TRANSITION METAL CATALYSIS OF ACETALS AND PIVALATES: ENANTIOSELECTIVE AND ENANTIOSPECIFIC METHODS FOR C-C & C-B BOND FORMATION

by

Srinivas H. Harathi Dwarakanath

A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry and Biochemistry

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by

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ABSTRACT

This dissertation focuses on the development of transition metal-catalyzed reactions of acetal and pivalate substrates. These new methods enable efficient synthesis of highly enantioenriched organic molecules. The first chapter discusses an enantioselective alkynylation of chromene acetals using copper (I) catalysts. In this method, we have observed wide substrate scope, and high enantioselectivities were observed especially with 4-aryl chromene acetals. Use of dilute conditions, $BF_3{\cdot}OEt_2$ as Lewis acid and Cy_2NMe as base are critical for achieving high enantioselectivities. In this chapter, a mechanism and stereochemical model are proposed that rationalize the observed substituent effects and enantioselectivities. This method demonstrates the advantage of using transition metal catalysis to facilitate reactions involving oxocarbenium ion intermediates.

Chapter 2 discusses enantiospecific, nickel-catalyzed cross-couplings of benzylic pivalates with mild and functional group tolerant arylboroxines as cross-coupling partners. The diarylalkane and triarylmethane products formed were obtained in high yields and levels of stereochemical fidelity. The success of this method depends on the use of $Ni(cod)_2$ as catalyst and NaOMe as base. In this method, we have shown broad substrate scope and wide functional group tolerance.

Chapter 3 discusses an enantiospecific, nickel-catalyzed cross-coupling of 1,3-disubstituted secondary allylic pivalates with mild and functional group tolerant arylboroxines. The 1,3-diaryl allyl products are obtained with high levels of stereochemical fidelity and yields. Excellent regioselectivity and *E*/*Z* selectivity are also

observed in this method. A wide variety of functional groups are tolerated, and the utility of this method is demonstrated in the synthesis of the anti-inflammatory drug (*S*)-ketoprofen.

Chapter 4 discusses an enantiospecific, nickel-catalyzed cross-coupling of 1,3-disubstituted secondary allylic pivalates and bis(pinacolato)diboron (B_2Pin_2) to form γ-aryl allyl boronates in high yields and ee's. In this method, the absolute configuration of the allylboronate product depends on the ligand and the solvent used. Thus, either enantiomer of allyl boronate is available from the same enantiomer of pivalate starting material. The optimized conditions for obtaining both retention and inversion products are discussed.

Chapter 1

ENANTIOSELECTIVE ADDITION OF ALKYNES TO CHROMENE ACETALS

1.1 Introduction

Cyclic ether scaffolds with α-stereogenic centers are present in many bioactive molecules (Figure 1.1). This important class of bioactive compounds has found many applications, such as potential antibacterial agents, DNA polymerase inhibitors, and in the treatment of atherosclerosis.[1-11]

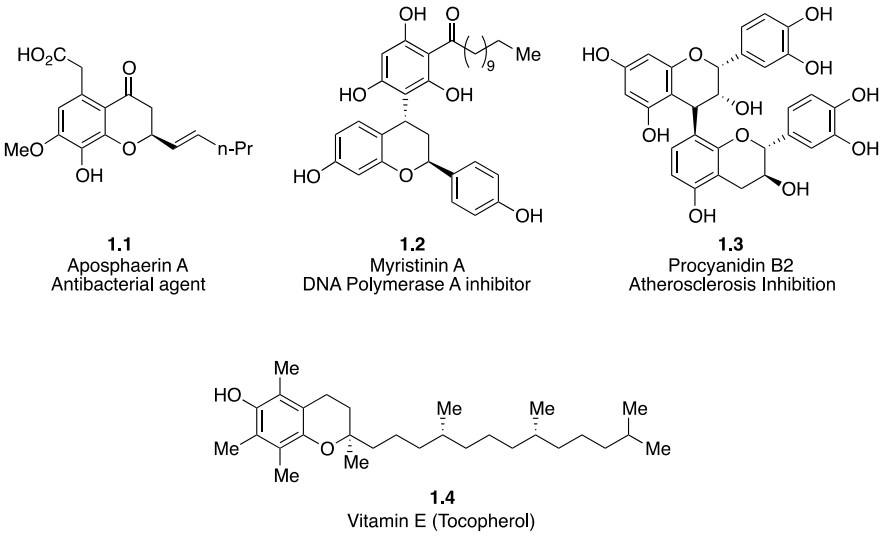


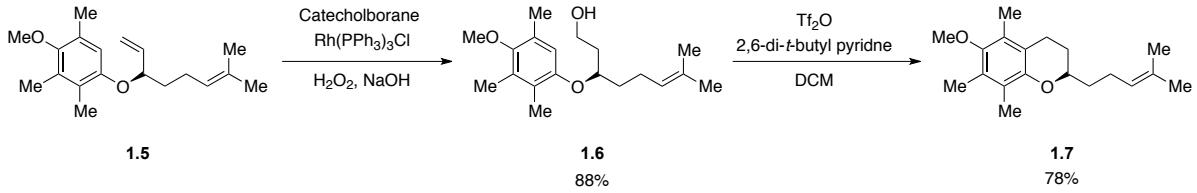
Figure 1.1. Biologically Active Cyclic Ethers with α-Stereocenters

State-of-the-Art in the Synthesis of Enantioenriched α-Substituted Cyclic Ethers

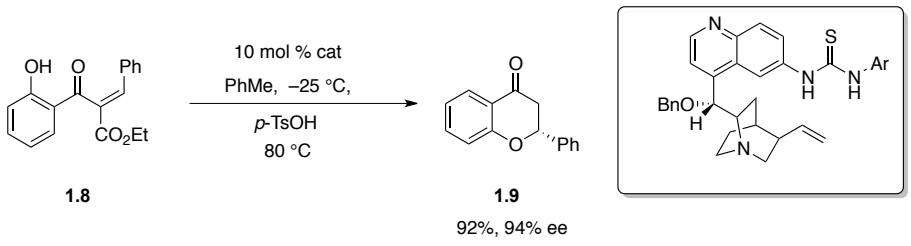
Methods Not Involving Oxocarbenium Ions

Various methods have been developed to synthesize these important molecular scaffolds. Many routes involve formation of the stereocenter prior to cyclization.[9,12-24] The Trost group has used the chemoselective hydroboration strategy followed by electrophilic cycloalkylation to form a pyran ring, which is an important scaffold of the Vitamin E molecule (Scheme 1.1).[9]

Scheme 1.1 Stereocenter Formation Before Cyclization (Trost)



Scheme 1.2. Concurrent Stereocenter and Ring Formation (Scheidt)

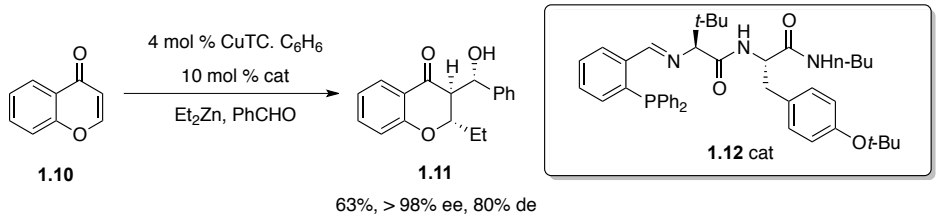


Alternative strategies like hetero-Diels-Alder cycloadditions, Wacker-type cyclizations and conjugate additions involve concurrent ring-forming and stereocenter-forming steps.[25-30] The Scheidt group reported a method to form α-stereocenters of

flavanones from α-substituted chalcones by intramolecular conjugate addition using thiourea catalysts. Scheidt's strategy involves concurrent ring and stereocenter center formation (Scheme 1.2).[25]

A third strategy involves stereocenter formation after cyclization. For example, the Hoveyda group has developed an enantioselective copper-catalyzed conjugate addition of alkyl zinc reagents to chromenone using a phosphine ligand containing amino acid core **1.12**. High enantioselectivities were observed, but the scope of this reaction is limited (Scheme 1.3).[31]

Scheme 1.3: Stereocenter Formation After Cyclization (Hoveyda)



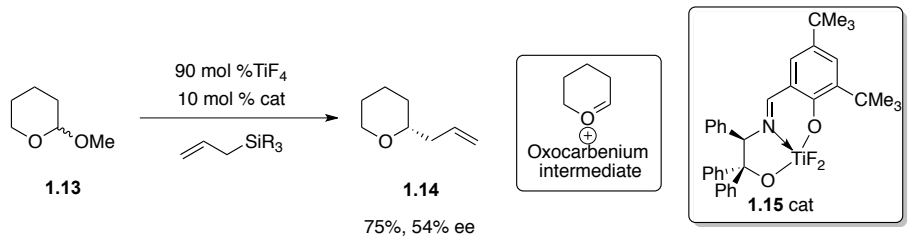
Additions to Oxocarbenium Ion Intermediates

Within the strategy of forming the stereocenter on a cyclic substrate, enantioselective addition to a prochiral oxocarbenium ion is an attractive approach. The requisite oxocarbenium ions can be formed insitu from ionization of acetal precursors. These acetals inturn can be easily prepared and are widely available. However, despite advances in the field of asymmetric catalysis, controlling enantioselectivity in additions to prochiral cyclic oxocarbenium ions remains a significant challenge, as the

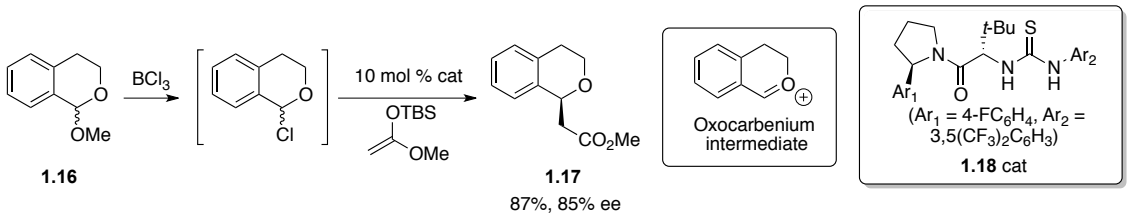
oxocarbenium ion lacks a Lewis basic functional site for coordination to chiral catalysts in a well-defined orientation. Moreover, oxocarbenium ions are very reactive intermediates, making uncatalyzed background reactions possible, which is detrimental to the enantioselectivity. When I began my work in this field, only four methods involving enantioselective additions to cyclic oxocarbenium ions were known. Braun reported a single example of allylation of dihydropyranyl acetal **1.13** catalyzed by a chiral titanium (IV) **1.15** (Scheme 1.4A).[32] The Jacobsen group has developed enantioselective additions of silyl ketene acetals to 1-chloroisochroman using chiral thiourea catalyst **1.18 (**Scheme 1.4B**)**.[33] The Schaus group has shown the use of tartramide catalyst **1.20** for the enantioselective addition of vinyl and electron-rich aryl boronic esters to chromene acetals (Scheme 1.4C).[34]

Scheme 1.4: Methods Involving Additions to Oxocarbenium Ions

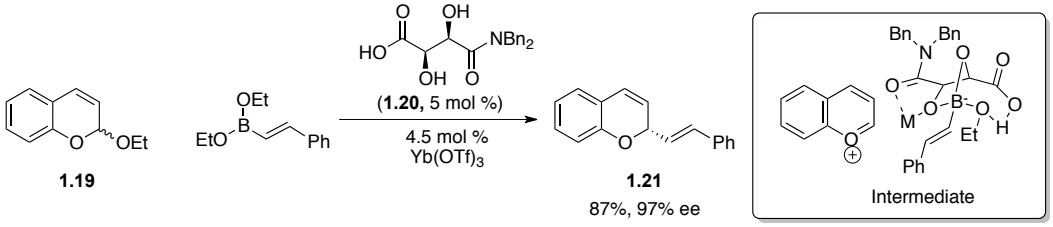
A) Lewis Acid Catalysis (Braun)



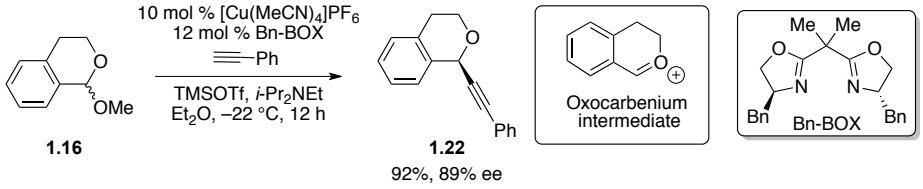
B) Thiourea Catalysis (Jacobsen)



C) Diol and Lewis Acid Catalysis (Schaus)

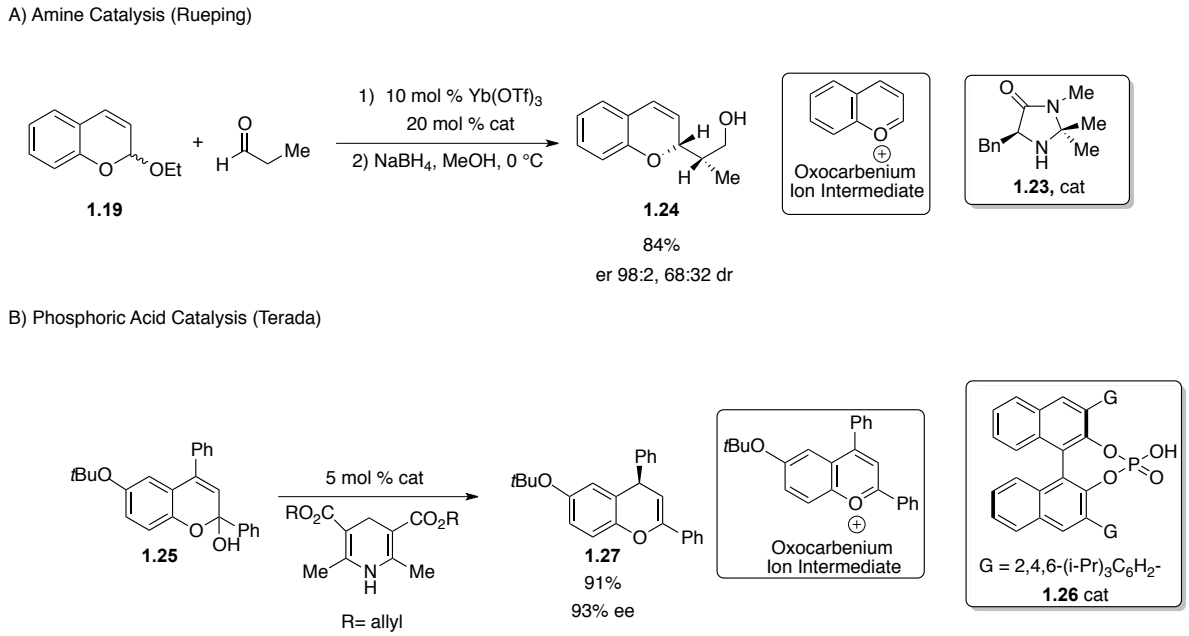


D) Transition Metal Catalysis (Watson)



In our lab, we have shown a copper(I)-catalyzed alkynylation of isochroman acetals, which represents the first example of an enantioselective addition of an organometallic nucleophile to a prochiral cyclic oxocarbenium ion (Scheme 1.4D).[35] More recently, Rueping has demonstrated the enantioselective addition of enamines to oxocarbenium ions using organocatalyst **1.23** (Scheme 1.5A)[36] and Terada has demonstrated an asymmetric 1,4-addition of a hydride to an the oxocarbenium ion using chiral Bronsted acid **1.26** (Scheme 1.5B).[37]

Scheme 1.5: Recent Methods Involving Additions to Oxocarbenium Ions

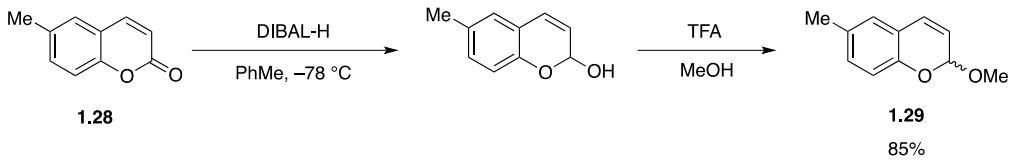


As shown in Schemes 1.4 and 1.5, catalytic, enantioselective additions to oxocarbenium ion interemediates is possible. However, these methods are largely limited to single classes of cyclic oxocarbenium ions, and a general strategy remains unknown. I envisioned that our enantioselective Cu(I)-catalyzed alkynylation may represent a general strategy. Towards this goal, I have developed an enantioselective, copper-catalyzed addition of alkynes to chromene acetals.

1.2 Results and Discussion

Synthesis of Chromene Acetals Substrates

Scheme 1.6: Synthesis of Chromene Acetals



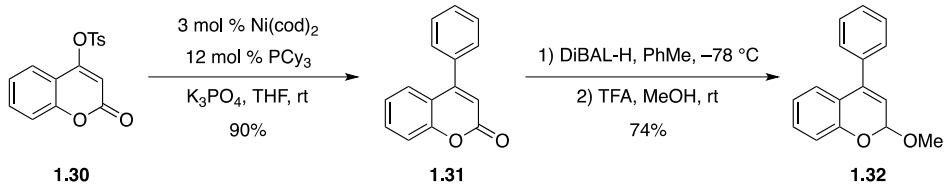
1.28 **1.29**

85%

As shown for substrate **1.29** in Scheme 1.6, acetal substrates were prepared via reduction of the coumarin precursor using DIBAL-H and subsequent acetal formation under acidic conditions. As these compounds decompose on silica gel, they required the use of deactivated silica gel for purification. These acetals are stable and can be stored at room temperature.

Synthesis of 4-Aryl Substituted Chromene Acetal

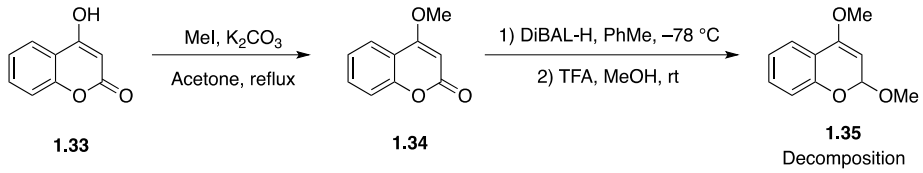
Scheme 1.7: Synthesis of 4-Phenyl Chromene Acetal



4-aryl chromene acetals have been prepared from a two-step synthetic route from 4-tosyl chromenone **1.30**. Nickel-catalyzed Heck reaction of tosylates installs the aryl group on the chromenone. DIBAL-H reduction and subsequent acetal formation delivers 4-arylated chromene acetals in very good yields. The representative reaction is shown in (Scheme 1.7).

Synthesis of 2,4-Dimethoxy-2*H*-Chromene

Scheme 1.8: Attempted synthesis of 2,4-Dimethoxy-*2H*-Chromene

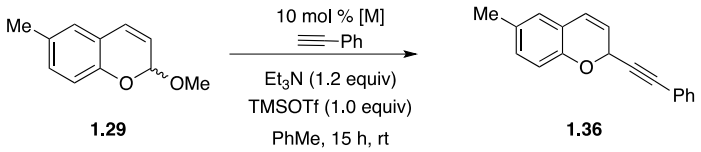


Given the beneficial effect of electron-rich aryl groups at the 4-position of the chromene acetal (discussed below), we wanted to study the influence of even more electron-donating groups at this position. We wanted to prepare of 2,4-dimethoxy-2*H*-chromene from 4-hydroxycoumarin by the two-step sequence shown in Scheme 1.8. However, we were not able to form 2,4-dimethoxy-2*H*-chromene **1.35**, instead we

observed various decomposition products by thin layer chromatography in the reduction step.

Alkynylation with Achiral Catalysts

Table1.1: Alkynylation using Phenylacetylene[a]



1.29 **1.36**

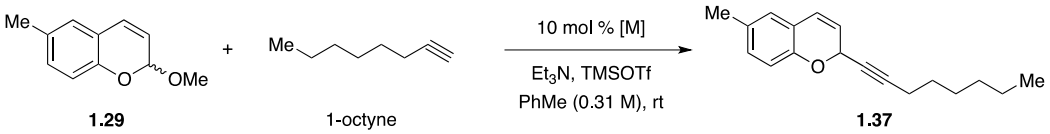
entry	[Metal]	Yield (%)
1	CuI	73
2	$ZnBr_2$	78

[a] Conditions: acetal 1.29 (0.2, 1.0 equiv), [M] (0.02 mmol, 10 mol %), phenyl acetylene (0.24 mmol, 1.2 equiv), Et_3N (0.24 mmol, 1.2 equiv), TMSOTf (0.2 mmol, 1.0 equiv), PhMe (0.31 M), 15 h.

When we tried alkynylation of chromene acetal **1.29** with phenylacetylene, we obtained alkynylated chromene **1.36** in good yields with both CuI and $ZnBr_2$ (Table 1.1).

I have also synthesized various other racemic alkynyl chromenes in good yields using above metal-catalyzed conditions. The alkynylated chromene product **1.37** was obtained in decent yields both with CuI and $ZnBr_2$ when 1-octyne was used (Table 1.2).

Table 1.2: Alkynylation using 1-Octyne[a]

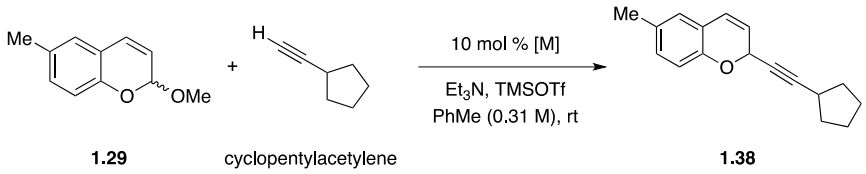


entry	[Metal]	NMR Yield (%)
1	CuI	54
2	$ZnBr_2$	[65]

[a] Conditions: acetal **1.29** (0.284 mmol, 1.0 equiv), [Metal] (0.028 mmol, 10 mol %), 1-octyne (0.315 mmol, 1.1 equiv), Et_3N (0.355 mmol, 1.25 equiv), TMSOTf (0.312 mmol, 1.1 equiv), PhMe (0.31M). NMR yields were determined using 1,3,5-trimethoxy benzene as internal standard. Yield in parentheses are isolated.

When cyclopentylacetylene was used as a reaction partner, we observed excellent yields of alkynylated chromene **1.38** with both CuI and $ZnBr_2$ (Table 1.3).

Table 1.3: Alkynylation using Cyclopentylacetylene[a]

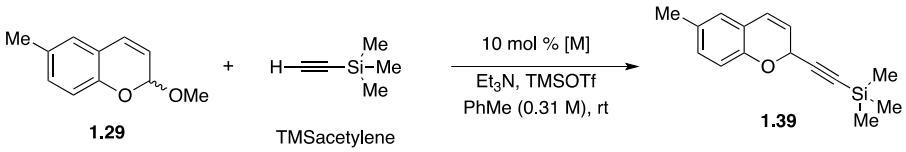


entry	[Metal]	NMR Yield (%)
1	CuI	80
3	$ZnBr_2$	[93]

[a]Conditions: acetal **1.29** (0.142 mmol, 1.0 equiv), [Metal] (0.014 mmol, 10 mol %), Et_3N (0.177 mmol, 1.25 equiv), alkyne (0.142 mmol, 1.0 equiv) TMSOTf (0.156 mmol, 1.1 equiv), PhMe (0.31M). NMR yields were determined using 1,3,5-trimethoxy benzene as internal standard. Yield in parentheses are isolated.

Using trimethylsilylacetylene as a reaction partner, both CuI, and $ZnBr_2$ gave compound **1.39** in excellent yields (Table 1.4)**.**

Table 1.4: Alkynylation using Trimethylsilylacetylene[a]



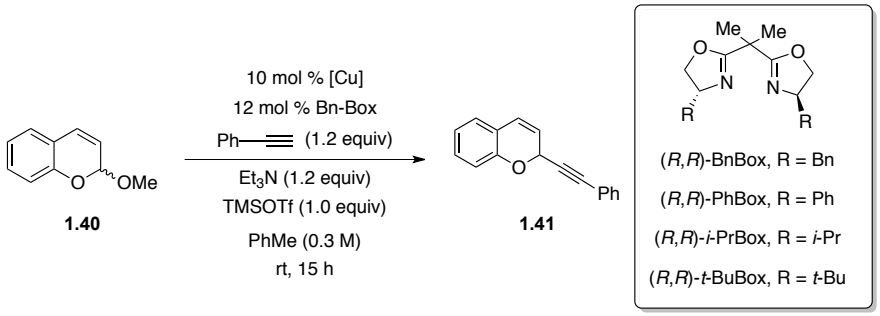
entry	[Metal]	NMR Yield (%)
1	CuI	[85]
3	$ZnBr_2$	76

[a]Conditions: acetal **1.29** (0.283 mmol, 1.0 equiv), [Metal] (0.028 mmol, 10 mol %), Et_3N (0.354 mmol, 1.25 equiv), alkyne (0.283 mmol, 1.0 equiv) TMSOTf (0.312 mmol, 1.1 equiv), PhMe (0.31M). NMR yields were determined using 1,3,5-trimethoxy benzene as an internal standard. Yield in parentheses are isolated.

Enantioselective Alkynylation

Initial studies began with using phenyl acetylene and chromene acetal **1.40** in the presence of chiral ligands. In our previous optimization of the alkynylation of isochroman acetal **1.16 (**Scheme 1.4D**)**[35], we had found that use of Cu(I) catalysts with weakly coordinating counterions was crucial for high levels of enantioselectivity. In particular, $Cu(MeCN)_4PF_6$ had proven best. However, under similar conditions to those optimal for the alkynylation of isochroman acetal **1.16**, low enantioselectivity (40% ee) of α-alkynyl chromene **1.41** was observed (Table 1.5, entry 1).

Table 1.5: Identification of Catalyst[a]



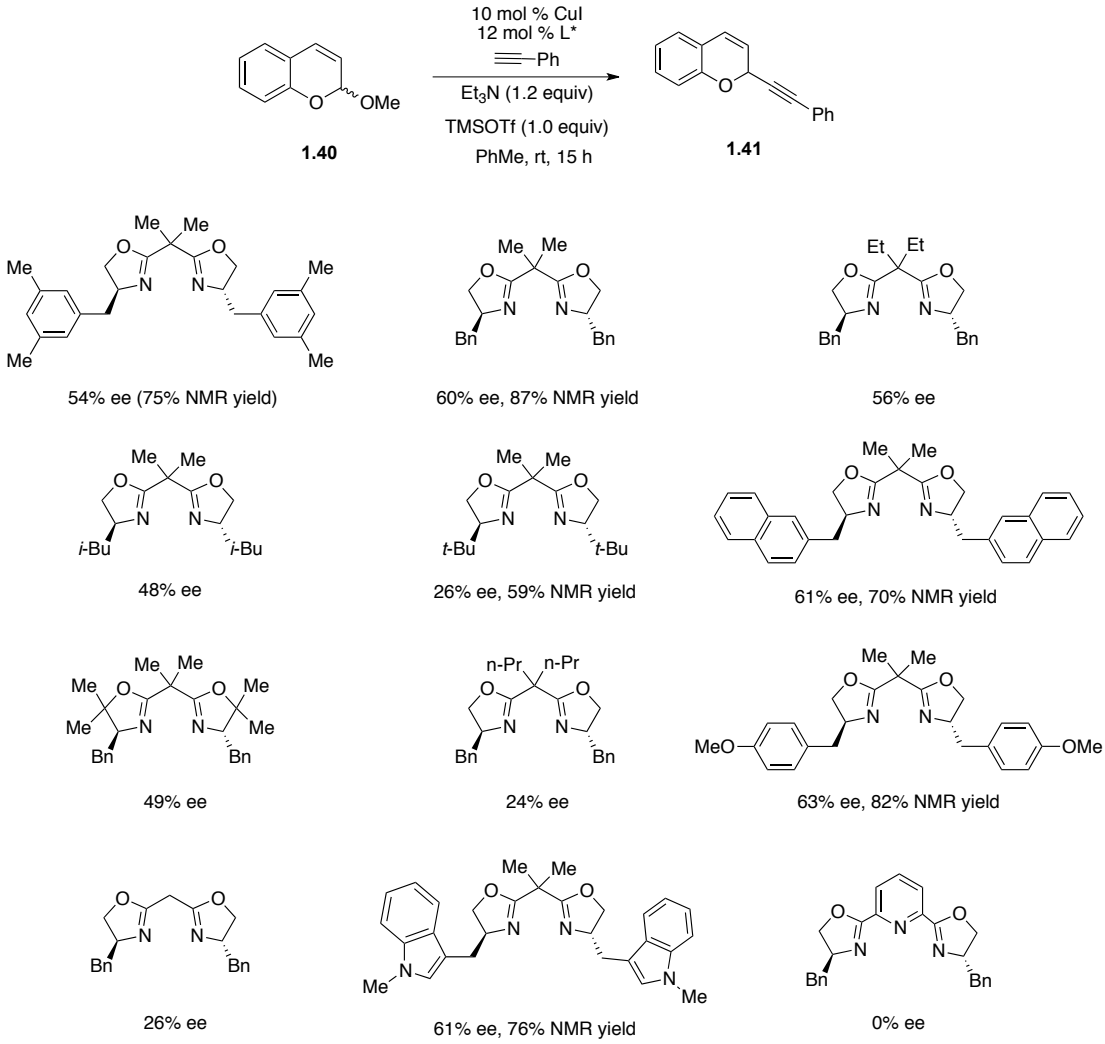
entry	[Cu]	ligand	yield (%)[b]	ee (%) [c]
1	$Cu(MeCN)_4PF_6$	BnBox	49	40
2	$Cu(MeCN)_4BF_4$	BnBox	58	42
3	$Cu(OAc)_2$	BnBox	60	21
4	CuBr	BnBox	55	20
5	CuI	BnBox	87	60
6	CuI	PhBox	63	26
7	CuI	*i*-PrBox	57	48
8	CuI	*t*-BuBox	59	26

[a] Conditions: acetal **1.40** (0.124 mmol, 1.0 equiv), [Cu] (0.012 mmol, 10 mol %), Ligand (0.014 mmol, 12 mol %), alkyne (0.148 mmol, 1.2 equiv), Et_3N (0.148 mmol, 1.2 equiv), TMSOTf (0.124 mmol, 1.0 equiv), PhMe (0.31 M), 15 h. [b] Determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as internal standard. [c] Determined by HPLC analysis using a chiral stationary phase.

In examining the effect of the Cu counterion, we were surprised to find that catalysts derived from CuI provided much greater enantioselectivity (60% ee) in the alkynylation of chromene acetal **1.40** than Cu salts with other counterions (entries 1-5). This result is in direct contrast to the alkynylation of isochroman acetals, in which CuI provided some of the lowest enantioselectivities. The reason for this discrepancy is unclear at this point.

After screening a variety of chiral ligands, (+)(2,2′-Isopropylidenebis[(4R)-4-benzyl-2-oxazoline] (Benzyl Box) was identified as optimal ligand (Table 1.5, entry 5). Alternative bis(oxazoline) ligands resulted in lower enantioselectivities (entries 6-8). Our efforts to improve the enantioselectivity by identifying an alternative ligand around the BnBox scaffold were unsuccessful (Scheme 1.9).

Scheme 1.9: Screening of Box Ligands[a]

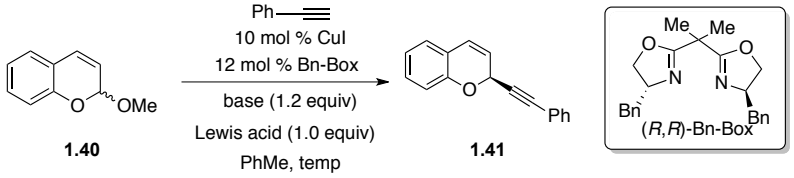


[a] Conditions: acetal 1.40 (0.124 mmol, 1.0 equiv), [Cu] (0.012 mmol, 10 mol %), L* (0.014 mmol, 12 mol %), phenyl acetylene (0.148 mmol, 1.2 equiv), Et_3N (0.148 mmol, 1.2 equiv), TMSOTf (0.124 mmol, 1.0 equiv), PhMe (0.31 M), 15 h. Enantioselectivities were determined by HPLC using a chiral stationary phase.

Effect of Concentration

At a reaction temperature of 0 °C, the CuI/BnBox catalyst provided alkynylated chromene **1.41** in 71% yield and 63% ee (Table 1.6, entry 1). However, lowering the reaction temperature further did not result in further increase in enantioselectivity. At this stage, we undertook a careful examination of each reaction variable and observed that overall reaction concentration influenced the enantioselectivity.

Table 1.6: Optimization Table[a]



1.40 **1.41**

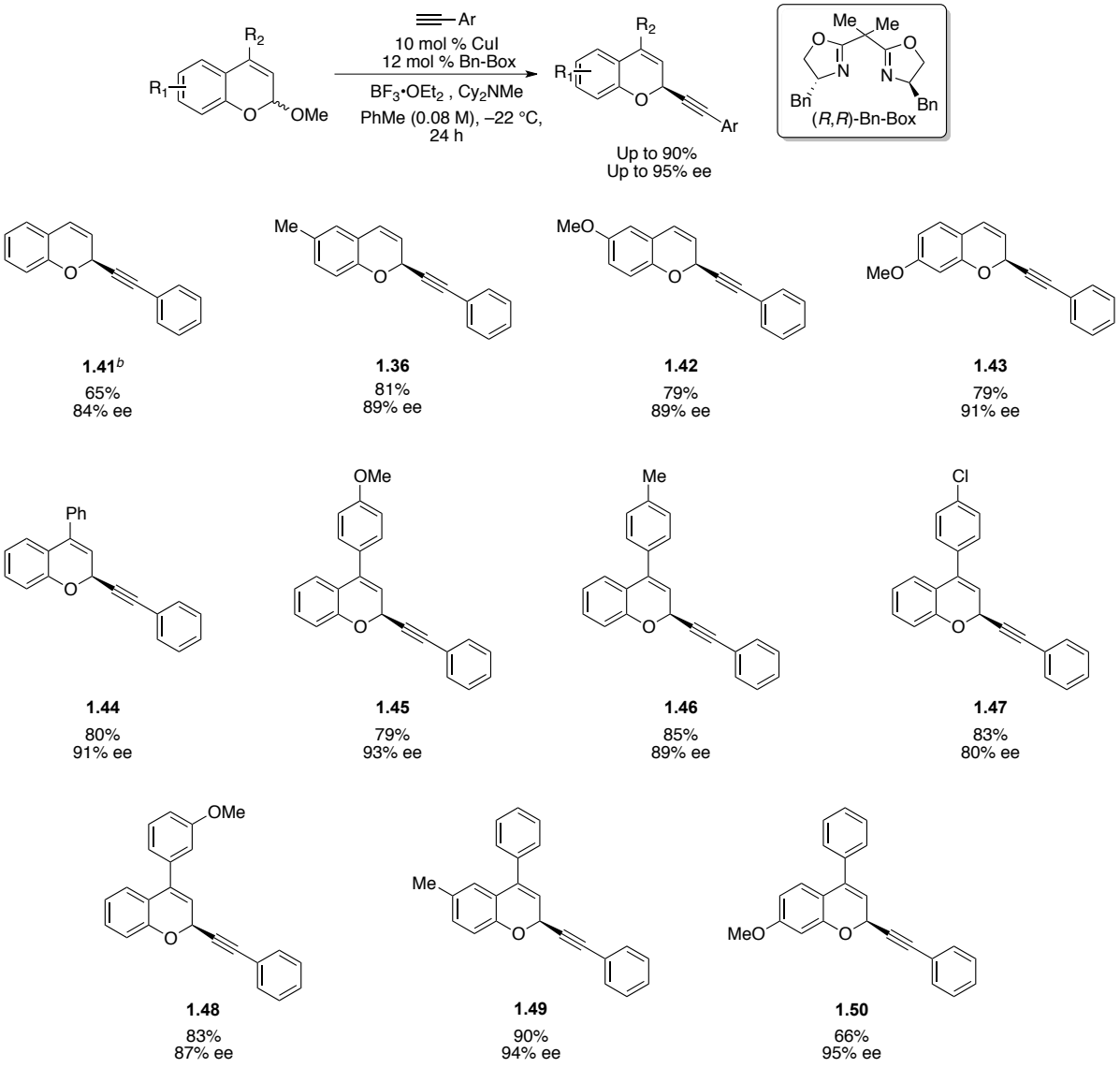
entry	acetal [M]	base	Lewis acid	temp (°C)	yield (%)[b]	ee (%)[c]
1	0.31	Et_3N	TMSOTf	0	[71]	63
2	0.08	Et_3N	TMSOTf	0	56	73
3	0.08	Cy_2NMe	TMSOTf	0	45	77
4	0.08	Cy_2NMe	$BF_3.OEt_2$	0	40	80
5	0.08	Cy_2NMe	$BF_3.OEt_2$	-22	31	83
6[d]	0.08	Cy_2NMe	$BF_3.OEt_2$	-22	[71]	83

[a] Conditions: acetal **1.40** (0.124 mmol, 1.0 equiv), [Cu] (0.012 mmol, 10 mol %), BnBox (0.014 mmol, 12 mol %), alkyne (0.148 mmol, 1.2 equiv), base (0.148 mmol, 1.2 equiv), Lewis acid (0.124 mmol, 1.0 equiv), PhMe, unless otherwise noted. [b] Determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as internal standard and yields in parentheses are isolated yields. [c] Determined by HPLC using a chiral stationary phase. [d] 1.75 equiv $BF_3{\cdot}OEt_2$ was used.

By lowering the concentration to 0.08 M, **1.41** was achieved in 73% ee, but with diminished yield (entry 2). Under these more dilute conditions, optimization of the base and Lewis acid revealed that the use of dicyclohexyl methyl amine (Cy_2NMe) and $BF_3{\cdot}OEt_2$ resulted in even higher enantioselectivity (entries 3-4). At a reaction temperature to –22 °C, chromene **1.41** was formed in 83% ee in a modest 31% yield (entry 5). However, we found that increasing the equivalents of $BF_3{\cdot}OEt_2$ led to synthetically useful yields of chromene **1.41** (entry 6). Under these optimal conditions, chromene **1.41** was isolated in 71% yield and 83% ee.

Scope in Chromenes

Scheme 1.10: Scope in Chromene Acetals[a]



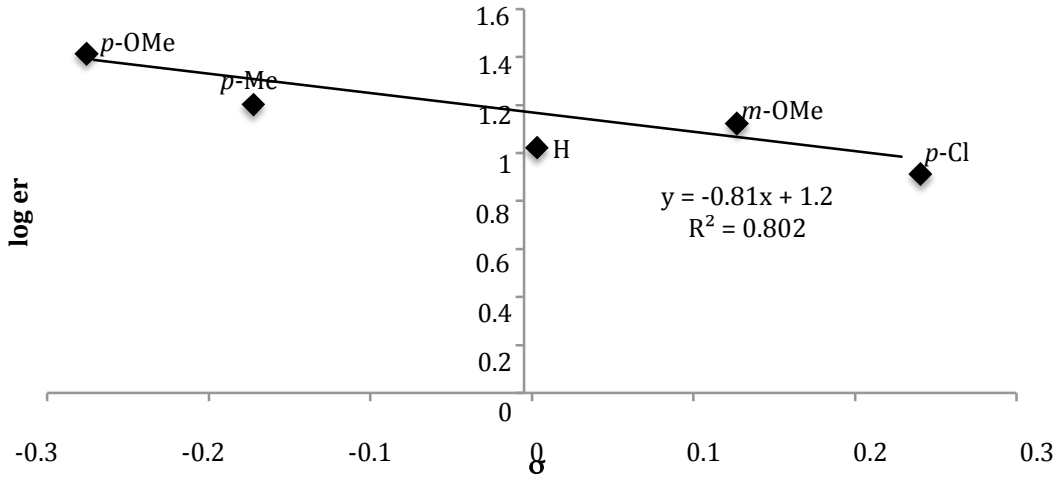
[a] Conditions: acetal (0.254 mmol, 1.0 equiv), CuI (0.025 mmol, 10 mol %), (*R,R*)- BnBox (0.030 mmol, 12 mol %), phenyl acetylene (0.381 mmol, 1.5 equiv), Cy_2NMe (0.305 mmol, 1.2 equiv), $BF_3{\cdot}OEt_2$ (0.444 mmol, 1.75 equiv), PhMe (0.08M). Yields reported are isolated and average of two experiments. Enantiomeric excess was determined by HPLC analysis using a chiral stationary phase. [b] 1.5 equiv of alkyne and 1.45 equiv of $BF_3{\cdot}OEt_2$ was used.

We have determined the scope with respect to the chromene acetal (Scheme 1.10). Alkynylation of our model substrate **1.40** occurs in good yield and enantioselectivity to give the product **1.41** under the optimized conditions. Installing methyl & methoxy group at the 6th and 7th carbon of the chromene scaffold (**1.36, 1.42, & 1.43**) results in higher enantioselectivity and yields. Compounds **1.42** & **1.43** with methoxy group at 6th and 7th carbon on the chromene ring undergo decomposition when stored neat for long time, however, they are stable in solution at – 5 ºC. We have also demonstrated the method with 4-aryl chromene acetals. By installing the aryl group at the 4th carbon of the chromene ring, excellent enantioselectivity was observed with good yields (**1.44, 1.45, 1.46, 1.49** and **1.50**). 7-methoxy-4-phenyl-2-(phenylethynyl)-2*H*-chromene, which has an electron-donating methoxy group at the 7th carbon and phenyl group at 4th carbon showed the highest enantioselectivity with moderate yield. This compound (**1.50**) is not stable to air and decomposes on long time exposure to air, hence column purification of this compound was performed under nitrogen atmosphere. This compound was stored in chloroform at – 5 ºC in the refrigerator. This compound is stable in solution, but decomposes when stored neat.

Electronic effects were probed by varying the functional groups on the 4-phenyl ring of the chromene acetal. Compound **1.45** which has an electron-donating methoxy group on the 4-phenyl ring was formed in excellent enantioselectivity and yield, whereas products **1.47** and **1.48** with electron-withdrawing chlorine and methoxy groups at the

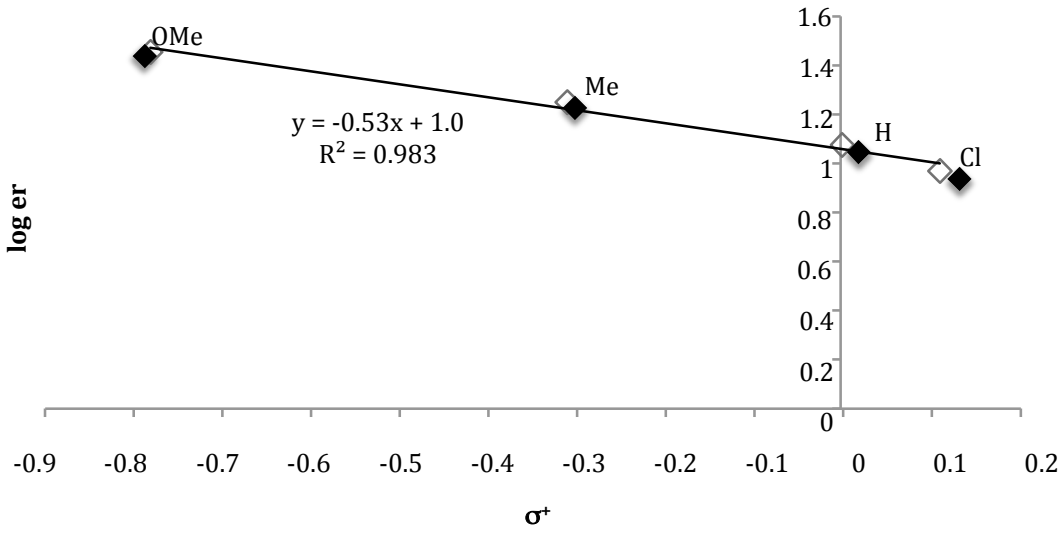
para and *meta* positions, were formed in lower enantioselectivity. When plotted σ vs log er for methyl, methoxy, and chloro groups, we obtained a linear plot and complete linear correlation was obtained when σ+ vs log er was plotted for the *p*-methoxy, *p*-methyl and *p*-chloro groups. This trend suggests higher enantioselectivity may result with more stable oxocarbenium ions and later transition state (Table 1.7 and 1.8).

Table 1.7: Plot of log er vs σ for compound 1.45, 1.46, 1.47, and 1.48



entry	Functional group	sigma value (σ)	ee	er	log er
1	*m*-OMe	0.12	87	14.38	1.157
2	*p*-Cl	0.23	80	9.00	0.954
3	*p*-OMe	-0.27	93	27.57	1.440
4	*p*-Me	-0.17	89	17.18	1.235
5	H	0	84	11.5	1.060

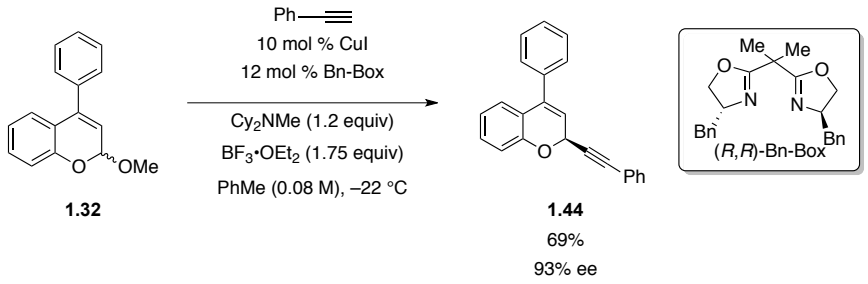
Table 1.8: Plot of log er vs σ+ for compound 1.45, 1.46, and 1.47



entry	Functional group	sigma plus (σ+)	ee	er	log er
1	*m*-OMe	-	87	14.38	1.157
2	*p*-Cl	0.11	80	9.00	0.954
3	*p*-OMe	-0.78	93	27.57	1.440
4	*p*-Me	-0.31	89	17.18	1.235
5	H	0	84	11.50	1.060

Experimental Set-Up Outside the Glovebox

Scheme 1.11: Outside the Glovebox Experiment[a]



1.32

1.44
69%
93% ee

[a]Conditions: acetal (0.254 mmol, 1.0 equiv), CuI (0.025 mmol, 10 mol %), (*R,R*)-BnBox (0.030 mmol, 12 mol %), alkyne (0.381 mmol, 1.5 equiv), Cy_2NMe (0.305 mmol, 1.2 equiv), $BF_3{\cdot}OEt_2$ (0.444 mmol, 1.75 equiv), PhMe (0.08M). Yields reported are isolated and average of two experiments. Enantiomeric excess was determined by HPLC analysis using a chiral stationary phase.

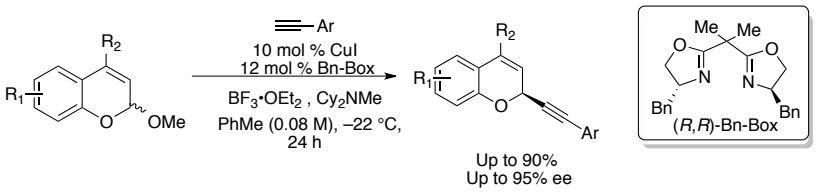
We have performed all the substrate scope experiments inside glove box. However, when we performed the reaction outside glove box on bench top using schlenk technique, we obtained compound **1.42** with excellent enantioselectivity and good yield. These conditions facilitate a benchtop set up of the alkynylation of chromene acetals (Scheme 1.11).

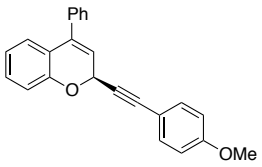
Scope in Alkynes

Under our optimized conditions, we have shown great scope in the types of alkynes that can be tolerated (Scheme 1.12). Alkynes with electron-rich groups such as methoxy and methyl work well under the optimized conditions (**1.51&1.52)**. Increased steric bulk was well tolerated, as highlighted by compound **1.56,** which was formed with 91% ee, when we used sterically encumbered 3,5-dimethyl phenyl acetylene. We have also

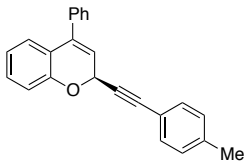
demonstrated the method in high enantiomeric excess with alkynes having strongly electron-withdrawing nitrile, ester and trifluromethyl functionalities **(1.54, 1.55, 1.61 1.63 & 1.64**). Under the given conditions, halides are also well tolerated. Compounds **1.53, 1.58, 1.59, 1.60, 1.66 &1.67**, which contain arylchloride, fluoride and bromide functionalities, were formed in high enantiomeric excess and yields. In particular, the chloride and bromide groups can be further utilized in the late state functionalization using various cross-coupling strategies. When comparing compounds **1.58, 1.59 &1.60**, which contain bromide, chloride and flouride functional group at the *meta*-position of the phenyl ring, we observed a decrease in enantioselectivity that follows a periodic trend. We hypothesize that this trend may be due to the steric size of the halogen group. We also showed the enyne addition to the oxocarbenium ion intermediate and the product **1.62** was formed in moderate enantioselectivity and yield, signifying the importance of the aromatic character of the alkyne. Furthermore, when we use an electron-rich chromene, we observe much higher enantioselectivity with a variety of alkynes (**1.63, 1.64, 1.65, 1.66** and **1.67**).

Scheme 1.12: Scope in Alkyne[a]

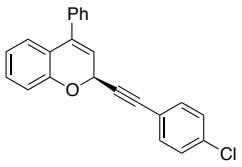




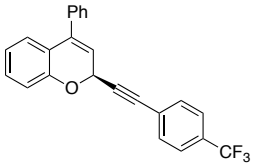
1.51
75%
86% ee



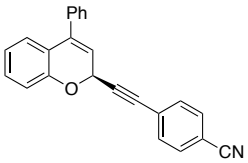
1.52
75%
89% ee



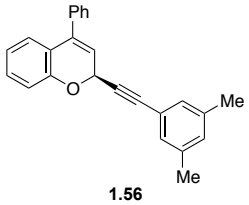
1.53
74%
89% ee



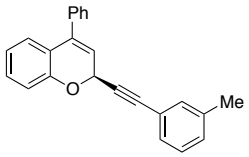
1.54
75%
83% ee



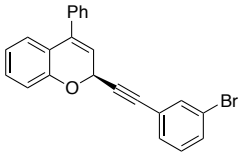
1.55
75%
85% ee



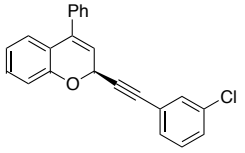
1.56
83%
91% ee



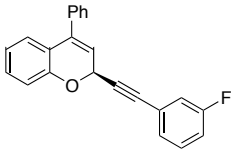
1.57
80%
90% ee



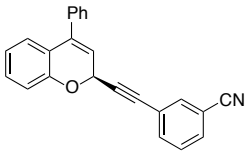
1.58
75%
87% ee



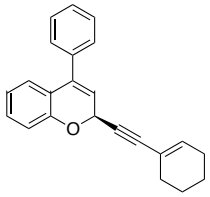
1.59
83%
89% ee



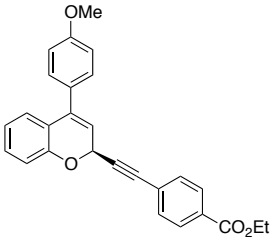
1.60
76%
93% ee



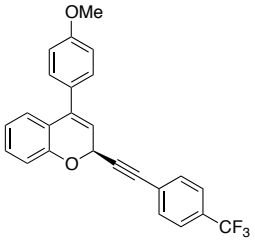
1.61
77%
88% ee



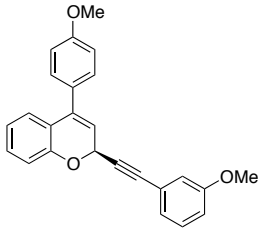
1.62
49%
70% ee



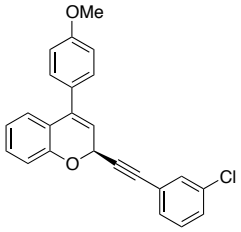
1.63
86%
89% ee



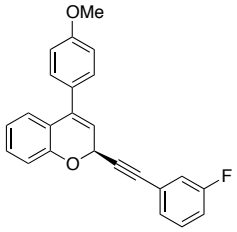
1.64
77%
87% ee



1.65
84%
90% ee



1.66
78%
91% ee



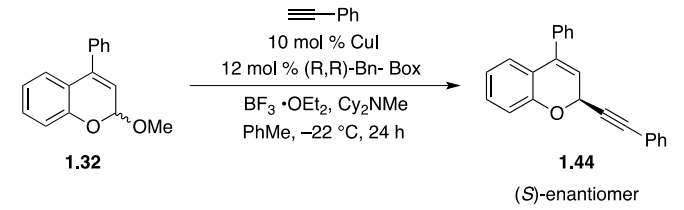
1.67
88%
91% ee

[a]Conditions: acetal (0.254 mmol, 1.0 equiv), CuI (0.025 mmol, 10 mol %), (*R*,*R*)-BnBox (0.030 mmol, 12 mol %), alkyne (0.305 mmol, 1.2 equiv), Cy_2NMe (0.305 mmol, 1.2 equiv), $BF_3{\cdot}OEt_2$ (0.444 mmol, 1.75 equiv), PhMe (0.08M). Yields reported are isolated and average of two experiments. Enantiomeric excess was determined by HPLC using a chiral stationary phase.

Determination of the Absolute Configuration

The stereochemistry of compound **1.44,** formed via alkynylation using CuI and (*R*,*R*)-Benzyl Box, was determined by X-ray crystallographic analysis (Figure 1.2).

Scheme 1.13: Determination of Absolute Configuration



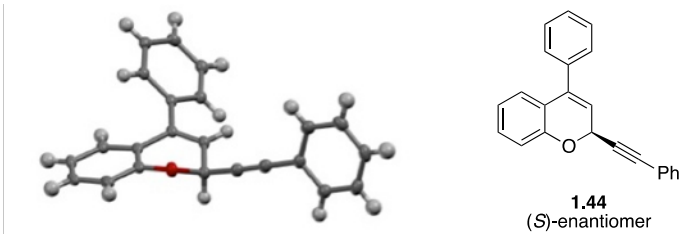
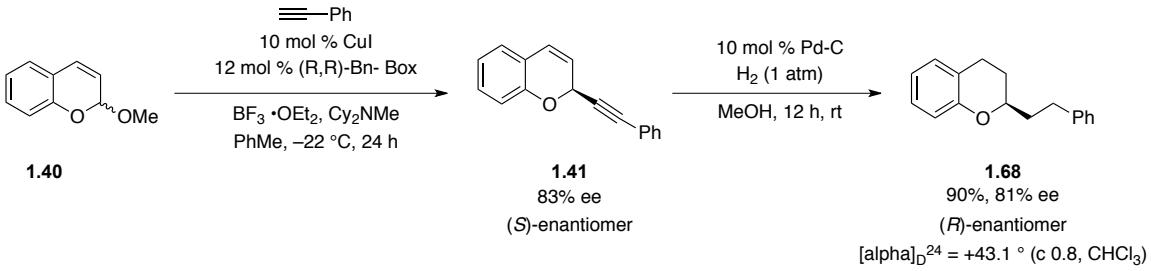


Figure 1.2: Crystal Structure of Compound 1.44

The absolute configuration of product **1.41,** was also determined. Compound **1.41** formed via alkynylation using CuI and (*R*,*R*)-BnBox was further reduced using palladium on carbon to form compound **1.68** in excellent yield and ee. The sign of observed optical rotation of the reduced product **1.68** is opposite to that of (*S*)-**1.68**

reported in literature, allowing assignment of the absolute configuration of **1.68** as *R*. The absolute configuration of alkyne **1.41** is thus assigned as *S* (Scheme 1.14).

Scheme 1.14: Determination of Absolute Configuration of Compound 1.41



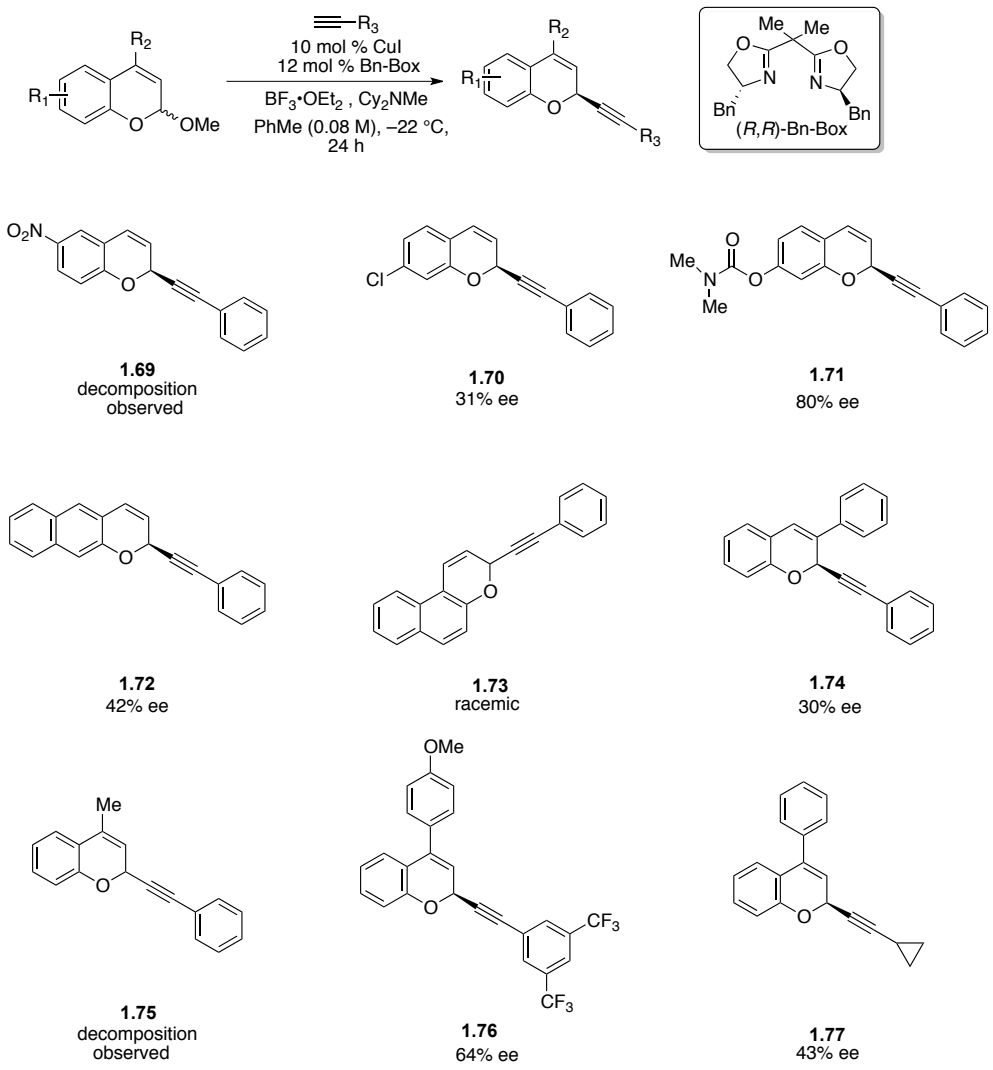
1.40

1.41
83% ee
(*S*)-enantiomer

1.68
90%, 81% ee
(*R*)-enantiomer
$[\alpha]_D^{24}$ = +43.1 ° (c 0.8, $CHCl_3$)

Unsuccessful Substrates

Scheme 1.15: Unsuccessful Substrates[a]



[a] Conditions: acetal (0.124 mmol, 1.0 equiv), CuI (0.012 mmol, 10 mol %), (*R*,*R*)-BnBox (0.014 mmol, 12 mol %), alkyne (0.148 mmol, 1.2 equiv), Cy_2NMe (0.148 mmol, 1.2 equiv), $BF_3{\cdot}OEt_2$ (0.217 mmol, 1.75 equiv), PhMe (0.08M). Enantiomeric excess was determined by HPLC using a chiral stationary phase.

In terms of the chromene acetal, several limitations were observed (Scheme 1.15). We did not observe the product **1.69**, when 2-methoxy-7-nitro-2*H*-chromene was tried

and observed varying degrees of decomposition by thin layer chromatography. We obtained **1.70** in 30% ee and **1.71** with 80% ee. Carbamate **1.71** was obtained in lower ee than the analogues ether (**1.43**, Scheme 1.10). These results are consistent with our observation that lower ee's are obtained with acetals that form less stable oxocarbenium ions. Extended π-systems **1.72** and **1.73** were obtained in 42% ee and racemic form, which may be due to steric hindrance between the napthyl group and the catalyst backbone. We obtained compound **1.74** in 30% ee, the reason for this might be due to steric hindrance and electro withdrawing nature of 3-phenyl group, which could destabilize the oxocarbenium ion. When 2-methoxy-4-methyl-2*H*-chromene was tried, we did not see the formation of alkynylated compound **1.75**, rather we observed the decomposition by thin layer chromatography.

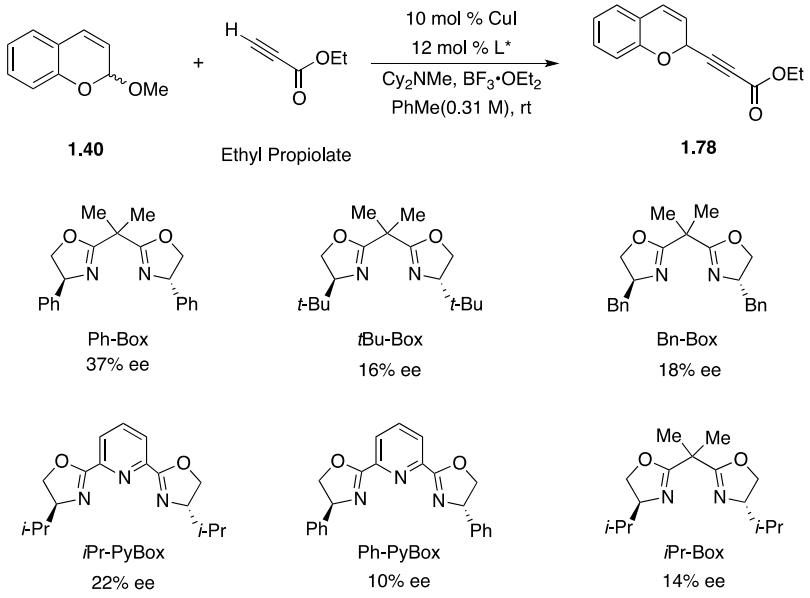
With respect to the alkyne, the 3,5-bis(trifluromethyl)phenyl acetylene with trifluromethyl groups at 3rd and 5th carbons, gives the alkynylated product **1.76** in low enantiomeric excess. A reason for this might be due to a combination of steric and electronic factors. When cyclopropyl acetylene was used, we obtained the corresponding alkynated product **1.77** in 41% enantiomeric excess. The lack of success with cyclopropylacetylene is consistent with the results, we obtained with 1-ethynylcyclohex-1-ene (**1.62**, Scheme 1.12) and also with isochroman acetal[35], which indicates that, as the

aromatic character of the alkyne substituent (aryl→sp2→cyclopropyl) decreases the enantioselectivity also decreases. The reason for this is unclear currently.

Alkynylation with Propiolates

Alkynylation of our model substrate **1.40** with ethyl propiolate under copper-catalyzed conditions in presence of various chiral ligands was tested (Scheme 1.16). Under the conditions shown in Scheme 1.16, we observed that the CuI/ Ph-Box catalyst system proved to be best, giving **1.78** in 37% ee, however with diminished yields due to significant decomposition.

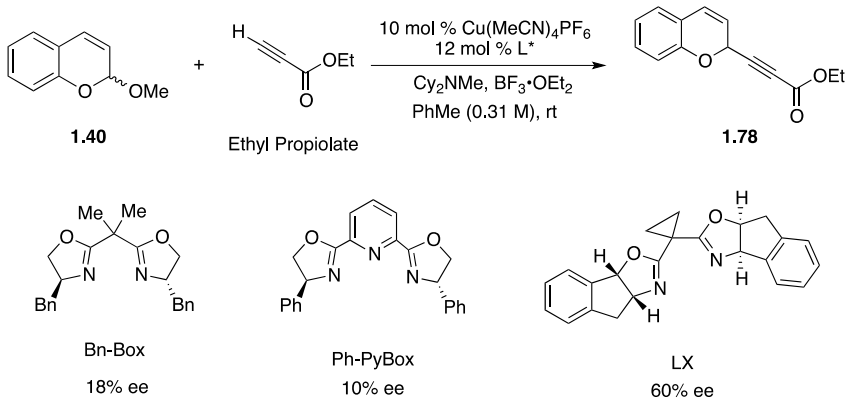
Scheme 1.16: Reaction with Ethyl Propiolate using CuI[a]



[a]Conditions: acetal **1.40** (0.308 mmol, 1.0 equiv), CuI (0.030 mmol, 10 mol %), L* (0.036 mmol, 12 mol %), alkyne (0.616 mmol, 2.0 equiv), Cy_2NMe (0.338 mmol, 1.1 equiv), $BF_3{\cdot}OEt_2$ (0.616 mmol, 2.0 equiv), PhMe (0.31M). Enantiomeric excess was determined by HPLC using a chiral stationary phase.

To further optimize the reaction, we then changed the copper salt to $Cu(MeCN)_4PF_6$ and screened several bis(oxazoline) ligands (Scheme 1.17). Among them box ligand **LX** ligand gave moderate ee of 60% with 30% yield. TLC observed significant decomposition. To overcome competitive coordination to carbonyl group of the ester functionality, excess of Lewis acid was used. Under more dilute conditions (0.08 M), only trace product was observed by thin layer chromatography.

Scheme 1.17: Reaction with Ethyl Propiolate using $Cu(MeCN)_4PF_6$[a]



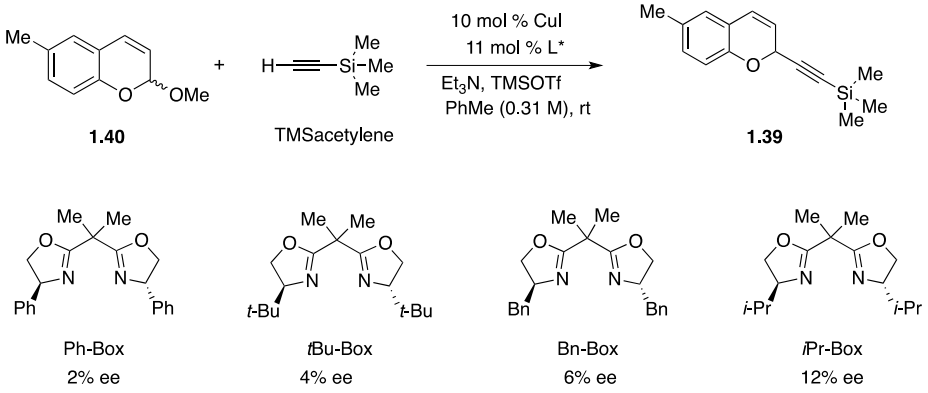
[a]Conditions: acetal **1.40** (0.308 mmol, 1.0 equiv), $Cu(MeCN)_4PF_6$ (0.030 mmol, 10 mol %), L* (0.036 mmol, 12 mol %), alkyne (0.616 mmol, 2.0 equiv), Cy_2NMe (0.338 mmol, 1.1 equiv), $BF_3{\cdot}OEt_2$ (0.616 mmol, 2.0 equiv), PhMe (0.31M). Enantiomeric excess was determined by HPLC using a chiral stationary phase.

Alkynylation with Trimethylsilylacetylene

We also attempted to use TMSacetylene as the alkyne. The trimethylsilyl group of the alkyne can be easily removed to enable derivitization of the acetylide product. However, when we tried the alkynylation of chromene acetal **1.40** using

trimethylsilylacetylene under asymmetric conditions, we obtained very low enantioselectivities with bis(oxazoline) ligands (Scheme 1.18).

Scheme 1.18: Reaction with Trimethylsilylacetylene[a]

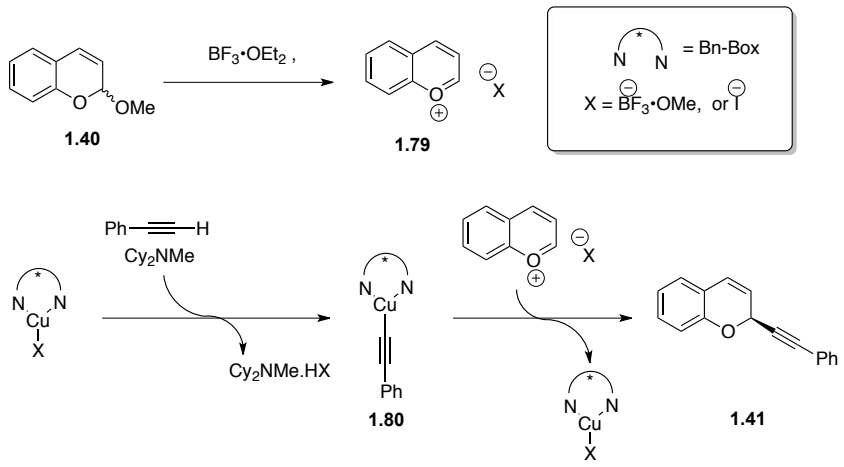


[a] Conditions: acetal **1.40** (0.113 mmol, 1.0 equiv), CuI (0.011 mmol, 10 mol %), L* (0.012 mmol, 11 mol %), alkyne (0.113 mmol, 1.0 equiv), Et_3N (0.141 mmol, 1.25 equiv), TMSOTf (0.113 mmol, 1.0 equiv), PhMe (0.31M). Enantiomeric excess was determined by HPLC using a chiral stationary phase.

Mechanism

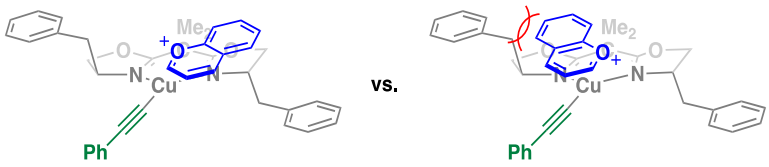
Our current mechanistic hypothesis is shown in Scheme 1.19. Exposure of chromene acetal **1.40** to $BF_3{\cdot}OEt_2$ leads to formation of oxocarbenium ion **1.79**, which reacts with the catalytically generated chiral copper acetylide **1.80** formed from phenyl acetylene, CuI, Bn-Box and Cy_2NMe to give alkynylated chromene product **1.41**. We hypothesize that the C-C bond formation is likely the enantiodetermining step. The observation that more stable oxocarbenium ions result in higher ee's is consistent with the C-C bond formation as the enantiodetermining step. More stable oxocarbenium ions will participate in a later transition state, and therefore feel more effect of the chiral ligand in this step.

Scheme 1.19: Proposed Mechanism



Stereochemical Hypothesis

Our current stereochemical hypothesis is shown in Figure 1.3. We envision that, in the enantiodetermining carbon-carbon bond-forming step, steric clash between the aromatic ring of the oxocarbenium ion and benzyl ring of the BnBox ligand disfavors the approach shown in **TS-2**. We have made two assumptions in this model: (1) the Cu(BnBox)acetylide geometry is trigonal planar analogous to (BnBox)CuI complex (Figure 1.5) and (2) the approach of acetylide is from Bürgi–Dunitz angle.

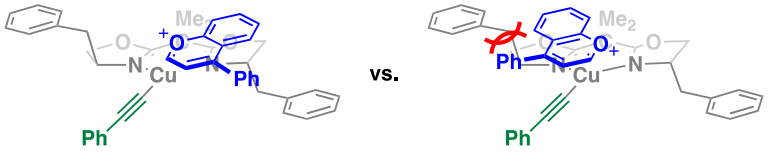


favored **TS-1** *disfavored* **TS-2**

Figure 1.3: Stereochemical Model

In the case of the 4-aryl chromene acetal, as the steric hindrance between the 4-aryl group and benzyl substituent on the BnBox ligand is greater than the steric hindrance

of the unsubstituted chromene oxocarbenium ions, our model rationalizes why higher ee's are observed for the oxocarbenium ions with substituents in the 4-position (Figure 1.4). Notably, however, aryl substituents also stabilize the oxocarbenium ion and likely lead to a later transition state, which would also contribute to high enantioselectivites with these substrates.



favored **TS-1** *disfavored* **TS-2**

Figure 1.4. Stereochemical Model with the 4-Aryl Group

Dilution Effect

My colleague, Dr. Prantik Maity, obtained a crystal structure of [(*S*,*S*)-(BnBox)]CuI, which is a tricoordinated copper(I) complex as shown in Figure 1.5. When we tried the alkynylation reaction of our model substrate with this complex, we obtained similar enantioselectivities both in dilute and concentrated solution (Table 1.9). The slight reduction in ee, when compared to our standard conditions might be due to partial oxidation of Cu(I) to Cu(II) during preparation of crystallographic sample. This result contrasts the results described above for our standard reaction set-up (dilute conditions 84% ee and concentrated conditions 63% ee). Typically, the catalyst is prepared in situ by stirring CuI and BnBox for 30 min. Under this procedure, lower ee (63% ee) is observed

under more concentrated conditions. Based on these results, we envision that (BnBox)CuI may be the active catalyst in dilute solution, but that other CuL_n or Cu_nL_m species may form when we generate our catalyst in situ. These other catalysts may provide lower enantioselectivities.

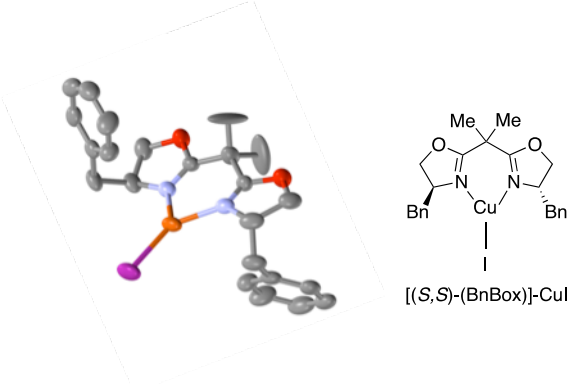
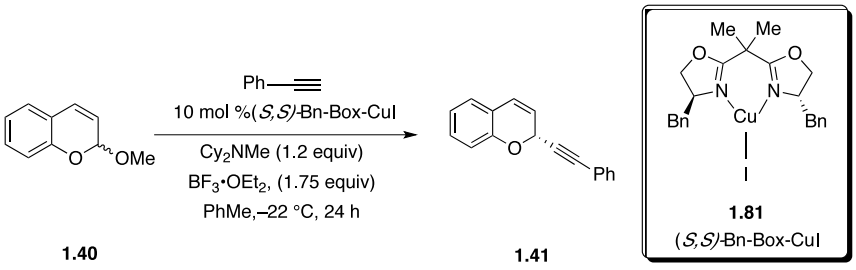


Figure 1.5: Crystal Structure of [(*S,S*)-(BnBox)]-CuI

Table 1.9: Reaction with [(*S,S*)-(BnBox)]-CuI [a]

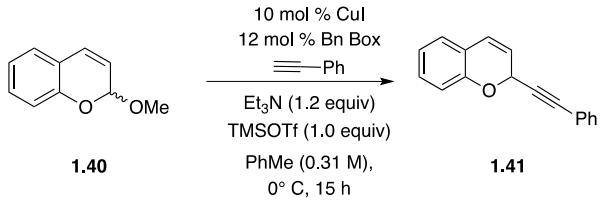


Entry	Acetal [M]	ee (%)
1	031	78
2[b]	0.08	80

[a]Conditions: acetal **1.40** (0.124 mmol, 1.0 equiv), (*S,S*) Benzyl Box CuI (0.012 mmol, 10 mol %), Cy_2NMe (0.148 mmol, 1.2 equiv), alkyne (0.148 mmol, 1.2 equiv), $BF_3{\cdot}OEt_2$ (0.217 mmol, 1.75 equiv), PhMe

(0.31M).[b] $BF_3 \cdot OEt_2$ (0.124 mmol, 1.0 equiv). PhMe (0.08 M) was used. Enantiomeric excess was determined by HPLC using a chiral stationary phase.

To investigate the possible formation of copper species with more than one BnBox ligand, I conducted non-linear effect experiments. In a typical scenario for enantioselective catalysis, the enantiomeric excess of the catalyst and the enantiosmeric excess of the product share a linear relationship. If the ee of the product vs ee of the catalyst deviates from linearity this is known as non-linear effect,[38-41] and indicates the presence of a catalyst aggregate. When we conducted these experiments, using various ee's of BnBox, we observed a linear relationship between ee of product vs. ee of catalyst (Figure 1.6). We conducted these experiments at 0.3 M, because we envisioned that there might be catalyst aggregation in concentrated solution, based on the above experiments (Table 1.9). The absence of a nonlinear effect suggests that either no catalyst aggregation occurs or that its formation does not affect the enantioselectivity of the reaction. Thus, it is still not clear why there is an effect of dilution on the enantioselectivity.



1.40 **1.41**

entry	ee (%) of cat	ee (%) of product
1	100	64
2	83	51
3	67	44
4	50	32
5	33	17
6	17	9
7	0	0

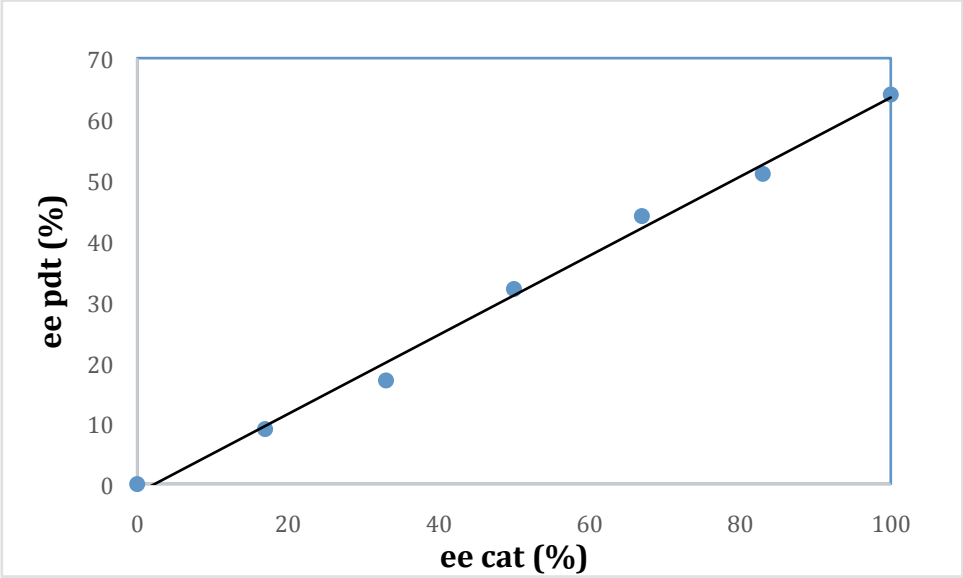
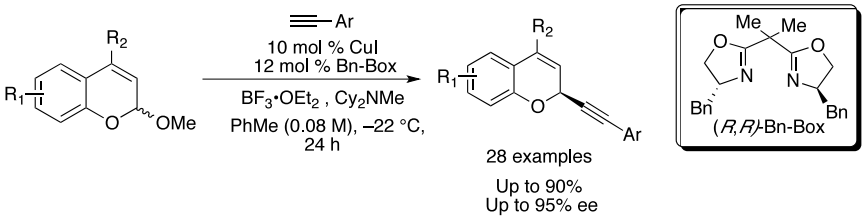


Figure 1.6: Non-linear Effect

[a] Conditions: acetal **1.40** (0.3 mmol, 1.0 equiv), [Cu] (0.030 mmol, 10 mol %), Benzyl box (0.036 mmol, 12 mol %), phenyl acetylene (0.36 mmol, 1.2 equiv), Et_3N (0.36, 1.2 equiv), TMSOTf (0.3 mmol, 1.0 equiv), PhMe (0.31 M), 15 h. Enantiomeric excess were determined using HPLC using a chiral stationary phase.

1.3 Conclusions

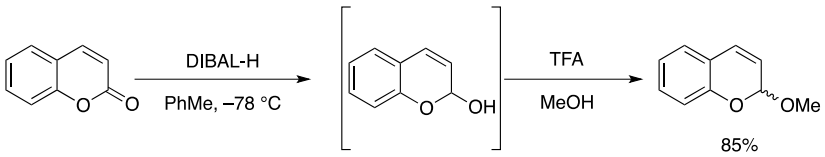
Scheme 1.20: Enantioselective Alkynylation of Chromene Acetals



We have developed the first enantioselective alkynylation of chromene acetals using Cu(I) catalysts (Scheme 1.20). The key factors to achieve high enantioselectivity include dilute conditions, use of $BF_3{\cdot}OEt_2$ as Lewis acid and Cy_2NMe as base. We have observed wide substrate scope, and high enantioselectivities were observed especially with 4-aryl chromene acetals. We have proposed a mechanism and stereochemical model that rationalizes our substituent effects and enantioselectivities. These results demonstrate the high utility of exploiting transition metal catalysis to enable reactions of oxocarbenium ion intermediates.

1.4 Experimental Information

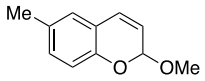
General Procedure for the Preparation of Chromene Acetals: Synthesis of 2-methoxy-2*H*-chromene (**1.40**)



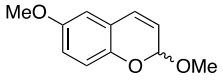
This procedure was adapted from literature.[34] To a flame-dried, 250-mL round-bottomed flask was added coumarin (6.0 g, 41.05 mmol, 1.0 equiv) and CH_2Cl_2 (60 mL). The solution was cooled to –78 °C and DIBAL-H (1.2 M in PhMe, 36.0 mL, 43.1 mmol, 1.05 equiv) was added via syringe over 15 min. The solution was then stirred for an additional 2 h at –78 °C and then allowed to warm to 0 °C and stirred for 15 min. The solution was then diluted with EtOAc (200 mL) and quenched with H_2O (200 mL). The resulting mixture was vigorously stirred for 1 h and then filtered through Celite. The aqueous layer was extracted with EtOAc (2 x 200 mL). The combined organic layers were washed with sat. NaCl (200 mL), dried (Na_2SO_4), filtered and concentrated. The hemiacetal was used in the subsequent step without further purification.

The crude hemiacetal was dissolved in MeOH (50 mL). Trifluoroacetic acid (95.4 μL, 1.2 mmol, 3 mol %) was added, and the solution was stirred for 4 h at room temperature. K_2CO_3(228 mg, 1.65 mmol, 0.04 equiv) was added. The mixture was filtered, and the filtrate was concentrated. The resulting residue was purified by silica gel

chromatography (2–4% Et_2O/hexanes with 5% Et_3N; R_f = 0.44 to afford **1.40** (5.65 g, 85%) as pale yellow oil: ^1H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.20 (m, 1H), 7.15 – 7.13 (m, 1H), 7.00 – 6.94 (m, 2H), 6.74 (d, *J* = 9.6 Hz, 1H), 5.87 (dd, *J* = 9.7, 3.8 Hz, 1H), 5.60 (d, *J* = 3.8 Hz, 1H), 3.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.3, 129.4, 127.1, 126.7, 121.6, 120.7, 119.7, 116.6, 95.9, 55.08; FTIR (NaCl, thin film) 2912, 2830, 1642, 1606, 1488, 1457, 1403, 1205 cm^{-1}; LRMS (EI+) $[M]^+$ calculated for $C_{10}H_{10}O_2$: 162.07, found: 162.1.

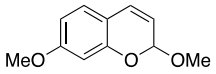


2-methoxy-6-methyl-2*H*-chromene (1.29). Prepared via the general procedure described above on a 31.0 mmol scale. The crude product was purified by silica gel chromatography (3–4% Et_2O/hexanes with 5% Et_3N; R_f = 0.5) to give **1.29** (5.1 g, 93%) as colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ 7.03– 7.01 (m, 1H), 6.96 – 6.94 (m, 1H), 6.90 – 6.88 (m, 1H), 6.70 (d, *J* = 9.6 Hz, 1H), 5.85 (dd, *J* = 9.6, 3.8 Hz, 1H), 5.56 (d, *J* = 3.8 Hz, 1H), 3.48 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.1, 130.8, 130.0, 127.4, 126.7, 120.4, 119.7, 116.3, 95.8, 54.9, 20.6; FTIR (NaCl, thin film) 2914, 1641, 1493, 1083, 1023 cm^{-1}; LRMS (EI+) $[M]^+$ calculated for $C_{11}H_{12}O_2$: 176.08, found: 176.1.

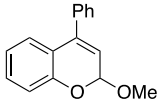


2,6-dimethoxy-2*H*-chromene (1.82). Prepared via the general procedure described above on a 12.5 mmol scale. 6-methoxy coumarin preparation

method was adapted from literature.[42] The crude product was purified by silica gel chromatography (10% Et_2O/hexanes with 5% Et_3N; R_f = 0.4) to give **1.82** (1.96 g, 82%) as colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (d, *J* = 8.8 Hz, 1H), 6.79 (dd, *J* = 8.8, 3.0 Hz, 1H), 6.70 – 6.68 (m, 2H), 5.90 (dd, *J* = 9.7, 3.8 Hz, 1H), 5.53 (d, *J* = 3.8 Hz, 1H), 3.77 (s, 3H), 3.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 145.2, 126.6, 121.2, 120.4, 117.2, 115.3, 111.5, 95.8, 55.8, 55.1; FTIR (NaCl, thin film) 2932, 2831, 1611, 1604, 1578, 1492, 1263, 1207 cm^{-1}; LRMS (EI+) $[M]^+$ calculated for $C_{11}H_{12}O_3$: 192.08, found: 192.1.

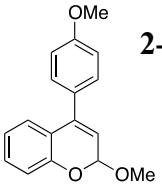


2,7-dimethoxy-2*H*-chromene (1.83). Prepared via the general procedure described above on a 12.5 mmol scale. 7-methoxy coumarin was prepared as reported in the literature.[42] The crude product was purified by silica gel chromatography (10% Et_2O/hexanes with 5% Et_3N; R_f = 0.42) to give **1.83** (1.46g, 61%) as colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (d, *J* = 8.3 Hz, 1H), 6.69 (d, *J* = 9.7 Hz, 1H), 6.59 – 6.48 (m, 2H), 5.73 (dd, *J* = 9.6, 3.7 Hz, 1H), 5.58 (d, *J* = 3.7 Hz, 1H), 3.80 (s, 3H), 3.49 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8, 152.6, 127.8, 126.4, 116.9, 114.1, 107.8, 102.09, 96.2, 55.4, 54.9; FTIR (NaCl, thin film) 2933, 2830, 1641, 1615, 1569, 1506, 1274 cm^{-1}; LRMS (EI+) $[M]^+$ calculated for $C_{11}H_{12}O_3$: 192.08, found: 192.1.

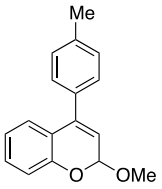


2-methoxy-4-phenyl-2*H*-chromene (1.32). Prepared via the general procedure described above on a 4.86 mmol scale. 4-phenyl coumarin was prepared as

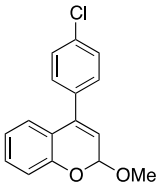
reported in the literature.[43] The crude product was purified by silica gel chromatography (3–4% Et_2O/hexanes with 5% Et_3N; R_f = 0.45) to give **1.32** (856 mg, 74 %) as a white solid (mp 81–83 °C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 5H), 7.28 – 7.24 (m, 1H), 7.14 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.10 – 7.08 (m, 1H), 6.95 – 6.91 (m, 1H), 5.86 (d, *J* = 4.2 Hz, 1H), 5.66 (d, *J* = 4.1 Hz, 1H), 3.54 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.5, 138.8, 137.6, 129.5, 128.8, 128.4, 128.1, 126.3, 121.7, 121.4, 117.9, 117.0, 95.8, 55.2; FTIR (NaCl, thin film) 2928, 2827, 1637, 1636, 1604, 1483, 1483, 1452, 1219, 1045 cm^{-1}; LRMS (EI+) $[M]^+$ calculated for $C_{16}H_{14}O_2$: 238.1, found: 238.1.



2-methoxy-4-(4-methoxyphenyl)-2*H*-chromene (1.84). Prepared via the general procedure described above on a 3.98 mmol scale. 4-(4-methoxyphenyl) coumarin was prepared as reported in the literature.[43] The crude product was purified by silica gel chromatography (7–8% Et_2O/hexanes with 5% Et_3N; R_f = 0.33) to give **1.84** (810 mg, 76%) as a white solid (mp 79–82 °C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.31 (m, 2H), 7.26 – 7.22 (m, 1H), 7.17 – 7.14 (m, 1H), 7.08 – 7.06 (m, 1H), 6.95 – 6.90 (m, 3H), 5.81 (d, *J* = 4.2 Hz, 1H), 5.62 (d, *J* = 4.1 Hz, 1H), 3.85 (s, 3H), 3.53 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 151.6, 138.3, 130.1, 129.9, 129.4, 126.3, 121.9, 121.4, 117.3, 117.1, 113.7, 95.9, 55.3, 55.2; FTIR (NaCl, thin film) 2930, 2833, 1696, 1636, 1606, 1573, 1612, 1452, 1248, 1095, cm^{-1}; LRMS (EI+) $[M]^+$ calculated for $C_{17}H_{16}O_3$: 268.1, found: 268.1.

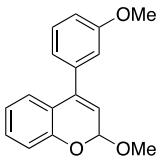


2-methoxy-4-(*p*-tolyl)-2*H*-chromene (1.85). Prepared via the general procedure described above on a 3.26 mmol scale. 4-(*p*-Tolyl) coumarin was prepared as reported in the literature.[43] The crude product was purified by silica gel chromatography (3–4% Et_2O/hexanes with 5% Et_3N; R_f = 0.45) to give **1.85** (517 mg, 63%) as a white solid (mp 85–88 °C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.21 (m, 5H), 7.16 – 7.14 (m, 1H), 7.09 – 7.07 (m, 1H), 6.94 – 6.90 (m, 1H), 5.86 (d, *J* = 4.2 Hz, 1H), 5.66 (d, *J* = 4.1 Hz, 1H), 3.55 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.5, 138.7, 137.9, 134.6, 129.4, 129.1, 128.7, 126.4, 121.8, 121.4, 117.5, 117.05, 95.8, 55.2, 21.2; FTIR (NaCl, thin film) 2923, 2827, 1639, 1603, 1558, 1484, 1452, 1220, 1095, 1045, cm^{-1}; LRMS (EI+) $[M]^+$ calculated for $C_{17}H_{16}O_2$: 252.2, found: 252.1.

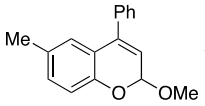


4-(4-chlorophenyl)-2-methoxy-2*H*-chromene (1.86). Prepared via the general procedure described above on a 1.75 mmol scale. 4-(4-chlorophenyl) coumarin was prepared as reported in the literature.[44] The crude product was purified by silica gel chromatography (5% Et_2O/hexanes with 5% Et_3N; R_f = 0.44) to give **1.86** (286 mg, 60%) as a white solid (mp 99–102 °C): ^{1}H NMR (400 MHz, $CDCl_3$) 7.41 – 7.33 (m, 4H), 7.25 – 7.29 (m, 1H), 7.08 – 7.10 (m, 2H) 6.96 – 6.92 (m, 1H), 5.84 (d, *J* = 4.2 Hz, 1H), 5.64 (d, *J* = 4.1 Hz, 1H), 3.54 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 132.6, 130.8, 128.9, 125.02, 124.5, 123.4, 120.8, 116.3,

116.2, 113.0, 112.01, 90.5, 50.1; FTIR (NaCl, thin film) 2926, 2827, 1652, 1636, 1558, 1483, 1455, 1219, 1088, 1045, cm^{-1}; LRMS (EI+) $[M]^+$ calculated for $C_{16}H_{13}ClO_2$: 272.1, found: 272.1.

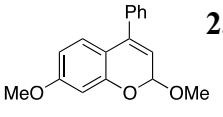


2-methoxy-4-(3-methoxyphenyl)-2*H*-chromene (1.87). Prepared via the general procedure described above on a 2.78 mmol scale. 4-(3-Methoxyphenyl) coumarin was prepared as reported in the literature.[43] The crude product was purified by silica gel chromatography (6–7% Et_2O/hexanes with 5% Et_3N; $R_f = 0.34$) to give **1.87** (469 mg, 63%) as a white solid (mp 87–90 °C): ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.23 (m, 2H), 7.17 – 7.15 (m, 1H), 7.09 – 7.07 (m, 1H), 6.99 – 6.90 (m, 4H), 5.87 (d, J = 4.1 Hz, 1H), 5.65 (d, J = 4.1 Hz, 1H), 3.82 (s, 3H), 3.54 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 151.4, 139.03, 138.8, 129.5, 129.4, 126.3, 121.70, 121.5, 121.3, 117.8, 117.1, 114.1, 113.9, 95.8, 55.3, 55.2; FTIR (NaCl, thin film) 2931, 2831, 1636, 1604, 1577, 1483, 1453, 1218, 1097, 1045, cm^{-1}; LRMS (EI+) $[M]^+$ calculated for $C_{17}H_{16}O_3$: 268.1, found: 268.1.



2-methoxy-6-methyl-4-phenyl-2*H*-chromene (1.88). Prepared via the general procedure described above on a 2.39 mmol scale. 6-methyl-4-phenyl coumarin was prepared as reported in the literature.[45] The crude product was purified by silica gel chromatography (4% Et_2O/hexanes with 5% Et_3N; $R_f = 0.45$) to give **1.88** (500 mg, 83%) as a white solid (mp 89–92 °C): ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.40 (m, 5H), 7.09

– 7.07 (m, 1H), 7.02 – 7.00 (m, 1H), 6.96 – 6.94 (m, 1H), 5.87 (d, J = 4.2 Hz, 1H), 5.64 (d, J = 4.2 Hz, 1H), 3.55 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$), δ 149.2, 138.9, 137.8, 130.7, 130.1, 128.9, 128.4, 128.08, 126.5, 121.5, 118.03, 116.8, 95.7, 55.2, 20.8; FTIR (NaCl, thin film) 2923, 2827, 1637, 1489, 1445, 1227, 1093, 1045 cm^{-1}; LRMS (EI+) $[M]^+$ calculated for $C_{17}H_{16}O_2$: 252.1, found: 252.1.

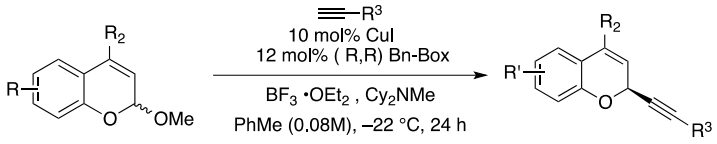


2,7-dimethoxy-4-phenyl-2*H*-chromene (1.89). Prepared via the general procedure described above on a 1.50 mmol scale. 7-Methoxy-4-phenyl coumarin was prepared as reported in the literature.[45] The crude product was purified by silica gel chromatography (7–8% Et_2O/hexanes with 5% Et_3N; R_f = 0.4) to give **1.89** (210 mg, 52%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.42 (m, 5H), 7.07 (d, J = 8.6 Hz, 1H), 6.68 (d, J = 2.5 Hz, 1H), 6.52 (dd, J = 8.6, 2.6 Hz, 1H), 5.74 (d, J = 4.1 Hz, 1H), 5.67 (d, J = 4.1 Hz, 1H), 3.84 (s, 3H), 3.57 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8, 152.9, 138.7, 137.8, 128.8, 128.3, 128.1, 127.2, 115.2, 115.11, 107.6, 102.4, 96.3, 55.4, 55.1; FTIR (NaCl, thin film) 2925, 2830, 1612, 1567, 1504, 1444, 1157, 1043 cm^{-1}; LRMS (EI+) $[M]^+$ calculated for $C_{17}H_{16}O_3$: 268.1, found: 268.1.

Enantioselective Alkynylation of Acetals

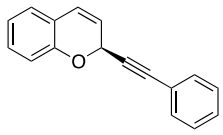
Racemic products were obtained using catalytic CuI, Cy_2NMe and $BF_3{\cdot}OEt_2$ in toluene at room temperature.

General Procedure for the Enantioselective, Copper-Catalyzed Alkynylation of Chromene Acetals



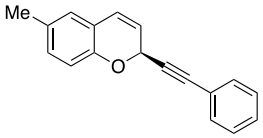
In a N_2-atmosphere glovebox, CuI (4.8 mg, 0.025 mmol, 10 mol %) was weighed into a 10-mL round-bottomed flask. (+)-2,2'-Isopropylidene[(4*R*)-4-benzyl-2-oxazoline] (BnBox**,** 11.0 mg, 0.030 mmol, 12 mol %) and toluene (3.2 mL, 0.08 M) were added. The round-bottomed flask was sealed with a septum. The mixture was stirred for 60 minutes at room temperature. Then the alkyne (0.305 mmol, 1.2 equiv), dicyclohexylmethyl amine (65.5 μL, 0.305 mmol, 1.2 equiv) and chromene acetal (0.254 mmol, 1.0 equiv) were added. The flask was again sealed with a septum, removed from the glovebox, and cooled to –22 °C. After 10 min, $BF_3{\cdot}OEt_2$ (55.0 μL, 0.444 mmol, 1.75 equiv) was added via syringe, and the reaction mixture was stirred for 24 h at –22 °C. The reaction mixture was quenched MeOH (3.0 ml), allowed to warm to room temperature, diluted with Et_2O

(10 mL), and filtered through a short plug of silica gel, which was then washed with Et_2O (10 mL). The filtrate was concentrated and purified by silica gel chromatography.



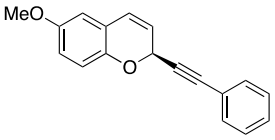
(*S*)-2-(phenylethynyl)-2*H*-chromene (1.41). Chromene **1.41** was prepared according to the General Procedure described above, except that 1.5 equiv of alkyne and 1.45 equiv $BF_3{\cdot}OEt_2$ was used. In a N_2-atmosphere glovebox, CuI (4.8 mg, 0.025 mmol, 10 mol %) was weighed into a 10-mL round-bottomed flask. (+)-2,2'-Isopropylidene[(4*R*)-4-benzyl-2-oxazoline] (BnBox**,** 11.0 mg, 0.030 mmol, 12 mol %) and toluene (3.18 mL, 0.08 M) were added. The round-bottomed flask was sealed with a septum. The mixture was stirred for 60 minutes at room temperature. Then phenyl acetylene (38.9 mg, 0.381 mmol, 1.5 equiv), dicyclohexylmethyl amine (65.5 μL, 0.305 mmol, 1.2 equiv) and chromene acetal **1.41** (41.1 mg, 0.254 mmol, 1.0 equiv) were added. The flask was again sealed with a septum, removed from the glovebox, and cooled to –22 °C. After 10 min, $BF_3{\cdot}OEt_2$ (45.5 μL, 0.368 mmol, 1.45 equiv) was added via syringe, and the reaction mixture was stirred for 24 h at –22 °C. The reaction mixture was quenched MeOH (3.0 ml), allowed to warm to room temperature, diluted with Et_2O (10 mL), and filtered through a short plug of silica gel, which was then washed with Et_2O (10 mL). The filtrate was concentrated and purified by silica gel chromatography (3% Et_2O/hexanes, R_f = 0.40) to give **1.41** (run 1: 39.3 mg, 67%; run 2: 36.9 mg, 63%) as a colorless oil. The enantiomeric excess was

determined to be 84% (run 1: 84% ee; run 2: 83% ee) by chiral HPLC analysis (CHIRALPAK IB, 0.8 mL/min, 1% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 10.9 min, t_R(minor) = 10.30 min. $[\alpha]_D^{24}$ = –110.1° (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.41 (m, 2H), 7.34 – 7.26 (m, 3H), 7.20 – 7.14 (m, 1H), 7.07 –7.03 (m, 1H), 6.96 – 6.90 (m, 2H), 6.53 (d, *J* = 9.5 Hz, 1H), 5.87 – 5.81 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.4, 131.9, 129.5, 128.7, 128.2, 126.8, 124.6, 122.15, 122.10, 121.8, 121.4, 116.5, 86.0, 85.7, 65.0 ; HRMS (EI+) $[M]^+$ calculated for $C_{17}H_{12}O$: 232.0888, found: 232.0895.The compound data matches with literature values.

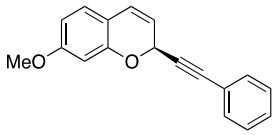


(*S*)-6-methyl-2-(phenylethynyl)-2*H*-chromene (1.36). Prepared via the General Procedure. The crude material was purified by silica gel chromatography (2–3% Et_2O/hexanes, R_f = 0.5) to give **1.36** (run 1: 52.8 mg, 84%; run 2: 48 mg, 77%) as a colorless oil. The enantiomeric excess was determined to be 89% (run 1: 89% ee; run 2: 89% ee) by chiral HPLC analysis (CHIRALPAK IB, 0.8 mL/min, 1% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 11.00 min, t_R(minor) = 10.24 min. $[\alpha]_D^{24}$ = –223.5° (c 1.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.43 (m, 2H), 7.35 – 7.27 (m, 3H), 6.98 (dd, *J* = 8.2, 1.7 Hz, 1H), 6.88 – 6.87 (m, 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 6.52 – 6.49 (m, 1H), 5.86 (dd, *J* = 9.5, 4.0 Hz, 1H), 5.79 (dd, *J* = 4.0, 1.6 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 131.9, 131.1, 129.9, 128.6, 128.2, 127.2, 124.8, 122.2, 122.1, 121.2, 116.2, 86.1, 85.5, 65.0, 20.6; FTIR (NaCl, thin film)

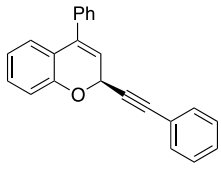
2918, 2830, 2214, 1725, 1665, 1632, 1586, 1487, 1442, 1206, 1022 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{18}H_{14}O$: 246.1044, found: 246.1048.



(*S*)-6-methoxy-2-(phenylethynyl)-2*H*-chromene (1.42). Prepared via the General Procedure. The crude material was purified by silica gel chromatography (5% Et_2O/hexanes, R_f = 0.38) to give **1.42** (run 1: 51 mg, 77%; run 2: 54 mg, 81%) as a colorless oil. After the column fractions were concentrated, HPLC and NMR analysis were immediately performed on compound **1.42**. When stored neat at room temperature, compound **1.42** decomposes, but can be stored in solution below –5 °C. The enantiomeric excess was determined to be 89% (run 1: 89% ee; run 2: 88% ee) by chiral HPLC analysis (CHIRALPAK IC, 0.8 mL/min, 2% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 9.21 min, t_R(minor) = 10.71 min. $[\alpha]_D^{24}$ = –173.1° (c 1.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.40 (m, 2H), 7.29 – 7.26 (m, 3H), 6.85 (d, *J* = 8.7 Hz, 1H), 6.72 (dd, *J* = 8.8, 3.0 Hz, 1H), 6.61 (d, *J* = 3.0 Hz, 1H), 6.49 (d, *J* = 9.6, 1H), 5.89 (dd, *J* = 9.6, 4.1 Hz, 1H), 5.74 – 5.73 (m, 1H), 3.77 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.5, 146.3, 131.9, 128.6, 128.2, 124.8, 123.1, 122.2, 122.1, 117.1, 114.6, 111.8, 86.0, 85.6, 65.0, 55.7; FTIR (NaCl, thin film) 2935, 2832, 2216, 1635, 1609, 1577, 1489, 1450, 1269, 1199 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{18}H_{14}O_2$: 262.0993, found: 262.0988.

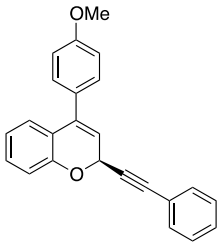


(*S*)-7-methoxy-2-(phenylethynyl)-2*H*-chromene (1.43). Prepared via the General Procedure. The crude material was purified by silica gel chromatography (4% Et_2O/hexanes, R_f = 0.4) to give **1.43** (run 1: 56.3 mg, 85%; run 2: 48 mg, 72%) as light yellow oil. After the column fractions were concentrated, HPLC and NMR analysis were immediately performed on compound **1.43**. When stored neat at room temperature, compound **1.43** decomposes, but can be stored in solution below –5 °C. The enantiomeric excess was determined to be 91% (run 1: 90% ee; run 2: 91% ee) by chiral HPLC analysis (CHIRALPAK IC, 0.8 mL/min, 2% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 10.14 min, t_R(minor) = 9.53 min. $[\alpha]_D^{24}$ = –110.8° (c 1.2, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.2 Hz, 2H), 7.34 – 7.28 (m, 3H), 6.97 (d, *J* = 8.1 Hz, 1H), 6.52 – 6.48 (m, 3H), 5.80 – 5.79 (m, 1H), 5.73 (dd, *J* = 9.6, 4.0 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.9, 153.7, 131.9, 128.6, 128.2, 127.5, 124.3, 122.2, 119.1, 114.7, 107.7, 102.3, 86.2, 85.5, 65.2, 55.3; FTIR (NaCl, thin film) 2932, 2830, 2213, 1635, 1612, 1550, 1481, 1269 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{18}H_{14}O2$: 262.0993, found: 262.0985.



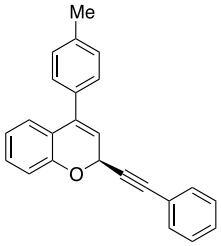
(*S*)-4-phenyl-2-(phenylethynyl)-2*H*-chromene (1.44). Prepared via the General Procedure. The crude material was purified by silica gel chromatography (3% Et_2O/hexanes, R_f = 0.40) to give **1.44** (run 1: 60.0 mg, 77%; run 2: 64.0 mg, 82%) as a white solid (mp 111–114 °C). The

enantiomeric excess was determined to be 91% (run 1: 91% ee; run 2: 90% ee) by chiral HPLC analysis (CHIRALPAK IC, 0.8 mL/min, 1% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 7.66 min, t_R(minor) = 7.30 min. $[\alpha]_D^{24}$ = –103.7° (c 1.6, $CHCl_3$); ^{1}H NMR (600 MHz $(CD_3)_2CO$) δ 7.48-7.33 (m, 10H), 7.25 (t, *J* = 7.8, Hz, 1H), 7.04 (d, *J*= 7.6 Hz, 1H), 7.00 (d, 1 *J* = 8.1 Hz, 1H), 6.95 (t, *J* = 7.5 Hz 1H), 5.98 (d, *J* = 4.7 Hz, 1H), 5.95 (d, *J* = 4.6, 1H); ^{13}C NMR (151 MHz, $(CD_3)_2CO$) δ 153.1, 137.6, 136.7, 131.6, 129.6, 128.8, 128.6, 128.54, 128.51, 128.1, 125.8, 122.7, 122.1, 121.6, 120.4, 116.9, 86.2, 85.1, 64.5; FTIR (NaCl/thin film) 2922, 2850, 2215, 1629, 1601, 1573, 1481, 1451, 1214, 1110 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{23}H_{16}O$: 308.1201, found: 308.1191.

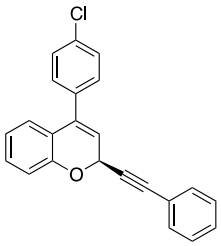


(*S*)-4-(4-methoxyphenyl)-2-(phenylethynyl)-2*H*-chromene (1.45). Prepared via the General Procedure. The crude material was purified by silica gel chromatography (5% Et_2O/hexanes, R_f = 0.4) to give **1.45** (run 1: 70 mg, 81%; run 2: 65.8 mg, 77%) as a white solid (mp 94–97 °C). The enantiomeric excess was determined to be 93% (run 1: 93% ee; run 2: 92% ee) by chiral HPLC analysis (CHIRALPAK IB, 0.8 mL/min, 3% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 8.67 min, t_R(minor) = 7.38 min. $[\alpha]_D^{24}$ = –140.5° (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.45 – 7.33 (m, 7H), 7.29 – 7.25 (m, 1H), 7.10 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.05 – 6.96 (m, 4H), 6.00 – 5.94 (m, 2H), 3.85 (s, 3H); ^{13}C NMR (101 MHz, $(CD_3)_2CO$) δ 159.8, 153.2, 136.2, 131.6, 129.8, 129.7, 129.5, 128.8, 128.5, 125.9, 122.9,

122.2, 121.6, 119.5, 116.9, 113.8, 86.3, 84.9, 64.5, 54.7; FTIR (NaCl, thin film) 2929, 2832, 2216, 1608, 1571, 1481, 1450, 1346, 1247, 1213 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{24}H_{18}O2$: 338.1306, found: 338.1300.

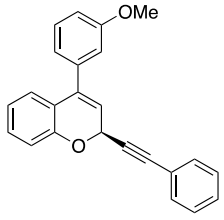


(*S*)-2-(phenylethynyl)-4-(*p*-tolyl)-2*H*-chromene (1.46). Prepared via the General Procedure. The crude material was purified by silica gel chromatography (3% Et_2O/hexanes, R_f = 0.5) to give **1.46** (run 1: 70 mg, 86%; run 2: 67.7 mg, 83%) as a colorless oil. The enantiomeric excess was determined to be 89% (run 1: 89% ee; run 2: 89% ee) by chiral HPLC analysis (CHIRALPAK IB, 0.8 mL/min, 1% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 10.45 min, t_R(minor) = 7.32 min. $[\alpha]_D^{24}$ = –38.3° (c 1.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.44 (m, 2H), 7.34 – 7.28 (m, 5H), 7.25 – 7.21 (m, 3H), 7.11 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.05 – 7.03 (m, 1H), 6.95 – 6.91 (m, 1H), 5.88 – 5.85 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.1, 137.9, 137.1, 134.7, 131.9, 129.5, 129.1, 128.7, 128.6, 128.2, 126.1, 122.9, 122.2, 121.6, 119.6, 116.9, 86.1, 85.7, 65.1, 21.2; FTIR (NaCl, thin film) 2920, 2826, 2230, 1683, 1635, 1601,1481, 1456, 1213 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{24}H_{18}O$: 322.1357, found: 322.1360.



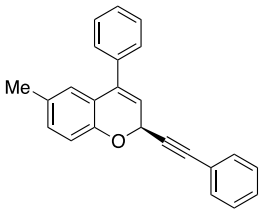
(*S*)-4-(4-chlorophenyl)-2-(phenylethynyl)-2*H*-chromene (1.47). Prepared via the General Procedure. The crude material was purified by silica gel chromatography (3% Et_2O/hexanes, R_f = 0.45) to give

1.47 (run 1: 75.4 mg, 87%; run 2: 68.7 mg, 79%) as a colorless oil. The enantiomeric excess was determined to be 80% (run 1: 80% ee; run 2: 80% ee) by chiral HPLC analysis (CHIRALPAK IB, 0.8 mL/min, 3% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 8.62 min, t_R(minor) = 6.47 min. $[\alpha]_D^{24}$ = –31.0° (c 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.54 – 7.51 (m, 2H), 7.48 – 7.33 (m, 7H), 7.30 – 7.26 (m, 1H), 7.06 – 6.94 (m, 3H), 6.04 (d, *J* = 4.7 Hz, 1H), 5.96 (d, *J* = 4.7 Hz, 1H); ^{13}C NMR (101 MHz, $(CD_3)_2CO$) δ 153.1, 136.3, 135.5, 133.5, 131.6, 130.3, 129.8, 128.9, 128.6, 128.5, 125.7, 122.3, 122.1, 121.8, 120.9, 117.0, 86.0, 85.2, 64.4; FTIR (NaCl, thin film) 2924, 2840, 2216, 2235, 1635, 1658, 1506, 1488, 1481, 1213, 1110, 1088 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{23}H_{15}OCl$: 342.0811, found: 342.0804.

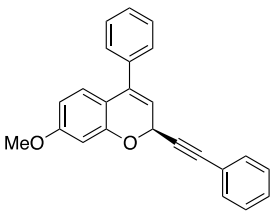


(*S*)-4-(3-methoxyphenyl)-2-(phenylethynyl)-2*H*-chromene (1.48). Prepared via the General Procedure. The crude material was purified by silica gel chromatography (5% Et_2O/hexanes, R_f = 0.4) to give **1.48** (run 1: 68.5 mg, 80%; run 2: 73.5 mg, 86%) as a white solid **(**mp 97–100 °C). The enantiomeric excess was determined to be 87% (run 1: 87% ee; run 2: 86% ee) by chiral HPLC analysis (CHIRALPAK IB, 0.8 mL/min, 3% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 8.00 min, t_R(minor) = 7.16 min. $[\alpha]_D^{24}$ = –123° (c 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.43 – 7.33 (m, 6H), 7.28 – 7.23 (m, 1H), 7.09 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.00 – 6.94 (m, 5H), 6.01 (d, *J* = 4.6 Hz, 1H), 5.95 (d, *J* = 4.6 Hz, 1H), 3.83 (s, 3H);

^{13}C NMR (101 MHz, $(CD_3)_2CO$) δ 159.9, 153.1, 138.9, 136.5, 131.6, 129.6, 129.5, 128.9, 128.5, 125.9, 122.6, 122.1, 121.7, 120.8, 120.3, 116.9, 114.0, 113.7, 86.2, 85.1, 64.5, 54.7; FTIR (NaCl, thin film) 2929, 2843, 2217, 1597, 1481, 1451, 1211 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{24}H_{18}O_2$: 338.1306, found: 338.1310.

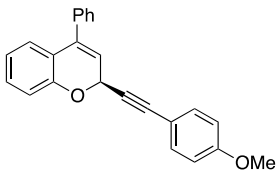


(*S*)-6-methyl-4-phenyl-2-(phenylethynyl)-2*H*-chromene (1.49). Prepared via the General Procedure. The crude material was purified by silica gel chromatography (4% Et_2O/hexanes, R_f = 0.6) to give **1.49** (run 1: 73 mg, 89%; run 2: 73.4 mg, 90%) as a white solid (mp 152–154 °C). The enantiomeric excess was determined to be 94% (run 1: 93% ee; run 2: 95% ee) by chiral HPLC analysis (CHIRALPAK IB, 0.8 mL/min, 2% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 7.38 min, t_R(minor) = 6.21 min. $[\alpha]_D^{24}$ = –80.6° (c 1.6, $CHCl_3$); ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.48 – 7.34 (m, 10H), 7.06 (d, *J* = 8.2 Hz, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 6.85 (s, 1H), 5.96 (d, *J* = 4.6 Hz, 1H), 5.90 (d, *J* = 4.6 Hz, 1H), 2.19 (s, 3H); ^{13}C NMR (101 MHz ($CDCl_3$) δ 150.9, 137.8, 137.3, 131.9, 131.0, 130.09, 128.8, 128.6, 128.4, 128.2 128.03, 126.4, 122.6, 122.2, 120.2, 116.7, 86.1, 85.7, 65.1, 20.82; FTIR (NaCl, thin film) 2922, 2830, 2217, 1683, 1635, 1601, 1481, 1456, 1213 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{24}H_{18}O$: 322.1357, found: 322.1363.



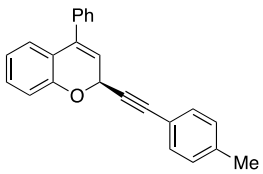
(*S*)-7-methoxy-4-phenyl-2-(phenylethynyl)-2*H*-chromene (1.50). Prepared via the General Procedure. The crude material

was purified by silica gel chromatography under N_2 atmosphere (3–5% Et_2O/hexanes, R_f = 0.42) to give **1.50** (run 1: 59 mg, 69%; run 2: 54 mg, 63%) as a colorless oil. After the column fractions were concentrated, HPLC and NMR analysis were immediately performed on compound **1.50.** When stored neat at room temperature, compound **1.50** decomposes, but can be stored in solution under a N_2 atmosphere below –5 °C. The enantiomeric excess was determined to be 95% (run 1: 95% ee; run 2: 94% ee) by chiral HPLC analysis (CHIRALPAK IB, 0.8 mL/min, 3% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 8.35 min, t_R(minor) = 7.11 min. $[\alpha]_D^{24}$ = –66.2° (c 1.6, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 7H), 7.33 – 7.27 (m, 3H), 6.98 (d, *J* = 8.6 Hz, 1H), 6.61 – 6.60 (m, 1H), 6.47 (dd, *J* = 8.6, 2.5 Hz, 1H), 5.84 (d, *J* = 4.2 Hz, 1H), 5.73 (d, *J* = 4.2 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.8, 154.5, 137.9, 137.1, 132.0, 128.7, 128.6, 128.3, 128.2, 128.0, 127.0, 122.2, 117.2, 116.1, 107.7, 102.5, 86.1, 85.6, 65.4, 55.4; FTIR (NaCl, thin film) 2930, 2835, 2215, 1630, 1602, 1480, 1450, 1348, 1213 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{24}H_{18}O_2$: 338.1306, found: 338.1298.



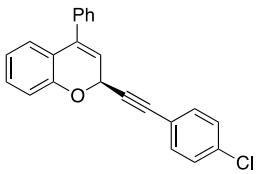
(*S*)-2-((4-methoxyphenyl)ethynyl)-4-phenyl-2*H*-chromene (1.51). Prepared via the General Procedure. The crude material was purified by silica gel chromatography (7% Et_2O/hexanes, R_f = 0.35) to give **1.51** (run 1: 61.5 mg, 72%; run 2: 65.8 mg, 77%) as a colorless oil. The enantiomeric excess was determined to be 86% (run 1: 85% ee; run 2: 86% ee) by chiral

HPLC analysis (CHIRALPAK IC, 0.8 mL/min, 2% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 8.69 min, t_R(minor) = 8.18 min. $[\alpha]_D^{24}$ = –72.9° (c 1.4, $CHCl_3$); ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.51 - 7.34 (m, 7H), 7.28 - 7.24 (m, 1H), 7.06 (dd, *J*= 7.7 Hz, 1.7 Hz, 1H), 7.01-6.90 (m, 4H), 5.99 (d, *J* = 4.6 Hz, 1H), 5.94 (d, *J* = 4.6 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (101 MHz, $(CD_3)_2CO$) δ 160.2, 153.2, 137.6, 136.5, 133.2, 129.6, 128.6, 128.5, 128.1, 125.8, 122.8, 121.6, 120.6, 116.9, 114.1, 114.0, 85.2, 84.7, 64.6, 54.8; FTIR (NaCl, thin film) 2928, 2836, 2216, 1604, 1570, 1480, 1451, 1249 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{24}H_{18}O_2$: 338.1306, found: 338.1315.

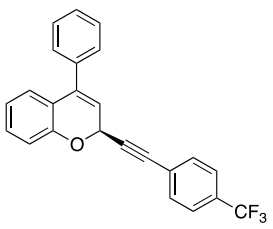


(*S*)-4-phenyl-2-(*p*-tolylethynyl)-2*H*-chromene (1.52). Prepared via the General Procedure. The crude material was purified by silica gel chromatography (3% Et_2O/hexanes, R_f = 0.5) to give **1.52** (run 1: 64 mg, 78%; run 2: 58.8 mg, 72%) as a white solid (mp 147–149 °C). The enantiomeric excess was determined to be 89% (run 1: 89% ee; run 2: 89% ee) by chiral HPLC analysis (CHIRALPAK IB, 0.8 mL/min, 1% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 10.89 min, t_R(minor) = 7.23 min. $[\alpha]_D^{24}$ = –117.0° (c 0.8, $CHCl_3$); ^{1}H NMR (600 MHz, $(CD_3)_2CO$) δ 7.47 - 7.38 (m, 5H), 7.30 (d, *J* =7.8 Hz, 2H), 7.25 (t, *J*= 7.7 Hz, 1H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.04 (d, *J* = 7.7 Hz, 1H), 6.99 (d, *J* = 8.1 Hz, 1H), 6.94 (t, *J* = 7.6 Hz, 1H), 5.97 (d, *J* = 4.6 Hz, 1H), 5.93 (d, *J* = 4.6 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (151 MHz, $(CD_3)_2CO$) δ 153.2, 139.0, 137.7, 136.6, 131.6, 129.6, 129.2, 128.6, 128.5,

128.1, 125.8, 122.8, 121.6, 120.5, 119.2, 116.9, 85.6, 85.3, 64.6, 20.5; FTIR (NaCl/thin film) 2916, 2848, 2214, 1635, 1508, 1450, 1453, 1212 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{24}H_{18}O$: 322.1357, found: 322.1365.

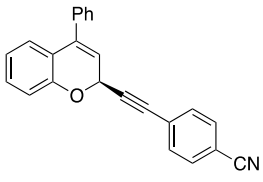


(*S*)-2-((4-chlorophenyl)ethynyl)-4-phenyl-2*H*-chromene (1.53). Prepared via the General Procedure. The crude material was purified by silica gel chromatography (6% Et_2O/hexanes, R_f = 0.5) to give **1.53** (run 1: 63.4 mg, 73%; run 2: 65.3 mg, 75%) as a light yellow solid (mp 142–145 °C). The enantiomeric excess was determined to be 89% (run 1: 89% ee; run 2: 89% ee) by chiral HPLC analysis (CHIRALPAK IB, 0.8 mL/min, 2% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 7.24 min, t_R(minor) = 6.46 min. $[\alpha]_D^{24}$ = –134.2° (c 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.51-7.40 (m, 9H), 7.30-7.25 (m, 1H), 7.07 – 6.95 (m, 3H), 5.97-6.00 (m, 2H); ^{13}C NMR (101 MHz, $(CD_3)_2CO$) δ 153.0, 137.5, 136.7, 134.4, 133.3, 129.7, 128.8, 128.57, 128.56, 128.2, 125.8, 122.7, 121.7, 120.9, 120.1, 116.9, 87.3, 83.8, 64.4; FTIR (NaCl, thin film) 2921, 2820, 2240, 1659, 1631, 1481, 1452, 1214 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{23}H_{15}OCl$: 342.0811, found: 342.0808.



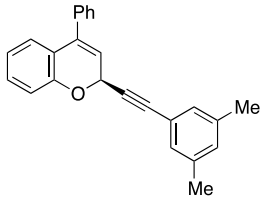
(*S*)-4-phenyl-2-((4-(trifluoromethyl)phenyl)ethynyl)-2*H*-chromene (1.54). Prepared via the General Procedure. The crude material was purified by silica gel chromatography (4% Et_2O/hexanes, R_f = 0.55) to give **1.54** (run 1: 72.3 mg, 76%; run 2: 69.2 mg, 73%) as a

light yellow solid (mp 123–126 °C). The enantiomeric excess was determined to be 83% (run 1: 82% ee; run 2: 83% ee) by chiral HPLC analysis (CHIRALPAK IB, 0.8 mL/min, 1% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 8.30 min, t_R(minor) = 6.98 min. $[\alpha]_D^{24}$ = –81.2° (c 1.6, $CHCl_3$); ^{1}H NMR (600 MHz, $(CD_3)_2CO$) δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.48 – 7.40 (m, 5H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 6.0 Hz, 1H), 7.02 (d, *J* = 8.1 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.05 – 6.00 (m, 2H); ^{13}C NMR (151 MHz, $(CD_3)_2CO$) δ 153.0, 137.5, 137.0, 129.9 (q, J_{C-F} = 31.7 Hz), 129.7,129.2 128.4, 128.2,127.8, 126.3, 125.9, 125.4 (q, J_{C-F} = 3.0 Hz), 124.0 (q, J_{C-F} = 271.8 Hz), 122.7, 121.8, 119.9, 116.9, 88.9, 83.6, 64.4; FTIR (NaCl, thin film) 2925, 2820, 2232, 1615, 1481, 1452 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{24}H_{15}OF_3$: 376.1075, found: 376.1070.

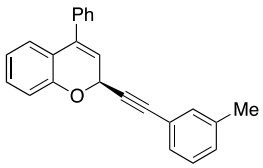


(*S*)-4-((4-phenyl-2*H*-chromen-2-yl)ethynyl)benzonitrile (1.55). Prepared via the General Procedure. The crude material was purified by silica gel chromatography (9% Et_2O/hexanes, R_f = 0.3) to give **1.55** (run 1: 62.2 mg, 74%; run 2: 63.8 mg, 76%) as light yellow oil. The enantiomeric excess was determined to be 85% (run 1: 85% ee; run 2: 85% ee) by chiral HPLC analysis (CHIRALPAK IB, 0.8 mL/min, 3% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 13.24 min, t_R(minor) = 11.74 min. $[\alpha]_D^{24}$ = –106.7° (c 0.8, $CHCl_3$); ^{1}H NMR (600 MHz, $(CD_3)_2CO$) δ 7.77 (d, *J* = 8.1 Hz, 2H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.48 – 7.40

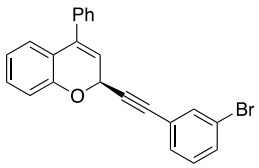
(m, 5H), 7.27 (t, J = 7.7 Hz, 1H), 7.05 (d, J = 7.8 Hz, 1H), 7.01 (d, J = 8.1 Hz, 1H), 6.97 (t, J = 7.5 Hz, 1H), 6.07 – 5.99 (m, 2H); ^{13}C NMR (151 MHz, $(CD_3)_2CO$) δ 152.9, 137.5, 137.1, 132.4, 132.3, 129.7, 128.6, 128.5, 128.2, 126.8, 125.9, 122.7, 121.8, 119.7, 117.9, 116.9, 112.2, 90.3, 83.5, 64.4; FTIR (NaCl, thin film) 2924, 2853, 2228, 2235, 1717, 1683, 1652, 1603, 1558, 1480, 1213 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{24}H_{15}ON$: 333.1153, found: 333.1148.



(*S*)-2-((3,5-dimethylphenyl)ethynyl)-4-phenyl-2*H*-chromene (1.56). Prepared via the General Procedure. The crude material was purified by silica gel chromatography (2–3% Et_2O/hexanes, R_f = 0.57) to give **1.56** (run 1: 68 mg, 80%; run 2: 73.3 mg, 86%) as a colorless oil. The enantiomeric excess was determined to be 91% (run 1: 90% ee; run 2: 92% ee) by chiral HPLC analysis (CHIRALPAK IB, 0.8 mL/min, 1% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 10.59 min, t_R(minor) = 7.63 min. $[\alpha]_D^{24}$ = –214.5° (c 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.51 – 7.41 (m, 5H), 7.29 – 7.25 (m, 1H), 7.07 – 6.94 (m, 6H), 5.99 (d, J = 4.7 Hz, 1H), 5.96 (d, J = 4.7 Hz, 1H), 2.26 (s, 6H); ^{13}C NMR (101 MHz, $(CD_3)_2CO$) δ 153.1, 138.1, 137.6, 136.5, 130.5, 129.6, 129.2, 128.6, 128.5, 128.1, 125.8, 122.7, 121.8, 121.6, 120.4, 116.9, 85.49, 85.48, 64.5, 20.1; FTIR (NaCl, thin film) 2917, 2820, 2212, 1637, 1599, 1481, 1452, 1214 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{25}H_{20}O$: 336.1514, found: 336.1509.

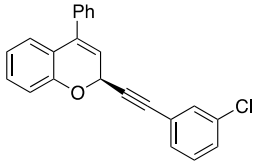


(*S*)-4-phenyl-2-(*m*-tolylethynyl)-2*H*-chromene (1.57). Prepared via the General Procedure. The crude material was purified by silica gel chromatography (3% Et_2O/hexanes, R_f = 0.5) to give **1.57** (run 1: 70.3 mg, 86%; run 2: 65 mg, 80%) as a white solid (mp 98–102°C). The enantiomeric excess was determined to be 90% (run 1: 90% ee; run 2: 89% ee) by chiral HPLC analysis (CHIRALPAK IC, 0.8 mL/min, 1% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 7.35 min, t_R(minor) = 6.78 min. $[\alpha]_D^{24}$ = –126.6° (c 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.51 – 7.41 (m, 5H), 7.30 – 7.20 (m, 5H), 7.07 – 6.95 (m, 3H), 6.00 (d, *J* = 4.7 Hz, 1H), 5.97 (d, *J* = 4.7 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $(CD_3)_2CO$) δ 153.1, 138.2, 137.6, 136.6, 132.1, 129.7, 129.6, 128.7, 128.58, 128.56, 128.4, 128.1, 125.8, 122.7, 122.0, 121.6, 120.4, 116.9, 85.8, 85.2, 64.5, 20.1; FTIR (NaCl, thin film) 2920, 2823, 2216, 1601, 1481, 1451, 1341, 1294, 1214 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{24}H_{18}O$: 322.1357, found: 322.1352.



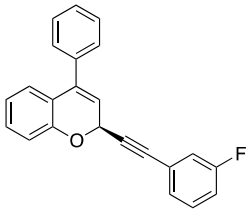
(*S*)-2-((3-bromophenyl)ethynyl)-4-phenyl-2*H*-chromene (1.58). Prepared via the General Procedure. The crude material was purified by silica gel chromatography (4% Et_2O/hexanes, R_f = 0.5) to give **1.58** (run 1: 72.4 mg, 74%; run 2: 74 mg, 76%) as a yellow oil. The enantiomeric excess was determined to be 87% (run 1: 87% ee; run 2: 86% ee) by chiral HPLC analysis (CHIRALPAK IB, 0.8 mL/min, 2% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 7.03 min,

t_R(minor) = 6.43 min. $[\alpha]_D^{24}$ = –129° (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.58 – 7.56 (m, 2H), 7.48 – 7.39 (m, 6H), 7.34 – 7.24 (m, 2H), 7.05 – 6.94 (m, 3H), 6.00 – 5.96 (m, 2H); ^{13}C NMR (101 MHz, $(CD_3)_2CO$) δ 153.0, 137.5, 136.8, 134.1, 132.0, 130.6, 130.5, 129.7, 128.59, 128.57, 128.2, 125.9, 124.3, 122.7, 121.8, 121.7, 120.0, 116.9, 87.7, 83.40, 64.4; FTIR (NaCl, thin film) 2919, 2849, 2214, 1589, 1554, 1480, 1349, 1213, 1110 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{23}H_{15}O$ Br: 386.0306, found: 386.0302.

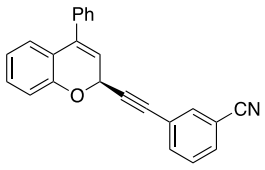


(*S*)-2-((3-chlorophenyl)ethynyl)-4-phenyl-2*H*-chromene (1.59). Prepared via the General Procedure. The crude material was purified by silica gel chromatography (4% Et_2O/hexanes, R_f = 0.4) to give **1.59** (run 1: 70.3 mg, 81%; run 2: 73 mg, 84%) as a yellow oil. The enantiomeric excess was determined to be 89% (run 1: 90% ee; run 2: 88% ee) by chiral HPLC analysis (CHIRALPAK IB, 0.8 mL/min, 1% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 8.58 min, t_R(minor) = 7.32 min. $[\alpha]_D^{24}$ = –71.2° (c 0.8, $CHCl_3$); ^{1}H NMR (600 MHz, $(CD_3)_2CO$) δ 7.48 – 7.36 (m, 9H), 7.26 (t, *J* = 7.7 Hz, 1H), 7.05 (d, *J* = 7.7 Hz, 1H), 7.01 (d, *J* = 8.1 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 5.98 (m, 2H); ^{13}C NMR (151 MHz, $(CD_3)_2CO$) δ 153.0, 137.5, 136.9, 133.8, 131.2, 130.3, 130.2, 129.7, 129.08, 128.59, 128.55, 128.2, 125.8, 124.09, 122.7, 121.7, 120.1, 116.9, 87.3, 83.8, 64.4; FTIR (NaCl, thin film) 2922,

2832, 2215, 1683, 1652, 1558, 1540, 1506, 1521, 1457, 1436 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{23}H_{15}OCl$: 342.0811, found: 342.0821.

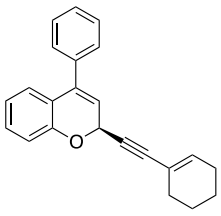


(*S*)-2-((3-fluorophenyl) ethynyl)-4-phenyl-2*H*-chromene (1.60). Prepared via the General Procedure. The crude material was purified by silica gel chromatography (4% Et_2O/hexanes, R_f = 0.4) to give **1.60** (run 1: 65 mg, 79%; run 2: 60.2 mg, 73%) as a colorless oil. The enantiomeric excess was determined to be 93% (run 1: 93% ee; run 2: 92% ee) by chiral HPLC analysis (CHIRALPAK IB, 0.8 mL/min, 2% *i*-PrOH/hexane, λ= 220 nm); t_R(major) = 6.64 min, t_R(minor) = 6.12 min. $[\alpha]_D^{24}$ = –180.0° (c 0.4, $CHCl_3$); ^{1}H NMR (600 MHz, $(CD_3)_2CO$) δ 7.48 – 7.38 (m, 6H), 7.27 – 7.24 (m, 2H), 7.18 – 7.15 (m, 2H), 7.05 (d, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 8.1 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 5.99 – 5.96 (m, 2H); ^{13}C NMR (151 MHz, $(CD_3)_2CO$) δ 162.3 (d, J_{C-F} = 246.1 Hz), 153.1, 137.5, 136.8, 130.6 (d, J_{C-F} = 7.6 Hz), 129.7, 128.6, 128.5, 128.1, 127.8 (d, J_{C-F} = 3.02 Hz), 125.8, 124.1 (d, J_{C-F} = 10.5 Hz), 122.7, 121.7, 120.1, 118.1(d, J_{C-F} = 22.6 Hz), 116.9, 116.1(d, J_{C-F} = 21.1 Hz), 87.3, 83.7(d, J_{C-F} = 3.02 Hz), 64.4; FTIR (NaCl, thin film) 2916, 2848, 2224, 1601, 1581, 1481, 1452, 1264 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{23}H_{15}OF$: 326.1107, found: 326.1106.



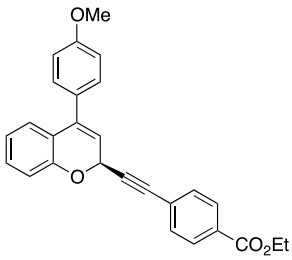
(*S*)-3-((4-phenyl-2*H*-chromen-2-yl) ethynyl) benzonitrile (1.61). Prepared via the General Procedure. The crude material

was purified by silica gel chromatography (8% Et_2O/hexanes, $R_f = 0.33$) to give **1.61** (run 1: 65.8 mg, 78%; run 2: 63.2 mg, 75%) as a colorless oil. The enantiomeric excess was determined to be 88% (run 1: 87% ee; run 2: 89% ee) by chiral HPLC analysis (CHIRALPAK IB, 0.8 mL/min, 3% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 12.66 min, t_R(minor) = 11.59 min). $[\alpha]_D^{24} = -140.8°$ (c 1.2, $CHCl_3$); ^{1}H NMR (600 MHz, $(CD_3)_2CO$) δ 7.81 (s, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.60 (t, *J* = 7.8 Hz, 1H), 7.48 – 7.40 (m, 5H), 7.28 – 7.25 (m, 1H), 7.05 (d, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 8.1 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.00 – 5.98 (m, 2H); ^{13}C NMR (151 MHz, $(CD_3)_2CO$) δ 153.0, 137.5, 137.0, 135.9, 134.8, 132.2, 129.8, 129.7, 128.6, 128.5, 128.2, 125.9, 123.6, 122.7, 121.8, 119.8, 117.5, 116.9, 112.9, 88.5, 82.9, 64.4; FTIR (NaCl, thin film) 2924, 2853, 2226, 2232, 1600, 1572, 1451, 1293 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{24}H_{15}ON$: 333.1153, found: 333.1149.



(*S*)-2-(cyclohex-1-en-1-ylethynyl)-4-phenyl-2*H*-chromene (1.62). Prepared via the General Procedure. The crude material was purified by silica gel chromatography (2–3% Et_2O/hexanes, $R_f = 0.5$) to give **1.62** (run 1: 40.1 mg, 51%; run 2: 36.2 mg, 46%) as a colorless oil. The enantiomeric excess was determined to be 71% (run 1: 70% ee; run 2: 70% ee) by chiral HPLC analysis (CHIRALPAK IB, 0.8 mL/min, 1% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 6.74 min, t_R(minor) = 6.15 min. $[\alpha]_D^{24} = -82.0°$ (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz,

$CDCl_3$), δ 7.42 – 7.35 (m, 5H), 7.21 – 7.17 (m, 1H), 7.04 – 7.02 (m, 1H), 6.99 – 6.98 (m, 1H), 6.90 – 6.87 (m, 1H), 6.15 – 6.13 (m, 1H), 5.81 (d, *J* = 4.1 Hz, 1H), 5.76 (d, *J* = 4.1 Hz, 1H), 2.28 – 2.08 (m, 4H), 1.69 – 1.47 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.2, 137.7, 136.9, 136.5, 129.5, 128.8, 128.4, 128.0, 126.0, 122.9, 121.5, 120.6, 119.8, 116.9, 87.8, 83.2, 65.2, 29.0, 25.7, 22.2, 21.4; FTIR (NaCl, thin film) 2925, 2855, 2214, 1630, 1602, 1 1480, 1450, 1348, 1213 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{23}H_{20}O$: 312.1514, found: 312.1522.

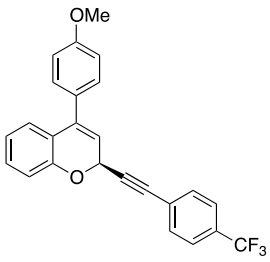


(*S*)-ethyl 4-((4-(4-methoxyphenyl)-2*H*-chromen-2-yl) ethynyl) benzoate (1.63).

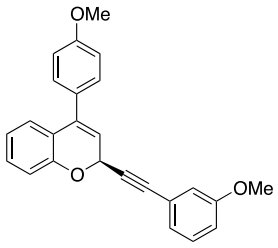
Prepared via the General Procedure. The crude material was purified by silica gel chromatography (12% Et_2O/hexanes, R_f = 0.33) to give **1.63** (run 1: 88 mg, 85%; run 2: 89.8 mg, 86%) as a colorless oil. The enantiomeric excess was determined to be 89% (run 1: 88% ee; run 2: 89% ee) by chiral HPLC analysis (CHIRALPAK IA, 0.8 mL/min, 3% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 17.69 min, t_R(minor) = 14.33 min. $[\alpha]_D^{24}$ = –105° (c 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.03 – 8.00 (m, 2H), 7.58 – 7.55 (m, 2H), 7.39 – 7.37 (m, 2H), 7.32 – 7.28 (m, 1H), 7.11 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.08 – 6.99 (m, 4H), 6.03 – 5.98 (m, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $(CD_3)_2CO$) δ 165.1, 159.8, 153.1, 136.4, 131.7, 130.5, 129.7, 129.63, 129.60, 129.3,

126.6, 125.9, 122.9, 121.7, 119.1, 116.9, 113.8, 89.3, 84.1, 64.4, 60.8, 54.7, 13.6; FTIR (NaCl, thin film) 2931, 2835, 2232, 1716, 1678, 1606, 1572, 1511, 1481 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{27}H_{22}O_4$: 410.1518, found: 410.1527.

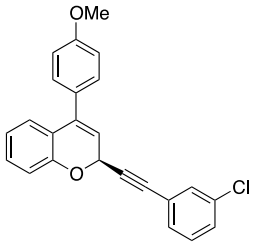
(*S*)-4-(4-methoxyphenyl)-2-((4-(trifluoromethyl)phenyl)ethynyl)-2*H*-chromene



(1.64). Prepared via the General Procedure. The crude material was purified by silica gel chromatography (6% Et_2O/hexanes, R_f = 0.33) to give **1.64** (run 1: 76.4 mg, 74%; run 2: 81.3 mg, 79%) as a colorless oil. The enantiomeric excess was determined to be 87% (run 1: 87% ee; run 2: 87% ee) by chiral HPLC analysis (CHIRALPAK IB, 0.8 mL/min, 1% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 11.72 min, t_R(minor) = 10.55 min. $[\alpha]_D^{24}$ = – 19.2 ° (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.36 – 7.31 (m, 2H), 7.29 – 7.24 (m, 1H), 7.09 (dd, J = 1.6, 7.7 Hz, 1H), 7.05 – 6.95 (m, 4H), 6.02 – 5.90 (m, 2H), 3.85 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.6, 153.1, 137.0, 132.2, 130.3 (q, J_{C-F} = 33.2 Hz) , 129.9, 129.86, 129.6, 126.2, 126.1 125.1(q, J_{C-F} = 3.02 Hz), 123.8 (q, J_{C-F} = 271.8 Hz), 123.0, 121.8 118.7, 116.9, 113.9, 88.6, 84.2, 64.9, 55.4; FTIR (NaCl, thin film) 2929, 2834, 2226, 1608, 1570, 1511, 1481, 1451, 1323, 1290, 1248 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{25}H_{17}O_2F_3$: 406.1180, found: 406.117.

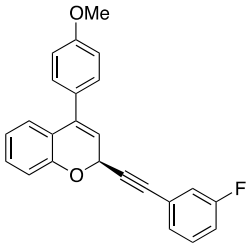


(*S*)-4-(4-methoxyphenyl)-2-((3-methoxyphenyl)ethynyl)-2*H*-chromene (1.65). Prepared via the General Procedure. The crude material was purified by silica gel chromatography (8% Et_2O/hexanes, R_f = 0.3) to give **1.65** (run 1: 80.7 mg, 86%; run 2: 77.0 mg, 82%) as a colorless oil. The enantiomeric excess was determined to be 90% (run 1: 90% ee; run 2: 89% ee) by chiral HPLC analysis (CHIRALPAK IA, 0.8 mL/min, 2% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 16.46 min, t_R(minor) = 13.94 min. $[\alpha]_D^{24}$ = –56.8 ° (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.37 – 7.33 (m, 2H), 7.30 – 7.242 (m, 2H), 7.09 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.05 – 6.95 (m, 7H), 5.96 – 5.93 (m, 2H), 3.87 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 159.2, 153.2, 136.7, 130.0, 129.9 129.5, 129.3, 126.1, 124.5, 123.2, 123.06, 121.7, 119.3, 116.9, 116.6, 115.4, 113.8, 85.9, 85.6, 65.1, 55.36, 55.31; FTIR (NaCl, thin film) 2928, 2832, 2228, 2221, 1604, 1573, 1511, 1480 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{25}H_{20}O_3$: 368.1412, found: 368.1404.



(*S*)-2-((3-chlorophenyl)ethynyl)-4-(4-methoxyphenyl)-2*H*-chromene (1.66). Prepared via the General Procedure. The crude material was purified by silica gel chromatography (4% Et_2O/hexanes, R_f = 0.5) to give **1.66** (run 1: 75.7 mg, 80%; run 2: 70.8 mg, 75%) as a light yellow solid (mp 112–115 °C). The enantiomeric excess was determined to be 91%

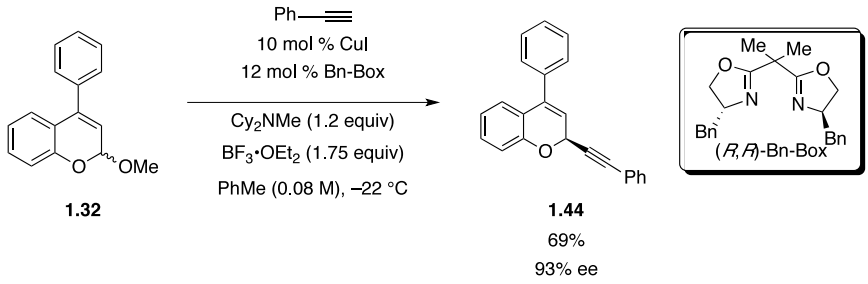
(run 1: 91% ee; run 2: 90% ee) by chiral HPLC analysis (CHIRALPAK IB, 0.8 mL/min, 1% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 11.23 min, t_R(minor) = 10.17 min. $[\alpha]_D^{24}$ = –70.8° (c 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.45 – 7.33 (m, 6H), 7.30 – 7.25 (m, 1H), 7.10 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.06 – 6.96 (m, 4H), 6.00 – 5.94 (m, 2H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, $(CD_3)_2CO$) δ 159.8, 153.1, 136.4, 133.8, 131.1, 130.3, 130.1, 129.7, 129.62, 129.61, 129.1, 125.9, 124.1, 122.9, 121.7, 119.1, 116.9, 113.9, 87.8, 83.3, 64.3, 54.7; FTIR (NaCl, thin film) 2930, 2832, 2216, 2235, 1608, 1627, 1529, 1560, 1480, 1214 cm^{-1}; HRMS (EI+) [M+] calculated for $C_{24}H_{17}O_2$ Cl: 372.0917, found: 372.0913.



(*S*)-2-((3-fluorophenyl)ethynyl)-4-(4-methoxyphenyl)-2*H*-chromene (1.67). Prepared via the General Procedure. The crude material was purified by silica gel chromatography (4% Et_2O/hexanes, R_f = 0.4) to give **1.67** (run 1: 77.6 mg, 86%; run 2: 81.3 mg, 90%) as a colorless oil. The enantiomeric excess was determined to be 91% (run 1: 91% ee; run 2: 91% ee) by chiral HPLC analysis (CHIRALPAK IB, 0.8 mL/min, 1% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 11.07 min, t_R(minor) = 9.84 min. $[\alpha]_D^{24}$ = –115.7° (c 1.4, $CHCl_3$); ^{1}H NMR (600 MHz, $(CD_3)_2CO$) δ 7.45 – 7.41 (m, 1H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.26 (m, 2H), 7.20 – 7.18 (m, 2H), 7.12 (d, *J* = 7.6 Hz, 1H), 7.05 – 6.98 (m, 4H), 5.98 – 5.95 (m, 2H), 3.88 (s, 3H); ^{13}C NMR (151MHz, $(CD_3)_2CO$) δ 162.3 (d, J_{C-F} = 247.6 Hz),

159.9, 153.1, 136.4, 130.6 (d, J_{C-F} = 9.06 Hz), 129.7, 129.6, 129.5, 127.8 (d, J_{C-F} = 3.0 Hz), 125.9, 124.2 (d, J_{C-F} = 10.57 Hz), 122.9, 121.7, 119.2, 118.1 (d, J_{C-F} = 24.16 Hz), 116.8, 116.07 (d, J_{C-F} = 21.1 Hz), 113.9, 87.5, 83.6 (d, J_{C-F} = 3.0 Hz), 64.5, 54.8; FTIR (NaCl, thin film) 2930, 2835, 2222, 1667, 1580, 1510, 1481, 1463, 1450, 1247, 1213 cm^{-1}; HRMS (EI+) $[M]^+$ HRMS (EI+) [M+] calculated for $C_{24}H_{17}O_2F$: 356.1212, found: 356.1203.

Procedure for Reaction Set-Up Outside the Glovebox

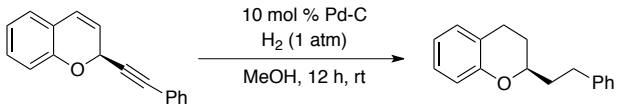


1.32 **1.44** 69% 93% ee

(S)-4-phenyl-2-(phenylethynyl)-2*H*-chromene (1.44). In a flame-dried, 10-mL round-bottomed flask, CuI (4.8 mg, 0.025 mmol, 10 mol %) and (+)-2,2'-isopropylidene[(4*R*)-4-benzyl-2-oxazoline] (BnBox**,** 11.0 mg, 0.0305 mmol, 12 mol %) were combined. The flask was sealed with a septum. The flask was evacuated and refilled with N_2 three times before PhMe (3.18 mL, 0.08 M) was added. The solution was stirred for 60 min at room temperature. Then phenyl acetylene (38.9 mg, 0.381 mmol, 1.5 equiv), dicyclohexylmethyl amine (65.5 μL, 0.305 mmol, 1.2 equiv) and chromene acetal **1.32** (60.5 mg, 0.254 mmol, 1.0 equiv) were added. The flask was cooled to –22 °C.

After 10 min, $BF_3 \cdot OEt_2$ (55.0 μL, 0.444 mmol, 1.75 equiv) was added via syringe, and the reaction mixture was stirred for 24 h at –22 °C. MeOH (3.0 mL,) was then added. After warming to room temperature, the mixture was diluted with Et_2O (10 mL) and filtered through a short plug of silica gel, which was then washed with Et_2O (10 mL). The filtrate was concentrated. The crude product was purified by silica gel chromatography (3% Et_2O/hexanes, R_f = 0.40) to give **1.44** (run 1: 54.3 mg, 69%; run 2: 53.0 mg, 68%) as a white solid. The enantiomeric excess was determined to be 93% (run 1: 93% ee; run 2: 93% ee) by chiral HPLC analysis (CHIRALPAK IC, 0.8 mL/min, 1% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 7.10 min, t_R(minor) = 6.77 min. The spectral data for this compound matches that reported above.

Determination of Absolute Configuration



1.41
83% ee
(*S*)-enantiomer

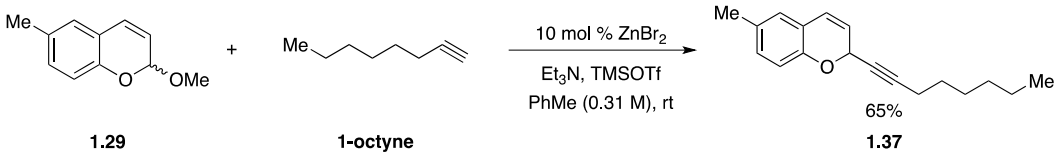
1.68
90%, 81% ee
(*R*)-enantiomer
$[\alpha]_D^{24}$ = +43.1 ° (c 0.8, $CHCl_3$)

Alkyne **1.41** (25.0 mg, 0.107 mmol, 83% ee prepared from acetal **1.40** and phenylacetylene using (*R*,*R*)-BnBox as ligand) and MeOH (2.5 mL) were combined in a 10-mL flame dried round-bottomed flask fitted with a 3-way adapter with a T-bore stopcock. Via this adapter, the reaction vessel was connected to a N_2/vacuum manifold

and to a H_2-filled balloon. The flask was evacuated and refilled with nitrogen three times. 10% Pd/C (3.0 mg, 0.0028 mmol, 0.026 equiv) was added, and the flask was again evacuated and refilled with nitrogen three times. The flask was then evacuated and refilled with H_2 five times. The reaction mixture was stirred under H_2 (1 atm) for 12 h. After consumption of alkyne **1.41** as determined by TLC analysis, the mixture was filtered through a short pad of celite, which was then washed with Et_2O (10 mL). The filtrate was concentrated, and the crude material was purified by silica gel chromatography (1–3% Et_2O/hexanes, R_f = 0.4) to give **1.68** (22.3 mg, 87%) as colorless oil. The enantiomeric excess was determined to be 82% by chiral HPLC analysis (CHIRALPAK IA, 0.8 mL/min, 0.5% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 7.72 min, t_R(minor) = 8.6 min. $[\alpha]_D^{24}$ = +43.1 ° (c 0.8, $CHCl_3$). The sign of observed rotation is opposite to that of (*S*)-**1.68** reported in literature,[10] allowing assignment of the absolute configuration of **1.68** as *R* via our synthesis. The absolute configuration of alkyne **1.41** is thus assigned as *S*. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.29 (m, 4H), 7.22 – 7.20 (m, 1H), 7.12 (t, *J* = 7.8 Hz, 1H), 7.06 (d, *J* = 7.5 Hz, 1H), 6.87 – 6.84 (m, 2H), 4.01 – 3.99 (m, 1H), 2.95– 2.76 (m, 4H), 2.13 – 2.07 (m, 1H), 2.02 – 2.00 (m, 1H), 1.95 – 1.89 (m, 1H), 1.83 – 1.76 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.0, 141.9, 129.5, 128.6, 128.4, 127.2, 125.8, 122.1, 120.0, 116.8, 74.8, 37.1, 31.5, 27.5, 24.8; HRMS (EI+) $[M]^+$ calculated for $C_{17}H_{18}O$: 238.1357, found: 238.1353.

Synthesis of racemic 1-alkynyl chromenes

Synthesis of 6-methyl-2-(oct-1-yn-1-yl)-2H-chromene **1.37**

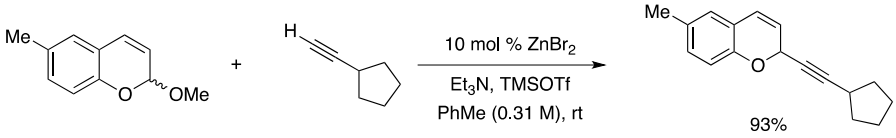


1.29 **1-octyne** **1.37**

In a N_2-atmosphere glovebox, $ZnBr_2$ (6.4 mg, 0.028 mmol, 10 mol %) was weighed into a 1-dram vial. 1-Octyne (34.4 mg, 0.312 mmol, 1.1 equiv) and toluene (916 μL, 0.31 M) were added. Then, triethyl amine (50.0 μL, 0.355 mmol, 1.25 equiv) and chromene acetal **1.29** (50.0 mg, 0.284 mmol, 1.0 equiv) were added. The vial was sealed and removed from the glovebox. After 10 min, TMSOTf (56.9 μL, 0.312 mmol, 1.1 equiv) was added via syringe, and the reaction mixture was stirred for 12 h at rt. The reaction mixture was quenched MeOH (1.0 ml), diluted with Et_2O (5.0 mL), and filtered through a short plug of silica gel, which was then washed with Et_2O (5.0 mL). The filtrate was concentrated and purified by silica gel chromatography (1-2 % Et_2O/hexanes, R_f = 0.40) to give **1.37** (46.9 mg, 65%;) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (dd, *J* = 8.12, 1.8 Hz, 1H), 6.85 – 6.84 (m, 1H), 6.79 (d, *J* = 8.1 Hz, 1H), 6.43 (dd, *J* = 9.6, 1.1 Hz, 1H), 5.76 (dd, *J* = 9.6, 3.8 Hz, 1H), 5.54 – 5.52 (m, 1H), 2.28 (s, 3H), 2.23 – 2.19 (m, 2H), 1.51 – 1.46 (m, 2H) 1.38 – 1.23 (m, 6H), 0.89 (t, *J* = 6.9, 3H); ^{13}C NMR (101 MHz, $(CD_3)_2CO$) δ 150.3, 130.6, 129.5, 127.08, 123.7, 123.3, 121.6, 115.9, 85.9, 77.7, 64.3,

31.1, 28.2, 28.1, 22.3, 19.6, 18.1, 13.4; FTIR (NaCl, thin film) 3077, 2990, 2812, 2338, 2311, 2281, 1900, 1719, 1623, 1547, 1271, 1088 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{18}H_{22}O$: 254.1671, found: 254.1686.

Synthesis of 2-(cyclopentylethynyl)-6-methyl-2*H*-chromene (**1.38**)

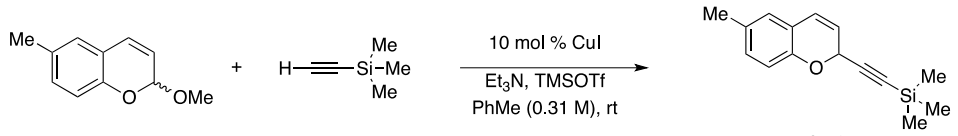


1.29 **cyclopentylacetylene** **1.38**

In a N_2-atmosphere glovebox, $ZnBr_2$ (3.2 mg, 0.014 mmol, 10 mol %) was weighed into a 1-dram vial. Cyclopentylacetylene (18.5 μL, 0.142 mmol, 90% assay, 1.0 equiv) and toluene (460 μL, 0.31 M) were added. Then, triethyl amine (24.8 μL, 0.177 mmol, 1.25 equiv) and chromene acetal **1.29** (25.0 mg, 0.142 mmol, 1.0 equiv) were added. The vial was sealed and removed from the glovebox. After 10 min, TMSOTf (28.5 μL, 0.156 mmol, 1.1 equiv) was added via syringe, and the reaction mixture was stirred for 12 h at rt. The reaction mixture was quenched MeOH (1.0 ml), diluted with Et_2O (5.0 mL), and filtered through a short plug of silica gel, which was then washed with Et_2O (5.0 mL). The filtrate was concentrated and purified by silica gel chromatography (1-2 % Et_2O/hexanes, R_f = 0.40) to give **1.38** (31.4 mg, 93%;) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 6.96 (dd, *J* = 8.12, 1.8 Hz, 1H), 6.84–6.83 (m, 1H), 6.79 (d, *J* = 8.1 Hz, 1H), 6.42 (dd, *J* = 9.6, 1.5 Hz, 1H), 5.74 (dd, *J* = 9.6, 3.7 Hz, 1H), 5.56 – 5.54 (m, 1H),

2.68 – 2.60 (m, 1H), 2.27 (s, 3H), 1.95 – 1.88 (m, 2H), 1.75– 1.66 (m, 2H) 1.65 – 1.47 (m, 4H); ^{13}C NMR (101 MHz, $(CD_3)_2CO$) δ 150.4, 130.5, 129.5, 127.09, 123.7, 123.4, 121.5, 115.9, 90.01, 77.2, 64.4, 33.42, 33.41, 24.5, 19.6; FTIR (NaCl, thin film) 3077, 2958, 2868, 2311, 2222, 1652, 1558, 1489, 1209, 1125, 1024 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{17}H_{18}O$: 238.1358, found: 238.1381.

