DESIGN AND SYNTHESIS OF HEMILABILE HETEROCYCLIC PHOSPHINE LIGANDS AND THEIR APPLICATIONS IN PALLADIUM-CATALYZED CARBON-CARBON AND CARBON-NITROGEN BOND-CONSTRUCTION PROCESSES

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2015

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Design and Synthesis of Hemilabile Heterocyclic Phosphine Ligands and Their Applications in Palladium-Catalyzed Carbon-Carbon and Carbon-Nitrogen Bond-Construction Processes

WONG Shun Man

A Thesis Submitted in Partial Fulfillment of the Requirements

for the Degree of Doctor of Philosophy

June, 2014

Certificate of Originality

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WONG Shun Man

June, 2014

Abstract

Abstract of thesis entitled "**Design and Synthesis of Hemilabile Heterocyclic Phosphine Ligands and Their Applications in Palladium-Catalyzed Carbon-Carbon and Carbon-Nitrogen Bond-Construction Processes**"

Submitted by WONG Shun Man

for the Degree of Doctor of Philosophy

at The Hong Kong Polytechnic University

in June, 2014

A new family of hemilabile benzimidazolyl phosphine ligands was designed and synthesized. The benzimidazole scaffold of this family of ligands could be easily prepared and diversified from inexpensive substituted *o*-phenylenediamines and substituted carboxylic acids by conventional Phillips benzimidazole synthesis.

Two classes of ligands, *P*,*N*-type 2-arylated benzimidazolyl phosphine ligands and alterable *P*,*O*- or *P*,*N*-type 2-phosphino-substituted benzimidazolyl ligands, were successfully synthesized by a "Cross-matching" approach.

The 2-arylated benzimidazolyl phosphine ligands showed excellent catalytic activities for the Suzuki-Miyaura coupling of aryl chlorides with arylboronic acids, especially under very-low-catalyst-loading down to 1 ppm. In addition, these ligands were efficient towards Suzuki-Miyaura coupling of aryl chlorides with potassium aryltrifluoroborates. Notably, the X-ray crystallographic

data confirmed that the ligand was coordinated in a κ^2-*P*,*N* fashion to the palladium center.

On the other hand, the palladium complexes of 2-phosphino-substituted benzimidazolyl ligands showed coordination in a κ^2-*P*,*N* fashion and potential *P*,*O*-hemilabile ability, which could be altered by tuning the steric bulkiness of phosphino group. Interestingly, the complexes with *P*,*O*-coordination and *P*,*N*-coordination showed high efficacy towards Suzuki-Miyaura coupling and Buchwald-Hartwig amination of aryl chlorides, respectively. Particularly noteworthy, to probe with these fascinating hemilabile properties, chemoselective cross-coupling of aryl chlorides was also examined. The palladium-ligand complexes showed essentially complete orthogonal property (>99%) to afford Suzuki coupling products when carrying out competitive cross-coupling of aryl chlorides with arylboronic acids and amines.

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Wong, S. M.; So, C. M.; Kwong, F. Y., The Recent Development of Phosphine Ligands Derived from 2-Phosphino-Substituted Heterocycles and Their Applications in Palladium-Catalyzed Cross-Coupling Reactions. *Synlett* **2012**, 1132-1153.

Chung, K. H.; So, C. M.; Wong, S. M.; Luk, C. H.; Zhou, Z.; Lau, C. P.; Kwong, F. Y., An efficient palladium-benzimidazolyl phosphine complex for the Suzuki-Miyaura coupling of aryl mesylates: facile ligand synthesis and metal complex characterization. *Chemical Communications* **2012**, *48*, 1967-1969.

Wong, S. M.; So, C. M.; Chung, K. H.; Lau, C. P.; Kwong, F. Y., An Efficient Class of P,N-Type "PhMezole-phos" Ligands: Applications in Palladium-Catalyzed Suzuki Coupling of Aryl Chlorides. *European Journal of Organic Chemistry* **2012**, 4172-4177.

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Wong, S. M.; Choy, P. Y.; Yuen, O. Y.; So, C. M.; Kwong, F. Y., Palladium-catalyzed Buchwald-Hartwig amination and Suzuki-Miyaura cross-coupling reaction of aryl mesylates: Preparation of 4-(*tert*-butyl)-*N*-methyl-*N*-phenylaniline and 4-(*tert*-butyl)-1,1'-biphenyl. *Organic Syntheses*, in press.

Wong, S. M.; So, C. M.; Kwong, F. Y., "Pd-catalyzed C-O & C-N bond-forming reactions" In *Applied Homogeneous Catalysis with Organometallic Compounds*, Cornils, Herrmann, Beller, Paciello, Eds., Wiley-VCH:Weinheim, 2014, *in press*.

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Acknowledgments

I would like to express my deepest gratitude to my supervisor Dr. Kwong Fuk Yee for his invaluable advice, supervision, and guidance throughout the course of my study.

I wish to give my special thanks to my mentor Mr. Yeung Chung Chiu who taught me technical skills from the very early stage of my study and his valuable guidance and discussion.

I would also like to thank you all my postgraduate colleagues for their valuable discussion and giving me an unforgettable memory.

I am obliged to the staff and technical service crew of the Chemical Technology Section of the Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University for their assistance throughout my postgraduate study, especially to Prof. Zhou Zhongyuan for X-ray crystallographic study and Dr. So Pui Kin for HRMS analysis.

I would like to acknowledge the Research Degree Committee of The Hong Kong Polytechnic University for the award of studentship.

Last but not least, I am thankful to my family for their love and fully support in various ways during the course of my study.

Contents

List of Figures

List of Schemes

List of Tables

Abbreviations

δ	Chemical shift (NMR)
η	Descriptor for hapticity
κ	Shows hapticity in σ-bonding ligands
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
equiv.	Equivalent
h	Hour
r.t.	Room temperature
THF	Tetrahydrofuran
MeOH	Methanol
E.A.	Ethyl acetate
DMF	Dimethyl formamide
DCM	Dichloromethane
t-BuOH	*tert*-butanol
$ClPPh_2$	Chlorodiphenylphosphine
$ClPCy_2$	Chlorodicyclohexylphosphine
Cl*P*t-Bu_2	Di-*tert*-butylchorophosphine
n-BuLi	*n*-Butyllithium
R	Generalized alkyl group
Me	Methyl
Et	Ethyl
n-Bu	*n*-Butyl
i-Pr	Isopropyl

t-Bu	*t*-Butyl
Ar	Aryl
Ph	Phenyl
Bn	Benzyl
Cy	Cyclohexyl
Cyp	Cyclopentyl
o-Tol	*ortho*-Tolyl
1-Ad	1-Adamantyl
P*t*-Bu_3	Tri-*tert*-butylphosphine

Chapter 1 Introduction

1.1 Background

The development of efficient and convenient methods for organic synthesis remains an important topic in modern organic chemistry. The straightforward and modular features of these methods empower scientists to synthesize highly complex, yet diversified molecules in a relatively simple way. Palladium-catalyzed cross-coupling reactions are state-of-the-art methods among various other synthetic processes in organic synthesis.[1] Although transition-metal-catalyzed bond construction protocols, such as the Suzuki-Miyaura coupling[2] and amination reaction,[3] were first reported in the early 1980s, substantial improvements on such reactions have only been achieved since the mid-1990s.[4]

Before the late 1990s, aryl iodides, bromides, and triflates were often employed as electrophiles in various kinds of cross-coupling reactions owing to their relatively high reactivity. However, the more-abundant and inexpensive, but also more-inert aryl chlorides were applied less frequently in the coupling reactions. To expand the scope of the cross-coupling reactions, significant efforts have been made in recent decades. Since the recognition of the significant effects of supporting ligands on the efficiency of coupling reactions, novel electron-rich (enhancement of oxidative addition) and sterically bulky phosphine (improvement of reductive elimination) ligands have been developed since the late 1990s. Within the last decade, Beller,[5] Buchwald,[6] Fu,[7] Hartwig,[8] other research groups[9] and our group [10] have contributed a huge amount of work to the area of phosphine

ligand design and synthesis (**Figure 1.1**). Although progress has been made, there are still efforts to increase the scope of these reactions.

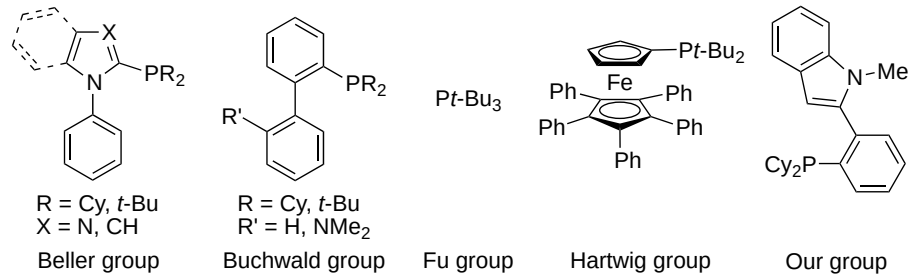
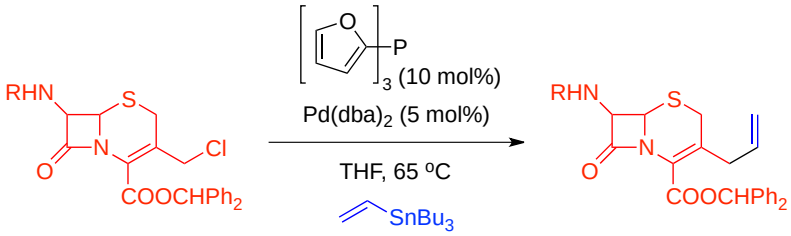


Figure 1.1 Phosphine Ligands Development by Different Research Groups

Among several series of phosphines developed, heterocyclic phosphines in which the phosphino group is attached to a heterocyclic ring are a unique type of supporting ligand for coupling reactions. In fact, heterocyclic phosphines have been applied to coupling reactions since 1988, Farina showed that tri-2-furylphosphine and tri-2-thienylphosphine were effective ligands in palladium-catalyzed Stille coupling instead of using traditional triphenylphosphine (**Scheme 1.1**).[11] However, these simple heterocyclic phosphines have inherent limitations since there is no further room for steric and electronic fine-tuning. In 2004, Beller and co-workers reported the design and synthesis of a new class of heterocyclic phosphines PAPs,[5c] which using pyrrole as the main scaffold and integrating with different phosphino groups and an aryl group, to allow the heterocyclic phosphines having different steric and electronic fine-tuning.



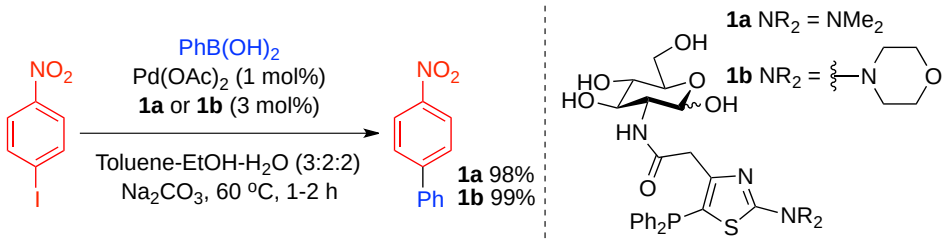
Scheme 1.1 The First Palladium-Catalyzed Stille Coupling by Using Heterocyclic Phosphines

1.2 Suzuki-Miyaura Coupling Reaction

The palladium-catalyzed Suzuki-Miyaura cross-coupling reaction has become a widely used protocol and is one of the most efficient tools for the synthesis of biaryl motifs.[12] This methodology has many advantages, including excellent functional group compatibility and that it uses organoboron compounds of low toxicity as well as arylboronic acids that are mostly commercially available.

1.2.1 Development of Heterocyclic Phosphines Towards Palladium-Catalyzed Suzuki-Miyaura Coupling Reaction of Aryl Halides

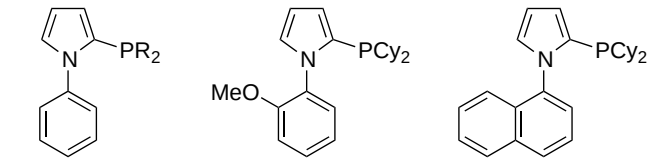
In 2003, Sinou reported a class of easily obtainable phosphine ligands bearing a carbohydrate skeleton.[13] The Pd/**1a** and Pd/**1b** systems showed efficacy in the Suzuki-Miyaura coupling of 1-iodo-4-nitrobenzene with phenylboronic acid (**Scheme 1.2**). However, when the coupling partners were changed to aryl chlorides, no biaryl product formation could be observed.



Scheme 1.2 Palladium-Catalyzed Suzuki Coupling of Aryl Iodide by Sinou

In late 2003, Beller revealed a novel class of phosphino-substituted 1-arylpyrroles, PAPs **2a** to **2d**, **3** and **4** (**Figure 1.2**).[5c] Particularly noteworthy is that the coupling of a nonactivated aryl chloride at room temperature could be

achieved with a turnover number (TON) of 800 (**Table 1.1**, entry 1). Moreover, the catalyst loading could be reduced to 0.005 mol% when the reaction temperature was elevated to 100 °C (**Table 1.1**, entry 3).

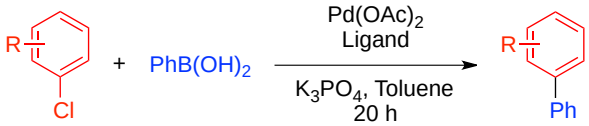


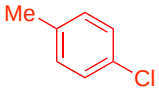
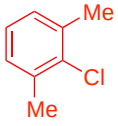
2a R = Ph
2b R = Cy
2c R = *t*-Bu
2d R = 1-Ad

3 **4**

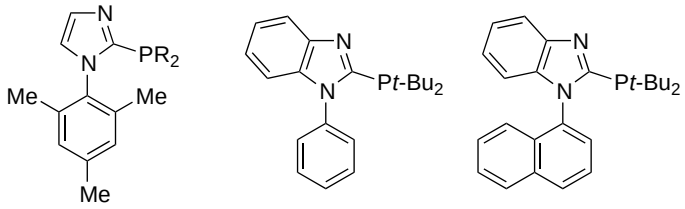
Figure 1.2 Beller's PAP Ligands

Table 1.1 Palladium-Catalyzed Suzuki Coupling of Aryl Chlorides by Beller



Entry	ArCl	Ligand	mol% Pd	Temp. °C	% Yield	TON
1		**2c**	0.1	r.t.	80	800
2		**2c**	0.01	60	99	9,900
3		**2c**	0.005	100	98	19,600
4		**2b**	0.05	60	72	1,440
5		**2c**	0.05	60	16	320
6		**2d**	0.05	60	15	300
7		**3**	0.05	60	55	1,100
8		**4**	0.05	60	35	700

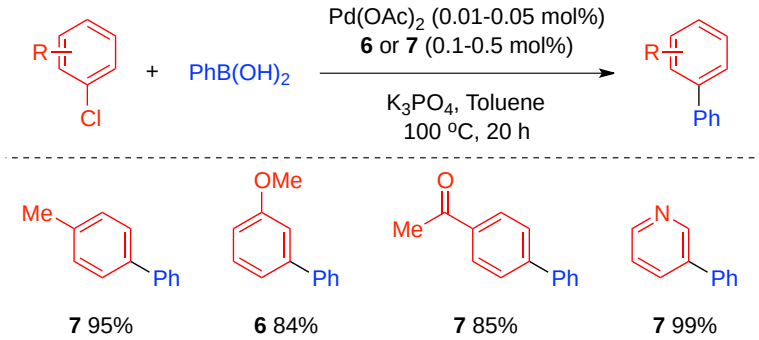
In addition to those compounds containing a pyrrole backbone, Beller soon after reported another series of phosphine ligands featuring imidazole and benzimidazole moieties: 1-aryl-2-(dialkylphosphino)imidazoles and -benzimidazoles **5** to **7** (**Figure 1.3**).[14] These types of ligand also feature easy tunability, and their synthesis can be conveniently scaled up. These ligands showed excellent catalytic activity in two palladium-catalyzed coupling reactions: Suzuki-Miyaura coupling reaction and Buchwald-Hartwig amination reaction (see **Section 1.3.1**). The superior ligands, **6** and **7**, were applied in the coupling reactions of different aryl and heteroaryl chlorides (**Scheme 1.3**). The coupling results using the Pd/**6** and Pd/**7** systems showed excellent product yields with low catalyst loading, which could even be down to 0.01 mol% of Pd.



5a R = Cy
5b R = *t*-Bu

6 **7**

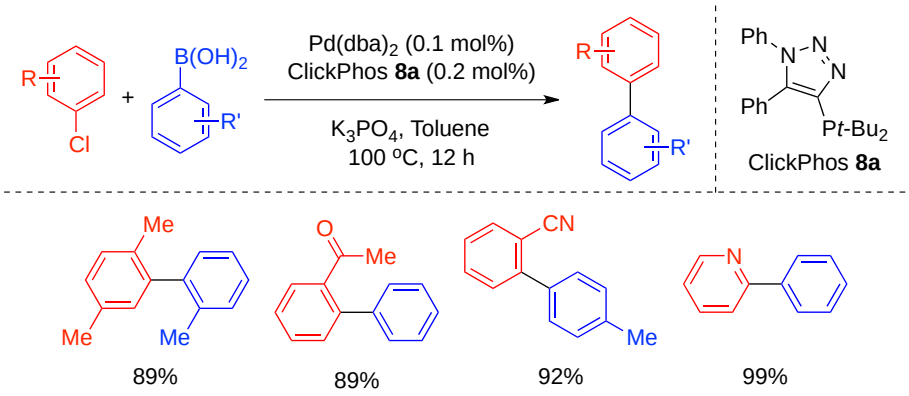
Figure 1.3 1-Aryl-2-(dialkylphosphino)imidazole and -benzimidazole Ligands



7 95% **6** 84% **7** 85% **7** 99%

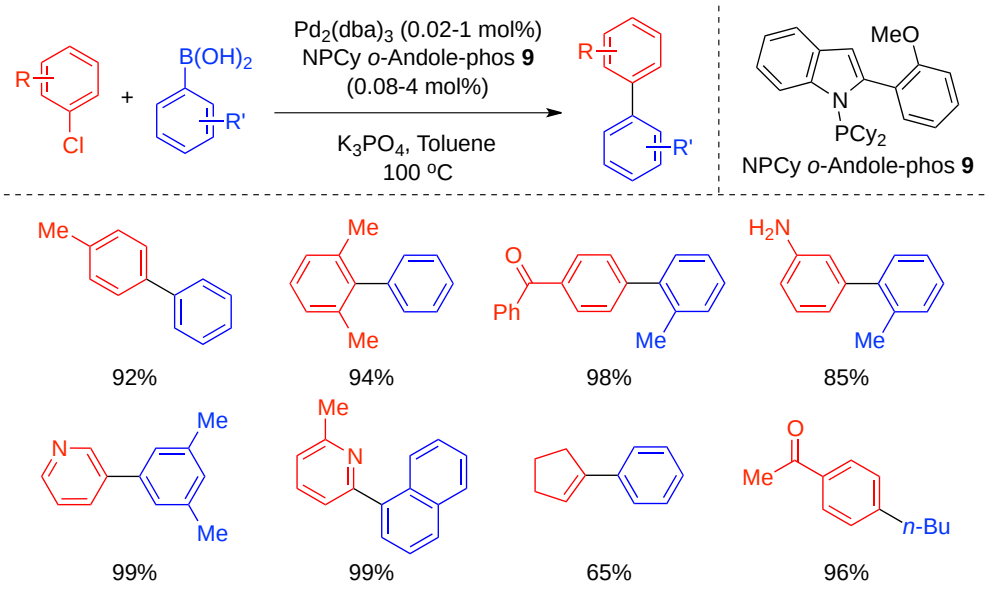
Scheme 1.3 Palladium-Catalyzed Suzuki Coupling of Aryl Chlorides by Beller

In 2005[15] and 2006,[9g] Zhang reported a new class of triazole-based monophosphines ClickPhos, the palladium complexes with these ligands showed excellent catalytic activities in both the Suzuki coupling and amination reactions (see **Section 1.3.1**). The general effectiveness of Pd/ClickPhos **8a** was extensively demonstrated by coupling a broad range of aryl and heteroaryl chlorides with several arylboronic acids (**Scheme 1.4**).



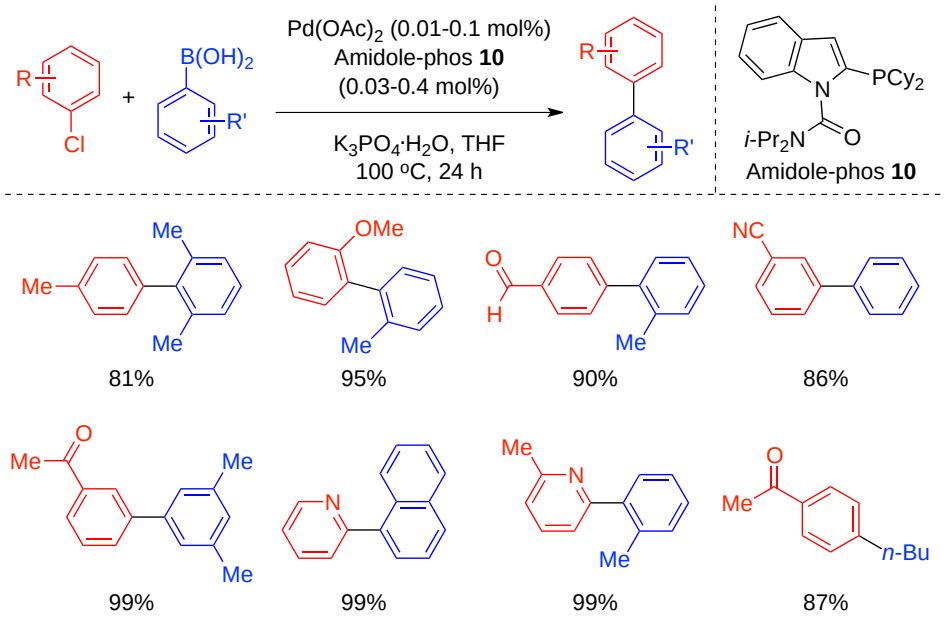
Scheme 1.4 Palladium-Catalyzed Suzuki Coupling of Aryl Chlorides by Zhang

In 2007, we developed a new class of easily accessible indolyl phosphines, NPCy *o*-Andole-phos **9**,[10b] which could be prepared easily *via* an efficient protocol involving Fischer indolization from commercially available phenylhydrazine and substituted acetophenones. The combination of this ligand with $Pd_2(dba)_3$ provided good efficacy towards Suzuki coupling of an array of aryl, heteroaryl chlorides and alkenyl chloride (**Scheme 1.5**). In addition, coupling with alkylboronic acid was also successful.



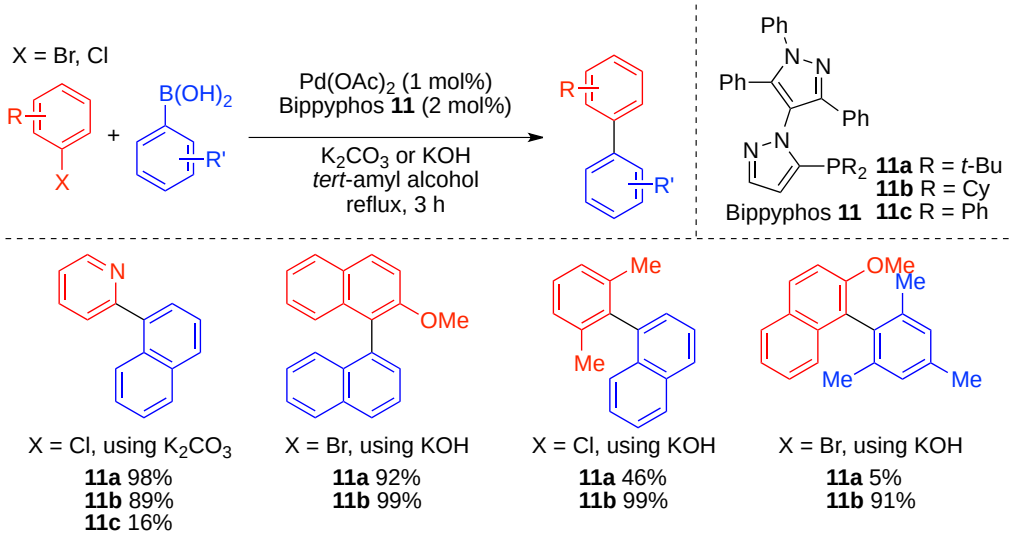
Scheme 1.5 Palladium-Catalyzed Suzuki Coupling of Aryl Chlorides by Kwong

Later on, we reported a new class of indolylphosphine ligands, Amidole-phos **10**,[10f] which could be easily accessed using a simple one-pot assembly from commercially available indoles, acid chlorides, and chlorophosphines. The Pd/**10** system was further applied to the Suzuki coupling of aryl and heteroaryl chlorides and an array of arylboronic acids (**Scheme 1.6**). This system showed good efficacy in the Suzuki-Miyaura coupling of aryl chlorides.



Scheme 1.6 Palladium-Catalyzed Suzuki Coupling of Aryl Chlorides by Kwong

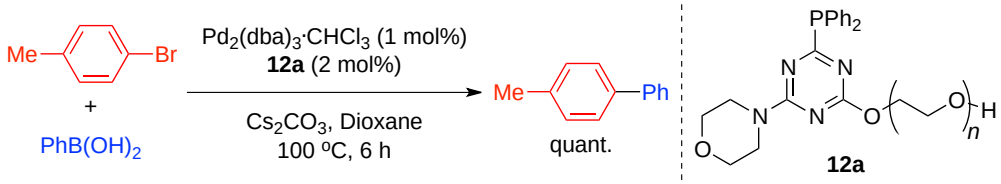
In 2008, Singer described a new family of ligands, Bippyphos compounds **11**.[9j] Palladium-catalyzed Suzuki coupling and amination (see **Section 1.3.1**), were possible using the Pd/Bippyphos **11** systems. In case of the Suzuki coupling reaction, Cy-Bippyphos **11b** generally succeeded in coupling aryl halides and arylboronic acids to afford tri-*ortho*-substituted biaryls, and one example involving the coupling of an aryl bromide gave the corresponding tetra-*ortho*-substituted biaryl in excellent yield (**Scheme 1.7**).



Scheme 1.7 Palladium-Catalyzed Suzuki Coupling of Aryl Halides by Singer

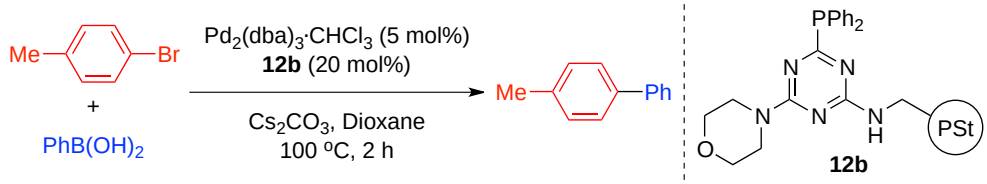
In 2009, Hayashi reported a novel class of phosphinotriazines **12**.[16] The ligand structures could be extended to include water-soluble chains **12a** and polymer supports **12b**. The Suzuki-Miyaura coupling reaction using these phosphinotriazines was excellent. Interestingly, the solubility of ligand **12a** could be tuned by varying the length of the polyethylene glycol chain and the substituent on the other site. The Pd/**12a** system demonstrated excellent performance in the palladium-catalyzed Suzuki coupling of an aryl bromide in water (**Scheme 1.8**). The polystyrene-supported ligand **12b** could readily be

recycled in the Suzuki coupling and the reactivity of this system remained active even after being reused for five times (**Table 1.2**).



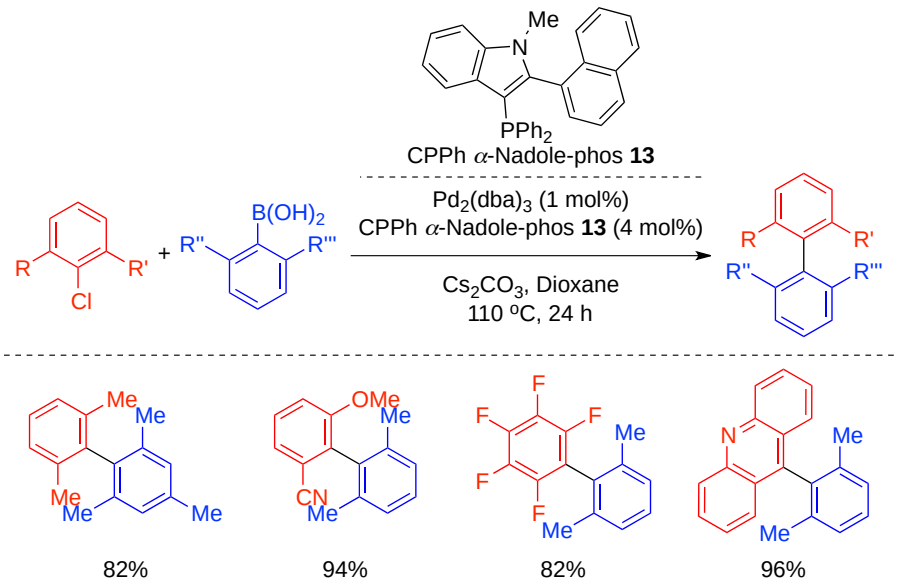
Scheme 1.8 Palladium-Catalyzed Suzuki Coupling of Aryl Bromide in Water by Hayashi

Table 1.2 Repetitive Use of Palladium-Catalyzed Suzuki Coupling of Aryl Bromide by Hayashi



Entry	Run	Reuse	% Yield
1	1	0	>99
2	2	1	>99
3	3	2	>99
4	4	3	>99
5	5	4	98
6	6	5	76
7	7	6	43

In 2010, we showed a novel C-P type indolyl phosphine, CPPh α-Nadole-phos **13**, with $-PPh_2$ moiety and its application towards palladium-catalyzed Suzuki-Miyaura coupling for challenging tetra-*ortho*-substituted biaryl syntheses (**Scheme 1.9**).[10j] With the employment of $Pd_2(dba)_3$ and CPPh α-Nadole-phos **13**, deactivated, activated aryl and herteroaryl chlorides were good partners for this challenging coupling reaction.



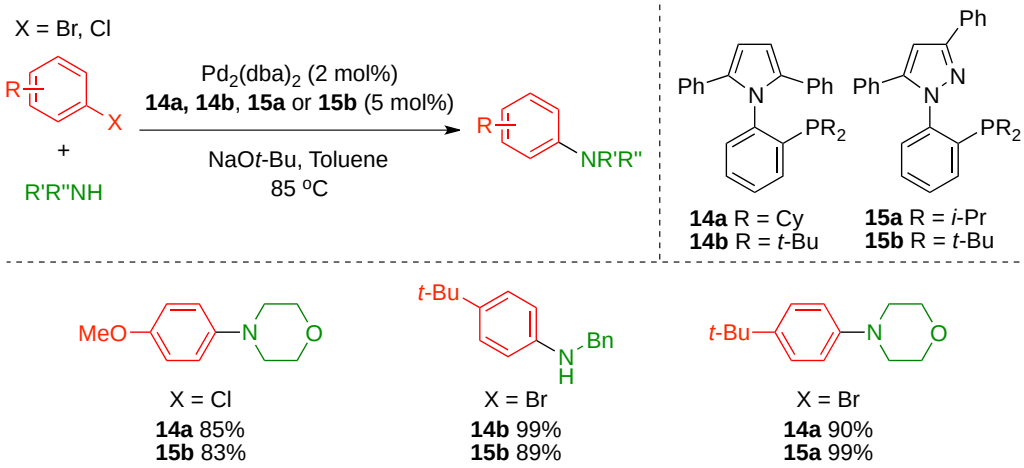
Scheme 1.9 Palladium-Catalyzed Tetra-*Ortho*-Substituted Suzuki Coupling of Aryl Chlorides by Kwong

1.3 Buchwald-Hartwig Amination Reaction

Palladium-catalyzed carbon-nitrogen bond coupling was firstly disclosed by Migita and co-workers in the early 1980s,[3, 17] and was extensively developed and further generalized by the groups of Buchwald[18] and Hartwig[19] in the mid-1990s. This so-called Buchwald–Hartwig amination has become an extremely useful method for constructing aromatic carbon–nitrogen bonds. These coupling processes are versatile and have widespread applications in pharmaceutical syntheses.[20]

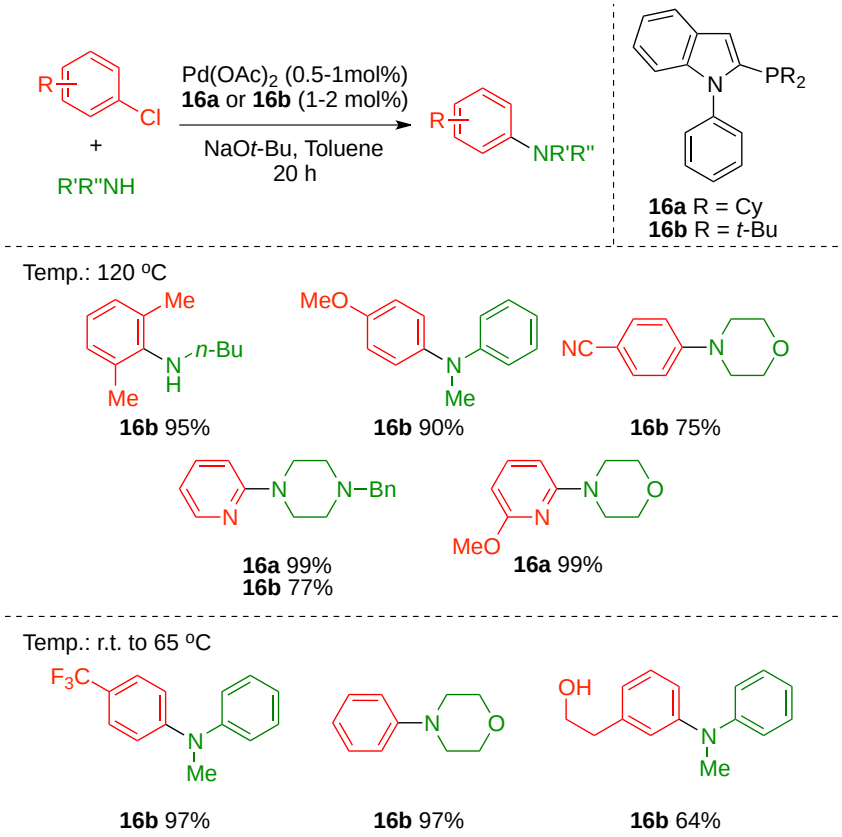
1.3.1 Development of Heterocyclic Phosphines Towards Palladium-Catalyzed Buchwald-Hartwig Amination Reaction of Aryl Halides

In 2003, Singer and co-workers firstly reported $Pd_2(dba)_3$ catalyzed amination of aryl halides using **14a**, **14b**, **15a** or **15b** as the ligand.[9d] These pyrrole- and pyrazole-based ligands are easily synthesized yet the reactivity for the amination reactions is limited (**Scheme 1.10**).



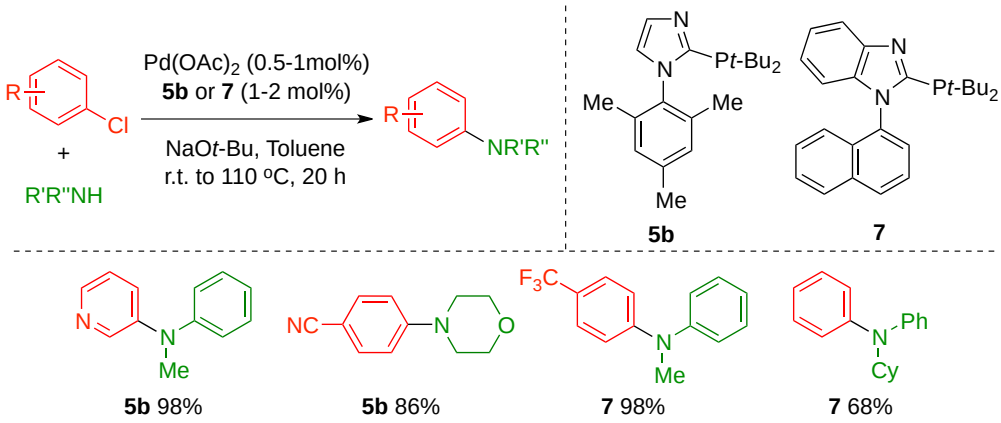
Scheme 1.10 Palladium-Catalyzed Amination of Aryl Halides by Singer

In 2004, Beller reported new monodentate *N*-substituted heteroarylphosphines, dialkyl(1-arylindol-2-yl)phosphines **16a** and **16b**, which showed generally excellent catalytic activity in the palladium-catalyzed amination of aryl and heteroaryl chlorides, even under mild conditions.[5d] Ligand **16b** was found to be the most efficient phosphine for this reaction. The Pd/**16b** system showed general application in the amination of various aryl and heteroaryl chlorides (**Scheme 1.11**). Both aliphatic and aromatic amines were efficient coupling partners. Remarkably, the amination could also occur under milder reaction conditions, such as at room temperature.



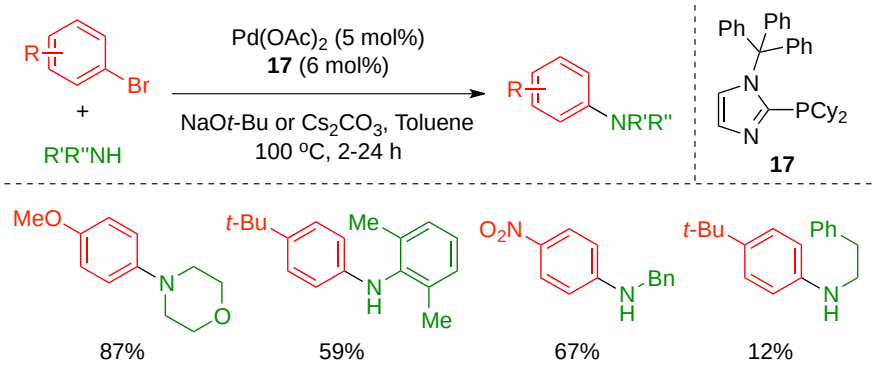
Scheme 1.11 Palladium-Catalyzed Amination of Aryl Chlorides by Beller

In the same year, Beller and co-workers developed 1-aryl-2-(dialkylphosphino)imidazoles and -benzimidazoles (see **Section 1.2.1**),[14] which also showed good to excellent catalytic performance in Buchwald-Hartwig amination reactions. The usefulness of these ligands was also examined by coupling an array of aryl and heteroaryl chlorides with different amines (**Scheme 1.12**). It should be noted that both aliphatic and aromatic amines were feasible coupling partners, and the amination could also be accomplished smoothly at room temperature.



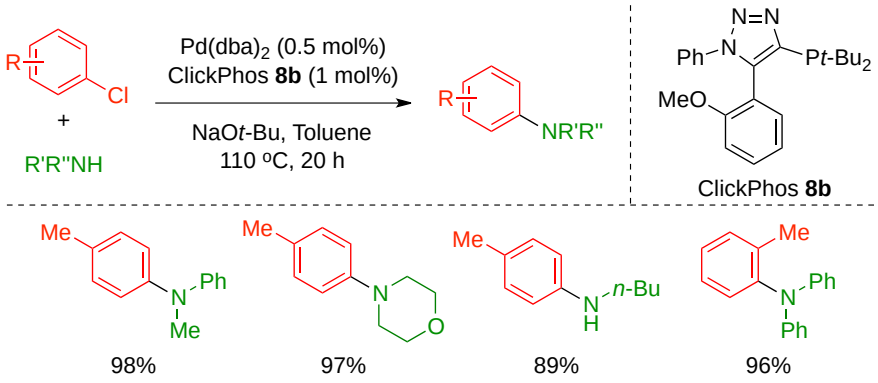
Scheme 1.12 Palladium-Catalyzed Amination of Aryl Chlorides by Beller

In 2004, Tom and co-workers described three families of ligands, including tritylimidazole-based **17**, for the palladium-catalyzed amination of aryl bromides.[21] The efficacy of ligand **17** in the amination was evaluated (**Scheme 1.13**). However, this phosphine showed moderate general application to this reaction in terms of substrate scope.



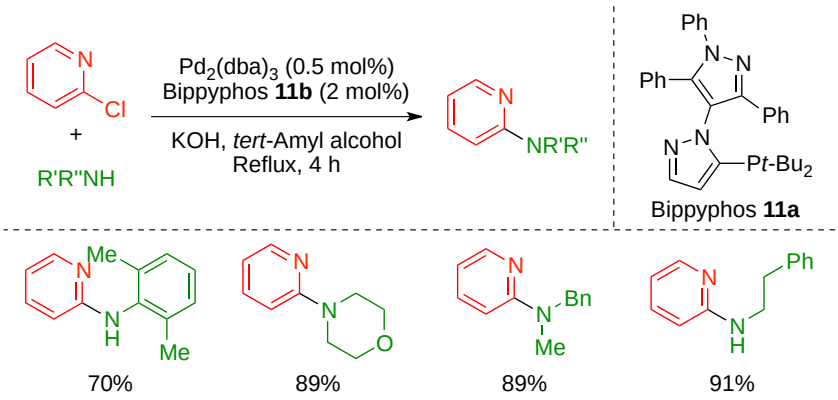
Scheme 1.13 Palladium-Catalyzed Amination of Aryl Bromides by Tom

As described in previous section (see **Section 1.2.1**), Zhang and co-workers reported that the ClickPhos family showed excellent catalytic activities in both the Suzuki coupling and amination reactions. This ligand family could allow up to 98% yield in the amination reaction.[15, 9g] The activities of Pd/ClickPhos **8b** were evaluated in the amination of aryl chlorides and a diverse array of primary and secondary amines (**Scheme 1.14**). The Pd/ClickPhos **8b** system demonstrated high catalytic activity and a broad substrate scope in the amination reaction.



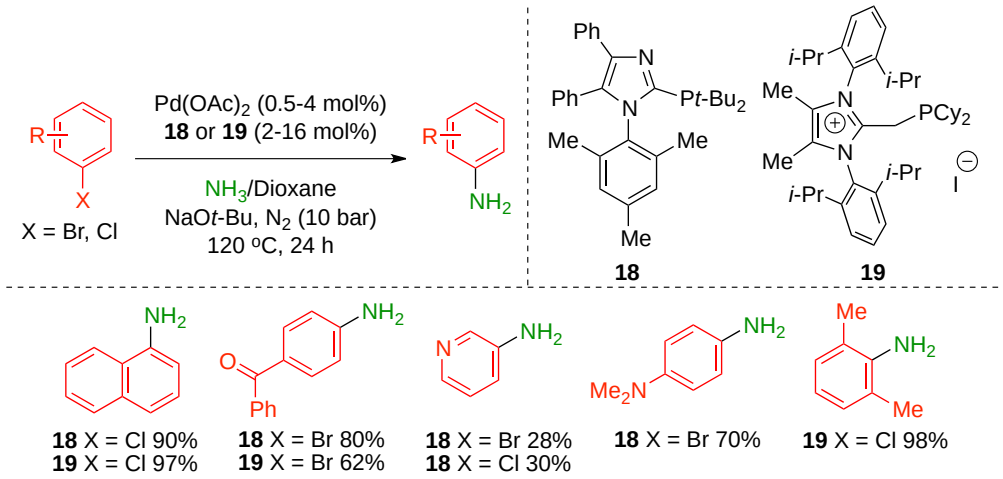
Scheme 1.14 Palladium-Catalyzed Amination of Aryl Chlorides by Zhang

In 2008, Singer and co-workers disclosed the family of Bippyphos ligands, compounds **11** (see **Section 1.2.1**).[9j] The ligand Bippyphos **11a** showed high efficiency in the amination reaction of chloropyridine (**Scheme 1.15**).



Scheme 1.15 Palladium-Catalyzed Amination of Chloropyridine by Singer

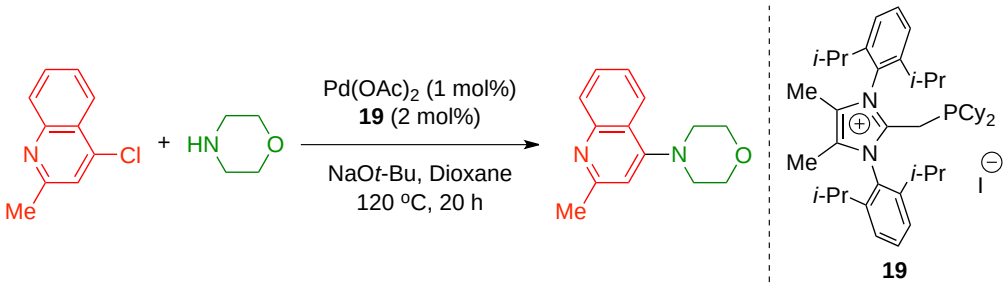
Anilines are important intermediates in the manufacture of agrochemicals, pharmaceuticals, dyes, etc.[22] In 2009, Beller reported the Pd-catalyzed amination of aryl halides with ammonia.[23] In spite of the remarkable results for the production of secondary and tertiary amines, relatively little work has been done on the amination of aryl halides with ammonia for producing primary arylamines. The authors established a new ancillary ligand **18** for the Pd-catalyzed coupling reactions. The scope of the reaction using the $Pd(OAc)_2$/**18** complex was evaluated for the amination of aryl bromines or chlorides with ammonia (**Scheme 1.16**). The optimized catalytic system allowed good substrate scope, including the use of deactivated and activated aryl or heteroaryl halides.



Scheme 1.16 Palladium-Catalyzed Amination of Aryl Halides with Ammonia by Beller

Additionally, in 2011, Beller and coworkers reported the recyclable ligand **19** for the amination reactions.[24] Palladium catalyst supported with ligand **19** could catalyze the amination of aryl halides with ammonia (**Scheme 1.16**), primary, and secondary amines. Moreover, the catalyst can be recycled at least for 3 times without significant decrease of its catalytic activity (**Table 1.3**).

Table 1.3 The Catalyst Recycling Amination of 4-Chloroquinaldine with Morpholine by Beller



Entry	Run	% Yield
1	1	99
2	2	98
3	3	89

1.4 Strategies and Exploration of Heterocyclic Phosphines Towards Palladium-Catalyzed Cross-Couplings of Aryl Halides

According to previous reviews on the development of heterocyclic phosphines towards palladium-catalyzed Suzuki-Miyaura cross-coupling and Buchwald-Hartwig amination reaction, heterocyclic phosphines have found a wide range of applications in palladium-catalyzed coupling reactions. Palladium catalysts supported by these heterocyclic phosphines demonstrated superior reactivity in both Suzuki-Miyaura cross-coupling and Buchwald-Hartwig amination processes.

Not only can aryl iodides and bromides be used as eletrophiles in these coupling reactions, but also inert aryl chlorides are applicable. Yet, the syntheses of these effective heterocyclic phosphine ligands are relatively simple and convenient. Owing to their ease of synthesis and diversification, designing and synthesizing new generations of heterocyclic phosphine ligands should be a great urgency and potential to improve the reactivity as well as substrate scope of palladium-catalyzed cross-coupling reactions.

Therefore, for the purpose of exploring the palladium-catalyzed cross-coupling of aryl halides, we herein plan to design strategically new classes of heterocyclic phosphines with high diversity that provide an appropriate steric and electronic properties for coupling reactions. Then, the applications of these new classes of heterocyclic phosphines towards palladium-catalyzed cross-couplings of aryl halides will also be undergone.

1.5 References

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Chapter 2 Strategic Design and Synthesis of New Classes of Benzimidazolyl Phosphine Ligands

2.1 Introduction

The structure of the phosphine ligand has been recognized to significantly influence the efficiency of cross-coupling reactions. Novel ligand design was found to be important for number of considerable advancements. During the past decade, pioneering establishments in designing effective phosphines for palladium-catalyzed cross-couplings, such as Beller,[1] Buchwald,[2] Fu,[3] Hartwig,[4] our group,[5] and other groups,[6] have contributed a huge amount of work. Although significant progress has been made, the ligand syntheses featuring simple, straightforward, streamlined, and large-scale-viable advantages are still highly desirable for more widespread applications of cross-coupling reactions.

2.1.1 Strategic Design of New Classes of Ligands

As in previous discussion, it showed an idea that a strategic ligand design is a key to be successful towards the palladium-catalyzed cross-coupling reactions. We herein propose designing a new class of heterocyclic phosphine ligand based on several strategic points: (1) the starting materials should be inexpensive and readily available; (2) the ligand synthetic route should be straightforward; (3) the ligand diversity and tuning should be easily accessible. Based on the above strategic points, benzimidazole was chosen as the ligand framework to develop a new class of benzimidazolyl phosphine ligands.

Benzimidazole is a heterocyclic aromatic organic compound consists of a phenyl ring fused to an imidazole ring. Benzimidazole is key system both in nature such as vitamin B_{12}, purines (component of DNA base structure), and obviously in pharmaceutical, veterinary and agrochemical products such as thiabendazole, benomyl (**Figure 2.1**).

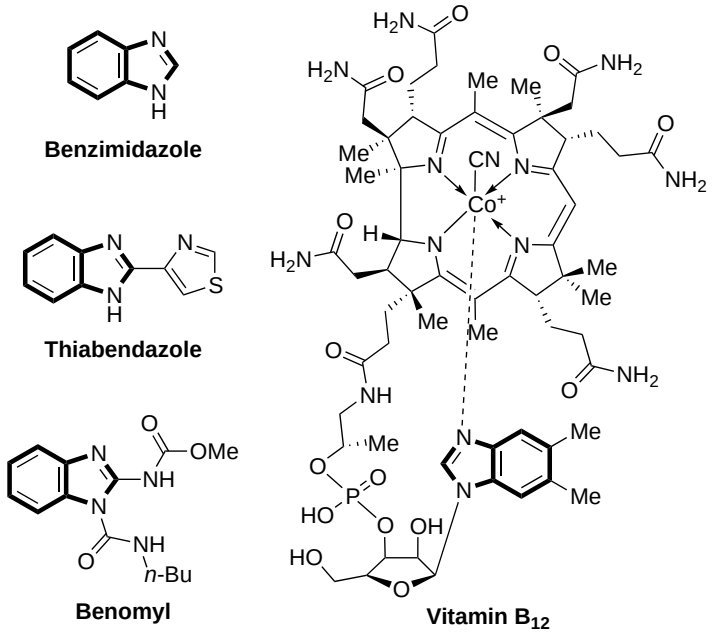


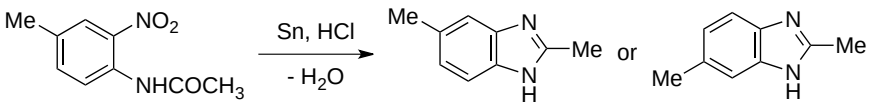
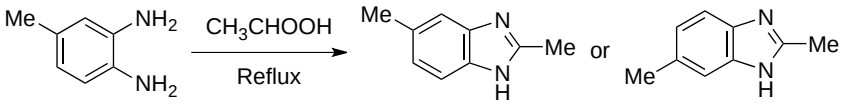
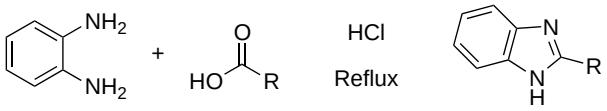
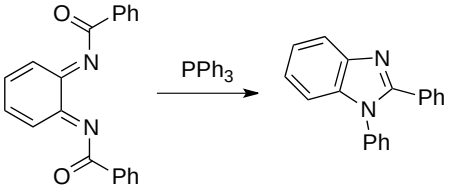
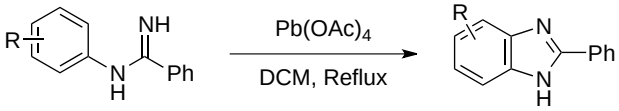
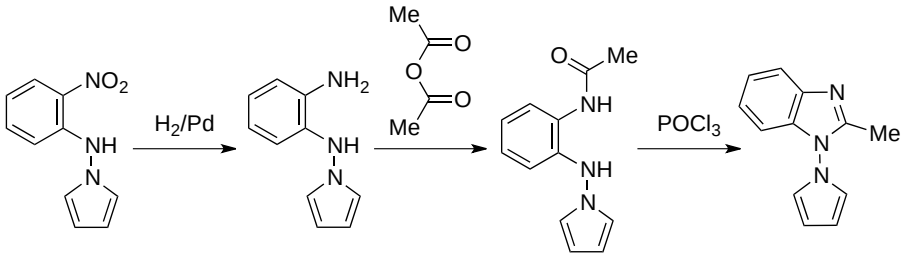
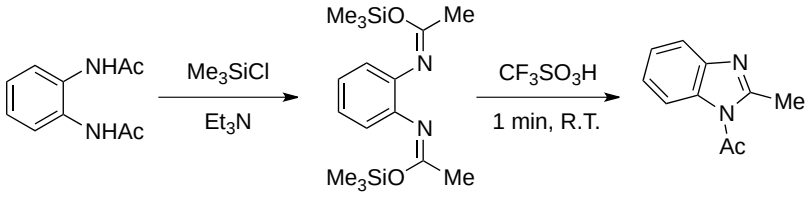
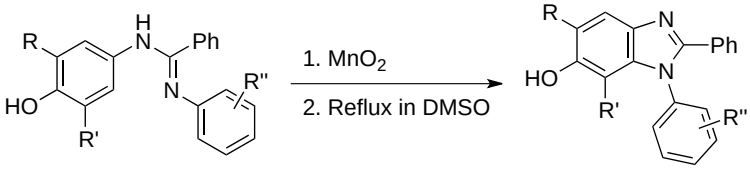
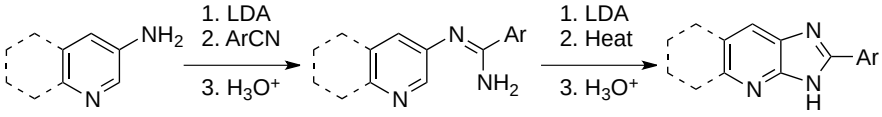
Figure 2.1 Structures of Benzimidazole, Vitamin B_{12}, Thiabendazole and Benomyl

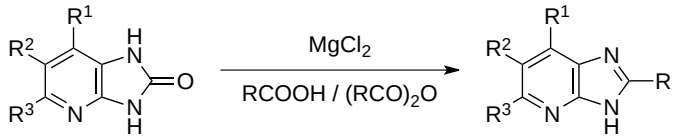
2.1.2 Considerations of Benzimidazole as Ligand Scaffold

There are several reasons for selecting benzimidazole as ligand framework: (1) benzimidazole is an inexpensive chemical and costs USD 140 per 500 g; (2) the cost of substituted benzimidazole is also reasonable, such as 5,6-dimethylbenzimidazole, USD 90 per 100 g; (3) the starting materials of synthesizing benzimidazole derivatives, such as *o*-phenylenediamine, USD 176 per kg, and formic acid, USD 74 per liter, are also relatively inexpensive.[7]

Benzimidazole and its derivatives are readily available. In addition, benzimidazole is a key system in nature, pharmaceutical, veterinary and agrochemical, thus a wide range of synthetic methods have been reported since 1872. Those methods including from the most general Phillips benzimidazole organic synthesis to recent metal-catalyzed synthesis have been well addressed to provide us a “cookery book” to prepare benzimidazole derivatives. Herein, some benzimidazole synthetic methods have been selected and showed below (**Table 2.1**).

Table 2.1 The Development of Benzimidazole Synthesis (1872-1994)

Researcher / Year	Synthetic Scheme
The first Benzimidazole synthesis by Hobrecker, F.[8] / **1872**	
Ladenburg, A.[9] / **1875**	
Phillips, M. A.[10] / **1928**	
Sprecher, M.[11] / **1969**	
Mahajan, M. P.[12] / **1982**	
Artico, M.[13] / **1983**	
Rigo, B.[14] / **1988**	
Sannicolò, F.[15] / **1988**	
Wakefield, B. J.[16] / **1992**	

Senanayake, C. H.[17] / **1994**	

Last but not least, it is notable that the chemical properties of benzimidazole provide a potential for diversifying the ligand structures since the benzimidazole scaffold allows both steric and electronic fine tunings. Particularly noteworthy is that the 3-position of benzimidazole is a potentially hemilabile *N*-chelating group providing weak coordinating property to offer the dynamic interaction for catalyst longevity. Therefore, there is one more strategic point for our ligand design: the presence of hemilabile group to enhance the catalyst longevity. Herein, the concept of a hemilabile phosphine ligand will be discussed in the following section.

2.2 Concept of Hemilabile Ligands

Hemilabile ligands, *P*,*N*-type or *P*,*O*-type, are the ligands that possess both of the soft and hard donor atoms. The development of this type of ligands is of current interest. Different features of the donor atoms provide the metal complexes with unique reactivity (**Figure 2.2**).[18] The hard donor, such as nitrogen and oxygen atoms, weakly coordinates to soft metal centers, such as palladium, a vacant site can be easily afforded by dissociation of nitrogen/oxygen atom from the metal center, for further oxidation addition of the substrate binding to the catalyst.[19]

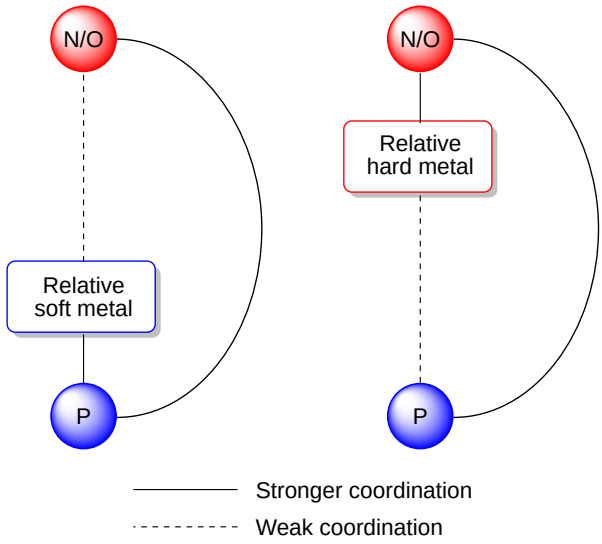


Figure 2.2 Concept of Hemilabile Ligand

To contribute the ligand with an attractive and versatile system, a highly tunable aryl backbone should be combined with phosphorous and nitrogen/oxygen donors, which have a tremendous different electronic and steric characteristics. This ligand design can also demonstrate a "On and Off" mechanism by either providing a vacant site for substrate or coordinating with metal (**Figure 2.3**).

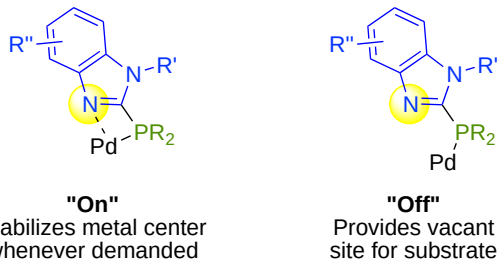


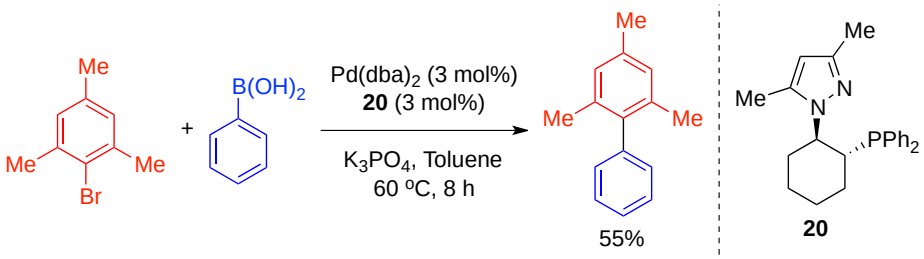
Figure 2.3 Potential Dynamic "On and Off" Mechanism of Benzimidazole-Derived Ligand

In order to show the potential and importance of hemilabile ligands, the development of both *P*,*N*- and *P*,*O*-type ligands towards palladium-catalyzed cross-coupling reactions will be herein presented.

2.2.1 *P,N*-Type Ligands

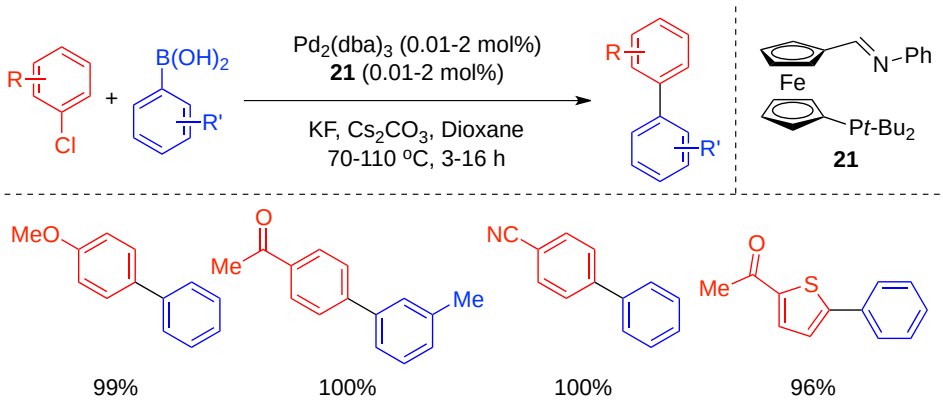
2.2.1.1 Development of *P,N*-Type Ligands Towards Palladium-Catalyzed Suzuki-Miyaura Coupling Reaction of Aryl Halides

In 2002, Yudin reported a new class of cyclohexane-based *P,N*-type ligand **20**,[20] which showed high stability towards oxidation at the phosphorus atom. The combination of $Pd(dba)_2$ and ligand **20** was found to be active to catalyze the Suzuki-Miyaura coupling for 2-bromomesitylene and phenylboronic acid in 55% yield (**Scheme 2.1**).



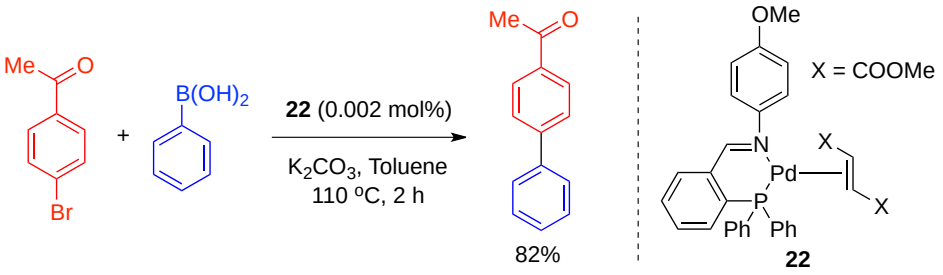
Scheme 2.1 Palladium-Catalyzed Suzuki Coupling of Aryl Bromide by Yudin

In 2004, Hor and co-workers described a combination of $Pd_2(dba)_3$ and ligand **21** efficiently catalyzed the Suzuki-Miyaura coupling of an array of arylboronic acids and aryl chlorides, affording the desired biaryl products in excellent yields (**Scheme 2.2**).[21] Notably, X-Ray crystallography showed Pd(0) species with heterodifunctional chelation with ligand **21**.



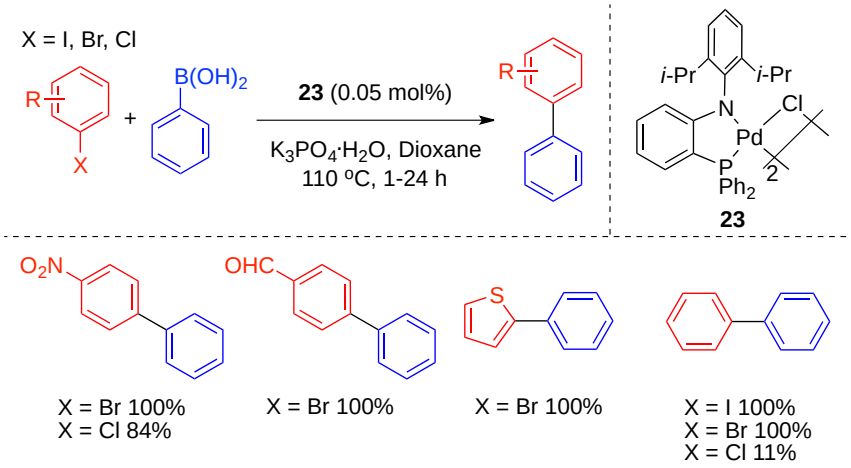
Scheme 2.2 Palladium-Catalyzed Suzuki Coupling of Aryl Chlorides by Hor

In 2005, Scrivanti and co-workers reported η^2-(olefin)palladium(0)(iminophosphine) complex **22** for the Suzuki-Miyaura coupling reaction.[22] High reaction rate was obtained in the coupling of 4-bromoacetophenone with phenylboronic acid (**Scheme 2.3**).



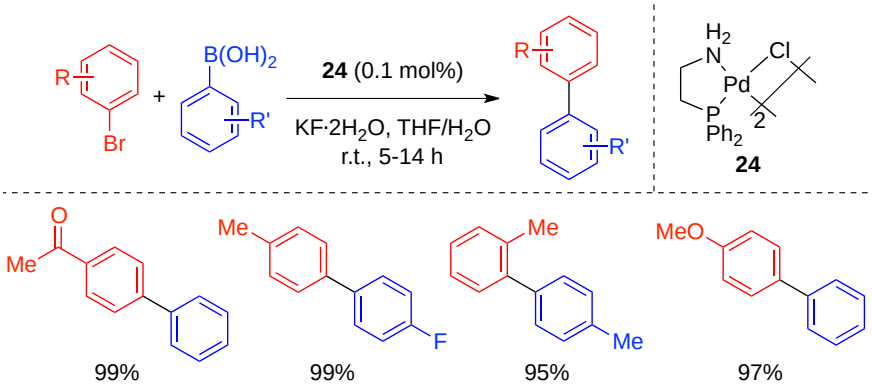
Scheme 2.3 Palladium-Catalyzed Suzuki Coupling of Aryl Bromide by Scrivanti

In the same year, Liang showed a phosphine palladacycle {[NP]PdCl}$_2$ **23** was highly active catalyst precursor for Suzuki-Miyaura coupling of wide range of aryl iodides, bromides and chlorides (**Scheme 2.4**).[23]



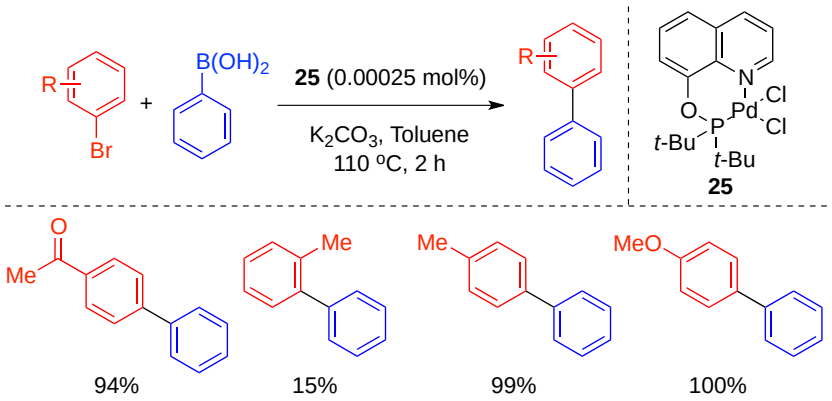
Scheme 2.4 Palladium-Catalyzed Suzuki Coupling of Aryl Halides by Liang

In 2006, He developed a air-stable *P*,*N*-chelated palladium(II) complex **24**,[24] which was a highly efficient and simple catalyst for Suzuki-Miyaura coupling reaction of aryl bromides with arylboronic acids at room temperature (**Scheme 2.5**).



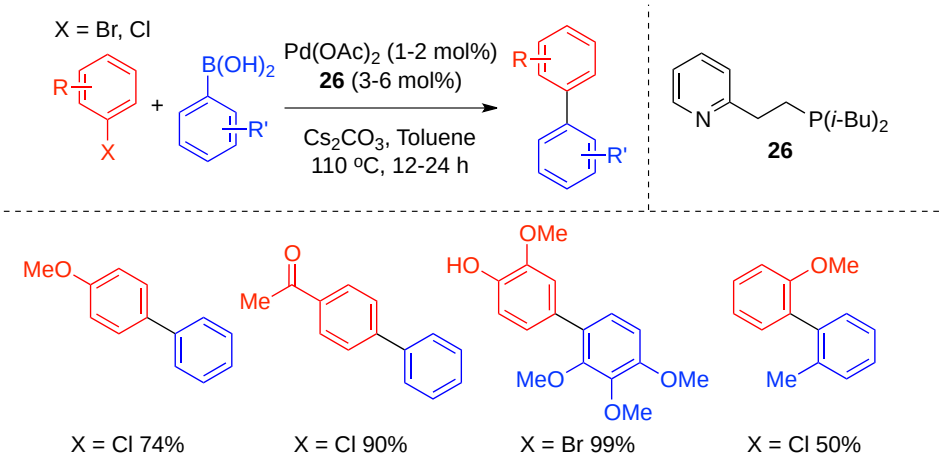
Scheme 2.5 Palladium-Catalyzed Suzuki Coupling of Aryl Bromides by He

As mentioned previously, Scrivanti reported a *P*,*N*-coordinated η^2-(olefin)palladium(0)(iminophosphine) complexes **22** for the Suzuki-Miyaura coupling reaction with high rate.[22] In 2009, Scrivanti and co-workers developed another *P*,*N*-type coordination ({8-[(di-*tert*-butylphosphinyl)oxy]quinoline}-$PdCl_2$) complex **25** for low-catalyst-loading Suzuki coupling of aryl bromides, down to 0.00025 mol% Pd (**Scheme 2.6**).[25]



Scheme 2.6 Palladium-Catalyzed Suzuki Coupling of Aryl Bromides by Scrivanti

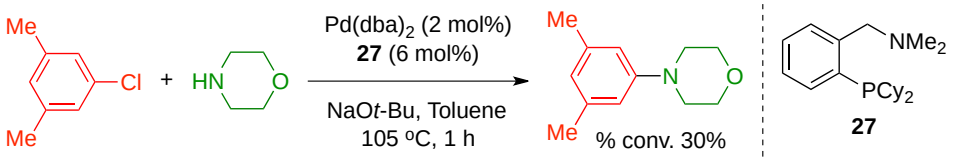
In 2011, McNulty demonstrated a direct synthesis of *P*,*N*- and *P*,*O*-type (see **Section 2.2.2.1**) heterocyclic phosphine ligand.[26] Palladium complex of the *P*,*N*-ligand **26** was determined to be highly active in the Suzuki coupling reaction of aryl halides, especially aryl chlorides (**Scheme 2.7**).



Scheme 2.7 Palladium-Catalyzed Suzuki Coupling of Aryl Halides by McNulty

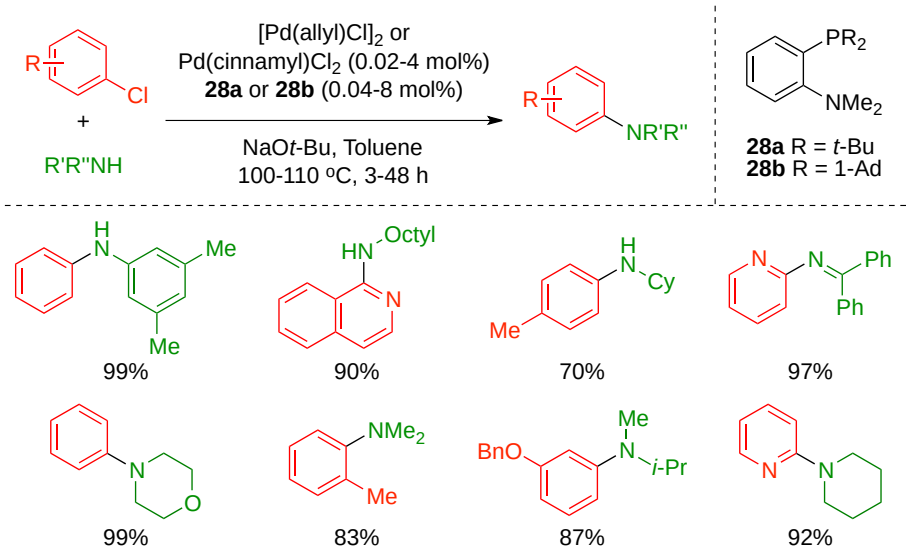
2.2.1.2 Development of *P,N*-Type Ligands Towards Palladium-Catalyzed Buchwald-Hartwig Amination Reaction of Aryl Halides

In 1999, Guram, Bei and co-workers reported a class of phenyl backbone-derived *P,N*- and *P,O*-type (see **Section 2.2.2**) ligands and their application in Buchwald-Hartwig amination reaction.[27] They showed a preliminary study of *P,N*-type ligand towards amination reaction of aryl chlorides (**Scheme 2.8**). This ligand **27** showed only low activity, but it demonstrated the possibility of using *P,N*-type ligands towards amination reaction.

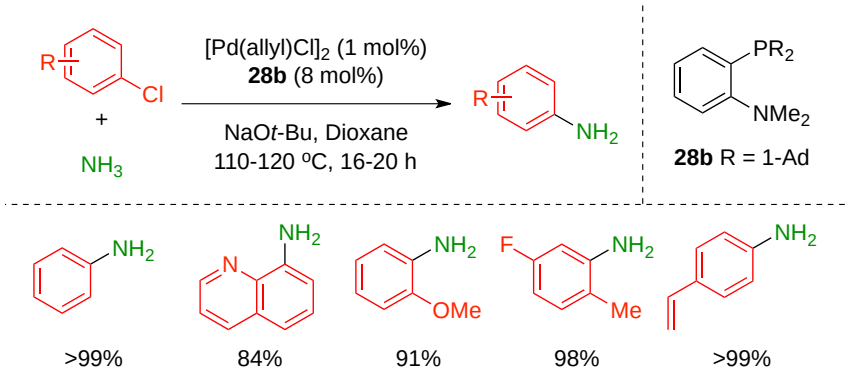


Scheme 2.8 Palladium-Catalyzed Amination of Aryl Chloride by Guram and Bei

In 2010, Stradiotto reported the syntheses of 2-(di-*tert*-butylphosphino)-*N,N*-dimethylaniline **28a**, and 2-(di-1-adamantylphosphino)-*N,N*-dimethylaniline **28b**, and their applications in Buchwald-Hartwig amination.[28] These air-stable *P,N*-type ligands enabled the amination of aryl and heteroaryl chlorides with a diverse range of primary alkyl- and arylamines, cyclic and acyclic secondary amines, N-H imines, hydrazones, lithium amide, and ammonia (**Scheme 2.9** & **2.10**).

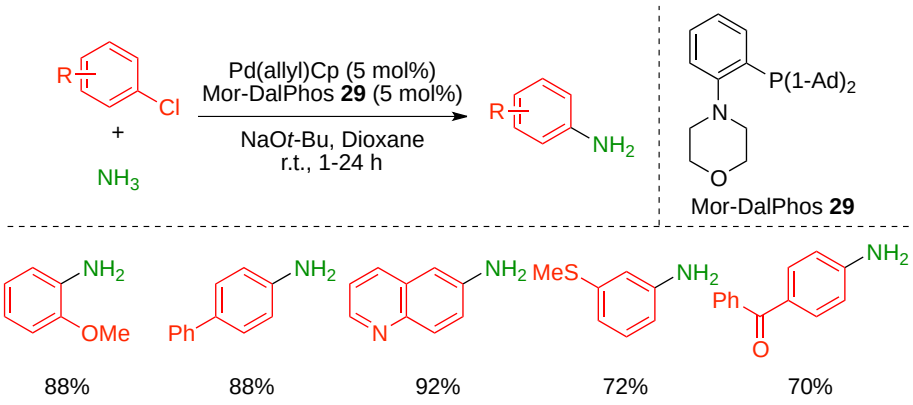


Scheme 2.9 Palladium-Catalyzed Amination of Aryl Chlorides by Stradiotto



Scheme 2.10 Palladium-Catalyzed Amination of Aryl Chlorides with Ammonia by Stradiotto

In the same year, Stradiotto and co-workers reported a new air-stable *P*,*N*-ligand Mor-DalPhos **29**.[29] The [Pd(cinnamyl)Cl]$_2$/Mor-DalPhos **29** system could catalyze the *N*-arylation of ammonia from both aryl chlorides and aryl tosylates with high chemoselectivity and, for the first time, at room temperature (**Scheme 2.11**).

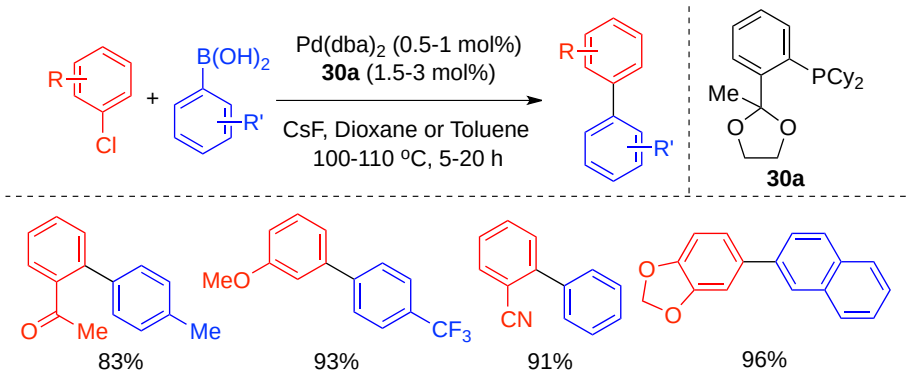


Scheme 2.11 The First Palladium-Catalyzed Amination of Aryl Chlorides with Ammonia at Room Temperature by Stradiotto

2.2.2 *P,O*-Type Ligands

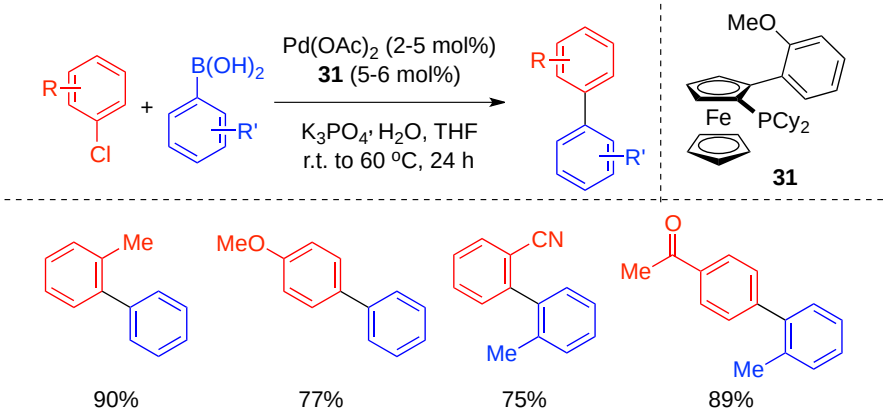
2.2.2.1 Development of *P,O*-Type Ligands Towards Palladium-Catalyzed Suzuki-Miyaura Coupling Reaction of Aryl Halides

In 1999, Guram and Bei reported a *P,O*-type ligand **30a** for Suzuki-Miyaura cross-coupling reactions.[30] The reactivity of $Pd(dba)_2$/**30a** catalytic systems for general Suzuki coupling reaction of aryl chlorides was also demonstrated (**Scheme 2.12**). The effectiveness of ligand **30a** was further extended to carbon-nitrogen bond coupling reactions (see **Section 2.2.2.2**).[27] Notably, the X-ray crystal structure showed both the phosphorus and oxygen donors bound to the palladium center.



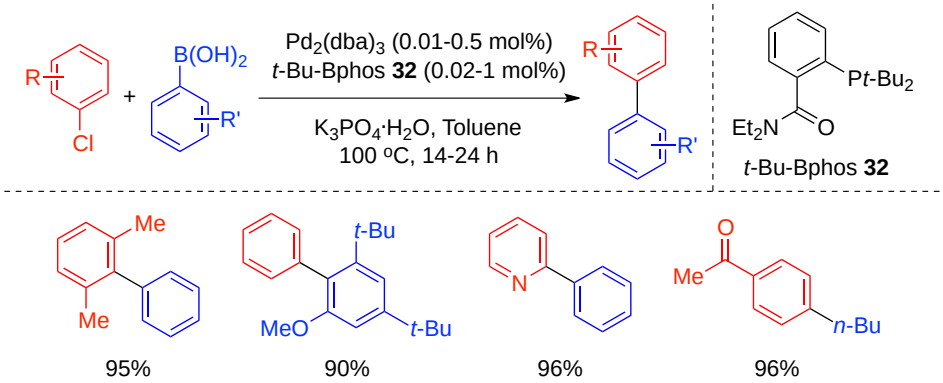
Scheme 2.12 Palladium-Catalyzed Suzuki Coupling of Aryl Chlorides by Guram and Bei

In 2003, Johannsen reported a novel class of planar chiral phosphine **31**,[31] possessing a ferrocenylarene scaffold, was active in the Suzuki-Miyaura coupling reaction of aryl chlorides even at room temperature (**Scheme 2.13**).



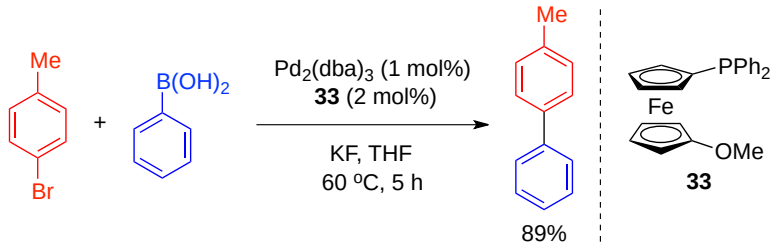
Scheme 2.13 Palladium-Catalyzed Suzuki Coupling of Aryl Chlorides by Johannsen

In 2004, we reported a simple and efficient air-stable benzamide-derived monophosphine Bphos **32**, which was prepared in one step based on an economically attractive approach from commercially available benzamide starting material.[32] The $Pd_2(dba)_3$/*t*-Bu-Bphos **32** system showed high catalytic activity in aryl/heteroaryl chlorides and aryl/alkylboronic acids couplings (**Scheme 2.14**).



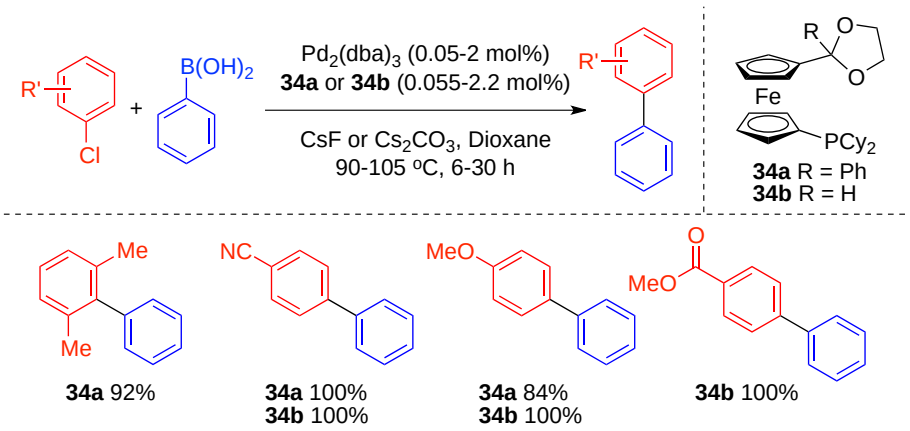
Scheme 2.14 Palladium-Catalyzed Suzuki Coupling of Aryl Chlorides by Kwong

In the same year, Gibson, Long and co-worker reported a 1,1'-disubstituted ferrocenyl *P*,*O*-type ligand **33**.[33] Preliminary studies showed that the combination of $Pd_2(dba)_3$ and ligand **33** could act as a catalyst for Suzuki-Miyaura coupling reaction of 4-bromotoluene with phenylboronic acid (**Scheme 2.15**).



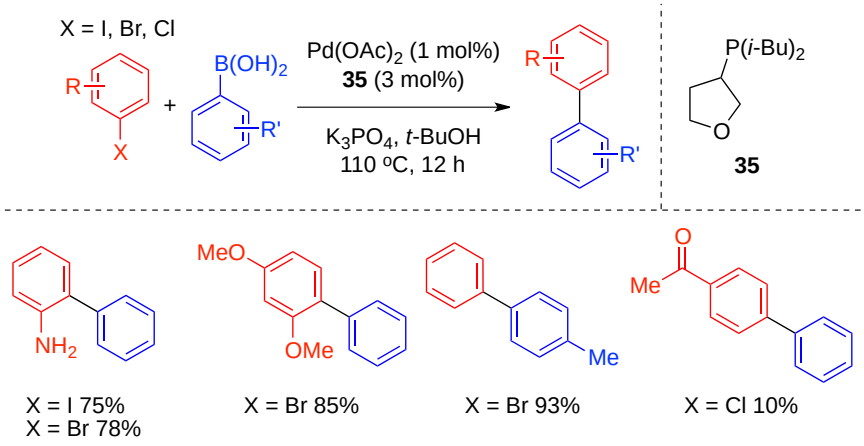
Scheme 2.15 Palladium-Catalyzed Suzuki Coupling of Aryl Bromide by Gibson and Long

In 2006, Hor reported ferrocenyl *P*,*O*-type ligands **34a** and **34b** with acetal protection moieties.[34] Noteworthy, the authors investigated the oxidative addition intermediates from the reaction of ligand **34b** with a palladium precursor and an aryl iodide, which showed a major *P*,*O*-coordination as judged by NMR spectroscopic analysis. The catalytic activity of ligands **34a** and **34b** were investigated in palladium-catalyzed Suzuki coupling of aryl chlorides with phenylboronic acid, very good yields of desired products were also observed (**Scheme 2.16**).



Scheme 2.16 Palladium-Catalyzed Suzuki Coupling of Aryl Chlorides by Hor

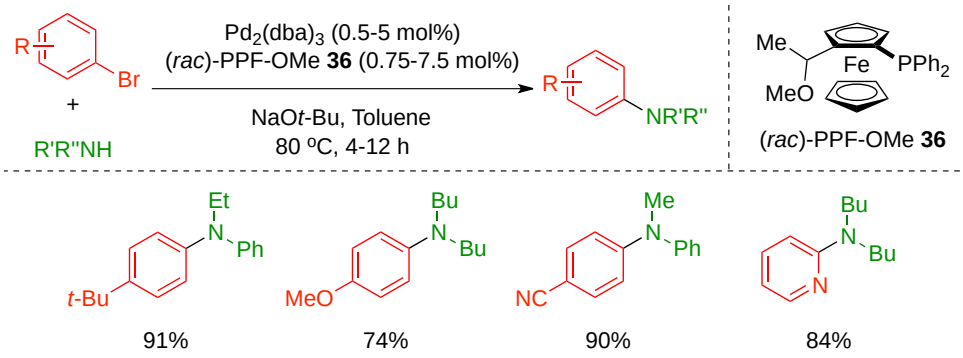
As discussed previously (see **Section 2.2.1.1**), in 2011, McNulty demonstrated a direct synthesis of *P*,*N*- and *P*,*O*-type heterocyclic phosphine ligand.[26] The combination of $Pd(OAc)_2$ and *P*,*O*-type ligand **35** showed that the catalytic activity towards Suzuki coupling reaction of aryl halides was not as good as *P*,*N*-type ligand **26**, and it was difficult to activate aryl chloride (**Scheme 2.17**).



Scheme 2.17 Palladium-Catalyzed Suzuki Coupling of Aryl Halides by McNulty

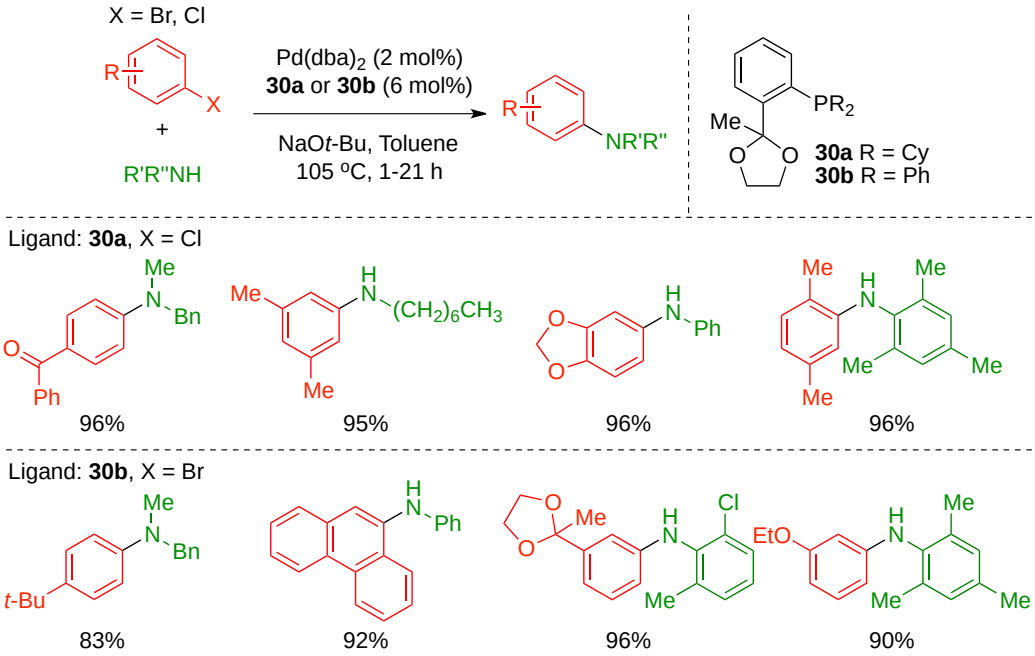
2.2.2.2 Development of *P,O*-Type Ligands Towards Palladium-Catalyzed Buchwald-Hartwig Amination Reaction of Aryl Halides

As early in 1997, Buchwald reported a general palladium-catalyzed amination of aryl bromides by using ferrocenyl *P,O*-type ligand (*rac*)-PPF-OMe **36** (**Scheme 2.18**).[35]



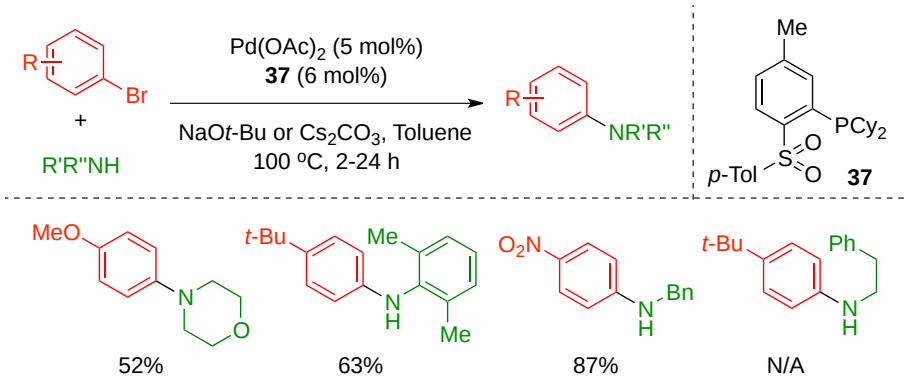
Scheme 2.18 Palladium-Catalyzed Amination of Aryl Bromides by Buchwald

As described is previously (see **Section 2.2.1.2**), in 1999, Guram, Bei and co-workers reported a class of phenyl backbone-derived *P,N*- and *P,O*-type ligands and their application in Buchwald-Hartwig amination reaction.[27] The $Pd(dba)_2$/*P,O*-type ligands **30a** and **30b** were efficient for aminations of aryl bromides and aryl chlorides respectively (**Scheme 2.19**).



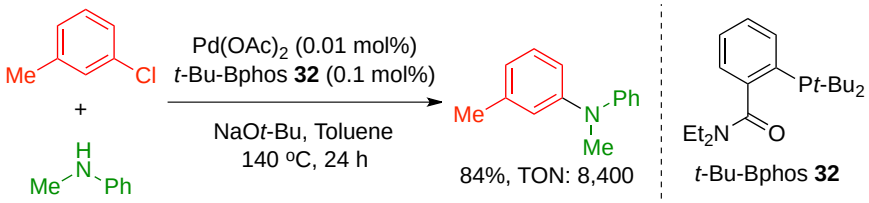
Scheme 2.19 Palladium-Catalyzed Amination of Aryl Halides by Guram and Bei

In 2004, Singer reported a new sulfone-type ligand **37** that consisted of a hemilabile sulfonyl oxygen and a dialkylphosphino group.[36] The authors demonstrated the efficacy of ligand **37** in the amination of aryl bromides (**Scheme 2.20**). Notably, the authors stated that this class of *P*,*O*-type ligand did not have the general scope or the exceptional catalytic activity.



Scheme 2.20 Palladium-Catalyzed Amination of Aryl Bromides by Singer

As mentioned previously, in 2004, we reported a simple and efficient air-stable benzamide-derived monophosphine Bphos **32**, which was efficient towards palladium-catalyzed Suzuki coupling of aryl chlorides (see **Section 2.2.2.1**).[32] Later on in 2007, we demonstrated $Pd(OAc)_2$/*t*-Bu-Bphos **32** system towards palladium-catalyzed amination of aryl and heteroaryl chlorides with high activity.[37] Particularly noteworthy, we presented the first example of *P*,*O*-type ligand providing turnover numbers up to 8,400 (**Scheme 2.21**).



Scheme 2.21 Palladium-Catalyzed Amination of Aryl Chloride with High Turnover Number by Kwong

2.3 Ligand Design Blueprint

As previous discussion of the ligand scaffold choosing and the development and potential of hemilabile ligands, the ligand design "blueprint" has been decided. In our blueprint, there are two possible series of ligand that can be readily prepared (**Figure 2.4**).

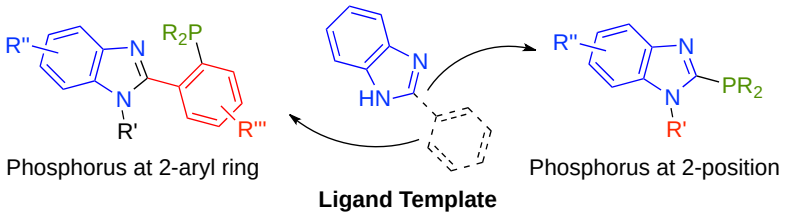


Figure 2.4 Two Possible Ligand Series

Inspired by the unique feature of *P*,*N*-type ligands in cross-couplings of aryl halides and the effectiveness of the monophosphines, such as CM-phos for the cross-coupling reactions, we are interested in designing a new family of hemilabile *P*,*N*-type ligands. Noteworthy, this new family of ligands embodies a highly tunable, yet easily accessible, main skeleton with a hemilabile coordinating site (**Figure 2.5**).

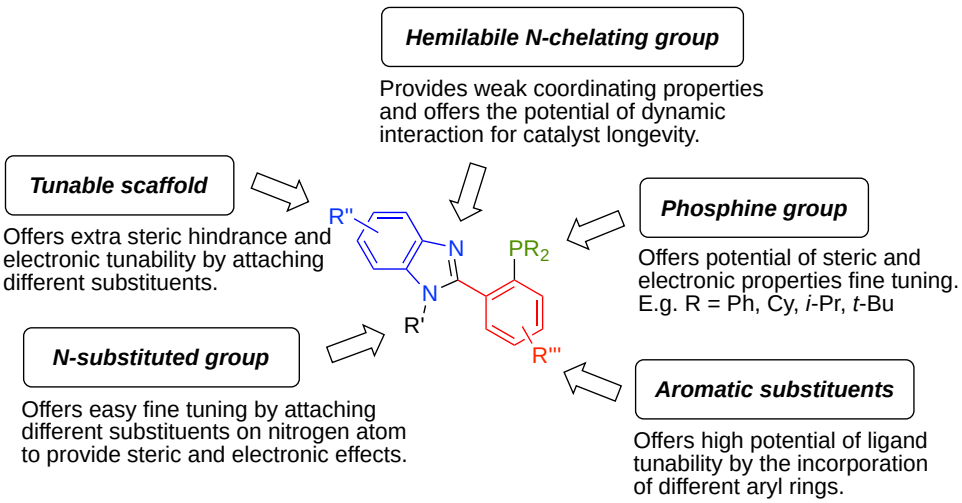


Figure 2.5 Features of New *P*,*N*-type Phosphine Ligand Family

After we have finished the design of a new *P*,*N*-type phosphine ligand family, and inspired by our previous report of *P*,*O*-type ligand, Amidole-phos.[5e] To the best of our knowledge, there has been no successful example reported to-date for ligand which derived from the same parent structure that has either *P*,*O* or *P*,*N* coordination ability. In continuing our research program of developing heterocyclic phosphines, we herein investigate another new family of benzimidazolyl phosphines having unique coordinating manner (**Figure 2.6**).

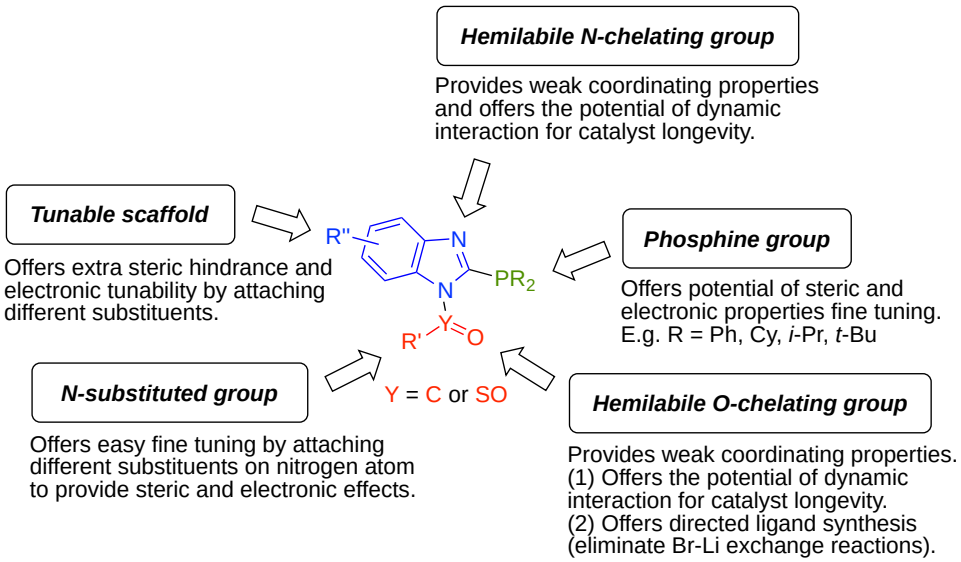


Figure 2.6 Features of New Alterable *P*,*N* and *P*,*O*-type Phosphine Ligand Family

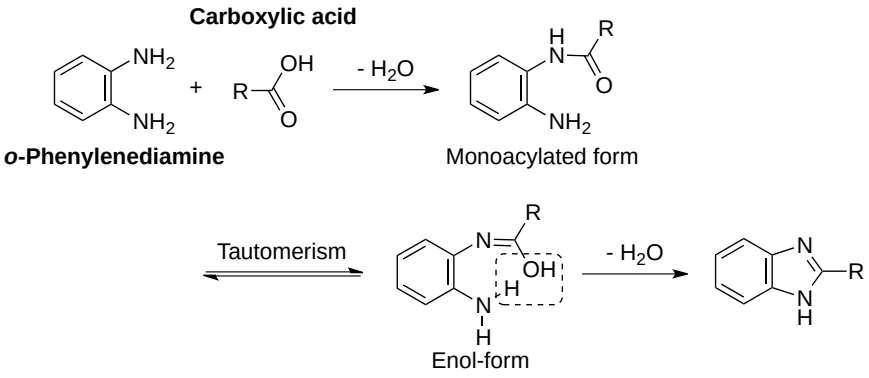
Sum up, the benzimidazole as ligand scaffold (1) is inexpensive and readily available; (2) can be synthesized straightforwardly; (3) can be easily accessed with high diversification and tunability; (4) contains hemilabile group to enhance the catalyst longevity. Based on the above strategic points, benzimidazole was chosen as the ligand framework to develop a new class of hemilabile benzimidazolyl phosphine ligands.

2.4 Results and Discussion

2.4.1 Preparation of the Benzimidazolyl Phosphine Ligands

Among those benzimidazole synthetic methods shown in **Table 2.1**, Phillips benzimidazole synthesis was selected for the protocol to synthesize the benzimidazole templates. While conventional Phillips benzimidazole synthesis work well for the preparation of 2-alkyl-substituted derivatives which involving heating the organic acid with *o*-phenylenediamine in aqueous hydrochloric acid, they frequently fail or give low yields in the preparation of 2-aryl-substituted benzimidazoles. Therefore, we finally chose polyphosphoric acid as catalyst instead of aqueous hydrochloric acid, which is highly effective, convenient, and general for promoting condensations of 2-aryl-substituted benzimidazoles.[38] Phillips benzimidazole synthesis is one of the most versatile methods which using the commercially available and inexpensive *o*-phenylenediamine with carboxylic acid as starting materials for synthesizing the benzimidazole. A combination of these two starting materials provides a high diversification of benzimidazolyl derivatives.

Phillips benzimidazole synthesis involves heating the carboxylic acid with *o*-phenylenediamine in aqueous hydrochloric acid to form the monoacyl derivative of free arylamine first.[39] Then, the monoacyl derivative undergoes tautomerism to afford enol-form intermediate, followed by ring closure involving dehydration.[40] The mechanism is briefly shown as **Scheme 2.22**.



Scheme 2.22 Mechanism of Benzimidazole Synthesis

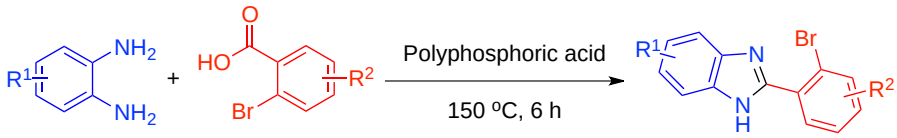
2.4.2 Preparation of the 2-Arylated Benzimidazolyl Phosphine Ligands

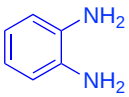
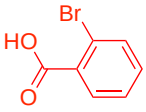
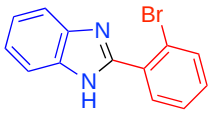
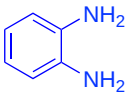
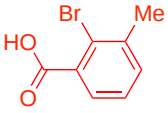
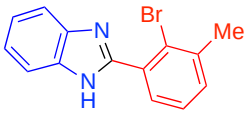
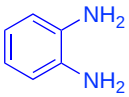
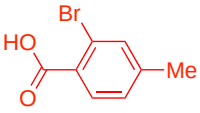
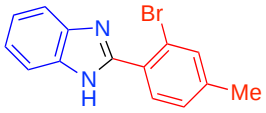
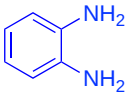
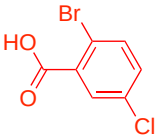
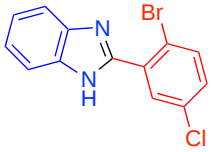
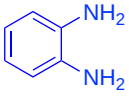
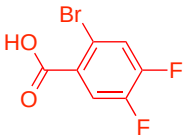
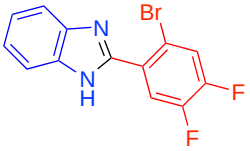
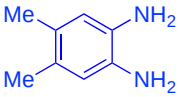
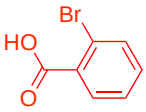
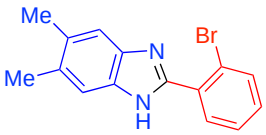
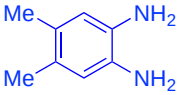
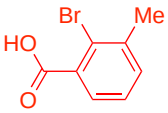
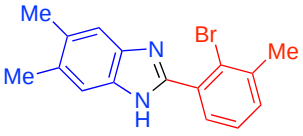
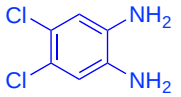
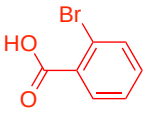
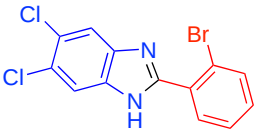
According to our ligand design blueprint (see **Figure 2.5** and **2.6**), the first series of ligand family, phosphorus atom at 2-aryl ring, has been synthesized as follow.

2.4.2.1 Synthesis of 2-Arylbenzimidazolyl Ligand Templates

An array of 2-arylbenzimidazolyl ligand template was successfully synthesized in moderate to excellent yields by condensation of commercially available and inexpensive *o*-phenylenediamine with 2-bromobenzoic acid in the presence of polyphosphoric acid (**Table 2.2**). This synthetic protocol could provide multiple entries of ligand template *via* a "Cross-matching" approach from two components. Even though both of the *o*-phenylenediamine and 2-bromobenzoic acid were being substituted, the product yields did not drop significantly. Noteworthy, the ligand template, 2-(2-bromophenyl)-1*H*-benzoimidazole (**Table 2.2**, entry 1), could be synthesized in a 100 mmol scale with good yields yet without difficulties in both synthetic and purification processes.

Table 2.2 Synthesis of 2-Arylbenzimidazolyl Ligand Templates[a]



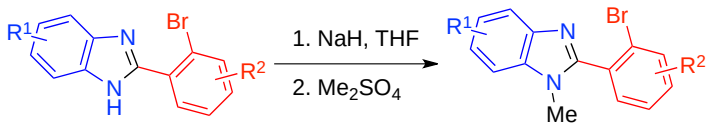
Entry	*o*-Phenylenediamine	2-Bromobenzoic acid	Product	% Yield[b]
1				84
2				77
3				80
4				46
5				72
6				78
7				95
8				84

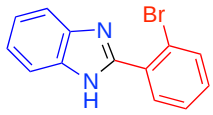
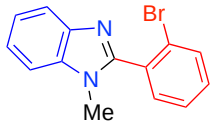
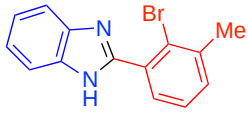
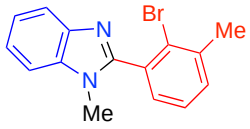
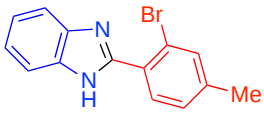
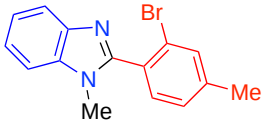
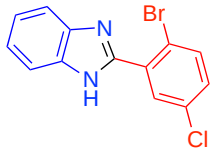
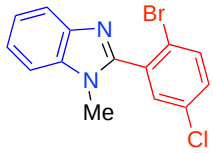
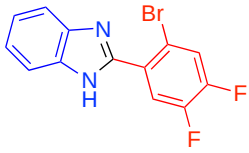
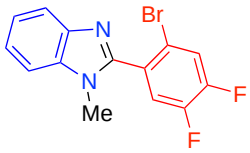
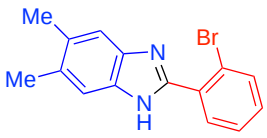
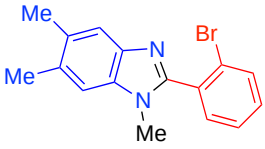
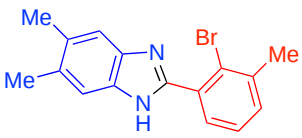
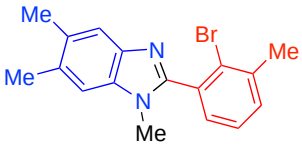
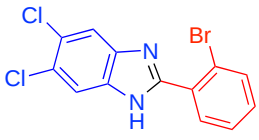
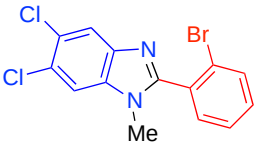
[a]Reaction conditions: *o*-Phenylenediamine (1 equiv.) and 2-bromobenzoic acid (1 equiv.) were stirred in polyphosphoric acid at 150 °C for 6 h under ambient atmosphere. [b]Isolated yield.

2.4.2.2 Synthesis of *N*-Substituted 2-Arylbenzimidazolyl Ligand Precursors

After synthesizing an array of 2-arylbenzimidazolyl ligand template, different *N*-substituted 2-arylbenzimidazolyl ligand precursors were also prepared. In this part, there were two arrays of *N*-substituted, methylated and *iso*-propylated, ligand precursors were synthesized. For the methylated ligand precursor, the benzimidazole N-H proton was deprotonated by sodium hydride and then reacted with dimethyl sulfate to give a series of *N*-methylated ligand precursors in good to excellent yields (**Table 2.3**). In addition, even though there was presence of different substituent in either benzimidazole part or 2-aryl part, the yields did not diminish significantly.

Table 2.3 Synthesis of *N*-Methylated 2-Arylbenzimidazolyl Ligand Precursors[a]

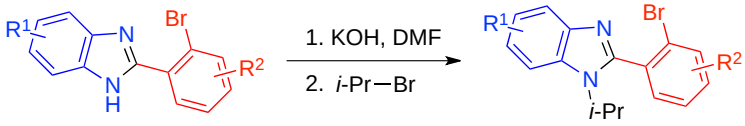


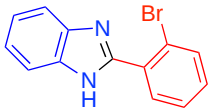
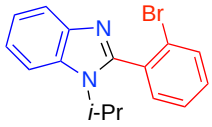
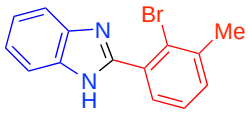
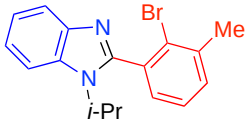
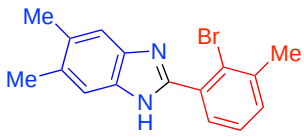
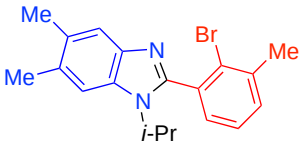
Entry	Ligand template	Product	% Yield[b]
1			82
2			80
3			82
4			45
5			63
6			79
7			96
8			79

[a]Reaction conditions: Ligand template (1 equiv.), NaH (1.2 equiv.) and Me_2SO_4 (1.1 equiv.) were stirred in THF for overnight under nitrogen. [b]Isolated yield.

On the other hand, for *iso*-propylated ligand precursors, the benzimidazole N-H proton was deprotonated by potassium hydroxide and then reacted with 2-bromopropane to give different types of *N-iso*-propylated ligand precursor in good yields (**Table 2.4**).

Table 2.4 Synthesis of *N-iso*-Propylated 2-Arylbenzimidazolyl Ligand Precursors[a]

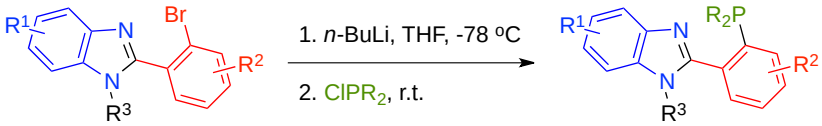


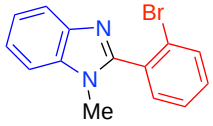
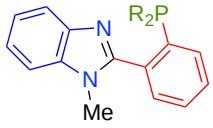
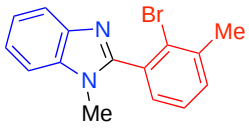
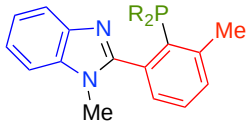
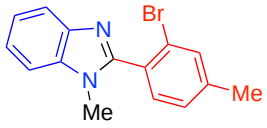
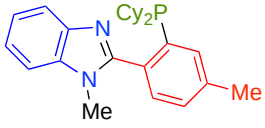
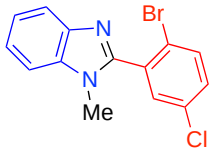
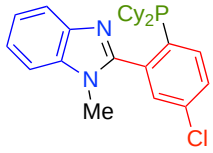
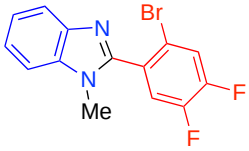
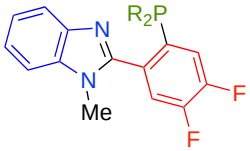
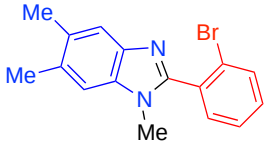
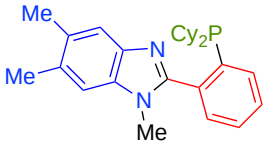
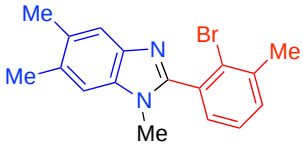
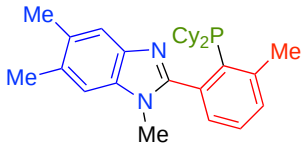
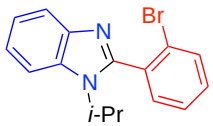
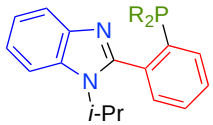
Entry	Ligand template	Product	% Yield[b]
1			75
2			67
3			75

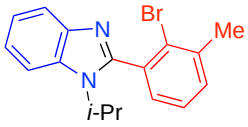
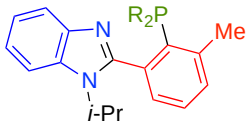
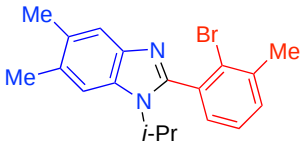
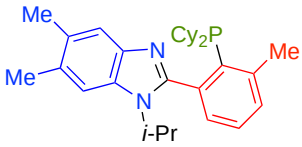
[a]Reaction conditions: Ligand template (1 equiv.), KOH (2 equiv.) and *i*-Pr–Br (3 equiv.) were stirred in DMF for overnight under nitrogen. [b]Isolated yield.

2.4.2.3 Synthesis of 2-Arylated Benzimidazolyl Phosphine Ligands

Table 2.5 Synthesis of 2-Arylated Benzimidazolyl Phosphine Ligands[a]



Entry	Ligand precursor	$ClPR_2$	Product		% Yield[b]
1		$ClPPh_2$		R = Ph	76
2		$ClPCy_2$		R = Cy	72
3		$ClPi\text{-}Pr_2$		R = *i*-Pr	72
4		$ClPPh_2$		R = Ph	67
5		$ClPCy_2$		R = Cy	50
6		$ClPCy_2$			69
7		$ClPCy_2$			72
8		$ClPPh_2$		R = Ph	20
9		$ClPCy_2$		R = Cy	29
10		$ClPCy_2$			70
11		$ClPCy_2$			56
12		$ClPPh_2$		R = Ph	31
13		$ClPCy_2$		R = Cy	66

14		$ClPPh_2$		R = Ph	57
15		$ClPCy_2$		R = Cy	53
16		$ClPCy_2$			55

[a]Reaction conditions: Ligand precursor (1 equiv.), *n*-Bu-Li (1 equiv.) and $ClPR_2$ (1 equiv.) were stirred in THF at 1.) -78 °C for 30 min, 2.) room temperature for overnight under nitrogen. [b]Isolated yield.

As mentioned in the previous part, an array of ligand skeleton was successfully obtained in moderated to excellent yields from condensation of commercially available *o*-phenylenediamine and 2-bromobenzoic acid (**Table 2.2**) followed by simple *N*-substitution reaction (**Table 2.3** and **2.4**). Thus, a simple lithium/bromo exchange could be undergone by lithiation and subsequently trapping with different chlorophosphines to afford corresponding benzimidazolyl phosphine ligands in reasonable to good yields (**Table 2.5** and **Figure 2.7**). This family of ligand exhibits excellent air stability in both solid and solution states.[41] In addition, it should be noted that no chromatographic purification is needed in most of the ligand syntheses shown above, which offers additional advantage to this family of ligand.

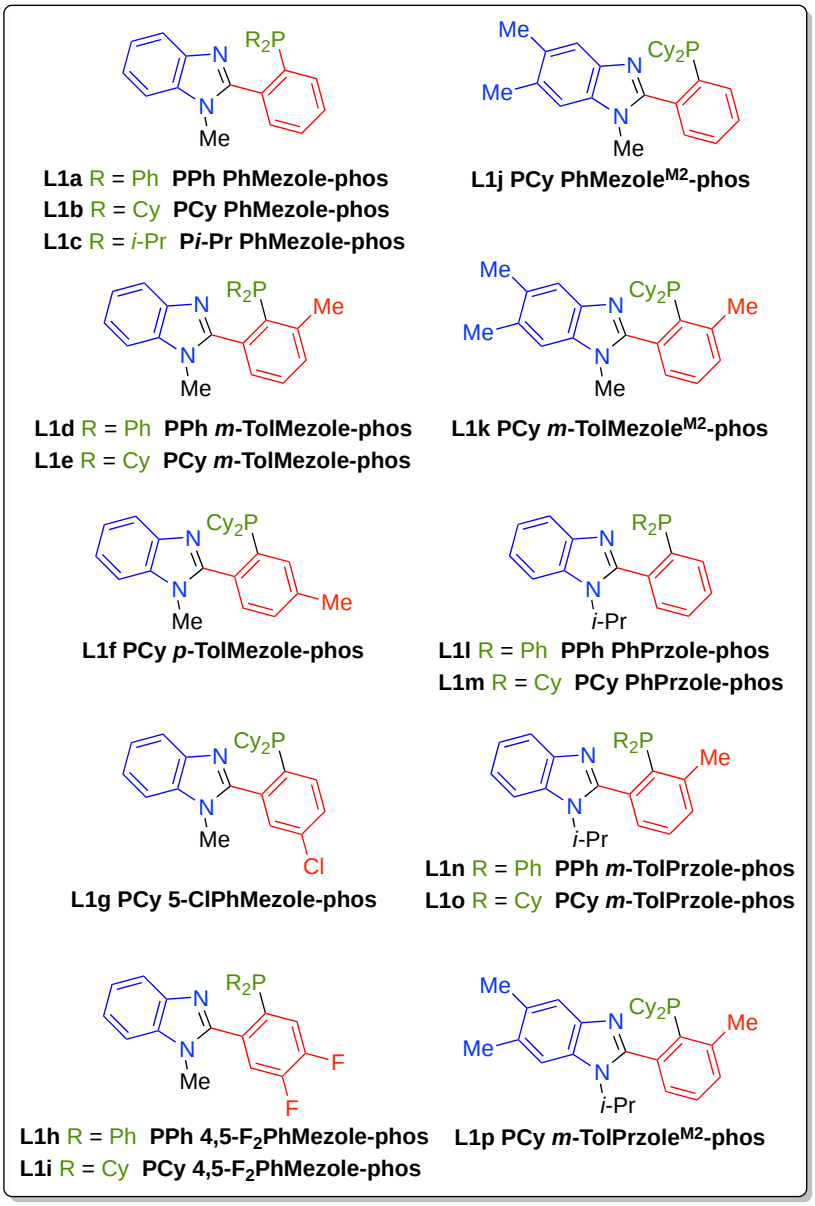


Figure 2.7 Summary of 2-Arylated Benzimidazolyl Phosphine Ligands

2.4.2.4 Structural Insight of 2-Arylated Benzimidazolyl Phosphine Ligands

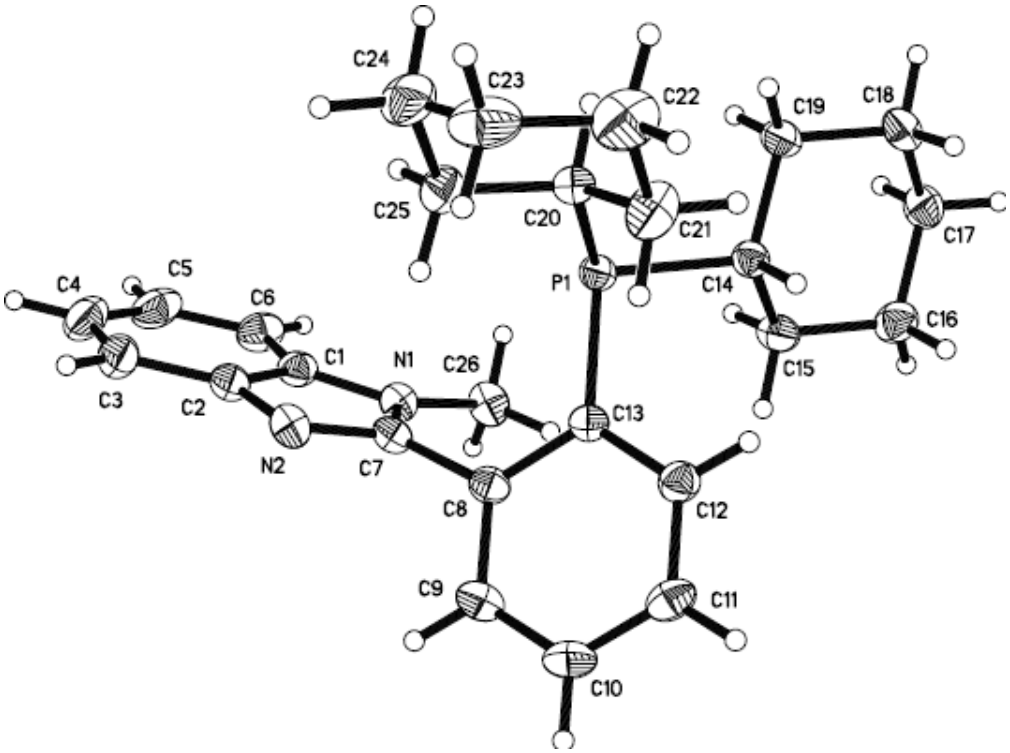


Figure 2.8 ORTEP Representation of Ligand PCy PhMezole-phos **L1b** (30% probability ellipsoids, hydrogen atoms have been omitted for clarity purpose.)

Table 2.6 Selected Bond Distances (Å) and Angles (°)

Bond Distances (Å)			
P(1)-C(13)	1.8536(14)	P(1)-C(14)	1.8583(15)
P(1)-C(20)	1.8597(15)		
Angles (°)			
C(13)-P(1)-C(14)	101.22(6)	C(13)-P(1)-C(20)	102.88(7)
C(14)-P(1)-C(20)	104.06(7)		

Table 2.7 Crystal Data and Structure Refinement for PCy PhMezole-phos **L1b**

Empirical formula	C_{26} H_{33} N_2 P	
Formula weight	404.51	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 11.9517(3) Å	α= 90°.
	b = 13.6898(3) Å	b= 90.7170(10)°.
	c = 13.8621(3) Å	γ = 90°.
Volume	2267.89(9) $Å^3$	
Z	4	
Density (calculated)	1.185 Mg/m^3	
Absorption coefficient	0.136 mm^{-1}	
F(000)	872	
Crystal size	0.50 x 0.40 x 0.40 mm^3	
Theta range for data collection	2.24 to 27.53°.	
Index ranges	-12<=h<=15, -17<=k<=17, -17<=l<=18	
Reflections collected	27624	
Independent reflections	5195 [R(int) = 0.0305]	
Completeness to theta = 27.53°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.746 and 0.689	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5195 / 0 / 263	
Goodness-of-fit on F^2	1.005	
Final R indices [I>2sigma(I)]	R1 = 0.0389, wR2 = 0.1077	
R indices (all data)	R1 = 0.0558, wR2 = 0.1223	
Extinction coefficient	0.0159(15)	
Largest diff. peak and hole	0.255 and -0.197 $e.Å^{-3}$	

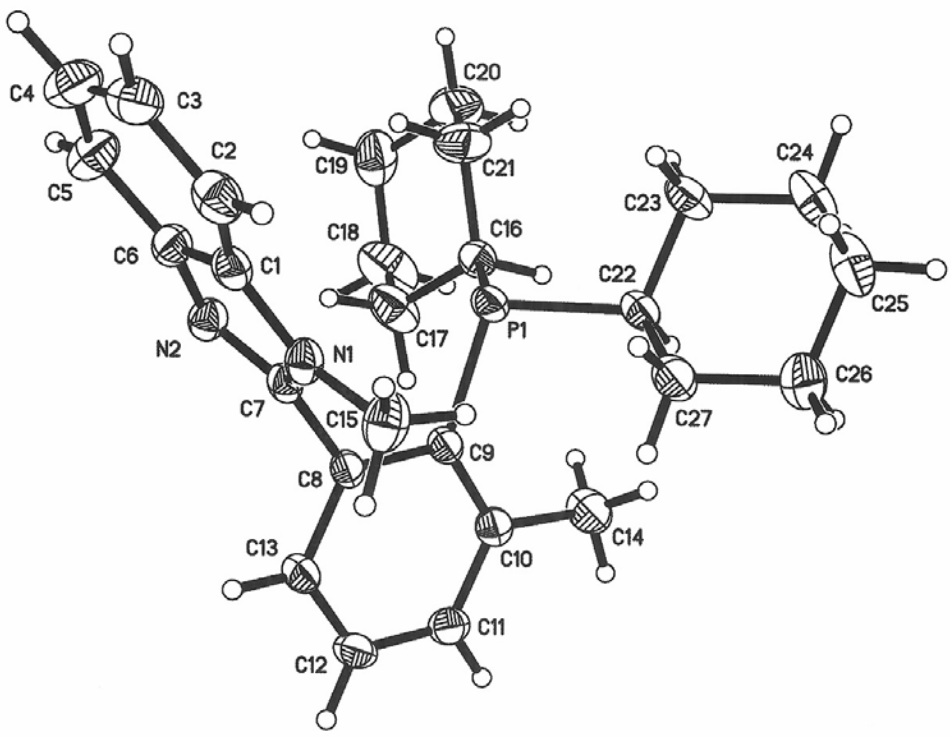


Figure 2.9 ORTEP Representation of Ligand PCy *m*-TolMezole-phos **L1e** (30% probability ellipsoids, hydrogen atoms have been omitted for clarity purpose.)

Table 2.8 Selected Bond Distances (Å) and Angles (°)

Bond Distances (Å)			
P(1)-C(22)	1.864(2)	P(1)-C(9)	1.865(2)
P(1)-C(16)	1.871(3)		
Angles (°)			
C(22)-P(1)-C(9)	105.20(10)	C(22)-P(1)-C(16)	103.37(11)
C(9)-P(1)-C(16)	103.04(11)		

Table 2.9 Crystal Data and Structure Refinement for PCy *m*-TolMezole-phos **L1e**

Empirical formula	C_{27} H_{35} N_2 P	
Formula weight	418.54	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 34.4485(10) Å	α= 90°.
	b = 8.0070(2) Å	b= 97.054(2)°.
	c = 17.8633(5) Å	γ = 90°.
Volume	4889.9(2) $Å^3$	
Z	8	
Density (calculated)	1.137 Mg/m^3	
Absorption coefficient	0.128 mm^{-1}	
F(000)	1808	
Crystal size	0.40 x 0.38 x 0.38 mm^3	
Theta range for data collection	2.30 to 27.42°.	
Index ranges	-43<=h<=44, -10<=k<=9, -22<=l<=23	
Reflections collected	24666	
Independent reflections	5377 [R(int) = 0.0368]	
Completeness to theta = 27.42°	96.3 %	
Absorption correction	None	
Max. and min. transmission	0.7456 and 0.4856	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5377 / 0 / 272	
Goodness-of-fit on F^2	1.003	
Final R indices [I>2sigma(I)]	R1 = 0.0708, wR2 = 0.1484	
R indices (all data)	R1 = 0.1345, wR2 = 0.2059	
Extinction coefficient	0.00105(10)	
Largest diff. peak and hole	0.467 and -0.714 $e.Å^{-3}$	

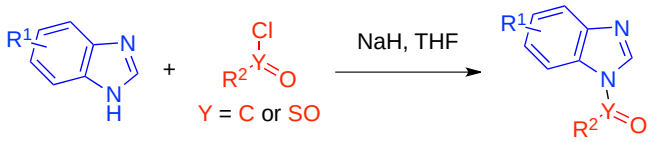
2.4.3 Preparation of 2-Phosphino-Substituted Benzimidazolyl Ligands

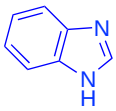
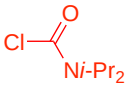
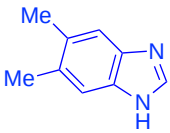
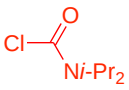
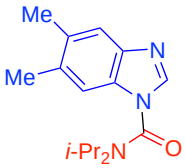
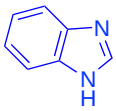
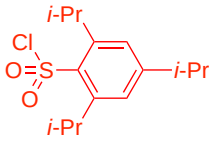
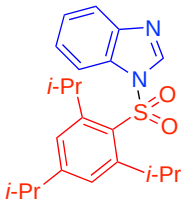
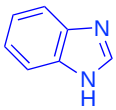
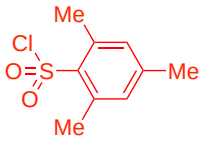
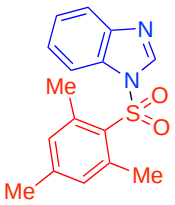
After we have synthesized the first series of 2-arylated benzimidazolyl phosphine ligands, there is still one more ligand design idea in our blueprint (see **Figure 2.4** and **2.6**). Another possible ligand series, phosphorus atom at 2-position, will herein be started to prepare.

2.4.3.1 Synthesis of *N*-Substituted Benzimidazolyl Ligand Precursors

In this part, different *N*-substituted benzimidazolyl ligand precursors were synthesized. Commercially available benzimidazole and 5,6-dimethylbenzimidazole was chosen as the starting materials, the benzimidazole NH proton was deprotonated by sodium hydride and then reacted with different acid chlorides or sulfonyl chlorides to afford an array of *N*-methylated ligand precursors in moderate to excellent yields (**Table 2.6**). Particularly noteworthy, these ligand precursors could be prepared in a large scale (up to 100 mmol scale).

Table 2.10 Synthesis of *N*-Substituted Benzimidazolyl Ligand Precursors[a]

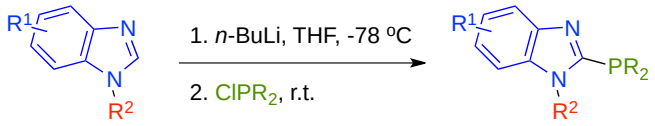


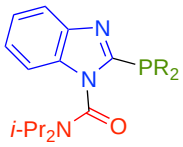
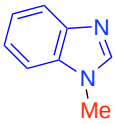
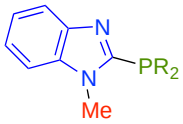
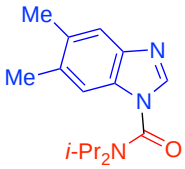
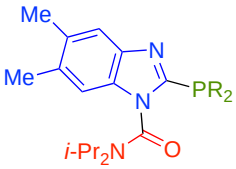
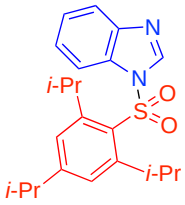
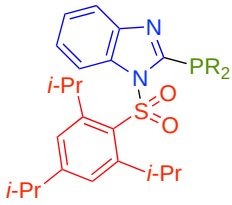
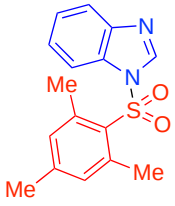
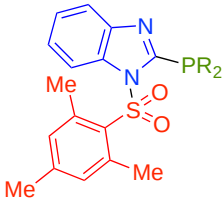
Entry	Benzimidazole	Acid / Sufonyl chloride	Product	% Yield[b]
1				73
2				92
3				85
4				62

[a]Reaction conditions: Benzimidazole (1 equiv.), NaH (1.2 equiv.) and acid / sulfonyl chloride (1.1 equiv.) were stirred in THF for overnight under nitrogen. [b]Isolated yield.

2.4.3.2 Synthesis of 2-Phosphino-Substituted Benzimidazolyl Ligands

Table 2.11 Synthesis of 2-Phosphino-Substituted Benzimidazolyl Ligands[a]



Entry	Ligand precursor	$ClPR_2$	Product		% Yield[b]
1		$ClPCy_2$		R = Cy	73
2		$ClPt\text{-}Bu_2$		R = *t*-Bu	65
3		$ClPi\text{-}Pr_2$		R = *i*-Pr	67
4		$ClPPh_2$		R = Ph	58
5		$ClPEt_2$		R = Et	52
6		$ClPCy_2$		R = Cy	60
7		$ClPt\text{-}Bu_2$		R = *t*-Bu	37
8		$ClPCyp_2$		R = Cyp	65
9		$ClPCy_2$		R = Cy	77
10		$ClPt\text{-}Bu_2$		R = *t*-Bu	48
11		$ClPi\text{-}Pr_2$		R = *i*-Pr	57
12		$ClPPh_2$		R = Ph	42
13		$ClPo\text{-}Tol_2$		R = *o*-Tol	77
14		$ClPCyp_2$		R = Cyp	62
15		$ClP(1\text{-}Ad)_2$		R = 1-Ad	19
16		$ClPCy_2$		R = Cy	77
17		$ClPt\text{-}Bu_2$		R = *t*-Bu	29
18		$ClPCy_2$		R = Cy	60
19		$ClPt\text{-}Bu_2$		R = *t*-Bu	44

[a]Reaction conditions: Ligand precursor (1 equiv.), *n*-Bu-Li (1.1 equiv.) and $ClPR_2$ (1.2 equiv.) were stirred in THF at 1.) -78 °C for 10-60 min, 2.) room temperature for overnight under nitrogen. [b]Isolated yield.

After we have synthesized different *N*-substituted benzimidazolyl ligand precursors. These ligand precursors were then subject to phosphine compounds. The 2-H on the benzimidazole ring relatively acidic that could be effectively abstracted by direct *ortho*-metalation (DoM)[42] using *n*-butyllithium and then trapped with corresponding chlorophosphines to afford a newly family of 2-phosphino-substituted benzimidazolyl phosphines in good yields (**Table 2.11** and **Figure 2.10**). Notably, most of the crude products could be simply purified by washing with methanol/hexane/ethanol mixture without tedious chromatographic purification process. However, if we used much more sterically hindered chlorophosphine, such as di(1-adamantanyl)chlorophosphine (**Table 2.11**, entry 15) and di-*tert*-butylchlorophosphine (**Table 2.11**, entries 7, 17 and 19), the product yields were much lower and column chromatographic purification was needed to applied. Noteworthy, these ligands could exhibit exceptionally high stability in both solid and solution states.[41]

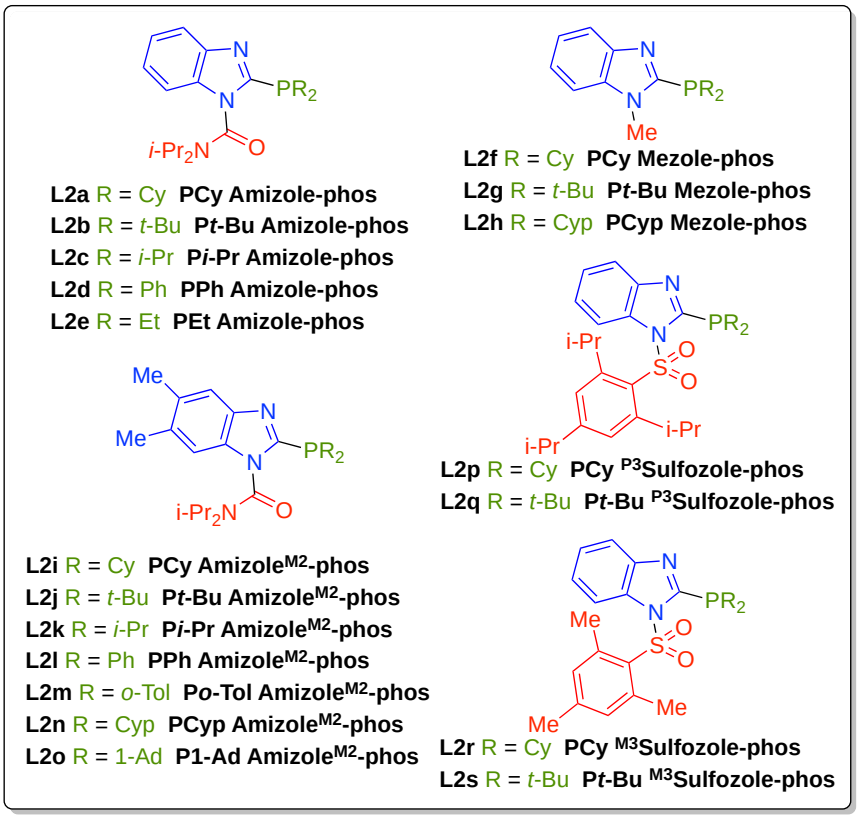


Figure 2.10 Summary of 2-Phosphino-Substituted Benzimidazolyl Ligands

2.4.3.3 Structural Insight of 2-Phosphino-Substituted Benzimidazolyl Ligands

Since some of the X-Ray structure of the ligands have been established and reported by our former groupmate,[43] we herein only showed selected ligands for structural insight.

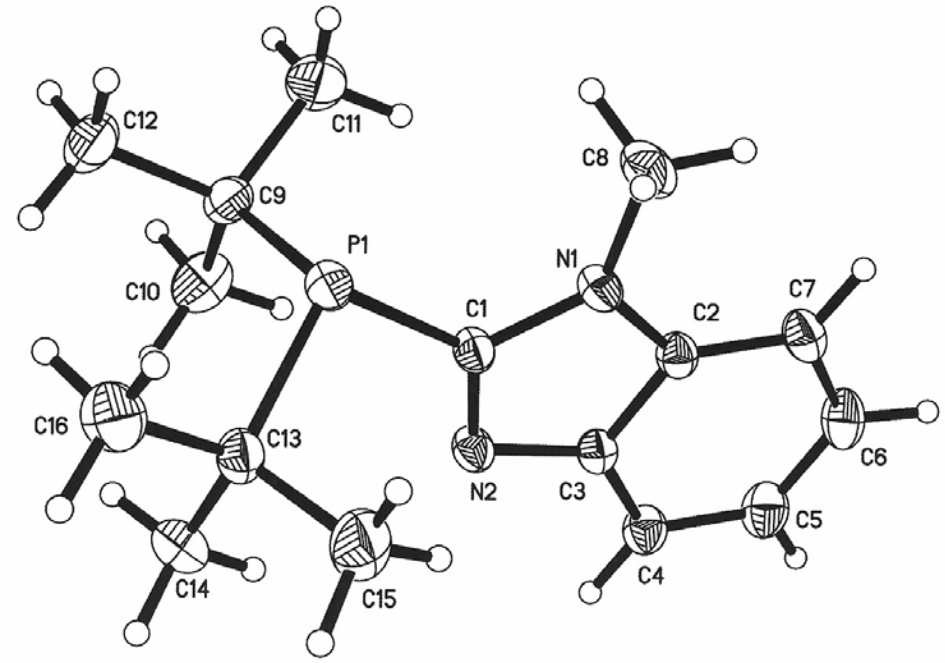


Figure 2.11 ORTEP Representation of Ligand P*t*-Bu Mezole-phos **L2g** (30% probability ellipsoids, hydrogen atoms have been omitted for clarity purpose.)

Table 2.12 Selected Bond Distances (Å) and Angles (°)

Bond Distances (Å)			
P(1)-C(1)	1.831(2)	P(1)-C(13)	1.870(3)
P(1)-C(9)	1.889(3)		
Angles (°)			
C(1)-P(1)-C(13)	102.61(11)	C(1)-P(1)-C(9)	100.54(11)
C(13)-P(1)-C(9)	112.57(12)		

Table 2.13 Crystal Data and Structure Refinement for P*t*-Bu Mezole-phos **L2g**

Empirical formula	$C_{16}H_{25}N_2P$	
Formula weight	276.35	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 10.5609(3) Å	α= 90°.
	b = 20.2219(6) Å	b= 101.783(2)°.
	c = 7.9641(2) Å	γ = 90°.
Volume	1664.98(8) $Å^3$	
Z	4	
Density (calculated)	1.102 Mg/m^3	
Absorption coefficient	0.156 mm^{-1}	
F(000)	600	
Crystal size	0.40 x 0.32 x 0.28 mm^3	
Theta range for data collection	1.97 to 27.51°.	
Index ranges	-13<=h<=13, -25<=k<=26, -10<=l<=10	
Reflections collected	16504	
Independent reflections	3736 [R(int) = 0.0353]	
Completeness to theta = 27.51°	97.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6130	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3736 / 0 / 190	
Goodness-of-fit on F^2	1.000	
Final R indices [I>2sigma(I)]	R1 = 0.0673, wR2 = 0.1459	
R indices (all data)	R1 = 0.1195, wR2 = 0.2006	
Extinction coefficient	0.0115(10)	
Largest diff. peak and hole	0.715 and -0.826 e.$Å^{-3}$	

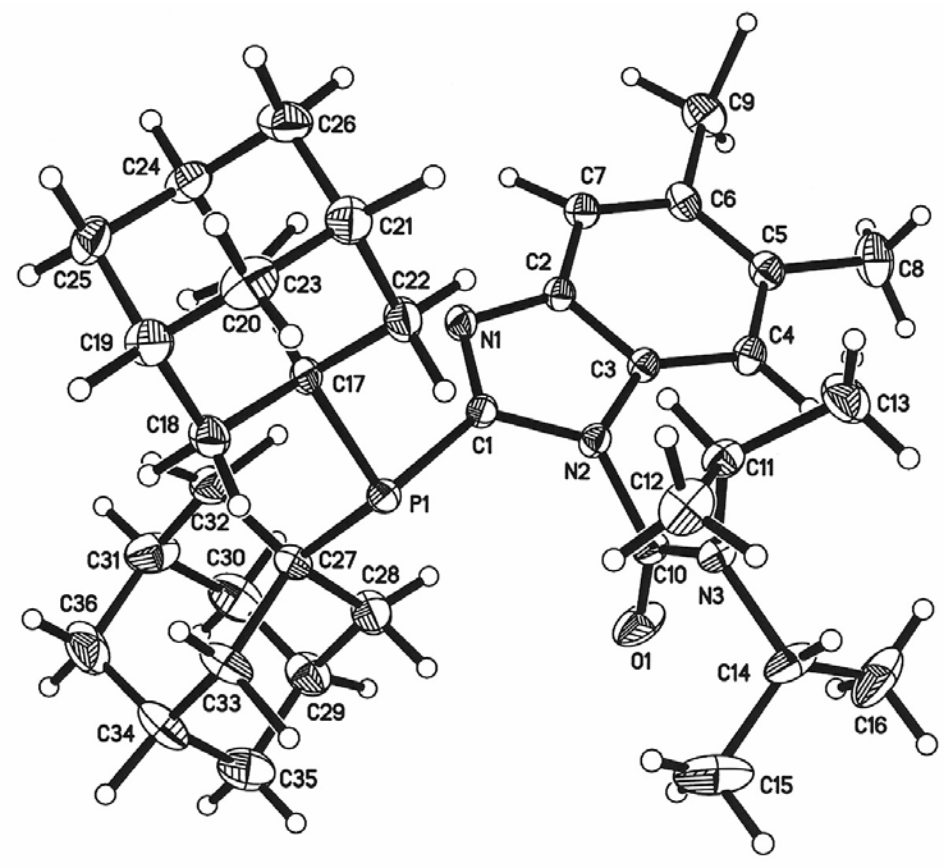


Figure 2.12 ORTEP Representation of Ligand P1-Ad Amizole^{M2}-phos **L2o** (30% probability ellipsoids, hydrogen atoms have been omitted for clarity purpose.)

Table 2.14 Selected Bond Distances (Å) and Angles (°)

Bond Distances (Å)			
P(1)-C(1)	1.829(3)	P(1)-C(27)	1.883(3)
P(1)-C(17)	1.884(3)		
Angles (°)			
C(1)-P(1)-C(27)	102.24(13)	C(1)-P(1)-C(17)	100.64(12)
C(27)-P(1)-C(17)	113.63(12)		

Table 2.15 Crystal Data and Structure Refinement for P1-Ad Amizole^{M2}-phos **L2o**

Empirical formula	C_{36} H_{52} N_3 O P
Formula weight	573.78
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 12.9682(8) Å α= 90°.
	b = 18.5528(13) Å b= 109.159(4)°.
	c = 14.4697(10) Å γ = 90°.
Volume	3288.5(4) Å^3
Z	4
Density (calculated)	1.159 Mg/m^3
Absorption coefficient	0.115 mm^{-1}
F(000)	1248
Crystal size	0.30 x 0.24 x 0.24 mm^3
Theta range for data collection	1.85 to 27.61°.
Index ranges	-16<=h<=16, -24<=k<=24, -18<=l<=18
Reflections collected	35992
Independent reflections	7527 [R(int) = 0.1202]
Completeness to theta = 27.61°	98.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.2947
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7527 / ? / 487
Goodness-of-fit on F^2	1.002
Final R indices [I>2sigma(I)]	R1 = 0.0924, wR2 = 0.2054
R indices (all data)	R1 = 0.1785, wR2 = 0.2632
Largest diff. peak and hole	0.682 and -0.425 e.Å^{-3}

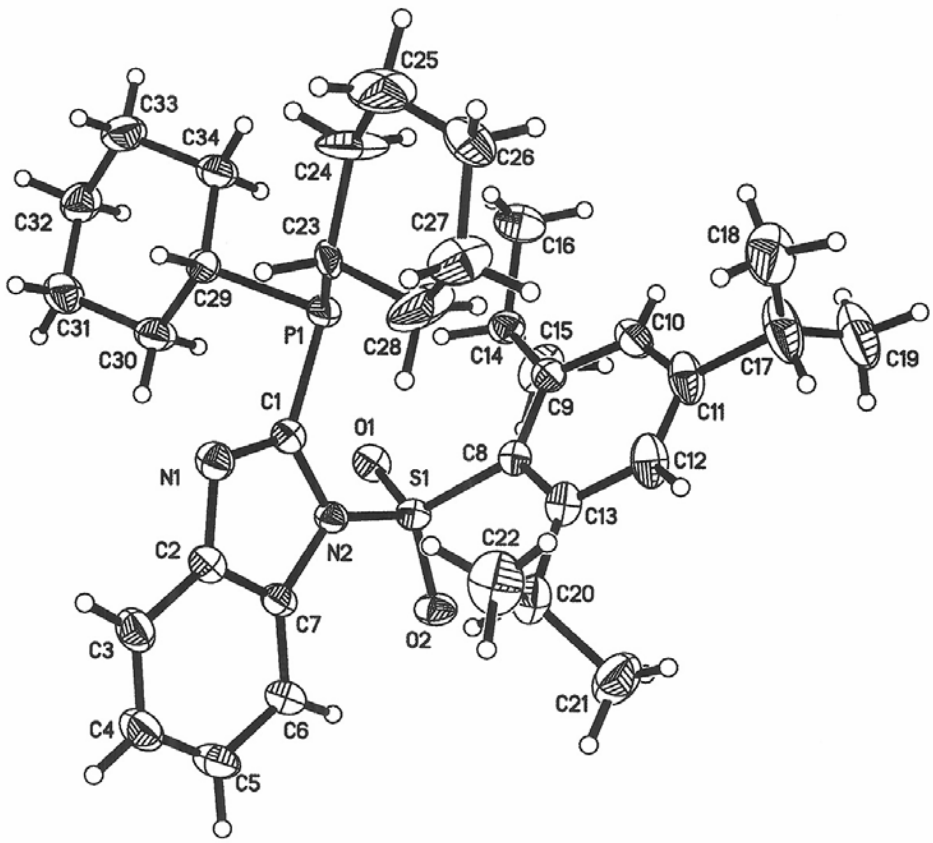


Figure 2.13 ORTEP Representation of Ligand PCy ^{P3}Sulfozole-phos **L2p** (30% probability ellipsoids, hydrogen atoms have been omitted for clarity purpose.)

Table 2.16 Selected Bond Distances (Å) and Angles (°)

Bond Distances (Å)			
P(1)-C(1)	1.835(2)	P(1)-C(29)	1.858(2)
P(1)-C(23)	1.876(4)		
Angles (°)			
C(1)-P(1)-C(29)	98.66(10)	C(1)-P(1)-C(23)	95.38(17)
C(29)-P(1)-C(23)	100.45(16)		

Table 2.17 Crystal Data and Structure Refinement for PCy ^{P3}Sulfozole-phos **L2p**

Empirical formula	$C_{34} H_{49} N_2 O_2 P S$	
Formula weight	580.78	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 9.9526(18) Å	α= 90°.
	b = 10.6286(18) Å	b= 99.114(9)°.
	c = 31.305(5) Å	γ = 90°.
Volume	3269.7(10) $Å^3$	
Z	4	
Density (calculated)	1.180 Mg/m^3	
Absorption coefficient	0.180 mm^{-1}	
F(000)	1256	
Crystal size	0.60 x 0.60 x 0.50 mm^3	
Theta range for data collection	2.27 to 27.51°.	
Index ranges	-12<=h<=12, -13<=k<=13, -40<=l<=39	
Reflections collected	31650	
Independent reflections	7190 [R(int) = 0.0695]	
Completeness to theta = 27.51°	95.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.5905	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7190 / 11 / 464	
Goodness-of-fit on F^2	1.001	
Final R indices [I>2sigma(I)]	R1 = 0.0774, wR2 = 0.1671	
R indices (all data)	R1 = 0.1284, wR2 = 0.1930	
Largest diff. peak and hole	0.283 and -0.345 $e.Å^{-3}$	

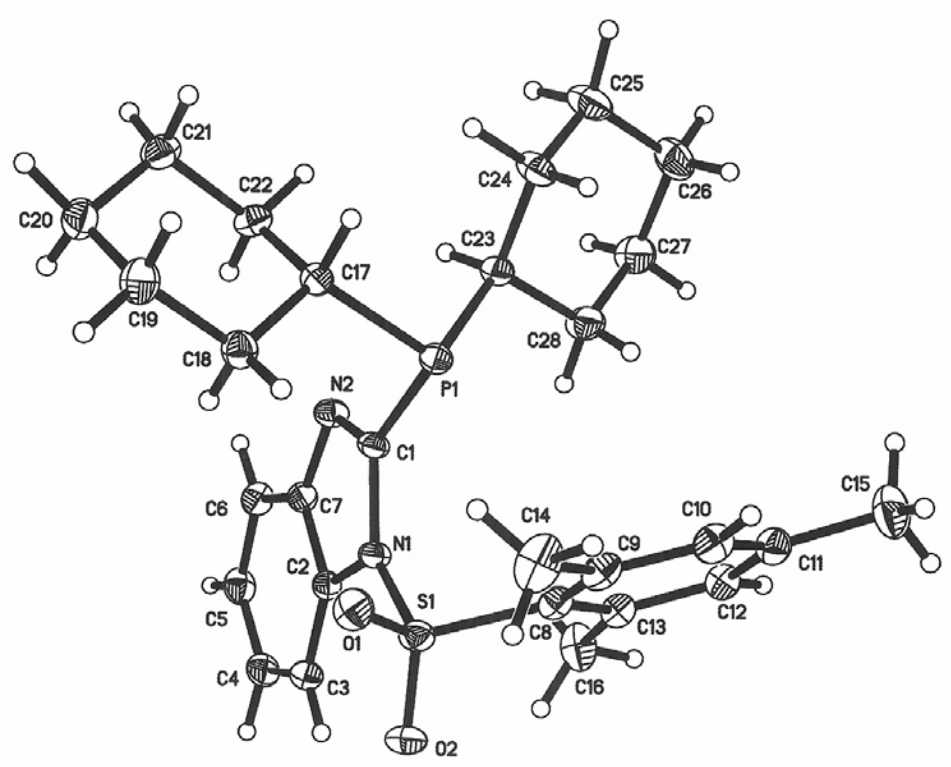


Figure 2.14 ORTEP Representation of Ligand PCy ^{M3}Sulfozole-phos **L2r** (30% probability ellipsoids, hydrogen atoms have been omitted for clarity purpose.)

Table 2.18 Selected Bond Distances (Å) and Angles (°)

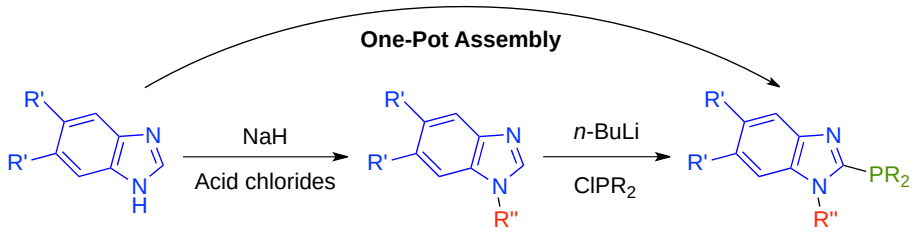
Bond Distances (Å)			
P(1)-C(1)	1.846(2)	P(1)-C(23)	1.856(2)
P(1)-C(17)	1.862(2)		
Angles (°)			
C(1)-P(1)-C(23)	97.23(10)	C(1)-P(1)-C(17)	101.37(10)
C(23)-P(1)-C(17)	103.32(10)		

Table 2.19 Crystal Data and Structure Refinement for PCy ^{M3}Sulfozole-phos **L2r**

Empirical formula	$C_{28}\ H_{37}\ N_2\ P\ S\ O_2$	
Formula weight	496.63	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 17.3725(4) Å	α= 90°.
	b = 9.5702(2) Å	b= 116.2830(10)°.
	c = 18.2919(4) Å	γ = 90°.
Volume	2726.78(10) $Å^3$	
Z	4	
Density (calculated)	1.210 Mg/m^3	
Absorption coefficient	0.204 mm^{-1}	
F(000)	1064	
Crystal size	0.50 x 0.50 x 0.42 mm^3	
Theta range for data collection	2.17 to 27.48°.	
Index ranges	-22<=h<=22, -12<=k<=12, -23<=l<=23	
Reflections collected	30636	
Independent reflections	6267 [R(int) = 0.0507]	
Completeness to theta = 27.48°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.5390	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6267 / 0 / 435	
Goodness-of-fit on F^2	1.000	
Final R indices [I>2sigma(I)]	R1 = 0.0627, wR2 = 0.1422	
R indices (all data)	R1 = 0.1008, wR2 = 0.1820	
Extinction coefficient	0.0042(4)	
Largest diff. peak and hole	0.588 and -0.454 $e.Å^{-3}$	

2.4.3.4 Synthesis of 2-Phosphino-Substituted Benzimidazolyl Ligands by One-Pot Assembly Approach

During the synthesis of the *N*-substituted benzimidazolyl ligand precursors, we observed that the reactions completed from GC analysis. In addition, the resultant precursors were found in a yield of about 80% to 90%. Therefore, we attempted to prepare this novel class of benzimidazolyl phosphine ligands *via* a simple one-pot assembly from benzimidazoles, acid chlorides and chlorophosphines. Since a combination of these starting materials provides a high diversification of the ligand structures, the synthetic protocol could generate diversified entities of ligand structures *via* "One-pot assembly" and "Cross-matching" approaches. Fortunately, the "One-pot assembly" approach was succeeded and the final product yields were only diminished by 10% to 20% when comparing with individual procedures (**Scheme 2.23**).



L2a R' = H, R'' = C(O)N*i*-Pr$_2$, R = Cy, 59%
L2b R' = H, R'' = C(O)N*i*-Pr$_2$, R = *t*-Bu, 50%
L2c R' = H, R'' = C(O)N*i*-Pr$_2$, R = *i*-Pr, 55%
L2d R' = H, R'' = C(O)N*i*-Pr$_2$, R = Ph, 48%
L2e R' = H, R'' = C(O)N*i*-Pr$_2$, R = Et, 40%
L2f R' = H, R'' = Me, R = Cy, 60%
L2g R' = H, R'' = Me, R = *t*-Bu, 37%
L2h R' = H, R'' = Me, R = Cyp, 65%
L2i R' = Me, R'' = C(O)N*i*-Pr$_2$, R = Cy, 65%
L2j R' = Me, R'' = C(O)N*i*-Pr$_2$, R = *t*-Bu, 30%
L2k R' = Me, R'' = C(O)N*i*-Pr$_2$, R = *i*-Pr, 49%
L2l R' = Me, R'' = C(O)N*i*-Pr$_2$, R = Ph, 32%
L2m R' = Me, R'' = C(O)N*i*-Pr$_2$, R = *o*-Tol, 64%
L2n R' = Me, R'' = C(O)N*i*-Pr$_2$, R = Cyp, 48%
L2o R' = Me, R'' = C(O)N*i*-Pr$_2$, R = 1-Ad, 10%
L2p R' = H, R'' = SO$_2$-2,4,6-*i*-Pr$_3$C$_6$H$_2$, R = Cy, 77%
L2q R' = H, R'' = SO$_2$-2,4,6-*i*-Pr$_3$C$_6$H$_2$, R = *t*-Bu, 29%
L2r R' = H, R'' = SO$_2$-2,4,6-Me$_3$C$_6$H$_2$, R = Cy, 60%
L2s R' = H, R'' = SO$_2$-2,4,6-Me$_3$C$_6$H$_2$, R = *t*-Bu, 44%
L2t R' = H, R'' = C(O)NEt$_2$, R = Cy, 30%

Scheme 2.23 Ligand Synthesis by One-Pot Assembly Approach

2.5 Conclusion

To conclude, we have designed two new classes of hemilabile benzimidazolyl phosphine ligands *via* "Cross-matching" and "One-pot assembly" approaches. The benzimidazole as ligand scaffold (1) is inexpensive and readily available; (2) can be synthesized straightforwardly; (3) can be easily accessed with high diversification and tunability; (4) contains hemilabile group to enhance the catalyst longevity potentially.

Phillips benzimidazole synthesis was selected for the protocol to synthesize the benzimidazole templates. In addition, polyphosphoric acid was chosen as catalyst instead of aqueous hydrochloric acid, which is highly effective, convenient, and general for promoting condensations of 2-aryl-substituted benzimidazoles.

Particularly, these two classes of benzimidazolyl phosphine ligands exhibited high air stability in both solid and solution forms.

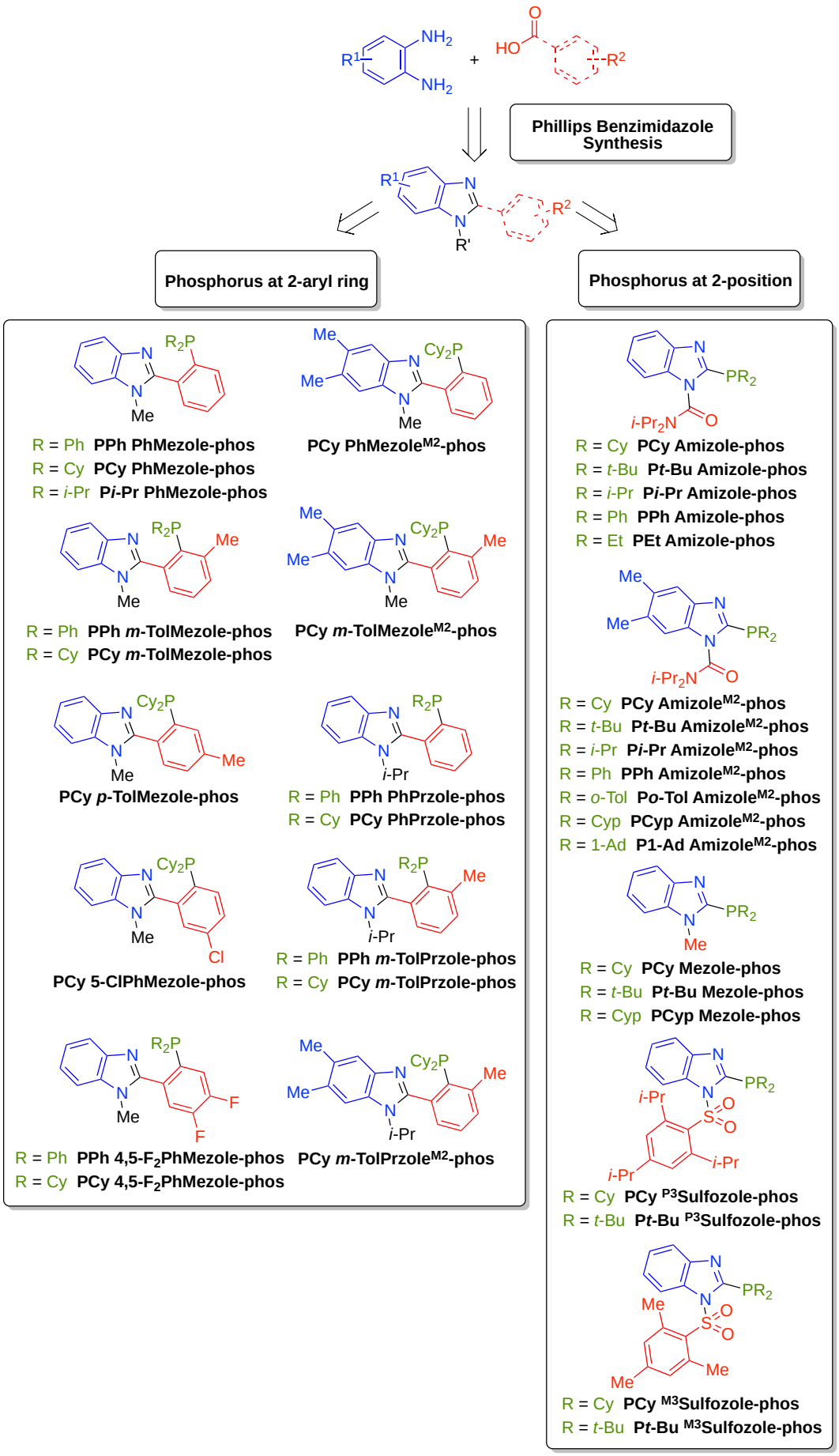


Figure 2.15 A Summary of Newly Prepared Benzimidazolyl Phosphines

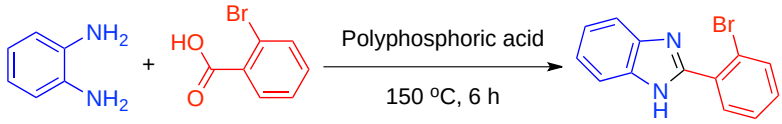
2.6 Experimental Section

2.6.1 General Considerations

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under nitrogen.[44] Chlorodiphenylphosphine (Tech. grade) was distilled under vacuum prior to use.[44] New bottle of *n*-butyllithium was used (*Note*: since the concentration of *n*-BuLi from old bottle may vary, we highly recommend to perform a titration prior to use). 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. Melting points were recorded on an uncorrected instrument. ^{1}H NMR spectra were recorded on a Bruker (400 MHz) spectrometer. Spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.26 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 mass spectrometer. High-resolution mass spectra (HRMS) were obtained on ESIMS. GC-MS analysis was conducted on a GCD system using a column with 30 m $\times$ 0.25 mm.

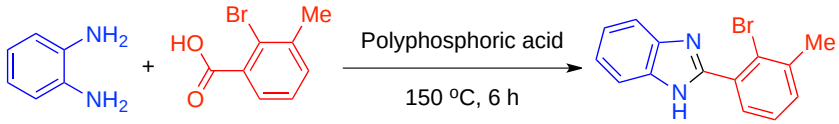
2.6.2 General Procedures for Preparation of the 2-Arylated Benzimidazolyl Phosphine Ligands

2-(2-Bromophenyl)-1*H*-benzo[*d*]imidazole (**Table 2.2**, entry 1)



General procedure for precursor synthesis: 2-Bromobenzoic acid (100 mmol) and 1,2-phenylenediamine (100 mmol) were taken in polyphosphoric acid (~120 g) and heated to 150 °C for 6 h. The reaction mixture was poured over crushed ice and kept in a refrigerator overnight. The resulting violet solid precipitate was filtered and added to 0.5 M Na_2CO_3 solution (500 mL), stirred for 30 min and filtered. The precipitate was dissolved in methanol (300 mL), and filtered through celite. The solution was evaporated to yield a white solid. Hexane was used to further wash the product. The product was then dried under vacuum to afford 2-(2-bromophenyl)-1*H*-benzo[*d*]imidazole (22.8 g, 84%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.35 (m, 3H), 7.43-7.47 (m, 1H), 7.53-7.56 (m, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.85-7.87 (m, 1H), 8.25 (d, J = 7.6 Hz, 1H), 10.52 (s, 1H); ^{13}C NMR (100 MHz, MeOD) δ 114.6, 121.7, 122.5, 127.2, 131.1, 131.7, 131.8, 133.1, 138.0, 150.7; MS (EI): *m/z* (relative intensity) 272.0 (M^+, 100), 193.0 (53), 90.0 (28).

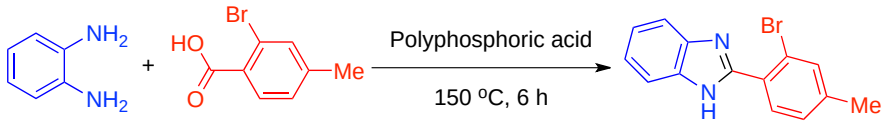
2-(2-Bromo-3-methylphenyl)-1*H*-benzo[*d*]imidazole (**Table 2.2**, entry 2)



General procedure for precursor synthesis was followed. 2-Bromo-3-methylbenzoic acid (10 mmol), 1,2-phenylenediamine (10 mmol) and

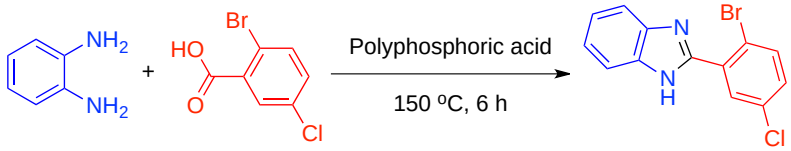
polyphosphoric acid (~25 g) were used to afford 2-(2-bromo-3-methylphenyl)-1*H*-benzo[*d*]imidazole (2.20 g, 77%) as a pale yellow solid. Melting point: 238.4-240.4 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 2.54 (s, 3H), 5.35 (s, 1H), 7.31-7.42 (m, 4H), 7.68 (s, 2H), 7.89 (d, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 23.9, 115.7, 122.5, 124.7 127.8, 130.2, 132.5, 133.8, 139.1, 151.6; IR (cm^{-1}): 3049.99, 2974.46, 2876.73, 2767.63, 2683.26, 1621.25, 1590.10, 1572.81, 1532.81, 1448.13, 1419.06, 1385.91, 1371.96, 1316.70, 1282.73, 1267.19, 1243.26, 1228.31, 1148.71, 1099.50, 1024.82, 983.10, 913.53, 874.99, 795.60, 786.48, 765.94, 751.62, 742.03, 727.31, 706.64, 617.36, 544.01, 441.65, 429.63; HRMS: calcd. for $C_{14}H_{11}N_2BrH^+$: 287.0184, found 287.0175.

