The Hong Kong Polytechnic University

Department of Applied Biology and Chemical Technology

Transition Metal-catalyzed Cyanation and Isocyanation of Aryl Halides and Sulfonates

YEUNG Pui-yee

A Thesis submitted in Partial Fulfillment of the Requirements for the Degree of Master of Philosophy

January 2012

Certificate of originality

I hereby declare that this thesis is my own research work carried out since my registration at the Hong Kong Polytechnic University for the degree of Master of Philosophy in February, 2010. To the best of my knowledge and belief, it reproduces no material previously published, or neither written, nor material that has been accepted for the award of any other degree or diploma, except where due acknowledgement has been made in the text.

YEUNG Pui-yee

January, 2012

Abstract

The mildest cyanation has been developed for aryl halides and sulfonates with environmental friendly cyanating source: $K_4[Fe(CN)_6]\cdot 3H_2O$.

In the presence of highly effective Pd/CMPhos catalyst, cyanation of aryl chlorides proceeds at 70 ℃ in general, which is the mildest reaction temperature achieved so far for this process. Moreover, sterically hindered non-activated *ortho-ortho*-disubstituted electrophile was also a feasible coupling partner in cyanation.

In addition, palladium-catalyzed cyanation of aryl bromides was also achieved general application of aryl halides in cyanation. The reactions were completed at 50℃ under mixed solvents (water/MeCN = 1:1). This result is the mildest temperature published so far for palladium-catalyzed aryl bromides cyanation.

In order to further explore cyanation, the coupling of aryl mesylates was investigated. Interestingly, the use of water as the solvent or a co-solvent was found to be essential. Moreover, this system was also applicable to the cyanation of other aryl and alkenyl tosylates.

The one-pot cyanation–amination sequence demonstrated the suitability of

the cyanation of aryl chlorides and tosylates for the introduction of a nitrile group and manipulation of a further functional group in a synthetic pathway without isolation of the initial nitrile-substituted intermediates. These palladium catalyst systems tolerated common functional-groups: nitriles, esters, ketos, aldehydes, free amines, and heterocyclic groups are found compatible.

Lastly, a palladium-catalyzed decarboxylative coupling of potassium cyanoacetate with aryl bromides and chlorides was also described. The reaction conditions featured the absence of additional strong inorganic bases and provided ester functional group tolerance. With $Pd(dba)_2$ and XPhos ligand as the catalyst system, α-diaryl nitriles could be obtained in good yields.

Publications

1. Yeung, P. Y.; So, C. M.; Lau, C. P.; Kwong, F. Y.* *Angew. Chem.Int. Ed.* **2010**, *49*, 8918.

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Table of content

Certificate of originality i

Abstract ii

Publications iv

Acknowledgement v

Table of content vii

Abbreviation xi

List of figures xiv

List of schemes xv

List of tables xviii

Chapter 1 Introduction 1

1.1. Background 1

1.2. Mechanistic considerations 5

1.3. Cyanation with potassium cyanide 9

1.4. Cyanation with zinc cyanide 13

1.5. Cyanation with potassium hexacyanoferrate(II) trihydrate ($K_4[Fe(CN)_6]•3H_2O$) 29

1.6. Cyanation with cyanohydrins 42

1.7. Cyanation with trimethylsilyl cyanide (TMSCN) 44

1.8. Miscellaneous cyanation 46

1.9. Decarboxylative arylation of potassium cyanoacetate 50

1.10. Conclusion 52

Chapter 2 Palladium-catalyzed cyanation of aryl sulfonates 54

2.1. Introduction 54

2.2. Results and discussion 55

2.2.1 Base and solvent screening 57

2.2.2 Ligand screening 59
2.2.3 Catalyst loading screening 61
2.2.4 Effect of co-solvent (water) added to the reaction system of ArOMs 62
2.2.5 Effect of co-solvent (water) added to the reaction system of ArOTs 63
2.2.6 Scope of palladium-catalyzed cyanation of aryl mesylates 65
2.2.7 Scope of palladium-catalyzed cyanation of aryl tosylates 68
2.3. Conclusion 71
2.4. Experimental section 72
2.4.1 General considerations 72
2.4.2 Procedures for aryl mesylates and tosylates synthesis 74
2.4.3 Procedures for indolyl phosphine ligands synthesis 74
2.4.4 General procedures for optimization of cyanation 75
2.4.5 General procedures for cyanation of aryl mesylates (Table 2.3 entry 1) and tosylates (Table 2.4, entry 1): 76
2.4.6 General procedures for one-pot sequential cyanation-amination reaction: 78
2.4.7 Characterization data of aryl nitriles from ArOMs 80
2.4.8 Characterization data of aryl nitriles from ArOTs 87
2.4.9 One-pot sequential cyanation-amination reaction 92
Chapter 3 Palladium-catalyzed cyanation of aryl halides 93
3.1. Introduction 93
3.2. Results and discussion of aryl chlorides 96
3.2.1 Ligand screening 96
3.2.2 Base and solvent screening 98
3.2.3 Effect of co-solvent (water) added to the benchmark conditions 100
3.2.4 Scope of palladium-catalyzed cyanation of aryl chlorides 101
3.3. Results and Discussion of aryl bromides 104
3.3.1 Ligands screening 105

3.3.2 Reaction optimization 106
3.3.3 Scope of palladium-catalyzed cyanation of aryl bromides 109
3.4. Conclusion 110
3.5. Experimental Section 112
3.5.1 General considerations 112
3.5.2 Procedures for indolyl phosphine ligand synthesis 114
3.5.3 General procedures for optimization of cyanation 114
3.5.4 General procedures for palladium-catalyzed cyanation of aryl chlorides: 115
3.5.5 General procedures for one-pot sequential cyanation-amination reaction: 116
3.5.6 General procedures for palladium-catalyzed cyanation of aryl bromides: 119
3.5.7 Characterization data of nitriles from aryl chlorides 120
3.5.8 One-pot sequential cyanation-amination 128
3.5.9 Characterization data of nitriles from aryl bromides 129
Chapter 4 Palladium-catalyzed decarboxylative arylation of aryl halides 134
4.1. Introduction 134
4.2. Result and discussion 135
4.2.1 Ligand screening 137
4.2.2 Metal screening 138
4.2.3 Scope of palladium-catalyzed decarboxylative diarylation of aryl chlorides 140
4.2.4 Scope of palladium-catalyzed decarboxylative diarylation of aryl bromides 142
4.2.5 Scope of palladium-catalyzed decarboxylative diarylation of aryl sulfonates 143
4.3. Conclusion 144
4.4. Experimental section 144
4.4.1 General considerations 144
4.4.2 Procedures for indolyl phosphine ligands synthesis 145
4.4.3 Procedures for potassium cyanoacetate synthesis 146
4.4.4 General procedures for optimization of cyanation 146

4.4.5 General procedures for the synthesis of α-diaryl nitriles: 148

4.4.6 Characterization data of nitriles from aryl chlorides..... 149

4.4.7 Characterization data of nitriles from aryl bromides 152

Chapter 5 Palladium-catalyzed amidation of aryl halides by isocyanides 156

5.1. Introduction..... 156

5.2. Progress..... 158

Conclusion 160

Appendices..... 163

Characterizations of products from palladium-catalyzed cyanation 163

^{1}H-, ^{13}C-NMR spectra of products from palladium-catalyzed cyanation of aryl mesylates..... 163

^{1}H-, ^{13}C-NMR spectra of products from palladium-catalyzed cyanation of aryl tosylates..... 213

^{1}H-, ^{13}C-NMR spectra of products from palladium-catalyzed cyanation of aryl chlorides..... 264

^{1}H-, ^{13}C-NMR spectra of products from palladium-catalyzed cyanation of aryl bromides..... 301

Characterizations of products from palladium-catalyzed decarboxylative diarylation.... 328

^{1}H-, ^{13}C-NMR spectra of palladium-catalyzed decarboxylative diarylation of aryl chlorides..... 328

^{1}H-, ^{13}C-NMR spectra of palladium-catalyzed decarboxylative diarylation of aryl bromides..... 345

References..... 356

Abbreviation

Ac	Acetyl
Ar	Aromatic
BINAP	2,2’-Bis(diphenylphosphino)-1,1’-binaphthalene
BrettPhos	2-(Dicyclohexylphosphino)3,6-dimethoxy-2’,4’,6’-triiso propyl-1, 1’-biphenyl
C_6D_6	d-benzene
Calcd.	Calculated
CataCXium A	Di(1-adamantyl)-*n*-butylphosphine
CataCXium PCy	2-(Dicyclohexylphosphino)-1-phenyl-1H-pyrrole
CataCXium PInCy	2-(Dicyclohexylphosphino)-1-phenylindole
$CDCl_3$	d-chloroform
CMPhos	2-[2-(Dicyclohexylphosphino)phenyl]-1-methyl-1H-indole
CN	Nitrile, cyano
Cy	Cyclohexyl
D	Deuterium
dba	Dibenzylideneacetone
DCM	Dichloromethane
DMA	*N*,*N*-Dimethylacetamide
DMAC	*N*,*N*-Dimethylacetamide
DME	Dimethoxyethane
DMF	*N*,*N*-Dimethylformamide
DMSO	Dimethyl sulfoxide
DPCB	1,2-diphenyl-3,4-bis(2,4,6-tri-tert-butylphenylphosphinidene) cyclobutene
DPEphos	(Oxydi-2,1-phenylene)bis(diphenylphosphine)
dppb	1,4-Bis(diphenylphosphino)butane
dppf	1,1'-Bis(diphenylphosphino)ferrocene
dppp	1,3-Bis(diphenylphosphino)propane
dpppe	1,5-Bis(diphenylphosphino)pentane
EA	Ethyl acetate
EI-MS	Electron ionized mass spectrometry
equiv	Equivalent
ES-MS / ESIMS	Electrospray ionization mass spectrometry

et al	et alii
FID	Flame ionization detector
GC	Gas chromatography
h	Hour
HCN	Hydrogen cyanide
HRMS	High-resolution mass spectra
hrs	Hours
i-	*Iso*-
i.e.	id est
^{i}Pr	*iso*-Propyl
$K_4[Fe(CN)_6]•3H_2O$	Potassium hexacyanoferrate(II) trihydride
L	Ligand
M	Molarity
MCPBA	*meta*-Chloroperoxybenzoic acid
MDP	1,1-Methylenedipiperidine
Me	Methyl
MHz	Mega-hertz
min	Minute
MS	Mass spectroscopy
-Ms	Mesyl, methylsulfonyl
n-BuLi	*n*-Butyl lithium
$-NH_2$	Primary amino-
NMP	1-Methyl-2-pyrrolidinone
NMR	Nuclear magnetic resonance
o-	*ortho*-
pK_a	Acid dissociation constant
ppm	Part per million
Py	Pyridine
QPhos	1,2,3,4,5-Pentaphenyl-1′-(di-tert-butylphosphino)ferrocene
R_f	Response factor
rt	Room temperature
s	second
SPhos	2-Dicyclohexylphosphino-2’,6’-dimethoxybiphenyl
^{t}Bu	Tertiary Butyl
tert-	Tertiary
-Tf	Trifluoromethanesulfonyl
TFA	Trifluoroacetic acid
THF	Tetrahydrofuran

TMEDA	N,N,N′,N′-Tetramethylethylenediamine
TMS	Tetramethylsilane
TMSCN	Trimethylsilyl cyanide
tol	Toluene
TON	Turnover number
-Ts	*p*-Tosyl, *p*-toluenesulfonyl
vs	Verse
wt	Weight
X	Halides
Xantphos	4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene
XPhos	2-Dicyclohexylphosphino-2’,4’,6’-triisopropylbiphenyl
δ	Chemical shifts

List of figures

Figure 1.1 Selected example of medicine. 1
Figure 1.2 Bulky heterocyclic phosphine ligands being tested.....34
Figure 1.3 Ligands for the cyanation of challenging aryl chloride.....34
Figure 1.4 XPhos and XPhos-SO_3Na.....36
Figure 1.5 Heterogenized ligands developed by Islam *et al* 39
Figure 1.6 Polyimidazole-based ligand.....41
Figure 1.7 Selected examples of pharmaceutically useful α-diarylated nitriles.....50
Figure 2.1 Effect of co-solvent(water) added to the benchmark conditions. 62
Figure 2.2. Effect of co-solvent (water) added to the aryl tosylate reaction conditions 63
Figure 3.1 Effect of co-solvent (water) in the palladium catalyzed cyanation of aryl chloride.....100

List of schemes

Scheme 1.1 Synthetic method of Fluvoxamine 2
Scheme 1.2 Traditional methods of synthesis for arene-containing nitriles.....3
Scheme 1.3 First palladium-catalyzed cyanation with KCN developed by Takagi *et al* 5
Scheme 1.4 Plausible mechanism for the cyanation according to Tagaki *et al*.....6
Scheme 1.5 Classical Catalytic circle of cyanation 7
Scheme 1.6 Catalytic Cycle for Pd-Catalyzed Cyanation of Aryl Bromides Promoted by Tin Ate Complexes.....10
Scheme 1.7 One-pot palladium-catalyzed sequential cyanation / *N*-addition / *N*-arylation 11
Scheme 1.8 Catalytic cyanation of chlorobenzene in the presence of different co-catalysts 13
Scheme 1.9 First palladium-catalyzed cyanation with $Zn(CN)_2$ developed by Tschaen *et al* 14
Scheme 1.10 Palladium-catalyzed cyanation with $Zn(CN)_2$ developed by Maligares *et al*.....15
Scheme 1.11 Palladium-catalyzed cyanation for the synthesis of cyano-substituted calixarene 15
Scheme 1.12 Palladium-catalyzed cyanation of aryl bromides with $Zn(CN)_2$ using DPCB ligand.....16
Scheme 1.13 Palladium-catalyzed cyanation with $Zn(CN)_2$ developed by Jin *et al* 17
Scheme 1.14 Pharmaceutical application of Jin's protocol.....18
Scheme 1.15 Room temperature palladium-catalyzed cyanation developed by Maddaford *et al*.....19
Scheme 1.16 A robust palladium-catalyzed cyanation of aryl bromides in the presence of zinc acetate.....20
Scheme 1.17 The mildest palladium-catalyzed cyanation of aryl bromides developed by Ryberg *et al* till 2008 21
Scheme 1.18 Palladium-catalyzed cyanation of aryl chlorides with sulfate additives.....23

Scheme 1.19 Microwave-assisted palladium-catalyzed cyanation for the synthesis of a HIV-1 protease inhibitor 25
Scheme 1.20 Microwave-assisted palladium-catalyzed cyanation reaction with aryl triflate 26
Scheme 1.21 Microwave-assisted palladium-catalyzed cyanation of citalopram 26
Scheme 1.22 Microwave-assisted palladium-catalyzed cyanation of aryl chlorides 27
Scheme 1.23 Microwave assisted polymer-supported palladium-catalyzed cyanation of aryl halides and triflates 27
Scheme 1.24 Cyanation of aryl bromides with zinc cyanides in the presence of heterogeneous Pd/C 28
Scheme 1.25 Ligand free catalyzed cyanation of aryl bromide. 30
Scheme 1.26 Effect of concentration of H_2O on the cyanation of bromobenzene. 31
Scheme 1.27 Effect of concentration of i-propanol on the cyanation of bromobenzene. 31
Scheme 1.28 Palladium-catalyzed cyanation of aryl bromide developed by Grossman *et al* 32
Scheme 1.29 Cyanation of aryl chlorides with cyclopalladated ferrocenylimine developed by Cheng *et al* 33
Scheme 1.30 Cyanation of aryl chlorides developed by Beller *et al* 33
Scheme 1.31 Catalytic system for microwave assisted palladium catalyzed cyanation of aryl bromides 37
Scheme 1.32 Cyanation reaction of various aryl halides using $K_4[Fe(CN)_6]$ in the presence of palladacycle under microwave irradiation. 38
Scheme 1.33 Synthetic method of hybrid silica catalyst I-Pd 40
Scheme 1.34 Acetone cyanohydrin, a useful HCN equivalent 42
Scheme 1.35 Synthesis of aryl nitriles *via* decarboxylative cyanation of aryl carboxylic acids 44
Scheme 1.36 Pd-catalyzed cyanation of aryl iodides with TMSCN developed by Chatani *et al* 44
Scheme 1.37 Palladium-catalyzed cyanation of aryl bromide with TMSCN developed by Beller *et al* 45
Scheme 1.38 Palladium-catalyzed cyanation of aryl halides and with CuCN developed Sakamoto *et al* 46
Scheme 1.39 Chelation-Assisted Palladium-Catalyzed Direct

Cyanation of 2-Arylpyridine C-H Bonds developed by Jia *et al* 47
Scheme 1.40 Concise pathway to a key intermediate of *Menispermum dauricum* DC (Menispermaceae) 47
Scheme 1.41 Synthesis and application of dialkyl cyanoboronates developed by Jiang *et al*. 48
Scheme 1.42 Palladium-catalyzed cyanation of porphyrins with cyanoethylzinc bromide 48
Scheme 1.43 Mechanistic proposal for the "CN" Formation 50
Scheme 1.44 Traditional methods for synthesizing α-aryl nitriles.....51
Scheme 2.1 Preliminary condition for palladium-catalyzed cyanation of 4-*tert*-butylphenyl tosylate 55
Scheme 2.2 Ligand screening for the palladium-catalyzed cyanation of 4-*tert*-butylphenyl mesylate 59
Scheme 2.3 One-pot sequential cyanation-amination reaction (see experimental section for detailed procedure).....70
Scheme 3.1 Ligand screening in palladium-catalyzed cyanation of aryl chloride.....97
Scheme 3.2 One-pot sequential cyanation –amination reaction 103
Scheme 3.3 Ligands screening in palladium-catalyzed cyanation of aryl bromide 106
Scheme 4.1 Investigations on the protocol for α-diaryl nitrile synthesis...135
Scheme 4.2 Palladium-catalyzed diarylation of potassium cyanoacetates with aryl sulfonates 143
Scheme 5.1 The formation of amides from carboxylic acids and amines .156
Scheme 5.2 A modified Ritter reaction develop by Baum *et al* 156
Scheme 5.3 Palladium-catalyzed synthesis of aryl amides from aryl chlorides and isocyanide 158

List of tables

Table 1.1 Evaluation of catalyst systems for the palladium-catalyzed cyanation 22
Table 1.2 The performance of recycled Pd/C 38
Table 1.3 Recyclability of catalyst I-Pd 40
Table 1.4 Palladium-catalyzed cyanation of 4-bromobenzotrifluoride using acetone cyanohydrins 43
Table 2.1 Initial base and solvent screening of the palladium-catalyzed cyanation of a non-activated aryl mesylate 57
Table 2.2 Initial catalyst loading and cyanating source screenings of the palladium-catalyzed cyanation of a non-activated aryl mesylate 61
Table 2.3. Palladium-catalyzed cyanation of aryl mesylates 66
Table 2.4 Palladium-catalyzed cyanation of tosylates 69
Table 3.1 Effect of base and solvent on the cyanation of 4-chlorotoluene 98
Table 3.2 Palladium-catalyzed cyanation of aryl chlorides 102
Table 3.3 Effect of metal, base and the loading of cyanide source on the cyanation of 3-bromotoluene 107
Table 3.4 Palladium-catalyzed cyanation of aryl bromides 110
Table 4.1 Screening of ligand 137
Table 4.2 Screening of reaction condition 138
Table 4.3 Palladium-catalyzed diarylation of potassium/sodium cyanoacetate with aryl chlorides 141
Table 4.4 Palladium-catalyzed diarylation of potassium cyanoacetates with aryl bromides 142
Table 5.1 Parameters checked for the failure 159

Chapter 1 Introduction

1.1. Background

Benzonitriles are important constituents in constructing organic synthetic blocks,[1-3] synthesis of pharmaceuticals,[4] agrochemicals, dyes, herbicides, insecticides and natural products.[5] Some of selected examples of drugs are shown in Figure 1.1 and a synthetic example is selected to demonstrate the usefulness of cyanation (Scheme 1.1).[6]

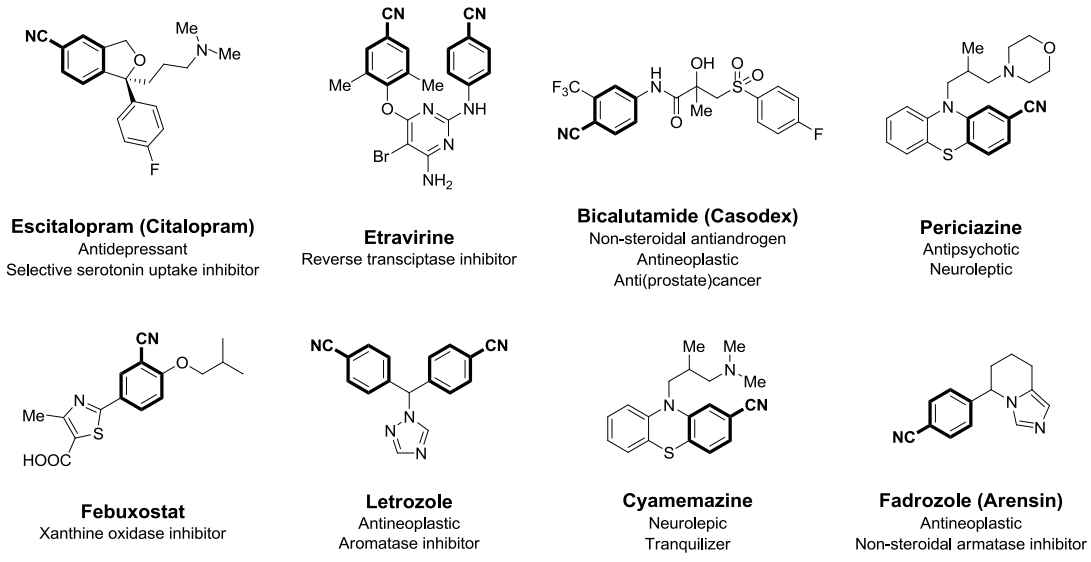
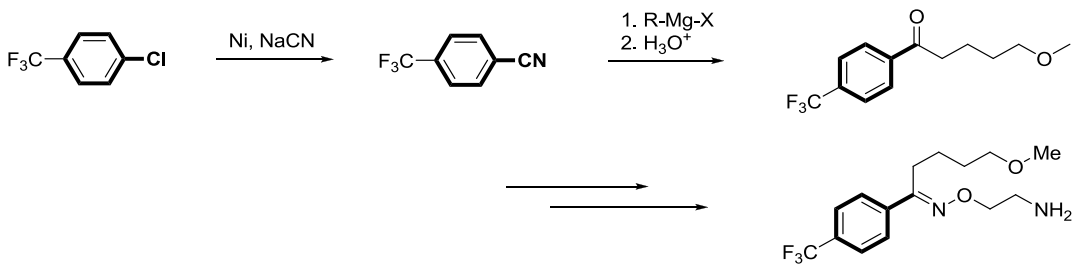


Figure 1.1 Selected example of medicine.

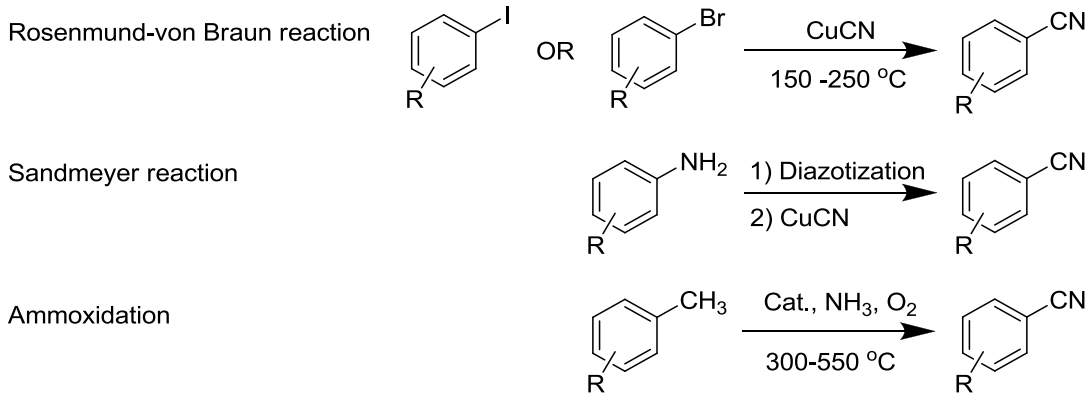


Scheme 1.1 Synthetic method of Fluvoxamine

The ton-scale synthesis of 4-(trifluoromethyl)benzonitrile is made by nickel-catalyzed cyanation from 4-chlorobenzotrifluoride, which is a key intermediate for the synthesis of fluvoxamine.[7,8] Further transformation of organic compounds indicate that aryl nitriles can be converted to benzoic acids / esters, amines, amides, imidoesters, benzamidines, aldehydes, as well as nitrogen-containing heterocyles.[9-13]

In fact, there are numerous methods to afford aryl nitriles.[1,5] Traditional laboratorial scaled reactions for the production of aryl nitriles are Rosenmun-von Braun,[14-19] Sandmeyer[20-23] reaction and ammoxidation.[17,24-27] The Rosenmun-von Braun and Sandmeyer reaction, generally, concern the reaction between aryl iodides / bromides and aryl diazonium salts, respectively, with stoichiometric amount of cuprous cyanide at high temperatures (i.e. 150 – 250 ℃). Ammoxidation is restricted to the production of simple aromatic nitriles such as benzonitrile, terphthalodinitrile as well as chlorobenzonitriles[28]

from the corresponding toluene derivatives under harsh condition, whereby high pressure and temperature (220-550 ℃) in the presence of heterogeneous fixed-bed catalysts are necessary (Scheme 1.2).



Scheme 1.2 Traditional methods of synthesis for arene-containing nitriles

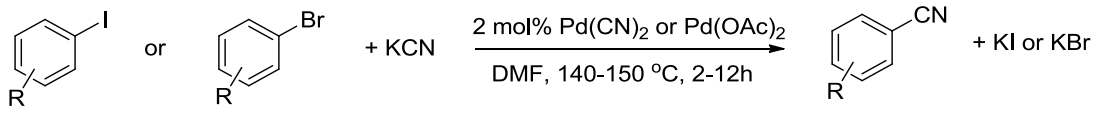
The disadvantages of utilizing stoichiometric amount of cuprous cyanide in the Rosenmund-von Braun and Sandmeyer reaction is the generation of an equimolar amount of heavy metal waste and hence pollutes the environment. In addition, holding at high reaction temperature consumes much energy and the Rosenmund-von Braun protocol is only applicable to expensive aryl iodides. There are many limitations in ammoxidation. Firstly, functionalized molecules are not preferable in ammoxidation due to the substrate decomposition at high temperature, high pressure and the presence of large excess of ammonia. Secondly, the variety of applicable toluene derivatives on process scale is limited.[28,29]

Despite the drawbacks of the traditional synthetic method, an alternative

synthetic methodology for more diversified substituted aryl nitriles is developed by the application of transition metals.[17,30-33] The transition metal complex catalyzes a cyanation of aryl halides and pseudo-halides with commercial cyanating surrogates.[17,31-34] The reactivity of the aryl halides is inversely proportional to the bond dissociation energy.[35,36] The order of reactivity is: C-Cl < C-Br < C-I ≈ C-OTf.[35] On the other hand, the reactivity of the aryl sulfonates is based on pK_a value of the corresponding conjugate acid. The order of reactivity is: Ar-OMs < Ar-OTs < Ar-OTf.[37] Common catalysts used in cyanation of aryl halides and pseudo-halides are copper,[38-43] nickel[44-49] and palladium complexes. Although copper and nickel are cheaper than palladium, copper is incompatible in cyanation of aryl chlorides particularly. Nickel is relatively sensitive towards oxygen and moisture. Also, the crucial point of little popularity of nickel is its small functional group compatibility. Hence, the main role in the transition metal-catalyzed cyanation of aryl halides and aryl sulfonates belongs to palladium because of its tolerance towards a wide spectrum of functional groups and having higher stability than nickel complexes.

1.2. Mechanistic considerations

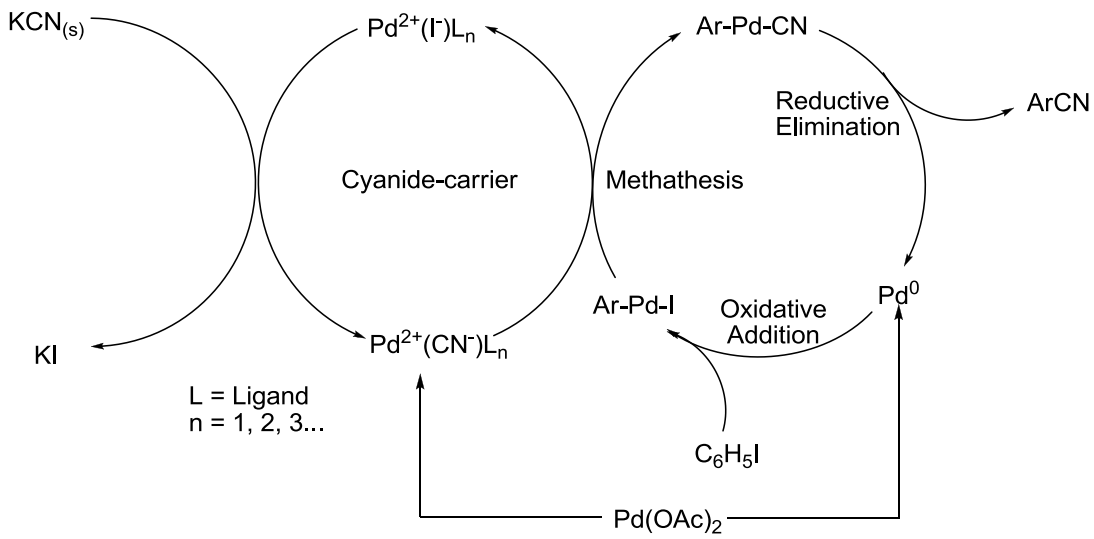
The first palladium catalyzed cyanation of aryl halides was developed by Takagi *et al.* in 1973. This protocol involved both aryl iodides and aryl bromides with potassium cyanide (Scheme 1.3).[50,51]



Scheme 1.3 First palladium-catalyzed cyanation with KCN developed by Takagi *et al*

This reaction required no additional ligands.[51] The addition of phosphine or phosphate retarded the reaction completely.[51] The reaction temperature and time varied from 140-150℃ and 2-12 hours depending on substrates, respectively.

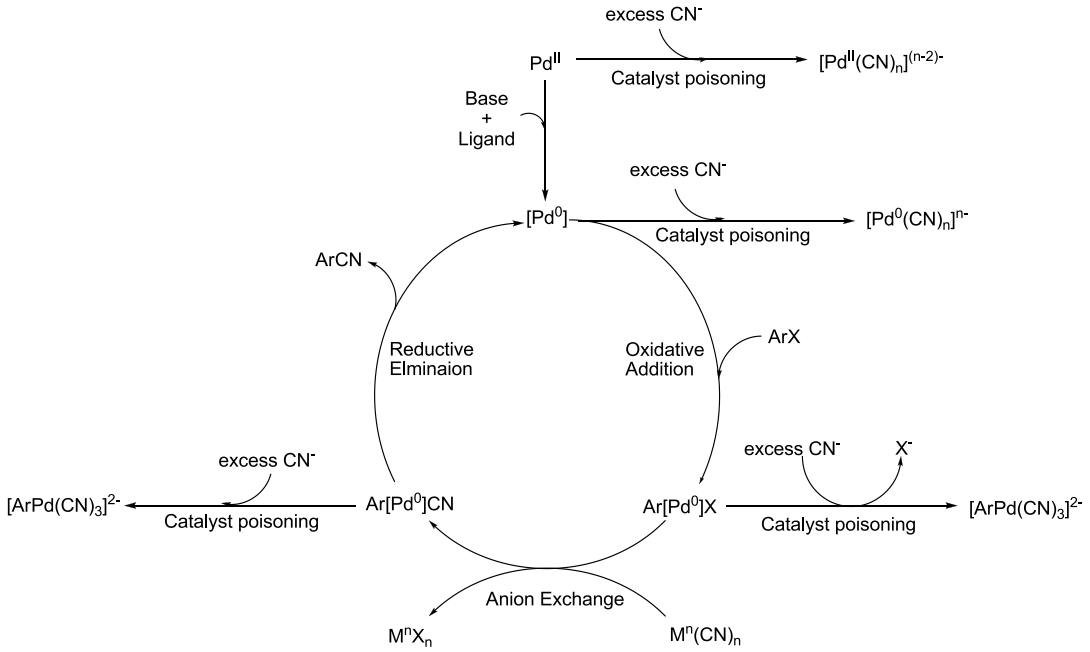
The earliest catalytic cycle is done by Takagi and co-workers (Scheme 1.5).[52]



Scheme 1.4 Plausible mechanism for the cyanation according to Tagaki *et al*

The cyanide anions involved in the cyanation are originated from the solid potassium cyanide. The activity of the catalysts depends on the cyanide solubility which varied from a solvent to another.[52] It is noteworthy that excess cyanide ions inhibits the cycle, by forming inactive palladium (II) cyano compounds such as potassium tetracyanopalladate (II) or palladium (II) cyanide irreversibly.[52] Recently literatures showed co-catalysts such as potassium hydroxide, sodium ethoxide, potassium carbonate or sodium phenoxide, promoted the formation of active palladium (0) species from less active palladium (II) species.[53,54] Moreover, the substrate scope of the methodology was broadened. A number of methodologies and catalysts were recently developed and the insights into the mechanistic studies were also explored by other research groups,[55-58] especially Beller *et al*.[3,59,60]

The proposed mechanism of palladium catalyzed cyanation is shown in Scheme 1.5. [3,56-60]



Scheme 1.5 Classical Catalytic cycle of cyanation

Before the beginning of catalytic cycle, inactive Pd(II) species was suggested to coordinate by ligands in the presence of base and then activated to Pd(0) complexes.[60] The active Pd(0) catalyst no longer acted as the cyanide-carrier as proposed by Tagaki *et al*.[52,60] Then, the catalytic cycle starts with the oxidative addition of Pd(0) species to the aryl halide.[60] The aryl Pd(II) halide complex undergoes an anion exchange with metal cyanide.[60] The aryl nitrile is formed by reductive elimination.[60] The active Pd(0) complex is re-generated for next catalytic cycle.[60] However, high concentration of cyanating agent shut down the catalytic cycle, due to the formation of inactive cyanide complexes,

$Pd(II)(CN)_x^{(x-2)-}$ (x = 3, 4), which was the "dead end" of the cycle.[60] The catalytic cycle was proposed based on a working hypothesis which assumed cyanation process was similar to other standard coupling reaction.[60] One of the supporting finding was the ease of displacement of halogen atoms from the aromatic nucleus following the trend of ArI > ArBr > ArCl.[51,60] All intermediates within the cycle and the inactive Pd(II) species were possible to be deactivated under the high concentration of cyanide ions.[60]

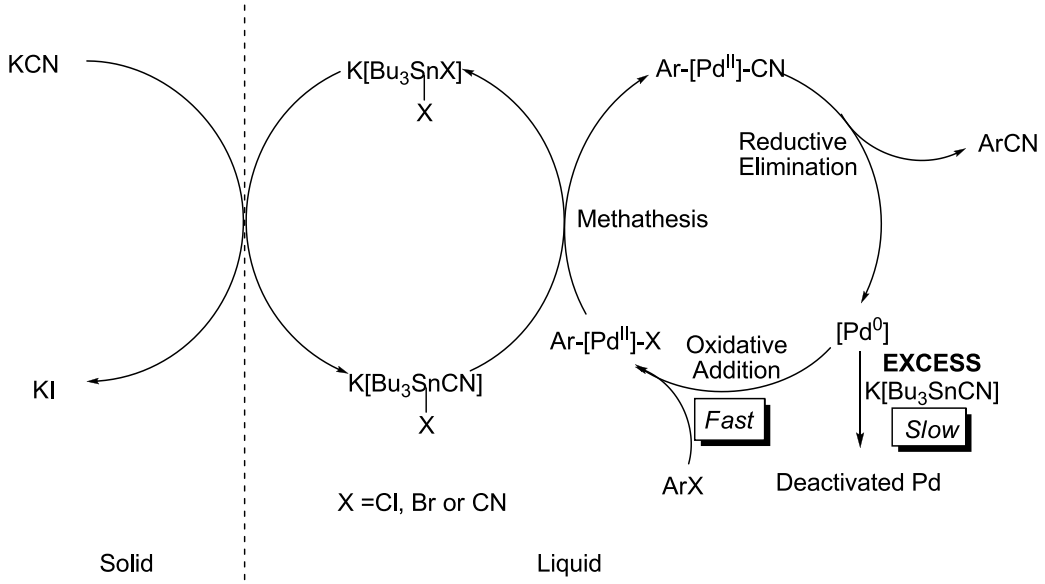
In 2003, Beller and co-workers began to study the effect of additives towards the cyanation.[3] They reported that the catalysts could be protected by bidentate amine ligands such as TMEDA from being "cyano-poisoning". Marcantonio *et al.* further proved that the concentration of cyanide ions governed the feasibility of the catalyst turnover.[61] The concentration of cyanide ions in solution could be monitored by either slow injection of liquid cyanation sources through micro-syringe which was controlled by syringe pump, or the rate of dissolution of solid cyanation sources.[56,62] Buono *et al.* found that $Zn(CN)_2$ dissociated slowly in the presence of optimum amount of water.[56] Either too much or too less water altered the concentration of cyanide ions in the reaction media, due to the dissolution of $Zn(CN)_2$.[56] Because of the critical amount of water, Grushin *et al.* conducted a series of NMR experiment in order

to study the role of water in cyanation.[63,64] Interestingly, the presence of water helped metal cyanide to dissociate into ionic form in the organic media.[63,64] Aryl nitrile was only product upon condition that the concentration of cyanide ions was optimized. However, in case of excess cyanide ions, the ligand exchange between ligands and cyanide ions was dominant over the reductive elimination due to the formation of catalytically inactive $[(CN)_3PdAr]^{2-}$ complexes.[63,64] By means of the reducing properties of zinc,[65] *iso*-propanol[66] and PMHS[62,67], inactive $[(CN)_3PdAr]^{2-}$ complexes were reduced to generate active complexes so that the catalytic cycle could be continued.

1.3. Cyanation with potassium cyanide

Since Takagi *et al.* reported the first palladium-catalyzed cyanation of aryl iodides and bromides with potassium cyanide, a number of publications about cyanation were published.[51] Until the late 1990's, only aryl iodides and bromides were applicable in cyanation but the development in aryl chloride cyanation was limited.[60] In 2004, Yang and Williams revealed an advanced cyanation method for the aryl bromides, using a catalytic amount of organotin compound as additive. The proposed mechanism was similar to that reported by

Tagaki *et al*.[52,68] The key step focused on the middle cycle (Scheme 1.6). With the NMR analysis, it was found that the formation of "tin ate complex" in the middle cycle is the key step. It served similarily to the phase transfer catalyst.[68]

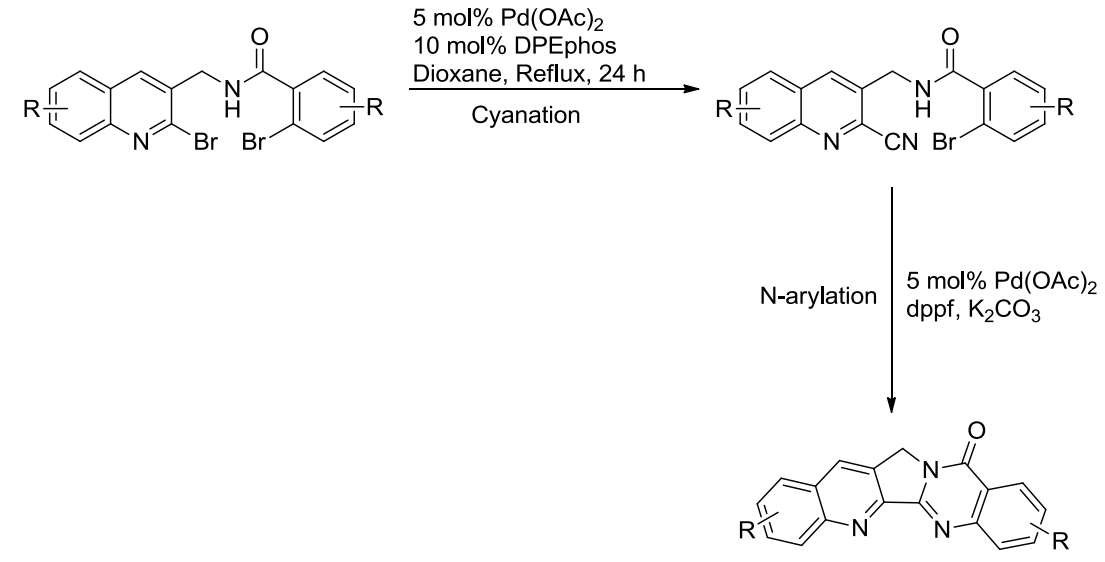


Scheme 1.6 Catalytic Cycle for Pd-Catalyzed Cyanation of Aryl Bromides Promoted by Tin Ate Complexes

In the cyanation reaction of aryl bromides, KCN reacted with tributylstannyl halides to form a more soluble intermediate, tributyltin cyanide, in the catalytic cycle.[68] The reaction media was found insoluble towards KCN and the deactivation of catalyst by KCN was thus eliminated.[68] The optimal molar ratio of tributyltin chloride to Pd was about 1:3.7.[68] This protocol was shown to be general for cyanation of activated, deactivated, non-activated, and hetero-aryl bromides.[68] The disadvantage of this method was that the ratio of tributyltin chloride to Pd must be adjusted precisely.[68] Too high or low

R_3SnCl/Pd ratio slowed down the reaction or caused incomplete conversion, respectively.[68]

In 2009, Li and co-workers enhanced the palladium catalyzed cyanation of aryl iodide using KCN as the cyanating agent (Scheme 1.7).[13] Luotonin A was a human DNA topoisomerase I poison and exhibited potent cytotoxicity against P-388 cells, which was firstly isolated from a Chinese medicinal plant (*Peganum nigellastrum*) in 1997.[13] Both cyanation and *N*-arylation were mainly controlled by the choice of ligands, that spurred the two reactions to one-pot, two-stage manner sequentially.[13]

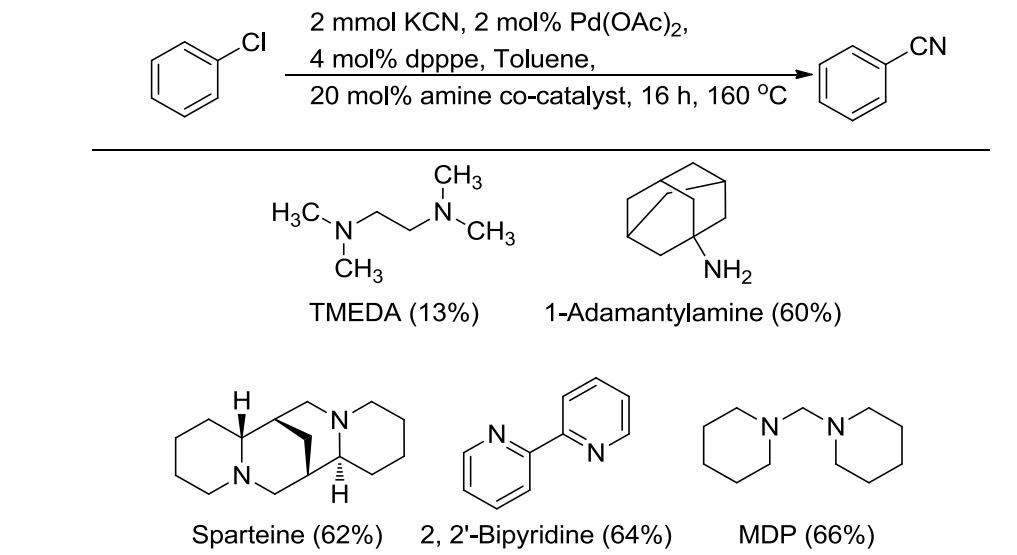


Scheme 1.7 One-pot palladium-catalyzed sequential cyanation / *N*-addition / *N*-arylation

In 2001, general conditions for cyanation of activated, non-activated and even deactivated aryl chlorides and hetero-aryl chlorides were firstly disclosed by Beller and co-worker.[69] Beller reported a cyanation using KCN as cyanating

sources in the present of amine co-catalyst.[69] However, KCN poisoned the catalyst by dissociation into potassium cation and cyanide anion when dissoluted in the reaction medium.[69] It was reported that 0.2 equivalent TMEDA could protect the palladium catalyst from the poison of KCN.[69] It is supported by evidence because it substituted cyanide ions on the palladium center, so an active palladium catalyst can be regenerated.[69] Based on NMR studies, the presence of di-amine also increased the stability of the phosphine ligands.[69]

Inspired by the positive effect of TMEDA, Beller expanded the investigation to a variety of di-amines and other bulky primary amines for the co-catalytic effect on the palladium-catalyzed cyanation of aryl chlorides.[3] Amines such as sparteine, MDP, 2,2-bipyridine and 1-adamantylamine showed superior results over TMEDA, with approximately 60-66% yield, whereas TMEDA only gave 13% yield (Scheme 1.8).[3]



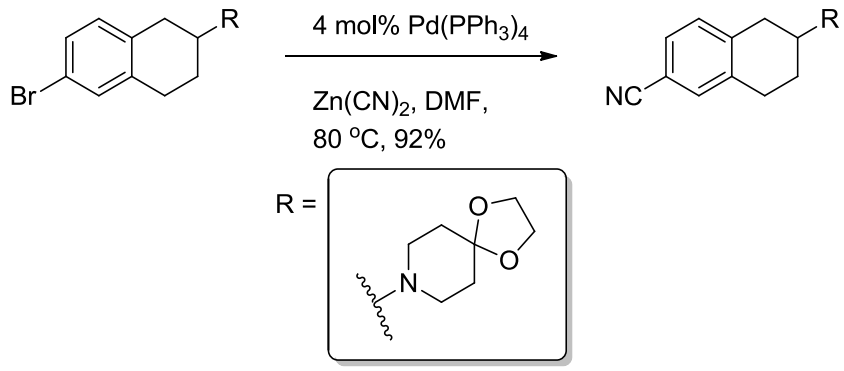
Scheme 1.8 Catalytic cyanation of chlorobenzene in the presence of different co-catalysts

There was no side reaction, palladium-catalyzed amination was observed.[3] From the catalytic results, it could conclude that the catalytic activity was independent on structural and electronic properties of amines.[3]

1.4. Cyanation with zinc cyanide

Zinc(II) cyanide is also a popular cyanide source.[60] The most attractive advantage of zinc(II) cyanide is its relatively low toxicity compared to other alternative cyanide sources, except potassium ferrocyanide.[70] In particular, its solubility in common organic solvents is relatively low.[60,71,72] Moreover, there are two cyanide ions available for cyanation but the dissociation of zinc cyanide is slowly due to the highly covalent nature of the zinc cyanide bond.[60] This gave rise to the low concentration of cyanide ion in the reaction medium, which led to deceleration of the rate of catalyst inhibition.[60,73]

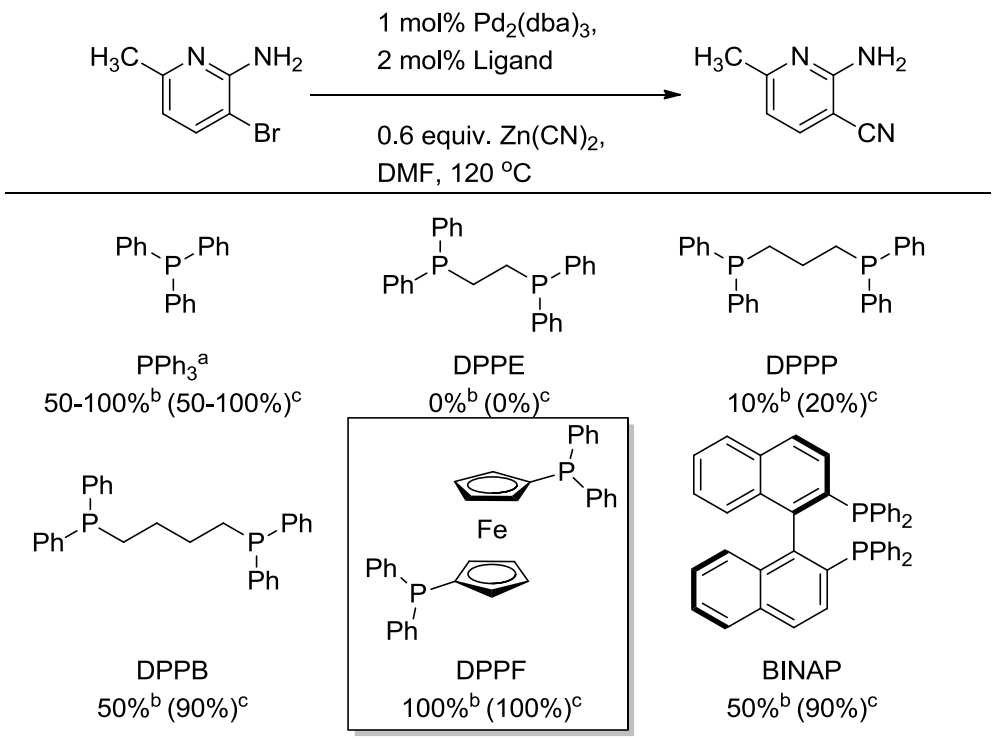
Tschaen *et al.* were the first chemist who utilized zinc(II) cyanide in palladium-catalyzed cyanations of aryl iodides and bromides (Scheme 1.9).[73] It is an important development because the respective aryl bromide is the essential intermediate in the synthesis of potent potassium channel blocker, MK-0499, which mediates repolarization of cardiac tissue.[73]



Scheme 1.9 First palladium-catalyzed cyanation with $Zn(CN)_2$ developed by Tschaen *et al*

Subsequent to Tschaen's report, Selnick *et al.* modified the conditions of Tschaen group so that 6-cyano-1,2,3,4-tetrahydroisoquinoline could be generated conveniently from the catalytic cyanation of aryl triflate.[74] Moreover, Rice *et al.* investigated a more advanced cyanation condition for sterically hindered and electron-rich 2-methoxyphenyl triflate.[75]

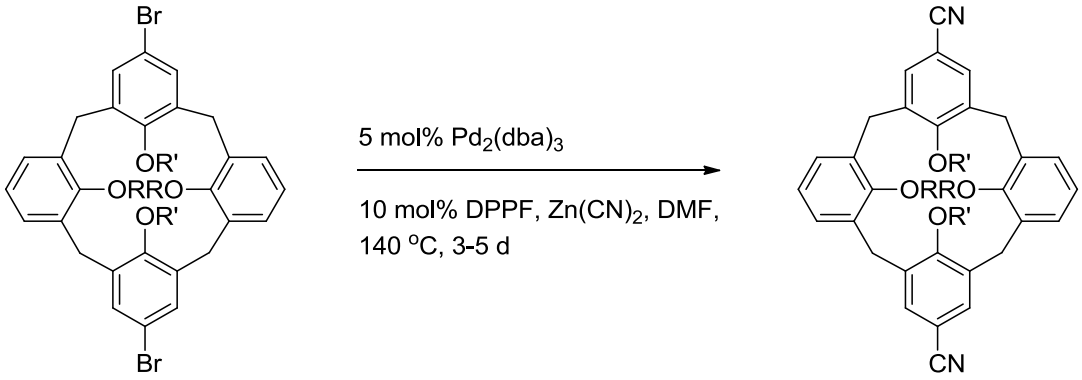
Maligares *et al.* pioneered the study of the influence of ligands on palladium-catalyzed cyanations of aryl iodides and bromides (Scheme 1.10).[76]



[a] 8 mol%; [b] % conversion at 22 h; [c] % conversion at 48 h

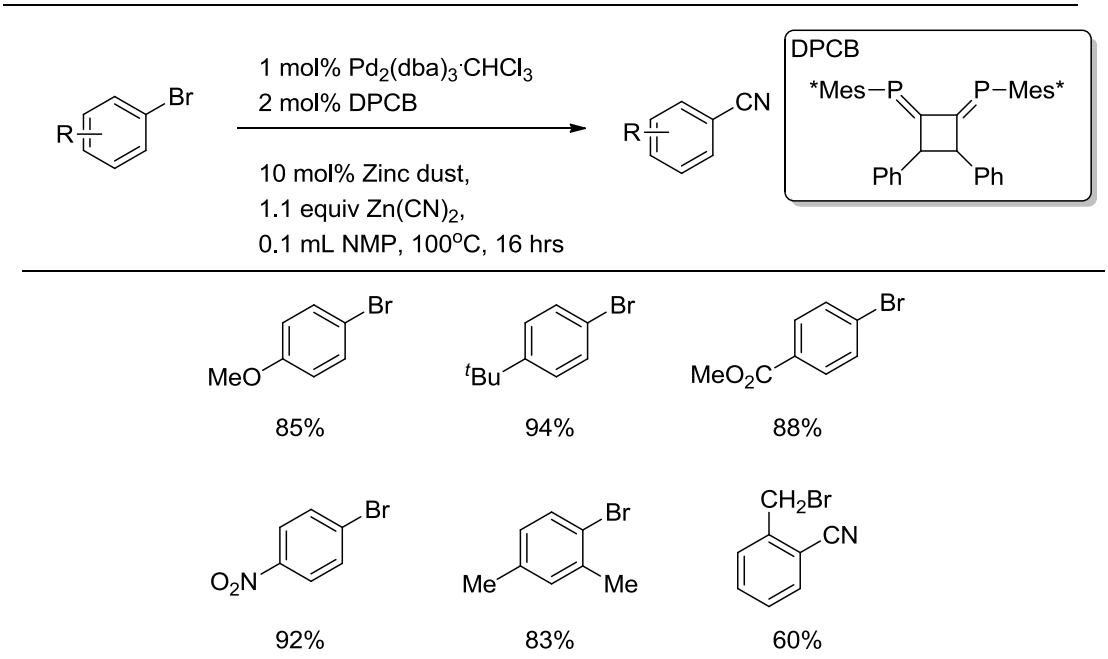
Scheme 1.10 Palladium-catalyzed cyanation with $Zn(CN)_2$ developed by Maligares *et al*

It was found that DPPF was the best ligand for successful cyanation of simple as well as sterically hindered and deactivated aryl bromides and their derivatives.[76] This system was further modified by Hioki and coworkers for the production of cyano-substituted calixarenes which was the scaffold of calixarene-based host molecules (Scheme 1.11).[70]



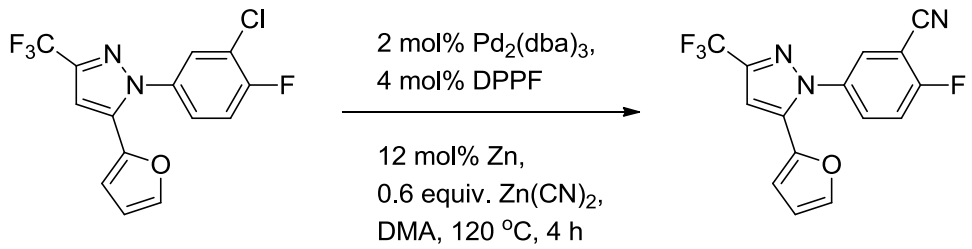
Scheme 1.11 Palladium-catalyzed cyanation for the synthesis of cyano-substituted calixarene

Particularly, Yoshifuji *et al.* keened on the development of a unique bidentate phosphorus ligand. They devoted considerable effort to the chemistry of low-coordinated phosphorus compounds with sp^2-hybridized phosphorus atoms.[71] They applied DPCB as the catalyst (Scheme 1.12), which was formed an effective ligand for palladium-catalyzed cyanation of aryl bromides.[71] This type of ligand bore extremely low-lying π* orbital mainly located around the phosphorus so it tended to engage in metal-to-phosphorus π-back bonding.[71] This feature was anticipated to stabilize low-vacant metal species with high electron density that facilitated the reduction of transition metal complexes.[71]



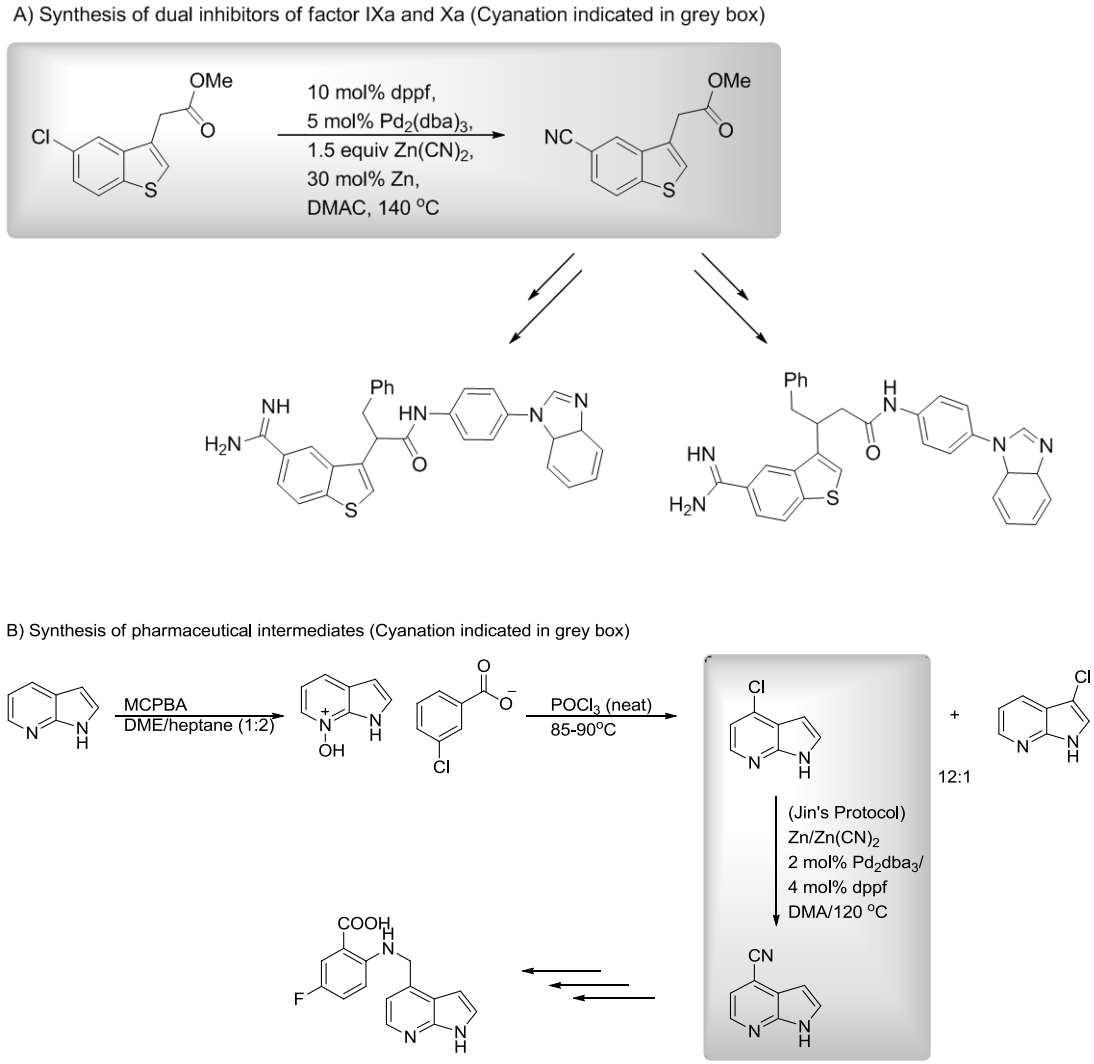
Scheme 1.12 Palladium-catalyzed cyanation of aryl bromides with $Zn(CN)_2$ using DPCB ligand

In 2000, Jin *et al.* investigated a new protocol for palladium-catalyzed cyanation of aryl chlorides with zinc(II) cyanide (Scheme 1.13).[65]



Scheme 1.13 Palladium-catalyzed cyanation with $Zn(CN)_2$ developed by Jin *et al*

Taking the advantages of Jin's protocol, it was pharmaceutically utilized in the preparation of 5-amidinobenzo[b]thiophene which is the dual fIXa and fXa inhibitors,[12] and the amino-methyl moiety in the practical synthesis of a key pharmaceutical intermediate, 2-[(1H-pyrrolo[2,3-b]pyridine-4-yl)methylamino]-5-fluoronicotinic acid (Scheme 1.14).[72]

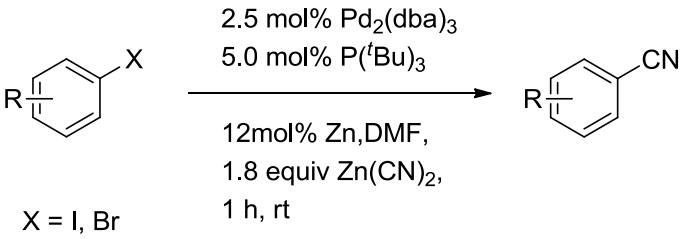


Scheme 1.14 Pharmaceutical applications of Jin's protocol

Both protocols of Maligres *et al.*[76] and Jin *et al.* used the same Pd(0) catalyst species, but the latter could be applied to deactivated and activated aryl chlorides.[65] Activated aryl chlorides reacted faster than deactivated aryl chlorides as well as neutral aryl chlorides at lower temperature. Electron-rich aryl and neutral aryl chlorides required higher catalyst loading in order to furnish the corresponding aryl nitriles.[65] Notably, the application of zinc dust in catalytic amount facilitated the reduction of deactivated palladium(II)

cyano-compound to catalytically active palladium(0) species.[65] This breakthrough was adopted to synthesize thienyl nitriles and their derivatives.[77]

Based on the strategy developed by Jin *et al.*[65], Maddaford and co-workers exmained conditions for cyanation of aryl bromides and iodides at room temperature by applying various ligands including tri-*tert*-butylphosphine, triphenylphosphine, dppf, XantPhos, and 2'-dicyclohexylphosphinobiphenyl (Scheme 1.15).[78]

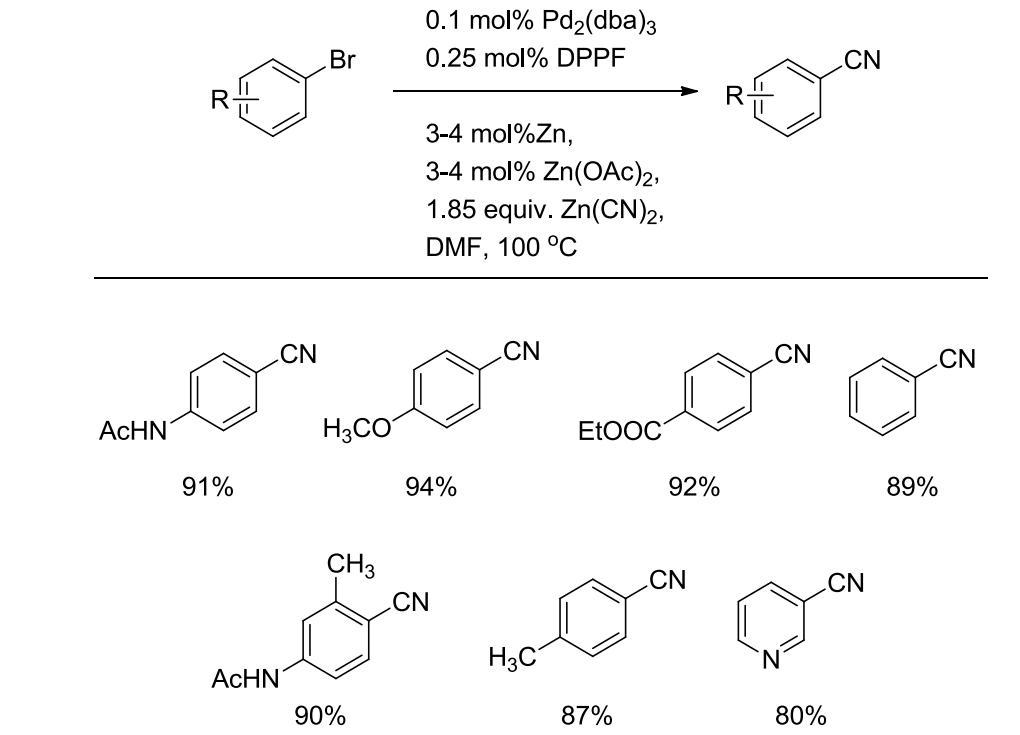


Scheme 1.15 Room temperature palladium-catalyzed cyanation developed by Maddaford *et al*

Interestingly, the optimal molar ratio of Pd to ligand was always be 1:1.[78] Electrion-deficient and electron-rich *ortho*-substituted aryl bromides gave moderate to good yield whereas excellent yields were observed in aryl iodides, irrespective of *ortho*-substitution.[78]

In addition to the concept of Maddafold *et al.*, Chidambaram manipulated zinc acetate to work with zinc dust to ensure a higher catalyst activity.[79] Interestingly, Chidambaram discovered the importance of acetic acid accidentally.[79] However, the presence of acetic acid possibly reacted with zinc cyanide, forming toxic hydrogen cyanide, so the need of safer alternates was

craved.[79] It was reported that the catalytic effect of 3–4 mol% zinc acetate was as effective as acetic acid (Scheme 1.16).[79] Zinc acetate worked with zinc dust to protect the palladium from being deactivated.[79] Nevertheless, it was ascertain not applicable to aryl chlorides.[79]



Scheme 1.16 A robust palladium-catalyzed cyanation of aryl bromides in the presence of zinc acetate

Martin *et al.* replaced the zinc-based reductants by PMHS, which was capable of imparting the reaction to a remarkable protective effect: protecting active palladium(0) species from oxidation.[67] This discovery of using PMHS represented a significant advancement in the development of open air robust catalytic reactions.[67]

In 2008, Ryberg noticed that the palladium-catalyzed cyanation with

potassium hexacyanoferrate suffered from a number of problems such as lack of robustness, the demand of long reaction times and at high temperatures (typically > 100 ℃), and notorious difficulty to run the reaction in gram-scale.[72,76,80] Ryberg reported the first palladium-catalyzed cyanation of aryl bromides operating successfully on 6.7 kg scale under mild conditions, i.e. 3 h at 50 ℃, with an isolated yield of 90% corresponding to the model substrate (Scheme 1.17).[81]

Scheme 1.17 The mildest palladium-catalyzed cyanation of aryl bromides developed by Ryberg *et al* till 2008

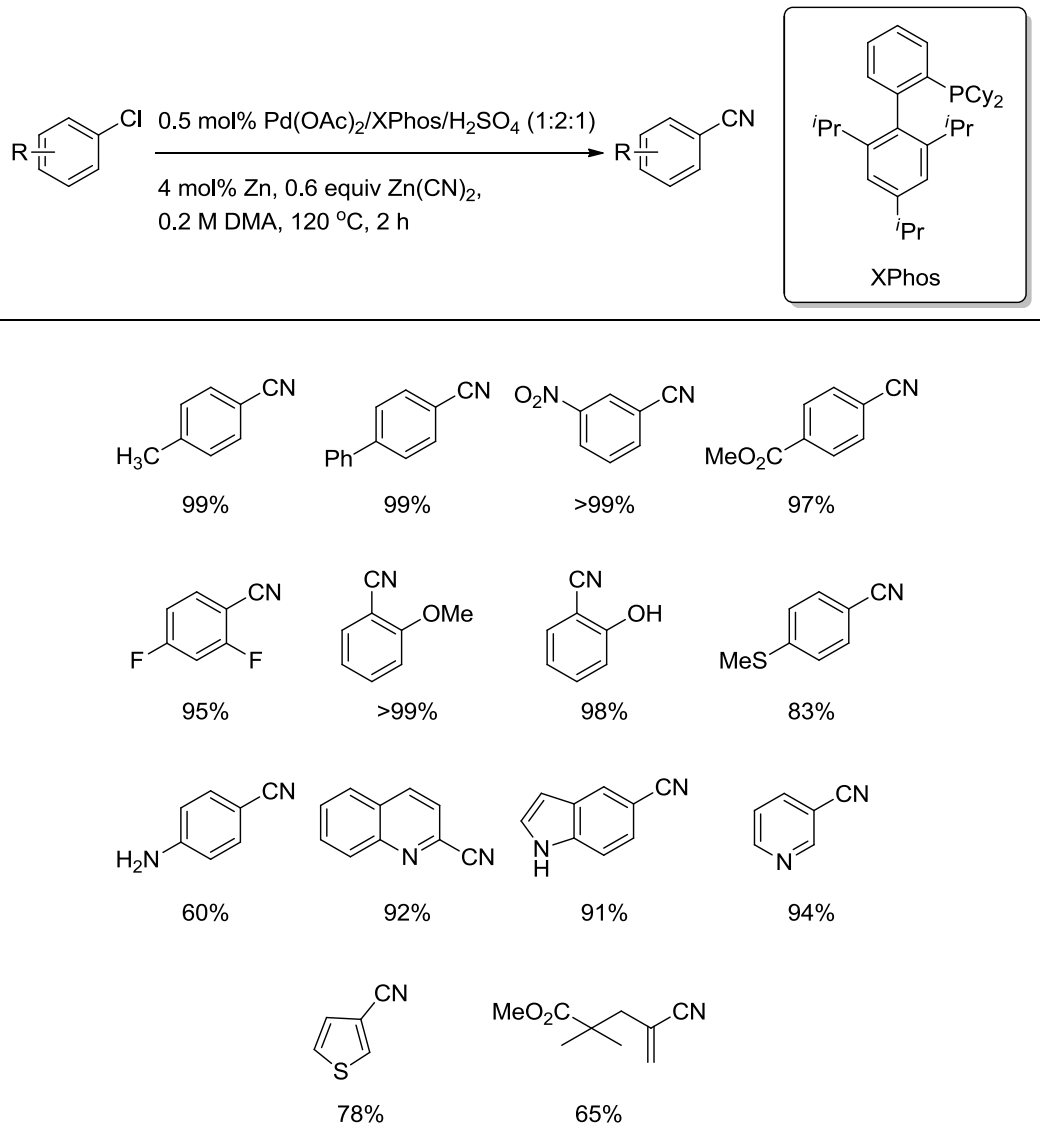
Entry	Catalyst System	Conversion (%) (1h)
1	$Pd(dba)_2$ + $P(^tBu)_3$	100
2	$Pd[P(^tBu)_3]$	100
3	$[BrPdP(^tBu)_3]_2$	100
4	$Pd(dba)_2$ + QPhos	100
5	$Pd(dba)_2$ + 2-$(^tBu)_2$P-biphenyl	100
6	$Pd(dba)_2$ + 2-Cy_2P-biphenyl	100
7	$Pd(dba)_2$ + XPhos	100
8	$Pd(dba)_2$ + P(*o*-tol)$_3$	100

Table 1.1 Evaluation of catalyst systems for the palladium-catalyzed cyanation

A series of experiments were conducted to explore robust conditions for the reaction where the addition order of the reagents was the key for success.[81] It was found that $Zn(CN)_2$ was added lastly to a pre-heated mixture of other reactants. They were mixed and heated at 50 ℃ in degassed DMF and kept at this temperature for 5−10 min.[81] A number of catalytic systems were tested whether the robust conditions were feasible as well as the reagent additional sequence (Table 1.1).[81] For the scale-up experiments, the commercially available $[BrPdP(^tBu)_3]_2$ complex was selected since it was reasonably air stable and gave the cleanest reaction.[81]

Most recently, Shevlin *et al* replaced the zinc acetate by sulfuric acid in an active and robust catalytic system for the cyanation of aryl chlorides (Scheme 1.18).[82] The role of the additives in the catalytic cycle was mystery. This system

was more advanced because it was applicable for aryl chlorides and also alkenyl chlorides.[82] Hetero-aryl chlorides were converted to corresponding aryl nitriles in moderate to good yield.[82]



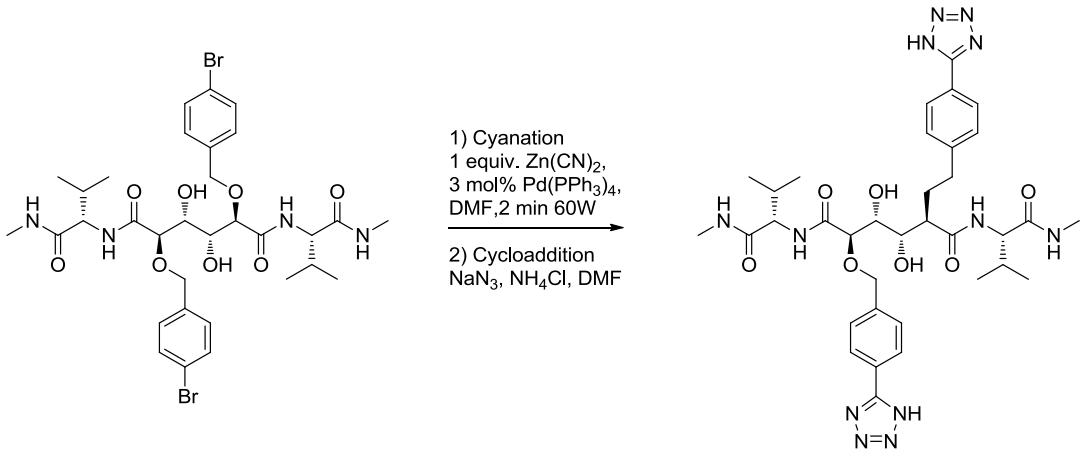
Scheme 1.18 Palladium-catalyzed cyanation of aryl chlorides with sulfate additives

The palladium-catalyzed cyanation of aryl chlorides remained problematic and was only possible at high temperature generally.[82] In 2007, Littke *et al.* reported a milder cyanation condition for aryl chlorides using two highly

reactive palladium-based catalysts, including $Pd(TFA)_2$/(binaphthyl)$P(^tBu)_2$ (Catalyst A) and $Pd[P(^tBu)_3]_2$ (Catalyst B).[83] Catalyst A was effective for very electron-rich aryl chlorides, electron-neutral as well as electron-deficient substrates.[83] Besides, catalyst B was not only efficient for highly hindered aryl chlorides as well as sulfur-containing substrates, e.g. 2-nitro-2-chlorotoluene and 2-chlorothioanisole, respectively, but also sufficient for less challenging electron-neutral and electron-deficient aryl chlorides.[83] They firstly demonstrated palladium-catalyzed cyanation of highly challenging 4-chloroaniline and 2-chlorophenol successfully.[83] Despite the mildest condition (80-95 ℃) at that moment, the catalyst loading (5 mol%) and the need of zinc flakes (20 mol%) were required.[83]

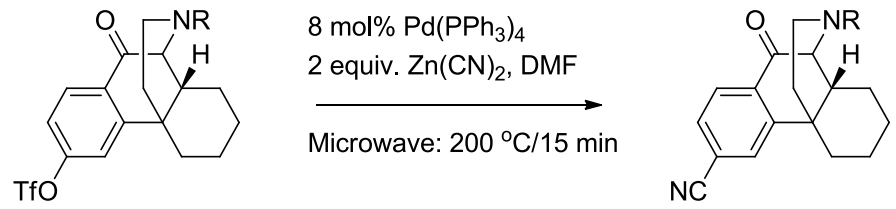
Since the first publication of palladium-catalyzed cyanation of aryl bromides with zinc cyanide was reported by Tschaen *et al.* in 1994, combinatorial and robotized parallel catalytic synthesis have been demanded for faster and efficient reaction conditions. In 2000, the first microwave assisted palladium-catalyzed cyanation of aryl bromides with zinc cyanide was reported by Hallberg and Alterman.[84] Flash heating by microwave irradiation enabled the fast conversion within approximately 2-2.5 min.[84] By combination of this process with cycloaddition reaction of sodium azide, one pot transformation of

aryl halides for accessing aryl tetrazoles could be accomplished.[84] A potent C2-symmetric HIV-1 protease inhibitor,[85] with two carboxyl group bio-isosteres, was prepared in one-pot from the corresponding aryl bromo-precursor *via* microwave assisted cyanation and cycloaddition (Scheme 1.19).[84]



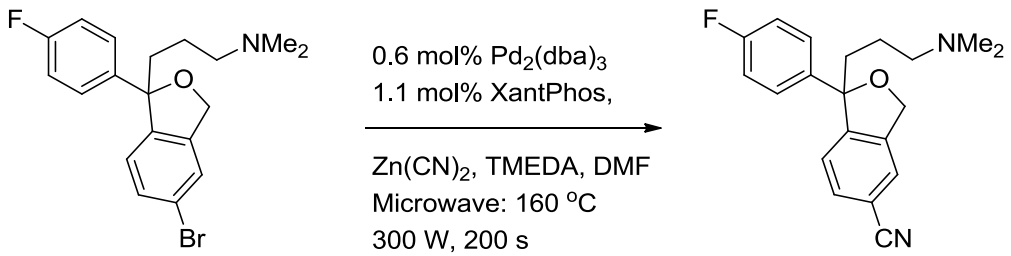
Scheme 1.19 Microwave-assisted palladium-catalyzed cyanation for the synthesis of a HIV-1 protease inhibitor

Until 2003, there had been no reports about the preparation of nitriles from the corresponding aryl triflates under microwave-assisted conditions.[86] Zhang *et al.* reported the first flash heating by microwave irradiation assisted palladium catalyzed cyanation of aryl triflates (Scheme 1.20).[86] The disadvantage of this system was the requirement of a *para*-keto group in the triflate.[86]



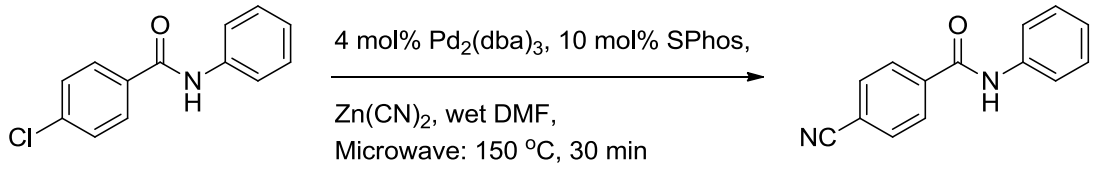
Scheme 1.20 Microwave-assisted palladium-catalyzed cyanation reaction with aryl triflate

In 2006, Pitts *et al.* devoted to the investigation of the ligand effect and additives in the microwave assisted palladium-catalyzed cyanation of aryl bromides.[80] They modified the last step in the synthesis of citalopram from the parent aryl bromide and developed a condition for palladium-catalyzed cyanation with the lowest catalyst loading ever reported in microwave enhanced palladium-catalyzed cyanation.[80] XantPhos and TMEDA were the best performed catalyst and additive for the reaction.[80]



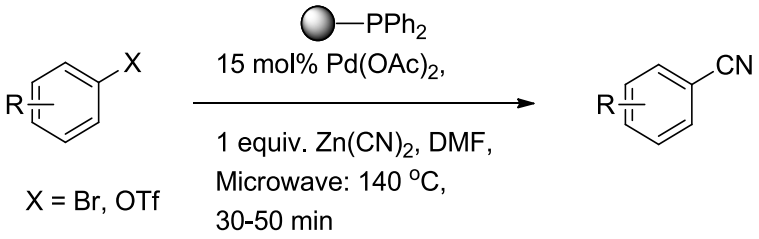
Scheme 1.21 Microwave-assisted palladium-catalyzed cyanation of citalopram

In the same year, Chobanian *et al.* accomplished the microwave-assisted palladium-catalyzed cyanation of aryl chlorides, using commercially available SPhos as ligand.[87] This system gave a better protocol than Jin *et al.* because the reaction could be performed effectively and efficiently in the absence of any reductants (Scheme 1.22).[87]



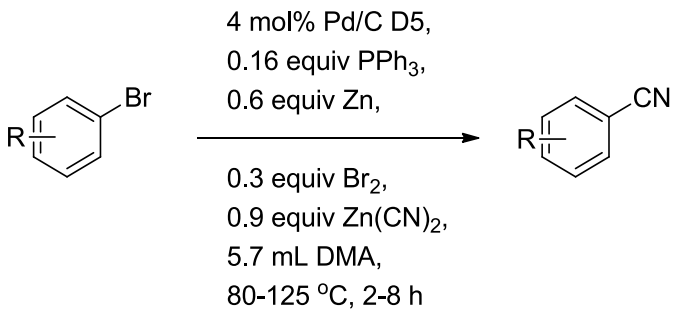
Scheme 1.22 Microwave-assisted palladium-catalyzed cyanation of aryl chlorides

Srivastave *et al.* elucidated the utilization of resin-bound triphenylphosphine as ligand in order to extend the scope of microwave assisted palladium-catalyzed cyanation of aryl halides and triflates (Scheme 1.23).[88,89] This inexpensive heterogeneous ligand is available in a variety of commercial sources.[88,89] This heterogeneous protocol simplified the purification steps and was amenable to high throughput synthesis.[88,89]



Scheme 1.23 Microwave assisted polymer-supported palladium-catalyzed cyanation of aryl halides and triflates

Heterogeneous catalyst, Pd/C, was used by Seki *et al.* for palladium-catalyzed cyanation of aryl bromides with zinc cyanide (Scheme 1.24).[90,91] Oxidic thick-shell type catalyst Pd/C was found to furnish the fastest reaction and highest yield.[90] The additive, zinc bromide, was *in situ* generated from the reaction of zinc dust and bromine.[91,92] Excellent recovery of Pd/C was achieved through the simple filtration and followed by combustion.[90]



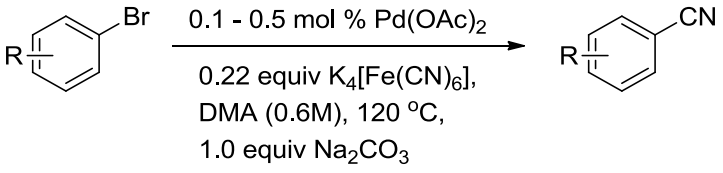
Scheme 1.24 Cyanation of aryl bromides with zinc cyanides in the presence of heterogeneous Pd/C

1.5. Cyanation with potassium hexacyanoferrate(II) trihydrate ($K_4[Fe(CN)_6]•3H_2O$)

In the previous section, the major disadvantages of cyanating sources used for palladium catalyzed cyanation were their toxicity to environment and the formation of inactive palladium(II) cyano compounds which no longer participating in the reaction. This gaves rise to the intriguing development of a novel cyanation using an extraordinary ideal cyanating source, potassium hexacyanoferrate(II) trihydrate ($K_4[Fe(CN)_6]\cdot 3H_2O$), by Beller *et al*. in 2004.[93-95] The most attractive advantage of $K_4[Fe(CN)_6\cdot 3H_2O]$ is non-toxic and even can be used in food industry for metal precipitation in wine.[70,95] It has also been used as anti-agglutinating auxiliary for table salt.[95] It is water soluble and stable.[95] Even in the presence of hydrochloric acid, HCN is generated only by boiling.[95] In particular, $K_4[Fe(CN)_6\cdot 3H_2O]$ is commercially available on ton-scale and the price is comparable or even cheaper than KCN.[96] It is known to be the least labile cyano-complexes of transition metal ions.[97] The cyanide ions are covalently bonded to the iron center with intensive π-back bonding, so the ferrocyanide ion has high stability / low dissociation.[60] Besides, the fourfold charged anion of the

ferrocyanide ion contributes to the low solubility in organic solvents.[60] Also, the ferrocyanide is defaulted to be reducing agent.[60] These are responsible for the success of cyanating reagent in palladium-catalyzed cyanation.[60] In the initial publication, Beller and co-worker demonstrated the highest TON of 18000 for un-activated substrate.[95] However, up to date, there has been no literature about the mechanistic investigations on the function of $K_4[Fe(CN)_6{\cdot}3H_2O]$ in the palladium-catalyzed cyanation of aryl halides and pseudo-halides.[60]

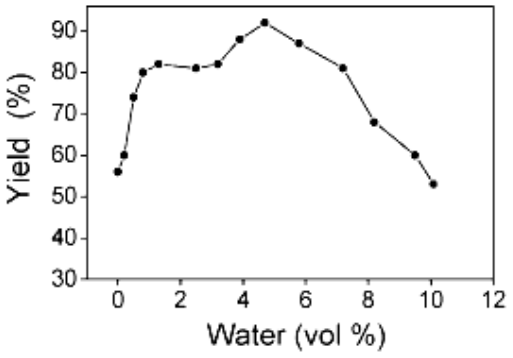
In addition to the breakthrough of cyanation reported by Beller and co-worker, the ligand-free system was published by Weissman (Scheme 1.25).[98]



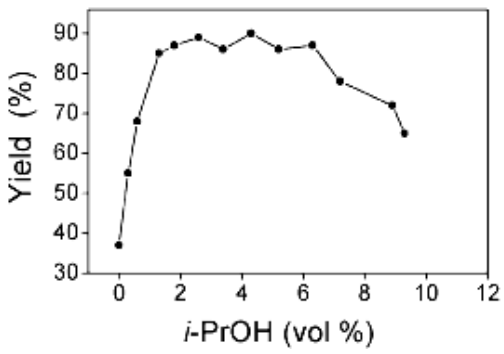
Scheme 1.25 Ligand free Pd-catalyzed cyanation of aryl bromides.

Air / moisture stable palladium(II) acetate was used for the cyanation.[98] As suggested by Beller,[94] all six cyanide ligands of $K_4[Fe(CN)_6{\cdot}3H_2O]$ are labile for the cyanation. The 0.22 equivalent was sufficient enough for the loading of $K_4[Fe(CN)_6{\cdot}3H_2O]$.[98] At this low loading, successful cyanation of a board scope of aryl bromides were demonstrated with excellent yield (83-96 %) within a shorter period of time (5-8 h).[98] But the TON was just half comparing to the report by Beller *et al*.[98] This is a significant breakthrough for ligand-free palladium-catalyzed cyanation of aryl bromides.[98]

Recently, Ren developed an environmental friendly and highly efficient cyanation protocol.[66] The additive, *i*-propanol, could reduce the oxidized inactive Pd (II) to active Pd (0). It was found effective in protection of palladium complex under air.[66] Moreover, water facilitated the cyanation because water assisted to stabilize $K_4[Fe(CN)_6 \cdot 3H_2O]$.[66] The critical volumes of *i*-propanol and water were analyzed by a series of optimization experiment (Scheme 1.26 and Scheme 1.27).[66]



Scheme 1.26 Effect of concentration of H_2O on the cyanation of bromobenzene.



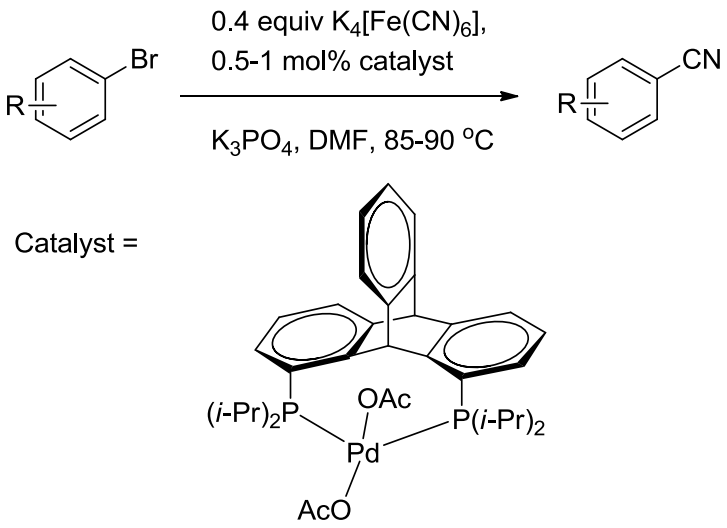
Scheme 1.27 Effect of concentration of i-propanol on the cyanation of bromobenzene.

Reaction conditions: iodobenzene (1 mmol), *i*-PrOH (2.4 vol. %), Na_2CO_3 (1.5 mmol), $Pd(OAc)_2$ (0.4 mmol%), NMP (2 mL), $K_4[Fe(CN)_6]$ (0.6 mmol), 140 ℃, time (40 min)[66]

Hence, there no longer needed an inert atmosphere and dry solvents for palladium catalyzed cyanation of aryl bromides with $K_4[Fe(CN)_6] \cdot 3H_2O$

Multitude extensions to the pioneering study by Beller *et al.* have been published since 2004.[94,95] Chemists focused on the investigation of novel catalyst systems for handling aryl halides, tosylates and mesylates by alternating the metal complex, solvent as well as co-solvents.[60] Grossman *et al.* made use of a

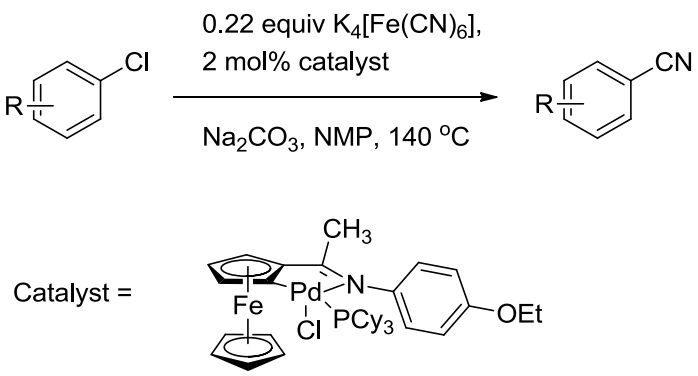
wide bite angle ligand on palladium center as catalyst for efficient cyanation of aryl bromides (Scheme 1.28).[99]



Scheme 1.28 Palladium-catalyzed cyanation of aryl bromides developed by Grossman *et al*

The palladium metal center is protected by ligand from air oxidation.[99] This catalyst was found insensitive against air. It worked well for the cyanation of aryl bromides at comparably mild reaction temperatures (85-90 ℃).[99] It was found not suitable in the cyanation of aryl chlorides, only yield 21% (GC yield) of the corresponding nitrile from methyl 4-chlorobenzoate was obtained.[99]

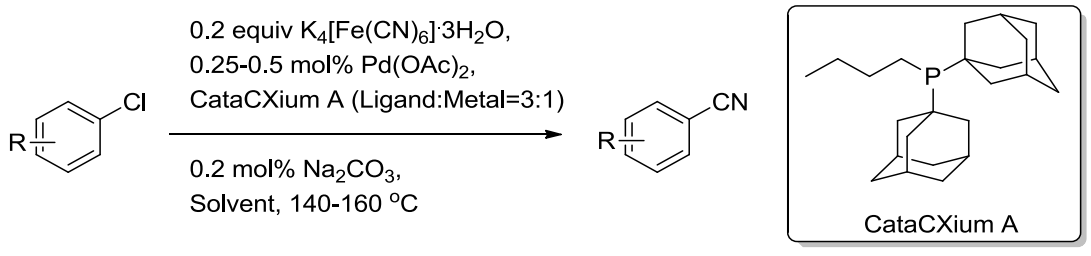
Cheng *et al.* was the first inventor of the palladium-catalyzed cyanation of aryl chlorides using a cyclopalladated ferrocenylimine as catalyst (Scheme 1.29).[100]



Scheme 1.29 Cyanation of aryl chlorides with cyclopalladated ferrocenylimine developed by Cheng *et al*

Most model substrates, such as 2-chloroanisole and 1-chloronaphthalene yielded 66% and 97% respectively under such conditions.[99]

Beller *et al.* used commercially available sterically hindered and electron-rich ligand CataCXium A[101] for successful palladium-catalyzed cyanation of aryl chlorides (Scheme 1.30).[102] The catalyst loading was low, only 0.25-0.5 mmol% $Pd(OAc)_2$, were enough for the conversion of electron-rich, electron-poor, hetero-cyclic and sterically hindered aryl chlorides to aryl nitriles.[102]



Scheme 1.30 Cyanation of aryl chlorides developed by Beller *et al*

More efforts were put to extend the scope of the aryl chloride cyanations, especially amino- and hydroxy- substituents.[103] Beller *et al*. had tested 16

ligands but none of each could give generality for cyanation (Figure 1.2).[103]

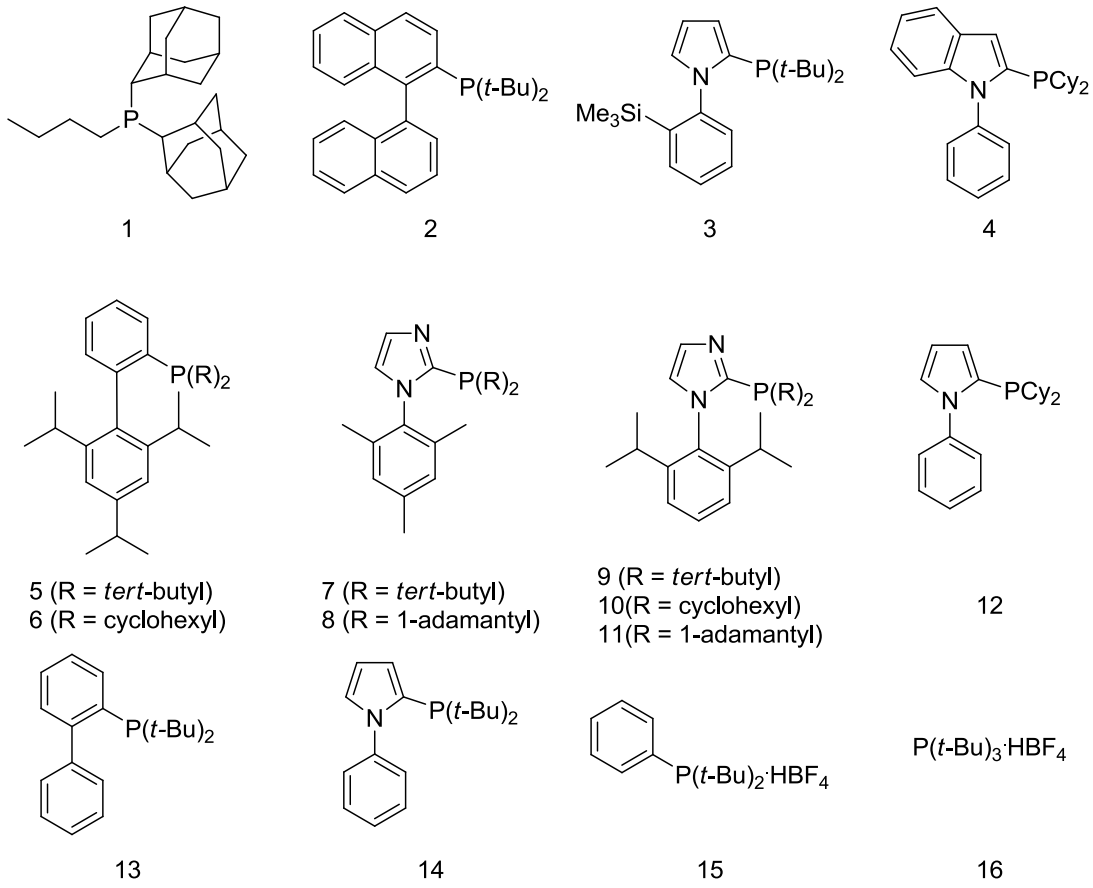


Figure 1.2 Bulky heterocyclic phosphine ligands being tested

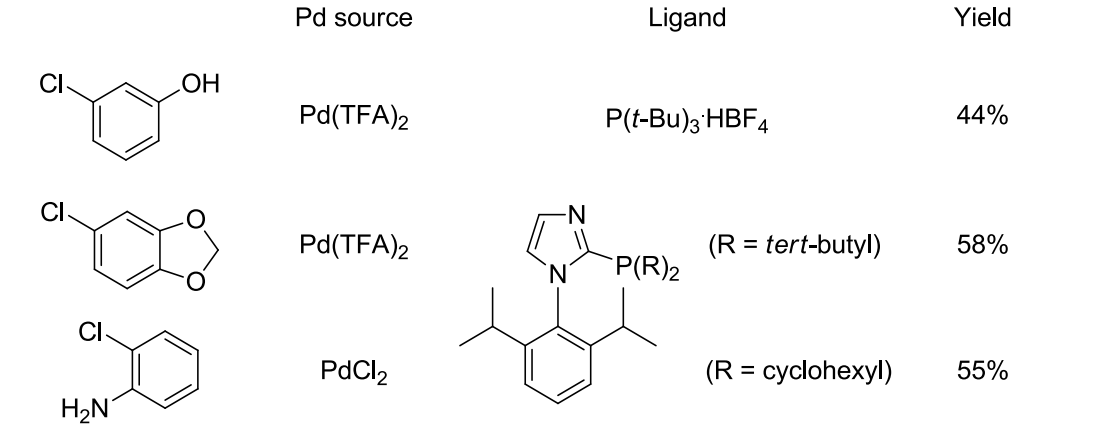


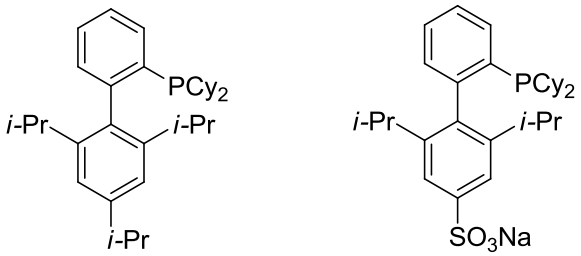
Figure 1.3 Ligands for the cyanation of challenging aryl chloride

Although difficult substrates such as chlorophenols and chloroanilines could be cyanated, different phosphine ligands were needed (Figure 1.3).[103] An all-purpose ligand did not find and almost each substrate needed its optimized

ligands and conditions.[103] This system only demonstrated the effectiveness of novel bulky heterocyclic phosphine ligands in cyanation, but lacked of generality and the reaction temperature was high (140 ℃).[103]

Cai *et al.* was the one discovered the palladium catalyzed cyanation of aryl trifluoromethylsufonates (triflates).[104] The high catalyst loading, 5 mol% palladium(II) acetate, was needed to achieve good yields.[104] For relatively active substrates such as perfluorooctylsulfonates, 1-2 mol% palladium(II) acetate together with triphenylphosphine were sufficient for cyanation.[104]

Zhang *et al*. realized ligands XPhos and XPhos-SO_3Na (Figure 1.4) were functionable in aqueous system (water / dioxane = 1:1) but the reaction temperature was high (140 ℃).[93] Because of their low solubility in aqueous media, they performed well for the cyanation of aryl chlorides, aryl tosylates and aryl benzenesulfonates with good yield, especially for naphthyl tosylates.[93] The good yields were attributed to the presence of K_2CO_3.[93] It was found important in the cyanation because it could reactivate the catalyst.[93] The solubility of $K_4[Fe(CN)_6]$ in water was also another factor for the success.[93]



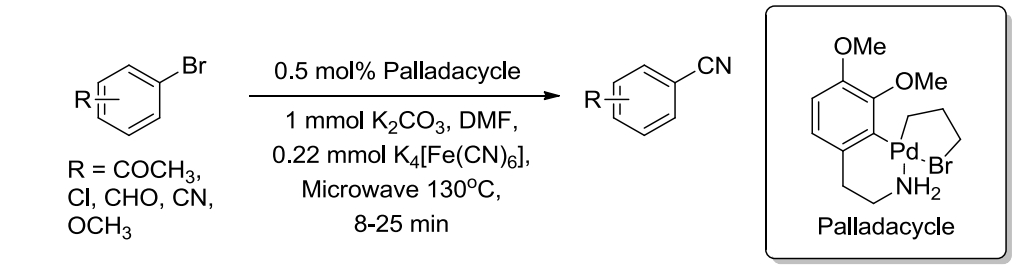
XPhos XPhos-SO_3Na

Figure 1.4 XPhos and XPhos-SO_3Na

In my MPhil study, the mildest reaction condition using 8 mol% CMPhos together with 2 mol% palladium(II) acetate achieved the generality of palladium-catalyzed cyanation.[34] The reaction temperature of 80 ℃ was the mildest ever reported for the cross-coupling of aryl mesylates.[34] Interestingly, water was found necessary as co-solvent to facilitate the cyanation.[34] Inspired by Zhang, our catalyst system had been applied for the hitherto mildest cyanation of aryl chlorides.[105] Sequential cyanation/amination of aryl sulfonates and chlorides were described in Chapter 2 and Chapter 3.[34,105]

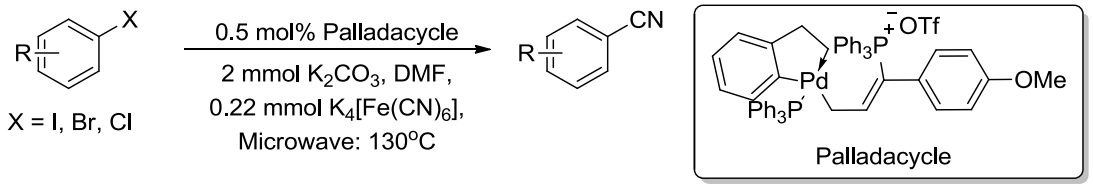
Direct transition metal-catalyzed C-H activation have emerged as a more attractive method for synthesizing aromatic nitriles.[57] $K_4[Fe(CN)_6]$ was applicable in the direct non-chelated cyanation of indoles.[57] The introduction of a cyano group into the 3-position of indoles could be found regioselective.[57] Interestingly, chelation-assisted palladium-catalyzed cascade bromination / cyanation of 2-arylpyridine and 1-arylpyrazole C−H bonds with $K_3[Fe(CN)_6]$ as a nontoxic and safe cyanating reagent was also reported.[96]

However, potassium hexacyanoferrate(II) was only used in a homogeneous catalyst system. The existing methods using homogeneous palladium catalyst still suffered from some drawbacks: quite expensive and hazardous phosphine ligand was needed and recycling of the catalyst was tedious.[106] Beginning with aryl iodides and bromides, various novel catalysts were developed to facilitate the reaction time and catalytic efficiency. Hajipour *et al*. took the advantages of microwave, 0.5 mol% palladacycle catalyst and $K_4[Fe(CN)_6]$ for a better catalytic cyanation (Scheme 1.31).[107]



Scheme 1.31 Catalytic system for microwave assisted palladium catalyzed cyanation of aryl bromides

This catalytic system was successful for the cyanation of aryl iodides and non-activated aryl bromides with good yields.[107] In 2011, Hajipour and co-workers explored a new palladacycle catalyst for aryl chlorides with satisfied product yields (Scheme 1.32).[108]



Scheme 1.32 Cyanation reaction of various aryl halides using $K_4[Fe(CN)_6]$ in the presence of palladacycle under microwave irradiation.

Cai *et al.* published the usage of heterogeneous catalyst, Pd/C, to catalyze the ligand-free cyanation of aryl iodides using potassium hexacyanoferrate(II) trihydrate as the cyanating agent.[106] This system demonstrated the cyanation of aryl iodides successfully with good to excellent yields.[106] The Pd/C was simply recycled by filtration and followed by washing with water and dichloromethane for 3 times.[106] The dried recycled catalyst can be further used for additional 3 cycles of catalysis without deteriorations (Table 1.2).[106]

Entry[a]	Pd/C	Yield (%)[b]
1	Fresh	95
2	First reuse	92
3	Second reuse	90
4	Third reuse	85

[a] Reaction conditions: 3.0 mmol of β-bromonaphthalene, 20 mol% dry $K_4[Fe(CN)_6]$, 5 mL of DMAc, 100 mol% Na_2CO_3, 140 ℃.

[b] Yields were determined by GC with 1,3-dimethoxybenzene as the internal standard.

Table 1.2 The performance of recycled Pd/C

Cai and co-workers further published a recyclable palladium-catalyzed (Pd/C) cyanation of aryl bromides.[109] In Cai's new study, tri-*n*-butylamine was the key component because it stabilized the catalyst in the catalytic cycle.[109] As other system using $K_4[Fe(CN)_6]$, polar solvent gave the best performance in the

cyanation and the base was the essential element.[109] This heterogeneous catalytic condition took the advantages of homogeneous catalysis to some extent.[109] Similar to that of aryl iodides reported by Cai,[106] the catalytic activity was slightly deteriorated in the fourth cycle.[109] This catalyst was easy for recover and usable in industrial scale.[109] Based on the previous study, Cai *et al.* eventually combined the benefits of the usages of tri-*n*-butylamine (50 mol%) and Pd/C (5 wt%), elucidating a novel microwave assisted palladium-catalyzed cyanation conditions for aryl iodides and aryl bromides.[110] In 2010, Islam and co-workers developed a series of polymer-bound palladium catalyst with polystyrene framework (Figure 1.5). In gerneral, 1 mol% catalyst was sufficient to cyanate reactive aryl iodides.[111-113]

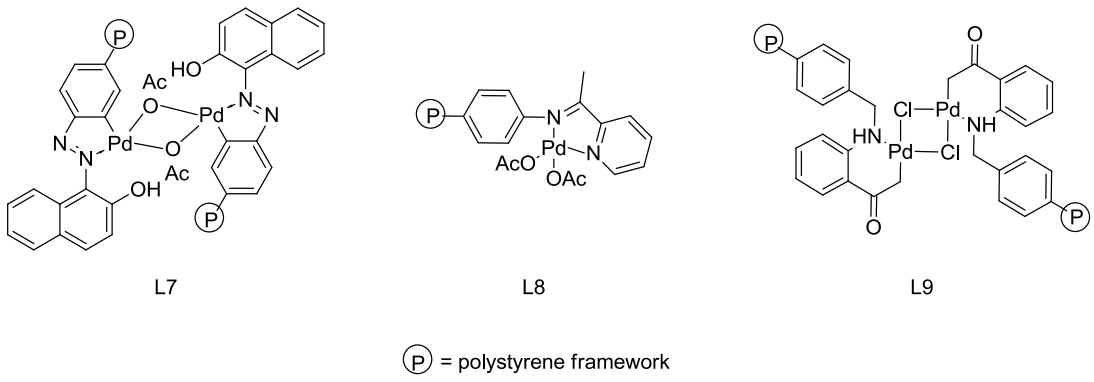
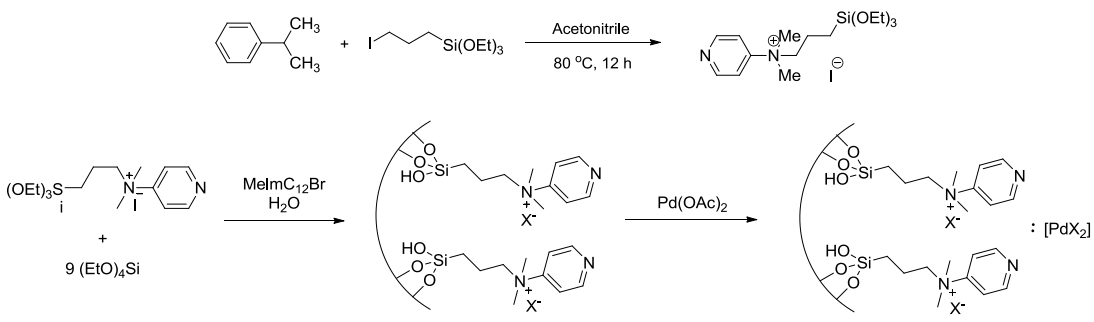


Figure 1.5 Heterogenized ligands developed by Islam *et al*

Polshettiwar and co-workers synthesized a nano-structural hybrid silica catalyst (Scheme 1.33).[114]



Scheme 1.33 Synthetic method of hybrid silica catalyst I-Pd

This catalyst successfully demonstrated a ligand-free cyanation of aryl iodides with good yield, using potassium hexacyanoferrate(II) trihydrate as cyanating agent.[114] The used catalyst was recovered by filtration, washed with dichloromethane and acetone, and dried for an hour. It could be reused for the first 3 cycles and deteriorated dramatically in the fourth cycle (Table 1.3).[114]

Entry[a]	Reuse	Conversion Yield(%)[b]
1	1	81
2	2	76
3	3	74
4	4	52

[a] Reaction was carried out using 1 mmol of aryl iodide, 0.7 mmol of $K_4[Fe(CN)_6]$, 2 mmol of triethylamine, and 500 mg nano-structured hybrid silica catalyst in refluxed DMF.

[b] Yield was determined by GC with dodecane as internal standard with respect to aryl iodide.

Table 1.3 Recyclability of catalyst I-Pd

A more powerful heterogeneous and recyclable palladium catalyst was the palladium(II) dichloride supported on the polyimidazole-based ligand which was copolymerized with a caprolactame monomer (Figure 1.6).[115] 1 mol% catalyst was enough for the conversion of aryl bromides to the corresponding

aryl nitriles but the conditions did not suitable for the cyanation of aryl chlorides.[115] This catalyst did not deteriorate until the tenth cycle.[115]

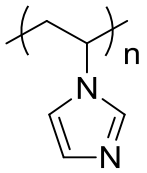
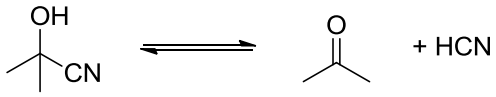


Figure 1.6 Polyimidazole-based ligand

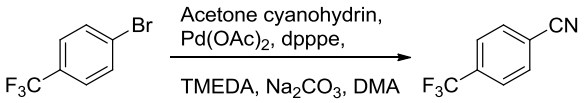
1.6. Cyanation with cyanohydrins

Acetone cyanohydrin could function as an equivalent of HCN (Scheme 1.34), which was applied as a cyanide source for nickel-catalyzed cyanation reactions in 1974.[116]



Scheme 1.34 Acetone cyanohydrin, a useful HCN equivalent

A slow and reproducible dosage of acetone cyanohydrin prevented the catalyst from cyanide poisoning, leading to successful coupling cyanations and solving the major concern in palladium-catalyzed cyanations in early 2000.[62] The presence of an excess of cyanide resulted lower catalyst TON (typically 10–50), compared to other palladium-catalyzed coupling reactions (TON 10 000 to 100 000).[62] In 2003, Beller *et al*. used syringe pump to assure a continuous addition of small volumes, so that the cyanide concentration would not be excessive.[62] Table 1.4 was the screening table for palladium-catalyzed cyanation using acetone cyanohydrin.[62]



Entry	$Pd(OAc)_2$ [mol%]	Pd/P	TMEDA [mol%]	Dosage rate [mmol h^{-1}]	t [h]	T [°C]	Yield[a] [%]	TON
1	2	1:4	20	0.1	21	80	>99	49.5
2	1	1:4	20	0.1	21	100	>99	99
3	0.5	1:4	10	0.1	21	100	>99	198
4	0.1	1:4	10	0.1	21	120	0	0
5	0.1	1:8	10	0.05	42	120	80	800
6	0.05	1:16	10	0.05	42	140	95	1900

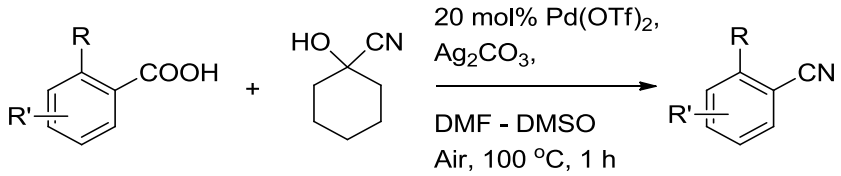
[a] GC yield (Internal standard = diethyleneglycol di-*n*-butyl ether)

Table 1.4 Palladium-catalyzed cyanation of 4-bromobenzotrifluoride using acetone cyanohydrins

In Table 1.4, 0.5 mol% catalyst was possible for success palladium-catalyzed cyanation (entry 3).[62] However, at 0.1 mol% palladium (Table 1.4, entry 5), a higher phosphine to palladium ratio and a slower addition of acetone cyanohydrin were essential to protect the catalyst.[62] Eventually, TON up to 1900 were achieved, which was the highest TON reported at that moment.[62]

The protocol of Beller *et al* was successfully applied in palladium-catalyzed cyanation of a variety of functionalized aryl halides.[62] In 2010, cyclohexanone cyanohydrin was discovered by Taran *et al.* and employed in palladium-catalyzed decarboxylative cyanation reaction of aryl carboxylic acids (Scheme 1.35).[117] However, the applications of cyclohexanone still need further investigation because in the publication of Taran *et al.*, the results were

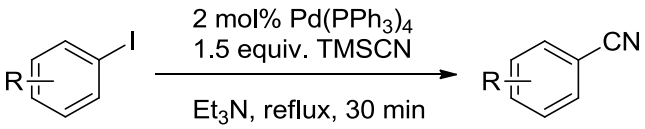
unsatisfactory.[117]



Scheme 1.35 Synthesis of aryl nitriles *via* decarboxylative cyanation of aryl carboxylic acids

1.7. Cyanation with trimethylsilyl cyanide (TMSCN)

The demand of TMSCN in organic synthesis as a useful reagent for cyanation was increasing in the last decade.[118-121] Chatani *et al.* was the first one employing TMSCN as cyanating agent for palladium-catalyzed cyanation of aryl iodides (Scheme 1.36).[122]

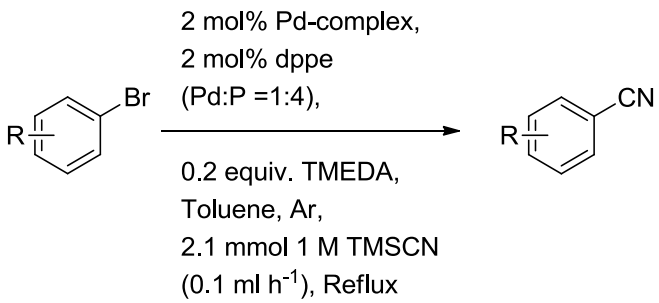


Scheme 1.36 Pd-catalyzed cyanation of aryl iodides with TMSCN developed by Chatani *et al*

The aryl iodides were cyanated in the presence of $Pd(PPh_3)_4$ catalyst to give good to excellent yield.[122] The critical points for the success were the choice of solvent (both polar and non-polar) and the use of triethylamine.[122] However, more effort is needed for the cyanations of aryl bromides and aryl chlorides.[122]

In 2003, Beller *et al.* explored an efficient catalytic system for the cyanation of aryl bromides with the aid of TMSCN (Scheme 1.37).[59] Two aryl palladium(II) complexes,

trans-bromo[4-(trifluoromethyl)phenyl]bis(triphenylphosphine)palladium(II) and *trans*-bromo(3-tolyl)bis(triphenylphosphine)palladium(II), offered similarly good results.[59]

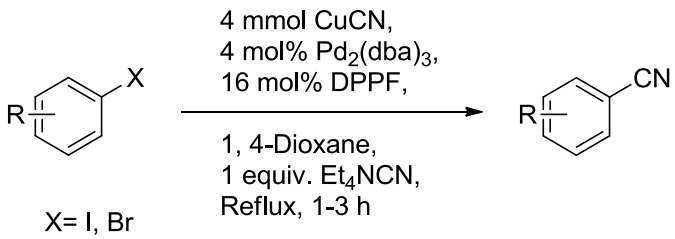


Scheme 1.37 Palladium-catalyzed cyanation of aryl bromide with TMSCN developed by Beller *et al*

The reaction between TMSCN and aryl palladium(II) halide complexes was simple and selective. Good to excellent yield of corresponding benzonitriles were obtained.[59] Similar to acetone cyanohydrin, the dosage of TMSCN must be controlled carefully so that the palladium-catalyzed cyanation of aryl bromides could be proceeded smoothly.[59] Successful cyanation of different activated, nonactivated, and deactivated aryl or heteroaryl bromides indicated the generality of the protocol.[59] To the best of our knowledge there has been no palladium-catalyzed cyanations of aryl chlorides and sulfonates with TMSCN reported in the literature.[60]

1.8. Miscellaneous cyanation

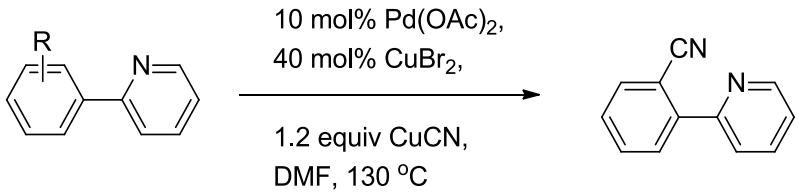
Apart from those cyanating surrogate mentioned in the previous sections, there are many alternative cyanide sources employed in the palladium-catalyzed cyanations. Cuprous cyanide is the oldest cyanation agent used in Rosenmund-von Braun and the Sandmeyer reaction (*vide supra)*. Sakamoto *et al.* was the first one to use cuprous cyanide in palladium-catalyzed cyanation of aryl and hetero-aryl iodides as well as bromides (Scheme 1.38).[123]



Scheme 1.38 Palladium-catalyzed cyanation of aryl halides and with CuCN developed Sakamoto *et al*

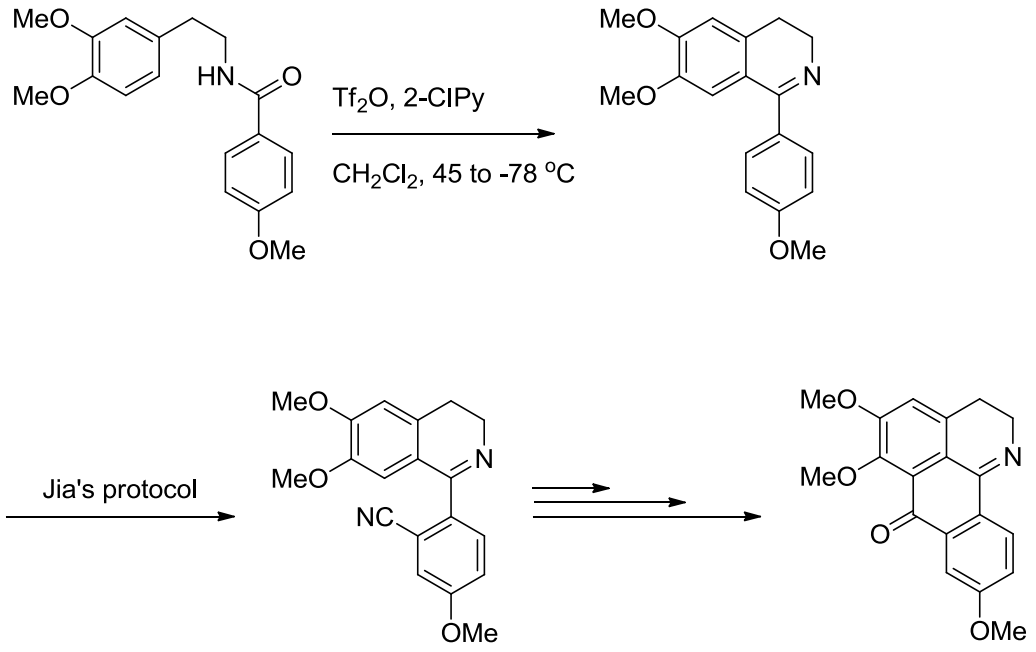
This cyanation method was generally applicable to arene, π-deficient, and π-sufficient hetero-aryl iodides as well as bromides such as *N*-(phenylsulfonyl) indoles, the pyrrole derivatives, and quinoline derivatives.[123] In the absence of palladium metal, the reaction of aryl bromides or iodides gave the corresponding nitriles in zero or low yields and the starting aryl bromides or iodides were recovered in high amount.[123] The presence of stoichiometric amount of Et_4NCN was critical for the palladium-catalyzed cyanation. The role of Et_4NCN was an additive.[123]

Recently, Jia *et al.* employed CuCN as a cyanating reagent in the palladium-catalyzed *ortho*-cyanation of aromatic C-H bonds (Scheme 1.39).[58]



Scheme 1.39 Chelation-Assisted Palladium-Catalyzed Direct Cyanation of 2-Arylpyridine C-H Bonds developed by Jia *et al*

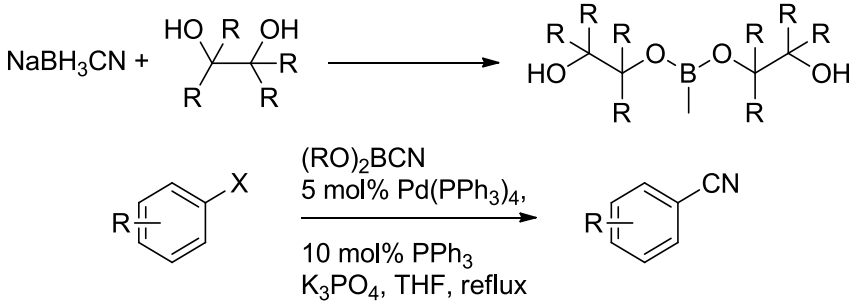
Successful cyanation of various 2-aryl nitrogen heterocycles was demonstrated in the presence of 10 mol% $Pd(OAc)_2$ with 0.4 equivalent $CuBr_2$ in DMF under air.[58] Noteworthy, this transformation neither required strong bases or expensive ligands, or the rigorous exclusion of air/moisture.[58] Jia *et al.* prepared the key intermediate of *Menispermum dauricum* DC (Menispermaceae) with their developed method (Scheme 1.40).[58]



Scheme 1.40 Concise pathway to a key intermediate of *Menispermum dauricum* DC

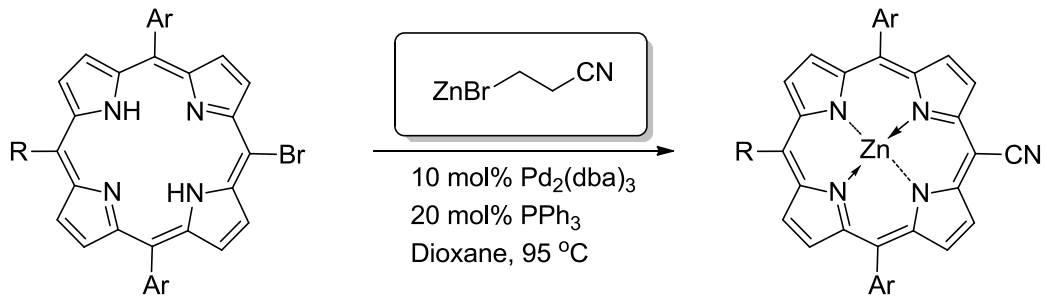
(Menispermaceae)

In 2001, Jiang *et al.* introduced a novel cyano- group source, dialkyl cyano-boronates, which could be used in palladium-catalyzed cyanation of aryl and hetero-aryl iodides, bromides and strongly activated chlorides. However, the yields were unsatisfactory (Scheme 1.41).[124] The synthetic method of dialkyl cyano-boronates was simple. It could be obtained from sodium cyano-borohydride and 1,2-diols (Scheme 1.41).[124]



Scheme 1.41 Synthesis and application of dialkyl cyanoboronates developed by Jiang *et al.*

In 2005, Suda *et al.* introduced another new cyanating agent, cyanoethylzinc bromide, for palladium-catalyzed cyanation of bromoporphyrins (Scheme 1.42).[125]

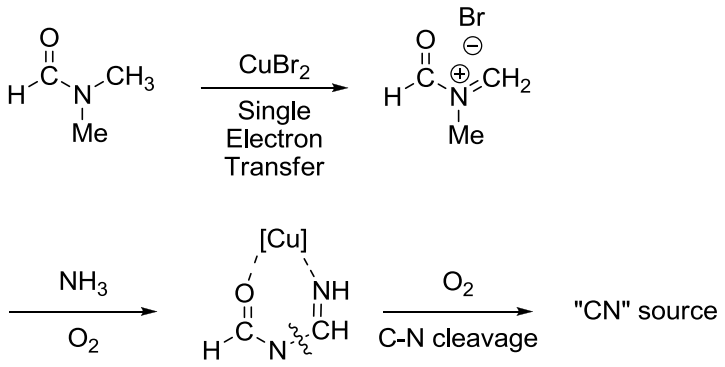


Scheme 1.42 Palladium-catalyzed cyanation of porphyrins with cyanoethylzinc bromide

Various Zn(II) porphyrins, including *meso*-mono-, *meso*-di-, and β-mono-cyano-substituted Zn(II) complexes were cyanated successfully with

this protocol.[125] After the oxidative addition of Pd(0) to the C-Br bond of the bromoporphyrin, subsequent metal ion insertion from the cyanoethylzinc bromide to the porphyrin core synchronously produced the cyanide ion and ethylene as a side product.[125] In 2010, Trapp *et al*. developed similar cyanation of aryl iodides to affprd the corresponding aryl nitriles and applied in a micro-capillary column reactor as the stationary phase (cyano-ethylmethyl-phenylmethyl-siloxane).[126] The low yield of transformation could be improved by tuning the flow rate of the reactor.[126]

More recently, Chang *et al* realized ammonia and DMF were the new cyanide source, which was demonstrated in the palladium-catalyzed cyanation of aryl C-H bonds.[127] A series of isotopic labeling experiments were performed and found that the carbon atom of cyanide was come from DMF whereas the nitrogen atom of cyanide was come from ammonia.[127] It was elucidated that the copper complex was presumably involved in the single electron transfer step to give an imine species, which was attacked by ammonia to provide an amidine intermediate (Scheme 1.43).[127] C-N bond cleavage in amidine intermediate occurred under the aerobic conditions, leading to "CN".[127]



Scheme 1.43 Mechanistic proposal for the "CN" Formation

Although the mechanistic study is not detail enough, the influence of such discovery is preeminent.[127] A number of arenes bearing various substituents at the *para-*, *meta-*, or *ortho-* position were readily cyanated in good yield and high selectivity.[127] This highly regioselective reaction afforded only one isomeric product even two different reacting sites were present.[127]

1.9. Decarboxylative arylation of potassium cyanoacetate

α-Arylated nitriles are essential structural motifs in natural product and pharmaceutically useful compounds (Figure 1.7).[128-133]

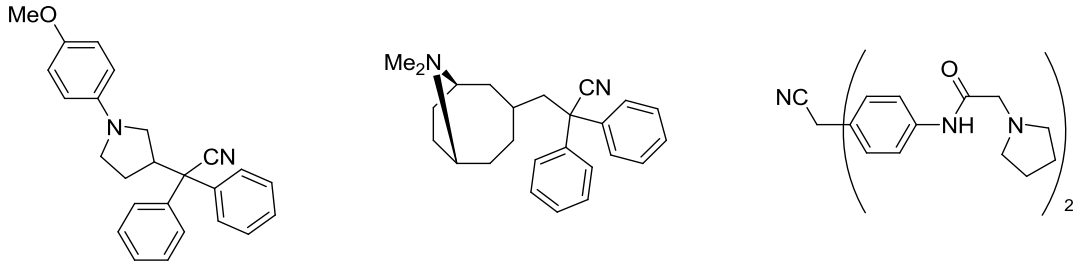
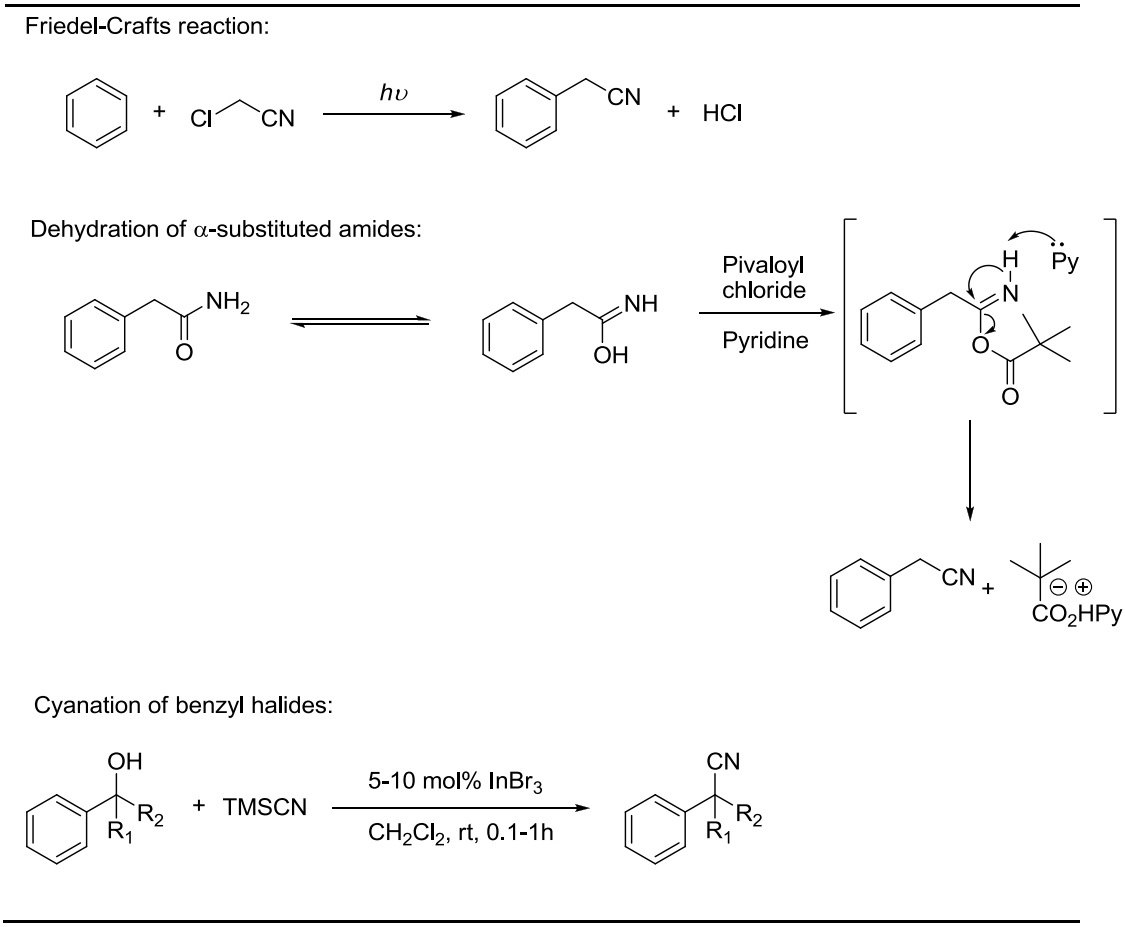


Figure 1.7 Selected examples of pharmaceutically useful α-diarylated nitriles

The nitrile moiety is a versatile functional group that allows further organic

transformations to give the corresponding substituted carboxylic acids, aldehydes, amides, and amines, as well as nitrogen heterocycles.[134] There a number of methodologies for the production of α-nitrile, for example, the Friedel-Crafts reactions,[135] dehydration of α-substituted amides,[136] and cyanation of benzyl halides[137] in traditional (Scheme 1.44).