Synthesis of trimethyl((6-methyl-2*H*-chromen-2-yl)ethynyl)silane (**1.39**)

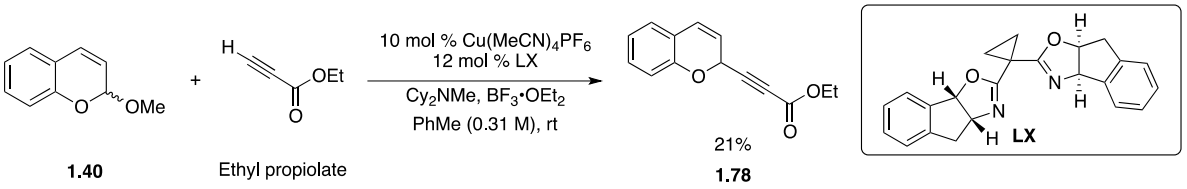


1.29 **Trimethylsilyl acetylene** **1.39**

In a N_2-atmosphere glovebox, CuI (5.4 mg, 0.028 mmol, 10 mol %) was weighed into a 1-dram vial. Trimethylsilylacetylene (40.0 μL, 0.283 mmol, 1.0 equiv) and toluene (912 μL, 0.31 M) were added. Then, triethyl amine (50.0 μL, 0.354 mmol, 1.25 equiv) and chromene acetal **1.29** (50.0 mg, 0.283 mmol, 1.0 equiv) were added. The vial was sealed and removed from the glovebox. After 10 min, TMSOTf (56.8 μL, 0.312 mmol, 1.1 equiv) was added via syringe, and the reaction mixture was stirred for 12 h at rt. The reaction mixture was quenched MeOH (1.0 ml), diluted with Et_2O (5.0 mL), and filtered through a short plug of silica gel, which was then washed with Et_2O (5.0 mL). The filtrate was concentrated and purified by silica gel chromatography (1 % Et_2O/hexanes, R_f = 0.5) to give **1.39** (58.5 mg, 85%;) as a white solid (M.P 72–75 °C). ^{1}H NMR (400 MHz,

$CDCl_3$) δ 6.96 (dd, *J* = 8.12, 1.9 Hz, 1H), 6.84 – 6.83 (m, 2H), 6.79 (d, *J* = 8.1 Hz, 1H), 5.74 (dd, *J* = 9.6, 1.6 Hz, 1H), 5.57–5.55 (m, 1H), 2.28 (s, 3H), 0.18 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 131.02, 129.9, 127.2, 124.7, 122.2, 121.1, 116.1, 102.1, 90.8, 65.1, 20.5, 0.21; FTIR (NaCl, thin film) 2966, 2896, 2167, 1684, 1652, 1489, 1250, 1206, 1026 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{15}H_{18}OSi$: 242.1127, found: 242.1148.

Synthesis of ethyl 3-(2*H*-chromen-2-yl)propiolate **1.78**



In a N_2-atmosphere glovebox, $Cu(ACN)_4PF_6$ (11.5 mg, 0.030 mmol, 10 mol %) and ligand **LX** (13.2 mg, 0.036 mmol, 12 mol %) was weighed into a 1-dram vial. Ethyl propiolate (62.4 μL, 0.616 mmol, 2.0 equiv) and toluene (993 μL, 0.31 M) were added. Then, dicyclohexylmethyl amine (79.1 μL, 0.369 mmol, 1.2 equiv) and chromene acetal **1.40** (50.0 mg, 0.308 mmol, 1.0 equiv) were added. The vial was sealed and removed from the glovebox. After 10 min, $BF_3{\cdot}OEt_2$ (76.0 μL, 0.616 mmol, 2.0 equiv) was added via syringe, and the reaction mixture was stirred for 12 h at rt. The reaction mixture was quenched MeOH (1.0 ml), diluted with Et_2O (5.0 mL), and filtered through a short plug of silica gel, which was then washed with Et_2O (5.0 mL). The filtrate was concentrated and purified by silica gel chromatography (3–4% Et_2O/hexanes, R_f = 0.4) to give **1.78** (14.7 mg, 21%;) as a colorless oil. ^1H NMR (400 MHz, $(CD_3)_2CO$) δ 7.25–7.21 (m, 1H),

7.18–7.16 (m, 1H), 7.01 –6.97 (m, 1H), 6.89 (d, *J* = 8.1 Hz, 1H), 6.70 (d, *J* = 9.4 Hz, 1H), 5.97–5.93 (m, 1H), 5.89–5.91 (m, 1H), 4.18 (q, *J* = 7.14 Hz, 3H), 1.24 ((t, *J* = 7.14 Hz, 2H); ^{13}C NMR (101 MHz, $(CD_3)_2CO$) δ 152.4, 151.8, 129.8, 127.1, 125.3, 122.3, 121.3, 120.3, 116.3, 83.1, 76.4, 63.4, 61.9, 13.2; FTIR (NaCl, thin film) 3077, 2986, 2232, 1713, 1606, 1456, 1404, 1388, 1366, 1247, 1224 cm^{-1}; HRMS (EI+) [M+] calculated for $C_{14}H_{12}O_3$: 228.0786, found: 228.0803.

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Chapter 2

NICKEL-CATALYZED CROSS-COUPLINGS OF BENZYL PIVALATES WITH ARYLBOROXINES

2.1 Introduction

Diarylalkanes and triarylmethanes are important scaffolds in pharmaceuticals and other biologically active molecules.[1-5] A strategic disconnection to form these molecules would be between the benzylic stereocenter and an aryl substituent, as shown with dotted lines in Figure 2.1. An enantiospecific or enantioselective cross coupling of a benzylic electrophile and an aryl nucleophile would enable preparation of these scaffolds in high enantiopurity. Although such cross couplings have been accomplished, before our work, the majority of these methods relied on air-sensitive and functional group-intolerant aryl nucleophiles.[6-12] As described herein, we have now developed an enantiospecific, nickel-catalyzed cross-coupling of benzylic pivalates with arylboroxines, which are air-stable and functional group tolerant. [13]

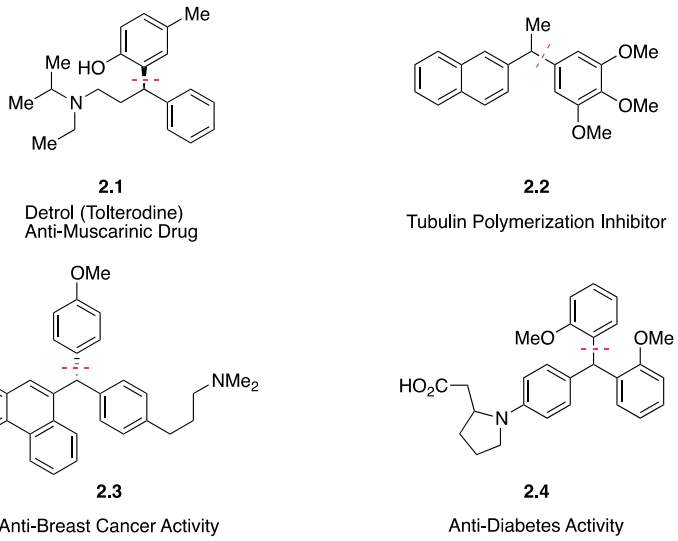


Figure 2.1: Bioactive Diarylethane and Triarylmethane Molecules

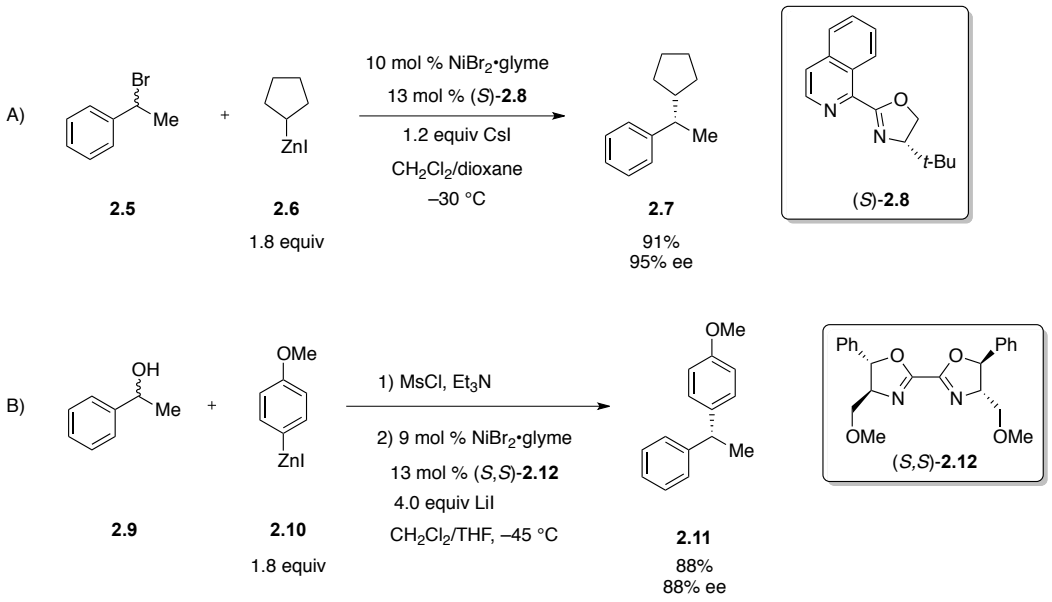
Prior-Art

Historically, cross-coupling reactions have generally relied on Pd-based catalysis in concert with aryl halide or pseudohalide electrophiles. Initial work by Wenkert[14] and other recent methods[15] have shown that stronger C–O bonds of aryl and vinyl ethers, carboxylates and carbamates can be activated by nickel catalysts. In the context of alkyl electrophiles, nickel catalysis has largely focused on the development of stereoconvergent, enantioselective cross couplings of alkyl halides, which undergo oxidative addition via single-electron transfer mechanisms.[6,7,16,17,18] Recently, however, enantiospecific cross couplings of alcohol-derived alkyl electrophiles have been realized, showing that nickel catalysts can also undergo oxidative addition to alkyl electrophiles via two-electron elementary steps.[8,11,12] The details of both enantioselective and enantiospecific nickel-catalyzed cross couplings of benzylic electrophiles are described in detail below.

With respect to enantioselective cross couplings, the Fu group has done pioneering work in stereoselective cross-couplings of secondary alkyl electrophiles. They have shown the enantioselective Negishi cross-coupling of racemic benzyl bromides with zincates using a nickel(II) catalyst equipped with a isoquinoline oxazoline chiral ligand (Scheme 2.1 A).[6,7] Recently, the Fu group has also shown the enantioselective nickel-catalyzed cross-coupling of benzyl alchohols and zincates through an insitu formed

mesylate. Control studies have shown that the oxidative addition takes place through benzyl iodide intermediate formed via a Finkelstein reaction of the mesylate with LiI (Scheme 2.1 B).[18]

Scheme 2.1: Stereoselective Cross-Couplings of Secondary Alkyl Bromides and Alcohols

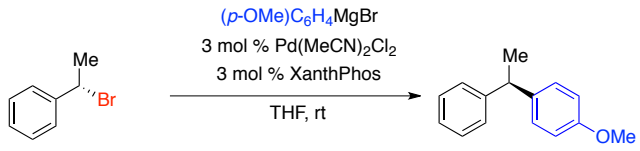


Over the past few years, stereospecific cross-couplings have been known to form diarylethanes. Carretero and Adrio[9] have demonstrated enantiospecific cross-coupling of secondary benzylic bromides with aryl Grignard reagents to form diarylethanes with high chirality transfer (Scheme 2.2A). The Jarvo group has shown the nickel-catalyzed enantiospecific cross-coupling of Grignard reagents with benzyl alcohol derivatives in high levels of chirality transfer and yields (Scheme 2.2B).[8,11,12] The Tian group has reported the formation of diarylethanes from copper-catalyzed cross-coupling of enantioenriched benzylic sulfonimides with Grignard reagents with modest levels of

stereochemical fidelity (Scheme 2.2C).[10] In contrast to the above methods, Crudden and coworkers have used secondary benzylic boronates as a chiral nucleophilic coupling partner to cross couple with aryl bromides to form diarylethanes with high chirality transfer (Scheme 2.2D).[19] Recently in our lab, we have shown the enantiospecific nickel-catalyzed cross-coupling of benzylic ammonium triflates and arylboronic acid to form diarylethanes with high levels of chirality transfer and yields (Scheme 2.2E).[20] I realize the importance and utility of alcohol derivatives in addition to amines. Despite the above advances, these starting materials are not easy to obtain in higher enantioselectivity except the benzylic ethers, and benzyl amine derivatives, which are obtained from readily available benzyl alcohol and amines. The limitation with the Jarvo's method is the use of air-sensitive Grignard reagents as cross-coupling partners which restricts the use of base-sensitive functional groups like ester, nitriles due to the nucleophilic nature of the Grignard reagents (Scheme 2.2B).[8,11,12]

Scheme 2.2: Stereospecific Cross-Couplings to Form Enantioenriched Diarylethanes

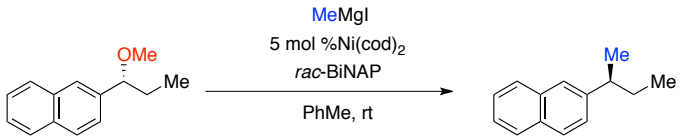
A) Benzylic Bromides (Carretero & Adrio)



2.5
85–86% ee

2.11
86%
98% ee

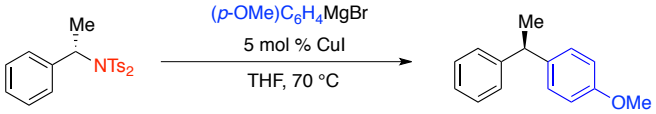
B) Benzylic Ethers (Jarvo)



2.13
96% ee

2.14
72%
94% ee

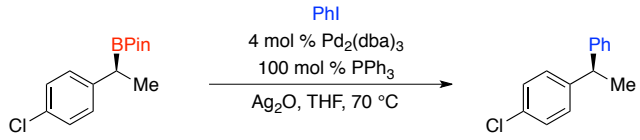
C) Benzylic Sulfonimides (Tian)



2.15
99% ee
single example

2.11
71%
44% ee

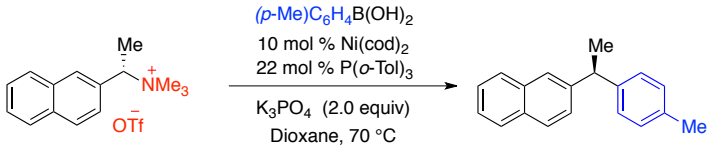
D) Benzylic Boronates (Crudden)



2.16
64% ee

2.17
84%
54% ee

E) Benzylic Ammonium Triflates (Watson)

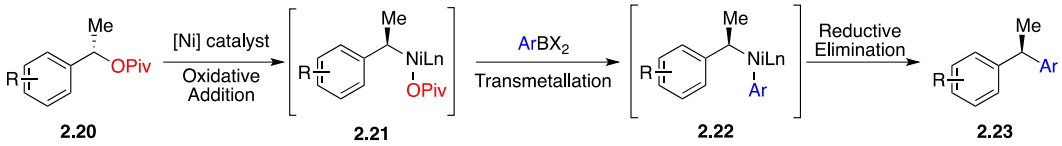


2.18
99% ee

2.19
72%

The use of mild organoboranes as cross-coupling partners would greatly advance the state-of-the-art in cross-coupling of benzylic electrophiles by improving the functional group tolerance and convenience of reaction set up. Very few reactions of stereospecific cross-couplings of organoboranes to form these type of products are known.[19-23] Towards this goal, in collaboration with fellow colleague Qi Zhou, I have developed an enantiospecific cross-coupling of benzylic pivalates with arylboroxines (Scheme 2.3).[13]

Scheme 2.3: Enantiospecific Cross-Couplings of Benzylic Pivalates and Arylboroxines



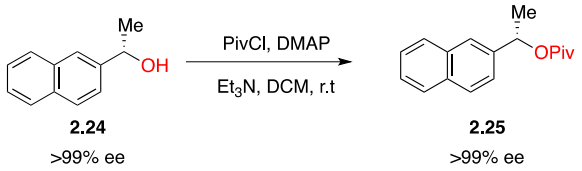
2.2 Results and Discussion

Earlier work in our laboratory had shown the Heck reaction of styrenes with aryl pivalates using nickel(0) catalyst.[24] Having the precedence of nickel(0) catalyzed C–O bond activation of aryl pivalates, we envisoned that a nickel(0)-catalyzed cross-coupling of benzyl pivalates and arylboranes would be a powerful and practical alternative to the use of harsh organometallic coupling partners. In particular, we envisioned that benzylic nickel intermediate **2.21** would undergo more facile transmetallation with a more mild transmetallating agent due to the greater cationic character of nickel and weaker

coordinating ability of the pivalate counterion, as compared to an alkoxide counterion present in Jarvo's couplings (Scheme 2.2B).

Synthesis of (*S*)-1-(Naphthalen-2-yl)Ethyl Pivalate, **2.25**

Scheme 2.4: Synthesis of Benzyl Pivalates



2.24
>99% ee

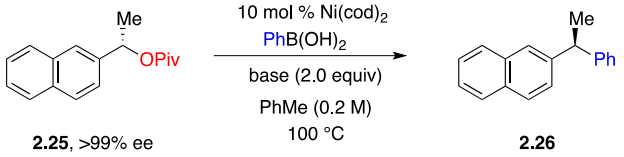
2.25
>99% ee

Benzyl pivalates were easily prepared from readily available enantioenriched benzylic alcohols using catalytic DMAP, pivaloyl chloride, and triethylamine in excellent yields in high enantioselectivity (Scheme 2.4).

Optimization

The cross-coupling of pivalate **2.25** and phenylboronic acid was chosen as the model reaction for optimization. Initial screens were performed at 100 °C using $Ni(cod)_2/PCy_3$ (Table 2.1). Although CsF and K_3PO_4 resulted in low yields, NaOMe gave decent yield (entries 1-3). When PCy_2Ph was used as a ligand, we obtained diarylethane **2.26** in 93% yield but only 54% ee with retention in stereochemistry (entry 4). Gratifyingly, in the absence of phosphine ligand, we observed 99% yield and 93% ee with inversion of stereochemistry (entry 5). Furthermore, by increasing the phenylboronic acid equivalents, we observed excellent enantioselectivity and yield (entry 6).

Table 2.1: Initial Screening[a]



2.25, >99% ee

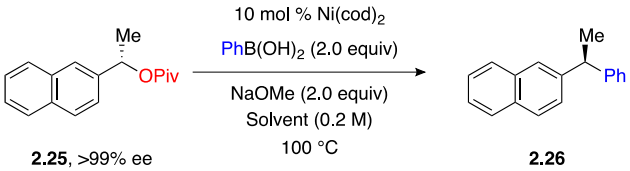
2.26

entry	ligand (mol %)	equiv of $PhB(OH)_2$	base	yield (%)[b]	ee (%)[c]
1	PCy_3 (24)	3.0	CsF	14	n.d.[d]
2	PCy_3 (24)	3.0	K_3PO_4	14	n.d.[d]
3	PCy_3 (24)	3.0	NaOMe	78	n.d.[d]
4	PCy_2Ph (22)	2.0	NaOMe	93	54 (*R*)
5	(0)	2.0	NaOMe	99	93 (*S*)
6	(0)	3.0	NaOMe	83	99 (*S*)

[a] Conditions: pivalate **2.25** (0.1 mmol, 1.0 equiv), $Ni(cod)_2$, $PhB(OH)_2$, base (0.2 mmol, 2.0 equiv) and PhMe (0.2M), unless otherwise noted. [b]Determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as internal standard. [c] Determined by HPLC using a chiral stationary phase. The absolute configuration of the major enantiomer is shown in the parentheses. [d] n.d. = not determined.

When we examined different solvents (Table 2.2), we observed that the ee of the reaction depends upon the polarity of the solvent used. Lower levels stereochemical fidelity were observed in more polar solvents. Although the reason for this is not entirely understood, it is consistent with the possible ionization of the benzylic pivalate **2.25** to form a benzylic cation in more polar solvents. Another possibility is that there is a higher concentration of base in more polar solvents, which may also lead to epimerization (see below)

Table 2.2: Solvent Screen[a]



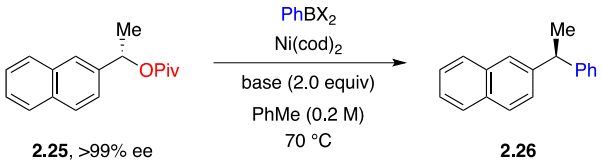
2.25, >99% ee

2.26

entry	solvent	yield (%)[b]	ee (%)[c]
1	benzene	89	94
2	PhMe	87	94
3	THF/PhMe (1:1)	56	16
4	DME	24	10
5	dioxane	63	7

[a] Conditions: pivalate **2.25** (0.1 mmol, 1.0 equiv), $Ni(cod)_2$, $PhB(OH)_2$, NaOMe (0.2 mmol, 2.0 equiv) and PhMe (0.2M), unless otherwise noted. [b] Determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as internal standard. [c] Determined by HPLC using a chiral stationary phase.

Table 2.3: Optimization



2.25, >99% ee

2.26

entry	$Ni(cod)_2$	$PhBX_2$ (equiv)	base	Temp (°C)	yield (%)[b]	ee (%)[c]
1	10	$PhB(OH)_2$ (3.0 equiv)	KOMe	70	74	69
2	10	$PhB(OH)_2$ (3.0 equiv)	LiOMe	70	0	n.d
3	5	$PhB(OH)_2$ (3.0 equiv)	NaOMe	70	87	98
4[d]	5	$(PhBO)_3$ (0.83 equiv)	NaOMe	70	98	97
5[d,e]	5	$(PhBO)_3$ (0.83 equiv)	NaOMe	70	59	94
6	0	$PhB(OH)_2$ (2.5 equiv)	NaOMe	70	0	n.d
7	0	$(PhBO)_3$ (0.83 equiv)	NaOMe	70	0	n.d

[a]Conditions: pivalate **2.25** (0.1 mmol, 1.0 equiv), $Ni(cod)_2$, $PhB(OH)_2$, base (0.2 mmol, 2.0 equiv) and PhMe (0.2M), unless otherwise noted. [b]Determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as internal standard. [c]Determined by HPLC using chiral stationary phase. [d]0.4 M. [e]Added 1.0 equiv of water.

Having obtained higher levels of stereochemical fidelity using sodium methoxide as a base, we wanted to examine the role of base by screening other methoxides (Table 2.3). Using potassium methoxide, we obtained only 69% ee, and with lithium methoxide we did not see any reaction (entries 1&2). We thus hypothesize that the solubility of the base is critical for the reaction. Potassium methoxide is more soluble in toluene, so greater concentration of base may lead to the observed ee. In contrast, lithium methoxide

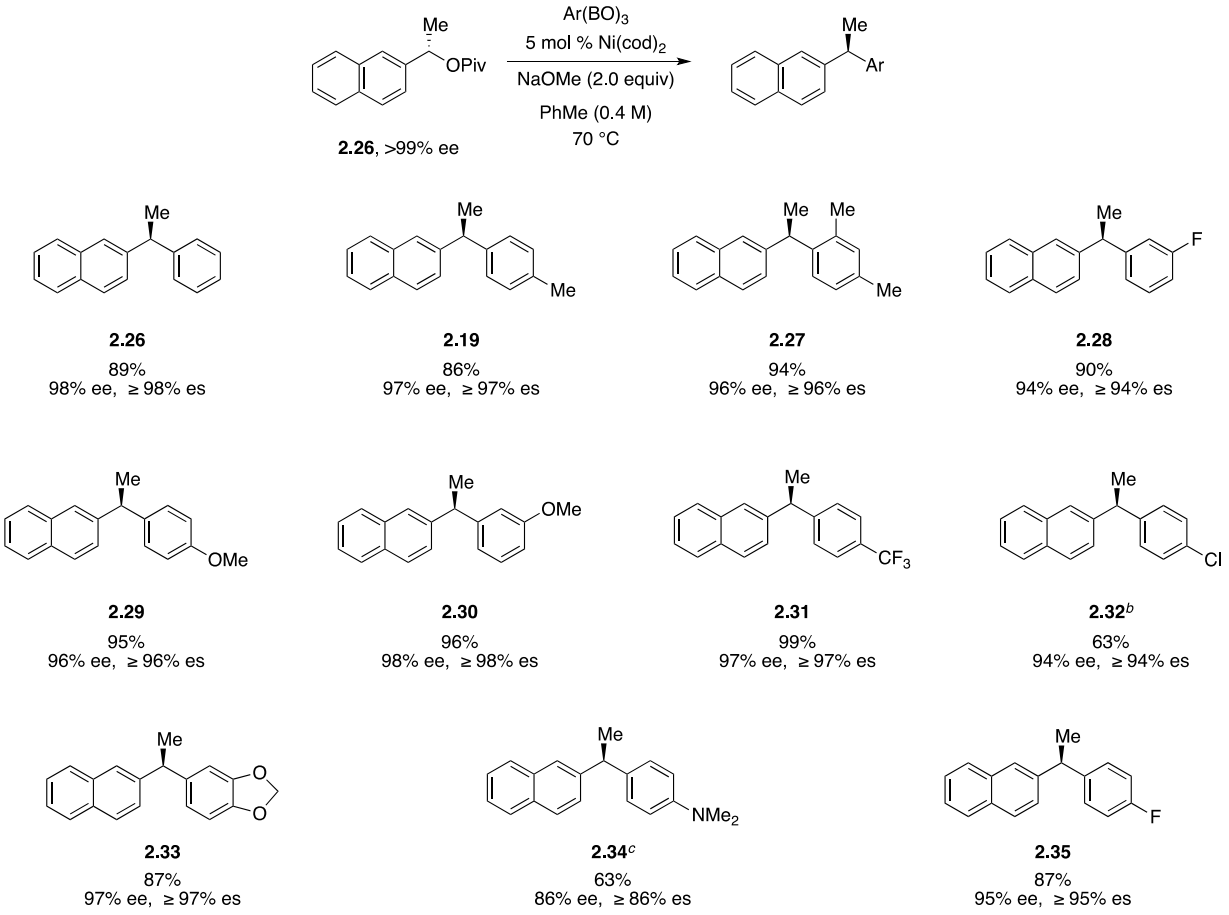
may not be soluble enough in toluene for the reaction to happen. This is also consistent with solvent screen where we observe lower ee's in polar solvents (Table 2.2). Also, there was no significant change in ee, when we used phenylboroxine as a cross-coupling partner instead of phenylboronic acid (entry 4). When we examined other arylboronic acids, arylboroxines gave more consistent results and higher yields than arylboronic acids, probably due to the presence of water in some commercially available boronic acids. We confirmed that water has a detrimental effect. When we added one equivalent of water to the reaction, we observed diminished yield and chirality transfer (entry 5). Our optimized conditions include 5 mol % of $Ni(cod)_2$ at 70 ° C in PhMe as solvent, using arylboroxines in the presence of sodium methoxide (entry 4). When we ran the control experiments in the absence of $Ni(cod)_2$, we did not see any cross-coupling product **2.26**, demonstrating that nickel is required for the reaction.

Scope in Arylboroxine

Under our optimized conditions, we observed broad scope with respect to the arylboroxine (Scheme 2.5). With electron-rich and electron-deficient arylboroxines, we obtained diarylethanes with high levels of stereochemical fidelity and in high yields. This method shows wide functional group tolerance, where fluoride (**2.28** and **2.35)**, chloride (**2.32)**, trifluromethyl (compound **2.31)**, ether (compound **2.29** & **2.30)**, acetal (**2.33)** and amine (**2.34)** functional groups are well tolerated. In particular, the formation of chloride compound **2.32** in 63% yield and 94% ee highlights the mildness and orthogonality of

this method. Notably, aryl chloride functional groups are not tolerated in the coupling of benzylic ammonium triflates and arylboronic acids. Increased steric bulk on the arylboroxine is well tolerated, which is shown by formation of compound **2.27** in 94% yield and 96% ee.

Scheme 2.5: Scope in Arylboroxines



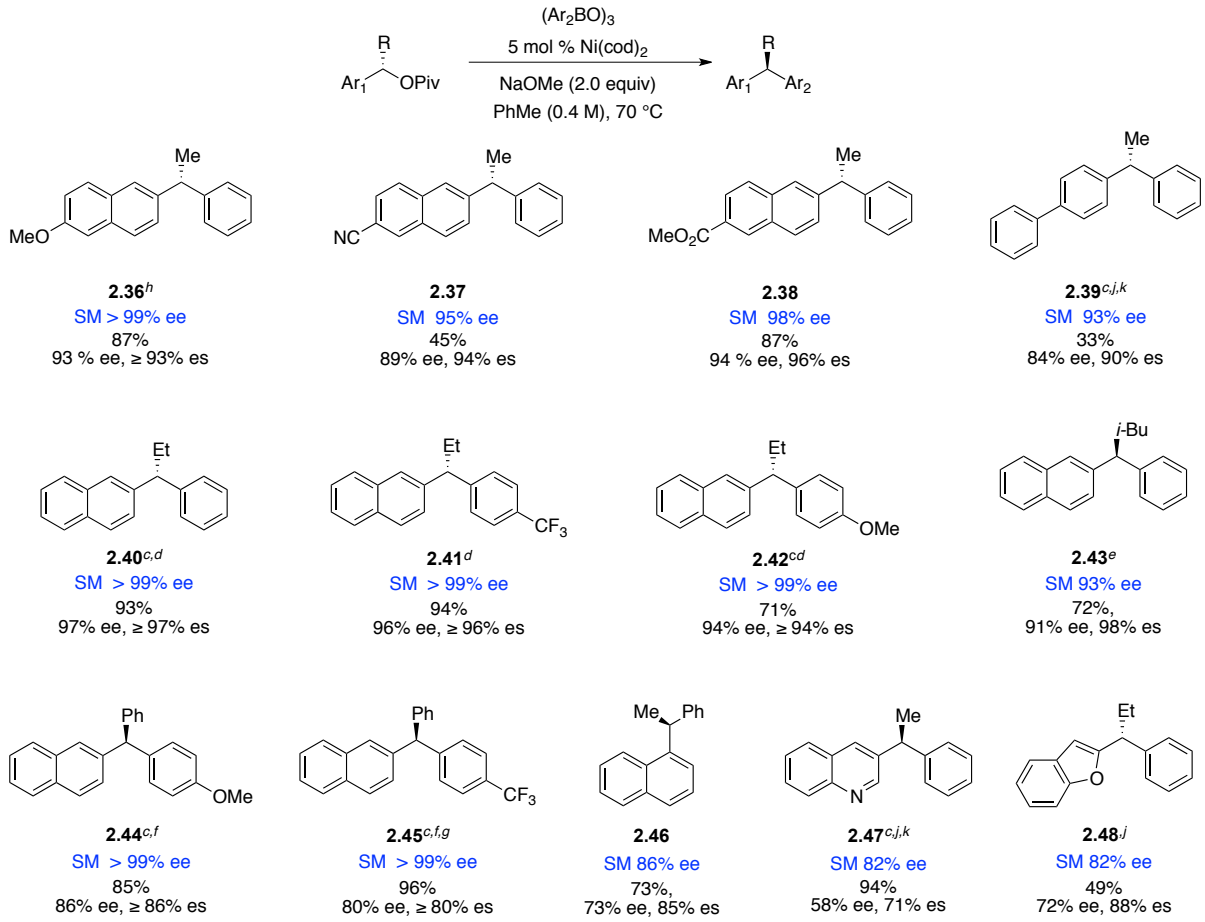
[a]Conditions: pivalate **2.26** (0.20 mmol, 1.0 equiv), arylboroxine (1.66 mmol, 0.83 equiv), $Ni(cod)_2$ (5 mol %, 0.01 mmol, 0.05 equiv) and NaOMe (0.4 mmol, 2.0 equiv) in PhMe (0.4 M) at 70 ° C for 3h, unless otherwise noted. Yields are average of duplicate experiments (± 0-2%) and ee's are average of duplicate experiments (± 0-1%) determined by HPLC on a chiral stationary phase. % es = enantiospecificity= [(ee of product/ (ee of starting material)] × 100%. [b]at 40 ºC for 24 h. [c]10 mol% $Ni(cod)_2$ at 90 ºC for 12 h.

Scope in Pivalate

By varying the pivalate coupling partner, a variety of diaryl and triarylalkane products were obtained with high levels of stereochemical fidelity and in high yields yields (Scheme 2.6). The compound **2.36** was obtained in 87% yield and 93% ee from electron-rich pivalate. Notably, we have obtained diarylethanes **2.37** and **2.38** with high enantiospecificity with base-sensitive nitrile and ester functional groups, which demonstrates the increased functional group tolerance enabled by use of an arylboroxine coupling partner. When biphenyl-substituted pivalate was used for cross-coupling with arylboroxine, we obtained compound **2.39** in 90% es and 33% yield. The decreased yield might be due to absence of an extended *pi*-system, which appears important in oxidative addition of nickel(0) to the pivalate.[8] Increased steric bulk on the alkyl substituent was well tolerated in this method as shown by compounds **2.40–2.43.** In particular, compound **2.43** with isobutyl substituent was formed in 72% yield and 98% es.

Triarylmethane compounds **2.44** and **2.45** were also formed in good yields and enantiospecificities, when diaryl-substituted pivalates were used as cross-coupling partners. Further, diarylethane **2.46** with a 1-napthyl substituent was obtained 73% yield and 85% es. Steric hindrance due to ortho-substitution on the aromatic ring might be reason for the slightly lowered enantiospecificity. Heteroaromatic compounds **2.47** and **2.48** were also obtained with decent yields and levels of chiral transfer.

Scheme 2.6: Scope in Pivalate



2.36[h]
SM > 99% ee
87%
93 % ee, ≥ 93% es

2.37
SM 95% ee
45%
89% ee, 94% es

2.38
SM 98% ee
87%
94 % ee, 96% es

2.39[c,j,k]
SM 93% ee
33%
84% ee, 90% es

2.40[c,d]
SM > 99% ee
93%
97% ee, ≥ 97% es

2.41[d]
SM > 99% ee
94%
96% ee, ≥ 96% es

2.42[cd]
SM > 99% ee
71%
94% ee, ≥ 94% es

2.43[e]
SM 93% ee
72%,
91% ee, 98% es

2.44[c,f]
SM > 99% ee
85%
86% ee, ≥ 86% es

2.45[c,f,g]
SM > 99% ee
96%
80% ee, ≥ 80% es

2.46
SM 86% ee
73%,
73% ee, 85% es

2.47[c,j,k]
SM 82% ee
94%
58% ee, 71% es

2.48[j]
SM 82% ee
49%
72% ee, 88% es

[a]Conditions: pivalate (0.20 mmol, 1.0 equiv), arylboroxine (1.66–2.6 mmol, 0.83–1.3 equiv), $Ni(cod)_2$ (5 mol %, 0.01 mmol, 0.05 equiv) and NaOMe (0.4 mmol, 2.0 equiv) in PhMe (0.4 M) at 70 ° C for 3h, unless otherwise noted. Yields are average of duplicate experiments (± 0-2%) and ee's are average of duplicate experiments (± 0-1%) determined by HPLC on a chiral stationary phase. [b] % es = enantiospecificity= [(ee of product/ (ee of starting material)] × 100%. [c] 10 mol% $Ni(cod)_2$. [d] 80 ° C. [e] 12 h. [f] 90 ° C. [g] Results of a single experiment. [h] 50 ° C. [i] 32 ° C. [j] 24 h. [k] 100 ° C.

Determination of Absolute Configuration

By comparing the absolute configuration of product **2.19** to that of authentic sample prepared in our laboratory,[20] we confirmed that our enantiospecific cross-coupling of benzylic pivalates with arylboroxines occurs with inversion at the benzylic stereocenter.

The absolute configuration of other diarylethanes and triarylmethanes was assigned analogously.

Proposed Mechanism and Related Experiments

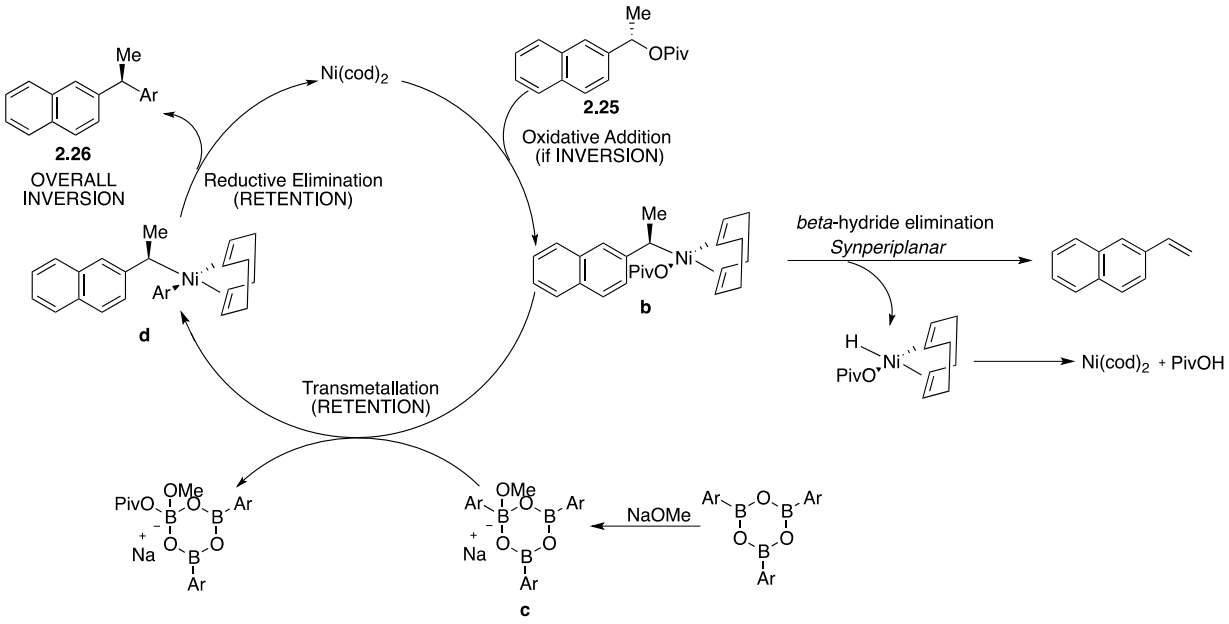
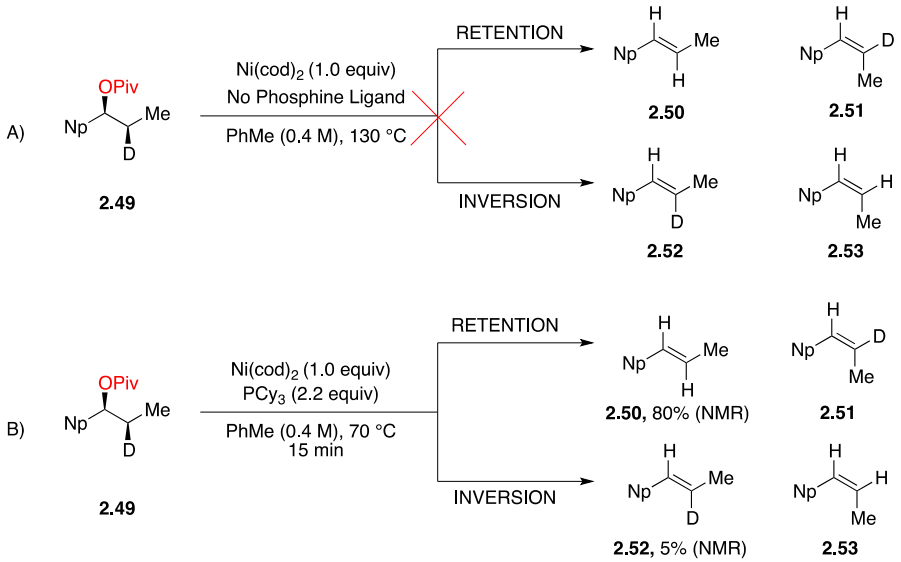


Figure 2.2: Proposed Catalytic Cycle

A plausible mechanism of the reaction is given in Figure 2.2. The first step involves the oxidative addition of nickel(0) to the benzylic pivalate **2.25** with inversion of configuration to form intermediate **b**, which undergoes transmetallation with activated arylboroxine to form intermediate **d.** Intermediate **d** undergoes reductive elimination to furnish final product **2.26** with overall inversion of stereochemistry.

With this mechanism in mind, we wanted to probe the stereochemical outcome of the oxidative addition step. My colleague Qi Zhou conducted a series of β-hydride elimination experiments using deuterated pivalate **2.49**.[25] We expected to see olefin **2.50** and /or **2.51**, if oxidative addition occurs with retention of configuration. If it proceeds with inversion of configuration, we would see formation of olefin **2.52** and/or **2.53** **(**Scheme 2.7**)**.

Scheme 2.7: β-Hydride Elimination Study

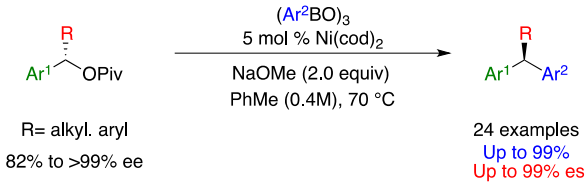


However, when pivalate **2.49** was subjected to stoichiometric $Ni(cod)_2$, we did not observe any reaction, even at an elevated temperature of 130 °C **(**Scheme 2.7A**)**. However, when reaction was conducted in presence of a phosphine-supported nickel(0) catalyst at 70 °C **(**Scheme 2.7B**)**, we observed 80% yield of olefin **2.50** and 5% yield of olefin **2.52**. Because pivalate **2.49** also undergoes slight epimerization under these conditions, we believe that minor product **2.52** arises from β-hydride elimination of

epimerized starting material. These results suggest that the oxidative addition occurs with retention in configuration at the benzylic stereocenter, when a phosphine-supported nickel catalyst is used. The formation of olefin **2.50** by the cleavage of carbon-deuterium bond, may be due to steric clash between the napthyl and methyl groups in the transition state favoring the formation of olefin **2.50** over **2.51.** These results also suggest that the transmetallation and reductive elimination occur with retention of configuration,[26] when $Ni(cod)_2$ without a of phosphine ligand is used. Because, we observe overall inversion at the benzylic stereocenter these results suggest that the oxidative addition with this Ni catalyst likely occurs with inversion.

2.3 Conclusions

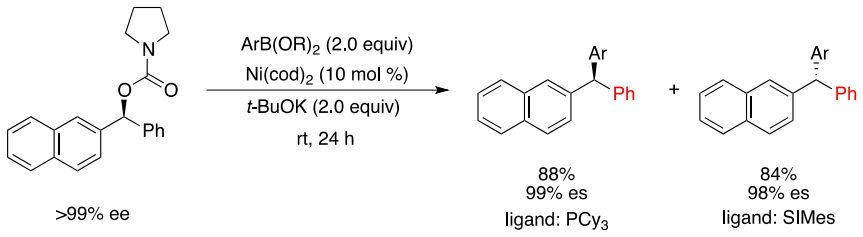
Scheme 2.8: Enantiospecific Nickel-Catalyzed Cross-Coupling of Benzylic Pivalates with Arylboroxines



In summary, we have developed an enantiospecific, nickel-catalyzed cross-coupling of benzylic pivalates with arylboroxines (Scheme 2.8). The diarylalkane and triarylmethane products were obtained in high yields and with high levels of chiral transfer. In this method, broad substrate scope is achieved, and a wide variety of functional groups are well tolerated. The success of this method relies on use of $Ni(cod)_2$ as a metal catalyst and NaOMe as a base. This report was published in *Journal of the*

American Chemical Society.[13] A related cross-coupling method for coupling benzyl carbamates and arylboronates using phosphine or NHC-supported Ni(0) catalysts was published from the Jarvo laboratory at the same time (Scheme 2.9).[27]

Scheme 2.9: Jarvo's Enantiospecific Nickel-Catalyzed Cross-Coupling of Benzylic Carbamates and Arylboronates



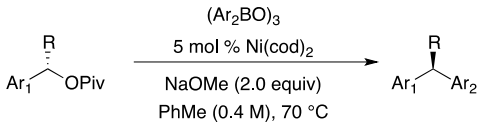
2.4 Experimental Information

Reactions were performed either in a N_2-atmosphere glovebox in oven-dried 1-dram vials with Teflon-lined caps or in oven-dried round-bottomed flasks unless otherwise noted. Flasks were fitted with rubber septa, and reactions were conducted under a positive pressure of N_2. Stainless steel syringes or cannulae were used to transfer air- and moisture-sensitive liquids. Flash chromatography was performed on silica gel 60 (40-63 μm, 60Å). Thin layer chromatography (TLC) was performed on glass plates coated with silica gel 60 with F254 indicator. Commercial reagents were purchased from Sigma Aldrich, Acros, Fisher, Strem, TCI, Combi Blocks, Alfa Aesar, or Cambridge Isotopes Laboratories and used as received with the following exceptions: toluene, CH_2Cl_2, dioxane, and Et_2O were dried by passing through drying columns. Toluene was then degassed by sparging with N_2 and stored over activated 4Å MS in a N_2-atmosphere glovebox. Anhydrous K_3PO_4 was purchased from Acros and used as received. Pivaloyl chloride was purchased from Sigma Aldrich, and used as received. Boronic acids were purchased from Combi Blocks and were converted to the boroxines according to literature procedure.[28] $CDCl_3$ was stored over oven-dried potassium carbonate. Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on both 400 MHz and 600 MHz spectrometers. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$ = δ

7.28). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$ =δ 77.07). Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, dd = doublet of doublets, h = heptet), coupling constants in Hertz (Hz), integration. Infrared (IR) spectra were obtained using FTIR spectrophotometers with material loaded onto a NaCl plate. The mass spectral data were obtained at the University of Illinois, Urbana–Champagne, mass spectrometry facility and the University of Delaware mass spectrometry facility. Optical rotations were measured using a 2.5 mL cell with a 1 dm path length. Melting points were taken on a Stuart SMP10 instrument.

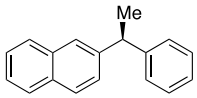
Stereospecific Cross Couplings of Benzyl Pivalates to Give Diarylalkanes and Triarylmethanes

General Procedure

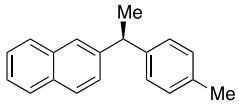


In a N_2-atmosphere glovebox, $Ni(cod)_2$ (2.8 mg, 0.01 mmol, 5 mol %) and NaOMe (21.6 mg, 0.4 mmol, 2.0 equiv) were weighed into a 1-dram vial. Benzylic pivalate (0.2 mmol, 1.0 equiv) and boroxine (0.167 mmol, 0.83 equiv) were added, followed by toluene (0.5 mL, 0.4 M). The vial was capped with a Teflon-lined cap and removed from the glovebox. The mixture was heated for 3 h at 70 °C. The reaction mixture was then diluted

with Et_2O (1.5 mL) and filtered through a plug of silica gel, which was rinsed with Et_2O (10 mL). The filtrate was concentrated and purified by silica gel chromatography to give the diaryl- or triarylmethane product.



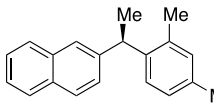
(*S*)-2-(1-phenylethyl)naphthalene (2.26). Diarylethane **2.26** was prepared via the General Procedure using pivalate **2.25** (prepared in >99% ee). The crude material was purified by silica gel chromatography (2–3% Et_2O/hexanes) to give compound **2.26** (run 1: 41.8 mg, 90%; run 2: 40.4 mg, 87%) as a colorless oil. The enantiomeric excess was determined to be 98% ee (run 1: 98% ee; run 2: 98% ee) by chiral HPLC analysis (CHIRACEL OD-H, 0.8 mL/min, 100% hexane, λ=220 nm); t_R(major)=21.40 min, t_R(minor)=27.35 min. $[\alpha]_D^{24}$ = +21.0° (c 1.00, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.80 (m, 2H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.75 – 7.72 (m, 1H), 7.55 – 7.41 (m, 2H), 7.37 – 7.27 (m, 5H), 7.26 – 7.19 (m, 1H), 4.36 (q, *J* = 7.2 Hz, 1H), 1.78 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.2, 143.8, 133.5, 132.1, 128.4, 127.9, 127.8, 127.7, 127.6, 126.9, 126.1, 125.9, 125.4, 125.3, 44.9, 21.8. The spectral data for this compound matches that reported in the literature.[9]



(*S*)-2-(1-(*p*-tolyl)ethyl)naphthalene (2.19). Diarylethane **2.19** was prepared via the General Procedure using pivalate **2.25** (prepared in >99% ee). The crude material was purified by silica gel chromatography (2% Et_2O/hexanes) to give compound **2.19** (run 1: 43.1 mg, 87%; run 2: 41.4 mg, 84%) as a colorless oil. The

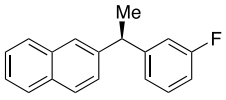
enantiomeric excess was determined to be 97% ee (run 1: 97% ee; run 2: 97% ee) by chiral HPLC analysis (CHIRACEL OD-H, 0.8 mL/min, 100% hexane, λ=220 nm); t_R(major)=20.43 min, t_R(minor)=23.63 min. $[\alpha]_D^{24}$ = +51.2° (c 0.80, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.80 (m, 2H), 7.78 (d, 1H), 7.76 – 7.72 (m, 1H), 7.52 – 7.43 (m, 2H), 7.34 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.22 – 7.11 (m, 4H), 4.32 (q, *J* = 7.2 Hz, 1H), 2.35 (s, 3H), 1.76 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 143.3, 135.6, 133.5, 132.1, 129.1, 127.9, 127.7, 127.6, 127.6, 126.9, 125.9, 125.3, 125.3, 44.5, 21.9, 21.0. The spectral data for this compound matches that reported in the literature.[29]

The absolute configuration of this compound was assigned as *S* by comparison of the HPLC of this compound to an authentic sample previously prepared in our group via a different method.[20]



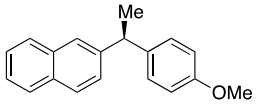
(*R*)-2-(1-(2,4-dimethylphenyl)ethyl)naphthalene (2.27). Diarylethane **2.27** was prepared via the General Procedure using pivalate **2.25** (prepared in >99% ee). The crude material was purified by silica gel chromatography (3% Et_2O/hexanes) to give compound **2.27** (run 1: 49.1 mg, 93%; run 2: 49.3 mg, 96%) as a colorless oil. The enantiomeric excess was determined to be 96% ee (run 1: 96% ee; run 2: 96% ee) by chiral HPLC analysis (CHIRACEL OD-H, 0.8 mL/min, 100% hexane, λ=220 nm); t_R(major)=17.61 min, t_R(minor)=14.35 min. $[\alpha]_D^{24}$ = +11.0° (c 1.00, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.79 (m, 2H), 7.76 (d,

J = 8.5 Hz, 1H), 7.68 – 7.64 (m, 1H), 7.51 – 7.41 (m, 2H), 7.31 (dd, J = 8.5, 1.8 Hz, 1H), 7.22 (d, J = 7.8 Hz, 1H), 7.10 – 7.04 (m, 1H), 7.02 (s, 1H), 4.49 (q, J = 7.2 Hz, 1H), 2.35 (s, 3H), 2.29 (s, 3H), 1.72 (d, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 140.9, 136.0, 135.6, 133.5, 131.9, 131.3, 127.9, 127.7, 127.6, 126.9, 126.9, 126.7, 125.9, 125.4, 125.3, 40.8, 22.0, 20.9, 19.8; FTIR (NaCl/thin film) 3052, 3015, 2965, 2922, 1600, 1500, 1451, 1373, 1043, 855 cm^{-1}; HRMS (EI+) $[M]^+$calculated for $C_{20}H_{20}$: 260.1565, found: 260.1573.

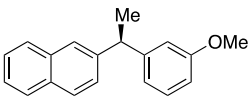


(*R*)-2-(1-(3-fluorophenyl)ethyl)naphthalene 2.28. Diarylethane (**2.28)** was prepared via the General Procedure using pivalate **2.25** (prepared in >99% ee). The crude material was purified by silica gel chromatography (3% Et_2O/hexanes) to give compound **2.28** (run 1: 44.3 mg, 88%; run 2: 45.5 mg, 91%) as a colorless oil. The enantiomeric excess was determined to be 94% ee (run 1: 94% ee; run 2: 94% ee) by chiral HPLC analysis (CHIRACEL OD-H, 0.8 mL/min, 100% hexane, λ=220 nm); t_R(major)=24.61 min, t_R(minor)=35.64 min. $[\alpha]_D^{24}$ = +22.5° (c 1.20, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.81 (m, 2H), 7.79 (d, J = 8.5 Hz, 1H), 7.75 – 7.71 (m, 1H), 7.54 – 7.45 (m, 2H), 7.36 – 7.30 (m, 1H), 7.29 – 7.24 (m, 1H), 7.10 – 7.05 (m, 1H), 7.02 – 6.97 (m, 1H), 6.95 – 6.89 (m, 1H), 4.34 (q, J = 7.2 Hz, 1H), 1.76 (d, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0 (d, J_{C-F} = 246.4 Hz), 148.9 (d, J_{C-F} = 6.1 Hz), 143.0, 133.5, 132.2, 129.8 (d, J_{C-F} = 8.1 Hz), 128.1, 127.8, 127.6, 126.6, 126.1, 125.6, 125.4,

123.5 (d, J_{C-F} = 3.0 Hz), 114.6 (d, J_{C-F} = 22.2 Hz), 113.0 (d, J_{C-F} = 21.2 Hz), 44.6, 21.6; FTIR (NaCl/thin film) 3055, 2967, 2928, 2873, 1726, 1613, 1559, 1487, 912, 818 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{18}H_{15}F$: 250.1158, found: 250.1164.

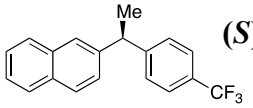


(*S*)-2-(1-(4-methoxyphenyl)ethyl)naphthalene (2.29). Diarylethane **2.29** was prepared via the General Procedure using pivalate **2.25** (prepared in >99% ee). The crude material was purified by silica gel chromatography (3% Et_2O/hexanes) to give compound **2.29** (run 1: 49.3 mg, 94%; run 2: 50.1 mg, 95%) as a colorless oil. The enantiomeric excess was determined to be 96% ee (run 1: 96% ee; run 2: 96% ee) by chiral HPLC analysis (CHIRAlPAK 1A, 1.0 mL/min, 0.2% *i*-PrOH/hexane, λ=254 nm); t_R(major)=8.64 min, t_R(minor)=8.09 min. $[\alpha]_D^{24}$ = –14.0° (c 1.00, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.81 (m, 2H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.73 (s, 1H), 7.54 – 7.43 (m, 2H), 7.34 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.25 – 7.17 (m, 2H), 6.94 – 6.81 (m, 2H), 4.31 (q, *J* = 7.2 Hz, 1H), 3.82 (s, 3H), 1.75 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 144.2, 138.4, 133.5, 132.1, 128.7, 127.9, 127.7, 127.6, 126.8, 125.9, 125.3, 125.2, 113.8, 55.3, 44.0, 22.0. The spectral data for this compound matches that reported in the literature.[30]



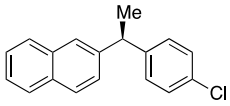
(*R*)-2-(1-(3-methoxyphenyl)ethyl)naphthalene (2.30). Diarylethane **2.25** was prepared via the General Procedure using pivalate **2.30** (prepared in >99% ee). The crude material was purified by silica gel chromatography (2% Et_2O/hexanes) to give

compound **2.30** (run 1: 49.5 mg, 94%; run 2: 51.2 mg, 97%) as a white solid (mp 88–91 °C). The enantiomeric excess was determined to be 98% ee (run 1: 97% ee; run 2: 98% ee) by chiral HPLC analysis (CHIRAlPAK 1A, 1.0 mL/min, 0.2% *i*-PrOH/hexane, λ=254 nm); t_R(major)=7.54 min, t_R(minor)=8.69 min. $[\alpha]_D^{24}$ = –23.3° (c 1.20, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.80 (m, 2H), 7.77 (d, *J* = 8.5 Hz, 1H), 7.74 – 7.72 (m, 1H), 7.52 – 7.42 (m, 2H), 7.35 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.24 (t, *J* = 7.9 Hz, 1H), 6.89 – 6.87 (m, 1H), 6.85 (t, *J* = 2.1 Hz, 1H), 6.77 (dd, 1H), 4.32 (q, *J* = 7.2 Hz, 1H), 3.79 (s, 3H), 1.76 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 147.9, 143.6, 133.5, 132.1, 129.4, 128.0, 127.8, 127.6, 126.8, 126.0, 125.4, 125.3, 120.3, 113.9, 111.0, 55.2, 44.9, 21.7; FTIR (NaCl/thin film) 3052, 2963, 2926, 1598, 1485, 1150, 1039, 818 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{19}H_{18}O$: 262.1358, found: 262.1366.



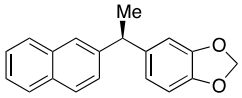
(*S*)-2-(1-(4-(trifluoromethyl)phenyl)ethyl)naphthalene (2.31). Diarylethane **2.31** was prepared via the General Procedure using pivalate **2.25** (prepared in >99% ee). The crude material was purified by silica gel chromatography (3% Et_2O/hexanes) to give compound **2.31** (run 1: 59.4 mg, 99%; run 2: 60.0 mg, 100%) as a colorless oil. The enantiomeric excess was determined to be 97% ee (run 1: 96% ee; run 2: 97% ee) by chiral HPLC analysis (CHIRACEL OD-H, 0.8 mL/min, 100% hexane, λ=220 nm); t_R(major)=28.30 min, t_R(minor)=39.14 min. $[\alpha]_D^{24}$ = +36.4° (c 1.60, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.82 (m, 2H), 7.80 (d, *J* = 8.5 Hz, 1H), 7.75 – 7.72

(m, 1H), 7.58 (d, J = 8.1 Hz, 2H), 7.54 – 7.46 (m, 2H), 7.42 – 7.38 (m, 2H), 7.31 (dd, J = 8.6, 1.8 Hz, 1H), 4.41 (q, J = 7.2 Hz, 1H), 1.79 (d, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.3 (q, $J_{C–F}$ = 1.1 Hz), 142.6, 133.5, 132.2, 128.4 (q, $J_{C–F}$ = 32.3 Hz), 128.3 (q, $J_{C–F}$ = 1.0 Hz), 128.1, 127.8, 127.6, 126.6, 126.2, 125.7, 125.5, 125.4 (q, $J_{C–F}$ = 4.0 Hz), 124.8 (q, $J_{C–F}$ = 272.7 Hz), 44.7, 21.6; FTIR (NaCl/thin film) 3056, 2970, 2932, 2876, 1919, 1618, 1600, 1416, 1326, 1164, 1118, 1071, 1017, 842 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{19}H_{15}F_3$: 300.1126, found: 300.1129.

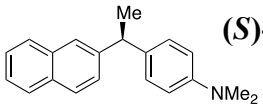


(*S*)-2-(1-(4-chlorophenyl)ethyl)naphthalene (2.32). Diarylethane **2.32** was prepared via the General Procedure using pivalate **2.25** (prepared in >99% ee) except that the reaction was done at 40 °C for 24 h. The crude material was purified by silica gel chromatography (100% petroleum ether) to give compound **2.32** (run 1: 34.5 mg, 65%; run 2: 32.5 mg, 61%) as a colorless oil. The enantiomeric excess was determined to be 94% ee (run 1: 94% ee; run 2: 94% ee) by chiral HPLC analysis (CHIRACEL OD-H, 0.8 mL/min, 100% hexane, λ=220 nm); t_R(major)=25.82 min, t_R(minor)=34.31 min. $[\alpha]_D^{24}$ = –27.7° (c 1.00, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.4 Hz, 2H), 7.77 (d, J = 8.5 Hz, 1H), 7.69 (s, 1H), 7.51 – 7.44 (m, 2H), 7.31 – 7.26 (m, 3H), 7.23 – 7.18 (m, 2H), 4.31 (q, J = 7.2 Hz, 1H), 1.74 (d, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 143.2, 133.5, 132.2, 131.8, 129.2, 128.5, 128.1, 127.7, 127.6, 126.7, 126.1, 125.6,

125.4, 44.3, 21.8; FTIR (NaCl/thin film) 3054, 2966, 2925, 2851, 1600, 1491, 1375, 1092, 1014, 856 cm^{-1}; HRMS (EI+) $[M]^+$calculated for $C_{18}H_{15}Cl$: 266.0862, found: 266.0855.

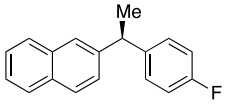


(*R*)-5-(1-(naphthalen-2-yl)ethyl)benzo[*d*][1,3]dioxole (2.33). Diarylethane **2.33** was prepared via the General Procedure using pivalate **2.25** (prepared in >99% ee). The crude material was purified by silica gel chromatography (2% Et_2O/hexanes) to give compound **2.33** (run 1: 48.2 mg, 88%; run 2: 47.1 mg, 85%) as a colorless oil. The enantiomeric excess was determined to be 97% ee (run 1: 97% ee; run 2: 96% ee) by chiral HPLC analysis (CHIRAlPAK 1B, 1.0 mL/min, 0.3% *i*-PrOH/hexane, λ=254 nm); t_R(major)=9.30 min, t_R(minor)=10.14 min. $[\alpha]_D^{24}$ = –10.8° (c 1.20, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.77 (m, 2H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.71 – 7.66 (m, 1H), 7.52 – 7.39 (m, 2H), 7.30 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.78 – 7.66 (m, 3H), 5.91 (s, 2H), 4.24 (q, *J* = 7.2 Hz, 1H), 1.70 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 145.8, 143.8, 140.3, 133.5, 132.1, 127.9, 127.7, 127.6, 126.7, 125.9, 125.4, 125.2, 120.5, 108.4, 108.1, 100.9, 44.6, 21.9; FTIR (NaCl/thin film) 3065, 2964, 2919, 1726, 1603, 1507, 1484, 1435, 1370, 1231, 1036, 940, 861 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{19}H_{16}O_2$: 276.1150, found: 276.1154.



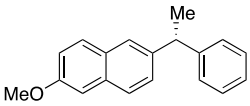
(*S*)-*N*,*N*-dimethyl-4-(1-(naphthalen-2-yl)ethyl)aniline (2.34). Diarylethane **2.34** was prepared via the General Procedure using pivalate **2.25** (prepared in >99% ee), except that 10 mol% $Ni(cod)_2$ was used and the

reaction mixture was heated at 90 °C for 12 h. The crude material was purified by silica gel chromatography (5–6% Et_2O/hexanes) to give compound **2.34** (run 1: 35.2 mg, 64%; run 2: 34.1 mg, 62%) as a colorless oil. The enantiomeric excess was determined to be 86% ee (run 1: 86% ee; run 2: 86% ee) by chiral HPLC analysis (CHIRAlPAK 1A, 1.0 mL/min, 0.3% *i*-PrOH/hexane, λ=254 nm); t_R(major)=10.87 min, t_R(minor)=9.35 min. $[\alpha]_D^{24}$ = –62.5° (c 0.60, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.76 (m, 2H), 7.73 (d, *J* = 8.5 Hz, 1H), 7.69 (d, *J* = 1.9 Hz, 1H), 7.48 – 7.38 (m, 2H), 7.32 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.16 – 7.11 (m, 2H), 6.73 – 6.67 (m, 2H), 4.24 (q, *J* = 7.2 Hz, 1H), 2.91 (s, 6H), 1.70 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.1, 144.7, 134.4, 133.5, 132.1, 128.3, 127.8, 127.7, 127.5, 126.9, 125.8, 125.2, 125.1, 112.8, 43.9, 40.8, 21.9; FTIR (NaCl/thin film) 3051, 2962, 2925, 2852, 2799, 1614, 1520, 1479, 1445, 1348, 1163, 1126, 948, 855, 816 cm^{-1}; HRMS (ESI) $[M]^+$ calculated for $C_{20}H_{22}N$: 276.1752, found: 276.1751.



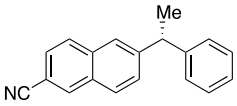
(*S*)-2-(1-(4-fluorophenyl)ethyl)naphthalene (2.35). Diarylethane **2.35** was prepared via the General Procedure using pivalate **2.25** (prepared in >99% ee). The crude material was purified by silica gel chromatography (2–2.5% Et_2O/hexanes) to give compound **2.35** (run 1: 44.2 mg, 88%; run 2: 42.8 mg, 85%) as a white solid (mp 57–61 °C). The enantiomeric excess was determined to be 96% ee (run 1: 97% ee; run 2: 95% ee) by chiral HPLC analysis (CHIRACEL OD-H, 0.8 mL/min, 100% hexane, λ=220 nm);

t_R(major)=26.20 min, t_R(minor)=34.62 min. $[\alpha]_D^{24}$ = –31.0° (c 1.60, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.81 (m, 2H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.72 – 7.68 (m, 1H), 7.53 – 7.44 (m, 2H), 7.31 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.27 – 7.22 (m, 2H), 7.05 – 6.97 (m, 2H), 4.33 (q, *J* = 7.2 Hz, 1H), 1.75 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3 (d, $J_{C–F}$ = 245.4 Hz), 143.6, 141.9 (d, $J_{C–F}$ = 3.0 Hz), 133.5, 132.1, 129.1 (d, $J_{C–F}$ = 8.1 Hz), 128.1, 127.7, 127.6, 126.7, 126.1, 125.5, 125.3, 115.1 (d, $J_{C–F}$ = 21.2 Hz), 44.1, 22.0. The spectral data for this compound matches that reported in the literature.[20]

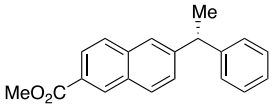


(*R*)-2-methoxy-6-(1-phenylethyl)naphthalene (2.36). Diarylethane **2.36** was prepared via the General Procedure using pivalate **2.54** (prepared in >99% ee) except that 1.0 equiv of boroxine was used and the reaction mixture was heated at 50 °C. The crude material was purified by silica gel chromatography (1–2% Et_2O/hexanes) to give compound **2.36** (run 1: 45.6 mg, 87%; run 2: 45.5 mg, 87%) as a white solid (mp 97–101 °C). The enantiomeric excess was determined to be 93% ee (run 1: 93% ee; run 2: 93% ee) by chiral HPLC analysis (CHIRALPAK 1B, 0.6 mL/min, 1.0% *i*-PrOH/hexane, λ=254 nm); t_R(major)=11.29 min, t_R(minor)=9.83 min. $[\alpha]_D^{24}$ = –28.2° (c 1.00, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.9 Hz, 1H), 7.69 (s, 1H), 7.68 – 7.66 (m, 1H), 7.36 – 7.28 (m, 5H), 7.26 – 7.20 (m, 1H), 7.17 (dd, *J* = 8.8, 2.6 Hz, 1H), 7.15 – 7.12 (m, 1H), 4.32 (q, *J* = 7.2 Hz, 1H), 3.94 (s, 3H), 1.76 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 146.5, 141.5, 133.1, 129.2, 128.9, 128.4, 127.8, 127.4,

126.9, 126.1, 125.2, 118.7, 105.6, 55.3, 44.7, 21.9; FTIR (NaCl/thin film) 3026, 2965, 2935, 2871, 1605, 1489, 1451, 1266, 1166, 1034, 851 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{19}H_{18}O$: 262.1358, found: 262.1353.

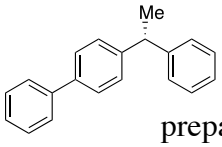


(*R*)-6-(1-phenylethyl)-2-naphthonitrile (2.37). Diarylethane **2.37** was prepared via the General Procedure using pivalate **2.55** (prepared in 95% ee). The crude material was purified by silica gel chromatography (5–10% EtOAc/hexanes) to give compound **2.37** (run 1: 23.6 mg, 46%; run 2: 22.1 mg, 43%) as viscous colorless oil. The enantiomeric excess was determined to be 90% ee (run 1: 90% ee; run 2: 89% ee) by chiral HPLC analysis (CHIRALPAK 1A, 1.0 mL/min, 0.5% *i*-PrOH/hexane, λ=254 nm); t_R(minor)=34.2 min, t_R(major)=37.2 min. $[\alpha]_D^{24}$ = –75.0° (c 0.40, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.86 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.73 (s, 1H), 7.58 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.44 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.25 – 7.20 (m, 3H), 4.34 (q, *J* = 7.2 Hz, 1H), 1.74 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.6, 145.3, 134.9, 133.8, 131.0, 129.0, 128.7, 128.6, 128.5, 127.7, 126.6, 126.5, 125.5, 119.4, 108.8, 45.0, 21.6; FTIR (NaCl/thin film) 3025, 2967, 2929, 2226, 1629, 1600, 1493, 1451, 1377, 1158, 894 cm^{-1}; HRMS (CI+) $[M+H]^+$ calculated for $C_{16}H_{18}O_3$: 258.1283, found: 258.1277.



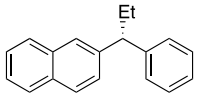
(*R*)-methyl 6-(1-phenylethyl)-2-naphthoate (2.38). Diarylethane **2.38** was prepared via the General Procedure using pivalate **2.56** (prepared

in 98% ee). The crude material was purified by silica gel chromatography (5–6% Et_2O/hexanes) to give compound **2.38** (run 1: 49.2 mg, 85%; run 2: 47.4 mg, 82%) as viscous colorless oil. The enantiomeric excess was determined to be 94% ee (run 1: 93% ee; run 2: 94% ee) by chiral HPLC analysis (CHIRALPAK 1B, 1.0 mL/min, 2.0% *i*-PrOH/hexane, λ=254 nm); t_R(minor)=6.75 min, t_R(major)=7.40 min. $[\alpha]_D^{24}$ = –31.8° (c 1.92, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.04 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.84 (dd, *J* = 8.5, 5.4 Hz, 2H), 7.73 (s, 1H), 7.38 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.33 – 7.24 (m, 4H), 7.23 – 7.18 (m, 1H), 4.33 (q, *J* = 7.2 Hz, 1H), 3.97 (s, 3H), 1.74 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.4, 146.6, 145.7, 135.7, 131.1, 130.8, 129.4, 128.5, 128.0, 127.8, 127.7, 126.9, 126.3, 125.4, 125.2, 52.2, 45.0, 21.7; FTIR (NaCl/thin film) 2966, 2929, 1719, 1632, 1494, 1437, 1289, 1237, 1201, 1097, 912 cm^{-1}; HRMS (CI+) $[M+H]^+$ calculated for $C_{15}H_{19}N_2O_4$: 291.1385, found: 291.1387.



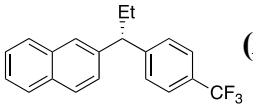
(*S*)-4-(1-phenylethyl)biphenyl (2.39). Diarylethane **2.39** was prepared via the General Procedure using pivalate **2.57** (prepared in 93% ee) except that 10 mol % $Ni(cod)_2$ and 1.0 equiv of boroxine were used and the reaction mixture was heated at 100 °C for 24 h. The crude material was purified by silica gel chromatography (100% petroleum ether) to give compound **2.39** (run 1: 17.0 mg, 33%; run 2: 17.2 mg, 33%) as a white solid (mp 37–41 °C). The enantiomeric excess was determined to be 84% ee (run 1: 84% ee; run 2: 84% ee) by chiral HPLC analysis

(CHIRALPAK 1B, 1.0 mL/min, 100% hexane, λ=254 nm); t_R(minor)=15.34 min, t_R(major)=24.22 min. $[\alpha]_D^{24}$ = –51.6° (c 0.60, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 – 7.57 (m, 2H), 7.57 – 7.52 (m, 2H), 7.47 – 7.43 (m, 2H), 7.38 – 7.29 (m, 7H), 7.25 – 7.12 (m, 1H), 4.23 (q, *J* = 7.3 Hz, 1H), 1.71 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.3, 145.5, 141.0, 139.0, 128.7, 128.4, 128.0, 127.6, 127.11, 127.05, 127.0, 126.1, 44.5, 21.9. The spectral data for this compound matches that reported in the literature.[9]

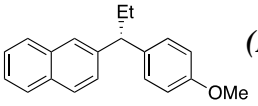


(*R*)-2-(1-phenylpropyl)naphthalene (2.40). Diarylpropane **2.40** was prepared via the General Procedure using pivalate **2.58** (prepared in >99% ee) except that 1.2 equiv of boroxine was used and the reaction mixture was heated at 80 °C. The crude material was purified by silica gel chromatography (3% Et_2O/hexanes) to give compound **2.40** (run 1: 44.6 mg, 91%; run 2: 47.2 mg, 94%) as a colorless oil. The enantiomeric excess was determined to be 97% ee (run 1: 96% ee; run 2: 98% ee) by chiral HPLC analysis (CHIRACEL OD-H, 1.0 mL/min, 100% hexanes, λ=220 nm); t_R(major)=19.18 min, t_R(minor)=14.40 min. $[\alpha]_D^{24}$ = –32.5° (c 0.80, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.72 (m, 4H), 7.54 – 7.41 (m, 3H), 7.37 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.35 – 7.29 (m, 3H), 7.26 – 7.16 (m, 1H), 4.00 (t, *J* = 7.7 Hz, 1H), 2.28 – 2.15 (m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 142.6, 133.5, 132.1, 128.4, 128.1, 128.0, 127.7, 127.6, 126.9, 126.1, 125.9, 125.9, 125.3, 53.3, 28.4, 12.9; FTIR (NaCl/thin

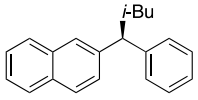
film) 3056, 3025, 2962, 2928, 2872, 1727, 1599, 1506, 1493, 1377, 1155, 855 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{19}H_{18}$: 246.1409, found: 246.1414.



(*R*)-2-(1-(4-(trifluoromethyl)phenyl)propyl)naphthalene (2.41). Diarylpropane **2.41** was prepared via the General Procedure using pivalate **2.58** (prepared in >99% ee) except that 1.2 equiv of boroxine was used and the reaction mixture was heated at 80 °C. The crude material was purified by silica gel chromatography (3% Et_2O/hexanes) to give compound **2.41** (run 1: 58.4 mg, 93%; run 2: 59.2 mg, 94%) as a colorless oil. The enantiomeric excess was determined to be 96% ee (run 1: 96% ee; run 2: 96% ee) by chiral HPLC analysis (CHIRACEL OD-H, 0.8 mL/min, 100% hexanes, λ=220 nm); t_R(major)=31.94 min, t_R(minor)=19.93 min. $[\alpha]_D^{24}$ = –78.3° (c 0.60, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.81 (m, 2H), 7.80 (d, *J* = 8.5 Hz, 1H), 7.76 – 7.73 (m, 1H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.54 – 7.45 (m, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.34 (dd, *J* = 8.5, 1.8 Hz, 1H), 4.06 (t, *J* = 7.7 Hz, 1H), 2.35 – 2.11 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.1 (q, $J_{C–F}$ = 1.1 Hz), 141.5, 133.5, 133.2, 128.4 (q, $J_{C–F}$ = 32.3 Hz), 128.4 (q, $J_{C–F}$ = 1.0 Hz), 128.3, 127.8, 127.6, 126.7, 125.2, 125.1, 125.6, 125.4 (q, $J_{C–F}$ = 4.0 Hz), 124.3 (q, $J_{C–F}$ = 272.7 Hz), 53.1, 28.2, 12.7; FTIR (NaCl/thin film) 3056, 2965, 2932, 2875, 1921, 1766, 1618, 1417, 1326, 1164, 1120, 1068, 1018, 815 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{20}H_{17}F_3$: 314.1282, found: 314.1287.

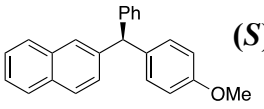


***(R)*-2-(1-(4-methoxyphenyl)propyl)naphthalene (2.42).** Diarylpropane **2.42** was prepared via the General Procedure using pivalate **2.58** (prepared in >99% ee) except that 10 mol % $Ni(cod)_2$ and 1.2 equiv of boroxine were used, and the reaction mixture was heated at 80 °C. The crude material was purified by silica gel chromatography (2.5% Et_2O/hexanes) to give compound **2.42** (run 1: 38.1 mg, 69%; run 2: 40.2 mg, 73%) as a colorless oil. The enantiomeric excess was determined to be 94% ee (run 1: 94% ee; run 2: 94% ee) by chiral HPLC analysis (CHIRACEL OD-H, 0.8 mL/min, 0.1% *i*-PrOH/hexane, λ=254 nm); t_R(major)=14.00 min, t_R(minor)=13.23 min. $[\alpha]_D^{24}$ = –19.0° (c 1.00, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.69 (m, 4H), 7.55 – 7.39 (m, 2H), 7.34 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.26 – 7.18 (m, 2H), 6.91 – 6.79 (m, 2H), 3.93 (t, *J* = 7.7 Hz, 1H), 3.79 (s, 3H), 2.30 – 2.05 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 142.9, 137.2, 133.5, 132.1, 128.9, 127.9, 127.7, 127.6, 126.8, 125.9, 125.8, 125.3, 113.7, 55.2, 52.4, 28.5, 12.9; FTIR (NaCl/thin film) 3050, 2959, 2929, 2872, 2834, 1726, 1609, 1510, 1462, 1249, 1178, 1038, 815 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{20}H_{20}O$: 276.1514, found: 276.1505.



(*S*)-2-(3-methyl-1-phenylbutyl)naphthalene (2.43). Diarylmethane **2.43** was prepared via the General Procedure using pivalate **2.59** (prepared in 93% ee) except that 1.3 equiv of boroxine was used and the reaction time was 12 h. The crude material was purified by silica gel chromatography (1–2% Et_2O/hexanes) to give

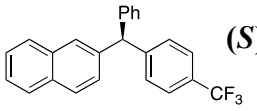
compound **2.43** (run 1: 40.2 mg, 73%; run 2: 39.0 mg, 71%) as a colorless oil. The enantiomeric excess was determined to be 91% ee (run 1: 90% ee; run 2: 91% ee) by chiral HPLC analysis (CHIRACEL OD-H, 0.8 mL/min, 100% hexanes, λ=220 nm); t_R(major)=15.47 min, t_R(minor)=25.37 min. $[\alpha]_D^{24}$ = –32.8° (c 0.60, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 12.7, 8.0 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 1H), 7.64 – 7.62 (m, 1H), 7.39 – 7.31 (m, 2H), 7.28 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.24 – 7.17 (m, 4H), 7.11 – 7.07 (m, 1H), 4.11 (t, *J* = 8.0 Hz, 1H), 2.02 – 1.88 (m, 2H), 1.46 – 1.37 (m, 1H), 0.87 (d, *J* = 2.4 Hz, 3H), 0.87 (d, *J* = 2.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.1, 142.7, 133.5, 132.1, 128.4, 128.01, 128.0, 127.6, 127.5, 126.8, 126.07, 125.8, 125.8, 125.3, 48.9, 44.7, 25.5, 22.7, 22.6; FTIR (NaCl/thin film) 3056, 2965, 2932, 2875, 1921, 1766, 1618, 1417, 1326, 1164, 1120, 1068, 1018, 815 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{21}H_{22}$: 274.1722, found: 274.1717.



(*S*)-2-((4-methoxyphenyl)(phenyl)methyl)naphthalene (2.44)

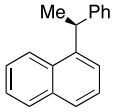
Triarylmethane **2.44** was prepared via the General Procedure using pivalate **2.60** (prepared in >99% ee) except that 10 mol % of $Ni(cod)_2$ and 1.0 equiv of boroxine were used and the reaction mixture was heated at 90 °C. The crude material was purified by silica gel chromatography (5% Et_2O/hexanes) to give compound **2.44** (run 1: 55.2 mg, 85%; run 2: 54.3 mg, 84%) as a colorless oil. The enantiomeric excess was determined to be 86% ee (run 1: 86% ee; run 2: 86% ee) by chiral HPLC analysis (CHIRACEL OD-H,

0.8 mL/min, 0.1% *i*-PrOH/hexane, λ=254 nm); t_R(major)=24.00 min, t_R(minor)=22.03 min. $[\alpha]_D^{24}$ = +3.7° (c 1.60, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.81 (m, 1H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.76 – 7.71 (m, 1H), 7.50 – 7.44 (m, 3H), 7.35 – 7.30 (m, 3H), 7.28 – 7.23 (m, 1H), 7.21 – 7.16 (m, 2H), 7.13 – 7.08 (m, 2H), 6.90 – 6.84 (m, 2H), 5.69 (s, 1H), 3.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1, 144.0, 141.9, 135.9, 133.4, 132.1, 130.5, 129.5, 128.4, 128.1, 127.9, 127.9, 127.7, 127.6, 126.3, 125.9, 125.6, 113.7, 56.1, 55.3. The spectral data for this compound matches that reported in the literature.[11]

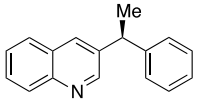


(*S*)-2-(phenyl(4-(trifluoromethyl)phenyl)methyl)naphthalene (2.45). Triarylmethane **2.45** was prepared via the General Procedure using pivalate **2.60** (prepared in >99% ee) except that 10 mol % of $Ni(cod)_2$ and 1.0 equiv of boroxine were used and the reaction mixture was heated at 90 °C. The crude material was purified by silica gel chromatography (1% Et_2O/hexanes) to give compound **2.45** (70.4 mg, 96%) as a colorless oil. The enantiomeric excess was determined to be 80% ee by chiral HPLC analysis (CHIRAlPAK 1B, 0.6 mL/min, 100% hexane, λ=254 nm); t_R(major)= 21.44 min, t_R(minor)= 23.27 min. $[\alpha]_D^{24}$ = –8.8° (c 1.92, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.72 (m, 1H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.66 – 7.62 (m, 1H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.40 – 7.36 (m, 3H), 7.27 – 7.22 (m, 2H), 7.22 – 7.16 (m, 4H), 7.07 (dd, *J* = 7.2, 1.7 Hz, 2H), 5.68 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.8, 142.8, 140.5, 133.4, 132.3, 129.9, 129.0, 128.8 (q, J_{C-F} = 32.1 Hz), 128.6, 128.5, 128.2, 128.9 (q, J_{C-F} = 1.5 Hz),

127.8,127.6,126.8, 126.2, 125.9, 125.4 (q, J_{C-F} = 3.9 Hz), 124.3 (q, J_{C-F} = 273. 5), 56.8; FTIR (NaCl/thin film) 3058, 3027, 2926, 1924, 1600, 1494, 1416, 1326, 1165, 1068, 814 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{24}H_{17}F_3$: 362.1824, found: 362.1276.

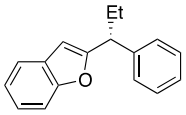


(*S*)-1-(1-phenylethyl)naphthalene (2.46). Diarylethane **2.46** was prepared via the General Procedure using pivalate **2.61** (prepared in 86% ee). The crude material was purified by silica gel chromatography (3% Et_2O/hexanes) to give compound **2.46** (run 1: 34.3 mg, 74%; run 2: 32.9 mg, 71%) as a colorless oil. The enantiomeric excess was determined to be 73% ee (run 1: 73% ee; run 2: 72% ee) by chiral HPLC analysis (CHIRALPAK 1B, 0.8 mL/min, 100% hexanes, λ=220 nm); t_R(major)=19.13 min, t_R(minor)=26.13 min. $[\alpha]_D^{24}$ = –23.3° (c 0.60, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.94 (m, 1H), 7.78 – 7.75 (m, 1H), 7.66 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.41 – 7.31 (m, 4H), 7.20 – 7.14 (m, 4H), 7.10 – 7.06 (m, 1H), 4.85 (q, *J* = 7.1 Hz, 1H), 1.69 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.7, 141.6, 134.0, 131.7, 128.8, 128.4, 127.6, 127.0, 126.0, 125.9, 125.5, 125.3, 124.4, 124.0, 40.6, 22.6; FTIR (NaCl/thin film) 3058, 2966, 2929, 2872, 1597, 1508, 1493, 1449, 1396, 1372, 1026, 800 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{18}H_{16}$: 232.1252, found: 232.1255. The spectral data for this compound matches that reported in the literature. [31,32]



(*S*)-3-(1-phenylethyl)quinoline (2.47). Diarylethane **2.47** was prepared via the General Procedure using pivalate **2.62** (prepared in 83% ee). The crude material

was purified by silica gel chromatography (20% EtOAc/hexanes) to give compound **2.47** (run 1: 43.2 mg, 93%; run 2: 44.3 mg, 94%) as pale yellow oil. The enantiomeric excess was determined to be 58% ee (run 1: 58% ee; run 2: 57% ee) by chiral HPLC analysis (CHIRALPAK 1C, 1.0 mL/min, 3.0% *i*-PrOH/hexane, λ=210 nm); t_R(minor)=14.95 min, t_R(major)=16.50 min. $[\alpha]_D^{24}$ = +12.1° (c 0.98, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.80 (d, *J* = 2.3 Hz, 1H), 8.07 (d, *J* = 8.5 Hz, 1H), 7.94 (d, *J* = 2.3 Hz, 1H), 7.77 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.69 – 7.63 (m, 1H), 7.56 – 7.47 (m, 1H), 7.36 – 7.29 (m, 2H), 7.29 – 7.20 (m, 3H), 4.37 (q, *J* = 7.2 Hz, 1H), 1.77 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.8, 146.8, 144.9, 138.9, 133.0, 129.1, 128.8, 128.7, 128.1, 127.7, 127.6, 126.6, 126.5, 42.6, 21.6; FTIR (NaCl/thin film) 3060, 3026, 2967, 2930, 2873, 1602, 1570, 1494, 1380, 1333, 1125, 1028, 961 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{17}H_{15}N$: 233.1204, found: 233.1198.

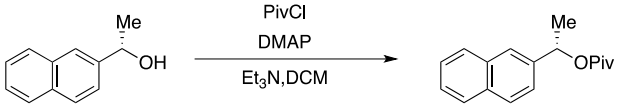


(*R*)-2-(1-phenylpropyl)benzofuran (2.48). Diarylpropane **2.48** was prepared via the General Procedure using pivalate **2.63** (prepared in 82% ee) except that 1.2 equiv of boroxine was used and the reaction mixture was heated at 32 °C for 24 h. The crude material was purified by silica gel chromatography (4% Et_2O/hexanes) to give compound **2.48** (run 1: 24.0 mg, 51%; run 2: 22.2 mg, 47%) as a colorless oil. The enantiomeric excess was determined to be 72% ee (run 1: 72% ee; run 2: 72% ee) by chiral HPLC analysis (CHIRALPAK 1B, 1.0 mL/min, 0.2% *i*-PrOH/hexane, λ=254 nm);

t_R(major)=37.28 min, t_R(minor)=34.31 min. $[\alpha]_D^{24}$ = –38.1° (c 0.80, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.40 (m, 1H), 7.33 – 7.30 (m, 1H), 7.26 – 7.21 (m, 4H), 7.18 – 7.14 (m, 1H), 7.14 – 7.07 (m, 2H), 6.38 (s, 1H), 3.88 (t, *J* = 7.7 Hz, 1H), 2.24 – 2.14 (m, 1H), 1.99 – 1.88 (m, 1H), 0.88 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2, 154.8, 141.9, 128.7, 128.5, 128.0, 126.7, 123.3, 122.4, 120.4, 110.9, 102.4, 47.6, 27.6, 12.4; HRMS (EI+) $[M]^+$calculated for $C_{17}H_{16}O$: 236.1201, found: 236.1195. The spectral data for this compound matches that reported in the literature.[33]

Preparation of Benzyl Pivalates

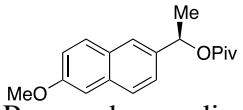
General Procedure for the Preparation of Benzyl Pivalates: Preparation of (*S*)-1-(naphthalen-2-yl)ethyl pivalate (2.25).



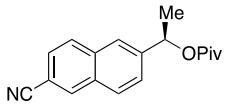
2.24 **2.25**

(*S*)-1-(Naphthalen-2-yl)ethanol (**2.24**, 1.17 g, 6.8 mmol, 1.0 equiv) and DMAP (83 mg, 0.68 mmol, 0.10 equiv) were dissolved in CH_2Cl_2 (10 mL, 0.68 M). Et_3N (1.94 mL, 1.35 mmol, 2.0 equiv) and pivaloyl chloride (1.02 mL, 8.15 mmol, 1.2 equiv) were then added. The reaction mixture was then stirred for 12 h at room temperature, before H_2O (20 mL) was added. The organic layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layers were washed with 10% aq. KOH (20 mL), dried ($MgSO_4$), filtered and concentrated. The resulting residue was purified by silica gel chromatography (5% Et_2O/hexanes) to give compound **2.25** (1.58 g, 91%) as a white solid. The

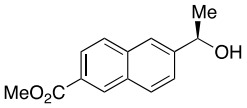
enantiomeric excess was determined to be >99% ee by chiral HPLC analysis (CHIRALPAK IA, 0.6 mL/min, 1.0% *i*-PrOH/hexane, λ=254 nm); t_R(minor)=8.23 min, t_R(major)=10.31 min. $[\alpha]_D^{24}$ = –82.1° (c 0.80, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 – 7.81 (m, 3H), 7.80 – 7.77 (m, 1H), 7.50 – 7.45 (m, 3H), 6.02 (q, *J* = 6.6 Hz, 1H), 1.60 (d, *J* = 6.6 Hz, 3H), 1.23 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.7, 139.5, 133.2, 132.9, 128.3, 128.0, 127.7, 126.2, 126.0, 124.7, 124.0, 72.1, 38.8, 27.2, 22.3; HRMS (EI+) $[M]^+$ calculated for $C_{17}H_{20}O_2$: 256.1463, found: 256.1469. The spectral data for this compound matches that reported in the literature for the racemic compound.[34]



(*R*)-1-(6-methoxynaphthalen-2-yl)ethyl pivalate (2.54). Prepared according to the General Procedure on a 1.89 mmol scale to give **2.54** (460 mg, 85%) as a white solid (mp 78–82°C). The enantiomeric excess was determined to be >99% ee by chiral HPLC analysis (CHIRALPAK IA, 0.8 mL/min, 1.0% *i*-PrOH/hexane, λ=254 nm); t_R(major)=6.88 min, t_R(minor)=6.02 min. $[\alpha]_D^{24}$ = +81.2° (c 0.80, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 – 7.69 (m, 3H), 7.43 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.17 – 7.11 (m, 2H), 5.99 (q, *J* = 6.6 Hz, 1H), 3.92 (s, 3H), 1.59 (d, *J* = 6.6 Hz, 3H), 1.22 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.7, 157.8, 137.2, 134.1, 129.5, 128.6, 127.1, 124.7, 124.6, 118.9, 105.7, 72.1, 55.3, 38.8, 27.2, 22.2; FTIR (NaCl/thin film) 2979, 1724, 1608, 1506, 1487, 1391, 1284, 1237, 1166, 1031, 859 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{18}H_{22}O_3$: 286.1569, found: 286.1561.

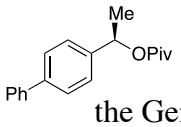


(*R*)-1-(6-cyanonaphthalen-2-yl)ethyl pivalate (2.55). Prepared according to the General Procedure on a 0.89 mmol scale to give **2.55** (170 mg, 67%) as a white solid (mp 74–76°C). The enantiomeric excess was determined to be 95% ee by chiral HPLC analysis (CHIRALPAK IA, 1.0 mL/min, 2.0% *i*-PrOH/hexane, λ=254 nm); t_R(major)=9.71 min, t_R(minor)=14.42 min. $[\alpha]_D^{24}$ = +78.6° (c 0.90, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.91 (d, *J* = 4.0 Hz, 1H), 7.89 (d, *J* = 4.1 Hz, 1H), 7.83 (s, 1H), 7.63 – 7.57 (m, 2H), 6.00 (q, *J* = 6.6 Hz, 1H), 1.60 (d, *J* = 6.6 Hz, 3H), 1.23 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.6, 143.1, 134.6, 133.9, 131.7, 129.3, 128.9, 126.8, 125.7, 124.7, 119.2, 109.4, 71.7, 38.8, 27.1, 22.3; FTIR (NaCl/thin film) 3059, 2977, 2227, 1727, 1634, 1470, 1281, 1157, 1133, 1064 cm^{-1}; HRMS (CI+) $[M+H]^+$ calculated for $C_{18}H_{20}NO_2$: 282.1494, found: 282.1491.

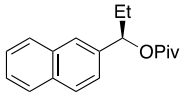


(*R*)-methyl-6-(1-(pivaloyloxy)ethyl)-2-naphthoate (2.56). Prepared according to the General Procedure on a 1.84 mmol scale to give **2.56** (470 mg, 81%) as a white solid (mp 85–88°C). The enantiomeric excess was determined to be 98% ee by chiral HPLC analysis (CHIRALPAK IA, 1.0 mL/min, 2.0% *i*-PrOH/hexane, λ=254 nm); t_R(major)=8.99 min, t_R(minor)=13.21 min. $[\alpha]_D^{24}$ = +40.9° (c 0.62, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.59 (s, 1H), 8.06 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.87 (d, *J* = 8.6 Hz, 1H), 7.82 (s, 1H), 7.52 (dd, *J* = 8.5, 1.7 Hz, 1H), 6.01 (q, *J* = 6.6 Hz, 1H), 3.98 (s, 3H), 1.60 (d, *J* = 6.6 Hz, 3H), 1.24 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$)

δ 177.7, 167.2, 142.2, 135.4, 132.0, 130.8, 129.8, 128.3, 127.5, 125.6, 124.7, 124.44, 71.9, 52.3, 38.8, 27.1, 22.3; FTIR (NaCl/thin film) 2977, 2872, 1724, 1635, 1480, 1436, 1281, 1156, 1097 cm^{-1}; HRMS (CI+) $[M+H]^+$ calculated for $C_{19}H_{23}O_4$: 315.1596, found: 315.1593.

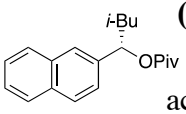


(*R*)-1-([1,1'-biphenyl]-4-yl)ethyl pivalate (2.57). Prepared according to the General Procedure on a 1.5 mmol scale to give **2.57** (295 mg, 70%) as a white solid (mp 78–82°C). The enantiomeric excess was determined to be 93% ee by chiral HPLC analysis (CHIRALPAK IA, 1.0 mL/min, 0.3% *i*-PrOH/hexane, λ=254 nm); t_R(major)=9.02 min, t_R(minor)=10.74 min. $[\alpha]_D^{24}$ = +68.7° (c 0.82, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 – 7.57 (m, 4H), 7.50 – 7.42 (m, 4H), 7.41 – 7.35 (m, 1H), 5.92 (q, *J* = 6.6 Hz, 1H), 1.58 (d, *J* = 6.6 Hz, 3H), 1.26 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.7, 141.2, 140.8, 140.6, 128.8, 127.3, 127.2, 127.1, 126.2, 71.7, 38.8, 27.2, 22.4; FTIR (NaCl/thin film) 3029, 2981, 1720, 1486, 1367, 1284, 1176, 1071, 1009, 836 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{19}H_{22}O_2$: 282.1620, found: 282.1629.

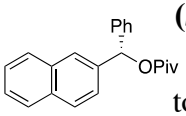


(*R*)-1-(naphthalen-2-yl)propyl pivalate (2.58). Prepared according to the General Procedure on a 4.03 mmol scale to give **2.58** (900 mg, 83%) as a colorless oil. The enantiomeric excess was determined to be >99% ee by chiral HPLC analysis (CHIRALPAK IA, 0.6 mL/min, 1.0% *i*-PrOH/hexane, λ=254 nm); t_R(major)=8.26 min, t_R(minor)=10.45 min. $[\alpha]_D^{24}$ = +160.9° (c 4.20, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ

7.88 – 7.75 (m, 4H), 7.54 – 7.44 (m, 3H), 5.83 (t, *J* = 7.0 Hz, 1H), 2.07 – 1.87 (m, 2H), 1.27 (s, 9H), 0.95 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.7, 138.4, 133.2, 133.0, 128.2, 128.0, 127.7, 126.1, 125.9, 125.4, 124.2, 38.9, 29.5, 27.2, 26.5, 10.0; FTIR (NaCl/thin film) 3057, 2971, 2934, 2875, 1728, 1479, 1396, 1153, 817 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{18}H_{22}O_2$: 270.1620, found: 270.1626.

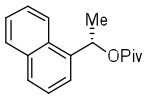


(*S*)-3-methyl-1-(naphthalen-2-yl)butyl pivalate (2.59). Prepared according to the General Procedure on a 1.17 mmol scale to give **2.59** (302 mg, 87%) as a colorless oil. The enantiomeric excess was determined to be 93% ee by chiral HPLC analysis (CHIRALPAK 1A, 0.8 mL/min, 1.0% *i*-PrOH/hexane, λ=254 nm); t_R(major)=8.22 min, t_R(minor)=10.31 min. $[\alpha]_D^{24}$ = –77.8° (c 0.84, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 – 7.79 (m, 3H), 7.78 – 7.75 (m, 1H), 7.50 – 7.43 (m, 3H), 5.93 (m, 1H), 1.95 (dd, *J* = 8.9, 7.8 Hz, 1H), 1.68 – 1.61 (m, 2H), 1.21 (s, 9H), 0.98 (d, *J* = 6.6 Hz, 3H), 0.95 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.7, 138.9, 133.2, 132.9, 128.3, 128.0, 127.7, 126.1, 125.9, 125.4, 124.2, 74.4, 45.7, 38.2, 27.1, 24.8, 22.9, 22.3; FTIR (NaCl/thin film) 2958, 2360, 1728, 1652, 1558, 1506, 1457, 1282, 1164 cm^{-1}; H RMS (EI+) $[M]^+$ calculated for $C_{20}H_{26}O_2$: 298.1933, found: 298.1938.

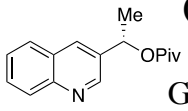


(*S*)-naphthalen-2-yl(phenyl)methyl pivalate (2.60). Prepared according to the General Procedure on a 6.40 mmol scale to give **2.60** (1.18 g, 88%) as a colorless oil. The enantiomeric excess was determined to be >99% ee by chiral

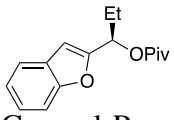
HPLC analysis (CHIRALPAK 1B, 0.8 mL/min, 1.0% *i*-PrOH/hexane, λ=254 nm); t_R(major)=7.06 min, t_R(minor)=6.43 min. $[\alpha]_D^{24}$ = –46.2° (c 0.80, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 – 7.80 (m, 4H), 7.53 – 7.48 (m, 2H), 7.45 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.43 – 7.34 (m, 4H), 7.33 – 7.30 (m, 1H), 7.02 (s, 1H), 1.30 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.3, 140.4, 137.9, 133.1, 132.9, 128.5, 128.4, 128.1, 127.8, 127.7, 126.9, 126.3, 126.2, 126.0, 124.9, 77.2, 38.9, 27.2; FTIR (NaCl/thin film) 2971, 1727, 1478, 1278, 1147, 1123, 1031, 818 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{22}H_{22}O_2$: 318.1620, found: 318.1617.



(*S*)-1-(naphthalene-1yl)ethyl pivalate (2.61). Prepared according to the General Procedure on a 2.33 mmol scale to give **2.61** (580 mg, 97%) as a colorless oil. The enantiomeric excess was determined to be 85% ee by chiral HPLC analysis (CHIRALPAK IA, 0.6 mL/min, 1.0% *i*-PrOH/hexane, λ=254 nm); t_R(major)=9.52 min, t_R(minor)=8.00 min. $[\alpha]_D^{24}$ = –39.2° (c 3.80, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.6 Hz, 1H), 7.87 (d, *J* = 8.3 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.59 (d, *J* = 7.0 Hz, 1H), 7.55 – 7.46 (m, 3H), 6.61 (q, *J* = 6.6 Hz, 1H), 1.68 (d, *J* = 6.6 Hz, 3H), 1.24 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.7, 137.9, 133.8, 130.2, 128.9, 128.3, 126.2, 125.6, 125.4, 123.3, 123.0, 69.3, 38.9, 27.2, 21.8; FTIR (NaCl/thin film) 2977, 2932, 1728, 1479, 1458, 1397, 1368, 1283, 1157, 1068, 1045 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{17}H_{20}O_2$: 256.1463, found: 256.1467.



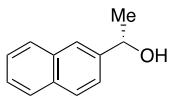
(*S*)-1-(quinolin-3-yl)ethyl pivalate (2.62). Prepared according to the General Procedure on a 1.60 mmol scale to give **2.62** (132.7 mg, 30%) as pale yellow oil. The enantiomeric excess was determined to be 82% ee by chiral HPLC analysis (CHIRALPAK IA, 1.0 mL/min, 1.0% *i*-PrOH/hexane, λ=254 nm); t_R(minor)=29.83 min, t_R(major)=33.26 min. $[\alpha]_D^{24}$ = –96.8° (c 0.96, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.96 (d, *J* = 2.2 Hz, 1H), 8.13 (d, *J* = 8.5 Hz, 1H), 8.11 (d, *J* = 2.1 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.63 – 7.53 (m, 1H), 6.09 (q, *J* = 6.6 Hz,1H), 1.68 (d, *J* = 6.7 Hz, 3H), 1.26 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.6, 149.2, 147.8, 134.6, 132.9, 129.5, 129.3, 127.9, 127.7, 126.9, 70.1, 38.8, 27.1, 22.0; FTIR (NaCl/thin film) 2977, 2933, 2872, 1728, 1497, 1480, 1281, 1154, 1126, 1067, 909 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{16}H_{19}O_2N$: 257.1416, found: 257.1411.



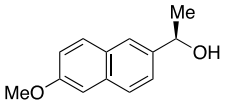
(*R*)-1-(benzofuran-2-yl)propyl pivalate (2.63). Prepared according to the General Procedure on a 1.66 mmol scale to give **2.63** (320 mg, 74%) as a colorless oil. The enantiomeric excess was determined to be 82% ee by chiral HPLC analysis (CHIRALPAK IC, 1.0 mL/min, 0.3% *i*-PrOH/hexane, λ=254 nm); t_R(major)=9.25 min, t_R(minor)=8.49 min. $[\alpha]_D^{24}$ = +172.7° (c 1.30, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 – 7.54 (m, 1H), 7.51 – 7.46 (m, 1H), 7.33 – 7.21 (m, 2H), 6.67 (s, 1H), 5.91 (t, *J* = 12.0 Hz, 1H), 2.13 – 2.03 (m, 2H), 1.25 (s, 9H), 0.99 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.7, 155.7, 154.8, 127.9, 124.2, 122.7, 121.1, 111.3, 104.2, 70.2, 38.9,

27.1, 26.0, 9.6; FTIR (NaCl/thin film) 2793, 2936, 2877, 1732, 1454, 1396, 1279, 1151, 1083, 1031, 950, 807 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{16}H_{20}O_3$: 260.1413, found: 260.1411.

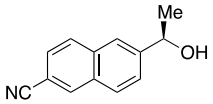
Preparation of Benzyl Alcohols



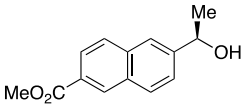
2.24



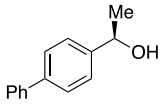
2.64



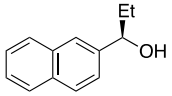
2.65



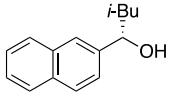
2.66



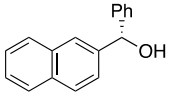
2.67



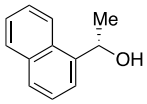
2.68



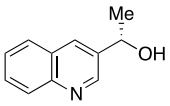
2.69



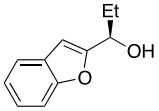
2.70



2.71



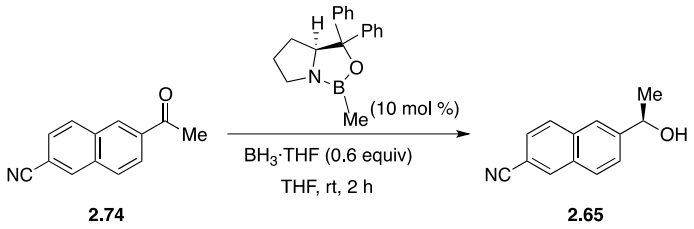
2.72



2.73

(*S*)-1-(Naphthalen-2-yl)ethanol **2.24** was purchased from Sigma Aldrich. Alcohols **2.68**,[12] **2.70**[11] and **2.73**[12] were prepared according to literature procedures using asymmetric addition of diethyl zinc to the aldehydes. The enantiomeric excesses of crystalline compounds **2.68** and **2.69** were then increased via recrystallization from hexanes. Alcohols **2.64**, **2.65**, **2.66**, and **2.67** were prepared via Corey-Bakshi-Shibata reduction of ketones.[35] Alcohols **2.69**, **2.71**, and **2.72** were prepared by asymmetric transfer hydrogenation of ketones.[36] Because alcohols **2.65, 2.66**, **2.67**, **2.69**, and **2.72** have not been prepared via these methods previously, experimental procedures are given below.

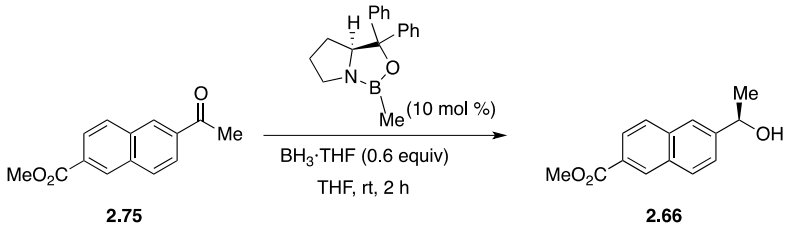
(*R*)-6-(1-hydroxyethyl)-2-naphthonitrile (2.65).



2.74 **2.65**

The following procedure is adapted from the literature.[35] A solution of CBS catalyst (30.7.0 mg, 0.11 mmol, 10 mol %) and THF (2.0 mL) was slowly added to a solution of ketone **2.74** (216.3 mg, 1.1 mmol, 1.0 equiv), BH_3·THF (1 M in THF, 0.66 mL, 0.66 mmol, 0.60 equiv), and THF (20 mL). After stirring at room temperature for 2 h, H_2O (50 mL) was added. The mixture was extracted with Et_2O (15 mL x 3). The combined organic layers were then dried ($MgSO_4$), filtered, concentrated. The resulting residue was purified by column chromatography (elution 60 % EtOAc/ hexanes) to give alcohol **2.65** (202 mg, 93%) as a white solid (mp 75–77 °C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.93 – 7.88 (m, 3H), 7.67 – 7.60 (m, 2H), 5.09 (q, *J* = 6.5 Hz, 1H), 2.10 (s, 1H), 1.57 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8, 134.7, 133.9, 131.7, 129.2, 128.8, 126.7, 125.8, 123.8, 119.3, 109.1, 70.2, 25.4; FTIR (NaCl/thin film) 3445, 2973, 2926, 2872, 2227, 1632, 1369, 1272, 1159, 1088, 895 cm $^{-1}$; HRMS (CI+) $[M+H]^+$ calculated for $C_{13}H_{12}NO$: 198.0919, found: 198.0917.

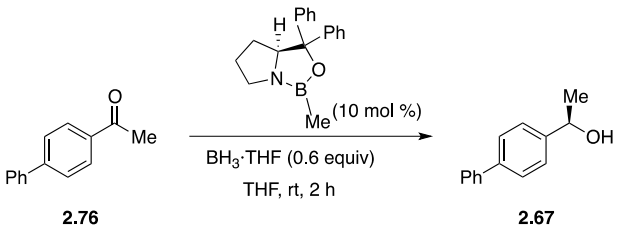
(*R*)-methyl 6-(1-hydroxyethyl)-2-naphthoate (2.66).



2.75 **2.66**

The following procedure is adapted from the literature.[35] A solution of CBS catalyst (83.2 mg, 0.30 mmol, 10 mol %) and THF (5.0 mL) was slowly added to a solution of ketone **2.75** (685.0 mg, 3.0 mmol, 1.0 equiv), BH_3·THF (1 M in THF, 1.0 mL, 1.8 mmol, 0.60 equiv), and THF (55 mL). After stirring at room temperature for 2 h, H_2O (30 mL) was added. The mixture was extracted with Et_2O (30 mL x 3). The combined organic layers were then dried ($MgSO_4$), filtered, concentrated. The resulting residue was purified by column chromatography (elution 40 % EtOAc/ hexanes) to give alcohol **2.66** (460 mg, 67%) as a white solid (mp 74–77 °C): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.05 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.87 (s, 1H), 7.85 (s, 1H), 7.56 (dd, *J* = 8.5, 1.7 Hz, 1H), 5.16 – 5.06 (m, 1H), 3.97 (s, 3H), 1.96 (d, *J* = 3.5 Hz, 1H), 1.58 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.3, 145.8, 135.5, 131.9, 130.8, 129.8, 128.2, 127.3, 125.6, 124.7, 123.6, 70.4, 52.3, 25.3; FTIR (NaCl/thin film) 3279, 2974, 2887, 1715, 1632, 1437, 1290, 1202, 1130, 1073, 898 cm^{-1}; HRMS (CI+) $[M+H]^+$ calculated for $C_{14}H_{15}O_3$: 231.1021, found: 231.1019.

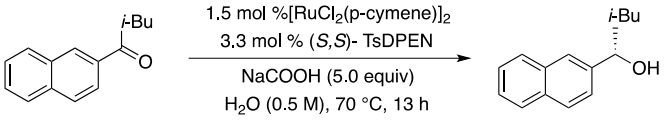
(*R*)-1-(biphenyl-4-yl)ethanol (2.76).



2.76 **2.67**

The following procedure is adapted from the literature.[35] A solution of CBS catalyst (97.0 mg, 0.35 mmol, 10 mol %) and THF (5.0 mL) was slowly added to a solution of 4-acetylbiphenyl (687.0 mg, 3.50 mmol, 1.0 equiv), BH_3·THF (1 M in THF, 2.1 mL, 2.1 mmol, 0.60 equiv), and THF (70 mL). After stirring at room temperature for 2 h, H_2O (50 mL) was added. The mixture was extracted with Et_2O (30 mL x 3). The combined organic layers were then dried ($MgSO_4$), filtered, concentrated. The resulting residue was purified by recrystallization (hexanes) to give compound **2.67** (640.7 mg, 92%, 93% ee) as a white solid. The spectral data for this compound matches that reported in the literature for the racemic compound.[37]

(*S*)-3-methyl-1-(naphthalene-2-yl)butan-1-ol (2.69).

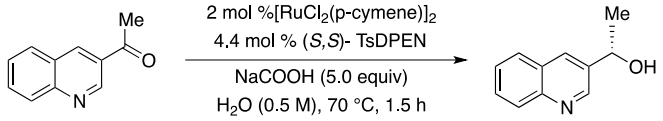


2.77 **2.69**

The following procedure is adapted from the literature.[36] In a N_2-atmosphere glovebox, $[RuCl_2(p\text{-cymene})]_2$ (21.9 mg, 0.0358 mmol, 1.5 mol %) and (*S*,*S*)-TsDPEN (28.8 mg,

0.0787 mmol, 3.3 mol %) were weighed into a vial. The vial was then capped and removed from glovebox. H_2O (degassed by sparging with N_2, 6.0 mL) was added, and the resulting mixture was stirred at 40 °C for 1 h. 3-Methyl-1-(naphthalene-2-yl)butan-1-one **2.77** (387.0 mg, 2.39 mmol, 1.0 equiv) and NaCOOH (811.4 mg, 11.9 mmol, 5.0 equiv) were added. The vial was evacuated and refilled with N_2 three times and then heated at 60 °C for 13 h. The reaction mixture was diluted with Et_2O (10 mL) and filtered through silica gel, which was then rinsed with additional Et_2O (10 mL x 2). The combined organic layers were concentrated. The resulting residue was purified by silica gel chromatography (15% Et_2O/hexanes) and then recrystallized (hexanes) to give compound **2.69** (238.3 mg, 61%, 93% ee) as a white solid. The spectral data for this compound matches that reported in literature.[38]

(*S*)-1-(quinolin-3-yl)ethanol (2.72).

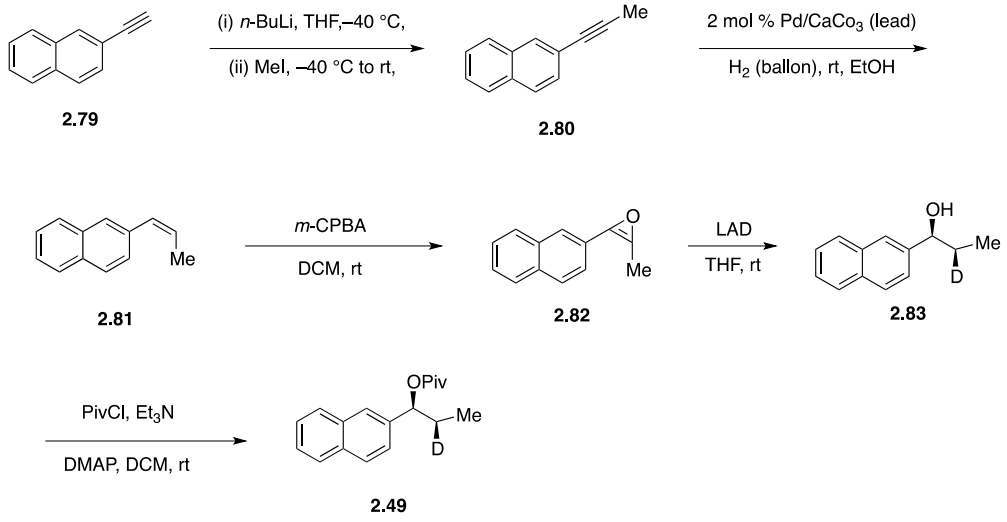


2.78 **2.72**

The following procedure is adapted from the literature.[36] In a N_2-atmosphere glovebox, $[RuCl_2(p\text{-cymene})]_2$ (3.58 mg, 0.0058 mmol, 2.0 mol %) and (*S*,*S*)-TsDPEN (4.71 mg, 0.0129 mmol, 4.4 mol %) were weighed into a vial. The vial was then capped and removed from glovebox. H_2O (degassed by sparging with N_2, 0.6 mL) was added, and the resulting mixture was stirred at 40 °C for 1 h. 3-Acetylquinoline **2.78** (50.0 mg, 0.292

mmol, 1.0 equiv) and NaCOOH (99.3 mg, 1.46 mmol, 5.0 equiv) were added. The vial was evacuated and refilled with N_2 three times and then heated at 40 °C for 1.5 h. The reaction mixture was diluted with Et_2O (1 mL) and filtered through silica gel, which was then rinsed with additional Et_2O (1 mL x 2). The combined organic layers were concentrated. The resulting residue was purified by silica gel chromatography (50–90% EtOAc/hexanes) to give compound **2.72** (45.7 mg, 90%, 85% ee) as a light brown oil. The spectral data for this compound matches to that reported in literature.[39]

Preparation of Pivalate (2.49)



2-(prop-1-ynyl)naphthalene 2.80. The following procedure is adapted from the literature.[40] A solution of terminal alkyne **2.79** (507.8 mg, 3.38 mmol, 1.0 equiv) and THF (20 mL) was cooled to –40 °C in a 50-mL round-bottomed flask. *n*-BuLi (2.5 M in Hexanes, 2.7 mL, 6.76 mmol, 2.0 equiv) was added. After stirring at – 40 °C for 1 h, a

solution of iodomethane (0.44 mL, 7.10 mmol, 2.1 equiv) and THF (2.5 mL) was added. The mixture was then stirred for 1 h at room temperature. Sat. aq. NH_4Cl (2 mL) and then water (40 mL) was added, and the mixture was extracted with Et_2O (30 mL x 3). The combined organic layers were then dried ($MgSO_4$), filtered, and concentrated. The resulting residue was purified by silica gel chromatography (100% petroleum ether) to give compound **2.80** (457.0 mg, 81%) as a colorless oil. The spectral data for compound **2.80** matches that reported in literature.[40]

(*Z*)-2-(prop-1-enyl)naphthalene 2.81. The following procedure is adapted from the literature.[41] In a 25-mL flask, $Pd/CaCO_3$ (5%, poisoned with lead, 80.4 mg, 0.0378 mmol 2 mol %) and ethanol (5.0 mL) were combined. The flask was evacuated and refilled with H_2 (balloon) three times, then a solution of alkyne **2.80** (314.1 mg, 1.89 mmol, 1.0 equiv) and ethanol (4.5 mL) was added slowly. The reaction mixture was stirred at room temperature for 40 minutes. It was then filtered through Celite and concentrated. The resulting residue was purified by silica gel chromatography (100% petroleum ether) to give **2.81** (282.3 mg, 89%) as colorless oil. The ratio of *Z:E* olefins was 19:1, as determined by ^1H NMR analysis.[42] This mixture was directly used in next step.

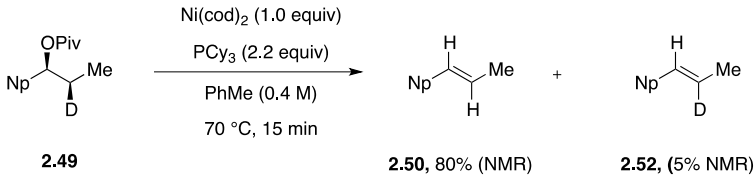
***Cis*-2-methyl-3-(naphtha-2-yl)oxirane (2.82)**. The following procedure is adapted from the epoxidation of (*E*)-2-(prop-1-enyl)naphthalene **2.81** in literature.[43] In a 50-mL flask, olefin **2.81** (247.8 mg, 1.34 mmol, 1.0 equiv) and CH_2Cl_2 (5.0 mL) were combined. A solution of *meta*-chloroperoxybenzoic acid (400.0 mg, 1.62 mmol, 1.2 equiv) and CH_2Cl_2 (10 mL) was added. After stirring at 35 °C for 30 min, sat. Na_2SO_3 (6 mL), water (10 mL) and then sat. NaCl were added. The organic layer was separated, dried (Na_2SO_4), filtered, concentrated. The resulting residue was purified by silica gel chromatography (5% Et_2O/hexanes) to give compound **2.82** (182.9 mg, 74%) as a colorless oil. The ^1H NMR showed that the ratio of *cis:trans* was 17:1.[44] This mixtures was directly used in next step.

1-(naphthalene-2-yl)-2-deuterio-propan-1-ol (2.83). In a 10-mL flask, lithium aluminum deuteride (105 mg, 2.5 mmol, 2.5 equiv) and THF (2 mL) were combined and cooled to 0 °C. A solution of **2.82** (183.0 mg, 1.0 mmol, 1.0 equiv) and THF (8 mL) was slowly added via addition funnel. After the addition was complete, the reaction mixture was warmed to room temperature and stirred for 2 hours. The reaction was then quenched by the addition of 1 N aq. HCl (5 mL). The organic layer was washed with sat. NaCl, dried ($MgSO_4$), filtered and concentrated. The resulting residue was purified by silica gel chromatography (17% Et_2O/hexanes) to give compound **2.83** (80.0 mg, 73%) as a colorless oil: ^1H NMR (600 MHz, $CDCl_3$) δ 7.89 – 7.84 (m, 3H), 7.81 (s, 1H), 7.54 – 7.47 (m, 3H), 4.80 (d, J = 5.8 Hz, 1H), 1.96 (s, 1H), 1.91 – 1.83 (m, 1H), 0.97 (d, J = 7.4

Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.9, 133.3, 133.0, 128.3, 127.9, 127.7, 126.1, 125.8, 124.7, 124.2, 76.1, 31.4 (t, J = 19.6 Hz), 10.0; FTIR (NaCl/thin film) 3357 (br), 3055, 2962, 2931, 2874, 1602, 1508, 1457, 1376, 1270, 1124, 1059, 1017, 857 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{13}H_{13}OD$: 187.1106, found: 187.1114.

1-(naphthalene-2-yl)-2-deuterio-propyl pivalate (2.49). Prepared according to the General Procedure for pivalate synthesis (see above) on a 0.176 mmol scale to give **2.49** (38.2 mg, 80%) as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 – 7.72 (m, 3H), 7.68 (s, 1H), 7.43 – 7.35 (m, 3H), 5.72 (d, J = 6.0 Hz, 1H), 1.81 (p, *J* = 7.3 Hz, 1H), 1.16 (s, 9H), 0.85 (d, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.8, 138.4, 133.2, 133.0, 128.2, 128.0, 127.7, 126.1, 125.9, 125.4, 124.2, 77.2, 38.9, 29.2 (t, *J* = 16.5 Hz), 27.2, 9.9; FTIR (NaCl/thin film) 3057, 2971, 2934, 2874, 1728, 1479, 1459, 1283, 1154, 1125, 856 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{18}H_{21}O_2D$: 271.1683, found: 271.1675

β-Hydride Elimination Experiment



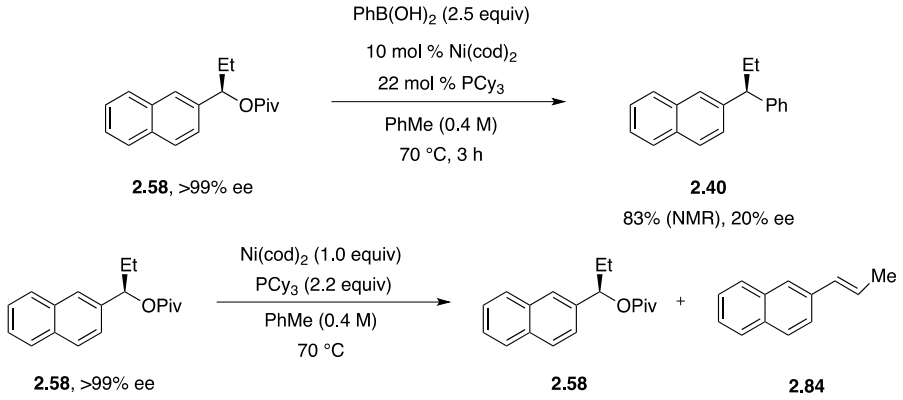
2.49 **2.50,** 80% (NMR) **2.52, (**5% NMR)

In a N_2-atmosphere glovebox, $Ni(cod)_2$ (45.7 mg, 0.166 mmol, 1.0 equiv) and PCy_3 (102.3 mg, 0.365 mmol, 2.2 equiv) were weighed into a 1-dram vial. Pivalate **2.49** (45.0 mg, 0.166 mmol, 1.0 equiv) was added, followed by toluene (0.41 mL, 0.4 M). The vial

was capped with a Teflon-lined cap and removed from the glovebox. The mixture was heated for 15 minutes at 70 °C. The reaction mixture was then diluted with Et_2O (2.0 mL) and filtered through a plug of silica gel, which was rinsed with Et_2O (15 mL). The solution was concentrated. Then 1,3,5-trimethoxybenzene (27.9 mg, 0.166 mmol, 1.0 equiv) was added as an internal standard for ^1H NMR analysis. Based on the ^1H NMR spectrum, pivalate **2.49** underwent quantitative conversion to give products **2.50**[42] (80%) and **2.52** (5%).[45]

Control Experiments for β-Hydride Elimination Experiment

Although the cross coupling proceeds with low levels of chirality transfer using a Ni/PCy_3 catalyst, we have determined that the starting material does not epimerize to a significant extent under the conditions used in the β-hydride elimination experiment.

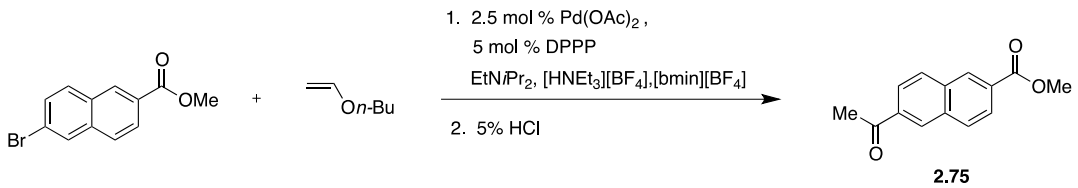


entry	time (min)	yield of 2.58 (%)[a]	ee of 2.58 (%)[b]	yield of 2.84 (%)[a]
1	15	0	n.d.	>95
2	1.5	19	95	81

[a] Determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. [b] Determined by HPLC on a chiral stationary phase.

Preparation of Ketones 2.75 and 2.74

methyl 6-acetyle-2-naphtoate (2.75).

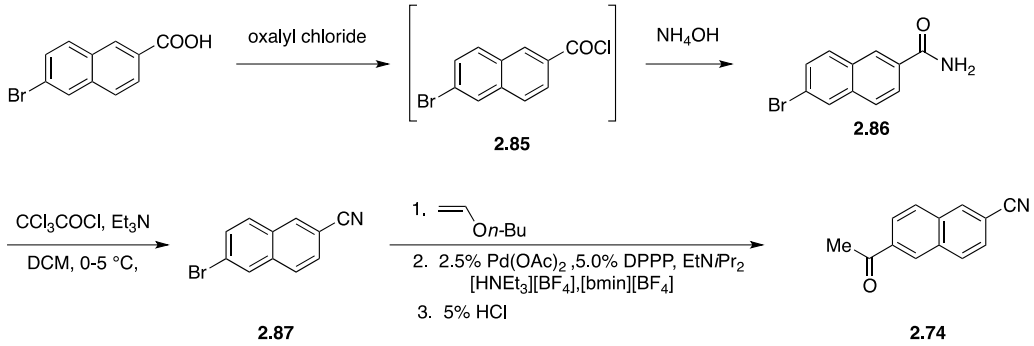


2.75

The following procedure is adapted from the literature.[46] An oven-dried, two-necked round-bottomed flask was charged with methyl 6-bromo-2-naphthoate (1.25 g, 4.72 mmol, 1.0 equiv), $Pd(OAc)_2$ (26.4 mg, 0.12 mmol, 2.5 mol %), dppp (97.0 mg, 0.24 mmol, 5 mol %), $[HNEt_3][BF_4]$ (1.38 g, 7.06 mmol, 1.5 equiv) and [bmin]][BF_4] (10 mL). The flask was then evacuated and refilled with N_2 three times. 1-(Vinyloxy)butane (1.27 mL, 9.43 mmol, 2.0 equiv) and then *i*-Pr_2NEt (1.3 mL, 7.06 mmol, 1.5 equiv) were added via syringe. The reaction mixture heated at 115 °C. After 8 h, the mixture was cooled to room temperature. Aq. HCl (5%, 15 mL) was added, and the mixture was stirred at room temperature for 0.5 h. CH_2Cl_2 (30 mL) was then added, and the layers were separated. The aqueous layer was then extracted with CH_2Cl_2 (2 x 30 mL). The combined organic layers were washed with H_2O until neutral, dried (Na_2SO_4), filtered, and concentrated. The crude material was purified by silica gel chromatography (12% EtOAc/hexanes) to give compound **2.75** (700.0 mg, 65%) as a white solid (mp 147–150 °C): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.48 (s, 1H), 8.13 (dd, *J* = 8.6, 1.6 Hz, 1H), 8.08 (dd, *J* =

8.6, 1.7 Hz, 1H), 8.01 (dd, J = 8.6, 2.5 Hz, 2H), 4.00 (s, 3H), 2.74 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.8, 166.8, 136.3, 134.7, 134.6 130.6, 129.9, 129.8 129.7, 129.6, 126.2, 124.7, 52.4, 26.8; FTIR (NaCl/thin film) 3058, 2952, 1711, 1608, 1438, 1360, 1338, 1291, 1264, 1180, 1097, 956 cm^{-1}; HRMS (CI+) $[M+H]^+$ calculated for $C_{14}H_{13}O_3$: 229.0865, found: 229.0869.

6-acetyl 2-naphthonitrile (2.74).



In a round-bottomed flask equipped with a nitrogen inlet and an oil bubbler to monitor gas flow, a solution of 6-bromo-2-naphthoic acid (4.0 g, 15.9 mmol, 1.0 equiv), DMF (0.25 mL, 3.18 mmol, 0.2 equiv) and CH_2Cl_2 (40.0 mL) was cooled to 0 °C. Oxalyl chloride (2.05 mL, 23.9 mmol, 1.5 equiv) was then added dropwise via syringe, and the immediate evolution of gas was observed by increased flow through the bubbler. The reaction mixture was stirred at 0 °C until gas flow slowed and was then stirred at room temperature for 1 hour. The resulting solution of acid chloride **2.85** was used in the subsequent step without purification.

After the oil bubbler was removed, the solution of acid chloride **2.85** was cooled to 0 °C. A solution of aq. NH_4OH (25%, 2.15 mL, 55.7 mmol, 3.5 equiv) was added dropwise via syringe. A precipitate immediately formed. The reaction mixture was then stirred at room temperature for 30 min. H_2O (40 mL) was added. The mixture was extracted with EtOAc (60 mL). The organic layer was washed with sat. NaCl (30 mL), dried ($MgSO_4$), filtered, and concentrated to give amide **2.86 (**2.5g, 63%) as a white solid: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.35 – 8.28 (m, 1H), 8.06 (d, *J* = 1.9 Hz, 1H), 7.89 (d, *J* = 1.7 Hz, 1H), 7.87 (d, *J* = 1.8 Hz, 1H), 7.85 – 7.78 (m, 1H), 7.63 (dd, *J* = 8.7, 2.0 Hz, 1H), 6.20 (s, 1H), 5.72 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.8, 135.9, 131.0, 130.9, 130.6, 130.4, 129.9, 128.1, 127.7, 124.8, 122.3. Amide **2.86** was used in the subsequent step without further purification.

The following procedure is adapted from the literature.[47] A mixture of amide **2.86** (2.5 g, 10 mmol, 1.0 equiv), triethylamine (2.3 mL, 22 mmol, 2.2 equiv) and CH_2Cl_2 (30 mL) was cooled to 0 °C. A solution of trichloroacetyl chloride (2.3 mL, 20 mmol, 2.2 equiv) and CH_2Cl_2 (20 mL) was added, while the bath temperature was maintained between 0–5 °C. After the addition was finished, ice-cooled water (25 mL) was added and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (10 mL). The combined organic layers were then washed with aq. KOH (5%, 30 mL), and the resulting aqueous layer was extracted with CH_2Cl_2 (10 mL). The combined organic

layers were then washed with aq. H_2SO_4 (5%, 30 mL), and the resulting aqueous layer was extracted with CH_2Cl_2 (10 mL). Finally, the combined organic layers were washed with H_2O (30 mL), and the resulting aqueous layer was extracted with CH_2Cl_2 (10 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated. The resulting residue was recrystallized (1:1 Et_2O/hexanes) to give **2.87** (1.81 g, 78%) as orange crystals: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (s, 1H), 8.07 (d, *J* = 1.2 Hz, 1H), 7.83 (d, *J* = 8.5 Hz, 1H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.69 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.64 (dd, *J* = 8.5, 1.6 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 135.5, 134.0, 131.3, 130.7, 130.2, 129.9, 128.3, 127.5, 123.6, 118.8, 109.9.

The following procedure is adapted from the literature.[46] An oven-dried, two-necked round-bottomed flask was charged with aryl halide **2.87** (348.0 mg, 1.50 mmol, 1.0 equiv), $Pd(OAc)_2$ (6.7 mg, 0.09 mmol, 3 mol %), dppp (74.2 mg, 0.18 mmol, 6 mol %), $[HNEt_3][BF_4]$ (439 mg, 2.25 mmol, 1.5 equiv) and [bmin][BF_4] (2.5 mL). The flask was then evacuated and refilled with N_2 three times. 1-(Vinyloxy)butane (0.33 mL, 3.0 mmol, 2.0 equiv) and then *i*-Pr_2NEt (0.37 mL, 2.25 mmol, 1.5 equiv) were added via syringe. The reaction mixture was heated at 115 °C. After 8 h, the mixture was cooled to room temperature. Aq. HCl (5%, 5 mL) was added, and the mixture was stirred at room temperature for 0.5 h. CH_2Cl_2 (20 mL) was added, and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layers were

washed with H_2O until neutral, dried (Na_2SO_4), filtered, and concentrated. The crude material was purified by silica gel chromatography (20% Et_2O/hexanes) to give compound **2.74** (235.0 mg, 40%) as a yellow solid (mp 134–136 °C): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.27 (s, 1H), 8.15 (dd, *J* = 8.6, 1.6 Hz, 1H), 8.07 (d, *J* = 8.5 Hz, 1H), 7.98 (d, *J* = 8.6 Hz, 1H), 7.69 (dd, *J* = 8.4, 1.5 Hz, 1H), 2.75 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.4, 136.9, 134.3, 134.0, 133.8, 130.7, 129.7, 129.0, 127.3, 125.8, 118.7, 111.9, 26.8; FTIR (NaCl/thin film) 3057, 2225, 1686, 1476, 1374, 1368, 1273, 1238, 1189, 902 cm^{-1}; HRMS (CI+) [M+H]+ calculated for $C_{13}H_{10}NO$: 196.0762, found: 196.0762.

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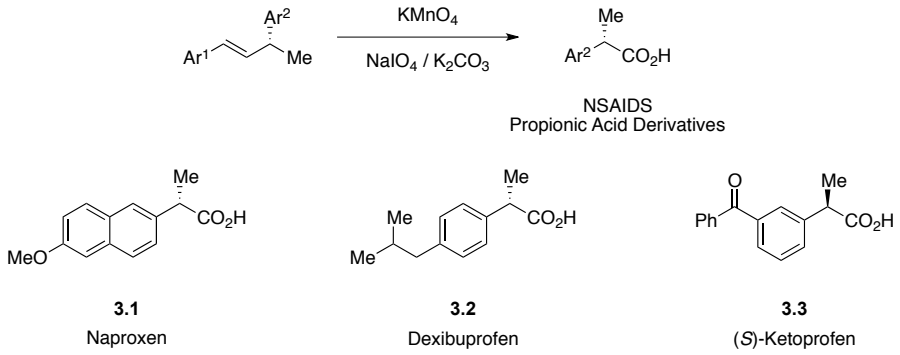
Chapter 3

ENANTIOSPECIFIC NICKEL-CATALYZED CROSS-COUPLINGS OF ALLYLIC PIVALATES AND ARYLBOROXINES

3.1. Introduction

Transition metal-catalyzed allylic arylation is an important class of reaction for carbon-carbon bond formation.[1-4] The allylic arylation of unsymmetrical, secondary 1,3-disubstituted electrophiles will give access to allyl arenes with vinyl-substituted benzylic stereocenters. These compounds often display bioactivity and are powerful synthetic intermediates in the preparation of many propionic acid derivatives (Scheme 3.1), which are potent non-steroidal anti-inflammatory drugs. [5,6]

Scheme 3.1: Allyl Arenes as Synthetic Intermediates

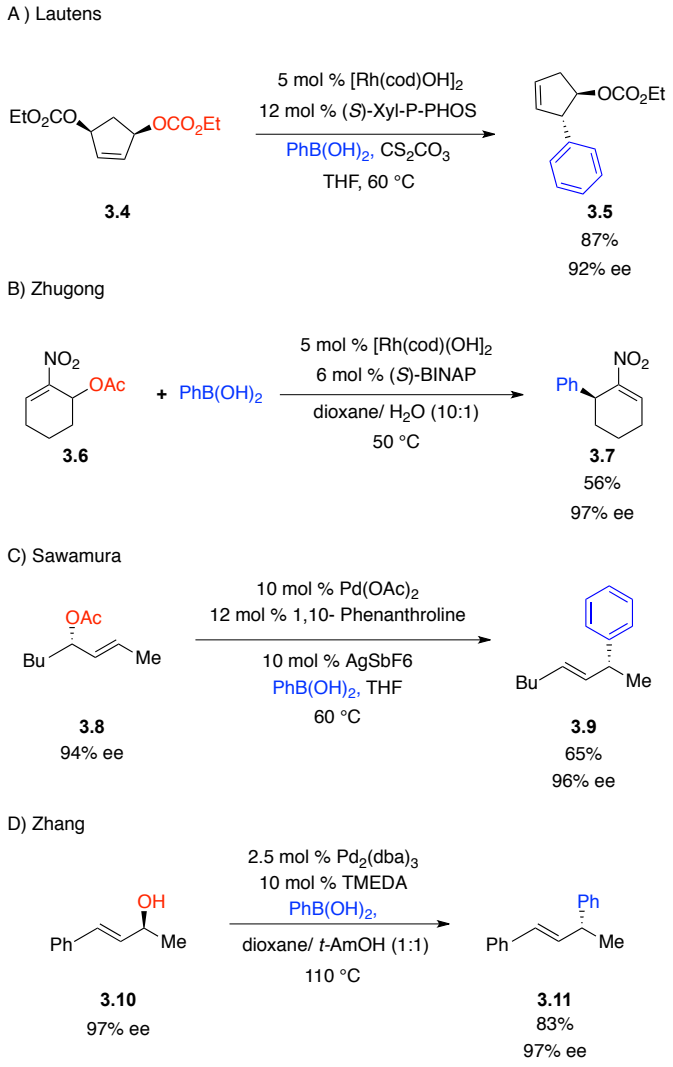


Prior-Art

A powerful method to access to these products in high enantioselectivity and regioselectivity is through cross-coupling strategies involving non-precious metal catalysts and mild, air-stable coupling partners like organoboranes [7,8] to enable wide functional group tolerance. There are methods involving cross-couplings of allylic electrophiles and organoboranes using precious metal catalysts like rhodium[9-14] and

palladium (Scheme 3.2). [6,15-21] However, the use of non-precious metal catalysis is less developed, but would facilitate a reliable supply of metal catalysts for large-scale industrial applications and would have a significant impact on the environment.[22-24]

Scheme 3.2: Examples of Allylic Arylations using Precious Metals

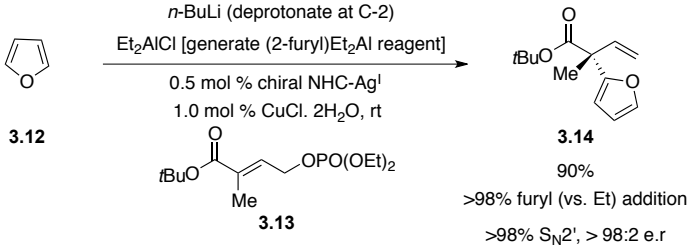


Enantiospecific or enantioselective allylic arylations using non-precious metal catalysts are less developed and usually involve air-sensitive and harsh organometallic reagents. For example, with copper catalysts, Grignard,[25-31] organoaluminum[32,33] or organozinc reagents,[34] are often required, which limit the functional groups that can be

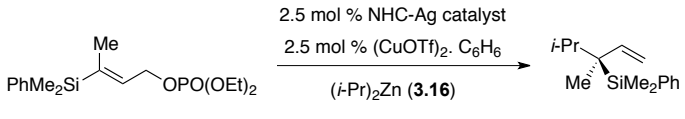
tolerated (Scheme 3.3). Only a few methods of copper-catalyzed allylic arylations are known using organoborane cross-coupling partners, which result in the formation of the γ-substituted product (Scheme 3.4).[35-37]

Scheme 3.3: Examples of Copper-Catalyzed Allylic Arylation involving Air-Sensitive Coupling Partner

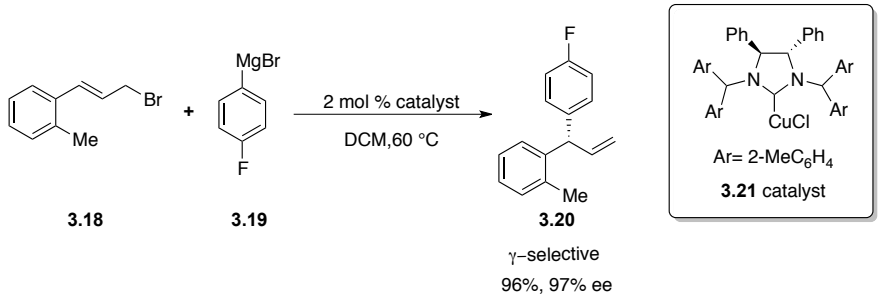
A) With Organoaluminum (Hoveyda)



B) With Organozinc (Hoveyda)



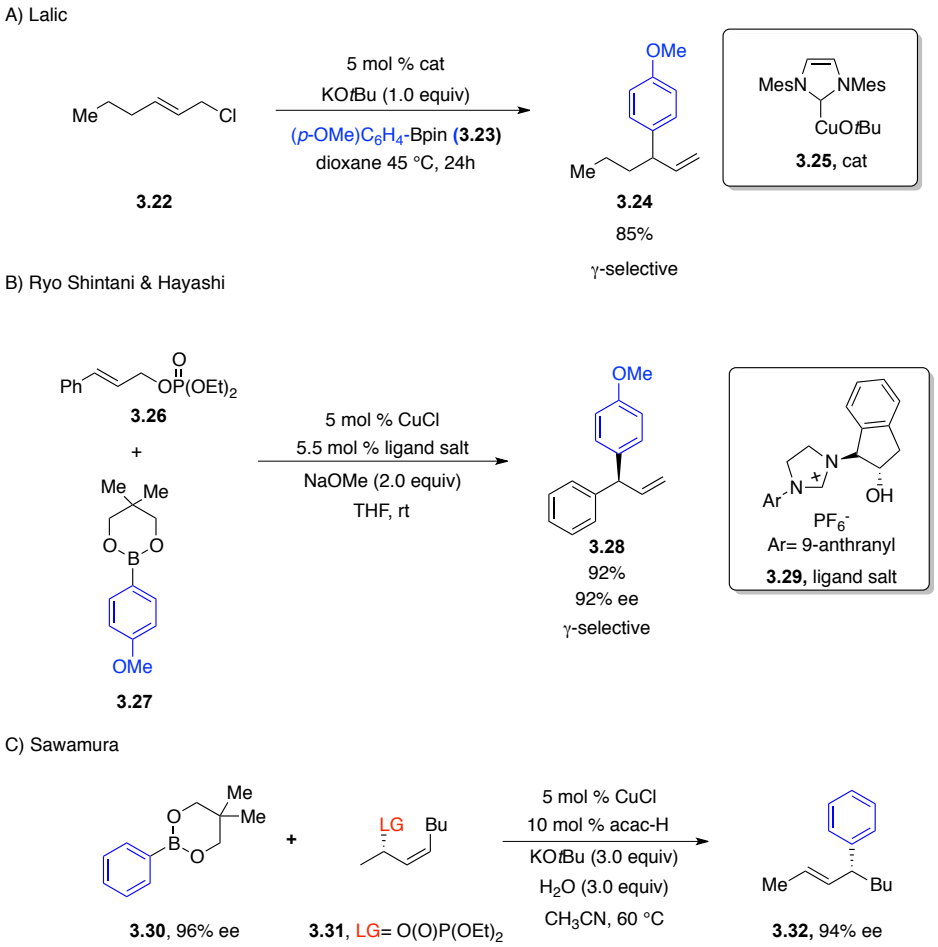
C) With Grignards (Tomioka)



Inspired by enantiospecific nickel-catalyzed cross-coupling of benzylic pivalates and arylboroxines in our laboratory,[38] we envisioned that nickel-catalyzed cross-coupling of allylic pivalates with organoboranes would give access to 1,3-disubstituted, allyl arenes with high levels of stereochemical fidelity and regioselectivity. Prior art in nickel-

catalyzed cross-coupling of allylic electrophiles includes the use of Grignard reagents with both enantioselective and diastereoselective variants. [39-44]

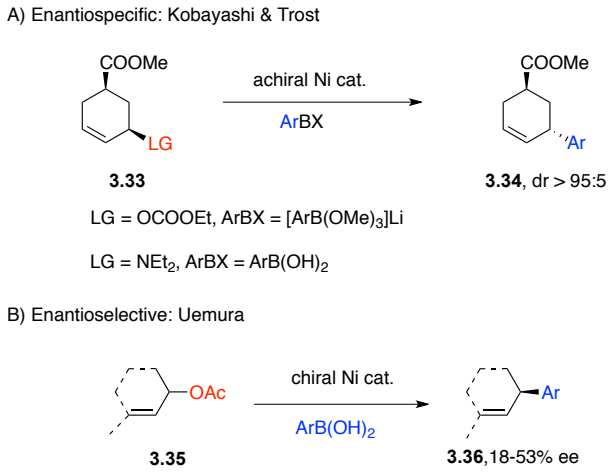
Scheme 3.4: Copper-Catalyzed Allylic Arylation using Organoboranes



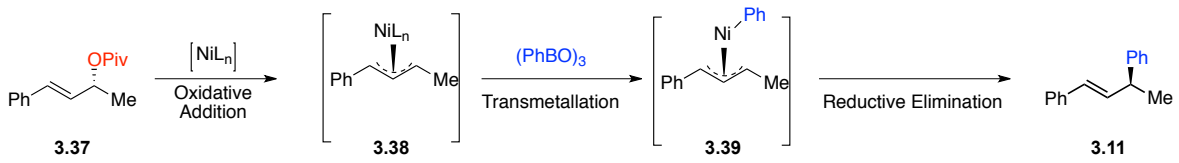
In terms of organoborane coupling partners, Trost[45] and Kobayashi[46-50] have shown cross-couplings of allylic electrophiles (amines and carbonates) with organoborate and boronic acids. With prototypical cyclic substrate **3.33,** they demonstrated that the reaction proceeds with inversion of stereochemistry (Scheme 3.5A). Uemura[51] has shown the nickel-catalyzed cross-coupling between aryl boronic acids with allylic acetates with moderate enantioselectivity (Scheme 3.5B). To the best of my knowledge, however, no

enantiospecific or enantioselective nickel-catalyzed cross-coupling of acyclic allylic electrophiles and organoboranes to form enantioenriched allylarenes has been reported. Towards this goal, I, in collaboration with my colleague Qi Zhou, have developed an enantiospecific, nickel-catalyzed arylation of allylic pivalates using organoboranes as cross-coupling partners (Scheme 3.6).

Scheme 3.5: Nickel-Catalyzed Enantioselective and Enantiospecific Arylation.



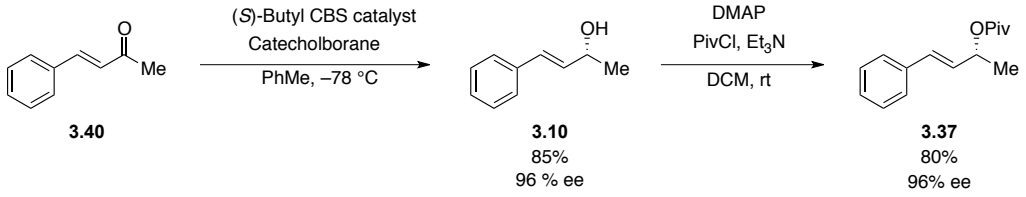
Scheme 3.6: Enantiospecific Cross-Couplings of Allylic Pivalates and Arylboroxines



3.2 Results and Discussion

Our initial studies were focused on studying the arylation of enantioenriched allylpivalate **3.37,** which was readily prepared from enantioenriched allyl alcohol, obtained through CBS-reduction of cinnamyl ketone **3.40** in high enantioselectivity and yield (Scheme 3.7).

Scheme 3.7: Synthesis of Allylic Pivalates



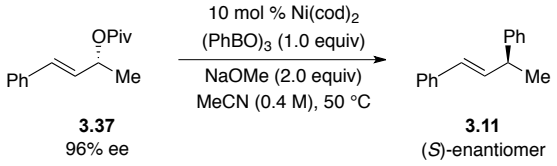
3.40

3.10
85%
96 % ee

3.37
80%
96% ee

When we tested the optimized conditions for the arylation of benzylic pivalates,[38] using $Ni(cod)_2$ without added phosphine ligand, and sodium methoxide as base, the desired arylated product **3.11** was obtained in only 18 % ee (Table 3.1, entry1). When we used acetonitrile as solvent, we obtained a moderate enantiomeric excess of 57% with similar yield (entry 2). In order to further increase the ee of the product, we examined various phosphine ligands. With bidendate phosphine ligands, poor ee's were observed (entries 3 and 4). However, with monodentate phosphine ligands, a significant improvement in the enantiomeric excess (entries 5–7) was observed. Among the monodentate phosphine ligands examined, benzyldiphenyl phosphine gave the highest ee of the arylated product **3.11**(entry 7).

Table 3.1: Initial Results[a]



3.37
96% ee

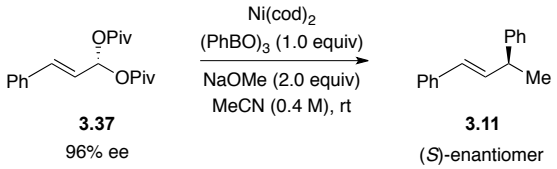
3.11
(*S*)-enantiomer

entry	ligand (mol %)	yield[b] (%)	ee[c] (%)
1[d]	none	95	18
2	none	96	57
3	dppp (11)[e]	90	57
4	XantPhos (11)[e]	30	27
5	PCy_3 (22)	80	84
6	$CyPPh_2$ (22)	83	85
7	$BnPPh_2$ (22)	85	87

[a]Conditions: pivalate **3.37** (96% ee, 0.1 mmol, 1.0 equiv), $(PhBO)_3$ (0.1 mmol, 1.0 equiv), $Ni(cod)_2$, NaOMe (0.2 mmol, 2.0 equiv), MeCN (0.4 M), 4h, unless otherwise noted. [b]Determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as internal standard. [c] Determined by HPLC on a chiral stationary phase. [d] Used PhMe instead of MeCN. [e] dppp = 1,3-bis(diphenylphosphino)propane. XantPhos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene.

In efforts to further optimize the reaction, we lowered the temperature of the reaction and observed an increase in yield (Table 3.2, entry 1). Reducing the catalyst loading to 2 mol % (entry 3) resulted in excellent enantiomeric excess and yield. The fact that higher ee's are observed with reduced catalyst loading suggests that nickel may have a role in the epimerization pathway.

Table 3.2: Further Optimization[a]



3.37
96% ee

3.11
(*S*)-enantiomer

entry	Ni (mol %)	ligand (mol %)	yield[b] (%)	ee[c] (%)
1	10	$BnPPh_2$ (22)	90	87
2	5	$BnPPh_2$ (10)	90	92
3	2	$BnPPh_2$ (5)	92	94
4[d]	2	$BnPPh_2$ (5)	72	93
5[e]	2	$BnPPh_2$ (5)	86	94

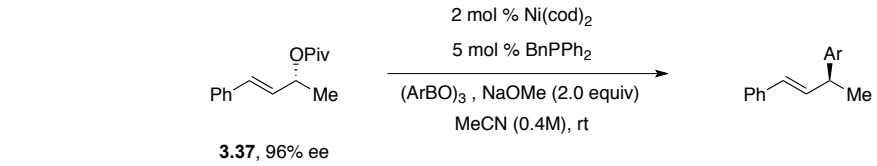
[a]Conditions: pivalate **3.37** (96% ee, 0.1 mmol, 1.0 equiv), $(PhBO)_3$ (0.1 mmol, 1.0 equiv), $Ni(cod)_2$, NaOMe (0.2 mmol, 2.0 equiv), MeCN (0.4 M), 4h, unless otherwise noted. [b]Determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as internal standard. [c] Determined by HPLC on a chiral stationary phase. [d] $PhB(OH)_2$ (0.3 mmol, 3.0 equiv). [e] Added H_2O (0.15 mmol, 1.5 equiv).

When we used phenylboronic acid instead of phenylboroxine under the optimized conditions, we observed the same levels of enantioselectivity but with reduced yield (entry 4). The reason for this is not clear and may not be due to the presence of water. When we add 1.5 equiv of water, we observe good ee and yield of the product (entry 5).

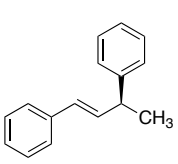
Scope in Boroxine

Under the optimized conditions, we observed wide scope with respect to the arylboroxine (Scheme 3.8). The *E*-isomer with α-selectivity was formed exclusively with high levels of chirality transfer and in excellent yields with both electron-deficient and electron-rich arylboroxines. A wide variety of functional groups, such as chloride (**3.41**), bromide (**3.42**), ketone (**3.43**), ester (**3.44**), nitrile (**3.45**), trifluromethyl (**3.46**), vinyl (**3.47**), acetal (**3.48**), ether (**3.49**), fluoride (**3.50**) and thioether (**3.51**) groups, are well tolerated under our optimized conditions. Specifically, the chloride, bromide, vinyl, thioether, and acetal products highlight the mildness and orthogonality of our optimized conditions. We did not observe any undesired *β*-hydride elimination products under our reaction conditions.

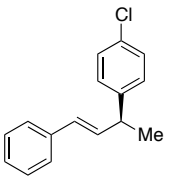
Scheme 3.8: Scope in Arylboroxine[a]



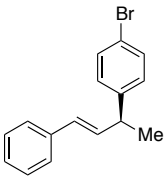
3.37, 96% ee



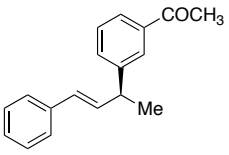
3.11, 88%
95% ee, 99% es



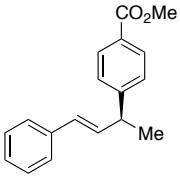
3.41, 75%
94% ee, 98% es



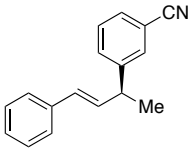
3.42, 63%
96% ee, 100% es



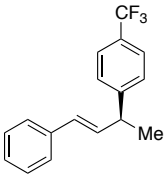
3.43[b], 86%
91% ee, 96% es



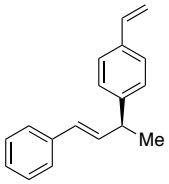
3.44, 93%
89% ee, 93% es



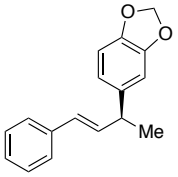
3.45, 84%
93% ee, 97% es



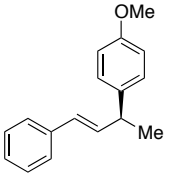
3.46, 78%
91% ee, 95% es



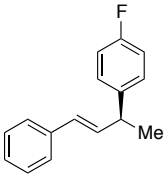
3.47, 93%
91% ee, 95% es



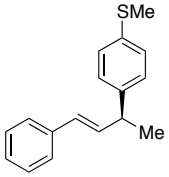
3.48, 88%
92% ee, 96% es



3.49, 90%
88% ee, 92% es



3.50, 86%
93% ee, 97% es



3.51, 95%
93% ee, 97% es

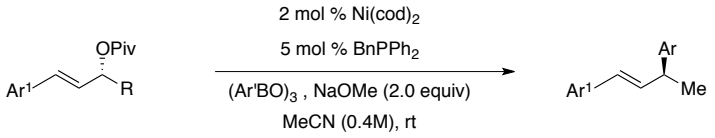
[a]Conditions: pivalate **3.37** (96% ee, 0.3 mmol, 1.0 equiv), $(PhBO)_3$ (0.3 mmol, 1.0 equiv), $Ni(cod)_2$ (2 mol %), $BnPPh_2$ (5 mol %), NaOMe (0.6 mmol, 2.0 equiv), MeCN (0.4 M), 4h, rt, unless otherwise noted. Yields are average of duplicate experiments (± 0-3%) and ee's are average of duplicate experiments (± 0-1%) determined by HPLC on a chiral stationary phase, % es = enantiospecificity= [(ee of product/ (ee of starting material)] × 100%. [b] ee of the SM is 95%.

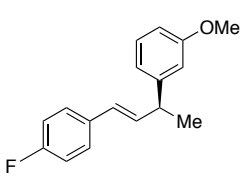
Scope in Pivalate

With regard to the allylic pivalate, a wide variety of allylic pivalates including both electron-rich and electron-poor were cross-coupled successfully with high levels of stereochemical fidelity and high yields (Scheme 3.9).

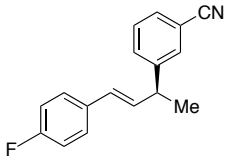
As with the arylboroxines, chloride functionality on the pivalate is well tolerated (**3.54**, **3.55** and **3.56**). The formation of dichloride compound **3.55** in high enantomeric excess highlights the mildness and orthogonality our optimized reaction conditions. Naphthyl product **3.59,** which contains an extended π-system, was formed in 77% yield and 91% ee. A tertiary amine functionality was well tolerated, as demonstrated by the formation of compound **3.56** in high ee. Compound **3.61** containing furyl substituent was also formed in good ee and yield. Increased steric bulk on the alkyl substituent was also well tolerated, which is demonstrated by ethyl and cyclohexyl products (**3.60** and **3.62**), however, the cyclohexyl product **3.62** was obtained in lower enantiomeric excess.