2-(2-Bromo-4-methylphenyl)-1*H*-benzo[*d*]imidazole (**Table 2.2**, entry 3)



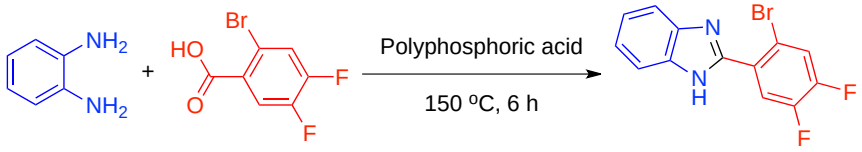
General procedure for precursor synthesis was followed. 2-Bromo-4-methylbenzoic acid (10 mmol), 1,2-phenylenediamine (10 mmol) and polyphosphoric acid (~25 g) were used to afford 2-(2-bromo-4-methylphenyl)-1*H*-benzo[*d*]imidazole (2.31 g, 80%) as a pale yellow solid. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 2.44 (s, 3H), 7.30-7.33 (m, 3H), 7.58-7.59 (m, 2H), 7.79-7.81 (m, 1H), 8.21 (d, J = 8.0 Hz, 1H), 10.24 (s, 1H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 20.8, 121.6, 128.9, 129.8, 132.3, 134.1, 142.0, 150.9; HRMS: calcd. for $C_{14}H_{11}N_2BrH^+$: 287.0184, found 287.0169.

2-(2-Bromo-5-chlorophenyl)-1*H*-benzo[*d*]imidazole (**Table 2.2**, entry 4)



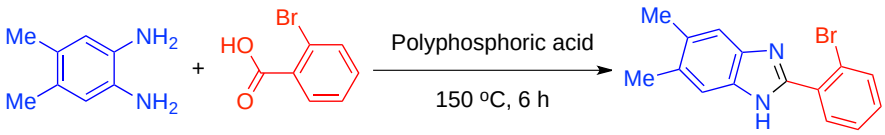
General procedure for precursor synthesis was followed. 2-Bromo-5-chlorobenzoic acid (10 mmol), 1,2-phenylenediamine (10 mmol) and polyphosphoric acid (~25 g) were used to afford 2-(2-bromo-5-chlorophenyl)-1*H*-benzo[*d*]imidazole (1.41 g, 46%) as a pale yellow solid. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.32-7.27 (m, 3H), 7.66-7.71 (m, 3H), 8.31 (d, J = 2.4 Hz, 1H), 10.48 (s, 1H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 112.2, 119.7, 120.4, 122.3, 131.5, 132.0, 132.9, 134.3, 135.6, 149.4; HRMS: calcd. for $C_{13}H_8N_2BrClH^+$: 306.9638, found 306.9641.

2-(2-Bromo-4,5-difluorophenyl)-1*H*-benzo[*d*]imidazole (**Table 2.2**, entry 5)



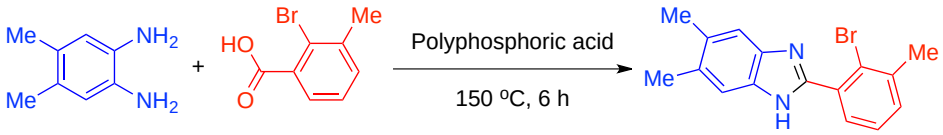
General procedure for precursor synthesis was followed. 2-Bromo-4,5-difluorobenzoic acid (10 mmol), 1,2-phenylenediamine (10 mmol) and polyphosphoric acid (~25 g) were used to afford 2-(2-bromo-4,5-difluorophenyl)-1*H*-benzo[*d*]imidazole (2.22 g, 72%) as a pale yellow solid. ^{1}H NMR (400 MHz, d_6-DMSO) δ 7.25-7.27 (m, 2H), 7.64 (s, 2H), 7.90-7.95 (m, 1H), 8.06-8.10 (m, 1H), 12.84 (s, 1H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 116.6, 121.1, 121.3, 122.9, 123.0, 123.2, 130.0, 147.7, 147.8, 149.0, 149.1, 150.2, 150.3, 151.5, 151.6; HRMS: calcd. for $C_{13}H_7N_2F_2BrH^+$: 308.9839, found 308.9846.

2-(2-Bromophenyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole (**Table 2.2**, entry 6)



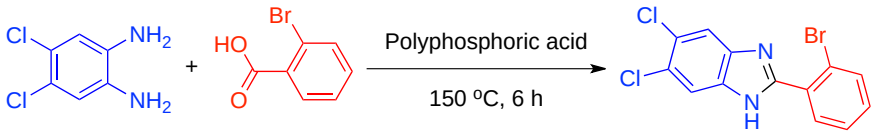
General procedure for precursor synthesis was followed. 2-Bromobenzoic acid (10 mmol), 4,5-dimethyl-1,2-phenylenediamine (10 mmol) and polyphosphoric acid (~25 g) were used to afford 2-(2-bromophenyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole (2.33 g, 78%) as a pale yellow solid. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 2.40 (s, 6H), 3.45 (s. 1H), 7.31-7.46 (m, 4H), 7.71 (d, J = 8.0 Hz, 1H), 8.14 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 20.0, 120.5, 127.7, 130.7, 131.2, 132.1, 132.4, 133.8, 149.0; HRMS: calcd. for $C_{15}H_{13}N_2BrH^+$: 301.0340, found 301.0339.

2-(2-Bromo-3-methylphenyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole (**Table 2.2**, entry 7)



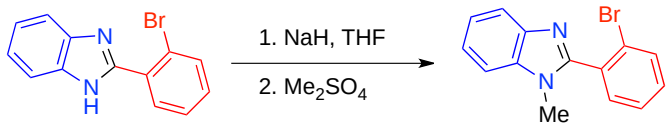
General procedure for precursor synthesis was followed. 2-Bromo-3-methylbenzoic acid (10 mmol), 4,5-dimethyl-1,2-phenylenediamine (10 mmol) and polyphosphoric acid (~25 g) were used to afford 2-(2-bromo-3-methylphenyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole (2.99 g, 95%) as a pale yellow solid. ^{1}H NMR (400 MHz, d_6-DMSO) δ 2.32 (s, 6H), 2.46 (s, 3H), 7.35 (s, 2H), 7.41 (t, J = 7.2 Hz, 1H), 7.48-7.51 (m, 2H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 20.4, 23.9, 124.7, 127.7, 130.2, 130.8, 132.2, 134.0, 139.1, 150.7; HRMS: calcd. for $C_{16}H_{15}N_2BrH^+$: 315.0497, found 315.0500.

2-(2-Bromophenyl)-5,6-dichloro-1*H*-benzo[*d*]imidazole (**Table 2.2**, entry 8)



General procedure for precursor synthesis was followed. 2-Bromobenzoic acid (10 mmol), 4,5-dichloro-1,2-phenylenediamine (10 mmol) and polyphosphoric acid (~25 g) were used to afford 2-(2-bromophenyl)-5,6-dichloro-1*H*-benzo[*d*]imidazole (2.87 g, 84%) as a pale yellow solid. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.41 (t, J = 6.8 Hz, 1H), 7.53 (t, J = 7.2 Hz, 1H), 7.70 (s, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.91 (s, 1H), 8.24 (d, J = 6.8 Hz, 1H), 10.44 (s, 1H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 121.9, 125.1, 128.3, 132.0, 132.3, 132.7, 133.9, 153.5; HRMS: calcd. for $C_{13}H_7N_2Cl_2BrH^+$: 340.9248, found 340.9242.

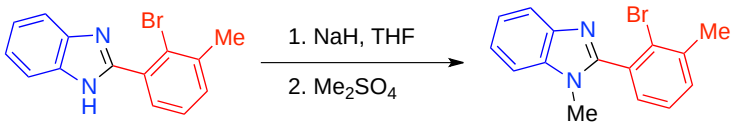
2-(2-Bromophenyl)-1-methyl-1*H*-benzo[*d*]imidazole (**Table 2.3**, entry 1)



General procedure for methylation: 2-(2-Bromophenyl)-1*H*-benzo[*d*]imidazole (10.9 g, 40 mmol) was dissolved in 500 mL THF in dropping funnel and added dropwise to the 1 L THF solution contained 1.2 equiv. NaH (60% in mineral oil, 1.92 g, 48 mmol) at room temperature. NaH was washed with hexane (10 mL × 3) under N_2. The mixture was stirred for 1 h at room temperature. Dimethylsulfate (4.16 mL, 44 mmol) was then added to the mixture dropwise. The mixture was refluxed for 30 min and stirred at room temperature for 3 h. Solvent was removed by vacuum. Ethyl acetate and water were added to the mixture and the organic phase was separated. The combined organic phase was washed with brine several times and concentrated. The concentrated mixture

was applied to 3 × 3 cm silica pad and eluted with ethyl acetate. The organic solvent was dried over Na_2SO_4 and evaporated in vacuum. The white solid of 2-(2-bromophenyl)-1-methyl-1*H*-benzo[*d*]imidazole (9.41 g, 82%) was obtained. ^{1}HNMR (400 MHz, $CDCl_3$) δ 3.66 (s, 3H), 7.34-7.49 (m, 5H), 7.55 (dd, J = 7.4 Hz, 1.6 Hz, 1H), 7.72 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 7.85-7.89 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.7, 109.6, 120.0, 122.3, 122.8, 123.7, 127.4, 131.3, 132.0, 132.3, 132.7, 135.4, 142.7, 152.4; MS (EI): *m/z* (relative intensity) 286.0 (M^+, 100), 207.1 (93), 103.1 (22), 77.0 (43).

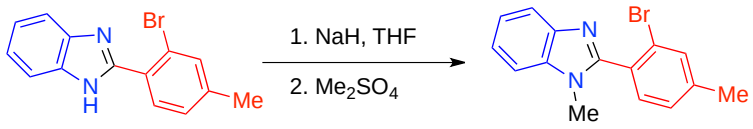
2-(2-Bromo-3-methylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole (**Table 2.3**, entry 2)



General procedure for methylation was followed. 2-(2-Bromo-3-methylphenyl)-1*H*-benzo[*d*]imidazole (1.435 g, 5.0 mmole) in 30 mL THF, NaH (60% in mineral oil, 0.24 g, 6.0 mmol) in 20 mL THF and dimethylsulfate (0.48 mL, 5.0 mmole) were used to afford 2-(2-bromo-3-methylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole (1.20 g, 80%) as a pale yellow solid. Melting point: 104.3-106.5 ºC; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 2.55 (s, 3H), 3.65 (s, 3H), 7.33-7.42 (m, 4H), 7.47-7.50 (m, 2H), 7.79 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 23.3, 30.5, 109.7, 119.6, 122.1, 122.7, 126.1, 127.2, 129.5, 132.2, 132.8, 135.5, 139.1, 142.8, 153.2; IR (cm^{-1}): 3051.61, 2951.27, 1611.46, 1572.09, 1518.69, 1482.36, 1457.82, 1450.68, 1431.16, 1397.90, 1378.25, 1324.36, 1278.70, 1244.13, 1173.27, 1152.84, 1129.09, 1115.73, 1097.10, 1081.53, 1025.76, 1005.21, 981.65, 919.53, 879.09, 796.63, 763.46, 741.64, 718.37, 698.59, 590.43,

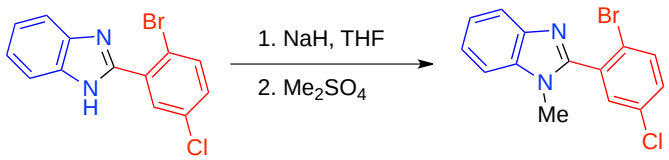
549.53, 486.47, 429.23; HRMS: calcd. for $C_{15}H_{13}N_2BrH^+$: 301.0340, found 301.0333.

2-(2-Bromo-4-methylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole (**Table 2.3**, entry 3)



General procedure for methylation was followed. 2-(2-Bromo-4-methylphenyl)-1*H*-benzo[*d*]imidazole (1.435 g, 5.0 mmole) in 30 mL THF, NaH (60% in mineral oil, 0.24 g, 6.0 mmol) in 20 mL THF and dimethylsulfate (0.48 mL, 5.0 mmole) were used to afford 2-(2-bromo-4-methylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole (1.23 g, 82%) as a pale yellow solid. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 2.48 (s, 3H), 3.66 (s, 3H), 7.32-7.48 (m, 5H), 7.62 (s, 1H), 7.78 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 20.8, 30.6, 109.70, 119.7, 122.0, 122.6, 123.3, 128.3, 129.3, 131.9, 133.2, 135.6, 142.2, 142.9, 152.6; HRMS: calcd. for $C_{15}H_{13}N_2BrH^+$: 301.0340, found 301.0326.

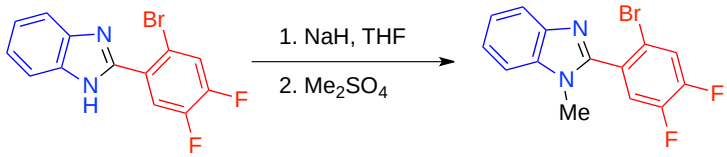
2-(2-Bromo-5-chlorophenyl)-1-methyl-1*H*-benzo[*d*]imidazole (**Table 2.3**, entry 4)



General procedure for methylation was followed. 2-(2-Bromo-5-chlorophenyl)-1*H*-benzo[*d*]imidazole (1.23 g, 4.0 mmole) in 30 mL THF, NaH (60% in mineral oil, 0.19 g, 4.8 mmol) in 20 mL THF and dimethylsulfate (0.39

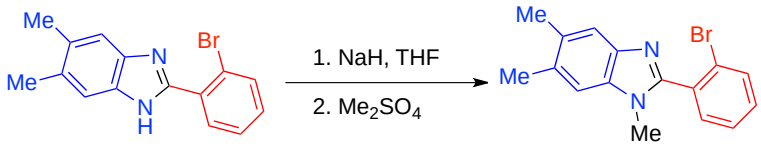
mL, 4.0 mmole) were used to afford 2-(2-bromo-5-chlorophenyl)-1-methyl-1*H*-benzo[*d*]imidazole (0.58 g, 45%) as a pale yellow solid. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.69 (s, 3H), 7.34-7.50 (m, 4H), 7.57 (s, 1H), 7.72 (d, J = 8.8 Hz, 1H), 7.82 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 30.8, 109.8, 119.9, 121.8, 122.3, 123.0, 131.4, 132.2, 133.6, 133.9, 134.0, 135.6, 142.8, 151.1; HRMS: calcd. for $C_{14}H_{10}N_2ClBrH^+$: 320.9794, found 320.9781.

2-(2-Bromo-4,5-difluorophenyl)-1-methyl-1*H*-benzo[*d*]imidazole (**Table 2.3**, entry 5)



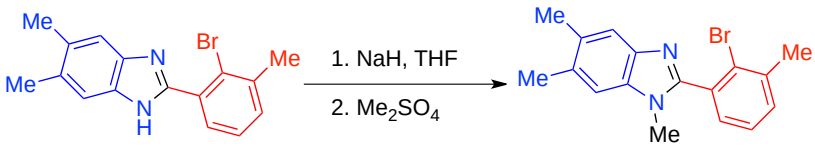
General procedure for methylation was followed. 2-(2-Bromo-4,5-difluorophenyl)-1*H*-benzo[*d*]imidazole (1.54 g, 5.0 mmole) in 35 mL THF, NaH (60% in mineral oil, 0.24 g, 6.0 mmol) in 20 mL THF and dimethylsulfate (0.48 mL, 5.0 mmole) were used to afford 2-(2-bromo-4,5-difluorophenyl)-1-methyl-1*H*-benzo[*d*]imidazole (1.01 g, 63%) as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.68 (s, 3H), 7.33-7.45 (m, 4H), 7.54-7.58 (m, 1H), 7.83-7.85 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.8, 109.7, 117.9 (overlapped), 118.0, 120.0, 121.0, 121.2, 121.8, 122.0, 122.6, 123.3, 128.6, 128.7 (overlapped), 135.2, 142.3, 148.0, 148.1, 149.7, 149.8, 150.3, 150.5, 150.6, 152.3, 152.4 (unresolved complex C-F splittings were observed); HRMS: calcd. for $C_{14}H_9N_2F_2BrH^+$: 322.9995, found 322.9985.

2-(2-Bromophenyl)-1,5,6-trimethyl-1*H*-benzo[*d*]imidazole (**Table 2.3**, entry 6)



General procedure for methylation was followed. 2-(2-Bromophenyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole (1.505 g, 5.0 mmole) in 30 mL THF, NaH (60% in mineral oil, 0.24 g, 6.0 mmol) in 20 mL THF and dimethylsulfate (0.48 mL, 5.0 mmole) were used to afford 2-(2-bromophenyl)-1,5,6-trimethyl-1*H*-benzo[*d*]imidazole (**2c**) (1.23 g, 79%) as a pale yellow solid. Melting point: 153.9-155.7 ºC; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 2.44 (s, 3H), 2.47 (s, 3H), 3.62 (s, 3H), 7.25 (s, 1H), 7.43-7.56 (m, 4H), 7.77 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 20.0, 20.3, 30.6, 109.8, 119.7, 123.8, 127.5, 131.1, 131.2, 132.1, 132.3, 132.6, 132.7, 134.2, 141.5, 151.6; IR (cm^{-1}): 3058.87, 3015.58, 2962.86, 2936.58, 1738.11, 1691.11, 1624.33, 1597.64, 1563.63, 1520.96, 1479.04, 1438.85, 1389.87, 1336.11, 1319.74, 1263.57, 1249.71, 1185.53, 1141.08, 1122.68, 1078.17, 1060.90, 1024.28, 1000.61, 870.99, 846.40, 821.75, 766.37, 728.53, 705.75, 665.42, 645.16, 607.35, 540.93, 514.11, 480.73, 456.26, 423.71; HRMS: calcd. for $C_{16}H_{15}N_2BrH^+$: 315.0497, found 315.0498.

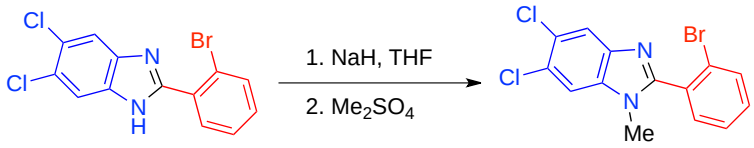
2-(2-Bromo-3-methylphenyl)-1,5,6-trimethyl-1*H*-benzo[*d*]imidazole (**Table 2.3**, entry 7)



General procedure for methylation was followed. 2-(2-Bromo-3-methylphenyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole (1.575 g, 5.0 mmole) in 30

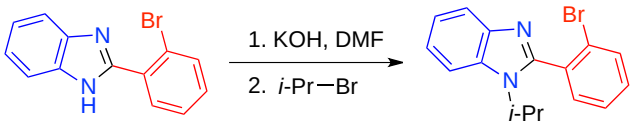
mL THF, NaH (60% in mineral oil, 0.24 g, 6.0 mmol) in 20 mL THF and dimethylsulfate (0.48 mL, 5.0 mmole) were used to afford 2-(2-bromo-3-methylphenyl)-1,5,6-trimethyl-1*H*-benzo[*d*]imidazole (1.58 g, 96%) as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3H), 2.45 (s, 3H), 2.51 (s, 3H), 3.62 (s, 3H), 7.21 (s, 1H), 7.35 (d, J = 4.8 Hz, 2H), 7.41 (t, J = 4.4 Hz, 1H), 7.63 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.2, 20.6, 23.5, 30.7, 109.9, 119.9, 126.4, 127.2, 129.7, 131.5, 132.3, 133.8, 139.0, 152.2; HRMS: calcd. for $C_{17}H_{17}N_2BrH^+$: 329.0653, found 329.0646.

2-(2-Bromophenyl)-5,6-dichloro-1-methyl-1*H*-benzo[*d*]imidazole (**Table 2.3**, entry 8)



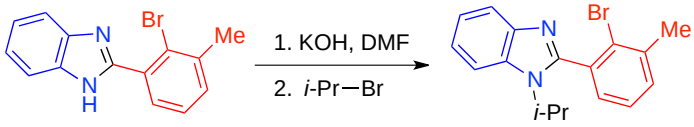
General procedure for methylation was followed. 2-(2-Bromophenyl)-5,6-dichloro-1*H*-benzo[*d*]imidazole (1.368 g, 4.0 mmole) in 15 mL THF, NaH (60% in mineral oil, 0.19 g, 4.8 mmol) in 20 mL THF and dimethylsulfate (0.39 mL, 4.0 mmole) were used to afford 2-(2-Bromophenyl)-5,6-dichloro-1-methyl-1*H*-benzo[*d*]imidazole (1.12 g, 79%) as a pale yellow solid. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.63 (s, 3H), 7.46-7.52 (m, 1H), 7.53-7.55 (m, 2H), 7.61 (s, 1H), 7.77-7.80 (m, 1H), 7.92 (s, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 31.0, 111.3, 121.0, 123.4, 126.0, 126.6, 127.6, 131.4, 131.8, 132.1, 132.9, 134.9, 142.2, 154.5; HRMS: calcd. for $C_{14}H_9N_2Cl_2BrH^+$: 354.9404, found 354.9388.

2-(2-Bromophenyl)-1-isopropyl-1*H*-benzo[*d*]imidazole (**Table 2.4**, entry 1)



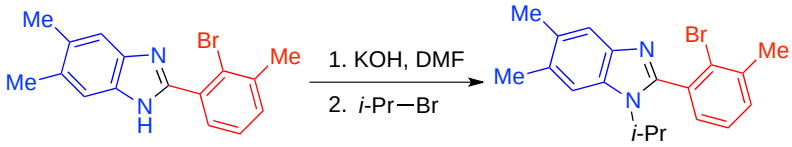
General procedure for propylation: 2-(2-Bromophenyl)-1*H*-benzo[*d*]imidazole (0.816 g, 3.0 mmole), 1.5 equiv. sodium hydroxide (0.18 g, 4.5 mmole) and 3.0 equiv. 2-bromopropane (0.845 mL, 9 mmole) were dissolved in DMF at room temperature and stirred for overnight. Water was added to the reaction mixture until the reaction mixture turn milky, and the reaction mixture was then kept in a refrigerator overnight. A pale yellow solid was grown and filtered. Small amount cold methanol and cold hexane was further used to wash the product. The pale yellow solid of 2-(2-bromophenyl)-1-isopropyl-1*H*-benzo[*d*]imidazole (1.18 g, 75%) was obtained. Melting point: 124.0-125.1 ºC; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 1.52 (d, J = 6.4 Hz, 3H), 1.74 (d, J = 6.8 Hz, 3H), 4.34 (septet, J = 6.8 Hz, 1H), 7.29-7.35 (m, 2H), 7.44-7.54 (m, 3H), 7.69-7.71 (m, 1H), 7.77-7.81 (m, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 21.0, 21.2, 49.2, 112.1, 120.2, 121.7, 122.3, 123.8, 127.4, 131.2, 131.8, 132.7, 132.8, 133.2, 143.8, 151.7; IR (cm^{-1}): 3421.58, 3058.43, 2976.14, 2931.40, 1610.13, 1562.20, 1517.54, 1451.74, 1424.11, 1397.01, 1375.76, 1336.71, 1306.49, 1283.67, 1245.85, 1180.18, 1160.95, 1149.25, 1132.92, 1103.52, 1059.01, 1029.39, 1017.71, 957.70, 908.35, 885.70, 850.69, 828.74, 769.13, 755.67, 748.48, 733.64, 705.77, 682.37, 648.75, 624.77, 536.46, 447.35, 430.92; HRMS: calcd. for $C_{16}H_{15}N_2BrH^+$: 315.0497, found 315.0491.

2-(2-Bromo-3-methylphenyl)-1-isopropyl-1*H*-benzo[*d*]imidazole (**Table 2.4**, entry 2)



General procedure for propylation was followed. 2-(2-Bromo-3-methylphenyl)-1*H*-benzo[*d*]imidazole (5.74 g, 20 mmole), sodium hydroxide (2.24 g, 40 mmole) and 2-bromopropane (5.63 mL, 60 mmole) in 35 mL DMF were used to afford 2-(2-bromo-3-methylphenyl)-1-isopropyl-1*H*-benzo[*d*]imidazole (4.41 g, 67%) as a pale yellow solid. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 1.52 (d, J = 6.8 Hz, 3H), 1.74 (d, J = 6.8 Hz, 3H), 2.56 (s, 3H), 4.34 (septet, J = 6.8 Hz, 1H), 7.28-7.34 (m, 3H), 7.40 (t, J = 7.2 Hz, 1H), 7.46-7.48 (m, 1H), 7.69-7.72 (m, 1H), 7.79-7.82 (m, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 21.0, 21.2, 23.3, 112.1, 120.1, 121.7, 122.2, 126.2, 127.1, 129.1, 132.0, 132.8, 133.7, 139.2, 143.8, 152.4; HRMS: calcd. for $C_{17}H_{17}N_2BrH^+$: 329.0653, found 329.0652.

2-(2-Bromo-3-methylphenyl)-1-isopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole (**Table 2.4**, entry 3)

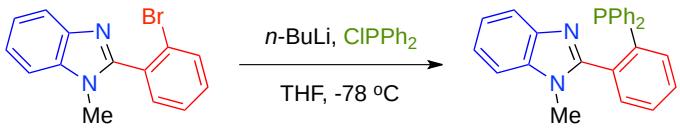


General procedure for propylation was followed. 2-(2-Bromo-3-methylphenyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole (1.575 g, 5 mmole), sodium hydroxide (0.56 g, 10 mmole) and 2-bromopropane (1.40 mL, 15 mmole) in 20 mL DMF were used to afford 2-(2-bromo-3-methylphenyl)-1-isopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole (1.33 g, 75%) as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.50 (d, J = 7.2 Hz, 3H), 1.73 (d, J = 6.8 Hz, 3H), 2.41 (s,

3H), 2.45 (s, 3H), 2.51 (s, 3H), 4.304 (septet, J = 6.8 Hz, 1H), 7.26 (d, J = 7.6 Hz, 1H), 7.33 (t, J = 7.6 Hz, 1H), 7.39-7.42 (m, 2H), 7.62 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.1, 20.7, 21.2, 21.5, 23.5, 48.9, 112.2, 120.2, 126.5, 127.0, 129.2, 130.9, 132.0, 139.0; HRMS: calcd. for $C_{19}H_{21}N_2BrH^+$: 357.0966, found 357.0978.

2-(2-(Diphenylphosphino)phenyl)-1-methyl-1*H*-benzo[*d*]imidazole

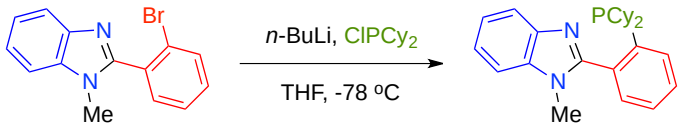
(PPh PhMezole-phos **L1a**) (**Table 2.5**, entry 1)



General procedure for ligand synthesis: 2-(2-Bromophenyl)-1-methyl-1*H*-benzo[*d*] imidazole (0.86 g, 3.0 mmol) was dissolved in freshly distilled THF (20 mL) at room temperature under N_2. The solution was cooled to -78 °C in dry ice/acetone bath. Titrated *n*-BuLi (3.0 mmol) was added dropwise by syringe. After the reaction mixture was stirred for 30 min at -78 °C, chlorodiphenylphosphine (0.55 mL, 3.0 mmol) was added. The reaction was allowed to warm to room temperature and stirred for 5 h. Solvent was removed under reduced pressure. DCM and water were added to the mixture and the organic phase was separated. The combined organic phase was washed with brine several times and concentrated. The concentrated mixture was applied to 2 × 10 cm silica pad and eluted with 200 mL E.A./Hexane (1:9). This fraction was discarded and further eluted with ethyl E.A./Hexane (4:6). The collected solvent was removed under vacuum. The solid product was further purified by washing with small amount of cold diethyl ether. The product was then dried under vacuum. White solid of 2-(2-(diphenylphosphino)phenyl)-1-methyl-1*H*-benzo[*d*]

imidazole (0.89 g, 76%) was obtained. Melting point: 174.2-176.2 ℃; ^{31}P NMR (161MHz, CD_2Cl_2) δ -11.7; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.46 (s, 3H), 7.25-7.38 (m, 14H), 7.49-7.55 (m, 3H), 7.72-7.74 (m, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 30.5, 109.3, 119.5, 121.7, 122.2, 128.1, 128.2, 128.5, 129.5, 130.4, 130.5, 133.5, 133.7, 133.8, 135.4, 136.0, 136.3, 136.6, 136.7, 139.5, 139.7, 142.7, 153.1 (unresolved complex C-P splittings were observed); IR (cm^{-1}): 3051.12, 1613.13, 1478.90, 1462.03, 1424.04, 1377.53, 1327.71, 1282.58, 1244.50, 1148.55, 1125.98, 1093.06, 1027.09, 1005.94, 773.97, 745.88, 695.76, 521.56, 493.47, 469.17; MS (EI): *m/z* (relative intensity) 392.1 (M^+, 2), 315.1 (100), 223.0 (22), 207.0 (26); HRMS: calcd. for $C_{26}H_{21}N_2PH^+$: 393.1521, found 393.1524.

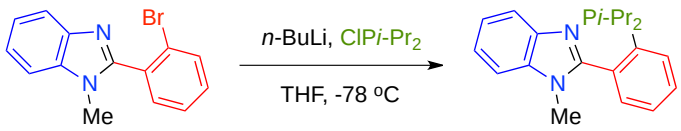
2-(2-(Dicyclohexylphosphino)phenyl)-1-methyl-1*H*-benzo[*d*]imidazole (PCy PhMezole-phos **L1b**) (**Table 2.5**, entry 2)



General procedure for ligand synthesis was followed. 2-(2-Bromophenyl)-1-methyl-1*H*-benzo[*d*]imidazole (2.86 g, 10.0 mmol), *n*-BuLi (10.0 mmol), chlorodicyclohexylphosphine (2.20 mL, 10.0 mmol), and 40 mL THF were used to afford 2-(2-(dicyclohexylphosphino)phenyl)-1-methyl-1*H*-benzo[*d*]imidazole (2.90 g, 72%) as a white solid. Small amount of cool hexane instead of diethyl ether was used for washing the products. Melting point: 155.7-158.1 ºC; ^{31}P NMR (161MHz, CD_2Cl_2) δ -8.07; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 1.10-1.31 (m, 10H), 1.67-1.78 (m, 10H), 1.91-1.94 (m, 2H), 3.56 (s, 3H), 7.30-7.37 (m, 2H), 7.43-7.61 (m, 4H), 7.71-7.79 (m, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 26.3, 27.1, 27.1, 27.2, 29.2, 29.3, 30.0, 30.2, 30.6, 30.7, 33.6, 33.7, 109.4, 119.3, 121.5, 122.0,

128.5, 128.8, 130.5, 1306, 132.6, 132.7, 135.3, 137.0, 137.2, 138.8, 139.1, 142.9, 154.6, 154.6 (unresolved complex C-P splittings were observed); IR (cm^{-1}): 3049.23, 2922.74, 2846.49, 1444.05, 1420.25, 1380.93, 1323.98, 1279.02, 1236.37, 1179.81, 1150.92, 1121.29, 1041.62, 1001.29, 885.48, 849.19, 773.73, 746.94, 526.06, 457.22; MS (EI): *m/z* (relative intensity) 404.2 (M^+, 0), 321.1 (100), 238.0 (39), 223.0 (28), 55.1 (7); HRMS: calcd. for $C_{26}H_{33}N_2PH^+$: 405.2460, found 405.2445.

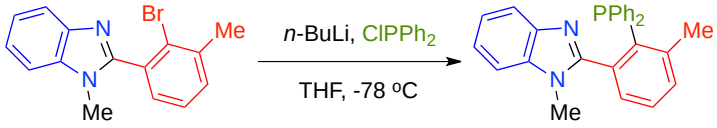
2-(2-(Diisopropylphosphino)phenyl)-1-methyl-1*H*-benzo[*d*]imidazole (P*i*-Pr PhMezole-phos **L1c**) (**Table 2.5**, entry 3)



General procedure for ligand synthesis was followed. 2-(2-Bromophenyl)-1-methyl-1*H*-benzo[*d*]imidazole (0.86 g, 3.0 mmol), *n*-BuLi (3.0 mmol), chlorodiisopropylphosphine (0.47 mL, 3.0 mmol) were used to afford 2-(2-(diisopropylphosphino)phenyl)-1-methyl-1*H*-benzo[*d*]imidazole (0.69 g, 72%) as a white solid. Small amount of cool hexane instead of diethyl ether was used for washing the products. Melting point: 147.7-149.7 °C; ^{31}P NMR (161MHz, CD_2Cl_2) δ 0.45; ^1H NMR (400 MHz, CD_2Cl_2) δ 1.02-1.09 (m, 12H), 2.14-2.18 (m, 2H), 3.59 (s, 3H), 7.31-7.38 (m, 2H), 7.44-7.46 (m, 1H), 7.50-7.63 (m, 3H), 7.71-7.73 (m, 1H), 7.78-7.80 (m, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 19.1, 19.2, 19.5, 19.6, 23.6, 23.8, 30.5, 30.6, 109.3, 119.3, 121.5, 122.1, 128.6, 128.9, 130.5, 130.6, 132.2, 132.3, 135.2, 137.4, 137.6, 138.5, 138.8, 142.9, 154.4, 154.5 (unresolved complex C-P splittings were observed); IR (cm^{-1}): 2959.77, 2941.70, 2859.58, 1441.13, 1421.73, 1382.81, 1325.73, 1279.50, 1239.22, 1150.84, 1119.29,

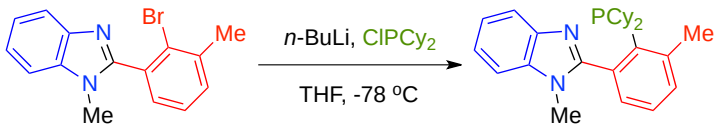
1032.32, 1002.00, 881.61, 775.91, 749.74, 653.87, 609.59, 596.19, 515.71; MS (EI): *m/z* (relative intensity) 324.2 (M^+, 0), 281.1 (100), 238.0 (56), 223.0 (38), 207.0 (48); HRMS: calcd. for $C_{20}H_{25}N_2PH^+$: 325.1834, found 325.1822.

2-(2-(Diphenylphosphino)-3-methylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole (PPh *m*-TolMezole-phos **L1d**) (**Table 2.5**, entry 4)



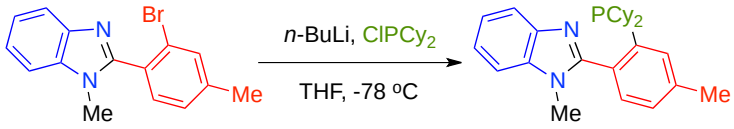
General procedure for ligand synthesis was followed. 2-(2-Bromo-3-methylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole (0.903 g, 3.0 mmole), *n*-BuLi (3.0 mmol), chlorodiphenylphosphine (0.55 mL, 3.0 mmol), and 20 mL THF were used to afford 2-(2-(diphenylphosphino)-3-methylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole (0.81 g, 67%) as a white solid. ^{31}P NMR (161MHz, CD_2Cl_2) δ -9.13; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 2.10 (s, 3H), 3.45 (s, 3H), 7.27-7.56 (m, 16H), 7.67-7.68 (m, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 22.6, 22.7, 30.7, 109.3, 119.4, 121.7, 122.1, 127.7, 128.1, 128.7 (overlapped), 129.7, 131.9, 132.1, 133.0, 135.0, 135.2, 135.4, 139.0, 139.3, 142.7, 145.2 (overlapped), 154.5 (overlapped) (unresolved complex C-P splittings were observed); HRMS: calcd. for $C_{27}H_{23}N_2PH^+$: 407.1677, found 407.1681.

2-(2-(Dicyclohexylphosphino)-3-methylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole (PCy *m*-TolMezole-phos **L1e**) (**Table 2.5**, entry 5)



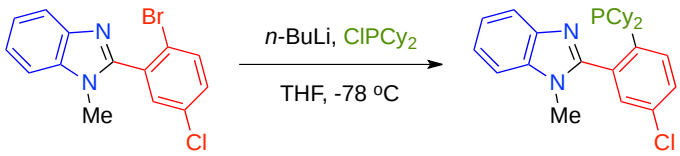
General procedure for ligand synthesis was followed. 2-(2-Bromo-3-methylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole (0.903 g, 3.0 mmole), *n*-BuLi (3.0 mmol), chlorodicyclohexylphosphine (0.66 mL, 3.0 mmol), and 20 mL THF were used to afford 2-(2-(dicyclohexylphosphino)-3-methylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole (0.62 g, 50%) as a white solid. Melting point: 175.9-176.5 ºC; ^{31}P NMR (161MHz, CD_2Cl_2) δ 4.85; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 1.28-1.79 (m, 22H), 2.70 (s, 3H), 3.65 (s, 3H), 7.27 (s, 1H), 7.38-7.45 (m, 4H), 7.51 (d, J = 7.2 Hz, 1H), 7.86 (d, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 22.6, 26.2, 26.9, 27.0, 27.3, 27.4, 30.7, 30.8, 33.0, 33.3, 35.6, 35.7, 109.4, 119.3, 121.6, 122.0, 128.0, 128.1, 128.5, 132.1, 135.2, 136.0, 136.2, 143.0, 144.5 (unresolved complex C-P splittings were observed); IR (cm^{-1}): 3426.80, 3054.44, 2923.97, 2846.57, 1614.56, 1591.11, 1516.29, 1458.32, 1446.75, 1434.63, 1386.29, 1325.45, 1299.50, 1278.05, 1243.64, 1193.38, 1173.27, 1149.17, 1129.44, 1109.44, 1087.25, 1039.54, 1002.89, 922.96, 888.59, 876.45, 848.13, 797.98, 765.62, 748.48, 722.84, 704.03, 616.21, 592.11, 560.57, 523.88, 496.14, 457.60, 438.18; HRMS: calcd. for $C_{27}H_{35}N_2PH^+$: 419.2616, found 419.2602.

2-(2-(Dicyclohexylphosphino)-4-methylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole (PCy *p*-TolMezole-phos **L1f**) (**Table 2.5**, entry 6)



General procedure for ligand synthesis was followed. 2-(2-Bromo-4-methylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole (0.903 g, 3.0 mmole), *n*-BuLi (3.0 mmol), chlorodicyclohexylphosphine (0.66 mL, 3.0 mmol), and 20 mL THF were used to afford 2-(2-(dicyclohexylphosphino)-4-methylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole (0.86 g, 69%) as a white solid. ^{31}P NMR (161MHz, CD_2Cl_2) δ -8.14; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 1.17-1.31 (m, 11H), 1.75-1.97 (m, 11H), 2.55 (s, 3H), 3.58 (s, 3H), 7.35-7.45 (m, 5H), 7.54 (s, 1H), 7.81 (d, J = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 21.3, 26.4, 27.2 (overlapped), 27.3, 29.3, 29.4, 30.2, 30.3, 30.7 (overlapped), 33.7, 33.8, 109.4, 119.3, 121.5, 122.0. 129.5, 130.4, 130.5, 133.1 (overlapped), 135.4, 135.9, 136.3, 136.6, 136.9, 138.8, 143.0, 154.8, 154.9 (unresolved complex C-P splittings were observed); HRMS: calcd. for $C_{27}H_{35}N_2PH^+$: 419.2616, found 419.2603.

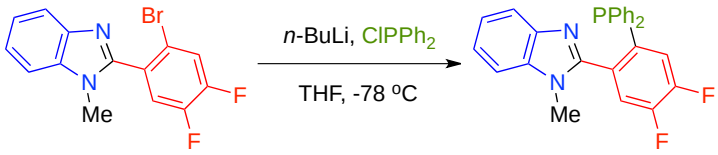
2-(5-Chloro-2-(dicyclohexylphosphino)phenyl)-1-methyl-1*H*-benzo[*d*]imidazole (PCy 5-ClPhMezole-phos **L1g**) (**Table 2.5**, entry 7)



General procedure for ligand synthesis was followed. 2-(2-Bromo-5-chlorophenyl)-1-methyl-1*H*-benzo[*d*]imidazole (0.482 g, 1.5 mmole), *n*-BuLi (1.5 mmol), chlorodicyclohexylphosphine (0.35 mL, 1.5 mmol), and 10 mL THF were

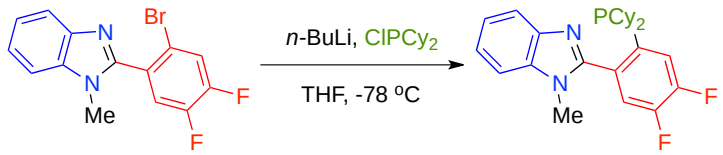
used to afford 2-(5-chloro-2-(dicyclohexylphosphino)phenyl)-1-methyl-1*H*-benzo[*d*]imidazole (0.47 g, 72%) as a white solid. ^{31}P NMR (161MHz, CD_2Cl_2) δ -8.91; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 0.95-1.28 (m, 11H), 1.69-1.93 (m, 11H), 3.59 (s, 3H), 7.35-7.65 (m, 6H), 7.80 (s, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 26.3, 27.1, 27.20, 27.26, 29.2, 29.3, 30.0, 30.2, 30.8, 30.9, 33.6, 33.7, 109.6, 119.5, 121.8, 122.4, 129.1, 130.6, 134.1, 134.7, 135.3, 135.8, 136.0, 140.4, 140.7, 142.9, 153.2 (unresolved complex C-P splittings were observed); HRMS: calcd. for $C_{26}H_{32}N_2ClPH^+$: 439.2070, found 439.2075.

2-(2-(Diphenylphosphino)-4,5-difluorophenyl)-1-methyl-1*H*-benzo[*d*]imidazole (PPh 4,5-F_2PhMezole-phos **L1h**) (**Table 2.5**, entry 8)



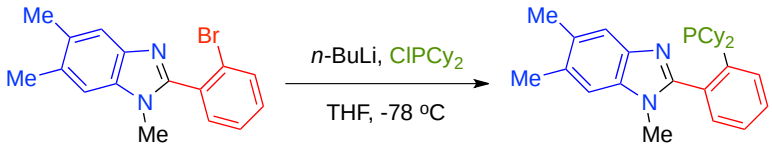
General procedure for ligand synthesis was followed. 2-(2-Bromo-4,5-difluorophenyl)-1-methyl-1*H*-benzo[*d*]imidazole (0.969 g, 3.0 mmole), *n*-BuLi (3.0 mmol), chlorodiphenylphosphine (0.55 mL, 3.0 mmol), and 15 mL THF were used to afford 2-(2-(diphenylphosphino)-4,5-difluorophenyl)-1-methyl-1*H*-benzo[*d*]imidazole (0.26 g, 20%) as a white solid. ^{31}P NMR (161MHz, CD_2Cl_2) δ -13.63 (d, $J_{P\text{-}F}$ = 12.8 Hz); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.56 (s, 3H), 7.31-7.46 (m, 15H), 7.77 (d, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 30.7, 109.6, 119.1, 119.3, 119.7, 122.1, 122.8, 127.2, 128.3, 128.4, 128.7, 132.5, 132.7, 134.7, 134.8, 135.4, 142.7 (unresolved complex C-P splittings were observed); HRMS: calcd. for $C_{26}H_{19}N_2F_2PH^+$: 429.1332, found 429.1331.

2-(2-(Dicyclohexylphosphino)-4,5-difluorophenyl)-1-methyl-1*H*-benzo[*d*] imidazole (PCy 4,5-F_2PhMezole-phos **L1i**) (**Table 2.5**, entry 9)



General procedure for ligand synthesis was followed. 2-(2-Bromo-4,5-difluorophenyl)-1-methyl-1*H*-benzo[*d*]imidazole (0.969 g, 3.0 mmole), *n*-BuLi (1.5 mmol), chlorodicyclohexylphosphine (0.66 mL, 3.0 mmol), and 15 mL THF were used to afford 2-(2-(dicyclohexylphosphino)-4,5-difluorophenyl)-1-methyl-1*H*-benzo[*d*]imidazole (0.38 g, 29%) as a white solid. ^{31}P NMR (161MHz, CD_2Cl_2) δ 3.25 (d, $J_{P\text{-}F}$ = 19.3 Hz); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 1.11-1.30 (m, 11H), 1.63-1.85 (m, 11H), 3.58 (s, 3H), 7.24-7.38 (m, 4H), 7.44 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 26.2, 26.8, 27.1, 27.2, 30.6, 30.7, 30.8, 31.5, 31.7, 109.6, 118.1, 118.3, 119.5, 121.8, 122.4, 127.1, 135.2, 135.9, 142.8, 153.0 (unresolved complex C-P splittings were observed); HRMS: calcd. for $C_{26}H_{31}N_2F_2PH^+$: 441.2271, found 441.2270.

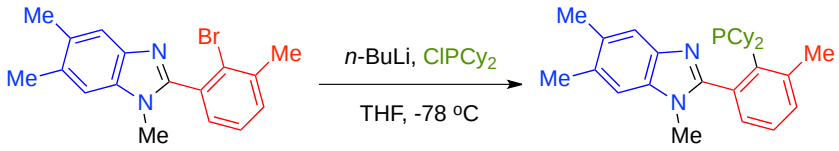
2-(2-(Dicyclohexylphosphino)phenyl)-1,5,6-trimethyl-1*H*-benzo[*d*]imidazole (PCy PhMezole^{M2}-phos **L1j**) (**Table 2.5**, entry 10)



General procedure for ligand synthesis was followed. 2-(2-Bromophenyl)-1,5,6-trimethyl-1*H*-benzo[*d*]imidazole (0.945 g, 3.0 mmole), *n*-BuLi (3.0 mmol), chlorodicyclohexylphosphine (0.66 mL, 3.0 mmol), and 20 mL THF were used to afford 2-(2-(dicyclohexylphosphino)phenyl)-1,5,6-trimethyl-1*H*-benzo[*d*]

imidazole (0.89 g, 70%) as a white solid. Melting point: 163.8-165.3 ºC; ^{31}P NMR (161MHz, CD_2Cl_2) δ -8.02; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 1.06-1.30 (m, 10H), 1.62-1.94 (m, 12H), 2.44 (s, 3H), 2.47 (s, 3H), 3.50 (s, 3H), 7.19 (s, 1H), 7.46-7.58 (m, 4H), 7.69 (d, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 19.9, 20.2, 26.4, 27.1, 27.2, 27.3, 29.3, 29.4, 30.1, 30.3, 30.6, 30.7, 33.6, 33.8, 109.6, 119.4, 128.5, 128.6, 130.4, 130.6, 130.7, 131.2, 132.6, 132.7, 133.9, 137.1, 137.3, 139.0, 139.4, 141.5, 153.7, 153.8 (unresolved complex C-P splittings were observed); IR (cm^{-1}): 3047.73, 2921.06, 2846.50, 1738.77, 1630.96, 1518.75, 1484.32, 1445.60, 1422.70, 1388.42, 1342.50, 1323.03, 1261.76, 1177.31, 1141.90, 1122.34, 1064.74, 1042.81, 1022.99, 995.70, 951.64, 916.17, 889.40, 858.70, 821.37, 773.15, 742.62, 723.16, 676.80, 653.67, 607.25, 517.62, 511.07, 490.76, 464.09, 447.60, 427.36, 417.95; HRMS: calcd. for $C_{28}H_{37}N_2PH^+$: 433.2773, found 433.2758.

2-(2-(Dicyclohexylphosphino)-3-methylphenyl)-1,5,6-trimethyl-1*H*-benzo[*d*] imidazole (PCy *m*-TolMezole^{M2}-phos **L1k**) (**Table 2.5**, entry 11)

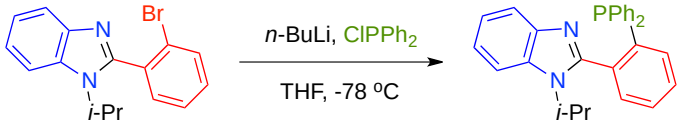


General procedure for ligand synthesis was followed. 2-(2-Bromo-3-methylphenyl)-1,5,6-trimethyl-1*H*-benzo[*d*]imidazole (0.987 g, 3.0 mmole), *n*-BuLi (3.0 mmol), chlorodicyclohexylphosphine (0.66 mL, 3.0 mmol), and 50 mL THF were used to afford 2-(2-(dicyclohexylphosphino)-3-methylphenyl)-1,5,6-trimethyl-1*H*-benzo[*d*]imidazole (0.75 g, 56%) as a white solid. ^{31}P NMR (161MHz, CD_2Cl_2) δ 4.72; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 0.99-1.68 (m, 22H), 2.44 (s, 3H), 2.47 (s, 3H), 2.59 (s, 3H), 3.51 (s, 3H), 7.20 (s, 2H), 7.35-7.37 (m,

2H), 7.51 (s, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 19.9, 20.2, 22.6, 25.2, 26.2, 26.9, 27.0, 27.2, 27.3, 30.6 (overlapped), 30.7, 30.8, 33.0, 33.3, 34.6, 35.5, 35.7, 109.6, 119.4, 128.1, 128.3, 130.3, 131.0, 131.9, 133.7, 136.1, 136.3, 141.6 (unresolved complex C-P splittings were observed); HRMS: calcd. for $C_{29}H_{39}N_2PH^+$: 447.2929, found 447.2909.

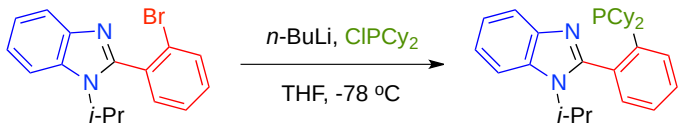
2-(2-(Diphenylphosphino)phenyl)-1-isopropyl-1*H*-benzo[*d*]imidazole

(PPh PhPrzole-phos **L1l**) (**Table 2.5**, entry 12)



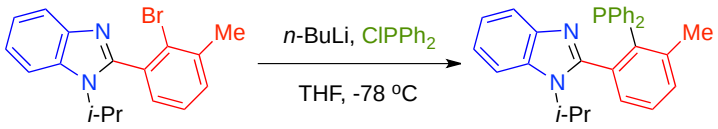
General procedure for ligand synthesis was followed. 2-(2-Bromophenyl)-1-isopropyl-1*H*-benzo[*d*]imidazole (0.945 g, 3.0 mmole), *n*-BuLi (3.0 mmol), chlorodiphenylphosphine (0.55 mL, 3.0 mmol), and 20 mL THF were used to afford 2-(2-(diphenylphosphino)phenyl)-1-isopropyl-1*H*-benzo[*d*]imidazole (0.39 g, 31%) as a white solid. ^{31}P NMR (161MHz, CD_2Cl_2) δ -15.00; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 1.53 (s, 3H), 1.55 (s, 3H), 4.39 (septet, J = 6.8 Hz, 1H), 7.24-7.31 (m, 7H), 7.36-7.37 (m, 6H), 7.49-7.57 (m, 3H), 7.65-7.67 (m, 1H), 7.70-7.72 (m, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 21.0, 48.9, 112.0, 120.0, 121.5, 121.9, 128.4 (overlapped), 128.5, 129.0, 129.7, 130.2, 130.3, 132.8, 133.3, 133.5, 134.7, 134.7, 137.1, 137.2, 137.9, 138.2, 138.7, 138.8, 143.8, 152.8, 152.8 (unresolved complex C-P splittings were observed); HRMS: calcd. for $C_{28}H_{25}N_2PH^+$: 421.1834, found 421.1820.

2-(2-(Dicyclohexylphosphino)phenyl)-1-isopropyl-1*H*-benzo[*d*]imidazole (PCy PhPrzole-phos **L1m**) (**Table 2.5**, entry 13)



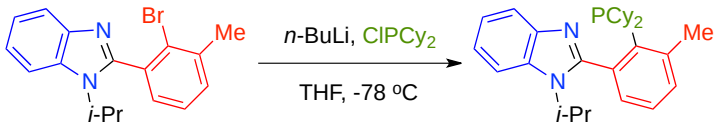
General procedure for ligand synthesis was followed. 2-(2-Bromophenyl)-1-isopropyl-1*H*-benzo[*d*]imidazole (0.945 g, 3.0 mmole), *n*-BuLi (3.0 mmol), chlorodicyclohexylphosphine (0.66 mL, 3.0 mmol), and 20 mL THF were used to afford 2-(2-(dicyclohexylphosphino)phenyl)-1-isopropyl-1*H*-benzo[*d*]imidazole (0.85 g, 66%) as a white solid. Melting point: 82.5-83.8 °C; ^{31}P NMR (161MHz, CD_2Cl_2) δ -9.49; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 0.917-1.50 (m, 17H), 1.71 (s, 11H), 4.21-4.28 (m, 1H), 7.26-7.30 (m, 2H), 7.39-7.41 (m, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.56 (t, J = 7.2 Hz, 1H), 7.64-7.66 (m, 1H), 7.70 (d, J = 7.6 Hz, 1H), 7.74-7.76 (m, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 21.2, 25.2, 26.2, 26.4, 26.8, 26.9, 27.0, 27.5, 28.8, 29.0, 30.0, 30.2, 30.4, 32.6, 34.6, 48.6, 111.9, 119.8, 121.2, 121.7, 128.3, 128.7, 130.2, 130.3, 132.70, 132.73, 132.76, 137.4, 137.7, 139.6, 139.9, 143.8, 153.8, 153.9 (unresolved complex C-P splittings were observed); IR (cm^{-1}): 3422.10, 3051.66, 2922.87, 2847.27, 1611.76, 1521.94, 1447.51, 1428.73, 1399.82, 1368.61, 1306.98, 1282.20, 1266.35, 1179.27, 1155.75, 1130.42, 1101.74, 1068.67, 1024.13, 999.98, 885.75, 849.94, 770.41, 742.29, 724.16, 629.15, 523.07, 472.27, 429.31; HRMS: calcd. for $C_{28}H_{37}N_2PH^+$: 433.2773, found 433.2758.

2-(2-(Diphenylphosphino)-3-methylphenyl)-1-isopropyl-1*H*-benzo[*d*]imidazole (PPh *m*-TolPrzole-phos **L1n**) (**Table 2.5**, entry 14)



General procedure for ligand synthesis was followed. 2-(2-Bromo-3-methylphenyl)-1-isopropyl-1*H*-benzo[*d*]imidazole (0.987 g, 3.0 mmole), *n*-BuLi (3.0 mmol), chlorodiphenylphosphine (0.55 mL, 3.0 mmol), and 20 mL THF were used to afford 2-(2-(diphenylphosphino)-3-methylphenyl)-1-isopropyl-1*H*-benzo[*d*]imidazole (0.74 g, 57%) as a white solid. ^{31}P NMR (161MHz, CD_2Cl_2) δ -10.42; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 1.36 (d, J = 7.2 Hz, 3H), 1.55 (d, J = 6.8 Hz, 3H), 1.91 (s, 3H), 4.38 (septet, J = 6.8 Hz, 1H), 7.25-7.45 (m, 14H), 7.55 (t, J = 7.6 Hz, 1H), 7.59-7.62 (m, 1H), 7.72-7.74 (m, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 20.5, 21.2, 22.7, 48.9, 111.9, 119.8, 121.5, 121.8, 127.5, 127.7, 127.9, 128.0, 128.2, 128.3, 128.4, 128.5, 130.1, 130.9, 131.1, 131.4, 131.6, 132.6, 133.3, 134.5, 135.5, 135.8, 141.2, 141.7, 143.8, 145.5, 154.5 (unresolved complex C-P splittings were observed); HRMS: calcd. for $C_{29}H_{27}N_2PH^+$: 435.1990, found 435.1983.

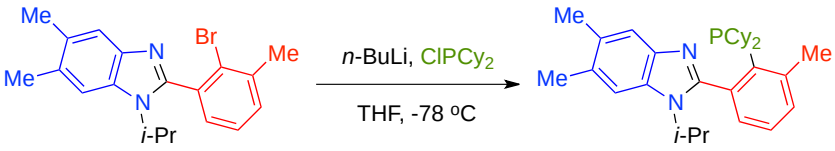
2-(2-(Dicyclohexylphosphino)-3-methylphenyl)-1-isopropyl-1*H*-benzo[*d*] imidazole (PCy *m*-TolPrzole-phos **L1o**) (**Table 2.5**, entry 15)



General procedure for ligand synthesis was followed. 2-(2-Bromo-3-methylphenyl)-1-isopropyl-1*H*-benzo[*d*]imidazole (0.987 g, 3.0 mmole), *n*-BuLi (3.0 mmol), chlorodicyclohexylphosphine (0.66 mL, 3.0 mmol), and 20 mL THF

were used to afford 2-(2-(dicyclohexylphosphino)-3-methylphenyl)-1-isopropyl-1*H*-benzo[*d*]imidazole (0.71 g, 53%) as a white solid. ^{31}P NMR (161MHz, CD_2Cl_2) δ 4.07; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 0.90-0.94 (m, 3H), 1.16-1.36, (m, 12H), 1.55 (d, J = 6.8 Hz, 3H), 1.73-1.81 (m, 8H), 2.13-2.18 (m, 1H), 2.25-2.33 (m, 1H), 2.58 (s, 3H), 4.29-4.37 (m, 1H), 7.13-7.16 (m, 1H), 7.26-7.30 (m, 2H), 7.36-7.37 (m, 2H), 7.66 (t, J = 4.0 Hz, 1H), 7.74 (t, J = 5.2 Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 13.8, 21.2, 21.5 (overlapped), 21.5, 22.2, 22.6, 26.1, 26.3, 26.8, 27.0, 27.1, 27.3, 27.4 (overlapped), 30.1, 30.2, 30.8 (overlapped), 31.5, 32.9, 33.1, 33.3, 33.5, 35.5, 35.7, 36.3, 36.4, 48.4, 111.9, 119.7, 121.2, 121.5, 127.6, 127.7, 128.4, 131.9, 132.4, 135.7, 143.9, 144.1, 155.2 (unresolved complex C-P splittings were observed); HRMS: calcd. for $C_{29}H_{39}N_2PH^+$: 447.2929, found 447.2920.

2-(2-(Dicyclohexylphosphino)-3-methylphenyl)-1-isopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole (PCy *m*-TolPrzole^{M2}-phos **L1p**) (**Table 2.5**, entry 16)

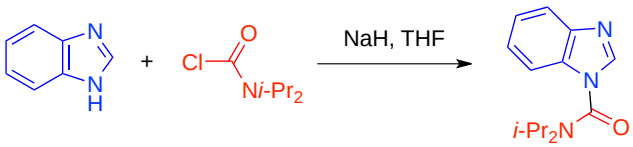


General procedure for ligand synthesis was followed. 2-(2-Bromo-3-methylphenyl)-1-isopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole (1.071 g, 3.0 mmole), *n*-BuLi (3.0 mmol), chlorodicyclohexylphosphine (0.66 mL, 3.0 mmol), and 20 mL THF were used to afford 2-(2-(dicyclohexylphosphino)-3-methylphenyl)-1-isopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole (0.78 g, 55%) as a white solid. ^{31}P NMR (161MHz, CD_2Cl_2) δ 4.11; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 0.92-0.96 (m, 1H), 1.19-1.45 (m, 13H), 1.56 (d, J = 6.8 Hz, 3H), 1.67-1.84 (m, 9H), 2.15-2.18 (m, 1H), 2.31-2.32 (m, 1H), 2.45 (s, 3H), 2.49 (s, 3H), 2.60 (s,

3H), 4.26-4.35 (m, 1H), 7.16-7.19 (m, 1H), 7.36-7.38 (m, 2H), 7.46 (s, 1H), 7.54 (s, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 20.4, 21.3, 21.5 (overlapped), 22.3, 26.2, 26.4, 26.9, 27.0, 27.2, 27.4, 27.5, 30.1, 30.2, 30.8, 30.9, 33.0, 33.3, 33.5, 35.6, 35.8, 36.3, 36.4, 48.2, 112.1, 119.7, 127.6, 127.7, 128.3, 129.9, 130.4, 130.9, 131.8, 135.9, 136.2, 141.9, 142.6, 144.0, 144.1, 154.4 (overlapped) (unresolved complex C-P splittings were observed); HRMS: calcd. for $C_{31}H_{43}N_2PH^+$: 475.3242, found 475.3240.

2.6.3 General Procedures for Preparation of 2-Phosphino-Substituted Benzimidazolyl Ligands

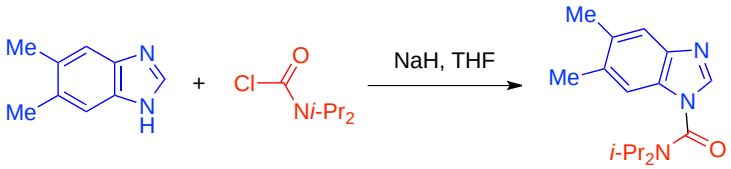
N,*N*-Diisopropyl-1*H*-benzo[*d*]imidazole-1-carboxamide (**Table 2.10**, entry 1)



General procedure for condensation reaction: Benzimidazole (2.36 g, 20.0 mmol) was dissolved in anhydrous THF (20 mL). The resultant solution was added dropwise to the THF (25 mL) solution containing 1.2 equiv. of NaH (60% in mineral oil, 0.96 g, 24.0 mmol) at 0 °C. (Note: NaH was pre-washed with dry hexane, 5 mL × 3, under nitrogen). The mixture was stirred for 30 min at room temperature. Then, 1.1 equiv. of *N*,*N*-diisopropylcarbamoylchloride (3.60 g, 22 mmol) was added directly to the reaction and the mixture was refluxed for 30 min and stirred at room temperature for overnight. Solvent was removed under reduced pressure. Ethyl acetate (~300 mL) and water (~100 mL) were added to the mixture and the aqueous phase was separated. The organic phase was further washed with brine (~50 mL × 3), and dried by Na_2SO_4 and concentrated. The concentrated mixture was applied to 2 × 2 inch silica pad and eluted with ethyl acetate. After the solvent was removed under vacuum, the white crystals (3.58 g, 73%) were obtained after re-crystallization from ethyl acetate/hexane. Melting point: 95.3-96.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.44 (t, J = 6.8 Hz, 12H), 3.78-3.85 (m, 2H), 7.28 (s, 1H), 7.35-7.39 (m, 1H), 7.61-7.83 (m, 1H), 7.84 (d, J = 2.0 Hz, 1H), 8.06 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 20.9, 49.0, 112.0, 120.3, 123.3, 124.3, 132.5, 140.3, 143.0, 149.4; IR (cm^{-1}) 3081.14, 3004.29, 2971.89, 2932.78, 1690.49, 1481.08, 1445.25, 1377.46, 1344.46, 1301.23, 1213.79, 1136.61, 1064.74, 1027.83, 952.93, 890.93, 829.02, 758.54, 609.88; MS

(EI): *m/z* (relative intensity) 245 (M^+, 42), 145 (11), 128 (74), 118 (58), 86 (100); HRMS: calcd. for $C_{14}H_{19}N_3OH^+$: 246.1606, found 246.1610.

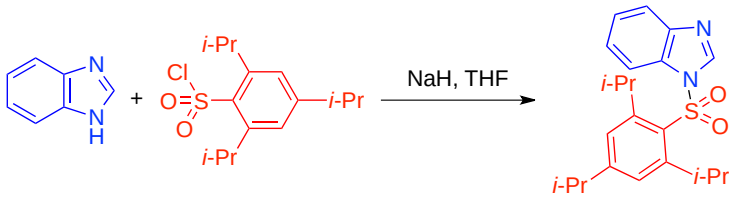
N,*N*-Diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide (**Table 2.10**, entry 2)



General procedure for condensation reaction was followed. 5,6-Dimethylbenzimidazole (14.6 g, 100 mmol) was dissolved in anhydrous THF (230 mL) and transferred dropwise to the THF (150 mL) solution containing 1.2 equiv. of NaH (60% in mineral oil, 4.8 g, 120 mmol) at 0 °C. (Note: NaH was pre-washed with dry hexane, 10 mL × 3, under nitrogen). The mixture was stirred for 1 h at room temperature. Then, 1.1 equiv. of *N*,*N*-diisopropylcarbamoylchloride (18.0 g, 110 mmol) was added directly to the reaction and the mixture was refluxed for 1 h and stirred at room temperature for overnight. Solvent was removed under reduced pressure. Ethyl acetate (~500 mL) and water (~200 mL) were added to the mixture and the aqueous phase was separated. The organic phase was further washed with brine (~100 mL × 3), and dried by Na_2SO_4 and concentrated. The concentrated mixture was applied to 2 × 2 inch silica pad and eluted with ethyl acetate. After the solvent was removed under vacuum, the pale yellow powder (25.2 g, 92%) was obtained after re-crystallization from ethyl acetate/hexane. Melting point: 117.1-119.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.44 (d, J = 6.8 Hz, 12H), 2.41 (d, J = 2.8 Hz, 6H), 3.79-3.86 (m, 2H), 7.41 (s, 1H), 7.58 (s, 1H), 7.95 (s, 1H); ^{13}C NMR (100MHz,

$CDCl_3$) δ 20.0, 20.3, 20.8, 48.8, 112.2, 120.1, 130.9, 132.1, 133.5, 139.4, 141.5, 149.7; IR (cm^{-1}) 2971.93, 1681.36, 1496.99, 1433.01, 1345.52, 1304.23, 1248.68, 1211.19, 1144.93, 1097.41, 1044.36, 1019.94, 994.95, 909.64, 842.74, 754.86, 646.71, 616.50, 585.00, 554.32, 524.15, 433.79; MS (EI): *m/z* (relative intensity) 273 (M^+, 42), 173 (11), 145 (26), 128 (61), 86 (100); HRMS: calcd. for $C_{16}H_{23}N_3OH^+$: 274.1919, found 274.1922.

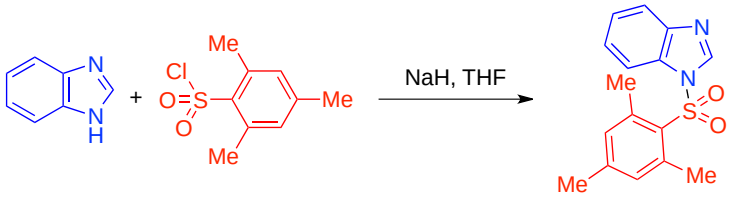
1-(2,4,6-Triisopropylphenylsulfonyl)-1*H*-benzo[*d*]imidazole (**Table 2.10**, entry 3)



General procedure for condensation reaction was followed. Benzimidazole (2.36 g, 20.0 mmol) was dissolved in anhydrous THF (20 mL) and added dropwise to the THF (25 mL) solution containing 1.2 equiv. of NaH (60% in mineral oil, 0.96 g, 24.0 mmol) at 0 °C. (Note: NaH was pre-washed with dry hexane, 10 mL × 3, under nitrogen). The mixture was stirred for 30 min at room temperature. Then, 1.1 equiv. of 2,4,6-triisopropylbenzenesulfonyl chloride (6.66 g, 22 mmol) was added directly to the reaction and the mixture was refluxed for 30 min and stirred at room temperature for overnight. Solvent was removed under reduced pressure. Ethyl acetate (~300 mL) and water (~100 mL) were added to the mixture and the aqueous phase was separated. The organic phase was further washed with brine (~50 mL × 3), and dried by Na_2SO_4 and concentrated. The concentrated mixture was applied to 1 × 1 inch silica pad and eluted with ethyl acetate. After the solvent was removed under vacuum, the white crystal (6.50 g, 85%) was obtained after re-crystallization from ethyl

acetate/hexane. Melting point: 134.6-136.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.14 (d, J = 6.8 Hz, 12H), 1.26 (d, J = 6.8 Hz, 6H), 2.93 (septet, J = 7.2 Hz, 1H), 4.18 (septet, J = 6.8 Hz, 2H), 7.23 (s, 2H), 7.28-7.35 (m, 3H), 7.80 (d, J = 8.0 Hz, 1H), 8.36 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 23.5, 24.3, 29.5, 34.2, 111.6, 120.9, 124.2, 124.5, 125.1, 130.0, 131.2, 140.5, 143.4, 151.6, 155.5; IR (cm^{-1}) 3447.58, 3128.15, 3057.52, 3032.29, 2967.19, 2929.17, 2870.96, 1781.20, 1611.42, 1597.78, 1555.05, 1495.68, 1475.97, 1460.62, 1447.83, 1387.03, 1371.52, 1344.48, 1306.68, 1293.92, 1258.78, 1197.09, 1182.66, 1173.06, 1159.16, 1141.02, 1104.25, 1071.32, 1061.47, 1038.33, 1022.20, 1009.98, 957.90, 939.78, 930.63, 892.40, 884.25, 844.06, 781.29, 761.95, 754.37, 743.33, 675.47; MS (EI): *m/z* (relative intensity) 384 (M^+, 35), 305 (17), 267 (100), 251 (61), 218 (54), 203 (43), 175 (79), 159 (24), 133 (33), 118 (99), 91 (85); HRMS: calcd. for $C_{22}H_{28}N_2O_2SH^+$: 385.1950, found 385.1952.

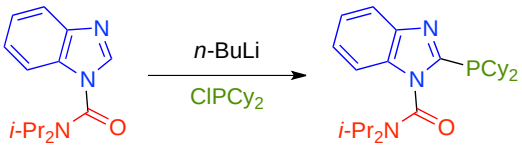
1-(Mesitylsulfonyl)-1*H*-benzo[*d*]imidazole (**Table 2.10**, entry 4)



General procedure for condensation reaction was followed. Benzimidazole (2.36 g, 20.0 mmol) was dissolved in anhydrous THF (20 mL) and added dropwise to the THF (25 mL) solution containing 1.2 equiv. of NaH (60% in mineral oil, 0.96 g, 24.0 mmol) at 0 °C. (Note: NaH was pre-washed with dry hexane, 10 mL × 3, under nitrogen). The mixture was stirred for 30 min at room temperature. Then, 1.1 equiv. of 2-mesitylenesulfonyl chloride (4.81 g, 22 mmol) was added directly to the reaction and the mixture was refluxed for 30 min and

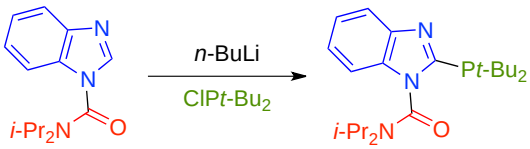
stirred at room temperature for overnight. Solvent was removed under reduced pressure. Ethyl acetate (~300 mL) and water (~100 mL) were added to the mixture and the aqueous phase was separated. The organic phase was further washed with brine (~50 mL × 3), and dried by Na_2SO_4 and concentrated. The concentrated mixture was applied to 1 × 1 inch silica pad and eluted with ethyl acetate. After the solvent was removed under vacuum, the white crystal (3.69 g, 62%) was obtained after re-crystallization from ethyl acetate/hexane. Melting point: 113.7-115.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 3H), 2.60 (s, 1H). 7.01 (s, 2H), 7.27-7.36 (m, 3H), 7.81 (d, J = 8.0 Hz, 1H), 8.45 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 21.0, 22.5, 111.6, 121.0, 124.3, 125.2, 130.8, 131.3, 132.6, 140.4, 141.4, 143.7, 145.1; IR (cm^{-1}) 3447.21, 3125.47, 2980.62, 1772.53, 1700.33, 1684.45, 1653.26, 1635.63, 1616.87, 1601.46, 1576.53, 1559.09, 1539.82, 1521.46, 1516.93, 1506.62, 1496.31, 1472.33, 1445.56, 1419.45, 1401.03, 1387.17, 1352.33, 1309.51, 1288.61, 1253.98, 1190.14, 1165.72, 1127.65, 1056.36, 1033.40, 1021.04, 939.68, 893.10, 882.96, 857.45, 779.42, 765.57, 749.40, 711.67, 677.48, 650.43, 616.39, 590.90, 580.23, 526.97, 486.01, 418.71; MS (EI): *m/z* (relative intensity) 300 (M^+, 28), 235 (7), 183 (9), 119 (100), 103 (7), 91 (24), 77 (11), 63 (7); HRMS: calcd. for $C_{16}H_{16}N_2O_2SH^+$: 301.1011, found 301.0998.

2-(Dicyclohexylphosphino)-*N*,*N*-diisopropyl-1*H*-benzo[*d*]imidazole-1-carboxamide (PCy Amizole-phos **L2a**) (**Table 2.11**, entry 1)



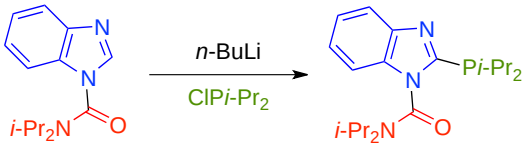
General procedure for ligand synthesis: *N*,*N*-Diisopropyl-1*H*-benzo[*d*]imidazole-1-carboxamide (1.23 g, 5.0 mmol) was dissolved in freshly distilled THF (30 mL) at room temperature under nitrogen. The solution was cooled to -78 °C in dry ice/acetone bath. Titrated *n*-BuLi (5.5 mmol) was added dropwise by syringe. After the reaction mixture was stirred for an hour at -78 °C, chlorodicyclohexylphosphine (1.33 mL, 6.0 mmol) dissolved in 5 ml THF was added dropwise by syringe. The reaction was allowed to warm to room temperature and stirred overnight. MeOH (~10 mL) was added slowly to quench the reaction. Solvent was removed under vacuum. The crude product was applied to column chromatography and the pure product was then dried under vacuum. White solid (1.61g, 73%) was obtained. Melting point: 205.2-206.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11-2.70 (m, 34H), 3.39-3.60 (m, 2H), 7.29-7.36 (m, 3 H), 7.89-7.91 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 20.8, 26.2, 27.0, 30.0, 33.0, 34.9, 110.0, 120.0, 122.7, 123.5, 133.9, 143.7, 150.0, 153.0, 153.3 (Complex unresolved C-P splitting was observed); ^{31}P NMR (202 MHz, $CDCl_3$) δ -15.95; IR (cm^{-1}) 2926.88, 2848.80, 1693.42, 1437.21, 1371.58, 1329.53, 1300.93, 1255.22, 1201.02, 1147.90, 1028.78, 1002.16, 829.67, 748.43; MS (EI): *m/z* (relative intensity) 440 (M^+, 3), 398 (31), 358 (73), 276 (33), 244 (100), 231 (25), 198 (14), 149 (29); HRMS: calcd. for $C_{26}H_{40}N_3OPH^+$: 442.2987, found 442.3004.

2-(Di-*tert*-butylphosphino)-*N*,*N*-diisopropyl-1*H*-benzo[*d*]imidazole-1-carboxamide (P*t*-Bu Amizole-phos **L2b**) (**Table 2.11**, entry 2)



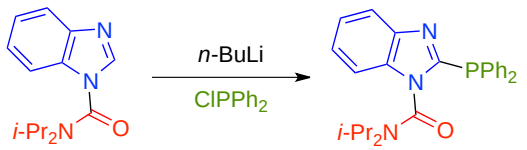
General procedure for ligand synthesis was followed. *N*,*N*-Diisopropyl-1*H*-benzo[*d*]imidazole-1-carboxamide (1.23 g, 5.0 mmol), titrated *n*-BuLi (5.5 mmol), and di-*tert*-butylchlorophosphine (1.14 mL, 6.0 mmol) were used to afford 2-(di-*tert*-butylphosphino)-*N*,*N*-diisopropyl-1*H*-benzo[*d*]imidazole-1-carboxamide (1.26 g, 65%) as white solid compound. Melting point: 179.2-181.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11-1.71 (m, 30H), 3.63 (m, 2H), 7.28-7.37 (m, 3H), 7.86-7.89 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 20.3, 21.4, 30.3, 30.5, 33.7, 46.7, 51.1, 110.2, 120.3, 122.6, 123.6, 132.9, 133.8, 133.8, 143.9, 149.8, 153.0, 153.5 (Complex unresolved C-P splitting was observed); ^{31}P NMR (202 MHz, $CDCl_3$) δ 14.35; IR (cm^{-1}) 2966.55, 1698.01, 1467.64, 1436.03, 1369.71, 1320.08, 1257.55, 1200.60, 1072.82, 1029.41, 914.88, 827.80, 748.38, 596.73, 546.15; MS (EI): *m/z* (relative intensity) 388 (M^+, 0), 346 (2), 332 (100), 276 (12), 234 (11), 205 (15), 149 (8); HRMS: calcd. for $C_{22}H_{36}N_3OPH^+$: 390.2674, found 390.2676.

2-(Diisopropylphosphino)-*N*,*N*-diisopropyl-1*H*-benzo[*d*]imidazole-1-carboxamide (P*i*-Pr Amizole-phos **L2c**) (**Table 2.11**, entry 3)



General procedure for ligand synthesis was followed. *N*,*N*-Diisopropyl-1*H*-benzo[*d*]imidazole-1-carboxamide (1.23 g, 5.0 mmol), titrated *n*-BuLi (5.5 mmol), and chlorodiisopropylphosphine (0.95 mL, 6.0 mmol) were used to afford 2-(diisopropylphosphino)-*N*,*N*-diisopropyl-1*H*-benzo[*d*]imidazole-1-carboxamide (1.21 g, 67%) as orange solid compound. Melting point: 103.4-104.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.12-1.66 (m, 26H), 2.19-2.79 (m, 2H), 3.48-3.53 (m, 2H), 7.29-7.37 (m, 3H), 7.86-7.89 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 19.7, 20.6, 23.1, 25.1, 110.0, 120.0, 122.7, 123.6, 133.8, 133.9, 143.6, 149.5, 153.2, 153.5 (Complex unresolved C-P splitting was observed); ^{31}P NMR (202 MHz, $CDCl_3$) δ -7.66; IR (cm^{-1}) 2967.35, 2869.78, 1696.43, 1456.76, 1434.64, 1373.05, 1330.37, 1304.47, 1258.39, 1206.15, 1151.88, 1032.17, 829.88, 746.24; MS (EI): *m/z* (relative intensity) 361 (M^+, 2), 318 (2), 276 (37), 244 (18), 233 (18), 191 (24), 149 (17); HRMS: calcd. for $C_{20}H_{32}N_3OPH^+$: 362.2361, found 362.2365.

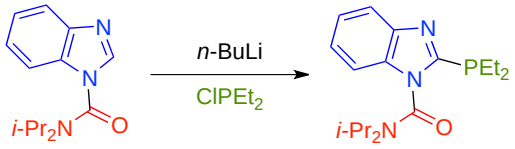
2-(Diphenylphosphino)-*N*,*N*-diisopropyl-1*H*-benzo[*d*]imidazole-1-carboxamide (PPh Amizole-phos **L2d**) (**Table 2.11**, entry 4)



General procedure for ligand synthesis was followed. *N*,*N*-Diisopropyl-1*H*-benzo[*d*]imidazole-1-carboxamide (1.23 g, 5.0 mmol), titrated *n*-BuLi (5.5

mmol), and chlorodiphenylphosphine (1.33 mL, 6.0 mmol) were used to afford 2-(diphenylphosphino)-*N*,*N*-diisopropyl-1*H*-benzo[*d*]imidazole-1-carboxamide (1.24 g, 58%) as white solid compound. Melting point: 182.5-184.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22-1.46 (m, 12H), 3.48-3.60 (m, 2H), 7.28-7.39 (m, 9H), 7.60-7.87 (m, 4H), 7.872 (d, J = 0.8Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 20.5, 49.2, 110.1, 120.7, 123.0, 124.1, 128.5, 128.6, 129.3, 133.9, 134.1, 134.2, 144.0, 149.4, 152.7, 152.8 (Complex unresolved C-P splitting was observed); ^{31}P NMR (202 MHz, $CDCl_3$) δ -25.44; IR (cm^{-1}) 2974.70, 1694.01, 1434.97, 1371.91, 1332.10, 1303.00, 1255.05, 1201.96, 1154.08, 1028.23, 829.83, 747.36, 693.97; MS (EI): *m/z* (relative intensity) 428 (M^+, 1), 386 (14), 344 (57), 301 (25), 244 (100), 223 (20), 201 (29), 183 (45), 159 (16); HRMS: calcd. for $C_{26}H_{28}N_3OPH^+$: 430.2048, found 430.2047.

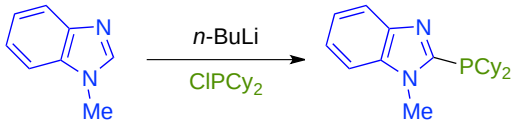
2-(Diethylphosphino)-*N*,*N*-diisopropyl-1*H*-benzo[*d*]imidazole-1-carboxamide (PEt Amizole-phos **L2e**) (**Table 2.11**, entry 5)



General procedure for ligand synthesis was followed. *N*,*N*-Diisopropyl-1*H*-benzo[*d*]imidazole-1-carboxamide (1.23 g, 5.0 mmol), titrated *n*-BuLi (5.5 mmol), and chlorodiethylphosphine (0.73 mL, 6.0 mmol) were used to afford 2-(diethylphosphino)-*N*,*N*-diisopropyl-1*H*-benzo[*d*]imidazole-1-carboxamide (0.86 g, 52%) as white solid compound. Melting point: 89.6-92.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.12-1.16 (m, 6H), 1.45 (d, J = 6.4 Hz, 12H), 1.88-1.98 (m, 2H), 2.12-2.19 (m, 2H), 3.52 (t, J = 5.6 Hz, 2H), 7.29-7.34 (m, 3H), 7.86-7.87 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 9.8, 10.0, 18.4, 20.1, 20.4, 20.6, 109.8, 119.8,

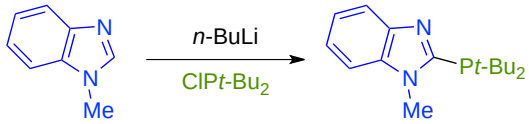
120.9, 122.8, 123.6, 134.2, 143.6, 149.7, 155.1, 155.3 (Complex unresolved C-P splitting was observed); ^{31}P NMR (202 MHz, $CDCl_3$) δ -28.99; IR (cm^{-1}) 2964.92, 2931.77, 2873.92, 1692.74, 1458.29, 1430.67, 1372.97, 1329.45, 1303.45, 1261.05, 1205.70, 1154.14, 1029.23, 830.66, 744.74; MS (EI): *m/z* (relative intensity) 332 (M^+, 3), 304 (45), 290 (38), 262 (15), 248 (100), 228 (23), 207 (22), 177 (28), 149 (28); HRMS: calcd. for $C_{18}H_{28}N_3OPH^+$: 334.2048, found 334.2043.

2-(Dicyclohexylphosphino)-1-methyl-1*H*-benzo[*d*]imidazole (PCy Mezole-phos **L2f**) (**Table 2.11**, entry 6)



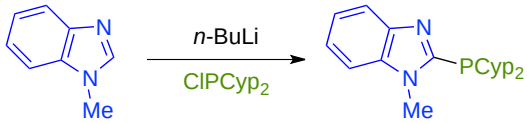
General procedure for ligand synthesis was followed. 1-Methylbenzimidazole (0.66 g, 5.0 mmol) which is commercially available, titrated *n*-BuLi (5.5 mmol), and chlorodicyclohexylphosphine (1.33 mL, 6.0 mmol) were used to afford 2-(dicyclohexylphosphino)-1-methyl-1*H*-benzo[*d*]imidazole (0.98 g, 60%) as white solid compound. Melting point: 113.2-114.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21-1.39 (m, 10H), 1.76-1.80 (m, 8H), 1.97-1.99 (m, 2H), 2.32-2.39 (m, 2H), 3.98 (d, J = 1.6 Hz, 2H), 7.30-7.41 (m, 3H), 7.87-7.91 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 26.2, 26.6, 26.8, 27.0, 29.2, 29.3, 30.2, 30.3, 31.1, 31.3, 33.4, 33.5, 109.4, 119.8, 121.9, 122.5, 136.3, 144.1, 154.4, 154.6 (Complex unresolved C-P splitting was observed); ^{31}P NMR (202 MHz, $CDCl_3$) δ -22.55; IR (cm^{-1}) 2921.43, 2847.08, 1443.52, 1406.85, 1318.98, 1270.75, 1235.00, 1002.19, 809.49, 758.68, 724.40; MS (EI): *m/z* (relative intensity) 328 (M^+, 8), 245 (100), 213 (2), 164 (25); HRMS: calcd. for $C_{20}H_{29}N_2PH^+$: 329.2147, found 329.2133.

2-(Di-*tert*-butylphosphino)-1-methyl-1*H*-benzo[*d*]imidazole (P*t*-Bu Mezole-phos **L2g**) (**Table 2.11**, entry 7)



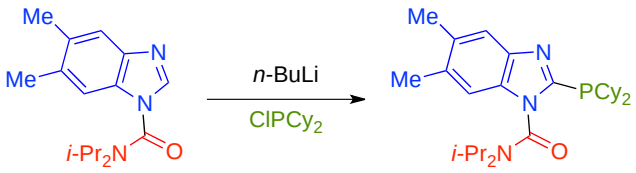
General procedure for ligand synthesis was followed. 1-Methylbenzimidazole (0.66 g, 5.0 mmol) which is commercially available, titrated *n*-BuLi (5.5 mmol), and di-*tert*-butylchlorophosphine (1.33 mL, 6.0 mmol) were used to afford 2-(di-*tert*-butylphosphino)-1-methyl-1*H*-benzo[*d*]imidazole (0.51 g, 37%) as white solid compound. Melting point: 91.7-92.1 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 1.29 (s, 9H), 1.32 (s, 9H), 4.03 (s, 3H), 7.27-7.34 (m, 2H), 7.44 (d, J = 7.2 Hz, 1H), 7.80 (d, J = 7.2 Hz, 1H); ^{13}C NMR (100MHz, CD_2Cl_2) δ 29.7, 29.8, 31.2, 31.4, 33.1, 33.3, 109.7, 109.8, 119.7, 121.7, 122.4, 135.8, 144.0, 154.8, 155.0 (Complex unresolved C-P splitting was observed); ^{31}P NMR (202 MHz, CD_2Cl_2) δ 5.97; IR (cm^{-1}) 3061.02, 3046.17, 2971.12, 2939.42, 2858.50, 2361.90, 1928.69, 1893.90, 1776.58, 1672.39, 1608.70, 1591.17, 1481.15, 1467.01, 1454.30, 1430.03, 1404.22, 1384.08, 1365.23, 1351.58, 1335.71, 1314.41, 1275.81, 1232.62, 1211.35, 1176.15, 1149.73, 1137.35, 1078.10, 1027.46, 1014.59, 1004.86, 965.92, 960.42, 931.89, 896.78, 808.51, 767.34, 743.75, 726.76, 686.94, 601.94, 574.85, 555.50, 546.14, 459.20, 446.09, 416.94; MS (EI): *m/z* (relative intensity) 276 (M^+, 21), 220 (62), 205 (65), 164 (100); HRMS: calcd. for $C_{16}H_{25}N_2PH^+$: 277.1834, found 227.1825.

2-(Dicyclopentylphosphino)-1-methyl-1*H*-benzo[*d*]imidazole (PCyp Mezole-phos **L2h**) (**Table 2.11**, entry 8)



General procedure for ligand synthesis was followed. 1-Methylbenzimidazole (0.66 g, 5.0 mmol) which is commercially available, titrated *n*-BuLi (5.5 mmol), and chlorodicyclopentylphosphine (1.29 mL, 6.0 mmol) were used to afford 2-(dicyclopentylphosphino)-1-methyl-1*H*-benzo[*d*]imidazole (1.17 g, 65%) as white solid compound. Melting point: 74.5-78.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26-1.29 (m, 2H), 1.48-1.73 (m, 12H), 2.02-2.06 (m, 2H), 2.63-2.66 (m, 2H), 4.01 (d, J = 1.6 Hz, 3H), 7.29-7.32 (m, 2H), 7.38-7.40 (m, 1H), 7.85-7.87 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 25.5, 26.5, 26.6, 31.1, 37.0, 37.1, 110.0, 120.0, 122.0, 122.6, 136.1, 144.1, 156.8, 157.0 (Complex unresolved C-P splitting was observed); ^{31}P NMR (202 MHz, $CDCl_3$) δ -24.34; IR (cm^{-1}) 2944.91, 2857.45, 1447.26, 1406.21, 1365.01, 1314.55, 1272.97, 1233.63, 1129.77, 1084.77, 904.08, 807.87, 733.84, 681.80, 541.10, 427.17; MS (EI): *m/z* (relative intensity) 300 (M^+, 11), 231 (100), 199 (5), 164 (27); HRMS: calcd. for $C_{18}H_{25}N_2PH^+$: 301.1834, found 301.1826.

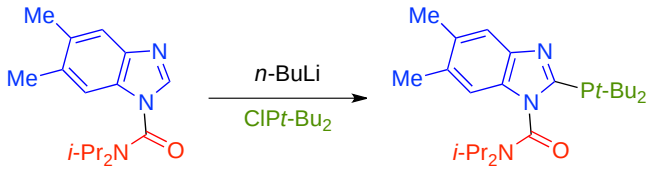
2-(Dicyclohexylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole -1-carboxamide (PCy Amizole[M2]-phos **L2i**) (**Table 2.11**, entry 9)



N,*N*-Diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide (1.365 g, 5.0 mmol) was dissolved in freshly distilled THF (2 mL) and toluene (40 mL, the reaction mixture THF/toluene = 1:20) at room temperature under nitrogen atmosphere. The solution was cooled to -98 °C in methanol/liquid N_2 bath. Titrated *n*-BuLi (5.5 mmol) was added dropwise by syringe. The reaction mixture was further stirred for 10 min at -98 °C and chlorodicyclohexylphosphine (1.33 mL, 6.0 mmol) was then added dropwise by syringe. The reaction was allowed to reach room temperature and stirred for 3 h. MeOH (~10 mL) was added slowly to quench the reaction. Solvent was removed under reduced pressure. Ethyl acetate (~200 mL) and water (~100 mL) were added to the mixture and the aqueous phase was separated. The organic phase was further washed with brine (~50 mL × 3), and dried by Na_2SO_4 and concentrated. The concentrated mixture was applied to 1 × 1 inch silica pad and eluted with diethyl ether. After the solvent was removed under vacuum, the white crystals (1.81 g, 77%) were obtained after re-crystallization from ether/hexane. Melting point: 162.5-165.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26-1.95 (m, 34H), 2.39 (d, J = 3.6 Hz, 6H), 3.49 (m, 2H), 7.09 (s, 1H), 7.65 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 19.9, 20.2, 20.4, 20.5, 20.6, 46.2, 50.6, 110.4, 120.7, 131.0, 132.2, 133.6, 139.9, 146.8, 149.2, 160.5 (Complex unresolved C-P splitting was observed); ^{31}P NMR (202 MHz, $CDCl_3$) δ -16.35; IR (cm^{-1}) 2970.33, 1697.80, 1634.45, 1515.61, 1438.33, 1373.10, 1331.74, 1298.93,

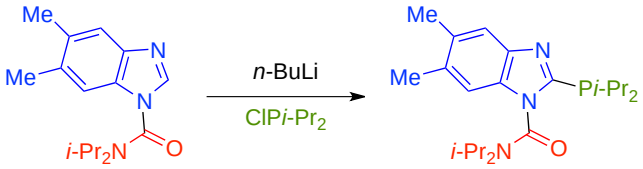
1234.28, 1208.02, 1157.10, 1035.95, 810.58, 626.04; MS (EI): *m/z* (relative intensity) 468 (M^+, 9), 426 (27), 386 (64), 343 (9), 304 (18), 272 (100), 259 (23), 177 (55); HRMS: calcd. for $C_{28}H_{44}N_3OPH^+$: 470.3300, found 470.3292.

2-(Di-*tert*-butylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide (P*t*-Bu Amizole^{M2}-phos **L2j**) (**Table 2.11**, entry 10)



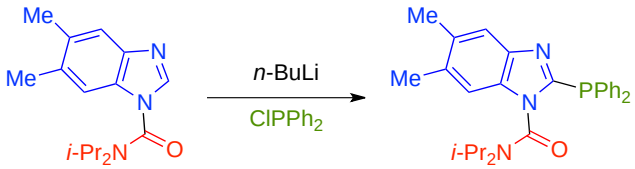
General procedure for ligand synthesis was followed. *N*,*N*-Diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide (1.365 g, 5.0 mmol), titrated *n*-BuLi (5.5 mmol), and di-*tert*-butylchlorophosphine (1.14 mL, 6.0 mmol) were used to afford 2-(di-*tert*-butylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide (1.00g, 48%) as white solid compound. Melting point: 168.4-171.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.14-1.68 (m, 30H), 2.63 (d, J = 2.8 Hz, 6H), 3.62-3.65 (m, 2H), 7.10 (s, 1H), 7.65 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 20.2, 20.5, 30.3, 30.5, 33.7, 110.3, 120.2, 131.5, 132.4, 132.9, 142.6, 150.1, 151.9, 152.2 (Complex unresolved C-P splitting was observed); ^{31}P NMR (202 MHz, $CDCl_3$) δ 13.95; IR (cm^{-1}) 2966.65, 1696.82, 1466.79, 1436.62, 1368.95, 1311.06, 1202.72, 1169.01, 1061.29, 1026.91, 910.66, 889.34, 864.47, 837.57, 807.97, 623.78, 591.78, 527.86; MS (EI): *m/z* (relative intensity) 416 (M^+, 0), 374 (3), 360 (100), 318 (5), 304 (10), 262 (15), 233 (28), 177 (20); HRMS: calcd. for $C_{24}H_{40}N_3OPH^+$: 418.2987, found 418.2992.

2-(Diisopropylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide (P*i*-Pr Amizole[M2]-phos **L2k**) (**Table 2.11**, entry 11)



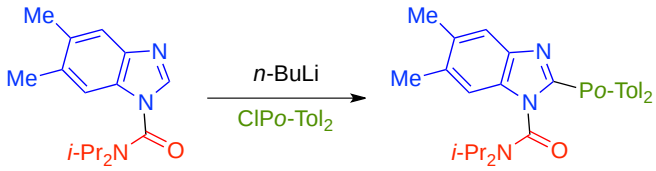
General procedure for ligand synthesis was followed. *N*,*N*-Diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide (1.365 g, 5.0 mmol), titrated *n*-BuLi (5.5 mmol), and chlorodiisopropylphosphine (0.95 mL, 6.0 mmol) were used to afford 2-(diisopropylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide (1.11 g, 57%) as orange solid compound. Melting point: 94.8-96.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07-1.95 (m, 26H), 2.39 (d, J = 2.0 Hz, 6H), 3.51 (s, 2H), 7.10 (s, 1H), 7.63 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 19.7, 20.2, 20.4, 20.6, 110.1, 119.8, 131.6, 132.5, 132.9, 142.3, 149.8, 152.0, 152.3 (Complex unresolved C-P splitting was observed); ^{31}P NMR (202 MHz, $CDCl_3$) δ -8.07; IR (cm^{-1}) 2963.39, 2868.49, 1695.01, 1464.11, 1434.71, 1373.01, 1332.31, 1308.69, 1209.16, 1154.84, 1027.41, 1003.84, 878.00, 838.52, 619.02; MS (EI): *m/z* (relative intensity) 389 (M^+, 2), 346 (100), 304 (46), 273 (15), 262 (18), 219 (28), 177 (28), 86 (18); HRMS: calcd. for $C_{22}H_{36}N_3OPH^+$: 390.2674, found 390.2660.

2-(Diphenylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide (PPh Amizole^{M2}-phos **L2l**) (**Table 2.11**, entry 12)



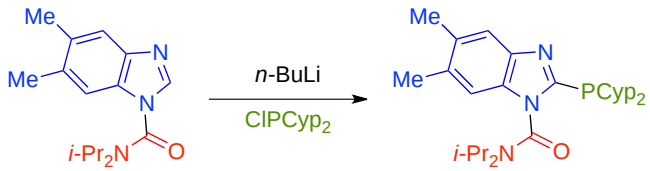
General procedure for ligand synthesis was followed. *N*,*N*-Diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide (1.365 g, 5.0 mmol), titrated *n*-BuLi (5.5 mmol), and chlorodiphenylphosphine (0.53 mL, 2.4 mmol) were used to afford 2-(diphenylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide (0.38 g, 42%) as white solid compound. Melting point: 174.6-176.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28-1.37 (m, 12H), 2.38 (d, J = 5.6 Hz, 6H), 3.4-3.61 (m, 2H), 7.11-7.36 (m, 7H), 7.55-8.33 (m, 5H); ^{13}C NMR (100MHz, $CDCl_3$) δ 20.2, 20.5, 110.2, 120.6, 128.4, 128.5, 129.1, 132.0, 132.8, 132.9, 133.5, 133.8, 134.0, 134.5, 142.7, 149.7, 151.4, 151.5 (Complex unresolved C-P splitting was observed); ^{31}P NMR (202 MHz, $CDCl_3$) δ -25.66; IR (cm^{-1}) 3050.16, 2967.16, 2928.78, 1691.23, 1434.42, 1405.18, 1371.81, 1334.72, 1304.95, 1208.83, 1152.97, 1090.58, 1025.99, 883.41, 840.40, 746.11, 692.54, 623.60, 586.65, 507.68, 431.67; MS (EI): *m/z* (relative intensity) 456 (M^+, 1), 414 (15), 372 (45), 346 (9), 329 (27), 272 (100), 256 (22), 201 (25), 183 (49); HRMS: calcd. for $C_{28}H_{32}N_3OPH^+$: 458.2361, found 458.2369.

2-(Di*o*-tolylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide (P*o*-Tol Amizole[M2]-phos **L2m**) (**Table 2.11**, entry 13)



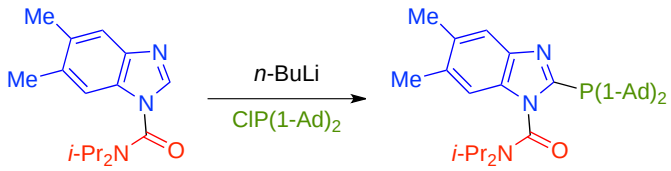
General procedure for ligand synthesis was followed. *N*,*N*-Diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide (1.365 g, 5.0 mmol), titrated *n*-BuLi (5.5 mmol), and chlorodi(*o*-tolyl)phosphine (1.492 g, 6.0 mmol) were used to afford 2-(di*o*-tolylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide (1.60 g, 77%) as white solid compound. Melting point: 188.2-191.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22-1.46 (m, 12H), 2.38 (d, J = 6.8 Hz, 6H), 2.42 (s, 6H), 3.50-3.58 (m, 2H), 7.11-7.31 (m, 9H), 7,61 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 20.2, 20.5, 20.6, 21.0, 21.3, 110.2, 120.5, 125.6, 126.3, 128.5, 129.2, 130.0, 131.7, 131.9, 132.0, 133.1, 133.2, 133.3, 133.6, 135.0, 142.2, 142.4, 142.9, 149.6, 150.7, 150.8 (Complex unresolved C-P splitting was observed); ^{31}P NMR (202 MHz, $CDCl_3$) δ -39.43; IR (cm^{-1}) 3051.33, 2966.69, 1690.59, 14444.41, 1372.89, 1327.06, 1204.19, 1155.99, 1058.60, 835.46, 748.82, 714.18, 586.55, 447.71; MS (EI): *m/z* (relative intensity) 442 (M^+, 9), 400 (18), 357 (19), 272 (100), 229 (18), 207 (73), 187 (19), 165 (13); HRMS: calcd. for $C_{30}H_{36}N_3OPH^+$: 486.2674, found 486.2661.

2-(Dicyclopentylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole -1-carboxamide (PCyp Amizole^{M2}-phos **L2n**) (**Table 2.11**, entry 14)



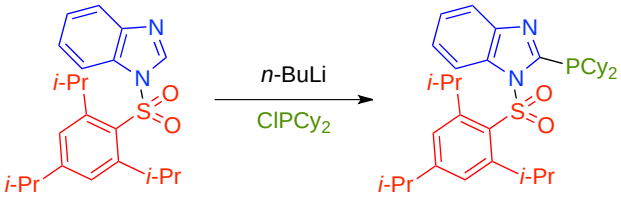
General procedure for ligand synthesis was followed. *N*,*N*-Diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide (1.365 g, 5.0 mmol), titrated *n*-BuLi (5.5 mmol), and chlorodicyclopentylphosphine (1.29 mL, 6.0 mmol) were used to afford 2-(dicyclopentylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide (1.37 g, 62%) as white solid compound. Melting point: 171.4-172.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27-2.44 (m, 30H), 2.54 (s, 6H), 3.54 (s, 2H), 7.10 (s, 1H), 7.61 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 20.2, 20.4, 25.5, 26.3, 30.5, 30.7, 110.1, 119.7, 131.6, 132.2, 132.8, 142.3, 149.7, 154.0, 154.2 (Complex unresolved C-P splitting was observed); ^{31}P NMR (202 MHz, $CDCl_3$) δ -19.70; IR (cm^{-1}) 2952.49, 2864.67, 1696.68, 1436.25, 1372.36, 1331.78, 1305.86, 1211.37, 1157.86, 1060.90, 1027.97, 1003.17, 894.49, 842.03, 625.66, 586.69, 523.09; MS (EI): *m/z* (relative intensity) 440 (M^+, 3), 398 (32), 358 (75), 331 (8), 315 (10), 276 (34), 259 (7), 244 (100), 228 (27); HRMS: calcd. for $C_{26}H_{40}N_3OPH^+$: 442.2987, found 442.2970.

2-(Di-1-adamantylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*] imidazole-1-carboxamide (P1-Ad Amizole[M2]-phos **L2o**) (**Table 2.11**, entry 15)



N,*N*-Diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide (0.735 g, 2.7 mmol) was dissolved in freshly distilled THF (2 mL) and toluene (30 mL) at room temperature under nitrogen atmosphere. The solution was cooled to -98 °C in methanol/liquid N_2 bath. Titrated *n*-BuLi (3.15 mmol) was added dropwise by syringe. The reaction mixture was further stirred for 10 min at -98 °C and chlorodi-1-adamantylphosphine (1.11 g, in THF/toluene, 5 mL/5 mL) was then added dropwise by syringe. The reaction was allowed to reach room temperature and stirred for overnight. MeOH (~10 mL) was added slowly to quench the reaction. Solvent was removed under reduced pressure. The white powder (0.29 g, 19%) were obtained after running column chromatography by E.A./hexane (1:9) system. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 0.93-2.42 (m, 48H), 3.65 (s, 2H), 7.13 (s, 1H), 7.61 (s, 1H); ^{13}C NMR (100MHz, CD_2Cl_2) δ 19.9, 20.2, 21.1, 21.5, 28.9, 29.0, 36.8, 38.2, 41.3, 110.3, 119.8, 131.5, 132.4, 132.8, 142.7, 150.0, 150.1, 150.4 (Complex unresolved C-P splitting was observed); ^{31}P NMR (202 MHz, CD_2Cl_2) δ 12.94; HRMS: calcd. for $C_{36}H_{52}N_3OPH^+$: 574.3926, found 574.3933.

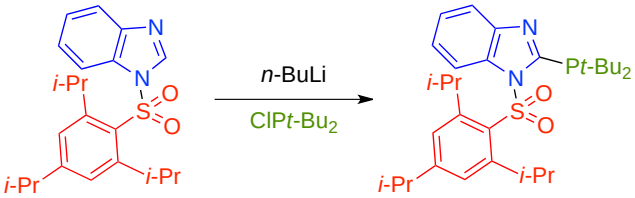
2-(Dicyclohexylphosphino)-1-(2,4,6-triisopropylphenylsulfonyl)-1*H*-benzo[*d*] imidazole (PCy ^{P3}Sulfozole-phos **L2p**) (**Table 2.11**, entry 16)



1-(2,4,6-Triisopropylphenylsulfonyl)-1*H*-benzo[*d*]imidazole (1.92 g, 5.0 mmol) was dissolved in freshly distilled THF (20 mL) and toluene (40 mL, the reaction mixture THF/toluene = 1:2) at room temperature under 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. The reaction mixture was further stirred for 15 min at -78 °C and chlorodicyclohexylphosphine (1.33 mL, 6.0 mmol) was then added dropwise by syringe. The reaction was allowed to reach room temperature and stirred for overnight. MeOH (~10 mL) was added slowly to quench the reaction. Solvent was removed under reduced pressure. Ethyl acetate (~200 mL) and water (~100 mL) were added to the mixture and the aqueous phase was separated. The organic phase was further washed with brine (~50 mL × 3), and dried by Na_2SO_4 and concentrated. The concentrated mixture was applied to 1 × 1 inch silica pad and eluted with diethyl ether. After the solvent was removed under vacuum, the white crystals (1.81 g, 77%) were obtained after re-crystallization from ether/hexane. Melting point: 208.8-210.0 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 0.87-1.36 (m, 30H), 1.53-1.86 (m, 8H), 2.05-2.11 (m, 2H), 2.91-2.98 (m, 1H), 4.23-4.29 (m, 2H), 7.20 (s, 2H), 7.37-7.44 (m, 2H), 7.78 (d, J = 7.2 Hz, 1H), 8.09 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100MHz, CD_2Cl_2) δ 26.7, 26.8, 26.9, 29.2, 29.3, 29.5, 29.6, 29.8, 34.3, 34.7, 34.8, 113.9, 120.1, 123.7, 123.8, 124.9, 133.8, 134.3, 142.8, 151.6, 155.0, 155.9, 156.3

(Complex unresolved C-P splitting was observed); ^{31}P NMR (202 MHz, CD_2Cl_2) δ -14.25; IR (cm^{-1}) 3447.50, 3048.54, 2927.62, 2850.75, 1599.22, 1583.18, 1560.10, 1550.26, 1459.10, 1445.69, 1426.76, 1375.85, 1346.95, 1332.42, 1292.71, 1251.55, 1229.16, 1181.46, 1157.48, 1142.31, 1106.33, 1057.58, 1037.79, 1023.23, 1011.10, 938.35, 902.43, 881.00, 850.61, 844.69, 816.68, 765.34, 746.69, 671.77, 654.25, 646.00, 624.02, 607.44, 575.97, 557.33, 542.45, 523.35, 433.64, 418.76; MS (EI): *m/z* (relative intensity) 580 (M^+, 0), 383 (100), 231 (23), 207 (19); HRMS: calcd. for $C_{34}H_{49}N_2O_2SPH^+$: 581.3331, found 581.3306.

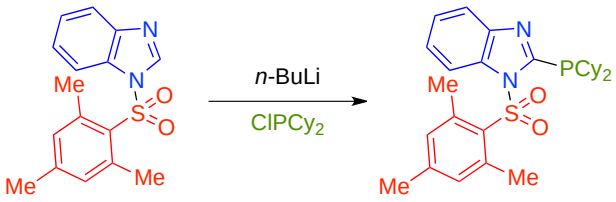
2-(Di-*tert*-butylphosphino)-1-(2,4,6-triisopropylphenylsulfonyl)-1*H*-benzo[*d*] imidazole (P*t*-Bu ^{P3}Sulfozole-phos **L2q**) (**Table 2.11**, entry 17)



1-(2,4,6-Triisopropylphenylsulfonyl)-1*H*-benzo[*d*]imidazole (1.15 g, 3.0 mmol) was dissolved in freshly distilled THF (20 mL) at room temperature under nitrogen atmosphere. The solution was cooled to -78 °C in dry ice/acetone bath. Titrated *n*-BuLi (3.3 mmol) was added dropwise by syringe. The reaction mixture was further stirred for 15 min at -78 °C and di-*tert*-butylchlorophosphine (0.68 mL, 3.6 mmol) was then added dropwise by syringe. The reaction was allowed to reach room temperature and stirred for overnight. MeOH (~10 mL) was added slowly to quench the reaction. Solvent was removed under reduced pressure. Ethyl acetate (~200 mL) and water (~100 mL) were added to the mixture and the aqueous phase was separated. The organic phase was further washed with brine

(~50 mL × 3), and dried by Na_2SO_4 and concentrated. The concentrated mixture was applied to 1 × 1 inch silica pad and eluted with diethyl ether. After the solvent was removed under vacuum, the orange solid (0.46 g, 29%) was obtained after re-crystallization from ether/hexane. Melting point: 165.6-166.2 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 1.04-1.09 (m, 30H), 1.24-1.29 (m, 8H), 2.88-2.98 (m, 1H), 4.35 (s, 2H), 7.20 (s, 2H), 7.40 (t, J = 7.6 Hz, 1H), 7.46 (t, J = 7.2 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 8.24 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100MHz, CD_2Cl_2) δ 23.2, 23.8, 24.4, 29.2, 29.3, 29.8, 29.9, 33.8, 34.0, 34.4, 114.4, 120.4, 123.6, 123.8, 125.2, 133.9, 134.2, 142.5, 151.9, 152.0, 154.8, 155.0, 155.2 (Complex unresolved C-P splitting was observed); ^{31}P NMR (202 MHz, CD_2Cl_2) δ 10.48; IR (cm^{-1}) 3287.51, 3053.72, 2966.91, 2894.06, 2865.47, 2361.74, 1601.34, 1566.93, 1460.26, 1430.30, 1374.55, 1346.83, 1331.45, 1251.48, 1225.27, 1177.87, 1130.04, 1107.20, 1070.78, 1057.94, 1035.59, 1012.81, 940.62, 903.40, 885.54, 846.26, 816.00, 762.51, 753.64, 742.24, 670.41, 627.58, 609.64, 576.50, 556.12, 547.25, 522.55, 459.86, 435.54, 434.83, 425.33; MS (EI): *m/z* (relative intensity) 528 (M^+, 13), 471 (6), 415 (7), 383 (16), 367 (34), 351 (31), 309 (21), 262 (37), 233 (12), 205 (33), 175 (20), 150 (100), 119 (24), 91 (27), 57 (56); HRMS: calcd. for $C_{30}H_{45}N_2O_2SPH^+$: 529.3018, found 529.3035.

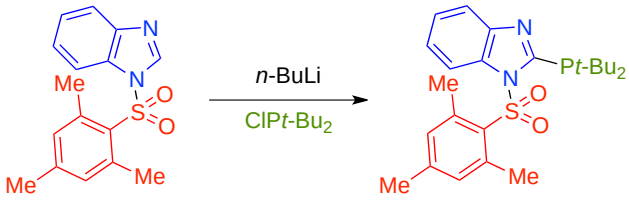
2-(Dicyclohexylphosphino)-1-(mesitylsulfonyl)-1*H*-benzo[*d*]imidazole (PCy ^{M3}Sulfozole-phos **L2r**) (**Table 2.11**, entry 18)



1-(Mesitylsulfonyl)-1*H*-benzo[*d*]imidazole (1.50 g, 5.0 mmol) was dissolved in freshly distilled THF (20 mL) and toluene (40 mL, the reaction mixture THF/toluene = 1:2) at room temperature under 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. The reaction mixture was further stirred for 15 min at -78 °C and chlorodicyclohexylphosphine (1.33 mL, 6.0 mmol) was then added dropwise by syringe. The reaction was allowed to reach room temperature and stirred for overnight. MeOH (~10 mL) was added slowly to quench the reaction. Solvent was removed under reduced pressure. Ethyl acetate (~200 mL) and water (~100 mL) were added to the mixture and the aqueous phase was separated. The organic phase was further washed with brine (~50 mL × 3), and dried by Na_2SO_4 and concentrated. The concentrated mixture was applied to 1 × 1 inch silica pad and eluted with diethyl ether. After the solvent was removed under vacuum, the white crystals (1.47 g, 60%) were obtained after re-crystallization from ether/hexane. Melting point: 169.1-170.8 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 0.89-1.35 (m, 12H), 1.55-1.81 (m, 8H), 2.05-2.11 (m, 2H), 2.34 (s, 3H), 2.47 (s, 6H), 6.99 (s, 2H), 7.37-7.44 (m, 2H), 7.79 (d, J = 6.4 Hz, 1H), 8.12 (d, J = 7.2 Hz, 1H); ^{13}C NMR (100MHz, CD_2Cl_2) δ 22.6, 26.2, 26.7, 26.8, 26.9, 29.4, 29.5, 29.7, 29.9, 34.8, 34.9, 114.7, 120.2, 123.8, 125.0, 131.8, 134.9, 135.3, 140.62, 140.64, 142.7, 144.5, 156.1, 156.5 (Complex unresolved C-P

splitting was observed); ^{31}P NMR (202 MHz, CD_2Cl_2) δ -13.58; IR (cm^{-1}) 3447.52, 2917.15, 2849.51, 1601.72, 1583.65, 1559.98, 1458.06, 1444.02, 1428.95, 1405.36, 1360.72, 1331.76, 1292.23, 1254.65, 1230.73, 1179.17, 1168.51, 1157.34, 1135.47, 1105.03, 1053.46, 1027.42, 1011.52, 903.46, 884.92, 850.87, 817.37, 768.05, 747.20, 718.29, 670.25, 643.83, 607.84, 587.04, 573.60, 562.09, 549.52, 532.72, 525.85, 510.92; MS (EI): *m/z* (relative intensity) 496 (M^+, 0), 349 (15), 299 (100), 267 (9), 207 (30), 149 (14), 117 (12); HRMS: calcd. for $C_{28}H_{37}N_2O_2SPH^+$: 497.2392, found 497.2375.

2-(Di-*tert*-butylphosphino)-1-(mesitylsulfonyl)-1*H*-benzo[*d*]imidazole (P*t*-Bu ^{M3}Sulfozole-phos **L2s**) (**Table 2.11**, entry 19)

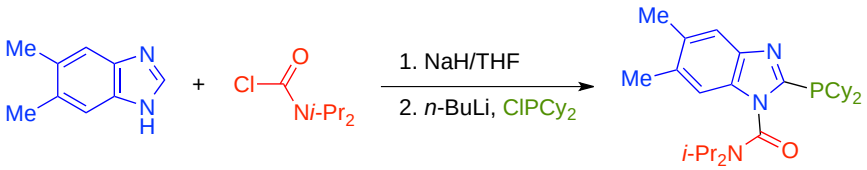


1-(Mesitylsulfonyl)-1*H*-benzo[*d*]imidazole (0.90 g, 3.0 mmol) was dissolved in freshly distilled THF (20 mL) at room temperature under nitrogen atmosphere. The solution was cooled to -78 °C in dry ice/acetone bath. Titrated *n*-BuLi (3.3 mmol) was added dropwise by syringe. The reaction mixture was further stirred for 15 min at -78 °C and di-*tert*-butylchlorophosphine (0.68 mL, 3.6 mmol) was then added dropwise by syringe. The reaction was allowed to reach room temperature and stirred for overnight. MeOH (~10 mL) was added slowly to quench the reaction. Solvent was removed under reduced pressure. Ethyl acetate (~200 mL) and water (~100 mL) were added to the mixture and the aqueous phase was separated. The organic phase was further washed with brine (~50 mL × 3), and dried by Na_2SO_4 and concentrated. The concentrated mixture

was applied to 1 × 1 inch silica pad and eluted with diethyl ether. After the solvent was removed under vacuum, the white crystals (0.58 g, 44%) were obtained after re-crystallization from ether/hexane. Melting point: 163.7-165.8 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 1.05-1.08 (m, 18H), 2.33 (s, 3H), 2.53 (s, 6H), 6.98 (s, 2H), 7.39-7.47 (m, 2H), 7.83 (d, J = 7.6 Hz, 1H), 8.25 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100MHz, CD_2Cl_2) δ 20.7, 22.8, 22.9, 29.6, 29.8, 33.8, 34.0, 115.3, 120.5, 123.7, 125.2, 131.8, 134.5, 135.6, 141.0, 141.1, 142.5, 144.5, 155.1, 155.5 (Complex unresolved C-P splitting was observed); ^{31}P NMR (202 MHz, CD_2Cl_2) δ 11.39; IR (cm^{-1}) 2972.67, 2941.30, 2894.51, 2860.87, 1604.42, 1566.07, 1467.32, 1425.26, 1400.93, 1378.77, 1356.37, 1340.87, 1334.53, 1291.59, 1249.27, 1229.65, 1193.68, 1174.23, 1129.38, 1117.80, 1050.78, 1026.04, 1015.68, 932.46, 901.17, 861.23, 816.95, 765.77, 749.16, 712.24, 680.80, 670.07, 643.40, 611.40, 587.30, 560.81, 551.86, 523.13, 461.50, 439.85, 419.51; MS (EI): *m/z* (relative intensity) 444 (M^+, 0), 387 (5), 331 (6), 299 (100), 267 (77), 253 (6), 235 (15), 205 (15), 189 (10), 165 (17), 149 (28), 119 (37), 105 (10), 91 (20), 77 (8), 57 (51); HRMS: calcd. for $C_{24}H_{33}N_2O_2SPH^+$: 445.2079, found 445.2085.

2.6.4 General Procedures for Preparation of 2-Phosphino-Substituted Benzimidazolyl Ligands by One-Pot Assembly Approach

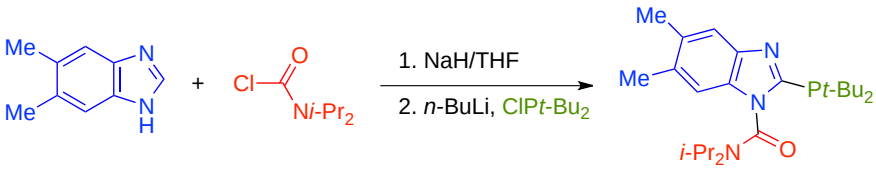
2-(Dicyclohexylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole -1-carboxamide (PCy Amizole^{M2}-phos **L2i**)



5,6-Dimethylbenzimidazole (1.46 g, 10.0 mmol) was dissolved in anhydrous THF (50 mL). The resultant solution was added dropwise to the THF (20 mL) solution containing 1.1 equiv. of NaH (60% in mineral oil, 0.44 g, 11.0 mmol) at 0 °C. (Note: NaH was pre-washed with dry hexane under nitrogen). The mixture was stirred for 20 min at room temperature. Then, 1.1 equiv. of *N*,*N*-diisopropylcarbamoylchloride (1.80 g, 11.0 mmol) was added directly to the reaction and the mixture was refluxed for 30 min. After the completion of the reaction as confirmed by GC-MS analysis, solvent was removed under reduced pressure. THF (4 mL) and toluene (80 mL, the reaction mixture THF/toluene = 1:20) were added. The solution was cooled to -98 °C in methanol/liquid N_2 bath. Titrated *n*-BuLi (11.0 mmol) was added dropwise by syringe. The reaction mixture was further stirred for 10 min at -98 °C and chlorodicyclohexylphosphine (2.65 mL, 12.0 mmol) was then added dropwise by syringe. The reaction was allowed to reach room temperature and stirred for 3 h. MeOH (~10 mL) was added slowly to quench the reaction. Solvent was removed under reduced pressure. Ethyl acetate (~200 mL) and water (~100 mL) were added to the mixture and the aqueous phase was separated. The organic phase was further washed with brine (~50 mL × 3), and dried by Na_2SO_4 and concentrated. The

concentrated mixture was applied to 1 × 1 inch silica pad and eluted with diethyl ether. After the solvent was removed under vacuum, the white crystals (3.03 g, 65%) were obtained after re-crystallization from ether/hexane.

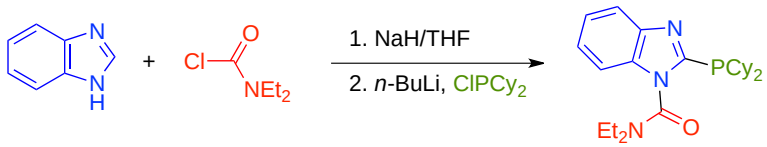
2-(Di-*tert*-butylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide (P*t*-Bu Amizole^{M2}-phos **L2j**)



5,6-Dimethylbenzimidazole (0.73 g, 5.0 mmol) was dissolved in anhydrous THF (30 mL). The resultant solution was added dropwise to the THF (10 mL) solution containing 1.1 equiv. of NaH (60% in mineral oil, 0.22 g, 5.5 mmol) at 0 °C. (Note: NaH was pre-washed with dry hexane under nitrogen). The mixture was stirred for 20 min at room temperature. Then, 1.1 equiv. of *N*,*N*-diisopropylcarbamoylchloride (0.90 g, 5.5 mmol) was added directly to the reaction and the mixture was refluxed for 30 min. After the completion of the reaction as confirmed by GC-MS analysis, the solution was cooled to -78 °C in dry ice/acetone bath. Titrated *n*-BuLi (6.0 mmol) was added dropwise by syringe. The reaction mixture was further stirred for 10 min at -78 °C and di-*tert*-butylchlorophosphine (1.14 mL, 6.0 mmol) was then added dropwise by syringe. The reaction was allowed to reach room temperature and stirred for 3 h. MeOH (~10 mL) was added slowly to quench the reaction. Solvent was removed under reduced pressure. Ethyl acetate (~100 mL) and water (~50 mL) were added to the mixture and the aqueous phase was separated. The organic phase was further washed with brine (~25 mL × 3), and dried by Na_2SO_4 and concentrated. The

concentrated mixture was applied to 1 × 1 inch silica pad and eluted with diethyl ether. After the solvent was removed under vacuum, the white solid (0.62 g, 30%) was obtained after re-crystallization from ether/hexane.

2-(Dicyclohexylphosphino)-*N*,*N*-diethyl-1*H*-benzo[*d*]imidazole-1-carboxamide (**Scheme 2.23**, **L2t**)



Benzimidazole (0.59 g, 5.0 mmol) was dissolved in anhydrous THF (20 mL). The resultant solution was added dropwise to the THF (10 mL) solution containing 1.1 equiv. of NaH (60% in mineral oil, 0.22 g, 5.5 mmol) at 0 °C. (Note: NaH was pre-washed with dry hexane under nitrogen). The mixture was stirred for 20 min at room temperature. Then, 1.1 equiv. of *N*,*N*-diisopropylcarbamoylchloride (0.90 g, 5.5 mmol) was added directly to the reaction and the mixture was refluxed for 30 min. After the completion of the reaction as confirmed by GC-MS analysis, solvent was removed under reduced pressure. THF (1 mL) and toluene (20 mL) were added. The solution was cooled to -78 °C in acetone/liquid N_2 bath. Titrated *n*-BuLi (5.5 mmol) was added dropwise by syringe. The reaction mixture was further stirred for 10 min at -78 °C and chlorodicyclohexylphosphine (1.35 mL, 6.0 mmol) was then added dropwise by syringe. The reaction was allowed to reach room temperature and stirred for overnight. MeOH (~10 mL) was added slowly to quench the reaction. Solvent was removed under reduced pressure. The white powder (0.65 g, 30%) was obtained after running column chromatography by E.A./hexane (1:9) system. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 1.08-3.65 (m, 33H), 7.31-7.37 (m, 3H), 7.79 (t, *J*

= 8.0 Hz, 1H); ^{13}C NMR (100MHz, CD_2Cl_2) δ 26.3, 27.1, 29.9, 110.3, 119.8, 122.7, 123.7, 134.0, 143.9, 151.2, 153.7, 153.9 (Complex unresolved C-P splitting was observed); ^{31}P NMR (202 MHz, CD_2Cl_2) δ -14.70; HRMS: calcd. for $C_{24}H_{36}N_3OPH^+$: 414.2674, found 414.2693.

2.7 References

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Chapter 3 An Efficient Class of *P,N*-Type 2-Arylated Benzimidazolyl Ligands for Palladium-Catalyzed Suzuki-Miyaura Coupling of Aryl Chlorides

3.1 Introduction

The palladium-catalyzed Suzuki-Miyaura cross-coupling is undoubtedly one of the most versatile and useful tool for the synthesis of diversified biaryls, which has numerous applications in pharmaceutical, materials, and agricultural chemistry.[1] To deal with the coupling reaction of aryl bromides as well as aryl chlorides, many effective supporting ligands have been developed in the past decade. The advancement of some notable ligands such as P*t*-Bu_3,[2] Beller's PAP,[3] Buchwald's biaryl–phosphines,[4] and Hartwig's Q-Phos[5] provide excellent catalytic activity in various cross-coupling reactions with aryl chlorides.[3c, 6] In view of the characteristics of the ligand structure, they are generally electron-rich and sterically hindered monophosphines. The increase of electron-richness can enhance oxidative addition. Meanwhile, sterically bulky skeletons can assist the catalyst complex to generate unsaturated palladium(0) species, which can facilitate both oxidative addition and reductive elimination steps. Indeed, monophosphine ligands may still give stable palladium catalysts. However, monophosphine ligands have limited coordinative flexibility for stabilizing the unstable low-coordinate and low-valent palladium complex, which is highly active but easily decomposed at high temperature or under prolonged heating. Consequent decomposition of the active catalysts would lead to the formation of inactive palladium black, which limits the maximum turnover, especially at extremely low-catalyst-loading conditions. Beller suggested that a several-fold

dosage increase of monophosphine ligand is an effective means of preventing decomposition of active low-valent palladium complexes, thus enabling the catalyst loading to be lowered and the TON to be maximized.[7, 3b] However, the choice between reactivity and the cost of sacrificing ligand becomes a dilemma and is clearly inefficient. The introduction of hemilabile phosphine ligands that have two basic sites with different donating ability provided a new way to address this problem. A hemilabile coordinating group offering both reactivity and stability towards the palladium center is sensitive to dynamic needs of the metal atom at different stages of the catalytic cycle. For instance, the nitrogen donor atom can weakly coordinate to soft metal centers (e.g., Pd and Rh) to stabilize low-valent metal complexes, yet can easily dissociate in solution to provide a vacant site whenever demanded.[8] In fact, phosphine ligands that possess potential hemilabile ability have been studied in the past decade (**Figure 3.1**, see also **Section 2.2.1**).[9]

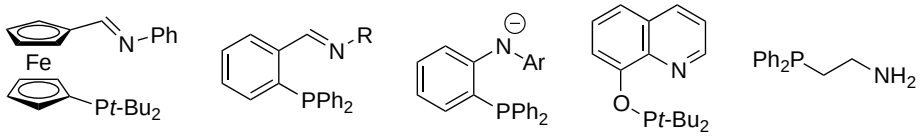
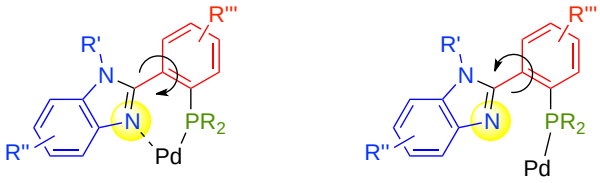


Figure 3.1 Recent Developments on *P*,*N*-Type Ligands for Suzuki Coupling

In respect to *P*,*N*-type ligands,[10] in 2004, Hor reported active ferrocenyl-derived *P*,*N*-type ligands with an imino group for the Suzuki coupling reaction.10[f] In 2005, a similar ligand with an aryl scaffold was also found to be effective in coupling processes.[11] Liang reported an amido-phosphinyl complex as an effective catalyst for the Suzuki coupling of aryl chlorides.[12] He and co-workers reported the use of bis(aminophosphine)-palladium chelated complexes for the

Suzuki coupling of aryl bromides.[10e] Scrivanti reported a *P,N*-type coordination ({8-[(di-*tert*-butylphosphinyl)oxy]quinoline}-$PdCl_2$) complex for low-catalyst-loading Suzuki coupling of aryl bromides.[13] Palladium complexes supported by these ligands demonstrated excellent catalytic activities towards the Suzuki coupling of aryl bromides and/or activated aryl chlorides at extremely low catalyst loadings (down to 1 ppm). However, currently developed hemilabile phosphine ligands, especially, *P,N*-type phosphine ligands, still have much room for improvement, particularly for the Suzuki coupling of neutral and deactivated aryl chlorides in systems with extremely low catalyst loadings. This challenge has still not been met.

To retain the advantage of an effective skeleton and further introduce beneficial hemilability to the ligand, we were inspired to use 2-arylated benzimidazolyl phosphine ligands (see **Section 2.4.2**). This framework features the same advantages as the 2-phenylindole scaffold[14] and allows high potential diversification from the rapid assembly of two starting components through the application of simple synthetic methods. Moreover, the additional nitrogen atom provides a weak coordinating site for potential dynamic interaction that could increase catalyst longevity (**Figure 3.2**). In 2012, we have successfully applied this class of benzimidazolyl phosphine ligands in the Suzuki-Miyaura coupling of aryl mesylates and Buchwald-Hartwig amination of aryl chlorides.[15] Herein, we disclose an extension to this class of ligands in the Suzuki-Miyaura coupling of aryl chlorides.



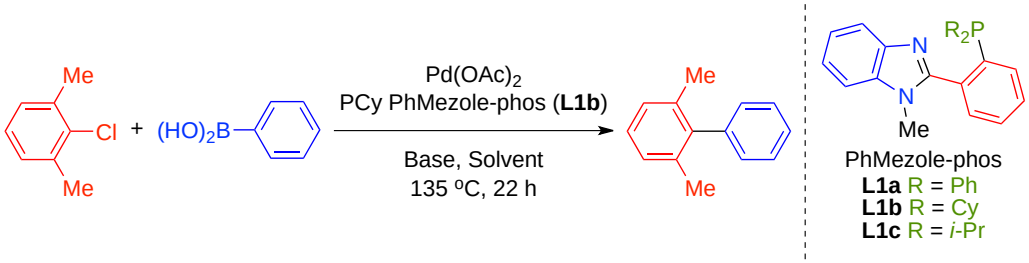
Hemilabile *N*-Chelating offers potential dynamic "**On** and **Off**" mechanism
by either providing a vacant site for substrate or coordinating with metal

Figure 3.2 Strategic Design and Potential Dynamic “On and Off” Mechanism

3.2 Results and Discussion

3.2.1 Study on the Effectiveness of *P,N*-Type Benzimidazolyl Phosphines

Table 3.1 Optimization of Reaction Conditions on Palladium-Catalyzed Suzuki-Miyaura Coupling of Aryl Chloride[a]



Entry	mol% Pd	Pd:L	Solvent	Base	% Yield
1	0.2	1:2	Dioxane	$K_3PO_4 \cdot H_2O$	99
2	0.2	1:2	Dioxane	K_3PO_4	58
3	0.2	1:2	Dioxane	K_2CO_3	44
4	0.2	1:2	Dioxane	Na_2CO_3	22
5	0.2	1:2	Dioxane	Cs_2CO_3	25
6	0.2	1:2	Dioxane	CsF	38
7	0.2	1:2	Dioxane	NaO*t*-Bu	36
8	0.2	1:2	THF	$K_3PO_4 \cdot H_2O$	24
9	0.2	1:2	Toluene	$K_3PO_4 \cdot H_2O$	34
10	0.2	1:2	DMF	$K_3PO_4 \cdot H_2O$	11
11	0.2	1:2	*t*-BuOH	$K_3PO_4 \cdot H_2O$	23
12	0.05	1:2	Mesitylene	$K_3PO_4 \cdot H_2O$	42
13	0.05	1:2	Dioxane	$K_3PO_4 \cdot H_2O$	74
14	0.05	1:3	Dioxane	$K_3PO_4 \cdot H_2O$	71
15	0.05	1:4	Dioxane	$K_3PO_4 \cdot H_2O$	65
16	0.05	1:2	Dioxane/Toluene	$K_3PO_4 \cdot H_2O$	51
17	0.05	1:2	Dioxane/Xylene	$K_3PO_4 \cdot H_2O$	52
18	0.05	1:2	Dioxane/Mesitylene	$K_3PO_4 \cdot H_2O$	99
19[b]	0.05	1:2	Dioxane/Mesitylene	$K_3PO_4 \cdot H_2O$	1
20[c]	0.05	1:2	Dioxane/Mesitylene	$K_3PO_4 \cdot H_2O$	81

[a]Reaction conditions: 1-Chloro-2,6-dimethylbenzene (1.0 mmol), phenylboronic acid (1.5 mmol), base (3.0 mmol), and solvent (3 mL) were stirred at 135 °C for 22 h under nitrogen. Calibrated GC yields were reported using dodecane as the internal standard, average of two runs. [b]**L1a** as ligand. [c]**L1c** as ligand.

In order to investigate the effectiveness of the new class of hemilabile *P*,*N*-type benzimidazolyl phosphines, PhMezole-phos **L1a** to **L1c**, these ligands were employed in palladium-catalyzed Suzuki-Miyaura coupling of aryl chlorides. Sterically hindered 2-chloro-*m*-xylene and phenylboronic acid were used as the model substrates in our benchmark reaction (**Table 3.1**).

An array of inorganic bases, such as $K_3PO_4 \cdot H_2O$, K_3PO_4, K_2CO_3, Na_2CO_3, Cs_2CO_3, CsF and NaO*t*-Bu, was first surveyed under 0.2 mol% of $Pd(OAc)_2$/PCy PhMezole-phos **L1b** system (**Table 3.1**, entries 1 to 7). $K_3PO_4 \cdot H_2O$ was found to be the best base in this catalytic system. Generally, organoboronic acid is easily dehydrated to give boroxine upon the elimination of one equivalent of water. Therefore, $K_3PO_4 \cdot H_2O$ could be suggested to generate more phenylboronic acid from boroxine.

For commonly used organic solvents, such as, tetrahydrofuran (THF), dioxane, *N*,*N*-dimethylformamide (DMF), toluene, mesitylene and *tert*-butanol (*t*-BuOH), they have different boiling points and solubility towards the catalytic system. In addition, the unique performance of the solvent is based on the principle of solvent effect. Then, non-polar dioxane was found to be the best single solvent (**Table 3.1**, entries 1 and 8 to 12). On the other hand, the effect of solvent mixing was also studied. When mixing dioxane with different solvents with higher boiling points, such as toluene, xylene and mesitylene (**Table 3.1**, entries 13 and 16 to 18), mixing dioxane with mesitylene was found to give the best result (**Table 3.1**, entry 18).

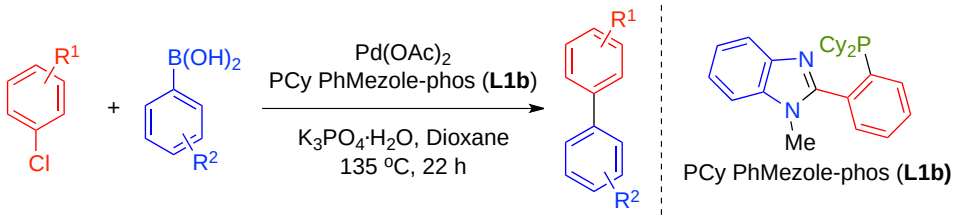
Upon investigating the metal to ligand ratio, the Pd-loading was tuned down to 0.05 mol%. The metal to ligand ratio from 1:2 to 1:4, ratio of 1:2 provided the highest yield (**Table 3.1**, entries 13 to 15). Therefore, the use of metal to ligand ratio of 1:2 was then chosen for the further screening trials.

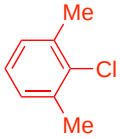
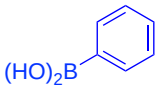
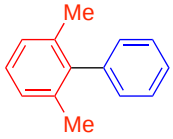
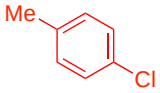
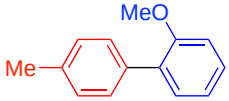
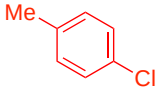
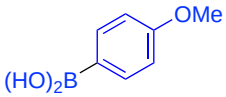
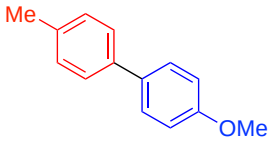
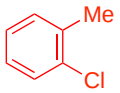
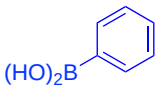
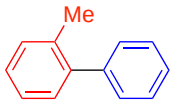
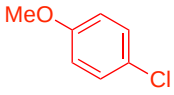
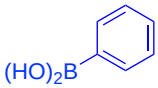
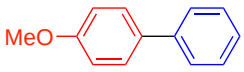
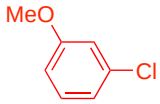
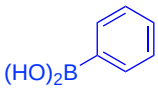
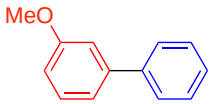
Last but not least, the effect of ligand with different phosphino moieties was examined. Ligand PPh PhMezole-phos **L1a** with a diphenylphosphinyl moiety provided only trace amount of substrate conversion (**Table 3.1**, entry 19), whereas the dicyclohexylphosphinyl analogue, PCy PhMezole-phos **L1b**, gave the best catalytic activity. On the contrary, ligand P*i*-Pr PhMezole-phos **L1c**, bearing a diisopropylphosphinyl moiety, showed a lower catalytic activity in the Suzuki coupling reaction (**Table 3.1**, entry 20). The possible reason was that dicyclohexylphosphino moiety was sufficiently electron-rich and sterically bulky to facilitate oxidative addition and reductive elimination respectively.

Finally, $K_3PO_4 \cdot H_2O$, mixing dioxane with mesitylene, metal to ligand ratio of 1:2 and PCy PhMezole-phos **L1b** were chosen in the optimization of reaction conditions for further substrate scope investigation.

3.2.2 Suzuki-Miyaura Coupling of Non-Activated Aryl Chlorides

Table 3.2 Palladium-Catalyzed Suzuki Coupling of Non-Activated Aryl Chlorides[a]

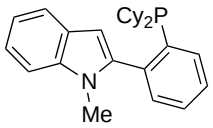


Entry	ArCl	Ar'B(OH)$_2$	Product	mol% Pd	% Yield[b] (TON)
1[c]				0.05	85 (1,700)
2				0.01	72 (7,200)
3				0.01	90 (9,000)
4				0.001	80 (80,000)
5[d]				0.001	39 (39,000)
6				0.002	74 (37,000)
7				0.005	90 (18,000)

[a]Reaction conditions: ArCl (1.0 mmol), Ar'B(OH)$_2$ (1.5 mmol), $K_3PO_4 \cdot H_2O$ (3.0 mmol), Pd(OAc)$_2$/PCy PhMezole-phos (**L1b**) = 1:2, and dioxane (3 mL) were stirred at 135 °C for 22 h under nitrogen. [b]Isolated yield. [c]Dioxane/mesitylene (1:1) as solvent (3 mL). [d]CM-phos as ligand, calibrated GC yield.

A range of aryl chlorides was examined under the preliminary optimized reaction conditions (**Table 3.2**). It was immediately clear that the palladium catalyst supported by the hemilabile benzimidazolyl phosphine, PCy PhMezole-

phos **L1b**, was highly active towards the Suzuki coupling reaction. The sterically hindered 2-chloro-*m*-xylene could be coupled with phenylboronic acid smoothly with high yield under 0.05 mol% Pd-loading (**Table 3.2**, entry 1). The catalyst loading and turnover number for the electron-neutral and deactivated aryl chloride could be reduced to 0.001 mol% Pd (80,000 TON) and 0.002 mol% Pd (37,000 TON), respectively (**Table 3.2**, entries 4 and 6). We then applied 2-[2-(dicyclohexylphosphinyl)phenyl]-*N*-methyl-1*H*-indole (CM-phos, **Figure 3.3**),[14] in which the 3-position of nitrogen group is replaced by carbon-hydrogen group, in the low-catalyst-loading coupling reaction (**Table 3.2**, Entries 4 and 5). The result showed that the hemilabile nitrogen coordinating group in the benzimidazole ring played an very important role in sustaining the high catalytic activity of the catalyst by prolonging the catalyst longevity.

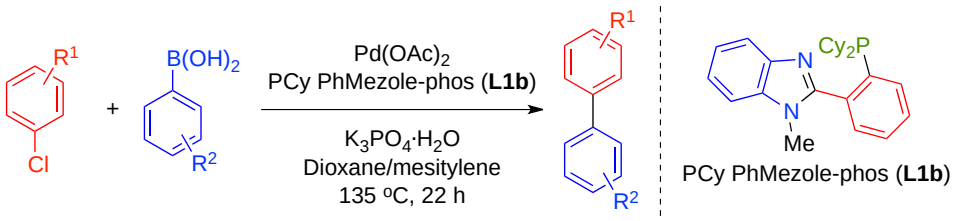


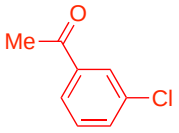
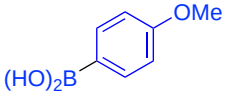
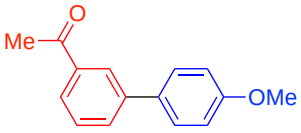
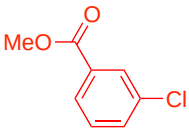
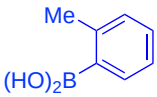
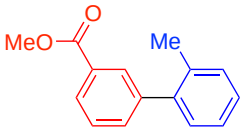
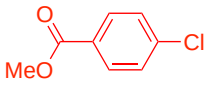
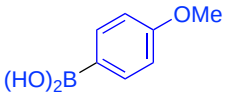
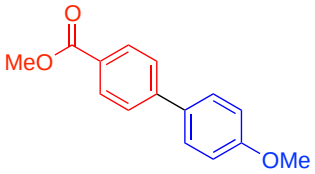
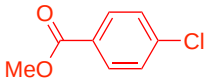
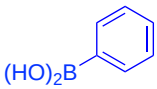
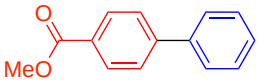
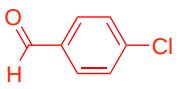
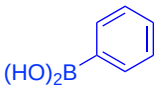
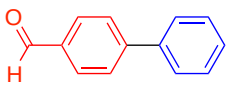
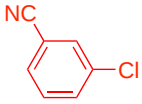
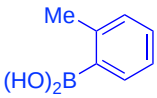
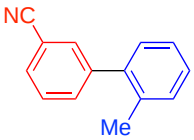
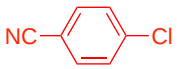
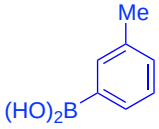
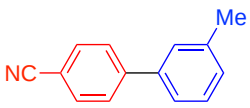
CM-phos

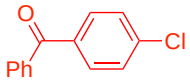
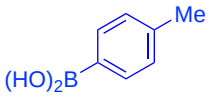
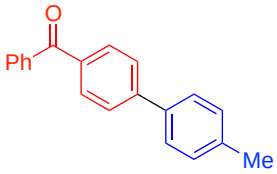
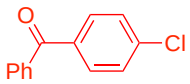
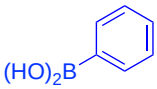
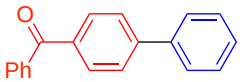
Figure 3.3 The Structure of CM-phos

3.2.3 Suzuki-Miyaura Coupling of Activated Aryl Chlorides

Table 3.3 Palladium-Catalyzed Suzuki Coupling of Activated Aryl Chlorides[a]



Entry	ArCl	Ar'B(OH)$_2$	Product	mol% Pd	% Yield[b] (TON)
1				0.01	>99 (10,000)
2				0.025	81 (3,240)
3[c]				0.01	94 (9,400)
4[c, d]				0.001	96 (96,000)
5[d]				0.001	85 (85,000)
6				0.02	81 (4,050)
7				0.01	96 (9,600)

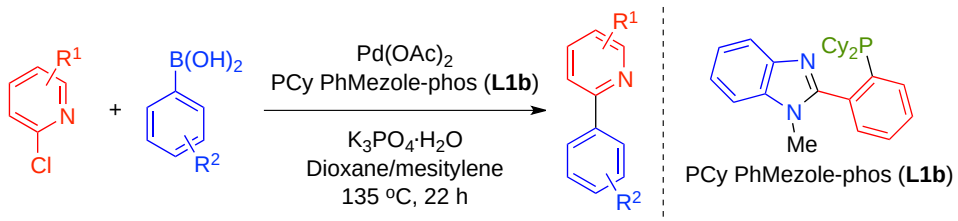
8				0.01	97 (9,700)
9[d]				0.001	>99 (100,000)
10[d]				0.0005	>99 (200,000)
11[d]				0.0002	97 (485,000)
12[d]				0.0001	72 (720,000)

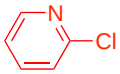
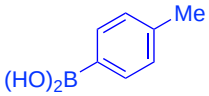
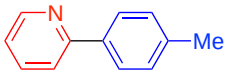
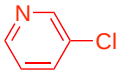
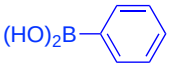
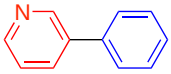
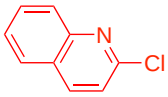
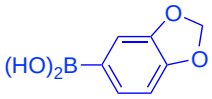
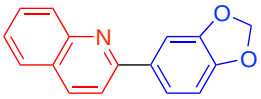
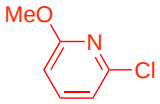
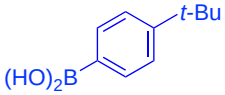
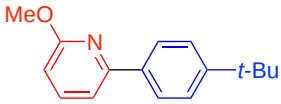
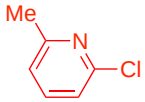
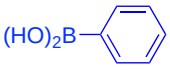
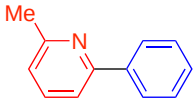
[a]Reaction conditions: ArCl (1.0 mmol), Ar'B(OH)$_2$ (1.5 mmol), $K_3PO_4 \cdot H_2O$ (3.0 mmol), Pd(OAc)$_2$/PCy PhMezole-phos (**L1b**) = 1:2, and dioxane/mesitylene (1:1, 3 mL) were stirred at 135 °C for 22 h under nitrogen. [b]Isolated yield. [c]K_2CO_3 as base. [d]Dioxane as solvent (3 mL).

Common functional groups, such as ketone, aldehyde, ester and nitrile, were compatible with these mild reaction conditions, and the catalyst loading could generally be reduced to 0.01 mol% to 0.001 mol% Pd-loading (**Table 3.3**, entries 1 to 8). Notably, the maximum catalytic activity of this new system was also probed (**Table 3.3**, entries 9 to 12). When the Pd-loading was reduced to 0.0005 mol% and 0.0002 mol%, this system was still effectively able to convert the substrate into the corresponding product in excellent yields. Although incomplete conversion of substrate was observed when 1 ppm of palladium catalyst was applied, turnover numbers as high as 720,000 (TON) were achieved. To the best of our knowledge, this is the lowest catalyst loading achieved by *P*,*N*-type phosphine ligands.

3.2.4 Suzuki-Miyaura Coupling of Heteroaryl Chlorides

Table 3.4 Palladium-Catalyzed Suzuki Coupling of Heteroaryl Chlorides[a]



Entry	Het-ArCl	Ar'B(OH)$_2$	Product	mol% Pd	% Yield[b] (TON)
1				0.01	98 (9,800)
2				0.01	>99 (10,000)
3				0.01	72 (7,200)
4				0.01	>99 (10,000)
5[c]				0.002	83 (41,500)
6[c, d]				0.001	>99 (100,000)

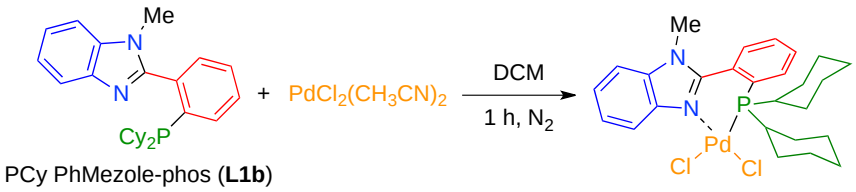
[a]Reaction conditions: Het-ArCl (1.0 mmol), Ar'B(OH)$_2$ (1.5 mmol), $K_3PO_4 \cdot H_2O$ (3.0 mmol), Pd(OAc)$_2$/PCy PhMezole-phos (**L1b**) = 1:2, and dioxane/mesitylene (1:1, 3 mL) were stirred at 135 °C for 22 h under nitrogen. [b]Isolated yield. [c]Dioxane as solvent (3 mL). [d]Pd(OAc)$_2$/PCy PhMezole-phos (**L1b**) = 1:4.

Generally, heteroaryl chlorides are classified as electron-deficient aryl chlorides due to the electron-withdrawing property of the heteroatom. However, under very-low-catalyst-loading conditions, the coordinating property of the heteroatom to the metal complex becomes significant and may be problematic for coupling reactions. Indeed, the high concentration of coordinating substrates may displace the phosphine ligands to generate inactive complexes and lead to a

reduction in the catalytic activity of the original active species. This newly developed system could effectively deal with pyridyl and quinolyl substrates when the metal to ligand ratio is 1:2 at a Pd-loading of 0.01 mol%. The isolated yield can be as high as 99% (**Table 3.4**, entries 1 to 4). Actually, the deleterious coordinating effect becomes serious when the catalyst loading was reduced to 0.002 mol% Pd (**Table 3.4**, entry 5). A slight increase of the metal to ligand ratio from 1:2 to 1:4 was required to compensate for the coordinating substrates under the extremely low-catalyst loading conditions. The Pd-loading could be further decreased to 0.001 mol%, and the isolated yield remained as high as 99% (**Table 3.4**, entry 6). This finding showed that the hemilabile group reduces the dependence of the reaction on the ligand concentration and can maintain the catalyst activity.

3.2.5 Structural Insight of Palladium-Ligand interaction

To further gain the insight into the metal-ligand interactions, our group had previously studied the X-ray crystallography of the palladium-ligand complex.[15a] We attempted to complex the $PdCl_2(CH_3CN)_2$ with one equivalent of PCy PhMezole-phos **L1b** in dichloromethane at room temperature (Scheme 3.1).



Scheme 3.1 Complexation of PCy PhMezole-phos with $PdCl_2(CH_3CN)_2$

The X-ray crystallographic data confirmed that the benzimidazolyl ligand PCy PhMezole-phos **L1b** was coordinated in a κ^2-*P*,*N* fashion to the palladium center (**Figure 3.4**).

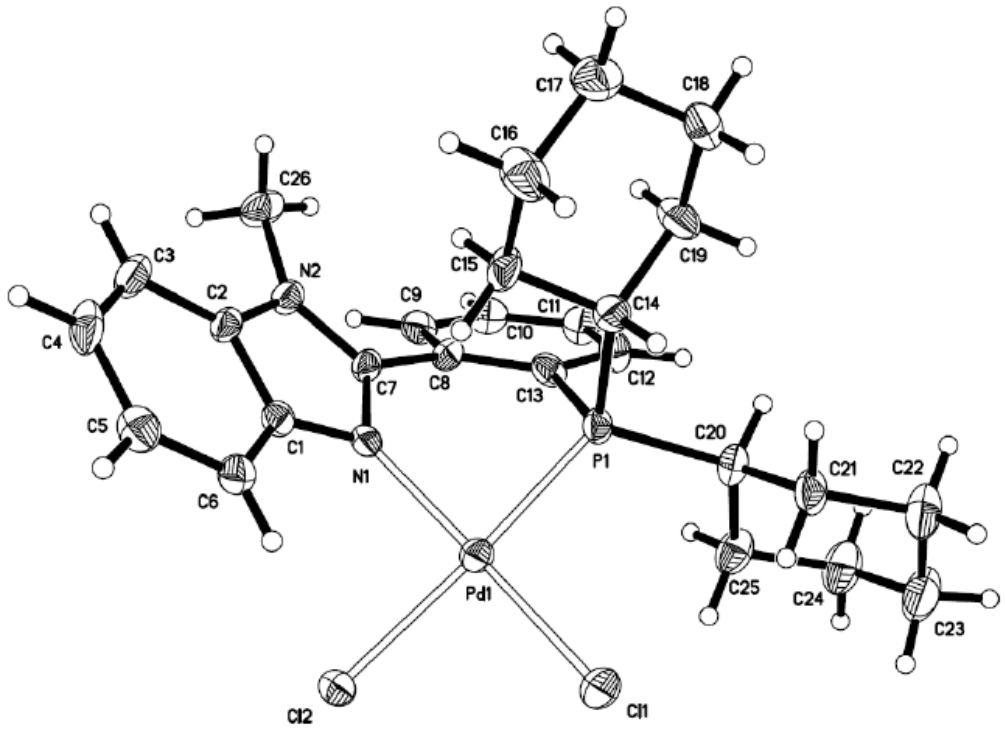


Figure 3.4 ORTEP Representation of Complex Pd-PCy PhMezole-phos **L1b** (30% probability ellipsoids, hydrogen atoms have been omitted for clarity purpose.)

Table 3.5 Selected Bond Distances (Å) and Angles (°)

Bond Distances (Å)			
Pd(1)-N(1)	2.0113(17)	Pd(1)-P(1)	2.2493(6)
Pd(1)-Cl(1)	2.2969(7)	Pd(1)-Cl(2)	2.3744(6)
P(1)-C(20)	1.8371(19)	P(1)-C(14)	1.846(3)
Angles (°)			
N(1)-Pd(1)-P(1)	86.05(5)	N(1)-Pd(1)-Cl(1)	170.26(5)
P(1)-Pd(1)-Cl(1)	96.35(2)	N(1)-Pd(1)-Cl(2)	88.90(5)
P(1)-Pd(1)-Cl(2)	168.21(2)		

Table 3.6 Crystal Data and Structure Refinement for Pd-PCy PhMezole-phos **L1b** Complex

Empirical formula	$PdCl_2(C_{26}H_{33}N_2P)\ .CH_2Cl_2$	
Formula weight	666.74	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.2097(6) Å	α= 99.428(6)°.
	b = 10.1097(6) Å	β= 97.595(6)°.
	c = 18.0481(16) Å	γ = 113.505(4)°.
Volume	1483.49(19) $Å^3$	
Z	2	
Density (calculated)	1.493 Mg/m^3	
Absorption coefficient	1.059 mm^{-1}	
F(000)	680	
Crystal size	0.50 x 0.40 x 0.18 mm^3	
Theta range for data collection	2.29 to 27.87°.	
Index ranges	-12<=h<=12, -13<=k<=13, -23<=l<=23	
Reflections collected	26578	
Independent reflections	6987 [R(int) = 0.4427]	
Completeness to theta = 27.87°	98.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8323 and 0.6196	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6987 / 4 / 335	
Goodness-of-fit on F^2	1.001	
Final R indices [I>2sigma(I)]	R1 = 0.0716, wR2 = 0.1649	
R indices (all data)	R1 = 0.2766, wR2 = 0.2023	
Largest diff. peak and hole	1.156 and -0.928 $e.Å^{-3}$	

3.3 Conclusion

We have developed a series of efficient hemilabile *P*,*N*-type benzimidazolyl phosphine ligands. Palladium complexes derived from these ligands showed excellent catalytic activities for the Suzuki-Miyaura coupling of aryl chlorides with arylboronic acids, especially under very-low-catalyst-loading condition. Benefiting from the hemilabile benzimidazolyl group, the Pd-loading for the Suzuki coupling of functionalized aryl chlorides can be reduced to 1 ppm; the palladium levels in neutral, deactivated and coordinating aryl chloride systems can be reduced to 0.001 mol%. To the best of our knowledge, this is the lowest catalyst loading achieved by *P*,*N*-type phosphine ligands up-to-date. We anticipate that further enhancements in reactivity and versatility of the ligand series will be attainable.

3.4 Experimental Section

3.4.1 General Considerations

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. All Suzuki-Miyaura coupling reactions were performed in resealable screw cap schlenk flask (approx. 20 mL volume) in the presence of Teflon coated magnetic stirrer bar (3mm × 10 mm). 1,4-Dioxane, mesitylene, *tert*-butanol and toluene were distilled from sodium under nitrogen.[16] Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under nitrogen.[16] Commercial aryl chlorides (liquid form only) were purified by passed through a short plug (0.5 cm wide × 4 cm high) of neutral alumina or distillation. Most commercially available boronic acids were used as received. Water content of arylboronic acids would affect the coupling results, some arylboronic acids may require further recrystallization depending on the received conditions. $K_3PO_4 \cdot H_2O$ were purchased from chemical supplier and used without 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. Melting points were recorded on an uncorrected instrument. ^{1}H NMR spectra were recorded on a Bruker (400 MHz) spectrometer. Spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.26 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 ESIMS. GC-MS analysis was conducted on a GCD system using a column with 30 m × 0.25 mm. The products

described in GC yield were accorded to the authentic samples/dodecane calibration standard from GC-FID system. Compounds described in the literature were characterized by comparison of their ^{1}H 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.

3.4.2 General Procedure for Initial Ligand and Reaction Conditions Screening

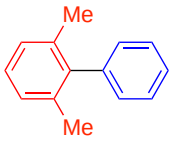
General procedure for initial ligand and reaction conditions screening: A stock solution of $Pd(OAc)_2$ (2.3 mg, 0.010 mmol) with ligand in freshly distilled solvent (10 mL) was initially prepared with continuously stirring at room temperature. Phenylboronic acid (0.1829 g, 1.5 mmol), base (3.0 equiv., 3.0 mmol) and magnetic stirrer bar (3 mm $\times$ 8 mm) were charged to an array of Schlenk tubes. Each tube was carefully evacuated and backfilled with nitrogen (3 cycles). 2-Chloro-1,3-dimethylbenzene (0.137 mL, 1.0 mmol) and stock solution (2.0 mL, 0.2 mol% Pd) were added *via* syringe. Further 1.0 mL solvent was added *via* syringe (final volume: 3 mL). This batch of Schlenk tube was resealed and magnetically stirred in a preheated 135 °C oil bath. The reactions were allowed to reach room temperature. Ethyl acetate (~10 mL), dodecane (227 μL, internal standard) water (~5 mL) were added. The organic layer was subjected to GC analysis. The GC yield was previously calibrated by authentic sample/dodecane calibration curve.

3.4.3 General Procedure for Suzuki-Miyaura Couplings of Aryl Chlorides

General procedure for Suzuki-Miyaura couplings of aryl chlorides: $Pd(OAc)_2$ (2.3 mg, 0.010 mmol) and ligand **L1b** (Pd:L = 1:2) in freshly distilled 10 mL 1,4-dioxane (0.1 mol% Pd per 1 mL stock solution) was initially prepared with continuously stirring at room temperature. Arylboronic acid (1.5 mmol), $K_3PO_4 \cdot H_2O$ (3.0 mmol) and magnetic stirrer bar (3 mm × 8 mm) were charged to an array of Schlenk tubes. Each tube was carefully evacuated and backfilled with nitrogen (3 cycles). Aryl chloride (1.0 mmol) was then added to the Schlenk tubes. The stock solution was further diluted to give different concentrations. The diluted stock solution was then transferred to Schlenk tubes *via* syringes. Further solvents were added (final volume: 3 mL). This batch of Schlenk tube was resealed and the reaction mixture was magnetically stirred in a preheated 135 °C oil bath. After the completion of reaction as judged by GC or TLC analysis, the reactions were allowed to reach room temperature. Water (~3 mL) and ethyl acetate (~10 mL × 3) were added. The organic layers were combined and concentrated. The crude products were purified by column chromatography on silica gel (230-400 mesh).

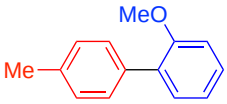
3.4.4 Characterization Data for Coupling Products

2,6-Dimethylbiphenyl (**Table 3.2**, entry 1)[17]



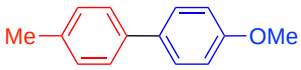
R_f = 0.5 (pure hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 2.22 (s, 6H), 7.28-7.36 (m, 5H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 20.7, 126.5, 127.0, 127.2, 128.3, 128.9, 135.9, 141.0, 141.8; MS (EI): *m/z* (relative intensity) 182.1 (M^+, 96), 167.1 (100).

2-Methoxy-4'-methylbiphenyl (**Table 3.2**, entry 2)[18]



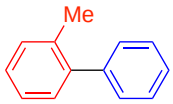
R_f = 0.6 (1:20 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 2.53 (s, 3H), 3.92 (s, 3H), 7.10 (d, *J* = 8.4 Hz, 1H), 7.14-7.18 (m, 1H), 7.37 (d, *J* = 7.6 Hz, 2H), 7.42-7.47 (m, 2H), 7.59 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 21.1, 55.4, 111.1, 120.7, 128.3, 128.6, 129.3, 130.6, 130.7, 135.5, 136.4, 156.4; MS (EI): *m/z* (relative intensity) 198.1 (M^+, 100), 183.1 (54), 168.1 (56).

4-Methoxy-4'-methylbiphenyl (**Table 3.2**, entry 3)[19]



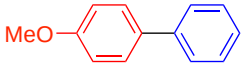
R_f = 0.6 (1:20 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 2.49 (s, 3H), 3.92 (s, 3H), 7.07 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 7.6 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 20.9, 55.2, 114.1, 126.5, 127.8, 129.3, 133.6, 136.2, 137.9, 158.9; MS (EI): *m/z* (relative intensity) 198.1 (M^+, 100), 183.1 (58), 155.1 (33).

2-Methylbiphenyl (**Table 3.2**, entry 4)[3b]



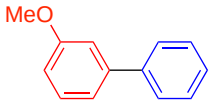
R_f = 0.5 (pure hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 2.45 (s, 3H), 7.41-7.43 (m, 4H), 7.49-7.50 (m, 3H), 7.57 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 20.4, 125.7, 126.7, 127.2, 128.0, 129.1, 129.7, 130.2, 135.2, 141.9, 141.9; MS (EI): *m/z* (relative intensity) 168.1 (M^+, 100), 153.1 (40).

4-Methoxybiphenyl (**Table 3.2**, entry 6)[3b]



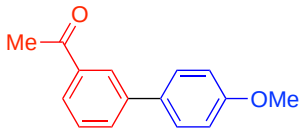
R_f = 0.4 (1:9 DCM/Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 3.93 (s, 3H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.53 (t, *J* = 7.2 Hz, 2H), 7.64-7.69 (m, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ 55.1, 114.1, 126.5, 126.6, 128.0, 128.6, 133.6, 140.7, 159.1; MS (EI): *m/z* (relative intensity) 184.1 (M^+, 100), 169.1 (49), 141.1 (48), 115.1 (36).

3-Methoxybiphenyl (**Table 3.2**, entry 7)[3b]



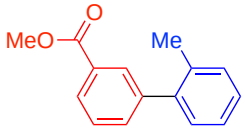
R_f = 0.5 (1:20 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 3.96 (s, 3H), 7.02-7.05 (m, 1H), 7.29-7.30 (m, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.46-7.50 (m, 2H), 7.56 (t, *J* = 7.2 Hz, 2H), 7.74 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 55.1, 112.5, 112.8, 119.5, 127.1, 127.3, 128.6, 129.6, 141.0, 142.6, 159.9; MS (EI): *m/z* (relative intensity) 184.1 (M^+, 100), 154.1 (24), 141.1 (33), 115.1 (36).

1-(4'-Methoxybiphenyl-3-yl)ethanone (**Table 3.3**, entry 1)[20]



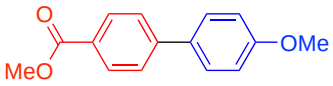
R_f = 0.4 (1:9 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 2.62 (s, 3H), 3.82 (s, 3H), 6.98 (d, J = 8.8 Hz, 2H), 7.47 (t, J = 8.0 Hz, 1H), 7.54 (d, J = 8.8 Hz, 2H), 7.72 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 7.6 Hz, 1H), 8.15 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 26.4, 55.0, 114.1, 126.0, 126.3, 127.9, 128.7, 130.9, 132.2, 137.3, 140.9, 159.3, 197.8; MS (EI): *m/z* (relative intensity) 226.1 (M^+, 100), 211.1 (91), 183.1 (49), 168.1 (26), 139.1 (35).

Methyl 2'-methylbiphenyl-3-carboxylate (**Table 3.3**, entry 2)[18]



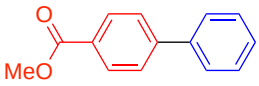
R_f = 0.5 (1:20 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 2.32 (s, 3H), 3.97 (s, 3H), 7.29-7.32 (m, 4H), 7.51-7.58 (m, 2H), 8.08-8.10 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 20.2, 51.9, 125.8, 127.5, 127.9, 128.0, 129.6, 130.0, 130.2, 130.3, 133.5, 135.1, 140.7, 142.1, 166.9; MS (EI): *m/z* (relative intensity) 226.1 (M^+, 98), 195.1 (52), 167.1 (100), 152.1 (43).

Methyl 4'-methoxybiphenyl-4-carboxylate (**Table 3.3**, entry 3)[21]



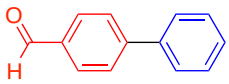
R_f = 0.3 (1:20 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 3.87 (s, 3H), 3.95 (s, 3H), 7.01 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H), 8.10 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 51.9, 55.2, 114.3, 126.3, 128.1, 128.2, 130.0, 132.3, 145.1, 159.8, 166.9; MS (EI): *m/z* (relative intensity) 242.1 (M^+, 100), 211.1 (68), 139.1 (24).

Methyl biphenyl-4-carboxylate (**Table 3.3**, entry 4)[22]



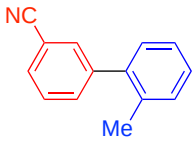
R_f = 0.5 (1:9 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 3.97 (s, 3H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 2H), 7.65 (d, *J* = 7.2 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 8.15 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 51.9, 126.9, 127.1, 128.0, 128.8, 130.0, 139.8, 145.5, 166.8; MS (EI): *m/z* (relative intensity) 212.1 (M^+, 63), 181.1 (100), 152.1 (57).

Biphenyl-4-carbaldehyde (**Table 3.3**, entry 5)[10f]



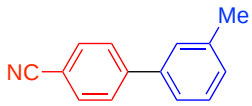
R_f = 0.5 (1:9 E.A./Hexane); ^{1}H NMR (400MHz, CD_2Cl_2) δ 7.47 (t, *J* = 7.2 Hz, 1H), 7.54 (t, *J* = 7.2 Hz, 2H), 7.71 (d, *J* = 7.2 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.99 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100MHz, CD_2Cl_2) δ 127.3, 127.6, 128.4, 129.0, 130.1, 135.3, 139.6, 146.9, 191.7; MS (EI): *m/z* (relative intensity) 181.1 (M^+, 100), 152.1 (74).