Scheme 1.44 Traditional methods for synthesizing α-aryl nitriles

Recently, Hartwig[129-131] *et al.* and Verkade[132,134] *et al.* established a palladium-catalyzed α-arylations of nitriles with aryl halides independently. Strong base such as $NaN(TMS_3)_2$ was required thus this protocol was not applicable to base-sensitive functional group substituted aryl halides. Later on,

Hartwig *et al.* reported a significantly improved method, but relatively expensive reagents, α-silyl nitriles and zinc cyanoalkyl, were employed.[128]

In addition to traditional cross-coupling reaction, decarboxylative couplings are the novel alternative method for the construction of C-C bond formation. Most recently, Forgione,[138] Glorius,[139,140] Goossen,[141-146] Liu,[147-150] Myers,[151-153] Tunge,[154-157] and others[158-161] reported significantly advanced systems for decarboxylative coupling using various electrophiles and nucleophiles. However, to the best of our knowledge, literature reports about the development of decarboxylative method for accessing 2-arylacetonitrile-related skeletons are limited.[128]

1.10. Conclusion

The ongoing development of palladium-catalyzed cyanation indicates that the palladium-catalyzed cyanation tends to be the major synthetic method for the production of functionalized benzonitriles on the laboratory scale. However, none of cross-coupling method is prefect, so this reaction will be expected to receive improvement in the future. In the last two decades, many catalyst optimization strategies have emerged. But the cost of production of benzonitriles is still high because the high catalyst loading required, especially the expensive ligand and palladium metal sources. The use of potassium

hexacyanoferrate can effectively minimize the cost and it is safe for human as well as environmentally friendly. The drawbacks of heavy toxic metal wastes were solved.

Particularly, there is a growth in the development of domino and tandem reactions. Thus sequential cyanation and other transition metal-catalyzed cross coupling reaction sequences are receiving attention.

Recent publications showed that there is a growth in the development of simple decarboxyalative arylation of cyanoacetates using aryl halides and sulfonates.

Chapter 2 Palladium-catalyzed cyanation of aryl sulfonates

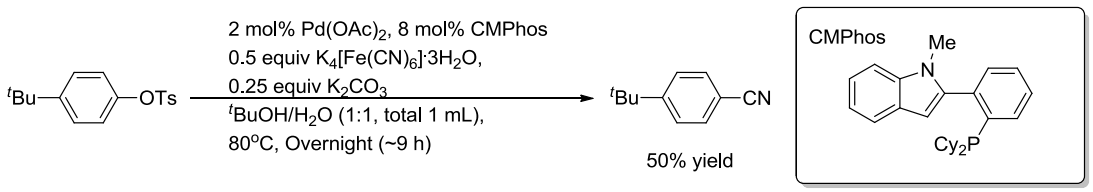
2.1. Introduction

Although the cyanation of aryl halides (mainly ArBr) is well established, the popularity of pseudo-halides (aryl triflates) in cyanation reactions is limited.[55,75,86,104,162,163] Possible constraints of this process may be the high cost of the triflating agent (e.g. Tf_2O), and the ease of decomposition of aryl triflates under basic reaction conditions, especially at high reaction temperatures (120–160 ℃). However, the development of phenolic derivatives as electrophilic partners is worthwhile. Since they may offer different or unique substitution of the aromatic ring, in which the corresponding aryl halides may not be commonly available or may require additional synthetic steps to manipulate the substitution pattern. Thus, the use of aryl mesylates or arene sulfonates, which are less expensive and more stable than aryl triflates, as cyanation substrates would be highly favorable.[164] Nickel-mediated processes with aryl mesylates were reported by Percec and co-workers in 1995.[165,166] Although aryl mesylates have several beneficial features, no

palladium-catalyzed cyanation was reported previously. Thus, a general palladium-catalyzed cyanation of aryl mesylates with potassium hexacyanoferrate(II) trihydrate is still in great demand.

2.2. Results and discussion

Initially, palladium-catalyzed cyanation of aryl tosylates was tested. The reaction of 4-*tert*-butylphenyl tosylate and potassium hexacyanoferrate(II) in the presence of catalytic amount of palladium(II) acetate and CMPhos in ^{t}BuOH/H_2O at 80℃ overnight (approximately 9 h) afforded the corresponding product in 50% yield according to GC analysis (Scheme 2.1). The usage of ^{t}BuOH for aryl sulfonates and the metal to ligand ratio were based on the previous studies of my group-mates.[37,167]

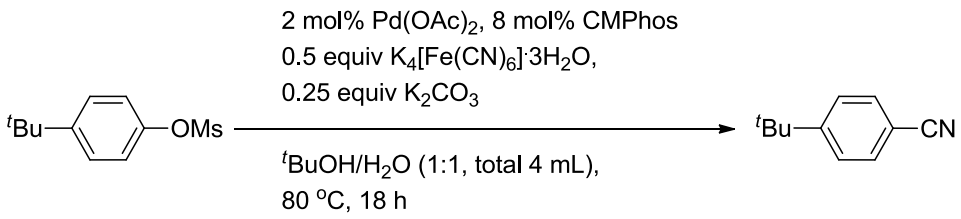


Scheme 2.1 Preliminary condition for palladium-catalyzed cyanation of 4-*tert*-butylphenyl tosylate

The positive results showed the potential of the palladium-catalyzed cyanation of aryl mesylate. Next, the investigation began with the palladium-catalyzed cyanation of electronically neutral 4-*tert*-butylphenyl mesylate. A series of different palladium species, bases and commercially available ligands,

especially our previously developed indolylphosphines were surveyed (Scheme 2.2). The effect of co-solvent for the reactions of aryl sufonates was also examined.

2.2.1 Base and solvent screening



Entry[a]	Base	Base loading (equiv to aryl mesylate)	Solvent	Yield [%][b]
1	K_2CO_3	0.5	^{t}BuOH/H_2O	36
2	K_2CO_3	0.25	^{t}BuOH/H_2O	43
3	K_2CO_3	0.125	^{t}BuOH/H_2O	90
4	K_2CO_3	0.05	^{t}BuOH/H_2O	0
5	K_2CO_3	0	^{t}BuOH/H_2O	0
6	Na_2CO_3	0.125	^{t}BuOH/H_2O	86
7	Cs_2CO_3	0.125	^{t}BuOH/H_2O	88
8	NaO^{t}Bu	0.125	^{t}BuOH/H_2O	10
9	KO^{t}Bu	0.125	^{t}BuOH/H_2O	52
10	K_3PO_4	0.125	^{t}BuOH/H_2O	90
11	K_2CO_3	0.125	MeCN/H_2O	89
12	K_2CO_3	0.125	Dioxane/H_2O	88
13	K_2CO_3	0.125	^{t}BuOH	3

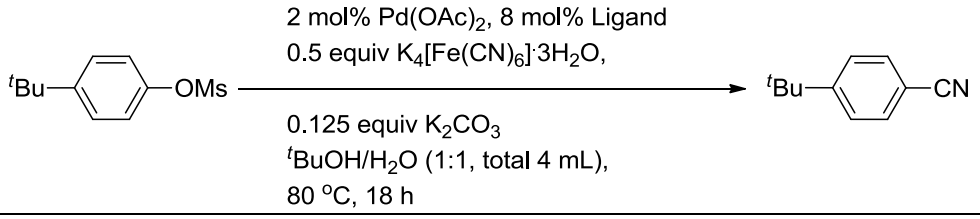
[a] Reaction conditions: 4-*tert*-butylphenyl mesylate (1.0 mmol), $K_4[Fe(CN)_6].3H_2O$ (0.5 mmol), 2 mol% $Pd(OAc)_2$, 8 mol% CMPhos, Base, Solvent (4.0 mL total), 80 °C, 18 h [b] GC yields with dodecane as internal standard

Table 2.1 Initial base and solvent screening of the palladium-catalyzed cyanation of a non-activated aryl mesylate

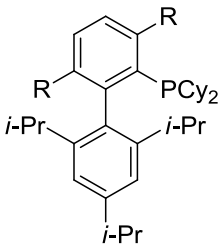
The amount of potassium carbonate was critical for the cyanation (Table 2.1, entries 1-5). Changing the amount of potassium carbonate gave significant

effect in the product yield (Table 2.1., entries 2, 4). Inorganic bases were found to assist the cyanation. Carbonated bases and K_3PO_4 were superior, whereas the reactions with NaO^tBu and KO^tBu provided poor product yield (Table 2.1, entries 3, 6-10). Attempted the cyanation with ^{t}BuOH as a solvent was inferior (Table 2.1, entry 13). These poor results might be attributed to low solubility of the cyanide source. Therefore, water was added as a co-solvent to the reaction system in attempt to improve the solubility of the $K_4[Fe(CN)]_6$ reagent. Under these improved conditions, the yield of aryl nitrile was increased dramatically to 90% (Table 2.1, entry 3). Inspired by these results, further experiments were conducted to determine the best solvent ratio. Surprisingly, the reaction even proceeded in water, without a co-solvent (Figure 2.1).

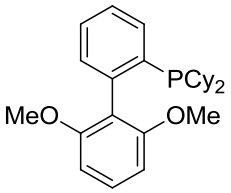
2.2.2 Ligand screening



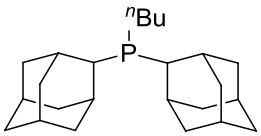
Ligand L:



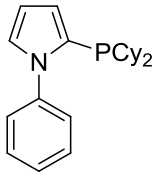
R = H, Xphos (2%)
R = OMe, BrettPhos (3%)



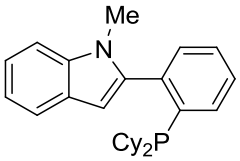
SPhos (11%)



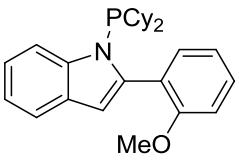
CataXium A (0%)



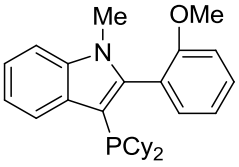
CataXium PCy (0%)



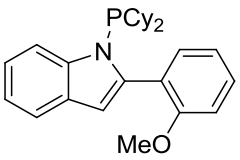
CM-Phos



L_1 (0%)



L_2 (0%)



L_3 (0%)

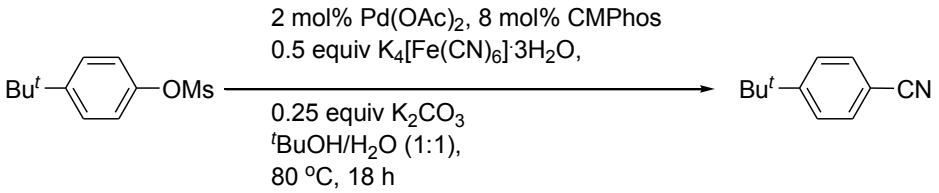
Reaction conditions: 1.0 mmol aryl mesylate, 0.5 mmol $K_4[Fe(CN)_6].3H_2O$, 2 mol% $Pd(OAc)_2$, 8 mol% Ligand, 0.125 mmol K_2CO_3, $^tBuOH/H_2O$ (1:1, total 4 mL), 80 °C, 18 h; Yields were determined by GC with dodecane as the internal standard. Cy = cyclohexyl

Scheme 2.2 Ligand screening for the palladium-catalyzed cyanation of 4-*tert*-butylphenyl mesylate

Poor conversion of the aryl mesylate was observed with the phosphine ligands XPhos,[168] BrettPhos,[169] and SPhos,[170] whereas the ligands CataCXium A[101] and CataCXium PCy[171] did not promote the cyanation. The

aminophosphine **L_1** and the C-P type phosphines **L_2** and **L_3** with a dicyclohexylphosphino group at the 3-position of the indole and N-H indole were also found to be inferior ligands for the desired reaction. Notably, with the ligand CMPhos,[37,172] in which the phosphino unit is attached to the non-indolyl ring, the desired product was obtained in 90% yield. A control experiment revealed that no cyanation product was formed in the absence of either the palladium precursor or CMPhos.

2.2.3 Catalyst loading screening



Entry[a]	"CN" source	Catalyst loading (mol% Pd)	Yield [%][b]
1	$K_4[Fe(CN)_6]\cdot 3H_2O$	4	55
2	$K_4[Fe(CN)_6]\cdot 3H_2O$	3	75
3	$K_4[Fe(CN)_6]\cdot 3H_2O$	2	90
4	$K_4[Fe(CN)_6]\cdot 3H_2O$	1	77
5	$K_4[Fe(CN)_6]\cdot 3H_2O$	0.8	28
6[c]	$K_4[Fe(CN)_6]\cdot 3H_2O$	2	65
7	NaCN	2	0
8	CuCN	2	0
9	$Zn(CN)_2$	2	2

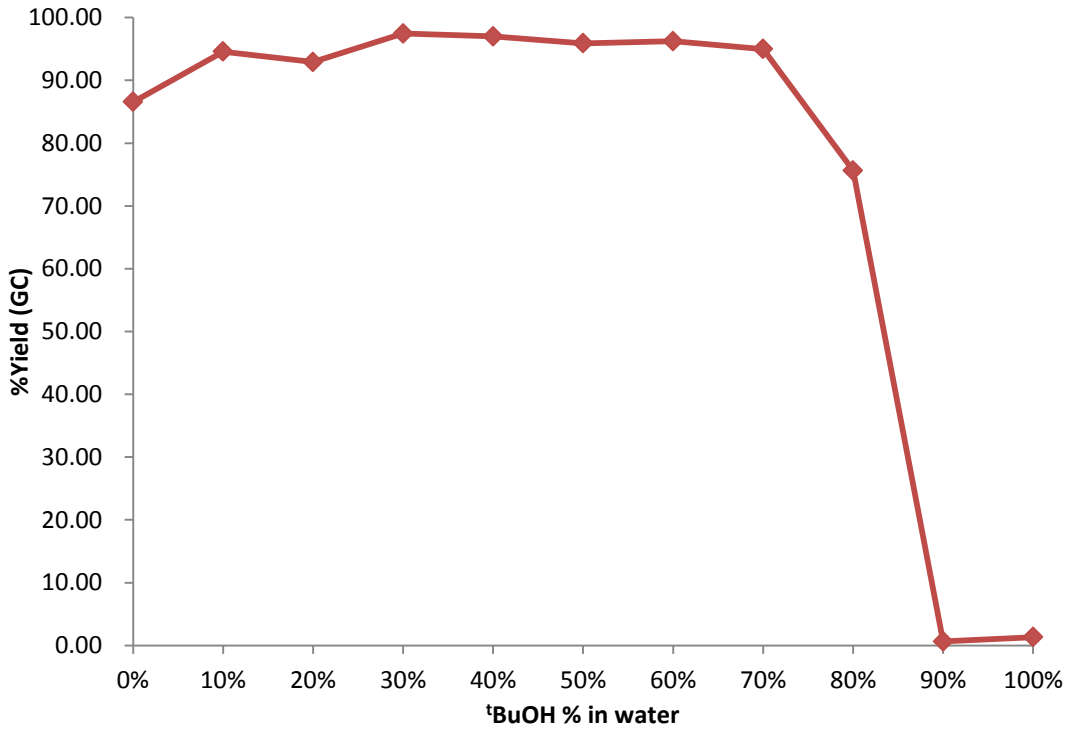
[a] Reaction conditions: 4-*tert*-butylphenyl mesylate (1.0 mmol), $K_4[Fe(CN)_6].3H_2O$ (0.5 mmol), 2 mol% $Pd(OAc)_2$, 8 mol% CMPhos, Base, solvent (4.0 mL total), 80 °C, 18 h. [b] GC yields with dodecane as internal standard. [c] Open to air

Table 2.2 Initial catalyst loading and cyanating source screenings of the palladium-catalyzed cyanation of a non-activated aryl mesylate

The optimal palladium loading was 2 mol% (Table 2.2, entry 3). Too high or low palladium loading gave poor results (Table 2.2, entries 1-2, 4-5). Besides, this catalytic system was found to be air sensitive. In the presence of air, the yield dropped from 90% to 65% (Table 2.2, entries 3 and 6). The other cyanide sources NaCN, CuCN, and $Zn(CN)_2$ did not promote the reaction (Table 2.2,

entries 7-9).

2.2.4 Effect of co-solvent (water) added to the reaction system of ArOMs



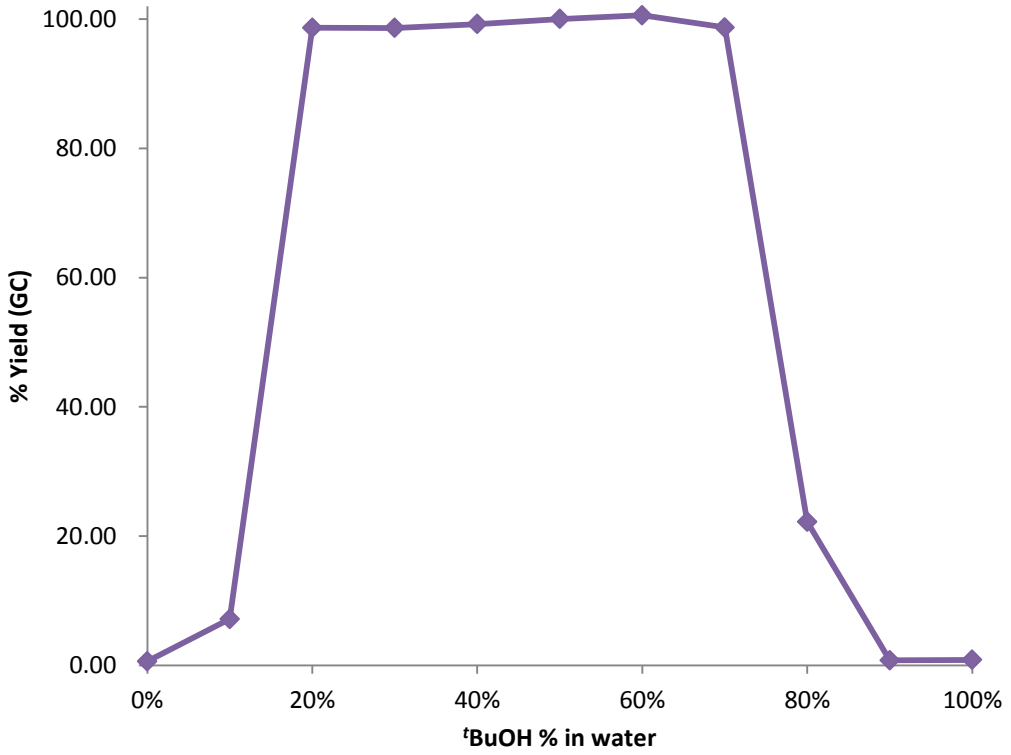
Reaction conditions: Aryl mesylate (1.0 mmol), $K_4[Fe(CN)_6] \cdot 3H_2O$ (0.5 mmol), $Pd(OAc)_2$ (0.02 mmol, 2 mol%), Pd : CMPhos (1:4), K_2CO_3 (0.125 mmol) in water/^{t}BuOH (indicated as the graph showed above) at 80 ℃ for 18 h. Calibrated GC yields were reported, using dodecane as the internal standard.

Figure 2.1 Effect of co-solvent(water) added to the benchmark conditions.

According to Figure 2.1, the reaction conditions were applicable in the range of 0% - 70% ^{t}BuOH in water. For above 80% ^{t}BuOH in water, $K_4[Fe(CN)_6]\cdot 3H_2O$ was hardly to be dissolved in the solvent, so the yields of product were dramatically dropped. Notably, the reaction was well conducted in sole water. It may be due to both $K_4[Fe(CN)_6]\cdot 3H_2O$ and 4-*tert*-butyl mesylate are soluble

in water at 80 ℃.

2.2.5 Effect of co-solvent (water) added to the reaction system of ArOTs



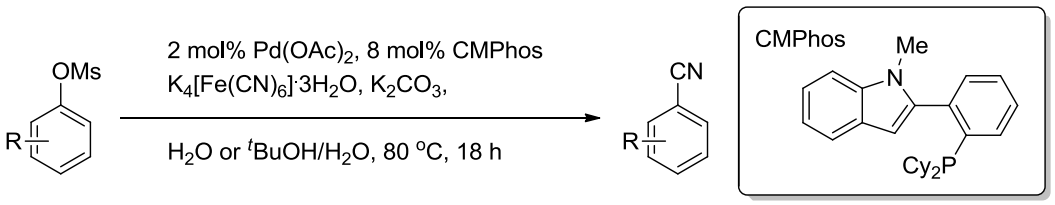
Reaction conditions: Aryl tosylate (1.0 mmol), $K_4[Fe(CN)_6]\cdot 3H_2O$ (0.5 mmol), $Pd(OAc)_2$ (0.02 mmol, 2 mol%), Pd : CMPhos (1:4), K_2CO_3 (0.125 mmol) in water/^{t}BuOH (indicated as the graph showed above) at 80 ℃ for 18 h. Calibrated GC yields were reported, using dodecane as the internal standard.

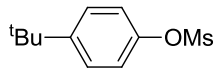
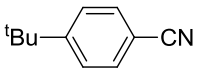
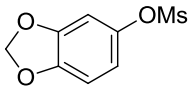
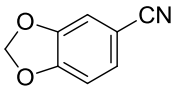
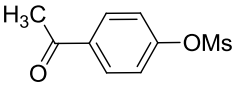
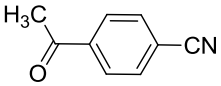
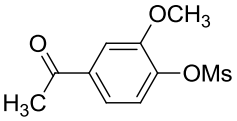
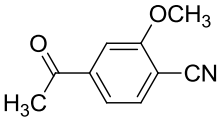
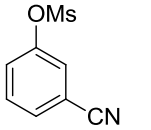
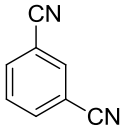
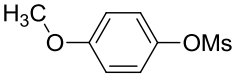
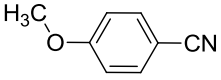
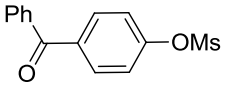
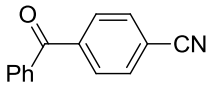
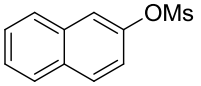
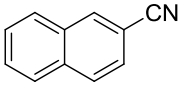
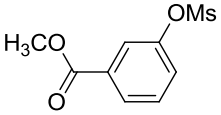
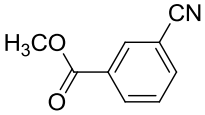
Figure 2.2. Effect of co-solvent (water) added to the aryl tosylate reaction conditions

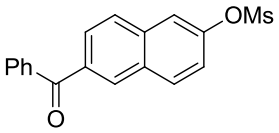
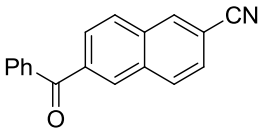
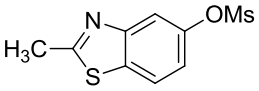
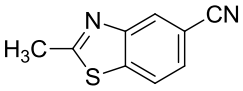
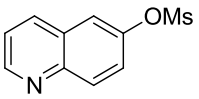
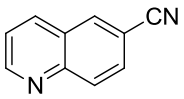
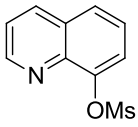
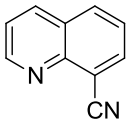
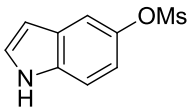
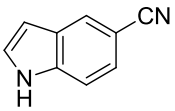
Unlike the aryl mesylate (Figure 2.1), aryl tosylate could not be cyanated when sole water medium was used (Figure 2.2). The workable range of aryl tosylate was narrower than aryl mesylate. Due to the convenience, 1:1 ratio (50% ^{t}BuOH in water) was selected for further investigation of scope of

palladium-catalyzed cyanation of aryl tosylates.

2.2.6 Scope of palladium-catalyzed cyanation of aryl mesylates



Entry[a]	ArOMs	ArCN	Solvent	Yield[b]
1 2[c]			Water ^{t}BuOH/H_2O	78%
3			Water	96%
4			Water	74%
5			Water	84%
6			Water	72%
7			^{t}BuOH/H_2O	91%
8			^{t}BuOH/H_2O	82%
9			^{t}BuOH/H_2O	72%
10			^{t}BuOH/H_2O	67%

11			^{t}BuOH/H_2O	81%
12			^{t}BuOH/H_2O	95%
13			^{t}BuOH/H_2O	96%
14			^{t}BuOH/H_2O	87%
15			^{t}BuOH/H_2O	93%

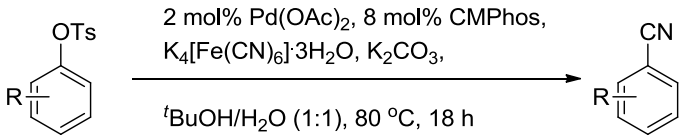
[a] Conditions: 1.0 mmol ArOMs; 0.5 mmol $K_4[Fe(CN_6)].3H_2O$; 2 mol%$Pd(OAc)_2$; $Pd(OAc)_2$: CMPhos = 1:4; 0.125 mmol K_2CO_3; 2.0 mL Deionized H_2O or 4.0 mL ^{t}BuOH/H_2O (3:1) [b] Isolated Yield [c] The reaction was carried out at 65 ^{o}C for 24h

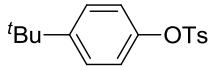
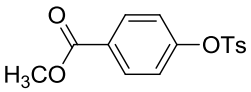
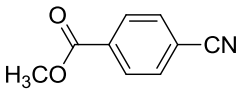
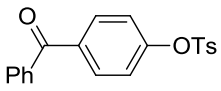
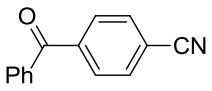
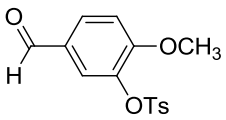
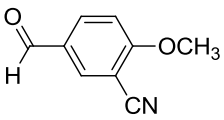
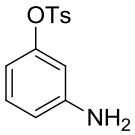
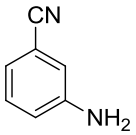
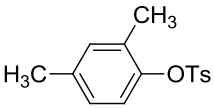
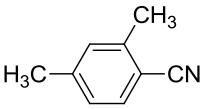
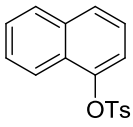
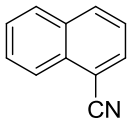
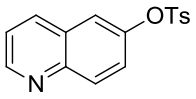
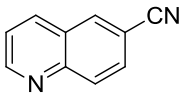
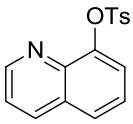
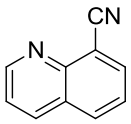
Table 2.3. Palladium-catalyzed cyanation of aryl mesylates

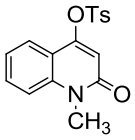
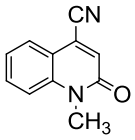
To test the effectiveness of the catalytic system, a variety of aryl mesylates were examined under the optimized reaction conditions (Table 2.3). Water was used as the only solvent when the substrates were soluble at 80 ℃ (Table 2.3, entries 1 and 3-6). When the reaction temperature was lowered to 65 ℃, the reaction still proceeded well and gave the desired product in good yield (Table 2.3, entry 2). However, in that case a ^{t}BuOH/H_2O mixture was necessary as the reaction medium. Common functional groups, such as keto, ester, and nitrile groups were compatible with the reaction conditions (Table 2.3, entries 3-11). Deactivated *para*-methoxyphenyl mesylate was a suitable coupling partner

(Table 2.3, entry 7). The cyanation of benzothiazolyl and quinolyl mesylates furnished the corresponding products in excellent yields (Table 2.3, entries 12-14). Notably, the cyanation of an unprotected indole afforded the nitrile product in 93% yield (Table 2.3, entry 15).

2.2.7 Scope of palladium-catalyzed cyanation of aryl tosylates



Entry[a]	ArOTs	ArCN	Solvent	Yield[b]
1 2			H_2O $^tBuOH/H_2O$	94%
3			$^tBuOH/H_2O$	69%
4			$^tBuOH/H_2O$	84%
5			$^tBuOH/H_2O$	89%
6			$^tBuOH/H_2O$	77%
7			$^tBuOH/H_2O$	43%
8			$^tBuOH/H_2O$	92%
9			$^tBuOH/H_2O$	96%
10			$^tBuOH/H_2O$	87%

11[c]			^{t}BuOH/H_2O	71%

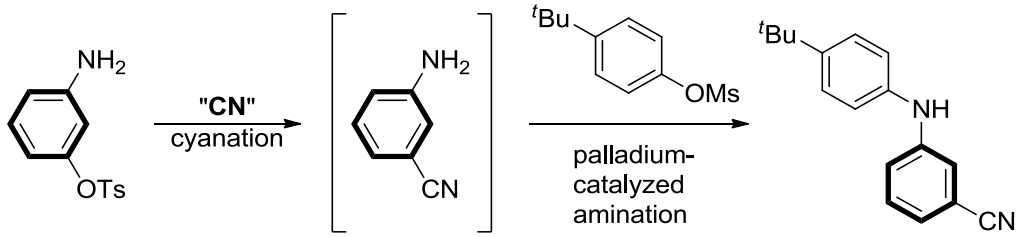
[a] Conditions: 1.0 mmol ArOTs; 0.5 equiv $K_4[Fe(CN_6)]\cdot 3H_2O$; 2 mol% $Pd(OAc)_2$; $Pd(OAc)_2$/CMPhos (1:4); 0.125 equiv K_2CO_3; ^{t}BuOH/H_2O=1:1 (total 2.0ml), 80 ^{o}C, 18 h
[b] Isolated Yield [c] 5 mol% $Pd(OAc)_2$; Ts = *p*-toluenesulfonyl.

Table 2.4 Palladium-catalyzed cyanation of tosylates

To further extend the catalytic system, an array of aryl tosylates was tested (Table 2.4). Interestingly, the reaction did not proceed when water was used as the only solvent (Table 2.4, entry 1 versus Table 2.3, entry 1), owing to the low solubility of the aryl tosylates. Hence, we used an organic co-solvent and finally identified the optimal reaction medium as a 1:3 ^{t}BuOH/water mixture. The yield was significantly improved (Table 2.4, entry 2). Ester, keto, aldehydes, and free amino groups were compatible under the reaction conditions (Table 2.4, entries 3-6). In addition to aryl tosylates, alkenyl tosylate was a suitable substrate for the cyanation reaction (Table 2.4, entry 11).

The manipulation of functionalized intermediates in a reaction sequence is crucial in organic synthesis.[133,173] Under the reaction conditions for cyanation, common functional groups were well tolerated. Thus, it was found possible to incorporate other functional groups, such as an NH_2 moiety, in the substrate for a further coupling reaction. To demonstrate the feasibility of this approach, a

one-pot sequential synthesis of an *N*-aryl amino-benzonitrile from the tosylate derived from 3-aminophenol by cyanation of the aryl tosylate and subsequent *N*-arylation of the amino group was carried out (Scheme 2.3).



Scheme 2.3 One-pot sequential cyanation-amination reaction (see experimental section for detailed procedure)

2.3. Conclusion

In summary, the palladium-catalyzed cyanation of aryl mesylates was demonstrated. The reaction temperature of 80 ℃ is the mildest ever reported for the coupling of aryl mesylates. Interestingly, the use of water as the solvent or a co-solvent was found to be essential. This palladium catalytic system exhibits excellent functional-group tolerance: nitrile, ester, keto, aldehyde, free amine, and heterocyclic groups remained intact during the course of reaction. Moreover, this system is also applicable to the cyanation of aryl and alkenyl tosylates. A one-pot cyanation–amination sequence demonstrated the suitability of this reaction for the introduction of a nitrile group and manipulation of another functional group in a synthetic pathway without isolation of the initial nitrile-substituted intermediate. Given the practical advantages of these sulfonating agents and the favorable cyanation conditions, we believe that this method will find widespread use in organic synthesis.

2.4. Experimental section

2.4.1 General considerations

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. All cyanation reactions were conducted in resealable screw cap Schlenk flask (approx. 20 mL volume) in the presence of Teflon coated magnetic stirrer bar (4 mm × 10 mm). Water was purified from deionized water under nitrogen. *tert*-Butanol was refluxing with sodium and distilled from calcium hydrides under nitrogen. Acetonitrile was distilled from calcium hydride under nitrogen.[174] Dioxane was distilled from sodium benzophenone ketyl under nitrogen.[174] Commercially available anhydrous NMP was distilled from dried molecular sieve under nitrogen. All cyanide sources were used as received. New bottle of *n*-butyl lithium was used (*Note*: since the concentration of *n*-BuLi from old bottle may vary, we recommend performing a titration prior to use).

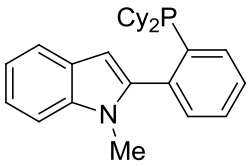
Thin layer chromatography was performed on pre-coated silica gel 60 F_{254} plates. Silica gel (70-230 and 230-400 mesh) was used for column chromatography. Melting points were recorded on an uncorrected Melting Point instrument. ^{1}H NMR spectra were recorded on a 400 MHz spectrometer.

Spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.26 ppm), or with acetone-D_6 (δ 2.05 ppm, the middle peak), or with C_6D_6 (δ 7.16 ppm), or with tetramethylsilane (TMS, δ 0.00 ppm) as the internal standard. Chemical shifts (δ) were reported as part per million (ppm) in δ scale downfield from TMS. ^{13}C NMR spectra were referenced to $CDCl_3$ (δ 77.0 ppm, the middle peak) or acetone-D_6 (δ 29.84 ppm, the middle peak) or with C_6D_6 (δ 128.06 ppm). ^{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 a mass spectrometer (ESIMS). GC-MS analysis was conducted on a GCD system using a column (30 m × 0.25 mm). The products described in GC yield were accorded to the authentic samples/dodecane calibration standard from GC-FID system. The known cyanation products were characterized by comparing to the corresponding ^{1}H- and ^{13}C-NMR reported in the literatures.

2.4.2 Procedures for aryl mesylates and tosylates synthesis

All mesylates used were generated from the corresponding phenols. The phenols and methanesulfonyl chloride reacted in dried dichloromethane with the presence of triethylamine according to the literature.[174]

2.4.3 Procedures for indolyl phosphine ligands synthesis



CMPhos was prepared according to the literature procedures.[37] Ligands **L_1- L_3** were synthesized based on the literature methods.[175,176]

2.4.4 General procedures for optimization of cyanation

General procedures for optimization:

$Pd(OAc)_2$ (4.5 mg, 0.020 mmol) and ligand (Pd:L = 1:4) were added into a Schlenk tube with the presence of magnetic stir bar which is Teflon-coated. The tube was evacuated and then pressurized with nitrogen for 3 cycles. Pre-complexation of palladium and ligand was initiated by injecting freshly distilled dry dichloromethane (2.0 mL) and Et_3N (0.1 mL) into the tube. The solution was stirred and warmed with hair drier till the solvent condensed on the tube wall. The solvent was removed under vacuum. 4-*tert*-Butylphenyl mesylate (1.0 mmol), K_2CO_3 (0.125 mmol) and potassium hexacyanoferrate (II) trihydrate (0.5 mmol) were charged successively to the tube followed by another 3 evacuation-nitrogen refill cycles. 2.0 ml water was used as solvent. The tube was immersed into a preheated 80 ℃ oil bath for 18 hours. After completion of reaction, the reaction tube was allowed to cool to room temperature. Dodecane (227 μL, internal standard), ethyl acetate and water were added. The organic layer was subjected to GC analysis. The GC yield obtained was previously calibrated by authentic sample/dodecane calibration curve.

2.4.5 General procedures for cyanation of aryl mesylates (Table 2.3 entry 1) and tosylates (Table 2.4, entry 1):

$Pd(OAc)_2$ (4.5 mg, 2 mol%) and CMPhos (32.3 mg, 8 mol%) were added into a Schlenk tube with the presence of magnetic stir bar which is Teflon-coated. The tube was evacuated and then pressurized with nitrogen for 3 cycles. Pre-complexation of palladium and ligand was initiated by injecting freshly distilled dry dichloromethane (2.0 mL) and Et_3N (0.1 mL) into the tube. The solution was stirred and warmed with hair drier till the solvent condensed on the tube wall. The solvent was removed under vacuum. Aryl mesylate (1.0 mmol), K_2CO_3 (0.125 mmol), and potassium hexacyanoferrate (II) trihydrate (0.5 mmol) were charged successively to the tube followed by another 3 evacuation-nitrogen refill cycles. 2.0 ml water was used as solvent. The tube was immersed into a preheated 80 ℃ oil bath for 18 hours. The reaction was quenched by cooling to ambient temperature and added with EtOAc and water. The organic supernatant was analyzed by GC. The organic layer was isolated and the remained aqua was further extracted with EtOAc (10.0 mL × 3). The combined organic phase was

concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (230-400 mesh). The pure fraction was collected, dried under vacuum, and followed proton (^{1}H) and carbon (^{13}C) NMR characterization.

2.4.6 General procedures for one-pot sequential cyanation-amination reaction:

Cyanation of aryl tosylate:

$Pd(OAc)_2$ (9.0 mg, 4 mol%) and CMPhos (32.3 mg, 8 mol%) were added into a Schlenk tube with the presence of magnetic stir bar which is Teflon-coated. The tube was evacuated and then re-filled with nitrogen for 3 cycles. Pre-complexation of palladium and ligand was initiated by injecting freshly distilled dichloromethane (1.0 mL) and Et_3N (0.2 mL) into the tube. The solution was stirred and warmed with hair drier till the solvent condensed on the tube wall. The solvent was removed under vacuum. 3-aminophenyl-4-methyl tosylate (1.0 mmol), K_2CO_3 (0.125 mmol), and potassium hexacyanoferrate (II) trihydrate (0.5 mmol) were charged successively to the tube followed by another 3 evacuation-nitrogen refill cycles. Water (1.0 mL) and acetonitrile (1.0 mL) was added as a solvent mixture. The tube was immersed into a preheated 70 ℃ oil bath for 18 hours. The reaction was allowed to reach ambient temperature.

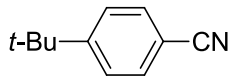
Amination between aryl mesylate and

tosylate:[37]

4-(*tert*-butyl) phenyl mesylate (1.2 mmol), potassium carbonate (2.5 mmol) and phenylboronic acid (5 mg) were poured into the tube under counter flow of nitrogen. ^{t}BuOH (1 mL) was used as solvent. The tube was immersed into a preheated 110 ℃ oil bath for 24 hours. The reaction was quenched by cooling to ambient temperature and added with EtOAc and water. The organic supernatant was analyzed by GC. The organic layer was separated and the remained aqua was further extracted with EtOAc (10mL × 3). The combined organic phase was concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (230-400 mesh). The pure fractions were collected, dried under vacuum, and followed by proton (^{1}H) and carbon (^{13}C) NMR characterization.

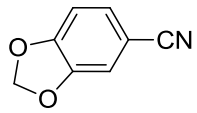
2.4.7 Characterization data of aryl nitriles from ArOMs

4-*tert*-Butylbenzonitrile (Table 2.3, entries 1 and 2) [177]



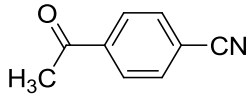
Ether : n-Hexane = 1:50, R_f = 0.2; ^{1}H NMR (400 MHz, $CDCl_3$). δ1.32 (s, 9H), 7.48 (d, 2H, *J* = 8.8Hz), 7.58 (d, 2H, *J* = 8.8Hz); ^{13}C NMR (100 MHz, $CDCl_3$). δ30.85, 35.17, 109.22, 119.06, 126.09, 131.87, 156.56; MS(EI) *m/z* (relative intensity) 159 (M^+, 19), 144 (100), 116 (65), 104 (14), 89 (8).

Piperonylnitrile (Table 2.3, entry 3) [178]



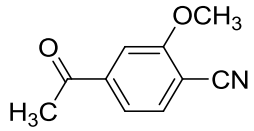
EA : n-Hexane = 2:8, R_f = 0.4; ^{1}H NMR (400 MHz, $CDCl_3$). δ6.05 (s, 2H), 6.84 (d, 1H, *J* = 8Hz), 6.99 (d, 1H, *J* = 1.6Hz), 7.18 (dd, 1H, *J* = 8Hz, 1.6Hz); ^{13}C NMR (100 MHz, $CDCl_3$). δ102.12, 104.73, 108.97, 111.20, 118.74, 128.04, 147.88, 151.40; MS(EI) *m/z* (relative intensity) 147 (M^+, 61), 146 (100), 89 (7), 62(15).

4-Acetylbenzonitrile (Table 2.3, entry 4) [179]



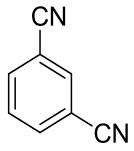
EA : n-Hexane = 2:8, R_f = 0.3; ^{1}H NMR (400 MHz, $CDCl_3$). δ2.60(s, 3H), 7.73 (d, 2H, *J* = 8.4Hz), 8.00 (d, 2H, *J* = 8.8Hz); ^{13}C NMR (100 MHz, $CDCl_3$). δ26.57, 116.15, 117.75, 128.52, 132.33, 139.75, 196.39; MS(EI) *m/z* (relative intensity) 145 (M^+, 17), 130 (100), 102 (48), 75 (13).

2-Methoxy-4-cyanoacetophenone (Table 2.3, entry 5)[180]



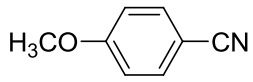
EA : n-Hexane = 2:8, R_f = 0.2; ^{1}H NMR (400 MHz, $CDCl_3$). δ2.58 (s, 3H), 3.93 (s, 3H), 7.48-7.52 (m, 2H), 7.60 (d, 1H, *J* = 8.0Hz); ^{13}C NMR (100 MHz, $CDCl_3$). δ26.66, 56.14, 105.64, 109.83, 115.40, 120.61, 133.88, 141.44, 161.10, 196.45; MS(EI) *m/z* (relative intensity) 175 (M^+, 42), 160 (100), 132 (17), 117 (23).

Isophthalonitrile (Table 2.3, entry 6)[181]



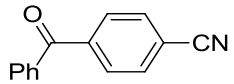
EA : n-Hexane = 2:8, R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$). δ7.66 (t, 1H, *J* = 7.8Hz), 7.89 (d, 1H, *J* = 1.6Hz), 7.91 (d, 1H, *J* = 1.6Hz), 7.96 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$). δ114.06, 116.52, 130.28, 135.35, 135.94; MS(EI) *m/z* (relative intensity) 128 (M^+, 100), 101 (20), 75 (11).

4-Methoxybenzonitrile (Table 2.3, entry 7)[178]



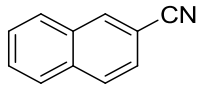
Ether : n-Hexane = 2:8, R_f = 0.3; ^{1}H NMR (400 MHz, $CDCl_3$). δ3.83 (s, 3H), 6.93 (d, 2H, *J* = 8.8Hz), 7.55 (d, 2H, *J* = 8.8Hz); ^{13}C NMR (100 MHz, $CDCl_3$). δ55.41, 103.76, 114.63, 119.08, 133.81, 162.72; MS(EI) *m/z* (relative intensity) 133 (M^+, 100), 118 (11), 103 (37), 90 (47), 76 (10).

4-Benzoylbenzonitrile (Table 2.3, entry 8)[182]



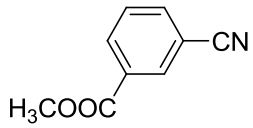
EA : n-Hexane = 2:8, R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$). δ7.49(t, 2H, *J* = 7.6Hz), 7.62(t, 1H, *J* = 7.4Hz), 7.76 (d, 4H, *J* = 8.8Hz), 7.85 (d, 2H, *J* = 8.8Hz); ^{13}C NMR (100 MHz, $CDCl_3$). δ115.47, 117.86, 128.48, 129.90, 130.06, 132.01, 133.16, 136.17, 141.05, 194.82; MS(EI) *m/z* (relative intensity) 207 (M^+, 60), 130 (24), 105 (100), 77 (42).

2-Naphthonitrile (Table 2.3, entry 9)[181]



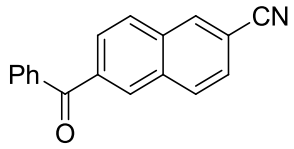
EA : n-Hexane = 2:8, R_f = 0.6; ^{1}H NMR (400 MHz, $CDCl_3$). δ7.54 – 7.64 (m, 3H), 7.84 (t, 3H, *J* = 7.4Hz), 8.16 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$). δ109.12, 119.07, 126.08, 127.46, 127.85, 128.19, 128.86, 128.98, 131.99, 133.90, 134.40; MS(EI) *m/z* (relative intensity) 153 (M^+, 100), 126 (17), 63 (5).

Methyl-3-cyanobenzoate (Table 2.3, entry 10) [183]



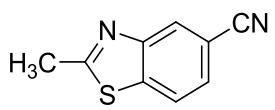
EA : n-Hexane = 2:8, R_f = 0.4; ^{1}H NMR (400 MHz, $CDCl_3$). δ3.93 (s, 3H), 7.57 (t, 1H, *J* = 7.8Hz), 7.81 (d, 1H, *J* = 7.6Hz), 8.24 (d, 1H, *J* = 7.6Hz), 8.29 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$). δ52.58, 112.82, 117.75, 129.35, 131.29, 133.12, 133.52, 135.86, 164.94; MS(EI) *m/z* (relative intensity) 161 (M^+, 26), 130 (100), 102 (47), 75 (16).

6-Benzoyl-2-naphthonitrile (Table 2.3, entry 11)[184]



EA : n-Hexane = 1:20, R_f = 0.1; ^{1}H NMR (400 MHz, $CDCl_3$). δ7.51 (t, 2H, *J* = 7.6Hz), 7.61-7.66 (m, 2H), 7.83 (d, 2H, *J* = 6.8Hz), 7.98 (d, 3H, *J* = 8.0Hz), 8.26 (s, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$). δ111.39, 118.55, 127.12, 127.35, 128.38, 128.65, 129.94, 130.39, 130.85, 132.77, 133.45, 133.66, 136.92, 137.43, 195.71; MS(EI) *m/z* (relative intensity) 257 (M^+, 90), 180 (78), 152 (55), 105 (100), 77 (67).

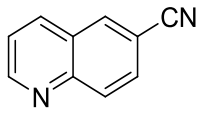
2-Methyl-5-benzothiazolecarbonitrile (Table 2.3, entry 12)[185]



EA : n-Hexane = 2:8, R_f = 0.3; ^{1}H NMR (400 MHz, $CDCl_3$). δ2.83 (s, 3H), 7.52

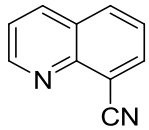
(dd, 1H, *J* = 8.4Hz, 1.6), 7.87 (d, 1H, *J* = 8.4Hz), 8.16 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$). δ20.13, 109.42, 118.65, 122.36, 126.30, 126.94, 140.51, 152.83, 169.66; MS(EI) *m/z* (relative intensity) 174 (M^+, 100), 133 (17), 69 (17).

Quinoline-6-carbonitrile (Table 2.3, entry 13)[89]



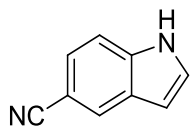
EA : n-Hexane = 4:6, R_f = 0.3; ^{1}H NMR (400 MHz, $CDCl_3$). δ7.51 (dd, 1H, *J* = 8.4Hz, 4.4Hz), 7.80 (d, 1H, *J* = 6.8Hz), 8.13-8.19 (m, 3H), 9.01 (d, 1H, *J* = 2.4Hz); ^{13}C NMR (100 MHz, $CDCl_3$). δ110.20, 118.34, 122.59, 127.37, 129.94, 130.89, 133.97, 136.22, 148.93, 153.12; MS(EI) *m/z* (relative intensity) 154 (M^+, 100), 127 (25), 100 (8).

8-Quinolinecarbonitrile (Table 2.3, entry 14)[55]



EA : n-Hexane = 4:6, R_f = 0.4; ^{1}H NMR (400 MHz, $CDCl_3$). δ7.43 (dd, 1H, *J* = 8.4Hz, 4.4Hz), 7.49 (t, 1H, *J* = 7.8Hz), 7.96 (t, 2H, *J* = 7.8Hz), 8.13 (d, 1H, *J* = 6.8Hz), 8.92 (d, 1H, *J* = 2.8Hz); ^{13}C NMR (100 MHz, $CDCl_3$). δ112.36, 116.98, 122.44, 125.53, 127.67, 132.70, 135.15, 136.22, 146.89, 152.03; MS(EI) *m/z* (relative intensity) 154 (M^+, 100), 127 (30), 100(9), 75(8).

1*H*-indole-5-carbonitrile (Table 2.3, entry 15) [186]

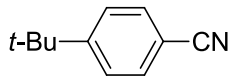


EA : n-Hexane = 2:8, R_f = 0.1; ^{1}H NMR (400 MHz, Acetone-D_6). δ6.64 (s, 1H), 7.41 (dd, 1H, *J* = 8.4Hz, 1.6Hz), 7.53 (t, 1H, *J* = 2.8Hz,), 7.61 (d, 1H, *J* =

8.8Hz), 8.04 (s, 1H), 10.76 (bs, 1H) ; ^{13}C NMR (100 MHz, Acetone-D_6). δ102.95, 103.26, 113.30, 121.23, 124.72, 126.54, 128.31, 128.77, 138.74 MS(EI) *m/z* (relative intensity) 142 (M^+, 100), 115 (36), 88 (10).

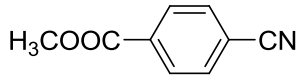
2.4.8 Characterization data of aryl nitriles from ArOTs

4-*tert*-Butylbenzonitrile (Table 2.4, entries 1 and 2)[177]



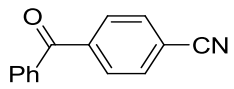
Ether: n-Hexane = 1:50, R_f = 0.20; ^{1}H NMR (400 MHz, $CDCl_3$). δ1.30 (s, 9H), 7.46 (d, 2H, *J* = 8.0Hz), 7.55 (d, 2H, *J* = 8.4Hz); ^{13}C NMR (100 MHz, $CDCl_3$). δ30.70, 35.01, 109.08, 118.88, 125.96, 131.70, 156.39; MS(EI) *m/z* (relative intensity) 159 (M^+, 19), 144 (100), 116 (65), 104 (14), 89 (8).

Methyl-4-cyanobenzoate (Table 2.4, entry 3)[181]



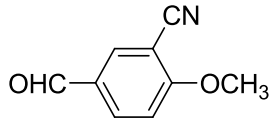
EA : n-Hexane = 2:8, R_f = 0.4; ^{1}H NMR (400 MHz, $CDCl_3$). δ3.93 (s, 3H), 7.72 (d, 2H, *J* = 8.8Hz), 8.10 (d, 2H, *J* = 8.4Hz); ^{13}C NMR (100 MHz, $CDCl_3$). δ52.58, 116.25, 117.82, 129.96, 132.10, 133.79, 165.27; MS(EI) *m/z* (relative intensity) 161 (M^+, 26), 130 (100), 102 (45), 75 (15).

4-Benzoylbenzonitrile (Table 2.4, entry 4)[182]



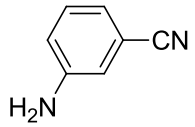
Ether : n-Hexane = 2:8, R_f = 0.35; ^{1}H NMR (400 MHz, $CDCl_3$). δ7.52 (t, 2H, *J* = 8.0Hz), 7.64 (t, 1H, *J* = 7.4Hz), 7.77 – 7.81 (m, 4H), 7.88 (d, 2H, *J* = 8.8Hz); ^{13}C NMR (100 MHz, $CDCl_3$). δ115.66, 117.98, 128.61, 130.04, 130.21, 132.14, 133.30, 136.33, 141.23, 194.99; MS(EI) *m/z* (relative intensity) 207 (M^+, 55), 130 (25), 105 (100), 77 (43), 51 (20).

5-Formyl-2-methoxybenzonitrile (Table 2.4, entry 5) [187]



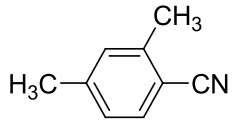
EA : n-Hexane = 2:8, R_f = 0.2; ^{1}H NMR (400 MHz, $CDCl_3$). δ4.04 (s, 3H), 7.13 (d, 1H, *J* = 8.8Hz), 8.09 (d, 2H, *J* = 8.0Hz), 9.90 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$). δ56.70, 102.99, 111.67, 115.02, 129.73, 135.56, 135.83, 165.17, 188.70; MS(EI) *m/z* (relative intensity) 161 (M^+, 61), 160 (100), 132 (8), 117 (17).

3-Aminobenzonitrile (Table 2.4, entry 6)[188]



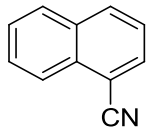
EA : n-Hexane = 2:8, R_f = 0.3; ^{1}H NMR (400 MHz, C_6D_6). δ2.88 (bs, 2H), 6.15 (d, 1H, *J* = 7.6Hz), 6.22 (s, 1H), 6.59 – 6.66 (m, 2H); ^{13}C NMR (100 MHz, C_6D_6). δ113.31, 117.26, 118.60, 119.49, 121.24, 129.91, 147.55; MS(EI) *m/z* (relative intensity) 118(M^+, 100), 91 (33), 64 (11).

2,4-Dimethylbenzonitrile (Table 2.4, entry 7)[102]



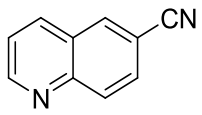
EA : n-Hexane = 2:8, R_f = 0.6; ^{1}H NMR (400 MHz, $CDCl_3$). δ2.36 (s, 3H), 2.48 (s, 3H), 7.05 (d, 1H, *J* = 8.0Hz), 7.11 (s, 1H), 7.45 (d, 1H, *J* = 7.6Hz); ^{13}C NMR (100 MHz, $CDCl_3$). δ20.21, 21.59, 109.56, 118.35, 126.93, 130.89, 132.25, 141.62, 143.36; MS(EI) *m/z* (relative intensity) 131(M^+, 100), 116 (100), 103 (12), 77 (12).

1-Naphthonitrile (Table 2.4, entry 8)[40]



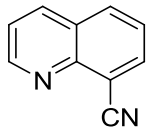
EA : n-Hexane = 2:8, R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$). δ7.50 (t, 1H, *J* = 7.6Hz), 7.61 (t, 1H, *J* = 6.8Hz), 7.68 (t, 1H, *J* = 7.0Hz), 7.90 (t, 2H, *J* = 7.2Hz), 8.06 (d, 1H, *J* = 8.0Hz), 8.22 (d, 1H, *J* = 8.4Hz); ^{13}C NMR (100 MHz, $CDCl_3$). δ110.06, 117.72, 124.82, 125.01, 127.45, 128.49, 128.56, 132.23, 132.51, 132.81, 133.18; MS(EI) *m/z* (relative intensity) 153 (M^+, 100), 126 (33), 99 (5), 87 (3), 76 (11), 63 (12), 50 (6).

Quinoline-6-carbonitrile (Table 2.4, entry 9)[89]



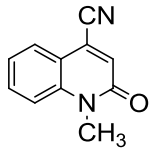
EA : n-Hexane = 4:6, R_f = 0.3; ^{1}H NMR (400 MHz, $CDCl_3$). δ7.50 (dd, 1H, *J* = 8.4Hz, 4.4Hz), 7.80 (d, 1H, *J* = 6.8Hz), 8.13-8.19 (m, 3H), 9.01 (d, 1H, *J* = 4.4Hz); ^{13}C NMR (100 MHz, $CDCl_3$). δ110.21, 118.34, 122.59, 127.38, 129.95, 130.90, 133.98, 136.22, 148.94, 153.12; MS(EI) *m/z* (relative intensity) 154 (M^+, 100), 127 (24), 100 (8), 75 (7).

8-Quinolinecarbonitrile (Table 2.4, entry 10)[55]



EA : n-Hexane = 4:6, R_f = 0.4; ^{1}H NMR (400 MHz, $CDCl_3$). δ7.48 (dd, 1H, *J* = 8.4Hz, 4.4Hz), 7.54 (t, 1H, 7.8Hz), 8.01 (t, 2H, *J* = 8.0Hz), 8.18 (d, 1H, *J* = 6.4Hz), 8.98 (d, 1H, *J* = 2.4Hz); ^{13}C NMR (100 MHz, $CDCl_3$). δ112.61, 117.07, 122.56, 125.65, 127.83, 132.78, 135.28, 136.32, 147.10, 152.19; MS(EI) *m/z* (relative intensity) 154 (M^+, 100), 127 (33), 100 (12), 75 (11).

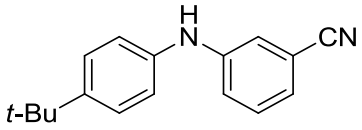
1-Methyl-2-oxo-1,2-dihydroquinoline-4-carbonitrile (Table 2.4, entry 11)[189]



EA : n-Hexane = 4:6, R_f = 0.4; ^{1}H NMR (400 MHz, $CDCl_3$). δ3.71 (s, 3H), 7.08 (s, 1H), 7.36 (t, 1H, *J* = 7.6Hz), 7.42 (d, 1H, *J* = 8.8Hz), 7.69 (t, 1H, *J* = 7.4Hz), 7.88 (d, 1H, *J* = 6.8Hz); ^{13}C NMR (100 MHz, $CDCl_3$). δ114.24, 114.72, 117.02, 122.47, 123.28, 126.56, 128.58, 132.53, 139.85, 159.64; MS(EI) *m/z* (relative intensity) 184 (M^+, 100), 156 (56), 128 (11), 114 (14), 101 (10), 88 (7), 77 (8), 63 (8), 51(7).

2.4.9 One-pot sequential cyanation-amination reaction

3-((4-(*tert*-Butyl)phenyl)amino)benzonitrile (Scheme 2.3)



Ether : n-Hexane = 2:8, R_f = 0.3; ^{1}H NMR (400 MHz, Acetone-D_6). δ1.31 (s, 9H), 7.09-7.15 (m, 3H), 7.31-7.34 (m, 2H), 7.35-7.39 (m, 2H), 7.66 (bs, 1H); ^{13}C NMR (100 MHz, Acetone-D_6). δ113.69, 118.28, 119.62, 120.24, 120.48, 122.80, 126.96, 131.12, 139.93, 145.84, 146.66; MS(EI) *m/z* (relative intensity) 251 (M^+, 27), 235 (100), 207 (8), 119 (4), 103 (5), 77 (2). HRMS: calc. For $C_{17}H_{18}N_2$: 251.1548, found 251.1552.

Chapter 3 Palladium-catalyzed cyanation of aryl halides

3.1. Introduction

The major disadvantages of mentioned cyanating sources used for palladium catalyzed cyanation are their toxicity to environment and the formation of inactive palladium(II) cyano compounds which no longer participating in the reaction. This gives rise to the intriguing development of a novel cyanation using an extraordinary ideal cyanating source, potassium hexacyanoferrate(II) trihydride ($K_4[Fe(CN)_6 \cdot 3H_2O]$), by Beller *et al*. in 2004.[93-95] However, up to date, there is no literature about the mechanistic investigations on the function of $K_4[Fe(CN)_6 \cdot 3H_2O]$ in the palladium-catalyzed cyanation of aryl halides and pseudo-halides.[60]

Recently, Ren developed an environmental friendly and high efficient reaction condition using commercially available *i*-propanol.[66] Water facilitates the cyanation because water helps to stabilize $K_4[Fe(CN)_6] \cdot 3H_2O$.[66] This reaction no longer needed an inert atmosphere and dry solvents for palladium catalyzed cyanation of aryl bromides with $K_4[Fe(CN)_6 \cdot 3H_2O]$. Grossman *et al.*

made use of ligand protected the palladium metal center from oxidation due to air. [99] Although this catalyst was insensitive against air, it worked well for the conversion of aryl bromides at comparably mild reaction temperature, approximate 85-90 ℃.[99] It hardly functioned in the cyanation of aryl chlorides.[99]

In 2008, Ryberg reported the first Pd-catalyzed cyanation of aryl bromides operating successfully on 6.7 kg scale under mild conditions, for example, 3 hours at 50 ℃ with an isolated yield of 90% corresponding to the model substrate.[81] Beller *et al.* used sterically hindered and electron-rich ligand - CataCXium A[101] which has been commercially available since 2004, in palladium-catalyzed cyanation of aryl chlorides.[102] The catalyst loading was low, only 0.25 - 0.5mmol $Pd(OAc)_2$, enough for the transformation of electron-rich, electron-poor, hetero-cyclic and sterically hindered aryl chlorides.[102] Although the difficult substrates such as chlorophenols and chloroanilines could be cyanated, the different phosphine ligands were needed.[103]

To the best of our knowledge, there has been limited literature report regarding cyanation of aryl chlorides mediated by $K_4[Fe(CN)_6]$ under mild reaction conditions.[103] Although the reaction temperature of 50℃ had been

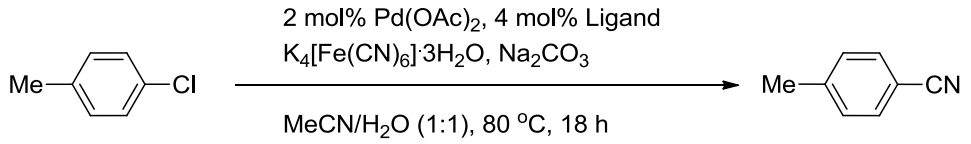
reported by Ryberg[81] using $ZnCN_2$ source, I would like to explore a cyanation procedure for aryl bromides mediated by environmentally benign potassium hexacyanaoferrate(II) at that temperature without any additives. Moreover, inspired by the described achievements, I would like to further investigate a general palladium-catalyzed cyanation for aryl chlorides so that the scope of palladium-catalyzed cyanation of aryl halides will be more solid.

3.2. Results and discussion of aryl chlorides

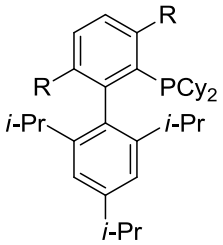
Initially, the palladium-catalyzed cyanation of aryl chloride was investigated, using electronically neutral 4-chlorotoluene as a benchmark substrate.

3.2.1 Ligand screening

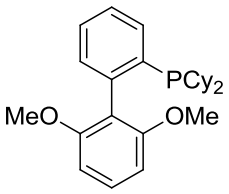
A series of commercially available ligands were tested for their efficacy in designed condition (Scheme 3.1).



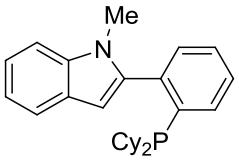
Ligand L:



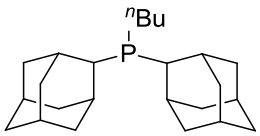
R = H, XPhos (73%)
R = OMe, BrettPhos (28%)



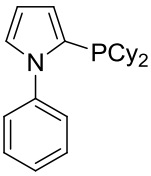
SPhos (58%)



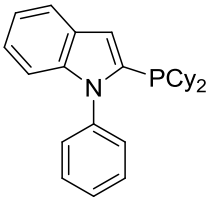
CMPhos (93%)



CataCXium A (0%)



CataCXium PCy (0%)



CataCXium PInCy (0%)

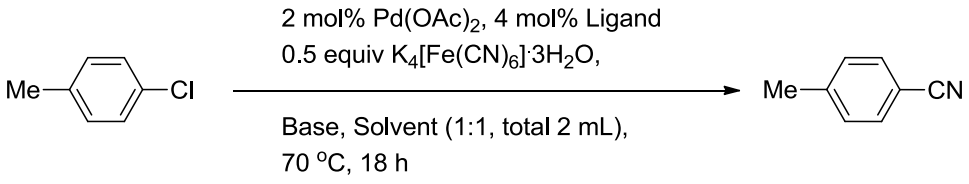
Reaction conditions: 1.0 mmol 4-chlorotoluene, 0.5 mmol $K_4[Fe(CN)_6].3H_2O$, 2 mol% $Pd(OAc)_2$, Pd/Ligand (1:2), 0.125 mmol Na_2CO_3, $MeCN/H_2O$ (1:1, total 2 mL), 70 °C, 18 h; Yields were determined by GC with dodecane as the internal standard.

Scheme 3.1 Ligand screening in palladium-catalyzed cyanation of aryl chloride

CMPhos[37,172] gave the best conversion (93% yield) of aryl chloride among (Scheme 3.1). The CataCXium[101,171,190] ligand series did not promote the cyanation reaction. XPhos,[168] BrettPhos[169] and SPhos[170] were inferior ligands for the cyanation reaction.

3.2.2 Base and solvent screening

Further experiments were conducted for optimization of the cyanation process (Table 3.1)



Entry[a]	Base (mmol)	Solvent (ratio)	Yield [%][b]
1	Na_2CO_3 (0.25)	MeCN/H_2O (1:1)	91
2	K_2CO_3 (0.25)	MeCN/H_2O (1:1)	81
3	Na_3PO_4 (0.25)	MeCN/H_2O (1:1)	80
4	Na_2CO_3 (1.0)	MeCN/H_2O (1:1)	69
5	Na_2CO_3 (0.5)	MeCN/H_2O (1:1)	57
6	Na_2CO_3 (0.125)	MeCN/H_2O (1:1)	65
7	Na_2CO_3 (0.063)	MeCN/H_2O (1:1)	96
8	Na_2CO_3 (0.125)	MeCN/H_2O (1:1)	92
9	Na_2CO_3 (0.125)	^{t}BuOH/H_2O (1:1)	22
10	Na_2CO_3 (0.125)	Dioxane/H_2O (1:1)	50
11	Na_2CO_3 (0.125)	MeCN	0
12[c]	Na_2CO_3 (0.125)	MeCN/H_2O (1:1)	66

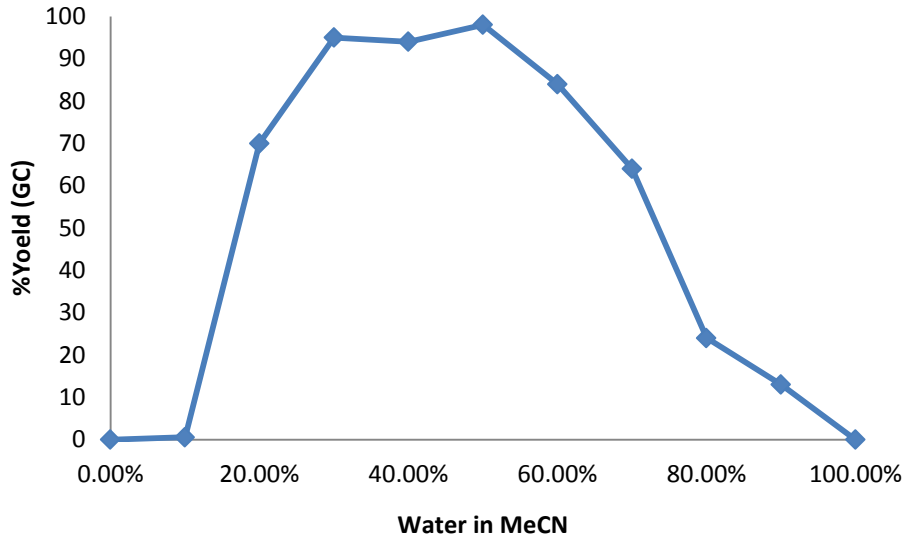
[a] Reaction conditions: 4-*tert*-butylphenyl mesylate (1.0 mmol), $K_4[Fe(CN)_6]\cdot 3H_2O$ (0.5 mmol), 2 mol% $Pd(OAc)_2$, 8 mol% CMPhos, Base, Solvent (4.0 mL total), 70 °C, 18 h. [b] Calibrated GC yields were reported using dodecane as the internal standard. [c] 2 mol% Pd_2dba_2 was used instead of $Pd(OAc)_2$

Table 3.1 Effect of base and solvent on the cyanation of 4-chlorotoluene

Inorganic bases were found to be important to promote this cyanation

(Table 3.1, entries 1-4). Na_2CO_3 afforded the best result (Table 3.1, entry 1). The stoichiometry of Na_2CO_3 used also affected the substrate conversion (Table 3.1, entries 1, 5-8). Acetonitrile/water mixtures were the best solvent medium of choice for this reaction (Table 3.1, entry 7 VS 9-10). It should be noted that no substrate conversions was observed when acetonitrile solvent was used alone (Table 3.1, entry 11). This inferior result might be due to the poor solubility of $K_4[Fe(CN)_6]\cdot 3H_2O$ in acetonitrile. Therefore, water was added into the reaction system in order to enhance the solubility of $K_4[Fe(CN)_6]\cdot 3H_2O$.

3.2.3 Effect of co-solvent (water) added to the benchmark conditions

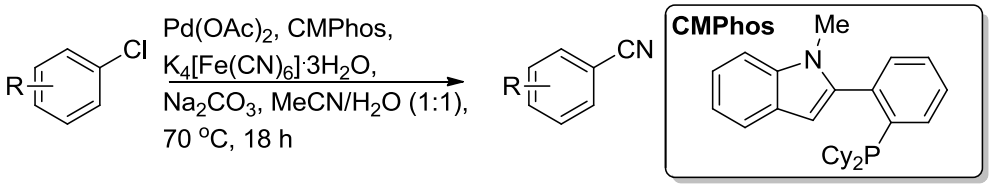


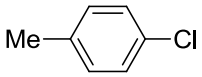
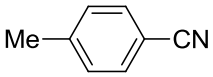
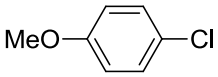
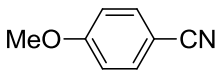
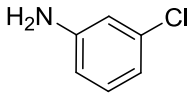
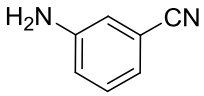
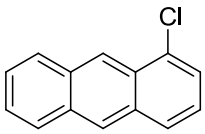
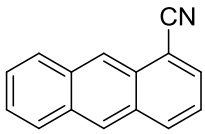
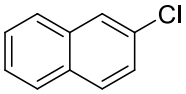
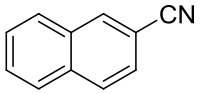
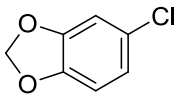
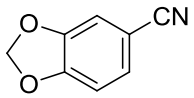
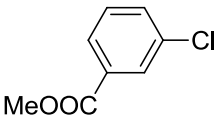
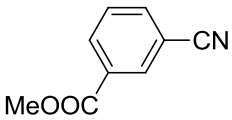
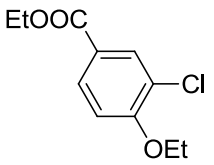
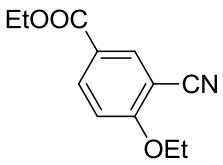
Reaction conditions: 1.0 mmol 4-Chlorotoleue, 0.5 mmol $K_4[Fe(CN)_6]\cdot 3H_2O$, 2 mol% $Pd(OAc)_2$, Pd/CMPhos (1:2), 0.125 mmol Na_2CO_3, total 2 mL mixed solvent at 70 ℃ for 18 h. Calibrated GC yields were reported using dodecane as the internal standard.

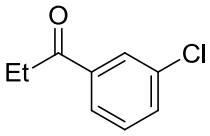
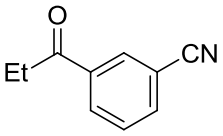
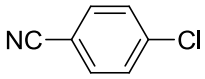
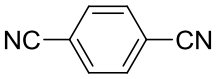
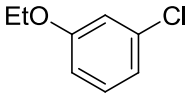
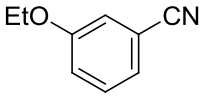
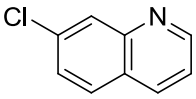
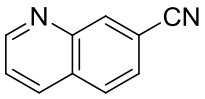
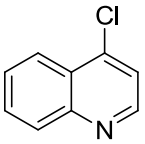
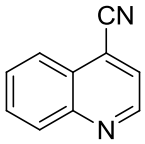
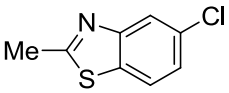
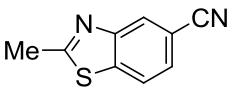
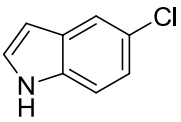
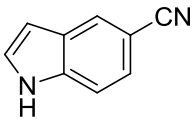
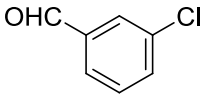
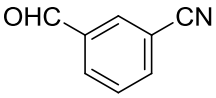
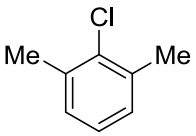
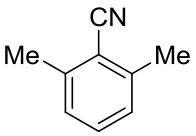
Figure 3.1 Effect of co-solvent (water) in the palladium catalyzed cyanation of aryl chloride

The influence of water on the cyanation reaction was summarized in Figure 3.1. Neither pure water nor pure acetonitrile supported substrate conversion. The best solvent mixtures ranged from 30-50% water in acetonitrile. Due to convenient purpose, 50% water in acetonitrile was used in the optimized reaction condition.

3.2.4 Scope of palladium-catalyzed cyanation of aryl chlorides



Entry[a]	ArCl	ArCN	Yield[b]
1			90%
2			85%
3			95%
4			86%
5			78%
6			90%
7			78%
8			74%

9			94%
10			75%
11			90%
12			96%
13[c]			81%
14[d]			97%
15[d]			91%
16[d]			71%
17[e]			77%

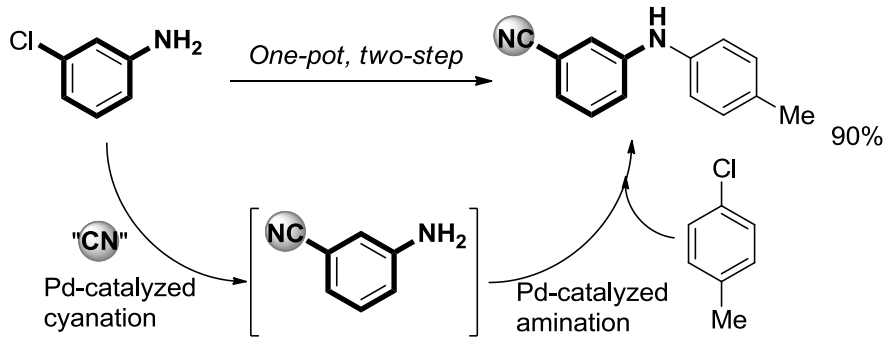
[a] Reaction conditions: ArCl (1.0 mmol), $K_4[Fe(CN)_6]\cdot 3H_2O$ (0.5mmol), $Pd(OAc)_2$ (0.02mmol, 2mol%), Pd/CMPhos (1:4), K_2CO_3 (0.125 mmol), MeCN/water (1:1, total 2 mL), 70 ^oC, 18 h. (The reaction time was not optimized for each substrate.) [b] Isolated yield. [c] 0.03 mmol, 3 mol% $Pd(OAc)_2$ [d] 0.04 mmol, 4 mol% $Pd(OAc)_2$ [e] 0.05 mmol, 5 mol% $Pd(OAc)_2$

Table 3.2 Palladium-catalyzed cyanation of aryl chlorides

Deactivated aryl chlorides afforded a good yield (Table 3.2, entries 2, 11).

Common functional groups, such as aldehydo, keto, ester, nitile, and free amino

groups were well tolerated under these reaction conditions (Table 3.2, entries 3, 6-10, 16). The cyanation of benzothiazolyl and quinolyl chlorides converted to the corresponding products in satisfactory yields (Table 3.2, entries 12-14). Notably, the cyanation of an unprotected indole group gave the nitrile product in 91% yield (Table 3.2, entry 15). The cyanation proceeded smoothly for sterically congested aryl chloride (Table 3.2, entry 17). A facile assembly of modular organic molecules using cross-coupling protocols is highly attractive.[133,173] Surprisingly, common functional groups were well tolerated under our reaction conditions. Thus it was possible to perform sequential coupling reactions to access multifunctional molecules. One-pot sequential catalytic cross-coupling cyanation-amination was attempted to demonstrate the reaction feasibility (Scheme 3.2).



Reaction conditions: Cyanation: same as in Table 3.2, entry 3. Amination: 4-chlorotoluene (0.6 mmol), Cs_2CO_3 (3.0 mmol), toluene (2 mL, additional) were added and stirred at 110 ^oC for 24 h (see experiment section for detailed procedures).

Scheme 3.2 One-pot sequential cyanation –amination reaction

3-chloroaniline was cyanated to give 3-amnobenzonitrile. Without further

addition of catalyst, the *N*-aryl amino-benzonitrile was obtained in excellent yield after the addition of 4-chlorotoluene (Scheme 3.2).

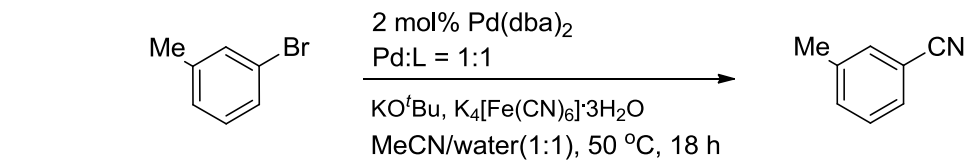
3.3. Results and Discussion of aryl bromides

A general palladium-catalyzed cyanation of aryl bromides under mild reaction conditions was reported. The first cyanation procedure for aryl bromides mediated by environmentally benign potassium hexacyanoferrate(II) at that temperature without any additives. The screening had included the optimization of the palladium source, ligand, ratio of metal to ligand, loading of cyanating agent and base.

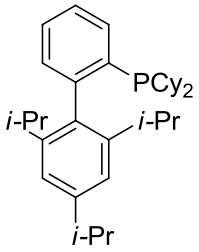
3.3.1 Ligands screening

The palladium-catalyzed cyanation used electron neutral 3-bromotoluene as the benchmark substrate in the presence of a series of commercially available ligands, as well as our group previously developed indolylphosphines **L_1-L_4**[175,176] (Scheme 3.3). It was interesting to show that well-known superior ligands for cross-coupling reactions such as XPhos[95], SPhos[191], CataCXium A[192] and CataCXium PCy[193] were less effective under the stated conditions. Moreover, we were surprised that our previously developed CMPhos,[34] which was found successful in aryl sulfonate coupling reactions, was also inferior. With our indolyl ligand family in hand, other ligand structures **L_1-L_4** that could offer efficacy was probed to this cyanation reaction. Surprisingly, **L_1** displayed lower yield than **L_2** (Scheme 3.3). It should be noted that **L_1** and **L_2** consisted the same skeletal structure except the $–PR_2$ group. In fact the ligand possessed $–PCy_2$ moiety should offer higher efficiency in general cross-coupling of aryl halides. Nevertheless, in our study of cyanation of aryl bromides, the **L_1** bearing only $–PPh_2$ could provide more superior activity than **L_2**. This finding offers us relevance to develop phosphine ligands that may not necessary to consist $–PCy_2$ group, yet can retain excellent activity in some unique cross-coupling reactions. Apart from **L_2**, the aminophosphine **L_3** also

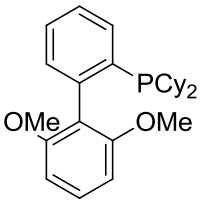
showed good activity. After fine tuning of the ligand structure, the best ligand choice was found to be **L_4**, named as Ph-*o*-Andole-phos.



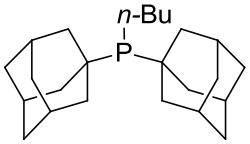
Ligand L:



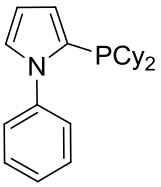
XPhos (13%)



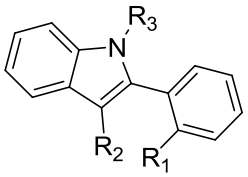
SPhos (34%)



CataCXium A (18%)



CataCXium PCy (24%)



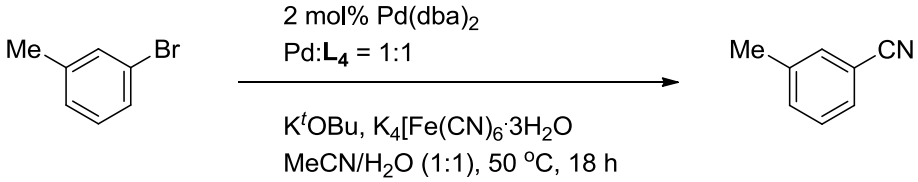
CM-Phos: R_1 = PCy_2, R_2 = H, R_3 = Me, (7%)
L1: R_1 = H, R_2 = PCy_2, R_3 = Me, (20%)
L2: R_1 = H, R_2 = PPh_2, R_3 = Me, (83%)
L3: R_1 = H, R_2 = H, R_3 = PPh_2, (80%)
L4: R_1 = OMe, R_2 = PPh_2, R_3 = Me, (93%)

[a] Reaction conditioins : 1.0 mmol 3-Bromotoluene, 2 mol% $Pd(dba)_2$, 2 mol% **L_4**, Pd:Ligand (1:1), Base (as indicated), $K_4[Fe(CN)_6]\cdot 3H_2O$ (as indicated) in MeCN/H_2O (1:1, 2 mL total) at 50 °C for 24 h. [b] Calculated GC-FID yields were reported using dodecane as the internal standard.

Scheme 3.3 Ligands screening in palladium-catalyzed cyanation of aryl bromide

3.3.2 Reaction optimization

With the aid of the Pd/**L_4** (Pd/Ph-*o*-Andole-phos) catalyst system, reaction parameters in this cyanation were investigated (Table 3.3).



Entry[a]	Pd source (mol%)	$K_4[Fe(CN)_6]$ loading	Base	Yield[b]
1	$PdCl_2$ (2)	0.25 mmol	K^tOBu	44
2	$Pd(OAc)_2$ (2)	0.25 mmol	K^tOBu	92
3	$Pd_2(dba)_3$ (2)	0.25 mmol	K^tOBu	93
4	$Pd(dba)_2$ (2)	0.25 mmol	K^tOBu	94
5	$Pd(OAc)_2$ (1)	0.25 mmol	K^tOBu	21
6	$Pd_2(dba)_3$ (1)	0.25 mmol	K^tOBu	88
7	$Pd(dba)_2$ (1)	0.25 mmol	K^tOBu	93
8	$Pd(dba)_2$ (2)	0.50 mmol	K^tOBu	31
9	$Pd(dba)_2$ (2)	0.27 mmol	K^tOBu	90
10	$Pd(dba)_2$ (2)	0.23 mmol	K^tOBu	96
11	$Pd(dba)_2$ (2)	0.21 mmol	K^tOBu	91
12	$Pd(dba)_2$ (2)	0.125 mmol	K^tOBu	23
13	$Pd(dba)_2$ (2)	0.25 mmol	$K_3PO_4·H_2O$	89
14	$Pd(dba)_2$ (2)	0.25 mmol	K_2CO_3	84
15	$Pd(dba)_2$ (2)	0.25 mmol	KOAc	70

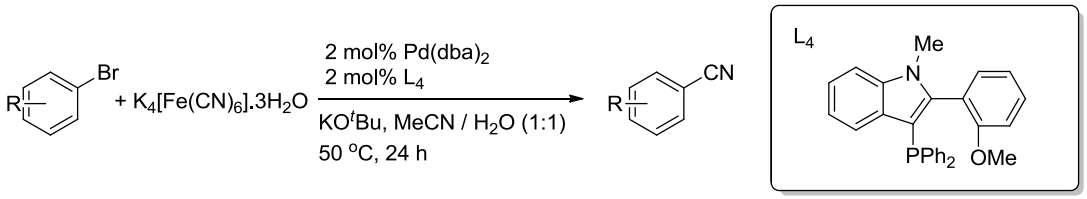
[a] Reaction conditioins : 1.0 mmol 3-Bromotoluene, 2 mol% $Pd(dba)_2$, 2 mol% **L_4**, Pd:Ligand (1:1), Base (as indicated), $K_4[Fe(CN)_6]·3H_2O$ (as indicated) in $MeCN/H_2O$ (1:1, 2 mL total) at 50 °C for 24 h. [b] Calculated GC-FID yields were reported using dodecane as the internal standard.

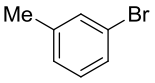
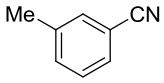
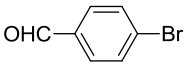
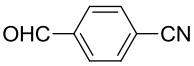
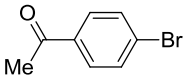
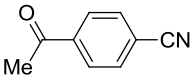
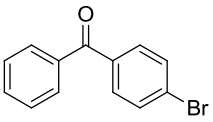
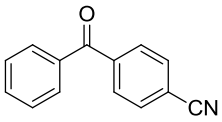
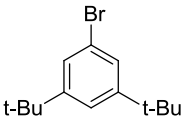
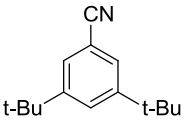
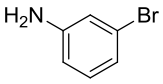
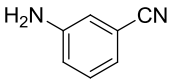
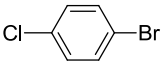
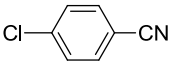
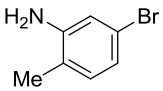
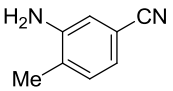
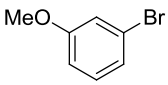
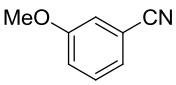
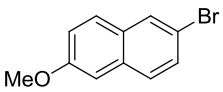
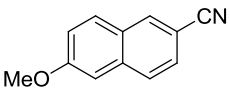
Table 3.3 Effect of metal, base and the loading of cyanide source on the cyanation of 3-bromotoluene

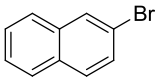
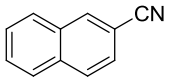
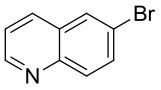
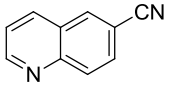
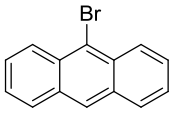
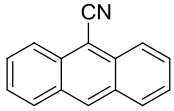
Palladium(0) salts were found to be more effective for promoting this

reaction (Table 3.3, entries 1-7). $Pd(dba)_2$ gave the best result (Table 3.3, entry 7). The concentration of $K_4[Fe(CN)_6]\cdot 3H_2O$ showed significant inhibition to the catalyst (Table 3.3, entries 4, 8-12). In fact, previous study also revealed that the concentration of CN^- source (from $Zn(CN)_2$) would suppress the cyanation efficiency. In my study, the optimal stoichiometry of $K_4[Fe(CN)_6]\cdot 3H_2O$ used was found to be 0.23 mmol (Table 3.3, entry 10). Inorganic bases were found to be essential for the fruitful performance of cyanation (Table 3.3, entries 4, 13-15). The best result was obtained in the presence of KO^tBu.

3.3.3 Scope of palladium-catalyzed cyanation of aryl bromides



Entry[a]	ArBr	ArCN	Yield[b]
1			96
2			89
3			88
4			92
5			66
6			91
7			94
8			75
9			87
10			89

11			95
12			91
13			62

[a] Reaction conditions : 3-Bromotoluene (1.0 mmol), $Pd(dba)_2$ (0.02 mmol), **L_4** (0.02 mmol), Pd:Ligand (1:1), KO^tBu (0.25 mmol), $K_4[Fe(CN)_6]\cdot 3H_2O$ (0.23 mmol) in MeCN:water (1:1, 2 mL total) at 50 °C for 24 h. [b] Isolated Yield

Table 3.4 Palladium-catalyzed cyanation of aryl bromides

A variety of *para*- and *meta*-substituted aryl bromides with functional groups such as chloro, methoxy, *tert*-butyl, amino, keto and especially aldehyde were compatible under our reaction conditions (Table 3.4, entries 2-11). It is surprised that there was no amination of 3-bromoaniline and 5-Bromo-2-methylaniline (Table 3.4, entries 6 and 8). It was observed that steric effect was not significant to the reaction (Table 3.4, entry 13). Hetero-cyclic substrate, 6-bromoquinoline, transformed the desired product in moderate yield (Table 3.4, entry 12).

3.4. Conclusion

In summary, a general and efficient palladium-catalyzed cyanation of aryl chlorides was developed. The reaction temperature of 70 ℃ is the mildest conditions reported so far. Particularly noteworthy is that water is found

necessary as co-solvent to facilitate the cyanation. This key finding will provide relevance for future cyanation investigations using $K_4[Fe(CN)_6]\cdot 3H_2O$ as the cyanide source. The one-pot cyanation-amination sequence showed the potential of this catalyst system for further functional group manipulation of a synthetic devise, yet without isolation of the intermediate or addition of extra catalyst.

Additionally, in couple with the investigation in palladium-catalyzed cyanation of aryl chlorides using $K_4[Fe(CN)_6]\cdot 3H_2O$ as cyanating source, the scope of this mild system to cyanation of aryl bromides was extended. The reaction condition is simple and mild. Particularly noteworthy is that water is found to be essential too.

The mild palladium systems described here exhibited excellent functional group compatibility. Nitrile, ester, keto, aldehyde, free amine, and heterocyclic groups remained intact during the course of reaction. This key finding may be useful for future cyanation investigations using $K_4[Fe(CN)_6]\cdot 3H_2O$ as the cyanide source.

3.5. Experimental Section

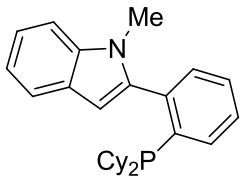
3.5.1 General considerations

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. All cyanation reactions were conducted in resealable screw cap Schlenk flask (approx. 20 mL volume) in the presence of Teflon coated magnetic stirrer bar (4 mm × 10 mm). Water was purified from deionized water under nitrogen. *tert*-Butanol was prior refluxed with sodium and the distillate was further distilled from calcium hydrides under nitrogen. Acetonitrile was distilled from calcium hydride under nitrogen.[174] Dioxane and toluene were distilled from sodium benzophenone ketyl under nitrogen.[174] All aryl chlorides and potassium hexacyanoferrate(II) trihydrate, $K_4[Fe(CN)_6]$, were used as received. New bottle of *n*-butyl lithium was used (*Note*: since the concentration of *n*-BuLi from old bottle may vary, we recommend performing a titration prior to use).

Thin layer chromatography was performed on pre-coated 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 Melting

Point instrument. ^{1}H NMR spectra were recorded on a 400 MHz spectrometer. Spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.26 ppm), or with C_6D_6 (δ 7.16 ppm), or with tetramethylsilane (TMS, δ 0.00 ppm) as the internal standard. Chemical shifts (δ) were reported as part per million (ppm) in δ scale downfield from TMS. ^{13}C NMR spectra were referenced to $CDCl_3$ (δ 77.0 ppm, the middle peak) or with C_6D_6 (δ 128.06 ppm). ^{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 a mass spectrometer (ESIMS). GC-MS analysis was conducted on a GCD system using a column (30 m × 0.25 mm). The products described in GC yield were accorded to the authentic samples/dodecane calibration standard from GC-FID system. The known cyanation products were characterized by comparing to the corresponding ^{1}H- and ^{13}C-NMR reported in the literatures.

3.5.2 Procedures for indolyl phosphine ligand synthesis



CMPhos was prepared according to the literature procedures.[37]

3.5.3 General procedures for optimization of cyanation

General procedures for optimization:

$Pd(OAc)_2$ (4.5 mg, 0.020 mmol) and ligand (Pd:L = 1:2) were added into a Schlenk tube with the presence of magnetic stir bar which is Teflon-coated. The tube was evacuated and then re-filled with nitrogen for 3 cycles. Pre-complexation of palladium and ligand was initiated by injecting freshly distilled anhydrous dichloromethane (1.0 mL) and Et_3N (0.1 mL) into the tube. The solution was stirred and warmed with hair drier till the solvent condensed on the tube wall. The solvent was removed under vacuum. 4-Chlorotlouene (1.0 mmol), base (as indicated) and potassium hexacyanoferrate(II) trihydrate (0.5 mmol) were charged successively to the tube followed by another 3 evacuation-nitrogen refill cycles. Water (1.0 mL) and acetonitrile (1.0 mL) (or

indicated solvent mixtures) were used as solvent. The tube was immersed into a preheated 70 ℃ oil bath for 18 h. After completion of reaction, the reaction tube was allowed to cool to room temperature. Dodecane (227.0 μL, internal standard), ethyl acetate and water were added. The organic layer was subjected to GC analysis. The GC yield obtained was previously calibrated by authentic sample/dodecane calibration curve.

3.5.4 General procedures for palladium-catalyzed cyanation of aryl chlorides:

$Pd(OAc)_2$ (4.5 mg, 2 mol%) and CMPhos (16.2 mg, 4 mol%) were added into a Schlenk tube with the presence of magnetic stir bar which is Teflon-coated. The tube was evacuated and then pressurized with nitrogen for 3 cycles. Pre-complexation of palladium and ligand was initiated by injecting freshly distilled dry dichloromethane (1.0 mL) and Et_3N (0.1 mL) into the tube. The solution was stirred and warmed with hair drier till the solvent condensed on the tube wall. The solvent was removed under vacuum. Aryl chloride (1.0 mmol), Na_2CO_3 (0.125 mmol), and potassium hexacyanoferrate (II) trihydrate (0.5 mmol) were discharged successively to the tube followed by another 3

evacuation-nitrogen refill cycles. 1.0 mL water and 1.0 mL was used as solvent. The tube was immersed into a preheated 70^{o}C oil bath for 18 hours. The reaction was quenched by cooling to ambient temperature and added with EtOAc and water. The organic supernatant was analyzed by GC. The organic layer was isolated and the remained aqua was further extracted with EtOAc (10.0 mL × 3). The combined organic phase was concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (230-400 mesh). The pure fraction was collected, dried under vacuum, and followed proton (^{1}H) and carbon (^{13}C) NMR characterization.

3.5.5 General procedures for one-pot sequential cyanation-amination reaction:

Cyanation of 3-Chloroaniline:

$Pd(OAc)_2$ (9.0 mg, 4 mol%) and CMPhos (32.3 mg, 8 mol%) were added into a Schlenk tube with the presence of magnetic stir bar which is Teflon-coated. The tube was evacuated and then re-filled with nitrogen for 3 cycles. Pre-complexation of palladium and ligand was initiated by injecting

freshly distilled dichloromethane (1.0 mL) and Et_3N (0.2 mL) into the tube. The solution was stirred and warmed with hair drier till the solvent condensed on the tube wall. The solvent was removed under vacuum. 3-Chloroaniline (1.0 mmol), Na_2CO_3 (0.125 mmol), and potassium hexacyanoferrate (II) trihydrate (0.5 mmol) were charged successively to the tube followed by another 3 evacuation-nitrogen refill cycles. Water (1.0 mL) and acetonitrile (1.0 mL) was added as a solvent mixture. The tube was immersed into a preheated 70℃ oil bath for 18 hours. The reaction was allowed to reach ambient temperature.

Amination of 3-Chloroaniline:

3-Chloroaniline (0.6 mmol), cesium carbonate (3.0 mmol) and phenylboronic acid (5 mg) were poured into the tube under counter flow of nitrogen. Toluene (1 mL) was used as solvent. The tube was immersed into a preheated 110 ℃ oil bath for 24 hours. The reaction was quenched by cooling to ambient temperature and added with EtOAc and water. The organic supernatant was analyzed by GC. The organic layer was separated and the remained aqua was further extracted with EtOAc (10 mL × 3). The combined organic phase was concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (230-400 mesh). The pure fractions were collected, dried under vacuum, and followed by proton (^1H)

and carbon (^{13}C) NMR characterization.

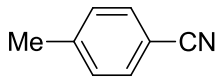
3.5.6 General procedures for palladium-catalyzed cyanation of aryl bromides:

An oven-dried Schlenk tube with the presence of magnetic stir bar which is Teflon-coated was charged with $Pd(dba)_2$ (11.5 mg, 0.02 mmol, 2 mol%) and ligand **L_4** (8.4 mg, 0.02 mmol, 2 mol%). The flask was evacuated and backfilled with nitrogen (3 cycles). Pre-complexation of palladium and ligand was initiated by injecting freshly distilled dry dichloromethane (2.0 mL) and Et_3N (0.1 mL) into the tube. The solution was stirred and warmed with hair drier till the solvent condensed on the tube wall. The solvent was removed under vacuum. Aryl bromide (1.0 mmol), K^{t}OBu (0.25 mmol), and potassium hexacyanoferrate(II) trihydrate (0.23 mmol) were charged successively to the tube followed by another 3 evacuation-nitrogen refill cycles. Water (1.0 mL) and acetonitrile (1.0 mL) were used as a solvent mixture. The tube was immersed into a preheated 50℃ oil bath for 24 hours. The reaction was quenched by cooling to ambient temperature and added with EtOAc and water. The organic supernatant was analyzed by GC. The organic layer was separated and the remained aqua medium was further extracted with EtOAc (10 mL × 3).

The combined organic phases were concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (230-400 mesh). The pure fractions were collected, dried under vacuum, and followed by proton (^{1}H) and carbon (^{13}C) NMR characterization.

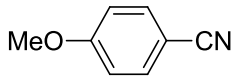
3.5.7 Characterization data of nitriles from aryl chlorides

4-Methylbenzonitrile (Table 3.2, entry 1)[194]



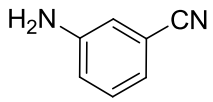
Ether : n-Pentane = 1 : 20, R_f = 0.2; ^{1}H NMR (400 MHz, $CDCl_3$). δ2.41 (s, 3H), 7.26 (d, 2H, *J* = 8.0 Hz), 7.52 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$). δ21.72, 109.20, 119.05, 129.74, 131.93, 143.61; MS(EI) *m/z* (relative intensity) 117 (M^+, 100), 90 (39), 63 (17).

4-Methoxybenzonitrile (Table 3.2, entry 2) [178]



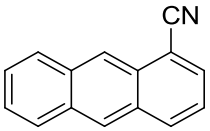
Ether : n-Pentane = 1 : 20, R_f = 0.1; ^{1}H NMR (400 MHz, $CDCl_3$). δ3.85 (s, 3H), 6.94 (d, 2H, *J* = 8.8 Hz), 7.57 (d, 2H, *J* = 9.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$). δ55.46, 103.84, 114.67, 129.14, 133.87, 162.76; MS(EI) *m/z* (relative intensity) 133 (M^+, 100), 90 (44), 63 (14).

3-Aminobenzonitrile (Table 3.2, entry 3) [188]



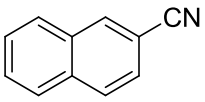
Ether : n-Pentane = 6 : 4, R_f = 0.3; ^{1}H NMR (400 MHz, C_6D_6). δ3.04 (bs, 2H), 6.21 (d, 1H, *J* = 8.0 Hz), 6.27 (s, 1H), 6.60 – 6.68 (m, 2H); ^{13}C NMR (100 MHz, C_6D_6). δ113.18, 117.25, 118.72, 119.57, 121.20, 129.96, 147.66; MS(EI) *m/z* (relative intensity) 118 (M^+, 100), 91 (41).

Anthracene-1-carbonitrile (Table 3.2, entry 4) [195]



Ether : n-Pentane = 1 : 20, R_f = 0.3; ^{1}H NMR (400 MHz, $CDCl_3$). δ7.41 (dd, 1H, *J* = 6.8 Hz, 2.0 Hz), 7.48 - 7.61 (m, 2H), 7.86 (d, 1H, *J* = 5.6 Hz), 7.95 – 8.02 (m, 2H), 8.13 (d, 1H, *J* = 8.8 Hz), 8.38 (s, 1H), 8.68 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$). δ110.13, 117.95, 123.58, 123.89, 126.54, 126.82, 127.51, 127.96, 128.22, 128.90, 130.15, 132.14, 132.58, 133.06, 133.62; MS (EI) *m/z* (relative intensity) 203 (M^+, 100), 176 (10).

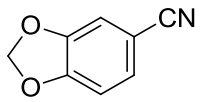
2-Naphthonitrile (Table 3.2, entry 5)[109]



Ether : n-Pentane = 1 : 20, R_f=0.3; ^{1}H NMR (400 MHz, $CDCl_3$). δ7.57-7.66 (m, 3H), 7.86-7.90 (m, 3H), 8.19 (s, 1H); ^{13}C NMR (100 MHz,

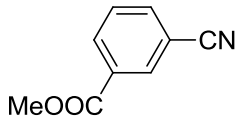
$CDCl_3$). δ126.20, 127.55, 127.94,128.29, 128.94, 129.07, 132.11, 134.01, 134.51; MS (EI) *m/z* (relative intensity) 153 (M^+, 100), 126 (18).

Piperonylnitrile (Table 3.2, entry 6)[188]



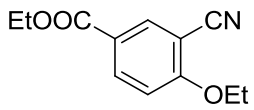
Ether : n-Pentane = 1 : 10, R_f = 0.3; ^{1}H NMR (400 MHz, $CDCl_3$). δ6.05 (s, 2H), 6.85 (d, 1H, *J* = 8.4 Hz), 7.01 (d, 1H, *J* = 1.6Hz), 7.19 (dd, 1H, *J* = 8.0 Hz, 1.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$). δ102.15, 104.82, 109.03, 111.28, 118.78, 128.10, 147.94, 151.44; MS (EI) *m/z* (relative intensity) 147 (M^+, 62), 146 (100), 89 (8), 62(16).

Methyl-3-cyanobenzoate (Table 3.2, entry 6)[196]



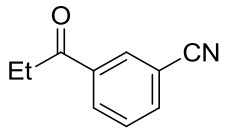
Ether : n-Pentane = 2 : 8, R_f = 0.4; ^{1}H NMR (400 MHz, $CDCl_3$). δ3.94 (s, 3H), 7.57 (t, 1H, *J* = 7.8 Hz), 7.82 (d, 1H, *J* = 7.6 Hz), 7.24 (d, 1H, *J* = 8.0 Hz), 8.30 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$). δ52.60, 112.87, 117.77, 129.37, 131.33, 133.15, 133.55, 135.88, 164.98; MS (EI) *m/z* (relative intensity) 161 (M^+, 29), 130 (100), 102 (41), 75 (13).

Ethyl 3-cyano-4-ethoxybenzoate (Table 3.2, entry 8)



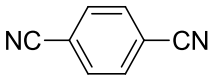
Ether : n-Pentane = 2 : 8, R_f = 0.2; ^{1}H NMR (400 MHz, $CDCl_3$). δ1.36 (t, 3H, *J* = 7.2Hz), 1.48 (t, 3H, *J* = 7.0 Hz), 4.20 (q, 2H, *J* = 7.0 Hz), 4.34 (q, 2H, *J* = 7.0 Hz), 6.97 (d, 1H, *J* = 9.2 Hz), 8.16 (dd, 1H, *J* = 9.2 Hz, 2.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$). δ14.17, 14.26, 61.21, 65.21, 102.05, 111.62, 115.46, 123.08, 135.44, 135.73, 1633.51, 164.47; MS (EI) *m/z* (relative intensity) 219 (M^+, 24), 163 (68), 146 (100), 118 (16), 90 (13). HRMS: calc. For $C_{12}H_{14}NO_3$: 220.0974, found 250.0973.

3-Propionylbenzonitrile (Table 3.2, entry 9)[197]



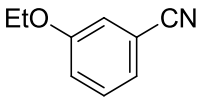
Ether : n-Pentane = 2 : 8, R_f = 0.3; ^{1}H NMR (400 MHz, $CDCl_3$). δ1.22 (t, 3H, *J* = 7.0 Hz), 3.00 (q, 2H, *J* = 7.2 Hz), 7.59 (t, 1H, *J* = 7.8 Hz), 7.81 (d, 1H, *J* = 8.0 Hz), 8.17 (d, 1H, *J* = 8.0 Hz), 8.21 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$). δ7.83, 31.87, 113.03, 117.91, 129.58, 131.61, 131.84, 135.71, 137.51, 198.48; MS (EI) *m/z* (relative intensity) 159 (M^+, 14), 130 (100), 102 (31), 75 (11).

Terephthalonitrile (Table 3.2, entry 10)[179]



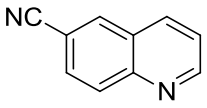
Ether, R_f = 0.8; ^{1}H NMR (400 MHz, $CDCl_3$). δ7.793 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$). δ116.67, 116.96, 132.75; MS (EI) *m/z* (relative intensity) 128 (M^+, 100), 101 (20), 75 (10).

3-Ethoxybenzonitrile (Table 3.2, entry 11)[198]



Ether : n-Pentane = 1 : 50, R_f = 0.6; ^{1}H NMR (400 MHz, $CDCl_3$). δ1.41 (t, 3H, *J* = 7.0 Hz), 4.02 (q, 2H, *J* = 7.0 Hz), 7.09 – 7.10 (m, 2H), 7.19 (d, 1H, *J* = 7.6 Hz), 7.31 – 7.35 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$). δ14.45, 63.78, 112.98, 117.24, 118.65, 119.60, 124.13, 130.17, 158.89; MS (EI) *m/z* (relative intensity) 147 (M^+, 31), 119 (100), 91 (16).

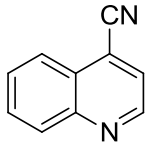
Quinoline-6-carbonitrile (Table 3.2, entry 12)[199]



Ether : n-Pentane = 1 : 1, R_f = 0.1; ^{1}H NMR (400 MHz, $CDCl_3$). δ7.50 (dd, 1H, *J* = 8.4 Hz, 4.4 Hz), 7.80 (dd, 1H, *J* = 8.8 Hz, 1.6 Hz), 8.12 – 8.18 (m, 3H), 9.01 (dd, 1H, *J* = 4.0 Hz, 1.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$). δ110.20, 118.33, 122.58, 127.37, 129.93, 130.89, 133.97, 136.21, 148.93,

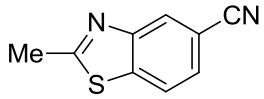
153.11; MS (EI) *m/z* (relative intensity) 154 (M^+, 100), 127 (26), 100 (9), 75 (7).

Quinoline-4-carbonitrile (Table 3.2, entry 13)[200]



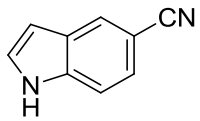
Ether : n-Pentane = 1 : 10, R_f = 0.2; ^{1}H NMR (400 MHz, $CDCl_3$). δ7.70 – 7.74 (m, 2H), 7.83 (t, 1H, *J* = 7.0 Hz), 8.16 (t, 2H, *J* = 8.2 Hz), 9.00 (d, 1H, *J* = 4.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$). δ115.41, 118.54, 124.72, 124.81, 125.61, 129.09, 130.27, 131.06, 148.00, 149.33; MS (EI) *m/z* (relative intensity) 154 (M^+, 100), 127 (36), 100 (7), 75 (6).

2-Methyl-5-benzothiazolecarbonitrile (Table 3.2, entry 14)[185]



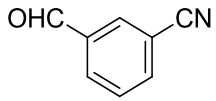
Ether : n-Pentane = 2 : 8, R_f = 0.2; ^{1}H NMR (400 MHz, $CDCl_3$). δ2.83 (s, 3H), 7.52 (dd, 1H, *J* = 8.0 Hz, 1.2), 7.87 (d, 1H, *J* = 8.4 Hz), 8.16 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$). δ20.13, 109.44, 118.65, 122.36, 126.30, 126.94, 140.52, 152.85, 169.64; MS (EI) *m/z* (relative intensity) 174 (M^+, 100), 133 (16), 69 (13).

1*H*-indole-5-carbonitrile (Table 3.2, entry 15)[186]



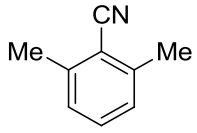
Ether : n-Pentane = 1 : 1, R_f = 0.3; ^{1}H NMR (400 MHz, $CDCl_3$). δ6.63 (s, 1H), 7.36 (t, 1H, *J* = 2.8 Hz), 7.42 (dd, 1H, *J* = 8.8 Hz, 1.6 Hz,), 7.49 (d, 1H, *J* = 8.4 Hz), 7.99 (s, 1H), 8.95 (bs, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$). δ102.28, 103.13, 112.06, 120.97, 124.59, 126.26, 126.60, 127.58, 137.53; MS (EI) *m/z* (relative intensity) 142 (M^+, 100), 115 (32), 88 (10).

3-Formylbenzonitrile (Table 3.2, entry 16)[106]



Ether : n-Pentane = 2 : 8, R_f = 0.3; ^{1}H NMR (400 MHz, $CDCl_3$). δ7.84 (d, 2H, *J* = 8.0 Hz), 7.99 (d, 2H, *J* = 8.8 Hz), 10.08 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$). δ117.50, 117.64, 129.81, 132.82, 138.66, 190.56; MS (EI) *m/z* (relative intensity) 131 (M^+, 69), 130 (100), 102 (54), 76 (21).

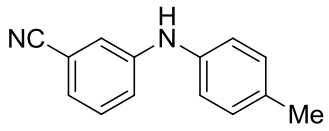
2,6-Dimethylbenzonitrile (Table 3.2, entry 17)[103]



Ether : n-Pentane = 1 : 50, R_f = 0.2; ^{1}H NMR (400 MHz, $CDCl_3$). δ2.52 (s, 6H), 7.11 (d, 2H, *J* = 7.6 Hz), 7.34 (t, 1H, *J* = 7.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$). δ20.69, 113.28, 117.19, 127.23, 132.00, 142.06; MS (EI) *m/z* (relative intensity) 131 (M^+, 71), 116 (100), 103 (16), 77 (14).

3.5.8 One-pot sequential cyanation-amination

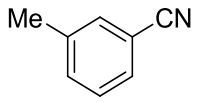
3-(p-Tolylamino)benzonitrile (Scheme 3.2, product)[201]



Ether : n-Pentane = 2 : 8, R_f = 0.6; ^{1}H NMR (400 MHz, $CDCl_3$). δ2.37 (s, 3H), 5.89 (bs, 1H), 7.05 – 7.31 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$). δ20.70, 112.86, 117.82, 119.11, 119.80, 120.67, 122.70, 129.98, 130.05, 132.91, 138.17, 145.29; MS (EI) *m/z* (relative intensity) 208 (M^+, 100), 192 (16), 103 (7), 77 (7).

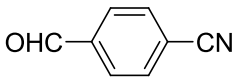
3.5.9 Characterization data of nitriles from aryl bromides

3-Methylbenzonitrile (Table 3.4, entry 1)[177]



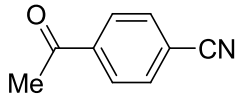
Ether : n-Pentane = 1 : 20, R_f = 0.2; ^{1}H NMR (400 MHz, $CDCl_3$). δ2.41 (s, 3H), 7.26 (d, 2H, *J* = 8.0 Hz), 7.52 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$). δ21.72, 109.20, 119.05, 129.74, 131.93, 143.61; MS(EI) *m/z* (relative intensity) 117 (M^+, 100), 90 (39), 63 (17).

2-Formylbenzonitrile (Table 3.4, entry 2)[108]



EA : n-Hexane = 2:8, R_f = 0.3; ^{1}H NMR (400 MHz, $CDCl_3$). δ7.82(D, 2H,*J*=7.6Hz), 7.97 (d, 2H,*J* = 8Hz), 10.06 (s, 1H,); ^{13}C NMR (100 MHz, $CDCl_3$). δ117.35, 117.57, 129.71, 132.73, 138.57, 190.55; MS(EI) *m/z* (relative intensity) 130 (M^+, 100), 102 (60), 76 (27), 63 (3), 50(21).

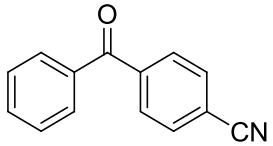
4-Acetylbenzonitrile (Table 3.4, entry 3)[43]



EA : n-Hexane = 2:8, R_f = 0.28; ^{1}H NMR (400 MHz, $CDCl_3$). δ2.65(s, 3H), 7.78 (d, 2H,*J* = 8.4Hz), 8.00 (d, 2H, *J* = 8.4Hz); ^{13}C NMR (100 MHz,

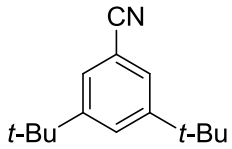
$CDCl_3$). δ26.48, 116.04,117.67, 128.44, 132.24, 139.68, 196.29; MS(EI) *m/z* (relative intensity) 145 (M^+, 17),130 (100), 102 (48), 75 (13).

4-Cyanobenzophenone (Table 3.4, entry 4)[108]



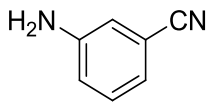
EA : n-Hexane = 2:8, R_f = 0.45 ; ^{1}H NMR (400 MHz, $CDCl_3$). δ7.51(t, 2H, J=7.6), 7.64 (t, 1H,*J* = 7.6Hz), 7.77 (t, 2H, *J* = 1.2Hz) ,7.79 (d, 2H,*J* =1.6 7.6Hz), 7.87 (d, 2H,*J* = 8.4Hz); ^{13}C NMR (100 MHz, $CDCl_3$). δ26.48, 115.63, 117.94, 128.58, 130.00, 130.17, 132.11, 133.26, 136.31, 141.2, 194.94; MS(EI) *m/z* (relative intensity) 207 (M+, 59),130 (24), 105 (100), 77 (44), 51(22).

3,5-di-tert-butylbenzonitrile (Table 3.4, entry 5)[202]



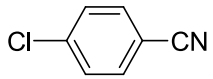
EA : n-Hexane = 1:20, R_f =0.31 ; ^{1}H NMR (400 MHz, $CDCl_3$). δ1.33(s, 18H), 7.48 (d, 2H,*J* = 2Hz), 7.6 (d, 1H, *J* = 1.6Hz); ^{13}C NMR (100 MHz, $CDCl_3$). δ 30.83, 34.68, 111.38, 119.54, 126.05, 126.81, 151.76; MS(EI) *m/z* (relative intensity) 216.2 ($M^{+\cdot}$ 13),200.2(100), 172.1 (14), 144.1 (6), 116.1(5), 100(1), 77.3(4). 57.1(13).

3-Aminobenzonitrile (Table 3.4, entry 6)[203]



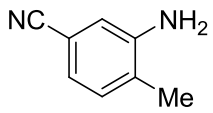
EA : n-Hexane = 2:8, R_f = 0.3; ^{1}H NMR (400 MHz, $CDCl_3$). δ2.88 (bs, 2H), 6.15 (d,1H, *J* = 7.6Hz), 6.22 (s, 1H), 6.59 – 6.66 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$). δ113.31, 117.26, 118.60, 119.49, 121.24, 129.91, 147.55;; MS(EI) *m/z* (relative intensity) 118.1 (M^+, 100),91.0 (33), 64.1 (12).

4-Chlorobenzonitrile (Table 3.4, entry 8)[62]



EA : n-Hexane = 1:9, R_f = 0.47; ^{1}H NMR (400 MHz, $CDCl_3$). δ7.44(d, 2H,*J*=8.4), 7.58 (d, 2H,*J*=8.8); ^{13}C NMR (100 MHz, $CDCl_3$). δ110.68, 117.83, 129.57, 133.27, 139.41; MS(EI) *m/z* (relative intensity) 137 (M^+, 100),102 (33), 75 (17), 50 (14).

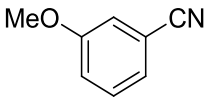
2-Amino-3methylbenzonitrile (Table 3.4, entry 7)[204]



EA : n-Hexane = 2:8, R_f = 0.3; ^{1}H NMR (400 MHz, C6D6). δ2.183(s, 3H), 3.827 (s, 2H), 6.87 (s,1H), 6.94 (d, 2H,J=7.6), 7.08(d, 2H,J=7.6); ^{13}C NMR (100 MHz, $CDCl_3$).δ17.35, 109.98, 116.82, 119.21, 121.7, 127.32, 130.72, 144.98; MS(EI) *m/z* (relative intensity) 131 (M^+, 100),115 (4), 104 (15),

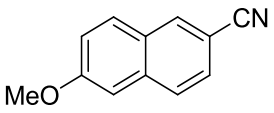
88(2),77(17),63(4),51(9).

3-Methoxybenzonitrile (Table 3.4, entry 9)[103]



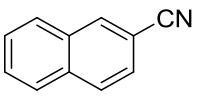
EA : n-Hexane = 1:9, R_f = 0.25; ^{1}H NMR (400 MHz, $CDCl_3$). δ3.748(s, 3H), 7.06 (d, 2H,*J*=8), 7.14(d,2H, *J*=7.6), 7.14(t,1H, *J*=7.6) ; ^{13}C NMR (100 MHz, $CDCl_3$). δ55.18,112.78, 116.58, 118.39, 118.89, 124.04, 130.04, 159.32; MS(EI) *m/z* (relative intensity) 133.1 (M^+, 100),118 (7), 103 (76), 90 (50), 76(17), 63(24), 51(10).

6-Methoxy-2-naphthonitrile (Table 3.4, entry 10)[42]



EA : n-Hexane = 1:9, R_f = 0.26; ^{1}H NMR (400 MHz, $CDCl_3$). δ3.939(s, 3H), 7.06 (d, 2H,*J*=8), 7.14(d,2H, *J*=7.6), 7.14(t,1H, *J*=7.6) ; ^{13}C NMR (100 MHz, $CDCl_3$). δ55.41, 105.84, 106.62, 119.49, 120.57, 126.95, 127.64, 127.71, 129.86, 133.63,136.32, 159.94; MS(EI) *m/z* (relative intensity) 183.1(M^+, 100),168 (4), 154 (17), 140 (100), 113(15), 88(6), 63(7).

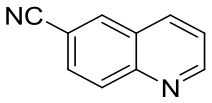
2-Naphthonitrile (Table 3.4, entry 11)[177]



EA : n-Hexane = 2:8, R_f = 0.6; ^{1}H NMR (400 MHz, $CDCl_3$). δ7.54 – 7.64

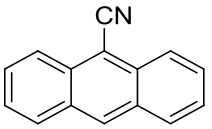
(m, 3H), 7.84 (t, 3H, *J* = 7.4Hz), 8.16 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$). δ109.36, 119.23, 126.09, 126.33, 127.63, 128.03, 128.39, 129.02, 129.18, 132.23, 134.14, 134.63; MS(EI) *m/z* (relative intensity) 153.1(M^+, 100),126 (14), 99 (4), 76 (5), 63(7).

6-Quinolinecarbonitrile (Table 3.4, entry 12)[105]



EA : n-Hexane = 1:9, R_f = 0.26; ^{1}H NMR (400 MHz, $CDCl_3$). δ7.53 (d, 1H, *J* = 4Hz, 4.4Hz), 7.85 (t, 1H, *J* = 6.8Hz), 8.13-8.19 (m, 3H), 9.05 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$). δ110.15, 118.13, 122.39, 127.26, 129.80, 130.80, 133.77, 137.01, 148.86, 152.93; MS(EI) *m/z* (relative intensity) 154(M^+, 100),127 (24), 100 (8), 87 (1), 75(6), 63(4), 50(8).

9-Anthracenecatbonitrile (Table 3.4, entry 13)[205]

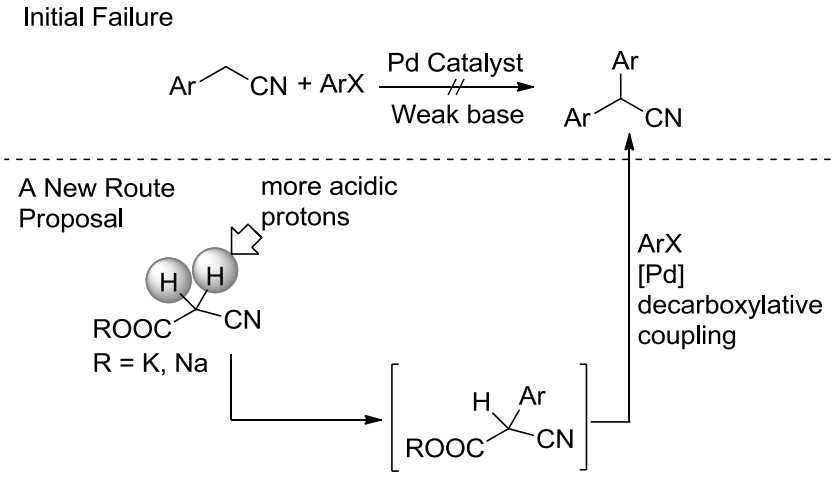


EA : n-Hexane = 1:9, R_f = 0.26; ^{1}H NMR (400 MHz, $CDCl_3$). δ7.53(t, 2H,*J*=6.8Hz), 7.65 (t, 2H,*J*=6.8Hz), 8.0(d,2H, *J*=8.4), 8.34(d,2H, *J*=8.8), 8.553(s, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$). δ105.26, 117.14, 125.12, 126.23, 128.81, 128.84, 130.46, 132.58, 133.13; MS(EI) *m/z* (relative intensity) 203(M^+, 100),176 (7), 150 (4), 126 (1), 110(0.5), 88(9), 63(1).

Chapter 4 Palladium-catalyzed decarboxylative arylation of aryl halides

4.1. Introduction

In the past decade, catalytic decarboxylative coupling drew the attention of chemists for the biarylation from aryl halides[142,143] and sulfonates with bi-catalystic system.[145,146] Recently, the decarboxylative couplings were used in α-arylation of nitriles and eventually in monoarylation of nitriles. Hence, I focused on investigation of monoarylation initially. During our investigation, Rui[128] published a paper a new synthetic strategy for α-monoarylated nitriles through palladium-catalyzed decarboxylative coupling of aryl halides and sulfonates with cyanoacetate salts, which was highly similar to my work. Embarked on the investigation from initial failure in the arylation of benzylic nitrile using weak bases under palladium catalysis (Scheme 4.1), our group was investigated an alternative method for diarylation of nitriles as the extension of palladium-catalyzed cyanation.



Scheme 4.1 Investigations on the protocol for α-diaryl nitrile synthesis

Hence, I altered the investigation to a new methodology for the synthesis of α-diarylated nitriles *via* palladium catalyzed decarboxylative arylation of potassium cyanoaetate. The reaction with aryl bromides and chlorides were described.

4.2. Results and discussion

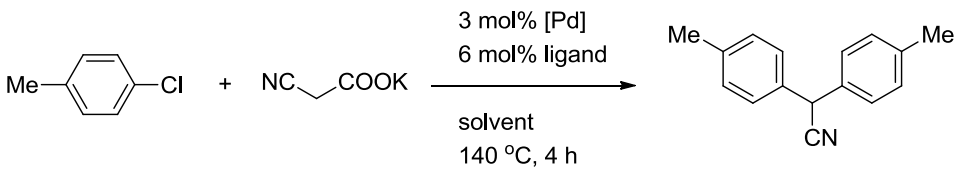
The reaction conditions feature the absence of additional strong inorganic bases and provide ester functional group tolerance. With $Pd(dba)_2$ and XPhos ligand as the catalyst system, α-diaryl nitriles can be obtained in good yields.

This reaction does not proceed, possibly because of the inefficient basicity of the weak base for assisting α-deprotonation of nitriles. Thus, if the acidity of the α-proton is increased by an additional neighboring activating group, this process will likely be viable.[206,207] Hence, cyanoacetate was chosen as the substrate for the attempted diarylation process (Scheme 4.1). Having the

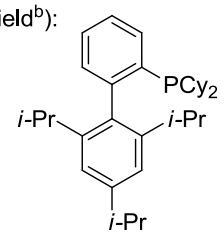
additional carboxylic group, this type of substrate offered both the feasibility of α-deprotonation/arylation and a subsequent decarboxylative arylation step.

At the beginning, potassium cyanoacetate and 4-chlorotoluene were used as the coupling partners for the investigation of the proposed study (Table 4.1).

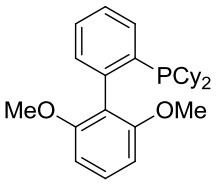
4.2.1 Ligand screening



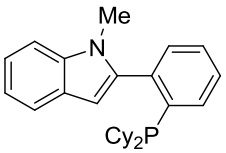
Ligand (Yield[b]):



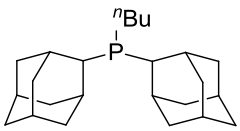
XPhos (96%)



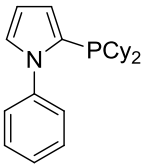
SPhos (81%)



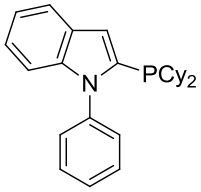
CMPhos (87%)



CataCXium A (31%)



CataCXium PCy (0%)



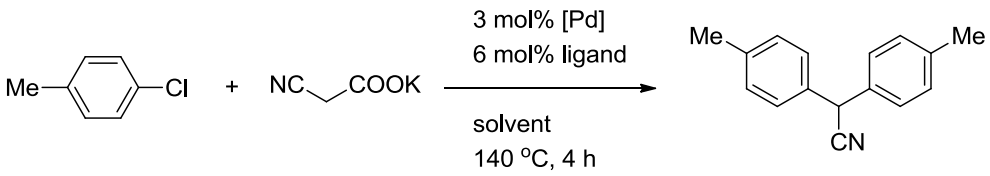
CataCXium PInCy (54%)

[a] Reaction conditions: 0.5 mmol 4-chlorotoluene, palladium precusor (3.0 mol% or 1.5 mol% for Pd dimer), 6.0 mol% ligand, 0.5 mmol potassium cyanoacetate and 1.0 mL xylene were stirred at 140 °C for 4 h under nitrogen. [b] Calibrated GC yields were reported using dodecane as the internal standard.

Table 4.1 Screening of ligand

Common phosphine ligands for aryl chloride coupling reactions were screened. XPhos[208] gave the best results, while SPhos[191] and CMPhos[37,209,210] provided slightly lower product yield (Table 4.1). CataCXium A,[192] CataCXium PCy,[171] and CataCXium PInCy[193] did not promote this reaction well (Table 4.1).