Scheme 3.9: Scope in Pivalate[a]

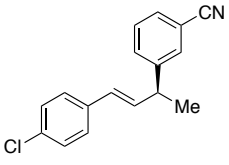




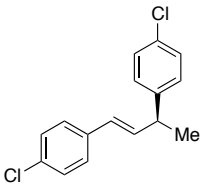
3.52, 90%
91% ee, 93% es
SM 98% ee



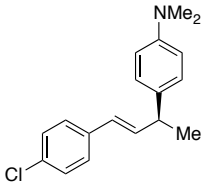
3.53, 74%
96% ee, 98% es
SM 98% ee



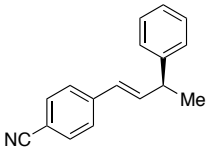
3.54, 86%
90% ee, 94% es
SM 96% ee



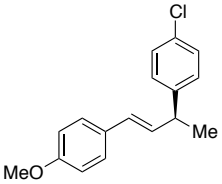
3.55, 86%
90% ee, 95% es
SM 96% ee



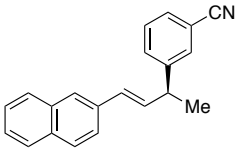
3.56, 83%
89% ee, 94% es
SM 96% ee



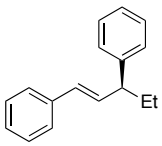
3.57, 85%
76% ee, 95% es
SM 80% ee



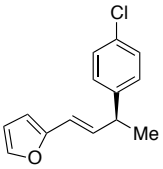
3.58, 83%
76% ee, 94% es
SM 82% ee



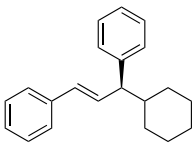
3.59, 77%
91% ee, 95% es
SM 96% ee



3.60, 81%
82% ee, 91% es
SM 90% ee



3.61[b], 82%
86% ee, 89% es
SM 97% ee



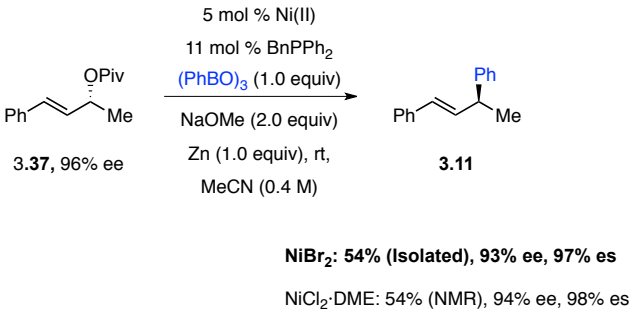
3.62, 91%
62% ee, 71% es
SM 87% ee

[a]Conditions: pivalates (0.3 mmol, 1.0 equiv), $(PhBO)_3$ (0.3 mmol, 1.0 equiv), $Ni(cod)_2$ (2 mol %), $BnPPh_2$ (5 mol %), NaOMe (0.6 mmol, 2.0 equiv), MeCN (0.4 M), 4h, rt, unless otherwise noted. Yields are average of duplicate experiments (± 0-3%) and ee's are average of duplicate experiments (± 0-1%) determined by HPLC on a chiral stationary phase, % es = enantiospecificity= [(ee of product/ (ee of starting material)] × 100%. [b] single experiment.

With Ni(II) salts

We were gratified to see that the catalyst generated in situ from $NiBr_2$, $BnPPh_2$ and Zn was effective in forming arylated product **3.11** in high levels of stereochemical fidelity and moderate yield. These conditions allow the reaction to be set up on the bench-top, without the need of an inert atmosphere glove box (Scheme 3.10).

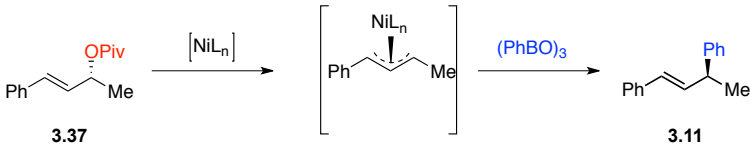
Scheme 3.10: Reaction with Ni(II) Salts



Mechanism and Regioselectivity

Based on the literature precedent in nickel-catalyzed allylations,[39-48,50-54] we propose the reaction proceeds through a π-allylnickel intermediate (Scheme 3.11).

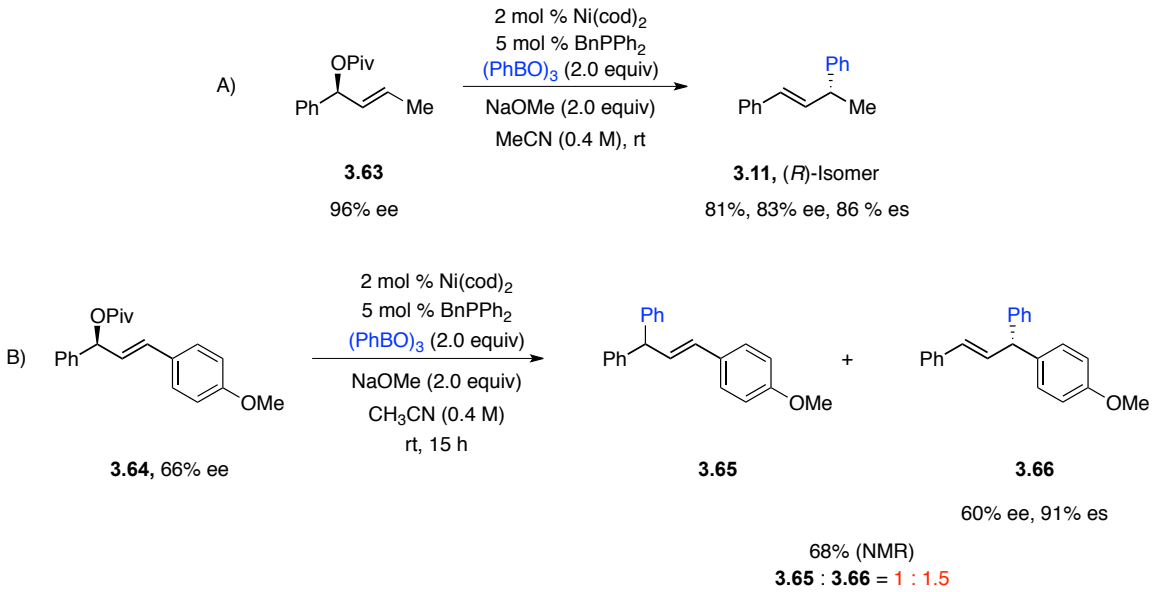
Scheme 3.11: Proposed Mechanism of Ni-Catalyzed Arylation



In order to test this hypothesis, we prepared pivalate **3.63,** the regioisomer of our model substrate **3.37,** and subjected it to the optimized reaction conditions (Scheme 3.12A). We obtained product **3.11** in 83% ee and 81% yield with inversion in stereochemistry. The decrease in ee may be due to the epimerization of the quickly

formed π-allylnickel intermediate. The observation that both the regioisomers of starting material give rise to the same product **3.11** suggests the intermediacy of an π-allylnickel intermediate. Also consistent with this proposal, the arylation of 1,3-diaryl substituted pivalate **3.64** gave the regioisomers **3.65** and **3.66** in 1:1.5 ratio and 68% combined yield. Regioisomer **3.66** was obtained in 91% es (Scheme 3.12B).

Scheme 3.12: Regioselectivity Experiments



Determination of Absolute Configuration

From X-ray crystallographic data, we confirmed the absolute configuration of the compound **3.55** as *S*, which indicates that the allylic arylation proceeds with inversion of configuration at the carbon stereocenter (Figure 3.1).

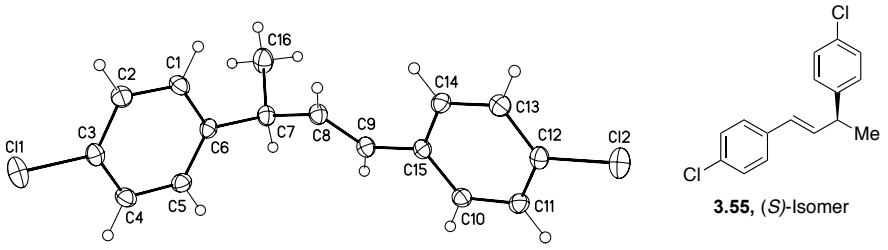
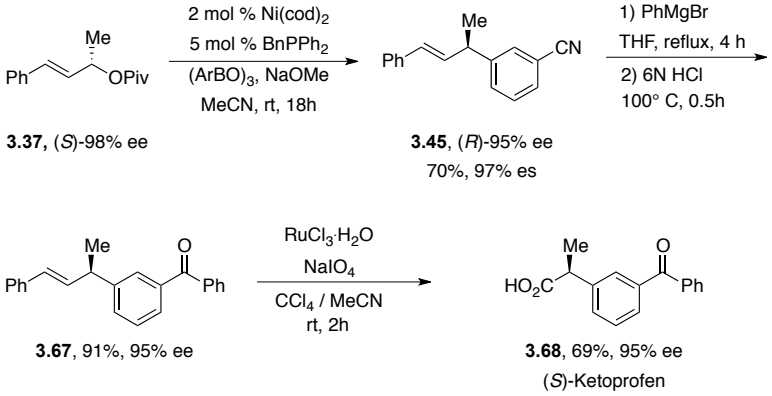


Figure 3.1: Molecular diagram of (*S*)-3.55 with ellipsoids at 30% probability. H-atoms depicted with arbitrary radii. (CCDC-973168)

To ascertain stereochemistry further and demonstrate the utility of our method, we elaborated compound **3.45,** obtained in 95% ee, to synthesize the non-steroidal anti-inflammaotory drug (*S*)-ketoprofen in two-steps. By comparing the optical rotation values of this ketoprofen sample to literature values,[55,56] the absolute configuration of compound **3.68** was confirmed to be *S,* again confirming that the allylic arylation proceeds with inversion of stereochemistry (Scheme 3.13).

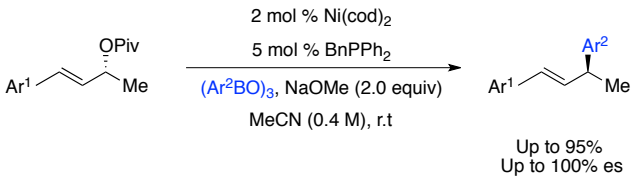
Scheme 3.13: Synthesis of (*S*)-Ketoprofen



3.3 Conclusions

We have developed an enantiospecific, nickel-catalyzed cross-coupling of 1,3-disubstituted secondary allylic pivalates and arylboroxines (Scheme 3.14). The 1,3-diaryl allyl products are obtained with high chirality transfer and in high yields with excellent levels of regioselectivity and *E*/*Z* selectivity. Wide functional group tolerance is observed both on the allyl pivalate and arylboroxine. Additionally, much cheaper and air-stable Ni(II) salts can be used as an alternative to $Ni(cod)_2$. This method was published in *Organic Letters*.[57]

Scheme 3.14: Enantiospecific Ni-Catalyzed Cross-Coupling of Allylic Pivalate and Arylboroxines



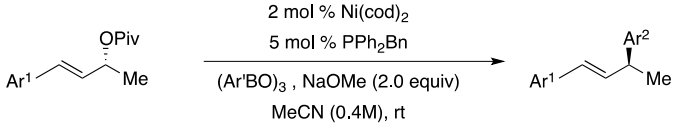
3.4 Experimental Information

Reactions were performed either in a N_2-atmosphere glovebox in oven-dried 1-dram vials with Teflon-lined caps or in oven-dried round-bottomed flasks unless otherwise noted. Flasks were fitted with rubber septa, and reactions were conducted under a positive pressure of N_2. Stainless steel syringes or cannulae were used to transfer air- and moisture-sensitive liquids. Flash chromatography was performed on silica gel 60 (40-63 μm, 60Å) unless otherwise noted. Thin layer chromatography (TLC) was performed on glass plates coated with silica gel 60 with F254 indicator. Commercial reagents were purchased from Sigma Aldrich, Acros, Fisher, Strem, TCI, Combi Blocks, Alfa Aesar, or Cambridge Isotopes Laboratories and used as received with the following exceptions: toluene, CH_2Cl_2, dioxane, MeCN and Et_2O were dried by passing through drying columns. Toluene and MeCN were then degassed by sparging with N_2 and stored over activated 4Å MS in a N_2-atmosphere glovebox. Pivaloyl chloride was purchased from Sigma Aldrich and distilled before use. Boronic acids were purchased from Combi Blocks and were converted to the boroxines according to literature procedure.[58] Racemic products were prepared from the corresponding racemic pivalates using the General Procedure for the cross coupling described below. $CDCl_3$ was stored over oven-dried potassium carbonate. Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on both 400 MHz and 600 MHz spectrometers. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$ = δ 7.26; $(CD_3)_2CO$ = δ 2.07). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon

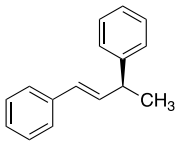
resonances of the solvent ($CDCl_3$ = δ 77.2; $(CD_3)_2CO$ = δ 28.94). Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, dd = doublet of doublets, h = heptet), coupling constants in Hertz (Hz), integration. Infrared (IR) spectra were obtained using FTIR spectrophotometers with material loaded onto a NaCl plate. The mass spectral data were obtained at the University of Delaware mass spectrometry facility. Optical rotations were measured using a 2.5 mL cell with a 0.1 dm path length. Melting points were taken on a Stuart SMP10 instrument.

Stereospecific Cross Coupling of Allylic Pivalates with Boroxines

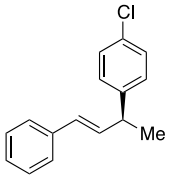
General Procedure for the Stereospecific, Nickel-Catalyzed Coupling of Allylic Pivalates with Boroxines



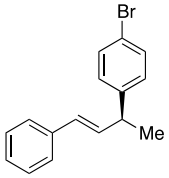
In a N_2-atmosphere glovebox, $Ni(cod)_2$ (1.7 mg, 0.06 mmol, 2 mol %), benzyl diphenyl phosphine (4.2 mg, 0.015 mmol, 5 mol %) and NaOMe (32.5 mg, 0.6 mmol, 2.0 equiv) were weighed into a 1-dram vial. Allylic pivalate (0.30 mmol, 1.0 equiv) and boroxine (0.30 mmol, 1.0 equiv) were added, followed by acetonitrile (0.75 mL, 0.4 M). The vial was capped with a Teflon-lined cap and removed from the glovebox. The mixture was stirred at room temperature for the time specified below. The reaction mixture was then diluted with Et_2O (1.5 mL) and filtered through a plug of silica gel, which was rinsed with Et_2O (10 mL). The filtrate was concentrated and then purified by silica gel chromatography to give the arylated product.



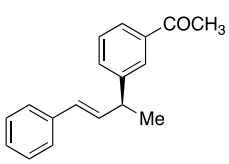
(*S*,*E*)-but-1-ene-1,3-diyldibenzene (3.11). Product **3.11** was prepared via the General Procedure using pivalate **3.37** (prepared in 96% ee). The reaction was stirred at room temperature for 4 h. The crude material was purified by silica gel chromatography (100% hexanes) to give compound **3.11** (run 1: 55.6 mg, 89%; run 2: 54.3 mg, 87%) as colorless oil. The enantiomeric excess was determined to be 95% (run 1: 95% ee; run 2: 95% ee) by chiral HPLC analysis (CHIRALCEL OD-H, 1.0 mL/min, 0.1% *i*-PrOH/hexane λ=254 nm); t_R(major)=6.07 min, t_R(minor)=6.48 min. $[\alpha]_D^{24}$ = –21.1° (c 1.42, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H), 7.35 – 7.27 (m, 6H), 7.25 – 7.19 (m, 2H), 6.46 – 6.37 (m, 2H), 3.69 – 3.63(m, 1H), 1.49 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $(CD_3)_2CO$) δ 145.8, 137.6, 135.2, 128.5, 128.43, 128.40, 127.1, 127.0, 126.11, 126.07, 42.6, 20.9. The spectral data for this compound matches that reported in the literature.[59]



(*S*,*E*)-1-chloro-4-(4-phenylbut-3-en-2-yl)benzene (3.41). Compound **3.41** was prepared via the General Procedure using pivalate **3.37** (prepared in 96% ee). The crude material was purified by silica gel chromatography (100% hexanes) to give compound **3.41** (run 1: 53.7 mg, 74%; run 2: 54.6 mg, 75%) as a yellow oil. The enantiomeric excess was determined to be 94% (run 1: 94% ee; run 2: 94% ee) by chiral HPLC analysis (CHIRALPAK IA, 1.0 mL/min, 100% hexanes, λ=254 nm); t_R(major)=7.38 min, t_R(minor)=8.11 min. $[\alpha]_D^{24}$ = –13.9 ° (c 3.36 $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 6H), 7.25 – 7.18 (m, 3H), 6.46 – 6.29 (m, 2H), 3.68 – 3.59 (m, 1H), 1.46 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 137.5, 134.7, 132.0, 129.0, 128.9, 128.74, 128.71, 127.4, 126.3, 42.1, 21.3. The spectral data for this compound matches that reported in the literature.[60]

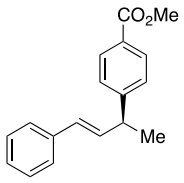


(*S*,*E*)-1-bromo-4-(4-phenylbut-3-en-2-yl)benzene (3.42). Compound **3.42** was prepared via the General Procedure using pivalate **3.37** (prepared in 96% ee). The crude material was purified by silica gel chromatography (100% hexanes) to give compound **3.42** (run 1: 53.4 mg, 62%; run 2: 54.2 mg, 63%) as a yellow oil. The enantiomeric excess was determined to be 96% (run 1: 96% ee; run 2: 95% ee) by chiral HPLC analysis (CHIRALPAK IA, 1.0 mL/min, 100% hexanes, λ=254 nm); t_R(major)=8.22 min, t_R(minor)=9.44 min. $[\alpha]_D^{24}$ = –5.8° (c 1.38, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.42 (m, 2H), 7.38 – 7.34 (m, 2H), 7.30 (dd, *J* = 8.5, 6.7 Hz, 2H), 7.24 – 7.19 (m, 1H), 7.18 – 7.13 (m, 2H), 6.47 – 6.29 (m, 2H), 3.66 – 3.57 (m, 1H), 1.45 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 137.4, 134.6, 131.7, 129.3, 129.1, 128.7, 127.4, 126.3, 120.1, 42.2, 21.3. The spectral data for this compound matches that reported in the literature.[61]

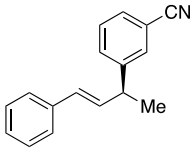


(*S*,*E*)-1-(3-(4-phenylbut-3-en-2-yl)phenyl)ethanone (3.43). Compound **3.43** was prepared via the General Procedure using pivalate **3.37** (prepared in 95% ee). The crude material was purified by silica gel chromatography (6% Et_2O/hexanes) to give compound **3.43** (run 1: 65.4 mg, 87%; run 2: 64.2 mg, 85%) as a colorless oil. The enantiomeric excess was determined to be 91% ee (run 1: 91% ee; run 2: 91% ee) by chiral HPLC analysis (CHIRALPAK IB, 1.0 mL/min, 0.5% *i*-PrOH/hexane, λ=254 nm); t_R(major)=18.72 min, t_R(minor)=21.37 min. $[\alpha]_D^{24}$ = –26.1° (c 2.64, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (t, *J* = 1.8 Hz, 1H), 7.81 (dt, *J* = 7.6, 1.5 Hz, 1H), 7.49 (dt, *J* = 7.7, 1.6 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.39 – 7.34 (m, 2H), 7.33 – 7.27 (m, 2H), 7.24 – 7.18 (m, 1H), 6.57 – 6.22 (m, 2H), 3.76 – 3.68 (m, 1H), 2.62 (s, 3H), 1.50 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ

198.5, 146.4, 137.5, 137.4, 134.6, 132.4, 129.2, 128.9, 128.7, 127.4, 127.1, 126.7, 126.3, 42.7, 26.9, 21.3; FTIR (NaCl/thin film) 3025, 2965, 2927, 1681, 1598, 1448, 1356, 1264, 966, 750, 693 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{18}H_{18}O$: 250.1358, found: 250.1376.

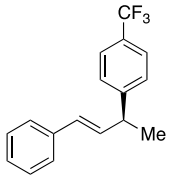


(*S*,*E*)-methyl 4-(4-phenylbut-3-en-2-yl)benzoate (3.44). Compound **3.44** was prepared via the General Procedure using pivalate **3.37** (prepared in 96% ee). The crude material was purified by silica gel chromatography (5% Et_2O/hexanes) to give compound **3.44** (run 1: 75.1 mg, 94%; run 2: 73.4mg, 92%) as a colorless oil. The enantiomeric excess was determined to be 89% (run 1: 89% ee; run 2: 89% ee) by chiral HPLC analysis (CHIRALPAK IA, 0.8 mL/min, 1% *i*-PrOH/hexane, λ=254 nm); t_R(major)=21.99 min, t_R(minor)=19.68 min. $[\alpha]_D^{24}$ = –30.2° (c 2.91, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.97 (m, 2H), 7.43 – 7.28 (m, 6H), 7.25 – 7.18 (m, 1H), 6.50 – 6.30 (m, 2H), 3.92 (s, 3H), 3.75 – 3.67 (m, 1H), 1.49 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 151.1, 137.4, 134.3, 130.0, 129.3, 128.7, 128.3, 127.5, 127.4, 126.3, 52.2, 42.8, 21.2. The spectral data for this compound matches that reported in the literature.[62]

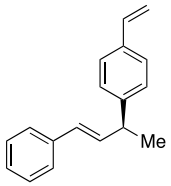


(*S*,*E*)-3-(4-phenylbut-3-en-2-yl)benzonitrile (3.45). Compound **3.45** was prepared via the General Procedure using pivalate **3.37** (prepared in 96% ee). The crude material was purified by silica gel chromatography (2% Et_2O/hexanes) to give compound **3.45** (run 1: 60.2 mg, 85%; run 2: 58.4 mg, 83%) as a colorless oil. The enantiomeric excess was determined to be 93% (run 1: 92% ee; run 2: 93% ee) by chiral HPLC analysis (CHIRALPAK IA, 1.0 mL/min, 2.0% *i*-PrOH/hexane, λ=254 nm); t_R(major)=9.53 min, t_R(minor)=10.52 min. $[\alpha]_D^{24}$ = –19.5° (c

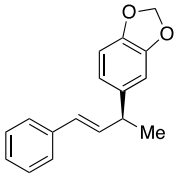
2.40, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (t, *J* = 1.7 Hz, 1H), 7.52 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.46 – 7.28 (m, 5H), 7.26 – 7.20 (m, 1H), 6.48 – 6.40 (m, 1H), 6.31 (dd, *J* = 15.9, 6.7 Hz, 1H), 3.73 – 3.64 (m, 1H), 1.48 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.1, 137.1, 133.6, 132.2, 131.1, 130.2, 129.8, 129.4, 128.7, 127.6, 126.3, 119.2, 112.6, 42.3, 21.1; FTIR (NaCl/thin film) 3025, 2967, 2930, 2228, 1590, 1481, 1446, 960, 798, 751 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{17}H_{15}N$: 233.1204, found: 233.1221.



(*S*,*E*)-1-(4-phenylbut-3-en-2-yl)-4-(trifluoromethyl)benzene (3.46). Compound **3.46** was prepared via the General Procedure using pivalate **3.37** (prepared in 96% ee). The crude material was purified by silica gel chromatography (100% hexanes) to give compound **3-xx** (run 1: 64.6 mg, 78%; run 2: 63.8 mg, 77%) as a colorless oil. The enantiomeric excess was determined to be 91% (run 1: 90% ee; run 2: 91% ee) by chiral HPLC analysis (CHIRALCEL OD-H, 0.6 mL/min, 0.1% *i*-PrOH/hexane, λ=254 nm); t_R(major)=11.14 min, t_R(minor)=12.14 min. $[\alpha]_D^{24}$ = – 9.4° (c 2.32, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.1 Hz, 2H), 7.43 – 7.35 (m, 4H), 7.31 (dd, *J* = 8.5, 6.7 Hz, 2H), 7.25 – 7.19 (m, 1H), 6.47 – 6.32 (m, 2H), 3.76 – 3.68 (m, 1H), 1.49 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.8 (q, J_{C-F} = 1.3 Hz), 137.3, 134.2, 129.5, 128.72, 128.69 (q, J_{C-F} = 32.2 Hz), 127.8, 127.5, 125.6 (q, J_{C-F} = 3.8 Hz), 124.5 (q, J_{C-F} = 271.6 Hz), 120.4, 42.6, 21.2. The spectral data for this compound matches that reported in the literature.[20]

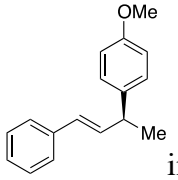


(*S*,*E*)-1-(4-phenylbut-3-en-2-yl)-4-vinylbenzene (3.47). Compound **3.47** was prepared via the General Procedure using pivalate **3.37** (prepared in 96% ee). The crude material was purified by silica gel chromatography (100% hexanes) to give compound **3.47** (run 1: 65.4 mg, 93%; run 2: 64.8 mg, 92%) as yellow oil. The enantiomeric excess was determined to be 91% (run 1: 91% ee; run 2: 91% ee) by chiral HPLC analysis (CHIRALPAK IA, 1.0 mL/min, 100% hexanes, λ=254 nm); t_R(major)=7.82 min, t_R(minor)=9.24 min. $[\alpha]_D^{24}$ = –22.6 ° (c 2.21, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.35 (m, 4H), 7.33 – 7.17 (m, 5H), 6.73 (dd, *J* = 17.6, 10.9 Hz, 1H), 6.49 – 6.34 (m, 2H), 5.75 (dd, *J* = 17.6, 1.0 Hz, 1H), 5.23 (dd, *J* = 10.8, 1.0 Hz, 1H), 3.66 (qd, *J* = 6.9, 5.4 Hz, 1H), 1.48 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5, 137.7, 136.7, 135.8, 135.2, 128.74, 128.67, 127.6, 127.3, 126.5, 126.3, 113.4, 42.5, 21.3; FTIR (NaCl/thin film) 3023, 2964, 2928, 1629, 1509, 1494, 965, 838, 746 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{18}H_{18}$: 234.1409, found: 234.1412.

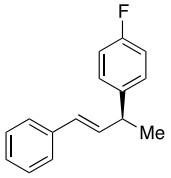


(*S*,*E*)-5-(4-phenylbut-3-en-2-yl)benzo[*d*][1,3]dioxole (3.48). Compound **3.48** was prepared via the General Procedure using pivalate **3.37** (prepared in 96% ee). The crude material was purified by silica gel chromatography (2% Et_2O/hexanes) to give compound **3.48** (run 1: 67.3 mg, 89%; run 2: 65.1 mg, 86%) as a colorless oil. The enantiomeric excess was determined to be 92% (run 1: 92% ee; run 2: 91% ee) by chiral HPLC analysis (CHIRALPAK IA, 0.6 mL/min, 0.1% *i*-PrOH/hexane, λ=254 nm); t_R(major)=13.70 min, t_R(minor)=14.68 min. $[\alpha]_D^{24}$ = –7.7° (c 2.98, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 2H), 7.29 (dd, *J* = 8.5, 6.8 Hz, 2H), 7.24 – 7.16 (m, 1H), 6.84 – 6.70 (m, 3H), 6.44 – 6.30 (m, 2H), 5.93 (s, 2H),

3.61 – 3.52 (m, 1H), 1.43 (d, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 146.0, 139.8, 137.6, 135.4, 128.6, 128.5, 127.2, 126.3, 120.2, 108.3, 108.0, 101.0, 42.4, 21.5; FTIR (NaCl/thin film) 3024, 2964, 2873, 2228, 1486, 1437, 1245, 1040, 938, 693 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{17}H_{16}O_2$: 252.1150, found: 252.1156.

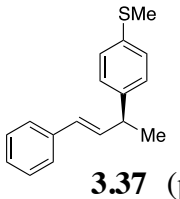


(*S*,*E*)-1-methoxy-4-(4-phenylbut-3-en-2-yl)benzene (3.49). Compound **3.49** was prepared via the General Procedure using pivalate **3.37** (prepared in 96% ee). The crude material was purified by silica gel chromatography (2% Et_2O/hexanes) to give compound **3.49** (run 1: 65.9 mg, 92%; run 2: 63.0 mg, 88%) as colorless oil. The enantiomeric excess was determined to be 88% (run 1: 87% ee; run 2: 89% ee) by chiral HPLC analysis (CHIRALCEL OD-H, 0.8 mL/min, 0.1% *i*-PrOH/hexane, λ=254 nm); t_R(major)=14.47 min, t_R(minor)=13.13 min. $[\alpha]_D^{24}$ = –2.8° (c 3.56, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 2H), 7. 34 – 7.26 (m, 2H), 7.25 – 7.16 (m, 3H), 6.93 – 6.84 (m, 2H), 6.45 – 6.34 (m, 2H), 3.81 (s, 3H), 3.66 – 3.55 (m, 1H), 1.46 (d, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1, 137.8, 137.7, 135.7, 128.6, 128.39, 128.36, 127.2, 126.3, 114.0, 55.4, 41.9, 21.5. The spectral data for this compound matches that reported in the literature.[63]

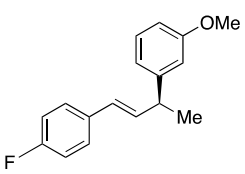


***(S,E)*-1-fluoro-4-(4-phenylbut-3-en-2-yl)benzene (3.50).** Compound **3.50** was prepared via the General Procedure using pivalate **3.37** (prepared in 95% ee). The crude material was purified by silica gel chromatography (100% hexanes) to give compound **3.50** (run 1: 57.6 mg, 87%; run 2: 58.9 mg, 85%) as a yellow oil. The enantiomeric excess was determined to be 93% (run 1: 93% ee; run 2: 93% ee) by chiral HPLC analysis (CHIRALPAK IB, 1.0 mL/min, 100% hexanes, λ=254 nm); t_R(major)=7.86 min, t_R(minor)=7.41 min. $[\alpha]_D^{24}$ = –15.4° (c

2.34, $CHCl_3$): ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.18 (m, 7H), 7.07 – 6.97 (m, 2H), 6.46 – 6.31 (m, 2H), 3.69 – 3.60 (m, 1H), 1.47 (d, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5 (d, $J_{C–F}$ = 243.8 Hz), 141.4 (d, $J_{C–F}$ = 3.2 Hz), 137.5, 135.1, 128.9, 128.8 (d, $J_{C–F}$ = 1.4 Hz), 128.7, 127.3, 126.3, 115.4 (d, $J_{C–F}$ = 21.0 Hz), 42.0, 21.5. The spectral data for this compound matches that reported in the literature.[64]

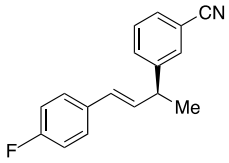


((*S*,*E*)-methyl(4-(4-phenylbut-3-en-2-yl)phenyl)sulfane (3.51). Compound **3.51** was prepared via the General Procedure using pivalate **3.37** (prepared in 96% ee). The crude material was purified by silica gel chromatography (100% hexanes) to give compound **3.51** (run 1: 73.2 mg, 96%; run 2: 70.6 mg, 93%) as a white amorphous solid (mp 49–51 °C). The enantiomeric excess was determined to be 93% (run 1: 93% ee; run 2: 92% ee) by chiral HPLC analysis (CHIRALPAK IA, 1.0 mL/min, 100% hexanes, λ=254 nm); t_R(major)=13.90 min, t_R(minor)=17.71 min. $[\alpha]_D^{24}$ = –8.3° (c 1.44, $CHCl_3$): ^1H NMR (600 MHz, $(CD_3)_2CO$) δ 7.43 – 7.38 (m, 2H), 7.32 – 7.16 (m, 7H), 6.48 – 6.44 (m, 2H), 3.68 – 3.60 (m, 1H), 2.46 (s, 3H), 1.43 (d, J = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.8, 137.5, 135.9, 135.0, 128.6, 128.5, 127.9, 127.2, 127.1, 126.2, 42.1, 21.2, 16.3; FTIR (NaCl/thin film) 3023, 2963, 2920, 2869, 1891, 1799, 1598, 1493, 1446, 1010, 964, 746; HRMS (EI+) $[M]^+$ calculated for $C_{17}H_{18}S$: 254.1129, found: 254.1134



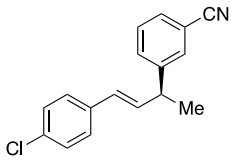
(*S*,*E*)-1-(4-(4-fluorophenyl)but-3-en-2-yl)-3-methoxybenzene (3.52). Compound **3.52** was prepared via the General Procedure using pivalate **3.69** (prepared in 98% ee). The crude material was purified by silica gel chromatography (2% Et_2O/hexanes) to give compound **3.52** (run 1: 69.4 mg, 90%; run 2:

68.2 mg, 89%) as a colorless oil. The enantiomeric excess was determined to be 91% (run 1: 91% ee; run 2: 91% ee) by chiral HPLC analysis (CHIRALPAK IB, 0.6 mL/min, 0.1% *i*-PrOH/hexane, λ=254 nm); t_R(major)=14.19 min, t_R(minor)=17.07 min. $[\alpha]_D^{24}$ = –18.9° (c 2.80, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 2H), 7.29 – 7.23 (m, 1H), 7.02 – 6.95 (m, 2H), 6.90 – 6.75 (m, 3H), 6.39 (d, *J* = 15.9 Hz, 1H), 6.29 (dd, *J* = 15.9, 6.5 Hz, 1H), 3.82 (s, 3H), 3.65 – 3.56 (m, 1H), 1.47 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.1 (d, J_{C-F} = 245.9 Hz), 159.9, 147.4, 134.93 (d, J_{C-F} = 2.3 Hz), 133.80 (d, J_{C-F} = 3.2 Hz), 129.64, 127.72 (d, J_{C-F} = 7.8 Hz), 127.53, 119.83, 115.47 (d, J_{C-F} = 21.5 Hz), 113.46, 111.34, 55.33, 42.73, 21.30; FTIR (NaCl/thin film) 2964, 2834, 1600, 1508, 1259, 1227, 1157, 779 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{17}H_{17}FO$: 256.1263, found: 256.1252.

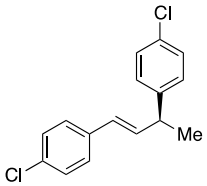


(*S*,*E*)-3-(4-(4-fluorophenyl)but-3-en-2-yl)benzonitrile (3.53). Compound **3.53** was prepared via the General Procedure using pivalate **3.69** (prepared in 98% ee). The crude material was purified by silica gel chromatography (5% Et_2O/hexanes) to give compound **3.53** (run 1: 56.4 mg, 75%; run 2: 55.2 mg, 73%) as a colorless oil. The enantiomeric excess was determined to be 96% (run 1: 96% ee; run 2: 95% ee) by chiral HPLC analysis (CHIRALPAK IA, 1.0 mL/min, 0.1% *i*-PrOH/hexane, λ=254 nm); t_R(major)=11.64 min, t_R(minor)=12.68 min. $[\alpha]_D^{24}$ = –5.0° (c 2.80, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.47 (m, 3H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.36 – 7.29 (m, 2H), 7.03 – 6.96 (m, 2H), 6.38 (dd, *J* = 15.9, 1.3 Hz, 1H), 6.22 (dd, *J* = 15.9, 6.8 Hz, 1H), 3.74 – 3.61 (m, 1H), 1.47 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3 (d, J_{C-F} = 246.6 Hz), 147.0, 133.4 (d, J_{C-F} = 2.2 Hz), 133.2 (d, J_{C-F} = 3.3 Hz), 132.1, 131.1, 130.2, 129.5, 128.7, 127.8 (d, J_{C-F} = 8.0 Hz), 119.2,

115.6 (d, J_{C-F} = 21.5 Hz), 112.7, 42.3, 21.1; FTIR (NaCl/thin film) 3038, 2968, 2228, 1600, 1507, 1481 1227, 1157, 967, 816, 693 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{17}H_{14}FN$: 251.1110, found: 251.1115.

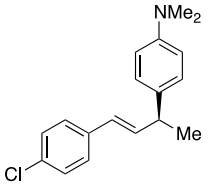


(*S*,*E*)-3-(4-(4-chlorophenyl)but-3-en-2-yl)benzonitrile (3.54). Compound **3.54** was prepared via the General Procedure using pivalate **3.70** (prepared in 96% ee). The crude material was purified by silica gel chromatography (5% Et_2O/hexanes) to give compound **3.54** (run 1: 69.6 mg, 87%; run 2: 68.3mg, 85%) as a colorless oil. The enantiomeric excess was determined to be 90% ee (run 1: 90% ee; run 2: 90% ee) by chiral HPLC analysis (CHIRALCEL OD-H, 0.8 mL/min, 1.0% *i*-PrOH/hexane, λ=254 nm); t_R(major)=15.06 min, t_R(minor)=17.46 min. $[\alpha]_D^{24}$ = –22.1° (c 2.76, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.48 (m, 3H), 7.45 – 7.40 (m, 1H), 7.27 (s, 4H), 6.37 (dd, *J* = 15.9, 1.1 Hz, 1H), 6.28 (dd, *J* = 15.9, 6.5 Hz, 1H), 3.71 – 3.63 (m, 1H), 1.47 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9, 135.6, 134.3, 133.2, 132.1, 131.1, 130.3, 129.5, 128.9, 128.7, 127.6, 119.2, 112.7, 42.3, 21.0; FTIR (NaCl/thin film) 3028, 2967, 2871, 2229, 1896, 1581, 1490, 1091, 968 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{17}H_{14}ClN$: 267.0815, found: 267.0807.

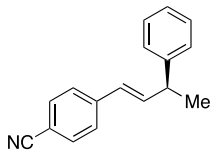


(*S*,*E*)-4,4'-(but-1-ene-1,3-diyl)bis(chlorobenzene) (3.55). Compound (**3.55**) was prepared via the General Procedure using pivalate **3.70** (prepared in 96% ee). The crude material was purified by silica gel chromatography (100% hexanes) to give compound **3.55** (run 1: 72.1 mg, 87%; run 2: 70.8 mg, 85%) as a white solid (mp 69–73 °C). The enantiomeric excess was determined to be 90% (run 1: 90% ee; run 2: 90% ee) by chiral HPLC analysis (CHIRALCEL OD-H, 0.4 mL/min, 100% hexanes, λ=254 nm); t_R(major)=26.72 min, t_R(minor)=24.66 min.

$[\alpha]_D^{24}$ = –11.7° (c 0.76, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.22 (m, 6H), 7.23 – 7.15 (m, 2H), 6.41 – 6.24 (m, 2H), 3.61 (qd, *J* = 7.0, 4.8 Hz, 1H), 1.44 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 136.0, 135.5, 132.9, 132.2, 128.83, 128.81, 128.79, 127.9, 127.5, 42.1, 21.2. The spectral data for this compound matches that reported in the literature.[65]

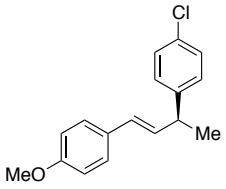


(*S*,*E*)-4-(4-(4-chlorophenyl)but-3-en-2-yl)-*N*,*N*-dimethylaniline (3.56). Compound **3.56** was prepared via the General Procedure using pivalate **3.70** (prepared in 96% ee). The crude material was purified by silica gel chromatography (5% Et_2O/hexanes) to give compound **3.56** (run 1: 71.8 mg, 84%; run 2: 70.2 mg, 82%) as a colorless oil. The enantiomeric excess was determined to be 89% (run 1: 89% ee; run 2: 88% ee) by chiral HPLC analysis (CHIRALPAK IA, 0.8 mL/min, 0.5% *i*-PrOH/hexane, λ=254 nm); t_R(major)=10.18 min, t_R(minor)=8.99 min. $[\alpha]_D^{24}$ = –14.8° (c 0.74, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.20 (m, 4H), 7.19 – 7.10 (m, 2H), 6.78 – 6.69 (m, 2H), 6.40 – 6.29 (m, 2H), 3.56 (qd, *J* = 7.0, 4.4 Hz, 1H), 2.93 (s, 6H), 1.43 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.5, 137.0, 136.4, 133.4, 132.5, 128.7, 128.0, 127.5, 126.8, 113.1, 41.7, 41.0, 21.3; FTIR (NaCl/thin film) 2962, 2926, 2799, 1895, 1646, 1521, 1489 1403, 1090, 1011, 947, 809 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{18}H_{20}ClN$: 285.1284, found: 285.1260.

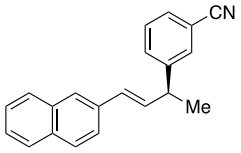


(*S*,*E*)-4-(3-phenylbut-1-en-1-yl)benzonitrile (3.57). Compound **3.57** was prepared via the General Procedure using pivalate **3.71** (prepared in 80% ee). The crude material was purified by silica gel chromatography (5% Et_2O/hexanes) to give compound **3.57** (run 1: 60.2 mg, 86%; run 2: 58.6 mg, 84%) as a colorless oil. The enantiomeric excess was determined to

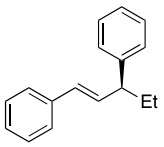
be 76% (run 1: 76% ee; run 2: 76% ee) by chiral HPLC analysis (CHIRALPAK IA, 0.8 mL/min, 1.0% *i*-PrOH/hexane, λ=254 nm); t_R(major)=15.73 min, t_R(minor)=14.13 min. $[\alpha]_D^{24}$ = –51.7° (c 2.28, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 2H), 7.38 – 7.31 (m, 2H), 7.27 – 7.21 (m, 3H), 6.54 (dd, *J* = 15.9, 6.7 Hz, 1H), 6.41 (dd, *J* = 15.8, 1.3 Hz, 1H), 3.75 – 3.63 (m, 1H), 1.49 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 142.2, 139.6, 132.5, 128.8, 127.4, 127.3, 126.8, 126.7, 119.3, 110.3, 42.9, 21.1; FTIR (NaCl/thin film) 3060, 3027, 2967, 2225, 1645, 1581, 1492, 1299, 1012, 969, 819 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{17}H_{15}N$: 233.1204, found: 233.1230.



(*S*,*E*)-1-chloro-4-(4-(4-methoxyphenyl)but-3-en-2-yl)benzene (3.58). Compound **3.58** was prepared via the General Procedure using pivalate **3.72** (prepared in 82% ee). The crude material was purified by silica gel chromatography (4% Et_2O/hexanes) to give compound **3.58** (run 1: 68.2 mg, 83%; run 2: 62.5 mg, 82%) as a white solid (mp 58–61 °C). The enantiomeric excess was determined to be 76% ee (run 1: 76% ee; run 2: 75% ee) by chiral HPLC analysis (CHIRALPAK IA, 0.8 mL/min, 0.1% *i*-PrOH/hexane, λ=254 nm); t_R(major)=11.45min, t_R(minor)=13.71 min. $[\alpha]_D^{24}$ = –8.3° (c 1.07, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 4H), 7.23 – 7.18 (m, 2H), 6.88 – 6.81 (m, 2H), 6.40 – 6.30 (m, 1H), 6.19 (dd, *J* = 15.9, 6.7 Hz, 1H), 3.80 (s, 3H), 3.66 – 3.55 (m, 1H), 1.44 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 144.5, 132.6, 131.9, 130.3, 128.9, 128.7, 128.4, 127.4, 114.1, 55.5, 42.1, 21.4; FTIR (NaCl/thin film) 3030, 2963, 2931, 2835, 1607, 1510, 1251, 1174, 1035, 816 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{17}H_{17}ClO$: 272.0968, found: 272.0960.

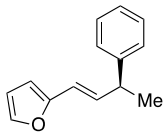


(*S*,*E*)-3-(4-(naphthalen-2-yl)but-3-en-2-yl)benzonitrile (3.59). Compound **3.59** was prepared via the General Procedure using pivalate **3.73** (prepared in 96% ee). The crude material was purified by silica gel chromatography (6% Et_2O/hexanes) to give compound **3.59** (run 1: 66.5 mg, 78%; run 2: 64.2 mg, 76%) as a white solid (mp 90–92 °C). The enantiomeric excess was determined to be 91% (run 1: 90% ee; run 2: 91% ee) by chiral HPLC analysis (CHIRALPAK IB, 1.0 mL/min, 1.0% *i*-PrOH/hexane, λ=254 nm); t_R(major)=18.77 min, t_R(minor)=23.33 min. $[\alpha]_D^{24}$ = –17.8° (c 0.56, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.75 (m, 3H), 7.71 (s, 1H), 7.63 – 7.51 (m, 4H), 7.50 – 7.40 (m, 3H), 6.59 (d, *J* = 15.9 Hz, 1H), 6.44 (dd, *J* = 15.9, 6.8 Hz, 1H), 3.78 – 3.69 (m, 1H), 1.52 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.1, 134.6, 134.1, 133.7, 133.0, 132.2, 131.2, 130.3, 130.0, 129.5, 128.4, 128.1, 127.8, 126.5, 126.2, 126.0, 123.6, 119.2, 112.7, 42.5, 21.2; FTIR (NaCl/thin film) 3057, 2967, 2927, 2228, 1627, 1597, 1481, 1267, 934, 813, 747, 694 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{21}H_{17}N$: 283.1361, found: 283.1335.

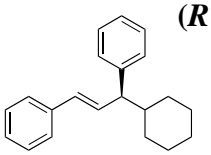


(*S*,*E*)-pent-1-ene-1,3-diyldibenzene (3.60). Compound **3.60** was prepared via the General Procedure using pivalate **3.74** (prepared in 90% ee). The crude material was purified by silica gel chromatography (100% hexanes) to give compound **3.60** (run 1: 52.7 mg, 79%; run 2: 54.7 mg, 82%) as a colorless oil. The enantiomeric excess was determined to be 82% (run 1: 82% ee; run 2: 81% ee) by chiral HPLC analysis (CHIRALCEL OD-H, 0.4 mL/min, 0.1% *i*-PrOH/hexane, λ=254 nm); t_R(major)=13.87min, t_R(minor)=14.76 min. $[\alpha]_D^{24}$ = –15.1° (c 1.45, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 2H), 7.33 – 7.30 (m, 2H), 7.29 – 7.25 (m, 4H), 7.24

– 7.18 (m, 2H), 6.41 (d, *J* = 15.9 Hz, 1H), 6.35 (dd, *J* = 15.9, 7.6 Hz, 1H), 3.32 (q, *J* = 7.5 Hz, 1H), 1.91 – 1.78 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $(CD_3)_2CO$) δ 145.7, 138.6, 135.1, 130.2, 129.30, 129.27 128.4, 127.8, 126.94, 126.90, 52.0, 29.7, 12.5. The spectral data for this compound matches that reported in the literature.[66]



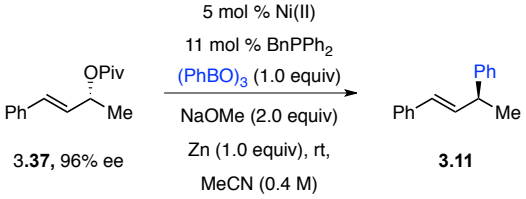
(*S*,*E*)-2-(3-(4-chlorophenyl)but-1-en-1-yl)furan (3.61). Compound **3.61** was prepared via the General Procedure using pivalate **3.75** (prepared in 97% ee). The crude material was purified by silica gel chromatography (100% hexanes) to give compound **3.61** (56.8mg mg, 82%) as colorless oil. The enantiomeric excess was determined to be 86% by chiral HPLC analysis (CHIRALCEL OD-H, 0.8 mL/min, 100% hexanes, λ=254 nm); t_R(major)=10.25 min, t_R(minor)=11.07 min. $[\alpha]_D^{24}$ = –48.5° (c 1.38, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 – 7.30 (m, 1H), 7.29 – 7.26 (m, 2H), 7.19 – 7.16 (m, 2H), 6.34 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.30 (dd, *J* = 15.9, 6.7 Hz, 1H), 6.20 – 6.13 (m, 2H), 3.65 – 3.53 (m, 1H), 1.42 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.0, 144.0, 141.7, 133.7, 132.1, 128.9, 128.8, 117.9, 111.4, 107.1, 41.9, 21.2; FTIR (NaCl/thin film) 2966, 2928, 2871, 1897, 1491 1454, 1150, 1094, 1012, 963, 826, 733 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{14}H_{13}ClO$: 232.0655, found: 232.0667.



(*R*,*E*)-(3-cyclohexylpent-1-en-1-yl)benzene (3.62). Compound **3.62** was prepared via the General Procedure using pivalate **3.76** (prepared in 87% ee). The crude material was purified by silica gel chromatography (0.5% Et_2O/hexanes) to give compound **3.62** (run 1: 73.8 mg, 89%; run 2: 76.2 mg, 92%) as a colorless oil. The enantiomeric excess was determined to be 62% (run 1: 62% ee; run 2: 61% ee) by chiral HPLC analysis (CHIRALCEL OD-H, 0.8 mL/min, 100% hexanes, λ=254 nm); t_R(major)=8.46min, t_R(minor)=8.04min. $[\alpha]_D^{24}$ = –6.8° (c 1.89, $CHCl_3$): ^{1}H

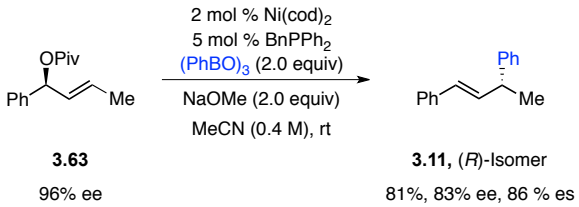
NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.25 (m, 5H), 7.24 – 7.15 (m, 5H), 6.49 – 6.19 (m, 2H), 3.08 (dt, *J* = 8.8, 4.5 Hz, 1H), 2.00 – 1.88 (m, 1H), 1.79 – 1.60 (m, 4H), 1.52 – 1.42 (m, 1H), 1.31 – 1.08 (m, 3H), 1.06 – 0.78 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 137.8, 133.4, 130.3, 128.59, 128.58, 128.1, 127.1, 126.3, 126.2, 56.9, 42.8, 33.2, 31.7, 31.6, 26.8, 26.5. The spectral data for this compound matches that reported in the literature.[67]

Benchtop Experiment: Preparation of (*S*,*E*)-but-1-ene-1,3-diyldibenzene (3.11)



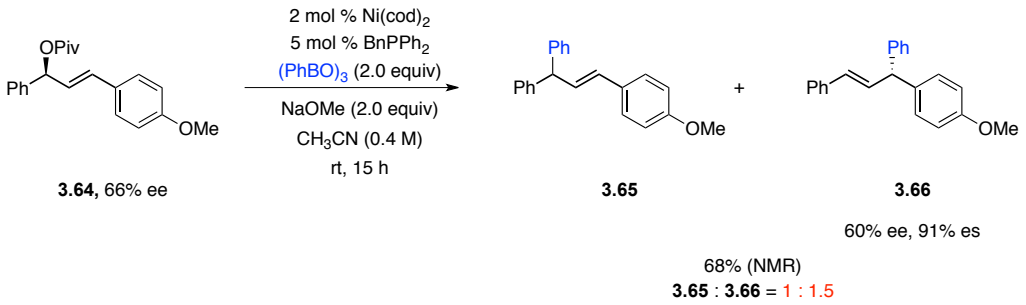
This experiment, including weighing of reagents, was conducted entirely on the benchtop without the use of a glovebox. $NiBr_2$ (5.5 mg, 0.025 mmol, 5 mol %), benzyldiphenyl phosphine (16.6 mg, 0.06 mmol, 12 mol %) and NaOMe (54.03 mg, 1.0 mmol, 2.0 equiv) were weighed into a 1-dram vial. Pivalate **3.37** (116.2 mg, 0.5 mmol, 1.0 equiv, 96% ee), phenylboroxine (156 mg, 0.5 mmol, 1.0 equiv) and zinc (32.6 mg, 0.5 mmol, 1.0 equiv) were added. Capped with a Teflon-lined cap, the vial was evacuated and backfilled with N_2 three times. Acetonitrile (1.25 mL, 0.4 M) was then added. The mixture was stirred for 24 h at room temperature. The reaction mixture was then diluted with Et_2O (3.0 mL) and filtered through a plug of silica gel, which was rinsed with Et_2O (15 mL). The filtrate was concentrated and purified by silica gel chromatography (100% hexanes) to give compound **3.11** (54.4 mg, 53%) as colorless oil. The enantiomeric excess of the product was determined to be 93% by chiral HPLC analysis.

Cross Coupling of Pivalate **3.63.**



The arylation of **3.63** was performed according to the General Procedure, but on a 0.2-mmol scale. In a N_2-atmosphere glovebox, $Ni(cod)_2$ (1.1 mg, 0.04 mmol, 2 mol %), benzyl diphenyl phosphine (2.8 mg, 0.010 mmol, 5 mol %) and NaOMe (21.7 mg, 0.40 mmol, 2.0 equiv) were weighed into a 1-dram vial. Allylic pivalate **3.63** (46.5 mg, 96% ee, 0.20 mmol, 1.0 equiv) and phenylboroxine (62.2 mg, 0.20 mmol, 1.0 equiv) were added, followed by acetonitrile (0.5 mL, 0.4 M). The vial was capped with a Teflon-lined cap and removed from the glovebox. The mixture was stirred at room temperature for 4 h. The reaction mixture was then diluted with Et_2O (1.5 mL) and filtered through a plug of silica gel, which was rinsed with Et_2O (10 mL). The filtrate was concentrated and purified by silica gel chromatography (1% Et_2O/hexanes) to afford (*R*)-**3.11** (33.8 mg, 81%) as a colorless oil. The absolute configuration was determined by comparison to the HPLC trace and optical rotation of (*S*)**-3.11.** The enantiomeric excess was determined by chiral HPLC analysis (CHIRALCEL OD-H, 1.0 mL/min, 0.1% *i*-PrOH/hexane λ=254 nm); t_R(major)=6.59 min, t_R(minor)=6.18 min. $[\alpha]_D^{24}$ = +12.9° (c 1.39, $CHCl_3$).

Cross-Coupling of Pivalate **3.64**.



3.64, 66% ee

3.65

3.66

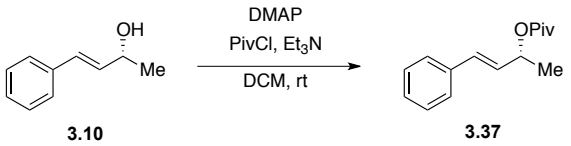
60% ee, 91% es

68% (NMR)

3.65 : **3.66** = 1 : 1.5

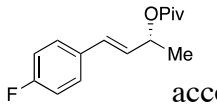
The arylation of **3.64** was performed according to the General Procedure, but on a 0.2-mmol scale. In a N_2-atmosphere glovebox, $Ni(cod)_2$ (1.1 mg, 0.04 mmol, 2 mol %), benzyl diphenyl phosphine (2.8 mg, 0.010 mmol, 5 mol %) and NaOMe (21.7 mg, 0.40 mmol, 2.0 equiv) were weighed into a 1-dram vial. Allylic pivalate **3.64** (64.9 mg, 66% ee, 0.20 mmol, 1.0 equiv) and phenylboroxine (62.2 mg, 0.20 mmol, 1.0 equiv) were added, followed by acetonitrile (0.5 mL, 0.4 M). The vial was capped with a Teflon-lined cap and removed from the glovebox. The mixture was stirred at room temperature for 18 h. The reaction mixture was then diluted with Et_2O (1.5 mL) and filtered through a plug of silica gel, which was rinsed with Et_2O (10 mL). The filtrate was concentrated and purified by silica gel chromatography (5% Et_2O/hexanes) to afford a 1: 1.5 mixture of **3.65** [68] and **3.66**[69] (41.7 mg, 69% combined yield) as colorless oil. The enantiomeric excess of **3.66** was determined by chiral HPLC analysis (CHIRALCEL OD-H, 0.4 mL/min, 0.1% *i*-PrOH/hexane λ=254 nm); t_R(major)=43.72 min, t_R(minor)=37.96 min. $[\alpha]_D^{24}$ = +22.6° (c 0.66, $CHCl_3$). The spectral data of each compound in the mixture matches that reported in the literature. [68,69]

General Procedure for the Preparation of Allylic Pivalates: Preparation of (R)-4-phenylbutan-2-yl Pivalate (**3.37**)

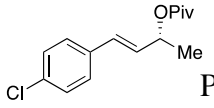


3.10 **3.37**

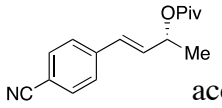
(*R*)-4-Phenyl-3-buten-2-ol **3.10** (1.80 g, 12.2 mmol, 1.0 equiv, 96% ee) and DMAP (149.5 mg, 1.22 mmol, 0.10 equiv) were dissolved in CH_2Cl_2 (20 mL, 0.61 M). Et_3N (3.5 mL, 24.5 mmol, 2.0 equiv) and pivaloyl chloride (1.80 mL, 14.7 mmol, 1.2 equiv) were then added. The reaction mixture was then stirred for 15 h at room temperature, before H_2O (20 mL) was added. The organic layer was extracted with CH_2Cl_2 (2 x 40 mL). The combined organic layers were washed with aq. KOH (2.0 M, 40 mL), dried ($MgSO_4$), filtered and concentrated. The resulting residue was purified by silica gel chromatography (5% Et_2O/hexanes) to give compound **3.37** (2.20 g, 77%) as a white solid (mp 47–50 °C). The enantiomeric excess was determined to be 96% by chiral HPLC analysis (CHIRALPAK IC, 0.8 mL/min, 1.0% *i*-PrOH/hexane, λ=254 nm); t_R(major)=6.80 min, t_R(minor)=8.01 min. $[\alpha]_D^{24}$ = +106.1° (c 2.78, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 2H), 7.34 – 7.28 (m, 2H), 7.25 – 7.21 (m, 1H), 6.59 (d, *J* = 16.0 Hz, 1H), 6.19 (dd, *J* = 16.0, 6.5 Hz, 1H), 5.54 – 5.46 (m, 1H), 1.39 (d, *J* = 6.5 Hz, 3H), 1.21 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.0, 136.6, 131.2, 129.3, 128.73, 128.70, 126.7, 70.7, 38.9, 27.3, 20.5; FTIR (NaCl/thin film) 2977, 2932, 1727, 1479, 1279, 1159, 1041, 965, 747, 692 cm^{-1}; HRMS (EI) $[M]^+$ calculated for $C_{15}H_{20}O_2$: 232.1463, found: 232.1479.



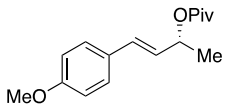
(*R*,*E*)-4-(4-fluorophenyl)but-3-en-2-yl pivalate (3.69). Prepared according to the General Procedure on a 3.32 mmol scale to give **3.69** (660 mg, 79%) as a colorless oil. The enantiomeric excess was determined to be 98% by chiral HPLC analysis (CHIRALPAK IA, 1.0 mL/min, 2.0% *i*-PrOH/hexane, λ=254 nm); t_R(major)=4.66 min, t_R(minor)=5.49 min. $[\alpha]_D^{24}$ = +134.2° (c 0.92, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 2H), 7.05 – 6.96 (m, 2H), 6.55 (d, *J* = 16.0 Hz, 1H), 6.10 (dd, *J* = 16.0, 6.5 Hz, 1H), 5.53 – 5.44 (m, 1H), 1.38 (d, *J* = 6.5 Hz, 3H), 1.24 – 1.19 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.9, 162.6 (d, *J* = 247.1 Hz), 132.76 (d, *J* = 3.3 Hz), 130.05, 129.02 (d, *J* = 2.3 Hz), 128.2 (d, *J* = 8.0 Hz), 115.6 (d, *J* = 21.6 Hz), 70.6, 38.9, 27.3, 20.5; FTIR (NaCl/thin film) 2977, 2935, 2873, 1727, 1509, 1231, 1157, 1041 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{15}H_{19}FO_2$: 250.1369, found: 250.1388.



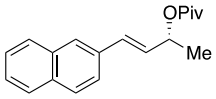
(*R*,*E*)-4-(4-chlorophenyl)but-3-en-2-yl pivalate (3.70). Prepared according to the General Procedure on a 5.40 mmol scale to give **3.70** (1.3 g, 92%) as a white solid (mp 72–74 °C). The enantiomeric excess was determined to be 96% by chiral HPLC analysis (CHIRALPAK IA, 0.8 mL/min, 1.0% *i*-PrOH/hexane, λ=254 nm); t_R(major)=6.09 min, t_R(minor)=7.06 min. $[\alpha]_D^{24}$ = +150.8° (c 0.68, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.24 (m, 4H), 6.53 (dd, *J* = 15.9, 1.2 Hz, 1H), 6.16 (dd, *J* = 16.0, 6.4 Hz, 1H), 5.53 – 5.44 (m, 1H), 1.38 (d, *J* = 6.5 Hz, 3H), 1.21 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.9, 135.1, 133.6, 130.0, 129.9, 128.9, 127.9, 70.5, 39.0, 27.3, 20.4; FTIR (NaCl/thin film) 2923, 2840, 1824, 1713, 1569, 1417, 1380, 1340, 1080 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{15}H_{19}ClO_2$: 266.1074, found: 266.1060.



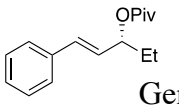
(*R*,*E*)-4-(4-cyanophenyl)but-3-en-2-yl pivalate (3.71). Prepared according to the General Procedure on a 2.49 mmol scale to give **3.71** (425 mg, 66%) as a white solid (mp 84–86 °C). The enantiomeric excess was determined to be 80% by chiral HPLC analysis (CHIRALPAK IC, 1.0 mL/min, 2.0% *i*-PrOH/hexane, λ=254 nm); t_R(major)=24.46 min, t_R(minor)=32.11 min. $[\alpha]_D^{24}$ = +115.0° (c 1.00, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.56 (m, 2H), 7.49 – 7.42 (m, 2H), 6.58 (d, *J* = 16.0 Hz, 1H), 6.31 (dd, *J* = 16.0, 6.1 Hz, 1H), 5.55 – 5.47 (m, 1H), 1.40 (d, *J* = 6.5 Hz, 3H), 1.22 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 141.1, 133.3, 132.7, 129.3, 127.2, 119.1, 111.2, 70.1, 39.0, 27.3, 20.3; FTIR (NaCl/thin film) 2978, 2935, 2872, 2227, 1717, 1604, 1480, 1282, 1173, 1039, 968 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{16}H_{19}NO_2$: 257.1416, found: 257.1408.



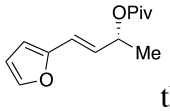
(*R*,*E*)-4-(4-methoxyphenyl)but-3-en-2-yl pivalate (3.72). Prepared according to the General Procedure on a 2.48 mmol scale to give **3.72** (500 mg, 77%) as a white solid (mp 76–80 °C). The enantiomeric excess was determined to be 82% by chiral HPLC analysis (CHIRALPAK IC, 0.7 mL/min, 2.0% *i*-PrOH/hexane, λ=254 nm); t_R(major)=9.23 min, t_R(minor)=10.47 min. $[\alpha]_D^{24}$ = +116.1° (c 1.08, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 2H), 6.89 – 6.81 (m, 2H), 6.53 (d, *J* = 15.9 Hz, 1H), 6.05 (dd, *J* = 15.9, 6.7 Hz, 1H), 5.52 – 5.43 (m, 1H), 3.81 (s, 3H), 1.37 (d, *J* = 6.5 Hz, 3H), 1.20 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.0, 159.5, 130.8, 129.4, 127.9, 127.1, 114.1, 70.9, 55.5, 38.9, 27.3, 20.6; FTIR (NaCl/thin film) 2830, 2821, 1714, 1573, 1380, 1080, 754 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{16}H_{22}O_3$: 262.1569, found: 262.1569.



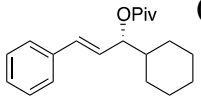
(*R*,*E*)-4-(naphthalen-2-yl)but-3-en-2-yl pivalate (3.73). Prepared according to the General Procedure on a 2.36 mmol scale to give **3.73** (515 mg, 77%) as a white solid (mp 103–105 °C). The enantiomeric excess was determined to be 96% by chiral HPLC analysis (CHIRALPAK IA, 1.0 mL/min, 1.0% *i*-PrOH/hexane, λ=254 nm); t_R(major)=6.12 min, t_R(minor)=6.92 min. $[\alpha]_D^{24}$ = +141.9° (c 0.82, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.71 (m, 4H), 7.59 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.51 – 7.40 (m, 2H), 6.75 (d, *J* = 15.7 Hz, 1H), 6.32 (dd, *J* = 16.0, 6.4 Hz, 1H), 5.60 – 5.52 (m, 1H), 1.43 (d, *J* = 6.5 Hz, 3H), 1.24 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.0, 134.1, 133.7, 133.2, 131.2, 129.6, 128.3, 128.1, 127.8, 126.8, 126.4, 126.1, 123.7, 70.7, 39.0, 27.3, 20.5; FTIR (NaCl/thin film) 2974, 1718, 1653, 1368, 1278, 1164, 1035, 972, 743 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{19}H_{22}O_2$: 282.1620, found: 282.1634.



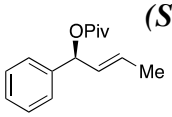
(*R*,*E*)-1-phenylpent-1-en-3-yl pivalate (3.74). Prepared according to the General Procedure on a 1.50 mmol scale to give **3.74** (295 mg, 70%) as a pale yellow oil. The enantiomeric excess was determined to be 90% by chiral HPLC analysis (CHIRALCEL OD-H, 0.8 mL/min, 1.0% i-PrOH/hexane, λ=254 nm); t_R(major)=7.37min, t_R(minor)=5.84min. $[\alpha]_D^{24}$ = +87.1° (c 2.41, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.27 – 7.21 (m, 1H), 6.59 (d, *J* = 15.9 Hz, 1H), 6.13 (dd, *J* = 16.0, 6.9 Hz, 1H), 5.37 – 5.30 (m, 1H), 1.78 – 1.69 (m, 2H), 1.23 (s, 9H), 0.95 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.0, 136.7, 132.1, 128.7, 128.0, 127.9, 126.7, 75.5, 39.10, 27.9, 27.4, 9.7. The spectral data for this compound matches that reported in the literature.[70]



***(R,E)*-4-(furan-2-yl)but-3-en-2-yl pivalate (3.75).** Prepared according to the General Procedure on a 1.66 mmol scale to give **3.75** (320 mg, 74%) as a colorless oil. The enantiomeric excess was determined to be 97% by chiral HPLC analysis (CHIRALPAK IA, 0.6 mL/min, 0.1% *i*-PrOH/hexane, λ=254 nm); t_R(major)=8.98 min, t_R(minor)=9.95 min. $[\alpha]_D^{24}$ = +124.1° (c 1.25, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 1H), 6.44 – 6.34 (m, 2H), 6.25 (d, *J* = 3.3 Hz, 1H), 6.12 (dd, *J* = 15.9, 6.4 Hz, 1H), 5.50 – 5.42 (m, 1H), 1.36 (d, *J* = 6.4 Hz, 3H), 1.21 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.9, 152.3, 142.3, 127.9, 119.5, 111.5, 108.7, 70.3, 39.0, 27.3, 20.4; FTIR (NaCl/thin film) 2976, 2933, 2872, 1727, 1480, 1280, 1161, 1040, 959, 734 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{13}H_{18}O_3$: 222.1256, found: 222.1262.

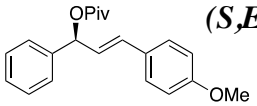


(*R,E*)-1-cyclohexyl-3-phenylallyl pivalate (3.76). Prepared according to the General Procedure on a 1.50 mmol scale to give **3.76** (295 mg, 70%) as a white solid (mp 69–71 °C). The enantiomeric excess was determined to be 87% by chiral HPLC analysis (CHIRALCEL OD-H, 0.8 mL/min, 1.0% i-PrOH/hexane, λ=254 nm); t_R(major)=6.89 min, t_R(minor)=5.32 min. $[\alpha]_D^{24}$ = +29.2° (c 0.82, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.19 (m, 5H), 6.55 (d, *J* = 15.9 Hz, 1H), 6.12 (dd, *J* = 15.9, 7.4 Hz, 1H), 5.23 – 5.14 (m, 1H), 1.85 – 1.59 (m, 6H), 1.22 (s, 10H), 1.22 – 0.99 (m, 4H);^{13}C NMR (101 MHz, $CDCl_3$) δ 177.9, 136.8, 132.8, 128.7, 127.9, 127.0, 126.7, 78.4, 42.3, 39.2, 29.07, 28.6, 27.4, 26.6, 26.2, 26.1; FTIR (NaCl/thin film) 3026, 2929, 2854, 1728, 1479, 1280, 1158, 966, 748 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{20}H_{28}O_2$: 300.2089, found: 300.2066.



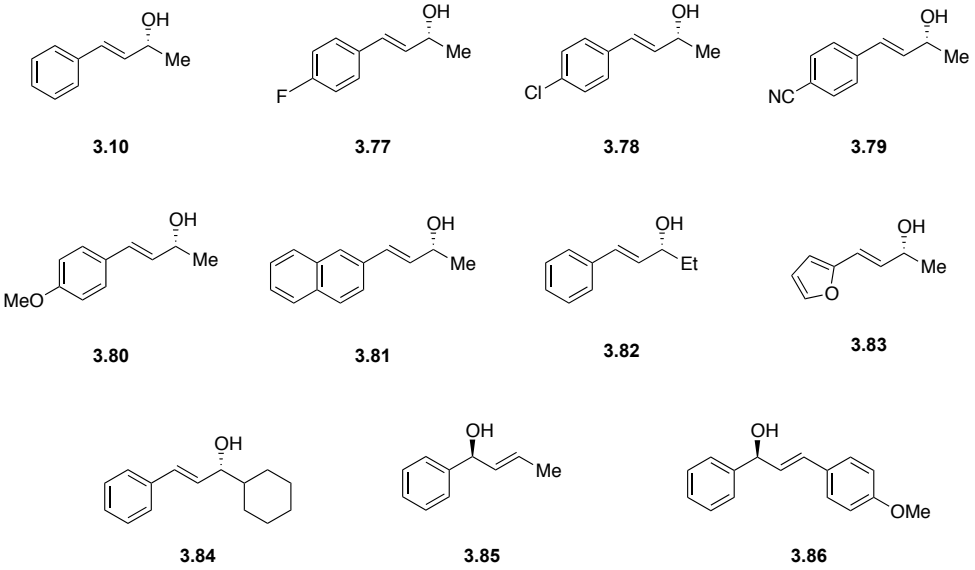
***(S,E)*-1-phenylbut-2-en-1-yl pivalate (3.63).** Prepared according to the General Procedure on a 0.6 mmol scale to give **3.63** (103.5 mg, 78%) as a

colorless oil. The enantiomeric excess was assumed to be unchanged from allylic alcohol **3.63** (96% ee). $[\alpha]_D^{24}$ = –10.2° (c 2.15, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.26 (m, 5H), 6.17 (d, *J* = 6.9 Hz, 1H), 5.80 – 5.70 (m, 1H), 5.67 – 5.60 (m, 1H), 1.71 (d, *J* = 6.6 Hz, 3H), 1.22 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.5, 140.3, 130.0, 129.2, 128.6, 127.8, 126.7, 76.0, 39.0, 27.3, 17.9; FTIR (NaCl/thin film) 2972, 1732, 1480, 1455, 1278, 1149, 963 cm^{-1}; HRMS (EI+) [M]+ calculated for $C_{21}H_{24}O_3$: 232.1463, found: 232.1470.



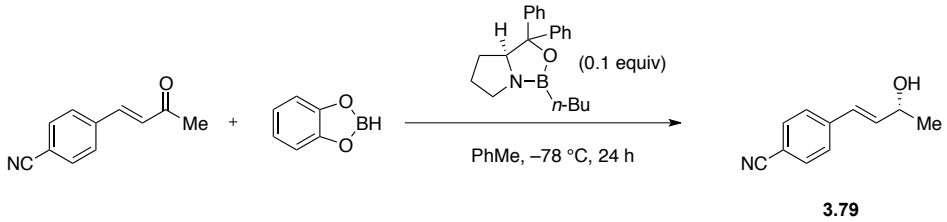
***(S,E)*-3-(4-methoxyphenyl)-1-phenylallyl pivalate (3.64).** Compound **3.64** was prepared via the General Procedure a 1.0 mmol scale. The crude material was purified by silica gel chromatography (5–7.5% Et_2O/hexanes, silica gel pre-saturated with Et_3N) to give **3.64** (167 mg, 54%) as a colorless oil. The enantiomeric excess was determined to be 66% by chiral HPLC analysis (CHIRALPAK IA, 1.0 mL/min, 5% *i*-PrOH/hexane, λ=210 nm); t_R(major)=7.21 min, t_R(minor)=6.26 min. $[\alpha]_D^{24}$ = +4.1° (c 4.83, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 7H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.46 (d, *J* = 15.6 Hz, 1H), 6.37 (d, *J* = 7.2 Hz, 1H), 6.17 (dd, *J* = 15.6, 6.8 Hz, 1H), 3.80 (s, 3H), 1.24 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.4, 159.5, 139.9, 131.9, 129.0, 128.6, 128.0, 127.9, 126.7, 125.6, 113.9, 76.0, 55.3, 38.9, 27.1; FTIR (NaCl/thin film) 2971, 2933, 1732, 1608, 1512, 1277,1252, 1149, 699 cm^{-1}; HRMS (LIFDI) [M]+ calculated for $C_{21}H_{24}O_3$: 324.1720, found: 324.1725.

Preparation of Enantioenriched Allylic Alcohols



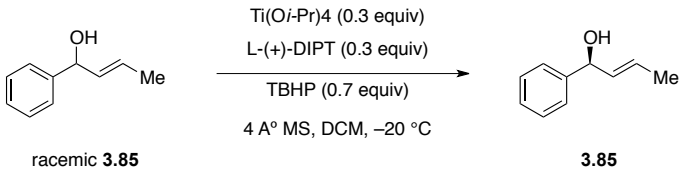
Enantioenriched allylic alcohols (**3.10** to **3.84)** were prepared via CBS reduction of the corresponding ketones according to the procedure reported in the literature.[71,72] These reductions are known to give the stereochemistry shown. A detailed example of the synthesis of **3.79** obtained by this method is given below. **3.85** and **3.86** were prepared according to a reported procedure.[73]

General Procedure for the Preparation of Allylic Alcohols 3-xx to 3-xx: Preparation of (*R*)-4-(4-cyanophenyl)-3-buten-2-ol (**3.79**).



In an oven-dried, 100-mL round-bottomed flask, (*E*)-4-(4-cyanophenyl)-3-buten-2-one (1.08 g, 5.84 mmol, 1.0 equiv) was dissolved in 10 mL PhMe. Under N_2, (*S*)-(−)-2-butyl-CBS-oxazaborolidine (0.58 mL, 0.58 mmol, 1.0 M in PhMe, 0.1 equiv) was added. After stirring at room temperature for 15 min, the mixture was cooled to −78 °C, and catecholborane (1.25 mL, 11.68 mmol, 2.0 equiv) was added slowly. The mixture was stirred at −78 °C for additional 24 h. Sat. $NaHCO_3$ (10 mL) was added, and the crude product was extracted with EtOAc (3 x 20 mL). Tthe combined organic layers were washed with aq. NaOH (1.5 M) until the color of the solution was light yellow, indicating the complete removal of residual catecholborane. The organic layers were then treated with sat. NaCl, dried ($MgSO_4$), filtered and concentrated. The resulting residue was purified by silica gel chromatography (50% Et_2O/hexanes) to give compound **3.79** (920 mg, 92%) as a yellow oil. The enantiomeric excess was determined to be 80% by chiral HPLC analysis (CHIRALPAK IA, 1.0 mL/min, 6.0% *i*-PrOH/hexane, λ=254 nm); t_R(major)=21.77 min, t_R(minor)=19.56 min. $[\alpha]_D^{24} = -9.2°$ (c 2.39, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, J = 8.2 Hz, 2H), 7.45 (d, J = 8.2 Hz, 2H), 6.60 (d, J = 16.0 Hz, 1H), 6.39 (dd, J = 15.9, 5.8 Hz, 1H), 4.57 – 450 (m, 1H), 1.65 (brs, 1H), 1.39 (d, J = 6.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.5, 137.6, 132.57, 127.6, 127.1, 119.1, 111.0, 68.6, 23.6; FTIR (NaCl/thin film) 3421(brs), 2973, 2226, 1604, 1504, 1142, 971 cm^{-1}; HRMS (EI) $[M]^+$ calculated for $C_{11}H_{11}NO$: 173.0841, found: 173.0867.

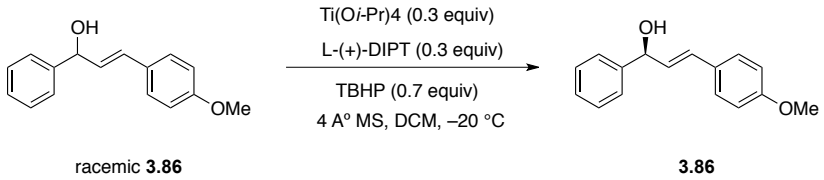
Preparation of Enantioenriched Alcohol (**3.85**)



racemic **3.85** **3.85**

In an oven-dried, 100-mL round-bottomed flask, L-(+)-DIPT (0.74 mL, 3.54 mmol, 0.3 equiv) was added to a suspension of (*E*)-1-phenyl-2-buten-1-ol (1.76g, 11.8 mmol, 1.0 equiv), 4 Å MS (0.85 g, crushed before use), and CH_2Cl_2 (47 mL). The suspension was then cooled to –20 °C, and $Ti(O^iPr)_4$ (1.06 mL, 3.54 mmol, 0.3 equiv) and TBHP (1.5 mL, 8.25 mmol, 5.5 M in decane, 0.7 equiv) were added. The mixture was stirred for 3 h at –20 °C. $FeSO_4 \square 7H_2O$ (6.5 g) and H_2O (40 mL) were then added, followed by tartaric acid (2.2 g), H_2O (20 mL), and aq. HCl (1.0 M, 30 mL) to dissolve the precipitate. The layers were separated. The organic layer was then washed with sat. NaCl, dried (Na_2SO_4), filtered, and concentrated. The resulting residue was purified by silica gel chromatography (15% Et_2O/hexanes) to give compound **3.85** (240 mg, 27%) as colorless oil. The enantiomeric excess was determined to be 96% by chiral GC analysis (Agilent 19091C-133/HP-225, 50% cyanopropyl, 50% phenylmethyl polysiloxane capillary column, initial temperature of 40 °C, ramp 1.0 °C/min to 180 °C, hold for 10 min); t_R(major)=105.67 min, t_R(minor)=106.02 min. $[\alpha]_D^{24}$ = +16.2° (c 3.29, $CHCl_3$). The absolute configuration was determined to be *S* by comparison of the optical rotation to that reported in the literature.[74]

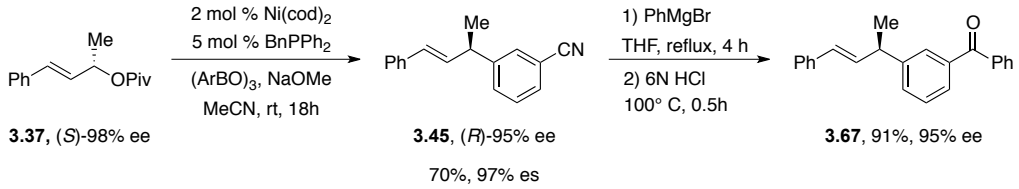
Preparation of Enantioenriched Alcohol (**3.86**)



racemic **3.86** **3.86**

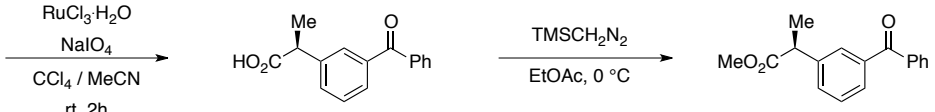
3.86 was prepared on a 8.0-mmol scale from (±)-**3.86** according to the procedure described for **3.85** above. **3.86** (662 mg, 70%) was obtained as a sticky yellow oil from the crude residue by silica gel chromatography (33% Et_2O/hexanes). The enantiomeric excess was determined to be 66% by chiral HPLC analysis (CHIRALPAK IA, 1.0 mL/min, 8.0% *i*-PrOH/hexane, λ=254 nm); t_R(major)=20.38 min, t_R(minor)=17.82 min. [mi$_D^{24}$ = –5.1° (c 4.26, $CHCl_3$). The spectral data for this compound matches that reported in the literature.[75]

Preparation of *(S)*-Ketoprofen



3.37, (*S*)-98% ee **3.45**, (*R*)-95% ee **3.67**, 91%, 95% ee

70%, 97% es



3.68, 69%, 95% ee **3.87**, 81%, 95% ee

(*S*)-Ketoprofen

Compound (*R*)-**3.45** was prepared in 95% ee via the General Procedure using pivalate (*S*)-**3.37** (prepared in 98% ee), as described above.

In a 25-mL, three-neck round-bottomed flask equipped with a reflux condenser, **3.45** (180 mg, 0.77 mmol, 95% ee, 1.0 equiv) and THF (1.6 mL) were combined.

PhMgBr (1.0 M in THF, 3.9 mL, 3.9 mmol, 5.0 equiv) was added slowly at room temperature. Upon completion of addition, the mixture was refluxed for 4 h. After cooling to room temperature, HCl (6 N, 2 mL) was added. The mixture was heated at 100 °C for 30 min. After cooling to room temperature, H_2O (20 mL) was added. The crude product was extracted with Et_2O (3 x 10 mL), dried ($MgSO_4$), filtered, and concentrated. The resulting material was purified by silica gel chromatography (5% Et_2O/hexanes) to give **3.67** (219 mg, 91%) as a light yellow oil. The enantiomeric excess was determined to be 95% by chiral HPLC analysis (CHIRALPAK IA, 1.0 mL/min, 1.0% *i*-PrOH/hexane, λ=220 nm); t_R(major)=13.43 min, t_R(minor)=14.41 min. $[\alpha]_D^{24}$ = –35.2° (c 1.7, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 – 7.79 (m, 2H), 7.75 (s, 1H), 7.64 – 7.61 (m, 1H), 7.60 – 7.56 (m, 1H), 7.53 – 7.45 (m, 3H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.38 – 7.34 (m, 2H), 7.32 – 7.27 (m, 2H), 7.23 – 7.18 (m, 1H), 6.48 – 6.34 (m, 2H), 3.76 –3.69 (m, 1H), 1.50 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.0, 146.2, 138.0, 137.8, 137.5, 134.7, 132.5, 131.6, 130.2, 129.2, 129.0, 128.7, 128.5, 128.39, 128.38, 127.4, 126.3, 42.7, 21.3; FTIR (NaCl/thin film) 3024, 2965, 1658, 1597, 1493, 1447, 1317,1178, 966 cm^{-1}; HRMS (EI) $[M]^+$ calculated for $C_{23}H_{20}O$: 312.1514, found: 312.1534.

A suspension of $RuCl_3 \cdot H_2O$ (7.3 mg, 0.035 mmol, 0.05 equiv) in H_2O (7.3 mL) was added to a solution of **3.67** (219 mg, 0.7 mmol, 1.0 equiv), $NaIO_4$ (749 mg, 3.5 mmol, 5.0 equiv), and CCl_4/MeCN (v/v = 1/1, 9.4 mL) at 0 °C. The mixture was then stirred at room temperature for 2 h.[28] Et_2O (30 mL) was added, and the crude product was then extracted with sat. $NaHCO_3$ (5 x 15 mL). The combined aqueous layers were then cooled to 0 °C, and HCl (6 N) was carefully added until the pH ≤ 1. The crude product was then extracted from aqueous layer with CH_2Cl_2 (5 x 15 mL). The combined organic

layers were dried (Na_2SO_4), filtered, and concentrated. The crude material was purified by silica gel chromatography (0–3% MeOH/CH_2Cl_2) to give (*S*)-ketoprofen **3.68** as an off-white solid (124 mg, 69%). The spectral data of **3.68** matches that reported in the literature.[55,56]

The enantiomeric excess of **3.68** was determined to be 95% based on the corresponding methyl ester **3.87**, which was prepared via a reported procedure on a 0.17 mmol scale.[55] The spectral data of **3.87** matches that reported in the literature.[76] The enantiomeric excess of **3.87** was determined to be 95% by chiral HPLC analysis (CHIRALPAK IB, 0.8 mL/min, 0.5% EtOH/hexane, λ=254 nm); t_R(major)=39.65 min, t_R(minor)=37.39 min. $[\alpha]_D^{24}$ = +43.5° (c 0.80, $CHCl_3$). The absolute configuration of **3.87** was determined to be ***S*** by comparing the optical rotation with reported data.[55,56]

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Chapter 4

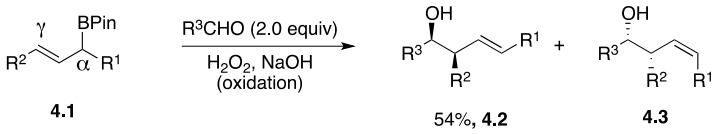
ENANTIOSPECIFIC, NICKEL-CATALYZED BORYLATION OF ALLYLIC PIVALATES

4.1 Introduction

Allylic boronates are powerful synthetic intermediates for carbon–carbon bond formation in organic synthesis via allylic transposition reactions.[1,2] For example, allylic borylation of aldehydes with α-chiral allyl boronate esters with a γ-substituent results in the formation of vicinal stereocenters often with high stereochemical fidelity (Scheme 4.1).1 Cross couplings have also been developed that enable allylic transposition of the stereocenter, as shown in Scheme 4.2.[3]

Scheme 4.1: Allylic Borylation of Aldehydes with α-Chiral Allyl Boronate

!



4.1

R^1= $PhCH_2CH_2$

R^2 = Bu

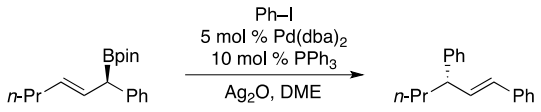
R^3 = Ph

54%, **4.2**

4.3

dr (**4.2**:**4.3**) 99:1

Scheme 4.2: Cross Coupling of Allylic Boronate with Aryl Iodides



4.4

96% ee

4.5

78%, 99:1 *E/Z*

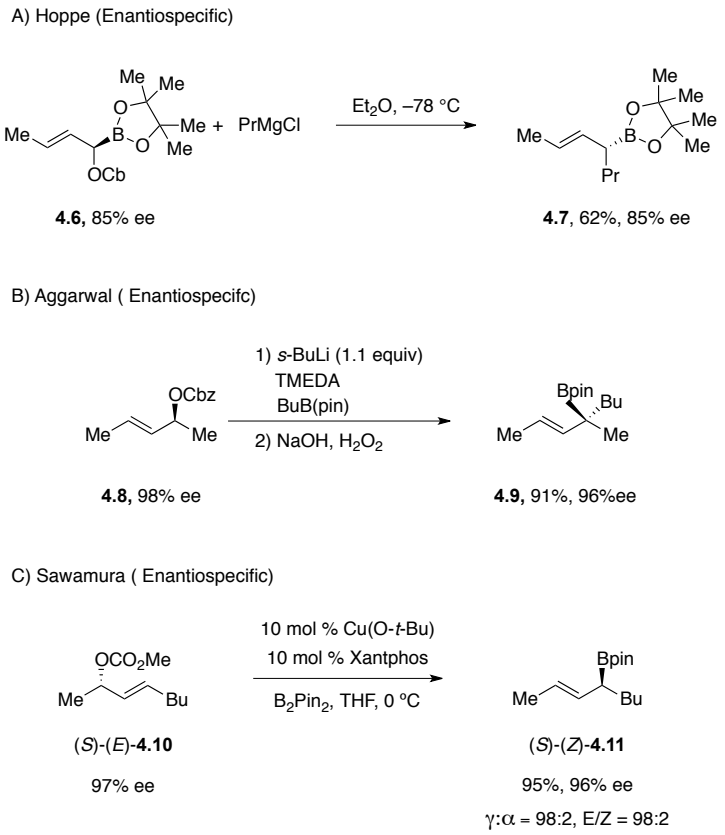
96% ee

Prior-Art

Although a γ-substituent is critical to set a stereocenter upon allylic transposition, most of the methods to form enantioenriched α-chiral allyl boronates result in the formation of products without a γ-substituent.[4-10] Only a few methods are known to form

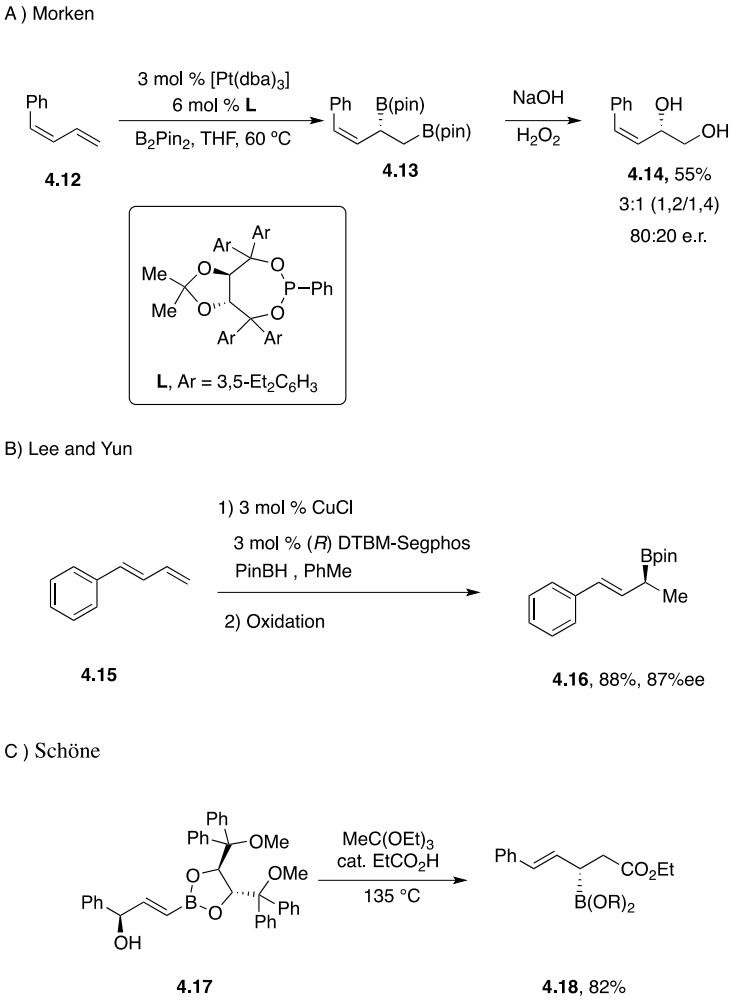
enantioenriched α-chiral allyl boronates with γ-substitution, and most of them are limited to alkyl substituents on the γ-carbon. For example, Hoppe has shown the addition of Grignard reagents to enantioenriched carbamoyloxy-2-alkenylboronates to form γ-alkyl allyl boronates in high stereochemical fidelity (Scheme 4.3A).[11] The Aggarwal group has utilized a lithiation-borylation strategy to form γ-alkyl substituted allyl boronates in high levels of chirality transfer and yields (Scheme 4.3B).[12] The Sawamura group has shown the copper-catalyzed addition of bis(pinacolato)diborane (B_2Pin_2) to enantioenriched allyl carbonates to form γ-alkyl substituted allyl boronates in high stereochemical fidelity and yields (Scheme 4.3C).[13]

Scheme 4.3: Examples of Methods to Form Enantioenriched γ-Alkyl Allyl Boronates[a]



[a]ee's determined above are for the corresponding alcohols obtained from oxidation of boronate.

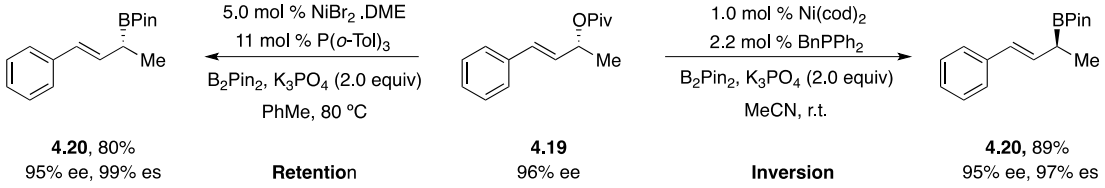
Scheme 4.4: Methods to Form Enantioenriched γ-Aryl Allylic Boronates



Few methods are known to form enantioenriched α-chiral allyl boronates with γ-aryl substitution.[14-16] The Morken group has shown the platinum-catalyzed enantioselective diboration of 1,4-dienes to form γ-aryl allyl boronates in moderate ee's (Scheme 4.4A).[14] Lee and Yun have shown a single example of enantioselective copper-catalyzed hydroboration of 1,4-dienes to form γ-phenyl allyl boronate in good ee and yield (Scheme 4.4B).[15] Schöne has utilized the Johnson Claisen rearrangement to form γ-aryl allyl boronates (Scheme 4.4C).[16] As there are limited methods to obtain enantioenriched α-chiral allyl boronates with γ-aryl substitution, we envisioned that a

nickel-catalyzed cross-coupling of allyl pivalates with bis(pinacolato) diborane (B_2Pin_2), would be a powerful strategy to form γ-aryl allyl boronates and would be complementary to Morken's and Schöne methods. Towards this goal, in collaboration with fellow colleague Qi Zhou, I have developed an enantiospecific cross coupling of allylic pivalates with B_2Pin_2 (Scheme 4.5).

Scheme 4.5: Enantiospecific Nickel-Catalyzed Cross-Coupling of Allylic Pivalates and B_2Pin_2



4.20, 80%
95% ee, 99% es

Retention

4.19
96% ee

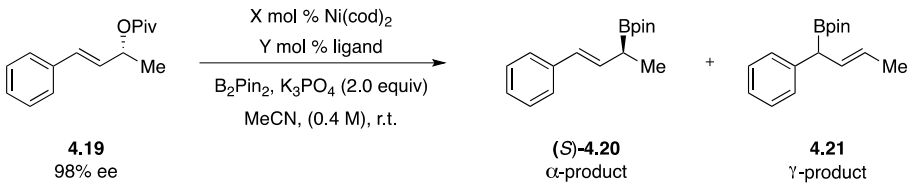
Inversion

4.20, 89%
95% ee, 97% es

4.2: Results and Discussion

We chose cinnamyl pivalate **4.19** as our model substrate. We first tried the borylation with conditions similar to those for our arylation of allylic pivalates.[17] We observed only 36% yield of the allylic boronate **4.20** in low ee (Table 4.1, entry 1). With K_3PO_4, which is a weaker base, improved yields and ee's were observed (entries 2-5). We were intrigued and excited to see that the stereochemistry of the product depends upon the solvent used. When we used toluene as a solvent, we observed retention of configuration (entry 3), whereas inversion of configuration was observed when acetonitrile was used as a solvent (entry 4& 5). The optimized conditions for the formation of (*S*)-**4.20** are 1 mol % $Ni(cod)_2$, 2.2 mol % $BnPPh_2$, K_3PO_4 as a base and acetonitrile as a solvent at room temperature. Under these optimized conditions, we observed 87% NMR yield, 95% ee, and 13:1 α/γ regioselectivity (entry 5).

Table 4.1: Optimization for Inversion Product[a]



4.19 98% ee

(*S*)-4.20 α-product

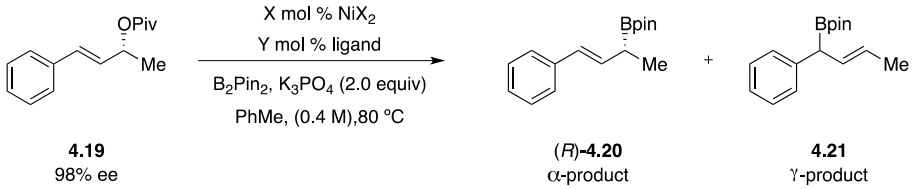
4.21 γ-product

entry	Ni source (mol %)	ligand (mol %)	base	solvent	yield (%)[b]	ee (%)[c]	(α:γ)[d]	stereochemistry
1	$Ni(cod)_2$ (5)	$BnPPh_2$ (11)	NaOMe	MeCN	23	36	n.d[e]	retention
2	$Ni(cod)_2$ (5)	dppb (5.5)	K_3PO_4	MeCN	37	79	100:1	inversion
3	$Ni(cod)_2$ (5)	$BnPPh_2$ (11)	K_3PO_4	PhMe	89	49	99:1	retention
4	$Ni(cod)_2$ (5)	$BnPPh_2$ (11)	K_3PO_4	MeCN	86	92	11:1	inversion
5	$Ni(cod)_2$ (1)	$BnPPh_2$ (2.2)	K_3PO_4	MeCN	87	95	13:1	inversion

[a] Conditions: pivalate **4.19** (0.2 mmol, 1.0 equiv), $Ni(cod)_2$, B_2Pin_2, base (0.2 mmol, 2.0 equiv) and solvent (0.4M). [b]Determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as internal standard. [c] ee was determined for the corresponding alcohol obtained via oxidation by HPLC using a chiral stationary phase. [d] Determined by ^1H NMR analysis. [e] n.d. = not determined.

We have also optimized the reaction conditions to obtain (*R*)-**4.20** in high yields and ee's via a borylation with inversion of configuration. In this case $Ni(cod)_2$ could be replaced with Ni(II) salts. We obtained high levels of chirality transfer and regioselectivity with P(*o*-Tol)$_3$ and Johnphos. Our optimized conditions for obtaining retention product include 5 mol % $NiBr_2$. diglyme, 11 mol % P(*o*-Tol)$_3$, K_3PO_4 as a base and toluene as a solvent at 80 ºC (Table 4.2, entry 3). Notably, these conditions utilize air-stable reagents, making a bench-top reaction set-up possible.

Table 4.2: Optimization for Retention Product[a]



4.19 98% ee | (*R*)-**4.20** α-product | **4.21** γ-product

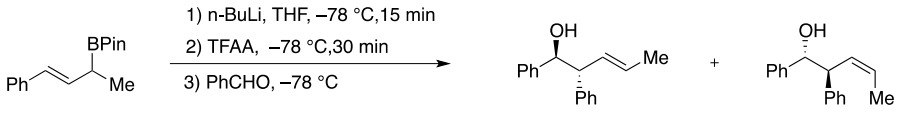
entry	Ni source (mol %)	ligand (mol %)	base	yield [b] (%)[b]	ee (%)[c]	α:γ[d]
1[e]	$NiCl_2$. DME (10)	Johnphos (22)	K_3PO_4	50	85	-
2	$NiBr_2$.diglyme (5)	P(*o*-Tol)$_3$ (11)	K_2CO_3	78	97	63:1
3	$NiBr_2$.diglyme (5)	P(*o*-Tol)$_3$ (11)	K_3PO_4	85	97	55:1
4	$NiBr_2$.diglyme (2)	P(*o*-Tol)$_3$ (5)	K_3PO_4	67	96	47:1

[a] Conditions: pivalate **4.19** (0.2 mmol, 1.0 equiv), B_2Pin_2, base (0.2 mmol, 2.0 equiv) and PhMe (0.4M). [b]Determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as internal standard. [c] ee was determined for the corresponding alcohol obtained via oxidation by HPLC using a chiral stationary phase. [d]The ratio of regioisomers were determined by ^{1}H NMR analysis. [e] ee of the starting material (91% ee).

Application of Allyl Boronates

My colleague Qi Zhou has shown the utility of our method by treating γ-phenyl substituted allyl boronate **4.20** with benzaldehyde. The selectivity in this reaction was 5: 1 as shown in Scheme 4.6.

Scheme 4.6: Allylic Borylation of Aldehydes



4.20 | **4.22** | **4.23**

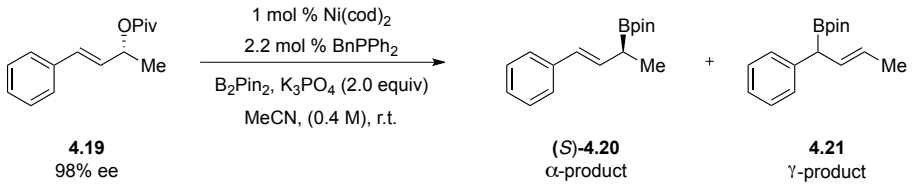
4.22: **4.23,** 5:1 (NMR)

4.3 Conclusion

We have developed an enantiospecific, nickel-catalyzed cross-coupling of 1,3-disubstituted secondary allylic pivalates and bis(pinacolato)diborane (B_2Pin_2) to form γ-aryl allyl boronates in high yields and ee's. We have found that the absolute configuration of allylboronate formed depends on the ligand and the solvent used. When $BnPPh_2$ is used as ligand and MeCN as solvent, the stereochemistry of allyl pivalate undergoes inversion of configuration upon borylation. However, with P(*o*-Tol)$_3$ as ligand in PhMe, retention of configuration was observed. High levels of stereochemical fidelity, yields, and regioselectivity are observed in both versions. Mechanistic studies and elucidation of substrate scope are ongoing in our laboratory.

4.4 Experimental Information

(*S*,*E*)-4,4,5,5-tetramethyl-2-(4-phenylbut-3-en-2-yl)-1,3,2-dioxaborolane, (*S*)-**4.20**



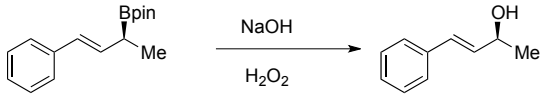
4.19 98% ee

(*S*)-**4.20** α-product

4.21 γ-product

In a N_2-atmosphere glovebox, $Ni(cod)_2$ (0.6 mg, 0.002 mmol, 1 mol %), $BnPPh_2$ (1.2 mg, 0.004 mmol, 2.2 mol %), and K_3PO_4 (85.0 mg, 0.4 mmol, 2.0 equiv) were weighed into a 1-dram vial. Allylic pivalate **4.19** (98% ee, 46.4 mg, 0.2 mmol, 1.0 equiv) and B_2Pin_2 (101.6 mg, 0.4 mmol, 2.0 equiv) were added, followed by MeCN (0.5 mL, 0.4 M). The vial was capped with a Teflon-lined cap and removed from the glovebox. The mixture was stirred at room temperature for 32h. The reaction mixture was then diluted with Et_2O (1.5 mL) and filtered through a plug of silica gel, which was rinsed with Et_2O (10 mL). The filtrate was concentrated and submitted for ^1H NMR analysis. Note: Product **4.20** decomposes on silica gel upon standing: ^1H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.36 (m, 2H), 7.31 – 7.28 (m, 2H), 7.20 – 7.18 (m, 1H), 6.37 – 6.36 (m, 2H), 2.07 – 2.09 (m, 1H), 1.26 (s, 12H), 1.21 (d, *J*= 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.2, 133.2, 128.3, 127.5, 126.4, 125.8, 83.2, 24.7, 24.6, 14.8. The spectral data for this compound matches to that reported in the literature.[18]

Scheme 4.7: Synthesis of Allyl Alcohol from Allyl Boronate

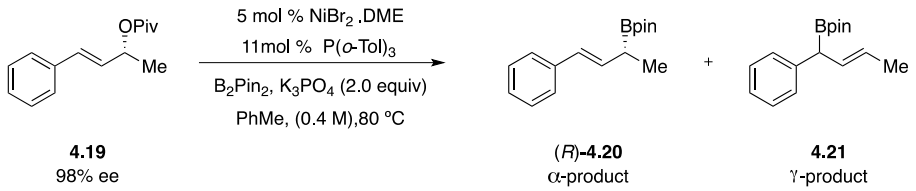


(*S*)-**4.20** (*S*)-**4.24**

To determine the enantiomeric excess, boronate **4.20** was converted to the corresponding alcohol **4.24** (Scheme 4.7). Allyl boronate **4.20** (20 mg, 0.134 mmol, 1.0 equiv) was

dissolved in Et_2O (0.25 mL, 0.53 M). The solution was cooled to 0 °C. Aq. NaOH (2N, 0.1 mL, 1.5 equiv) and H_2O_2 (30%, 0.075 mL, 7.2 equiv) were added slowly. The mixture was allowed to warm to room temperature and then stirred for 30 min. The alcohol product was isolated using preparative TLC and submitted for HPLC and NMR analysis. The NMR spectral data for this compound matches to that reported in the literature.[17,19] The enantiomeric excess was determined to be 95% by HPLC analysis using a chiral stationary phase (CHIRALPAK IB, 1.0 mL/min, 3.0% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 23.73 min, t_R(minor)=15.80 min.

(*R*,*E*)-4,4,5,5-tetramethyl-2-(4-phenylbut-3-en-2-yl)-1,3,2-dioxaborolane, (*R*)-**4.20**



In a N_2-atmosphere glovebox, $NiBr_2$.diglyme (3.1 mg, 0.01 mmol, 5 mol %), P(*o*-Tol)$_3$ (6.7 mg, 0.022 mmol, 11 mol %), and K_3PO_4 (85.0 mg, 0.4 mmol, 2.0 equiv) were weighed into a 1-dram vial. Allylic pivalate **4.19** (98% ee, 46.4 mg, 0.2 mmol, 1.0 equiv) and B_2Pin_2 (101.6 mg, 0.4 mmol, 2.0 equiv) were added, followed by PhMe (0.5 mL, 0.4 M). The vial was capped with a Teflon-lined cap and removed from the glovebox. The mixture was stirred at 80 °C for 32h. The reaction mixture was then diluted with Et_2O (1.5 mL) and filtered through a plug of silica gel, which was rinsed with Et_2O (10 mL). The filtrate was concentrated and submitted for ^{1}H NMR analysis. Note: Product **4.20** decomposes on silica gel upon standing. The spectral data for this compound matches to that reported for (*S*)-**4.20** above and that reported in the literature.[18]

To determine the enantiomeric excess, boronate (*R*)-**4.20** was converted to the corresponding alcohol (*R*)-**4.24**, as described above. The alcohol product was isolated using preparative TLC and submitted for HPLC and NMR analysis. The NMR spectral data for this compound matches to that reported in the literature.[17,19] The enantiomeric excess was determined to be 97% by HPLC analysis using a chiral stationary phase (CHIRALPAK IB, 1.0 mL/min, 3.0% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 14.88 min, t_R(minor)=22.20 min.

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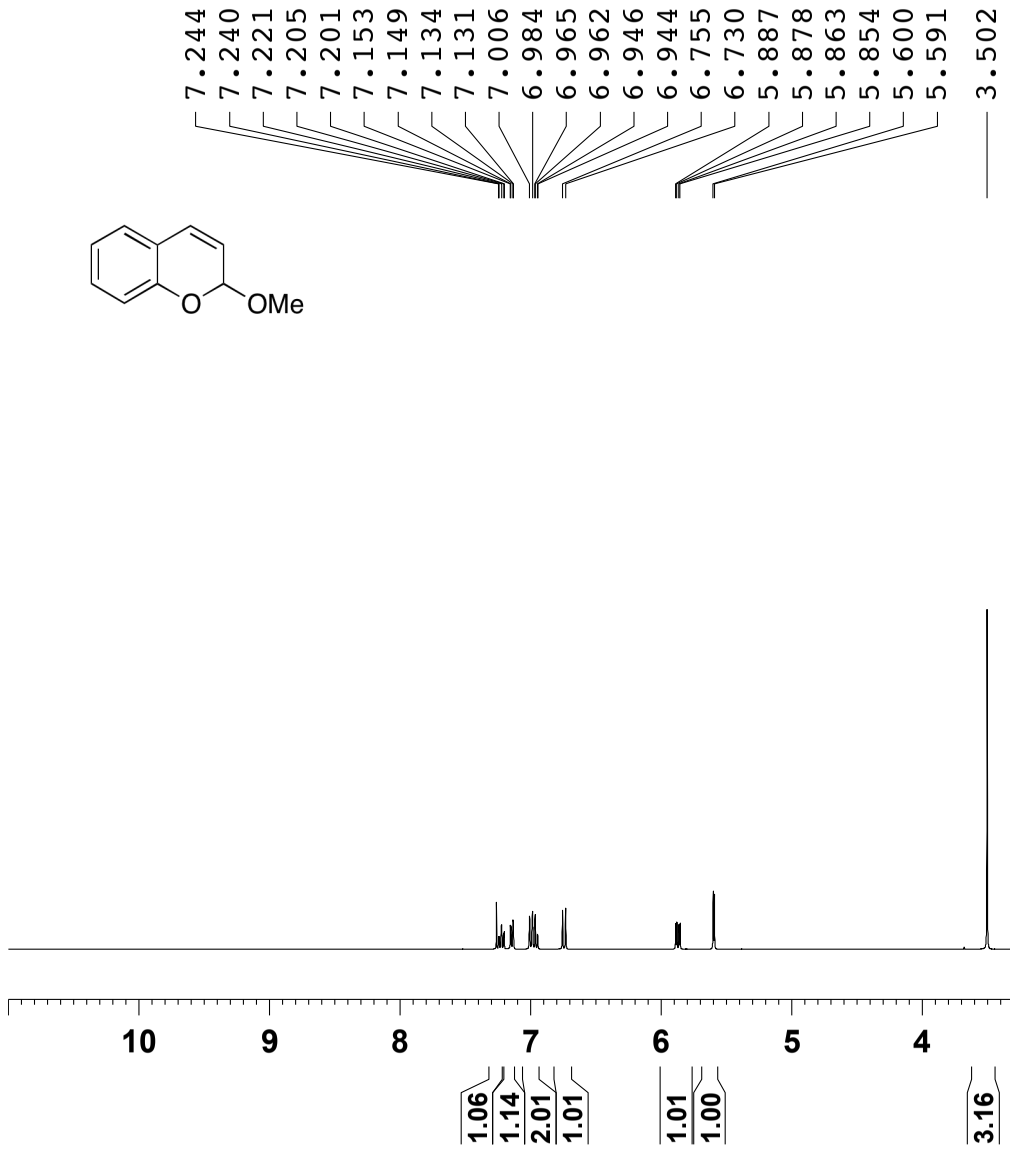
APPENDIX

APPENDIX A
CHAPTER 1 SPECTRAL DATA

Compound 1.40
1H NMR



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PROCNO 1

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PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 9
DW 60.400 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 4.90 dB
PL1W 3.30822015 W
SFO1 400.1324710 MHz

F2 - Processing parameters
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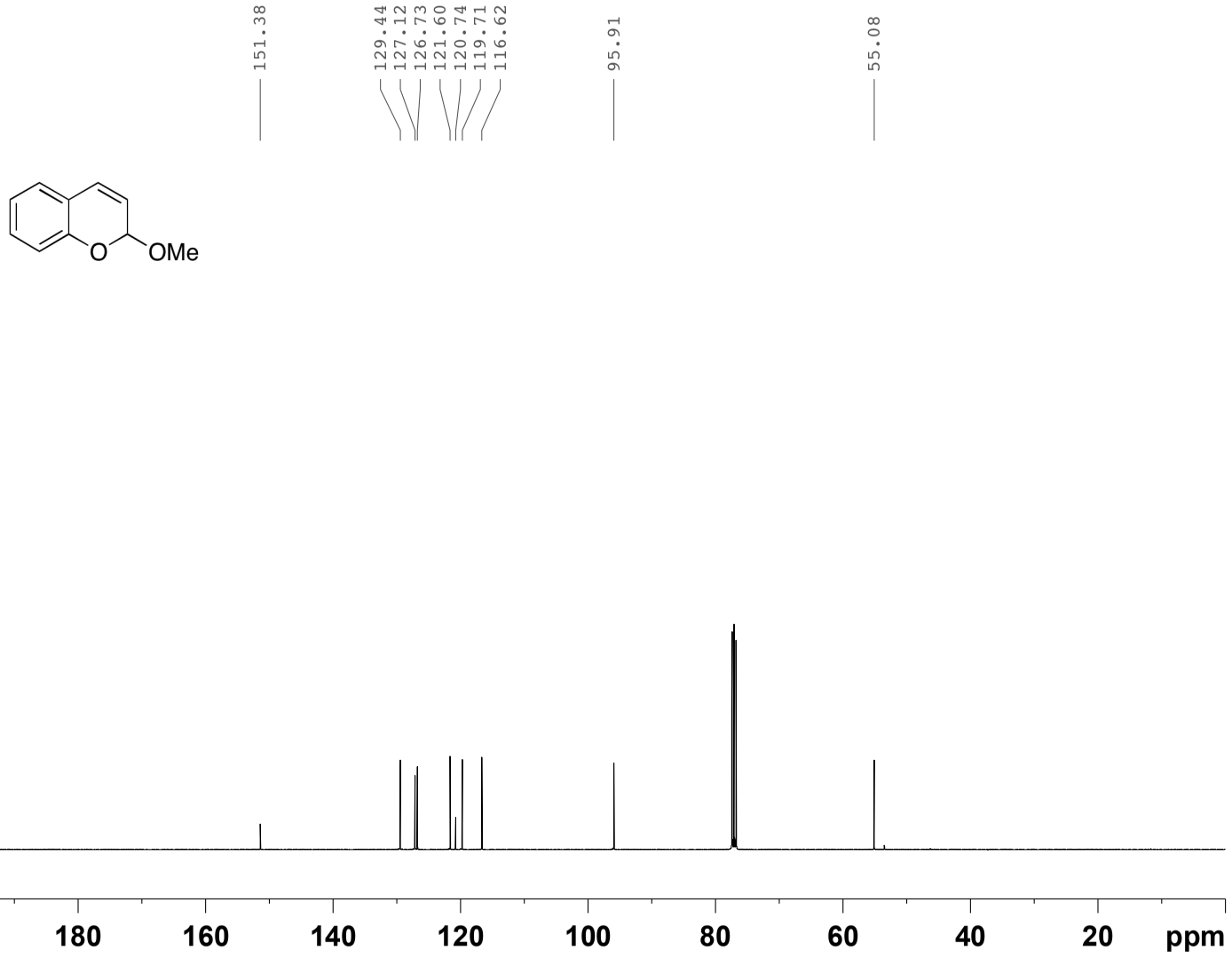
SF 400.1300098 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound 1.40
13C NMR



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PROCNO 1

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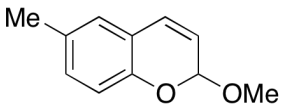
NS 1024
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 512
DW 20.850 usec
DE 18.00 usec
TE 298.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

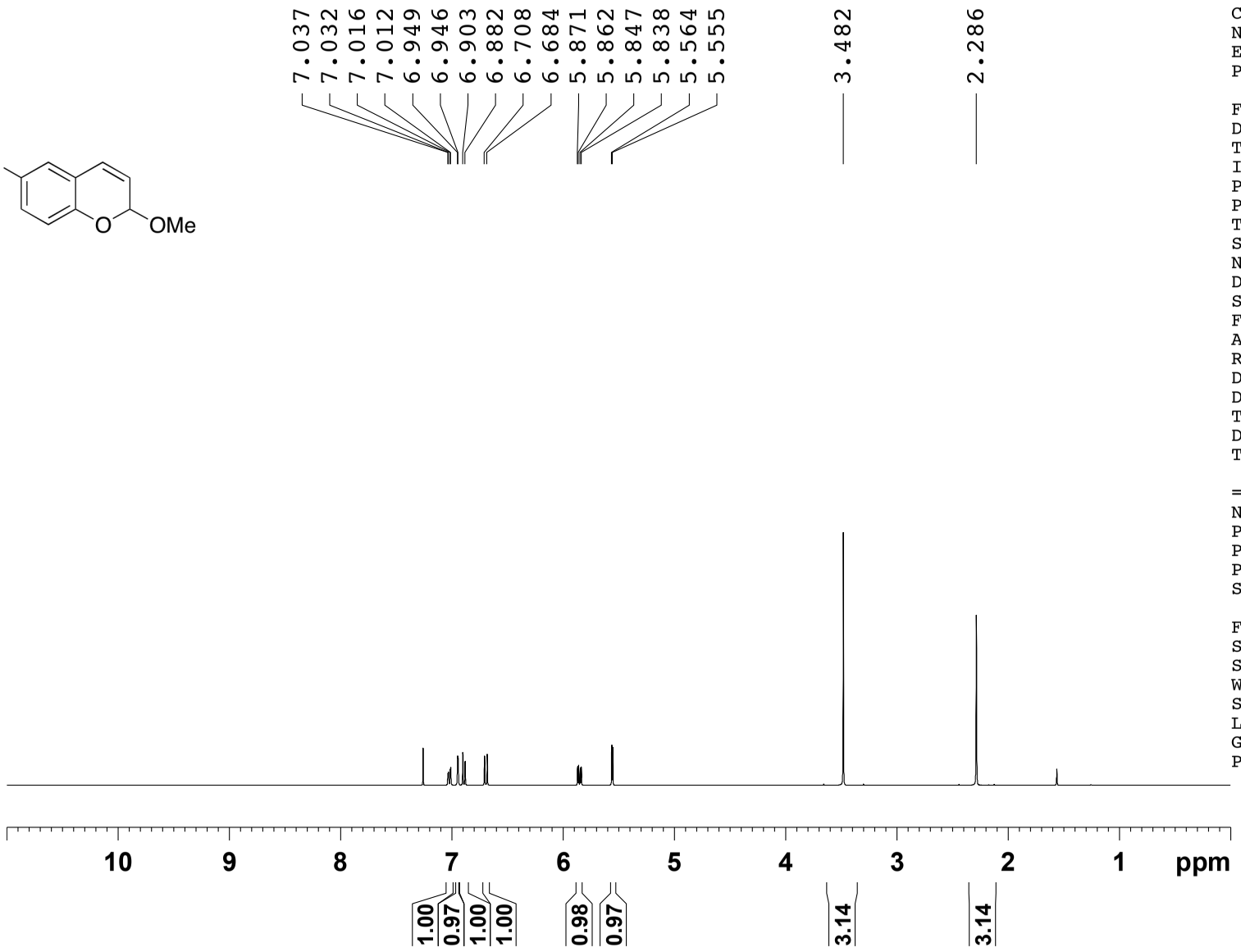
======== CHANNEL f1 ========
NUC1 13C
P1 9.25 usec
PL1 0.55 dB
PL1W 35.18820572 W
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 4.90 dB
PL12 20.46 dB
PL13 21.00 dB
PL2W 3.30822015 W
PL12W 0.09195905 W
PL13W 0.08120718 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Compound 1.29
1H NMR



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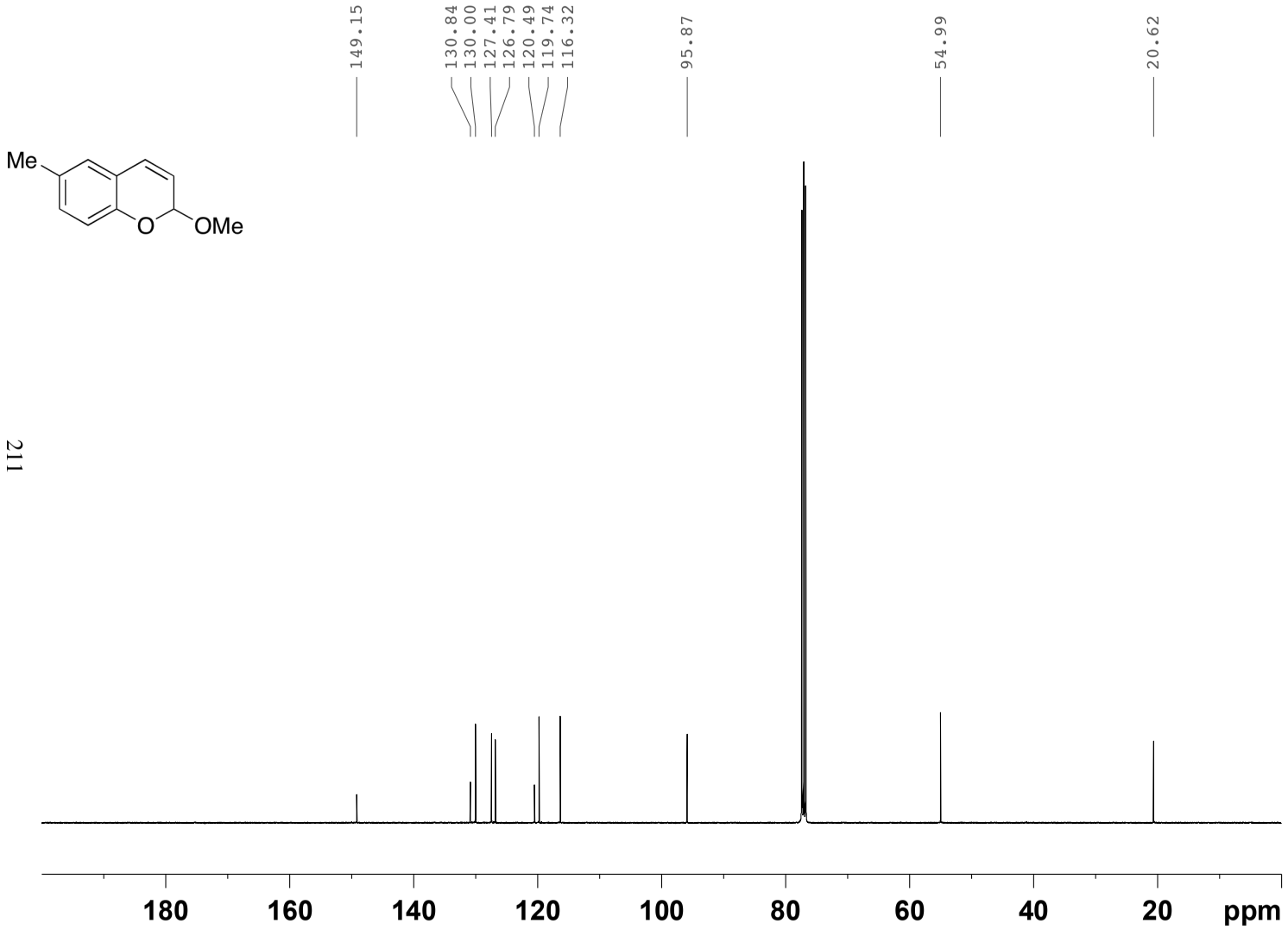
Current Data Parameters
NAME       HH-2-275aug14
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120814
Time               12.04
INSTRUM            spect
PROBHD   5 mm CPQNP 1H/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ              3.9584243 sec
RG                  10.1
DW                60.400 usec
DE                 6.00 usec
TE                298.2 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                15.00 usec
PL1                4.90 dB
PL1W         3.30822015 W
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300097 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                1.00
```

Compound 1.29 13CNMR



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Current Data Parameters
NAME HH-3-275aug14
EXPNO 1
PROCNO 1

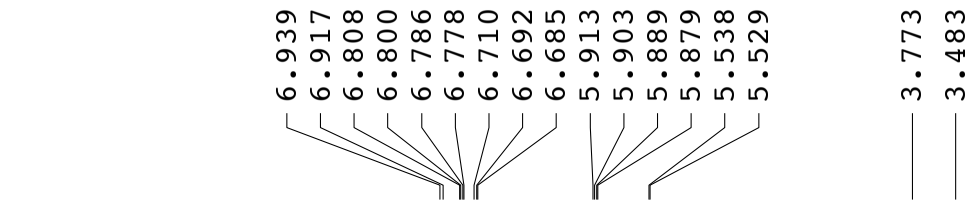
F2 - Acquisition Parameters
Date_ 20120815
Time 0.47
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 512
DW 20.850 usec
DE 18.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

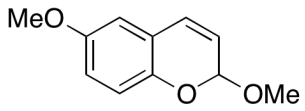
======== CHANNEL f1 ========
NUC1 13C
P1 9.25 usec
PL1 0.55 dB
PL1W 35.18820572 W
SFO1 100.6228298 MHz

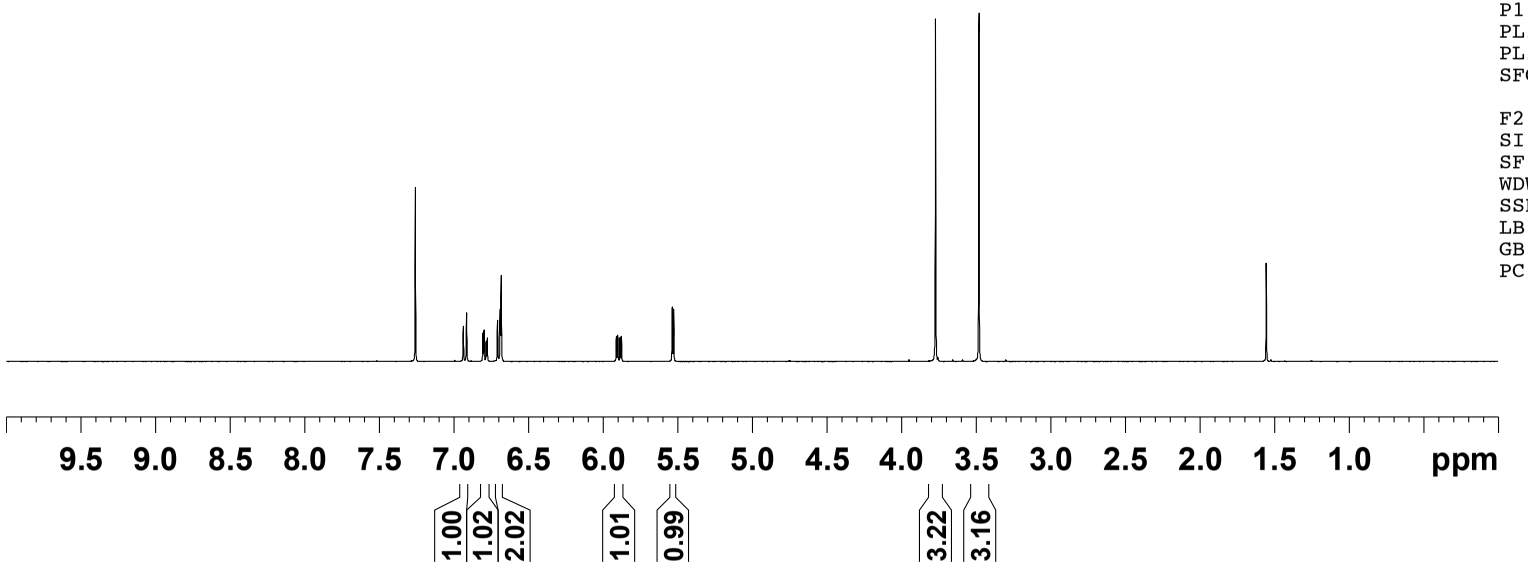
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 4.90 dB
PL12 20.46 dB
PL13 21.00 dB
PL2W 3.30822015 W
PL12W 0.09195905 W
PL13W 0.08120718 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Compound 1.82 1H NMR







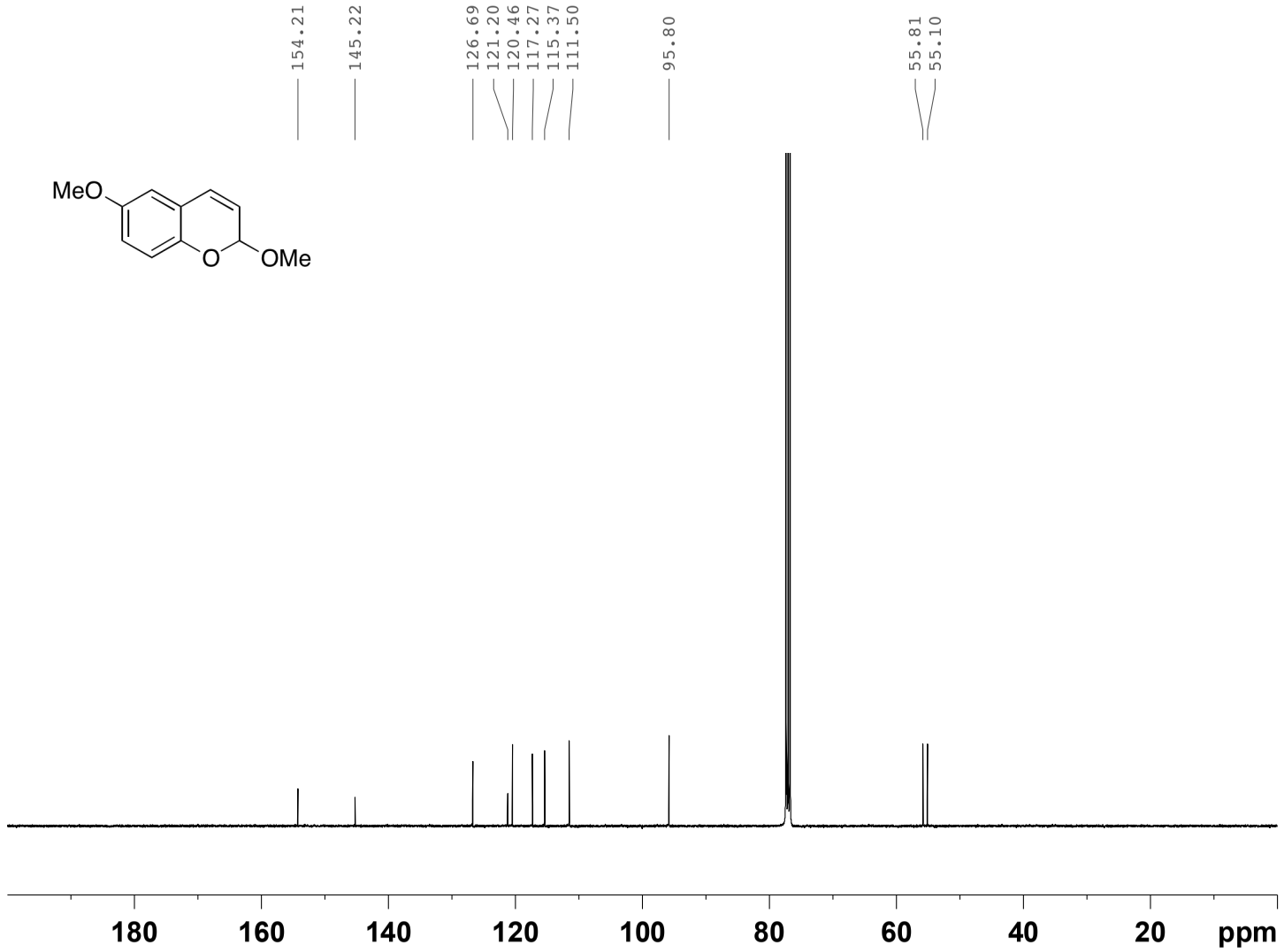
Current Data Parameters
NAME HH-3-113aug14
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120814
Time 12.23
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 9
DW 60.400 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 4.90 dB
PL1W 3.30822015 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300097 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound 1.82 13C NMRR



Current Data Parameters
NAME HH-3-113aug14
EXPNO 2
PROCNO 1

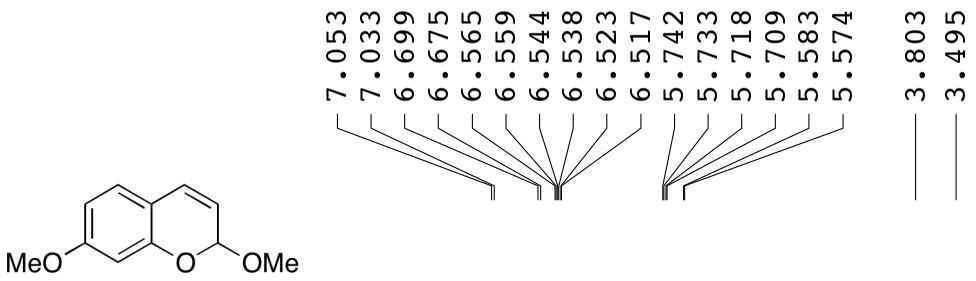
F2 - Acquisition Parameters
Date_ 20120815
Time 1.50
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 512
DW 20.850 usec
DE 18.00 usec
TE 298.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

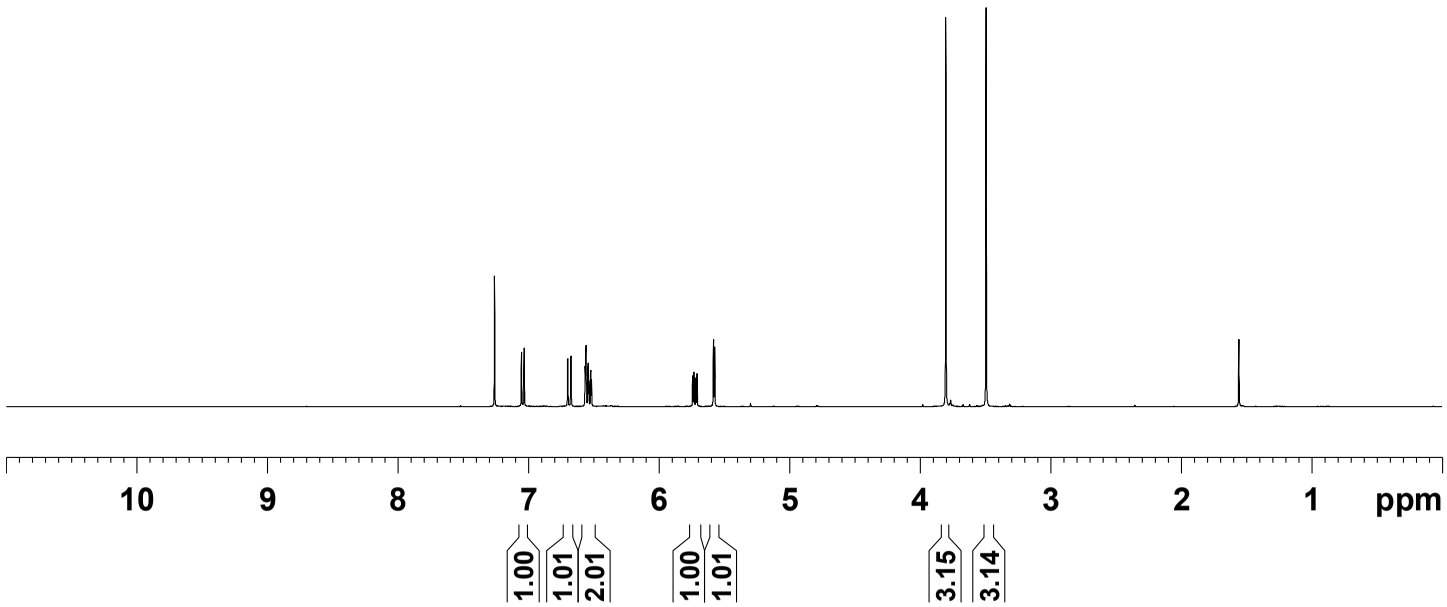
======== CHANNEL f1 ========
NUC1 13C
P1 9.25 usec
PL1 0.55 dB
PL1W 35.18820572 W
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 4.90 dB
PL12 20.46 dB
PL13 21.00 dB
PL2W 3.30822015 W
PL12W 0.09195905 W
PL13W 0.08120718 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Compound 1.83
1H NMR





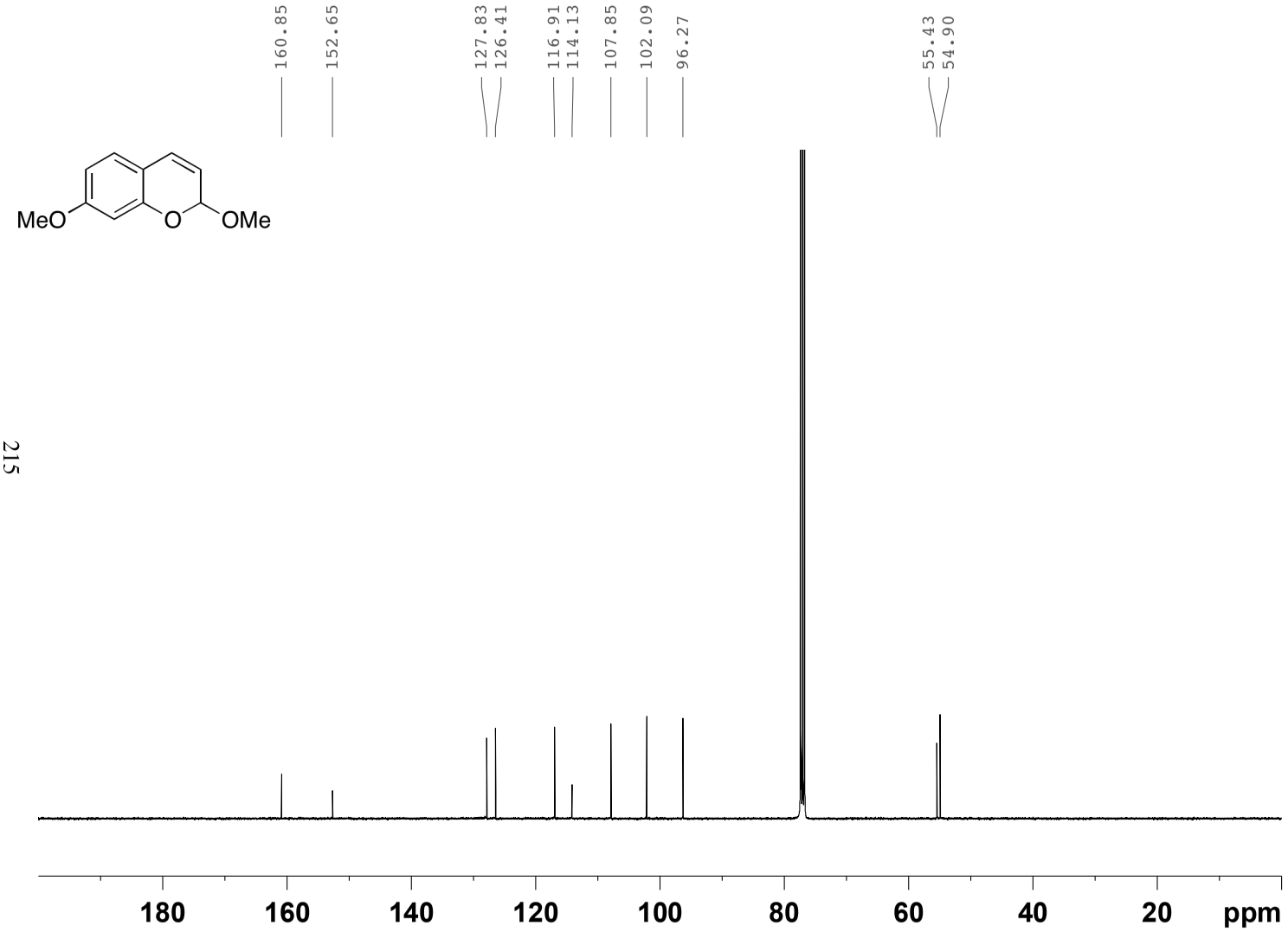

```
Current Data Parameters
NAME       HH-3-107aug14
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120814
Time               12.16
INSTRUM            spect
PROBHD   5 mm CPQNP 1H/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ              3.9584243 sec
RG                     9
DW                60.400 usec
DE                 6.00 usec
TE                298.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 15.00 usec
PL1                 4.90 dB
PL1W          3.30822015 W
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300099 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