2'-Methylbiphenyl-3-carbonitrile (**Table 3.3**, entry 6)[18]



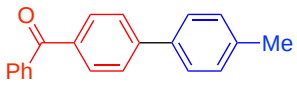
R_f = 0.5 (1:20 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 2.29 (s, 3H), 7.21 (d, *J* = 7.2 Hz, 1H), 7.29-7.34 (m, 3H), 7.54-7.48 (m, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ 20.0, 112.1, 118.6, 125.9, 128.8, 129.3, 130.2, 130.4, 132.4, 133.4, 134.8, 139.2, 142.9; MS (EI): *m/z* (relative intensity) 193.1 (M^+, 100), 165.1 (42).

3'-Methylbiphenyl-4-carbonitrile (**Table 3.3**, entry 7)[10f]



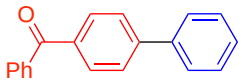
R_f = 0.5 (1:20 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 2.47 (s, 3H), 7.27 (s, 1H), 7.40-7.42 (m, 3H), 7.66-7.71 (m, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ 21.2, 110.4, 118.7, 124.0, 127.4, 127.6, 128.7, 129.1, 132.2, 138.5, 138.8, 145.4; MS (EI): *m/z* (relative intensity) 193.1 (M^+, 100), 165.1 (23).

(4'-Methylbiphenyl-4-yl)(phenyl)methanone (**Table 3.3**, entry 8)[23]



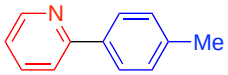
R_f = 0.5 (1:20 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 2.45 (s, 3H), 7.33 (d, *J* = 7.6 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.59-7.65 (m, 3H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 7.6 Hz, 2H), 7.94 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 21.0, 126.5, 126.9, 128.1, 129.5, 129.8, 130.5, 132.1, 135.7, 136.8, 137.6, 137.9, 144.9, 196.0; MS (EI): *m/z* (relative intensity) 272.1 (M^+, 83), 195.1 (100) 165.1 (22), 152.1 (32).

Biphenyl-4-yl(phenyl)methanone (**Table 3.3**, entry 9)[24]



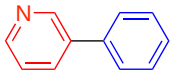
R_f = 0.5 (1:9 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 7.44 (t, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 7.2 Hz, 2H), 7.54 (d, *J* = 7.6 Hz, 2H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.69 (d, *J* = 7.2 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 7.2 Hz, 2H), 7.94 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 126.7, 127.1, 128.0, 128.1, 128.8, 129.8, 130.5, 132.2, 136.0, 137.6, 139.7, 145.0, 196.0; MS (EI): *m/z* (relative intensity) 258.1 (M^+, 81), 181.1 (100), 152.1 (44).

2-*p*-Tolylpyridine (**Table 3.4**, entry 1)[25]



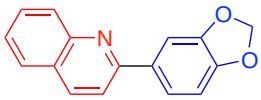
R_f = 0.5 (1:9 E.A./Hexane); ^{1}H NMR (400MHz, CD_2Cl_2) δ 2.50 (s, 3H), 7.24-7.27 (m, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.75-7.80 (m, 2H), 8.05 (d, *J* = 8.0 Hz, 2H), 8.76 (d, *J* = 4.4 Hz, 1H); ^{13}C NMR (100MHz, CD_2Cl_2) δ 21.0, 119.9, 121.8, 126.7, 129.4, 136.6, 136.6, 139.0, 149.6, 157.1; MS (EI): *m/z* (relative intensity) 169.1 (M^+, 100).

3-Phenylpyridine (**Table 3.4**, entry 2)[3b]



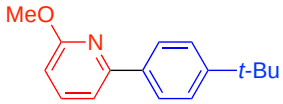
R_f = 0.2 (1:9 E.A./Hexane); ^{1}H NMR (400MHz, CD_2Cl_2) δ 7.38-7.48 (m, 2H), 7.54 (t, *J* = 7.2 Hz, 2H), 7.66 (d, *J* = 7.2 Hz, 2H), 7.91-7.94 (m, 1H). 8.64 (d, *J* = 4.8 Hz, 1H), 8.93 (s, 1H); ^{13}C NMR (100MHz, CD_2Cl_2) δ 123.5, 127.1, 128.0, 129.0, 134.1, 136.4, 137.9, 148.3, 148.5; MS (EI): *m/z* (relative intensity) 155.1 (M^+, 100).

2-(Benzo[*d*][1,3]dioxol-5-yl)quinoline (**Table 3.4**, entry 3)[26]



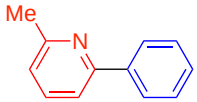
R_f = 0.5 (1:20 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 6.03 (s, 2H), 6.96 (d, *J* = 8.0 Hz, 1H), 7.48-7.52 (m, 1H), 7.66-7.68 (m, 1H), 7.70-7.78 (m, 4H), 8.12 (d, *J* = 8.8 Hz, 1H), 8.17 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 101.2, 107.7, 108.3, 118.3, 121.5, 125.8, 126.8, 127.2, 129.4, 129.4, 133.9, 136.4, 148.0, 148.2, 148.7, 156.4; MS (EI): *m/z* (relative intensity) 249.1 (M^+, 100), 191.1 (24).

2-(4-*tert*-Butylphenyl)-6-methoxypyridine (**Table 3.4**, entry 4)



R_f = 0.8 (1:9 E.A./Hexane); ^{1}H NMR (400MHz, CD_2Cl_2) δ 1.51 (s, 9H), 4.15 (s, 3H), 6.79 (d, J = 8.4 Hz, 1H), 7.44 (d, J = 7.6 Hz, 1H), 7.62 (d, J = 8.4 Hz, 2H), 7.70 (t, J = 7.6 Hz, 1H), 8.13 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100MHz, CD_2Cl_2) δ 31.1, 34.6, 53.0, 108.9, 112.4, 125.5, 126.4, 136.4, 139.1, 152.1, 154.7, 163.8; MS (EI): *m/z* (relative intensity) 241.1 (M^+, 35), 226.2 (100); HRMS: calcd. for $C_{16}H_{19}NOH^+$: 242.1545, found 242.1537.

2-Methyl-6-phenylpyridine (**Table 3.4**, entry 5)[27]



R_f = 0.5 (1:9 E.A./Hexane); ^{1}H NMR (400MHz, CD_2Cl_2) δ 2.69 (s, 3H), 7.17 (d, J = 7.6 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.55 (t, J = 7.2 Hz, 2H), 7.61 (d, J = 8.0 Hz, 1H), 7.69 (t, J = 7.6 Hz, 1H), 8.11 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100MHz, CD_2Cl_2) δ 24.4, 117.3, 121.6, 126.8, 128.6, 128.7, 136.8, 139.7, 156.4, 158.3; MS (EI): *m/z* (relative intensity) 169.1 (M^+, 100).

3.5 References

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Chapter 4 *P,N*-Type 2-Arylated Benzimidazolyl Ligands for Palladium-Catalyzed Suzuki-Miyaura Coupling of Aryl Chlorides with Potassium Aryltrifluoroborates

4.1 Introduction

As in **Chapter 3**, the 2-arylated benzimidazolyl phosphines **PhMezole-phos** showed excellent catalytic activities for the Suzuki-Miyaura coupling of aryl chlorides with arylboronic acids, especially under very-low-catalyst-loading conditions down to 1 ppm palladium loading.

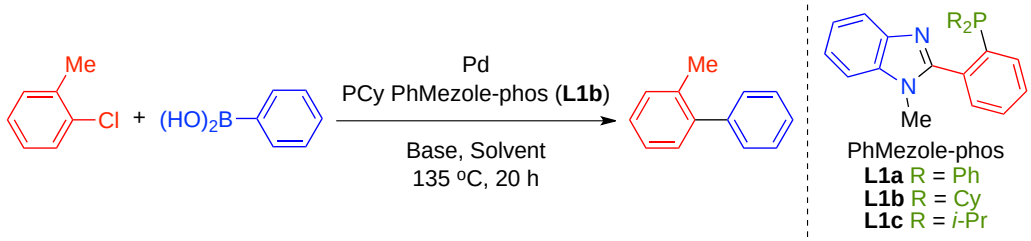
In general, arylboronic acids are good nucleophilic organoboron reagents in Suzuki-Miyaura coupling reaction.[1] However, boronic acids are noted to never be ideal because they exhibit several drawbacks such as the partial formation of dimeric and cyclic trimeric boroxines, which depend on storage water content. This structural ambiguity affects the stoichiometry of boronic acids added to the intended reaction. Organotrifluoroborate salts are attractive alternatives to aryl and heteroarylboronic acids because they are usually sold in high purity from commercial sources and are readily available from other organoboron compounds.[2, 3] Recently, Molander[4] and many other respected researchers[5] made superb efforts to make advancements toward transition metal-catalyzed Suzuki-Miyaura coupling using organotrifluoroborate salts as coupling partners.

Therefore, we herein attempt to explore the catalytic activity of this type of ligands towards palladium-catalyzed Suzuki-Miyaura coupling of aryl chlorides with potassium aryltrifluoroborates.

4.2 Results and Discussion

4.2.1 Study on the Effectiveness of *P,N*-Type Benzimidazolyl Phosphines

Table 4.1 Optimization of Reaction Conditions on Palladium-Catalyzed Suzuki-Miyaura Coupling of Aryl Chlorides with Potassium Aryltrifluoroborates[a]



Entry	Pd source	mol% Pd	Pd:L	Solvent	Base	% Yield
1	$Pd(OAc)_2$	0.5	1:2	*t*-BuOH	$K_3PO_4·H_2O$	70
2	$Pd(OAc)_2$	0.5	1:2	Toluene	$K_3PO_4·H_2O$	16
3	$Pd(OAc)_2$	0.5	1:2	Dioxane	$K_3PO_4·H_2O$	16
4	$Pd(OAc)_2$	0.5	1:2	DMF	$K_3PO_4·H_2O$	15
5	$Pd(OAc)_2$	0.5	1:2	*t*-Amyl alcohol	$K_3PO_4·H_2O$	60
6	$Pd(OAc)_2$	0.5	1:2	*t*-BuOH/Toluene	$K_3PO_4·H_2O$	99
7	$Pd(dba)_2$	0.2	1:2	*t*-BuOH/Toluene	$K_3PO_4·H_2O$	99
8	$Pd_2(dba)_3$	0.2	1:2	*t*-BuOH/Toluene	$K_3PO_4·H_2O$	34
9	$Pd(dba)_2$	0.2	1:1	*t*-BuOH/Toluene	$K_3PO_4·H_2O$	44
10	$Pd(dba)_2$	0.2	1:3	*t*-BuOH/Toluene	$K_3PO_4·H_2O$	55
11	$Pd(dba)_2$	0.2	1:4	*t*-BuOH/Toluene	$K_3PO_4·H_2O$	37
12	$Pd(dba)_2$	0.1	1:2	*t*-BuOH/Toluene	$K_3PO_4·H_2O$	82
13	$Pd(OAc)_2$	0.1	1:2	*t*-BuOH/Toluene	$K_3PO_4·H_2O$	28
14	$Pd(dba)_2$	0.1	1:2	*t*-BuOH/Toluene	NaO*t*-Bu	12
15	$Pd(dba)_2$	0.1	1:2	*t*-BuOH/Toluene	Cs_2CO_3	10
16	$Pd(dba)_2$	0.1	1:2	*t*-BuOH/Toluene	K_3PO_4	56
17	$Pd(dba)_2$	0.1	1:2	*t*-BuOH/Toluene	CsF	3
18	$Pd(dba)_2$	0.1	1:2	*t*-BuOH/Toluene	K_2CO_3	49
19	$Pd(dba)_2$	0.1	1:2	*t*-BuOH/Toluene	Na_2CO_3	44
20[b]	$Pd(dba)_2$	0.1	1:2	*t*-BuOH/Toluene	$K_3PO_4·H_2O$	1
21[c]	$Pd(dba)_2$	0.1	1:2	*t*-BuOH/Toluene	$K_3PO_4·H_2O$	80

[a]Reaction conditions: 2-Chlorotoluene (1.0 mmol), potassium phenyltrifluoroborate (1.5 mmol), base (3.0 mmol), and solvent (3 mL) were stirred at 135 °C for 20 h under nitrogen. Calibrated GC yields were reported using dodecane as the internal standard, average of two runs. [b]**L1a** as ligand. [c]**L1c** as ligand.

To test the effectiveness of the benzimidazolyl phosphine ligands, 2-chlorotoluene coupled with potassium phenyltriflouroborate was used as the benchmark entry (**Table 4.1**). Commonly used organic solvents, such as *tert*-butanol (*t*-BuOH), *t*-amyl alcohol, toluene, dioxane and *N*,*N*-dimethylformamide (DMF) were firstly examined under 0.5 mol% of $Pd(OAc)_2$/PCy PhMezole-phos **L1b** system. Alcoholic solvents such as *t*-BuOH and *t*-amyl alcohol showed superior result when compared to the other polar aprotic and non-polar solvents (**Table 4.1**, entries 1 to 5). The improvement in performance could be attributed to the increase in solubility of the triflouroborate salt. As we had experience for solvent mixing to promote the catalytic activity (see **Section 3.2.1**), mixing *t*-BuOH with toluene showed superior result among those single solvents (**Table 4.1**, entry 6).

Three kinds of palladium sources were examined. $Pd(dba)_2$ gave the best result among $Pd(OAc)_2$, $Pd(dba)_2$, and $Pd_2(dba)_3$ (**Table 4.1**, entries 7, 8, 12 and 13). Upon varying the metal to ligand ratio, the Pd-loading was tuned down from 0.5 mol% to 0.2 mol%. From metal to ligand ratio 1:1 to 1:4, the ratio of 1:2 provided the highest yield (**Table 4.1**, entries 7 and 9 to 11). The use of $Pd(dba)_2$ and metal to ligand ratio of 1:2 was then chosen for further screening process.

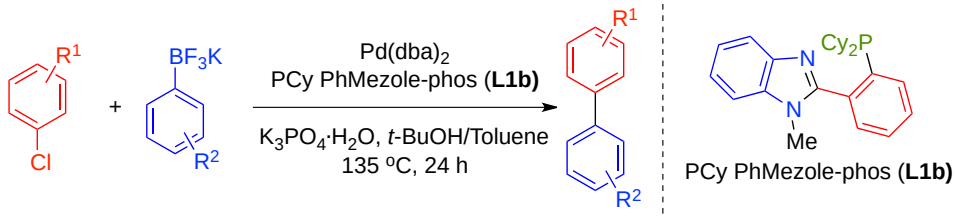
After that, several common inorganic bases, such as $K_3PO_4 \cdot H_2O$, K_3PO_4, K_2CO_3, Na_2CO_3, Cs_2CO_3, CsF and NaO*t*-Bu, were examined. In the presence of ligand PCy PhMezole-phos **L1b**, $K_3PO_4 \cdot H_2O$ was found to be the best base of choice in this catalytic system (**Table 4.1**, entries 12 and 14 to 19).

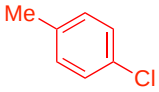
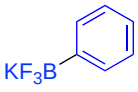
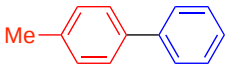
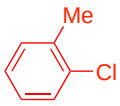
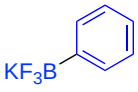
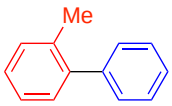
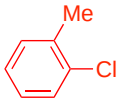
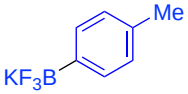
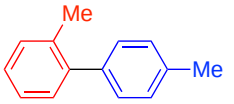
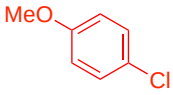
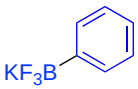
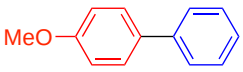
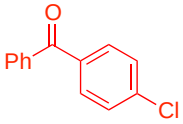
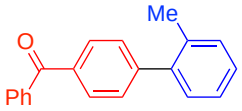
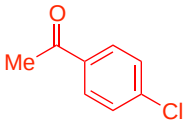
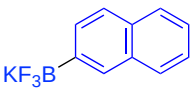
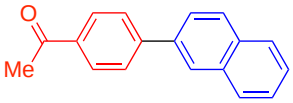
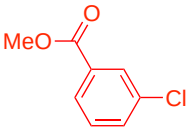
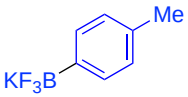
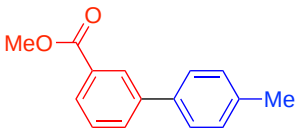
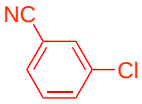
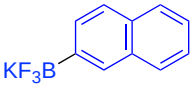
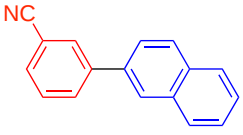
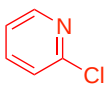
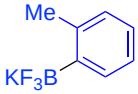
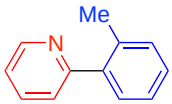
The effect of ligand with different phosphion moieties was also examined. Ligand PPh PhMezole-phos **L1a** with diphenylphosphino moiety provided trace conversion while the dicyclohexylphosphino analogue, PCy PhMezole-phos **L1b**, gave the best catalytic activity. In addition, ligand P*i*-Pr PhMezole-phos **L1c** bearing a diisopropylphosphino moiety showed a low catalytic activity (**Table 4.1**, entries 12, 20 and 21).

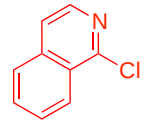
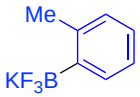
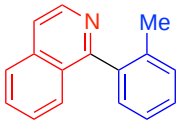
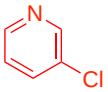
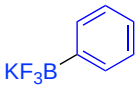
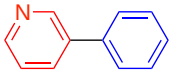
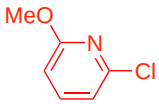
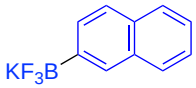
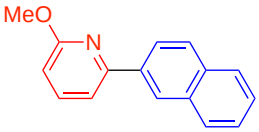
At last, $Pd(dba)_2$, PCy PhMezole-phos **L1b**, metal to ligand ratio of 1:2, $K_3PO_4 \cdot H_2O$ and mixing *t*-BuOH with toluene were chosen as the optimized reaction conditions which was used for further substrate scope development.

4.2.2 Suzuki-Miyaura Coupling of Aryl Chlorides with Potassium Aryltrifluoroborates

Table 4.2 Palladium-Catalyzed Suzuki Coupling of Aryl Chlorides with Potassium Aryltrifluoroborates[a]



Entry	ArCl	Ar'BF_3K	Product	mol% Pd	% Yield[b]
1				0.2	94
2				0.2	98
3				0.2	98
4				0.2	79
5				0.05	99
6				0.05	92
7				0.05	85
8				0.05	83
9				0.05	88

10				0.05	80
11				0.05	98
12				0.05	99

[a]Reaction conditions: ArCl (1.0 mmol), Ar'$BF_3K(OH)_2$ (1.5 mmol), $K_3PO_4 \cdot H_2O$ (3.0 mmol), $Pd(OAc)_2$/PCy PhMezole-phos (**L1b**) = 1:2, and *t*-BuOH/toluene (1:1, 3 mL) were stirred at 135 °C for 24 h under nitrogen. Catalyst loading and time for the reactions were not optimized. [b]Isolated yield.

The scope of this reaction was then investigated under the optimized conditions. A range of aryl chlorides was examined and the results are listed in **Table 4.2**. The deactivated aryl chlorides containing methyl or methoxy in *ortho*- or *para*- position were found to be a feasible coupling partner under 0.2 mol% Pd-loading (**Table 4.2**, entries 1 to 4). In addition, *ortho*-substituted aryltrifluoroborate was also good substrate for this reaction (**Table 4.2**, entries 5, 9 and 10).

On the other hand, a variety of common functional groups, such as ketone, ester and nitrile, were compatible under 0.05 mol% Pd-loading although the catalyst loading was not optimized (**Table 4.2**, entries 5 to 8).

Apart from a variety of aryl chlorides, heteroaryl chlorides were also examined. Quinolyl and pyridyl substrates could couple with potassium aryltrifluoroborates to furnish products in moderate to excellent yields. (**Table 4.2**, entries 9 to 12).

4.3 Conclusion

In conclusion, the combination of $Pd(dba)_2$ and PCy PhMezole-phos **L1b** was efficient towards Suzuki-Miyaura coupling of aryl chlorides with potassium aryltrifluoroborates. Non-activated, functionalized aryl and heteroaryl chlorides could also couple with potassium aryltrifluoroborates smoothly. Notably, the catalyst loading down to 0.05 mol% can also be achieved.

4.4 Experimental Section

4.4.1 General Considerations

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. All Suzuki-Miyaura coupling reactions were performed in resealable screw cap schlenk flask (approx. 20 mL volume) in the presence of Teflon coated magnetic stirrer bar (3mm × 10 mm). *tert*-Butanol, toluene, mesitylene and 1,4-dioxane were distilled from sodium under nitrogen.[6] Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under nitrogen.[6] Commercial aryl chlorides (liquid form only) were purified by passed through a short plug (0.5 cm wide × 4 cm high) of neutral alumina or distillation. Most commercially available potassium aryltrifluoroborates were used as received. $K_3PO_4 \cdot H_2O$ were purchased from chemical supplier and used without 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. Melting points were recorded on an uncorrected instrument. ^{1}H NMR spectra were recorded on a Bruker (400 MHz) spectrometer. Spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.26 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 ESIMS. GC-MS analysis was conducted on a GCD system using a column with 30 m × 0.25 mm. The products described in GC yield were accorded to the authentic samples/dodecane calibration standard from GC-FID system. Compounds described in the literature

were characterized by comparison of their ^{1}H 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.

4.4.2 General Procedure for Initial Ligand and Reaction Conditions Screening

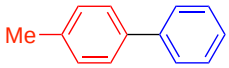
General procedure for initial ligand and reaction conditions screening: A stock solution of $Pd(dba)_2$ (5.8 mg, 0.010 mmol) with ligand in freshly distilled solvent (10 mL) was initially prepared with continuously stirring at room temperature. Potassium phenyltrifluoroborate (0.2760 g, 1.5 mmol), base (3.0 equiv., 3.0 mmol) and magnetic stirrer bar (3 mm $\times$ 8 mm) were charged to an array of Schlenk tubes. Each tube was carefully evacuated and backfilled with nitrogen (3 cycles). 2-Chlorotoluene (0.118 mL, 1.0 mmol) and stock solution (1.0 mL, 0.1 mol% Pd) were added *via* syringe. Further 2.0 mL solvent was added *via* syringe (final volume: 3 mL). This batch of Schlenk tube was resealed and magnetically stirred in a preheated 135 °C oil bath. The reactions were allowed to reach room temperature. Ethyl acetate (~10 mL), dodecane (227 μL, internal standard) water (~5 mL) were added. The organic layer was subjected to GC analysis. The GC yield was previously calibrated by authentic sample/dodecane calibration curve.

4.4.3 General Procedure for Suzuki-Miyaura Couplings of Aryl Chlorides with Potassium Aryltrifluoroborates

General procedure for Suzuki-Miyaura couplings of aryl chlorides with potassium aryltrifluoroborates: $Pd(dba)_2$ (5.8 mg, 0.010 mmol) and ligand **L1b** (Pd:L = 1:2) in freshly distilled 10 mL toluene (0.1 mol% Pd per 1 mL stock solution) was initially prepared with continuously stirring at room temperature. Potassium aryltrifluoroborate (1.5 mmol), $K_3PO_4 \cdot H_2O$ (3.0 mmol) and magnetic stirrer bar (3 mm × 8 mm) were charged to an array of Schlenk tubes. Each tube was carefully evacuated and backfilled with nitrogen (3 cycles). Aryl chloride (1.0 mmol) was then added to the Schlenk tubes. The stock solution was then transferred to Schlenk tubes *via* syringes. Further solvents were added (final volume: 3 mL, *t*-BuOH/ toluene, 1:1). This batch of Schlenk tube was resealed and magnetically stirred in a preheated 135 °C oil bath. After the completion of reaction as judged by GC or TLC analysis, the reactions were allowed to reach room temperature. Water (~3 mL) and ethyl acetate (~10 mL × 3) were added. The organic layers were combined and concentrated. The crude products were purified by column chromatography on silica gel (230-400 mesh).

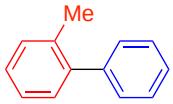
4.4.4 Characterization Data for Coupling Products

4-Methylbiphenyl (**Table 4.2**, entry 1)[7]



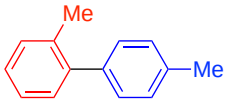
R_f = 0.5 (pure hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 2.56 (s, 3H), 7.41 (d, J = 8.0 Hz, 2H), 7.49 (t, J = 7.2 Hz, 1H), 7.59 (t, J = 7.2 Hz, 2H), 7.67 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 21.0, 126.9, 128.6, 129.4, 136.9, 138.31, 141.1; MS (EI): *m/z* (relative intensity) 168.1 (M^+, 100), 152.1 (24).

2-Methylbiphenyl (**Table 4.2**, entry 2)[8]



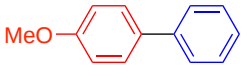
R_f = 0.5 (pure hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 2.44 (s, 3H), 7.40-7.42 (m, 4H), 7.48-7.50 (m, 3H), 7.54-7.58 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 20.4, 125.7, 126.7, 127.2, 128.0, 129.1, 129.7, 130.2, 135.2, 141.9, 141.9; MS (EI): *m/z* (relative intensity) 168.1 (M^+, 100), 153.0 (42).

2,4'-Dimethylbiphenyl (**Table 4.2**, entry 3)[8]



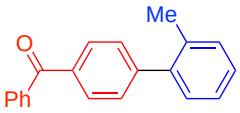
R_f = 0.5 (pure hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 2.48 (s, 3H), 2.59 (s, 3H), 7.42-7.43 (m, 8H); ^{13}C NMR (100MHz, $CDCl_3$) δ 20.4, 21.1, 125.7, 127.0, 128.7, 129.0, 129.8, 130.2, 135.3, 136.2, 139.0, 141.8; MS (EI): *m/z* (relative intensity) 182.1 (M^+, 88), 167.1 (100).

4-Methoxybiphenyl (**Table 4.2**, entry 4)[7]



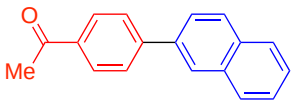
R_f = 0.5 (1:20 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 3.93 (s, 3H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.63-7.68 (m, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ 55.2, 114.1, 126.5, 128.0, 128.6, 133.6, 140.7, 159.1; MS (EI): *m/z* (relative intensity) 184.1 (M^+, 100), 169.1 (49), 141.1 (45), 115.1 (34).

(2'-Methylbiphenyl-4-yl)(phenyl)methanone (**Table 4.2**, entry 5)[8]



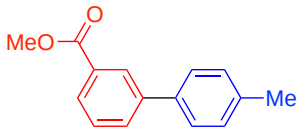
R_f = 0.5 (1:20 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 2.38 (s, 3H), 7.32-7.36 (m, 4H), 7.49-7.56 (m, 4H), 7.62-7.66 (m, 1H), 7.92-7.96 (m, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ 20.2, 125.7, 127.6, 128.0, 128.9, 129.3, 129.7, 130.3, 132.1, 134.8, 135.7, 137.4, 140.5, 146.0, 195.9; MS (EI): *m/z* (relative intensity) 272.1 (M^+, 80), 195.1 (100).

1-(4-(Naphthalen-2-yl)phenyl)ethanone (**Table 4.2**, entry 6)[9]



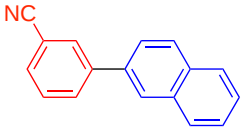
R_f = 0.3 (1:20 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 2.66 (s, 3H), 7.54-7.56 (m, 2H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.89-7.96 (m, 3H), 8.06 (s, 1H), 8.09 (d, *J* = 4.0 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 26.5, 125.0, 126.2, 126.3, 126.4, 127.3, 127.5, 128.2, 128.6, 128.8, 132.9, 133.4, 135.7, 136.9, 145.4, 197.5; MS (EI): *m/z* (relative intensity) 246.1 (M^+, 67), 231.1 (100), 202.1 (69).

Methyl 4'-methylbiphenyl-3-carboxylate (**Table 4.2**, entry 7)[10]



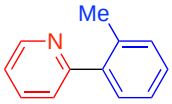
R_f = 0.5 (1:20 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 2.44 (s, 3H), 3.98 (s, 3H), 7.30 (d, J = 8.0 Hz, 2H), 7.50-7.58 (m, 3H), 7.80 (d, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 8.33 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 21.0, 52.0, 126.8, 127.9, 127.9, 128.69, 129.5, 130.5, 131.2, 137.1, 137.4, 141.2, 166.9; MS (EI): *m/z* (relative intensity) 226.1 (M^+, 100), 195.1 (71), 167.1 (35), 152.1 (39).

3-(Naphthalen-2-yl)benzonitrile (**Table 4.2**, entry 8)[11]



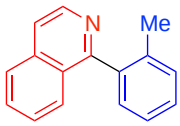
R_f = 0.4 (1:20 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 7.54-7.58 (m, 3H), 7.64-7.67 (m, 2H), 7.90-7.96 (m, 5H), 8.00 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 112.8, 118.7, 124.6, 126.0, 126.4, 126.5, 127.5, 128.1, 128.8, 129.4, 130.5, 130.6, 131.4, 132.8, 133.3, 135.8, 142.0; MS (EI): *m/z* (relative intensity) 229.1 (M^+, 100).

2-*o*-Tolylpyridine (**Table 4.2**, entry 9)[8]



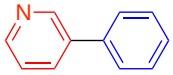
R_f = 0.5 (1:4 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 2.40 (s, 3H), 7.22 (t, *J* = 5.6 Hz, 1H), 7.30 (s, 3H), 7.38-7.44 (m, 2H), 7.71 (t, *J* = 7.2 Hz, 1H), 8.71 (d, *J* = 4.0 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 20.0, 121.3, 123.7, 125.6, 128.0, 129.3, 130.4, 135.4, 135.8, 140.1, 148.8, 159.7; MS (EI): *m/z* (relative intensity) 168.1 (M^+, 100).

1-*o*-Tolylisoquinoline (**Table 4.2**, entry 10)[12]



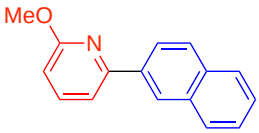
R_f = 0.5 (1:4 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 2.09 (s, 3H), 7.32-7.39 (m, 4H), 7.45 (t, J = 7.2 Hz, 1H), 7.62-7.68 (m, 3H), 7.85 (d, J = 8.0 Hz, 1H), 8.64 (d, J = 5.6 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 19.5, 119.6, 125.3, 126.6, 126.9, 127.1, 128.1, 129.3, 129.8, 130.0, 136.1, 136.1, 138.7, 141.9, 161.1; MS (EI): *m/z* (relative intensity) 218.1 (M^+, 100), 108.6 (16).

3-Phenylpyridine (**Table 4.2**, entry 11)[7]



R_f = 0.5 (1:4 E.A./Hexane); ^{1}H NMR (400MHz, CD_2Cl_2) δ 7.39-7.48 (m, 2H), 7.53 (t, J = 7.2 Hz, 2H), 7.65 (d, J = 7.6 Hz, 2H), 7.93 (d, J = 7.6 Hz, 1H). 8.63 (d, J = 4.8 Hz, 1H), 8.91 (s, 1H); ^{13}C NMR (100MHz, CD_2Cl_2) δ 123.5, 127.1, 128.0, 129.0, 134.1, 136.4, 137.9, 148.2, 148.4; MS (EI): *m/z* (relative intensity) 155.1 (M^+, 100).

2-Methoxy-6-(naphthalen-2-yl)pyridine (**Table 4.2**, entry 12)[13]



R_f = 0.6 (1:10 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 4.20 (s, 3H), 6.82 (d, J = 8.0 Hz, 1H), 7.50-7.70 (m, 4H), 7,94-8.01 (m, 3H), 8.29 (d, J = 8.4 Hz, 1H), 8.62 (d, J = 8.8 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 53.1, 109.1, 112.9, 124.4, 125.9, 126.0, 126.2, 127.5, 128.1, 128.5, 133.3, 133.5, 136.2, 139.0, 154.3, 163.6; MS (EI): *m/z* (relative intensity) 234.1 (M^+, 100), 294.1 (47).

4.5 References

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Chapter 5 Easily Accessible and Highly Tunable Alterable *P,O*- or *P,N*-Type 2-Phosphino-Substituted Benzimidazolyl Ligands for Palladium-Catalyzed Suzuki-Miyaura Coupling of Aryl Chlorides

5.1 Introduction

As mentioned previously in **Chapter 3**, palladium-catalyzed cross-couplings have received widespread applications in pharmaceutical, natural product and agricultural synthesis.[1] During the past decade, considerable efforts have been undertaken by researchers aiming to design unique phosphine ligands which allow challenging coupling reaction to proceed smoothly.[2]

Distinctive ligand scaffold has been underlined to be important in promoting cross-coupling reactions. In this regards, phosphine ligands in palladium-catalyzed cross-coupling of aryl halides generally contain electron-rich (to promote oxidative addition) and sterically bulky (to improve reductive elimination) features. In particular, phosphine containing a proximal dynamic hemilabile coordinating group would potentially offer additional catalyst longevity.[3] In 1999, Guram and Bei reported *P,O*-type ligands for Suzuki-Miyaura coupling and amination of aryl chlorides.[4] Recently, Hor,[5] Singer,[6] Stradiotto,[7] and other group[8] disclosed new entity of mixed-donor chelating ligands, which could tackle difficult cross-coupling processes. In 2011, McNulty reported *P,O* and *P,N*-type heterocyclic phosphines.[9] They suggested that different conformational feature of palladium-complexes would give dramatic

influence on catalytic activity.

We recently reported *P,O* and *P,N*-type ligands, Amidole-phos[10] and PhMezole-phos (see **Chapter 3** & **4**), respectively (**Figure 5.1**). We herein demonstrate our exploration of a new family of 2-phosphino-substituted benzimidazolyl ligands towards Suzuki-Miyaura cross-coupling of aryl chlorides.

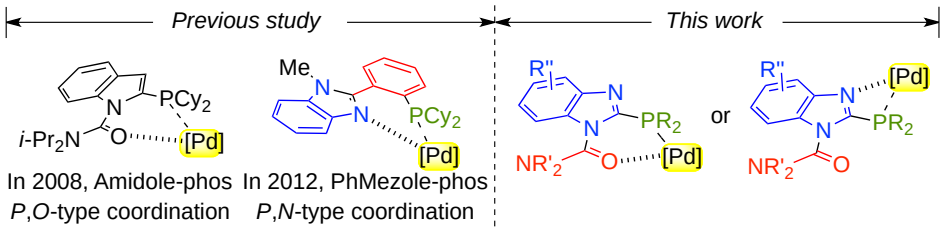
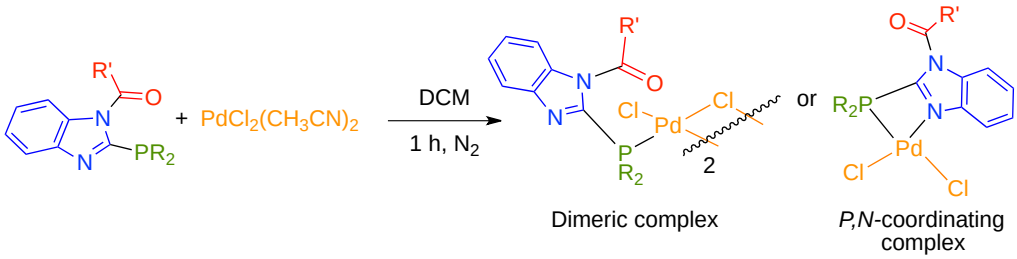


Figure 5.1 Previous Ligand Structures/Coordination and Present Investigation.

5.2 Results and Discussion

5.2.1 Structural Insight of Palladium-Ligand interaction

To investigate the unique binding properties of the 2-phosphino-substituted benzimidazolyl ligands series, we have grown single crystal of palladium complexes from $PdCl_2(CH_3CN)_2$ and ligands (**Scheme 5.1**).



Scheme 5.1 Complexation of 2-Phosphino-Substituted Benzimidazolyl Ligands with $PdCl_2(CH_3CN)_2$

After we have grown different crystal structures of complex, we found that phosphine with bulky –P*t*-Bu_2 moiety was found to coordinate in a κ^2-*P*,*N* fashion (**Figure 5.3**, **5.6** and **5.8** to **5.9**), while phosphine with less sterically congested, such as –PCy_2 and –P*i*-Pr moiety (**Figure 5.2**, **5.4**, **5.5** and **5.7**), was a dimeric complex, in which the bottom carbamoyl oxygen pointed towards the palladium center and showed a potential *P*,*O*-hemilabile ability. Hence, we deduced that adjusting the bulkiness of the phosphino group could alter the site of coordination of the ligand to metal.

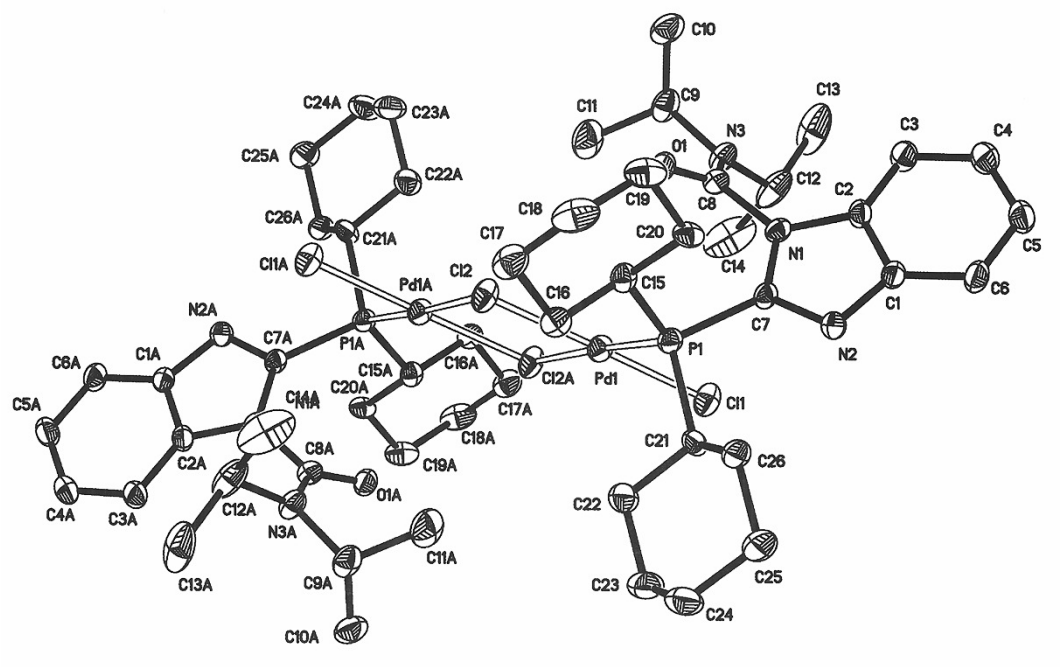


Figure 5.2 ORTEP Representation of Complex Pd-PCy Amizole-phos **L2a** (30% probability ellipsoids, hydrogen atoms have been omitted for clarity purpose.)

Table 5.1 Selected Bond Distances (Å) and Angles (°)

Bond Distances (Å)			
Pd(1)-P(1)	2.2257(9)	Pd(1)-Cl(1)	2.2816(11)
Pd(1)-Cl(2)	2.3240(11)	Pd(1)-Cl(2)#1	2.4236(9)
Cl(2)-Pd(1)#1	2.4236(9)	P(1)-C(7)	1.814(4)
P(1)-C(21)	1.842(4)	P(1)-C(15)	1.846(4)
Angles (°)			
P(1)-Pd(1)-Cl(1)	85.51(4)	P(1)-Pd(1)-Cl(2)	96.18(3)
Cl(1)-Pd(1)-Cl(2)	178.26(4)	P(1)-Pd(1)-Cl(2)#1	177.53(4)
Cl(1)-Pd(1)-Cl(2)#1	93.14(4)	Cl(2)-Pd(1)-Cl(2)#1	85.15(4)
Pd(1)-Cl(2)-Pd(1)#1	94.85(4)		

Table 5.2 Crystal Data and Structure Refinement for Pd-PCy Amizole-phos **L2a** Complex

Empirical formula	$[PdCl_2(C_{26}H_{40}N_3OP)]_2$
Formula weight	1237.76
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 13.8769(5) Å α= 90°.
	b = 24.3168(10) Å β= 101.287(2)°.
	c = 9.5464(3) Å γ = 113.505(4)°.
Volume	3159.0(2) $Å^3$
Z	2
Density (calculated)	1.301 Mg/m^3
Absorption coefficient	0.828 mm^{-1}
F(000)	1280
Crystal size	0.18 x 0.10 x 0.08 mm^3
Theta range for data collection	2.33 to 27.58°.
Index ranges	-17<=h<=17, -31<=k<=29, -12<=l<=12
Reflections collected	35115
Independent reflections	7203 [R(int) = 0.1233]
Completeness to theta = 27.58°	98.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.5803
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7203 / 0 / 308
Goodness-of-fit on F^2	1.001
Final R indices [I>2sigma(I)]	R1 = 0.0756, wR2 = 0.1535
R indices (all data)	R1 = 0.1710, wR2 = 0.2278
Extinction coefficient	0.0081(2)
Largest diff. peak and hole	1.077 and -1.145 $e.Å^{-3}$

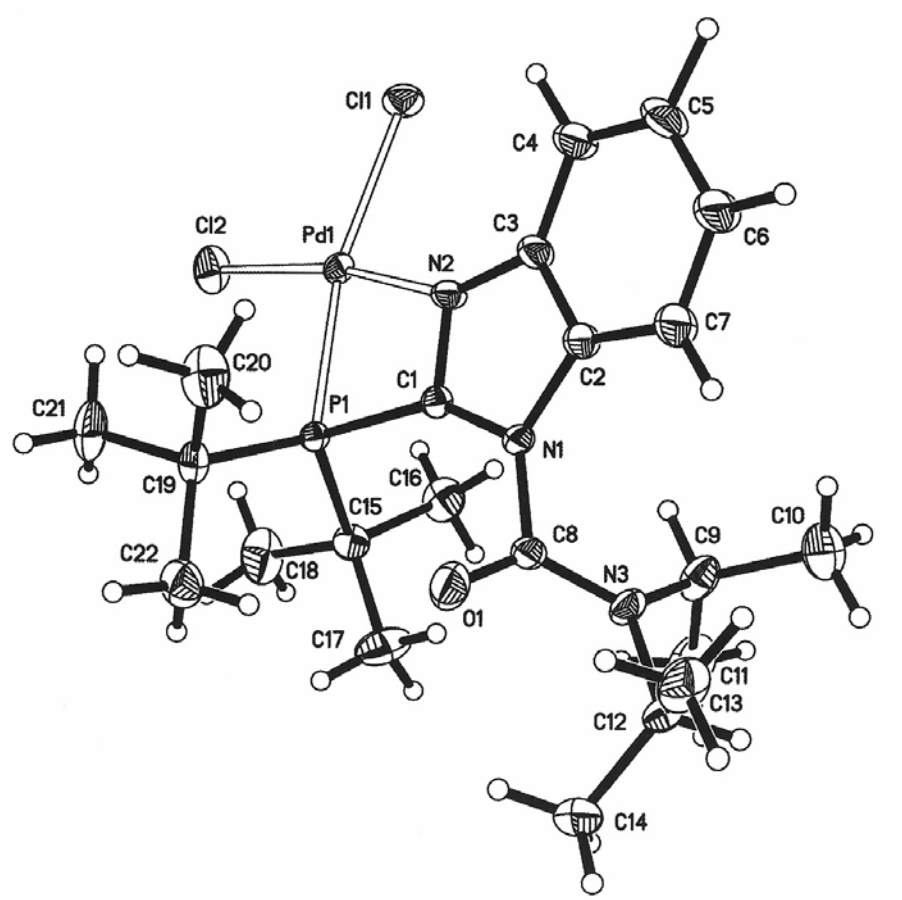


Figure 5.3 ORTEP Representation of Complex Pd-P*t*-Bu Amizole-phos **L2b** (30% probability ellipsoids, hydrogen atoms have been omitted for clarity purpose.)

Table 5.3 Selected Bond Distances (Å) and Angles (°)

Bond Distances (Å)			
Pd(1)-N(2)	2.029(3)	Pd(1)-P(1)	2.2569(8)
Pd(1)-Cl(2)	2.2827(10)	Pd(1)-Cl(1)	2.3688(10)
P(1)-C(1)	1.838(3)	P(1)-C(15)	1.850(3)
P(1)-C(19)	1.862(3)		
Angles (°)			
N(2)-Pd(1)-P(1)	70.84(7)	N(2)-Pd(1)-Cl(2)	169.14(8)
P(1)-Pd(1)-Cl(2)	98.37(3)	N(2)-Pd(1)-Cl(1)	95.88(8)
P(1)-Pd(1)-Cl(1)	166.04(4)	Cl(2)-Pd(1)-Cl(1)	94.97(4)

Table 5.4 Crystal Data and Structure Refinement for Pd-P*t*-Bu Amizole-phos **L2b** Complex

Empirical formula	$PdCl_2(C_{22}H_{36}N_3OP)$
Formula weight	566.81
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/n
Unit cell dimensions	a = 13.4083(3) Å α= 90°.
	b = 11.6455(3) Å β= 98.0390(10)°.
	c = 16.6487(4) Å γ = 90°.
Volume	2574.09(11) $Å^3$
Z	4
Density (calculated)	1.463 Mg/m^3
Absorption coefficient	1.009 mm^{-1}
F(000)	1168
Crystal size	0.48 x 0.28 x 0.24 mm^3
Theta range for data collection	1.83 to 27.42°.
Index ranges	-17<=h<=17, -15<=k<=15, -21<=l<=21
Reflections collected	39515
Independent reflections	5840 [R(int) = 0.0600]
Completeness to theta = 27.42°	99.6 %
Absorption correction	None
Max. and min. transmission	0.7456 and 0.4921
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5840 / 0 / 288
Goodness-of-fit on F^2	1.002
Final R indices [I>2sigma(I)]	R1 = 0.0651, wR2 = 0.1941
R indices (all data)	R1 = 0.0822, wR2 = 0.2254
Largest diff. peak and hole	1.006 and -0.930 e.$Å^{-3}$

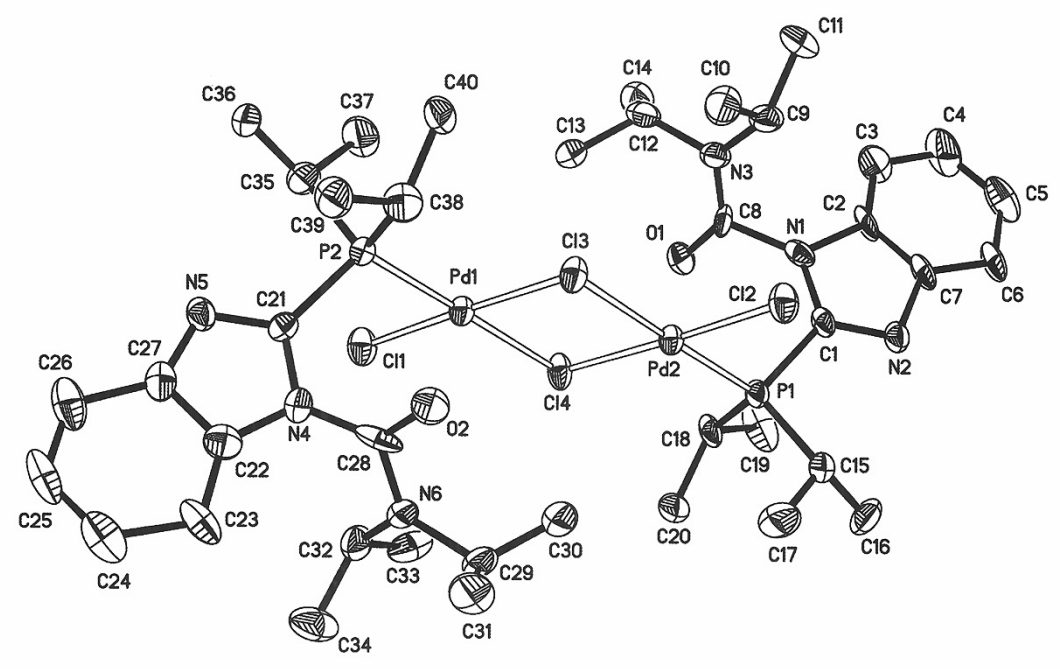


Figure 5.4 ORTEP Representation of Complex Pd-P*i*-Pr Amizole-phos **L2c** (30% probability ellipsoids, hydrogen atoms have been omitted for clarity purpose.)

Table 5.5 Selected Bond Distances (Å) and Angles (°)

Bond Distances (Å)			
Pd(1)-P(2)	2.2257(10)	Pd(1)-Cl(1)	2.2799(11)
Pd(1)-Cl(3)	2.3294(10)	Pd(1)-Cl(4)	2.4192(9)
Pd(2)-P(1)	2.2245(8)	Pd(2)-Cl(2)	2.2751(13)
Pd(2)-Cl(4)	2.3359(12)	Pd(2)-Cl(3)	2.4329(8)
Angles (°)			
P(2)-Pd(1)-Cl(1)	84.44(4)	P(2)-Pd(1)-Cl(3)	97.49(4)
Cl(1)-Pd(1)-Cl(3)	178.05(3)	P(2)-Pd(1)-Cl(4)	178.06(4)
Cl(1)-Pd(1)-Cl(4)	93.67(4)	Cl(3)-Pd(1)-Cl(4)	84.41(4)
Pd(1)-Cl(3)-Pd(2)	95.71(3)		

Table 5.6 Crystal Data and Structure Refinement for Pd-P*i*-Pr Amizole-phos **L2c** Complex

Empirical formula	$[PdCl_2(C_{20}H_{32}N_3OP)]_2$
Formula weight	1077.51
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	Cc
Unit cell dimensions	a = 31.8142(7) Å α= 90°.
	b = 11.9373(3) Å β= 115.0800(10)°.
	c = 14.0027(3) Å γ = 90°.
Volume	4816.50(19) $Å^3$
Z	4
Density (calculated)	1.486 Mg/m^3
Absorption coefficient	1.074 mm^{-1}
F(000)	2208
Crystal size	0.50 x 0.40 x 0.34 mm^3
Theta range for data collection	1.85 to 27.45°.
Index ranges	-31<=h<=41, -14<=k<=15, -18<=l<=18
Reflections collected	27296
Independent reflections	8494 [R(int) = 0.0379]
Completeness to theta = 27.45°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6418
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8494 / 2 / 577
Goodness-of-fit on F^2	1.005
Final R indices [I>2sigma(I)]	R1 = 0.0382, wR2 = 0.0768
R indices (all data)	R1 = 0.0607, wR2 = 0.0923
Absolute structure parameter	0.00
Largest diff. peak and hole	0.948 and -1.232 $e.Å^{-3}$

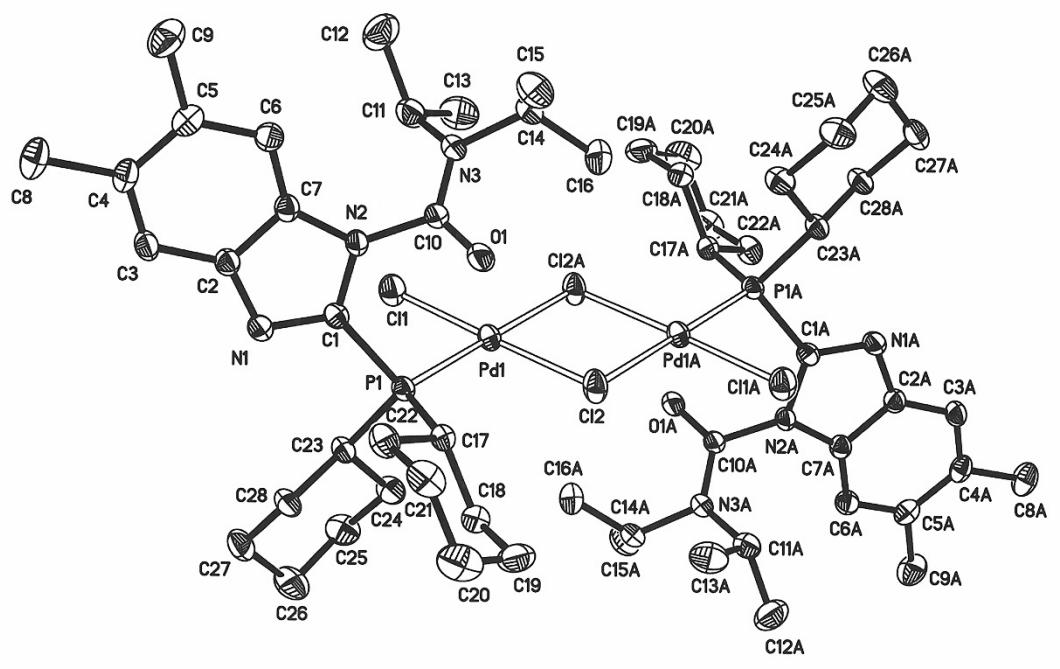


Figure 5.5 ORTEP Representation of Complex Pd-PCy Amizole^{M2}-phos **L2i** (30% probability ellipsoids, hydrogen atoms have been omitted for clarity purpose.)

Table 5.7 Selected Bond Distances (Å) and Angles (°)

Bond Distances (Å)			
Pd(1)-P(1)	2.2219(6)	Pd(1)-Cl(1)	2.2850(7)
Pd(1)-Cl(2)	2.3272(6)	Pd(1)-Cl(2)#1	2.4205(6)
Cl(2)-Pd(1)#1	2.4205(6)	P(1)-C(1)	1.815(2)
P(1)-C(23)	1.840(2)	P(1)-C(17)	1.845(2)
Angles (°)			
P(1)-Pd(1)-Cl(1)	85.35(2)	P(1)-Pd(1)-Cl(2)	96.47(2)
Cl(1)-Pd(1)-Cl(2)	178.15(2)	P(1)-Pd(1)-Cl(2)#1	177.16(2)
Cl(1)-Pd(1)-Cl(2)#1	93.04(2)	Cl(2)-Pd(1)-Cl(2)#1	85.15(2)
Pd(1)-Cl(2)-Pd(1)#1	94.85(2)		

Table 5.8 Crystal Data and Structure Refinement for Pd-PCy Amizole^{M2}-phos **L2i** Complex

Empirical formula	$[(PdCl)Cl(C_{28}H_{44}N_3OP)]_2 .2(CH_2Cl_2)$	
Formula weight	1463.72	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.6010(3) Å	α= 88.389(2)°.
	b = 13.0326(3) Å	β= 77.005(2)°.
	c = 14.0213(4) Å	γ = 81.740(2)°.
Volume	1691.75(8) $Å^3$	
Z	1	
Density (calculated)	1.437 Mg/m^3	
Absorption coefficient	0.938 mm^{-1}	
F(000)	756	
Crystal size	0.20 x 0.14 x 0.12 mm^3	
Theta range for data collection	1.49 to 27.53°.	
Index ranges	-12<=h<=12, -16<=k<=16, -18<=l<=18	
Reflections collected	31841	
Independent reflections	7762 [R(int) = 0.0750]	
Completeness to theta = 27.53°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6448	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7762 / 1 / 350	
Goodness-of-fit on F^2	1.001	
Final R indices [I>2sigma(I)]	R1 = 0.0494, wR2 = 0.1133	
R indices (all data)	R1 = 0.0897, wR2 = 0.1337	
Largest diff. peak and hole	0.960 and -0.937 e.$Å^{-3}$	

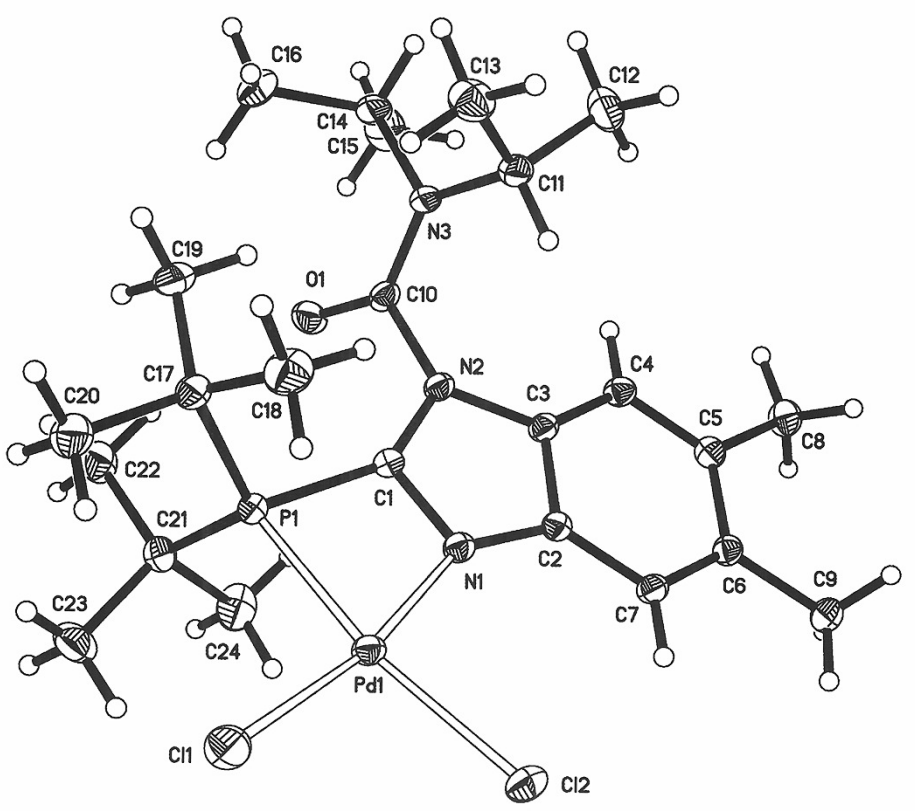


Figure 5.6 ORTEP Representation of Complex Pd-P*t*-Bu Amizole^{M2}-phos **L2j** (30% probability ellipsoids, hydrogen atoms have been omitted for clarity purpose.)

Table 5.9 Selected Bond Distances (Å) and Angles (°)

Bond Distances (Å)			
Pd(1)-N(1)	2.0402(16)	Pd(1)-P(1)	2.2509(5)
Pd(1)-Cl(1)	2.2796(6)	Pd(1)-Cl(2)	2.3486(6)
P(1)-C(1)	1.8373(19)	P(1)-C(17)	1.857(2)
P(1)-C(21)	1.869(2)		
Angles (°)			
N(1)-Pd(1)-P(1)	70.87(4)	N(1)-Pd(1)-Cl(1)	168.44(5)
P(1)-Pd(1)-Cl(1)	97.73(2)	N(1)-Pd(1)-Cl(2)	97.36(4)
P(1)-Pd(1)-Cl(2)	168.20(2)	Cl(1)-Pd(1)-Cl(2)	94.00(2)

Table 5.10 Crystal Data and Structure Refinement for Pd-P*t*-Bu Amizole^{M2}-phos **L2j** Complex

Empirical formula	$PdCl_2(C_{25}H_{40}N_2OP)\ .(CH_2Cl_2)$
Formula weight	679.79
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 11.4333(3) Å α= 90°.
	b = 13.5925(4) Å β= 91.390(2)°.
	c = 20.6057(6) Å γ = 90°.
Volume	3201.33(16) $Å^3$
Z	4
Density (calculated)	1.410 Mg/m^3
Absorption coefficient	0.985 mm^{-1}
F(000)	1400
Crystal size	0.50 x 0.34 x 0.14 mm^3
Theta range for data collection	1.78 to 27.46°.
Index ranges	-14<=h<=14, -17<=k<=17, -26<=l<=21
Reflections collected	49147
Independent reflections	7249 [R(int) = 0.0537]
Completeness to theta = 27.46°	99.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.5817
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7249 / 0 / 317
Goodness-of-fit on F^2	1.000
Final R indices [I>2sigma(I)]	R1 = 0.0374, wR2 = 0.0815
R indices (all data)	R1 = 0.0559, wR2 = 0.0905
Largest diff. peak and hole	0.735 and -0.818 $e.Å^{-3}$

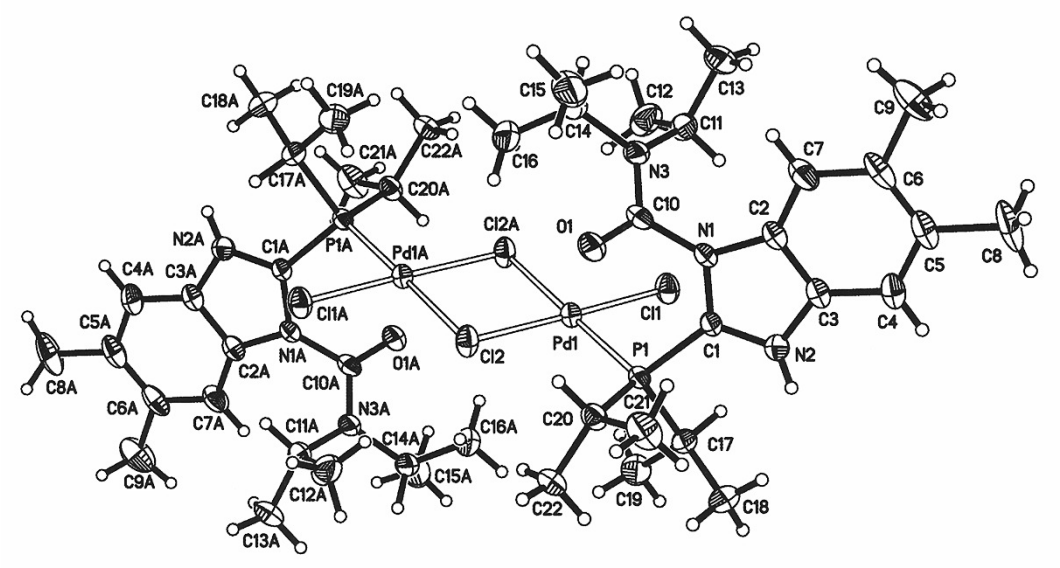


Figure 5.7 ORTEP Representation of Complex Pd-P*i*-Pr Amizole^{M2}-phos **L2k** (30% probability ellipsoids, hydrogen atoms have been omitted for clarity purpose.)

Table 5.11 Selected Bond Distances (Å) and Angles (°)

Bond Distances (Å)			
Pd(1)-P(1)	2.2238(8)	Pd(1)-Cl(1)	2.2790(9)
Pd(1)-Cl(2)	2.3311(9)	Pd(1)-Cl(2)#1	2.4231(9)
Cl(2)-Pd(1)#1	2.4231(8)	P(1)-C(1)	1.818(3)
P(1)-C(20)	1.848(3)	P(1)-C(17)	1.852(4)
Angles (°)			
P(1)-Pd(1)-Cl(1)	84.54(3)	P(1)-Pd(1)-Cl(2)	97.33(3)
Cl(1)-Pd(1)-Cl(2)	178.13(3)	P(1)-Pd(1)-Cl(2)#1	177.51(3)
Cl(1)-Pd(1)-Cl(2)#1	93.29(3)	Cl(2)-Pd(1)-Cl(2)#1	84.84(3)
Pd(1)-Cl(2)-Pd(1)#1	95.16(3)		

Table 5.12 Crystal Data and Structure Refinement for Pd-P*i*-Pr Amizole^{M2}-phos **L2k** Complex

Empirical formula	$[PdCl(Cl)(C_{22}H_{37}N_3OP)]_2 \cdot 2(H_2O)$	
Formula weight	1171.66	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 18.443(3) Å	α= 90°.
	b = 11.3457(18) Å	β= 112.822(7)°.
	c = 14.494(2) Å	γ = 90°.
Volume	2795.4(7) $Å^3$	
Z	2	
Density (calculated)	1.392 Mg/m^3	
Absorption coefficient	0.934 mm^{-1}	
F(000)	1212	
Crystal size	0.50 x 0.42 x 0.42 mm^3	
Theta range for data collection	2.16 to 27.53°.	
Index ranges	-23<=h<=23, -14<=k<=14, -18<=l<=17	
Reflections collected	32253	
Independent reflections	6057 [R(int) = 0.0425]	
Completeness to theta = 27.53°	94.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6089	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6057 / 0 / 296	
Goodness-of-fit on F^2	1.001	
Final R indices [I>2sigma(I)]	R1 = 0.0489, wR2 = 0.1413	
R indices (all data)	R1 = 0.0701, wR2 = 0.1798	
Largest diff. peak and hole	1.089 and -1.152 e.$Å^{-3}$	

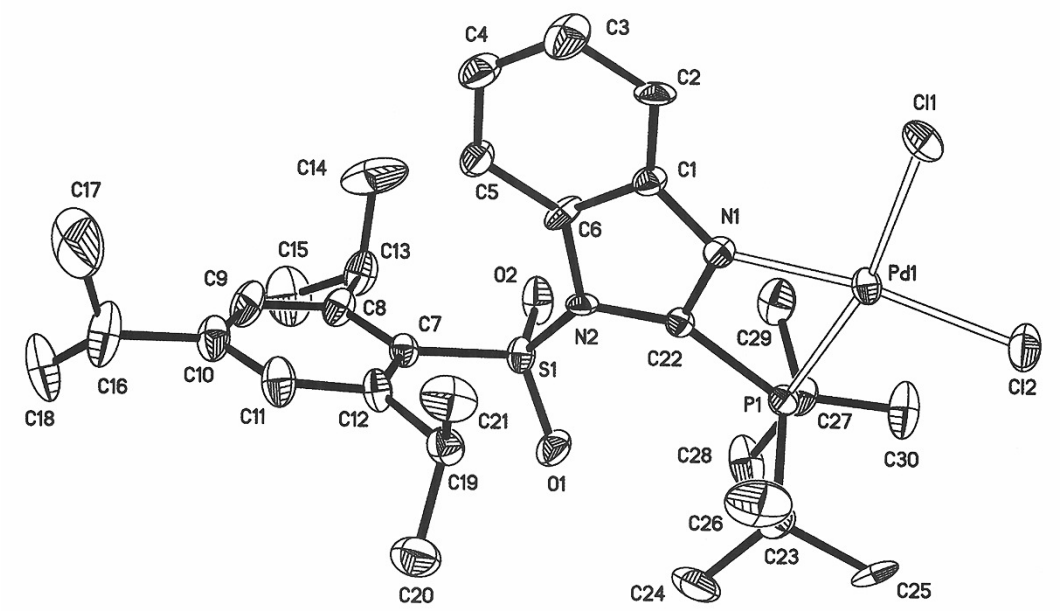


Figure 5.8 ORTEP Representation of Complex Pd-P*t*-Bu ^{P3}Sulfozole-phos **L2q** (30% probability ellipsoids, hydrogen atoms have been omitted for clarity purpose.)

Table 5.13 Selected Bond Distances (Å) and Angles (°)

Bond Distances (Å)			
Pd(1)-N(1)	2.035(2)	Pd(1)-P(1)	2.2598(8)
Pd(1)-Cl(2)	2.2814(9)	Pd(1)-Cl(1)	2.3348(9)
P(1)-C(22)	1.852(3)	P(1)-C(27)	1.854(4)
P(1)-C(23)	1.866(4)		
Angles (°)			
N(1)-Pd(1)-P(1)	71.27(8)	N(1)-Pd(1)-Cl(2)	170.95(8)
P(1)-Pd(1)-Cl(2)	99.78(3)	N(1)-Pd(1)-Cl(1)	96.15(8)
P(1)-Pd(1)-Cl(1)	167.36(3)	Cl(2)-Pd(1)-Cl(1)	92.83(4)

Table 5.14 Crystal Data and Structure Refinement for Pd-P*t*-Bu ^{P3}Sulfozole-phos **L2q** Complex

Empirical formula	$PdCl_2(C_{30}H_{46}N_2O_2SP)\ .CH_2Cl_2$
Formula weight	791.94
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pna2(1)
Unit cell dimensions	a = 28.5856(7) Å α= 90°.
	b = 12.8636(4) Å β= 90°.
	c = 10.0522(3) Å γ = 90°.
Volume	3696.33(18) $Å^3$
Z	4
Density (calculated)	1.423 Mg/m^3
Absorption coefficient	0.920 mm^{-1}
F(000)	1636
Crystal size	0.32 x 0.30 x 0.24 mm^3
Theta range for data collection	1.74 to 27.43°.
Index ranges	-37<=h<=35, -16<=k<=15, -13<=l<=9
Reflections collected	21451
Independent reflections	7050 [R(int) = 0.0502]
Completeness to theta = 27.43°	97.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.5681
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7050 / 1 / 375
Goodness-of-fit on F^2	1.005
Final R indices [I>2sigma(I)]	R1 = 0.0566, wR2 = 0.1278
R indices (all data)	R1 = 0.0803, wR2 = 0.1648
Absolute structure parameter	-0.05(5)
Largest diff. peak and hole	1.146 and -1.535 $e.Å^{-3}$

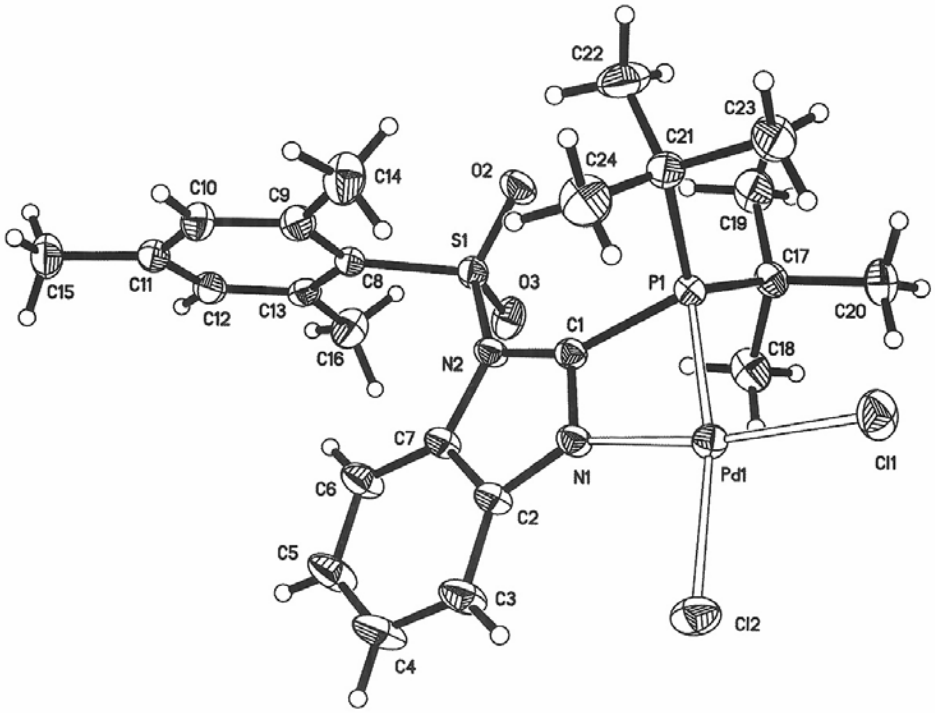


Figure 5.9 ORTEP Representation of Complex Pd-P*t*-Bu ^{M3}Sulfozole-phos **L2s** (30% probability ellipsoids, hydrogen atoms have been omitted for clarity purpose.)

Table 5.15 Selected Bond Distances (Å) and Angles (°)

Bond Distances (Å)			
Pd(1)-N(1)	2.0261(15)	Pd(1)-P(1)	2.2681(5)
Pd(1)-Cl(1)	2.2772(5)	Pd(1)-Cl(2)	2.3503(5)
P(1)-C(1)	1.8572(17)	P(1)-C(21)	1.8694(19)
P(1)-C(17)	1.8712(18)		
Angles (°)			
N(1)-Pd(1)-P(1)	70.53(4)	N(1)-Pd(1)-Cl(1)	170.90(4)
P(1)-Pd(1)-Cl(1)	100.375(19)	N(1)-Pd(1)-Cl(2)	97.93(4)
P(1)-Pd(1)-Cl(2)	168.428(19)	Cl(1)-Pd(1)-Cl(2)	91.16(2)

Table 5.16 Crystal Data and Structure Refinement for Pd-P*t*-Bu ^{M3}Sulfozole-phos **L2s** Complex

Empirical formula	$PdCl_2(C_{24}H_{33}N_2O_2SP)$
Formula weight	621.85
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/n
Unit cell dimensions	a = 13.0661(3) Å α= 90°.
	b = 15.4288(4) Å β= 100.8850(10)°.
	c = 13.6838(3) Å γ = 90°.
Volume	2708.94(11) $Å^3$
Z	4
Density (calculated)	1.525 Mg/m^3
Absorption coefficient	1.042 mm^{-1}
F(000)	1272
Crystal size	0.50 x 0.44 x 0.16 mm^3
Theta range for data collection	2.01 to 28.55°.
Index ranges	-17<=h<=15, -20<=k<=20, -18<=l<=18
Reflections collected	39631
Independent reflections	6850 [R(int) = 0.0467]
Completeness to theta = 28.55°	99.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.5717
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6850 / 0 / 353
Goodness-of-fit on F^2	1.002
Final R indices [I>2sigma(I)]	R1 = 0.0334, wR2 = 0.0729
R indices (all data)	R1 = 0.0510, wR2 = 0.0798
Largest diff. peak and hole	0.362 and -0.387 $e.Å^{-3}$

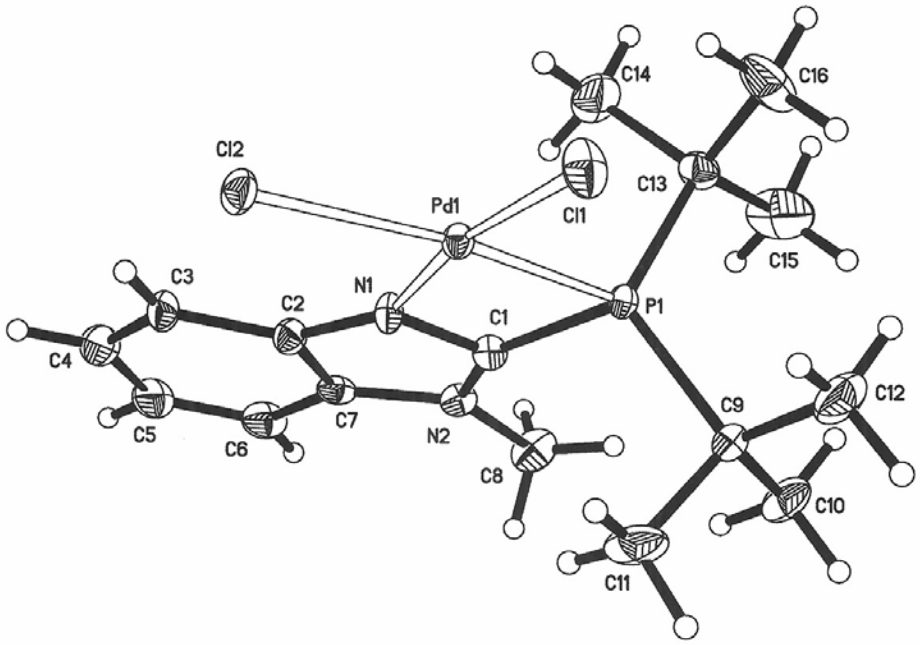


Figure 5.10 ORTEP Representation of Complex Pd-P*t*-Bu Mezole-phos **L2g** (30% probability ellipsoids, hydrogen atoms have been omitted for clarity purpose.)

Table 5.17 Selected Bond Distances (Å) and Angles (°)

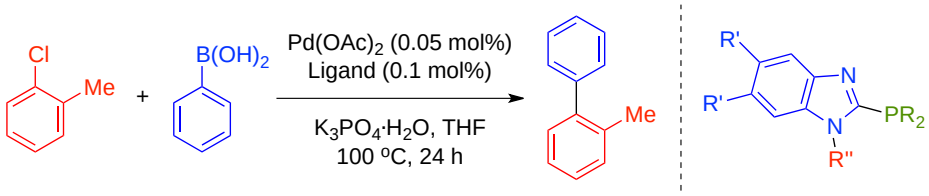
Bond Distances (Å)			
Pd(1)-N(1)	2.039(2)	Pd(1)-P(1)	2.2618(7)
Pd(1)-Cl(1)	2.2820(8)	Pd(1)-Cl(2)	2.3631(8)
P(1)-C(1)	1.833(3)	P(1)-C(9)	1.867(3)
P(1)-C(13)	1.880(3)		
Angles (°)			
N(1)-Pd(1)-P(1)	70.62(7)	N(1)-Pd(1)-Cl(1)	169.58(7)
P(1)-Pd(1)-Cl(1)	99.31(3)	N(1)-Pd(1)-Cl(2)	96.62(7)
P(1)-Pd(1)-Cl(2)	167.23(3)	Cl(1)-Pd(1)-Cl(2)	93.42(3)

Table 5.18 Crystal Data and Structure Refinement for Pd-P*t*-Bu Mezole-phos **L2g** Complex

Empirical formula	$PdCl_2(C_{16}H_{25}N_2P)$	
Formula weight	453.65	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 16.2011(4) Å	α= 90°.
	b = 12.5887(3) Å	β= 103.8050(10)°.
	c = 19.7586(4) Å	γ = 90°.
Volume	3913.37(16) $Å^3$	
Z	8	
Density (calculated)	1.540 Mg/m^3	
Absorption coefficient	1.301 mm^{-1}	
F(000)	1840	
Crystal size	0.50 x 0.40 x 0.40 mm^3	
Theta range for data collection	1.86 to 27.42°.	
Index ranges	-20<=h<=20, -15<=k<=16, -25<=l<=25	
Reflections collected	40456	
Independent reflections	8580 [R(int) = 0.0583]	
Completeness to theta = 27.42°	96.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.5123	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8580 / 0 / 379	
Goodness-of-fit on F^2	1.004	
Final R indices [I>2sigma(I)]	R1 = 0.0638, wR2 = 0.1831	
R indices (all data)	R1 = 0.0785, wR2 = 0.2080	
Largest diff. peak and hole	1.109 and -1.800 $e.Å^{-3}$	

5.2.2 Preliminary Study on the Effectiveness of 2-Phosphino-Substituted Benzimidazolyl Ligands

Table 5.19 Investigation on the Effectiveness of 2-Phosphino-Substituted Benzimidazolyl Ligands in Palladium-Catalyzed Suzuki-Miyaura Coupling of Aryl Chloride[a]



Entry	Ligand	% Yield
1	PCy Amizole-phos **L2a** (R' = H, R" = C(O)N*i*-Pr$_2$, R = Cy)	43
2	P*t*-Bu Amizole-phos **L2b** (R' = H, R" = C(O)N*i*-Pr$_2$, R = *t*-Bu)	8
3	P*i*-Pr Amizole-phos **L2c** (R' = H, R" = C(O)N*i*-Pr$_2$, R = *i*-Pr)	18
4	PPh Amizole-phos **L2d** (R' = H, R" = C(O)N*i*-Pr$_2$, R = Ph)	0
5	PEt Amizole-phos **L2e** (R' = H, R" = C(O)N*i*-Pr$_2$, R = Et)	0
6	PCy Mezole-phos **L2f** (R' = H, R" = Me, R = Cy)	18
7	P*t*-Bu Mezole-phos **L2g** (R' = H, R" = Me, R = *t*-Bu)	0
8	PCyp Mezole-phos **L2h** (R' = H, R" = Me, R = Cyp)	9
9	PCy Amizole^{M2}-phos **L2i** (R' = Me, R" = C(O)N*i*-Pr$_2$, R = Cy)	57
10	P*t*-Bu Amizole^{M2}-phos **L2j** (R' = Me, R" = C(O)N*i*-Pr$_2$, R = *t*-Bu)	13
11	P*i*-Pr Amizole^{M2}-phos **L2k** (R' = Me, R" = C(O)N*i*-Pr$_2$, R = *i*-Pr)	23
12	PPh Amizole^{M2}-phos **L2l** (R' = Me, R" = C(O)N*i*-Pr$_2$, R = Ph)	0
13	P*o*-Tol Amizole^{M2}-phos **L2m** (R' = Me, R" = C(O)N*i*-Pr$_2$, R = *o*-Tol)	0
14	PCyp Amizole^{M2}-phos **L2n** (R' = Me, R" = C(O)N*i*-Pr$_2$, R = Cyp)	38
15	PCy ^{P3}Sulfozole-phos **L2p** (R' = H, R" = SO$_2$-2,4,6-*i*-Pr$_3$C$_6$H$_2$, R = Cy)	3
16	P*t*-Bu ^{P3}Sulfozole-phos **L2q** (R' = H, R" = SO$_2$-2,4,6-*i*-Pr$_3$C$_6$H$_2$, R = *t*-Bu)	0
17	PCy ^{M3}Sulfozole-phos **L2r** (R' = H, R" = SO$_2$-2,4,6-Me$_3$C$_6$H$_2$, R = Cy)	3
18	P*t*-Bu ^{M3}Sulfozole-phos **L2s** (R' = H, R" = SO$_2$-2,4,6-Me$_3$C$_6$H$_2$, R = *t*-Bu)	0

[a]Reaction conditions: 2-Chlorotoluene (1.0 mmole), phenylboronic acid (1.5 mmole), $K_3PO_4 \cdot H_2O$ (3.0 mmole), $Pd(OAc)_2$/L = 1:2, and THF (3 mL) were stirred for 24 h at 100 °C under nitrogen. Calibrated GC yields were reported using dodecane as the internal standard, average of two runs.

In order to test the effectiveness of the 2-phosphino-substituted benzimidazolyl ligands, the 2-chlorotoluene and phenylboronic acid was used as the benchmark substrate. A combination of $Pd(OAc)_2$ with an array of 2-phosphino-substituted benzimidazolyl ligands was applied in probing the ligand efficacy (**Table 5.19**). Ligands PCy Amizole^{M2}-phos **L2i** showed the highest percentage yield of the desired product among the other ligands examined.

The efficacy of ligands Amizole-phos **L2a** to **L2e** in Suzuki-Miyaura coupling were firstly investigated (**Table 5.19**, entries 1 to 5). Ligand PCy Amizole-phos **L2a** with dicyclohexylphosphino moiety provided the best catalytic activity among the other corresponding ligands. Ligand P*t*-Bu Amizole-phos **L2b** bearing a sterically congested and electron-donating di-*tert*-butylphosphino moiety showed almost no conversion towards the coupling reaction while ligand P*i*-Pr Amizole-phos **L2c** bearing diisopropylphosphino moiety in which the steric bulkiness is similar to dicyclohexylphosphino moiety afforded lower conversion. On the other hand, ligand PPh Amizole-phos **L2d** with a diphenylphosphino moiety provided no conversion since the π-conjugated system in two phenyl rings decreased the electron richness in coordinated metal center by delocalization. In addition, ligand PEt Amizole-phos **L2e** bearing a less sterically congested diethylphosphino moiety showed also no conversion.

In order to indicate the importance of the bottom *N*-substituted group of the ligands, the carbamoyl-substituent ligands were changed to methyl group (ligands Mezole-phos **L2f**, **L2g** and **L2h**), and sulfonyl group (ligands

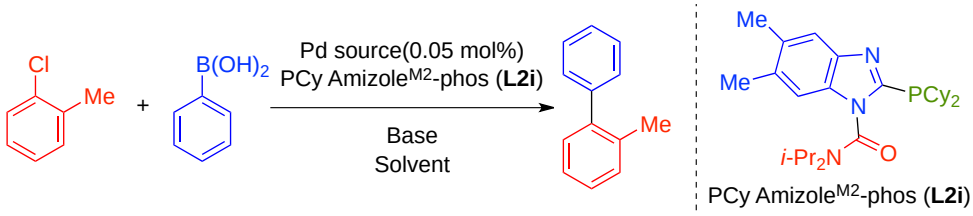
^{P3}Sulfozole-phos **L2p** and **L2q**, and ^{M3}Sulfozole-phos **L2r** and **L2s**). Steric bulkiness of the bottom *N*-substituted group can be arranged in ascending order, methyl < carbamoyl < mesitylsulfonyl < 2,4,6-triisopropylphenylsulfonyl. No matter increasing the steric bulkiness of the *N*-substituted group by replacing carbamoyl group with mesitylsulfonyl group or 2,4,6-triisopropylphenylsulfonyl group, or reducing the size to methyl group, they just gave a trace or even no conversion (**Table 5.19**, entries 6 to 8 and 15 to 18). Ligand PCy Amizole-phos **L2a** bearing carbamoyl group as the bottom *N*-substituted group showed a better catalytic result, which could also be implied that carbamoyl group offered the most suitable bulkiness for the dynamic "On and Off" interaction towards the metal center of the catalytic system and hence to enhance the performance on the reductive elimination.

In order to further enhance the catalytic activity of the newly developed 2-phosphino-substituted benzimidazolyl ligands, a fine tuning was made on the scaffold by incorporating two methyl groups to the benzimidazole 5,6-position. When comparing between ligands Amizole-phos **L2a** to **L2d** and Amizole^{M2}-phos **L2i** to **L2l**, ligands Amizole^{M2}-phos **L2i** to **L2l** bearing two methyl groups gave better catalytic activity towards the coupling reaction. The reason of this phenomenon could be explained by the enhancement of electron richness of the phosphorus atom to facilitate oxidative addition. In the chemical shifts of ^{31}P NMR of ligands Amizole^{M2}-phos **L2i** to **L2l** were at more up-field region than that of Amizole-phos **L2a** to **L2d** (**Table 5.20**). Therefore, the importance of two methyl groups substituted on the benzene ring of benzimidazole scaffold could be demonstrated.

Table 5.20 Direct Comparison of the Effectiveness between Ligands Amizole-phos **L2a** to **L2d** and Amizole^{M2}-phos **L2i** to **L2l**

Phosphino moiety	Ligand (R' = H)	δ of ^{31}P NMR	% Yield	Ligand (R' = H)	δ of ^{31}P NMR	% Yield
R = Cy	**L2a**	-15.95	43	**L2i**	-16.35	57
R = *t*-Bu	**L2b**	14.35	8	**L2j**	13.95	13
R = *i*-Pr	**L2c**	-7.66	18	**L2k**	-8.07	23
R = Ph	**L2d**	-25.44	0	**L2l**	-25.66	0

Table 5.21 Optimization of Reaction Conditions on Palladium-Catalyzed Suzuki-Miyaura Coupling of Aryl Chloride[a]



Entry	Pd source	Pd:L	Base	Solvent	Temp. °C	% Yield
1	$Pd_2(dba)_3$	1:2	$K_3PO_4 \cdot H_2O$	THF	100	44
2	$Pd(OAc)_2$	1:2	$K_3PO_4 \cdot H_2O$	THF	100	57
3	$Pd(dba)_2$	1:2	$K_3PO_4 \cdot H_2O$	THF	100	31
4	$PdCl_2$	1:2	$K_3PO_4 \cdot H_2O$	THF	100	0
5	$Pd(OAc)_2$	1:1	$K_3PO_4 \cdot H_2O$	THF	100	14
6	$Pd(OAc)_2$	1:2.5	$K_3PO_4 \cdot H_2O$	THF	100	67
7	$Pd(OAc)_2$	1:3	$K_3PO_4 \cdot H_2O$	THF	100	75
8	$Pd(OAc)_2$	1:4	$K_3PO_4 \cdot H_2O$	THF	100	34
9	$Pd(OAc)_2$	1:5	$K_3PO_4 \cdot H_2O$	THF	100	32
10	$Pd(OAc)_2$	1:10	$K_3PO_4 \cdot H_2O$	THF	100	11
11	$Pd(OAc)_2$	1:3	K_3PO_4	THF	100	55
12	$Pd(OAc)_2$	1:3	K_2CO_3	THF	100	62
13	$Pd(OAc)_2$	1:3	Na_2CO_3	THF	100	28
14	$Pd(OAc)_2$	1:3	Cs_2CO_3	THF	100	4
15	$Pd(OAc)_2$	1:3	CsF	THF	100	2
16	$Pd(OAc)_2$	1:3	NaO(*t*-Bu)	THF	100	0
17	$Pd(OAc)_2$	1:3	$K_3PO_4 \cdot H_2O$	Dioxane	100	35
18	$Pd(OAc)_2$	1:3	$K_3PO_4 \cdot H_2O$	Toluene	100	17
19	$Pd(OAc)_2$	1:3	$K_3PO_4 \cdot H_2O$	*t*-Butanol	100	13
20	$Pd(OAc)_2$	1:3	$K_3PO_4 \cdot H_2O$	THF	r.t.	0
21	$Pd(OAc)_2$	1:3	$K_3PO_4 \cdot H_2O$	THF	90	28
22	$Pd(OAc)_2$	1:3	$K_3PO_4 \cdot H_2O$	THF	110	93

[a]Reaction conditions: 2-Chlorotoluene (1.0 mmole), phenylboronic acid (1.5 mmole), base (3.0 mmole), and solvent (3 mL) were stirred for 24 h under nitrogen. Calibrated GC yields were reported using dodecane as the internal standard, average of two runs.

Ligand PCy Amizole^{M2}-phos **L2i** was selected to further optimize the reaction conditions (**Table 5.21**). Reaction parameters of metal source, metal to ligand ratio, base, solvent and temperature were varied for optimizing the reaction conditions.

Palladium source, such as $Pd(OAc)_2$, $Pd(dba)_2$, $Pd_2(dba)_3$ and $PdCl_2$, of the coupling reaction was first studied, 0.05 mol% $Pd(OAc)_2$ gave the highest yield towards coupling reaction (**Table 5.21**, entries 1 to 4). Upon investigating the metal to ligand ratio from 1:1 to 1:5 and 1:10, the ratio of 1:3 provided the highest catalytic activity (**Table 5.21**, entries 2 and 5 to 10). When the metal to ligand ratio increased form 1:1 to 1:3, the product yield increased. However, when adjusting metal to ligand ratio to 1:4 or higher even to 1:10, the % yield of the coupling reaction decreased significantly. The possible reason was that excess amount of ligand would cause coordinating effect which might block the coordinating site for the substrate approach, resulting in lowering the catalytic activity.

Several bases, such as $K_3PO_4 \cdot H_2O$, K_3PO_4, K_2CO_3, Na_2CO_3, Cs_2CO_3, CsF and NaO*t*-Bu, were examined in the presence of PCy Amizole^{M2}-phos **L2i** (**Table 5.21**, entries 7 and 11 to 16). $K_3PO_4 \cdot H_2O$ was found to be the best base of choice in this catalytic system and was finally chosen for further optimization.

Among the commonly used organic solvents, such as tetrahydrofuran (THF), dioxane, toluene and *tert*-butanol (*t*-BuOH), THF gave the best result

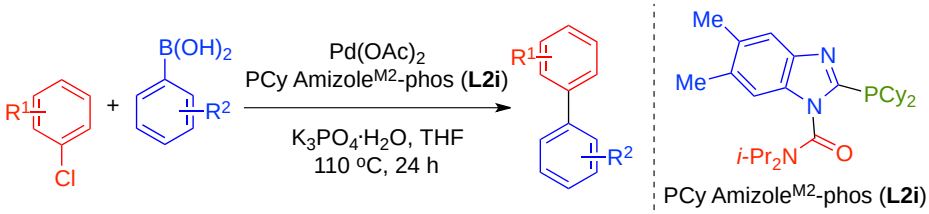
(**Table 5.21**, entries 7 and 17 to 19). As according to the principle of solvent effect, polar aprotic THF was the most suitable solvent for this catalytic system.

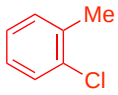
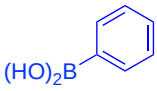
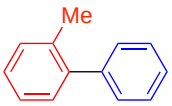
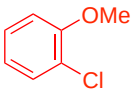
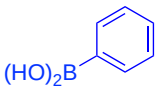
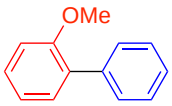
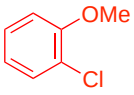
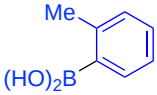
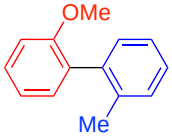
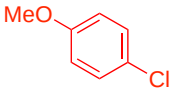
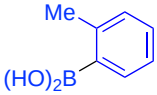
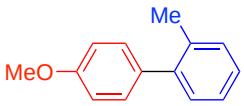
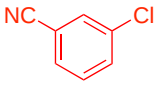
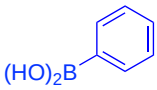
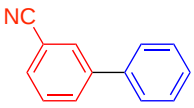
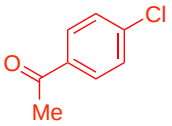
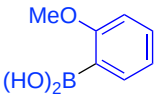
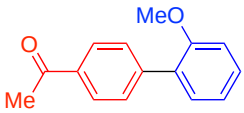
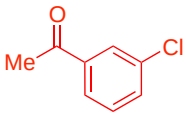
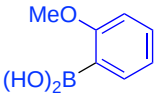
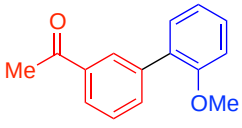
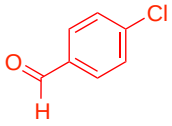
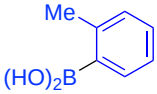
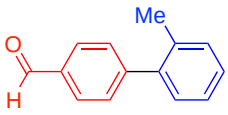
Last but not least, since temperature is an essential factor towards coupling reaction for overcoming the energy barrier, the effect on different temperature has been studied. At 110 °C, the catalytic system provided >90% yield while no conversion at room temperature (Table **5.21**, entries 7 and 20 to 22).

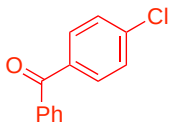
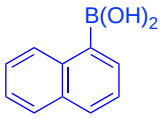
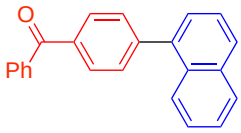
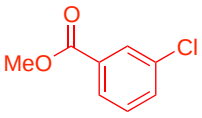
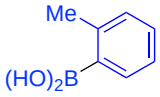
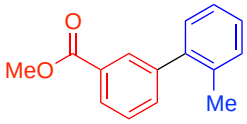
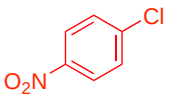
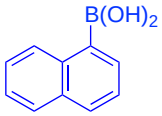
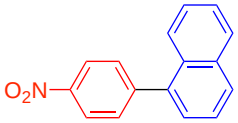
At last, $Pd(OAc)_2$, metal to ligand ratio of 1:3, $K_3PO_4 \cdot H_2O$, THF and 110 °C were chosen as the optimized condition for investigating substrate scope of this catalytic system.

5.2.3 Suzuki-Miyaura Coupling of Non-Activated and Functionalized Aryl Chlorides

Table 5.22 Palladium-Catalyzed Suzuki Coupling of Non-Activated and Functionalized Aryl Chlorides[a]



Entry	ArCl	Ar'B(OH)$_2$	Product	mol% Pd	% yield[b]
1				0.05	93
2				0.067	96
3				0.1	86
4				0.1	97
5				0.05	>99
6				0.02	81
7				0.05	80
8				0.01	94

9				0.01	81
10				0.025	87
11				0.01	99

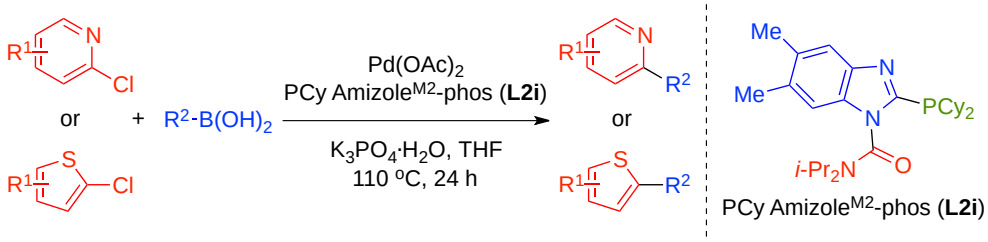
[a]Reaction conditions: ArCl (1.0 mmole), Ar'B(OH)$_2$ (1.5 mmole), $K_3PO_4 \cdot H_2O$ (3.0 mmole), Pd(OAc)$_2$/PCy Amizole^{M2}-phos (**L2i**) = 1:3, and THF (3 mL) were stirred at 110 °C for 24 h under nitrogen. [b]Isolated yields.

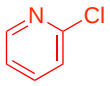
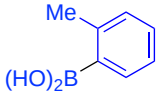
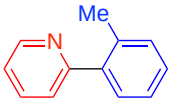
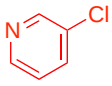
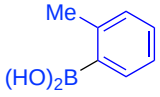
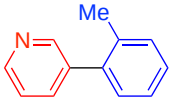
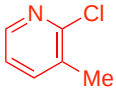
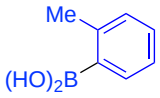
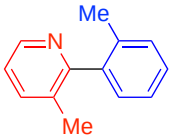
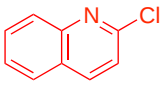
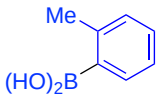
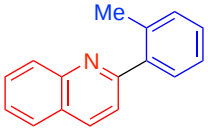
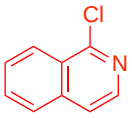
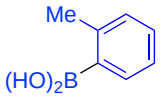
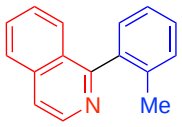
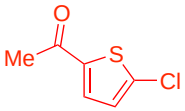
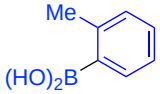
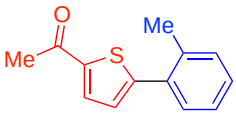
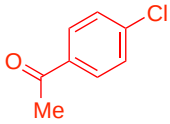
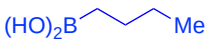
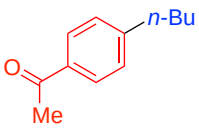
A variety of aryl chlorides were examined under the preliminary optimized conditions (**Table 5.22**). The deactivated aryl chlorides containing different substituted group, such as methyl and methoxy group, were studied in coupling with different arylboronic acids. In the presence of moderate Pd-loading, 0.05 to 0.1 mol%, aryl chlorides were coupled with arylboronic acids to give excellent product yields (**Table 5.22**, entries 1 to 4). Even though both aryl chlorides and arylboronic acids were *ortho*-substituted, an excellent product yield could also be achieved (**Table 5.22**, entry 3).

Apart from the studies in non-activated substrates, the substrates which consist of functional groups such as ketone, aldehyde, ester, nitrile and nitro group were compatible under this catalytic system. The Pd-loading of 0.01 to 0.05 mol% was also achieved (**Table 5.22**, entries 5 to 11).

5.2.4 Suzuki-Miyaura Coupling of Heteroaryl Chlorides

Table 5.23 Palladium-Catalyzed Suzuki Coupling of Heteroaryl Chlorides[a]



Entry	Het-ArCl	R'B(OH)$_2$	Product	mol% Pd	% Yield[b]
1				0.02	82
2				0.067	80
3				0.05	83
4				0.01	99
5				0.1	98
6				0.02	98
7[c]				0.05	87

[a]Reaction conditions: Het-ArCl (1.0 mmole), R'B(OH)$_2$ (1.5 mmole), $K_3PO_4 \cdot H_2O$ (3.0 mmole), Pd(OAc)$_2$/PCy Amizole^{M2}-phos (**L2i**) = 1:3, and THF (3 mL) were stirred at 110 °C for 24 h under nitrogen. [b]Isolated yields. [c]Reaction conditions: ArCl (1.0 mmole), *n*-BuB(OH)$_2$ (2.0 mmole), $K_3PO_4 \cdot H_2O$ (3.0 mmole), Pd(OAc)$_2$/PCy Amizole^{M2}-phos (**L2i**) = 1:3, and toluene (3 mL) were stirred at 110 °C for 24 h under nitrogen.

Apart from the studies in non-activated and functionalized substrates, the coupling of heteroaryl chlorides was also examined in the presence of PCy Amizole^{M2}-phos **L2i**. The results show that the heteroaryl chlorides were also effective substrates for Suzuki coupling under Pd-loading from 0.01 to 0.1 mol% (**Table 5.23**, entries 1 to 6). This catalytic system could effectively deal with pyridyl, quinolyl and thiophenyl substrates to give excellent isolated yields up to 99%.

Notably, preliminary study in the coupling of alkylboronic acid with aryl chloride was also success (**Table 5.23**, entry 7). The optimized reaction conditions were modified by increasing the alkylboronic acid ratio to two equivalents and changing the solvent to toluene. Particularly noteworthy, it showed that this catalyst system could tolerate against β-H elimination.

5.3 Conclusion

In conclusion, the structural insights of palladium to different 2-phosphino-substituted benzimidazolyl ligands have been studied. From the X-ray crystallographic data, we confirmed that the benzimidazolyl ligand with bulky –P*t*-Bu_2 moiety was coordinated in a κ^2-*P*,*N* fashion, while the phosphine with less sterically congested, such as –PCy_2 and –P*i*-Pr moiety, was a dimeric complex, in which the bottom carbamoyl oxygen pointed towards the palladium center and showed a potential *P*,*O*-hemilabile ability.

In order to test the effectiveness of 2-phosphino-substituted benzimidazolyl ligands, which have interesting alterable coordinating feature, preliminary study of Suzuki-Miyaura coupling of aryl chlorides in the presence of PCy Amizole^{M2}-phos **L2i** was conducted. A variety of non-activated, functionalized aryl and heteroaryl chlorides could be coupled smoothly with an array of arylboronic acids and even alkylboronic acid. Notably, Pd-loading down to 0.01 mol% could also be achieved. Further exploration and versatility of this hemilabile 2-phosphino-substituted benzimidazolyl ligands will be attainable.

5.4 Experimental Section

5.4.1 General Considerations

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. All Suzuki-Miyaura coupling reactions were performed in resealable screw cap schlenk flask (approx. 20 mL volume) in the presence of Teflon coated magnetic stirrer bar (3mm × 10 mm). *tert*-Butanol, toluene and 1,4-dioxane were distilled from sodium under nitrogen.[11] Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under nitrogen.[11] Commercial aryl chlorides (liquid form only) were purified by passed through a short plug (0.5 cm wide × 4 cm high) of neutral alumina or distillation. Most commercially available boronic acids were used as received. All bases were purchased from chemical supplier and used without 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. Melting points were recorded on an uncorrected instrument. ^{1}H NMR spectra were recorded on a Bruker (400 MHz) spectrometer. Spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.26 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 ESIMS. GC-MS analysis was conducted on a GCD system using a column with 30 m × 0.25 mm. The products described in GC yield were accorded to the authentic samples/dodecane calibration standard from GC-FID system. Compounds described in the literature

were characterized by comparison of their ^{1}H 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.

5.4.2 General Procedure for Initial Ligand and Reaction Conditions Screening

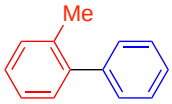
General procedure for initial ligand and reaction conditions screening: A stock solution of $Pd(OAc)_2$ (2.3 mg, 0.010 mmol) with ligand in freshly distilled solvent (10 mL) was initially prepared with continuously stirring at room temperature. Phenylboronic acid (0.1829 g, 1.5 mmol), base (3.0 equiv., 3.0 mmol) and magnetic stirrer bar (3 mm × 8 mm) were charged to an array of Schlenk tubes. Each tube was carefully evacuated and backfilled with nitrogen (3 cycles). 2-Chlorotoluene (0.117 ml, 1.0 mmol) and stock solution of palladium complex (0.5 mL, 0.05 mol% Pd) were added *via* syringe. Further 2.5 ml solvent was added *via* syringe (final volume: 3 mL). This batch of Schlenk tube was resealed and magnetically stirred in a preheated oil bath. The reactions were allowed to reach room temperature. Ethyl acetate (~10 mL), dodecane (227 μL, internal standard) water (~5 mL) were added. The organic layer was subjected to GC analysis. The GC yield was previously calibrated by authentic sample/dodecane calibration curve.

5.4.3 General Procedure for Suzuki-Miyaura Couplings of Aryl Chlorides

General procedure for Suzuki-Miyaura couplings of aryl chlorides: A stock solution of $Pd(OAc)_2$ (2.3 mg, 0.010 mmol) with ligand (Pd:L = 1:3) in freshly distilled 10 mL THF (0.1 mol% Pd per 1 mL stock solution) was initially prepared with continuously stirring at room temperature. Arylboronic acid (1.5 mmol), $K_3PO_4 \cdot H_2O$ (3.0 mmol) and magnetic stirrer bar (3 mm × 8 mm) were charged to an array of Schlenk tubes. Each tube was carefully evacuated and backfilled with nitrogen (3 cycles). Aryl chloride (1.0 mmol) was then added to the Schlenk tubes. The stock solution was further diluted to give different concentrations of palladium complex. The diluted solutions were then transferred to Schlenk tubes via syringes. Further solvent was added (final volume: 3 mL). This batch of Schlenk tube was resealed and magnetically stirred in a preheated oil bath. After the completion of reaction as judged by GC or TLC analysis, the reactions were allowed to reach room temperature. Water (~3 mL) and ethyl acetate (~10 mL × 3) were added. The organic layers were combined and concentrated. The crude products were purified by column chromatography on silica gel (230-400 mesh).

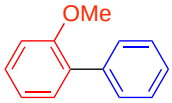
5.4.4 Characterization Data for Coupling Products

2-Methylbiphenyl (**Table 5.22**, entry 1)[12]



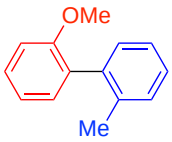
R_f = 0.5 (pure hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 2.39 (s, 3H), 7.34-7.37 (m, 4H), 7.42-7.45 (m, 3H), 7.49-7.43 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 20.4, 125.7, 126.7, 127.2, 128.0, 129.1, 129.7, 130.2, 135.2, 141.9, 141.9; MS (EI): *m/z* (relative intensity) 168 (M^+, 100), 153 (42).

2-Methoxybiphenyl (**Table 5.22**, entry 2)[13]



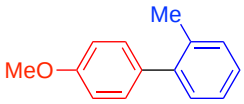
R_f = 0.5 (1:20 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 3.92 (s, 3H), 7.12 (d, J = 8.4 Hz, 2H), 7.45-7.51 (m, 3H), 7.55-7.59 (m, 2H), 7.70-7.73 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 55.3, 111.1, 120.7, 126.8, 127.8, 128.5, 129.4, 130.6, 130.7, 138.4, 156.3; MS (EI): *m/z* (relative intensity) 184 (M^+, 100), 169 (51), 141 (31), 115 (28).

2-Methoxy-2'-methylbiphenyl (**Table 5.22**, entry 3)[10]



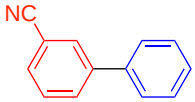
R_f = 0.5 (1:20 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 2.35 (s, 3H), 3.92 (s, 3H), 7.13 (d, J = 8.4 Hz, 1H), 7.18-7.22 (m, 1H), 7.34-7.36 (m, 1H), 7.38-7.46 (m, 4H), 7.50-7.54 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 19.8, 55.2, 110.5, 120.3, 125.3, 127.2, 128.4, 129.4, 129.9, 130.7, 130.9, 136.7, 138.5, 156.5; MS (EI): *m/z* (relative intensity) 198.2 (M^+, 100), 183.1 (36), 165.1 (47).

4'-Methoxy-2-methylbiphenyl (**Table 5.22**, entry 4)[10]



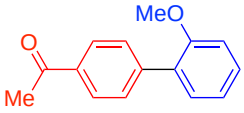
R_f = 0.4 (pure hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 2.37 (s, 3H), 3.92 (s, 3H), 7.02-7.06 (m, 2H), 7.31-7.36 (m, 6H); ^{13}C NMR (100MHz, $CDCl_3$) δ 20.4, 55.17, 113.4, 125.7, 126.9, 129.8, 130.1, 130.2, 134.3, 135.4, 141.5, 158.4; MS (EI): *m/z* (relative intensity) 198.2 (M^+, 100), 183.2 (24), 165.1 (27), 153.1 (29).

3-Phenylbenzonitrile (**Table 5.22**, entry 5)[10]



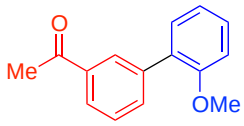
R_f = 0.5 (1:20 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 7.40-7.44 (m, 1H), 7.46-7.52 (m, 2H), 7.54-7.57 (m, 3H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.85 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 112.8, 118.7, 126.9, 128.30, 129.0, 129.5, 130.5, 131.3, 138.7, 142.3; MS (EI): *m/z* (relative intensity) 179.1 (M^+, 100), .151.0 (13).

1-(2'-Methoxybiphenyl-4-yl)ethanone (**Table 5.22**, entry 6)[14]



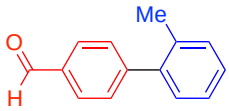
R_f = 0.4 (1:10 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 2.63 (s, 3H), 3.82 (s, 3H), 7.01 (d, *J* = 8.0 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 7.33-7.40 (m, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 8.01 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 26.4, 55.4, 111.2, 120.8, 127.9, 129.3, 129.3, 129.5, 130.5, 135.3, 143.4, 156.35, 197.6; MS (EI): *m/z* (relative intensity) 226.2 (M^+, 56), 211.1 (100), 168.1 (48), 139.1 (22).

1-(2'-Methoxybiphenyl-3-yl)ethanone (**Table 5.22**, entry 7)[15]



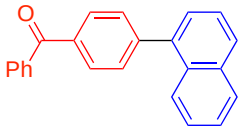
R_f = 0.4 (1:10 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 2.64 (s, 3H), 3.83 (s, 3H), 7.02 (d, J = 8.4 Hz, 1H), 7.05-7.09 (m, 1H), 7.34-7.39 (m, 2H), 7.49-7.53 (m, 1H), 7.74-7.77 (m, 1H), 7.92-7.95 (m, 1H), 8.14-8.15 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 26.5, 55.4, 111.1, 120.8, 126.6, 128.1, 129.1, 129.43, 129.5, 130.6, 134.1, 136.9, 138.9, 156.3, 198.0; MS (EI): *m/z* (relative intensity) 226.1 (M^+, 81), 211.1 (100), 168.1 (67), 139.1 (25).

2'-Methylbiphenyl-4-carbaldehyde (**Table 5.22**, entry 8)[10]



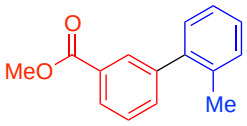
R_f = 0.4 (1:10 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 2.32 (s, 3H), 7.25-7.35 (m, 4H), 7.53 (d, J = 8.0 Hz, 2H), 7.97 (d, J = 8.0 Hz, 2H), 10.09 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 20.2, 125.8, 127.9, 129.3, 129.4, 129.8, 130.4, 134.83, 134.9, 140.4, 148.2, 191.8; MS (EI): *m/z* (relative intensity) 196.1 (M^+, 100), 165.1 (67), 152.1 (40).

(4-(Naphthalen-1-yl)phenyl)(phenyl)methanone (**Table 5.22**, entry 9)[10]



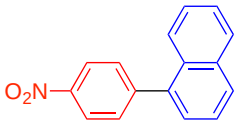
R_f = 0.3 (1:40 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 7.46-7.64 (m, 9H), 7.90-7.97 (m, 7H); ^{13}C NMR (100MHz, $CDCl_3$) δ 125.3, 125.6, 125.9, 126.3, 126.9, 128.3, 128.3, 130.00 (overlapped), 130.1, 131.2, 132.4, 133.7, 136.3, 137.6, 139.0, 145.1, 196.4; MS (EI): *m/z* (relative intensity) 308.1 (M^+, 100), 231.1 (57), 202.1 (58).

Methyl 2'-methylbiphenyl-3-carboxylate (**Table 5.22**, entry 10)[16]



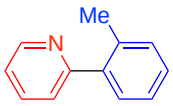
R_f = 0.5 (1:10 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 2.31 (s, 3H), 3.97 (s, 3H), 7.26-7.33 (m, 4H), 7.50-7.58 (m, 2H), 8.06-8.09 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 20.3, 51.0, 125.8, 127.6, 127.9, 128.1, 129.6, 130.0, 130.2, 130.3, 133.5, 135.1, 140.7, 142.1, 166.9; MS (EI): *m/z* (relative intensity) 226.1 (M^+, 99), 195.1 (53), 167.1 (100), 152.0 (44).

1-(4-Nitrophenyl)naphthalene (**Table 5.22**, entry 11)[17]



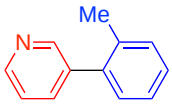
R_f = 0.5 (1:10 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 7.45-7.47 (m, 1H), 7.51-7.67 (m, 5H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.97-8.00 (m, 2H), 8.33-8.37 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 123.3, 124.9, 125.1, 126.0, 126.5, 126.9, 128.4, 128.8, 130.7, 130.7, 133.6, 137.5, 146.9, 147.4; MS (EI): *m/z* (relative intensity) 249.1 (M^+, 100), 202.1 (89).

2-*o*-Tolylpyridine (**Table 5.23**, entry 1)[10]



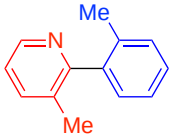
R_f = 0.6 (1:2 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 2.40 (s, 3H), 7.23-7.33 (m, 4H), 7.40-7.44 (m, 2H), 7.72-7.76 (m, 1H), 8.71-8.73 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 20.1, 121.4, 123.9, 125.7, 128.1, 129.4, 130.6, 135.6, 135.9, 140.3, 149.0, 159.9; MS (EI): *m/z* (relative intensity) 168.2 (M^+, 100).

3-*o*-Tolylpyridine (**Table 5.23**, entry 2)[10]



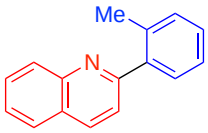
R_f = 0.5 (1:4 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 2.28 (s, 3H), 7.21-7.36 (m, 5H), 7.63-7.66 (m, 1H), 8.60-8.62 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 20.1, 122.8, 125.9, 127.9, 129.7, 130.4, 135.3, 136.2, 137.2, 137.9, 147.9, 149.8; MS (EI): *m/z* (relative intensity) 169.1 (M^+, 100), 141.1 (19), 115.1 (21).

3-Methyl-2-*o*-tolylpyridine (**Table 5.23**, entry 3)[18]



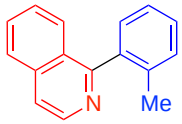
R_f = 0.4 (1:4 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 2.08 (s, 3H), 2.08 (s, 3H), 7.13-7.16 (m, 2H), 7.20-7.27 (m, 3H), 7.53-7.55 (m, 1H), 8.49-8.50 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 18.7, 19.0, 121.8, 125.3, 127.5, 128.1, 131.1, 135.1, 137.3, 139.9, 146.4, 159.3; MS (EI): *m/z* (relative intensity) 182.1 (M^+, 41), 168.1 (100).

2-*o*-Tolylquinoline (**Table 5.23**, entry 4)[10]



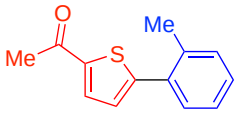
R_f = 0.5 (1:10 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 2.48 (s, 3H), 7.33-7.40 (m, 3H), 7.51-7.58 (m, 3H), 7.72-7.76 (m, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 8.27 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 20.0, 122.0, 125.7, 126.0, 126.3, 127.2, 128.2, 129.2, 129.3, 129.4, 130.5, 135.6, 135.7, 140.3, 147.5, 159.8; MS (EI): *m/z* (relative intensity) 218.2 (M^+, 100), 108.6 (20).

1-*o*-Tolylisoquinoline (**Table 5.23**, entry 5)[19]



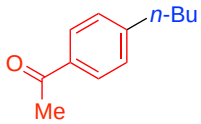
R_f = 0.4 (1:4 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 2.10 (s, 3H), 7.30-7.46 (m, 5H), 7.63-7.68 (m, 3H), 7.85 (d, *J* = 8.0 Hz, 1H), 8.64 (d, *J* = 5.6 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 19.5, 119.6, 125.3, 126.6, 126.9, 127.1, 128.1, 129.2, 129.8, 130.0, 136.0, 136.1, 138.7, 141.9, 161.1; MS (EI): *m/z* (relative intensity) 218.1 (M^+, 100), 108.6 (17).

1-(5-*o*-Tolylthiophen-2-yl)ethanone (**Table 5.23**, entry 6)[20]



R_f = 0.4 (1:10 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 2.42 (s, 3H), 2.56 (s, 3H), 7.07 (d, *J* = 3.6 Hz, 1H), 7.20-7.28 (m, 3H), 7.39 (d, *J* = 7.2 Hz, 1H), 7.66 (d, *J* = 3.6 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 20.7, 26.2, 125.8, 127.2, 128.5, 129.8, 130.7, 132.4, 132.8, 135.6, 143.4, 151.6, 190.2; MS (EI): *m/z* (relative intensity) 216.1 (M^+, 57), 201.1 (100), 129.1 (18).

1-(4-Butylphenyl)ethanone (**Table 5.23**, entry 7)[10]



R_f = 0.5 (1:10 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 0.93 (t, *J* = 7.2 Hz, 3H), 1.36 (sextet, J = 7.2 Hz, 2H), 1.61 (quintet, *J* = 7.2 Hz, 2H), 2.57 (s, 3H), 2.66 (t, *J* = 7.6 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 13.7, 22.1, 26.3, 33.1, 35.5, 128.3, 128.4, 134.7, 148.6, 197.5; MS (EI): *m/z* (relative intensity) 176.2 (M^+, 19), 161.2 (100), 133.1 (6), 105.1 (11).

5.5 References

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Chapter 6 Alterable *P,O*- or *P,N*-Type 2-Phosphino-Substituted Benzimidazolyl Ligands for Palladium-Catalyzed Buchwald-Hartwig Amination of Aryl Chlorides

6.1 Introduction

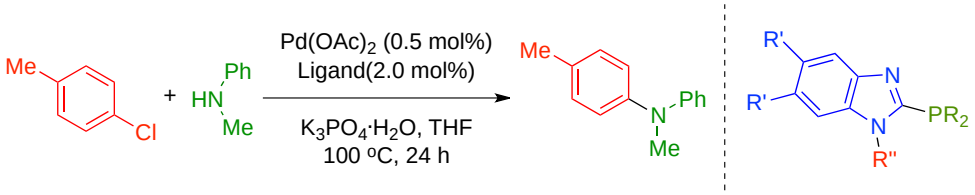
Buchwald-Hartwig amination is one of the most powerful tools available for constructing aromatic carbon-nitrogen bonds in the synthesis of pharmaceutical and biologically materials.[1] As the first catalytic amination protocol was discovered,[2] efforts toward increasing the reaction efficacy have been actively input.[3] Recently, many researchers reported the conversion of aryl iodides and bromides to corresponding aryl amines by employing copper[4] or iron[5] with various ligands as catalysts. However, the use of the easily available as well as inexpensive aryl chlorides still requires a highly active palladium catalyst for the amination reactions.

As previously discussed in **Chapter 5**, we have developed a series of 2-phosphino-substituted benzimidazolyl ligands which were employed towards palladium-catalyzed Suzuki-Miyaura cross-coupling reaction of aryl chlorides and showed a good catalytic activity. Herein, we would like to extent the scope of this catalytic system and apply it to palladium-catalyzed Buchwald-Hartwig amination reaction.

6.2 Results and Discussion

6.2.1 Preliminary Study on the Effectiveness of 2-Phosphino-Substituted Benzimidazolyl Ligands

Table 6.1 Investigation on the Effectiveness of 2-Phosphino-Substituted Benzimidazolyl Ligands in Palladium-Catalyzed Buchwald-Hartwig Amination of Aryl Chloride[a]



Entry	Ligand	% Yield
1	PCy Amizole-phos **L2a** (R' = H, R" = C(O)N*i*-Pr$_2$, R = Cy)	1
2	P*t*-Bu Amizole-phos **L2b** (R' = H, R" = C(O)N*i*-Pr$_2$, R = *t*-Bu)	57
3	P*i*-Pr Amizole-phos **L2c** (R' = H, R" = C(O)N*i*-Pr$_2$, R = *i*-Pr)	1
4	PPh Amizole-phos **L2d** (R' = H, R" = C(O)N*i*-Pr$_2$, R = Ph)	0
5	PCy Mezole-phos **L2f** (R' = H, R" = Me, R = Cy)	0
6	P*t*-Bu Mezole-phos **L2g** (R' = H, R" = Me, R = *t*-Bu)	5
7	PCy Amizole^{M2}-phos **L2i** (R' = Me, R" = C(O)N*i*-Pr$_2$, R = Cy)	6
8	P*t*-Bu Amizole^{M2}-phos **L2j** (R' = Me, R" = C(O)N*i*-Pr$_2$, R = *t*-Bu)	80
9	P*i*-Pr Amizole^{M2}-phos **L2k** (R' = Me, R" = C(O)N*i*-Pr$_2$, R = *i*-Pr)	3
10	PPh Amizole^{M2}-phos **L2l** (R' = Me, R" = C(O)N*i*-Pr$_2$, R = Ph)	0
11	P*o*-Tol Amizole^{M2}-phos **L2m** (R' = Me, R" = C(O)N*i*-Pr$_2$, R = *o*-Tol)	0
12	PCy ^{P3}Sulfozole-phos **L2p** (R' = H, R" = SO$_2$-2,4,6-*i*-Pr$_3$C$_6$H$_2$, R = Cy)	0
13	P*t*-Bu ^{P3}Sulfozole-phos **L2q** (R' = H, R" = SO$_2$-2,4,6-*i*-Pr$_3$C$_6$H$_2$, R = *t*-Bu)	2
14	PCy ^{M3}Sulfozole-phos **L2r** (R' = H, R" = SO$_2$-2,4,6-Me$_3$C$_6$H$_2$, R = Cy)	0
15	P*t*-Bu ^{M3}Sulfozole-phos **L2s** (R' = H, R" = SO$_2$-2,4,6-Me$_3$C$_6$H$_2$, R = *t*-Bu)	3

[a]Reaction conditions: 4-Chlorotoluene (1.0 mmole), *N*-methylaniline (1.5 mmole), K_2CO_3 (2.5 mmole), $Pd(OAc)_2$/L = 1:4, $PhB(OH)_2$ (0.02 mmole) and toluene (3 mL) were stirred at 110 °C for 24 h under nitrogen. Calibrated GC yields were reported using dodecane as the internal standard, average of two runs.

To investigate the efficacy of the 2-phosphino-substituted benzimidazolyl ligands in Buchwald-Hartwig amination reaction, 4-chlorotoluene and *N*-methylaniline were used as benchmark substrates. 1 mol % $Pd(OAc)_2$ was applied in probing the catalytic efficiency of different ligands using toluene as solvent and K_2CO_3 as base (**Table 6.1**). Ligand P*t*-Bu Amizole^{M2}-phos **L2j** performed the best in yielding desired product among the other ligands tested.

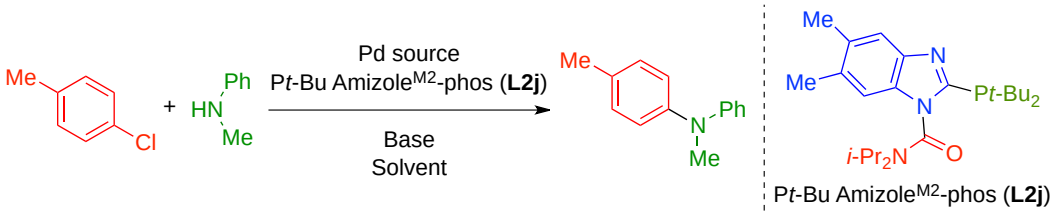
When investigating the usefulness of the ligands towards Buchwald-Hartwig amination reaction, we followed the same logical path as reported in **Section 5.22**. The efficiency of ligands Amizole-phos **L2a** to **L2d** were first examined in amination of 4-chlorotoulene with *N*-methylaniline (**Table 6.1**, entries 1 to 4). Ligand P*t*-Bu Amizole-phos **L2b** with di-*tert*-butylphosphino moiety afforded the best catalytic activity while others only gave trace or no conversion. Thus, we could deduce that ligand bearing a sterically congested and electron-donating di-*tert*-butylphosphino moiety might afford better catalytic activity towards the amination reaction.

Then, the importance of the bottom *N*-substituted group of the ligands was also examined (**Table 6.1**, entries 2, 5, 6 an 12 to 15). Ligands with different bottom *N*-substituted group, such as carbamoyl, methyl, mesitylsulfony and 2,4,6-triisopropylphenylsulfonyl, were employed to the catalytic system. Ligand P*t*-Bu Amizole-phos **L2b** with carbamoyl-substituent showed the best catalytic result among others, which could also be implied that carbamoyl group offered the most suitable bulkiness for the dynamic “On and Off” interaction towards the metal

center of the catalytic system and hence to enhance the performance on the reductive elimination.

As followed by the logical path, ligands Amizole^{M2}-phos **L2i** to **L2l** with dimethyl substitution on 5,6-position on benzimidazole ring were also applied to amination reaction. The catalytic result also showed that ligand P*t*-Bu Amizole^{M2}-phos **L2j** bearing dimethyl substitution had better performance when comparing with P*t*-Bu Amizole-phos **L2b** with no substitution. It could be explicated that the addition of two electron-donating methyl groups on the benzimidazole scaffold gave better catalytic activity (same as Suzuki coupling in **Chapter 5**). Therefore, ligand P*t*-Bu Amizole^{M2}-phos **L2j** with the optimized steric and electronic properties was selected for further optimization of reaction conditions.

Table 6.2 Optimization of Reaction Conditions on Palladium-Catalyzed Buchwald-Hartwig Amination of Aryl Chloride[a]



Entry	Pd source	Pd:L	mol% Pd	Base	Solvent	% Yield
1	$Pd_2(dba)_3$	1:4	0.5	K_2CO_3	Toluene	74
2	$Pd(OAc)_2$	1:4	0.5	K_2CO_3	Toluene	80
3	$Pd(dba)_2$	1:4	0.5	K_2CO_3	Toluene	20
4	$Pd(OAc)_2$	1:4	0.2	K_2CO_3	Toluene	30
5	$Pd(OAc)_2$	1:4	0.2	$K_3PO_4 \cdot H_2O$	Toluene	19
6	$Pd(OAc)_2$	1:4	0.2	Cs_2CO_3	Toluene	8
7	$Pd(OAc)_2$	1:4	0.2	NaO(*t*-Bu)	Toluene	3
8	$Pd(OAc)_2$	1:4	0.2	K_3PO_4	Toluene	18
9	$Pd(OAc)_2$	1:4	0.2	Na_2CO_3	Toluene	4
10	$Pd(OAc)_2$	1:4	0.2	KOH	Toluene	3
11	$Pd(OAc)_2$	1:4	0.2	NaOH	Toluene	2
12	$Pd(OAc)_2$	1:4	0.2	K_2CO_3	THF	14
13	$Pd(OAc)_2$	1:4	0.2	K_2CO_3	Dioxane	17
14	$Pd(OAc)_2$	1:4	0.2	K_2CO_3	Xylene	Trace
15	$Pd(OAc)_2$	1:1	0.5	K_2CO_3	Toluene	34
16	$Pd(OAc)_2$	1:2	0.5	K_2CO_3	Toluene	67
17	$Pd(OAc)_2$	1:3	0.5	K_2CO_3	Toluene	70
18	$Pd(OAc)_2$	1:5	0.5	K_2CO_3	Toluene	92
19	$Pd(OAc)_2$	1:6	0.5	K_2CO_3	Toluene	72
20[b]	$Pd(OAc)_2$	1:4	0.5	K_2CO_3	Toluene	65

[a]Reaction conditions: 4-Chlorotoluene (1.0 mmole), *N*-methylaniline (1.5 mmole), base (2.5 mmole), $PhB(OH)_2$ (0.02 mmole) and solvent (3 mL) were stirred at 110 °C for 24 h under nitrogen. Calibrated GC yields were reported using dodecane as the internal standard, average of two runs. [b]At 100 °C.

Ligand P*t*-Bu Amizole^{M2}-phos **L2j** was selected for optimizing the reaction conditions. The parameters were varied for optimizing the reaction conditions, including metal source, base, solvent, metal to ligand ratio and temperature.

For the preliminary study of the palladium precursors, $Pd(OAc)_2$, $Pd(dba)_2$, $Pd_2(dba)_3$ were examined. 0.5 mol% $Pd(OAc)_2$ offered a superior desired product yield among others (**Table 6.2**, entries 1 to 3).

Common inorganic bases, such as K_2CO_3, $K_3PO_4 \cdot H_2O$, K_3PO_4, Cs_2CO_3, Na_2CO_3, NaO*t*-Bu, KOH and NaOH, were also studied in the presence of the 0.2 mol% $Pd(OAc)_2$ and ligand P*t*-Bu Amizole^{M2}-phos **L2j** (**Table 6.2**, entries 4 to 11). K_2CO_3 led to notable efficiencies in yielding the desired product due to the mild basicity towards this amination reaction. However, a strong base, such as NaO(*t*-Bu), NaOH and KOH, only gave an inferior result when compared to the weaker bases.

Among the solvents investigated, such as toluene, tetrahydrofuran (THF), dioxane and xylene, toluene gave the best result (**Table 6.2**, entries 4 and 12 to 14). As each catalytic system had a highly selectivity in solvent and owned its unique solvent system. Thus, toluene was elucidated that was the most suitable solvent of choice in this catalytic system.

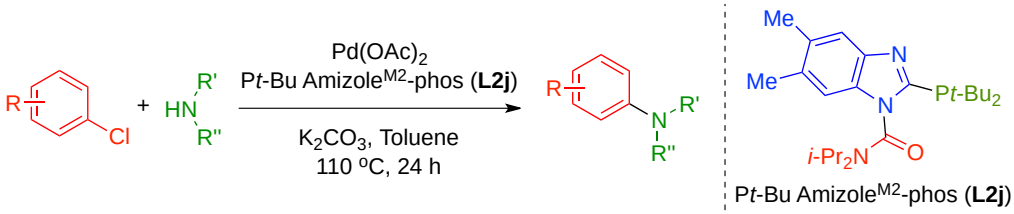
After that, upon investigating the metal to ligand ratio from 1:1 to 1:6 and 1:10, the ratio of 1:5 gave the highest product yield > 90% (**Table 6.2**, entries 2

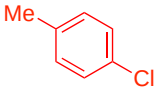
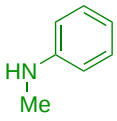
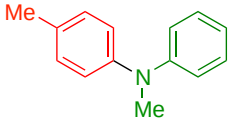
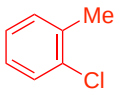
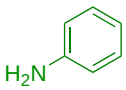
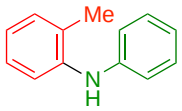
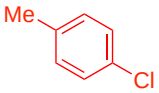
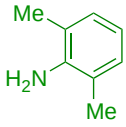
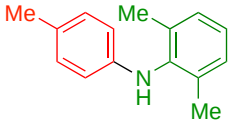
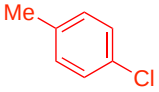
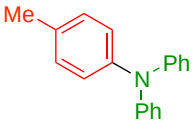
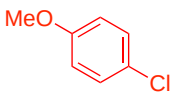
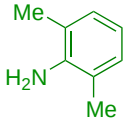
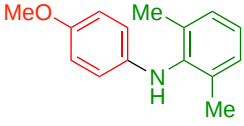
and 15 to 19). However, further increasing the metal to ligand ratio to 1:6 rendered the obviously dwindling of the percentage of product yield. In general, there is a coordinating property of amines to metal complexes, and it may be problematic for the reaction. Therefore, we observed that higher metal to ligand ratio of 1:5 was needed in amination reaction here when compared with that of 1:3 in Suzuki coupling (**Section 5.22**).

Finally, $Pd(OAc)_2$, metal to ligand ratio of 1:5, K_2CO_3 and toluene were chosen as the optimized condition for further establishing the substrate scope of amination.

6.2.2 Buchwald-Hartwig Amination of Aryl Chlorides with Aromatic Amines

Table 6.3 Palladium-Catalyzed Buchwald-Hartwig Amination of Aryl Chlorides with Aromatic Amines[a]



Entry	ArCl	Amine	Product	mol% Pd	% Yield[b]
1				0.5	89
2				1.5	93
3				1.2	89
4				1.5	81
5				2	87

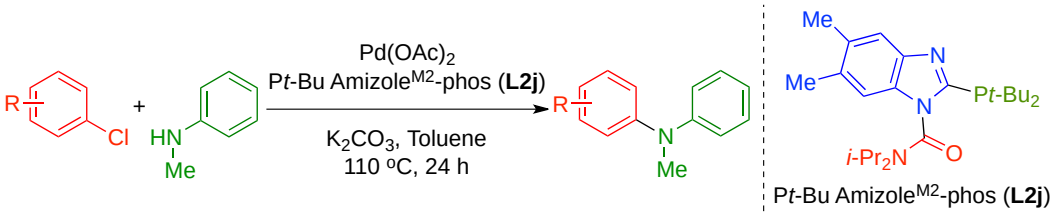
[a]Reaction conditions: ArCl (1.0 mmole), Amine (1.5 mmole), K_2CO_3 (2.5 mmole), $Pd(OAc)_2$/P*t*-Bu Amizole^{M2}-phos (**L2j**) = 1:5, $PhB(OH)_2$ (0.02 mmole) and toluene (3 mL) were stirred at 110 °C for 24 h under nitrogen. [b]Isolated yields.

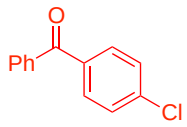
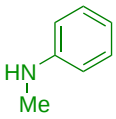
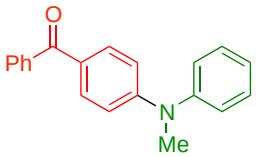
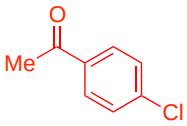
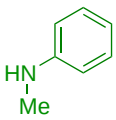
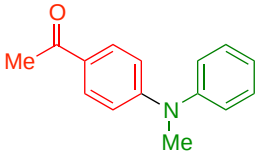
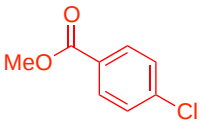
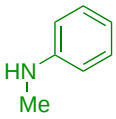
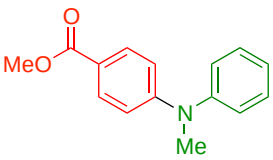
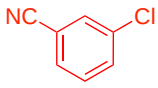
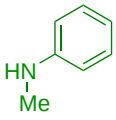
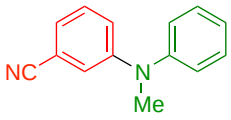
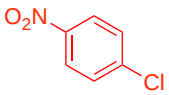
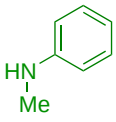
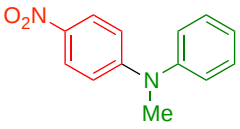
An array of aryl chlorides was examined in the coupling of aromatic amines under the optimized catalytic system in presence of P*t*-Bu Amizole^{M2}-phos **L2j** (**Table 6.3**). *N*-Methylaniline, aniline and diphenylamine were effective substrates to couple with chlorotoluene to afford excellent corresponding product yields (**Table 6.3**, entries 1, 2 and 4) under Pd-loading in range from 0.5 to 1.5 mol%.

Noteworthy, sterically congested 2,6-dimethylaniline was found to be a capable coupling partner towards this catalytic system (**Table 6.3**, entries 3 and 5). It was notable that deactivated 4-chloroanisole was also a capable partner for the reaction and excellent yield could be achieved under 2 mol% Pd-loading (**Table 6.3**, entry 5).

6.2.3 Buchwald-Hartwig Amination of Functionalized Aryl Chlorides with Aromatic Amines

Table 6.4 Palladium-Catalyzed Buchwald-Hartwig Amination of Functionalized Aryl Chlorides with Aromatic Amines[a]



Entry	ArCl	Amine	Product	mol% Pd	% Yield[b]
1				0.2	95
2				0.5	98
3				0.2	92
4				0.5	94
5				0.2	97

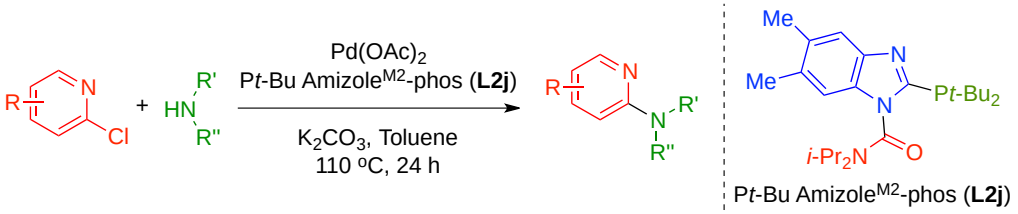
[a]Reaction conditions: ArCl (1.0 mmole), Amine (1.5 mmole), K_2CO_3 (2.5 mmole), $Pd(OAc)_2$/P*t*-Bu Amizole^{M2}-phos (**L2j**) = 1:5, $PhB(OH)_2$ (0.02 mmole) and toluene (3 mL) were stirred at 110 °C for 24 h under nitrogen. [b]Isolated yields.

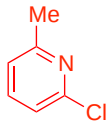
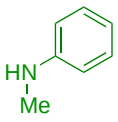
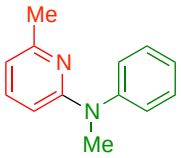
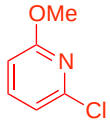
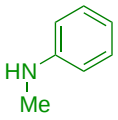
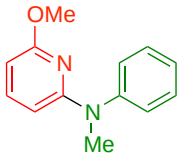
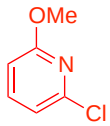
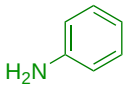
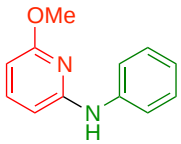
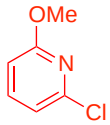
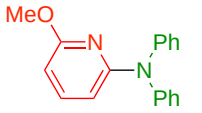
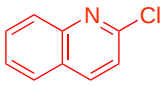
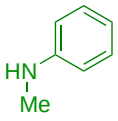
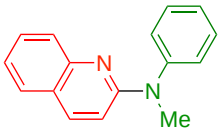
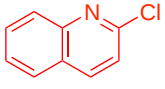
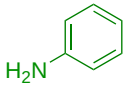
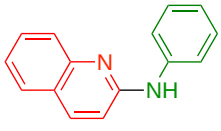
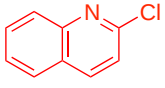
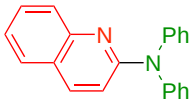
After the investigating the feasibility of the amination reaction of aryl chlorides with aromatic amines by employing P*t*-Bu Amizole^{M2}-phos **L2j**, the amination of functionalized aryl chlorides with *N*-methylaniline was then examined (**Table 6.4**).

Functionalized aryl chlorides containing ketone, ester, nitrile, nitro group were compatible furnished desired products in excellent yields. The Pd-loading could be even lowered to 0.2 mol % without deleterious effect. Since functional group tolerance is important in the applications of amination for synthesizing pharmaceutically useful intermediates, $Pd(OAc)_2$/P*t*-Bu Amizole^{M2}-phos **L2j** system showed excellent functional group compatibility towards different functional group.

6.2.4 Buchwald-Hartwig Amination of Heteroaryl Aryl Chlorides with Aromatic Amines

Table 6.5 Palladium-Catalyzed Buchwald-Hartwig Amination of Heteroaryl Chlorides with Aromatic Amines[a]



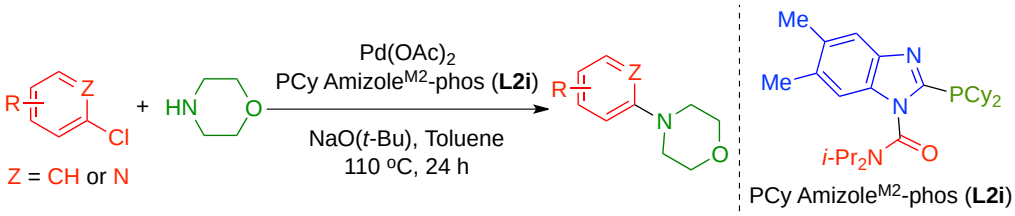
Entry	Het-ArCl	Amine	Product	mol%	% Yield[b]
1				0.5	84
2				1	97
3				1	89
4				1	97
5				0.5	81
6				1	92
7				0.5	83

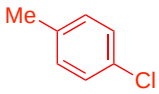
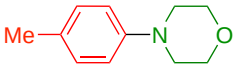
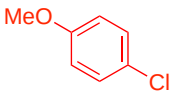
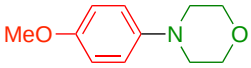
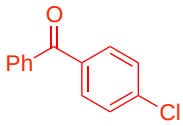
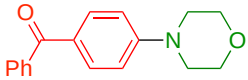
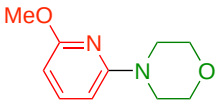
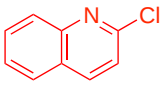
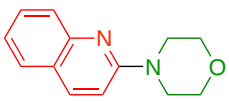
[a]Reaction conditions: Het-ArCl (1.0 mmole), Amine (1.5 mmole), K_2CO_3 (2.5 mmole), $Pd(OAc)_2$/P*t*-Bu Amizole^{M2}-phos (**L2j**) = 1:5, $PhB(OH)_2$ (0.02 mmole) and toluene (3 mL) were stirred at 110 °C for 24 h under nitrogen. [b]Isolated yields.

In order to further expand the substrate scope, a variety of heteroaryl chlorides were coupled with different amines in the presence of P*t*-Bu Amizole^{M2}-phos **L2j** (**Table 6.5**). Both pyridyl and quinolyl were effective substrates for coupling with a variety of amines and excellent yields were obtained in the presence of 0.5 to 1 mol% Pd-loading.

6.2.5 Buchwald-Hartwig Amination of Aryl/Heteroaryl Chlorides with Aliphatic Amines

Table 6.6 Palladium-Catalyzed Buchwald-Hartwig Amination of Aryl/Heteroaryl Chlorides with Aliphatic Amines[a]



Entry	ArCl	Amine	Product	mol% Pd	% Yield[b]
1				2	60, 0[c], 0[d]
2				1	33
3				1	87
4				1	89
5				1	93

[a]Reaction conditions: ArCl (1.0 mmole), Amine (1.5 mmole), NaO(*t*-Bu) (2.5 mmole), $Pd(OAc)_2$/PCy Amizole^{M2}-phos (**L2i**) = 1:5, $PhB(OH)_2$ (0.02 mmole) and toluene (3 mL) were stirred at 110 °C for 24 h under nitrogen. [b]Isolated yields. [c]**L2j** as ligand and GC yields. [d]K_2CO_3 as base and GC yields.

Finally, $Pd(OAc)_2$/ P*t*-Bu Amizole^{M2}-phos **L2j** system was examined towards palladium-catalyzed amination of aliphatic amines (**Table 6.6**), and however, this system gave almost no conversion (**Table 6.6**, entry 1). Therefore, fine-tuning of reaction conditions was carried out.

Ligand PCy Amizole^{M2}-phos **L2i** bearing dicyclohexylphosphino moiety showed catalytic active towards the amination of aliphatic amines with the presence of strong base NaO(*t*-Bu) (**Table 6.6**, entry 1). Non-activated, functionalized aryl and heteroaryl chlorides were also good partners in amination with morpholine under Pd-loading from 1 to 2 mol%.

Interestingly, this study implied that the different substrates or even reactions could match with different ligands with different phosphino analogues. From the experimental results we got in **Chapter 5** and **Chapter 6**, ligands PCy Amizole^{M2}-phos **L2i** and P*t*-Bu Amizole^{M2}-phos **L2j** were active towards Suzuki coupling and amination of aromatic amines respectively. It inspired us that this series of ligands with different phosphino analogues might have a feature to control the chemoselectivity of different reactions.

6.3 Conclusion

To conclude, the efficacy of 2-phosphino-substituted benzimidazolyl ligands towards Buchwald-Hartwig amination was studied. Ligands P*t*-Bu Amizole^{M2}-phos **L2j** with di-*tert*-butylphosphino moiety showed to be active in amination of non-activated, functionalized aryl and heteroaryl chlorides with aromatic amines, while ligand PCy Amizole^{M2}-phos **L2i** bearing dicyclohexylphosphino moiety showed catalytic active towards amination of aliphatic amines. Notably, a preliminary chemo-selection between aromatic and aliphatic amines controlled by ligands with different phosphino analogue was observed. Further exploration of ligand-control chemoselective couplings will be attainable.

6.4 Experimental Section

6.4.1 General Considerations

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. All Buchwald-Hartwig amination reactions were performed in resealable screw cap schlenk flask (approx. 20 mL volume) in the presence of Teflon coated magnetic stirrer bar (3mm × 10 mm). Toluene, xylene and 1,4-dioxane were distilled from sodium under nitrogen.[6] Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under nitrogen.[6] Commercial aryl chlorides (liquid form only) were purified by passed through a short plug (0.5 cm wide × 4 cm high) of neutral alumina or distillation. Commercially available amines were purified by distillation. All bases were purchased from chemical supplier and used without 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. Melting points were recorded on an uncorrected instrument. ^{1}H NMR spectra were recorded on a Bruker (400 MHz) spectrometer. Spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.26 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 ESIMS. GC-MS analysis was conducted on a GCD system using a column with 30 m × 0.25 mm. The products described in GC yield were accorded to the authentic samples/dodecane calibration standard from GC-FID system. Compounds described in the literature

were characterized by comparison of their ^{1}H 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.

6.4.2 General Procedure for Initial Ligand and Reaction Conditions Screening

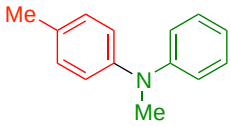
General procedure for initial ligand and reaction conditions screening: A stock solution of $Pd(OAc)_2$ (2.3 mg, 0.010 mmol) with ligand in freshly distilled solvent (4 mL) was initially prepared with continuously stirring at room temperature. Base (2.5 equiv., 2.5 mmol) and magnetic stirrer bar (3 mm × 8 mm) were charged to an array of Schlenk tubes. Each tube was carefully evacuated and backfilled with nitrogen (3 cycles). 4-Chlorotoluene (0.118 mL, 1.0 mmol), *N*-methylaniline (0.163 mL, 1.5 mmol), phenylboronic acid (0.02 mmol) and stock solution (2.0 mL, 0.5 mol% Pd or 0.8 mL, 0.2 mol%) were added *via* syringe. Further solvent was added *via* syringe (final volume: 3 mL). This batch of Schlenk tube was resealed and magnetically stirred in a preheated 110 °C oil bath. The reactions were allowed to reach room temperature. Ethyl acetate (~10 mL), dodecane (227 μL, internal standard) water (~5 mL) were added. The organic layer was subjected to GC analysis. The GC yield was previously calibrated by authentic sample/dodecane calibration curve.

6.4.3 General Procedure for Buchwald-Hartwig Amination of Aryl Chlorides

General procedure for Buchwald-Hartwig Amination of aryl chlorides: $Pd(OAc)_2$ (2.3 mg, 0.010 mmol) and ligand (Pd:L = 1:5) were loaded into a Schlenk tube equipped with a magnetic stirrer bar (3 mm × 8 mm). The tube was evacuated and flushed with nitrogen for several times. Precomplexation was applied by adding freshly distilled toluene (1 mL) and stirred for 5 min. Aryl chloride (1.0 mmol), amine (1.5 mmol), K_2CO_3 (2.5 mmol) were loaded to an array of Schlenk tubes. Further solvents were added (final volume 3 mL). This batch of Schlenk tube was resealed and magnetically stirred in a preheated 110 °C oil bath. After the completion of reaction as judged by GC or TLC analysis, the reactions were allowed to reach room temperature. Water (~3 mL) and ethyl acetate (~10 mL × 3) were added. The organic layers were combined and concentrated. The crude products were purified by column chromatography on silica gel (230-400 mesh).

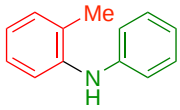
6.4.4 Characterization Data for Coupling Products

N-Methyl-*N*-*p*-tolylbenzenamine (**Table 6.3**, entry 1)[7]



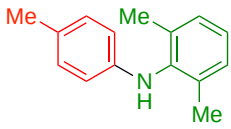
R_f = 0.8 (1:50 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 2.58 (s, 3H), 3.52 (s, 3.52), 7.13 (t, J = 7.2Hz, 1H), 7.20 (d, J = 8Hz, 2H), 7.26 (d, J = 8.4Hz, 2H), 7.36 (d, J = 8.4Hz, 2H), 7.48 (t, J = 7.6Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 20.6, 40.1, 118.1, 119.7, 122.4, 128.9, 129.8, 131.7, 146.5, 149.2.

N-*o*-Tolylbenzenamine (**Table 6.3**, entry 2)[8]



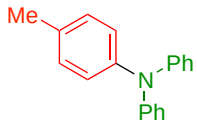
R_f = 0.4 (1:50 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 2.35 (s, 3H), 5.46 (s, 1H), 6.99-7.06 (m, 4H), 7.24 (t, J = 7.2Hz, 1H), 7.29-7.37 (m, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ 17.8, 117.3, 118.8, 120.3, 121.9, 126.7, 128.3, 129.2, 130.8, 141.1, 143.9.

2,6-Dimethyl-*N*-*p*-tolylbenzenamine (**Table 6.3**, entry 3)[9]



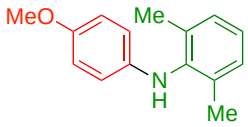
R_f = 0.7 (1:20 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 2.24(s, 6H), 2.28 (s, 3H), 6.47 (d, J = 8.4Hz, 3H), 7.00 (d, J = 8Hz, 2H), 7.07-7.15 (m, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 18.3, 20.4, 113.7, 125.3, 127.4, 128.4, 129.6, 135.4, 138.6, 143.8.

N-Phenyl-*N*-*p*-tolylbenzenamine (**Table 6.3**, entry 4)[10]



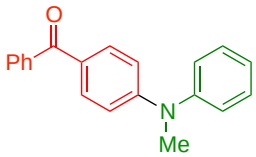
R_f = 0.6 (1:9 DCM/Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 2.52 (s, 3H), 7.16 (t, *J* = 7.2Hz, 2H), 7.25-7.30 (m, 8H), 7.39-7.43 (m, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ 20.7, 122.1, 123.5, 124.8, 129.0, 129.8, 132.5, 145.2, 147.9.

N-(4-Methoxyphenyl)-2,6-dimethylbenzenamine (**Table 6.3**, entry 5)[7]



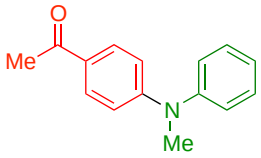
R_f = 0.3 (1:20 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 2.32 (s, 6H), 3.84 (s, 3H), 5.14 (s, 1H), 6.61 (d, *J* = 7.6Hz, 2H), 6.87 (d, *J* = 8.8Hz, 2H), 7.14-7.18 (m, 1H), 7.23 (d, *J* = 7.2Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 18.2, 55.5, 114.6, 115.1, 124.9, 128.4, 134.8, 139.1, 140.0, 152.5.

(4-(Methyl(phenyl)amino)phenyl)(phenyl)methanone (**Table 6.4**, entry 1)[11]



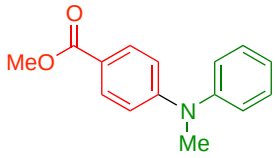
R_f =0.4 (1:4 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 3.34 (s, 3H), 6.80 (d, *J* = 8.8Hz, 2H), 7.21 (t, *J* = 6.4Hz, 3H), 7.37-7.52 (m, 5H), 7.76-7.79 (m, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ 39.75, 113.0, 125.2, 125.6, 126.2, 127.6, 129.0, 129.4, 130.9, 131.9, 138.5, 146.7, 152.0, 194.4.

1-(4-(Methyl(phenyl)amino)phenyl)ethanone (**Table 6.4**, entry 2)[7]



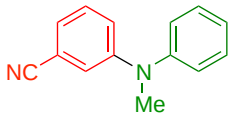
R_f = 0.4 (2:8 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 2.48 (s, 3H), 3.34 (s, 3H), 6.75 (d, *J* = 8.8Hz, 2H), 7.21 (t, 8.4Hz, 3H), 7.39 (t, *J* = 7.6Hz, 2H), 7.81 (d, *J* = 8.8Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 25.7, 39.8, 113.1, 125.3, 125.7, 126.7, 129.5, 129.8, 146.8, 152.2, 195.9.

Methyl 4-(methyl(phenyl)amino)benzoate (**Table 6.4**, entry 3)[7]



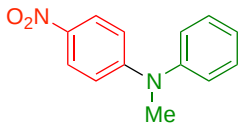
R_f = 0.4 (1:20 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 3.36 (s, 3H), 3.88 (s, 3H), 6.80 (d, *J* = 8.8, 2H), 7.23 (t, *J* = 3.2Hz, 3H), 7.41 (t, *J* = 8Hz, 2H), 7.91 (d, *J* = 8.8H, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 39.9, 51.3, 113.5, 118.9, 125.1, 125.6, 129.5, 130.8, 147.2, 152.3, 166.9.

3-(Methyl(phenyl)amino)benzonitrile (**Table 6.4**, entry 4)[12]



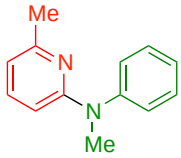
R_f = 0.5 (1: 20 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 3.34 (s, 3H), 7.06-7.09 (m, 3H), 7.18-7.23 (m, 3H), 7.28 (t, *J* = 7.2Hz, 1H), 7.40-7.44 (t, *J* = 8.4Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 39.8, 112.4, 118.3, 119.0, 119.8, 121.5, 124.4, 124.6, 129.4, 129.6, 147.2, 149.1.

N-Methyl-*N*-(4-nitrophenyl)benzenamine (**Table 6.4**, entry 5)[13]



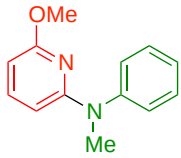
R_f = 0.3 (1: 20 EA: hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 3.39 (s, 3H), 6.64 (d, *J* = 9.2Hz, 2H), 7.23 (d, *J* = 7.6Hz, 2H), 7.30 (t, *J* = 7.6Hz, 1H), 7.45 (t, *J* = 8Hz, 2H), 7.99 (d, *J* = 9.2Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 40.1, 112.0, 125.3, 126.3, 126.4, 129.8, 137.6, 145.9, 153.4.

N,6-Dimethyl-*N*-phenylpyridin-2-amine (**Table 6.5**, entry 1)[14]



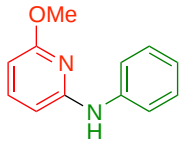
R_f = 0.3 (1: 50 EA: hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 2.55 (s, 3H), 3.59 (s, 3H), 6.45 (d, *J* = 8.4Hz, 1H), 6.56 (d, *J* = 7.2Hz, 1H), 7.23-7.28 (m, 2H), 7.34 (d, *J* = 7.2Hz, 2H), 7.44 (t, *J* = 7.2Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 24.4, 37.9, 106.0, 112.2, 124.7, 125.8, 129.3, 136.6, 146.9, 156.4, 158.3.

6-Methoxy-*N*-methyl-*N*-phenylpyridin-2-amine (**Table 6.5**, entry 2)[15]



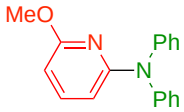
R_f = 0.9 (1:4 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 3.54 (s, 3H), 3.96 (s, 3H), 6.12 (d, *J* = 2.8Hz, 1H), 6.14 (d, *J* = 2.8Hz, 1H), 7.23-7.35 (m, 4H), 7.44 (t, *J* = 7.6Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 37.9, 52.9, 97.2, 100.0, 125.0, 126.1, 129.3, 139.2, 146.6, 157.5, 163.0.

6-Methoxy-*N*-phenylpyridin-2-amine (**Table 6.5**, entry 3)[16]



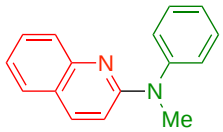
R_f = 0.3 (1:20 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 3.98 (s, 3H), 6.29 (d, *J* = 8Hz, 1H), 6.44 (d, *J* = 8Hz, 1H), 6.59 (s, 1H), 7.09 (t, *J* = 6.8Hz, 1H), 7.38 (t, *J* = 8Hz, 2H), 7.45 (t, *J* = 6.8Hz 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 53.2, 99.7, 99.9, 119.6, 122.0, 128.9, 139.9, 128.9, 139.9, 140.5, 154.2, 163.4.

6-Methoxy-*N*,*N*-diphenylpyridin-2-amine (**Table 6.5**, entry 4)



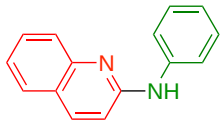
R_f = 0.8 (1:20 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 3.76 (s, 3H), 6.34 (d, *J* = 8Hz, 2H), 7.21 (t, *J* = 7.2Hz, 2H), 7.34 (d, *J* = 7.6Hz, 4H), 7.38-7.43 (m, 5H); ^{13}C NMR (100MHz, $CDCl_3$) δ 52.8, 101.2, 104.1, 124.2, 126.5, 128.8, 139.6, 145.7, 156.7, 162.6.

N-Methyl-*N*-phenylquinolin-2-amine (**Table 6.5**, entry 5)[17]



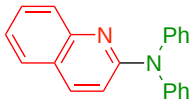
R_f = 0.4 (1:20 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 3.74 (s, 3H), 6.84 (d, *J* = 9.2Hz, 1H), 7.30-7.38 (m, 4H), 7.50 (t, *J* = 7.6Hz, 2H), 7.66 (t, *J* = 7.6Hz, 2H), 7.73 (d, *J* = 8.8Hz, 1H), 7.96 (d, *J* = 8.4Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 38.4, 111.8, 122.2, 123.1, 125.6, 126.4, 126.5, 127.1, 129.2, 129.6, 136.1, 146.3, 147.7, 156.8.

N-Phenylquinolin-2-amine (**Table 6.5**, entry 6)[18]



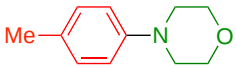
R_f = 0.2 (1:9 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 7.00 (d, J = 8.8Hz, 1H), 7.13 (t, J = 7.2Hz, 1H), 7.33 (t, J = 7.6Hz, 1H), 7.40 (t, J = 8.4Hz, 2H), 7.59-7.68 (m, 4H), 7.85 (d, J = 8.4Hz, 1H), 7.91 (d, J = 8.8Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 111.6, 115.0, 120.4, 122.9, 124.0, 126.5, 127.3, 129.1, 129.6, 137.6, 140.1, 147.5, 154.3.

N,*N*-Diphenylquinolin-2-amine (**Table 6.5**, entry 7)



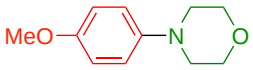
R_f = 0.3 (1: 20 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 6.99 (d, J = 8.8Hz, 1H), 7.24 (t, J = 7.2Hz, 2H), 7.33-7.43 (m, 9H), 7.61 (t, J = 7.6Hz, 1H), 7.69 (d, J = 8Hz, 1H), 7.80 (d, J = 8.4Hz, 1H), 7.90 (d, J = 9.2Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 115.1, 123.6, 124.4, 124.6, 126.4, 126.9, 127.4, 129.1, 129.3, 136.9, 145.6, 147.2, 157.0.

4-*p*-Tolylmorpholine (**Table 6.6**, entry 1)[7]



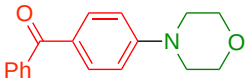
R_f = 0.3 (1:20 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 2.36 (s, 3H), 3.16 (t, J = 4.8Hz, 4H), 3.92 (t, J = 4.8Hz, 4H), 6.90 (d, J = 8.4Hz, 2H), 7.17 (d, J = 8.4Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 20.2, 49.7, 115.8, 129.2, 129.5, 149.0.

4-(4-Methoxyphenyl)morpholine (**Table 6.6**, entry 2)[19]



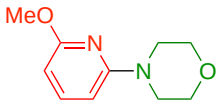
R_f = 0.3 (1:4 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 3.07 (t, J = 4.8Hz, 4H), 3.79 (s, 3H), 3.87 (t, J = 4.8Hz, 4H), 6.86-6.92 (m, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ 50.6, 55.4, 66.9, 114.3, 117.6, 145.5, 153.8.

(4-Morpholinophenyl)(phenyl)methanone (**Table 6.6**, entry 3)[20]



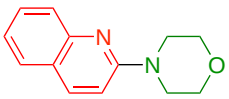
R_f = 0.2 (1:4 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 3.23 (t, J = 4.8Hz, 4H), 3.77 (t, J = 5.2Hz, 4H), 6.82 (d, J = 8.8Hz, 2H), 7.40 (t, J = 7.6Hz, 2H), 7.49 (t, J = 8Hz, 1H), 7.70 (d, J = 7.2Hz, 2H), 7.75 (d, J = 8.8Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 47.0, 66.1, 112.7, 127.1, 127.7, 129.1, 131.1, 132.0, 138.3, 153.6, 194.6.

4-(6-Methoxypyridin-2-yl)morpholine (**Table 6.6**, entry 4)[15]



R_f = 0.4 (1:10 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 3.45 (t, J = 4.8Hz, 4H), 3.79 (t, J = 4.8Hz, 4H), 3.85 (s, 3H), 6.10 (d, J = 4.4Hz, 1H), 6.12 (d, J = 4.8Hz, 1H), 7.39 (t, J = 8Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 45.3, 52.6, 66.4, 97.6, 98.5, 139.8, 158.1, 162.8.

2-Morpholinoquinoline (**Table 6.6**, entry 5)[11]



R_f = 0.35 (1:4 E.A./Hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 3.71 (t, J = 4.8Hz, 4H), 3.86 (t, J = 5.2Hz, 4H), 6.92 (d, J = 9.2Hz, 1H), 7.28 (t, J = 7.6Hz, 1H), 7.57-7.64 (m, 2H), 7.78 (d, J = 8.4Hz, 1H), 7.90 (d, J = 9.2Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 45.3, 66.6, 109.1, 122.4, 123.1, 126.5, 127.0, 129.4, 137.3, 147.5, 157.3.

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Chapter 7 Ligand-Controlled Chemoselective Cross-Coupling of Aryl Chlorides

7.1 Introduction

During the past decade, considerable efforts have been undertaken by researchers aiming to design unique phosphine ligands which allow challenging coupling reaction to proceed smoothly.[1] Actually, the synthetic versatility of cross-coupling would be further increased if catalysts are both highly reactive and particularly selective. This is significantly useful for a reaction system which can deal with the aimed site, yet remains other reactive groups intact. Therefore, it is valuable to develop a complementary set of catalysts which can enable chemoselective couplings. Well-known state-of-the-art ligands such as P*t*-Bu_3,[2] PAP,[1b, 3] and XPhos[4] provide excellent catalytic activity in palladium-catalyzed C-C and C-N couplings of aryl halides. However, the highly reactive nature of these ligands often show limited chemoselectivty, in view of aromatic C-C and C-N bond-forming reactions, no matter under modifying ligand-diversities (-phosphino moieties) and reaction conditions.

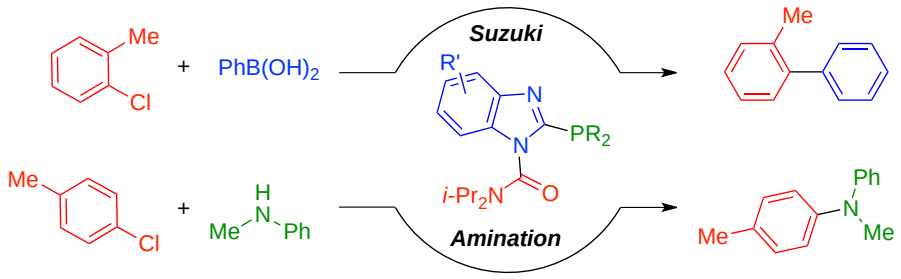
In addition, we have developed a series of 2-phosphino-substituted ligands which was highly active in both palladium-catalyzed Suzuki-Miyaura coupling and Buchwald-Hartwig amination reactions (see **Chapter 5** and **6**). Particularly noteworthy, this series of ligands showed a potential chemoselectivity, and herein we would like to test and prove this interestingly feature.

7.2 Results and Discussion

7.2.1 Study on the Ligand Structural Effect Towards Palladium-Catalyzed Suzuki Coupling and Amination Reactions

Having demonstrated the coordination ability of this ligand series (see **Section 5.2.1**), we next sought to study their effectiveness, with respected to their structures in palladium-catalyzed Suzuki coupling and amination of aryl chlorides (**Chapter 5** and **6**).

Table 7.1 Dramatic Ligand Structural Effect Towards Palladium-Catalyzed Suzuki Coupling and Amination Processes[a]



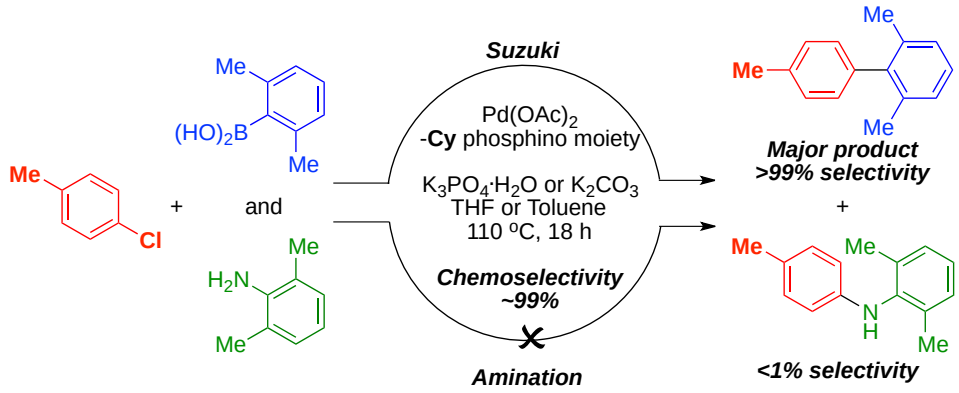
Ligand	Phosphino moiety	Dimethy-substitution on scaffold	Suzuki coupling[b]	Amination[b]
PCy Amizole-phos **L2a**	Cy	✗	43	1
PCy Amizole^{M2}-phos **L2i**		✓	57	6
P*t*-Bu Amizole-phos **L2b**	*t*-Bu	✗	8	57
P*t*-Bu Amizole ^{M2}-phos **L2j**		✓	13	80

[a]Reaction conditions: For Suzuki (C-C): 2-chlorotoluene (1.0 mmole), phenylboronic acid (1.5 mmole), $K_3PO_4 \cdot H_2O$ (3.0 mmole), 0.1 mol% Pd, $Pd(OAc)_2$/L = 1:2, and THF (3 mL) were stirred for 24 h at 100 °C under nitrogen. For amination (C-N): 4-chlorotoluene (1.0 mmole), *N*-methylaniline (1.5 mmole), K_2CO_3 (2.5 mmole), 1.0 mol% Pd, $Pd(OAc)_2$/L = 1:4, $PhB(OH)_2$ (0.02 mmol) and toluene (3 mL) were stirred for 24 h at 110 °C under nitrogen. [b]Calibrated GC yields were reported using dodecane as the internal standard, average of two runs.