4.2.2 Metal screening



Entry[a]	Palladium precursor (mol%)	Metal:Ligand	Yield[b] (%)
1	$PdCl_2$ (3 mol%)	1:2	77
2	$Pd(MeCN)_2Cl_2$ (3 mol%)	1:2	46
3	$Pd(COD)Cl_2$ (3 mol%)	1:2	30
4	$Pd(OAc)_2$ (3 mol%)	1:2	92
5	$[Pd(ally)Cl]_2$ (3 mol%)	1:2	66 (>99)[c]
6	$Pd_2(dba)_3$ (3 mol%)	1:2	96
7	$Pd_2(dba)_3$ (3 mol%)	1:1	86
8	$Pd_2(dba)_3$ (3 mol%)	1:3	90
9	$Pd_2(dba)_3$ (1 mol%)	1:2	57
10	$Pd_2(dba)_3$ (0.5 mol%)	1:2	49
11	$Pd_2(dba)_3$ (0.1 mol%)	1:2	0
12	$[Pd(ally)Cl]_2$ (3 mol%)	1:1	94[c]
13	$[Pd(ally)Cl]_2$ (3 mol%)	1:3	>99[c]

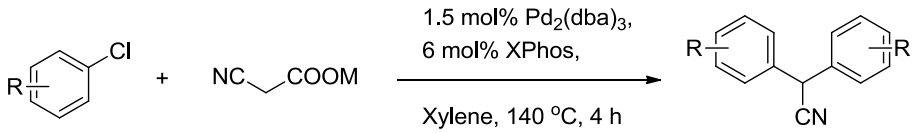
[a] Reaction conditions: 0.5 mmol 4-chlorotoluene, palladium precusor (3.0 mol% or 1.5 mol% for Pd dimer), 6.0 mol% ligand, 0.5 mmol potassium cyanoacetate and 1.0 mL xylene were stirred at 140 °C for 4 h under nitrogen. [b] Calibrated GC yields were reported using dodecane as the internal standard. [c] Mono-α-aryl nitrile was the product.

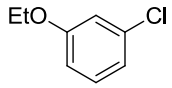
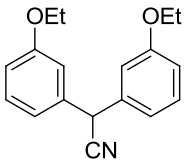
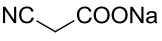
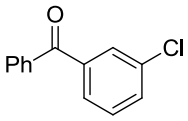
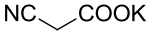
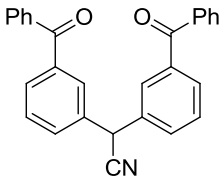
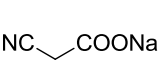
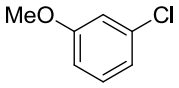
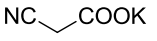
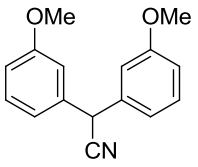
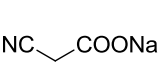
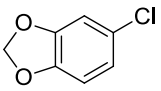
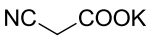
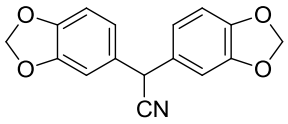
Table 4.2 Screening of reaction condition

A scanning of commercially available palladium precursors revealed that $Pd(dba)_2$ and $Pd(OAc)_2$ were the best choice (Table 4.2, entries 1-6). Accidentally, mono-α-arylation was observed when $[Pd(ally)Cl]_2$ was used

(Table 4.2, entries 5, 12-13). During the completion of the manuscript, a report about Pd-catalyzed mono-α-arylation of nitriles appeared.[128] Metal to ligand ratio 1:2 preformed the best diarylation (Table 4.2, entries 6-8). Lower catalyst loading (less than 3 mol%) leaded to significant decrease in yield (Table 4.2, entries 6, 9-11).

4.2.3 Scope of palladium-catalyzed decarboxylative diarylation of aryl chlorides



Entry[a]	ArCl	Cyanoacetate	Product	Yield[b]
1				87
2				53
3				58
4				62
5				83
6				85
7				72
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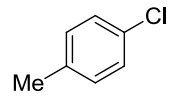
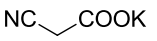
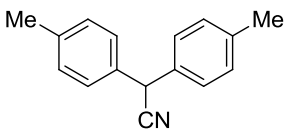
9				92
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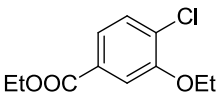
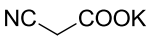
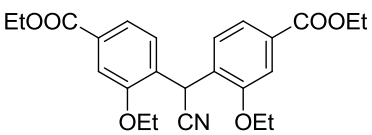
11				98
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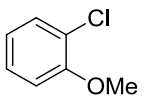
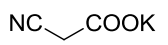
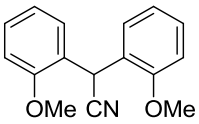
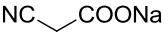
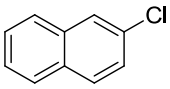
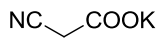
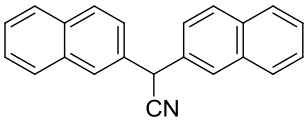
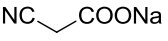
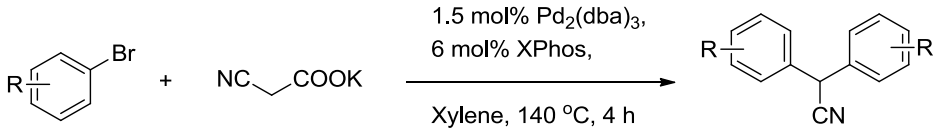
13[c]				90
14[c]				58
15				58
16				82

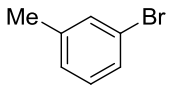
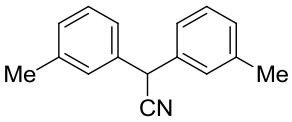
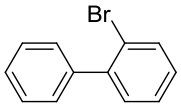
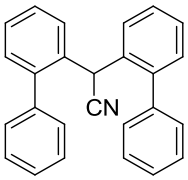
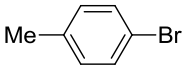
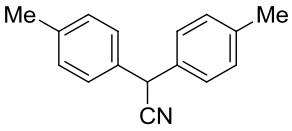
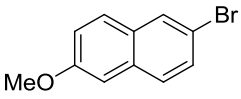
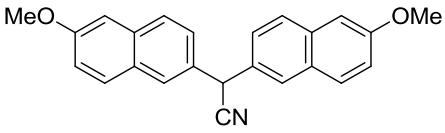
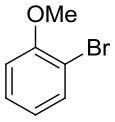
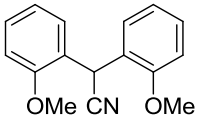
[a] Reaction conditions: ArCl (0.5 mmol), $Pd_2(dba)_3$ (1.5 mol %), XPhos (6.0 mol %), potassium/sodium cyanoacetate (0.5 mmol), xylene (1.0 mL) were stirred at 140 °C for 4 h under nitrogen (reaction times were not optimized for each substrate). [b] Isolated yields. [c] $[Pd(allyl)Cl]_2$ was used instead of $Pd_2(dba)_3$.

Table 4.3 Palladium-catalyzed diarylation of potassium/sodium cyanoacetate with aryl chlorides

Having the optimized reaction conditions in hand, a series of substituted aryl chlorides in this decarboxylative coupling was tested (Table 4.3). *Ortho*-, *meta*-, and *para*-substituted aryl chlorides coupled smoothly with cyanoacetates to generate α-diaryl nitriles. Keto and ester functional groups were found to be compatible under these reaction conditions (Table 4.3, entries 3, 4, 11, and 12). Sterically hindered aryl chlorides showed applicability in this decarboxylative coupling (Table 4.3, entries 11-14). Naphthyl chloride gave a moderate product yield, associated with naphthalene side product (Table 4.3, entries 15 and 16). In general, potassium cyanoacetate performed better than sodium cyanoacetate in this reaction, except for the naphthyl and keto-substituted coupling partners.

4.2.4 Scope of palladium-catalyzed decarboxylative diarylation of aryl bromides



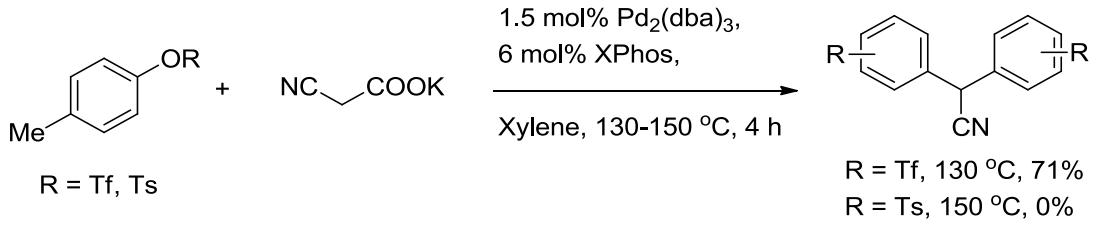
Entry[a]	ArBr	Product	Yield[b]
1			88%
2			73%
3			77%
4			53%
5			73%

[a] Reaction conditions: ArBr (0.5 mmol), $Pd(dba)_2$ (3.0 mol %), XPhos (6.0 mol %), potassium cyanoacetate (0.5 mmol), and xylene (1.0 mL) were stirred at 140 °C for 4 h under nitrogen (reaction times were not optimized for each substrate). [b] Isolated yields were reported.

Table 4.4 Palladium-catalyzed diarylation of potassium cyanoacetates with aryl bromides

Table 4.4 illustrated the arylation of potassium cyanoacetate using aryl bromides. No coupling products were found when the reaction temperature was lowered to 110 ℃. Substituted aryl bromides were coupled smoothly to desired products. Notably, a highly sterically hindered 2-bromobiphenyl was found to be a feasible coupling partner in this reaction.

4.2.5 Scope of palladium-catalyzed decarboxylative diarylation of aryl sulfonates



Scheme 4.2 Palladium-catalyzed diarylation of potassium cyanoacetates with aryl sulfonates

To expand the substrate scope further, we next investigated the possibility of using phenol-derived electrophiles as the coupling partners (Scheme 4.2). It should be noted that previous α-arylations of nitriles applied strong bases and were incompatible with base-sensitive aryl triflates.[129-132,134] Under our new reaction conditions, *p*-tolyl triflate was found to couple well with potassium cyanoacetate (Scheme 4.2).

4.3. Conclusion

In summary, we have developed a simple decarboxylative arylation of cyanoacetate using aryl chlorides, bromides, and sulfonates as the coupling partners. We believe this Pd system will be useful for α-diaryl nitrile synthesis. Further mechanistic studies are in progress.

4.4. Experimental section

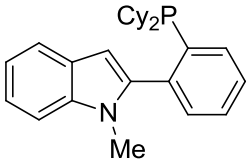
4.4.1 General considerations

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. All reactions were conducted in resealable screw cap Schlenk flask (approx. 20 mL volume) in the presence of Teflon coated magnetic stirrer bar (4 mm × 10 mm). All aryl halides were used as received.

Thin layer chromatography was performed on pre-coated 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 Melting Point instrument. ^{1}H NMR spectra were recorded on a 400 MHz spectrometer. Spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.26 ppm), or with D_2O (δ 4.79 ppm), or with

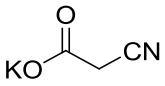
tetramethylsilane (TMS, δ 0.00 ppm) as the internal standard. Chemical shifts (δ) were reported as part per million (ppm) in δ scale downfield from TMS. ^{13}C NMR spectra were referenced to $CDCl_3$ (δ 77.0 ppm, the middle peak). Coupling constants (*J*) were reported in Hertz (Hz). Mass spectra (EI-MS and ES-MS) were recorded on a Mass Spectrometer. High-resolution mass spectra (HRMS) were obtained on a mass spectrometer (ESIMS). GC-MS analysis was conducted on a GCD system using a column (30 m × 0.25 mm). The products described in GC yield were accorded to GC-MS system. The known α-diaryl nitirile products were characterized by comparing to the corresponding ^{1}H- and ^{13}C-NMR reported in the literatures.

4.4.2 Procedures for indolyl phosphine ligands synthesis



CMPhos was prepared according to the literature procedures[172]

4.4.3 Procedures for potassium cyanoacetate synthesis[146]



A 200 ml, two-necked, round-bottomed flask was charged with 2-cyanoacetic acid (3.40 g, 40.0 mmol) and ethanol (40 ml). To this, a solution of potassium *tert*-butoxide (4.48 g, 40 mmol) in ethanol (40 ml) was added dropwise over 30 min. After completion of addition, the reaction mixture was stirred for another 1 hour at room temperature. After removing about 4/5 of the ethanol solvent by slow evaporation on rotary evaporator, 50 ml diethyl ether was wadded. The resulting solid was collected by filtration, washed sequentially with ethanol (5 ml x 2) and diethyl ether (10 ml x 2), transferred to a round-bottomed flask and dried under vacuum at 30℃ for 2 hours to provide potassium cyanoacetate in 94% yields.

4.4.4 General procedures for optimization of cyanation

$Pd(OAc)_2$ (3.4 mg, 0.015 mmol), XPhos (Pd:L = 1:2), and potassium cyanoacetate (0.5 mmol) were added into a Schlenk tube with the presence of magnetic stir bar which is Teflon-coated. The tube was evacuated and

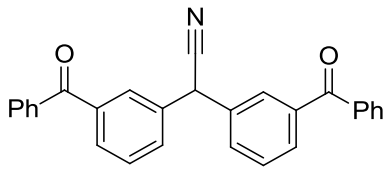
then pressurized with nitrogen for 3 cycles. 4-chlorotlouene (0.5 mmol) and 1.0 mL xylene was used as solvent. The tube was immersed into a preheated 140-150 ℃ oil bath for 4 hours. After completion of reaction, the reaction tube was allowed to cool to room temperature. Ethyl acetate and water were added for extraction. The organic layer was subjected to GC analysis. The GC yield obtained.

4.4.5 General procedures for the synthesis of α-diaryl nitriles:

$Pd_2(dba)_3$ (0.015 mmol), XPhos (0.06 mmol, Pd:L = 1:2), and potassium cyanoacetate (1.0 mmol) were added into a Schlenk tube in the presence of Teflon-coated magnetic stir bar. The tube was evacuated and re-filled with nitrogen for 3 cycles. ArCl (1.0 mmol) and xylene (2.0 mL) were then added. The tube was stirred for 1 min at room temperature and then immersed into a preheated 140 ℃ oil bath for 4 hours. The reaction was quenched by cooling to ambient temperature and EtOAc (~10 mL) and water (~10 mL) were added. The organic supernatant was analyzed by GC. The organic layer was isolated and the remained aqua was further extracted with EtOAc (~10 mL × 3). The combined organic phase was concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (230-400 mesh). The pure fraction was collected and dried under vacuum and followed proton (^1H) and carbon (^{13}C) NMR characterization.

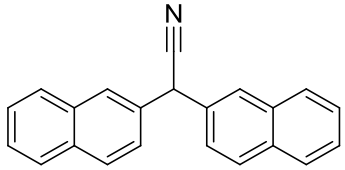
4.4.6 Characterization data of nitriles from aryl chlorides

2,2-bis(3-benzoylphenyl)acetonitrile (Table 4.3, entries 3 and 4)



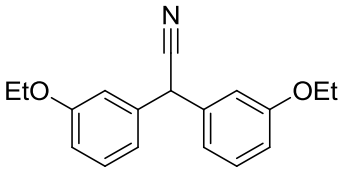
EA:Hexane=2:8, R_f=0.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.04 (s, 1H), 6.88-6.98 (m, 8H), 7.09-7.24 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.2, 119.4, 127.4, 128.1, 130.0, 130.4, 130.6, 131.3, 133.1, 137.1, 137.0, 137.3, 196.6; MS(EI) *m/z* (relative intensity) 221 (15), 194 (100), 165 (15), 144 (8); HRMS: calcd. for $C_{28}H_{19}NO_2H^+$: 424.1313, found.424.1310

2,2-di(naphthalen-2-yl)acetonitrile (Table 4.3, entries 15 and 16)[211]



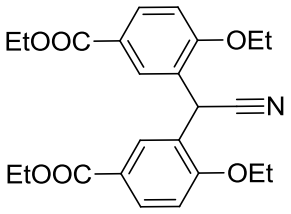
EA:Hexane=1:9, R_f=0.3; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.78 (s, 1H), 6.72-6.85 (m, 7H), 7.14-7.19 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.9, 125.2, 126.7, 126.8, 126.8, 127.7, 128.0, 129.2, 132.8, 132.9, 133.2; MS(EI) *m/z* (relative intensity) 293 (100, M^+), 265 (35), 207 (17), 132 (12).

2,2-bis(3-ethoxyphenyl)acetonitrile (Table 4.3, entries 1 and 2)



EA:Hexane=1:9, R_f=0.3; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37 (t, J=6.8 Hz, 6H), 3.98 (q, J=7.2 Hz, 4H), 5.02 (s, 1H), 6.81-6.91 (m, 6H), 7.22-7.26 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.6, 42.4, 63.4, 113.9, 114.1, 119.7, 130.1, 137.1, 159.4; MS(EI) *m/z* (relative intensity) 281 (100, M^+), 253 (15), 225 (63), 197 (27); HRMS: calcd. for $C_{18}H_{19}NO_2Na$: 304.1313, found 304.1311.

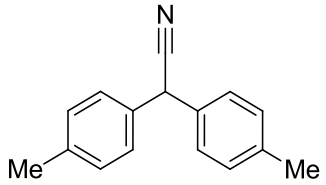
Diethyl 3,3'-(cyanomethylene)bis(4-ethoxybenzoate) (Table 4.3, entries 11 and 12)



EA:Hexane=1:9 , R_f=0.2; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37 (t, J=7.2 Hz, 6H), 1.48 (t, J=7.2 Hz, 6H), 4.03-4.11 (m, 4H), 4.34 (q, J=7.2 Hz, 4H), 5.58 (s, 1H), 6.84 (d, J=8.8 Hz, 2H), 7.96-7.99 (m, 2H), 8.19 (d, J=2.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 14.3, 33.2, 60.6, 64.2, 110.8, 118.7, 122.3, 122.6, 131.4, 131.6, 159.5, 165.8; MS(EI) *m/z* (relative intensity) 425 (15), 378 (100, M^+), 350 (17), 325 (25); HRMS: calcd. for

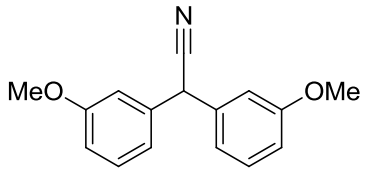
$C_{24}H_{27}NO_6Na$: 448.1736, found 448.1746.

2,2-di-*p*-tolylacetonitrile (Table 4.3, entries 9 and 10)[135]



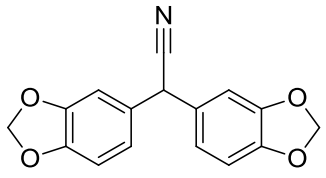
EA:Hexane=1:9, R_f=0.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 6H), 5.07 (s, 1H), 7.17 (d, J=8.0 Hz, 4H), 7.23 (d, J=8.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 41.9, 119.9, 127.5, 129.8, 133.2, 138.0; MS(EI) *m/z* (relative intensity) 221 (100, M^+), 206 (100), 179 (48), 129 (13).

2,2-bis(3-methoxyphenyl)acetonitrile (Table 4.3, entries 5 and 6)[136]



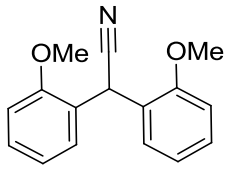
EA:Hexane=2:8, R_f=0.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 (s, 6H), 5.09 (s, 1H), 6.86-6.97 (m, 6H), 7.26-7.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.3, 55.2, 113.4, 113.5, 119.8, 130.1, 137.0, 160.0; MS(EI) *m/z* (relative intensity) 253 (100, M^+), 222 (17), 195 (9), 178 (9).

2,2-bis(benzo[d][1,3]dioxol-5-yl)acetonitrile (Table 4.3, entries 7 and 8)



EA:Hexane=2:8, R_f=0.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.26 (s, 1H), 5.226 (d, J=1.6 Hz, 4H), 6.05-6.15 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 41.8, 101.4, 108.0, 108.5, 119.6, 121.0, 129.6, 147.6, 148.3; MS(EI) *m/z* (relative intensity) 281 (100, M^+), 251 (10), 221 (34), 193 (36); HRMS: calcd. for $C_{16}H_{11}NO_4Na$: 304.0586, found 304.0597.

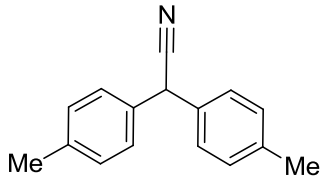
2,2-bis(2-methoxyphenyl)acetonitrile (Table 4.3, entries 13 and 14)[137]



EA:Hexane=1:9, R_f=0.2; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (s, 6H), 5.76 (s, 1H), 6.90-6.98 (m, 4H), 7.26-7.33 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.2, 55.5, 110.8, 120.0, 120.6, 123.4, 129.1, 129.4, 156.5; MS(EI) *m/z* (relative intensity) 253 (100,M^+), 238 (30), 222 (12), 207 (33).

4.4.7 Characterization data of nitriles from aryl bromides

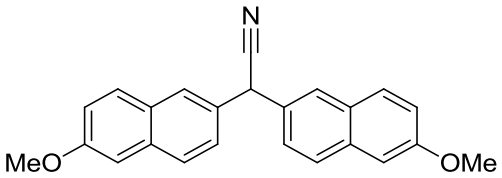
2,2-di-p-tolylacetonitrile (Table 4.4, entry 3)[135]



EA:Hexane=1:9, R_f=0.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 6H), 5.07

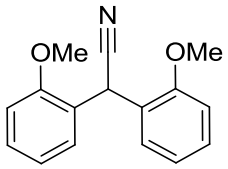
(s, 1H), 7.16-7.18 (m, 4H), 7.22-7.24 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 41.9, 119.9, 127.5, 129.8, 133.2, 138.0; MS(EI) *m/z* (relative intensity) 221 (100,M^+), 206 (100), 179 (53), 129 (16).

2,2-bis(6-methoxynaphthalen-2-yl)acetonitrile (Table 4.4, entry 4)



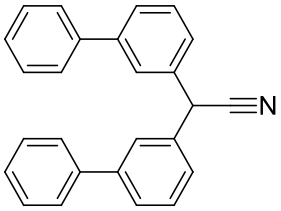
EA:Hexane=2:8, R_f=0.3; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.92 (s, 6H), 5.39 (s, 1H), 7.12-7.20 (m, 4H), 7.35-7.37 (m, 2H), 7.71-7.83 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.6, 55.4, 105.7, 119.6, 125.9, 126.6, 128.0, 128.7, 129.5, 130.9, 134.1, 158.3; MS(EI) *m/z* (relative intensity) 354 (2, M^+), 304 (100), 276 (39), 234 (26); HRMS: calcd. for $C_{24}H_{19}NO_2H^+$: 376.1313, found 376.1310.

2,2-bis(2-methoxyphenyl)acetonitrile (Table 4.4, entry 5)[137]



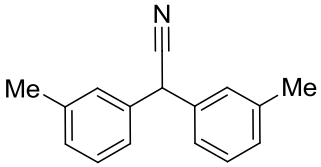
EA:Hexane=1:9, R_f=0.2; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (s, 6H), 5.74 (s, 1H), 6.89-6.97 (m, 4H), 7.26-7.32 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.2, 55.6, 110.9, 120.6, 123.5, 129.2, 129.4, 156.6; MS(EI) *m/z* (relative intensity) 253 (100, M^+), 207 (29), 181 (10), 152 (8).

2,2-di([1,1'-biphenyl]-3-yl)acetonitrile (Table 4.4, entry 2)



EA:Hexane=2:8, R_f=0.3; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.24 (s, 1H), 7.11-7.45 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.4, 127.3, 127.9, 128.0, 128.2, 128.8, 128.8, 130.7, 133.2, 139.6, 142.0; MS(EI) *m/z* (relative intensity) 345 (100, M^+), 267 (8), 190 (8), 165 (12); HRMS: calcd. for C26H19NH$^+$: 368.1415, found 368.1430.

2,2-di-m-tolylacetonitrile (Table 4.4, entry 1)[211]

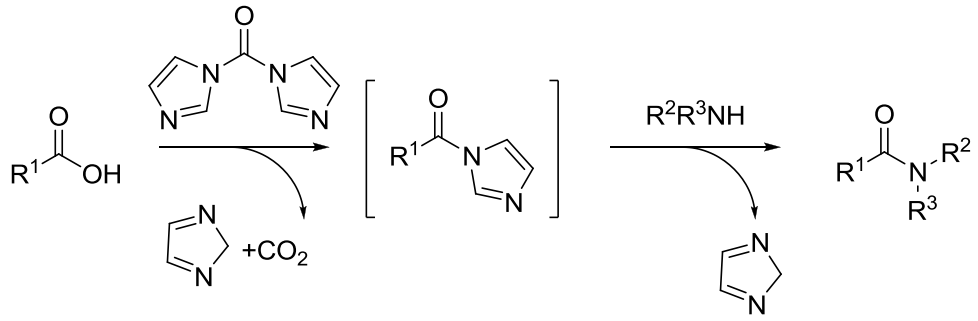


EA:Hexane=1:9, R_f=0.4;^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36 (s, 6H), 5.06 (s, 1H), 7.13-7.28 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 42.5, 119.9, 124.8, 128.3, 128.9, 129.0, 135.9, 139.0; MS(EI) *m/z* (relative intensity) 221 (100,M^+), 206 (82), 179 (54), 129 (16).

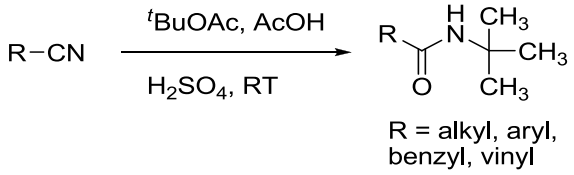
Chapter 5 Palladium-catalyzed amidation of aryl halides by isocyanides

5.1. Introduction

Amides are important substructures in *N*-containing compounds in organic chemistry and possible to transform a number of natural products, potent pharmaceuticals as well as bioactive polymers.[4,212-217] Traditionally, amides were converted from activated carboxylic acid derivatives[1,218-221] or rearrangement reactions[222] in the presence of base or acid (Scheme 5.1 and). The procedure was generally tedious and anhydrous condition is crucial.

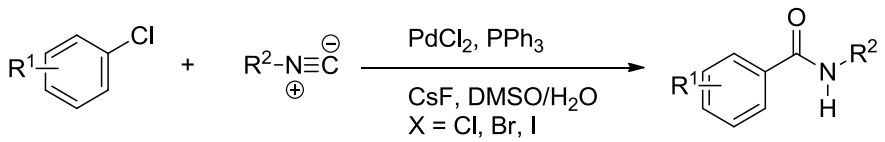


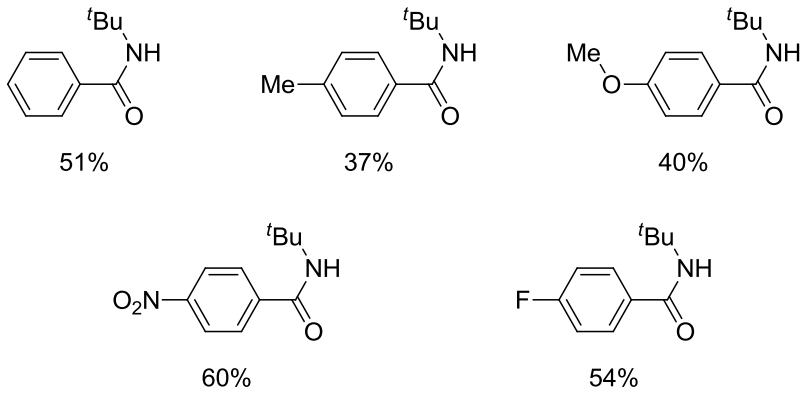
Scheme 5.1 The formation of amides from carboxylic acids and amines



Scheme 5.2 A modified Ritter reaction develop by Baum *et al*

This gave rise to transition-metal-catalyzed reactions as an effective tool for the formation of carbon-carbon and carbon-heteroatom bonds.[191,192,207] The most recently important development was direct amide synthesis from alcohols and amines using Ag-[193], Ru-[164,208-210,223], and Rh-[224,225] based catalytic systems with hydrogen gas as side-product. There were limited literatures about palladium-catalyzed aminocarbonylation for the synthesis of amides from aryl halides.[226-234] Some publications used carbon monoxide as the carbonyl source which restricted the scope of this type of reactions.[235-241] Thus, there was a demand for a palladium-catalyzed direct amidation of aryl halides under mild conditions in the absence of toxic reagents. Isocyanide is a kind of unsaturated molecules similar to carbon monoxide, but it has already had the basic motifs of the amide group (-C-N-R). Hence, it is believed that *iso*-nitriles are suitable for the substitution of toxic carbon monoxide for the amidation.[206] In 2011, Jiang *et al*. developed a novel and practical synthesis of amides *via* palladium-catalyzed C-C coupling of aryl halides with isocyanides.[206] Jiang and co-worker demonstrated the effectiveness of the reaction towards aryl bromide but aryl chlorides elucidated ungratified yields (Scheme 5.3).[206]





[a] Reaction condition: 1.0 mmol aryl halide, 1.2 mmol isocyanide, 5 mol% $PdCl_2$, 10 mol% PPh_3, 1.0 equiv CsF, and 0.1 mL of H_2O in 1.0 mL DMSO at 110 °C for 15 h.

Scheme 5.3 Palladium-catalyzed synthesis of aryl amides from aryl chlorides and isocyanide

Therefore, I would like to explore a palladium-catalyzed amidation of aryl chloride with isocyanide.

5.2. Progress

At the beginning, I repeated the reaction developed by Jiang *et al.*, but unfortunately, trace amount of the product was observed. There was no different for the reaction conducted under both nitrogen and oxygen. Several parameters were checked for the reason of failure (Table 5.1).

Entry[a]	Ambient	Solvent : water (ratio)	Metal : Ligand (ratio)	Yield[b]
1	Air	DMSO : H2O (10:1)	$PdCl_2$: PPh_3 (1:2)	Trace
2	Nitrogen	DMSO : H2O (10:1)	$PdCl_2$: PPh_3 (1:2)	Trace
3	Air	Extra Dried DMSO : H_2O (10:1)	$PdCl_2$: PPh_3 (1:2)	Trace
4	Air	DMSO : H2O (10:0.44)	$PdCl_2$: PPh_3 (1:2)	Trace
5	Air	DMSO : H2O (10:0.50)	$PdCl_2$: PPh_3 (1:2)	Trace
6	Air	DMSO : H2O (10:0.66)	$PdCl_2$: PPh_3 (1:2)	Trace
7	Air	DMSO : H2O (10:0.80)	$PdCl_2$: PPh_3 (1:2)	Trace
8	Air	DMSO : H2O (10:1)	$PdCl_2$: PPh_3 (1:3)	Trace
9	Air	DMSO : H2O (10:1)	$PdCl_2$: PPh_3 (1:4)	Trace

[a] Reaction conditions: 1.0 mmol 4-bromotolene, 1.2 mmol *tert*-butyl isocyanide, 5 mol% $PdCl_2$, 10 mol% PPh_3, 1.0 equiv CsF, 0.1 mL H_2O in 1.0 mL DMSO at 90 ^oC for 12 h. [b] Yields are detected by GC-FID with dodecane as internal stardard.

Table 5.1 Parameters checked for the failure

Although these parameters were checked, the reason of failure was still unknown. The purity of triphenylphosphine was then suspected, so it was purified by re-cystallization according to standard method.[174] I am purifying the triphenylphosphine to test the feasibility of the reaction. The reaction is still under investigation. Further experiments will be done in the future.

Conclusion

In summary, a general and efficient palladium-catalyzed cyanation of aryl chlorides is reported. The reaction temperature of 70 ℃ is the mildest condition reported so far for such reactions. Particularly, it is noteworthy that water is found necessary as co-solvent to facilitate the cyanation. This essential finding may be useful for the future cyanation investigations using $K_4[Fe(CN)_6]\cdot 3H_2O$ as the cyanide source.

In addition, the mildest palladium-catalyzed cyanation of aryl bromides using $K_4[Fe(CN)_6]\cdot 3H_2O$ as the cyanide source is preformed. The new palladium/Ph-*o*-Andole-phos catalyst system described here exhibits good functional group compatibility. Noticeably, the phosphine ligand bearing $–PPh_2$ moiety is found to have a better efficacy than the ligand with $–PCy_2$ group in this reaction. This unique finding is anticipate to be useful for further complementary investigation of aryl halide efficiency in cyanation and related reactions using $K_4[Fe(CN)_6]\cdot 3H_2O$ as the cyanide source.

Furthermore, the palladium-catalyzed cyanation of aryl mesylates is demonstrated. The reaction temperature of 80 ℃ is the mildest ever reported for the coupling of aryl mesylates. Interestingly, the use of water as the solvent

or a co-solvent was found to be essential.

These palladium catalyst systems exhibited excellent functional-group tolerance: nitrile, ester, keto, aldehydes, free amine, and heterocyclic groups remained intact during the course of reaction. Moreover, the system is also applicable to the cyanation of aryl and alkenyl tosylates. The one-pot cyanation-amination sequence of aryl sulfonates and aryl chlorides demonstrated the suitability of this reaction for the introduction of a nitrile group and manipulation of a further functional group in a synthetic pathway without isolation of the initial nitrile-substituted intermediate.

Given the practical advantages of these sulfonating agents and the favorable cyanation conditions, it is believed that this method will find widespread use in organic synthesis. Palladium-catalyzed cyanation with $K_4[Fe(CN)_6]\cdot 3H_2O$ as the cyanide source is going to be the best method for the synthesis of functionalized aryl nitriles on a laboratory scale. However, every type of chemical transformation has disadvantages too, so that future improvements will be done. Although $K_4[Fe(CN)_6]\cdot 3H_2O$ becomes popular as the cheapest cyanide source, the precious metal palladium and ligands are quite expensive, especially those cyanations preformed only with high catalyst loadings. Hence, it is expected that palladium-catalyzed cyanation can be

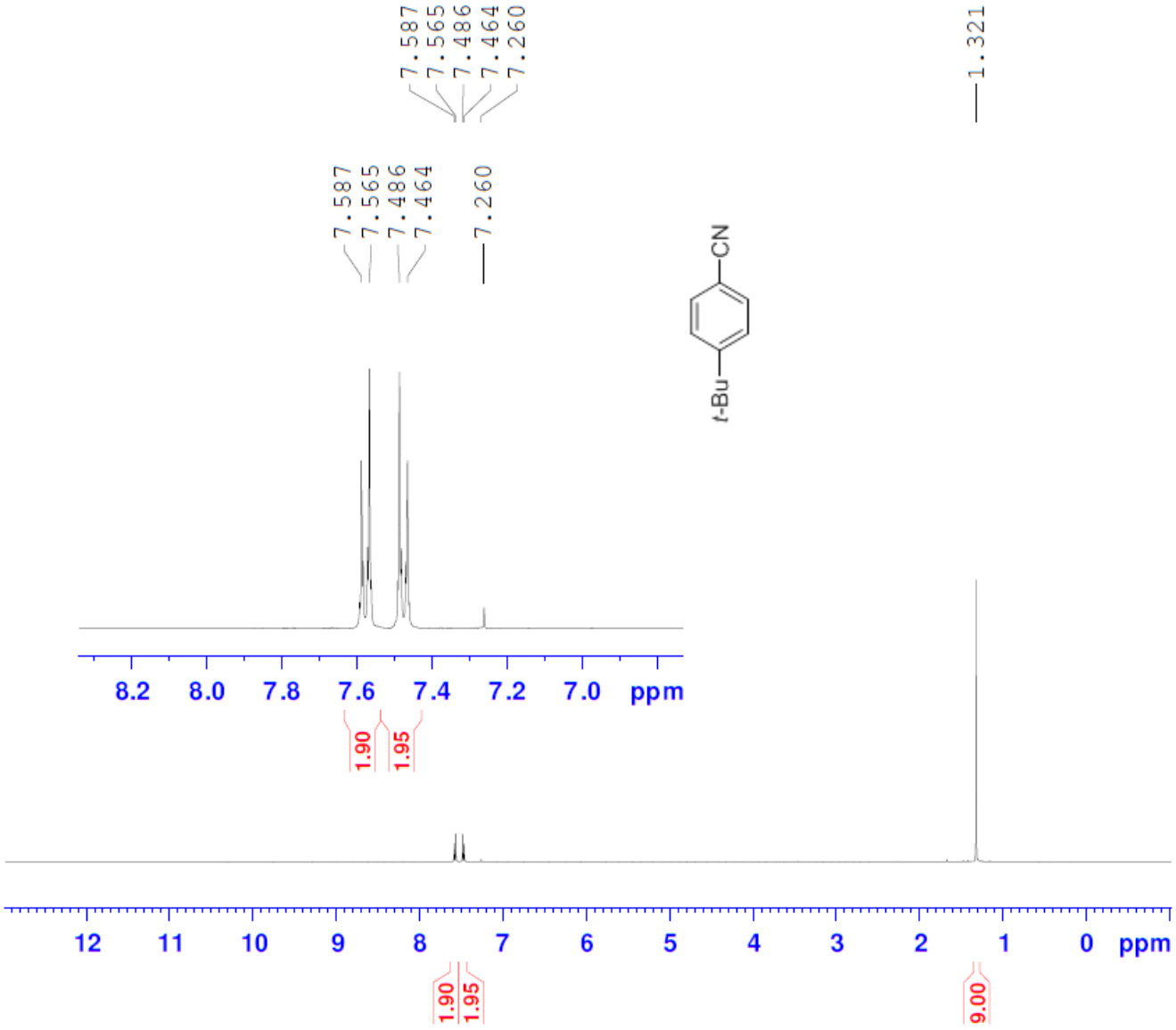
performed with low catalyst loading in the future. Finally, palladium-catalyzed cyanation will be applied in organic synthesis more frequently especially in the area of tandem reactions novel interesting reaction sequences.

Appendices

Characterizations of products from palladium-catalyzed cyanation

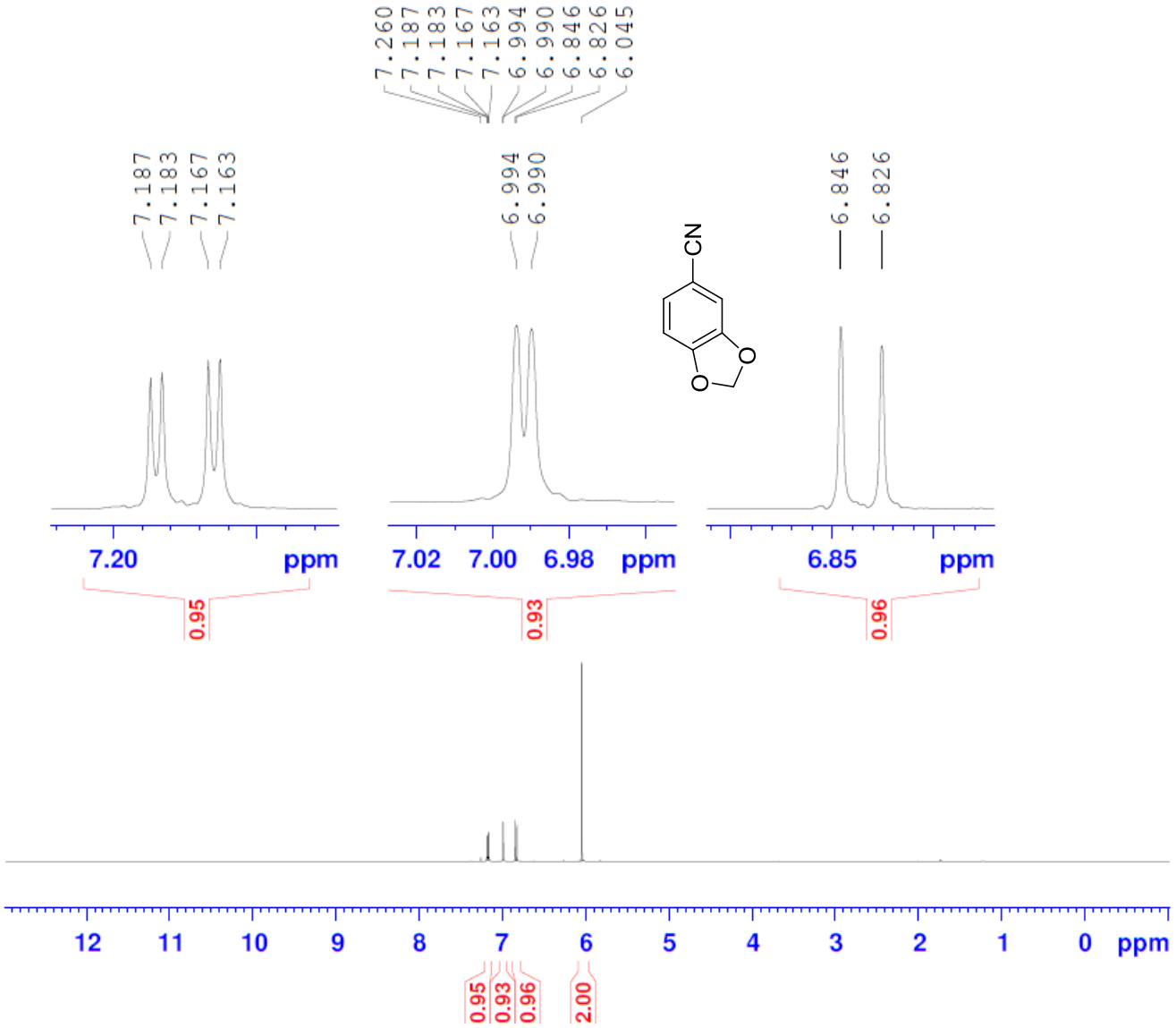
^{1}H-, ^{13}C-NMR spectra of products from palladium-catalyzed cyanation of aryl mesylates

pyy163Cyan-H

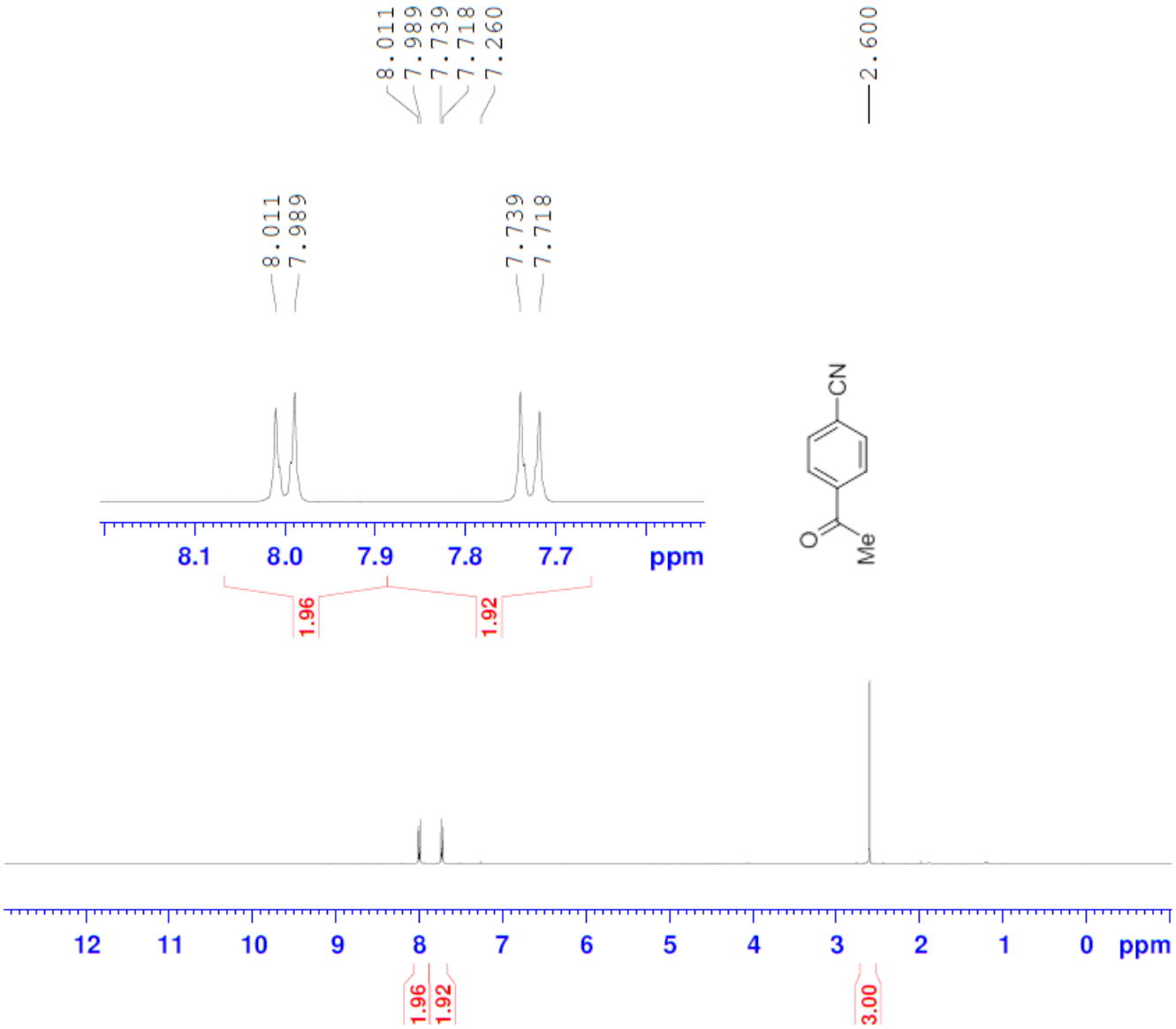


NAME	pyy163Cyan
EXPNO	1
PROCNO	1
Date_	20100420
Time	14.58
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	32
DW	89.333 usec
DE	6.50 usec
TE	296.1 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300098 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

pyy168Cyan-H

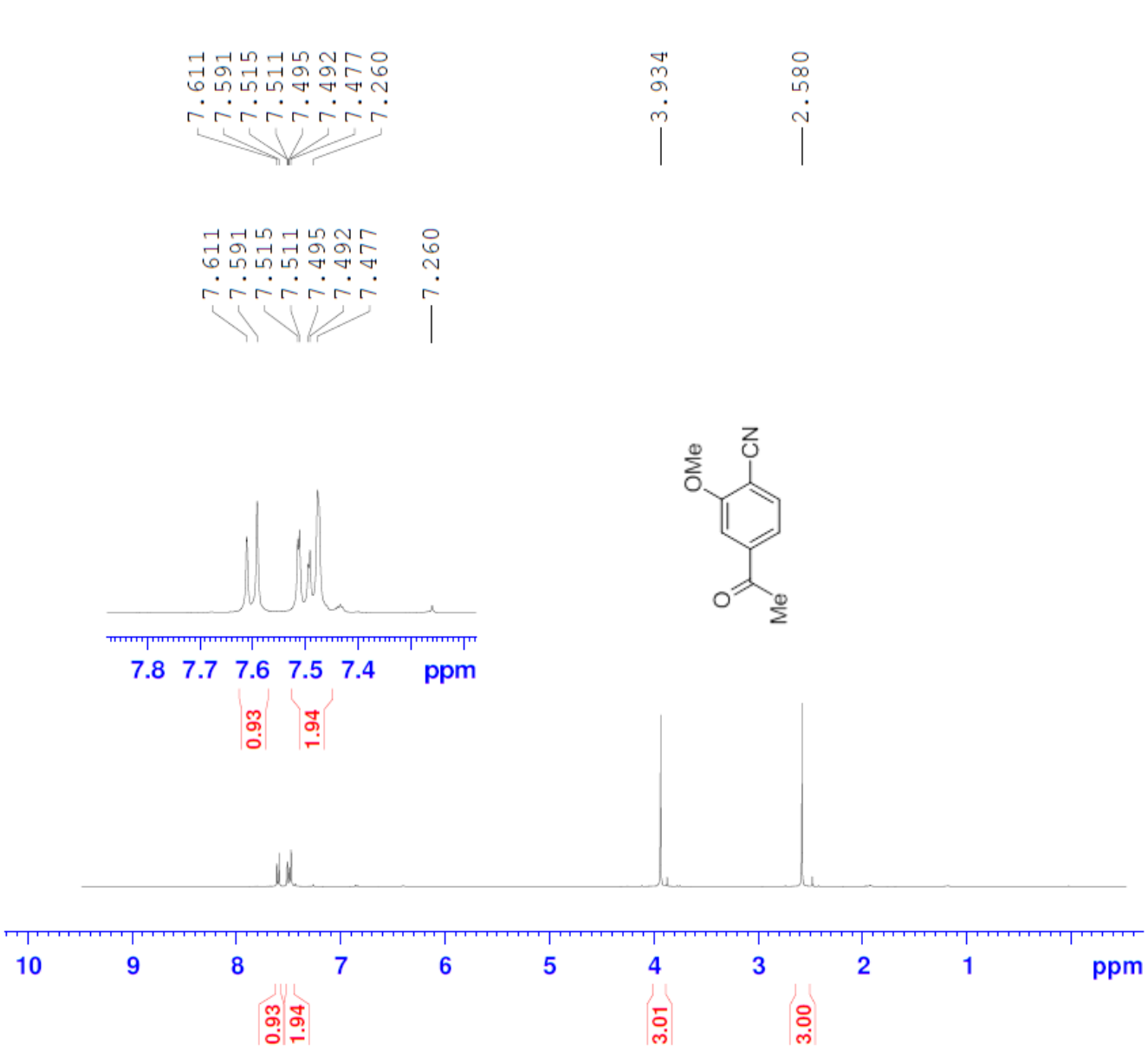


NAME	pyy168Cyan
EXPNO	1
PROCNO	1
Date_	20100420
Time	12.08
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	45.2
DW	89.333 usec
DE	6.50 usec
TE	295.9 K
D1	1.00000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300097 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



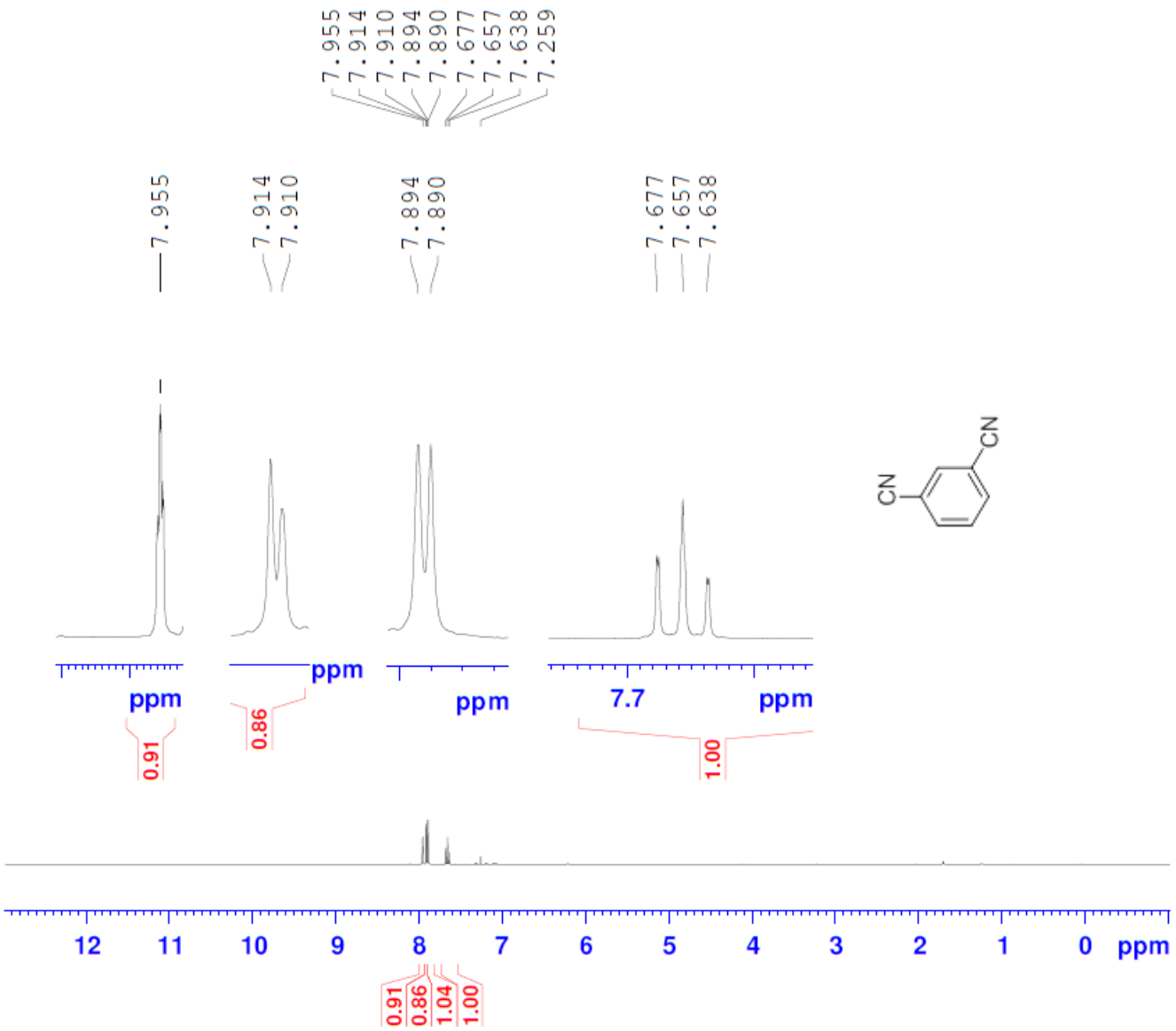
BRUKER

NAME	pyy174Cyan
EXPNO	1
PROCNO	1
Date_	20100421
Time	14.38
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	8
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	297.7 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	400.1300096 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



NAME	pyy175Cyan	
EXPNO	1	
PROCNO	1	
Date_	20100421	
Time	13.57	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zg30	
TD	32768	
SOLVENT	CDCl3	
NS	8	
DS	2	
SWH	4006.410	Hz
FIDRES	0.122266	Hz
AQ	4.0894966	sec
RG	28.5	
DW	124.800	usec
DE	6.50	usec
TE	297.8	K
D1	1.00000000	sec
TD0	1	
========	CHANNEL f1 ========	
NUC1	1H	
P1	14.70	usec
PL1	0.00	dB
PL1W	11.88122272	W
SFO1	400.1318007	MHz
SI	32768	
SF	400.1300095	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	

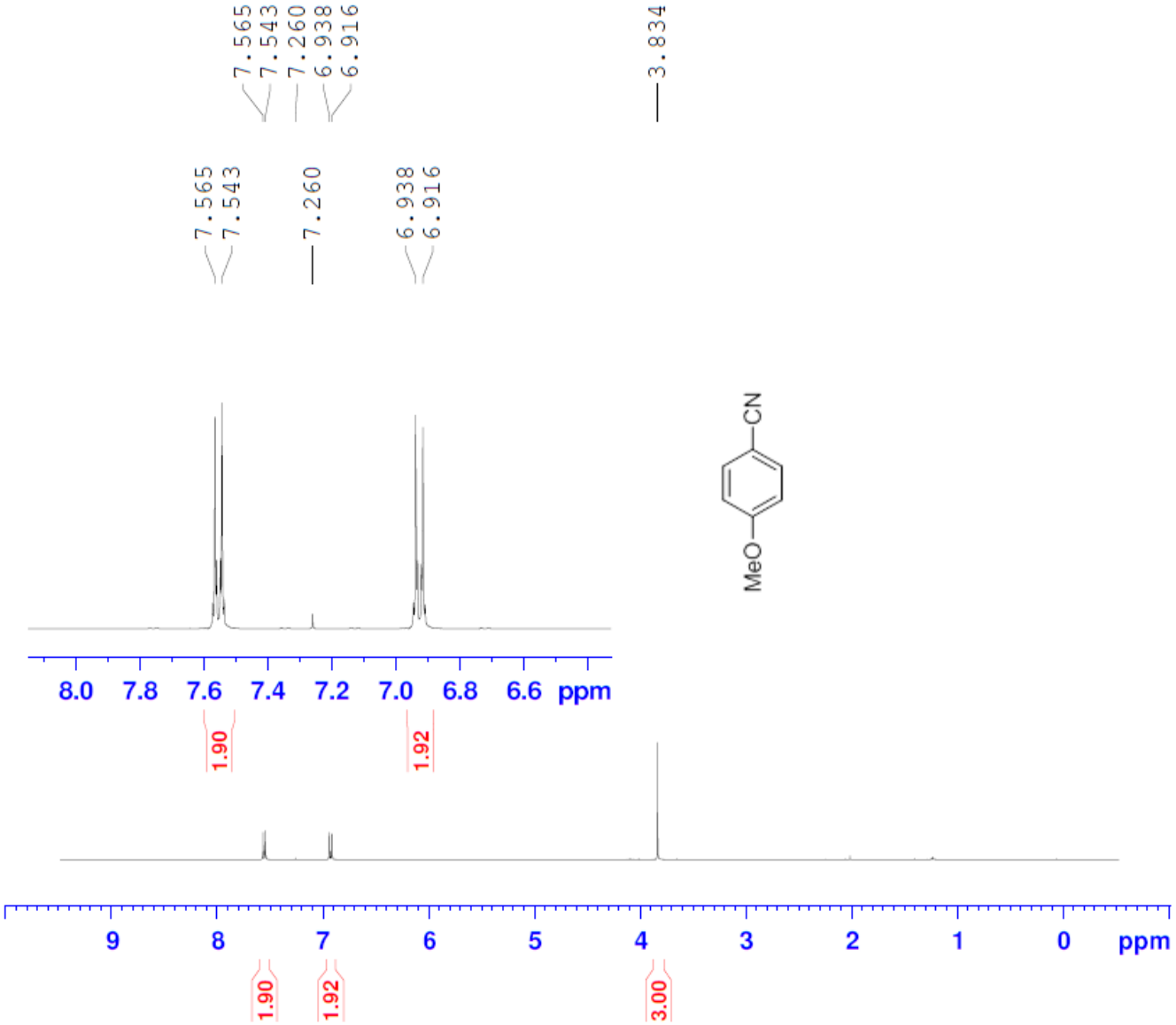
pyy179Cyan-H



BRUKER

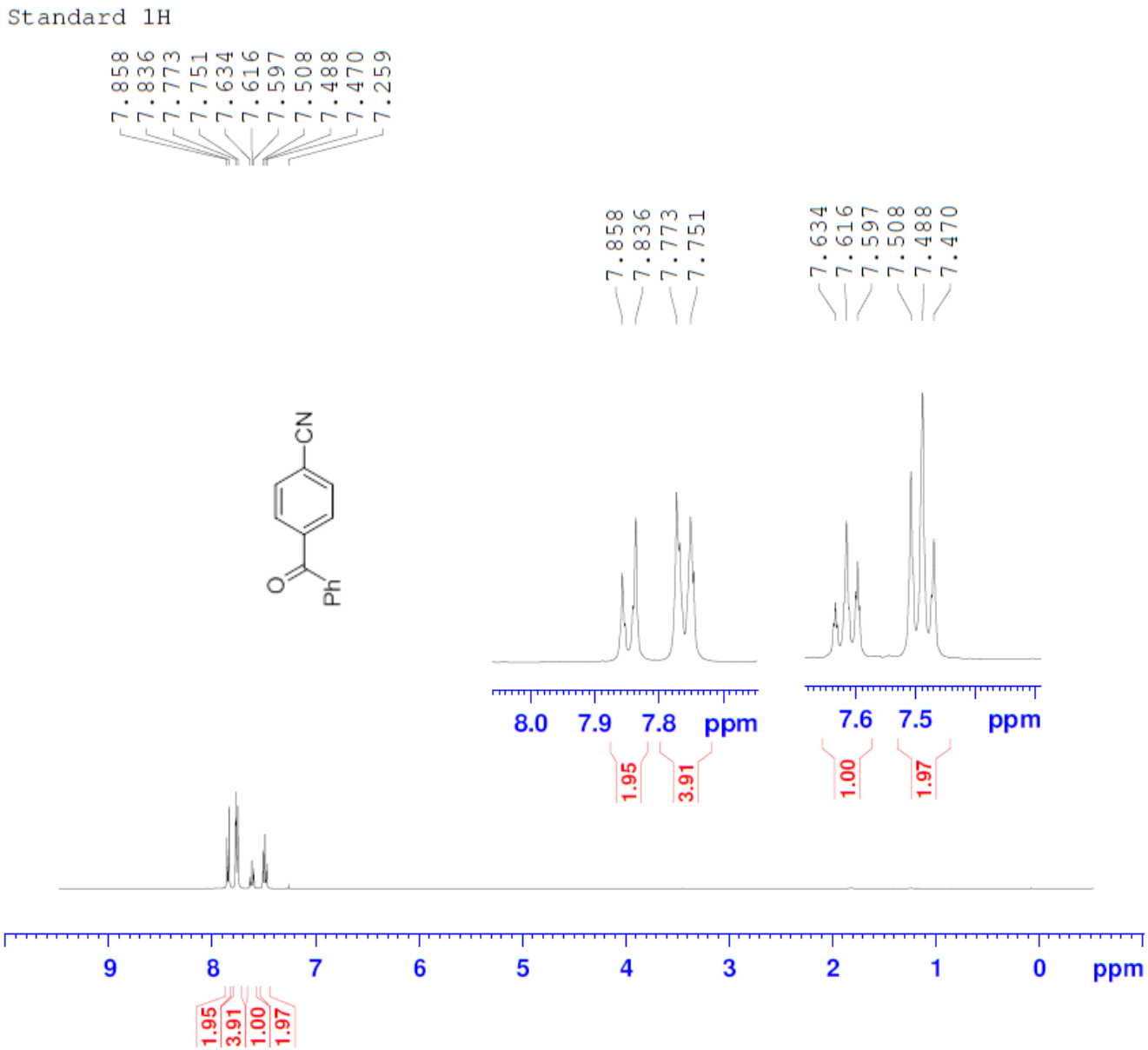
NAME	pyy179Cyan
EXPNO	1
PROCNO	1
Date_	20100421
Time	15.01
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	114
DW	89.333 usec
DE	6.50 usec
TE	297.8 K
D1	1.00000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300102 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Standard 1H



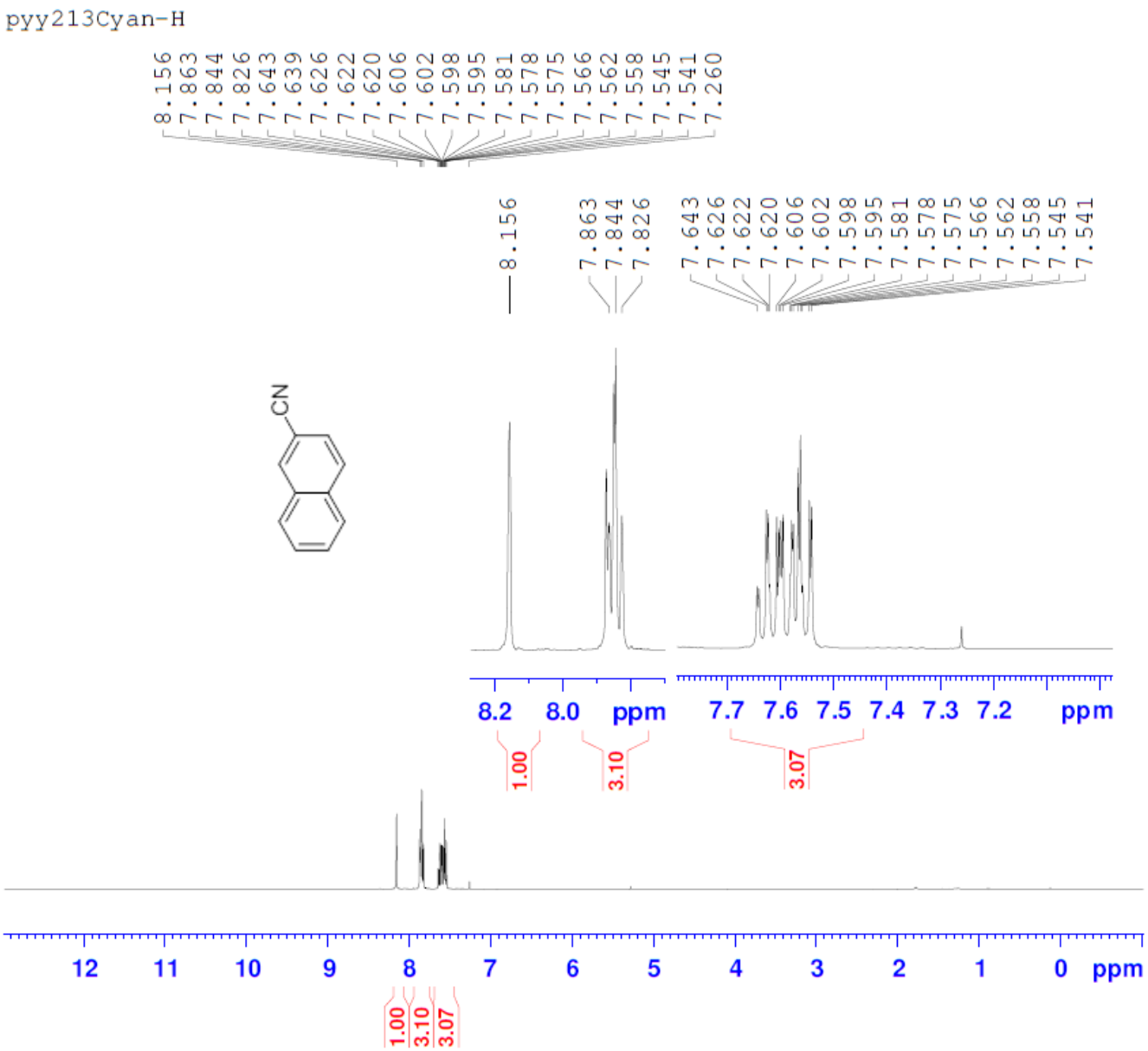
NAME	pyy196Cyan
EXPNO	1
PROCNO	1
Date_	20100504
Time	18.00
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	8
DS	2
SWH	4006.410 Hz
FIDRES	0.122266 Hz
AQ	4.0894966 sec
RG	40.3
DW	124.800 usec
DE	6.50 usec
TE	297.5 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1318007 MHz
SI	32768
SF	400.1300096 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Standard 1H



NAME	pyy207Cyan
EXPNO	3
PROCNO	1
Date_	20100507
Time	17.40
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	8
DS	2
SWH	4006.410 Hz
FIDRES	0.122266 Hz
AQ	4.0894966 sec
RG	40.3
DW	124.800 usec
DE	6.50 usec
TE	297.2 K
D1	1.00000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1318007 MHz
SI	32768
SF	400.1300096 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

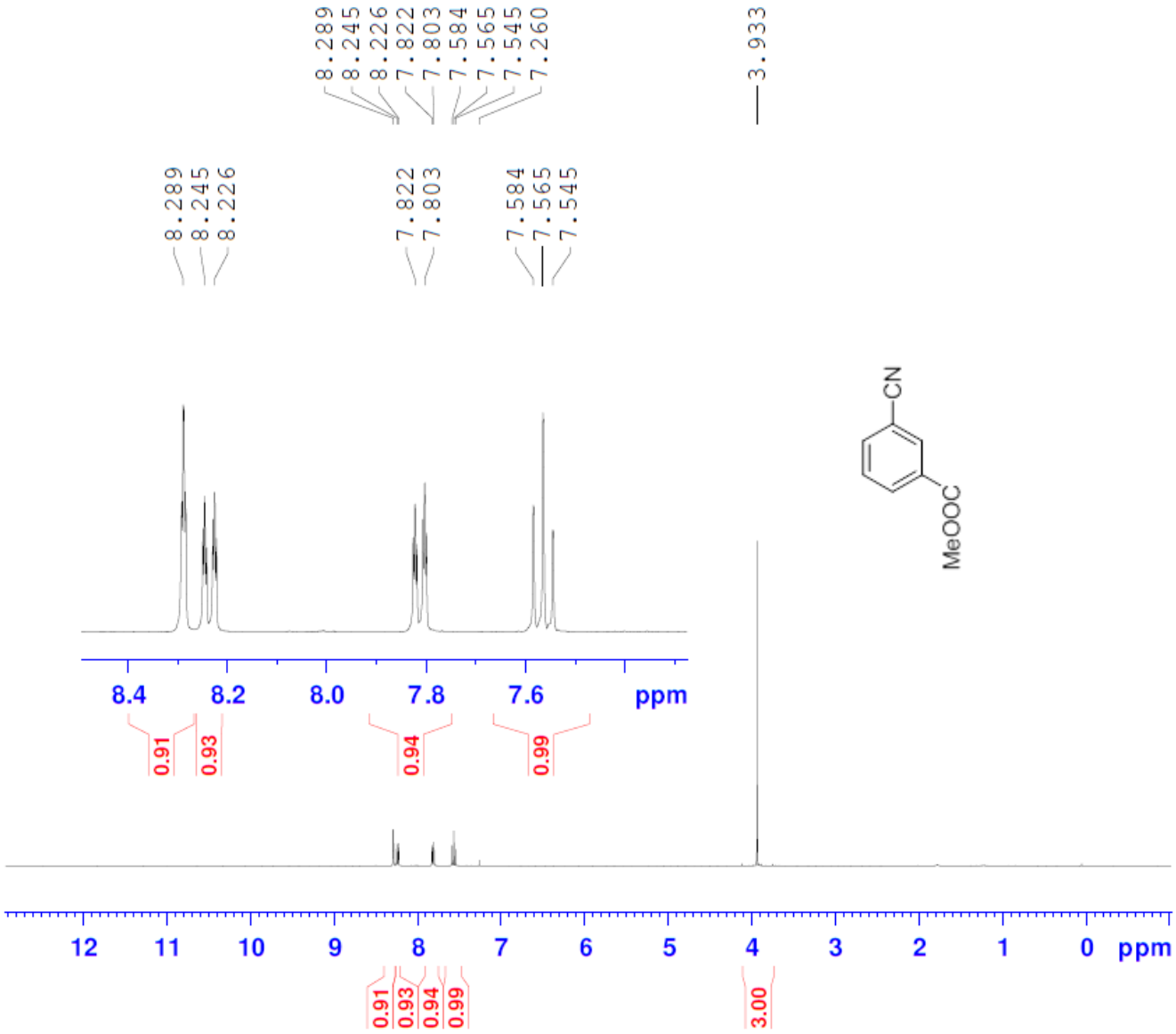
pyy213Cyan-H



BRUKER

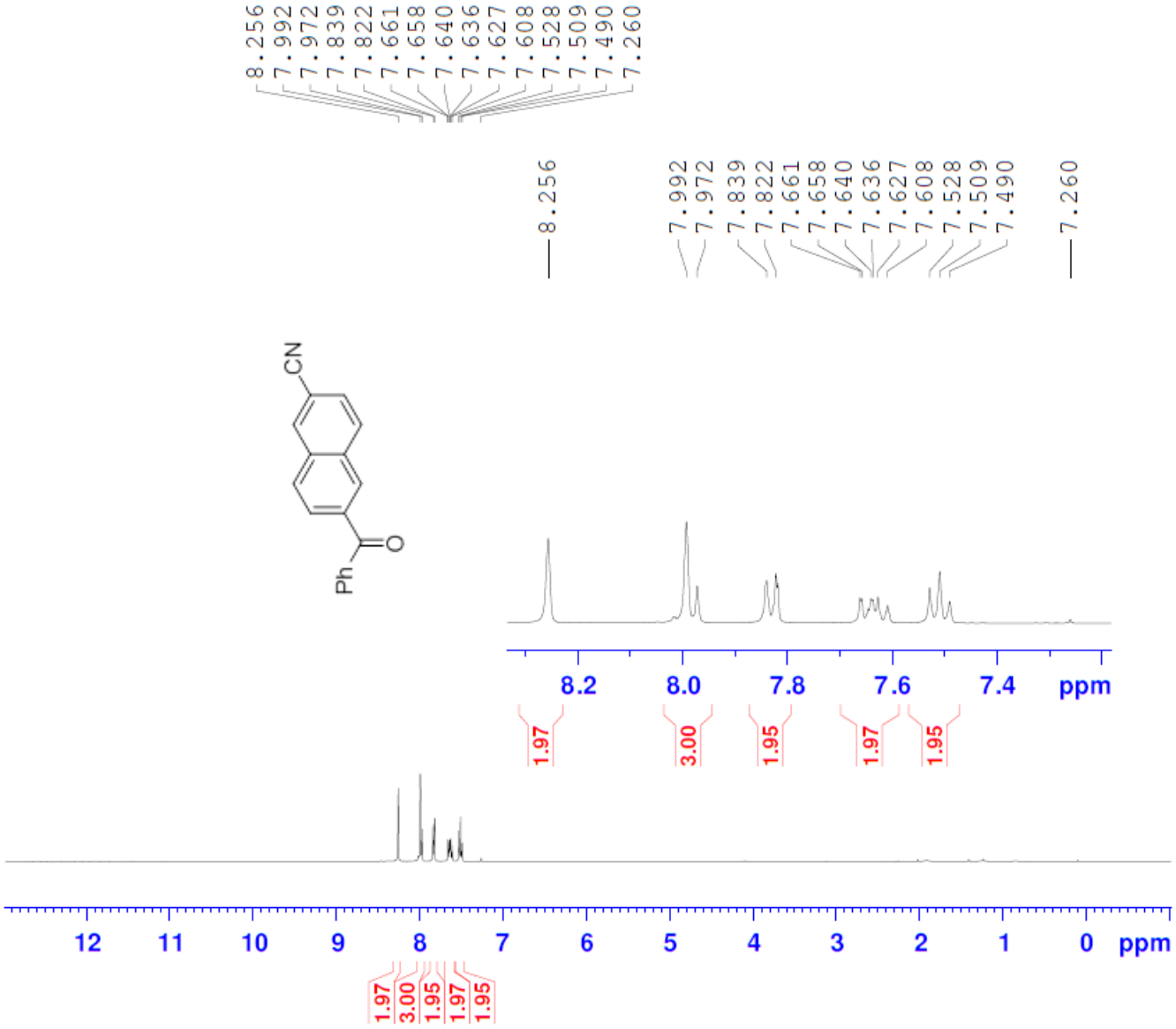
NAME	pyy213Cyan	
EXPNO	1	
PROCNO	1	
Date_	20100513	
Time	19.36	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zg30	
TD	32768	
SOLVENT	CDCl3	
NS	8	
DS	2	
SWH	5597.015	Hz
FIDRES	0.170807	Hz
AQ	2.9273248	sec
RG	32	
DW	89.333	usec
DE	6.50	usec
TE	296.4	K
D1	1.00000000	sec
TD0	1	
========	CHANNEL f1 ========	
NUC1	1H	
P1	14.70	usec
PL1	0.00	dB
PL1W	11.88122272	W
SFO1	400.1324008	MHz
SI	32768	
SF	400.1300094	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	

pyy214Cyan-H



NAME	pyy214Cyan	
EXPNO	1	
PROCNO	1	
Date_	20100512	
Time	11.09	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zg30	
TD	32768	
SOLVENT	CDCl3	
NS	8	
DS	2	
SWH	5597.015	Hz
FIDRES	0.170807	Hz
AQ	2.9273248	sec
RG	45.2	
DW	89.333	usec
DE	6.50	usec
TE	295.9	K
D1	1.00000000	sec
TD0	1	
========	CHANNEL f1 ========	
NUC1	1H	
P1	14.70	usec
PL1	0.00	dB
PL1W	11.88122272	W
SFO1	400.1324008	MHz
SI	32768	
SF	400.1300096	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	

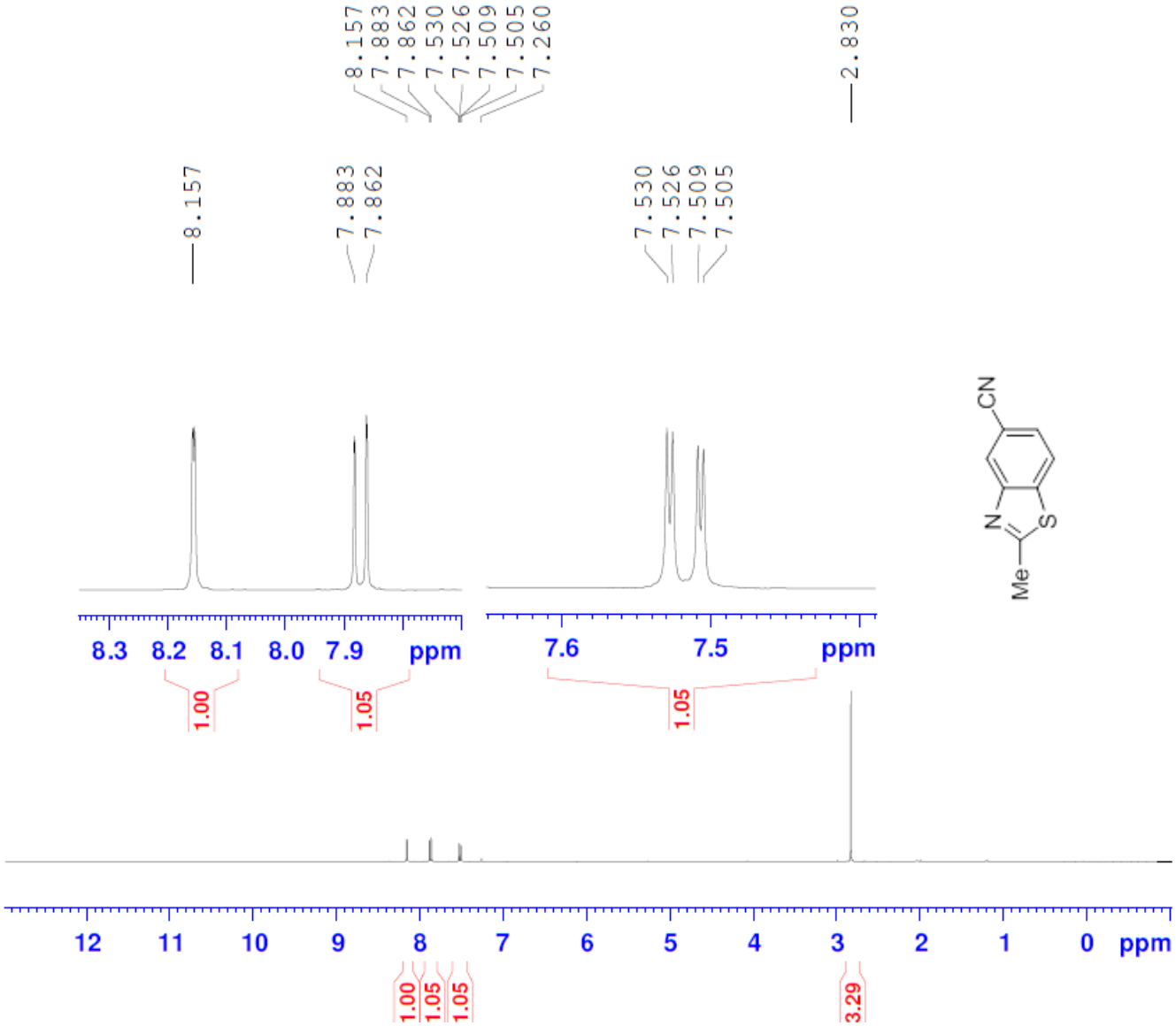
pyy363Cyan-H



BRUKER

NAME	pyy363Cyan
EXPNO	1
PROCNO	1
Date_	20100708
Time	12.00
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	4
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	36
DW	89.333 usec
DE	6.50 usec
TE	298.4 K
D1	1.00000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300095 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

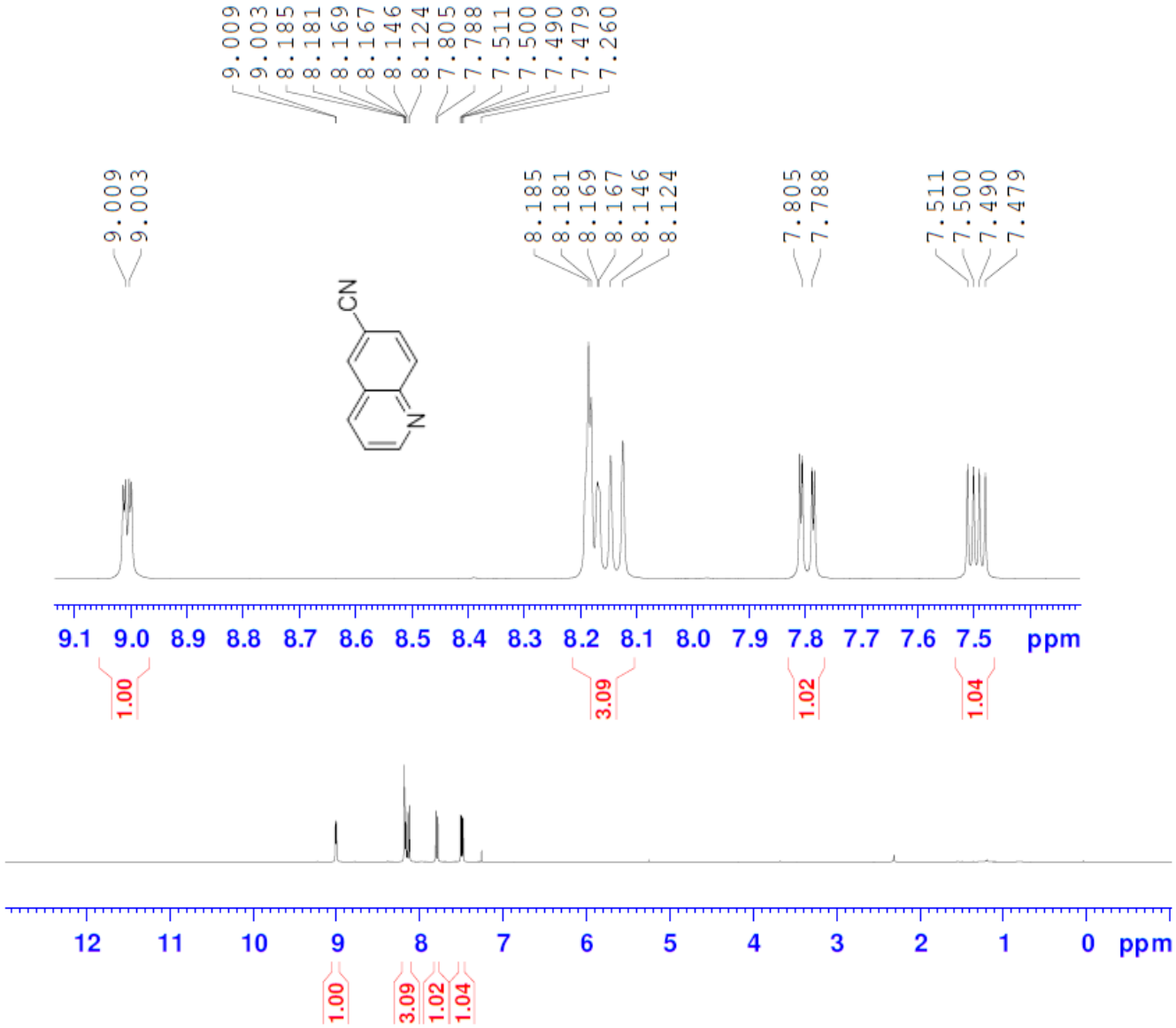
pyy231Cyan-H



BRUKER

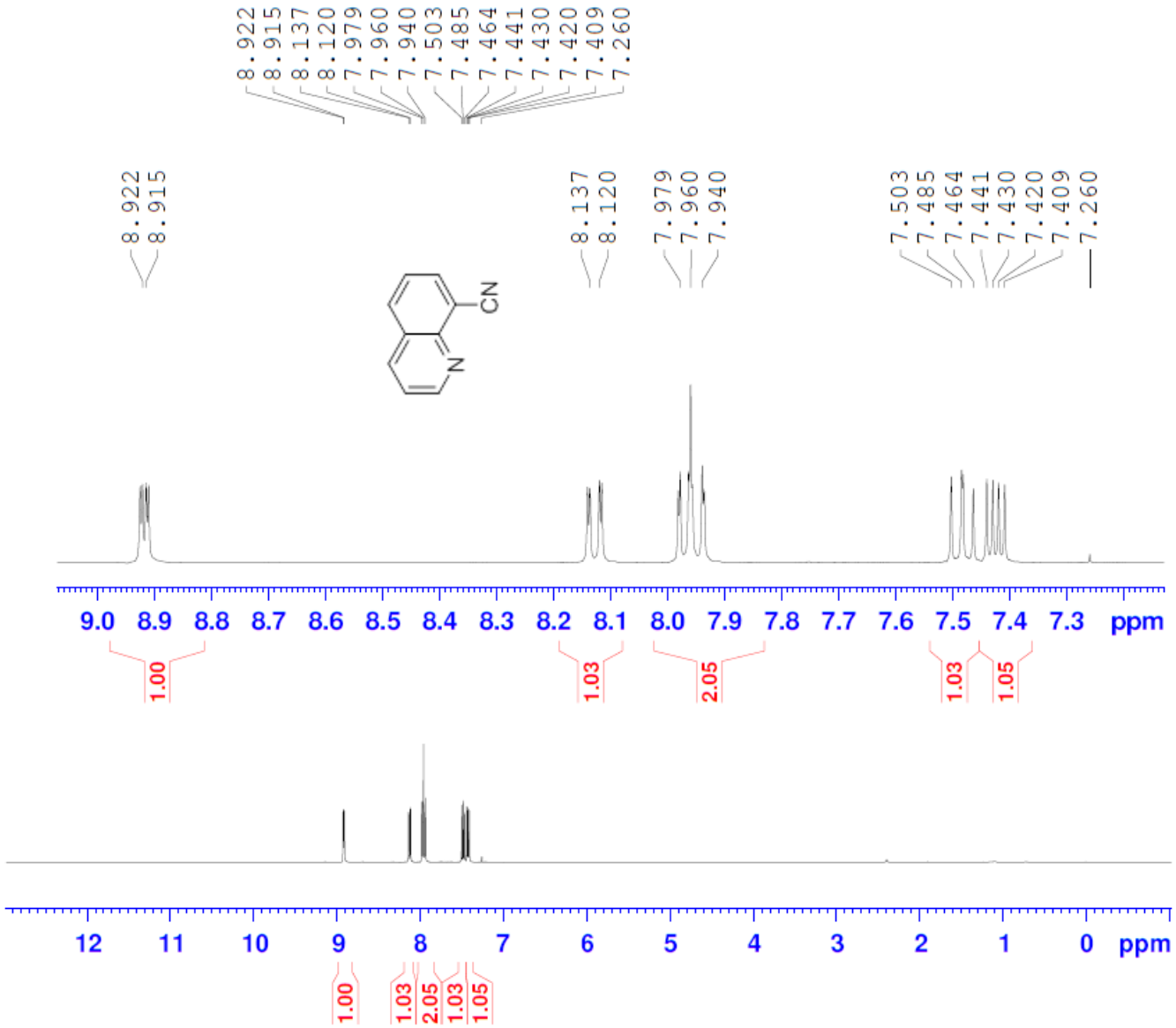
NAME	pyy231Cyan	
EXPNO	1	
PROCNO	1	
Date_	20100517	
Time	12.16	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zg30	
TD	32768	
SOLVENT	CDCl3	
NS	8	
DS	2	
SWH	5597.015	Hz
FIDRES	0.170807	Hz
AQ	2.9273248	sec
RG	45.2	
DW	89.333	usec
DE	6.50	usec
TE	295.9	K
D1	1.00000000	sec
TD0	1	
========	CHANNEL f1 ========	
NUC1	1H	
P1	14.70	usec
PL1	0.00	dB
PL1W	11.88122272	W
SFO1	400.1324008	MHz
SI	32768	
SF	400.1300097	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	

pyy225Cyan-H



NAME	pyy225Cyan	
EXPNO	1	
PROCNO	1	
Date_	20100513	
Time	20.13	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zg30	
TD	32768	
SOLVENT	CDCl3	
NS	8	
DS	2	
SWH	5597.015	Hz
FIDRES	0.170807	Hz
AQ	2.9273248	sec
RG	45.2	
DW	89.333	usec
DE	6.50	usec
TE	296.4	K
D1	1.00000000	sec
TD0	1	
========	CHANNEL f1 ========	
NUC1	1H	
P1	14.70	usec
PL1	0.00	dB
PL1W	11.88122272	W
SFO1	400.1324008	MHz
SI	32768	
SF	400.1300097	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	

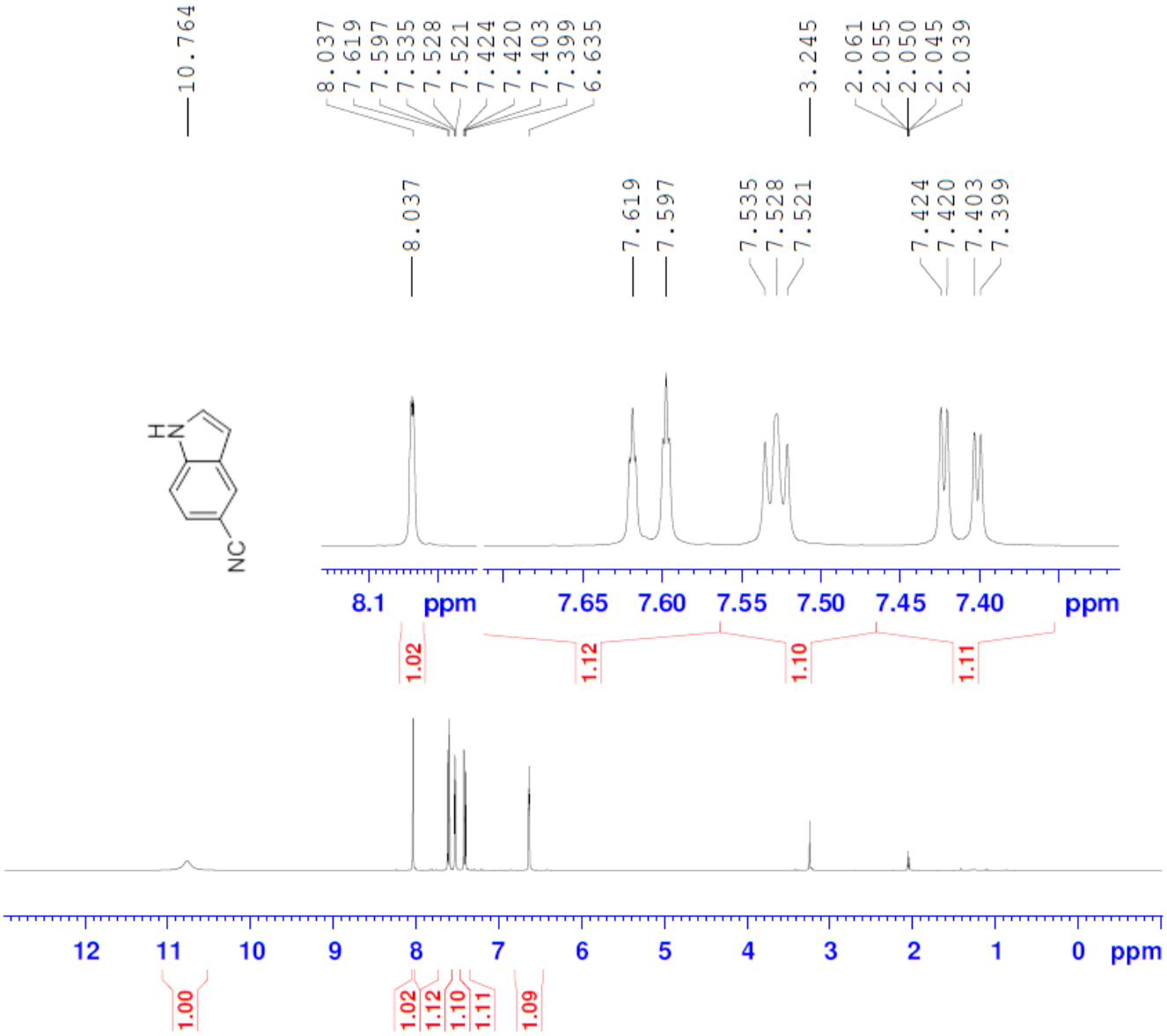
pyy227Cyan-H



BRUKER

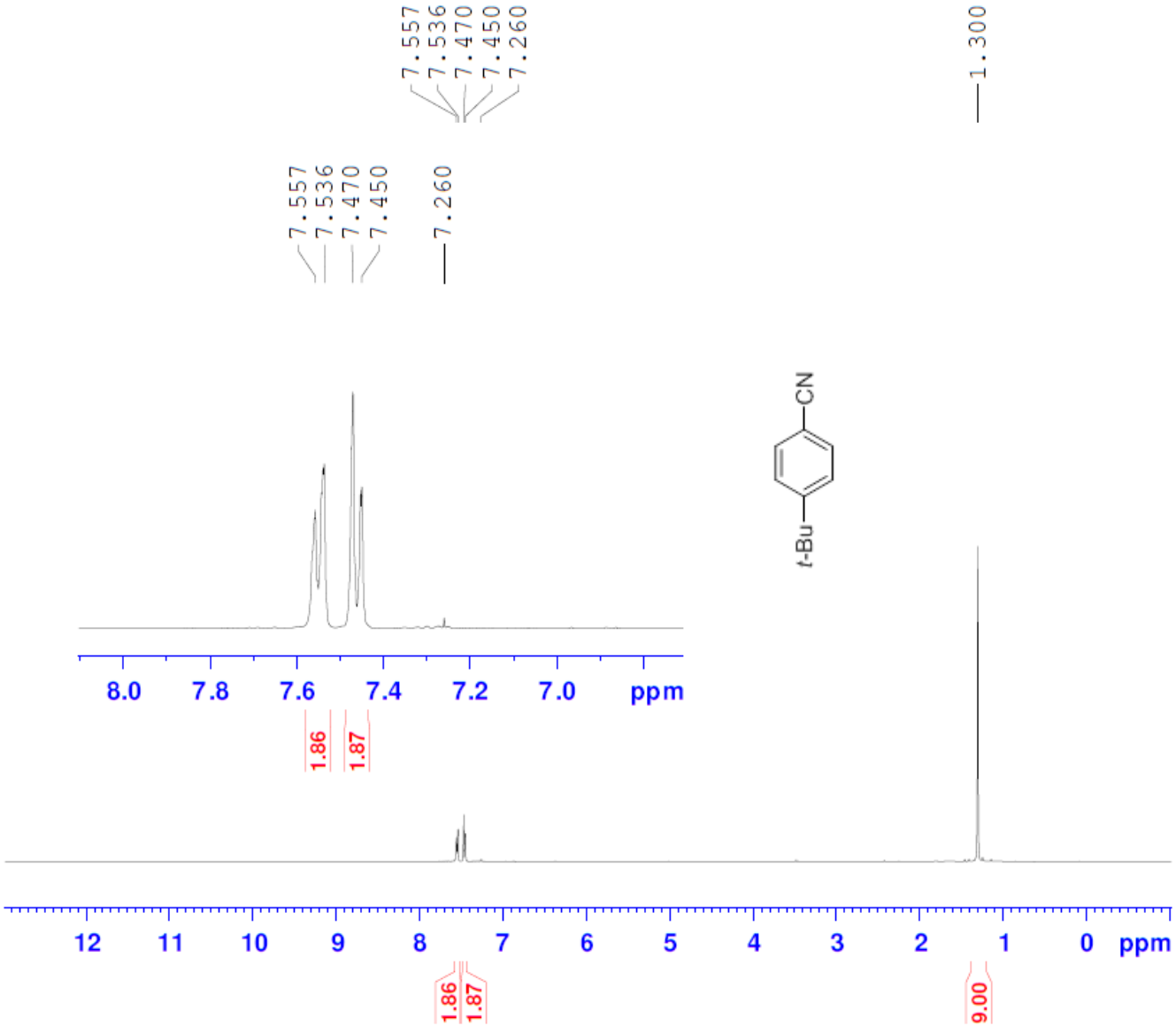
NAME	pyy227Cyan
EXPNO	1
PROCNO	1
Date_	20100517
Time	11.52
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	8
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	25.4
DW	89.333 usec
DE	6.50 usec
TE	295.9 K
D1	1.00000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300098 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

pyy378Cyan-H



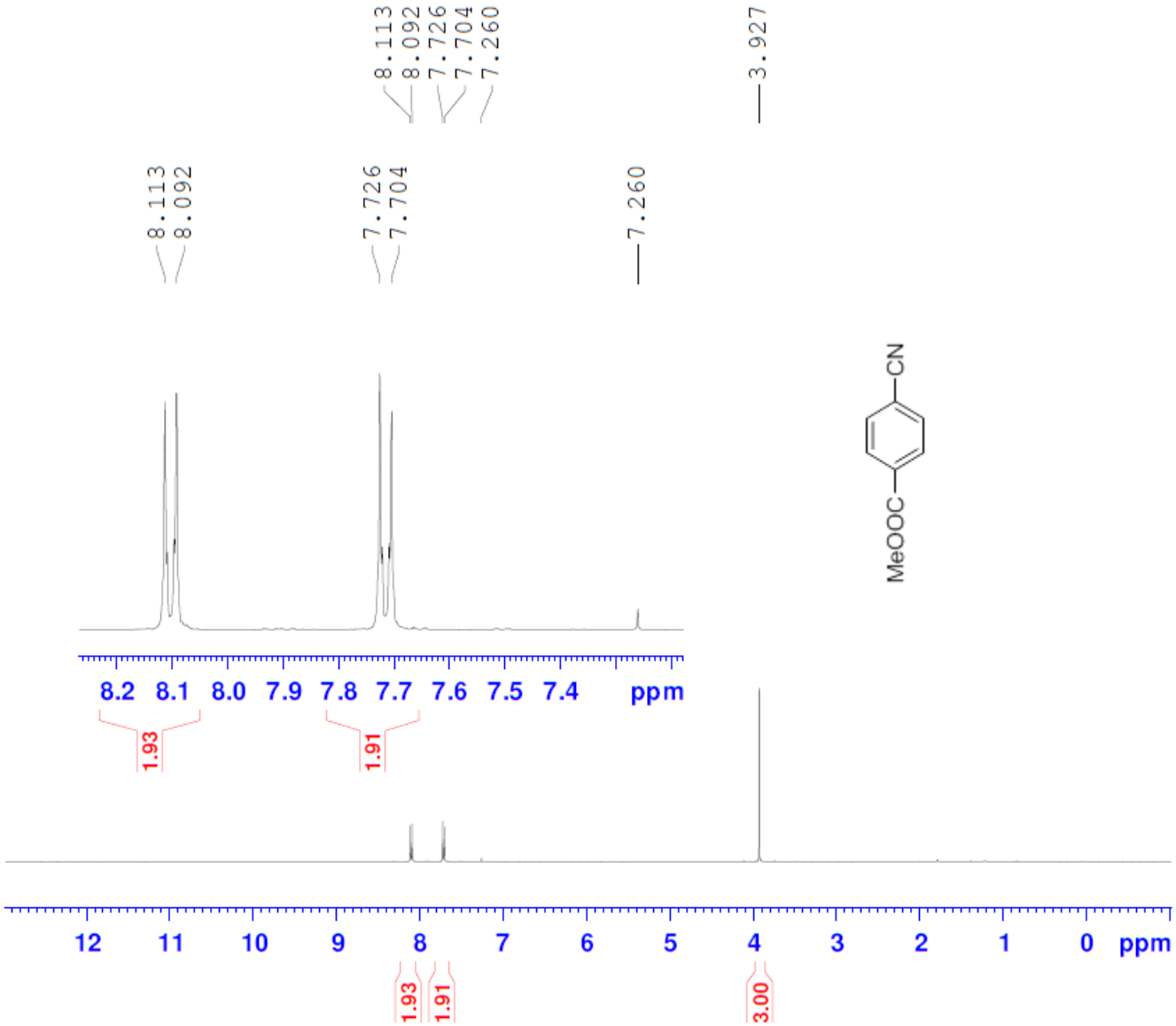
NAME	pyy378Cyan
EXPNO	1
PROCNO	1
Date_	20100721
Time	12.02
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	Acetone
NS	8
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	32
DW	89.333 usec
DE	6.50 usec
TE	298.5 K
D1	1.00000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300068 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

pyy099Cyan-H



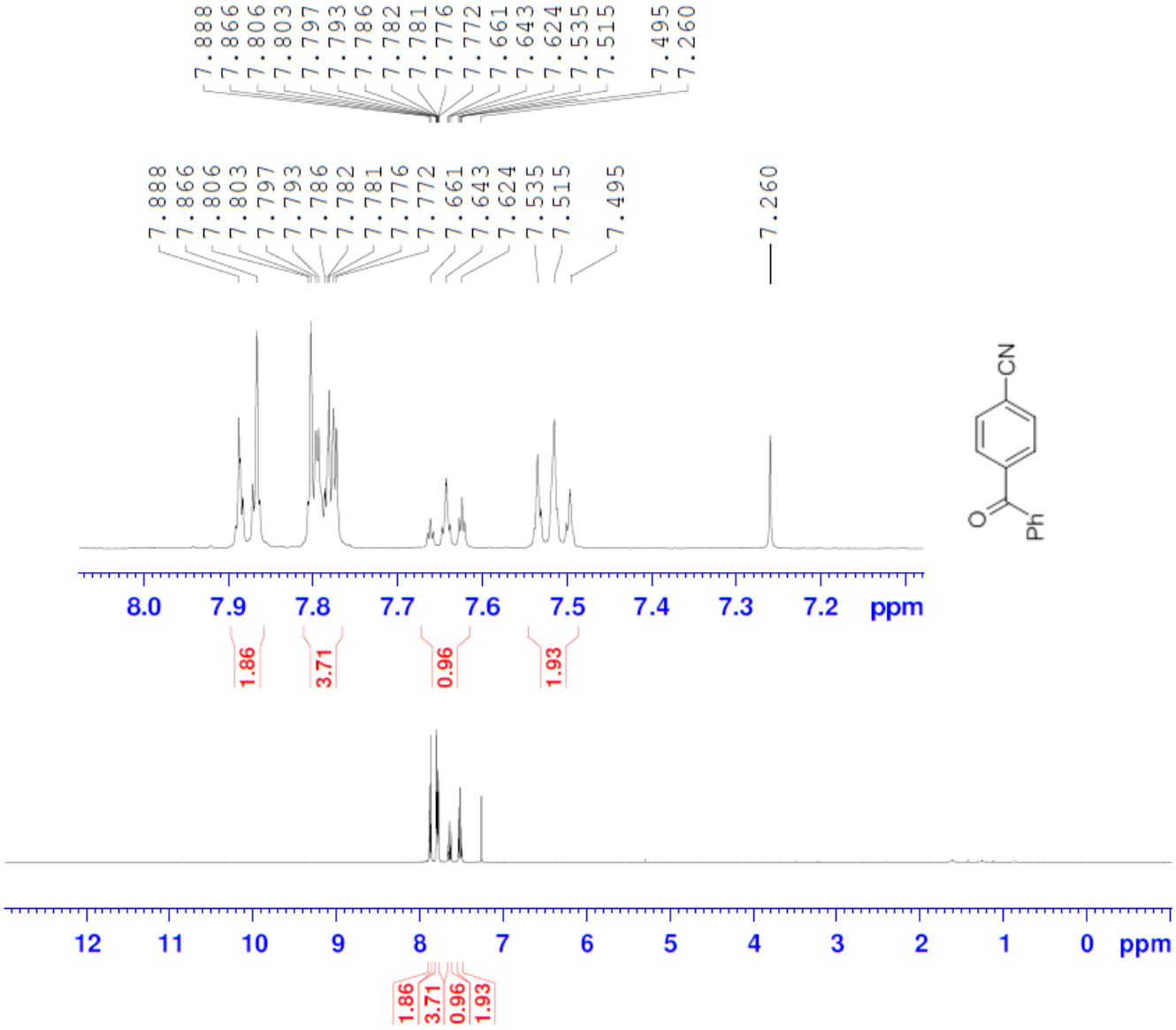
NAME	pyy099Cyan
EXPNO	1
PROCNO	1
Date_	20100330
Time	18.38
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	9
DW	89.333 usec
DE	6.50 usec
TE	295.7 K
D1	1.00000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300095 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

pyy136Cyan-H



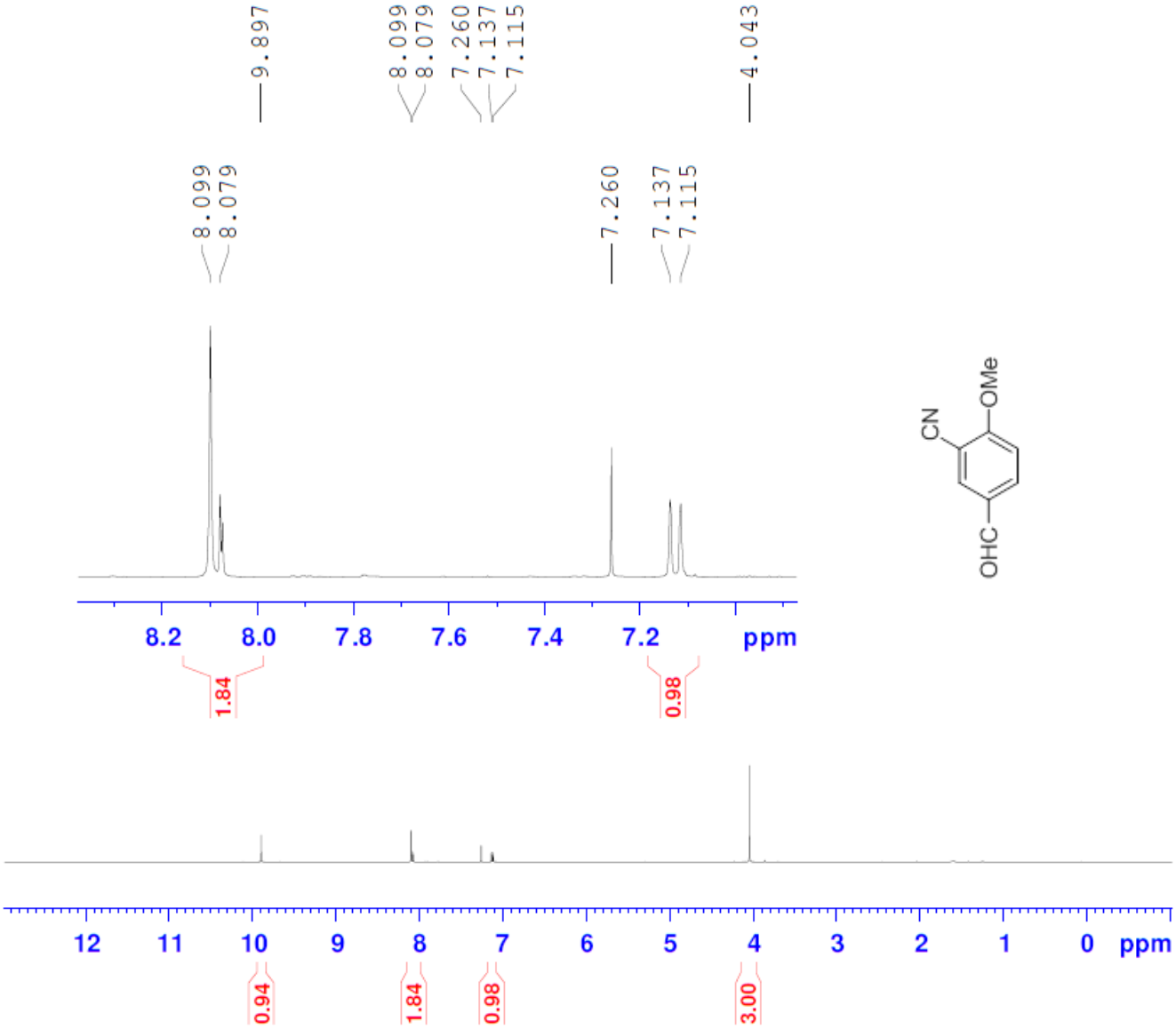
NAME	pyy136Cyan	
EXPNO	1	
PROCNO	1	
Date_	20100413	
Time	11.10	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zg30	
TD	32768	
SOLVENT	CDCl3	
NS	16	
DS	2	
SWH	5597.015	Hz
FIDRES	0.170807	Hz
AQ	2.9273248	sec
RG	45.2	
DW	89.333	usec
DE	6.50	usec
TE	296.0	K
D1	1.00000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	1H	
P1	14.70	usec
PL1	0.00	dB
PL1W	11.88122272	W
SFO1	400.1324008	MHz
SI	32768	
SF	400.1300095	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	

pyy139Cyan-H



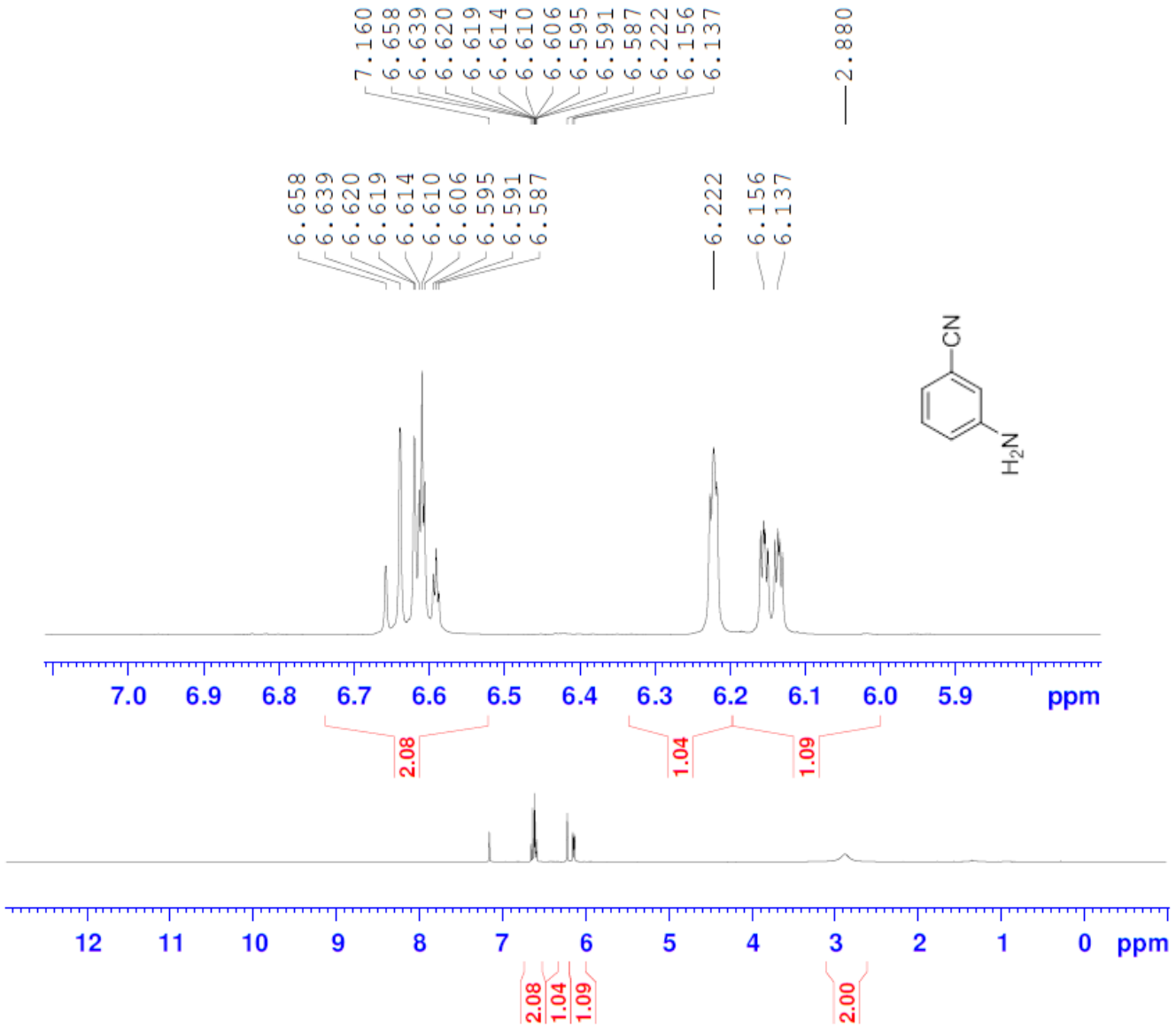
NAME	pyy139Cyan
EXPNO	1
PROCNO	1
Date_	20100412
Time	14.41
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	161
DW	89.333 usec
DE	6.50 usec
TE	296.9 K
D1	1.00000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300098 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

pyy145Cyan-H



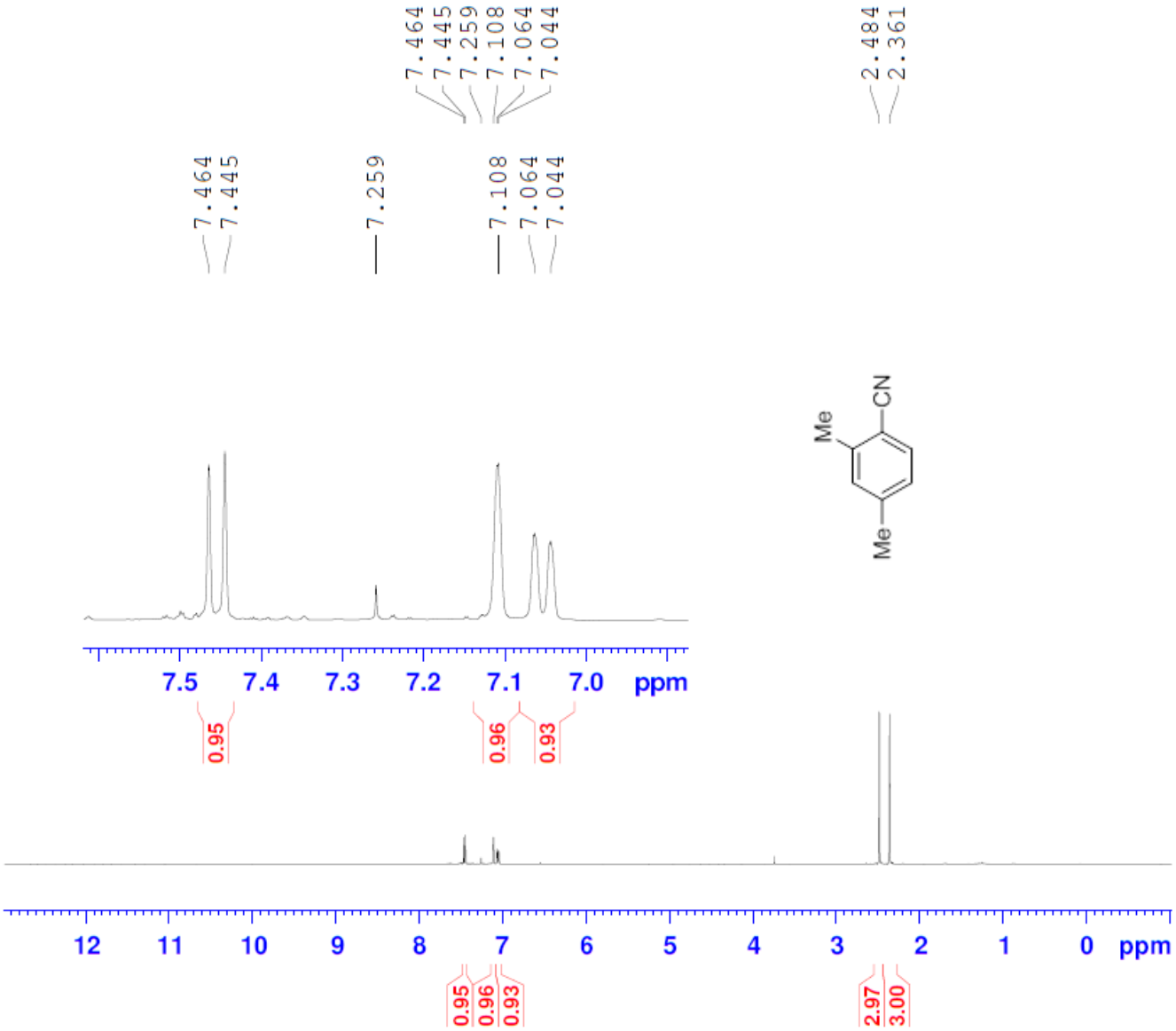
NAME	pyy145Cyan	
EXPNO	1	
PROCNO	1	
Date_	20100410	
Time	22.11	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zg30	
TD	32768	
SOLVENT	CDCl3	
NS	16	
DS	2	
SWH	5597.015	Hz
FIDRES	0.170807	Hz
AQ	2.9273248	sec
RG	203	
DW	89.333	usec
DE	6.50	usec
TE	294.7	K
D1	1.00000000	sec
TD0	1	
========	CHANNEL f1 ========	
NUC1	1H	
P1	14.70	usec
PL1	0.00	dB
PL1W	11.88122272	W
SFO1	400.1324008	MHz
SI	32768	
SF	400.1300097	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	

pyy142Cyan-H(Pure)



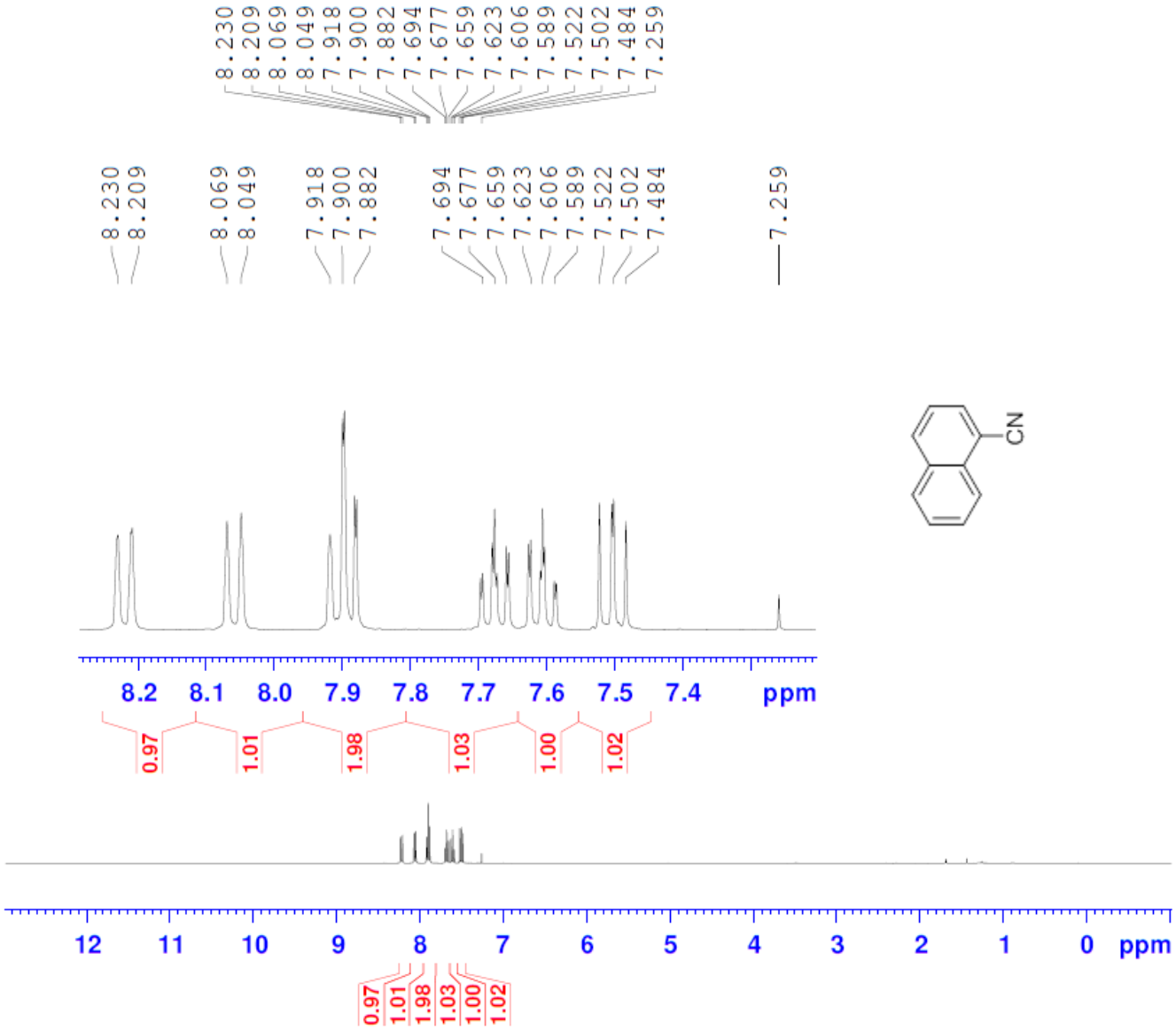
NAME	pyy142Cyan
EXPNO	7
PROCNO	1
Date_	20100420
Time	14.16
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	C6D6
NS	16
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	45.2
DW	89.333 usec
DE	6.50 usec
TE	296.0 K
D1	1.00000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1299967 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

pyy217Cyan-H



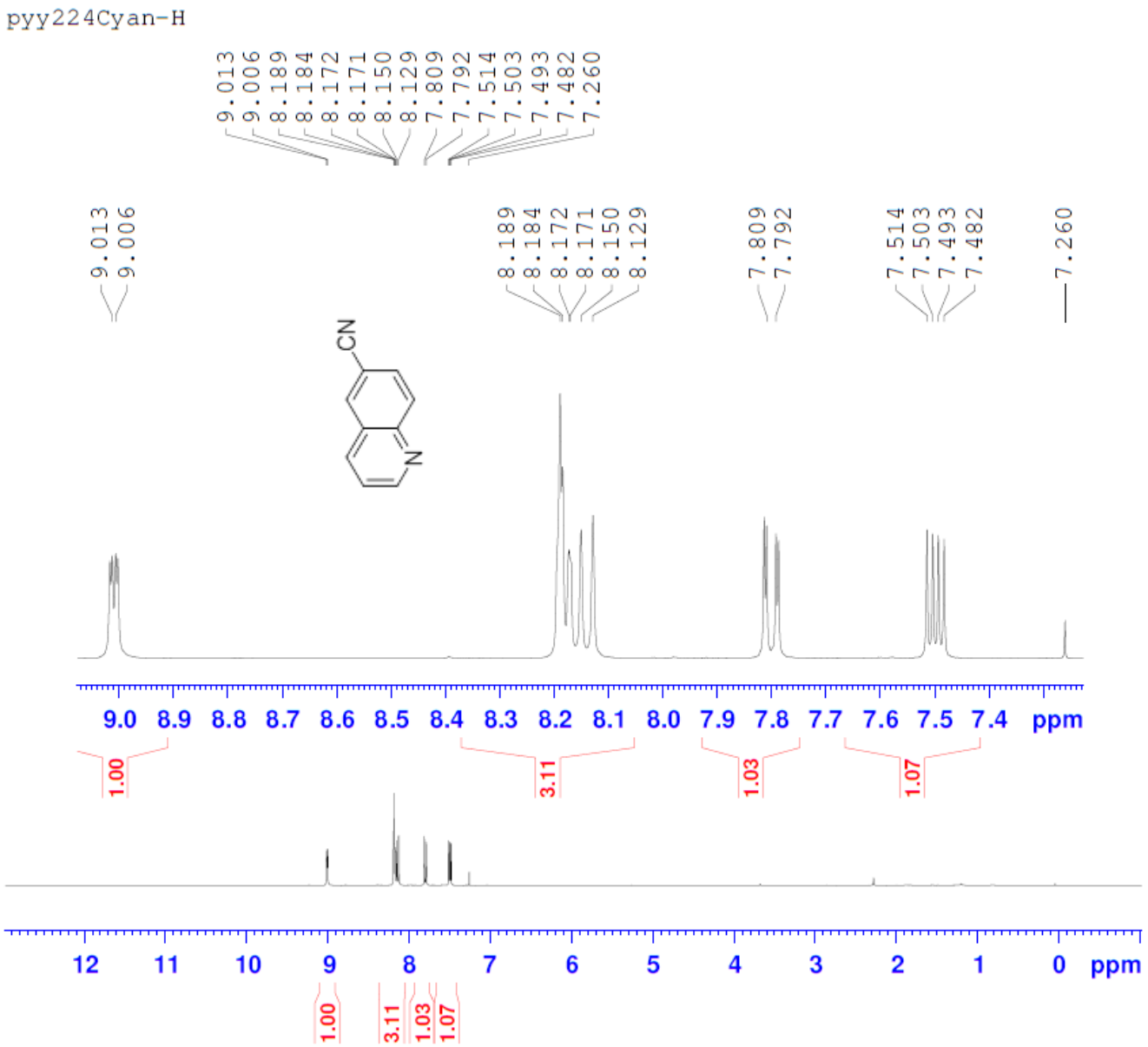
NAME	pyy217Cyan	
EXPNO	1	
PROCNO	1	
Date_	20100512	
Time	11.33	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zg30	
TD	32768	
SOLVENT	CDCl3	
NS	8	
DS	2	
SWH	5597.015	Hz
FIDRES	0.170807	Hz
AQ	2.9273248	sec
RG	45.2	
DW	89.333	usec
DE	6.50	usec
TE	296.0	K
D1	1.00000000	sec
TD0	1	
========	CHANNEL f1 ========	
NUC1	1H	
P1	14.70	usec
PL1	0.00	dB
PL1W	11.88122272	W
SFO1	400.1324008	MHz
SI	32768	
SF	400.1300103	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	

pyy137Cyan-H



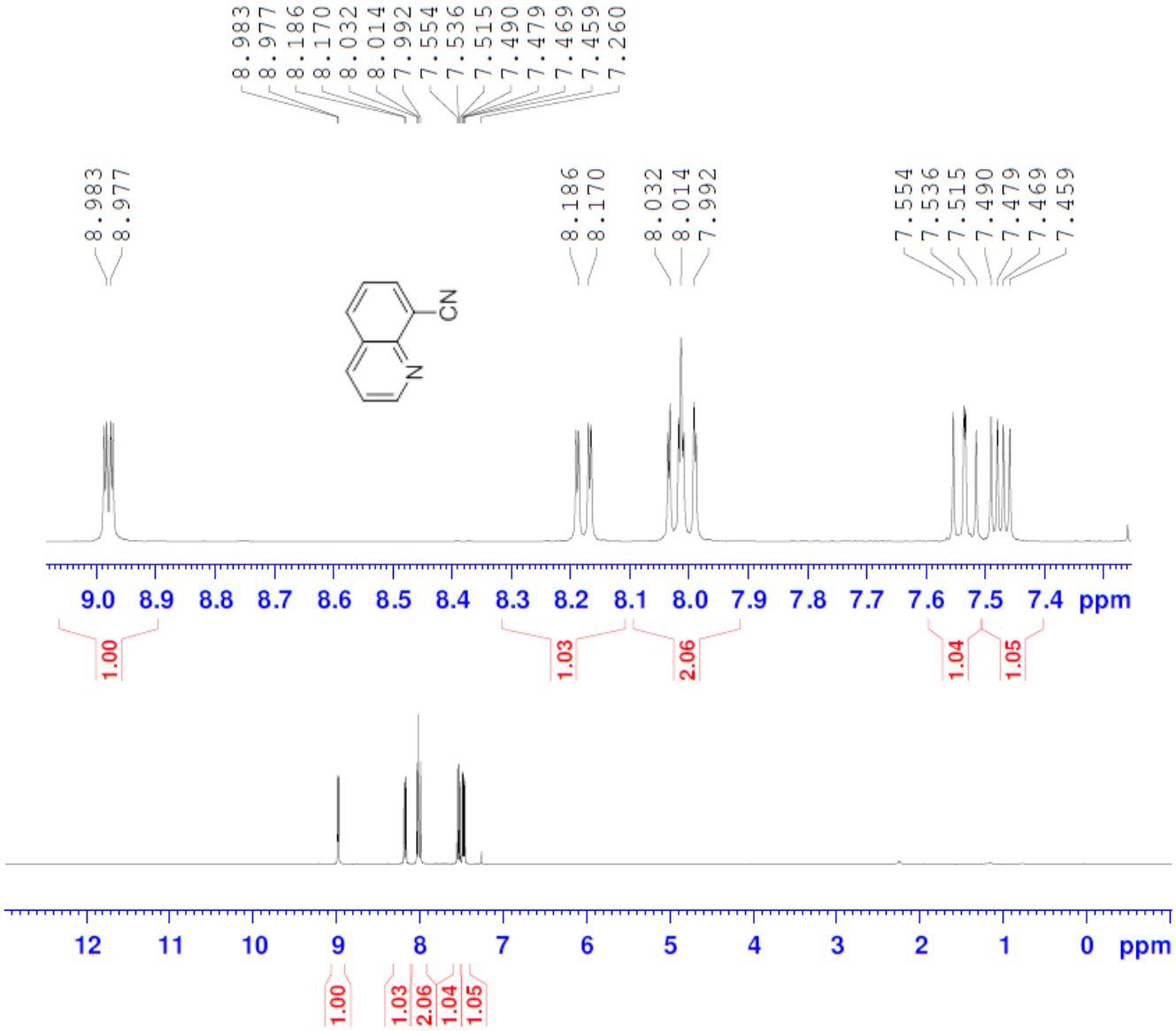
NAME	pyy137Cyan	
EXPNO	1	
PROCNO	1	
Date_	20100413	
Time	11.20	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zg30	
TD	32768	
SOLVENT	CDCl3	
NS	16	
DS	2	
SWH	5597.015	Hz
FIDRES	0.170807	Hz
AQ	2.9273248	sec
RG	45.2	
DW	89.333	usec
DE	6.50	usec
TE	296.1	K
D1	1.00000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	1H	
P1	14.70	usec
PL1	0.00	dB
PL1W	11.88122272	W
SFO1	400.1324008	MHz
SI	32768	
SF	400.1300101	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	

pyy224Cyan-H



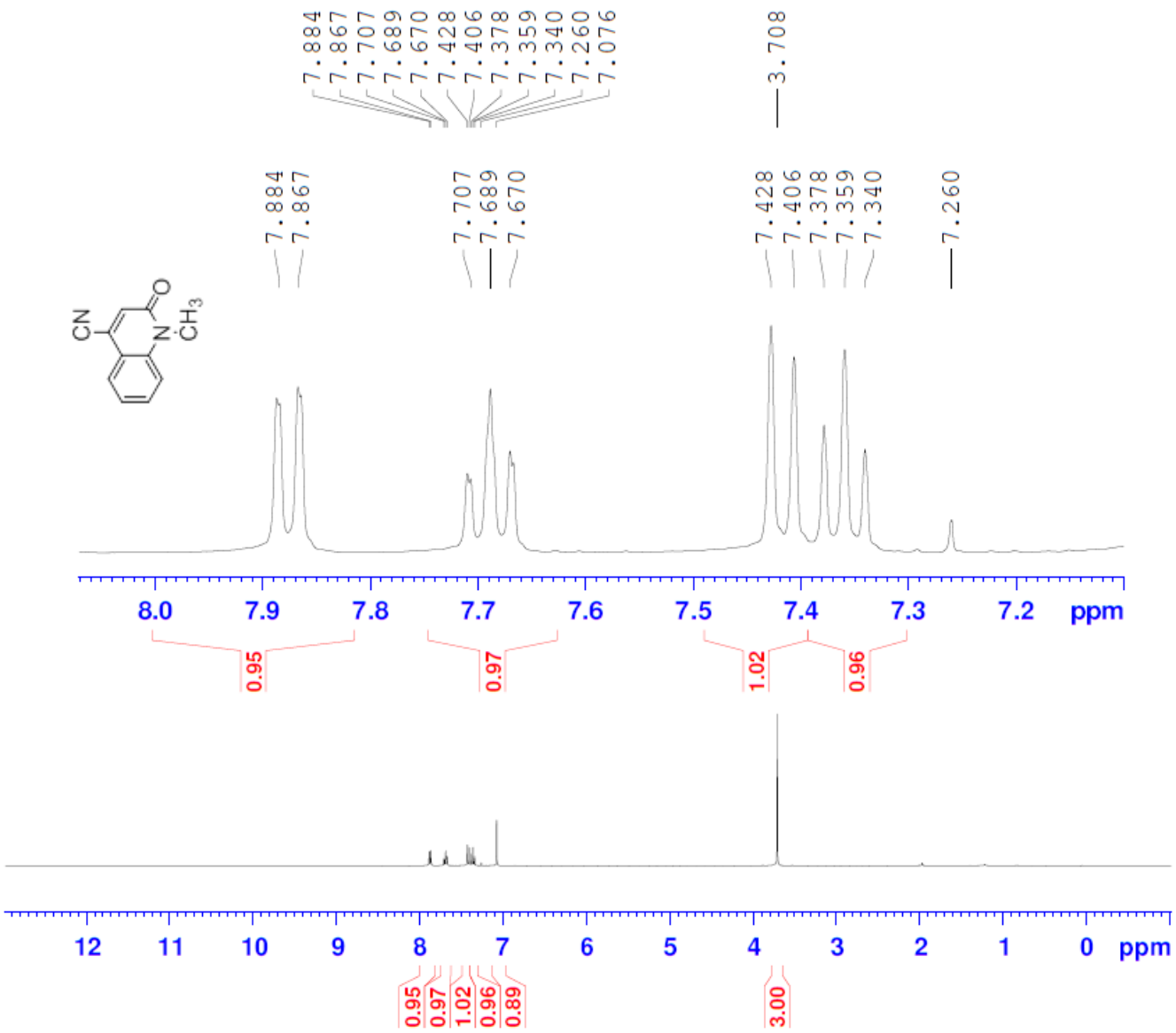
NAME	pyy224Cyan
EXPNO	1
PROCNO	1
Date_	20100513
Time	19.50
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	8
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	45.2
DW	89.333 usec
DE	6.50 usec
TE	296.5 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300097 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

pyy226Cyan-H



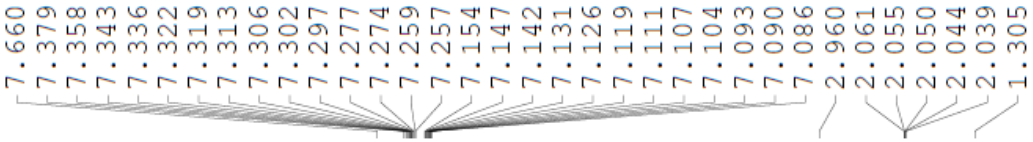
NAME	pyy226Cyan	
EXPNO	1	
PROCNO	1	
Date_	20100517	
Time	11.42	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zg30	
TD	32768	
SOLVENT	CDCl3	
NS	8	
DS	2	
SWH	5597.015	Hz
FIDRES	0.170807	Hz
AQ	2.9273248	sec
RG	45.2	
DW	89.333	usec
DE	6.50	usec
TE	295.8	K
D1	1.00000000	sec
TD0	1	
========	CHANNEL f1 ========	
NUC1	1H	
P1	14.70	usec
PL1	0.00	dB
PL1W	11.88122272	W
SFO1	400.1324008	MHz
SI	32768	
SF	400.1300097	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	