Compound 1.83 13C NMR




```
Current Data Parameters
NAME      HH-3-107aug14
EXPNO                 2
PROCNO                1

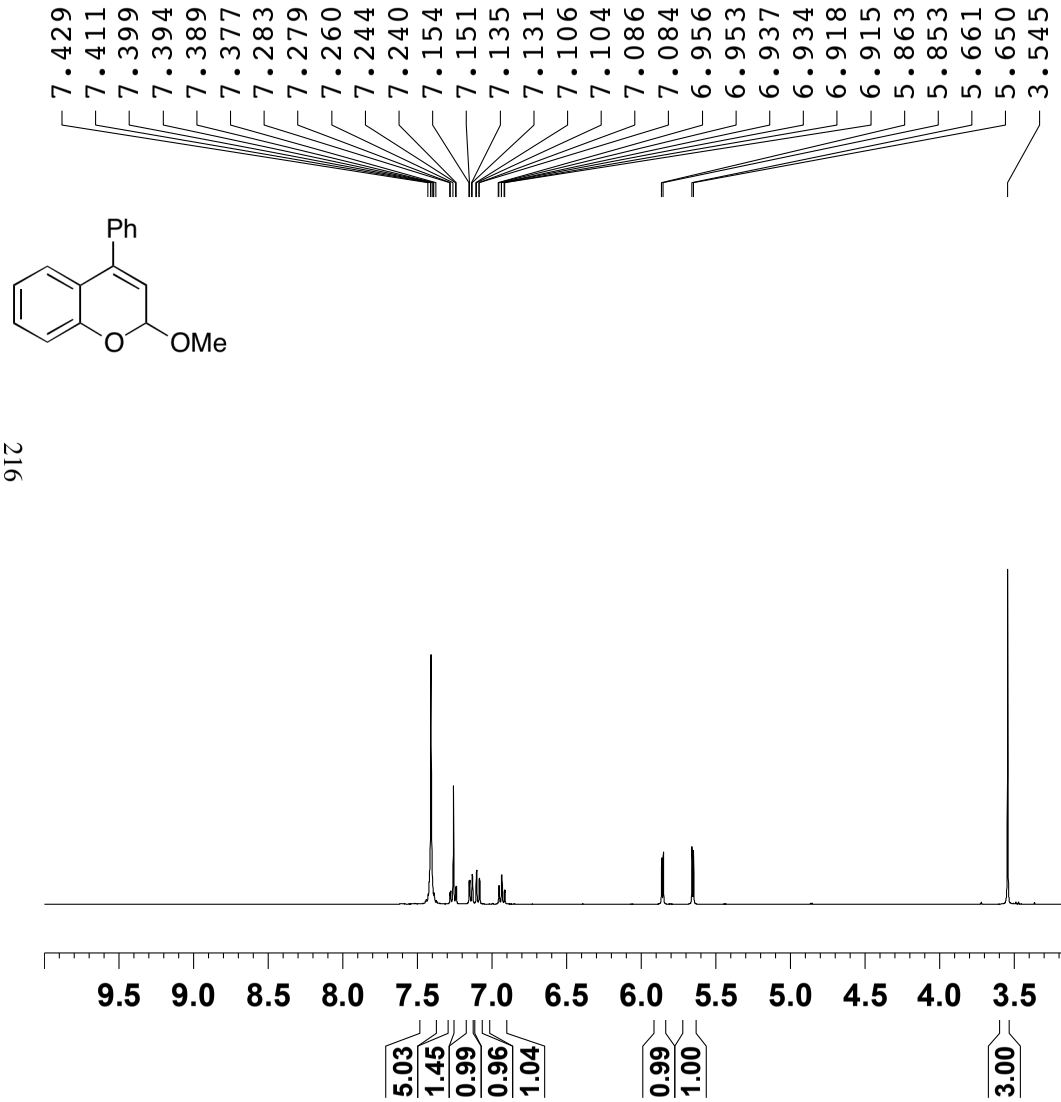
F2 - Acquisition Parameters
Date_          20120815
Time               2.53
INSTRUM           spect
PROBHD   5 mm CPQNP 1H/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ             1.3664756 sec
RG                  512
DW               20.850 usec
DE               18.00 usec
TE               298.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                 9.25 usec
PL1                0.55 dB
PL1W        35.18820572 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             90.00 usec
PL2                4.90 dB
PL12              20.46 dB
PL13              21.00 dB
PL2W         3.30822015 W
PL12W        0.09195905 W
PL13W        0.08120718 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127690 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

Compound 1.32 1H NMR



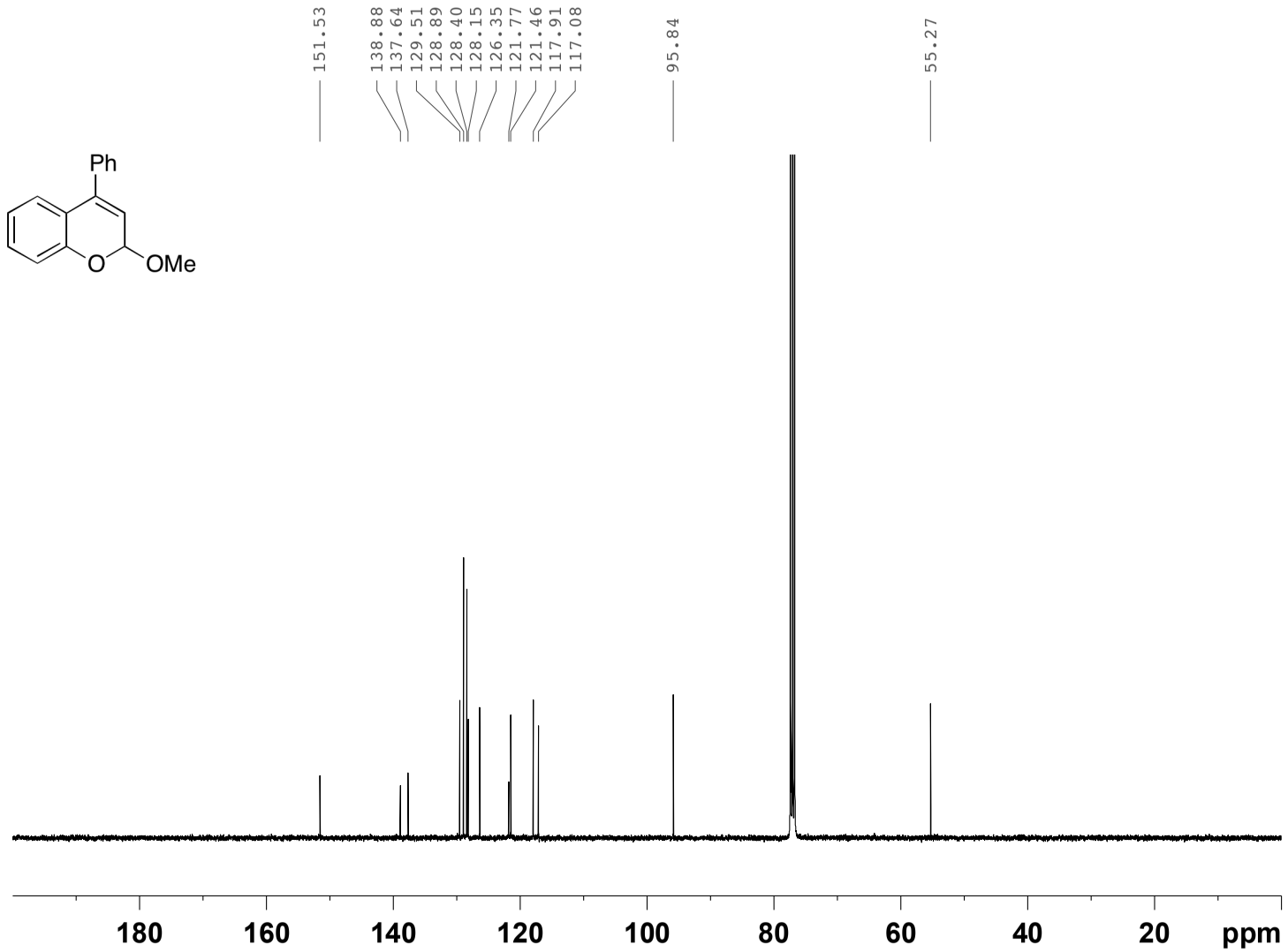
Current Data Parameters
NAME HH-3-190aug15
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120815
Time 12.58
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 12.7
DW 60.400 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 4.90 dB
PL1W 3.30822015 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300100 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound 1.32 13C NMR



Current Data Parameters
NAME HH-3-190aug15
EXPNO 2
PROCNO 1

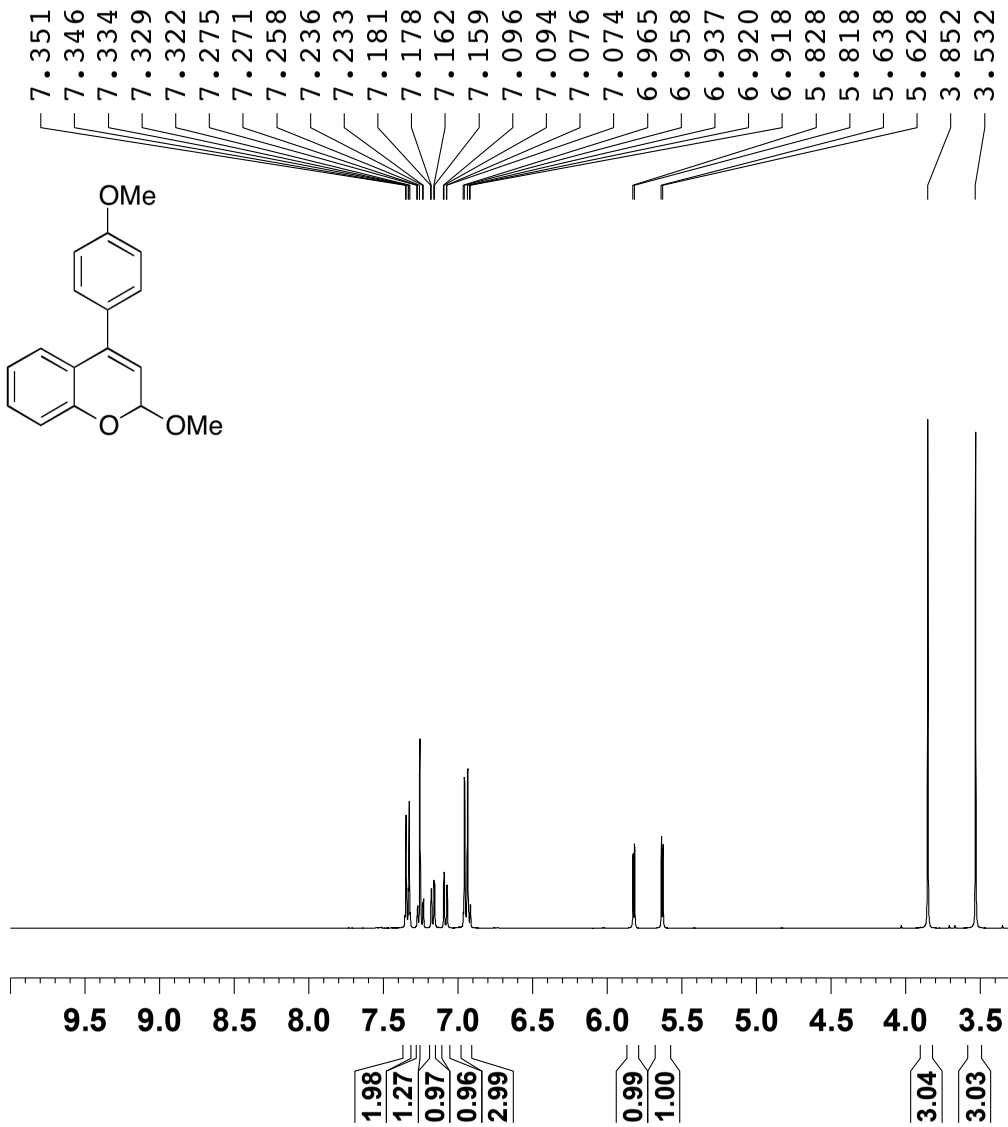
F2 - Acquisition Parameters
Date_ 20120815
Time 13.54
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 512
DW 20.850 usec
DE 18.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.25 usec
PL1 0.55 dB
PL1W 35.18820572 W
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 4.90 dB
PL12 20.46 dB
PL13 21.00 dB
PL2W 3.30822015 W
PL12W 0.09195905 W
PL13W 0.08120718 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Compound 1.84 1H NMR



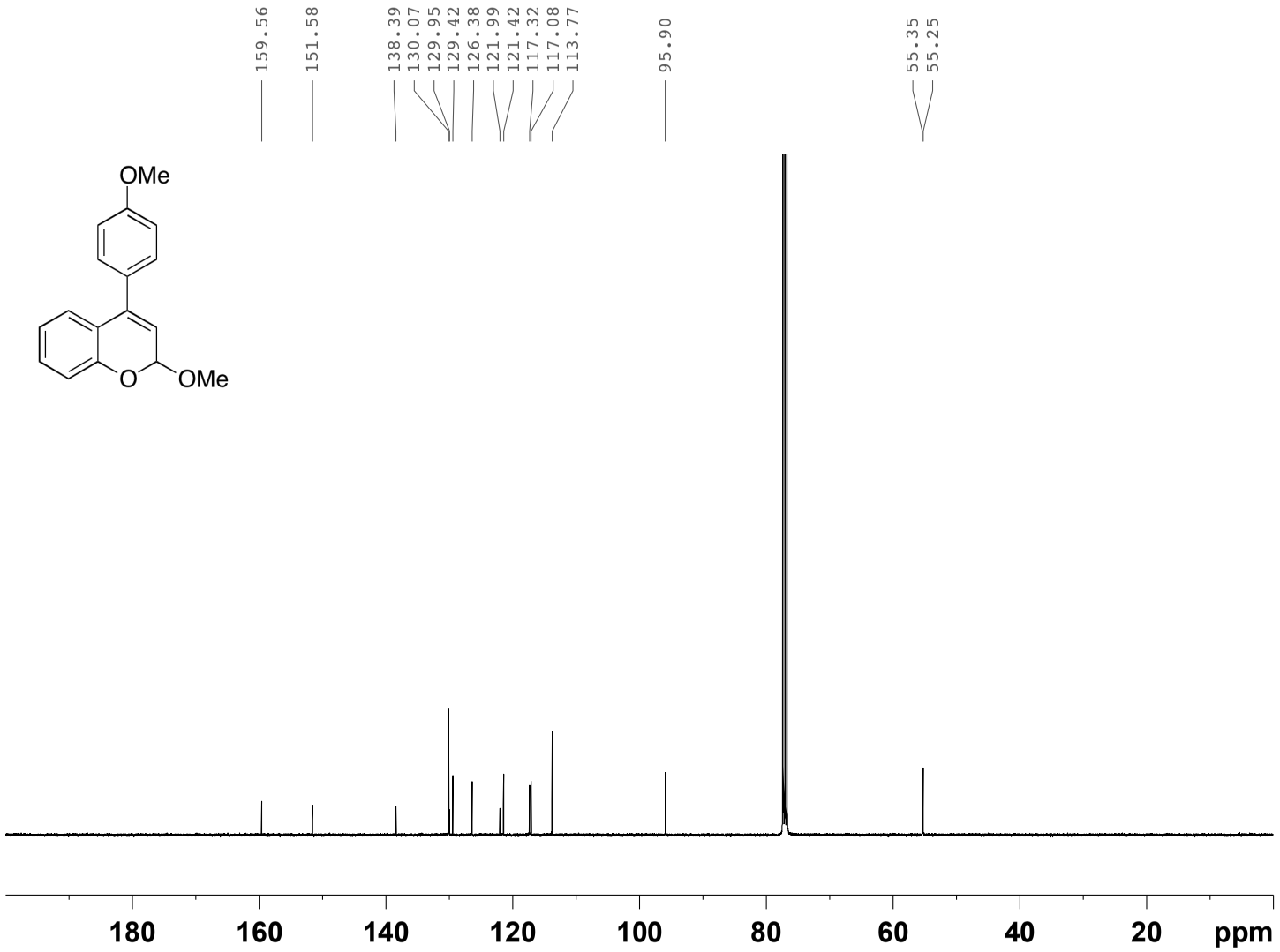
Current Data Parameters
NAME HH-3-191aug14
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120814
Time 12.10
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 10.1
DW 60.400 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 4.90 dB
PL1W 3.30822015 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300108 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound 1.84 13C NMR



Current Data Parameters
NAME HH-3-191aug14
EXPNO 2
PROCNO 1

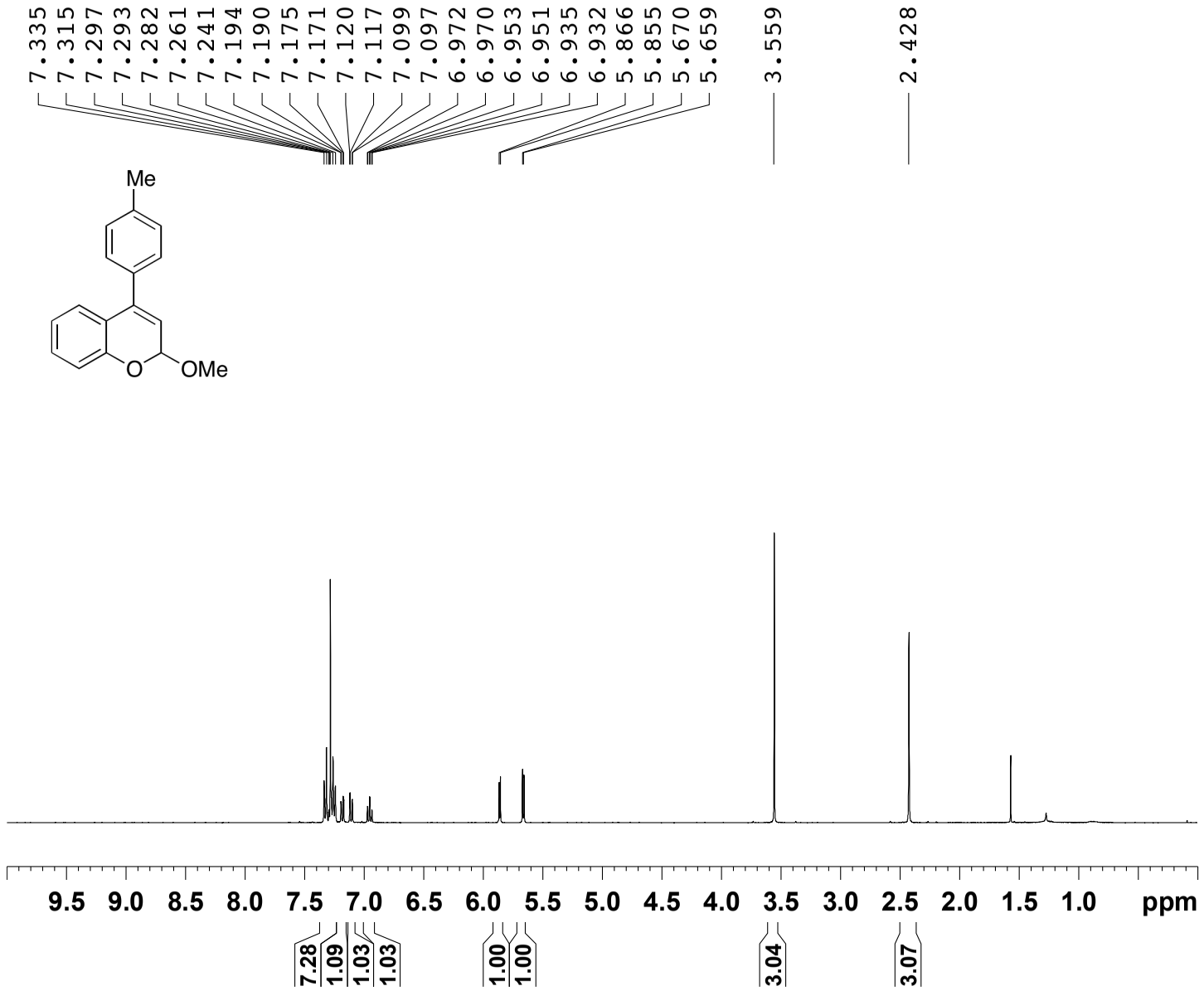
F2 - Acquisition Parameters
Date_ 20120814
Time 20.08
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 512
DW 20.850 usec
DE 18.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.25 usec
PL1 0.55 dB
PL1W 35.18820572 W
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 4.90 dB
PL12 20.46 dB
PL13 21.00 dB
PL2W 3.30822015 W
PL12W 0.09195905 W
PL13W 0.08120718 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Compound 1.85 1H NMR



220

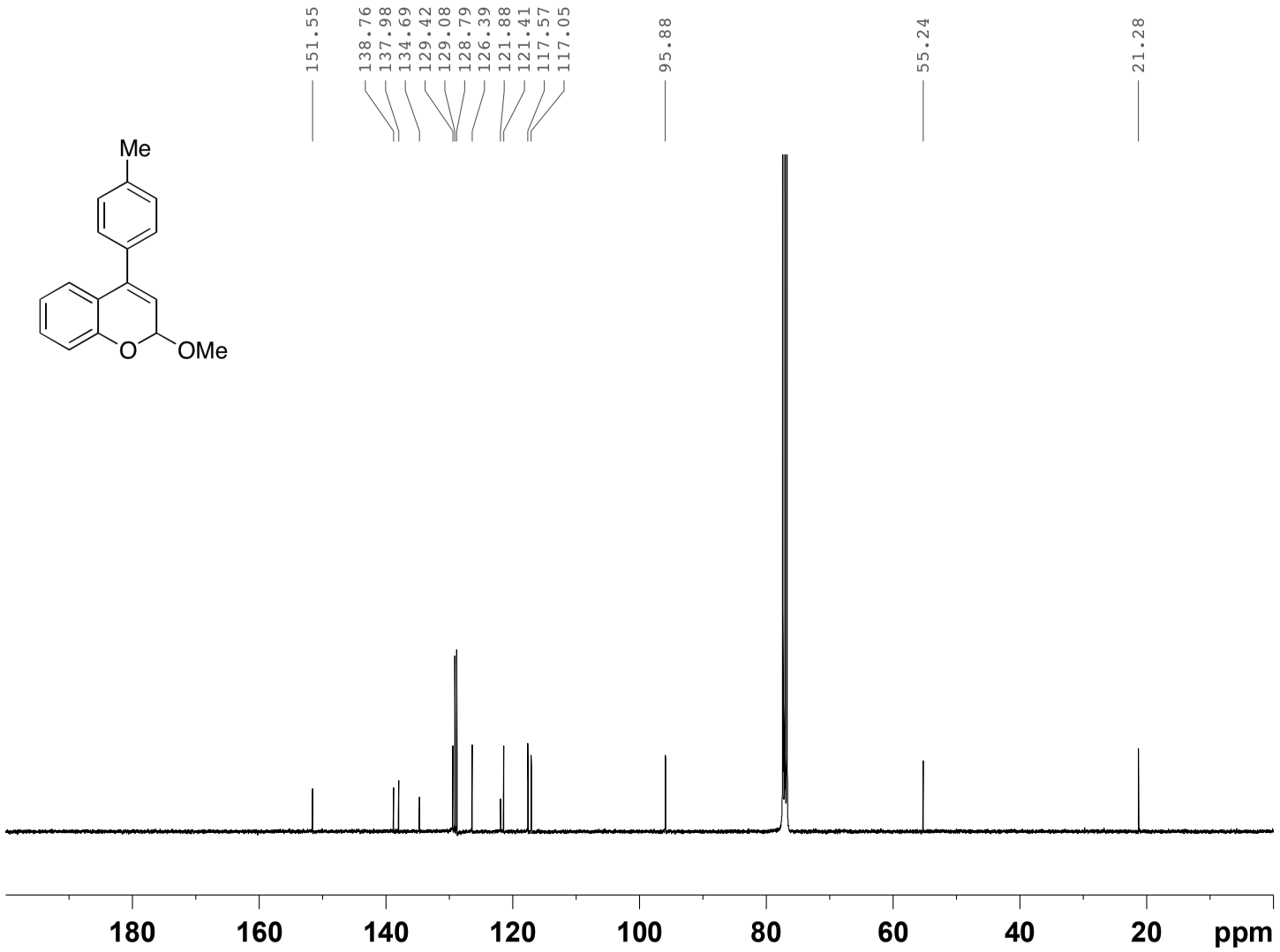
Current Data Parameters
NAME HH-3-201
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120428
Time 16.02
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 6.3
DW 60.400 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 4.90 dB
PL1W 3.30822015 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound 1.85 13C NMR

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Current Data Parameters
NAME            HH-3-201
EXPNO                  2
PROCNO                 1

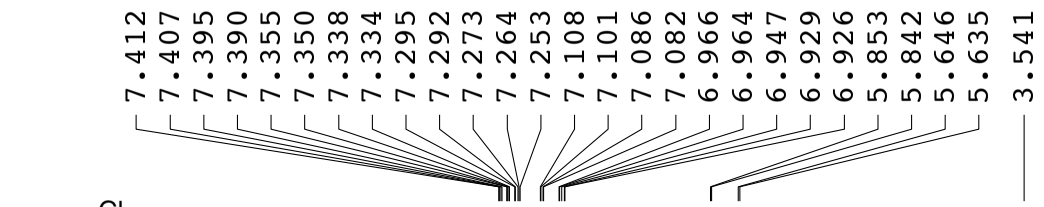
F2 - Acquisition Parameters
Date_           20120429
Time                2.44
INSTRUM            spect
PROBHD   5 mm CPQNP 1H/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ             1.3664756 sec
RG                   512
DW                20.850 usec
DE                18.00 usec
TE                298.1 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

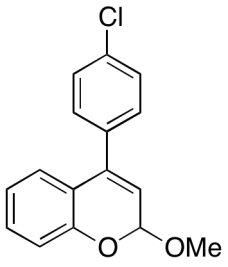
======== CHANNEL f1 ========
NUC1                 13C
P1                  9.25 usec
PL1                 0.55 dB
PL1W        35.18820572 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL2                 4.90 dB
PL12               20.46 dB
PL13               21.00 dB
PL2W         3.30822015 W
PL12W        0.09195905 W
PL13W        0.08120718 W
SFO2        400.1316005 MHz

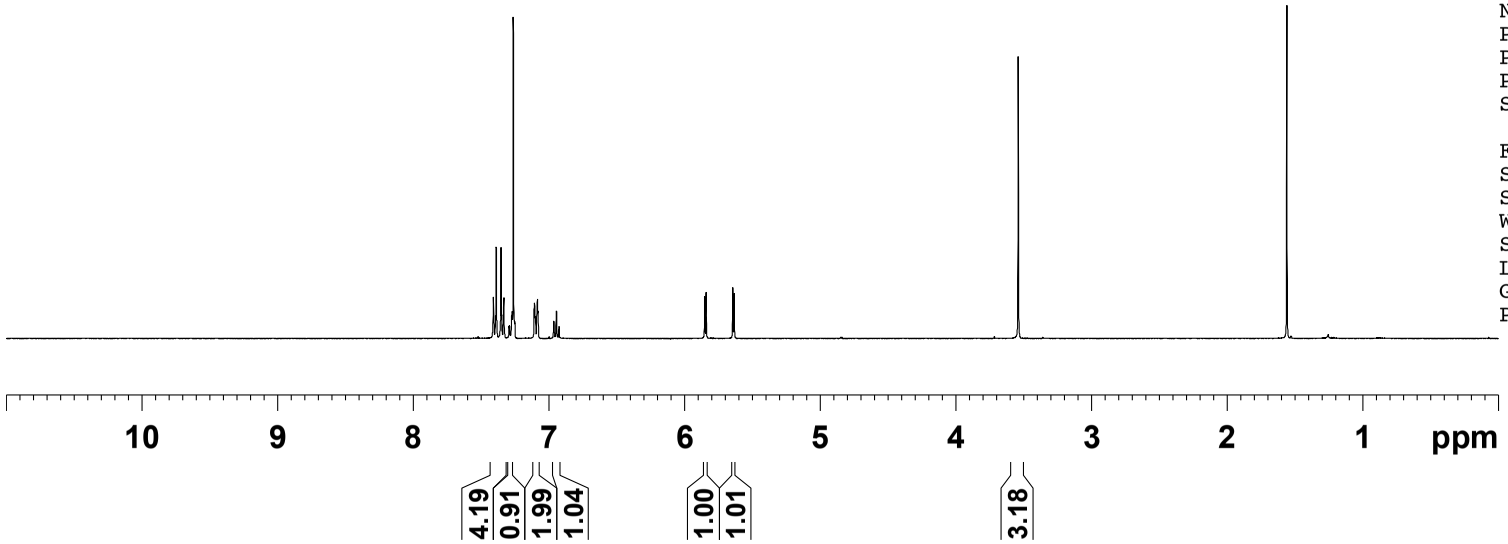
F2 - Processing parameters
SI                 32768
SF          100.6127690 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

Compound 1.86 1H NMR





222



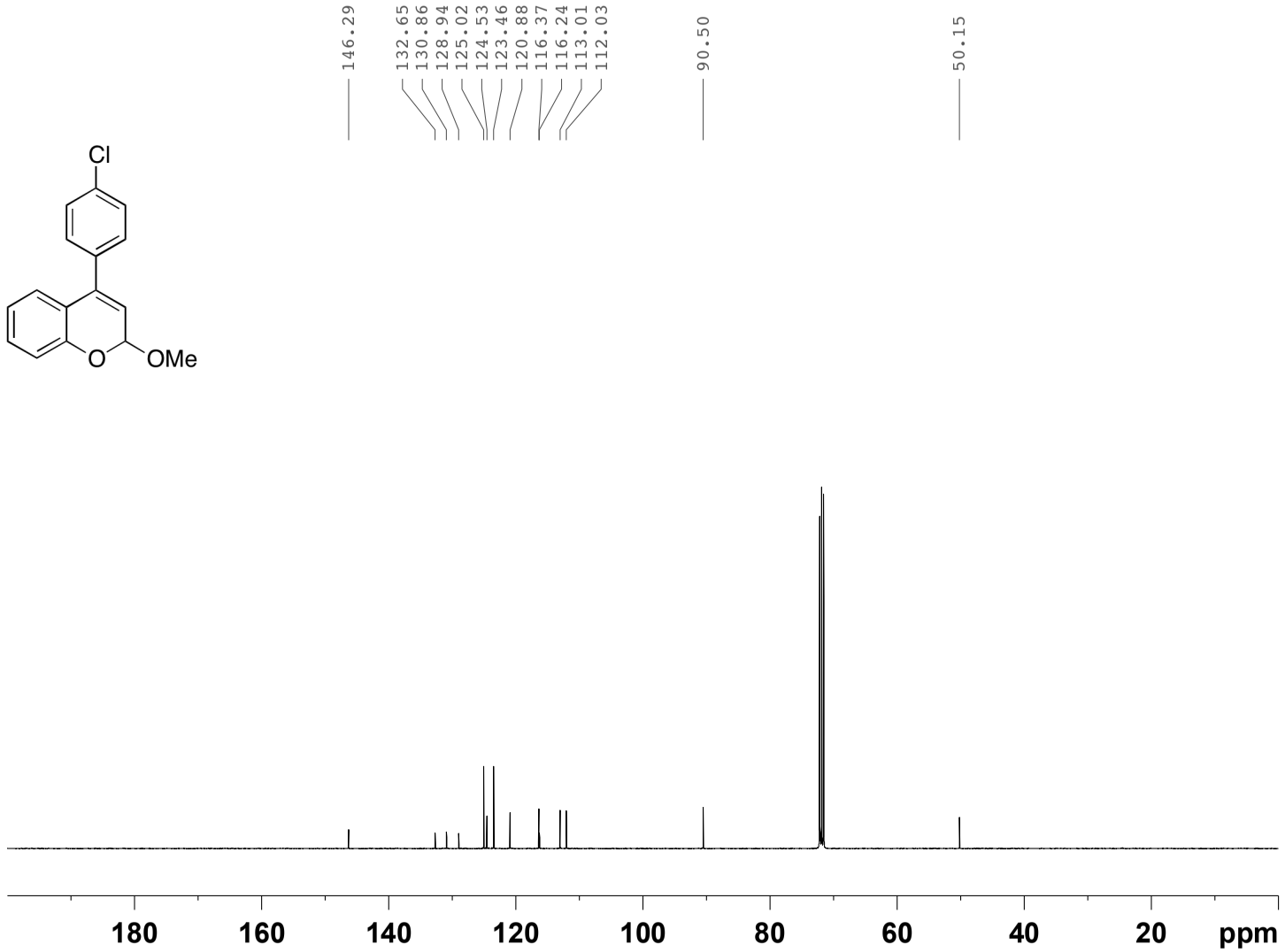
Current Data Parameters
NAME HH-3-247aug14
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120814
Time 11.41
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 9
DW 60.400 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 4.90 dB
PL1W 3.30822015 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300082 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound 1.86 13C NMR



223

Current Data Parameters
NAME HH-3-241aug14
EXPNO 1
PROCNO 1

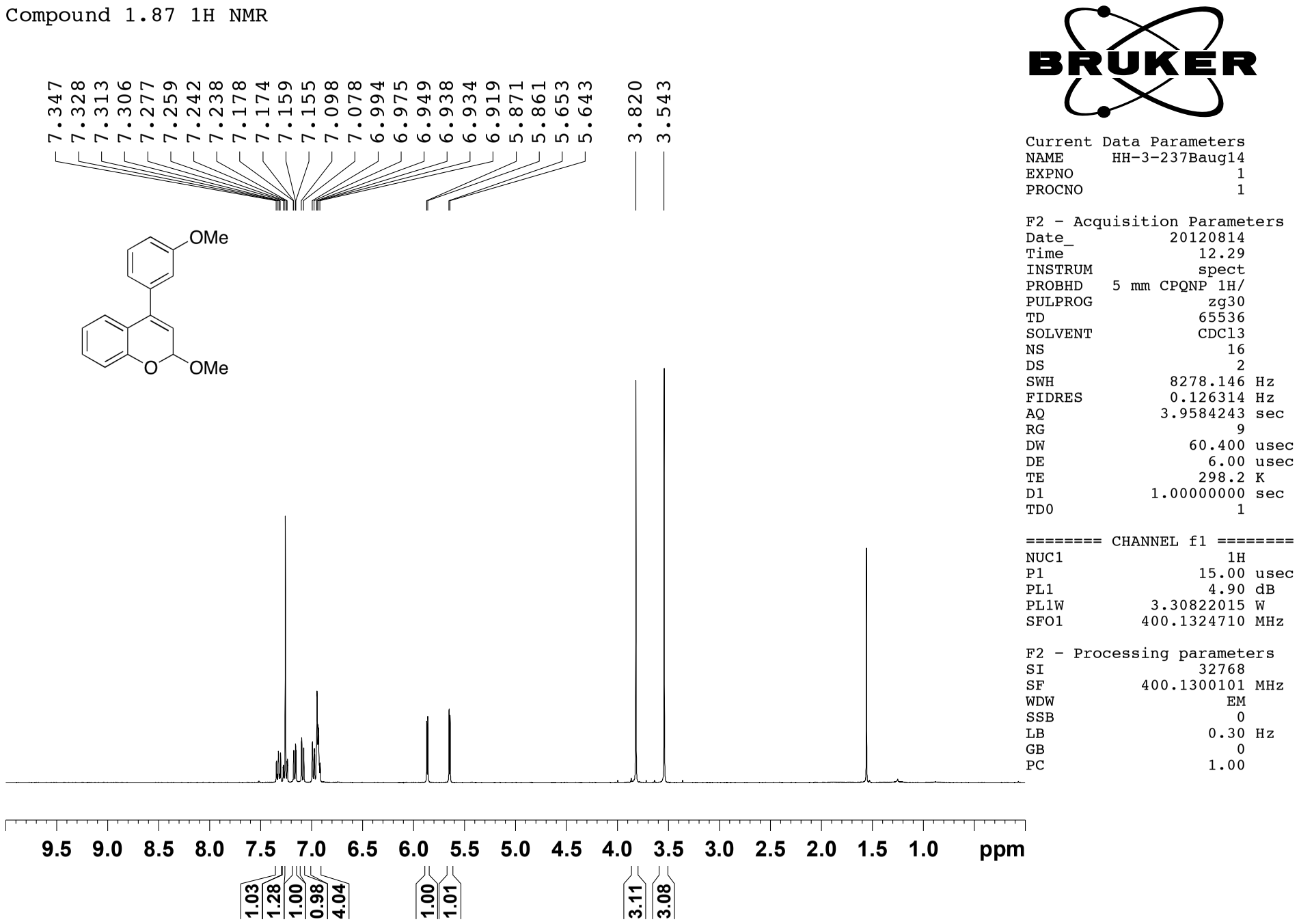
F2 - Acquisition Parameters
Date_ 20120815
Time 5.01
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 1024
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 512
DW 20.850 usec
DE 18.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.25 usec
PL1 0.55 dB
PL1W 35.18820572 W
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 4.90 dB
PL12 20.46 dB
PL13 21.00 dB
PL2W 3.30822015 W
PL12W 0.09195905 W
PL13W 0.08120718 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Compound 1.87 1H NMR



224

Current Data Parameters
NAME HH-3-237Baug14
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

Date_	20120814
Time	12.29
INSTRUM	spect
PROBHD	5 mm CPQNP 1H/
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	9
DW	60.400 usec
DE	6.00 usec
TE	298.2 K
D1	1.00000000 sec
TD0	1

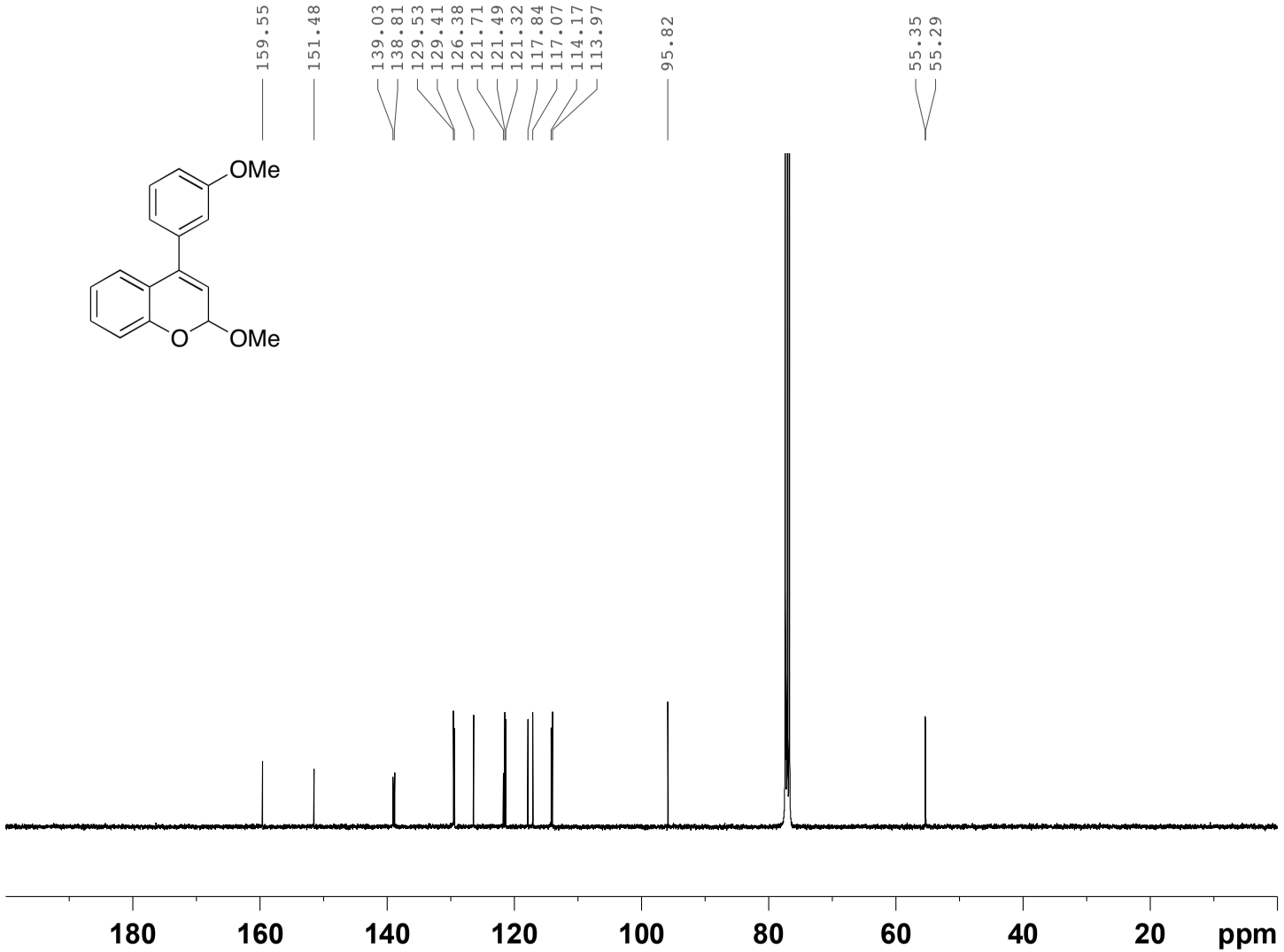
======== CHANNEL f1 ========

NUC1	1H
P1	15.00 usec
PL1	4.90 dB
PL1W	3.30822015 W
SFO1	400.1324710 MHz

F2 - Processing parameters

SI	32768
SF	400.1300101 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Compound 1.87 13C NMR



Current Data Parameters
NAME HH-3-237Baug14
EXPNO 2
PROCNO 1

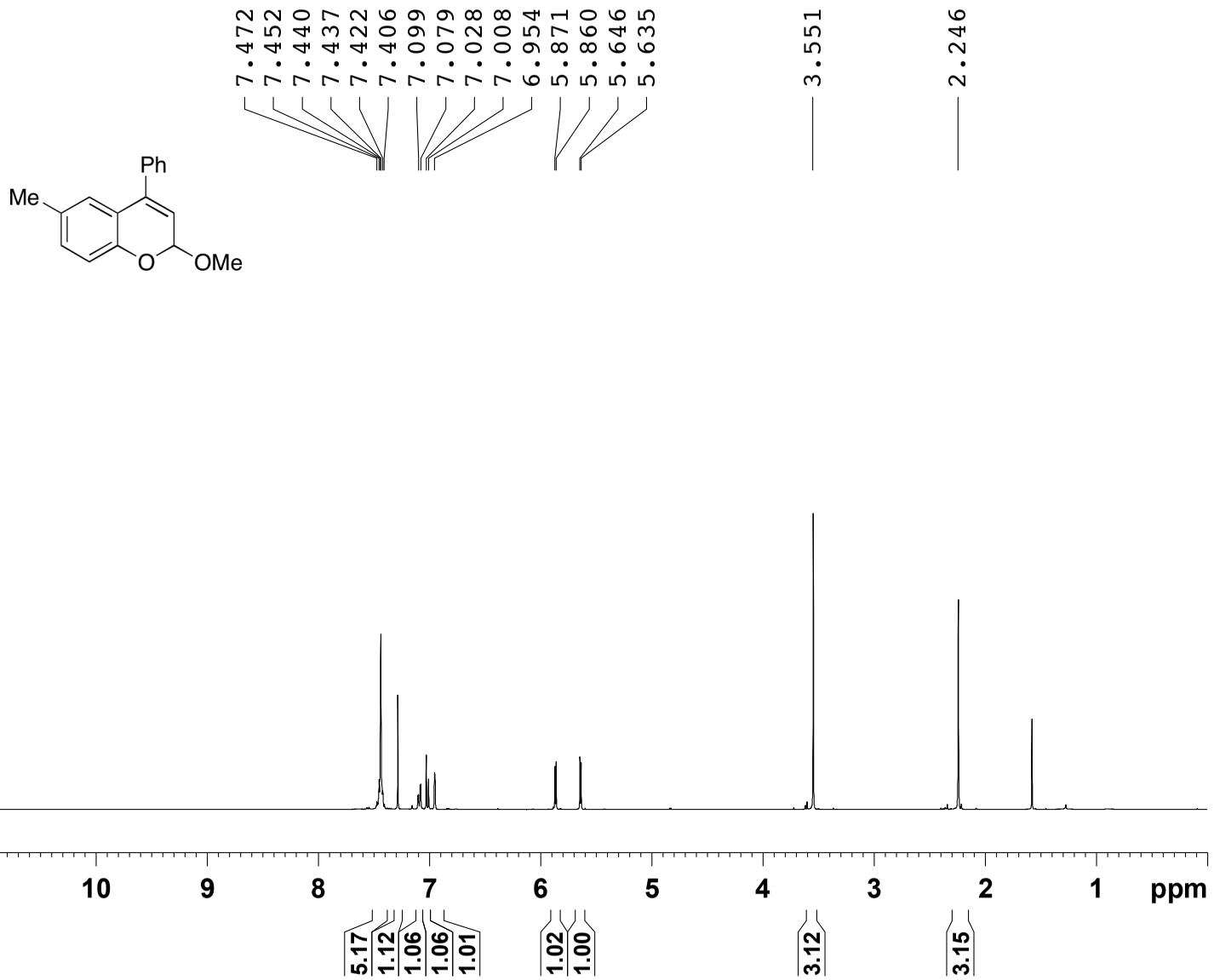
F2 - Acquisition Parameters
Date_ 20120814
Time 22.40
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 512
DW 20.850 usec
DE 18.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.25 usec
PL1 0.55 dB
PL1W 35.18820572 W
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 4.90 dB
PL12 20.46 dB
PL13 21.00 dB
PL2W 3.30822015 W
PL12W 0.09195905 W
PL13W 0.08120718 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Compound 1.88 1H NMR

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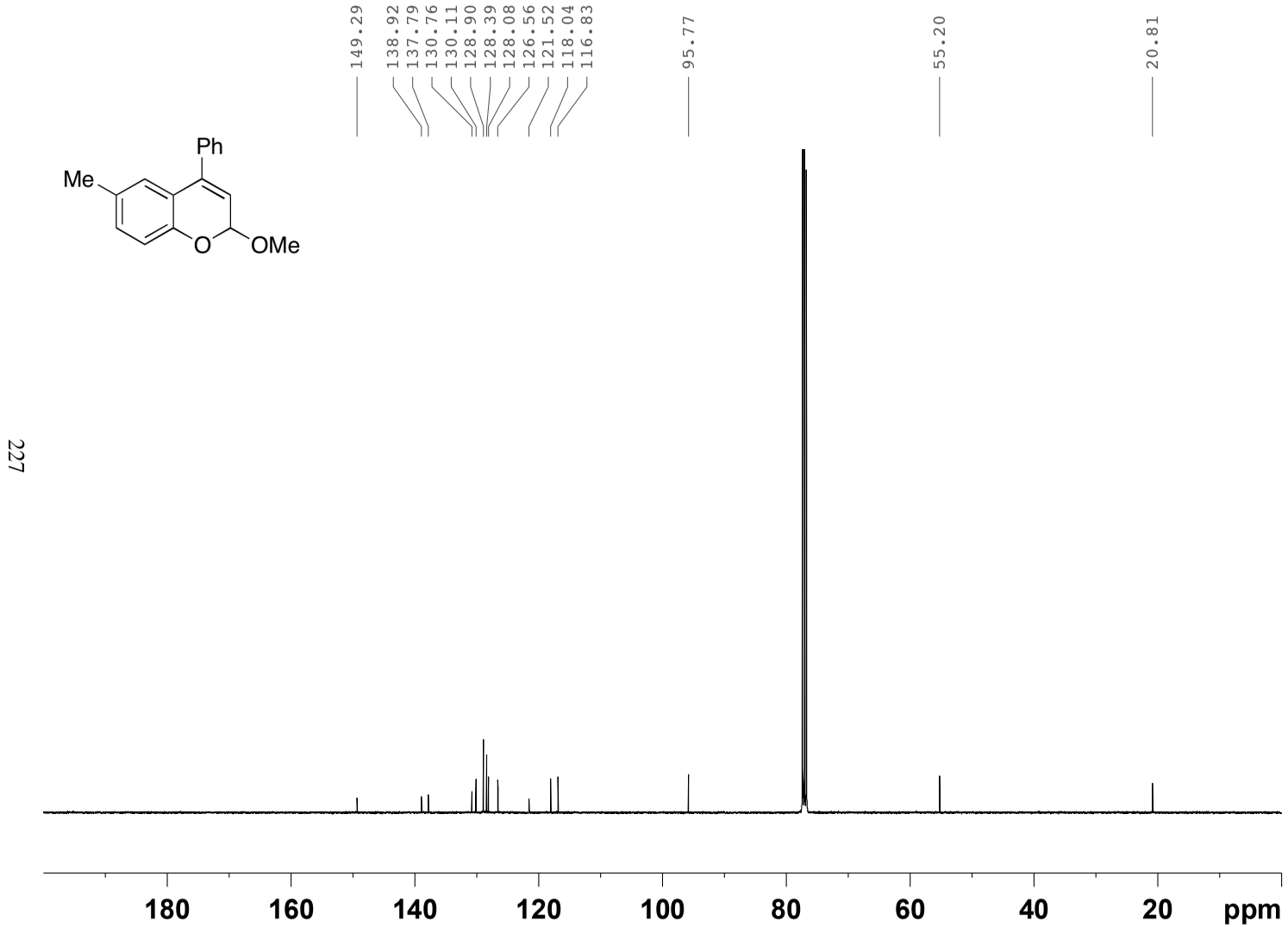
Current Data Parameters
NAME      HH-3-214aug14
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20120814
Time              11.35
INSTRUM           spect
PROBHD   5 mm CPQNP 1H/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ             3.9584243 sec
RG                    9
DW               60.400 usec
DE                6.00 usec
TE                298.2 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                15.00 usec
PL1                4.90 dB
PL1W         3.30822015 W
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

Compound 1.88 13C NMR



227

Current Data Parameters
NAME HH-3-214aug14
EXPNO 2
PROCNO 1

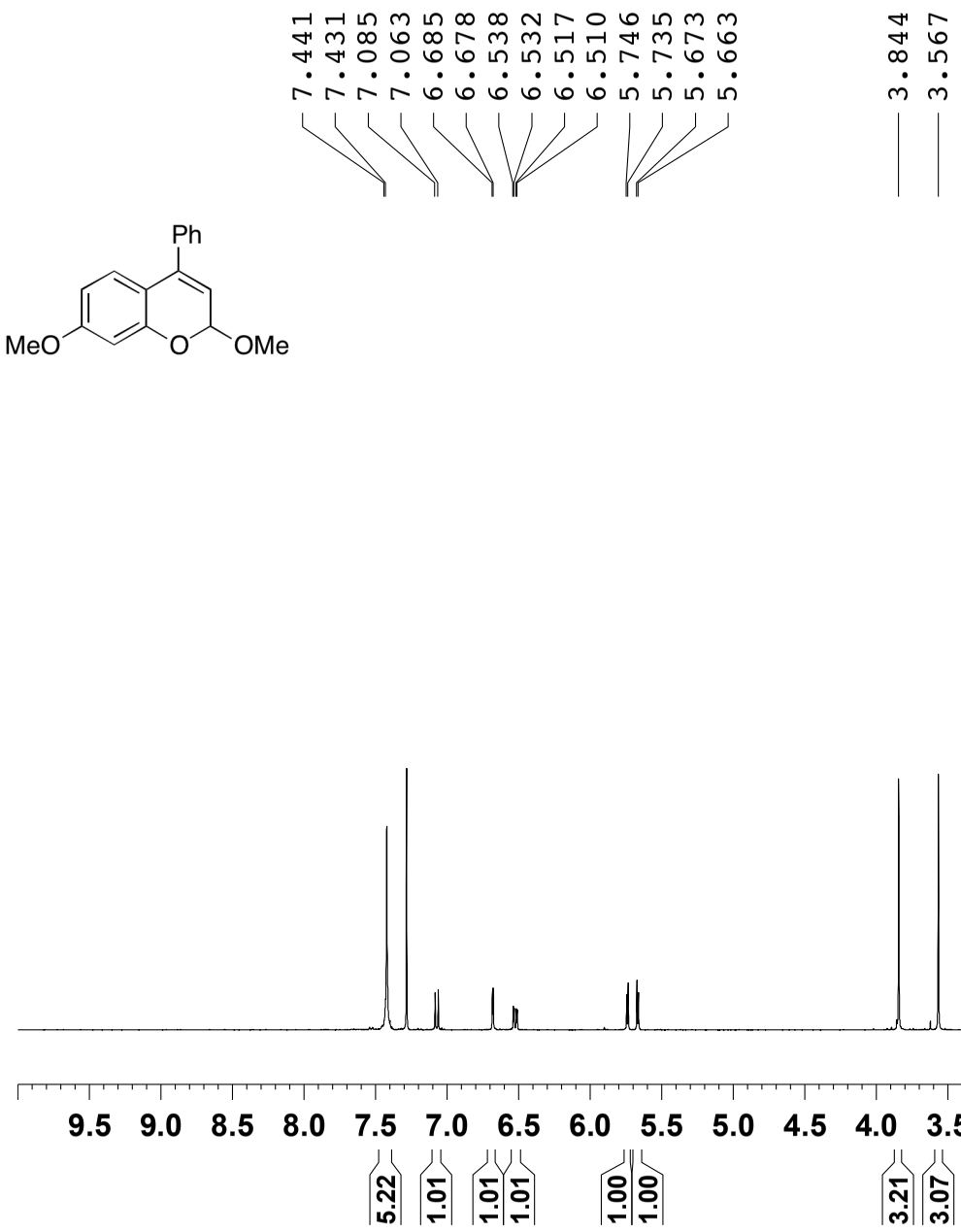
F2 - Acquisition Parameters
Date_ 20120814
Time 18.07
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 512
DW 20.850 usec
DE 18.00 usec
TE 298.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.25 usec
PL1 0.55 dB
PL1W 35.18820572 W
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 4.90 dB
PL12 20.46 dB
PL13 21.00 dB
PL2W 3.30822015 W
PL12W 0.09195905 W
PL13W 0.08120718 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Compound 1.89 1H NMR



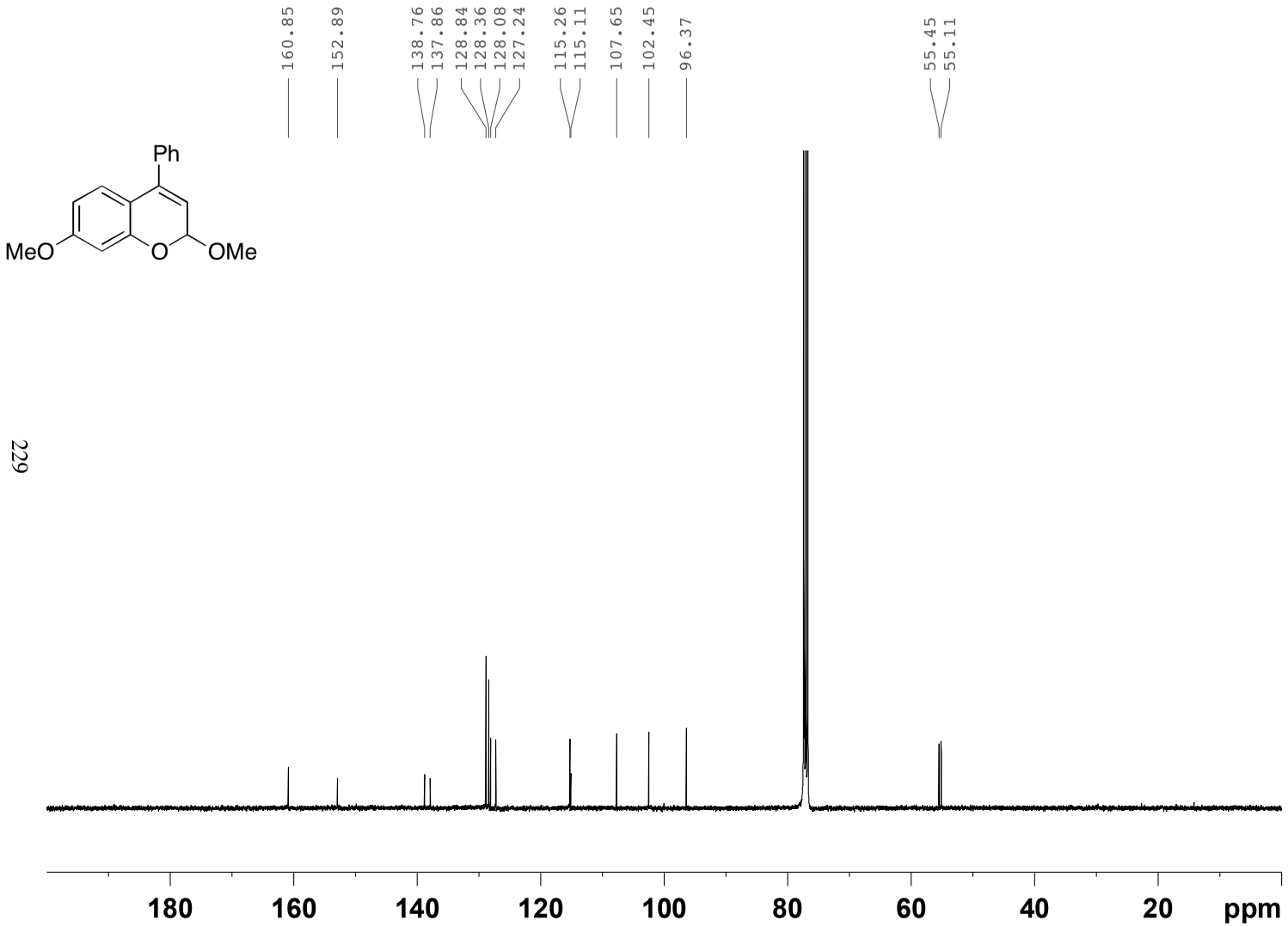
Current Data Parameters
NAME HH-3-175aug22
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120823
Time 0.11
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 6.3
DW 60.400 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 4.90 dB
PL1W 3.30822015 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound 1.89 13C NMR



229

Current Data Parameters
NAME HH-3-175aug22
EXPNO 2
PROCNO 1

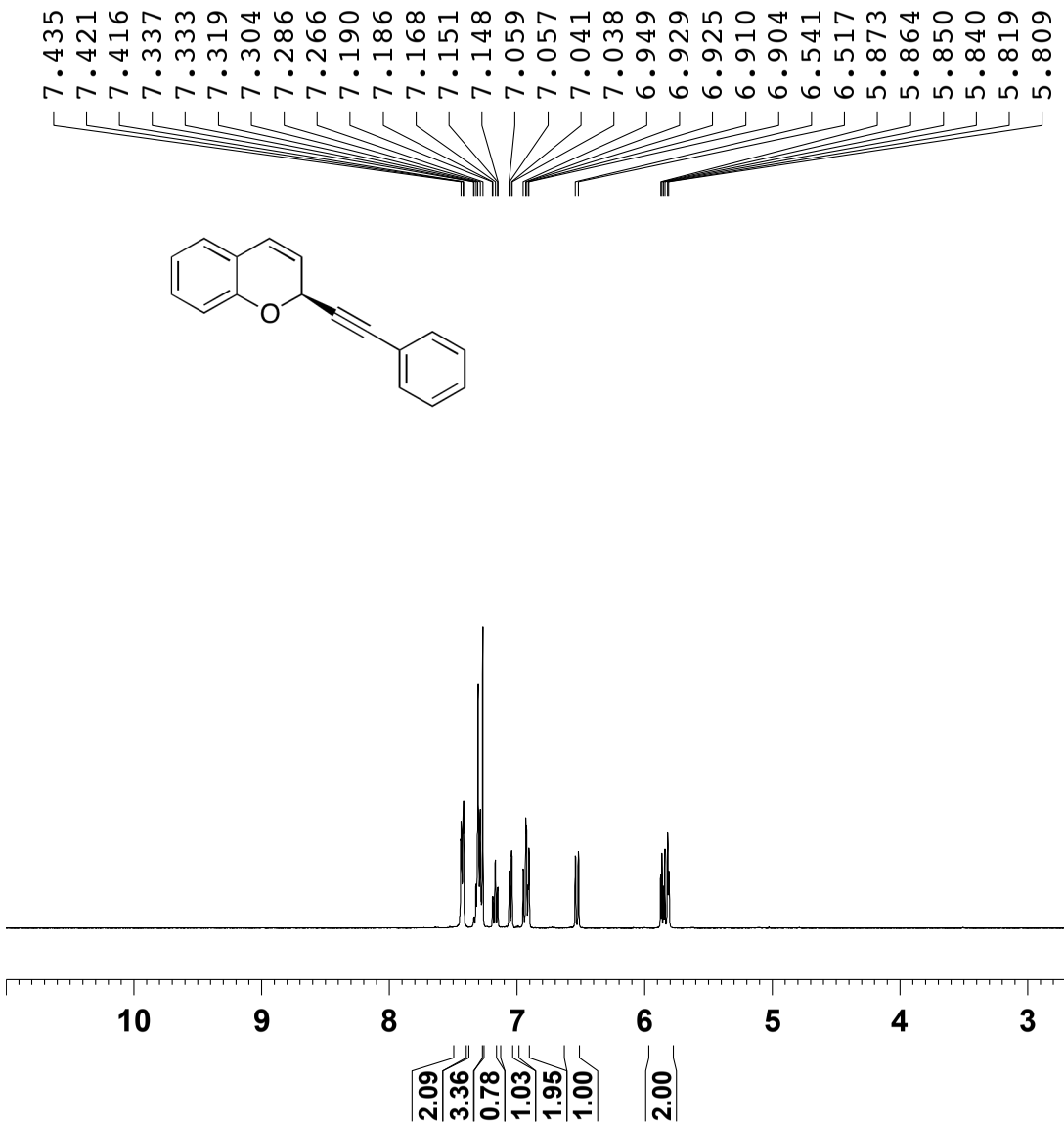
F2 - Acquisition Parameters
Date_ 20120823
Time 2.19
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 512
DW 20.850 usec
DE 18.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.25 usec
PL1 0.55 dB
PL1W 35.18820572 W
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 4.90 dB
PL12 20.46 dB
PL13 21.00 dB
PL2W 3.30822015 W
PL12W 0.09195905 W
PL13W 0.08120718 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Compound 1.41 1H NMR



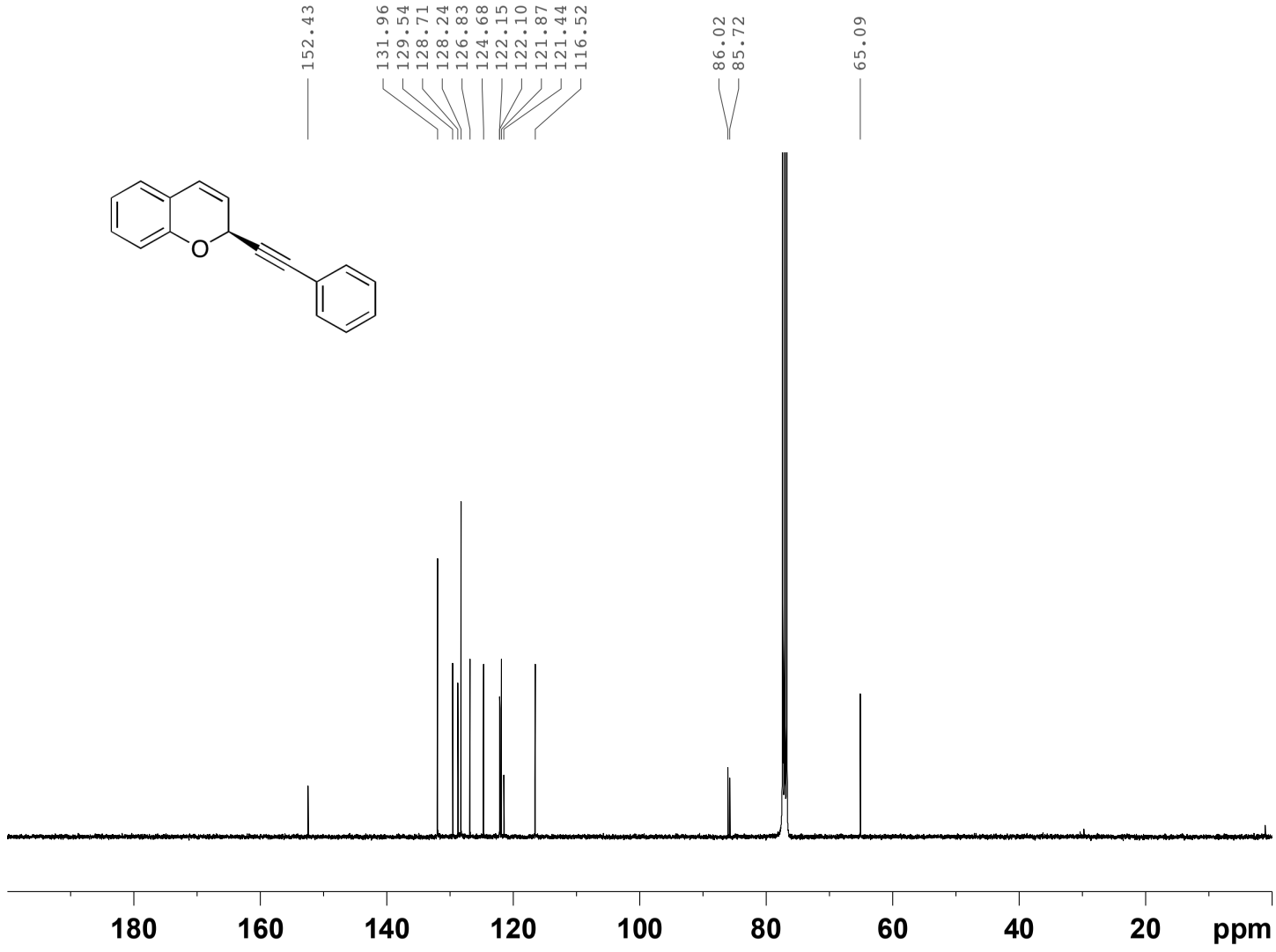
Current Data Parameters
NAME HH-3-246E1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120723
Time 16.10
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 11.3
DW 60.400 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 4.90 dB
PL1W 3.30822015 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300073 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound 1.41 13C NMR



Current Data Parameters
NAME HH-3-246E1
EXPNO 2
PROCNO 1

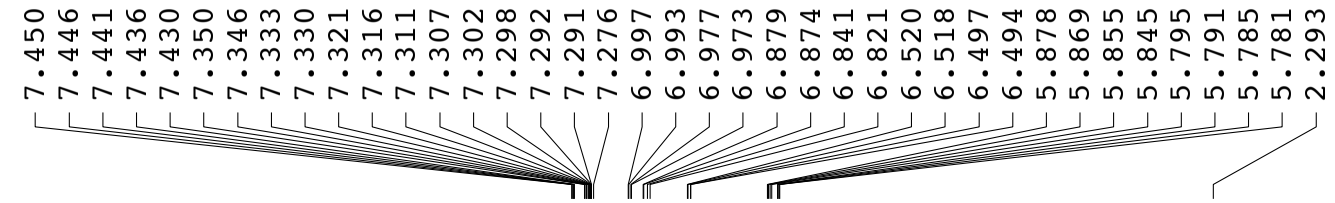
F2 - Acquisition Parameters
Date_ 20120724
Time 21.19
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 512
DW 20.850 usec
DE 18.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

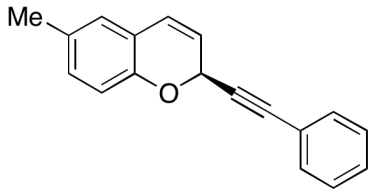
======== CHANNEL f1 ========
NUC1 13C
P1 9.25 usec
PL1 0.55 dB
PL1W 35.18820572 W
SFO1 100.6228298 MHz

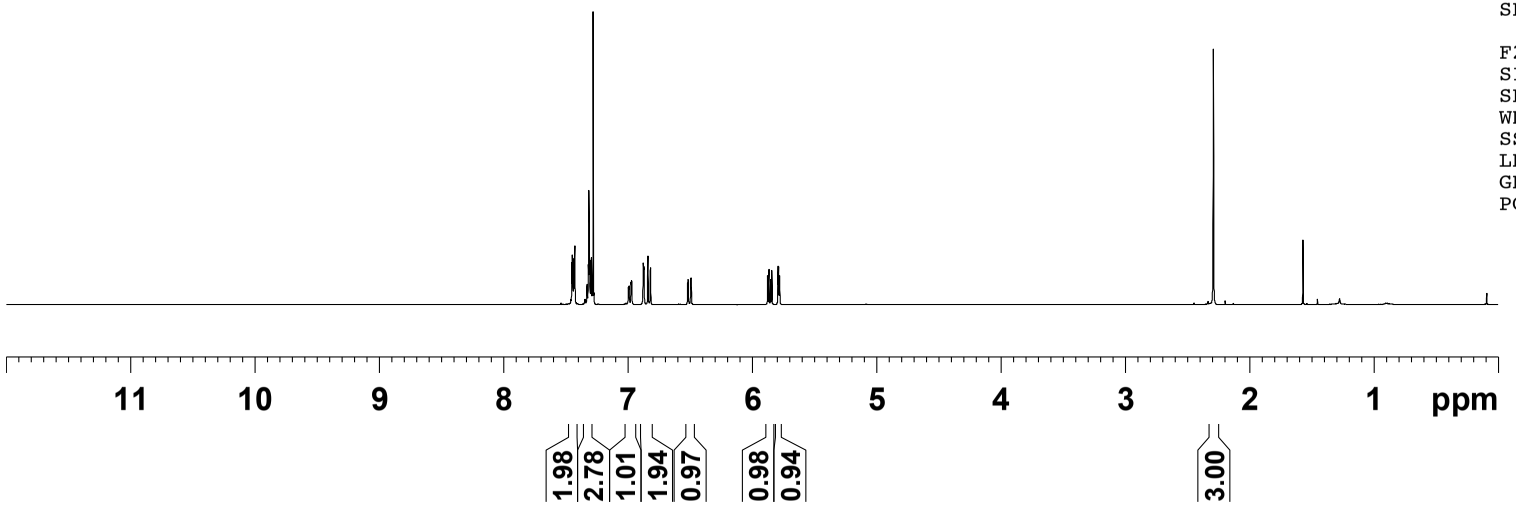
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 4.90 dB
PL12 20.46 dB
PL13 21.00 dB
PL2W 3.30822015 W
PL12W 0.09195905 W
PL13W 0.08120718 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Compound 1.36 1H NMR







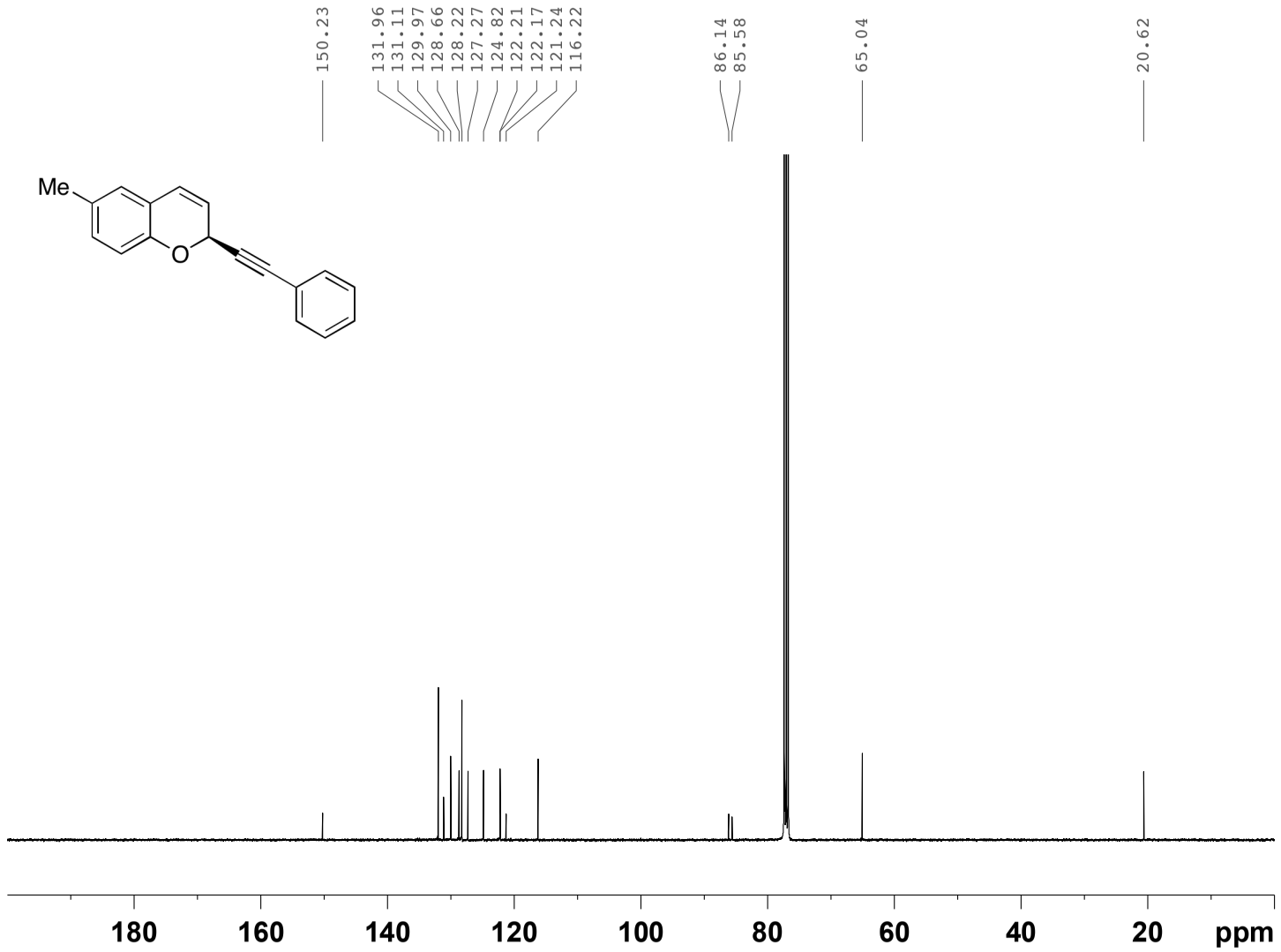
Current Data Parameters
NAME HH-3-207A2
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120511
Time 4.23
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 16
DW 60.400 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 4.90 dB
PL1W 3.30822015 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound 1.36 13C NMR




```
Current Data Parameters
NAME          HH-3-207A2
EXPNO                  2
PROCNO                 1

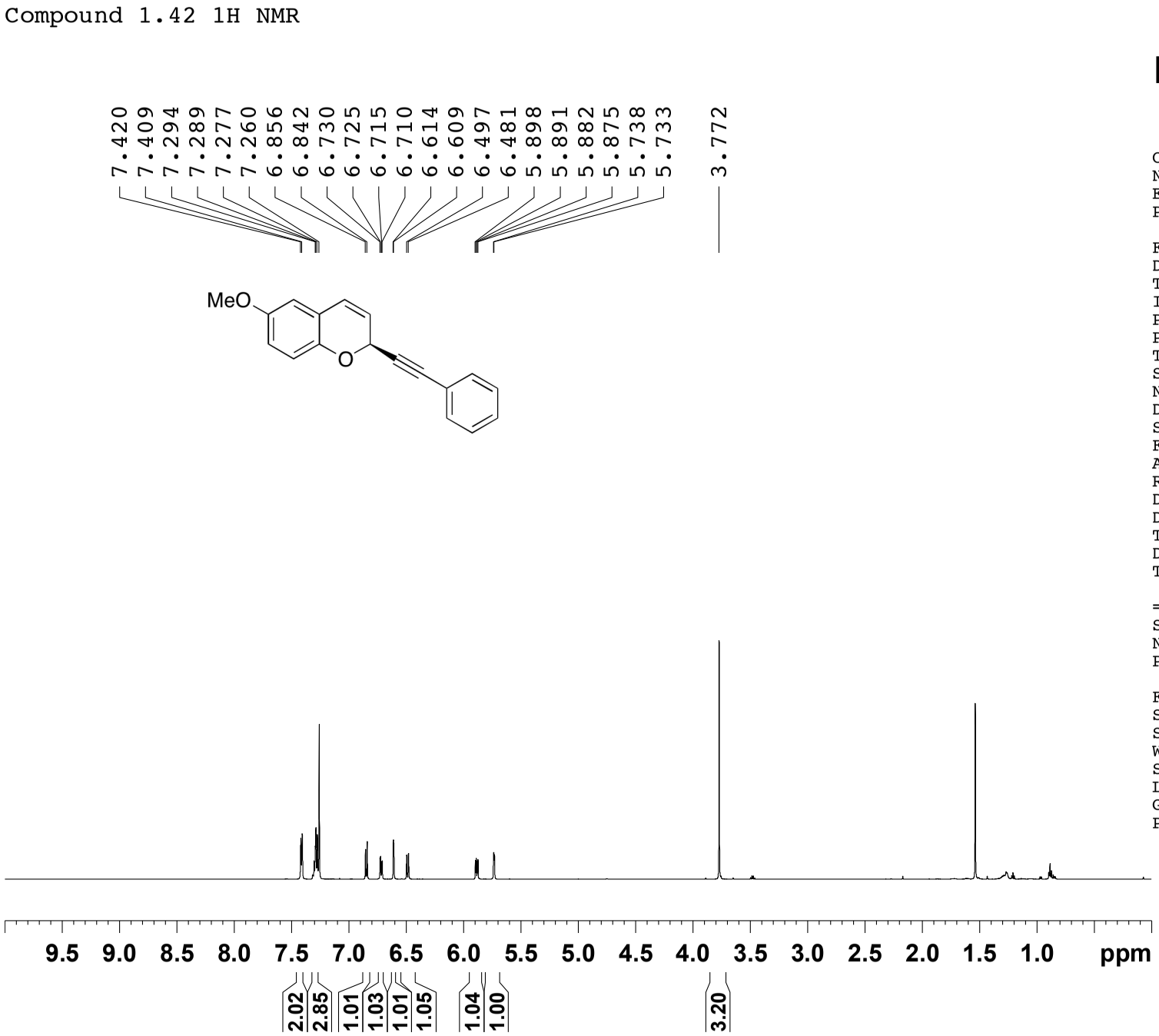
F2 - Acquisition Parameters
Date_           20120511
Time               5.23
INSTRUM           spect
PROBHD   5 mm CPQNP 1H/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ            1.3664756 sec
RG                  512
DW               20.850 usec
DE               18.00 usec
TE               298.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 9.25 usec
PL1                0.55 dB
PL1W        35.18820572 W
SFO1       100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             90.00 usec
PL2                4.90 dB
PL12              20.46 dB
PL13              21.00 dB
PL2W         3.30822015 W
PL12W        0.09195905 W
PL13W        0.08120718 W
SFO2       400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127690 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                 1.40
```

Compound 1.42 1H NMR



Current Data Parameters

NAME	HH-3-253A2_2
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20120719
Time	23.52
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	2
SWH	8403.361 Hz
FIDRES	0.128225 Hz
AQ	3.8994420 sec
RG	228
DW	59.500 usec
DE	17.39 usec
TE	300.2 K
D1	1.00000000 sec
TD0	1

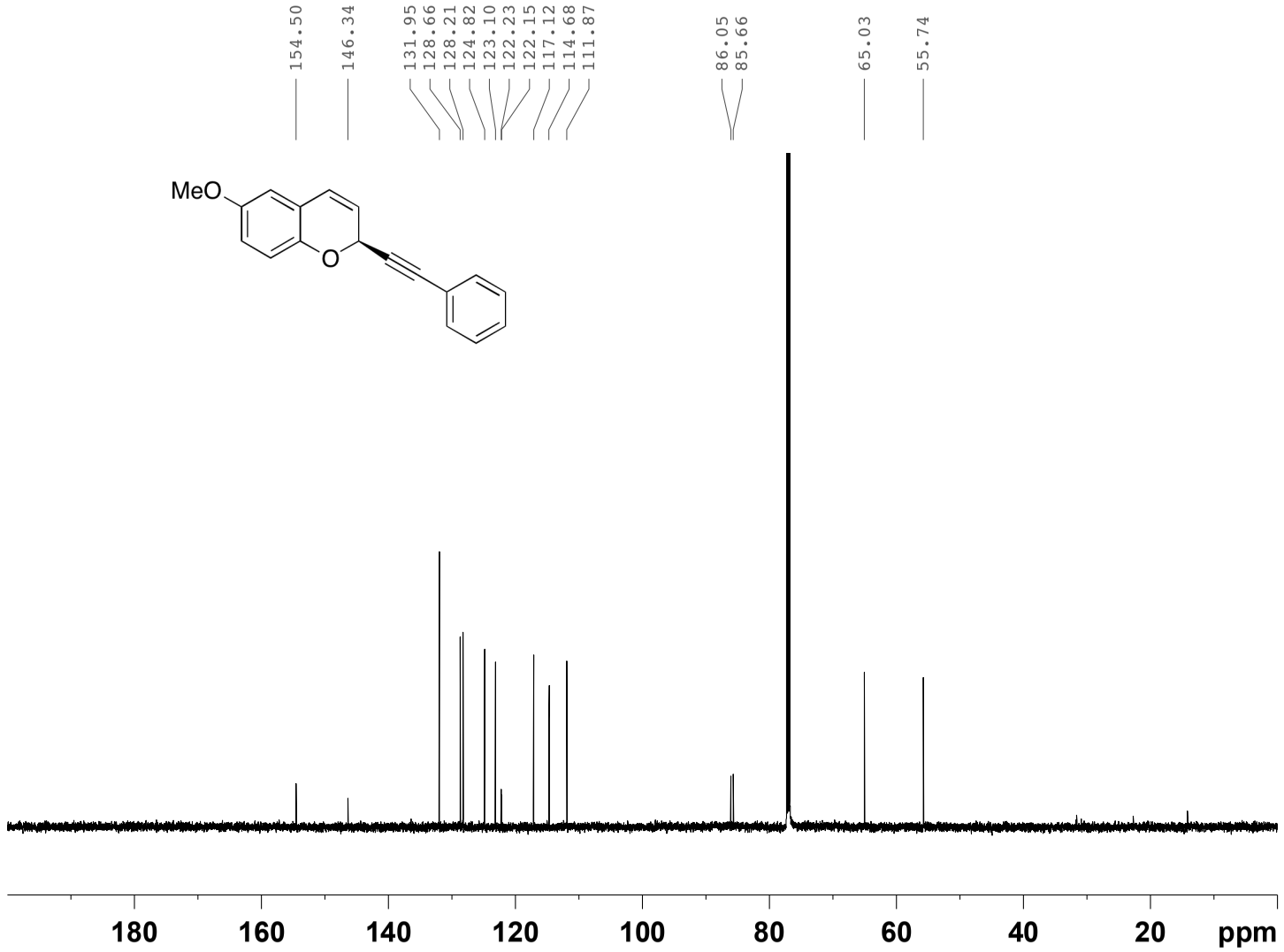
======== CHANNEL f1 ========

SFO1	600.3233018 MHz
NUC1	1H
P1	10.77 usec

F2 - Processing parameters

SI	65536
SF	600.3200159 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Compound 1.42 13C NMR



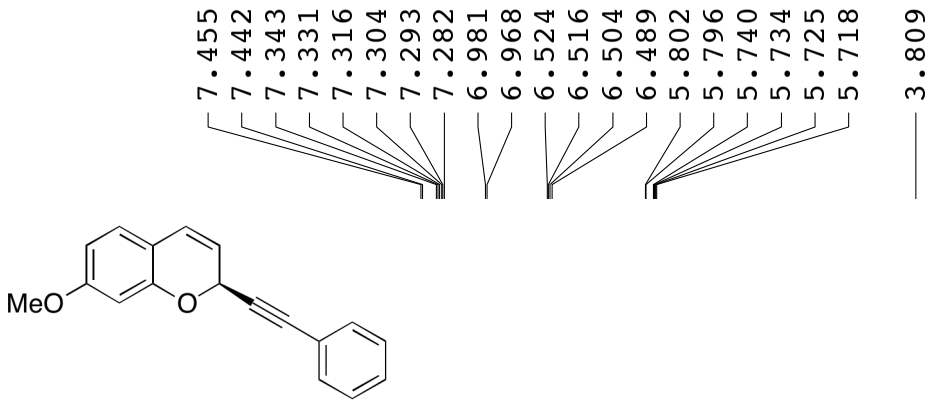
Current Data Parameters
NAME HH-3-253A2_2
EXPNO 2
PROCNO 1

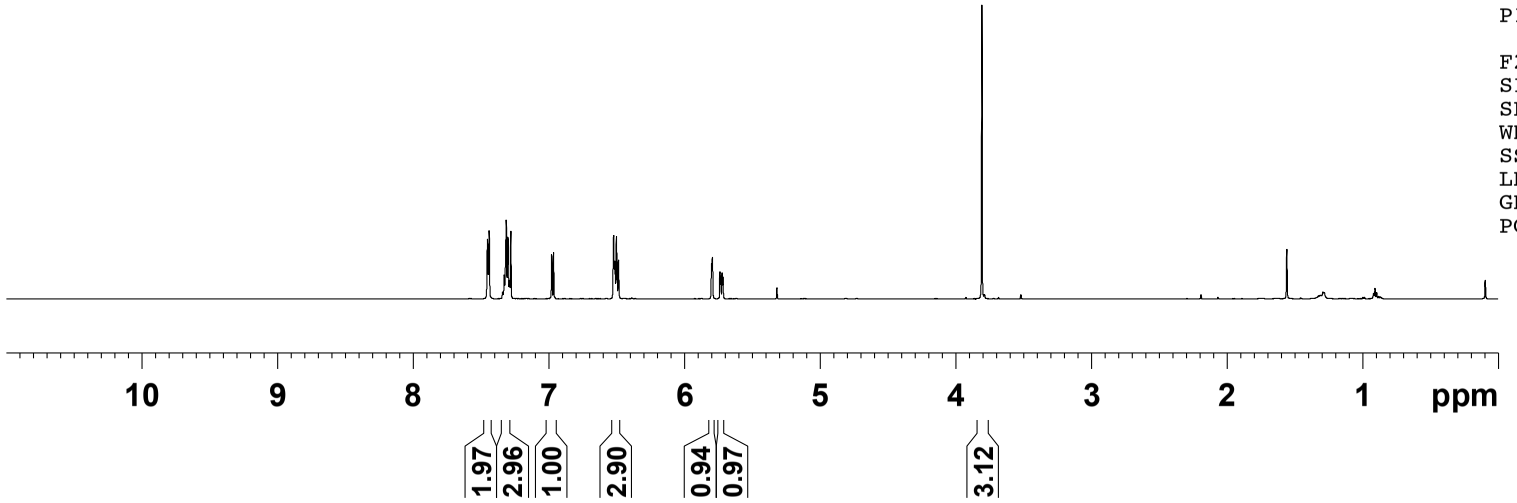
F2 - Acquisition Parameters
Date_ 20120720
Time 1.05
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg55
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 34722.223 Hz
FIDRES 0.529819 Hz
AQ 0.9437684 sec
RG 2050
DW 14.400 usec
DE 19.34 usec
TE 300.2 K
D1 1.10000002 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 150.9656784 MHz
NUC1 13C
P1 10.63 usec

F2 - Processing parameters
SI 32768
SF 150.9505840 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Compound 1.43 1H NMR





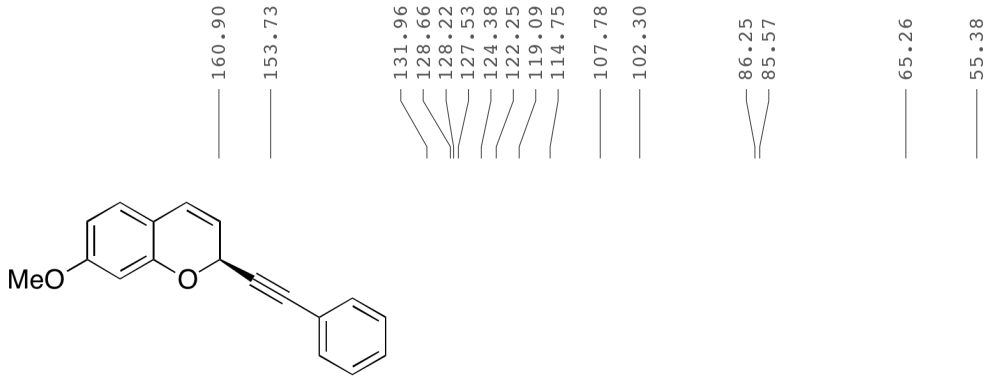
Current Data Parameters
NAME HH-3-232_2
EXPNO 1
PROCNO 1

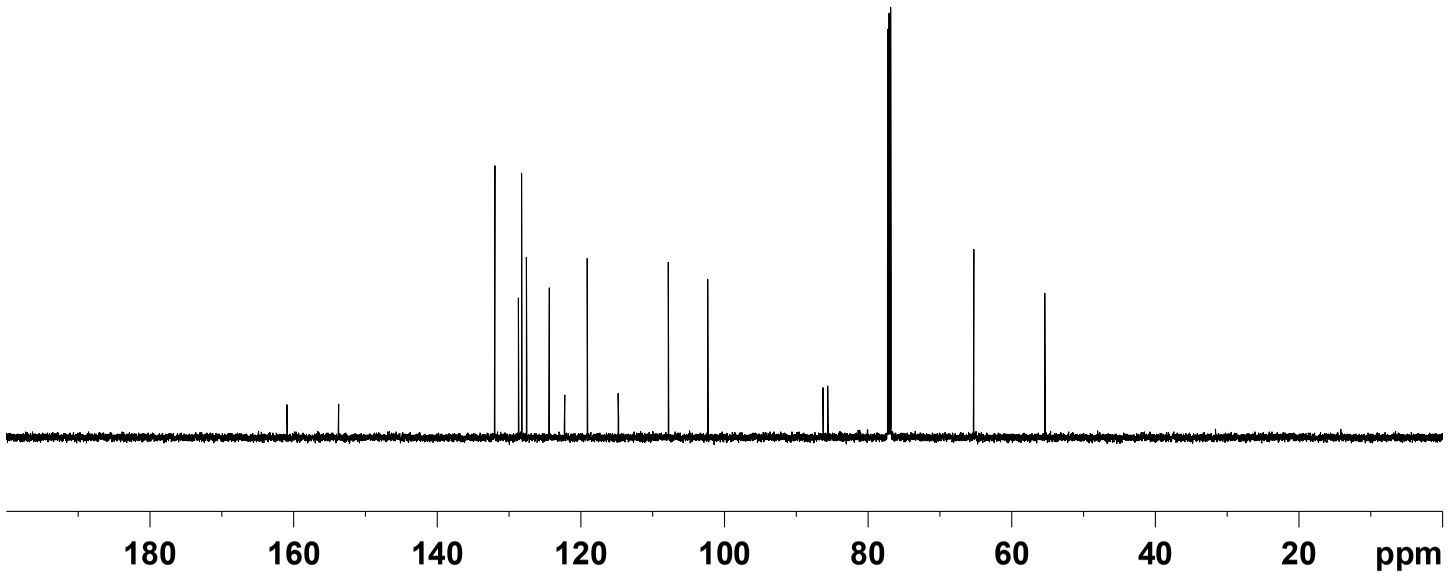
F2 - Acquisition Parameters
Date_ 20120708
Time 1.34
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8403.361 Hz
FIDRES 0.128225 Hz
AQ 3.8994420 sec
RG 161
DW 59.500 usec
DE 17.39 usec
TE 300.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 600.3233018 MHz
NUC1 1H
P1 10.77 usec

F2 - Processing parameters
SI 65536
SF 600.3200026 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound 1.43 13C NMR





237

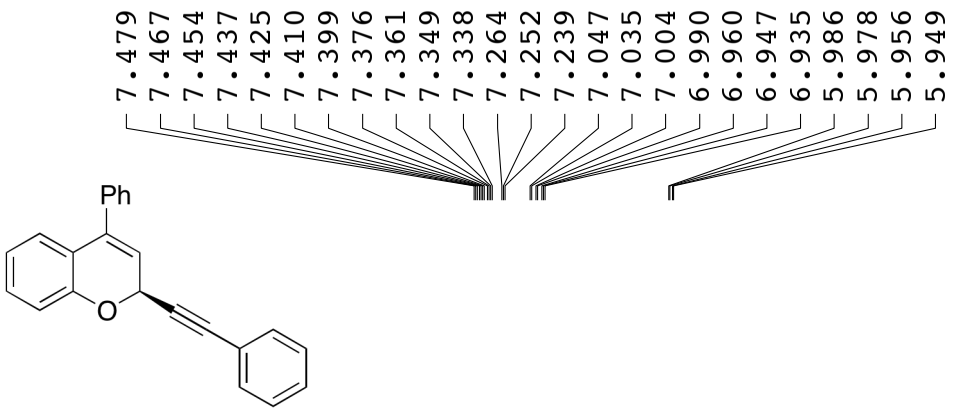
Current Data Parameters
NAME HH-3-232july8
EXPNO 3
PROCNO 1

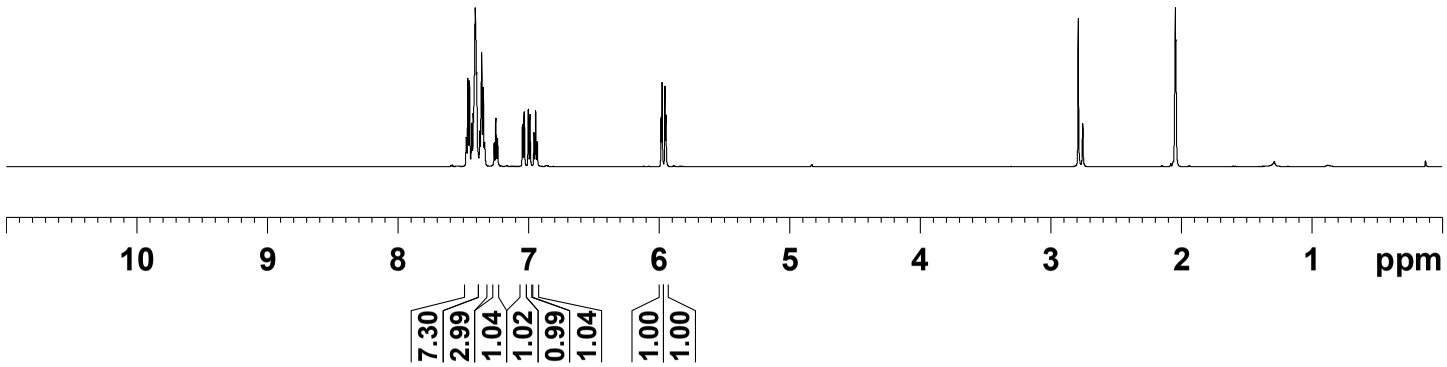
F2 - Acquisition Parameters
Date_ 20120708
Time 15.31
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg55
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 34722.223 Hz
FIDRES 0.529819 Hz
AQ 0.9437684 sec
RG 2050
DW 14.400 usec
DE 19.34 usec
TE 300.2 K
D1 1.10000002 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 150.9656784 MHz
NUC1 13C
P1 10.63 usec

F2 - Processing parameters
SI 32768
SF 150.9505840 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Compound 1.44 1H NMR





238

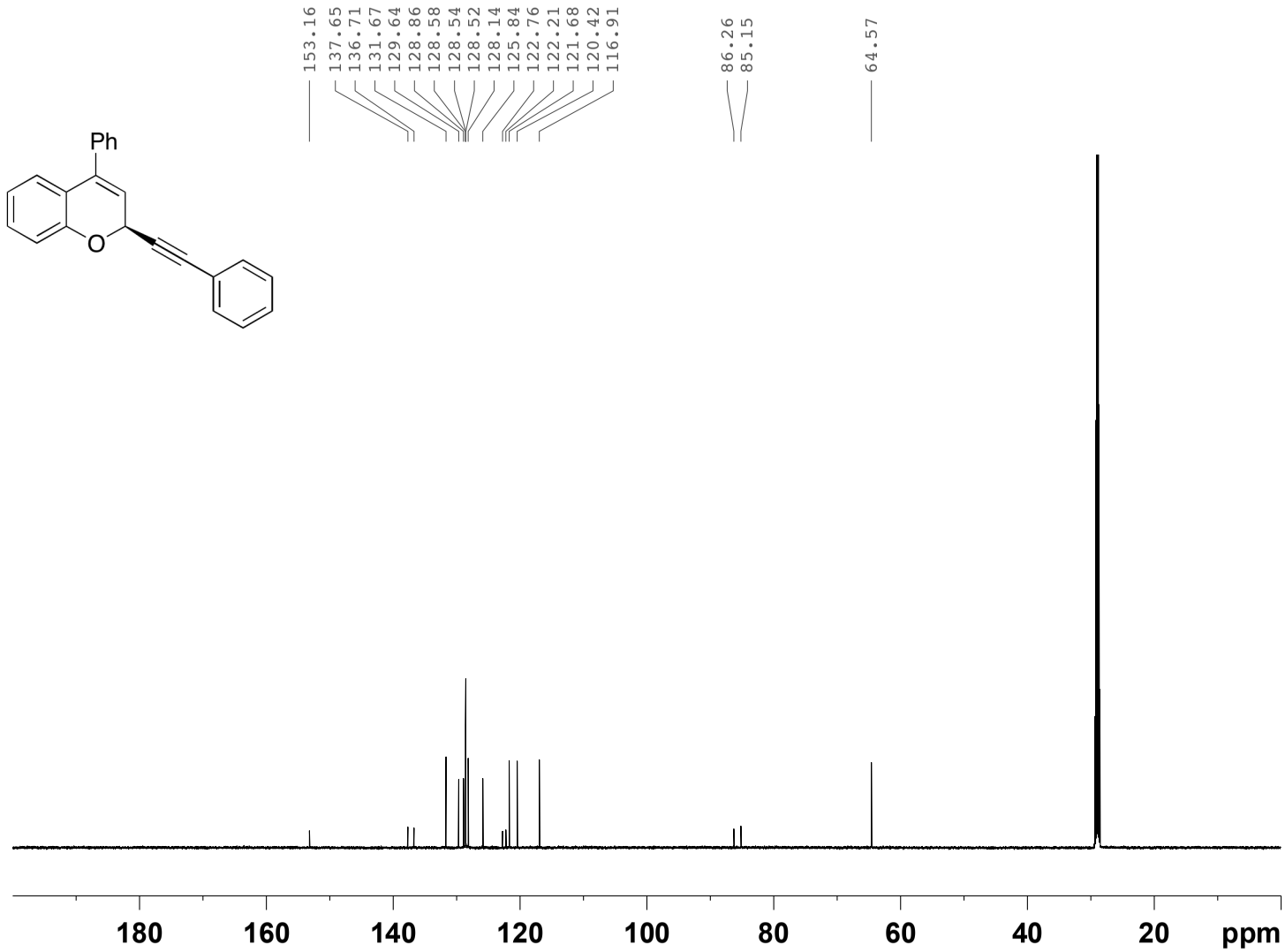
Current Data Parameters
NAME HH-3-192A1_3
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120731
Time 10.57
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT Acetone
NS 8
DS 2
SWH 8403.361 Hz
FIDRES 0.128225 Hz
AQ 3.8994420 sec
RG 181
DW 59.500 usec
DE 17.39 usec
TE 300.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 600.3233018 MHz
NUC1 1H
P1 10.77 usec

F2 - Processing parameters
SI 65536
SF 600.3200143 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound 1.44 13C NMR



239

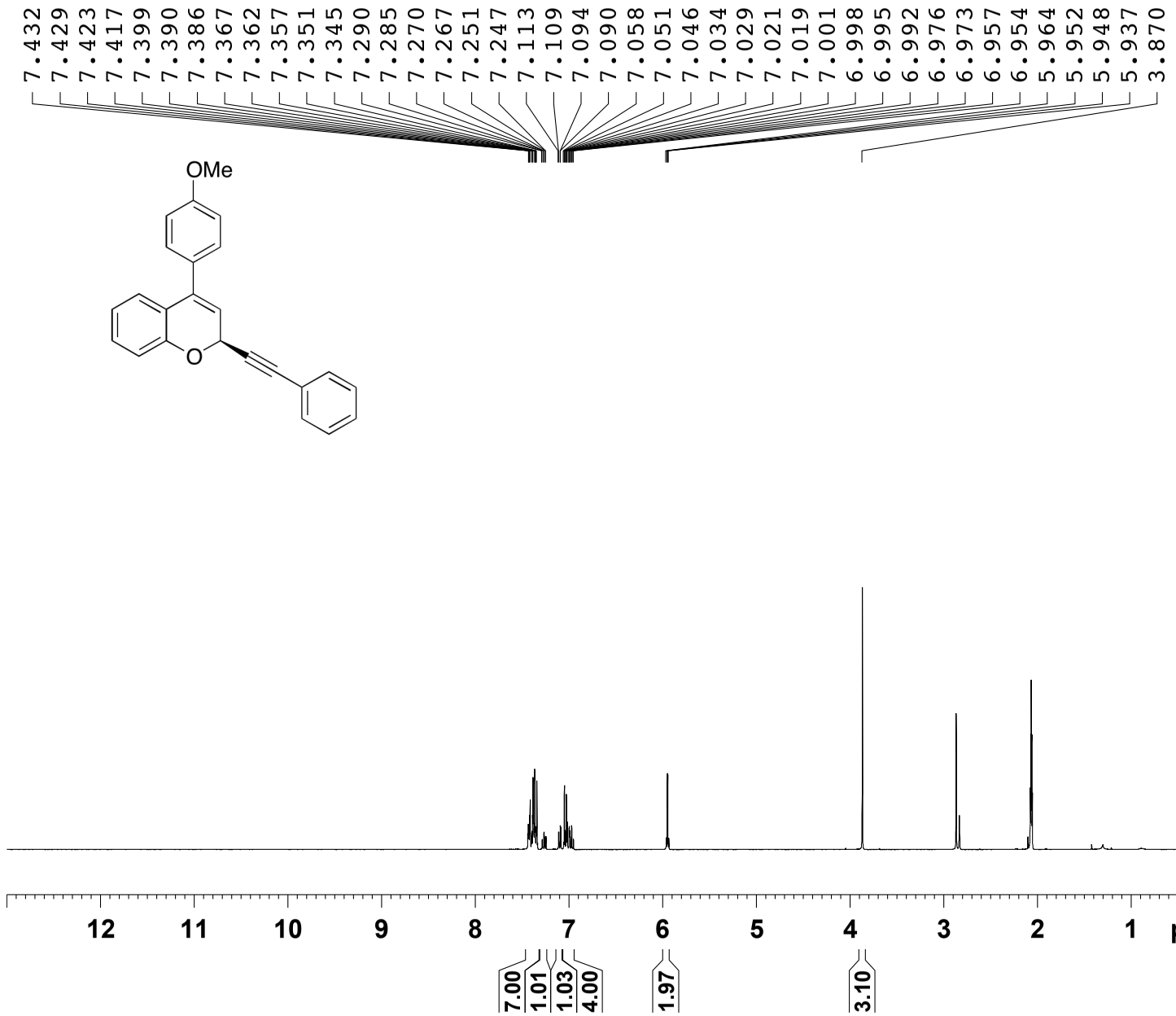
Current Data Parameters
NAME HH-3-192A2_2
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120731
Time 21.35
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg55
TD 65536
SOLVENT Acetone
NS 2048
DS 4
SWH 34722.223 Hz
FIDRES 0.529819 Hz
AQ 0.9437684 sec
RG 2050
DW 14.400 usec
DE 19.34 usec
TE 300.2 K
D1 1.10000002 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 150.9656784 MHz
NUC1 13C
P1 10.63 usec

F2 - Processing parameters
SI 32768
SF 150.9505840 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Compound 1.45 1H NMR



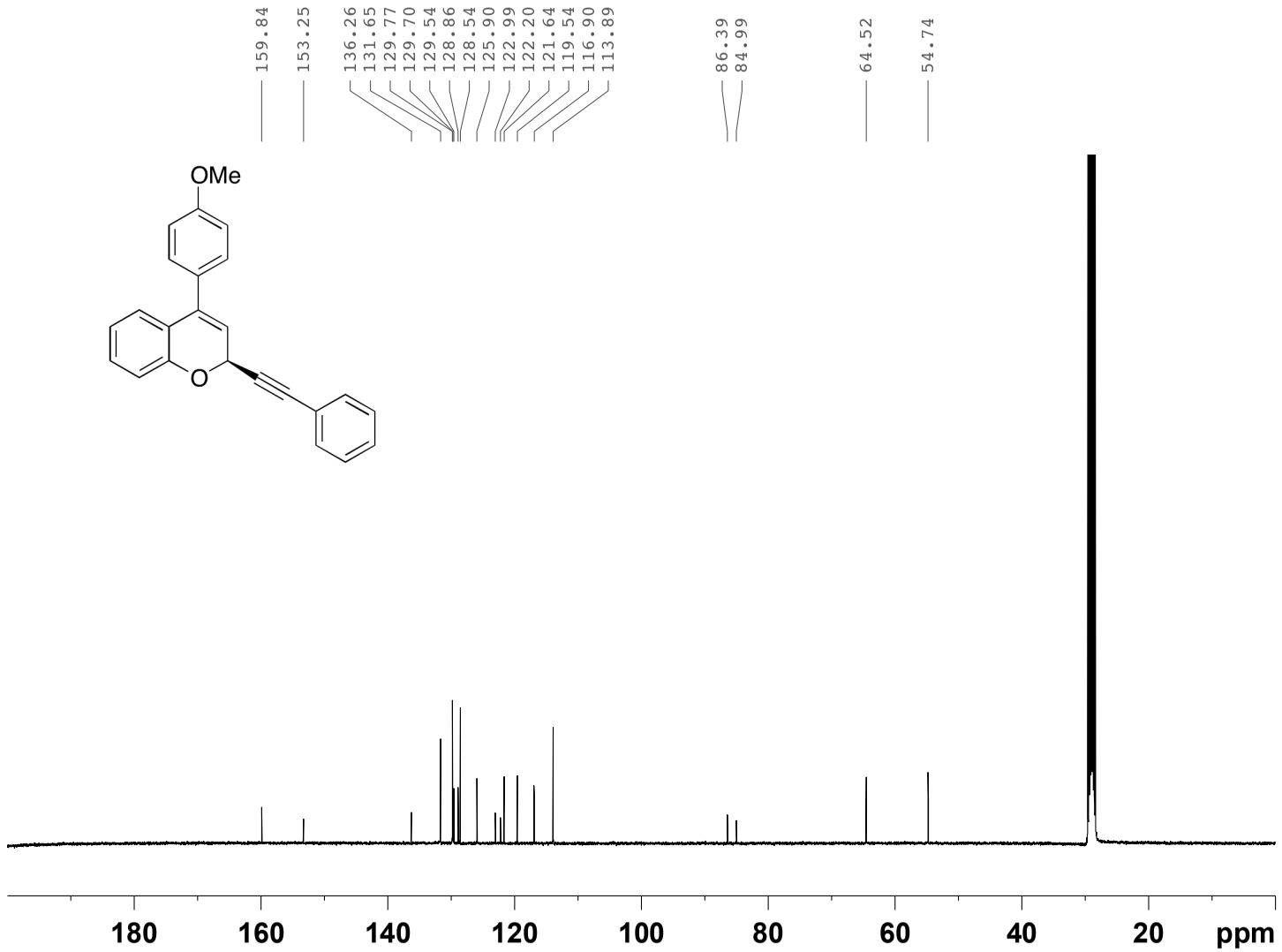
Current Data Parameters
NAME HH-3-209A1rs
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120725
Time 7.49
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zg30
TD 65536
SOLVENT Acetone
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 9
DW 60.400 usec
DE 6.00 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 4.90 dB
PL1W 3.30822015 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound 1.45 13C NMR



Current Data Parameters

NAME	HH-3-209A2rs
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20120726
Time	1.17
INSTRUM	spect
PROBHD	5 mm CPQNP 1H/
PULPROG	zgpg30
TD	65536
SOLVENT	Acetone
NS	1024
DS	4
SWH	23980.814 Hz
FIDRES	0.365918 Hz
AQ	1.3664756 sec
RG	512
DW	20.850 usec
DE	18.00 usec
TE	298.1 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1

======== CHANNEL f1 ========

NUC1	13C
P1	9.25 usec
PL1	0.55 dB
PL1W	35.18820572 W
SFO1	100.6228298 MHz

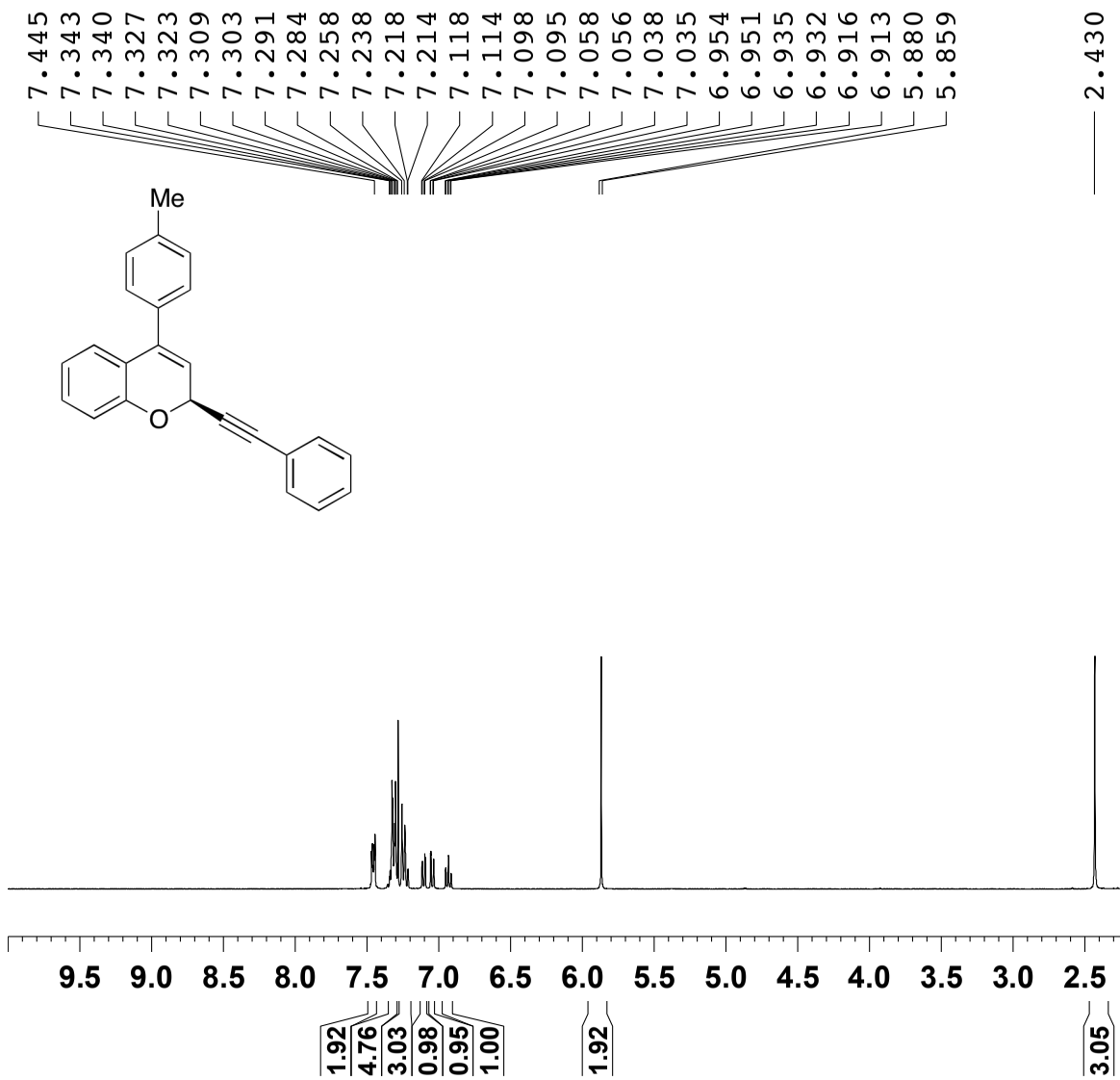
======== CHANNEL f2 ========

CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	4.90 dB
PL12	20.46 dB
PL13	21.00 dB
PL2W	3.30822015 W
PL12W	0.09195905 W
PL13W	0.08120718 W
SFO2	400.1316005 MHz

F2 - Processing parameters

SI	32768
SF	100.6127690 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

Compound 1.46 1H NMR



242

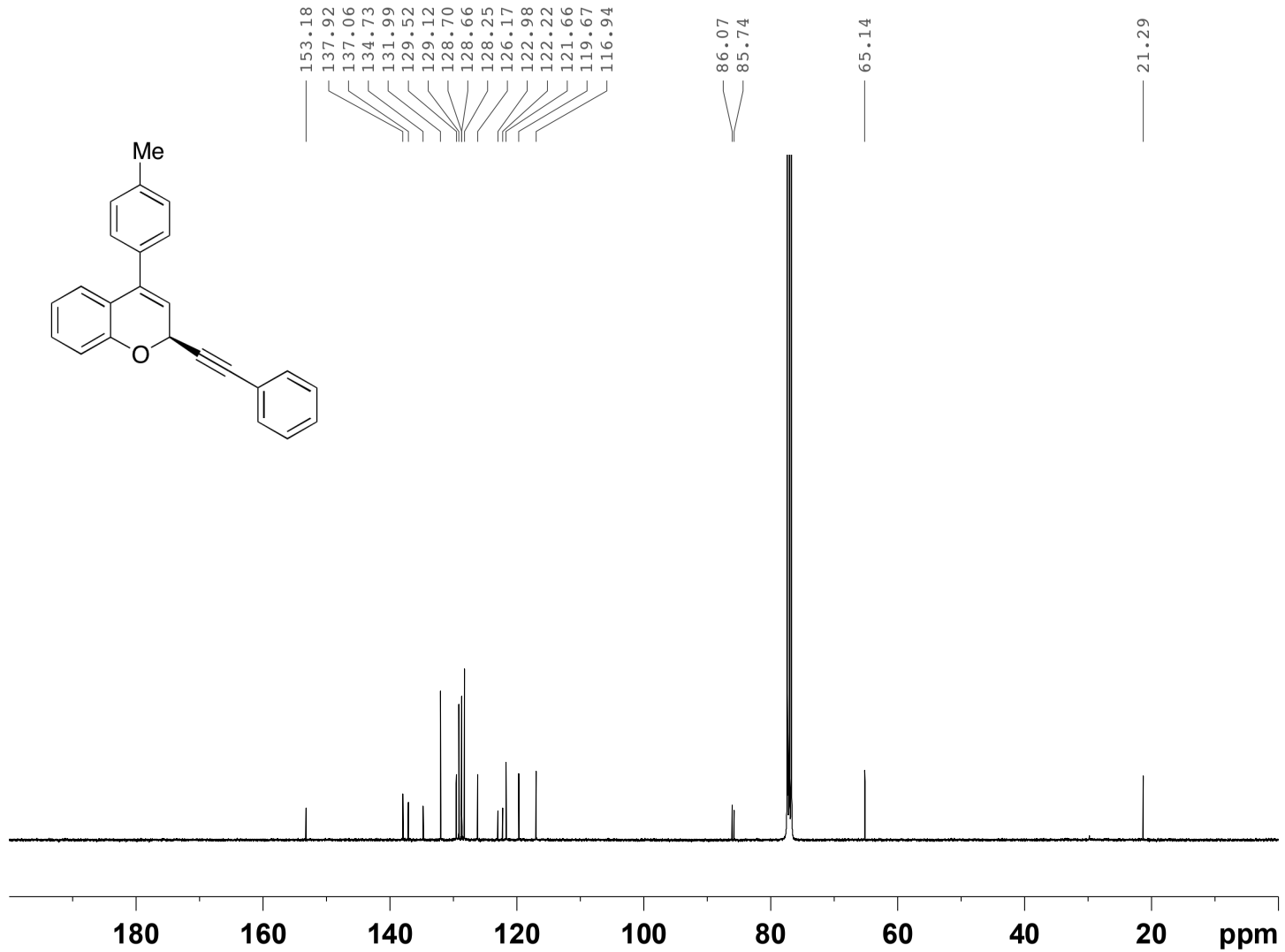
Current Data Parameters
NAME HH-3-203B1july29
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120729
Time 16.04
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 11.3
DW 60.400 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 4.90 dB
PL1W 3.30822015 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound 1.46 13C NMR

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Current Data Parameters
NAME      HH-3-203B1july29
EXPNO                    2
PROCNO                   1

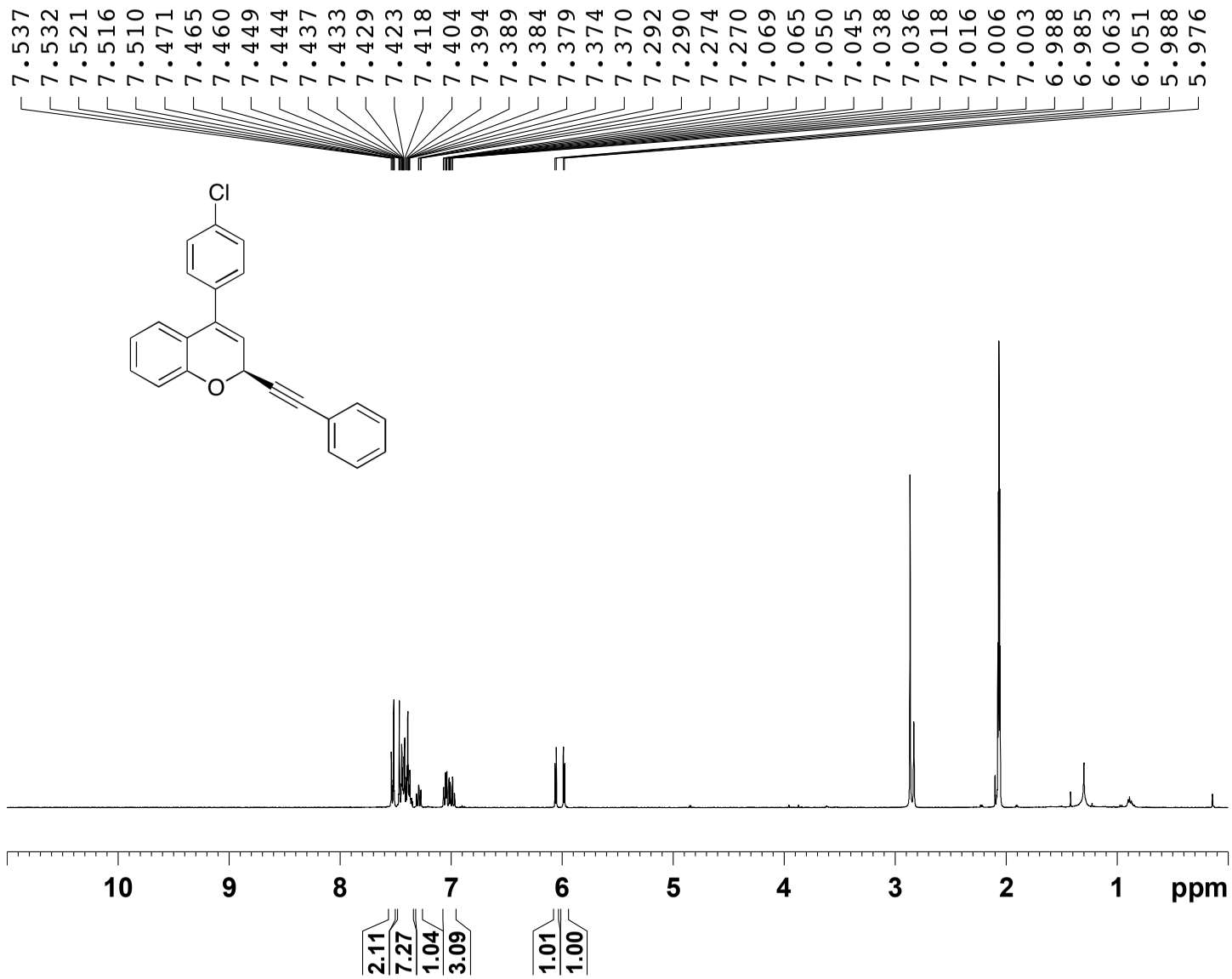
F2 - Acquisition Parameters
Date_             20120729
Time                 17.58
INSTRUM              spect
PROBHD   5 mm CPQNP 1H/
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    1500
DS                       4
SWH              23980.814 Hz
FIDRES            0.365918 Hz
AQ               1.3664756 sec
RG                     512
DW                  20.850 usec
DE                  18.00 usec
TE                  298.2 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    9.25 usec
PL1                   0.55 dB
PL1W          35.18820572 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2                90.00 usec
PL2                   4.90 dB
PL12                 20.46 dB
PL13                 21.00 dB
PL2W           3.30822015 W
PL12W          0.09195905 W
PL13W          0.08120718 W
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                   32768
SF           100.6127690 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

Compound 1.47 1H NMR



244

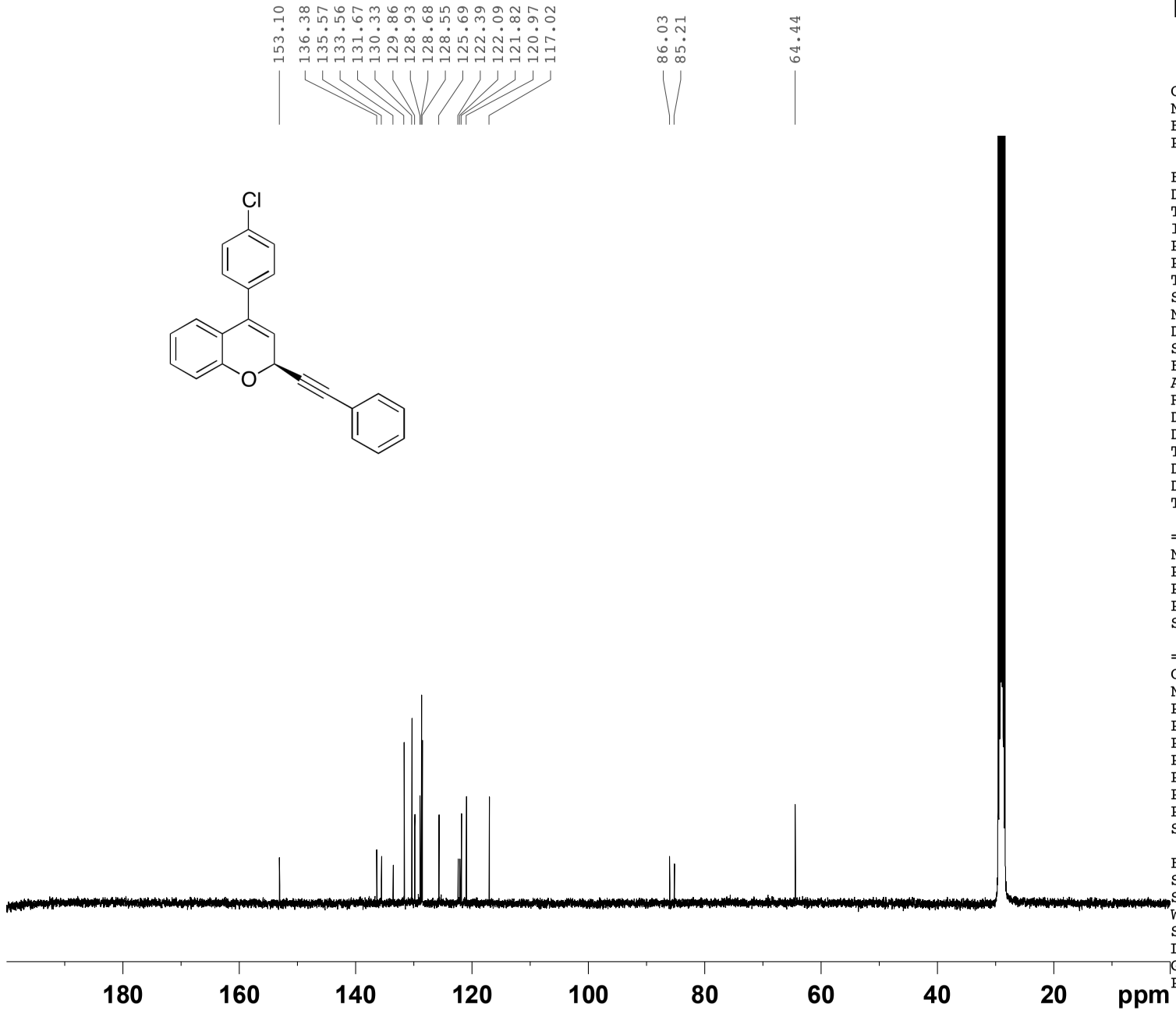
Current Data Parameters
NAME HH-3-243A2july28
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120727
Time 4.44
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zg30
TD 65536
SOLVENT Acetone
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 12.7
DW 60.400 usec
DE 6.00 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 4.90 dB
PL1W 3.30822015 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound 1.47 13C NMR




```
Current Data Parameters
NAME      HH-3-243A2july28
EXPNO                    2
PROCNO                   1

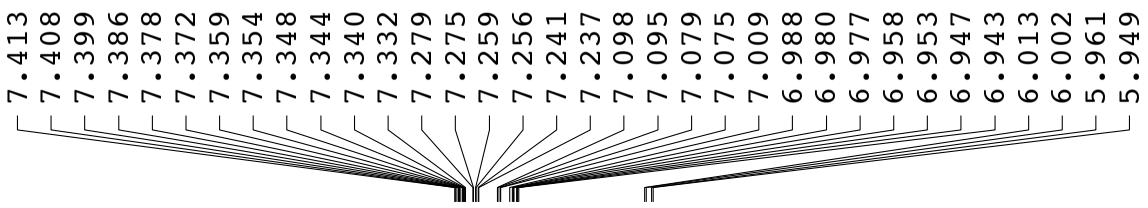
F2 - Acquisition Parameters
Date_             20120727
Time                  5.44
INSTRUM              spect
PROBHD   5 mm CPQNP 1H/
PULPROG             zgpg30
TD                   65536
SOLVENT            Acetone
NS                    1024
DS                       4
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ               1.3664756 sec
RG                     512
DW                20.850 usec
DE                18.00 usec
TE                298.1 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                      1

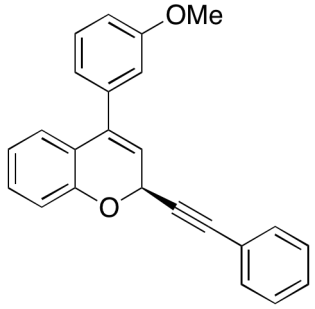
======== CHANNEL f1 ========
NUC1                   13C
P1                  9.25 usec
PL1                 0.55 dB
PL1W         35.18820572 W
SFO1         100.6228298 MHz

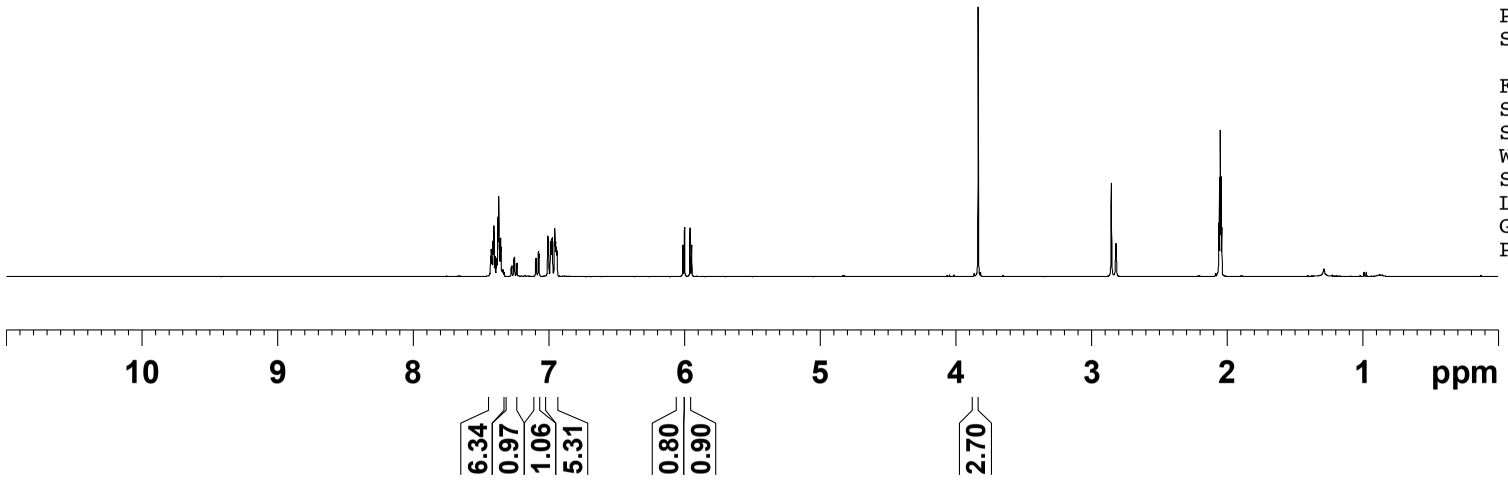
======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              90.00 usec
PL2                 4.90 dB
PL12               20.46 dB
PL13               21.00 dB
PL2W          3.30822015 W
PL12W         0.09195905 W
PL13W         0.08120718 W
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                   32768
SF           100.6127690 MHz
WDW                     EM
SSB                      0
LB                  1.00 Hz
GB                       0
PC                    1.40
```

Compound 1.48 1H NMR







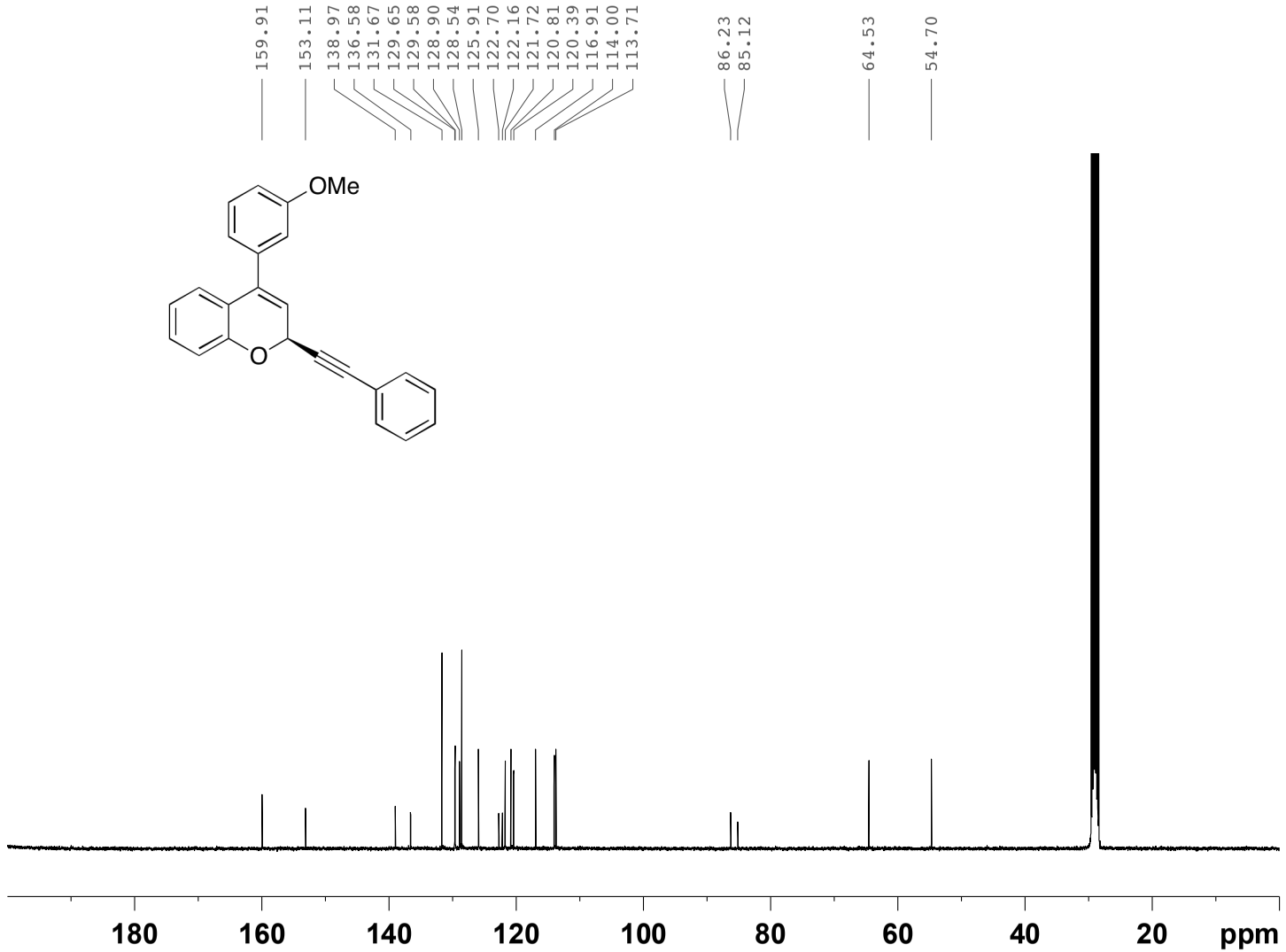
Current Data Parameters
NAME HH-3-238A1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120723
Time 15.52
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zg30
TD 65536
SOLVENT Acetone
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 10.1
DW 60.400 usec
DE 6.00 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 4.90 dB
PL1W 3.30822015 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300066 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound 1.48 13C NMR



Current Data Parameters
NAME HH-3-238A1
EXPNO 2
PROCNO 1

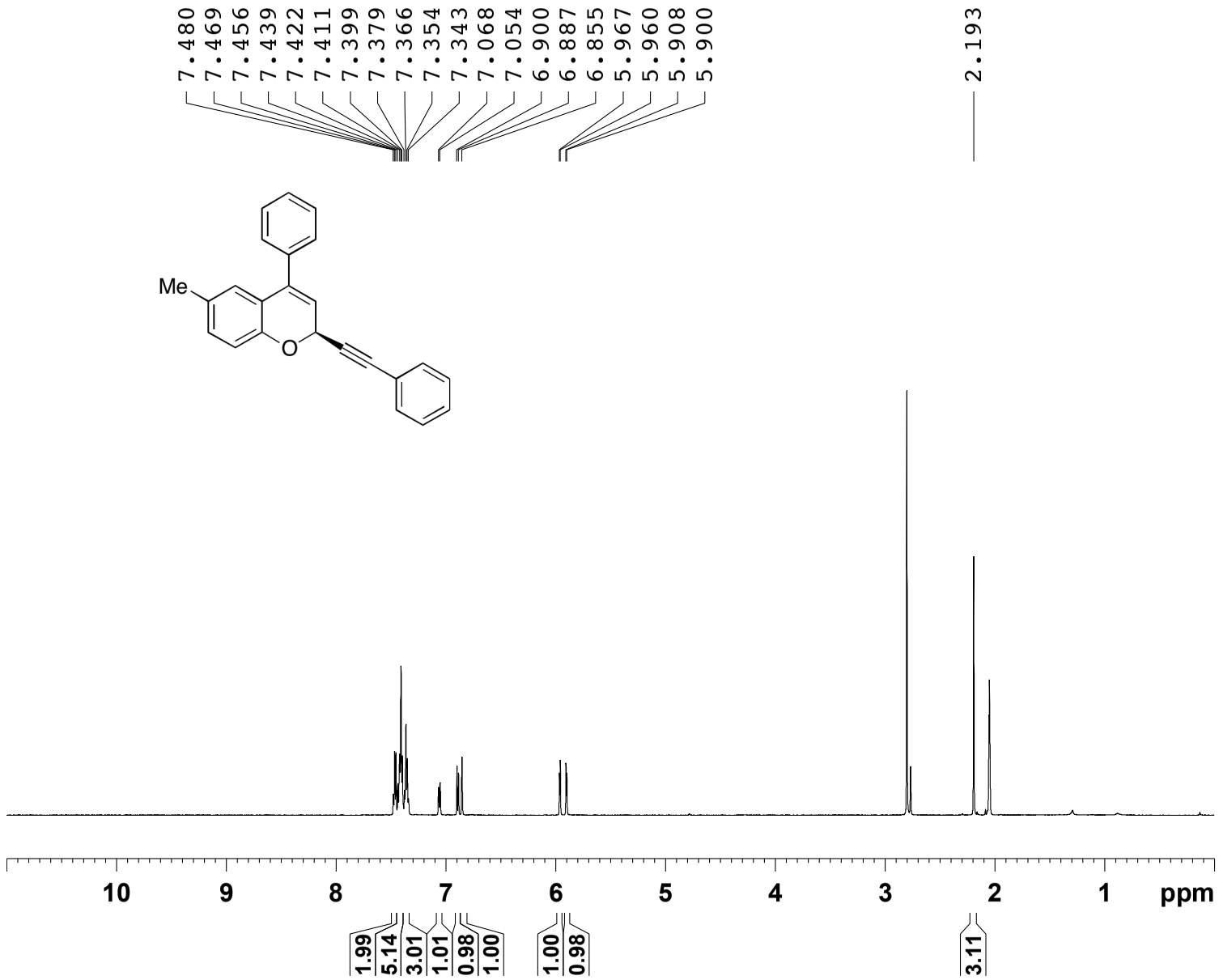
F2 - Acquisition Parameters
Date_ 20120724
Time 4.55
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 1024
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 512
DW 20.850 usec
DE 18.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.25 usec
PL1 0.55 dB
PL1W 35.18820572 W
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 4.90 dB
PL12 20.46 dB
PL13 21.00 dB
PL2W 3.30822015 W
PL12W 0.09195905 W
PL13W 0.08120718 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Com[pound 1.49 1H NMR



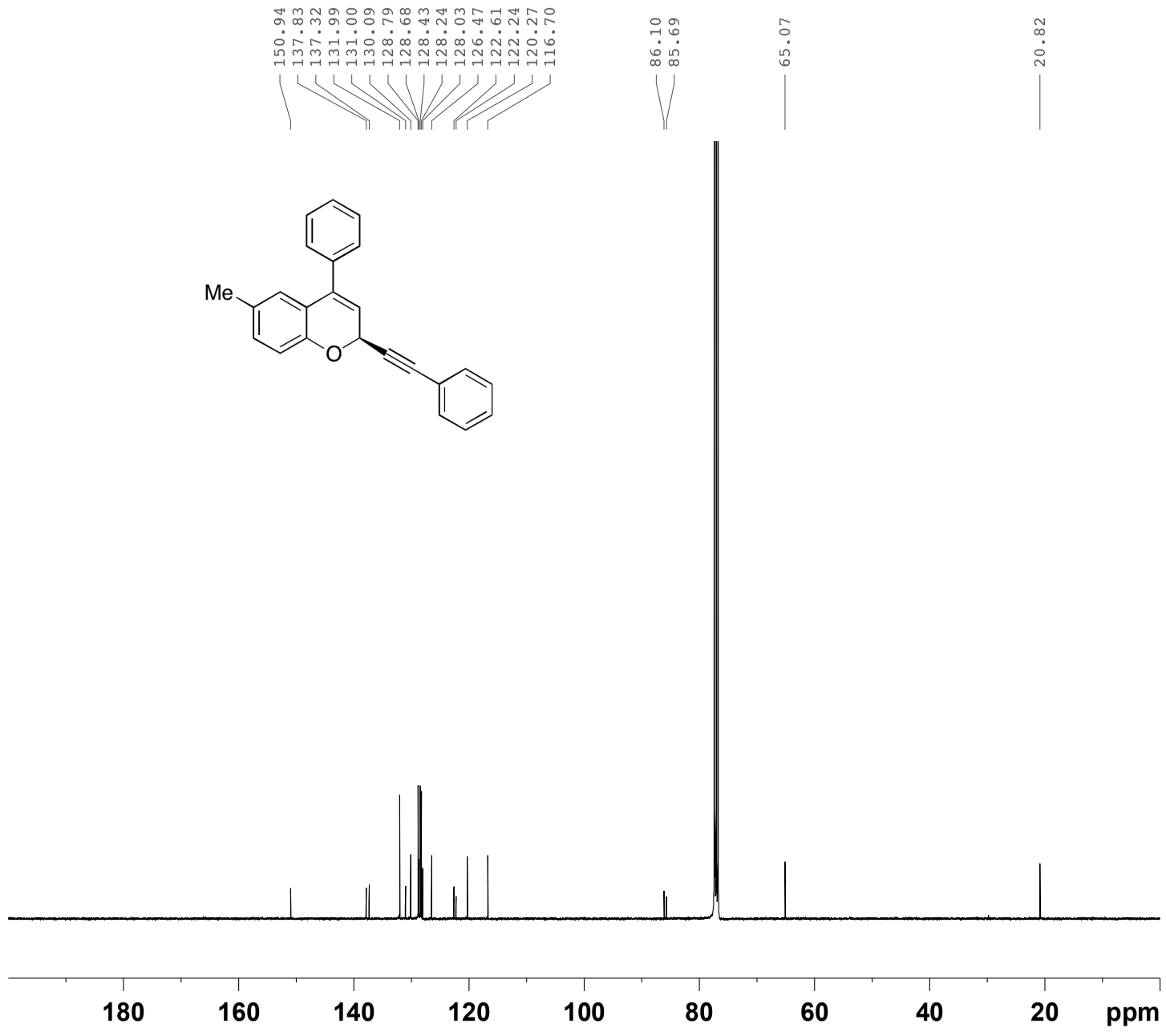
Current Data Parameters
NAME HH-3-216A2rs
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120730
Time 16.03
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT Acetone
NS 8
DS 2
SWH 8403.361 Hz
FIDRES 0.128225 Hz
AQ 3.8994420 sec
RG 181
DW 59.500 usec
DE 17.39 usec
TE 300.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 600.3233018 MHz
NUC1 1H
P1 10.77 usec

F2 - Processing parameters
SI 65536
SF 600.3200113 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound 1.49 13C NMR

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Current Data Parameters
NAME      HH-3-216A2 Dec2013
EXPNO                      2
PROCNO                     1

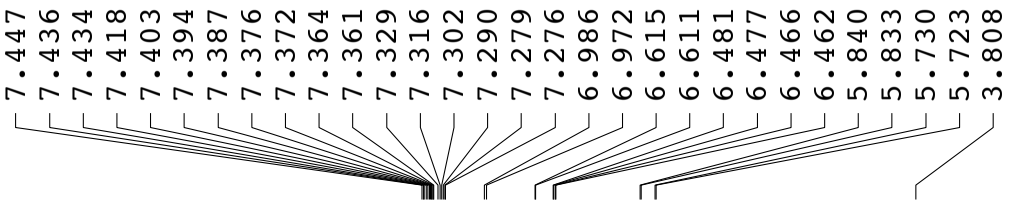
F2 - Acquisition Parameters
Date_           20131219
Time                1.32
INSTRUM            spect
PROBHD   5 mm CPQNP 1H/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ             1.3664756 sec
RG                  512
DW               20.850 usec
DE               18.00 usec
TE               298.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

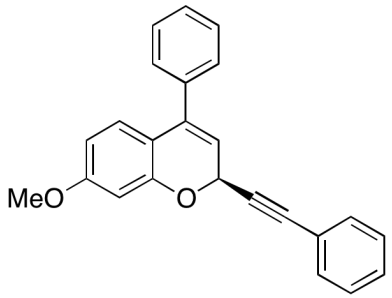
======== CHANNEL f1 ========
NUC1                 13C
P1                 9.25 usec
PL1                0.55 dB
PL1W        35.18820572 W
SFO1       100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             90.00 usec
PL2                4.90 dB
PL12              20.46 dB
PL13              21.00 dB
PL2W         3.30822015 W
PL12W        0.09195905 W
PL13W        0.08120718 W
SFO2       400.1316005 MHz

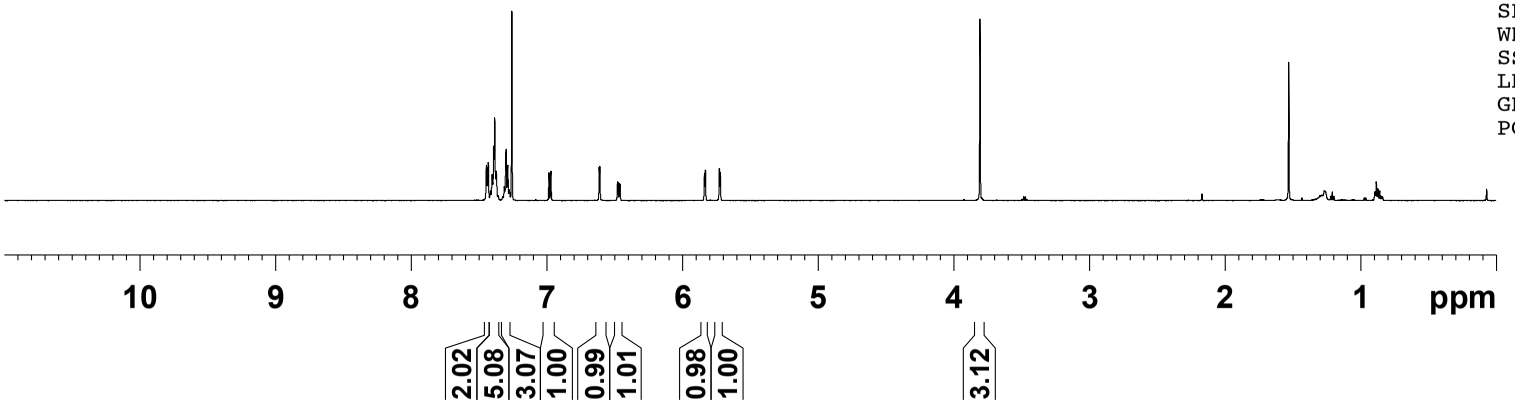
F2 - Processing parameters
SI                32768
SF          100.6127690 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

Compound 1.50 1H NMR





250



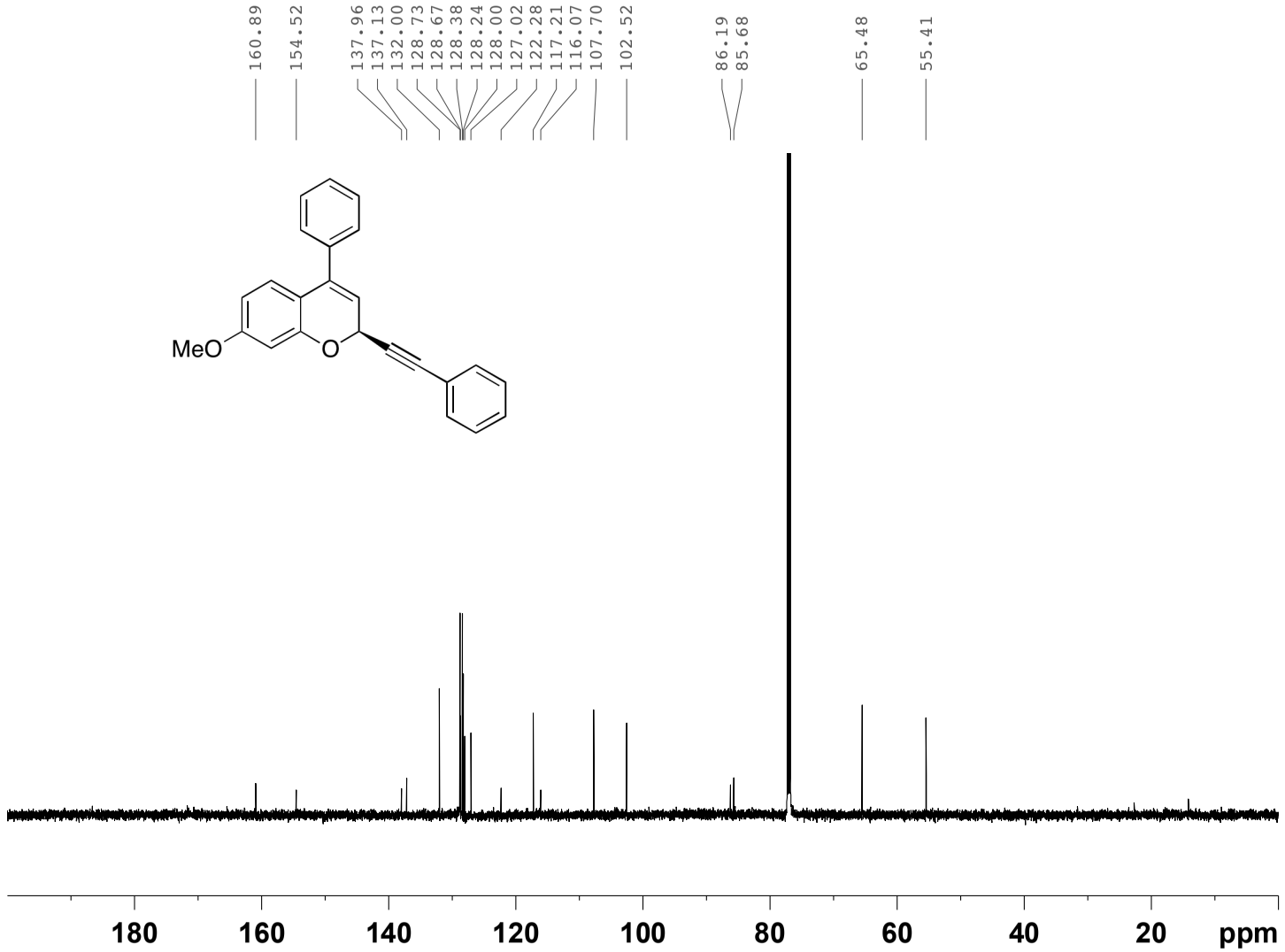
Current Data Parameters
NAME HH-3-255A1rs
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120722
Time 0.04
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8403.361 Hz
FIDRES 0.128225 Hz
AQ 3.8994420 sec
RG 228
DW 59.500 usec
DE 17.39 usec
TE 300.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 600.3233018 MHz
NUC1 1H
P1 10.77 usec

F2 - Processing parameters
SI 65536
SF 600.3200158 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound 1.50 13C NMR



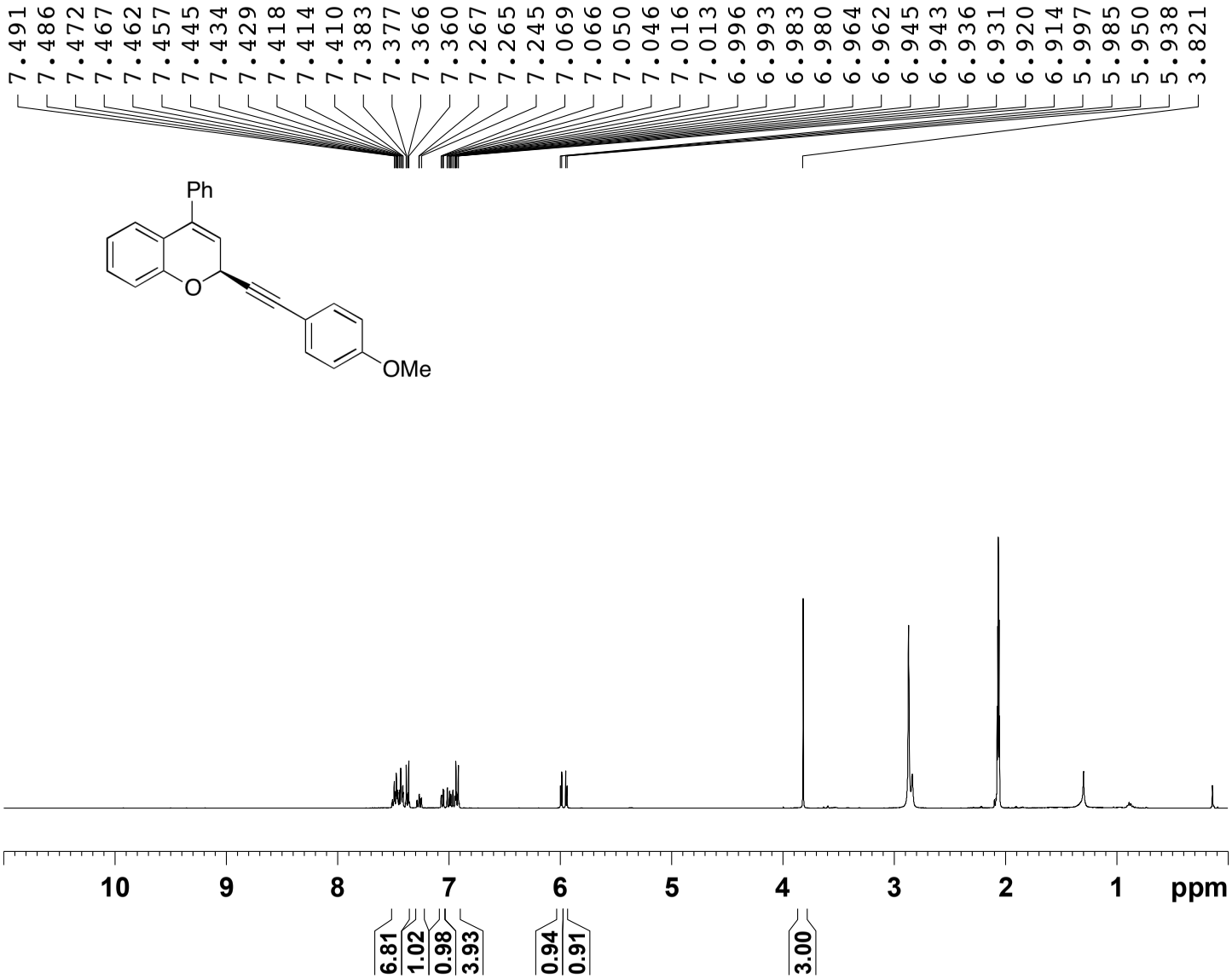
Current Data Parameters
NAME HH-3-255A1rs
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120722
Time 3.23
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg55
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 34722.223 Hz
FIDRES 0.529819 Hz
AQ 0.9437684 sec
RG 2050
DW 14.400 usec
DE 19.34 usec
TE 300.2 K
D1 1.10000002 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 150.9656784 MHz
NUC1 13C
P1 10.63 usec

F2 - Processing parameters
SI 32768
SF 150.9505840 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Compound 1.51 1H NMR



252

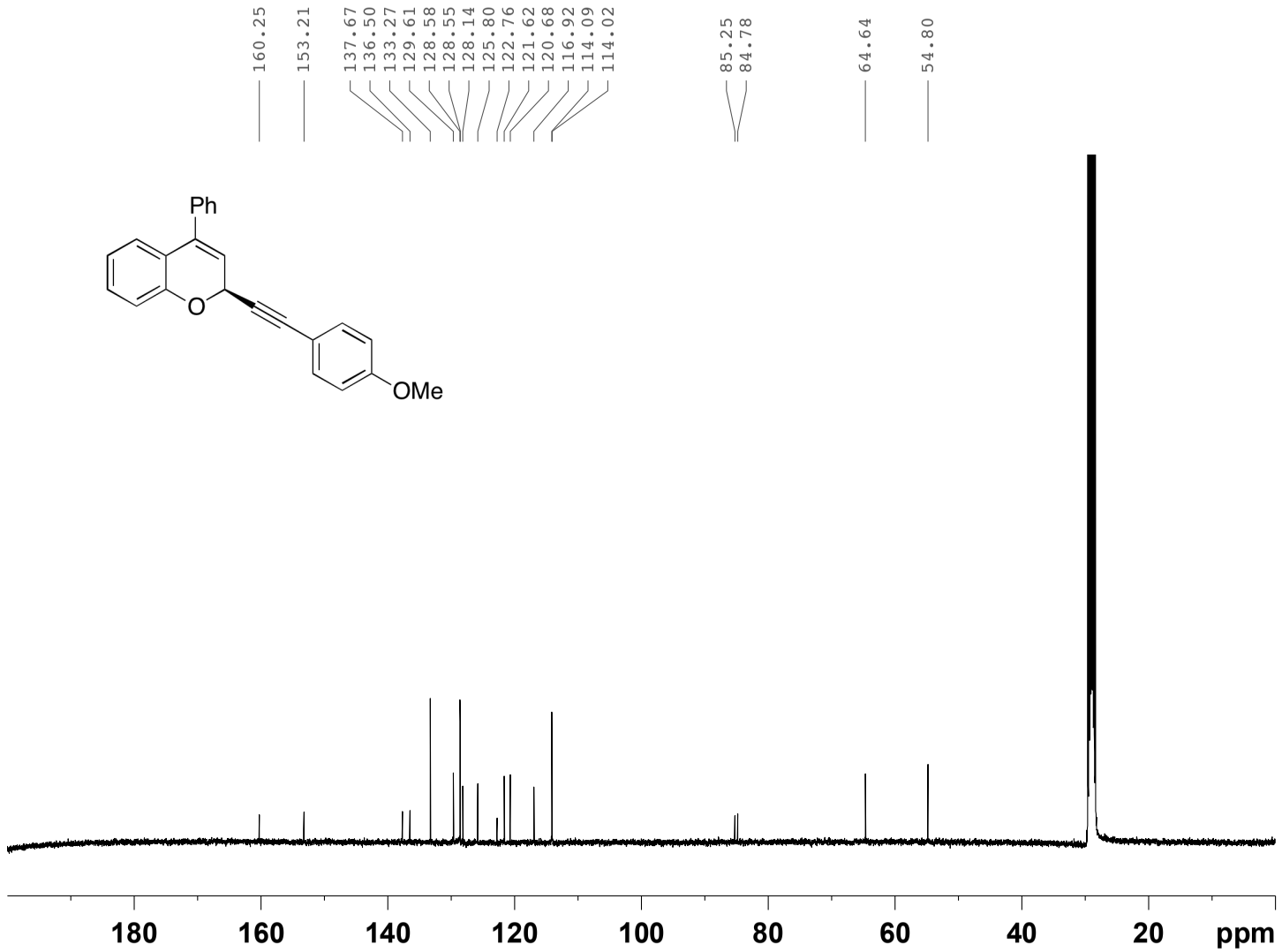
Current Data Parameters
NAME HH-3-211A2aug13_2
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120813
Time 15.49
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zg30
TD 65536
SOLVENT Acetone
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 12.7
DW 60.400 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 4.90 dB
PL1W 3.30822015 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound 1.51 13C NMR



Current Data Parameters
NAME HH-3-211A2aug13
EXPNO 2
PROCNO 1

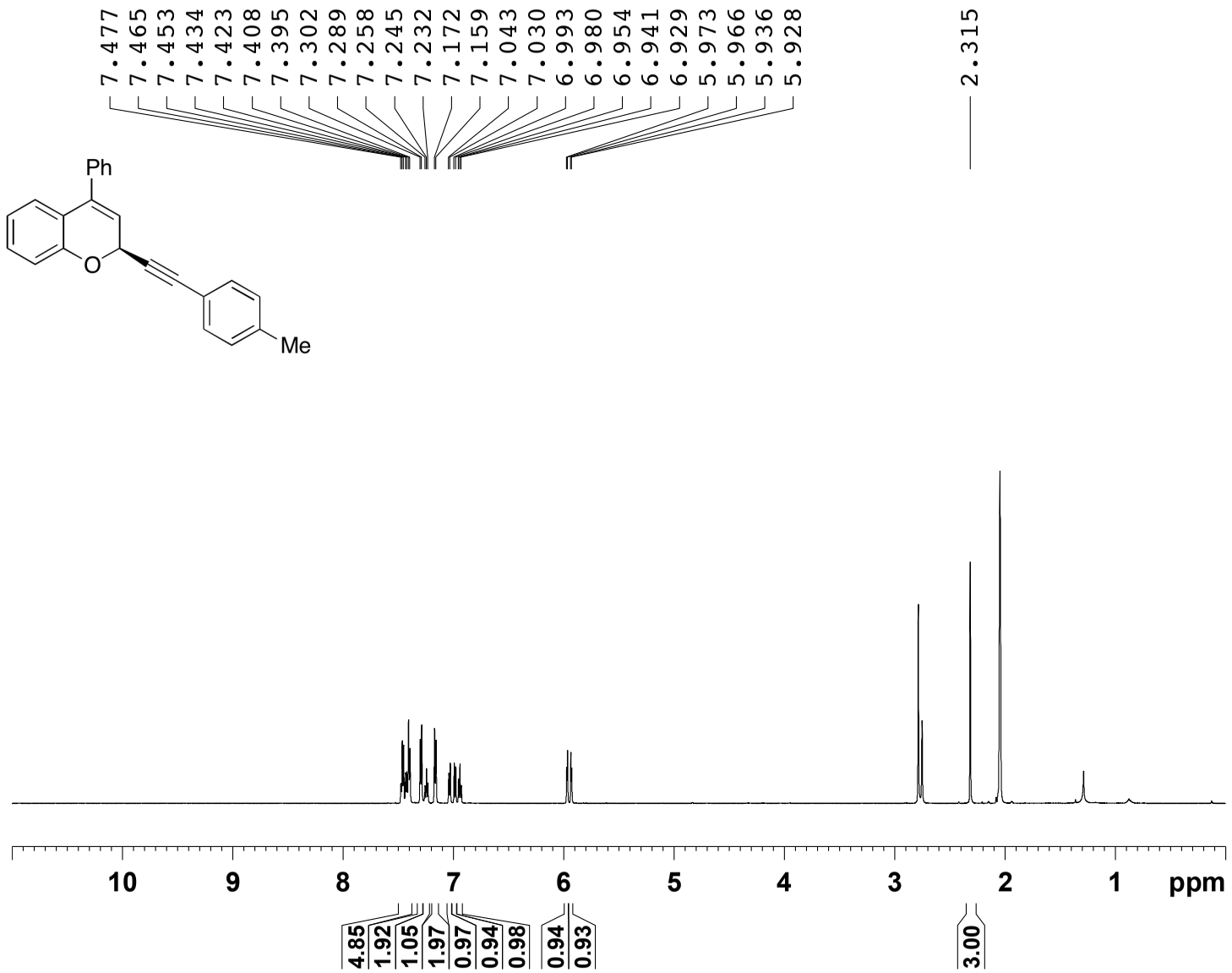
F2 - Acquisition Parameters
Date_ 20120814
Time 0.26
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 1024
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 512
DW 20.850 usec
DE 18.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.25 usec
PL1 0.55 dB
PL1W 35.18820572 W
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 4.90 dB
PL12 20.46 dB
PL13 21.00 dB
PL2W 3.30822015 W
PL12W 0.09195905 W
PL13W 0.08120718 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Compound 1.52 1H NMR



254

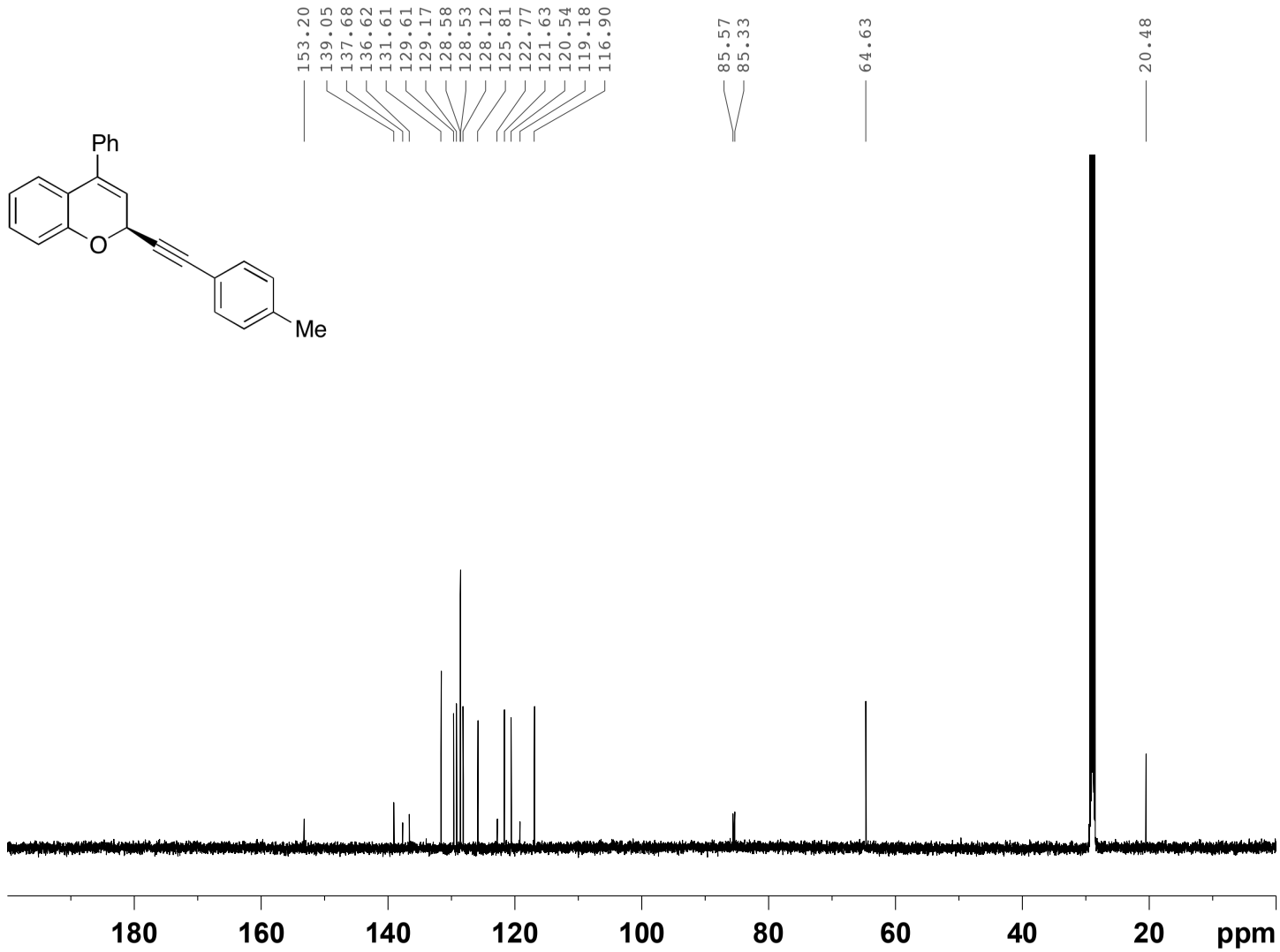
Current Data Parameters
NAME HH-3-197a1JULY30
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120731
Time 16.34
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT Acetone
NS 8
DS 2
SWH 8403.361 Hz
FIDRES 0.128225 Hz
AQ 3.8994420 sec
RG 228
DW 59.500 usec
DE 17.39 usec
TE 300.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 600.3233018 MHz
NUC1 1H
P1 10.77 usec

F2 - Processing parameters
SI 65536
SF 600.3200144 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound 1.52 13C NMR



Current Data Parameters

NAME	HH-3-197a1JULY30
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20120731
Time	20.14
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zgpg55
TD	65536
SOLVENT	Acetone
NS	2048
DS	4
SWH	34722.223 Hz
FIDRES	0.529819 Hz
AQ	0.9437684 sec
RG	2050
DW	14.400 usec
DE	19.34 usec
TE	300.2 K
D1	1.10000002 sec
D11	0.03000000 sec
TD0	1

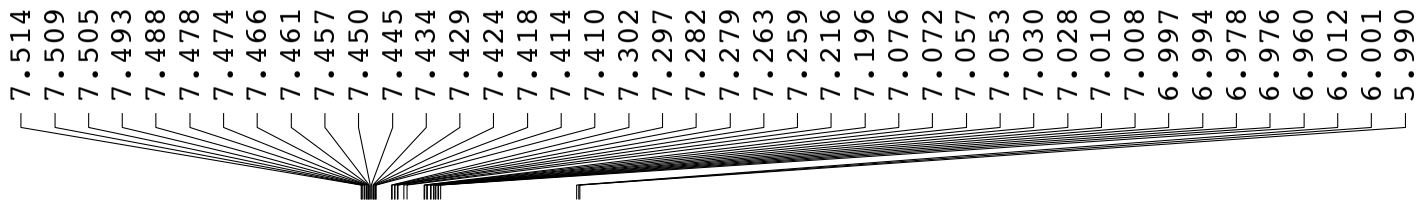
======== CHANNEL f1 ========

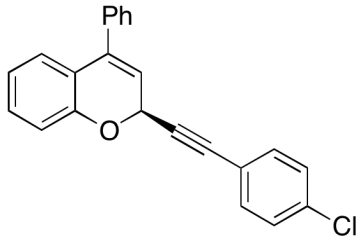
SFO1	150.9656784 MHz
NUC1	13C
P1	10.63 usec

F2 - Processing parameters

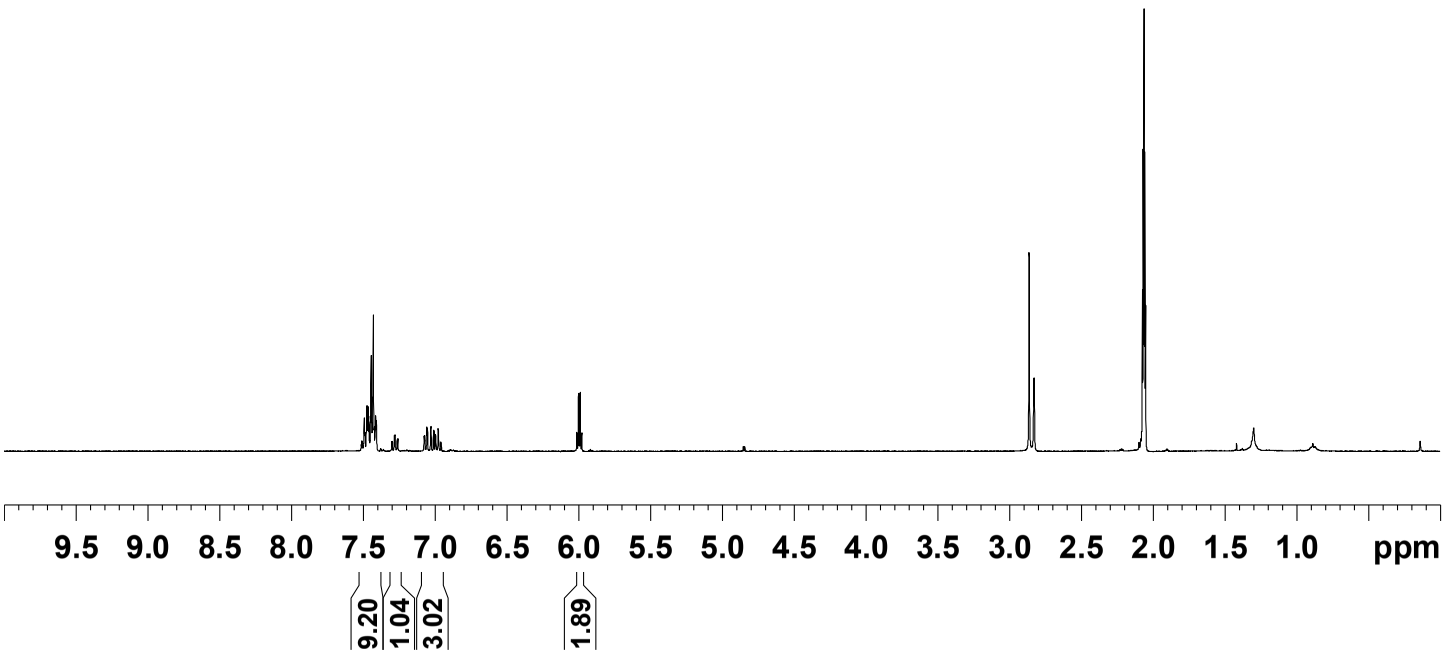
SI	32768
SF	150.9505840 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

Compound 1.53 1H NMR





256



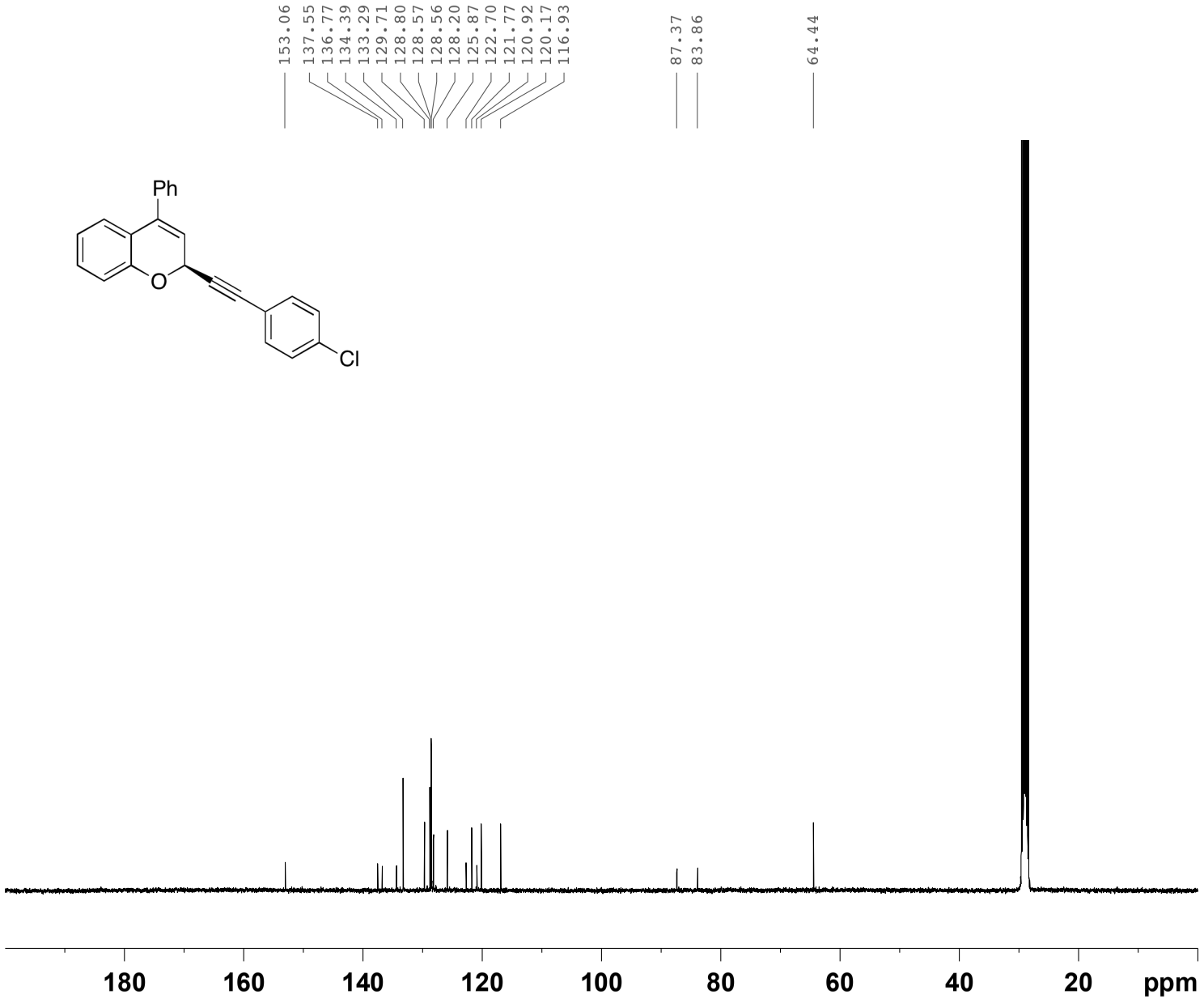
Current Data Parameters
NAME HH-3-204A1rs
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120725
Time 7.36
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zg30
TD 65536
SOLVENT Acetone
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 10.1
DW 60.400 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 4.90 dB
PL1W 3.30822015 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound 1.53 13C NMR



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```
Current Data Parameters
NAME          HH-3-204A1
EXPNO                  2
PROCNO                 1

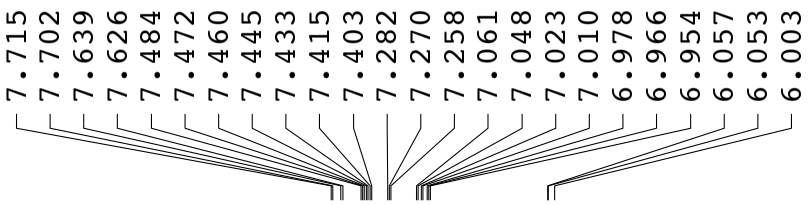
F2 - Acquisition Parameters
Date_           20120509
Time                7.03
INSTRUM            spect
PROBHD   5 mm CPQNP 1H/
PULPROG          zgpg30
TD                65536
SOLVENT          Acetone
NS                 1024
DS                    4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ            1.3664756 sec
RG                  512
DW               20.850 usec
DE               18.00 usec
TE                298.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

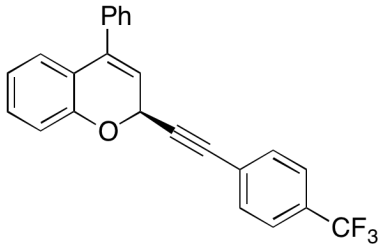
======== CHANNEL f1 ========
NUC1                 13C
P1                  9.25 usec
PL1                 0.55 dB
PL1W        35.18820572 W
SFO1       100.6228298 MHz

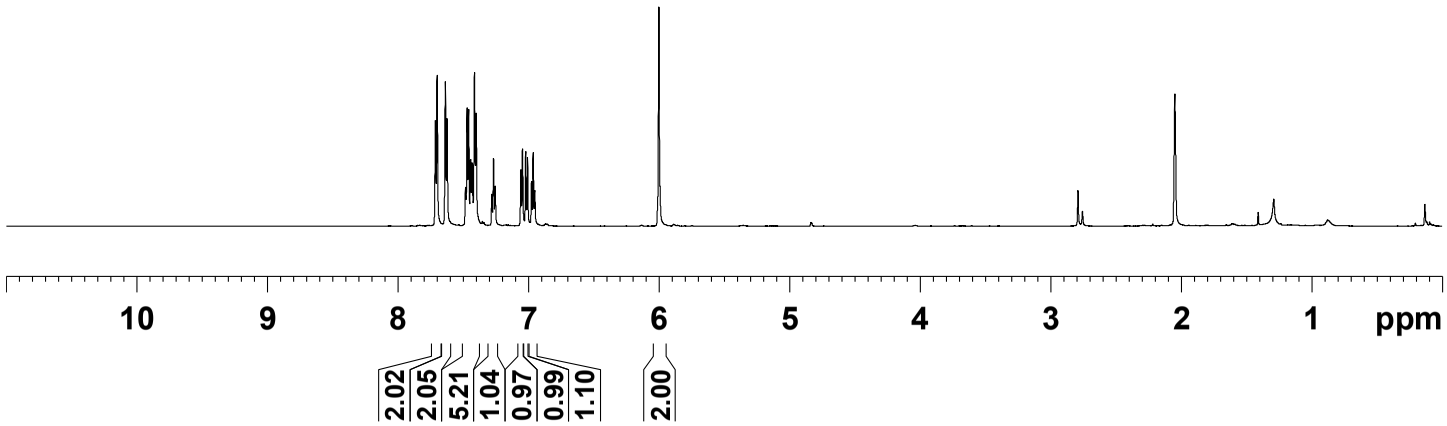
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL2                 4.90 dB
PL12               20.46 dB
PL13               21.00 dB
PL2W         3.30822015 W
PL12W        0.09195905 W
PL13W        0.08120718 W
SFO2       400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127690 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                 1.40
```

