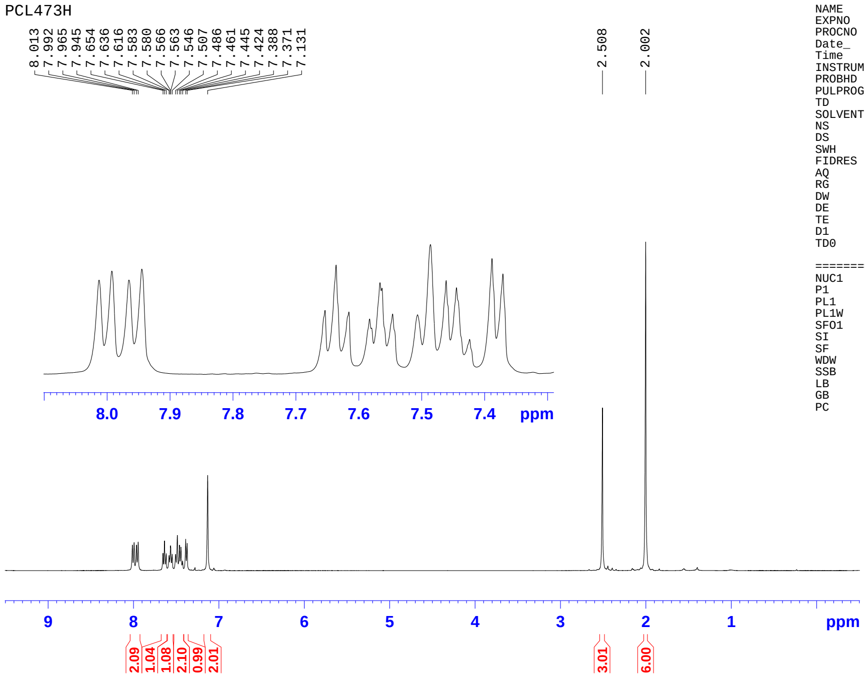
```
NAME              PCL864
EXPNO                  3
PROCNO                 1
Date_           20130228
Time               19.14
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    13
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                   228
DW                20.800 usec
DE                  6.50 usec
TE                 299.3 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127690 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

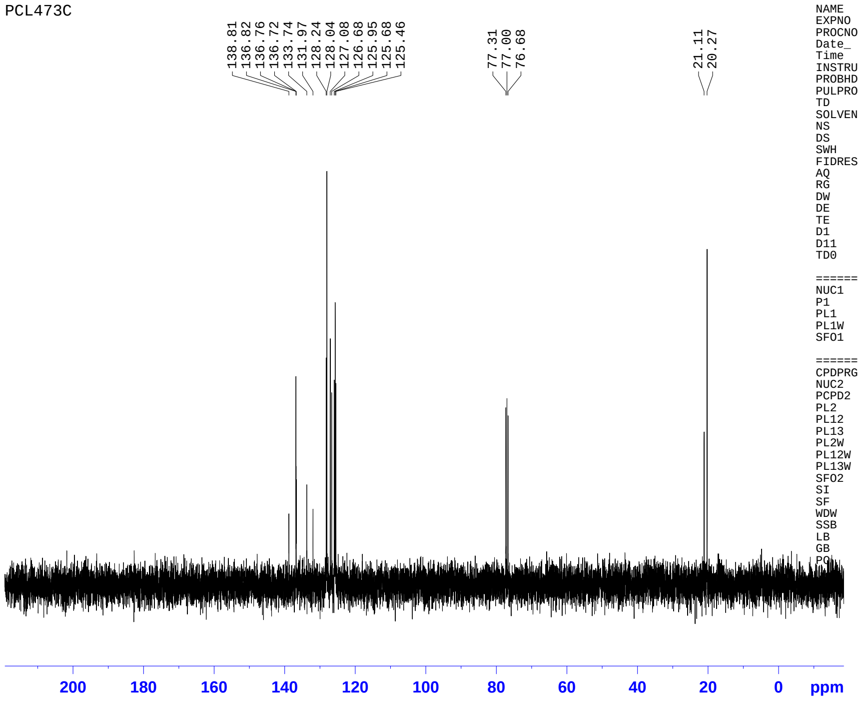
1-Mesitylnaphthalene (Table 7, entry 6)





```
NAME              PCL473
EXPNO                  1
PROCNO                 1
Date_           20110305
Time               16.53
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4006.410 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                     1
DW               124.800 usec
DE                  6.50 usec
TE                 299.4 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1         400.1318007 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



```
NAME              PCL473
EXPNO                  2
PROCNO                 1
Date_           20110305
Time               16.57
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                     1
DW                20.800 usec
DE                  6.50 usec
TE                 300.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -2.00 dB
PL1W         58.52175522 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127824 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```