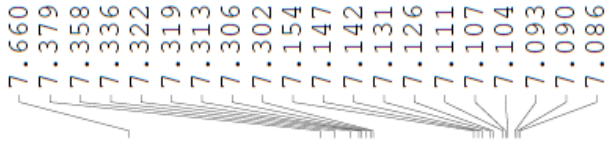
pyy235Cyan-H

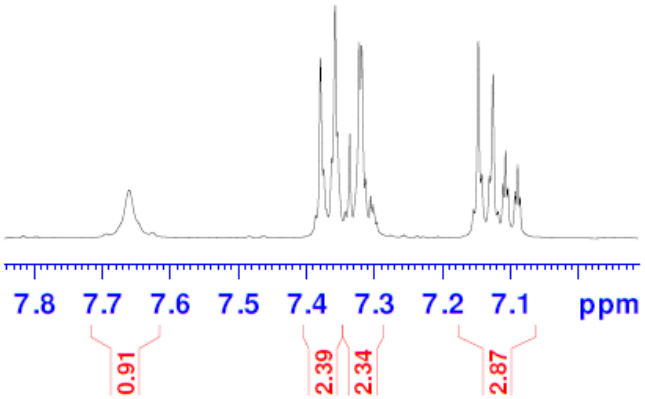


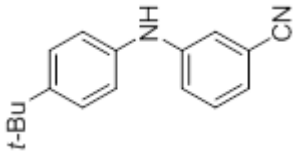
NAME	pyy235Cyan	
EXPNO	1	
PROCNO	1	
Date_	20100525	
Time	11.57	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zg30	
TD	32768	
SOLVENT	CDCl3	
NS	8	
DS	2	
SWH	5597.015	Hz
FIDRES	0.170807	Hz
AQ	2.9273248	sec
RG	45.2	
DW	89.333	usec
DE	6.50	usec
TE	297.3	K
D1	1.00000000	sec
TD0	1	
========	CHANNEL f1 ========	
NUC1	1H	
P1	14.70	usec
PL1	0.00	dB
PL1W	11.88122272	W
SFO1	400.1324008	MHz
SI	32768	
SF	400.1300094	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	

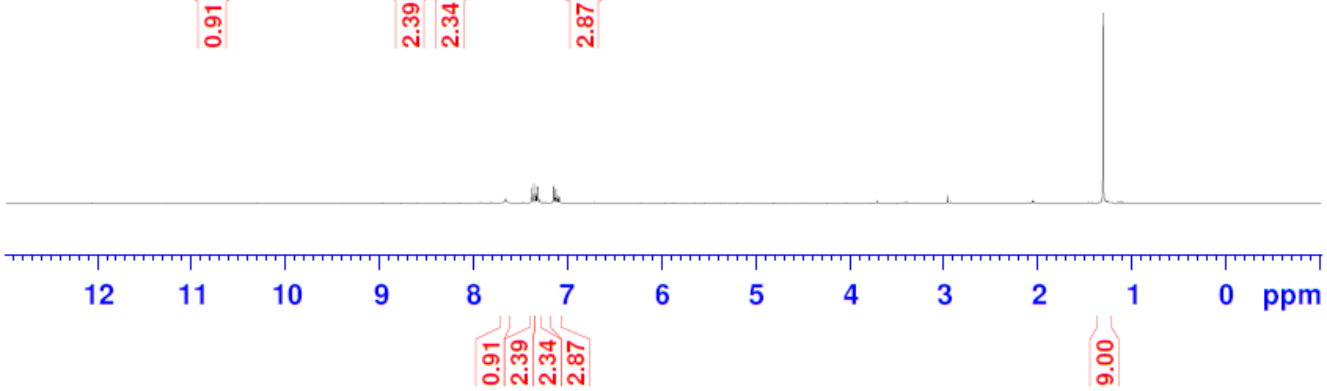
pyy400Cyan-H





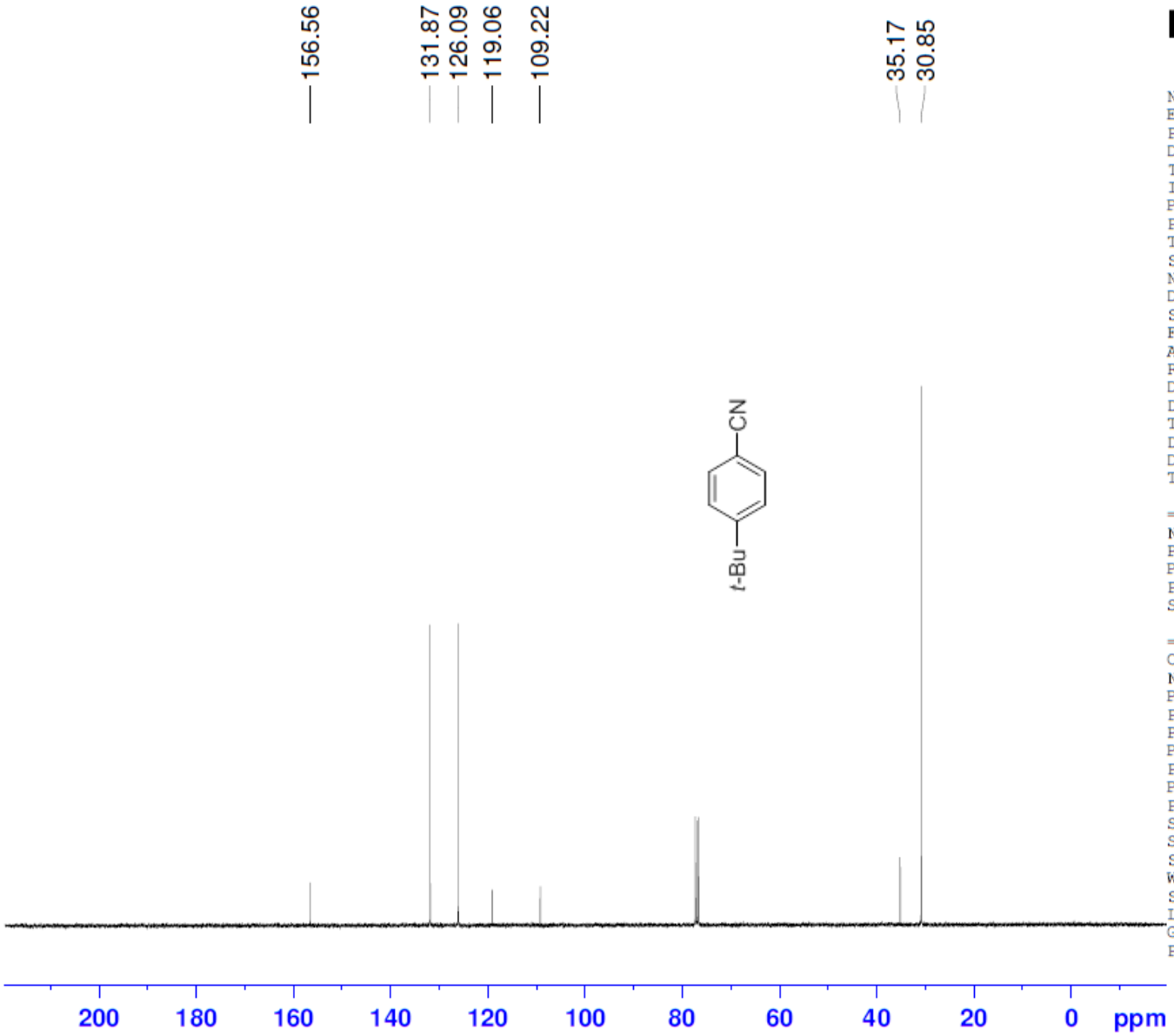






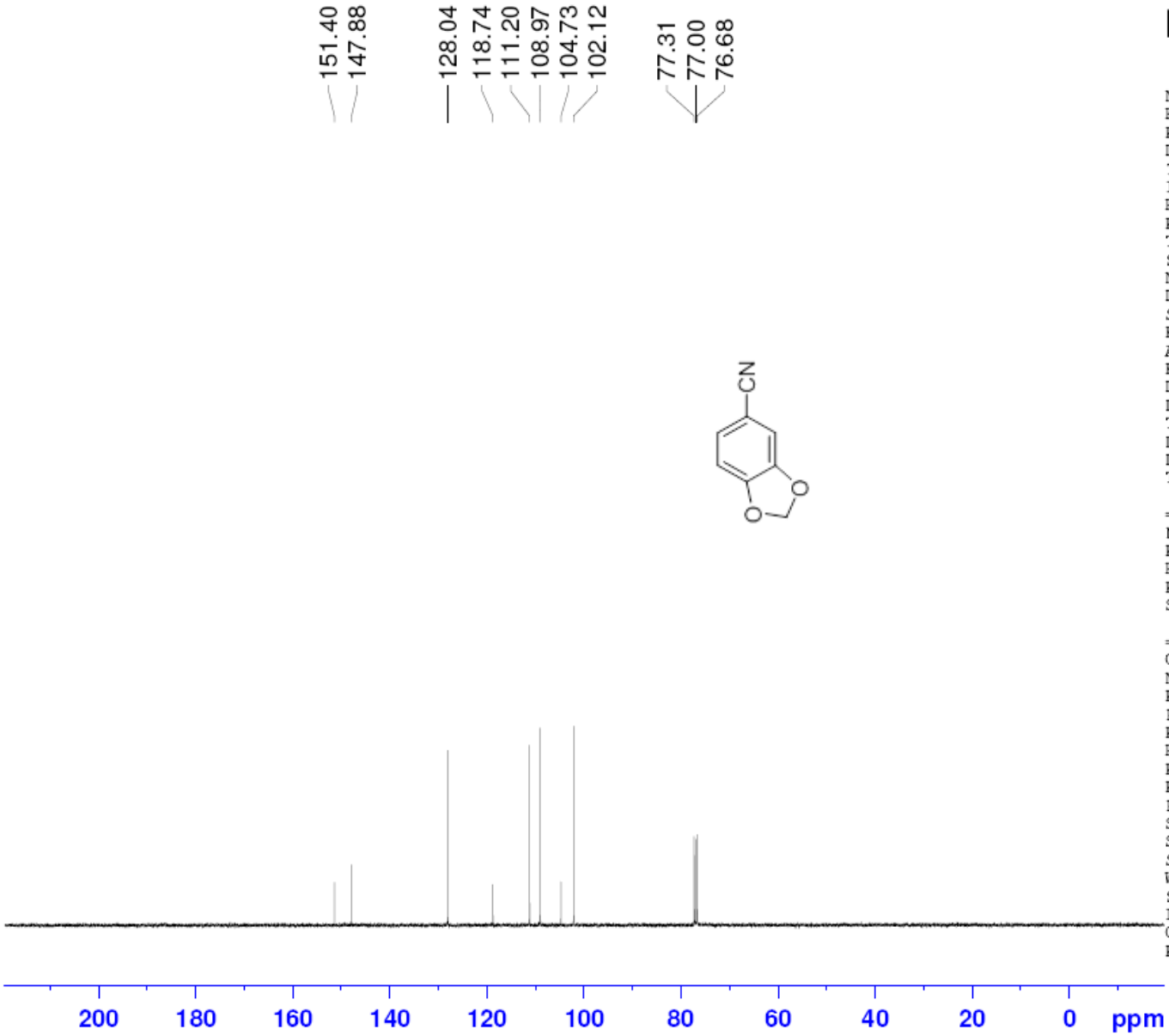
NAME	pyy400Cyan	
EXPNO	1	
PROCNO	1	
Date_	20100806	
Time	12.02	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zg30	
TD	32768	
SOLVENT	Acetone	
NS	8	
DS	2	
SWH	5597.015	Hz
FIDRES	0.170807	Hz
AQ	2.9273248	sec
RG	22.6	
DW	89.333	usec
DE	6.50	usec
TE	297.8	K
D1	1.00000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	1H	
P1	14.70	usec
PL1	0.00	dB
PL1W	11.88122272	W
SFO1	400.1324008	MHz
SI	32768	
SF	400.1300069	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	

pyy163Cyan-C



NAME	pyy163Cyan
EXPNO	2
PROCNO	1
Date_	20100420
Time	15.02
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	32
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	296.3 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	15.00 dB
PL2W	11.88122272 W
PL12W	0.37571725 W
PL13W	0.37571725 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127782 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

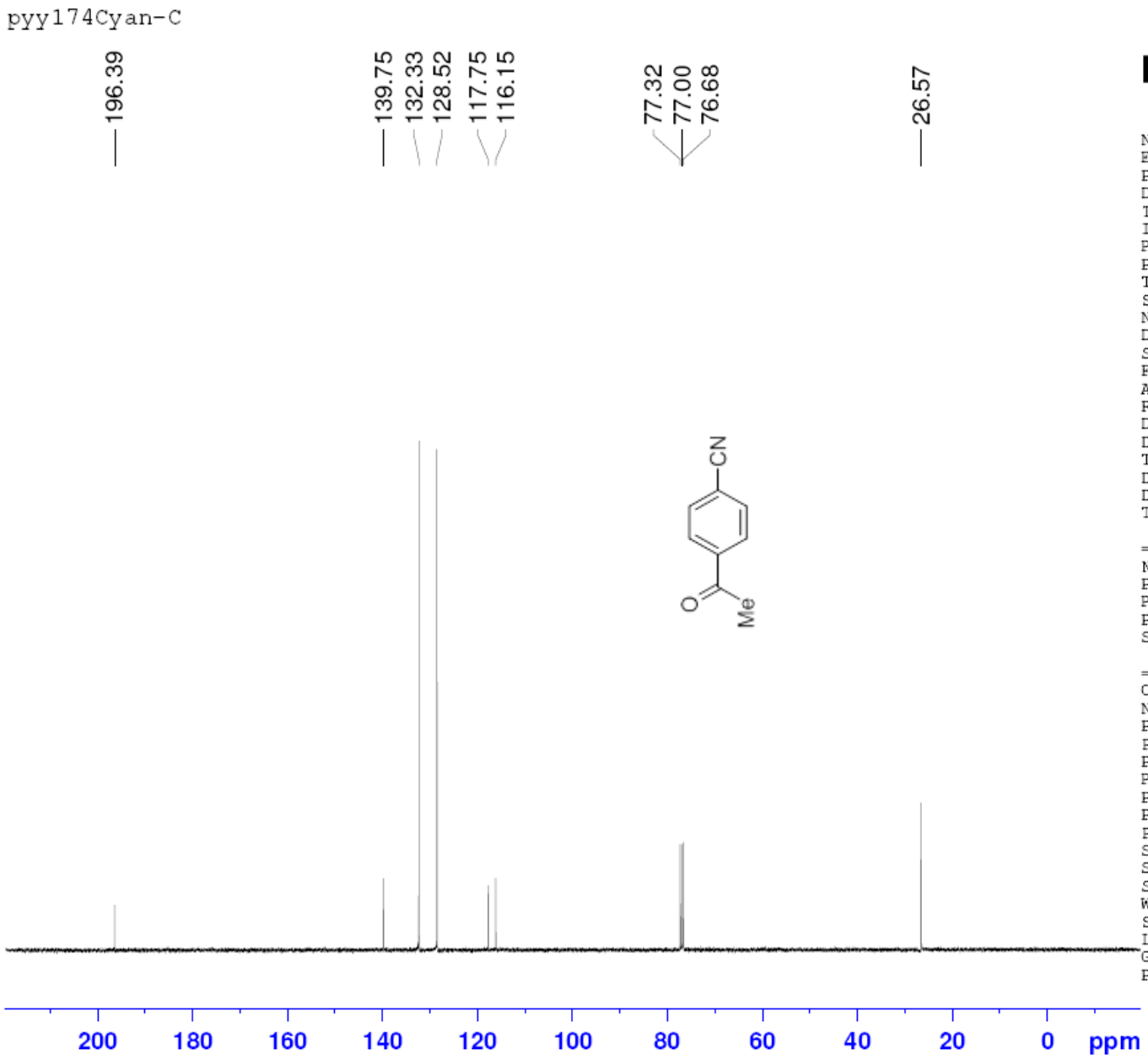
pyy168Cyan-C



BRUKER

NAME	pyy168Cyan
EXPNO	2
PROCNO	1
Date_	20100420
Time	12.12
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	24
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	296.1 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	15.00 dB
PL2W	11.88122272 W
PL12W	0.37571725 W
PL13W	0.37571725 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127848 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

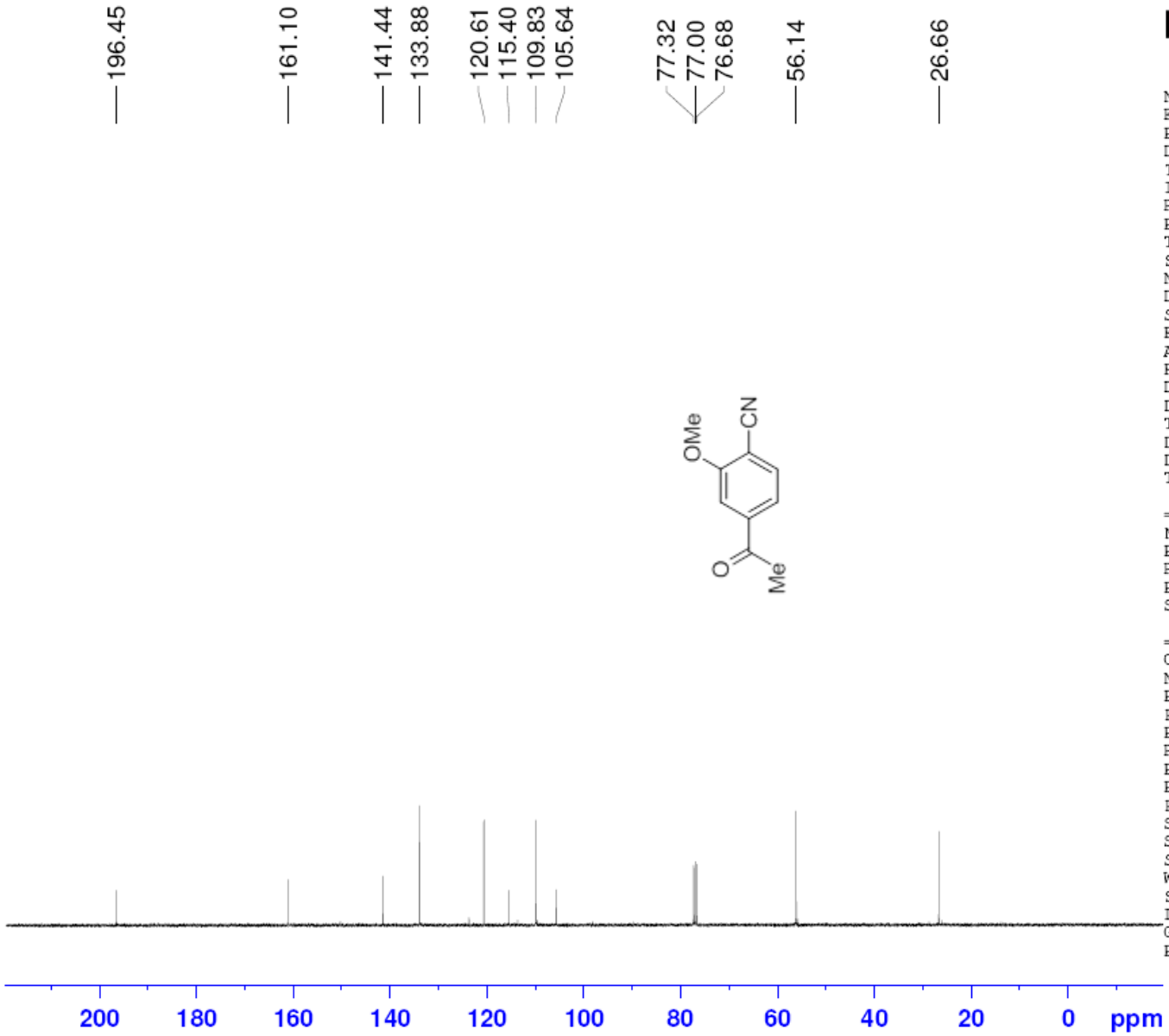
pyy174Cyan-C



BRUKER

NAME	pyy174Cyan
EXPNO	2
PROCNO	1
Date_	20100421
Time	14.54
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	203
DW	20.800 usec
DE	6.50 usec
TE	298.8 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	15.00 dB
PL2W	11.88122272 W
PL12W	0.37571725 W
PL13W	0.37571725 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127859 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

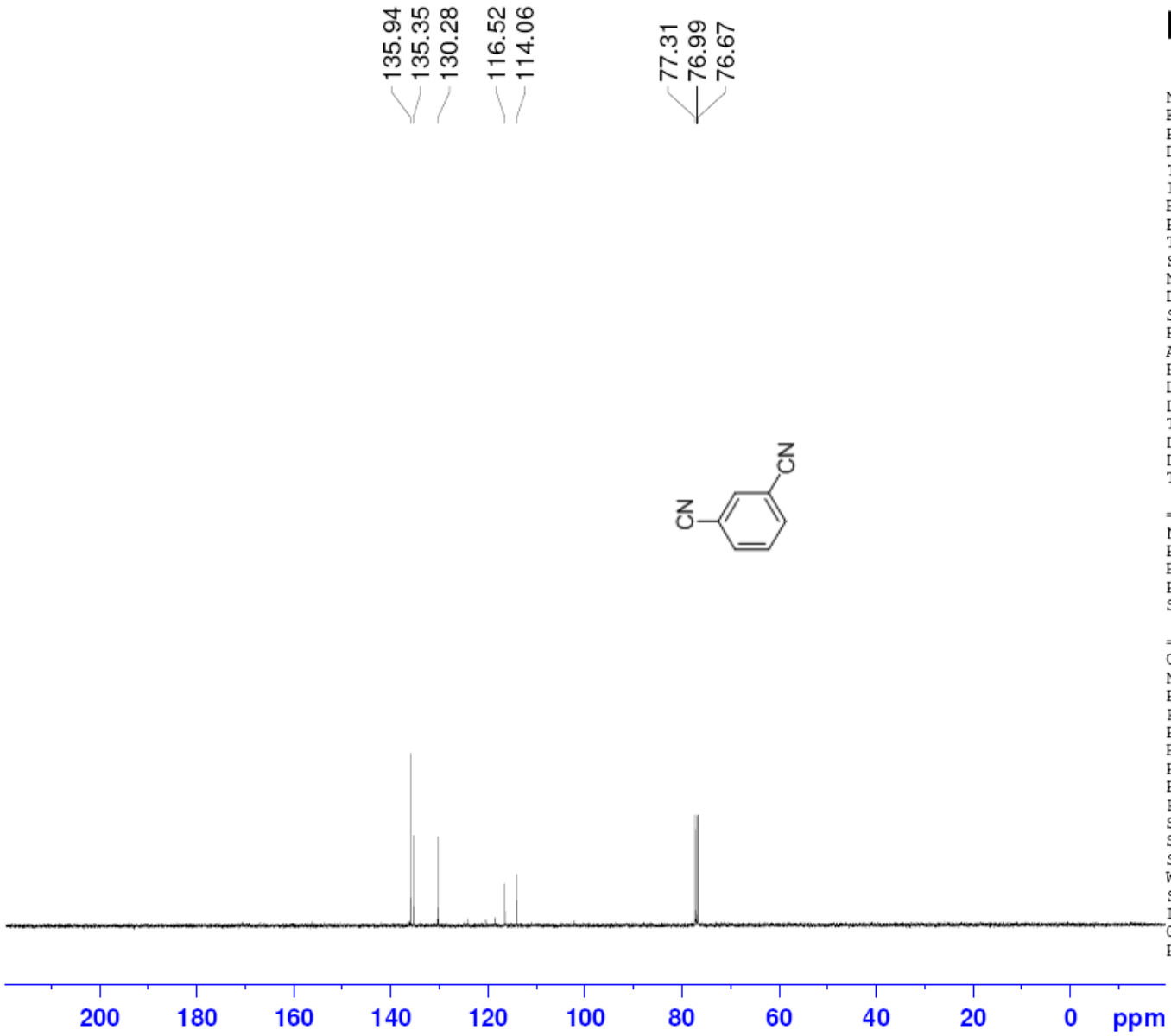
Standard 13C



BRUKER

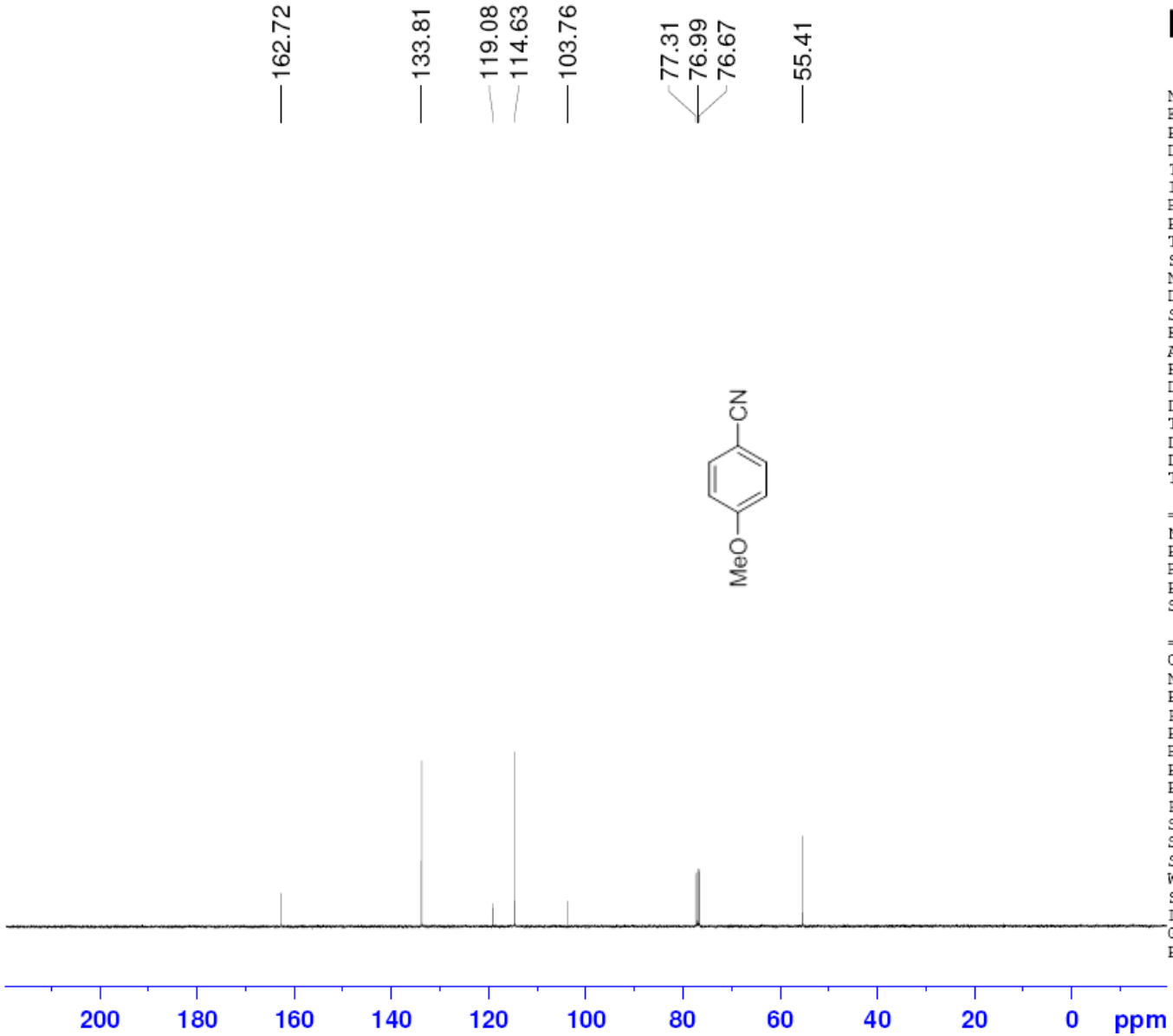
NAME	pyy175Cyan	
EXPNO	2	
PROCNO	1	
Date_	20100421	
Time	14.01	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	17	
DS	2	
SWH	24038.461	Hz
FIDRES	0.366798	Hz
AQ	1.3631988	sec
RG	203	
DW	20.800	usec
DE	6.50	usec
TE	298.5	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	9.50	usec
PL1	-2.00	dB
PL1W	58.52175522	W
SFO1	100.6228298	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	80.00	usec
PL2	0.00	dB
PL12	15.00	dB
PL13	15.00	dB
PL2W	11.88122272	W
PL12W	0.37571725	W
PL13W	0.37571725	W
SFO2	400.1316005	MHz
SI	32768	
SF	100.6127879	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

pyy179Cyan-C



NAME	pyy179Cyan
EXPNO	2
PROCNO	1
Date_	20100421
Time	15.08
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	298.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	15.00 dB
PL2W	11.88122272 W
PL12W	0.37571725 W
PL13W	0.37571725 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127785 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

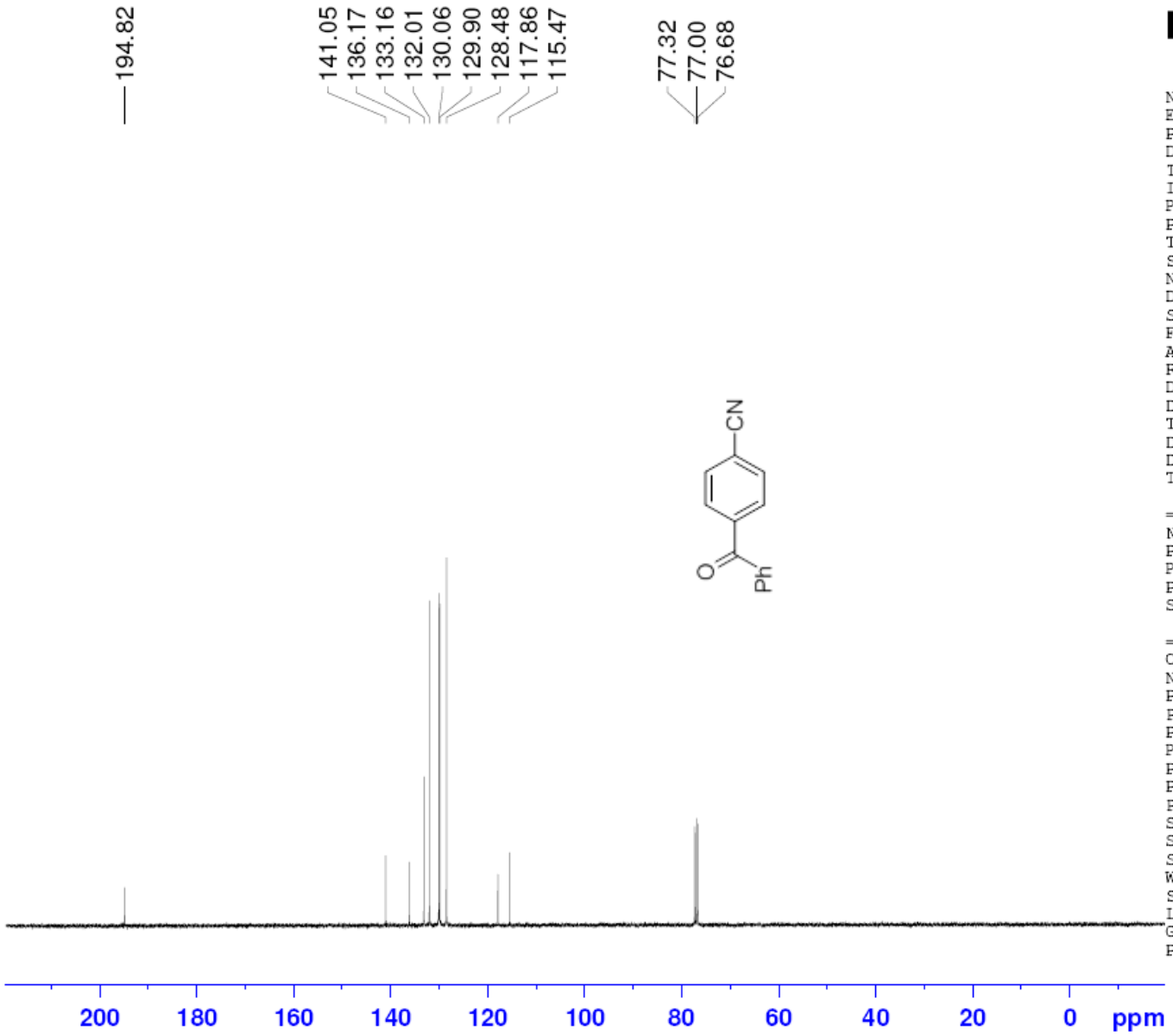
Standard 13C



BRUKER

NAME	pyy196Cyan	
EXPNO	2	
PROCNO	1	
Date_	20100504	
Time	18.04	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	13	
DS	2	
SWH	24038.461	Hz
FIDRES	0.366798	Hz
AQ	1.3631988	sec
RG	203	
DW	20.800	usec
DE	6.50	usec
TE	297.9	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	9.50	usec
PL1	-2.00	dB
PL1W	58.52175522	W
SFO1	100.6228298	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	80.00	usec
PL2	0.00	dB
PL12	15.00	dB
PL13	15.00	dB
PL2W	11.88122272	W
PL12W	0.37571725	W
PL13W	0.37571725	W
SFO2	400.1316005	MHz
SI	32768	
SF	100.6127834	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

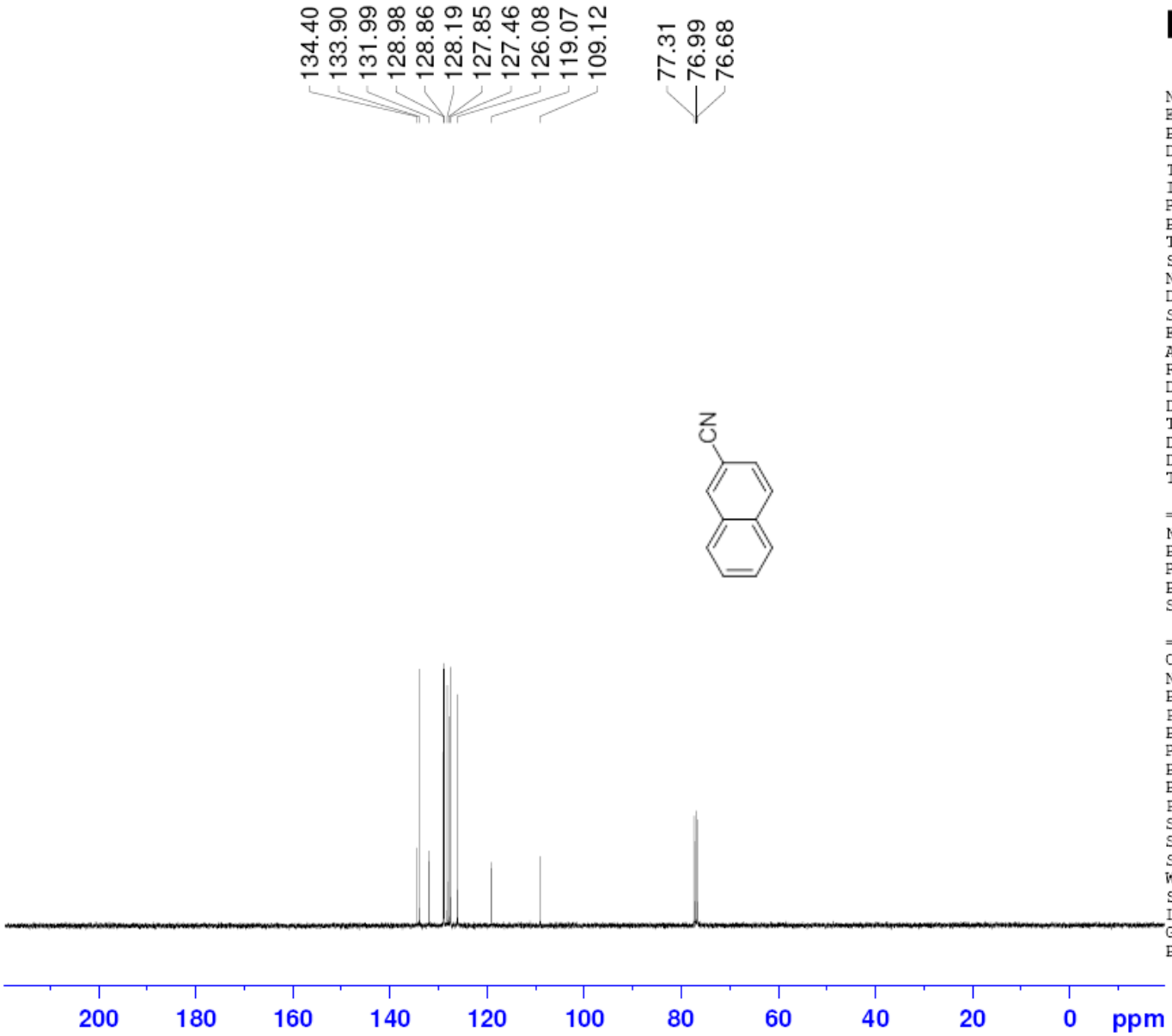
Standard 13C



BRUKER

NAME	pyy207Cyan	
EXPNO	4	
PROCNO	1	
Date_	20100507	
Time	17.44	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	32	
DS	2	
SWH	24038.461	Hz
FIDRES	0.366798	Hz
AQ	1.3631988	sec
RG	203	
DW	20.800	usec
DE	6.50	usec
TE	297.9	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	100.6127855	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

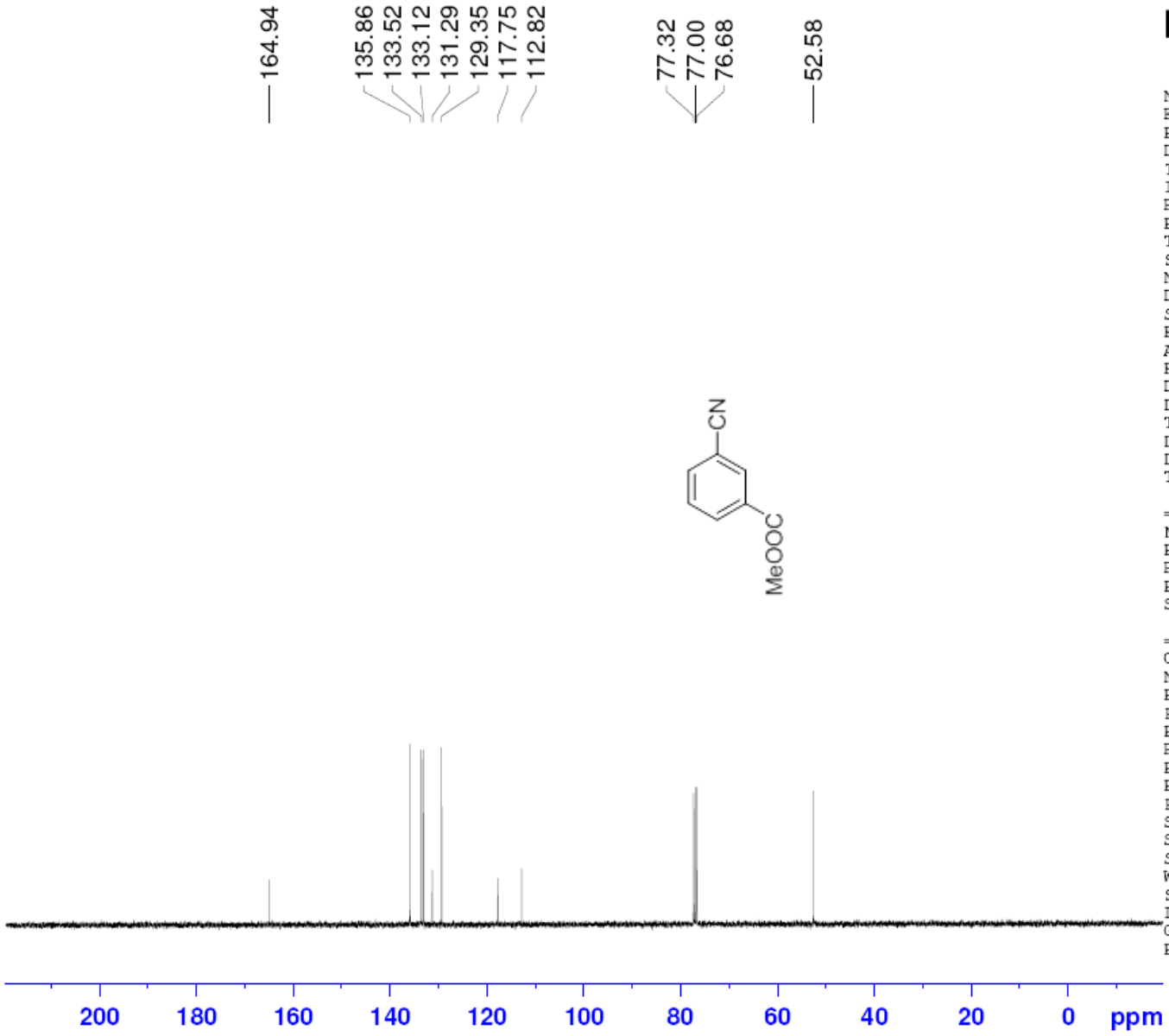
pyy213Cyan-C



BRUKER

NAME	pyy213Cyan
EXPNO	2
PROCNO	1
Date_	20100513
Time	19.44
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	181
DW	20.800 usec
DE	6.50 usec
TE	296.8 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	15.00 dB
PL2W	11.88122272 W
PL12W	0.37571725 W
PL13W	0.37571725 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127904 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

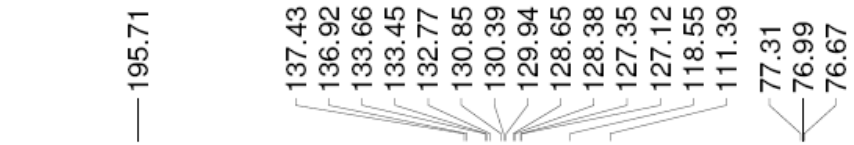
pyy214Cyan-C

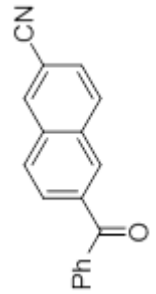


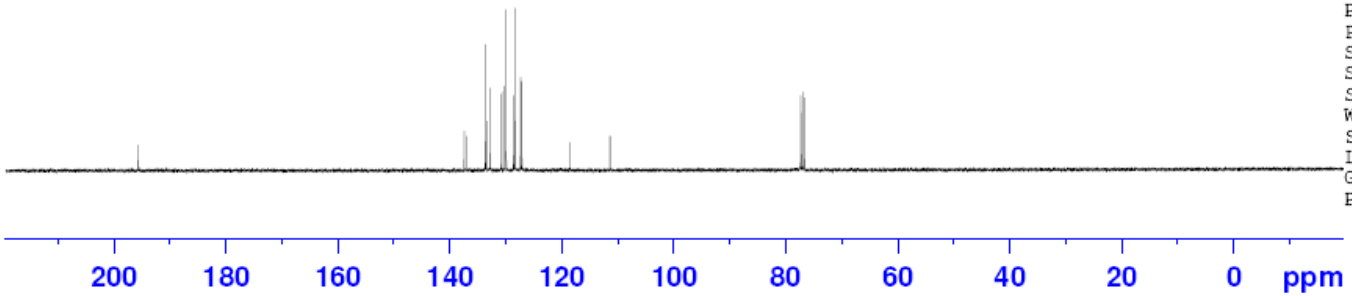
BRUKER

NAME	pyy214Cyan
EXPNO	2
PROCNO	1
Date_	20100512
Time	11.15
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	296.1 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	15.00 dB
PL2W	11.88122272 W
PL12W	0.37571725 W
PL13W	0.37571725 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127801 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

pyy363Cyan-C

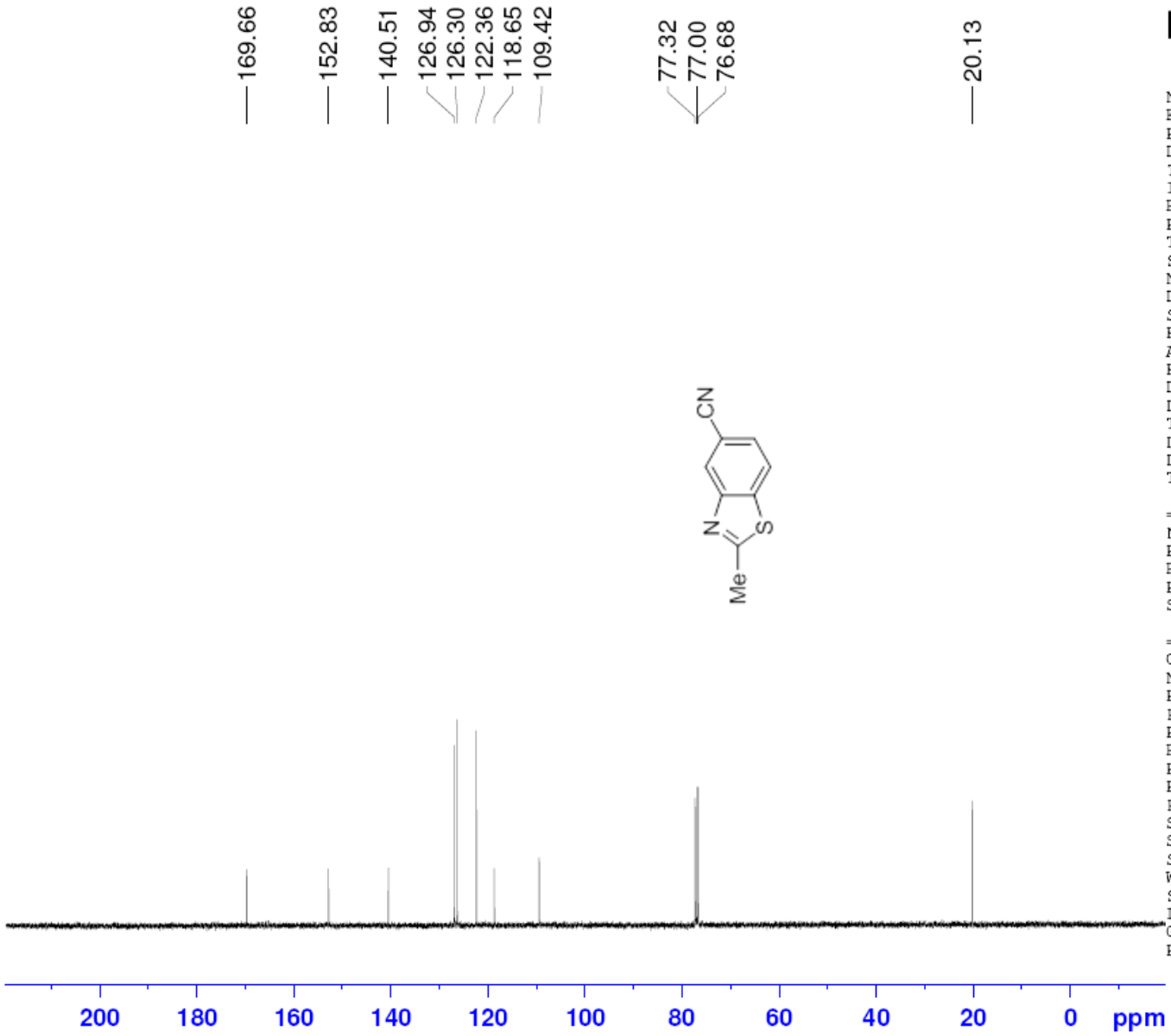






NAME	pyy363Cyan
EXPNO	2
PROCNO	1
Date_	20100708
Time	12.09
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	299.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL 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	100.6127877 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

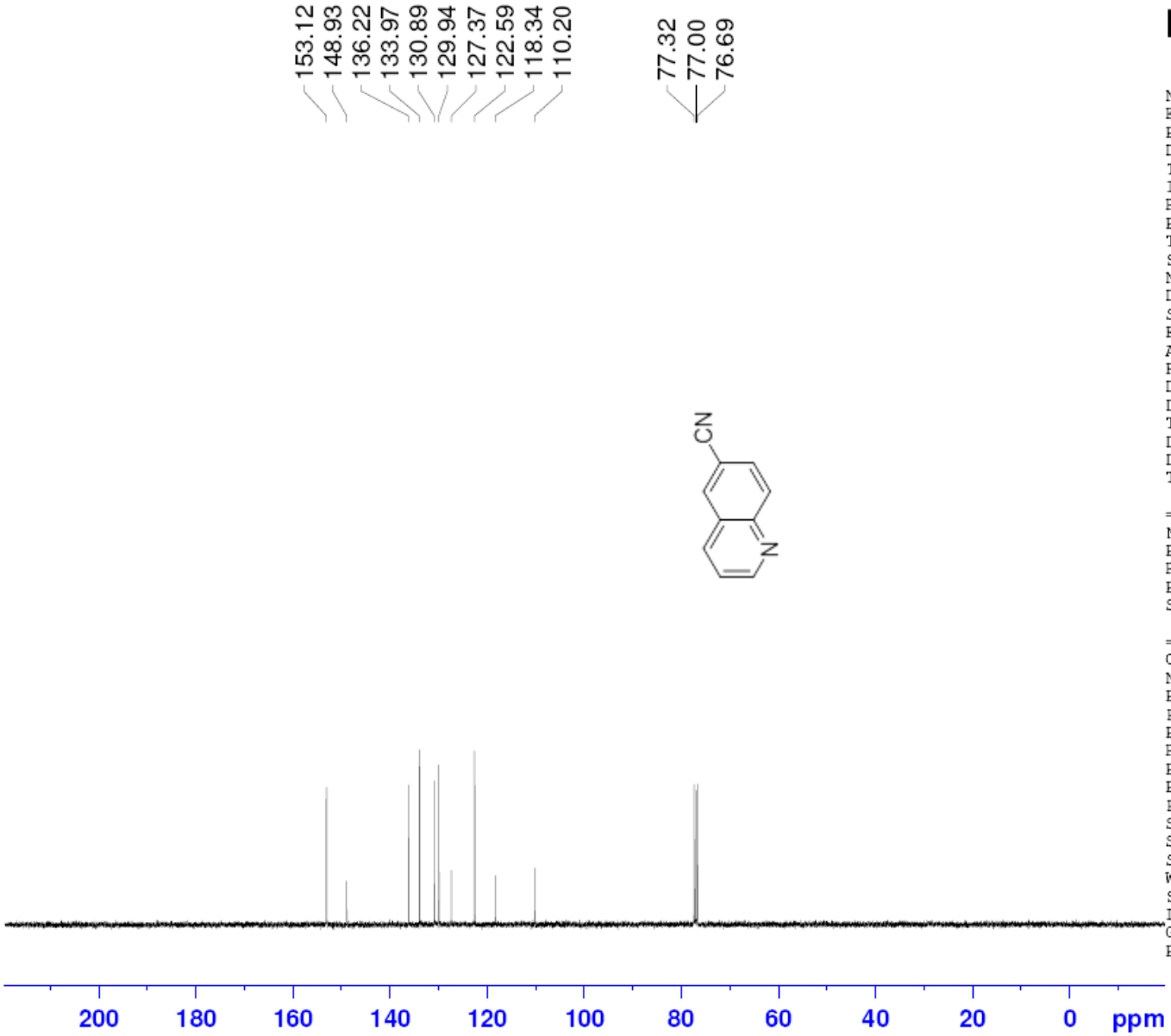
pyy230Cyan-C



BRUKER

NAME	pyy231Cyan	
EXPNO	2	
PROCNO	1	
Date_	20100517	
Time	12.20	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	16	
DS	2	
SWH	24038.461	Hz
FIDRES	0.366798	Hz
AQ	1.3631988	sec
RG	203	
DW	20.800	usec
DE	6.50	usec
TE	296.0	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	9.50	usec
PL1	-2.00	dB
PL1W	58.52175522	W
SFO1	100.6228298	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	80.00	usec
PL2	0.00	dB
PL12	15.00	dB
PL13	15.00	dB
PL2W	11.88122272	W
PL12W	0.37571725	W
PL13W	0.37571725	W
SFO2	400.1316005	MHz
SI	32768	
SF	100.6127847	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

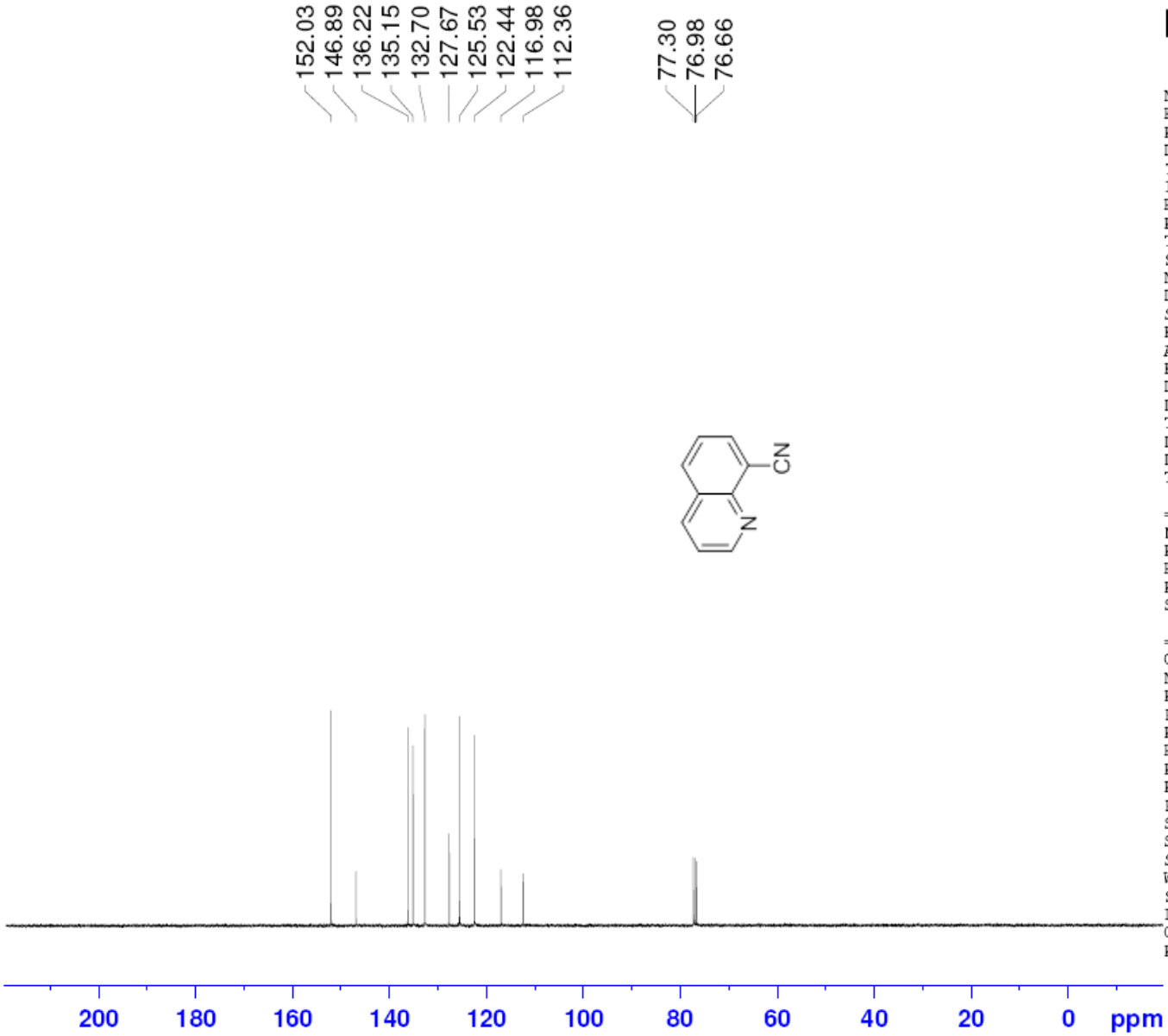
pyy225Cyan-C



BRUKER

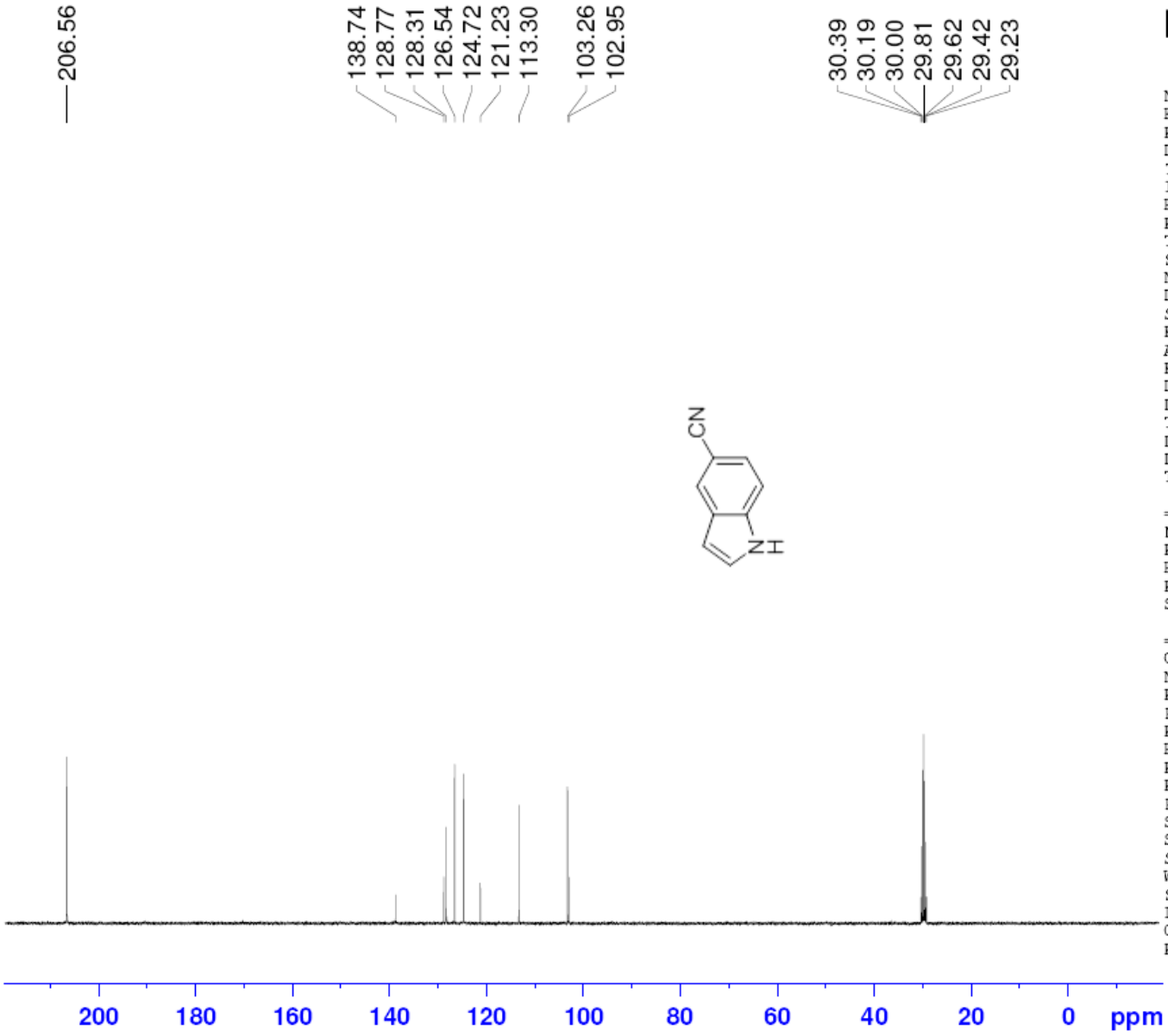
NAME	pyy225Cyan	
EXPNO	2	
PROCNO	1	
Date_	20100513	
Time	20.20	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	16	
DS	2	
SWH	24038.461	Hz
FIDRES	0.366798	Hz
AQ	1.3631988	sec
RG	203	
DW	20.800	usec
DE	6.50	usec
TE	297.1	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	9.50	usec
PL1	-2.00	dB
PL1W	58.52175522	W
SFO1	100.6228298	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	80.00	usec
PL2	0.00	dB
PL12	15.00	dB
PL13	15.00	dB
PL2W	11.88122272	W
PL12W	0.37571725	W
PL13W	0.37571725	W
SFO2	400.1316005	MHz
SI	32768	
SF	100.6127831	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

pyy227Cyan-C



NAME	pyy227Cyan
EXPNO	2
PROCNO	1
Date_	20100517
Time	11.57
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	296.5 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	15.00 dB
PL2W	11.88122272 W
PL12W	0.37571725 W
PL13W	0.37571725 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6128057 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

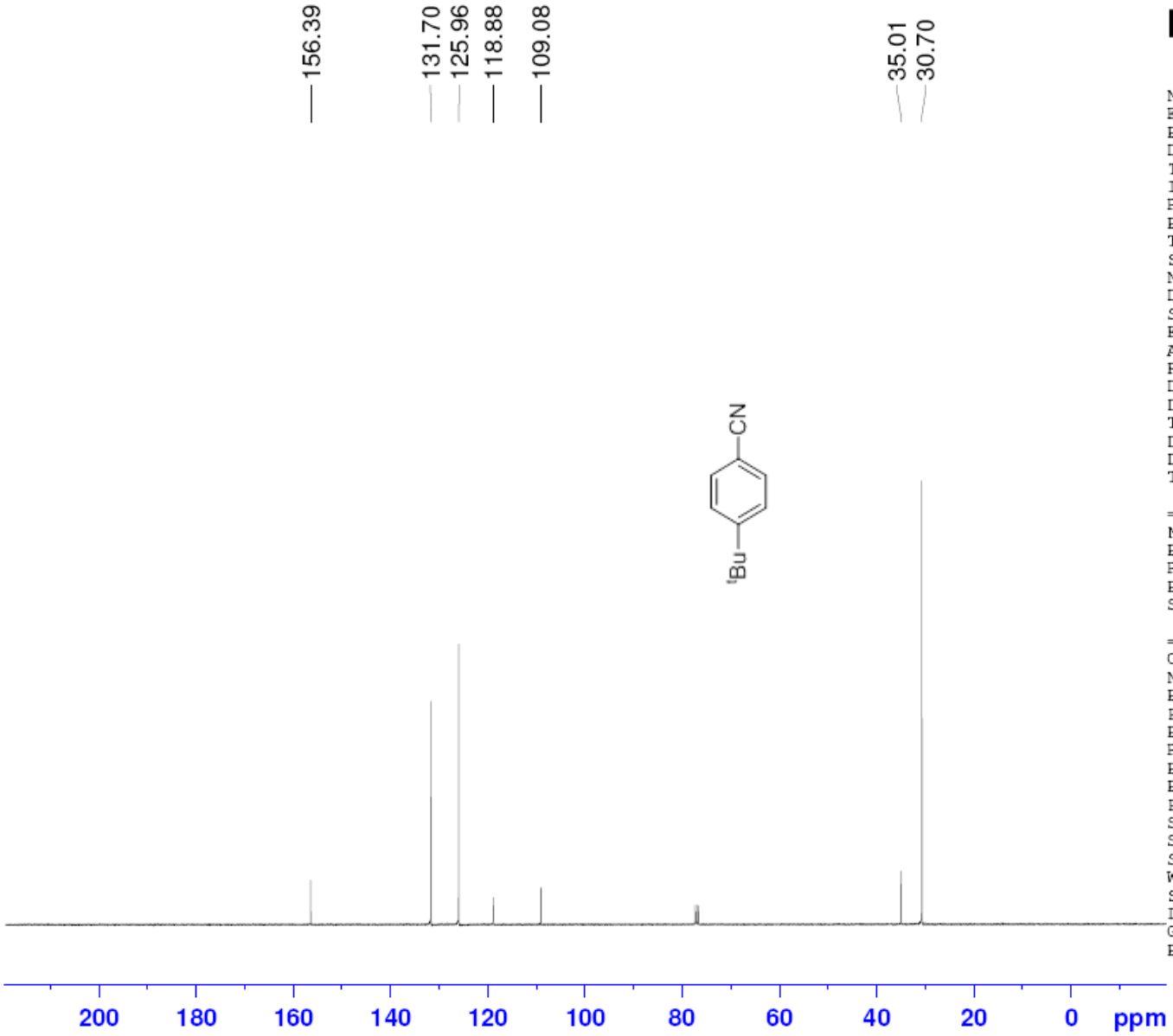
pyy378Cyan-C



BRUKER

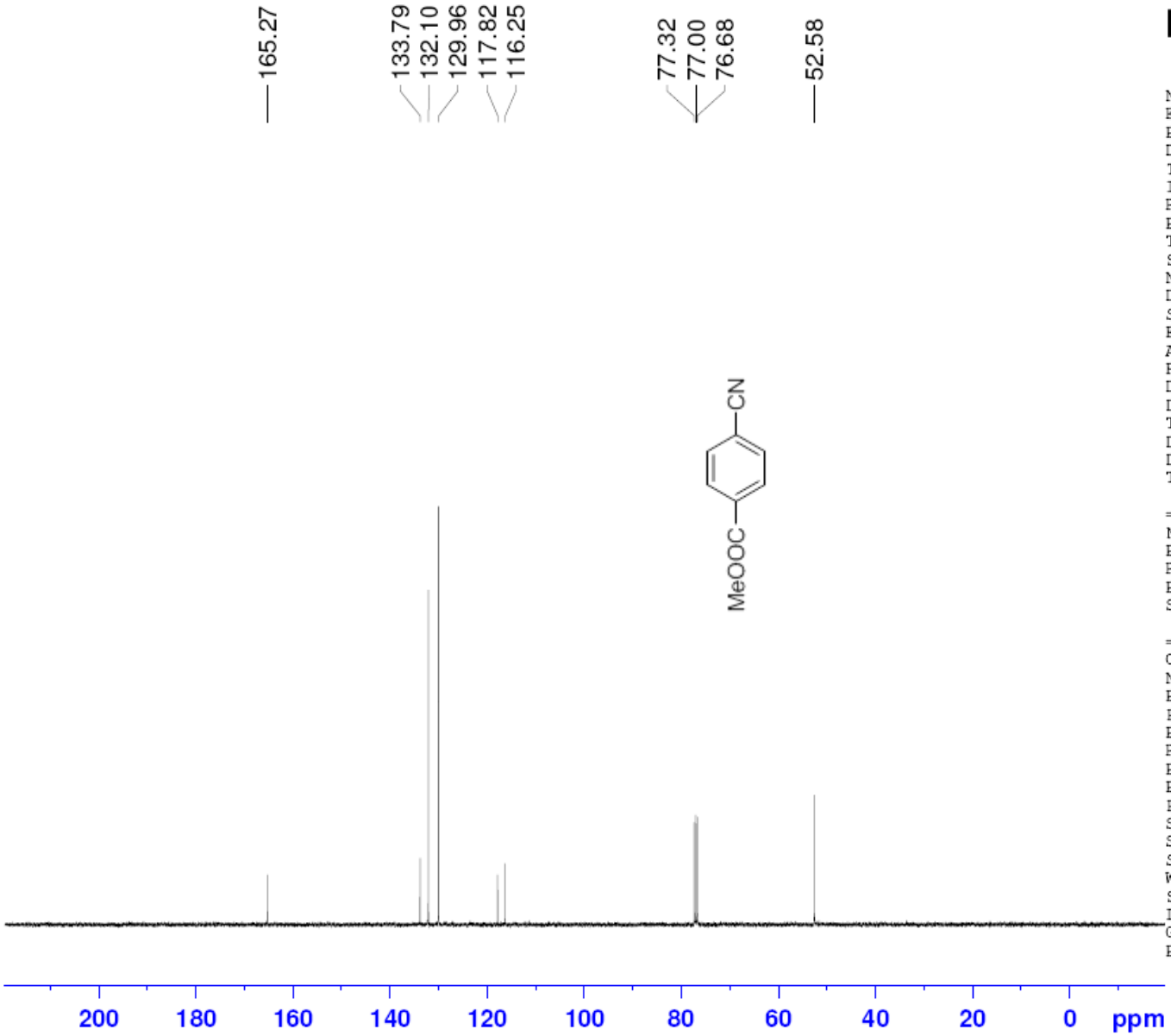
NAME	pyy378Cyan	
EXPNO	2	
PROCNO	1	
Date_	20100721	
Time	12.05	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	Acetone	
NS	16	
DS	2	
SWH	24038.461	Hz
FIDRES	0.366798	Hz
AQ	1.3631988	sec
RG	203	
DW	20.800	usec
DE	6.50	usec
TE	299.2	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
======== 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	100.6126938	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

pyy099Cyan-C



NAME	pyy099Cyan	
EXPNO	2	
PROCNO	1	
Date_	20100330	
Time	18.43	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	41	
DS	2	
SWH	24038.461	Hz
FIDRES	0.366798	Hz
AQ	1.3631988	sec
RG	128	
DW	20.800	usec
DE	6.50	usec
TE	295.9	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	9.50	usec
PL1	-2.00	dB
PL1W	58.52175522	W
SFO1	100.6228298	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	80.00	usec
PL2	0.00	dB
PL12	15.00	dB
PL13	15.00	dB
PL2W	11.88122272	W
PL12W	0.37571725	W
PL13W	0.37571725	W
SFO2	400.1316005	MHz
SI	32768	
SF	100.6127923	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

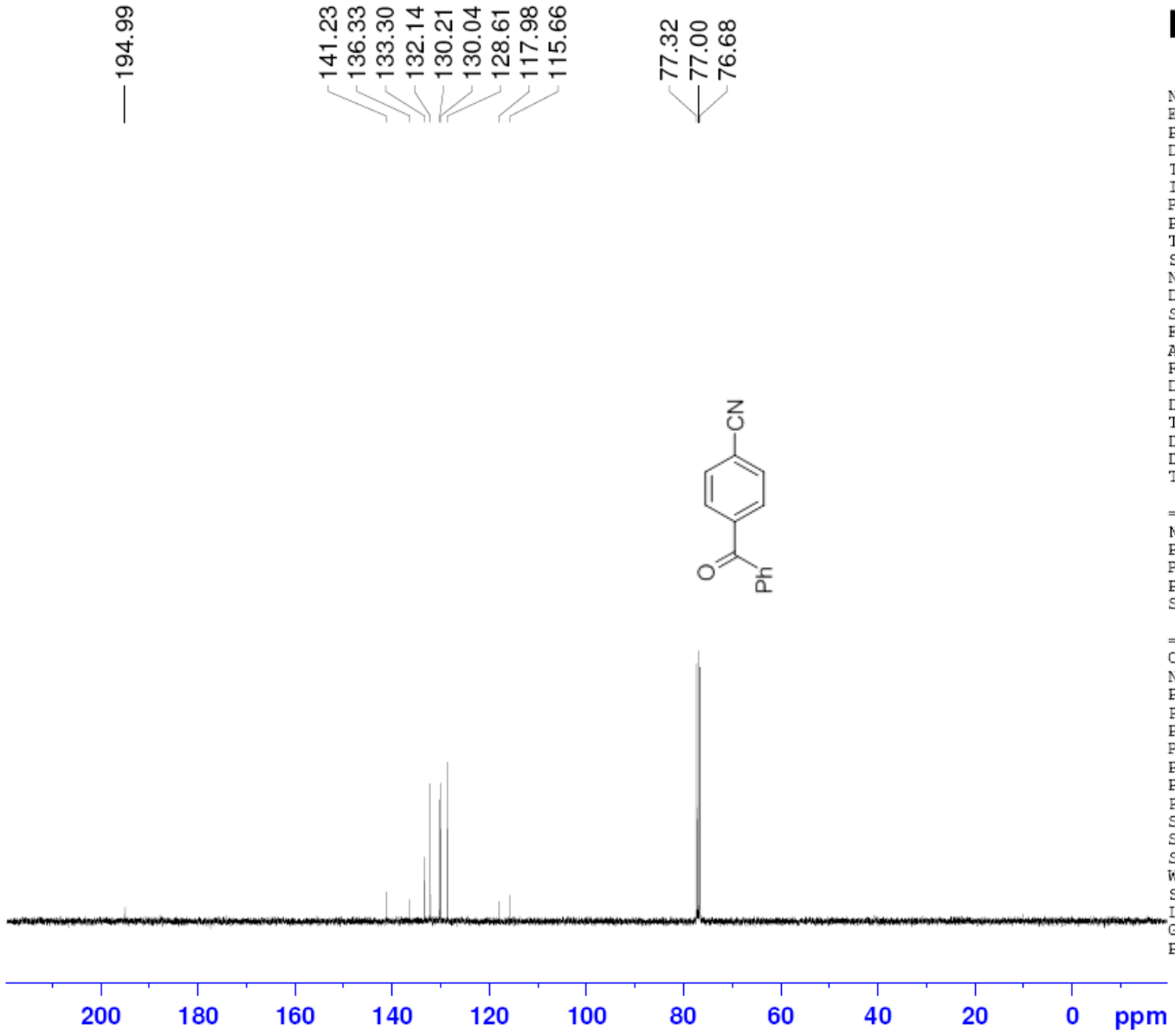
pyy136Cyan-C



BRUKER

NAME	pyy136Cyan	
EXPNO	2	
PROCNO	1	
Date_	20100413	
Time	11.14	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	32	
DS	2	
SWH	24038.461	Hz
FIDRES	0.366798	Hz
AQ	1.3631988	sec
RG	203	
DW	20.800	usec
DE	6.50	usec
TE	296.4	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	100.6127809	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

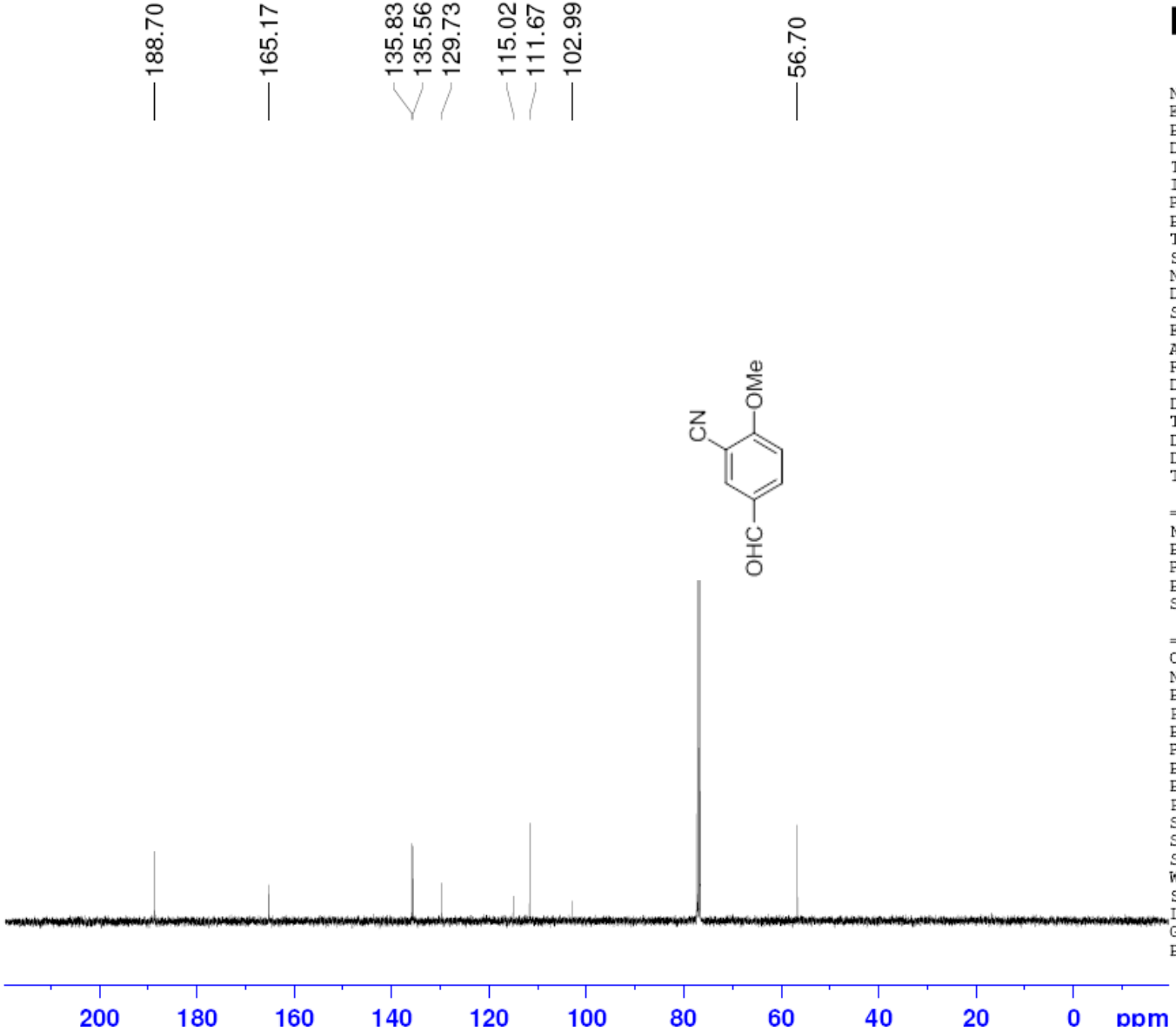
pyy139Cyan-C



BRUKER

NAME	pyy139Cyan	
EXPNO	2	
PROCNO	1	
Date_	20100412	
Time	14.48	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	101	
DS	2	
SWH	24038.461	Hz
FIDRES	0.366798	Hz
AQ	1.3631988	sec
RG	203	
DW	20.800	usec
DE	6.50	usec
TE	297.3	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	9.50	usec
PL1	-2.00	dB
PL1W	58.52175522	W
SFO1	100.6228298	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	80.00	usec
PL2	0.00	dB
PL12	15.00	dB
PL13	15.00	dB
PL2W	11.88122272	W
PL12W	0.37571725	W
PL13W	0.37571725	W
SFO2	400.1316005	MHz
SI	32768	
SF	100.6127716	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

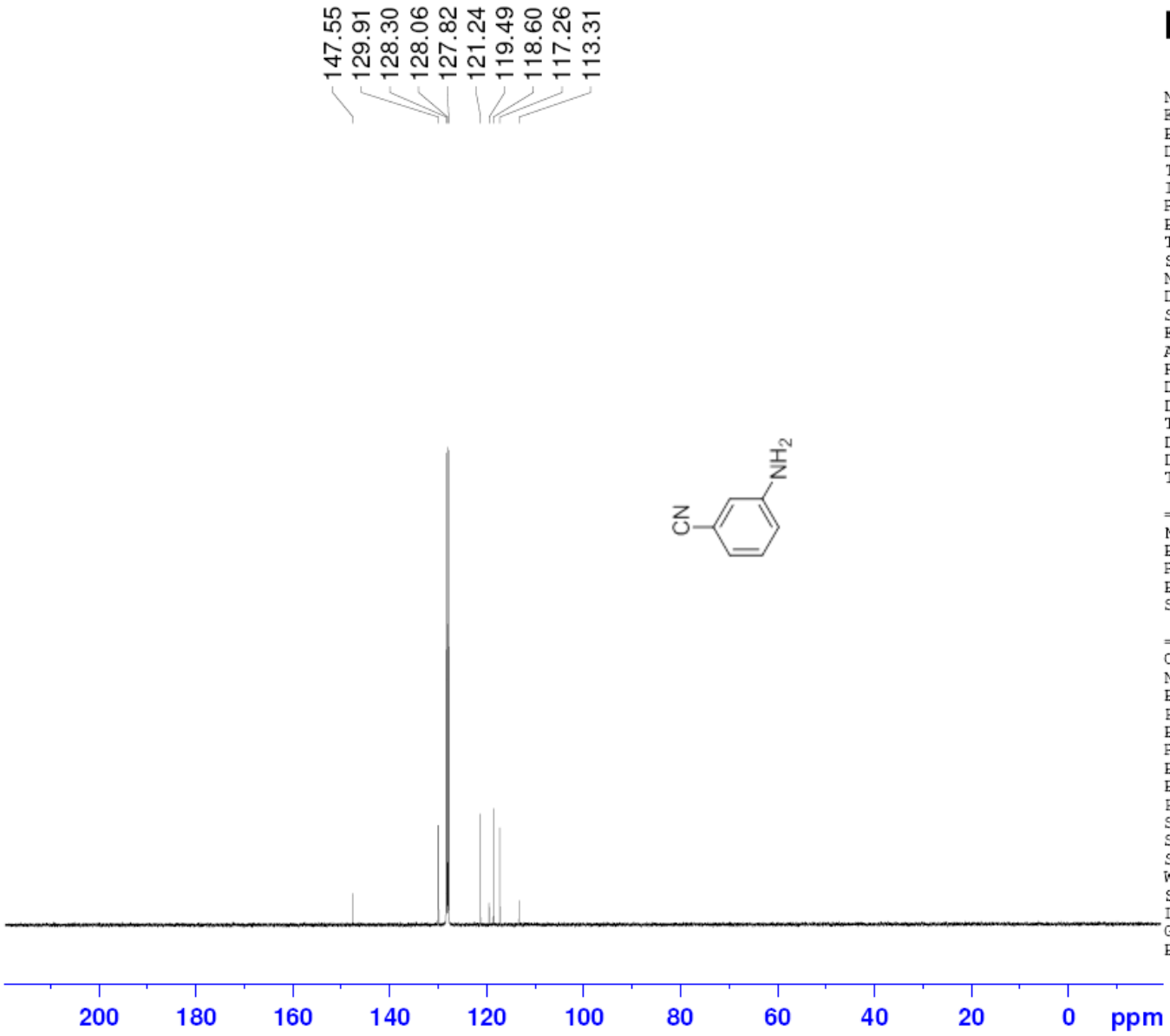
pyy145Cyan-C



BRUKER

NAME	pyy145Cyan	
EXPNO	2	
PROCNO	1	
Date_	20100410	
Time	22.25	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	132	
DS	2	
SWH	24038.461	Hz
FIDRES	0.366798	Hz
AQ	1.3631988	sec
RG	203	
DW	20.800	usec
DE	6.50	usec
TE	295.9	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	100.6127754	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

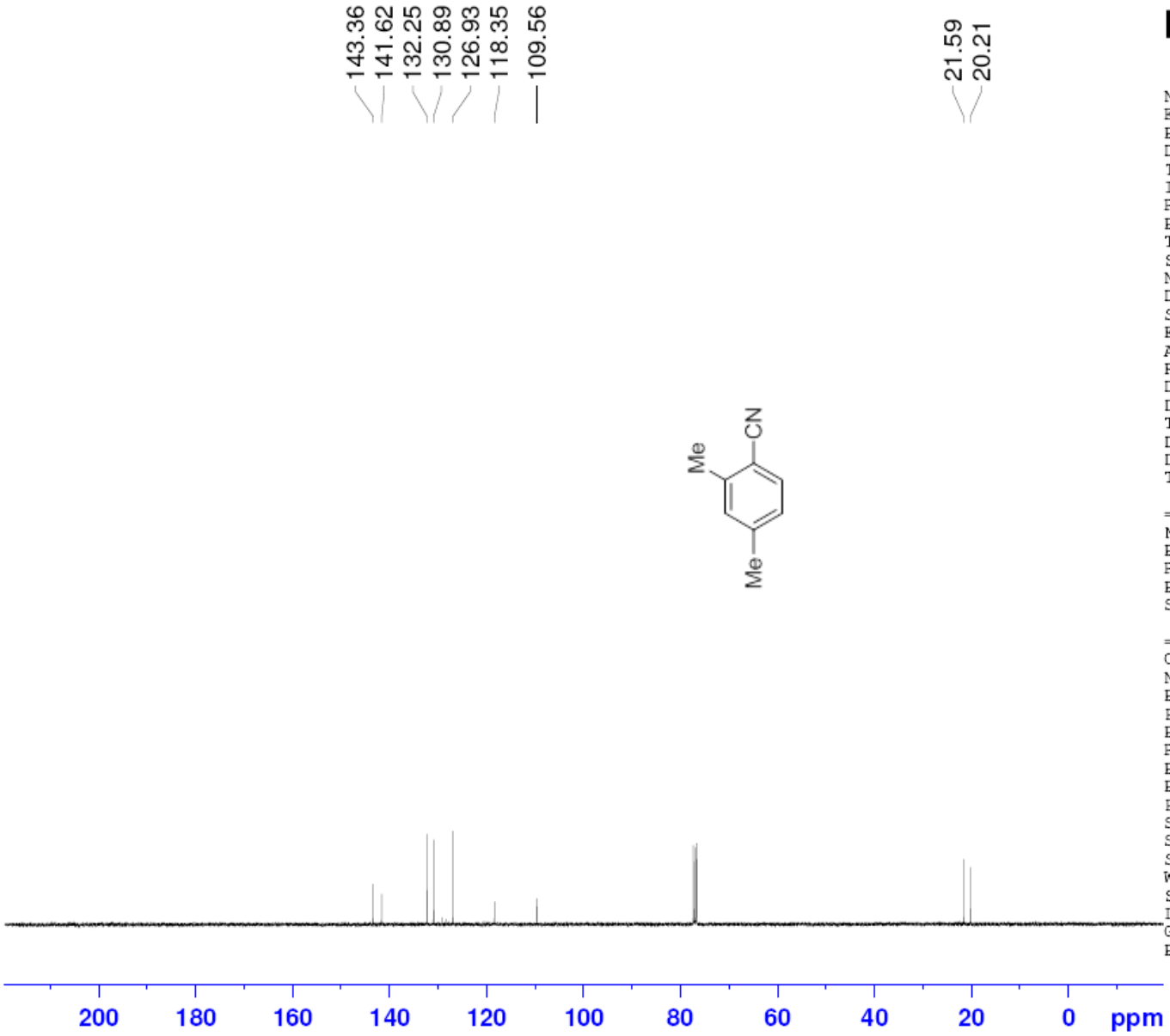
pyy142Cyan-C(Pure)



BRUKER

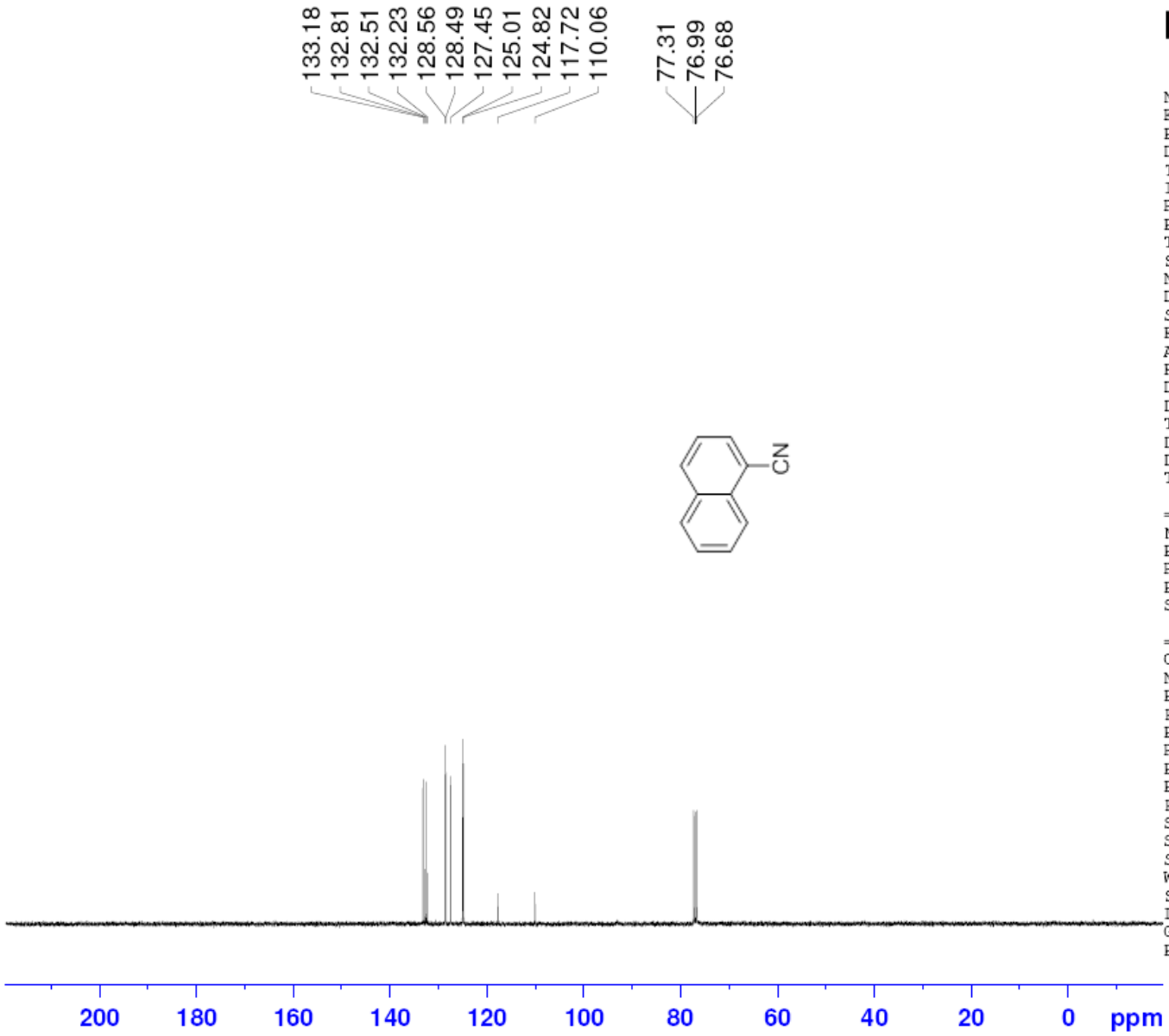
NAME	pyy142Cyan
EXPNO	8
PROCNO	1
Date_	20100420
Time	14.22
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	C6D6
NS	32
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	181
DW	20.800 usec
DE	6.50 usec
TE	296.3 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	15.00 dB
PL2W	11.88122272 W
PL12W	0.37571725 W
PL13W	0.37571725 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127333 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

pyy217Cyan-C



NAME	pyy217Cyan
EXPNO	2
PROCNO	1
Date_	20100512
Time	11.40
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	296.1 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	15.00 dB
PL2W	11.88122272 W
PL12W	0.37571725 W
PL13W	0.37571725 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127810 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

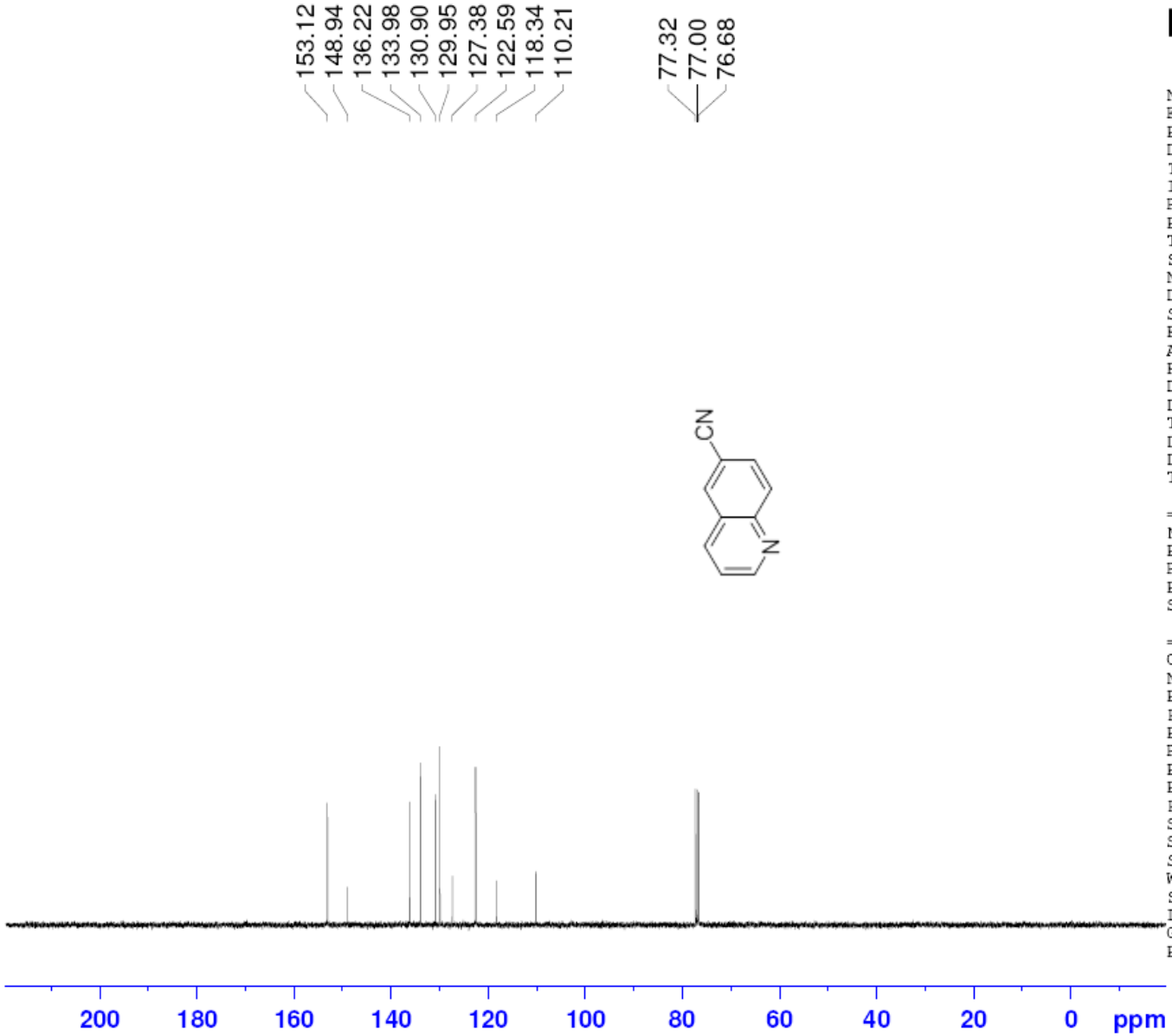
pyy137Cyan-C



BRUKER

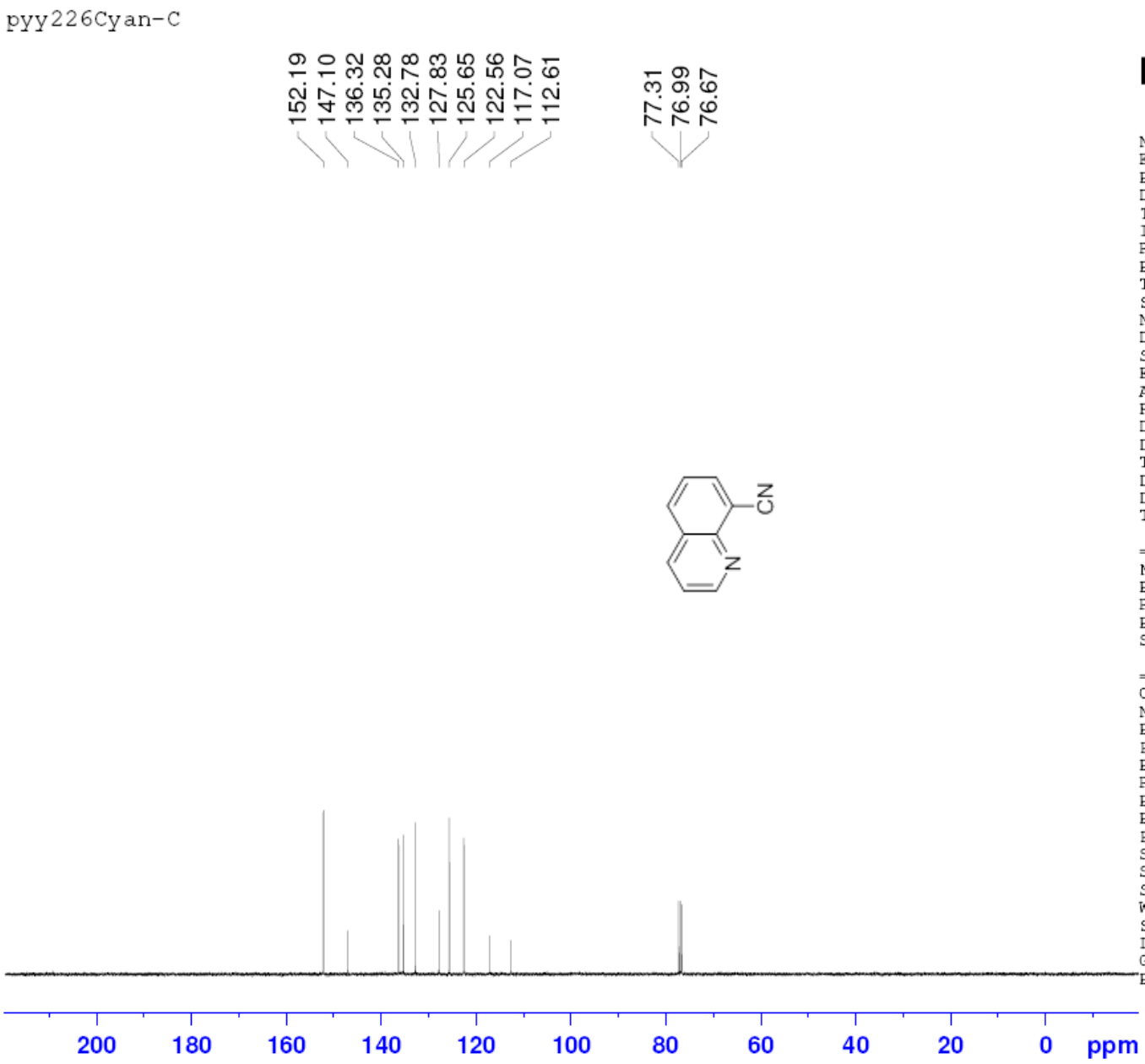
NAME	pyy137Cyan	
EXPNO	2	
PROCNO	1	
Date_	20100413	
Time	11.33	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	39	
DS	2	
SWH	24038.461	Hz
FIDRES	0.366798	Hz
AQ	1.3631988	sec
RG	203	
DW	20.800	usec
DE	6.50	usec
TE	297.0	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	9.50	usec
PL1	-2.00	dB
PL1W	58.52175522	W
SFO1	100.6228298	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	80.00	usec
PL2	0.00	dB
PL12	15.00	dB
PL13	15.00	dB
PL2W	11.88122272	W
PL12W	0.37571725	W
PL13W	0.37571725	W
SFO2	400.1316005	MHz
SI	32768	
SF	100.6127810	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

pyy224Cyan-C



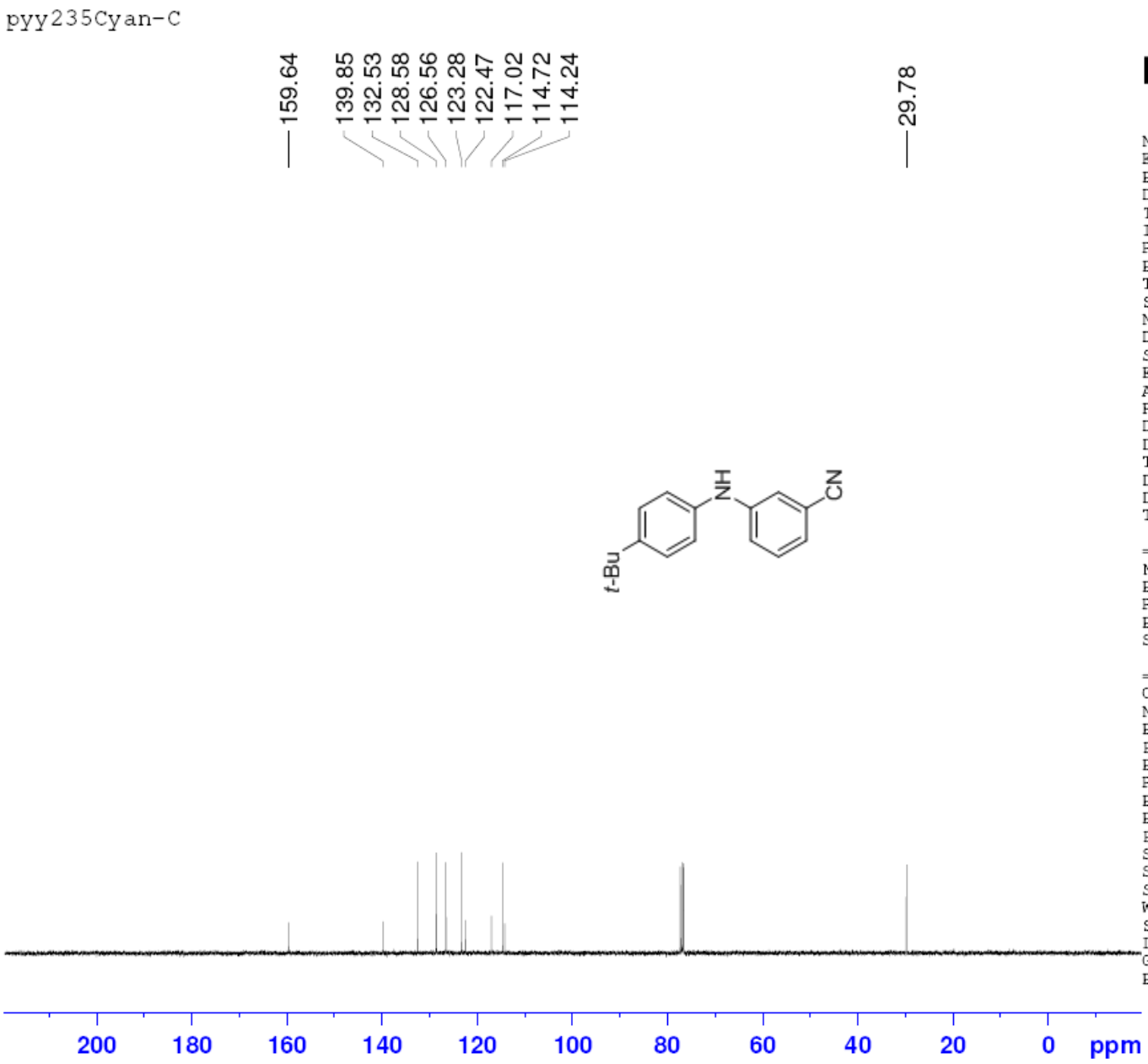
NAME	pyy224Cyan
EXPNO	2
PROCNO	1
Date_	20100513
Time	19.55
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	297.1 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	15.00 dB
PL2W	11.88122272 W
PL12W	0.37571725 W
PL13W	0.37571725 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127828 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

pyy226Cyan-C



NAME	pyy226Cyan	
EXPNO	2	
PROCNO	1	
Date_	20100517	
Time	11.47	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	16	
DS	2	
SWH	24038.461	Hz
FIDRES	0.366798	Hz
AQ	1.3631988	sec
RG	203	
DW	20.800	usec
DE	6.50	usec
TE	296.5	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	9.50	usec
PL1	-2.00	dB
PL1W	58.52175522	W
SFO1	100.6228298	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	80.00	usec
PL2	0.00	dB
PL12	15.00	dB
PL13	15.00	dB
PL2W	11.88122272	W
PL12W	0.37571725	W
PL13W	0.37571725	W
SFO2	400.1316005	MHz
SI	32768	
SF	100.6127950	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

pyy235Cyan-C

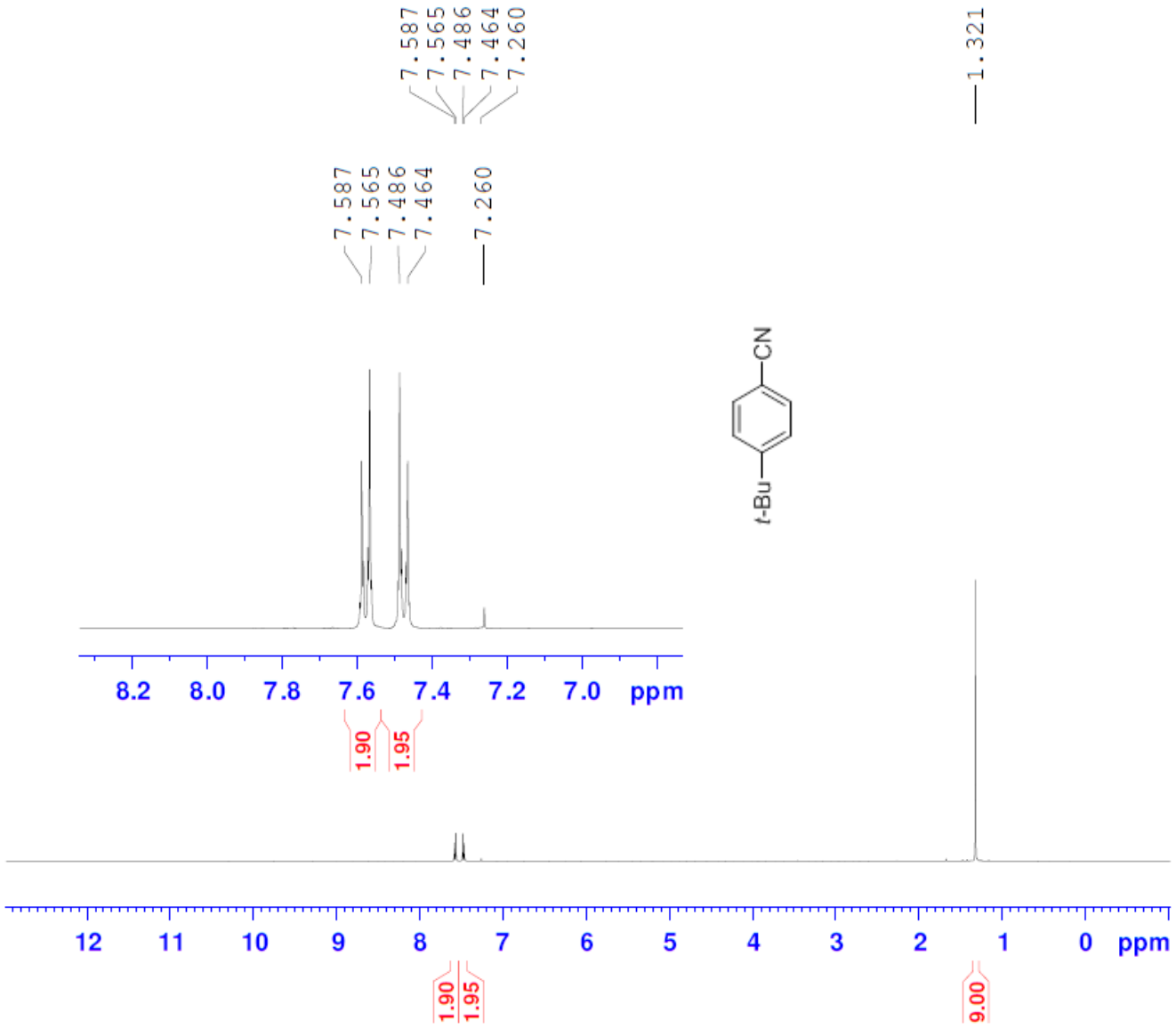


BRUKER

NAME	pyy235Cyan	
EXPNO	2	
PROCNO	1	
Date_	20100525	
Time	12.02	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	16	
DS	2	
SWH	24038.461	Hz
FIDRES	0.366798	Hz
AQ	1.3631988	sec
RG	203	
DW	20.800	usec
DE	6.50	usec
TE	298.0	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	9.50	usec
PL1	-2.00	dB
PL1W	58.52175522	W
SFO1	100.6228298	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	80.00	usec
PL2	0.00	dB
PL12	15.00	dB
PL13	15.00	dB
PL2W	11.88122272	W
PL12W	0.37571725	W
PL13W	0.37571725	W
SFO2	400.1316005	MHz
SI	32768	
SF	100.6127826	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

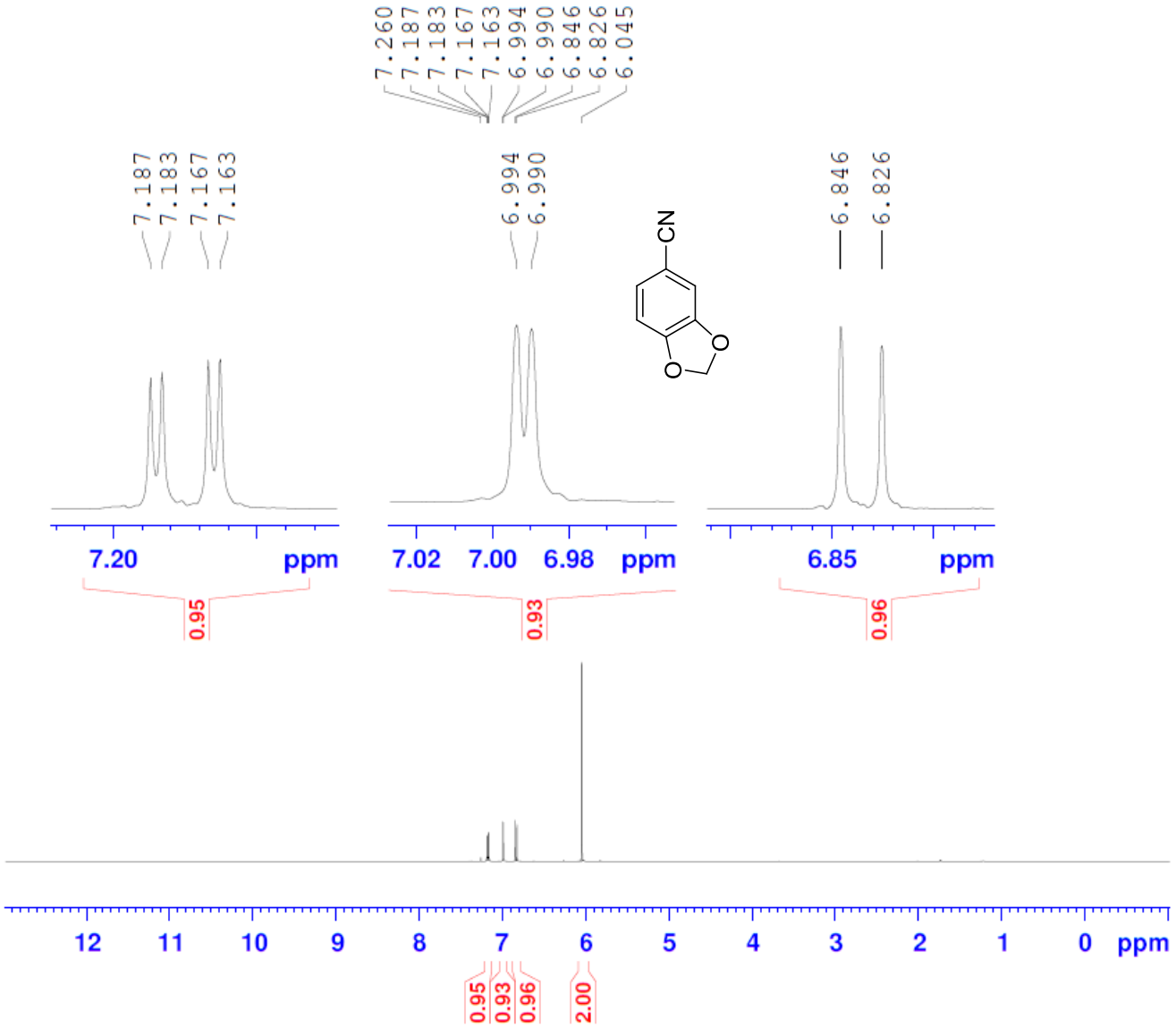
^{1}H-, ^{13}C-NMR spectra of products from palladium-catalyzed cyanation of aryl tosylates

pyy163Cyan-H

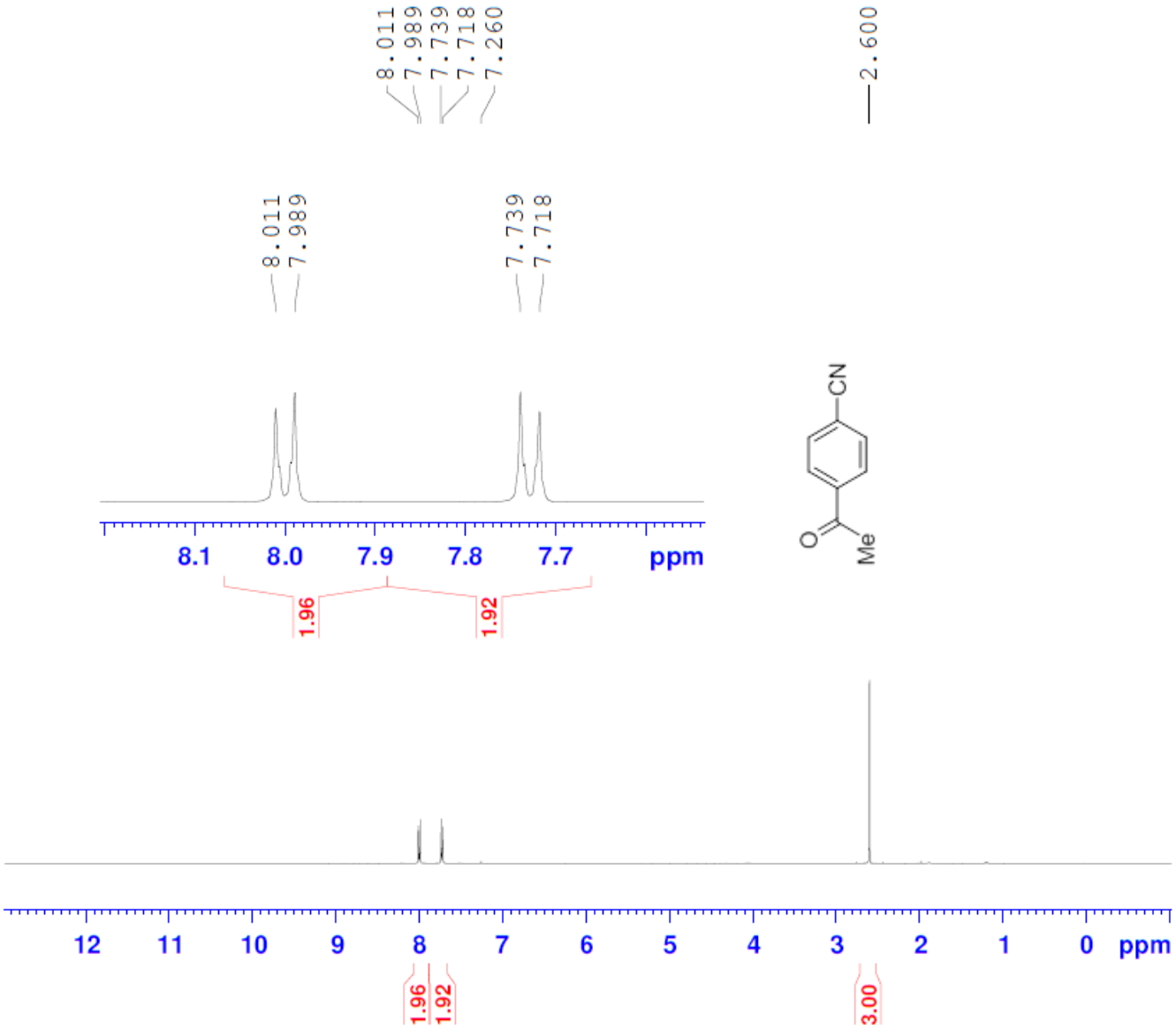


NAME	pyy163Cyan
EXPNO	1
PROCNO	1
Date_	20100420
Time	14.58
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	32
DW	89.333 usec
DE	6.50 usec
TE	296.1 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300098 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

pyy168Cyan-H

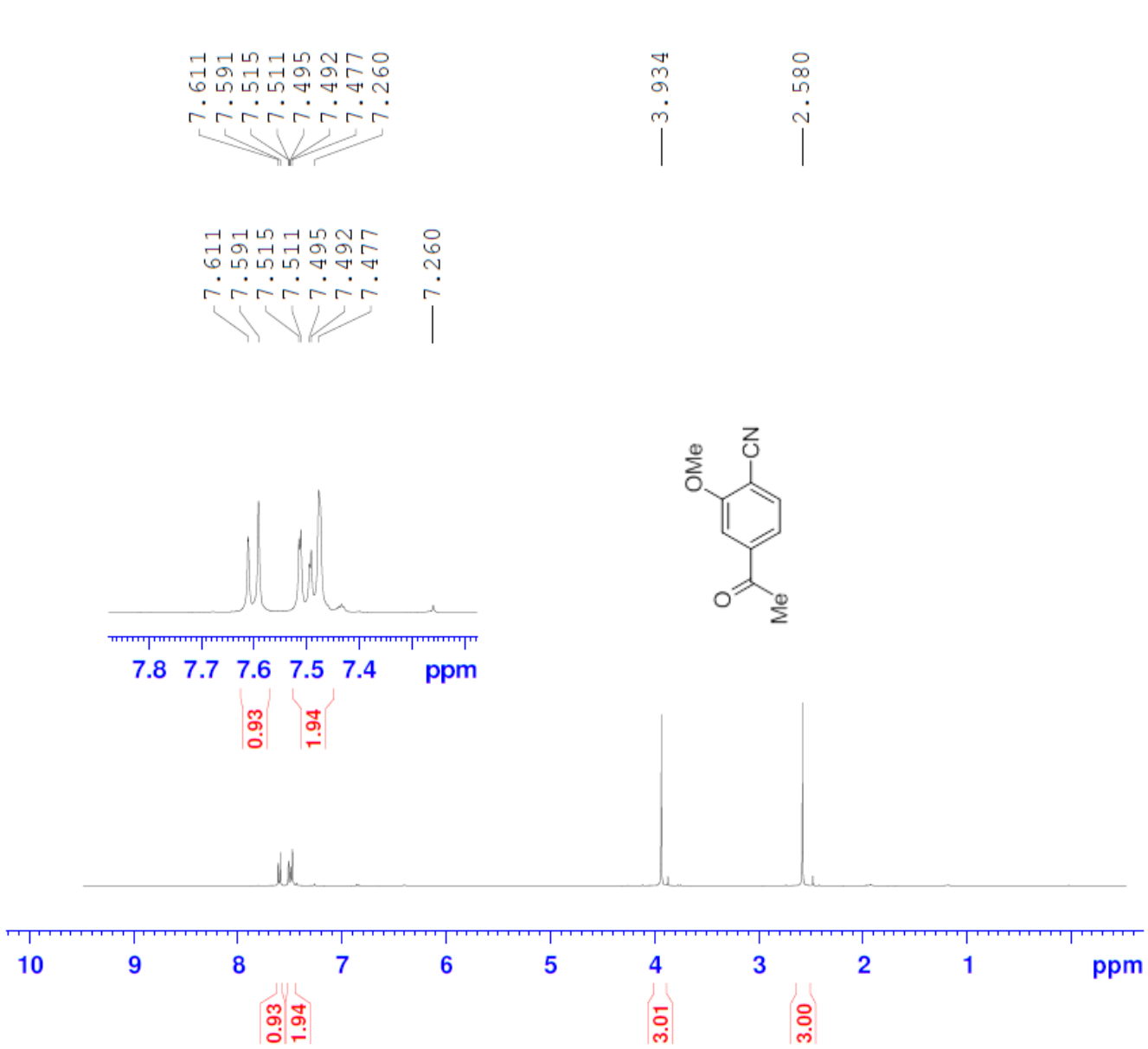


NAME	pyy168Cyan
EXPNO	1
PROCNO	1
Date_	20100420
Time	12.08
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	45.2
DW	89.333 usec
DE	6.50 usec
TE	295.9 K
D1	1.00000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300097 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



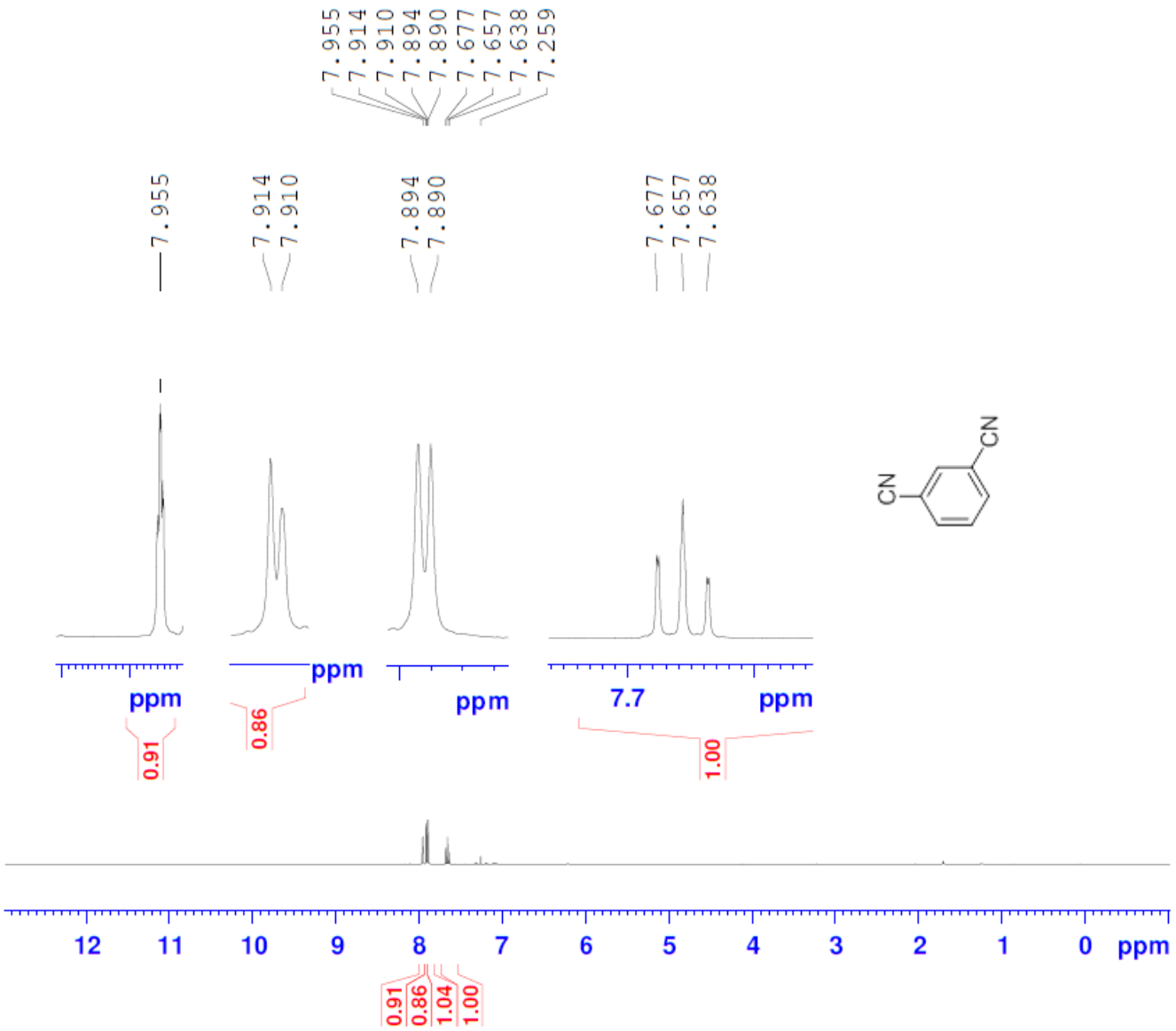
BRUKER

NAME	pyy174Cyan
EXPNO	1
PROCNO	1
Date_	20100421
Time	14.38
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	8
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	297.7 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	400.1300096 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