Compound 1.54 1H NMR







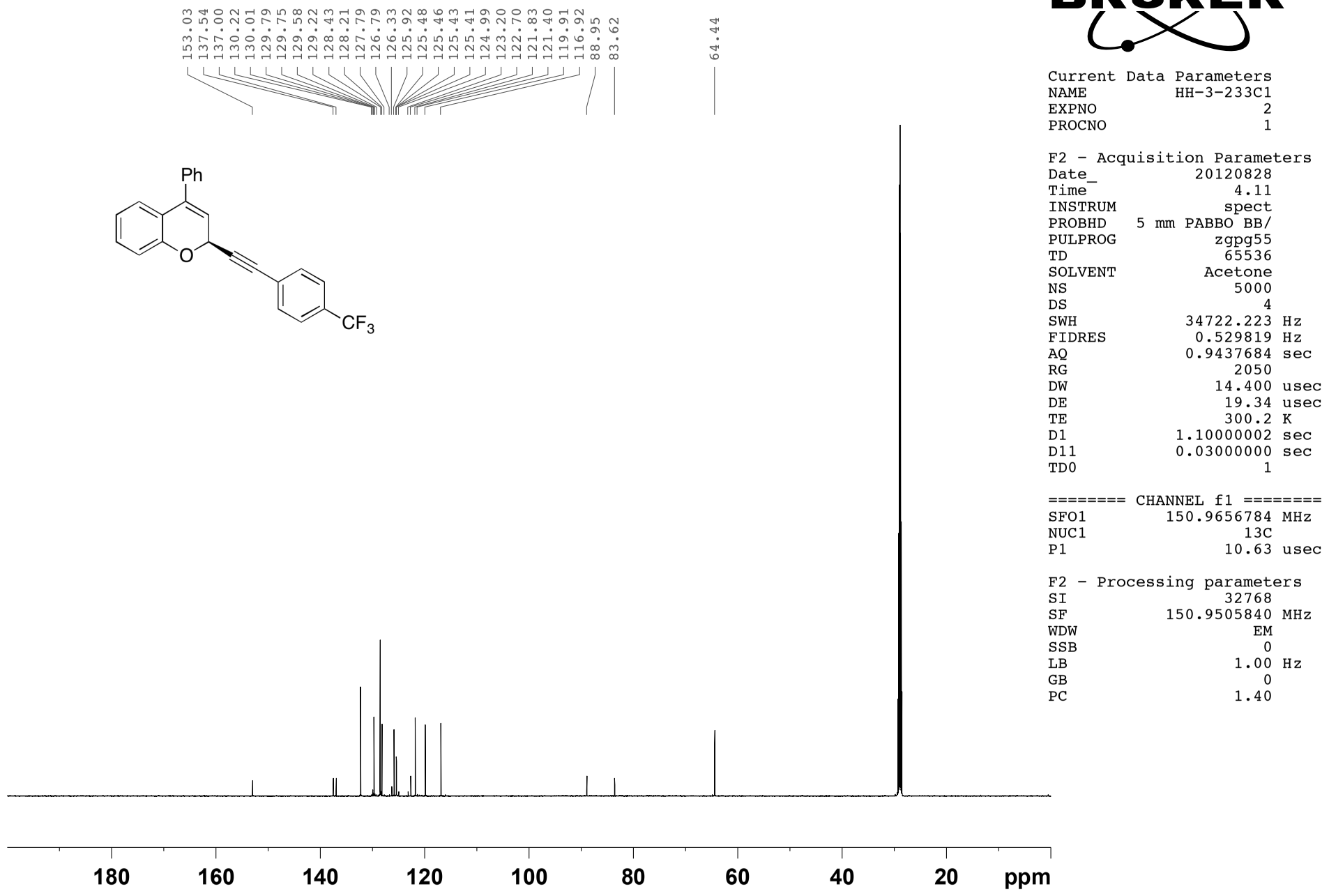
Current Data Parameters
NAME HH-3-233C1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120828
Time 1.09
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT Acetone
NS 8
DS 2
SWH 8403.361 Hz
FIDRES 0.128225 Hz
AQ 3.8994420 sec
RG 128
DW 59.500 usec
DE 17.39 usec
TE 300.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 600.3233018 MHz
NUC1 1H
P1 10.77 usec

F2 - Processing parameters
SI 65536
SF 600.3200120 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound 1.54 13C NMR



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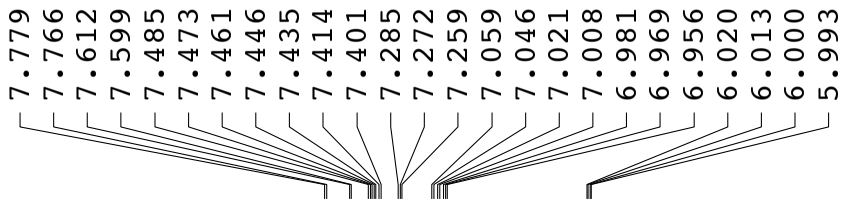
Current Data Parameters
NAME HH-3-233C1
EXPNO 2
PROCNO 1

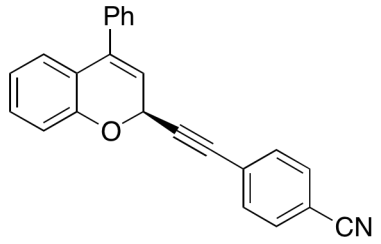
F2 - Acquisition Parameters
Date_ 20120828
Time 4.11
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg55
TD 65536
SOLVENT Acetone
NS 5000
DS 4
SWH 34722.223 Hz
FIDRES 0.529819 Hz
AQ 0.9437684 sec
RG 2050
DW 14.400 usec
DE 19.34 usec
TE 300.2 K
D1 1.10000002 sec
D11 0.03000000 sec
TD0 1

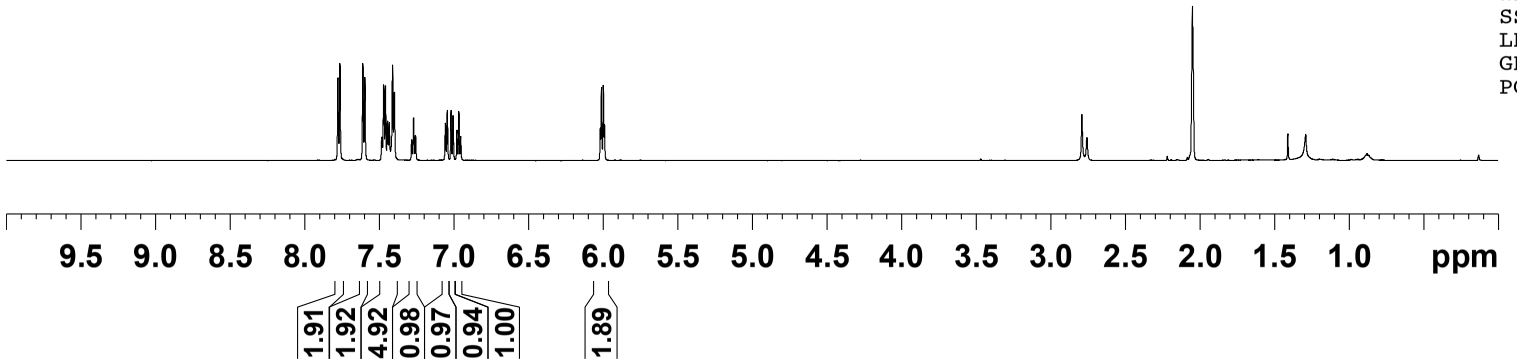
======== CHANNEL f1 ========
SFO1 150.9656784 MHz
NUC1 13C
P1 10.63 usec

F2 - Processing parameters
SI 32768
SF 150.9505840 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Compound 1.55 1H NMR







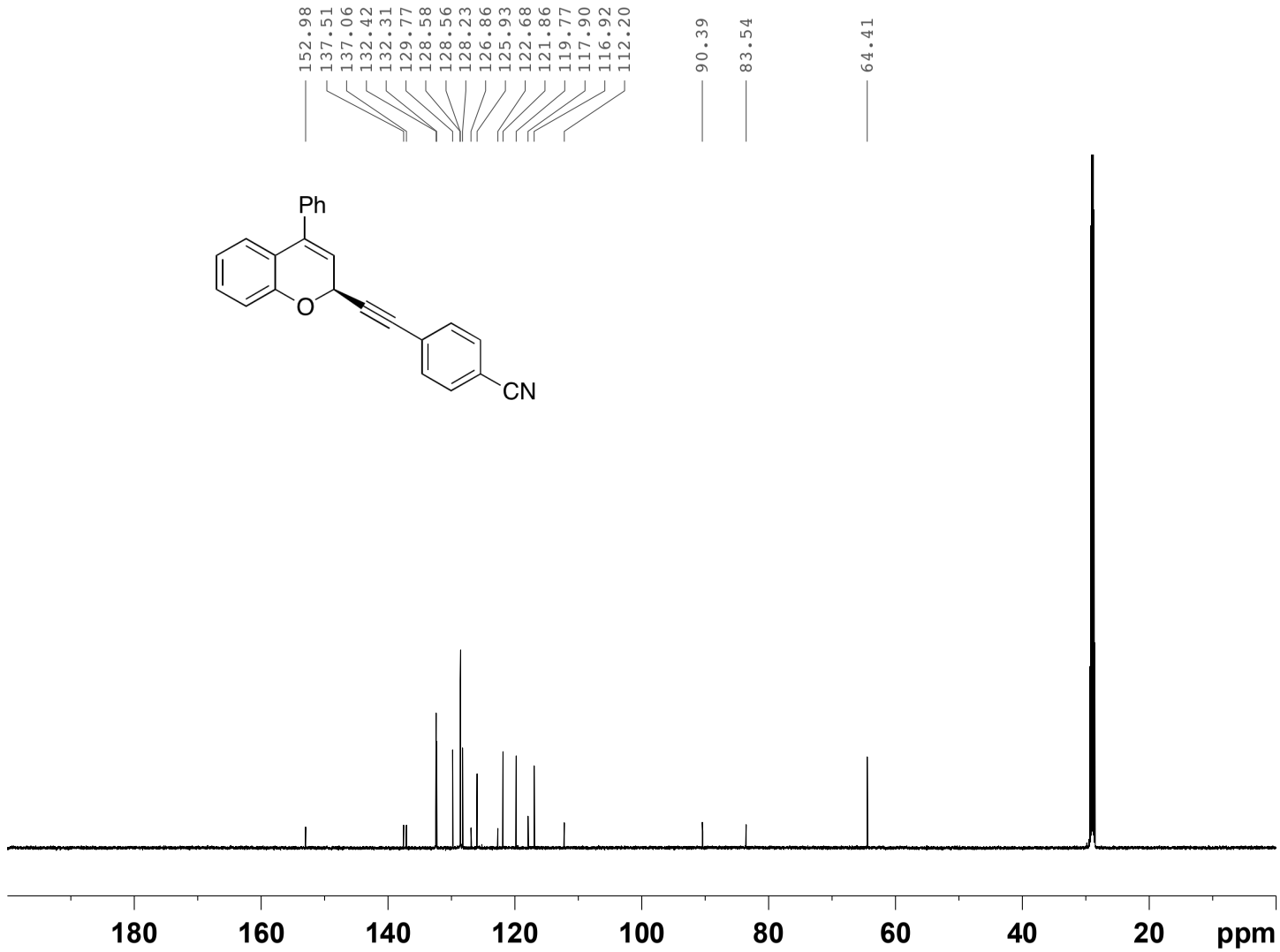
Current Data Parameters
NAME HH-3-222C1rs
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120730
Time 15.10
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT Acetone
NS 8
DS 2
SWH 8403.361 Hz
FIDRES 0.128225 Hz
AQ 3.8994420 sec
RG 181
DW 59.500 usec
DE 17.39 usec
TE 300.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 600.3233018 MHz
NUC1 1H
P1 10.77 usec

F2 - Processing parameters
SI 65536
SF 600.3200113 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound 1.55 13C NMR



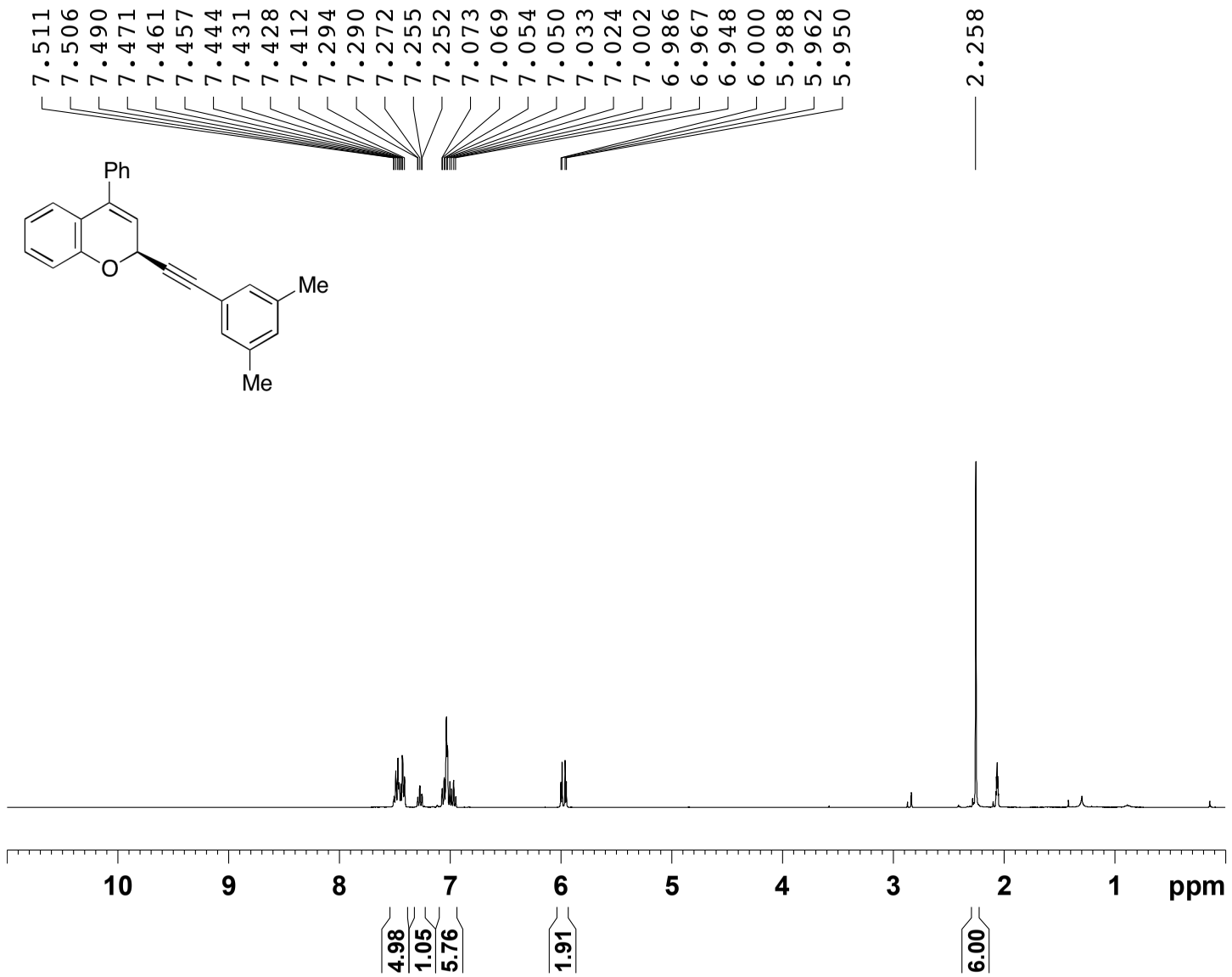

```
Current Data Parameters
NAME        HH-3-222C1rs
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120730
Time              20.16
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg55
TD                65536
SOLVENT         Acetone
NS                 2048
DS                    4
SWH           34722.223 Hz
FIDRES         0.529819 Hz
AQ            0.9437684 sec
RG                 2050
DW               14.400 usec
DE               19.34 usec
TE               300.2 K
D1           1.10000002 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        150.9656784 MHz
NUC1               13C
P1               10.63 usec

F2 - Processing parameters
SI                32768
SF          150.9505840 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```

Compound 1.56 1H NMR



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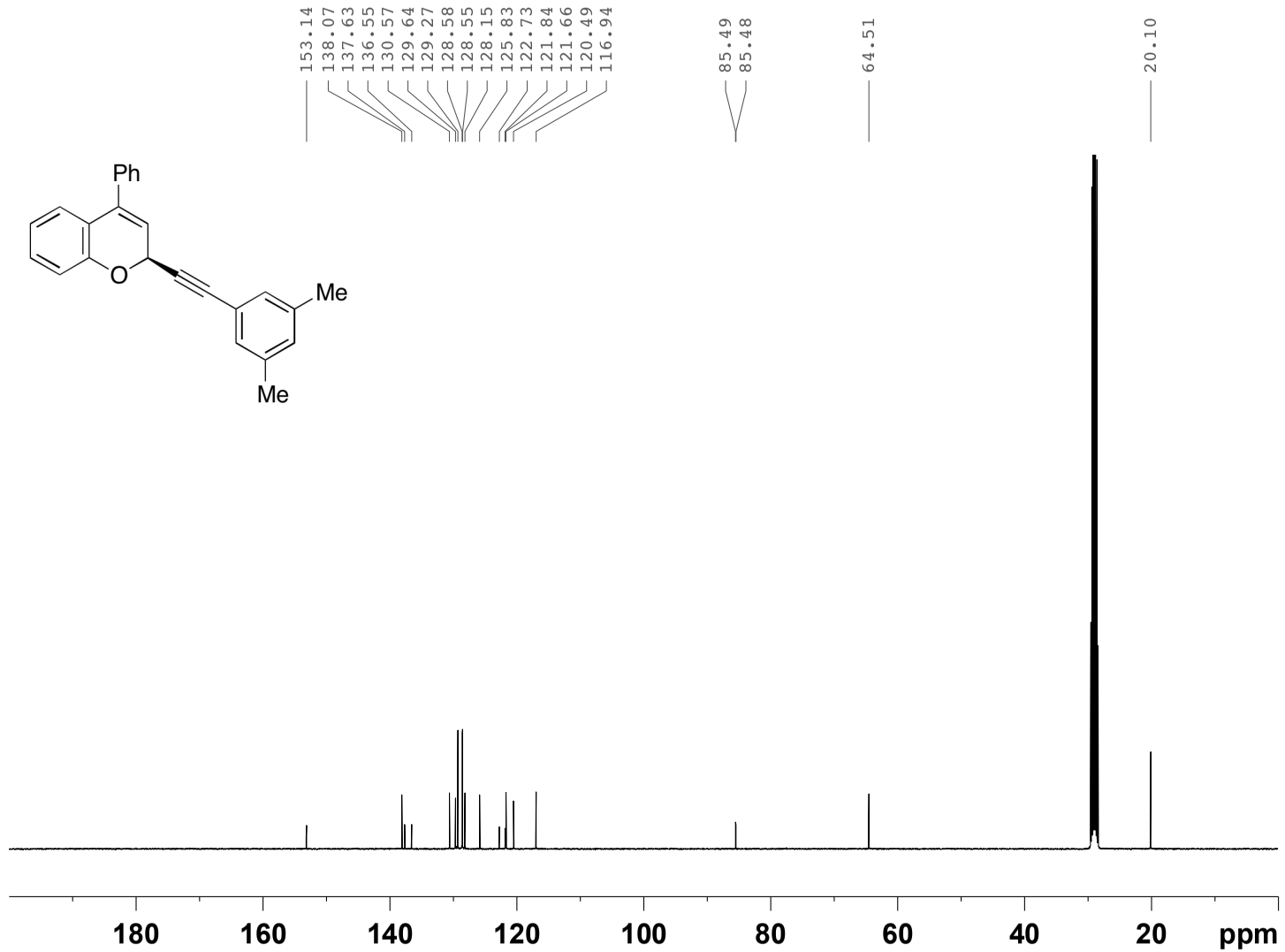
Current Data Parameters
NAME HH-3-202A1fr2
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120429
Time 21.51
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zg30
TD 65536
SOLVENT Acetone
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 6.3
DW 60.400 usec
DE 6.00 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 4.90 dB
PL1W 3.30822015 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound 1.56 13C NMR




```
Current Data Parameters
NAME      HH-3-202A1fr2
EXPNO                 2
PROCNO                1

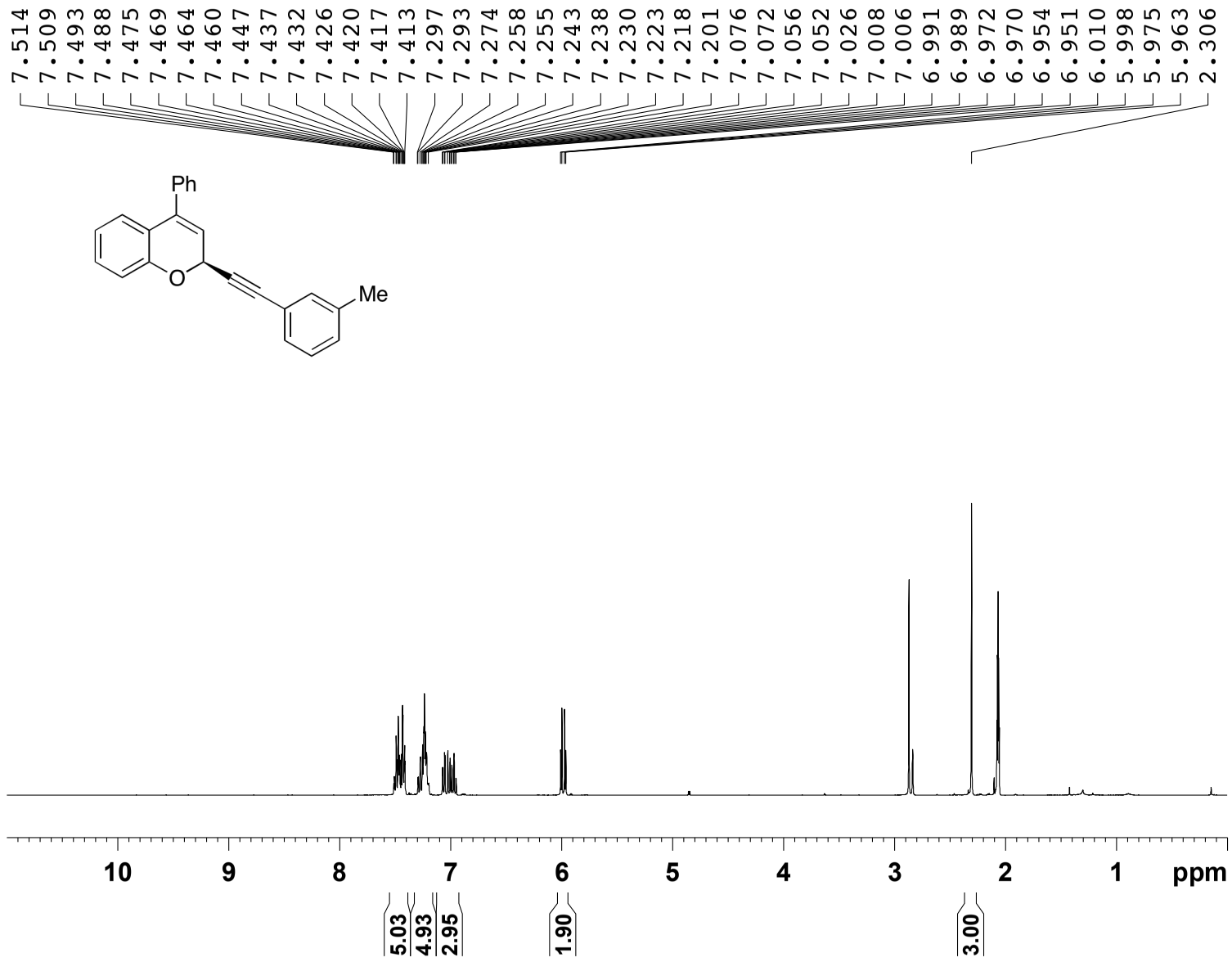
F2 - Acquisition Parameters
Date_          20120429
Time              22.51
INSTRUM           spect
PROBHD   5 mm CPQNP 1H/
PULPROG          zgpg30
TD                65536
SOLVENT         Acetone
NS                 1024
DS                    4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ             1.3664756 sec
RG                  512
DW               20.850 usec
DE               18.00 usec
TE               298.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                9.25 usec
PL1               0.55 dB
PL1W        35.18820572 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2            90.00 usec
PL2               4.90 dB
PL12             20.46 dB
PL13             21.00 dB
PL2W         3.30822015 W
PL12W         0.09195905 W
PL13W         0.08120718 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127690 MHz
WDW                EM
SSB                 0
LB                1.00 Hz
GB                  0
PC                1.40
```

Compound 1.57 1H NMR



Current Data Parameters

NAME	HH-3-206A1rs
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20120725
Time	8.38
INSTRUM	spect
PROBHD	5 mm CPQNP 1H/
PULPROG	zg30
TD	65536
SOLVENT	Acetone
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	9
DW	60.400 usec
DE	6.00 usec
TE	298.2 K
D1	1.00000000 sec
TD0	1

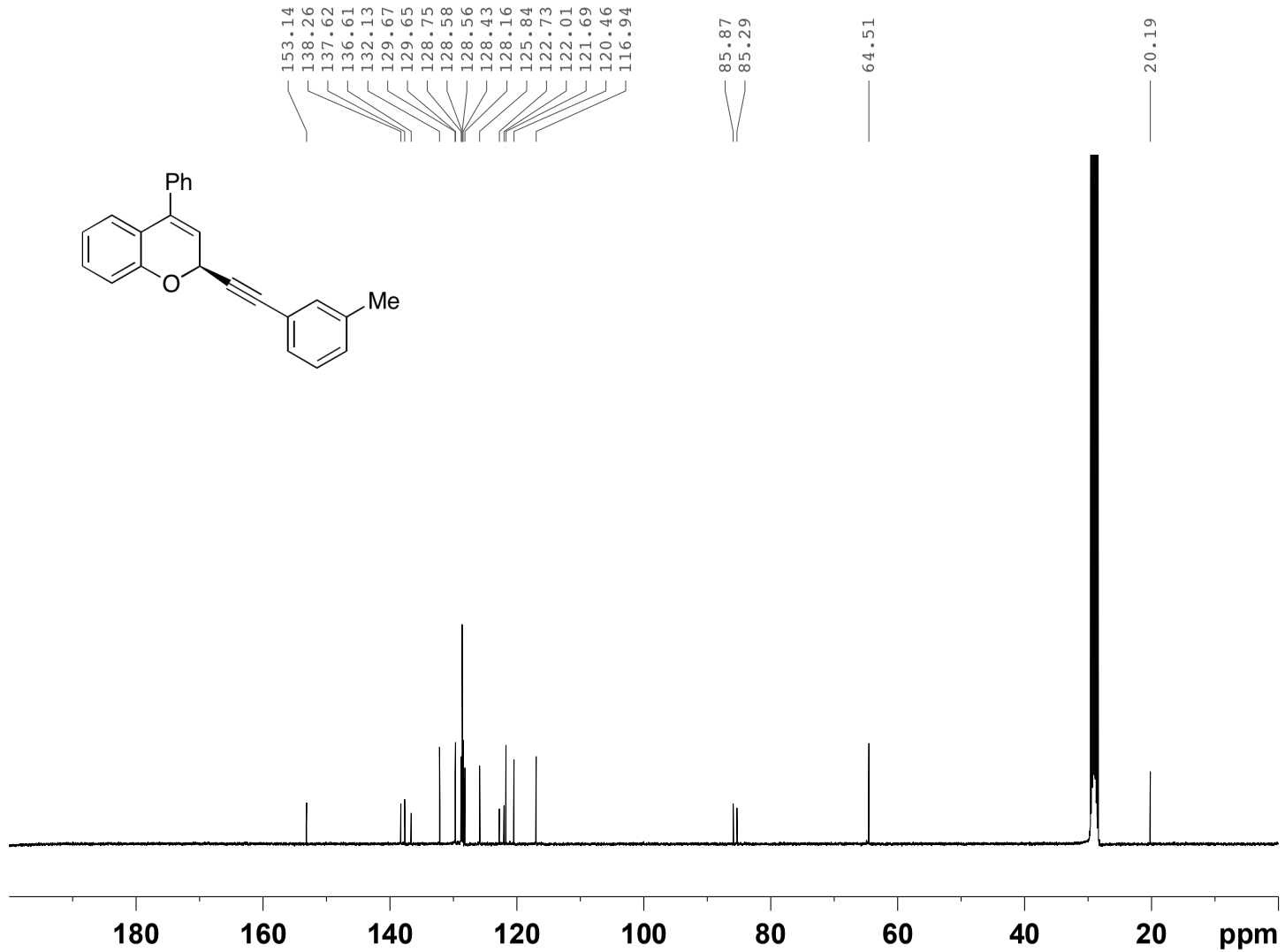
======== CHANNEL f1 ========

NUC1	1H
P1	15.00 usec
PL1	4.90 dB
PL1W	3.30822015 W
SFO1	400.1324710 MHz

F2 - Processing parameters

SI	32768
SF	400.1300000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Compound 1.57 13C NMR



Current Data Parameters
NAME HH-3-206A1rs
EXPNO 2
PROCNO 1

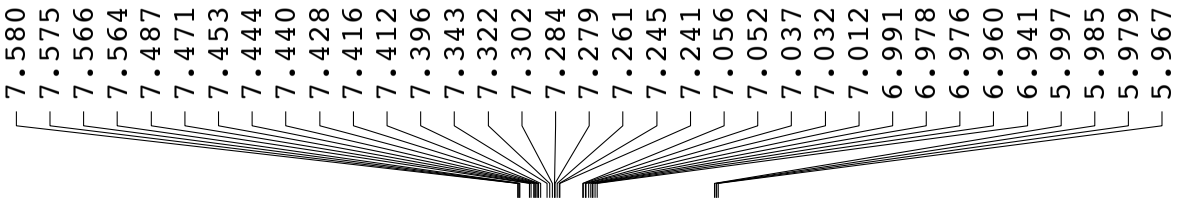
F2 - Acquisition Parameters
Date_ 20120726
Time 21.07
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 1024
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 512
DW 20.850 usec
DE 18.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

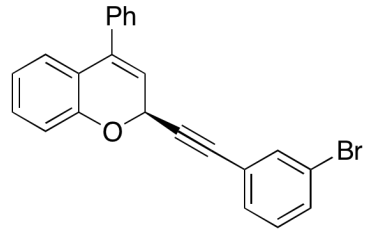
======== CHANNEL f1 ========
NUC1 13C
P1 9.25 usec
PL1 0.55 dB
PL1W 35.18820572 W
SFO1 100.6228298 MHz

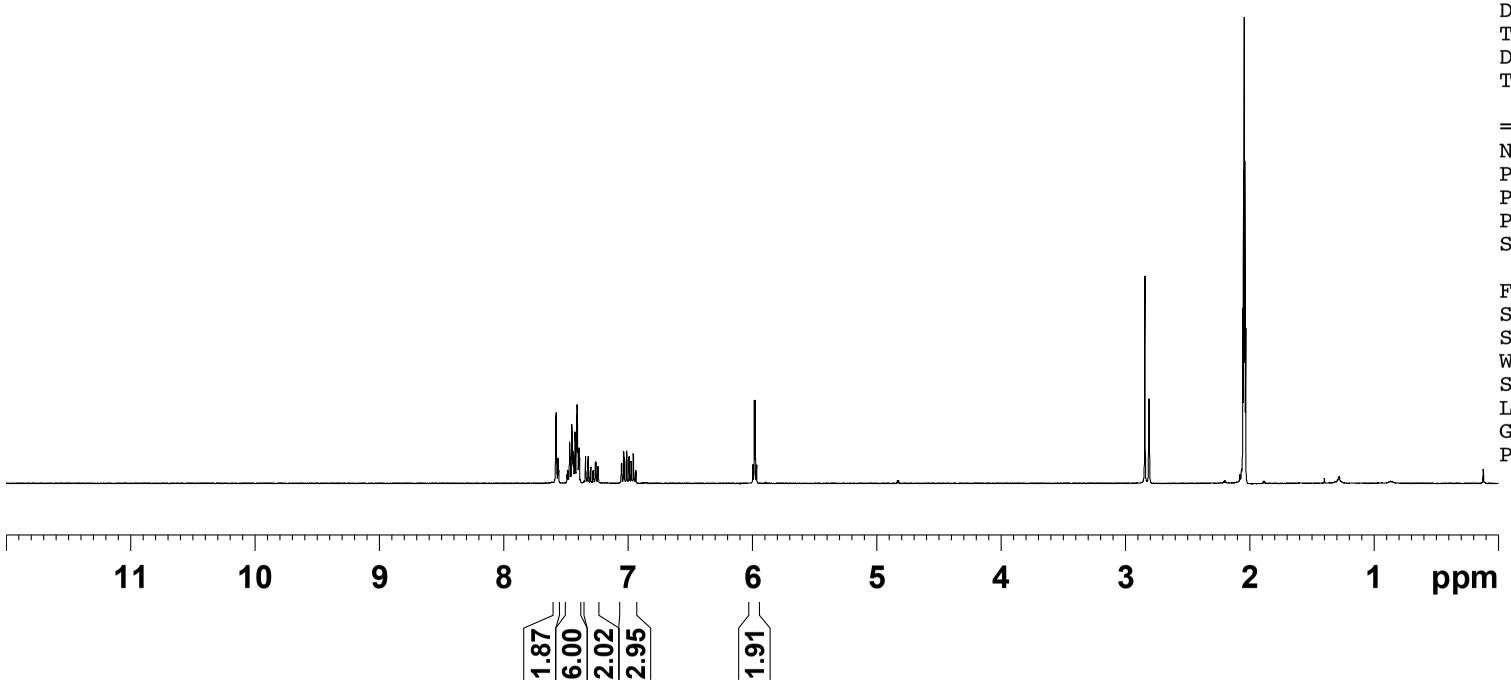
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 4.90 dB
PL12 20.46 dB
PL13 21.00 dB
PL2W 3.30822015 W
PL12W 0.09195905 W
PL13W 0.08120718 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Compound 1.58 1H NMR







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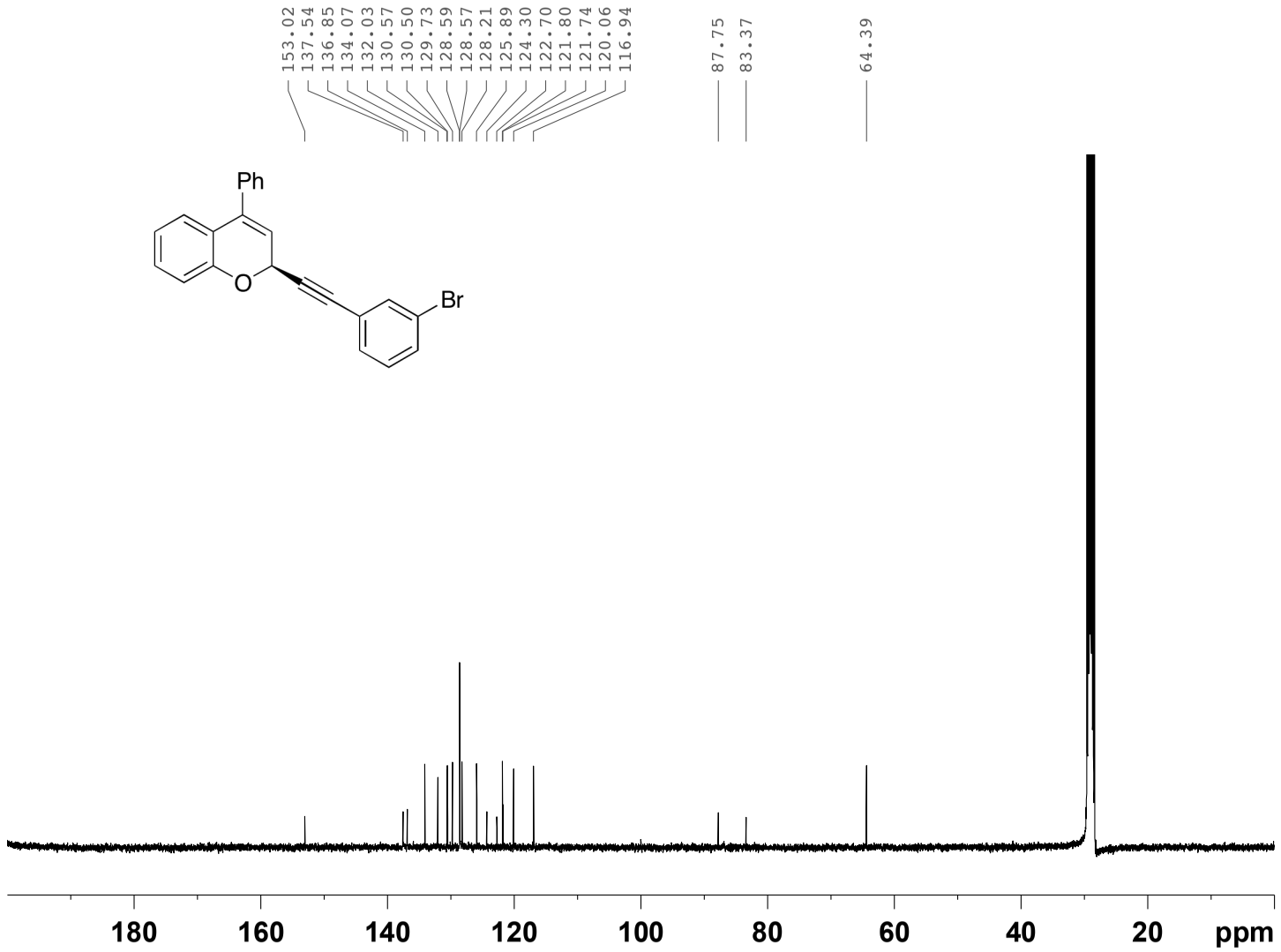
```
Current Data Parameters
NAME          HH-3-222Ars
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20120806
Time                 0.44
INSTRUM             spect
PROBHD   5 mm CPQNP 1H/
PULPROG              zg30
TD                  65536
SOLVENT           Acetone
NS                     16
DS                      2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ               3.9584243 sec
RG                   11.3
DW                 60.400 usec
DE                  6.00 usec
TE                 298.1 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  15.00 usec
PL1                  4.90 dB
PL1W          3.30822015 W
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF           400.1300090 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

Compound 1.58 13C NMR



Current Data Parameters
NAME HH-3-222Ars
EXPNO 2
PROCNO 1

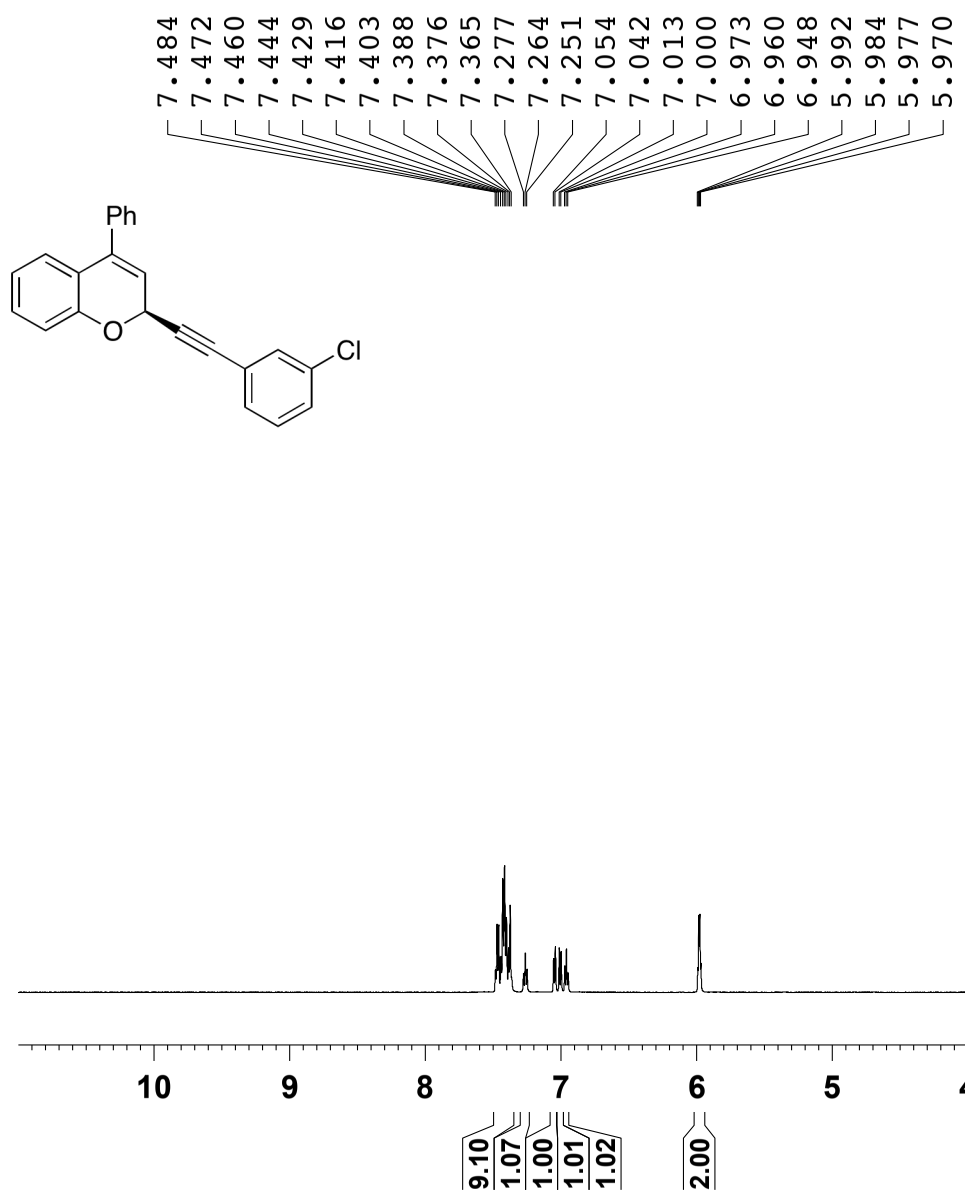
F2 - Acquisition Parameters
Date_ 20120806
Time 1.44
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 1024
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 512
DW 20.850 usec
DE 18.00 usec
TE 298.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.25 usec
PL1 0.55 dB
PL1W 35.18820572 W
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 4.90 dB
PL12 20.46 dB
PL13 21.00 dB
PL2W 3.30822015 W
PL12W 0.09195905 W
PL13W 0.08120718 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Compound 1.59 1H NMR



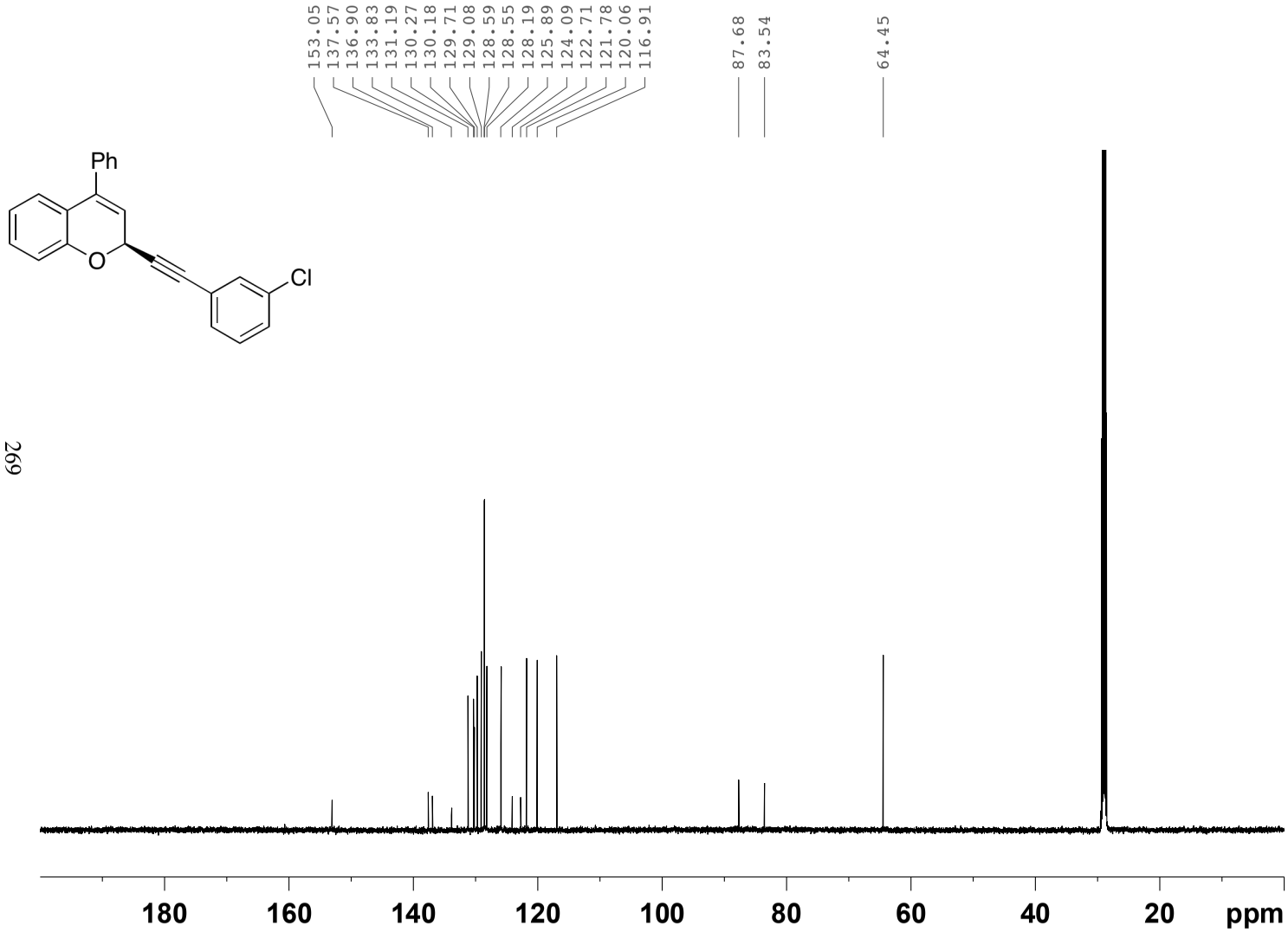
Current Data Parameters
NAME HH-3-196A1Aug1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120731
Time 23.30
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT Acetone
NS 8
DS 2
SWH 8403.361 Hz
FIDRES 0.128225 Hz
AQ 3.8994420 sec
RG 181
DW 59.500 usec
DE 17.39 usec
TE 300.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 600.3233018 MHz
NUC1 1H
P1 10.77 usec

F2 - Processing parameters
SI 65536
SF 600.3200115 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound 1.59 13C NMR



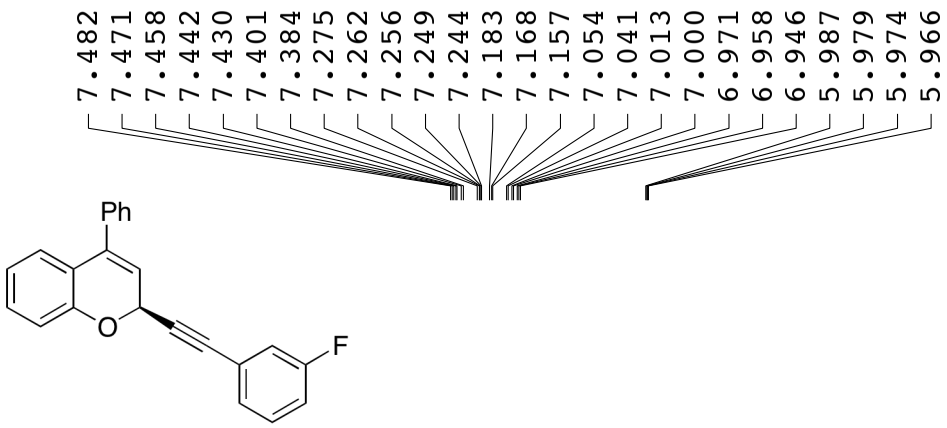
Current Data Parameters
NAME HH-3-196A1Aug1
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120801
Time 2.00
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg55
TD 65536
SOLVENT Acetone
NS 2048
DS 4
SWH 34722.223 Hz
FIDRES 0.529819 Hz
AQ 0.9437684 sec
RG 2050
DW 14.400 usec
DE 19.34 usec
TE 300.2 K
D1 1.10000002 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 150.9656784 MHz
NUC1 13C
P1 10.63 usec

F2 - Processing parameters
SI 32768
SF 150.9505840 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Compound 1.601H NMR



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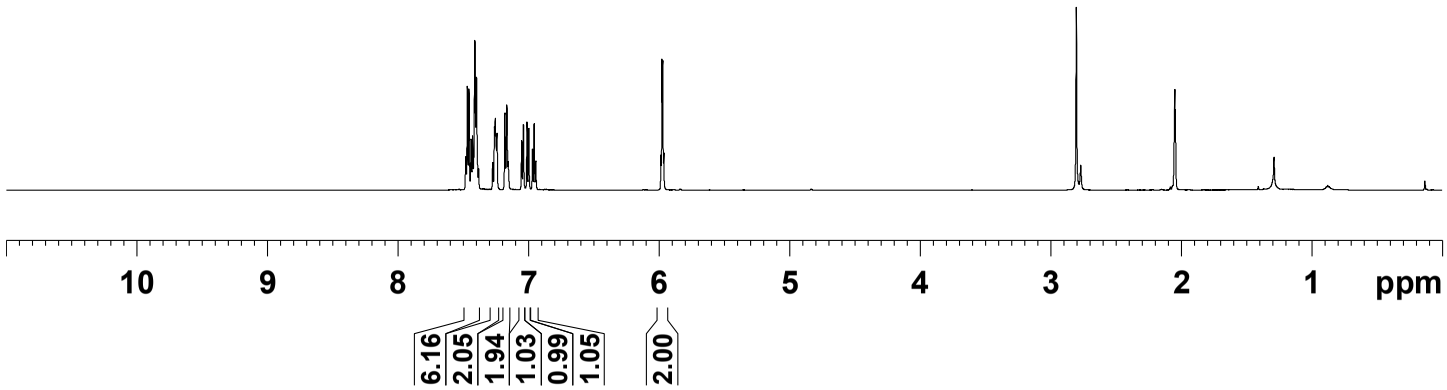


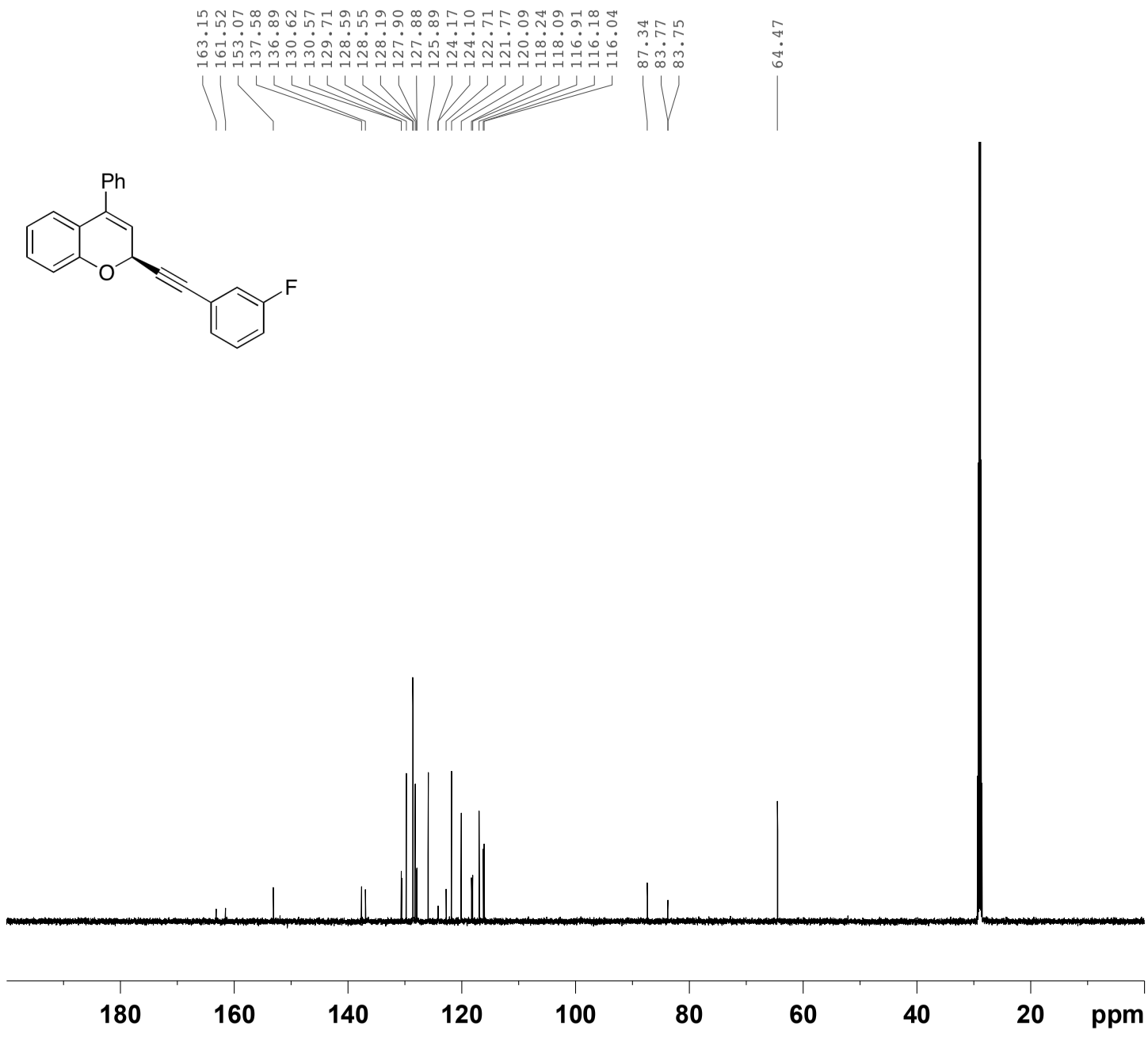
Current Data Parameters
NAME HH-3-200A1_2
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120802
Time 1.09
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT Acetone
NS 8
DS 2
SWH 8403.361 Hz
FIDRES 0.128225 Hz
AQ 3.8994420 sec
RG 144
DW 59.500 usec
DE 17.39 usec
TE 300.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 600.3233018 MHz
NUC1 1H
P1 10.77 usec

F2 - Processing parameters
SI 65536
SF 600.3200119 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound 1.60 13C NMR



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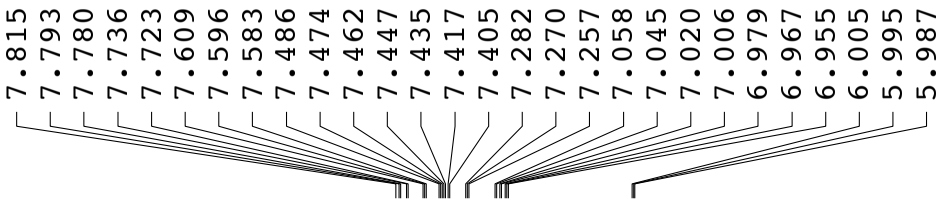
Current Data Parameters
NAME HH-3-200A1_2
EXPNO 2
PROCNO 1

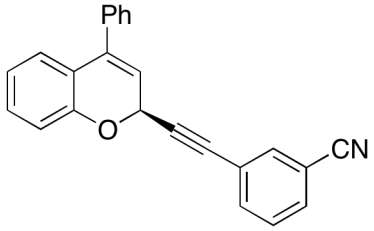
F2 - Acquisition Parameters
Date_ 20120802
Time 1.19
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg55
TD 65536
SOLVENT Acetone
NS 256
DS 4
SWH 34722.223 Hz
FIDRES 0.529819 Hz
AQ 0.9437684 sec
RG 2050
DW 14.400 usec
DE 19.34 usec
TE 300.2 K
D1 1.10000002 sec
D11 0.03000000 sec
TD0 1

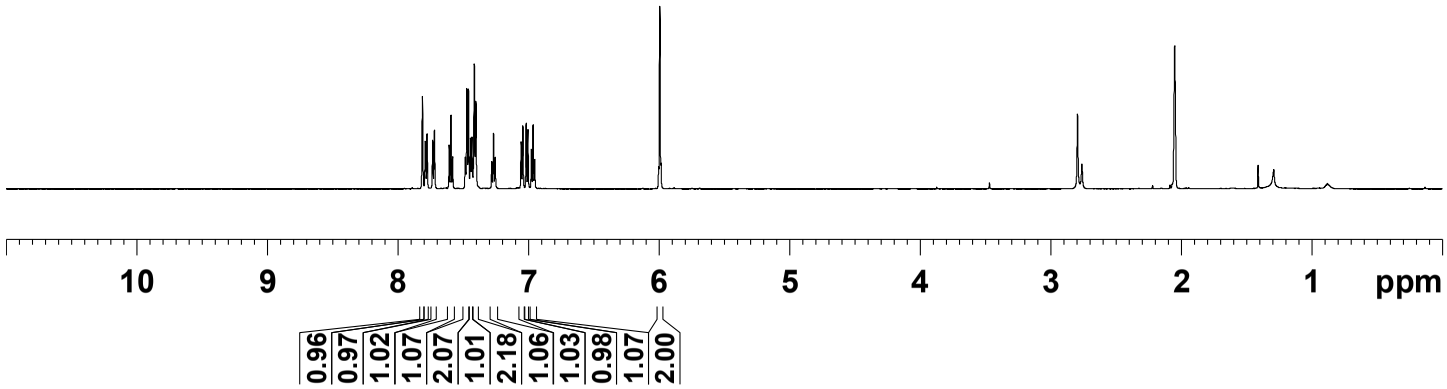
======== CHANNEL f1 ========
SFO1 150.9656784 MHz
NUC1 13C
P1 10.63 usec

F2 - Processing parameters
SI 32768
SF 150.9505840 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Compound 1.61 1H NMR







272

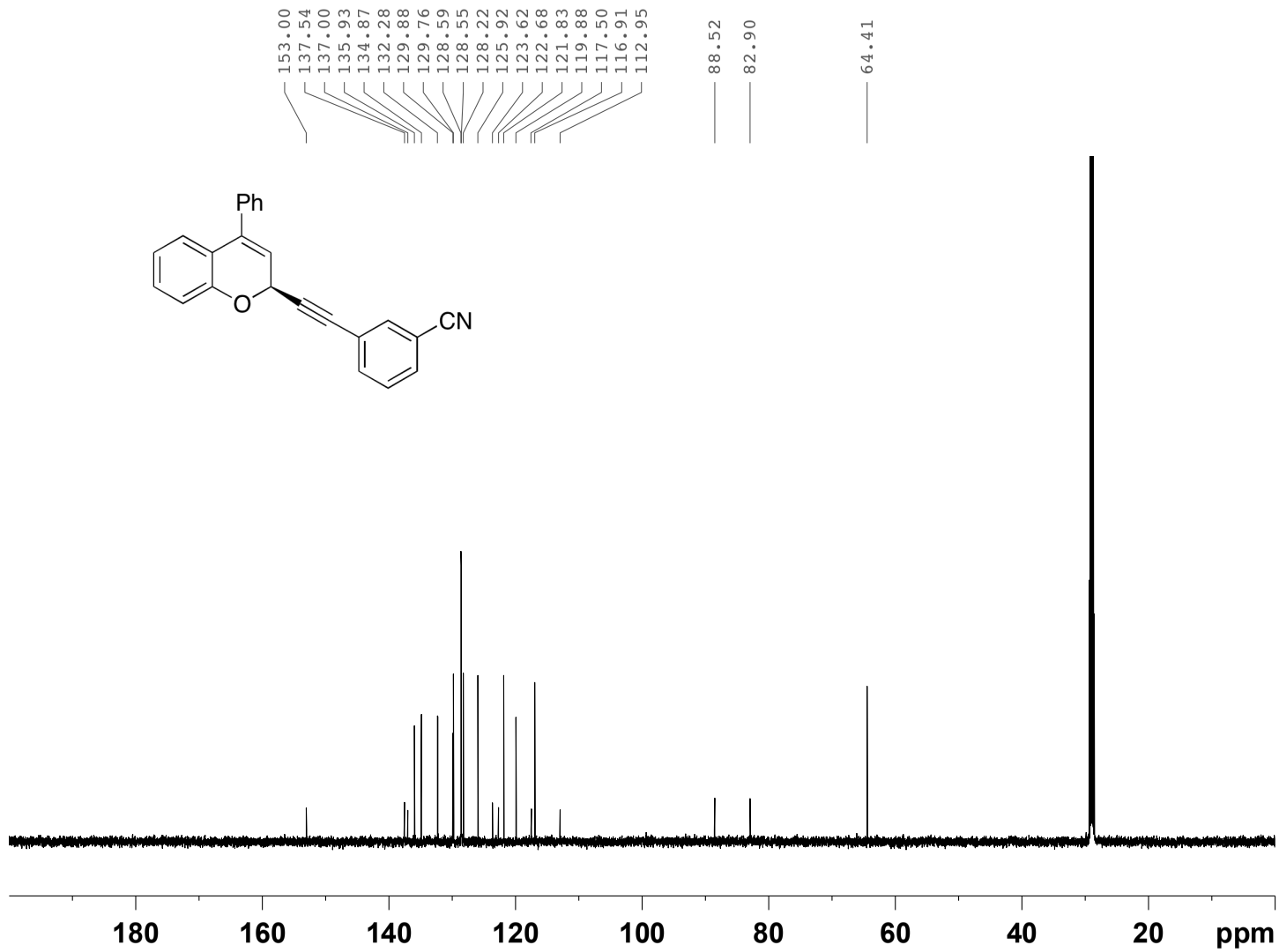
Current Data Parameters
NAME HH-3-222B1aug1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120801
Time 12.13
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT Acetone
NS 8
DS 2
SWH 8403.361 Hz
FIDRES 0.128225 Hz
AQ 3.8994420 sec
RG 161
DW 59.500 usec
DE 17.39 usec
TE 300.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 600.3233018 MHz
NUC1 1H
P1 10.77 usec

F2 - Processing parameters
SI 65536
SF 600.3200111 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound 1.61 13C NMR



273

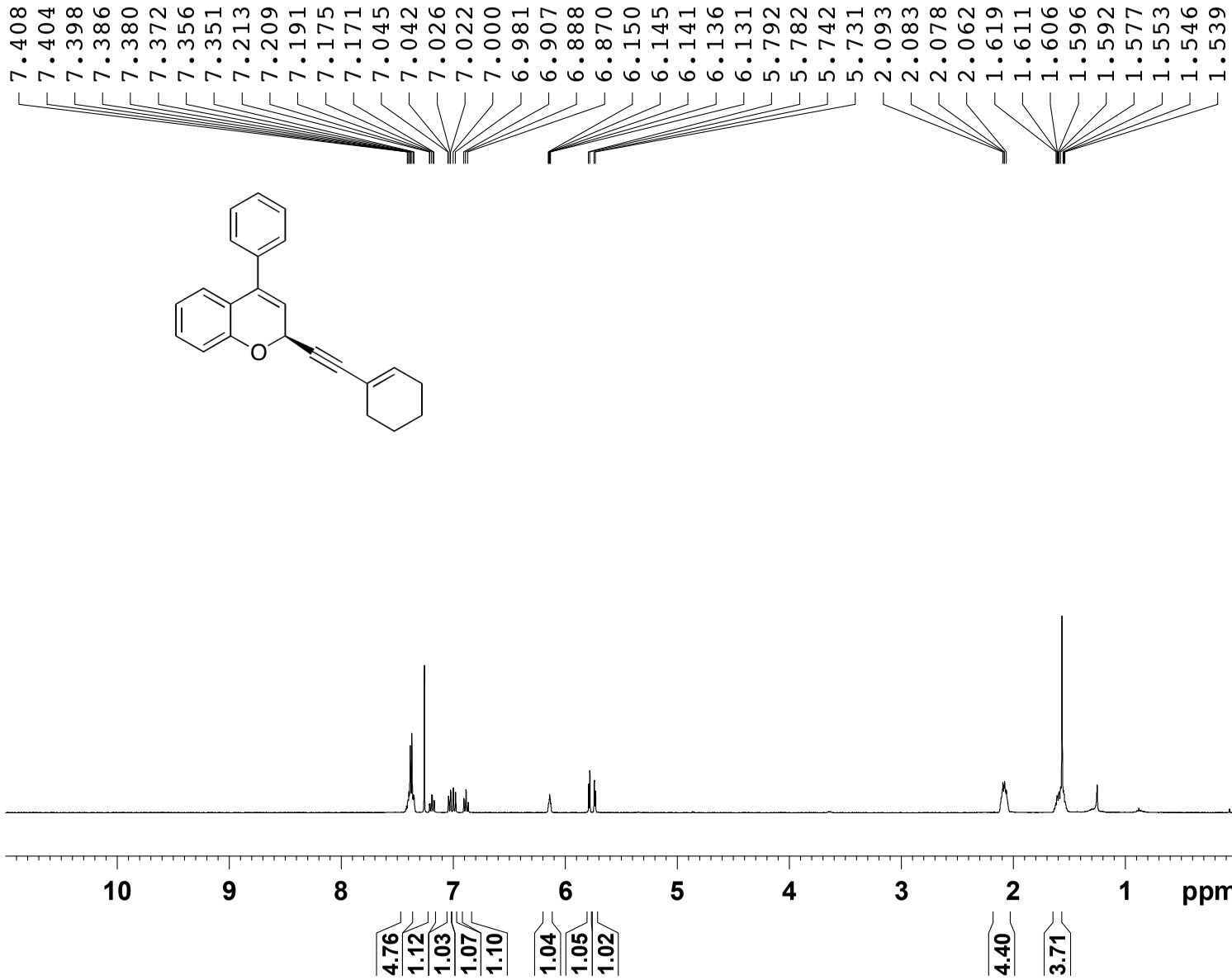
Current Data Parameters
NAME HH-3-222B1aug1
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120801
Time 12.45
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg55
TD 65536
SOLVENT Acetone
NS 256
DS 4
SWH 34722.223 Hz
FIDRES 0.529819 Hz
AQ 0.9437684 sec
RG 2050
DW 14.400 usec
DE 19.34 usec
TE 300.2 K
D1 1.10000002 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 150.9656784 MHz
NUC1 13C
P1 10.63 usec

F2 - Processing parameters
SI 32768
SF 150.9505840 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Compound 1.62 1H NMR



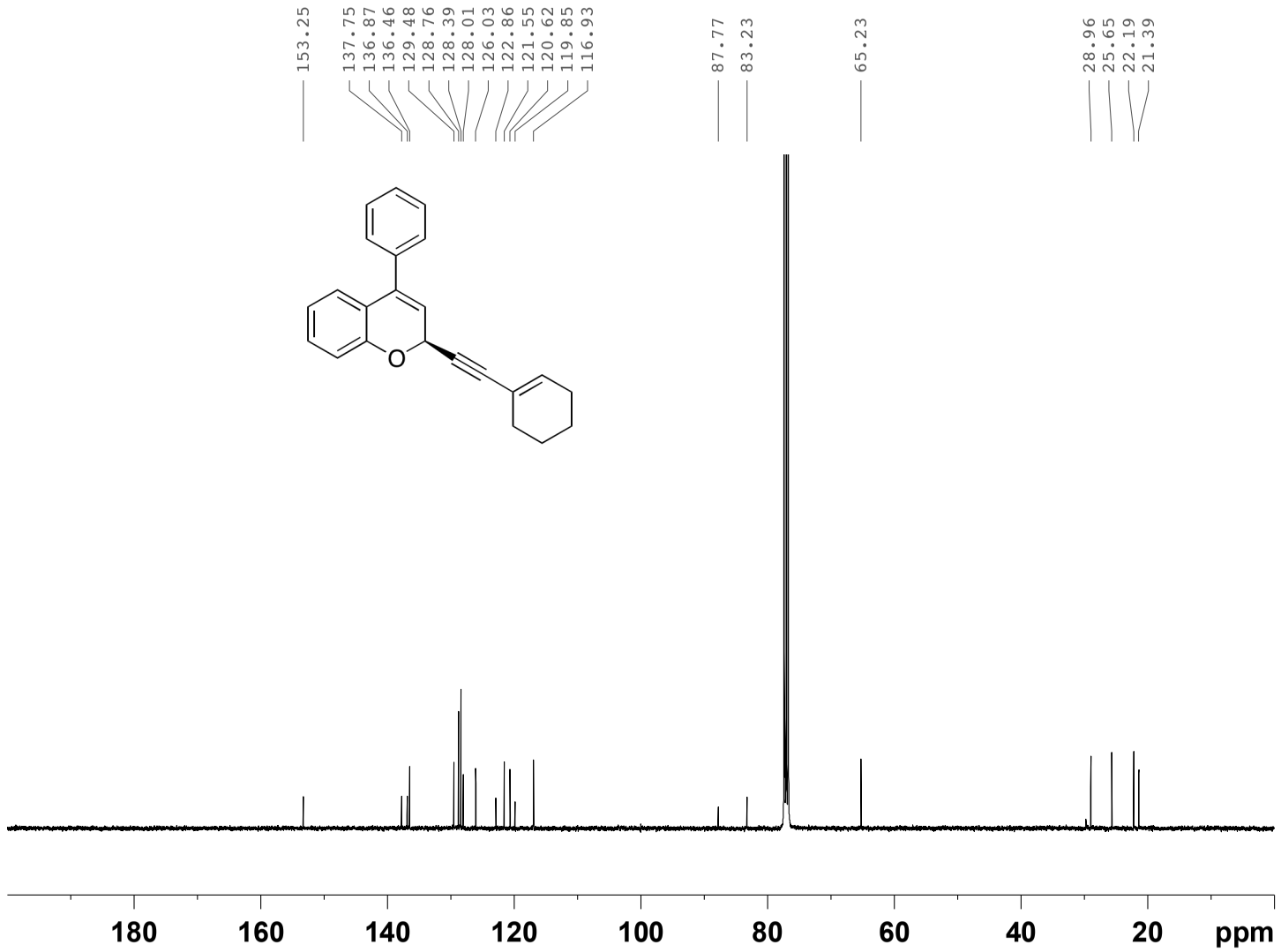
Current Data Parameters
NAME HH-3-256A2_2
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120814
Time 18.20
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 10.1
DW 60.400 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 4.90 dB
PL1W 3.30822015 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300098 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound 1.62 13C NMR



Current Data Parameters
NAME HH-3-256A2_2
EXPNO 2
PROCNO 1

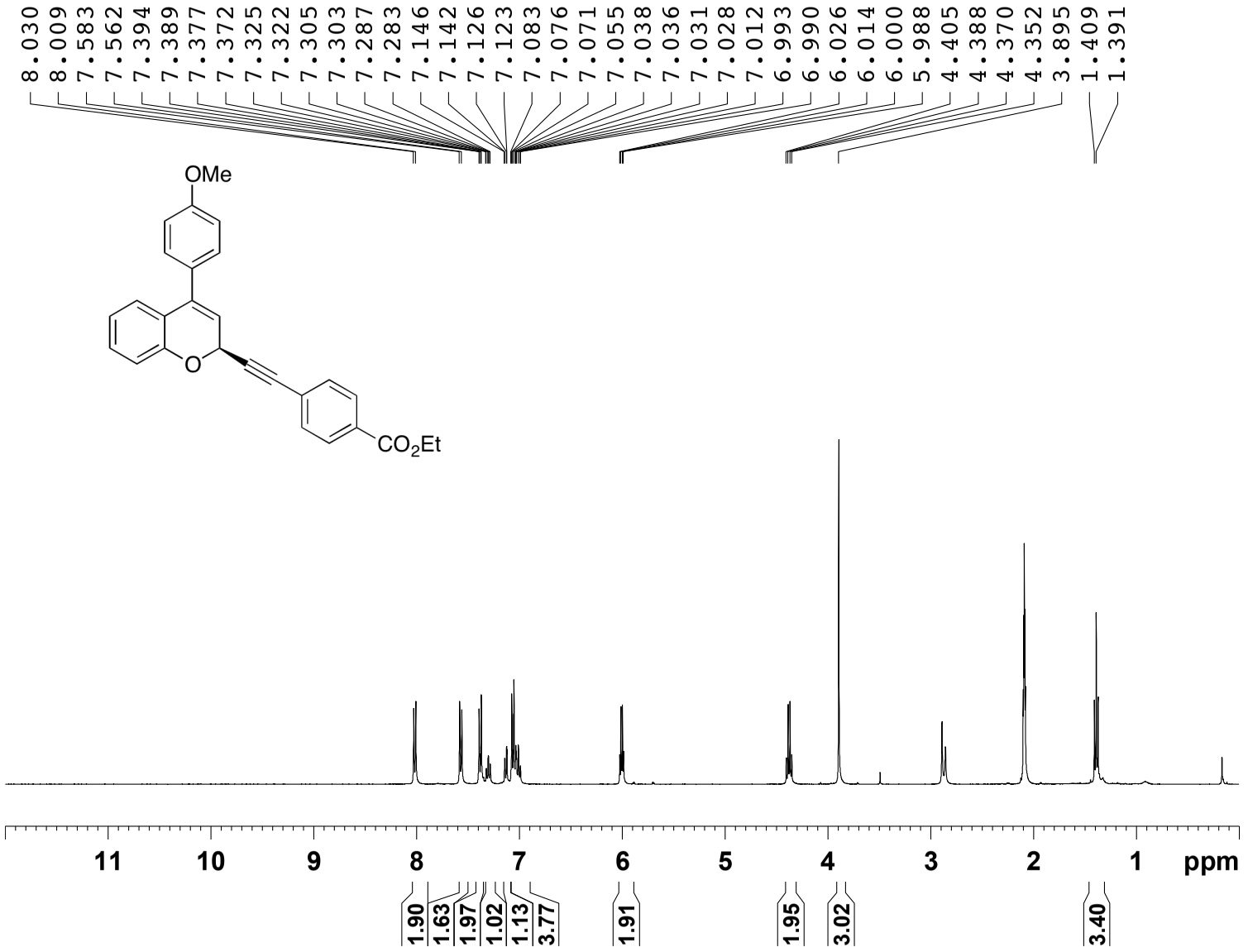
F2 - Acquisition Parameters
Date_ 20120814
Time 18.50
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 500
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 512
DW 20.850 usec
DE 18.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.25 usec
PL1 0.55 dB
PL1W 35.18820572 W
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 4.90 dB
PL12 20.46 dB
PL13 21.00 dB
PL2W 3.30822015 W
PL12W 0.09195905 W
PL13W 0.08120718 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Compound 1.63 1H NMR



276

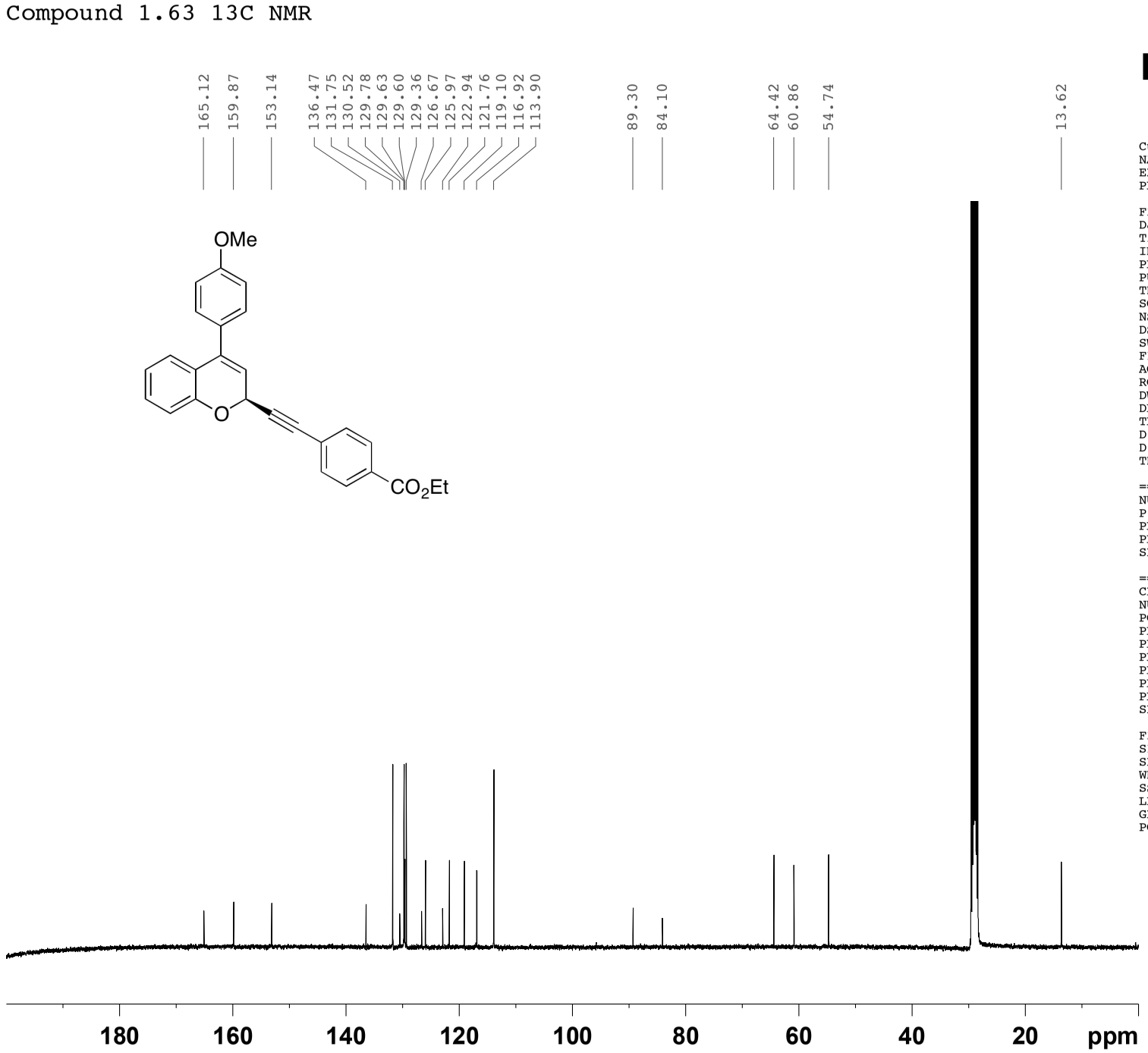
Current Data Parameters
NAME HH-3-240B2rs_2
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120806
Time 15.29
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zg30
TD 65536
SOLVENT Acetone
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 10.1
DW 60.400 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 4.90 dB
PL1W 3.30822015 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1299907 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound 1.63 13C NMR



Current Data Parameters
NAME HH-3-240B2rs_2
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters

Date_	20120807
Time	3.11
INSTRUM	spect
PROBHD	5 mm CPQNP 1H/
PULPROG	zgpg30
TD	65536
SOLVENT	Acetone
NS	1024
DS	4
SWH	23980.814 Hz
FIDRES	0.365918 Hz
AQ	1.3664756 sec
RG	512
DW	20.850 usec
DE	18.00 usec
TE	298.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1

======== CHANNEL f1 ========

NUC1	13C
P1	9.25 usec
PL1	0.55 dB
PL1W	35.18820572 W
SFO1	100.6228298 MHz

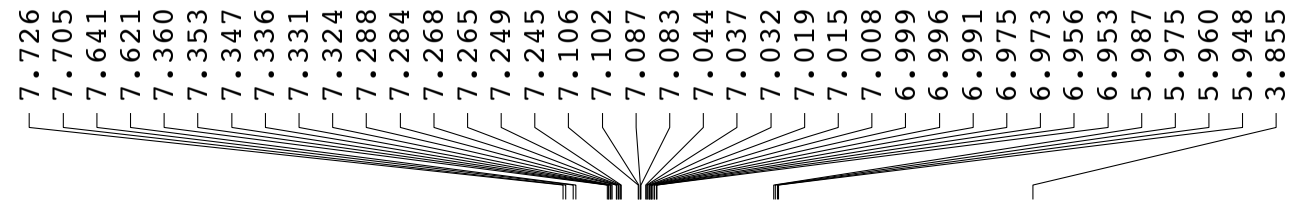
======== CHANNEL f2 ========

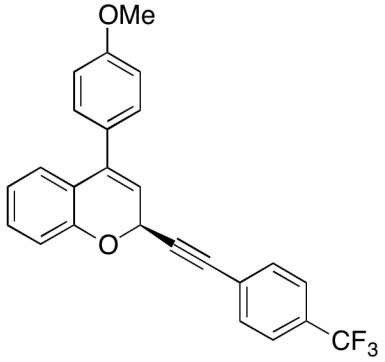
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	4.90 dB
PL12	20.46 dB
PL13	21.00 dB
PL2W	3.30822015 W
PL12W	0.09195905 W
PL13W	0.08120718 W
SFO2	400.1316005 MHz

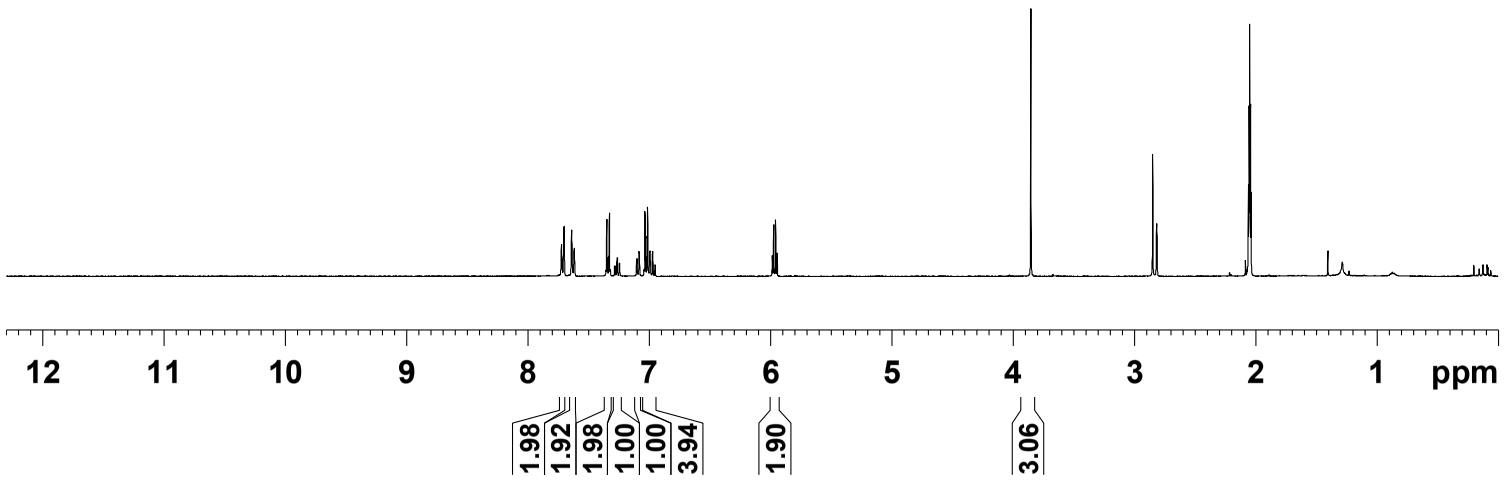
F2 - Processing parameters

SI	32768
SF	100.6127690 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

Compound 1.64 1H NMR







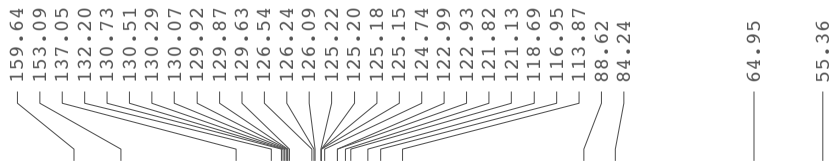
Current Data Parameters
NAME HH-3-233D1
EXPNO 1
PROCNO 1

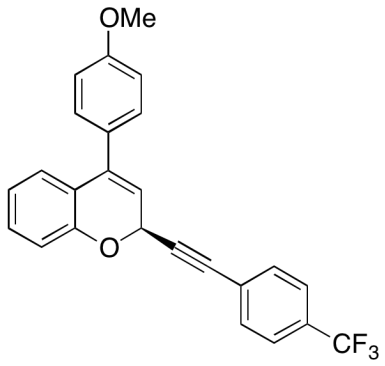
F2 - Acquisition Parameters
Date_ 20120723
Time 12.45
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zg30
TD 65536
SOLVENT Acetone
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 11.3
DW 60.400 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1

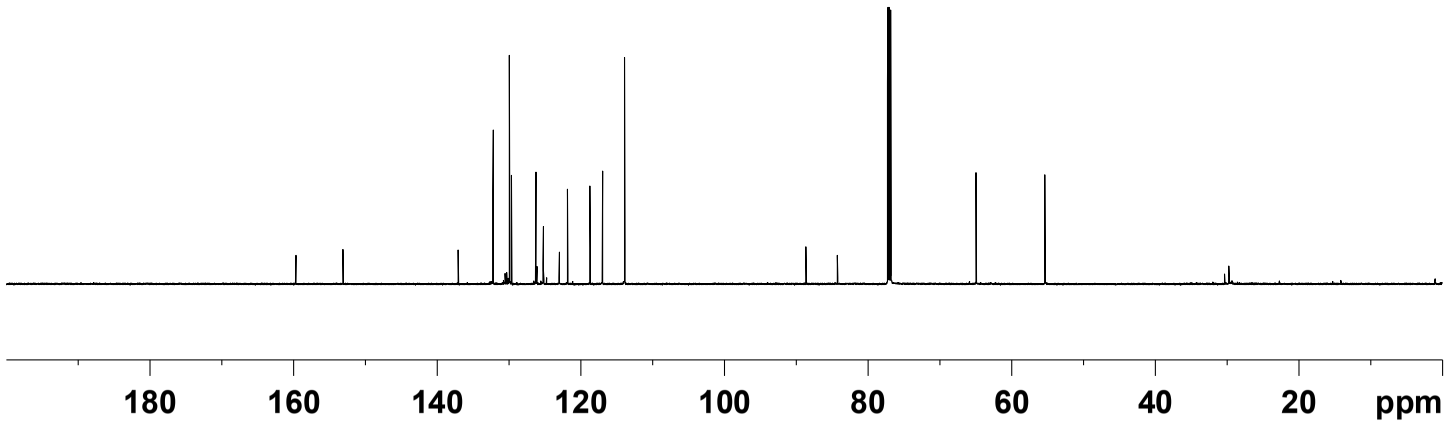
======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 4.90 dB
PL1W 3.30822015 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300067 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound 1.64 13C NMR







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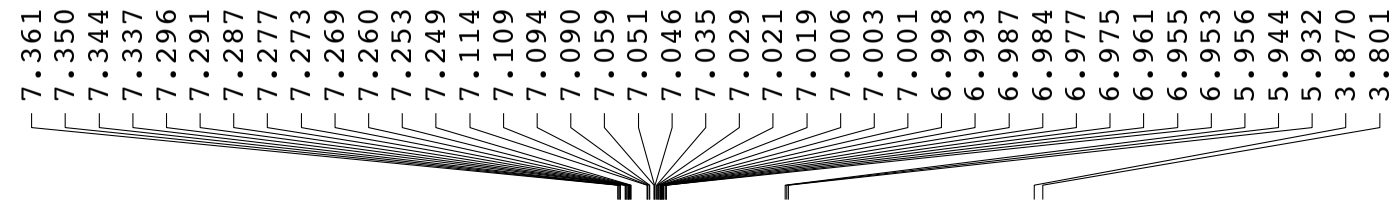
Current Data Parameters
NAME HH-3-233D sep8
EXPNO 1
PROCNO 1

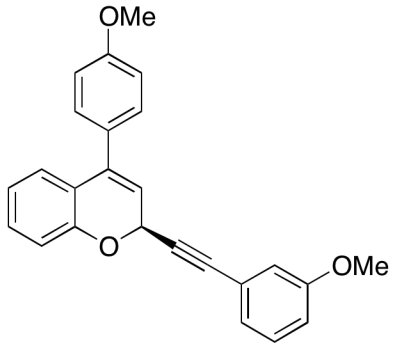
F2 - Acquisition Parameters
Date_ 20120908
Time 22.03
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg55
TD 65536
SOLVENT CDCl3
NS 5000
DS 4
SWH 34722.223 Hz
FIDRES 0.529819 Hz
AQ 0.9437684 sec
RG 2050
DW 14.400 usec
DE 19.34 usec
TE 298.0 K
D1 1.10000002 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 150.9656784 MHz
NUC1 13C
P1 10.63 usec

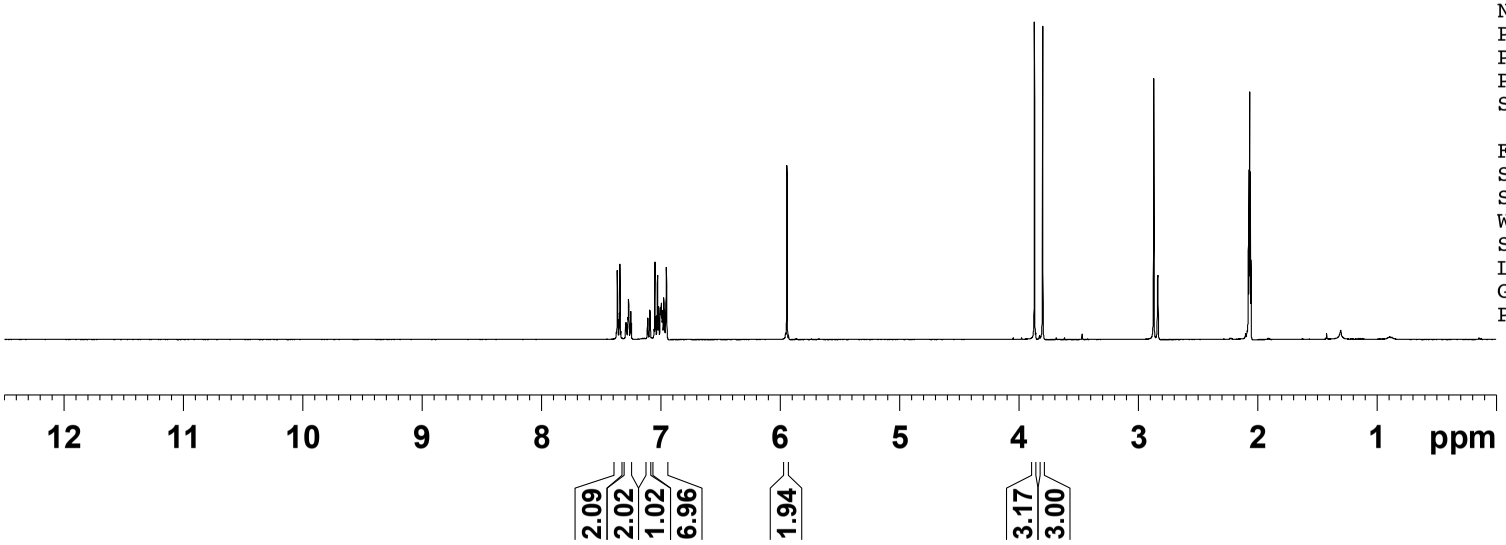
F2 - Processing parameters
SI 32768
SF 150.9505840 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Compound 1.65 1H NMR





280



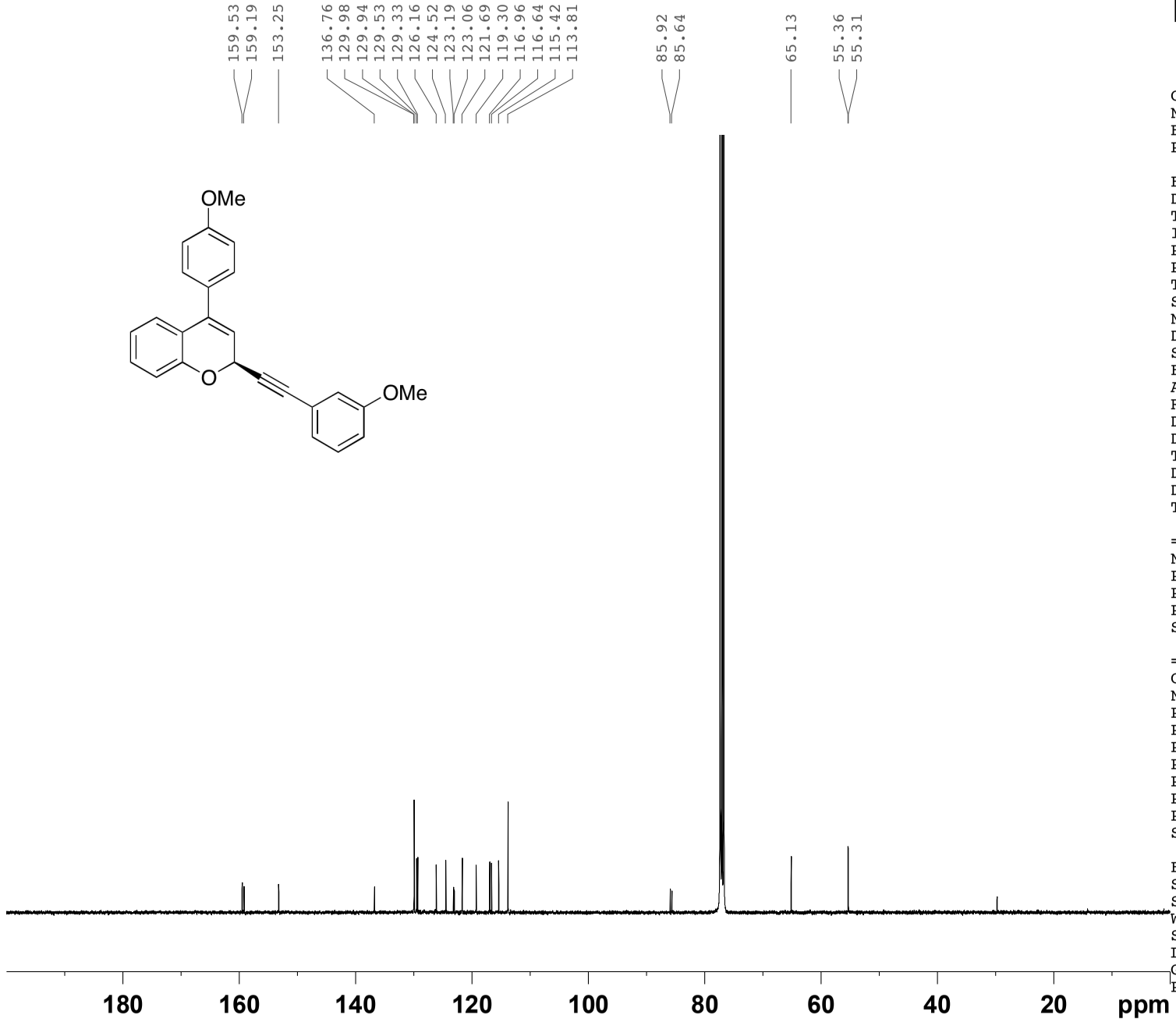
Current Data Parameters
NAME HH-3-233B2
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120723
Time 15.46
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zg30
TD 65536
SOLVENT Acetone
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 10.1
DW 60.400 usec
DE 6.00 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 4.90 dB
PL1W 3.30822015 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound 1.65 13C NMR



Current Data Parameters
NAME HH-3-233B2 dec29
EXPNO 2
PROCNO 1

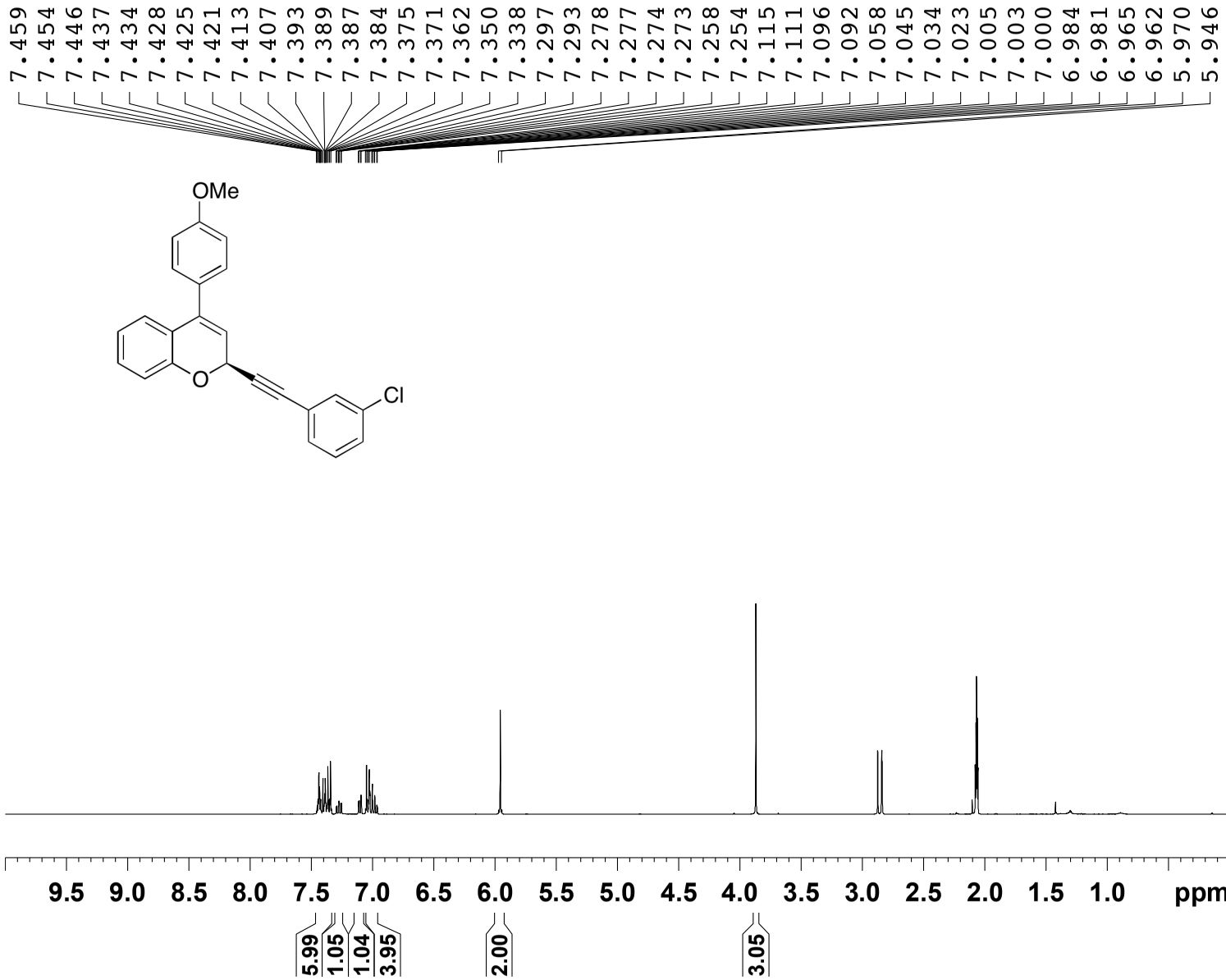
F2 - Acquisition Parameters
Date_ 20131229
Time 20.41
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 512
DW 20.850 usec
DE 18.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.25 usec
PL1 0.55 dB
PL1W 35.18820572 W
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 4.90 dB
PL12 20.46 dB
PL13 21.00 dB
PL2W 3.30822015 W
PL12W 0.09195905 W
PL13W 0.08120718 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Compound 1.66 1H NMR



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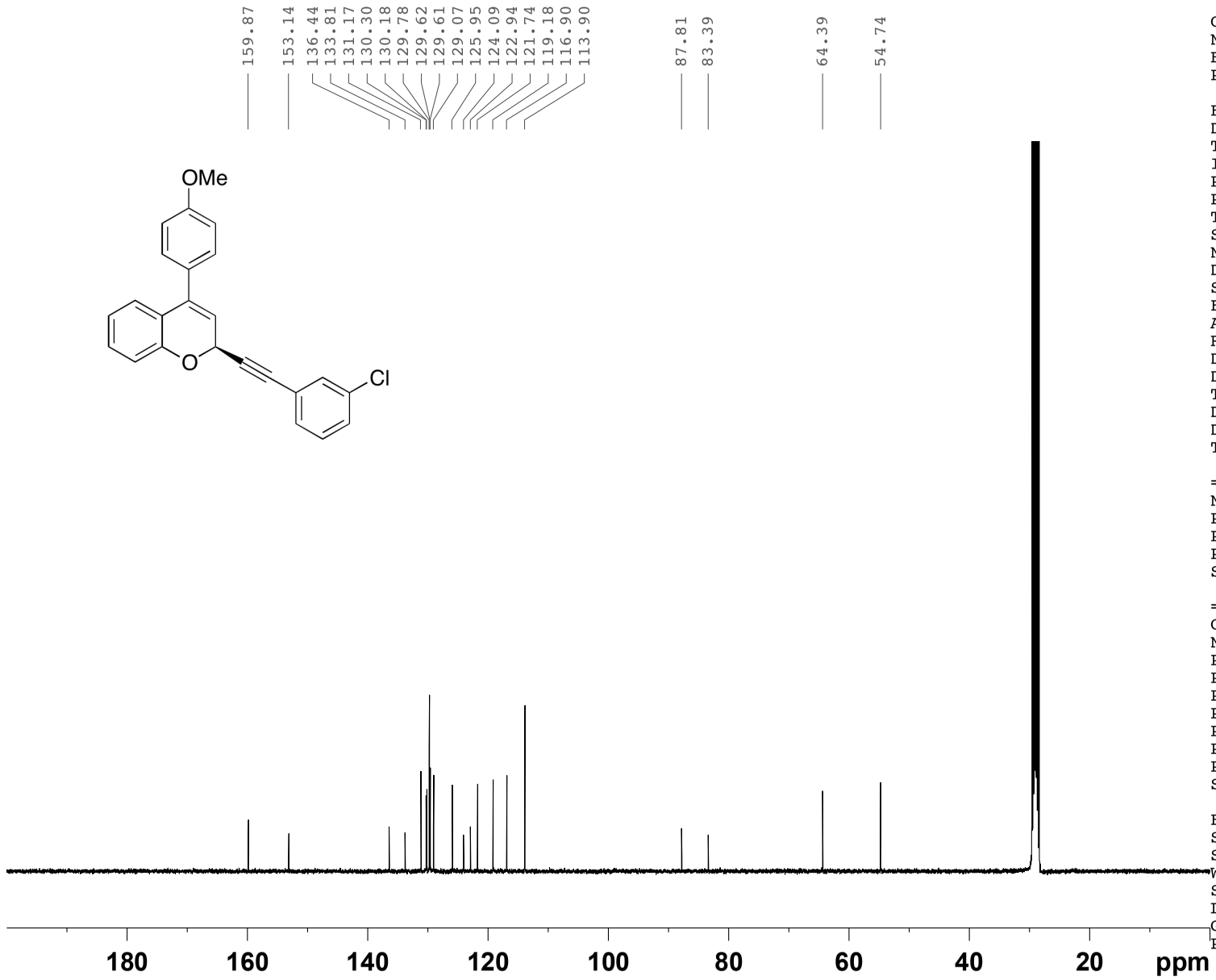
```
Current Data Parameters
NAME          HH-3-212A2
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120521
Time               14.34
INSTRUM            spect
PROBHD   5 mm CPQNP 1H/
PULPROG             zg30
TD                 65536
SOLVENT          Acetone
NS                    16
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ              3.9584243 sec
RG                  11.3
DW                60.400 usec
DE                 6.00 usec
TE                298.2 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                15.00 usec
PL1                4.90 dB
PL1W         3.30822015 W
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300000 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                 1.00
```

Compound 1.66 13C NMR



Current Data Parameters
NAME HH-3-212A1
EXPNO 2
PROCNO 1

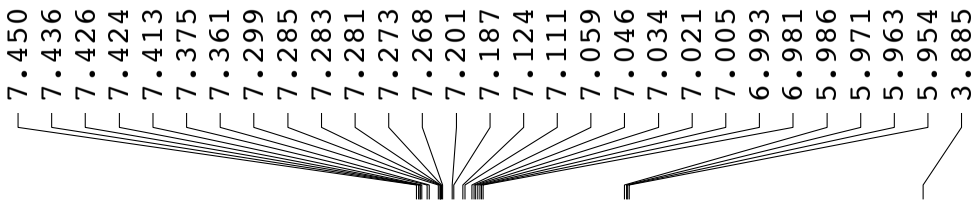
F2 - Acquisition Parameters
Date_ 20120522
Time 0.12
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 1024
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 512
DW 20.850 usec
DE 18.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

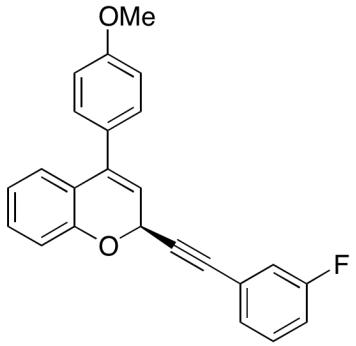
======== CHANNEL f1 ========
NUC1 13C
P1 9.25 usec
PL1 0.55 dB
PL1W 35.18820572 W
SFO1 100.6228298 MHz

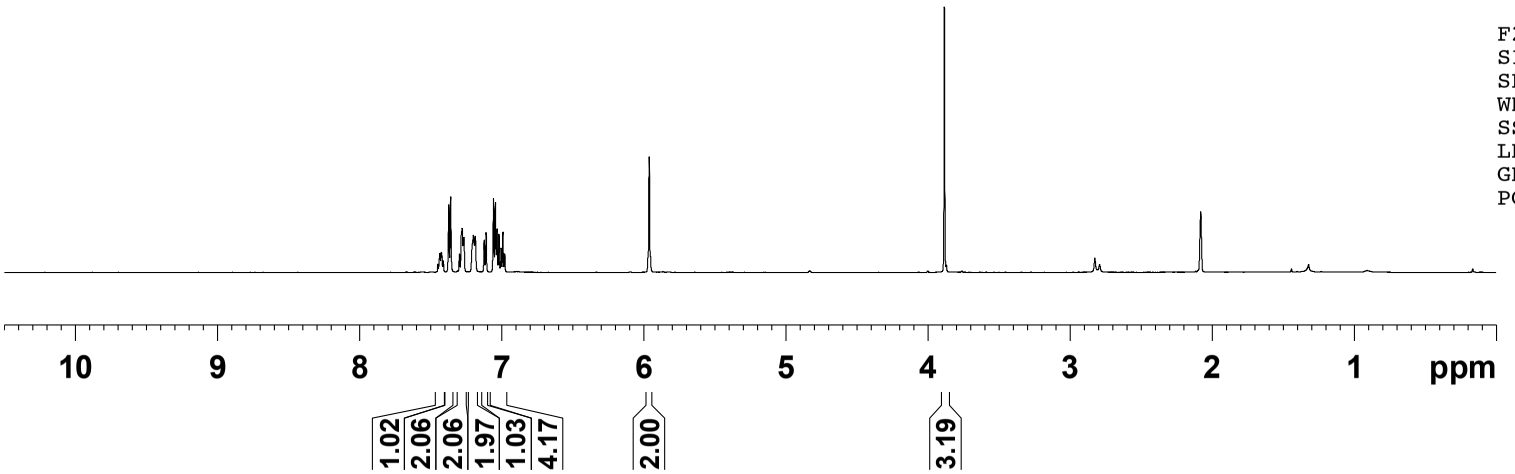
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 4.90 dB
PL12 20.46 dB
PL13 21.00 dB
PL2W 3.30822015 W
PL12W 0.09195905 W
PL13W 0.08120718 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Compound 1.67 1H NMR







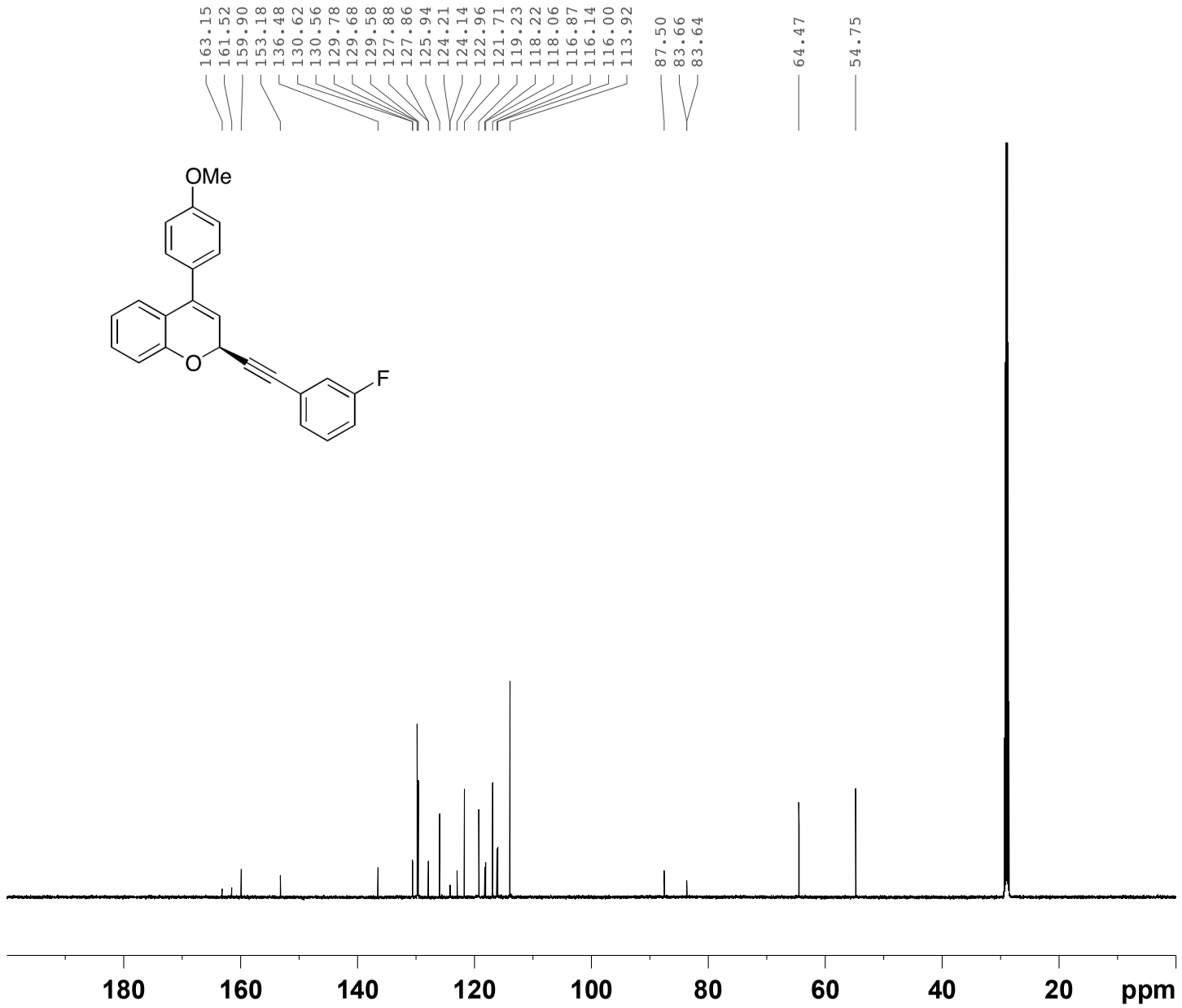
Current Data Parameters
NAME HH-3-212B1july31
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120731
Time 23.23
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT Acetone
NS 8
DS 2
SWH 8403.361 Hz
FIDRES 0.128225 Hz
AQ 3.8994420 sec
RG 144
DW 59.500 usec
DE 17.39 usec
TE 300.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 600.3233018 MHz
NUC1 1H
P1 10.77 usec

F2 - Processing parameters
SI 65536
SF 600.3199926 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound 1.67 13C NMR



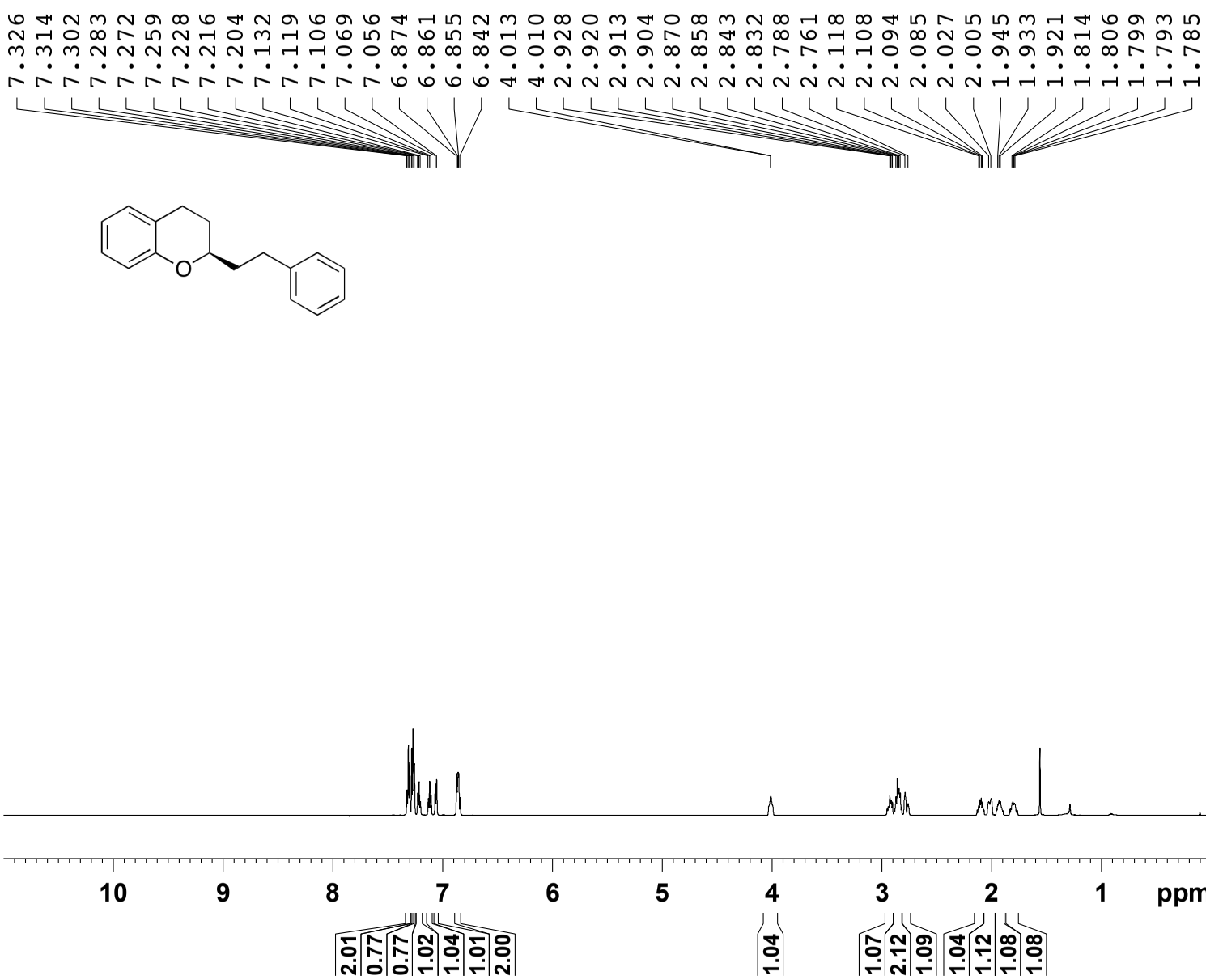
Current Data Parameters
NAME HH-3-212B2aug2
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120802
Time 4.03
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg55
TD 65536
SOLVENT Acetone
NS 2048
DS 4
SWH 34722.223 Hz
FIDRES 0.529819 Hz
AQ 0.9437684 sec
RG 2050
DW 14.400 usec
DE 19.34 usec
TE 300.2 K
D1 1.10000002 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 150.9656784 MHz
NUC1 13C
P1 10.63 usec

F2 - Processing parameters
SI 32768
SF 150.9505840 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Compound 1.68 1H NMR



BRUKER

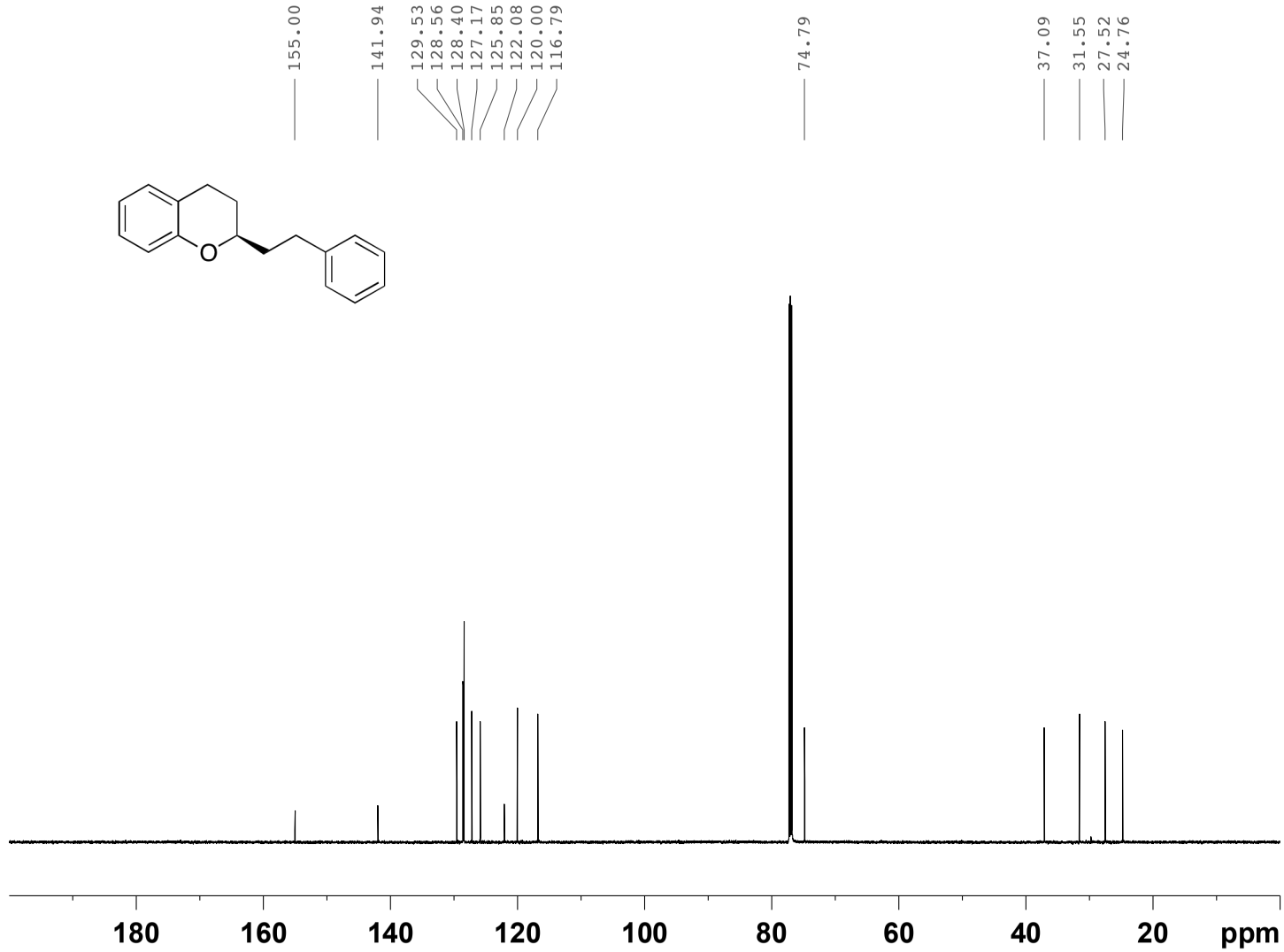
```
Current Data Parameters
NAME          HH-3-248cp
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120815
Time               2.53
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8403.361 Hz
FIDRES         0.128225 Hz
AQ             3.8994420 sec
RG                  181
DW               59.500 usec
DE               17.39 usec
TE                300.2 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        600.3233018 MHz
NUC1                  1H
P1                10.77 usec

F2 - Processing parameters
SI                65536
SF          600.3200019 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

Compound 1.68 13C NMR



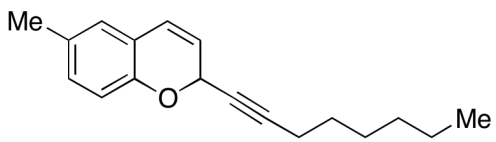
Current Data Parameters
NAME HH-3-248cp
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120815
Time 4.39
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg55
TD 65536
SOLVENT CDCl3
NS 3000
DS 4
SWH 34722.223 Hz
FIDRES 0.529819 Hz
AQ 0.9437684 sec
RG 2050
DW 14.400 usec
DE 19.34 usec
TE 300.2 K
D1 1.10000002 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 150.9656784 MHz
NUC1 13C
P1 10.63 usec

F2 - Processing parameters
SI 32768
SF 150.9505840 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

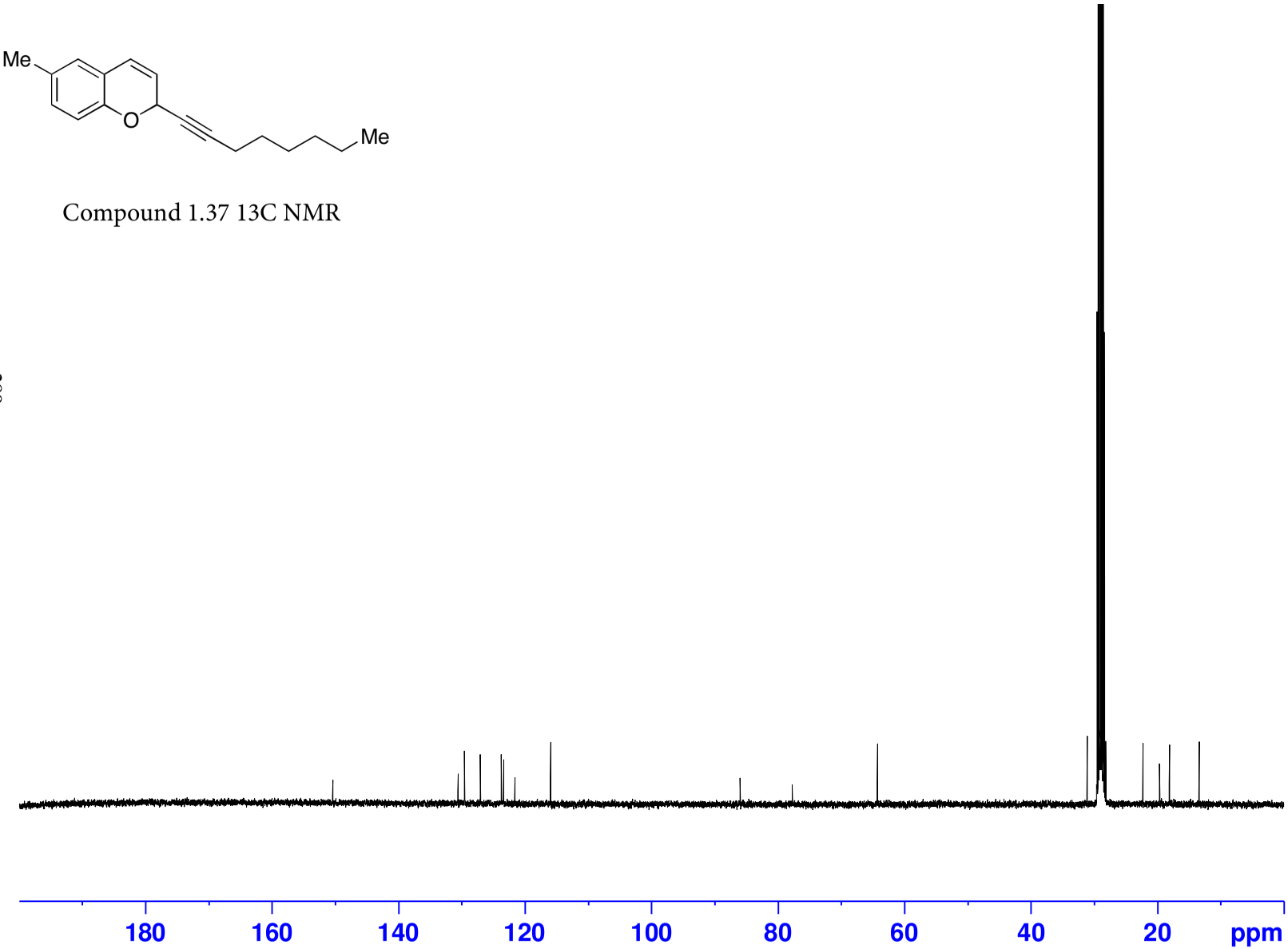
HH-2-061rs
PROTON_16 CDCl3 /opt/topspin3.1pl7



Compound 1.37 1H NMR

HH-2-061acetone
C13CPD32 Acetone /opt/topspin hari 7

Compound 1.37 13C NMR



rameters
61acetone
2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140416
Time 12.14
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 32
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664256 sec
RG 512
DW 20.850 usec
DE 18.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

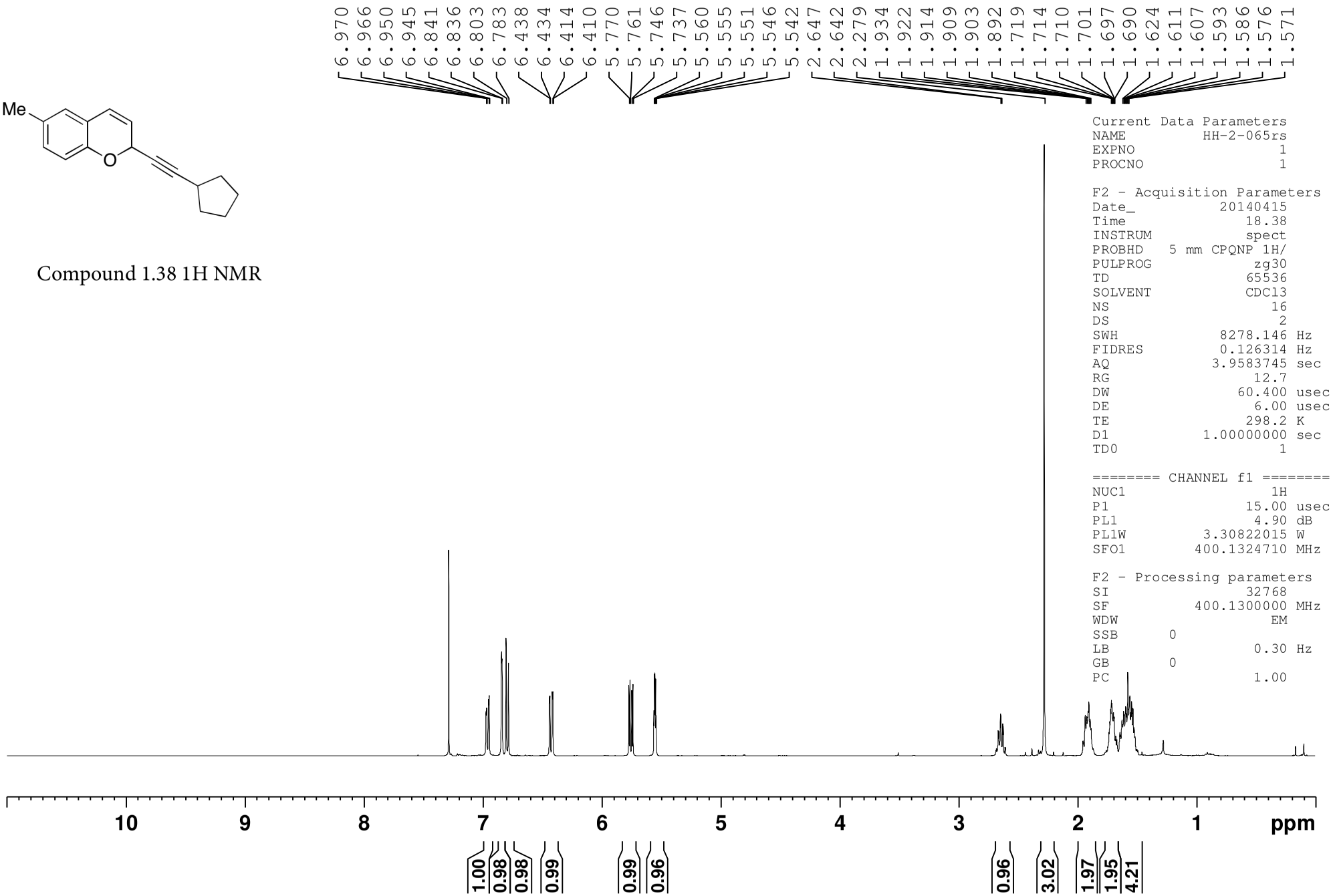
======== CHANNEL f1 ========
NUC1 13C
P1 9.25 usec
PL1 0.55 dB
PL1W 35.18820572 W
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 4.90 dB
PL12 20.46 dB
PL13 21.00 dB
PL2W 3.30822015 W
PL12W 0.09195905 W
PL13W 0.08120718 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

HH-2-065rs
PROTON_16 CDCl3 /opt/topspin hari 7

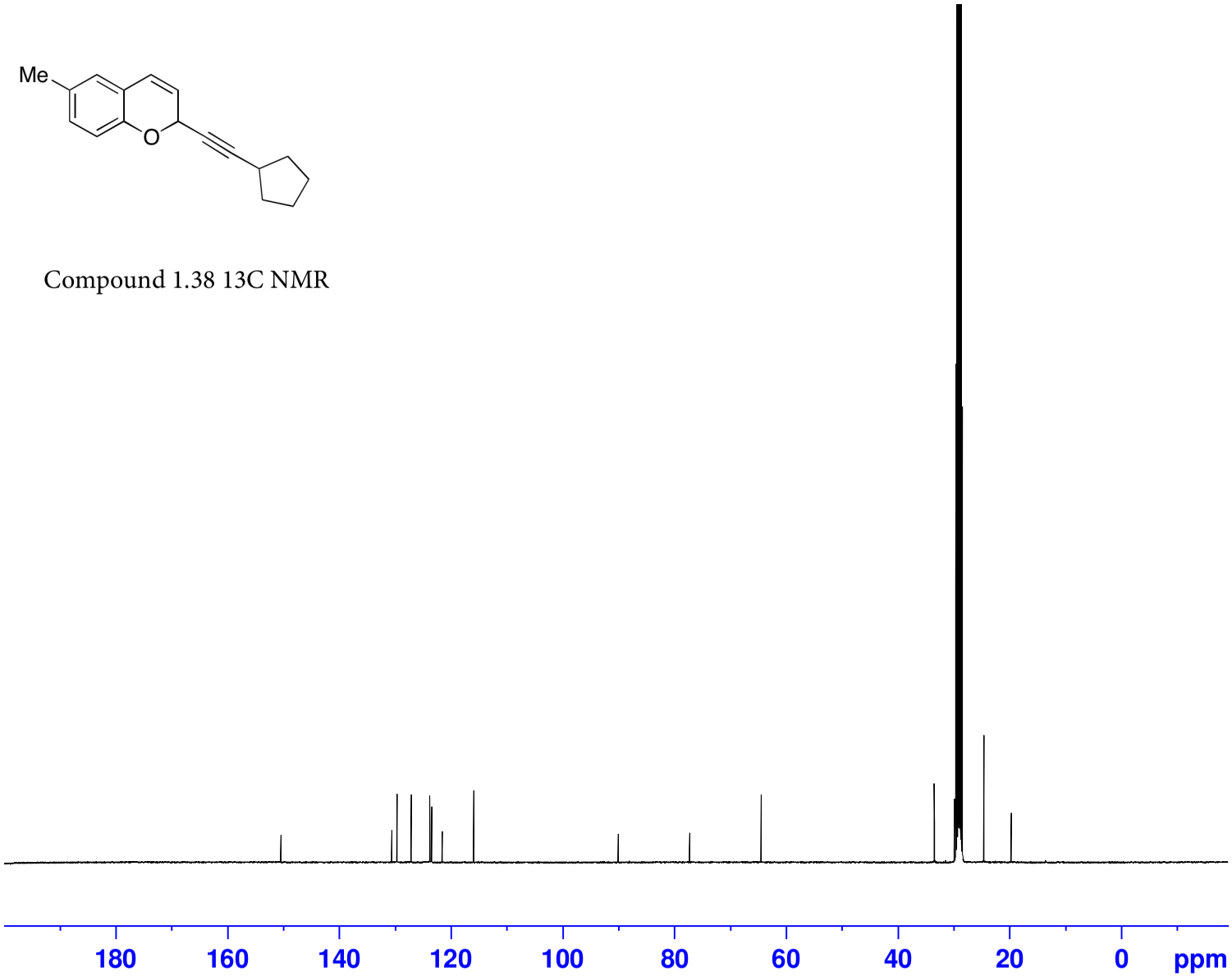
Compound 1.38 1H NMR



With Cyclopentyl alkyne
HH-2-065acetone

150.43
130.58
129.59
127.09
123.74
123.40
121.51
115.89
90.01
77.24
64.43
33.42
33.41
24.55
19.65

Compound 1.38 13C NMR




```
Current Data Parameters
NAME      HH-2-065acetoners
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_           20140418
Time                6.01
INSTRUM            spect
PROBHD   5 mm CPQNP 1H/
PULPROG           zgpg30
TD                65536
SOLVENT          Acetone
NS                 1024
DS                    4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ            1.3664256 sec
RG                  512
DW               20.850 usec
DE               18.00 usec
TE               298.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

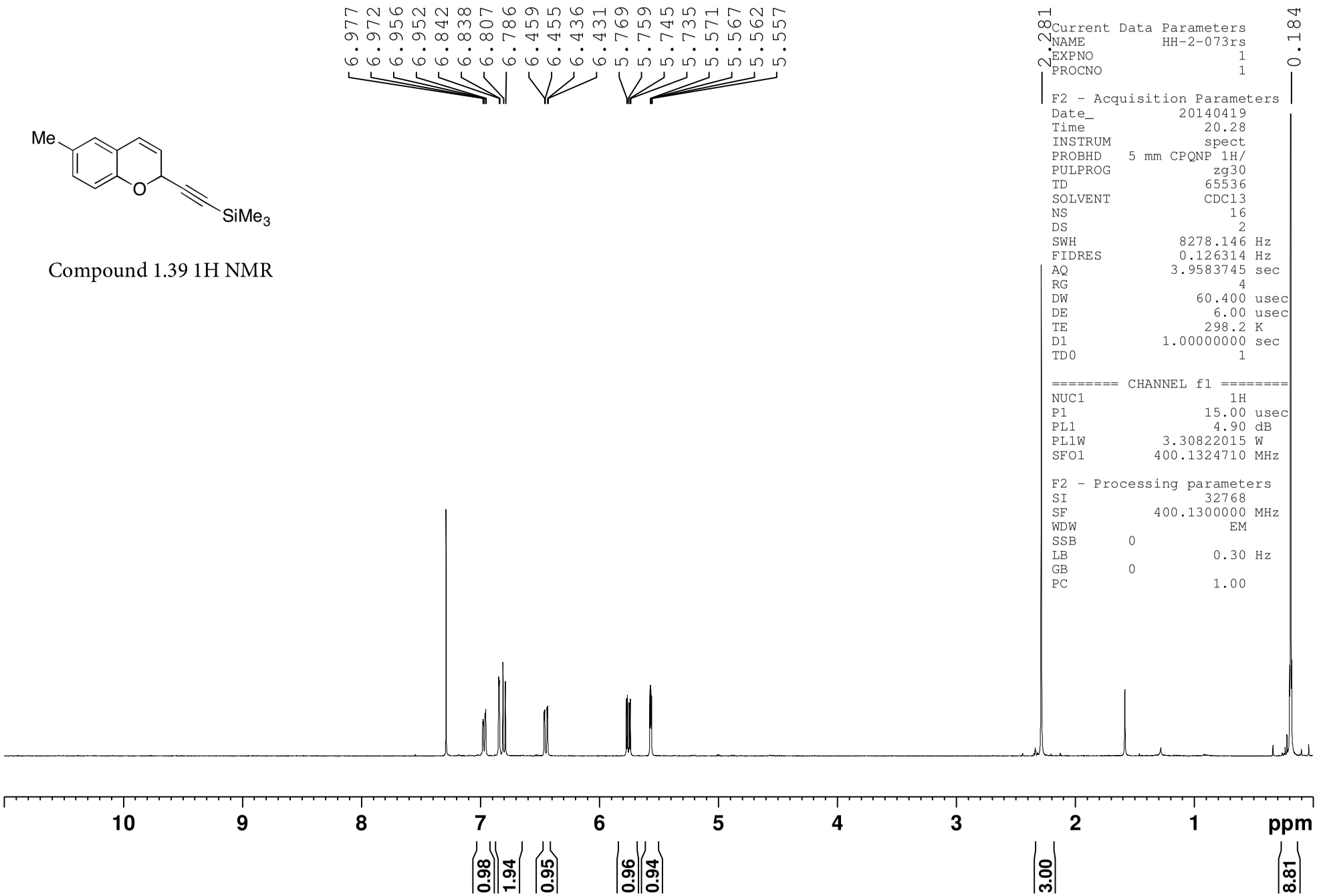
======== CHANNEL f1 ========
NUC1                 13C
P1                 9.25 usec
PL1                0.55 dB
PL1W        35.18820572 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                 1H
PCPD2             90.00 usec
PL2                4.90 dB
PL12              20.46 dB
PL13              21.00 dB
PL2W         3.30822015 W
PL12W        0.09195905 W
PL13W        0.08120718 W
SFO2        400.1316005 MHz

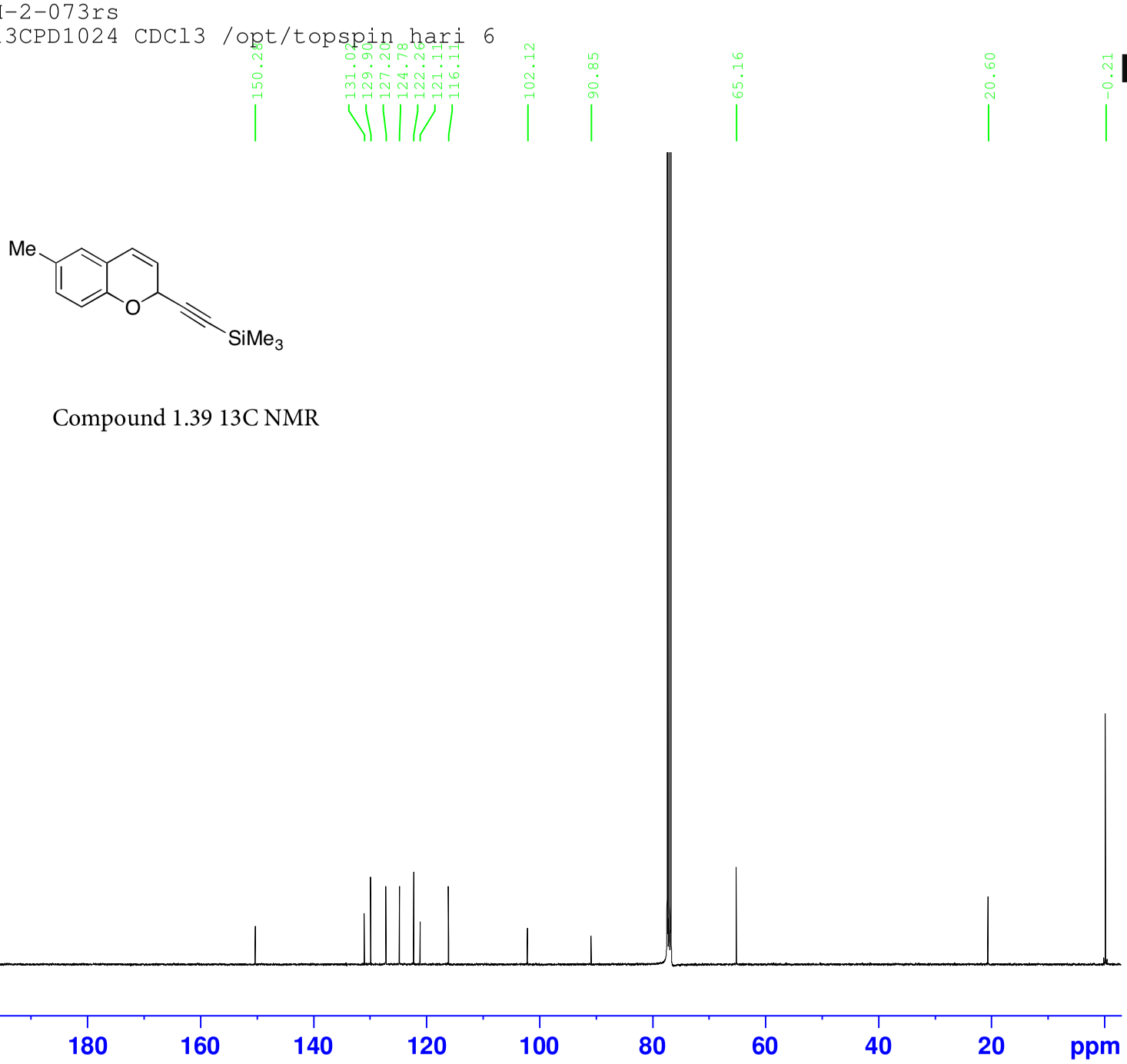
F2 - Processing parameters
SI                32768
SF          100.6127690 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

HH-2-073rs
PROTON_16 CDCl3 /opt/topspin hari 6

Compound 1.39 1H NMR



HH-2-073rs
C13CPD1024 CDCl3 /opt/topspin hari 6



Compound 1.39 13C NMR


```
Current Data Parameters
NAME          HH-2-073rs
EXPNO                  3
PROCNO                 1

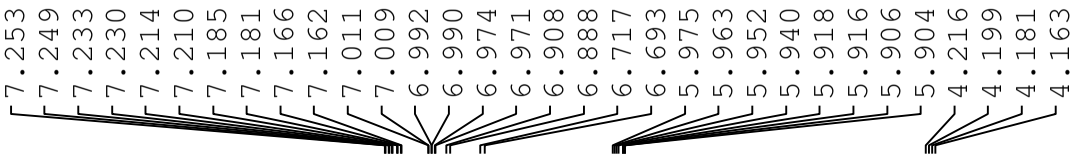
F2 - Acquisition Parameters
Date_           20140419
Time              21.32
INSTRUM           spect
PROBHD   5 mm CPQNP 1H/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ            1.3664256 sec
RG                  512
DW               20.850 usec
DE               18.00 usec
TE               298.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

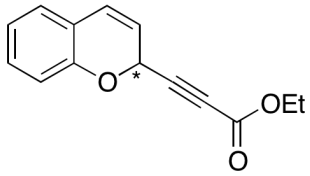
======== CHANNEL f1 ========
NUC1                13C
P1                9.25 usec
PL1               0.55 dB
PL1W        35.18820572 W
SFO1       100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                1H
PCPD2            90.00 usec
PL2               4.90 dB
PL12             20.46 dB
PL13             21.00 dB
PL2W         3.30822015 W
PL12W        0.09195905 W
PL13W        0.08120718 W
SFO2       400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127690 MHz
WDW                EM
SSB      0
LB                1.00 Hz
GB       0
PC                1.40
```

HH-5-172rs
PROTON_16 Acetone /opt/topspin hari 14





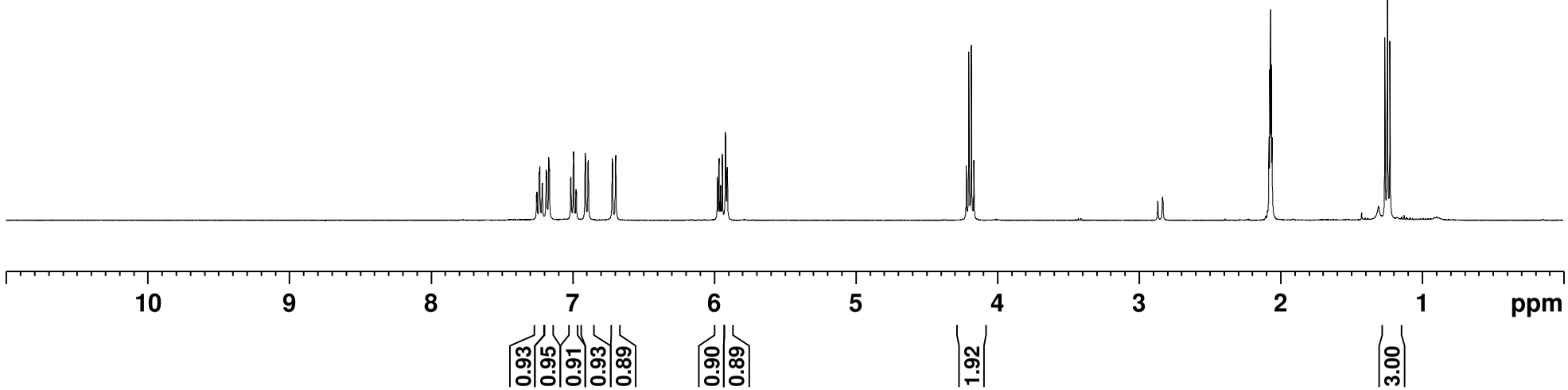
Compound 1.78 1H NMR

Current Data Parameters
NAME HH-5-172rs
EXPNO 1
PROCNO 1

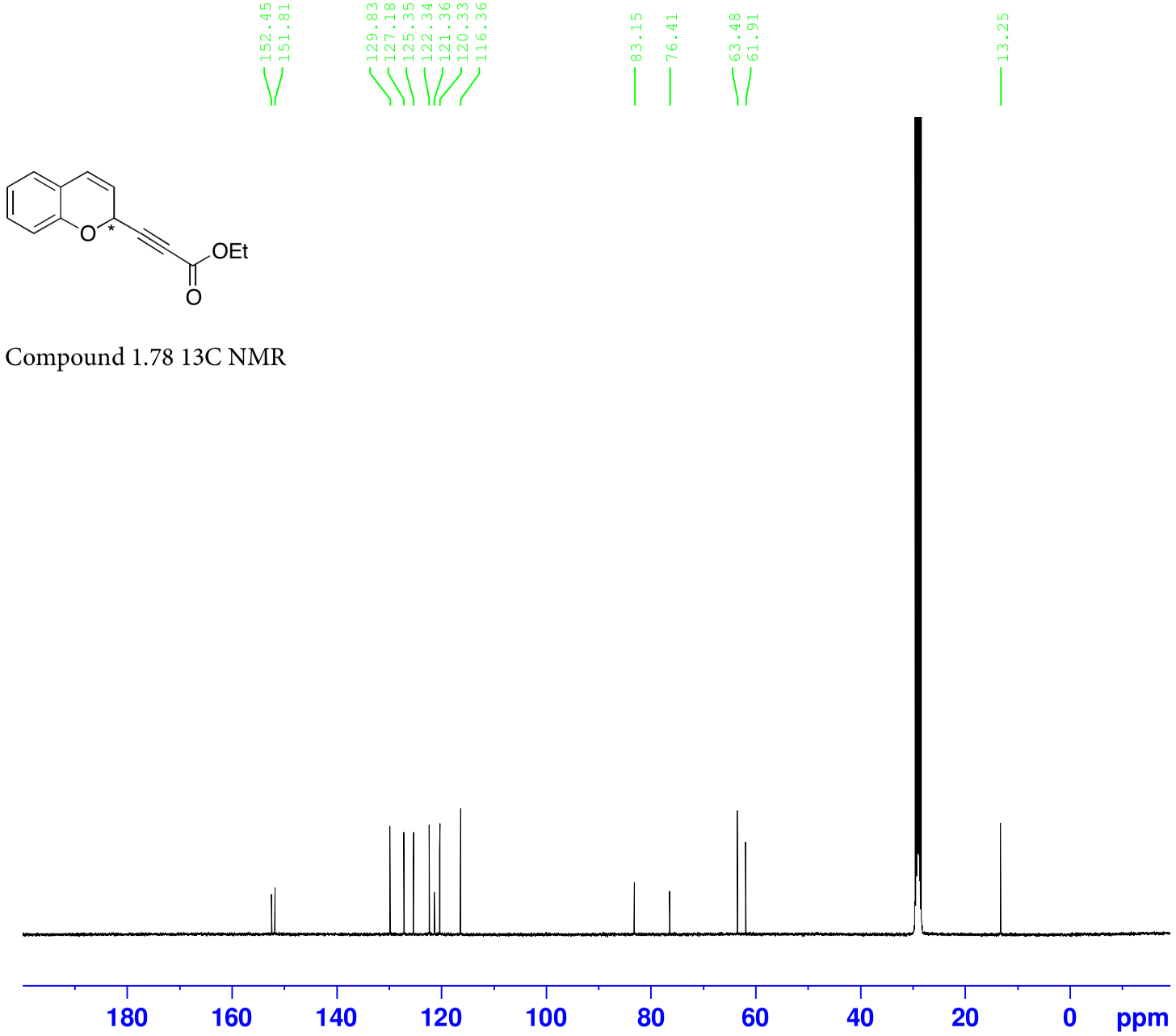
F2 - Acquisition Parameters
Date_ 20140506
Time 19.19
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zg30
TD 65536
SOLVENT Acetone
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9583745 sec
RG 4
DW 60.400 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 4.90 dB
PL1W 3.30822015 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