In Suzuki-Miyaura coupling, ligands PCy Amizole-phos **L2a** and PCy Amizole^{M2}-phos **L2i** bearing carbamoyl group with $–PCy_2$ moiety provided the

highest catalytic activity, while P*t*-Bu Amizole-phos **L2b** and P*t*-Bu Amizole^{M2}-phos **L2j** (with –P*t*-Bu_2 group) did not (**Table 7.1**). Ligand PCy Amizole^{M2}-phos **L2i** with dimethyl-substitution on the 5,6-positions of benzimidazole ring gave improvement in the coupling reactions (**Table 7.1**). In amination reaction, interestingly, a reversal of activity (**L2a**/**L2i** *versus* **L2b**/**L2j**) was observed in this reaction (**Table 7.1**).

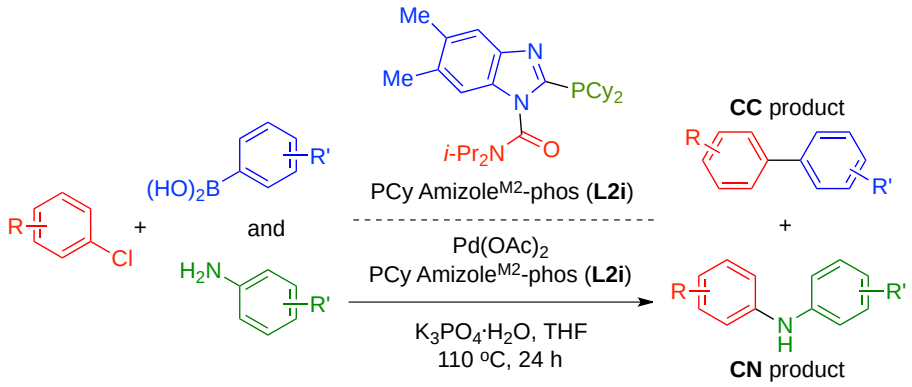
With the above selectivity between Suzuki coupling and amination, a competitive chemoselectivity of this catalytic system was studied (**Scheme 7.1**). Ligands bearing –PCy_2 moiety, PCy Amizole-phos **L2a** or PCy Amizole^{M2}-phos **L2i**, showed essentially complete orthogonal property (>99%) to afford Suzuki coupling product, no matter under either Suzuki or amination reaction conditions.

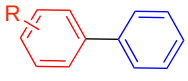


Scheme 7.1 Ligand-Controlled Orthogonal Palladium-Catalyzed Suzuki Coupling

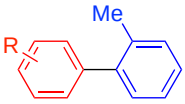
7.2.2 Competitive Palladium-Catalyzed Suzuki Couplings of Aryl Chlorides with Boronic Acids and Amines

Table 7.2 Competitive Palladium-Catalyzed Suzuki Couplings of Aryl Chlorides with Boronic Acids and Amines[a]

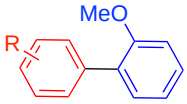




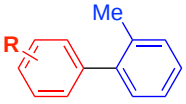
1: R = 2-Me, 0.05 mol%
91%, (**CC** : **CN** = 98 : 2)
2: R = 2-OMe, 0.067 mol%
94%, (**CC** : **CN** = 99:1)
3: = R = 3-CN, 0.05 mol%
98% (**CC** : **CN** = >99:1)



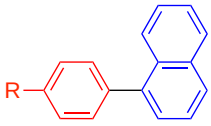
4: R = 2-OMe, 0.1 mol%
83%, (**CC** : **CN** = 98 : 2)
5: R = 4-OMe, 0.1 mol%
95%, (**CC** : **CN** = 98 : 2)



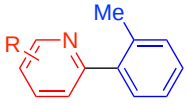
6: R = 4-C(O)Me, 0.02 mol%
80%, (**CC** : **CN** = >99 : 1)
7: R = 3-C(O)Me, 0.05 mol%
79%, (**CC** : **CN** = >99 : 1)



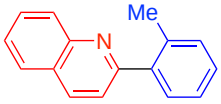
8: R = 4-CHO, 0.01 mol%
91%, (**CC** : **CN** = 98 : 2)
9: R = 3-C(O)OMe, 0.025 mol%
86%, (**CC** : **CN** = >99 : 1)



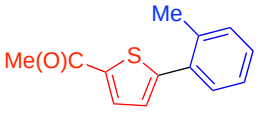
10: R = C(O)Ph, 0.01 mol%
80%, (**CC** : **CN** = >99 : 1)
11: R = NO_2, 0.01 mol%
98%, (**CC** : **CN** = >99 : 1)



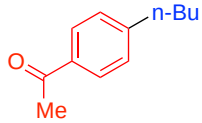
12: R = H, 0.02 mol%
80%, (**CC** : **CN** = 97 : 3)
13: R = 3-Me, 0.05 mol%
81%, (**CC** : **CN** = >99 : 1)



14: 0.01 mol%
98%, (**CC** : **CN** = >99 : 1)



15: 0.02 mol%
92%, (**CC** : **CN** = 96 : 4)



16: 0.05 mol%
84%[b] (**CC** : **CN** = 98 : 2)

[a]Reaction conditions: ArCl (1.0 mmole), Ar'$B(OH)_2$ (1.5 mmole), Ar'NH_2 (1.5 mmole), $K_3PO_4 \cdot H_2O$ (3.0 mmole), $Pd(OAc)_2$/PCy Amizole^{M2}-phos (**L2i**) = 1:3, and THF (3 mL) were stirred at 110 °C for 24 h under nitrogen. Isolated yields, average of two runs. Chemoselectivity determined by GC. [b]*n*-$BuB(OH)_2$ (2.0 mmole), *n*-$BuNH_2$ (2.0 mmole) and toluene (3 mL).

A range of aryl chlorides together with both arylboronic acids and amines (same substitution pattern) were further examined competitively (**Table 7.2**).

Non-activated, functionalized aryl and heteroaryl chlorides showed excellent chemoselectivity (~99% selectivity) to form Suzuki product under $Pd(OAc)_2$/PCy Amizole^{M2}-phos **L2i** system. In particular, the catalyst loading could be down to 0.01 mol% Pd. The competitive coupling could also be applied to alkylboronic acid and aliphatic amine (**Table 7.2**, example 16). To the best of our knowledge, there has been no successful example reported to-date that a carbon-carbon chemoselective bond-forming reaction can be simply controlled by phosphine ligand.

7.3 Conclusion

In summary, we have developed a new family of 2-phosphino-substituted ligands. To the best of our knowledge, we have succeeded in showing the first examples of a ligand family that have both *P,O* and *P,N* hemilabile features, and ligand-controlled chemoselective Suzuki coupling and amination reactions. We anticipate this unique structural finding from this ligand family would provide a useful direction of future ligand design in stepwise and specific cross-coupling reactions.

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 coupling reactions were performed in resealable screw cap schlenk flask (approx. 20 mL volume) in the presence of Teflon coated magnetic stirrer bar (3mm × 10 mm). Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under nitrogen.[5] Commercial aryl chlorides (liquid form only) were purified by passed through a short plug (0.5 cm wide × 4 cm high) of neutral alumina or distillation. Most commercially available boronic acids were used as received. Commercially available amines were purified by distillation. All bases were purchased from chemical supplier and used without 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. Melting points were recorded on an uncorrected instrument. ^{1}H NMR spectra were recorded on a Bruker (400 MHz) spectrometer. Spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.26 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 ESIMS. GC-MS analysis was conducted on a GCD system using a column with 30 m × 0.25 mm. The products described in GC yield were accorded to the authentic samples/dodecane calibration standard from GC-FID system. Compounds described in the literature were characterized by comparison of their

^{1}H 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 General Procedure for Competitive Suzuki-Miyaura Cross-Couplings of Aryl Chlorides with Boronic Acids and Amines

General procedure for competitive Suzuki-Miyaura cross-couplings of aryl chlorides with boronic acids and amines: A stock solution of $Pd(OAc)_2$ (2.3 mg, 0.010 mmol) with ligand (Pd:L = 1:3) in freshly distilled 10 mL THF (0.1 mol% Pd per 1 mL stock solution) was initially prepared with continuously stirring at room temperature. Arylboronic acid (1.5 mmol), $K_3PO_4 \cdot H_2O$ (3.0 mmol) and magnetic stirrer bar (3 mm × 8 mm) were charged to an array of Schlenk tubes. Each tube was carefully evacuated and backfilled with nitrogen (3 cycles). Aryl chloride (1.0 mmol), and corresponding amines (1.5 mmole) were then added to the Schlenk tubes. The stock solution was further diluted to give different concentrations of palladium complex. The diluted solutions were then transferred to Schlenk tubes via syringes. Further solvent was added (final volume: 3 mL). This batch of Schlenk tube was resealed and magnetically stirred in a preheated oil bath. After the completion of reaction as judged by GC or TLC analysis, the reactions were allowed to reach room temperature. Water (~3 mL) and ethyl acetate (~10 mL × 3) were added. The organic layers were combined and concentrated. The crude products were purified by column chromatography on silica gel (230-400 mesh).

7.5 References

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(2) For selected references, see: (a) Netherton, M. R.; Dai, C.; Neuschütz, K.; Fu, G. C. *J. Am. Chem. Soc.* **2001**, *123*, 10099. (b) Kirchhoff, J. H.; Netherton, M. R.; Hills, I. D.; Fu, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 13662. (c) Nishiyama, M.; Yamamoto, T.; Koie, Y. *Tetrahedron Lett.* **1998**, *39*, 617. (d) Netherton, M. R.; Fu, G. C. *Org. Lett.* **2001**, *3*, 4295.

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Summary

We have successfully designed and explored two classes of ligands, *P*,*N*-type 2-arylated benzimidazolyl phosphine ligands and alterable *P*,*O*- or *P*,*N*-type 2-phosphino-substituted benzimidazolyl ligands by a "Cross-matching" approach. The benzimidazole scaffold of this family of ligands could be easily synthesized and diversified from inexpensive substituted *o*-phenylenediamines and substituted carboxylic acids by Phillips benzimidazole synthesis.

For the 2-arylated benzimidazolyl phosphine ligands, a total of 16 examples have been prepared with moderate to excellent yields. When applying this class of ligands towards palladium-catalyzed Suzuki-Miyaura coupling of aryl chlorides, it showed excellent catalytic activities with arylboronic acids, especially under very-low-catalyst-loading down to 1 ppm. Furthermore, this class of ligands was also efficient towards Suzuki-Miyaura coupling of aryl chlorides with potassium aryltrifluoroborates. It is particularly noteworthy that the X-ray crystallographic data confirmed that the ligand was coordinated in a κ^2-*P*,*N* fashion to the palladium center.

On the other hand, for the 2-phosphino-substituted benzimidazolyl ligands, a total of 20 examples have been synthesized by "One-pot assembly" approaches. Palladium complexes of 2-phosphino-substituted benzimidazolyl ligands showed notable coordination in a κ^2-*P*,*N* fashion and potential *P*,*O*-hemilabile ability, which gave us evidence to believe the mode of coordination could be altered by tuning the steric bulkiness of the phosphino group. Interestingly, the complexes with *P*,*O*-coordination and *P*,*N*-coordination were

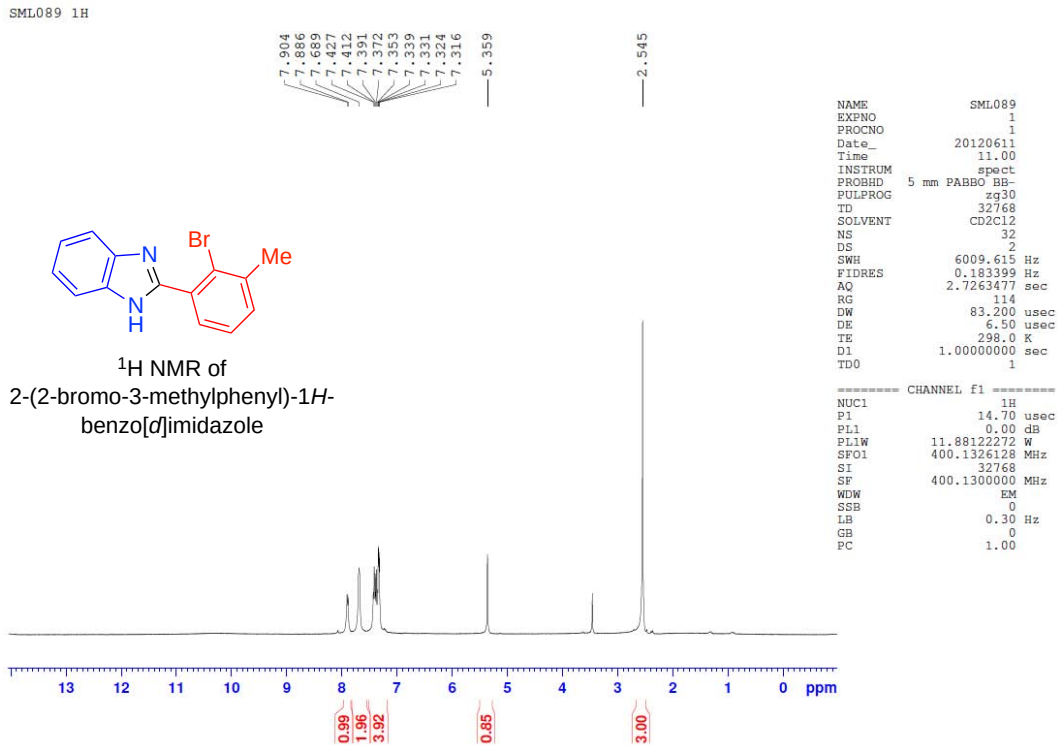
highly efficient towards Suzuki-Miyaura coupling and Buchwald-Hartwig amination of aryl chlorides respectively. Notably, in order to probe with these fascinating hemilabile properties, chemoselective cross-coupling of aryl chlorides was also examined, which showed essentially complete orthogonal property (>99%) to afford Suzuki coupling products when carrying out competitive cross-coupling of aryl chlorides with boronic acids and amines.

We believe that the contribution of work here would give us inspiration or even breakthrough to future exploration in the area of phosphine ligand syntheses and applications.

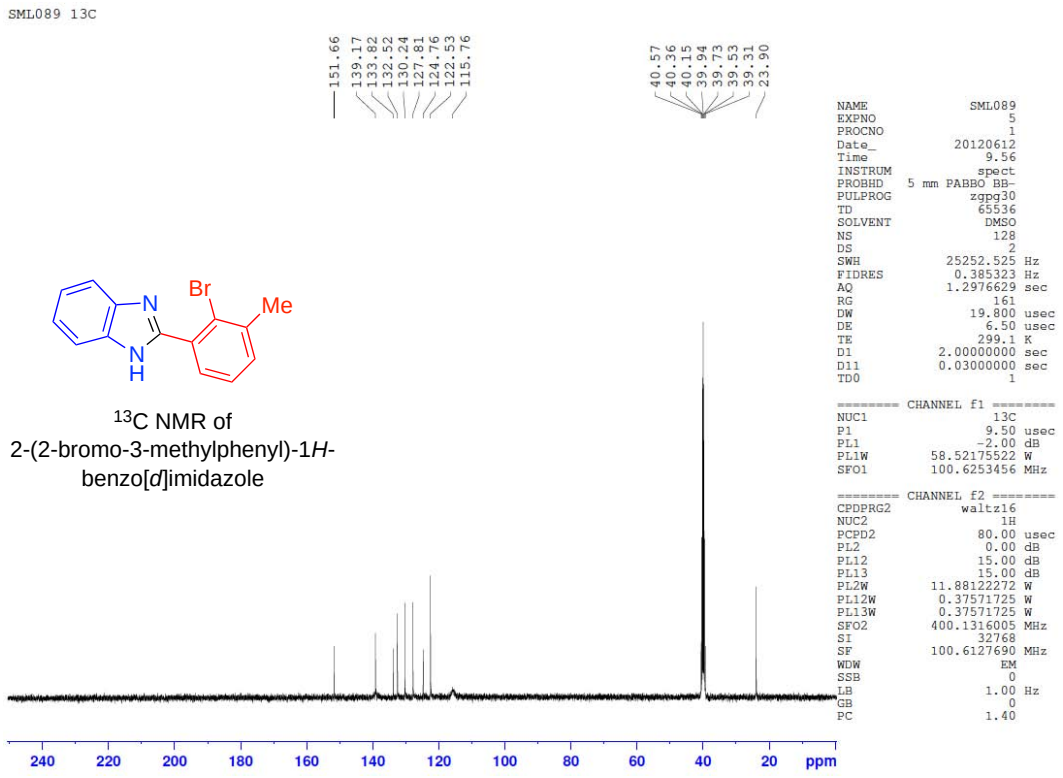
Appendix

Chapter 2 HMR and HRMS Spectra of 2-Arylbenzimidazolyl Ligand Templates

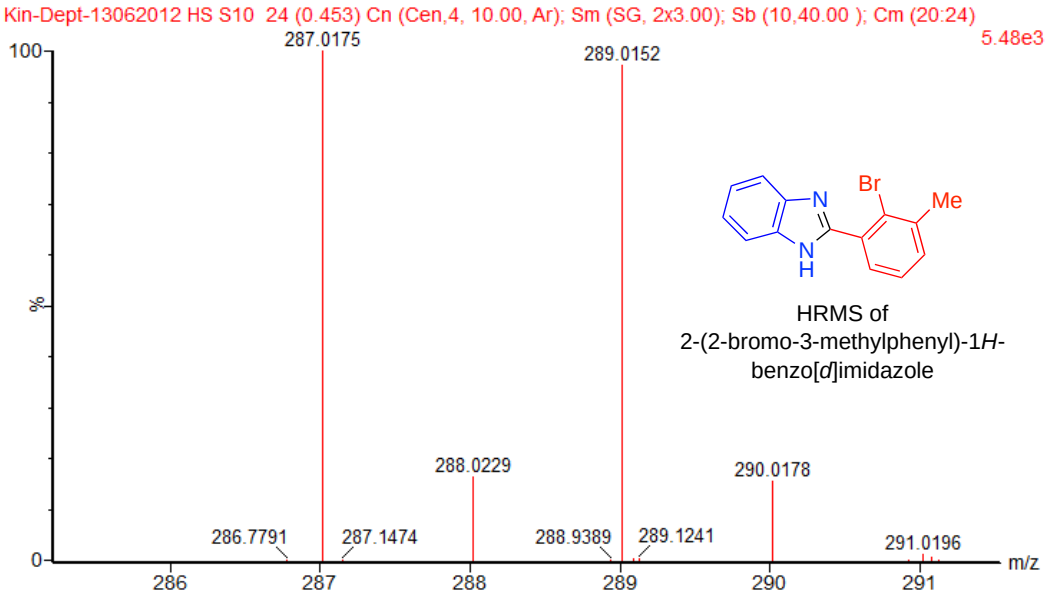
2-(2-Bromo-3-methylphenyl)-1*H*-benzo[*d*]imidazole (**Table 2.2**, entry 2)



^{1}H NMR of
2-(2-bromo-3-methylphenyl)-1*H*-
benzo[*d*]imidazole



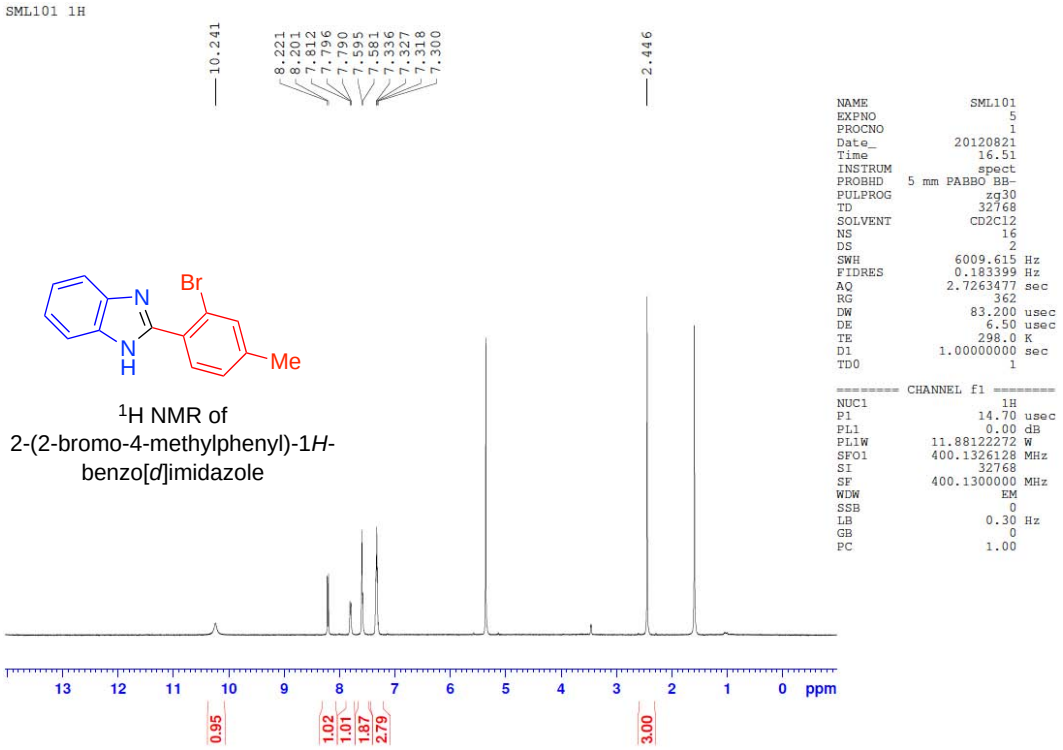
^{13}C NMR of
2-(2-bromo-3-methylphenyl)-1*H*-
benzo[*d*]imidazole



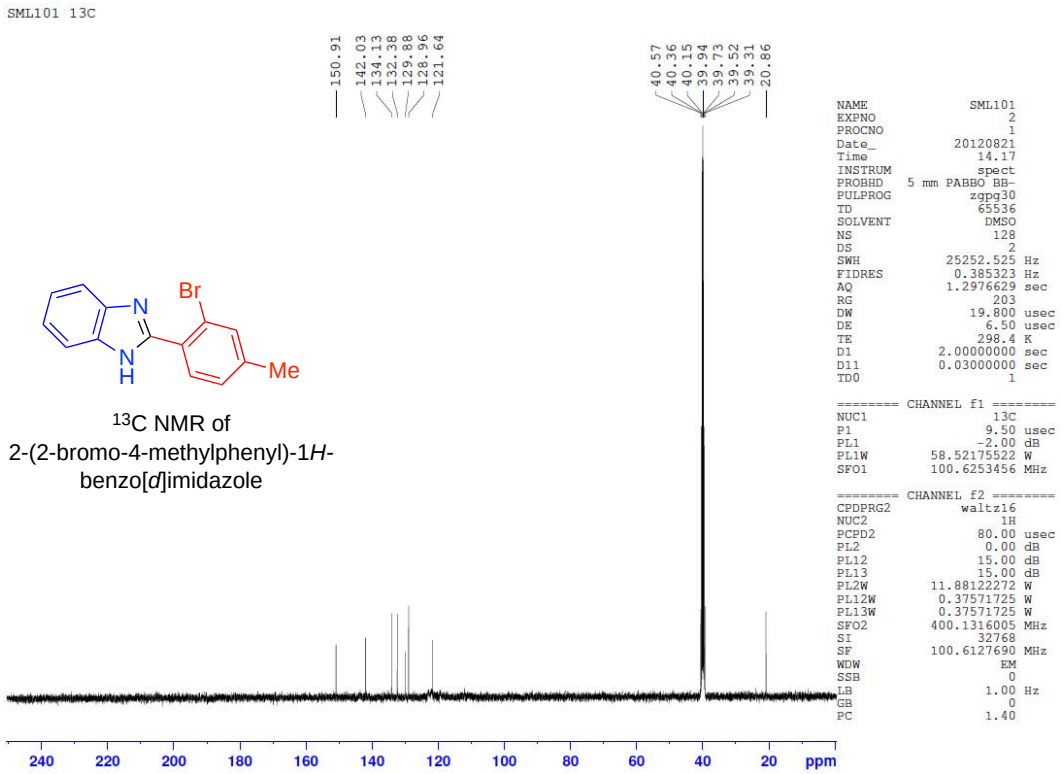
HRMS of
2-(2-bromo-3-methylphenyl)-1*H*-
benzo[*d*]imidazole

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
287.0175	287.0184	-0.9	-3.1	9.5	0.8	C14 H12 N2 Br

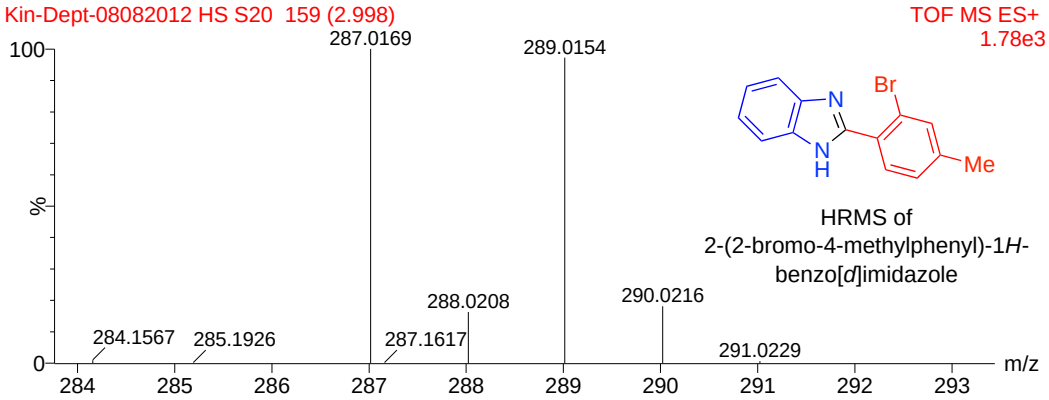
2-(2-Bromo-4-methylphenyl)-1*H*-benzo[*d*]imidazole (**Table 2.2**, entry 3)



^{1}H NMR of
2-(2-bromo-4-methylphenyl)-1*H*-
benzo[*d*]imidazole

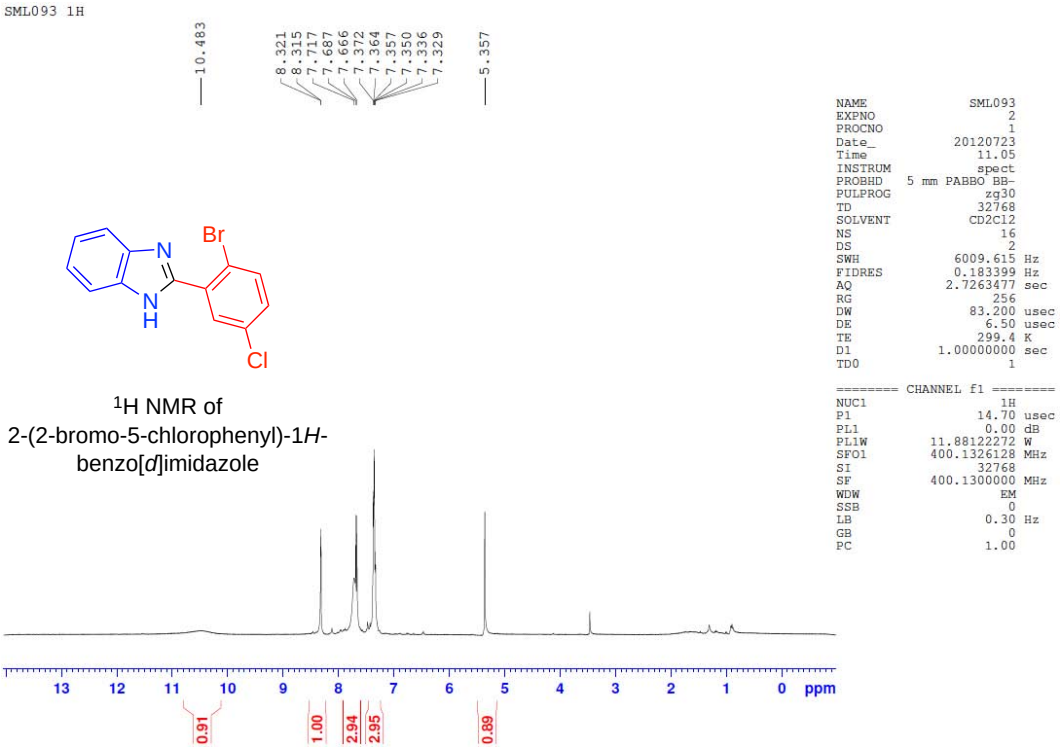


^{13}C NMR of
2-(2-bromo-4-methylphenyl)-1*H*-
benzo[*d*]imidazole

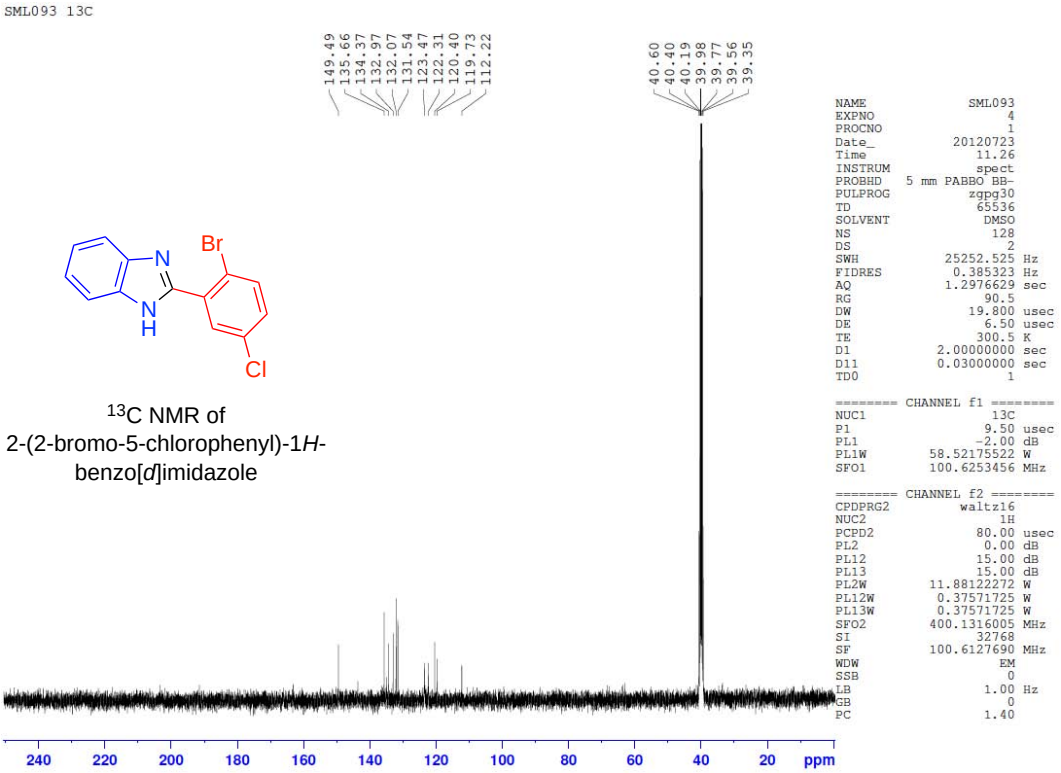


Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
287.0169	287.0184	-1.5	-5.2	9.5	0.3	C14 H12 N2 Br

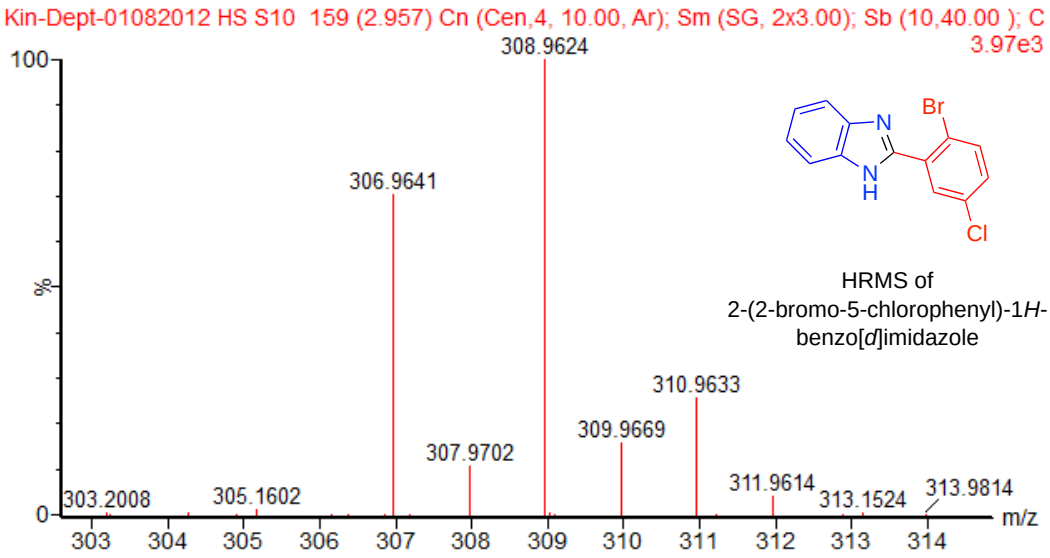
2-(2-Bromo-5-chlorophenyl)-1*H*-benzo[*d*]imidazole (**Table 2.2**, entry 4)



^{1}H NMR of
2-(2-bromo-5-chlorophenyl)-1*H*-
benzo[*d*]imidazole



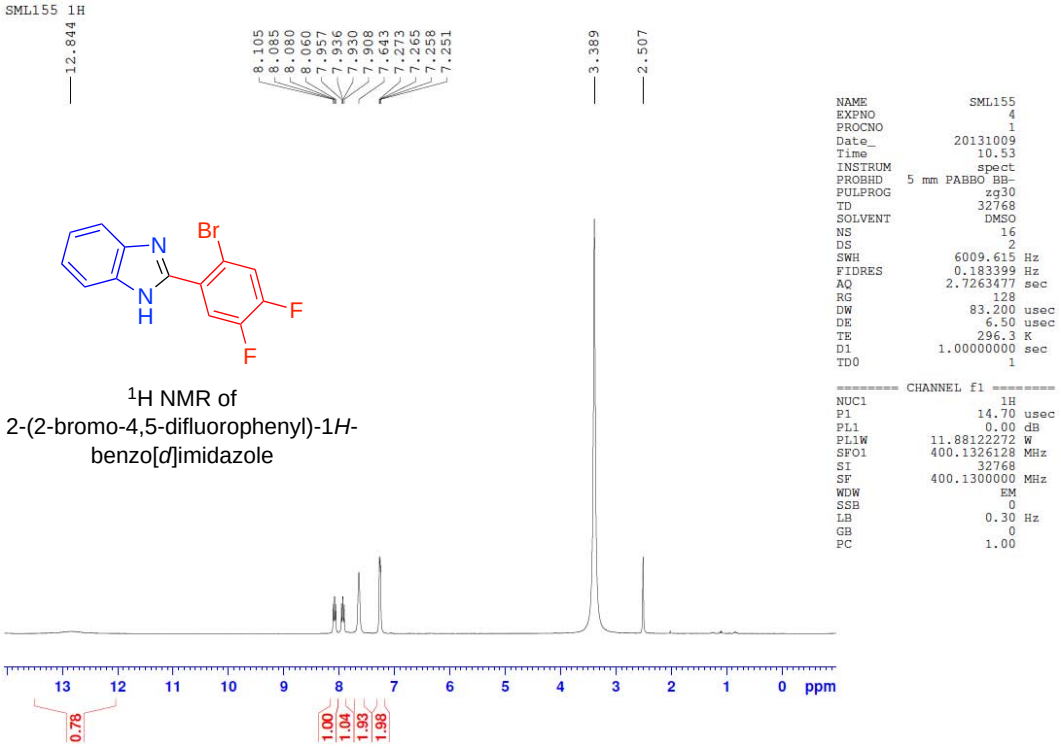
^{13}C NMR of
2-(2-bromo-5-chlorophenyl)-1*H*-
benzo[*d*]imidazole



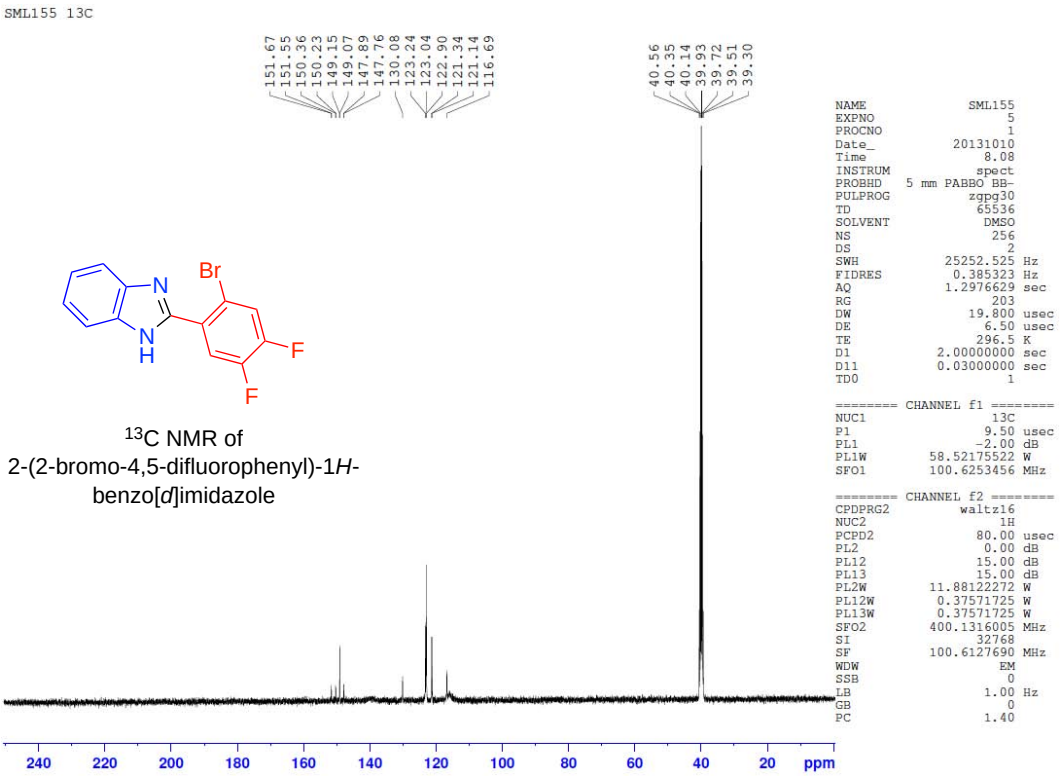
HRMS of
2-(2-bromo-5-chlorophenyl)-1*H*-
benzo[*d*]imidazole

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
306.9641	306.9638	0.3	1.0	9.5	7.4	C13 H9 N2 Cl Br

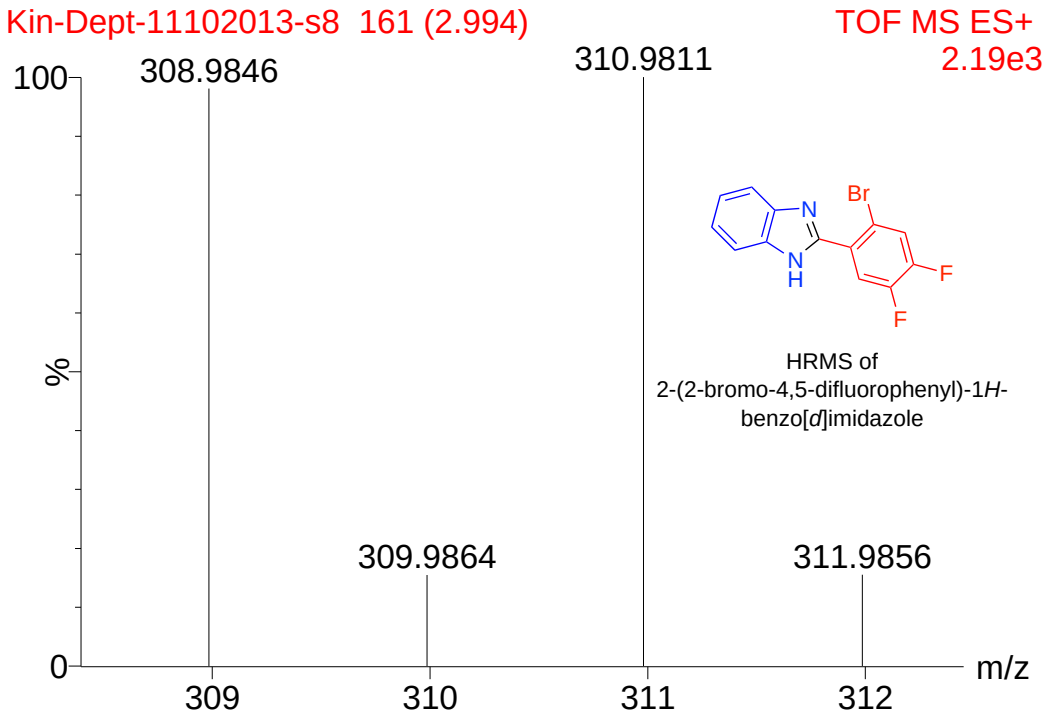
2-(2-Bromo-4,5-difluorophenyl)-1*H*-benzo[*d*]imidazole (**Table 2.2**, entry 5)



^{1}H NMR of
2-(2-bromo-4,5-difluorophenyl)-1*H*-
benzo[*d*]imidazole



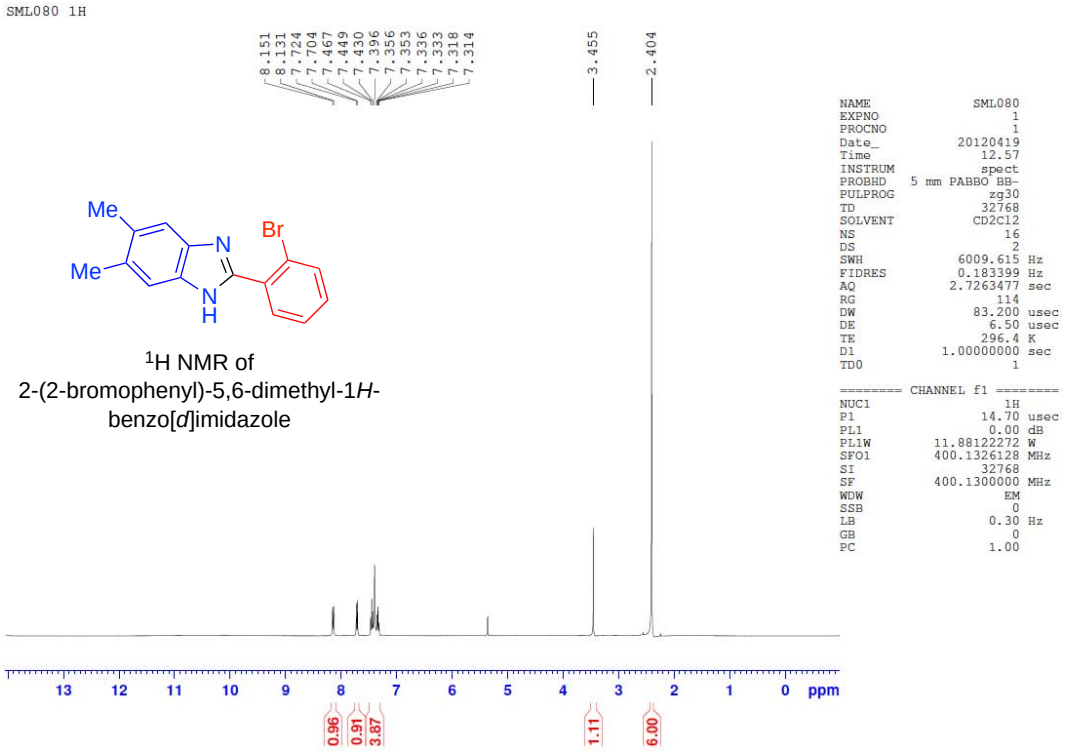
^{13}C NMR of
2-(2-bromo-4,5-difluorophenyl)-1*H*-
benzo[*d*]imidazole



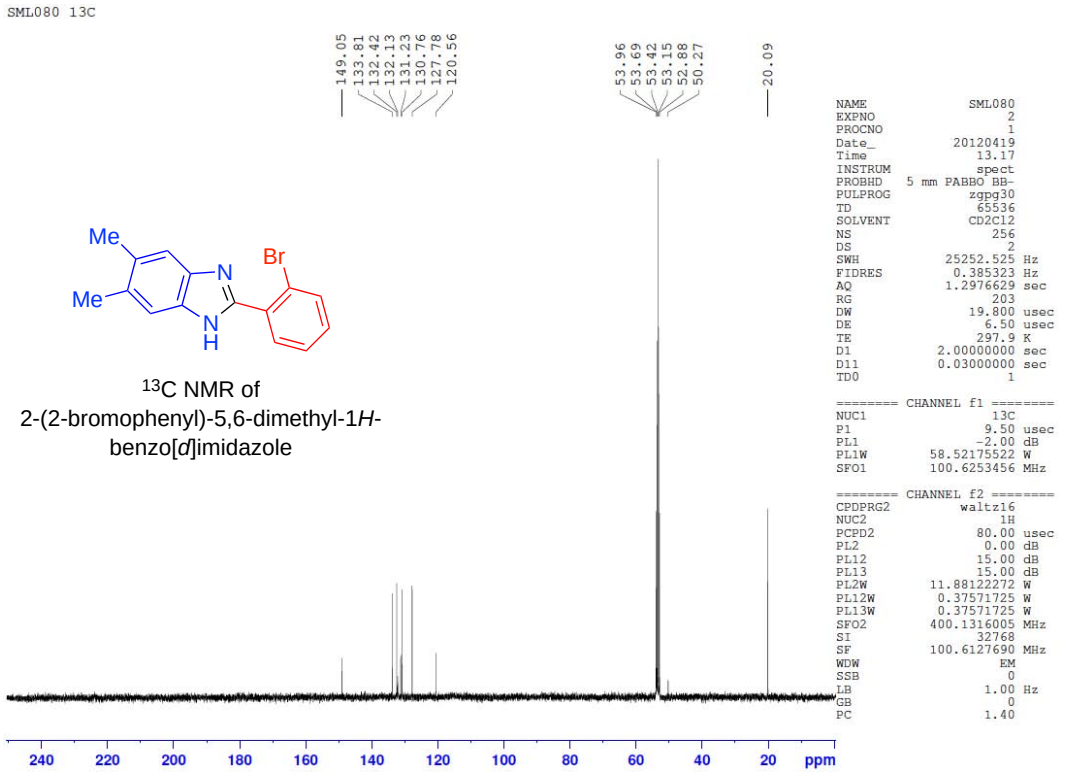
HRMS of
2-(2-bromo-4,5-difluorophenyl)-1*H*-
benzo[*d*]imidazole

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
308.9846	308.9839	0.7	2.3	9.5	0.8	C13 H8 N2 F2 Br

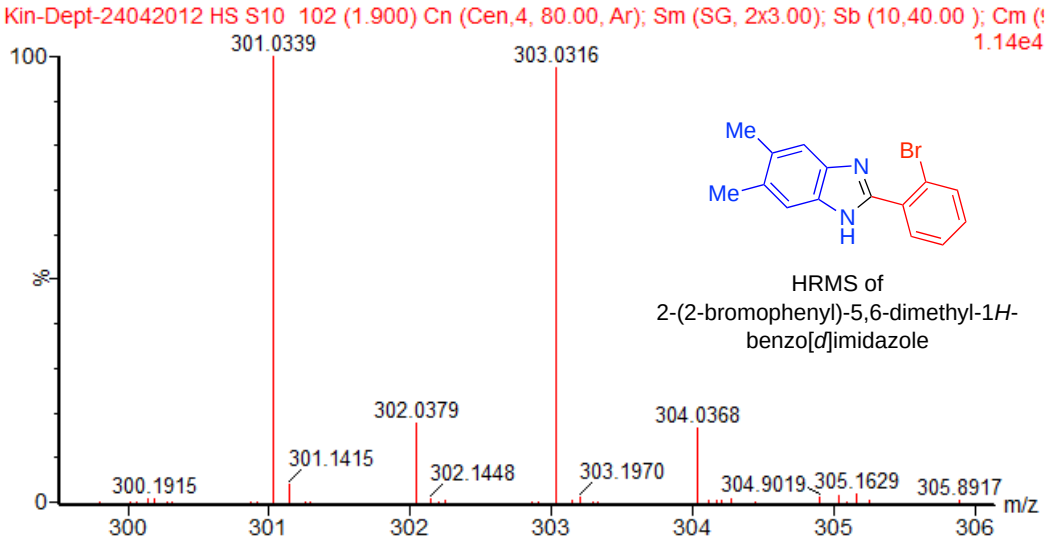
2-(2-Bromophenyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole (**Table 2.2**, entry 6)



^{1}H NMR of
2-(2-bromophenyl)-5,6-dimethyl-1*H*-
benzo[*d*]imidazole



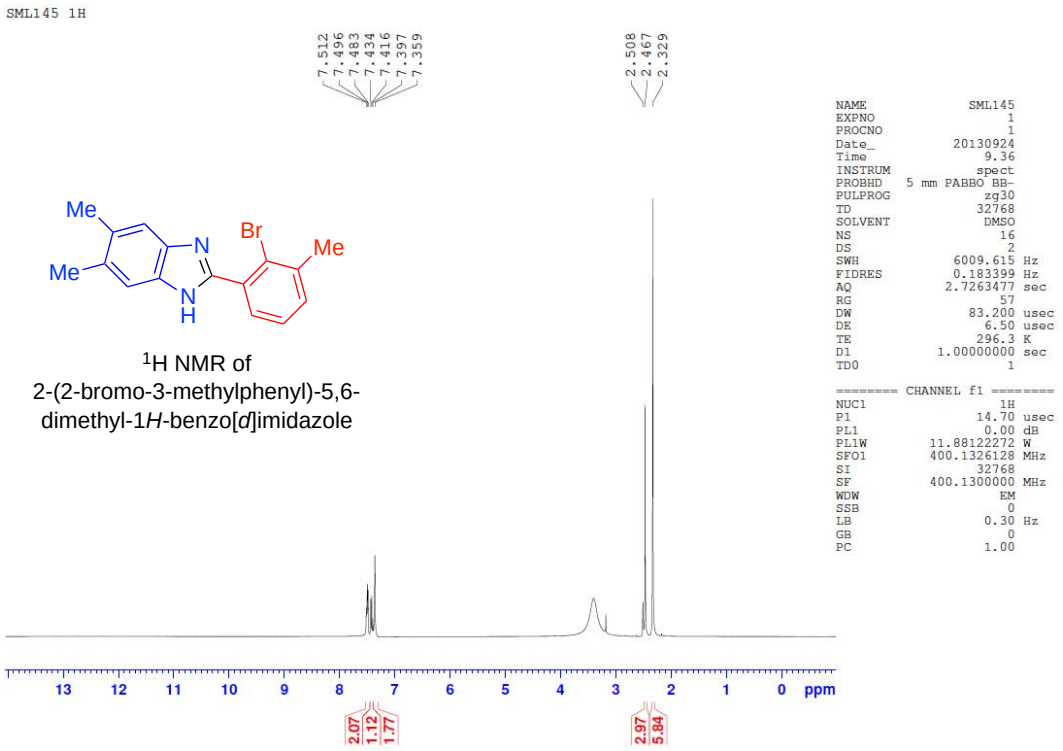
^{13}C NMR of
2-(2-bromophenyl)-5,6-dimethyl-1*H*-
benzo[*d*]imidazole



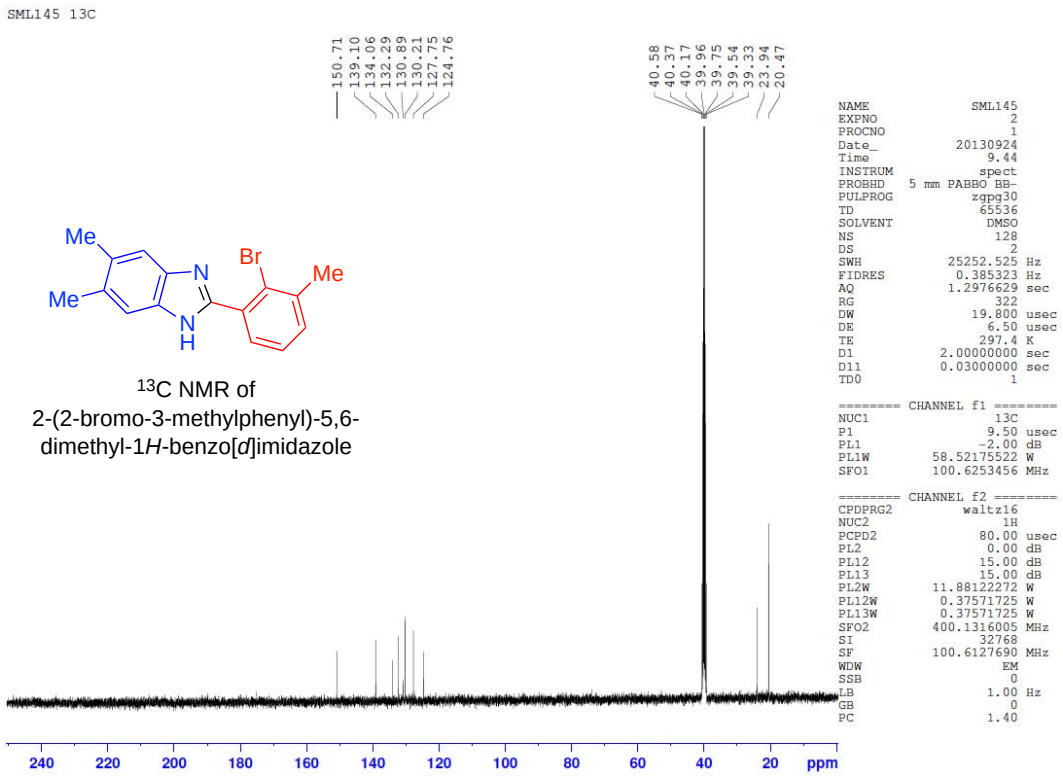
HRMS of
2-(2-bromophenyl)-5,6-dimethyl-1*H*-
benzo[*d*]imidazole

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
301.0339	301.0340	-0.1	-0.3	9.5	0.9	C15 H14 N2 Br

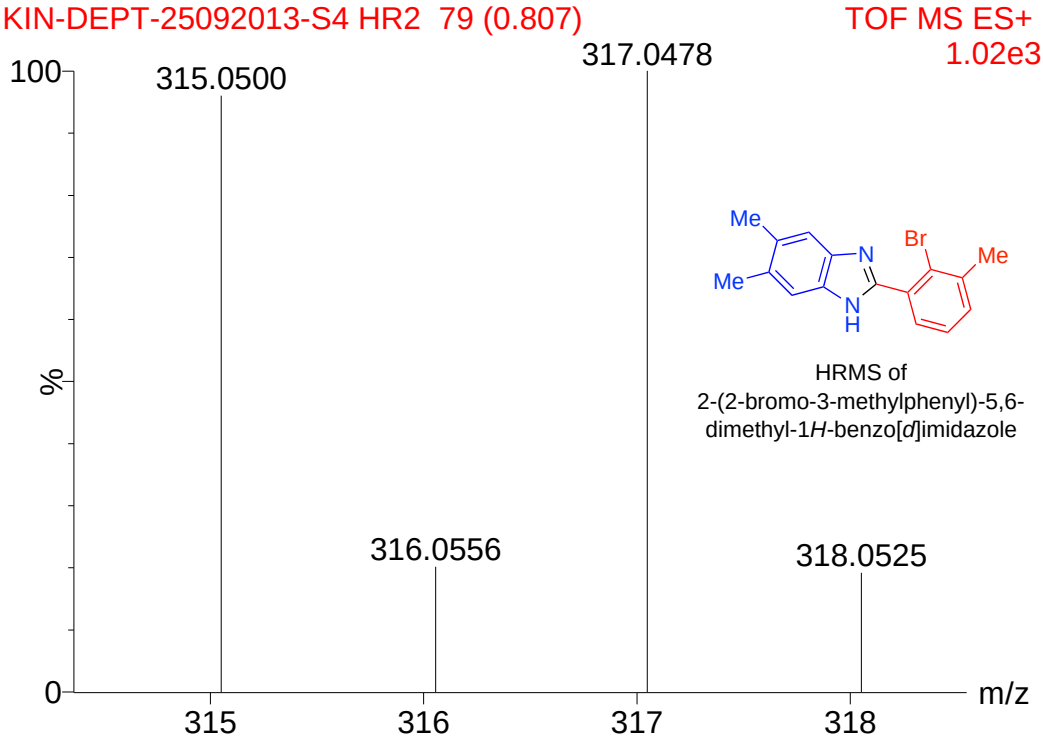
2-(2-Bromo-3-methylphenyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole (**Table 2.2**, entry 7)



^{1}H NMR of
2-(2-bromo-3-methylphenyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole



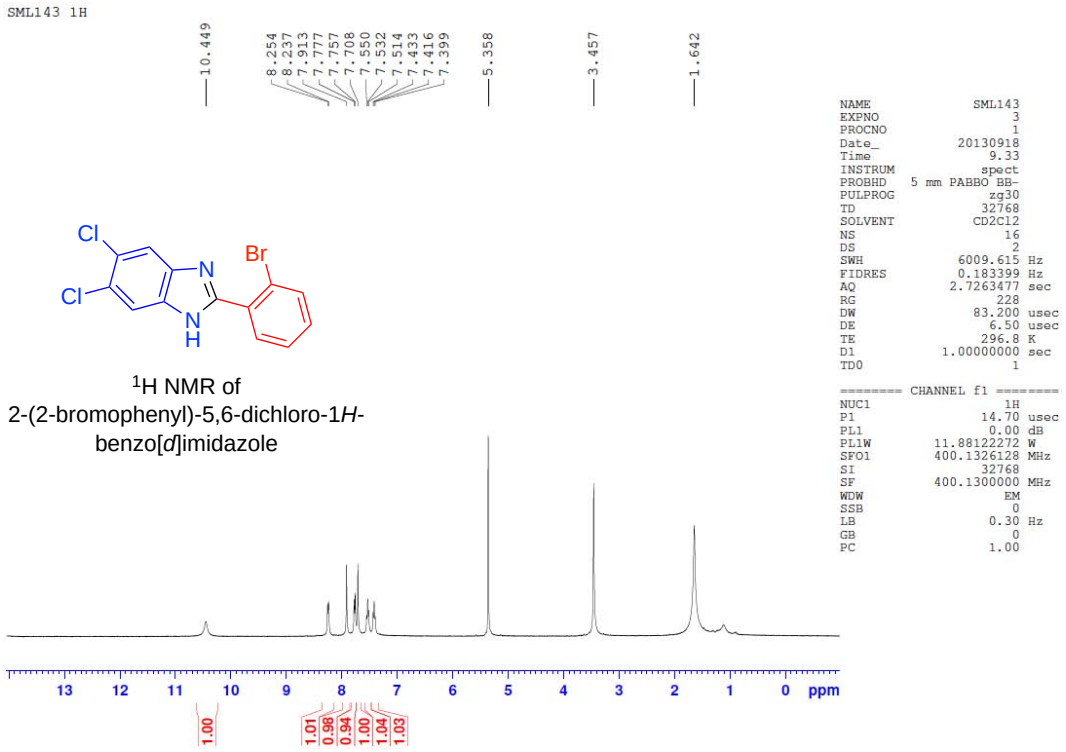
^{13}C NMR of
2-(2-bromo-3-methylphenyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole



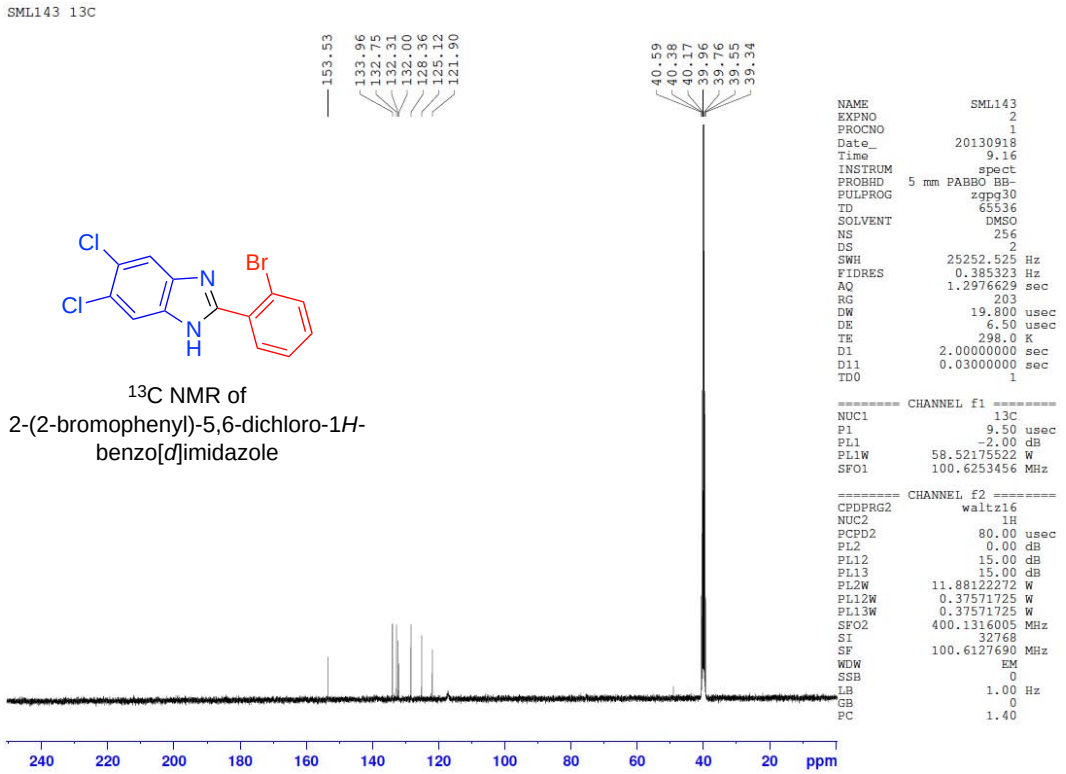
HRMS of
2-(2-bromo-3-methylphenyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
315.0500	315.0497	0.3	1.0	9.5	1.3	C16 H16 N2 Br

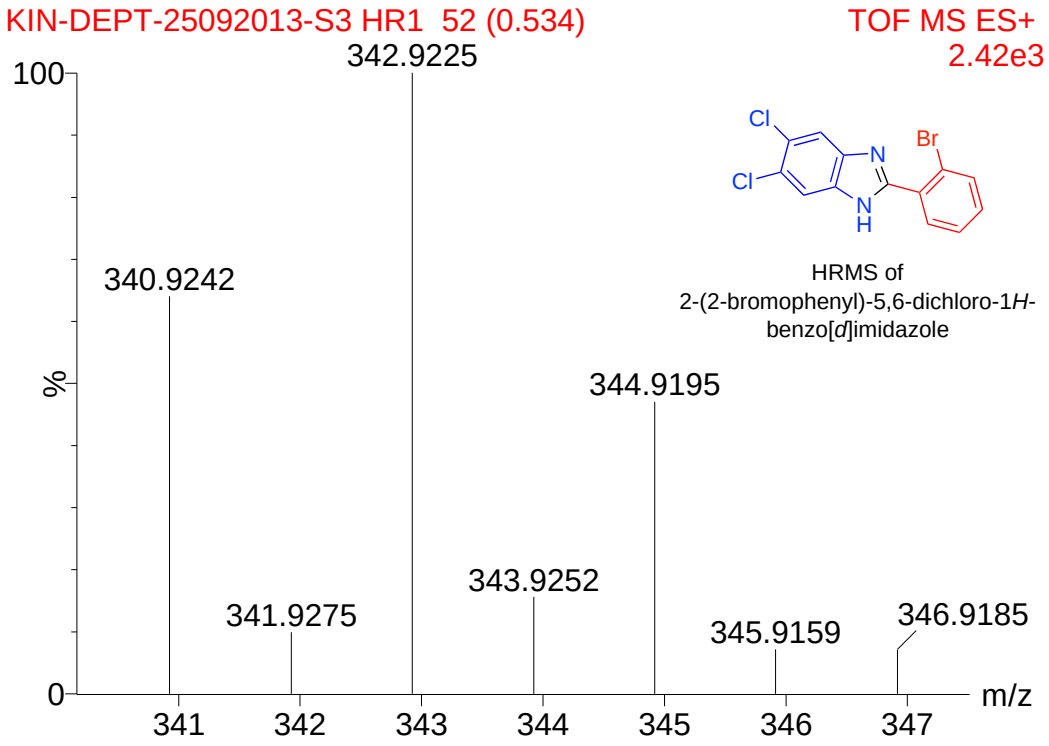
2-(2-Bromophenyl)-5,6-dichloro-1*H*-benzo[*d*]imidazole (**Table 2.2**, entry 8)



^{1}H NMR of 2-(2-bromophenyl)-5,6-dichloro-1*H*-benzo[*d*]imidazole



^{13}C NMR of 2-(2-bromophenyl)-5,6-dichloro-1*H*-benzo[*d*]imidazole

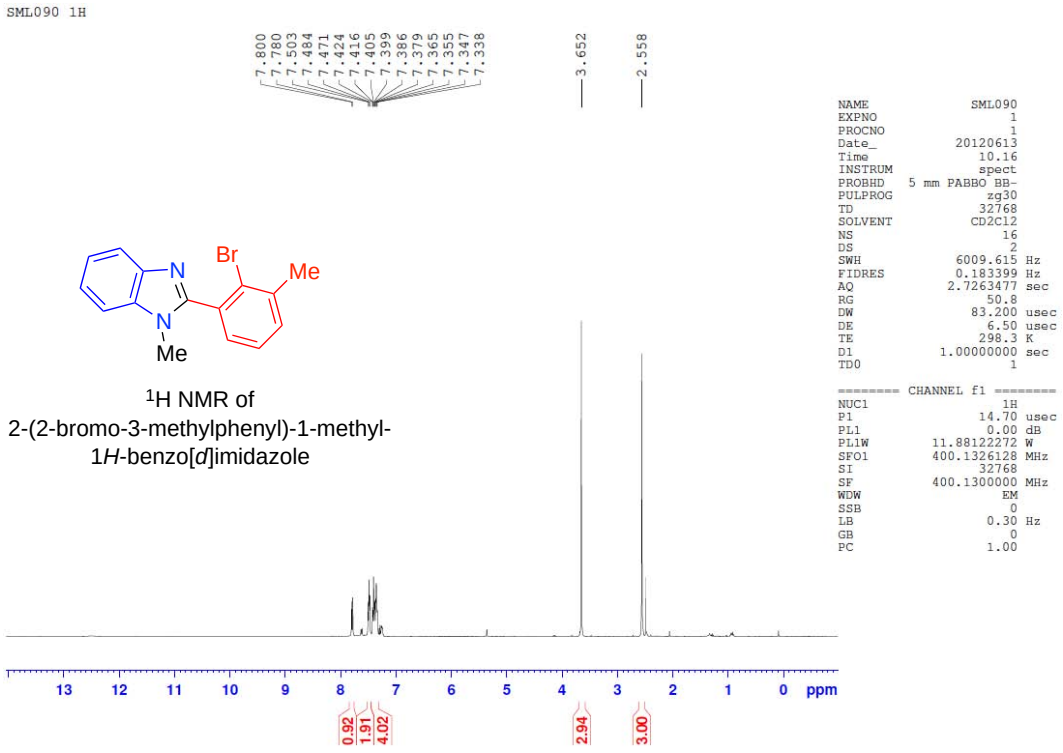


HRMS of
2-(2-bromophenyl)-5,6-dichloro-1*H*-
benzo[*d*]imidazole

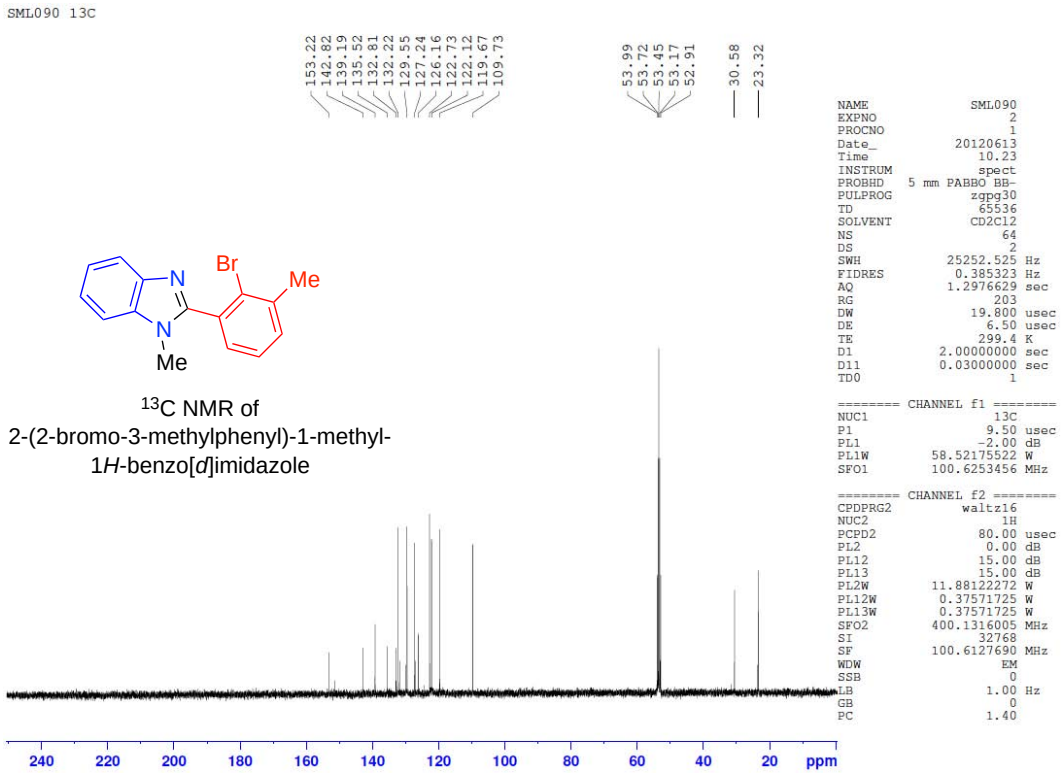
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
340.9242	340.9248	-0.6	-1.8	9.5	0.8	C13 H8 N2 Cl2 Br

Chapter 2 HMR and HRMS Spectra of *N*-Substituted 2-Arylbenzimidazolyl Ligand Precursors

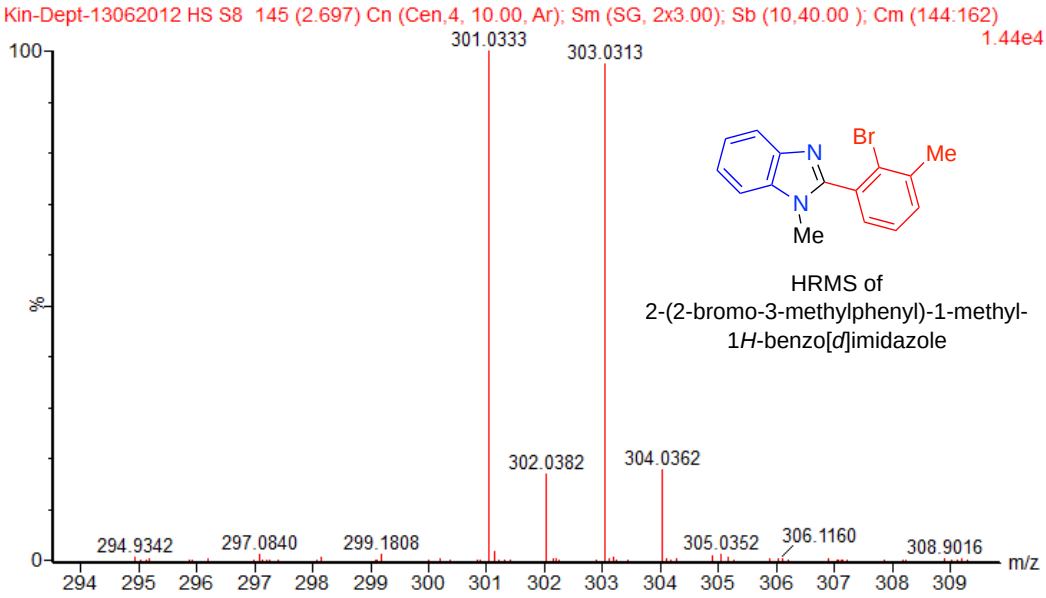
2-(2-Bromo-3-methylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole (**Table 2.3**, entry 2)



^{1}H NMR of
2-(2-bromo-3-methylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole



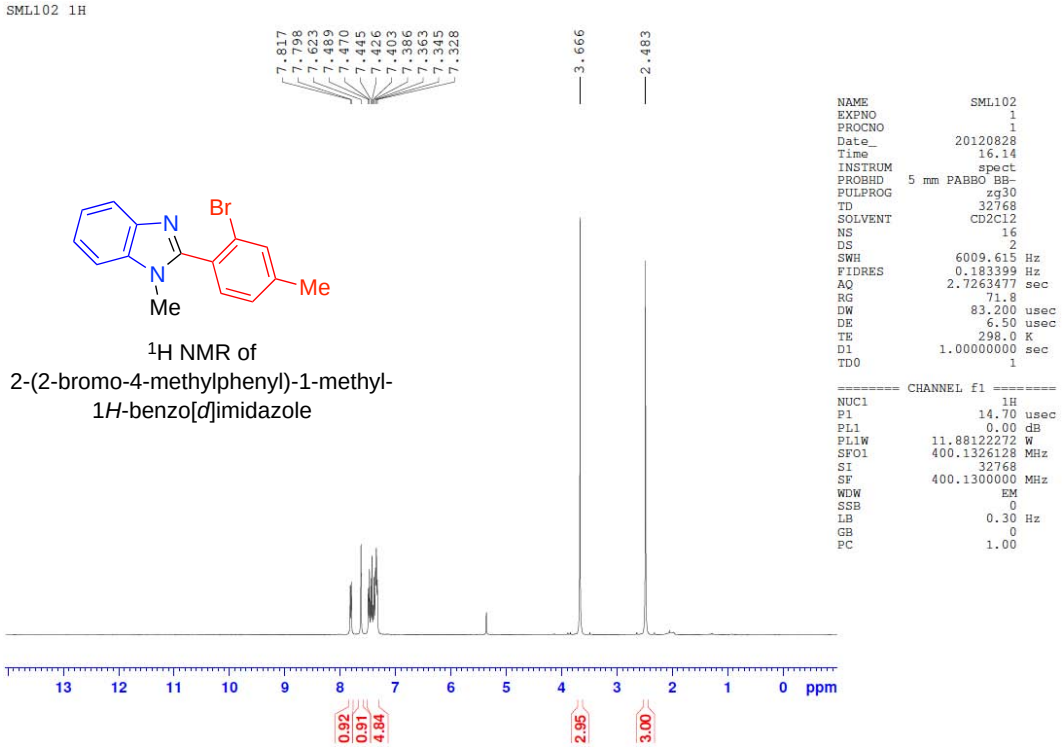
^{13}C NMR of
2-(2-bromo-3-methylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole



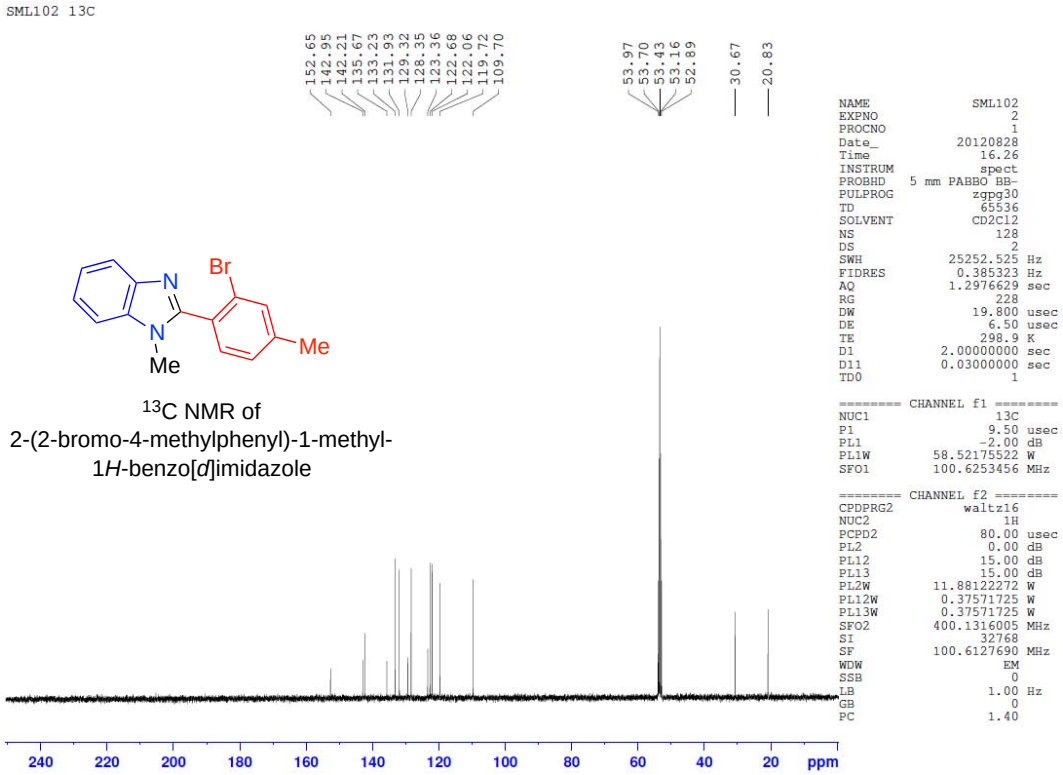
HRMS of
2-(2-bromo-3-methylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
301.0333	301.0340	-0.7	-2.3	9.5	2.1	C15 H14 N2 Br

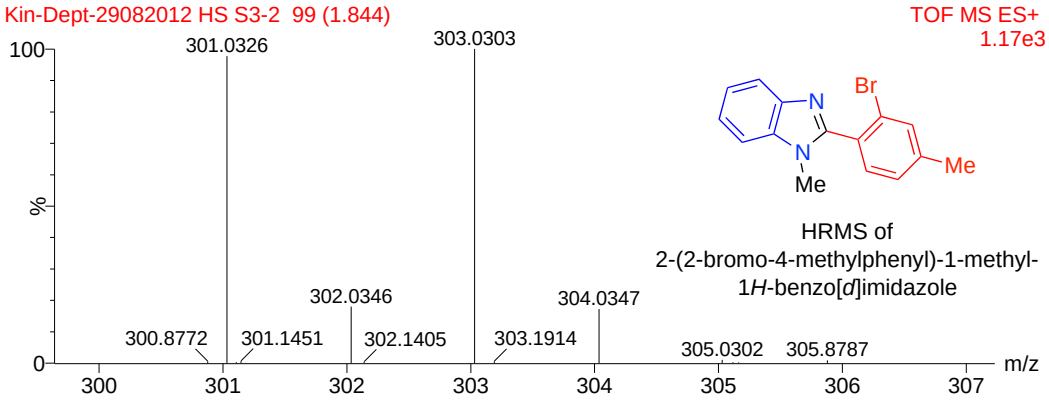
2-(2-Bromo-4-methylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole (**Table 2.3**, entry 3)



^{1}H NMR of
2-(2-bromo-4-methylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole



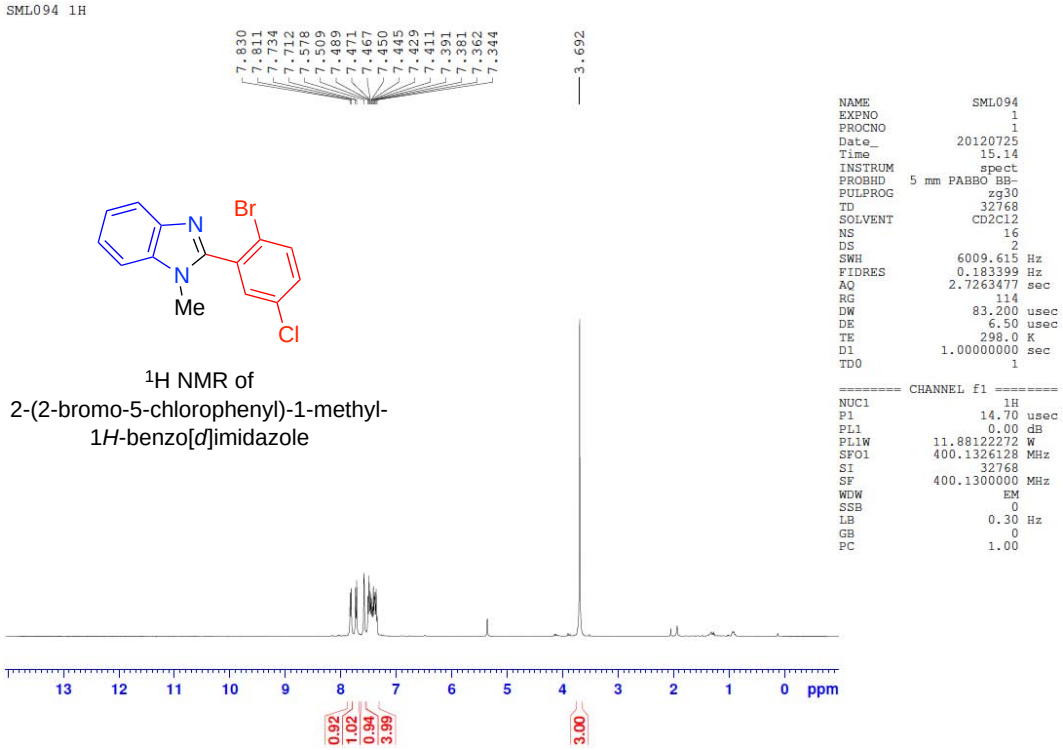
^{13}C NMR of
2-(2-bromo-4-methylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole



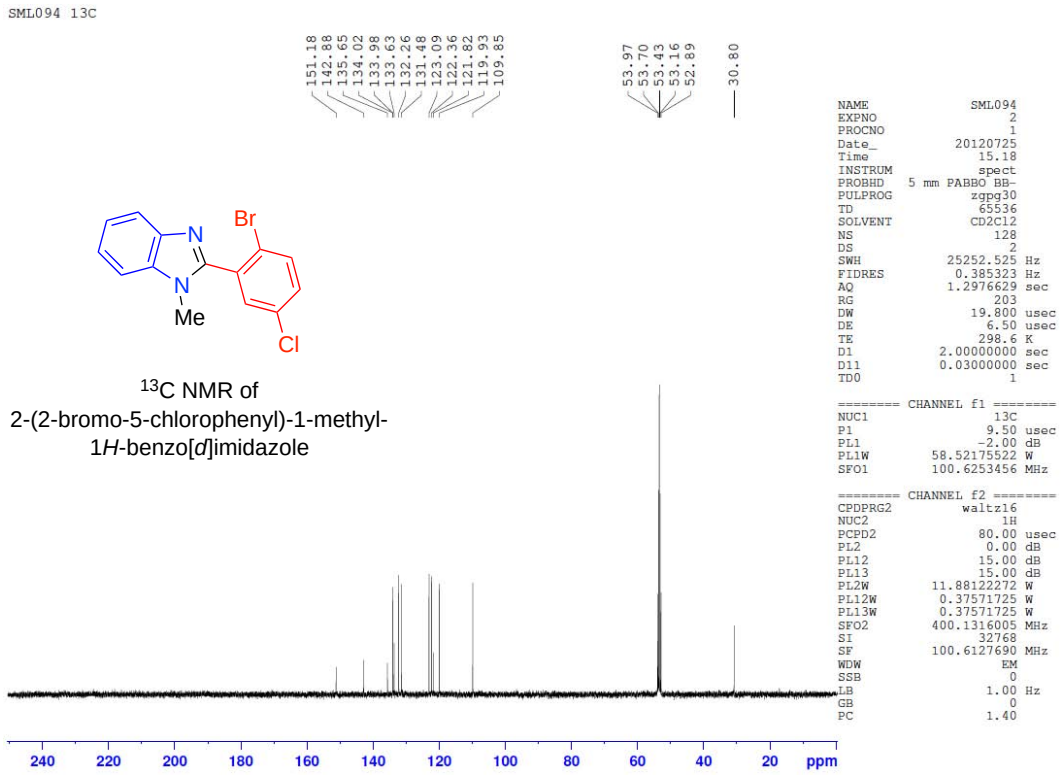
HRMS of
2-(2-bromo-4-methylphenyl)-1-methyl-
1*H*-benzo[*d*]imidazole

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
301.0326	301.0340	-1.4	-4.7	9.5	0.6	C15 H14 N2 Br

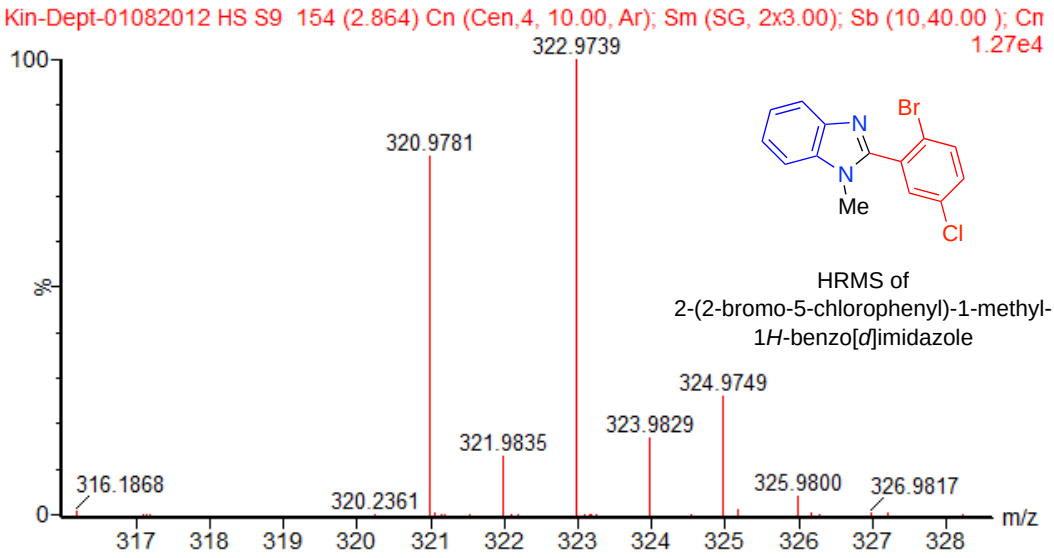
2-(2-Bromo-5-chlorophenyl)-1-methyl-1*H*-benzo[*d*]imidazole (**Table 2.3**, entry 4)



^{1}H NMR of
2-(2-bromo-5-chlorophenyl)-1-methyl-
1*H*-benzo[*d*]imidazole



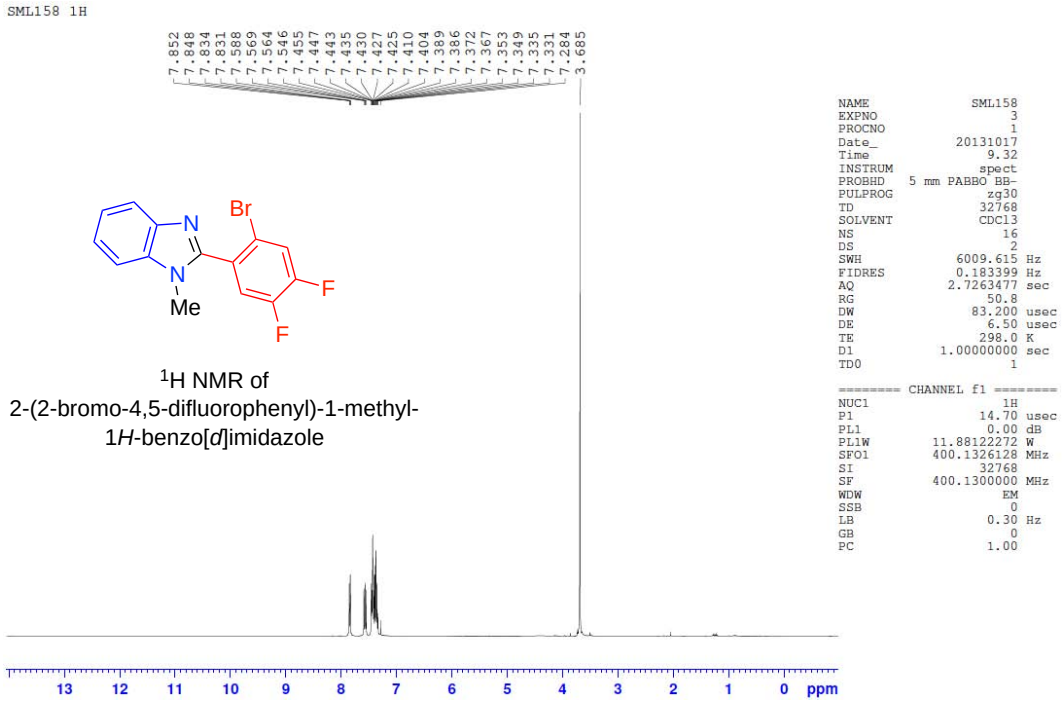
^{13}C NMR of
2-(2-bromo-5-chlorophenyl)-1-methyl-
1*H*-benzo[*d*]imidazole



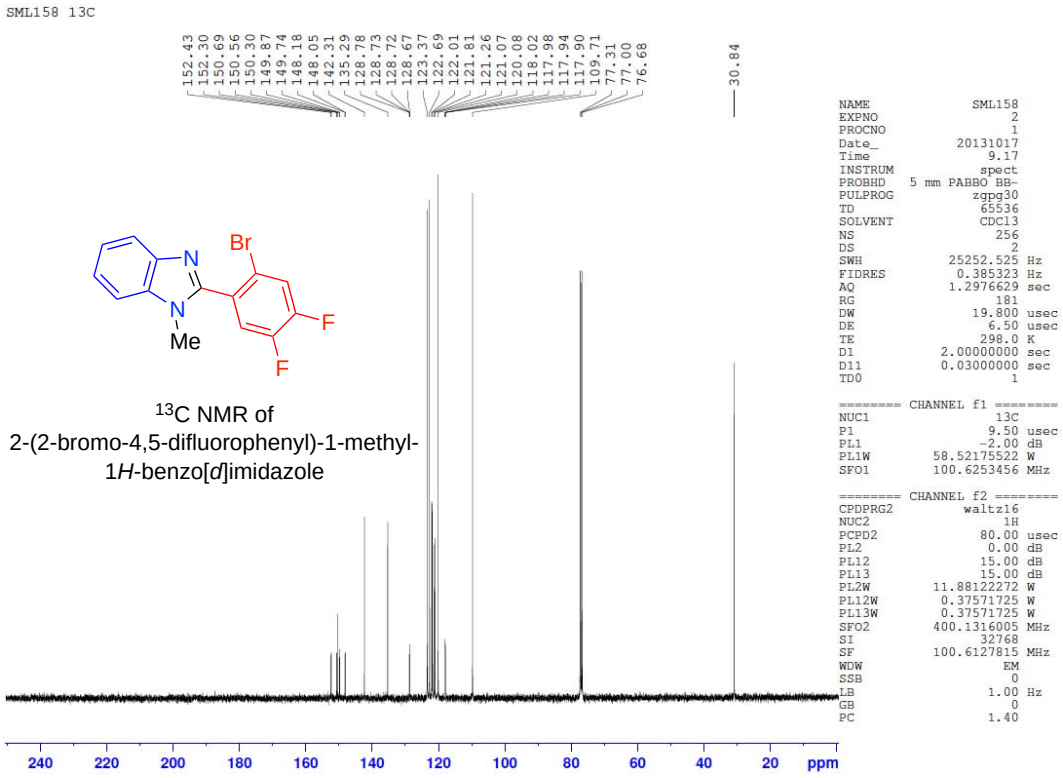
HRMS of
2-(2-bromo-5-chlorophenyl)-1-methyl-1*H*-benzo[*d*]imidazole

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
320.9781	320.9794	-1.3	-4.1	9.5	6.3	C14 H11 N2 Cl Br

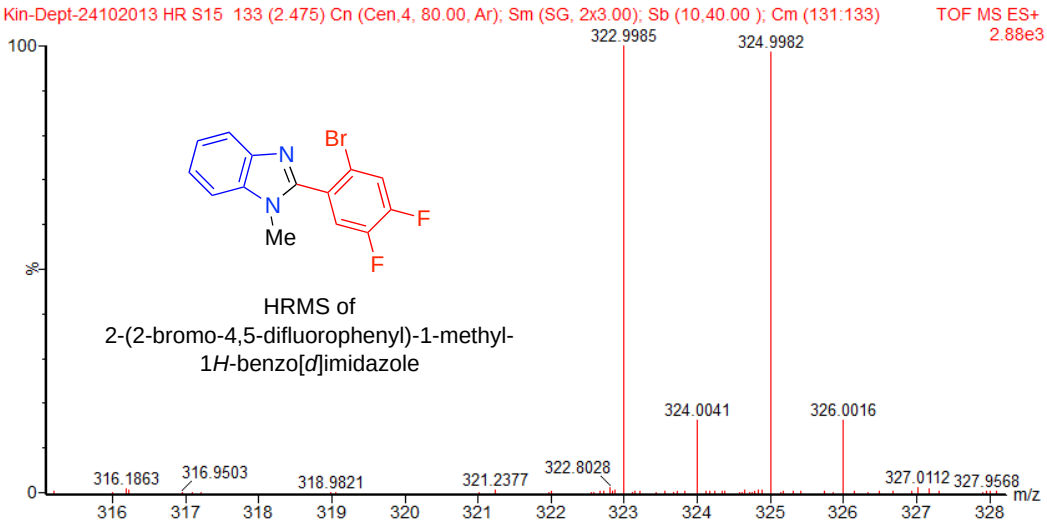
2-(2-Bromo-4,5-difluorophenyl)-1-methyl-1*H*-benzo[*d*]imidazole (**Table 2.3**, entry 5)



^{1}H NMR of 2-(2-bromo-4,5-difluorophenyl)-1-methyl-1*H*-benzo[*d*]imidazole

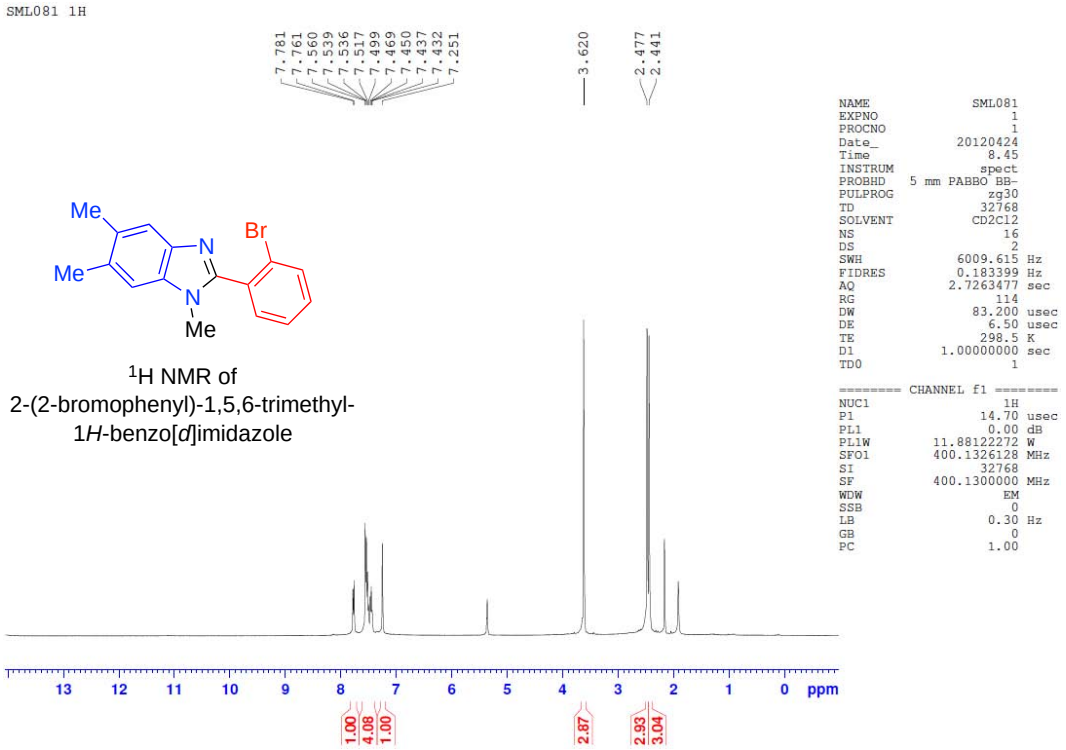


^{13}C NMR of 2-(2-bromo-4,5-difluorophenyl)-1-methyl-1*H*-benzo[*d*]imidazole

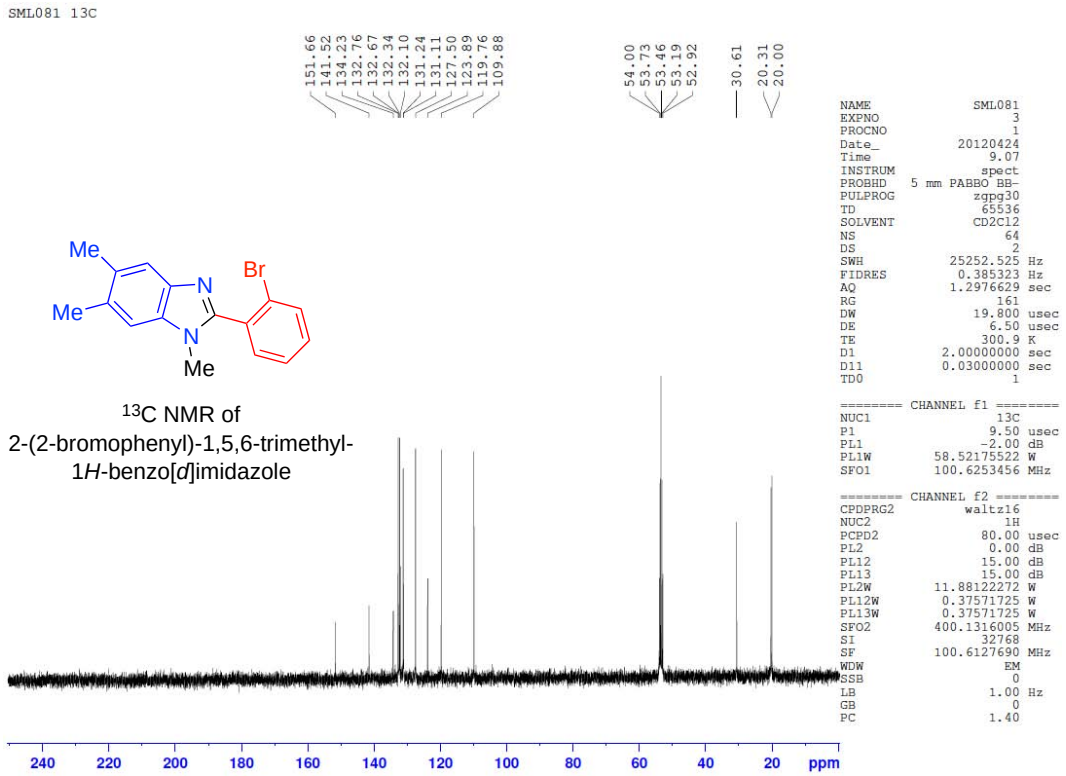


Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
322.9985	322.9995	-1.0	-3.1	9.5	0.2	C14 H10 N2 Br F2

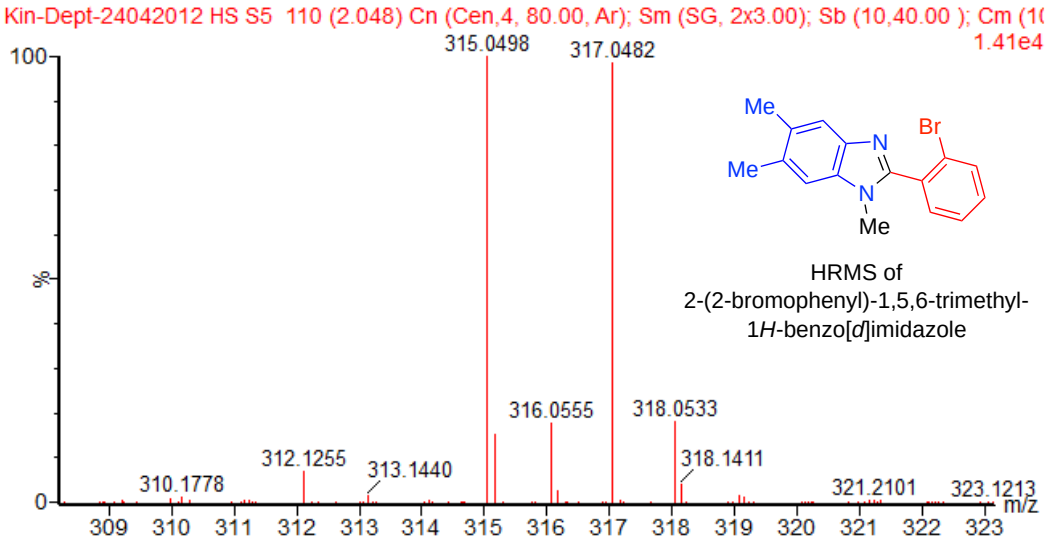
2-(2-Bromophenyl)-1,5,6-trimethyl-1*H*-benzo[*d*]imidazole (**Table 2.3**, entry 6)



^{1}H NMR of
2-(2-bromophenyl)-1,5,6-trimethyl-
1*H*-benzo[*d*]imidazole



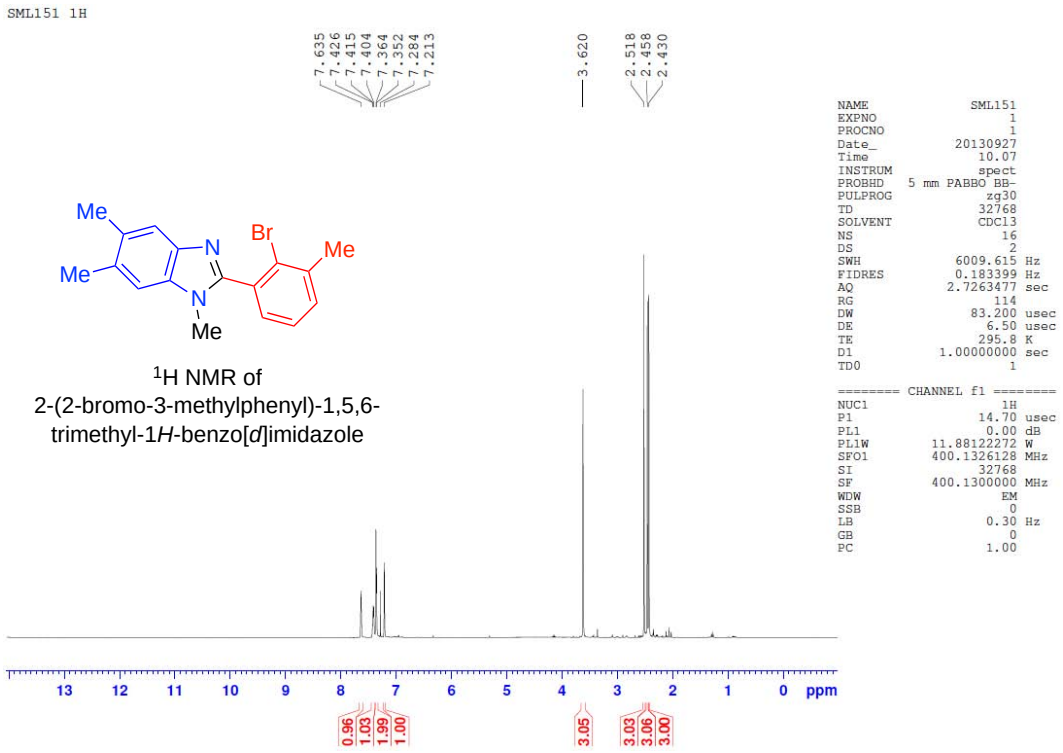
^{13}C NMR of
2-(2-bromophenyl)-1,5,6-trimethyl-
1*H*-benzo[*d*]imidazole



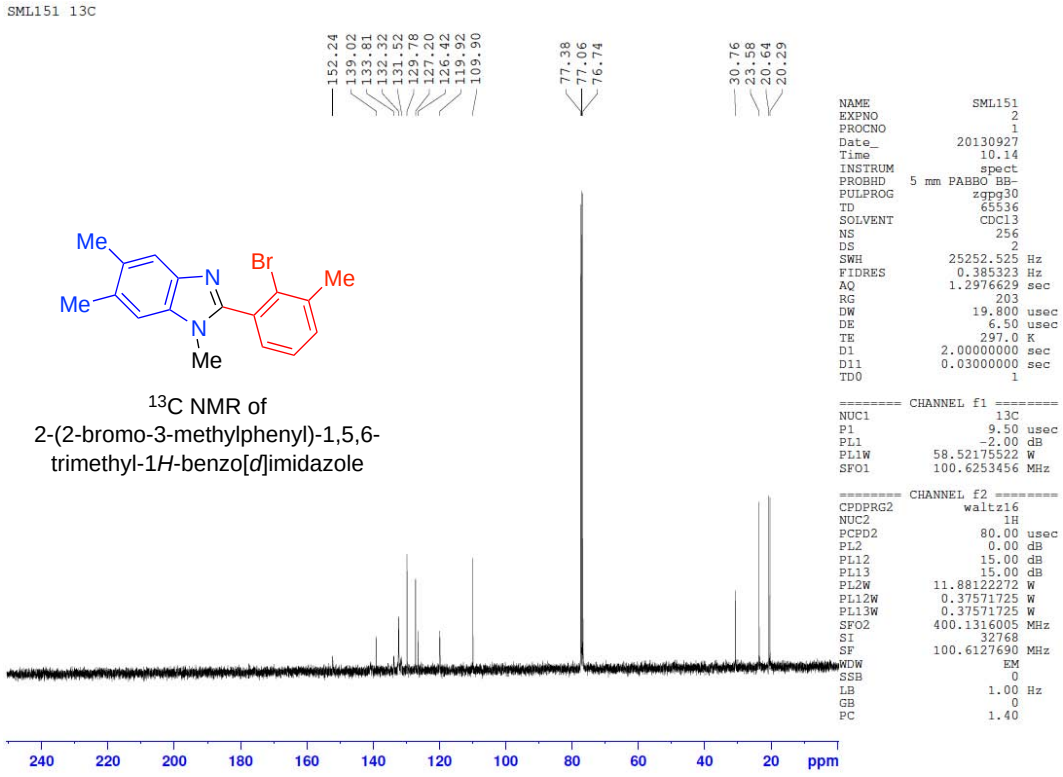
HRMS of
2-(2-bromophenyl)-1,5,6-trimethyl-
1*H*-benzo[*d*]imidazole

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
315.0498	315.0497	0.1	0.3	9.5	5.3	C16 H16 N2 Br

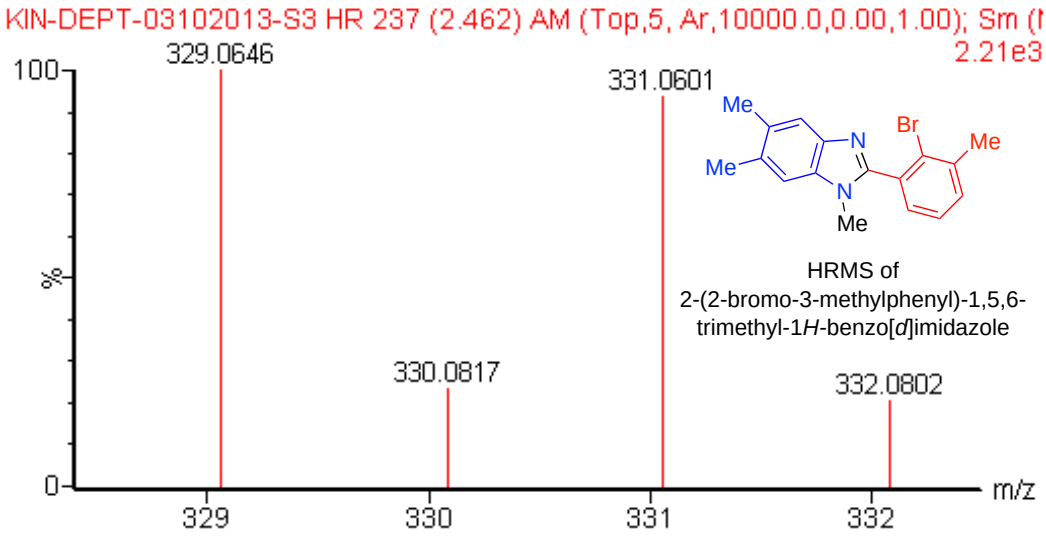
2-(2-Bromo-3-methylphenyl)-1,5,6-trimethyl-1*H*-benzo[*d*]imidazole (**Table 2.3**, entry 7)



^{1}H NMR of
2-(2-bromo-3-methylphenyl)-1,5,6-trimethyl-1*H*-benzo[*d*]imidazole



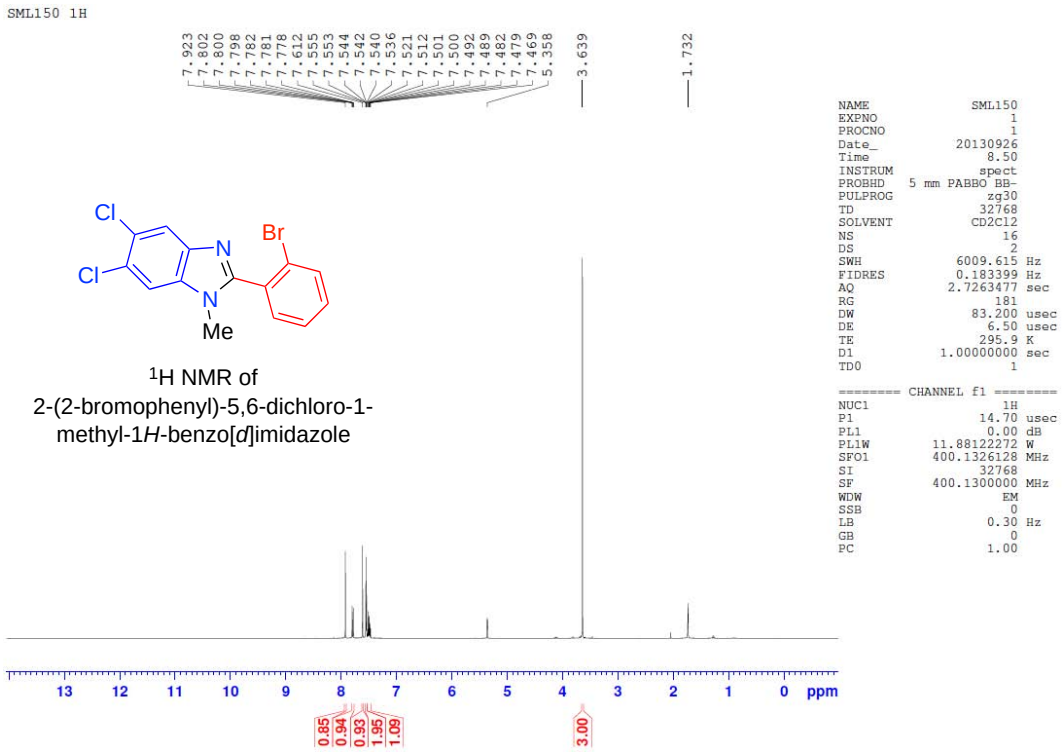
^{13}C NMR of
2-(2-bromo-3-methylphenyl)-1,5,6-trimethyl-1*H*-benzo[*d*]imidazole



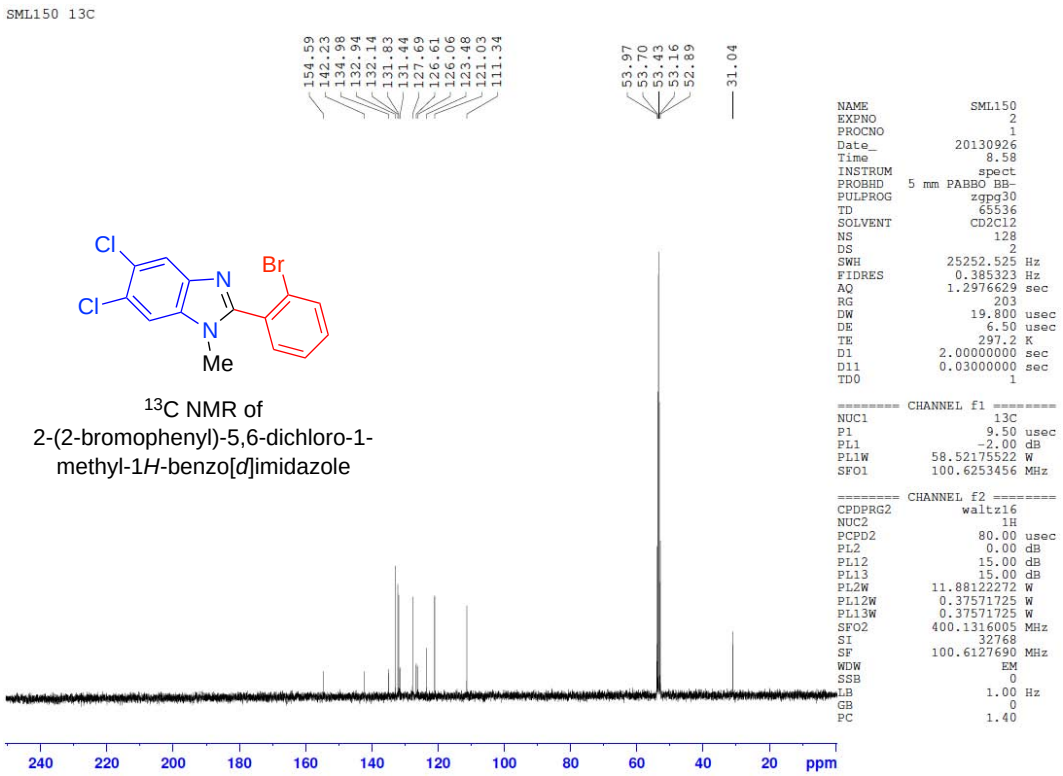
HRMS of
2-(2-bromo-3-methylphenyl)-1,5,6-trimethyl-1*H*-benzo[*d*]imidazole

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
329.0646	329.0653	-0.7	-2.1	9.5	11.5	C17 H18 N2 Br

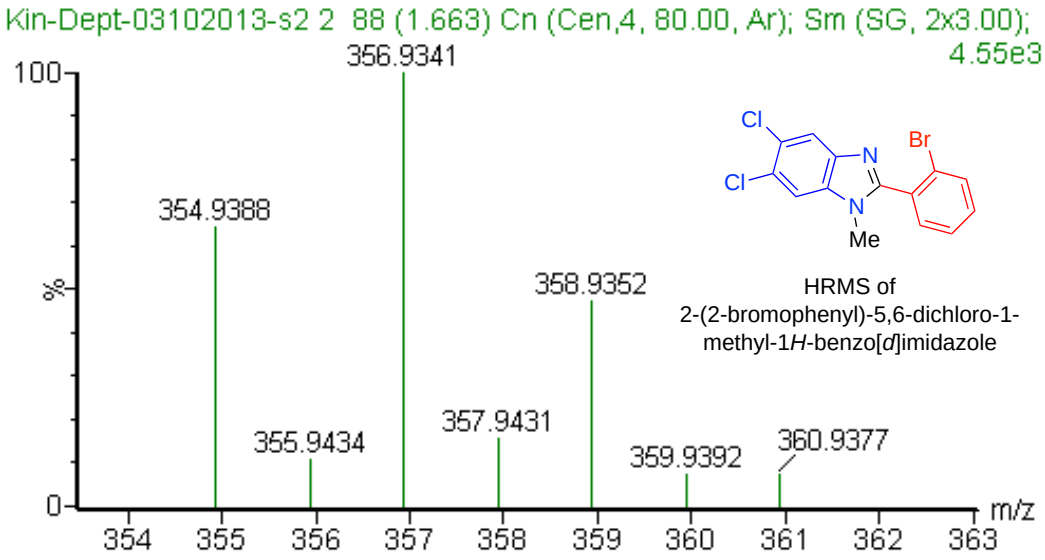
2-(2-Bromophenyl)-5,6-dichloro-1-methyl-1*H*-benzo[*d*]imidazole (**Table 2.3**, entry 8)



^{1}H NMR of 2-(2-bromophenyl)-5,6-dichloro-1-methyl-1*H*-benzo[*d*]imidazole



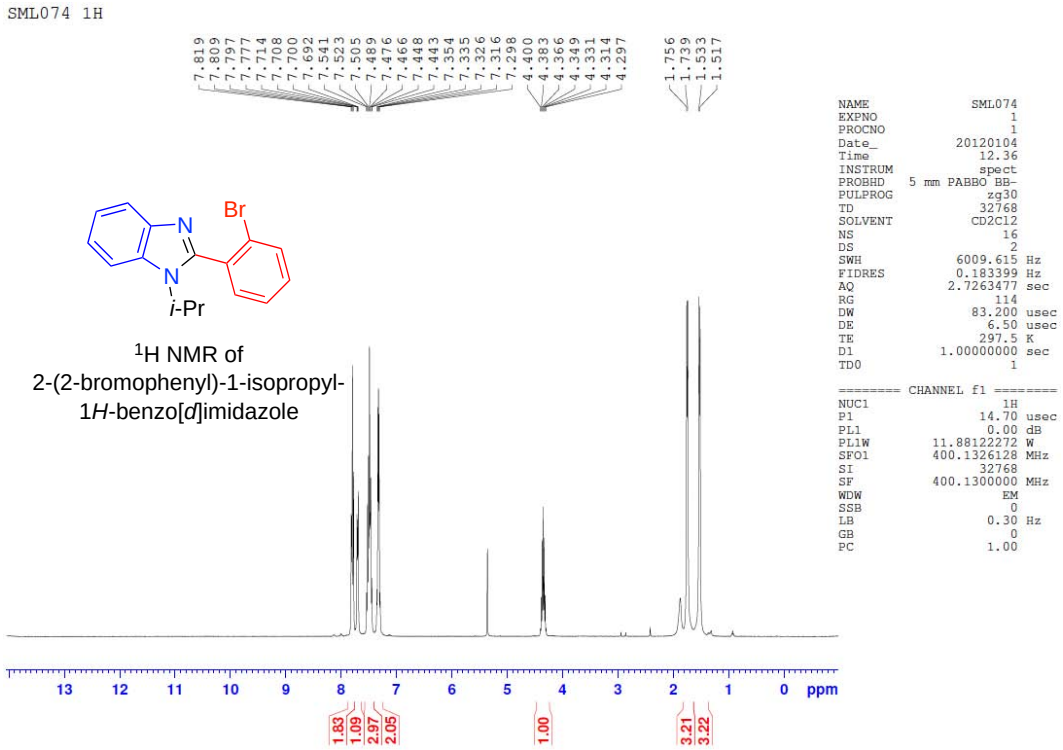
^{13}C NMR of 2-(2-bromophenyl)-5,6-dichloro-1-methyl-1*H*-benzo[*d*]imidazole



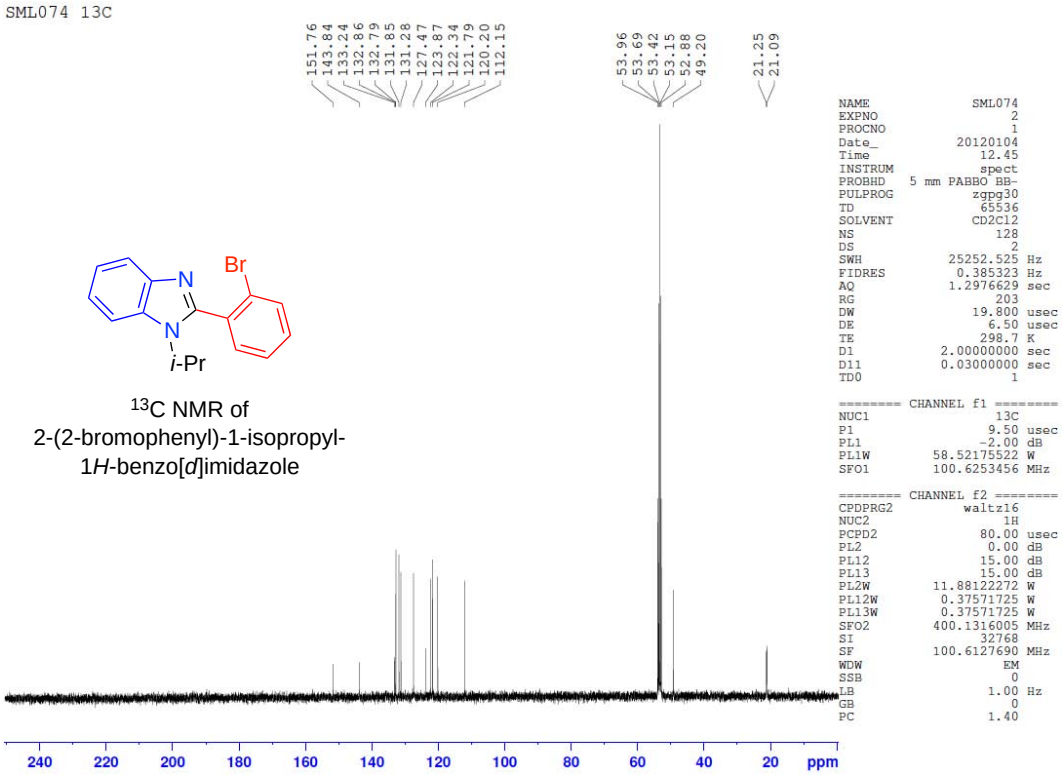
HRMS of
2-(2-bromophenyl)-5,6-dichloro-1-methyl-1*H*-benzo[*d*]imidazole

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
354.9388	354.9404	-1.6	-4.5	9.5	3.5	C14 H10 N2 Cl2 Br

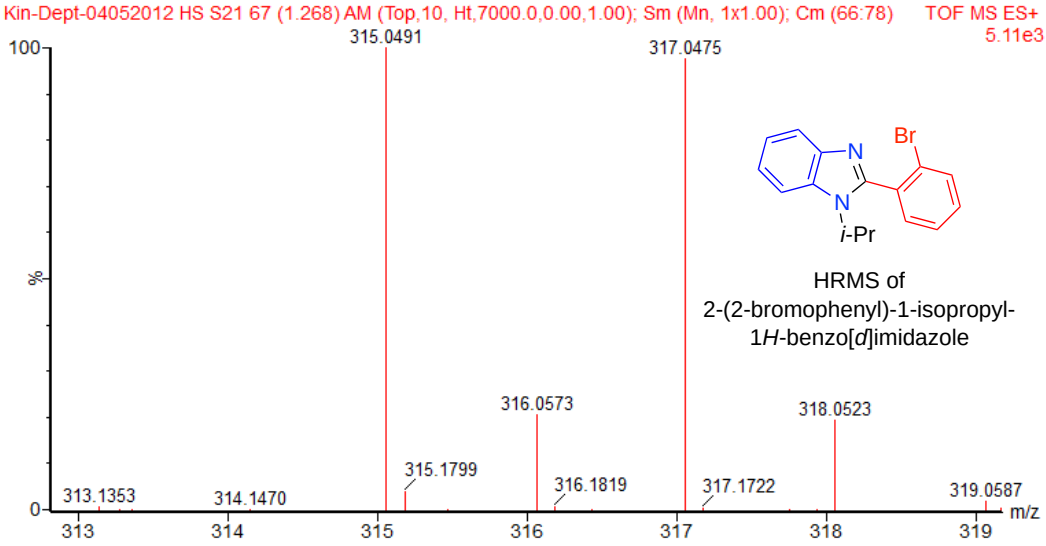
2-(2-Bromophenyl)-1-isopropyl-1*H*-benzo[*d*]imidazole (**Table 2.4**, entry 1)



^{1}H NMR of
2-(2-bromophenyl)-1-isopropyl-
1*H*-benzo[*d*]imidazole



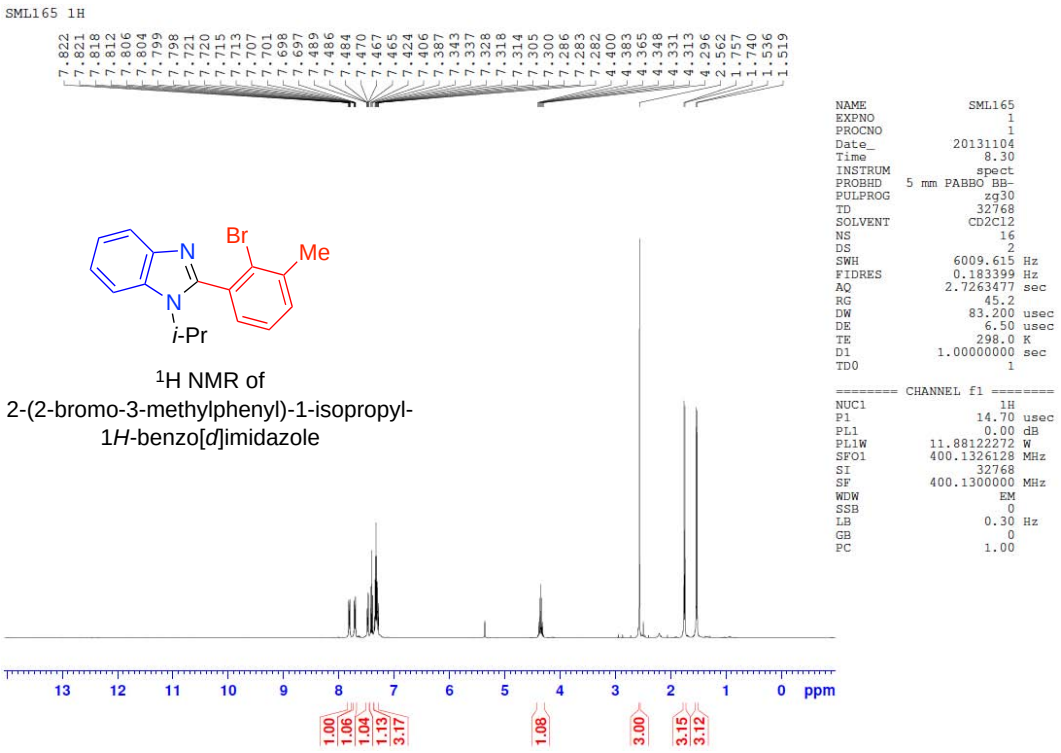
^{13}C NMR of
2-(2-bromophenyl)-1-isopropyl-
1*H*-benzo[*d*]imidazole



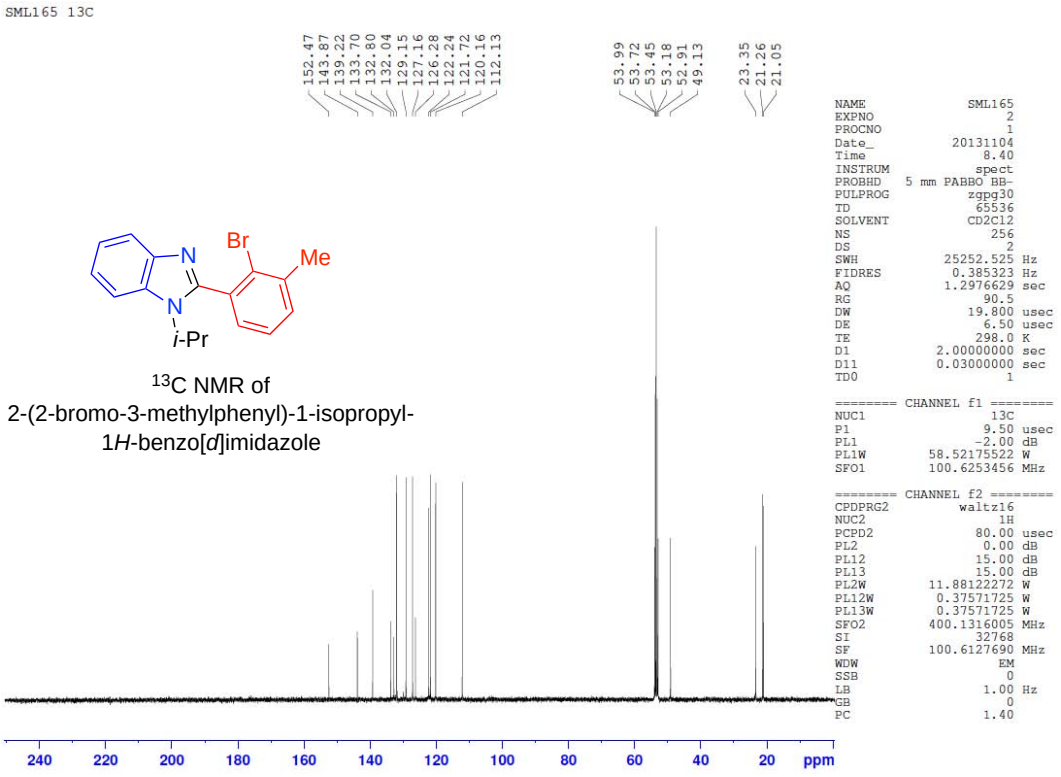
HRMS of
2-(2-bromophenyl)-1-isopropyl-
1*H*-benzo[*d*]imidazole

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
315.0491	315.0497	-0.6	-1.9	9.5	5.4	C16 H16 N2 Br

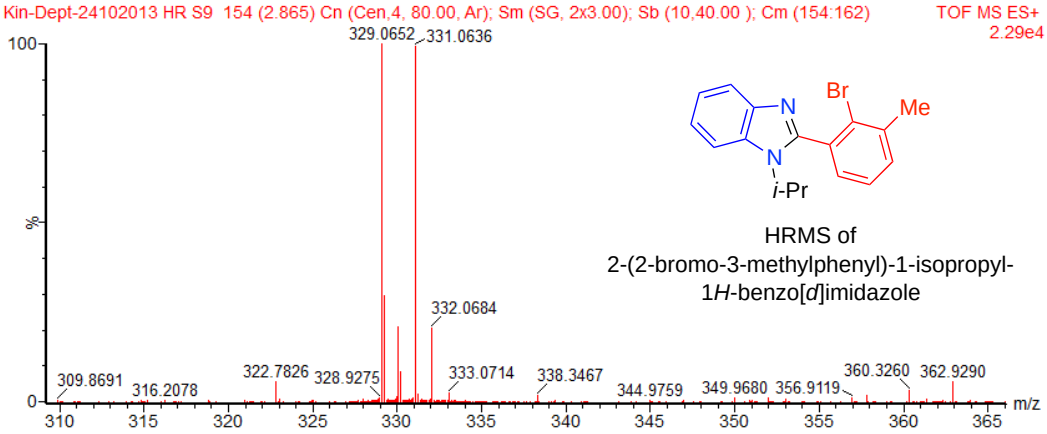
2-(2-Bromo-3-methylphenyl)-1-isopropyl-1*H*-benzo[*d*]imidazole (**Table 2.4**, entry 2)



^{1}H NMR of 2-(2-bromo-3-methylphenyl)-1-isopropyl-1*H*-benzo[*d*]imidazole



^{13}C NMR of 2-(2-bromo-3-methylphenyl)-1-isopropyl-1*H*-benzo[*d*]imidazole

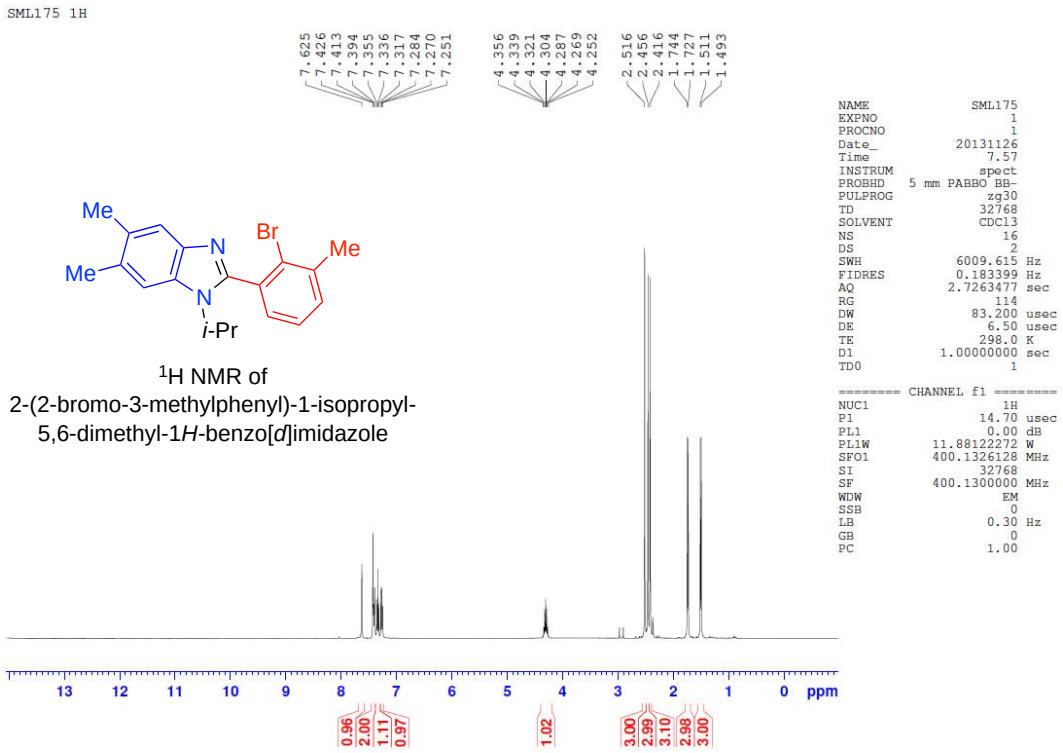


HRMS of
2-(2-bromo-3-methylphenyl)-1-isopropyl-
1*H*-benzo[*d*]imidazole

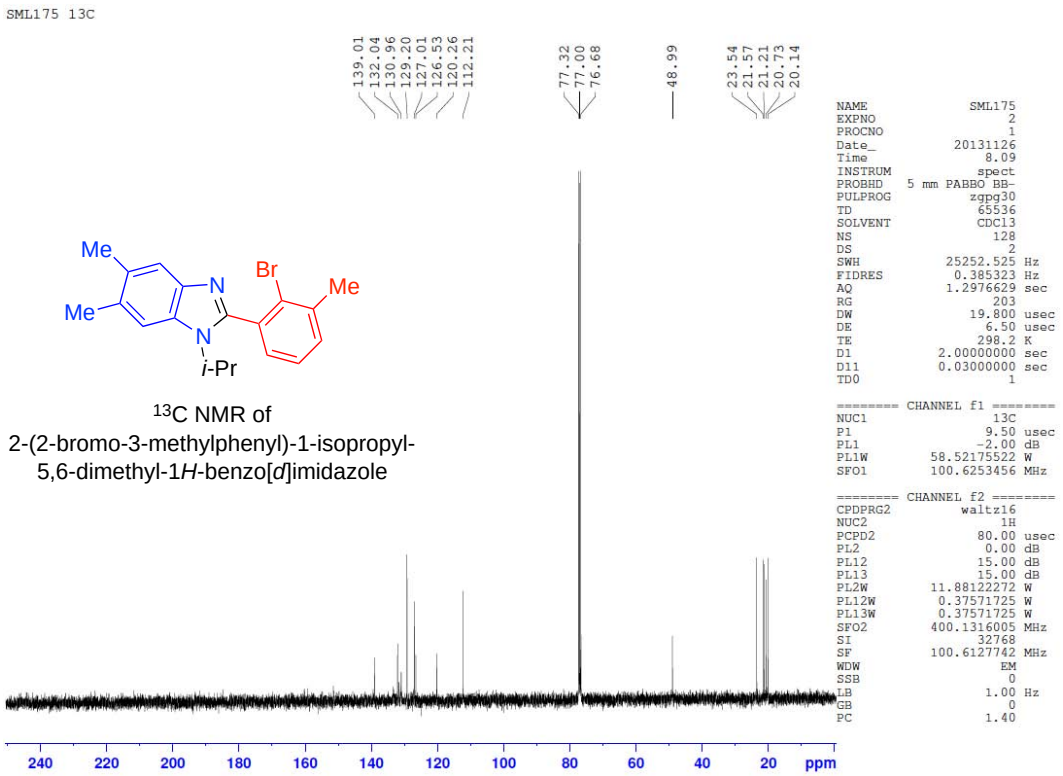
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
329.0652	329.0653	-0.1	-0.3	9.5	6.0	C17 H18 N2 Br

2-(2-Bromo-3-methylphenyl)-1-isopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole

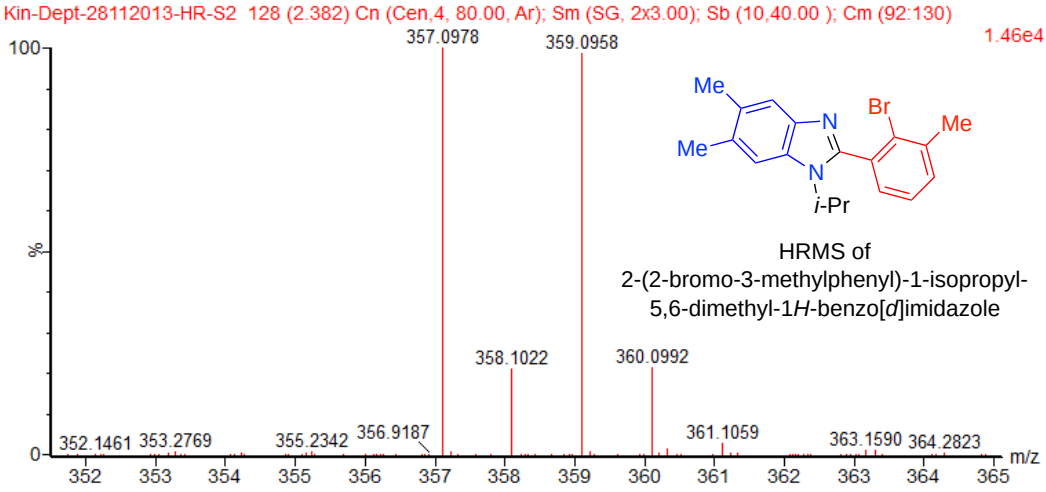
(**Table 2.4**, entry 3)



^{1}H NMR of
2-(2-bromo-3-methylphenyl)-1-isopropyl-
5,6-dimethyl-1*H*-benzo[*d*]imidazole



^{13}C NMR of
2-(2-bromo-3-methylphenyl)-1-isopropyl-
5,6-dimethyl-1*H*-benzo[*d*]imidazole

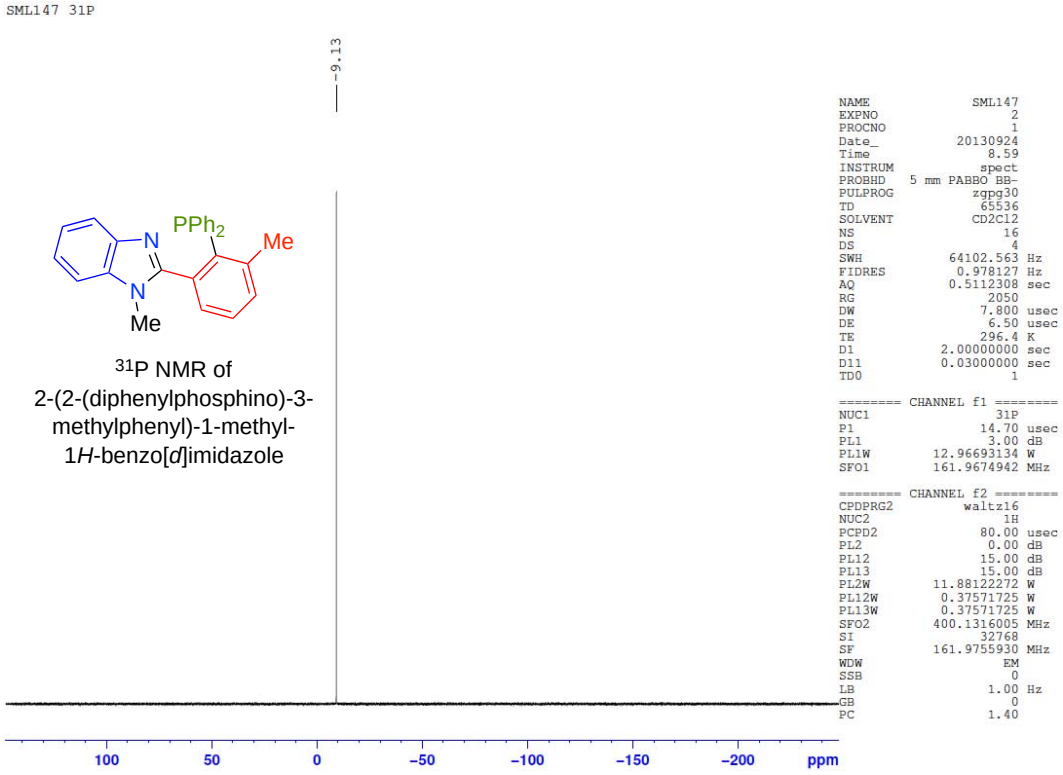


HRMS of
2-(2-bromo-3-methylphenyl)-1-isopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole

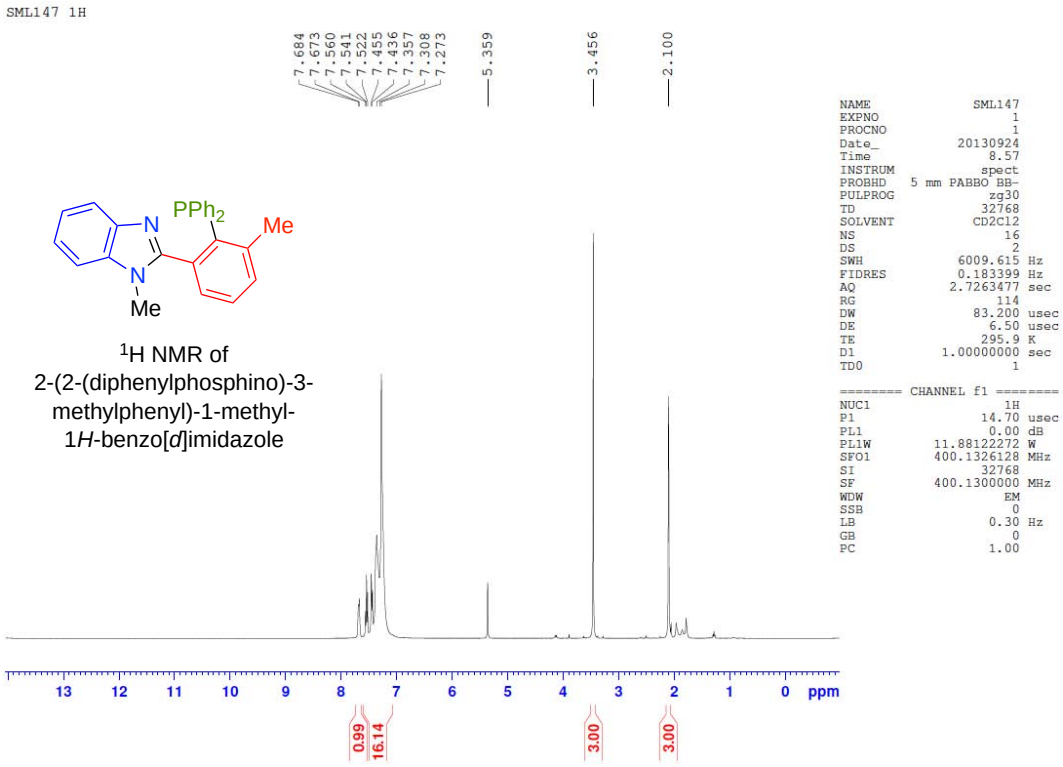
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
357.0978	357.0966	1.2	3.4	9.5	6.3	C19 H22 N2 Br

Chapter 2 HMR and HRMS Spectra of 2-Arylated Benzimidazolyl Phosphine Ligands

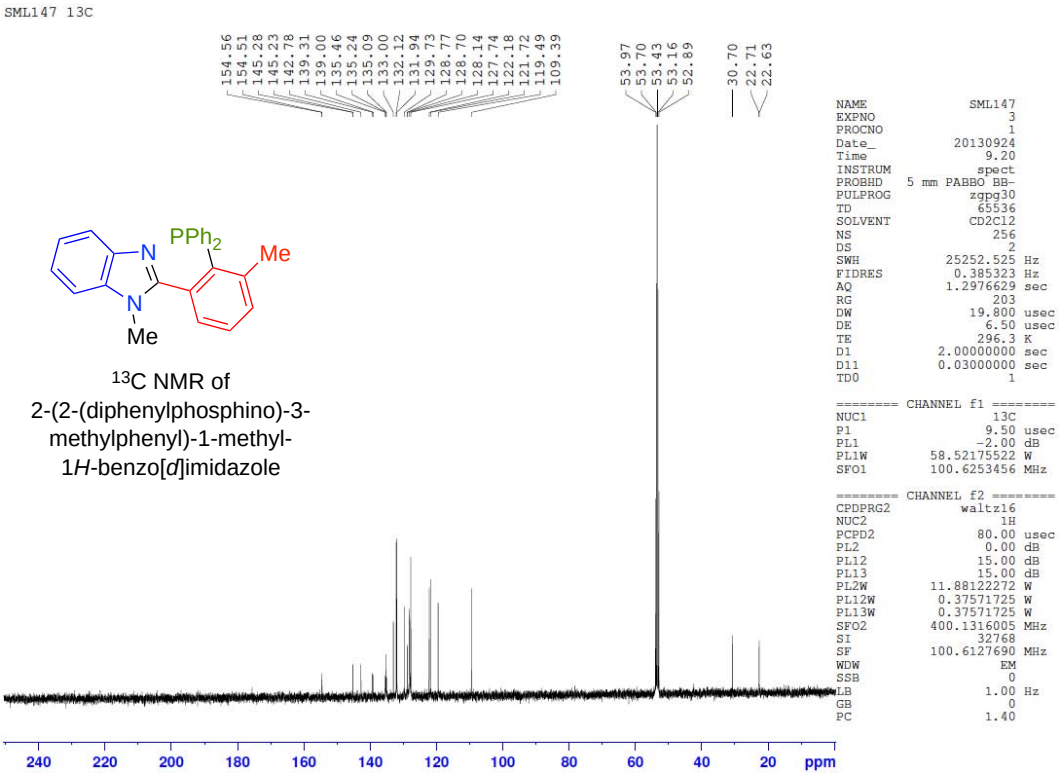
2-(2-(Diphenylphosphino)-3-methylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole (PPh *m*-TolMezole-phos **L1d**) (**Table 2.5**, entry 4)



^{31}P NMR of 2-(2-(diphenylphosphino)-3-methylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole



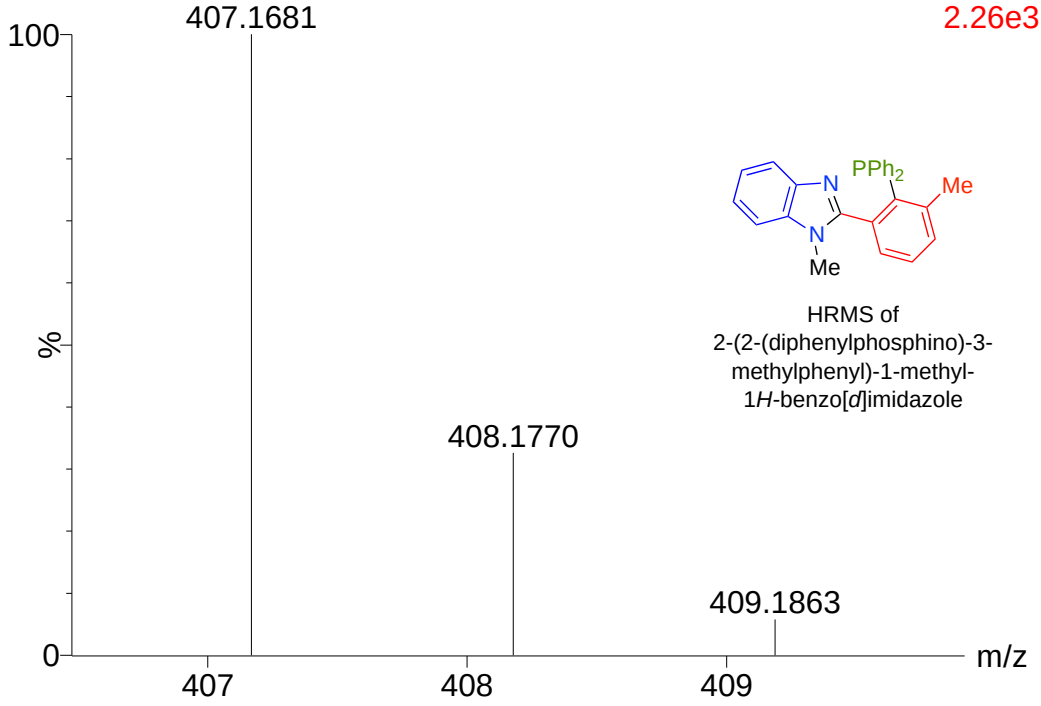
^{1}H NMR of 2-(2-(diphenylphosphino)-3-methylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole



^{13}C NMR of
2-(2-(diphenylphosphino)-3-methylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole

KIN-DEPT-25092013-S5 HR 83 (0.848)

TOF MS ES+
2.26e3

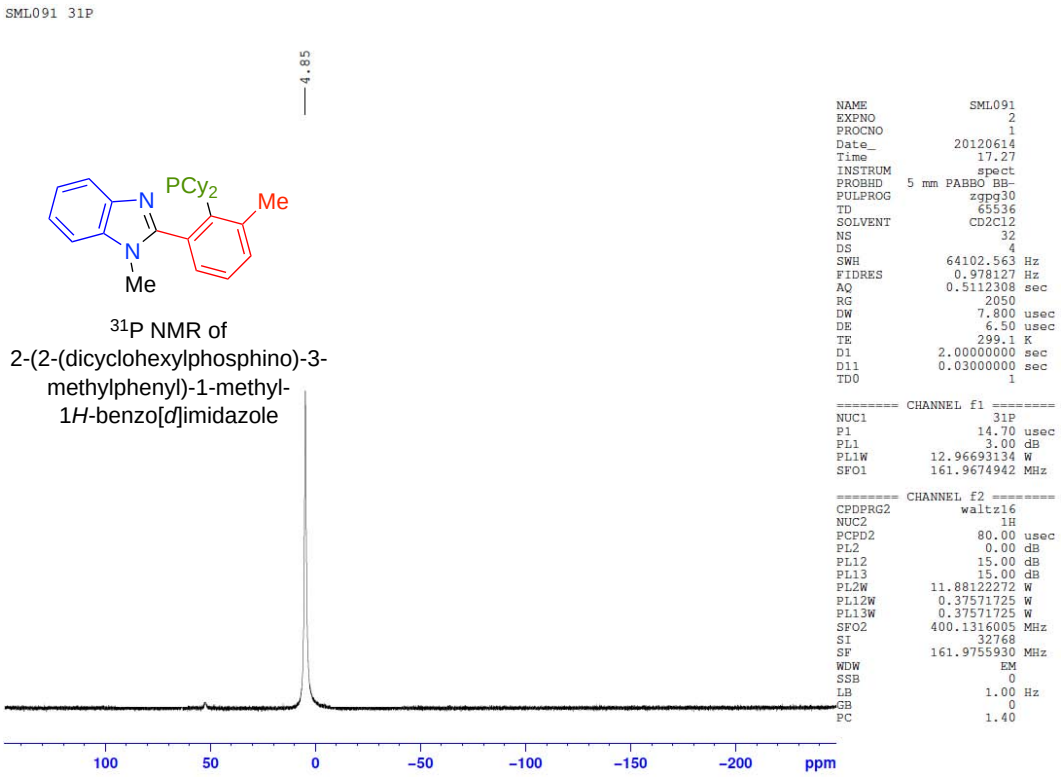


HRMS of
2-(2-(diphenylphosphino)-3-methylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole

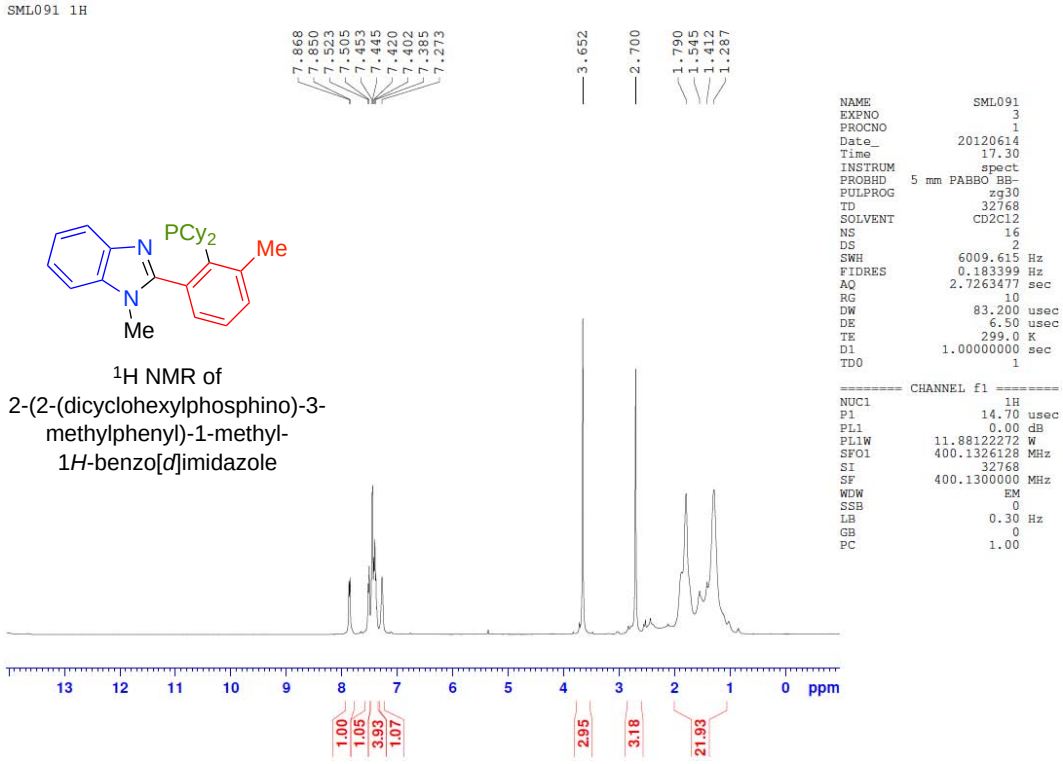
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
407.1681	407.1677	0.4	1.0	17.5	3.3	C27 H24 N2 P

2-(2-(Dicyclohexylphosphino)-3-methylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole

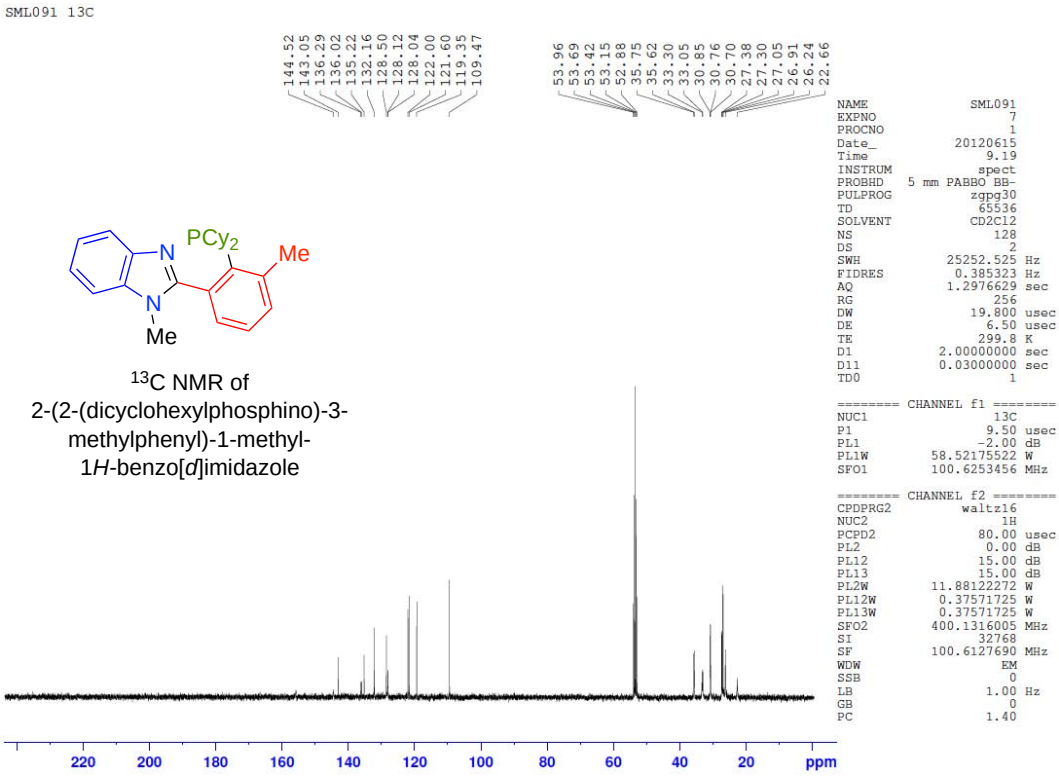
(PCy *m*-TolMezole-phos **L1e**) (**Table 2.5**, entry 5)



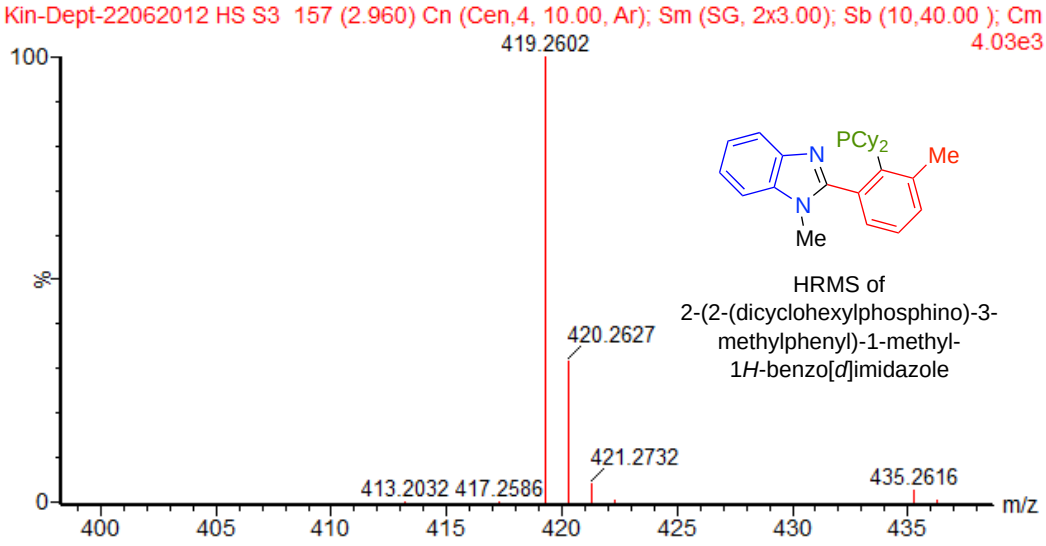
^{31}P NMR of 2-(2-(dicyclohexylphosphino)-3-methylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole



^{1}H NMR of 2-(2-(dicyclohexylphosphino)-3-methylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole



^{13}C NMR of
2-(2-(dicyclohexylphosphino)-3-methylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole

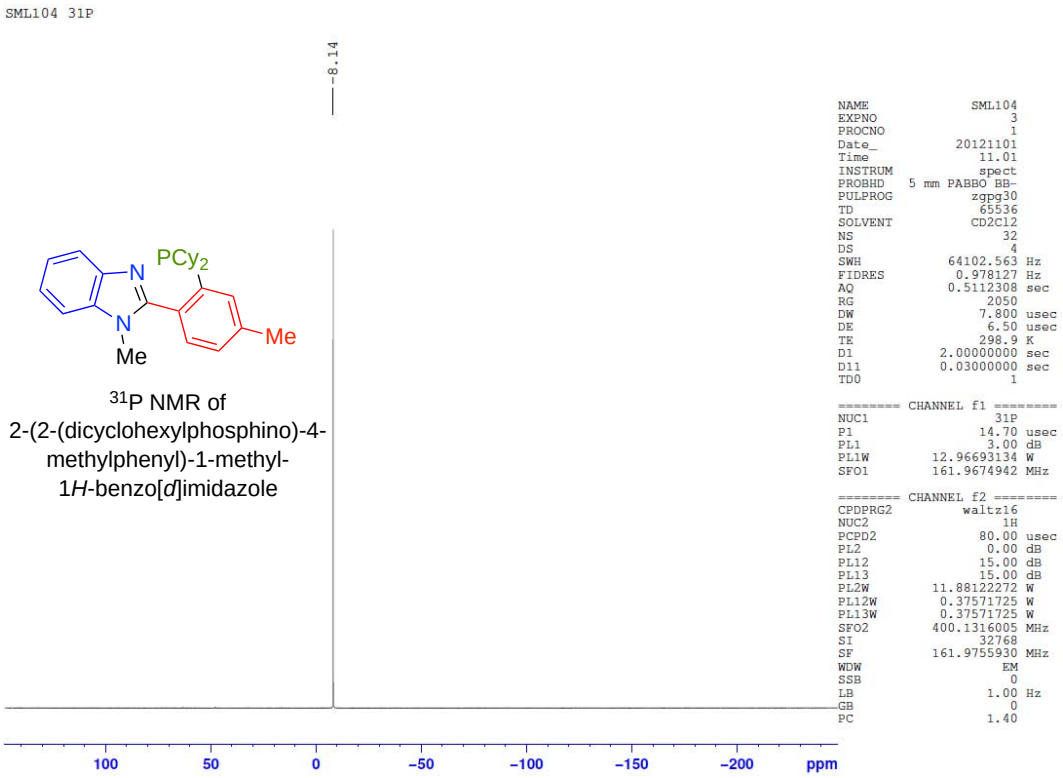


HRMS of
2-(2-(dicyclohexylphosphino)-3-methylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole

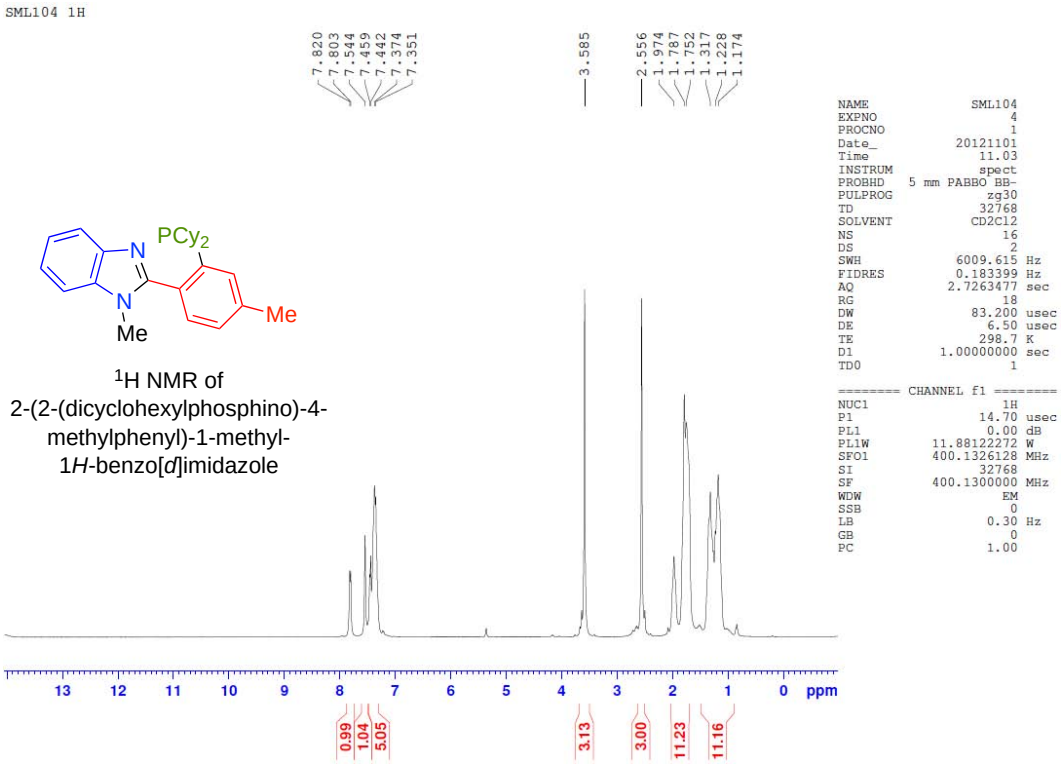
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
419.2602	419.2616	-1.4	-3.3	11.5	2.6	C27 H36 N2 P

2-(2-(Dicyclohexylphosphino)-4-methylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole