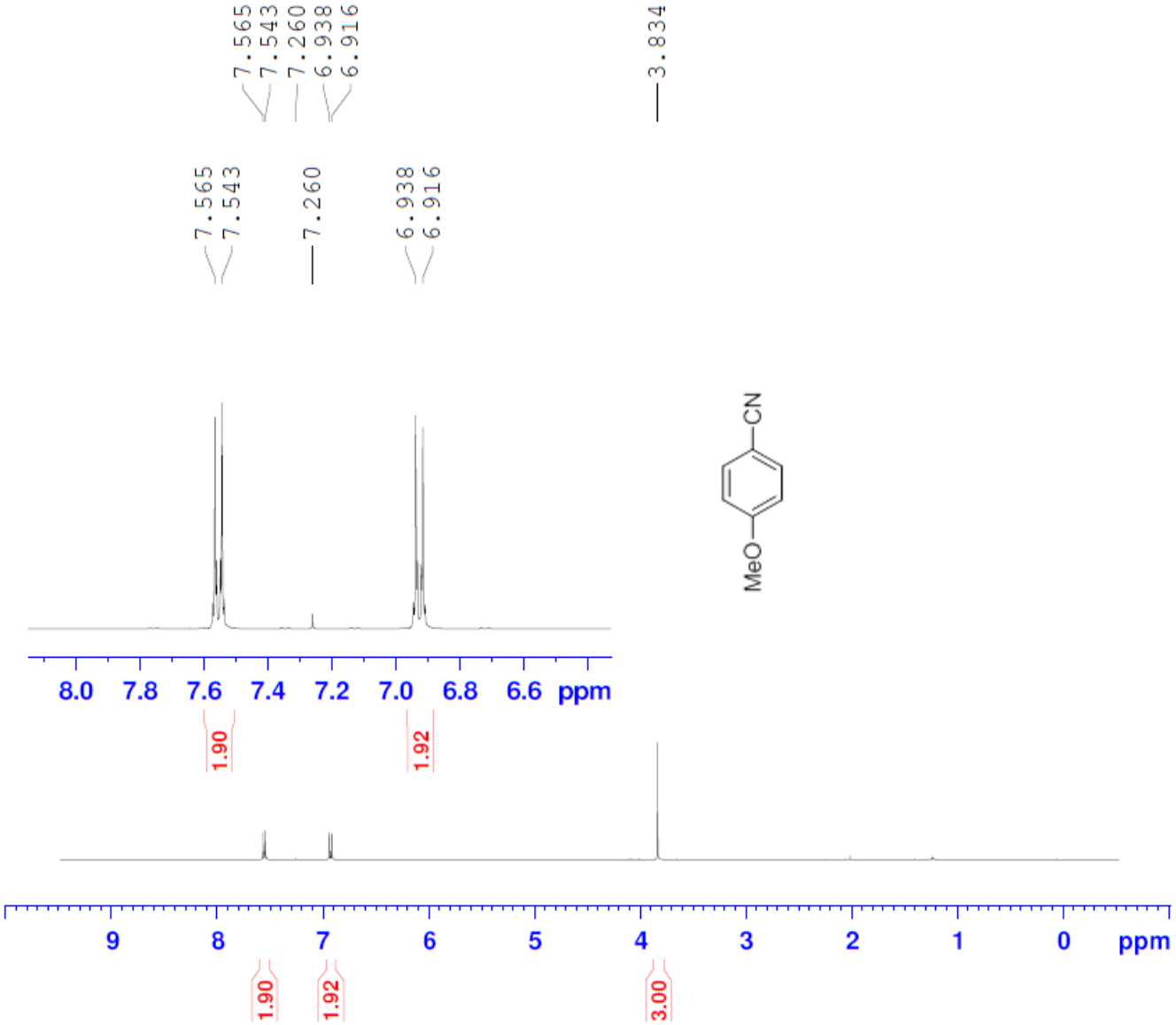
NAME	pyy175Cyan
EXPNO	1
PROCNO	1
Date_	20100421
Time	13.57
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	8
DS	2
SWH	4006.410 Hz
FIDRES	0.122266 Hz
AQ	4.0894966 sec
RG	28.5
DW	124.800 usec
DE	6.50 usec
TE	297.8 K
D1	1.00000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1318007 MHz
SI	32768
SF	400.1300095 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

pyy179Cyan-H



NAME	pyy179Cyan	
EXPNO	1	
PROCNO	1	
Date_	20100421	
Time	15.01	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zg30	
TD	32768	
SOLVENT	CDCl3	
NS	16	
DS	2	
SWH	5597.015	Hz
FIDRES	0.170807	Hz
AQ	2.9273248	sec
RG	114	
DW	89.333	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	400.1324008	MHz
SI	32768	
SF	400.1300102	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	

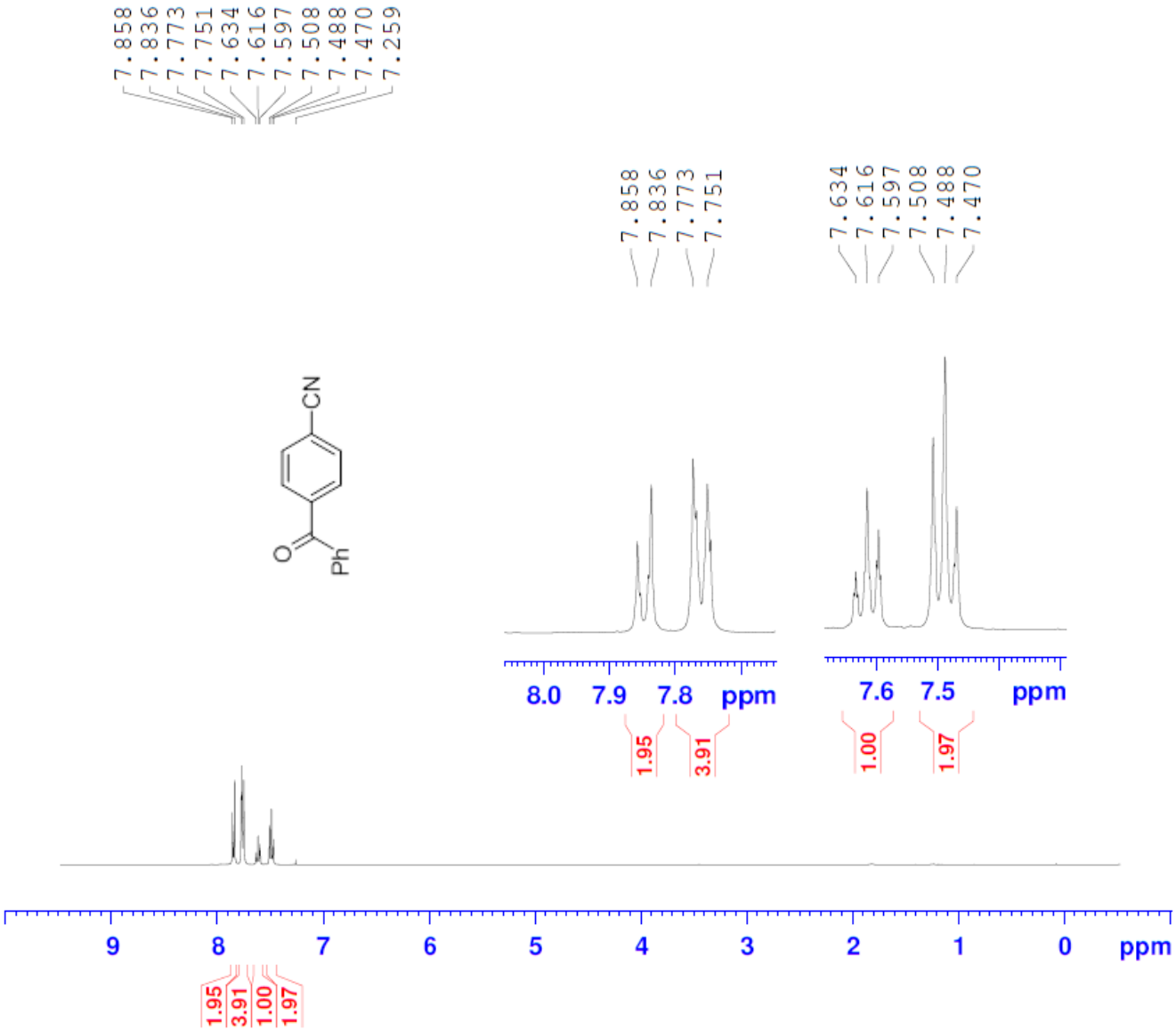
Standard 1H



BRUKER

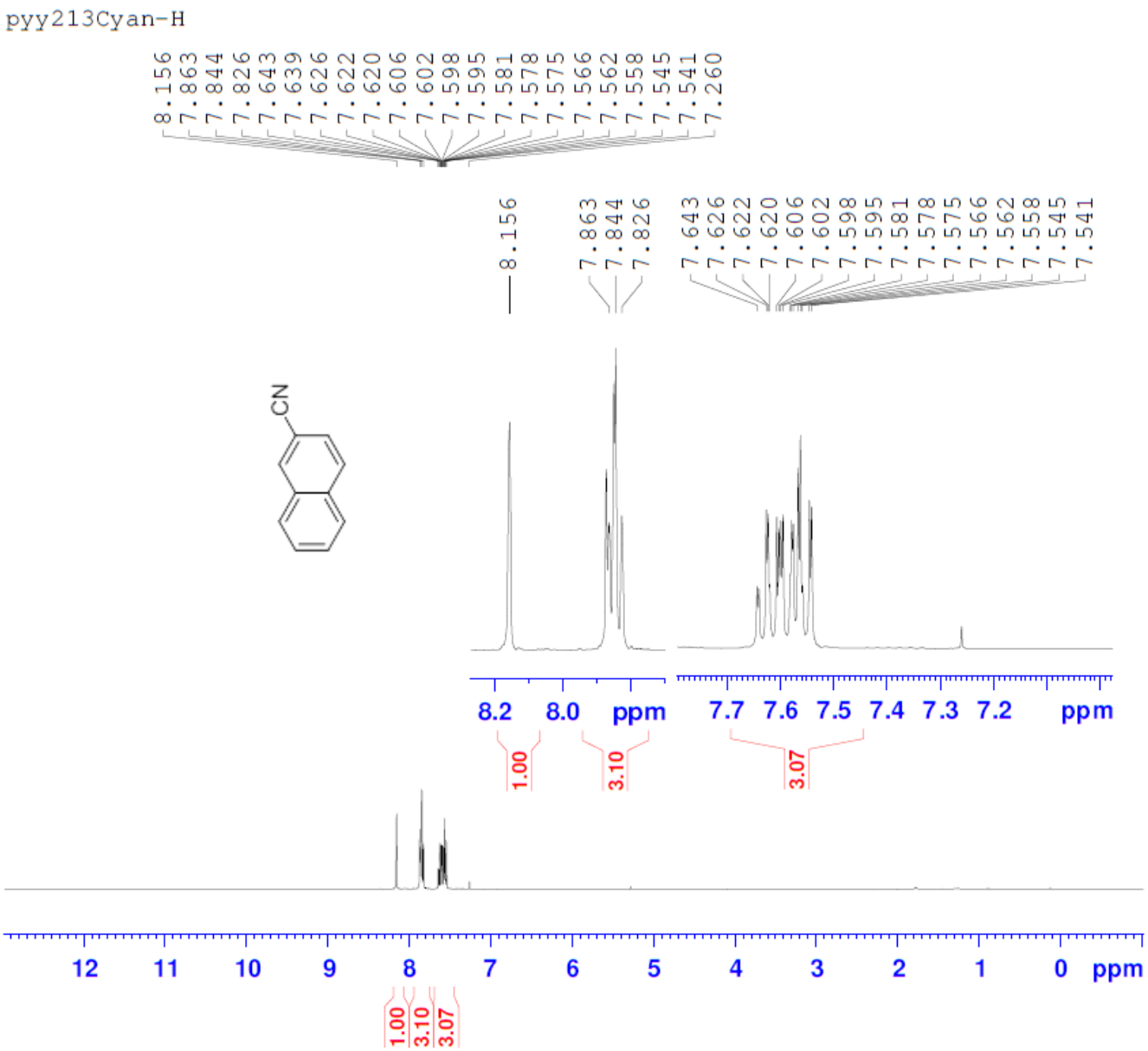
NAME	pyy196Cyan
EXPNO	1
PROCNO	1
Date_	20100504
Time	18.00
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	8
DS	2
SWH	4006.410 Hz
FIDRES	0.122266 Hz
AQ	4.0894966 sec
RG	40.3
DW	124.800 usec
DE	6.50 usec
TE	297.5 K
D1	1.00000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1318007 MHz
SI	32768
SF	400.1300096 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Standard 1H



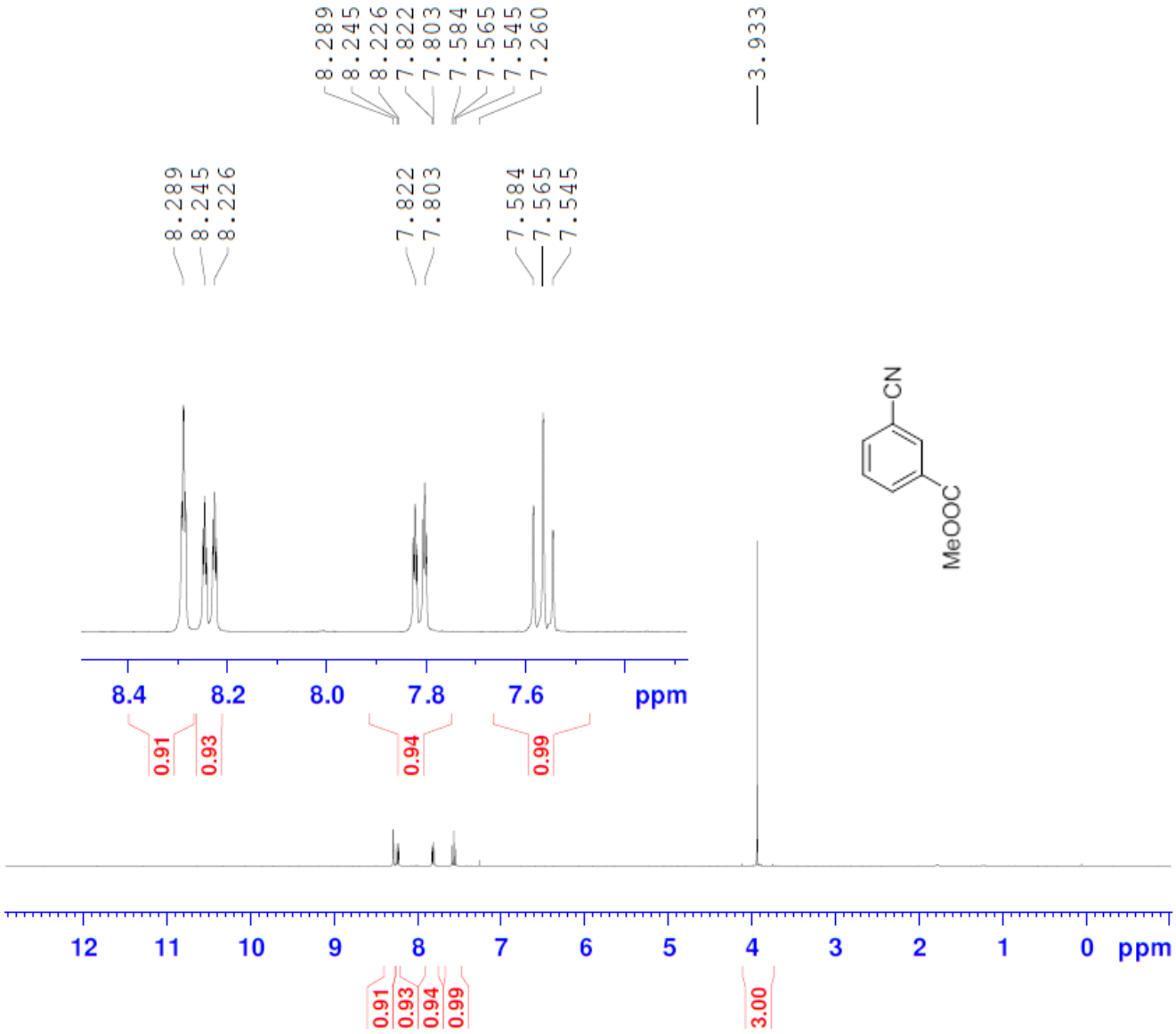
NAME	pyy207Cyan
EXPNO	3
PROCNO	1
Date_	20100507
Time	17.40
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	8
DS	2
SWH	4006.410 Hz
FIDRES	0.122266 Hz
AQ	4.0894966 sec
RG	40.3
DW	124.800 usec
DE	6.50 usec
TE	297.2 K
D1	1.00000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1318007 MHz
SI	32768
SF	400.1300096 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

pyy213Cyan-H



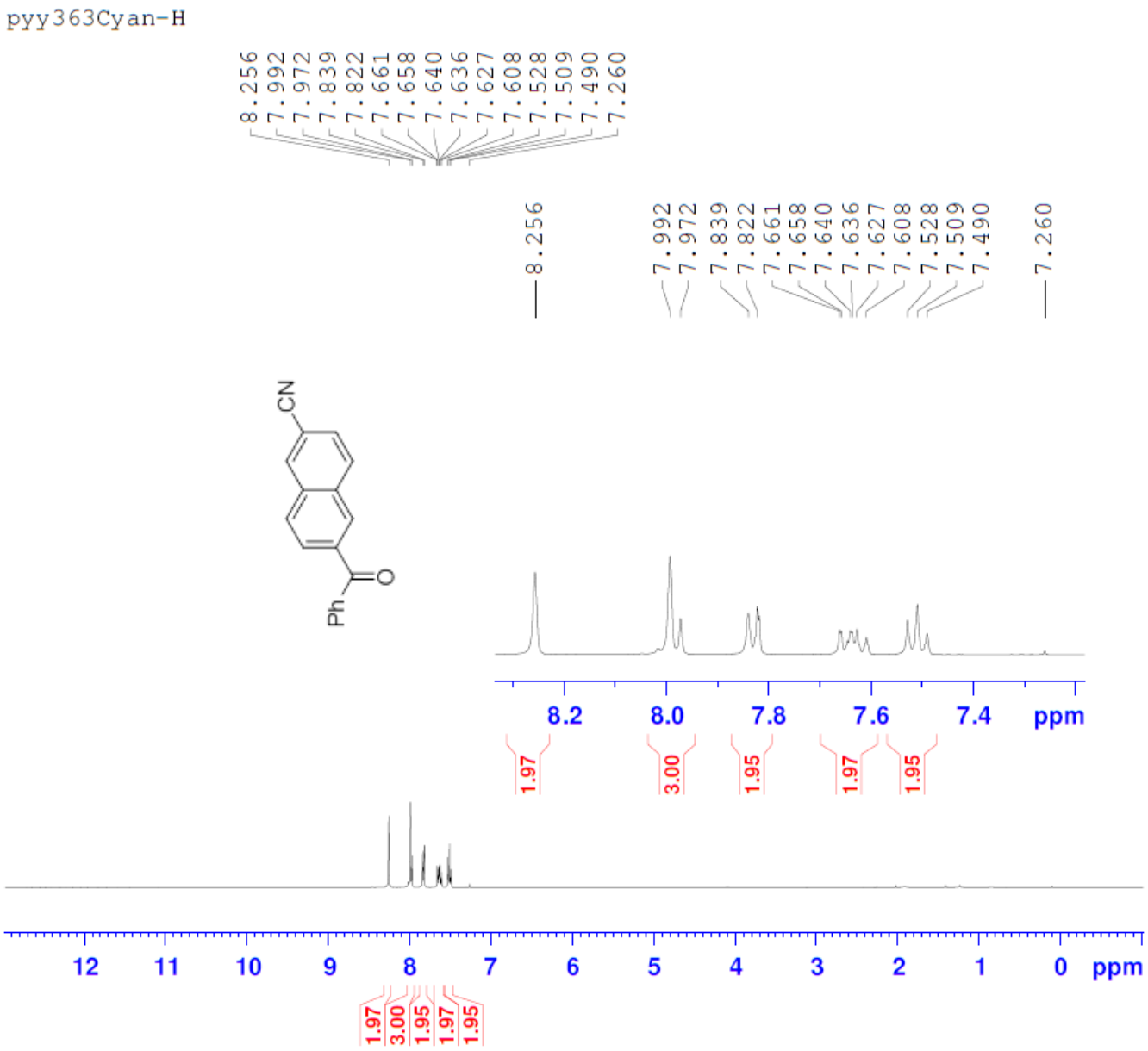
NAME	pyy213Cyan
EXPNO	1
PROCNO	1
Date_	20100513
Time	19.36
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	8
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	32
DW	89.333 usec
DE	6.50 usec
TE	296.4 K
D1	1.00000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300094 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

pyy214Cyan-H



NAME	pyy214Cyan	
EXPNO	1	
PROCNO	1	
Date_	20100512	
Time	11.09	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zg30	
TD	32768	
SOLVENT	CDCl3	
NS	8	
DS	2	
SWH	5597.015	Hz
FIDRES	0.170807	Hz
AQ	2.9273248	sec
RG	45.2	
DW	89.333	usec
DE	6.50	usec
TE	295.9	K
D1	1.00000000	sec
TD0	1	
========	CHANNEL f1 ========	
NUC1	1H	
P1	14.70	usec
PL1	0.00	dB
PL1W	11.88122272	W
SFO1	400.1324008	MHz
SI	32768	
SF	400.1300096	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	

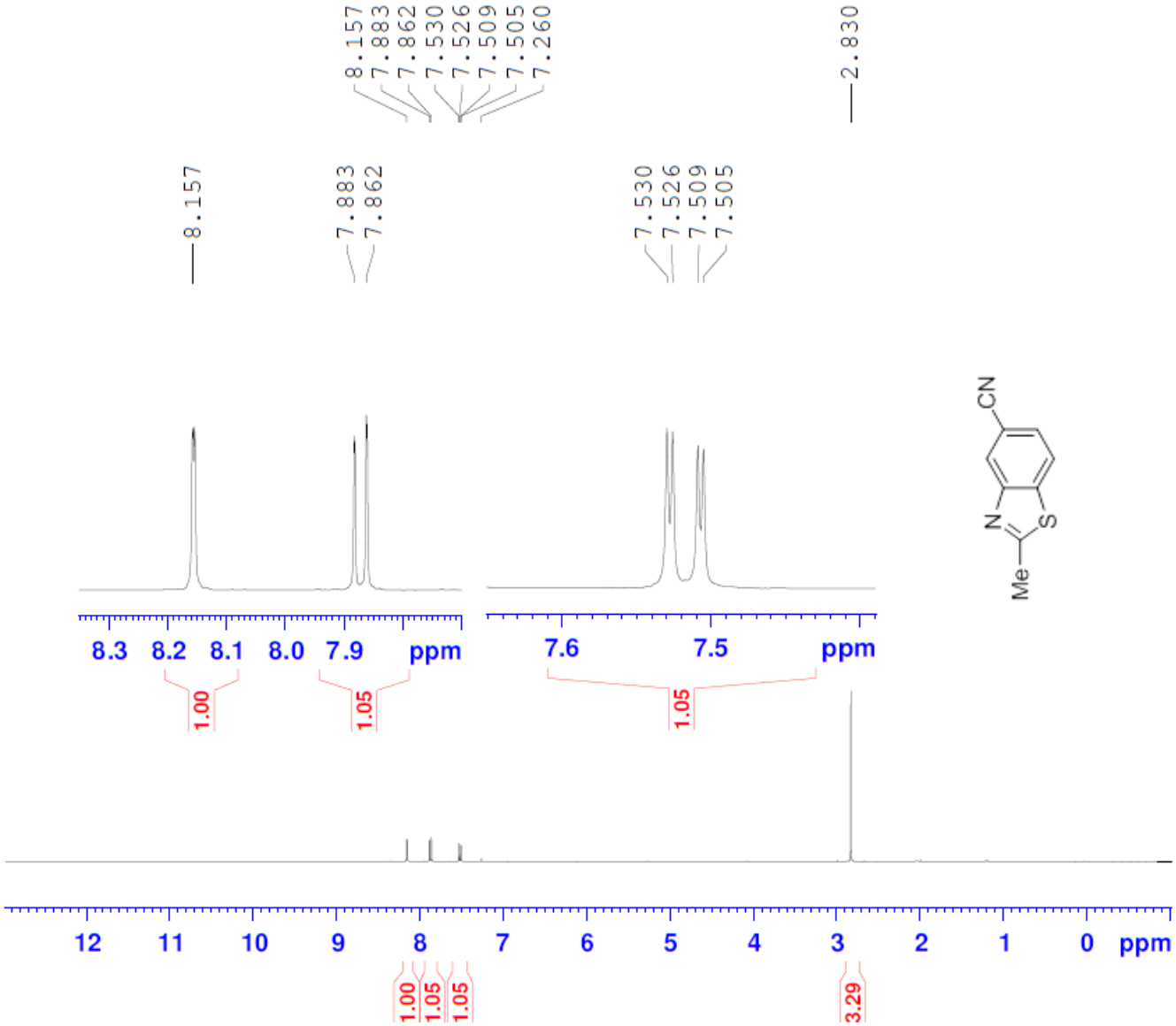
pyy363Cyan-H



BRUKER

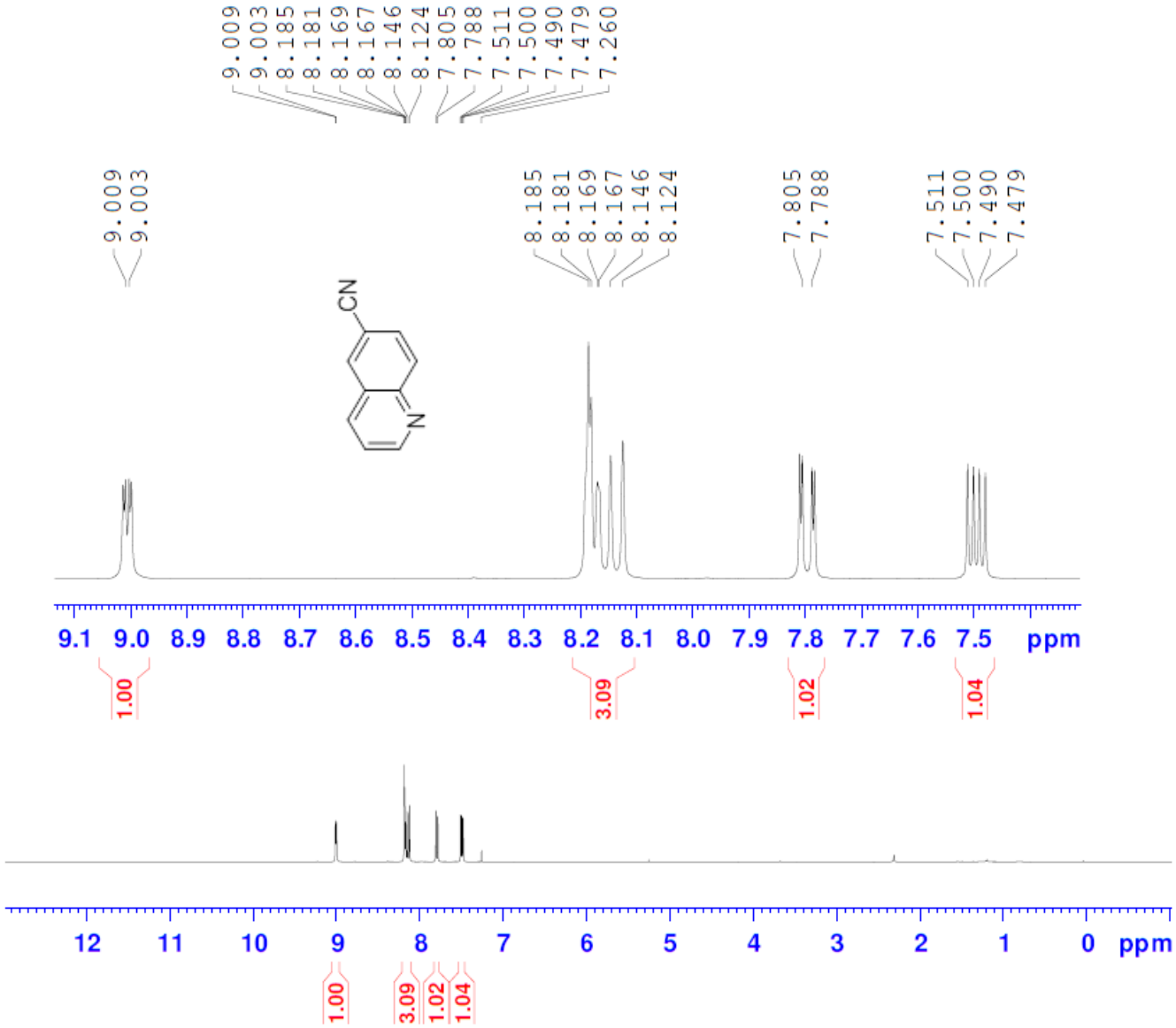
NAME	pyy363Cyan
EXPNO	1
PROCNO	1
Date_	20100708
Time	12.00
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	4
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	36
DW	89.333 usec
DE	6.50 usec
TE	298.4 K
D1	1.00000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300095 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

pyy231Cyan-H



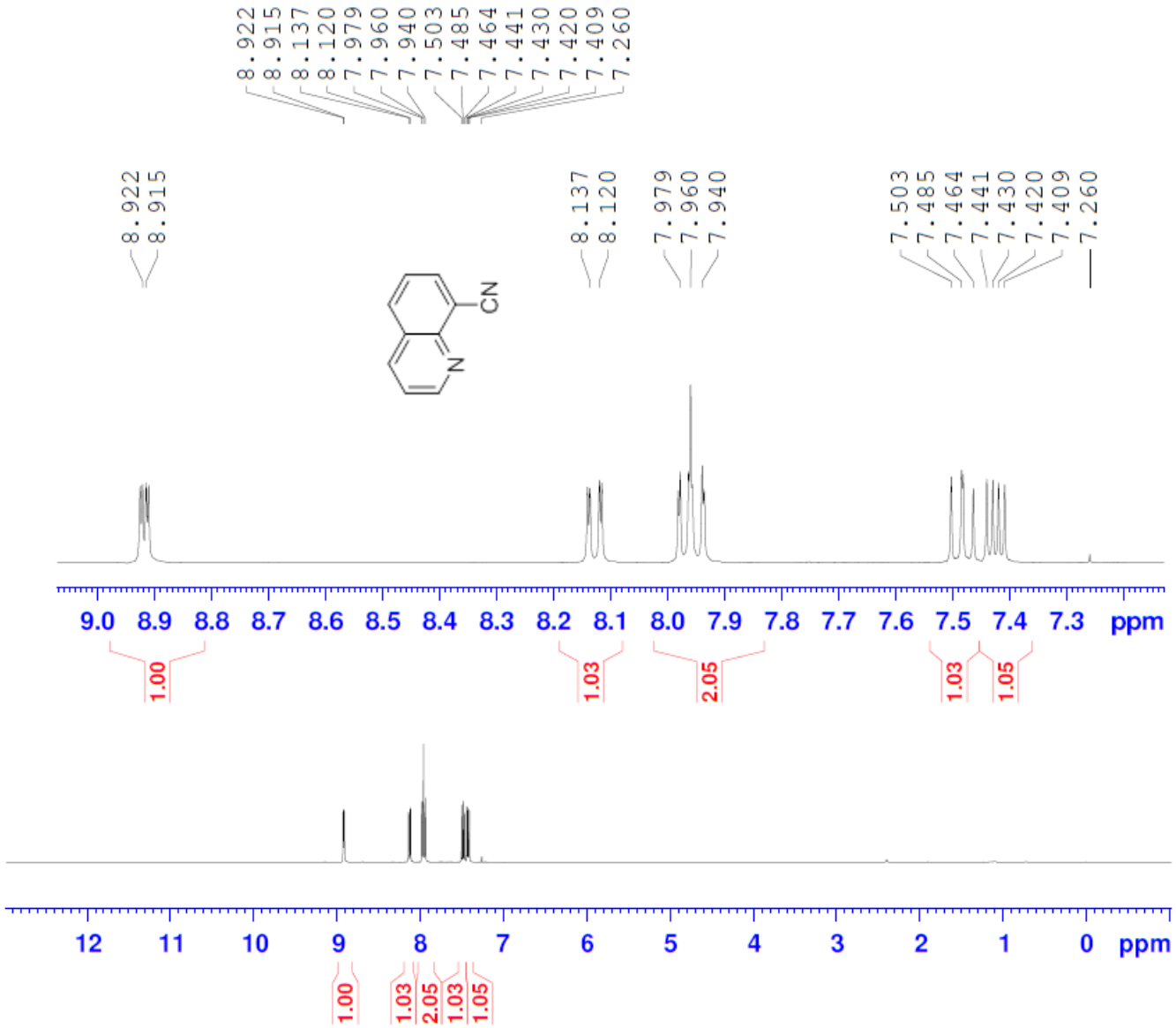
NAME	pyy231Cyan	
EXPNO	1	
PROCNO	1	
Date_	20100517	
Time	12.16	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zg30	
TD	32768	
SOLVENT	CDCl3	
NS	8	
DS	2	
SWH	5597.015	Hz
FIDRES	0.170807	Hz
AQ	2.9273248	sec
RG	45.2	
DW	89.333	usec
DE	6.50	usec
TE	295.9	K
D1	1.00000000	sec
TD0	1	
========	CHANNEL f1 ========	
NUC1	1H	
P1	14.70	usec
PL1	0.00	dB
PL1W	11.88122272	W
SFO1	400.1324008	MHz
SI	32768	
SF	400.1300097	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	

pyy225Cyan-H



NAME	pyy225Cyan	
EXPNO	1	
PROCNO	1	
Date_	20100513	
Time	20.13	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zg30	
TD	32768	
SOLVENT	CDCl3	
NS	8	
DS	2	
SWH	5597.015	Hz
FIDRES	0.170807	Hz
AQ	2.9273248	sec
RG	45.2	
DW	89.333	usec
DE	6.50	usec
TE	296.4	K
D1	1.00000000	sec
TD0	1	
========	CHANNEL f1 ========	
NUC1	1H	
P1	14.70	usec
PL1	0.00	dB
PL1W	11.88122272	W
SFO1	400.1324008	MHz
SI	32768	
SF	400.1300097	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	

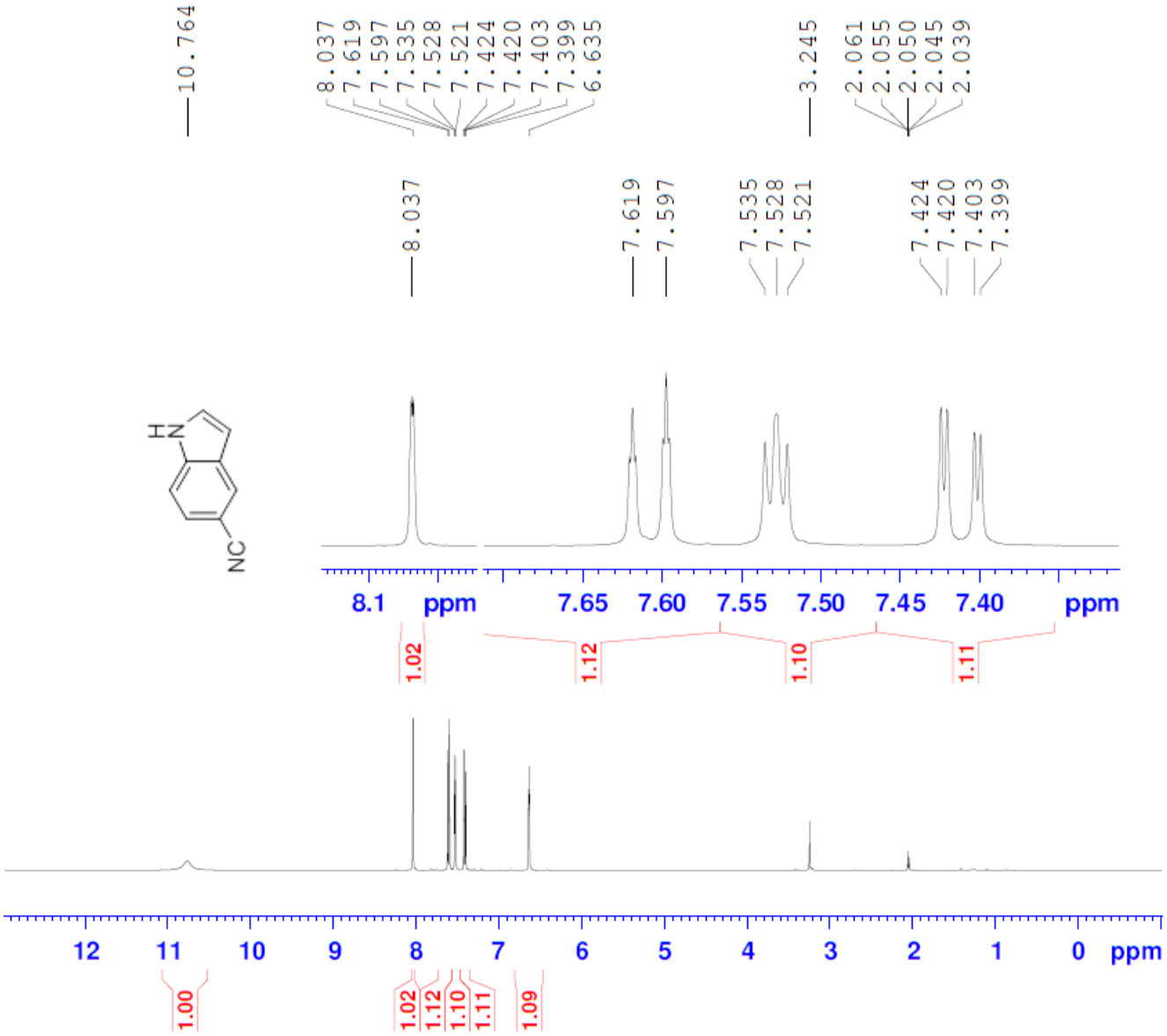
pyy227Cyan-H



BRUKER

NAME	pyy227Cyan
EXPNO	1
PROCNO	1
Date_	20100517
Time	11.52
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	8
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	25.4
DW	89.333 usec
DE	6.50 usec
TE	295.9 K
D1	1.00000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300098 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

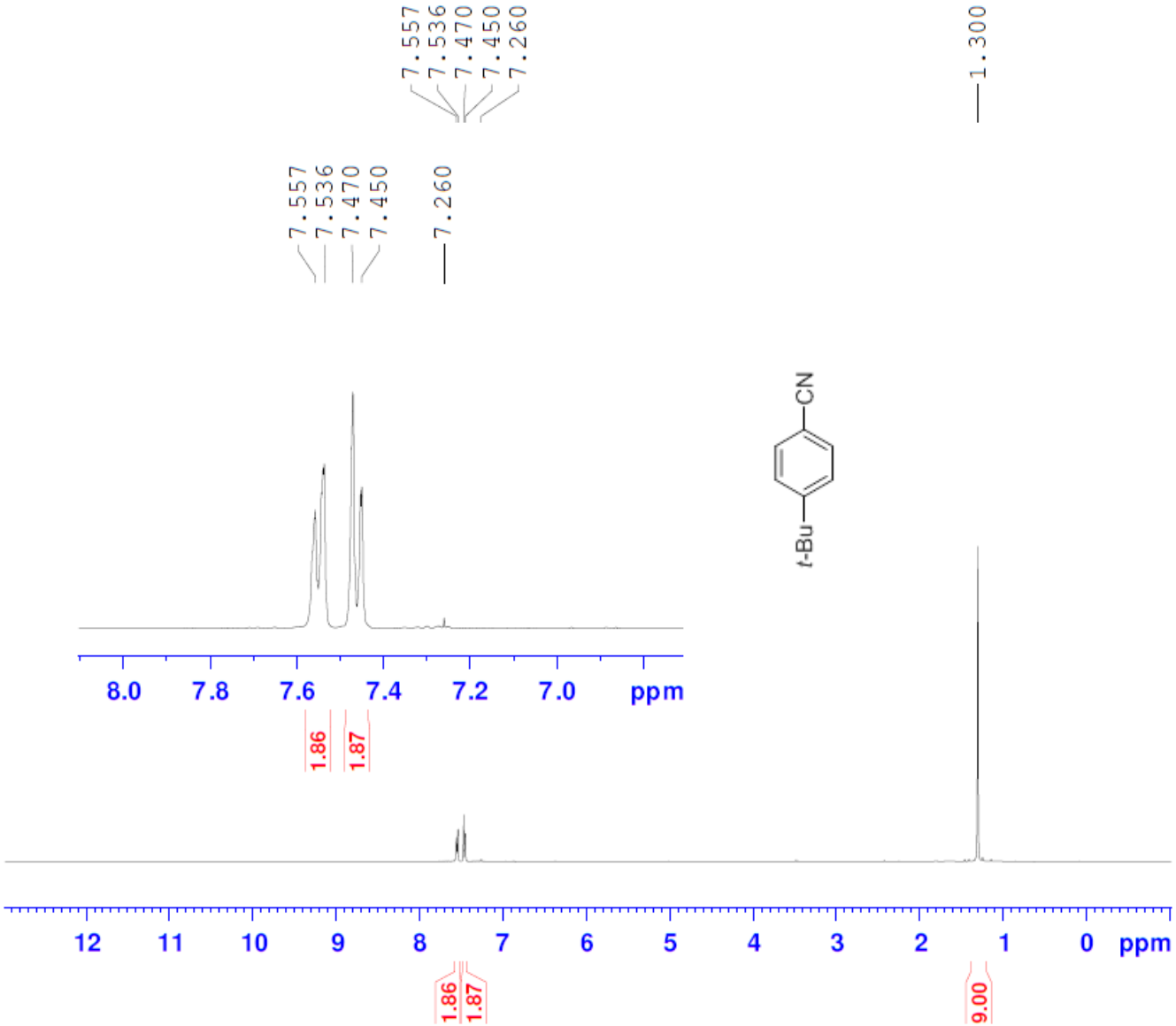
pyy378Cyan-H



BRUKER

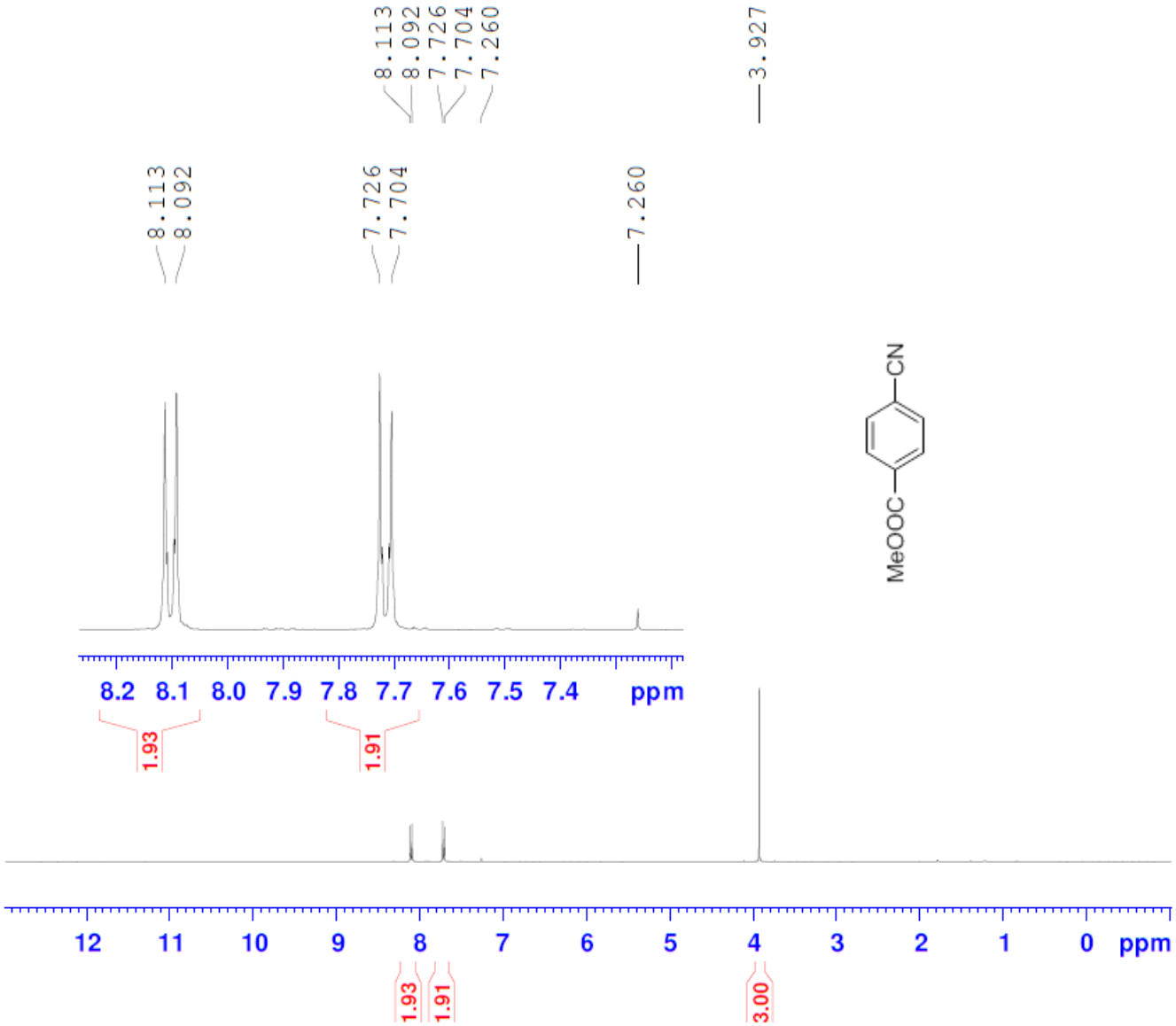
NAME	pyy378Cyan
EXPNO	1
PROCNO	1
Date_	20100721
Time	12.02
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	Acetone
NS	8
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	32
DW	89.333 usec
DE	6.50 usec
TE	298.5 K
D1	1.00000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300068 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

pyy099Cyan-H



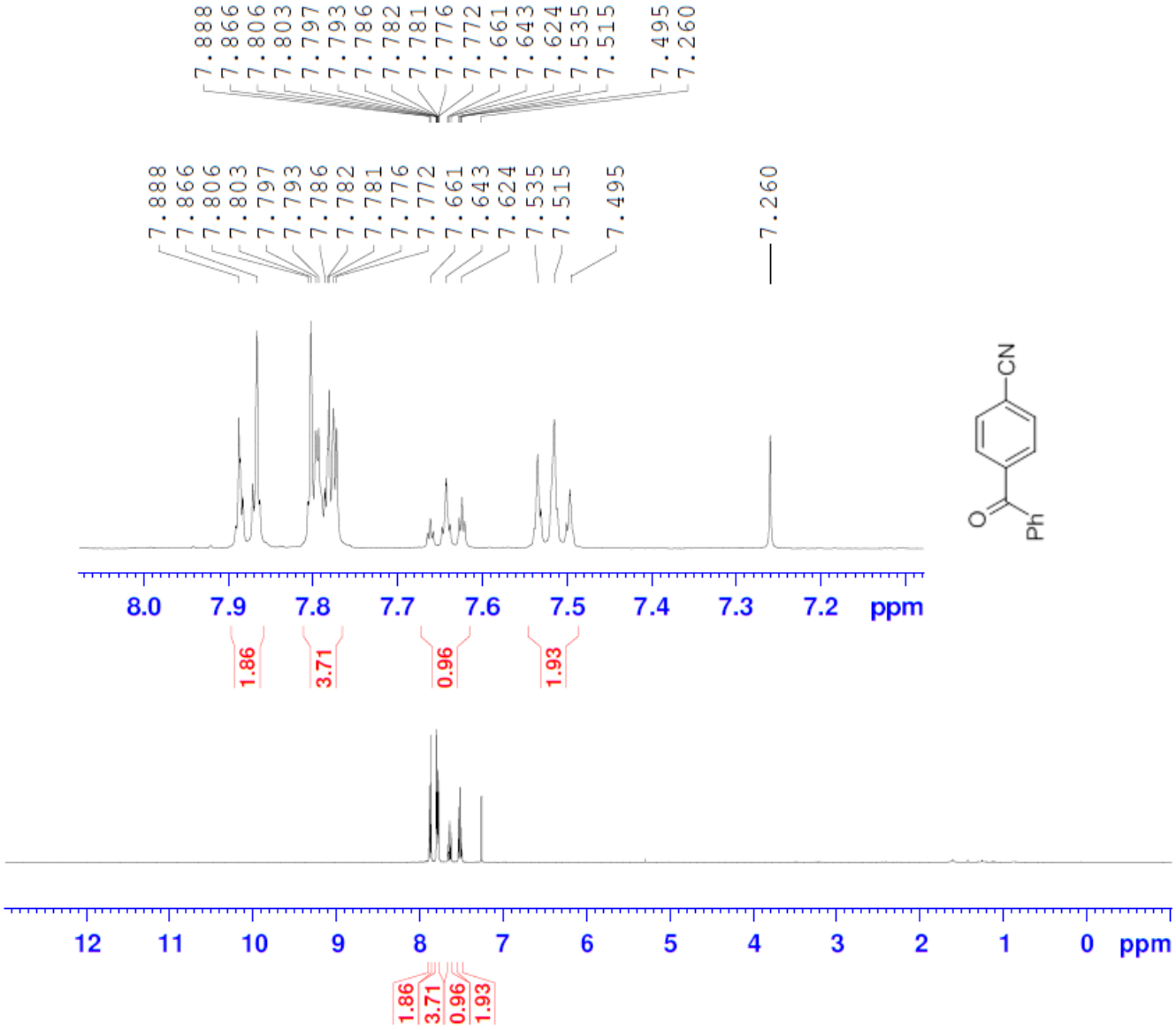
NAME	pyy099Cyan
EXPNO	1
PROCNO	1
Date_	20100330
Time	18.38
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	9
DW	89.333 usec
DE	6.50 usec
TE	295.7 K
D1	1.00000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300095 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

pyy136Cyan-H



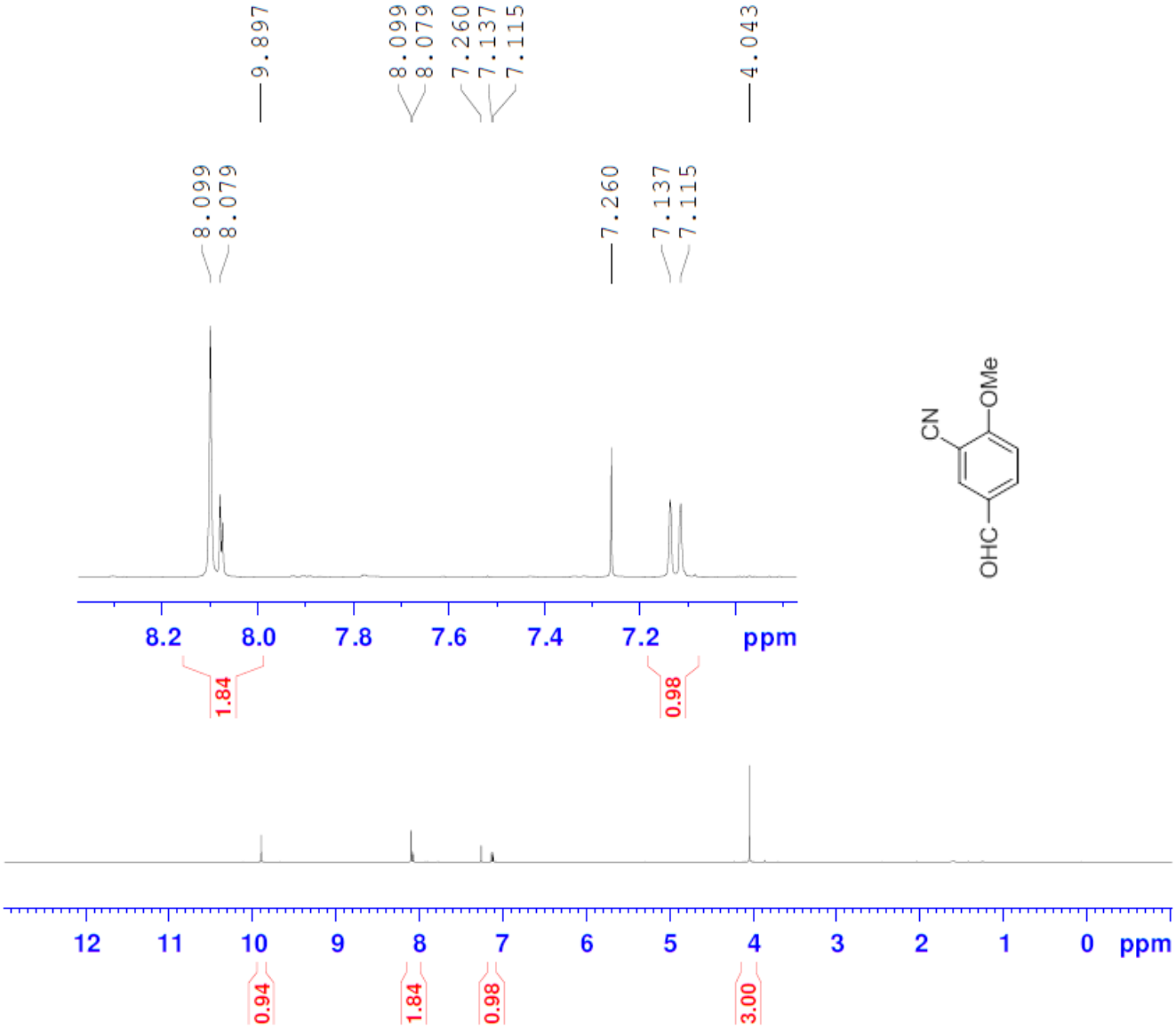
NAME	pyy136Cyan	
EXPNO	1	
PROCNO	1	
Date_	20100413	
Time	11.10	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zg30	
TD	32768	
SOLVENT	CDCl3	
NS	16	
DS	2	
SWH	5597.015	Hz
FIDRES	0.170807	Hz
AQ	2.9273248	sec
RG	45.2	
DW	89.333	usec
DE	6.50	usec
TE	296.0	K
D1	1.00000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	1H	
P1	14.70	usec
PL1	0.00	dB
PL1W	11.88122272	W
SFO1	400.1324008	MHz
SI	32768	
SF	400.1300095	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	

pyy139Cyan-H



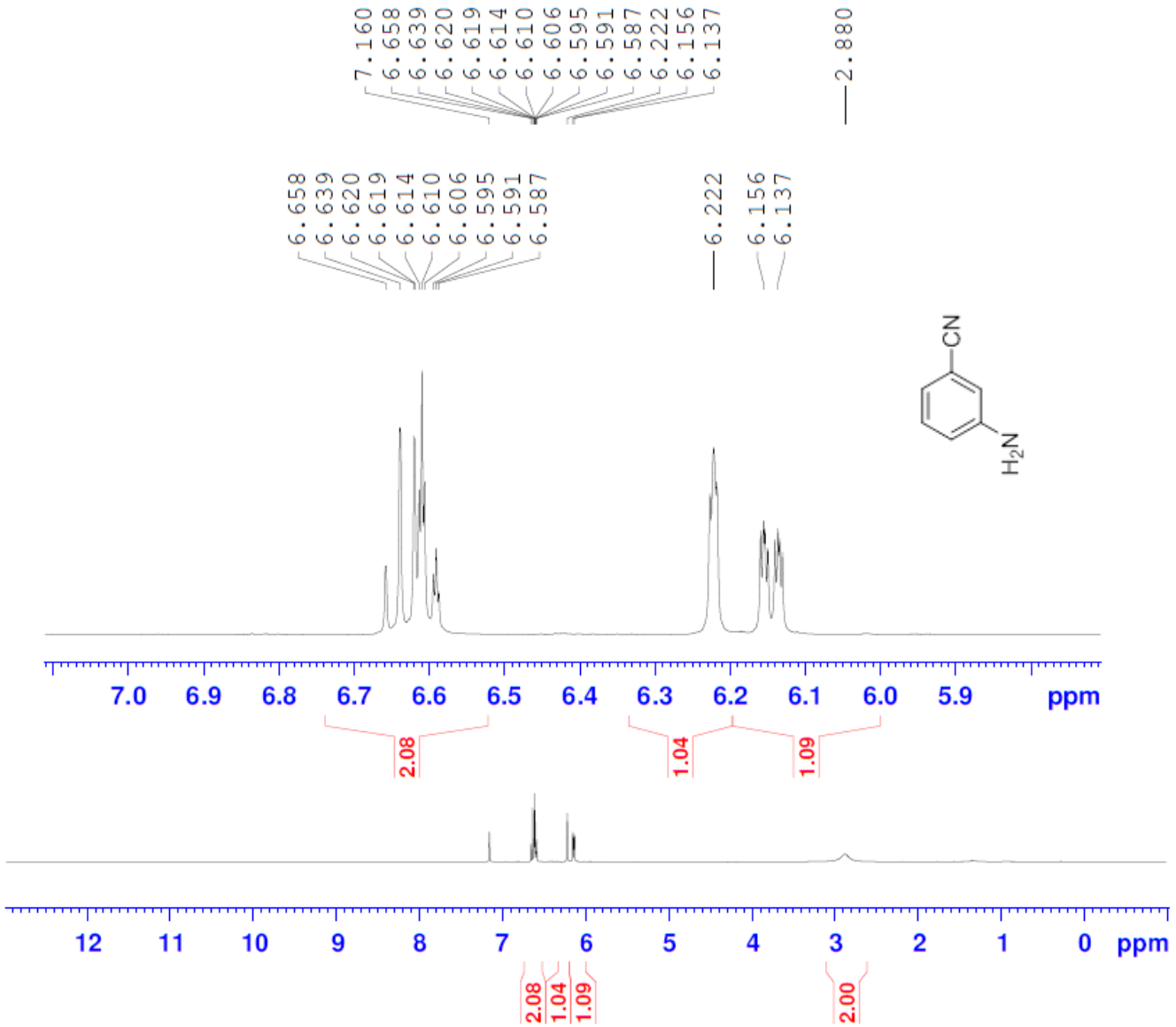
NAME	pyy139Cyan
EXPNO	1
PROCNO	1
Date_	20100412
Time	14.41
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	161
DW	89.333 usec
DE	6.50 usec
TE	296.9 K
D1	1.00000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300098 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

pyy145Cyan-H



NAME	pyy145Cyan	
EXPNO	1	
PROCNO	1	
Date_	20100410	
Time	22.11	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zg30	
TD	32768	
SOLVENT	CDCl3	
NS	16	
DS	2	
SWH	5597.015	Hz
FIDRES	0.170807	Hz
AQ	2.9273248	sec
RG	203	
DW	89.333	usec
DE	6.50	usec
TE	294.7	K
D1	1.00000000	sec
TD0	1	
========	CHANNEL f1 ========	
NUC1	1H	
P1	14.70	usec
PL1	0.00	dB
PL1W	11.88122272	W
SFO1	400.1324008	MHz
SI	32768	
SF	400.1300097	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	

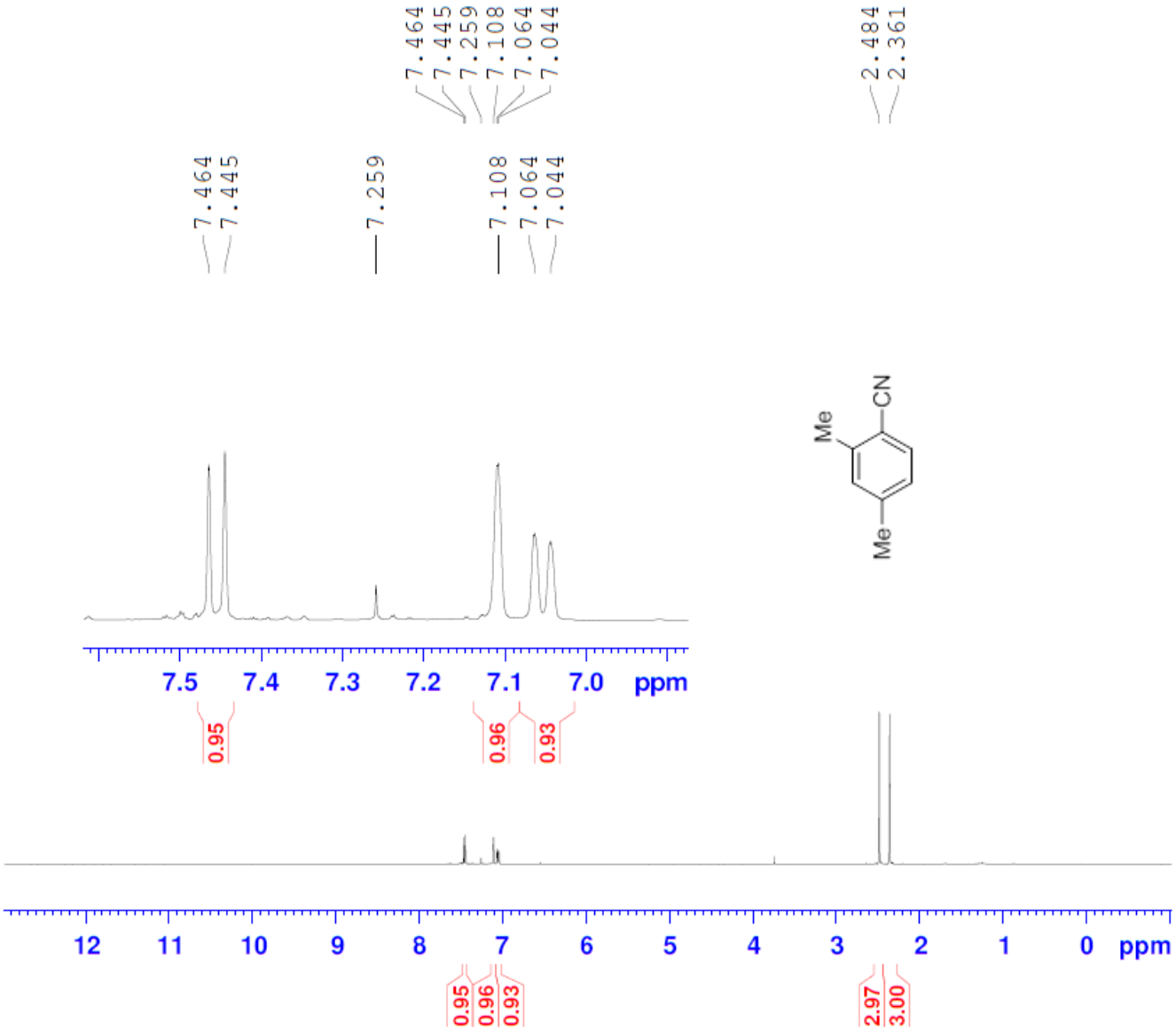
pyy142Cyan-H(Pure)



BRUKER

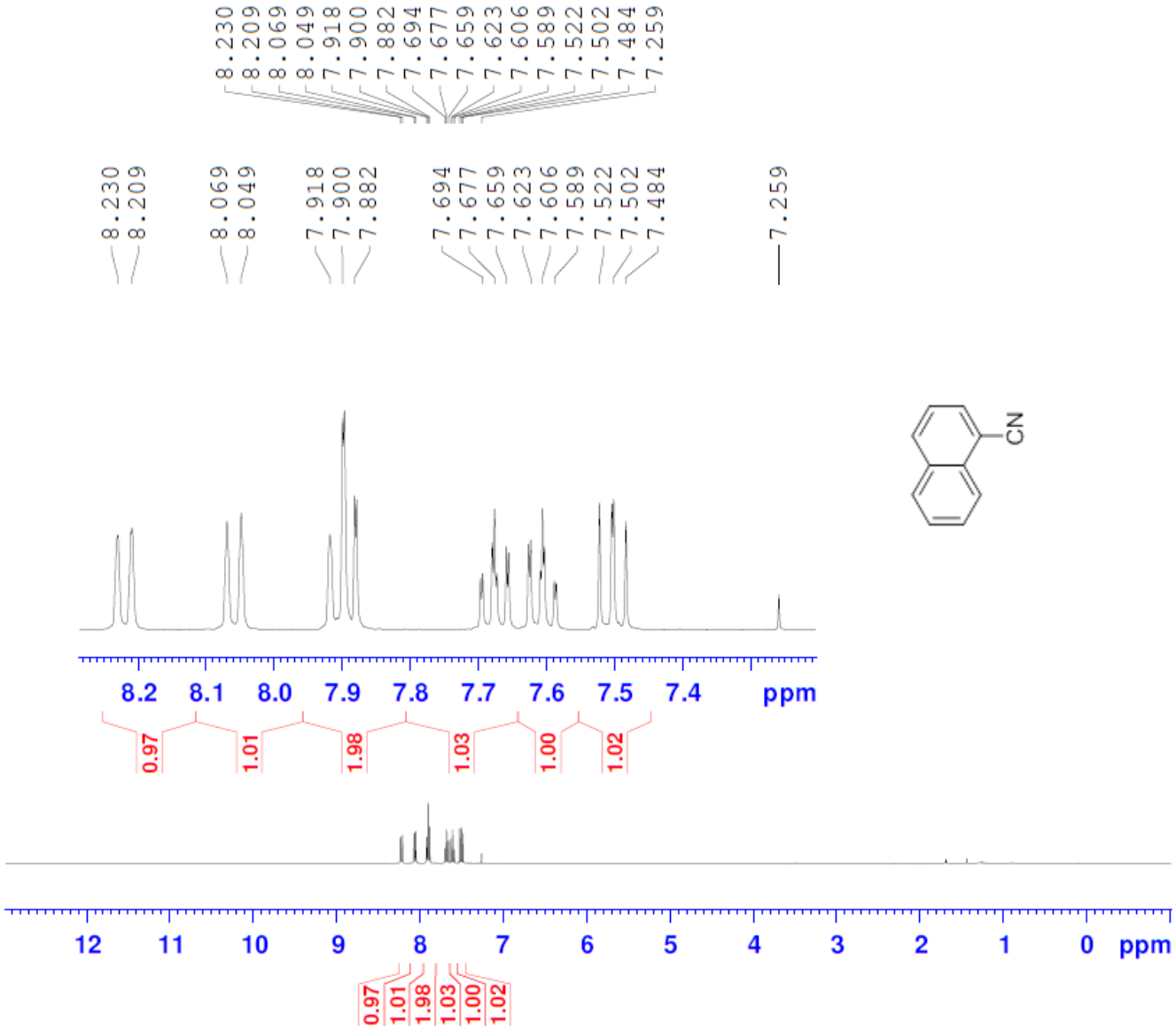
NAME	pyy142Cyan
EXPNO	7
PROCNO	1
Date_	20100420
Time	14.16
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	C6D6
NS	16
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	45.2
DW	89.333 usec
DE	6.50 usec
TE	296.0 K
D1	1.00000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1299967 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

pyy217Cyan-H



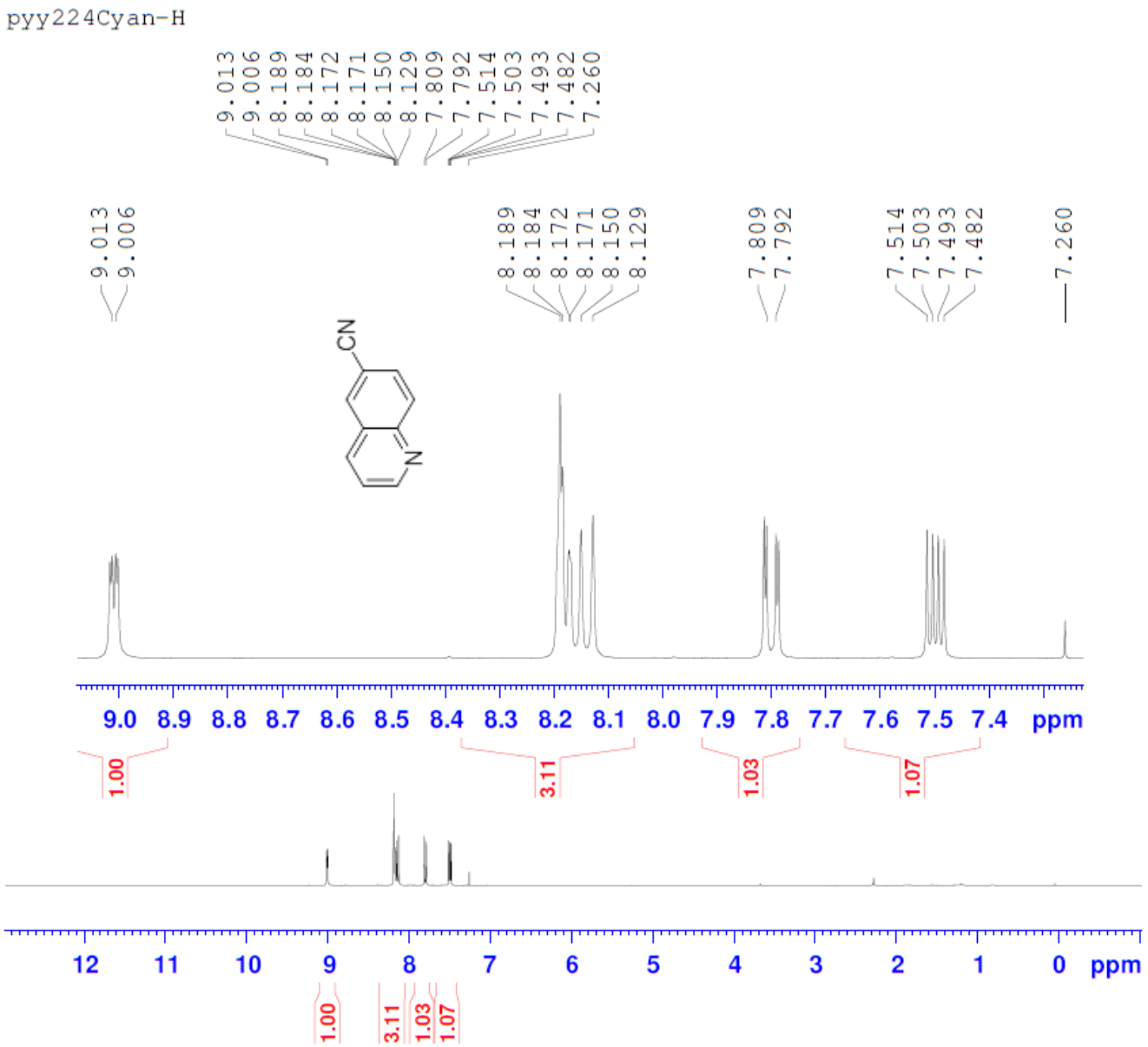
NAME	pyy217Cyan	
EXPNO	1	
PROCNO	1	
Date_	20100512	
Time	11.33	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zg30	
TD	32768	
SOLVENT	CDCl3	
NS	8	
DS	2	
SWH	5597.015	Hz
FIDRES	0.170807	Hz
AQ	2.9273248	sec
RG	45.2	
DW	89.333	usec
DE	6.50	usec
TE	296.0	K
D1	1.00000000	sec
TD0	1	
========	CHANNEL f1 ========	
NUC1	1H	
P1	14.70	usec
PL1	0.00	dB
PL1W	11.88122272	W
SFO1	400.1324008	MHz
SI	32768	
SF	400.1300103	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	

pyy137Cyan-H



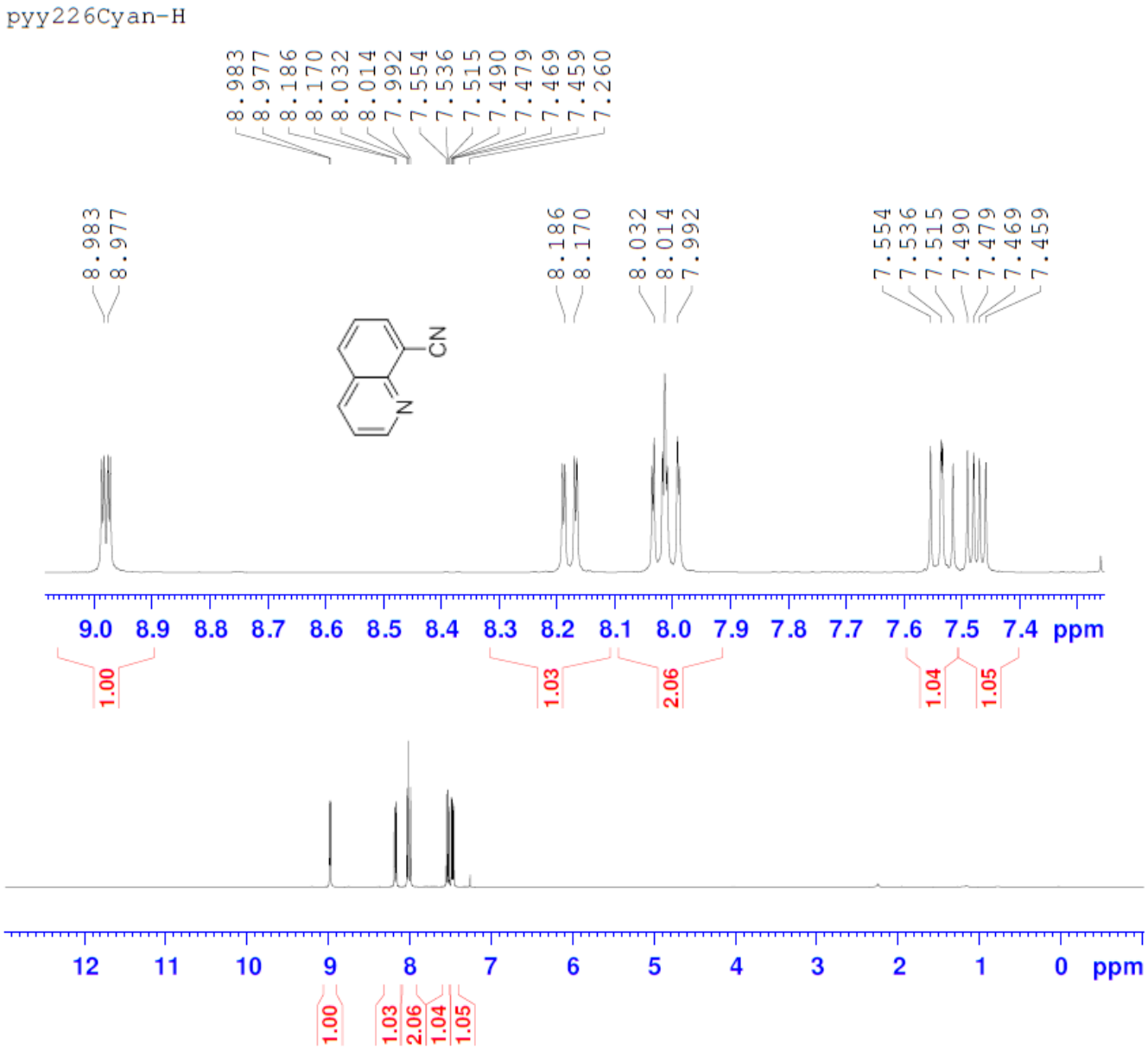
NAME	pyy137Cyan	
EXPNO	1	
PROCNO	1	
Date_	20100413	
Time	11.20	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zg30	
TD	32768	
SOLVENT	CDCl3	
NS	16	
DS	2	
SWH	5597.015	Hz
FIDRES	0.170807	Hz
AQ	2.9273248	sec
RG	45.2	
DW	89.333	usec
DE	6.50	usec
TE	296.1	K
D1	1.00000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	1H	
P1	14.70	usec
PL1	0.00	dB
PL1W	11.88122272	W
SFO1	400.1324008	MHz
SI	32768	
SF	400.1300101	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	

pyy224Cyan-H



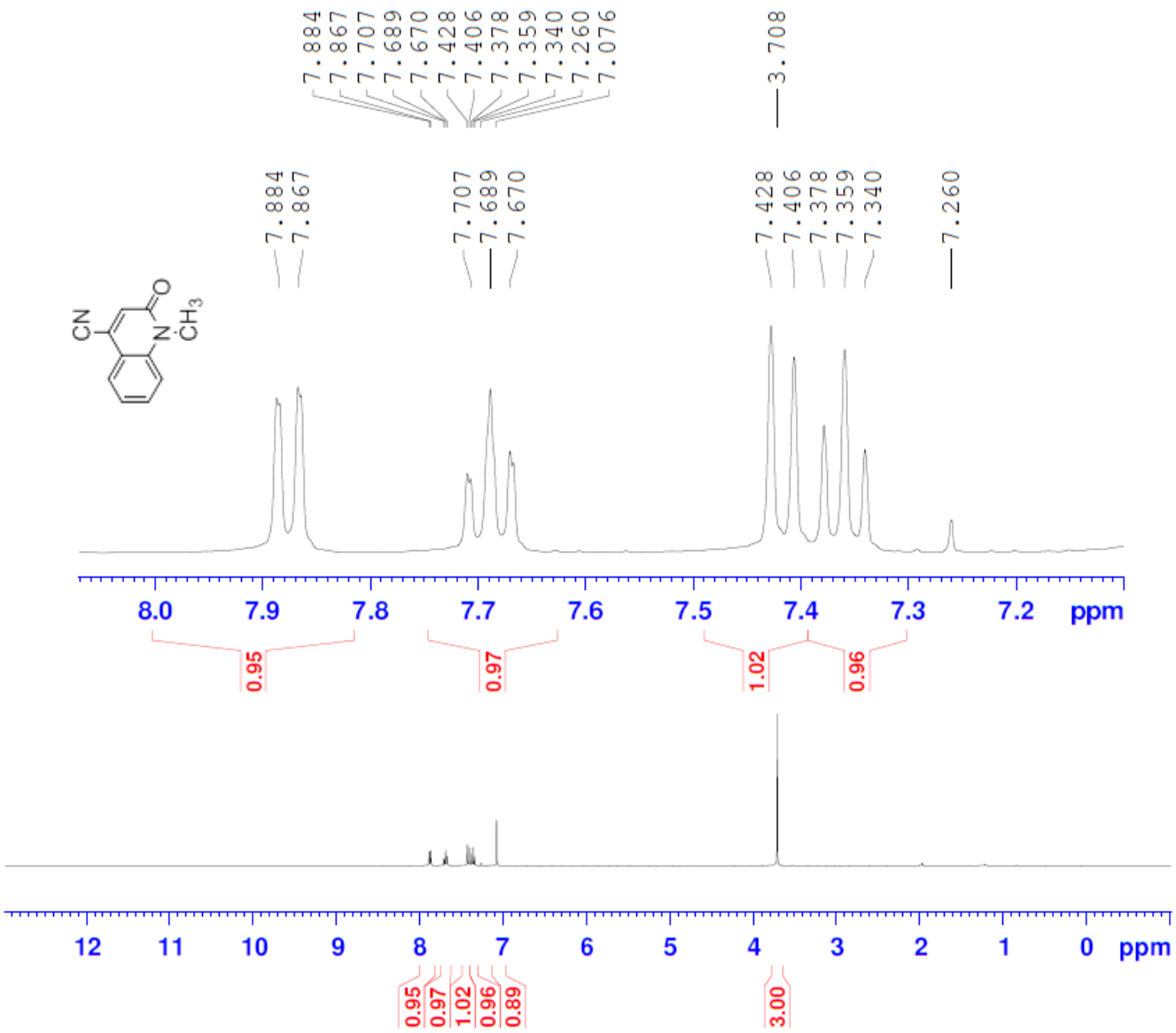
NAME	pyy224Cyan
EXPNO	1
PROCNO	1
Date_	20100513
Time	19.50
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	8
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	45.2
DW	89.333 usec
DE	6.50 usec
TE	296.5 K
D1	1.00000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300097 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

pyy226Cyan-H



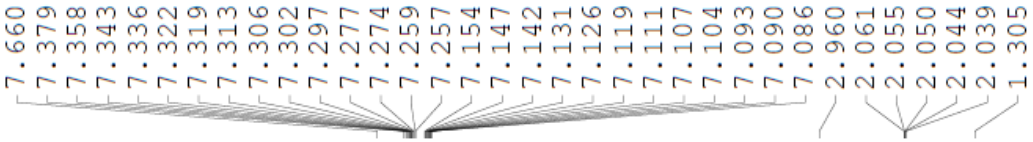
NAME	pyy226Cyan	
EXPNO	1	
PROCNO	1	
Date_	20100517	
Time	11.42	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zg30	
TD	32768	
SOLVENT	CDCl3	
NS	8	
DS	2	
SWH	5597.015	Hz
FIDRES	0.170807	Hz
AQ	2.9273248	sec
RG	45.2	
DW	89.333	usec
DE	6.50	usec
TE	295.8	K
D1	1.00000000	sec
TD0	1	
========	CHANNEL f1 ========	
NUC1	1H	
P1	14.70	usec
PL1	0.00	dB
PL1W	11.88122272	W
SFO1	400.1324008	MHz
SI	32768	
SF	400.1300097	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	

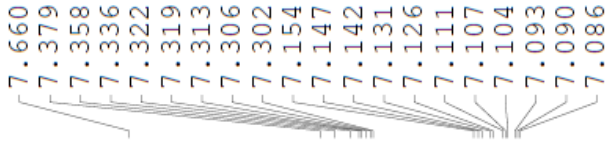
pyy235Cyan-H

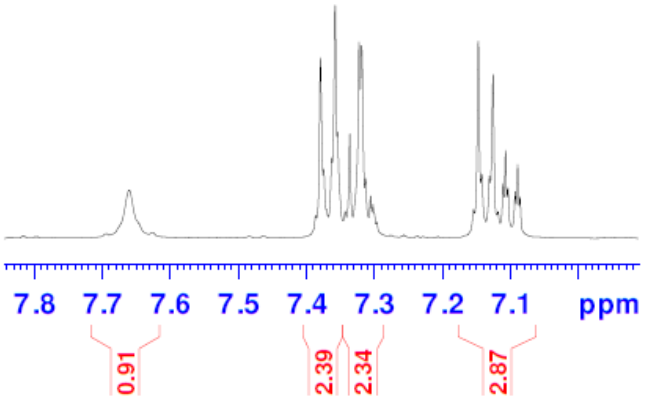


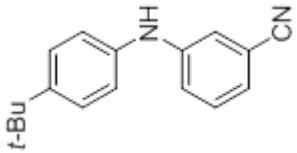
NAME	pyy235Cyan	
EXPNO	1	
PROCNO	1	
Date_	20100525	
Time	11.57	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zg30	
TD	32768	
SOLVENT	CDCl3	
NS	8	
DS	2	
SWH	5597.015	Hz
FIDRES	0.170807	Hz
AQ	2.9273248	sec
RG	45.2	
DW	89.333	usec
DE	6.50	usec
TE	297.3	K
D1	1.00000000	sec
TD0	1	
========	CHANNEL f1 ========	
NUC1	1H	
P1	14.70	usec
PL1	0.00	dB
PL1W	11.88122272	W
SFO1	400.1324008	MHz
SI	32768	
SF	400.1300094	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	

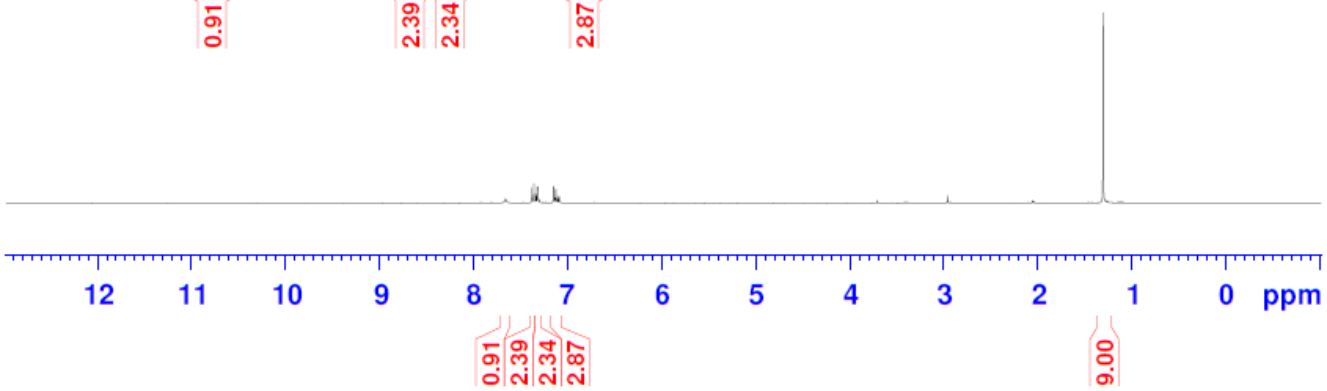
pyy400Cyan-H





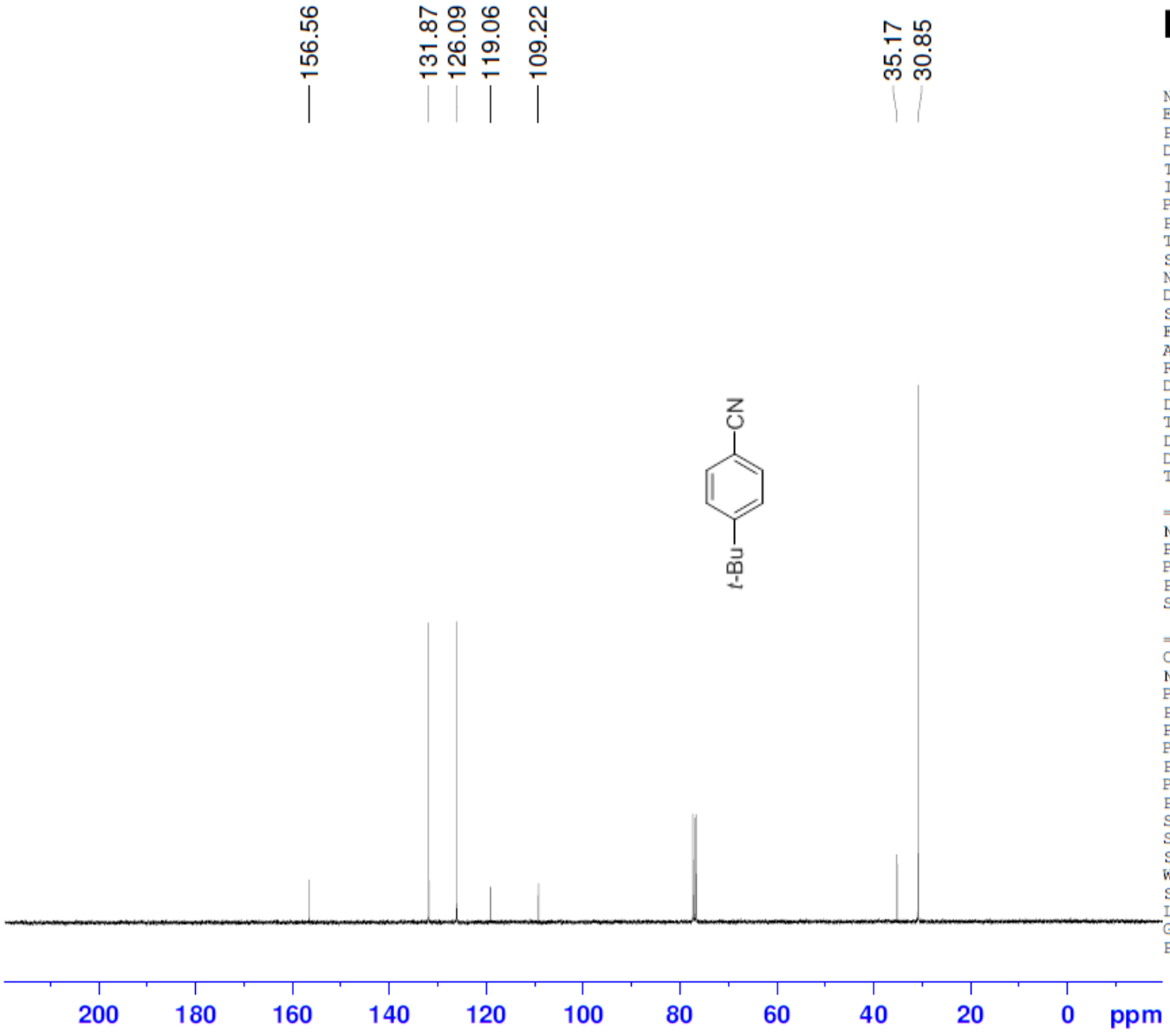






NAME	pyy400Cyan
EXPNO	1
PROCNO	1
Date_	20100806
Time	12.02
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	Acetone
NS	8
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	22.6
DW	89.333 usec
DE	6.50 usec
TE	297.8 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300069 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

pyy163Cyan-C

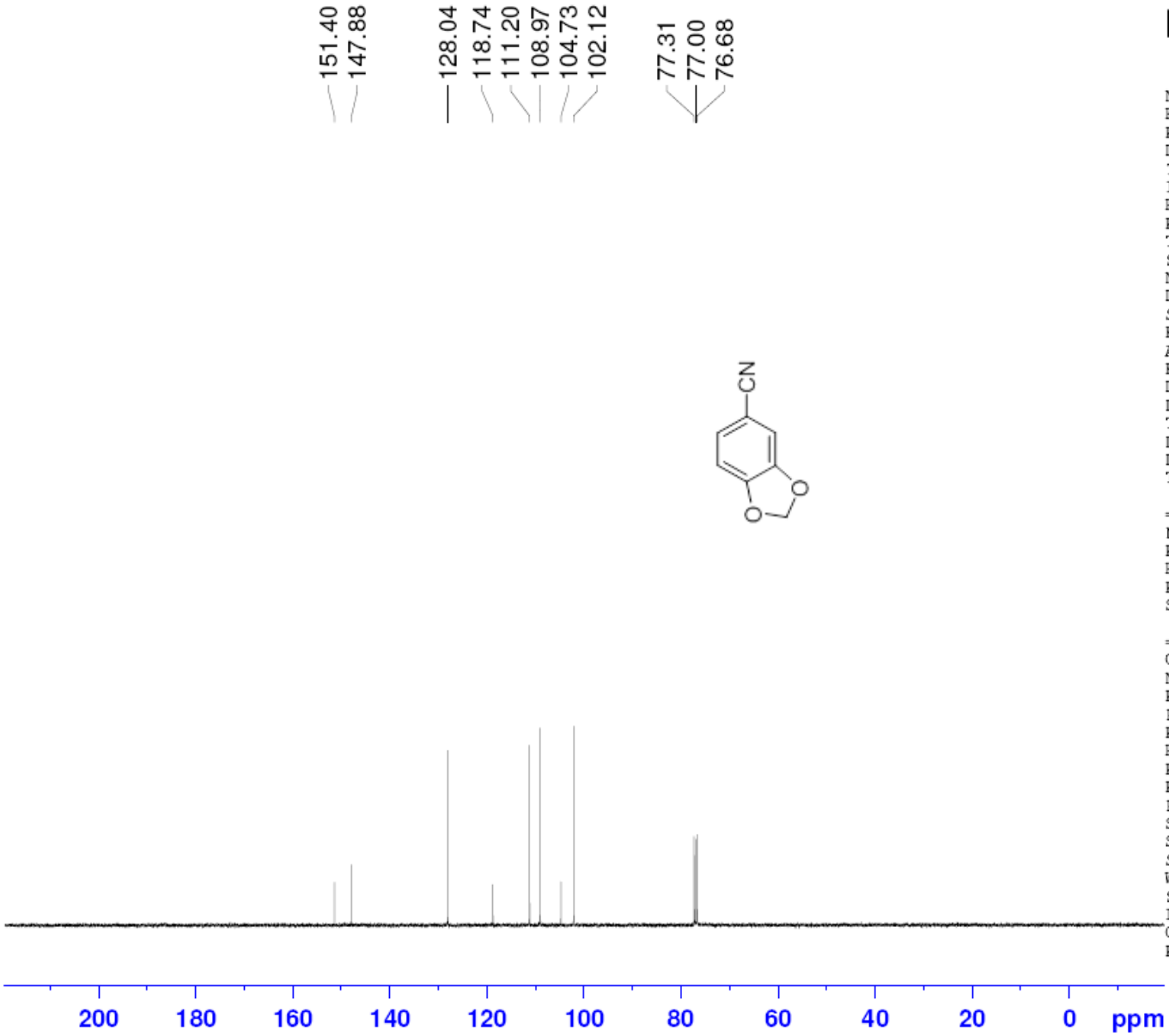



```
NAME                pyy163Cyan
EXPNO                        2
PROCNO                       1
Date_                 20100420
Time                     15.02
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                          32
DS                           2
SWH                24038.461 Hz
FIDRES              0.366798 Hz
AQ                  1.3631988 sec
RG                         203
DW                    20.800 usec
DE                     6.50 usec
TE                     296.3 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                          1

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

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                        1H
PCPD2                 80.00 usec
PL2                    0.00 dB
PL12                  15.00 dB
PL13                  15.00 dB
PL2W            11.88122272 W
PL12W            0.37571725 W
PL13W            0.37571725 W
SFO2           400.1316005 MHz
SI                      32768
SF             100.6127782 MHz
WDW                        EM
SSB                         0
LB                    1.00 Hz
GB                          0
PC                     1.40
```

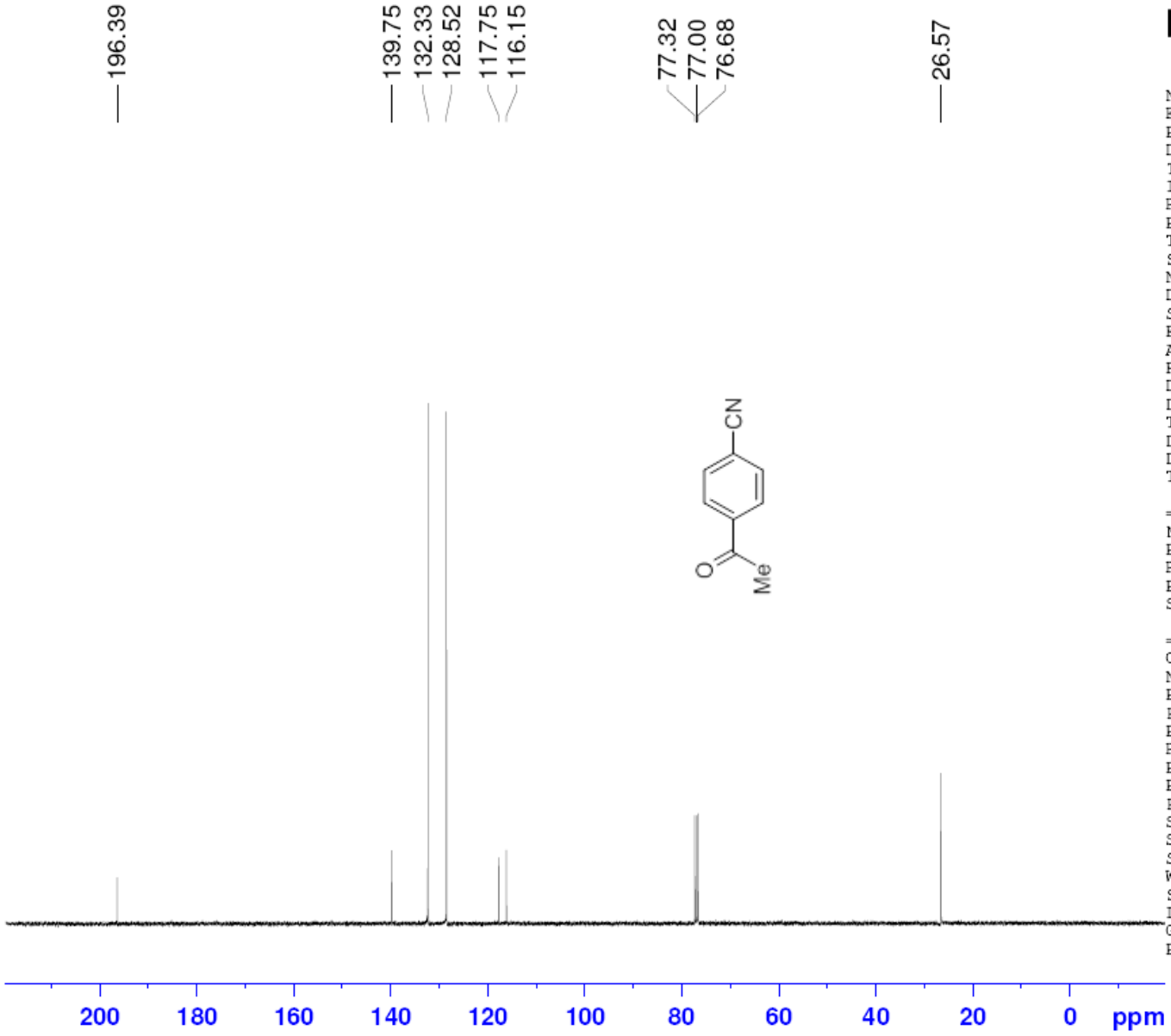
pyy168Cyan-C



BRUKER

NAME	pyy168Cyan	
EXPNO	2	
PROCNO	1	
Date_	20100420	
Time	12.12	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	24	
DS	2	
SWH	24038.461	Hz
FIDRES	0.366798	Hz
AQ	1.3631988	sec
RG	203	
DW	20.800	usec
DE	6.50	usec
TE	296.1	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	9.50	usec
PL1	-2.00	dB
PL1W	58.52175522	W
SFO1	100.6228298	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	80.00	usec
PL2	0.00	dB
PL12	15.00	dB
PL13	15.00	dB
PL2W	11.88122272	W
PL12W	0.37571725	W
PL13W	0.37571725	W
SFO2	400.1316005	MHz
SI	32768	
SF	100.6127848	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

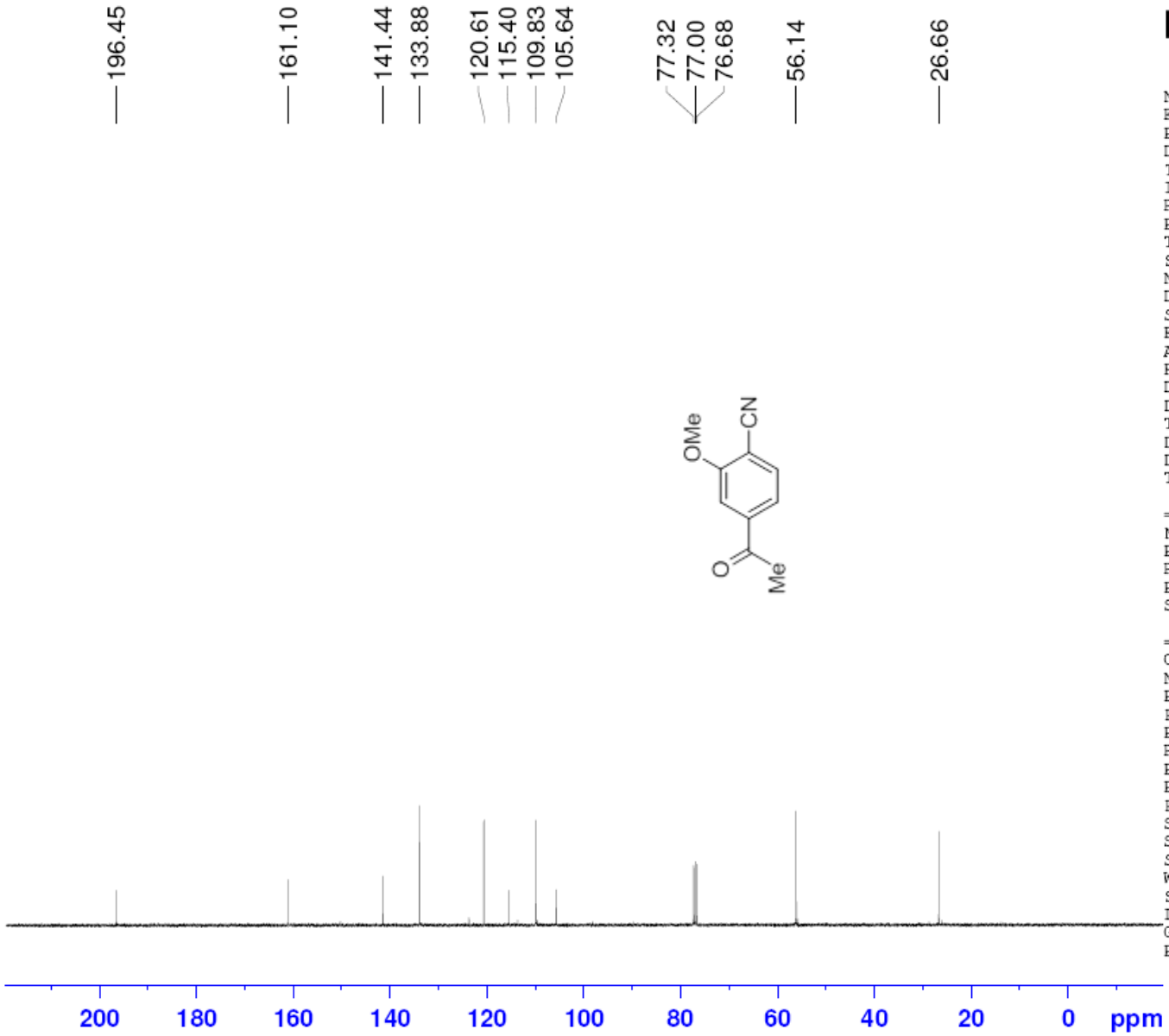
pyy174Cyan-C



BRUKER

NAME	pyy174Cyan
EXPNO	2
PROCNO	1
Date_	20100421
Time	14.54
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	203
DW	20.800 usec
DE	6.50 usec
TE	298.8 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	15.00 dB
PL2W	11.88122272 W
PL12W	0.37571725 W
PL13W	0.37571725 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127859 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

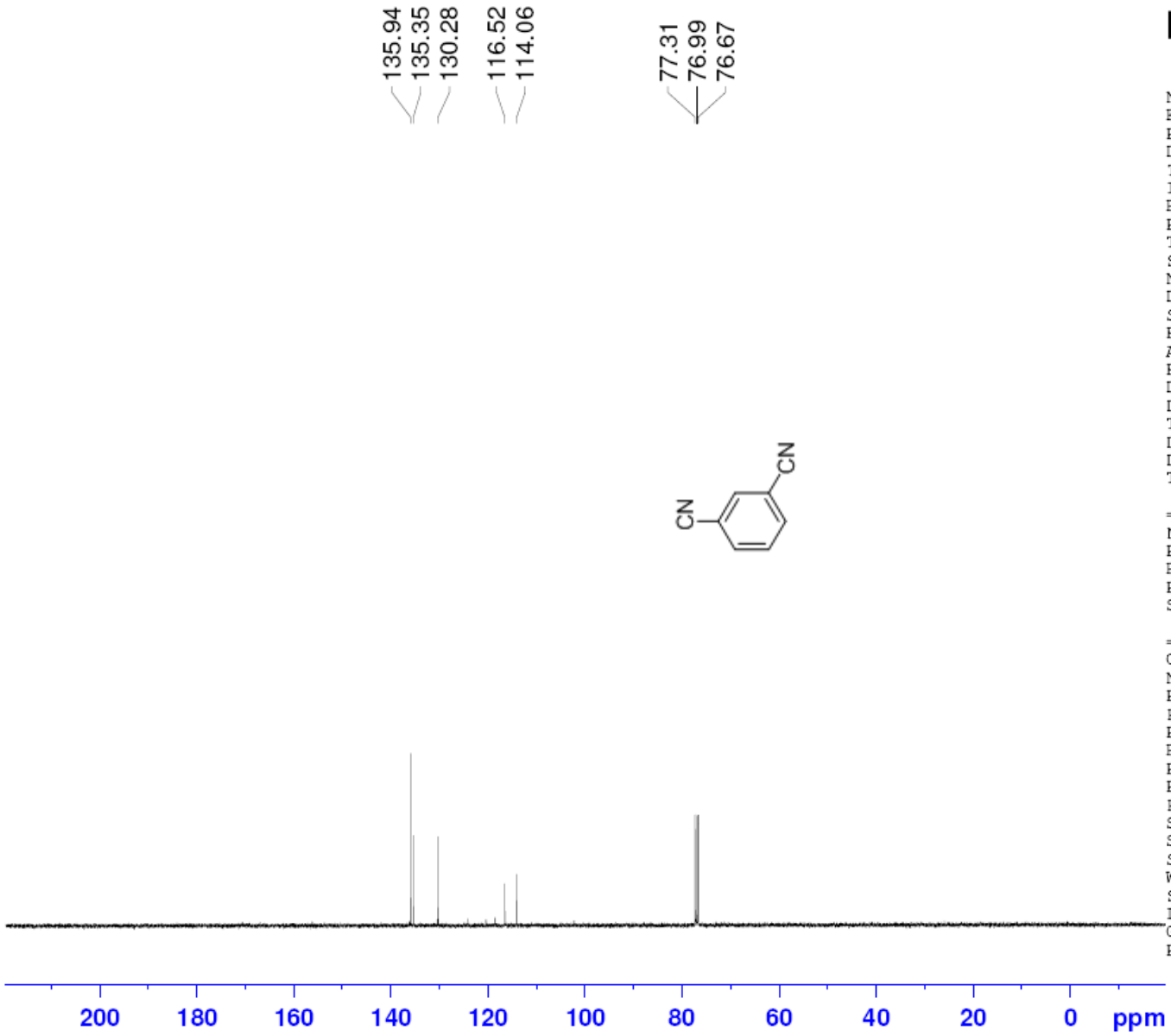
Standard 13C



BRUKER

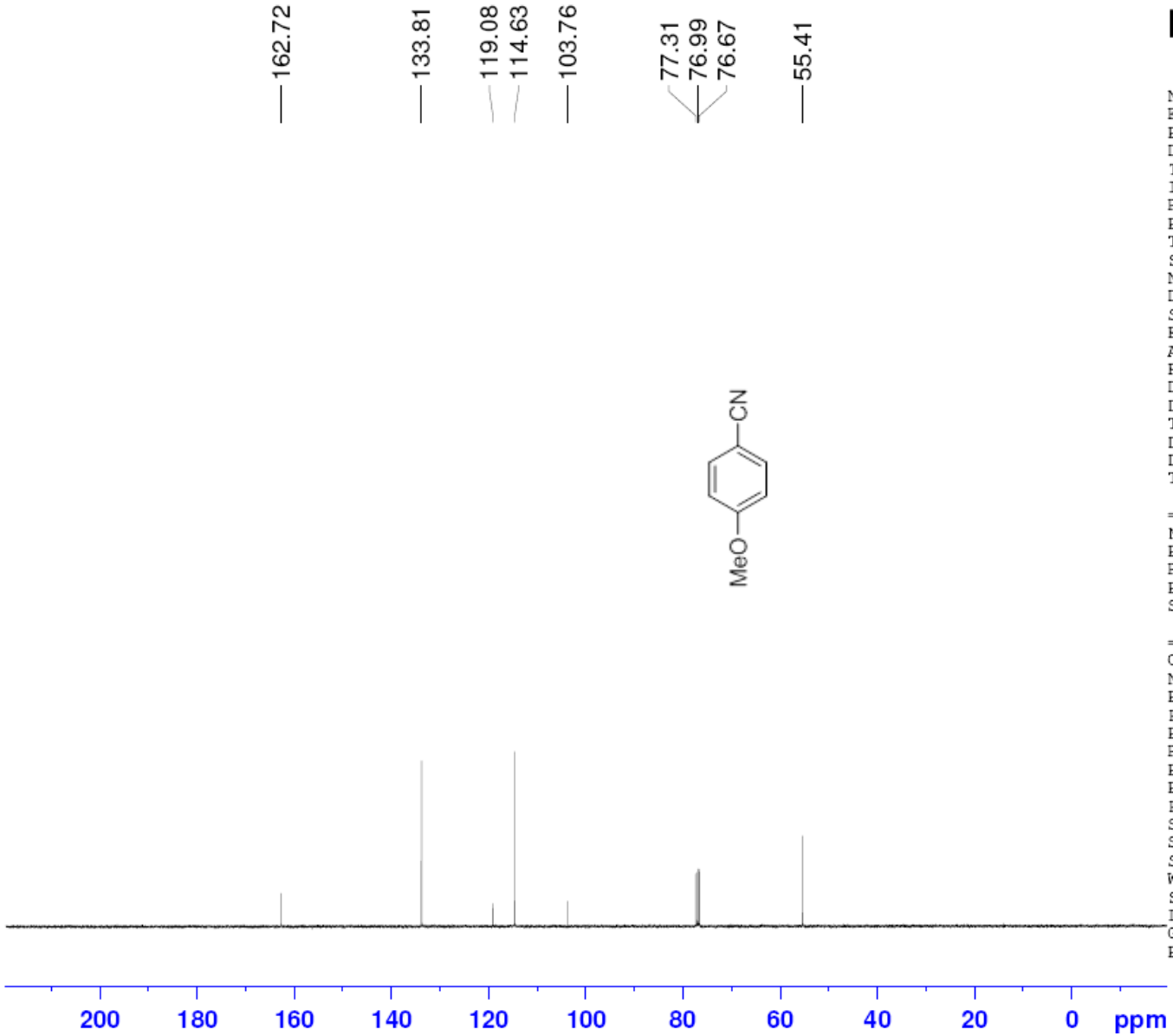
NAME	pyy175Cyan	
EXPNO	2	
PROCNO	1	
Date_	20100421	
Time	14.01	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	17	
DS	2	
SWH	24038.461	Hz
FIDRES	0.366798	Hz
AQ	1.3631988	sec
RG	203	
DW	20.800	usec
DE	6.50	usec
TE	298.5	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	9.50	usec
PL1	-2.00	dB
PL1W	58.52175522	W
SFO1	100.6228298	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	80.00	usec
PL2	0.00	dB
PL12	15.00	dB
PL13	15.00	dB
PL2W	11.88122272	W
PL12W	0.37571725	W
PL13W	0.37571725	W
SFO2	400.1316005	MHz
SI	32768	
SF	100.6127879	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

pyy179Cyan-C



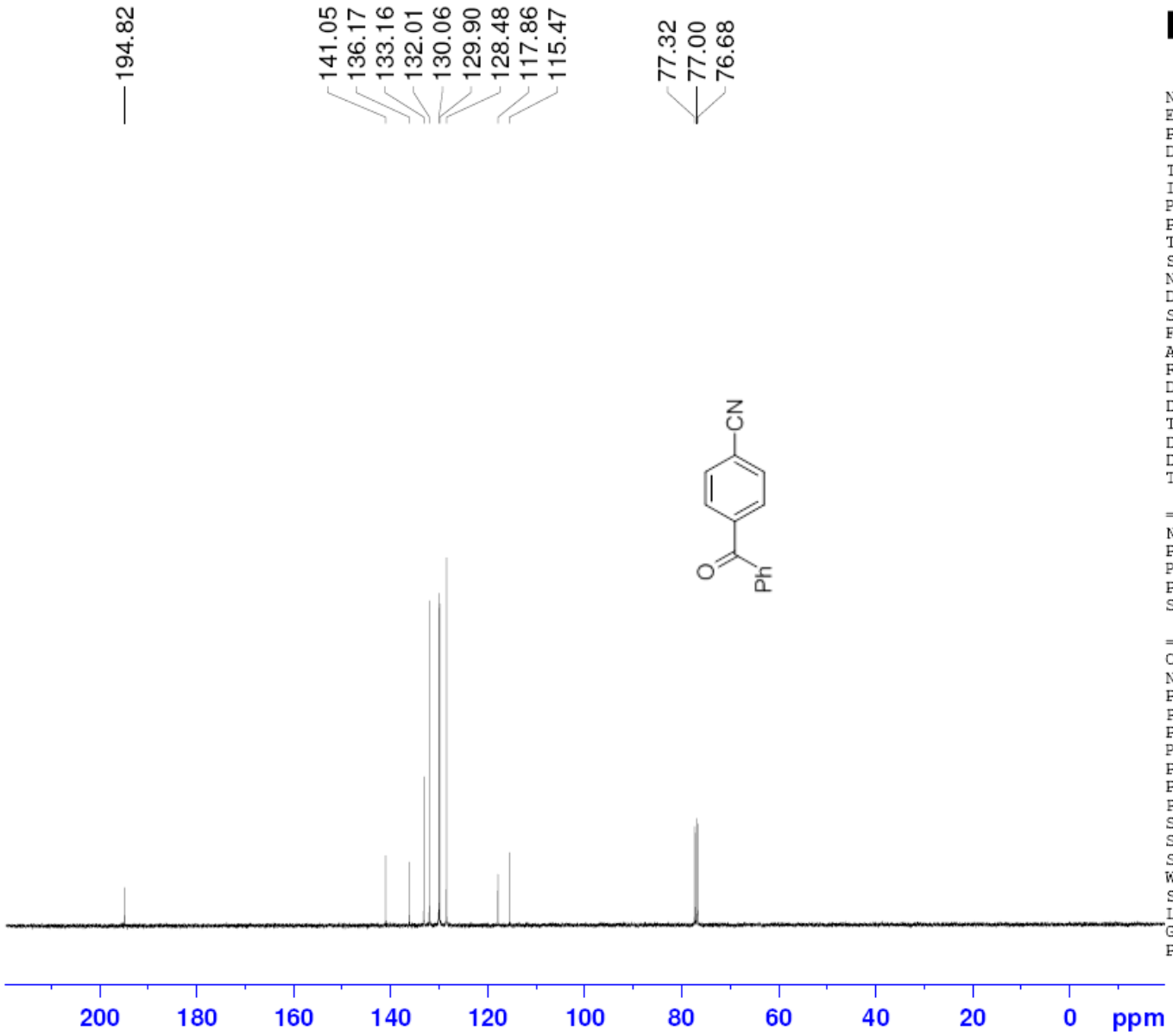
NAME	pyy179Cyan	
EXPNO	2	
PROCNO	1	
Date_	20100421	
Time	15.08	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	32	
DS	2	
SWH	24038.461	Hz
FIDRES	0.366798	Hz
AQ	1.3631988	sec
RG	203	
DW	20.800	usec
DE	6.50	usec
TE	298.0	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	9.50	usec
PL1	-2.00	dB
PL1W	58.52175522	W
SFO1	100.6228298	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	80.00	usec
PL2	0.00	dB
PL12	15.00	dB
PL13	15.00	dB
PL2W	11.88122272	W
PL12W	0.37571725	W
PL13W	0.37571725	W
SFO2	400.1316005	MHz
SI	32768	
SF	100.6127785	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

Standard 13C



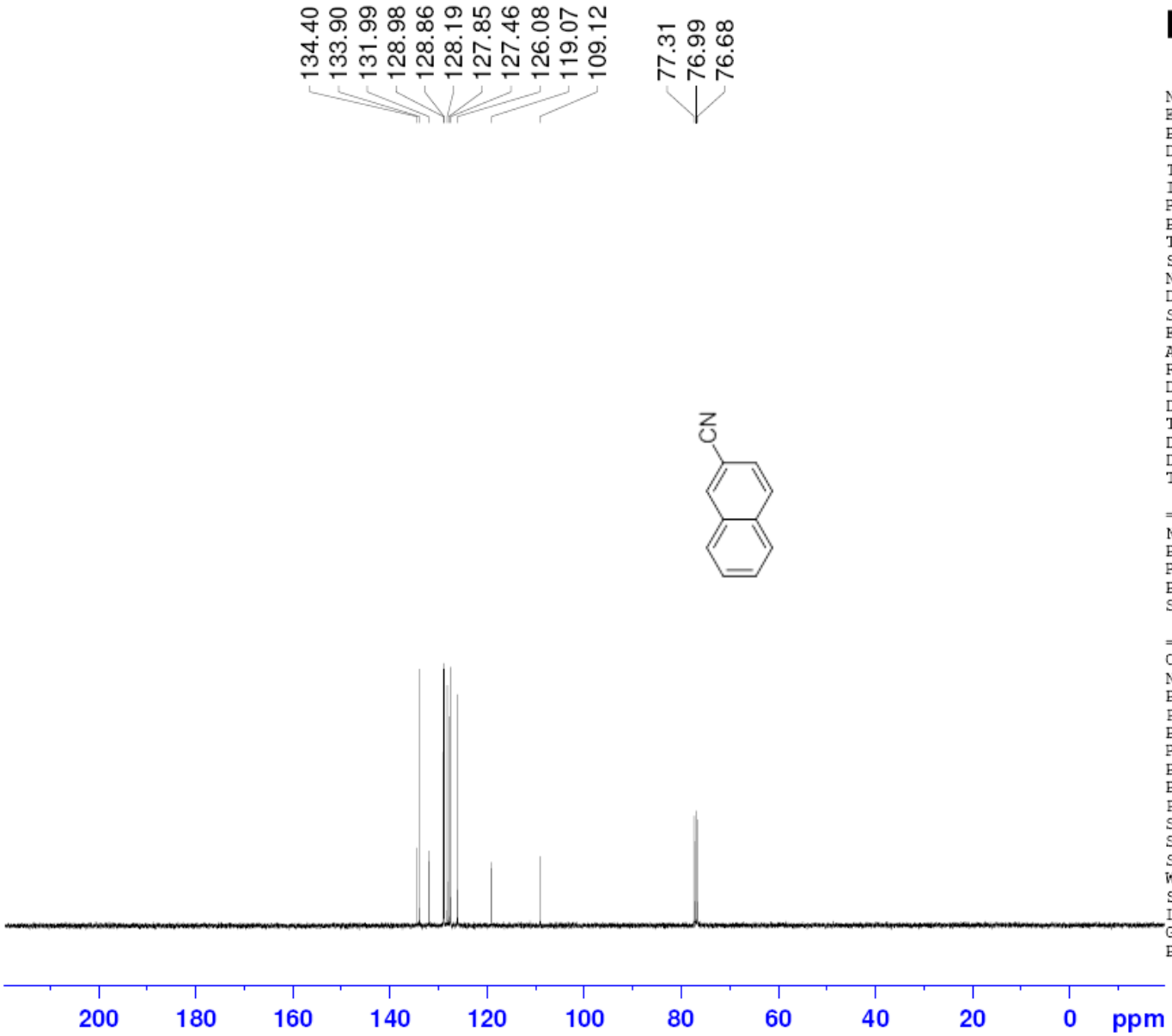
NAME	pyy196Cyan	
EXPNO	2	
PROCNO	1	
Date_	20100504	
Time	18.04	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	13	
DS	2	
SWH	24038.461	Hz
FIDRES	0.366798	Hz
AQ	1.3631988	sec
RG	203	
DW	20.800	usec
DE	6.50	usec
TE	297.9	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	9.50	usec
PL1	-2.00	dB
PL1W	58.52175522	W
SFO1	100.6228298	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	80.00	usec
PL2	0.00	dB
PL12	15.00	dB
PL13	15.00	dB
PL2W	11.88122272	W
PL12W	0.37571725	W
PL13W	0.37571725	W
SFO2	400.1316005	MHz
SI	32768	
SF	100.6127834	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

Standard 13C



NAME	pyy207Cyan	
EXPNO	4	
PROCNO	1	
Date_	20100507	
Time	17.44	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	32	
DS	2	
SWH	24038.461	Hz
FIDRES	0.366798	Hz
AQ	1.3631988	sec
RG	203	
DW	20.800	usec
DE	6.50	usec
TE	297.9	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	100.6127855	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

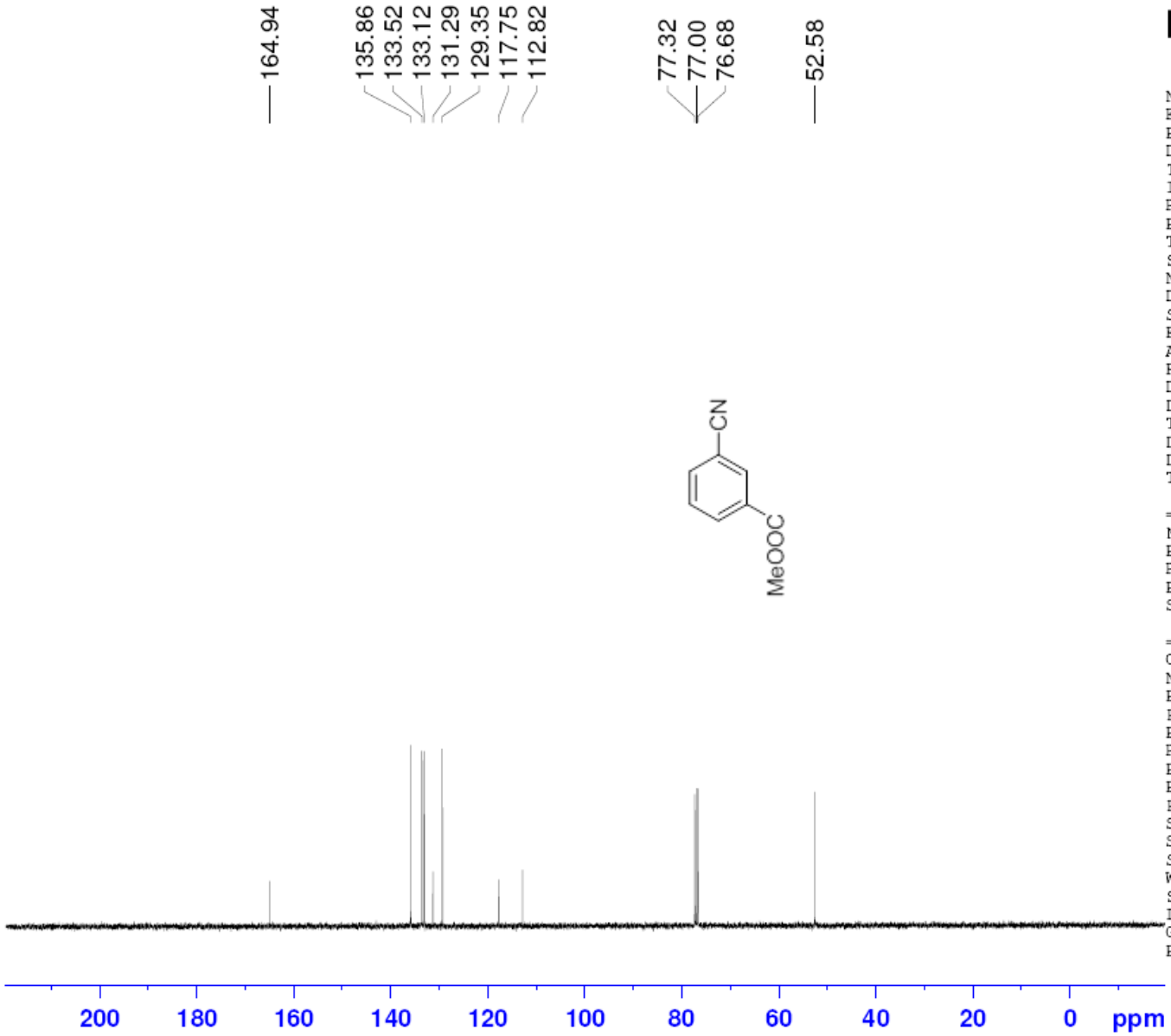
pyy213Cyan-C



BRUKER

NAME	pyy213Cyan
EXPNO	2
PROCNO	1
Date_	20100513
Time	19.44
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	181
DW	20.800 usec
DE	6.50 usec
TE	296.8 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	15.00 dB
PL2W	11.88122272 W
PL12W	0.37571725 W
PL13W	0.37571725 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127904 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