HH-5-172rs
C13CPD1024 Acetone /opt/topspin hari 14



Compound 1.78 13C NMR

```
Current Data Parameters
NAME          HH-5-172rs
EXPNO                  2
PROCNO                 1

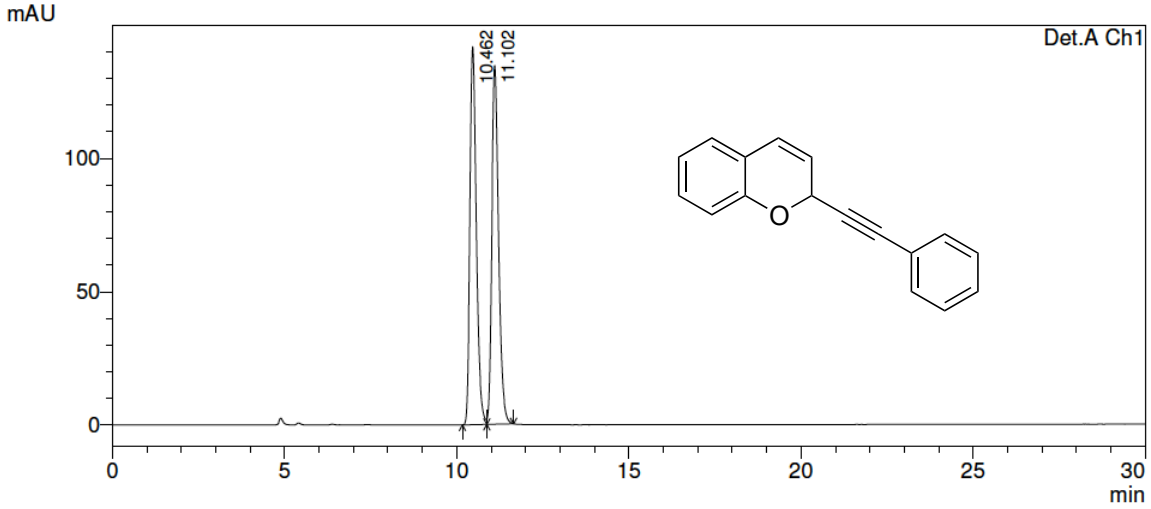
F2 - Acquisition Parameters
Date_           20140506
Time               23.29
INSTRUM            spect
PROBHD   5 mm CPQNP 1H/
PULPROG          zgpg30
TD                65536
SOLVENT         Acetone
NS                 1024
DS                    4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ            1.3664256 sec
RG                  512
DW               20.850 usec
DE               18.00 usec
TE               298.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.25 usec
PL1                 0.55 dB
PL1W         35.18820572 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                 1H
PCPD2              90.00 usec
PL2                 4.90 dB
PL12               20.46 dB
PL13               21.00 dB
PL2W          3.30822015 W
PL12W         0.09195905 W
PL13W         0.08120718 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127690 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

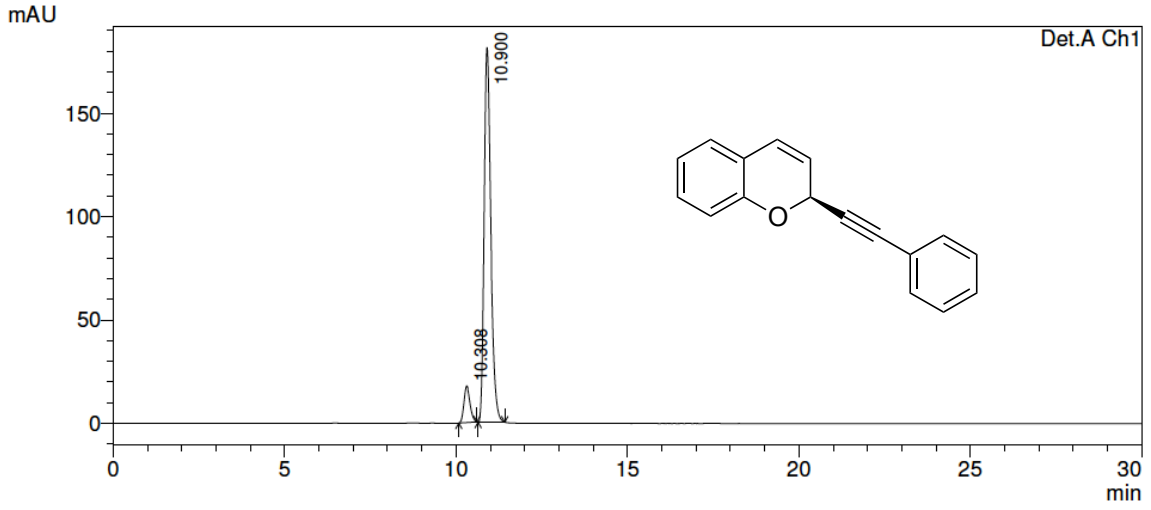
Compound 1.41, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.462	1837045	141778	50.039	51.312
2	11.102	1834150	134529	49.961	48.688
Total		3671194	276307	100.000	100.000

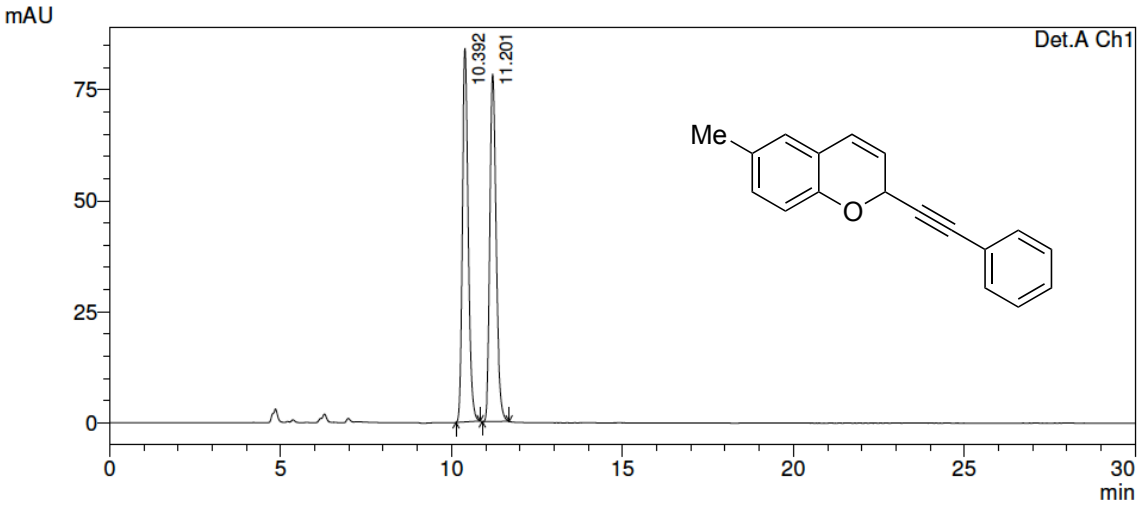
Compound 1.41, 84% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.308	217673	17761	8.210	8.923
2	10.900	2433526	181291	91.790	91.077
Total		2651199	199052	100.000	100.000

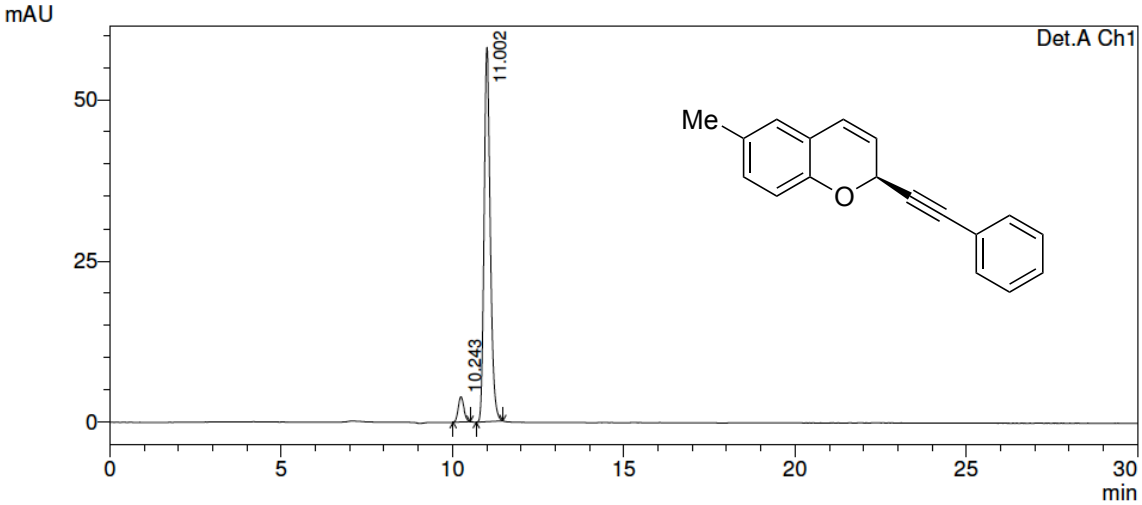
Compound 1.36, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.392	1006345	84176	50.104	51.809
2	11.201	1002161	78296	49.896	48.191
Total		2008506	162472	100.000	100.000

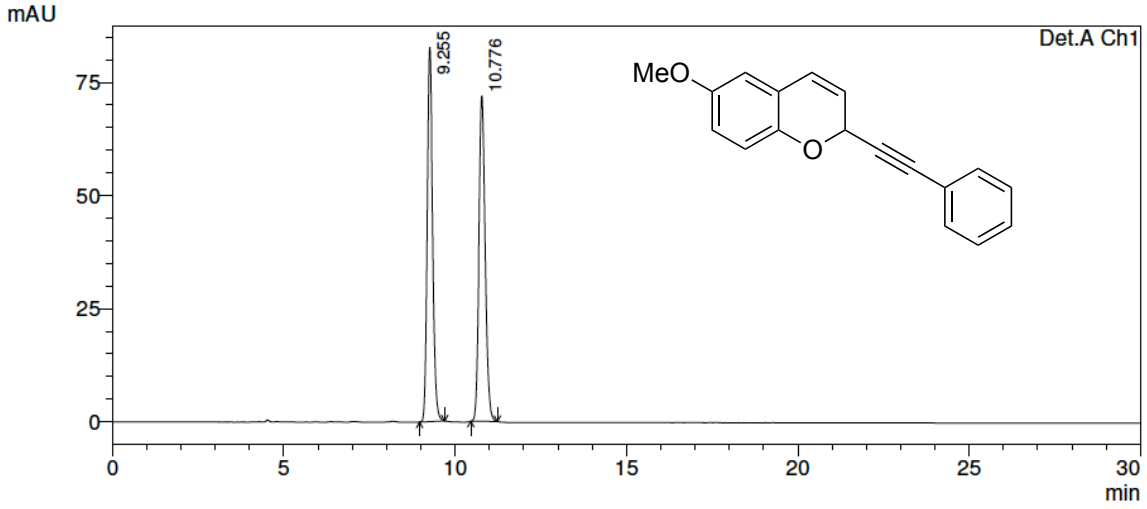
Compound 1.36, 89% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.243	44728	3916	5.744	6.322
2	11.002	733922	58036	94.256	93.678
Total		778650	61952	100.000	100.000

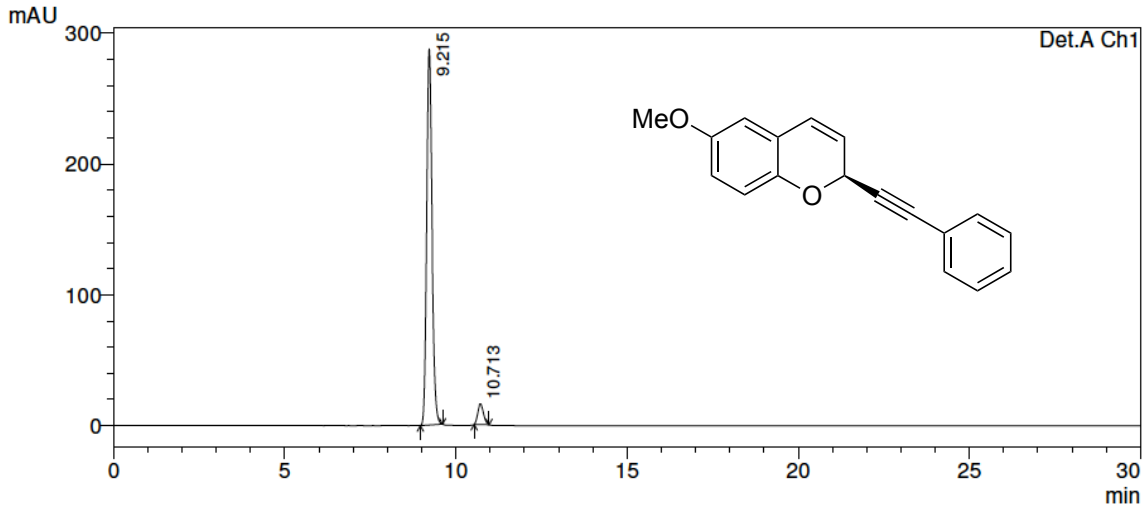
Compound 1.42, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.255	908040	82694	49.956	53.493
2	10.776	909650	71894	50.044	46.507
Total		1817689	154589	100.000	100.000

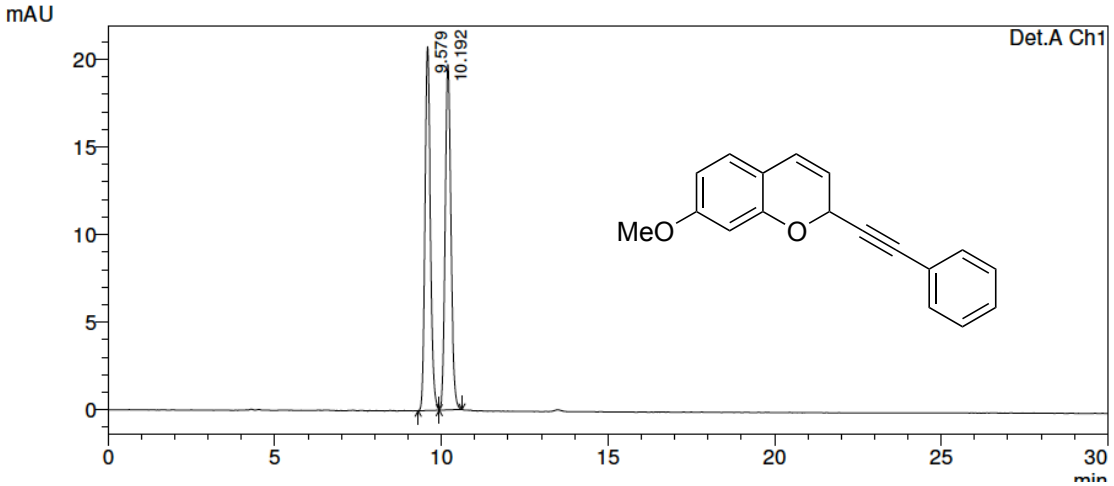
Compound 1.42, 89% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.215	3120669	287374	94.440	94.770
2	10.713	183709	15858	5.560	5.230
Total		3304378	303231	100.000	100.000

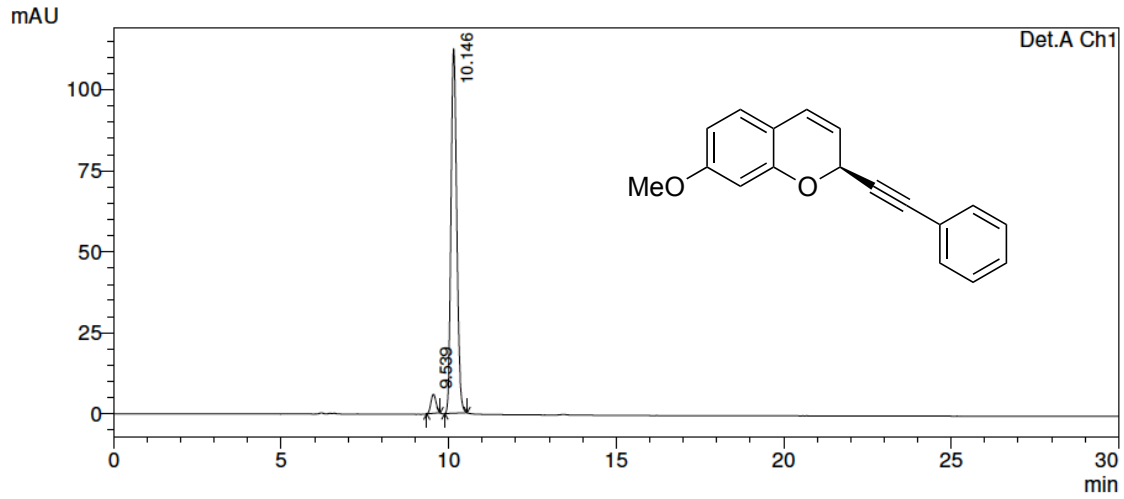
Compound 1.43, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.579	235878	20757	50.009	51.305
2	10.192	235796	19701	49.991	48.695
Total		471674	40458	100.000	100.000

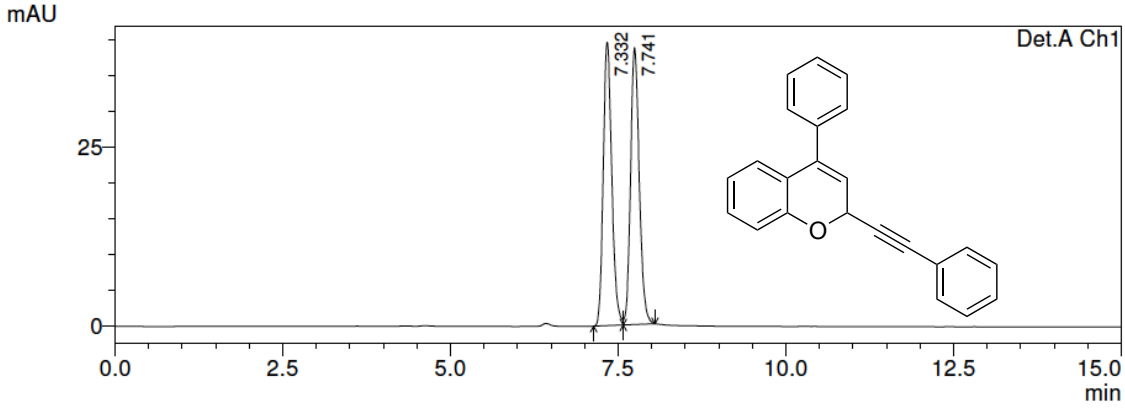
Compound 1.43, 91% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.539	62346	5912	4.470	4.995
2	10.146	1332316	112456	95.530	95.005
Total		1394662	118368	100.000	100.000

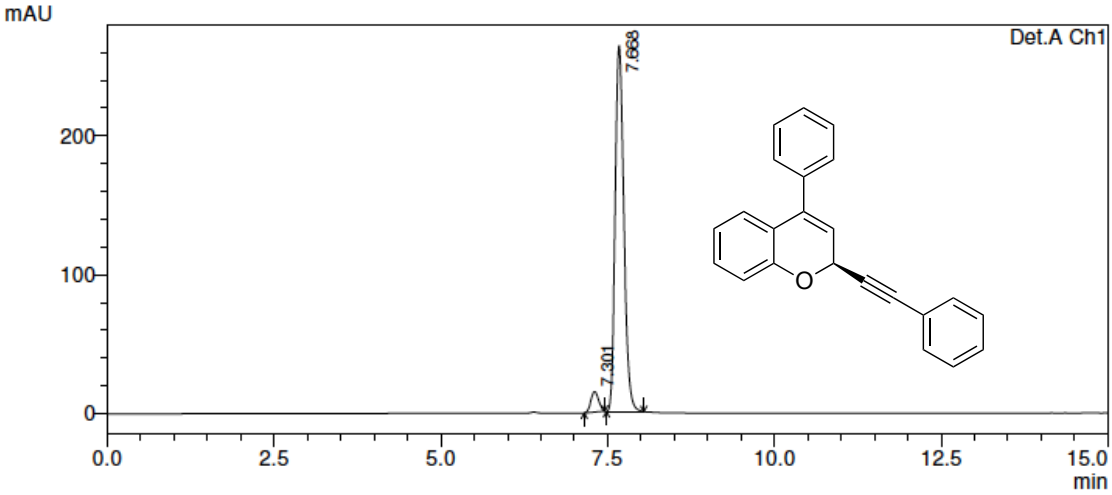
Compound 1.44, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.332	349615	39485	50.117	50.566
2	7.741	347986	38601	49.883	49.434
Total		697601	78086	100.000	100.000

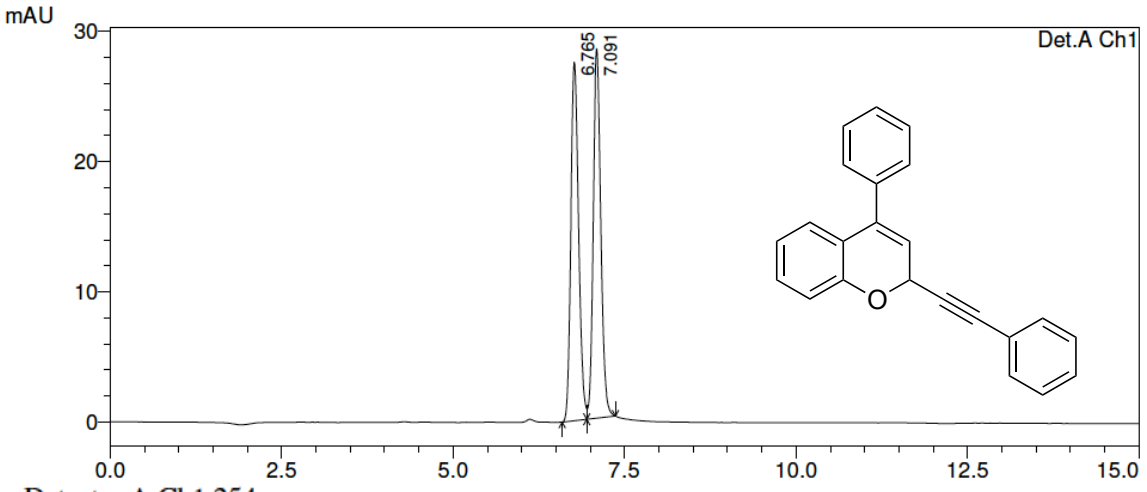
Compound 1.44, 91% ee (Inside glove box reaction)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.301	118382	14695	4.740	5.288
2	7.668	2379159	263179	95.260	94.712
Total		2497541	277875	100.000	100.000

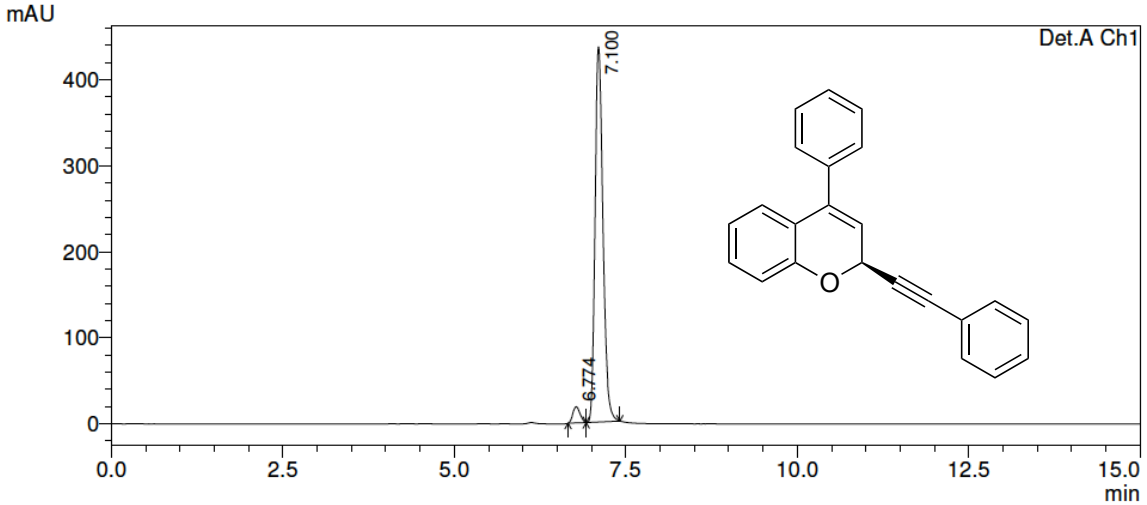
Compound 1.44, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.765	216346	27565	49.786	49.233
2	7.091	218206	28424	50.214	50.767
Total		434552	55989	100.000	100.000

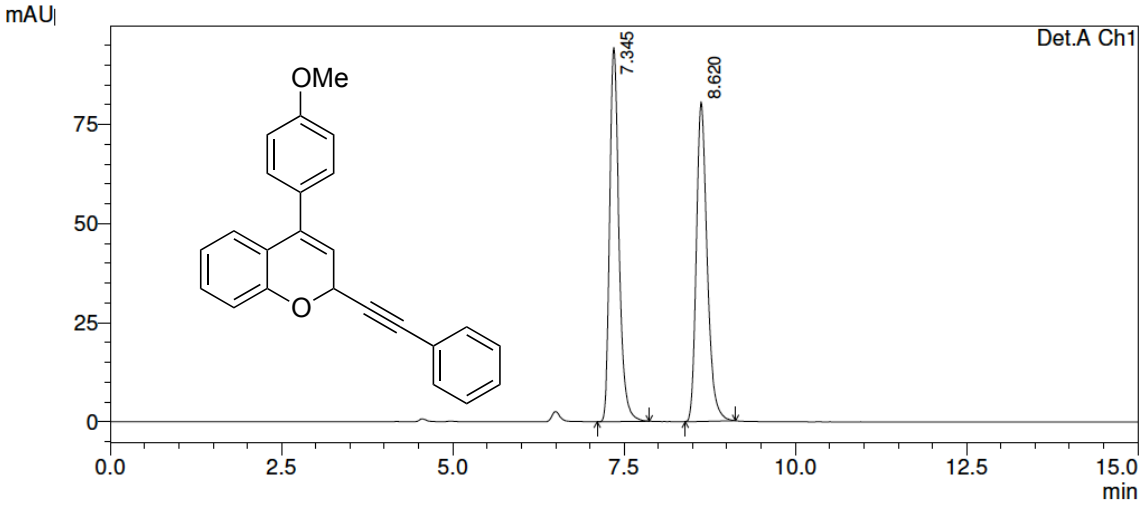
Compound 1.44, 93% ee (Outside the glove box reaction)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.774	136766	18775	3.747	4.129
2	7.100	3513228	435927	96.253	95.871
Total		3649994	454702	100.000	100.000

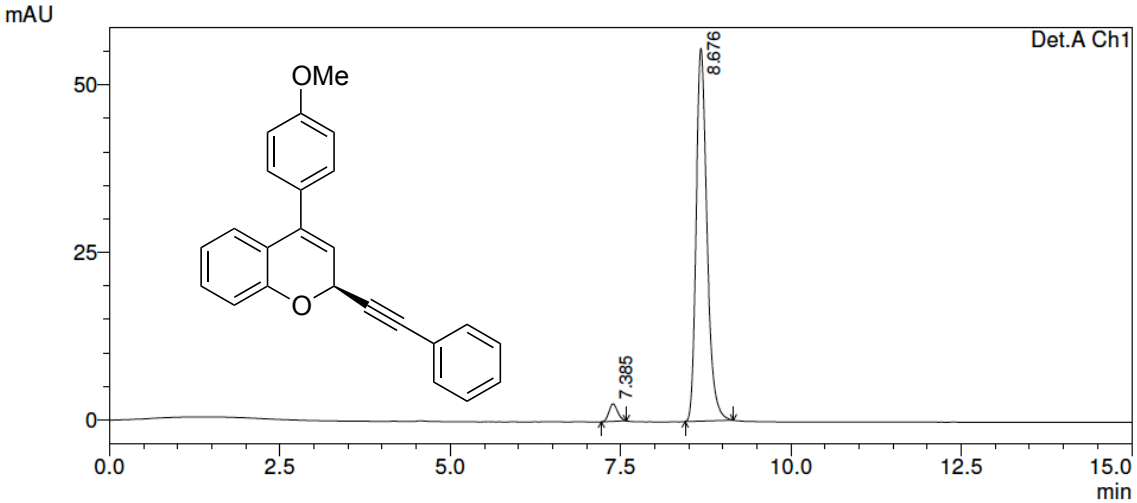
Compound 1.45, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.345	892914	94461	50.135	53.930
2	8.620	888091	80694	49.865	46.070
Total		1781005	175155	100.000	100.000

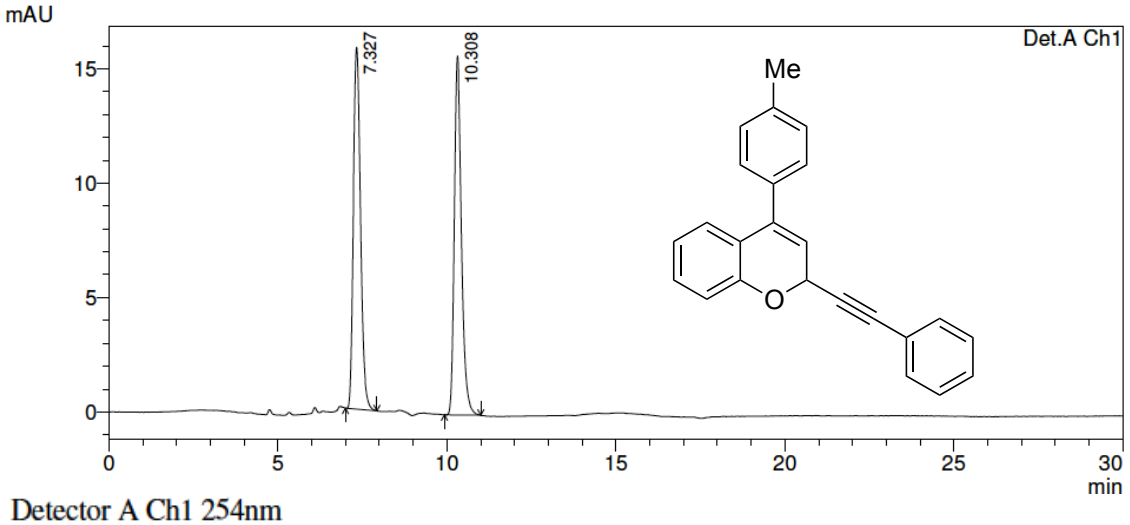
Compound 1.45, 93% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.385	23133	2621	3.622	4.501
2	8.676	615525	55600	96.378	95.499
Total		638658	58221	100.000	100.000

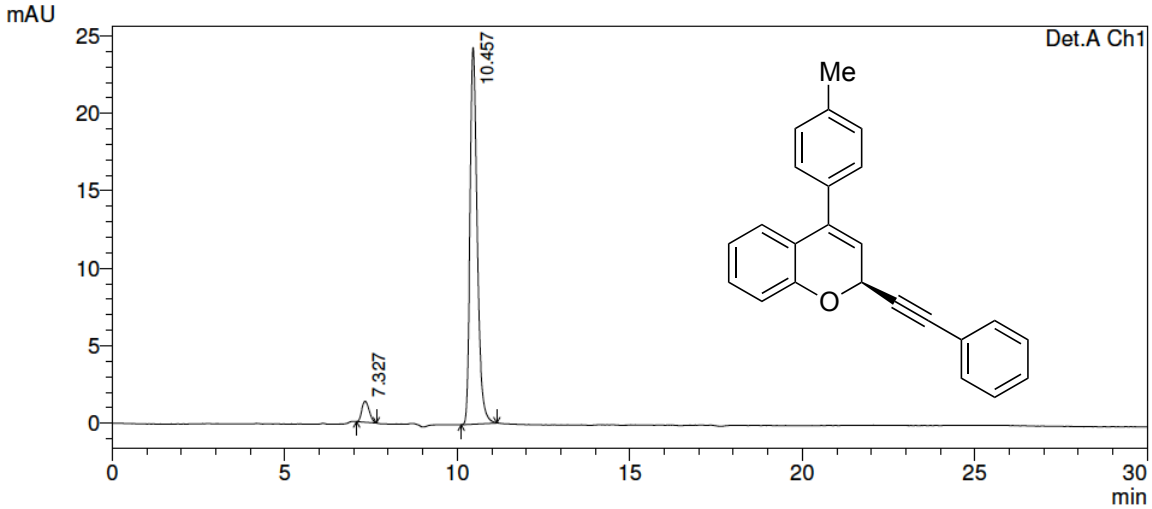
Compound 1.46, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.327	232299	15824	50.137	50.204
2	10.308	231034	15696	49.863	49.796
Total		463333	31520	100.000	100.000

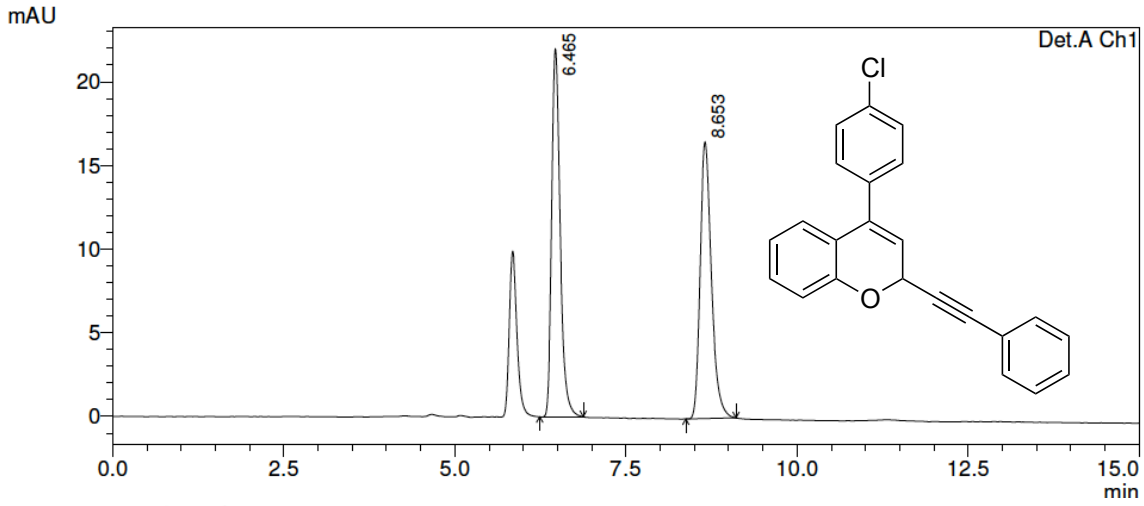
Compound 1.46, 89% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.327	20110	1354	5.378	5.278
2	10.457	353811	24308	94.622	94.722
Total		373921	25663	100.000	100.000

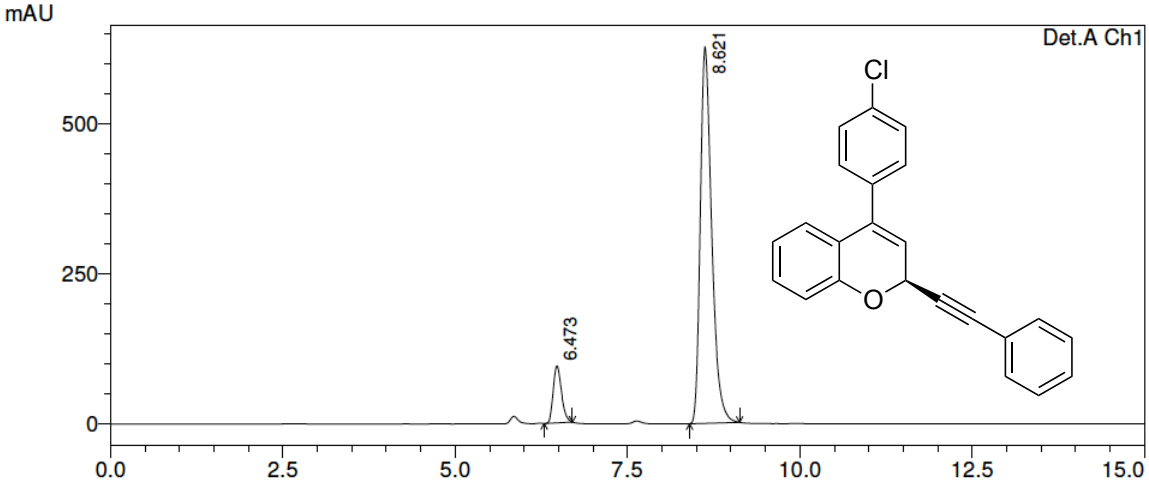
Compound 1.47, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.465	189285	22002	50.013	57.082
2	8.653	189188	16542	49.987	42.918
Total		378473	38544	100.000	100.000

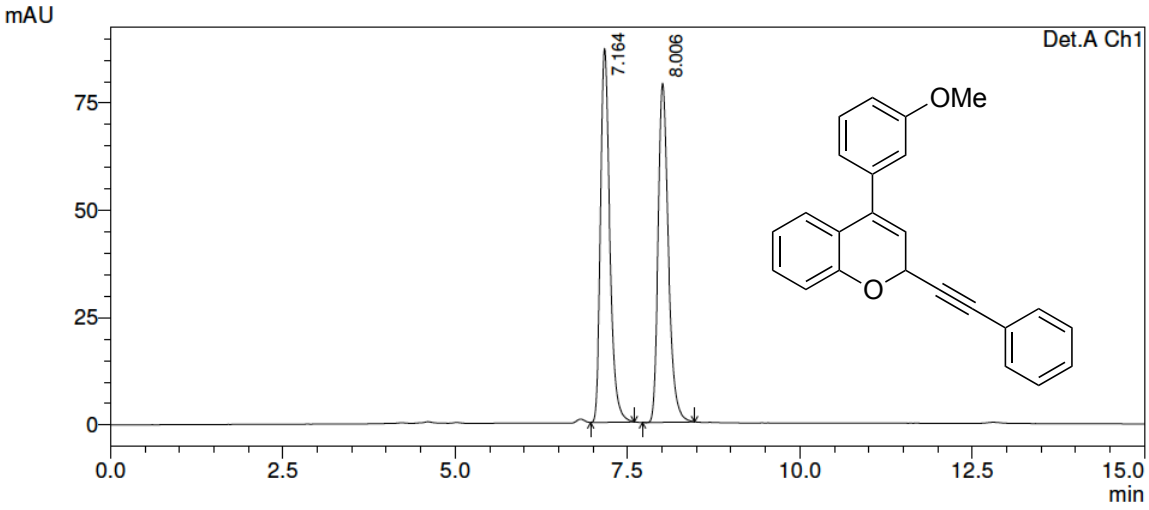
Compound 1.47, 80% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.473	792784	95100	9.879	13.149
2	8.621	7232308	628166	90.121	86.851
Total		8025092	723266	100.000	100.000

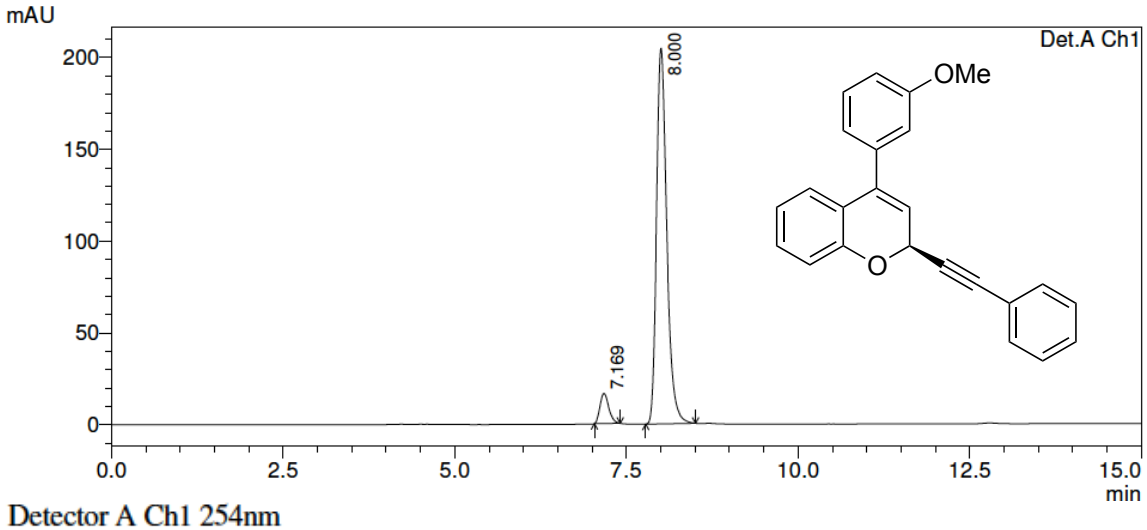
Compound 1.48, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.164	818415	87198	50.098	52.462
2	8.006	815209	79012	49.902	47.538
Total		1633624	166210	100.000	100.000

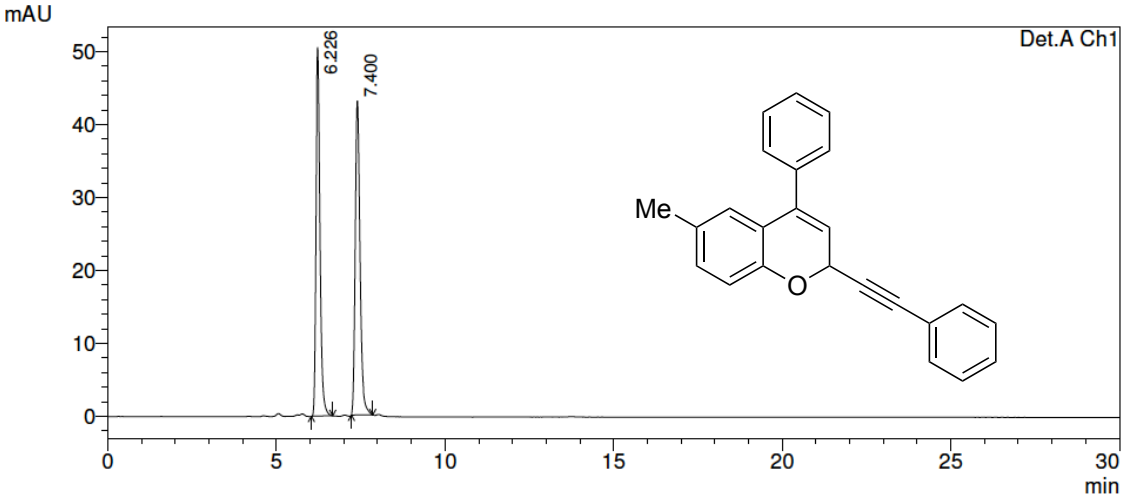
Compound 1.48, 87% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.169	145620	16405	6.414	7.420
2	8.000	2124877	204686	93.586	92.580
Total		2270497	221091	100.000	100.000

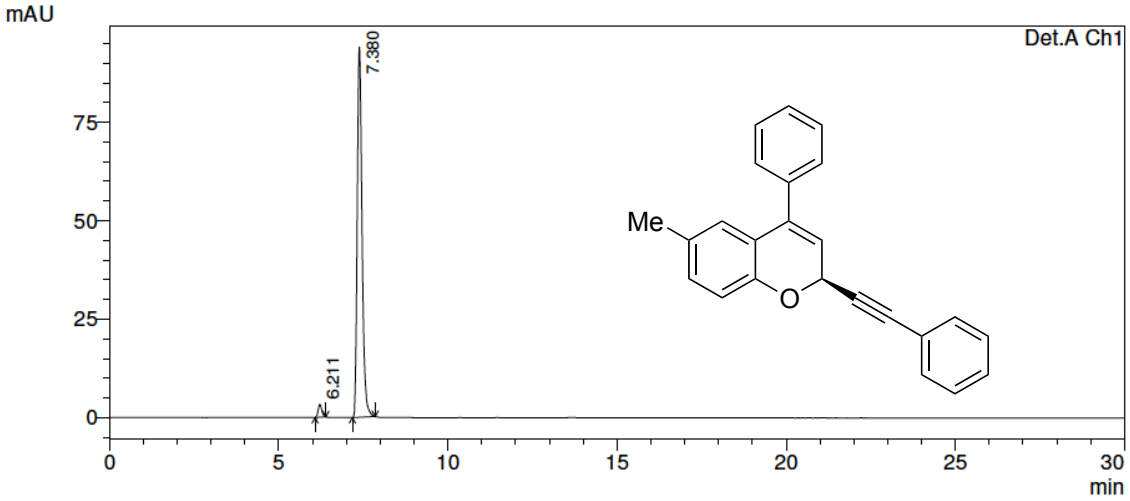
Compound 1.49, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.226	423424	50545	50.271	54.010
2	7.400	418864	43038	49.729	45.990
Total		842288	93583	100.000	100.000

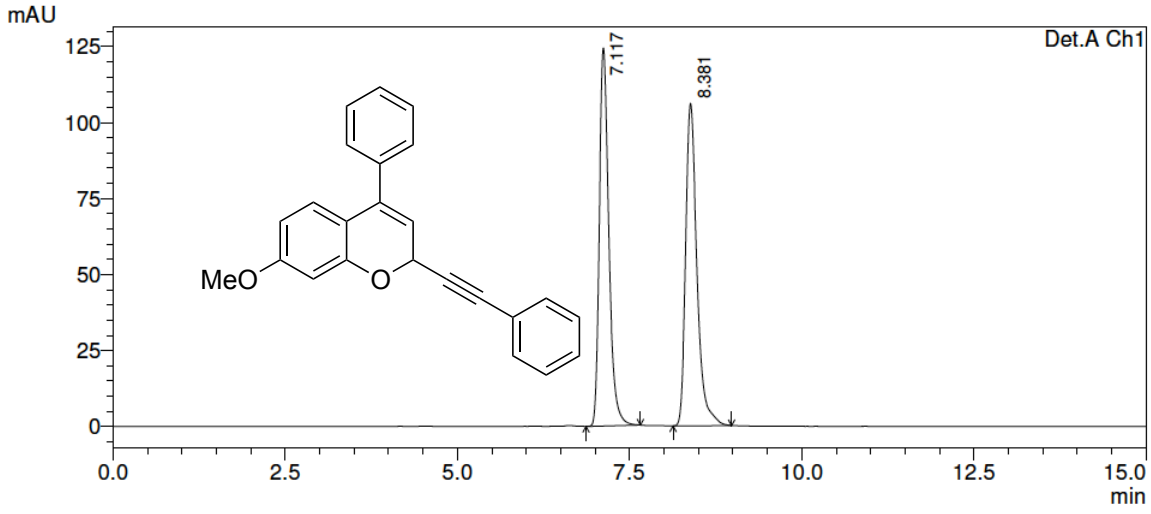
Compound 1.49, 95% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.211	25497	3300	2.720	3.392
2	7.380	912033	93987	97.280	96.608
Total		937529	97287	100.000	100.000

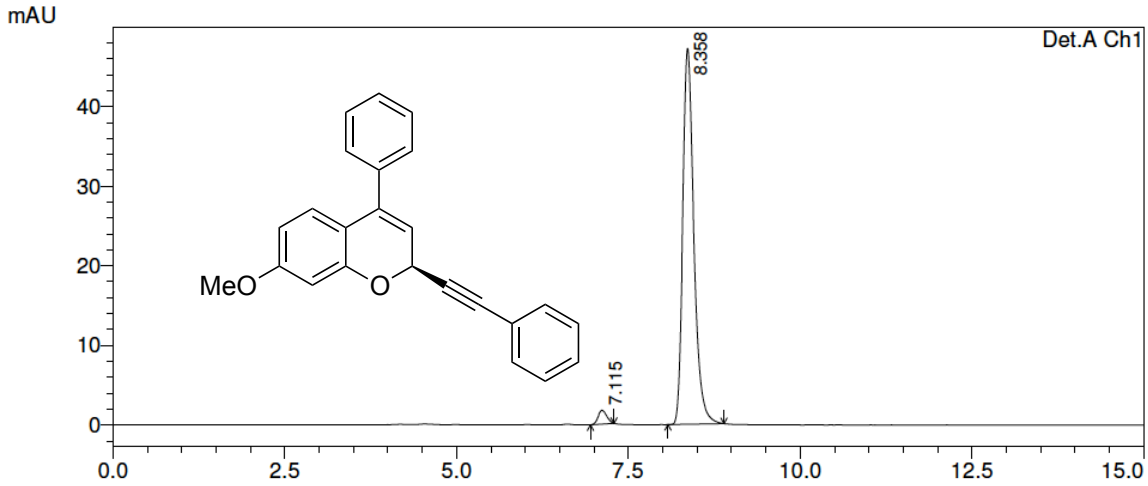
Compound 1.50, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.117	1192314	124339	49.700	53.965
2	8.381	1206695	106069	50.300	46.035
Total		2399008	230408	100.000	100.000

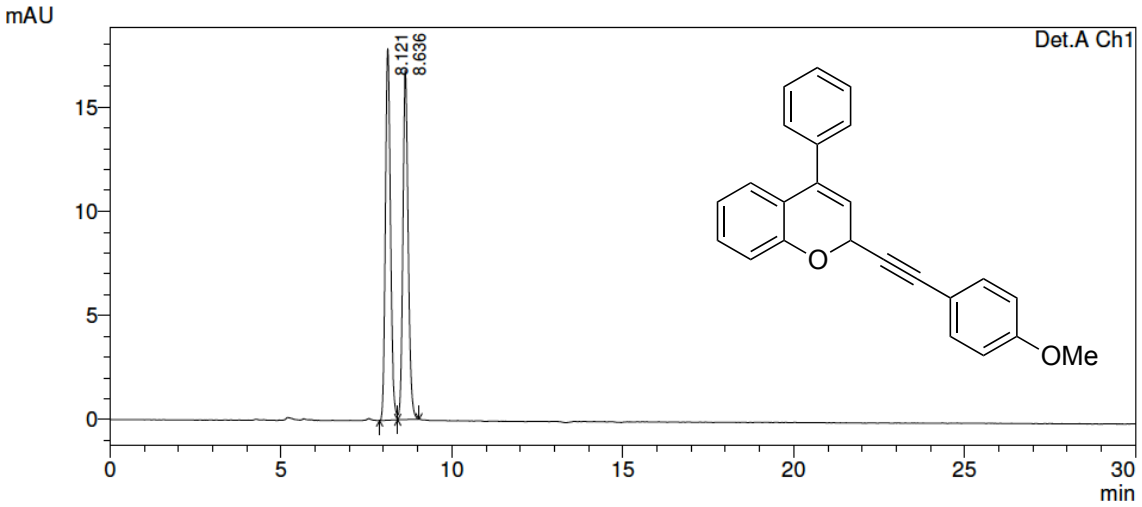
Compound 1.50, 95% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.115	14955	1724	2.750	3.521
2	8.358	528968	47234	97.250	96.479
Total		543923	48958	100.000	100.000

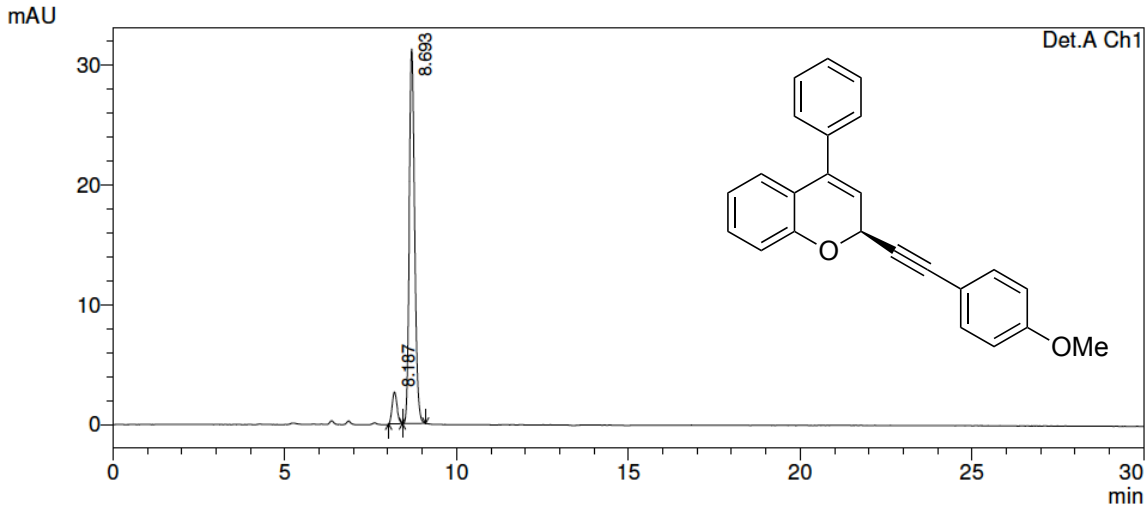
Compound 1.51, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.121	183164	17854	49.957	51.523
2	8.636	183481	16798	50.043	48.477
Total		366646	34652	100.000	100.000

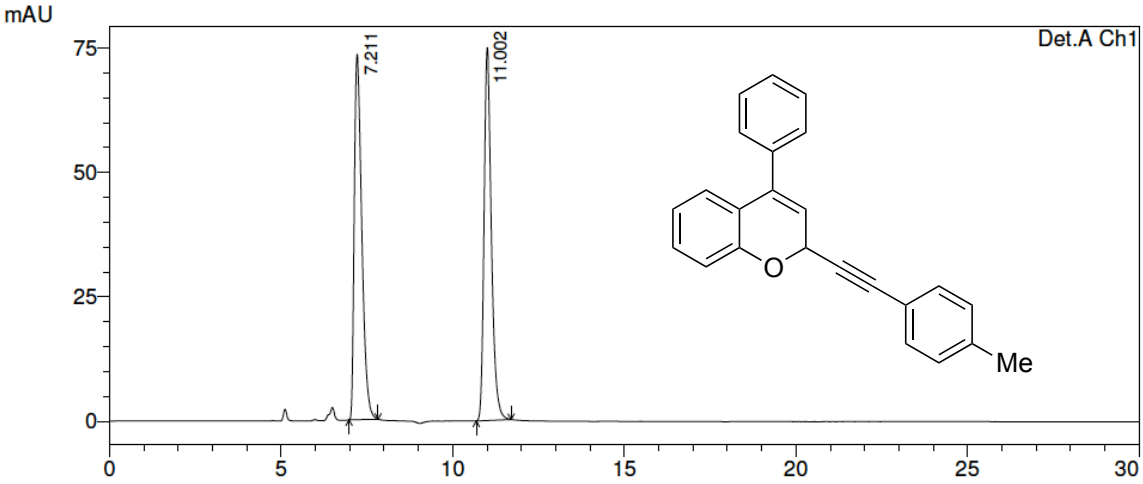
Compound 1.51, 86% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.187	26302	2651	7.143	7.816
2	8.693	341909	31269	92.857	92.184
Total		368212	33920	100.000	100.000

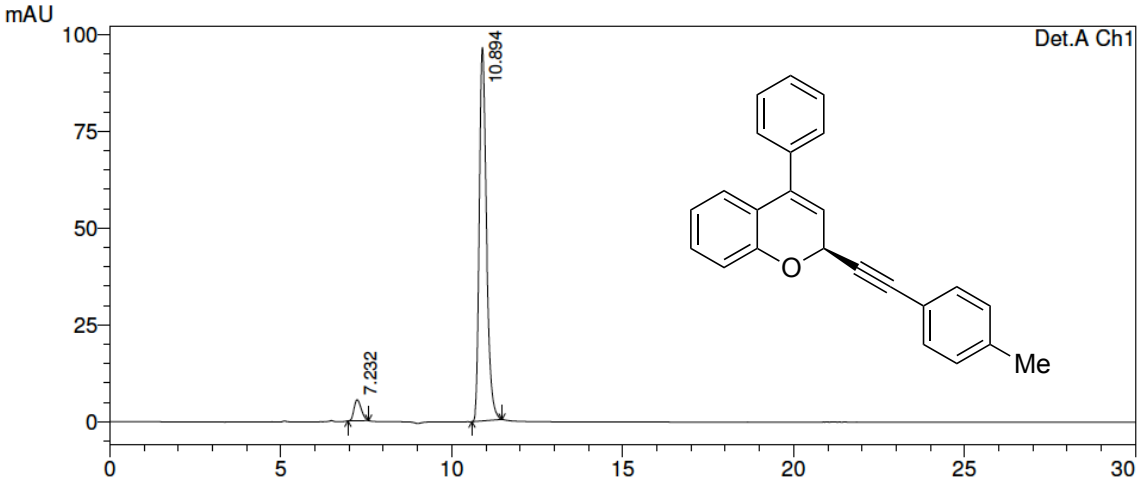
Compound 1.52, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.211	1125459	73453	50.187	49.475
2	11.002	1117056	75011	49.813	50.525
Total		2242516	148464	100.000	100.000

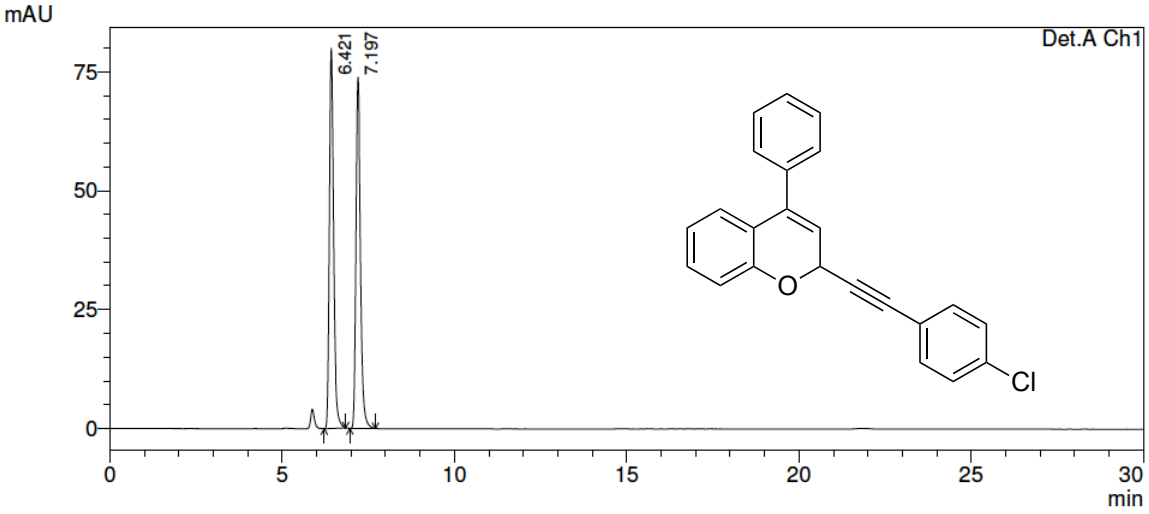
Compound 1.52, 89% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.232	80270	5425	5.400	5.324
2	10.894	1406204	96475	94.600	94.676
Total		1486474	101900	100.000	100.000

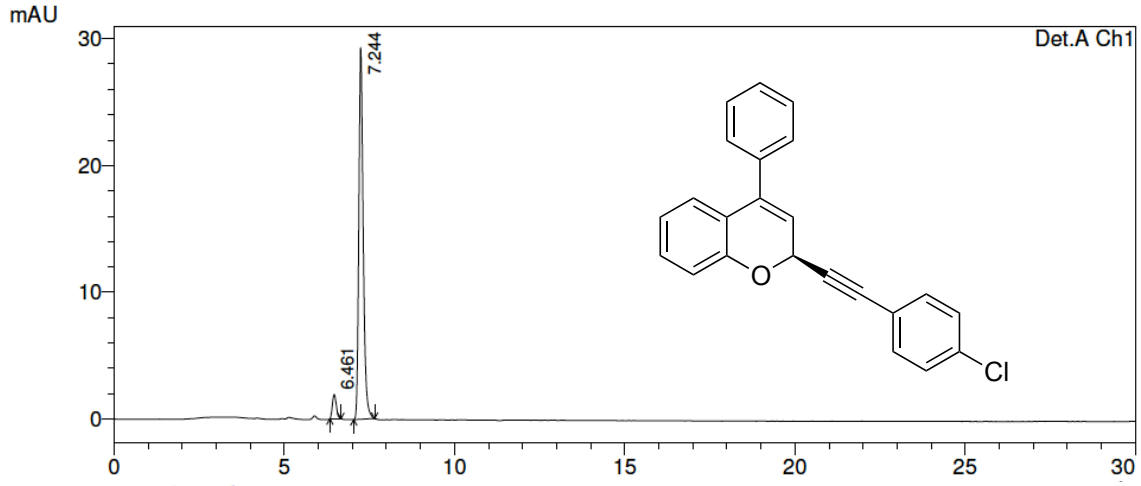
Compound 1.53, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.421	678626	79947	49.927	51.977
2	7.197	680606	73864	50.073	48.023
Total		1359232	153812	100.000	100.000

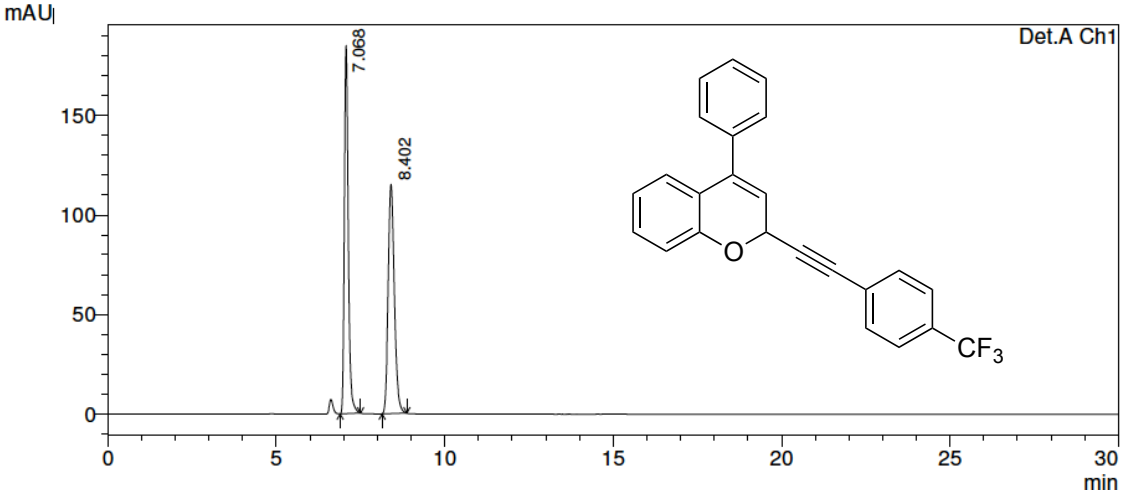
Compound 1.53, 89% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.461	15248	1916	5.340	6.138
2	7.244	270303	29305	94.660	93.862
Total		285551	31222	100.000	100.000

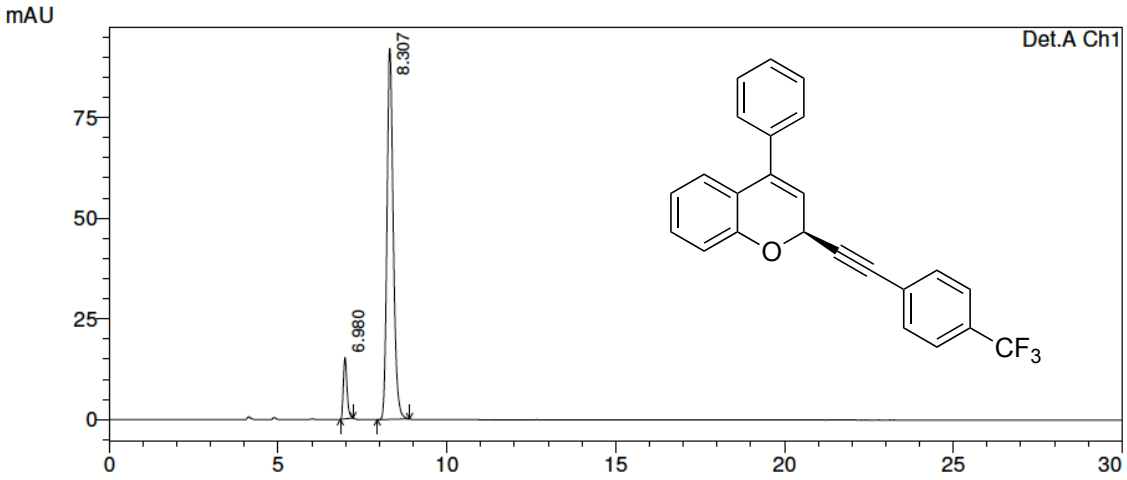
Compound 1.54, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.068	1464746	184723	50.061	61.641
2	8.402	1461160	114951	49.939	38.359
Total		2925906	299674	100.000	100.000

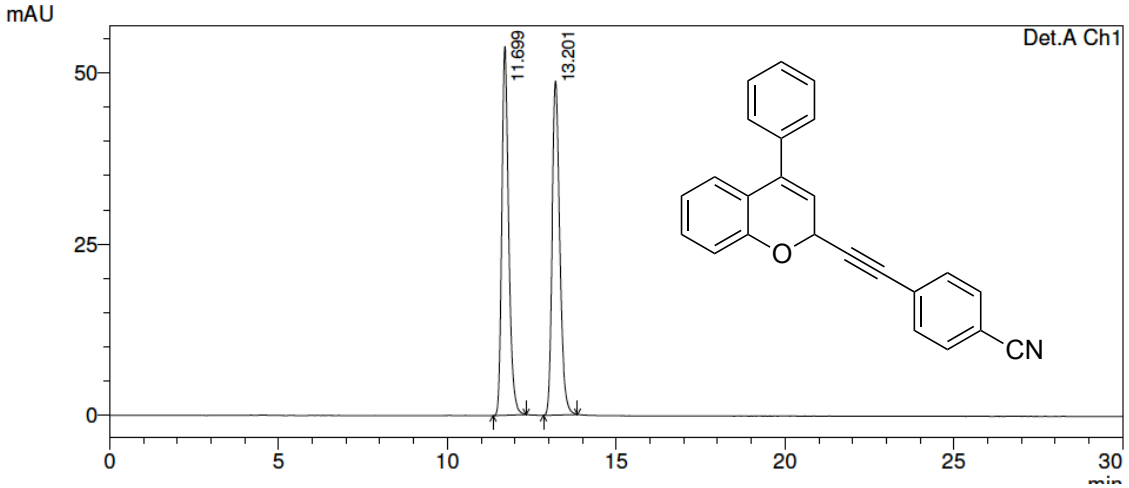
Compound 1.54, 83% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.980	113246	15241	8.567	14.195
2	8.307	1208628	92127	91.433	85.805
Total		1321873	107368	100.000	100.000

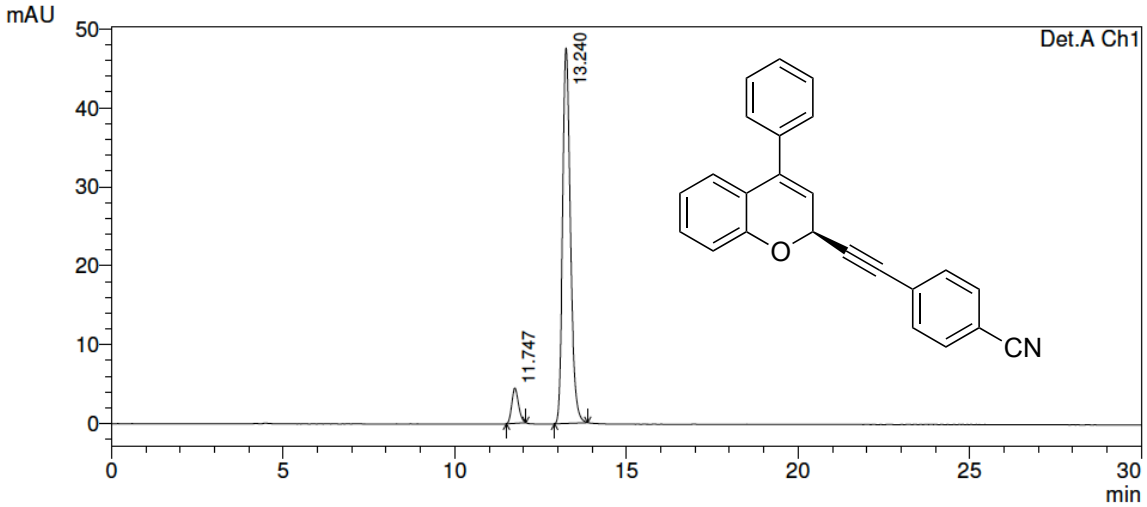
Compound 1.55, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.699	769004	53848	50.036	52.480
2	13.201	767907	48759	49.964	47.520
Total		1536911	102607	100.000	100.000

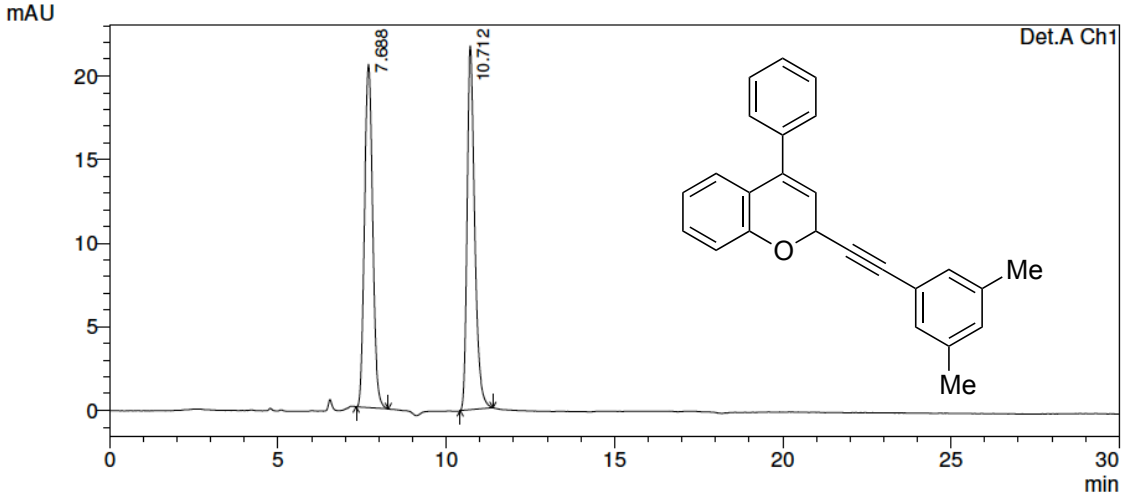
Compound 1.55, 85% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.747	61059	4468	7.519	8.586
2	13.240	751058	47573	92.481	91.414
Total		812117	52041	100.000	100.000

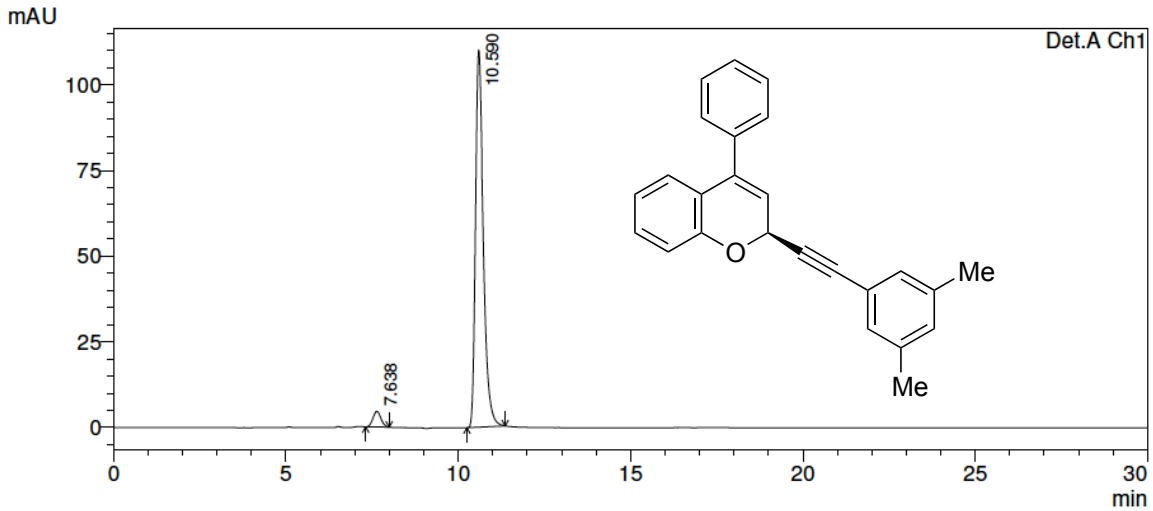
Compound 1.56, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.688	348241	20523	50.226	48.533
2	10.712	345108	21764	49.774	51.467
Total		693349	42287	100.000	100.000

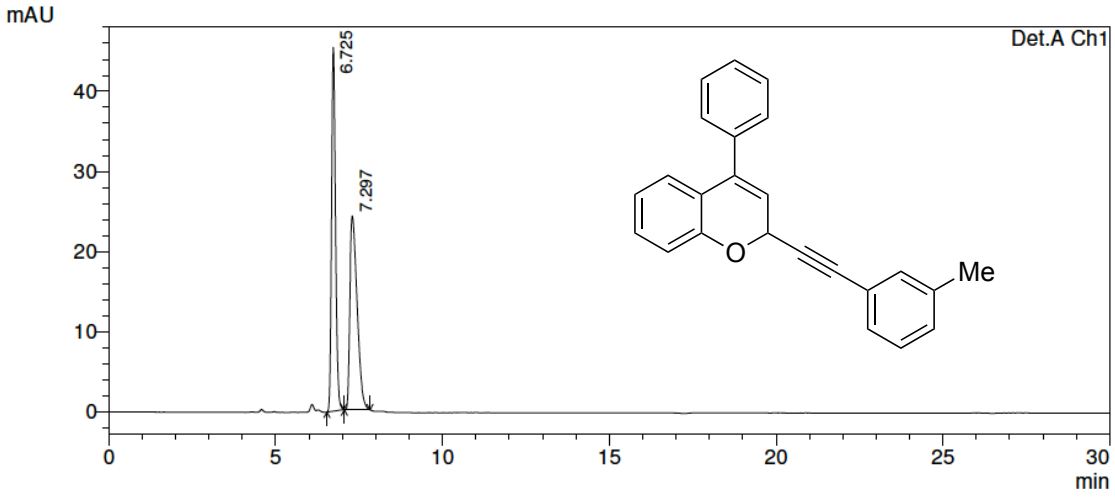
Compound 1.56, 92% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.638	73356	4560	4.059	3.972
2	10.590	1733974	110241	95.941	96.028
Total		1807330	114801	100.000	100.000

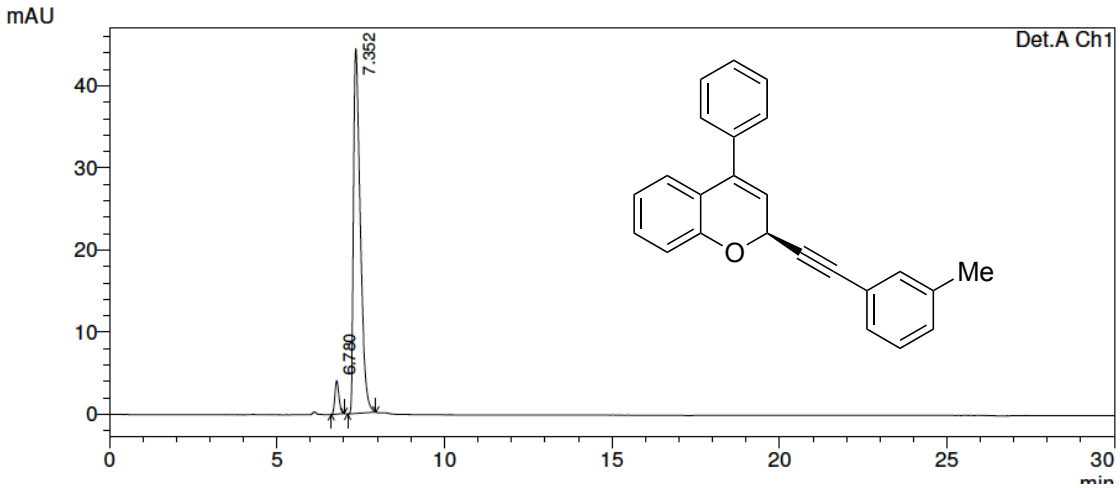
Compound 1.57, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.725	367661	45393	50.075	65.219
2	7.297	366558	24209	49.925	34.781
Total		734219	69602	100.000	100.000

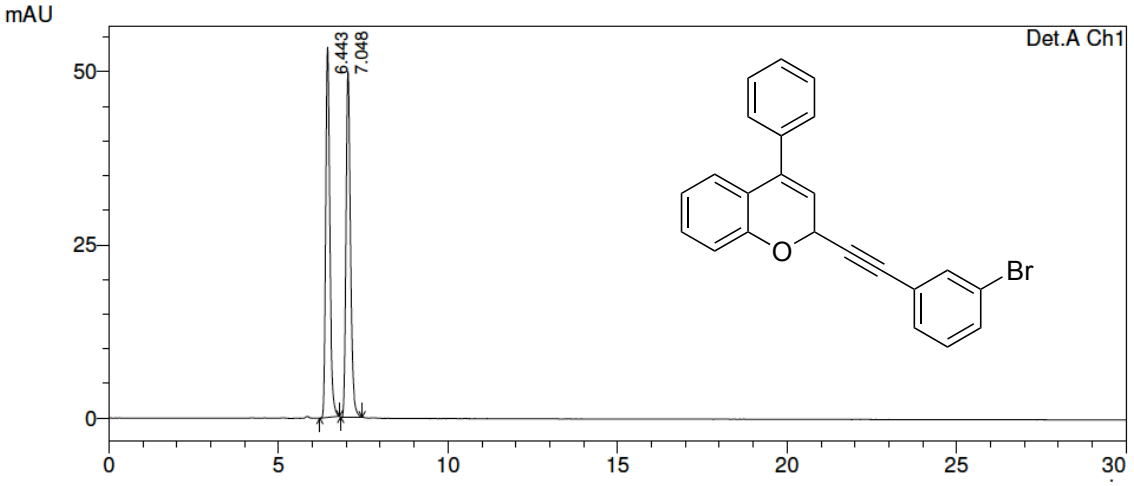
Compound 1.57, 90% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.780	33597	4092	5.135	8.433
2	7.352	620657	44428	94.865	91.567
Total		654254	48520	100.000	100.000

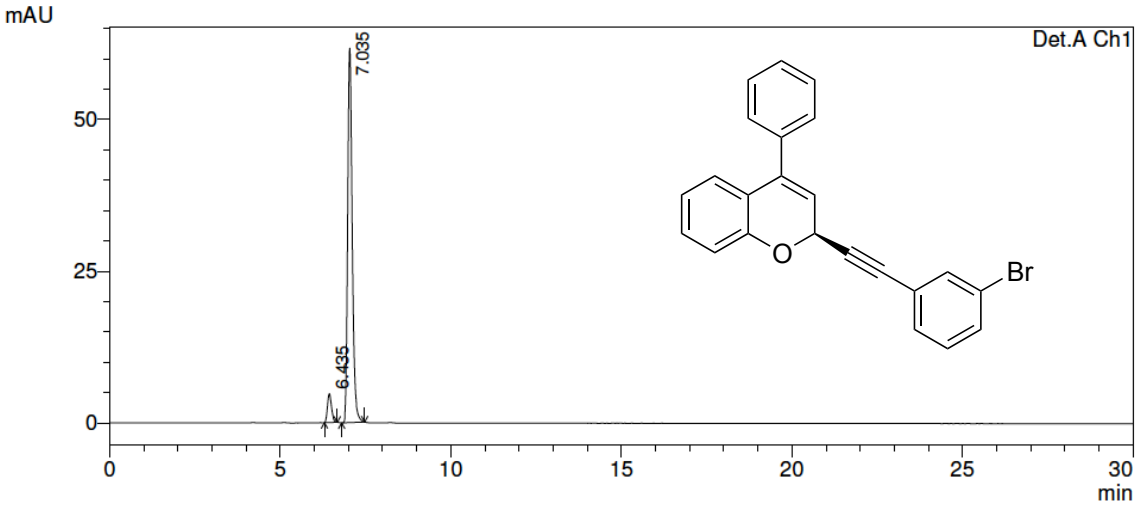
Compound 1.58, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.443	450129	53435	49.989	51.713
2	7.048	450327	49895	50.011	48.287
Total		900456	103330	100.000	100.000

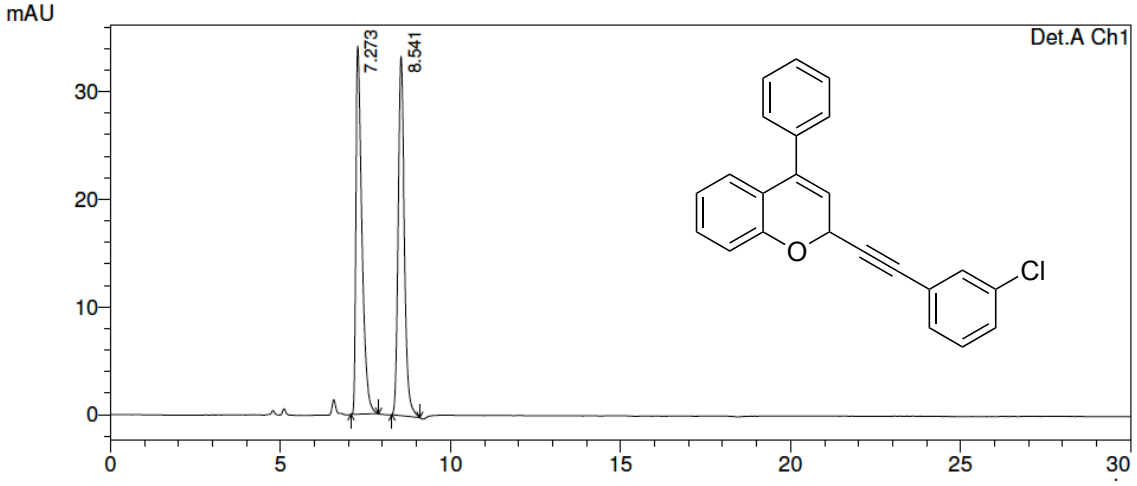
Compound 1.58, 87% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.435	38637	4744	6.446	7.133
2	7.035	560769	61760	93.554	92.867
Total		599406	66504	100.000	100.000

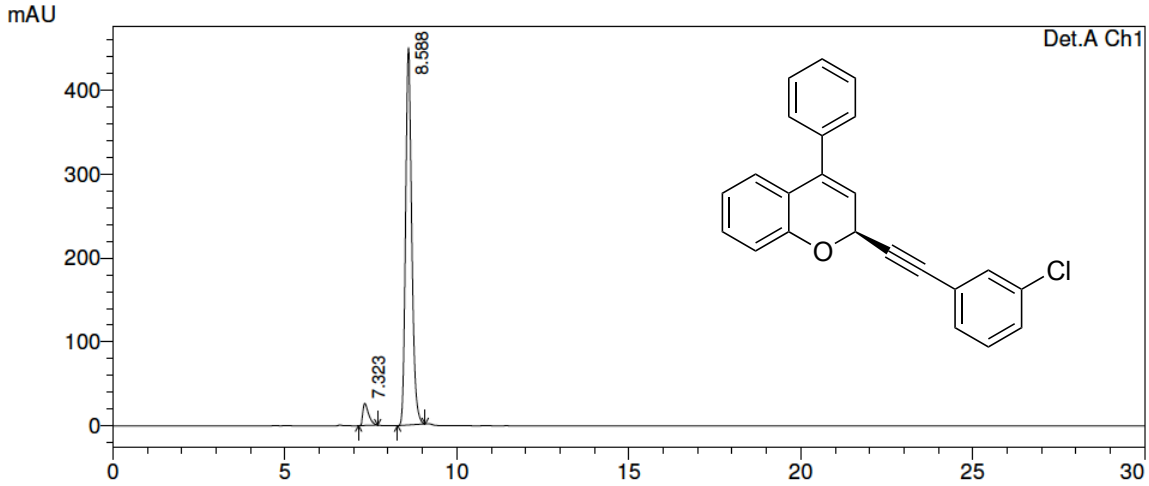
Compound 1.59, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.273	425044	34189	50.130	50.634
2	8.541	422837	33332	49.870	49.366
Total		847881	67521	100.000	100.000

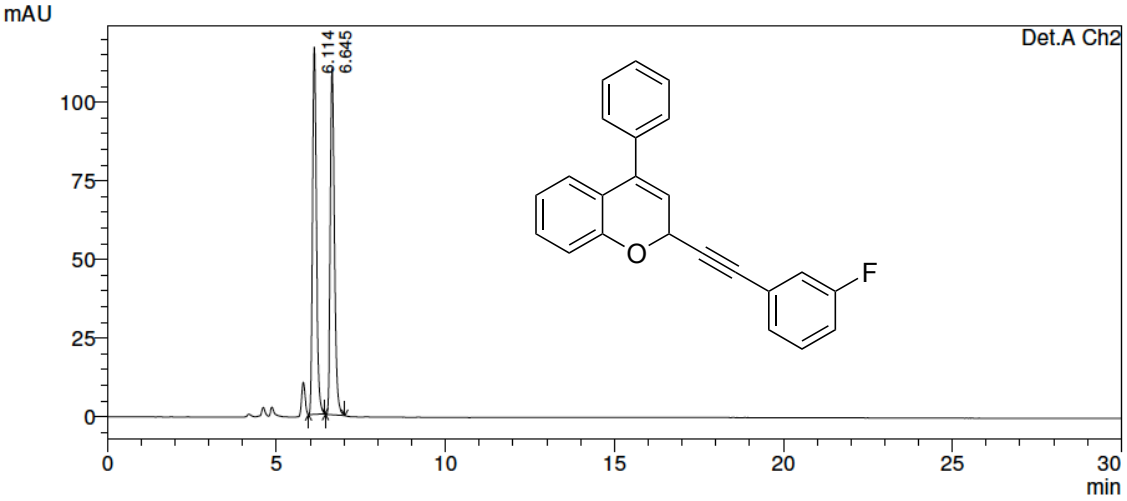
Compound 1.59, 90% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.323	305261	26436	5.086	5.549
2	8.588	5697204	449967	94.914	94.451
Total		6002465	476402	100.000	100.000

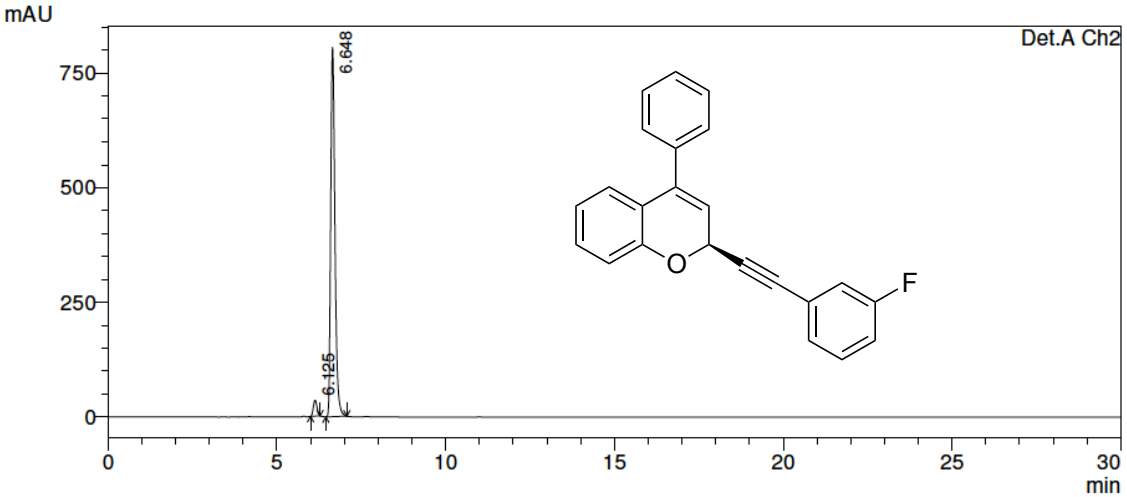
Compound 1.60, racemic



Detector A Ch2 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.114	936018	116766	49.862	51.460
2	6.645	941217	110140	50.138	48.540
Total		1877235	226905	100.000	100.000

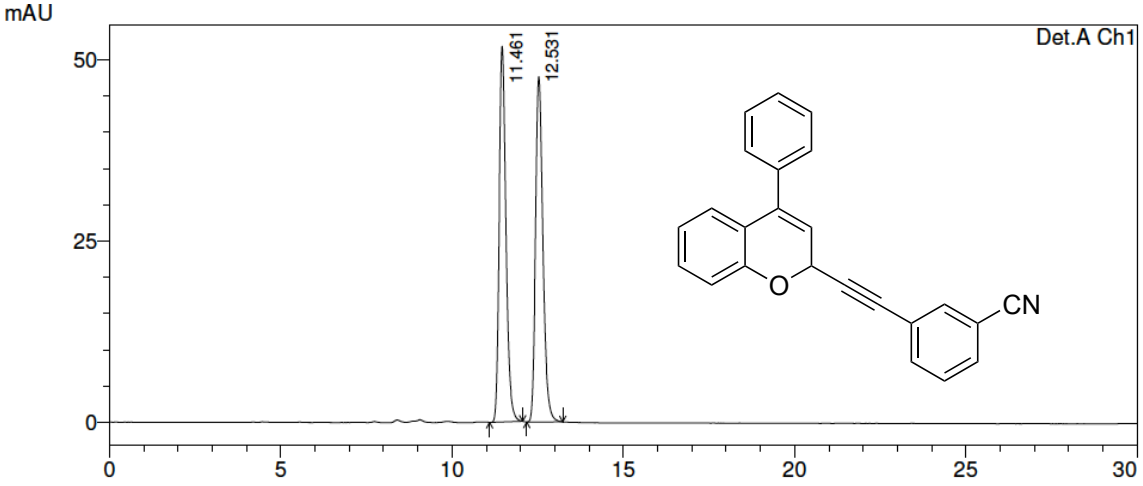
Compound 1.60, 93% ee



Detector A Ch2 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.125	257229	34556	3.579	4.115
2	6.648	6929224	805180	96.421	95.885
Total		7186453	839735	100.000	100.000

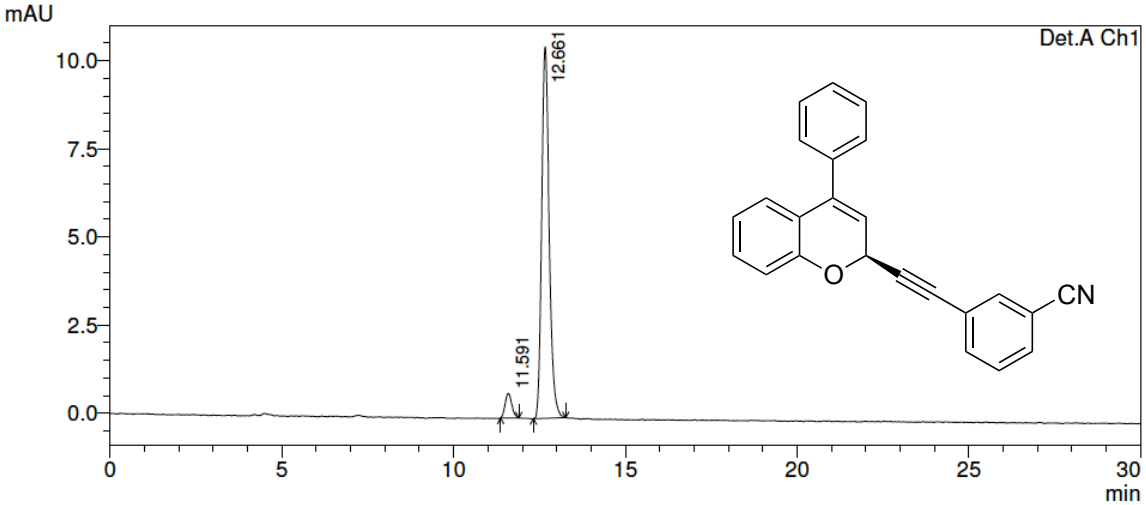
Compound 1.61, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.461	712903	51848	50.034	52.099
2	12.531	711940	47670	49.966	47.901
Total		1424843	99518	100.000	100.000

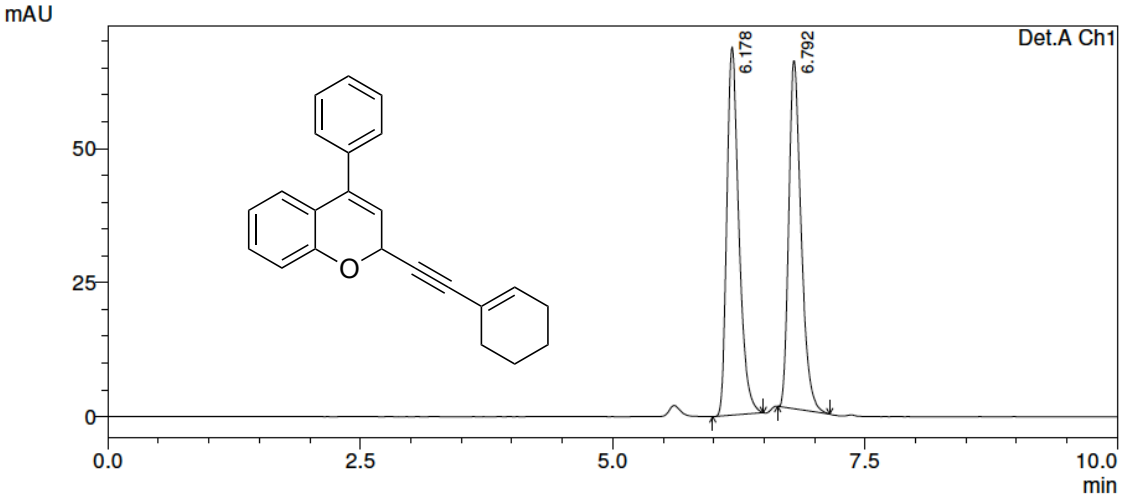
Compound 1.61, 89% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.591	9464	703	5.618	6.254
2	12.661	158992	10533	94.382	93.746
Total		168456	11236	100.000	100.000

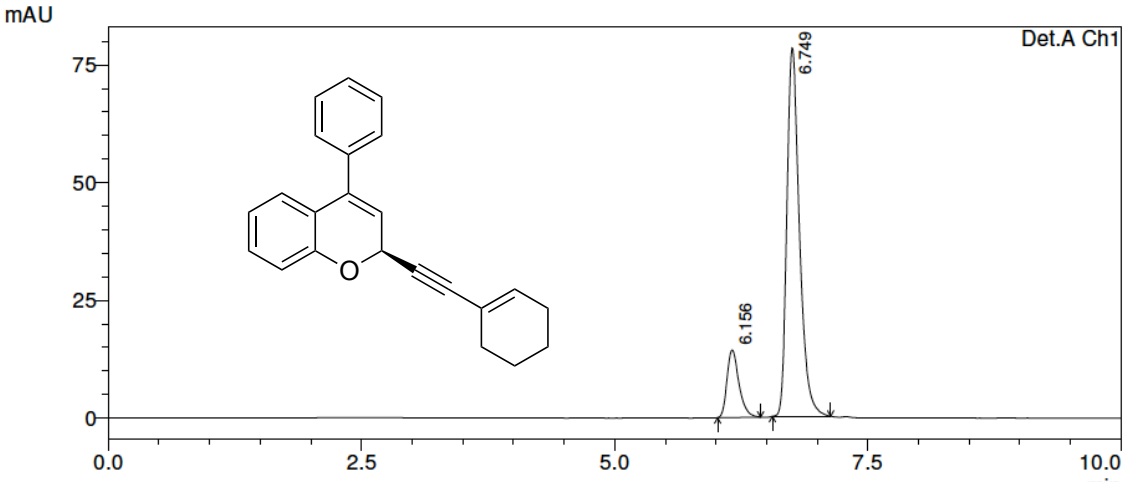
Compound 1.62, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.178	571073	68718	50.794	51.418
2	6.792	553212	64928	49.206	48.582
Total		1124285	133646	100.000	100.000

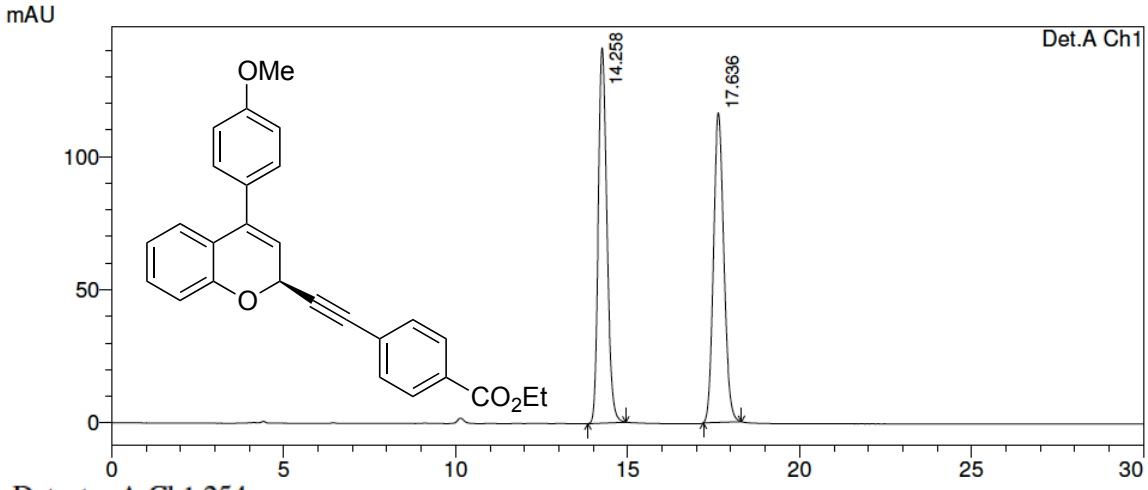
Compound 1.62, 70% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.156	118018	14380	14.854	15.512
2	6.749	676481	78324	85.146	84.488
Total		794499	92704	100.000	100.000

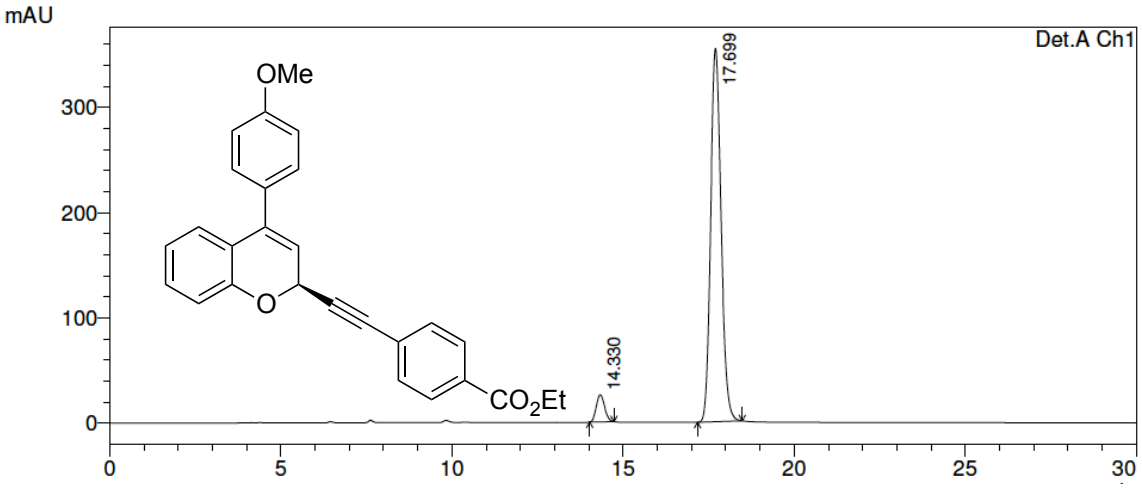
Compound 1.63, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.258	2462334	141006	50.190	54.790
2	17.636	2443684	116349	49.810	45.210
Total		4906018	257355	100.000	100.000

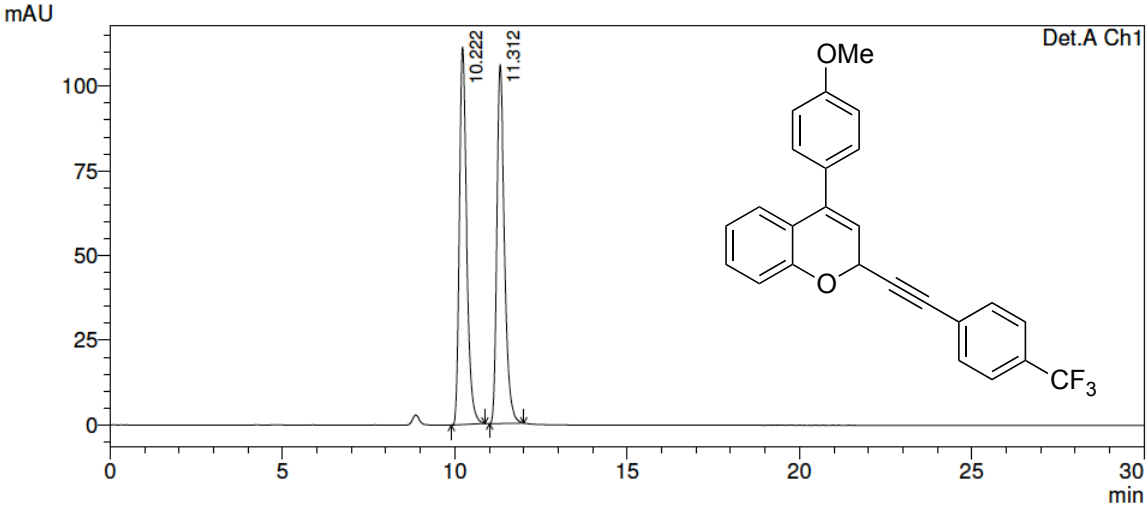
Compound 1.63, 89% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.330	437319	25854	5.490	6.787
2	17.699	7527731	355085	94.510	93.213
Total		7965050	380939	100.000	100.000

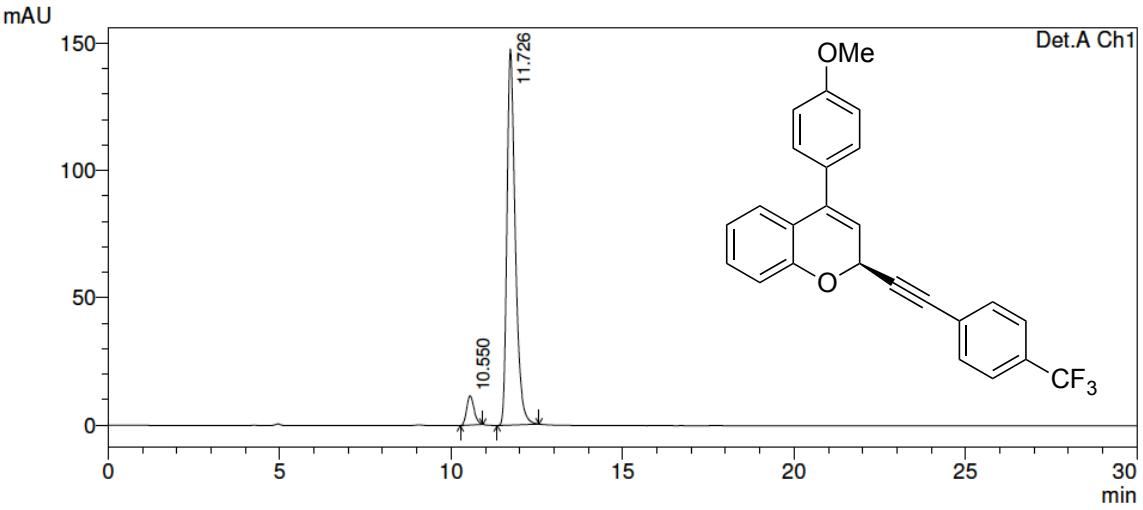
Compound 1.64, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.222	1626626	111427	50.105	51.266
2	11.312	1619783	105924	49.895	48.734
Total		3246410	217351	100.000	100.000

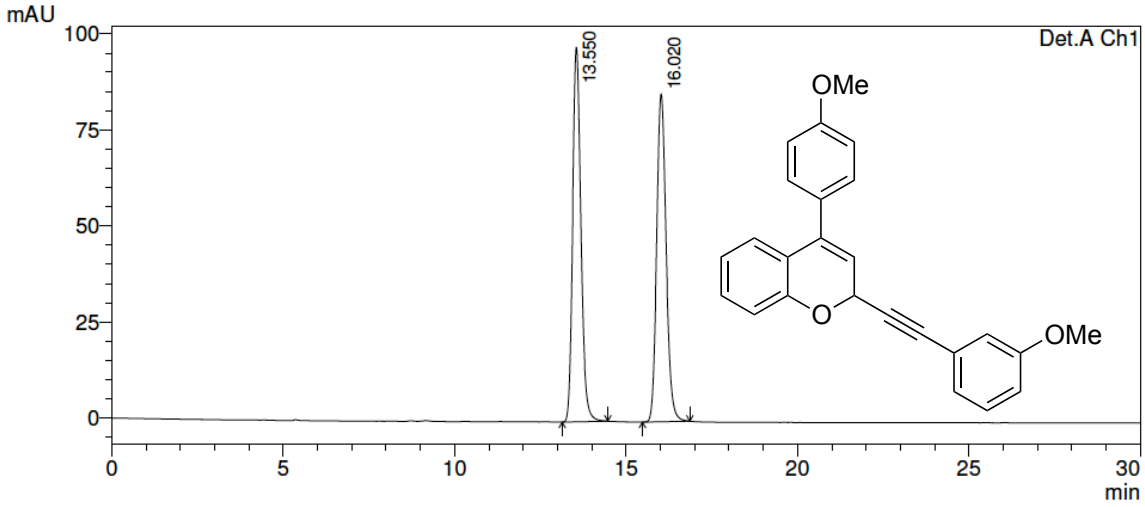
Compound 1.64, enantioenriched (87% ee)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.550	171369	11467	6.390	7.204
2	11.726	2510376	147708	93.610	92.796
Total		2681745	159175	100.000	100.000

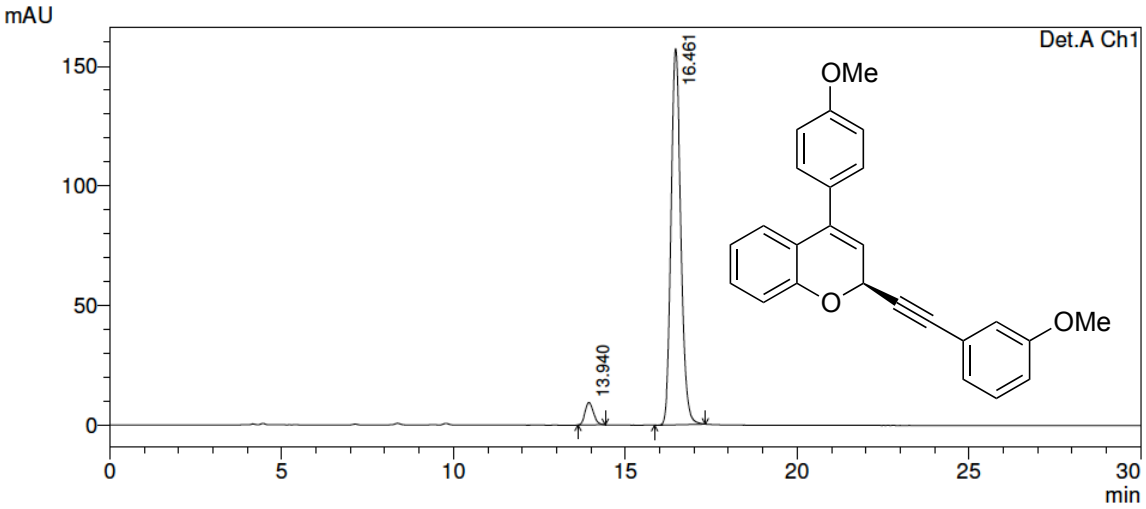
Compound 1.65, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.550	1631840	97481	50.030	53.329
2	16.020	1629909	85310	49.970	46.671
Total		3261749	182791	100.000	100.000

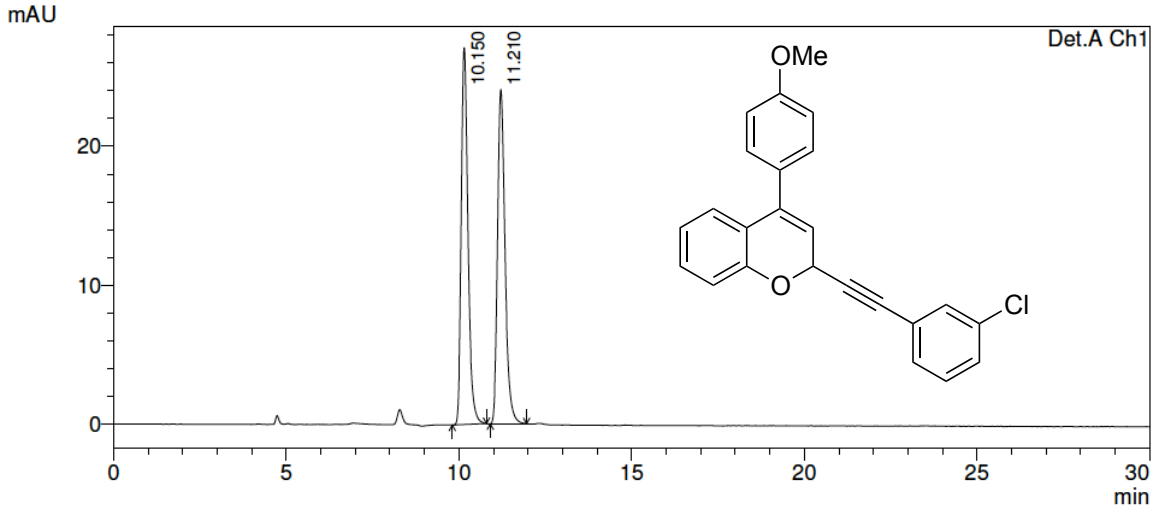
Compound 1.65, 90% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.940	160970	9422	4.923	5.648
2	16.461	3108980	157408	95.077	94.352
Total		3269950	166830	100.000	100.000

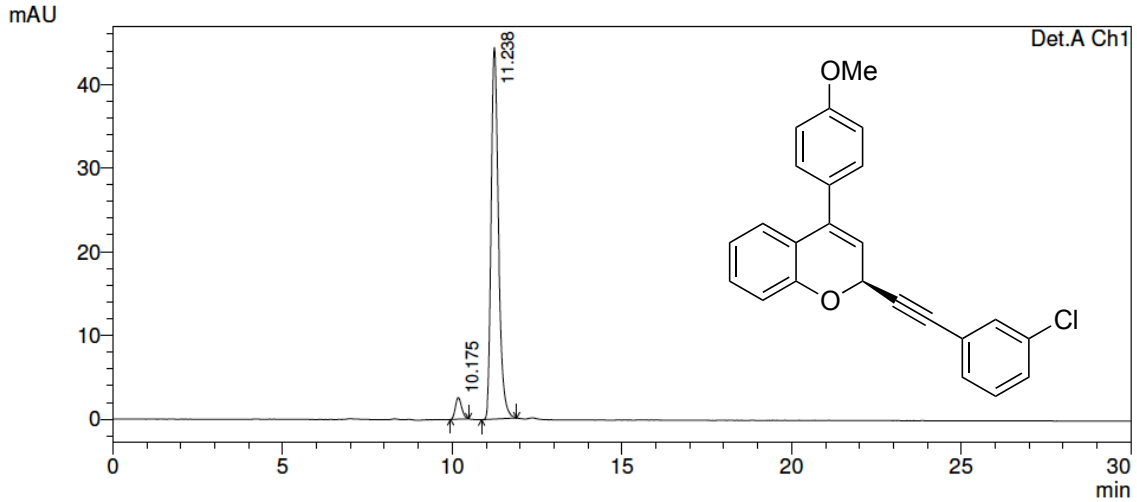
Compound 1.66, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.150	365887	27135	50.281	52.991
2	11.210	361794	24072	49.719	47.009
Total		727680	51208	100.000	100.000

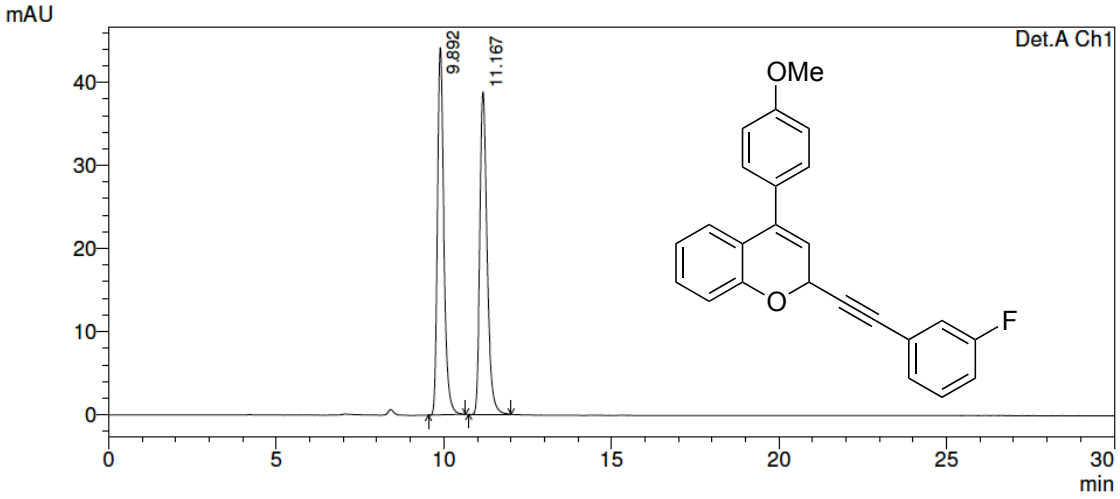
Compound 1.66, 91% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.175	32790	2580	4.697	5.491
2	11.238	665297	44405	95.303	94.509
Total		698087	46985	100.000	100.000

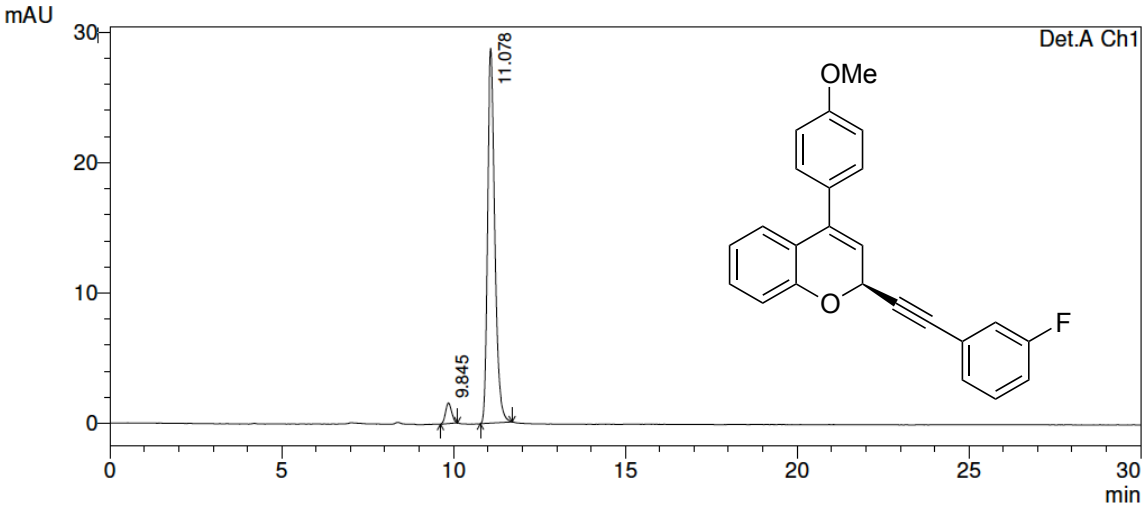
Compound 1.67, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.892	586543	44180	50.120	53.231
2	11.167	583725	38817	49.880	46.769
Total		1170268	82997	100.000	100.000

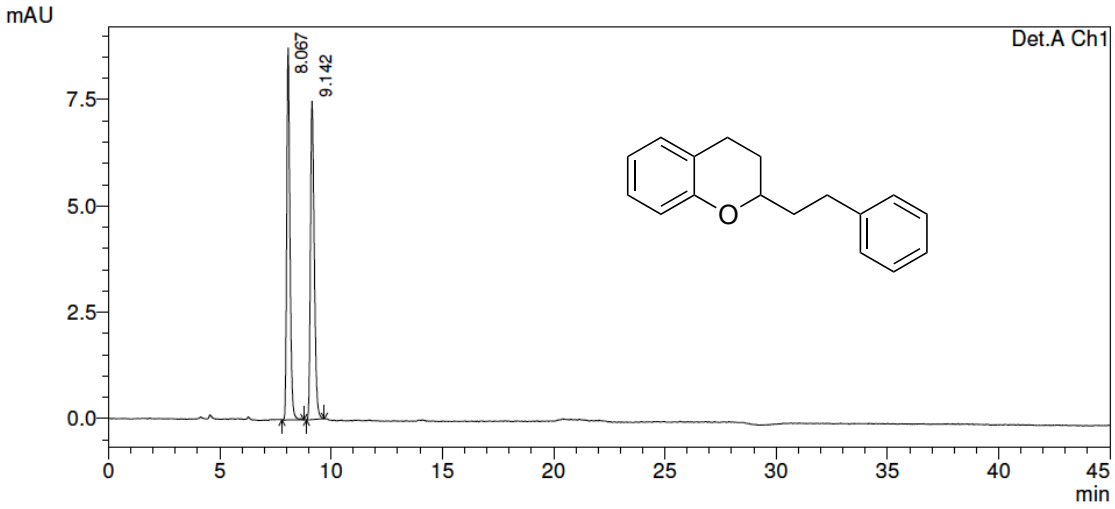
Compound 1.67, 91% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.845	19164	1580	4.344	5.201
2	11.078	421983	28799	95.656	94.799
Total		441147	30379	100.000	100.000

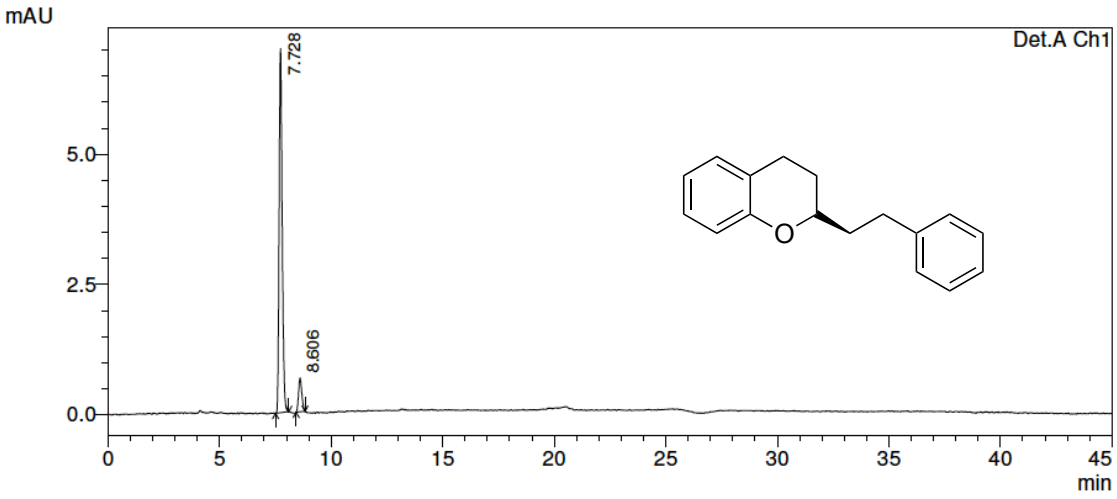
Compound 1.68, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.067	89714	8746	50.154	53.886
2	9.142	89164	7485	49.846	46.114
Total		178878	16231	100.000	100.000

Compound 1.68, 82% ee



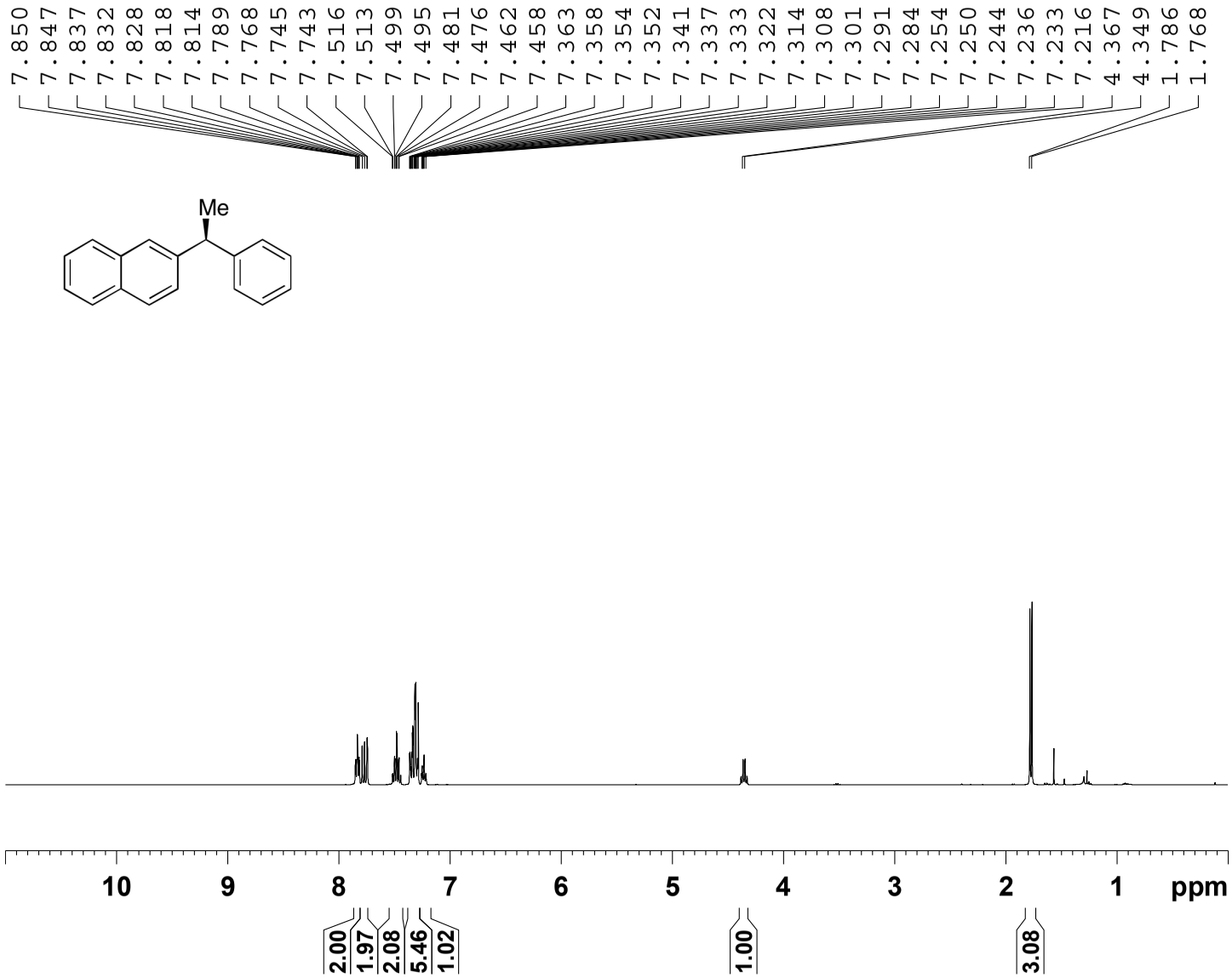
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.728	67071	6999	91.101	91.522
2	8.606	6551	648	8.899	8.478
Total		73622	7648	100.000	100.000

APPENDIX B

CHAPTER 2 SPECTRAL DATA

compound 2.26 1H NMR



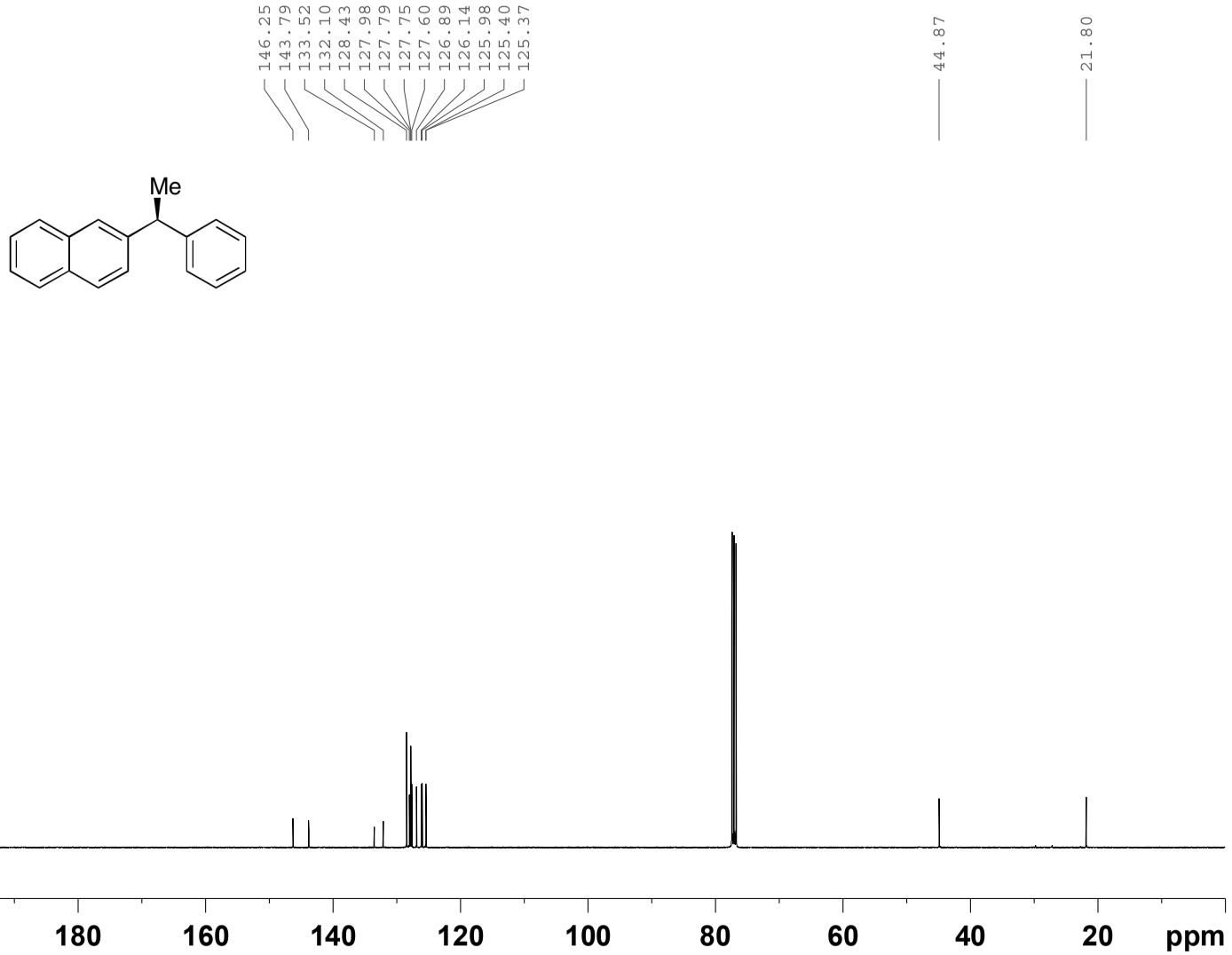
Current Data Parameters
NAME HH-4-046B
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121104
Time 20.20
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 11.3
DW 60.400 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 4.90 dB
PL1W 3.30822015 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound 2.26 13C NMR




```
Current Data Parameters
NAME            HH-4-046B
EXPNO                   2
PROCNO                  1

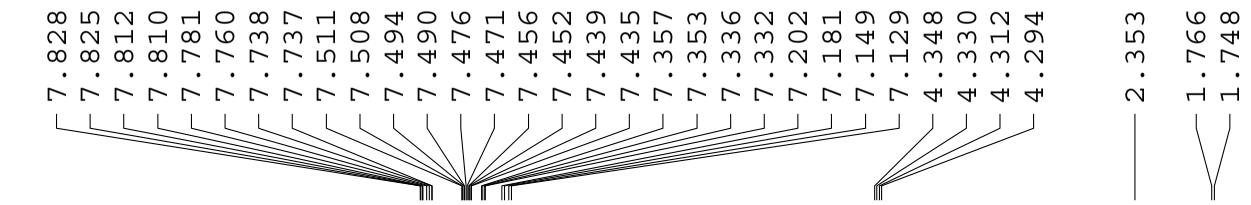
F2 - Acquisition Parameters
Date_            20121104
Time                20.37
INSTRUM             spect
PROBHD   5 mm CPQNP 1H/
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    256
DS                      4
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ               1.3664756 sec
RG                    512
DW                 20.850 usec
DE                 18.00 usec
TE                 298.1 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                     1

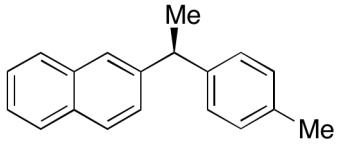
======== CHANNEL f1 ========
NUC1                  13C
P1                  9.25 usec
PL1                 0.55 dB
PL1W         35.18820572 W
SFO1        100.6228298 MHz

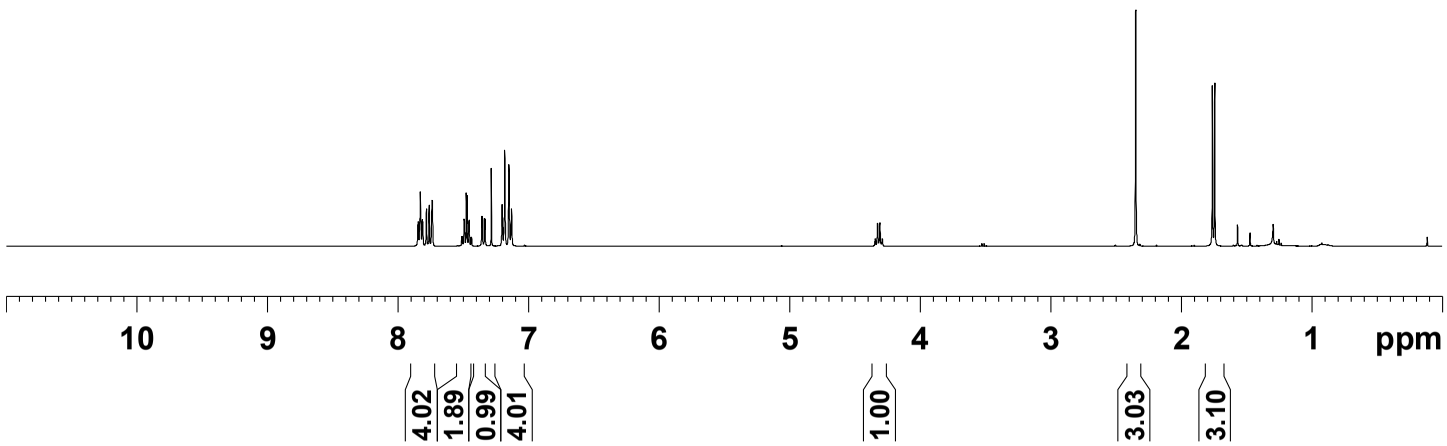
======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                 4.90 dB
PL12               20.46 dB
PL13               21.00 dB
PL2W          3.30822015 W
PL12W         0.09195905 W
PL13W         0.08120718 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                  32768
SF          100.6127690 MHz
WDW                    EM
SSB                     0
LB                  1.00 Hz
GB                      0
PC                   1.40
```

Compound 2.19 1H NMR







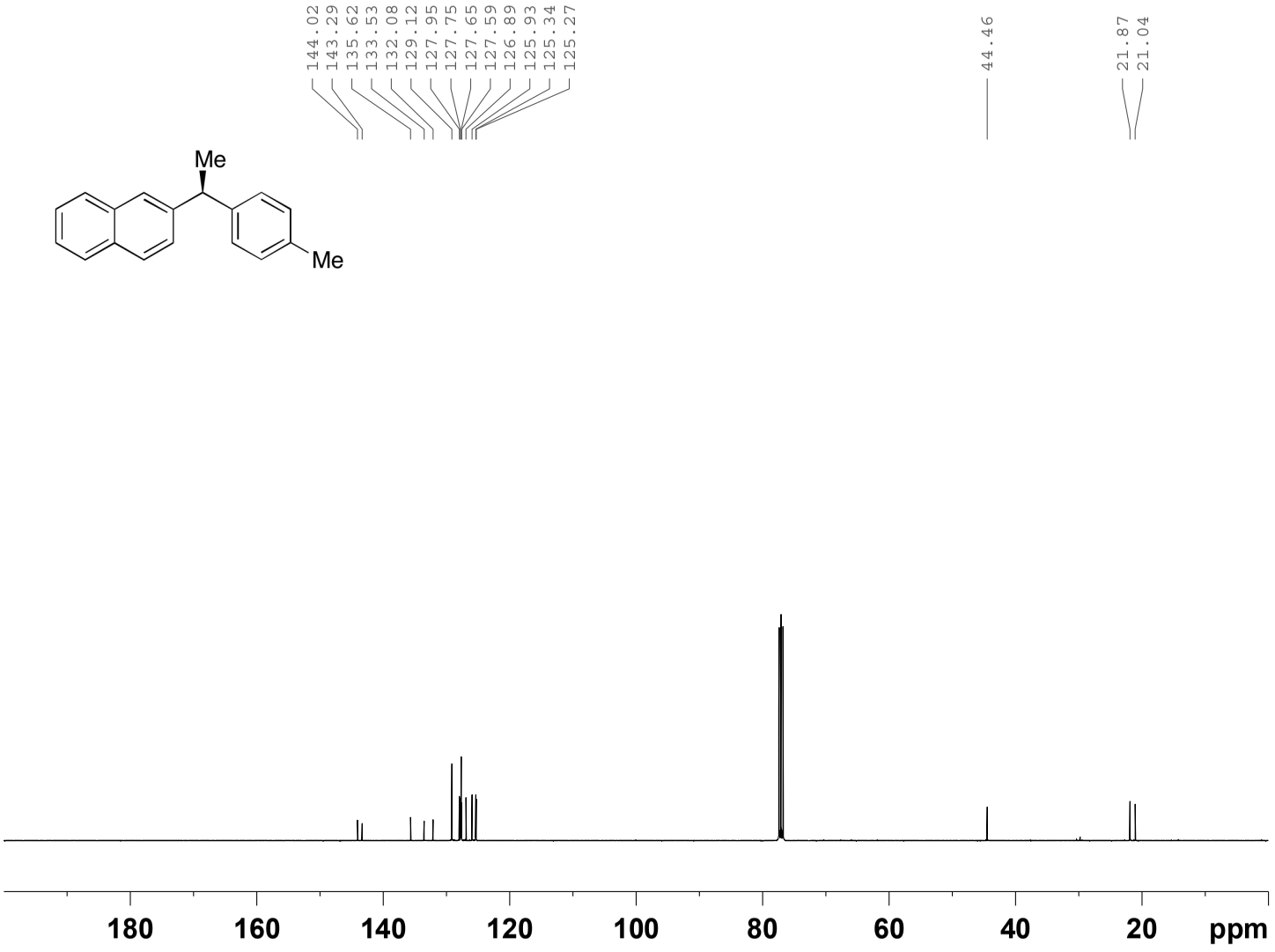

```
Current Data Parameters
NAME            HH-4-047A
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20121104
Time                20.43
INSTRUM             spect
PROBHD   5 mm CPQNP 1H/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ               3.9584243 sec
RG                   11.3
DW                 60.400 usec
DE                  6.00 usec
TE                 298.2 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                 15.00 usec
PL1                 4.90 dB
PL1W          3.30822015 W
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

Compound 2.19 13C NMR



330

Current Data Parameters
NAME HH-4-047A
EXPNO 2
PROCNO 1

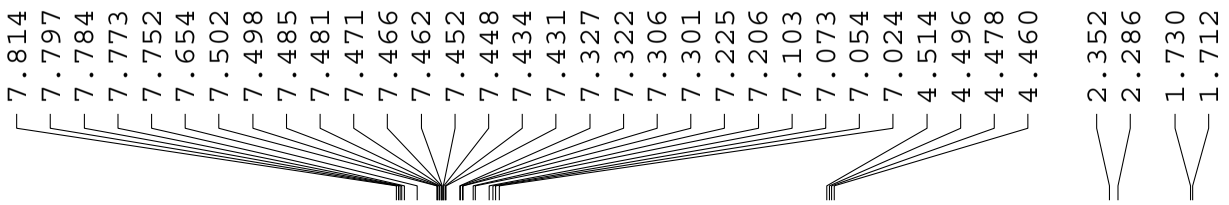
F2 - Acquisition Parameters
Date_ 20121104
Time 20.59
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 512
DW 20.850 usec
DE 18.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

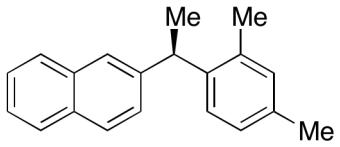
======== CHANNEL f1 ========
NUC1 13C
P1 9.25 usec
PL1 0.55 dB
PL1W 35.18820572 W
SFO1 100.6228298 MHz

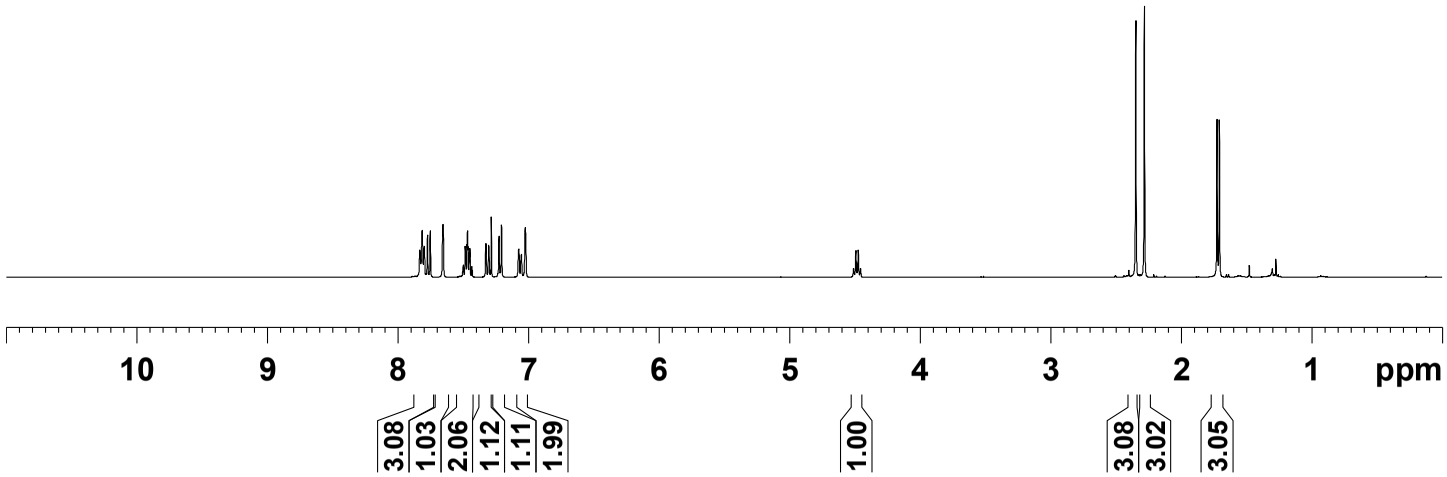
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 4.90 dB
PL12 20.46 dB
PL13 21.00 dB
PL2W 3.30822015 W
PL12W 0.09195905 W
PL13W 0.08120718 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Compound 2.27 1H NMR







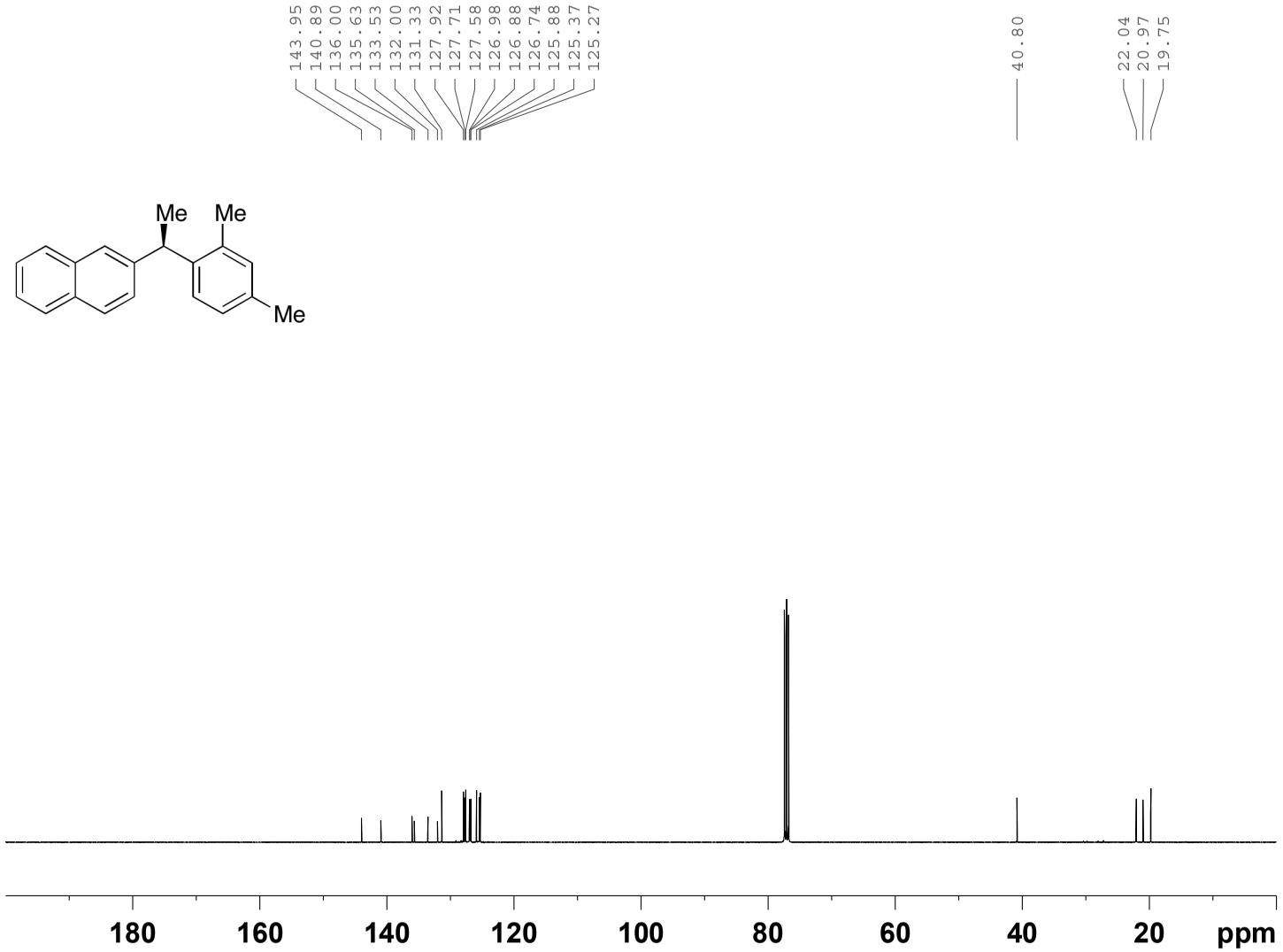
Current Data Parameters
NAME QZ-3-060A
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121104
Time 21.27
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 11.3
DW 60.400 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 4.90 dB
PL1W 3.30822015 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound 2.27 13C NMR



332

Current Data Parameters
NAME QZ-3-060A
EXPNO 2
PROCNO 1

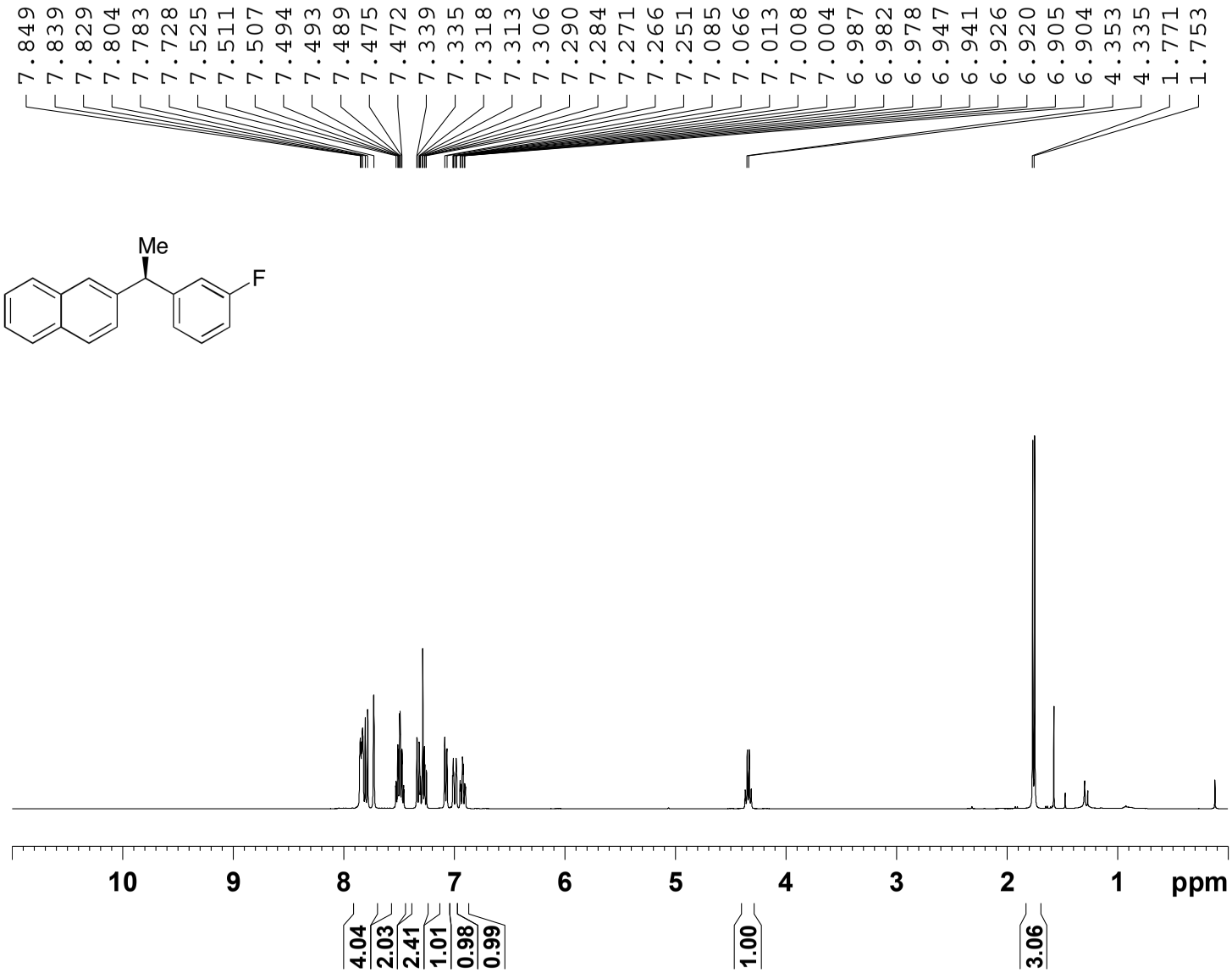
F2 - Acquisition Parameters
Date_ 20121104
Time 21.43
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 512
DW 20.850 usec
DE 18.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.25 usec
PL1 0.55 dB
PL1W 35.18820572 W
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 4.90 dB
PL12 20.46 dB
PL13 21.00 dB
PL2W 3.30822015 W
PL12W 0.09195905 W
PL13W 0.08120718 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Compound **2.28** 1H NMR



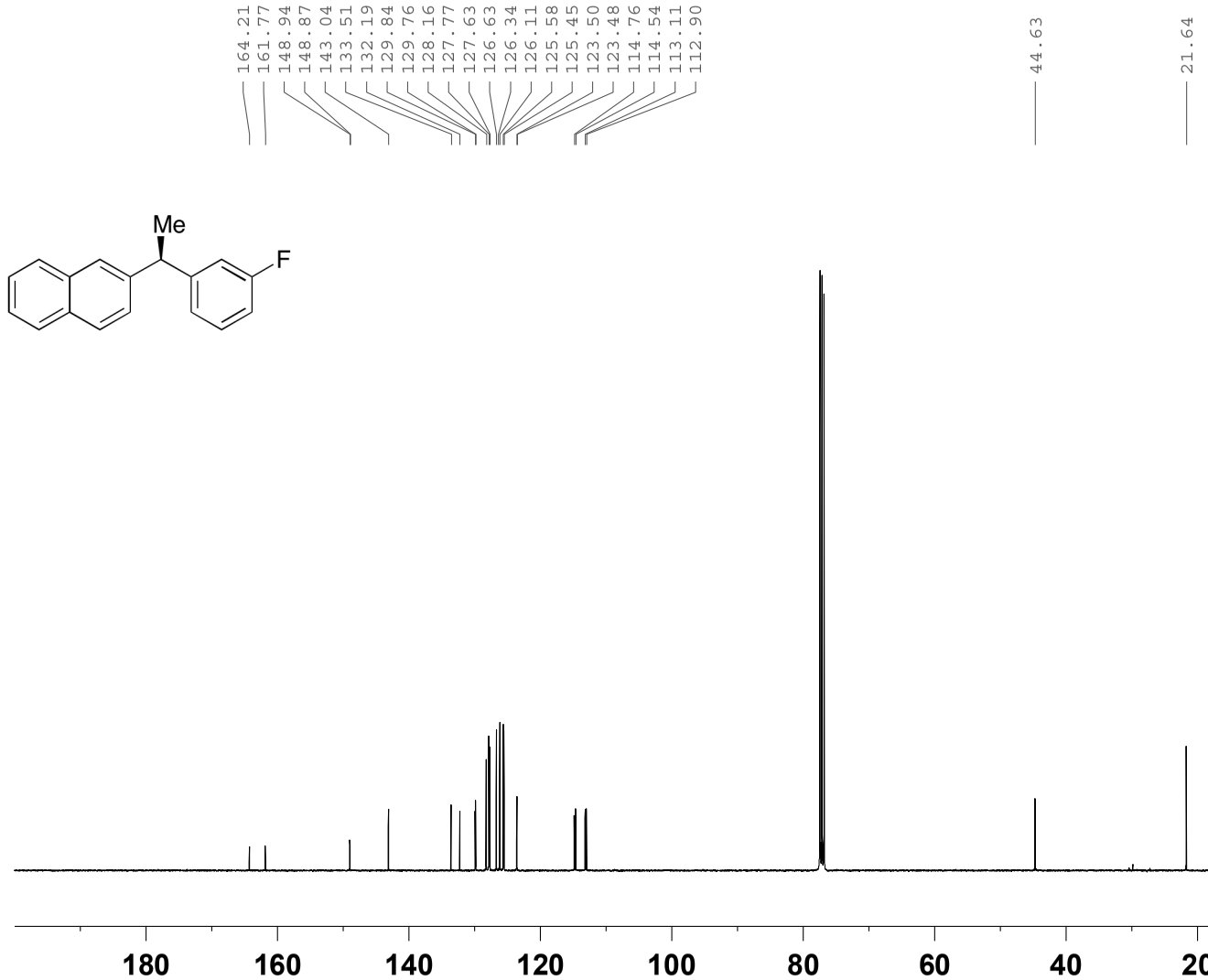

```
Current Data Parameters
NAME                  HH-4-51 B
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20121117
Time                       4.31
INSTRUM                   spect
PROBHD    5 mm CPQNP 1H/
PULPROG                   zg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                   8278.146 Hz
FIDRES                0.126314 Hz
AQ                    3.9584243 sec
RG                          11.3
DW                     60.400 usec
DE                      6.00 usec
TE                       298.1 K
D1                   1.00000000 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                         1H
P1                       15.00 usec
PL1                       4.90 dB
PL1W                 3.30822015 W
SFO1               400.1324710 MHz

F2 - Processing parameters
SI                        32768
SF                 400.1300000 MHz
WDW                          EM
SSB                           0
LB                       0.30 Hz
GB                            0
PC                        1.00
```

Compound **2.28** 13C NMR




```
Current Data Parameters
NAME          HH-4-51 B
EXPNO                 2
PROCNO                1

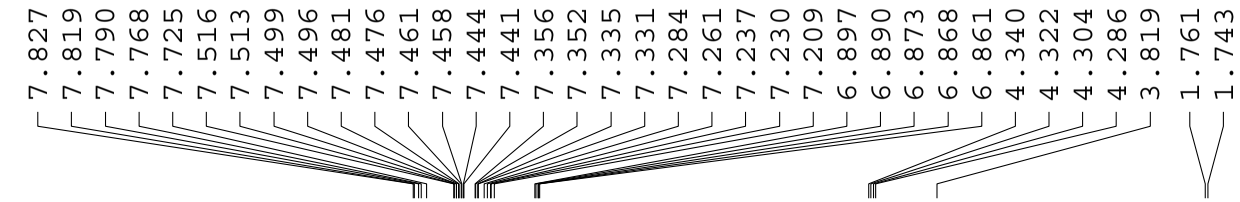
F2 - Acquisition Parameters
Date_          20121117
Time               4.47
INSTRUM           spect
PROBHD   5 mm CPQNP 1H/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ             1.3664756 sec
RG                  512
DW               20.850 usec
DE               18.00 usec
TE               298.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

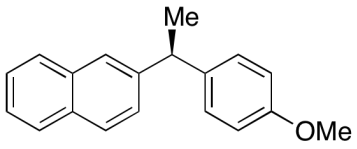
======== CHANNEL f1 ========
NUC1                13C
P1                9.25 usec
PL1               0.55 dB
PL1W        35.18820572 W
SFO1        100.6228298 MHz

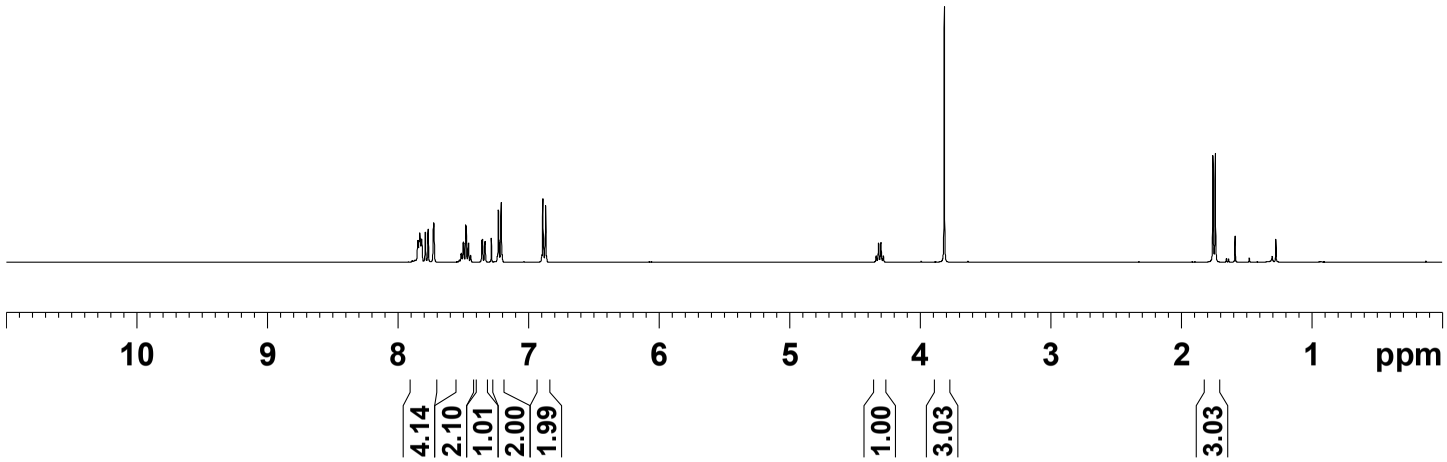
======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2            90.00 usec
PL2               4.90 dB
PL12             20.46 dB
PL13             21.00 dB
PL2W         3.30822015 W
PL12W        0.09195905 W
PL13W        0.08120718 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127690 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC                1.40
```