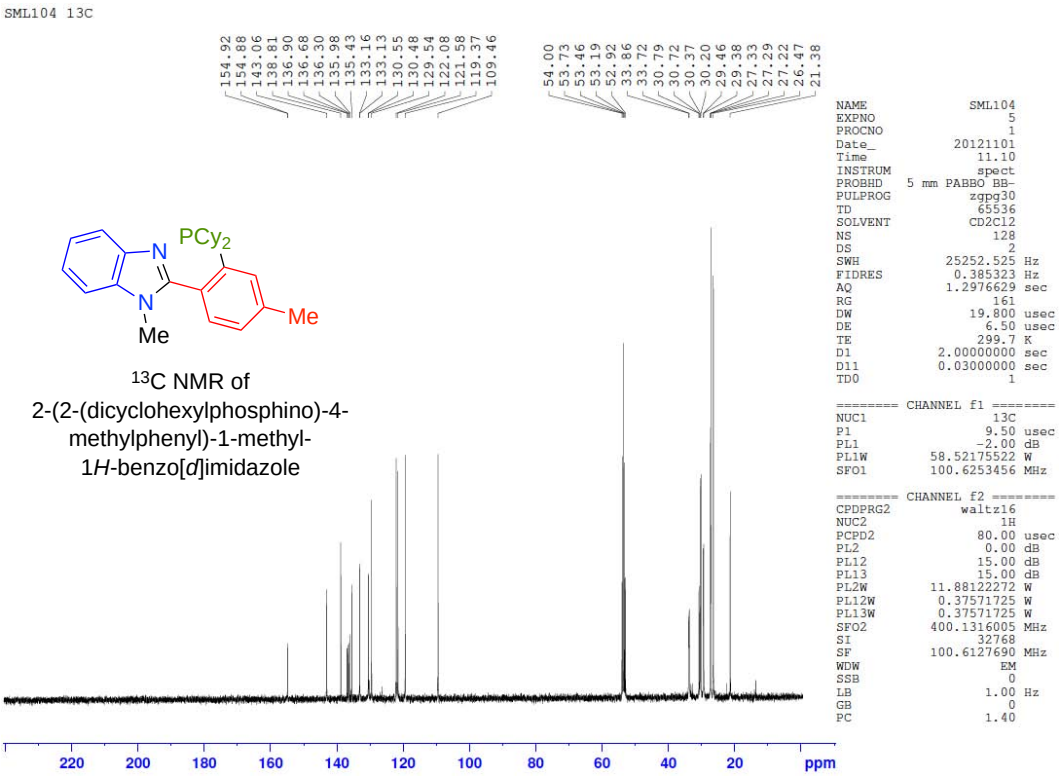
(PCy *p*-TolMezole-phos **L1f**) (**Table 2.5**, entry 6)



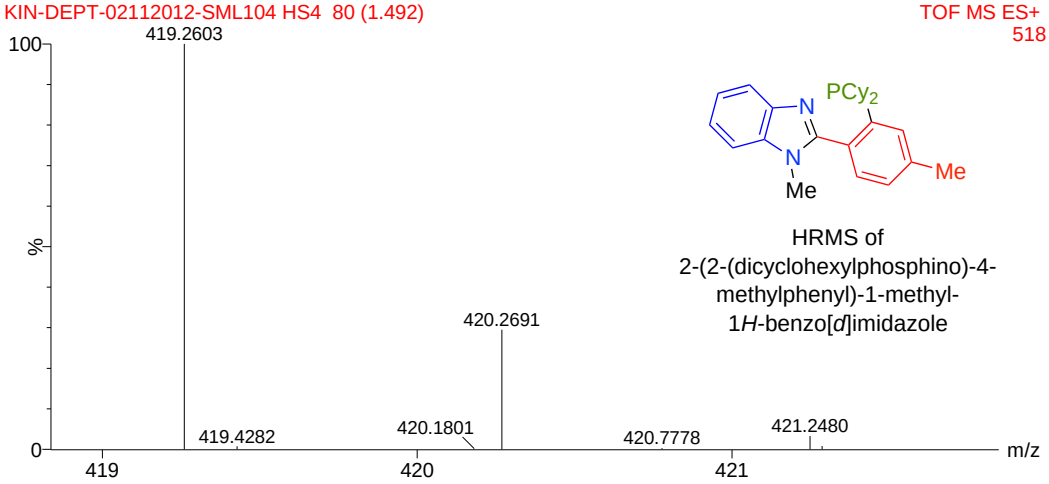
^{31}P NMR of 2-(2-(dicyclohexylphosphino)-4-methylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole



^{1}H NMR of 2-(2-(dicyclohexylphosphino)-4-methylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole



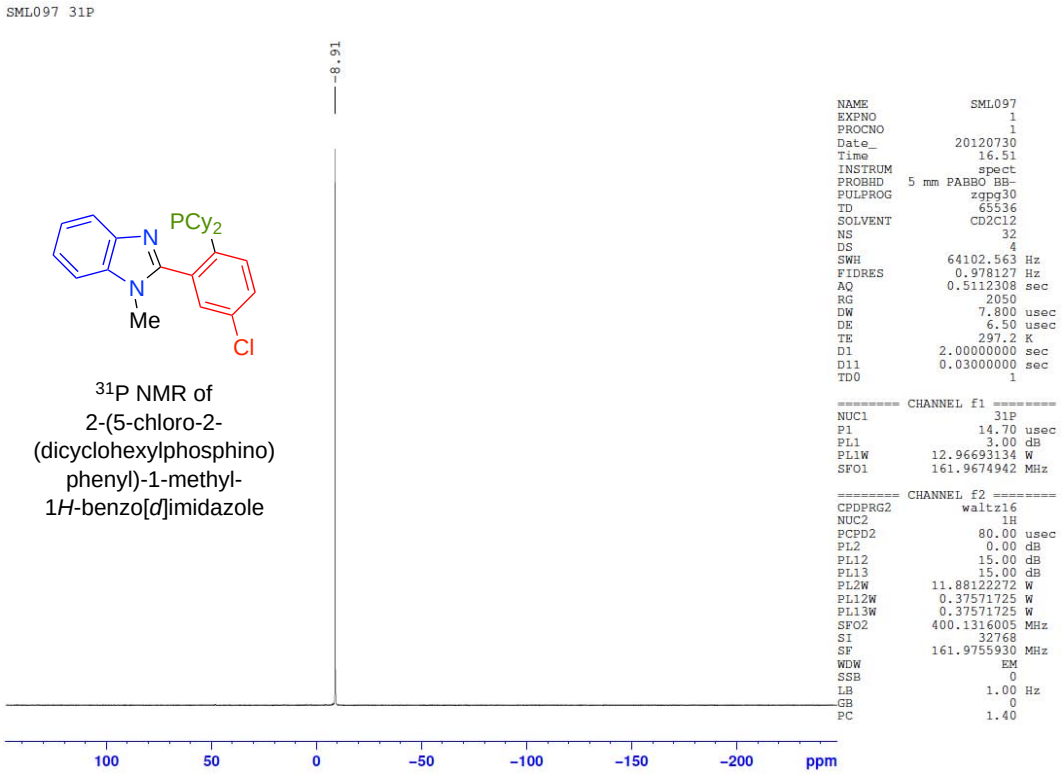
^{13}C NMR of
2-(2-(dicyclohexylphosphino)-4-methylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole



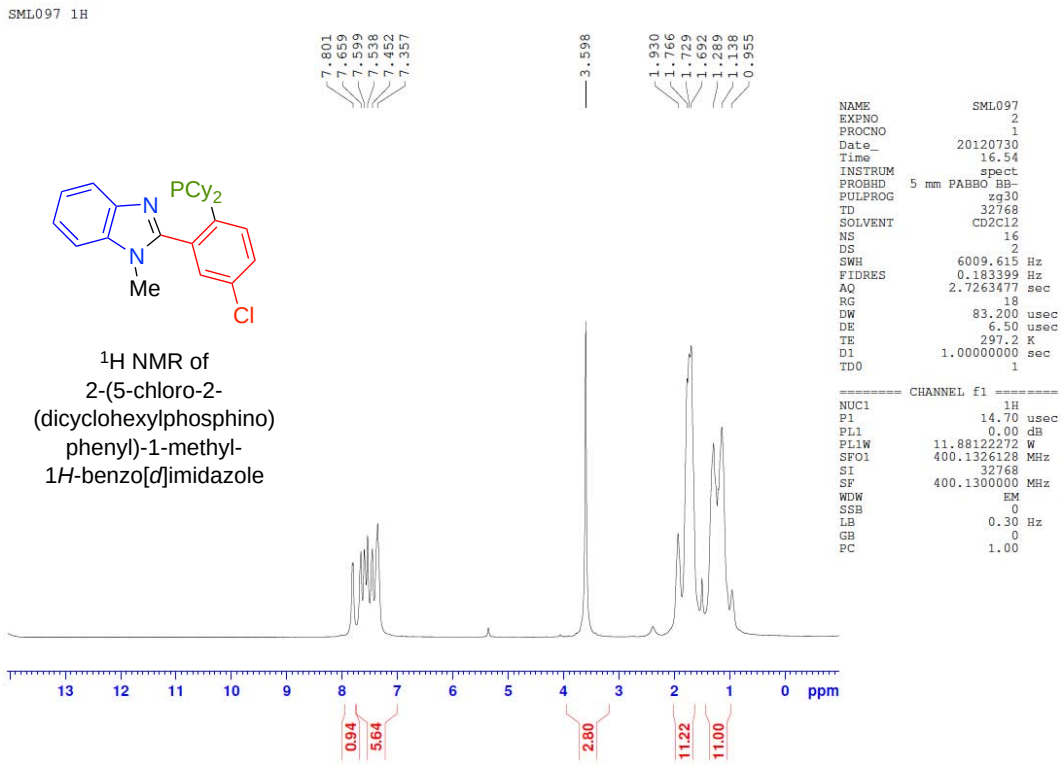
HRMS of
2-(2-(dicyclohexylphosphino)-4-methylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
419.2603	419.2616	-1.3	-3.1	11.5	2.0	C27 H36 N2 P

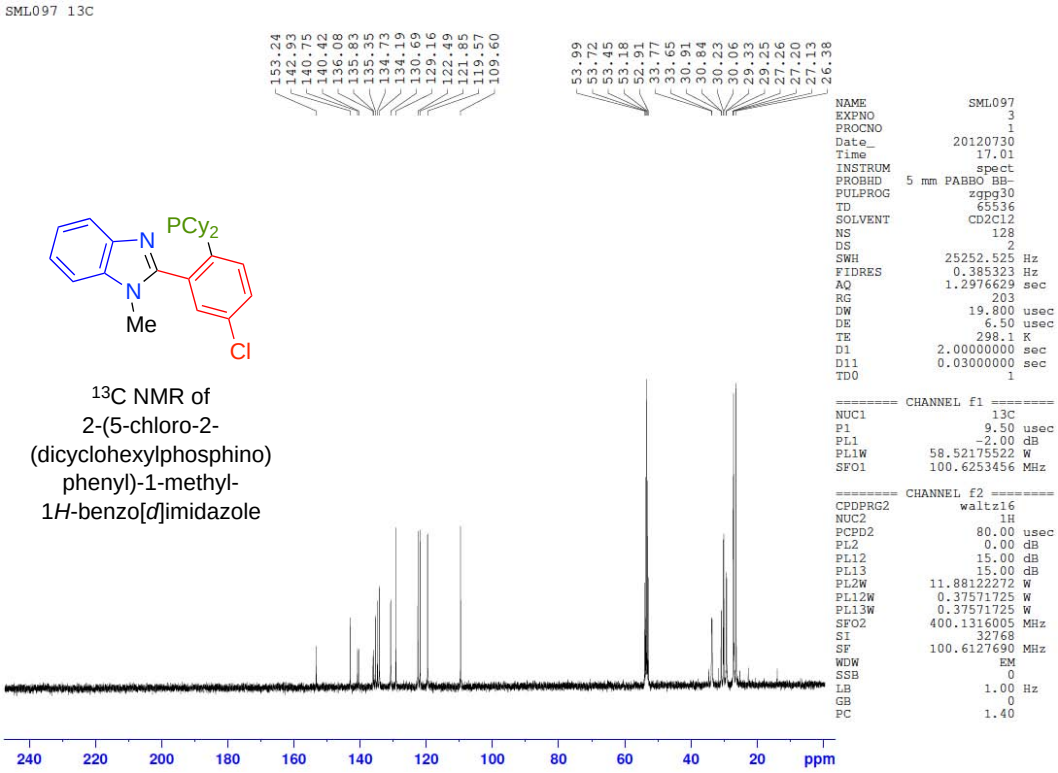
2-(5-Chloro-2-(dicyclohexylphosphino)phenyl)-1-methyl-1*H*-benzo[*d*]imidazole (PCy 5-ClPhMezole-phos **L1g**) (**Table 2.5**, entry 7)

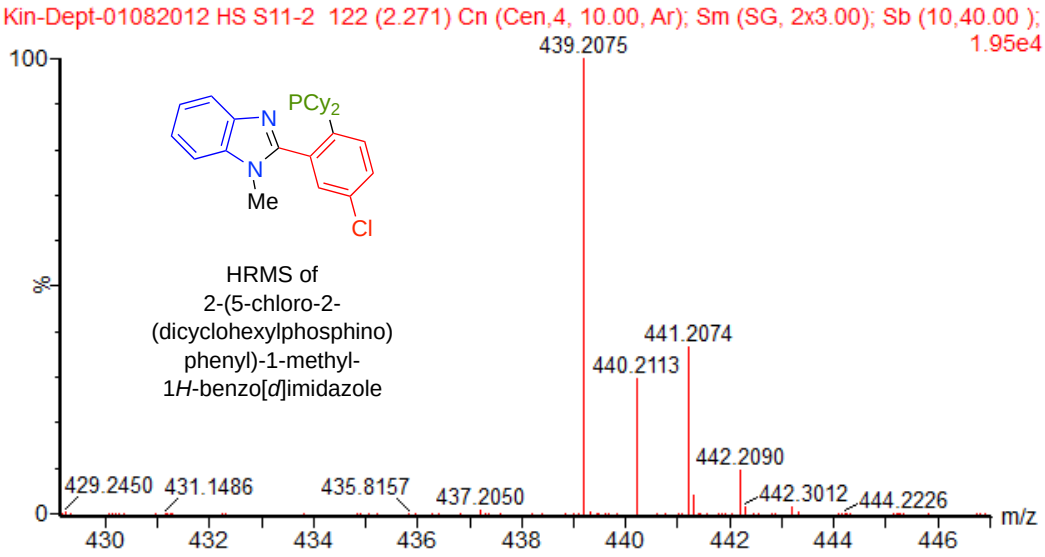


^{31}P NMR of 2-(5-chloro-2-(dicyclohexylphosphino) phenyl)-1-methyl-1*H*-benzo[*d*]imidazole



^{1}H NMR of 2-(5-chloro-2-(dicyclohexylphosphino) phenyl)-1-methyl-1*H*-benzo[*d*]imidazole

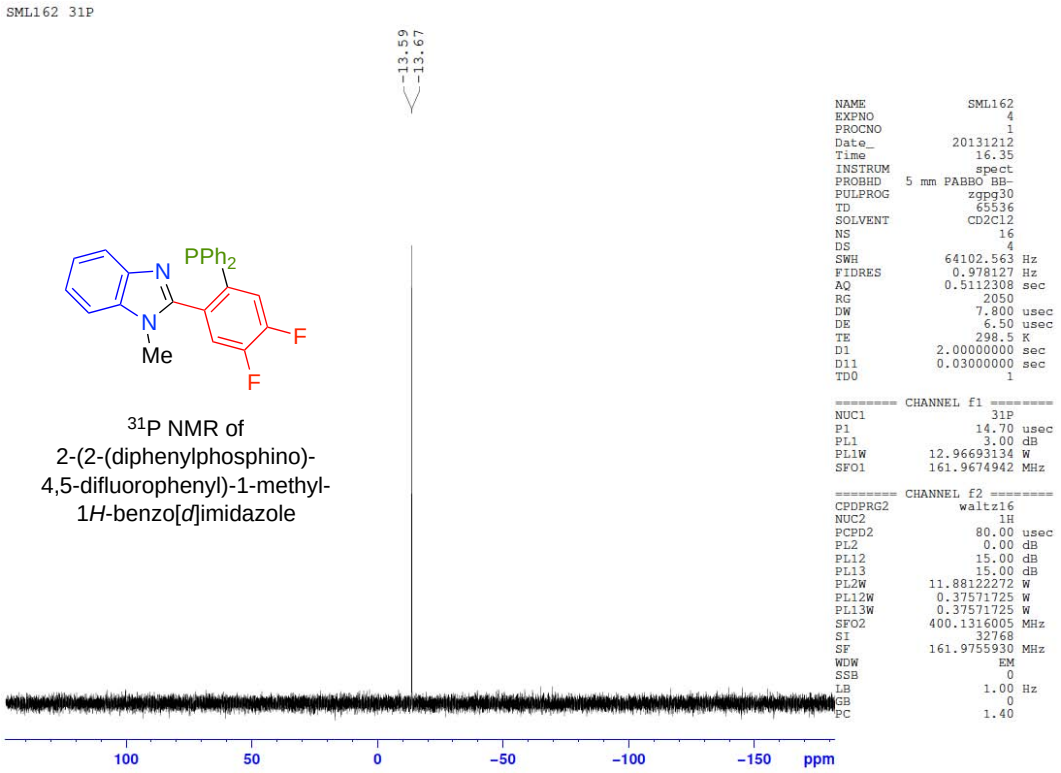




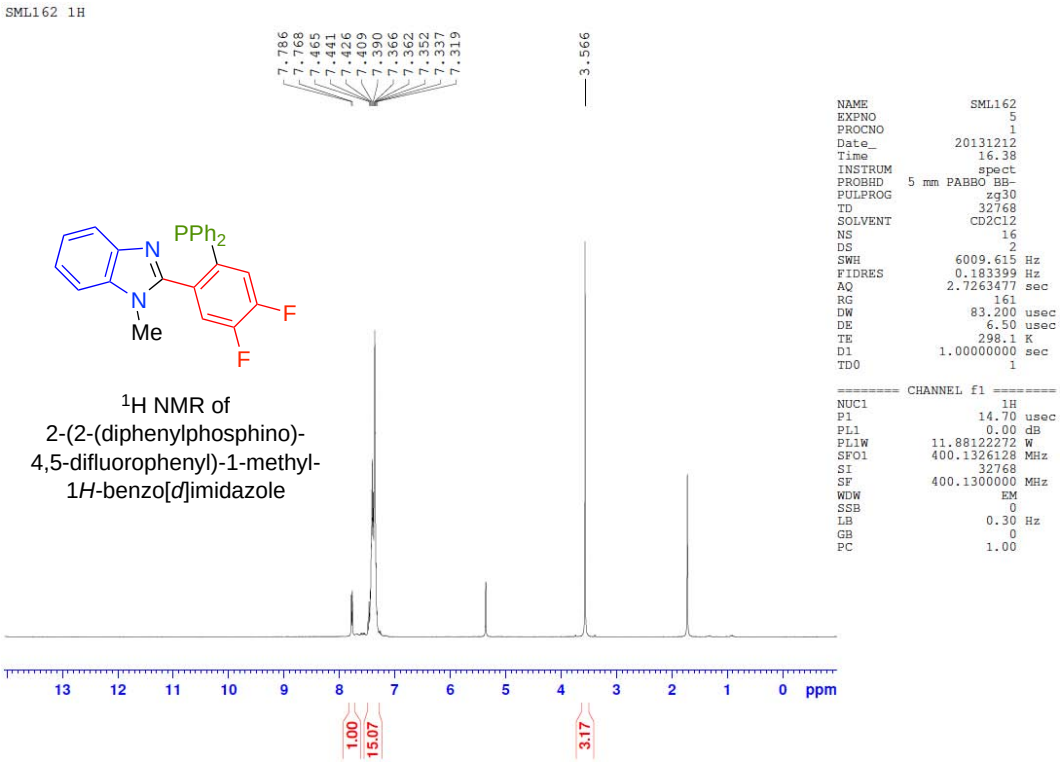
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
439.2075	439.2070	0.5	1.1	11.5	2.0	C26 H33 N2 P Cl

2-(2-(Diphenylphosphino)-4,5-difluorophenyl)-1-methyl-1*H*-benzo[*d*]imidazole

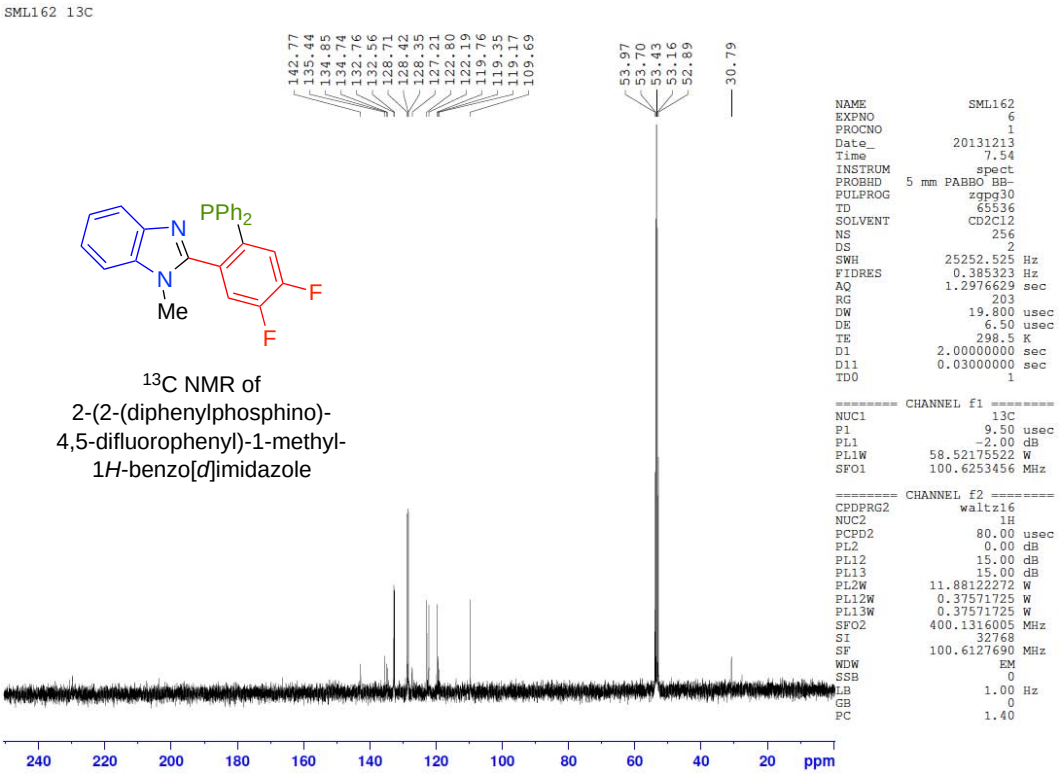
(PPh 4,5-F_2PhMezole-phos **L1h**) (**Table 2.5**, entry 8)



^{31}P NMR of 2-(2-(diphenylphosphino)-4,5-difluorophenyl)-1-methyl-1*H*-benzo[*d*]imidazole



^{1}H NMR of 2-(2-(diphenylphosphino)-4,5-difluorophenyl)-1-methyl-1*H*-benzo[*d*]imidazole



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PL12 15.00 dB
PL13 15.00 dB
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PL13W 0.37571725 W
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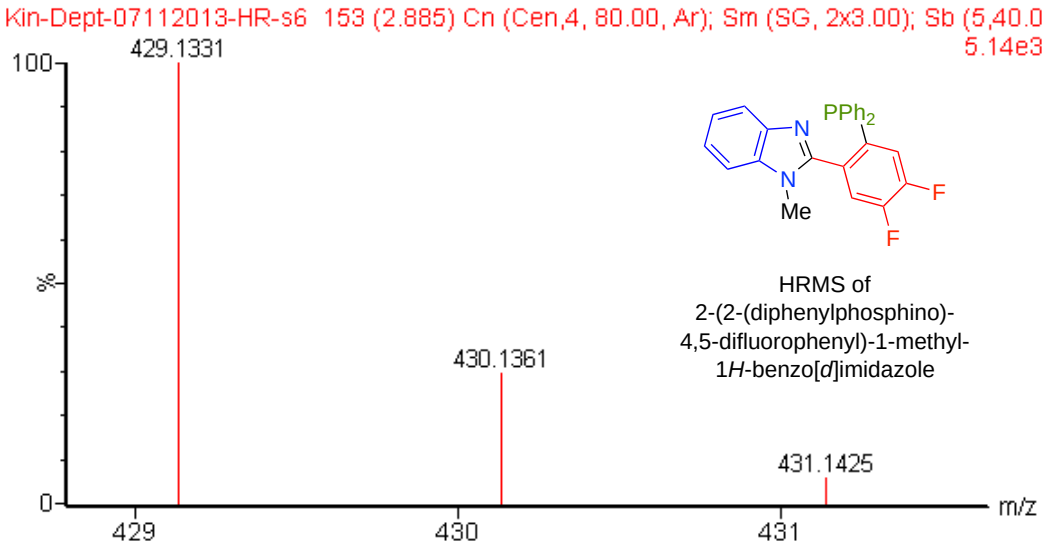
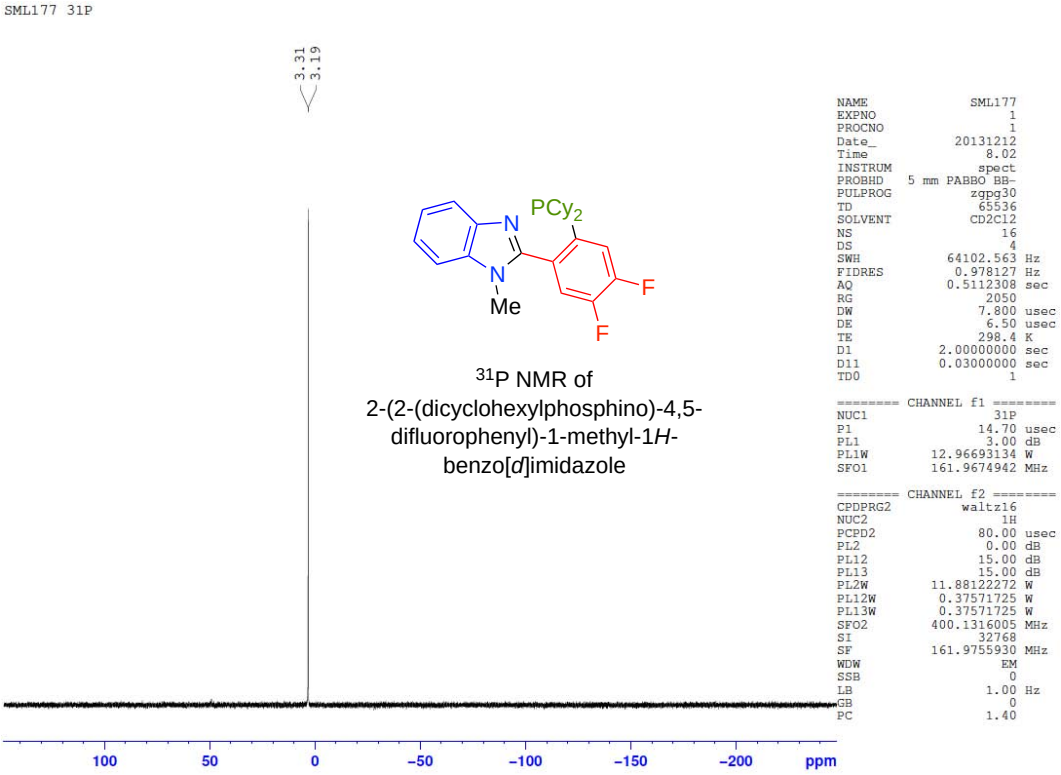
^{13}C NMR of
2-(2-(diphenylphosphino)-
4,5-difluorophenyl)-1-methyl-
1*H*-benzo[*d*]imidazole



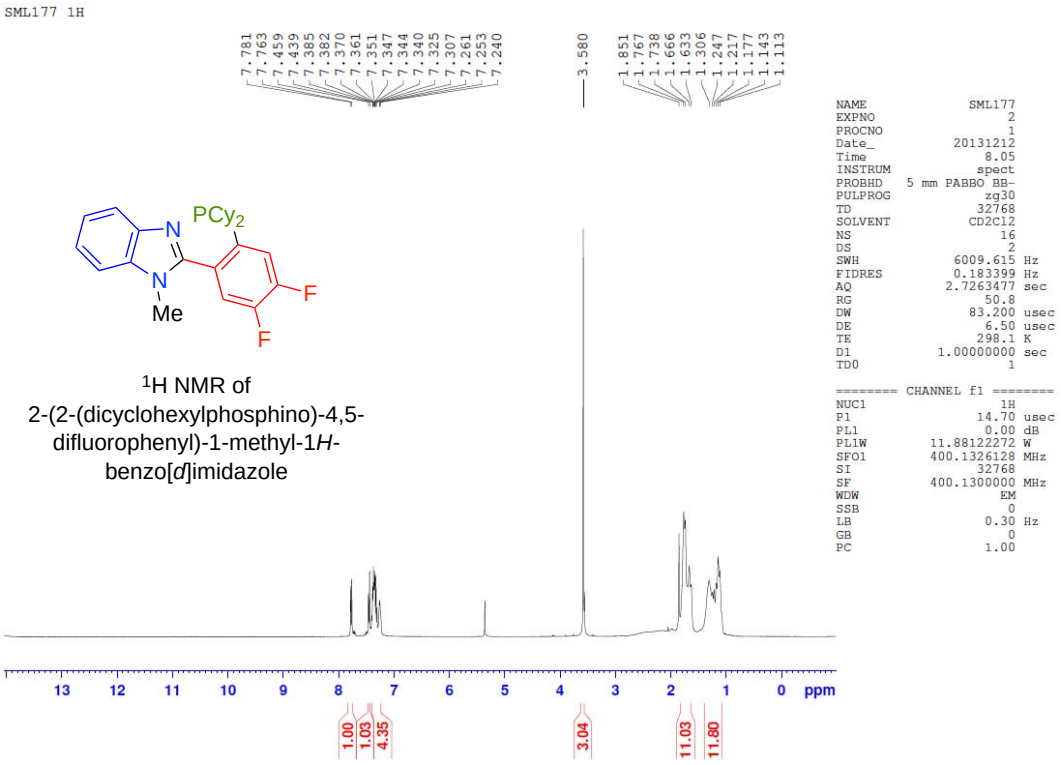
HRMS of
2-(2-(diphenylphosphino)-
4,5-difluorophenyl)-1-methyl-
1*H*-benzo[*d*]imidazole

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
429.1331	429.1332	-0.1	-0.2	17.5	8.3	C26 H20 N2 F2 P

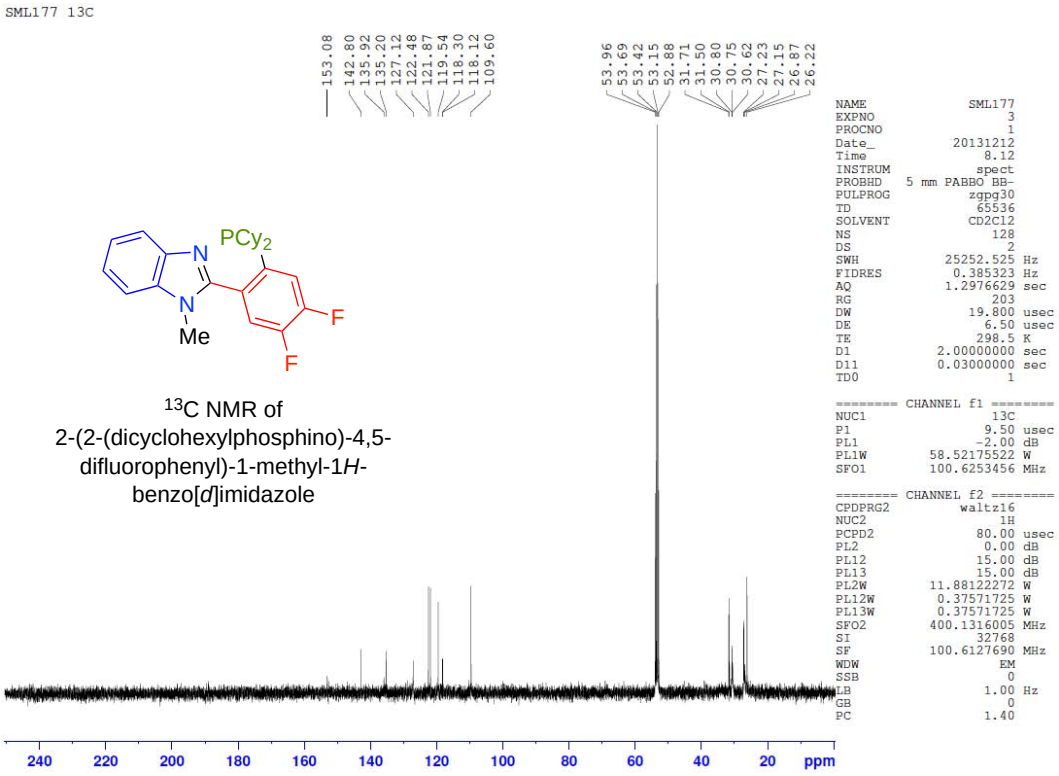
2-(2-(Dicyclohexylphosphino)-4,5-difluorophenyl)-1-methyl-1*H*-benzo[*d*]imidazole (PCy 4,5-F_2PhMezole-phos **L1i**) (**Table 2.5**, entry 9)



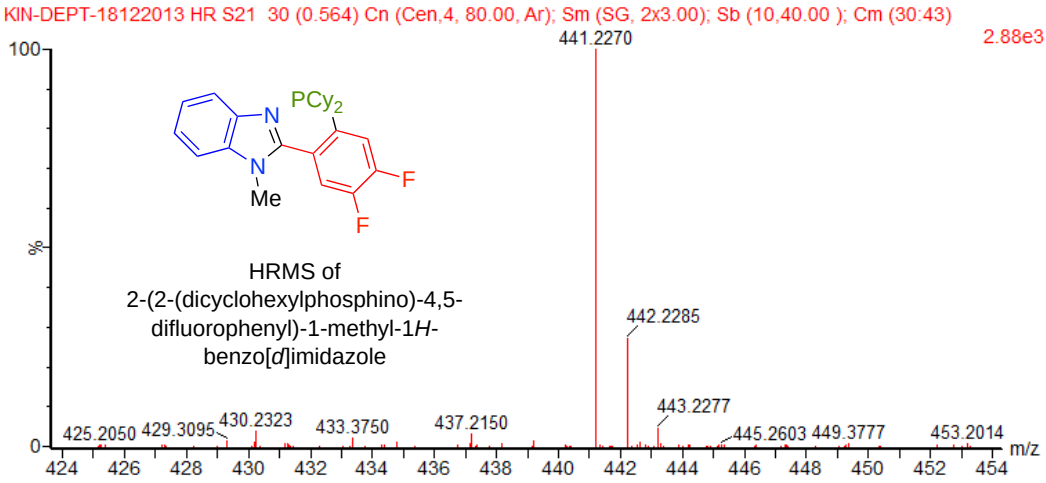
^{31}P NMR of 2-(2-(dicyclohexylphosphino)-4,5-difluorophenyl)-1-methyl-1*H*-benzo[*d*]imidazole



^{1}H NMR of 2-(2-(dicyclohexylphosphino)-4,5-difluorophenyl)-1-methyl-1*H*-benzo[*d*]imidazole



^{13}C NMR of
2-(2-(dicyclohexylphosphino)-4,5-difluorophenyl)-1-methyl-1*H*-benzo[*d*]imidazole

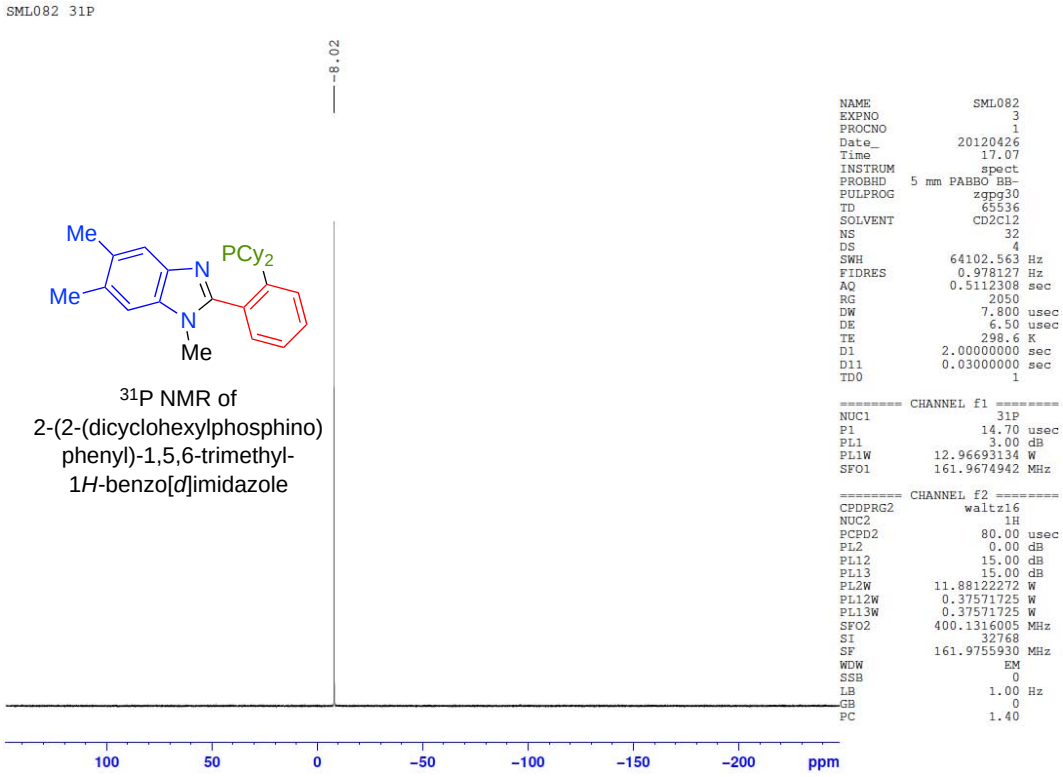


HRMS of
2-(2-(dicyclohexylphosphino)-4,5-difluorophenyl)-1-methyl-1*H*-benzo[*d*]imidazole

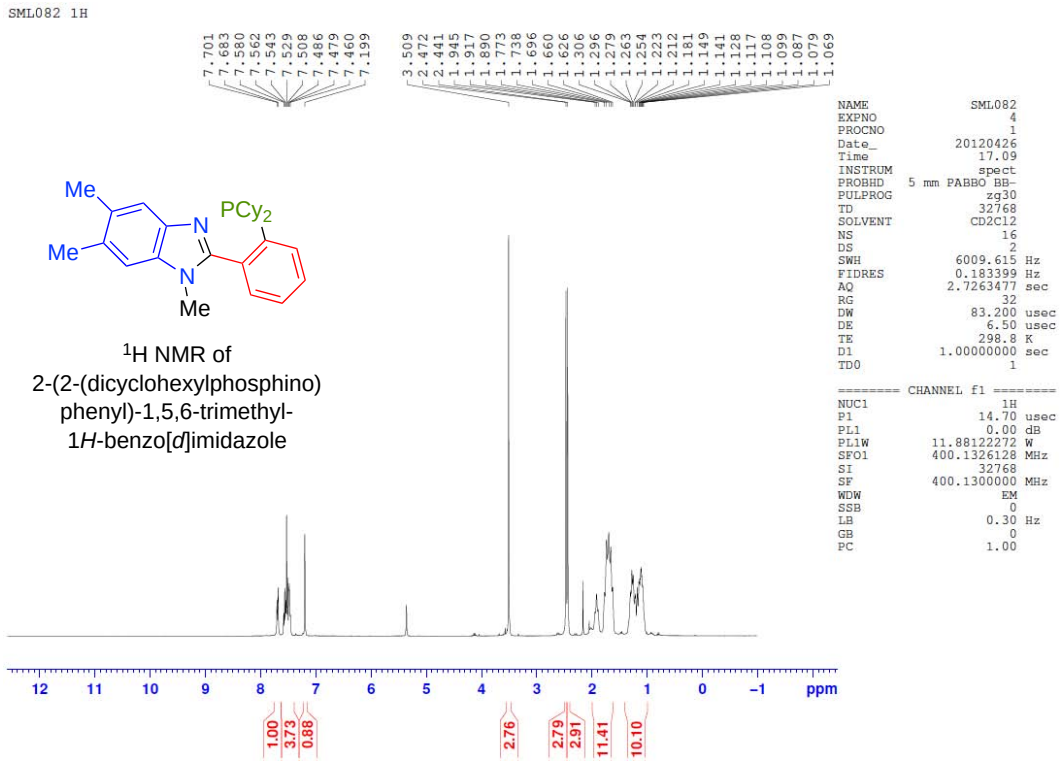
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
441.2270	441.2271	-0.1	-0.2	11.5	4.1	C26 H32 N2 F2 P

2-(2-(Dicyclohexylphosphino)phenyl)-1,5,6-trimethyl-1*H*-benzo[*d*]imidazole

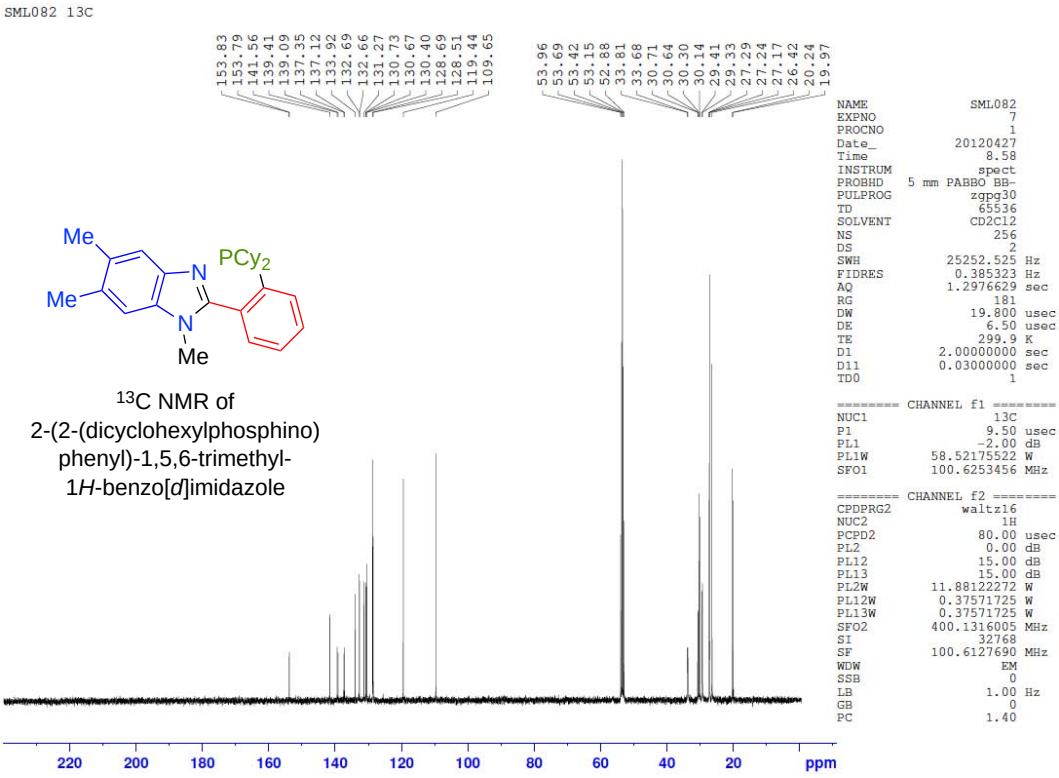
(PCy PhMezole^{M2}-phos **L1j**) (**Table 2.5**, entry 10)



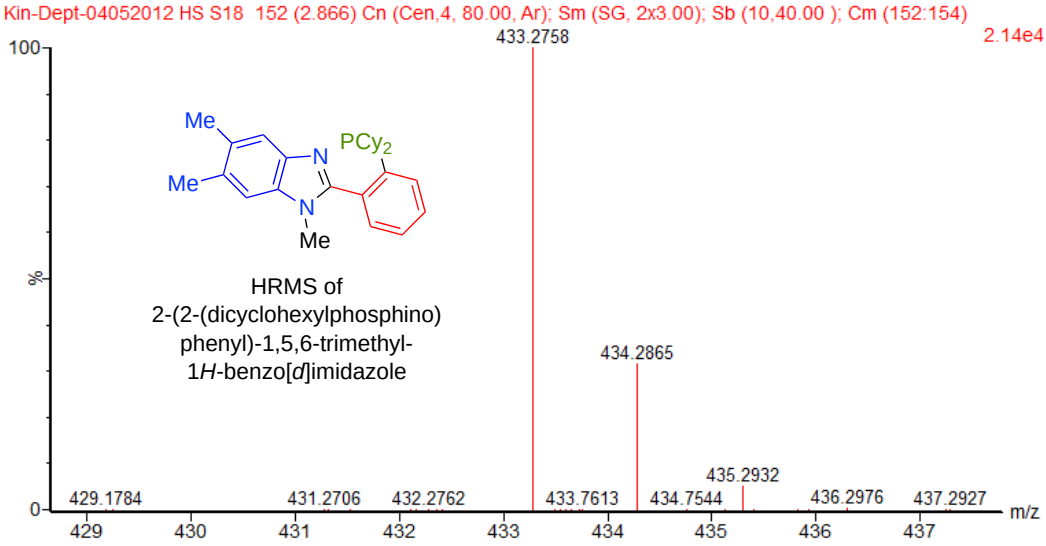
^{31}P NMR of 2-(2-(dicyclohexylphosphino) phenyl)-1,5,6-trimethyl-1*H*-benzo[*d*]imidazole



^{1}H NMR of 2-(2-(dicyclohexylphosphino) phenyl)-1,5,6-trimethyl-1*H*-benzo[*d*]imidazole



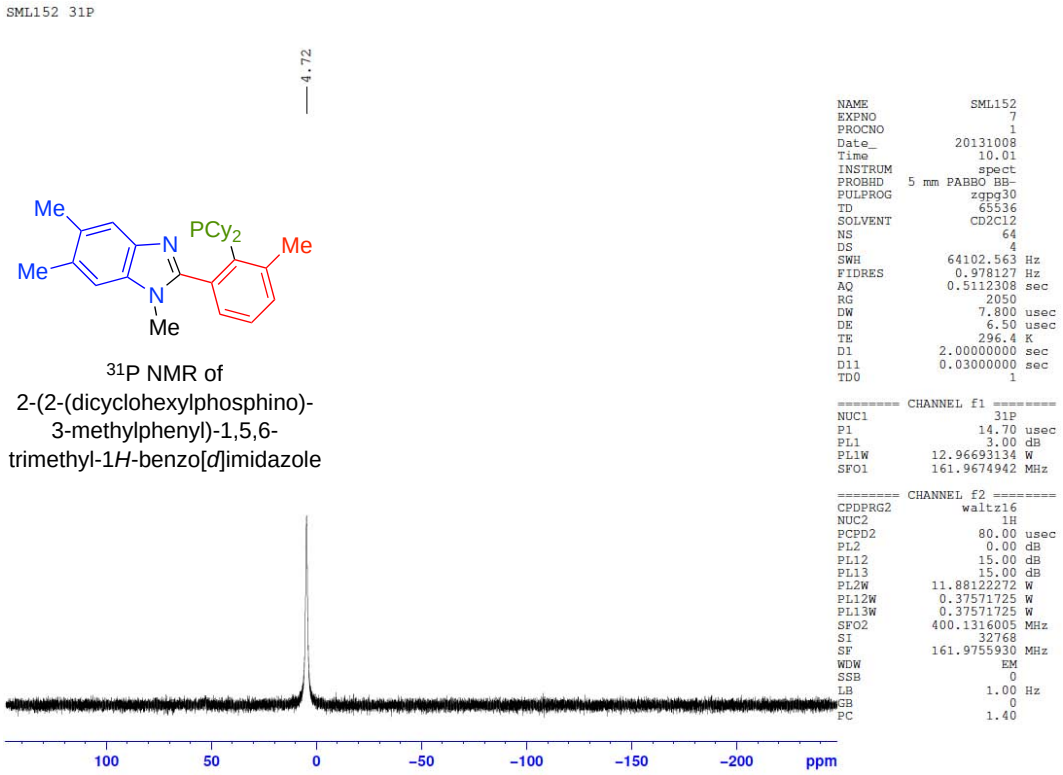
^{13}C NMR of
2-(2-(dicyclohexylphosphino)
phenyl)-1,5,6-trimethyl-
1*H*-benzo[*d*]imidazole



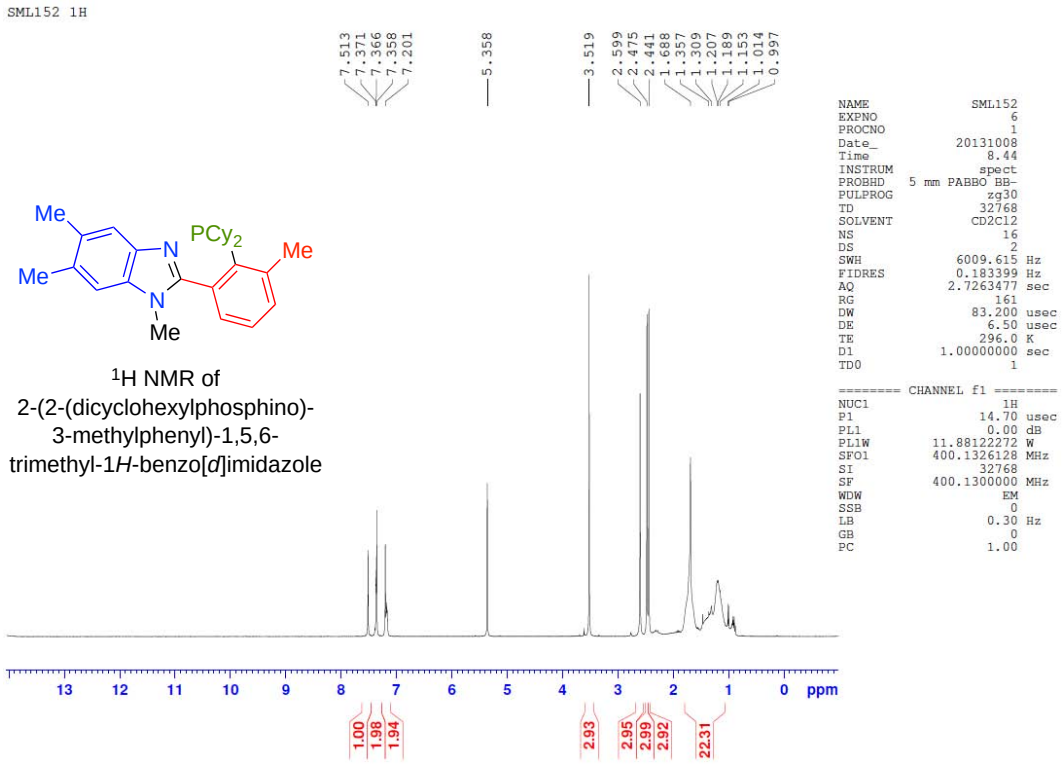
HRMS of
2-(2-(dicyclohexylphosphino)
phenyl)-1,5,6-trimethyl-
1*H*-benzo[*d*]imidazole

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
433.2758	433.2773	-1.5	-3.5	11.5	8.1	C28 H38 N2 P

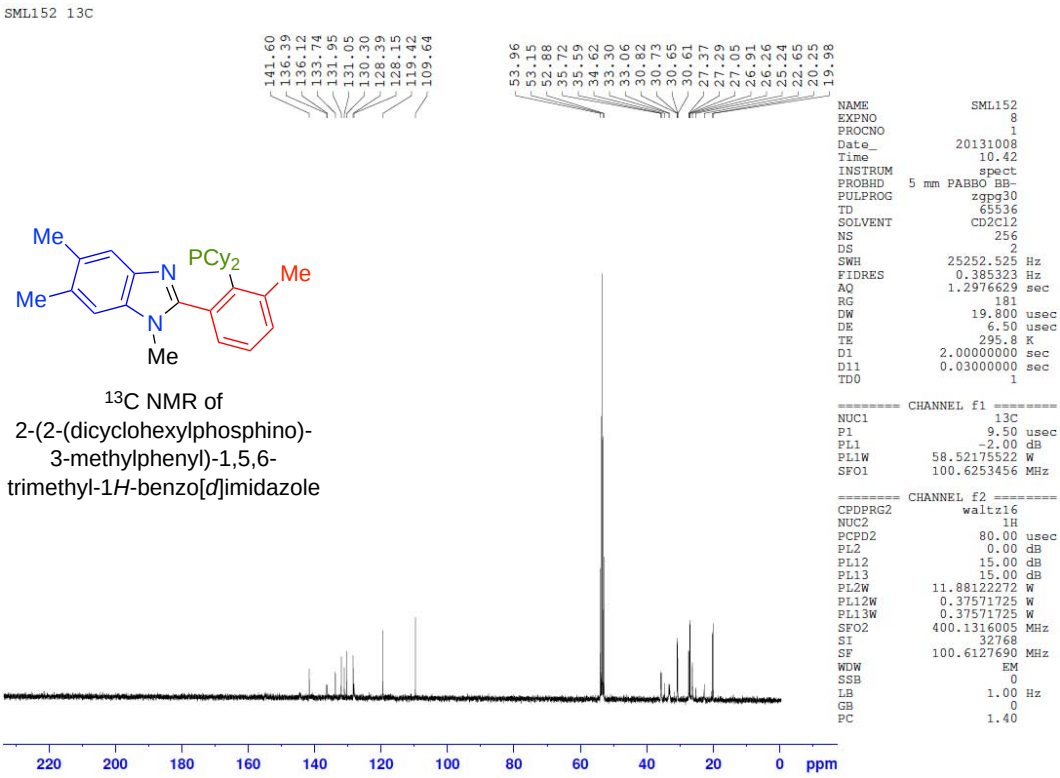
2-(2-(Dicyclohexylphosphino)-3-methylphenyl)-1,5,6-trimethyl-1*H*-benzo[*d*]imidazole (PCy *m*-TolMezole^{M2}-phos **L1k**) (**Table 2.5**, entry 11)



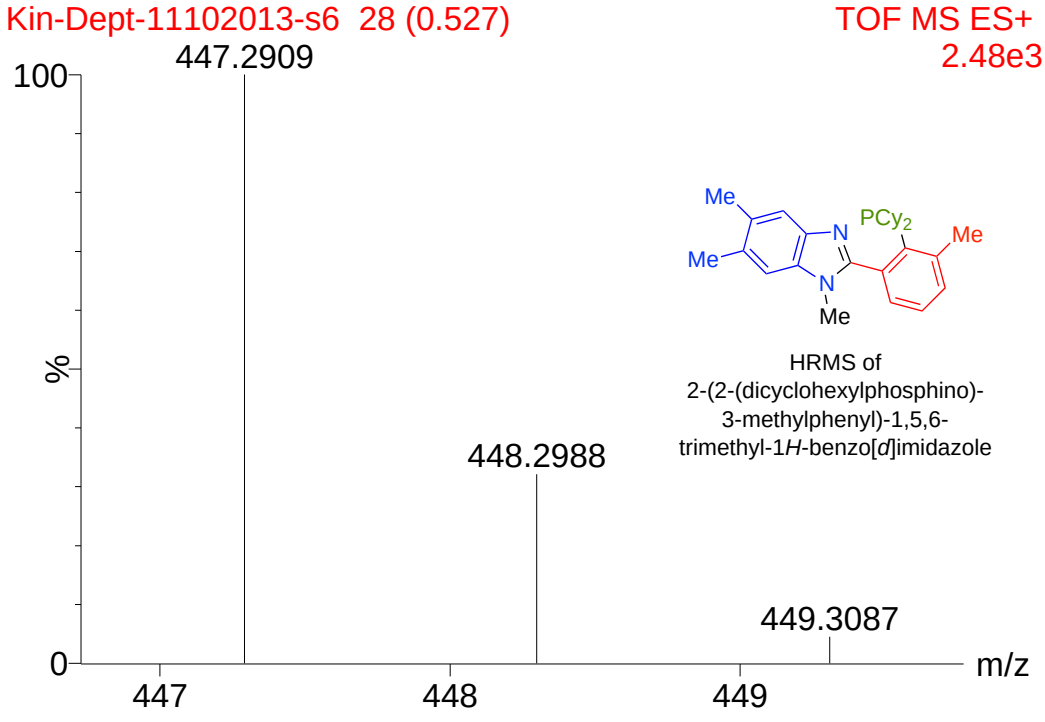
^{31}P NMR of 2-(2-(dicyclohexylphosphino)-3-methylphenyl)-1,5,6-trimethyl-1*H*-benzo[*d*]imidazole



^{1}H NMR of 2-(2-(dicyclohexylphosphino)-3-methylphenyl)-1,5,6-trimethyl-1*H*-benzo[*d*]imidazole



^{13}C NMR of
2-(2-(dicyclohexylphosphino)-
3-methylphenyl)-1,5,6-
trimethyl-1*H*-benzo[*d*]imidazole

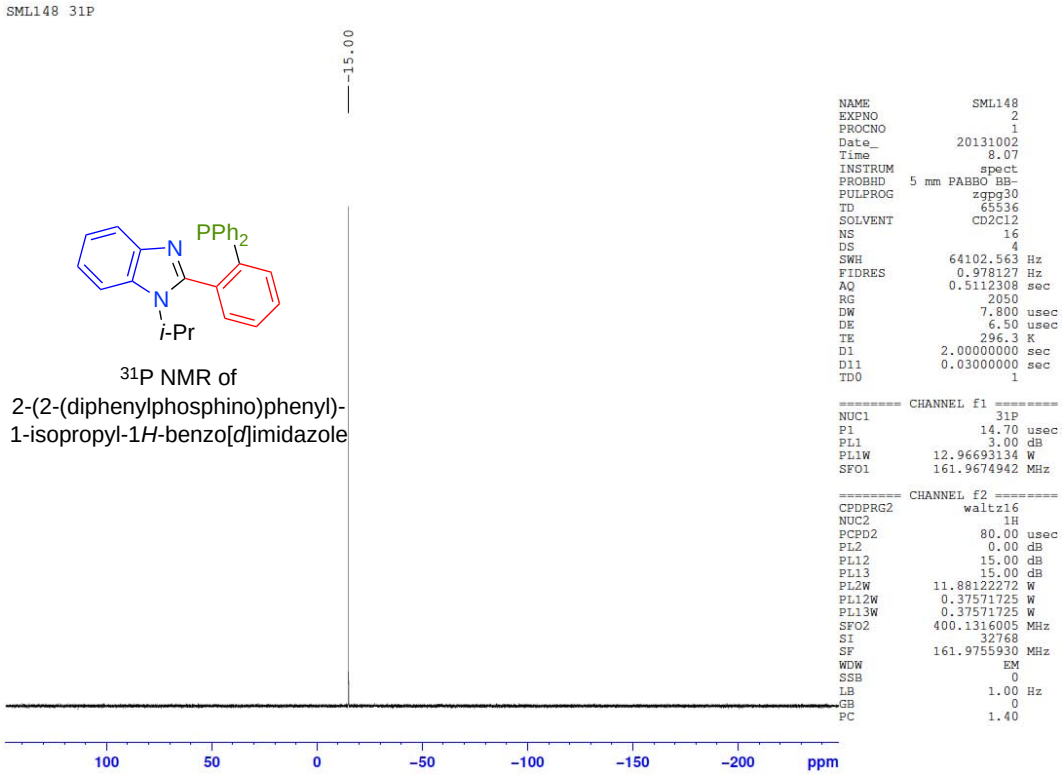


HRMS of
2-(2-(dicyclohexylphosphino)-
3-methylphenyl)-1,5,6-
trimethyl-1*H*-benzo[*d*]imidazole

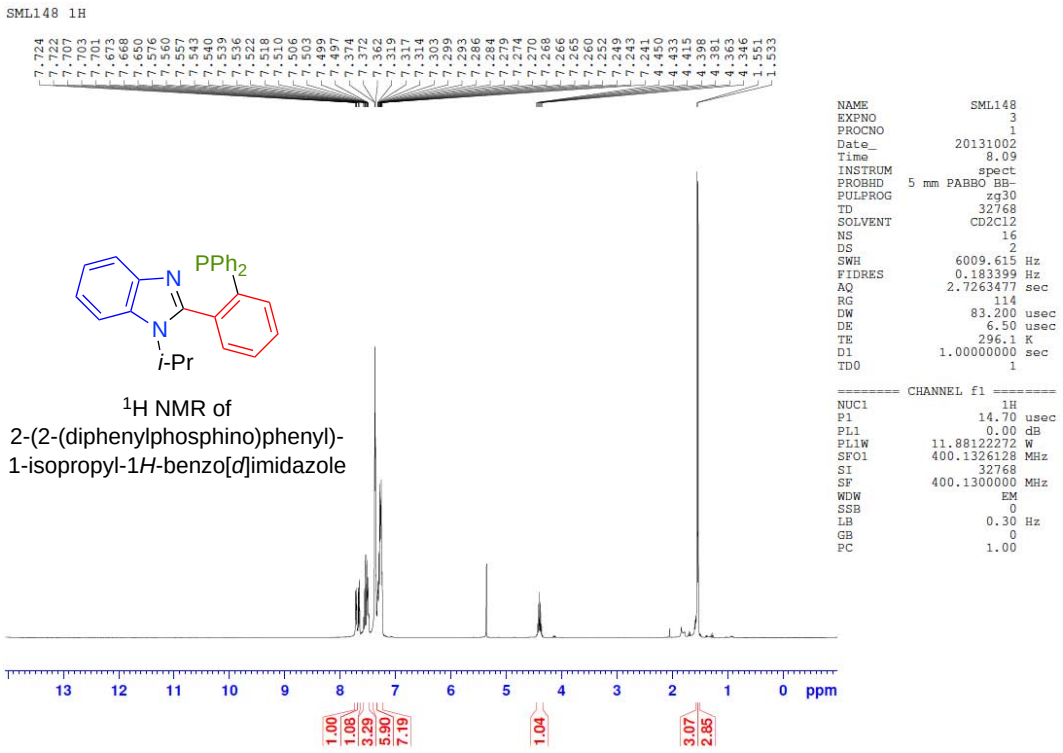
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
447.2909	447.2929	-2.0	-4.5	11.5	3.5	C29 H40 N2 P

2-(2-(Diphenylphosphino)phenyl)-1-isopropyl-1*H*-benzo[*d*]imidazole

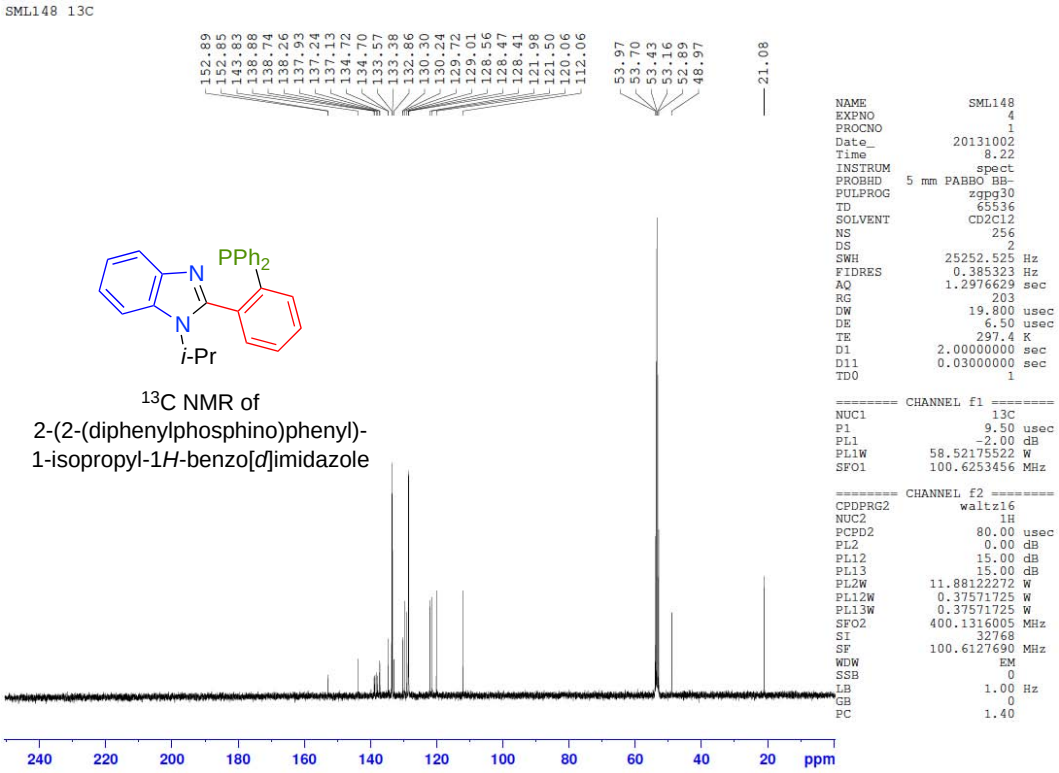
(PPh PhPrzole-phos **L1l**) (**Table 2.5**, entry 12)



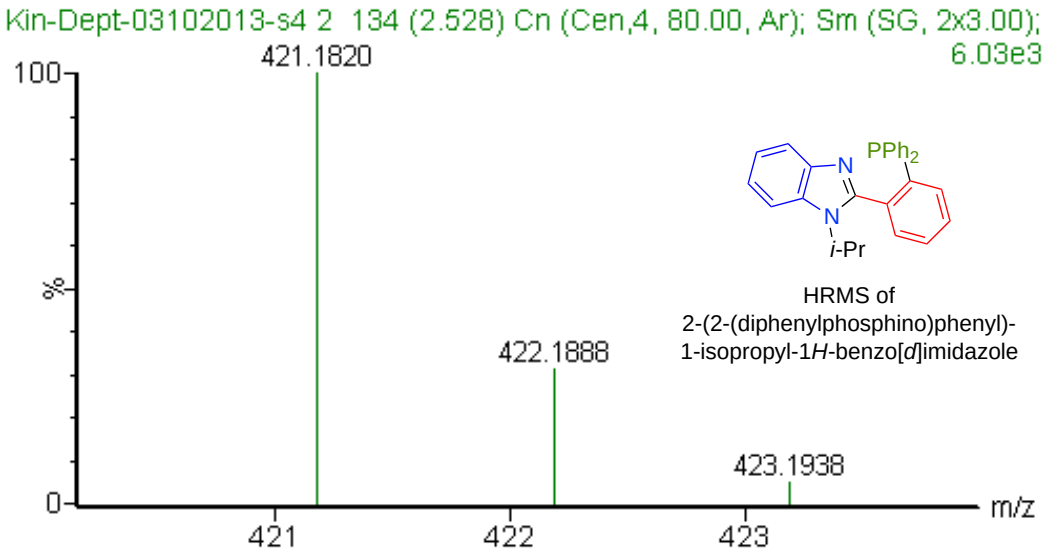
^{31}P NMR of
2-(2-(diphenylphosphino)phenyl)-
1-isopropyl-1*H*-benzo[*d*]imidazole



^{1}H NMR of
2-(2-(diphenylphosphino)phenyl)-
1-isopropyl-1*H*-benzo[*d*]imidazole



^{13}C NMR of
2-(2-(diphenylphosphino)phenyl)-
1-isopropyl-1*H*-benzo[*d*]imidazole

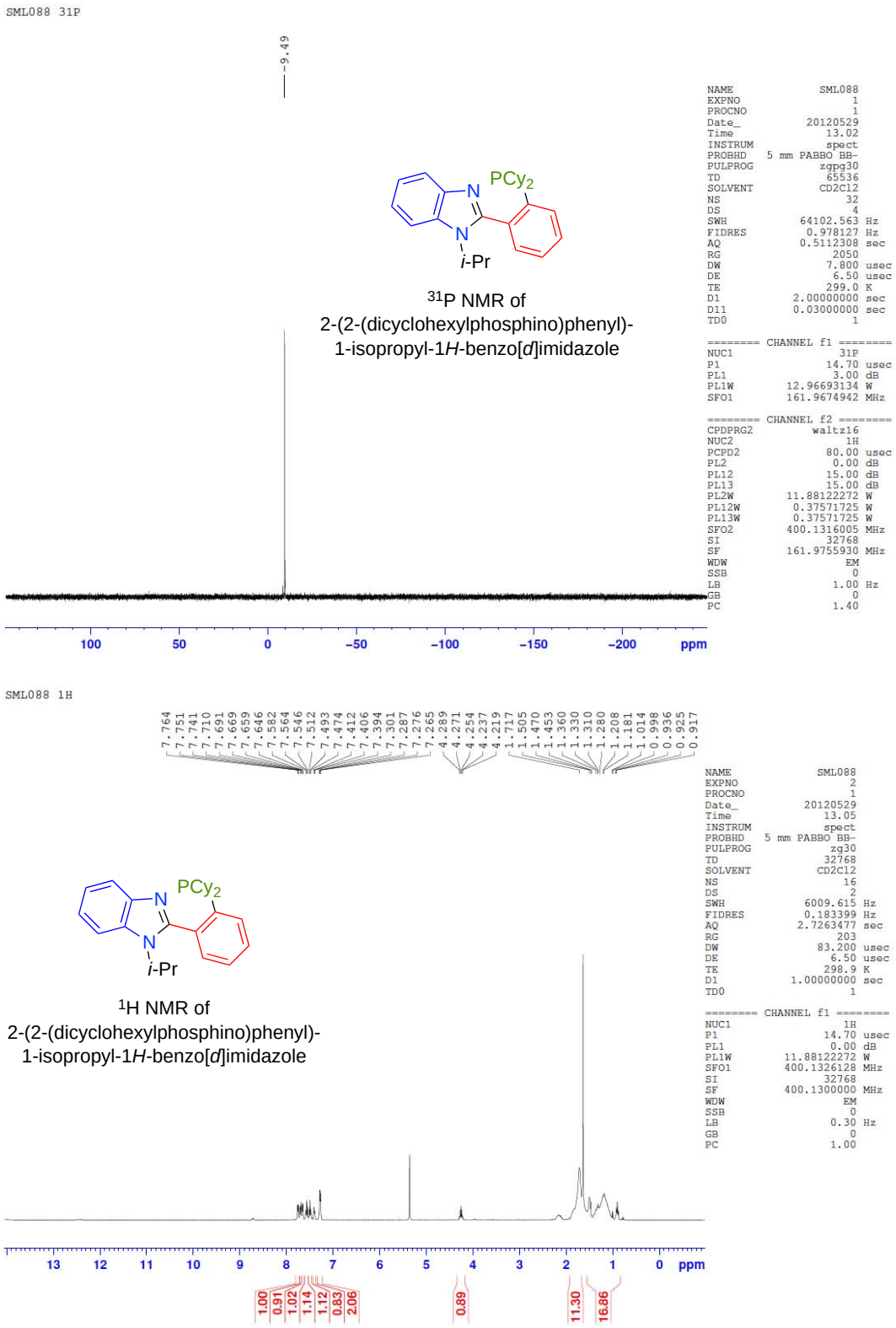


HRMS of
2-(2-(diphenylphosphino)phenyl)-
1-isopropyl-1*H*-benzo[*d*]imidazole

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
421.1820	421.1834	-1.4	-3.3	17.5	2.0	C28 H26 N2 P

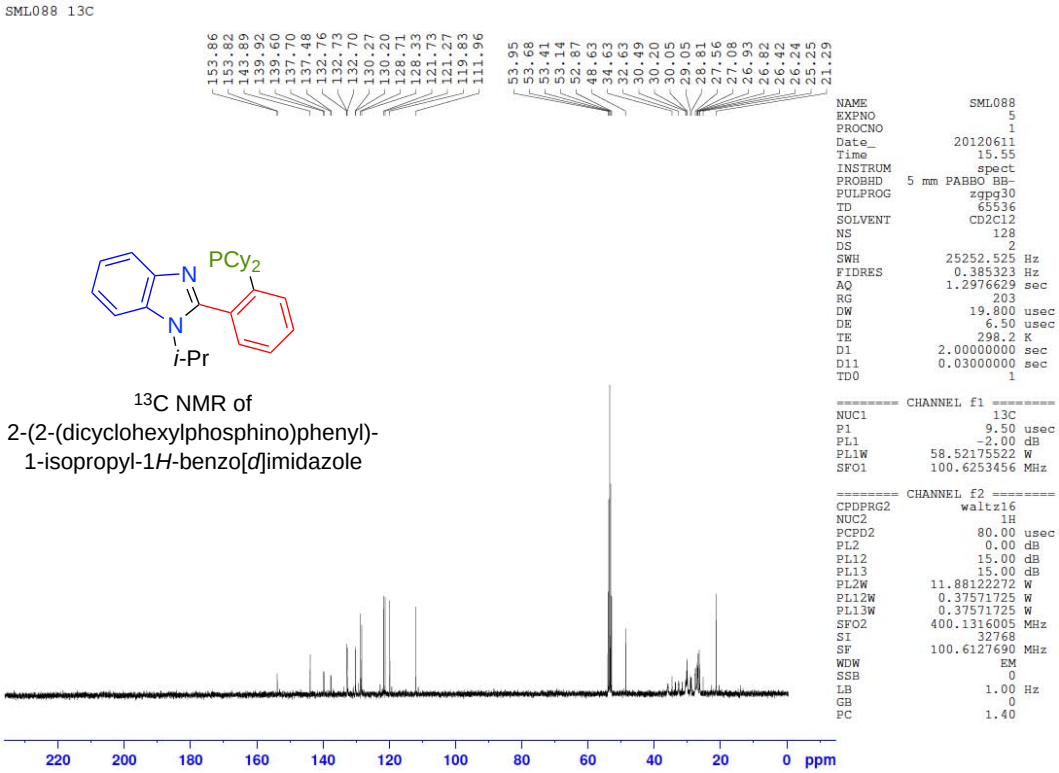
2-(2-(Dicyclohexylphosphino)phenyl)-1-isopropyl-1*H*-benzo[*d*]imidazole

(PCy PhPrzole-phos **L1m**) (**Table 2.5**, entry 13)



^{31}P NMR of
2-(2-(dicyclohexylphosphino)phenyl)-
1-isopropyl-1*H*-benzo[*d*]imidazole

^{1}H NMR of
2-(2-(dicyclohexylphosphino)phenyl)-
1-isopropyl-1*H*-benzo[*d*]imidazole



^{13}C NMR of
2-(2-(dicyclohexylphosphino)phenyl)-
1-isopropyl-1*H*-benzo[*d*]imidazole

```
NAME                SML088
EXPNO                    5
PROCNO                   1
Date_             20120611
Time                 15.55
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT             CD2Cl2
NS                       128
DS                         2
SWH               25252.525 Hz
FIDRES            0.385323 Hz
AQ                1.2976629 sec
RG                       203
DW                   19.800 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          100.6253456 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
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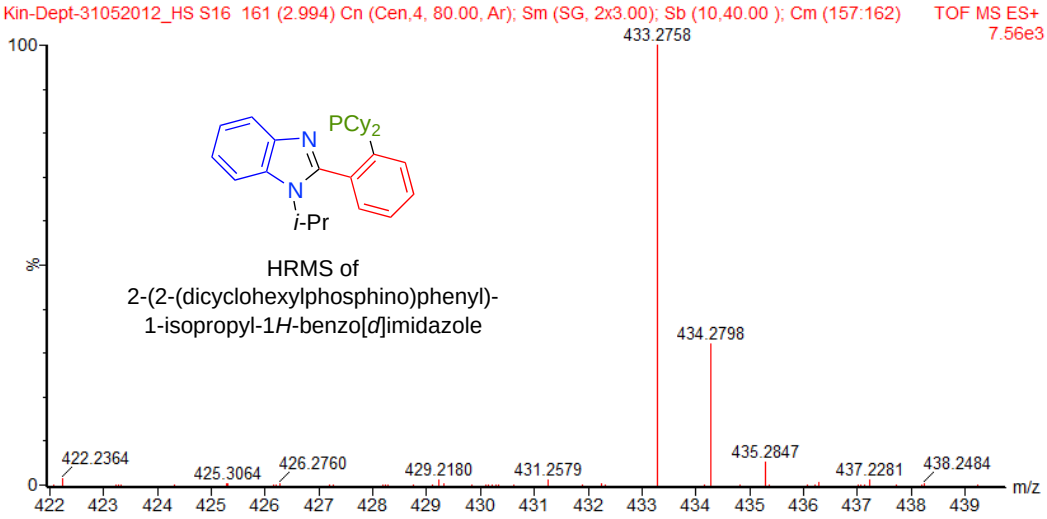
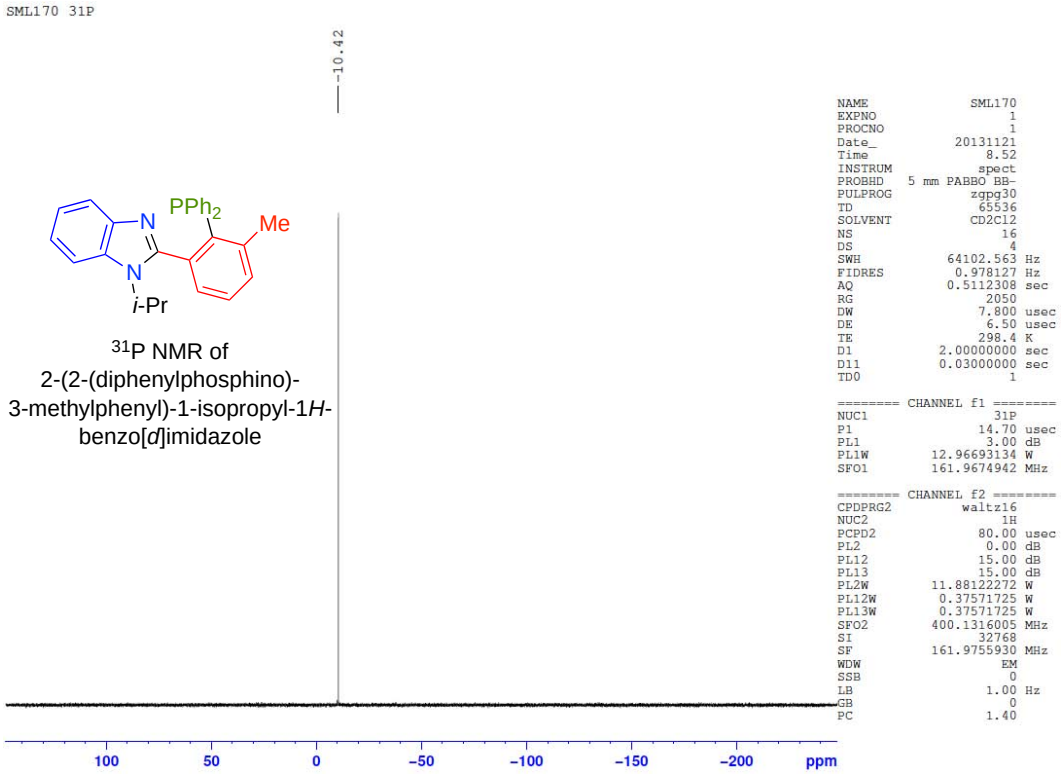


HRMS of
2-(2-(dicyclohexylphosphino)phenyl)-
1-isopropyl-1*H*-benzo[*d*]imidazole

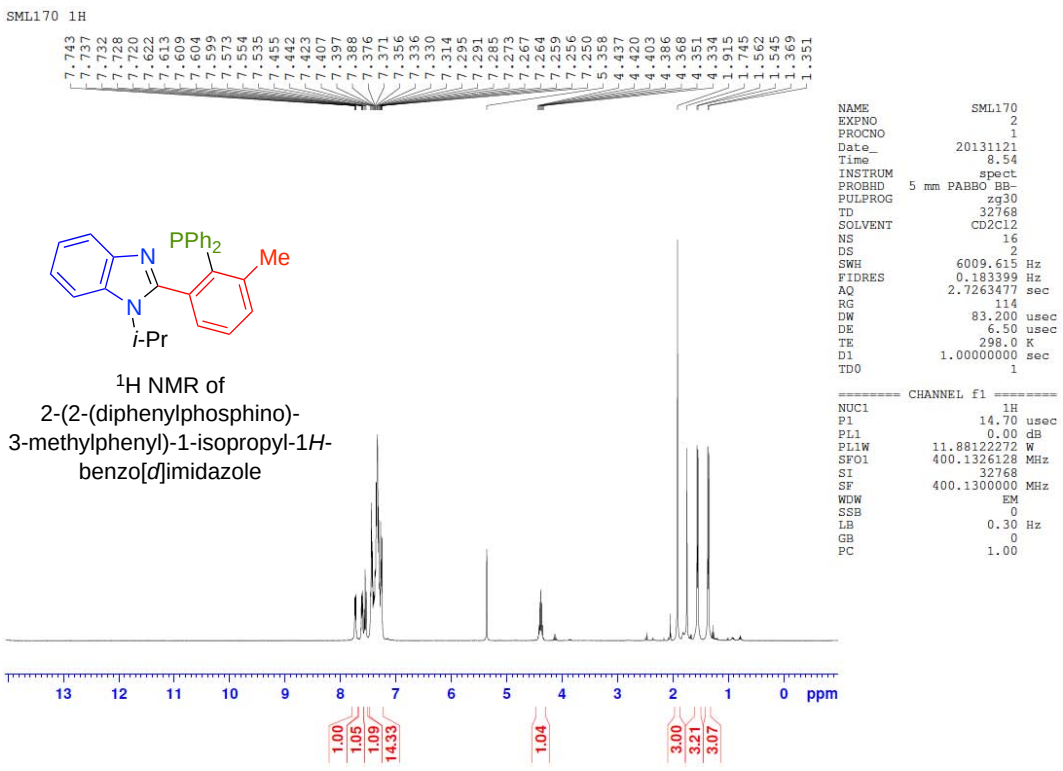
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
433.2758	433.2773	-1.5	-3.5	11.5	0.5	C28 H38 N2 P

2-(2-(Diphenylphosphino)-3-methylphenyl)-1-isopropyl-1*H*-benzo[*d*]imidazole

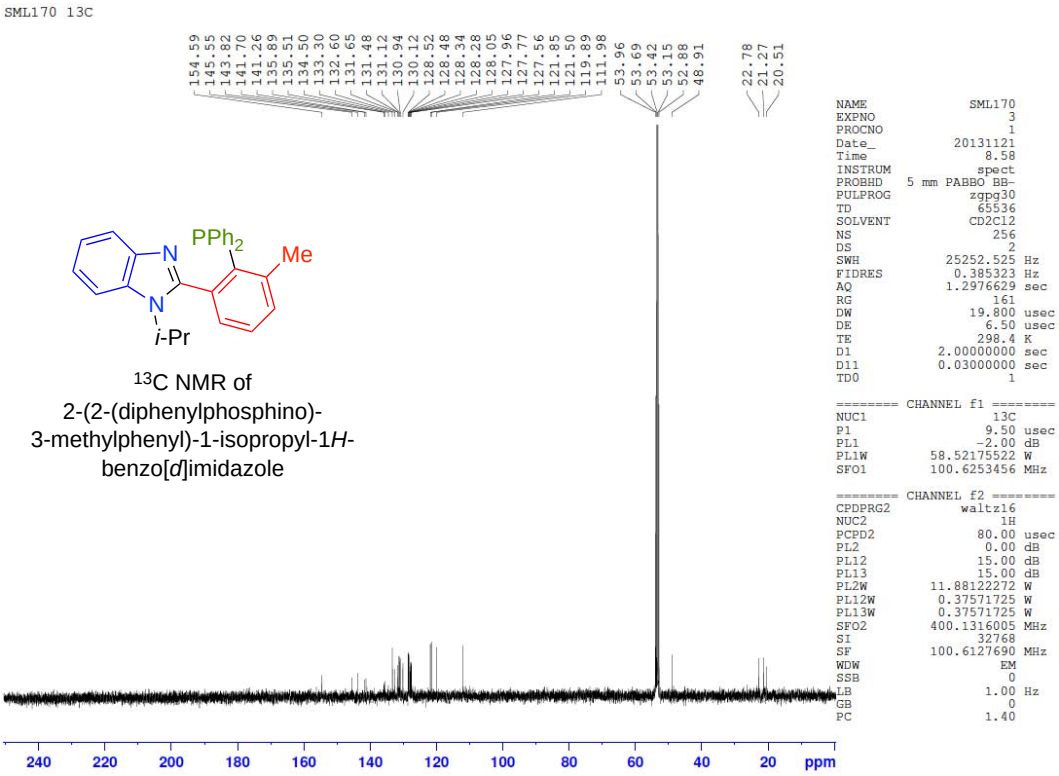
(PPh *m*-TolPrzole-phos **L1n**) (**Table 2.5**, entry 14)



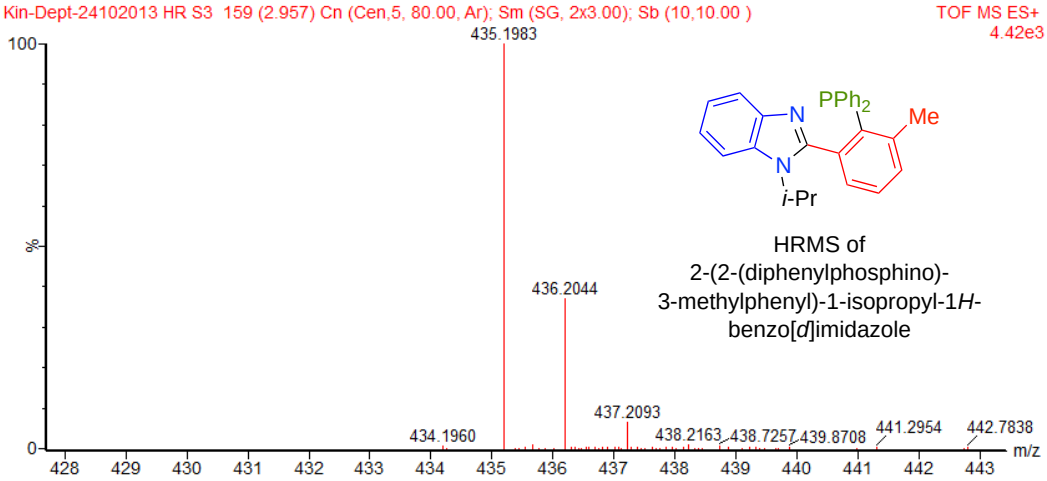
^{31}P NMR of 2-(2-(diphenylphosphino)-3-methylphenyl)-1-isopropyl-1*H*-benzo[*d*]imidazole



^{1}H NMR of 2-(2-(diphenylphosphino)-3-methylphenyl)-1-isopropyl-1*H*-benzo[*d*]imidazole



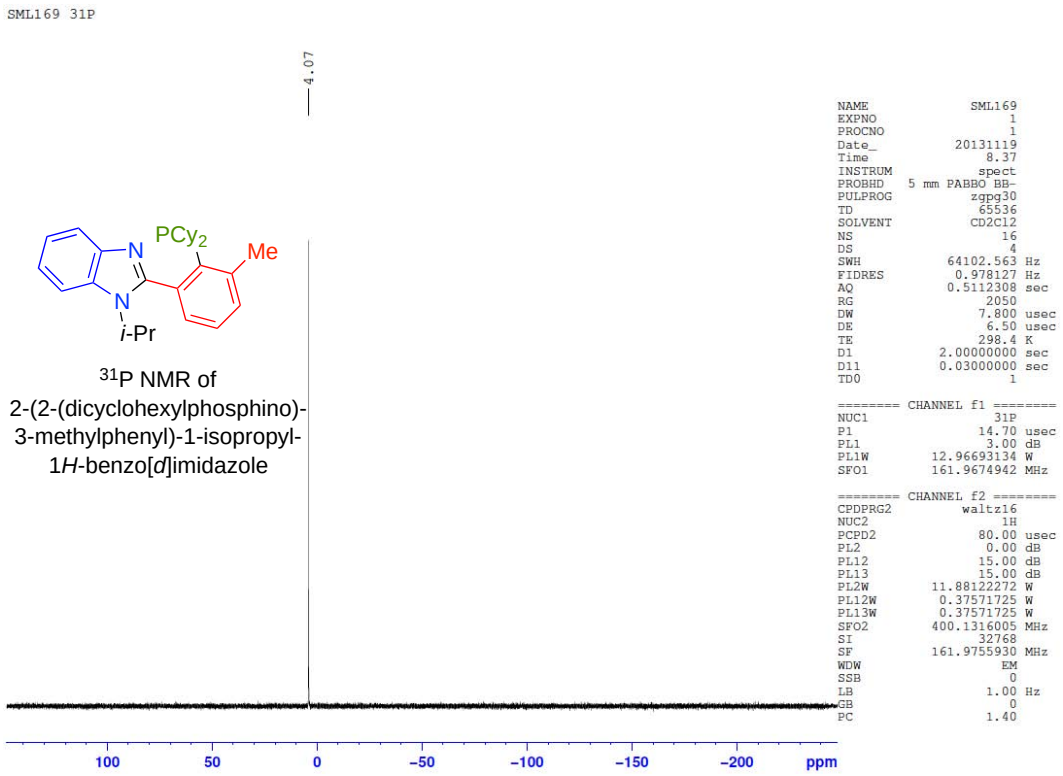
^{13}C NMR of
2-(2-(diphenylphosphino)-
3-methylphenyl)-1-isopropyl-1*H*-
benzo[*d*]imidazole



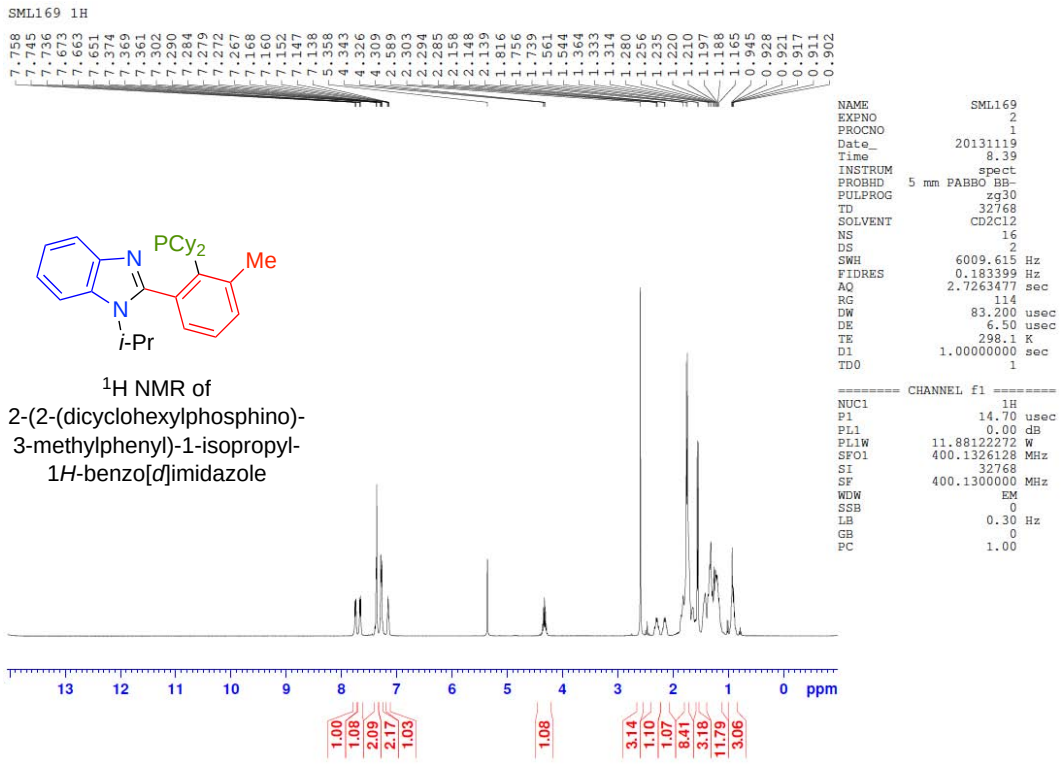
HRMS of
2-(2-(diphenylphosphino)-
3-methylphenyl)-1-isopropyl-1*H*-
benzo[*d*]imidazole

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
435.1983	435.1990	-0.7	-1.6	17.5	9.8	C29 H28 N2 P

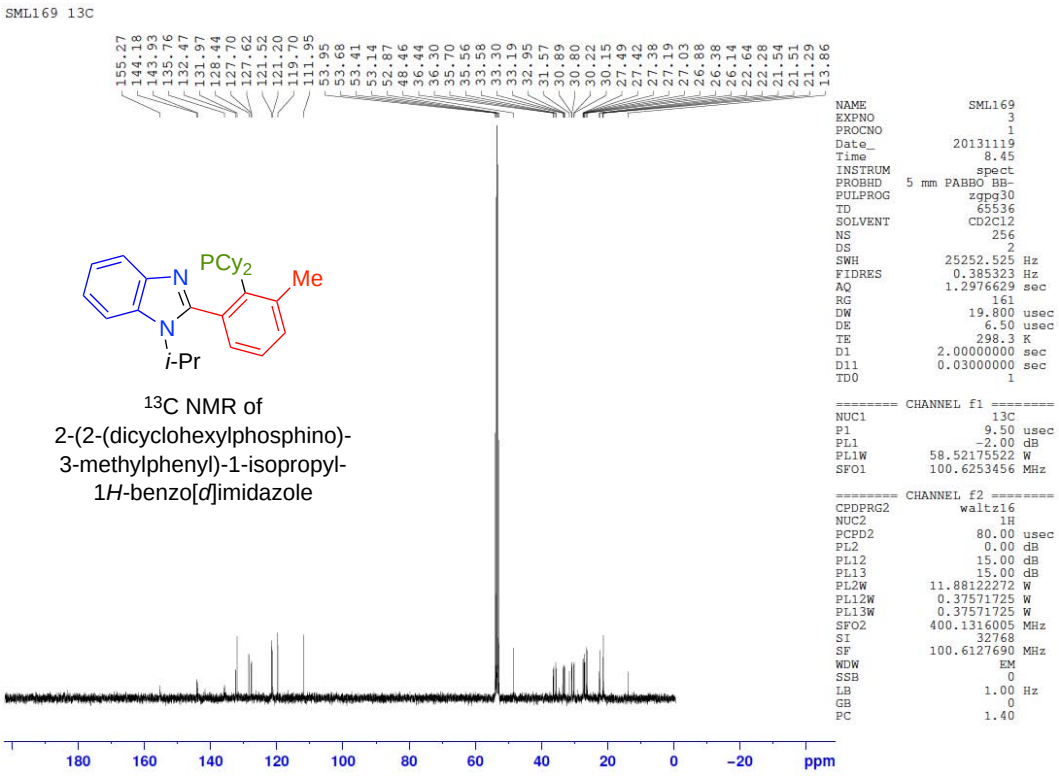
2-(2-(Dicyclohexylphosphino)-3-methylphenyl)-1-isopropyl-1*H*-benzo[*d*]imidazole (PCy *m*-TolPrzole-phos **L1o**) (**Table 2.5**, entry 15)



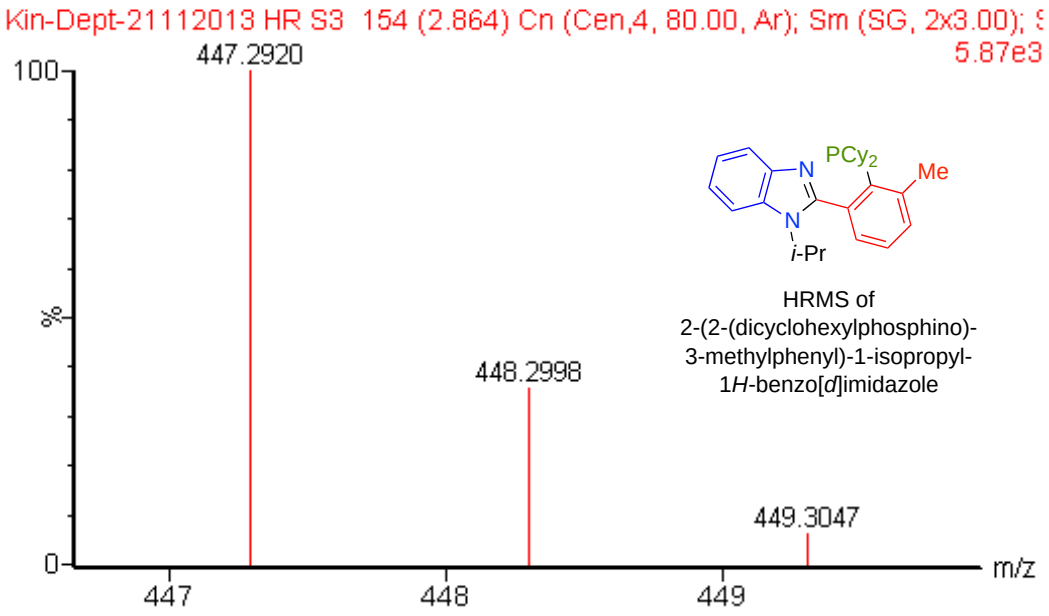
^{31}P NMR of 2-(2-(dicyclohexylphosphino)-3-methylphenyl)-1-isopropyl-1*H*-benzo[*d*]imidazole



^{1}H NMR of 2-(2-(dicyclohexylphosphino)-3-methylphenyl)-1-isopropyl-1*H*-benzo[*d*]imidazole



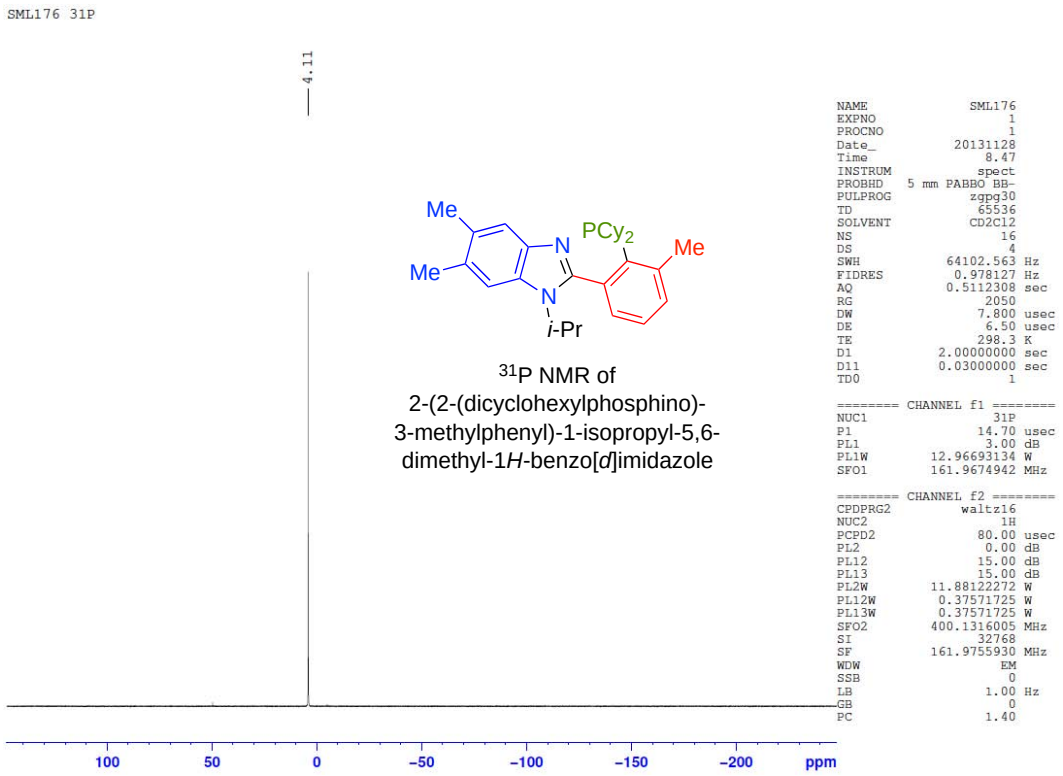
^{13}C NMR of
2-(2-(dicyclohexylphosphino)-
3-methylphenyl)-1-isopropyl-
1*H*-benzo[*d*]imidazole



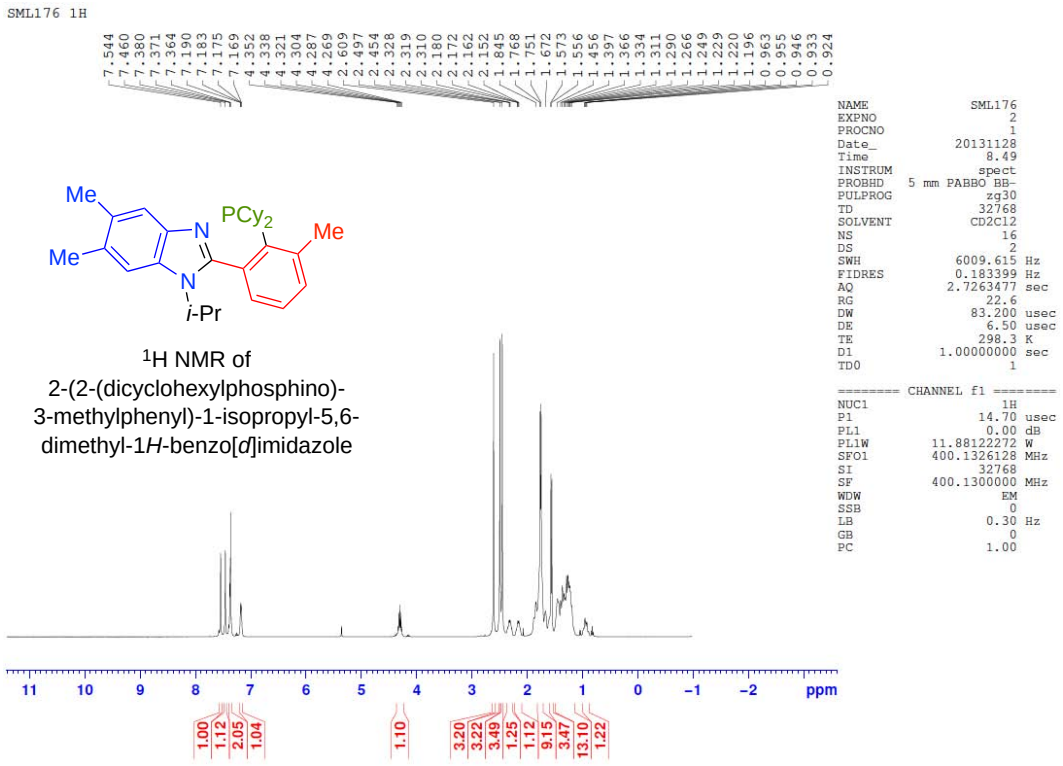
HRMS of
2-(2-(dicyclohexylphosphino)-
3-methylphenyl)-1-isopropyl-
1*H*-benzo[*d*]imidazole

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
447.2920	447.2929	-0.9	-2.0	11.5	4.1	C29 H40 N2 P

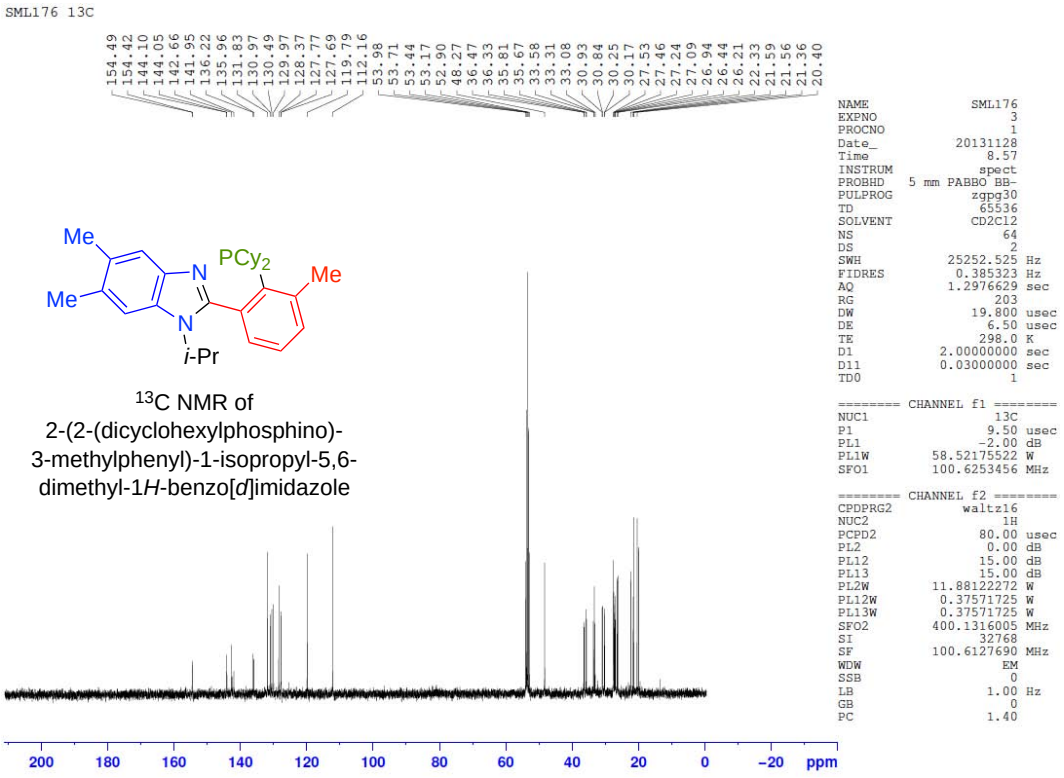
2-(2-(Dicyclohexylphosphino)-3-methylphenyl)-1-isopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole (PCy *m*-TolPrzole^{M2}-phos **L1p**) (**Table 2.5**, entry 16)



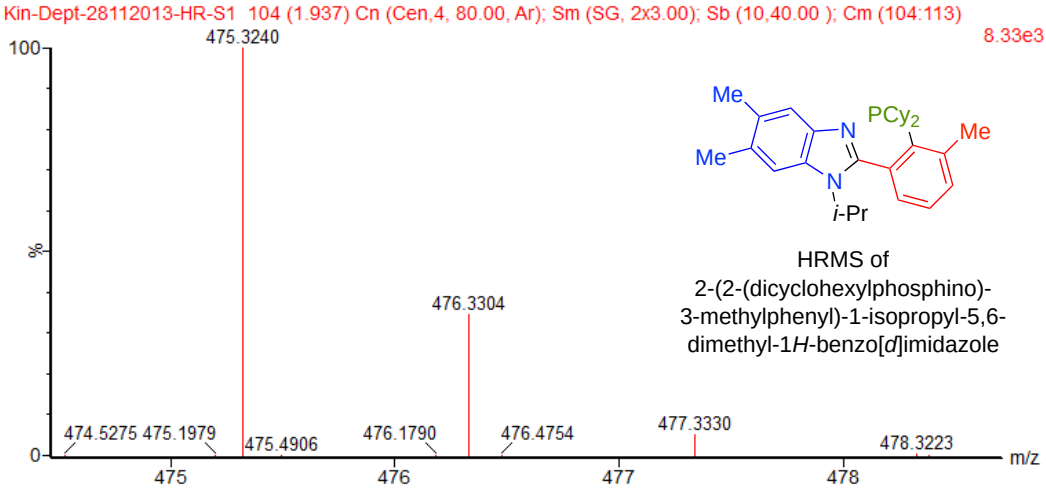
^{31}P NMR of 2-(2-(dicyclohexylphosphino)-3-methylphenyl)-1-isopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole



^{1}H NMR of 2-(2-(dicyclohexylphosphino)-3-methylphenyl)-1-isopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole



^{13}C NMR of
2-(2-(dicyclohexylphosphino)-
3-methylphenyl)-1-isopropyl-5,6-
dimethyl-1*H*-benzo[*d*]imidazole

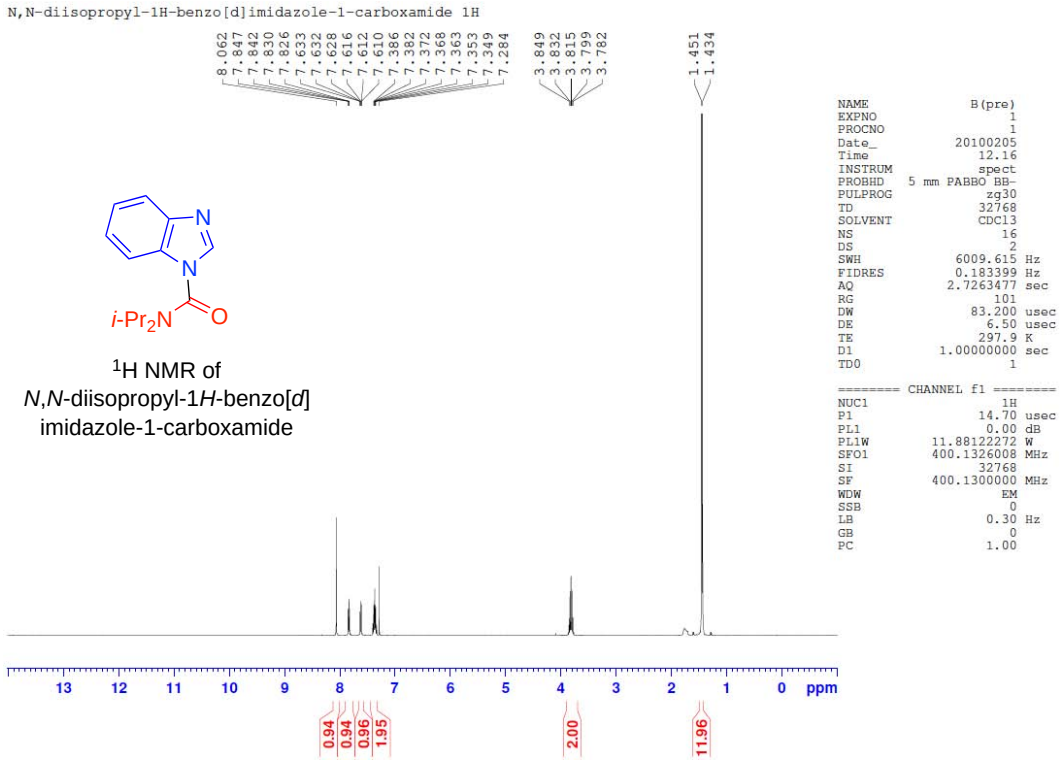


HRMS of
2-(2-(dicyclohexylphosphino)-
3-methylphenyl)-1-isopropyl-5,6-
dimethyl-1*H*-benzo[*d*]imidazole

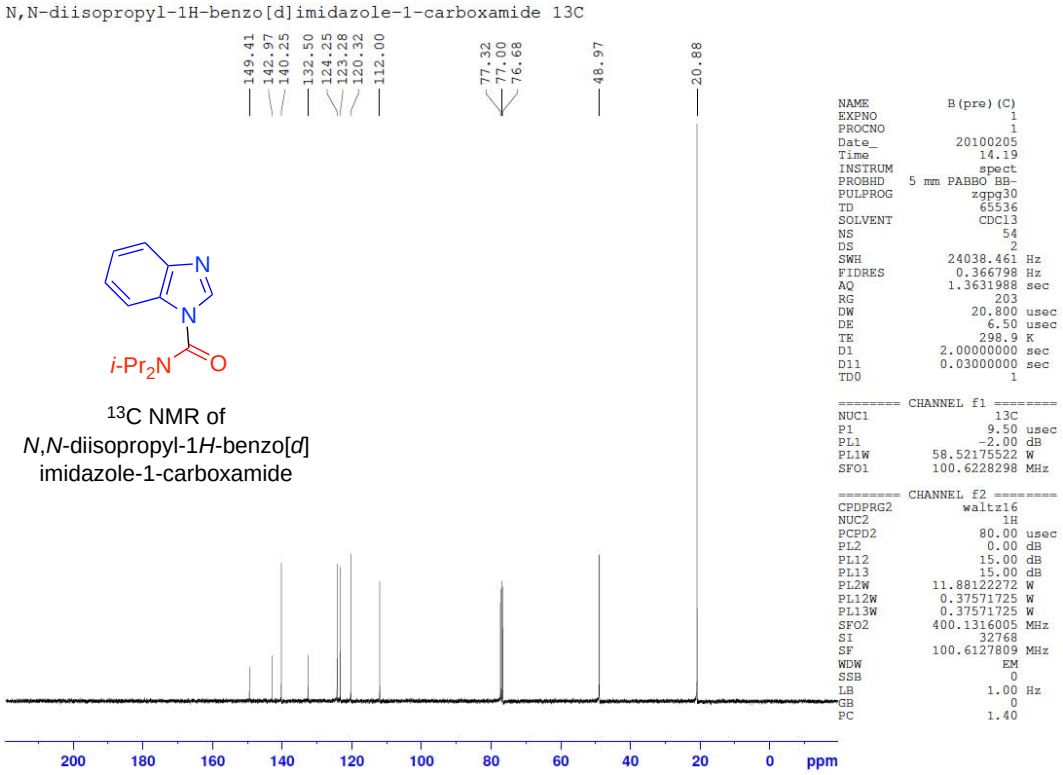
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
475.3240	475.3242	-0.2	-0.4	11.5	8.5	C31 H4 N2 P

Chapter 2 HMR and HRMS Spectra of *N*-Substituted Benzimidazolyl Ligand Precursors

N,*N*-Diisopropyl-1*H*-benzo[*d*]imidazole-1-carboxamide (**Table 2.10**, entry 1)

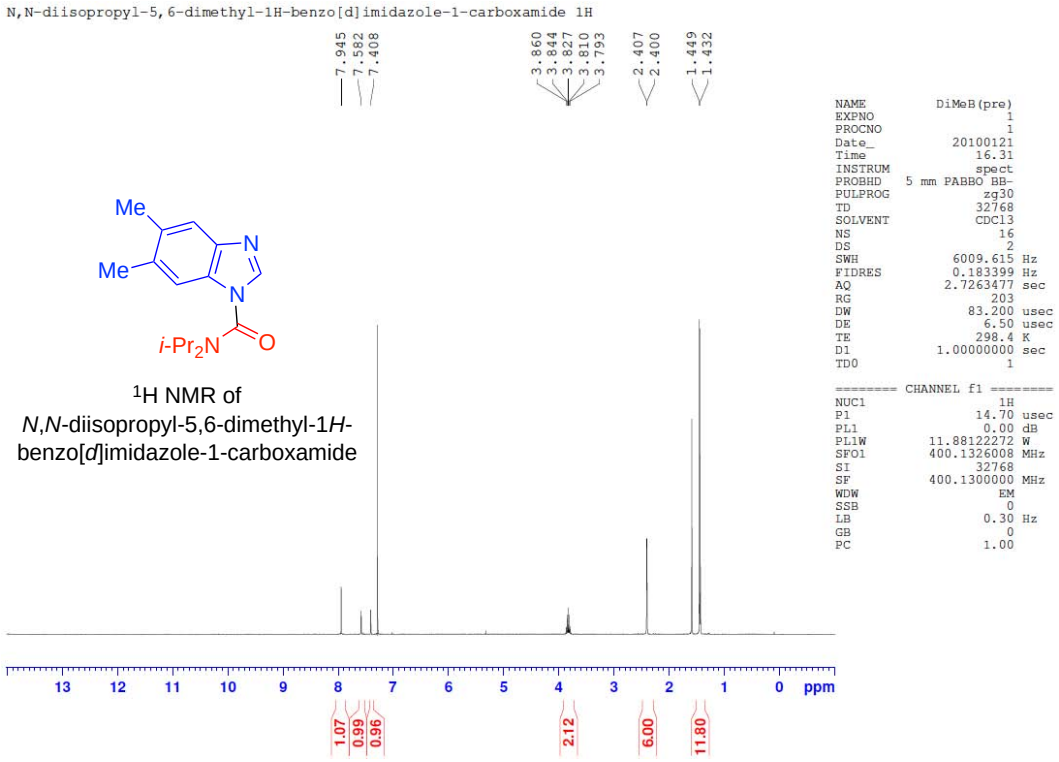


^{1}H NMR of *N*,*N*-diisopropyl-1*H*-benzo[*d*] imidazole-1-carboxamide

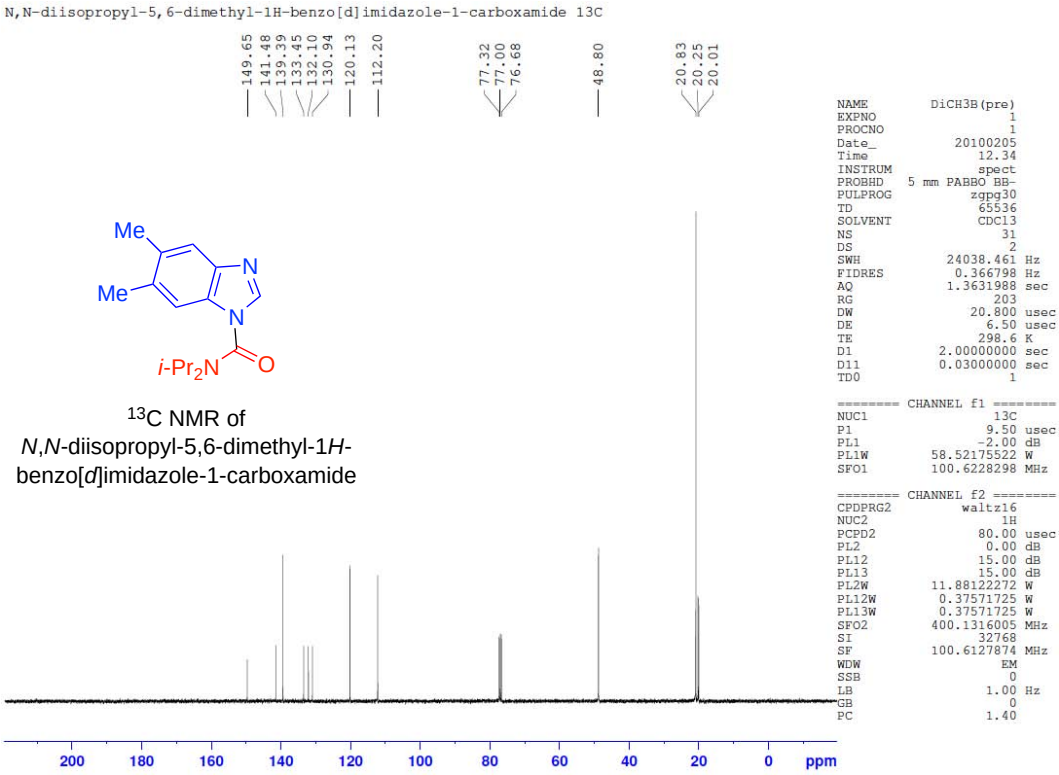


^{13}C NMR of *N*,*N*-diisopropyl-1*H*-benzo[*d*] imidazole-1-carboxamide

N,*N*-Diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide (**Table 2.10**, entry 2)



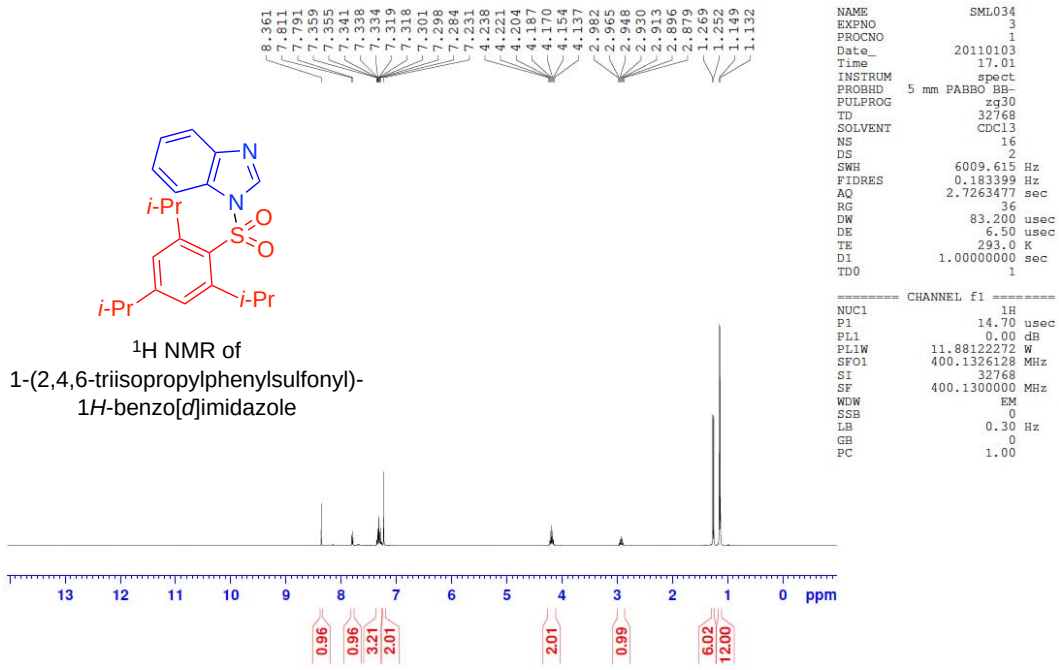
^{1}H NMR of *N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide



^{13}C NMR of *N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide

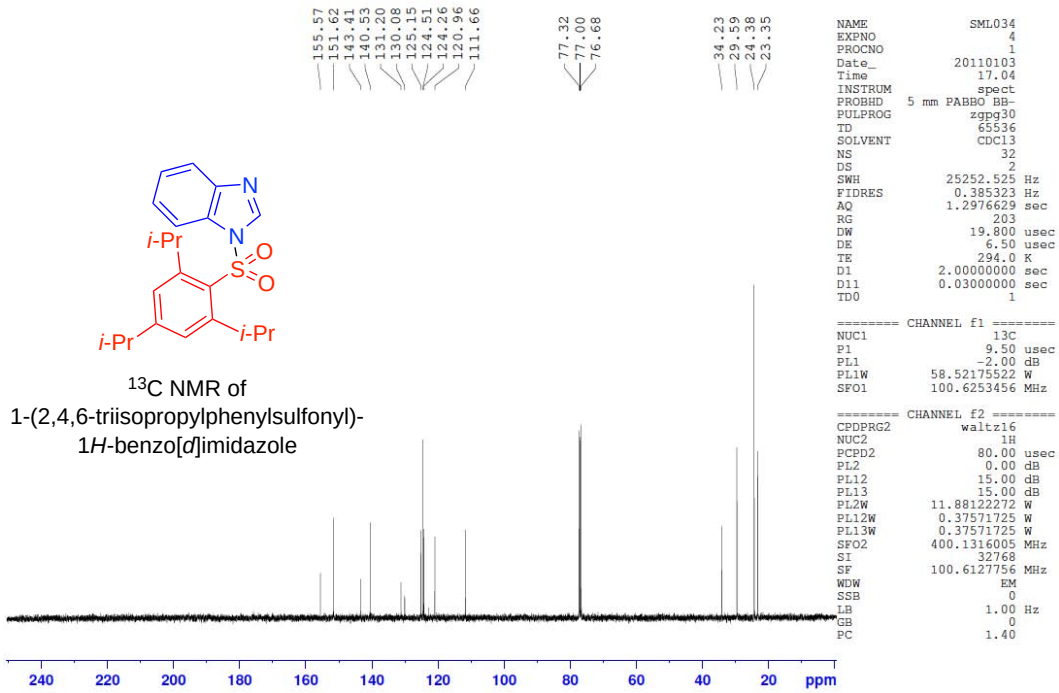
1-(2,4,6-Triisopropylphenylsulfonyl)-1*H*-benzo[*d*]imidazole (**Table 2.10**, entry 3)

SML034 1H



^{1}H NMR of
1-(2,4,6-triisopropylphenylsulfonyl)-
1*H*-benzo[*d*]imidazole

SML034 13C

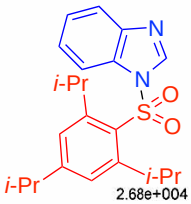


^{13}C NMR of
1-(2,4,6-triisopropylphenylsulfonyl)-
1*H*-benzo[*d*]imidazole

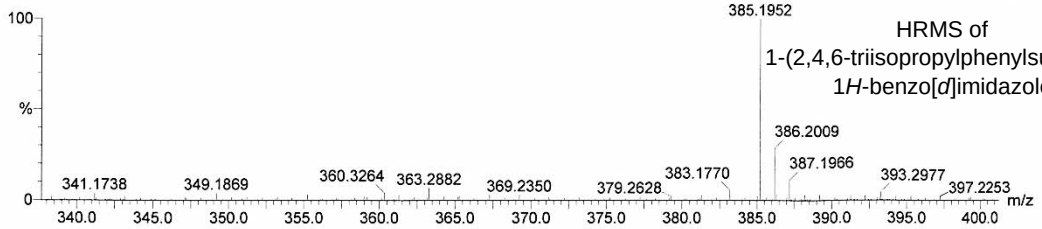
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Even Electron Ions
1313 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-22 H: 0-29 N: 0-3 O: 0-10 Na: 0-1 S: 0-6
Kin-Dept-10012011 HS S8 47 (0.880) Cn (Cen,10, 80.00, Ar); Sm (SG, 2x3.00); Sb (10,10.00); Cm (37:57)
TOF MS ES+



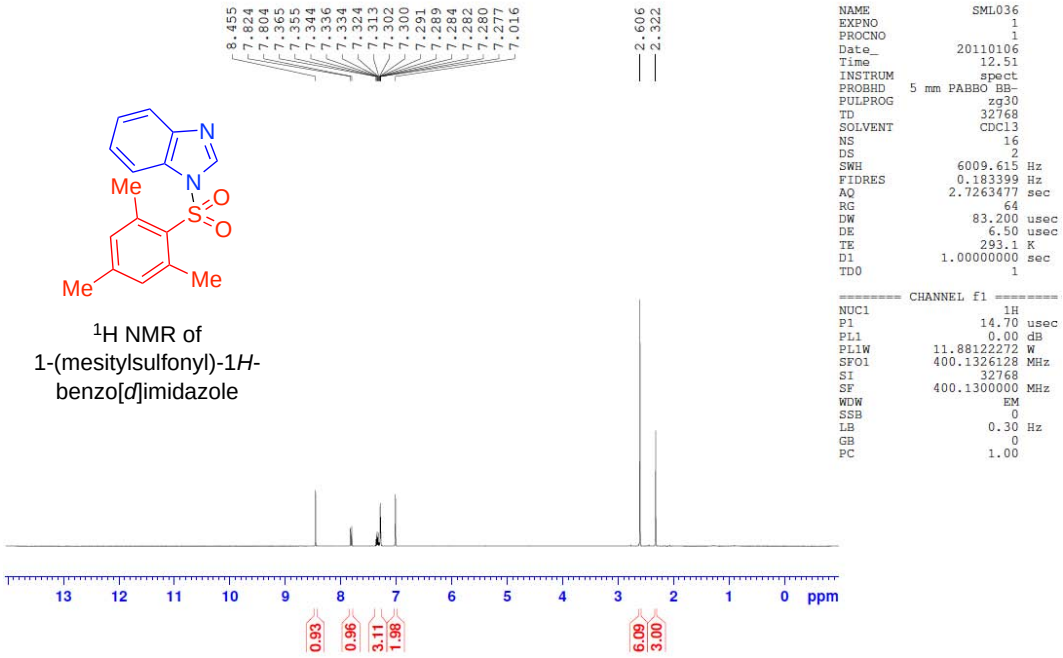
HRMS of
1-(2,4,6-triisopropylphenylsulfonyl)-
1*H*-benzo[*d*]imidazole



Minimum:				-1.5		
Maximum:		5.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
385.1952	385.1950	0.2	0.5	9.5	89.3	C22 H29 N2 O2 S

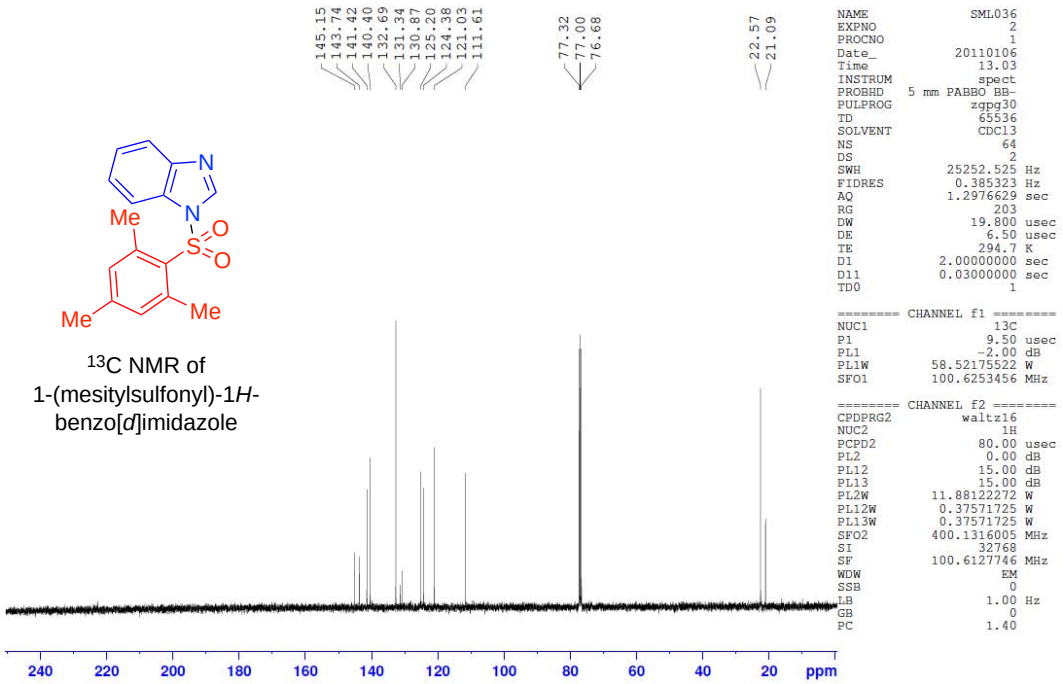
1-(Mesitylsulfonyl)-1*H*-benzo[*d*]imidazole (**Table 2.10**, entry 4)

SML036 1H



^{1}H NMR of 1-(mesitylsulfonyl)-1*H*-benzo[*d*]imidazole

SML036 13C

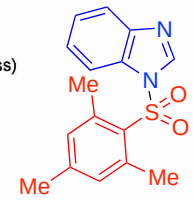


^{13}C NMR of 1-(mesitylsulfonyl)-1*H*-benzo[*d*]imidazole

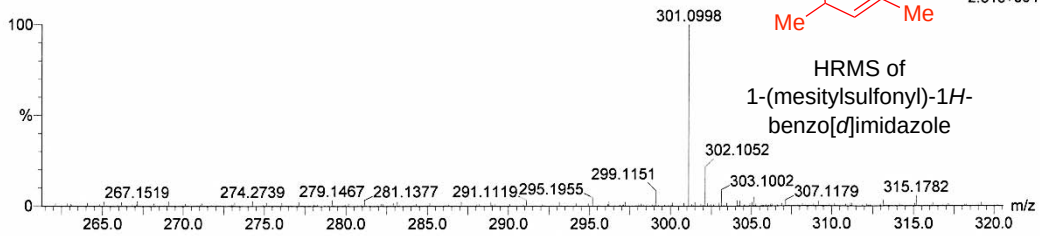
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Even Electron Ions
730 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-16 H: 0-17 N: 0-3 O: 0-10 Na: 0-1 S: 0-6
Kin-Dept-10012011 HS S9 46 (0.861) Cn (Cen,10, 80.00, Ar); Sm (SG, 2x3.00); Sb (10,10.00); Cm (36:59)
TOF MS ES+



2.31e+004

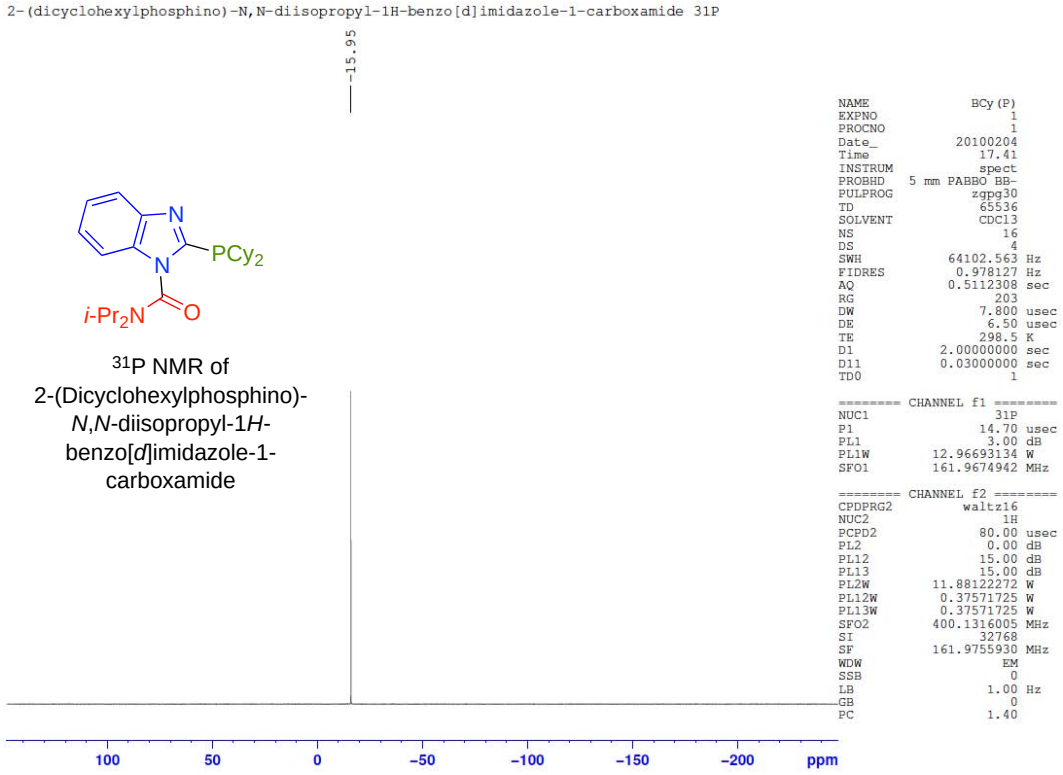


HRMS of
1-(mesitylsulfonyl)-1*H*-
benzo[*d*]imidazole

Minimum:				-1.5		
Maximum:		5.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
301.0998	301.1011	-1.3	-4.3	9.5	65.1	C16 H17 N2 O2 S

Chapter 2 HMR and HRMS Spectra of 2-Phosphino-Substituted Benzimidazolyl Ligands

2-(Dicyclohexylphosphino)-*N*,*N*-diisopropyl-1*H*-benzo[*d*]imidazole-1-carboxamide (PCy Amizole-phos **L2a**) (**Table 2.11**, entry 1)

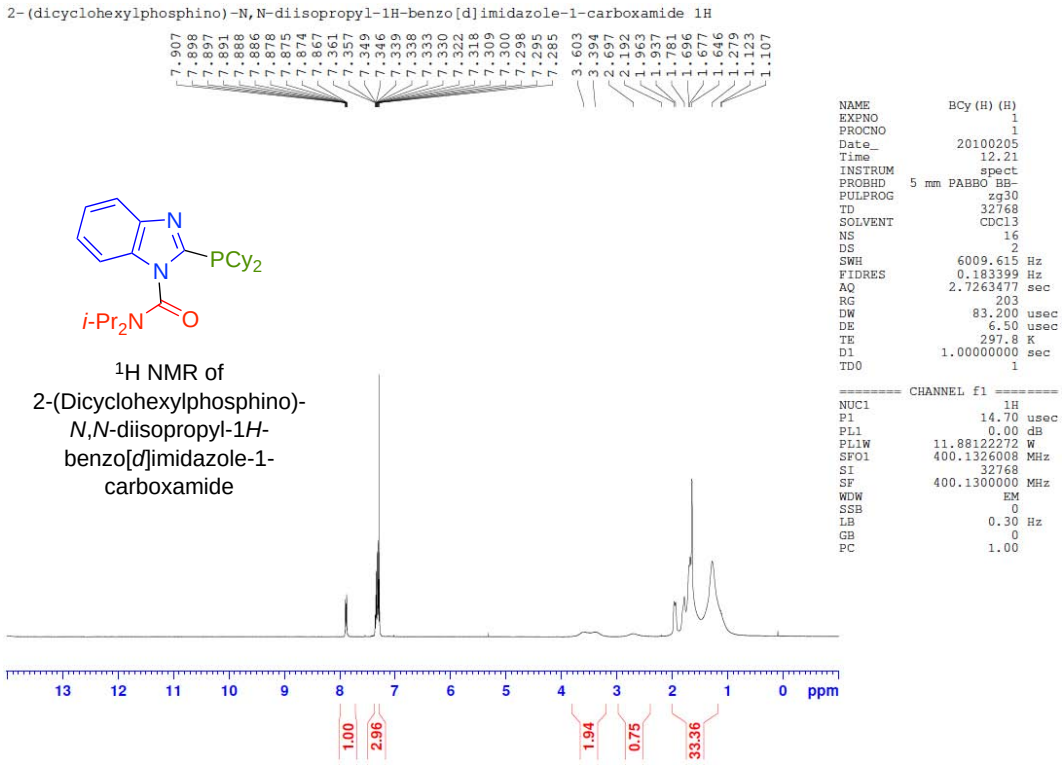


^{31}P NMR of 2-(Dicyclohexylphosphino)-*N*,*N*-diisopropyl-1*H*-benzo[*d*]imidazole-1-carboxamide

```
NAME                 BCy (P)
EXPNO                      1
PROCNO                     1
Date_               20100204
Time                   17.41
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                    298.5 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

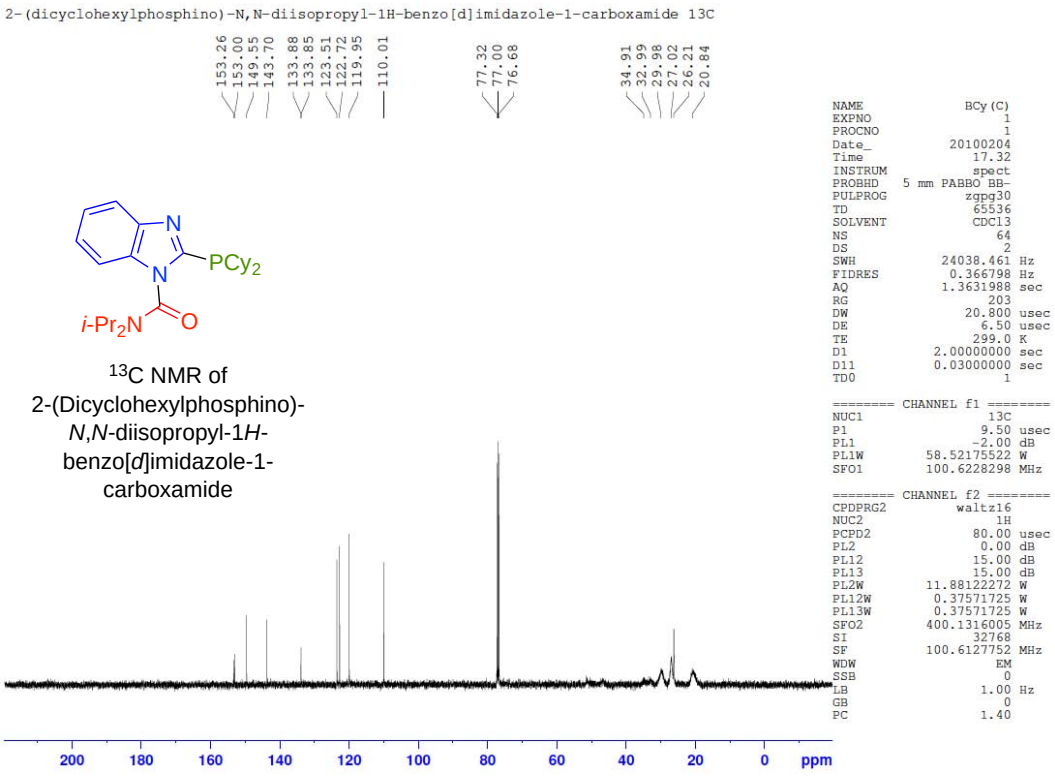
======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                     1H
PCPD2                 80.00 usec
PL2                    0.00 dB
PL12                  15.00 dB
PL13                  15.00 dB
PL2W              11.88122272 W
PL12W              0.37571725 W
PL13W              0.37571725 W
SFO2             400.1316005 MHz
SI                     32768
SF               161.9755930 MHz
WDW                       EM
SSB                        0
LB                     1.00 Hz
GB                         0
PC                      1.40
```



^{1}H NMR of 2-(Dicyclohexylphosphino)-*N*,*N*-diisopropyl-1*H*-benzo[*d*]imidazole-1-carboxamide

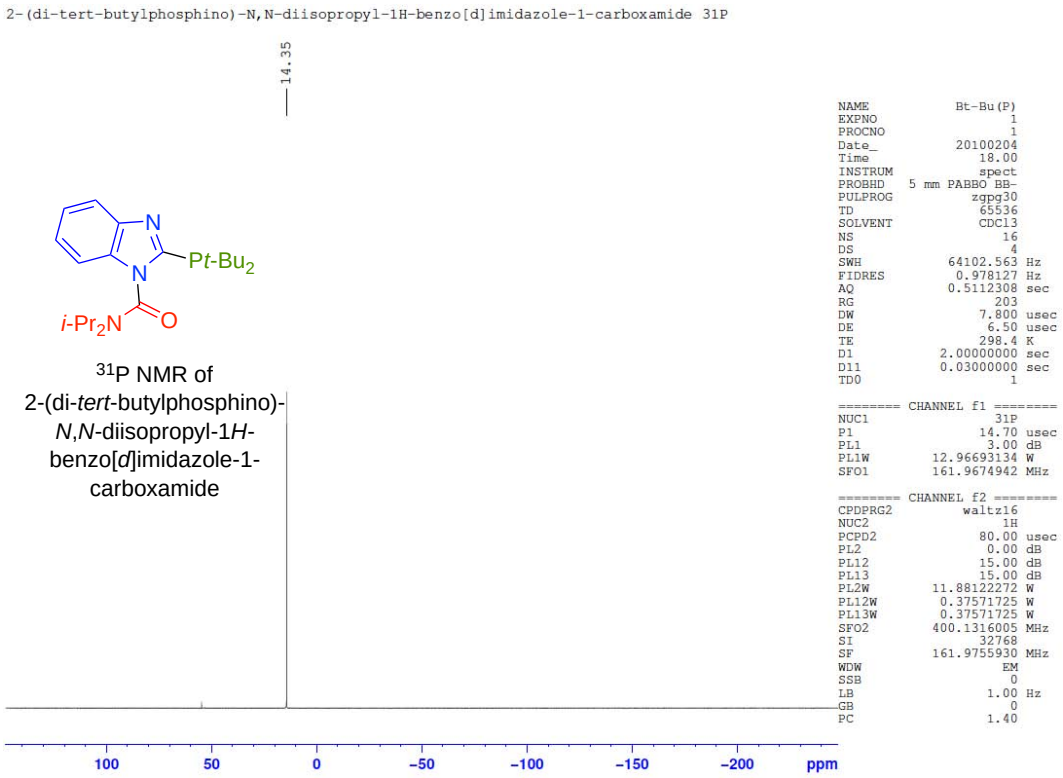
```
NAME              BCy (H) (H)
EXPNO                      1
PROCNO                     1
Date_               20100205
Time                   12.21
INSTRUM                spect
PROBHD     5 mm PABBO BB-
PULPROG                zg30
TD                     32768
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                6009.615 Hz
FIDRES             0.183399 Hz
AQ                 2.7263477 sec
RG                       203
DW                   83.200 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             400.1326008 MHz
SI                     32768
SF               400.1300000 MHz
WDW                       EM
SSB                        0
LB                     0.30 Hz
GB                         0
PC                      1.00
```

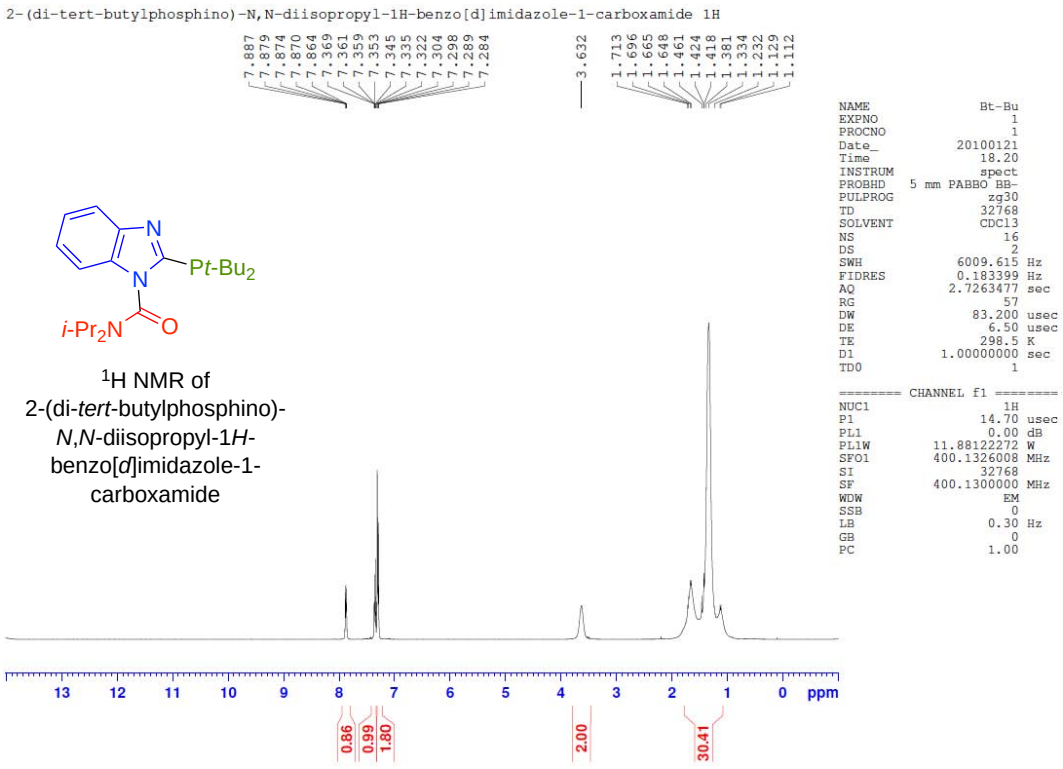


^{13}C NMR of 2-(Dicyclohexylphosphino)-*N*,*N*-diisopropyl-1*H*-benzo[*d*]imidazole-1-carboxamide

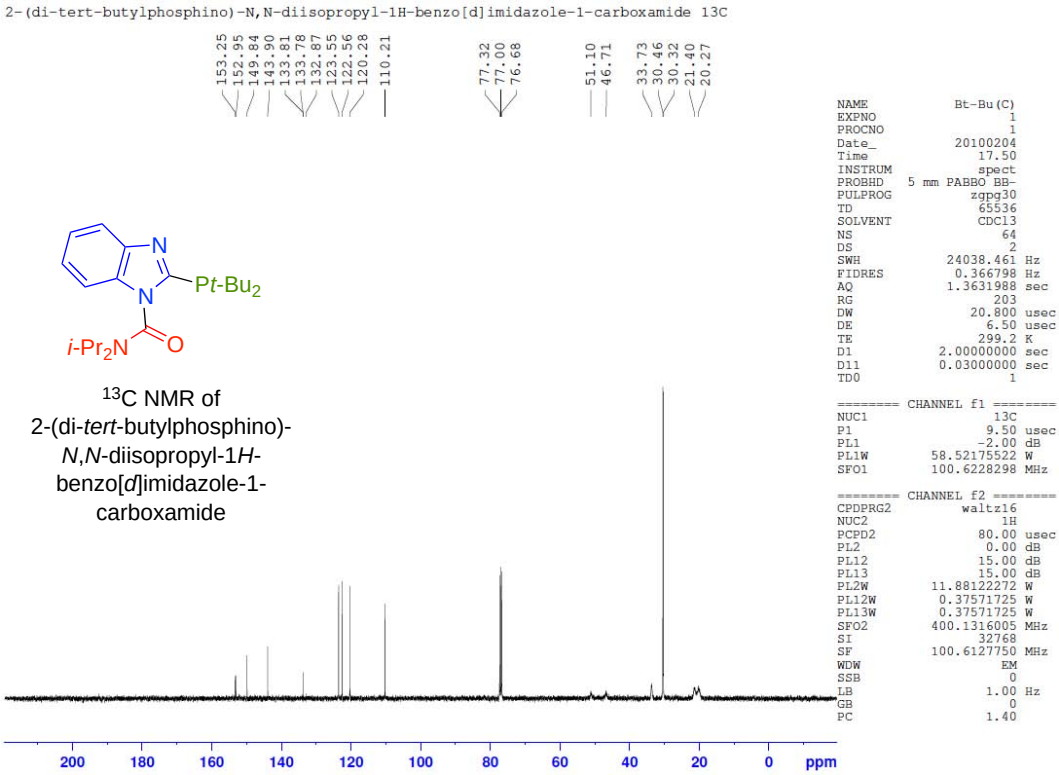
2-(Di-*tert*-butylphosphino)-*N*,*N*-diisopropyl-1*H*-benzo[*d*]imidazole-1-carboxamide (P*t*-Bu Amizole-phos **L2b**) (**Table 2.11**, entry 2)



^{31}P NMR of 2-(di-*tert*-butylphosphino)-*N*,*N*-diisopropyl-1*H*-benzo[*d*]imidazole-1-carboxamide



^{1}H NMR of 2-(di-*tert*-butylphosphino)-*N*,*N*-diisopropyl-1*H*-benzo[*d*]imidazole-1-carboxamide

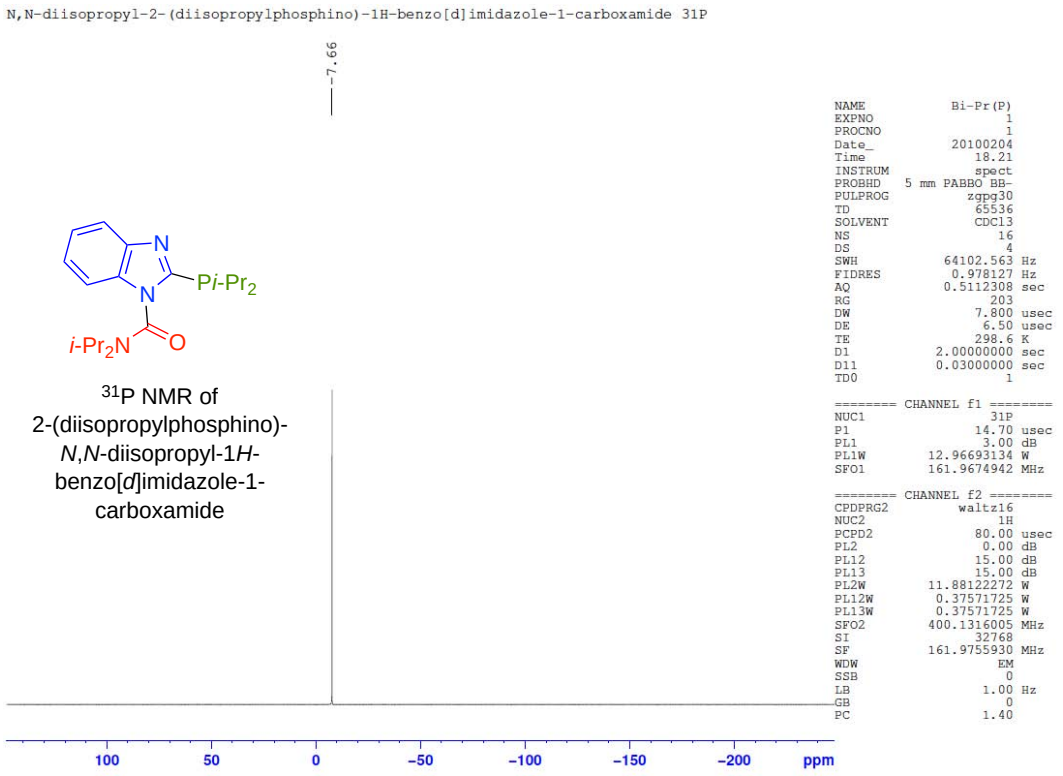


^{13}C NMR of 2-(di-*tert*-butylphosphino)-*N*,*N*-diisopropyl-1*H*-benzo[*d*]imidazole-1-carboxamide

NAME	Bt-Bu(C)
EXPNO	1
PROCNO	1
Date_	20100204
Time	17.50
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	64
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	100.6127750 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

2-(Diisopropylphosphino)-*N*,*N*-diisopropyl-1*H*-benzo[*d*]imidazole-1-carboxamide

(P*i*-Pr Amizole-phos **L2c**) (**Table 2.11**, entry 3)

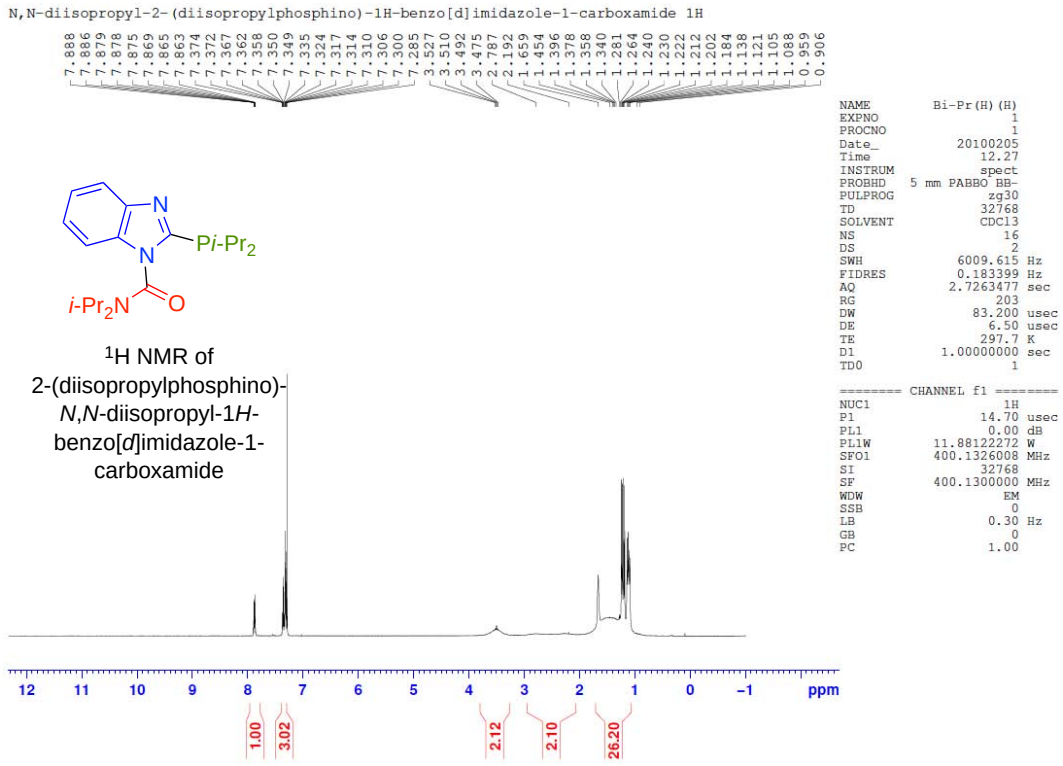


^{31}P NMR of 2-(diisopropylphosphino)-*N*,*N*-diisopropyl-1*H*-benzo[*d*]imidazole-1-carboxamide

```
NAME            Bi-Pr(P)
EXPNO                  1
PROCNO                 1
Date_           20100204
Time               18.21
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                 298.6 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

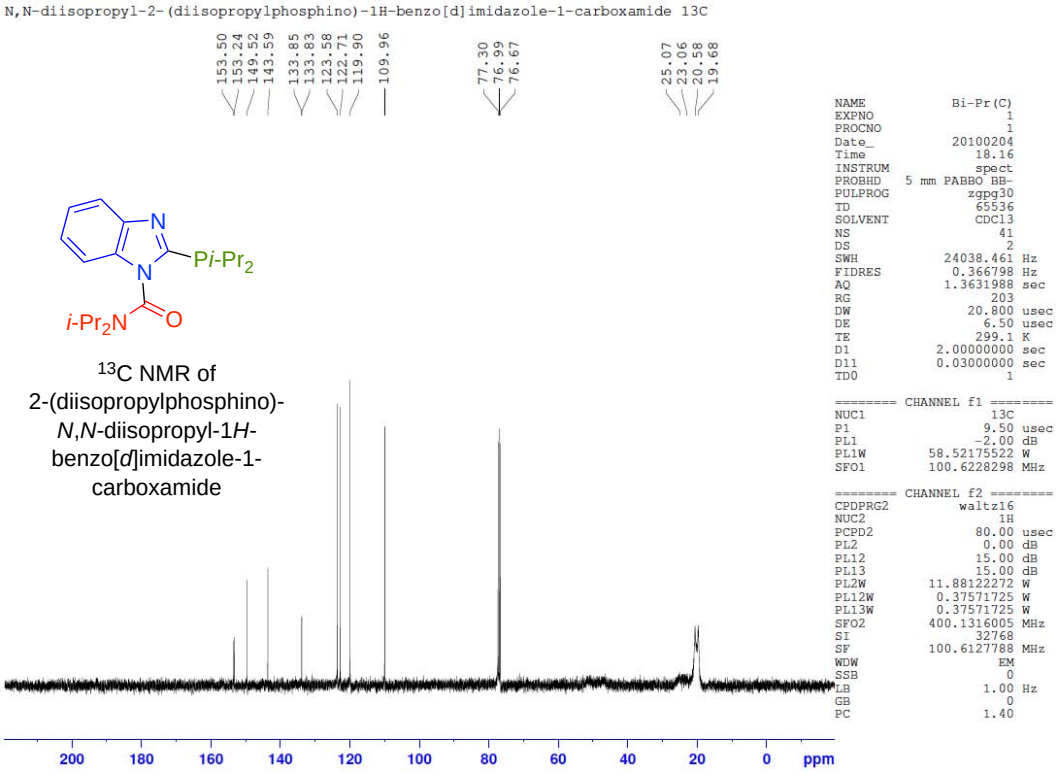
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.88122272 W
PL12W         0.37571725 W
PL13W         0.37571725 W
SFO2        400.1316005 MHz
SI                 32768
SF          161.9755930 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