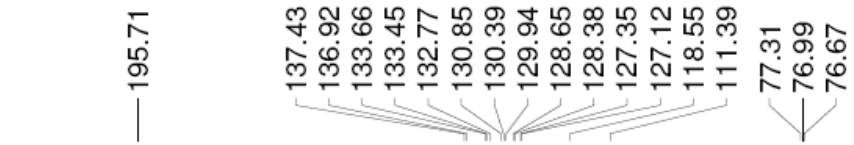
pyy214Cyan-C

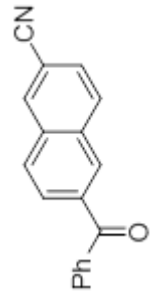


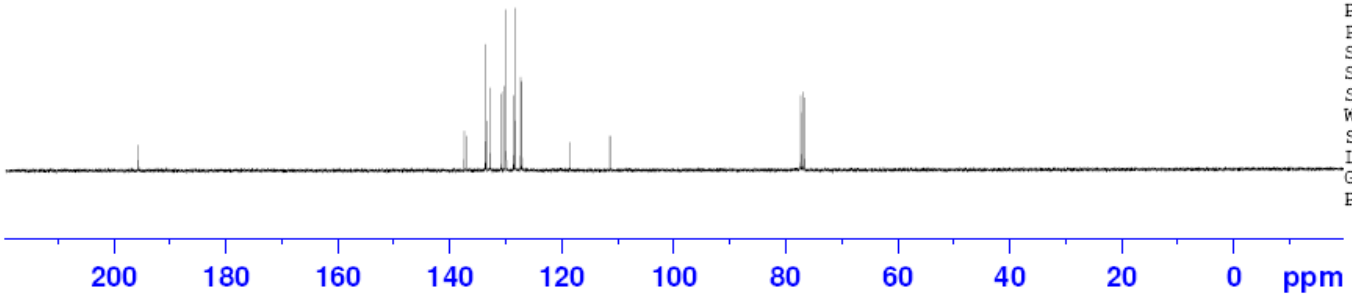
BRUKER

NAME	pyy214Cyan
EXPNO	2
PROCNO	1
Date_	20100512
Time	11.15
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	296.1 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	15.00 dB
PL2W	11.88122272 W
PL12W	0.37571725 W
PL13W	0.37571725 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127801 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

pyy363Cyan-C

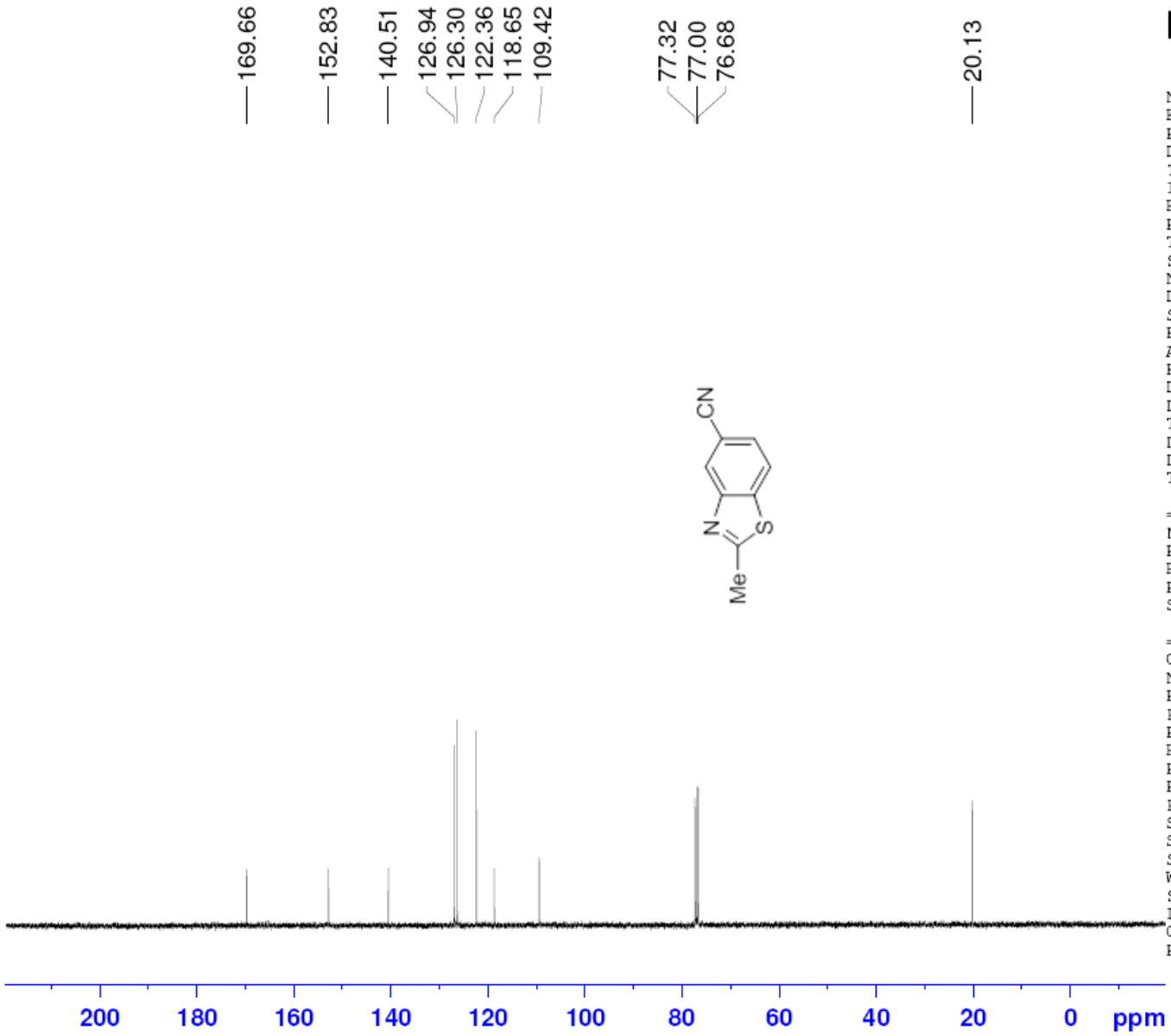






NAME	pyy363Cyan
EXPNO	2
PROCNO	1
Date_	20100708
Time	12.09
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	299.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL 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	100.6127877 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

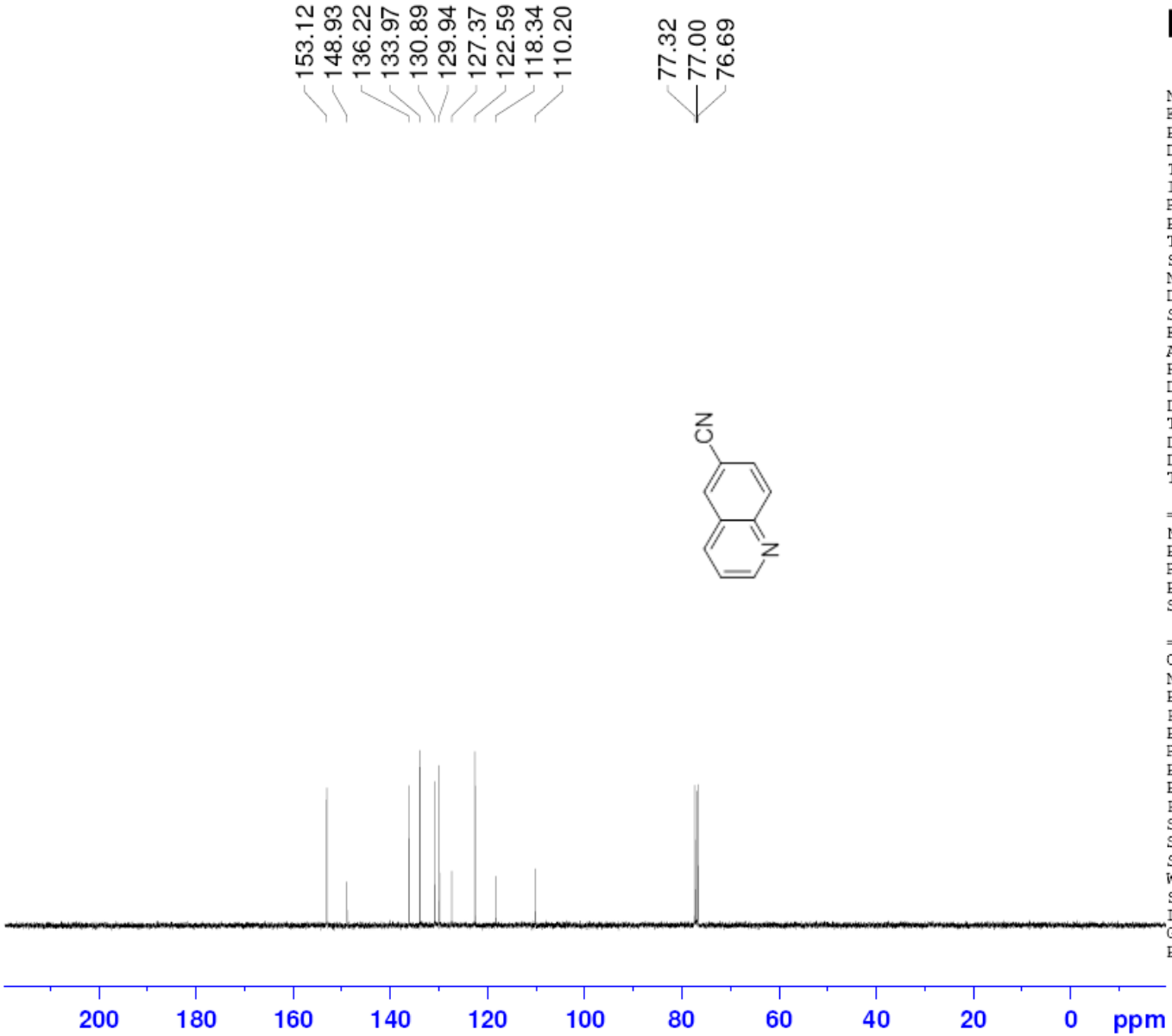
pyy230Cyan-C



BRUKER

NAME	pyy231Cyan	
EXPNO	2	
PROCNO	1	
Date_	20100517	
Time	12.20	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	16	
DS	2	
SWH	24038.461	Hz
FIDRES	0.366798	Hz
AQ	1.3631988	sec
RG	203	
DW	20.800	usec
DE	6.50	usec
TE	296.0	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	9.50	usec
PL1	-2.00	dB
PL1W	58.52175522	W
SFO1	100.6228298	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	80.00	usec
PL2	0.00	dB
PL12	15.00	dB
PL13	15.00	dB
PL2W	11.88122272	W
PL12W	0.37571725	W
PL13W	0.37571725	W
SFO2	400.1316005	MHz
SI	32768	
SF	100.6127847	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

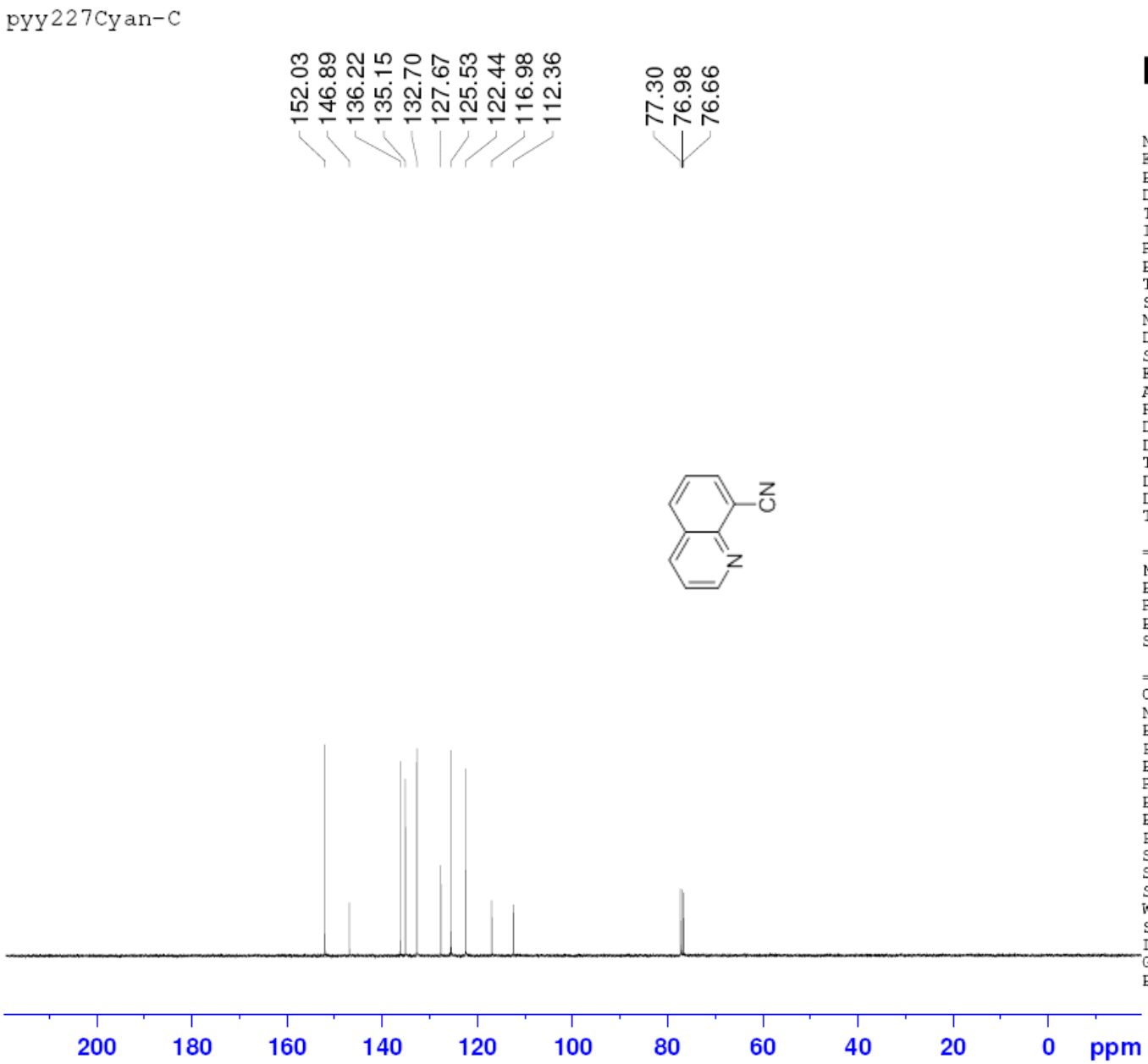
pyy225Cyan-C



BRUKER

NAME	pyy225Cyan	
EXPNO	2	
PROCNO	1	
Date_	20100513	
Time	20.20	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	16	
DS	2	
SWH	24038.461	Hz
FIDRES	0.366798	Hz
AQ	1.3631988	sec
RG	203	
DW	20.800	usec
DE	6.50	usec
TE	297.1	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	9.50	usec
PL1	-2.00	dB
PL1W	58.52175522	W
SFO1	100.6228298	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	80.00	usec
PL2	0.00	dB
PL12	15.00	dB
PL13	15.00	dB
PL2W	11.88122272	W
PL12W	0.37571725	W
PL13W	0.37571725	W
SFO2	400.1316005	MHz
SI	32768	
SF	100.6127831	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

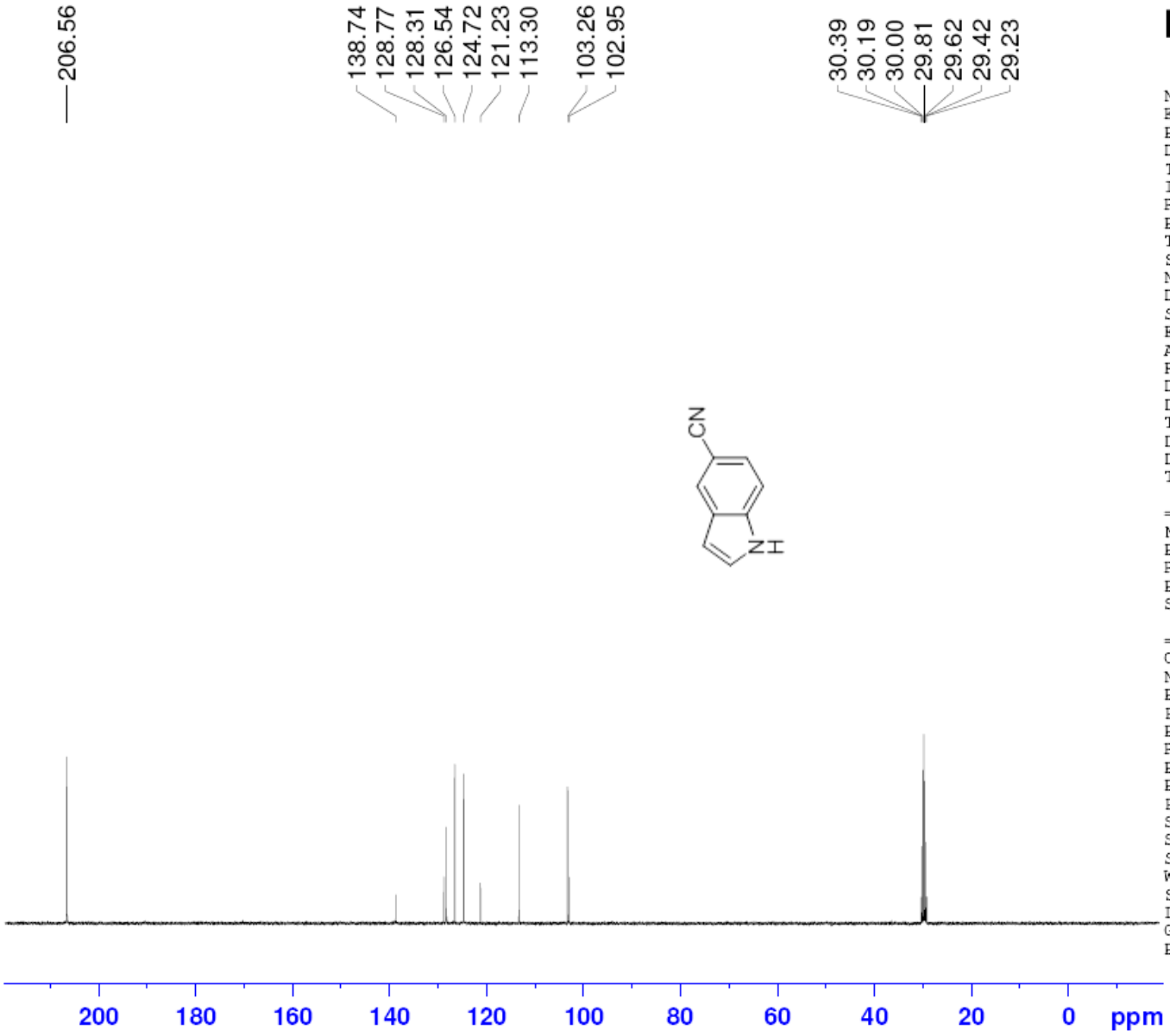
pyy227Cyan-C



BRUKER

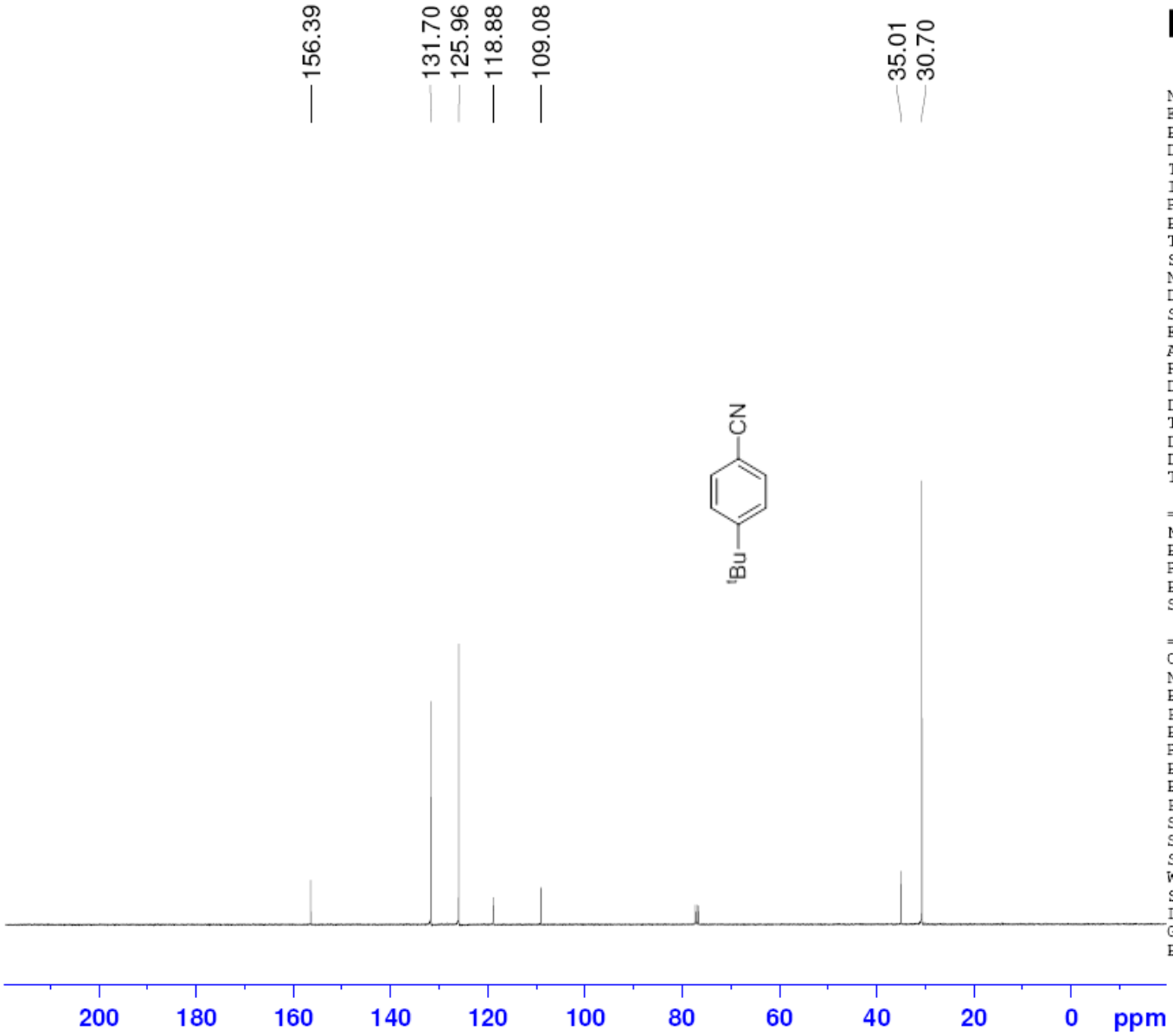
NAME	pyy227Cyan	
EXPNO	2	
PROCNO	1	
Date_	20100517	
Time	11.57	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	16	
DS	2	
SWH	24038.461	Hz
FIDRES	0.366798	Hz
AQ	1.3631988	sec
RG	203	
DW	20.800	usec
DE	6.50	usec
TE	296.5	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	9.50	usec
PL1	-2.00	dB
PL1W	58.52175522	W
SFO1	100.6228298	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	80.00	usec
PL2	0.00	dB
PL12	15.00	dB
PL13	15.00	dB
PL2W	11.88122272	W
PL12W	0.37571725	W
PL13W	0.37571725	W
SFO2	400.1316005	MHz
SI	32768	
SF	100.6128057	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

pyy378Cyan-C



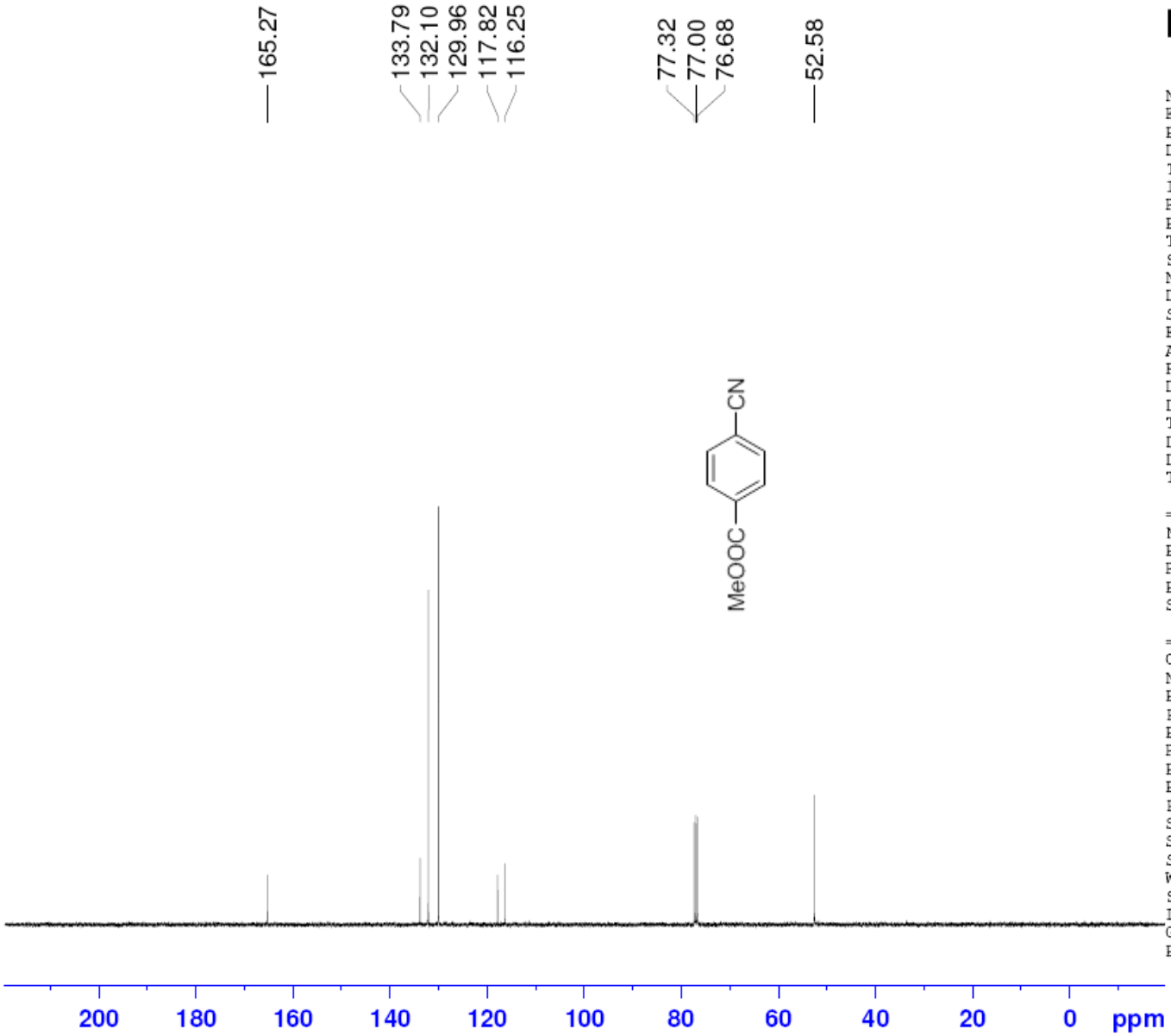
NAME	pyy378Cyan	
EXPNO	2	
PROCNO	1	
Date_	20100721	
Time	12.05	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	Acetone	
NS	16	
DS	2	
SWH	24038.461	Hz
FIDRES	0.366798	Hz
AQ	1.3631988	sec
RG	203	
DW	20.800	usec
DE	6.50	usec
TE	299.2	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
======== 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	100.6126938	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

pyy099Cyan-C



NAME	pyy099Cyan	
EXPNO	2	
PROCNO	1	
Date_	20100330	
Time	18.43	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	41	
DS	2	
SWH	24038.461	Hz
FIDRES	0.366798	Hz
AQ	1.3631988	sec
RG	128	
DW	20.800	usec
DE	6.50	usec
TE	295.9	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	9.50	usec
PL1	-2.00	dB
PL1W	58.52175522	W
SFO1	100.6228298	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	80.00	usec
PL2	0.00	dB
PL12	15.00	dB
PL13	15.00	dB
PL2W	11.88122272	W
PL12W	0.37571725	W
PL13W	0.37571725	W
SFO2	400.1316005	MHz
SI	32768	
SF	100.6127923	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

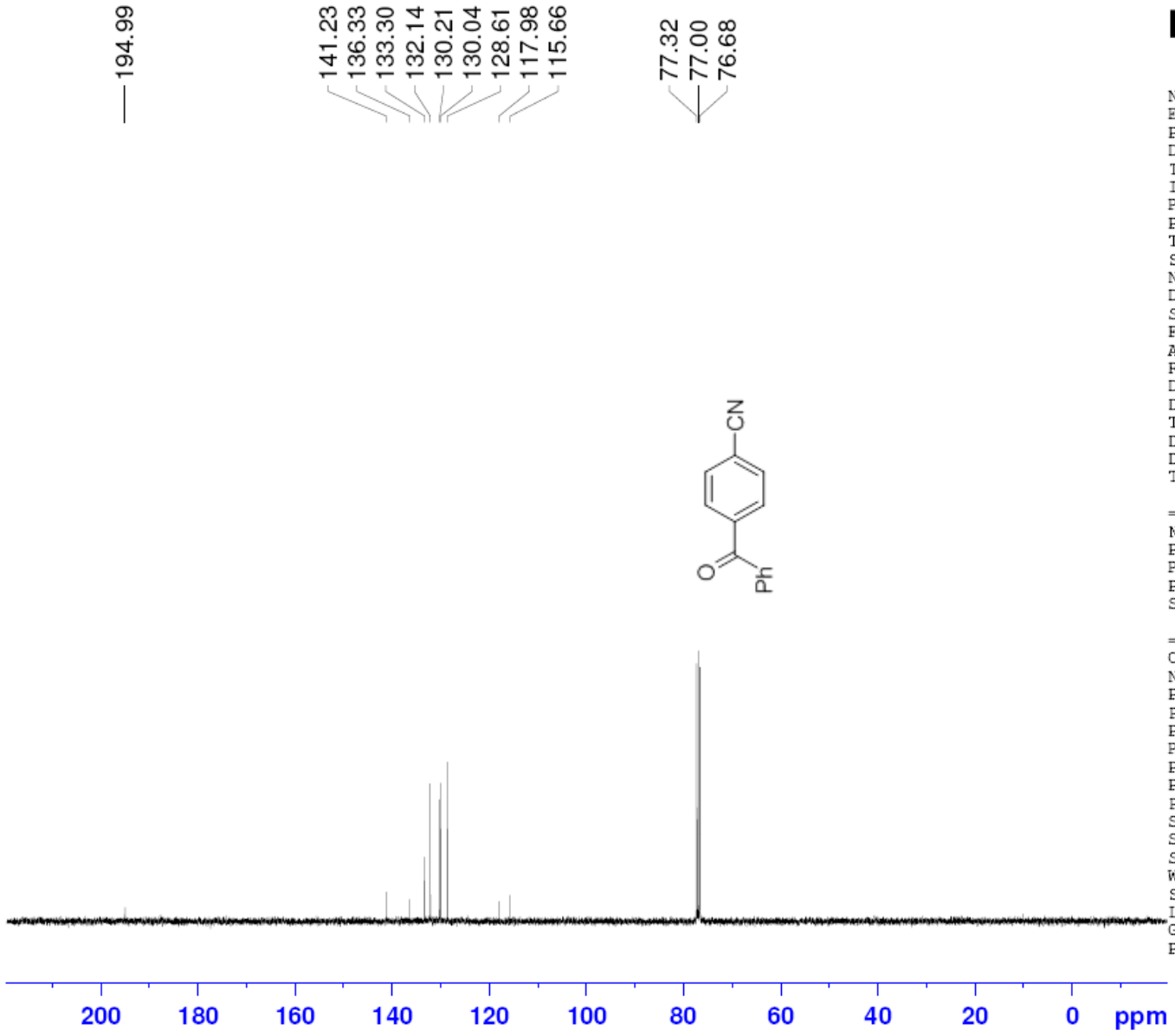
pyy136Cyan-C



BRUKER

NAME	pyy136Cyan
EXPNO	2
PROCNO	1
Date_	20100413
Time	11.14
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	32
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	296.4 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	100.6127809 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

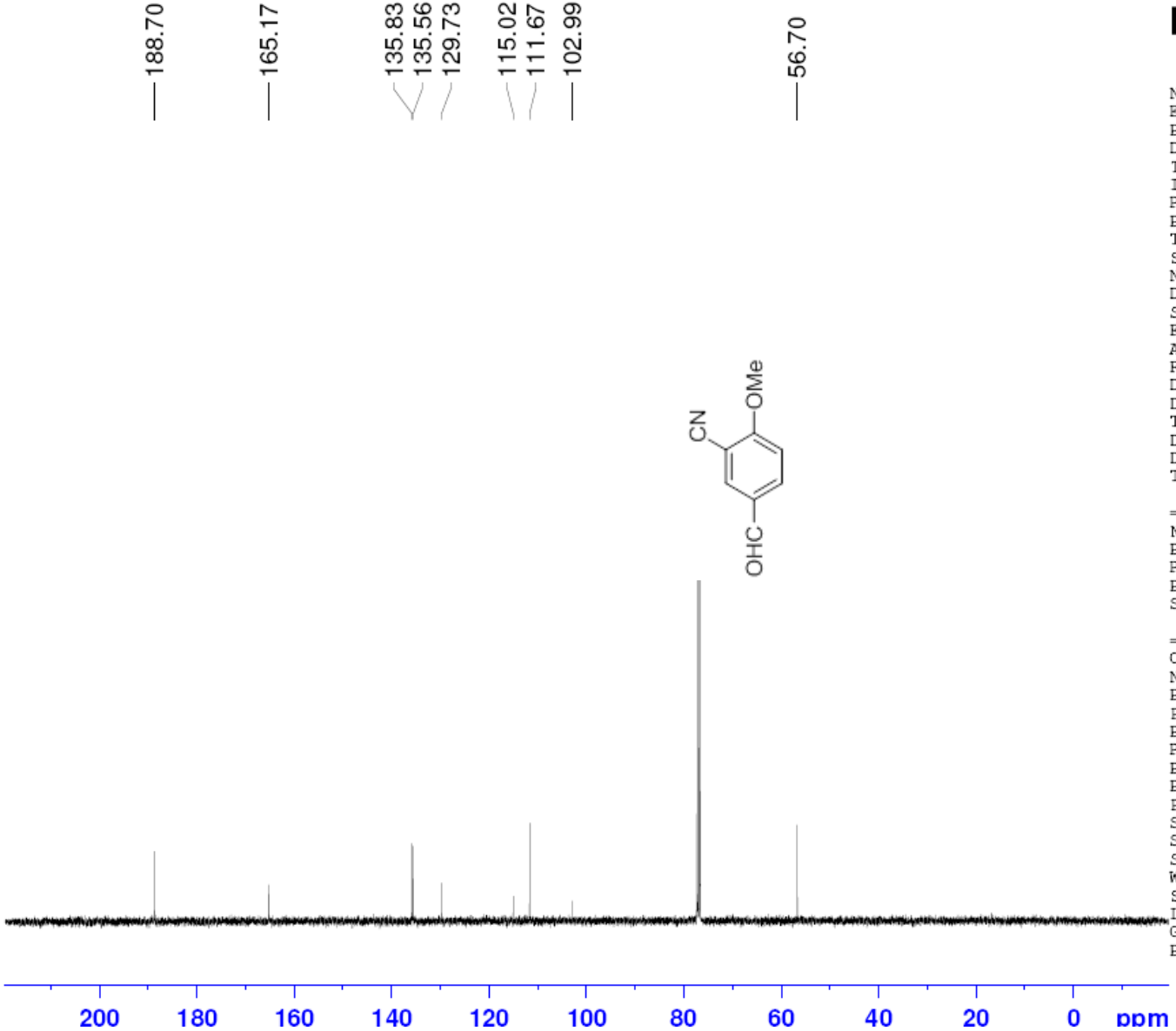
pyy139Cyan-C



BRUKER

NAME	pyy139Cyan	
EXPNO	2	
PROCNO	1	
Date_	20100412	
Time	14.48	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	101	
DS	2	
SWH	24038.461	Hz
FIDRES	0.366798	Hz
AQ	1.3631988	sec
RG	203	
DW	20.800	usec
DE	6.50	usec
TE	297.3	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	9.50	usec
PL1	-2.00	dB
PL1W	58.52175522	W
SFO1	100.6228298	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	80.00	usec
PL2	0.00	dB
PL12	15.00	dB
PL13	15.00	dB
PL2W	11.88122272	W
PL12W	0.37571725	W
PL13W	0.37571725	W
SFO2	400.1316005	MHz
SI	32768	
SF	100.6127716	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

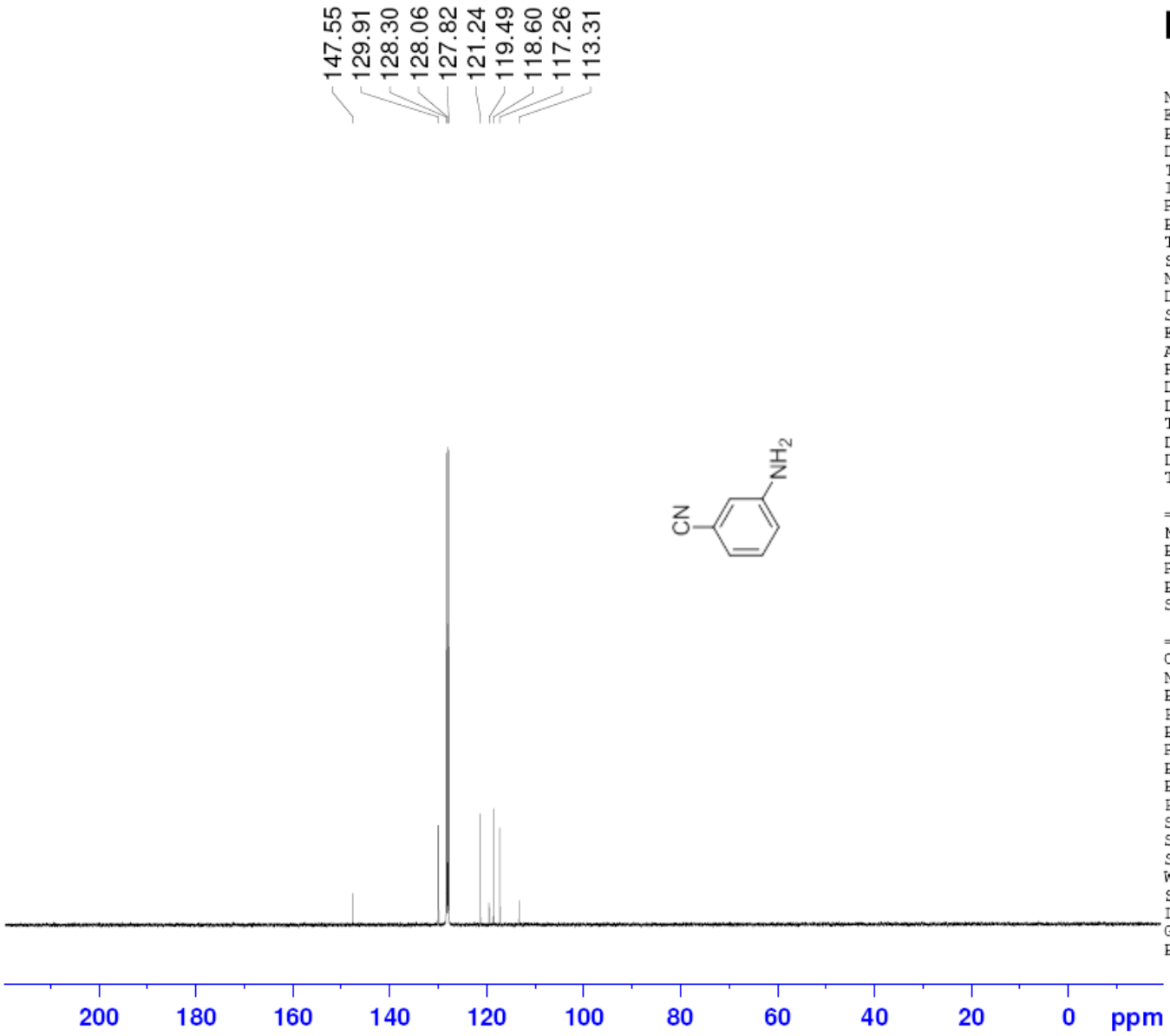
pyy145Cyan-C



BRUKER

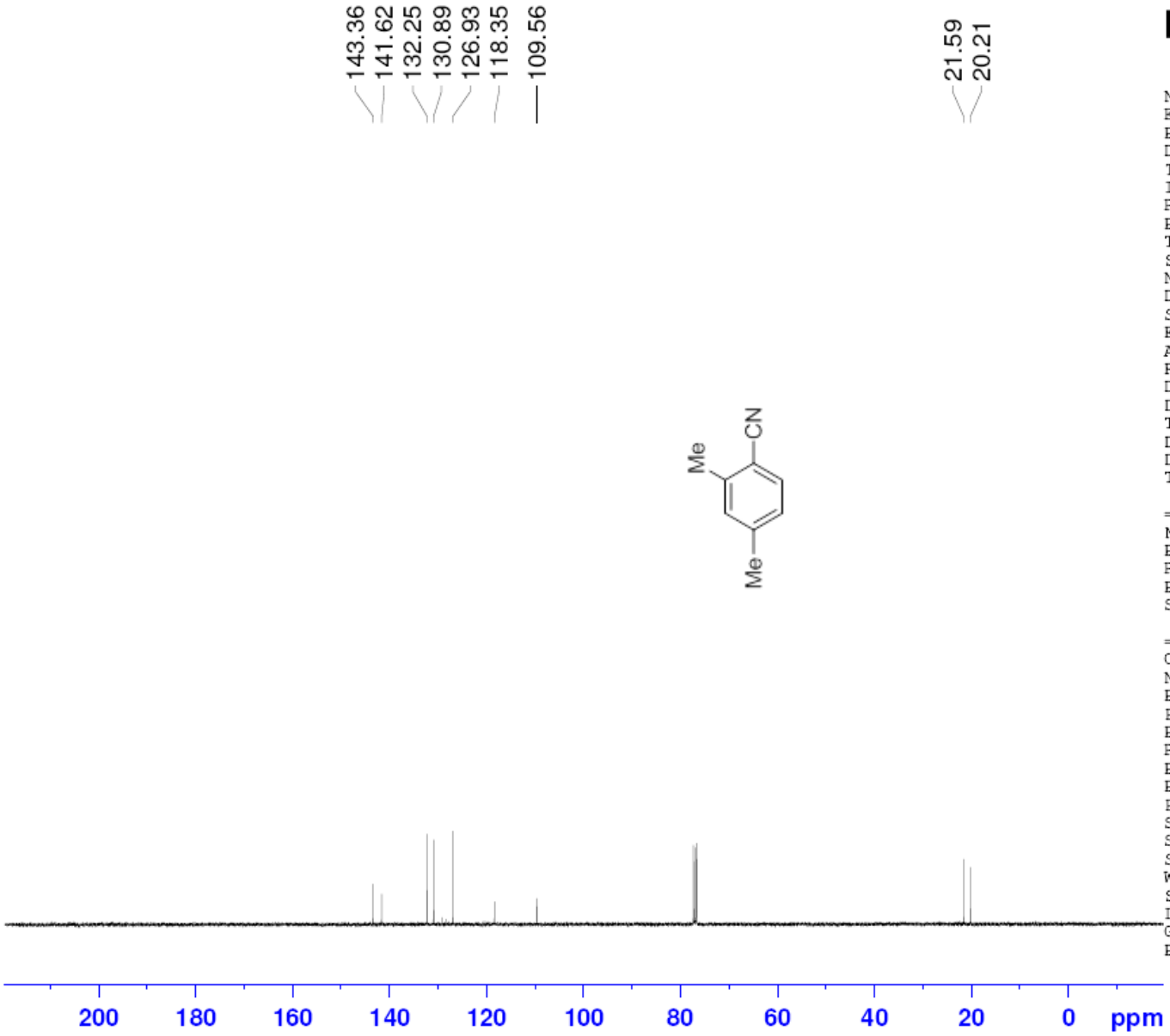
NAME	pyy145Cyan	
EXPNO	2	
PROCNO	1	
Date_	20100410	
Time	22.25	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	132	
DS	2	
SWH	24038.461	Hz
FIDRES	0.366798	Hz
AQ	1.3631988	sec
RG	203	
DW	20.800	usec
DE	6.50	usec
TE	295.9	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
======== 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	100.6127754	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

pyy142Cyan-C(Pure)



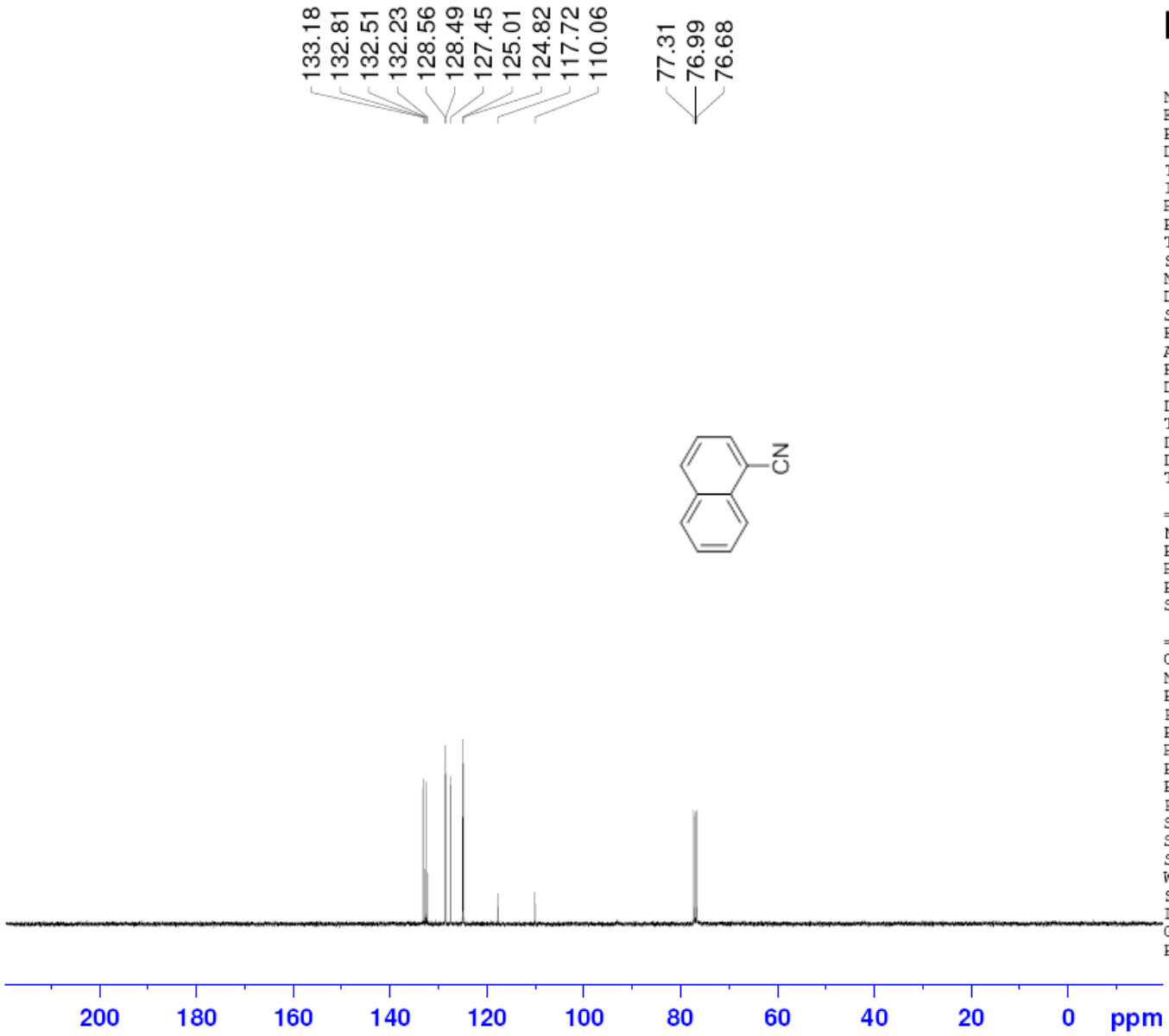
NAME	pyy142Cyan
EXPNO	8
PROCNO	1
Date_	20100420
Time	14.22
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	C6D6
NS	32
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	181
DW	20.800 usec
DE	6.50 usec
TE	296.3 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	15.00 dB
PL2W	11.88122272 W
PL12W	0.37571725 W
PL13W	0.37571725 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127333 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

pyy217Cyan-C



NAME	pyy217Cyan
EXPNO	2
PROCNO	1
Date_	20100512
Time	11.40
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	296.1 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	15.00 dB
PL2W	11.88122272 W
PL12W	0.37571725 W
PL13W	0.37571725 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127810 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

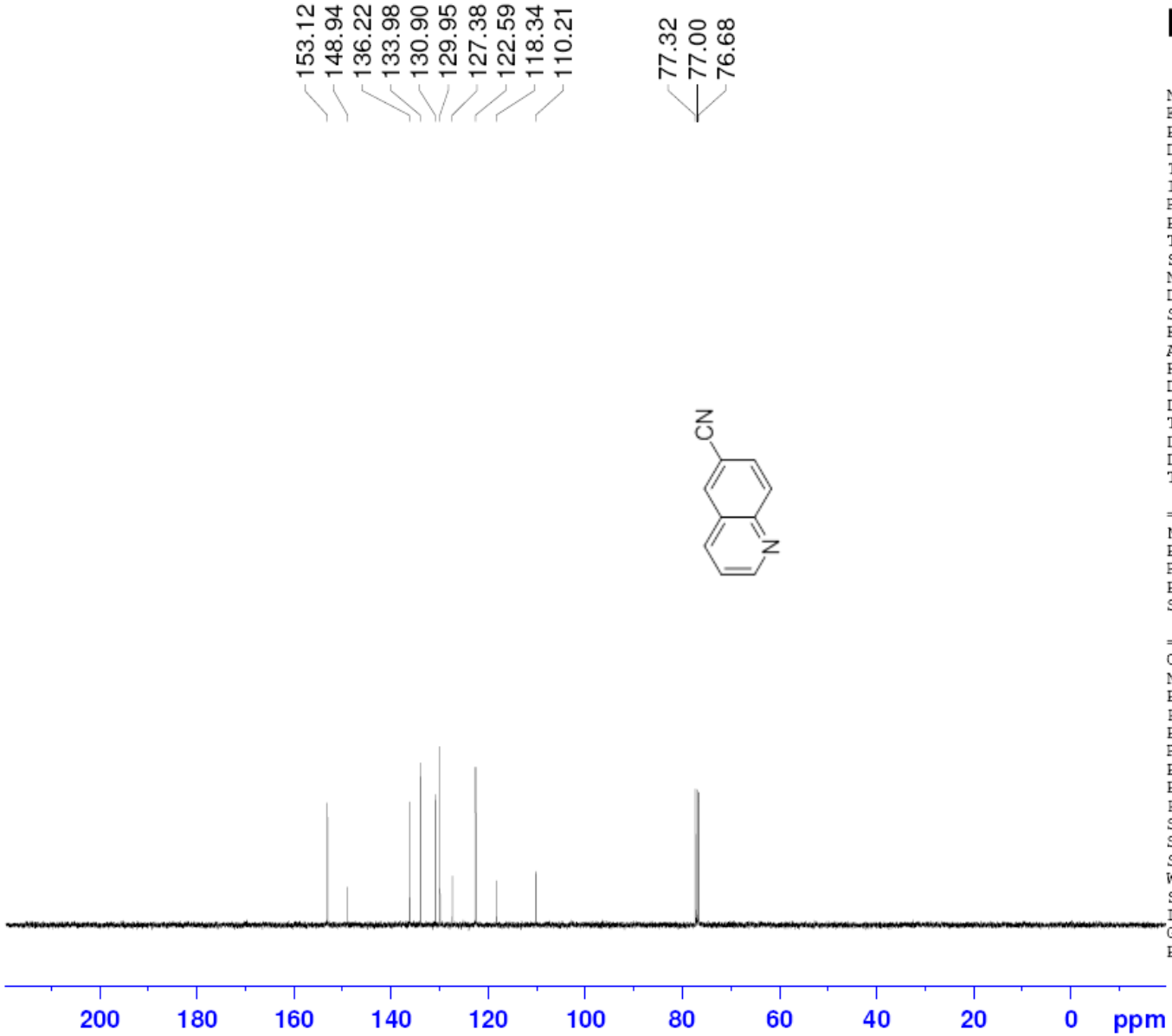
pyy137Cyan-C



BRUKER

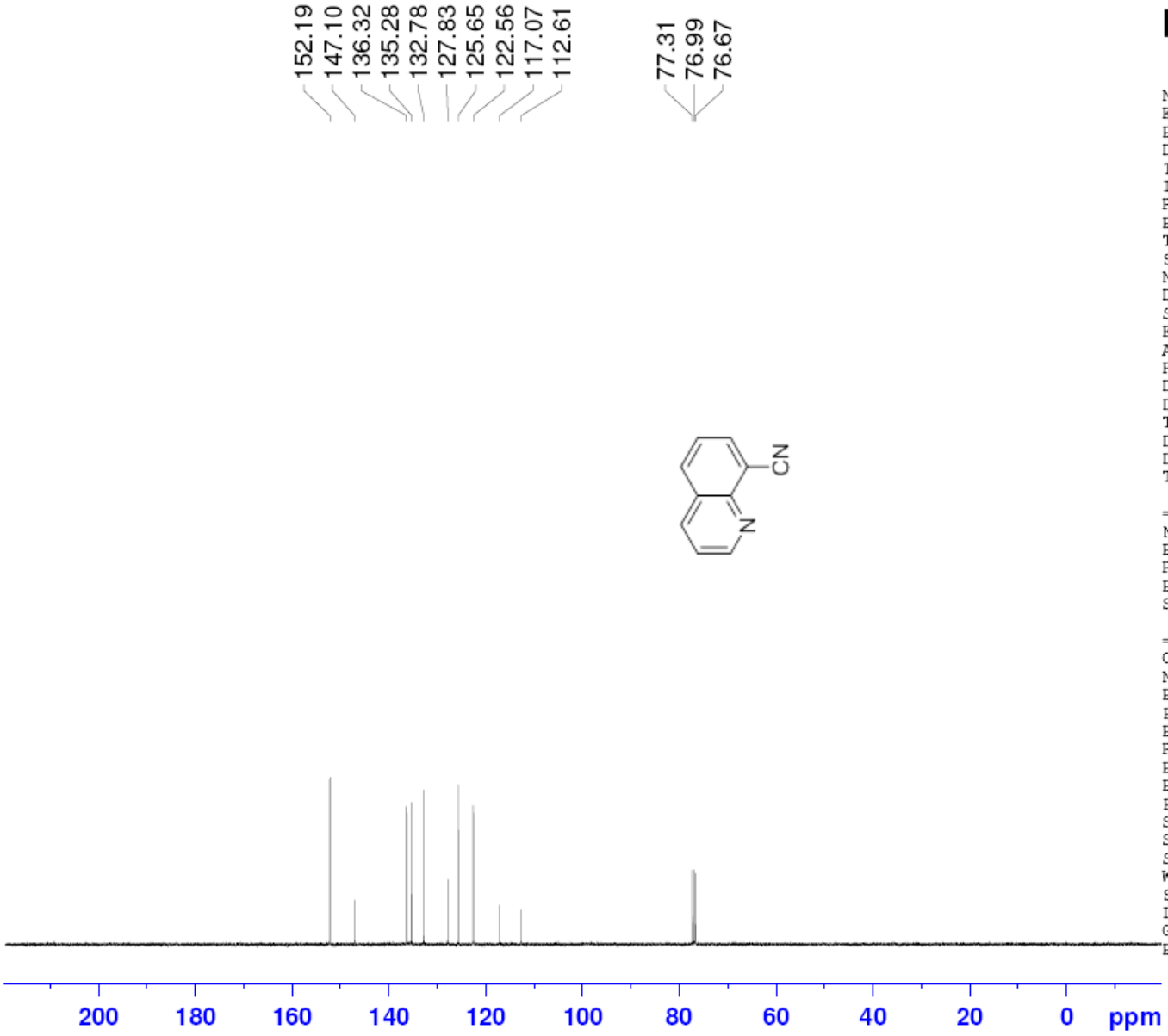
NAME	pyy137Cyan	
EXPNO	2	
PROCNO	1	
Date_	20100413	
Time	11.33	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	39	
DS	2	
SWH	24038.461	Hz
FIDRES	0.366798	Hz
AQ	1.3631988	sec
RG	203	
DW	20.800	usec
DE	6.50	usec
TE	297.0	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	9.50	usec
PL1	-2.00	dB
PL1W	58.52175522	W
SFO1	100.6228298	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	80.00	usec
PL2	0.00	dB
PL12	15.00	dB
PL13	15.00	dB
PL2W	11.88122272	W
PL12W	0.37571725	W
PL13W	0.37571725	W
SFO2	400.1316005	MHz
SI	32768	
SF	100.6127810	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

pyy224Cyan-C



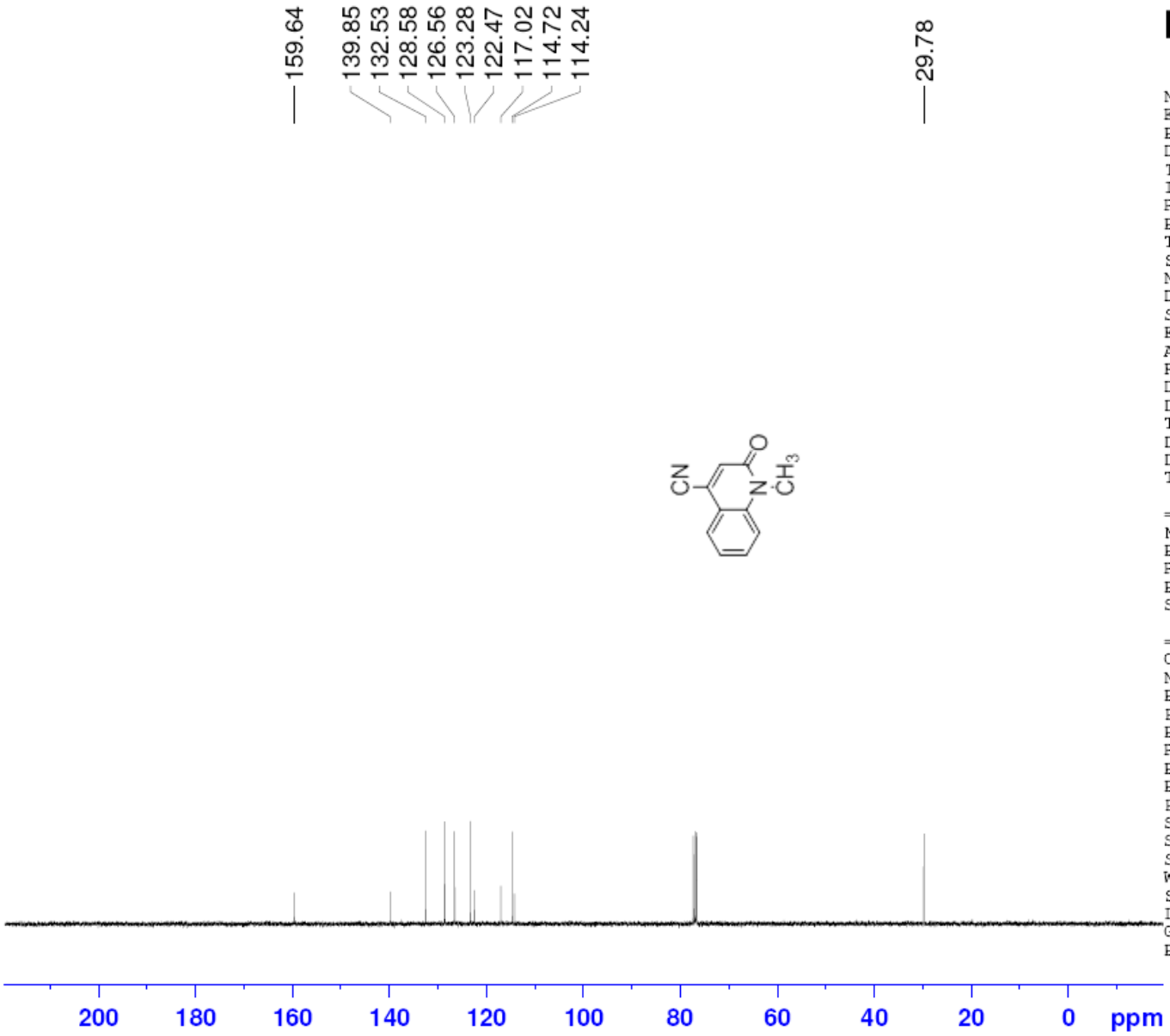
NAME	pyy224Cyan
EXPNO	2
PROCNO	1
Date_	20100513
Time	19.55
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	297.1 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	15.00 dB
PL2W	11.88122272 W
PL12W	0.37571725 W
PL13W	0.37571725 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127828 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

pyy226Cyan-C



NAME	pyy226Cyan	
EXPNO	2	
PROCNO	1	
Date_	20100517	
Time	11.47	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	16	
DS	2	
SWH	24038.461	Hz
FIDRES	0.366798	Hz
AQ	1.3631988	sec
RG	203	
DW	20.800	usec
DE	6.50	usec
TE	296.5	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	9.50	usec
PL1	-2.00	dB
PL1W	58.52175522	W
SFO1	100.6228298	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	80.00	usec
PL2	0.00	dB
PL12	15.00	dB
PL13	15.00	dB
PL2W	11.88122272	W
PL12W	0.37571725	W
PL13W	0.37571725	W
SFO2	400.1316005	MHz
SI	32768	
SF	100.6127950	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

pyy235Cyan-C



BRUKER

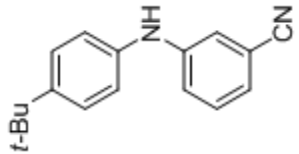
NAME	pyy235Cyan	
EXPNO	2	
PROCNO	1	
Date_	20100525	
Time	12.02	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	16	
DS	2	
SWH	24038.461	Hz
FIDRES	0.366798	Hz
AQ	1.3631988	sec
RG	203	
DW	20.800	usec
DE	6.50	usec
TE	298.0	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	9.50	usec
PL1	-2.00	dB
PL1W	58.52175522	W
SFO1	100.6228298	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	80.00	usec
PL2	0.00	dB
PL12	15.00	dB
PL13	15.00	dB
PL2W	11.88122272	W
PL12W	0.37571725	W
PL13W	0.37571725	W
SFO2	400.1316005	MHz
SI	32768	
SF	100.6127826	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

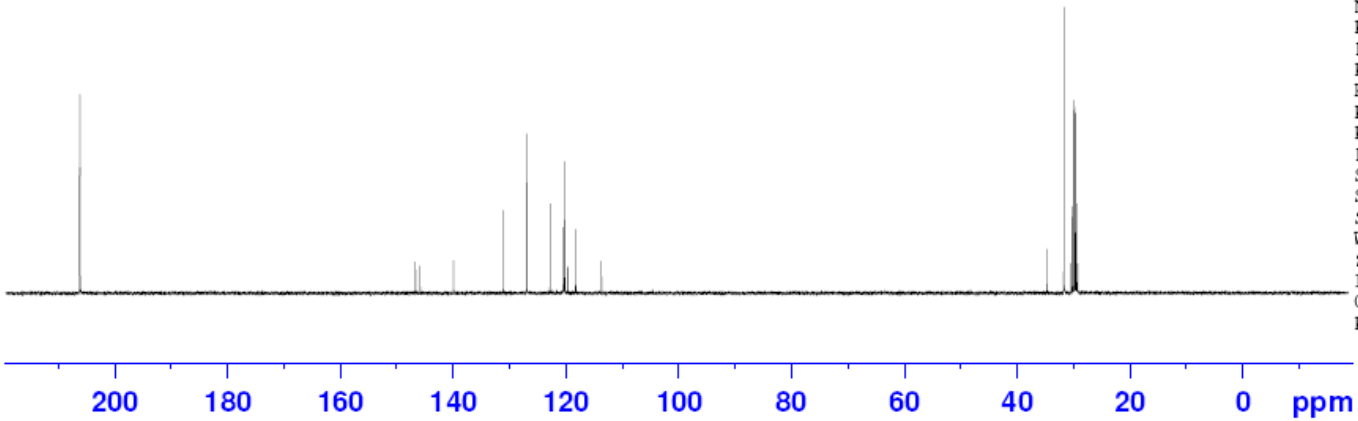
pyy400Cyan-C

206.18

146.66 145.84 139.93 131.12 126.96 122.80 120.48 120.24 119.62 118.28 113.69

34.71 31.70 30.41 30.21 30.02 29.83 29.64 29.45 29.25

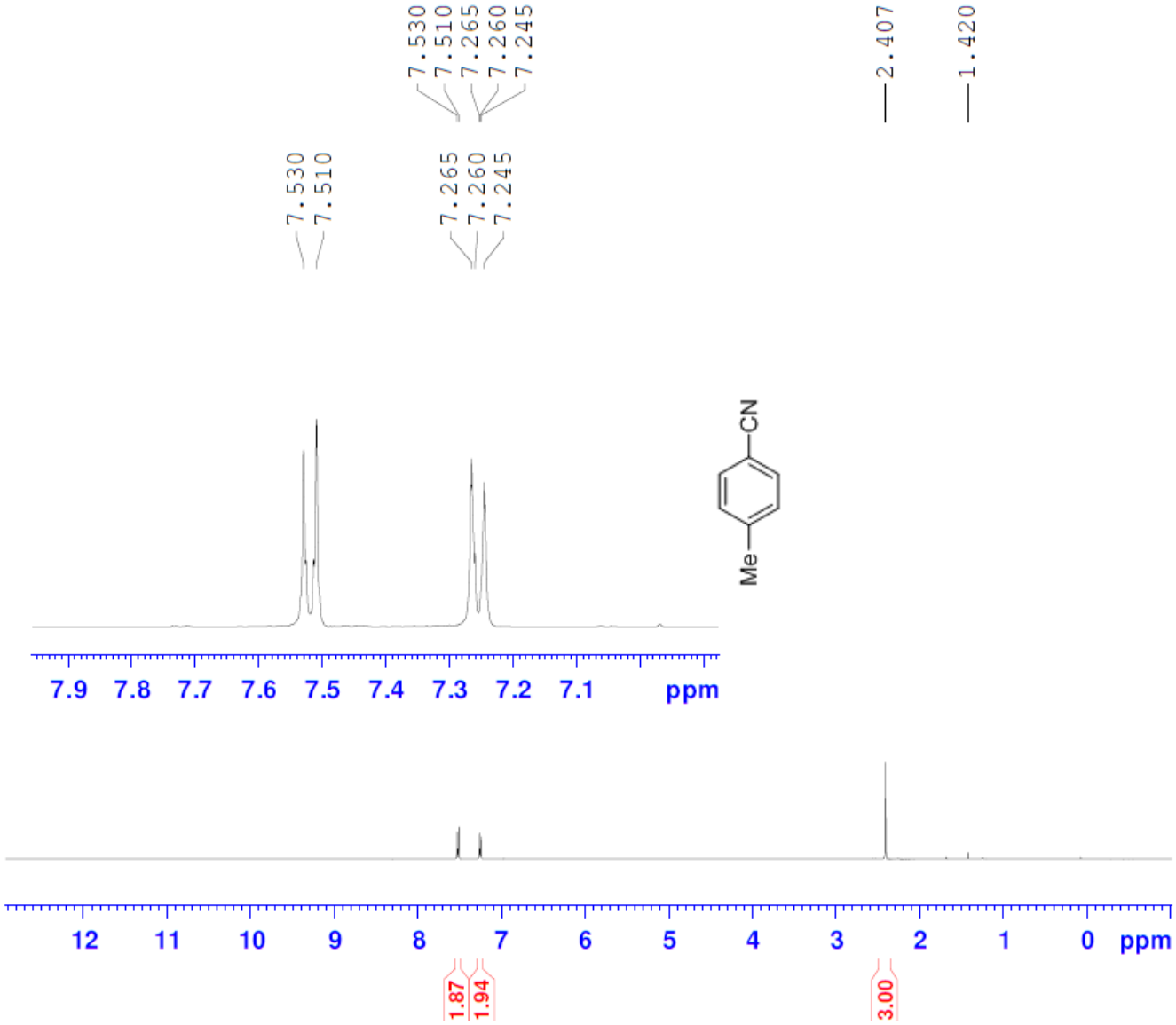




NAME	pyy400Cyan
EXPNO	2
PROCNO	1
Date_	20100806
Time	12.18
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	Acetone
NS	16
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	298.4 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL 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	100.6126884 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

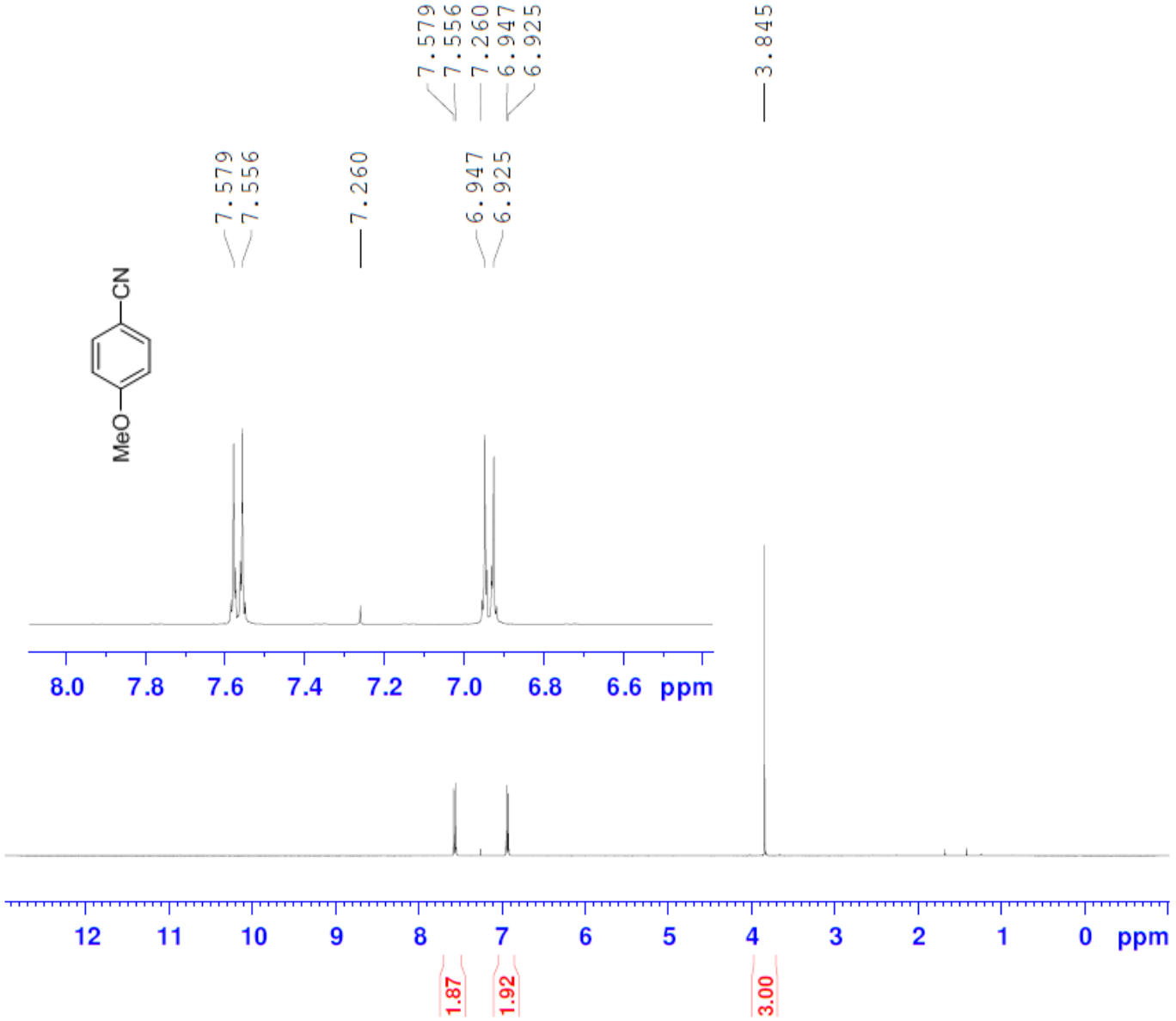
^{1}H-, ^{13}C-NMR spectra of products from palladium-catalyzed cyanation of aryl chlorides

pyy550Cyan-H



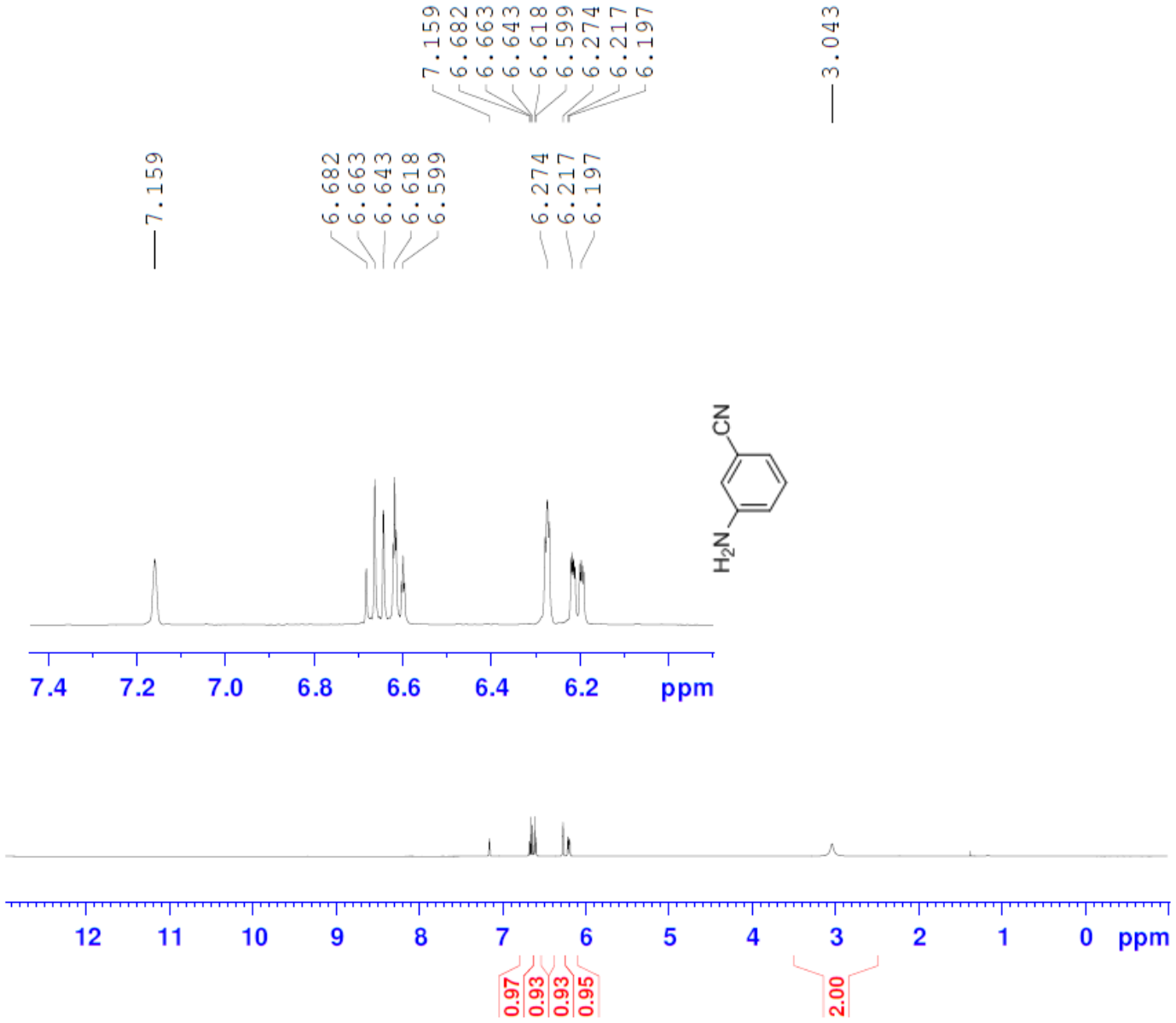
NAME	pyy550Cyan
EXPNO	1
PROCNO	1
Date_	20101124
Time	15.51
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	4
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	45.2
DW	89.333 usec
DE	6.50 usec
TE	297.3 K
D1	1.00000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300097 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

pyy487Cyan-H



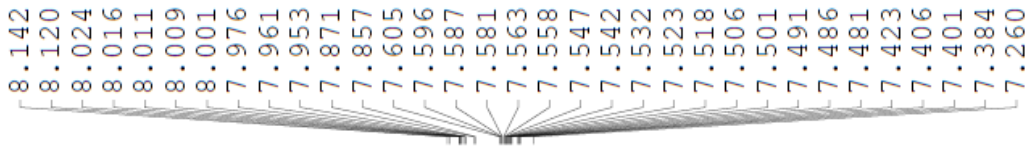
NAME	pyy487Cyan
EXPNO	1
PROCNO	1
Date_	20100929
Time	16.16
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	8
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	45.2
DW	89.333 usec
DE	6.50 usec
TE	297.4 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300095 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

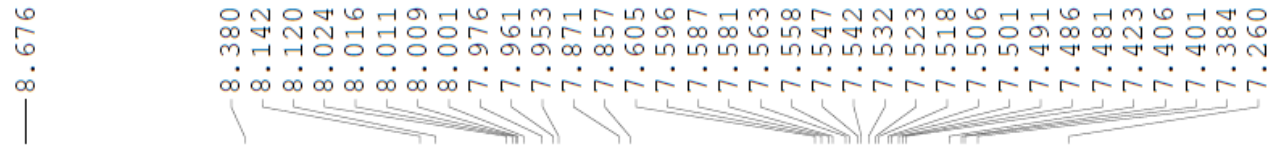
pyy501Cyan-H

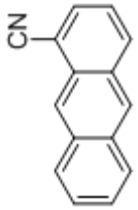


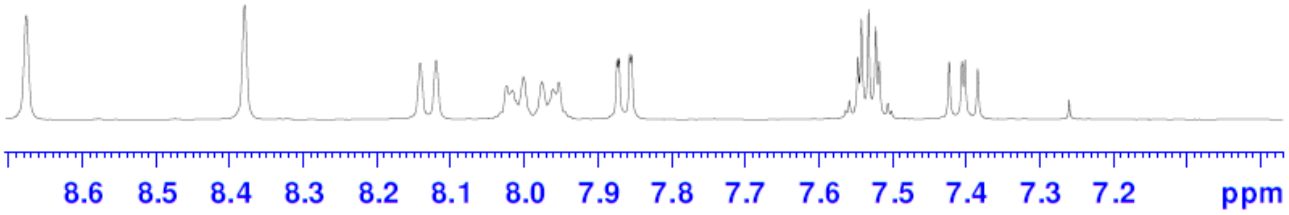
NAME	pyy501Cyan
EXPNO	1
PROCNO	1
Date_	20101008
Time	16.30
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	C6D6
NS	4
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	45.2
DW	89.333 usec
DE	6.50 usec
TE	297.7 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1299968 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

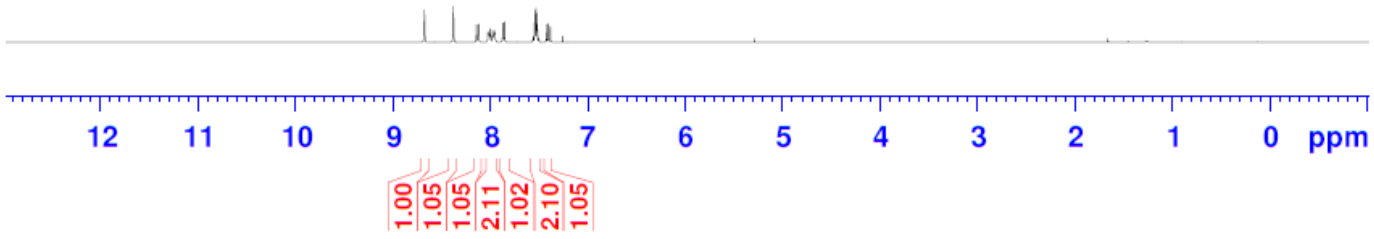
pyy502Cyan-H





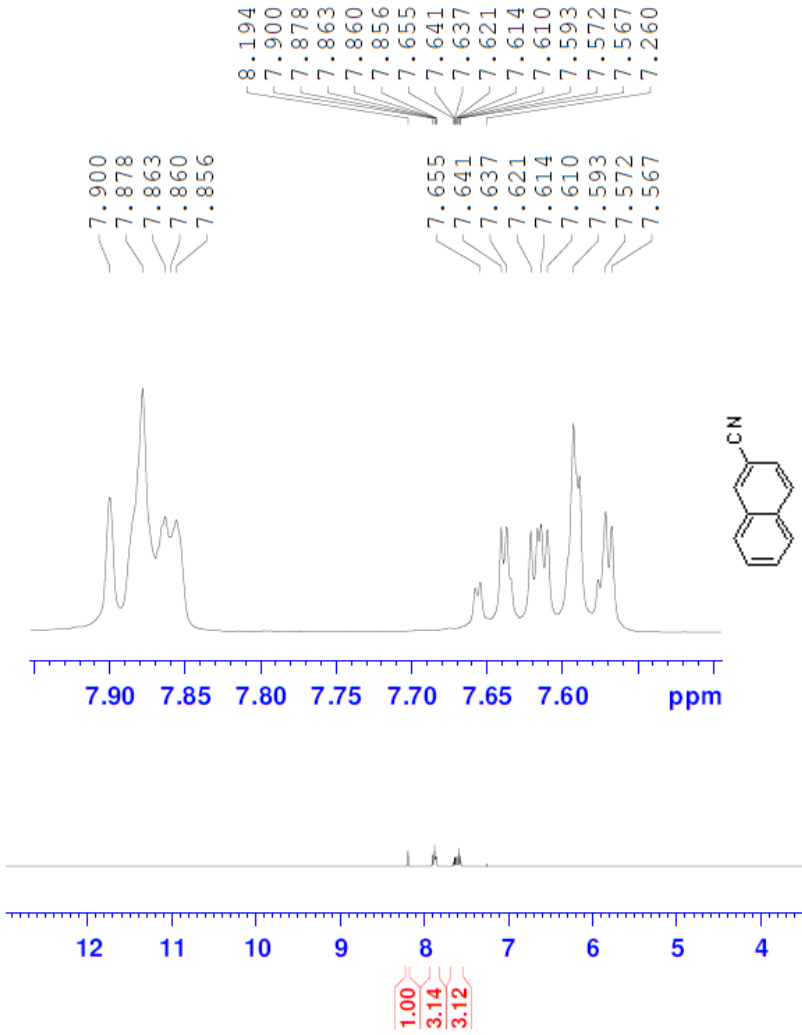






NAME	pyy502Cyan
EXPNO	1
PROCNO	1
Date_	20101011
Time	11.10
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	8
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	45.2
DW	89.333 usec
DE	6.50 usec
TE	297.8 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300095 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

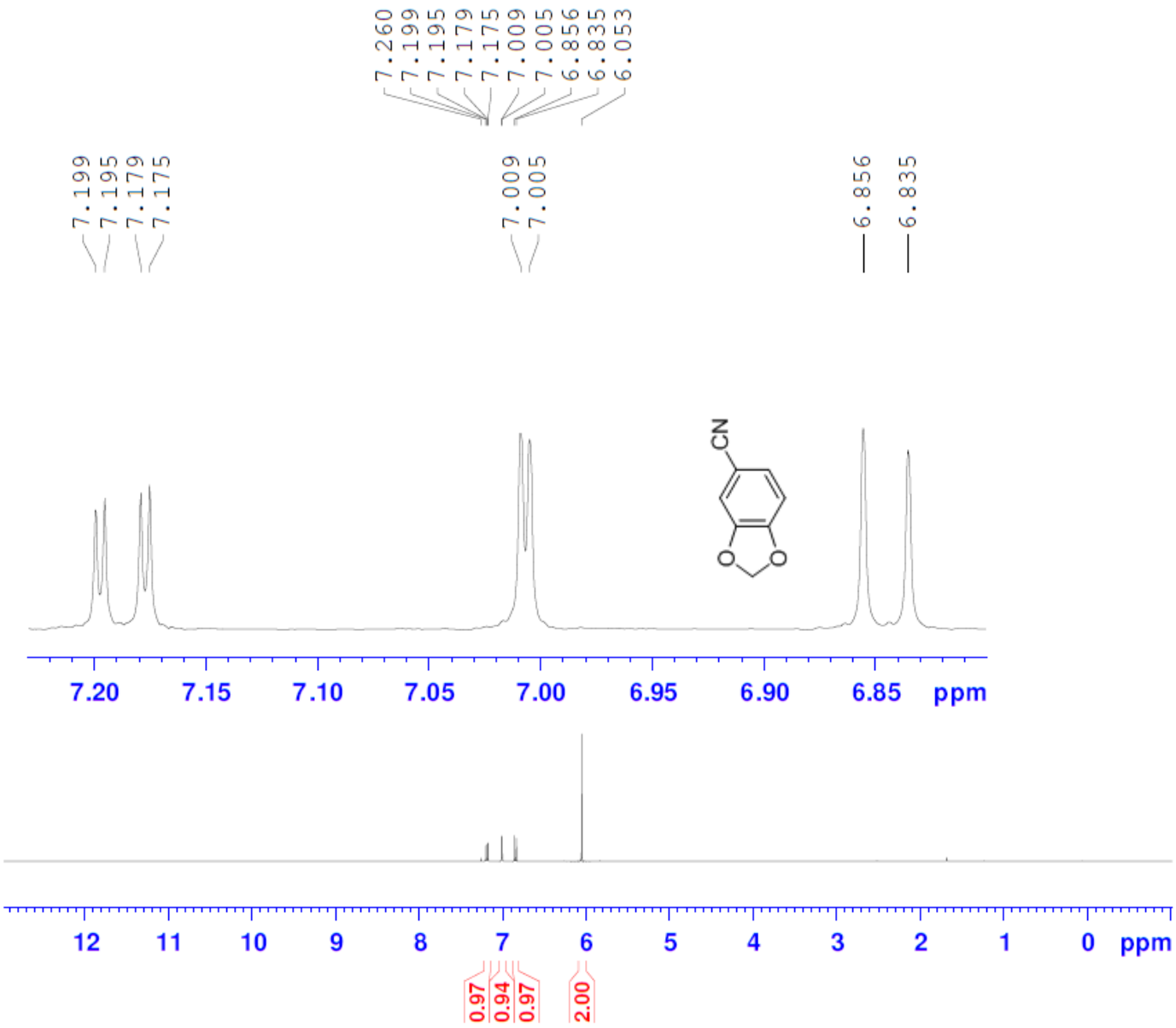
pyy504Cyan-H



BRUKER

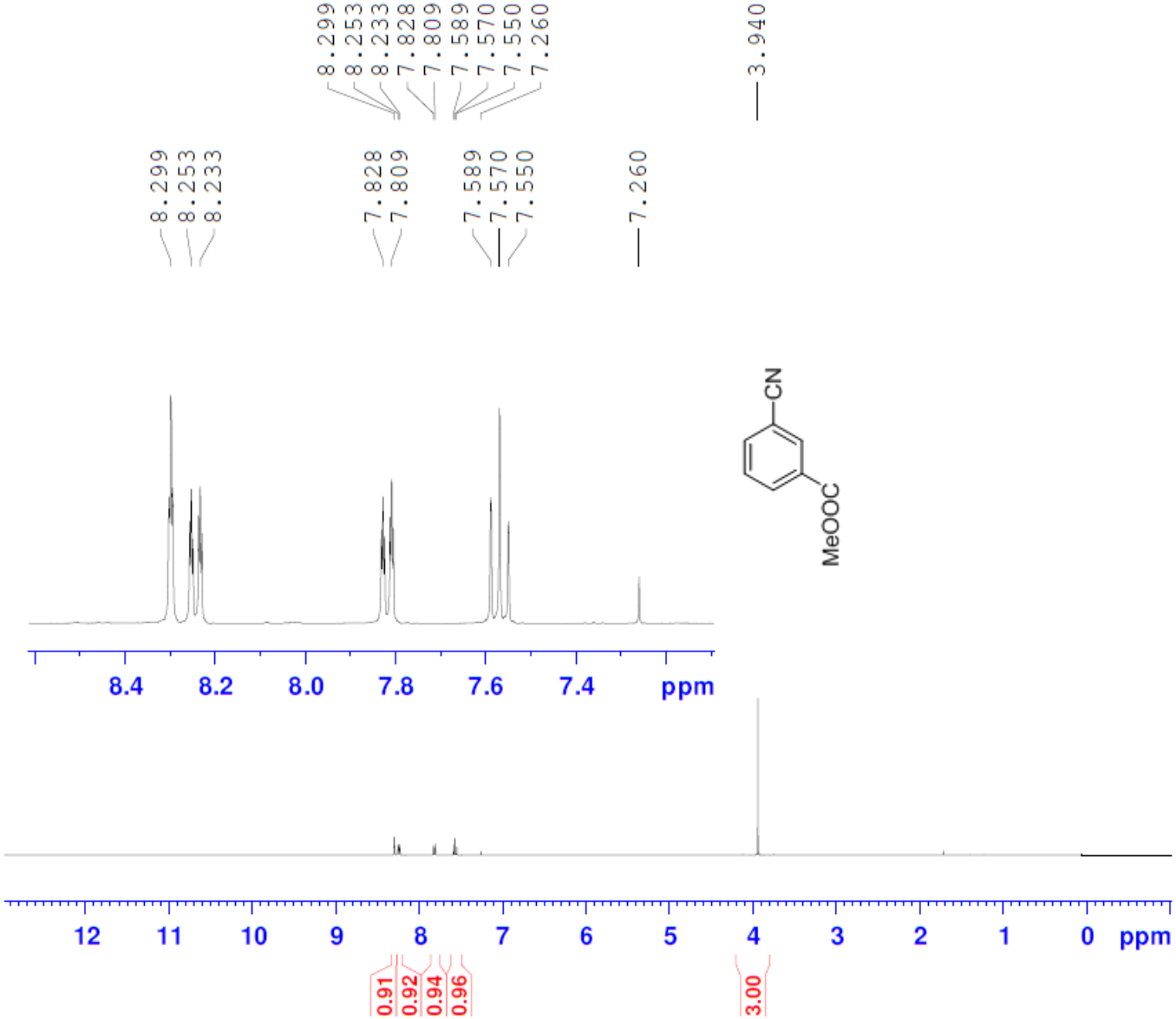
NAME	pyy504Cyan
EXPNO	1
PROCNO	1
Date_	20101011
Time	11.19
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	4
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	45.2
DW	89.333 usec
DE	6.50 usec
TE	297.8 K
D1	1.00000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300096 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

pyy508Cyan-H



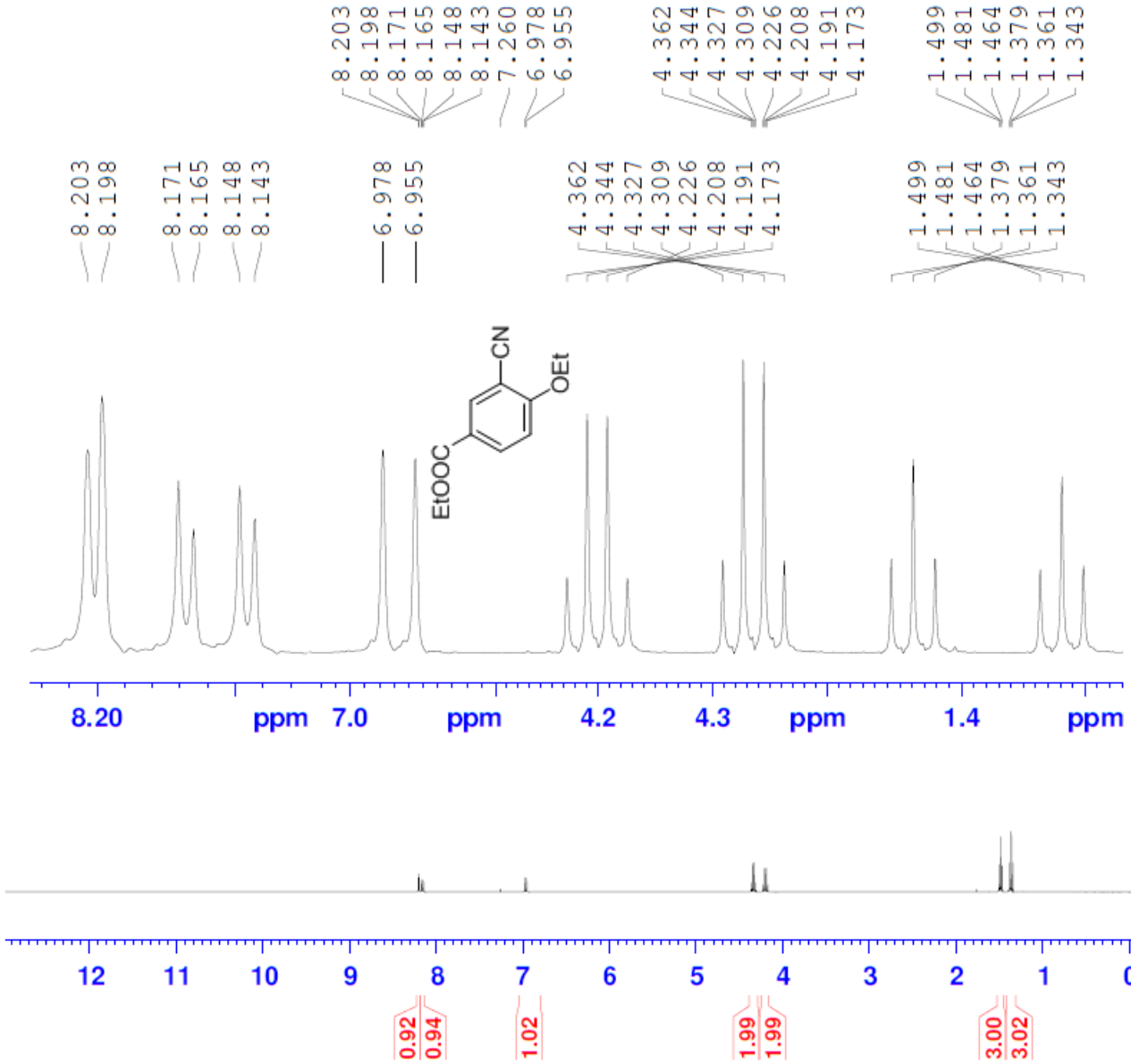
NAME	pyy508Cyan
EXPNO	1
PROCNO	1
Date_	20101014
Time	11.12
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	4
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	45.2
DW	89.333 usec
DE	6.50 usec
TE	297.7 K
D1	1.00000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300096 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

pyy510Cyan-H



NAME	pyy510Cyan
EXPNO	1
PROCNO	1
Date_	20101014
Time	11.21
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	4
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	45.2
DW	89.333 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	400.1324008 MHz
SI	32768
SF	400.1300095 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

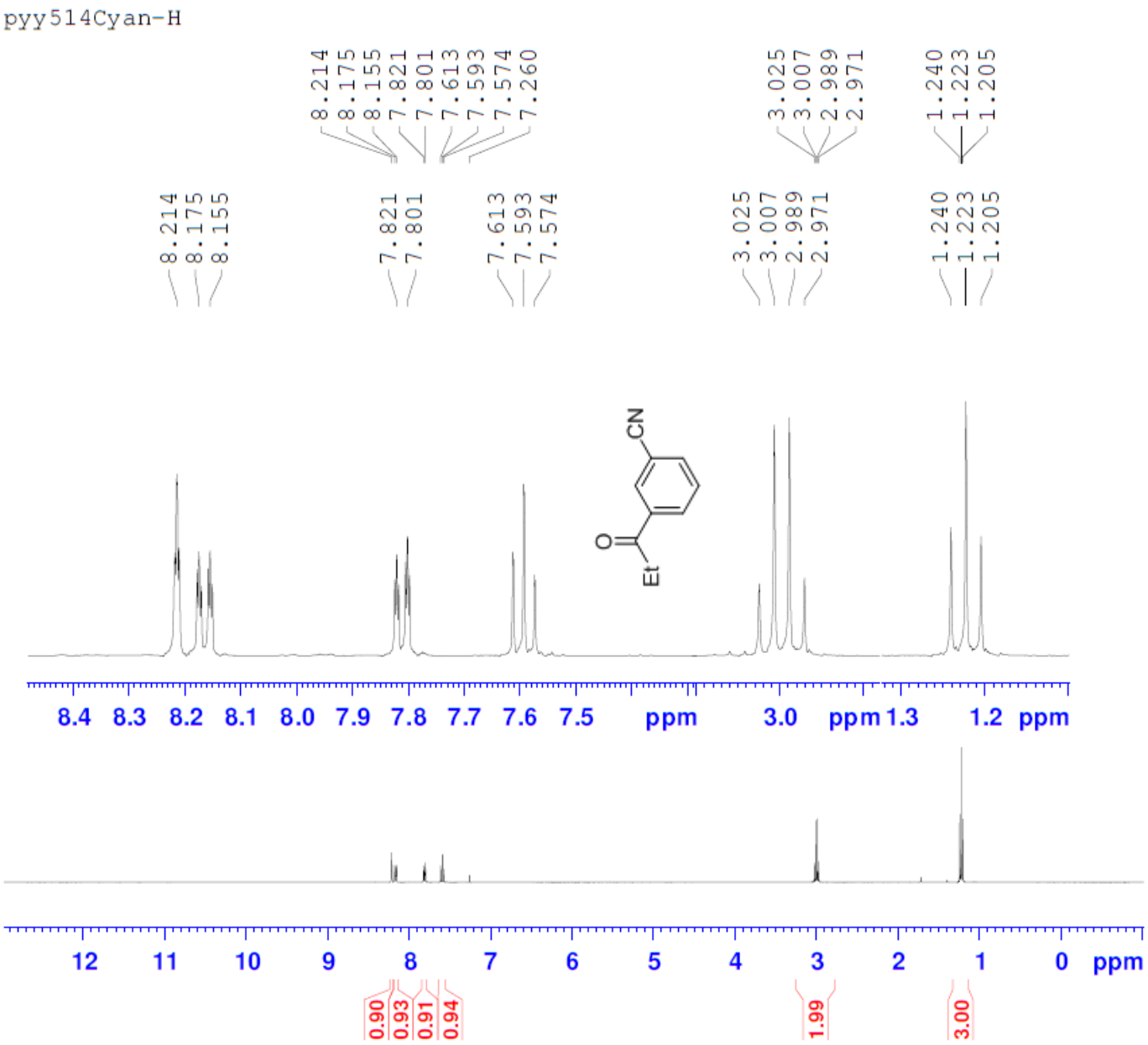
pyy513Cyan-H



BRUKER

NAME	pyy513Cyan
EXPNO	1
PROCNO	1
Date_	20101018
Time	11.59
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	4
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	40.3
DW	89.333 usec
DE	6.50 usec
TE	298.2 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300095 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

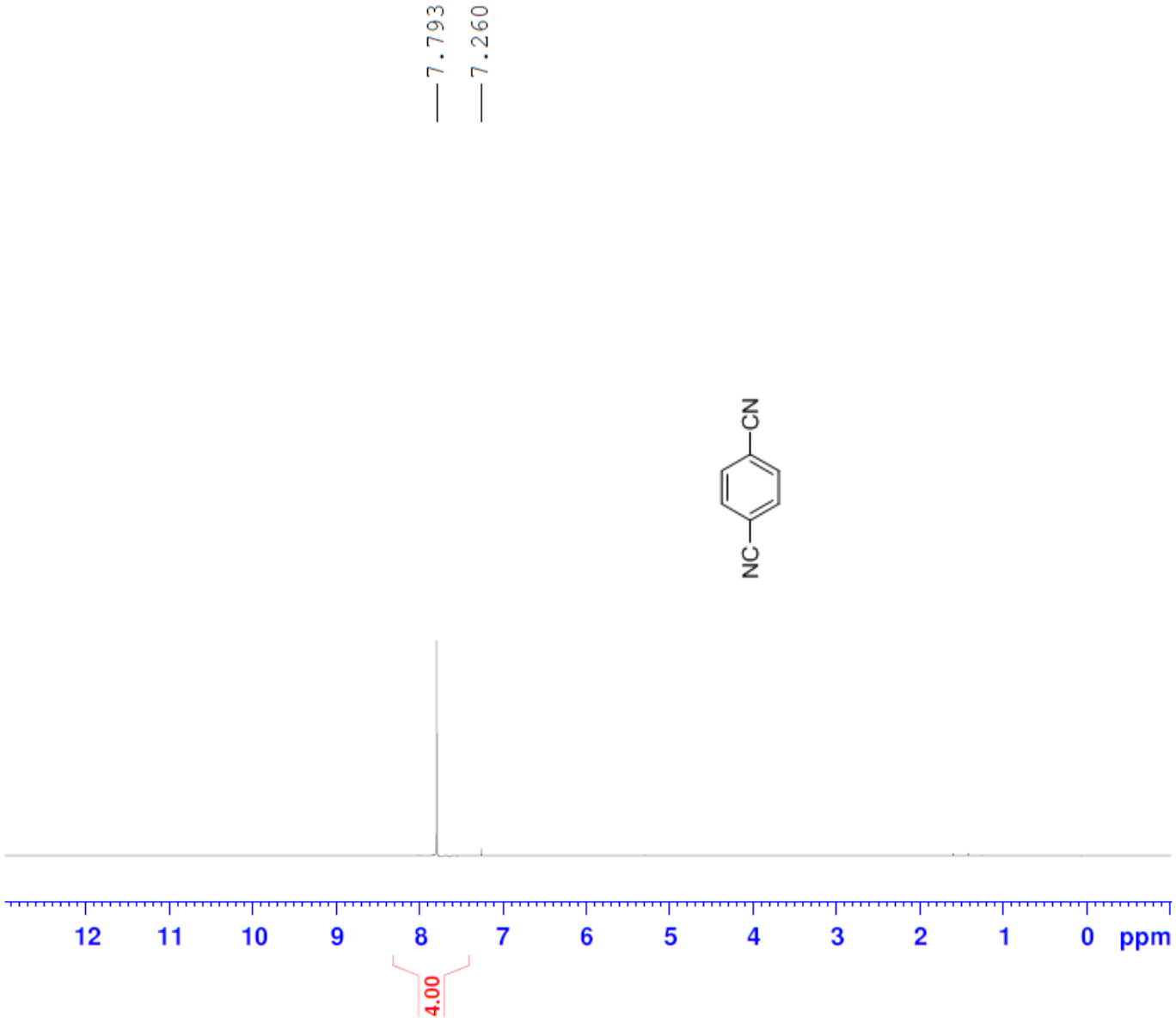
pyy514Cyan-H



BRUKER

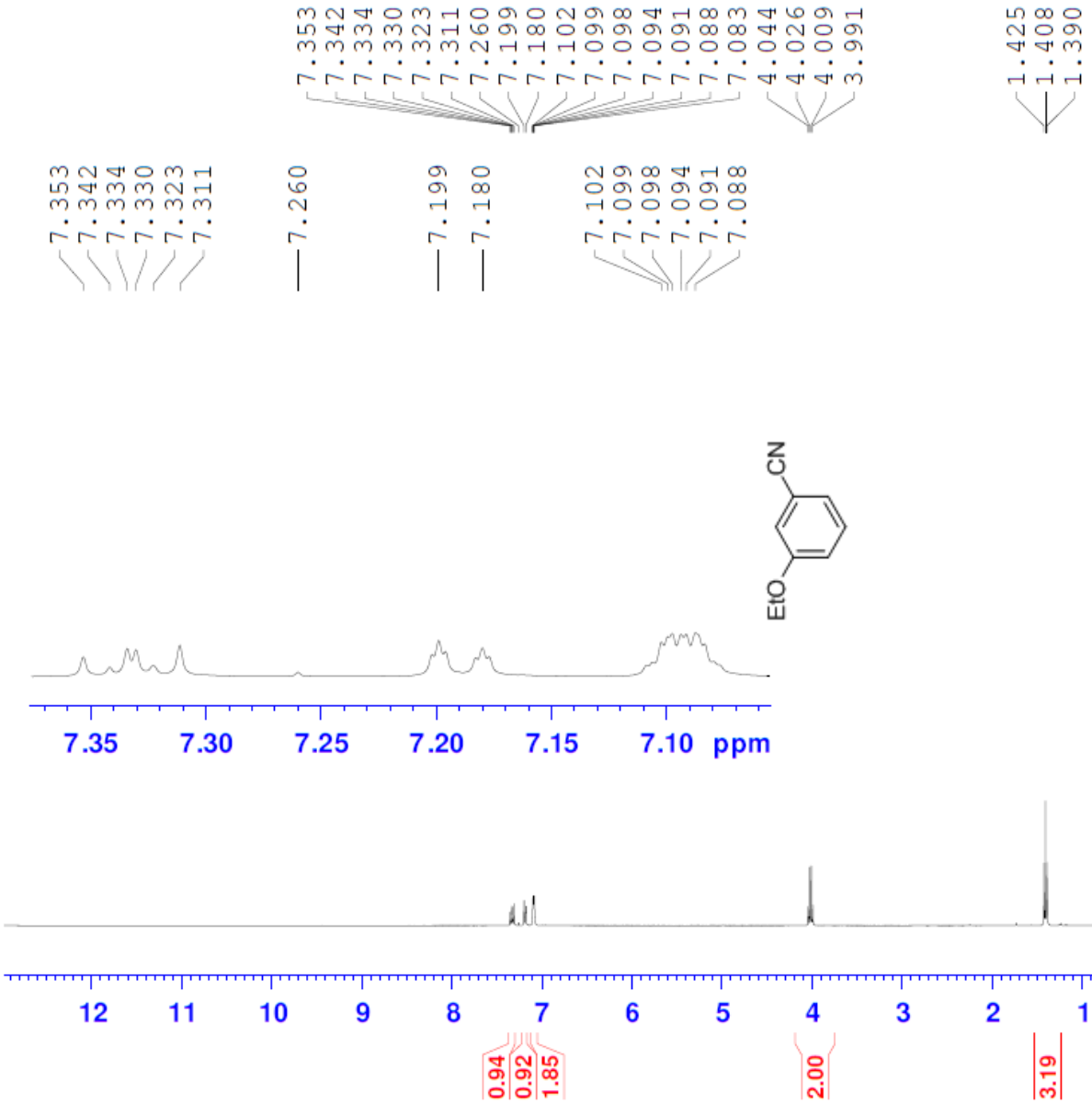
NAME	pyy514Cyan
EXPNO	1
PROCNO	1
Date_	20101018
Time	12.18
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	4
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	45.2
DW	89.333 usec
DE	6.50 usec
TE	298.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300096 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

pyy515Cyan-H



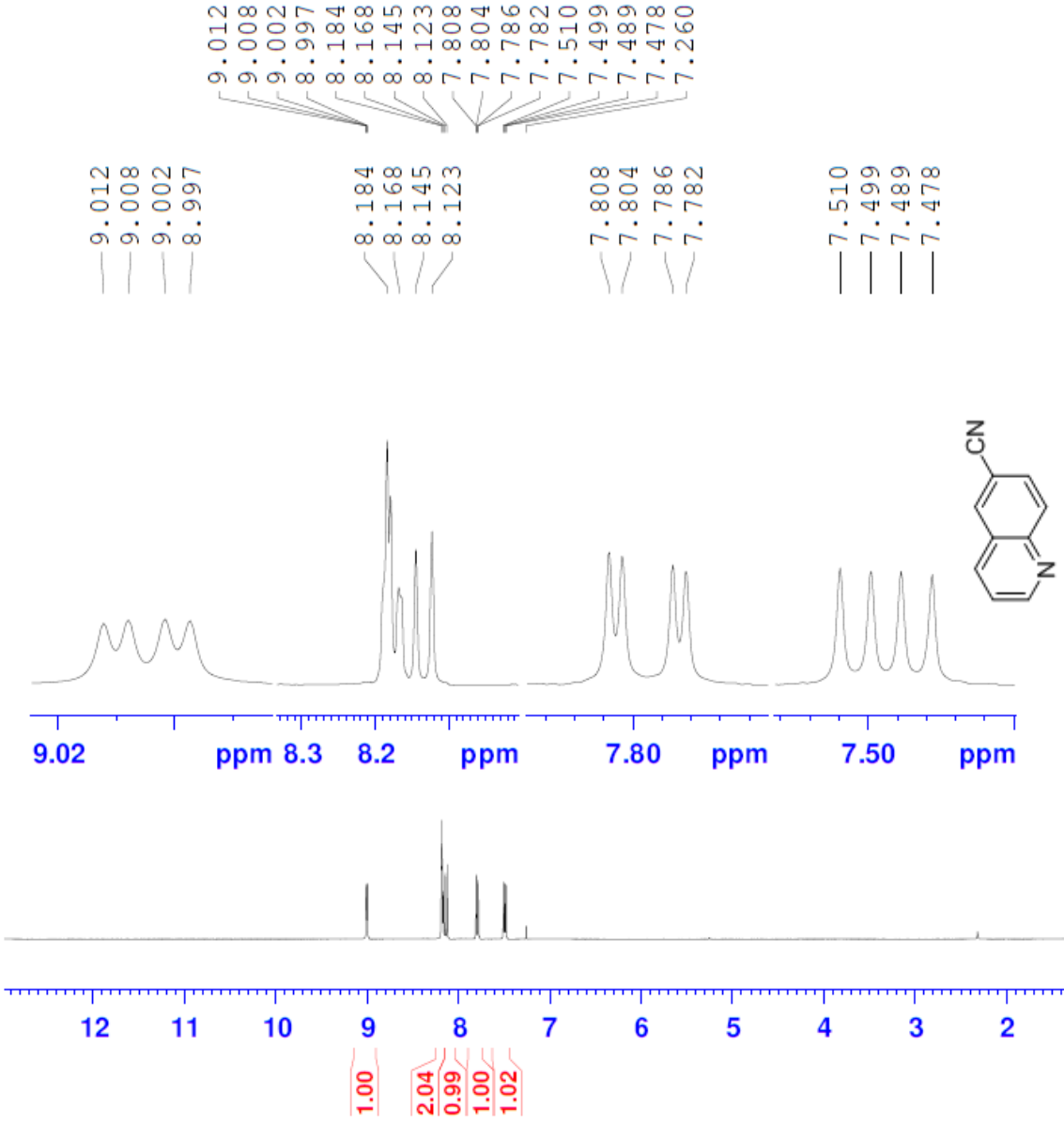
NAME	pyy515Cyan
EXPNO	1
PROCNO	1
Date_	20101018
Time	12.11
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	4
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	128
DW	89.333 usec
DE	6.50 usec
TE	298.1 K
D1	1.00000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300097 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

pyy516Cyan-H



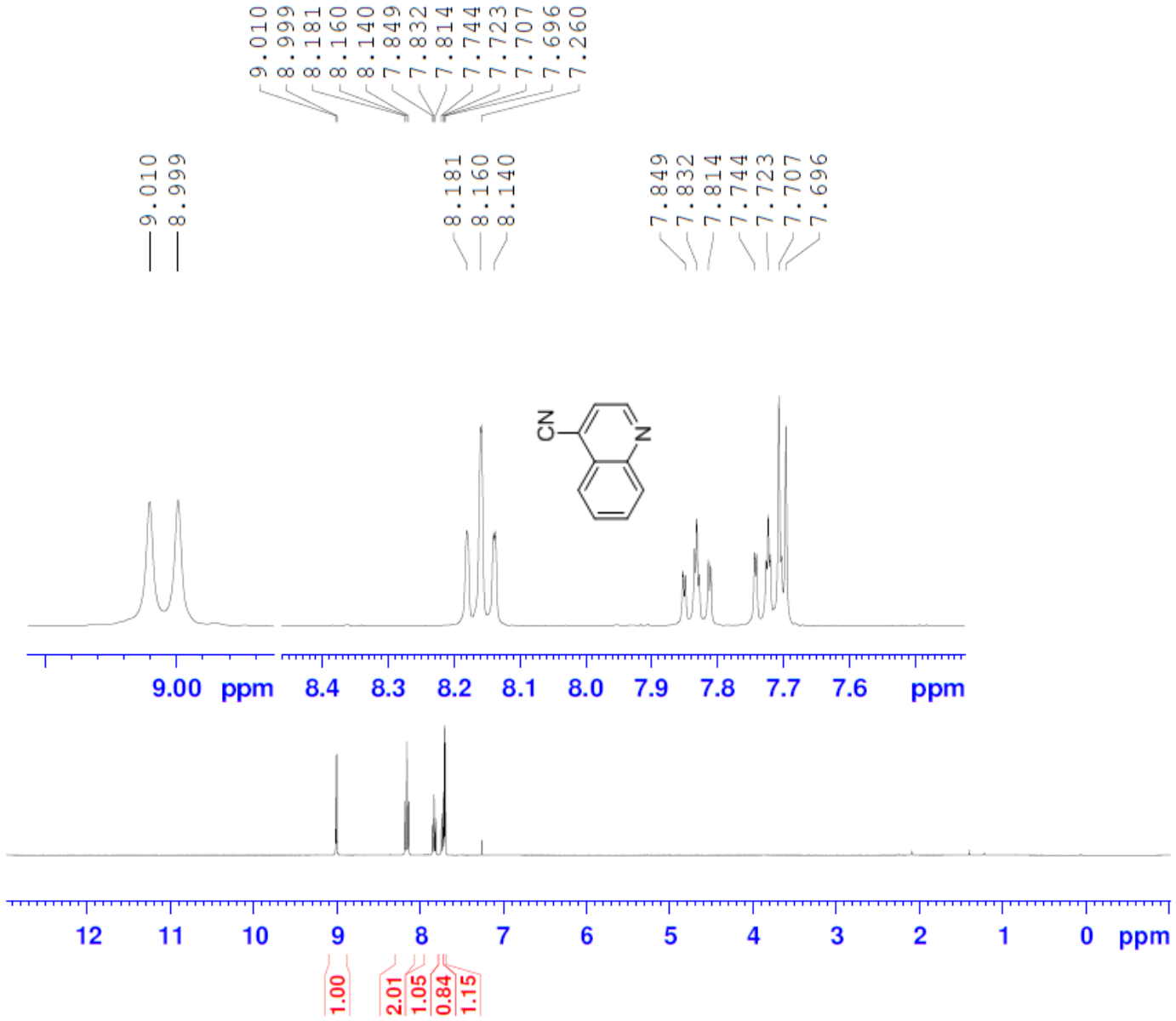
NAME	pyy516Cyan
EXPNO	1
PROCNO	1
Date_	20101026
Time	18.36
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	4
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	28.5
DW	89.333 usec
DE	6.50 usec
TE	297.7 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300094 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

pyy517Cyan-H



NAME	pyy517Cyan
EXPNO	1
PROCNO	1
Date_	20101025
Time	21.32
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	4
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	45.2
DW	89.333 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	400.1324008 MHz
SI	32768
SF	400.1300096 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

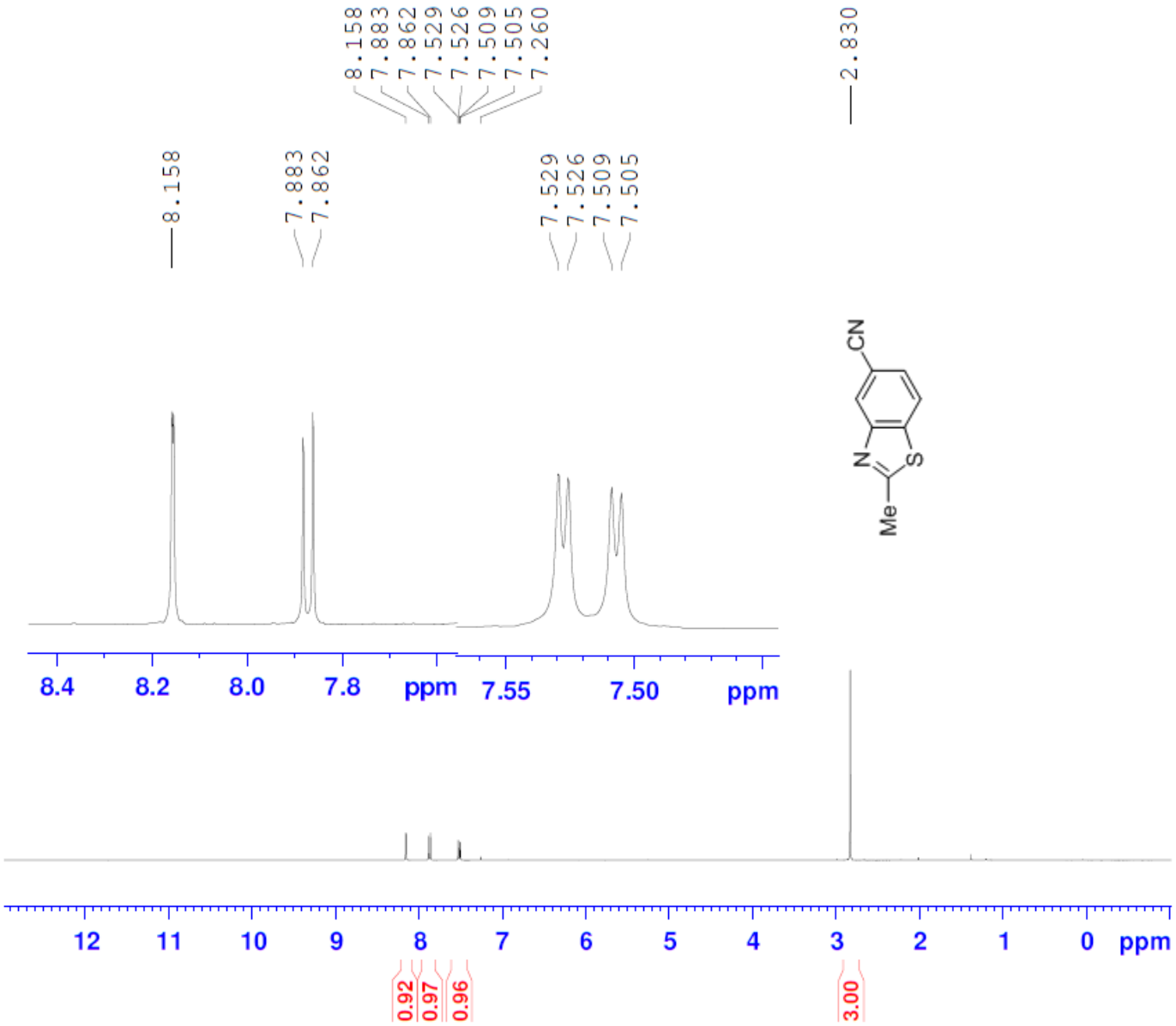
pyy521Cyan-H



BRUKER

NAME	pyy521Cyan
EXPNO	1
PROCNO	1
Date_	20101029
Time	12.14
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	4
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	45.2
DW	89.333 usec
DE	6.50 usec
TE	298.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300094 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

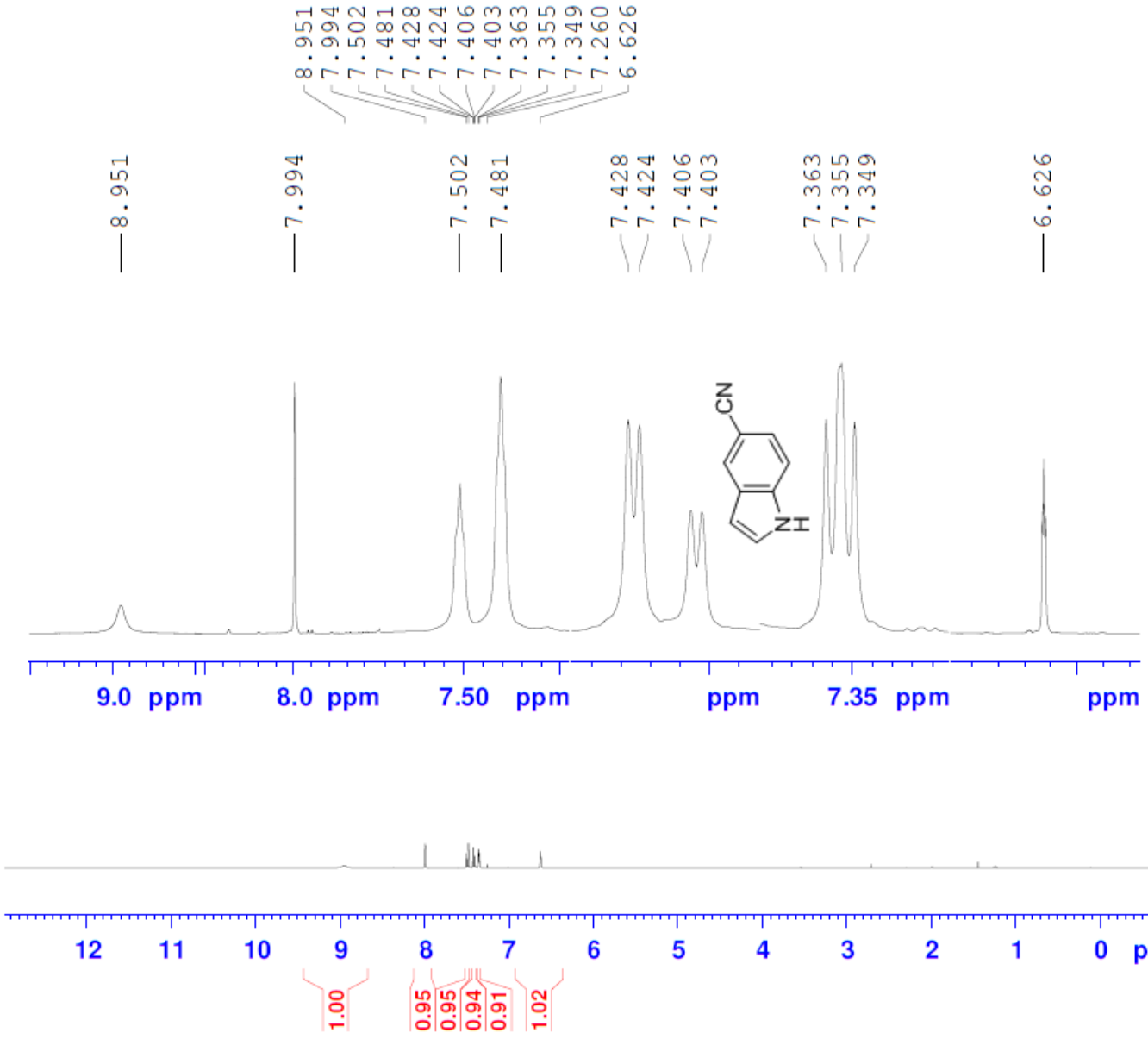
pyy530Cyan-H



BRUKER

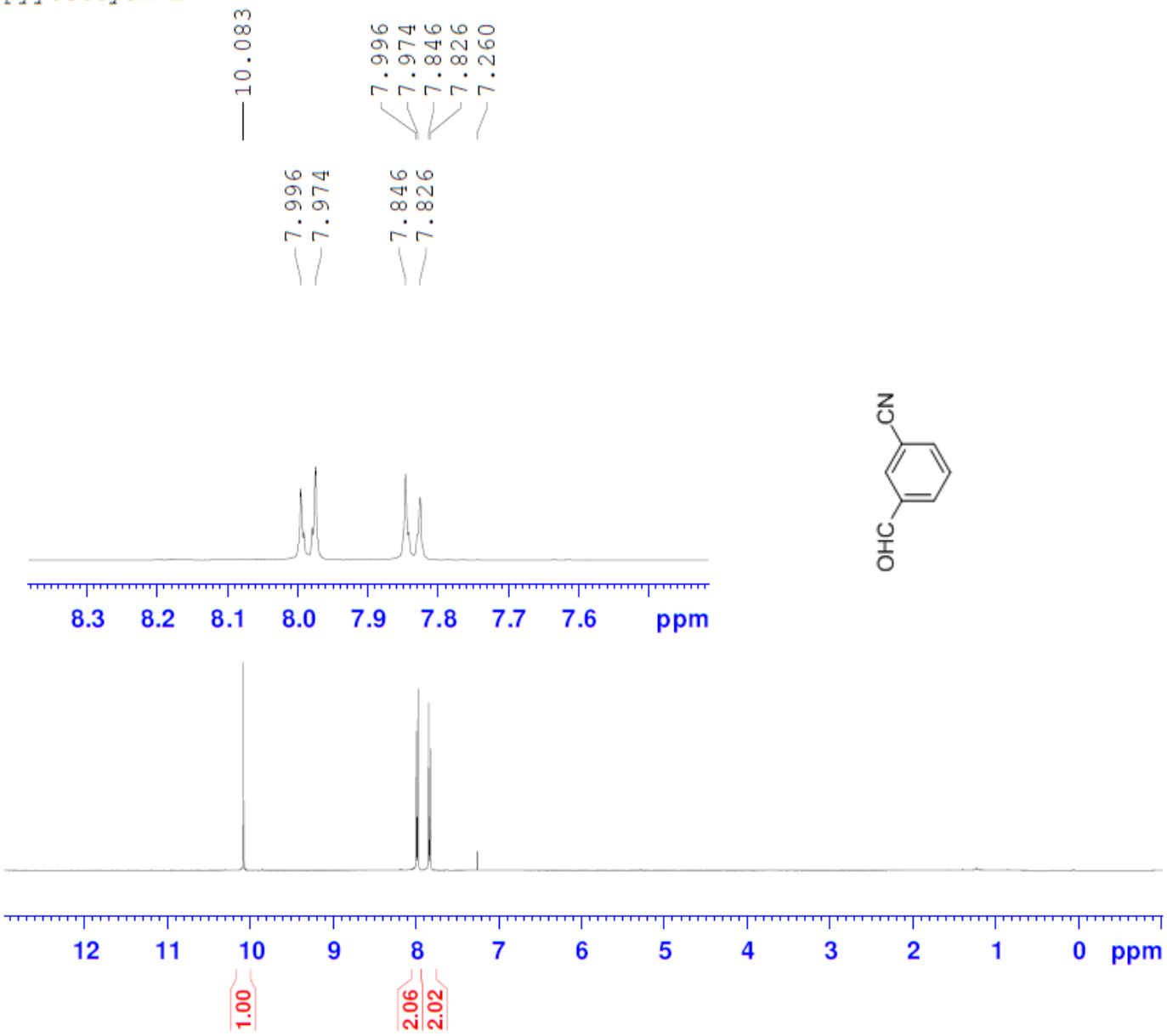
NAME	pyy530Cyan
EXPNO	1
PROCNO	1
Date_	20101029
Time	12.25
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	4
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	45.2
DW	89.333 usec
DE	6.50 usec
TE	298.0 K
D1	1.00000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300094 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

pyy533Cyan-H



NAME	pyy533Cyan	
EXPNO	1	
PROCNO	1	
Date_	20101029	
Time	12.33	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zg30	
TD	32768	
SOLVENT	CDCl3	
NS	4	
DS	2	
SWH	5597.015	Hz
FIDRES	0.170807	Hz
AQ	2.9273248	sec
RG	45.2	
DW	89.333	usec
DE	6.50	usec
TE	298.0	K
D1	1.00000000	sec
TD0	1	
========	CHANNEL f1 ========	
NUC1	1H	
P1	14.70	usec
PL1	0.00	dB
PL1W	11.88122272	W
SFO1	400.1324008	MHz
SI	32768	
SF	400.1300095	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	