Compound 2.29 1HNMR







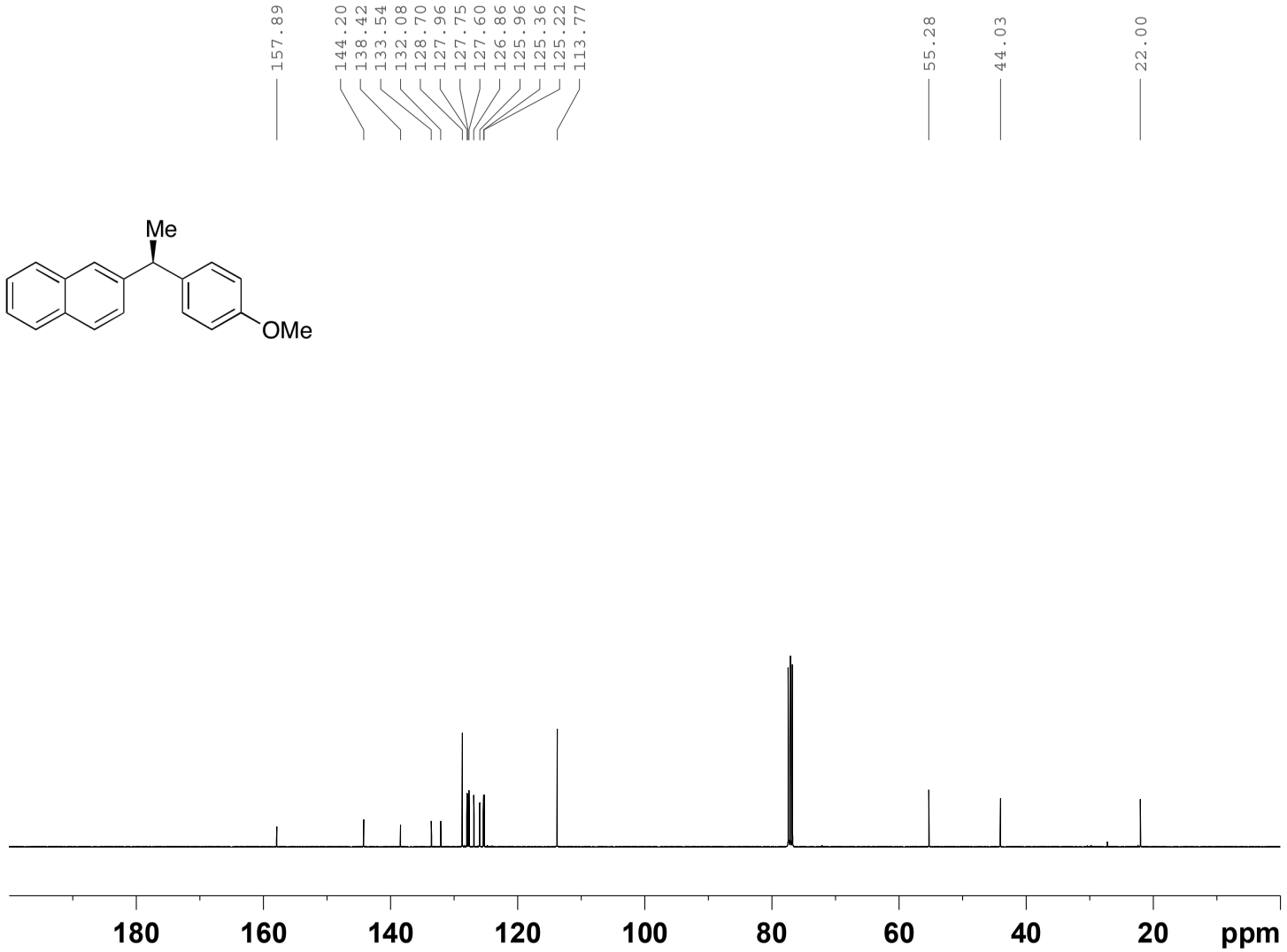

```
Current Data Parameters
NAME            HH-4-049A
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20121115
Time                16.26
INSTRUM             spect
PROBHD   5 mm CPQNP 1H/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ               3.9584243 sec
RG                     9
DW                60.400 usec
DE                 6.00 usec
TE                298.1 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 15.00 usec
PL1                 4.90 dB
PL1W          3.30822015 W
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

Compound 2.29 13CNMR



336

Current Data Parameters
NAME HH-4-049A
EXPNO 2
PROCNO 1

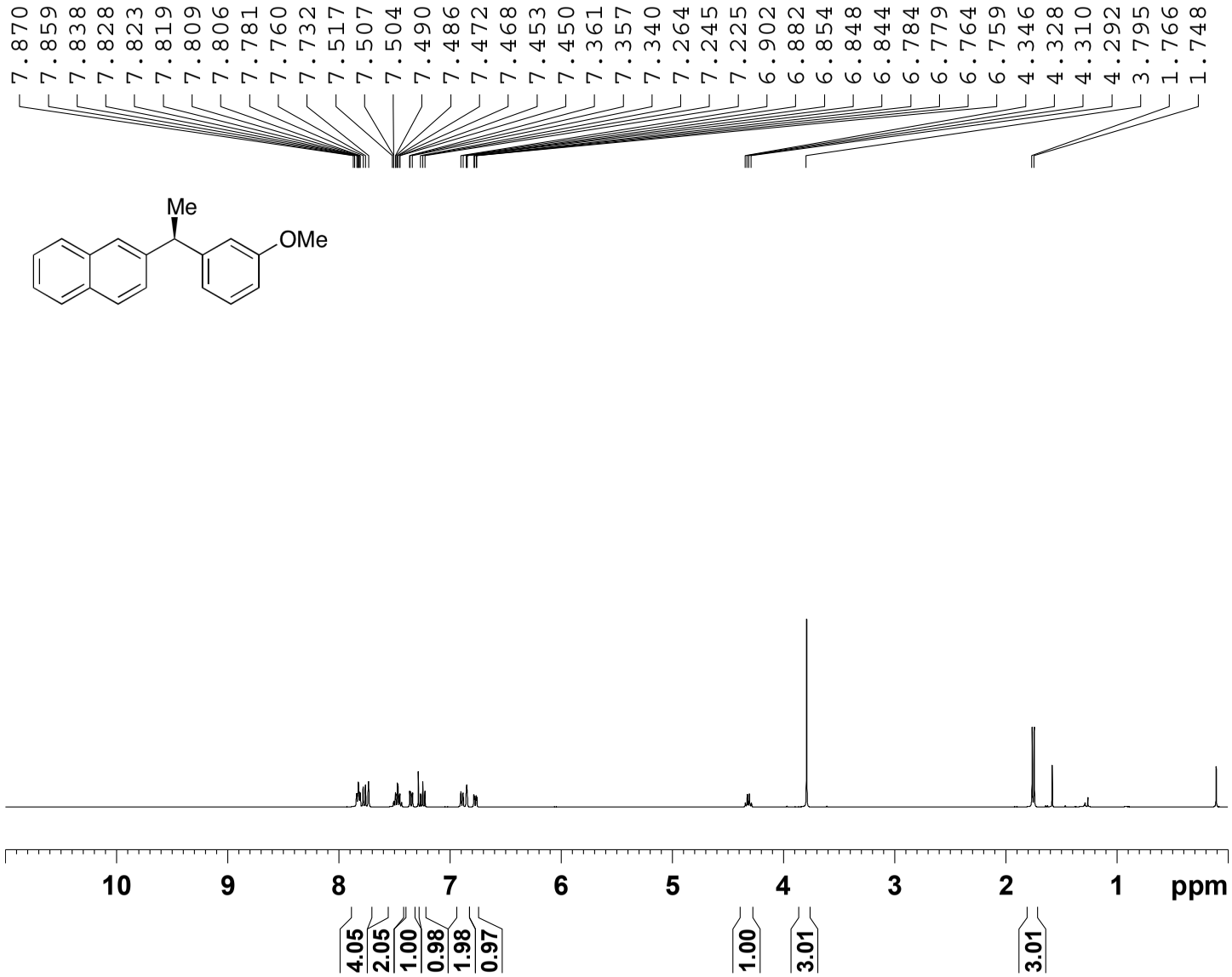
F2 - Acquisition Parameters
Date_ 20121115
Time 23.19
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 512
DW 20.850 usec
DE 18.00 usec
TE 298.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.25 usec
PL1 0.55 dB
PL1W 35.18820572 W
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 4.90 dB
PL12 20.46 dB
PL13 21.00 dB
PL2W 3.30822015 W
PL12W 0.09195905 W
PL13W 0.08120718 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Compound 2.30 1H NMR



Current Data Parameters

NAME	HH-4-050A
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20121115
Time	16.38
INSTRUM	spect
PROBHD	5 mm CPQNP 1H/
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	9
DW	60.400 usec
DE	6.00 usec
TE	298.1 K
D1	1.00000000 sec
TD0	1

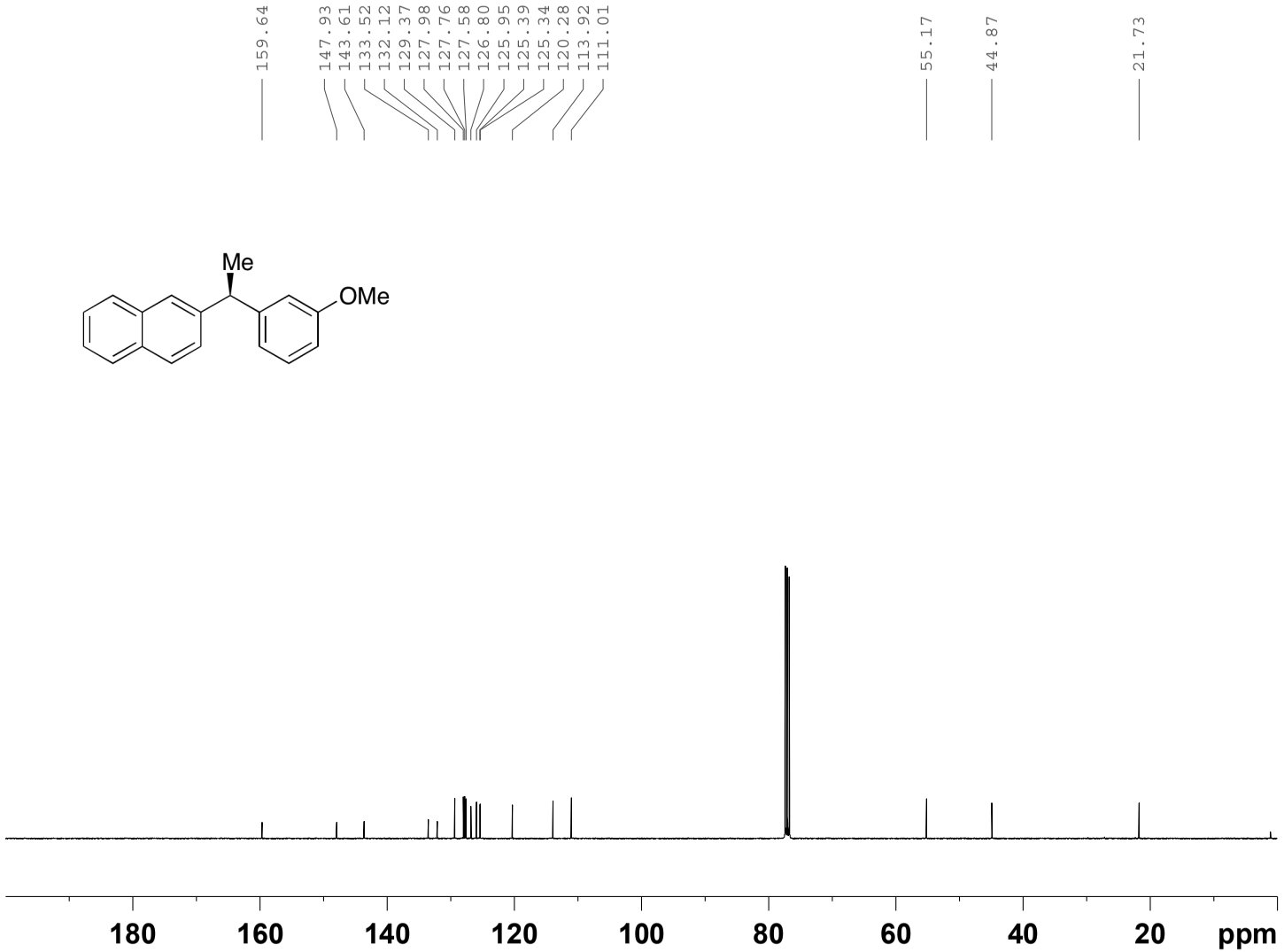
======== CHANNEL f1 ========

NUC1	1H
P1	15.00 usec
PL1	4.90 dB
PL1W	3.30822015 W
SFO1	400.1324710 MHz

F2 - Processing parameters

SI	32768
SF	400.1300000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Compound 2.30 13C NMR




```
Current Data Parameters
NAME          HH-4-050A
EXPNO                 2
PROCNO                1

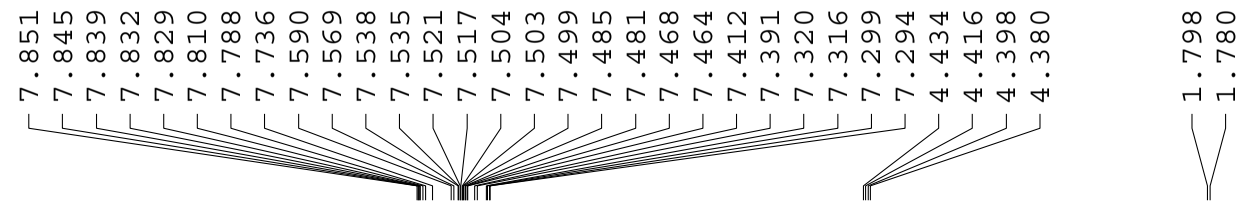
F2 - Acquisition Parameters
Date_          20121115
Time              23.39
INSTRUM           spect
PROBHD   5 mm CPQNP 1H/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ             1.3664756 sec
RG                  512
DW               20.850 usec
DE               18.00 usec
TE               298.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

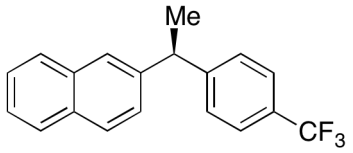
======== CHANNEL f1 ========
NUC1                13C
P1                9.25 usec
PL1               0.55 dB
PL1W        35.18820572 W
SFO1        100.6228298 MHz

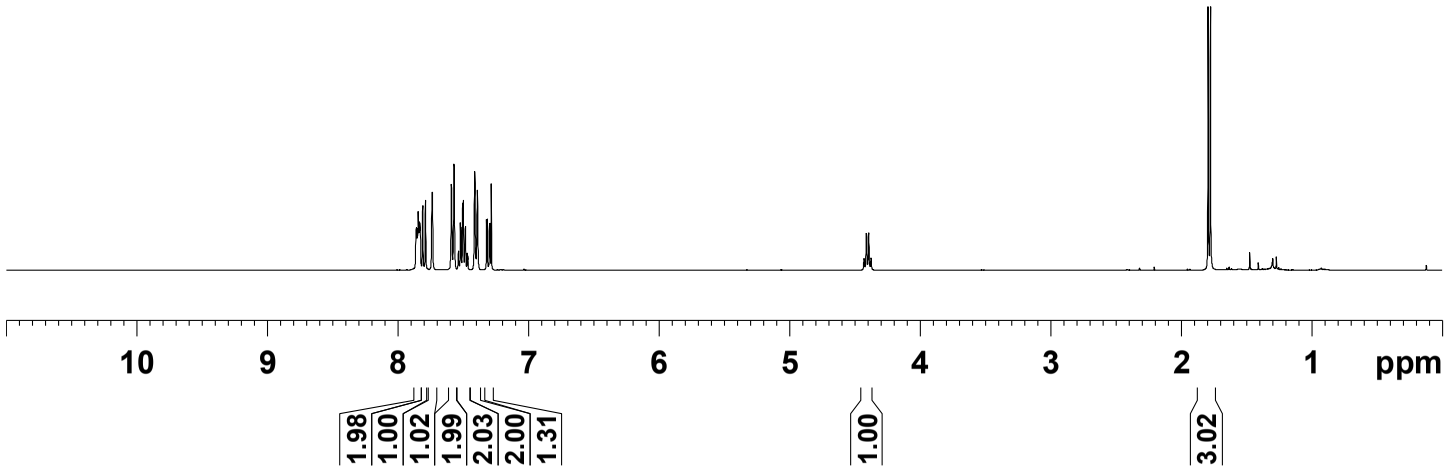
======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2            90.00 usec
PL2               4.90 dB
PL12             20.46 dB
PL13             21.00 dB
PL2W         3.30822015 W
PL12W        0.09195905 W
PL13W        0.08120718 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127690 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```

Compound 2.31 1H NMR







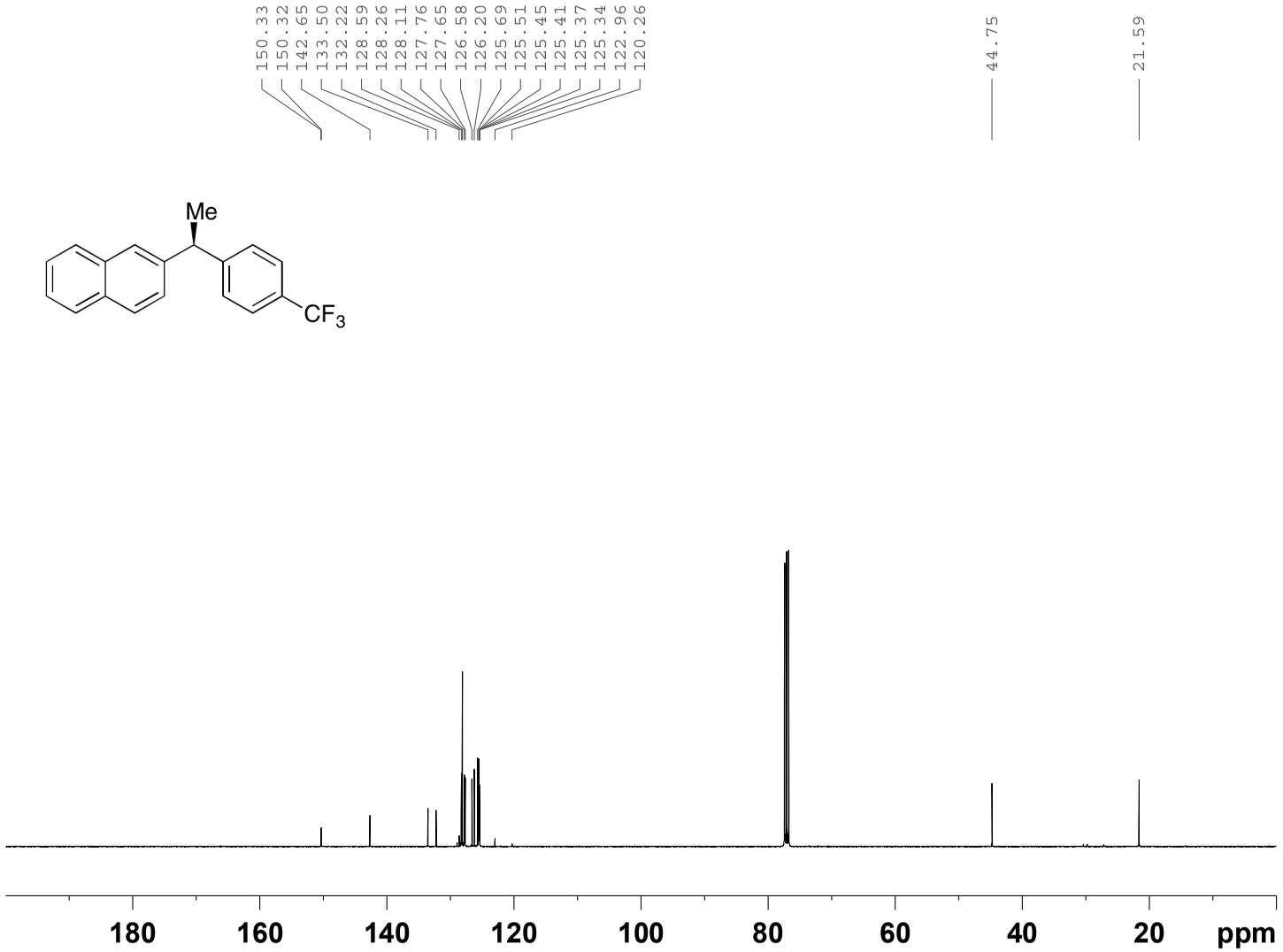
Current Data Parameters
NAME QZ-3-061A
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121104
Time 22.11
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 11.3
DW 60.400 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 4.90 dB
PL1W 3.30822015 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound 2.31 13C NMR



Current Data Parameters

NAME	QZ-3-061A
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20121104
Time	22.27
INSTRUM	spect
PROBHD	5 mm CPQNP 1H/
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	256
DS	4
SWH	23980.814 Hz
FIDRES	0.365918 Hz
AQ	1.3664756 sec
RG	512
DW	20.850 usec
DE	18.00 usec
TE	298.1 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1

======== CHANNEL f1 ========

NUC1	13C
P1	9.25 usec
PL1	0.55 dB
PL1W	35.18820572 W
SFO1	100.6228298 MHz

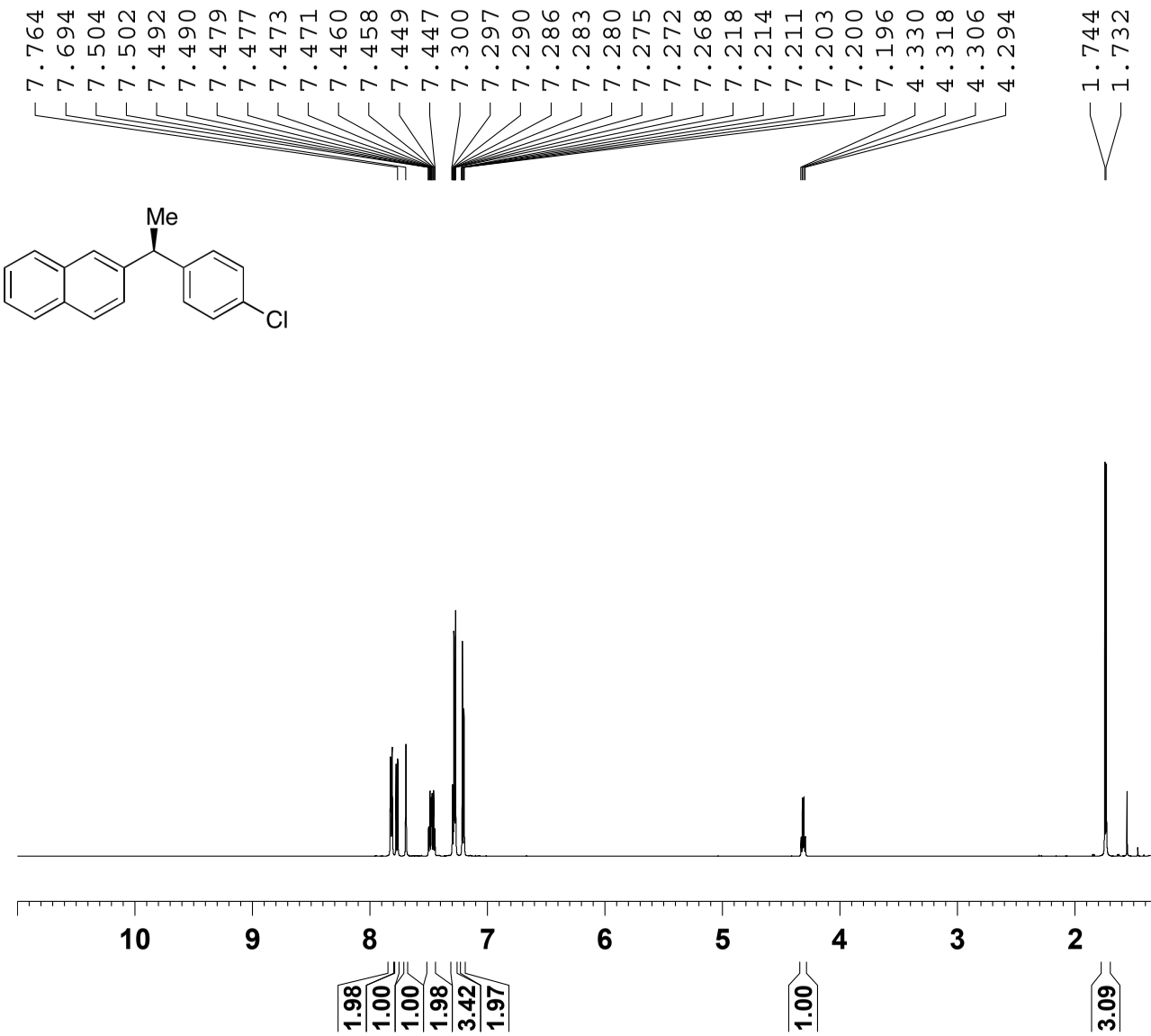
======== CHANNEL f2 ========

CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	4.90 dB
PL12	20.46 dB
PL13	21.00 dB
PL2W	3.30822015 W
PL12W	0.09195905 W
PL13W	0.08120718 W
SFO2	400.1316005 MHz

F2 - Processing parameters

SI	32768
SF	100.6127690 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

Compound 2.32 1H NMR



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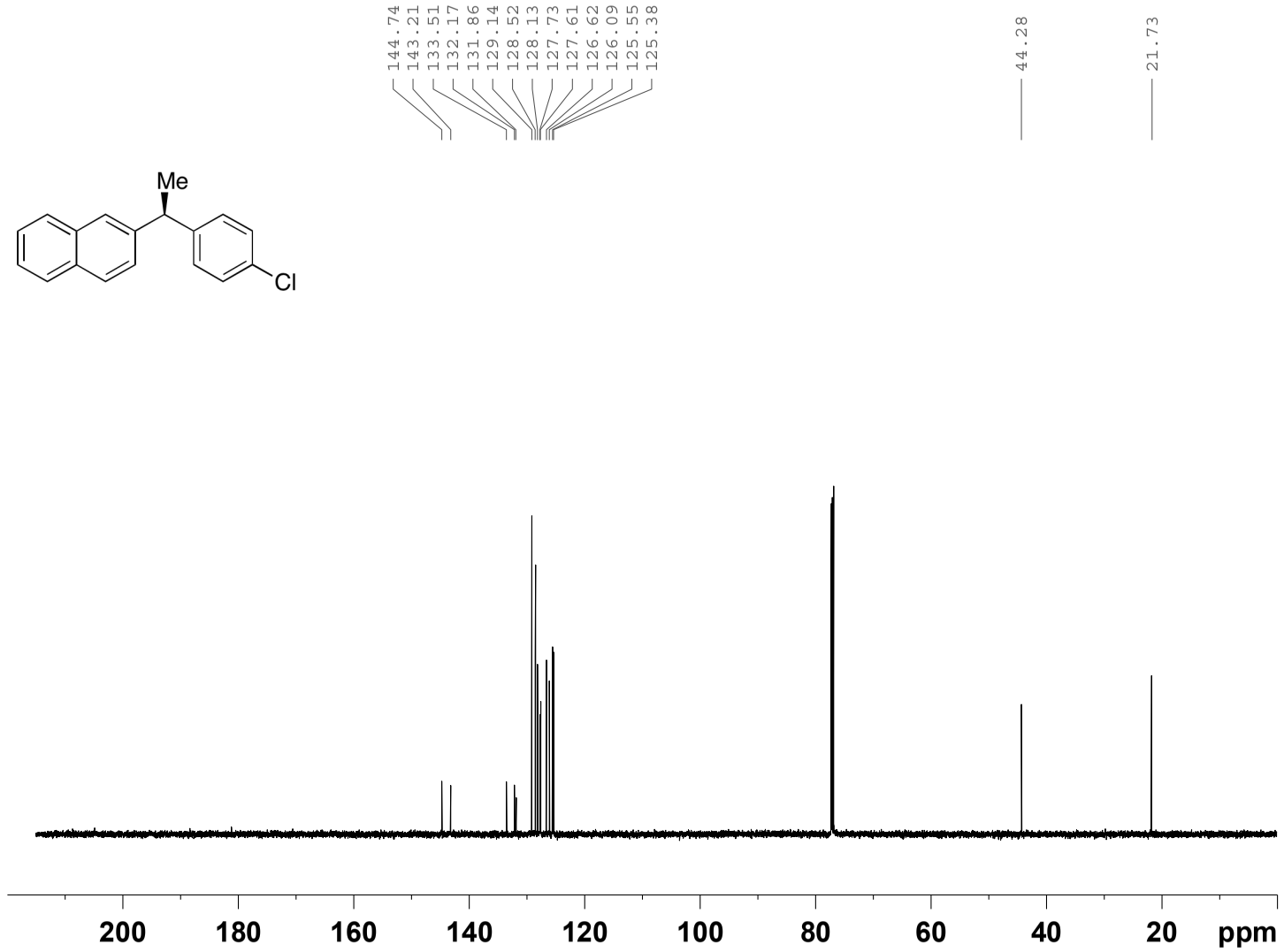
Current Data Parameters
NAME QZ-Compound 8
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121209
Time 13.13
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8403.361 Hz
FIDRES 0.128225 Hz
AQ 3.8994420 sec
RG 144
DW 59.500 usec
DE 17.39 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 600.3233018 MHz
NUC1 1H
P1 10.77 usec

F2 - Processing parameters
SI 65536
SF 600.3200047 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound **2.32** 13 CNMR



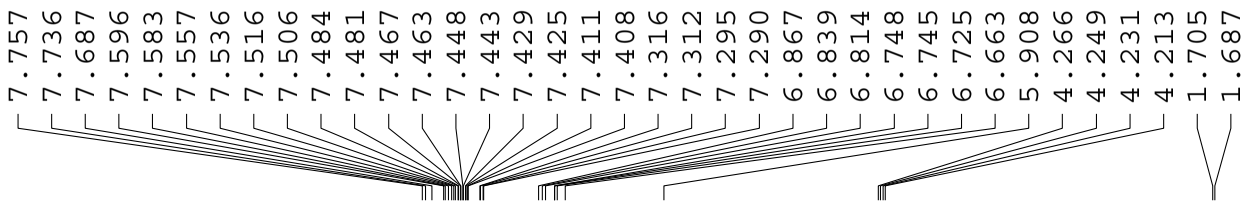

```
Current Data Parameters
NAME       QZ-Compound 8
EXPNO                 2
PROCNO                1

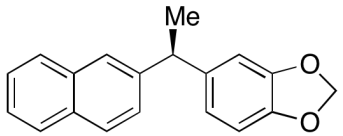
F2 - Acquisition Parameters
Date_          20121209
Time               13.23
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg55
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    4
SWH           34722.223 Hz
FIDRES         0.529819 Hz
AQ            0.9437684 sec
RG                 2050
DW               14.400 usec
DE                19.34 usec
TE                298.1 K
D1           1.10000002 sec
D11          0.03000000 sec
TD0                   1

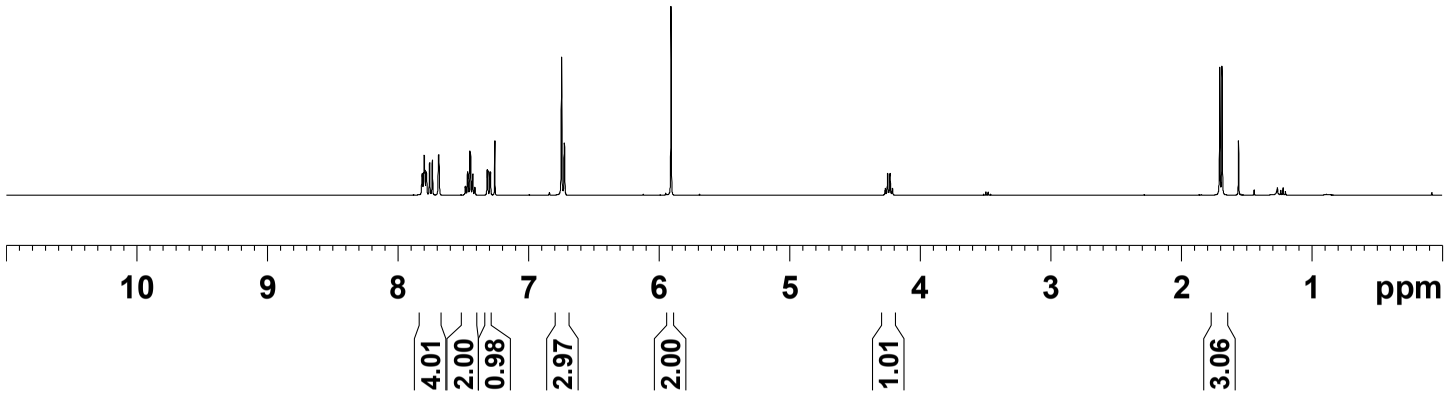
======== CHANNEL f1 ========
SFO1        150.9656784 MHz
NUC1                13C
P1                10.63 usec

F2 - Processing parameters
SI                32768
SF          150.9505840 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

Compound 2.33 1H NMR







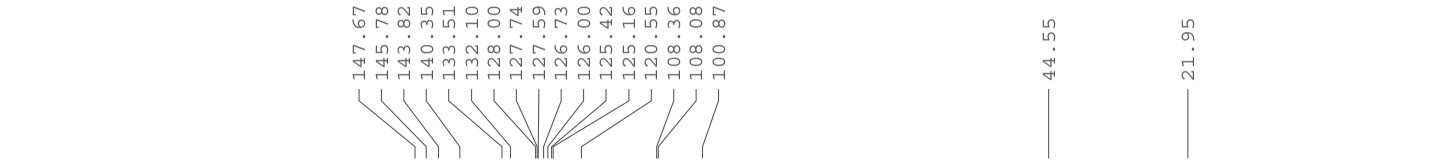
Current Data Parameters
NAME SDG-2-177B1
EXPNO 1
PROCNO 1

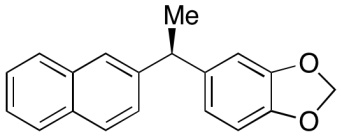
F2 - Acquisition Parameters
Date_ 20121118
Time 9.13
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 12.7
DW 60.400 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1

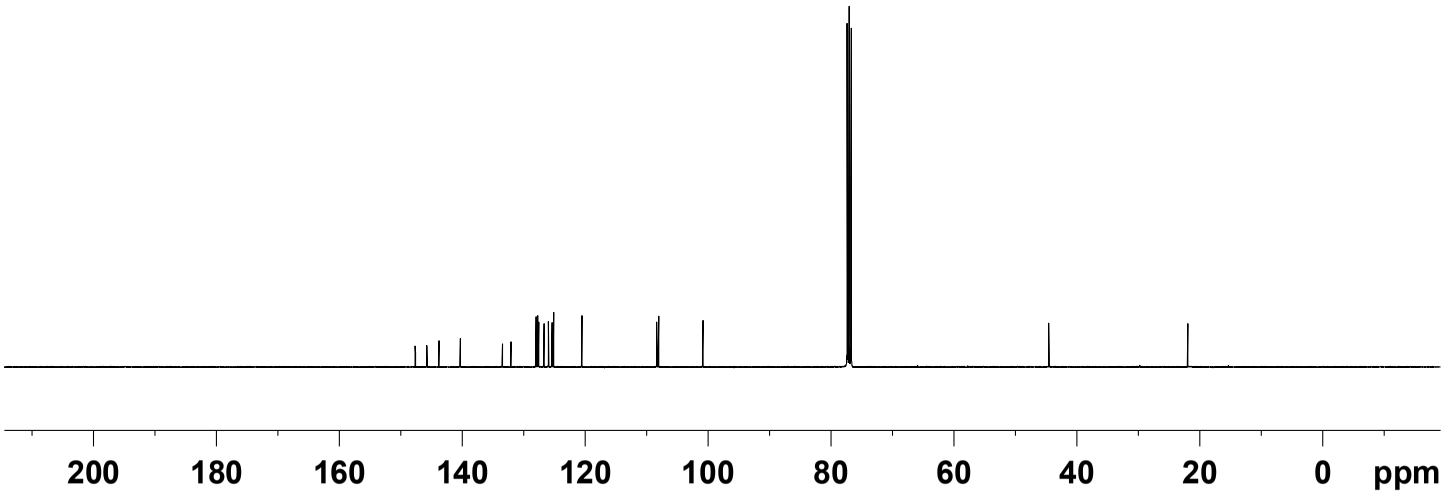
======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 4.90 dB
PL1W 3.30822015 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300105 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound **2.33** 13C NMR








```
Current Data Parameters
NAME         SDG-2-177B1
EXPNO                  2
PROCNO                 1

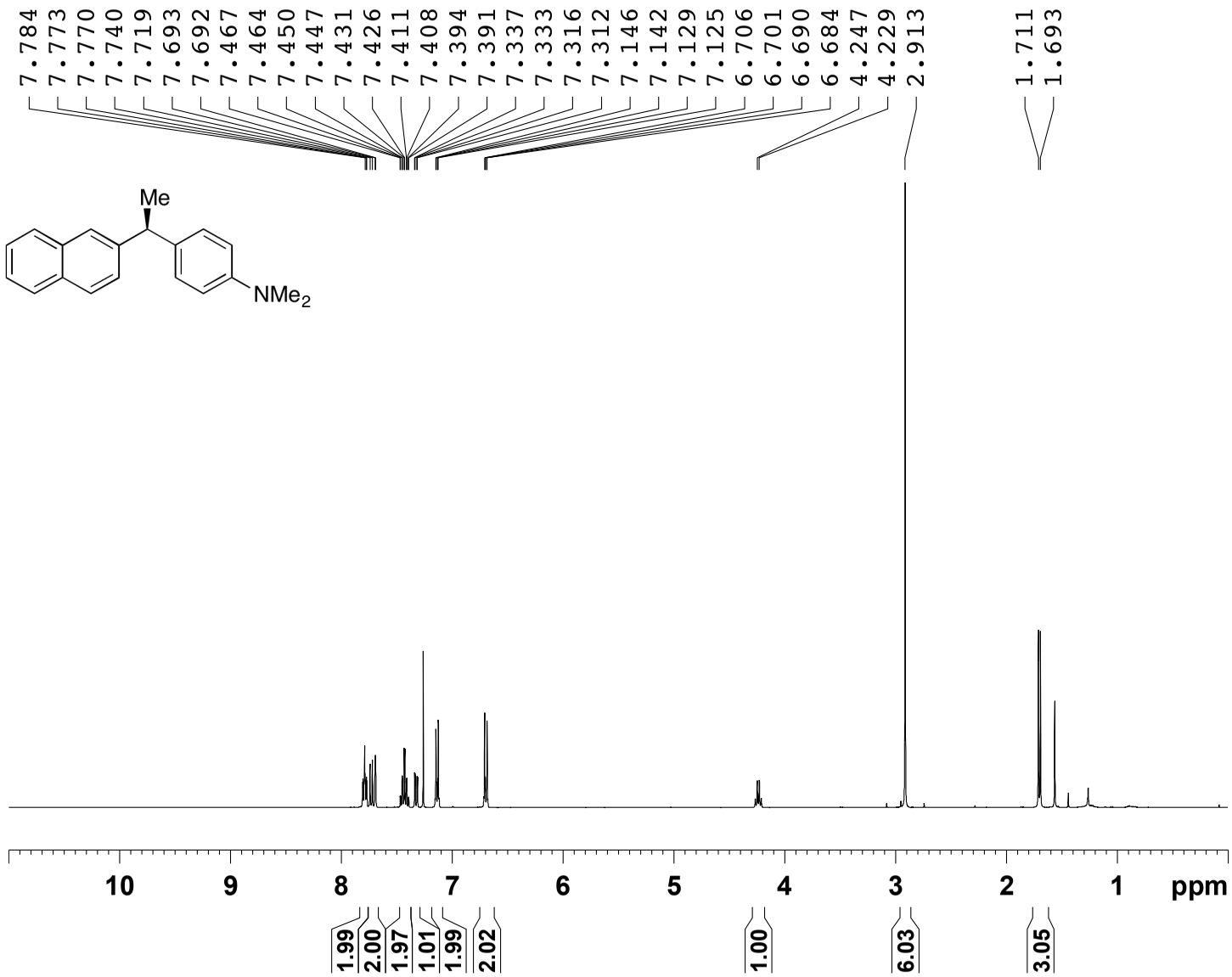
F2 - Acquisition Parameters
Date_           20121118
Time                9.29
INSTRUM            spect
PROBHD   5 mm CPQNP 1H/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   256
DS                     4
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG                   512
DW                20.850 usec
DE                18.00 usec
TE                298.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.25 usec
PL1                 0.55 dB
PL1W        35.18820572 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL2                 4.90 dB
PL12               20.46 dB
PL13               21.00 dB
PL2W         3.30822015 W
PL12W        0.09195905 W
PL13W        0.08120718 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127690 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

Compound 2.34 1HNMR



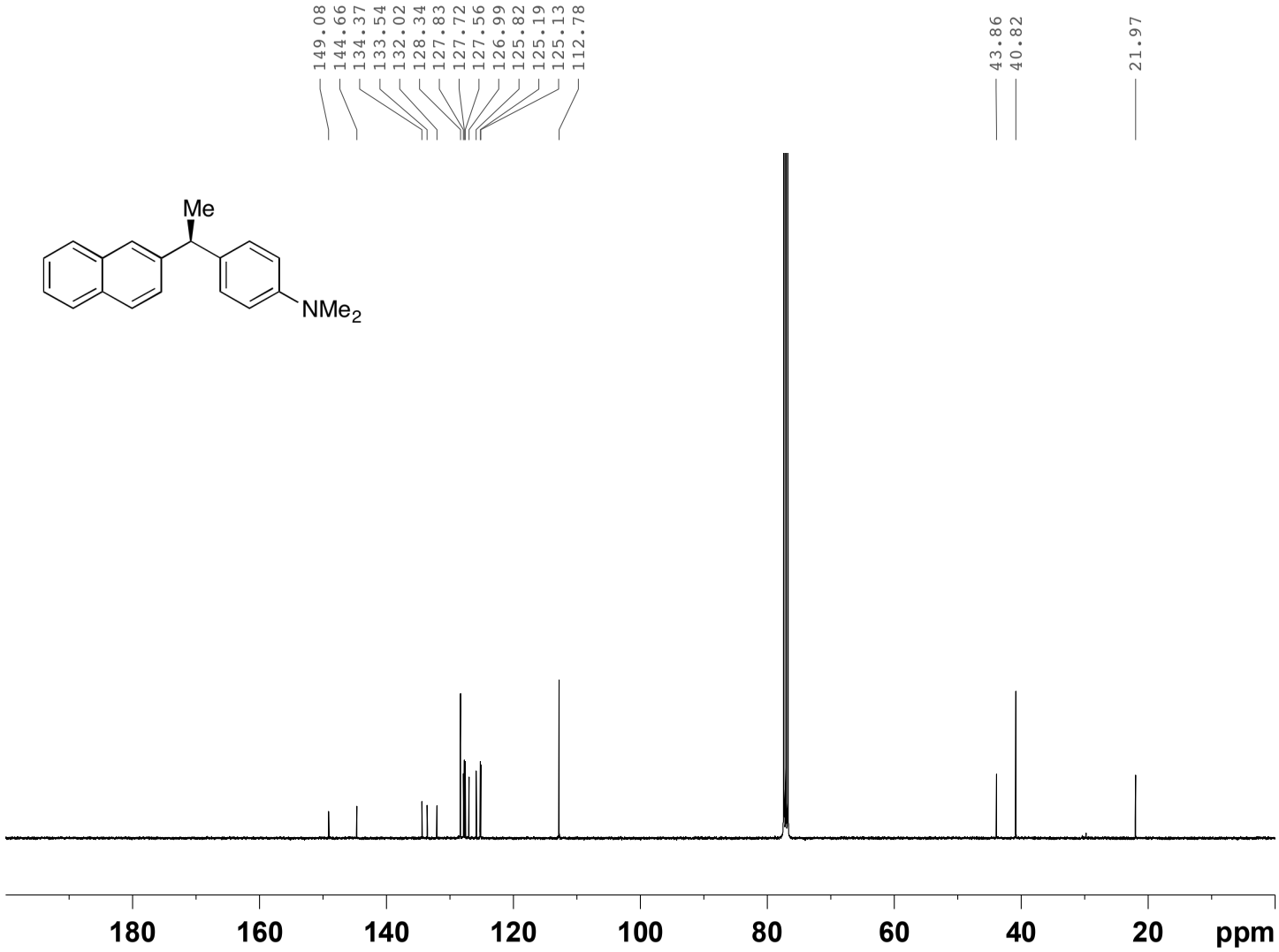
Current Data Parameters
NAME SDG-2-177A1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121118
Time 8.29
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 12.7
DW 60.400 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 4.90 dB
PL1W 3.30822015 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound 2.34 13 CNMR




```
Current Data Parameters
NAME         SDG-2-177A1
EXPNO                  2
PROCNO                 1

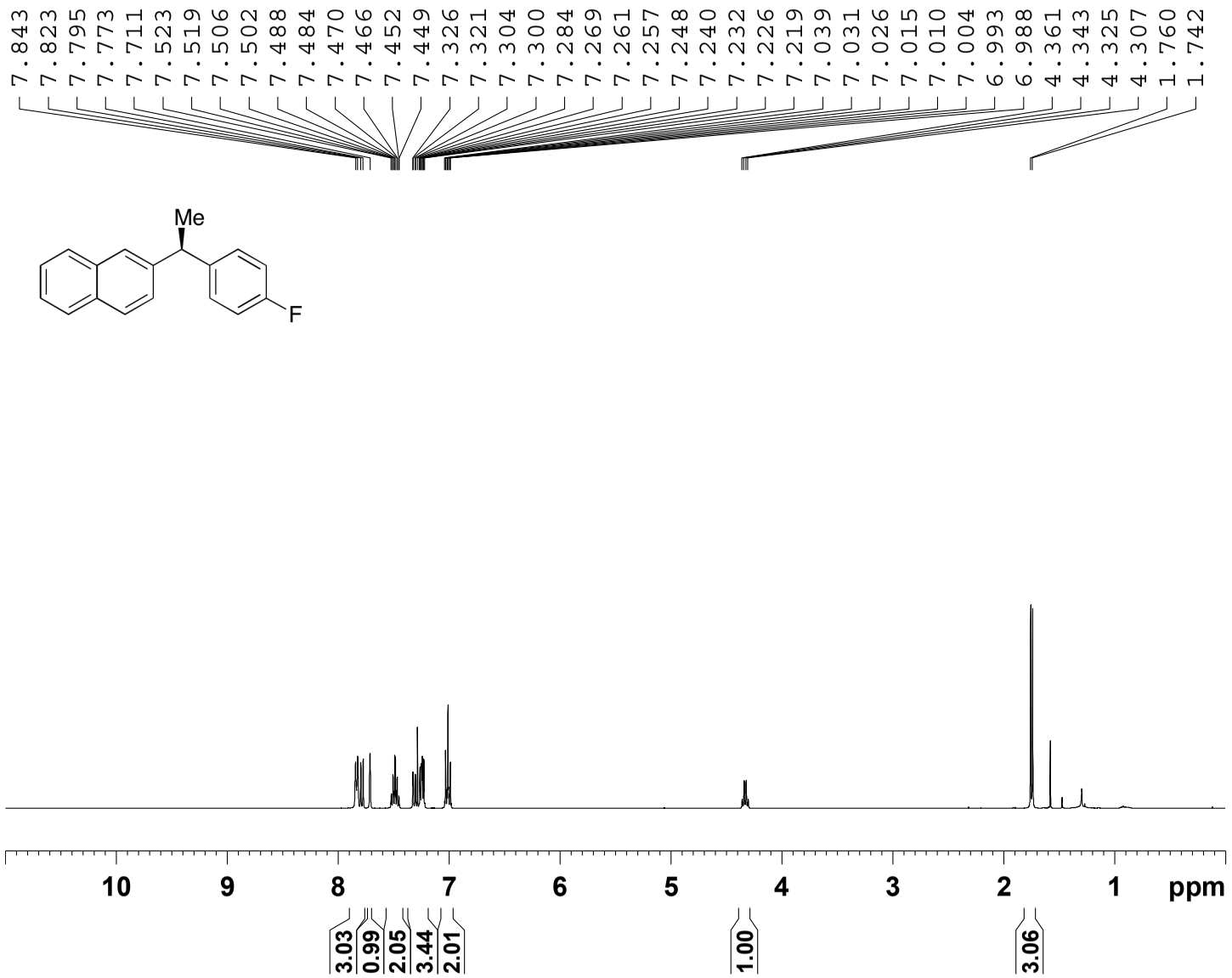
F2 - Acquisition Parameters
Date_           20121118
Time                8.45
INSTRUM            spect
PROBHD   5 mm CPQNP 1H/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   256
DS                     4
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ              1.3664756 sec
RG                   512
DW                20.850 usec
DE                18.00 usec
TE                298.2 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 9.25 usec
PL1                0.55 dB
PL1W        35.18820572 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             90.00 usec
PL2                4.90 dB
PL12              20.46 dB
PL13              21.00 dB
PL2W         3.30822015 W
PL12W        0.09195905 W
PL13W        0.08120718 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127690 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                 1.40
```

Compound 2.35 1H NMR



Current Data Parameters

NAME	HH-4-69 A
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20121117
Time	5.15
INSTRUM	spect
PROBHD	5 mm CPQNP 1H/
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	11.3
DW	60.400 usec
DE	6.00 usec
TE	298.1 K
D1	1.00000000 sec
TD0	1

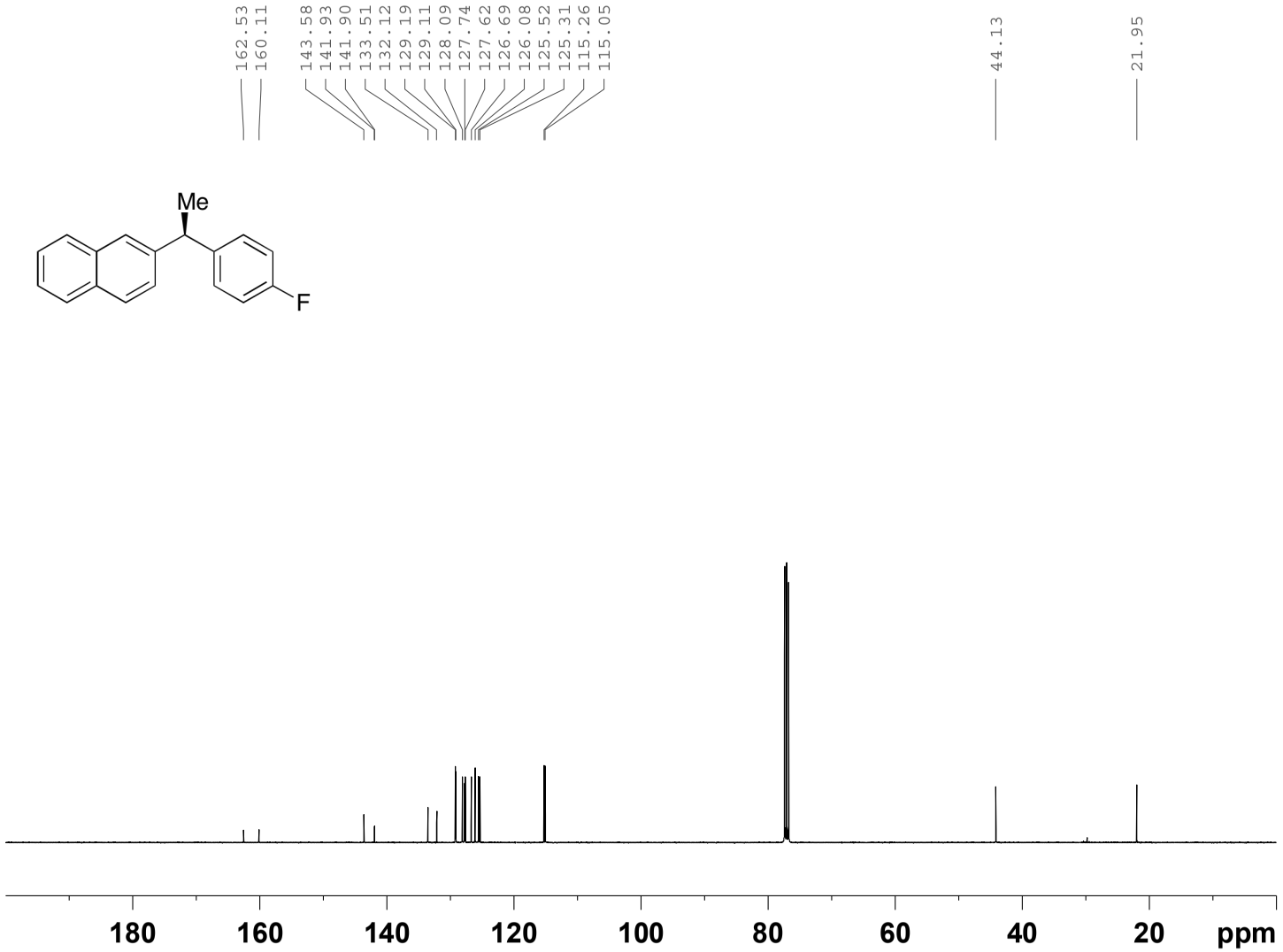
======== CHANNEL f1 ========

NUC1	1H
P1	15.00 usec
PL1	4.90 dB
PL1W	3.30822015 W
SFO1	400.1324710 MHz

F2 - Processing parameters

SI	32768
SF	400.1300000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Compound 2.35 13 CNMR



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Current Data Parameters
NAME HH-4-69 A
EXPNO 2
PROCNO 1

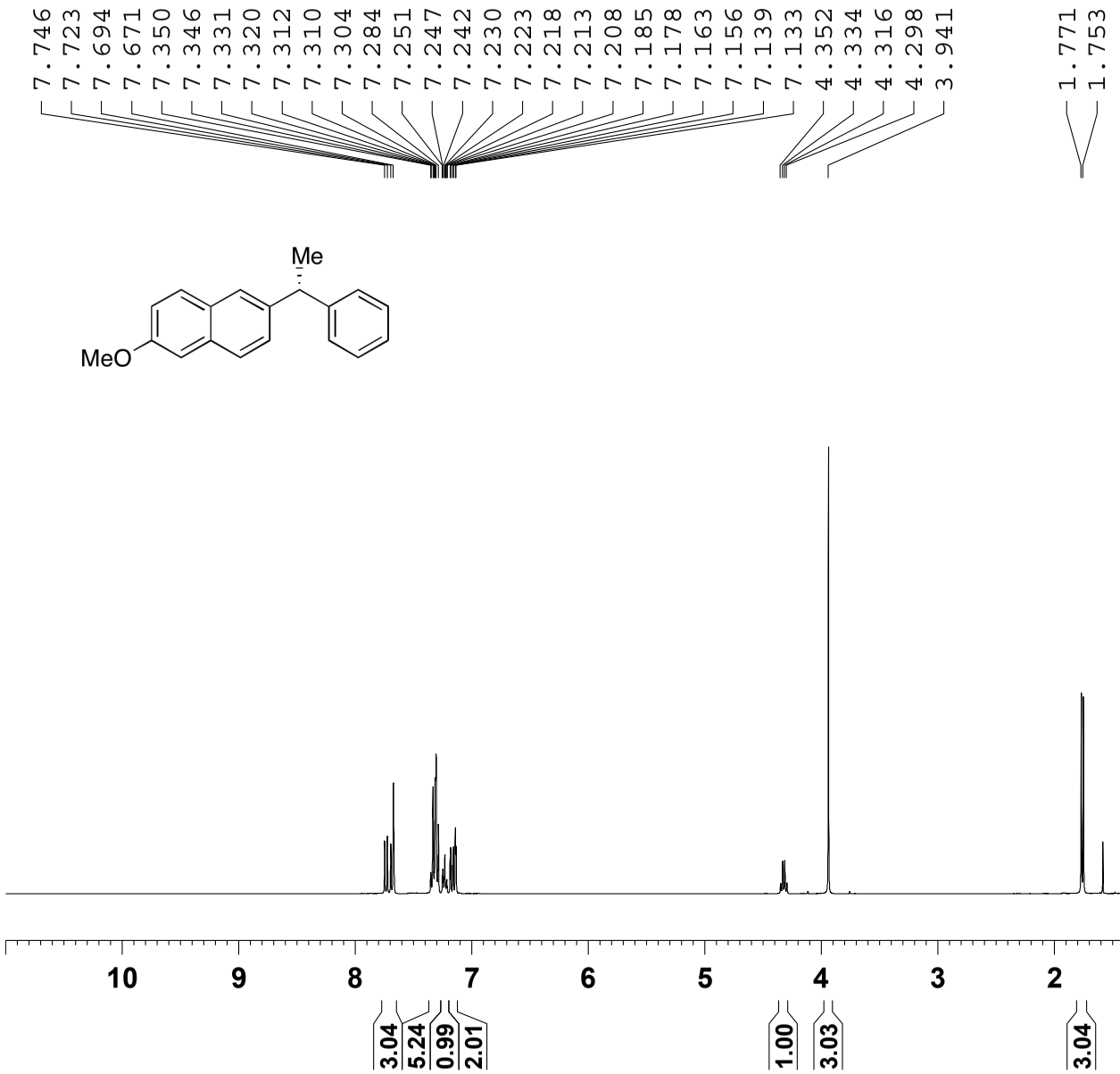
F2 - Acquisition Parameters
Date_ 20121117
Time 5.32
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 512
DW 20.850 usec
DE 18.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.25 usec
PL1 0.55 dB
PL1W 35.18820572 W
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 4.90 dB
PL12 20.46 dB
PL13 21.00 dB
PL2W 3.30822015 W
PL12W 0.09195905 W
PL13W 0.08120718 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Compound 2.36 1H NMR



Current Data Parameters

NAME	SDG-2-167-1
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20121115
Time	16.02
INSTRUM	spect
PROBHD	5 mm CPQNP 1H/
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	8
DW	60.400 usec
DE	6.00 usec
TE	298.2 K
D1	1.00000000 sec
TD0	1

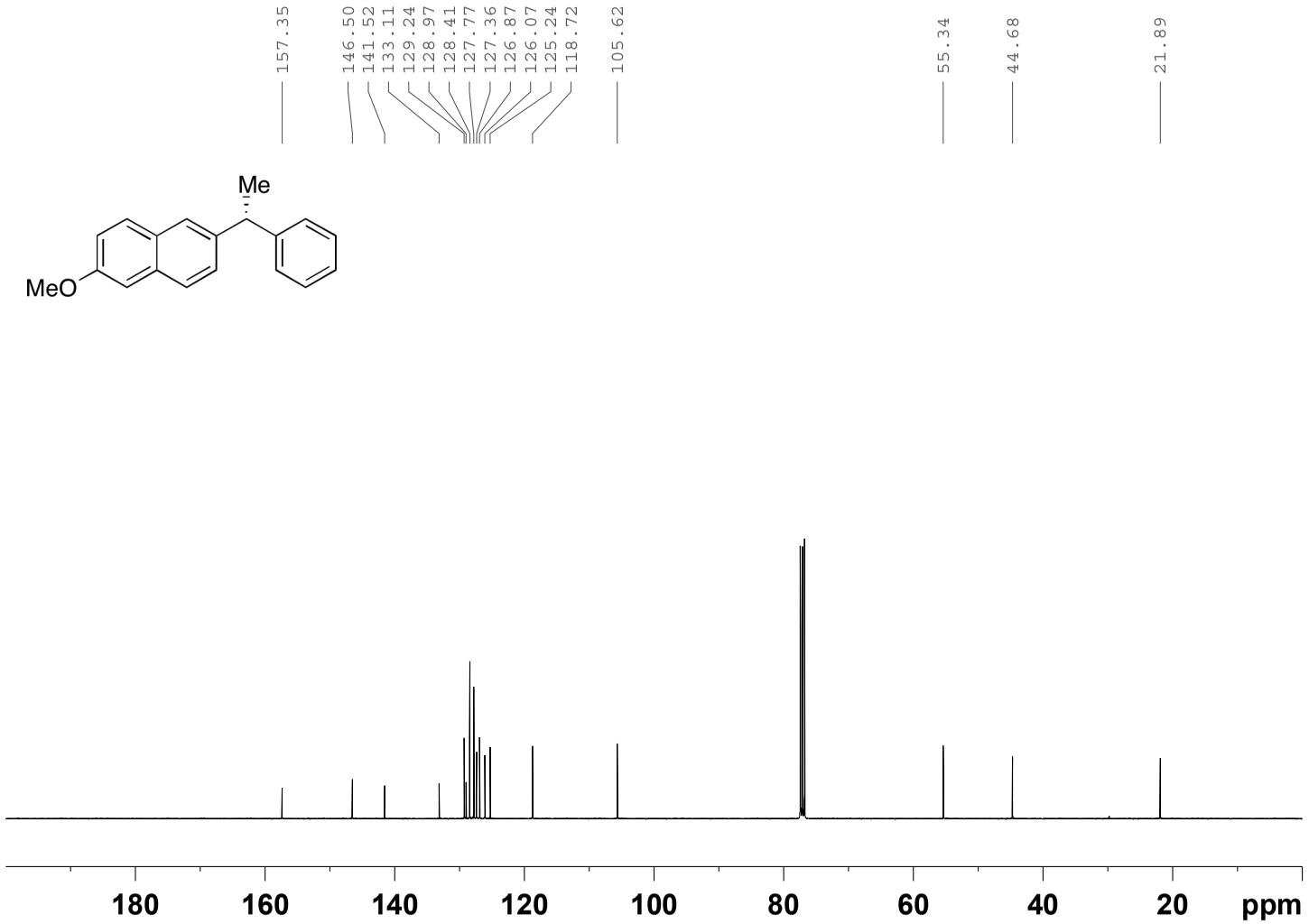
======== CHANNEL f1 ========

NUC1	1H
P1	15.00 usec
PL1	4.90 dB
PL1W	3.30822015 W
SFO1	400.1324710 MHz

F2 - Processing parameters

SI	32768
SF	400.1300000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Compound **2.36** 13C NMR



Current Data Parameters

NAME	SDG-2-167-1
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20121115
Time	22.03
INSTRUM	spect
PROBHD	5 mm CPQNP 1H/
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	256
DS	4
SWH	23980.814 Hz
FIDRES	0.365918 Hz
AQ	1.3664756 sec
RG	512
DW	20.850 usec
DE	18.00 usec
TE	298.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1

======== CHANNEL f1 ========

NUC1	13C
P1	9.25 usec
PL1	0.55 dB
PL1W	35.18820572 W
SFO1	100.6228298 MHz

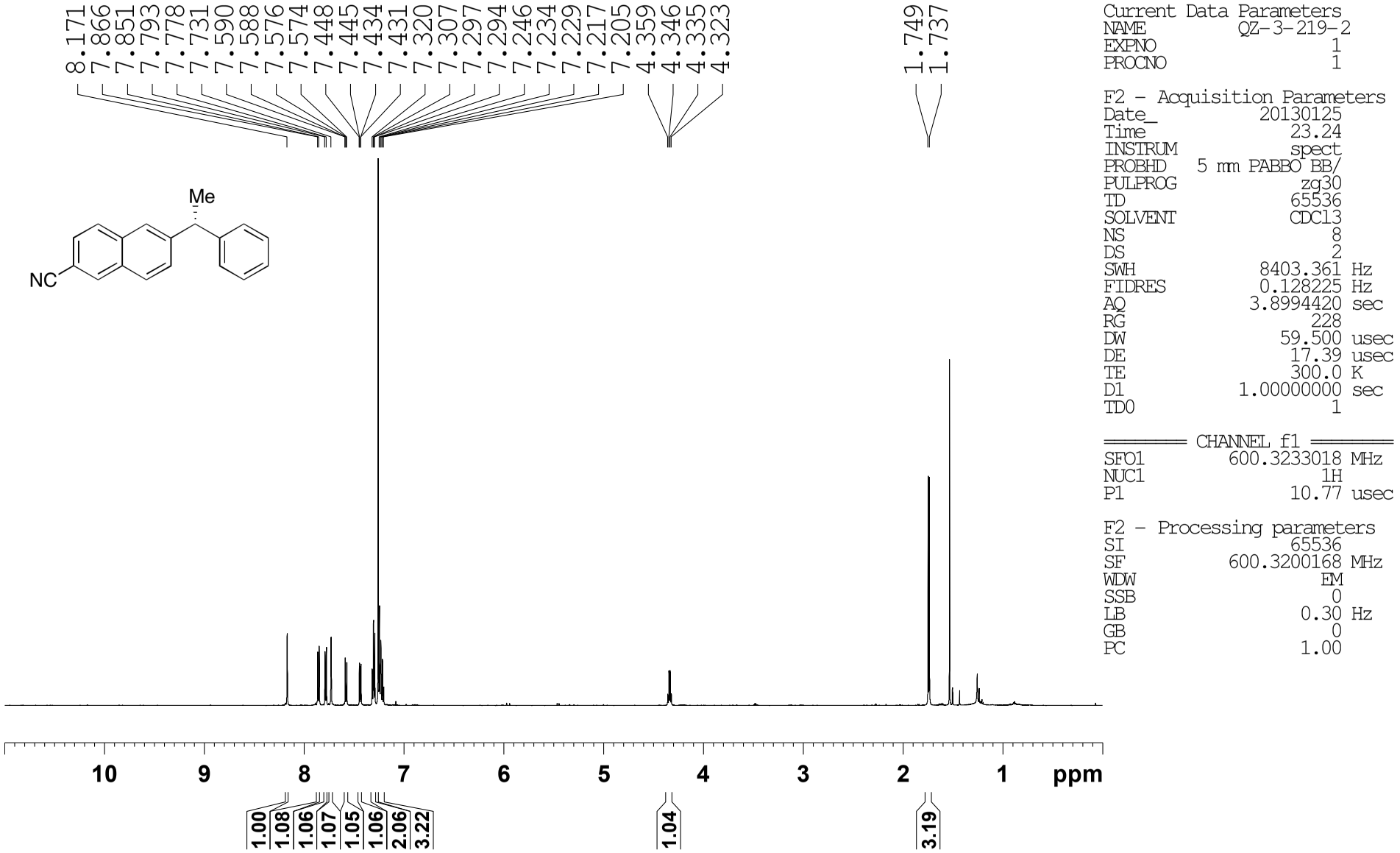
======== CHANNEL f2 ========

CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	4.90 dB
PL12	20.46 dB
PL13	21.00 dB
PL2W	3.30822015 W
PL12W	0.09195905 W
PL13W	0.08120718 W
SFO2	400.1316005 MHz

F2 - Processing parameters

SI	32768
SF	100.6127690 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

compound 2.37 1H NMR



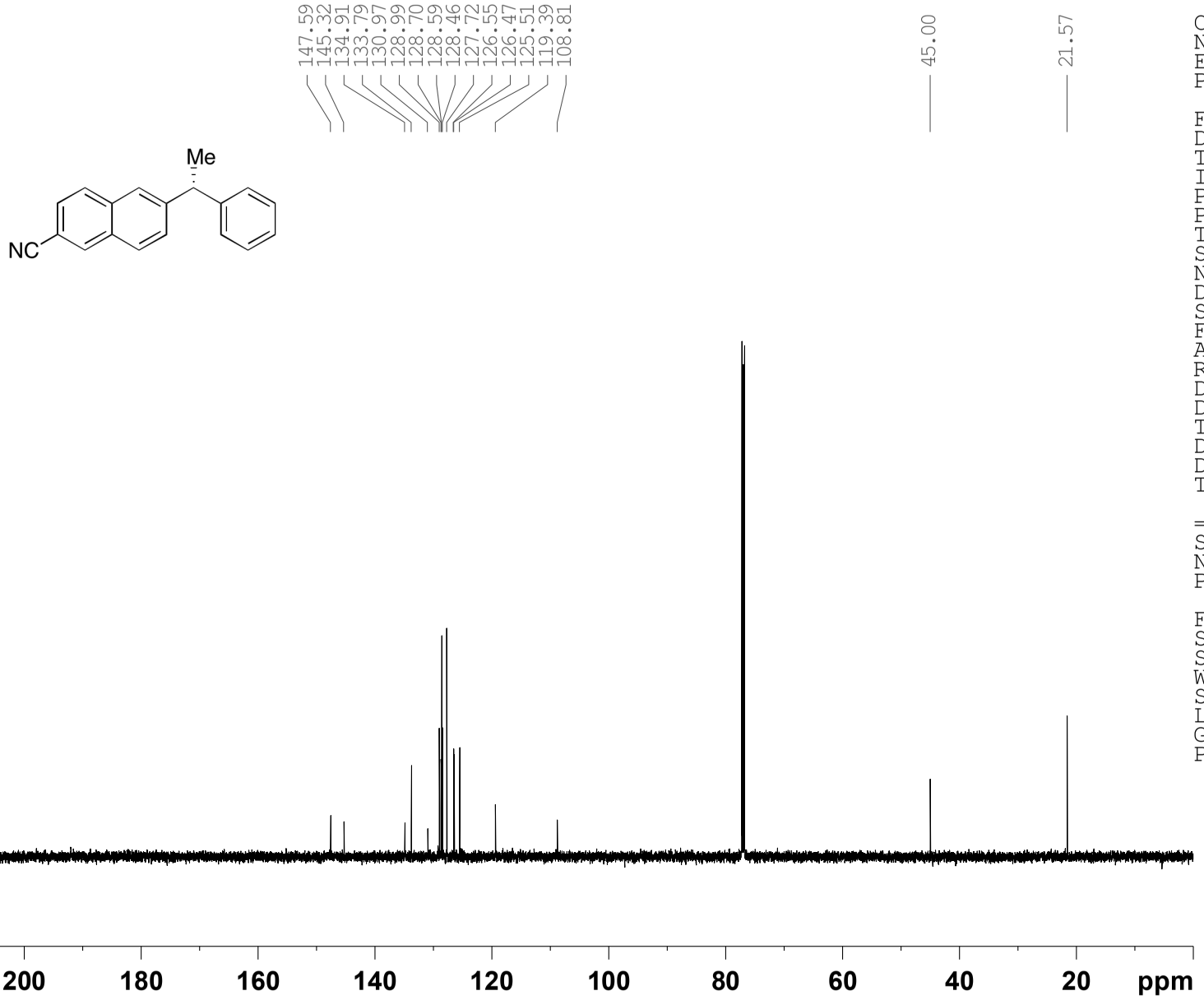
Current Data Parameters
NAME QZ-3-219-2
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130125
Time 23.24
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8403.361 Hz
FIDRES 0.128225 Hz
AQ 3.8994420 sec
RG 228
DW 59.500 usec
DE 17.39 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 600.3233018 MHz
NUC1 1H
P1 10.77 usec

F2 - Processing parameters
SI 65536
SF 600.3200168 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compopund 2.37 13C NMR



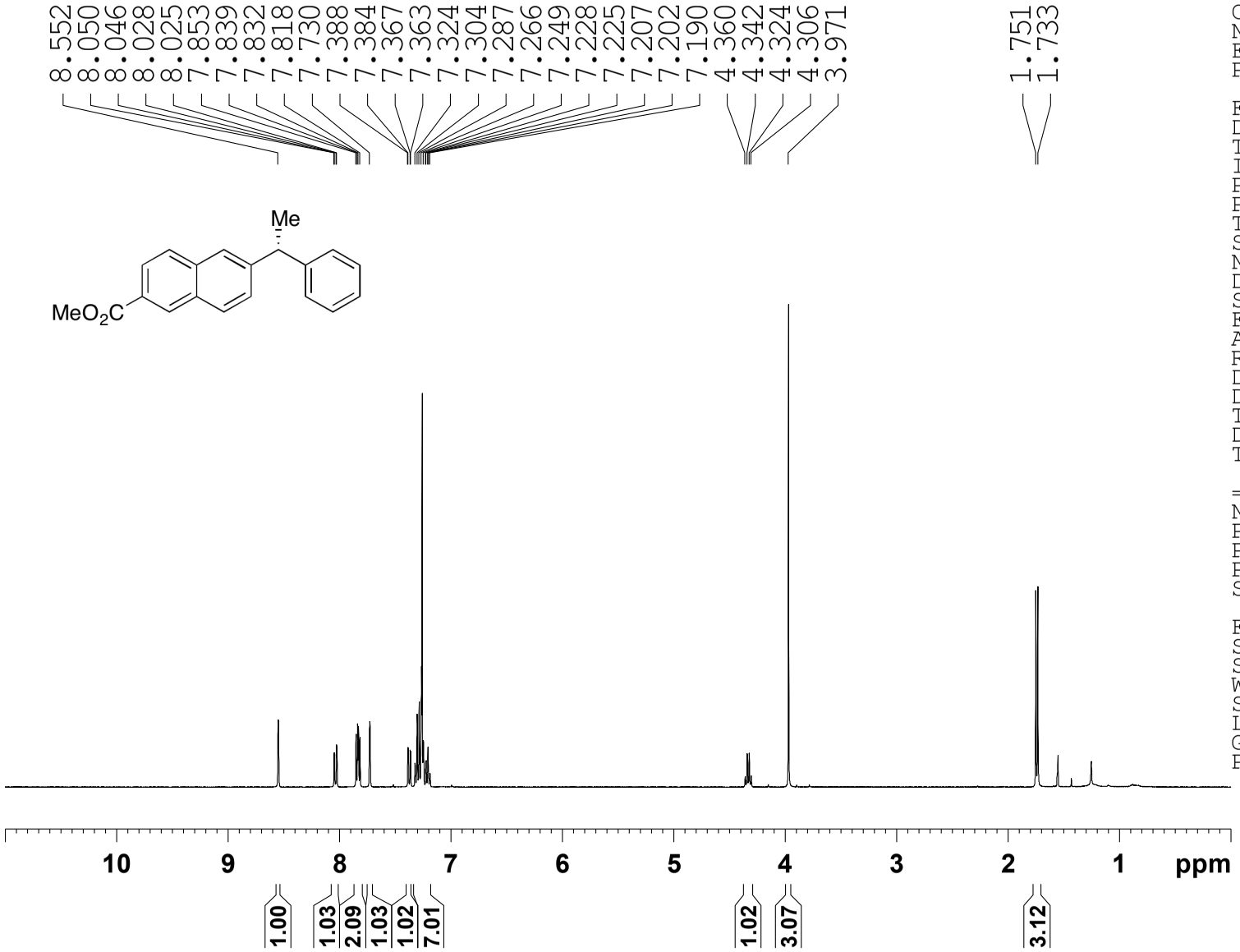
Current Data Parameters
NAME QZ-3-219-B-1
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130126
Time 1.08
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg55
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 34722.223 Hz
FIDRES 0.529819 Hz
AQ 0.9437684 sec
RG 2050
DW 14.400 usec
DE 19.34 usec
TE 300.0 K
D1 1.10000002 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 150.9656784 MHz
NUC1 13C
P1 10.63 usec

F2 - Processing parameters
SI 32768
SF 150.9505840 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Compound 2.38 1H NMR



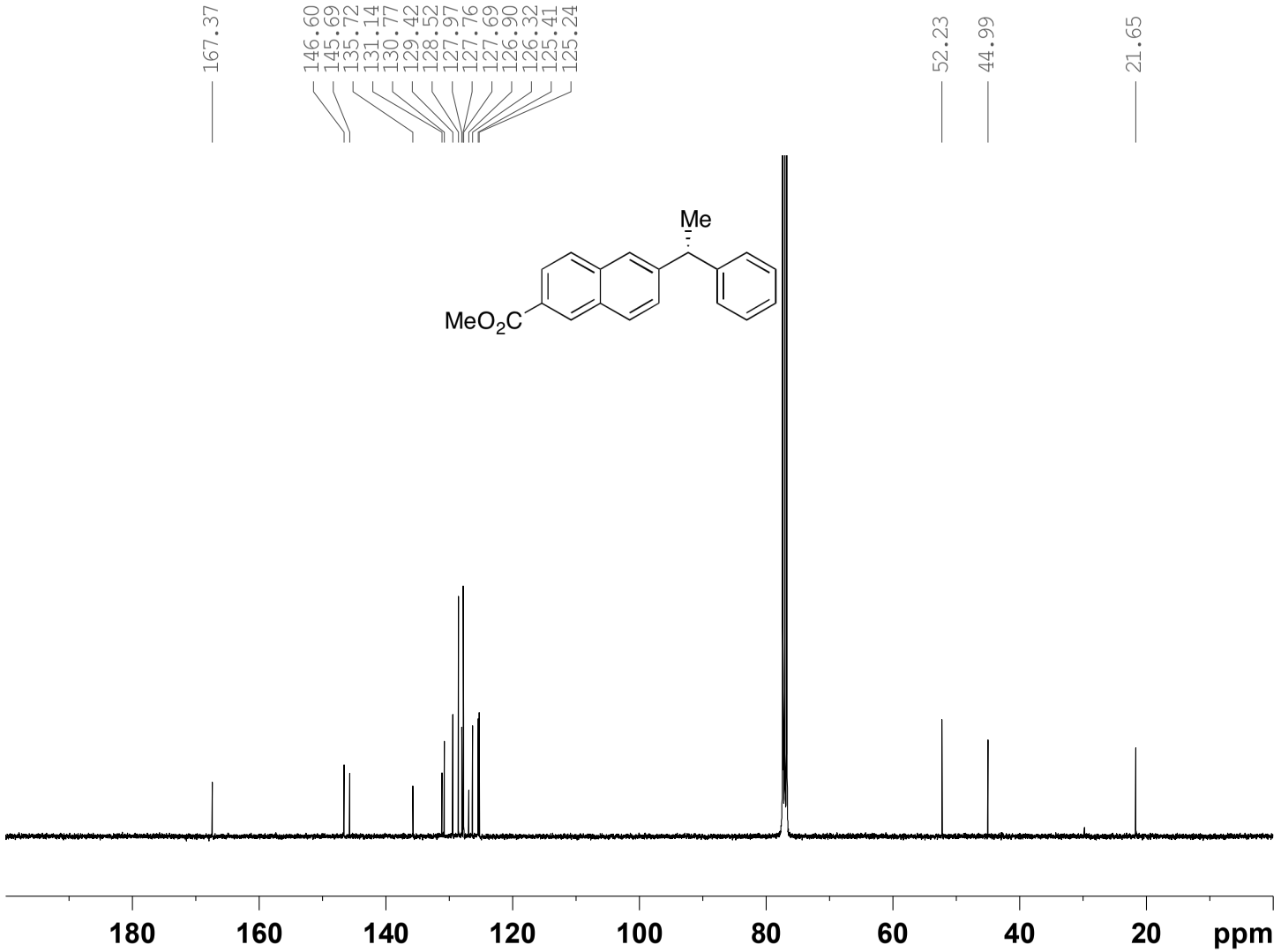
Current Data Parameters
NAME HH-4-143A
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130124
Time 14.48
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 9
DW 60.400 usec
DE 6.00 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1

CHANNEL f1
NUC1 1H
P1 15.00 usec
PL1 4.90 dB
PL1W 3.30822015 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300104 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound 2.38 13C NMR



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Current Data Parameters
NAME HH-4-143A
EXPNO 2
PROCNO 1

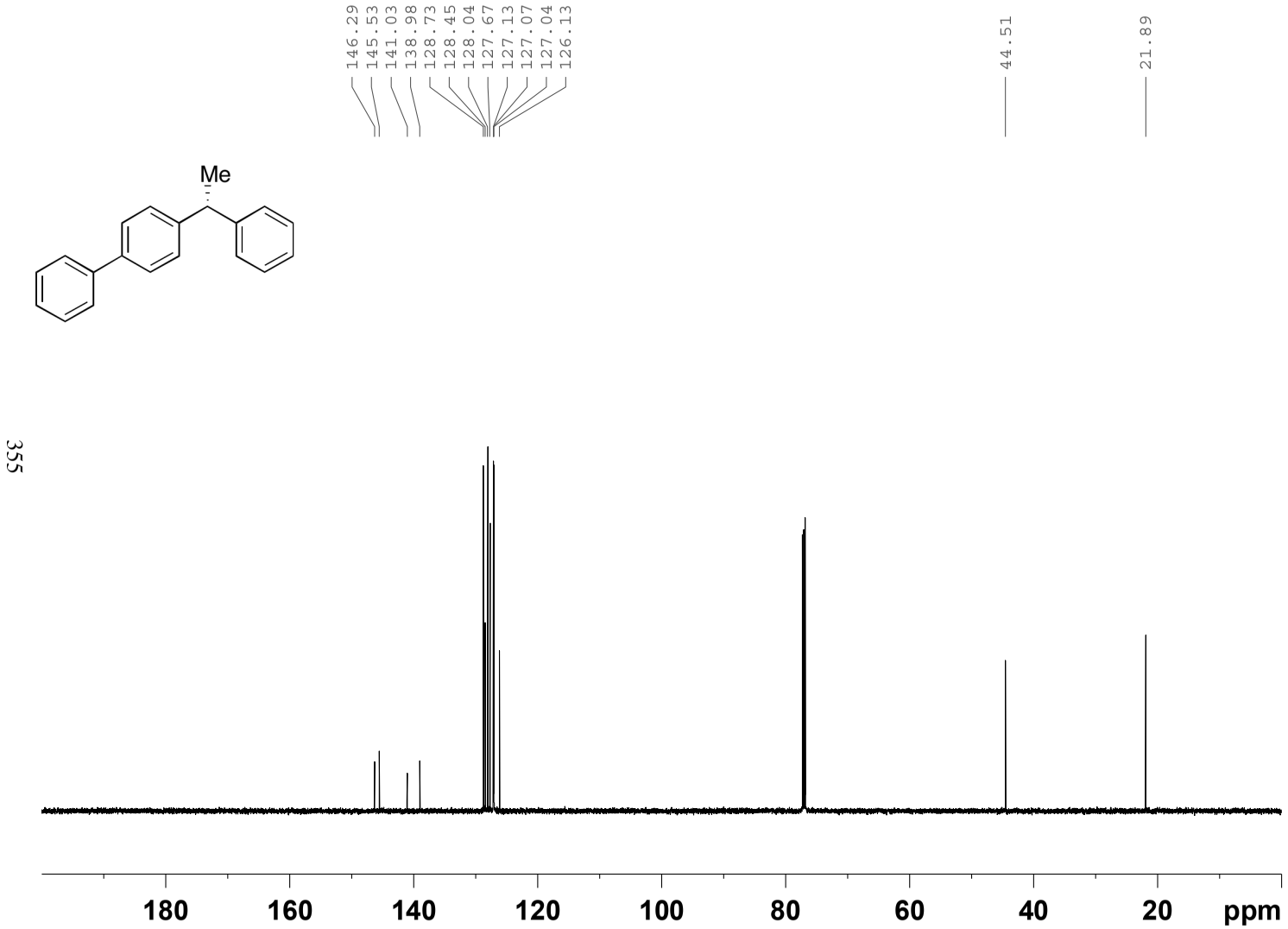
F2 - Acquisition Parameters
Date_ 20130124
Time 23.45
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 512
DW 20.850 usec
DE 18.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.25 usec
PL1 0.55 dB
PL1W 35.18820572 W
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 4.90 dB
PL12 20.46 dB
PL13 21.00 dB
PL2W 3.30822015 W
PL12W 0.09195905 W
PL13W 0.08120718 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Compound 2.39 13 C NMR



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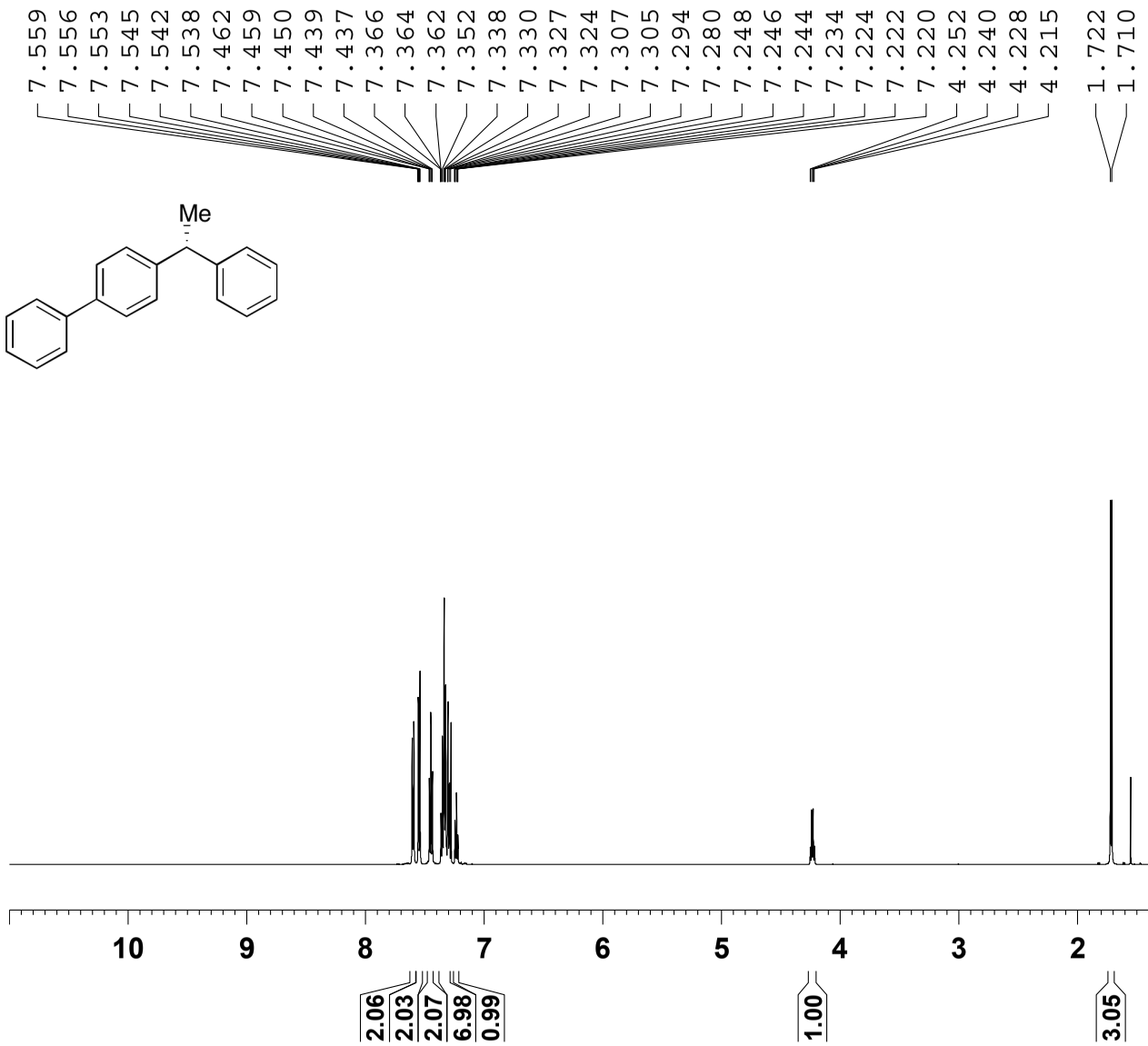
```
Current Data Parameters
NAME      QZ-Compound 23
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20121209
Time               14.18
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg55
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    4
SWH           34722.223 Hz
FIDRES         0.529819 Hz
AQ            0.9437684 sec
RG                 2050
DW               14.400 usec
DE                19.34 usec
TE                298.1 K
D1           1.10000002 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        150.9656784 MHz
NUC1                13C
P1                10.63 usec

F2 - Processing parameters
SI                32768
SF          150.9505840 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

Compound 2.39 1HNMR



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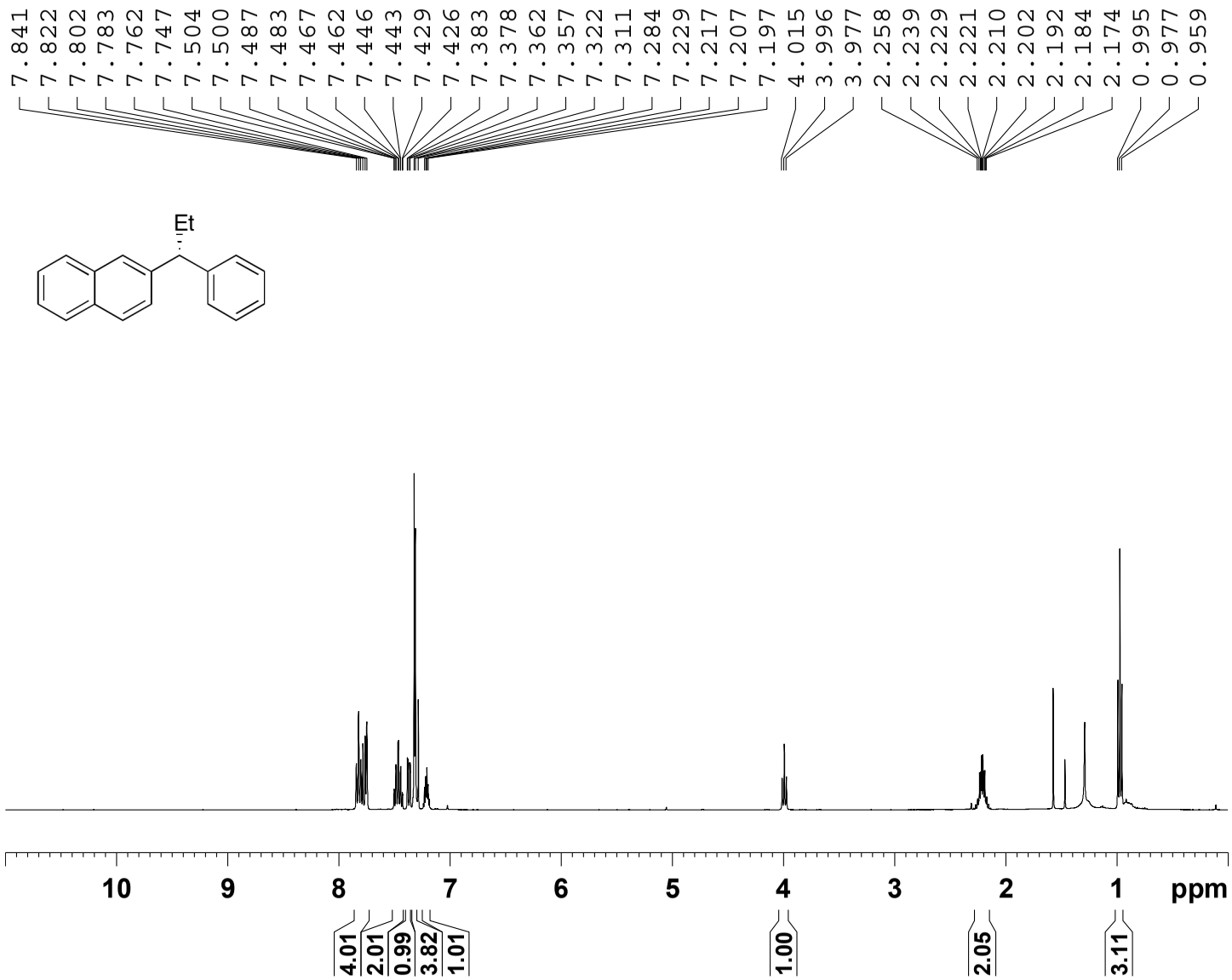
Current Data Parameters
NAME QZ-Compound 23
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121209
Time 14.07
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8403.361 Hz
FIDRES 0.128225 Hz
AQ 3.8994420 sec
RG 114
DW 59.500 usec
DE 17.39 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 600.3233018 MHz
NUC1 1H
P1 10.77 usec

F2 - Processing parameters
SI 65536
SF 600.3200047 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound 2.40 1H NMR



Current Data Parameters

NAME	SDG-2-165-1
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20121115
Time	16.14
INSTRUM	spect
PROBHD	5 mm CPQNP 1H/
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	9
DW	60.400 usec
DE	6.00 usec
TE	298.2 K
D1	1.00000000 sec
TD0	1

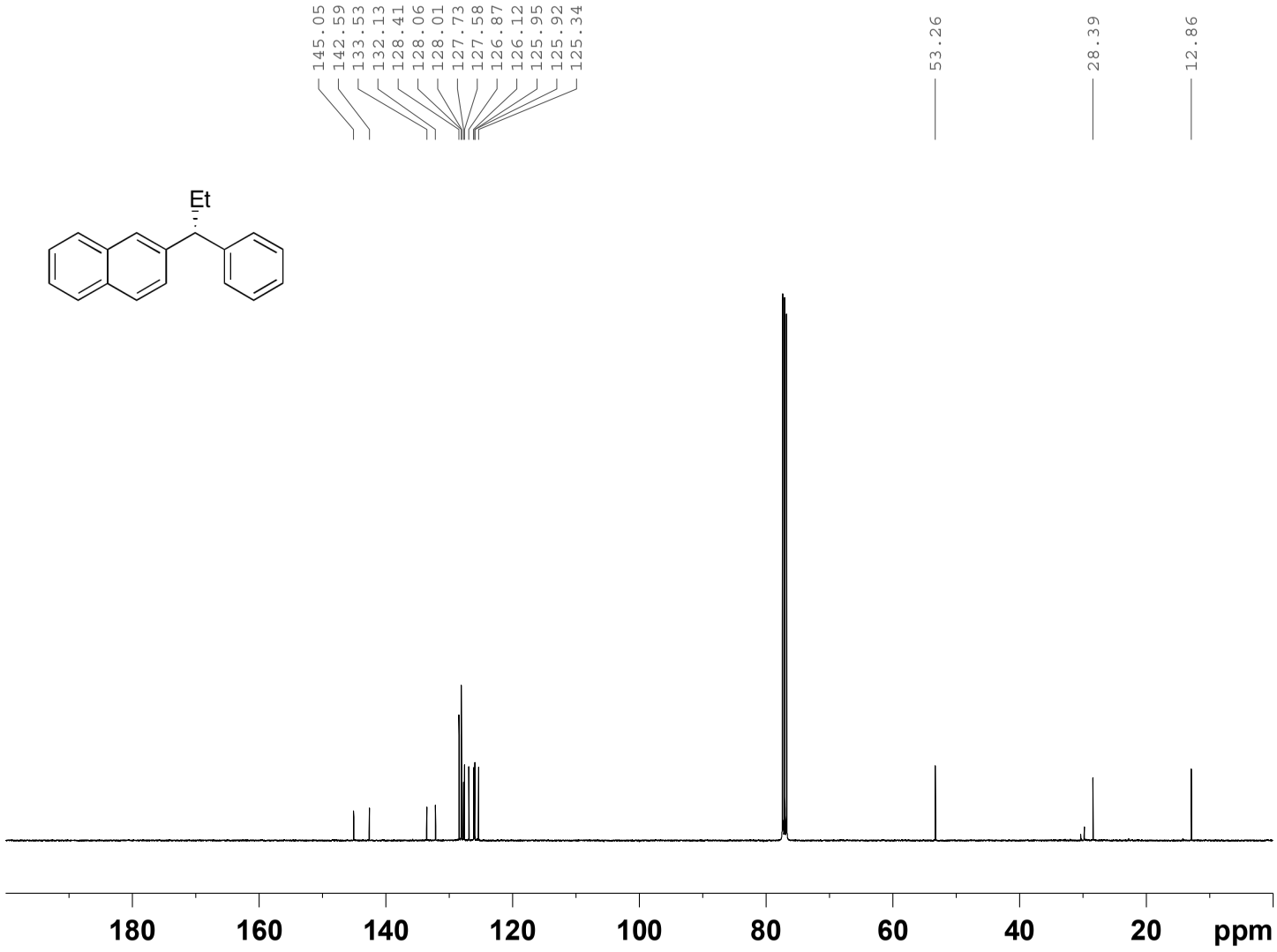
======== CHANNEL f1 ========

NUC1	1H
P1	15.00 usec
PL1	4.90 dB
PL1W	3.30822015 W
SFO1	400.1324710 MHz

F2 - Processing parameters

SI	32768
SF	400.1300000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Compound **2.40** 13C NMR



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```
Current Data Parameters
NAME         SDG-2-165-1
EXPNO                  2
PROCNO                 1

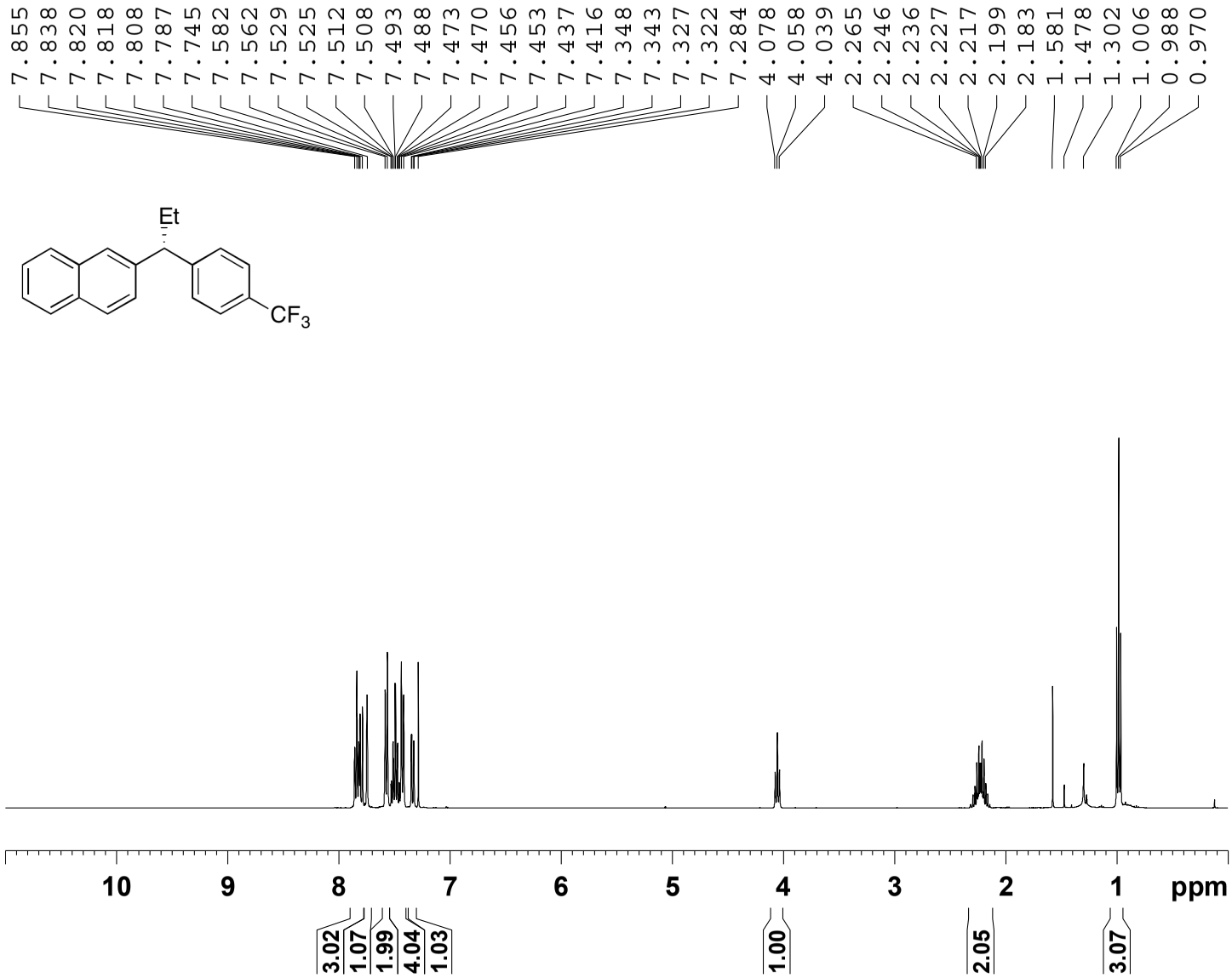
F2 - Acquisition Parameters
Date_           20121115
Time               22.41
INSTRUM            spect
PROBHD   5 mm CPQNP 1H/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ            1.3664756 sec
RG                  512
DW               20.850 usec
DE               18.00 usec
TE               298.1 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                9.25 usec
PL1               0.55 dB
PL1W        35.18820572 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2            90.00 usec
PL2               4.90 dB
PL12             20.46 dB
PL13             21.00 dB
PL2W         3.30822015 W
PL12W        0.09195905 W
PL13W        0.08120718 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127690 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC                1.40
```

Compound **2.41** 1H NMR



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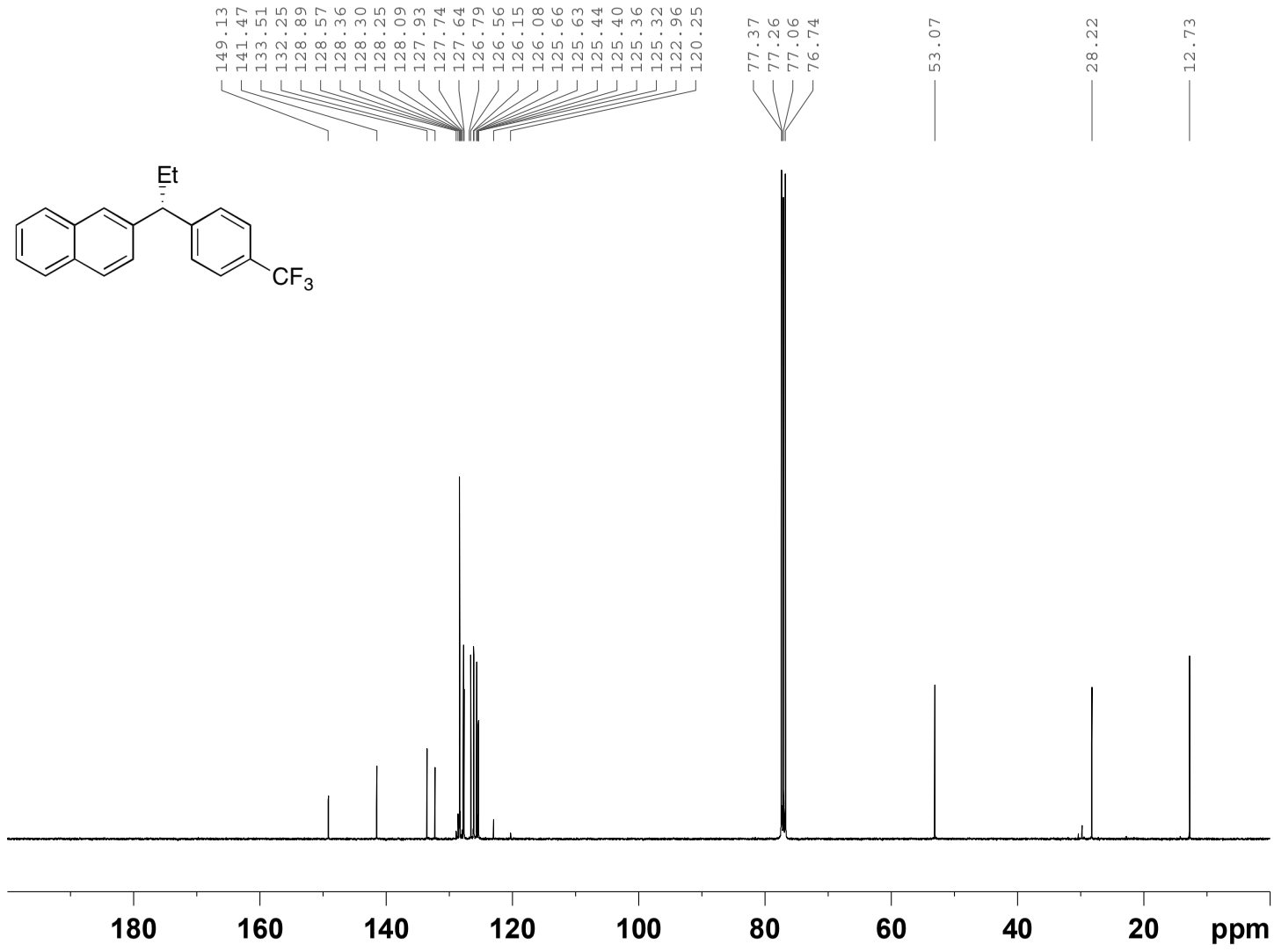
```
Current Data Parameters
NAME                  HH-4-52
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20121117
Time                   4.53
INSTRUM               spect
PROBHD    5 mm CPQNP 1H/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8278.146 Hz
FIDRES             0.126314 Hz
AQ                3.9584243 sec
RG                     12.7
DW                   60.400 usec
DE                    6.00 usec
TE                   298.1 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                    15.00 usec
PL1                    4.90 dB
PL1W           3.30822015 W
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                    32768
SF            400.1300000 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```

Compound **2.41** 13C NMR




```
Current Data Parameters
NAME                 HH-4-52
EXPNO                      2
PROCNO                     1

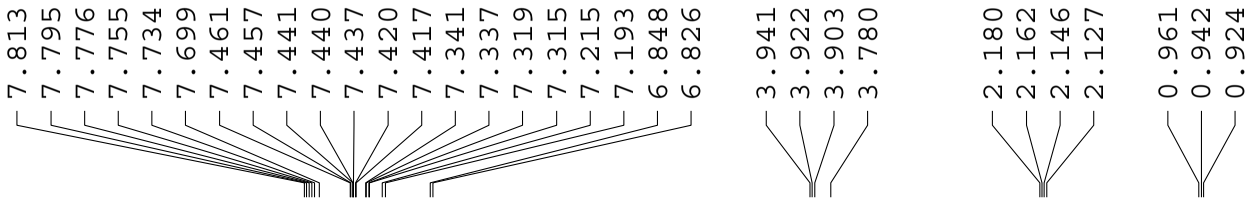
F2 - Acquisition Parameters
Date_               20121117
Time                    5.09
INSTRUM                spect
PROBHD    5 mm CPQNP 1H/
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                        256
DS                          4
SWH                23980.814 Hz
FIDRES              0.365918 Hz
AQ                  1.3664756 sec
RG                        512
DW                     20.850 usec
DE                     18.00 usec
TE                     298.2 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                        1

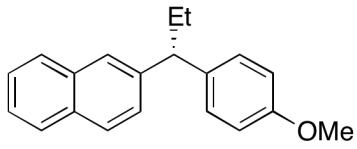
======== CHANNEL f1 ========
NUC1                      13C
P1                     9.25 usec
PL1                    0.55 dB
PL1W            35.18820572 W
SFO1           100.6228298 MHz

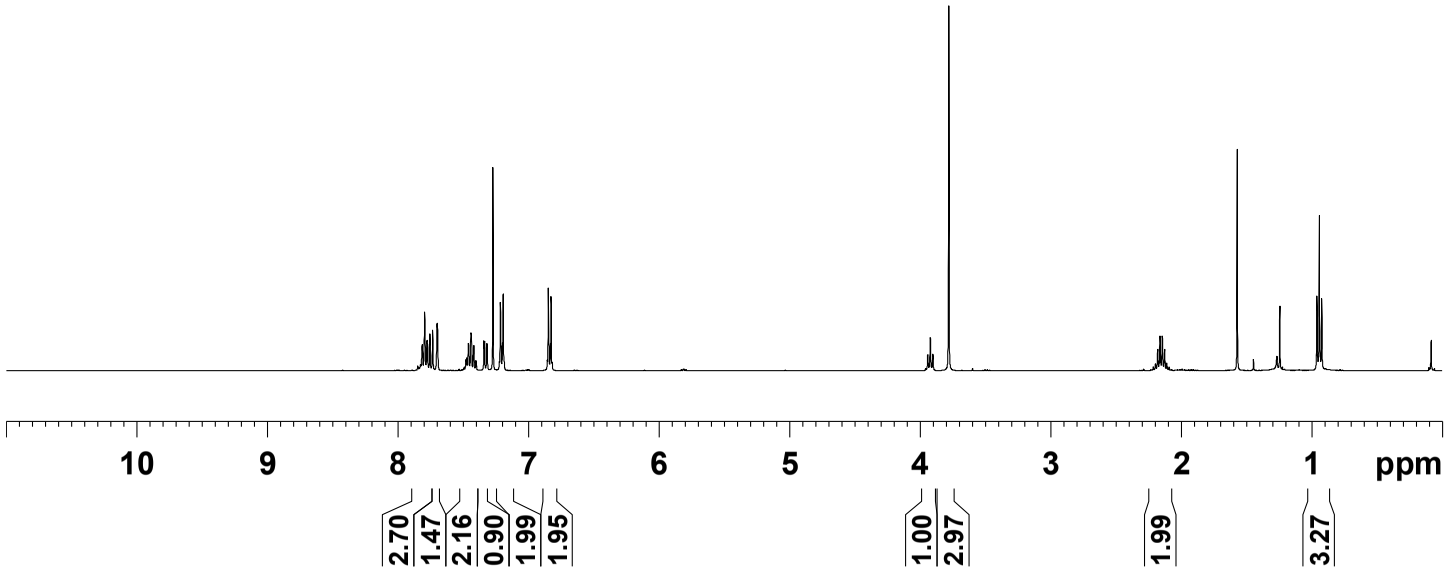
======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                      1H
PCPD2                 90.00 usec
PL2                    4.90 dB
PL12                  20.46 dB
PL13                  21.00 dB
PL2W            3.30822015 W
PL12W           0.09195905 W
PL13W           0.08120718 W
SFO2           400.1316005 MHz

F2 - Processing parameters
SI                     32768
SF              100.6127690 MHz
WDW                       EM
SSB                        0
LB                     1.00 Hz
GB                         0
PC                     1.40
```

Compound **2.42** 1H NMR







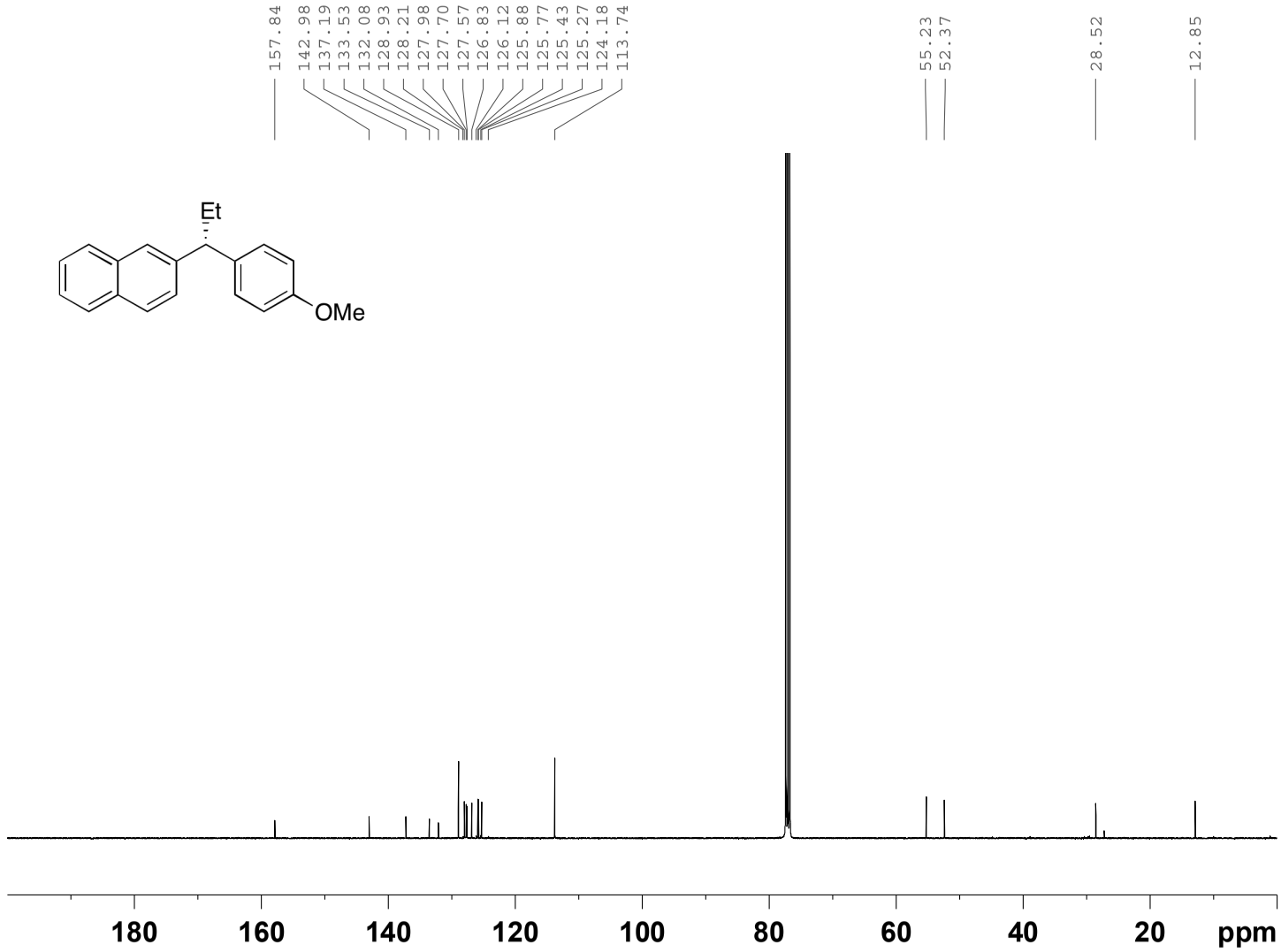

```
Current Data Parameters
NAME          SDG-2-164A
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20121118
Time                6.09
INSTRUM            spect
PROBHD   5 mm CPQNP 1H/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                   100
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ              3.9584243 sec
RG                     9
DW                60.400 usec
DE                 6.00 usec
TE                298.2 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                15.00 usec
PL1                4.90 dB
PL1W          3.30822015 W
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300049 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                1.00
```

Compound **2.42** 13C NMR



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```
Current Data Parameters
NAME          SDG-2-164A
EXPNO                  2
PROCNO                 1

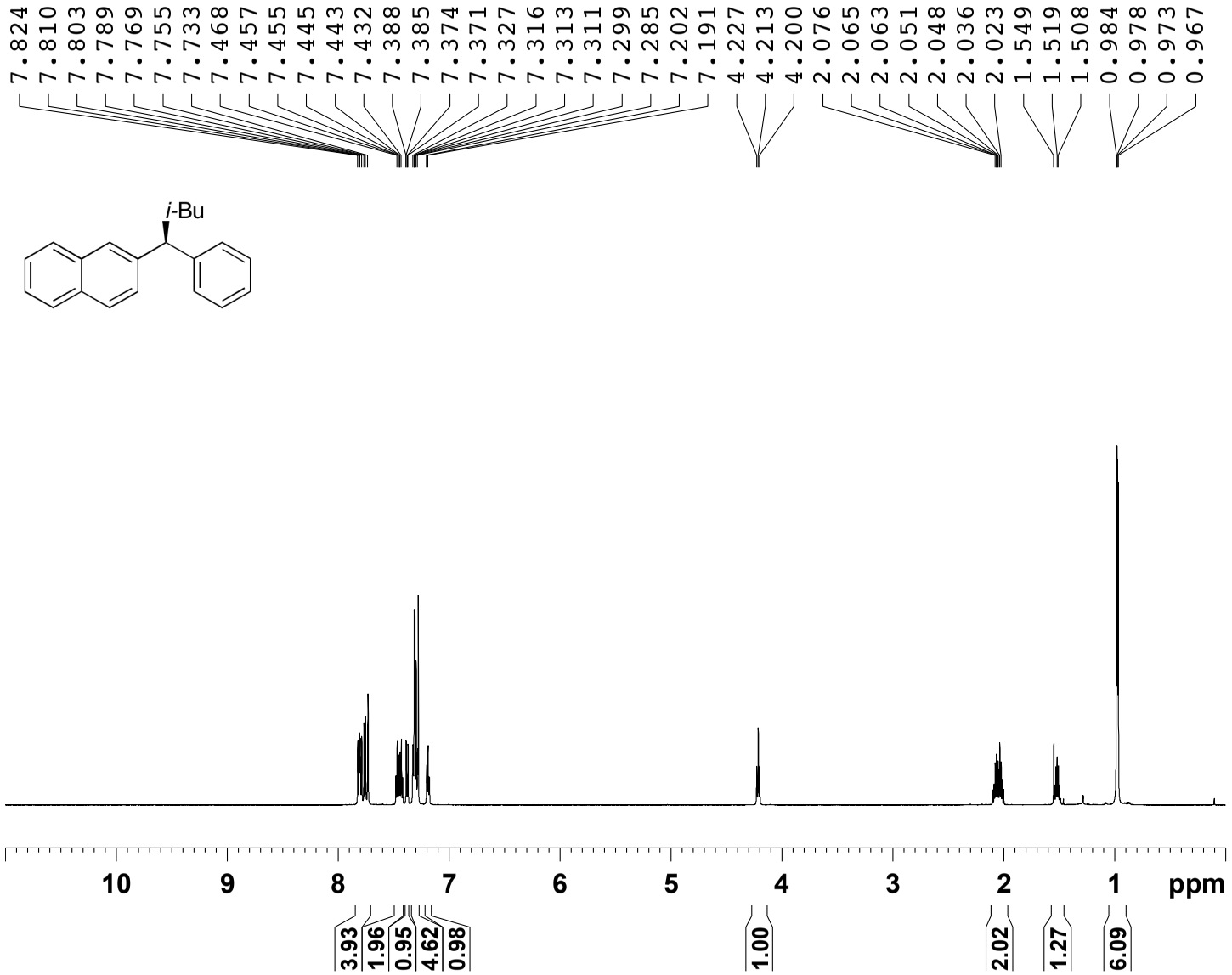
F2 - Acquisition Parameters
Date_           20121118
Time                7.09
INSTRUM            spect
PROBHD   5 mm CPQNP 1H/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ            1.3664756 sec
RG                   512
DW              20.850 usec
DE              18.00 usec
TE                298.1 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                9.25 usec
PL1               0.55 dB
PL1W        35.18820572 W
SFO1       100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2            90.00 usec
PL2               4.90 dB
PL12             20.46 dB
PL13             21.00 dB
PL2W         3.30822015 W
PL12W        0.09195905 W
PL13W        0.08120718 W
SFO2       400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127690 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                 1.40
```

Compound 2.43 1H NMR



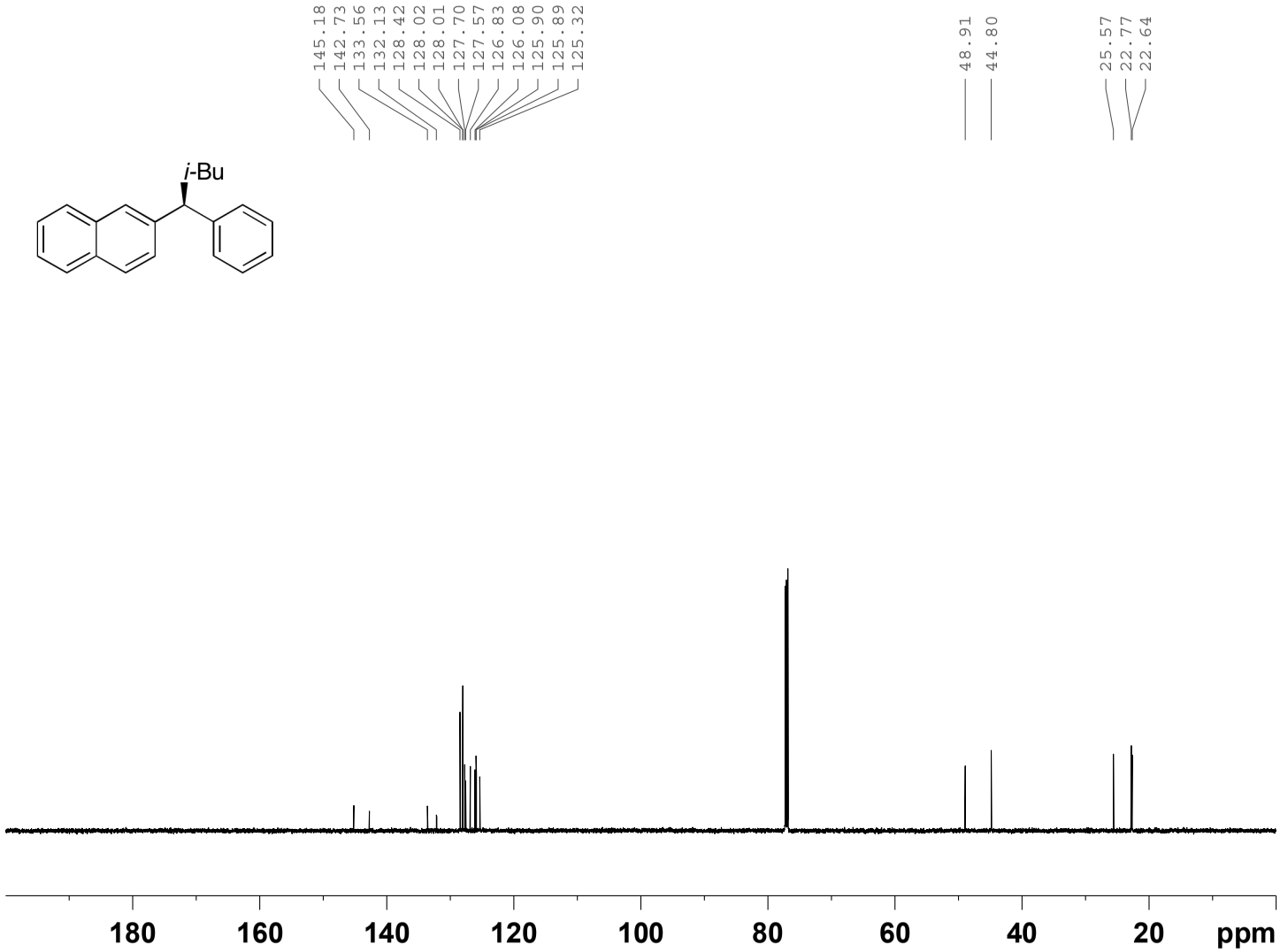

```
Current Data Parameters
NAME            HH-4-087B
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20121129
Time                11.12
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8403.361 Hz
FIDRES          0.128225 Hz
AQ              3.8994420 sec
RG                   256
DW                59.500 usec
DE                 9.10 usec
TE                298.1 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.3233018 MHz
NUC1                   1H
P1                 14.80 usec

F2 - Processing parameters
SI                 65536
SF           600.3200044 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

Compound **2.43** 13 CNMR



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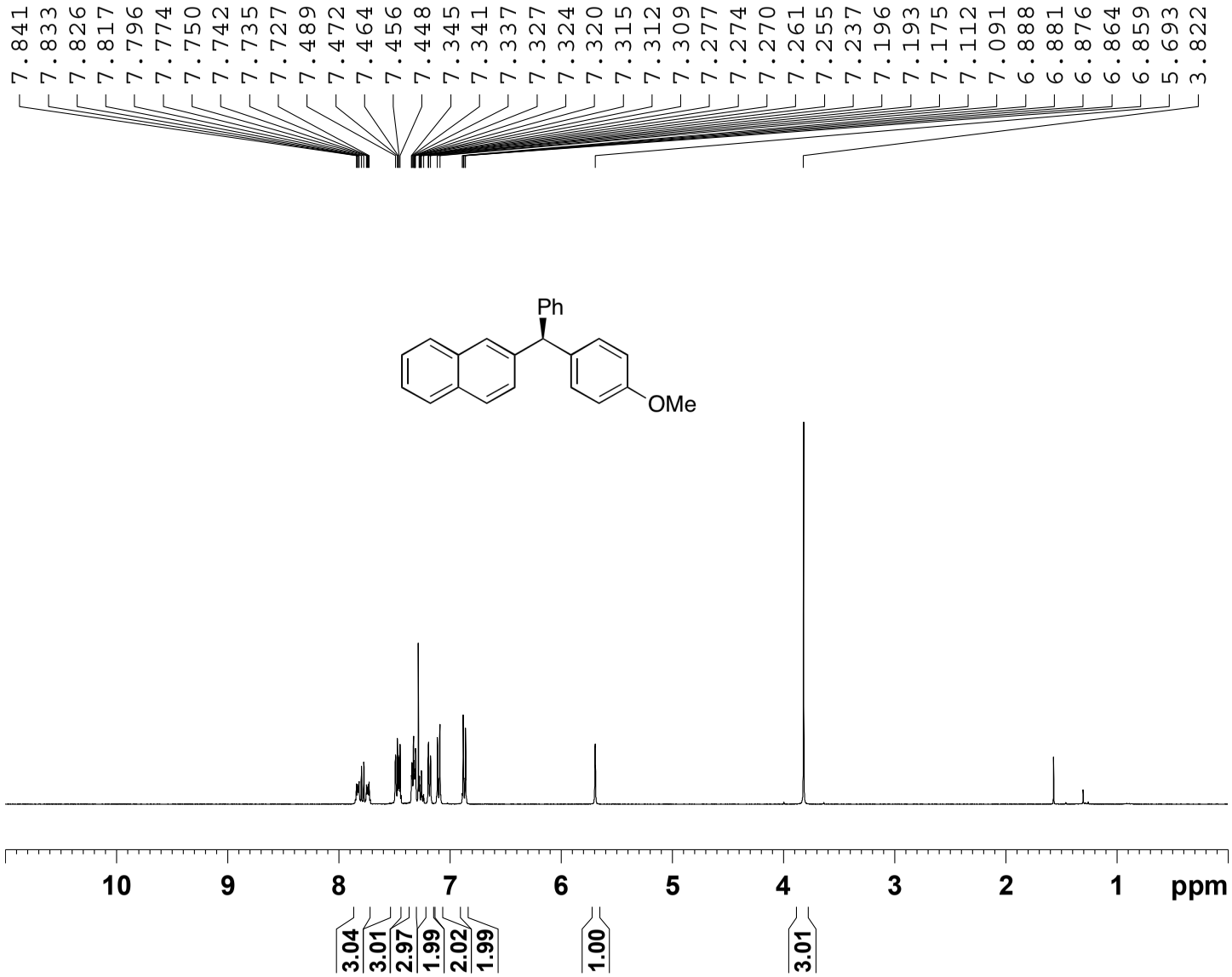
Current Data Parameters
NAME HH-4-087B
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121129
Time 11.22
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg55
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 34722.223 Hz
FIDRES 0.529819 Hz
AQ 0.9437684 sec
RG 2050
DW 14.400 usec
DE 8.88 usec
TE 298.1 K
D1 1.10000002 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 150.9656784 MHz
NUC1 13C
P1 9.00 usec

F2 - Processing parameters
SI 32768
SF 150.9505840 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Compound 2.44 1H NMR



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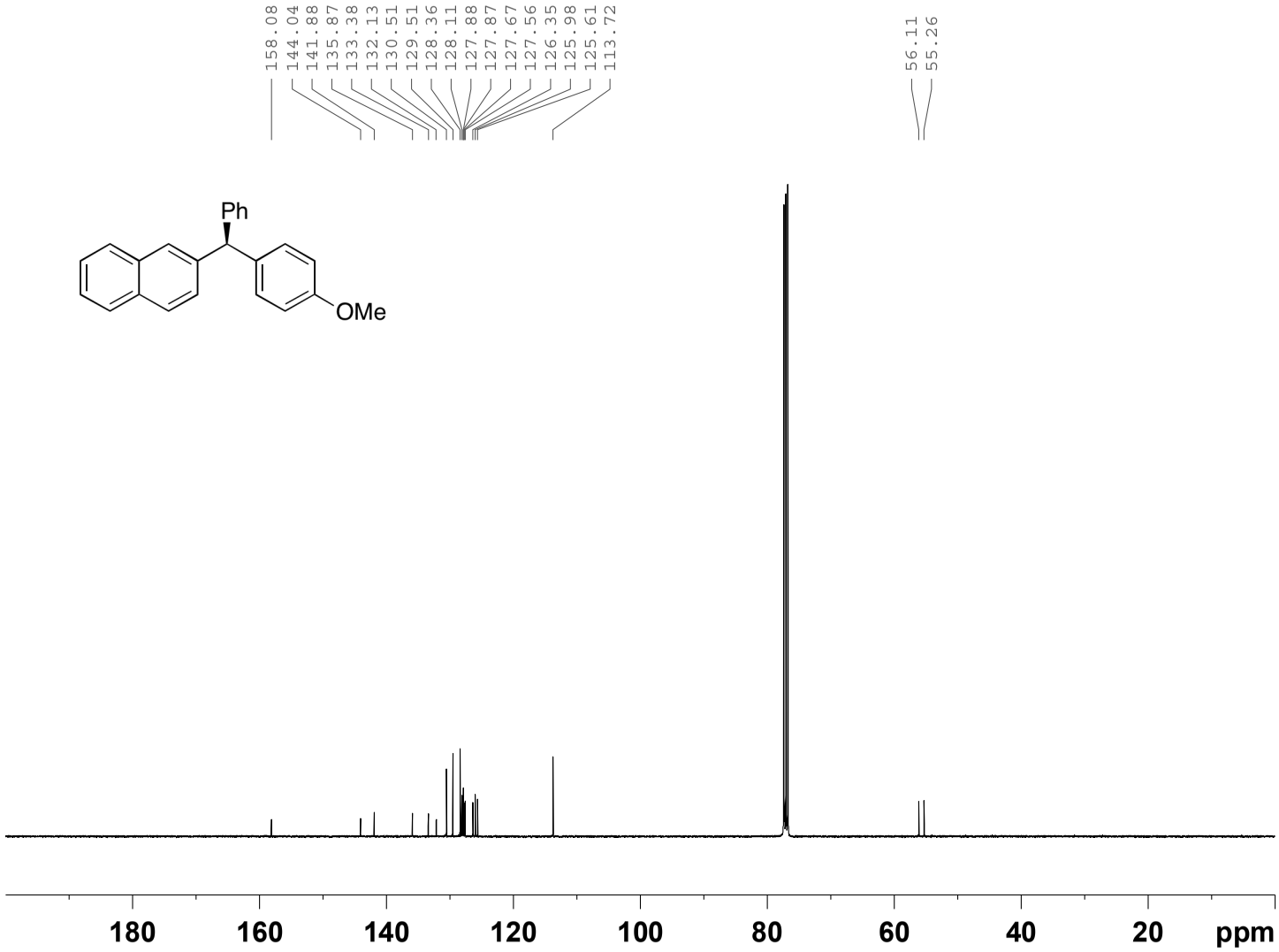
Current Data Parameters
NAME HH-4-082A
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121122
Time 18.07
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 4
DW 60.400 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 4.90 dB
PL1W 3.30822015 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound **2.44** 13C NMR



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Current Data Parameters

NAME	HH-4-082A
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20121122
Time	18.28
INSTRUM	spect
PROBHD	5 mm CPQNP 1H/
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	256
DS	4
SWH	23980.814 Hz
FIDRES	0.365918 Hz
AQ	1.3664756 sec
RG	512
DW	20.850 usec
DE	18.00 usec
TE	298.1 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1

======== CHANNEL f1 ========

NUC1	13C
P1	9.25 usec
PL1	0.55 dB
PL1W	35.18820572 W
SFO1	100.6228298 MHz

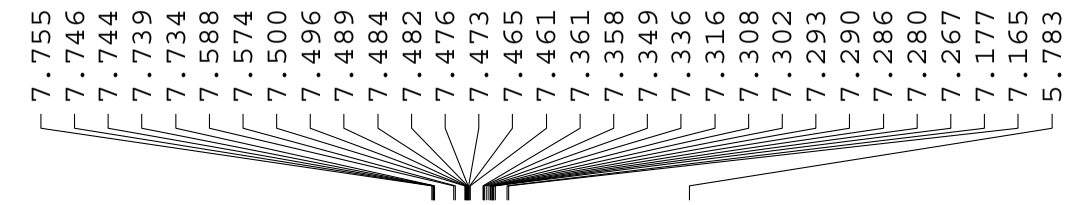
======== CHANNEL f2 ========

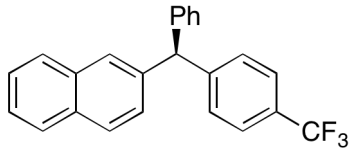
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	4.90 dB
PL12	20.46 dB
PL13	21.00 dB
PL2W	3.30822015 W
PL12W	0.09195905 W
PL13W	0.08120718 W
SFO2	400.1316005 MHz

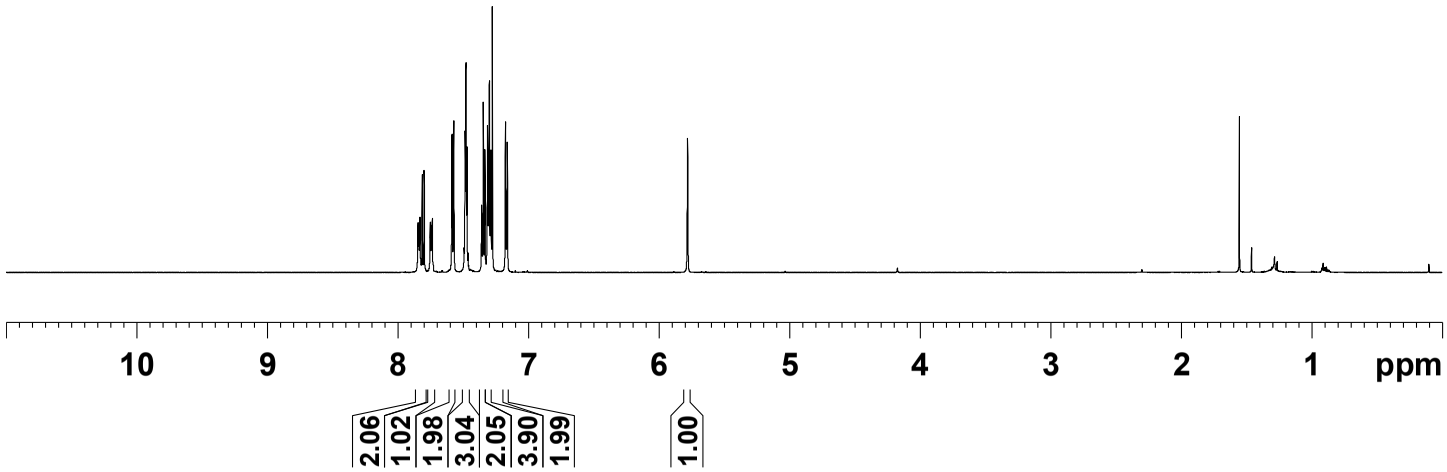
F2 - Processing parameters

SI	32768
SF	100.6127690 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

Compound 2.45 1H NMR







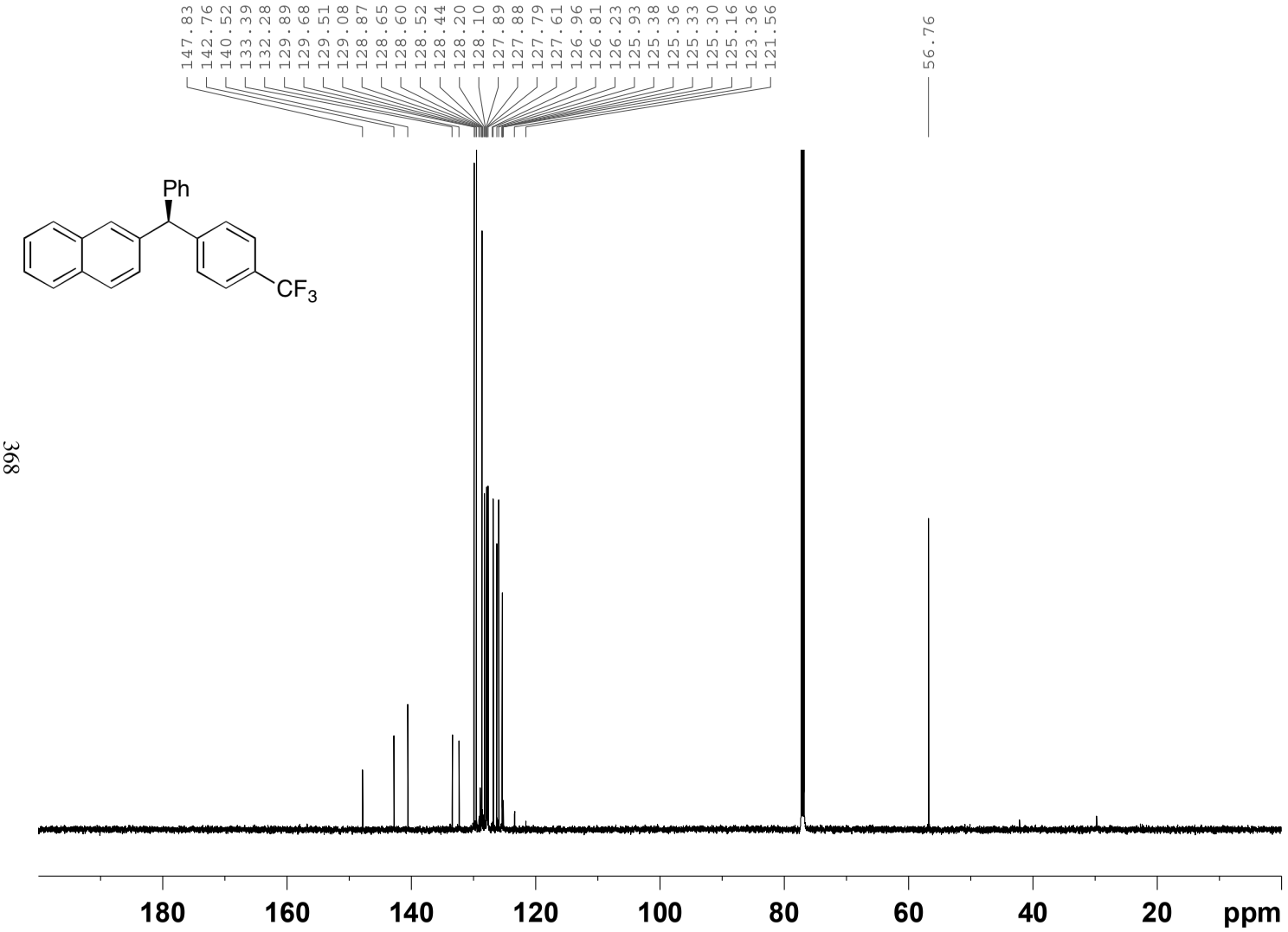
Current Data Parameters
NAME QZ-3-139rs
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121130
Time 11.35
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8403.361 Hz
FIDRES 0.128225 Hz
AQ 3.8994420 sec
RG 256
DW 59.500 usec
DE 9.10 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 600.3233018 MHz
NUC1 1H
P1 14.80 usec

F2 - Processing parameters
SI 65536
SF 600.3200039 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound **2.45** 13C NMR

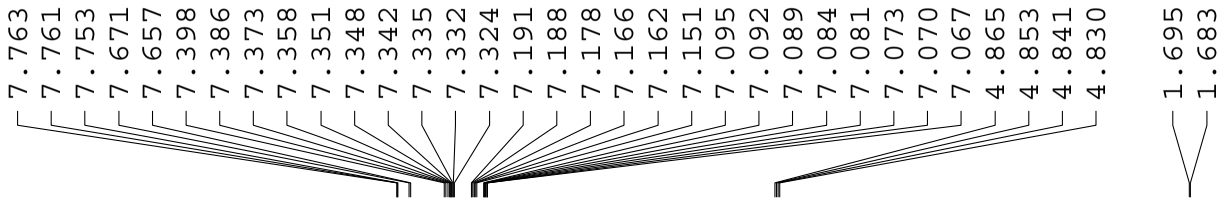


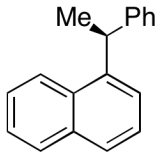

```
Current Data Parameters
NAME      QZ-3-139 3rd tim
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20121210
Time                 18.42
INSTRUM              spect
PROBHD    5 mm PABBO BB/
PULPROG             zgpg55
TD                   65536
SOLVENT              CDCl3
NS                    1024
DS                       4
SWH             34722.223 Hz
FIDRES           0.529819 Hz
AQ              0.9437684 sec
RG                    2050
DW                14.400 usec
DE                 19.34 usec
TE                 298.1 K
D1             2.50000000 sec
D11            0.03000000 sec
TD0                      1

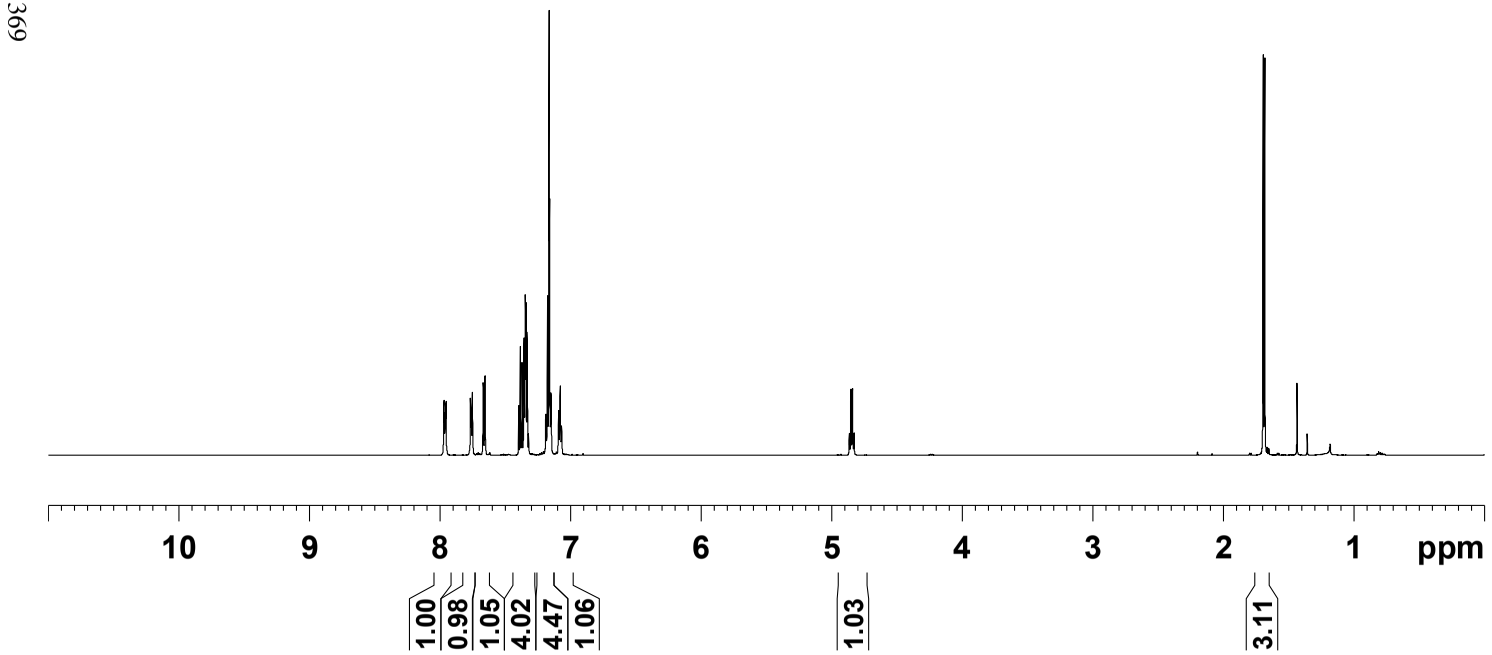
======== CHANNEL f1 ========
SFO1          150.9656784 MHz
NUC1                   13C
P1                 10.63 usec

F2 - Processing parameters
SI                   32768
SF            150.9505840 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```





Compound 2.46 1H NMR



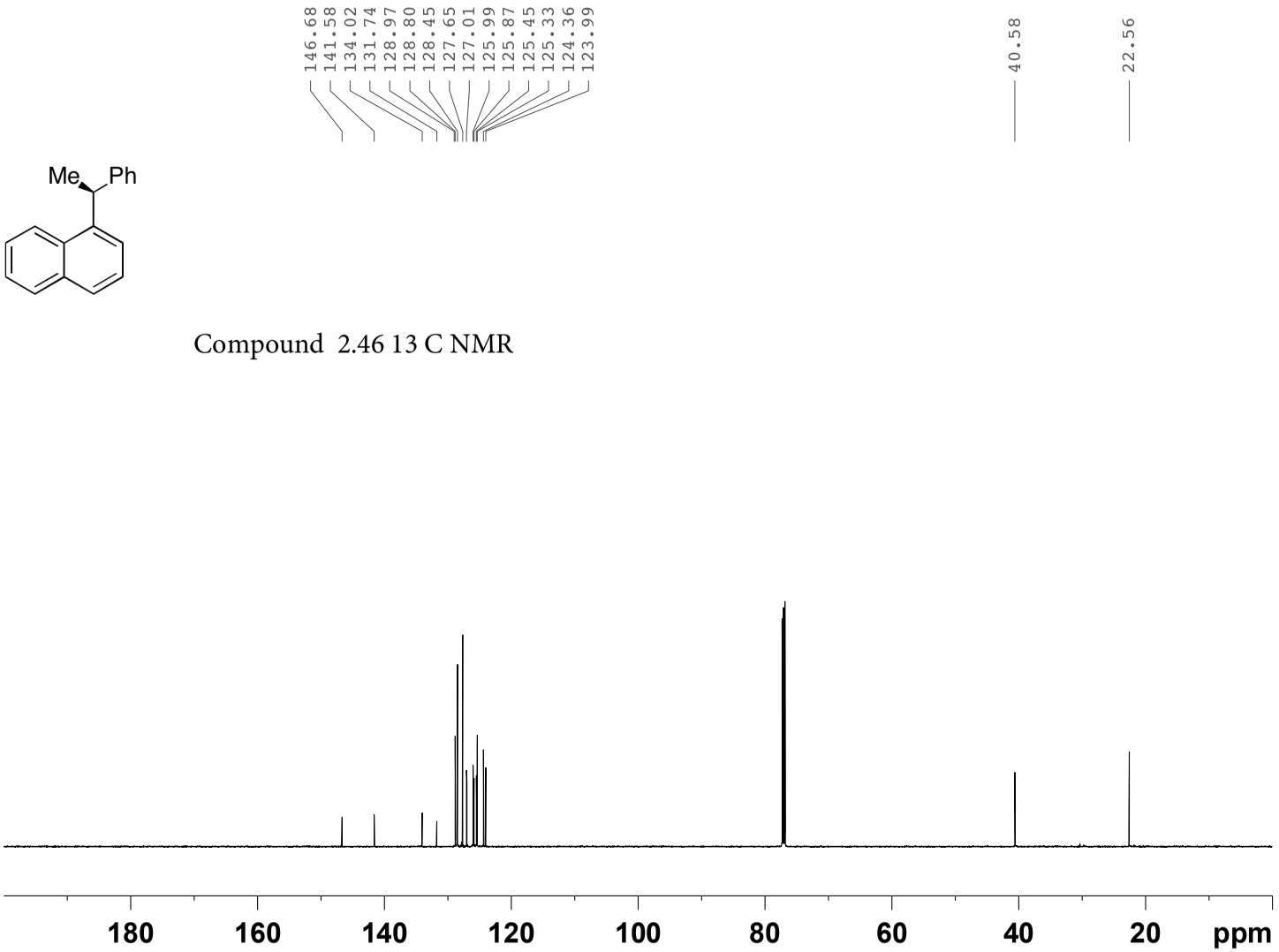

```
Current Data Parameters
NAME            HH-4-088A
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20121129
Time                18.26
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              8403.361 Hz
FIDRES           0.128225 Hz
AQ               3.8994420 sec
RG                    203
DW                 59.500 usec
DE                  9.10 usec
TE                 298.1 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         600.3233018 MHz
NUC1                   1H
P1                 14.80 usec

F2 - Processing parameters
SI                  65536
SF           600.3200718 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

Compound 2.46 13 C NMR



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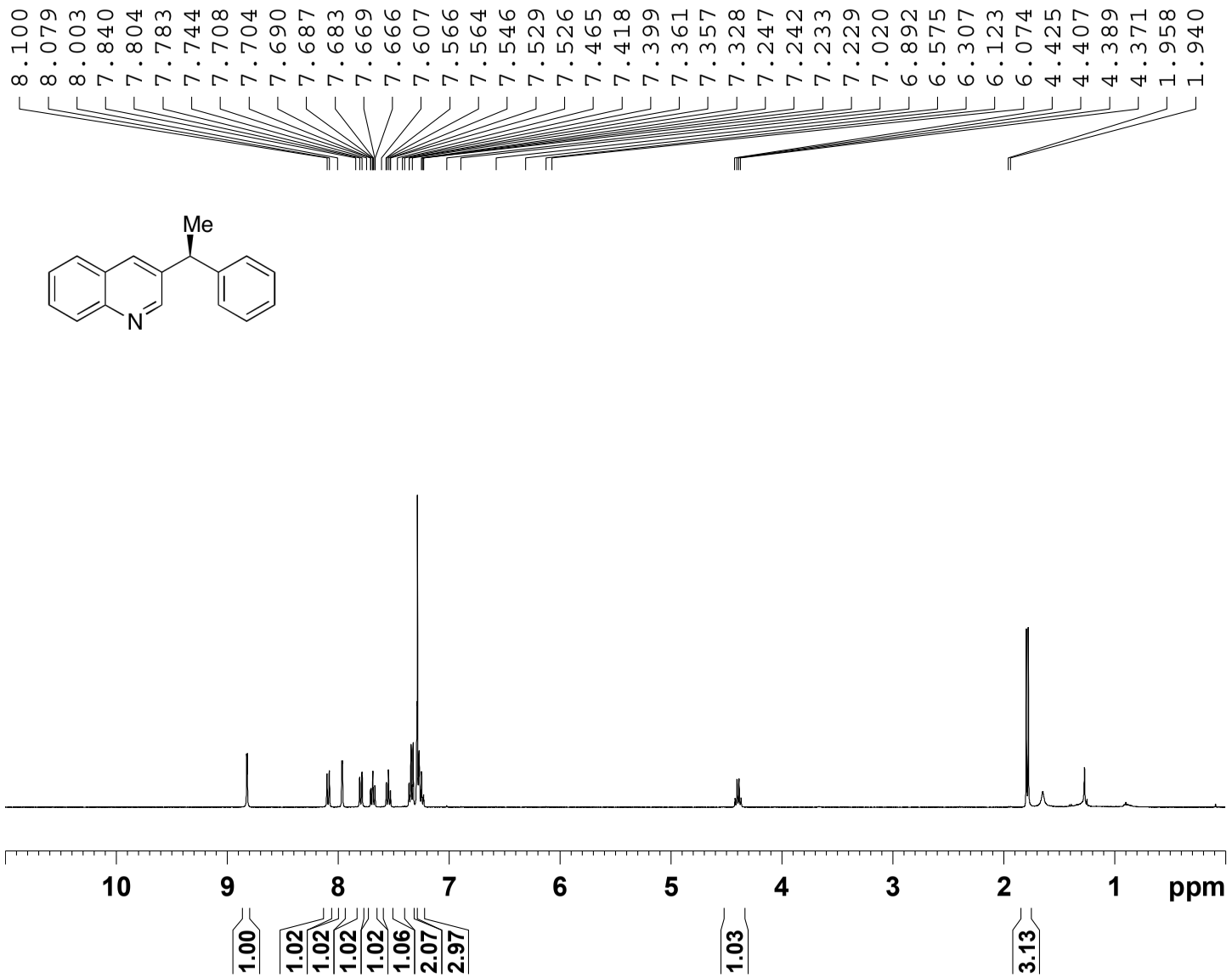
```
Current Data Parameters
NAME            HH-4-088A
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20121129
Time                22.39
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg55
TD                  65536
SOLVENT             CDCl3
NS                   3000
DS                      4
SWH             34722.223 Hz
FIDRES           0.529819 Hz
AQ              0.9437684 sec
RG                   2050
DW                 14.400 usec
DE                  8.88 usec
TE                 298.1 K
D1             1.10000002 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          150.9656784 MHz
NUC1                 13C
P1                  9.00 usec

F2 - Processing parameters
SI                  32768
SF            150.9505840 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

Compound 2.47 1H NMR



Current Data Parameters

NAME	QZ-3-157rs
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20121207
Time	10.02
INSTRUM	spect
PROBHD	5 mm CPQNP 1H/
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	6.3
DW	60.400 usec
DE	6.00 usec
TE	298.2 K
D1	1.00000000 sec
TD0	1

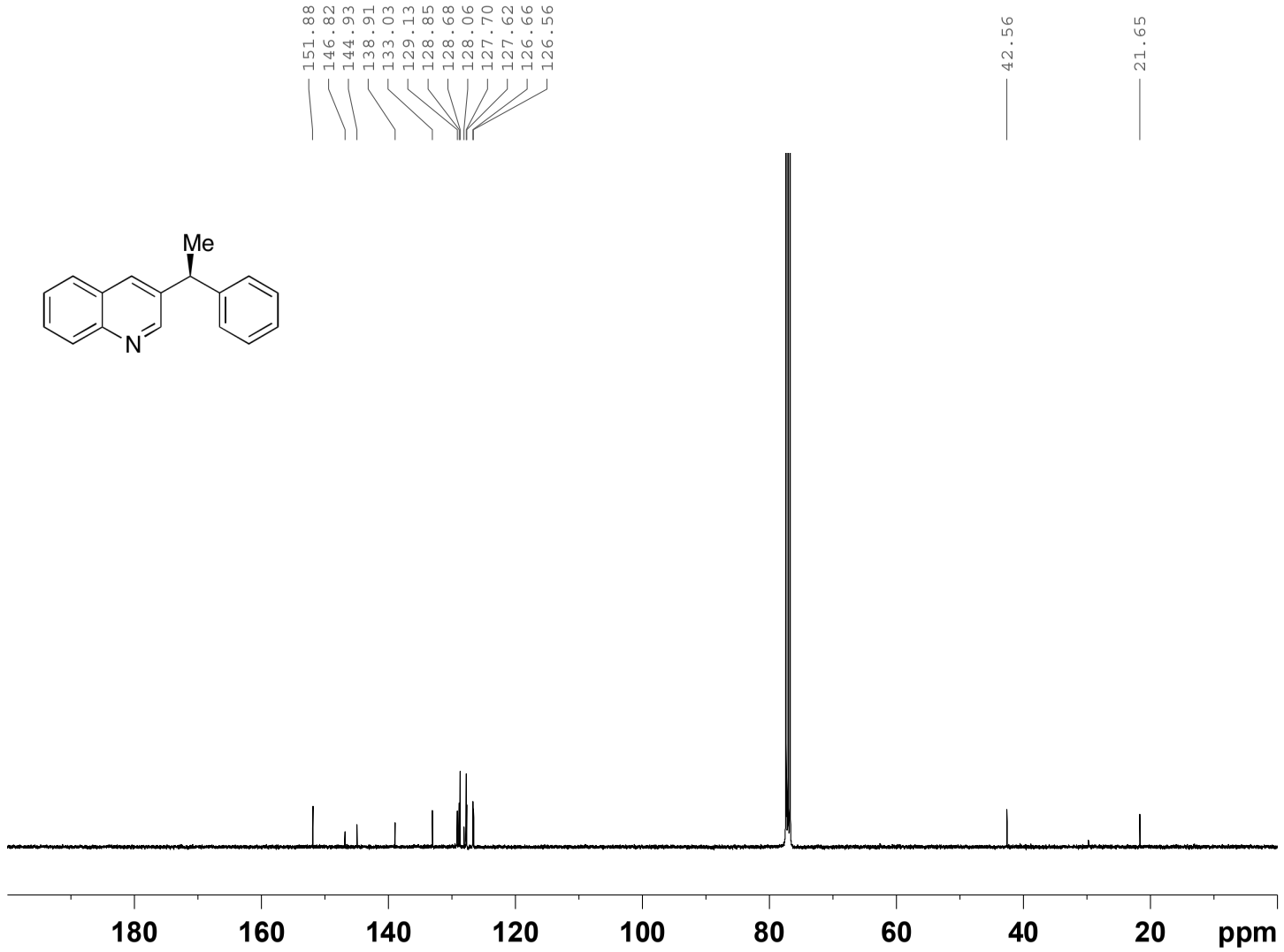
======== CHANNEL f1 ========

NUC1	1H
P1	15.00 usec
PL1	4.90 dB
PL1W	3.30822015 W
SFO1	400.1324710 MHz

F2 - Processing parameters

SI	32768
SF	400.1300000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Compound 2.47 13 C NMR



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S84

```
Current Data Parameters
NAME          QZ-3-157rs
EXPNO                  2
PROCNO                 1

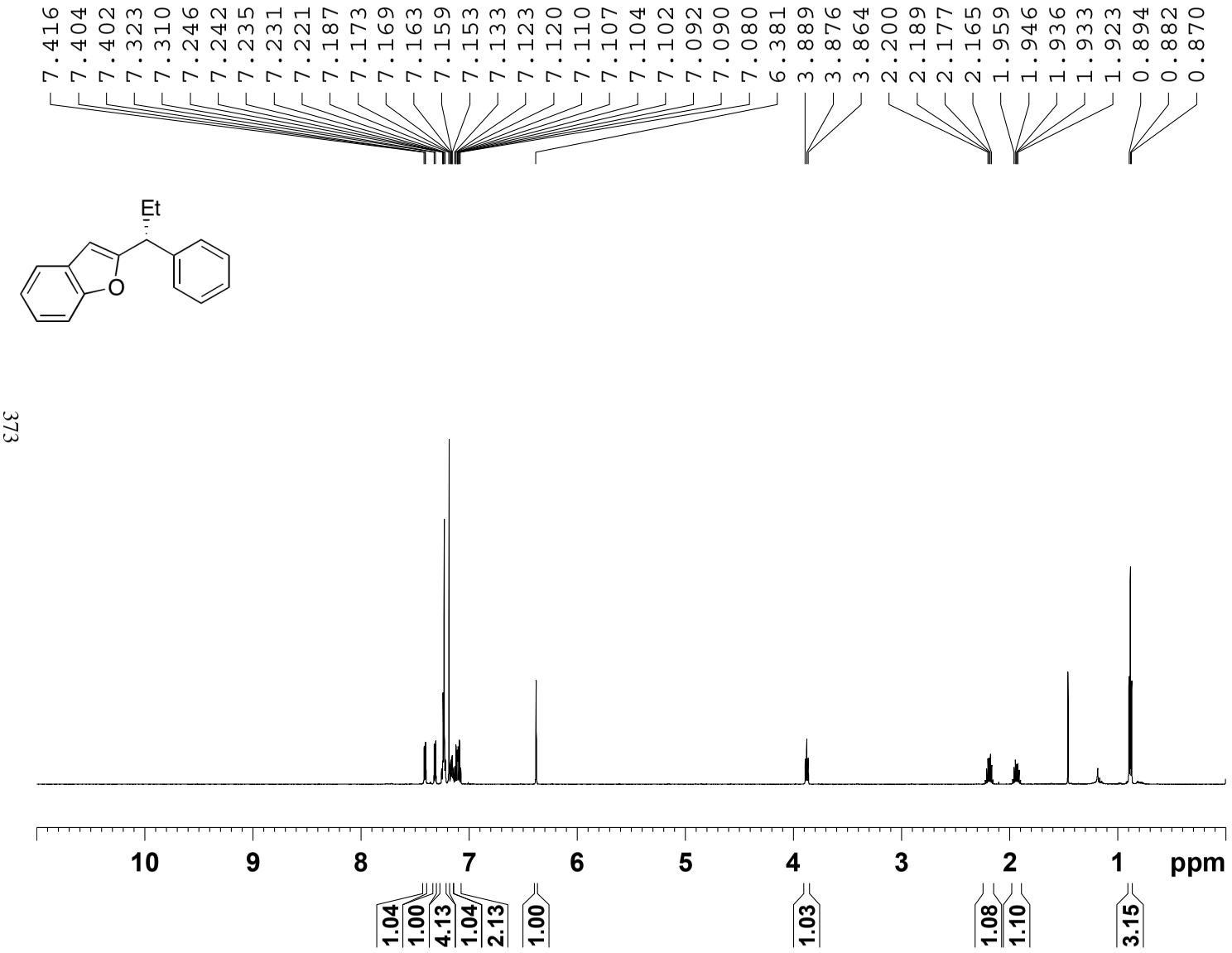
F2 - Acquisition Parameters
Date_           20121207
Time              23.46
INSTRUM           spect
PROBHD   5 mm CPQNP 1H/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ             1.3664756 sec
RG                  512
DW               20.850 usec
DE               18.00 usec
TE               298.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                9.25 usec
PL1               0.55 dB
PL1W        35.18820572 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2            90.00 usec
PL2               4.90 dB
PL12             20.46 dB
PL13             21.00 dB
PL2W         3.30822015 W
PL12W        0.09195905 W
PL13W        0.08120718 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127690 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC                1.40
```