^{1}H NMR of 2-(diisopropylphosphino)-*N*,*N*-diisopropyl-1*H*-benzo[*d*]imidazole-1-carboxamide

```
NAME         Bi-Pr(H)(H)
EXPNO                  1
PROCNO                 1
Date_           20100205
Time               12.27
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6009.615 Hz
FIDRES         0.183399 Hz
AQ             2.7263477 sec
RG                   203
DW                83.200 usec
DE                 6.50 usec
TE                 297.7 K
D1            1.00000000 sec
TD0                    1

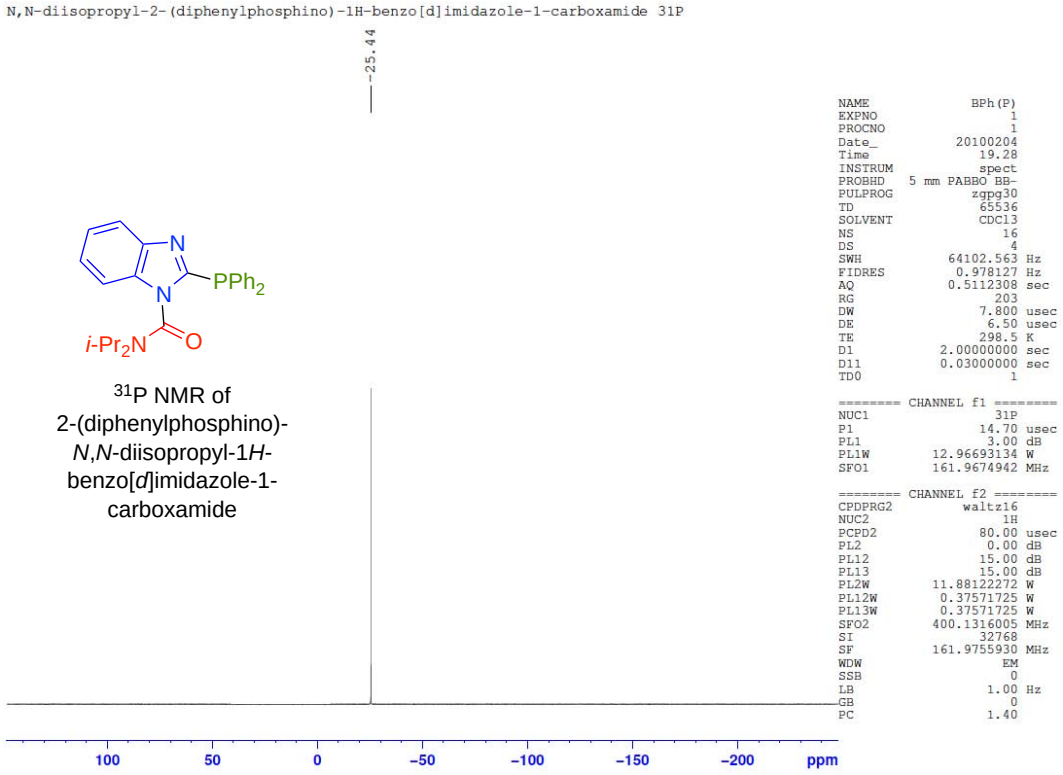
======== CHANNEL f1 ========
NUC1                 1H
P1                 14.70 usec
PL1                 0.00 dB
PL1W         11.88122272 W
SFO1        400.1326008 MHz
SI                 32768
SF          400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



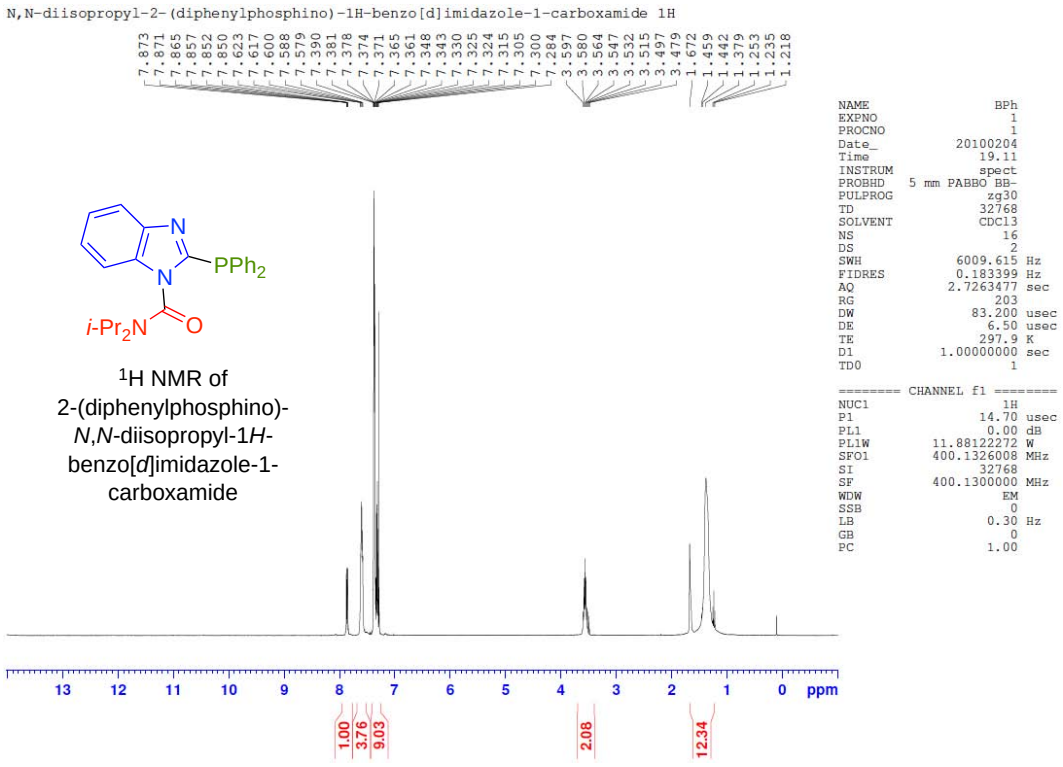
^{13}C NMR of 2-(diisopropylphosphino)-*N*,*N*-diisopropyl-1*H*-benzo[*d*]imidazole-1-carboxamide

2-(Diphenylphosphino)-*N*,*N*-diisopropyl-1*H*-benzo[*d*]imidazole-1-carboxamide

(PPh Amizole-phos **L2d**) (**Table 2.11**, entry 4)

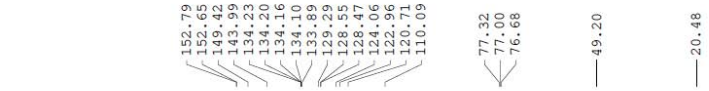


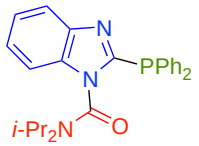
^{31}P NMR of 2-(diphenylphosphino)-*N*,*N*-diisopropyl-1*H*-benzo[*d*]imidazole-1-carboxamide



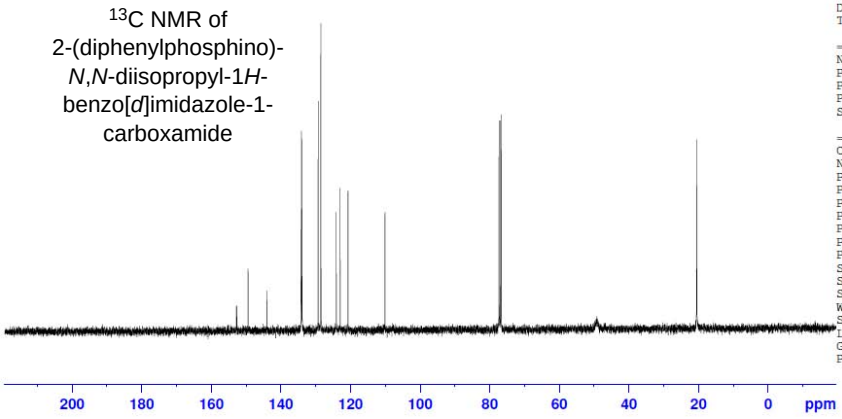
^{1}H NMR of 2-(diphenylphosphino)-*N*,*N*-diisopropyl-1*H*-benzo[*d*]imidazole-1-carboxamide

N,N-diisopropyl-2-(diphenylphosphino)-1H-benzo[d]imidazole-1-carboxamide 13C





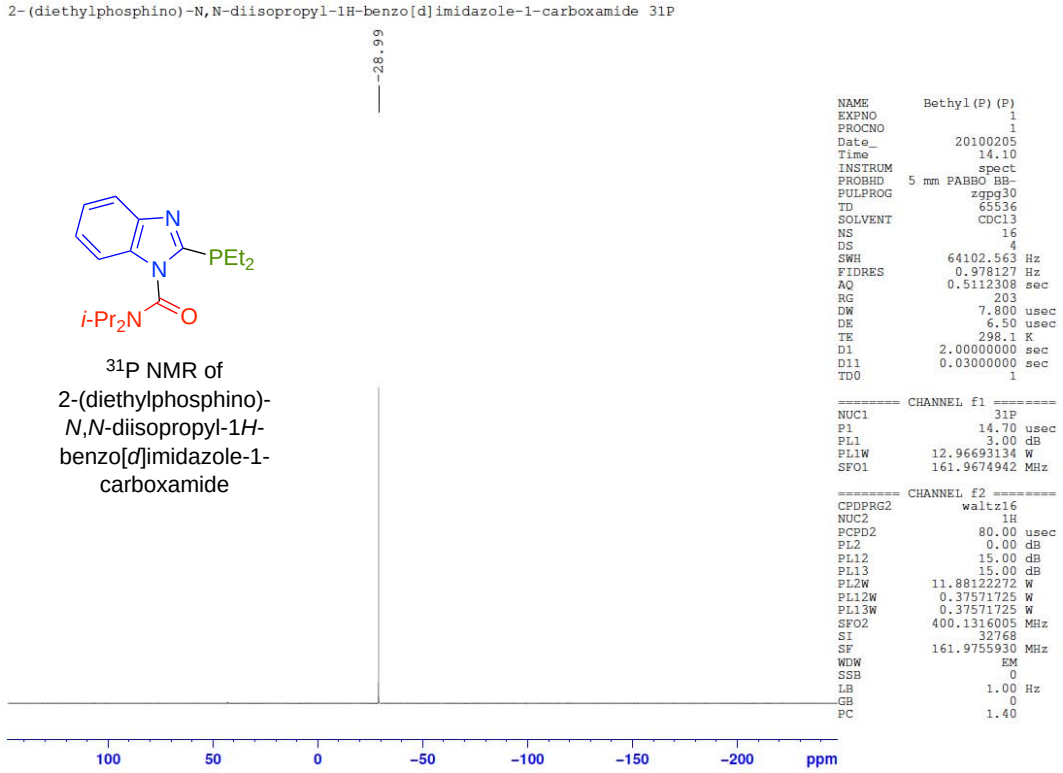
^{13}C NMR of 2-(diphenylphosphino)-*N*,*N*-diisopropyl-1*H*-benzo[*d*]imidazole-1-carboxamide



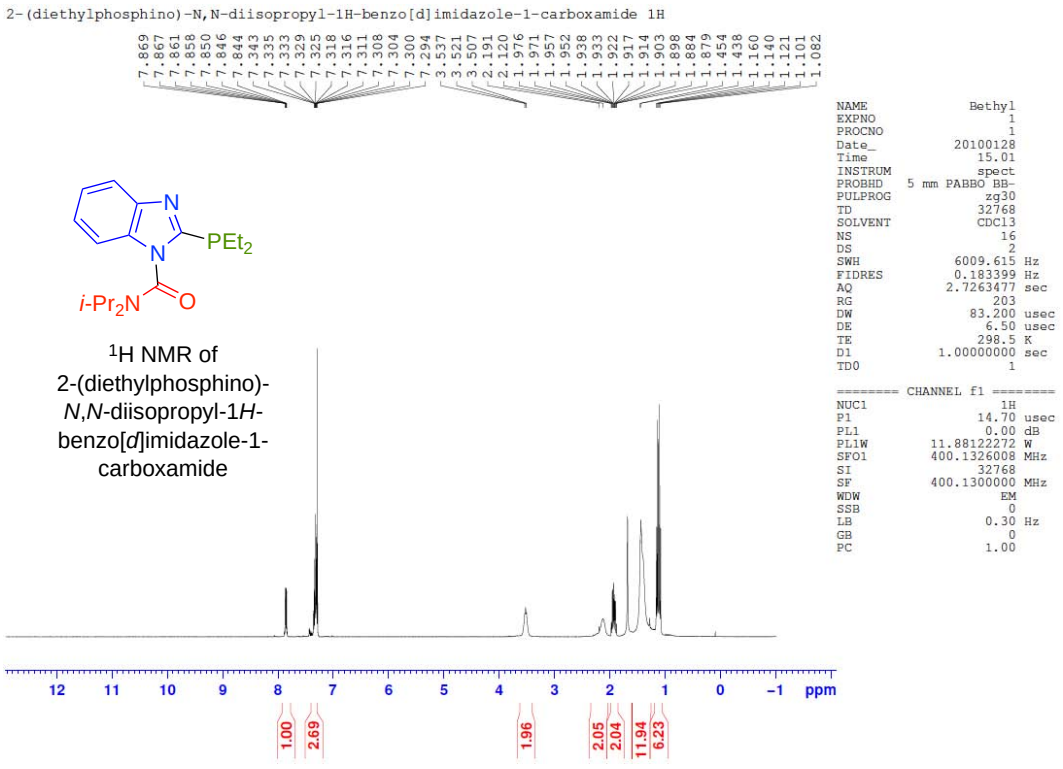
NAME	BPh(C)
EXPNO	1
PROCNO	1
Date_	20100204
Time	19.21
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	64
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	181
DW	20.800 usec
DE	6.50 usec
TE	299.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
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	100.6127778 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

2-(Diethylphosphino)-*N*,*N*-diisopropyl-1*H*-benzo[*d*]imidazole-1-carboxamide

(PEt Amizole-phos **L2e**) (**Table 2.11**, entry 5)

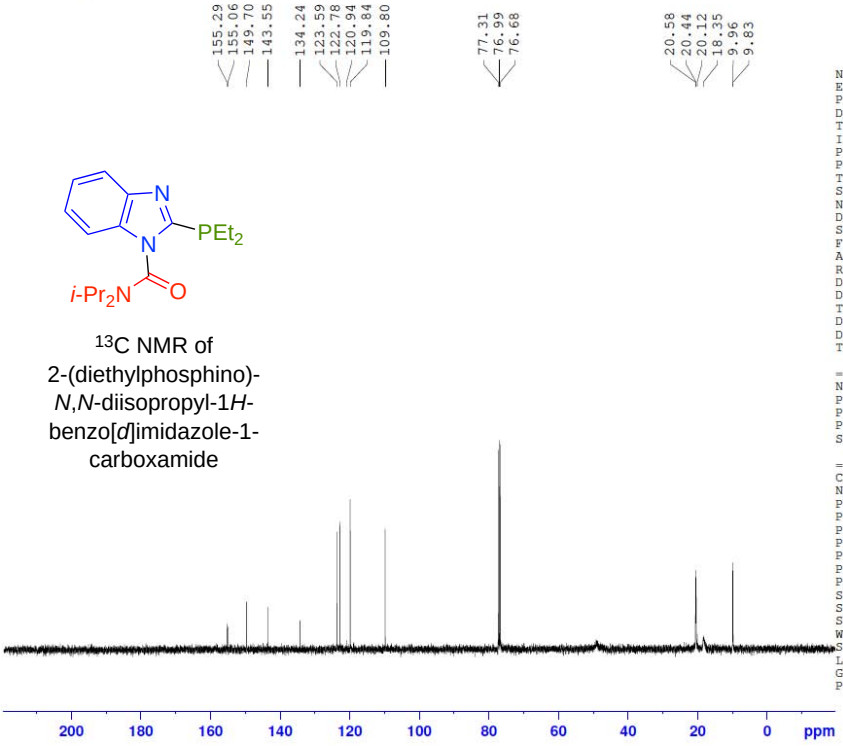


^{31}P NMR of 2-(diethylphosphino)-*N*,*N*-diisopropyl-1*H*-benzo[*d*]imidazole-1-carboxamide



^{1}H NMR of 2-(diethylphosphino)-*N*,*N*-diisopropyl-1*H*-benzo[*d*]imidazole-1-carboxamide

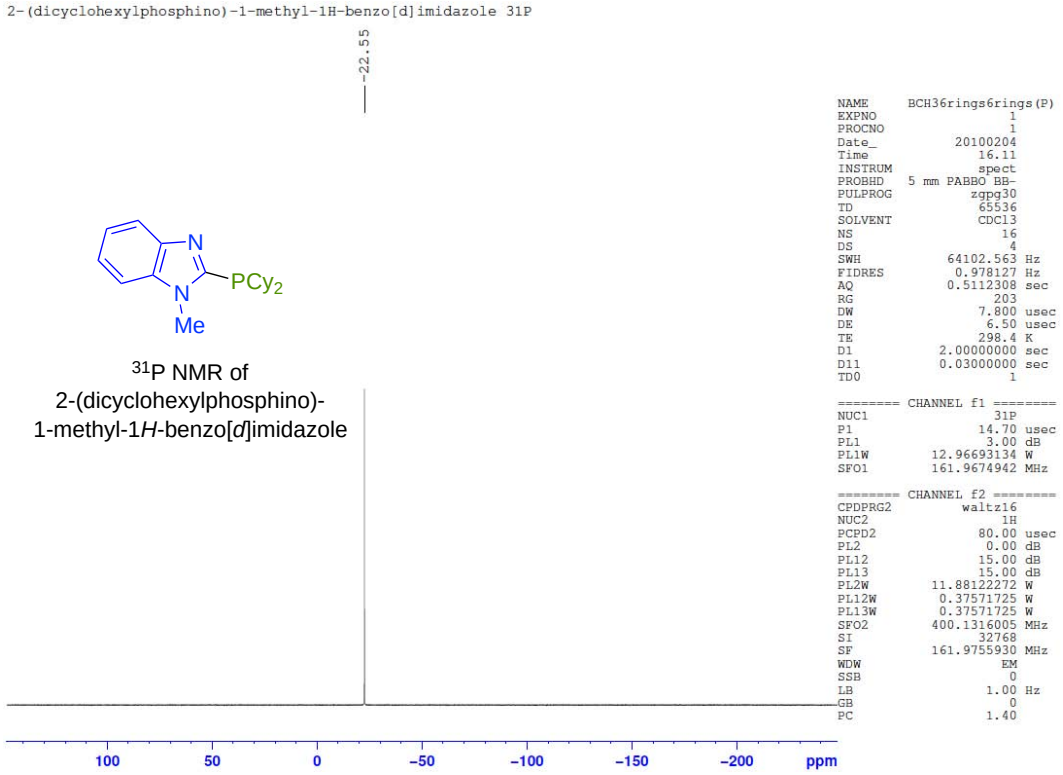
2-(diethylphosphino)-N,N-diisopropyl-1H-benzo[d]imidazole-1-carboxamide 13C



^{13}C NMR of 2-(diethylphosphino)-*N*,*N*-diisopropyl-1*H*-benzo[*d*]imidazole-1-carboxamide

NAME	BEth(C)
EXPNO	1
PROCNO	1
Date_	20100201
Time	15.44
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	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	100.6127755 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

2-(Dicyclohexylphosphino)-1-methyl-1*H*-benzo[*d*]imidazole (PCy Mezole-phos **L2f**) (**Table 2.11**, entry 6)

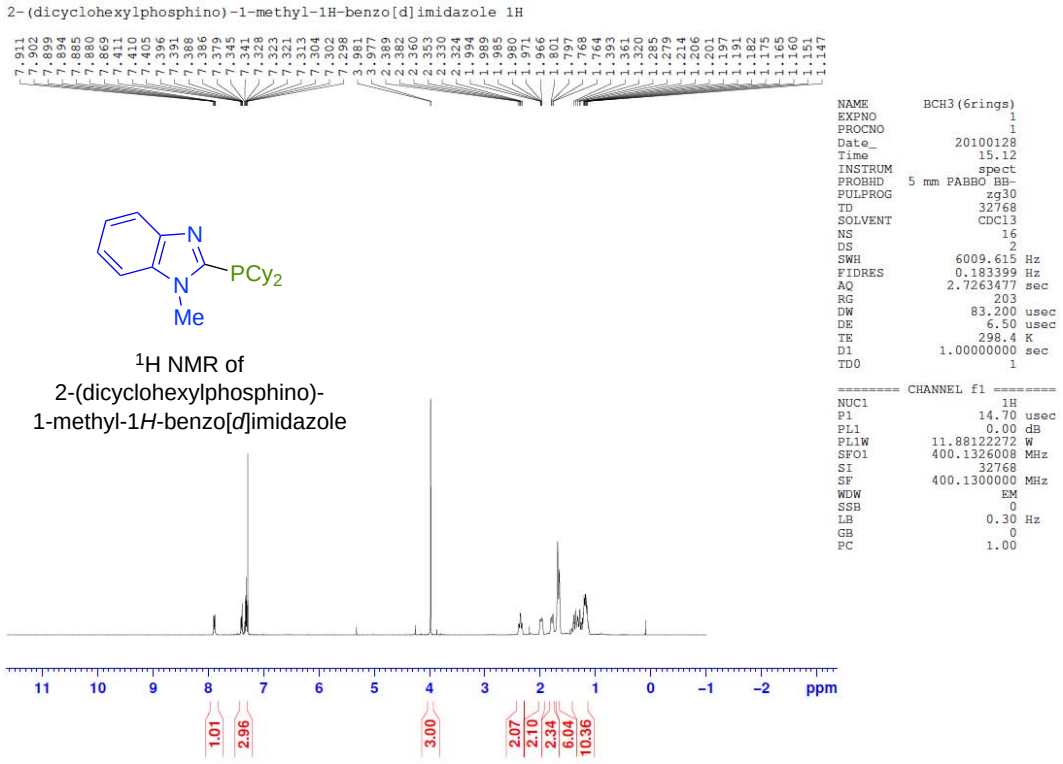


^{31}P NMR of 2-(dicyclohexylphosphino)-1-methyl-1*H*-benzo[*d*]imidazole

```
NAME          BCH36rings6rings(P)
EXPNO                           1
PROCNO                          1
Date_                    20100204
Time                        16.11
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                         298.4 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
```



^{1}H NMR of 2-(dicyclohexylphosphino)-1-methyl-1*H*-benzo[*d*]imidazole

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EXPNO                      1
PROCNO                     1
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Time                   15.12
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PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                        16
DS                         2
SWH                6009.615 Hz
FIDRES             0.183399 Hz
AQ                 2.7263477 sec
RG                       203
DW                    83.200 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           400.1326008 MHz
SI                    32768
SF             400.1300000 MHz
WDW                       EM
SSB                        0
LB                     0.30 Hz
GB                         0
PC                     1.00
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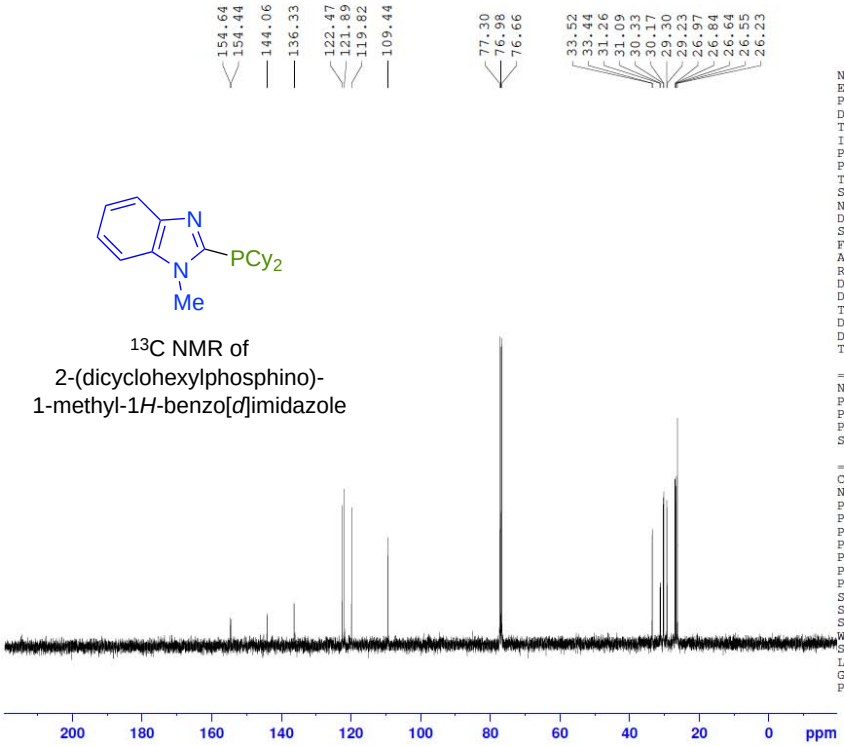
2-(dicyclohexylphosphino)-1-methyl-1H-benzo[d]imidazole 13C



^{13}C NMR of
2-(dicyclohexylphosphino)-
1-methyl-1*H*-benzo[*d*]imidazole

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PROCNO	1
Date_	20100201
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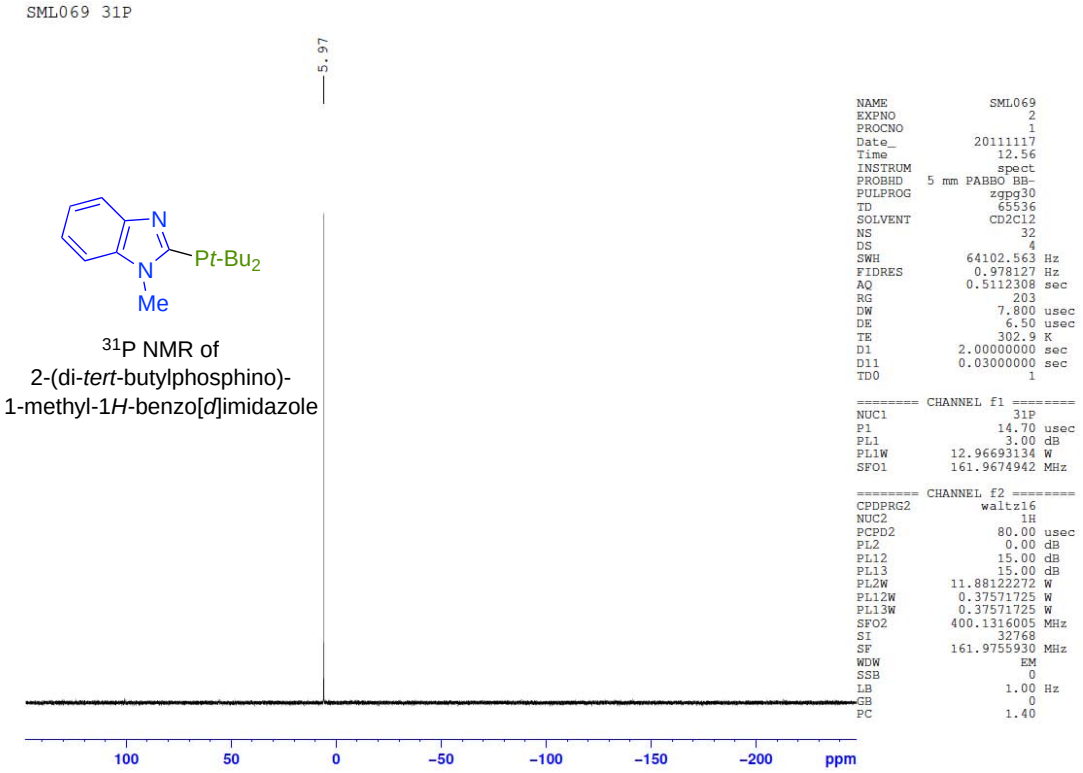
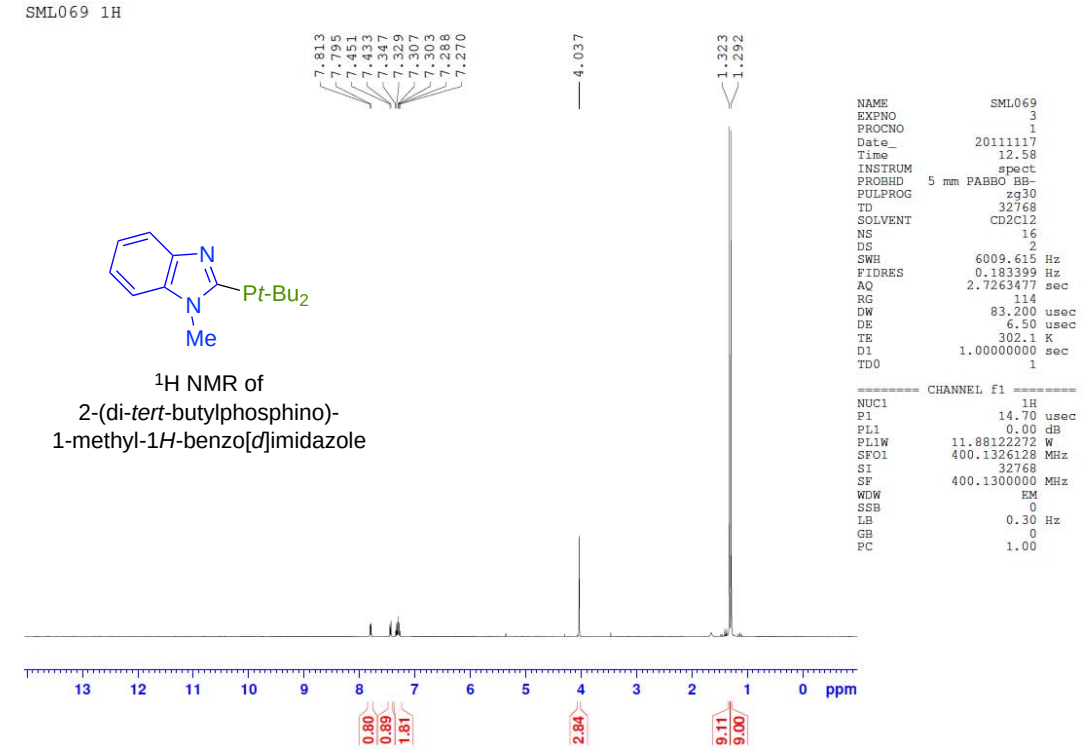
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	32
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	181
DW	20.800 usec
DE	6.50 usec
TE	299.9 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz
========	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-(Di-*tert*-butylphosphino)-1-methyl-1*H*-benzo[*d*]imidazole (P*t*-Bu Mezole-phos **L2g**) (**Table 2.11**, entry 7)

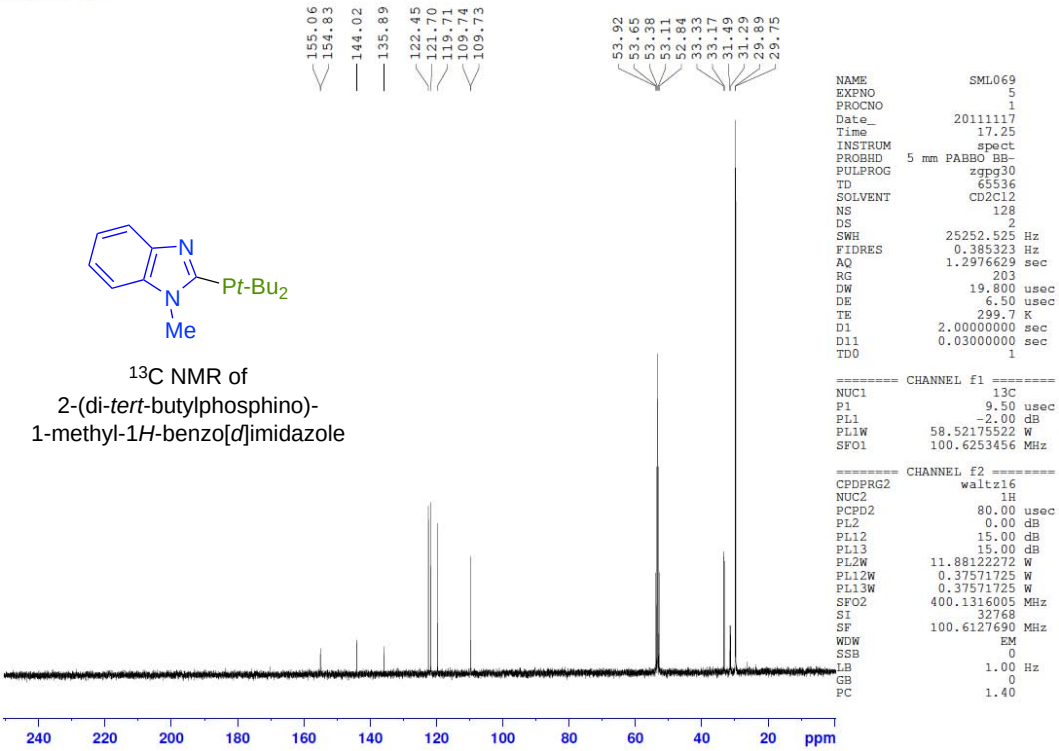




^{31}P NMR of 2-(di-*tert*-butylphosphino)-1-methyl-1*H*-benzo[*d*]imidazole

^{1}H NMR of 2-(di-*tert*-butylphosphino)-1-methyl-1*H*-benzo[*d*]imidazole

SML069 13C



NAME SML069
EXPNO 5
PROCNO 1
Date_ 20111117
Time 17.25
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CD2Cl2
NS 128
DS 2
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976629 sec
RG 203
DW 19.800 usec
DE 6.50 usec
TE 299.7 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 100.6253456 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

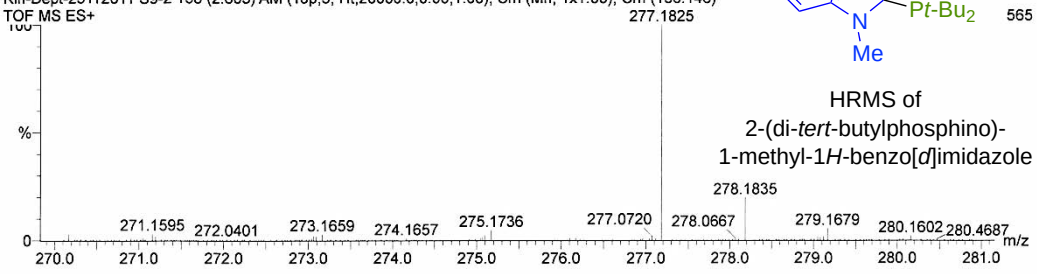
^{13}C NMR of
2-(di-*tert*-butylphosphino)-
1-methyl-1*H*-benzo[*d*]imidazole

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
105 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-16 H: 0-26 N: 0-4 Na: 0-1 P: 0-2 39K: 0-1

Kin-Dept-23112011 S9-2 138 (2.603) AM (Top,3, Ht,20000.0,0.00,1.00); Sm (Mn, 1x1.00); Cm (136:146)
TOF MS ES+

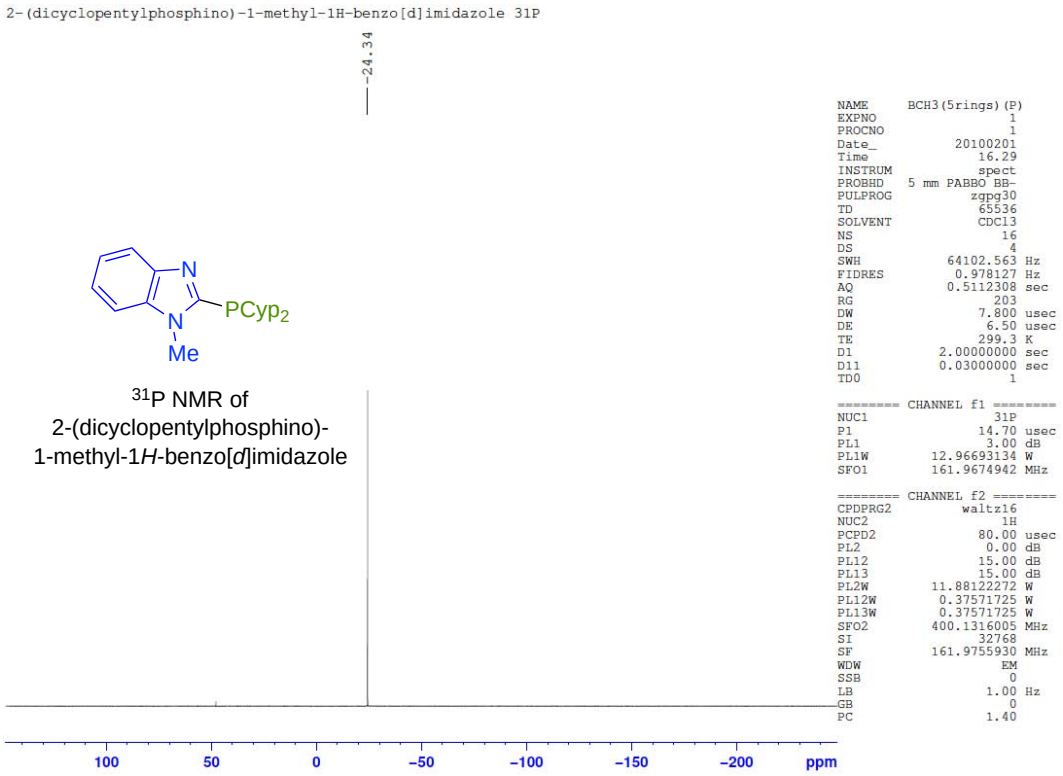


565

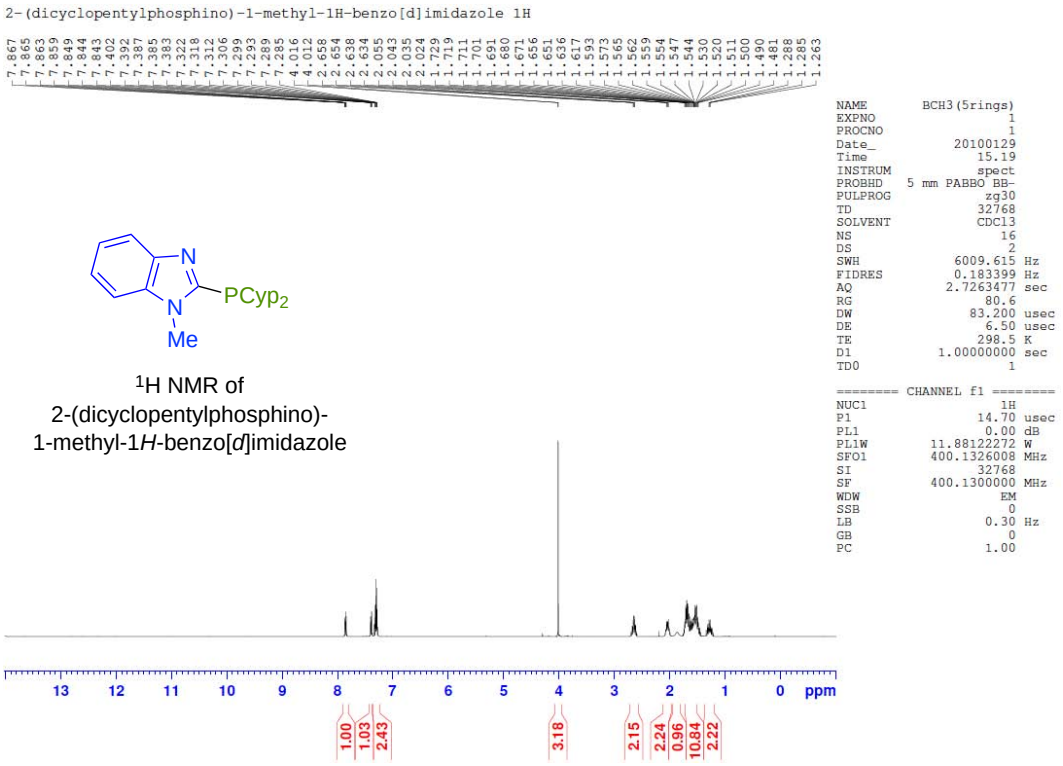
HRMS of
2-(di-*tert*-butylphosphino)-
1-methyl-1*H*-benzo[*d*]imidazole

Minimum:				-1.5		
Maximum:		5.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
277.1825	277.1834	-0.9	-3.2	5.5	7.7	C16 H26 N2 P

2-(Dicyclopentylphosphino)-1-methyl-1*H*-benzo[*d*]imidazole (PCyp Mezole-phos **L2h**) (**Table 2.11**, entry 8)

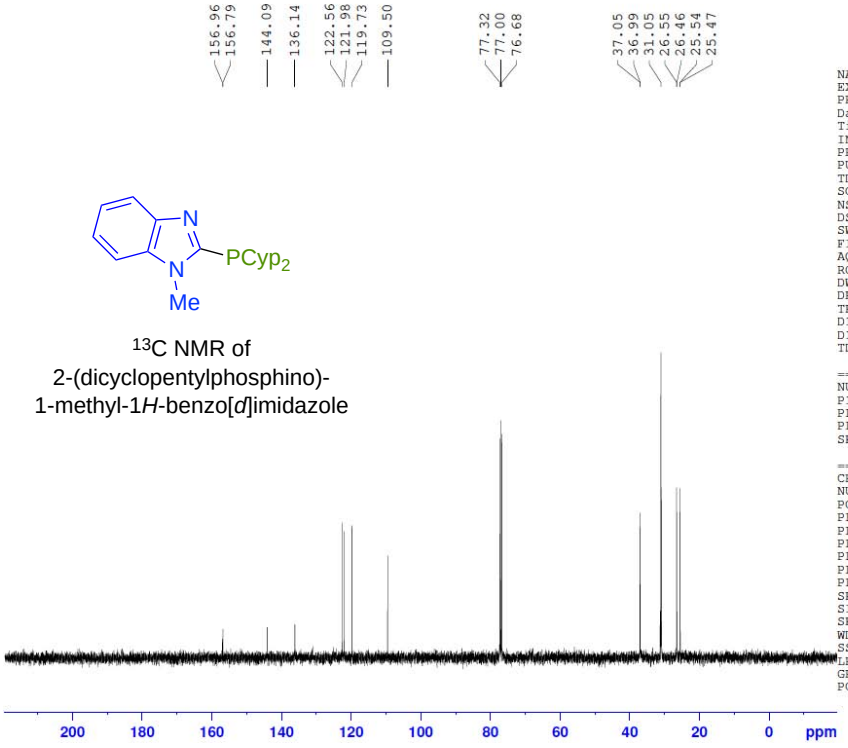


^{31}P NMR of 2-(dicyclopentylphosphino)-1-methyl-1*H*-benzo[*d*]imidazole



^{1}H NMR of 2-(dicyclopentylphosphino)-1-methyl-1*H*-benzo[*d*]imidazole

2-(dicyclopentylphosphino)-1-methyl-1H-benzo[d]imidazole 13C



^{13}C NMR of
2-(dicyclopentylphosphino)-
1-methyl-1*H*-benzo[*d*]imidazole

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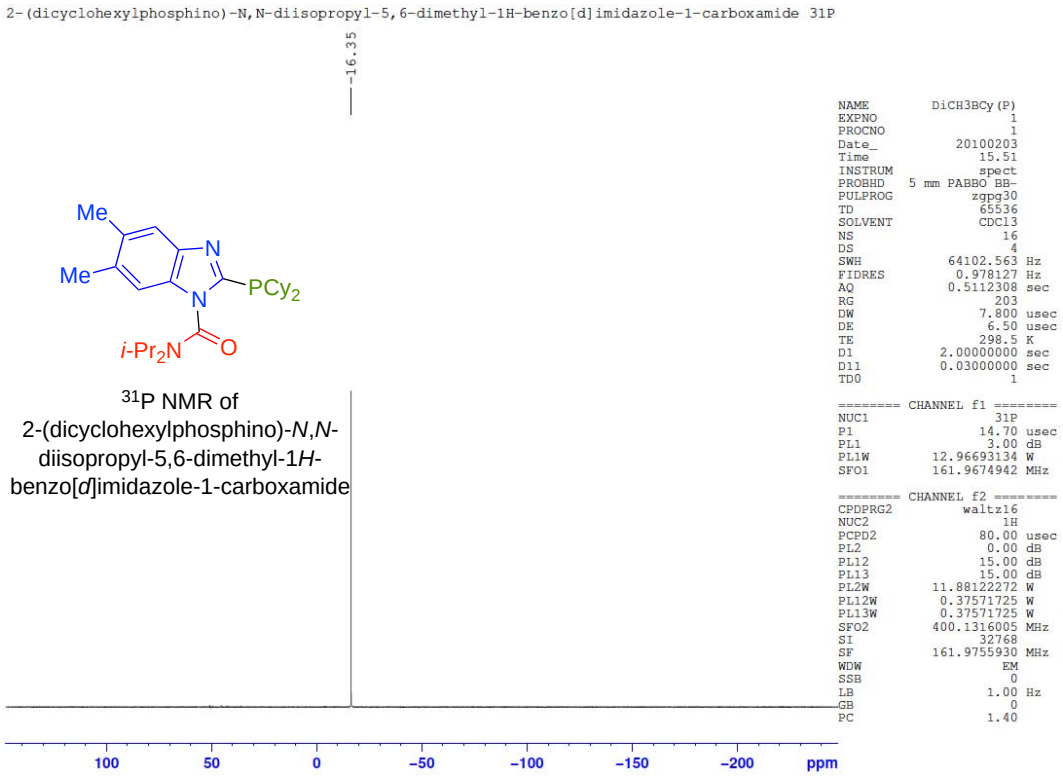
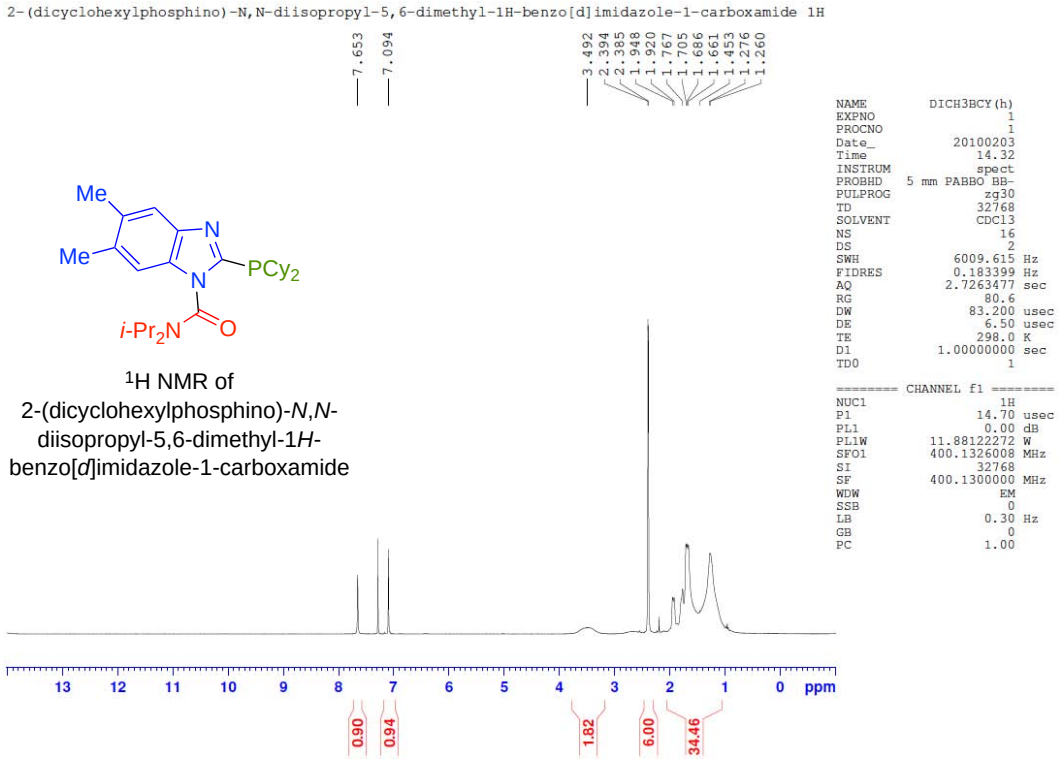
EXPNO	1	
PROCNO	1	
Date_	20100201	
Time	15.54	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	32	
DS	2	
SWH	24038.461	Hz
FIDRES	0.366798	Hz
AQ	1.3631988	sec
RG	114	
DW	20.800	usec
DE	6.50	usec
TE	299.8	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
======== CHANNEL f1 ========		
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	100.6127735	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

2-(Dicyclohexylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole -1-carboxamide (PCy Amizole^{M2}-phos **L2i**) (**Table 2.11**, entry 9)

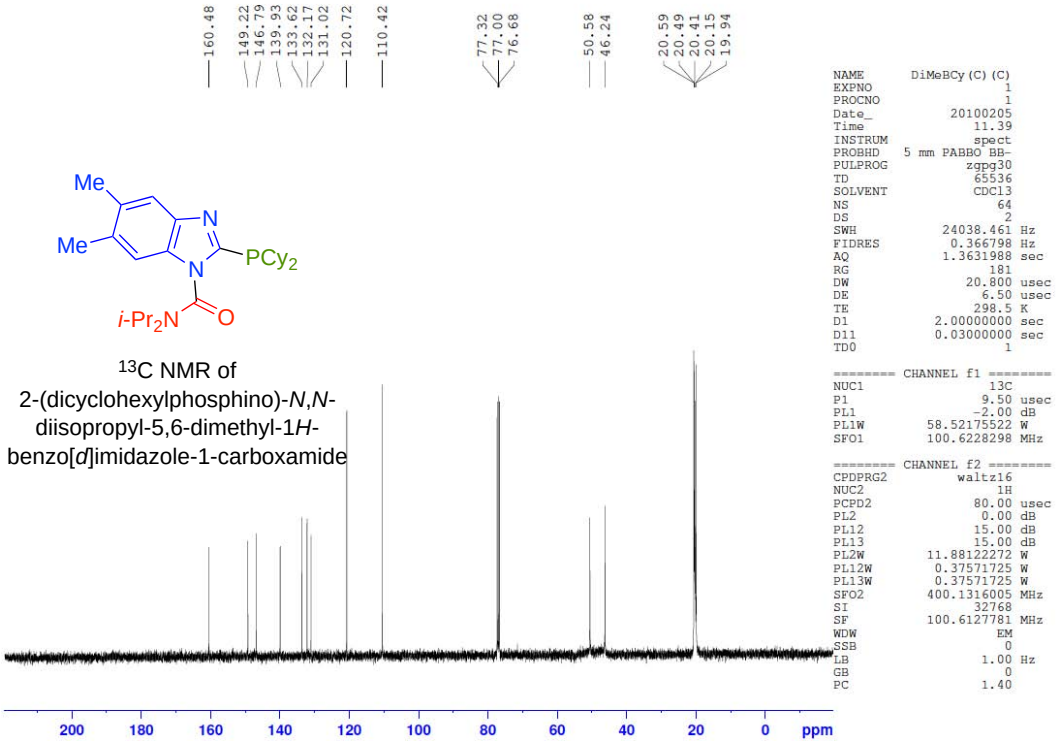


^{31}P NMR of 2-(dicyclohexylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide



^{1}H NMR of 2-(dicyclohexylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide

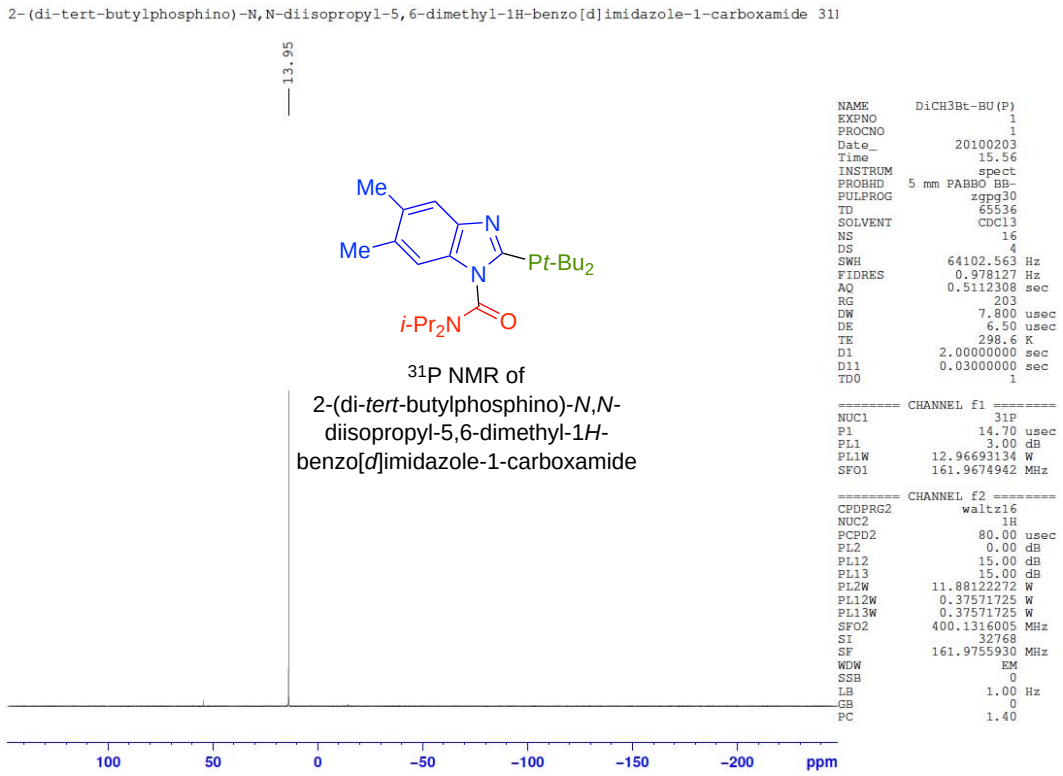
2-(dicyclohexylphosphino)-N,N-diisopropyl-5,6-dimethyl-1H-benzo[d]imidazole-1-carboxamide 13C



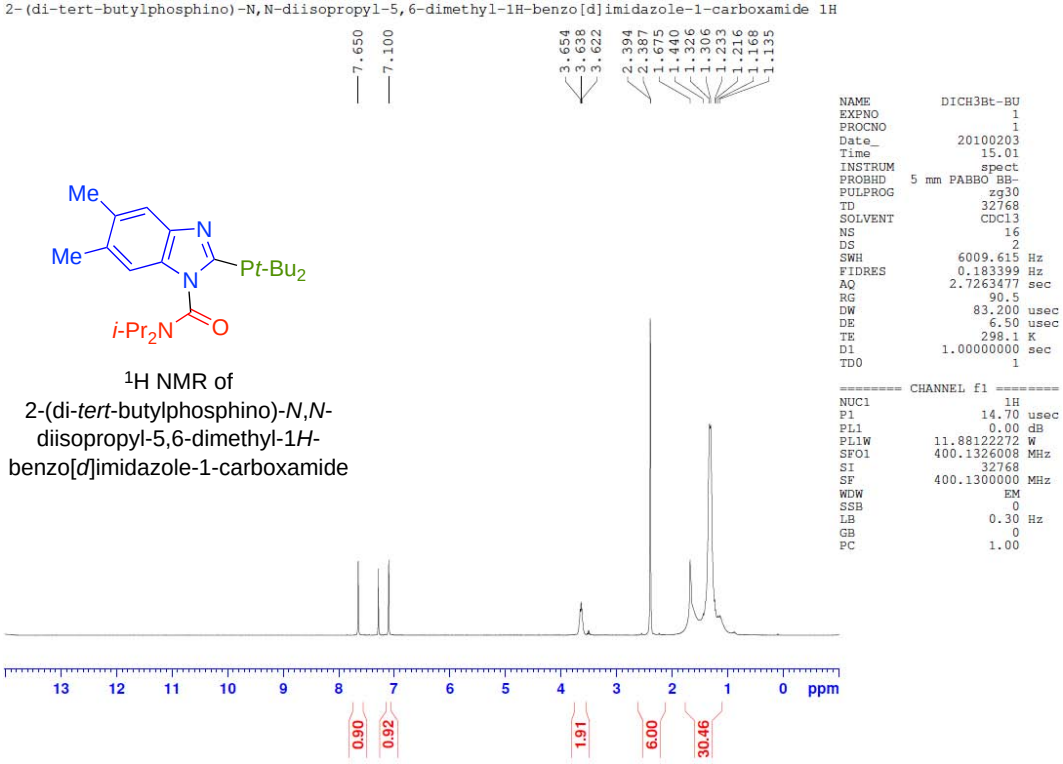
^{13}C NMR of 2-(dicyclohexylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide

NAME	DiMeBCy (C) (C)
EXPNO	1
PROCNO	1
Date_	20100205
Time	11.39
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	64
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	298.5 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	100.6127781 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

2-(Di-*tert*-butylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide (P*t*-Bu Amizole[M2]-phos **L2j**) (**Table 2.11**, entry 10)

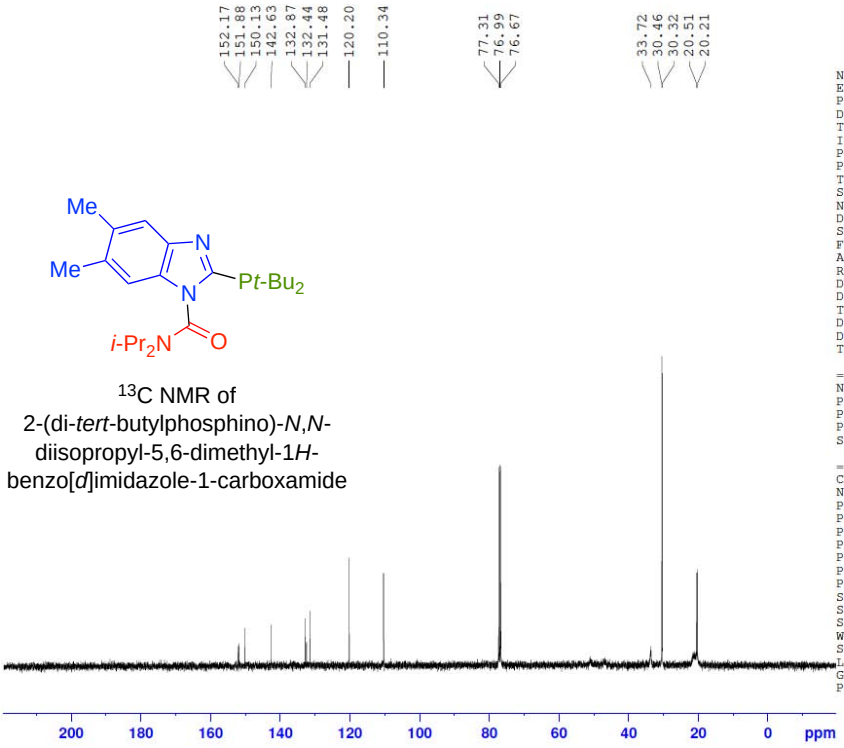


^{31}P NMR of 2-(di-*tert*-butylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide



^{1}H NMR of 2-(di-*tert*-butylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide

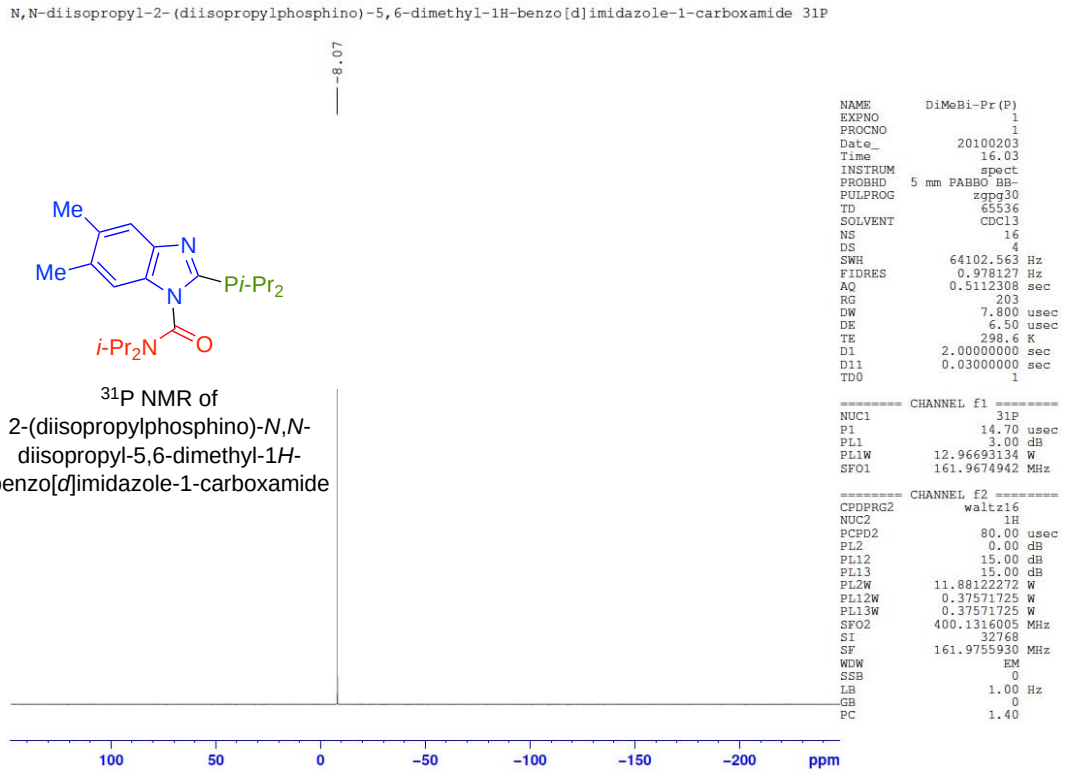
2-(di-tert-butylphosphino)-N,N-diisopropyl-5,6-dimethyl-1H-benzo[d]imidazole-1-carboxamide 13



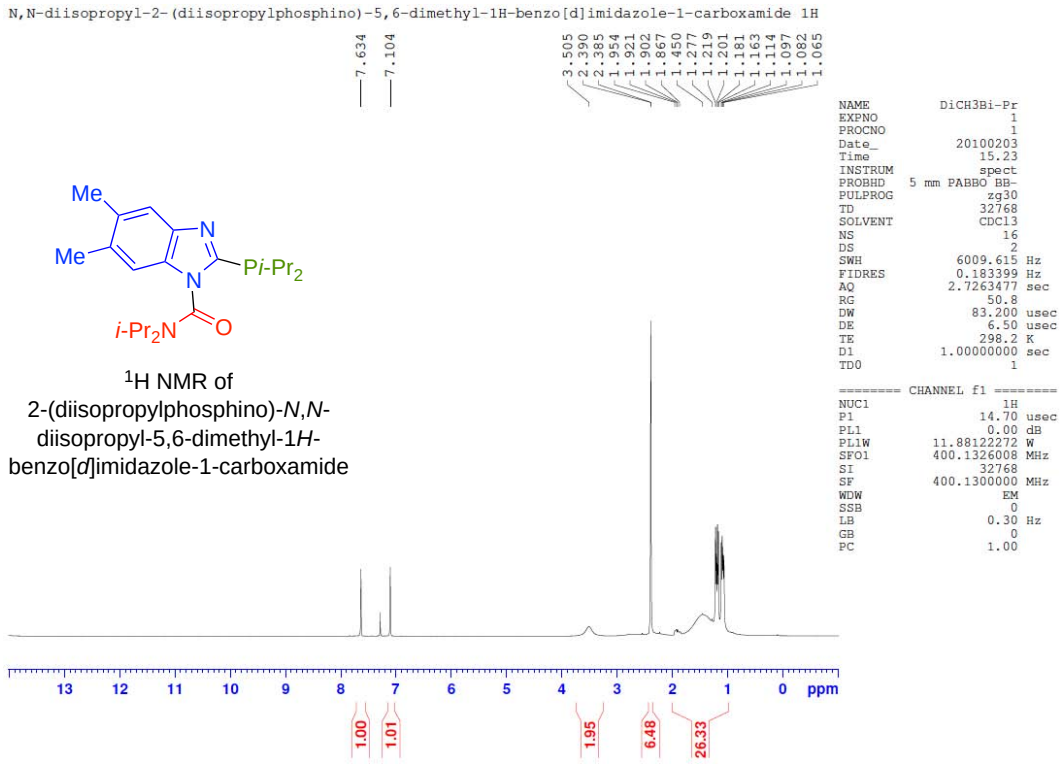
^{13}C NMR of
2-(di-*tert*-butylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide

NAME	DICH3Bt-BU(C)
EXPNO	1
PROCNO	1
Date_	20100203
Time	15.14
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	64
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	299.4 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	100.6127739 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

2-(Diisopropylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide (P*i*-Pr Amizole^{M2}-phos **L2k**) (**Table 2.11**, entry 11)

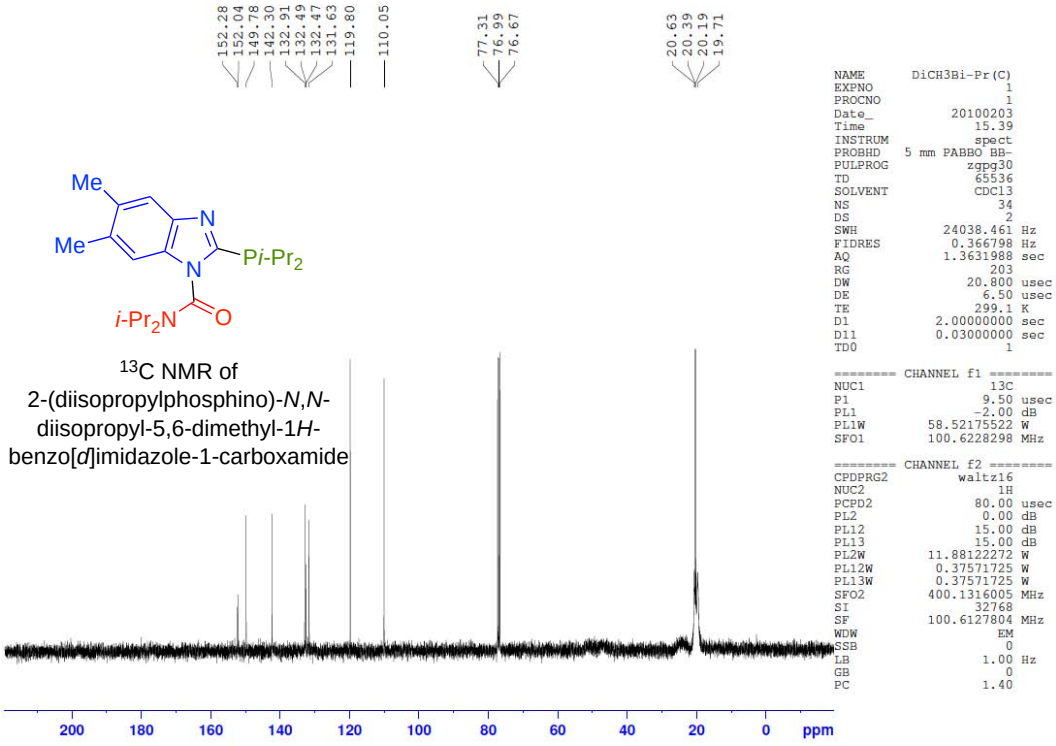


^{31}P NMR of 2-(diisopropylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide



^{1}H NMR of 2-(diisopropylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide

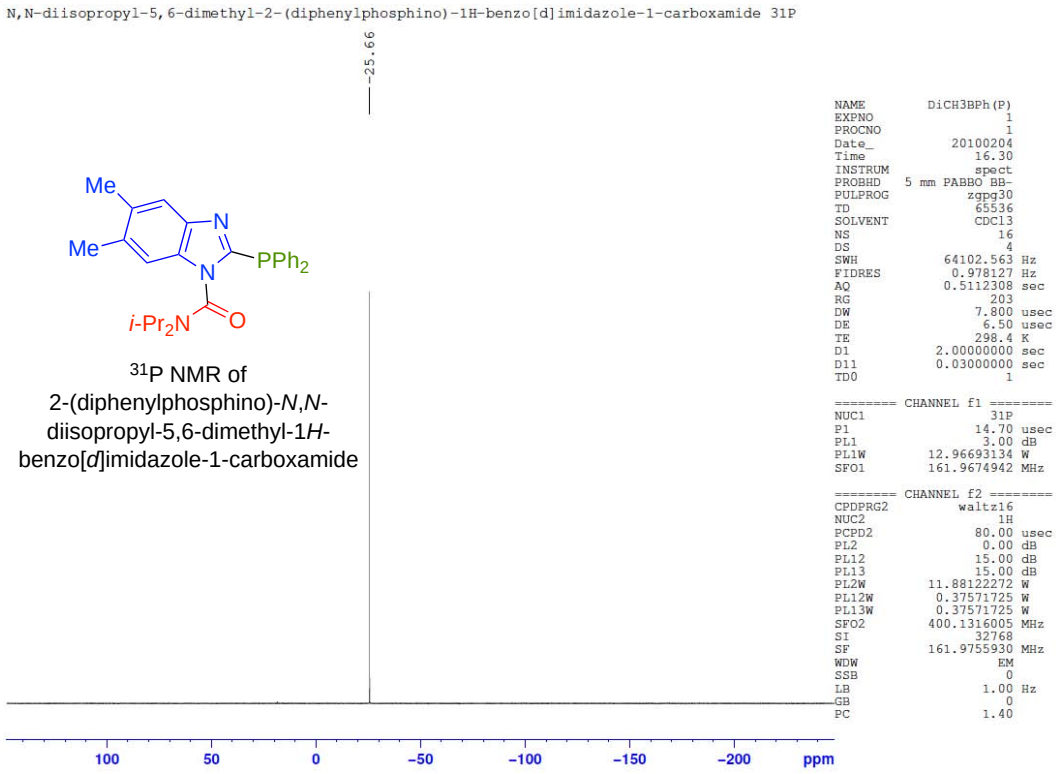
N,N-diisopropyl-2-(diisopropylphosphino)-5,6-dimethyl-1H-benzo[d]imidazole-1-carboxamide 13C



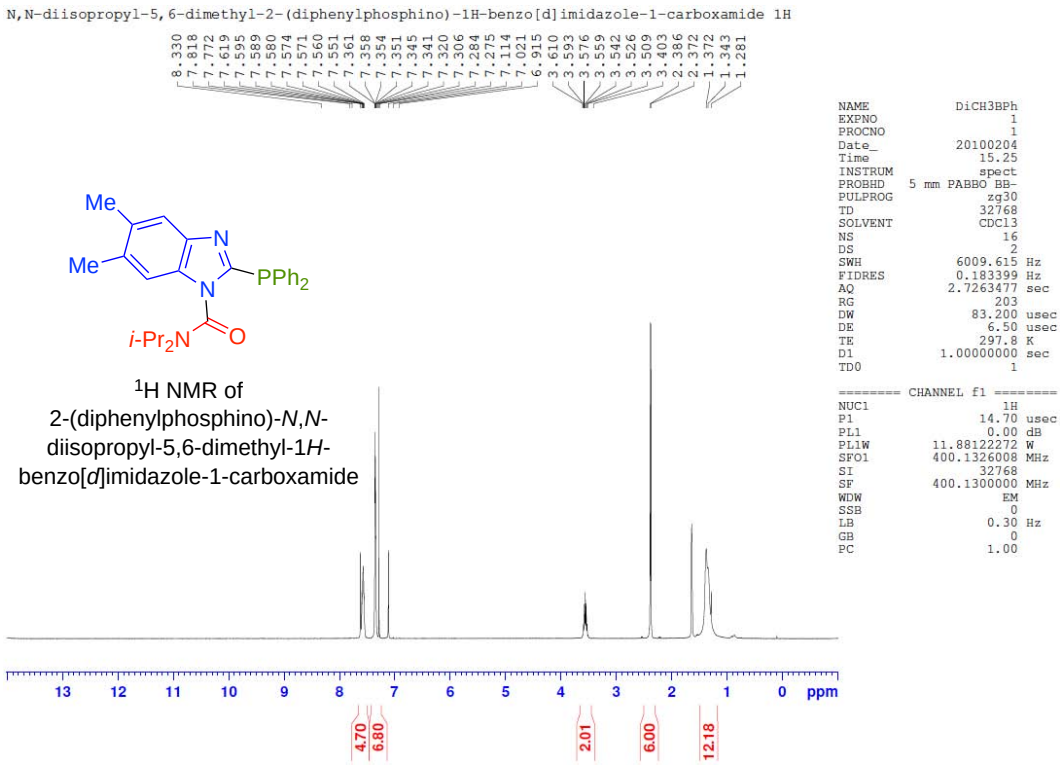
^{13}C NMR of 2-(diisopropylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide

NAME	DiCH3Bi-Pr(C)
EXPNO	1
PROCNO	1
Date_	20100203
Time	15.39
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	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	100.6127804 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

2-(Diphenylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide (PPh Amizole^{M2}-phos **L2l**) (**Table 2.11**, entry 12)

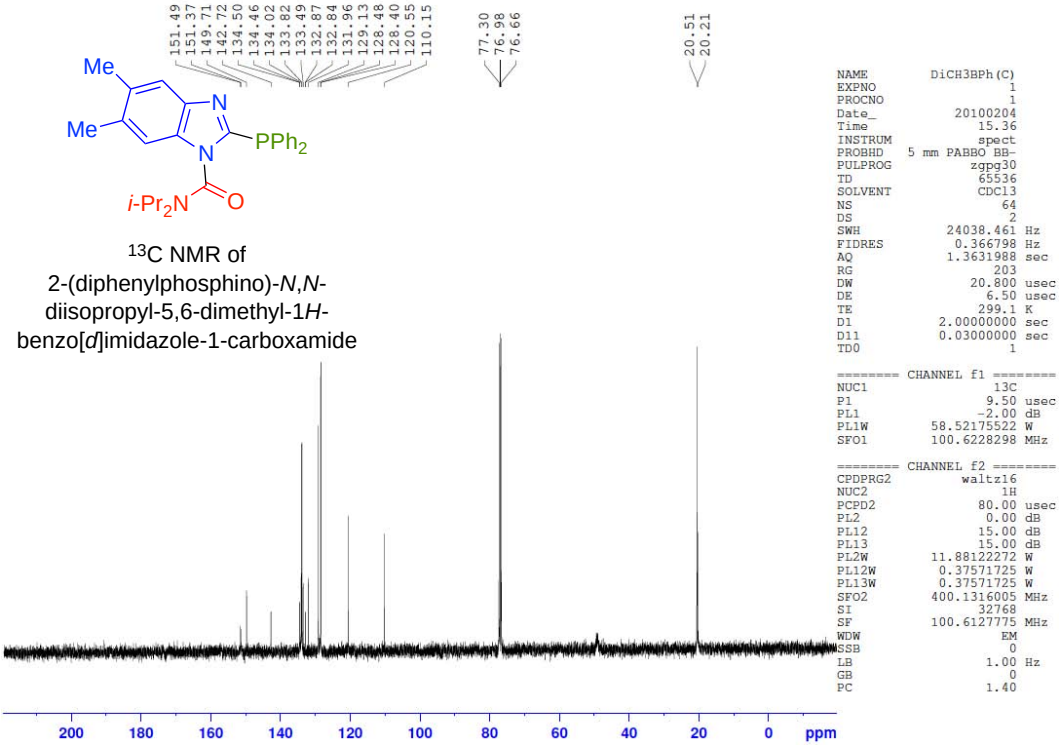


^{31}P NMR of 2-(diphenylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide



^{1}H NMR of 2-(diphenylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide

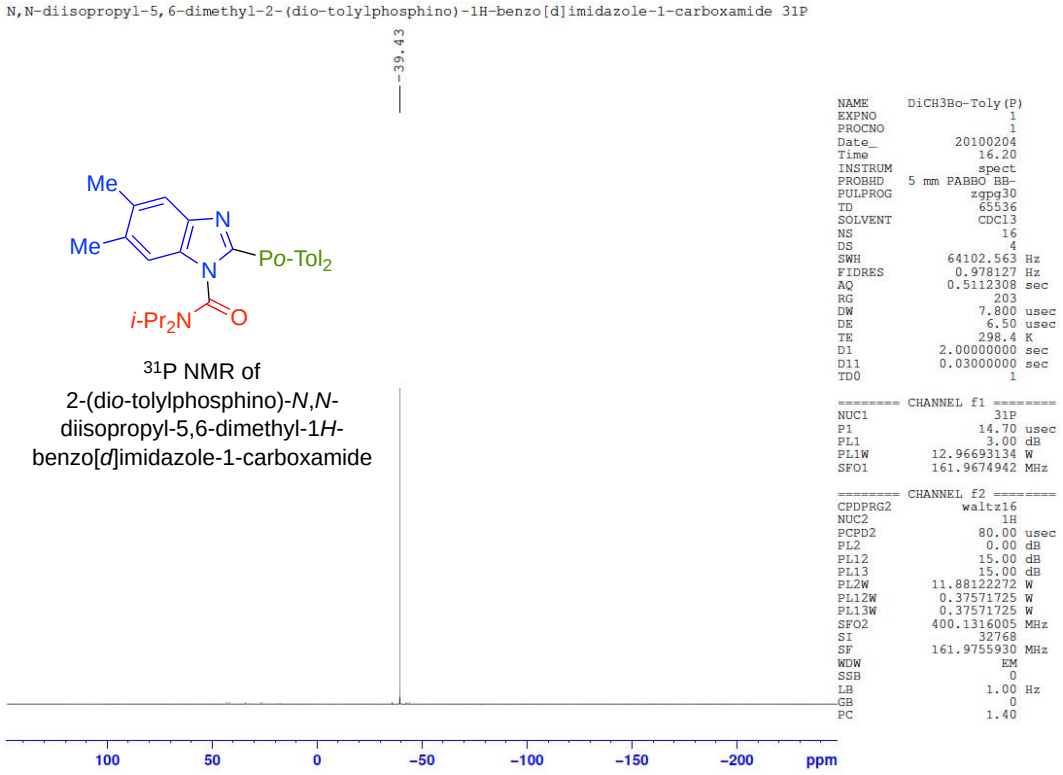
N,N-diisopropyl-5,6-dimethyl-2-(diphenylphosphino)-1H-benzo[d]imidazole-1-carboxamide 13C



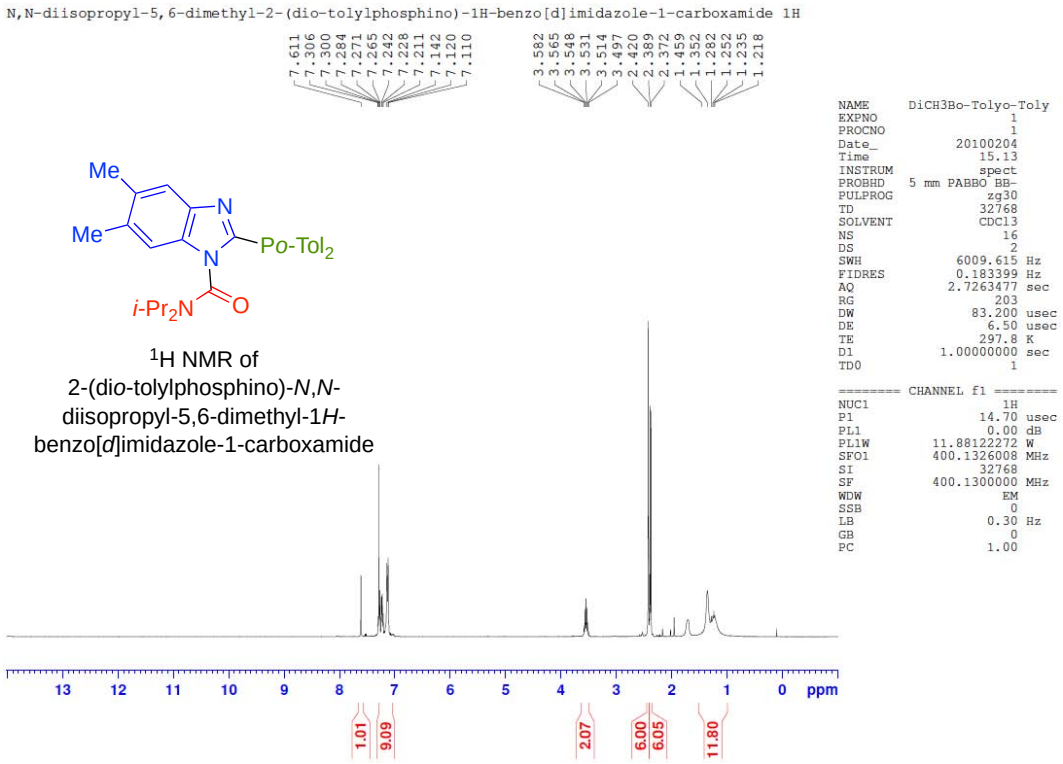
^{13}C NMR of
2-(diphenylphosphino)-*N*,*N*-
diisopropyl-5,6-dimethyl-1*H*-
benzo[*d*]imidazole-1-carboxamide

NAME	DiCH3BPh(C)
EXPNO	1
PROCNO	1
Date_	20100204
Time	15.36
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	64
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	100.6127775 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

2-(Di*o*-tolylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide (P*o*-Tol Amizole^{M2}-phos **L2m**) (**Table 2.11**, entry 13)

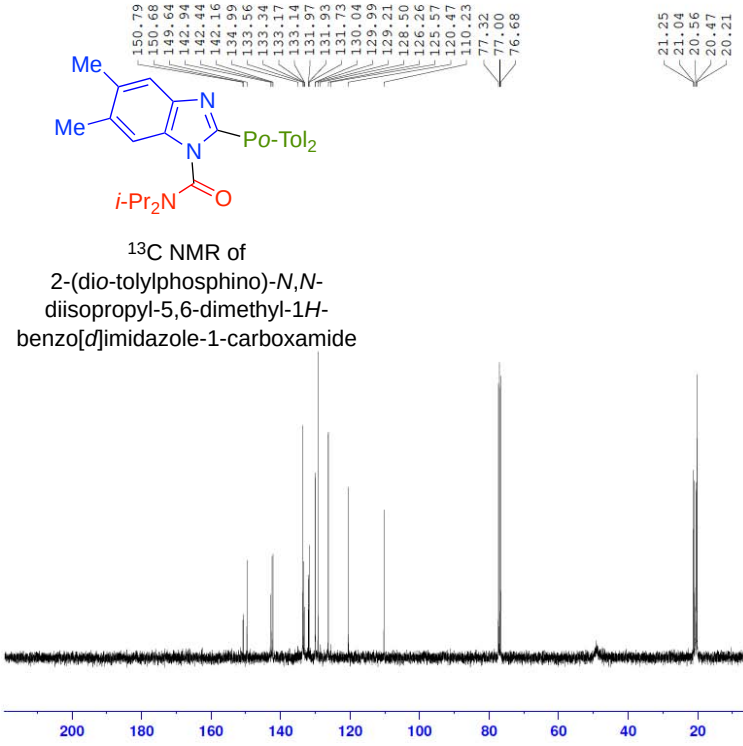


^{31}P NMR of 2-(di*o*-tolylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide



^{1}H NMR of 2-(di*o*-tolylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide

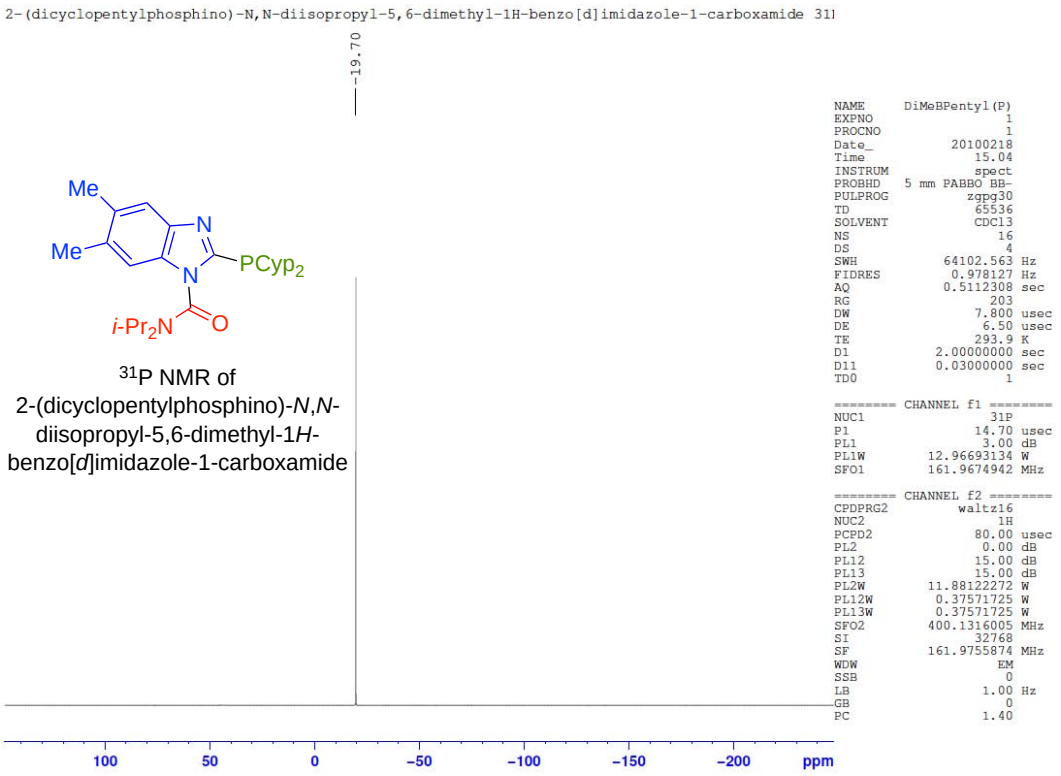
N,N-diisopropyl-5,6-dimethyl-2-(dio-tolylphosphino)-1H-benzo[d]imidazole-1-carboxamide 13C



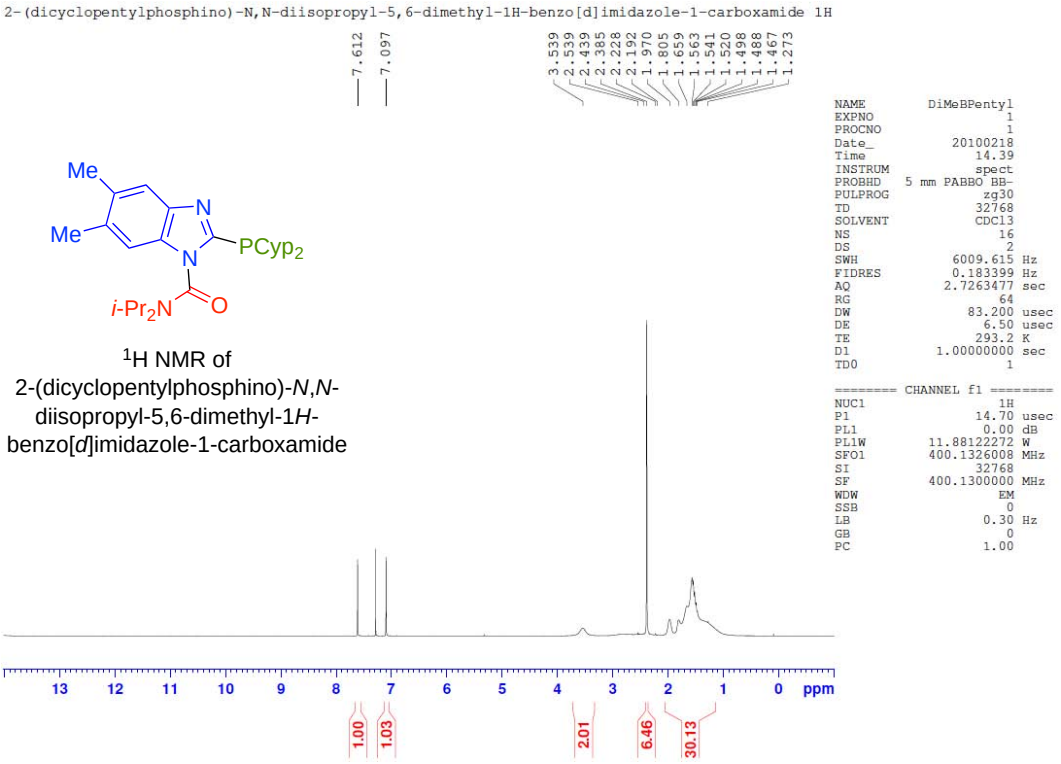
^{13}C NMR of
2-(dio-tolylphosphino)-*N*,*N*-
diisopropyl-5,6-dimethyl-1*H*-
benzo[*d*]imidazole-1-carboxamide

NAME	DiCH3Bo-Toly(C)
EXPNO	1
PROCNO	1
Date_	20100204
Time	16.38
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	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	100.6127838 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

2-(Dicyclopentylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole -1-carboxamide (PCyp Amizole^{M2}-phos **L2n**) (**Table 2.11**, entry 14)

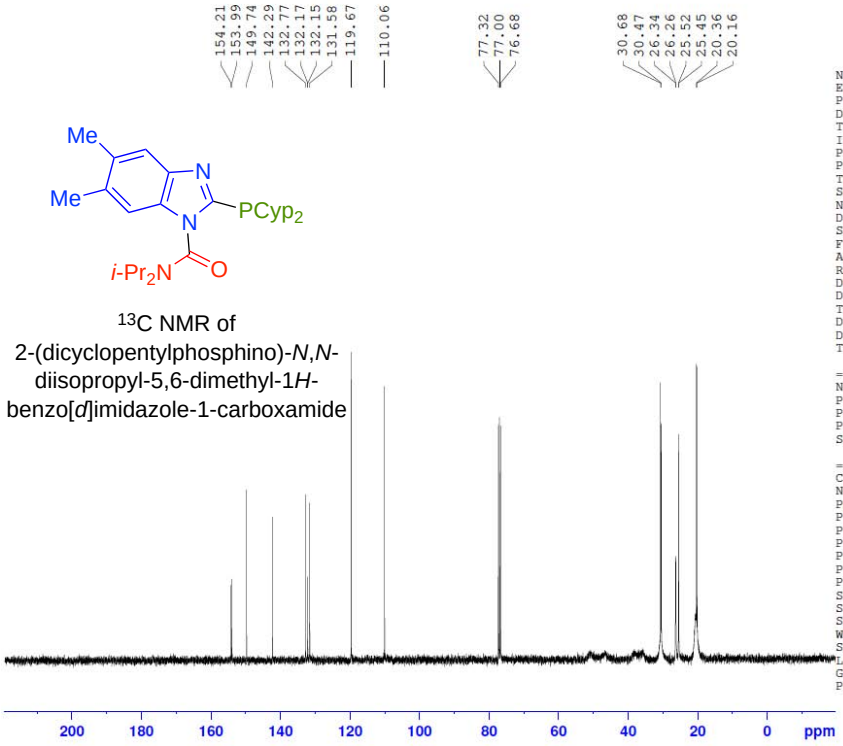


^{31}P NMR of 2-(dicyclopentylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide



^{1}H NMR of 2-(dicyclopentylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide

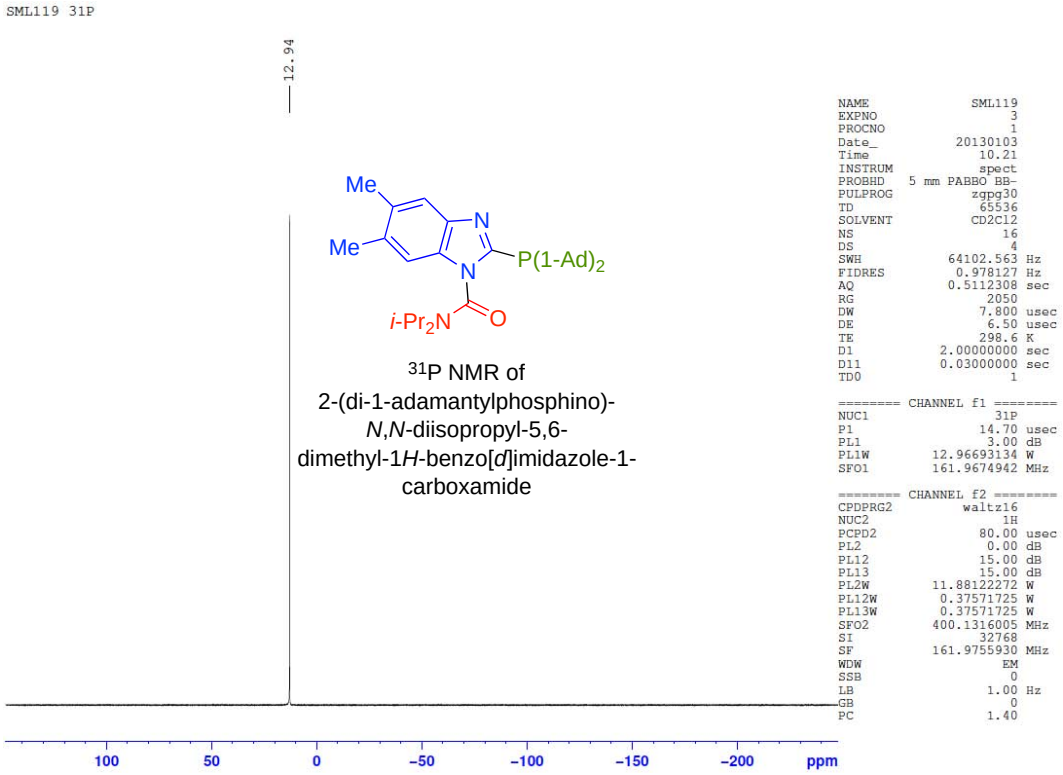
2-(dicyclopentylphosphino)-N,N-diisopropyl-5,6-dimethyl-1H-benzo[d]imidazole-1-carboxamide 13



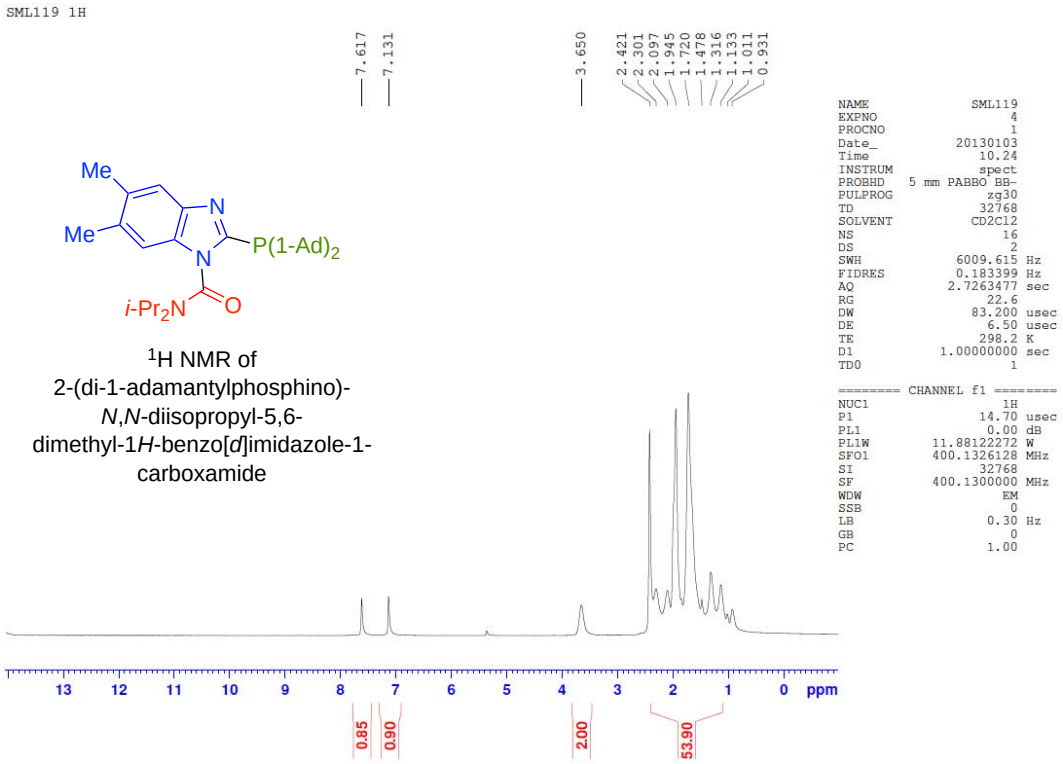
^{13}C NMR of 2-(dicyclopentylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide

NAME	DiMeBPentyl(C)
EXPNO	1
PROCNO	1
Date_	20100218
Time	14.50
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	64
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	294.2 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	100.6127854 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

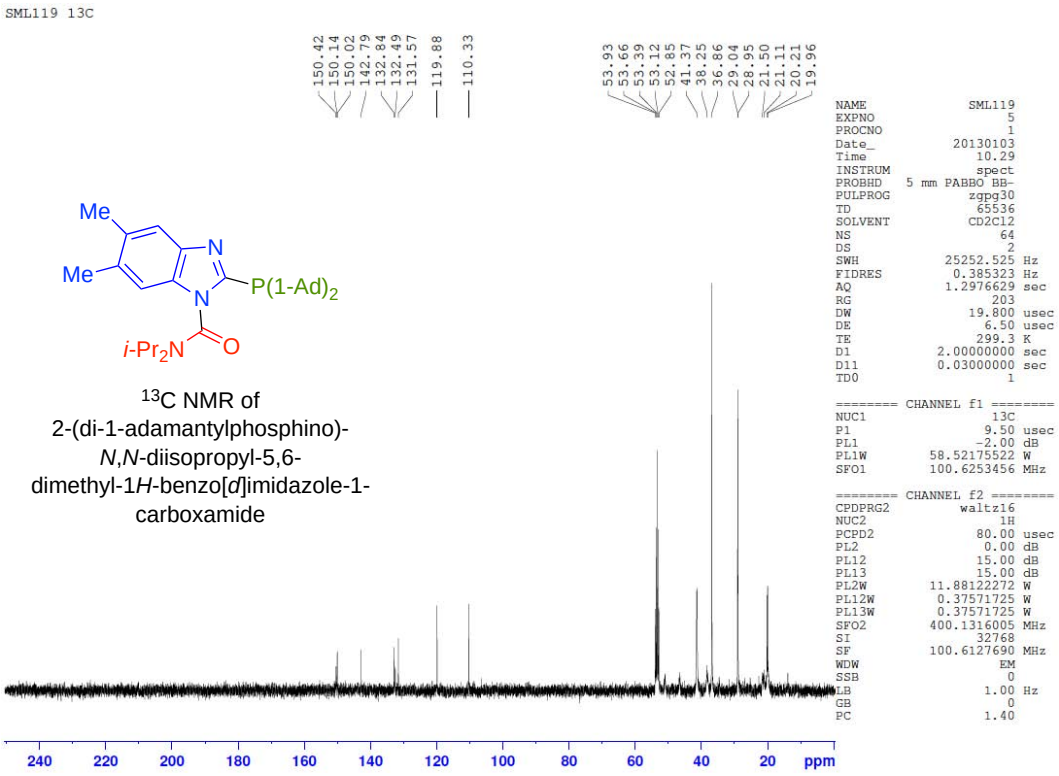
2-(Di-1-adamantylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*] imidazole-1-carboxamide (P1-Ad Amizole^{M2}-phos **L2o**) (**Table 2.11**, entry 15)



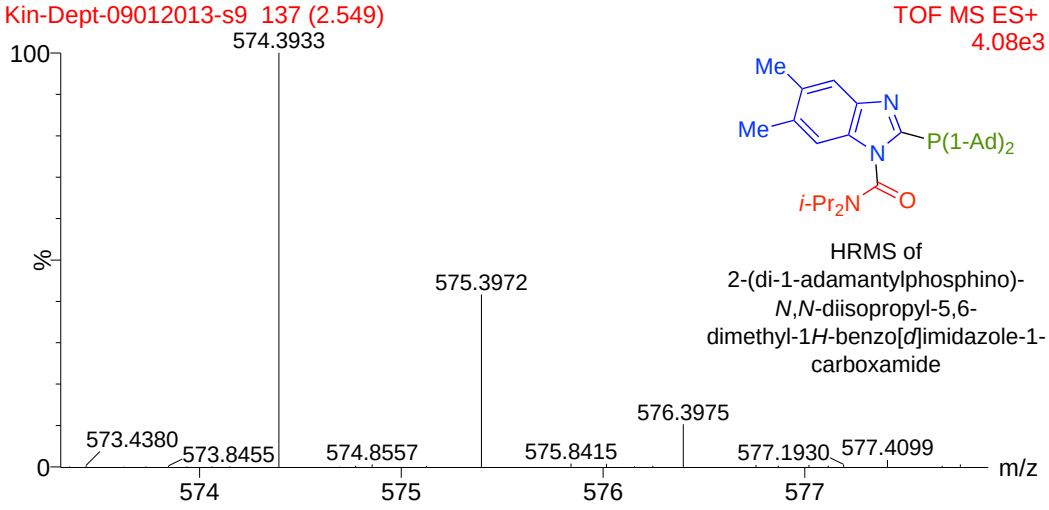
^{31}P NMR of 2-(di-1-adamantylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide



^{1}H NMR of 2-(di-1-adamantylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide



^{13}C NMR of 2-(di-1-adamantylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide

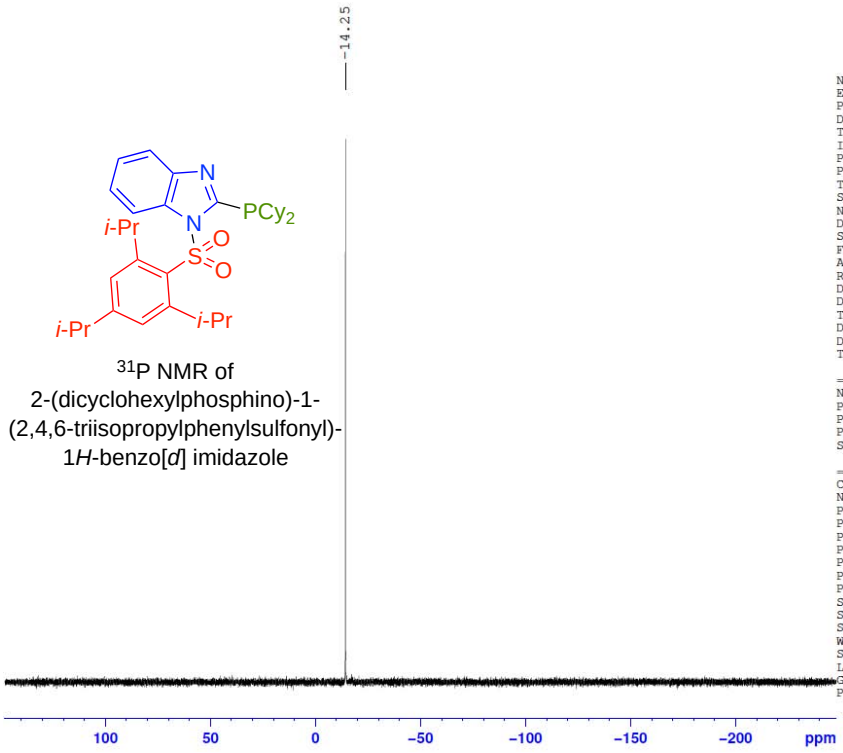


HRMS of 2-(di-1-adamantylphosphino)-*N*,*N*-diisopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazole-1-carboxamide

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
574.3933	574.3926	0.7	1.2	12.5	4.3	C36 H53 N3 O P

2-(Dicyclohexylphosphino)-1-(2,4,6-triisopropylphenylsulfonyl)-1*H*-benzo[*d*] imidazole (PCy ^{P3}Sulfozole-phos **L2p**) (**Table 2.11**, entry 16)

SML049 31P



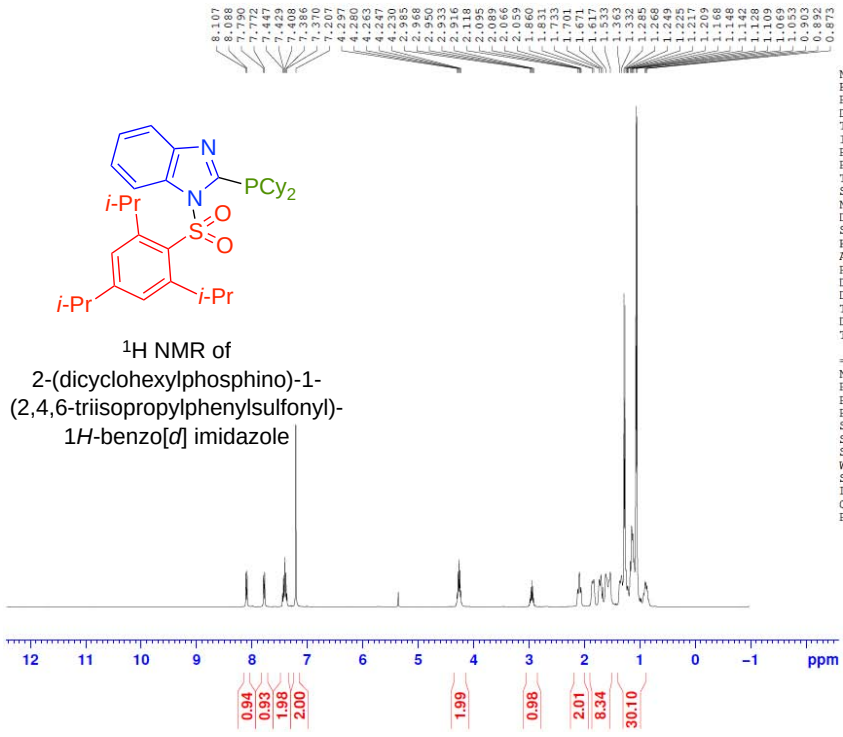
^{31}P NMR of 2-(dicyclohexylphosphino)-1-(2,4,6-triisopropylphenylsulfonyl)-1*H*-benzo[*d*] imidazole

```
NAME                SML049
EXPNO                    1
PROCNO                   1
Date_             20110815
Time                 11.13
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT              CD2Cl2
NS                       32
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                  299.3 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
```

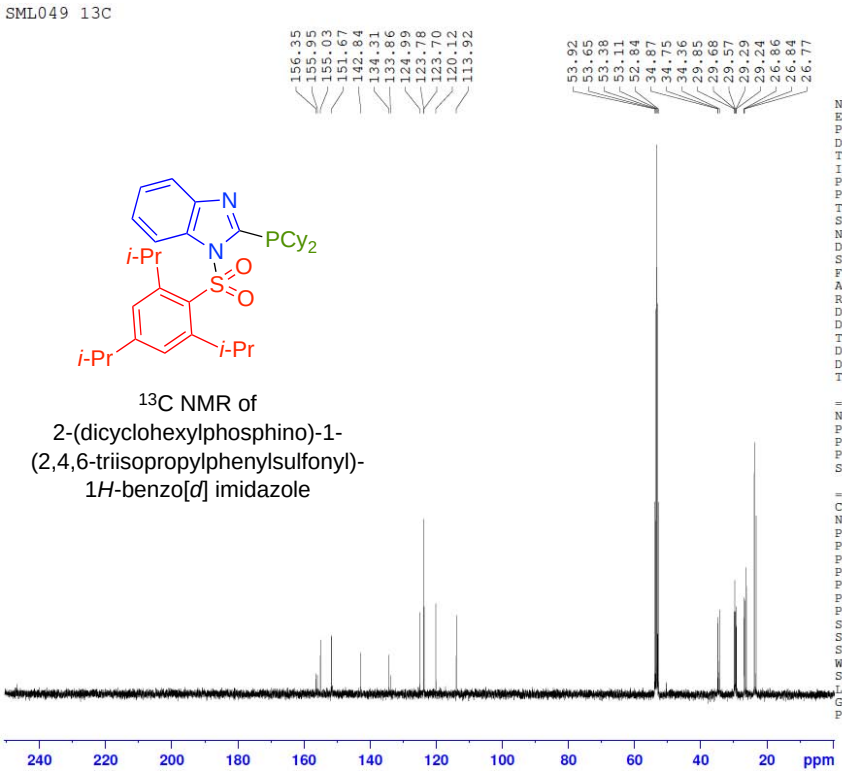
SML049 1H



^{1}H NMR of 2-(dicyclohexylphosphino)-1-(2,4,6-triisopropylphenylsulfonyl)-1*H*-benzo[*d*] imidazole

```
NAME                SML049
EXPNO                    5
PROCNO                   1
Date_             20110816
Time                  8.41
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                    32768
SOLVENT              CD2Cl2
NS                       16
DS                        2
SWH               6009.615 Hz
FIDRES           0.183399 Hz
AQ               2.7263477 sec
RG                       18
DW                  83.200 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          400.1326128 MHz
SI                    32768
SF            400.1300000 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

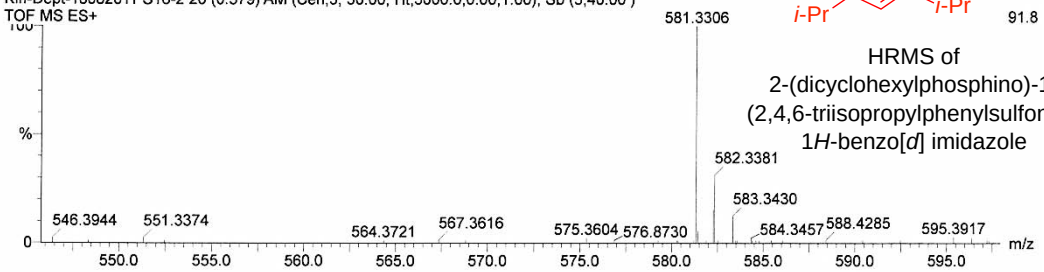


^{13}C NMR of
2-(dicyclohexylphosphino)-1-(2,4,6-triisopropylphenylsulfonyl)-1*H*-benzo[*d*] imidazole

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
55 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-34 H: 0-50 N: 0-2 O: 0-2 Na: 0-1 P: 0-1 S: 0-1

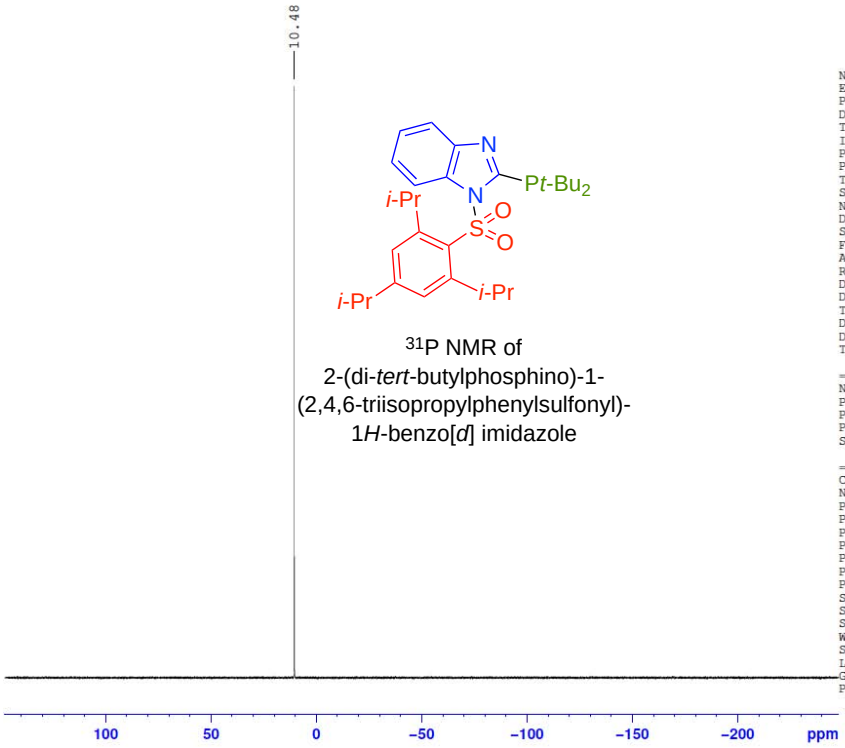


HRMS of
2-(dicyclohexylphosphino)-1-(2,4,6-triisopropylphenylsulfonyl)-1*H*-benzo[*d*] imidazole

Minimum:				-1.5		
Maximum:		5.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
581.3306	581.3331	-2.5	-4.3	11.5	0.8	C34 H50 N2 O2 P S

2-(Di-*tert*-butylphosphino)-1-(2,4,6-triisopropylphenylsulfonyl)-1*H*-benzo[*d*] imidazole (P*t*-Bu ^{P3}Sulfozole-phos **L2q**) (**Table 2.11**, entry 17)

SML070 31P



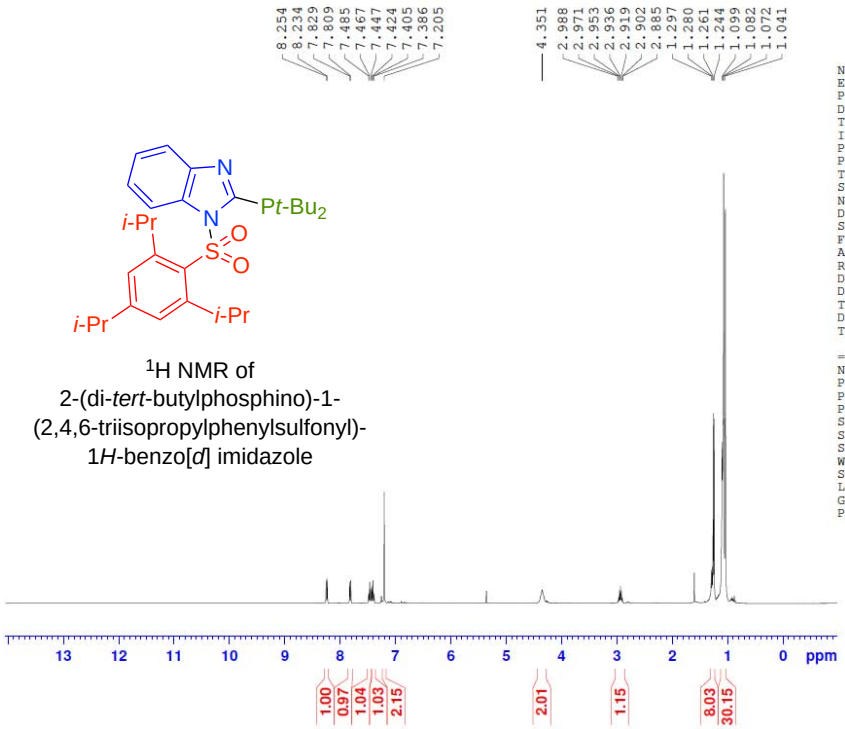
NAME SML070
EXPNO 1
PROCNO 1
Date_ 20111112
Time 12.52
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CD2Cl2
NS 64
DS 4
SWH 64102.563 Hz
FIDRES 0.978127 Hz
AQ 0.5112308 sec
RG 203
DW 7.800 usec
DE 6.50 usec
TE 297.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== 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

^{31}P NMR of 2-(di-*tert*-butylphosphino)-1-(2,4,6-triisopropylphenylsulfonyl)-1*H*-benzo[*d*] imidazole

SML070 1H

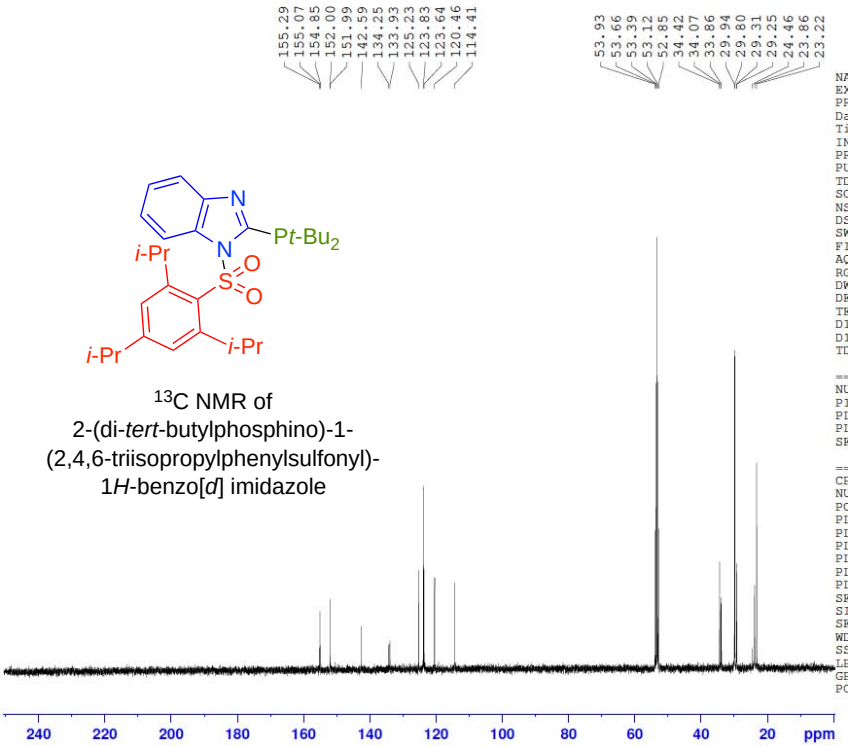


NAME SML070
EXPNO 2
PROCNO 1
Date_ 20111112
Time 12.58
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CD2Cl2
NS 32
DS 2
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 40.3
DW 83.200 usec
DE 6.50 usec
TE 297.8 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 14.70 usec
PL1 0.00 dB
PL1W 11.88122272 W
SFO1 400.1326128 MHz
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

^{1}H NMR of 2-(di-*tert*-butylphosphino)-1-(2,4,6-triisopropylphenylsulfonyl)-1*H*-benzo[*d*] imidazole

SML070 13C

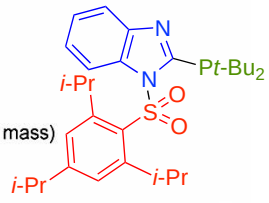


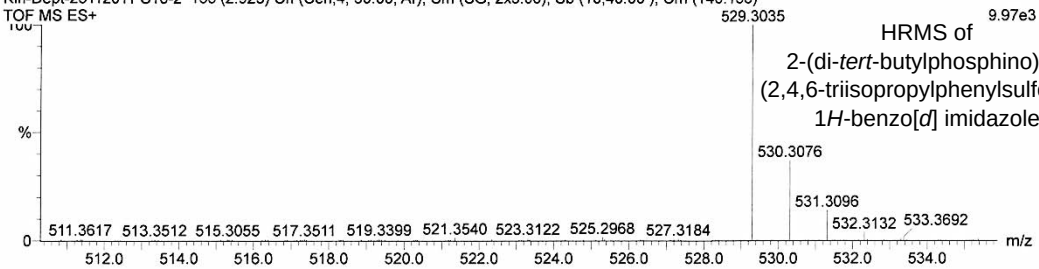
^{13}C NMR of
2-(di-*tert*-butylphosphino)-1-
(2,4,6-triisopropylphenylsulfonyl)-
1*H*-benzo[*d*] imidazole

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
951 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-30 H: 0-46 N: 0-2 O: 0-2 Na: 0-1 P: 0-2 S: 0-3 39K: 0-1
Kin-Dept-23112011 S10-2 155 (2.923) Cn (Cen,4, 50.00, Ar); Sm (SG, 2x3.00); Sb (10,40.00); Cm (140:156)





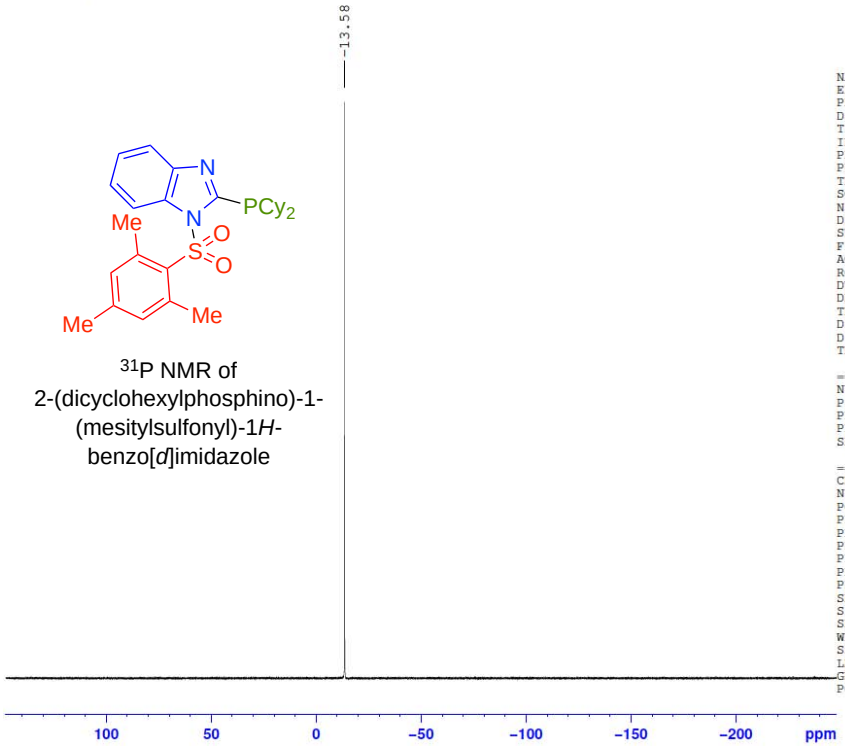
HRMS of
2-(di-*tert*-butylphosphino)-1-
(2,4,6-triisopropylphenylsulfonyl)-
1*H*-benzo[*d*] imidazole

Minimum:				-1.5		
Maximum:		5.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
529.3035	529.3018	1.7	3.2	9.5	30.2	C30 H46 N2 O2 P S

2-(Dicyclohexylphosphino)-1-(mesitylsulfonyl)-1*H*-benzo[*d*]imidazole

(PCy ^{M3}Sulfozole-phos **L2r**) (**Table 2.11**, entry 18)

SML050 31P



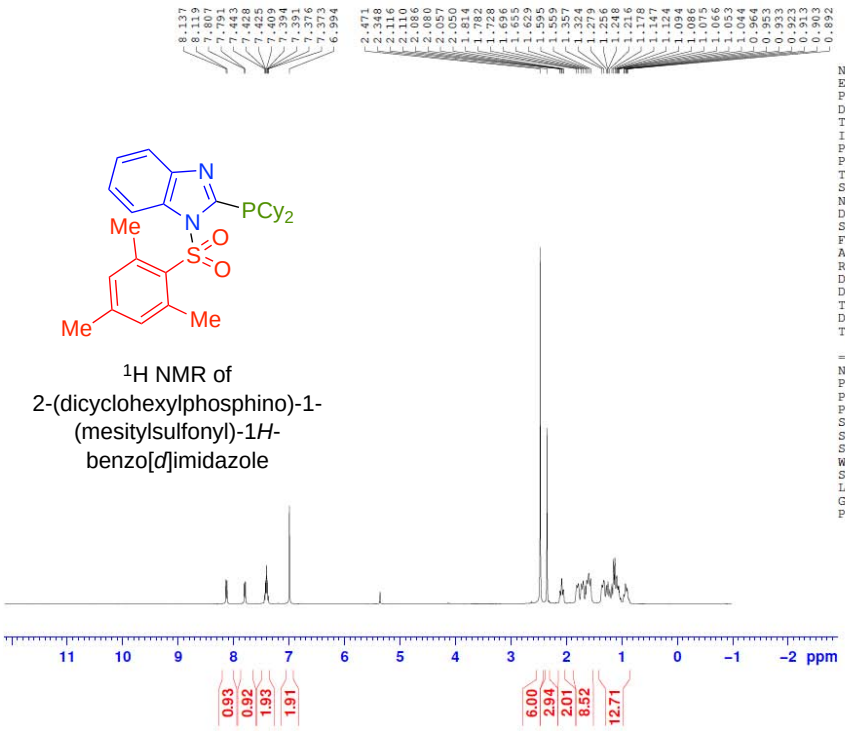
^{31}P NMR of 2-(dicyclohexylphosphino)-1-(mesitylsulfonyl)-1*H*-benzo[*d*]imidazole

```
NAME                SML050
EXPNO                    7
PROCNO                   1
Date_             20110823
Time                 8.17
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG              zgpg30
TD                   65536
SOLVENT              CD2Cl2
NS                       32
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                   298.3 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
```

SML050 1H

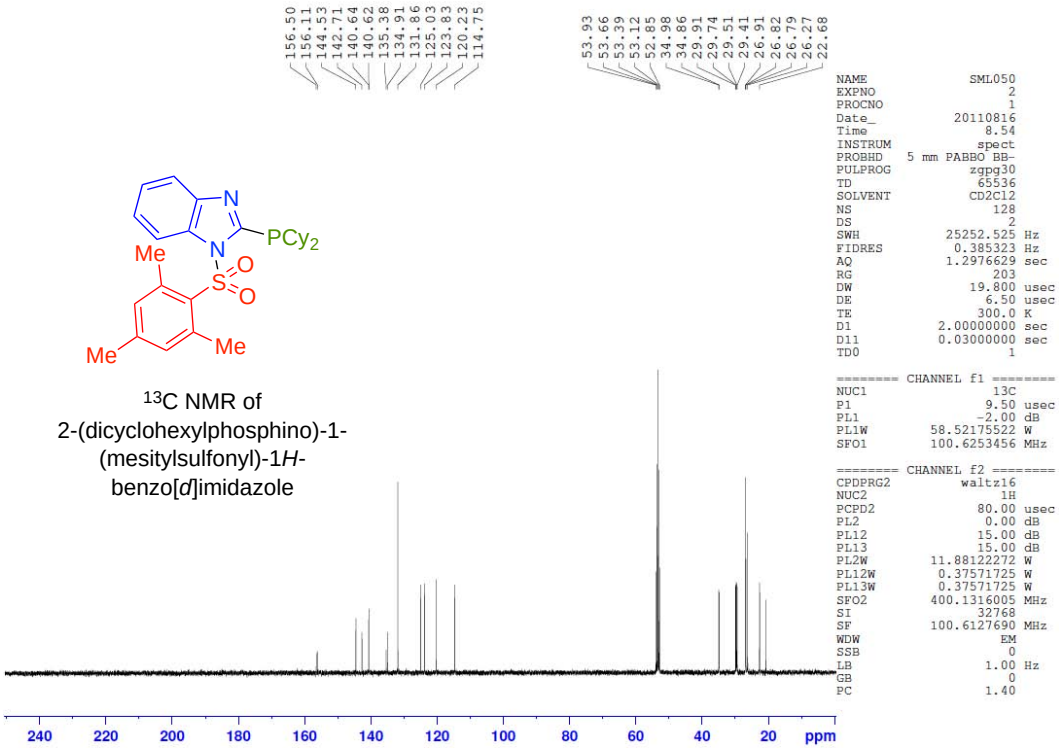


^{1}H NMR of 2-(dicyclohexylphosphino)-1-(mesitylsulfonyl)-1*H*-benzo[*d*]imidazole

```
NAME                SML050
EXPNO                    8
PROCNO                   1
Date_             20110823
Time                 8.20
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                   32768
SOLVENT              CD2Cl2
NS                       16
DS                        2
SWH               6009.615 Hz
FIDRES           0.183399 Hz
AQ               2.7263477 sec
RG                    28.5
DW                  83.200 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          400.1326128 MHz
SI                   32768
SF            400.1300000 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

SML050 13C

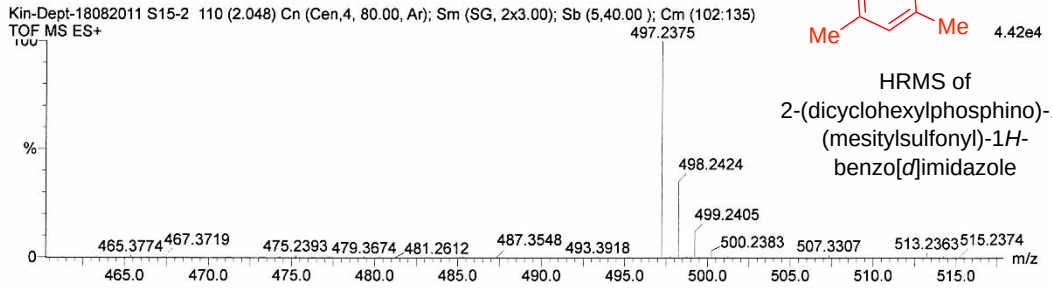


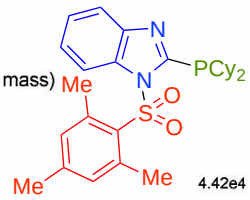
^{13}C NMR of
2-(dicyclohexylphosphino)-1-(mesitylsulfonyl)-1*H*-benzo[*d*]imidazole

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
201 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-28 H: 0-38 N: 0-2 O: 0-6 Na: 0-1 S: 0-1 P: 0-1





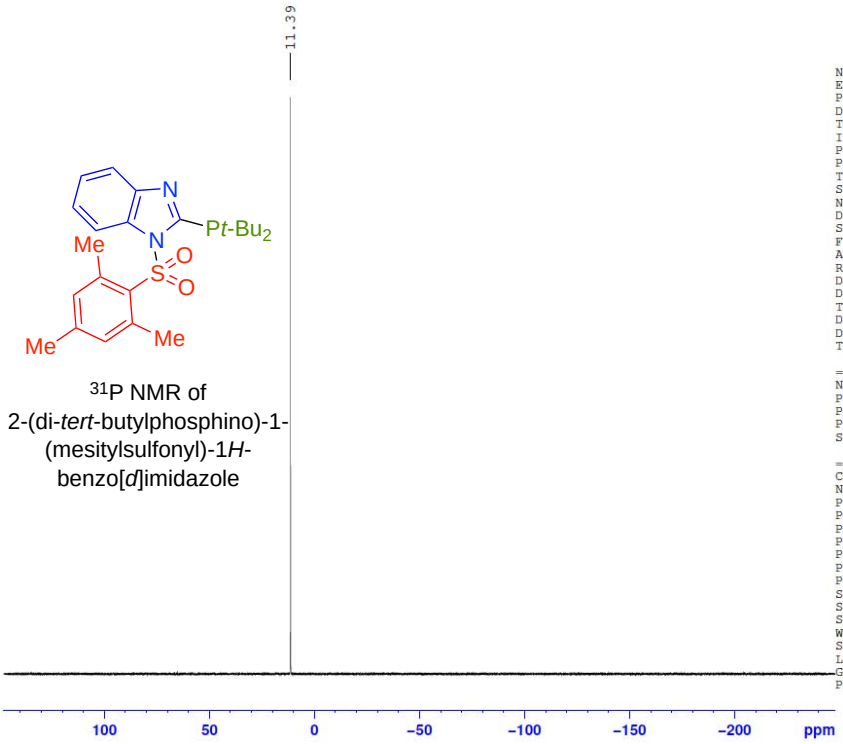
HRMS of
2-(dicyclohexylphosphino)-1-(mesitylsulfonyl)-1*H*-benzo[*d*]imidazole

Minimum:				-1.5		
Maximum:		5.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
497.2375	497.2392	-1.7	-3.4	11.5	59.9	C28 H38 N2 O2 S P

2-(Di-*tert*-butylphosphino)-1-(mesitylsulfonyl)-1*H*-benzo[*d*]imidazole

(P*t*-Bu ^{M3}Sulfozole-phos **L2s**) (**Table 2.11**, entry 19)

SML071 31P



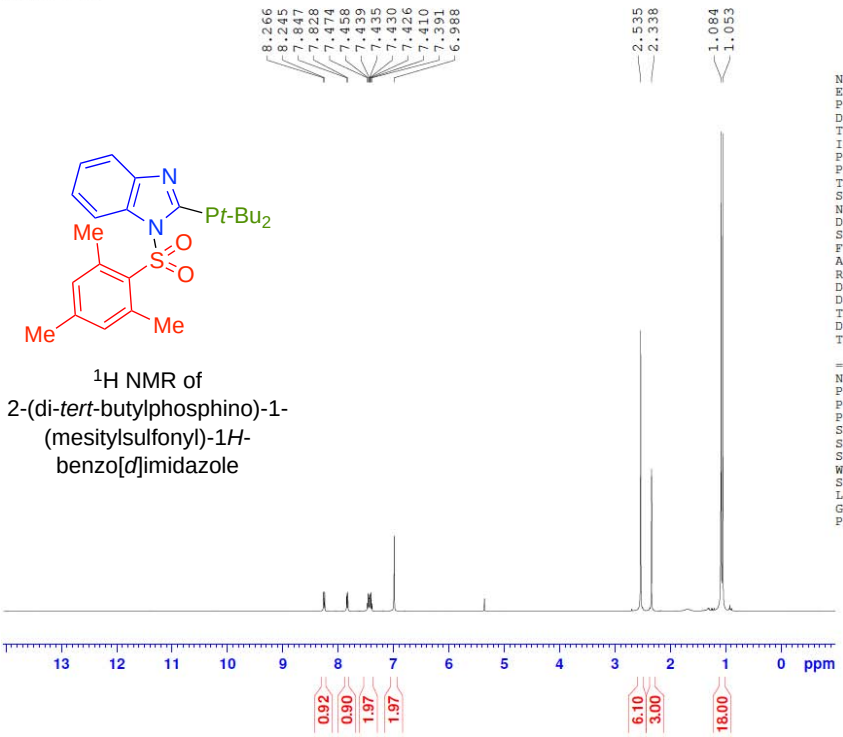
^{31}P NMR of 2-(di-*tert*-butylphosphino)-1-(mesitylsulfonyl)-1*H*-benzo[*d*]imidazole

```
NAME                SML071
EXPNO                    1
PROCNO                   1
Date_             20111112
Time                 13.23
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CD2Cl2
NS                       64
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                   300.0 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
```

SML071 1H

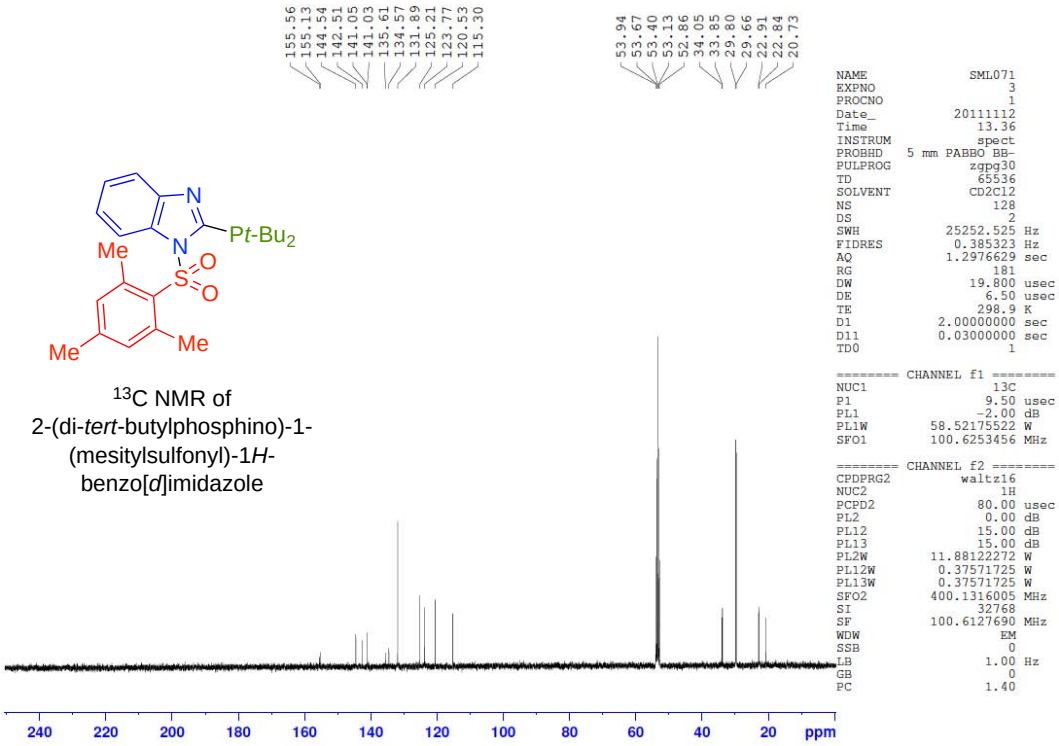


^{1}H NMR of 2-(di-*tert*-butylphosphino)-1-(mesitylsulfonyl)-1*H*-benzo[*d*]imidazole

```
NAME                SML071
EXPNO                    2
PROCNO                   1
Date_             20111112
Time                 13.26
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   32768
SOLVENT              CD2Cl2
NS                       32
DS                        2
SWH               6009.615 Hz
FIDRES           0.183399 Hz
AQ               2.7263477 sec
RG                    71.8
DW                   83.200 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           400.1326128 MHz
SI                    32768
SF             400.1300000 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```

SML071 13C

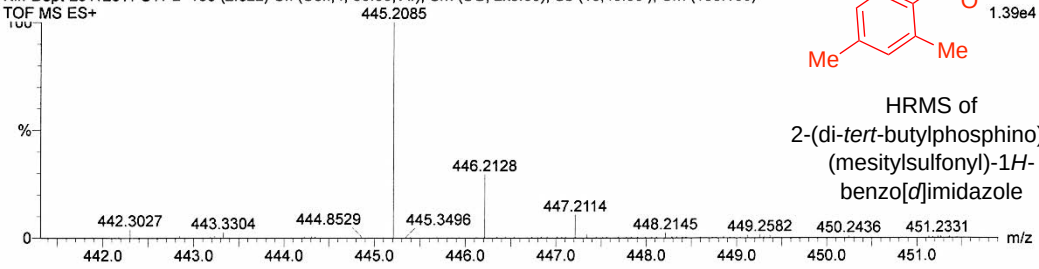


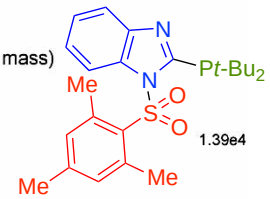
^{13}C NMR of
2-(di-*tert*-butylphosphino)-1-
(mesitylsulfonyl)-1*H*-
benzo[*d*]imidazole

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
794 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-24 H: 0-34 N: 0-2 O: 0-2 Na: 0-1 P: 0-2 S: 0-3 39K: 0-1
Kin-Dept-23112011 S11-2 139 (2.622) Cn (Cen,4, 50.00, Ar); Sm (SG, 2x3.00); Sb (10,40.00); Cm (133:160)
TOF MS ES+





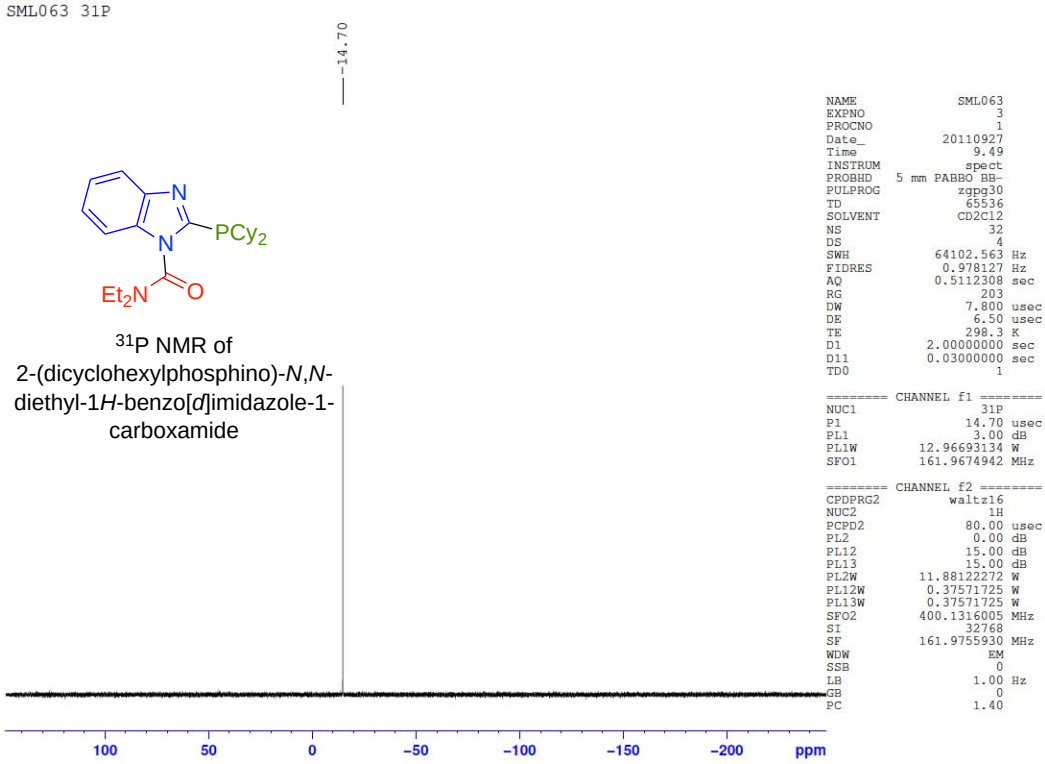
HRMS of
2-(di-*tert*-butylphosphino)-1-
(mesitylsulfonyl)-1*H*-
benzo[*d*]imidazole

Minimum:				-1.5		
Maximum:		5.0	20.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
445.2085	445.2079	0.6	1.3	9.5	18.2	C24 H34 N2 O2 P S

2-(Dicyclohexylphosphino)-*N*,*N*-diethyl-1*H*-benzo[*d*]imidazole-1-carboxamide

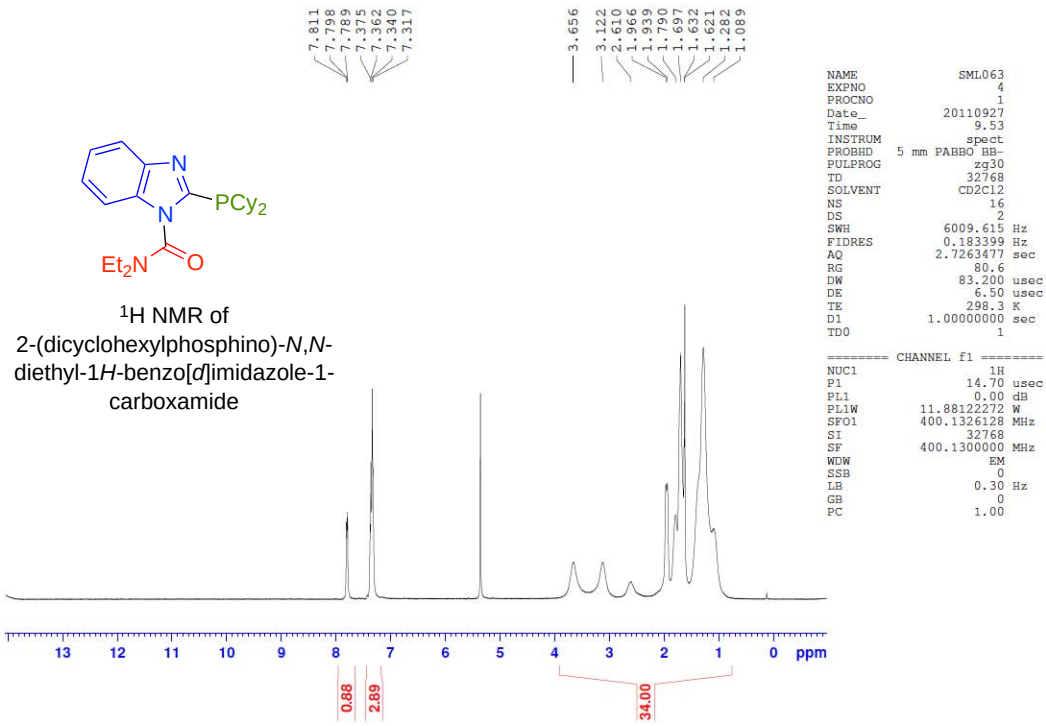
(**Scheme 2.23**, **L2t**)

SML063 31P



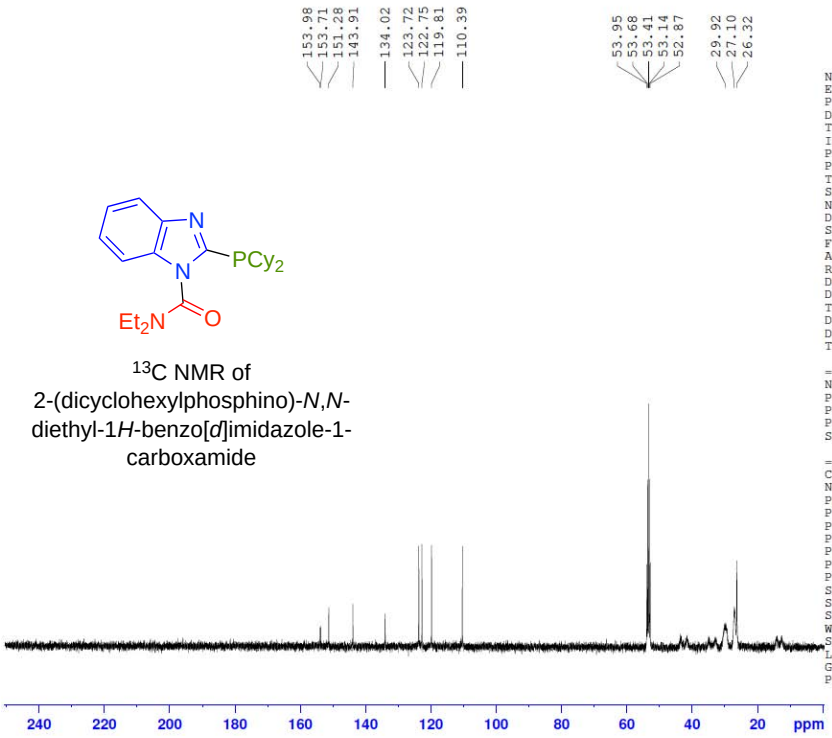
^{31}P NMR of 2-(dicyclohexylphosphino)-*N*,*N*-diethyl-1*H*-benzo[*d*]imidazole-1-carboxamide

SML063 1H



^{1}H NMR of 2-(dicyclohexylphosphino)-*N*,*N*-diethyl-1*H*-benzo[*d*]imidazole-1-carboxamide

SML063 13C



NAME SML063
EXPNO 6
PROCNO 1
Date_ 20110927
Time 10.21
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CD2Cl2
NS 128
DS 2
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976629 sec
RG 203
DW 19.800 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 100.6253456 MHz

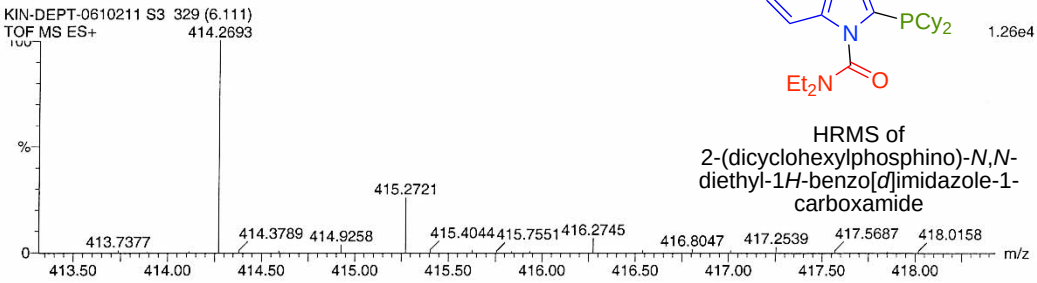
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 15.00 dB
PL13 15.00 dB
PL2W 11.88122272 W
PL12W 0.37571725 W
PL13W 0.37571725 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

^{13}C NMR of 2-(dicyclohexylphosphino)-*N*,*N*-diethyl-1*H*-benzo[*d*]imidazole-1-carboxamide

Elemental Composition Report **Page 1**

Single Mass Analysis (displaying only valid results)
Tolerance = 5.0 PPM / DBE: min = -100.0, max = 1000.0
Selected filters: None

Monoisotopic Mass, Even Electron Ions
538 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-24 H: 5-37 N: 0-3 O: 0-3 Na: 0-1 S: 0-2 P: 0-2



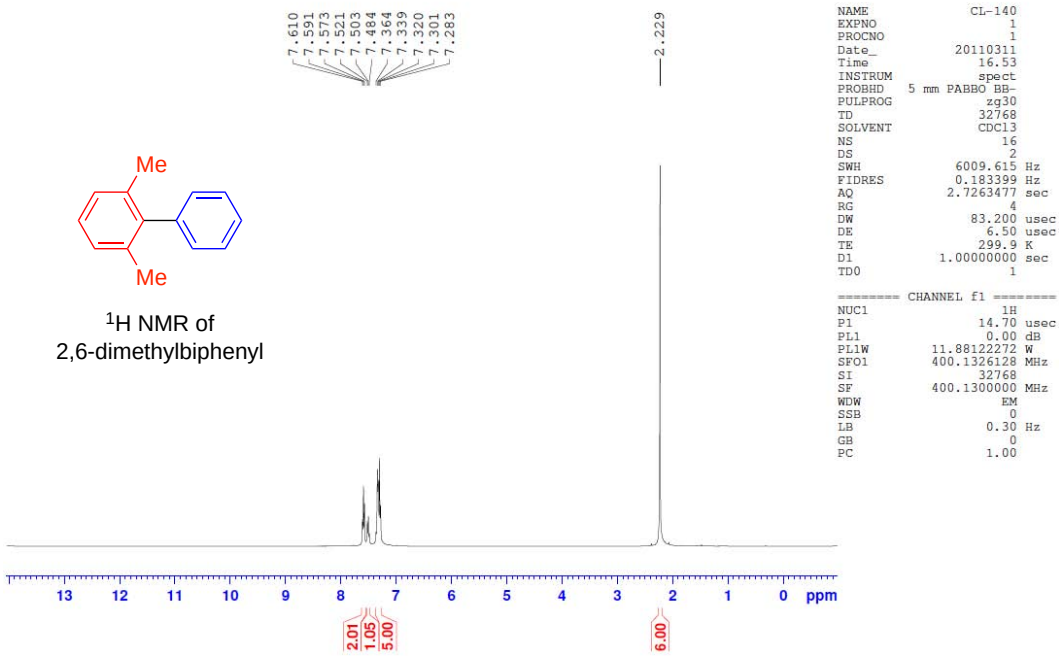
HRMS of 2-(dicyclohexylphosphino)-*N*,*N*-diethyl-1*H*-benzo[*d*]imidazole-1-carboxamide

Minimum:				-100.0		
Maximum:		5.0	5.0	1000.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
414.2693	414.2674	1.9	4.6	8.5	79.6	C24 H37 N3 O P

Chapter 3 NMR Spectra of Coupling products

2,6-Dimethylbiphenyl (**Table 3.2**, entry 1)

CL-140 1H

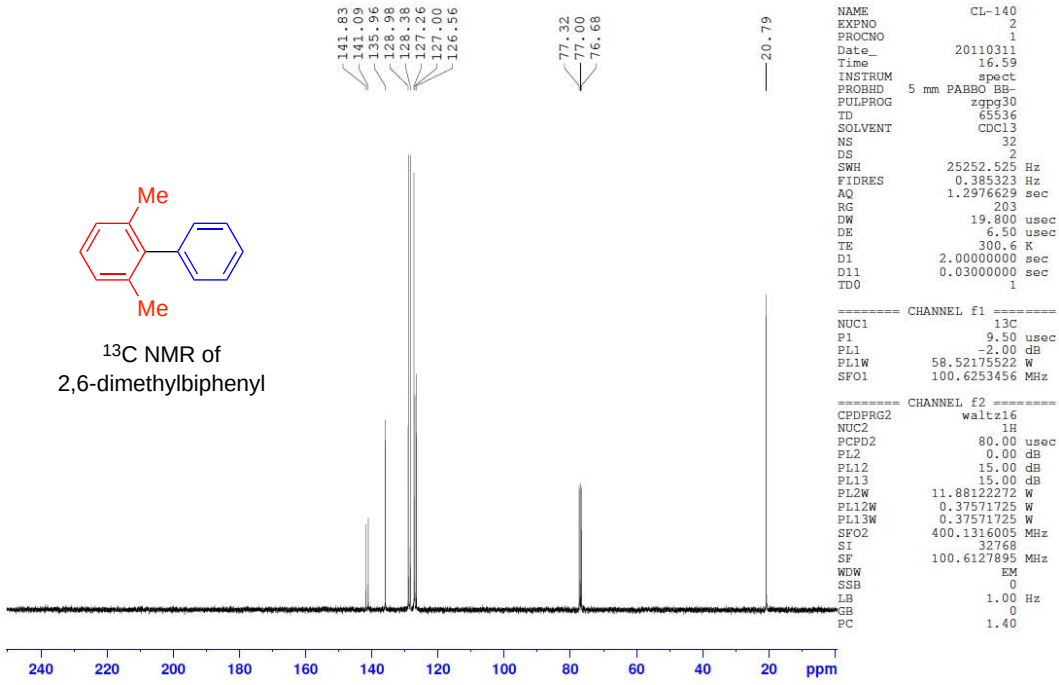


^{1}H NMR of
2,6-dimethylbiphenyl

```
NAME                CL-140
EXPNO                    1
PROCNO                   1
Date_             20110311
Time                 16.53
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                   32768
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               6009.615 Hz
FIDRES            0.183399 Hz
AQ                2.7263477 sec
RG                       4
DW                  83.200 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            400.1326128 MHz
SI                   32768
SF               400.1300000 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

CL-140 13C



^{13}C NMR of
2,6-dimethylbiphenyl

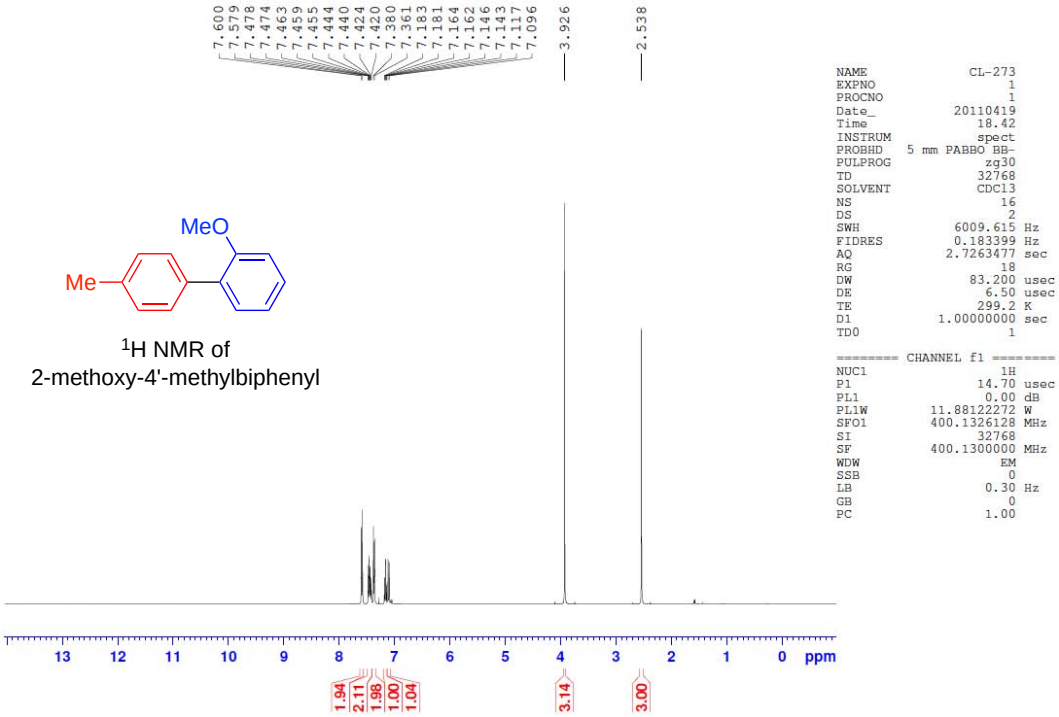
```
NAME                CL-140
EXPNO                    2
PROCNO                   1
Date_             20110311
Time                 16.59
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      32
DS                       2
SWH              25252.525 Hz
FIDRES            0.385323 Hz
AQ                1.2976629 sec
RG                     203
DW                  19.800 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            100.6253456 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               100.6127895 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

2-Methoxy-4'-methylbiphenyl (**Table 3.2**, entry 2)

CL-273 1H

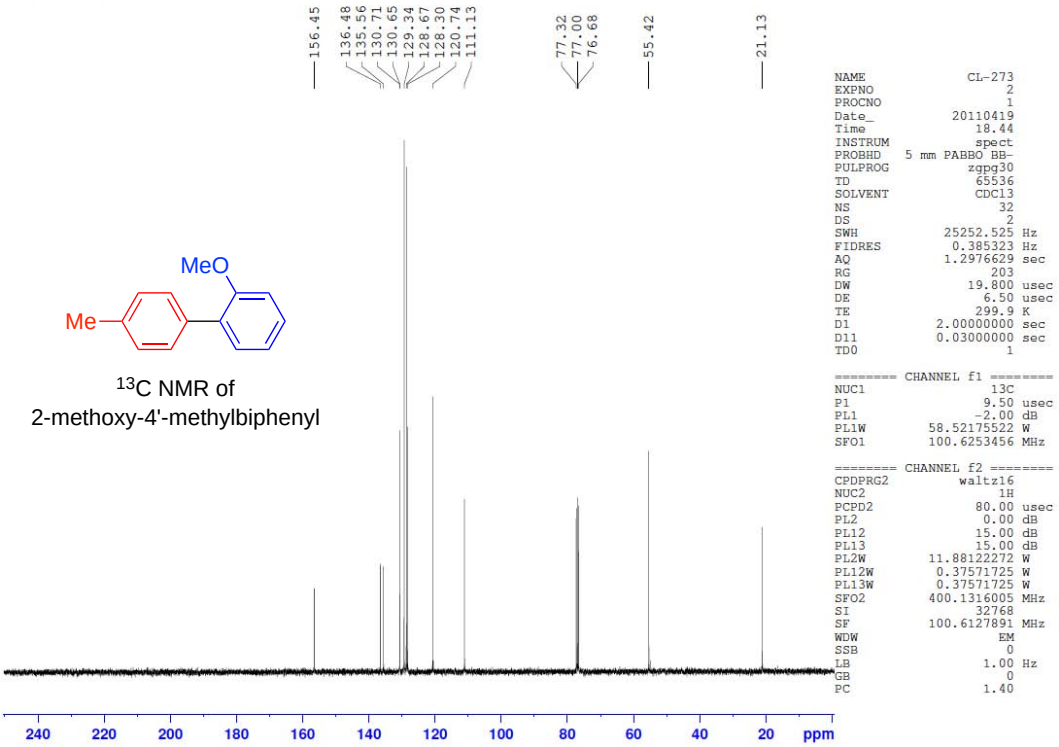


^{1}H NMR of
2-methoxy-4'-methylbiphenyl

```
NAME                CL-273
EXPNO                    1
PROCNO                   1
Date_             20110419
Time                 18.42
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               6009.615 Hz
FIDRES            0.183399 Hz
AQ                2.7263477 sec
RG                      18
DW                  83.200 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             400.1326128 MHz
SI                   32768
SF               400.1300000 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

CL-273 13C



^{13}C NMR of
2-methoxy-4'-methylbiphenyl

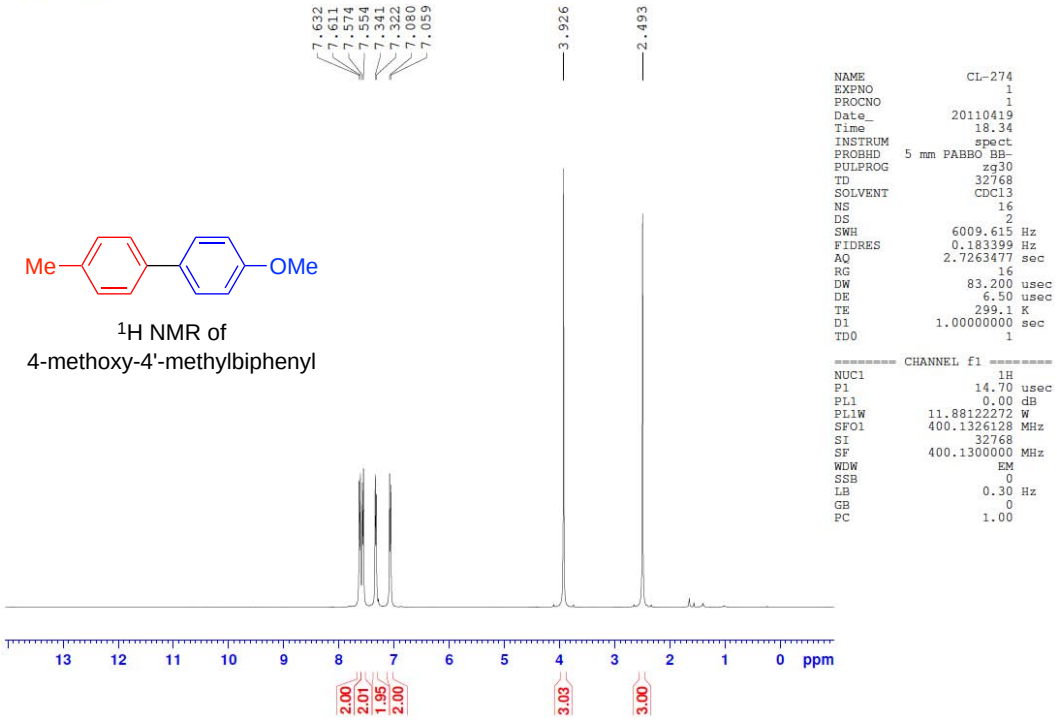
```
NAME                CL-273
EXPNO                    2
PROCNO                   1
Date_             20110419
Time                 18.44
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      32
DS                       2
SWH              25252.525 Hz
FIDRES            0.385323 Hz
AQ                1.2976629 sec
RG                     203
DW                  19.800 usec
DE                   6.50 usec
TE                  299.9 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             100.6253456 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               100.6127891 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

4-Methoxy-4'-methylbiphenyl (**Table 3.2**, entry 3)

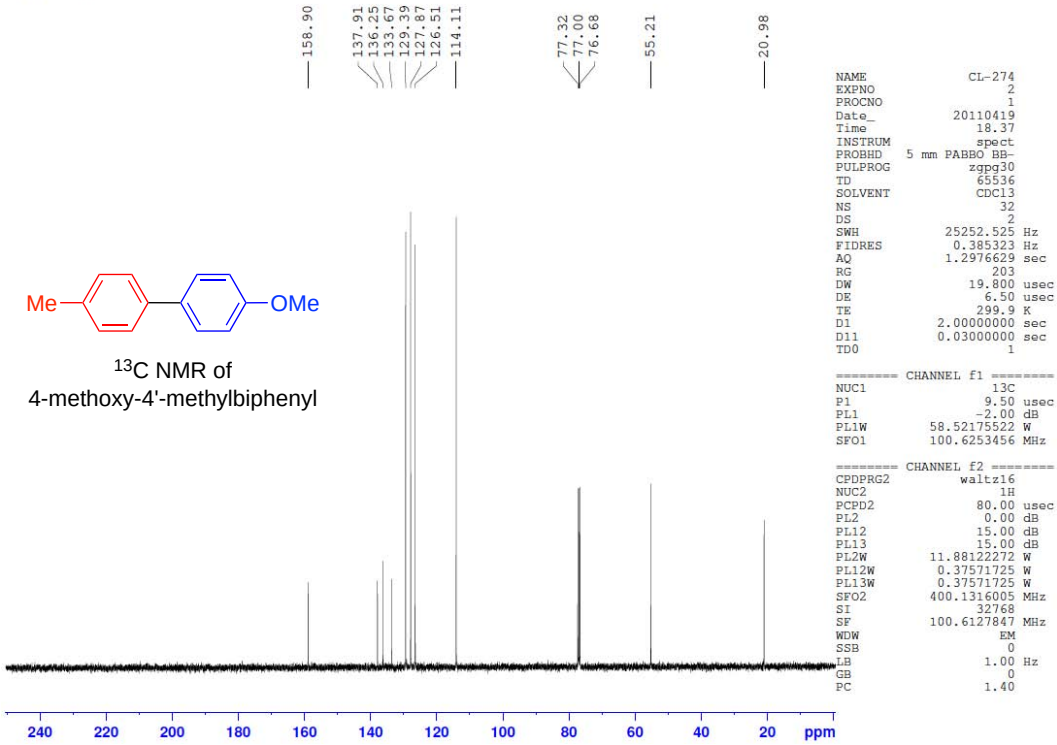
CL-274 1H



^{1}H NMR of
4-methoxy-4'-methylbiphenyl

NAME	CL-274
EXPNO	1
PROCNO	1
Date_	20110419
Time	18.34
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	6009.615 Hz
FIDRES	0.183399 Hz
AQ	2.7263477 sec
RG	16
DW	83.200 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	400.1326128 MHz
SI	32768
SF	400.1300000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

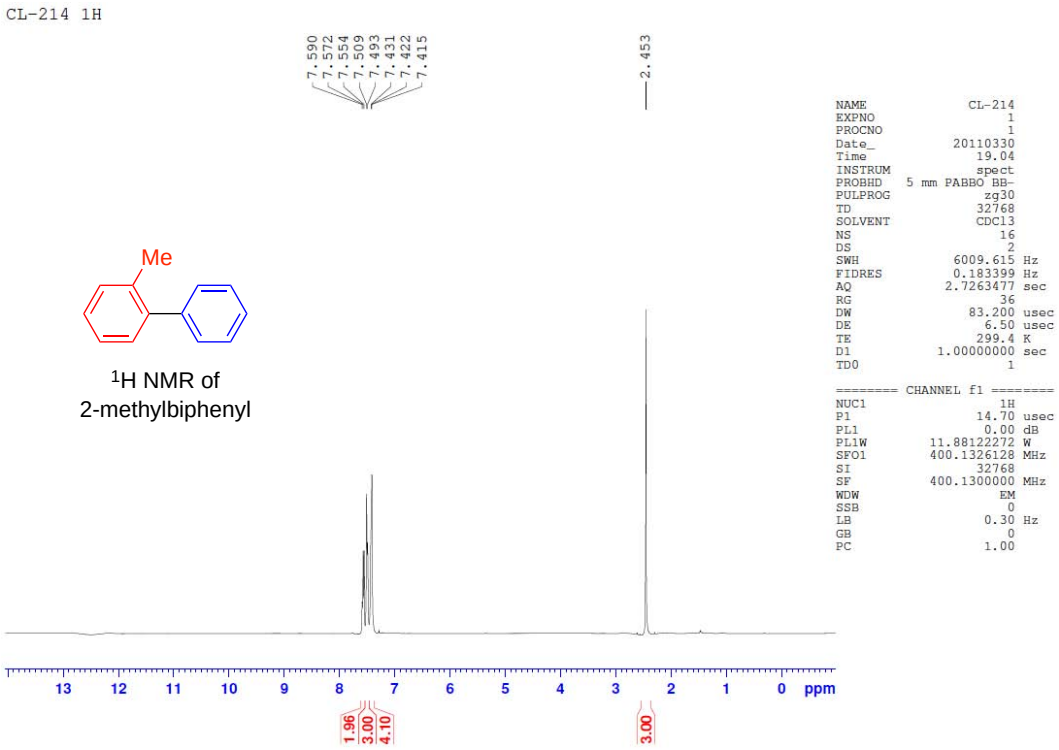
CL-274 13C



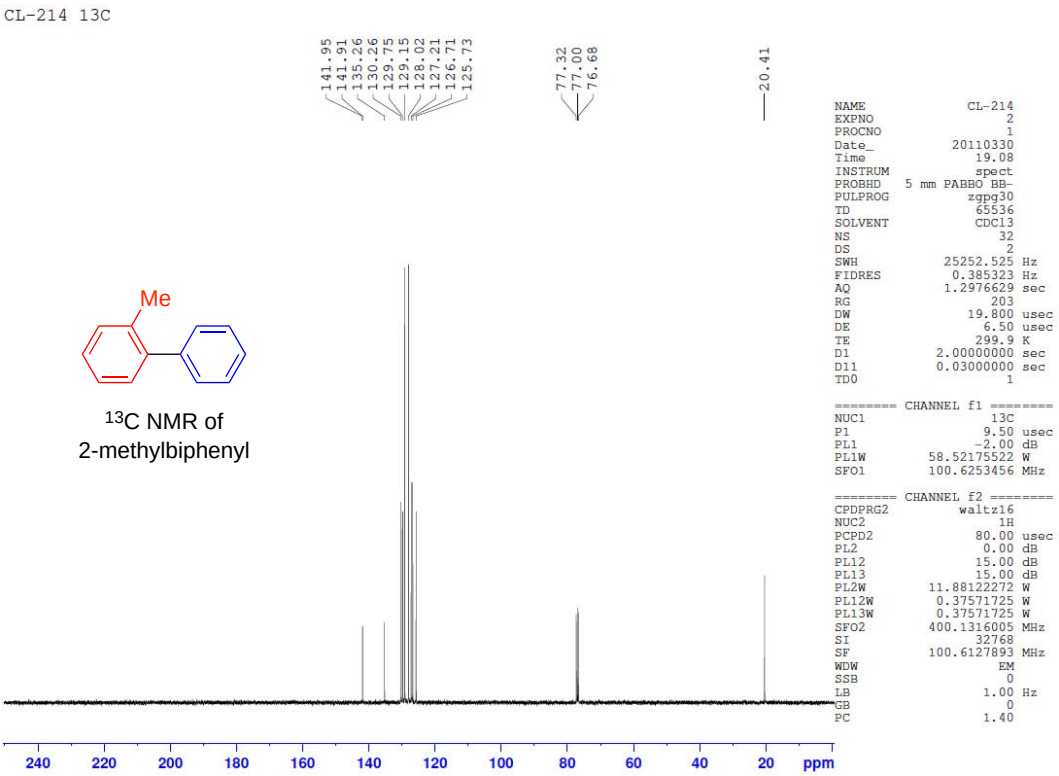
^{13}C NMR of
4-methoxy-4'-methylbiphenyl

NAME	CL-274
EXPNO	2
PROCNO	1
Date_	20110419
Time	18.37
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	32
DS	2
SWH	25252.525 Hz
FIDRES	0.385323 Hz
AQ	1.2976629 sec
RG	203
DW	19.800 usec
DE	6.50 usec
TE	299.9 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	100.6253456 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

2-Methylbiphenyl (**Table 3.2**, entry 4)

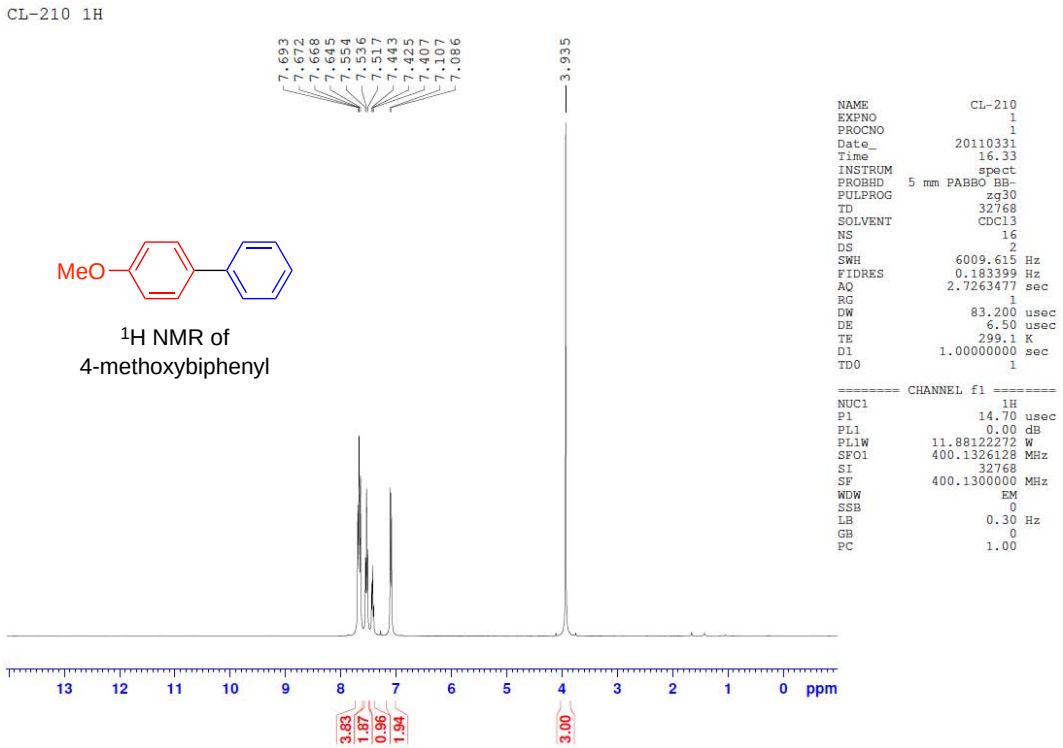


^{1}H NMR of
2-methylbiphenyl

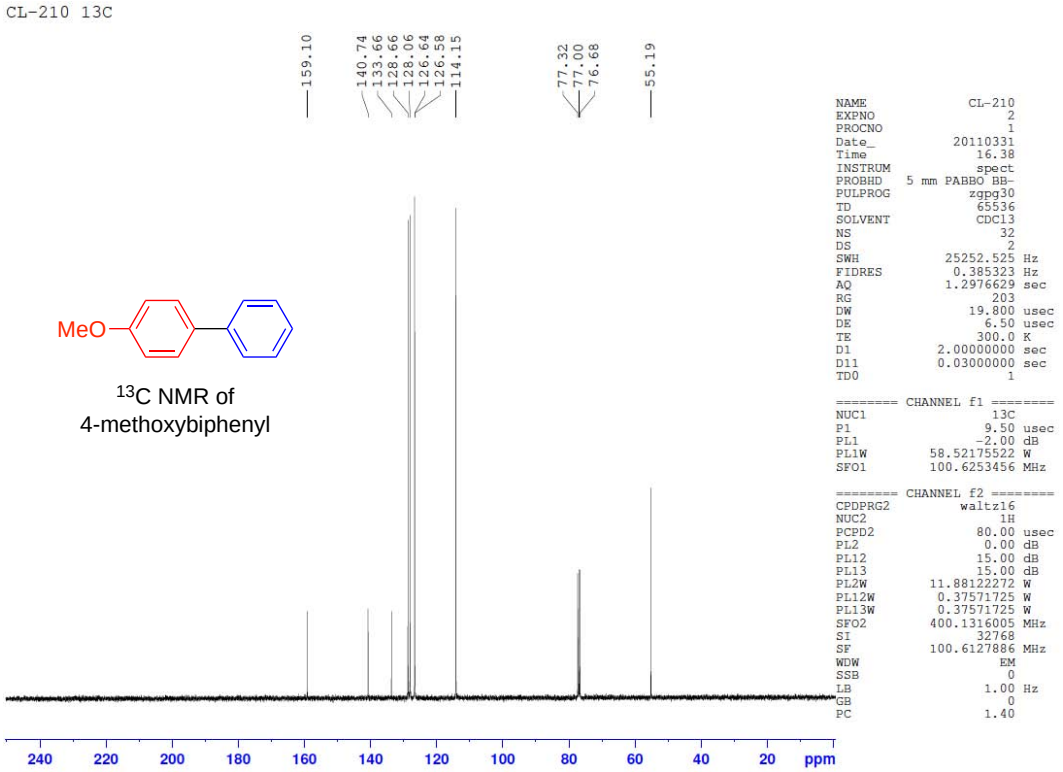


^{13}C NMR of
2-methylbiphenyl

4-Methoxybiphenyl (**Table 3.2**, entry 6)