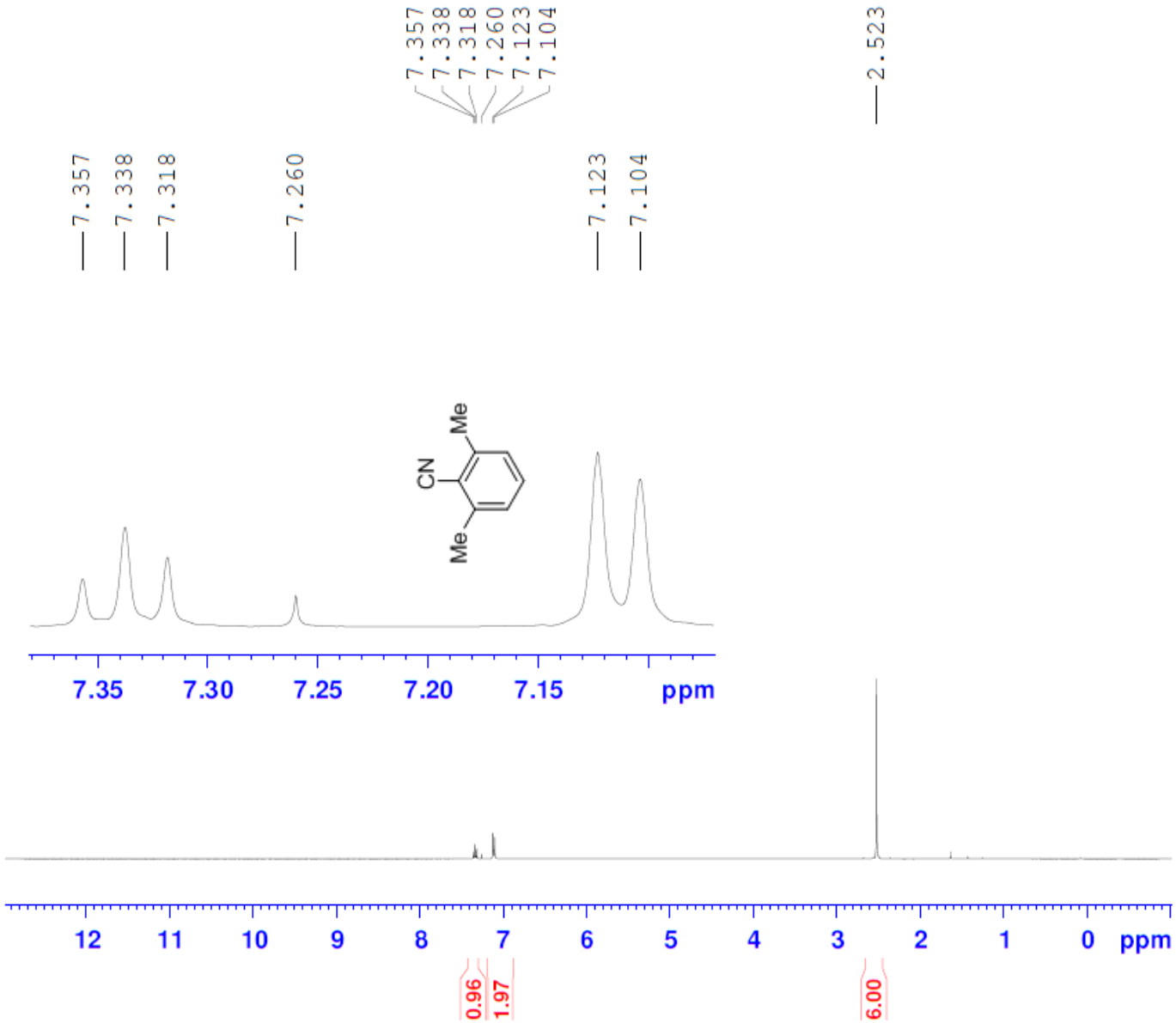
pyy536Cyan-H



BRUKER

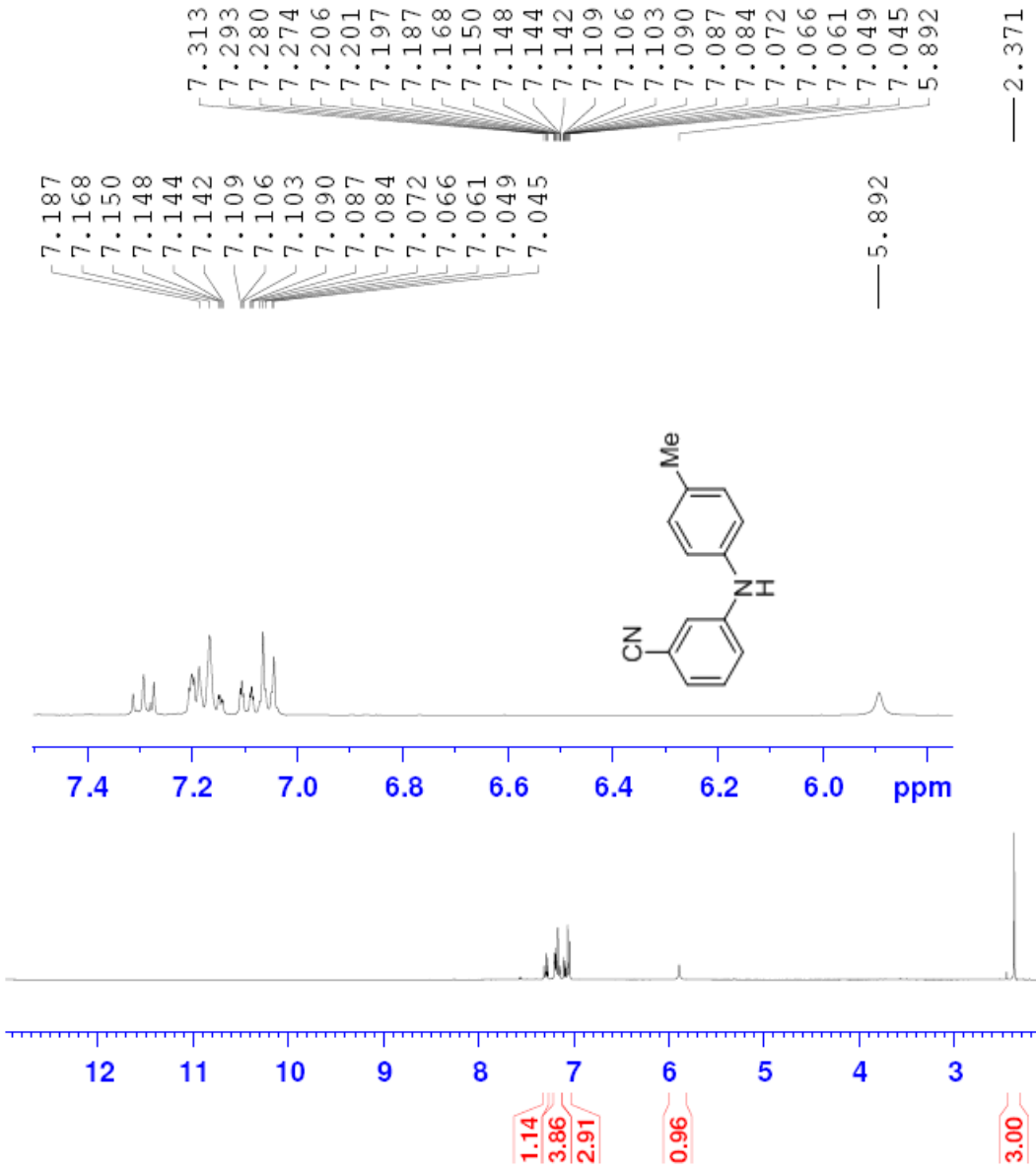
NAME	pyy536Cyan
EXPNO	1
PROCNO	1
Date_	20101103
Time	17.00
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	4
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	80.6
DW	89.333 usec
DE	6.50 usec
TE	297.5 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300095 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

pyy485Cyan-H



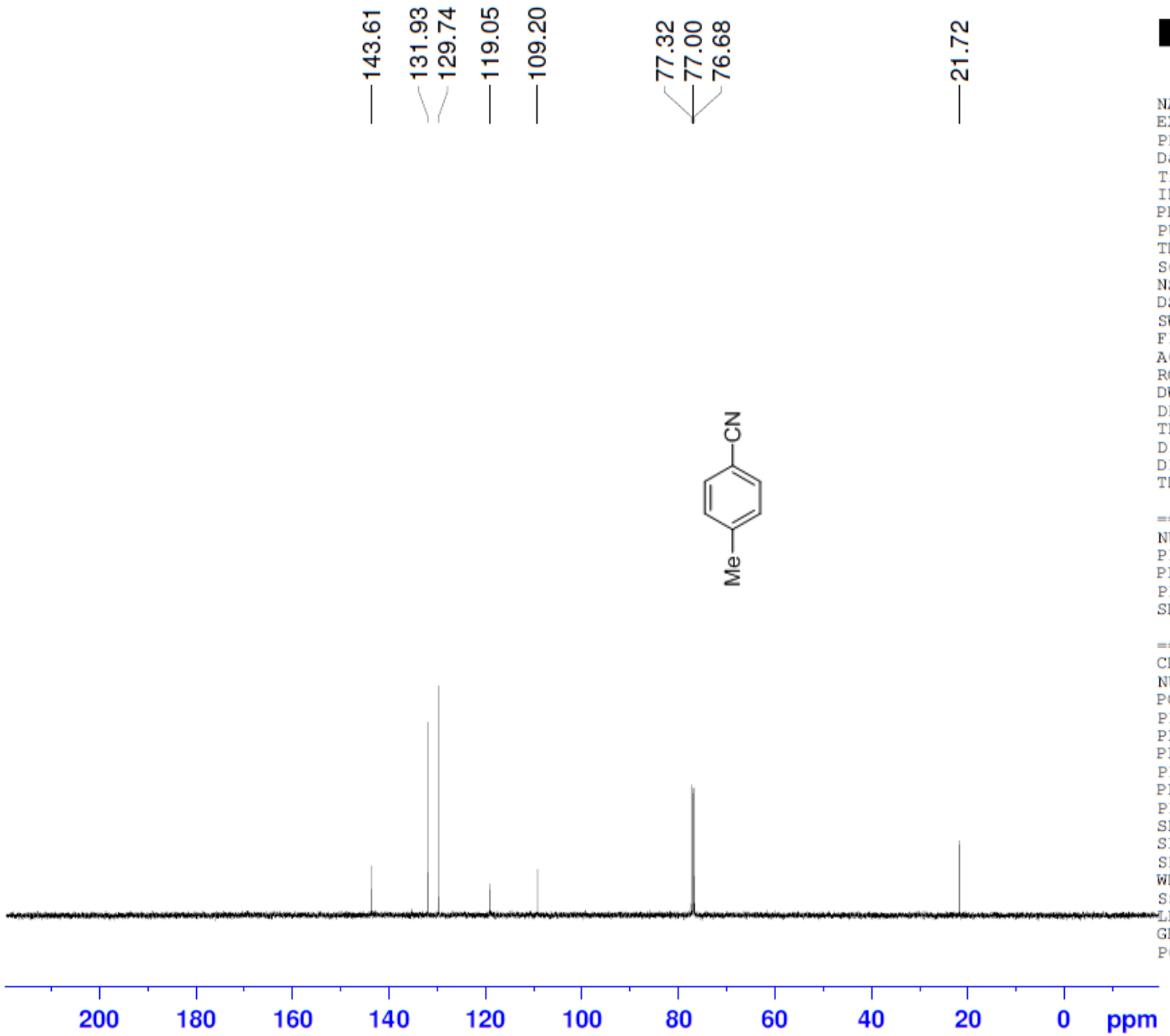
NAME	pyy485Cyan
EXPNO	1
PROCNO	1
Date_	20100929
Time	16.05
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	45.2
DW	89.333 usec
DE	6.50 usec
TE	297.2 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300095 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

pyy548Cyan-H



NAME	pyy548Cyan
EXPNO	1
PROCNO	1
Date_	20101111
Time	18.28
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	4
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	45.2
DW	89.333 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	400.1324008 MHz
SI	32768
SF	400.1300014 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

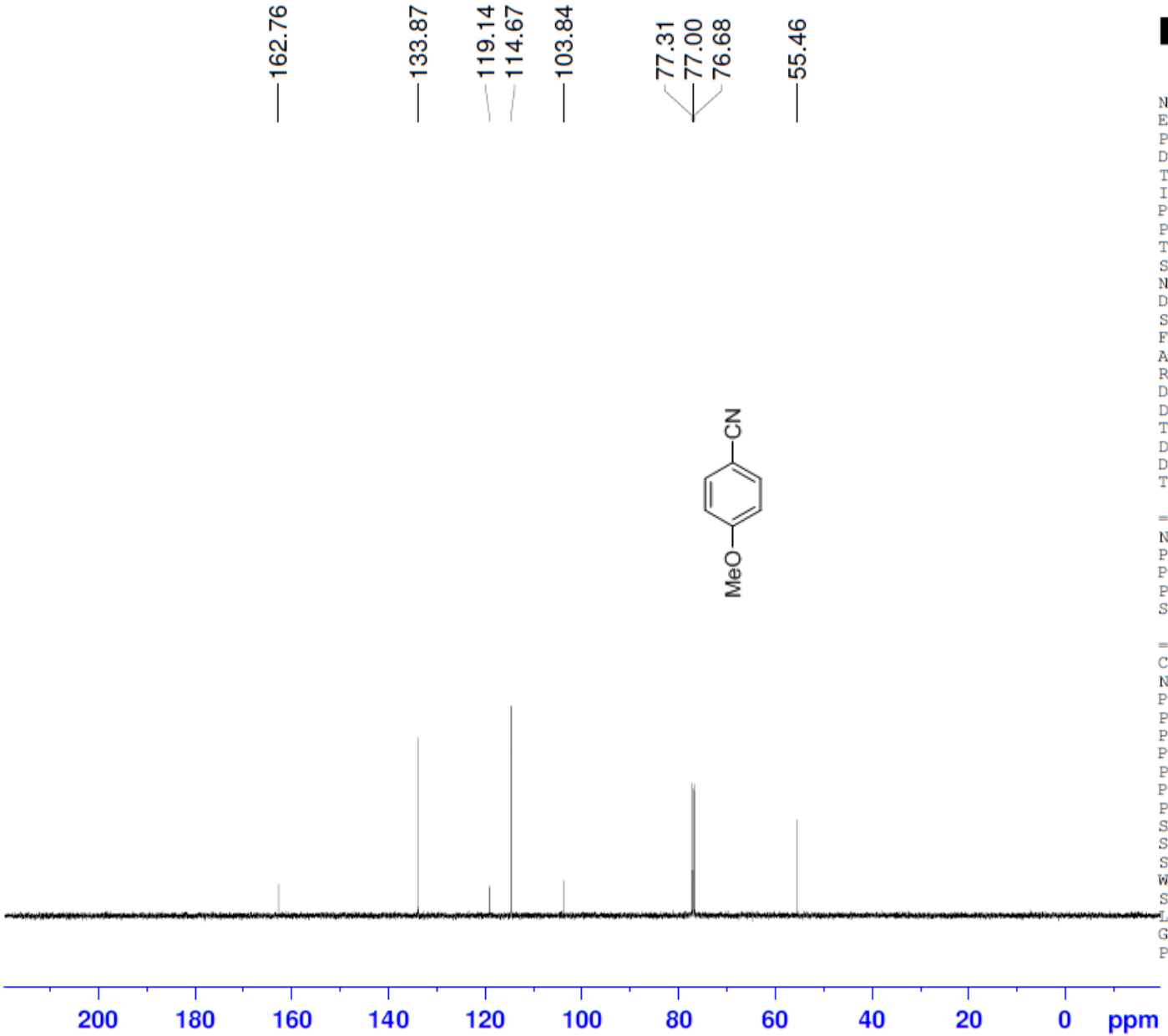
pyy550Cyan-C



BRUKER

NAME	pyy550Cyan
EXPNO	2
PROCNO	1
Date_	20101124
Time	15.55
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	297.7 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	15.00 dB
PL2W	11.88122272 W
PL12W	0.37571725 W
PL13W	0.37571725 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127797 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

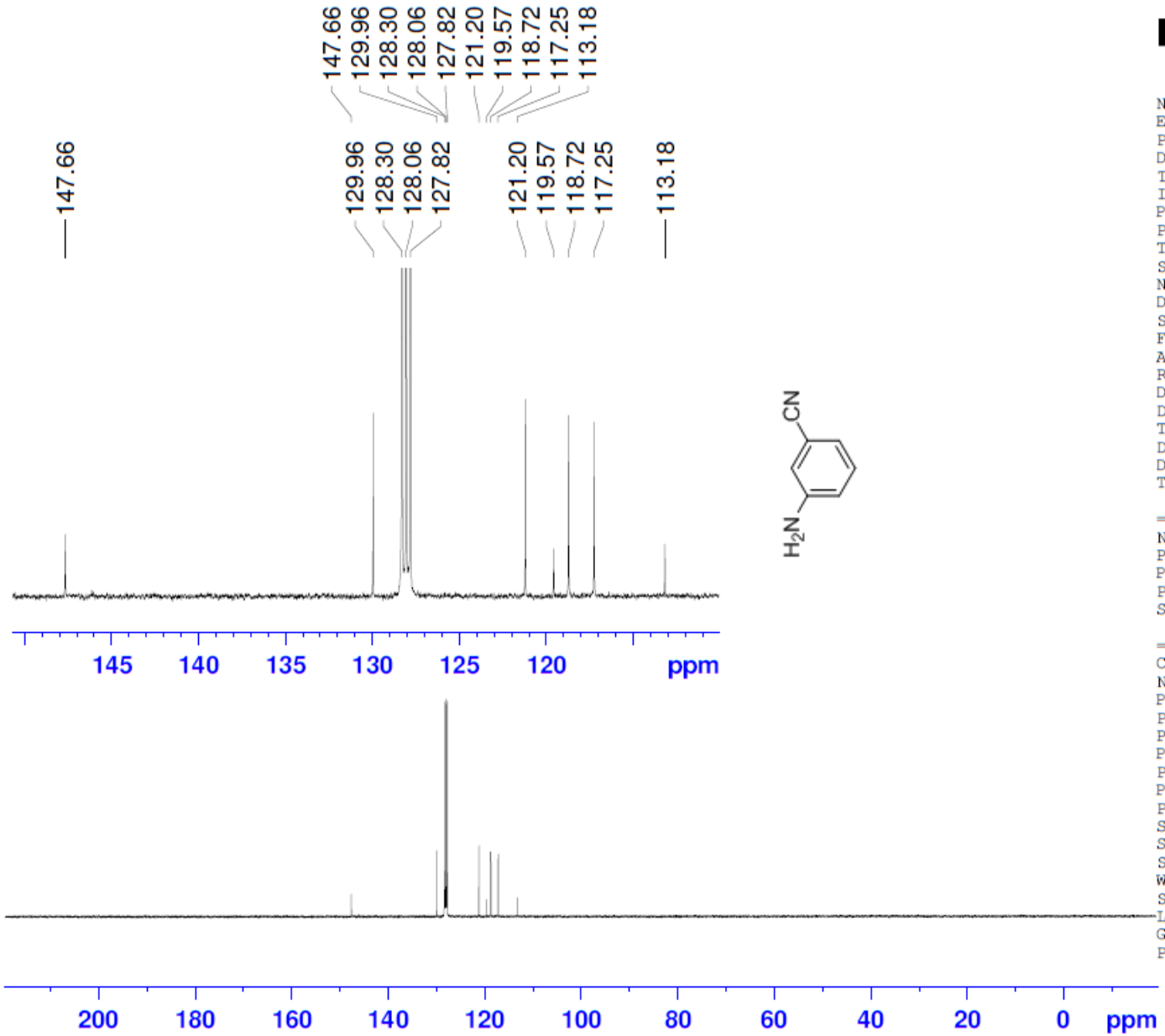
pyy487Cyan-C



BRUKER

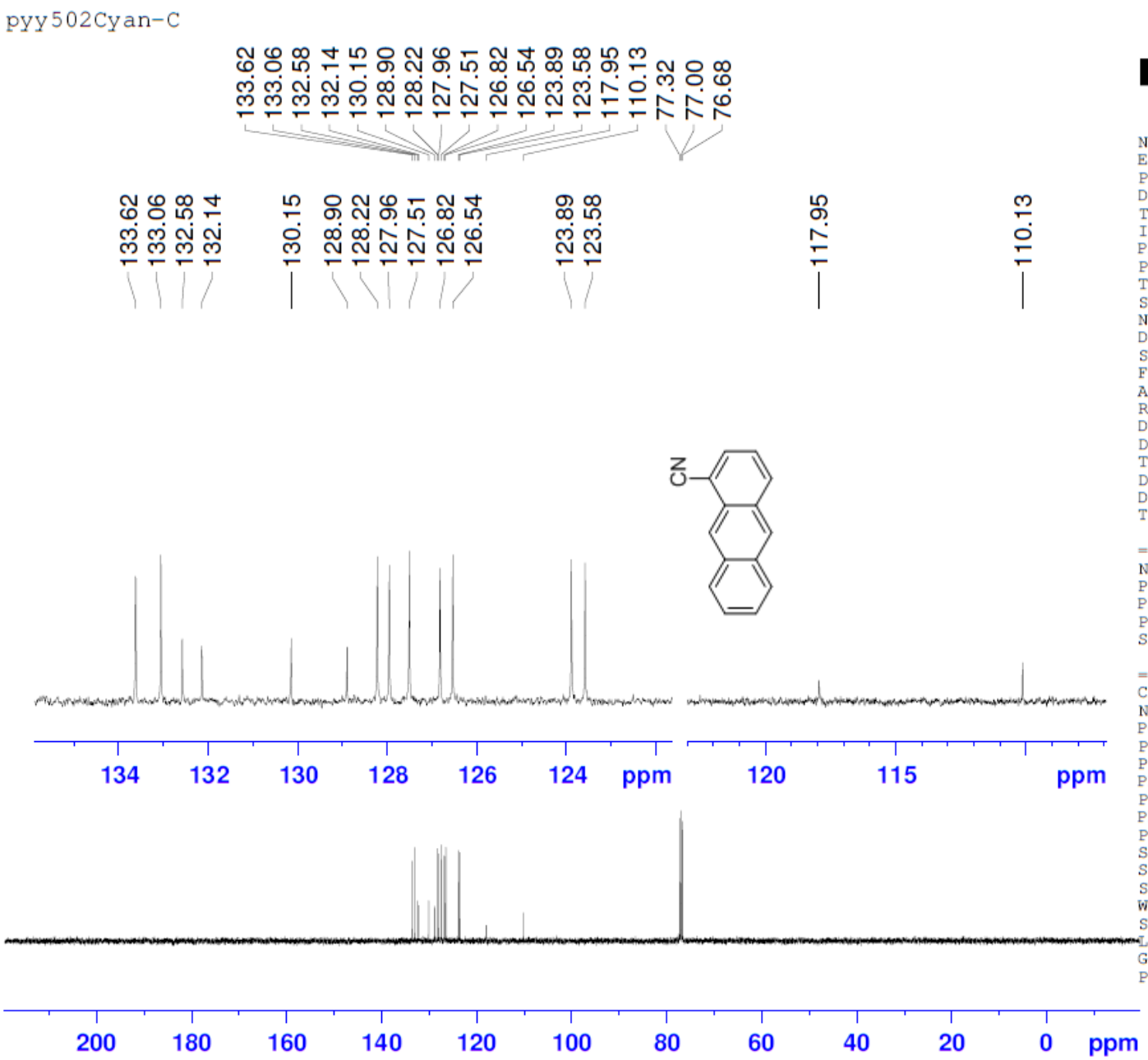
NAME	pyy487Cyan
EXPNO	2
PROCNO	1
Date_	20100929
Time	16.20
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	297.8 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	15.00 dB
PL2W	11.88122272 W
PL12W	0.37571725 W
PL13W	0.37571725 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127788 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

pyy501Cyan-C



NAME	pyy501Cyan
EXPNO	2
PROCNO	1
Date_	20101008
Time	16.40
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	C6D6
NS	16
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	298.3 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	100.6127342 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

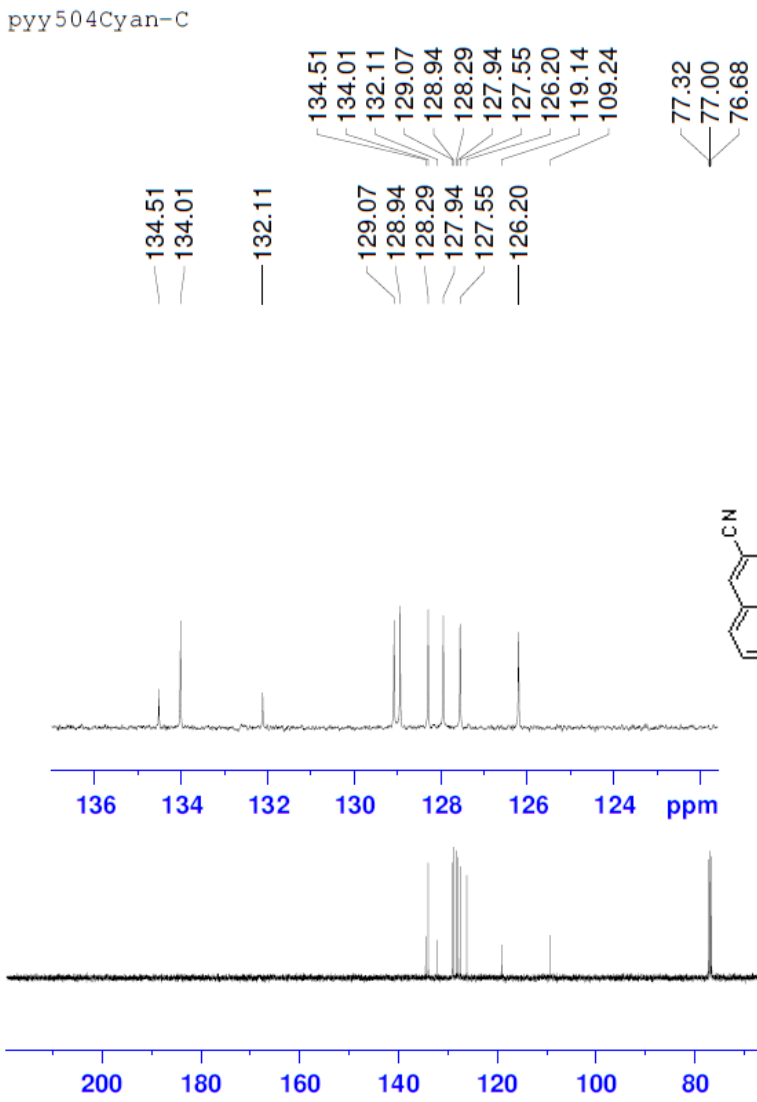
pyy502Cyan-C



BRUKER

NAME	pyy502Cyan
EXPNO	2
PROCNO	1
Date_	20101011
Time	11.13
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	298.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	15.00 dB
PL2W	11.88122272 W
PL12W	0.37571725 W
PL13W	0.37571725 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127810 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

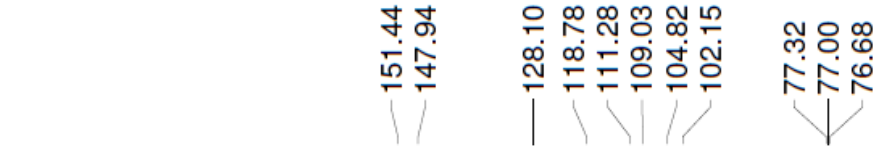
pyy504Cyan-C

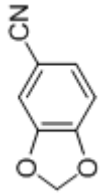


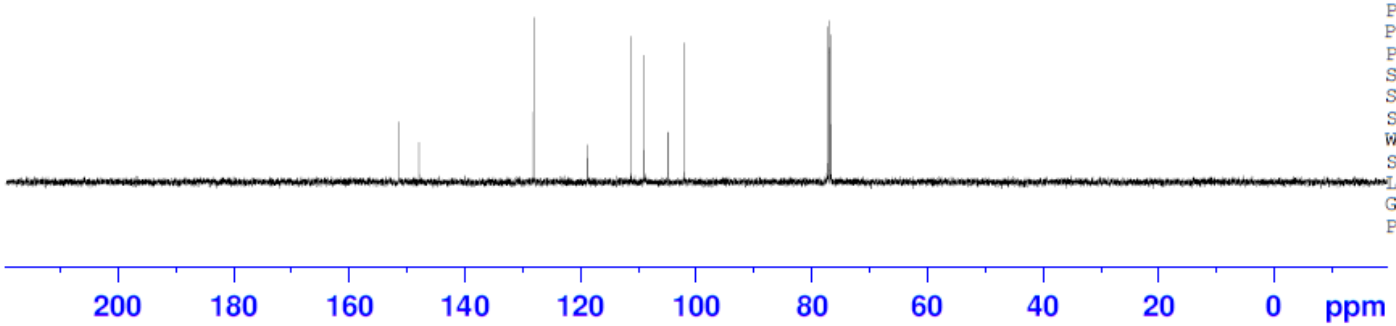
BRUKER

NAME	pyy504Cyan
EXPNO	2
PROCNO	1
Date_	20101011
Time	11.23
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	8
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	298.1 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	100.6127818 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

pyy508Cyan-C

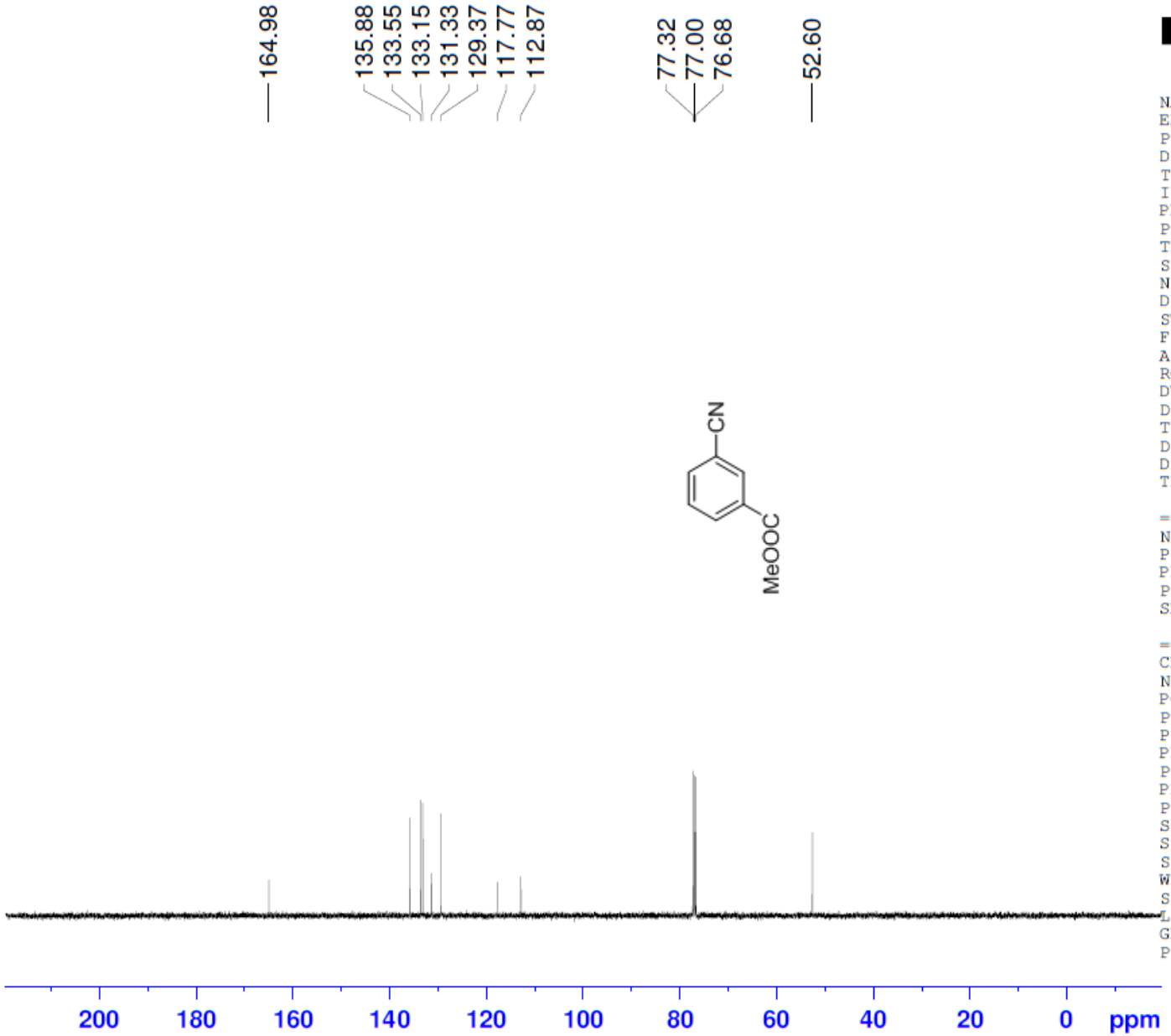






NAME	pyy508Cyan
EXPNO	2
PROCNO	1
Date_	20101014
Time	11.18
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	298.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	15.00 dB
PL2W	11.88122272 W
PL12W	0.37571725 W
PL13W	0.37571725 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127795 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

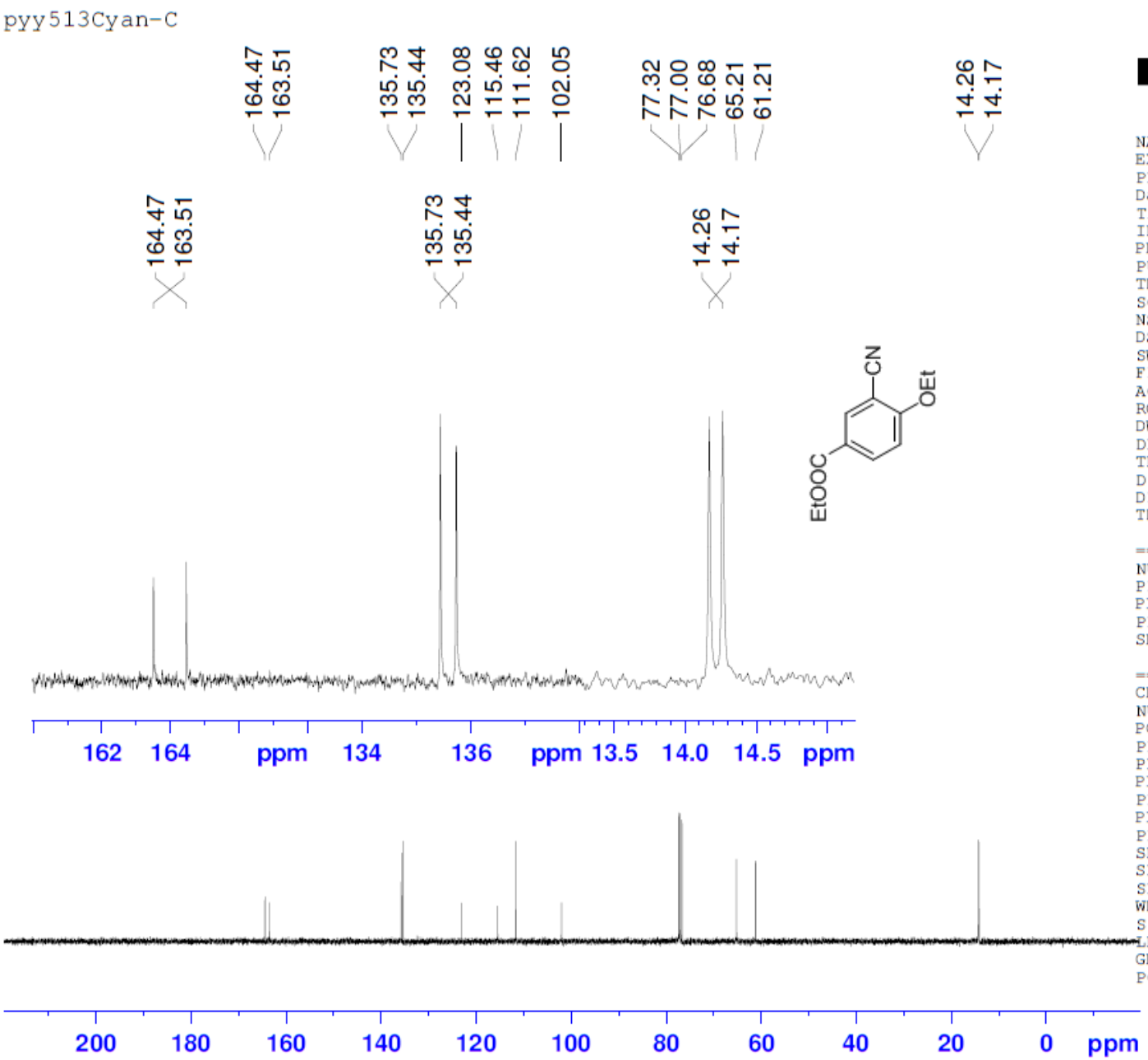
pyy510Cyan-C



BRUKER

NAME	pyy510Cyan
EXPNO	2
PROCNO	1
Date_	20101014
Time	11.27
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	8
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	298.1 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

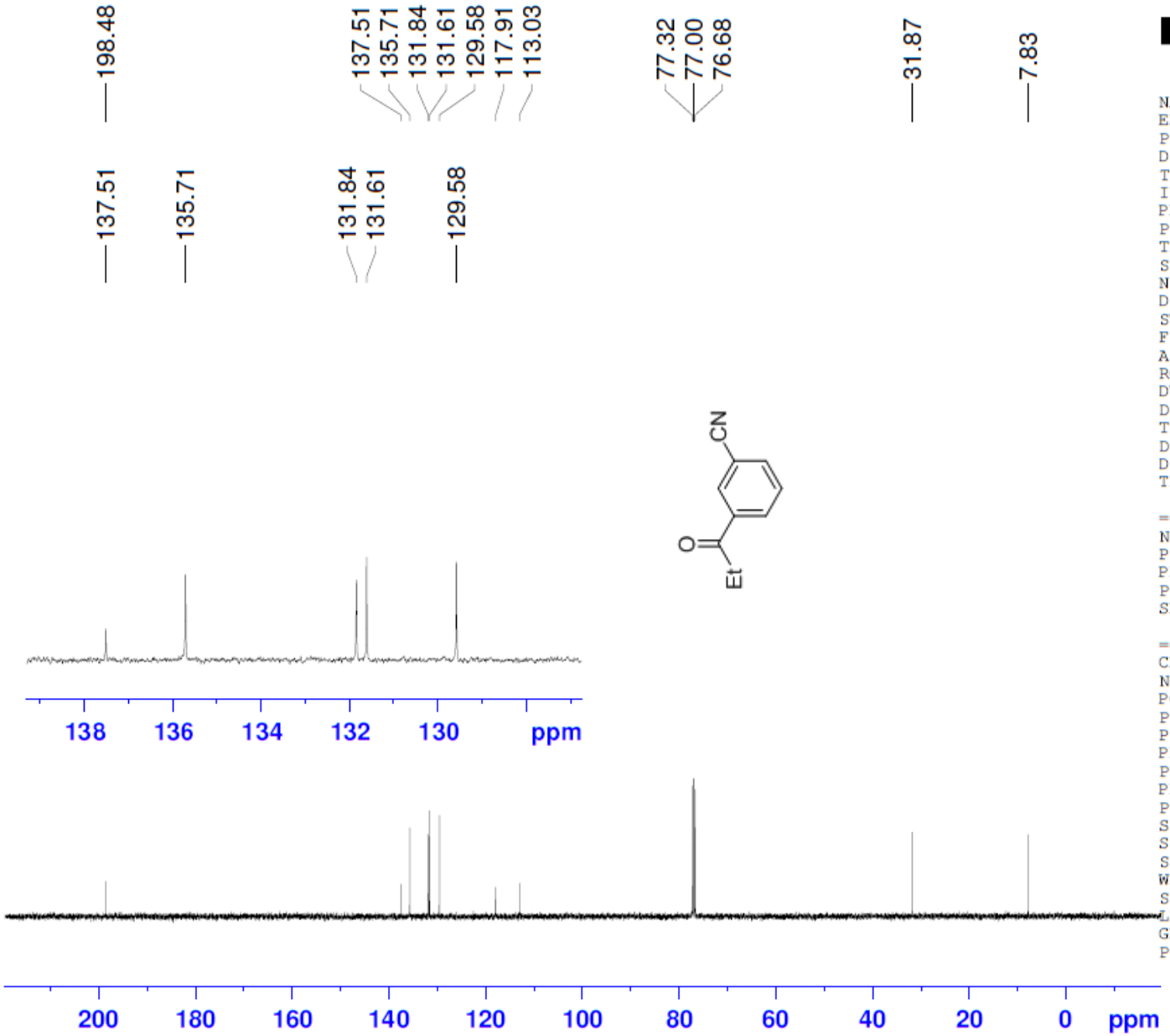
pyy513Cyan-C



BRUKER

NAME	pyy513Cyan
EXPNO	2
PROCNO	1
Date_	20101018
Time	12.06
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	8
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	298.3 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	100.6127788 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

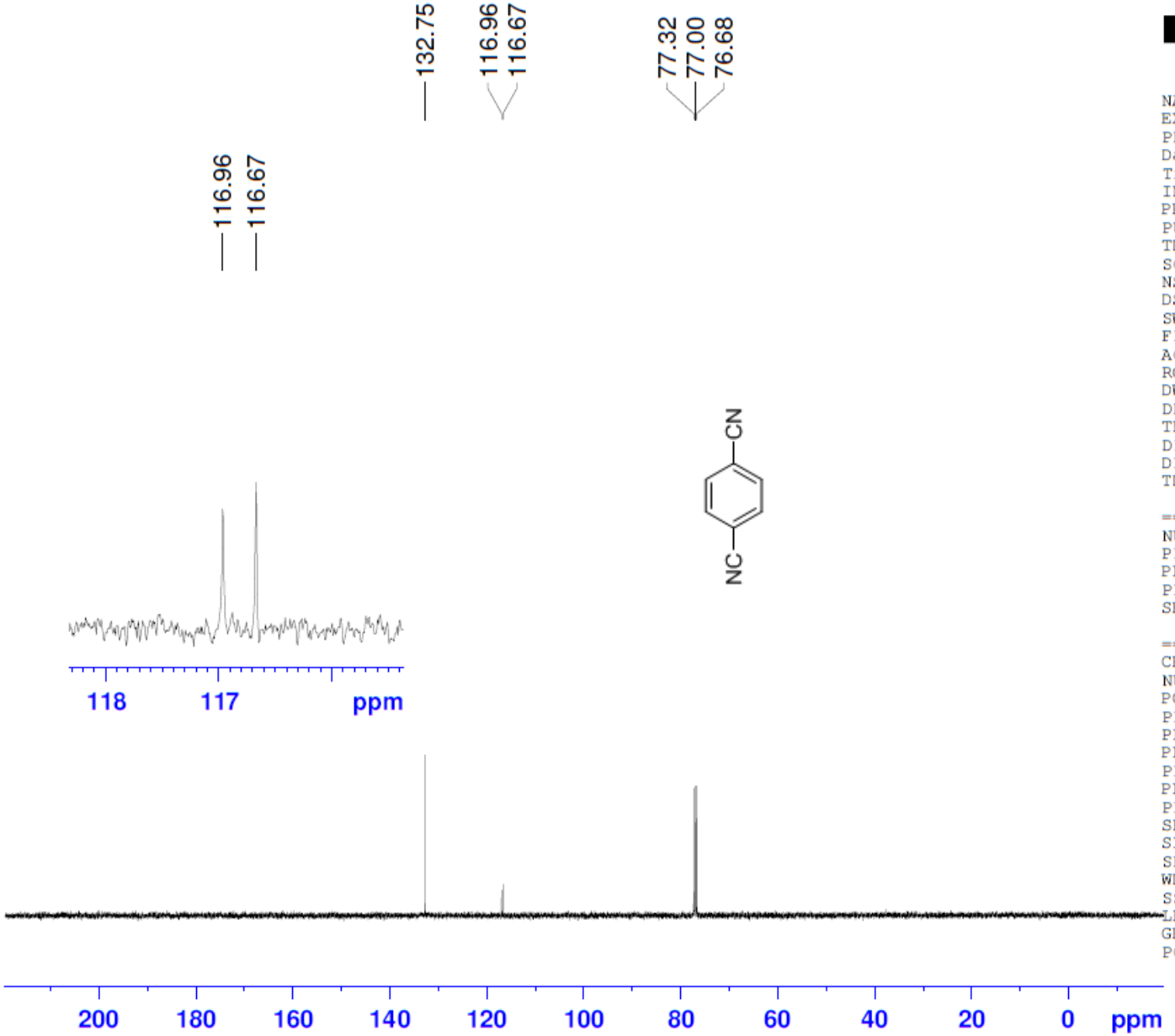
pyy514Cyan-C



BRUKER

NAME	pyy514Cyan
EXPNO	2
PROCNO	1
Date_	20101018
Time	12.23
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	8
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	298.3 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	100.6127773 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

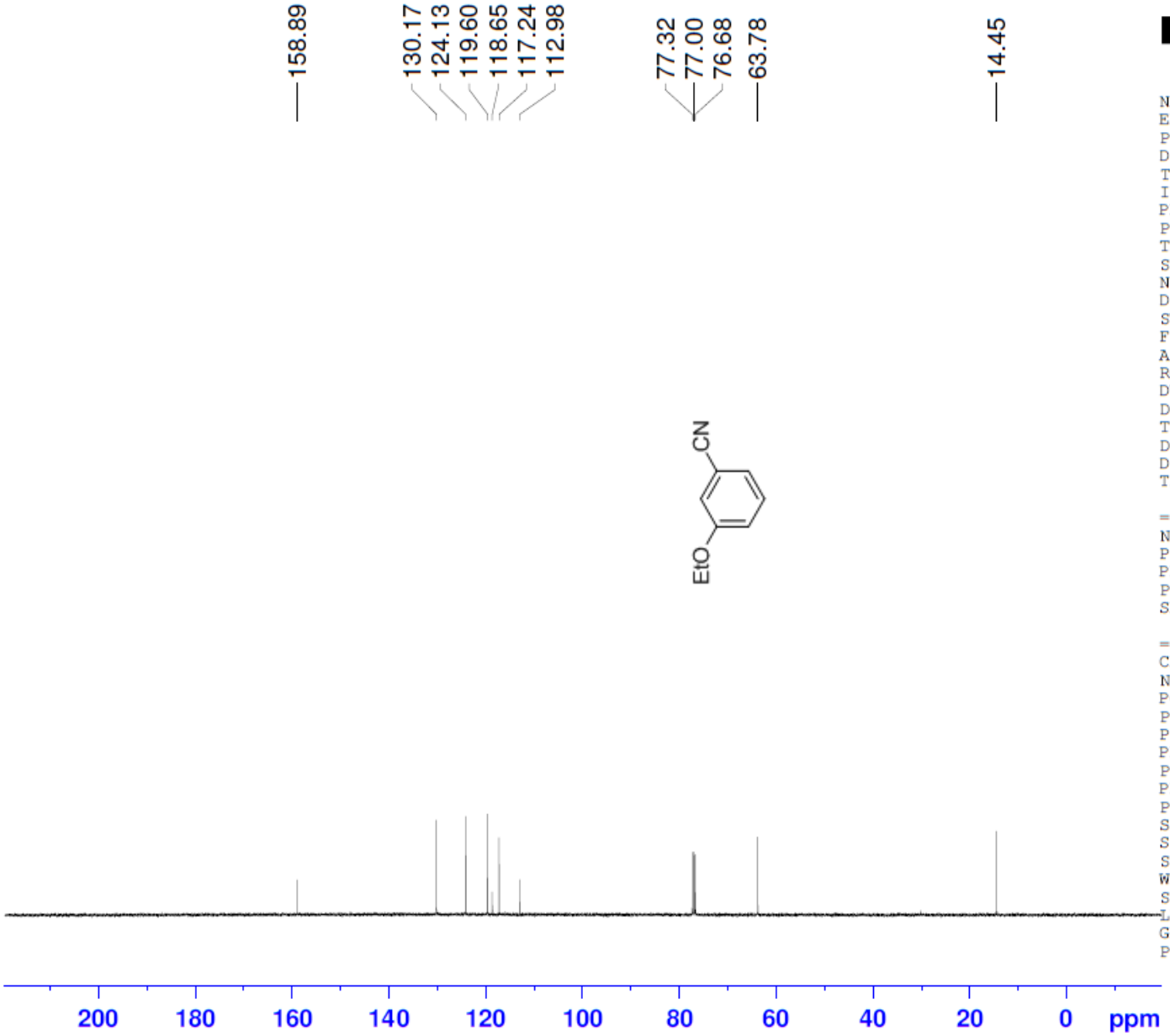
pyy515Cyan-C



BRUKER

NAME	pyy515Cyan
EXPNO	2
PROCNO	1
Date_	20101018
Time	12.13
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	298.4 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	15.00 dB
PL2W	11.88122272 W
PL12W	0.37571725 W
PL13W	0.37571725 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127749 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

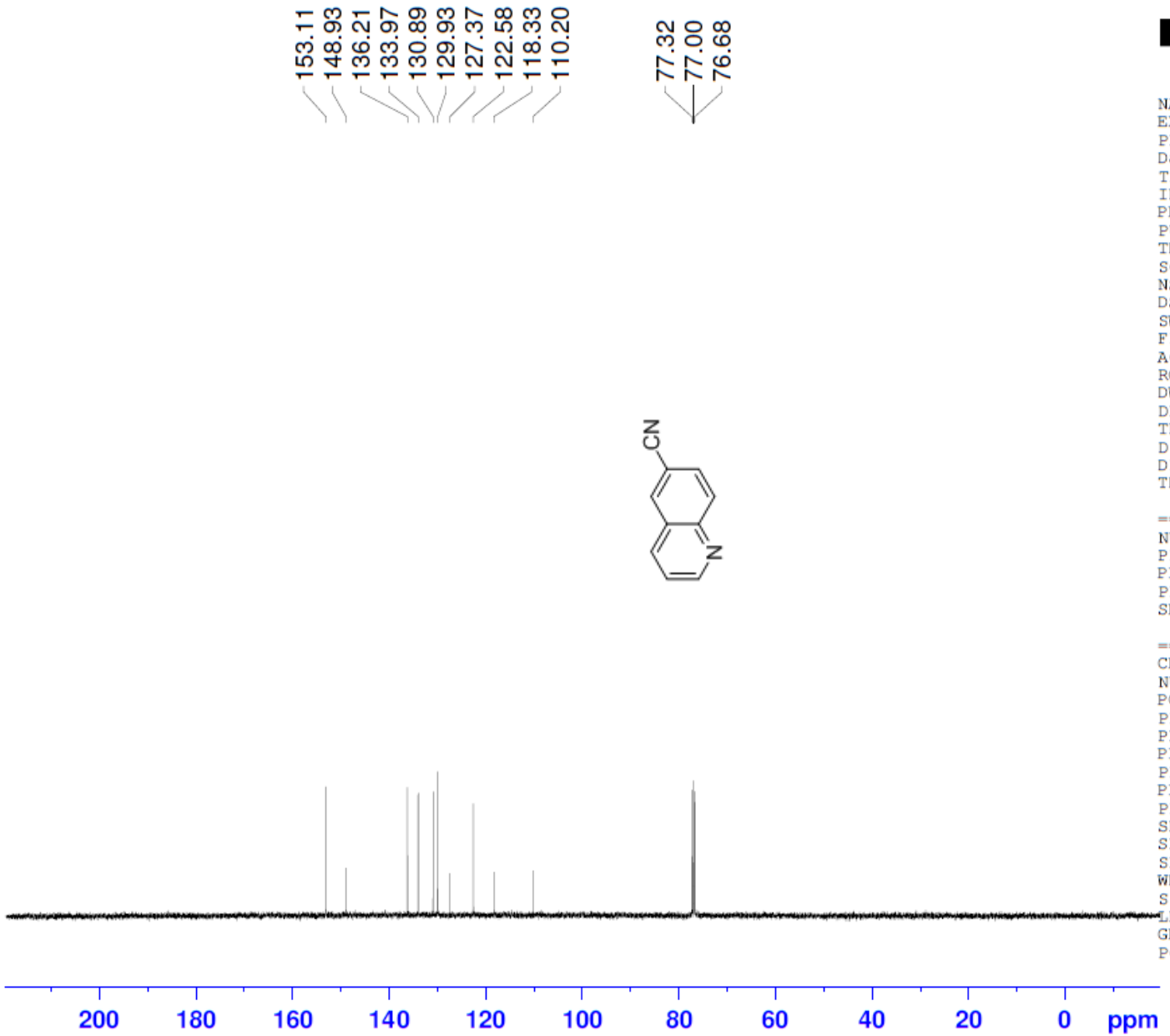
pyy516Cyan-C



BRUKER

NAME	pyy516Cyan
EXPNO	2
PROCNO	1
Date_	20101026
Time	18.42
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	298.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	15.00 dB
PL2W	11.88122272 W
PL12W	0.37571725 W
PL13W	0.37571725 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127826 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

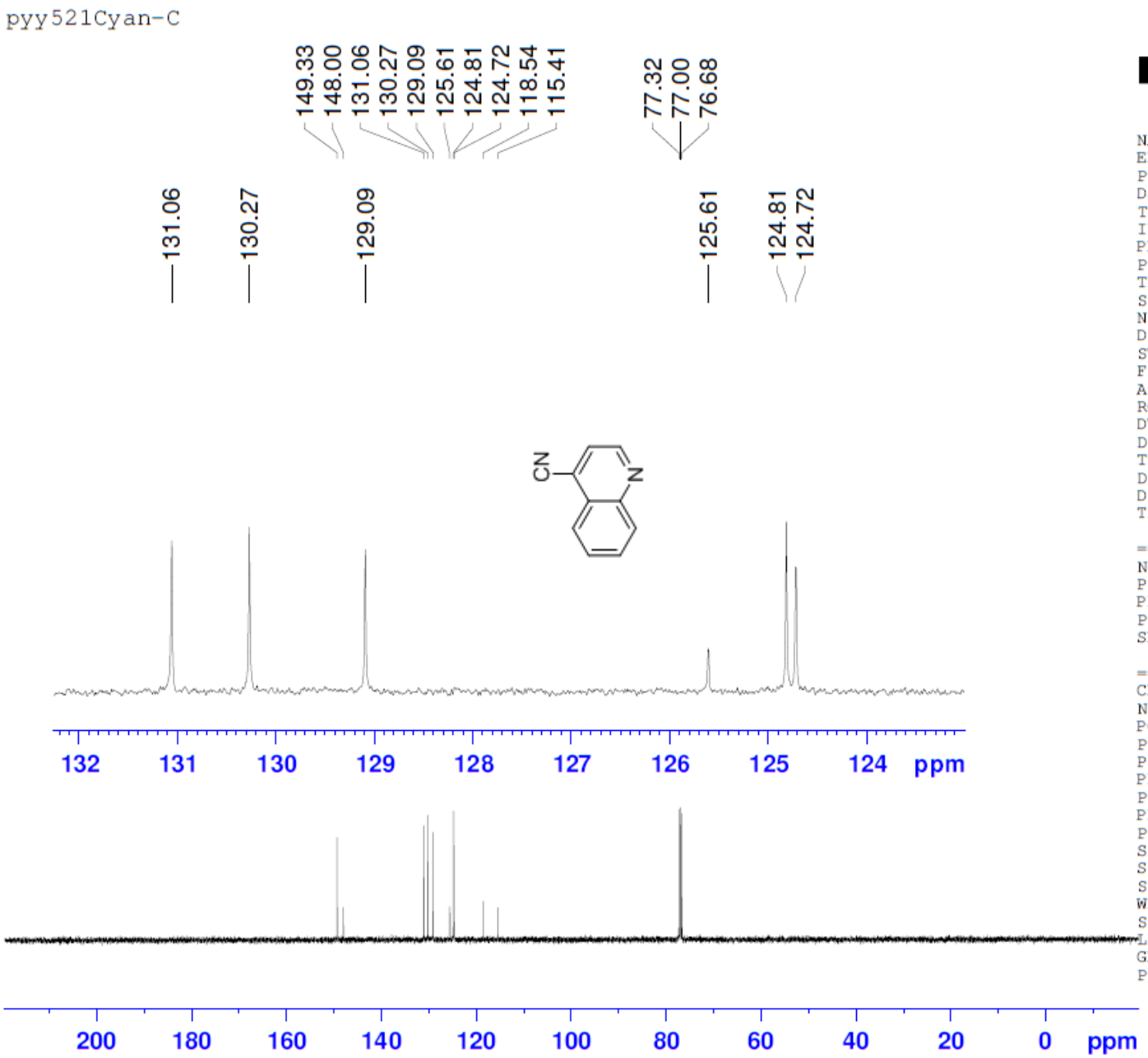
pyy517Cyan-C



BRUKER

NAME	pyy517Cyan
EXPNO	2
PROCNO	1
Date_	20101025
Time	21.36
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDC13
NS	8
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	298.1 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	100.6127832 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

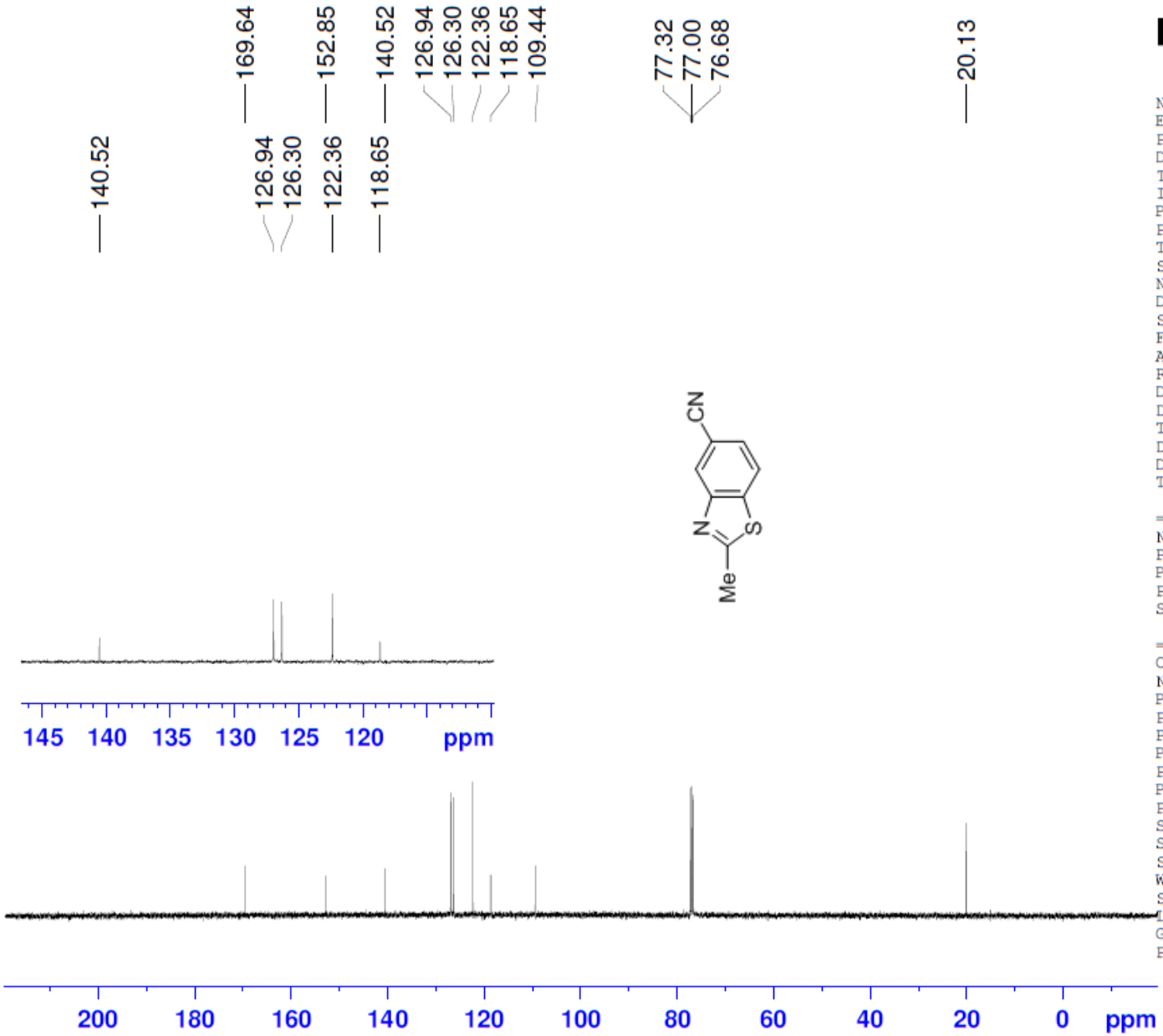
pyy521Cyan-C



BRUKER

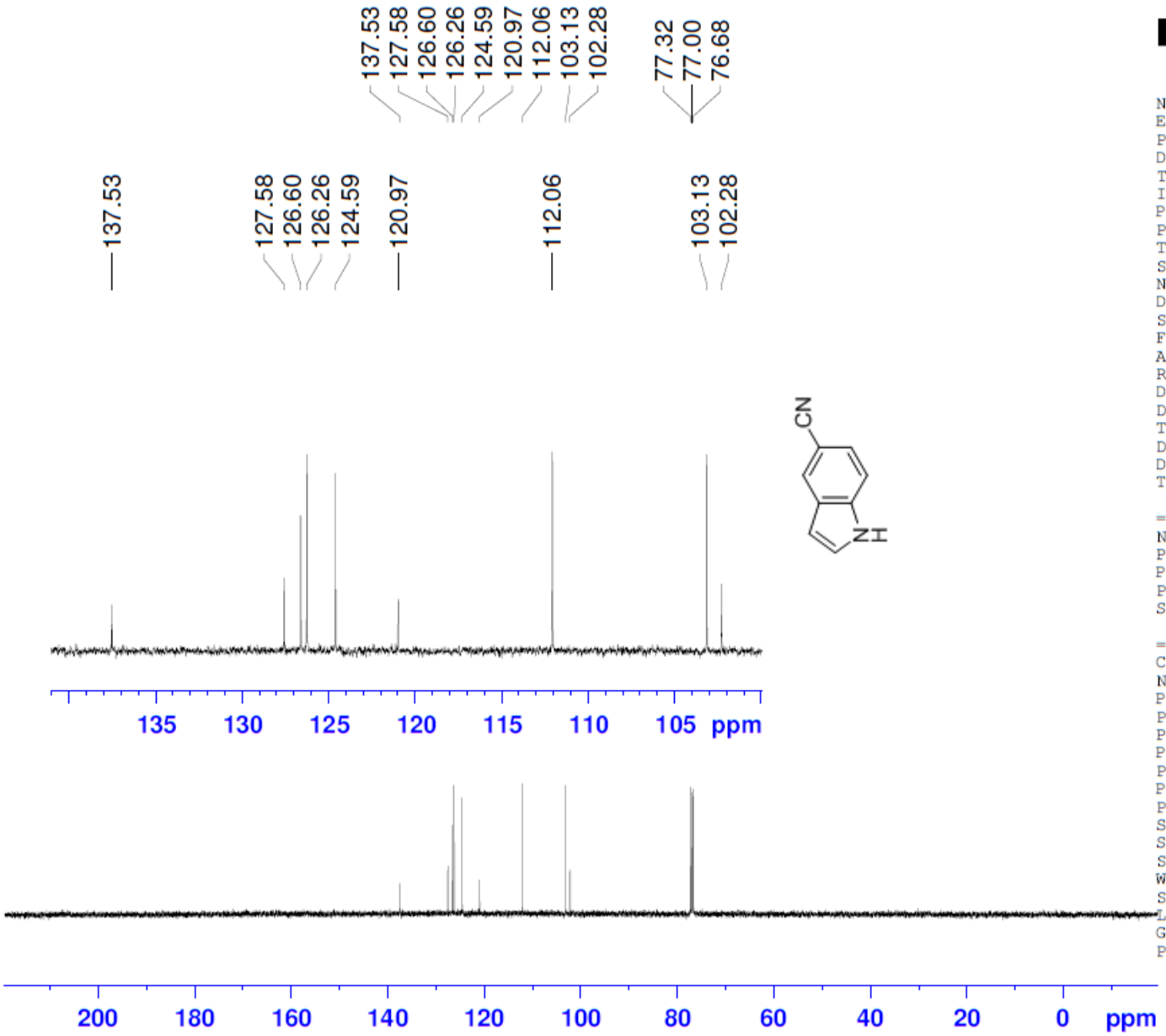
NAME	pyy521Cyan
EXPNO	2
PROCNO	1
Date_	20101029
Time	12.20
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	298.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	15.00 dB
PL2W	11.88122272 W
PL12W	0.37571725 W
PL13W	0.37571725 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127796 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

pyy530Cyan-C



NAME	pyy530Cyan
EXPNO	2
PROCNO	1
Date_	20101029
Time	12.28
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	298.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	15.00 dB
PL2W	11.88122272 W
PL12W	0.37571725 W
PL13W	0.37571725 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127840 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

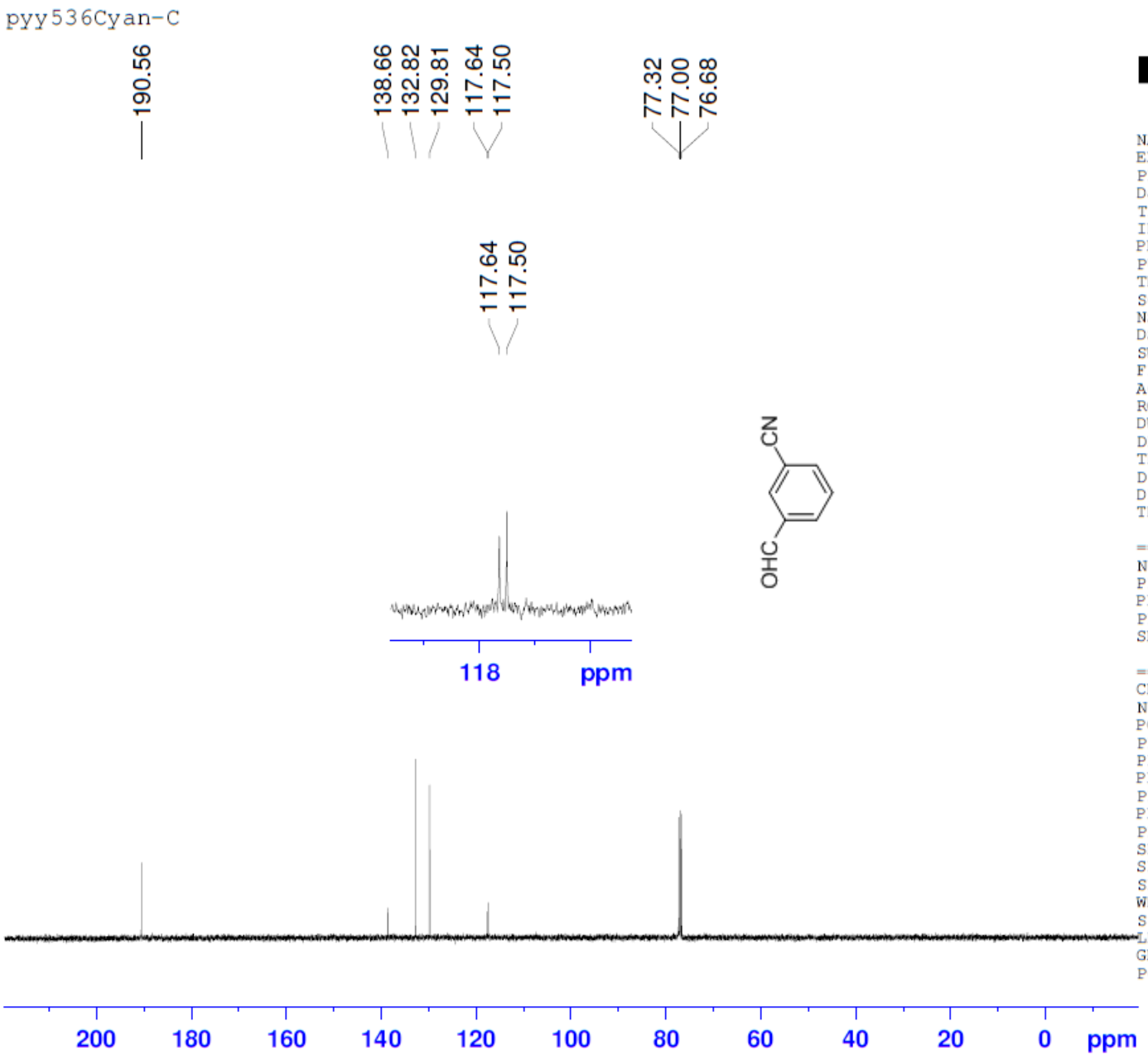
pyy533Cyan-C



BRUKER

NAME	pyy533Cyan
EXPNO	2
PROCNO	1
Date_	20101029
Time	12.42
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	298.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	15.00 dB
PL2W	11.88122272 W
PL12W	0.37571725 W
PL13W	0.37571725 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127835 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

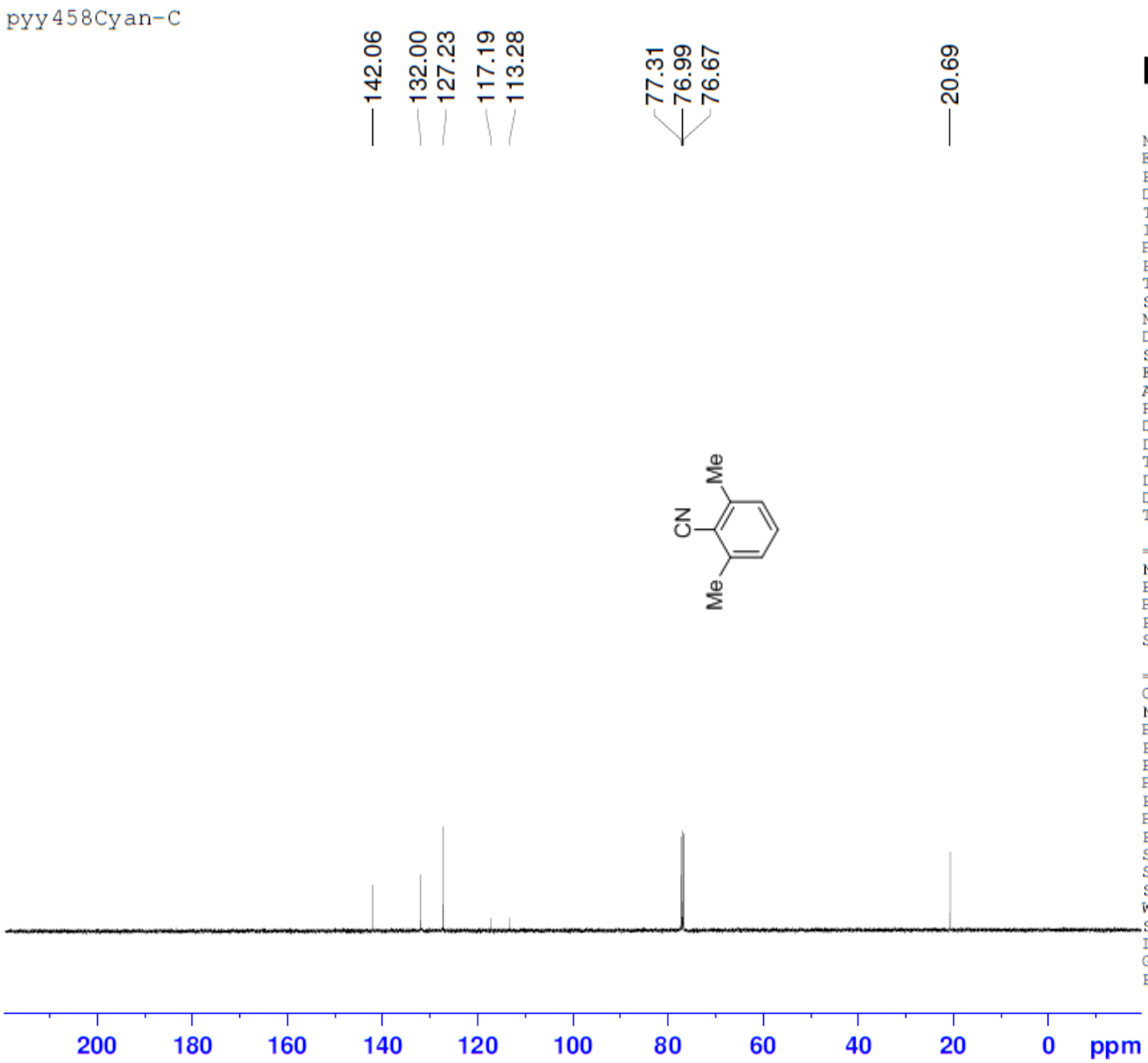
pyy536Cyan-C



BRUKER

NAME	pyy536Cyan
EXPNO	2
PROCNO	1
Date_	20101103
Time	17.04
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	297.9 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	15.00 dB
PL2W	11.88122272 W
PL12W	0.37571725 W
PL13W	0.37571725 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127780 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

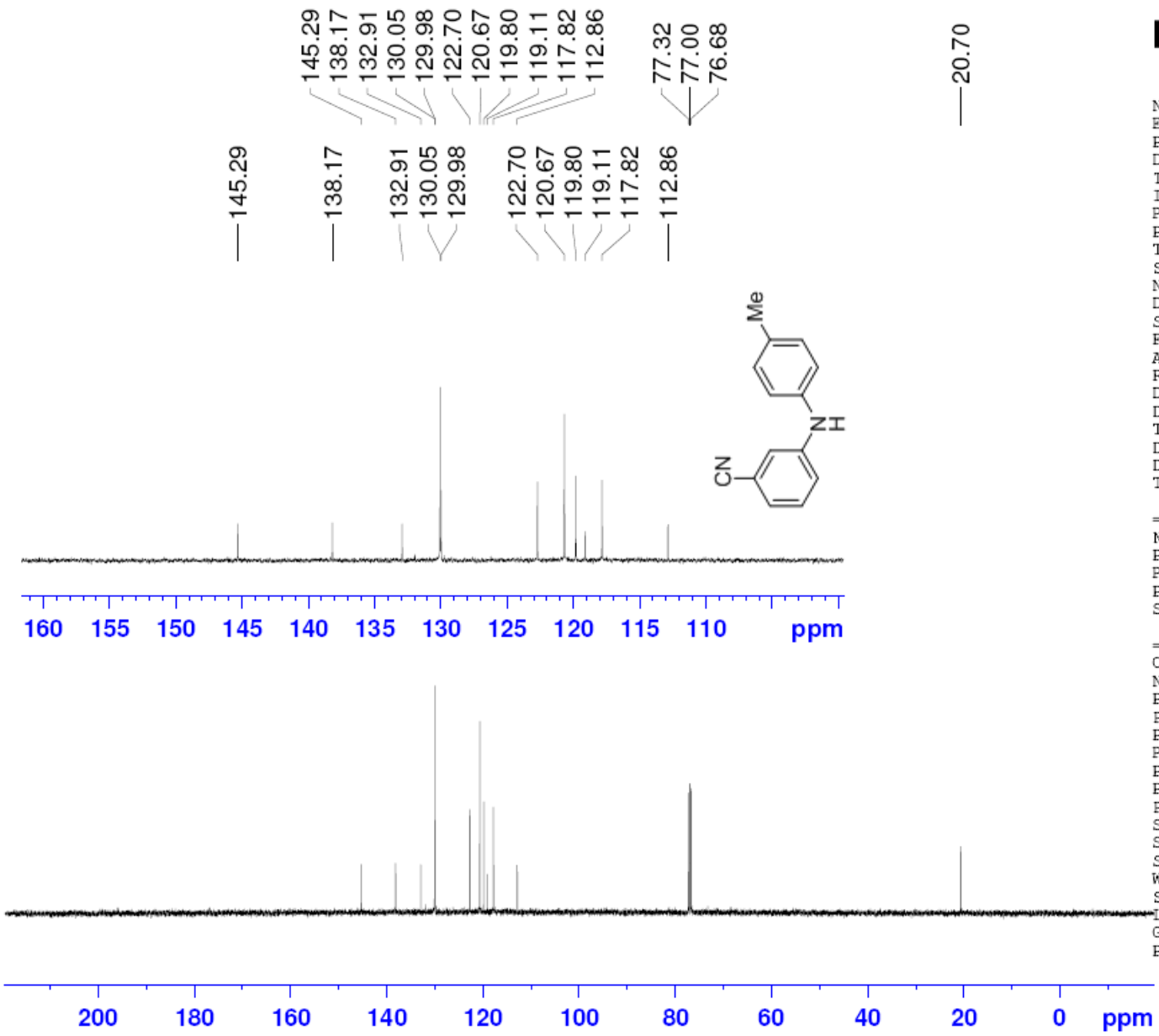
pyy458Cyan-C



BRUKER

NAME	pyy485Cyan	
EXPNO	2	
PROCNO	1	
Date_	20100929	
Time	16.12	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	16	
DS	2	
SWH	24038.461	Hz
FIDRES	0.366798	Hz
AQ	1.3631988	sec
RG	203	
DW	20.800	usec
DE	6.50	usec
TE	298.1	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	100.6127758	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

pyy548Cyan-C

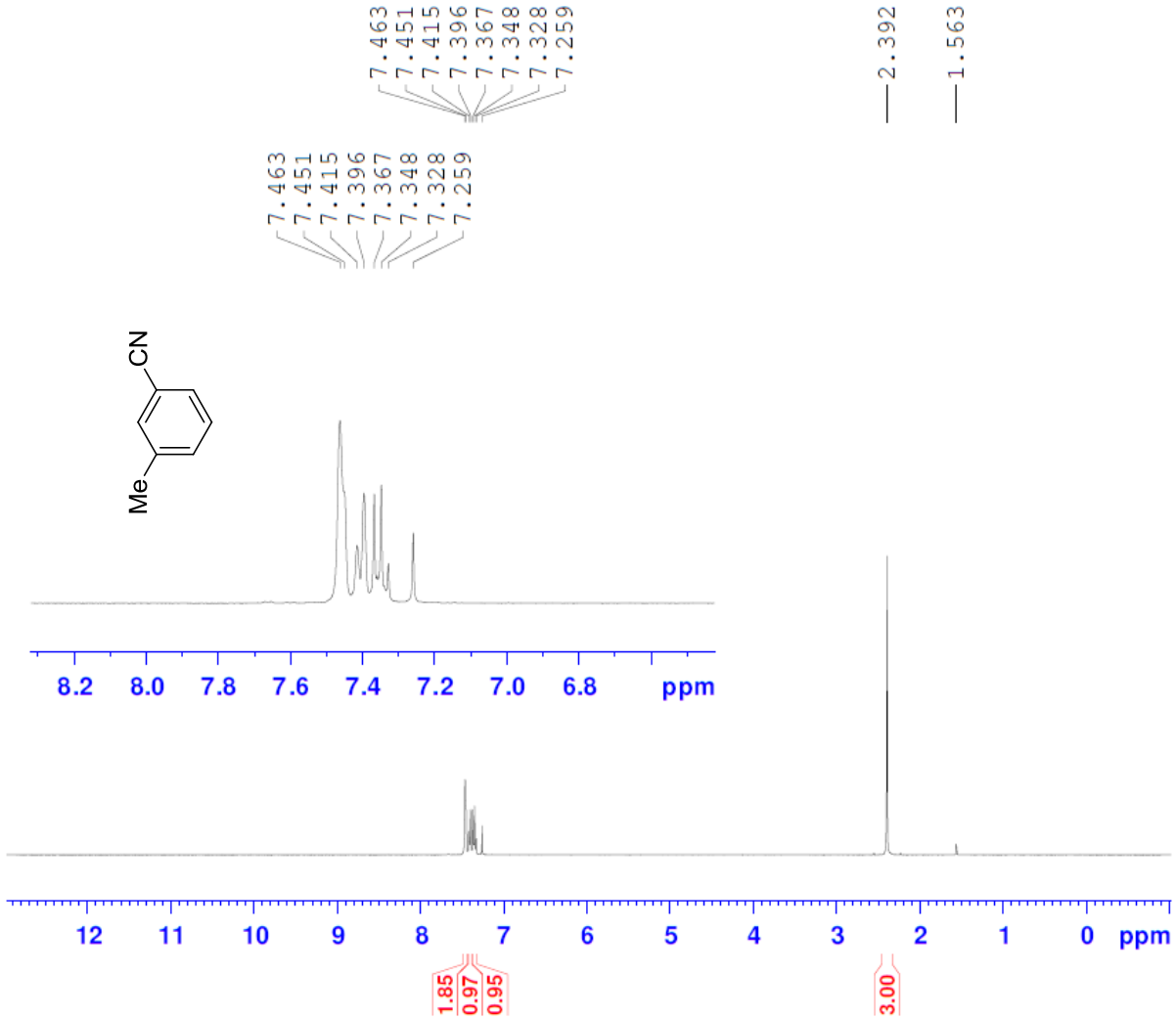


BRUKER

NAME	pyy548Cyan
EXPNO	2
PROCNO	1
Date_	20101111
Time	18.31
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	297.8 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	15.00 dB
PL2W	11.88122272 W
PL12W	0.37571725 W
PL13W	0.37571725 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127838 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

^{1}H-, ^{13}C-NMR spectra of products from palladium-catalyzed cyanation of aryl bromides

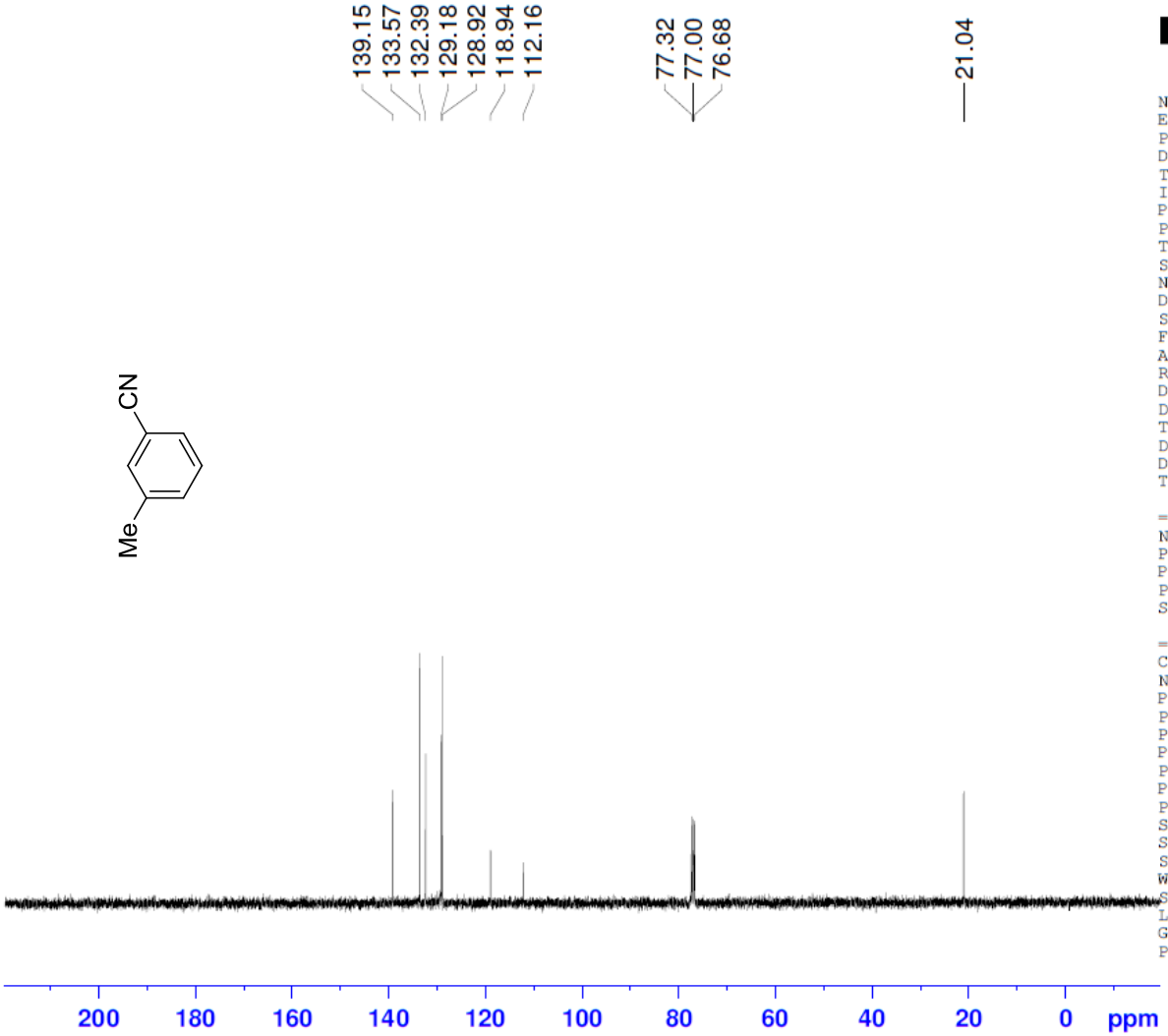
m-tolunitrile-H



BRUKER

NAME	test
EXPNO	11
PROCNO	1
Date_	20110628
Time	11.59
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	8
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	114
DW	89.333 usec
DE	6.50 usec
TE	298.6 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300099 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

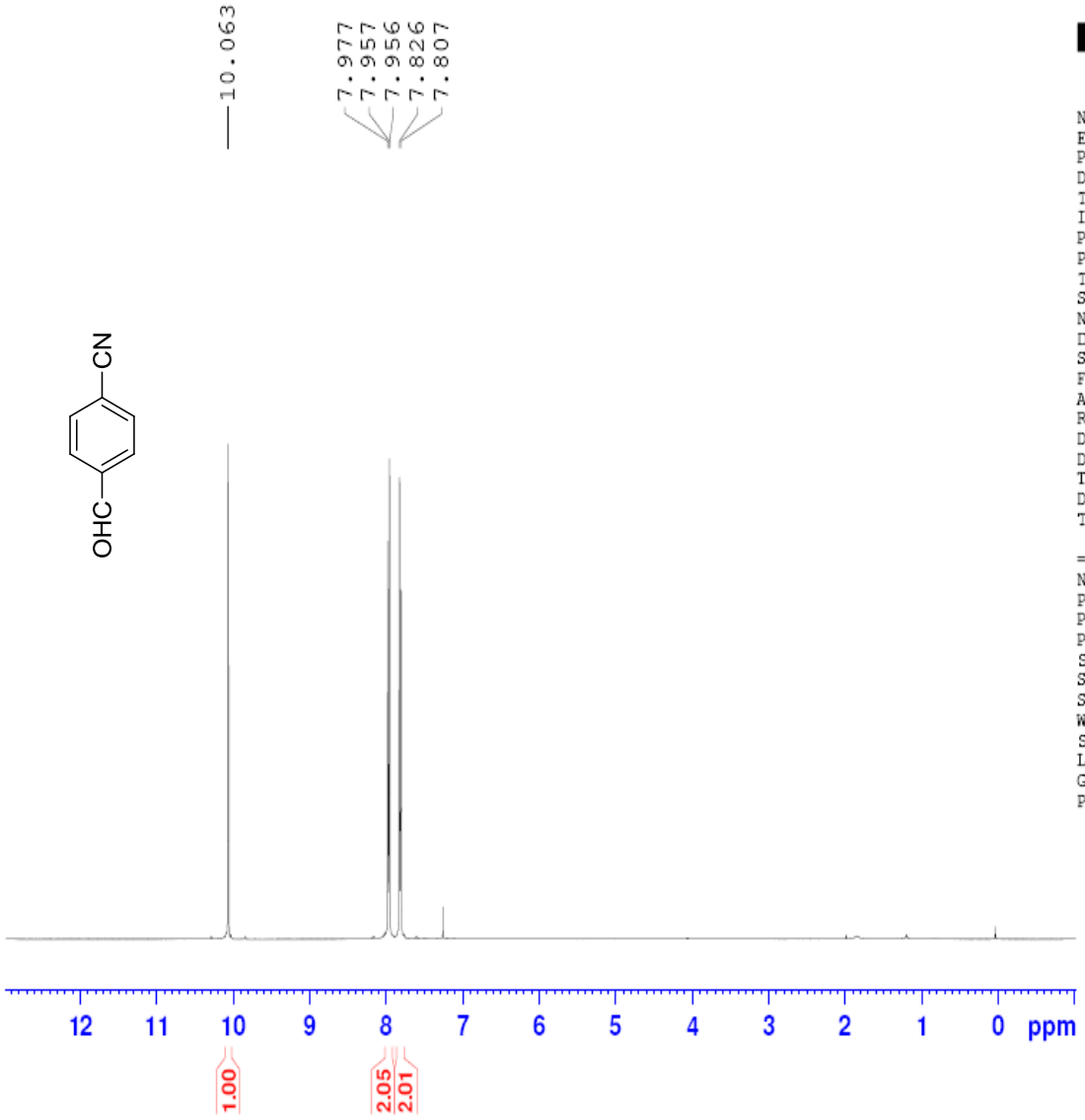
m-tolunitrile-C



BRUKER

NAME	test
EXPNO	12
PROCNO	1
Date_	20110628
Time	13.09
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	128
DW	20.800 usec
DE	6.50 usec
TE	298.5 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	15.00 dB
PL2W	11.88122272 W
PL12W	0.37571725 W
PL13W	0.37571725 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127776 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

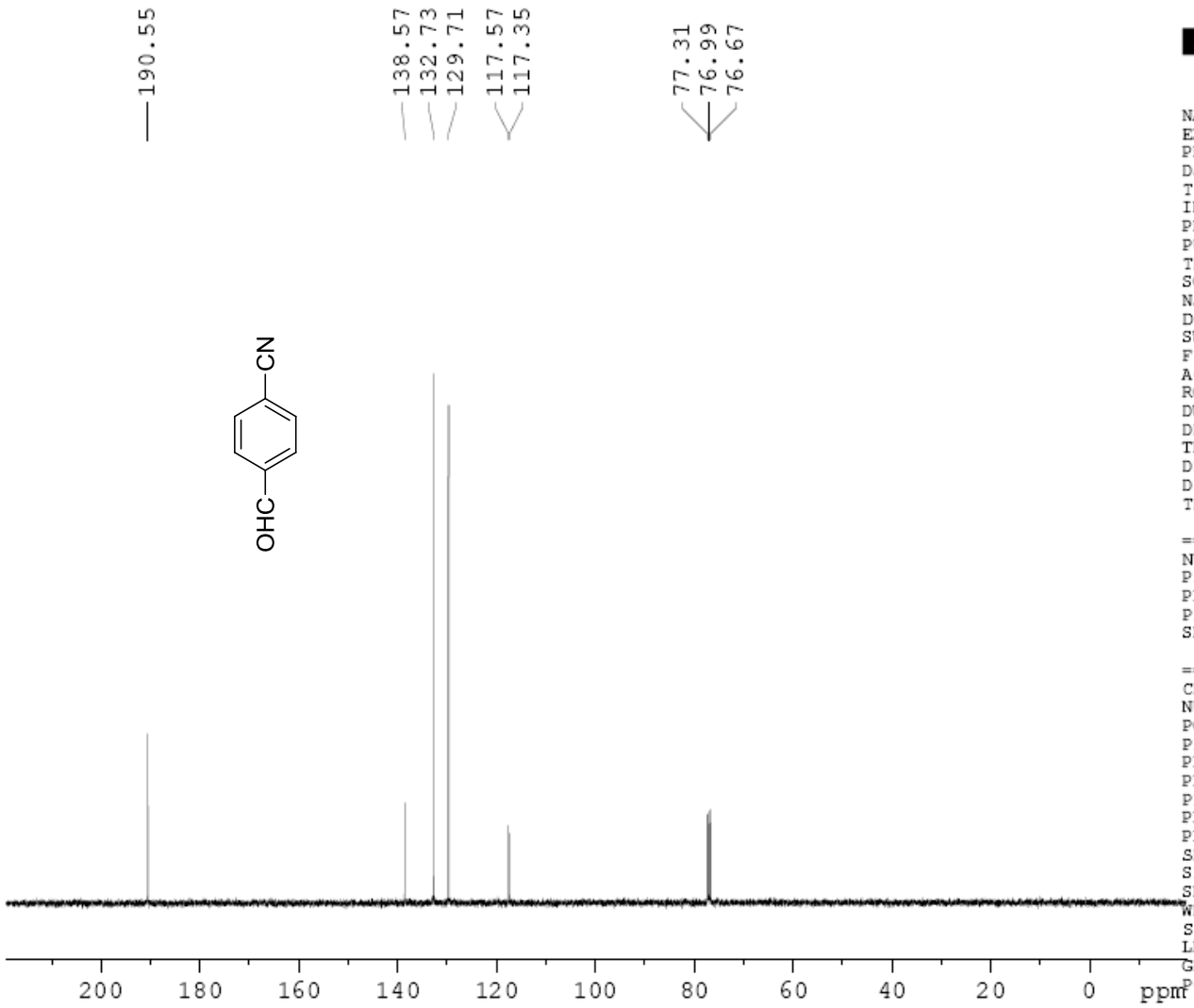
Standard 1H




```
NAME              aldehyde
EXPNO                    1
PROCNO                   1
Date_             20110408
Time                 20.15
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               5597.015 Hz
FIDRES            0.170807 Hz
AQ                2.9273248 sec
RG                    45.2
DW                  89.333 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          400.1324008 MHz
SI                   32768
SF            400.1300094 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

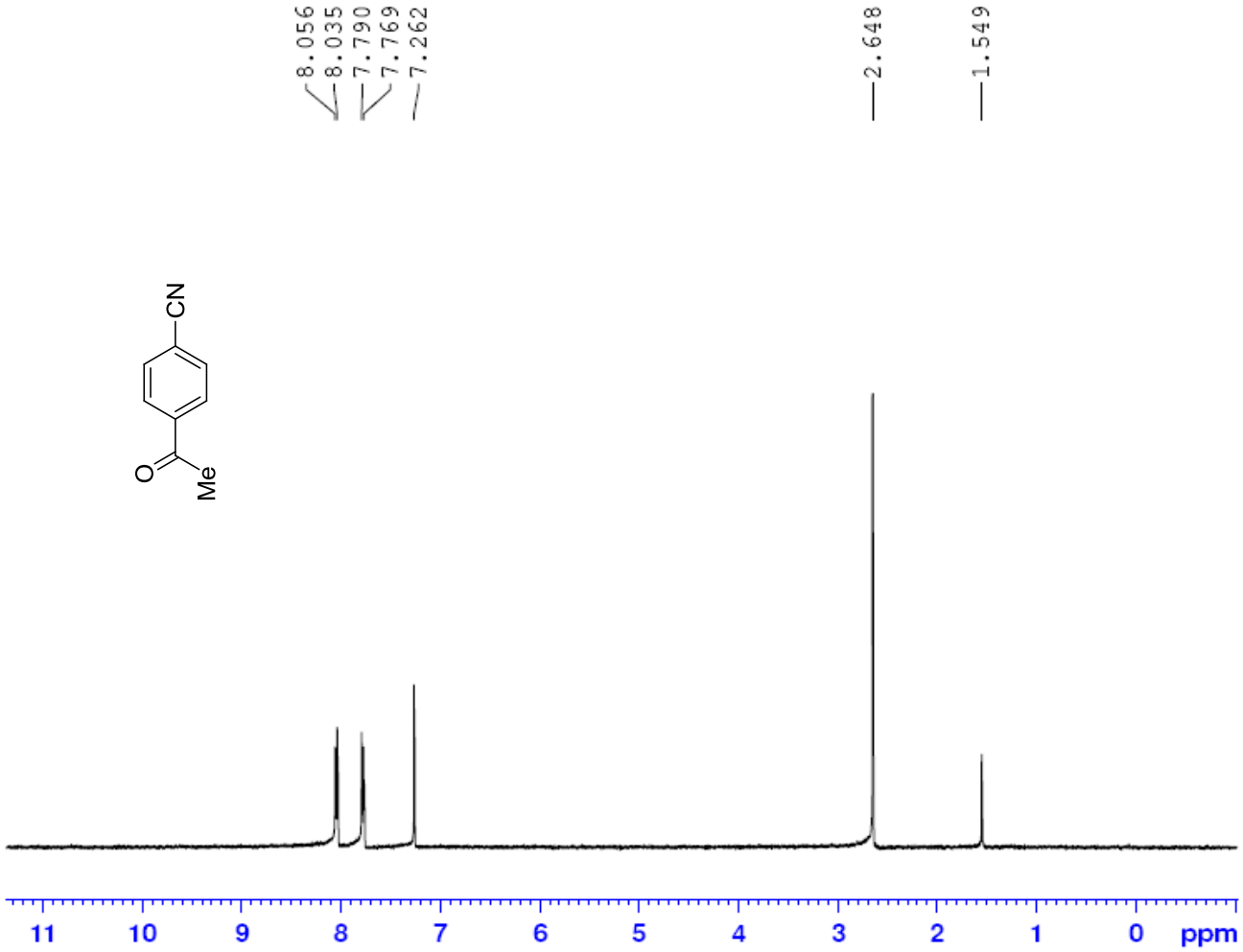
standard 13C



BRUKER

NAME	aldhyde-C
EXPNO	1
PROCNO	1
Date_	20110408
Time	20.21
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	299.5 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	15.00 dB
PL2W	11.88122272 W
PL12W	0.37571725 W
PL13W	0.37571725 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127869 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

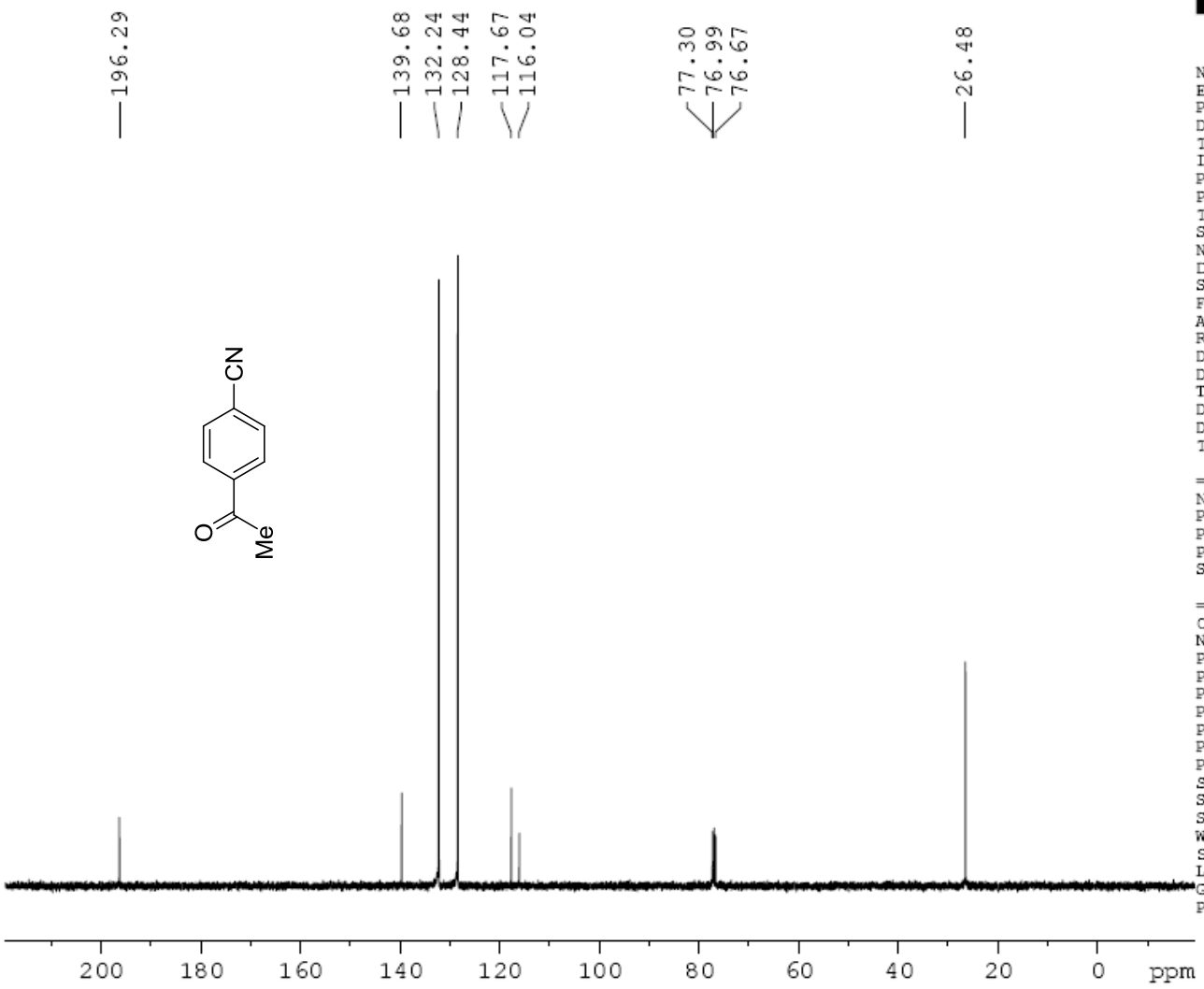
Standard 1H



BRUKER

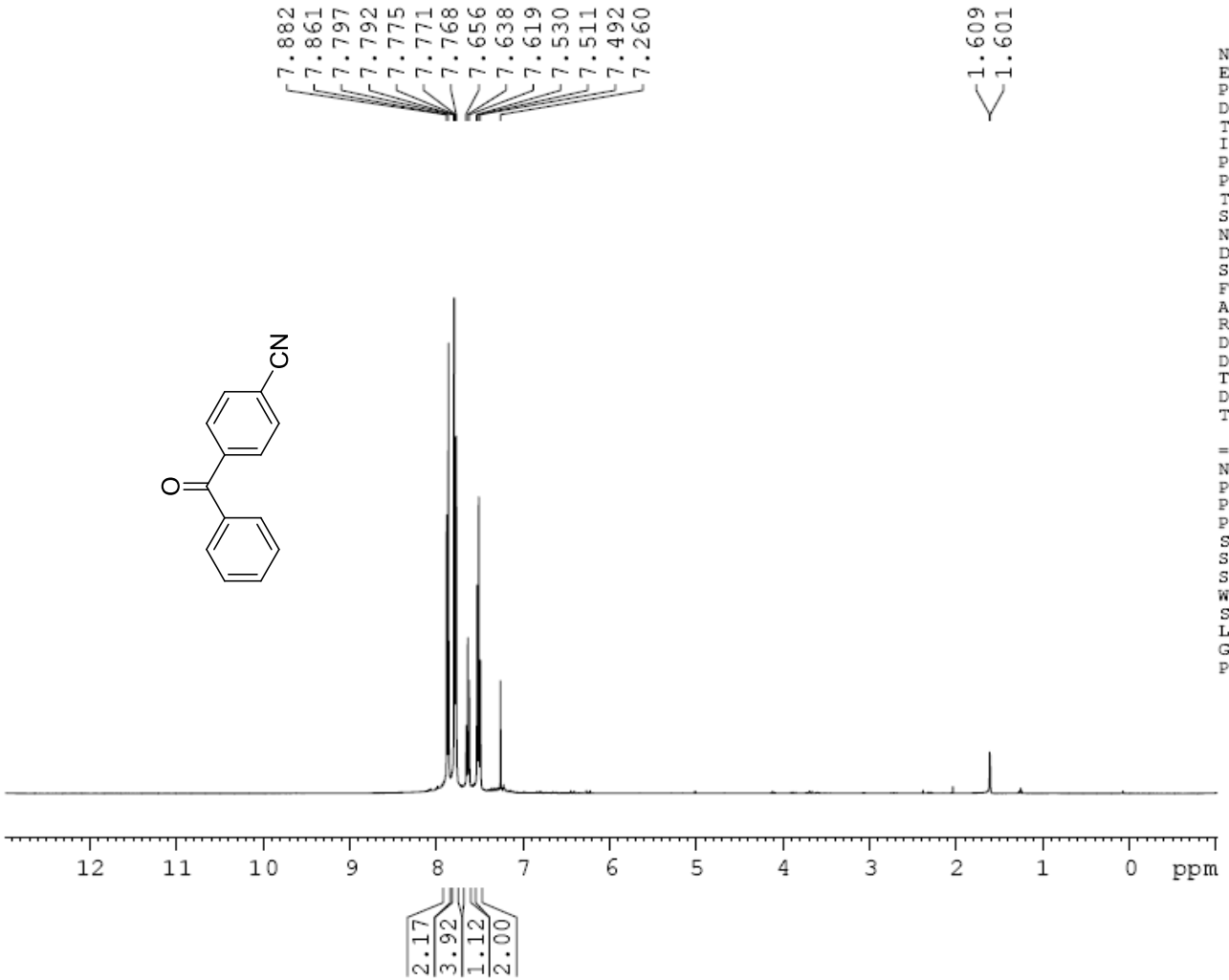
NAME	ketone
EXPNO	1
PROCNO	1
Date_	20110301
Time	16.38
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	1
DW	89.333 usec
DE	6.50 usec
TE	299.1 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300096 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Standard 13C



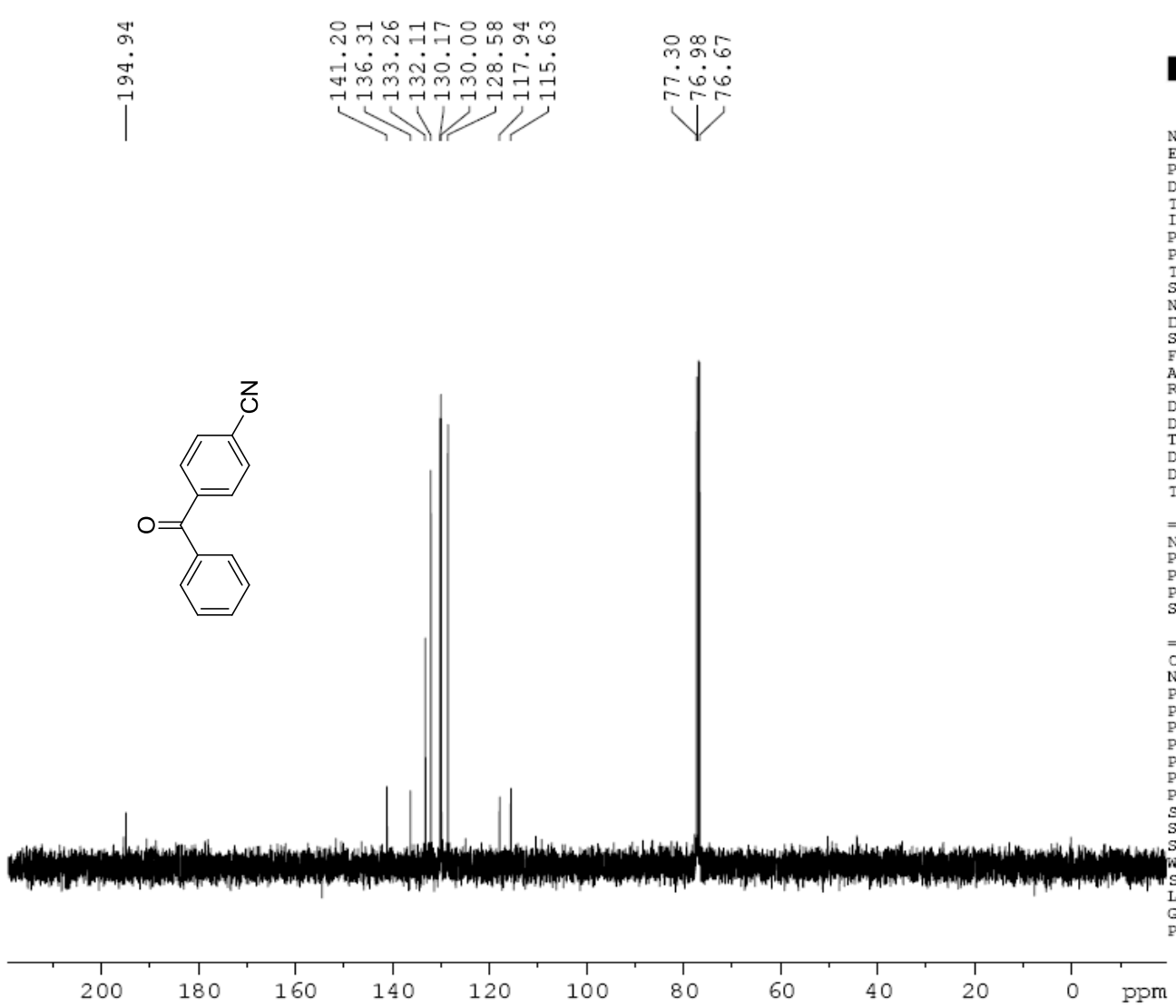
NAME	ketone-13C
EXPNO	3
PROCNO	1
Date_	20110407
Time	13.26
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	32
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	301.8 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL 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	100.6127929 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

Standard 1H



BRUKER

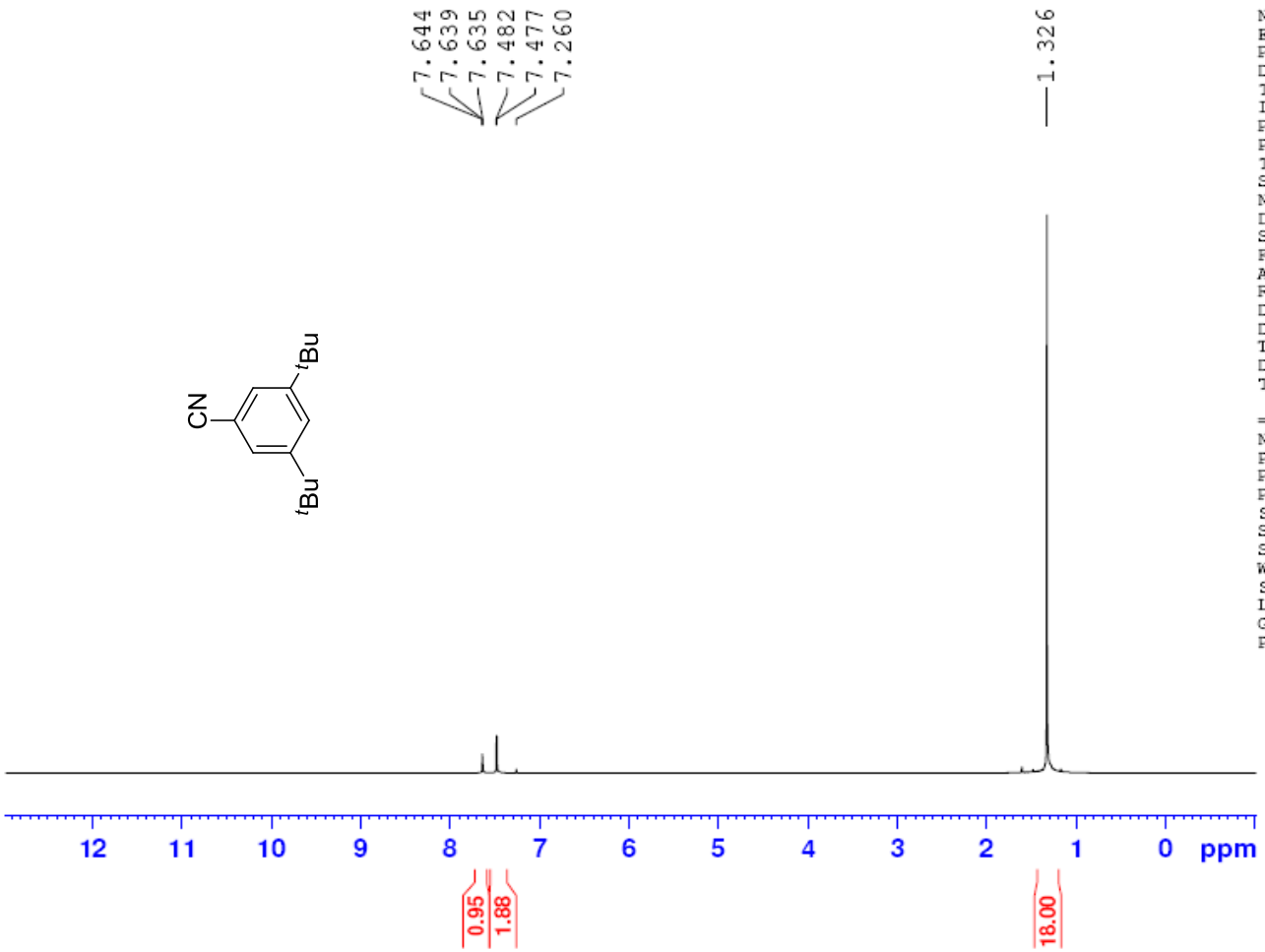
NAME	acetophenone-1H	
EXPNO	1	
PROCNO	1	
Date_	20110407	
Time	12.59	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zg30	
TD	32768	
SOLVENT	CDCl3	
NS	16	
DS	2	
SWH	5597.015	Hz
FIDRES	0.170807	Hz
AQ	2.9273248	sec
RG	101	
DW	89.333	usec
DE	6.50	usec
TE	301.9	K
D1	1.00000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	1H	
P1	14.70	usec
PL1	0.00	dB
PL1W	11.88122272	W
SFO1	400.1324008	MHz
SI	32768	
SF	400.1300097	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	



BRUKER

NAME	acetophenone-13C
EXPNO	1
PROCNO	1
Date_	20110407
Time	13.10
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	301.7 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	15.00 dB
PL2W	11.88122272 W
PL12W	0.37571725 W
PL13W	0.37571725 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127743 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

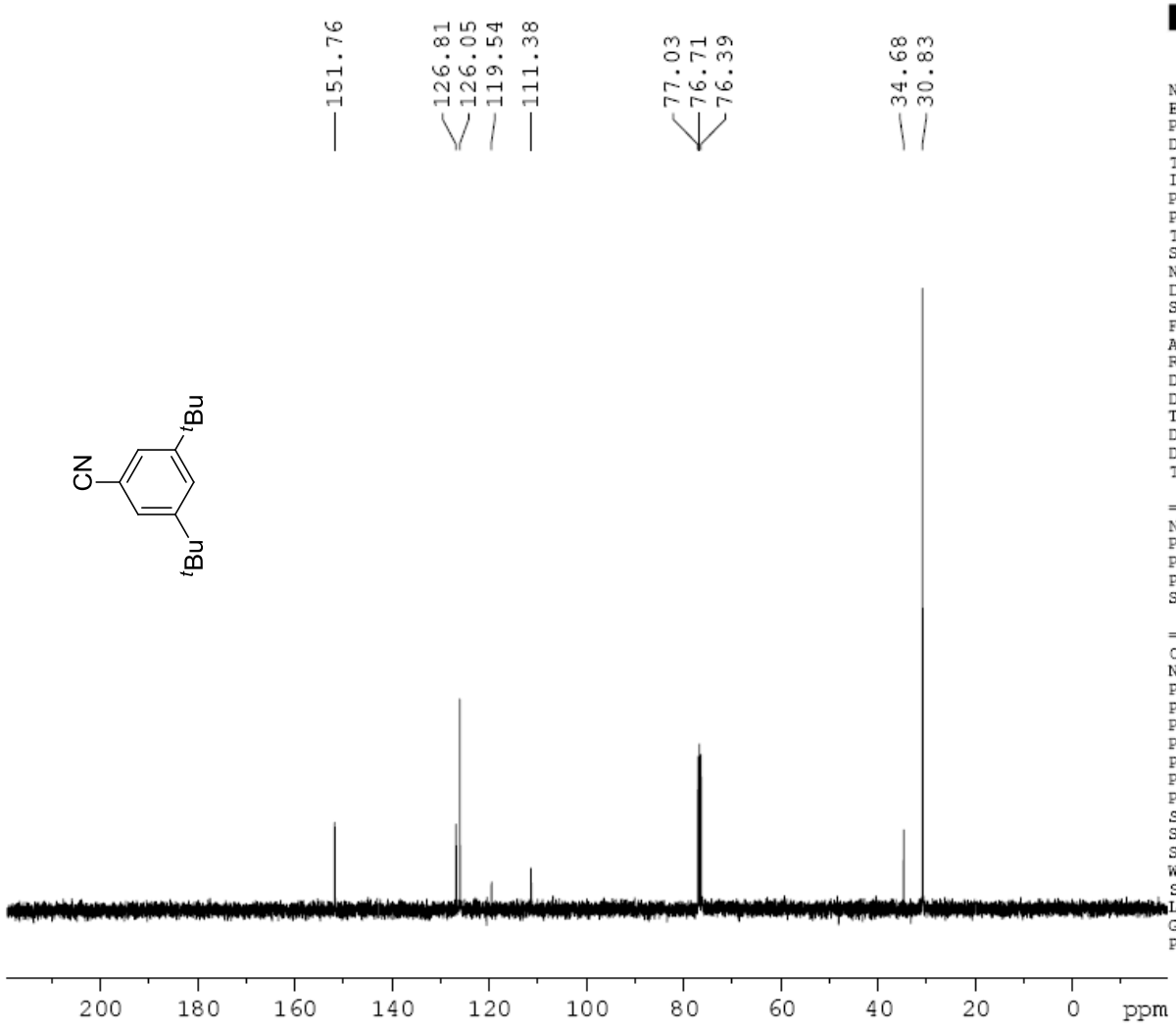
Standard 1H




```
NAME              t-butane-h
EXPNO                      1
PROCNO                     1
Date_               20110407
Time                   10.51
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                 zg30
TD                     32768
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                 5597.015 Hz
FIDRES              0.170807 Hz
AQ                  2.9273248 sec
RG                       45.2
DW                     89.333 usec
DE                       6.50 usec
TE                      300.8 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     14.70 usec
PL1                     0.00 dB
PL1W             11.88122272 W
SFO1             400.1324008 MHz
SI                     32768
SF               400.1300097 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```

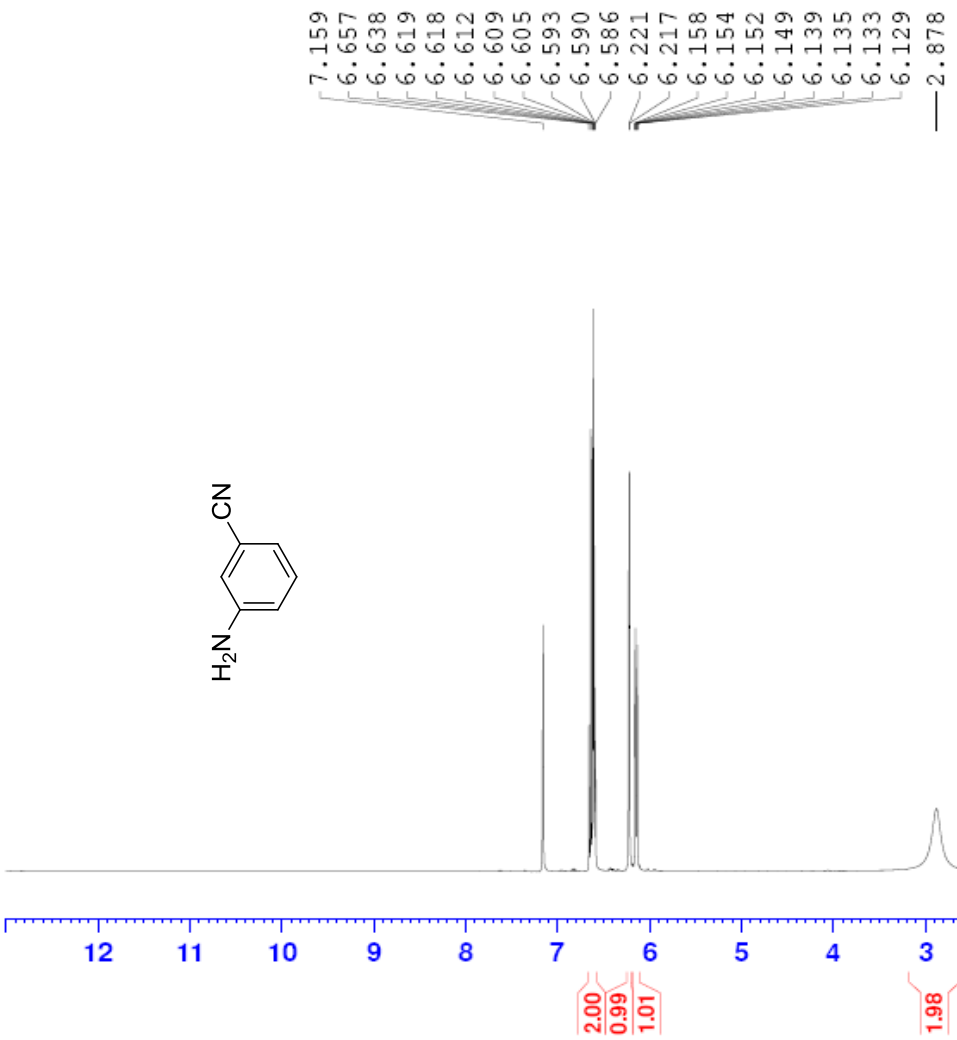
standard 13C



BRUKER

NAME	t-butane-13C	
EXPNO	1	
PROCNO	1	
Date_	20110407	
Time	11.11	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	16	
DS	2	
SWH	24038.461	Hz
FIDRES	0.366798	Hz
AQ	1.3631988	sec
RG	203	
DW	20.800	usec
DE	6.50	usec
TE	303.8	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	100.6128002	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

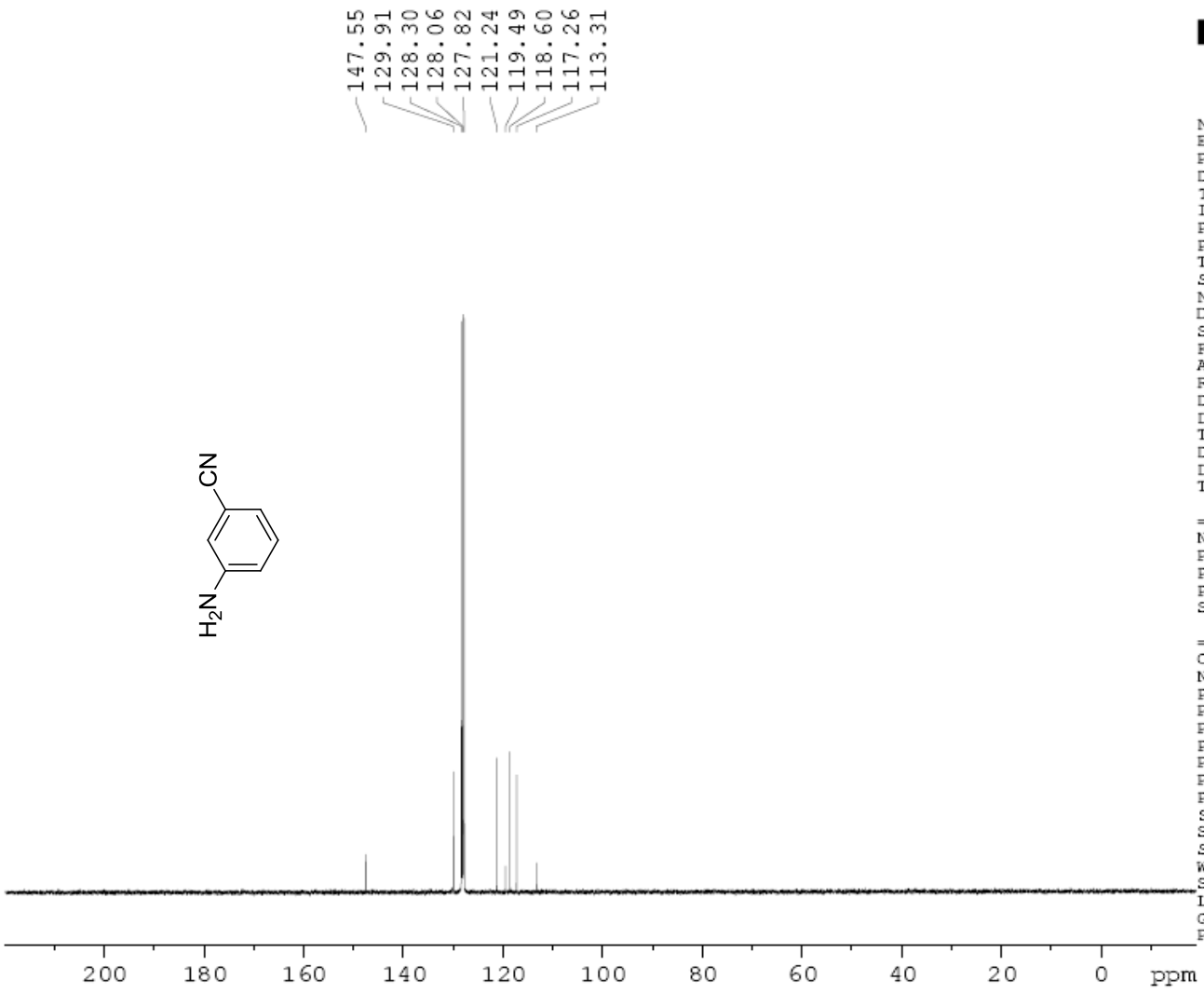
standard 1H



BRUKER

NAME	aniline
EXPNO	7
PROCNO	1
Date_	20110320
Time	14.16
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	C6D6
NS	16
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	45.2
DW	89.333 usec
DE	6.50 usec
TE	296.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1299972 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

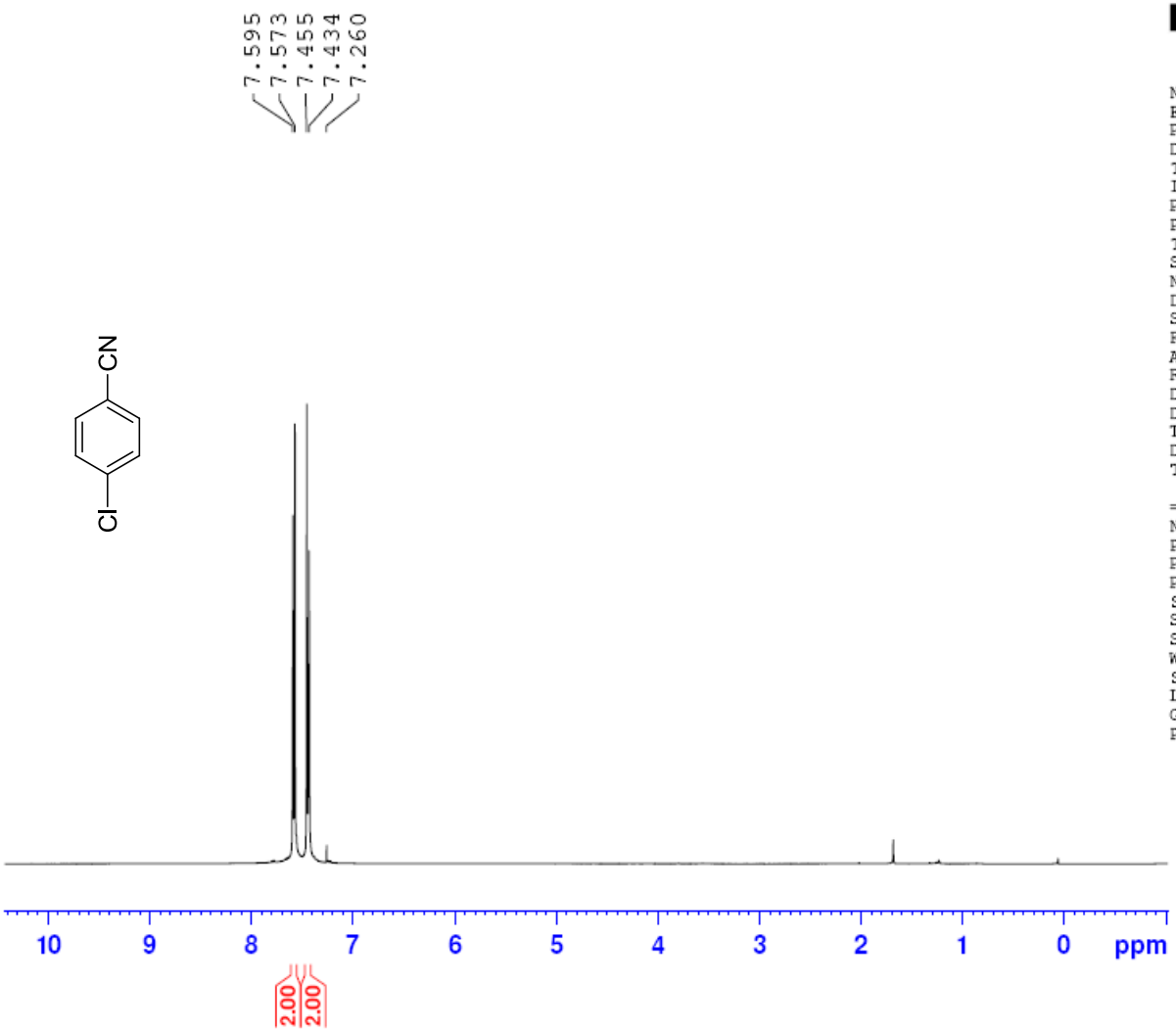
standard13C



BRUKER

NAME	aniline	
EXPNO	8	
PROCNO	1	
Date_	20110320	
Time	14.22	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	C6D6	
NS	32	
DS	2	
SWH	24038.461	Hz
FIDRES	0.366798	Hz
AQ	1.3631988	sec
RG	181	
DW	20.800	usec
DE	6.50	usec
TE	296.3	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
========	CHANNEL f1	========
NUC1	13C	
P1	9.50	usec
PL1	-2.00	dB
PL1W	58.52175522	W
SFO1	100.6228298	MHz
========	CHANNEL f2	========
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	80.00	usec
PL2	0.00	dB
PL12	15.00	dB
PL13	15.00	dB
PL2W	11.88122272	W
PL12W	0.37571725	W
PL13W	0.37571725	W
SFO2	400.1316005	MHz
SI	32768	
SF	100.6127333	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

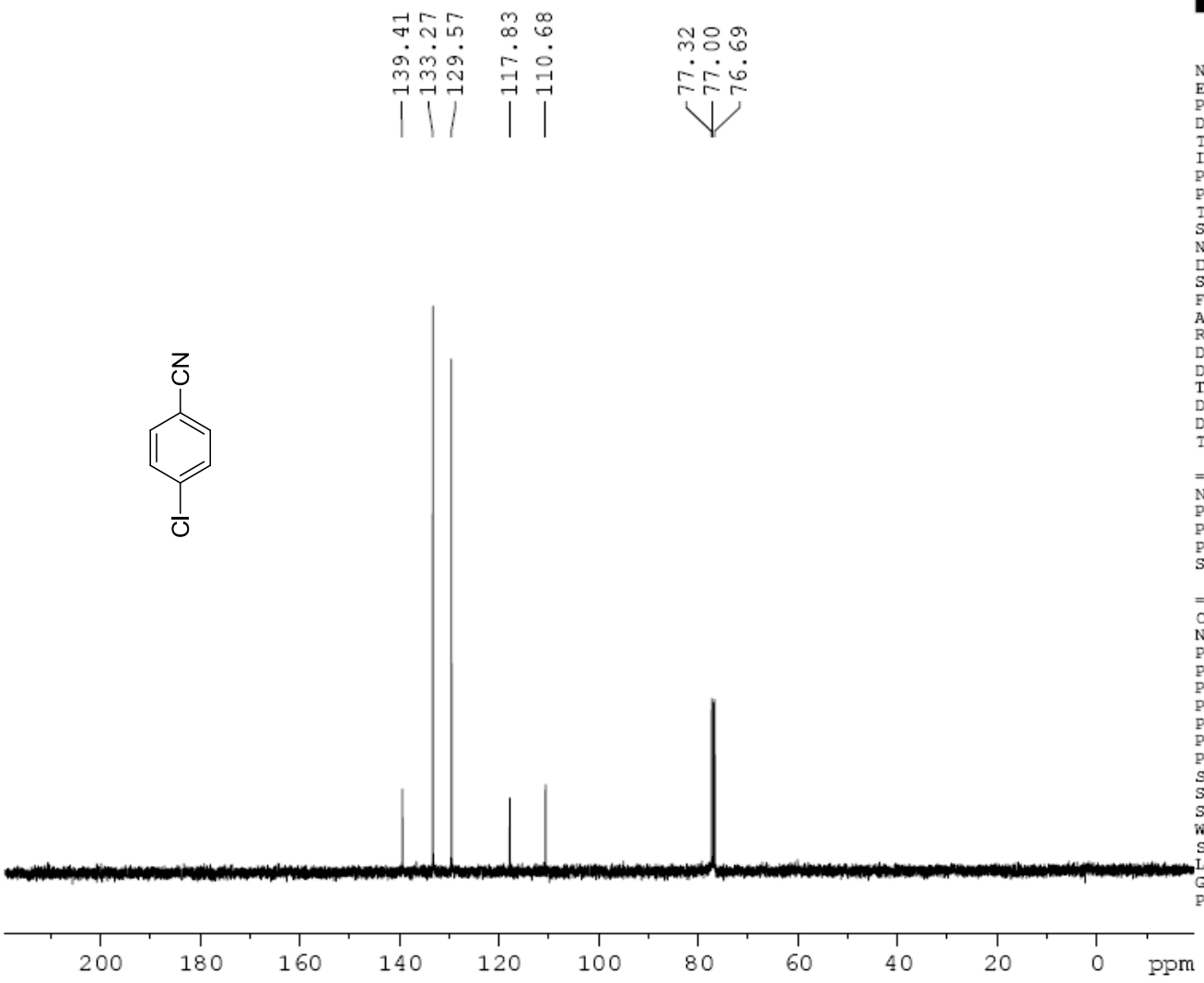
Standard 1H



BRUKER

NAME	cloro-H
EXPNO	1
PROCNO	1
Date_	20110406
Time	17.51
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	45.2
DW	89.333 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	400.1324008 MHz
SI	32768
SF	400.1300094 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

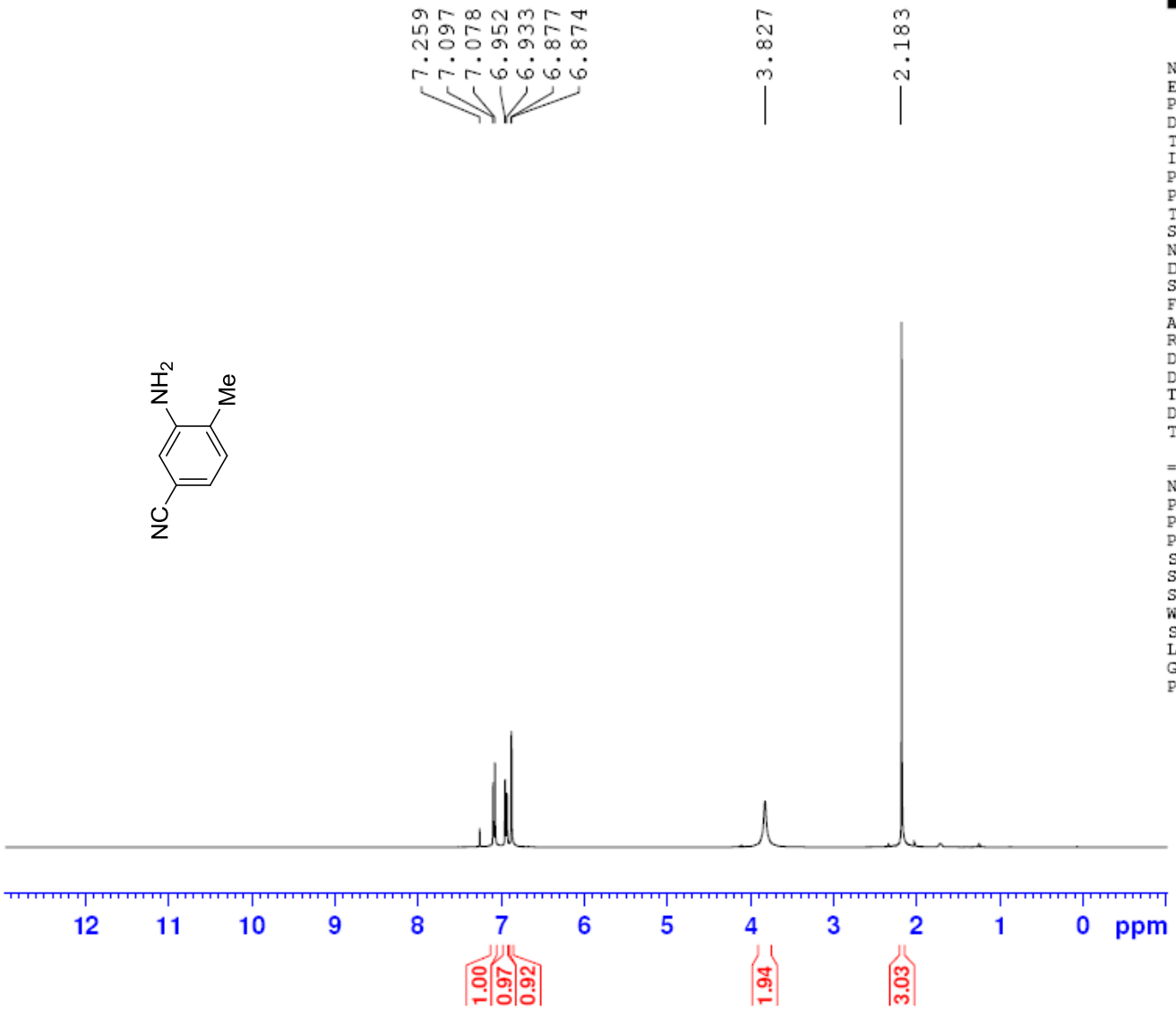
standard 13C



BRUKER

NAME	chloro-C
EXPNO	10
PROCNO	1
Date_	20110406
Time	17.56
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	300.4 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	15.00 dB
PL2W	11.88122272 W
PL12W	0.37571725 W
PL13W	0.37571725 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127809 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

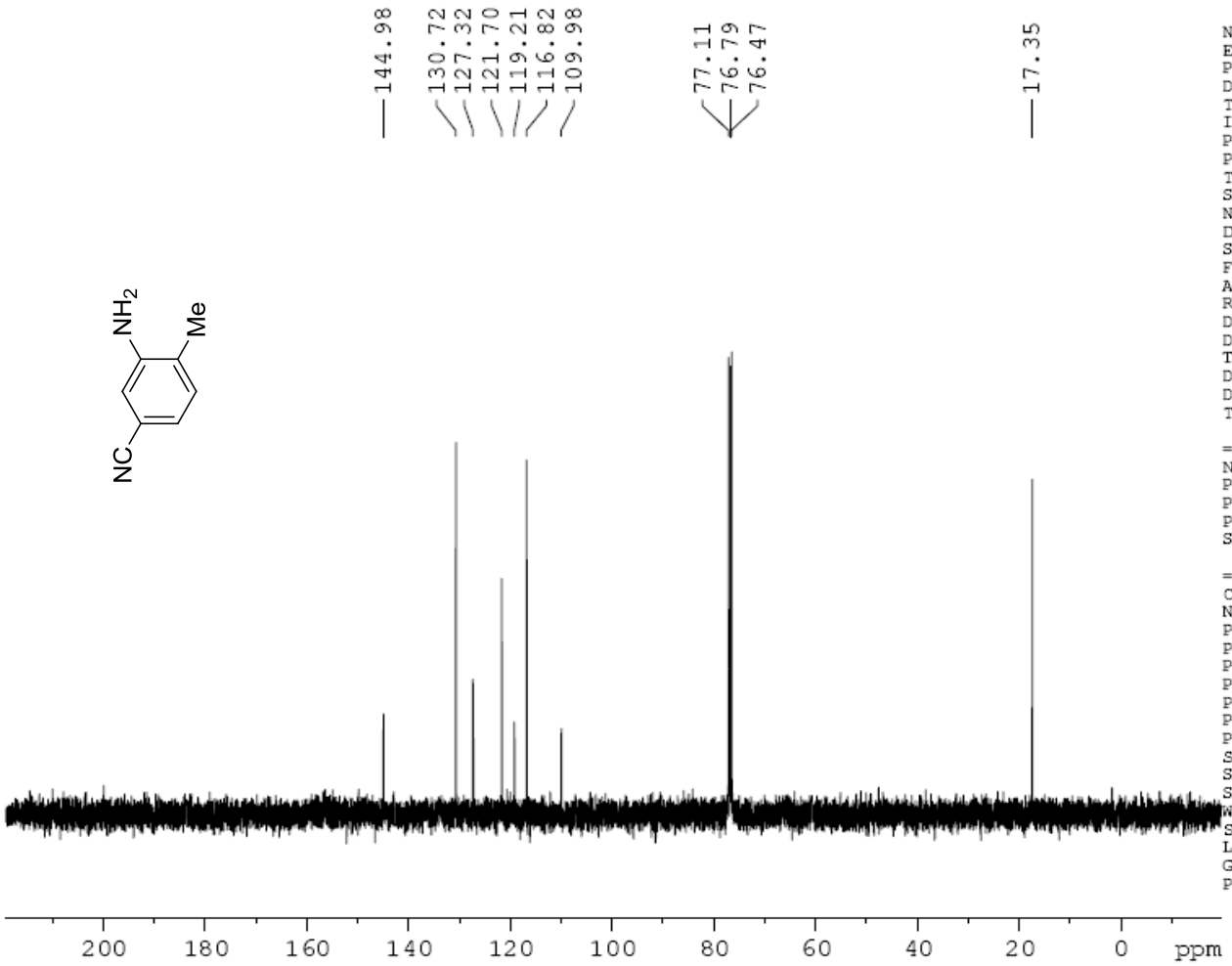
Standard 1H



BRUKER

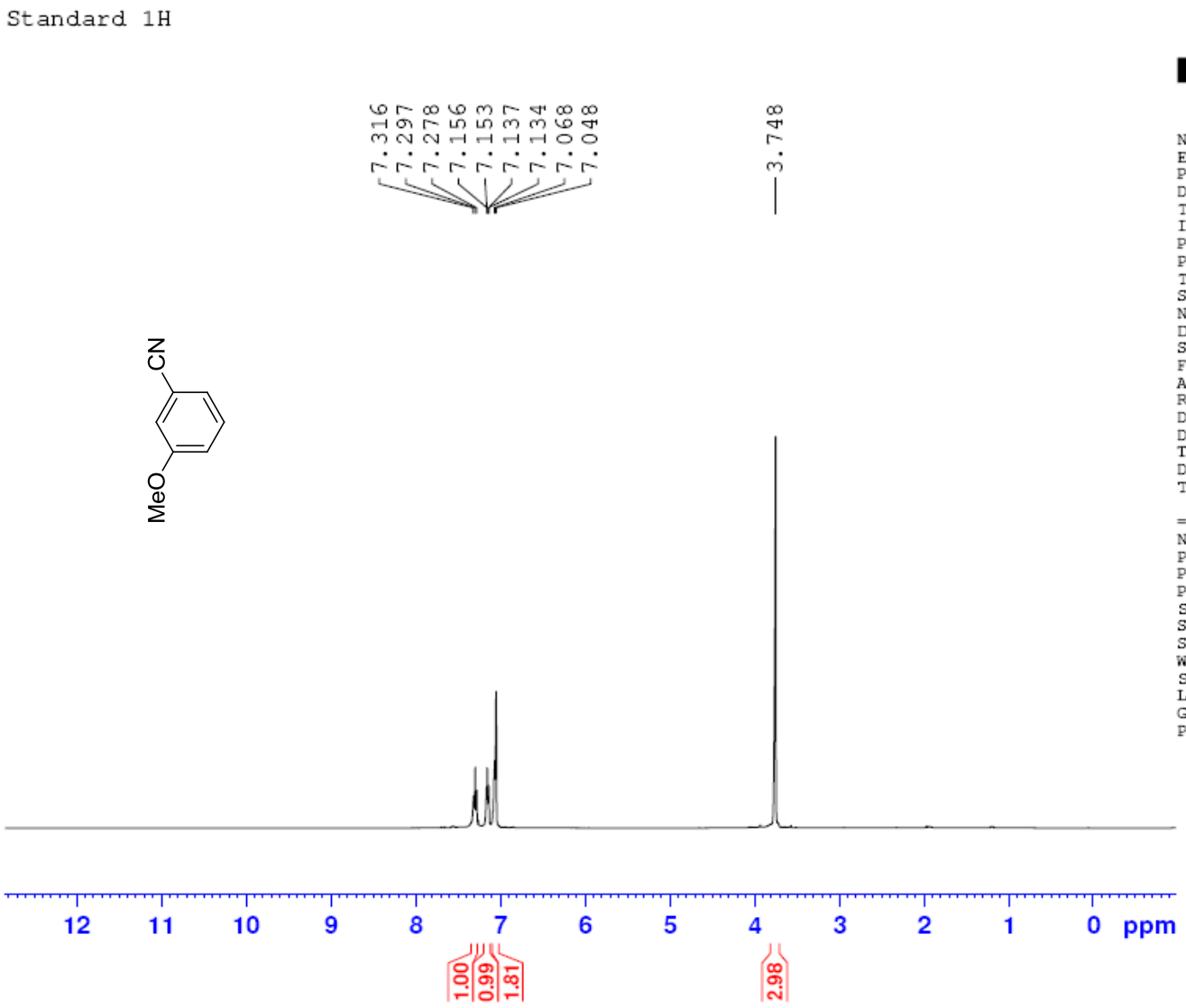
NAME	aniline-methane-1H
EXPNO	1
PROCNO	1
Date_	20110407
Time	9.54
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	71.8
DW	89.333 usec
DE	6.50 usec
TE	300.7 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300101 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Standard 13C



NAME	aniline-methane-13C
EXPNO	10
PROCNO	1
Date_	20110407
Time	10.10
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	301.5 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	100.6128002 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

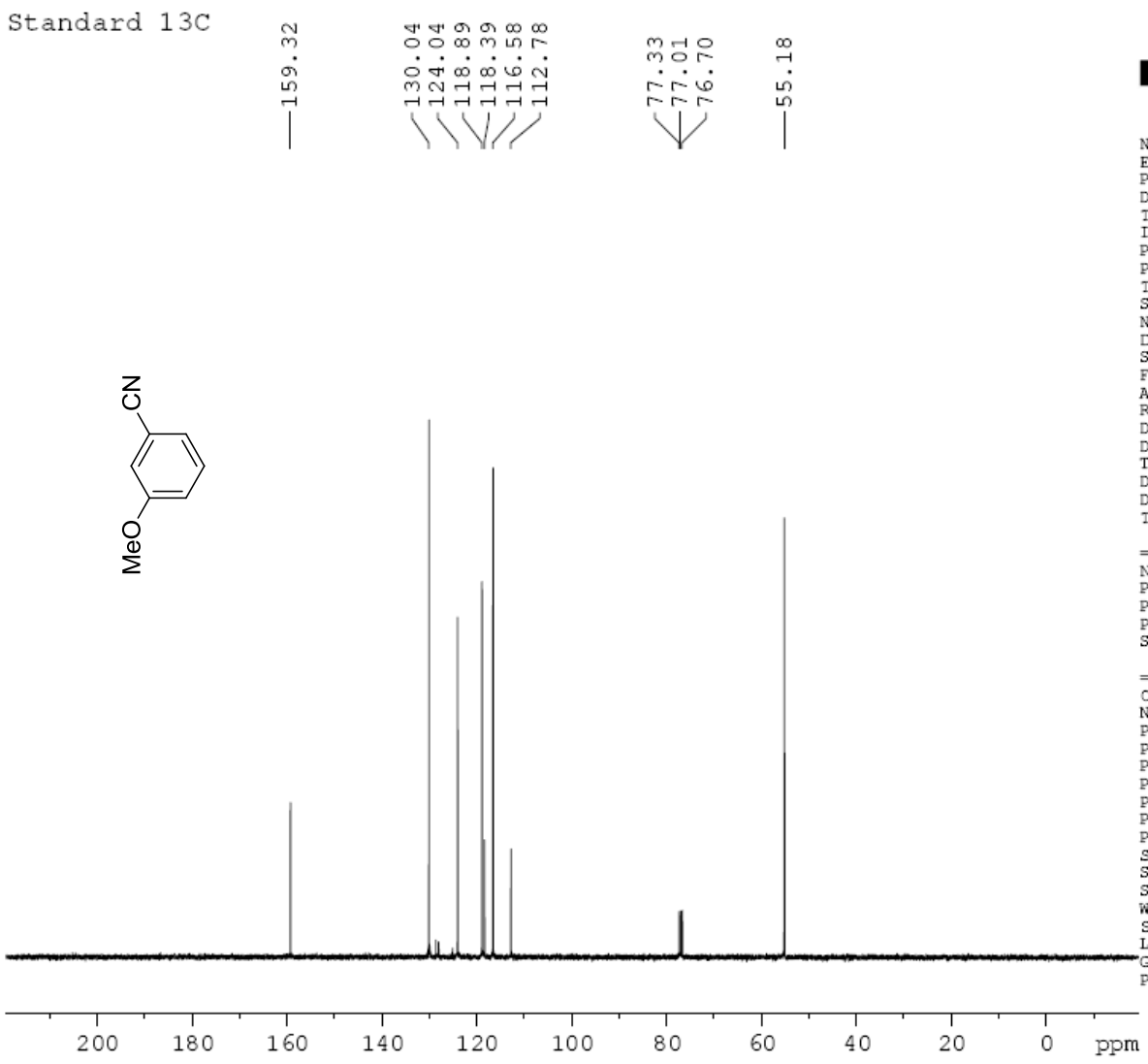
Standard 1H



BRUKER

NAME	methoxy
EXPNO	1
PROCNO	1
Date_	20110407
Time	16.33
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	14.2
DW	89.333 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	400.1324008 MHz
SI	32768
SF	400.1300099 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

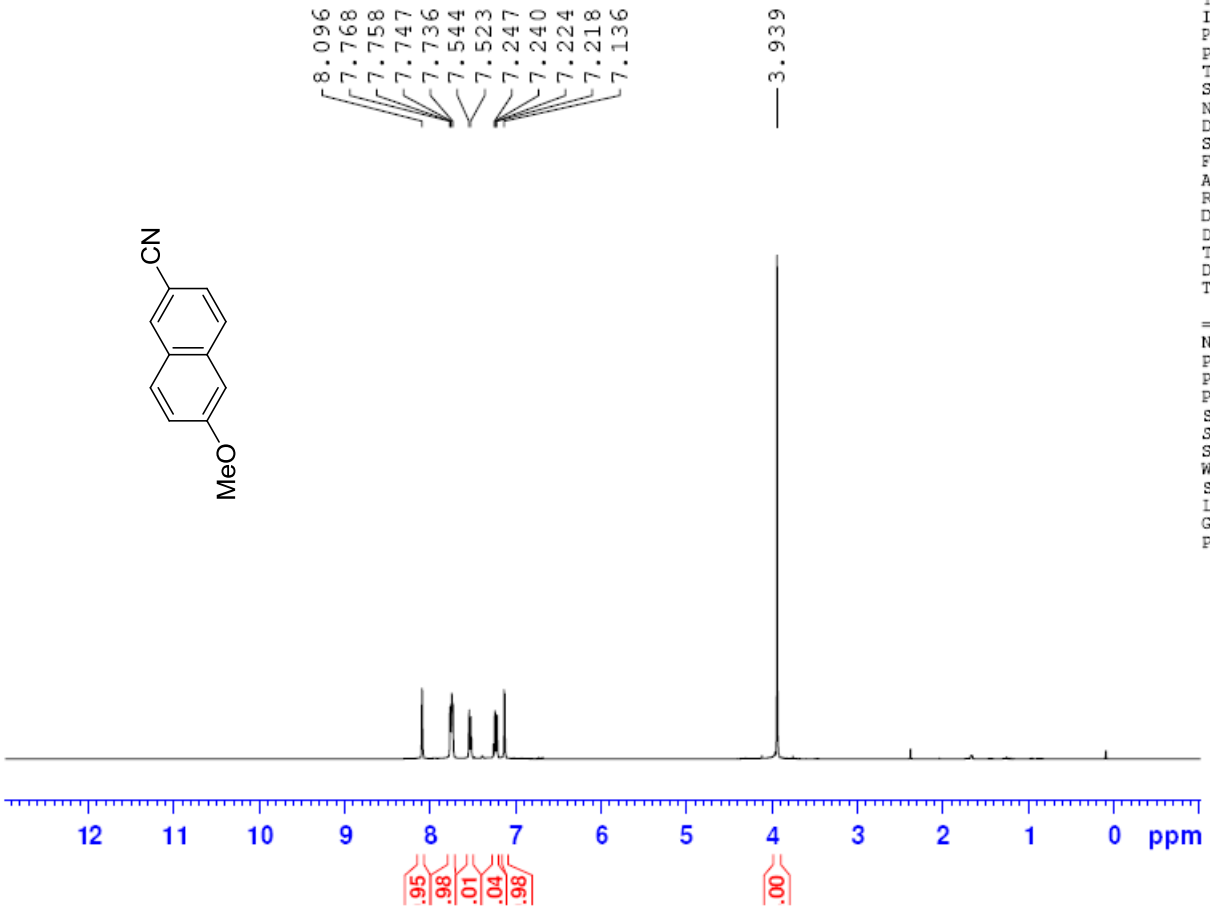
Standard 13C



BRUKER

NAME	methoxy-13C
EXPNO	3
PROCNO	1
Date_	20110407
Time	16.40
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	32
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	299.6 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	15.00 dB
PL2W	11.88122272 W
PL12W	0.37571725 W
PL13W	0.37571725 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127996 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

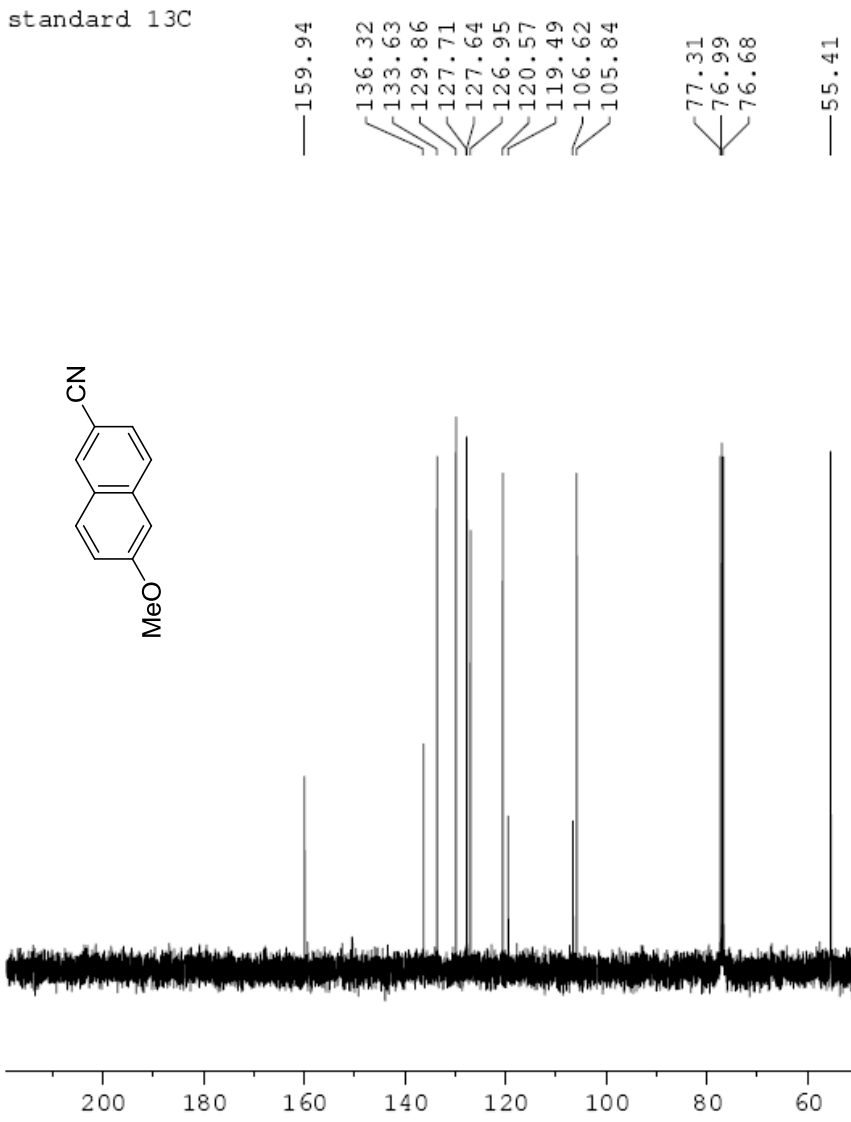
Standard 1H



BRUKER

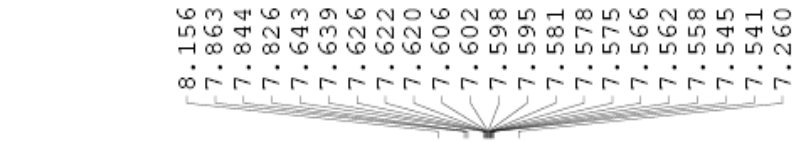
NAME	nathplene-methoxy-1H
EXPNO	1
PROCNO	1
Date_	20110407
Time	10.18
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDC13
NS	16
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	45.2
DW	89.333 usec
DE	6.50 usec
TE	300.7 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300092 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

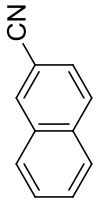
standard 13C



NAME	nathplene-methoxy-13C
EXPNO	10
PROCNO	1
Date_	20110407
Time	10.24
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	301.1 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	100.6127785 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

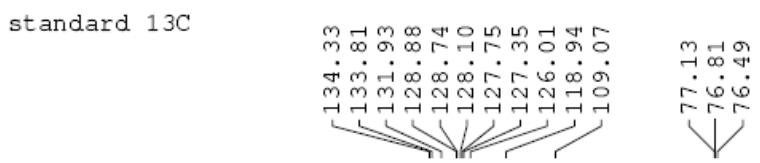
standard-H

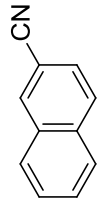




NAME	pyy213Cyan	
EXPNO	1	
PROCNO	1	
Date_	20100513	
Time	19.36	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zg30	
TD	32768	
SOLVENT	CDCl3	
NS	8	
DS	2	
SWH	5597.015	Hz
FIDRES	0.170807	Hz
AQ	2.9273248	sec
RG	32	
DW	89.333	usec
DE	6.50	usec
TE	296.4	K
D1	1.00000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	1H	
P1	14.70	usec
PL1	0.00	dB
PL1W	11.88122272	W
SFO1	400.1324008	MHz
SI	32768	
SF	400.1300094	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	

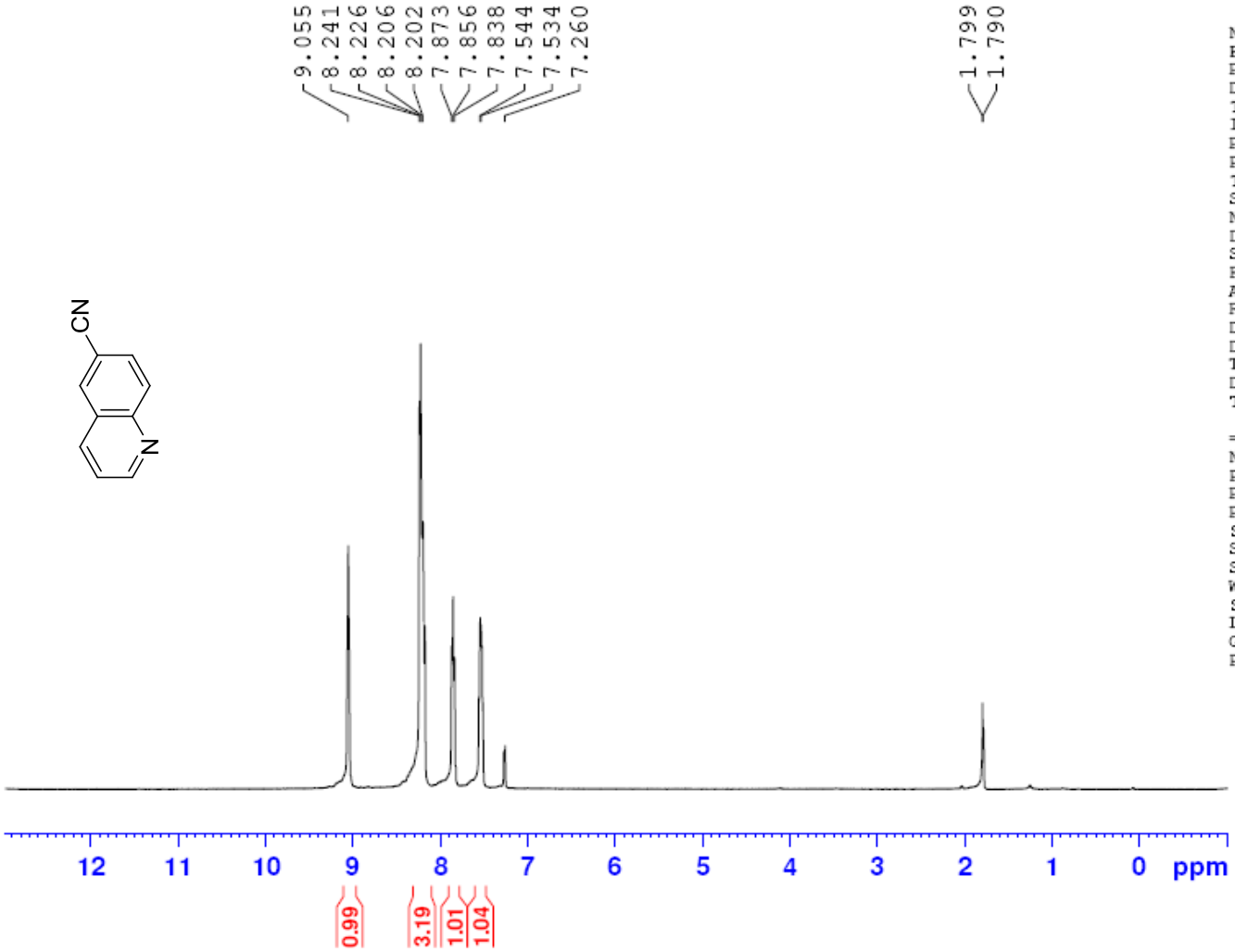
standard 13C





NAME	nathplene-13C
EXPNO	1
PROCNO	1
Date_	20110407
Time	13.52
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	301.4 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	100.6128002 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

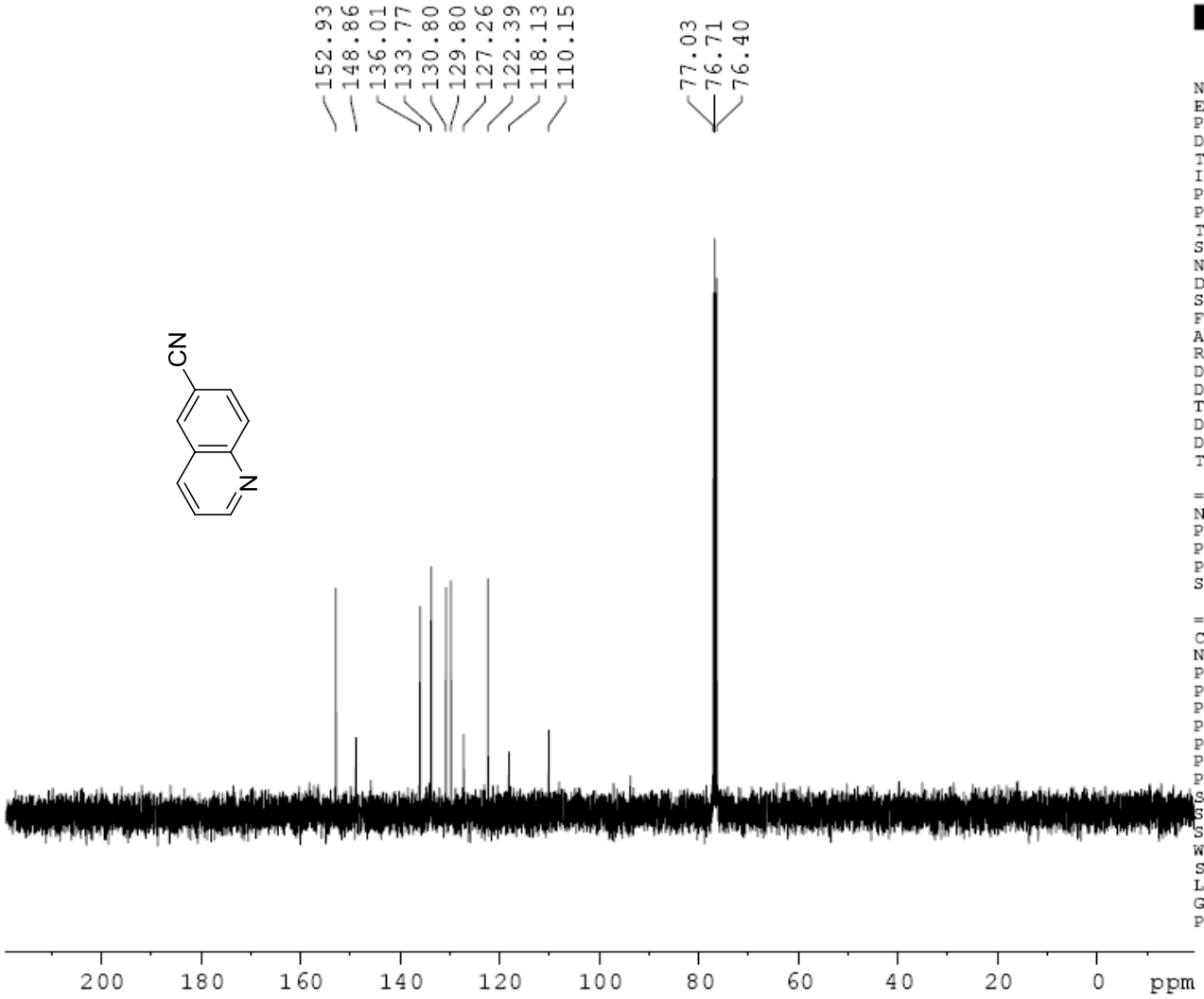
Standard 1H



BRUKER

NAME	quinline
EXPNO	1
PROCNO	1
Date_	20110407
Time	11.19
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	128
DW	89.333 usec
DE	6.50 usec
TE	305.2 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300064 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

standard 13C

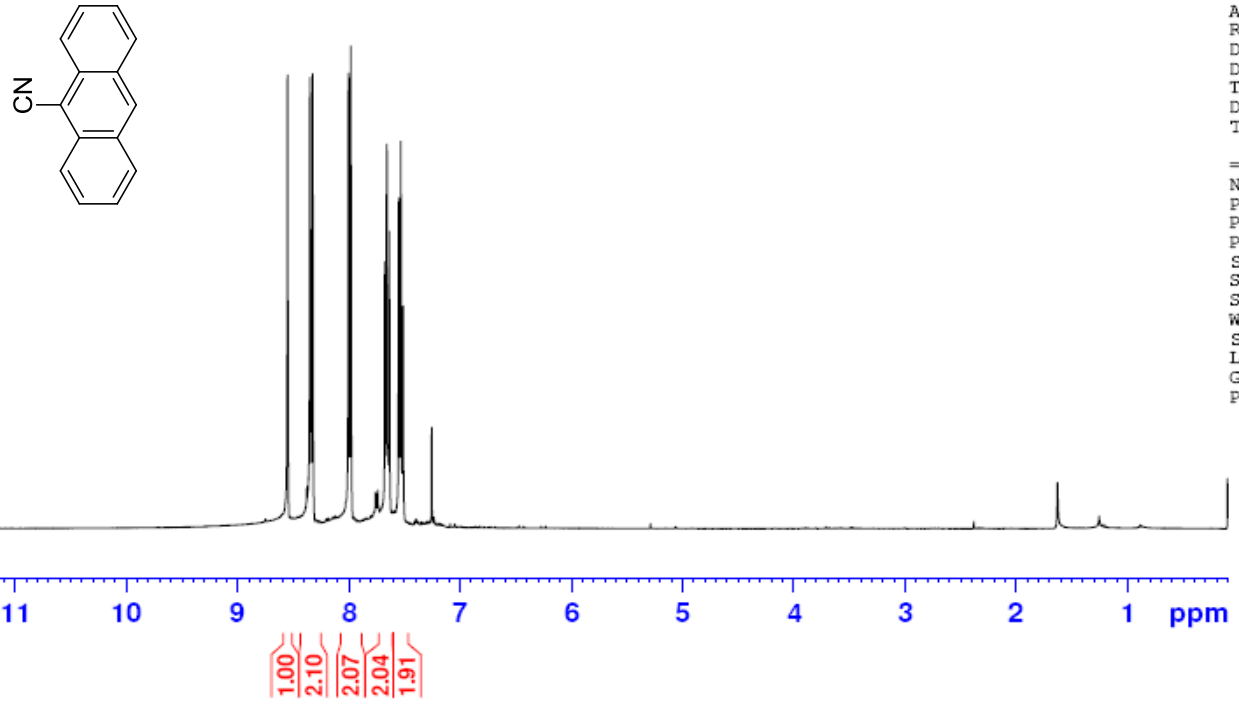


BRUKER

NAME	quiline-13C
EXPNO	1
PROCNO	1
Date_	20110407
Time	11.26
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	305.8 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	100.6128002 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

Standard 1H

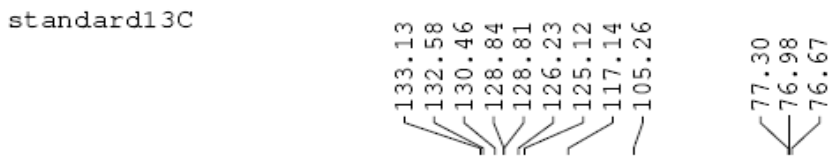
8.553 8.351 8.350 8.329 8.328 8.005 7.984 7.676 7.662 7.659 7.654 7.641 7.638 7.555 7.552 7.538 7.534 7.531 7.517 7.515 7.258

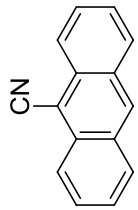


BRUKER

NAME	threebenzene-h	
EXPNO	1	
PROCNO	1	
Date_	20110407	
Time	9.45	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zg30	
TD	32768	
SOLVENT	CDCl3	
NS	16	
DS	2	
SWH	5597.015	Hz
FIDRES	0.170807	Hz
AQ	2.9273248	sec
RG	71.8	
DW	89.333	usec
DE	6.50	usec
TE	300.4	K
D1	1.00000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	1H	
P1	14.70	usec
PL1	0.00	dB
PL1W	11.88122272	W
SFO1	400.1324008	MHz
SI	32768	
SF	400.1300104	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	

standard13C





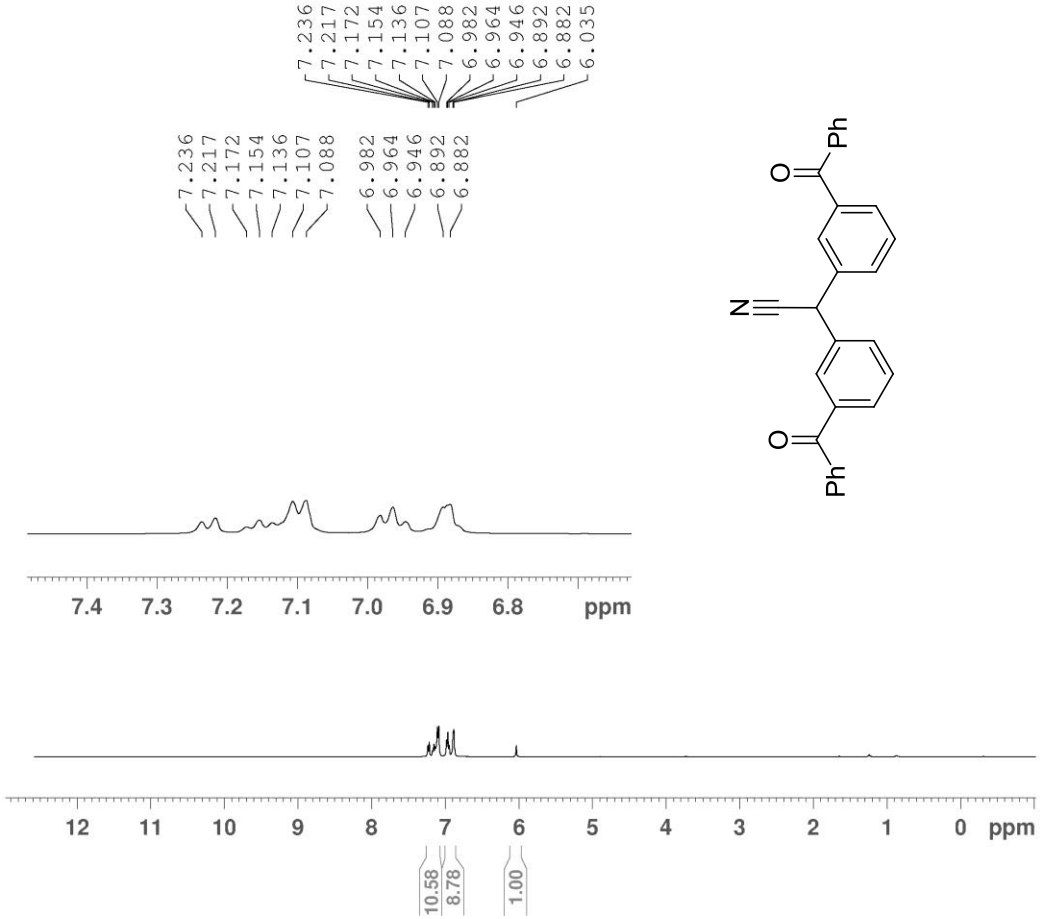
BRUKER

NAME	threebenzene-C	
EXPNO	10	
PROCNO	1	
Date_	20110407	
Time	9.39	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	16	
DS	2	
SWH	24038.461	Hz
FIDRES	0.366798	Hz
AQ	1.3631988	sec
RG	203	
DW	20.800	usec
DE	6.50	usec
TE	300.5	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	9.50	usec
PL1	-2.00	dB
PL1W	58.52175522	W
SFO1	100.6228298	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	80.00	usec
PL2	0.00	dB
PL12	15.00	dB
PL13	15.00	dB
PL2W	11.88122272	W
PL12W	0.37571725	W
PL13W	0.37571725	W
SFO2	400.1316005	MHz
SI	32768	
SF	100.6127774	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

Characterizations of products from palladium-catalyzed decarboxylative diarylation

^{1}H-, ^{13}C-NMR spectra of palladium-catalyzed decarboxylative diarylation of aryl chlorides

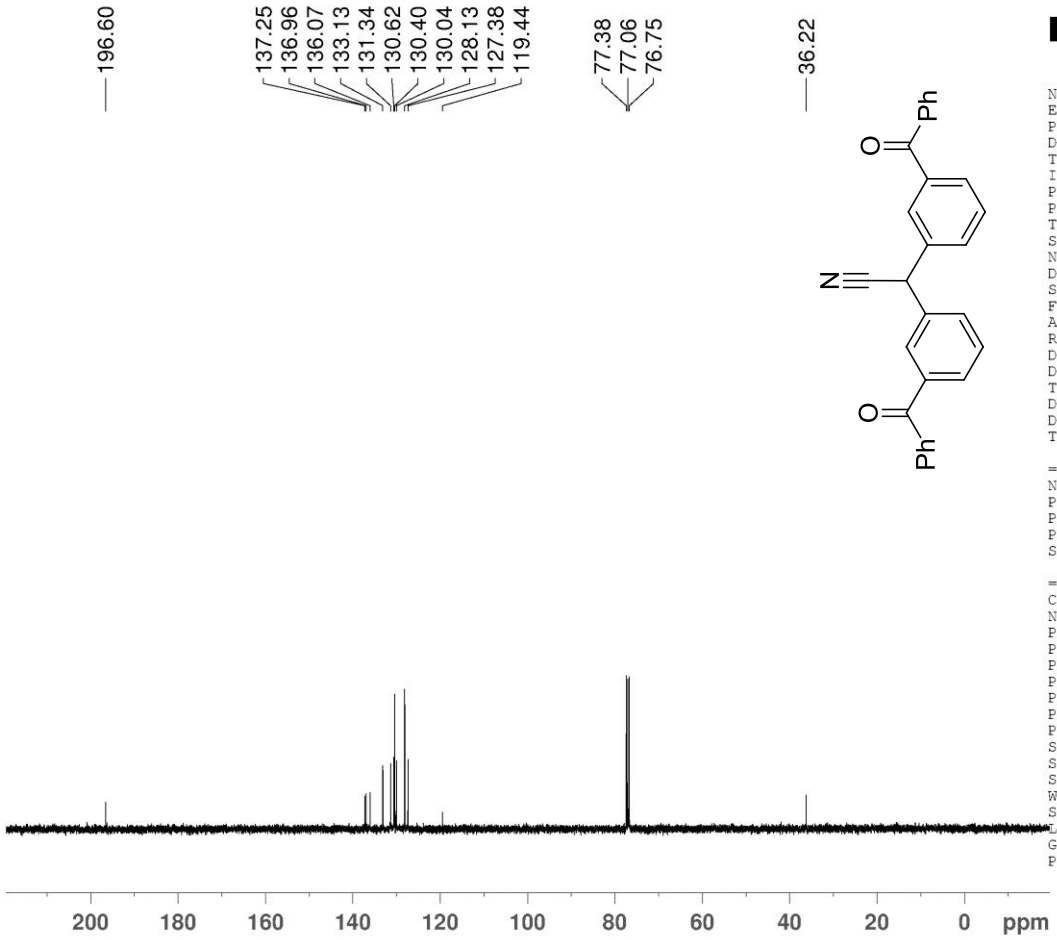
pyy713Deca2-c-H



BRUKER

NAME	pyy713Deca2
EXPNO	2
PROCNO	1
Date_	20110321
Time	13.53
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	8
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	16
DW	89.333 usec
DE	6.50 usec
TE	298.9 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1301661 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

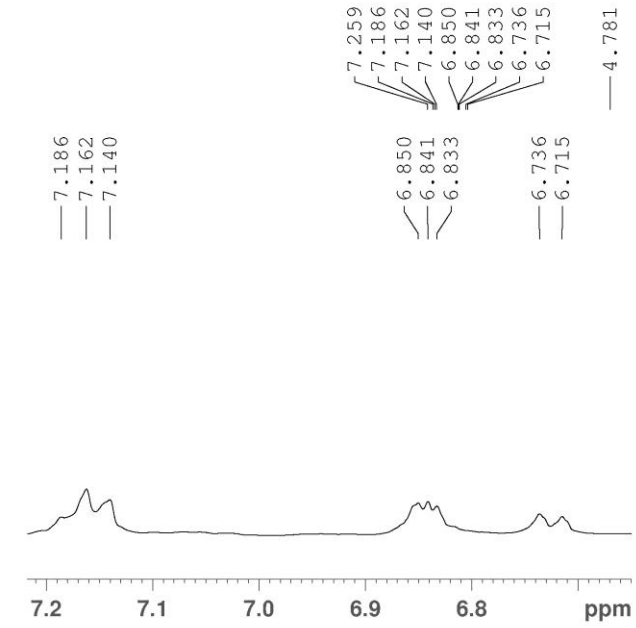
pyy713Deca2-c-C

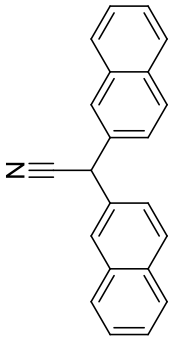


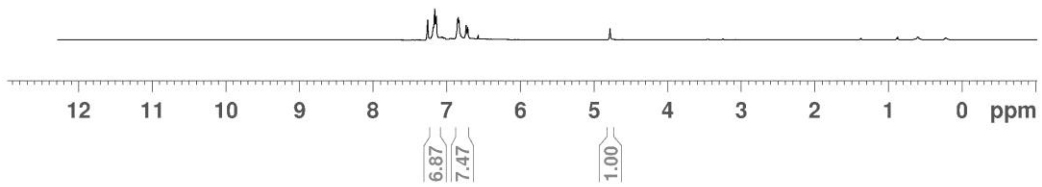
BRUKER

NAME	pyy713Deca2
EXPNO	3
PROCNO	1
Date_	20110321
Time	14.01
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	299.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	15.00 dB
PL2W	11.88122272 W
PL12W	0.37571725 W
PL13W	0.37571725 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127690 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

pyy698Deca2-H



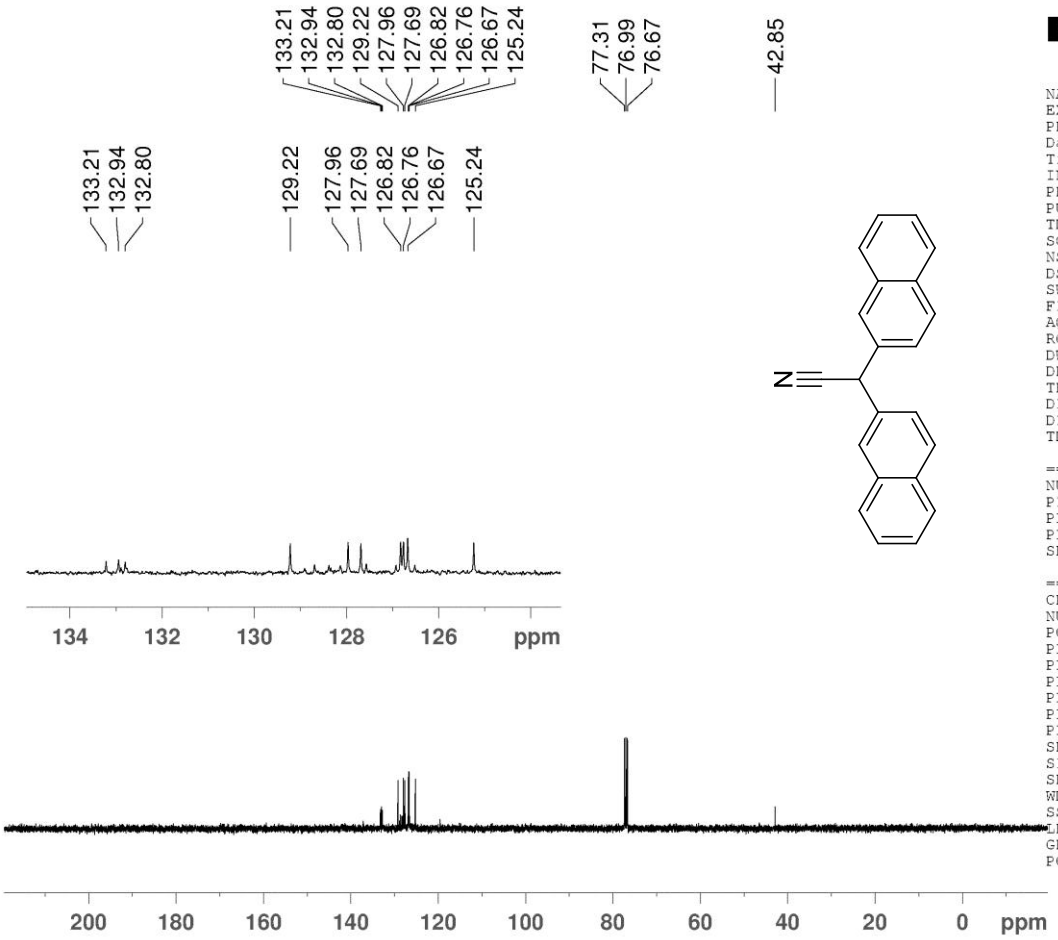




BRUKER

NAME	pyy698Deca2
EXPNO	3
PROCNO	1
Date_	20110309
Time	11.52
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	16
DW	89.333 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	400.1324008 MHz
SI	32768
SF	400.1302838 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

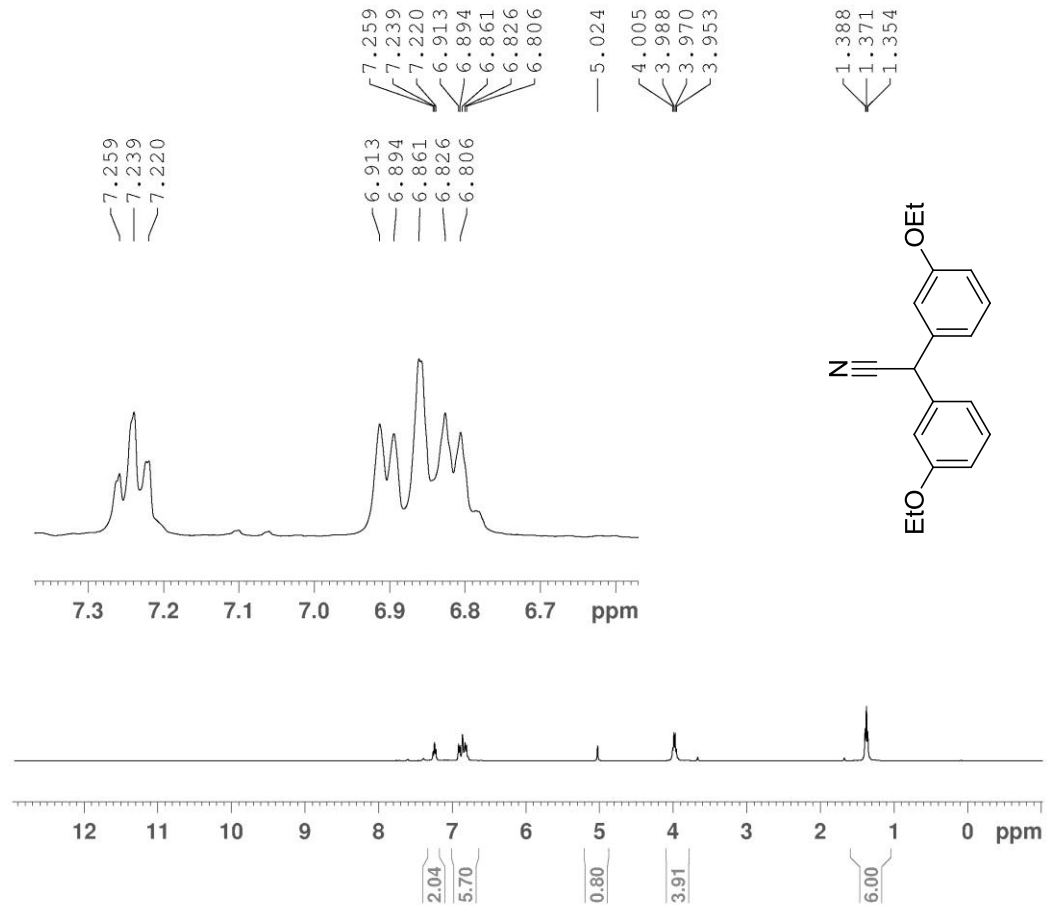
pyy698Deca2-C



BRUKER

NAME	pyy698Deca2
EXPNO	2
PROCNO	1
Date_	20110307
Time	13.52
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	8
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	299.8 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	100.6127797 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

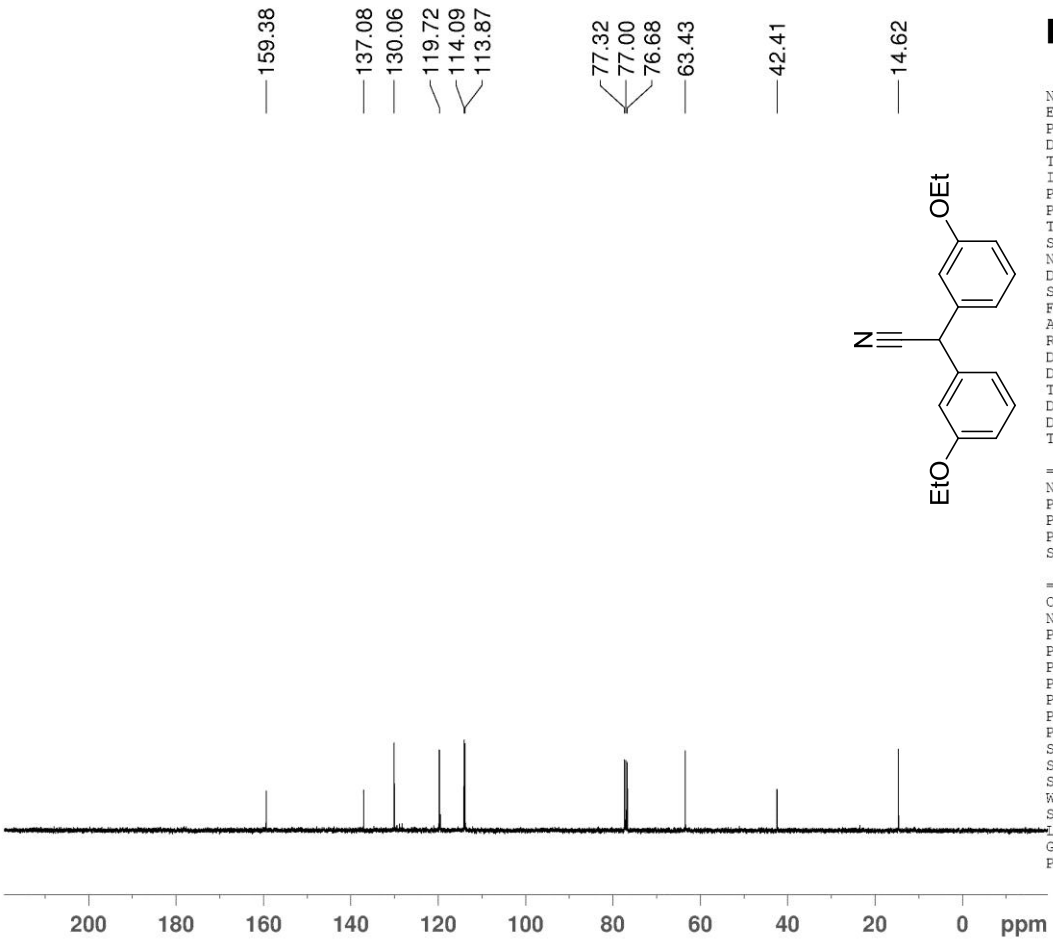
pyy697Deca2-H



BRUKER

NAME	pyy697Deca2	
EXPNO	1	
PROCNO	1	
Date_	20110307	
Time	11.55	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zg30	
TD	32768	
SOLVENT	CDCl3	
NS	8	
DS	2	
SWH	5597.015	Hz
FIDRES	0.170807	Hz
AQ	2.9273248	sec
RG	1	
DW	89.333	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	400.1324008	MHz
SI	32768	
SF	400.1300193	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	

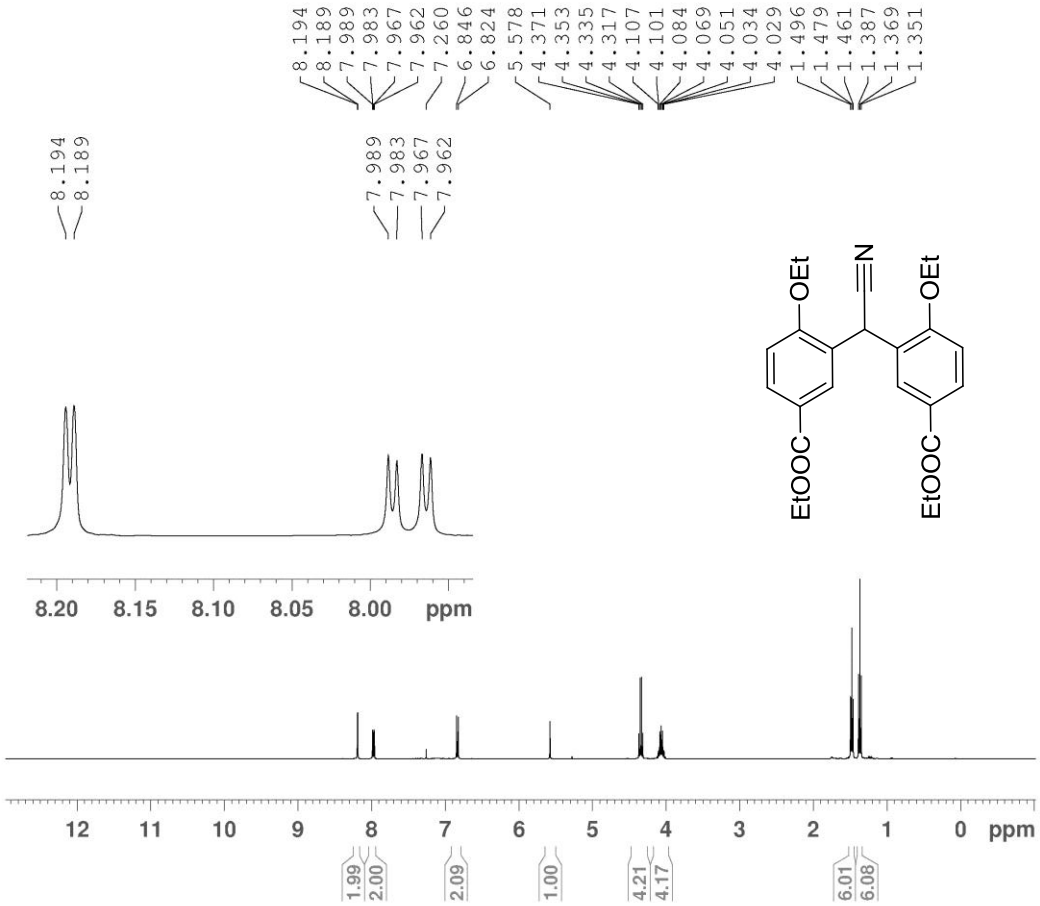
pyy697Deca2-C



BRUKER

NAME	pyy697Deca2
EXPNO	2
PROCNO	1
Date_	20110307
Time	11.59
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	8
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	299.8 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	100.6127820 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

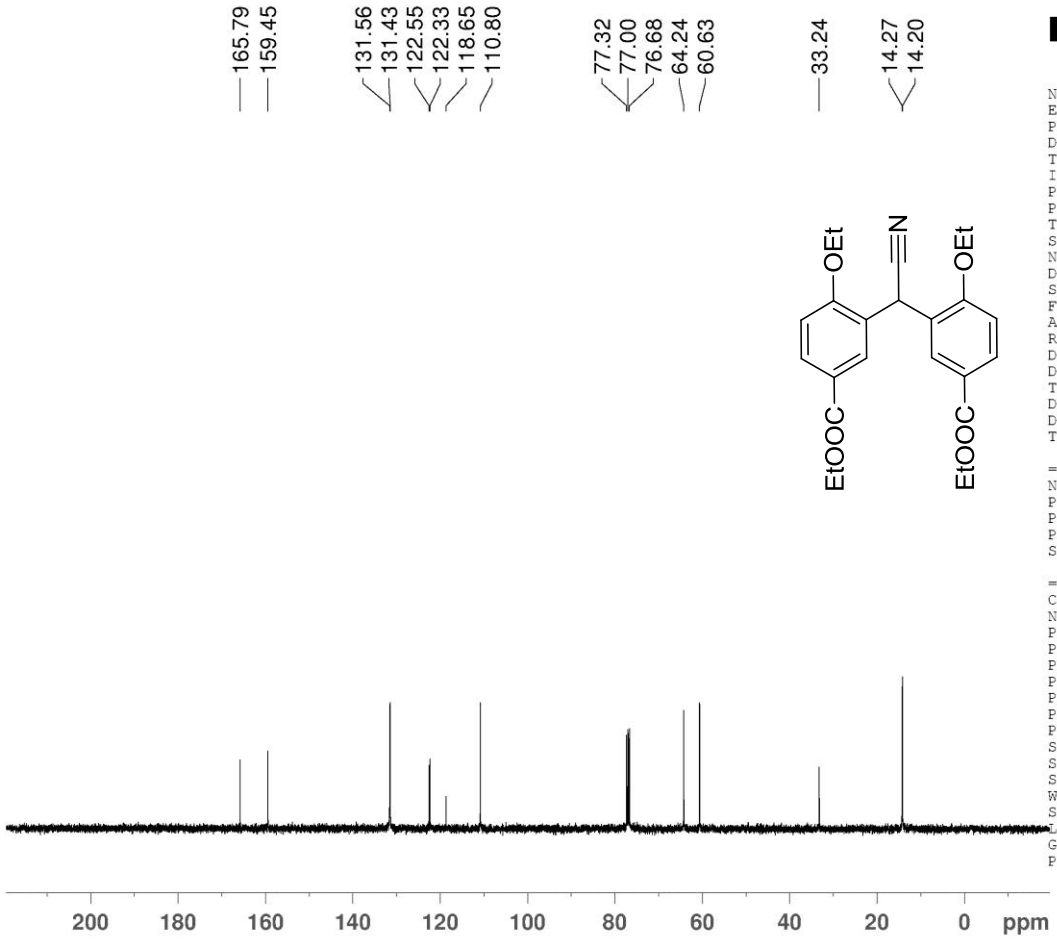
pyy701Deca2-H



BRUKER

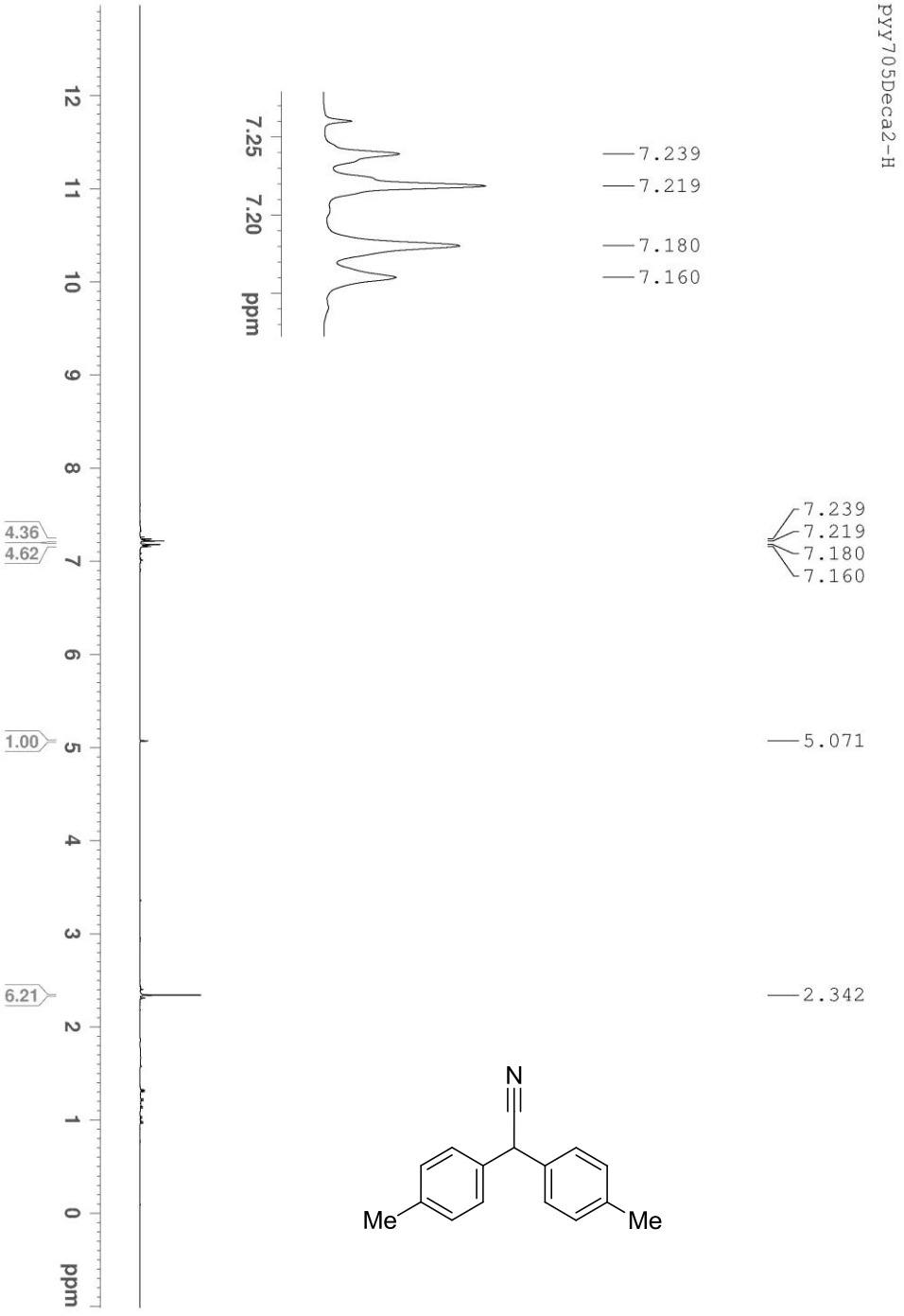
NAME	pyy701Deca2
EXPNO	3
PROCNO	1
Date_	20110408
Time	17.59
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	16
DW	89.333 usec
DE	6.50 usec
TE	300.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300094 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

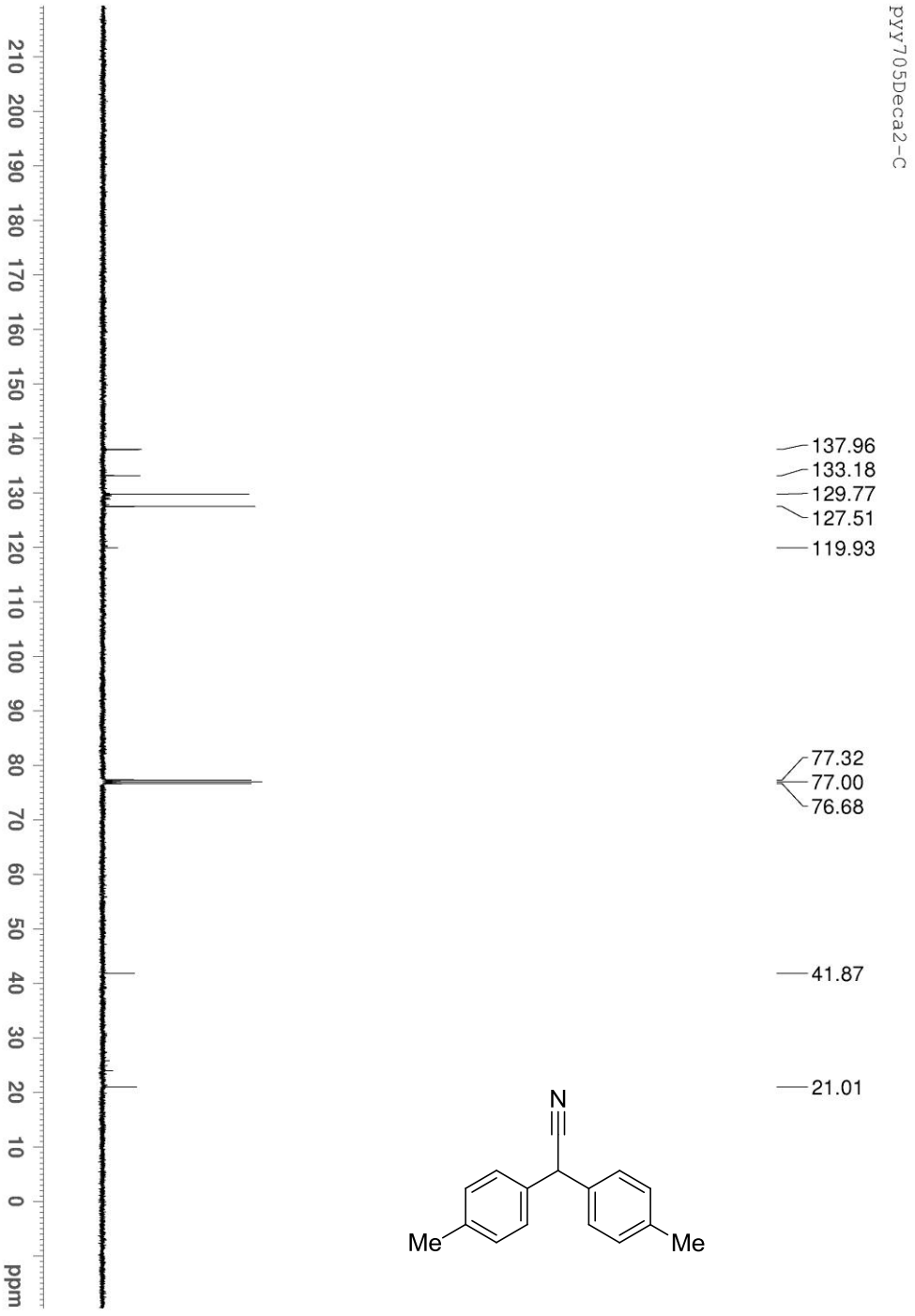
pyy701Deca2-C



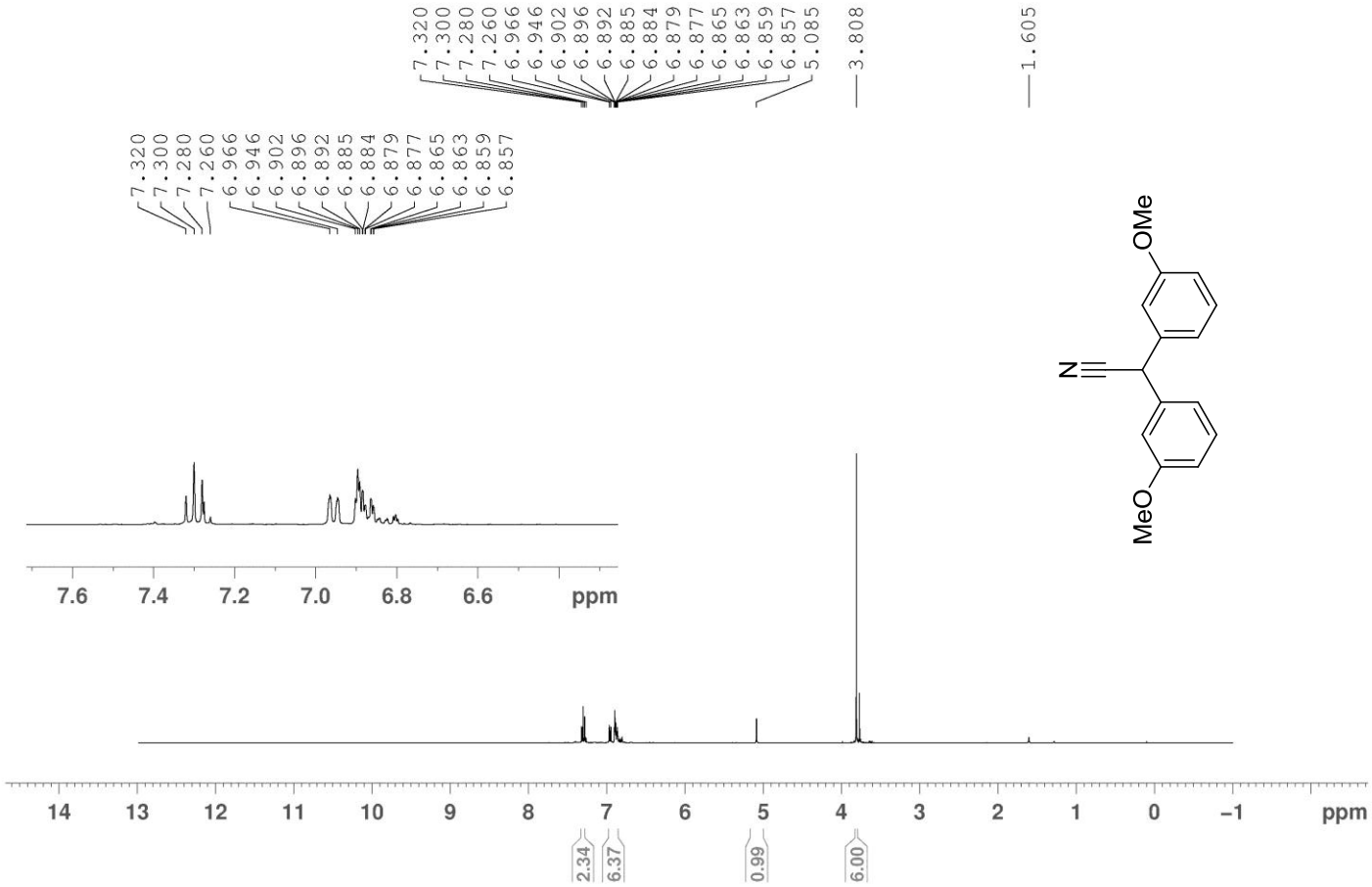
BRUKER

NAME	pyy701Deca2
EXPNO	2
PROCNO	1
Date_	20110308
Time	23.52
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	300.9 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	15.00 dB
PL2W	11.88122272 W
PL12W	0.37571725 W
PL13W	0.37571725 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127835 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

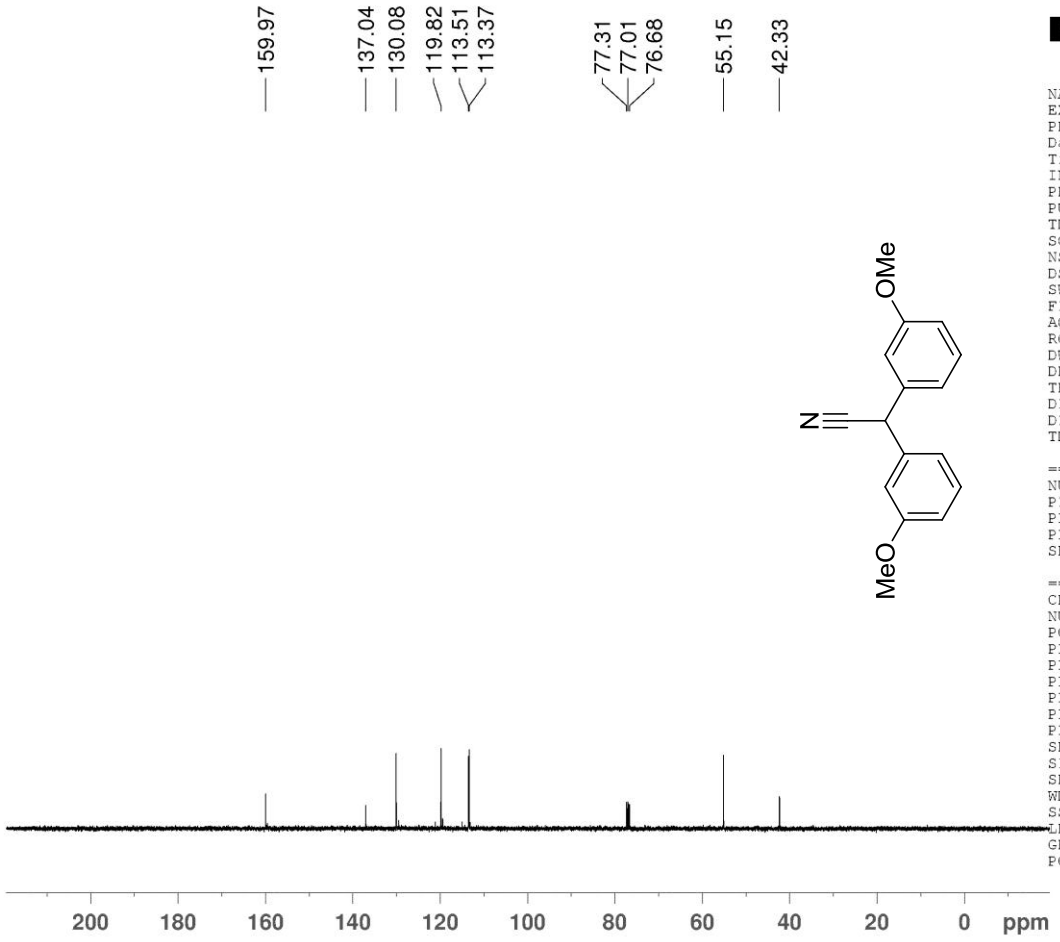

pyy705Deca2-H
7.25
7.20
ppm
7.239
7.219
7.180
7.160
4.36
4.62
1.00
6.21
5.071
2.342
N
Me
Me


pyy705Deca2-C
137.96
133.18
129.77
127.51
119.93
77.32
77.00
76.68
41.87
21.01
N
Me
Me
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

pyy693Deca2-H



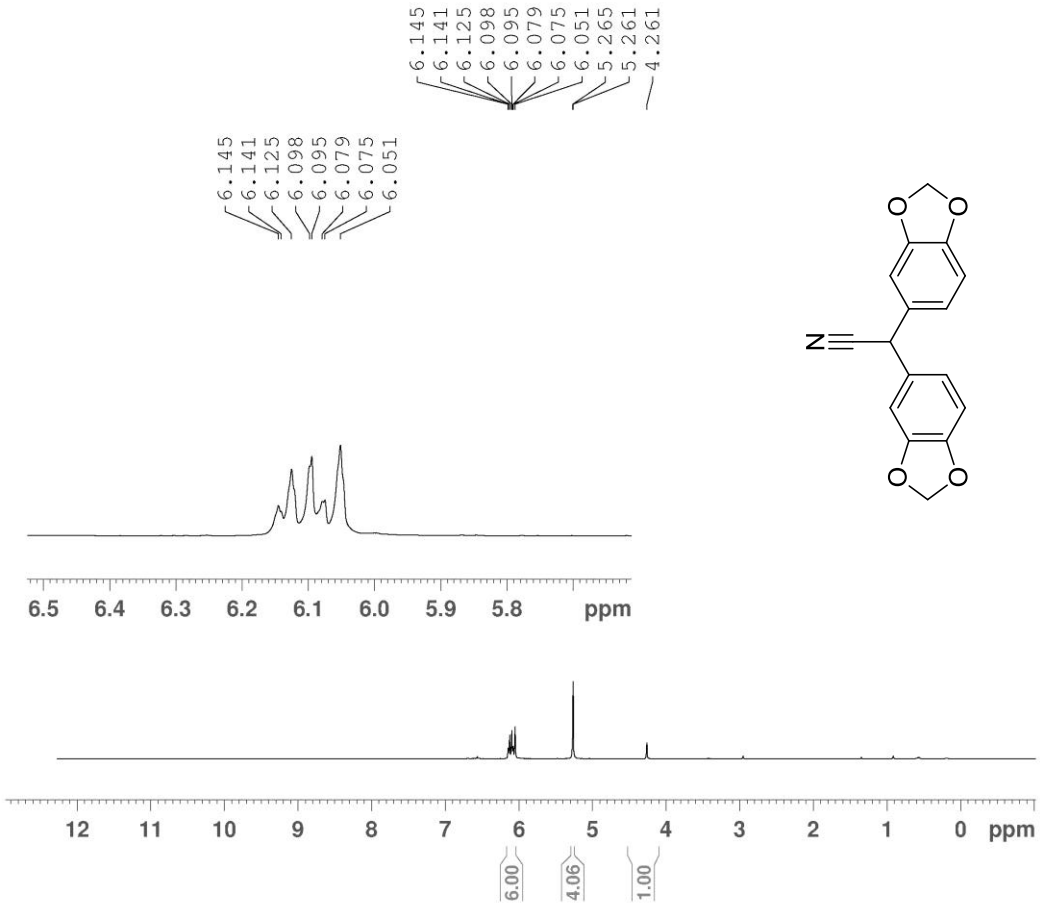
pyy693Deca2-C



BRUKER

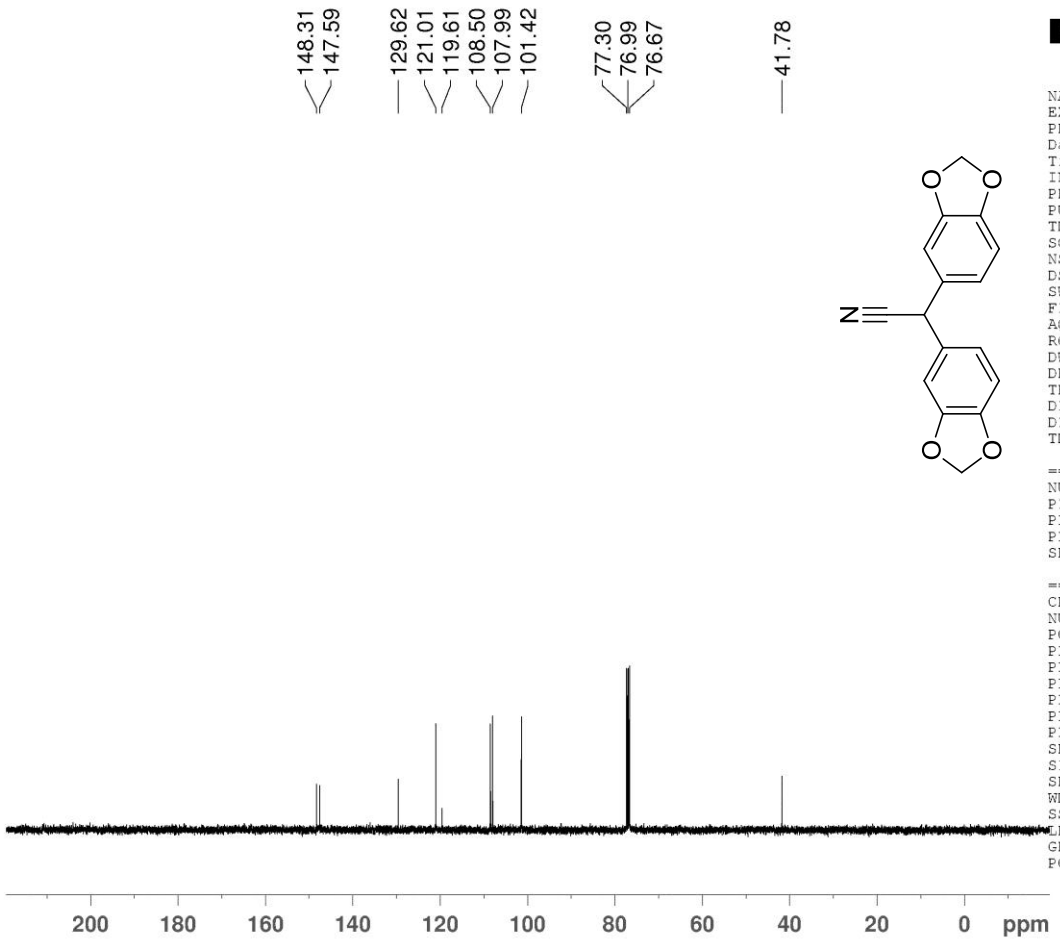
NAME	pyy693deca2
EXPNO	3
PROCNO	1
Date_	20110307
Time	12.04
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	5
DW	20.800 usec
DE	6.50 usec
TE	299.8 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL 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	100.6127868 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

pyy695Deca2-H



NAME	pyy695Deca2
EXPNO	1
PROCNO	1
Date_	20110308
Time	23.26
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	16
DW	89.333 usec
DE	6.50 usec
TE	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	400.1324008 MHz
SI	32768
SF	400.1302875 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

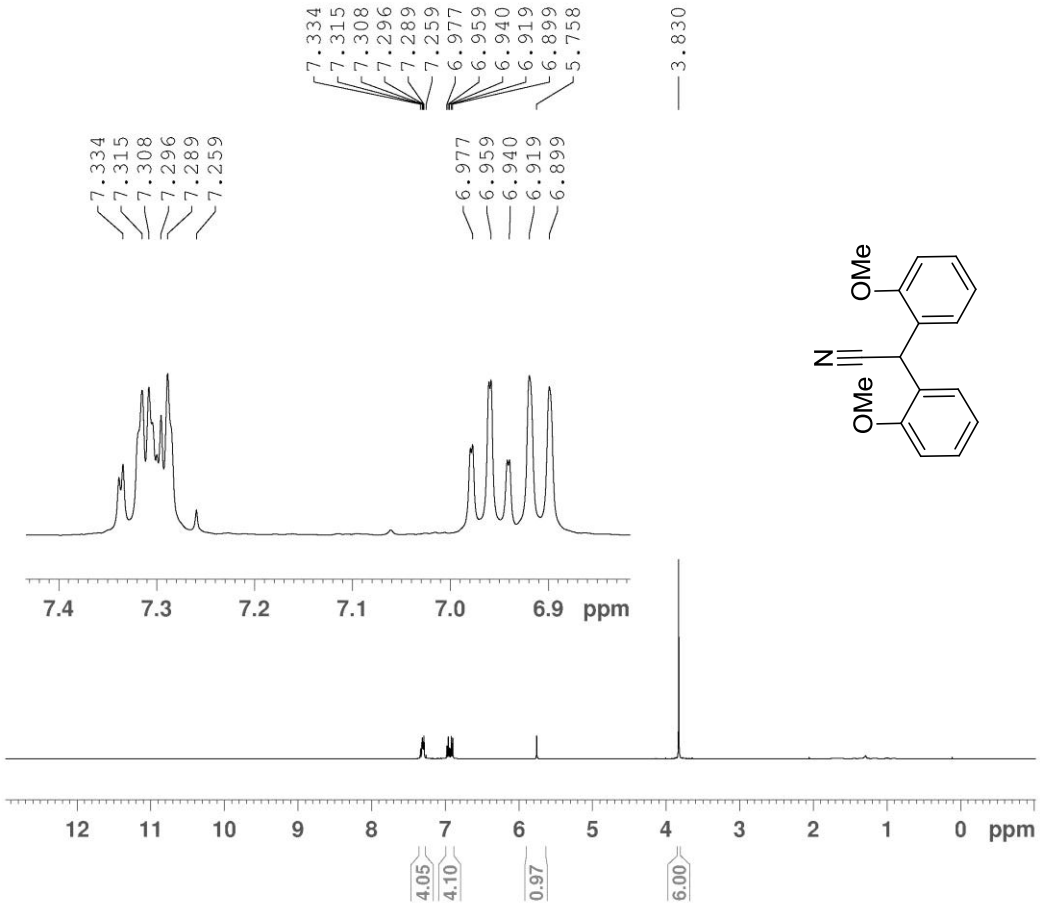
pyy695Deca2-C



BRUKER

NAME	pyy695Deca2
EXPNO	2
PROCNO	1
Date_	20110308
Time	23.32
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
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	100.6127767 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

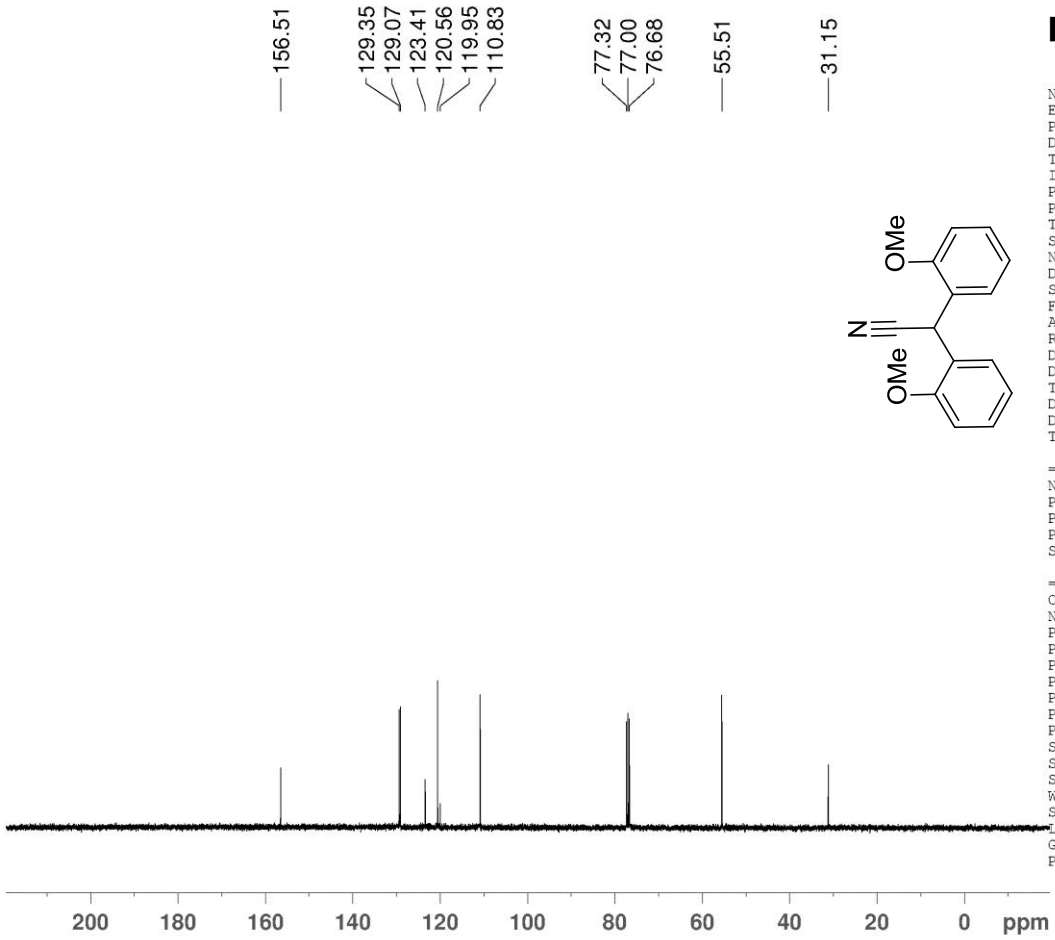
pyy632Deca-H



BRUKER

NAME	pyy632Deca
EXPNO	1
PROCNO	1
Date_	20110125
Time	14.59
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	4
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	25.4
DW	89.333 usec
DE	6.50 usec
TE	296.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300097 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

pyy632Deca-C

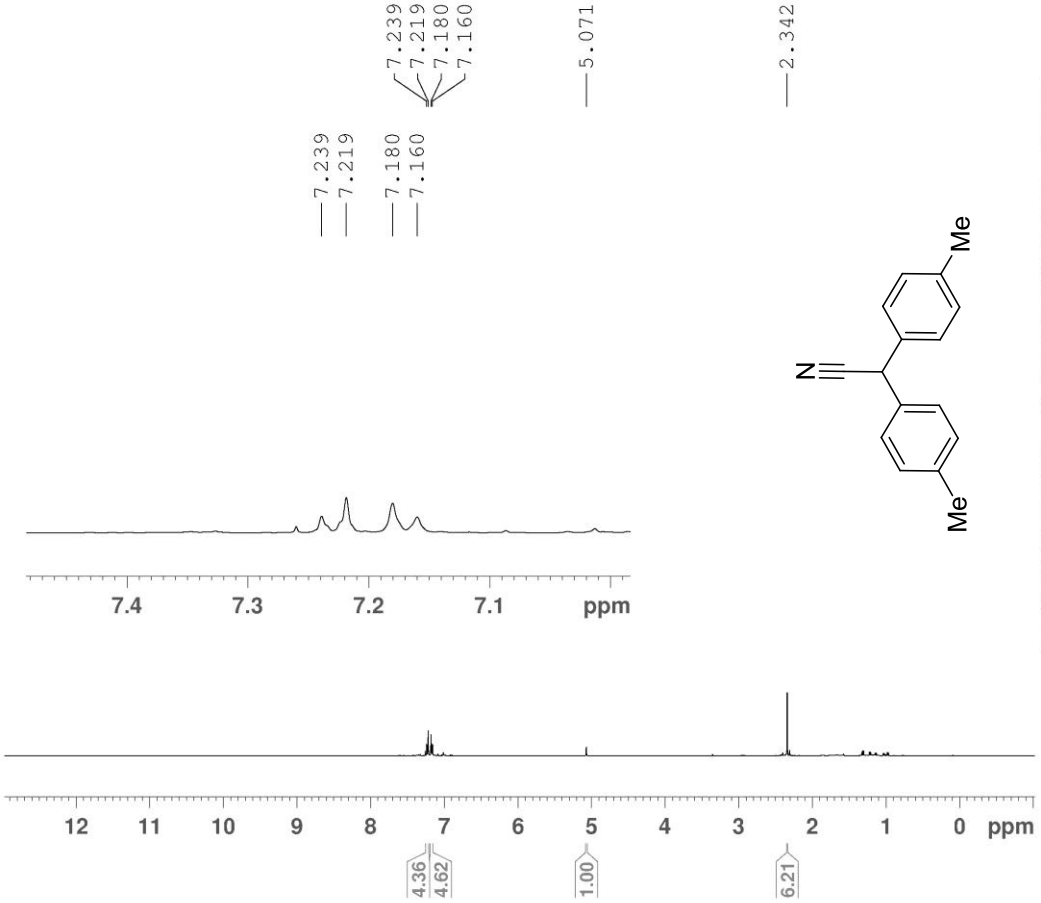


BRUKER

NAME	pyy632Deca
EXPNO	2
PROCNO	1
Date_	20110125
Time	15.05
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	296.2 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	100.6127825 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

^{1}H-, ^{13}C-NMR spectra of palladium-catalyzed decarboxylative diarylation of aryl bromides

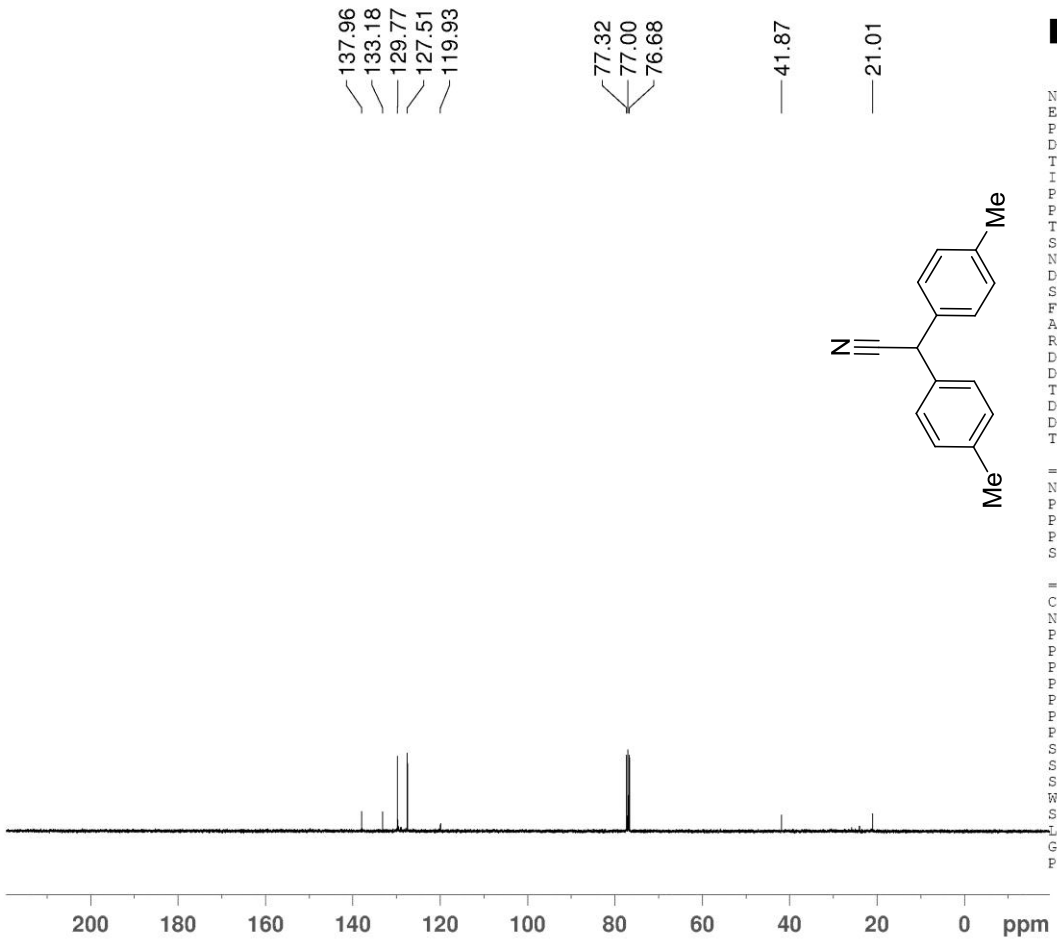
Standard 1H



BRUKER

NAME	pyy736Deca2
EXPNO	2
PROCNO	1
Date_	20110407
Time	23.23
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	5
DW	89.333 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	400.1324008 MHz
SI	32768
SF	400.1300096 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

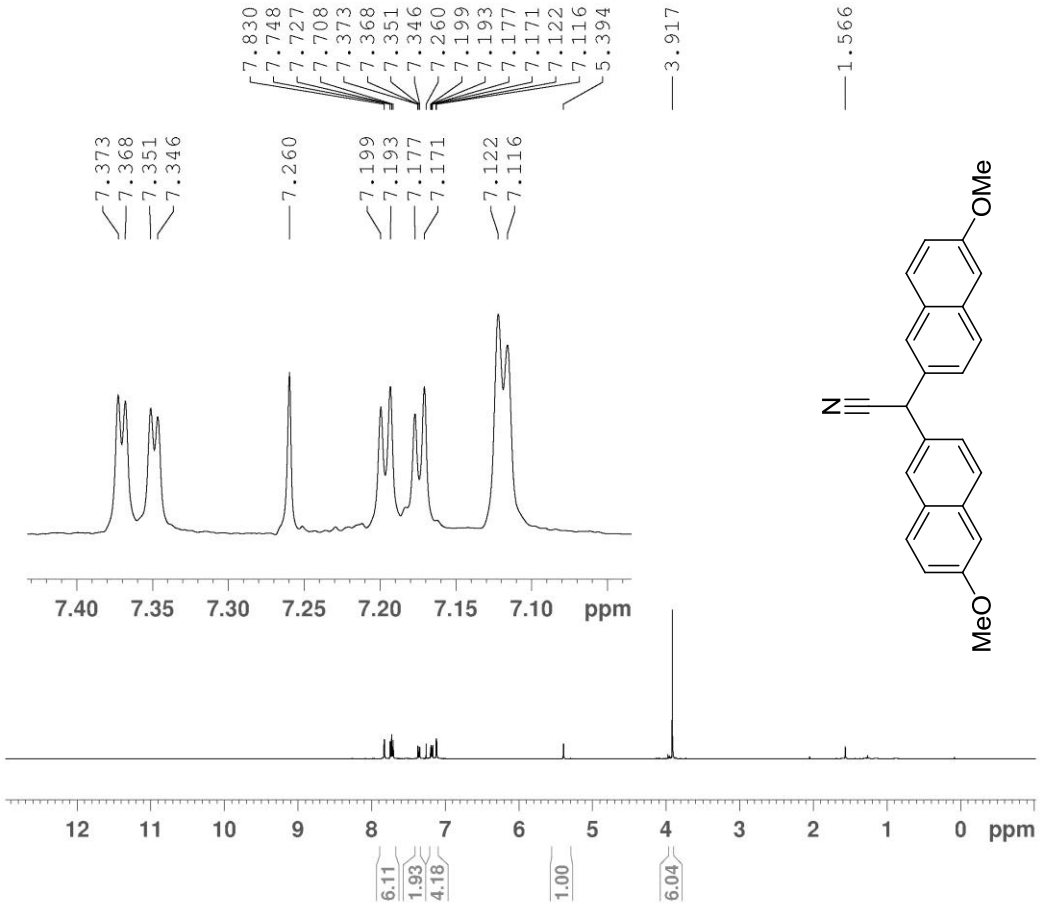
Standard 13C



BRUKER

NAME	pyy736Deca2
EXPNO	4
PROCNO	1
Date_	20110407
Time	23.30
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	100
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	144
DW	20.800 usec
DE	6.50 usec
TE	299.7 K
D1	1.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	15.00 dB
PL2W	11.88122272 W
PL12W	0.37571725 W
PL13W	0.37571725 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127729 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

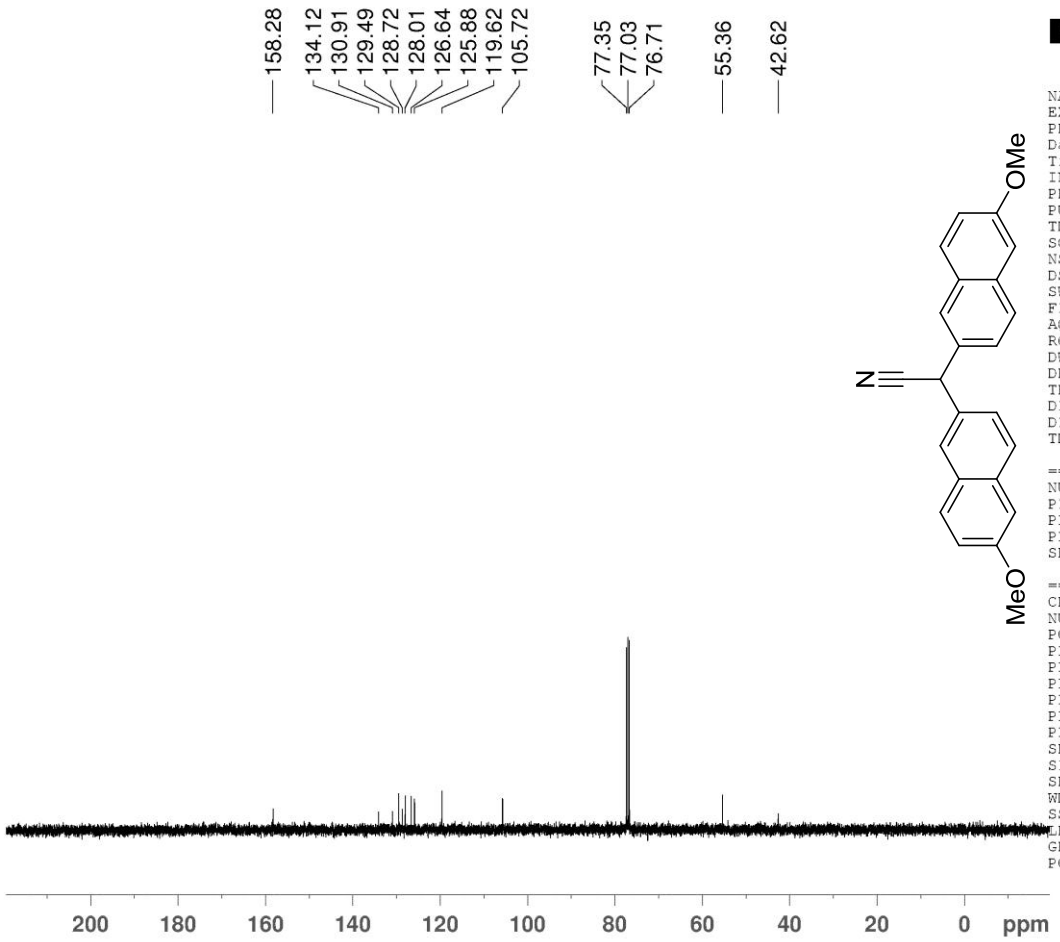
pyy732Deca2-H



BRUKER

NAME	pyy732Deca2	
EXPNO	1	
PROCNO	1	
Date_	20110402	
Time	17.54	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zg30	
TD	32768	
SOLVENT	CDCl3	
NS	8	
DS	2	
SWH	5597.015	Hz
FIDRES	0.170807	Hz
AQ	2.9273248	sec
RG	16	
DW	89.333	usec
DE	6.50	usec
TE	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	400.1324008	MHz
SI	32768	
SF	400.1300097	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	

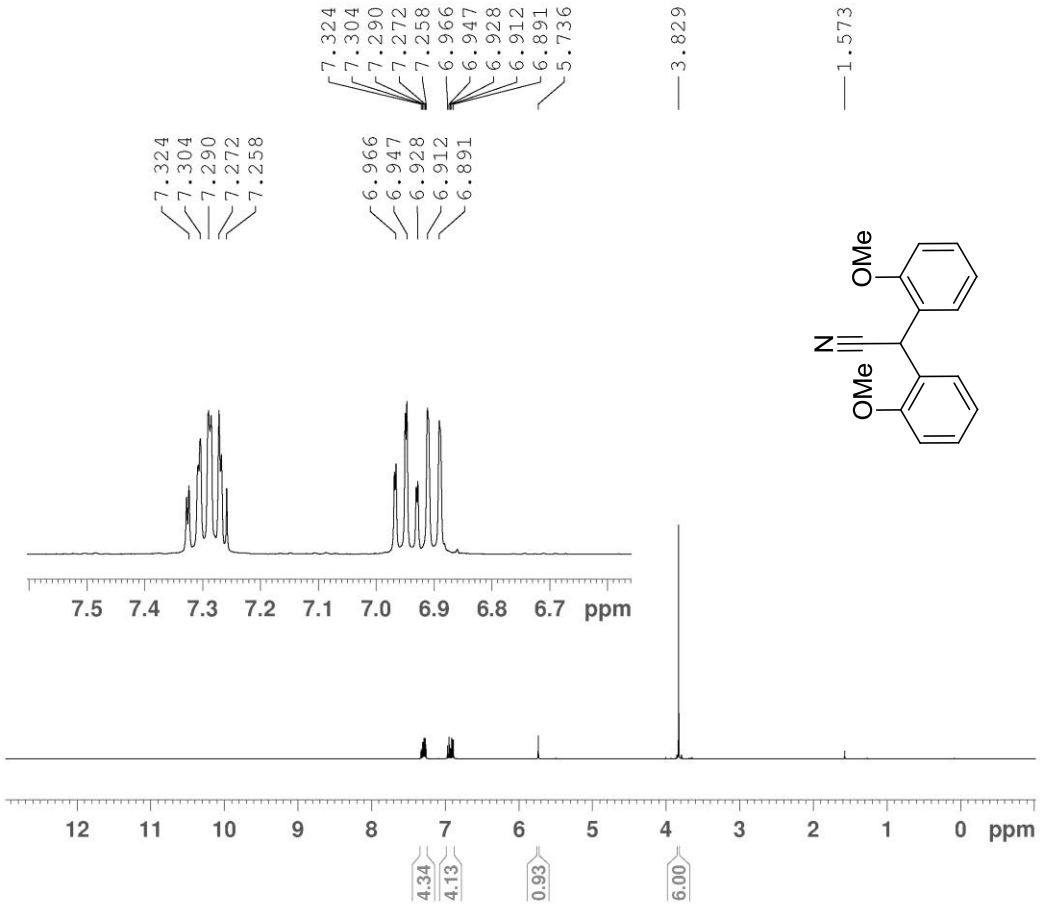
pyy732Deca2-C



BRUKER

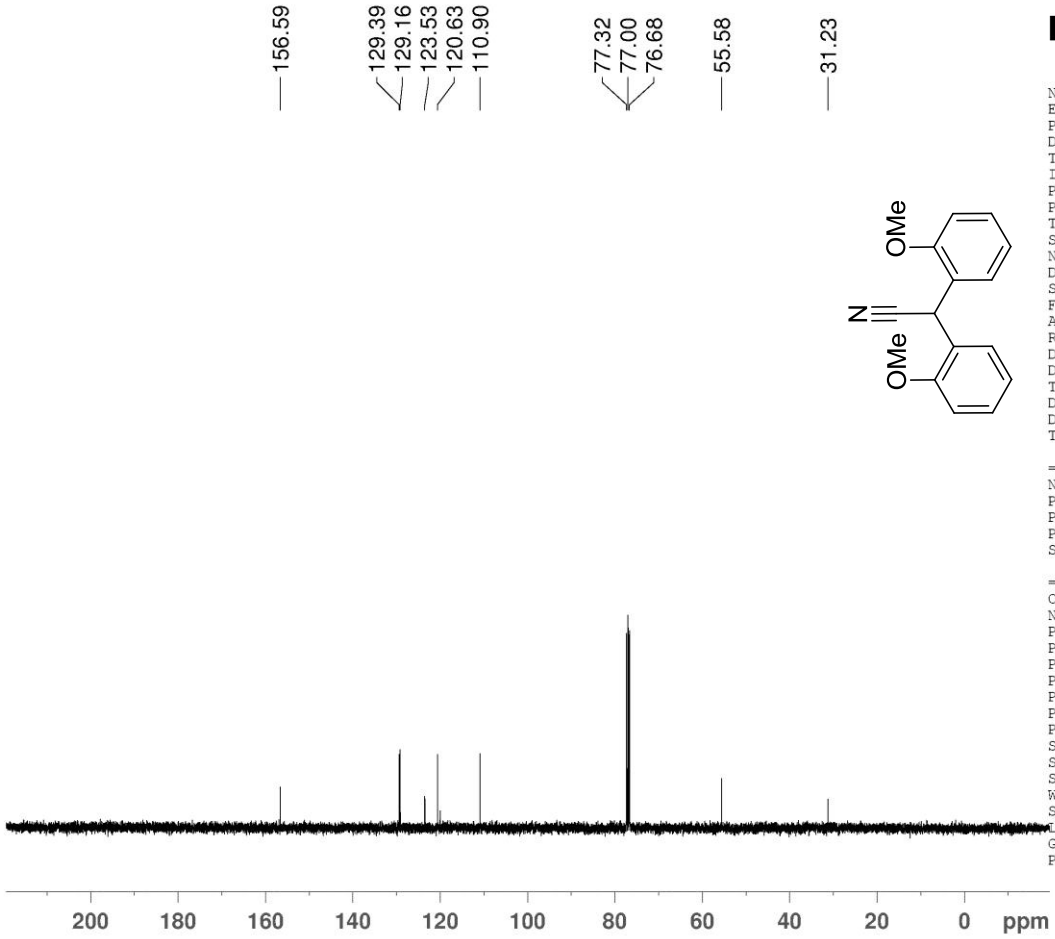
NAME	pyy732Deca2	
EXPNO	2	
PROCNO	1	
Date_	20110402	
Time	17.58	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	8	
DS	2	
SWH	24038.461	Hz
FIDRES	0.366798	Hz
AQ	1.3631988	sec
RG	203	
DW	20.800	usec
DE	6.50	usec
TE	299.7	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	9.50	usec
PL1	-2.00	dB
PL1W	58.52175522	W
SFO1	100.6228298	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	80.00	usec
PL2	0.00	dB
PL12	15.00	dB
PL13	15.00	dB
PL2W	11.88122272	W
PL12W	0.37571725	W
PL13W	0.37571725	W
SFO2	400.1316005	MHz
SI	32768	
SF	100.6127690	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

pyy738Deca2-H



NAME	pyy738Deca2
EXPNO	1
PROCNO	1
Date_	20110407
Time	23.38
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	8
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	8
DW	89.333 usec
DE	6.50 usec
TE	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	400.1324008 MHz
SI	32768
SF	400.1300103 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

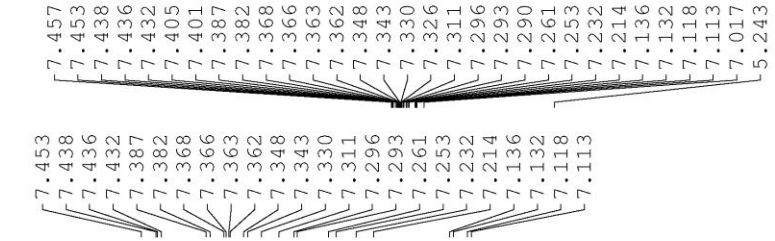
pyy738Deca2-C

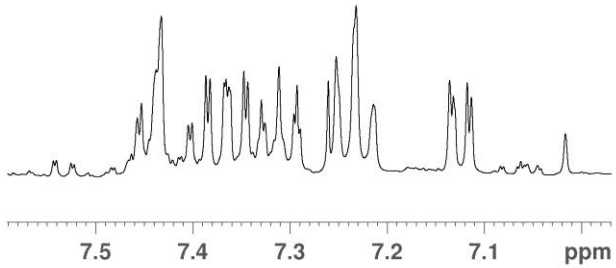


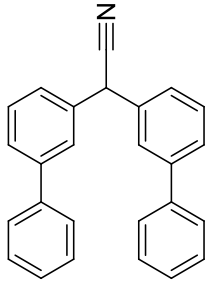
BRUKER

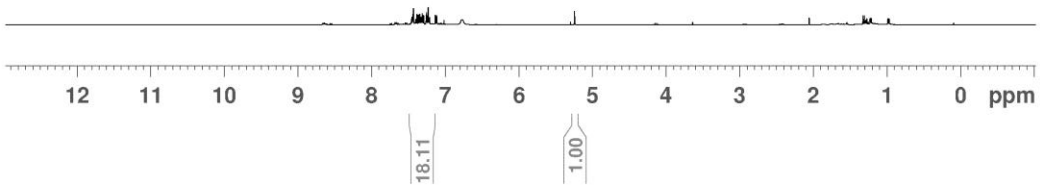
NAME	pyy738Deca2
EXPNO	2
PROCNO	1
Date_	20110407
Time	23.40
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	144
DW	20.800 usec
DE	6.50 usec
TE	299.7 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-2.00 dB
PL1W	58.52175522 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.00 dB
PL13	15.00 dB
PL2W	11.88122272 W
PL12W	0.37571725 W
PL13W	0.37571725 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127736 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

pyy740Deca2-H



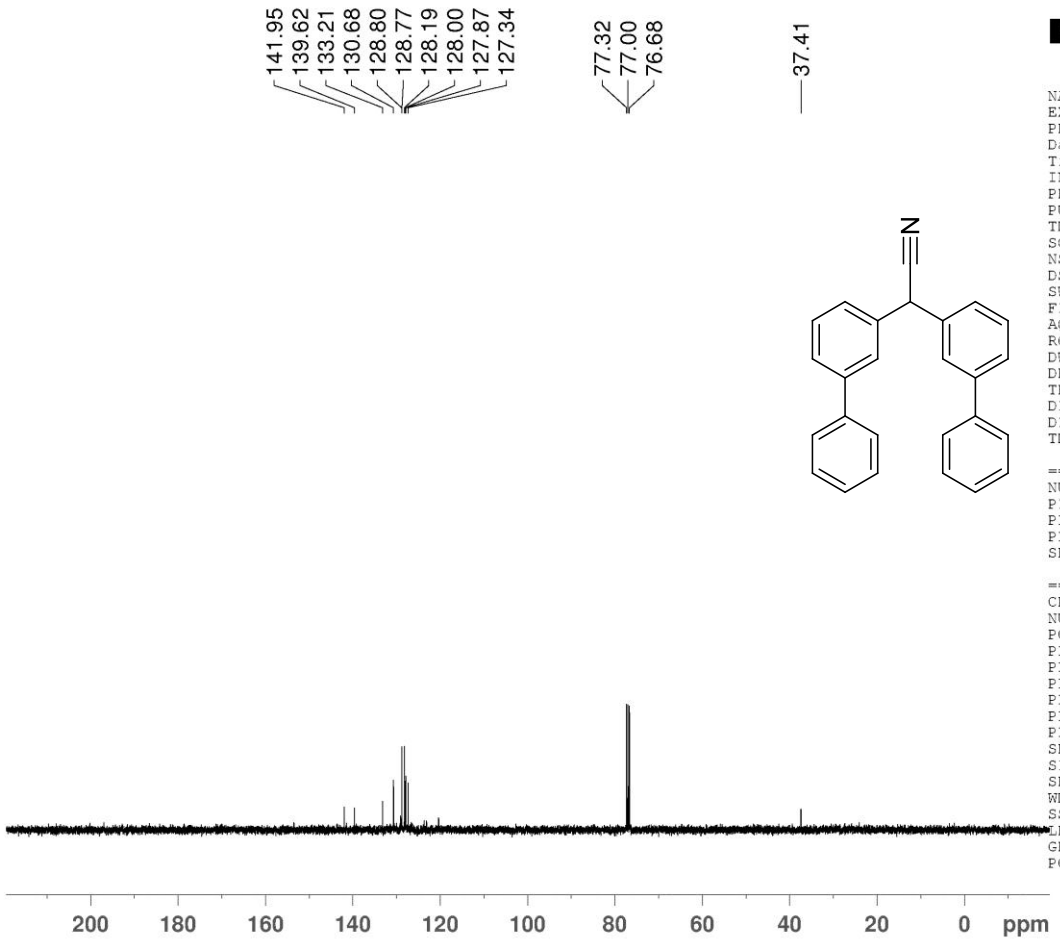






NAME	pyy740Deca2
EXPNO	2
PROCNO	1
Date_	20110408
Time	17.53
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	8
DW	89.333 usec
DE	6.50 usec
TE	299.1 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300092 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

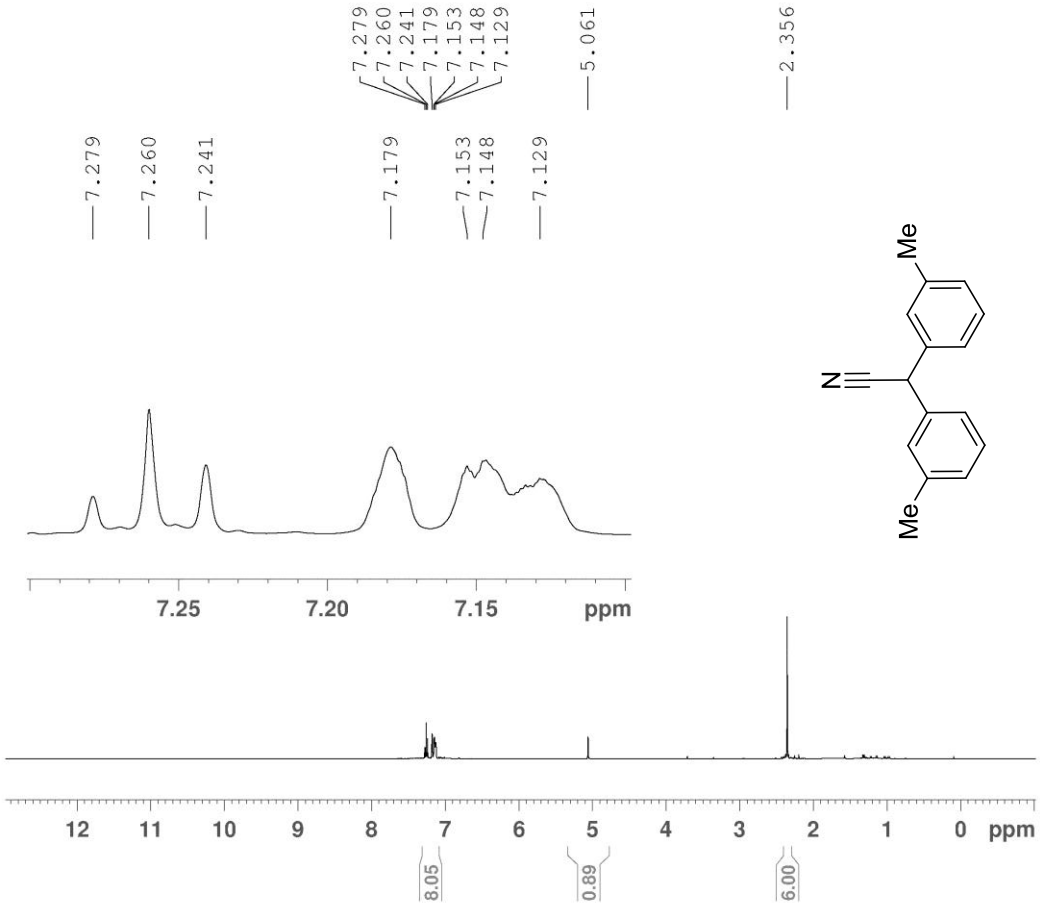
pyy740Deca2-C



BRUKER

NAME	pyy740Deca2
EXPNO	1
PROCNO	1
Date_	20110408
Time	17.51
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	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	100.6127727 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

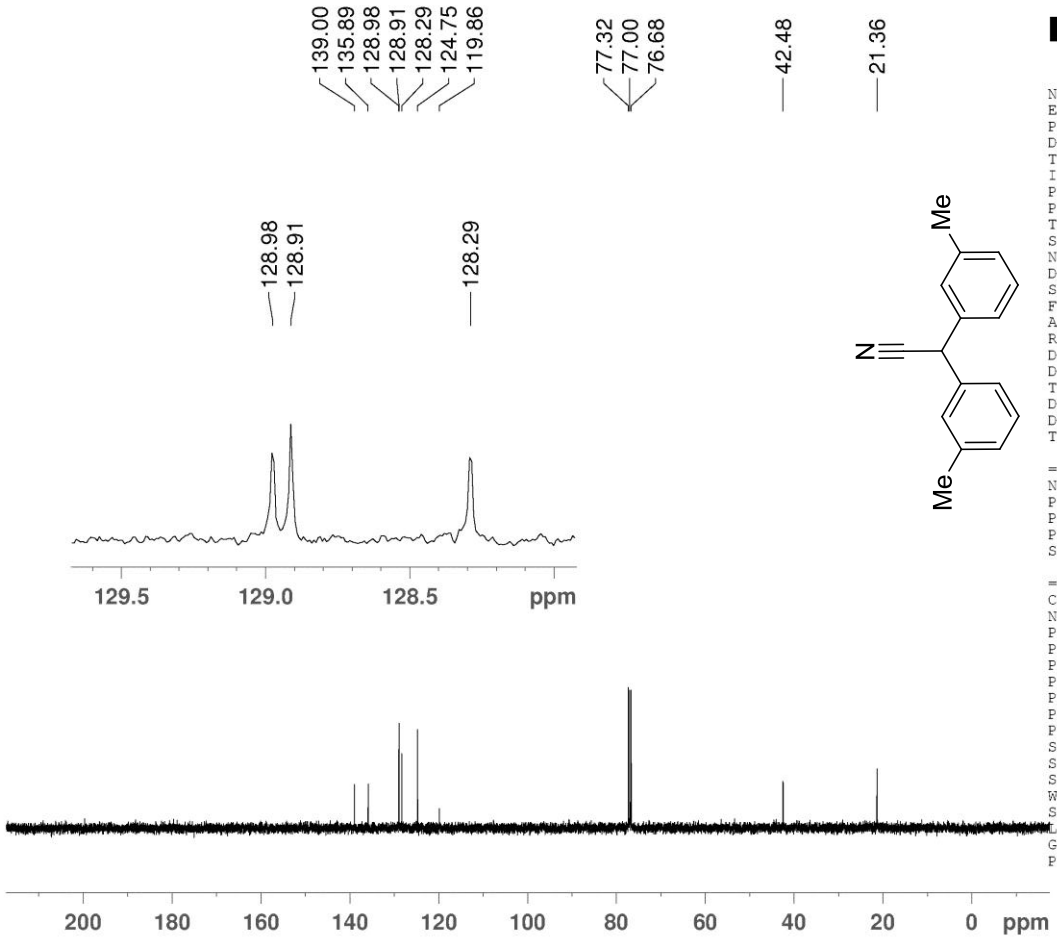
pyy737Deca2-H



BRUKER

NAME	pyy737Deca2
EXPNO	1
PROCNO	1
Date_	20110408
Time	17.37
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	4
DS	2
SWH	5597.015 Hz
FIDRES	0.170807 Hz
AQ	2.9273248 sec
RG	16
DW	89.333 usec
DE	6.50 usec
TE	300.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.70 usec
PL1	0.00 dB
PL1W	11.88122272 W
SFO1	400.1324008 MHz
SI	32768
SF	400.1300096 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

pyy737Deca2-C



BRUKER

NAME	pyy737Deca2
EXPNO	2
PROCNO	1
Date_	20110408
Time	17.40
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	8
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	100.6127738 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

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