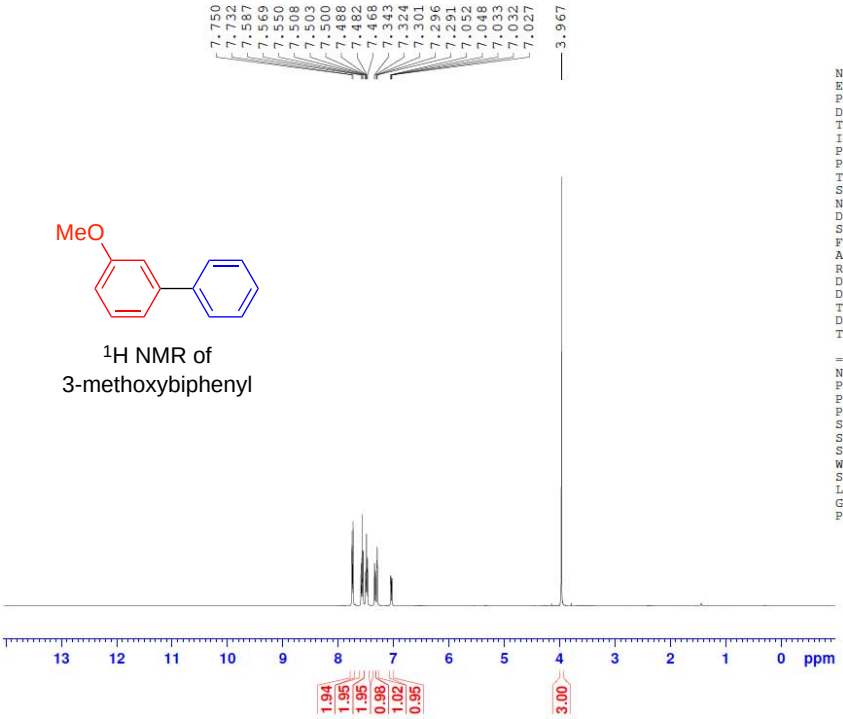
^{1}H NMR of
4-methoxybiphenyl



^{13}C NMR of
4-methoxybiphenyl

3-Methoxybiphenyl (**Table 3.2**, entry 7)

CL-230 1H

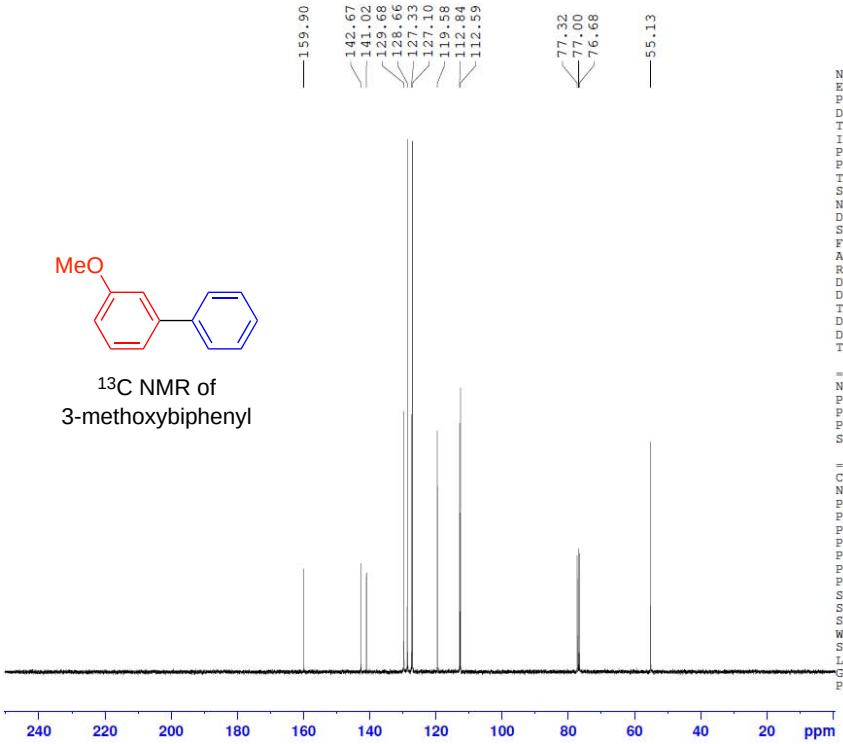


^{1}H NMR of
3-methoxybiphenyl

```
NAME              CL-230
EXPNO                  1
PROCNO                 1
Date_           20110408
Time               20.01
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6009.615 Hz
FIDRES          0.183399 Hz
AQ              2.7263477 sec
RG                    16
DW                83.200 usec
DE                 6.50 usec
TE                298.7 K
D1              1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                0.00 dB
PL1W          11.88122272 W
SFO1          400.1326128 MHz
SI                 32768
SF            400.1300000 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```

CL-230 13C



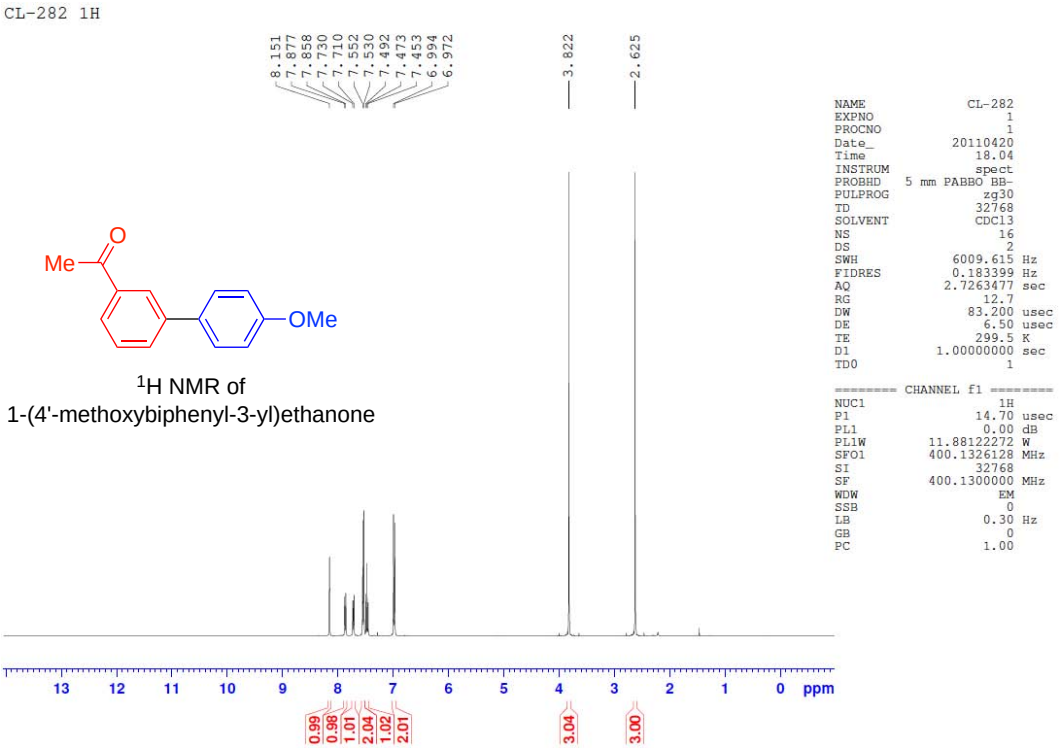
^{13}C NMR of
3-methoxybiphenyl

```
NAME              CL-230
EXPNO                  2
PROCNO                 1
Date_           20110408
Time               20.06
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            25252.525 Hz
FIDRES          0.385323 Hz
AQ              1.2976629 sec
RG                   203
DW                19.800 usec
DE                 6.50 usec
TE                299.7 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                    1

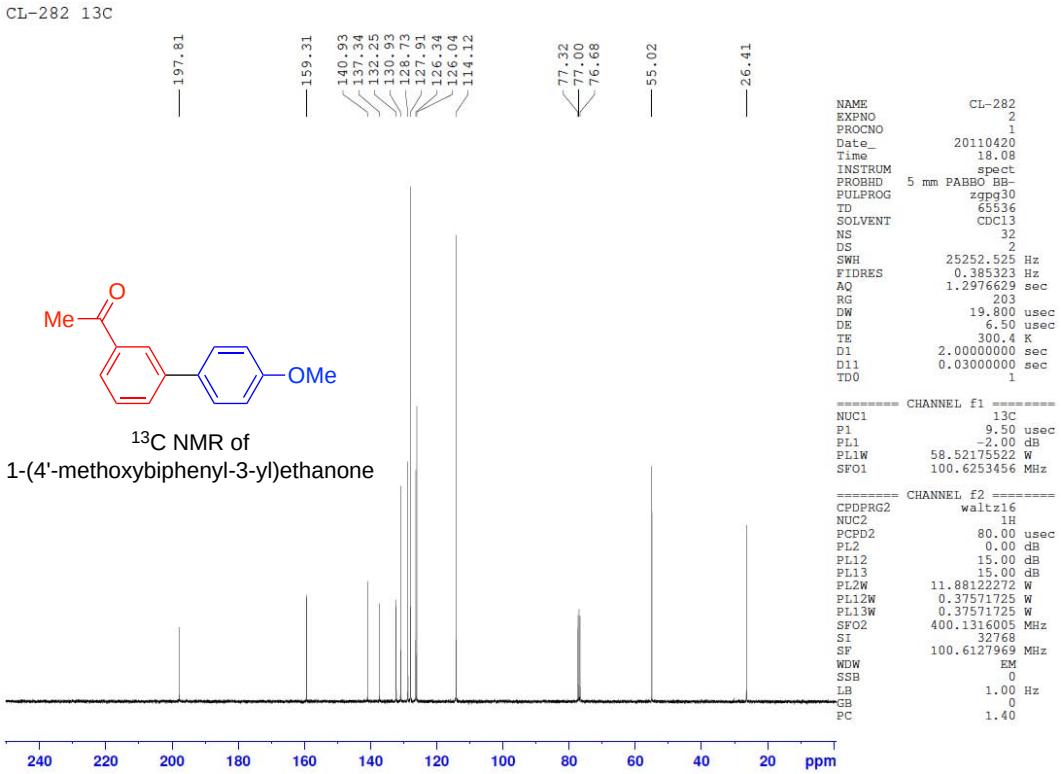
======== CHANNEL f1 ========
NUC1                 13C
P1                 9.50 usec
PL1               -2.00 dB
PL1W          58.52175522 W
SFO1          100.6253456 MHz

======== 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            100.6127915 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                 1.40
```

1-(4'-Methoxybiphenyl-3-yl)ethanone (**Table 3.3**, entry 1)



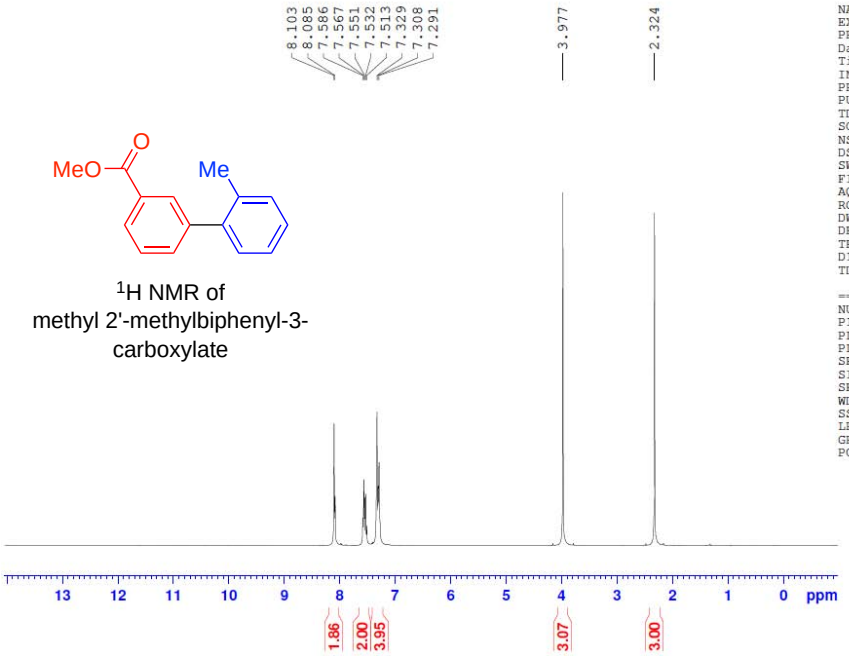
^{1}H NMR of
1-(4'-methoxybiphenyl-3-yl)ethanone



^{13}C NMR of
1-(4'-methoxybiphenyl-3-yl)ethanone

Methyl 2'-methylbiphenyl-3-carboxylate (**Table 3.3**, entry 2)

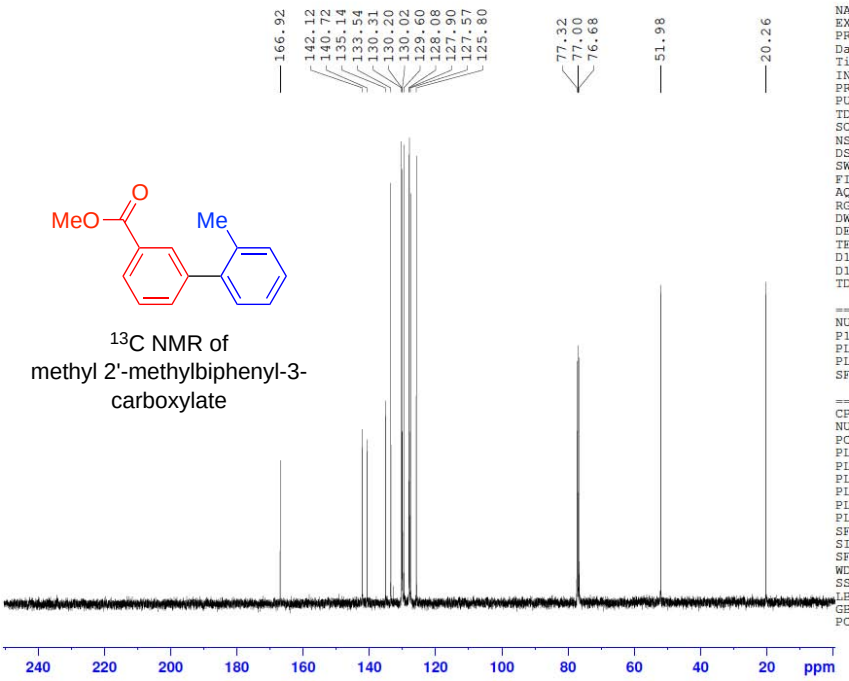
CL-156 1H



^{1}H NMR of methyl 2'-methylbiphenyl-3-carboxylate

NAME	CL-156
EXPNO	3
PROCNO	1
Date_	20110317
Time	12.59
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	6009.615 Hz
FIDRES	0.183399 Hz
AQ	2.7263477 sec
RG	10
DW	83.200 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	400.1326128 MHz
SI	32768
SF	400.1300000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

CL-156 13C

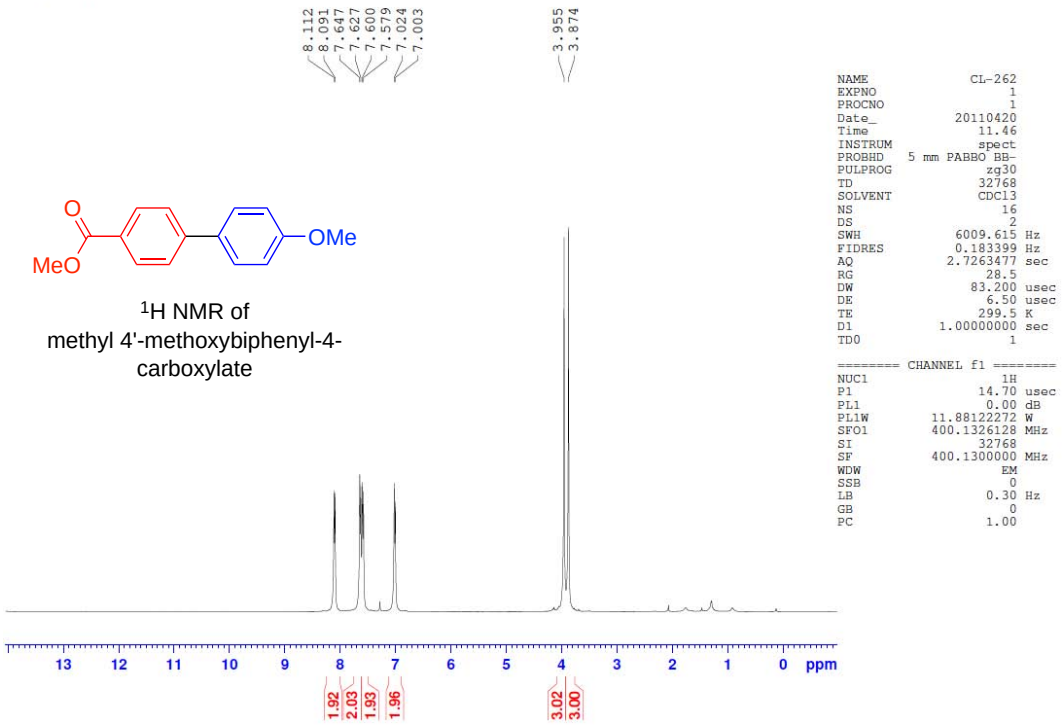


^{13}C NMR of methyl 2'-methylbiphenyl-3-carboxylate

NAME	CL-156
EXPNO	4
PROCNO	1
Date_	20110317
Time	13.03
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	32
DS	2
SWH	25252.525 Hz
FIDRES	0.385323 Hz
AQ	1.2976629 sec
RG	203
DW	19.800 usec
DE	6.50 usec
TE	300.1 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	100.6253456 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

Methyl 4'-methoxybiphenyl-4-carboxylate (**Table 3.3**, entry 3)

CL-262 1H

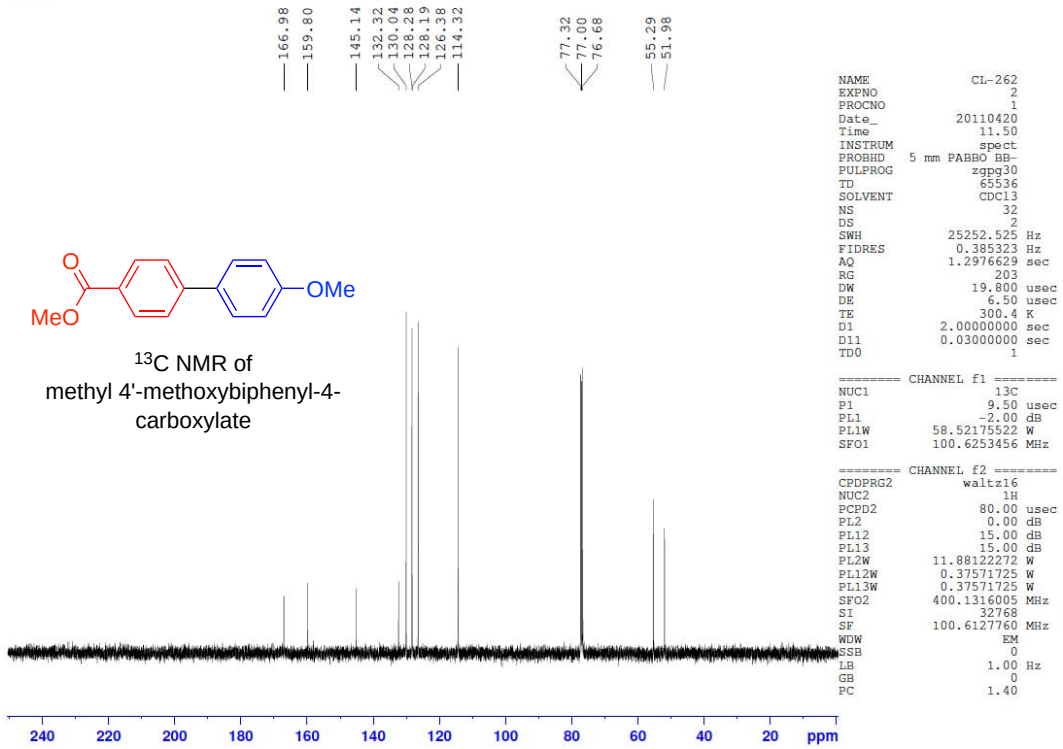


NAME CL-262
EXPNO 1
PROCNO 1
Date_ 20110420
Time 11.46
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 28.5
DW 83.200 usec
DE 6.50 usec
TE 299.5 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 14.70 usec
PL1 0.00 dB
PL1W 11.88122272 W
SFO1 400.1326128 MHz
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

^{1}H NMR of methyl 4'-methoxybiphenyl-4-carboxylate

CL-262 13C



NAME CL-262
EXPNO 2
PROCNO 1
Date_ 20110420
Time 11.50
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 32
DS 2
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976629 sec
RG 203
DW 19.800 usec
DE 6.50 usec
TE 300.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

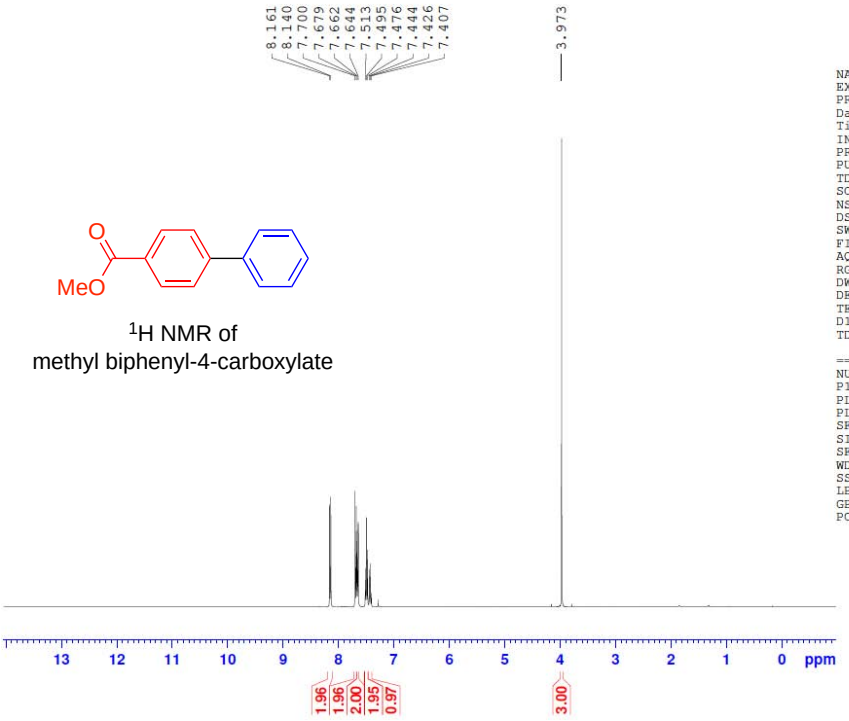
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 -2.00 dB
PL1W 58.52175522 W
SFO1 100.6253456 MHz

======== 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

^{13}C NMR of methyl 4'-methoxybiphenyl-4-carboxylate

Methyl biphenyl-4-carboxylate (**Table 3.3**, entry 4)

CL-234 1H

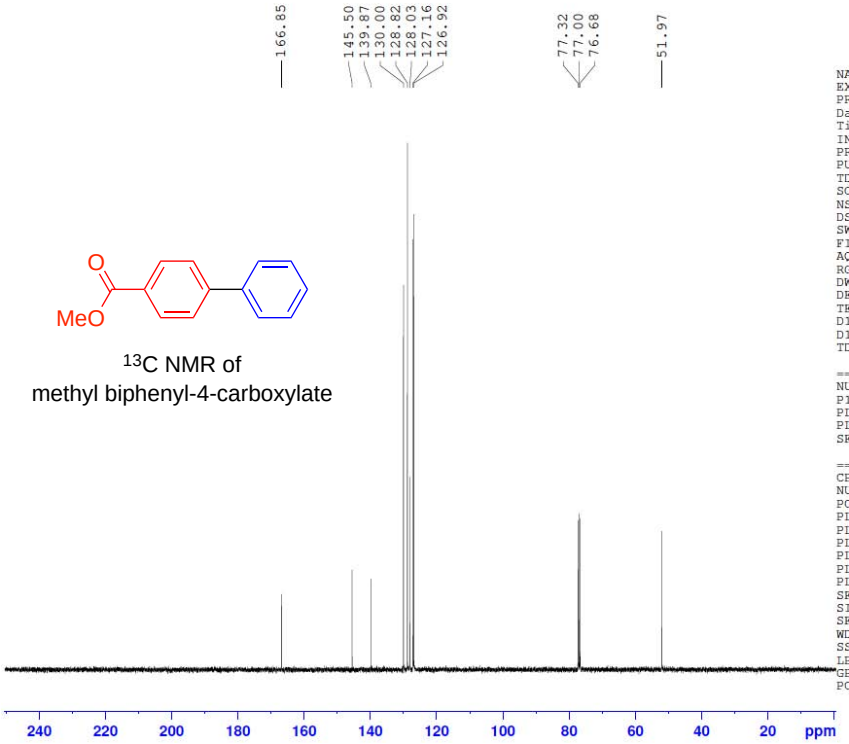


^{1}H NMR of
methyl biphenyl-4-carboxylate

```
NAME              CL-234
EXPNO                  1
PROCNO                 1
Date_           20110406
Time               18.40
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6009.615 Hz
FIDRES          0.183399 Hz
AQ              2.7263477 sec
RG                  20.2
DW                83.200 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        400.1326128 MHz
SI                 32768
SF          400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

CL-234 13C



^{13}C NMR of
methyl biphenyl-4-carboxylate

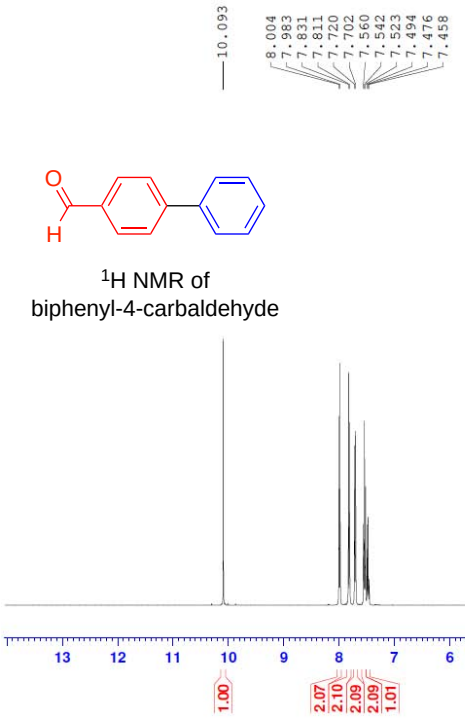
```
NAME              CL-234
EXPNO                  2
PROCNO                 1
Date_           20110406
Time               18.43
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            25252.525 Hz
FIDRES          0.385323 Hz
AQ              1.2976629 sec
RG                   203
DW                19.800 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        100.6253456 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          100.6127822 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

Biphenyl-4-carbaldehyde (**Table 3.3**, entry 5)

CL-233 1H

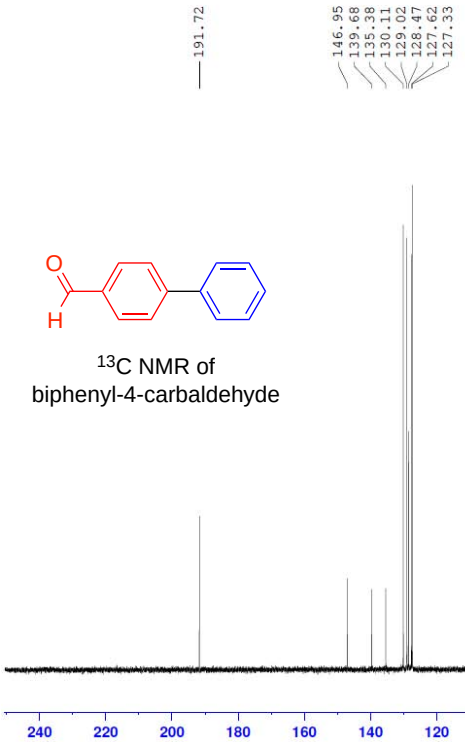


^{1}H NMR of biphenyl-4-carbaldehyde

```
NAME                CL-233
EXPNO                    3
PROCNO                   1
Date_             20110405
Time                 16.06
INSTRUM              spect
PROBHD     5 mm PABBO BB-
PULPROG               zg30
TD                   32768
SOLVENT             CD2Cl2
NS                       16
DS                        2
SWH               6009.615 Hz
FIDRES            0.183399 Hz
AQ                2.7263477 sec
RG                       1
DW                  83.200 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           400.1326128 MHz
SI                   32768
SF             400.1300000 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

CL-233 13C



^{13}C NMR of biphenyl-4-carbaldehyde

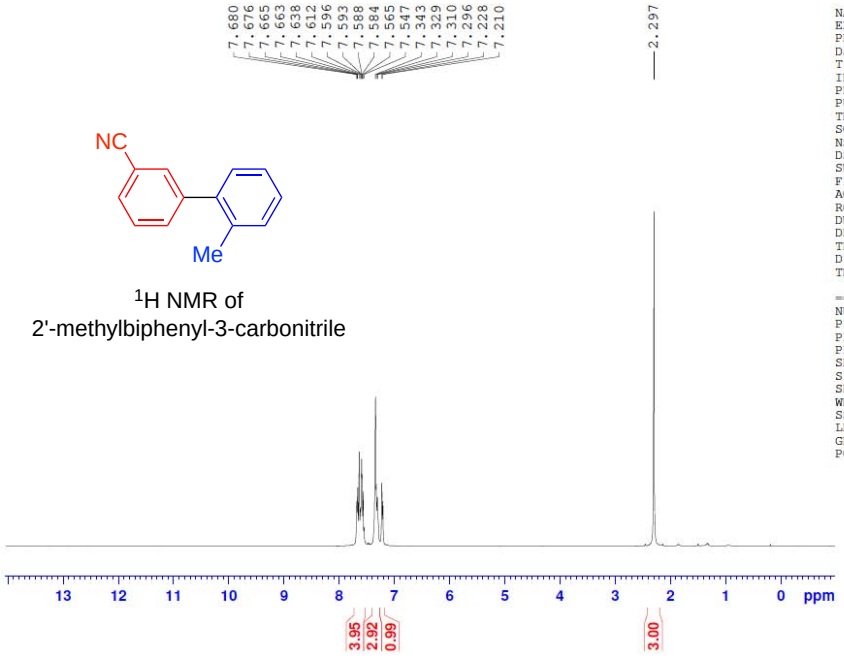
```
NAME                CL-233
EXPNO                    4
PROCNO                   1
Date_             20110405
Time                 16.10
INSTRUM              spect
PROBHD     5 mm PABBO BB-
PULPROG           zgpg30
TD                   65536
SOLVENT             CD2Cl2
NS                       32
DS                        2
SWH              25252.525 Hz
FIDRES            0.385323 Hz
AQ                1.2976629 sec
RG                     203
DW                  19.800 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          100.6253456 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'-Methylbiphenyl-3-carbonitrile (**Table 3.3**, entry 6)

CL-59 1H

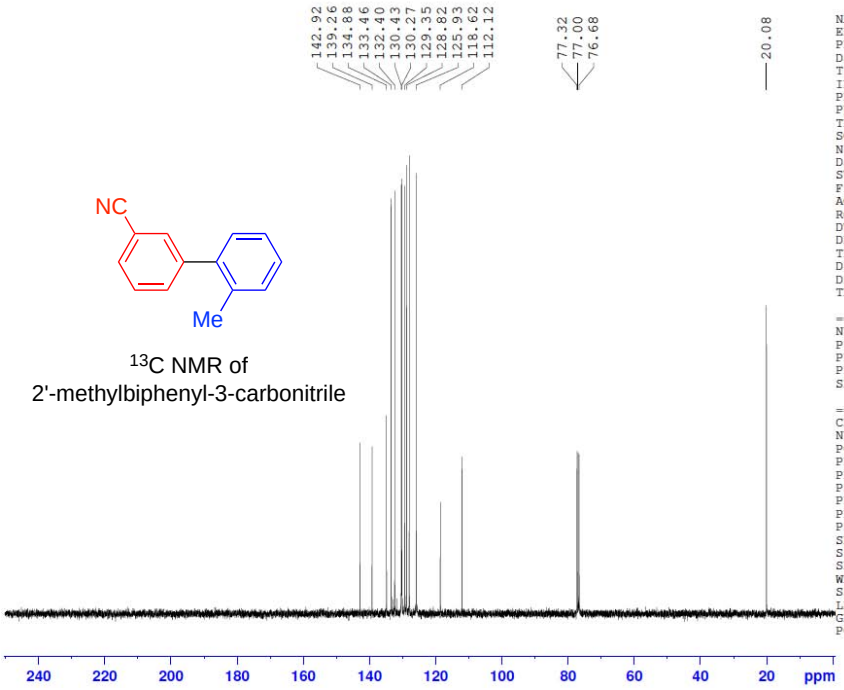


NAME CL-59
EXPNO 1
PROCNO 1
Date_ 20110222
Time 8.13
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 2.56
DW 83.200 usec
DE 6.50 usec
TE 296.5 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 14.70 usec
PL1 0.00 dB
PL1W 11.88122272 W
SFO1 400.1326128 MHz
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

^{1}H NMR of
2'-methylbiphenyl-3-carbonitrile

CL-59 13C



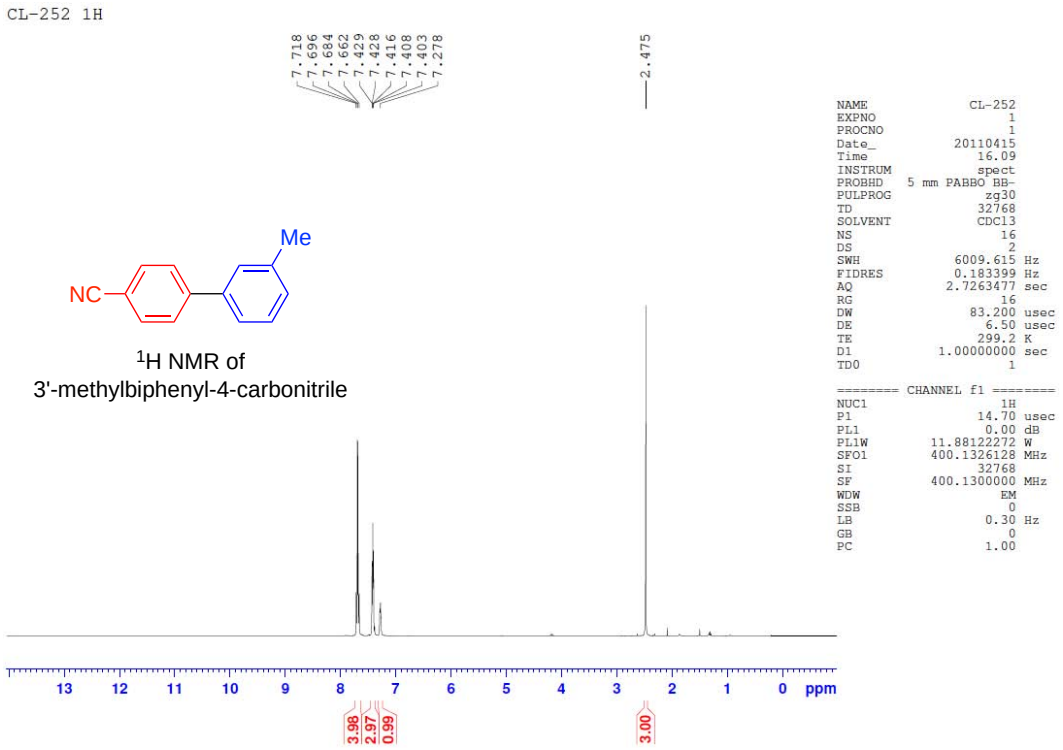
NAME CL-59
EXPNO 2
PROCNO 1
Date_ 20110222
Time 8.16
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 32
DS 2
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976629 sec
RG 203
DW 19.800 usec
DE 6.50 usec
TE 297.3 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 -2.00 dB
PL1W 58.52175522 W
SFO1 100.6253456 MHz

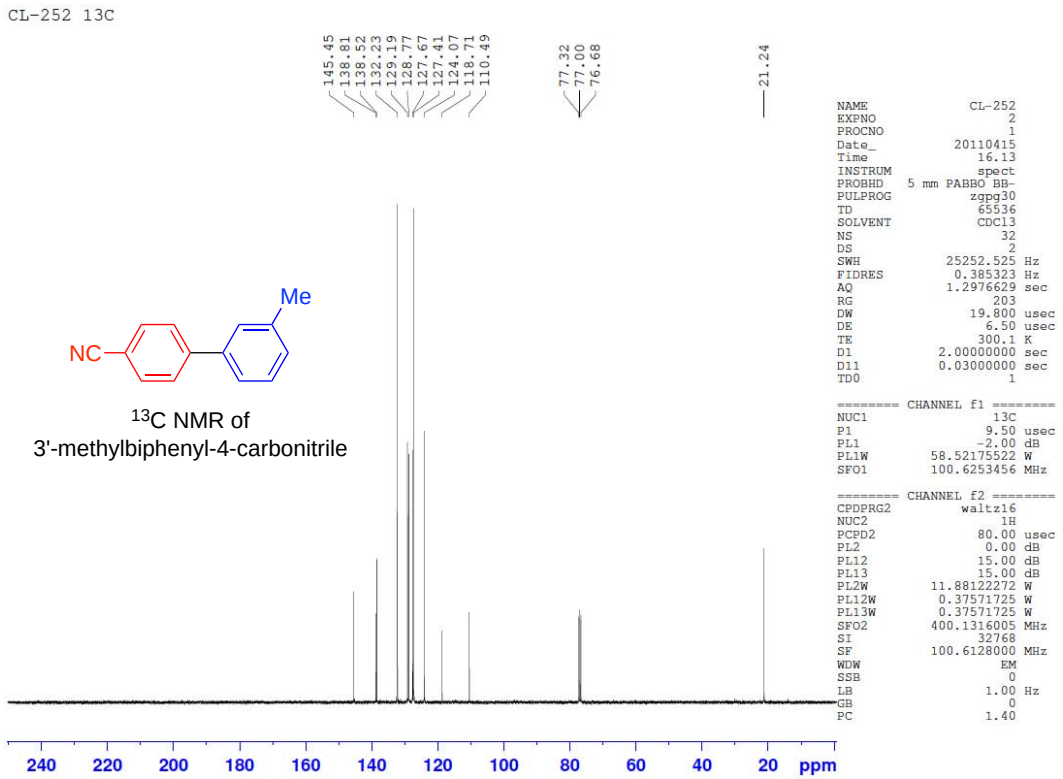
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 15.00 dB
PL13 15.00 dB
PL2W 11.88122272 W
PL12W 0.37571725 W
PL13W 0.37571725 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127970 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

^{13}C NMR of
2'-methylbiphenyl-3-carbonitrile

3'-Methylbiphenyl-4-carbonitrile (**Table 3.3**, entry 7)



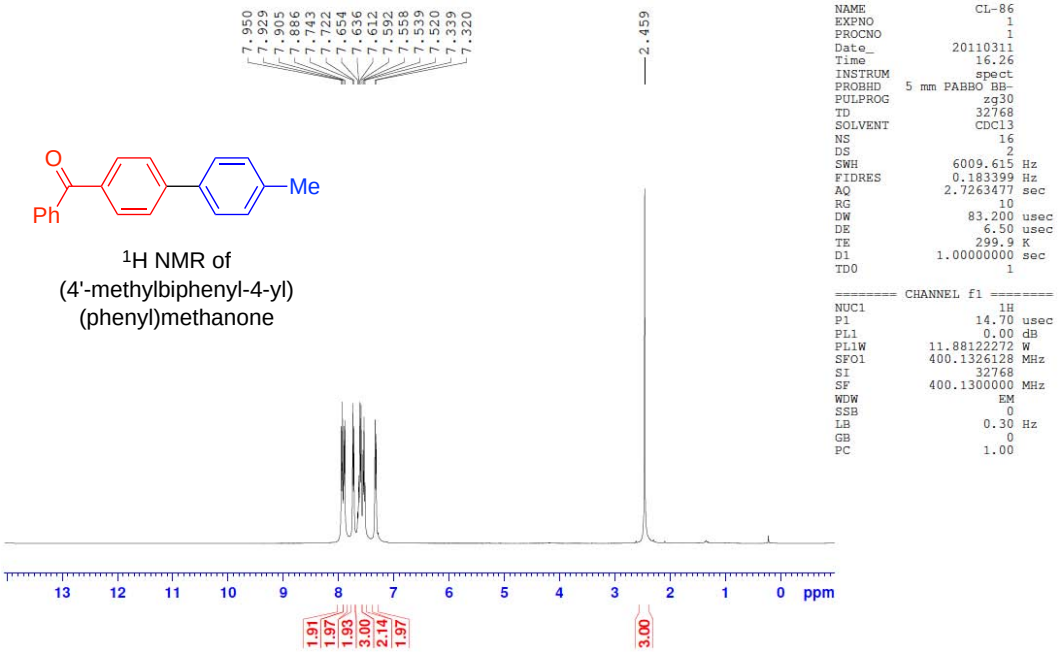
^{1}H NMR of
3'-methylbiphenyl-4-carbonitrile



^{13}C NMR of
3'-methylbiphenyl-4-carbonitrile

(4'-Methylbiphenyl-4-yl)(phenyl)methanone (**Table 3.3**, entry 8)

CL-86 1H

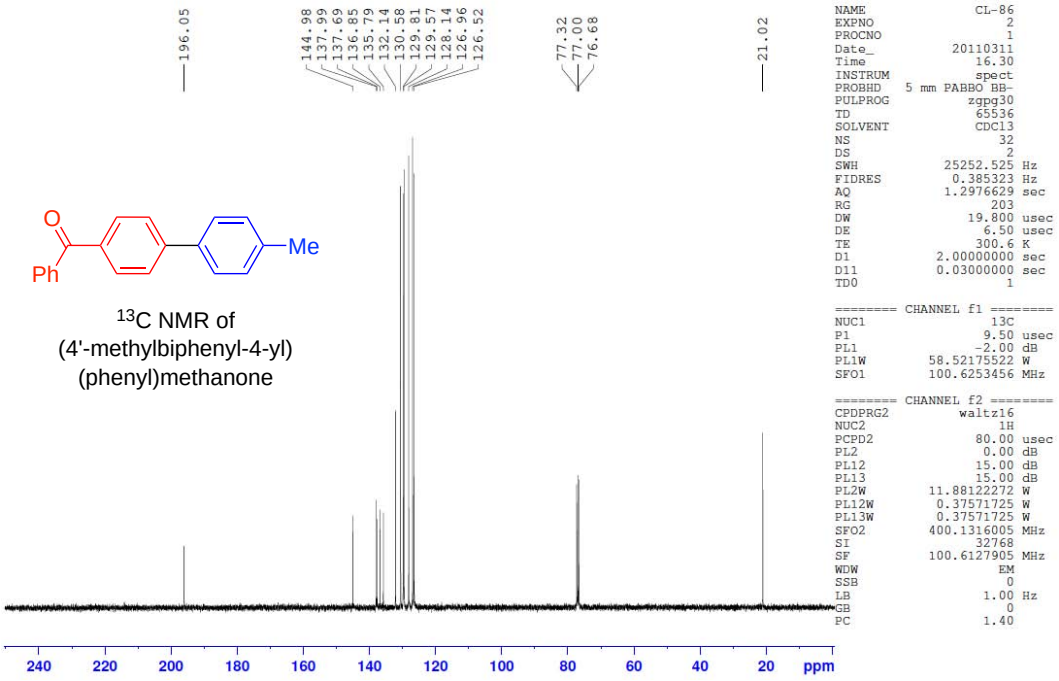


^{1}H NMR of
(4'-methylbiphenyl-4-yl)
(phenyl)methanone

```
NAME              CL-86
EXPNO                1
PROCNO               1
Date_         20110311
Time             16.26
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG           zg30
TD               32768
SOLVENT          CDCl3
NS                  16
DS                   2
SWH           6009.615 Hz
FIDRES        0.183399 Hz
AQ            2.7263477 sec
RG                  10
DW              83.200 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       400.1326128 MHz
SI               32768
SF         400.1300000 MHz
WDW                 EM
SSB                  0
LB               0.30 Hz
GB                   0
PC                1.00
```

CL-86 13C



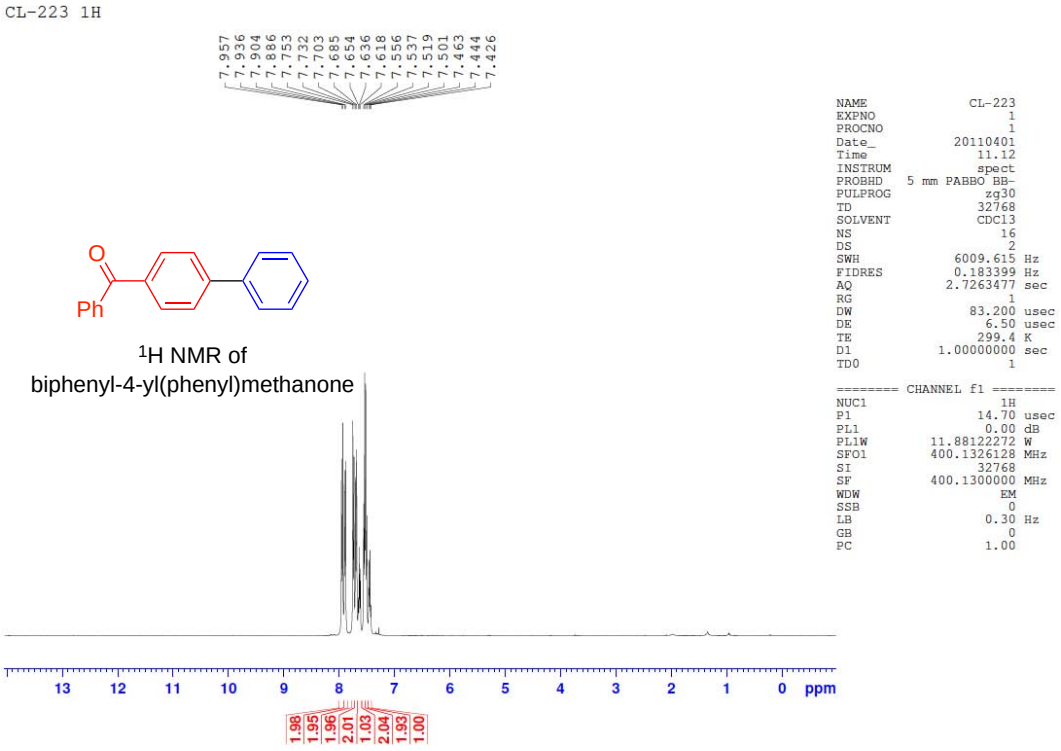
^{13}C NMR of
(4'-methylbiphenyl-4-yl)
(phenyl)methanone

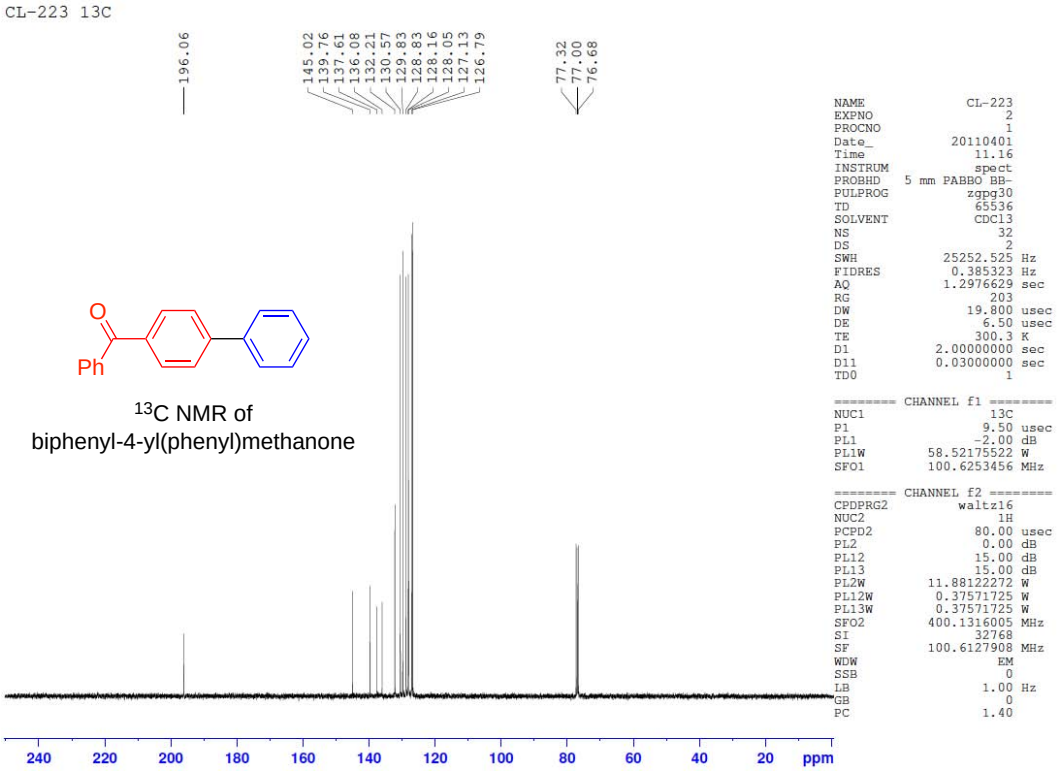
```
NAME              CL-86
EXPNO                2
PROCNO               1
Date_         20110311
Time             16.30
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                  32
DS                   2
SWH          25252.525 Hz
FIDRES        0.385323 Hz
AQ            1.2976629 sec
RG                 203
DW              19.800 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       100.6253456 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         100.6127905 MHz
WDW                 EM
SSB                  0
LB               1.00 Hz
GB                   0
PC                1.40
```

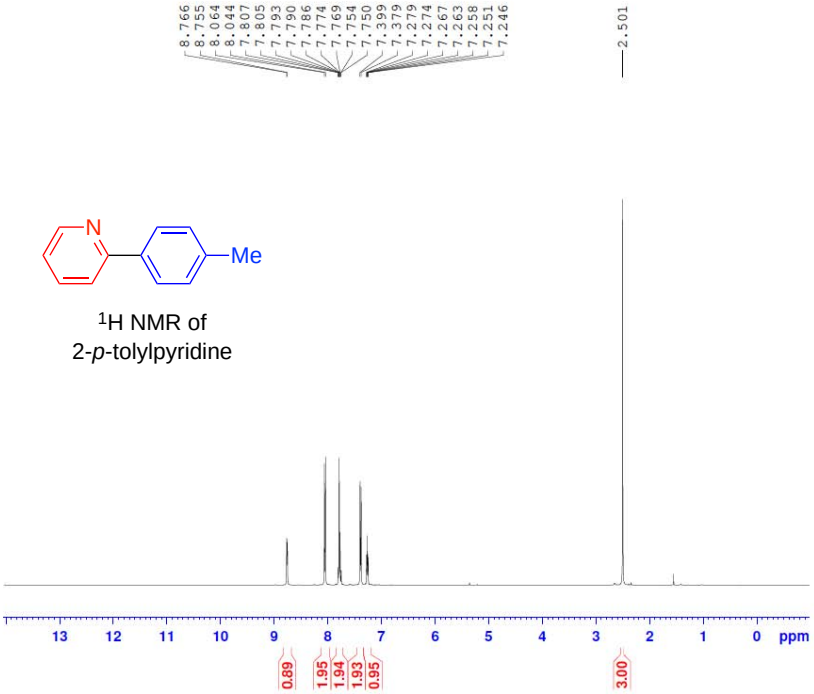
Biphenyl-4-yl(phenyl)methanone (**Table 3.3**, entry 9)





2-*p*-Tolylpyridine (**Table 3.4**, entry 1)

CL-255 1H

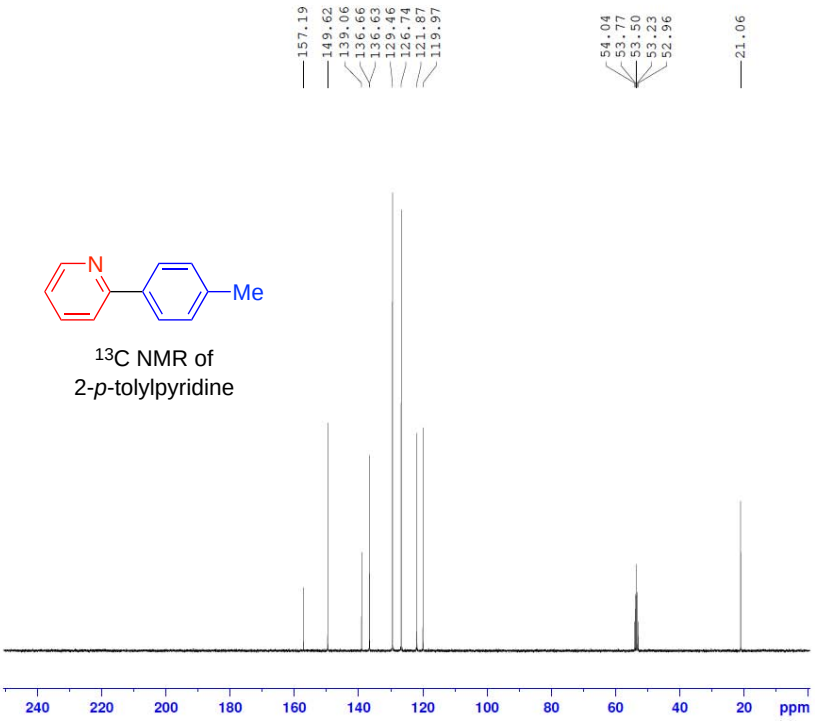


^{1}H NMR of
2-*p*-tolylpyridine

```
NAME                CL-255
EXPNO                    1
PROCNO                   1
Date_             20110414
Time                 16.51
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   32768
SOLVENT              CD2Cl2
NS                       16
DS                        2
SWH               6009.615 Hz
FIDRES            0.183399 Hz
AQ                2.7263477 sec
RG                    12.7
DW                  83.200 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         400.1326128 MHz
SI                   32768
SF           400.1300000 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

CL-255 13C



^{13}C NMR of
2-*p*-tolylpyridine

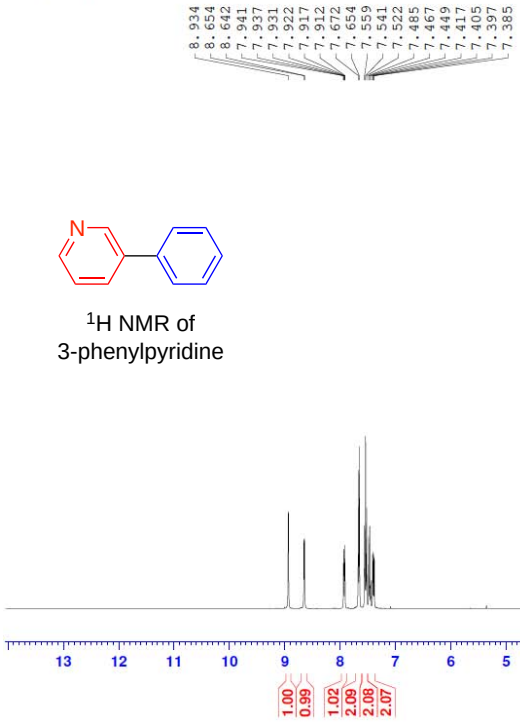
```
NAME                CL-255
EXPNO                    2
PROCNO                   1
Date_             20110414
Time                 16.53
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CD2Cl2
NS                       32
DS                        2
SWH              25252.525 Hz
FIDRES            0.385323 Hz
AQ                1.2976629 sec
RG                      203
DW                  19.800 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         100.6253456 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-Phenylpyridine (**Table 3.4**, entry 2)

CL-256 1H

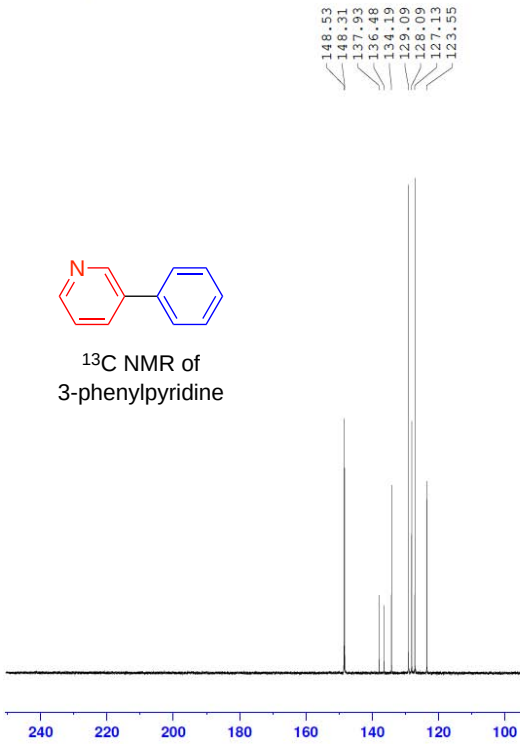


^{1}H NMR of
3-phenylpyridine

```
NAME                CL-256
EXPNO                    1
PROCNO                   1
Date_             20110413
Time                 16.50
INSTRUM              spect
PROBHD     5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT             CD2Cl2
NS                       16
DS                        2
SWH               6009.615 Hz
FIDRES               0.183399 Hz
AQ                2.7263477 sec
RG                      12.7
DW                   83.200 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            400.1326128 MHz
SI                   32768
SF               400.1300000 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

CL-256 13C



^{13}C NMR of
3-phenylpyridine

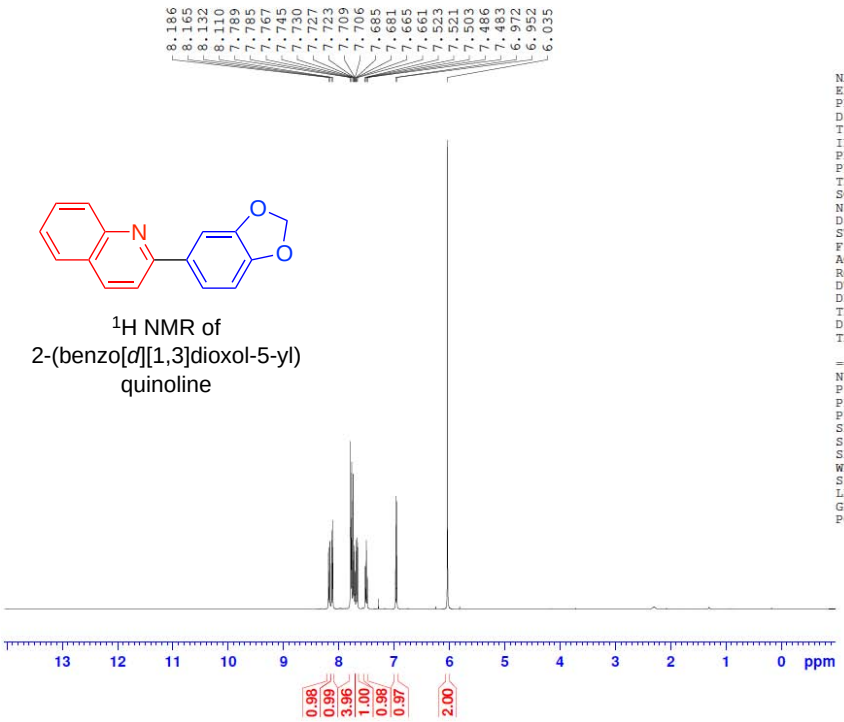
```
NAME                CL-256
EXPNO                    2
PROCNO                   1
Date_             20110413
Time                 16.53
INSTRUM              spect
PROBHD     5 mm PABBO BB-
PULPROG           zgpg30
TD                  65536
SOLVENT             CD2Cl2
NS                       32
DS                        2
SWH              25252.525 Hz
FIDRES               0.385323 Hz
AQ                1.2976629 sec
RG                      203
DW                   19.800 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            100.6253456 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-(Benzo[*d*][1,3]dioxol-5-yl)quinoline (**Table 3.4**, entry 3)

CL-266 1H

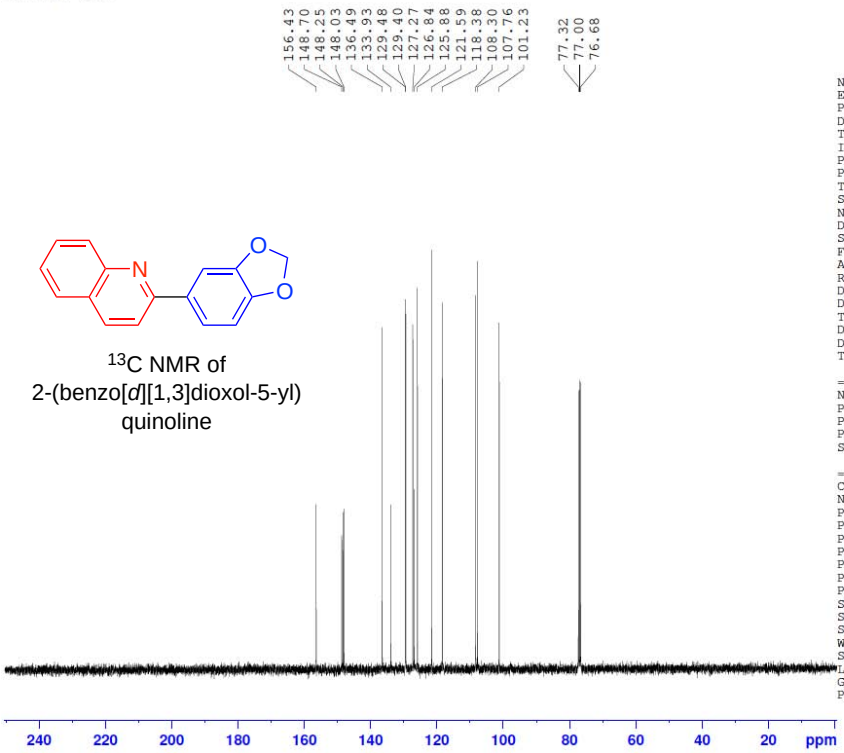


NAME CL-266
EXPNO 1
PROCNO 1
Date_ 20110419
Time 18.49
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 25.4
DW 83.200 usec
DE 6.50 usec
TE 299.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 14.70 usec
PL1 0.00 dB
PL1W 11.88122272 W
SFO1 400.1326128 MHz
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

^{1}H NMR of
2-(benzo[*d*][1,3]dioxol-5-yl)
quinoline

CL-266 13C



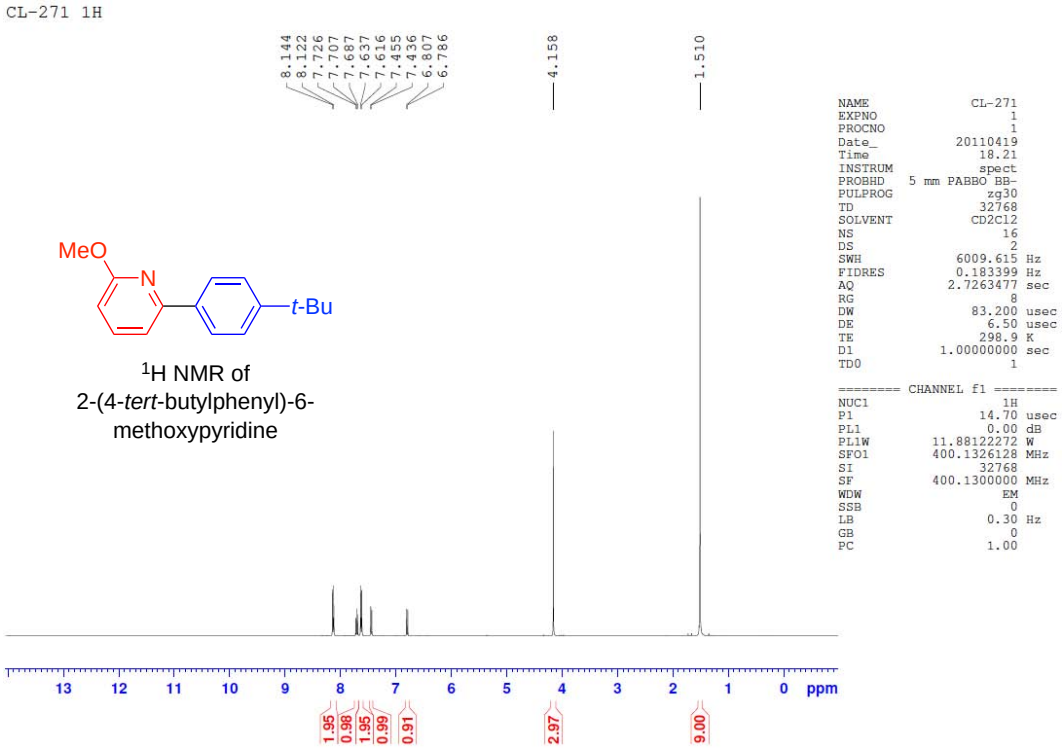
NAME CL-266
EXPNO 2
PROCNO 1
Date_ 20110419
Time 18.52
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 32
DS 2
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976629 sec
RG 203
DW 19.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 -2.00 dB
PL1W 58.52175522 W
SFO1 100.6253456 MHz

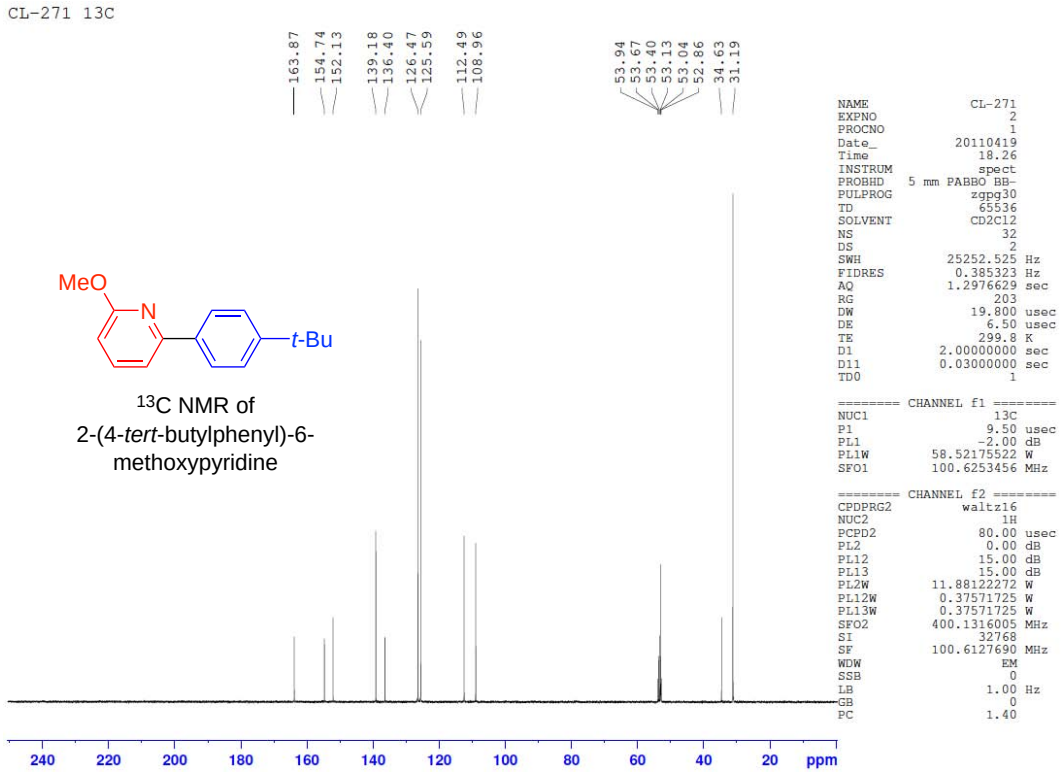
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 15.00 dB
PL13 15.00 dB
PL2W 11.88122272 W
PL12W 0.37571725 W
PL13W 0.37571725 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127861 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

^{13}C NMR of
2-(benzo[*d*][1,3]dioxol-5-yl)
quinoline

2-(4-*tert*-Butylphenyl)-6-methoxypyridine (**Table 3.4**, entry 4)



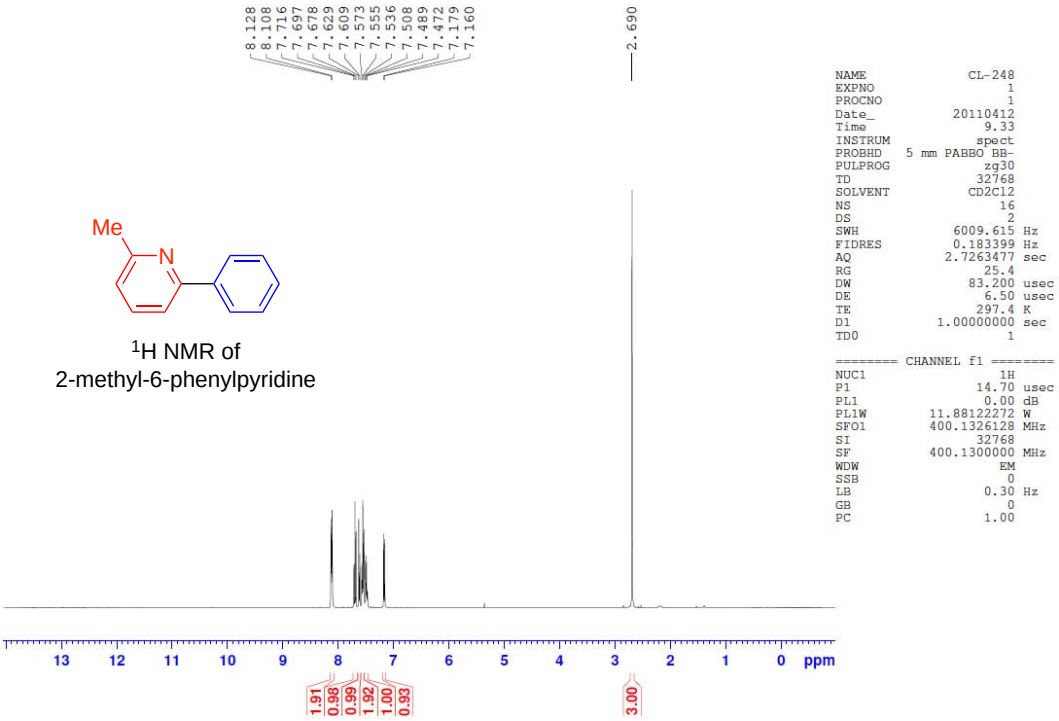
^{1}H NMR of
2-(4-*tert*-butylphenyl)-6-
methoxypyridine



^{13}C NMR of
2-(4-*tert*-butylphenyl)-6-
methoxypyridine

2-Methyl-6-phenylpyridine (**Table 3.4**, entry 5)

CL-248 1H

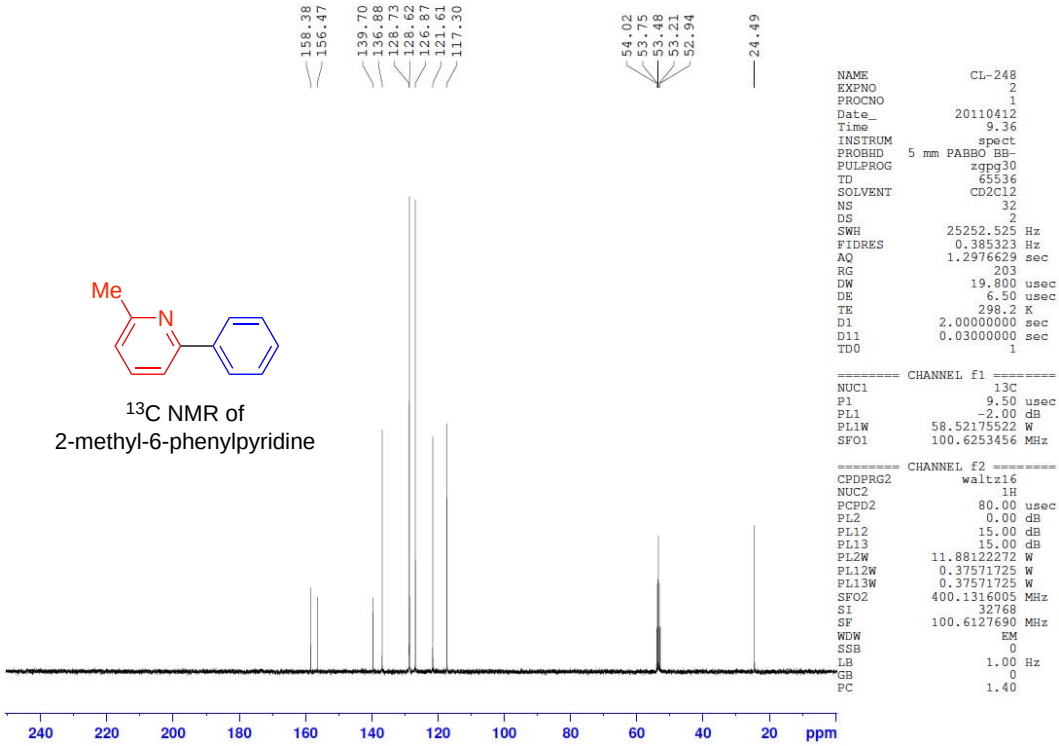


NAME CL-248
EXPNO 1
PROCNO 1
Date_ 20110412
Time 9.33
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CD2Cl2
NS 16
DS 2
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 25.4
DW 83.200 usec
DE 6.50 usec
TE 297.4 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 14.70 usec
PL1 0.00 dB
PL1W 11.88122272 W
SFO1 400.1326128 MHz
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

^{1}H NMR of
2-methyl-6-phenylpyridine

CL-248 13C



NAME CL-248
EXPNO 2
PROCNO 1
Date_ 20110412
Time 9.36
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CD2Cl2
NS 32
DS 2
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976629 sec
RG 203
DW 19.800 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 100.6253456 MHz

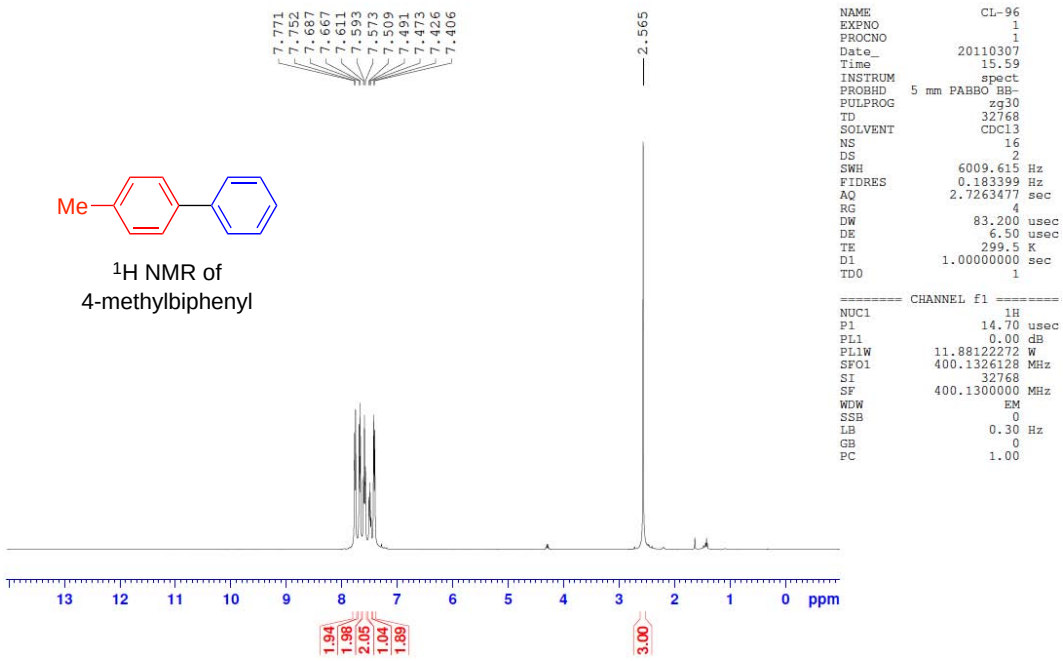
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 15.00 dB
PL13 15.00 dB
PL2W 11.88122272 W
PL12W 0.37571725 W
PL13W 0.37571725 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

^{13}C NMR of
2-methyl-6-phenylpyridine

Chapter 4 NMR Spectra of Coupling products

4-Methylbiphenyl (**Table 4.2**, entry 1)

CL-96 1H

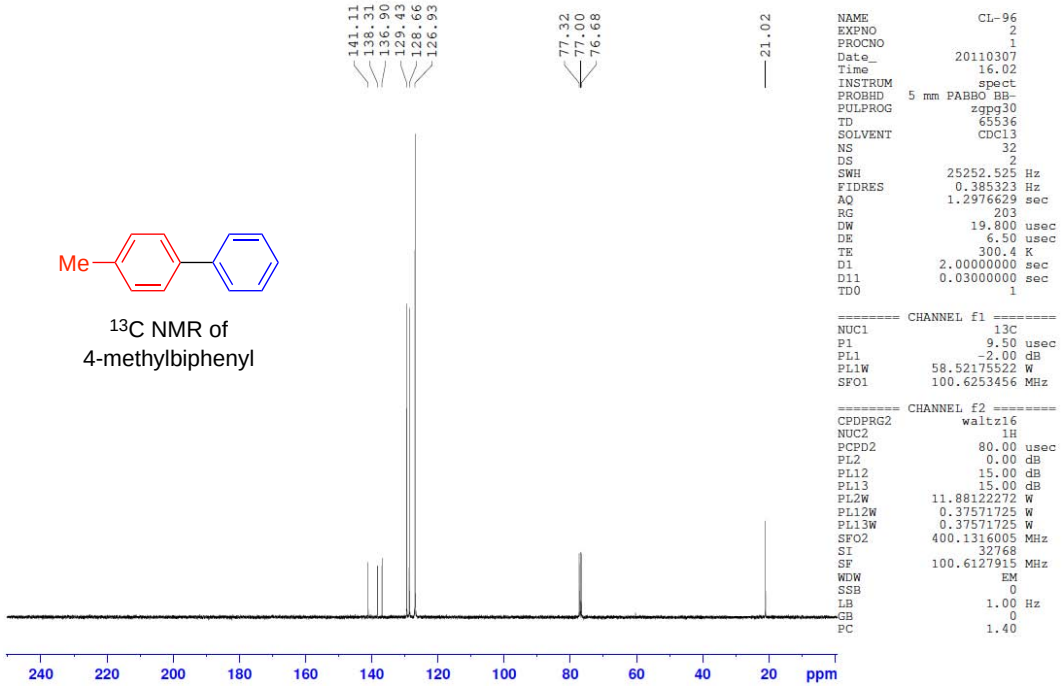


^{1}H NMR of
4-methylbiphenyl

```
NAME                CL-96
EXPNO                   1
PROCNO                  1
Date_            20110307
Time                15.59
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              6009.615 Hz
FIDRES           0.183399 Hz
AQ               2.7263477 sec
RG                      4
DW                 83.200 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          400.1326128 MHz
SI                  32768
SF            400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

CL-96 13C



^{13}C NMR of
4-methylbiphenyl

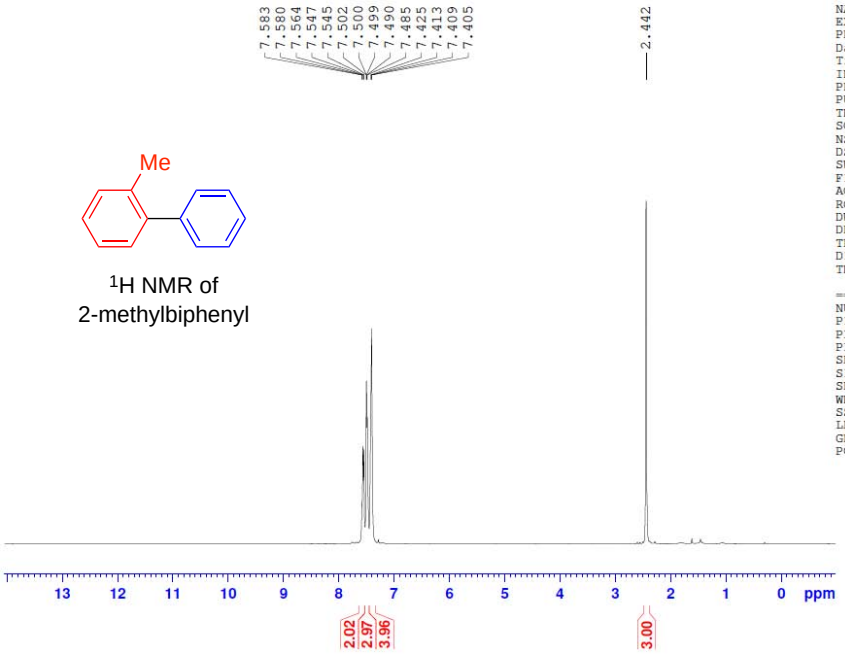
```
NAME                CL-96
EXPNO                   2
PROCNO                  1
Date_            20110307
Time                16.02
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      2
SWH             25252.525 Hz
FIDRES           0.385323 Hz
AQ               1.2976629 sec
RG                    203
DW                 19.800 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          100.6253456 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            100.6127915 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

2-Methylbiphenyl (**Table 4.2**, entry 2)

CL-87 1H



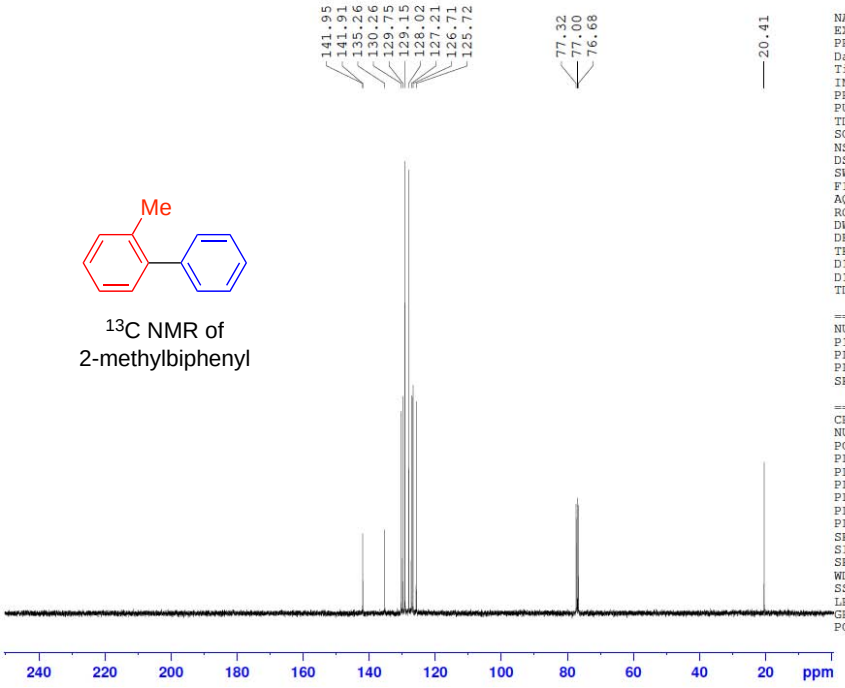
Me

^{1}H NMR of
2-methylbiphenyl

```
NAME              CL-87
EXPNO                1
PROCNO               1
Date_         20110228
Time              8.23
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG           zg30
TD               32768
SOLVENT          CDCl3
NS                  16
DS                   2
SWH           6009.615 Hz
FIDRES        0.183399 Hz
AQ            2.7263477 sec
RG                2.25
DW              83.200 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       400.1326128 MHz
SI               32768
SF         400.1300000 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.00
```

CL-87 13C



Me

^{13}C NMR of
2-methylbiphenyl

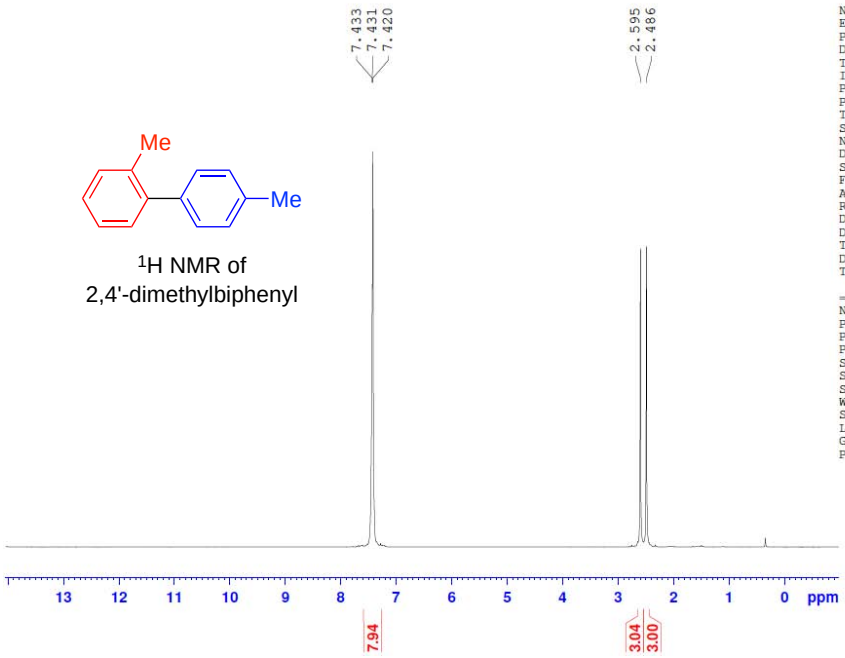
```
NAME              CL-87
EXPNO                2
PROCNO               1
Date_         20110228
Time              8.26
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                  32
DS                   2
SWH          25252.525 Hz
FIDRES        0.385323 Hz
AQ            1.2976629 sec
RG                 203
DW              19.800 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       100.6253456 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         100.6127884 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```

2,4'-Dimethylbiphenyl (**Table 4.2**, entry 3)

CL-88 1H

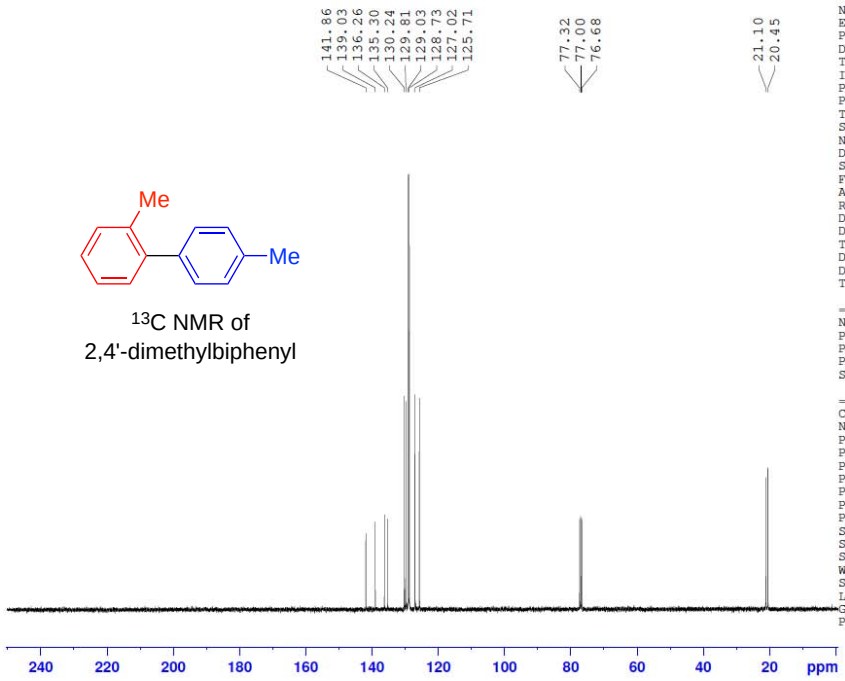


^{1}H NMR of
2,4'-dimethylbiphenyl

```
NAME              CL-88
EXPNO                1
PROCNO               1
Date_         20110228
Time              8.32
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG           zg30
TD               32768
SOLVENT          CDCl3
NS                  16
DS                   2
SWH           6009.615 Hz
FIDRES        0.183399 Hz
AQ            2.7263477 sec
RG                   1
DW              83.200 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       400.1326128 MHz
SI               32768
SF         400.1300000 MHz
WDW                 EM
SSB                  0
LB               0.30 Hz
GB                   0
PC                1.00
```

CL-88 13C



^{13}C NMR of
2,4'-dimethylbiphenyl

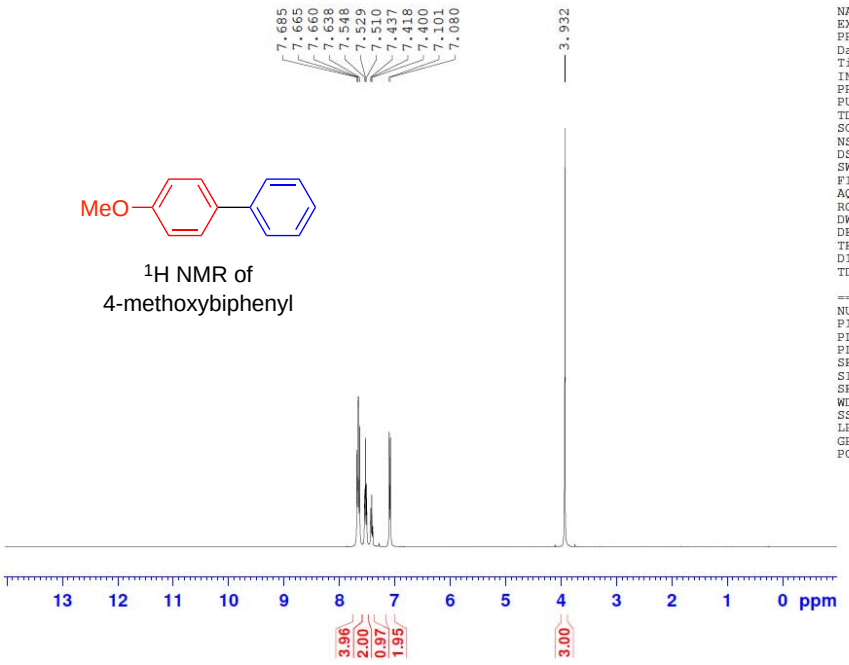
```
NAME              CL-88
EXPNO                2
PROCNO               1
Date_         20110228
Time              8.35
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                  32
DS                   2
SWH          25252.525 Hz
FIDRES        0.385323 Hz
AQ            1.2976629 sec
RG                 203
DW              19.800 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       100.6253456 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         100.6127922 MHz
WDW                 EM
SSB                  0
LB               1.00 Hz
GB                   0
PC                1.40
```

4-Methoxybiphenyl (**Table 4.2**, entry 4)

CL-97 1H

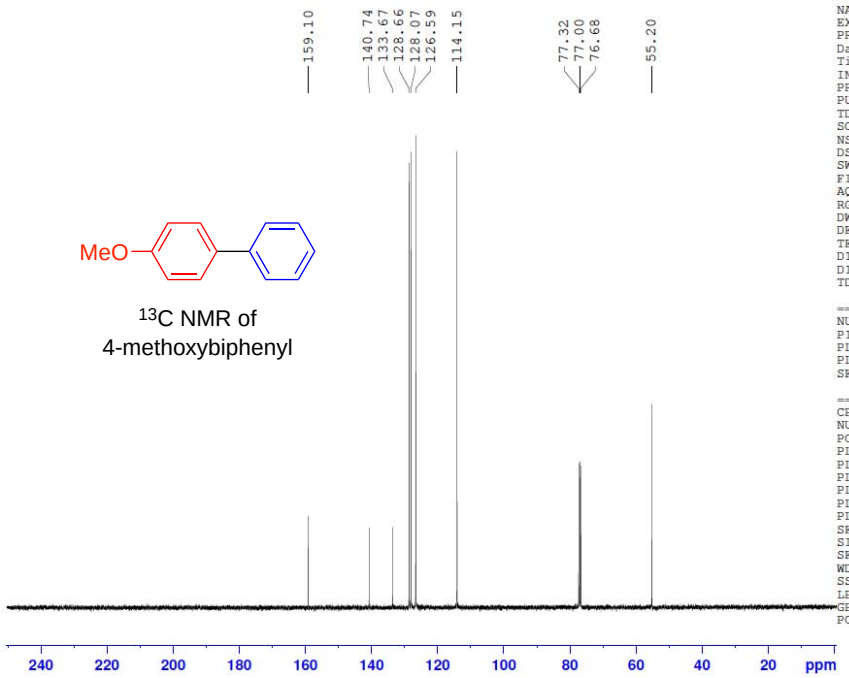


^{1}H NMR of
4-methoxybiphenyl

```
NAME                CL-97
EXPNO                  1
PROCNO                 1
Date_           20110307
Time                8.40
INSTRUM            spect
PROBHD    5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6009.615 Hz
FIDRES          0.183399 Hz
AQ              2.7263477 sec
RG                    10
DW                83.200 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        400.1326128 MHz
SI                 32768
SF          400.1300000 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```

CL-97 13C



^{13}C NMR of
4-methoxybiphenyl

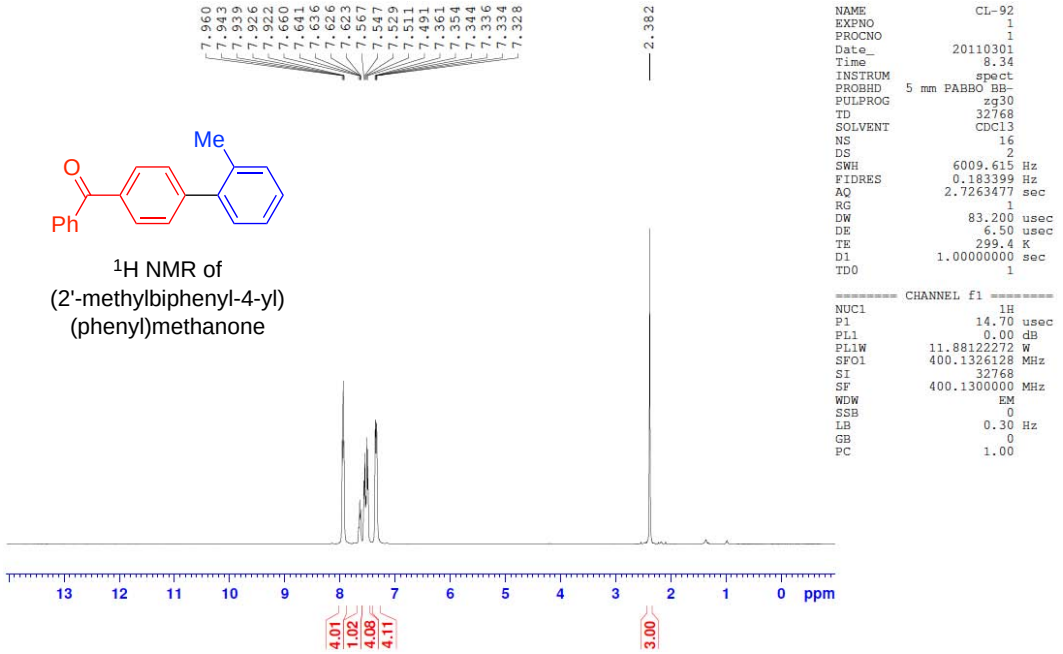
```
NAME                CL-97
EXPNO                  2
PROCNO                 1
Date_           20110307
Time                8.44
INSTRUM            spect
PROBHD    5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            25252.525 Hz
FIDRES          0.385323 Hz
AQ              1.2976629 sec
RG                   203
DW                19.800 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        100.6253456 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
```

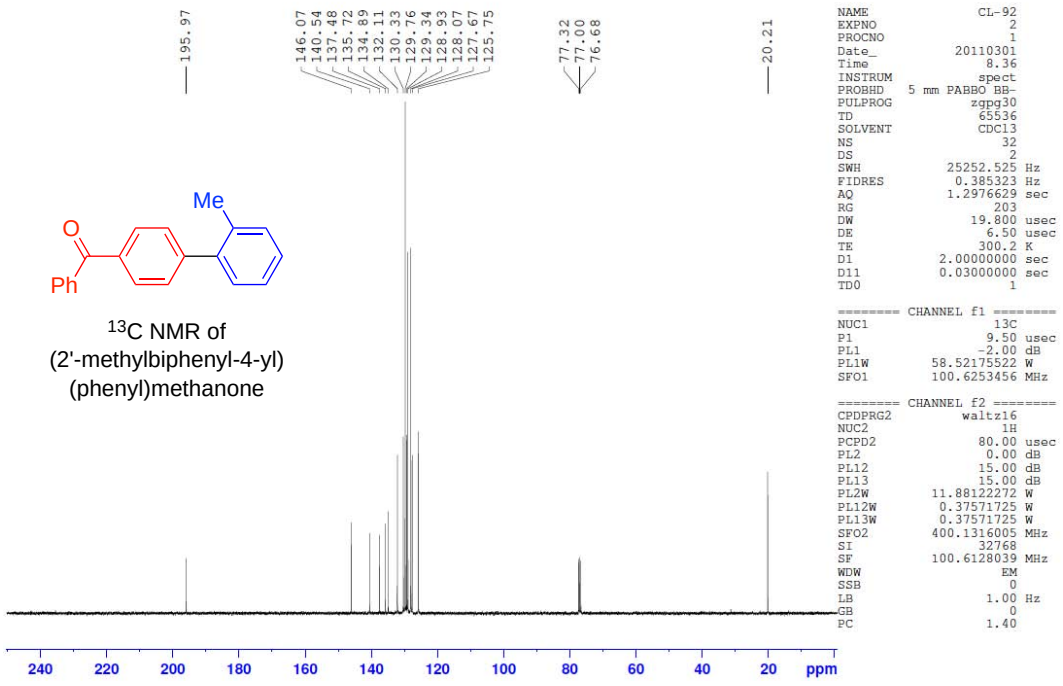
(2'-Methylbiphenyl-4-yl)(phenyl)methanone (**Table 4.2**, entry 5)

CL-92 1H



^{1}H NMR of (2'-methylbiphenyl-4-yl) (phenyl)methanone

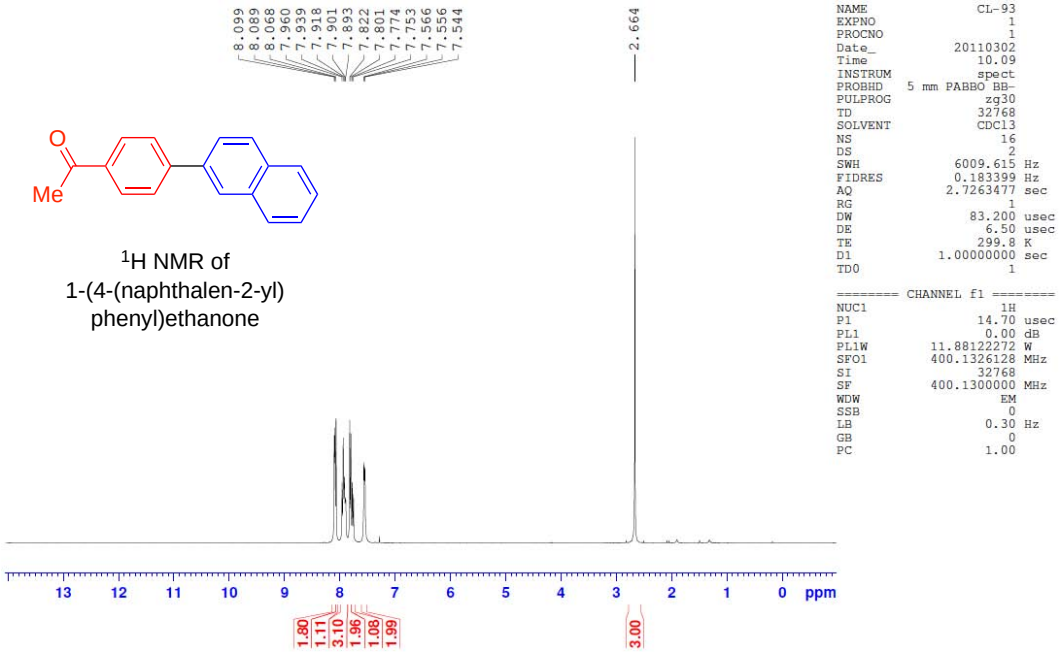
CL-92 13C



^{13}C NMR of (2'-methylbiphenyl-4-yl) (phenyl)methanone

1-(4-(Naphthalen-2-yl)phenyl)ethanone (**Table 4.2**, entry 6)

CL-93 1H

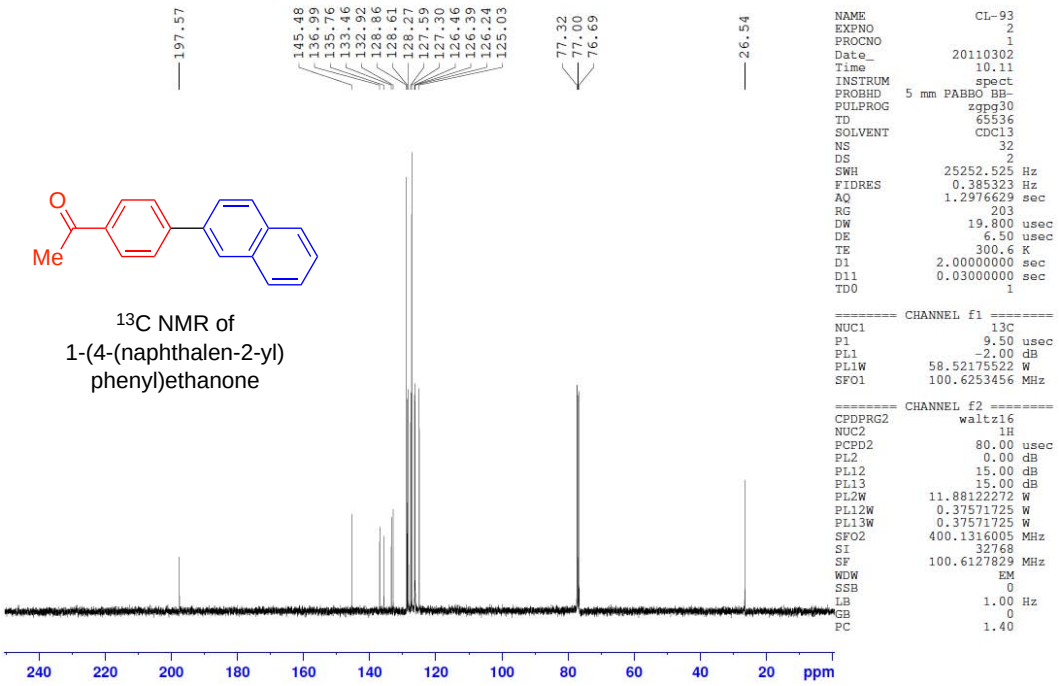


^{1}H NMR of
1-(4-(naphthalen-2-yl)
phenyl)ethanone

```
NAME              CL-93
EXPNO                1
PROCNO               1
Date_         20110302
Time             10.09
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG           zg30
TD               32768
SOLVENT          CDCl3
NS                  16
DS                   2
SWH           6009.615 Hz
FIDRES        0.183399 Hz
AQ            2.7263477 sec
RG                   1
DW              83.200 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       400.1326128 MHz
SI               32768
SF         400.1300000 MHz
WDW                 EM
SSB                  0
LB               0.30 Hz
GB                   0
PC                1.00
```

CL-93 13C



^{13}C NMR of
1-(4-(naphthalen-2-yl)
phenyl)ethanone

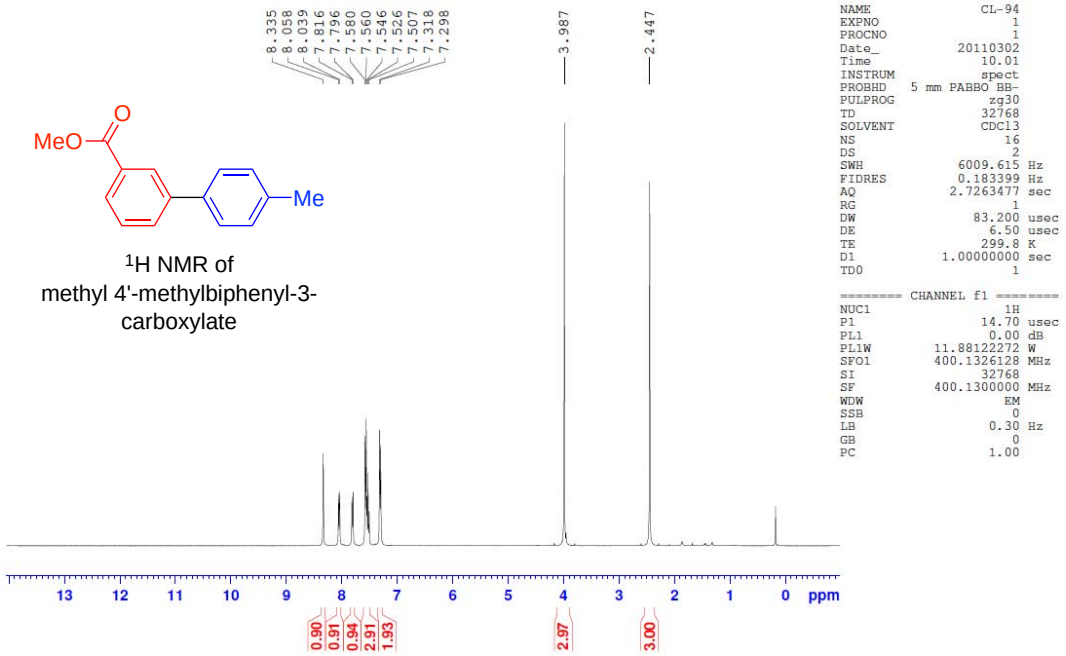
```
NAME              CL-93
EXPNO                2
PROCNO               1
Date_         20110302
Time             10.11
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD               65536
SOLVENT          CDCl3
NS                  32
DS                   2
SWH          25252.525 Hz
FIDRES        0.385323 Hz
AQ            1.2976629 sec
RG                 203
DW              19.800 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      100.6253456 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         100.6127829 MHz
WDW                 EM
SSB                  0
LB               1.00 Hz
GB                   0
PC                1.40
```

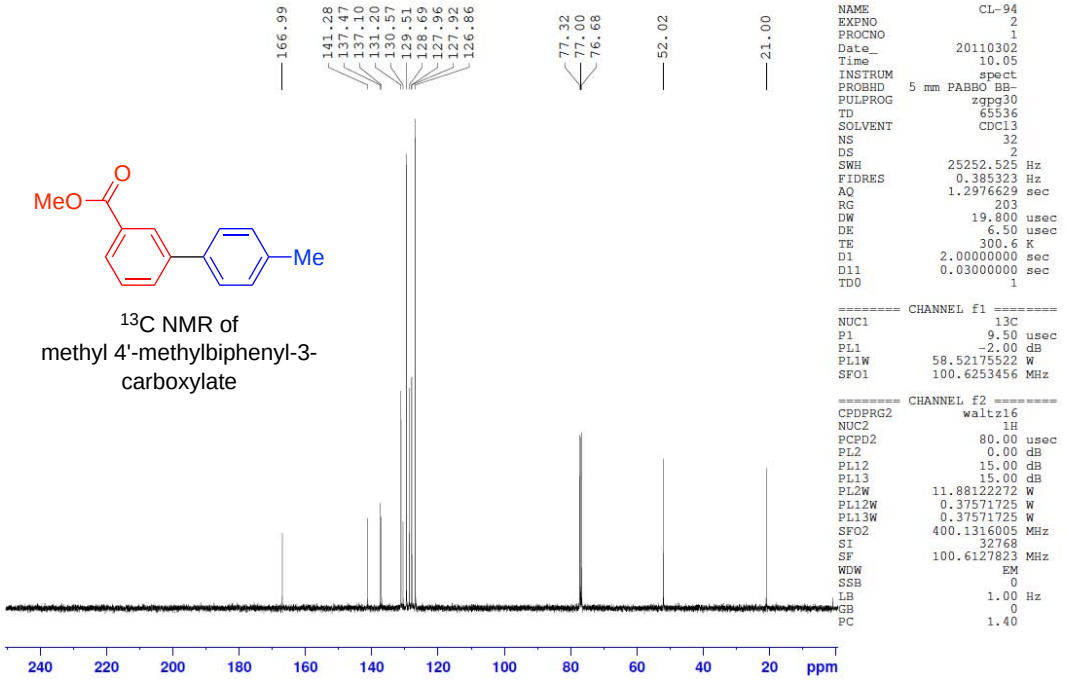
Methyl 4'-methylbiphenyl-3-carboxylate (**Table 4.2**, entry 7)

CL-94 1H



^{1}H NMR of methyl 4'-methylbiphenyl-3-carboxylate

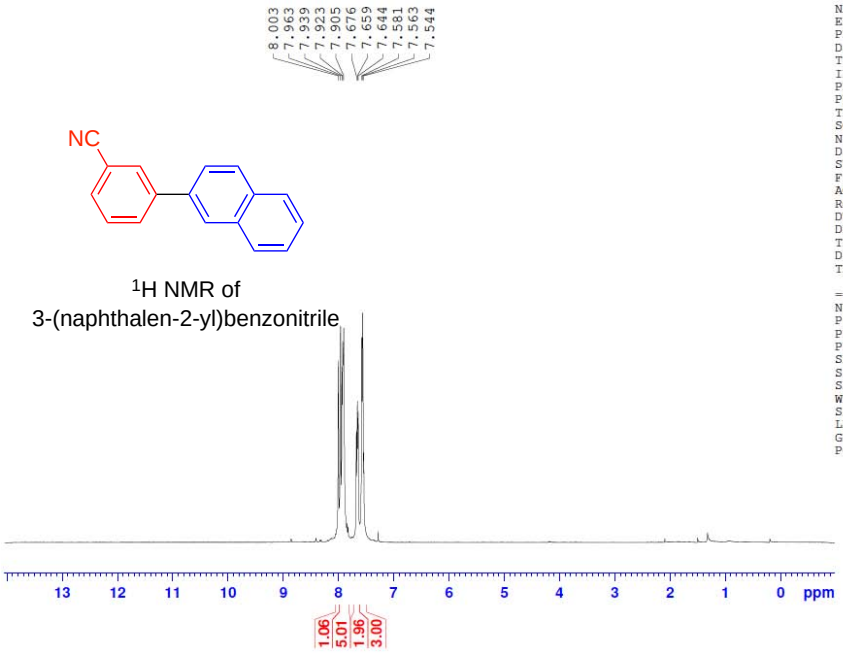
CL-94 13C



^{13}C NMR of methyl 4'-methylbiphenyl-3-carboxylate

3-(Naphthalen-2-yl)benzonitrile (**Table 4.2**, entry 8)

CL-95 1H

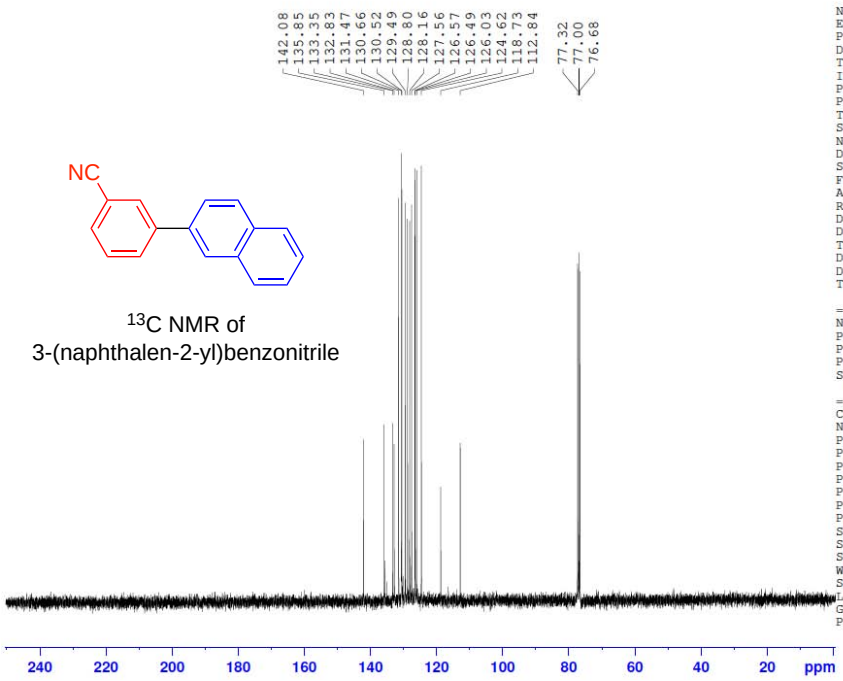


^{1}H NMR of
3-(naphthalen-2-yl)benzonitrile

```
NAME                CL-95
EXPNO                  1
PROCNO                 1
Date_           20110302
Time                10.15
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6009.615 Hz
FIDRES          0.183399 Hz
AQ              2.7263477 sec
RG                     1
DW                83.200 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          400.1326128 MHz
SI                 32768
SF            400.1300000 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```

CL-95 13C



^{13}C NMR of
3-(naphthalen-2-yl)benzonitrile

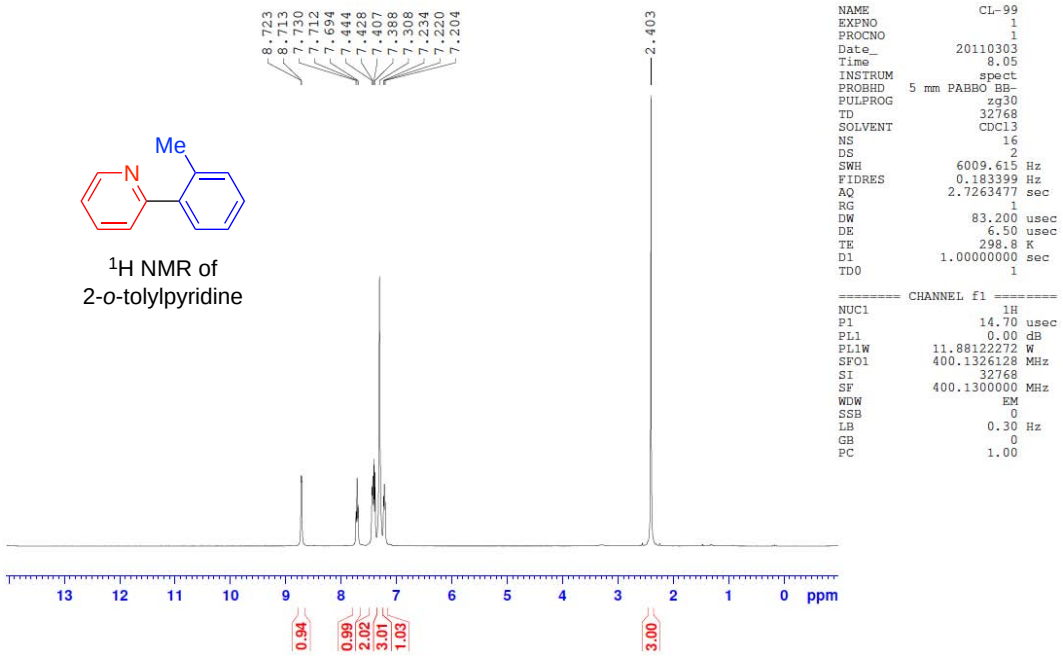
```
NAME                CL-95
EXPNO                  2
PROCNO                 1
Date_           20110302
Time                10.18
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            25252.525 Hz
FIDRES          0.385323 Hz
AQ              1.2976629 sec
RG                   203
DW                19.800 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          100.6253456 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            100.6127893 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                 1.40
```

2-*o*-Tolylpyridine (**Table 4.2**, entry 9)

CL-99 1H

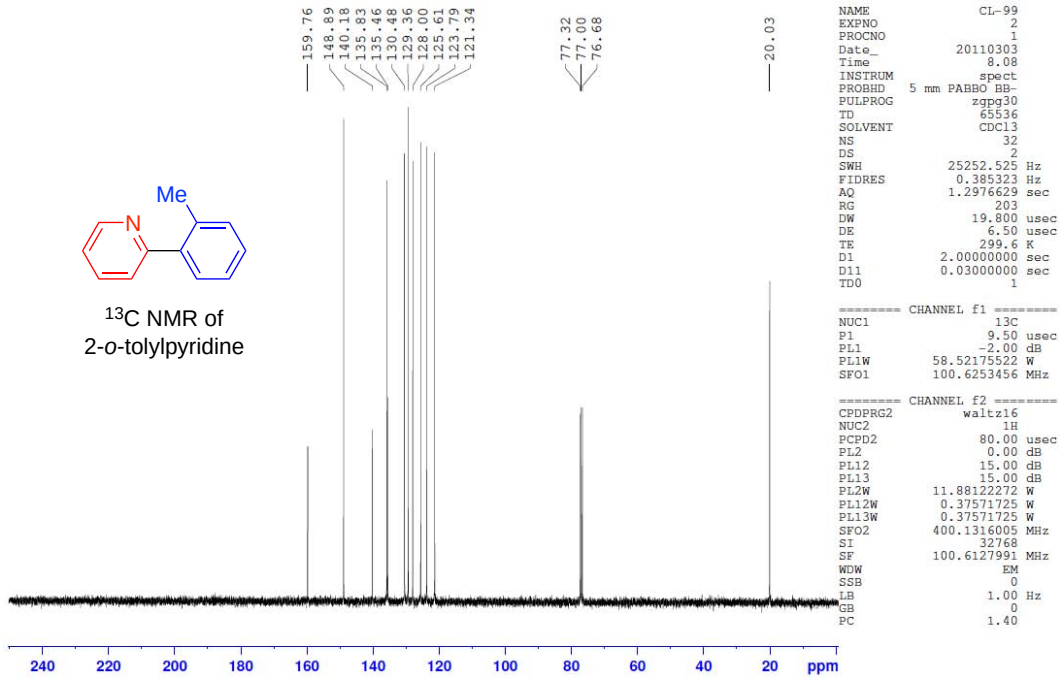


^{1}H NMR of
2-*o*-tolylpyridine

```
NAME                CL-99
EXPNO                  1
PROCNO                 1
Date_           20110303
Time                8.05
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                    16
DS                     2
SWH            6009.615 Hz
FIDRES         0.183399 Hz
AQ             2.7263477 sec
RG                     1
DW               83.200 usec
DE                6.50 usec
TE                298.8 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                14.70 usec
PL1                0.00 dB
PL1W         11.88122272 W
SFO1        400.1326128 MHz
SI                 32768
SF          400.1300000 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                1.00
```

CL-99 13C



^{13}C NMR of
2-*o*-tolylpyridine

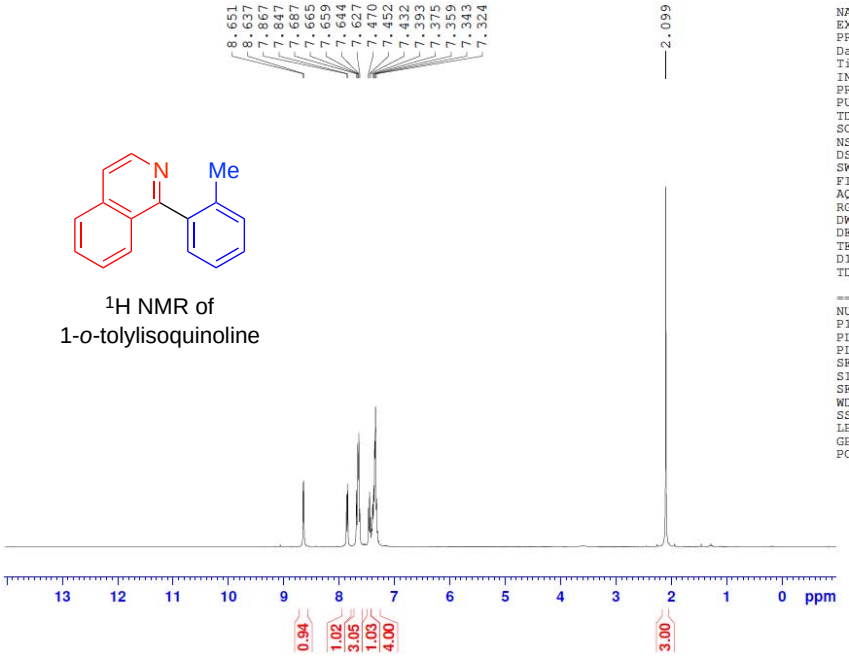
```
NAME                CL-99
EXPNO                  2
PROCNO                 1
Date_           20110303
Time                8.08
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                    32
DS                     2
SWH           25252.525 Hz
FIDRES         0.385323 Hz
AQ             1.2976629 sec
RG                   203
DW               19.800 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        100.6253456 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          100.6127991 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                1.40
```

1-*o*-Tolylisoquinoline (**Table 4.2**, entry 10)

CL-100 1H

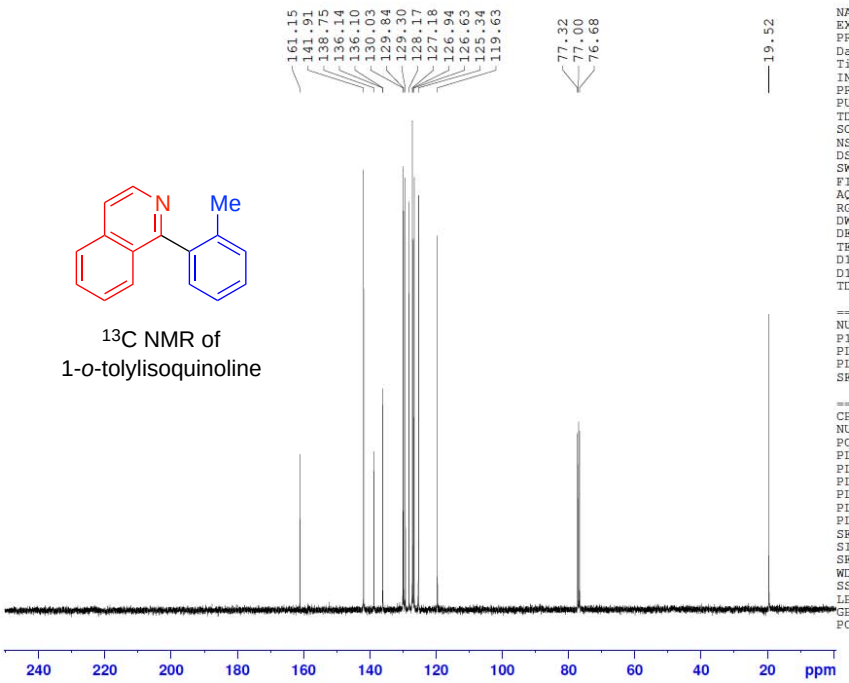


^{1}H NMR of
1-*o*-tolylisoquinoline

```
NAME            CL-100
EXPNO                1
PROCNO               1
Date_         20110304
Time             18.14
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG           zg30
TD               32768
SOLVENT          CDCl3
NS                  16
DS                   2
SWH           6009.615 Hz
FIDRES        0.183399 Hz
AQ            2.7263477 sec
RG                   1
DW              83.200 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       400.1326128 MHz
SI                32768
SF         400.1300000 MHz
WDW                  EM
SSB                  0
LB               0.30 Hz
GB                   0
PC                1.00
```

CL-100 13C



^{13}C NMR of
1-*o*-tolylisoquinoline

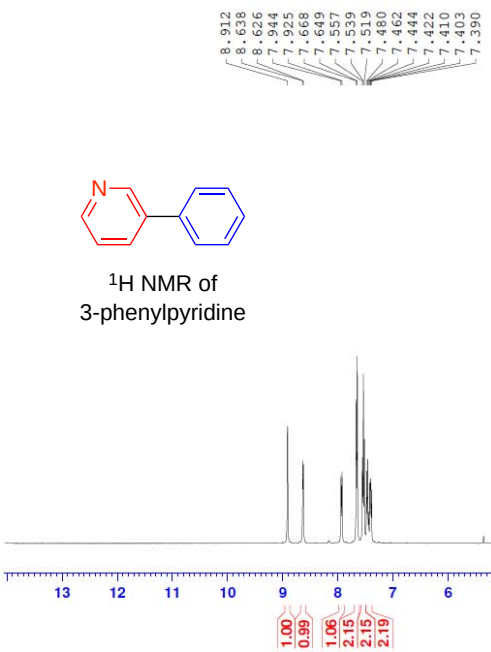
```
NAME            CL-100
EXPNO                2
PROCNO               1
Date_         20110304
Time             18.17
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                  32
DS                   2
SWH          25252.525 Hz
FIDRES        0.385323 Hz
AQ            1.2976629 sec
RG                 203
DW              19.800 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       100.6253456 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         100.6127984 MHz
WDW                  EM
SSB                  0
LB               1.00 Hz
GB                   0
PC                1.40
```

3-Phenylpyridine (**Table 4.2**, entry 11)

CL-101 1H

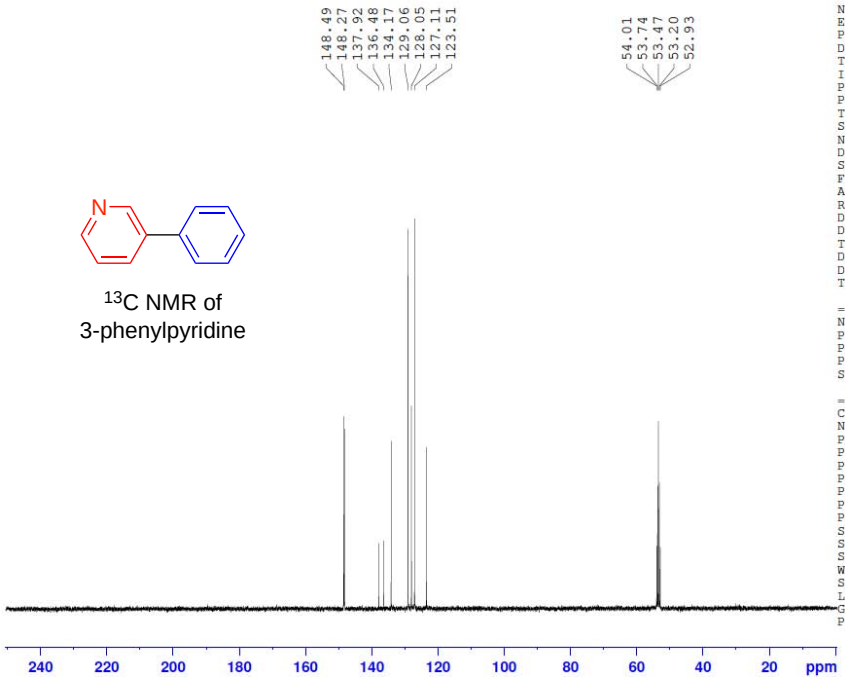


^{1}H NMR of
3-phenylpyridine

```
NAME                CL-101
EXPNO                    6
PROCNO                   1
Date_             20110307
Time                 13.10
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    32768
SOLVENT            CD2Cl2
NS                       16
DS                        2
SWH               6009.615 Hz
FIDRES            0.183399 Hz
AQ                2.7263477 sec
RG                       4
DW                  83.200 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         400.1326128 MHz
SI                    32768
SF           400.1300000 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

CL-101 13C



^{13}C NMR of
3-phenylpyridine

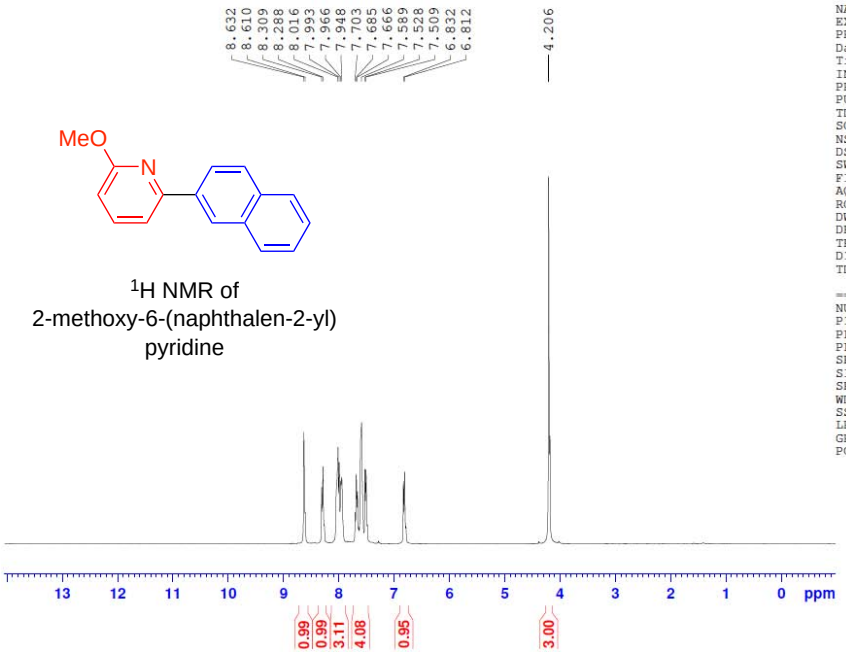
```
NAME                CL-101
EXPNO                    7
PROCNO                   1
Date_             20110307
Time                 13.14
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT            CD2Cl2
NS                       32
DS                        2
SWH              25252.525 Hz
FIDRES            0.385323 Hz
AQ                1.2976629 sec
RG                     203
DW                  19.800 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         100.6253456 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-6-(naphthalen-2-yl)pyridine (**Table 4.2**, entry 12)

CL-133 1H

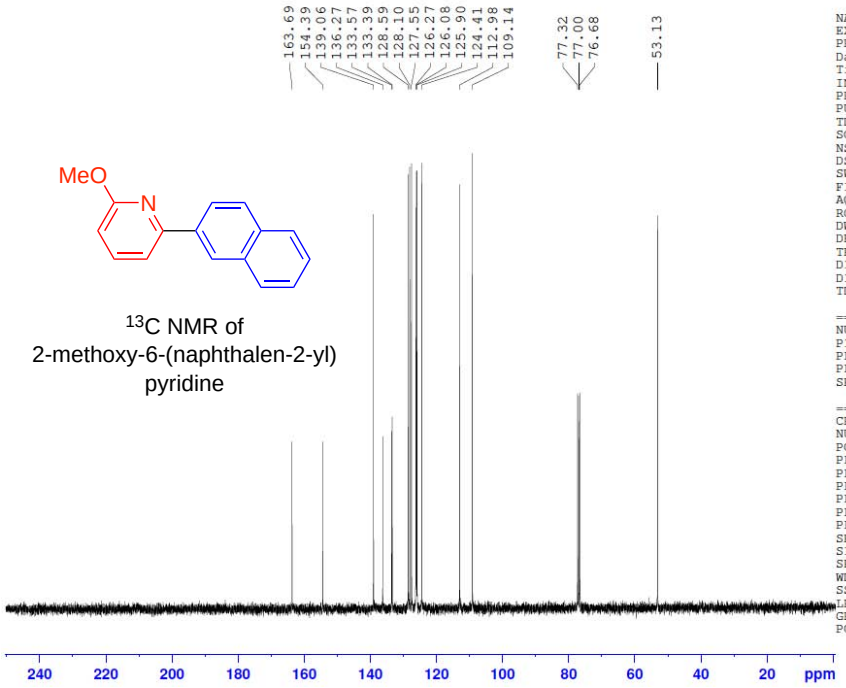


^{1}H NMR of
2-methoxy-6-(naphthalen-2-yl)
pyridine

```
NAME            CL-133
EXPNO                1
PROCNO               1
Date_         20110309
Time             16.30
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG          zg30
TD              32768
SOLVENT          CDCl3
NS                  16
DS                   2
SWH           6009.615 Hz
FIDRES        0.183399 Hz
AQ            2.7263477 sec
RG                   1
DW               83.200 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       400.1326128 MHz
SI              32768
SF         400.1300000 MHz
WDW                EM
SSB                 0
LB               0.30 Hz
GB                  0
PC               1.00
```

CL-133 13C



^{13}C NMR of
2-methoxy-6-(naphthalen-2-yl)
pyridine

```
NAME            CL-133
EXPNO                2
PROCNO               1
Date_         20110309
Time             16.34
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG        zgpg30
TD              65536
SOLVENT          CDCl3
NS                  32
DS                   2
SWH          25252.525 Hz
FIDRES        0.385323 Hz
AQ            1.2976629 sec
RG                 203
DW               19.800 usec
DE                6.50 usec
TE              300.1 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                  1

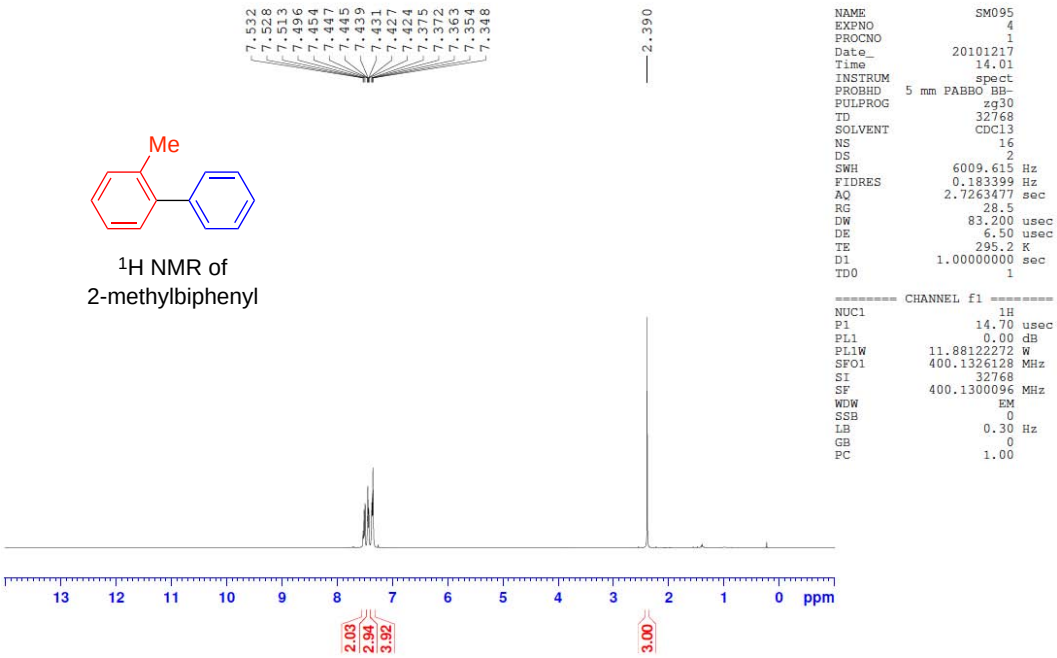
======== CHANNEL f1 ========
NUC1                13C
P1                9.50 usec
PL1              -2.00 dB
PL1W        58.52175522 W
SFO1       100.6253456 MHz

======== 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         100.6127932 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```

Chapter 5 NMR Spectra of Coupling products

2-Methylbiphenyl (**Table 5.22**, entry 1)

SM095 1H

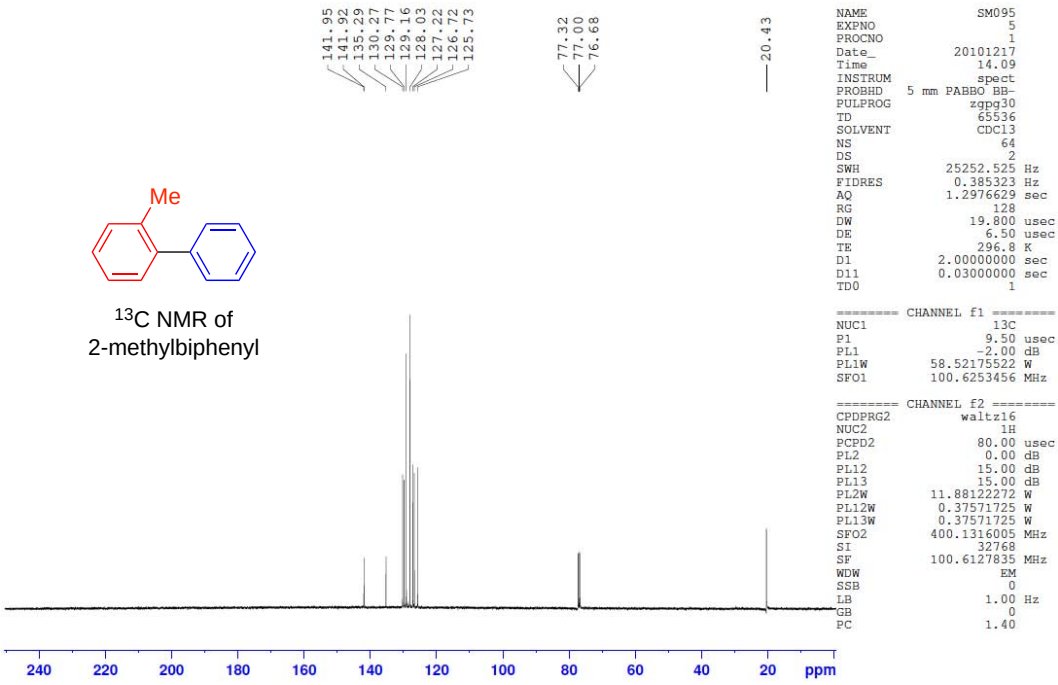


^{1}H NMR of
2-methylbiphenyl

```
NAME                SM095
EXPNO                   4
PROCNO                  1
Date_            20101217
Time                14.01
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              6009.615 Hz
FIDRES           0.183399 Hz
AQ               2.7263477 sec
RG                   28.5
DW                 83.200 usec
DE                  6.50 usec
TE                 295.2 K
D1               1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.70 usec
PL1                  0.00 dB
PL1W          11.88122272 W
SFO1          400.1326128 MHz
SI                  32768
SF            400.1300096 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

SM095 13C



^{13}C NMR of
2-methylbiphenyl

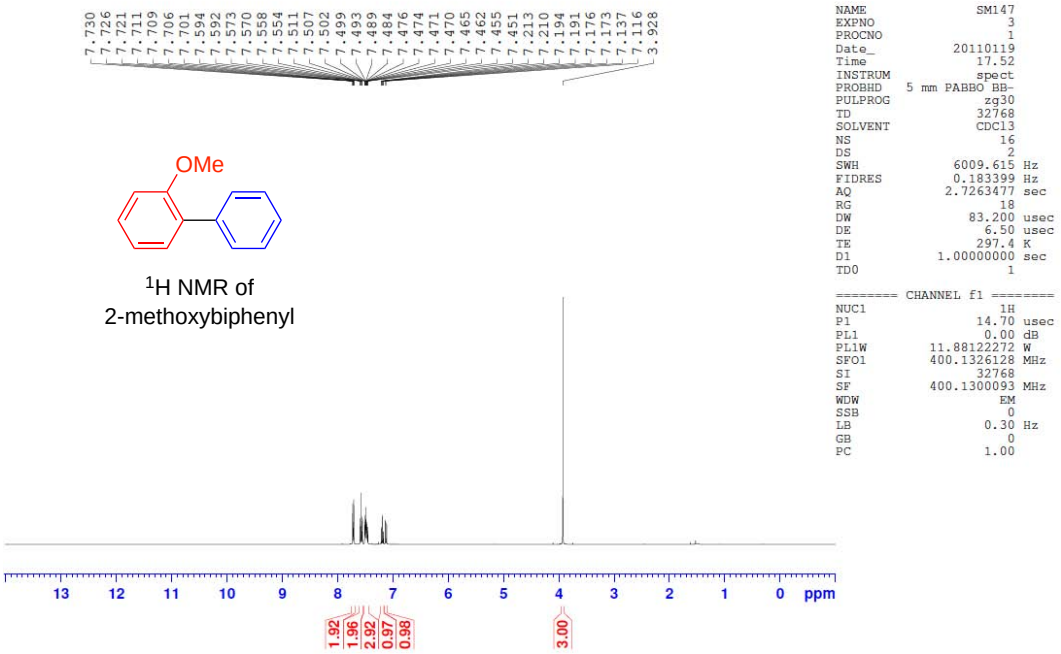
```
NAME                SM095
EXPNO                   5
PROCNO                  1
Date_            20101217
Time                14.09
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     64
DS                      2
SWH             25252.525 Hz
FIDRES           0.385323 Hz
AQ               1.2976629 sec
RG                    128
DW                 19.800 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          100.6253456 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            100.6127835 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

2-Methoxybiphenyl (**Table 5.22**, entry 2)

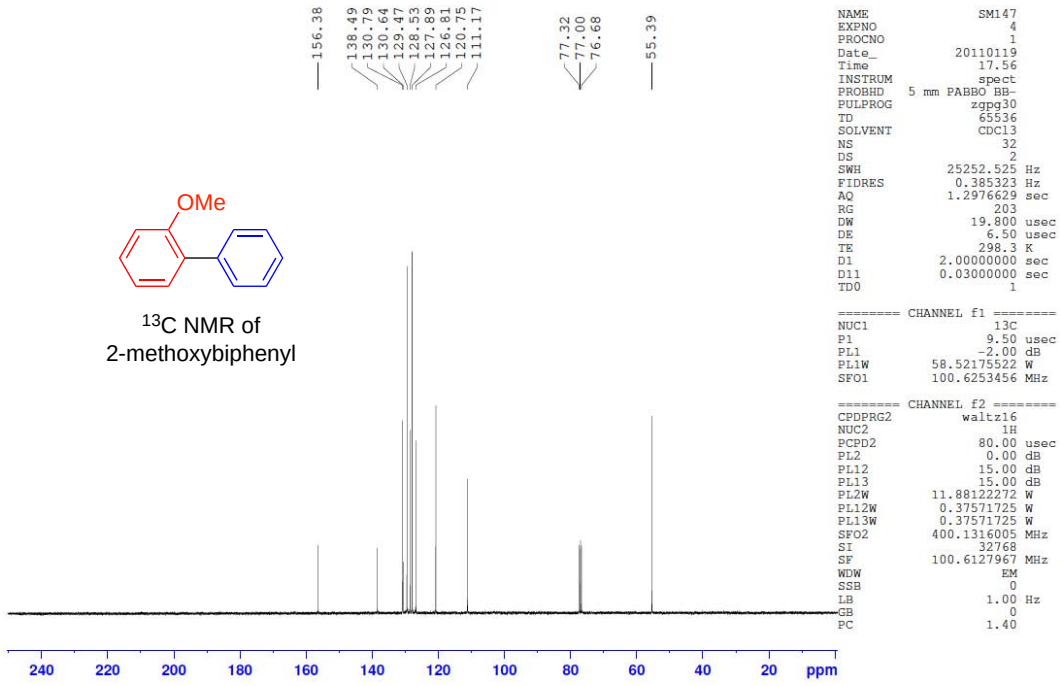
SM147 1H



^{1}H NMR of
2-methoxybiphenyl

NAME	SM147
EXPNO	3
PROCNO	1
Date_	20110119
Time	17.52
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	6009.615 Hz
FIDRES	0.183399 Hz
AQ	2.7263477 sec
RG	18
DW	83.200 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	400.1326128 MHz
SI	32768
SF	400.1300093 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

SM147 13C

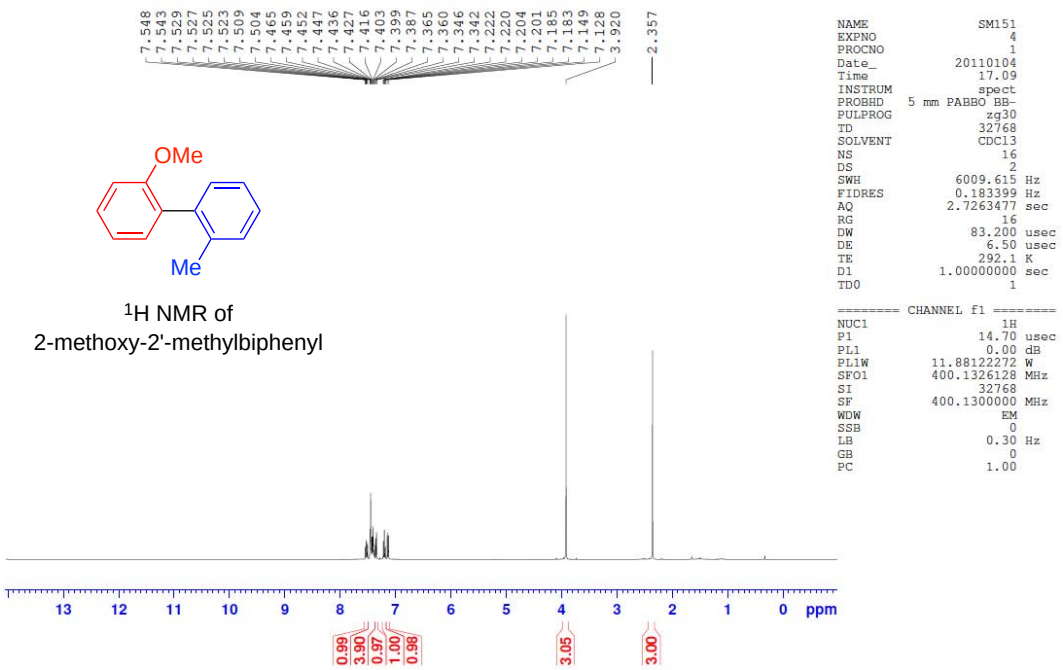


^{13}C NMR of
2-methoxybiphenyl

NAME	SM147
EXPNO	4
PROCNO	1
Date_	20110119
Time	17.56
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	32
DS	2
SWH	25252.525 Hz
FIDRES	0.385323 Hz
AQ	1.2976629 sec
RG	203
DW	19.800 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	100.6253456 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	100.6127967 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

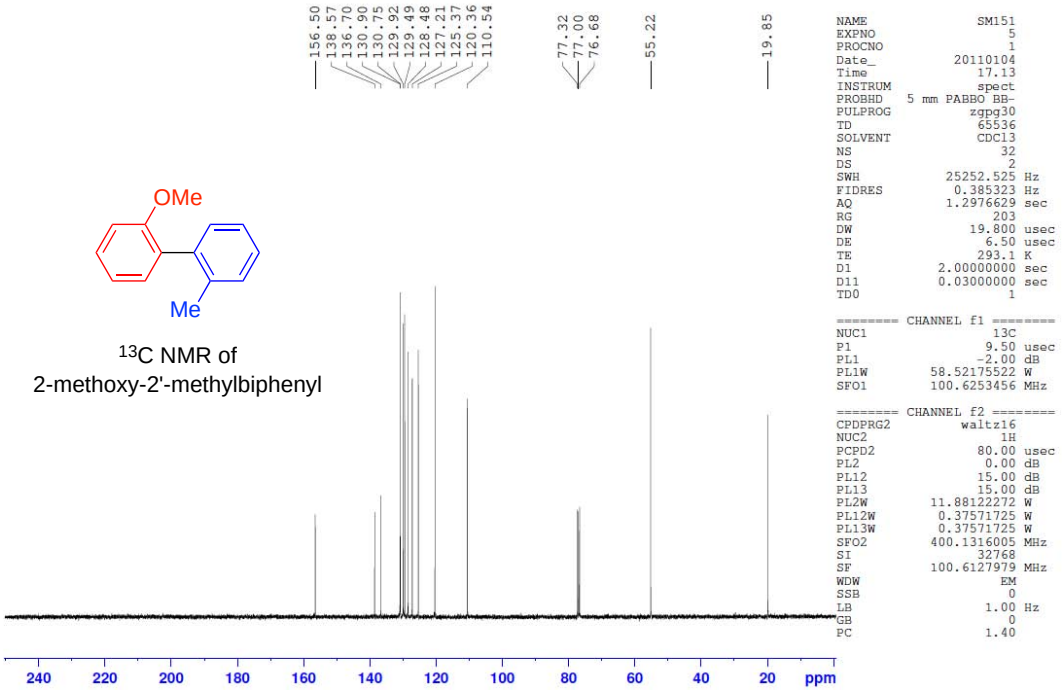
2-Methoxy-2'-methylbiphenyl (**Table 5.22**, entry 3)

SM151 1H



^{1}H NMR of
2-methoxy-2'-methylbiphenyl

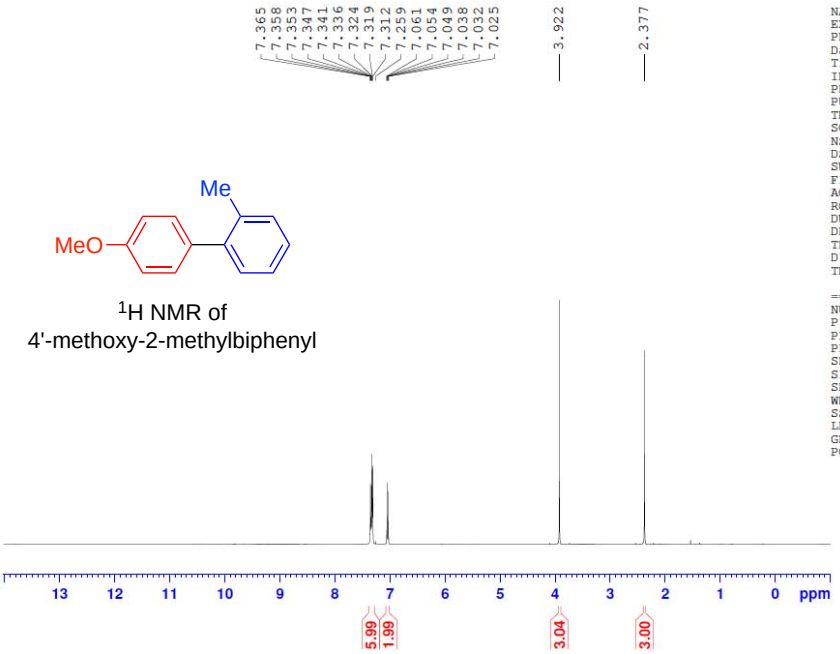
SM151 13C



^{13}C NMR of
2-methoxy-2'-methylbiphenyl

4'-Methoxy-2-methylbiphenyl (**Table 5.22**, entry 4)

SM149 1H

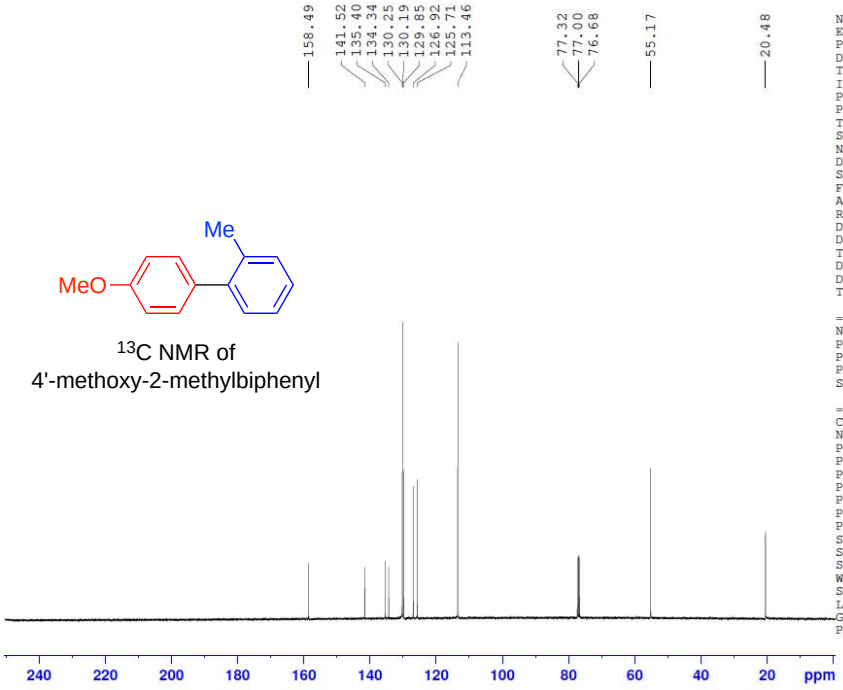


NAME SM149
EXPNO 4
PROCNO 1
Date_ 20101209
Time 15.01
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 25.4
DW 83.200 usec
DE 6.50 usec
TE 297.9 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 14.70 usec
PL1 0.00 dB
PL1W 11.88122272 W
SFO1 400.1326128 MHz
SI 32768
SF 400.1300094 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

^{1}H NMR of
4'-methoxy-2-methylbiphenyl

SM149 13C



NAME SM149
EXPNO 5
PROCNO 1
Date_ 20101209
Time 15.07
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 64
DS 2
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976629 sec
RG 203
DW 19.800 usec
DE 6.50 usec
TE 298.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

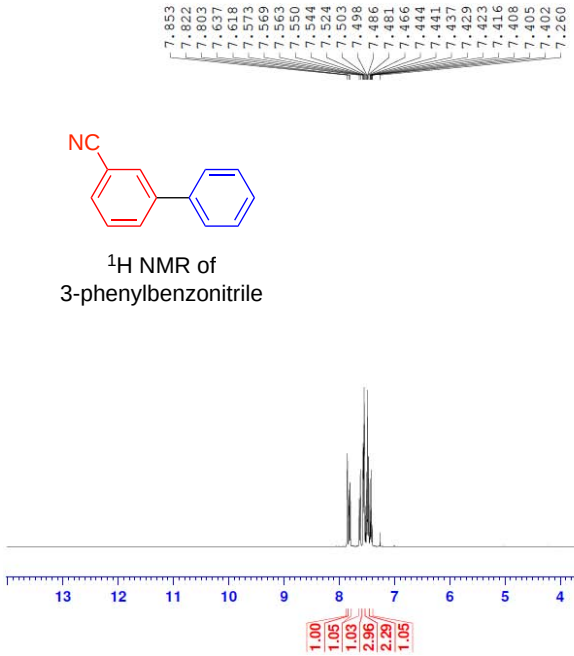
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 -2.00 dB
PL1W 58.52175522 W
SFO1 100.6253456 MHz

======== 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

^{13}C NMR of
4'-methoxy-2-methylbiphenyl

3-Phenylbenzonitrile (**Table 5.22**, entry 5)

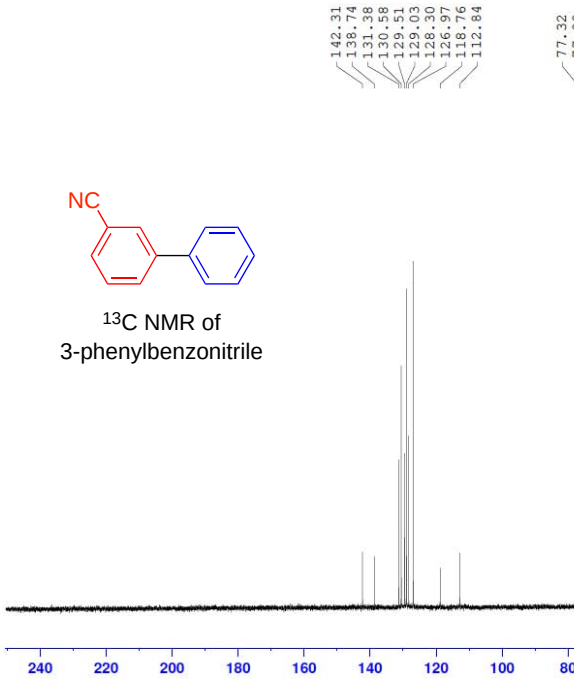
SM188 1H



^{1}H NMR of
3-phenylbenzonitrile

NAME	SM188
EXPNO	3
PROCNO	1
Date_	20110105
Time	17.22
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	6009.615 Hz
FIDRES	0.183399 Hz
AQ	2.7263477 sec
RG	45.2
DW	83.200 usec
DE	6.50 usec
TE	295.2 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1326128 MHz
SI	32768
SF	400.1300093 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

SM188 13C

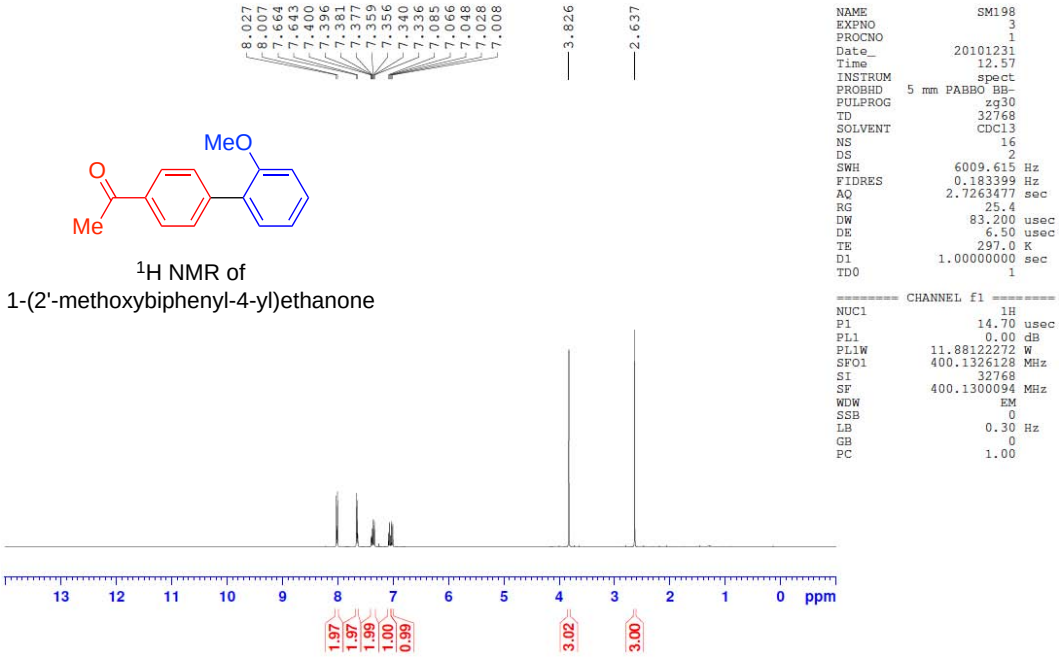


^{13}C NMR of
3-phenylbenzonitrile

NAME	SM188
EXPNO	4
PROCNO	1
Date_	20110105
Time	17.25
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	32
DS	2
SWH	25252.525 Hz
FIDRES	0.385323 Hz
AQ	1.2976629 sec
RG	203
DW	19.800 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	100.6253456 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-(2'-Methoxybiphenyl-4-yl)ethanone (**Table 5.22**, entry 6)

SM198 1H

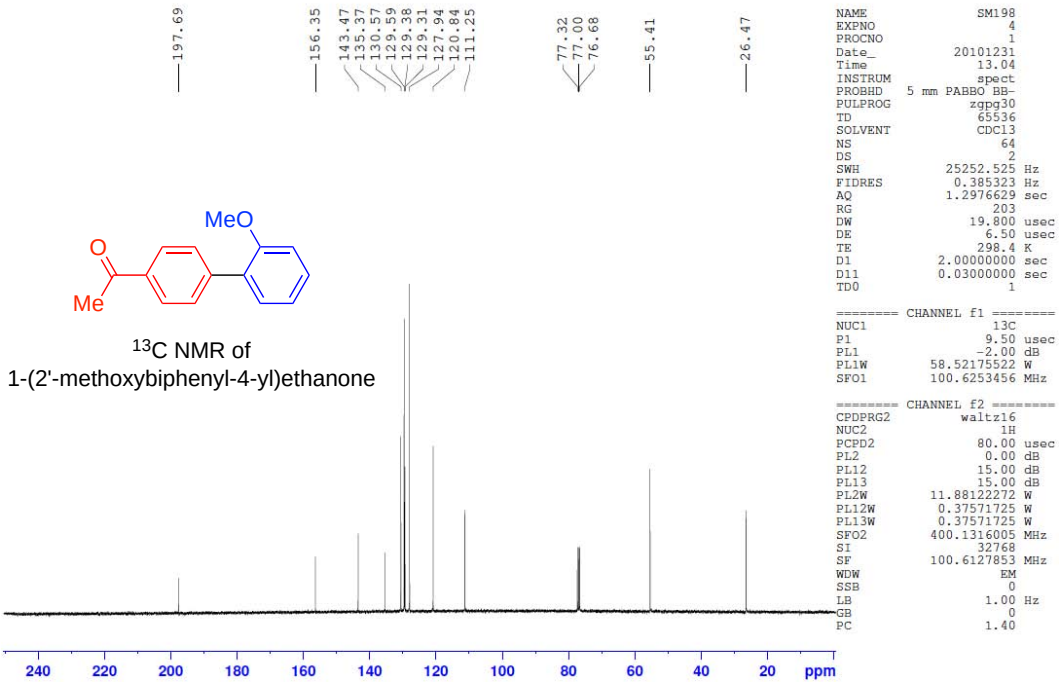


NAME SM198
EXPNO 3
PROCNO 1
Date_ 20101231
Time 12.57
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 25.4
DW 83.200 usec
DE 6.50 usec
TE 297.0 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 14.70 usec
PL1 0.00 dB
PL1W 11.88122272 W
SFO1 400.1326128 MHz
SI 32768
SF 400.1300094 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

^{1}H NMR of
1-(2'-methoxybiphenyl-4-yl)ethanone

SM198 13C



NAME SM198
EXPNO 4
PROCNO 1
Date_ 20101231
Time 13.04
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 64
DS 2
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976629 sec
RG 203
DW 19.800 usec
DE 6.50 usec
TE 298.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

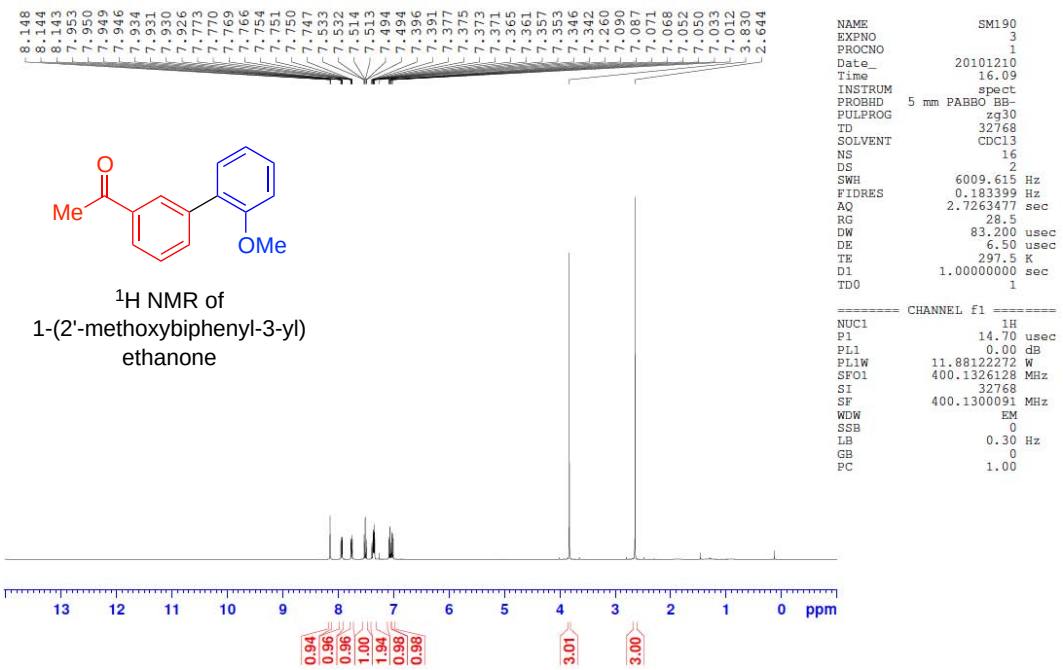
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 -2.00 dB
PL1W 58.52175522 W
SFO1 100.6253456 MHz

======== 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 100.6127853 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

^{13}C NMR of
1-(2'-methoxybiphenyl-4-yl)ethanone

1-(2'-Methoxybiphenyl-3-yl)ethanone (**Table 5.22**, entry 7)

SM190 1H

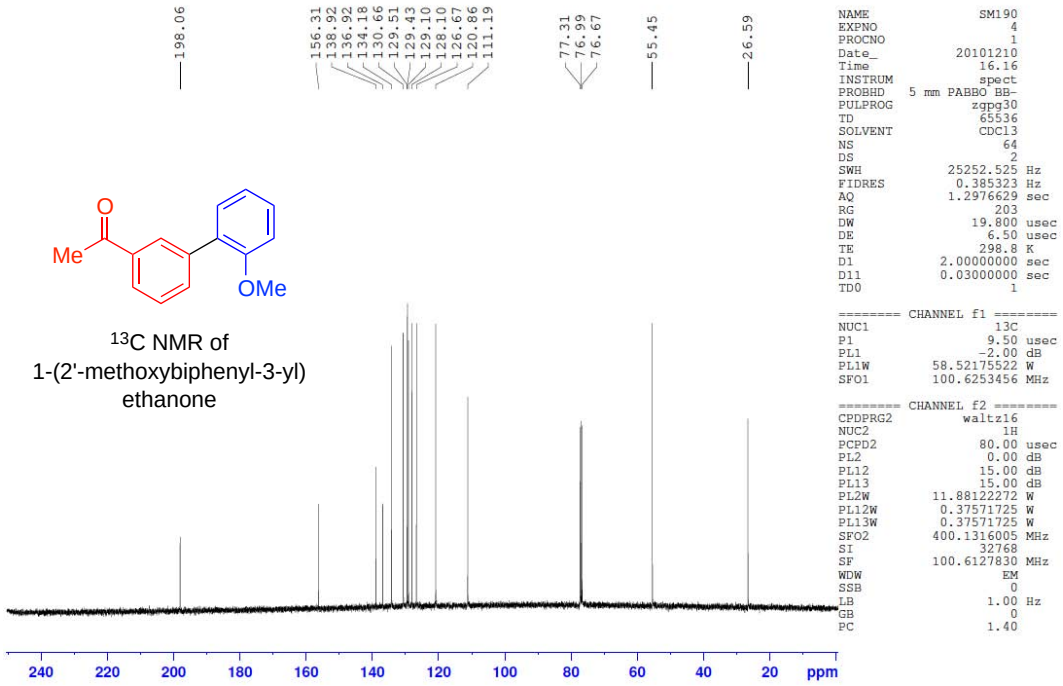


^{1}H NMR of 1-(2'-methoxybiphenyl-3-yl) ethanone

```
NAME                SM190
EXPNO                   3
PROCNO                  1
Date_            20101210
Time                16.09
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH             6009.615 Hz
FIDRES          0.183399 Hz
AQ              2.7263477 sec
RG                   28.5
DW                 83.200 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           400.1326128 MHz
SI                 32768
SF             400.1300091 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

SM190 13C



^{13}C NMR of 1-(2'-methoxybiphenyl-3-yl) ethanone

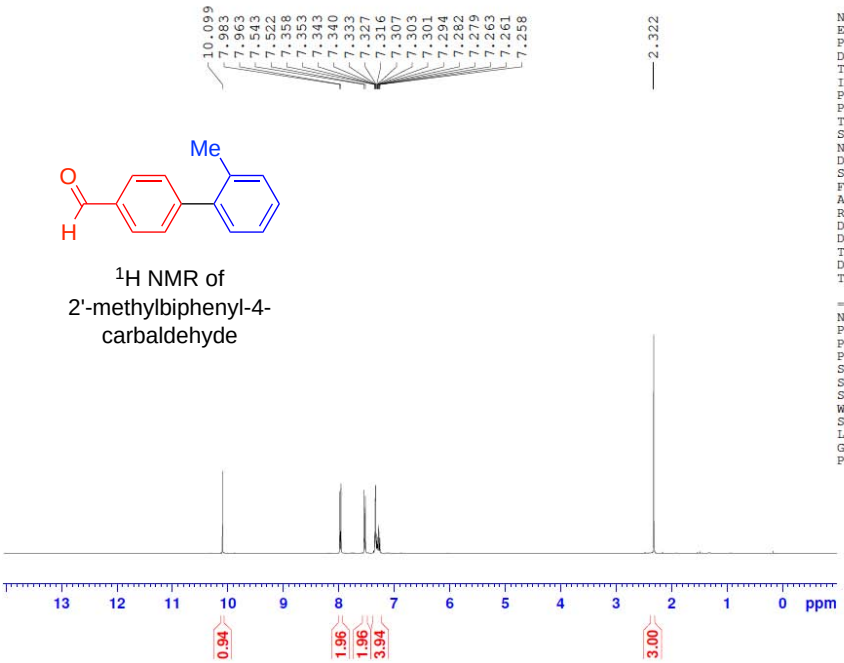
```
NAME                SM190
EXPNO                   4
PROCNO                  1
Date_            20101210
Time                16.16
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT             CDCl3
NS                     64
DS                      2
SWH            25252.525 Hz
FIDRES          0.385323 Hz
AQ              1.2976629 sec
RG                    203
DW                 19.800 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           100.6253456 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             100.6127830 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

2'-Methylbiphenyl-4-carbaldehyde (**Table 5.22**, entry 8)

SM209 1H

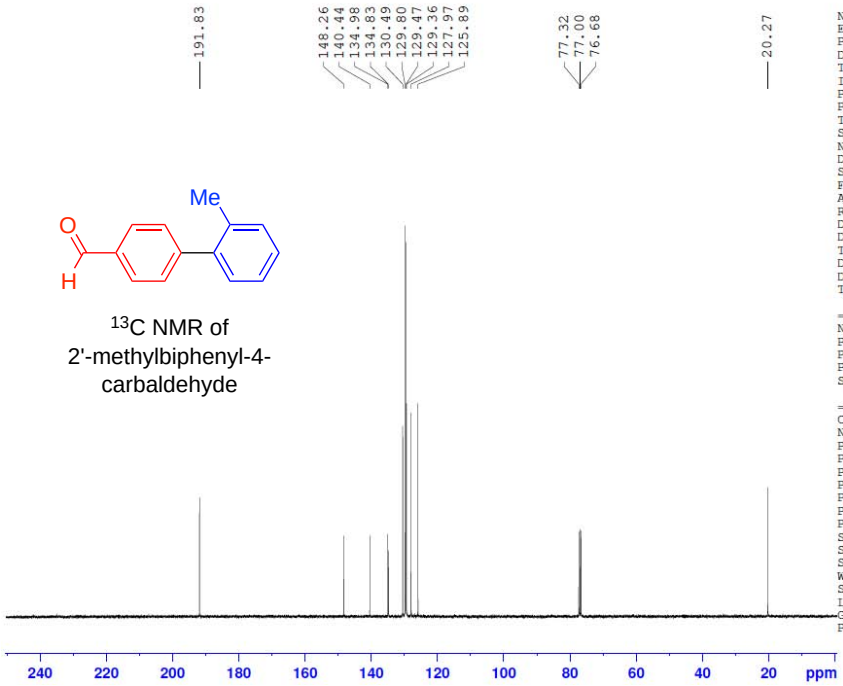


^{1}H NMR of 2'-methylbiphenyl-4-carbaldehyde

```
NAME              SM209
EXPNO                 3
PROCNO                1
Date_          20110111
Time              11.40
INSTRUM           spect
PROBHD    5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            6009.615 Hz
FIDRES        0.183399 Hz
AQ            2.7263477 sec
RG                 25.4
DW               83.200 usec
DE                6.50 usec
TE               293.3 K
D1            1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.70 usec
PL1                0.00 dB
PL1W         11.88122272 W
SFO1         400.1326128 MHz
SI                32768
SF           400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

SM209 13C



^{13}C NMR of 2'-methylbiphenyl-4-carbaldehyde

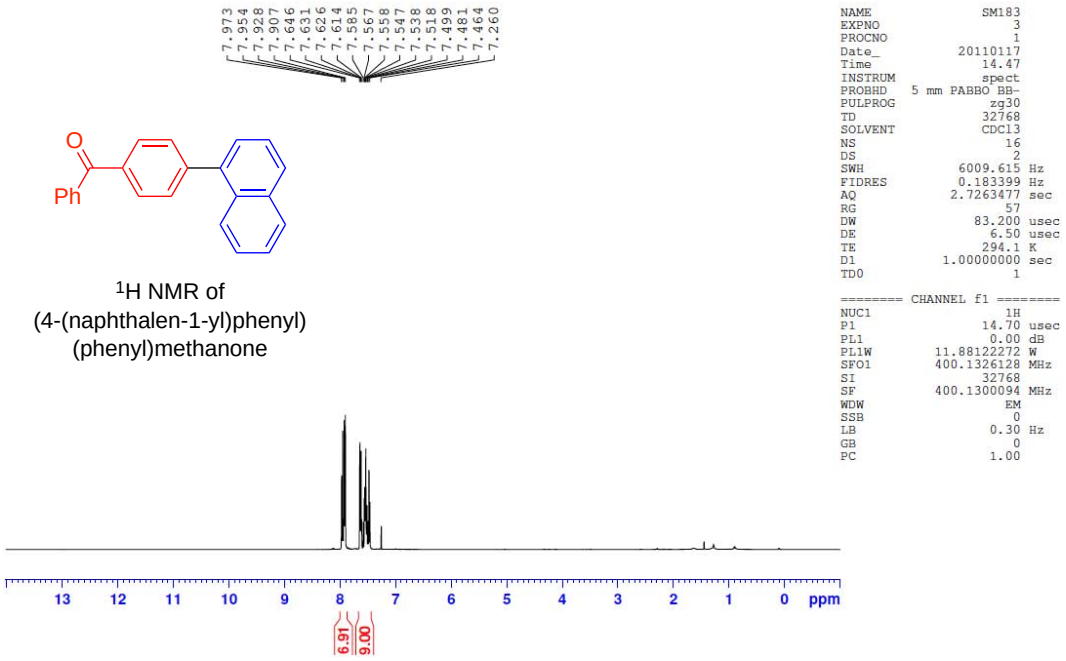
```
NAME              SM209
EXPNO                 4
PROCNO                1
Date_          20110111
Time              11.45
INSTRUM           spect
PROBHD    5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   64
DS                    2
SWH           25252.525 Hz
FIDRES        0.385323 Hz
AQ            1.2976629 sec
RG                  203
DW               19.800 usec
DE                6.50 usec
TE               294.9 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         100.6253456 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
```

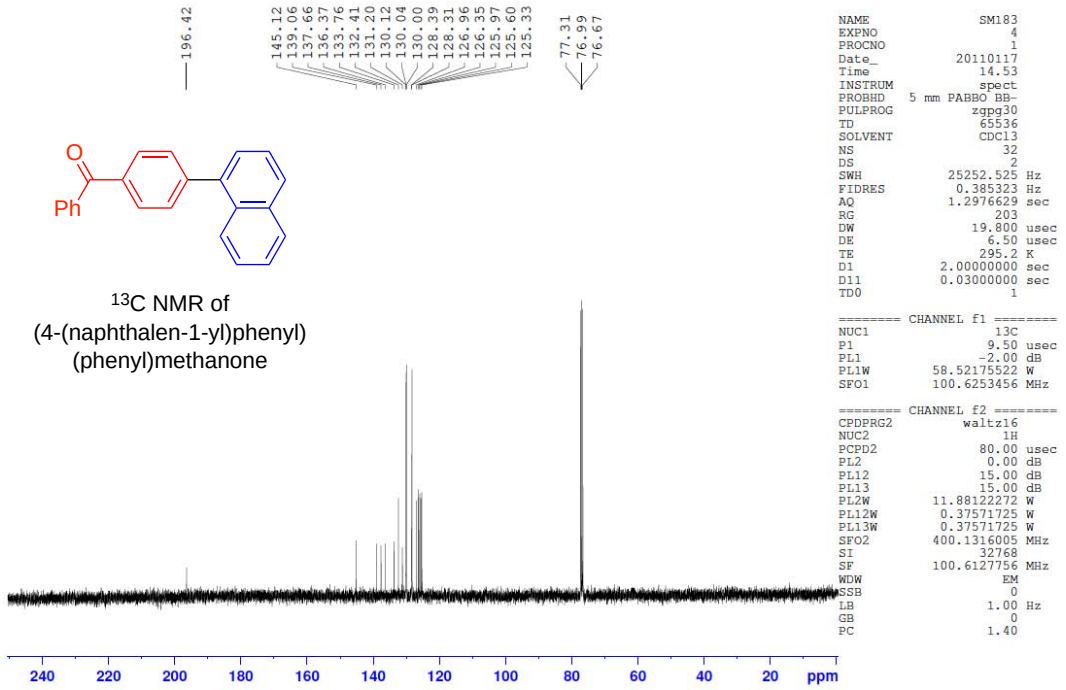
(4-(Naphthalen-1-yl)phenyl)(phenyl)methanone (**Table 5.22**, entry 9)

SM183 1H



^{1}H NMR of
(4-(naphthalen-1-yl)phenyl)
(phenyl)methanone

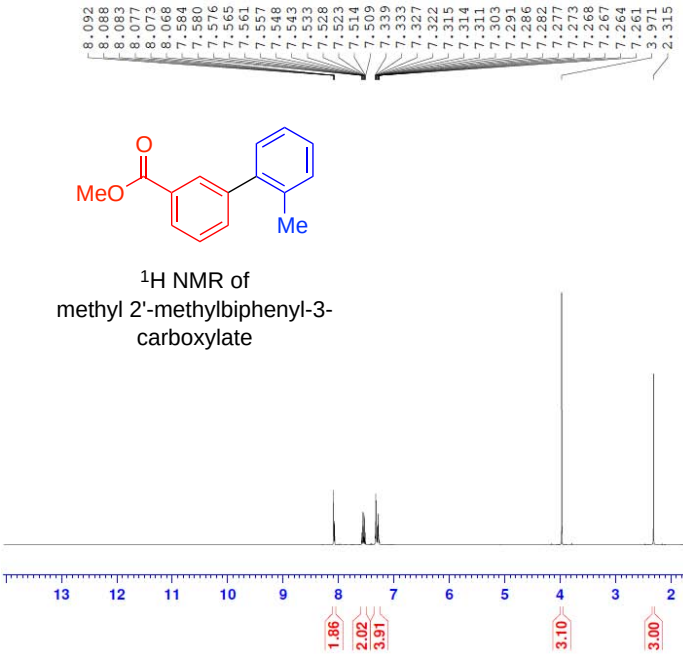
SM183 13C



^{13}C NMR of
(4-(naphthalen-1-yl)phenyl)
(phenyl)methanone

Methyl 2'-methylbiphenyl-3-carboxylate (**Table 5.22**, entry 10)

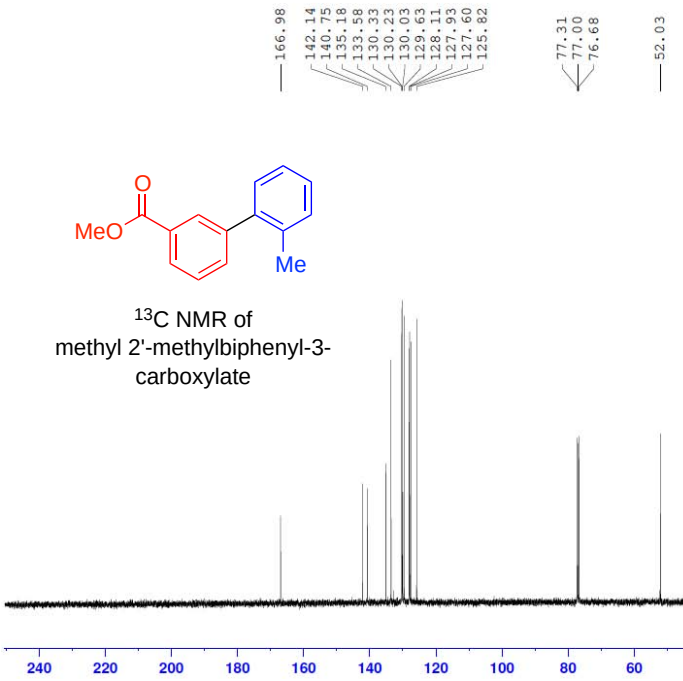
SM201 1H



^{1}H NMR of methyl 2'-methylbiphenyl-3-carboxylate

NAME	SM201
EXPNO	4
PROCNO	1
Date_	20110114
Time	12.38
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	6009.615 Hz
FIDRES	0.183399 Hz
AQ	2.7263477 sec
RG	25.4
DW	83.200 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	400.1326128 MHz
SI	32768
SF	400.1300000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

SM201 13C

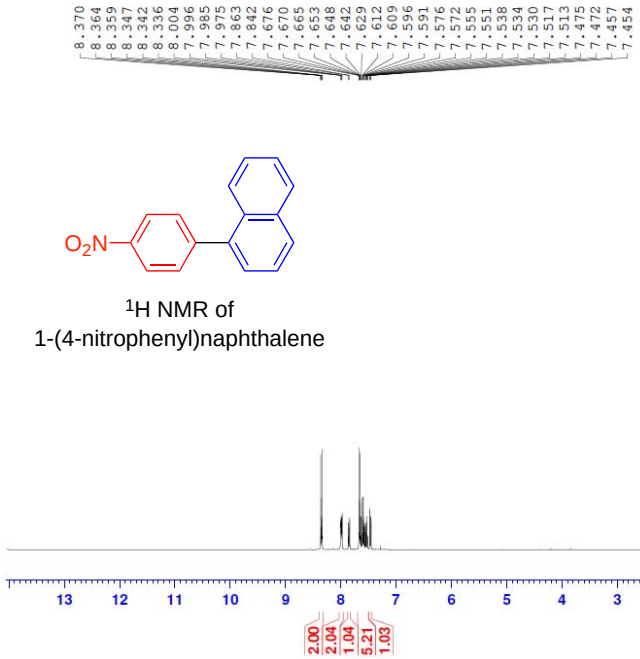


^{13}C NMR of methyl 2'-methylbiphenyl-3-carboxylate

NAME	SM201
EXPNO	5
PROCNO	1
Date_	20110114
Time	12.42
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	32
DS	2
SWH	25252.525 Hz
FIDRES	0.385323 Hz
AQ	1.2976629 sec
RG	203
DW	19.800 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	100.6253456 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	100.6127807 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1-(4-Nitrophenyl)naphthalene (**Table 5.22**, entry 11)

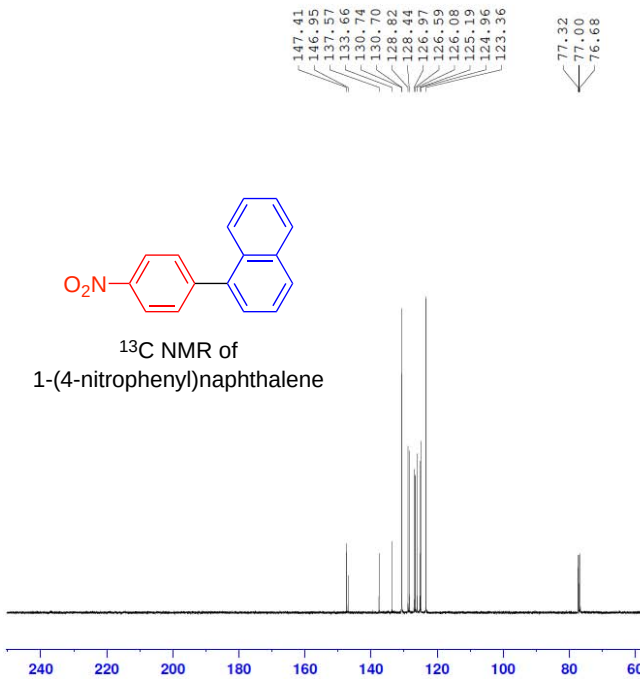
SM318 1H



^{1}H NMR of
1-(4-nitrophenyl)naphthalene

NAME	SM318
EXPNO	1
PROCNO	1
Date_	20101011
Time	9.57
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	6009.615 Hz
FIDRES	0.183399 Hz
AQ	2.7263477 sec
RG	22.6
DW	83.200 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	400.1326128 MHz
SI	32768
SF	400.1300000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

SM318 13C

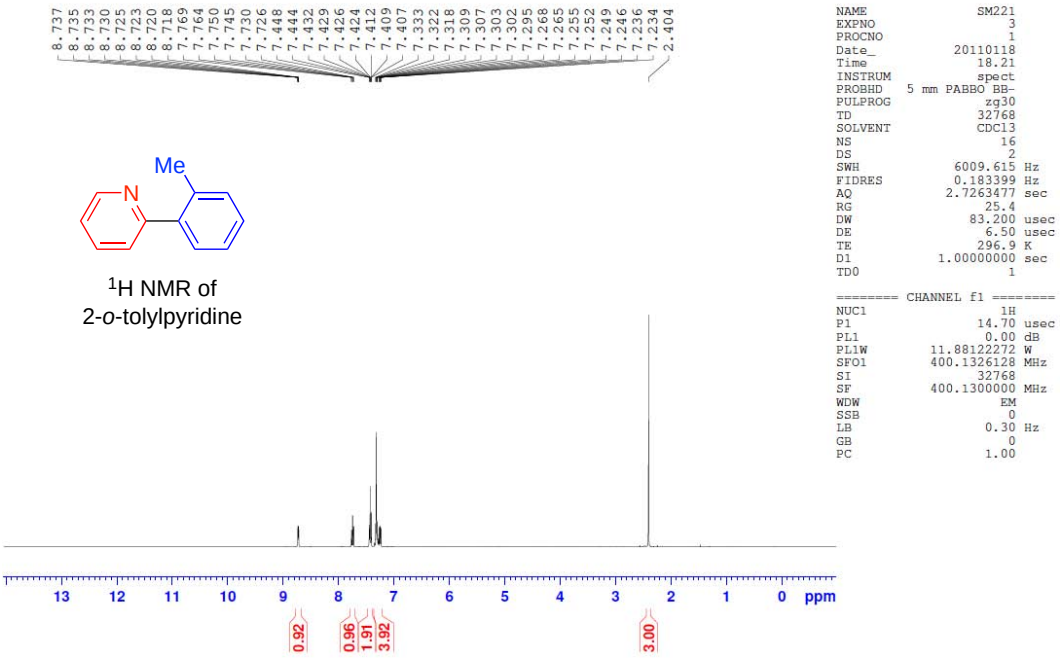


^{13}C NMR of
1-(4-nitrophenyl)naphthalene

NAME	SM318
EXPNO	2
PROCNO	1
Date_	20101011
Time	10.06
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	32
DS	2
SWH	25252.525 Hz
FIDRES	0.385323 Hz
AQ	1.2976629 sec
RG	203
DW	19.800 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	100.6253456 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	100.6127930 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

2-*o*-Tolylpyridine (**Table 5.23**, entry 1)

SM221 1H

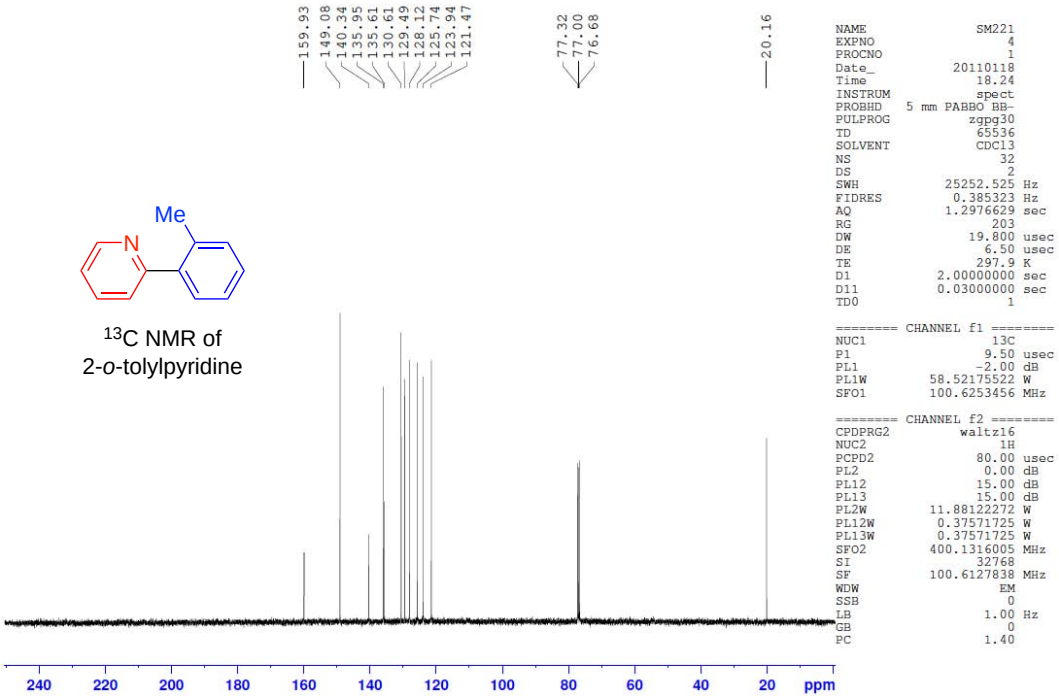


^{1}H NMR of
2-*o*-tolylpyridine

```
NAME                SM221
EXPNO                   3
PROCNO                  1
Date_            20110118
Time                18.21
INSTRUM             spect
PROBHD     5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              6009.615 Hz
FIDRES           0.183399 Hz
AQ               2.7263477 sec
RG                   25.4
DW                 83.200 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         400.1326128 MHz
SI                  32768
SF           400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

SM221 13C



^{13}C NMR of
2-*o*-tolylpyridine

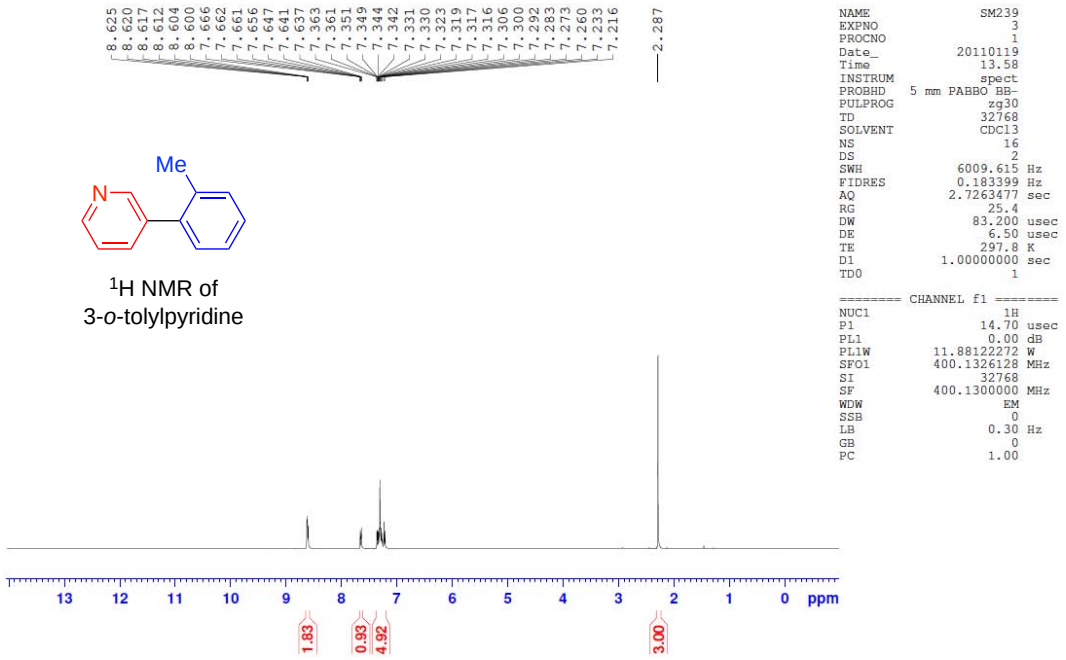
```
NAME                SM221
EXPNO                   4
PROCNO                  1
Date_            20110118
Time                18.24
INSTRUM             spect
PROBHD     5 mm PABBO BB-
PULPROG          zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      2
SWH             25252.525 Hz
FIDRES           0.385323 Hz
AQ               1.2976629 sec
RG                    203
DW                 19.800 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         100.6253456 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
```

3-*o*-Tolylpyridine (**Table 5.23**, entry 2)

SM239 1H

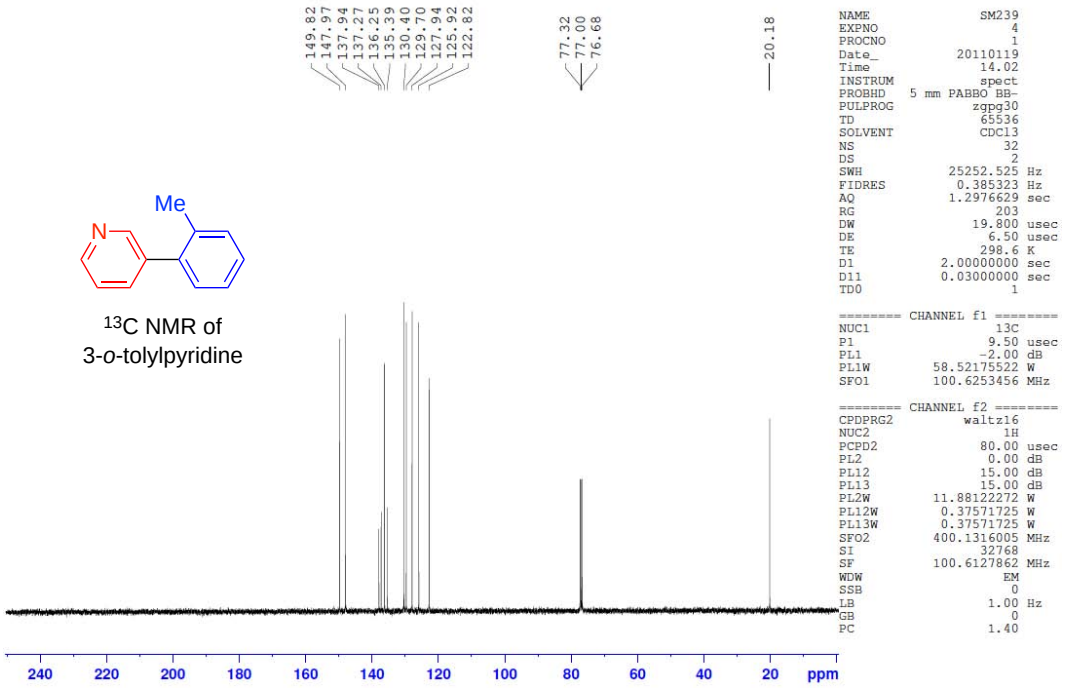


^{1}H NMR of
3-*o*-tolylpyridine

```
NAME                SM239
EXPNO                   3
PROCNO                  1
Date_            20110119
Time                13.58
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT             CDC13
NS                     16
DS                      2
SWH              6009.615 Hz
FIDRES           0.183399 Hz
AQ               2.7263477 sec
RG                   25.4
DW                 83.200 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          400.1326128 MHz
SI                  32768
SF            400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

SM239 13C



^{13}C NMR of
3-*o*-tolylpyridine

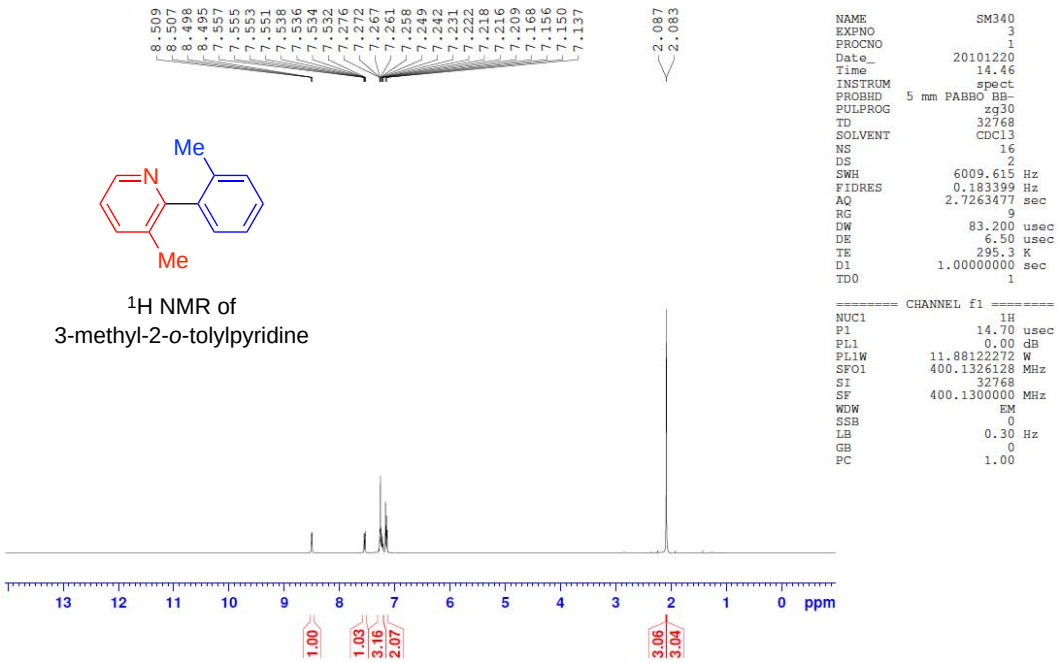
```
NAME                SM239
EXPNO                   4
PROCNO                  1
Date_            20110119
Time                14.02
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG           zgpg30
TD                  65536
SOLVENT             CDC13
NS                     32
DS                      2
SWH             25252.525 Hz
FIDRES           0.385323 Hz
AQ               1.2976629 sec
RG                    203
DW                 19.800 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          100.6253456 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
```

3-Methyl-2-*o*-tolylpyridine (**Table 5.23**, entry 3)

SM340 1H

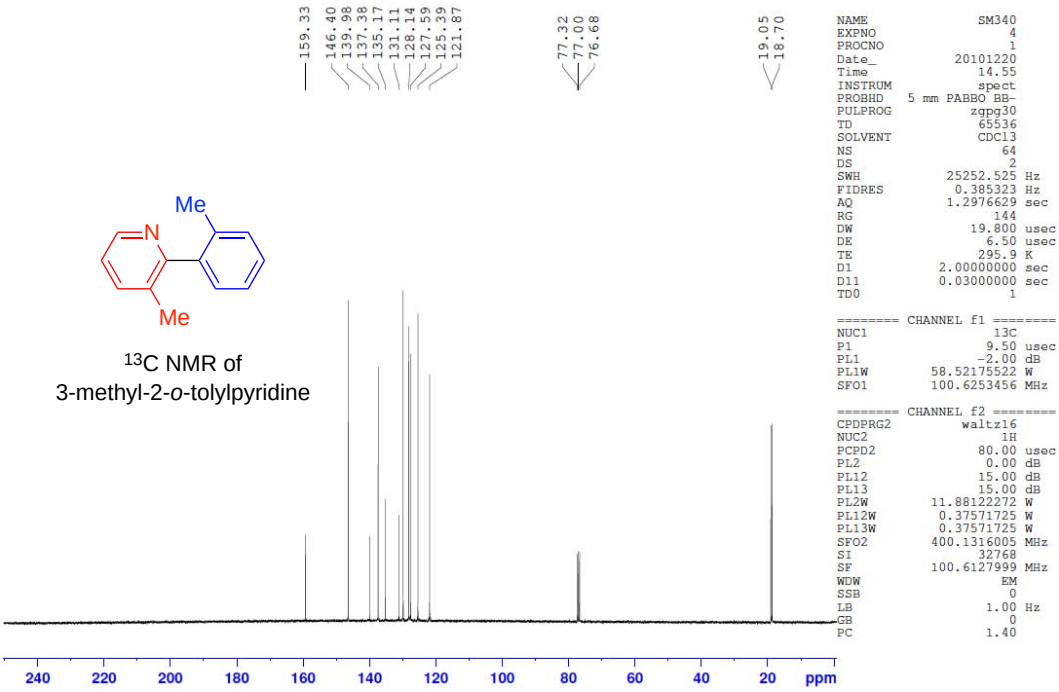


^{1}H NMR of
3-methyl-2-*o*-tolylpyridine

```
NAME              SM340
EXPNO                 3
PROCNO                1
Date_          20101220
Time              14.46
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            6009.615 Hz
FIDRES        0.183399 Hz
AQ            2.7263477 sec
RG                    9
DW               83.200 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        400.1326128 MHz
SI                32768
SF          400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

SM340 13C



^{13}C NMR of
3-methyl-2-*o*-tolylpyridine

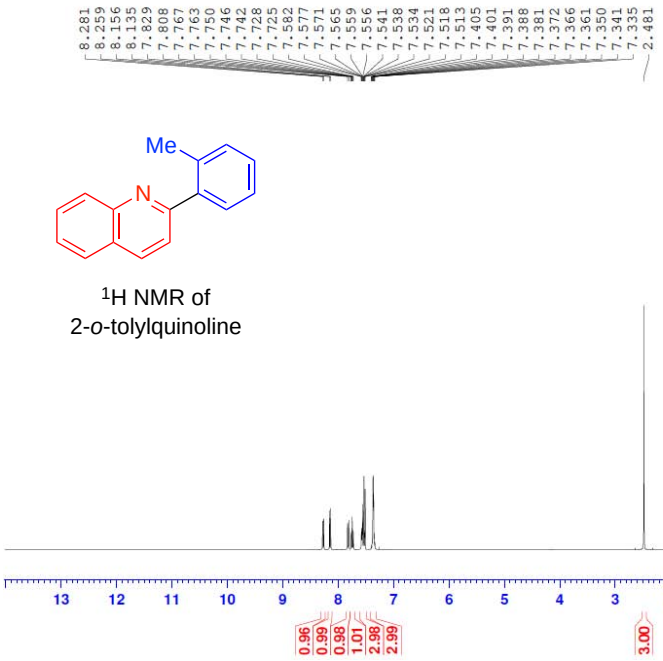
```
NAME              SM340
EXPNO                 4
PROCNO                1
Date_          20101220
Time              14.55
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   64
DS                    2
SWH           25252.525 Hz
FIDRES        0.385323 Hz
AQ            1.2976629 sec
RG                  144
DW               19.800 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        100.6253456 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          100.6127999 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

2-*o*-Tolylquinoline (**Table 5.23**, entry 4)

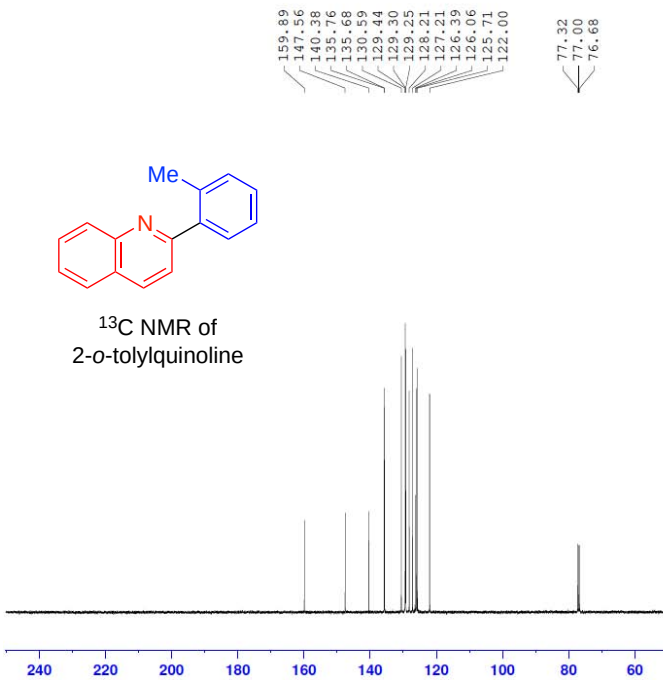
SM320 1H



^{1}H NMR of
2-*o*-tolylquinoline

NAME	SM320
EXPNO	1
PROCNO	1
Date_	20101013
Time	8.16
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	6009.615 Hz
FIDRES	0.183399 Hz
AQ	2.7263477 sec
RG	9
DW	83.200 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	400.1326128 MHz
SI	32768
SF	400.1300099 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

SM320 13C

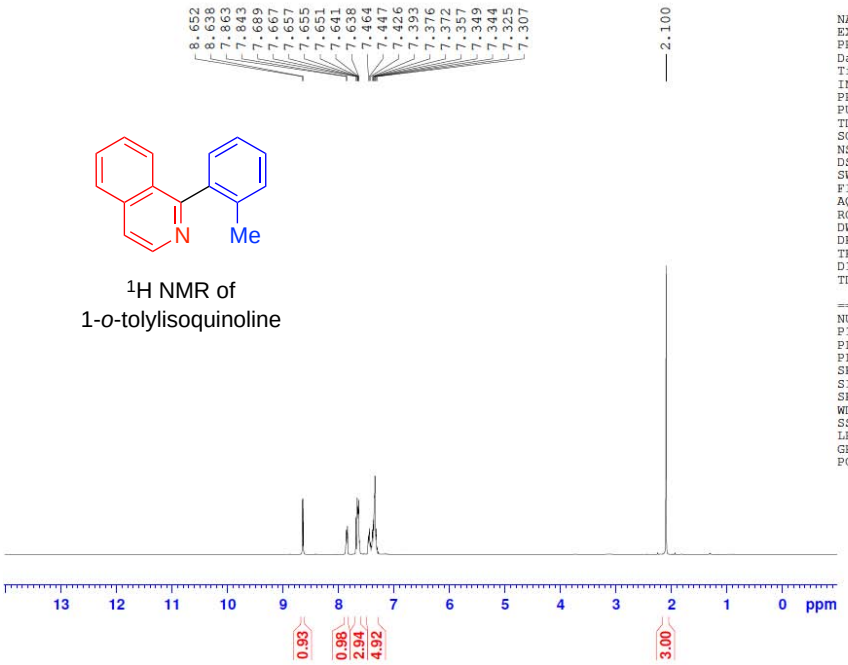


^{13}C NMR of
2-*o*-tolylquinoline

NAME	SM320
EXPNO	2
PROCNO	1
Date_	20101013
Time	8.32
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	32
DS	2
SWH	25252.525 Hz
FIDRES	0.385323 Hz
AQ	1.2976629 sec
RG	203
DW	19.800 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	100.6253456 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	100.6128107 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1-*o*-Tolylisoquinoline (**Table 5.23**, entry 5)

SM308 1H

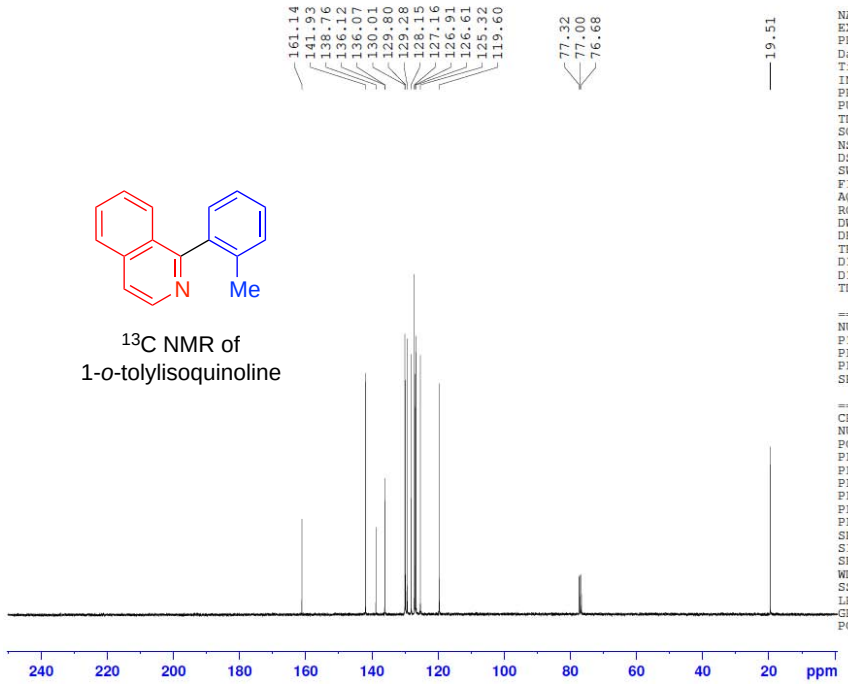


^{1}H NMR of
1-*o*-tolylisoquinoline

```
NAME                SM308
EXPNO                   3
PROCNO                  1
Date_            20101117
Time                14.26
INSTRUM             spect
PROBHD     5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     32
DS                      2
SWH              6009.615 Hz
FIDRES           0.183399 Hz
AQ               2.7263477 sec
RG                     16
DW                83.200 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          400.1326128 MHz
SI                  32768
SF            400.1300000 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                 1.00
```

SM308 13C



^{13}C NMR of
1-*o*-tolylisoquinoline

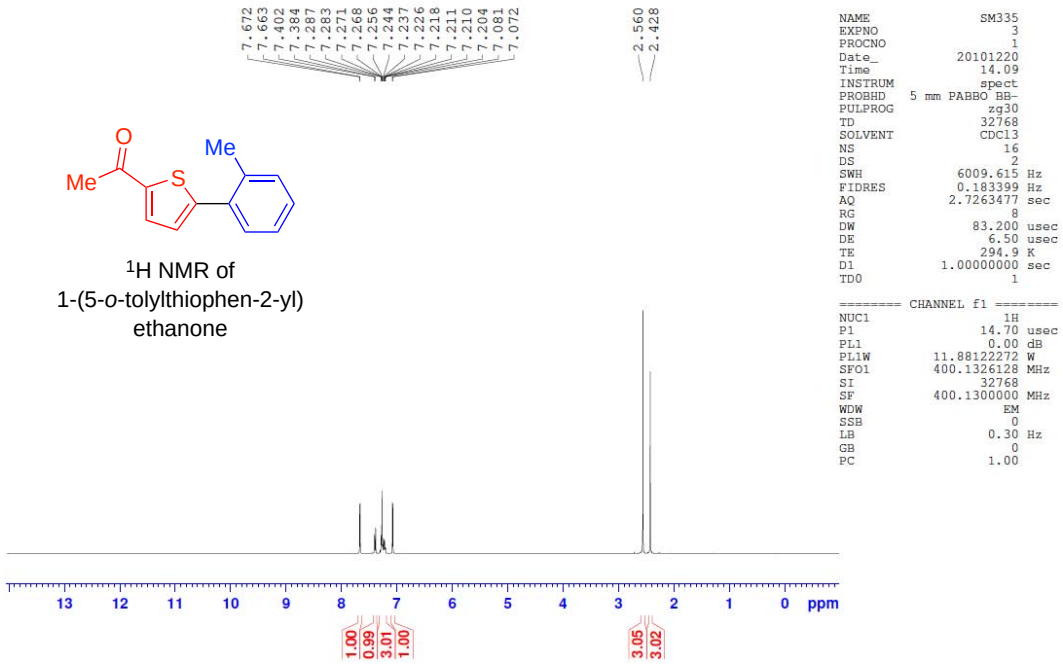
```
NAME                SM308
EXPNO                   4
PROCNO                  1
Date_            20101117
Time                14.36
INSTRUM             spect
PROBHD     5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     64
DS                      2
SWH             25252.525 Hz
FIDRES           0.385323 Hz
AQ               1.2976629 sec
RG                    203
DW                19.800 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          100.6253456 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            100.6128003 MHz
WDW                    EM
SSB                     0
LB                 1.00 Hz
GB                      0
PC                 1.40
```

1-(5-*o*-Tolylthiophen-2-yl)ethanone (**Table 5.23**, entry 6)

SM335 1H

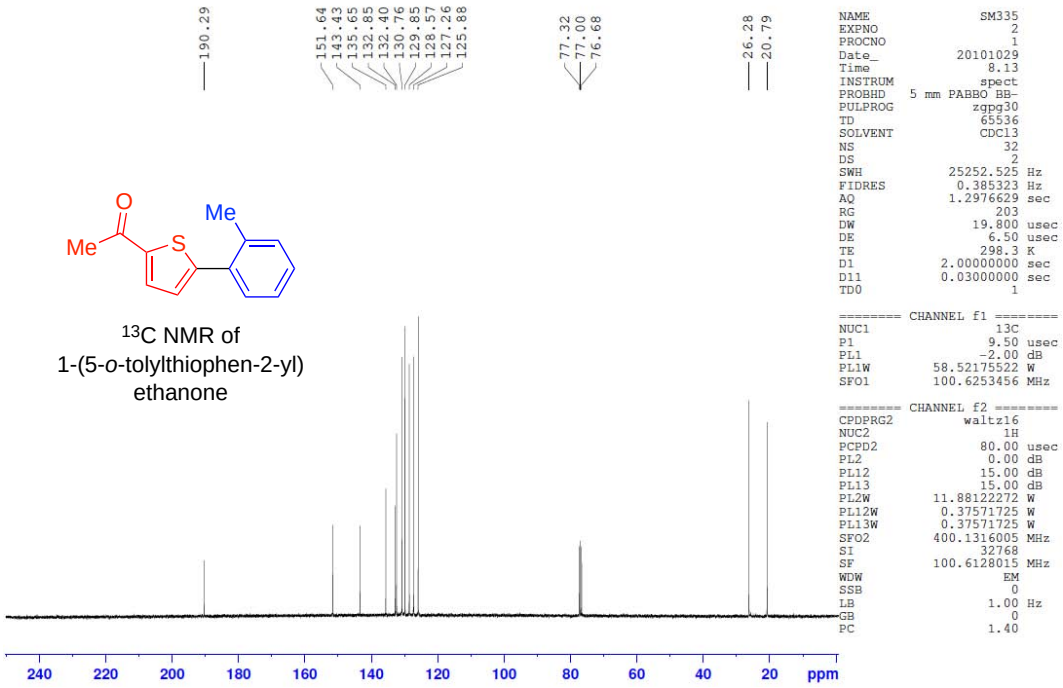


^{1}H NMR of 1-(5-*o*-tolylthiophen-2-yl) ethanone

```
NAME              SM335
EXPNO                 3
PROCNO                1
Date_          20101220
Time              14.09
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            6009.615 Hz
FIDRES        0.183399 Hz
AQ            2.7263477 sec
RG                    8
DW               83.200 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       400.1326128 MHz
SI                32768
SF         400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

SM335 13C



^{13}C NMR of 1-(5-*o*-tolylthiophen-2-yl) ethanone

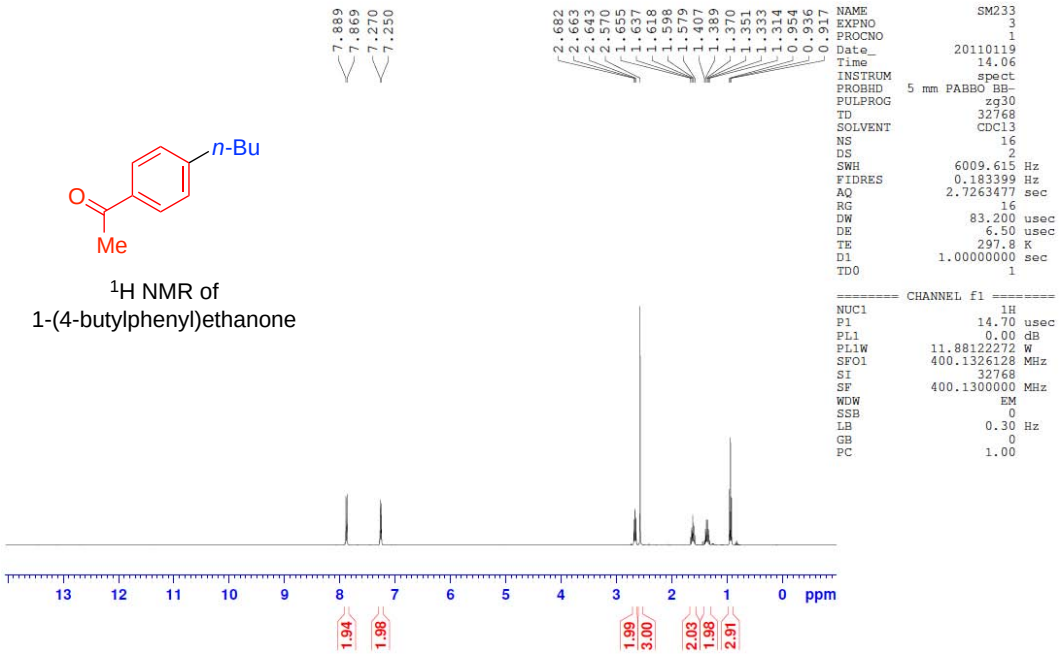
```
NAME              SM335
EXPNO                 2
PROCNO                1
Date_          20101029
Time               8.13
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    2
SWH           25252.525 Hz
FIDRES        0.385323 Hz
AQ            1.2976629 sec
RG                  203
DW               19.800 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       100.6253456 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         100.6128015 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

1-(4-Butylphenyl)ethanone (**Table 5.23**, entry 7)

SM233 1H

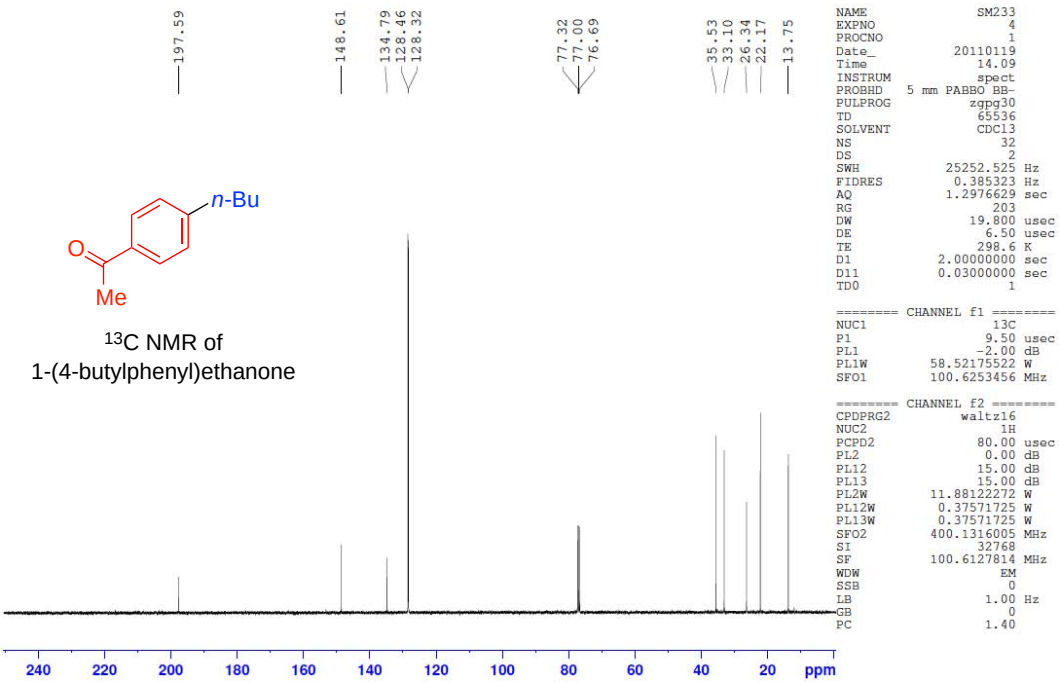


NAME SM233
EXPNO 3
PROCNO 1
Date_ 20110119
Time 14.06
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 16
DW 83.200 usec
DE 6.50 usec
TE 297.8 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 14.70 usec
PL1 0.00 dB
PL1W 11.88122272 W
SFO1 400.1326128 MHz
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

^{1}H NMR of
1-(4-butylphenyl)ethanone

SM233 13C



NAME SM233
EXPNO 4
PROCNO 1
Date_ 20110119
Time 14.09
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 32
DS 2
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976629 sec
RG 203
DW 19.800 usec
DE 6.50 usec
TE 298.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

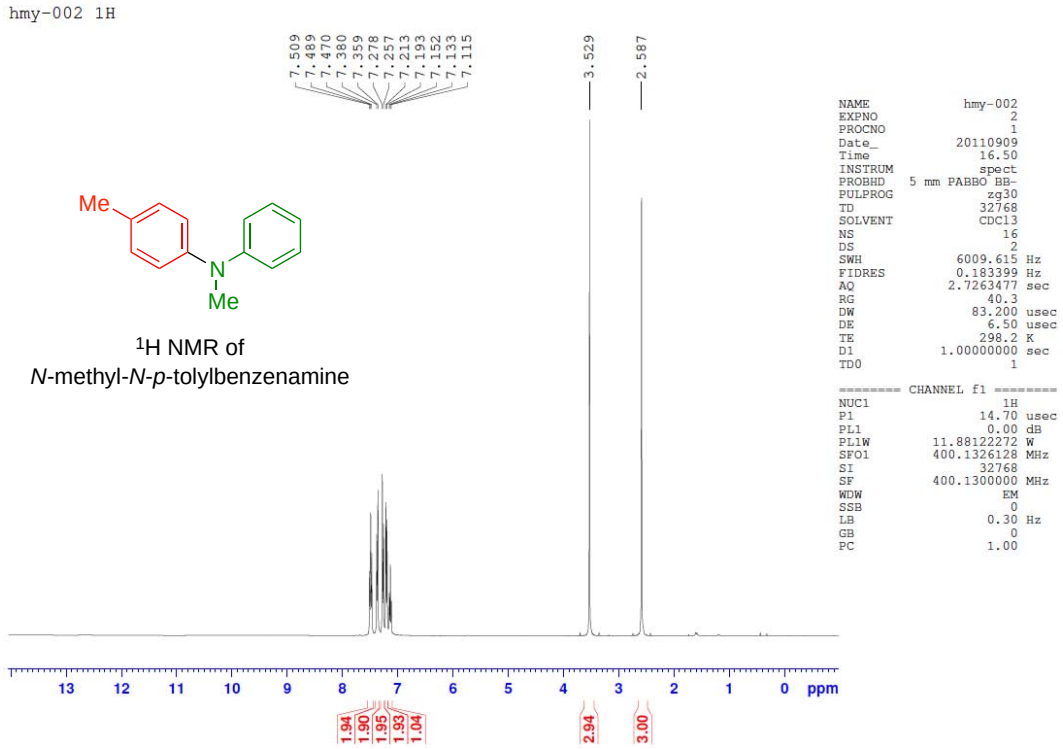
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 -2.00 dB
PL1W 58.52175522 W
SFO1 100.6253456 MHz

======== 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 100.6127814 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

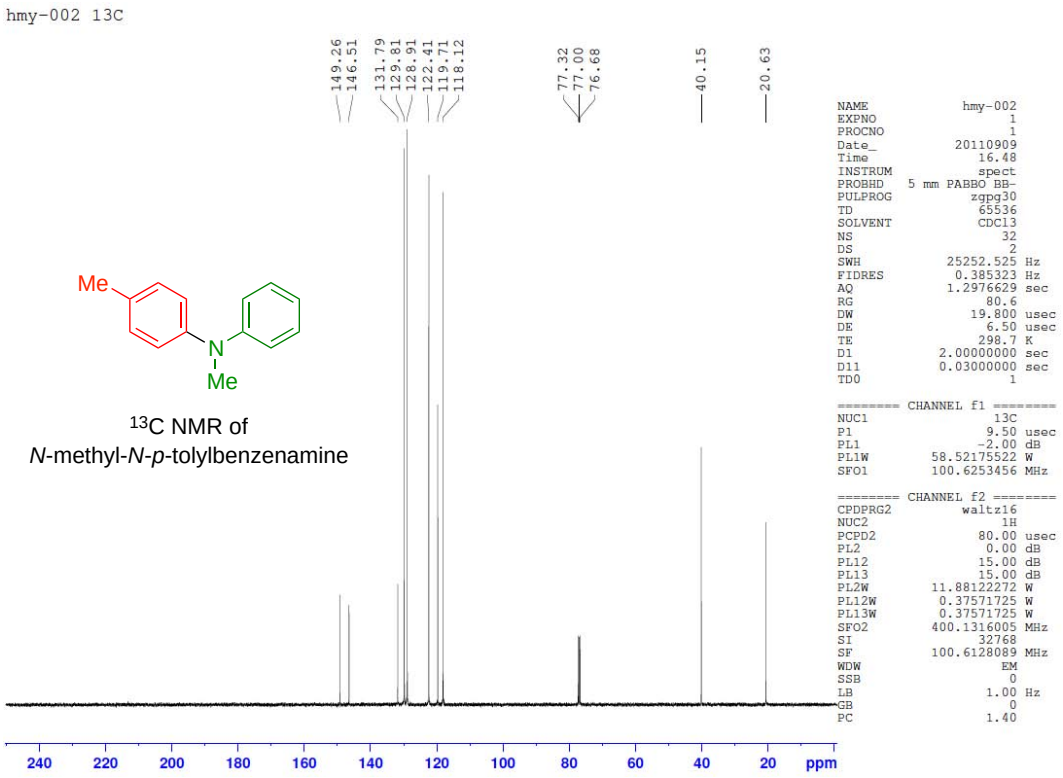
^{13}C NMR of
1-(4-butylphenyl)ethanone

Chapter 6 NMR Spectra of Coupling products

N-Methyl-*N*-*p*-tolylbenzenamine (**Table 6.3**, entry 1)



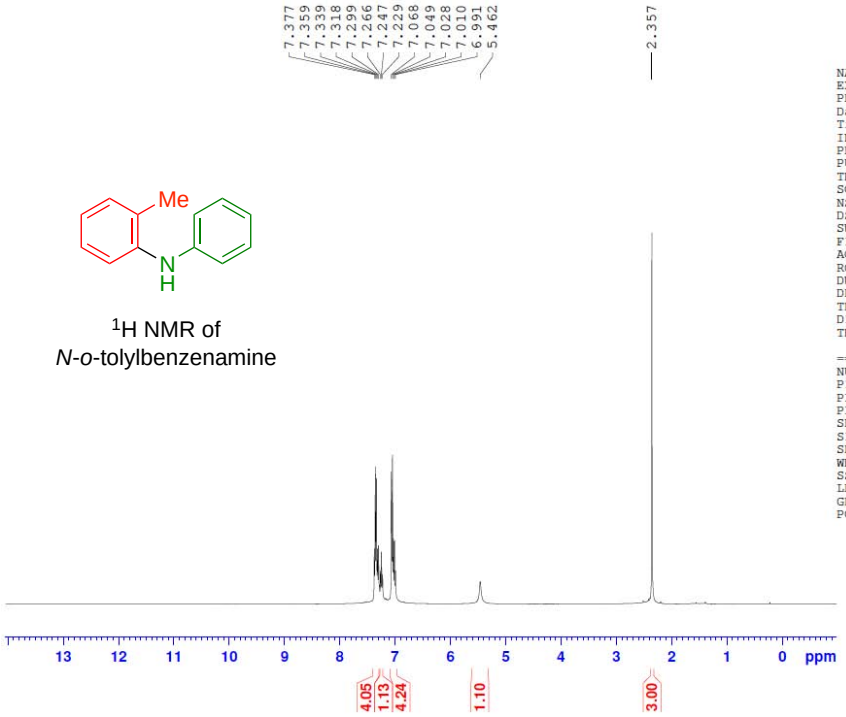
^{1}H NMR of
N-methyl-*N*-*p*-tolylbenzenamine



^{13}C NMR of
N-methyl-*N*-*p*-tolylbenzenamine

N-*o*-Tolylbenzenamine (**Table 6.3**, entry 2)

hmy-154 1H

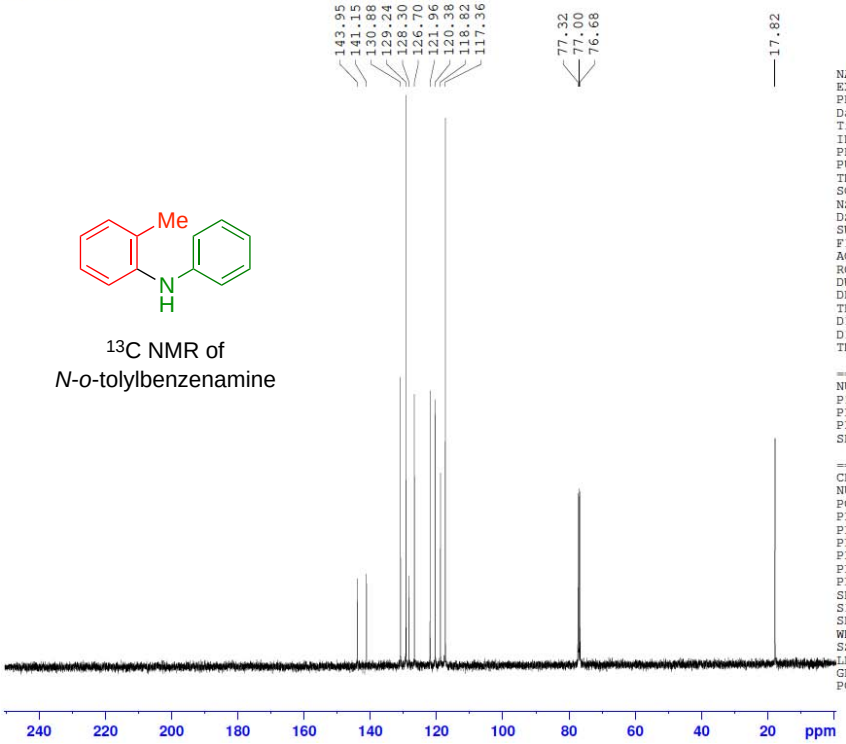


NAME hmy-154
EXPNO 1
PROCNO 1
Date_ 20120220
Time 14.57
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 32
DW 83.200 usec
DE 6.50 usec
TE 296.9 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 14.70 usec
PL1 0.00 dB
PL1W 11.88122272 W
SFO1 400.1326128 MHz
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

^{1}H NMR of
N-*o*-tolylbenzenamine

hmy-154 13C



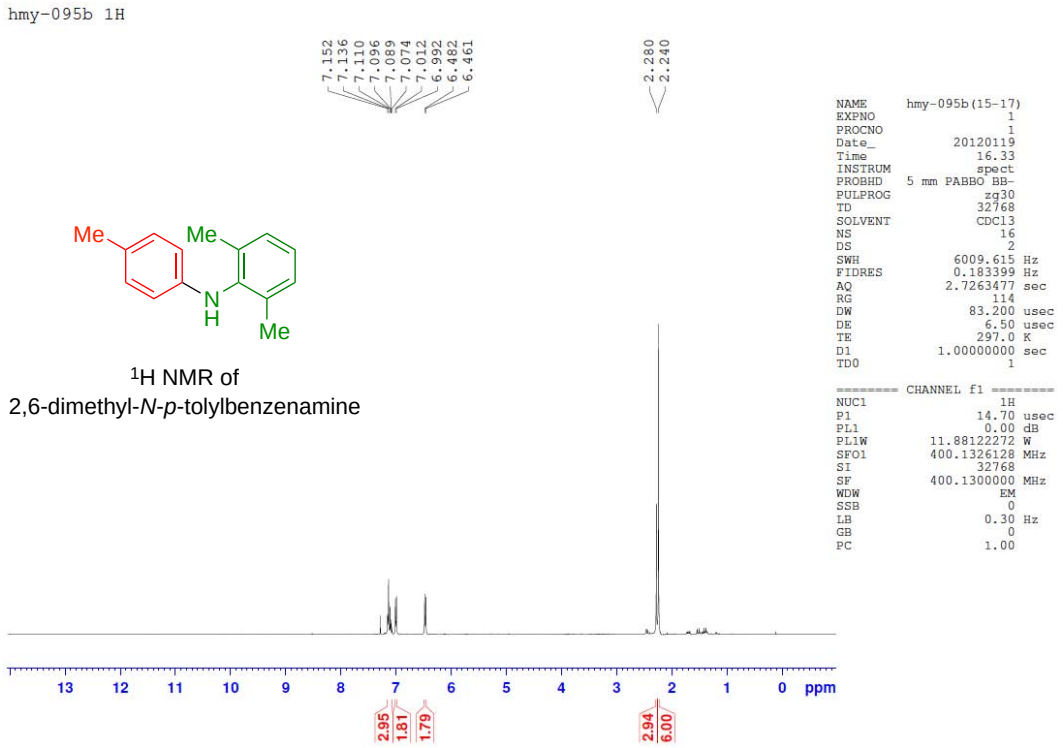
NAME hmy-154
EXPNO 2
PROCNO 1
Date_ 20120220
Time 15.03
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 64
DS 2
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976629 sec
RG 80.6
DW 19.800 usec
DE 6.50 usec
TE 298.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 -2.00 dB
PL1W 58.52175522 W
SFO1 100.6253456 MHz

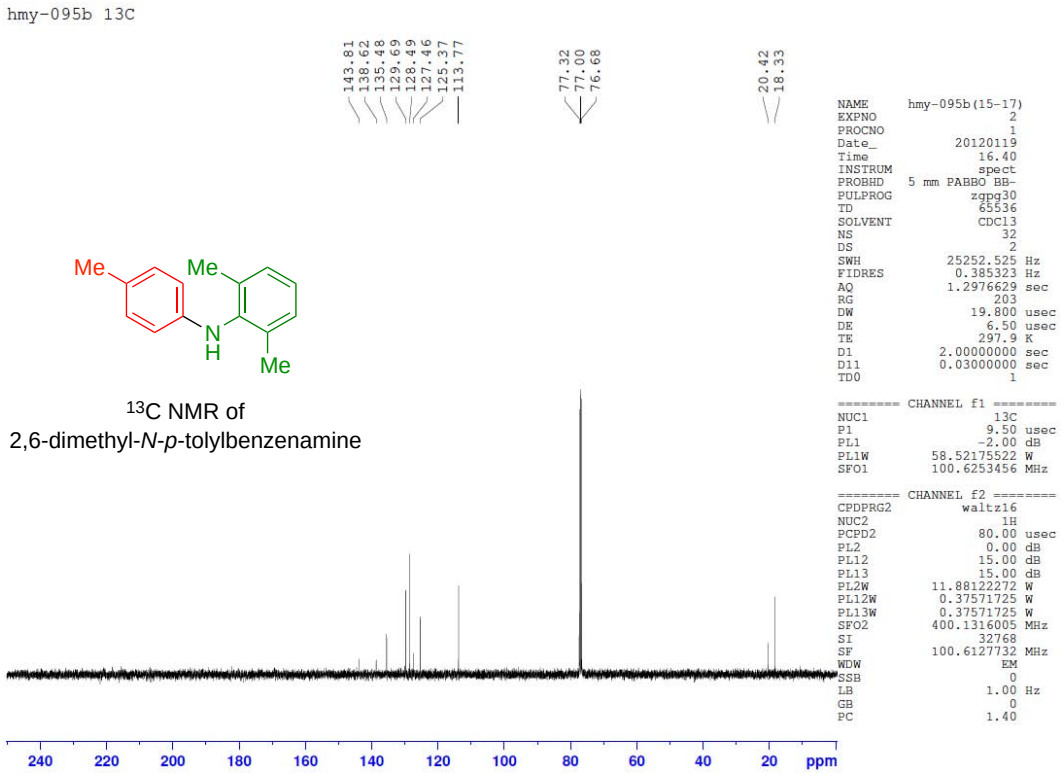
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 15.00 dB
PL13 15.00 dB
PL2W 11.88122272 W
PL12W 0.37571725 W
PL13W 0.37571725 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127853 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

^{13}C NMR of
N-*o*-tolylbenzenamine

2,6-Dimethyl-*N*-*p*-tolylbenzenamine (**Table 6.3**, entry 3)



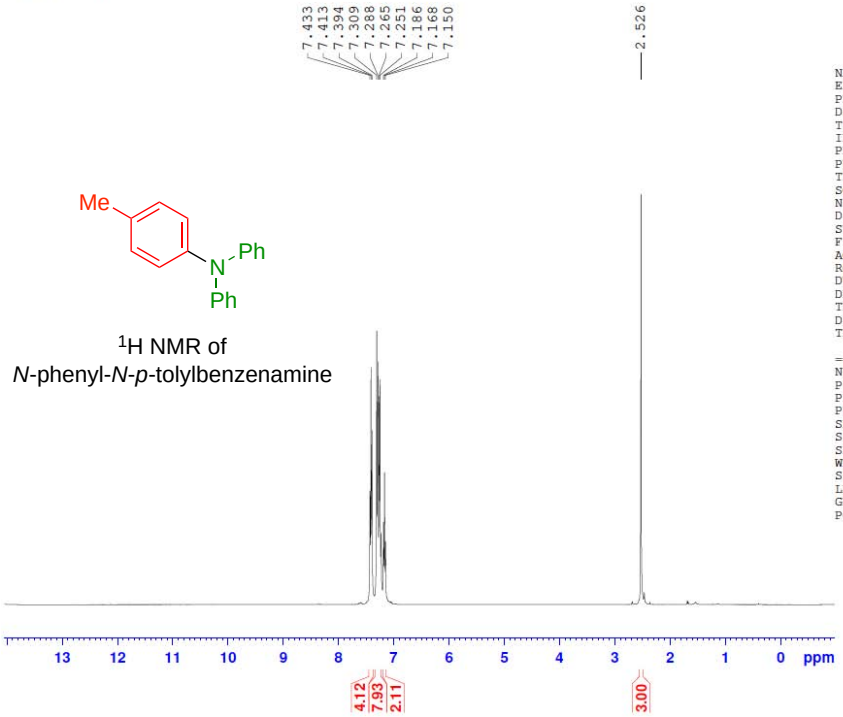
^{1}H NMR of
2,6-dimethyl-*N*-*p*-tolylbenzenamine



^{13}C NMR of
2,6-dimethyl-*N*-*p*-tolylbenzenamine

N-Phenyl-*N*-*p*-tolylbenzenamine (**Table 6.3**, entry 4)

hmy-100 1H

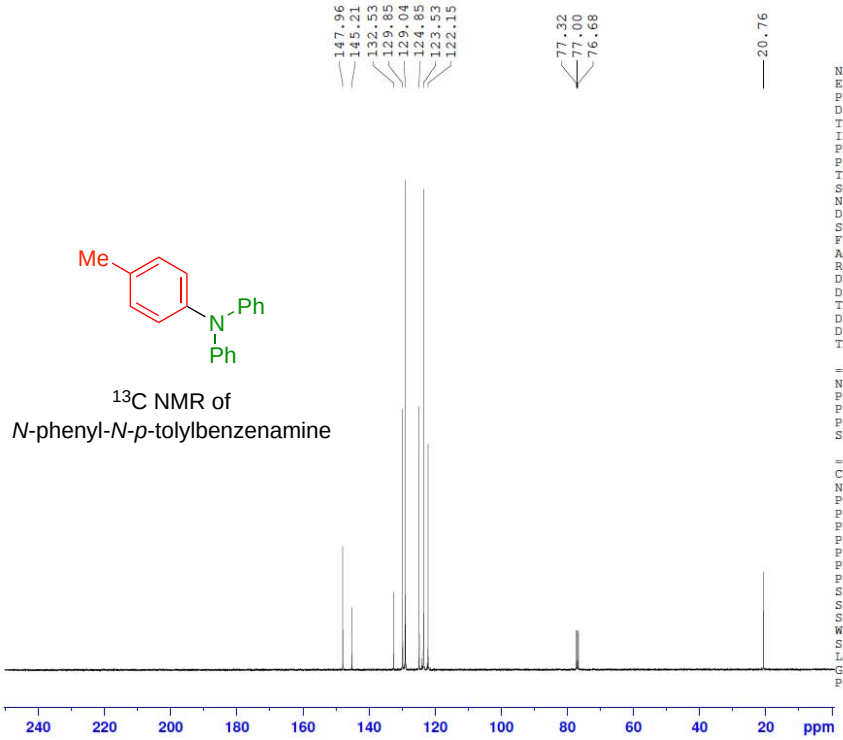


^{1}H NMR of
N-phenyl-*N*-*p*-tolylbenzenamine

```
NAME            hmy-100
EXPNO                 1
PROCNO                1
Date_          20120213
Time              15.03
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            6009.615 Hz
FIDRES        0.183399 Hz
AQ            2.7263477 sec
RG                 11.3
DW               83.200 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       400.1326128 MHz
SI                32768
SF         400.1300000 MHz
WDW                EM
SSB                 0
LB                0.30 Hz
GB                  0
PC                1.00
```

hmy-100 13C



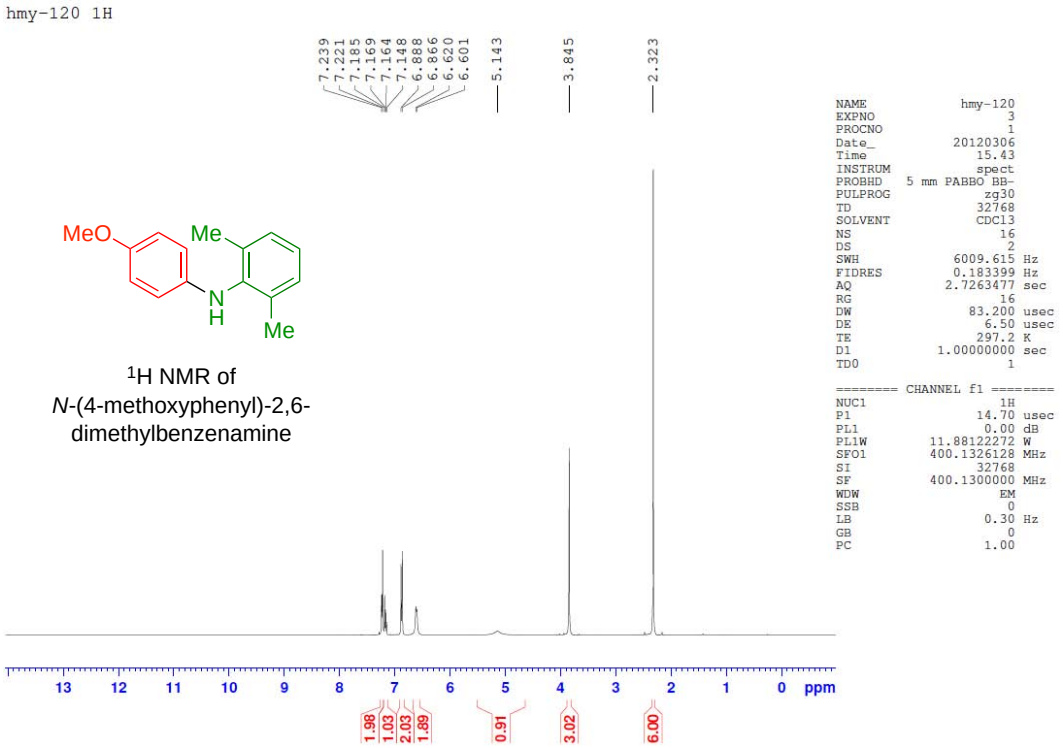
^{13}C NMR of
N-phenyl-*N*-*p*-tolylbenzenamine

```
NAME            hmy-100
EXPNO                 2
PROCNO                1
Date_          20120213
Time              15.12
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    2
SWH           25252.525 Hz
FIDRES        0.385323 Hz
AQ            1.2976629 sec
RG                  161
DW               19.800 usec
DE                6.50 usec
TE               298.3 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

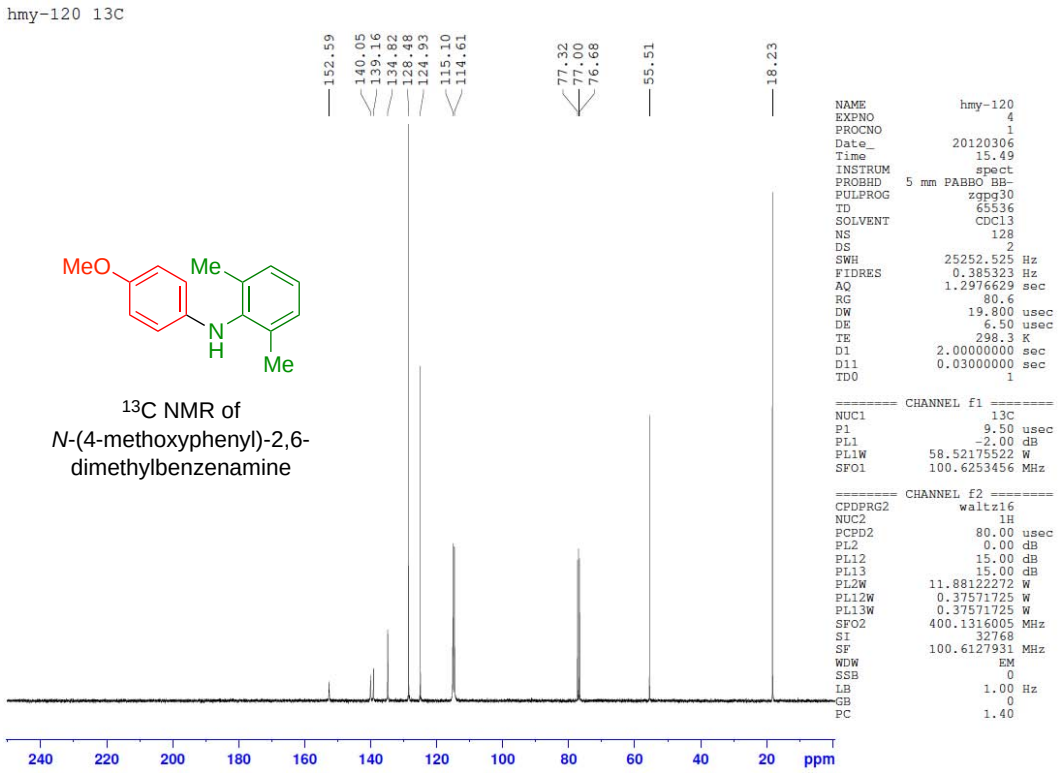
======== CHANNEL f1 ========
NUC1                13C
P1                9.50 usec
PL1              -2.00 dB
PL1W       58.52175522 W
SFO1       100.6253456 MHz

======== 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         100.6128027 MHz
WDW                EM
SSB                 0
LB                1.00 Hz
GB                  0
PC                1.40
```

N-(4-Methoxyphenyl)-2,6-dimethylbenzenamine (**Table 6.3**, entry 5)

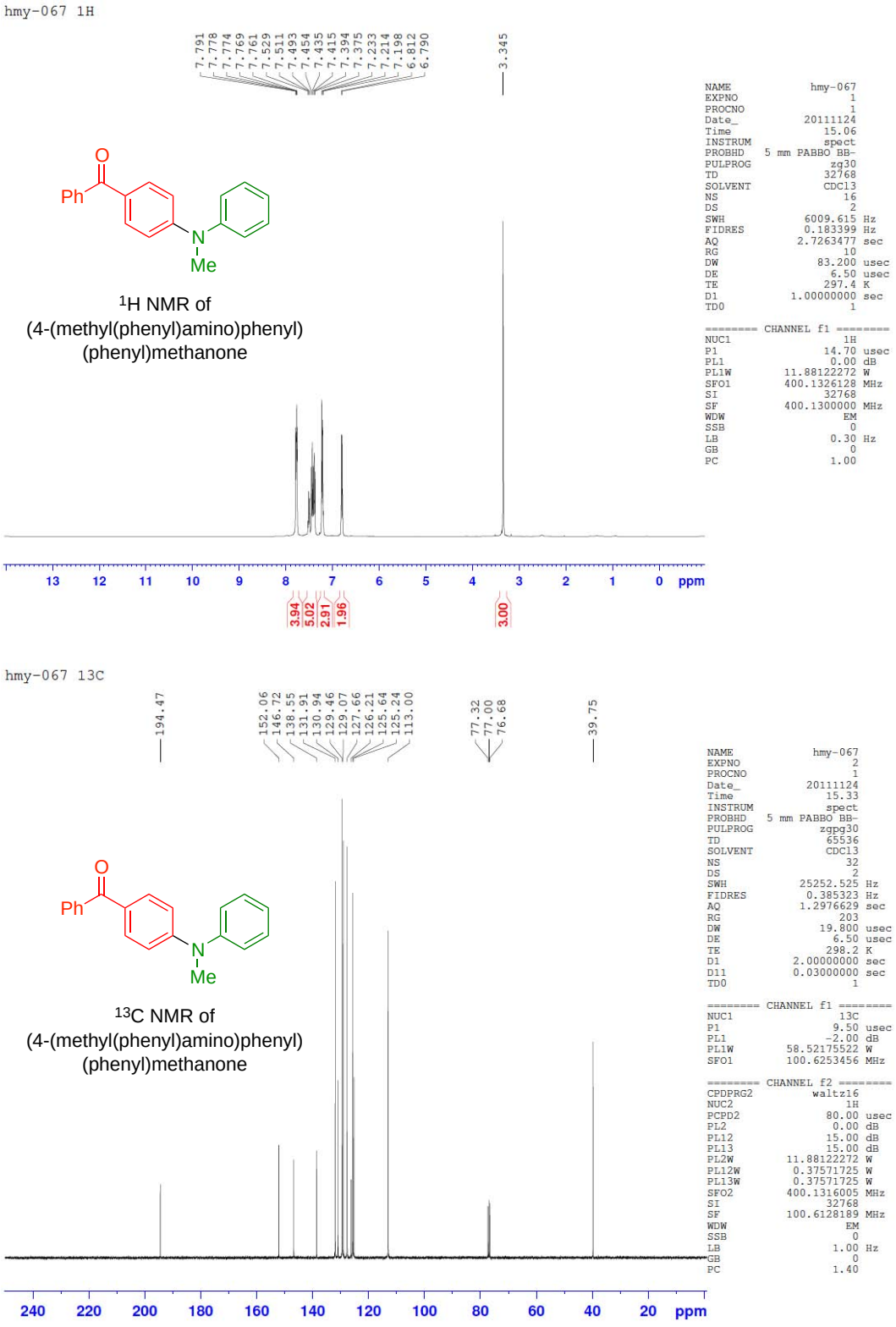


^{1}H NMR of *N*-(4-methoxyphenyl)-2,6-dimethylbenzenamine



^{13}C NMR of *N*-(4-methoxyphenyl)-2,6-dimethylbenzenamine

(4-(Methyl(phenyl)amino)phenyl)(phenyl)methanone (**Table 6.4**, entry 1)

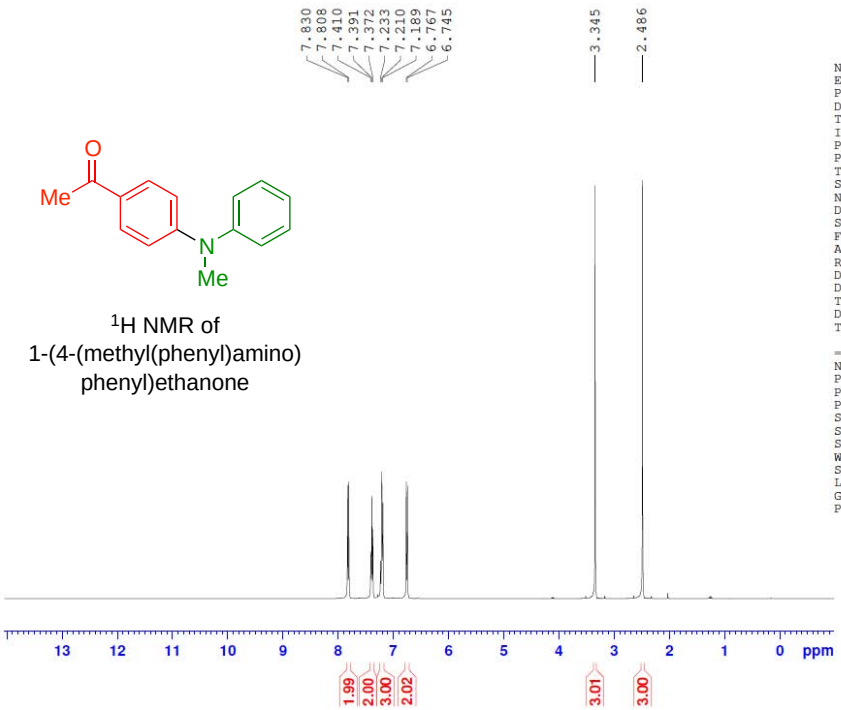


^{1}H NMR of
(4-(methyl(phenyl)amino)phenyl)
(phenyl)methanone

^{13}C NMR of
(4-(methyl(phenyl)amino)phenyl)
(phenyl)methanone

1-(4-(Methyl(phenyl)amino)phenyl)ethanone (**Table 6.4**, entry 2)

hmy-080 1H

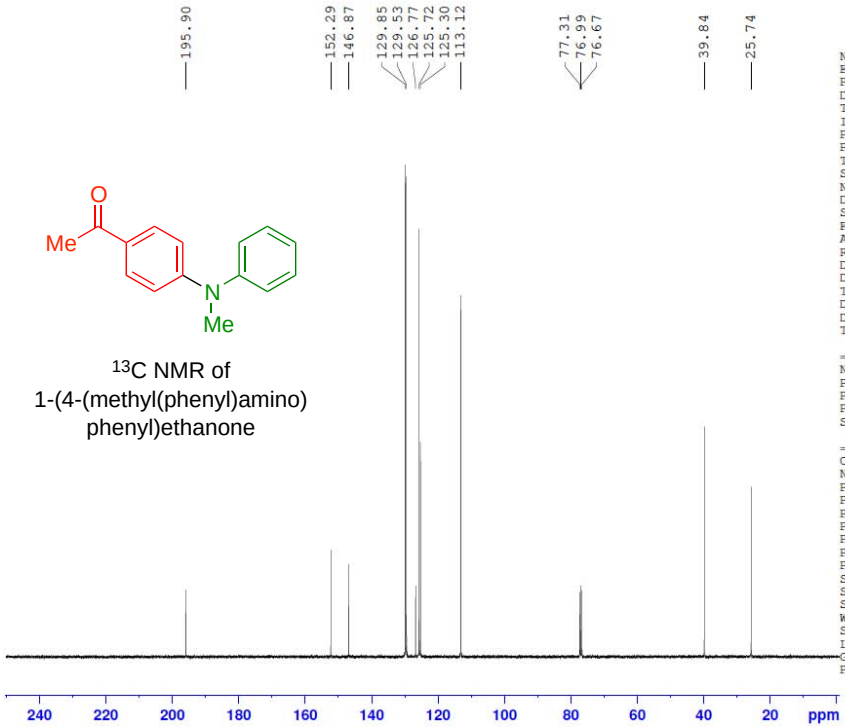


^{1}H NMR of
1-(4-(methyl(phenyl)amino)
phenyl)ethanone

```
NAME            hmy-080
EXPNO                 1
PROCNO                1
Date_          20120106
Time              16.29
INSTRUM           spect
PROBHD  5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            6009.615 Hz
FIDRES        0.183399 Hz
AQ            2.7263477 sec
RG                 14.2
DW               83.200 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       400.1326128 MHz
SI                32768
SF         400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

Standard 13C



^{13}C NMR of
1-(4-(methyl(phenyl)amino)
phenyl)ethanone

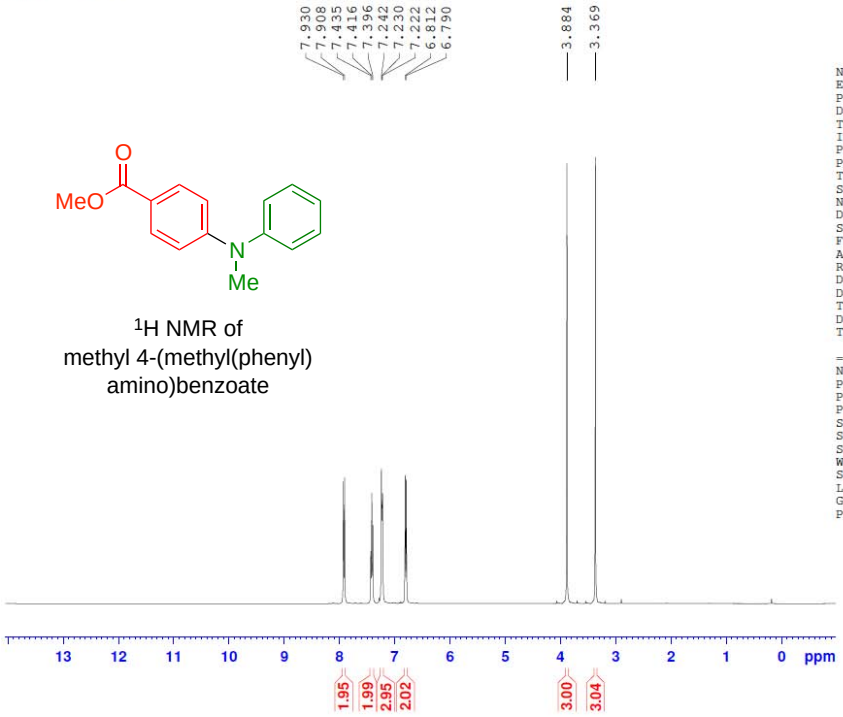
```
NAME       Standard 13C
EXPNO                 1
PROCNO                1
Date_          20120106
Time              16.37
INSTRUM           spect
PROBHD  5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    2
SWH           25252.525 Hz
FIDRES        0.385323 Hz
AQ            1.2976629 sec
RG                  203
DW               19.800 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       100.6253456 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         100.6128066 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

Methyl 4-(methyl(phenyl)amino)benzoate (**Table 6.4**, entry 3)

hmy-073 1H

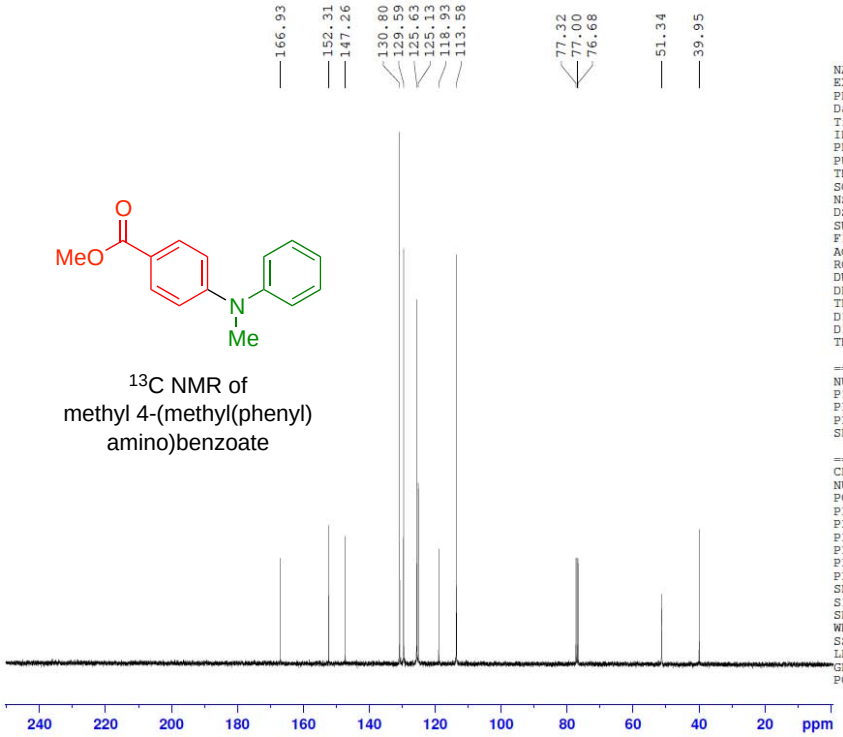


^{1}H NMR of methyl 4-(methyl(phenyl)amino)benzoate

```
NAME            hmy-073
EXPNO                 1
PROCNO                1
Date_          20120118
Time              13.17
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            6009.615 Hz
FIDRES        0.183399 Hz
AQ            2.7263477 sec
RG                   16
DW               83.200 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        400.1326128 MHz
SI                32768
SF          400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

hmy-073 13C



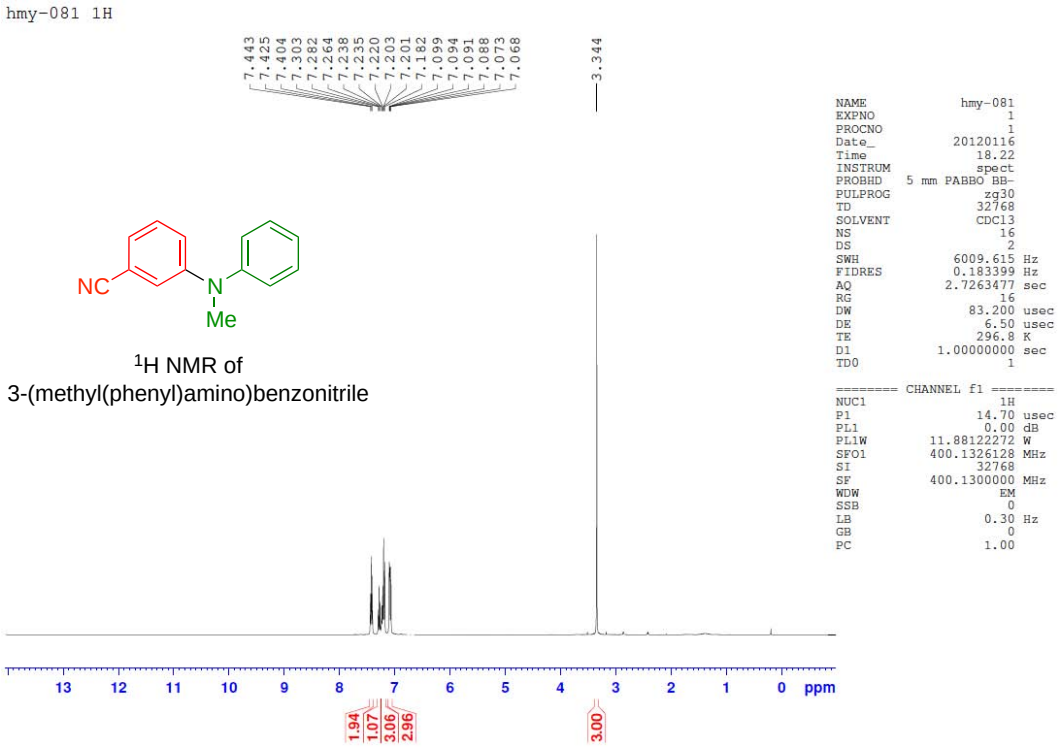
^{13}C NMR of methyl 4-(methyl(phenyl)amino)benzoate

```
NAME            hmy-073
EXPNO                 2
PROCNO                1
Date_          20120118
Time              13.34
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    2
SWH           25252.525 Hz
FIDRES        0.385323 Hz
AQ            1.2976629 sec
RG                 90.5
DW               19.800 usec
DE                6.50 usec
TE               298.4 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

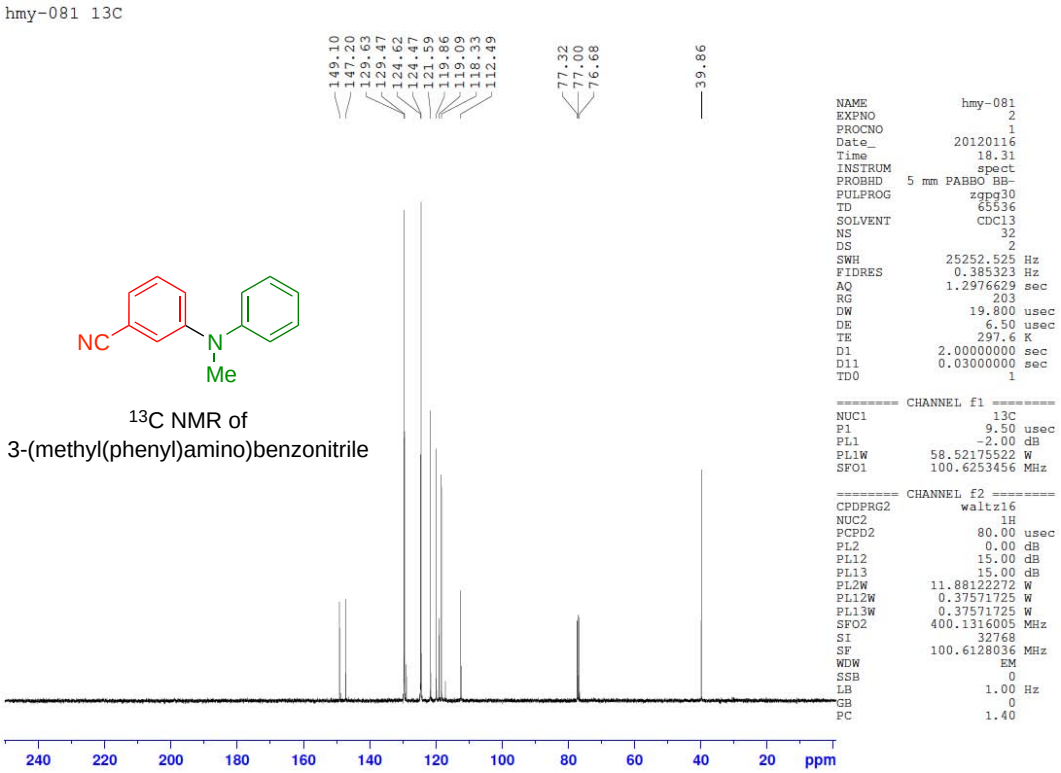
======== CHANNEL f1 ========
NUC1                 13C
P1                9.50 usec
PL1               -2.00 dB
PL1W        58.52175522 W
SFO1        100.6253456 MHz

======== 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          100.6127947 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

3-(Methyl(phenyl)amino)benzonitrile (**Table 6.4**, entry 4)



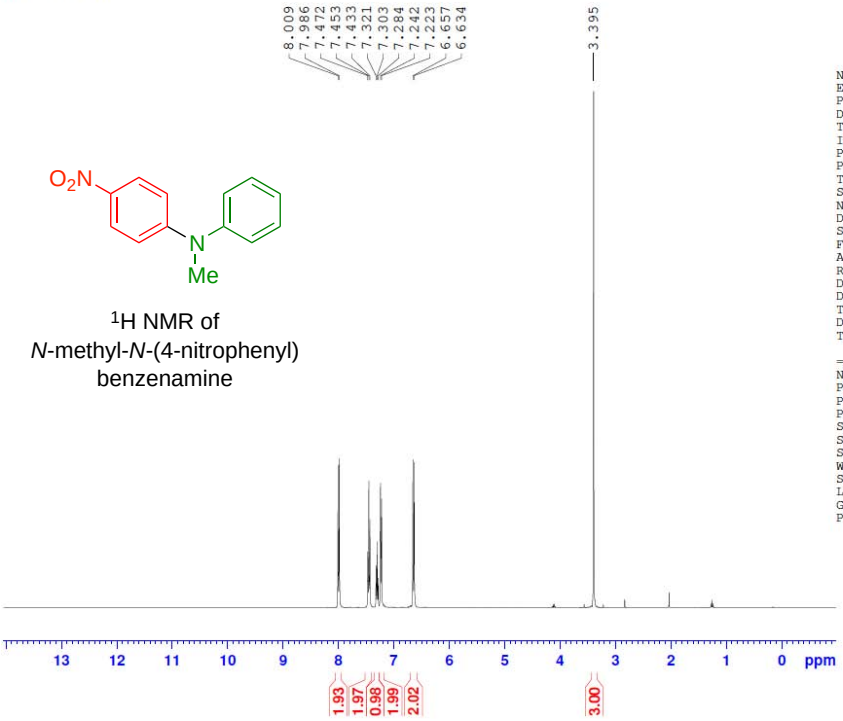
^{1}H NMR of
3-(methyl(phenyl)amino)benzonitrile



^{13}C NMR of
3-(methyl(phenyl)amino)benzonitrile

N-Methyl-*N*-(4-nitrophenyl)benzenamine (**Table 6.4**, entry 5)

hmy-079 1H

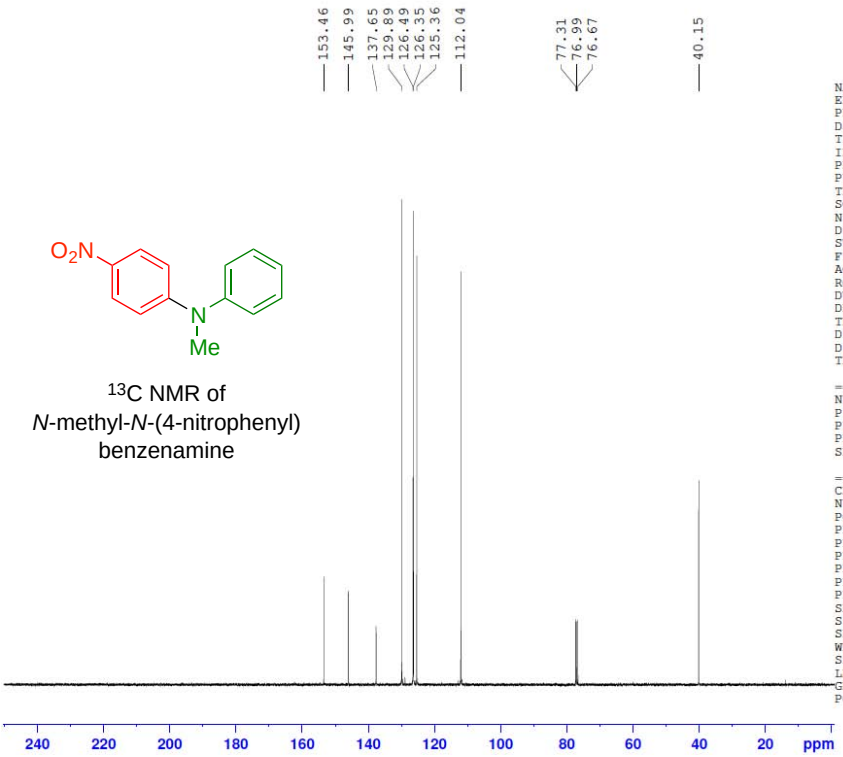


^{1}H NMR of
N-methyl-*N*-(4-nitrophenyl)
benzenamine

```
NAME            hmy-079
EXPNO                 1
PROCNO                1
Date_          20120104
Time              15.53
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            6009.615 Hz
FIDRES        0.183399 Hz
AQ            2.7263477 sec
RG                 14.2
DW                83.200 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       400.1326128 MHz
SI                32768
SF         400.1300000 MHz
WDW                EM
SSB                 0
LB                0.30 Hz
GB                  0
PC                1.00
```

hmy-079 13C



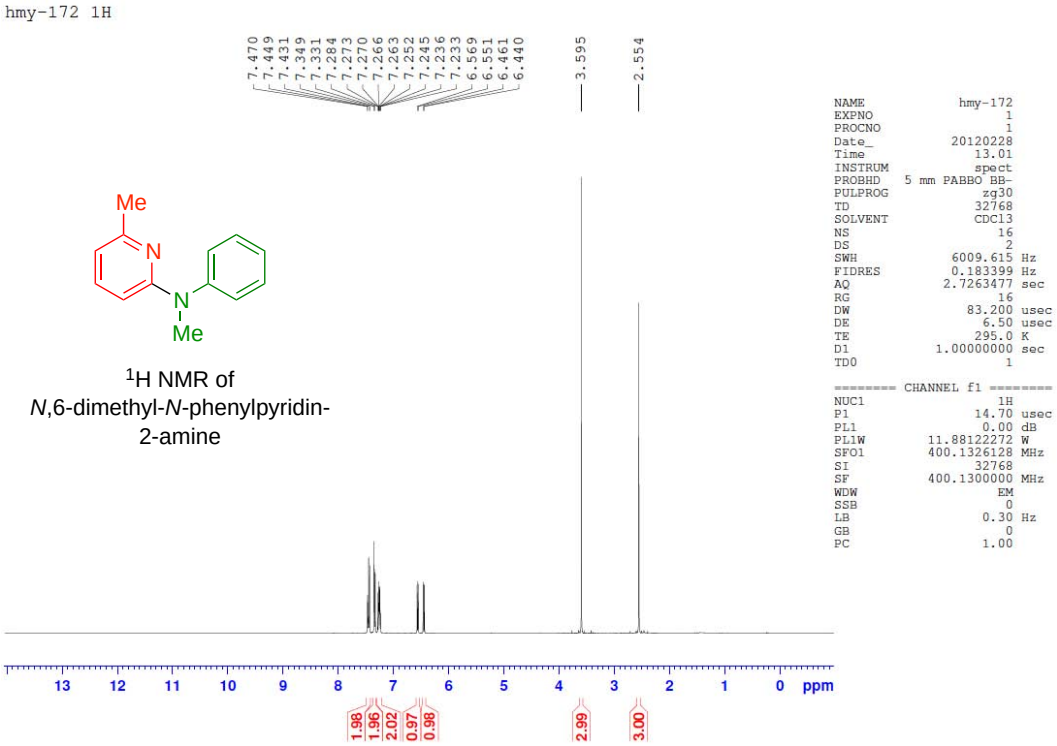
^{13}C NMR of
N-methyl-*N*-(4-nitrophenyl)
benzenamine

```
NAME            hmy-079
EXPNO                 2
PROCNO                1
Date_          20120104
Time              16.03
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    2
SWH           25252.525 Hz
FIDRES        0.385323 Hz
AQ            1.2976629 sec
RG                  203
DW                19.800 usec
DE                 6.50 usec
TE               299.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

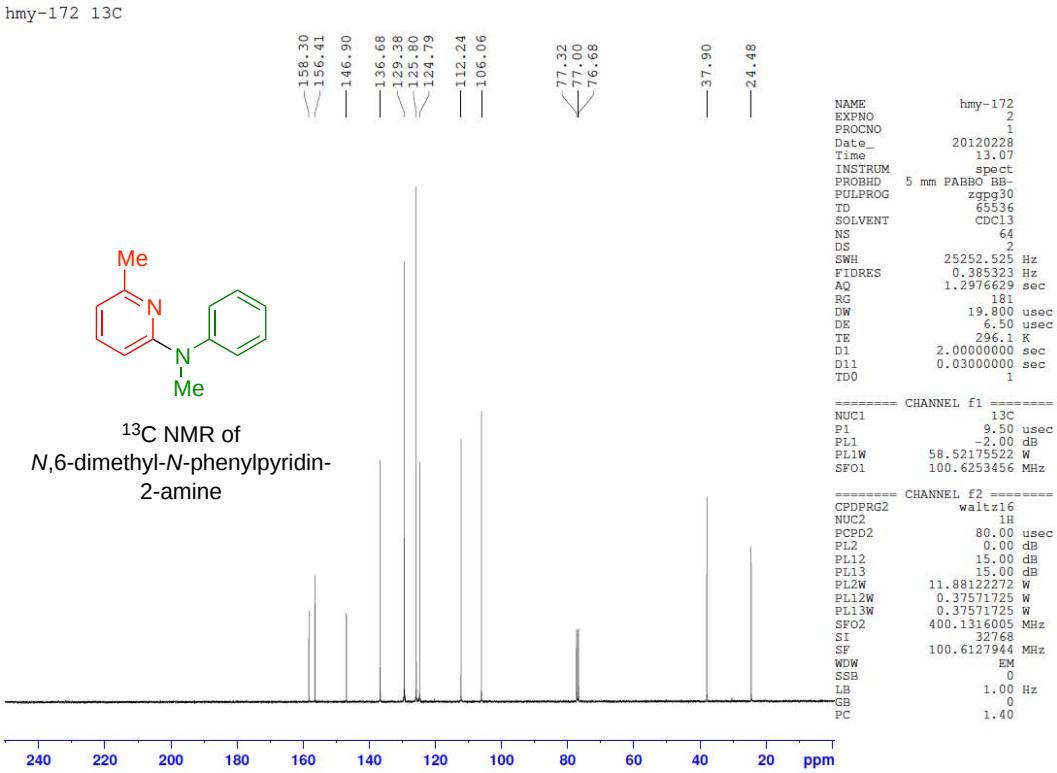
======== CHANNEL f1 ========
NUC1               13C
P1                 9.50 usec
PL1               -2.00 dB
PL1W       58.52175522 W
SFO1       100.6253456 MHz

======== 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         100.6128048 MHz
WDW                EM
SSB                 0
LB                1.00 Hz
GB                  0
PC                1.40
```

N,6-Dimethyl-*N*-phenylpyridin-2-amine (**Table 6.5**, entry 1)

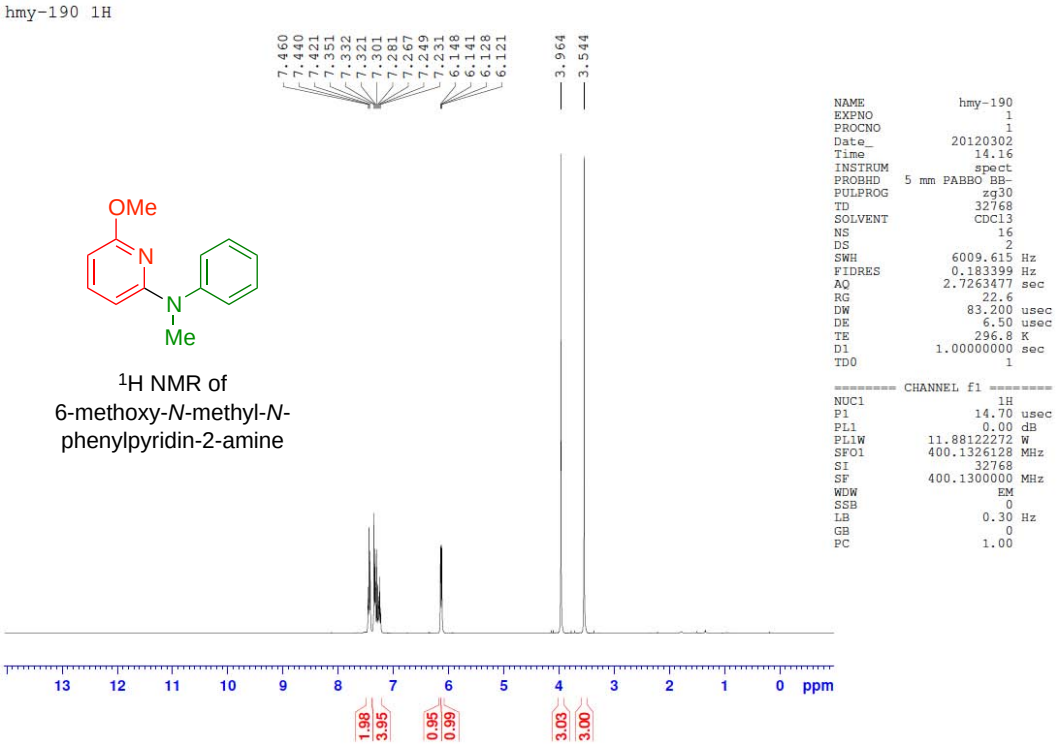


^{1}H NMR of *N*,6-dimethyl-*N*-phenylpyridin-2-amine

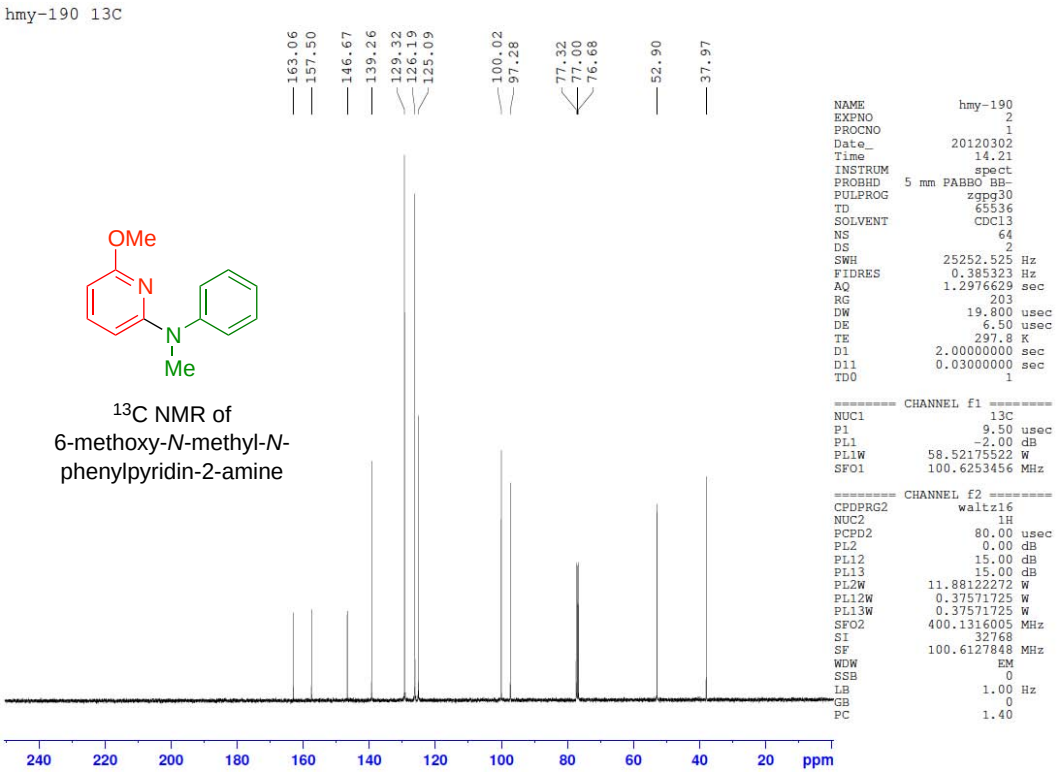


^{13}C NMR of *N*,6-dimethyl-*N*-phenylpyridin-2-amine

6-Methoxy-*N*-methyl-*N*-phenylpyridin-2-amine (**Table 6.5**, entry 2)

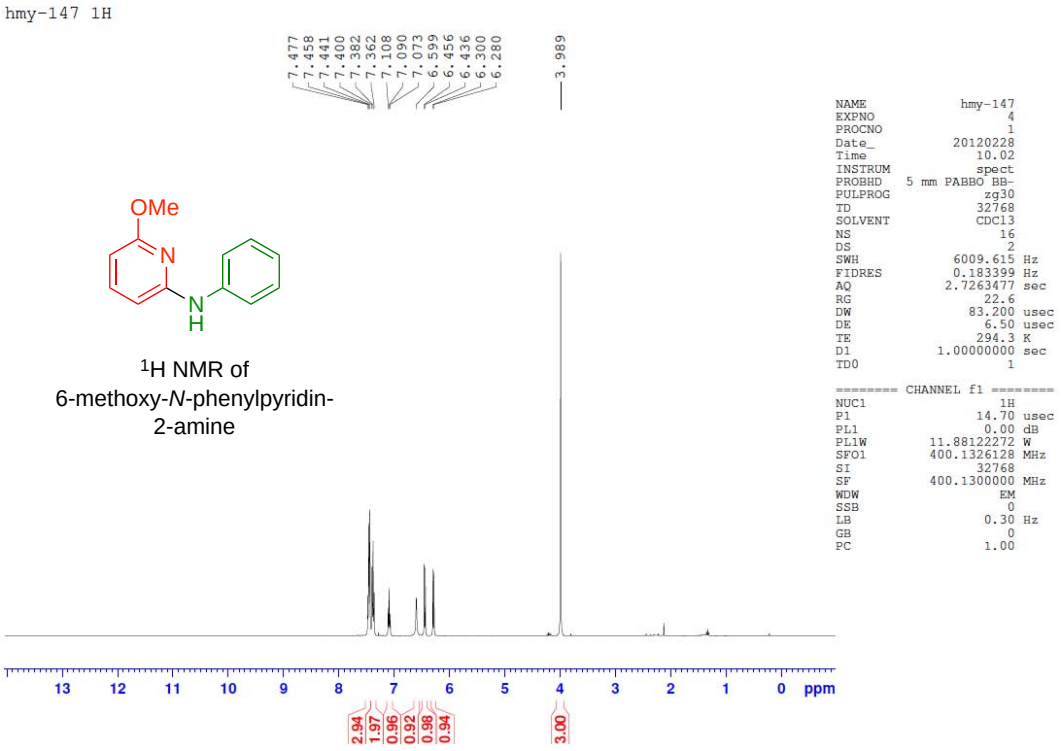


^{1}H NMR of
6-methoxy-*N*-methyl-*N*-
phenylpyridin-2-amine

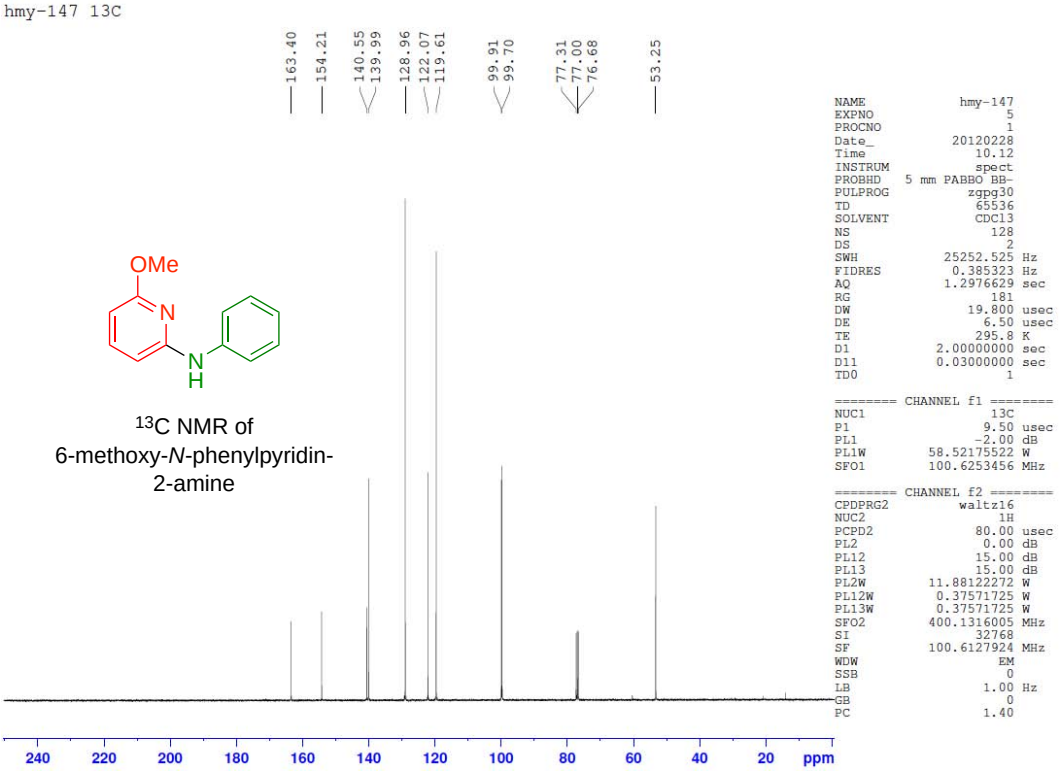


^{13}C NMR of
6-methoxy-*N*-methyl-*N*-
phenylpyridin-2-amine

6-Methoxy-*N*-phenylpyridin-2-amine (**Table 6.5**, entry 3)



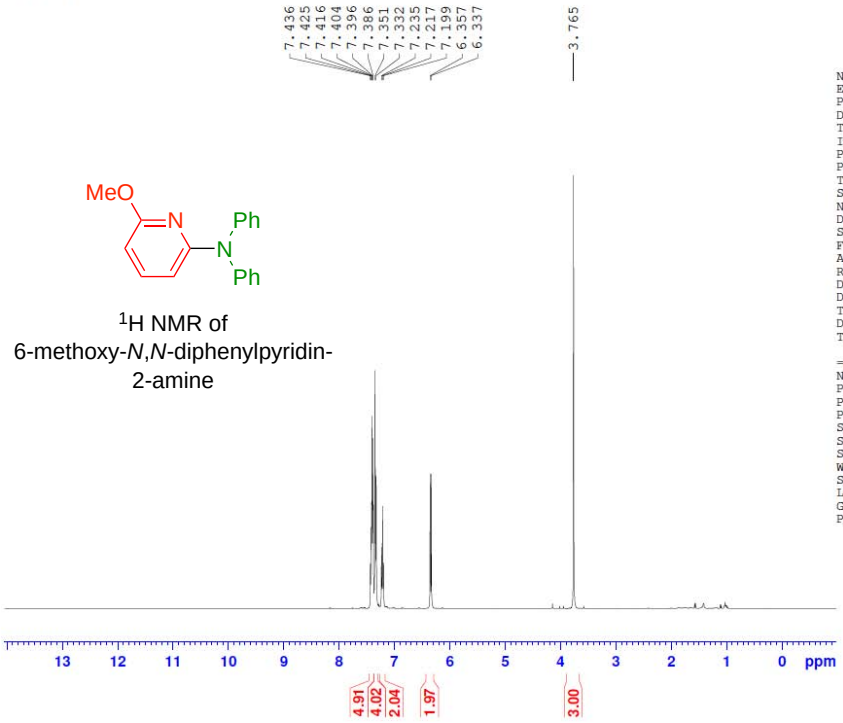
^{1}H NMR of
6-methoxy-*N*-phenylpyridin-
2-amine



^{13}C NMR of
6-methoxy-*N*-phenylpyridin-
2-amine

6-Methoxy-*N*,*N*-diphenylpyridin-2-amine (**Table 6.5**, entry 4)

hmy-191 1H

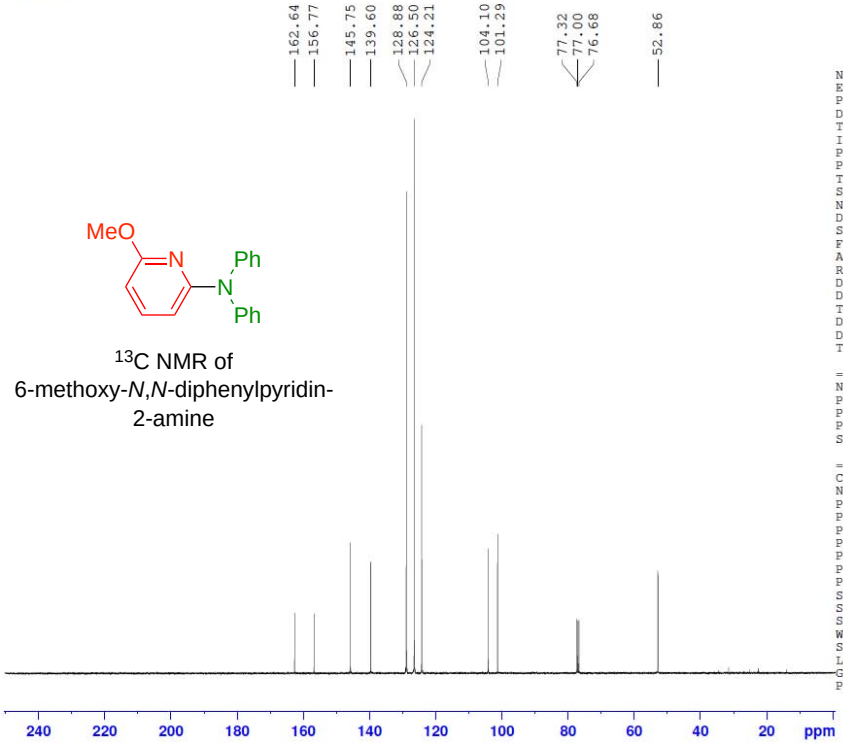


^{1}H NMR of 6-methoxy-*N*,*N*-diphenylpyridin-2-amine

```
NAME            hmy-191
EXPNO                 1
PROCNO                1
Date_          20120301
Time              18.09
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            6009.615 Hz
FIDRES        0.183399 Hz
AQ             2.7263477 sec
RG                 14.2
DW                83.200 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        400.1326128 MHz
SI                32768
SF          400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

hmy-191 13C



^{13}C NMR of 6-methoxy-*N*,*N*-diphenylpyridin-2-amine

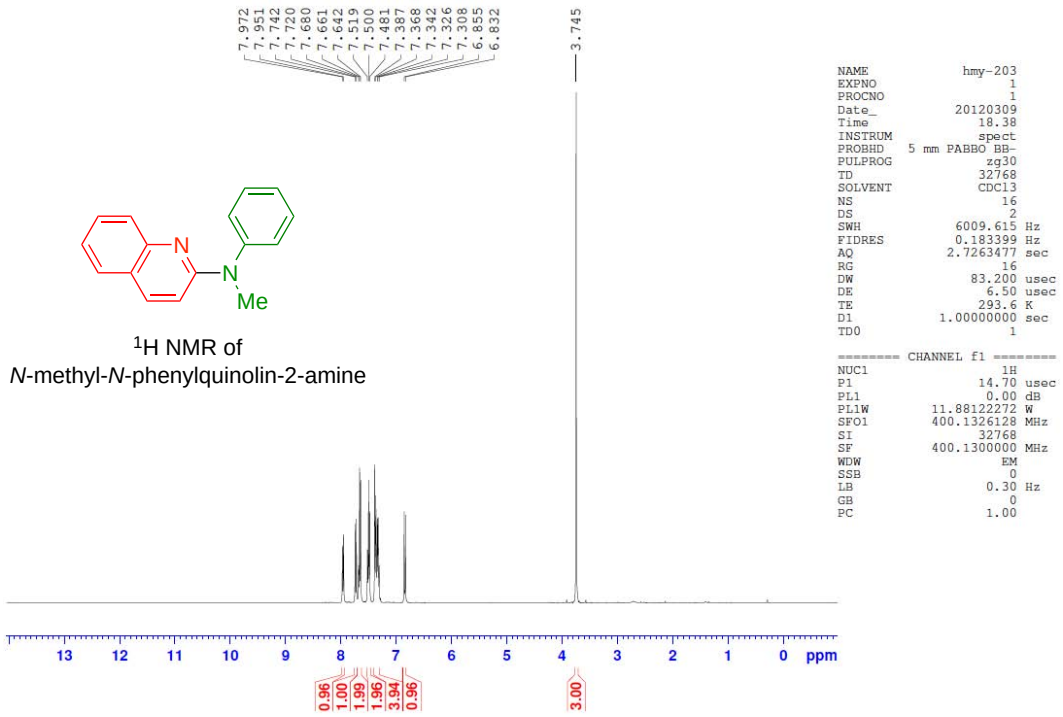
```
NAME            hmy-191
EXPNO                 2
PROCNO                1
Date_          20120301
Time              18.13
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    2
SWH           25252.525 Hz
FIDRES        0.385323 Hz
AQ             1.2976629 sec
RG                  203
DW                19.800 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        100.6253456 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          100.6127975 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

N-Methyl-*N*-phenylquinolin-2-amine (**Table 6.5**, entry 5)

hmy-203 1H

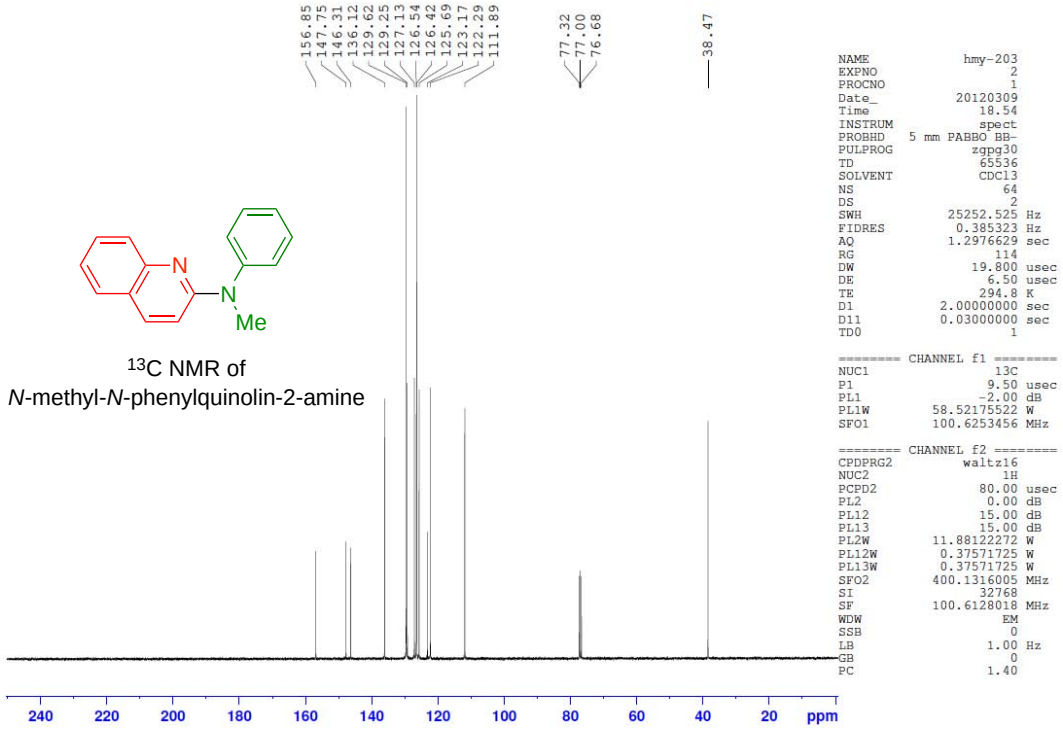


NAME hmy-203
EXPNO 1
PROCNO 1
Date_ 20120309
Time 18.38
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 16
DW 83.200 usec
DE 6.50 usec
TE 293.6 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 14.70 usec
PL1 0.00 dB
PL1W 11.88122272 W
SFO1 400.1326128 MHz
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

^{1}H NMR of
N-methyl-*N*-phenylquinolin-2-amine

hmy-203 13C



NAME hmy-203
EXPNO 2
PROCNO 1
Date_ 20120309
Time 18.54
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 64
DS 2
SWH 25252.525 Hz
FIDRES 0.385323 Hz
AQ 1.2976629 sec
RG 114
DW 19.800 usec
DE 6.50 usec
TE 294.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

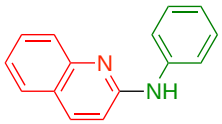
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 -2.00 dB
PL1W 58.52175522 W
SFO1 100.6253456 MHz

======== 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 100.6128018 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

^{13}C NMR of
N-methyl-*N*-phenylquinolin-2-amine

N-Phenylquinolin-2-amine (**Table 6.5**, entry 6)

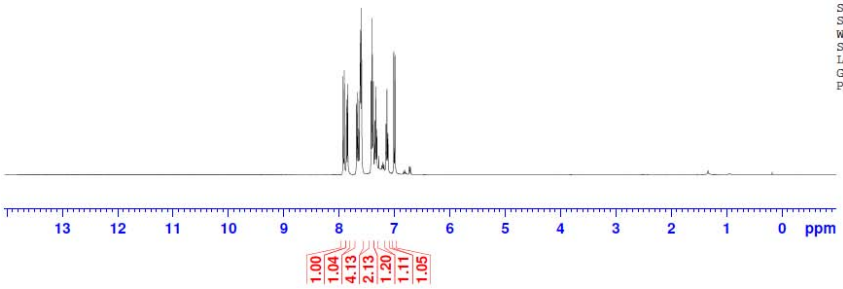
hmy-175 1H



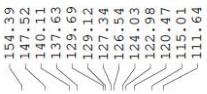
^{1}H NMR of
N-phenylquinolin-2-amine

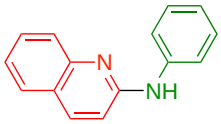
```
NAME              hmy-175
EXPNO                   1
PROCNO                  1
Date_            20120308
Time                16.56
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              6009.615 Hz
FIDRES           0.183399 Hz
AQ               2.7263477 sec
RG                     36
DW                83.200 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         400.1326128 MHz
SI                  32768
SF           400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



hmy-175 13C



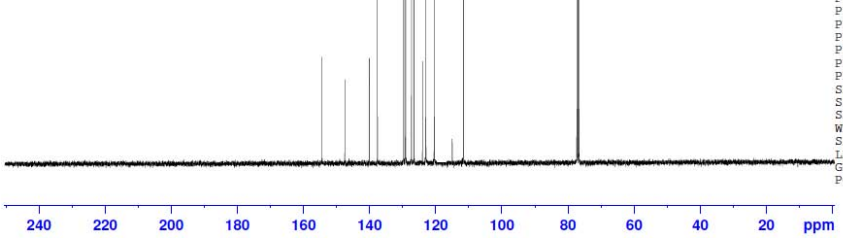


^{13}C NMR of
N-phenylquinolin-2-amine

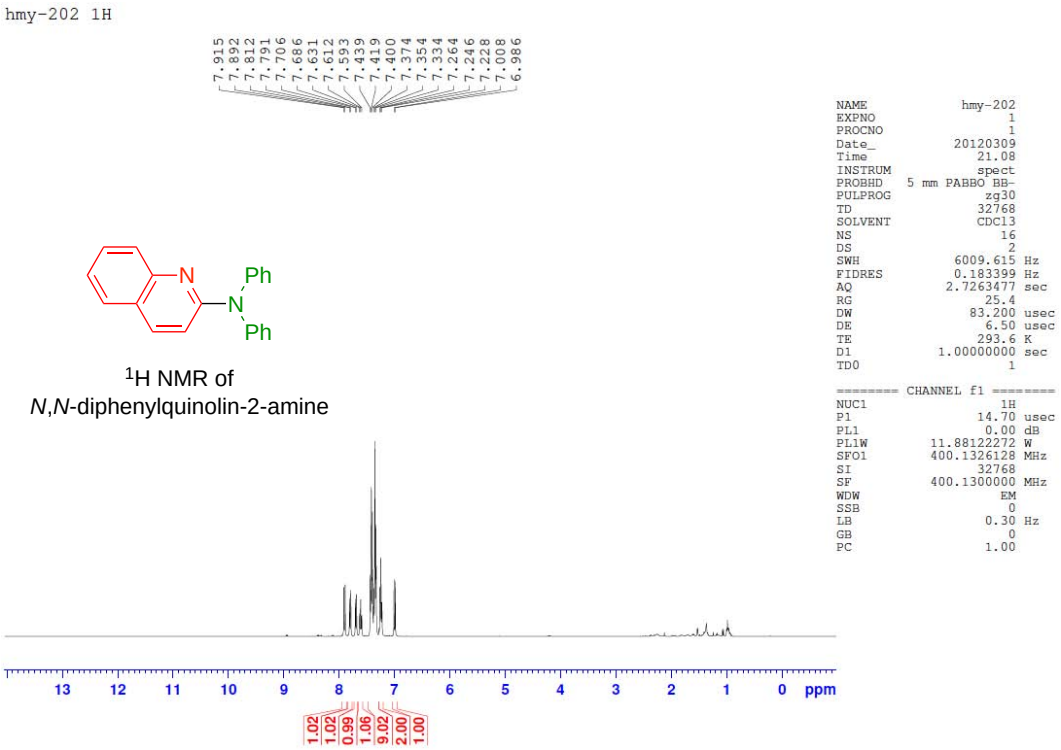
```
NAME              hmy-175
EXPNO                   2
PROCNO                  1
Date_            20120308
Time                17.02
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     64
DS                      2
SWH             25252.525 Hz
FIDRES           0.385323 Hz
AQ               1.2976629 sec
RG                    203
DW                19.800 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         100.6253456 MHz

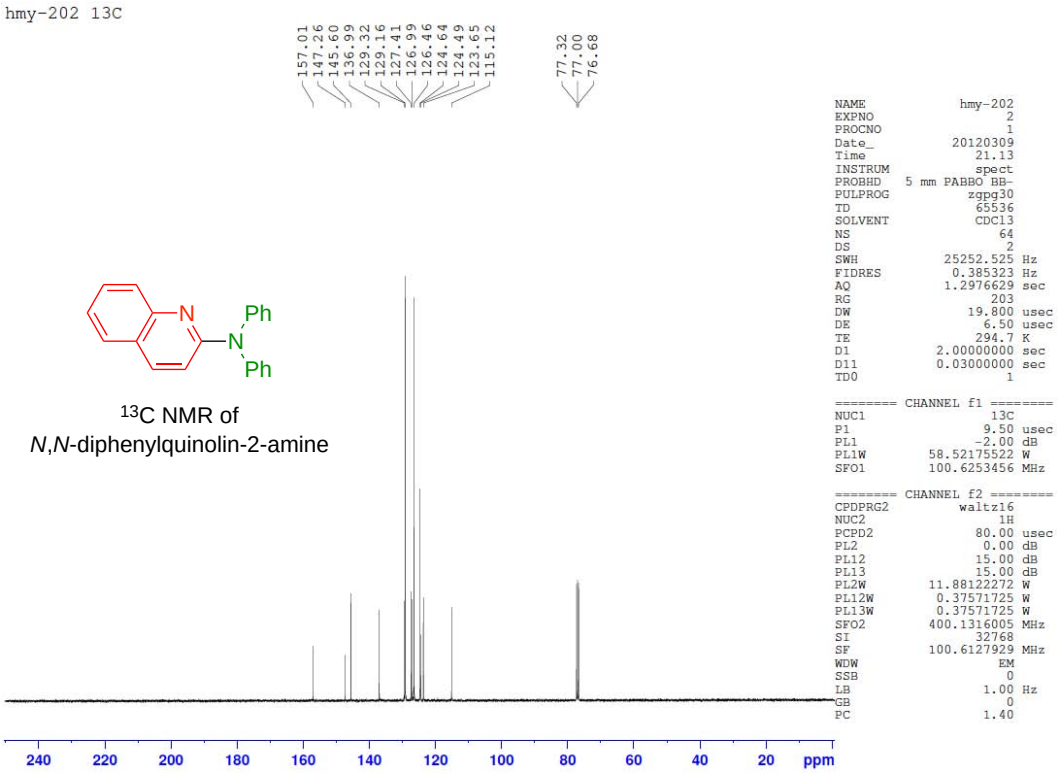
======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                15.00 dB
PL13                15.00 dB
PL2W          11.88122272 W
PL12W          0.37571725 W
PL13W          0.37571725 W
SFO2         400.1316005 MHz
SI                  32768
SF           100.6127861 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```



N,*N*-Diphenylquinolin-2-amine (**Table 6.5**, entry 7)



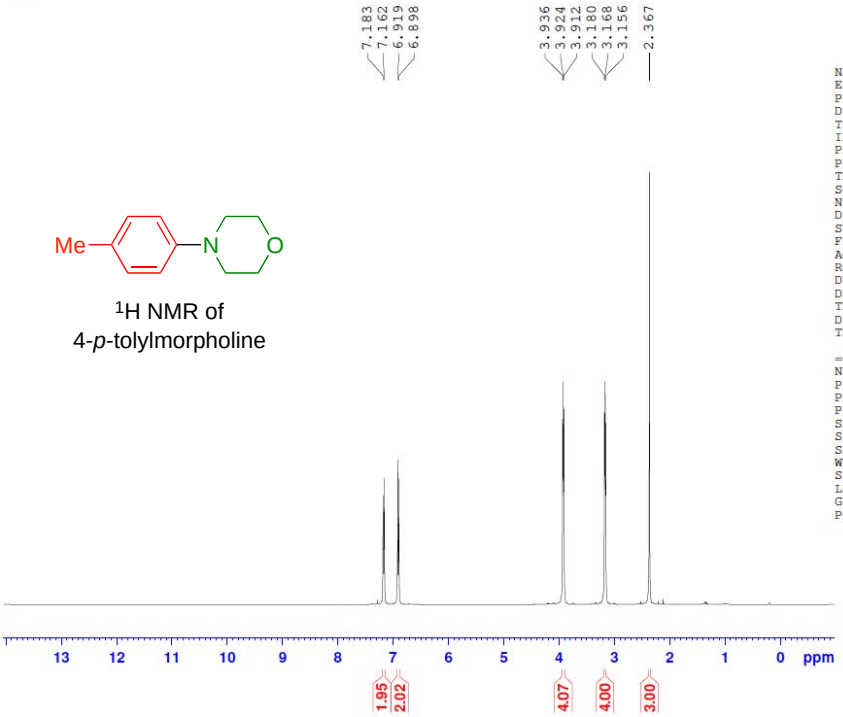
^{1}H NMR of
N,*N*-diphenylquinolin-2-amine



^{13}C NMR of
N,*N*-diphenylquinolin-2-amine

4-*p*-Tolylmorpholine (**Table 6.6**, entry 1)

hmy-122 1H

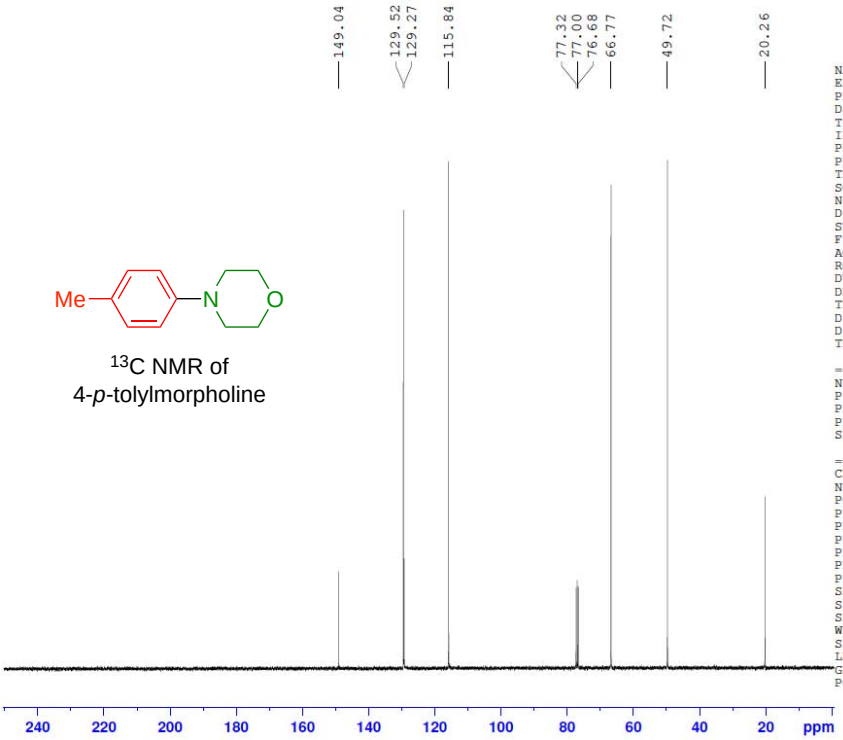


^{1}H NMR of
4-*p*-tolylmorpholine

```
NAME            hmy-122
EXPNO                 1
PROCNO                1
Date_          20120215
Time              14.36
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            6009.615 Hz
FIDRES        0.183399 Hz
AQ            2.7263477 sec
RG                 14.2
DW               83.200 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       400.1326128 MHz
SI                32768
SF         400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

hmy-122 13C



^{13}C NMR of
4-*p*-tolylmorpholine

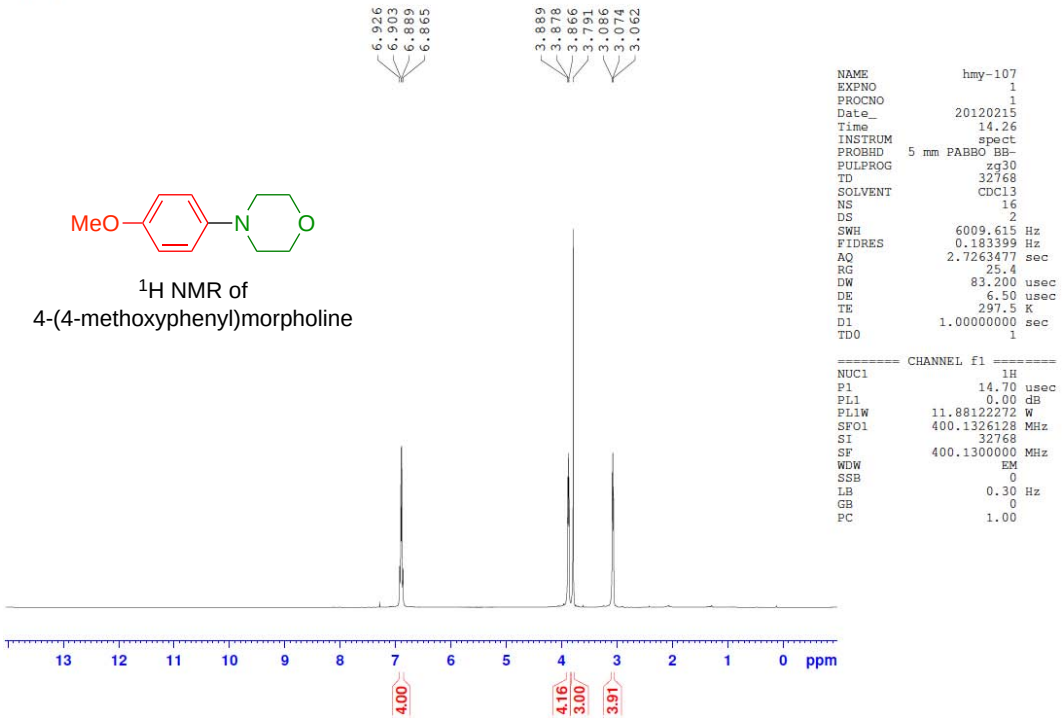
```
NAME            hmy-122
EXPNO                 2
PROCNO                1
Date_          20120215
Time              14.39
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    2
SWH           25252.525 Hz
FIDRES        0.385323 Hz
AQ            1.2976629 sec
RG                  203
DW               19.800 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       100.6253456 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         100.6127947 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

4-(4-Methoxyphenyl)morpholine (**Table 6.6**, entry 2)

hmy-107 1H

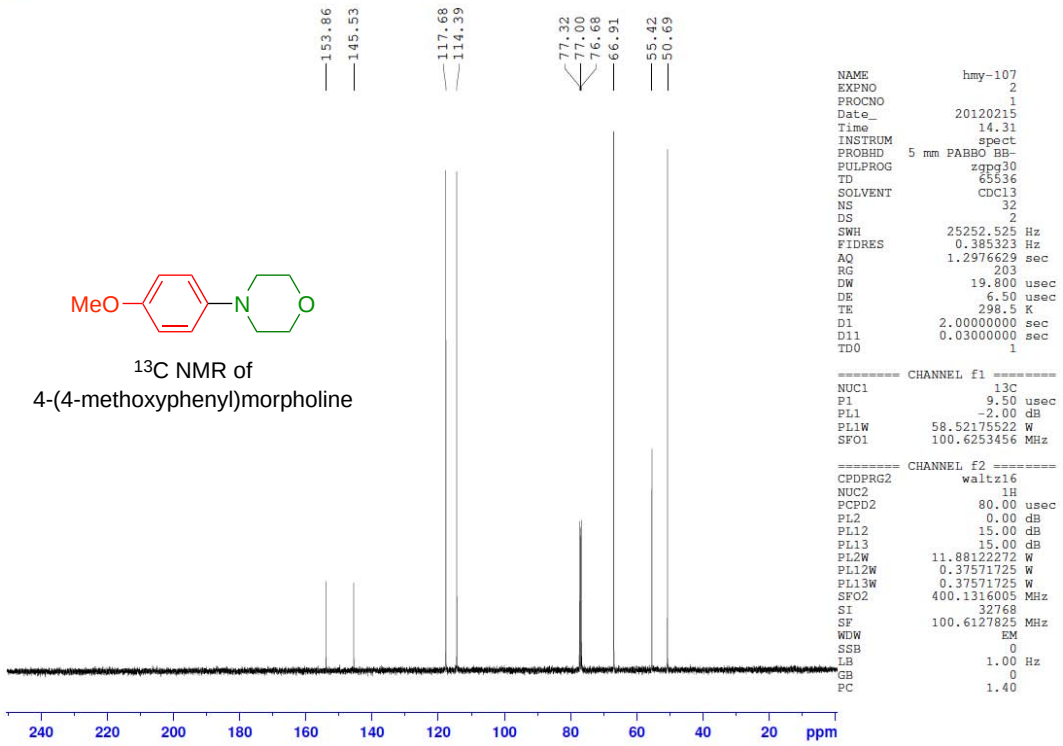


^{1}H NMR of
4-(4-methoxyphenyl)morpholine

```
NAME              hmy-107
EXPNO                   1
PROCNO                  1
Date_            20120215
Time                14.26
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              6009.615 Hz
FIDRES           0.183399 Hz
AQ               2.7263477 sec
RG                   25.4
DW                 83.200 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         400.1326128 MHz
SI                  32768
SF           400.1300000 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                 1.00
```

hmy-107 13C



^{13}C NMR of
4-(4-methoxyphenyl)morpholine

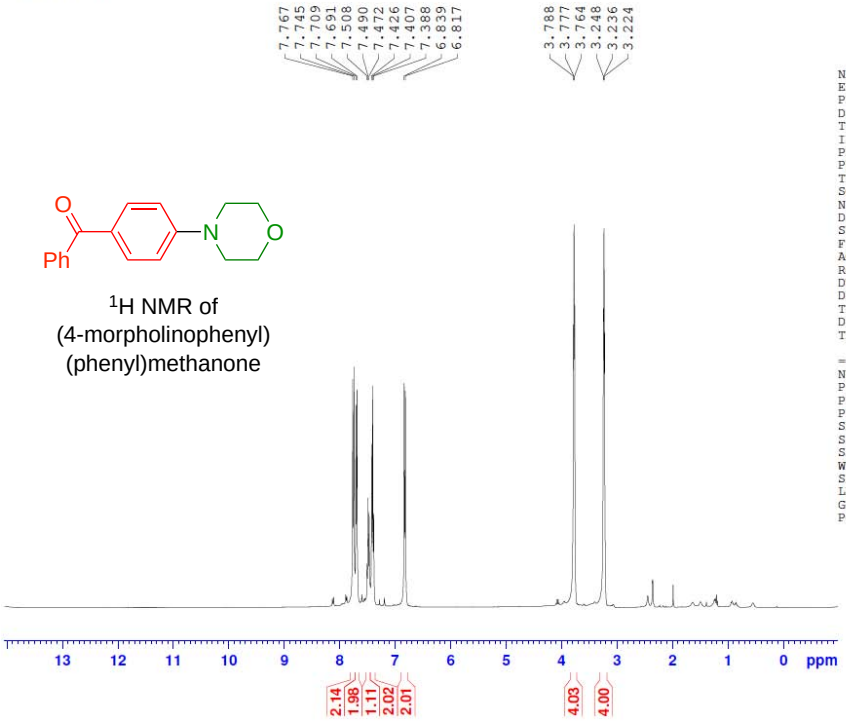
```
NAME              hmy-107
EXPNO                   2
PROCNO                  1
Date_            20120215
Time                14.31
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      2
SWH             25252.525 Hz
FIDRES           0.385323 Hz
AQ               1.2976629 sec
RG                    203
DW                 19.800 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         100.6253456 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
```

(4-Morpholinophenyl)(phenyl)methanone (**Table 6.6**, entry 3)

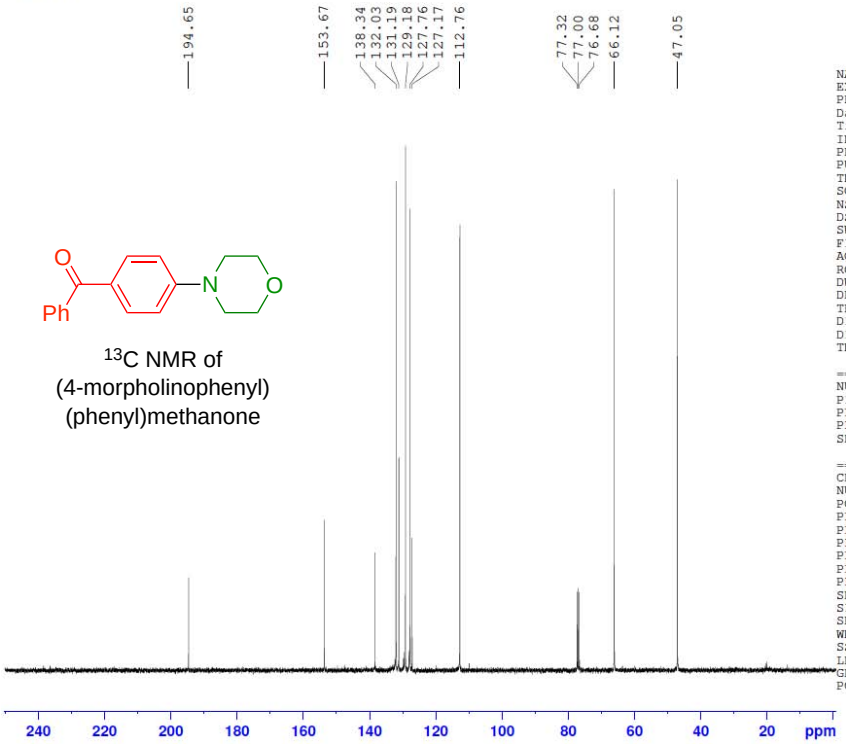
hmy-193 1H



^{1}H NMR of (4-morpholinophenyl)(phenyl)methanone

NAME	hmy-193
EXPNO	1
PROCNO	1
Date_	20120302
Time	15.14
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	6009.615 Hz
FIDRES	0.183399 Hz
AQ	2.7263477 sec
RG	12.7
DW	83.200 usec
DE	6.50 usec
TE	297.1 K
D1	1.00000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1326128 MHz
SI	32768
SF	400.1300000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

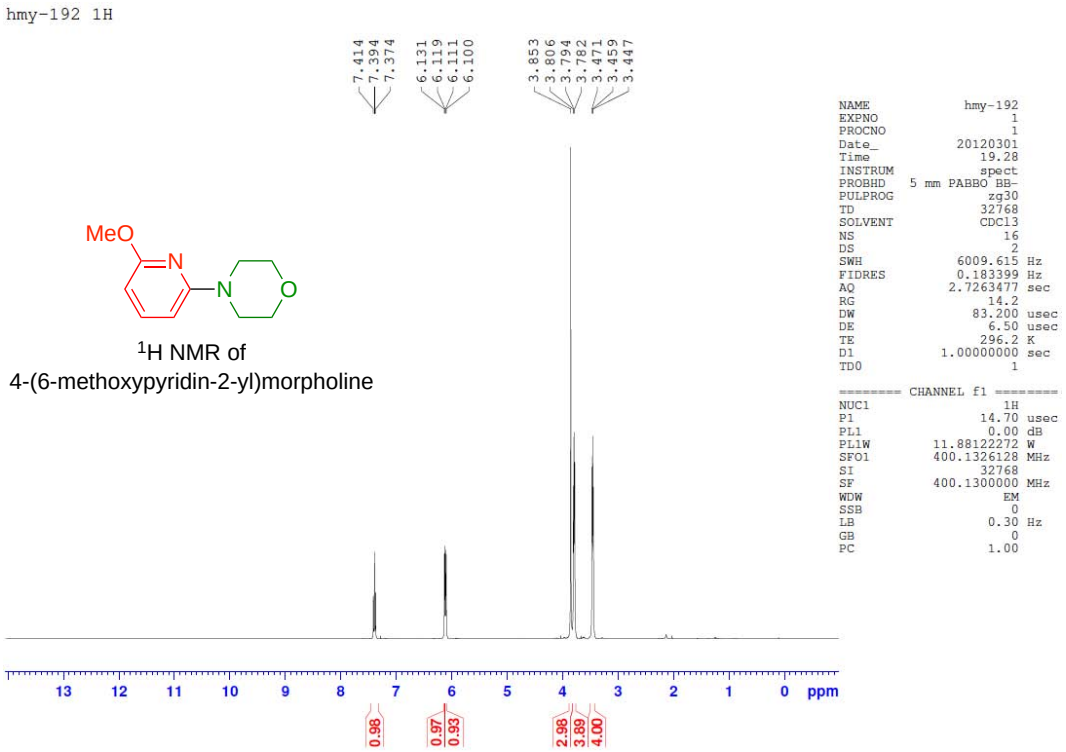
hmy-193 13C



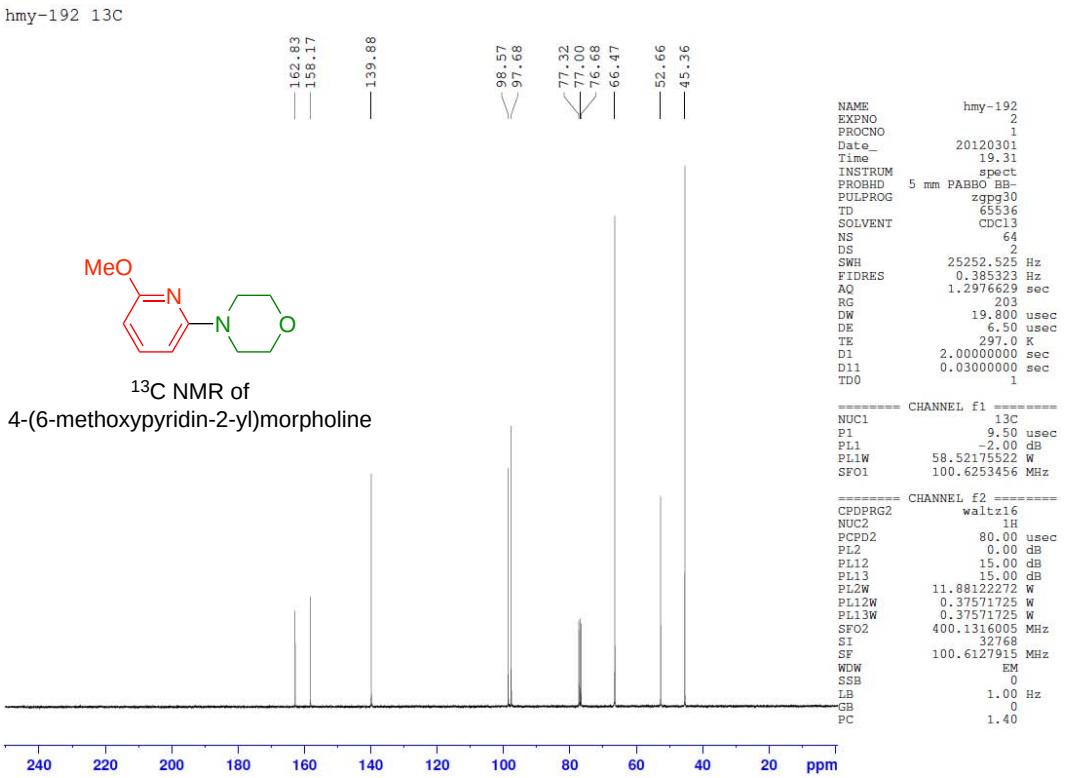
^{13}C NMR of (4-morpholinophenyl)(phenyl)methanone

NAME	hmy-193
EXPNO	2
PROCNO	1
Date_	20120302
Time	15.19
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	32
DS	2
SWH	25252.525 Hz
FIDRES	0.385323 Hz
AQ	1.2976629 sec
RG	203
DW	19.800 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	100.6253456 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	100.6128061 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

4-(6-Methoxypyridin-2-yl)morpholine (**Table 6.6**, entry 4)



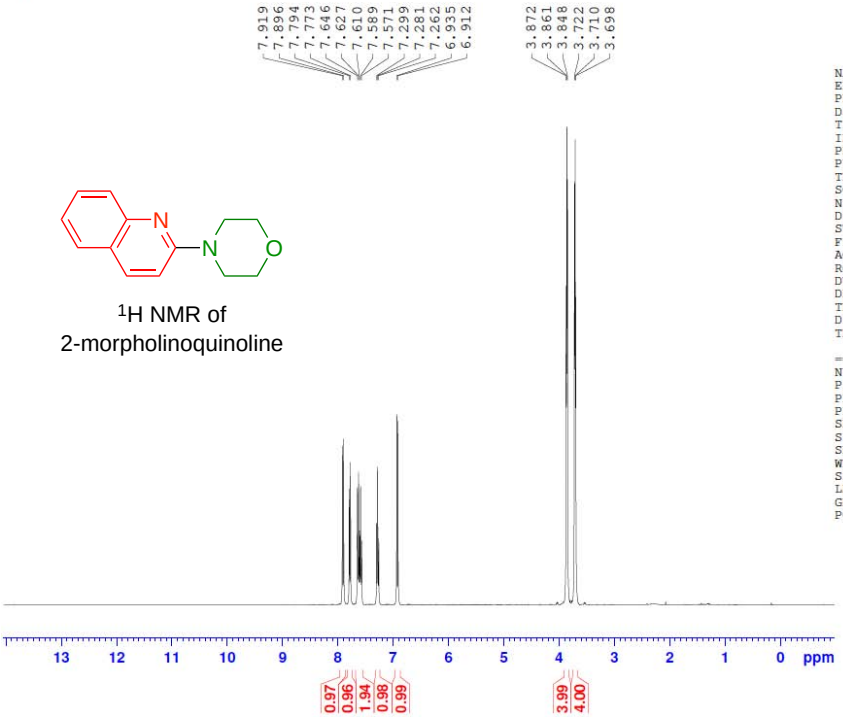
^{1}H NMR of
4-(6-methoxypyridin-2-yl)morpholine



^{13}C NMR of
4-(6-methoxypyridin-2-yl)morpholine

2-Morpholinoquinoline (**Table 6.6**, entry 5)

hmy-196 1H

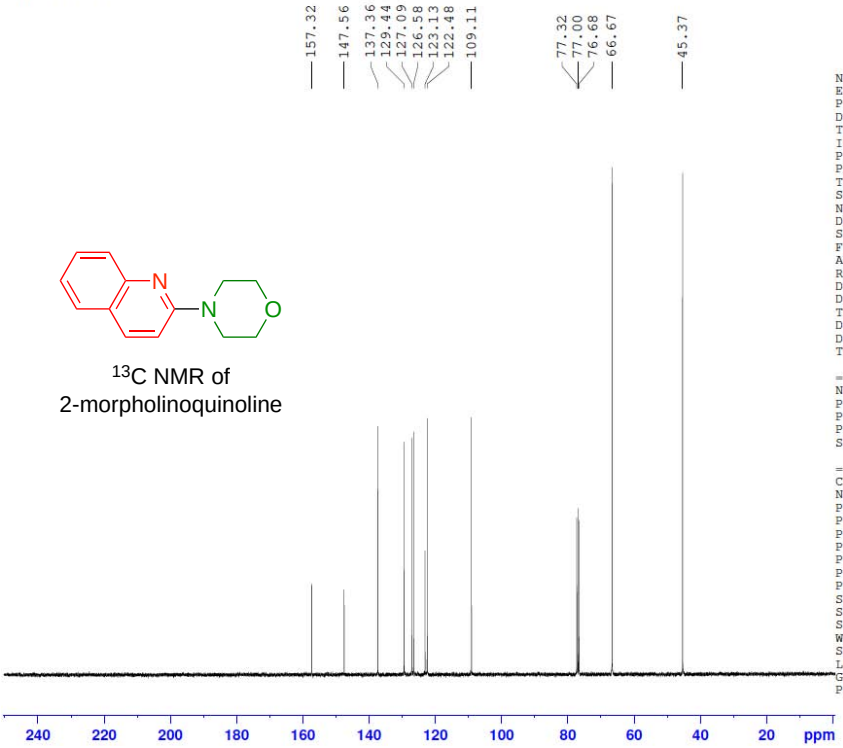


^{1}H NMR of
2-morpholinoquinoline

```
NAME            hmy-196
EXPNO                 1
PROCNO                1
Date_          20120301
Time              18.17
INSTRUM           spect
PROBHD  5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            6009.615 Hz
FIDRES        0.183399 Hz
AQ            2.7263477 sec
RG                 22.6
DW               83.200 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       400.1326128 MHz
SI                32768
SF         400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

hmy-196 13C



^{13}C NMR of
2-morpholinoquinoline

```
NAME            hmy-196
EXPNO                 2
PROCNO                1
Date_          20120301
Time              18.21
INSTRUM           spect
PROBHD  5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   64
DS                    2
SWH           25252.525 Hz
FIDRES        0.385323 Hz
AQ            1.2976629 sec
RG                  203
DW               19.800 usec
DE                6.50 usec
TE               297.5 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      100.6253456 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         100.6127907 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```