Compound 2.48 1H NMR

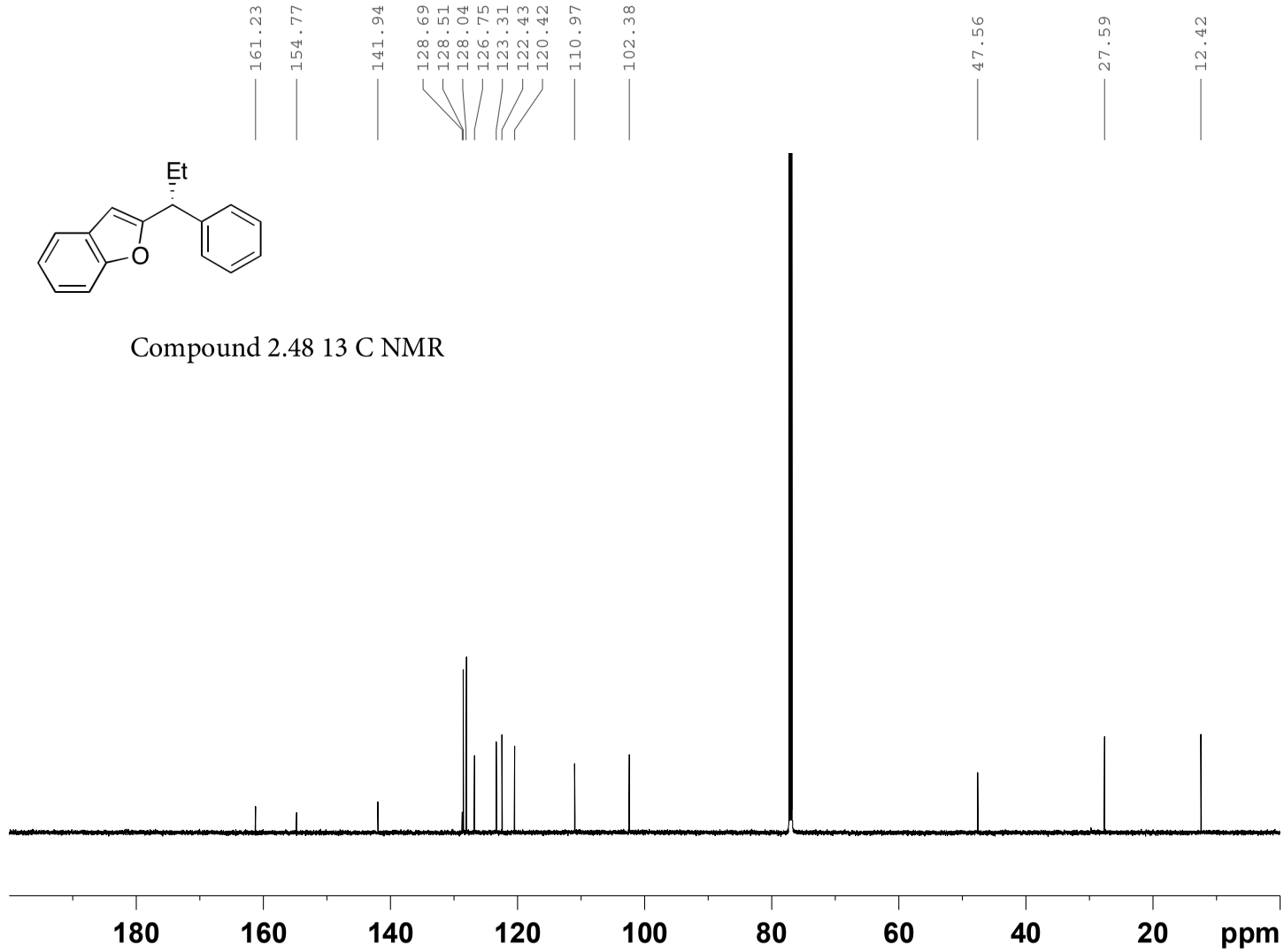



```
Current Data Parameters
NAME      HH-4-083 3rd time
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20121126
Time                  1.46
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       8
DS                       2
SWH              8403.361 Hz
FIDRES           0.128225 Hz
AQ               3.8994420 sec
RG                     362
DW                59.500 usec
DE                 9.10 usec
TE                 298.1 K
D1             1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1         600.3233018 MHz
NUC1                    1H
P1                 14.80 usec

F2 - Processing parameters
SI                   65536
SF           600.3200598 MHz
WDW                     EM
SSB                      0
LB                  0.30 Hz
GB                       0
PC                    1.00
```



Compound 2.48 13 C NMR

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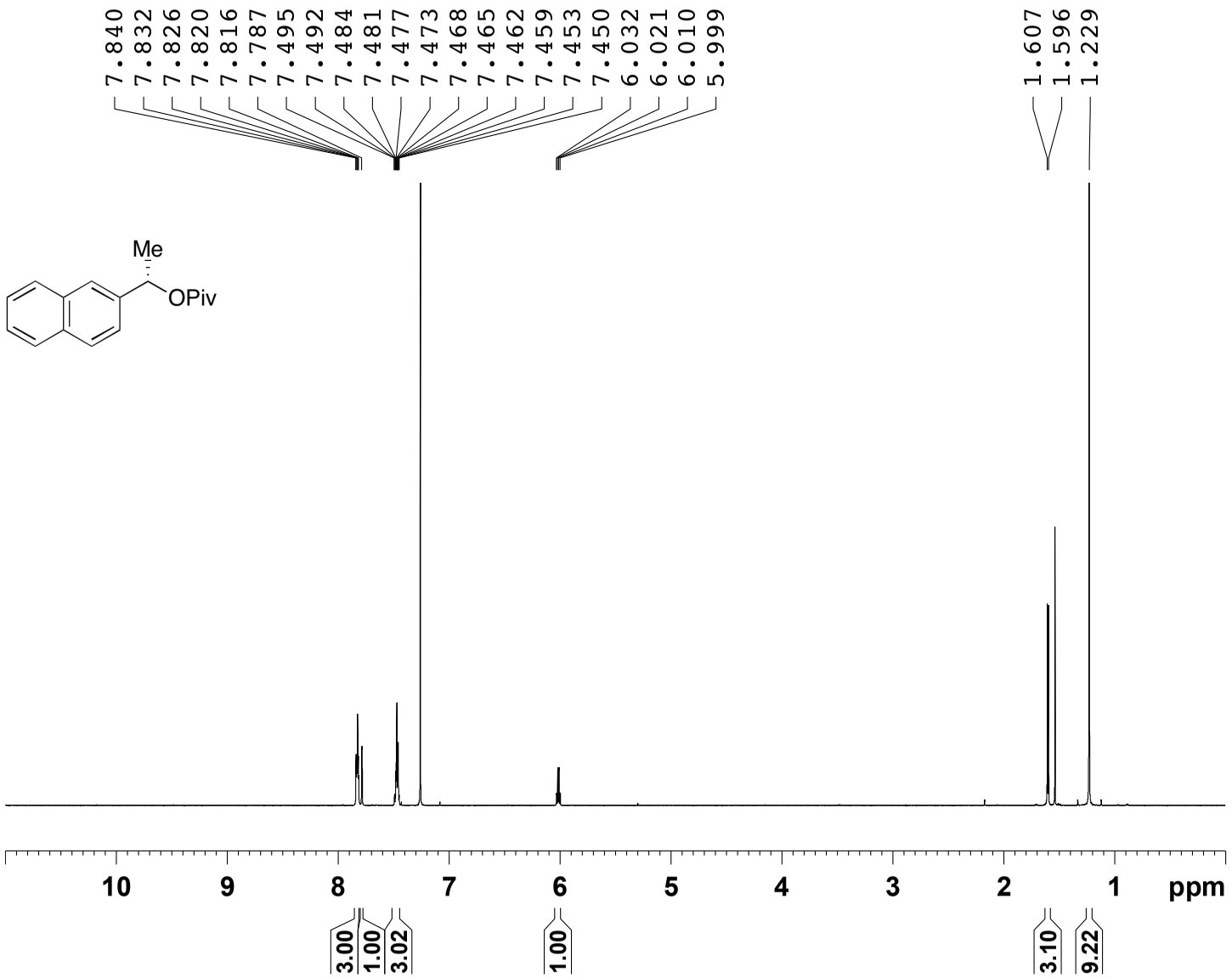
```
Current Data Parameters
NAME      HH-4-083 3rd time
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20121126
Time                 3.32
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg55
TD                  65536
SOLVENT             CDCl3
NS                   3000
DS                      4
SWH            34722.223 Hz
FIDRES          0.529819 Hz
AQ             0.9437684 sec
RG                   2050
DW                14.400 usec
DE                 8.88 usec
TE                 298.1 K
D1            1.10000002 sec
D11           0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         150.9656784 MHz
NUC1                  13C
P1                   9.00 usec

F2 - Processing parameters
SI                   32768
SF           150.9505840 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

Compound 2.25 1H NMR



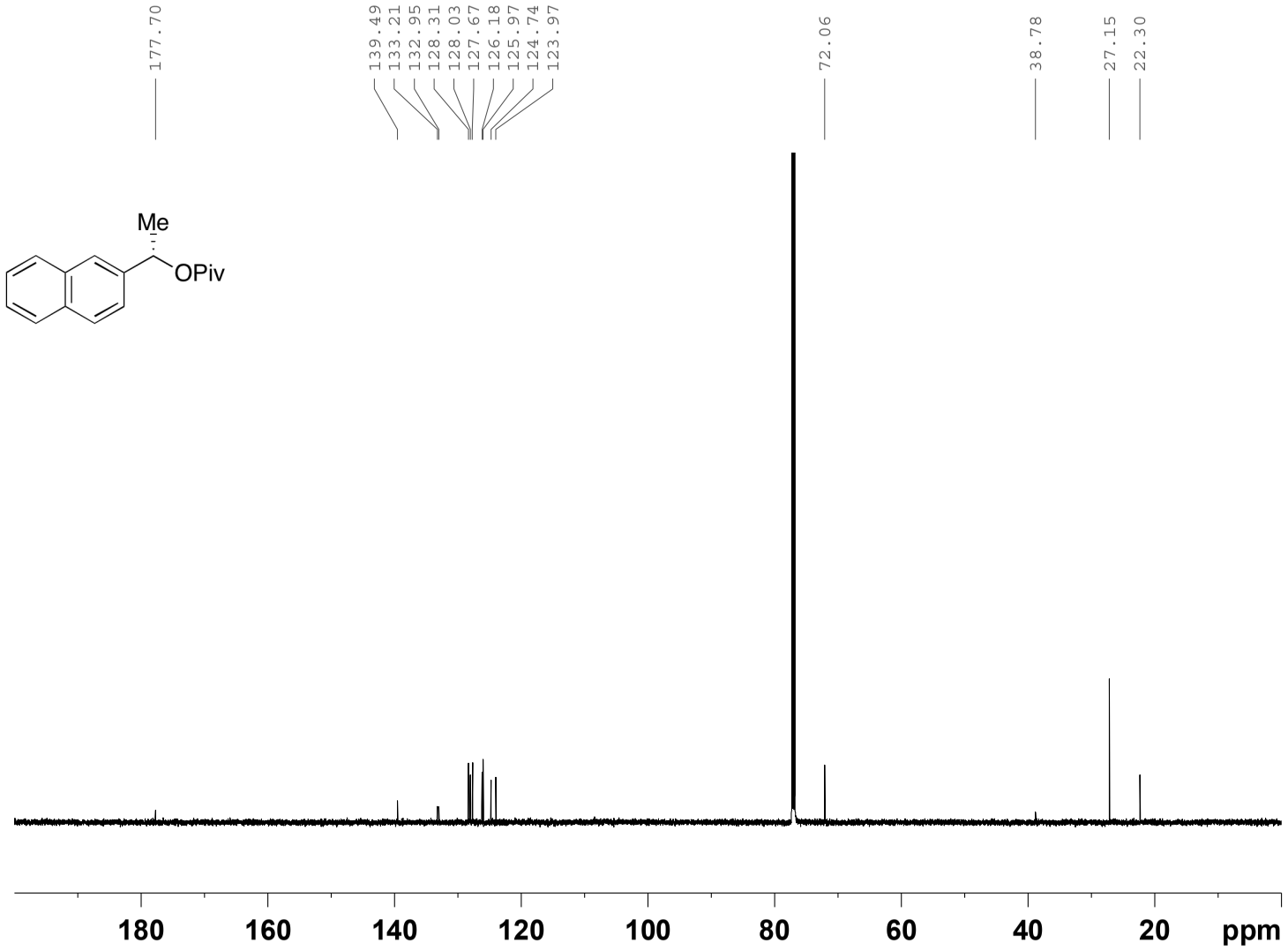

```
Current Data Parameters
NAME          methyl sub
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20121125
Time               18.30
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8403.361 Hz
FIDRES          0.128225 Hz
AQ              3.8994420 sec
RG                   406
DW                59.500 usec
DE                 9.10 usec
TE                298.1 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.3233018 MHz
NUC1                   1H
P1                14.80 usec

F2 - Processing parameters
SI                 65536
SF           600.3200156 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                1.00
```

Compound 2.25 13C NMR



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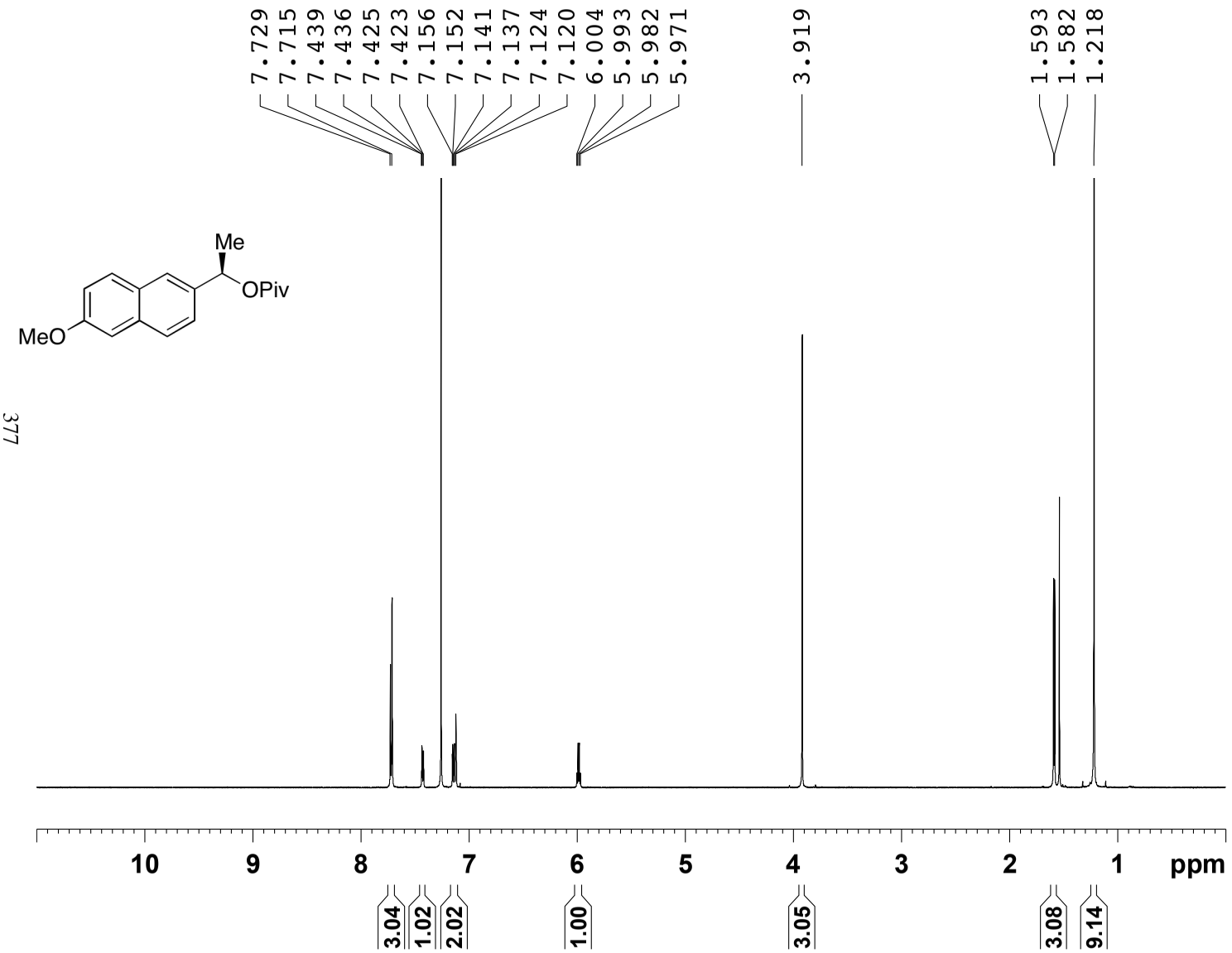
Current Data Parameters
NAME methyl sub
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121125
Time 22.39
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg55
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 34722.223 Hz
FIDRES 0.529819 Hz
AQ 0.9437684 sec
RG 2050
DW 14.400 usec
DE 8.88 usec
TE 298.1 K
D1 1.10000002 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 150.9656784 MHz
NUC1 13C
P1 9.00 usec

F2 - Processing parameters
SI 32768
SF 150.9505840 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Compound 2.54 1H NMR



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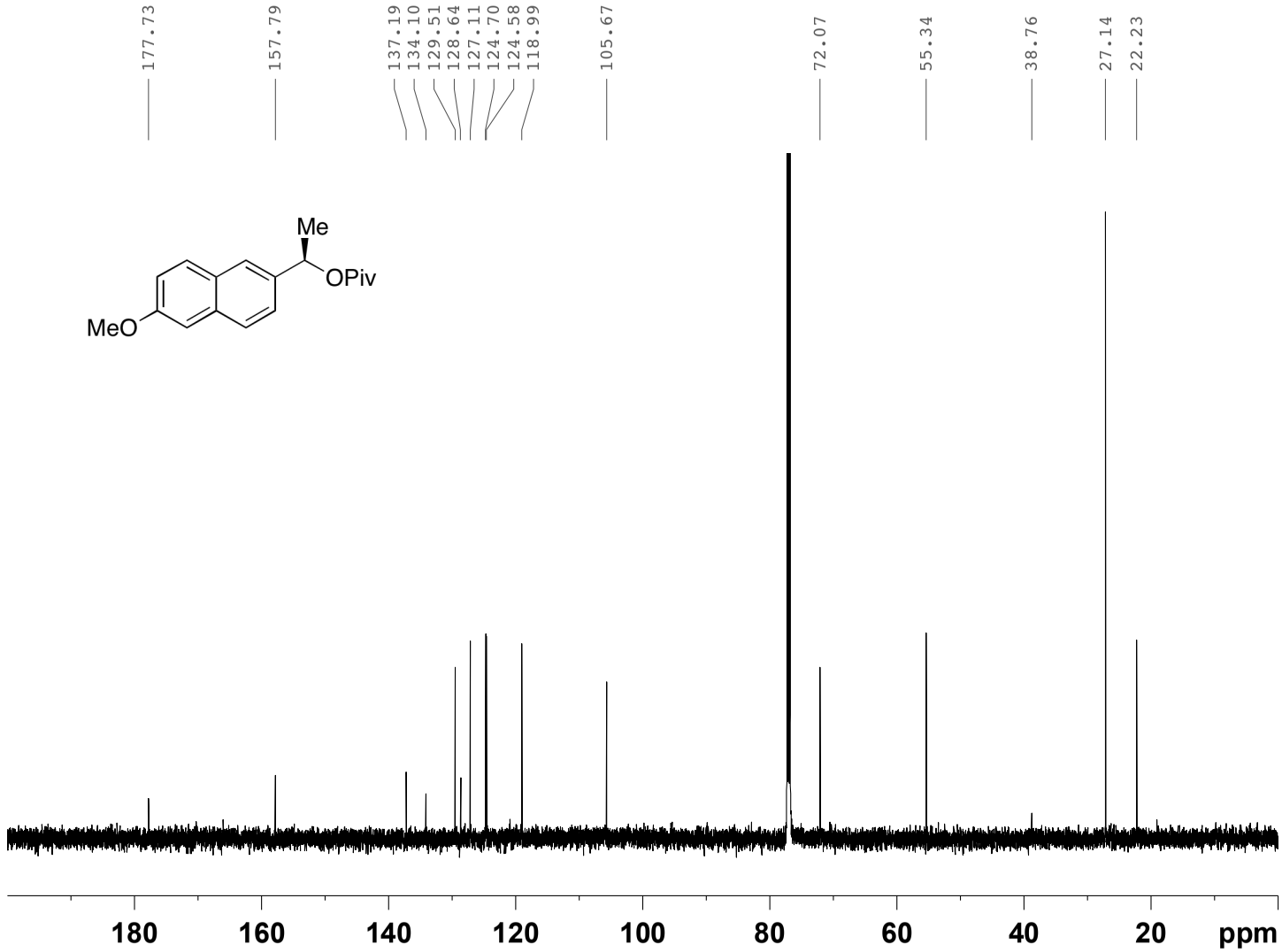
```
Current Data Parameters
NAME        6methoxy piv
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20121125
Time               18.34
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8403.361 Hz
FIDRES          0.128225 Hz
AQ              3.8994420 sec
RG                   406
DW                59.500 usec
DE                 9.10 usec
TE                298.1 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.3233018 MHz
NUC1                   1H
P1                14.80 usec

F2 - Processing parameters
SI                 65536
SF          600.3200157 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                1.00
```

Compound 2.54 13C NMR



Current Data Parameters

NAME	6methoxy piv
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20121125
Time	23.58
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg55
TD	65536
SOLVENT	CDCl3
NS	2048
DS	4
SWH	34722.223 Hz
FIDRES	0.529819 Hz
AQ	0.9437684 sec
RG	2050
DW	14.400 usec
DE	8.88 usec
TE	298.1 K
D1	1.10000002 sec
D11	0.03000000 sec
TD0	1

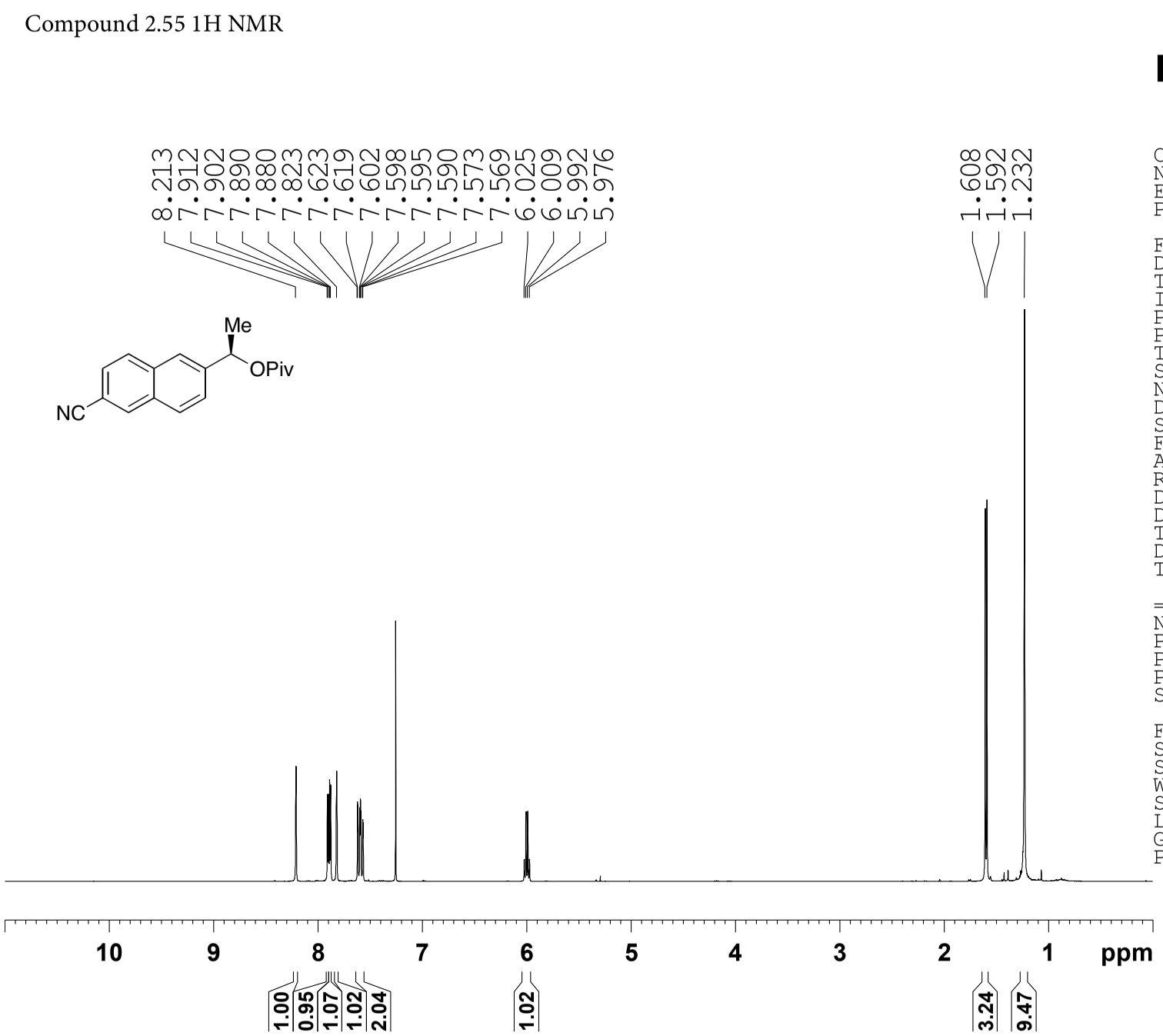
======== CHANNEL f1 ========

SFO1	150.9656784 MHz
NUC1	13C
P1	9.00 usec

F2 - Processing parameters

SI	32768
SF	150.9505840 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

Compound 2.55 1H NMR



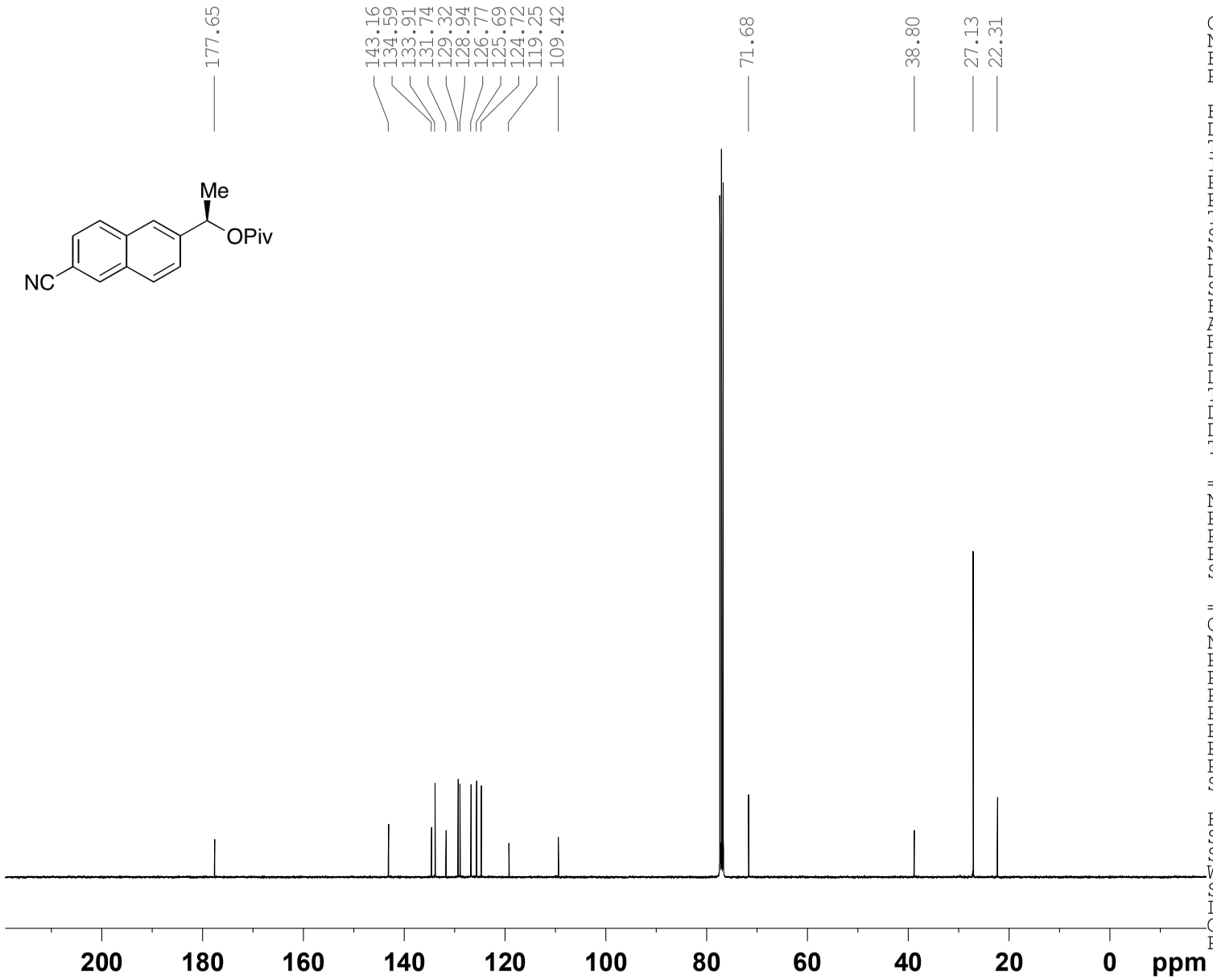
Current Data Parameters
NAME HH-4-142
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130124
Time 0.23
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 12.7
DW 60.400 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1

CHANNEL f1
NUC1 1H
P1 15.00 usec
PL1 4.90 dB
PL1W 3.30822015 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300111 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

compound 2.55 13C NMR



Current Data Parameters
NAME HH-4-142
EXPNO 2
PROCNO 1

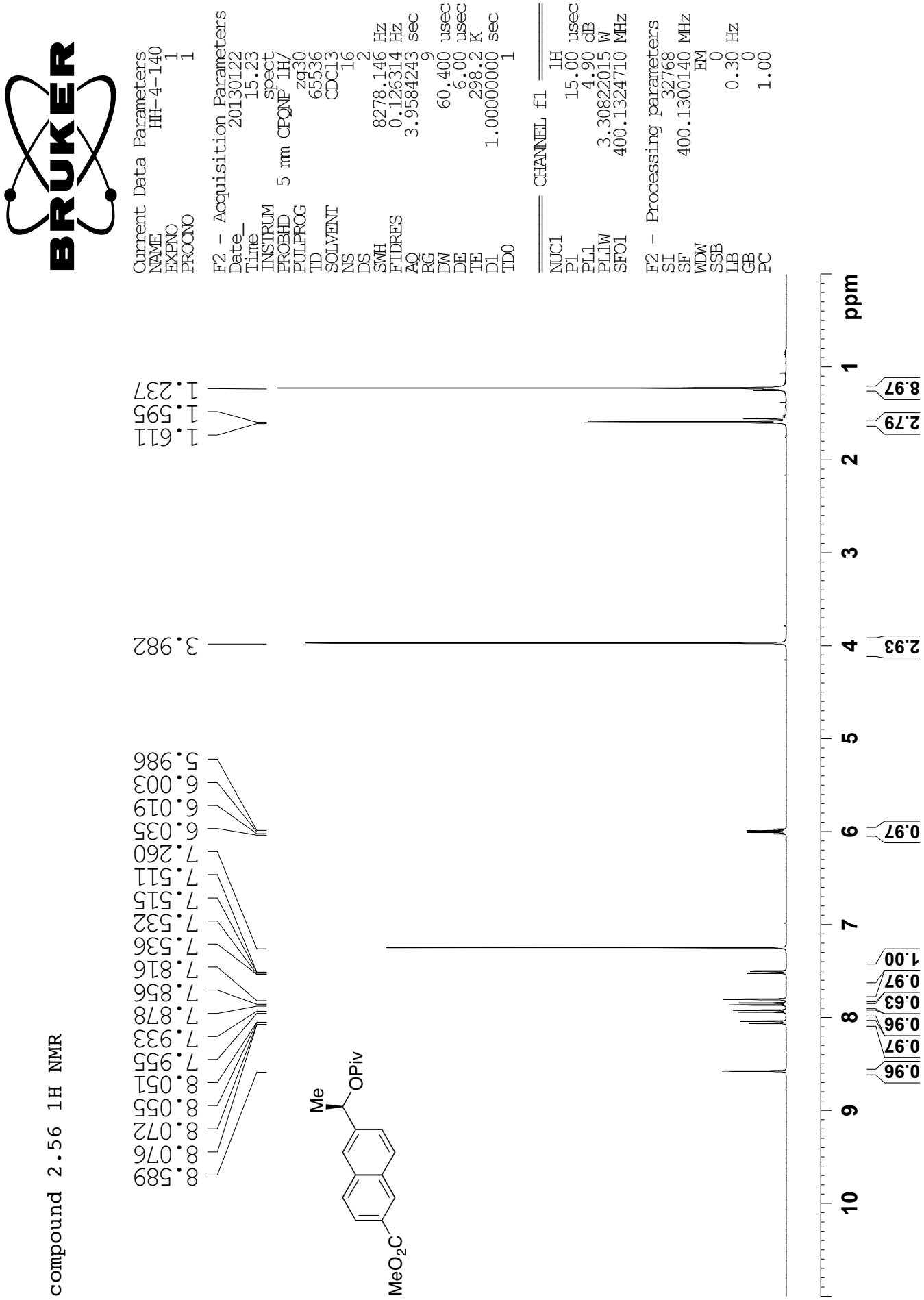
F2 - Acquisition Parameters
Date_ 20130124
Time 0.39
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 512
DW 20.850 usec
DE 18.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.25 usec
PL1 0.55 dB
PL1W 35.18820572 W
SFO1 100.6228298 MHz

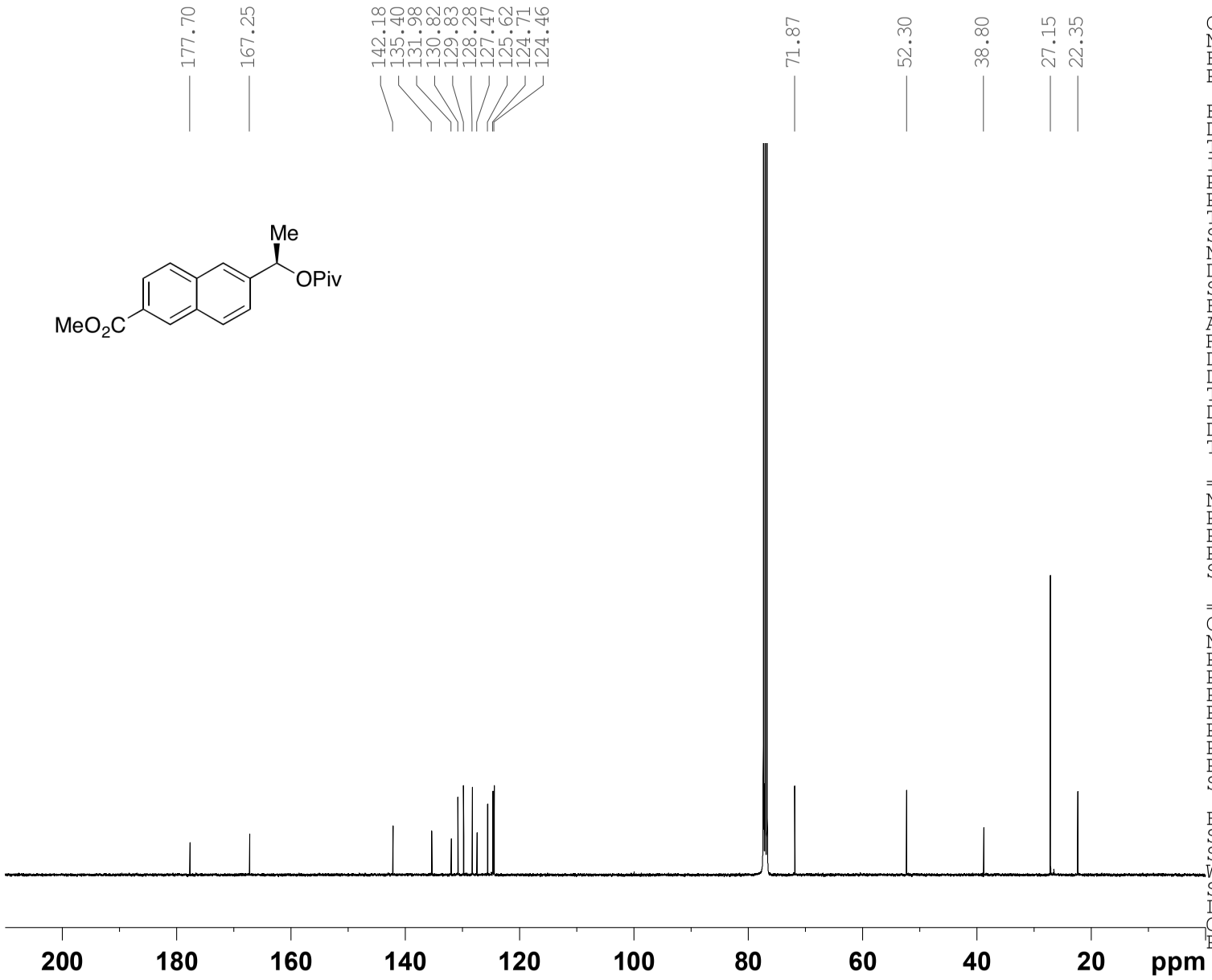
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 4.90 dB
PL12 20.46 dB
PL13 21.00 dB
PL2W 3.30822015 W
PL12W 0.09195905 W
PL13W 0.08120718 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

compound 2.56 1H NMR



compound 2.56 13C NMR



Current Data Parameters
NAME HH-4-140
EXPNO 2
PROCNO 1

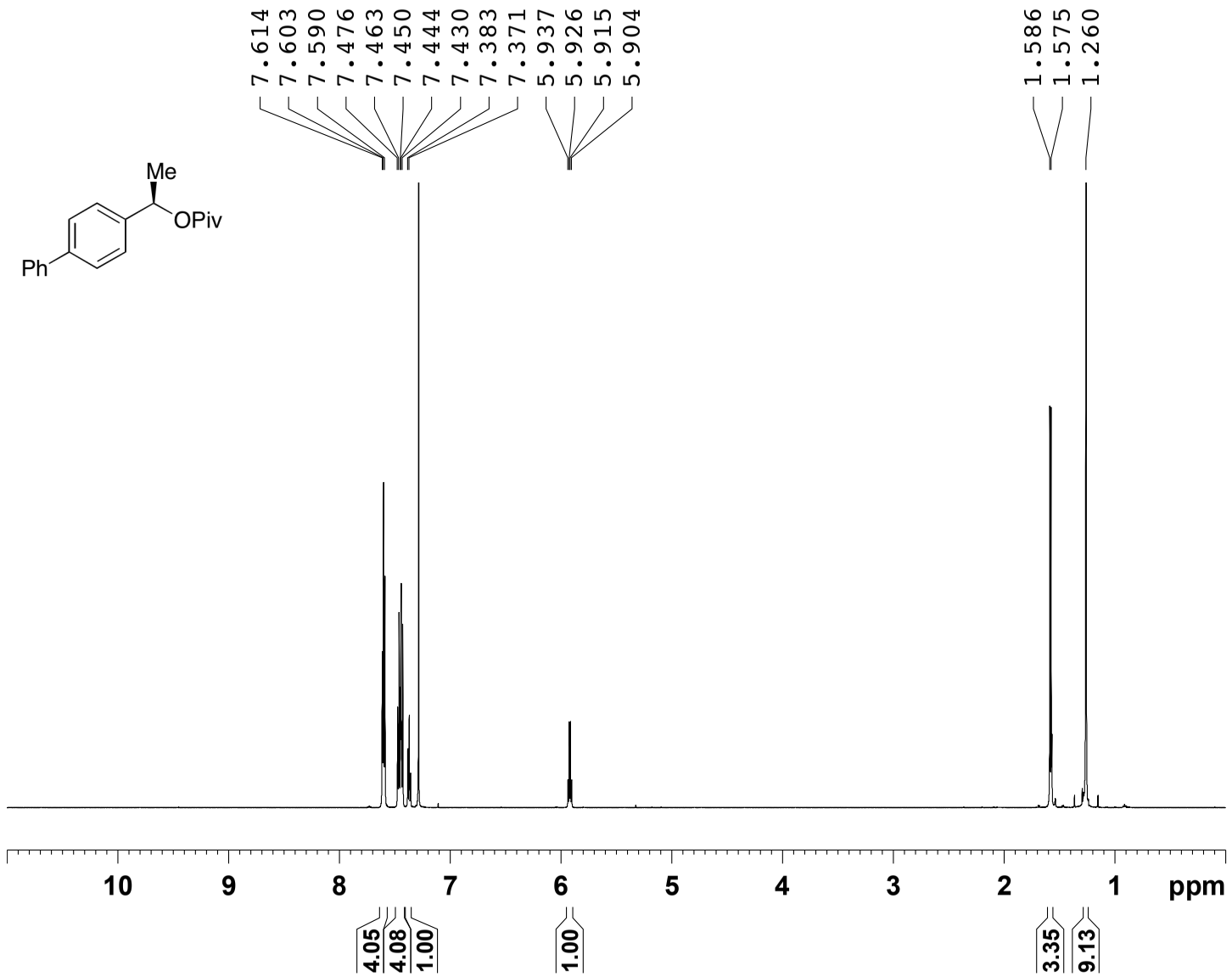
F2 - Acquisition Parameters
Date_ 20130123
Time 1.17
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 512
DW 20.850 usec
DE 18.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.25 usec
PL1 0.55 dB
PL1W 35.18820572 W
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 4.90 dB
PL12 20.46 dB
PL13 21.00 dB
PL2W 3.30822015 W
PL12W 0.09195905 W
PL13W 0.08120718 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Compound 2.57 1H NMR



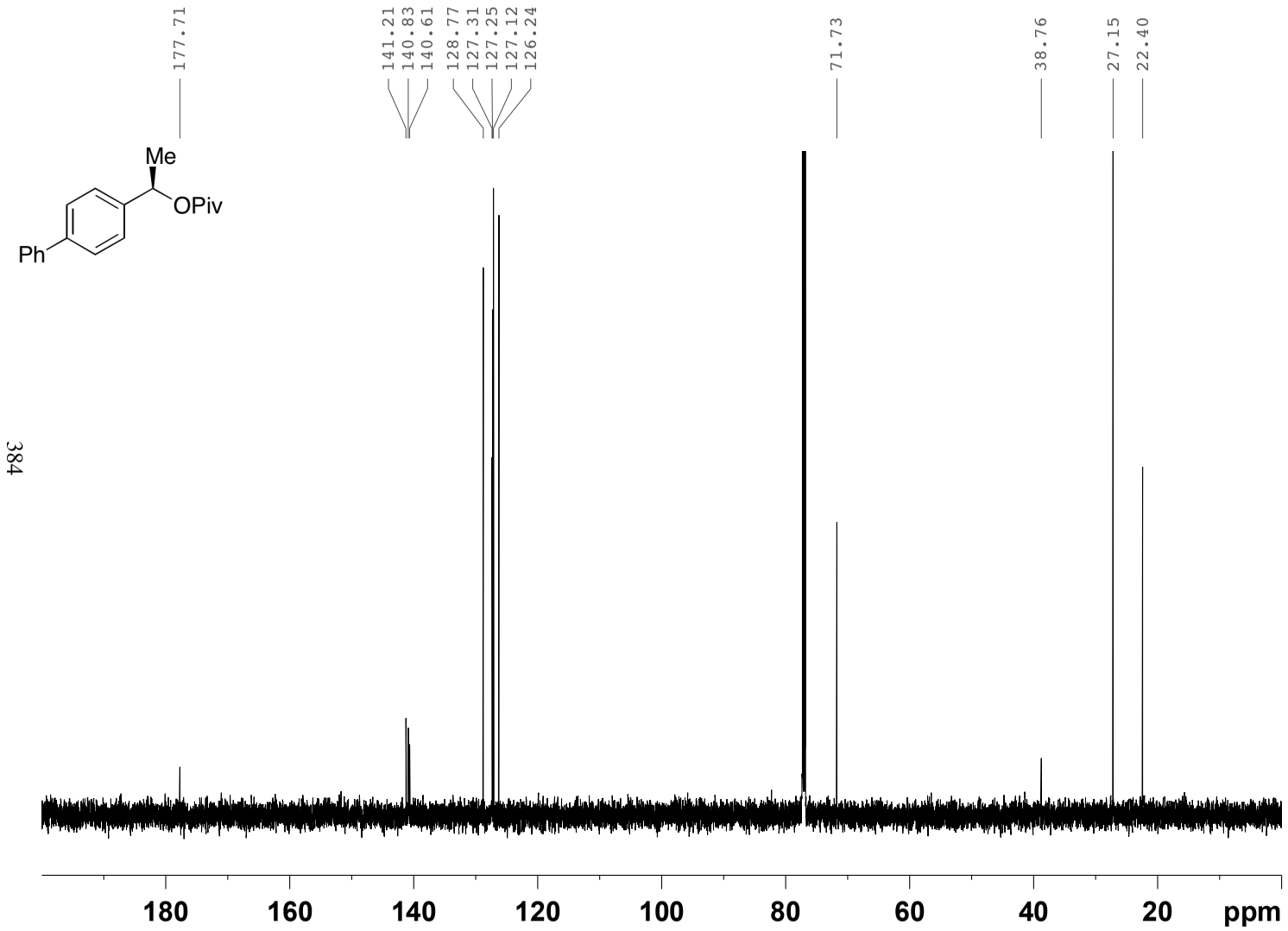

```
Current Data Parameters
NAME          QZ-3-145-1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20121201
Time              17.19
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8403.361 Hz
FIDRES         0.128225 Hz
AQ             3.8994420 sec
RG                  287
DW                59.500 usec
DE                 9.10 usec
TE                298.1 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        600.3233018 MHz
NUC1                  1H
P1                14.80 usec

F2 - Processing parameters
SI                65536
SF          600.3200000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

Compound 2.57 13C NMR



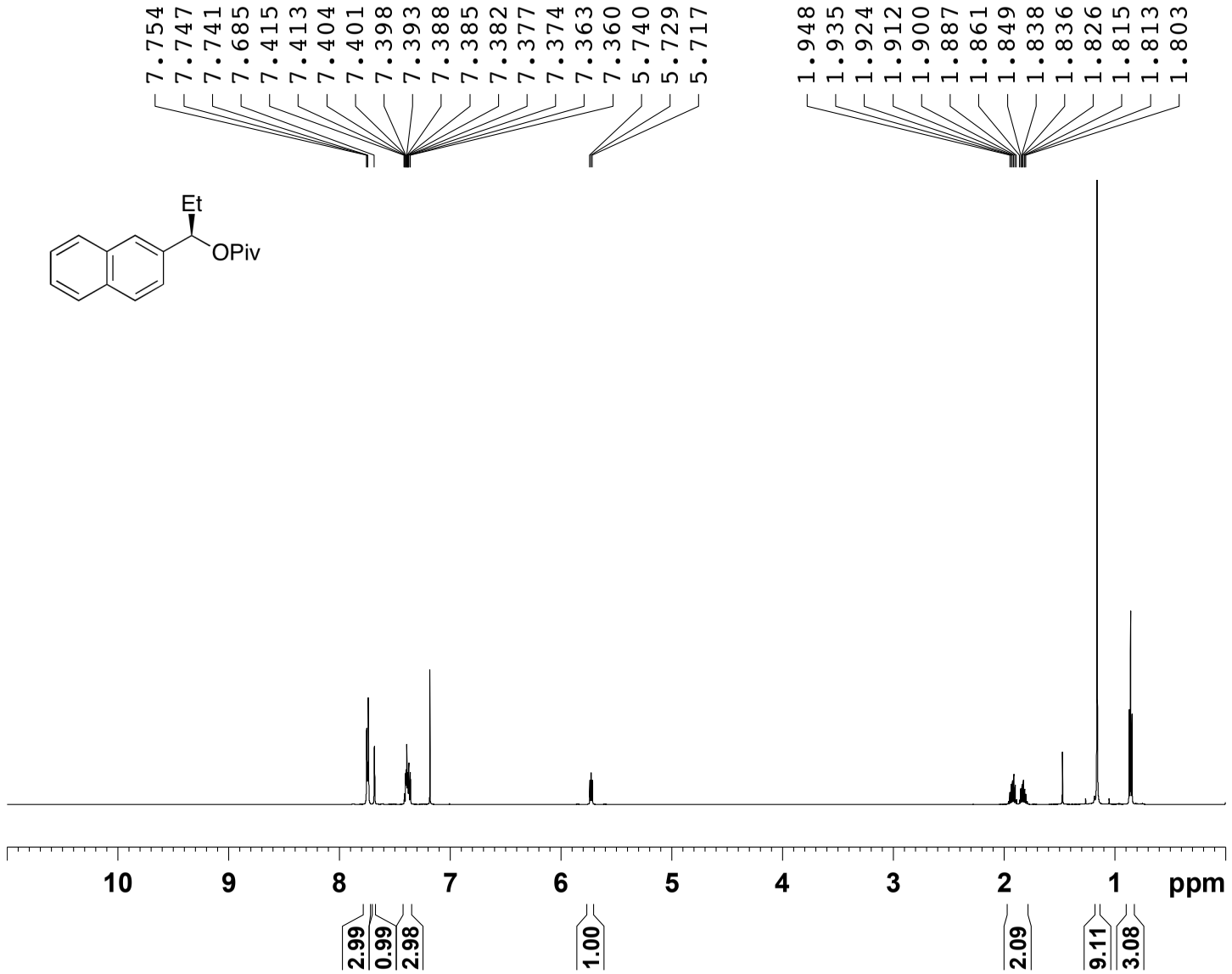

```
Current Data Parameters
NAME          QZ-3-145-1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20121201
Time              17.29
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg55
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    4
SWH           34722.223 Hz
FIDRES         0.529819 Hz
AQ            0.9437684 sec
RG                 2050
DW               14.400 usec
DE                8.88 usec
TE                298.1 K
D1           1.10000002 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        150.9656784 MHz
NUC1                13C
P1                9.00 usec

F2 - Processing parameters
SI                32768
SF          150.9505840 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

Compound 2.58 1H NMR



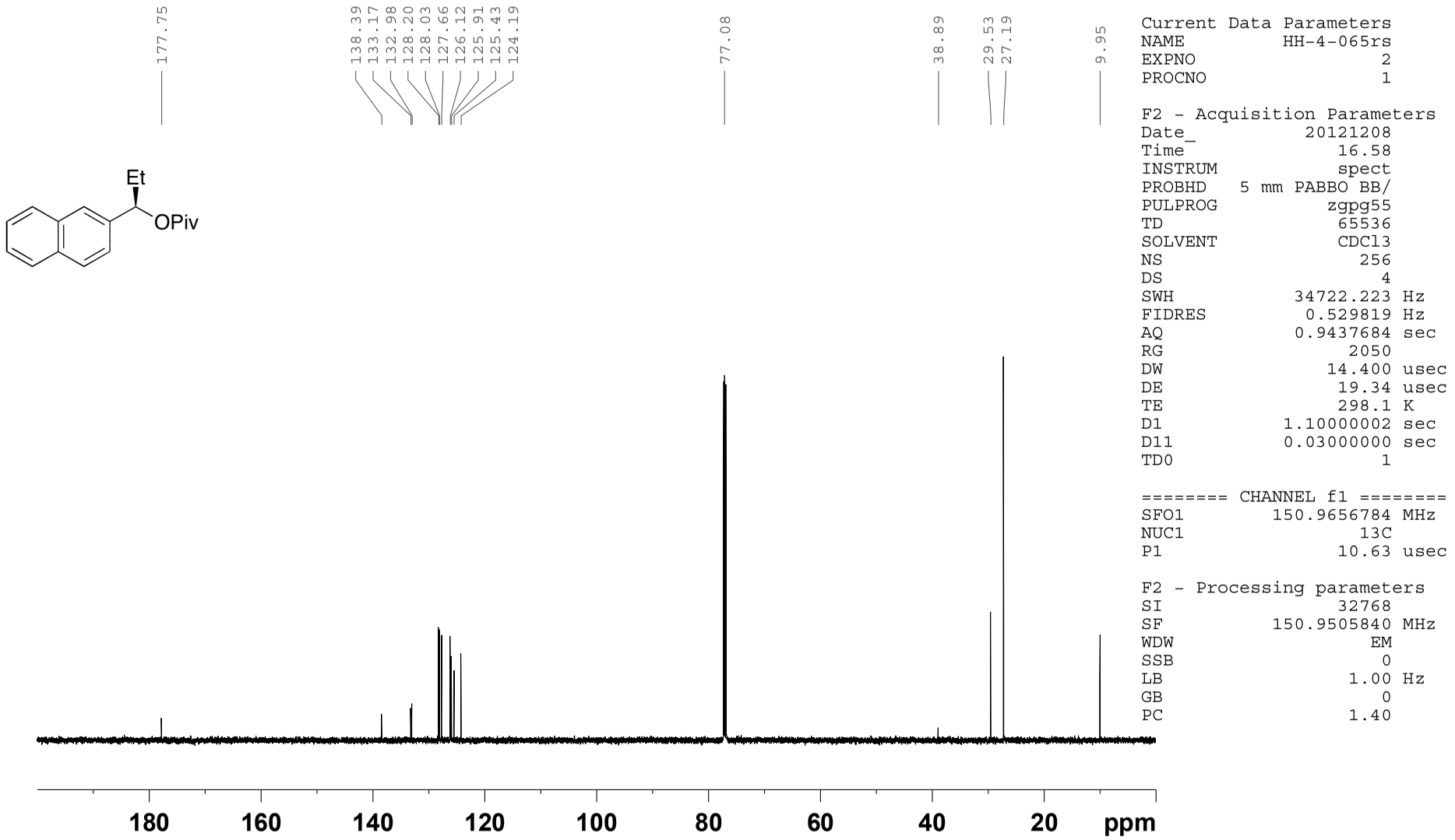

```
Current Data Parameters
NAME        HH-4-065rs_2
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20121208
Time              16.48
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8403.361 Hz
FIDRES         0.128225 Hz
AQ             3.8994420 sec
RG                  144
DW                59.500 usec
DE                17.39 usec
TE                298.1 K
D1             1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         600.3233018 MHz
NUC1                 1H
P1                10.77 usec

F2 - Processing parameters
SI                65536
SF           600.3200619 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

Compound 2.58 13C NMR



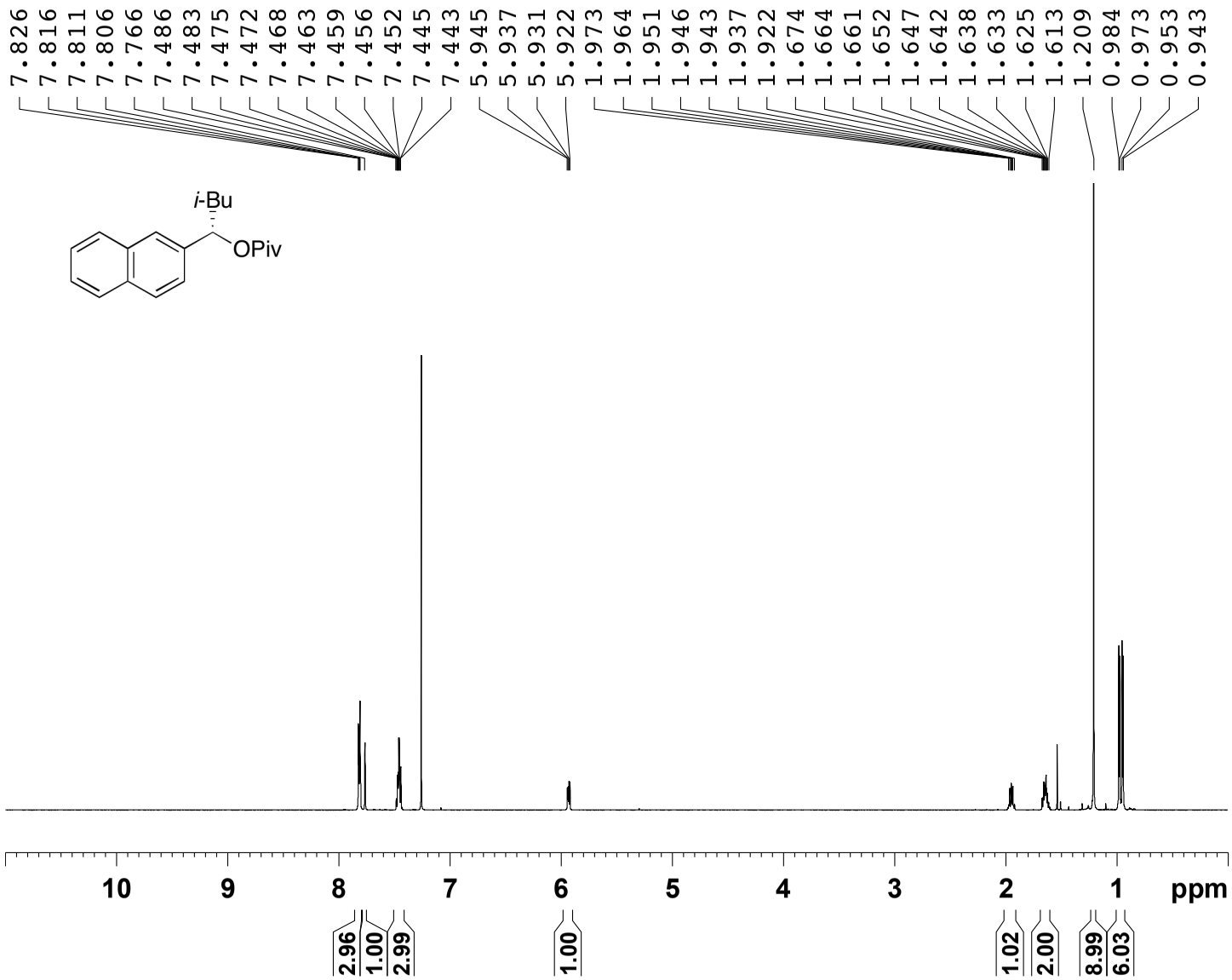

```
Current Data Parameters
NAME          HH-4-065rs
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20121208
Time               16.58
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg55
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    4
SWH           34722.223 Hz
FIDRES         0.529819 Hz
AQ            0.9437684 sec
RG                 2050
DW               14.400 usec
DE               19.34 usec
TE                298.1 K
D1           1.10000002 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        150.9656784 MHz
NUC1               13C
P1               10.63 usec

F2 - Processing parameters
SI                32768
SF          150.9505840 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```

Compound 2.59 1H NMR



387

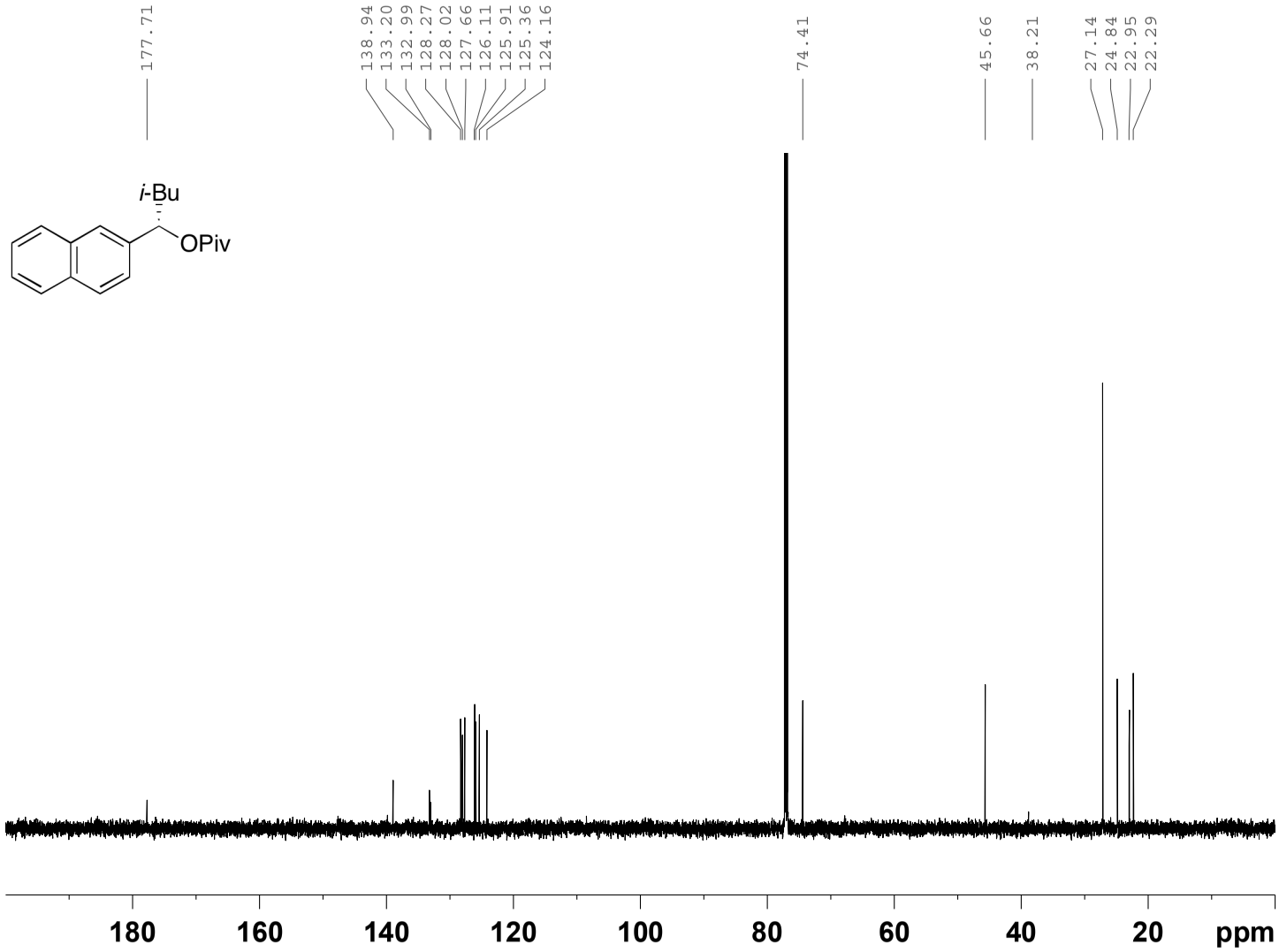
Current Data Parameters
NAME QZ-3-134
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121126
Time 12.44
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8403.361 Hz
FIDRES 0.128225 Hz
AQ 3.8994420 sec
RG 322
DW 59.500 usec
DE 9.10 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 600.3233018 MHz
NUC1 1H
P1 14.80 usec

F2 - Processing parameters
SI 65536
SF 600.3200160 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound **2.59** 13C NMR



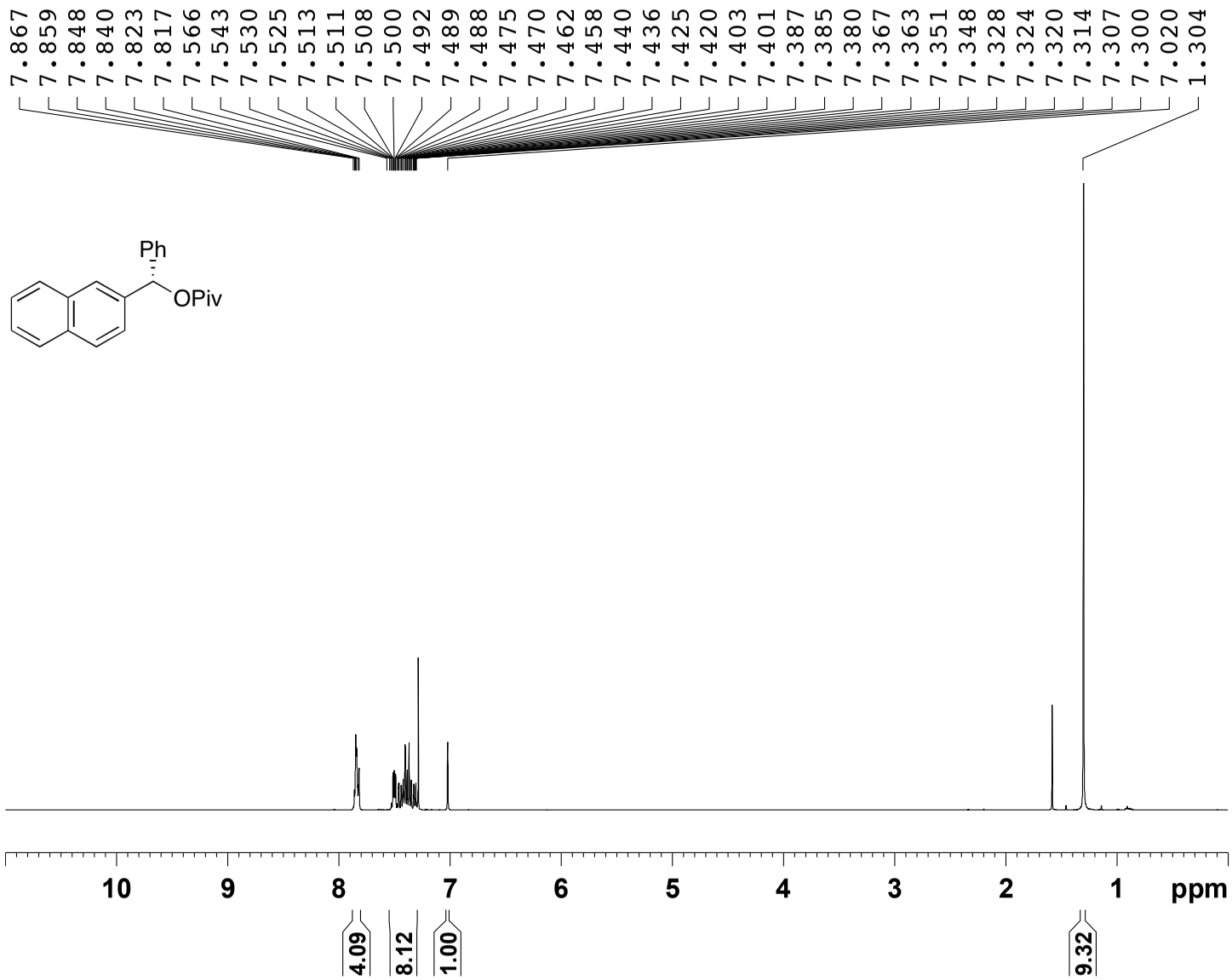

```
Current Data Parameters
NAME                  QZ-3-134
EXPNO                        2
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20121126
Time                     12.54
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG                 zgpg55
TD                       65536
SOLVENT                  CDCl3
NS                         256
DS                           4
SWH                34722.223 Hz
FIDRES              0.529819 Hz
AQ                  0.9437684 sec
RG                        2050
DW                     14.400 usec
DE                      8.88 usec
TE                      298.1 K
D1                 1.10000002 sec
D11                0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1             150.9656784 MHz
NUC1                     13C
P1                    9.00 usec

F2 - Processing parameters
SI                       32768
SF               150.9505840 MHz
WDW                         EM
SSB                          0
LB                    1.00 Hz
GB                           0
PC                        1.40
```

Compound 2.60 1H NMR



389

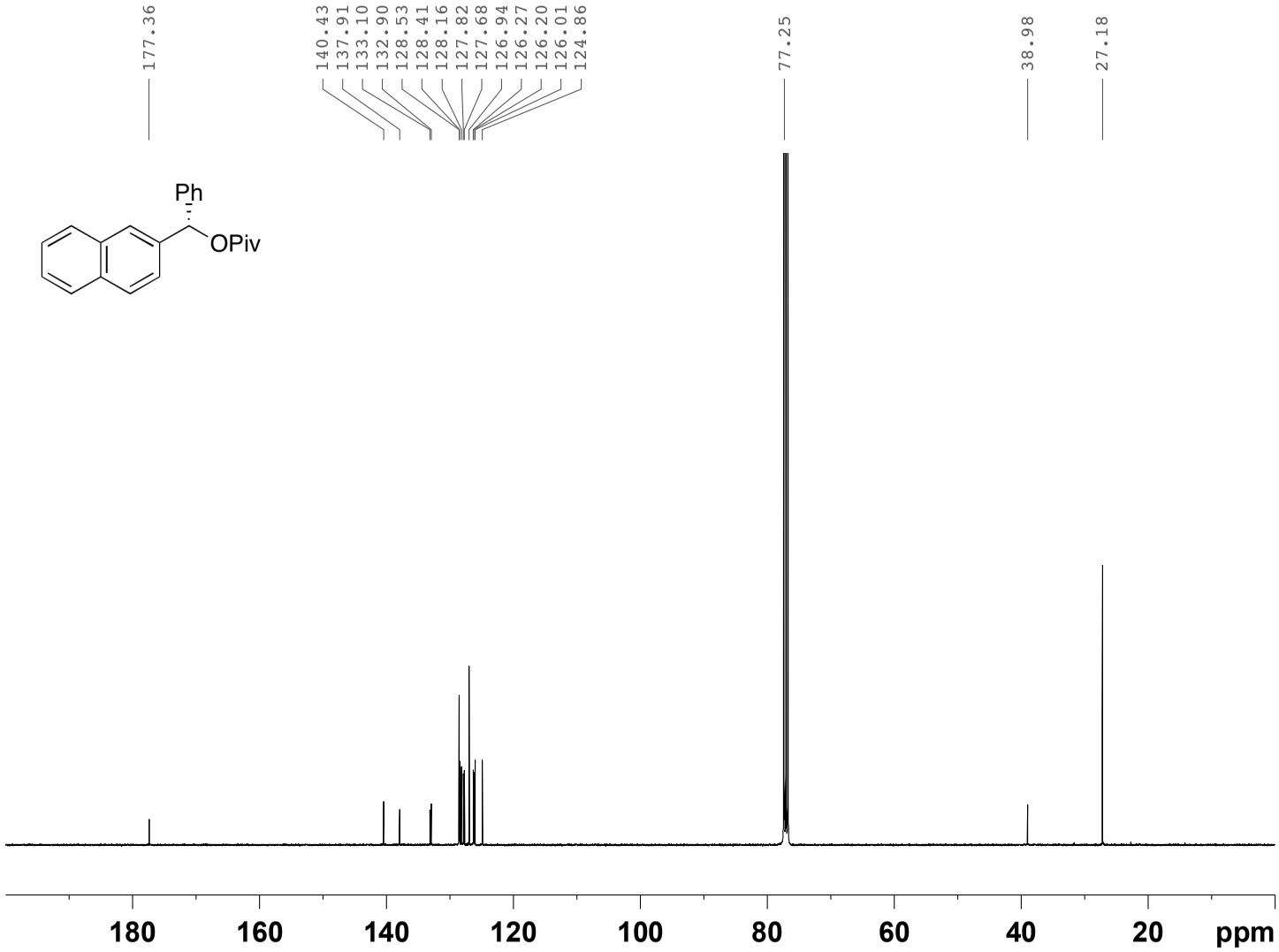
Current Data Parameters
NAME HH-3-266
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120914
Time 9.42
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 11.3
DW 60.400 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 4.90 dB
PL1W 3.30822015 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound 2.60 13CNMR



390

```
Current Data Parameters
NAME            HH-3-266
EXPNO                  2
PROCNO                 1

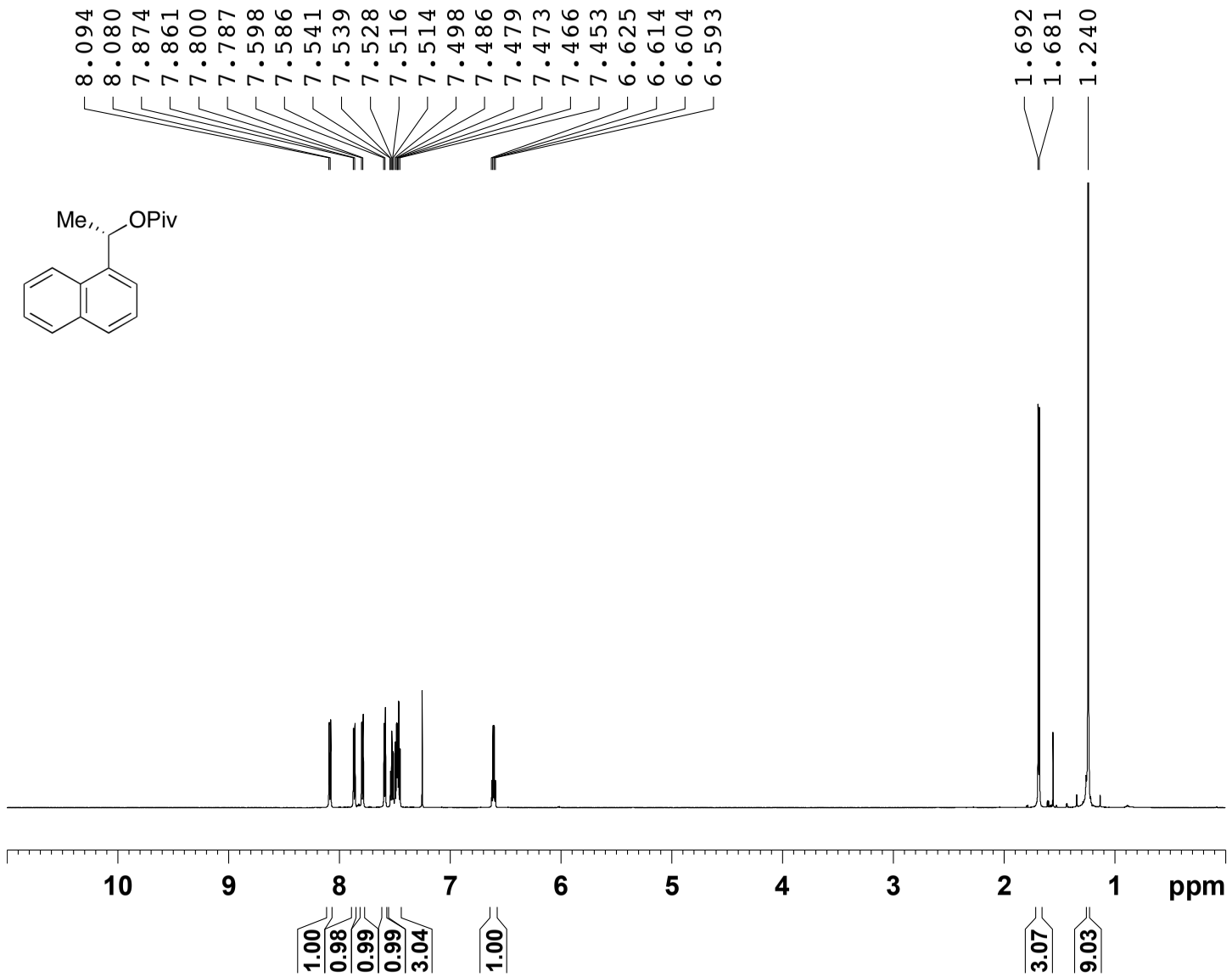
F2 - Acquisition Parameters
Date_           20120916
Time               14.48
INSTRUM            spect
PROBHD   5 mm CPQNP 1H/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG                   512
DW                20.850 usec
DE                18.00 usec
TE                298.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.25 usec
PL1                 0.55 dB
PL1W        35.18820572 W
SFO1       100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL2                 4.90 dB
PL12               20.46 dB
PL13               21.00 dB
PL2W         3.30822015 W
PL12W        0.09195905 W
PL13W        0.08120718 W
SFO2       400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF         100.6127690 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

Compound 2.61 1H NMR



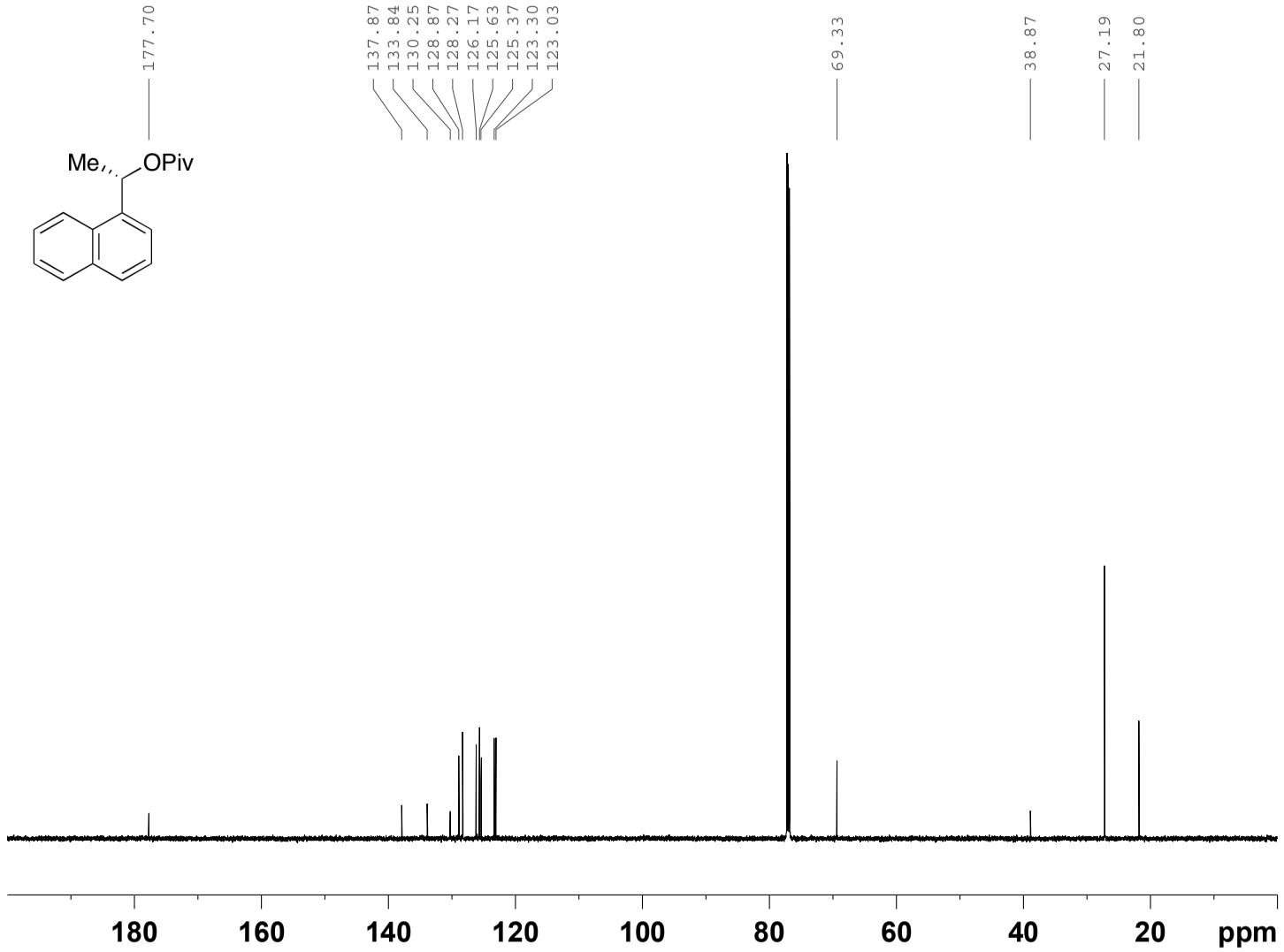

```
Current Data Parameters
NAME      QZ-Compound 1f 1HNMR
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20121210
Time                9.04
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8403.361 Hz
FIDRES          0.128225 Hz
AQ              3.8994420 sec
RG                  90.5
DW                59.500 usec
DE                17.39 usec
TE                298.1 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.3233018 MHz
NUC1                   1H
P1                 10.77 usec

F2 - Processing parameters
SI                 65536
SF           600.3200200 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

Compound 2.61 13C NMR



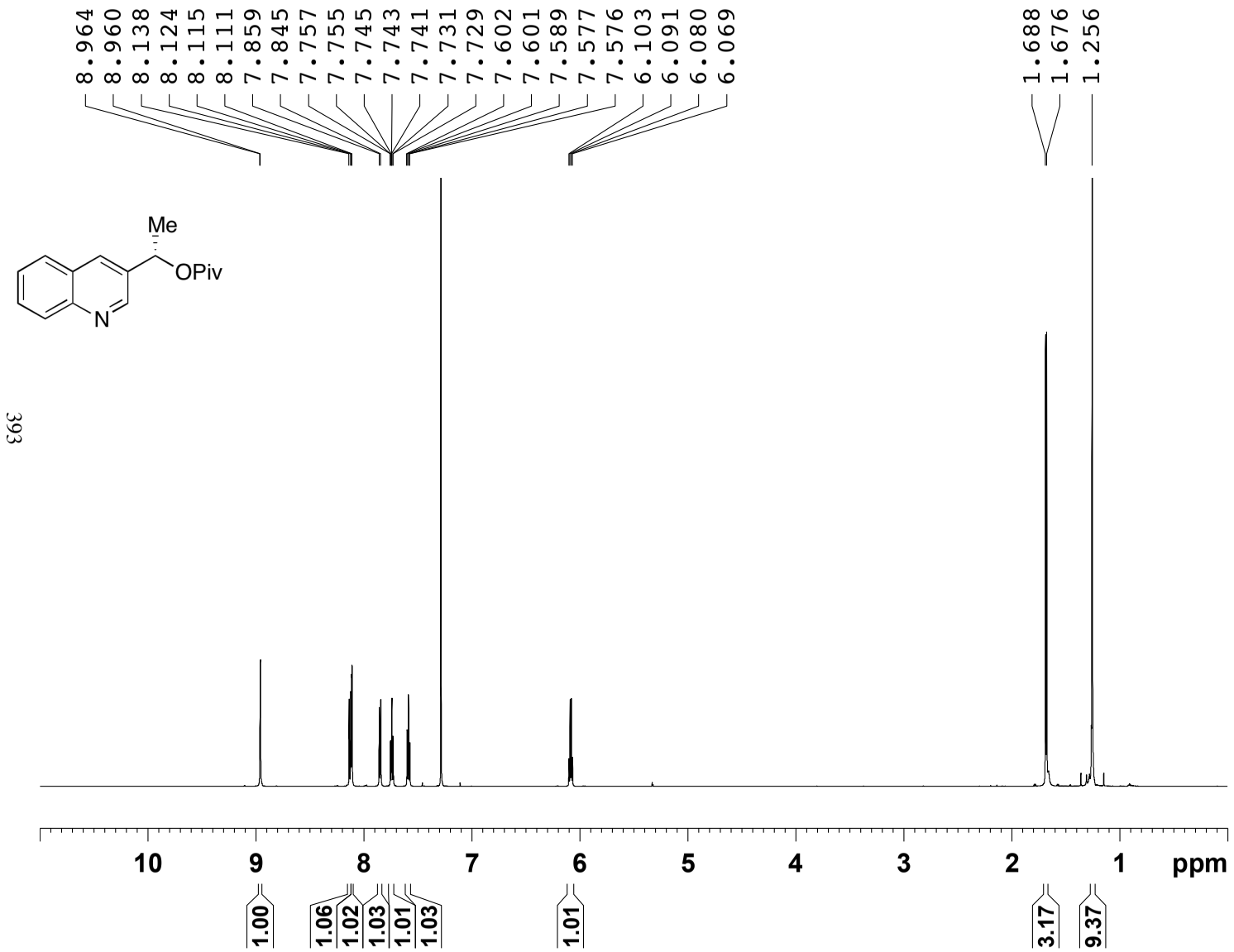

```
Current Data Parameters
NAME                  HH-4-077
EXPNO                        3
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20121129
Time                     20.50
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                 zgpg55
TD                       65536
SOLVENT                  CDCl3
NS                        2048
DS                           4
SWH                 34722.223 Hz
FIDRES               0.529819 Hz
AQ                   0.9437684 sec
RG                        1030
DW                      14.400 usec
DE                       8.88 usec
TE                      298.1 K
D1                  1.10000002 sec
D11                 0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               150.9656784 MHz
NUC1                       13C
P1                        9.00 usec

F2 - Processing parameters
SI                       32768
SF                 150.9505840 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```

Compound 2.62 1HNMR



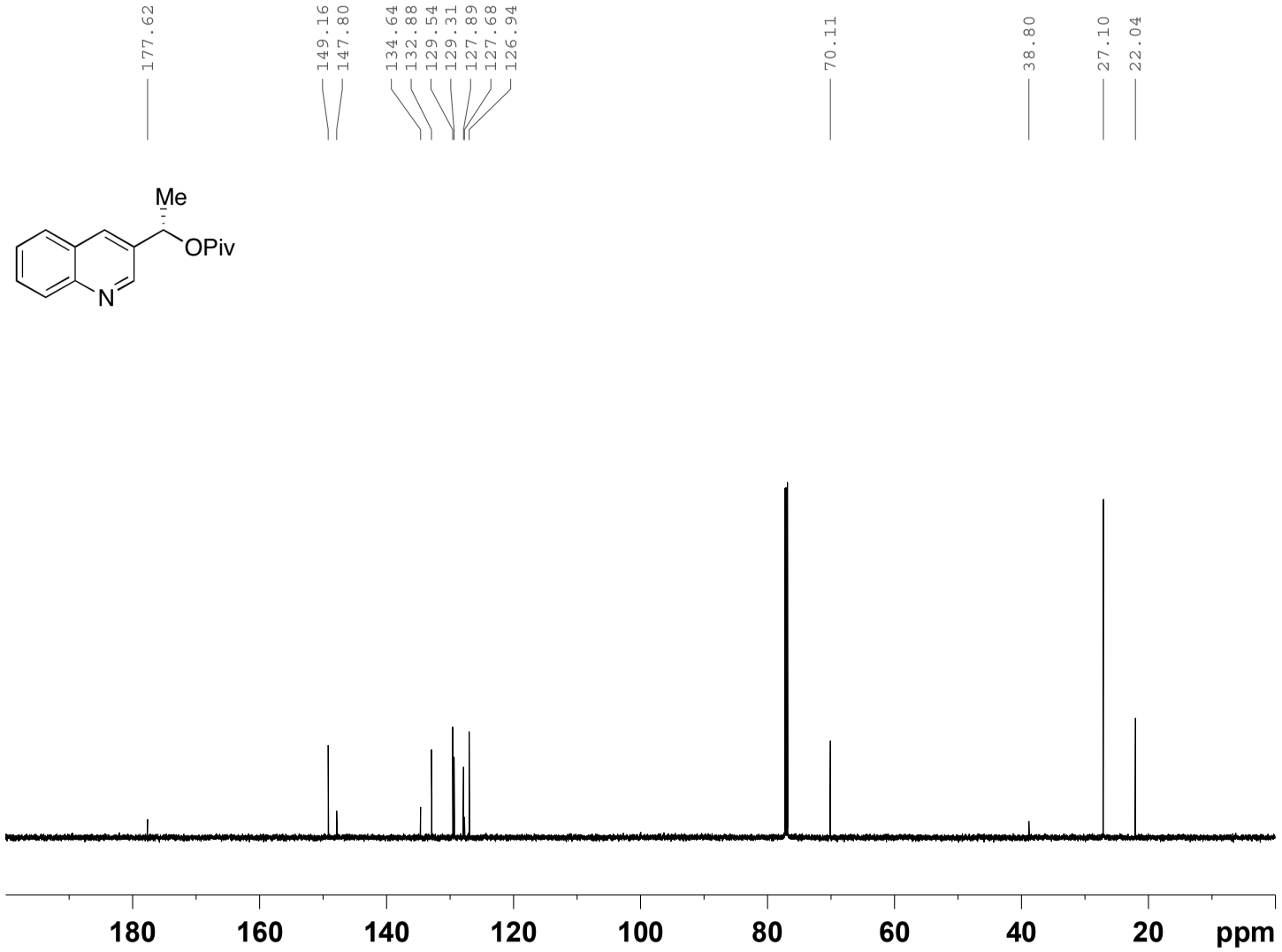

```
Current Data Parameters
NAME          QZ-2-290-2
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20121203
Time              22.51
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8403.361 Hz
FIDRES         0.128225 Hz
AQ             3.8994420 sec
RG                  161
DW               59.500 usec
DE               17.39 usec
TE                298.1 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        600.3233018 MHz
NUC1                  1H
P1                10.77 usec

F2 - Processing parameters
SI                65536
SF          600.3200000 MHz
WDW                  EM
SSB                   0
LB                0.30 Hz
GB                    0
PC                1.00
```

Compound 2.62 13C NMR



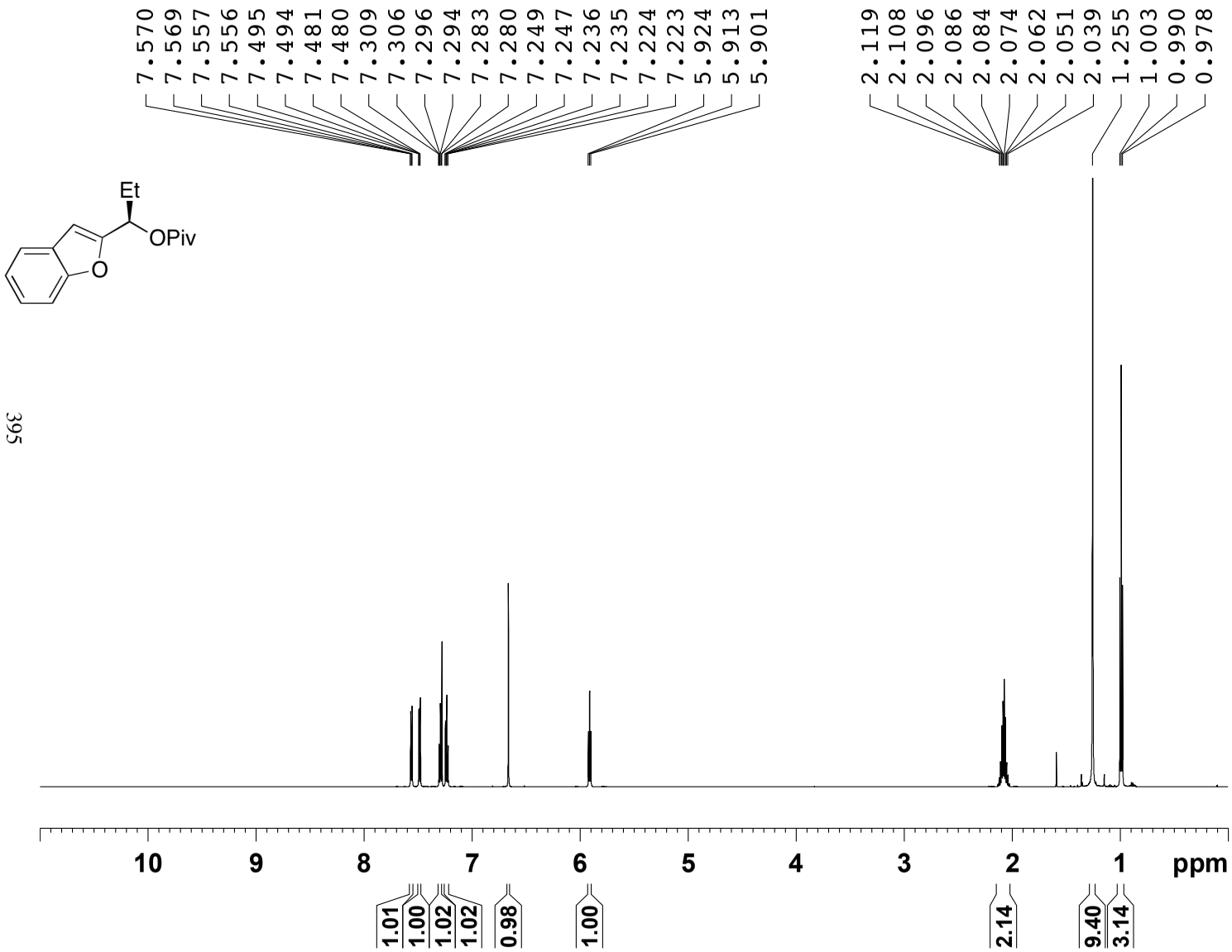
Current Data Parameters
NAME QZ-2-290-2
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121203
Time 23.01
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg55
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 34722.223 Hz
FIDRES 0.529819 Hz
AQ 0.9437684 sec
RG 2050
DW 14.400 usec
DE 19.34 usec
TE 298.1 K
D1 1.10000002 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 150.9656784 MHz
NUC1 13C
P1 10.63 usec

F2 - Processing parameters
SI 32768
SF 150.9505840 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Compound 2.63 1H NMR



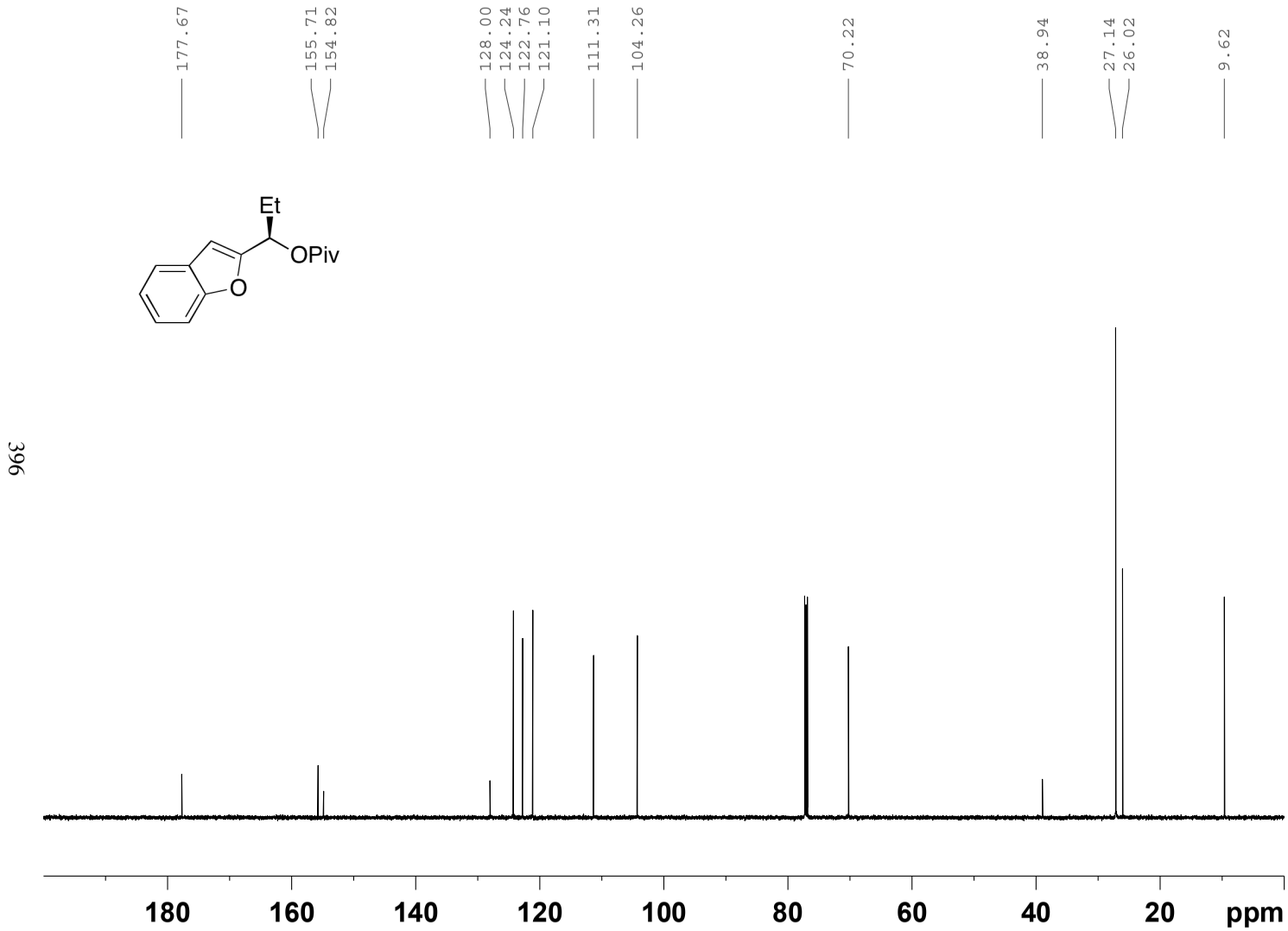

```
Current Data Parameters
NAME      QZ-Compound-1h
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20121209
Time               12.06
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8403.361 Hz
FIDRES          0.128225 Hz
AQ              3.8994420 sec
RG                    57
DW                59.500 usec
DE                17.39 usec
TE                298.1 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.3233018 MHz
NUC1                   1H
P1                 10.77 usec

F2 - Processing parameters
SI                 65536
SF           600.3200046 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

Compound 2.63 13C NMR



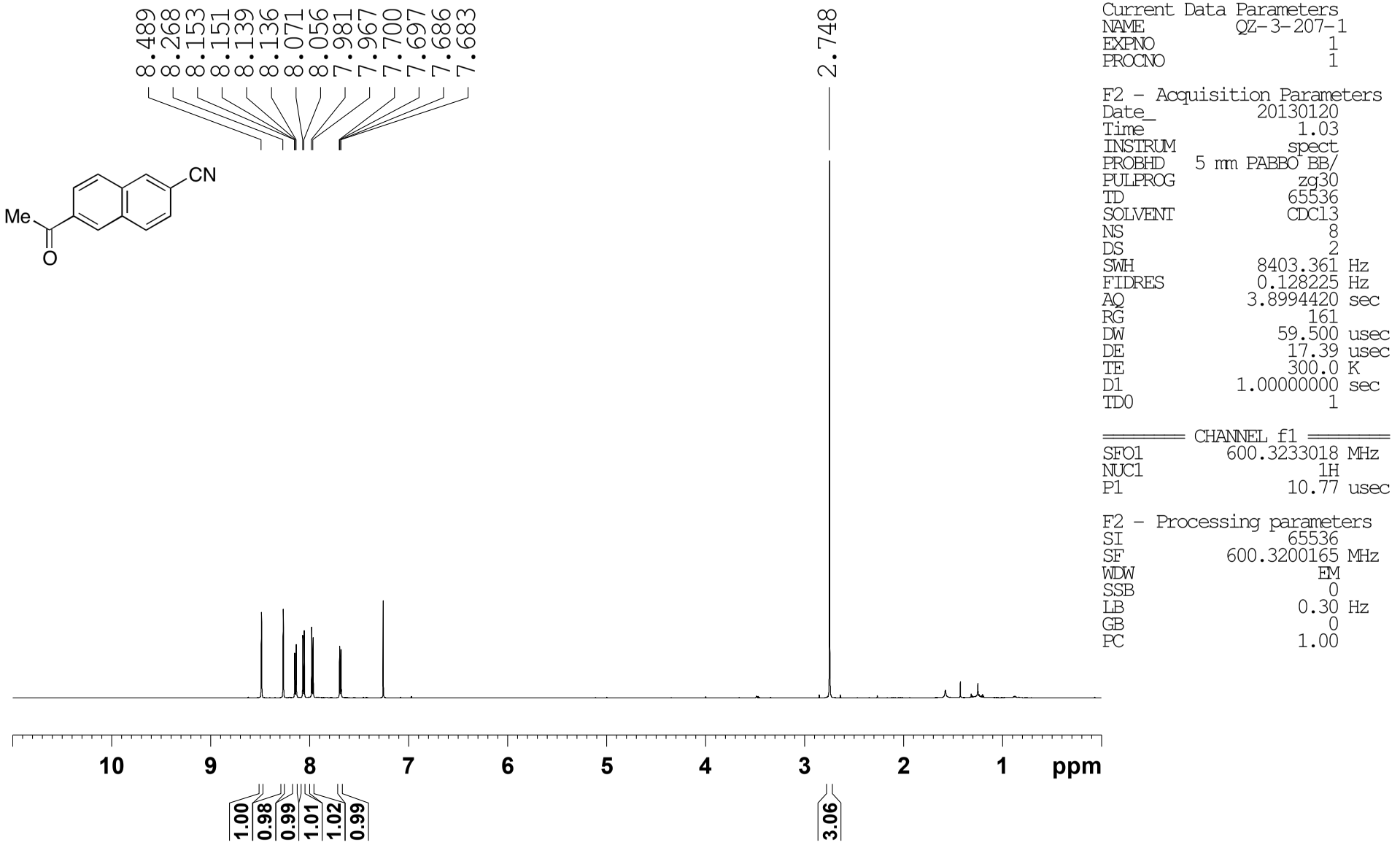

```
Current Data Parameters
NAME      QZ-Compound-1h
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20121209
Time                12.16
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg55
TD                 65536
SOLVENT            CDCl3
NS                   256
DS                     4
SWH            34722.223 Hz
FIDRES          0.529819 Hz
AQ             0.9437684 sec
RG                  2050
DW                14.400 usec
DE                19.34 usec
TE                298.1 K
D1             1.10000002 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         150.9656784 MHz
NUC1                  13C
P1                 10.63 usec

F2 - Processing parameters
SI                 32768
SF           150.9505840 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

compound 2.74 1H NMR



Current Data Parameters

NAME	QZ-3-207-1
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20130120
Time	1.03
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	2
SWH	8403.361 Hz
FIDRES	0.128225 Hz
AQ	3.8994420 sec
RG	161
DW	59.500 usec
DE	17.39 usec
TE	300.0 K
D1	1.00000000 sec
TD0	1

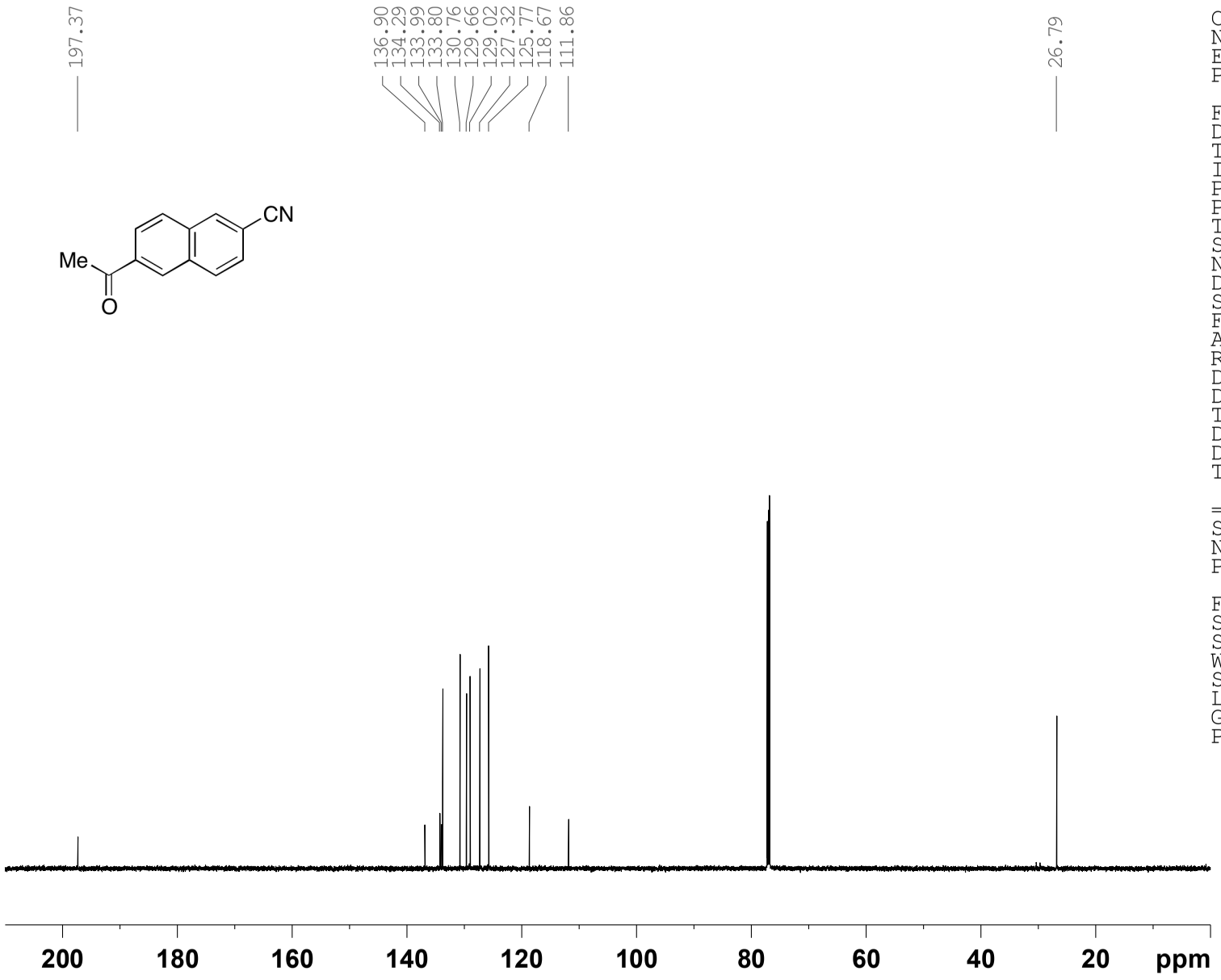
CHANNEL f1

SFO1	600.3233018 MHz
NUC1	1H
P1	10.77 usec

F2 - Processing parameters

SI	65536
SF	600.3200165 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

compound 2.74 13C NMR



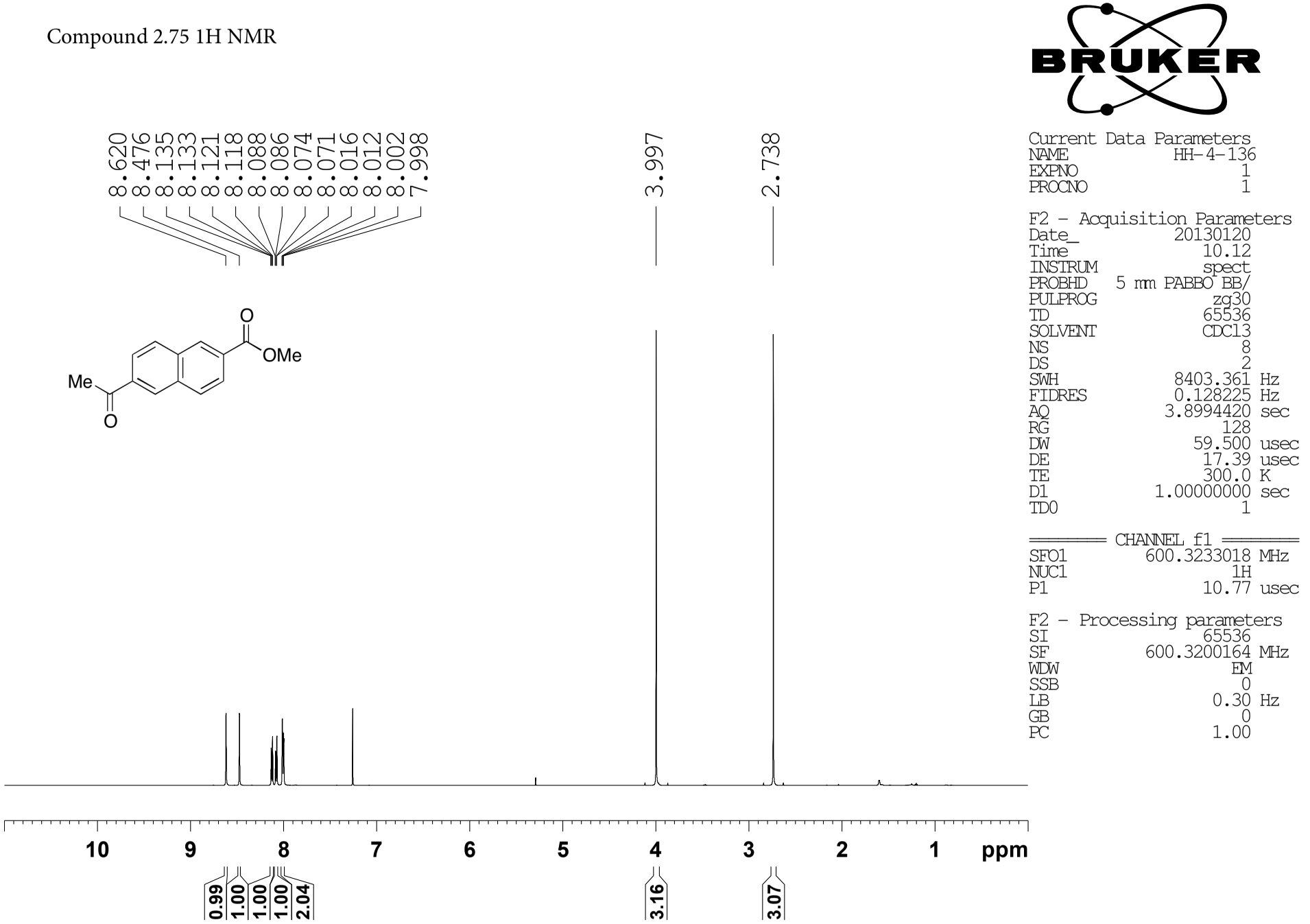
Current Data Parameters
NAME QZ-3-207-1
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130120
Time 1.22
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg55
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 34722.223 Hz
FIDRES 0.529819 Hz
AQ 0.9437684 sec
RG 2050
DW 14.400 usec
DE 19.34 usec
TE 300.0 K
D1 1.10000002 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 150.9656784 MHz
NUC1 13C
P1 10.63 usec

F2 - Processing parameters
SI 32768
SF 150.9505840 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Compound 2.75 1H NMR



Current Data Parameters

NAME	HH-4-136
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20130120
Time	10.12
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	2
SWH	8403.361 Hz
FIDRES	0.128225 Hz
AQ	3.8994420 sec
RG	128
DW	59.500 usec
DE	17.39 usec
TE	300.0 K
D1	1.00000000 sec
TD0	1

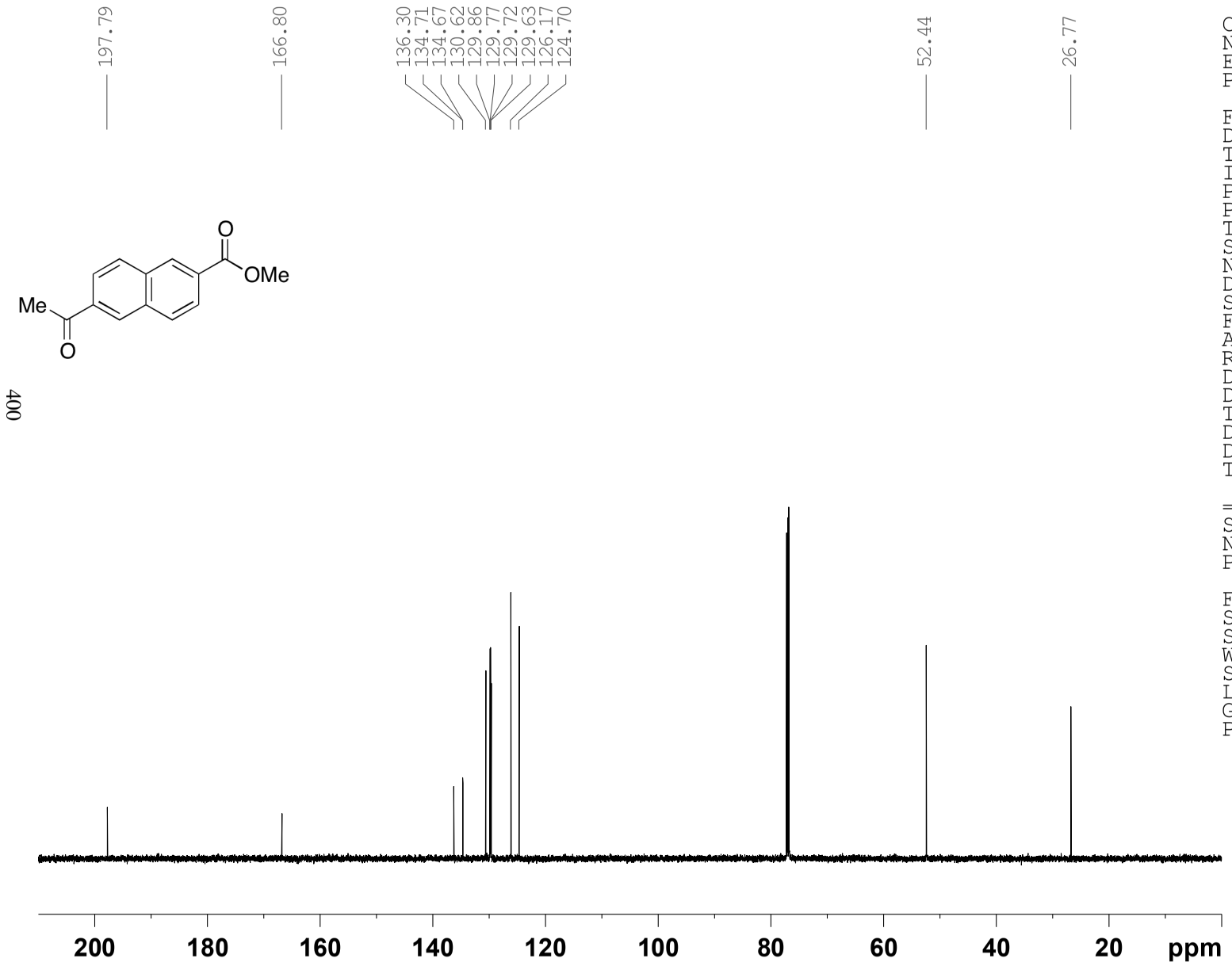
CHANNEL f1

SFO1	600.3233018 MHz
NUC1	1H
P1	10.77 usec

F2 - Processing parameters

SI	65536
SF	600.3200164 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Compound 2.75 13C NMR



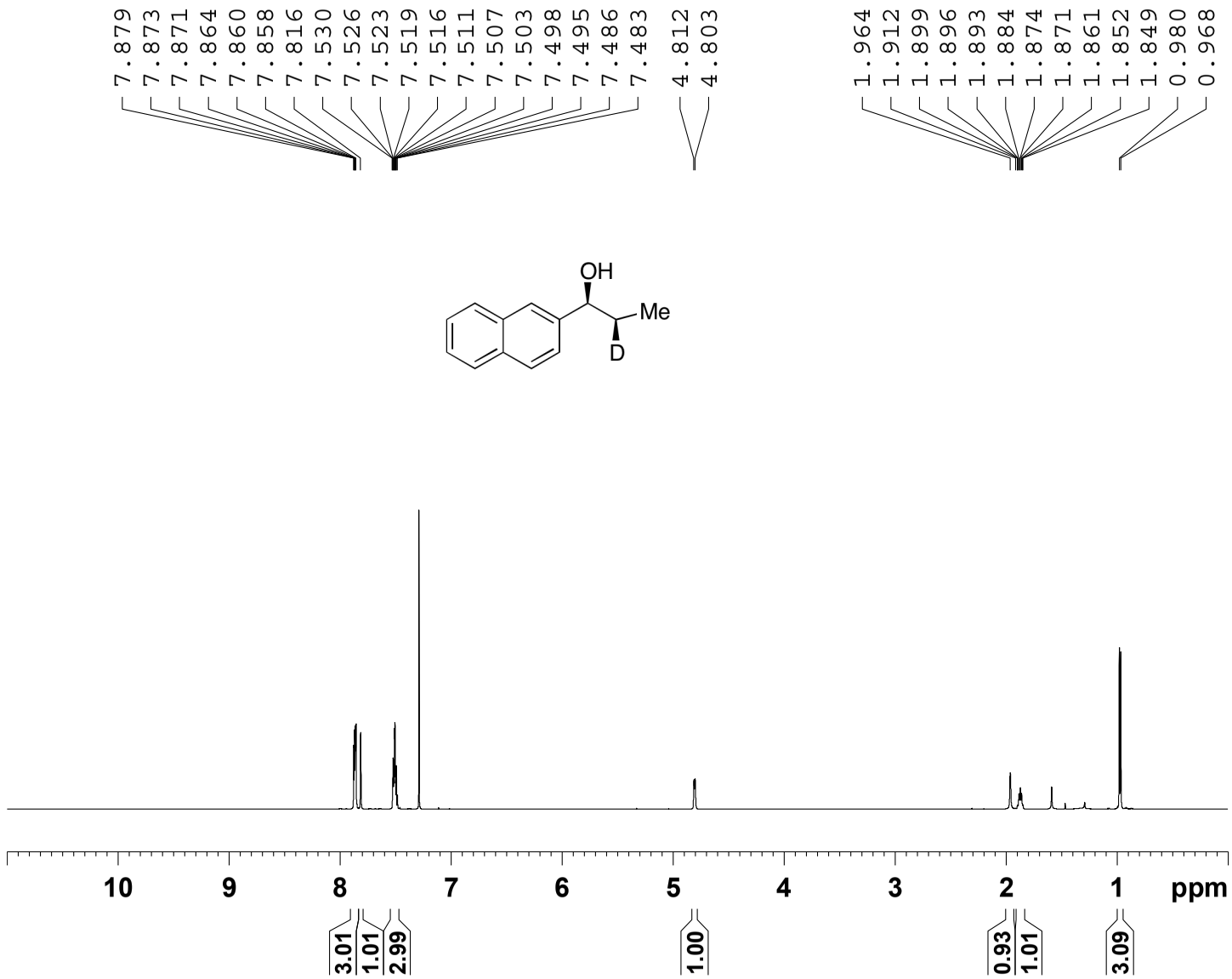
Current Data Parameters
NAME HH-4-136
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130120
Time 10.49
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg55
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 34722.223 Hz
FIDRES 0.529819 Hz
AQ 0.9437684 sec
RG 2050
DW 14.400 usec
DE 19.34 usec
TE 300.0 K
D1 1.10000002 sec
D11 0.03000000 sec
TD0 1

CHANNEL f1
SFO1 150.9656784 MHz
NUC1 13C
P1 10.63 usec

F2 - Processing parameters
SI 32768
SF 150.9505840 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Compound 2.83 1H NMR



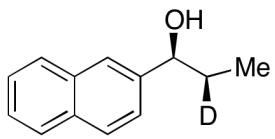
Current Data Parameters
NAME QZ-3-132-1
EXPNO 3
PROCNO 1

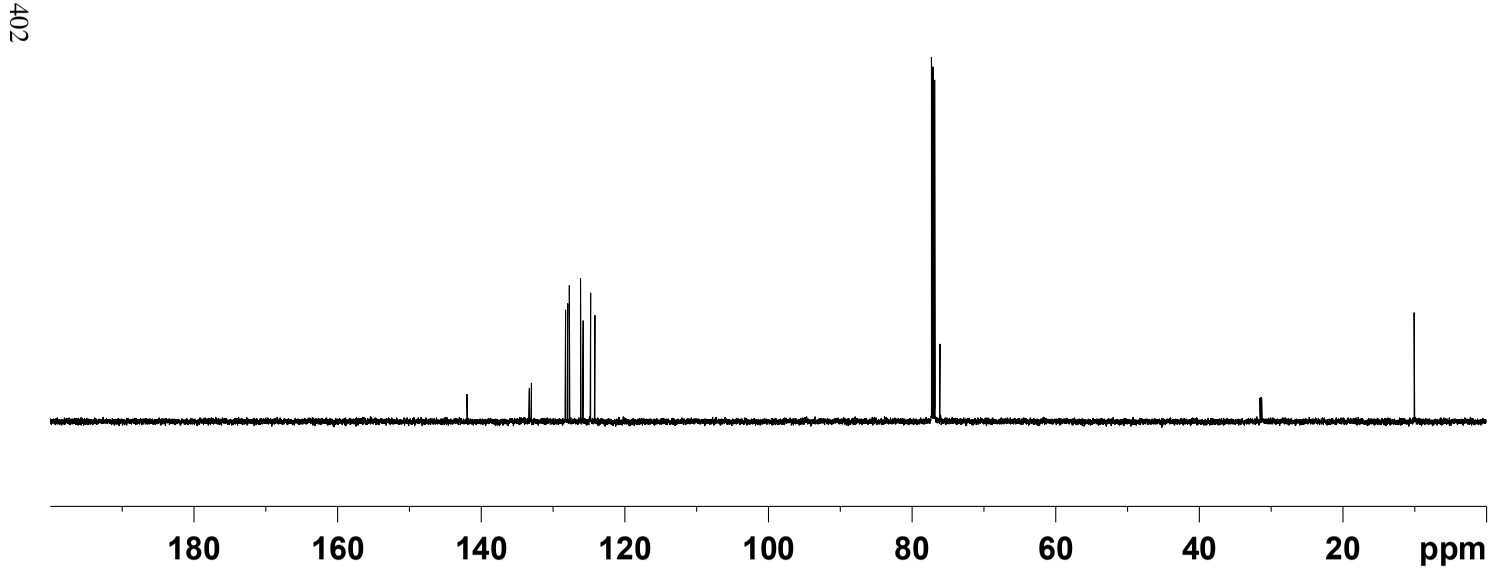
F2 - Acquisition Parameters
Date_ 20121203
Time 22.38
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8403.361 Hz
FIDRES 0.128225 Hz
AQ 3.8994420 sec
RG 144
DW 59.500 usec
DE 17.39 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 600.3233018 MHz
NUC1 1H
P1 10.77 usec

F2 - Processing parameters
SI 65536
SF 600.3199982 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Compound 2.83 13C NMR





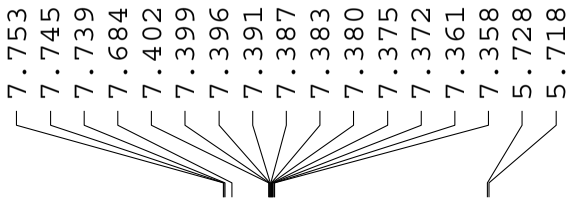

```
Current Data Parameters
NAME          QZ-3-132-1
EXPNO                  4
PROCNO                 1

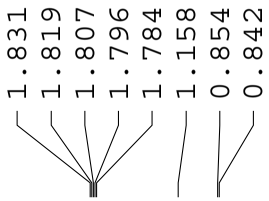
F2 - Acquisition Parameters
Date_           20121203
Time               22.48
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg55
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    4
SWH           34722.223 Hz
FIDRES         0.529819 Hz
AQ            0.9437684 sec
RG                 2050
DW               14.400 usec
DE               19.34 usec
TE               298.1 K
D1            1.10000002 sec
D11           0.03000000 sec
TD0                    1

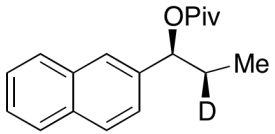
======== CHANNEL f1 ========
SFO1        150.9656784 MHz
NUC1                  13C
P1                10.63 usec

F2 - Processing parameters
SI                 32768
SF          150.9505840 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                1.40
```

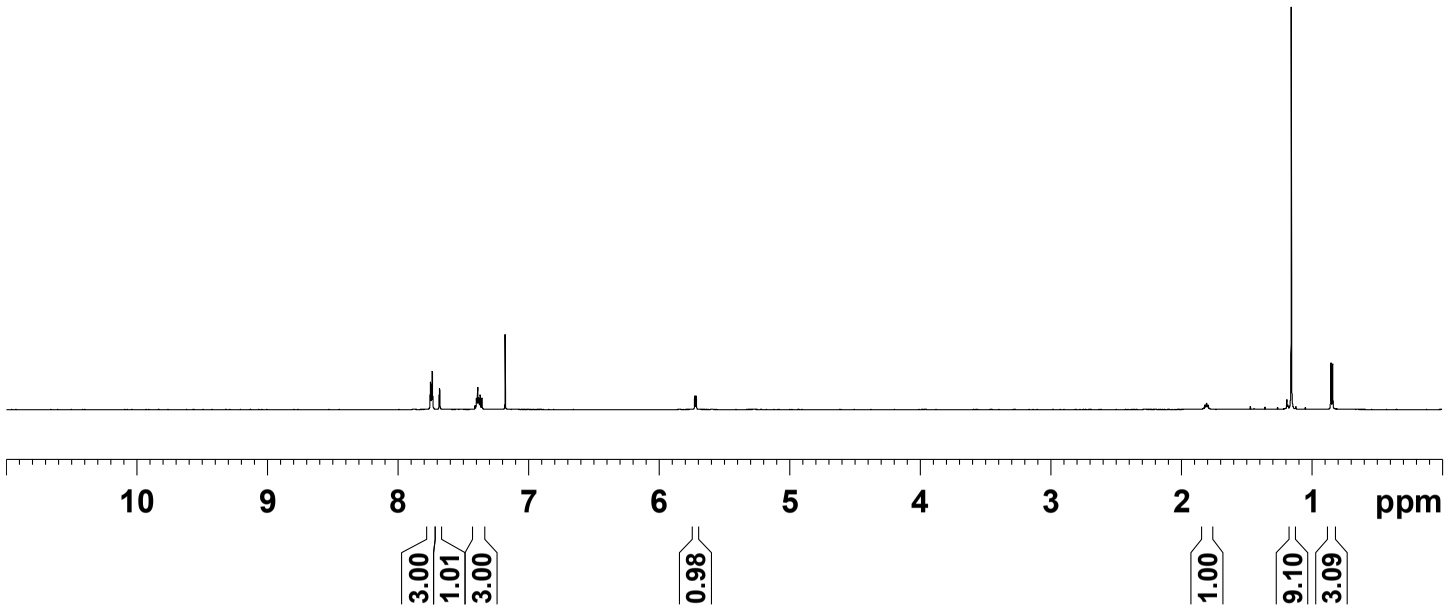
Compound 2.49 1H NMR







403



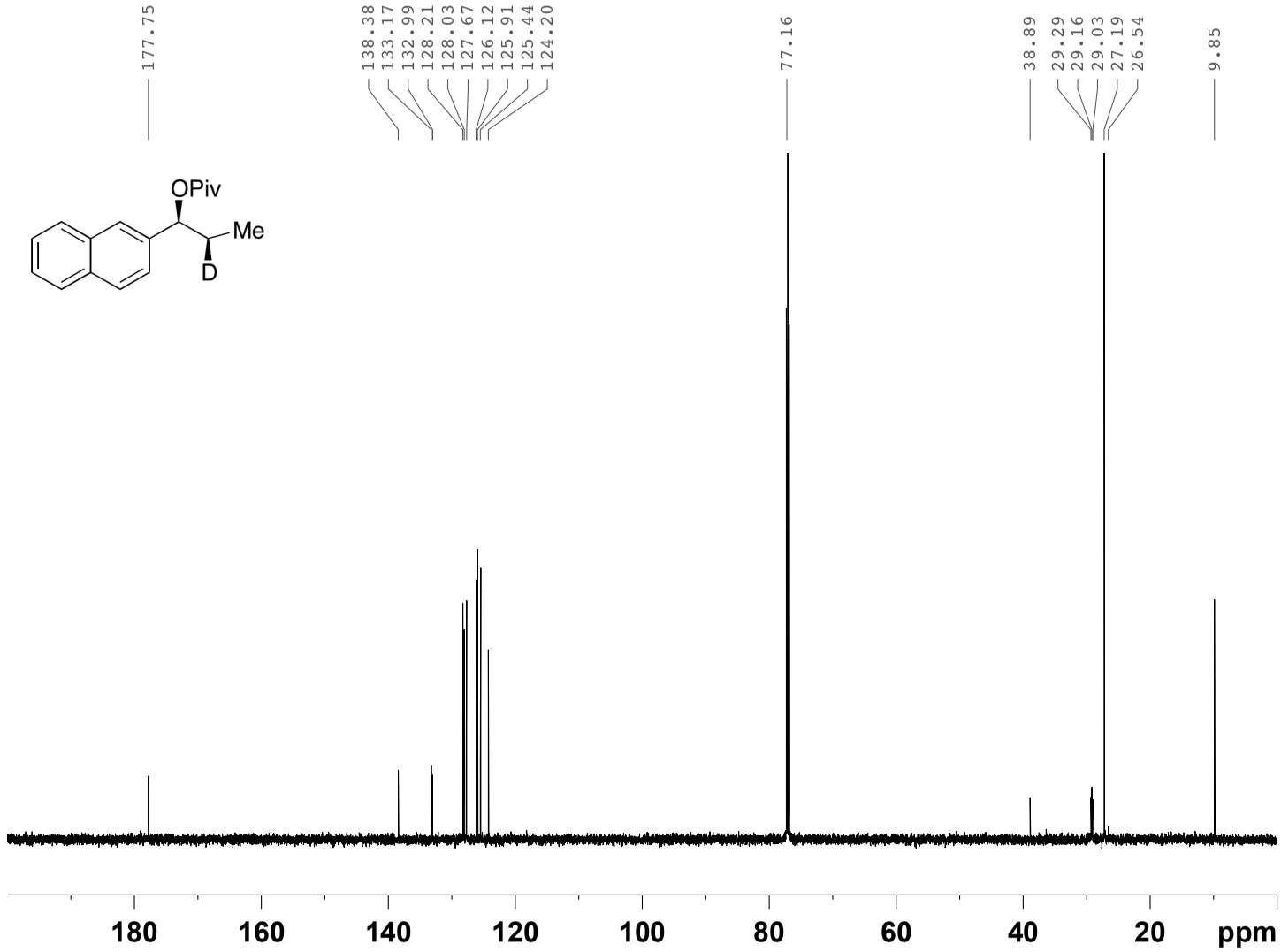

```
Current Data Parameters
NAME          QZ-3-156-1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20121205
Time               15.54
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8403.361 Hz
FIDRES          0.128225 Hz
AQ              3.8994420 sec
RG                   114
DW                59.500 usec
DE                17.39 usec
TE                298.1 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.3233018 MHz
NUC1                   1H
P1                 10.77 usec

F2 - Processing parameters
SI                 65536
SF           600.3200641 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

Compound 2.49 13 C NMR



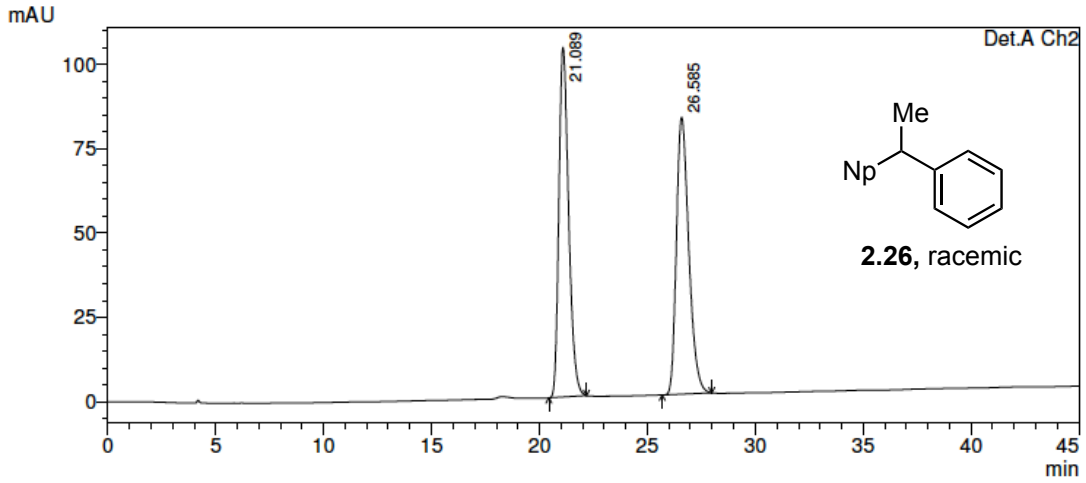
Current Data Parameters
NAME QZ-3-156-1
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121205
Time 16.04
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg55
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 34722.223 Hz
FIDRES 0.529819 Hz
AQ 0.9437684 sec
RG 2050
DW 14.400 usec
DE 19.34 usec
TE 298.1 K
D1 1.10000002 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 150.9656784 MHz
NUC1 13C
P1 10.63 usec

F2 - Processing parameters
SI 32768
SF 150.9505840 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

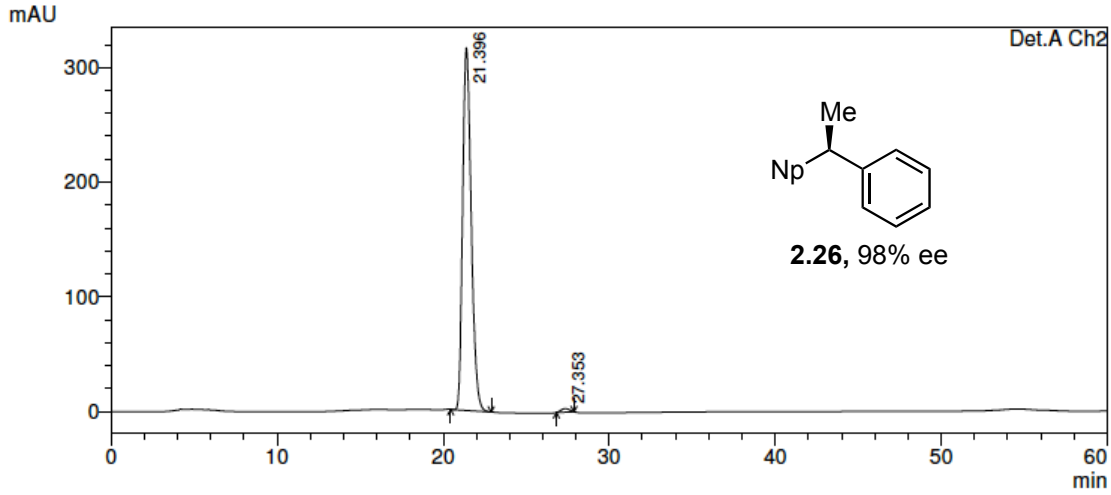
Compound 2.26, racemic



Detector A Ch2 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.089	3262561	103718	49.915	55.809
2	26.585	3273635	82125	50.085	44.191
Total		6536196	185843	100.000	100.000

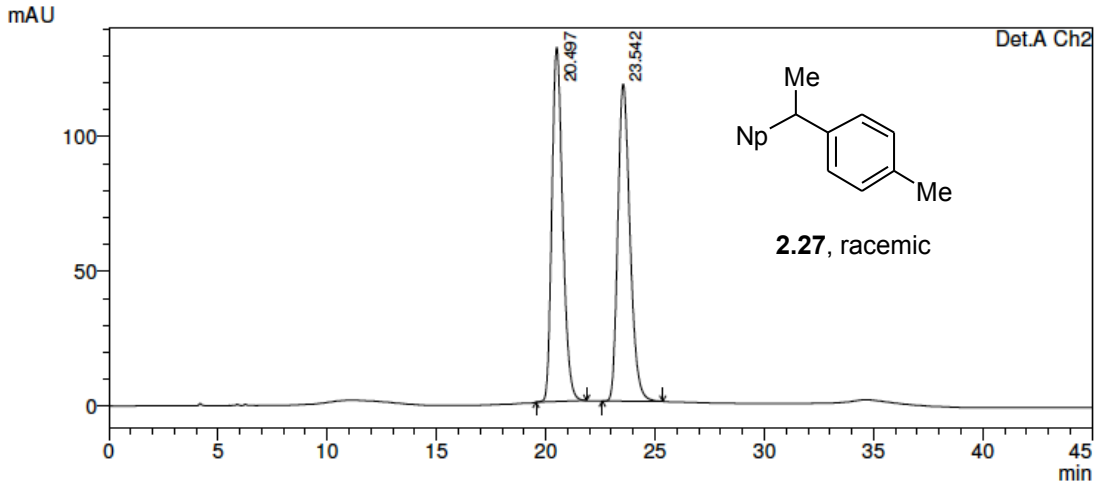
Compound 2.26, 98% ee



Detector A Ch2 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.396	11355848	316283	99.047	99.024
2	27.353	109219	3118	0.953	0.976
Total		11465067	319400	100.000	100.000

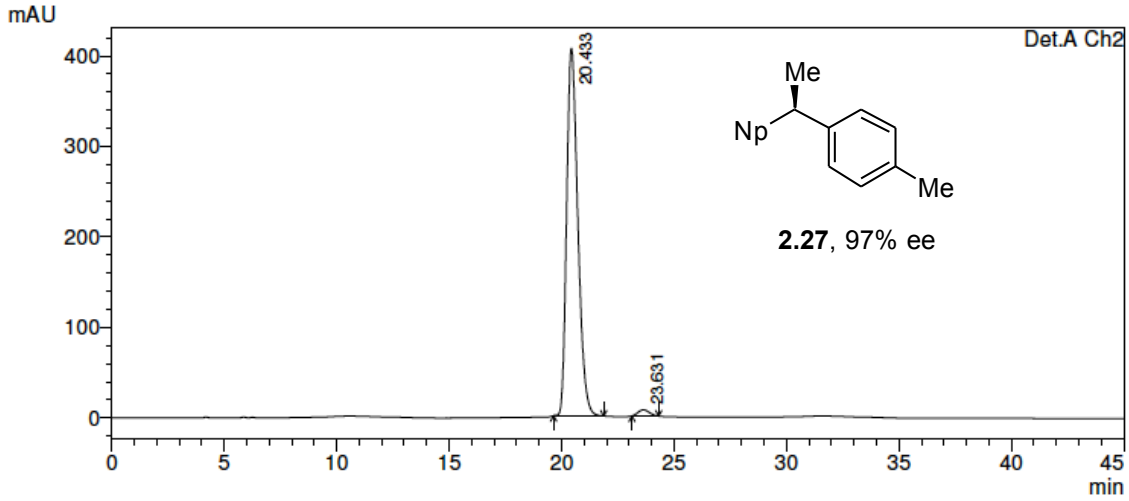
Compound 2.27, racemic



Detector A Ch2 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.497	4523871	131568	49.803	52.771
2	23.542	4559688	117752	50.197	47.229
Total		9083559	249320	100.000	100.000

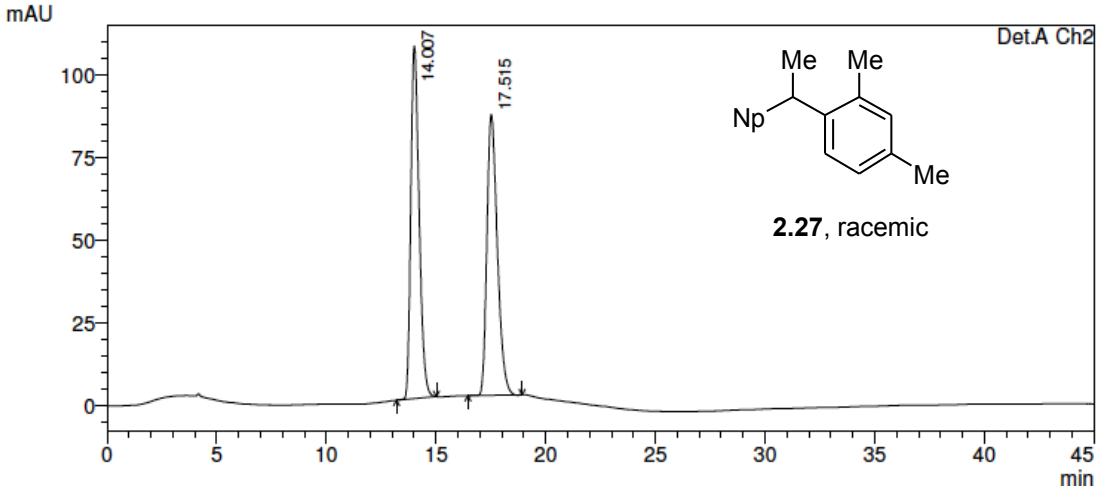
Compound 2.27, 97% ee



Detector A Ch2 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.433	14024628	406137	98.341	98.352
2	23.631	236613	6803	1.659	1.648
Total		14261242	412940	100.000	100.000

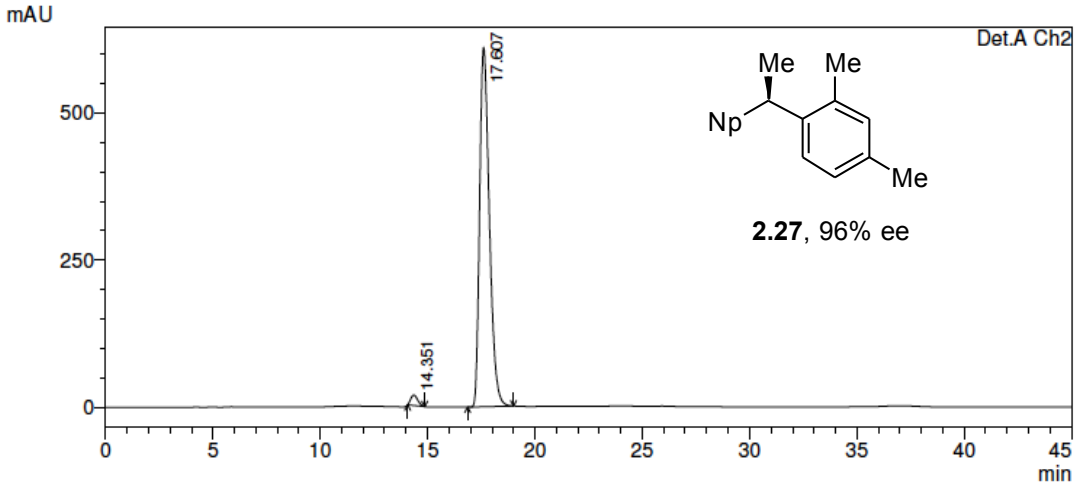
Compound 2.27, racemic



Detector A Ch2 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.007	2808009	106586	50.097	55.666
2	17.515	2797140	84887	49.903	44.334
Total		5605149	191474	100.000	100.000

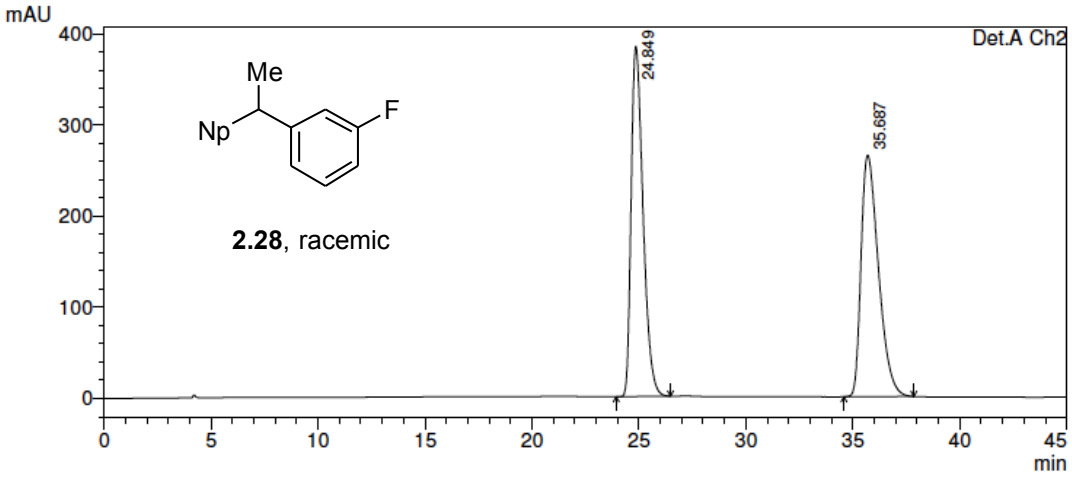
Compound 2.27, 96% ee



Detector A Ch2 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.351	393869	17724	2.008	2.823
2	17.607	19217322	610132	97.992	97.177
Total		19611191	627856	100.000	100.000

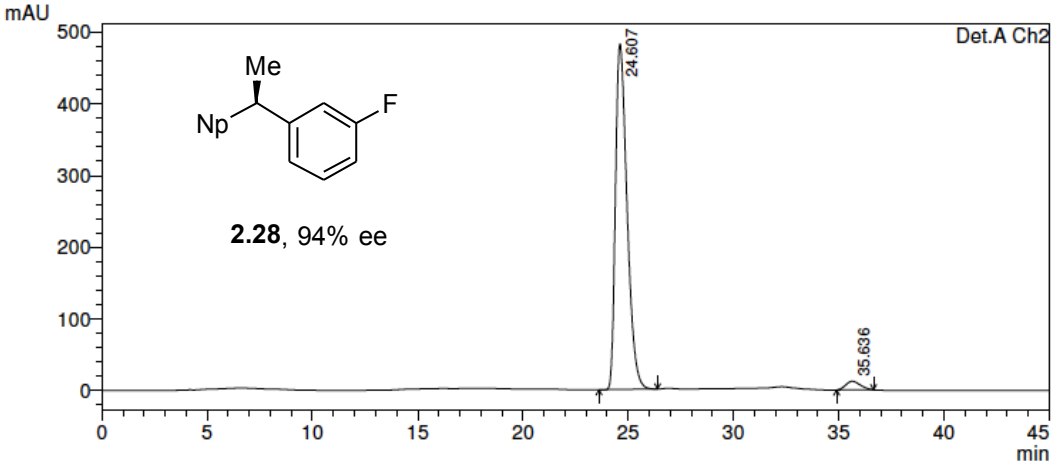
Compound 2.28, racemic



Detector A Ch2 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.849	14888201	384482	49.841	59.188
2	35.687	14983179	265111	50.159	40.812
Total		29871380	649593	100.000	100.000

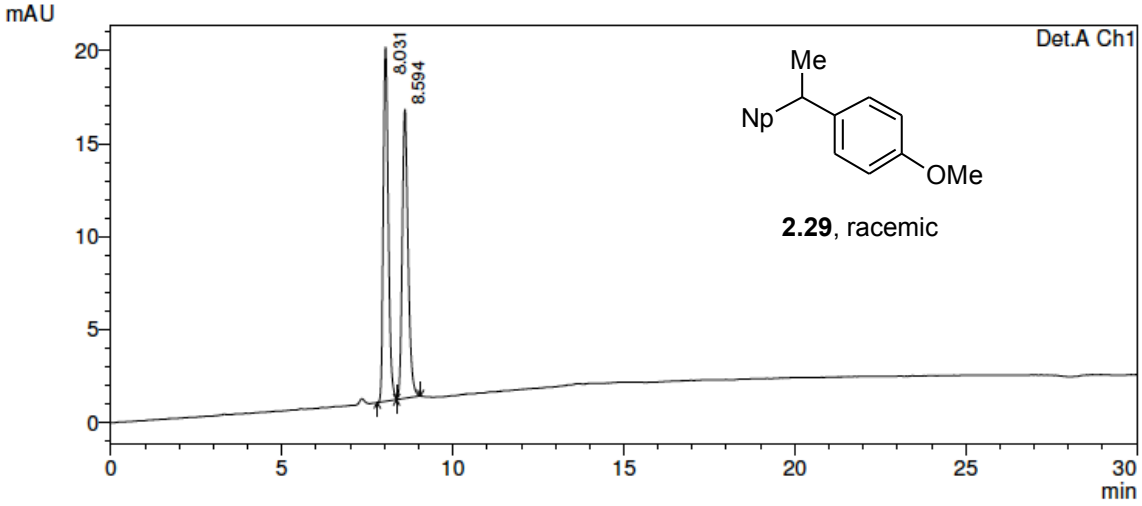
Compound 2.28, 94% ee



Detector A Ch2 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.607	18437656	482435	96.983	97.593
2	35.636	573579	11899	3.017	2.407
Total		19011234	494333	100.000	100.000

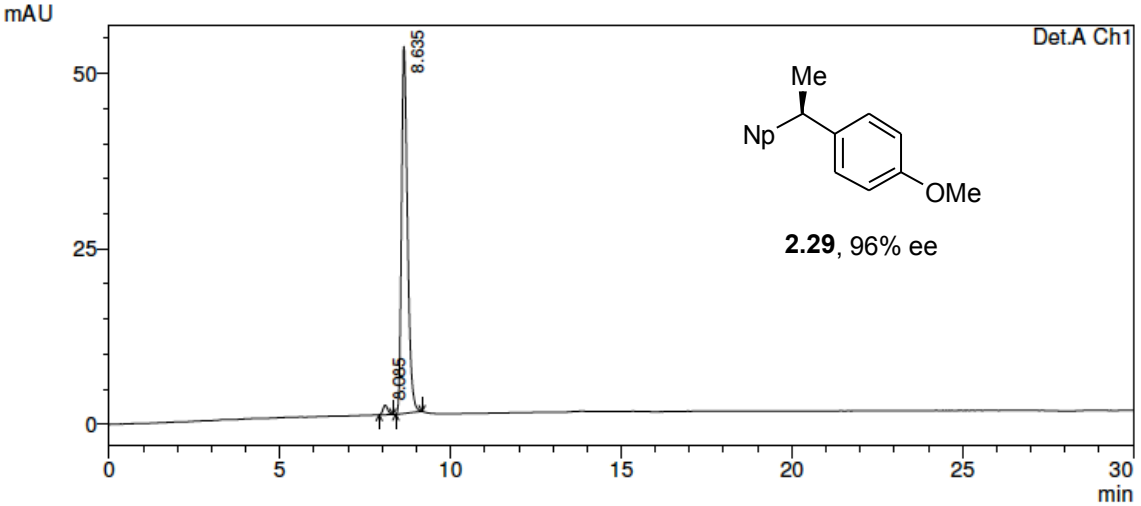
Compound 2.29, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.031	191673	19028	50.578	55.069
2	8.594	187296	15524	49.422	44.931
Total		378969	34552	100.000	100.000

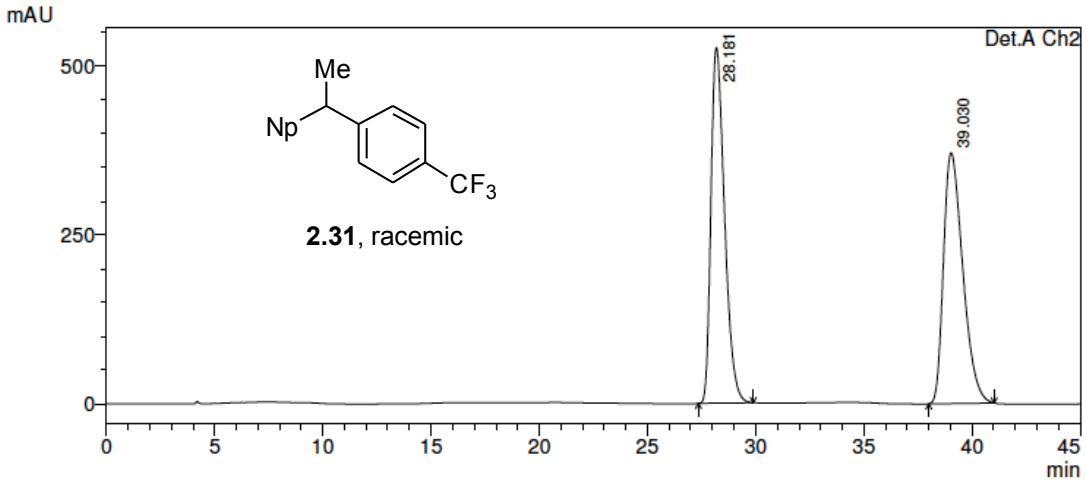
Compound 2.29, 96% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.085	13175	1356	1.992	2.529
2	8.635	648308	52277	98.008	97.471
Total		661483	53633	100.000	100.000

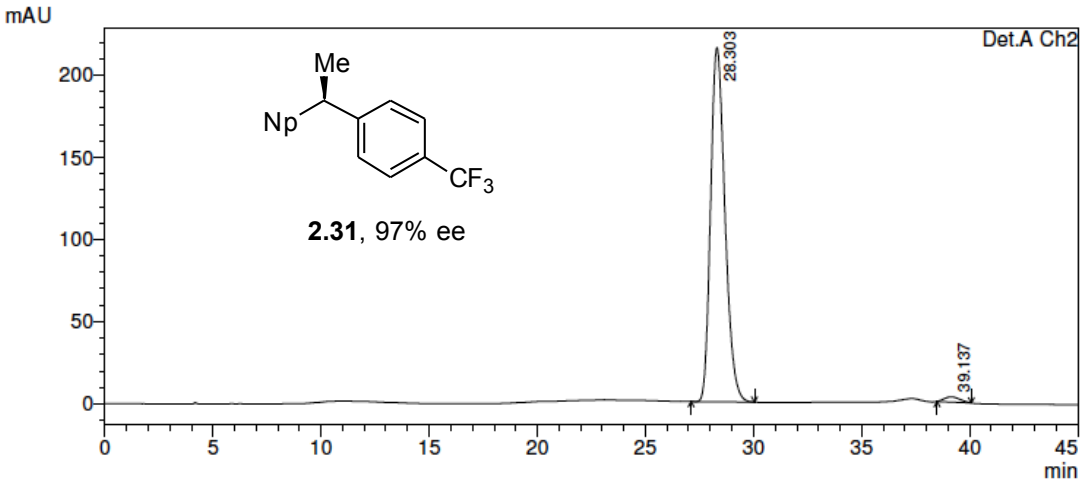
Compound 2.31, racemic



Detector A Ch2 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.181	23034505	527033	50.014	58.657
2	39.030	23021610	371471	49.986	41.343
Total		46056115	898503	100.000	100.000

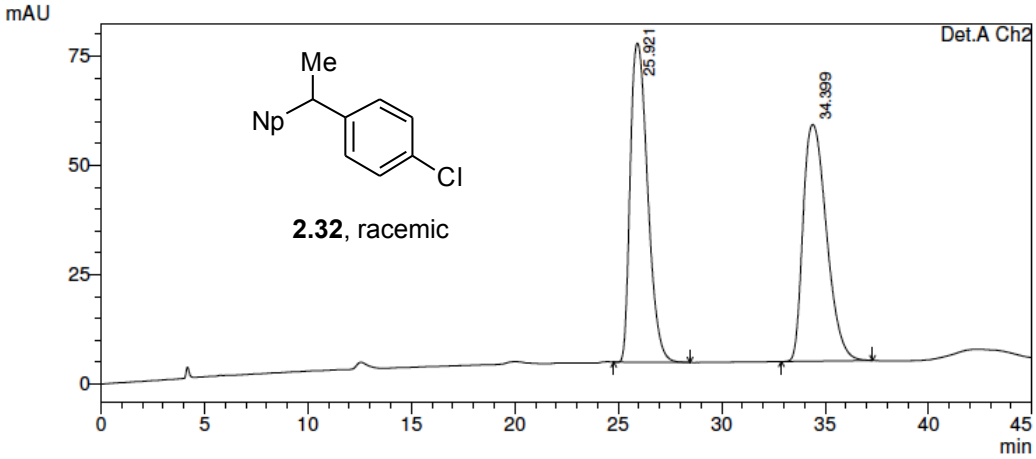
Compound 2.31, 97% ee



Detector A Ch2 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.303	9967337	215692	98.419	98.556
2	39.137	160085	3159	1.581	1.444
Total		10127422	218851	100.000	100.000

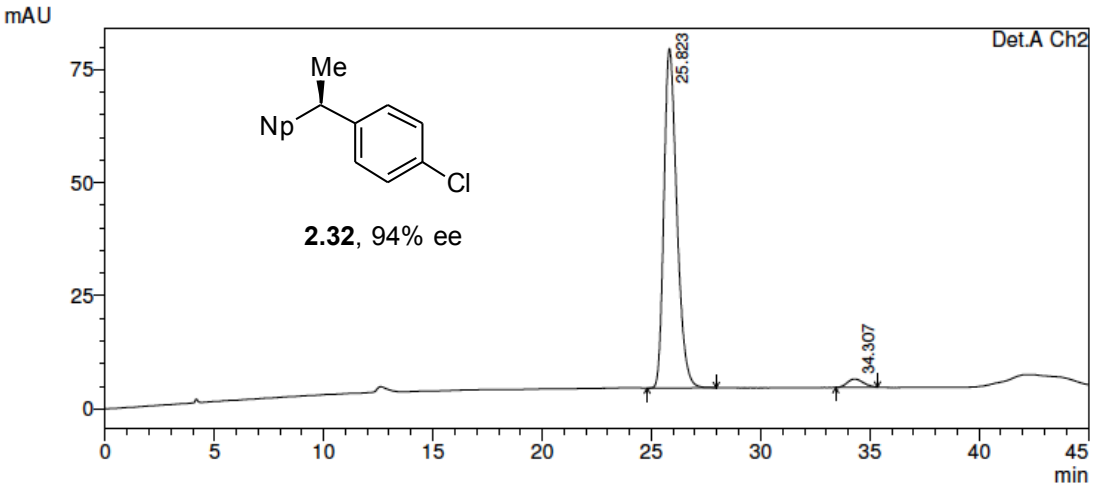
Compound 2.32, racemic



Detector A Ch2 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.921	4270293	73019	49.968	57.422
2	34.399	4275844	54144	50.032	42.578
Total		8546138	127164	100.000	100.000

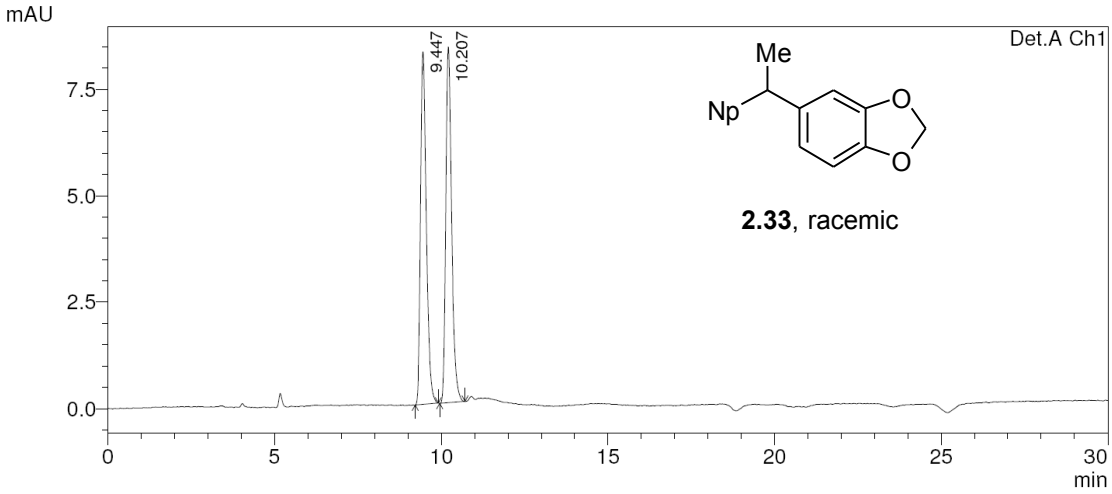
Compound 2.32, 94% ee



Detector A Ch2 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.823	3087241	75048	97.037	97.589
2	34.307	94277	1854	2.963	2.411
Total		3181518	76902	100.000	100.000

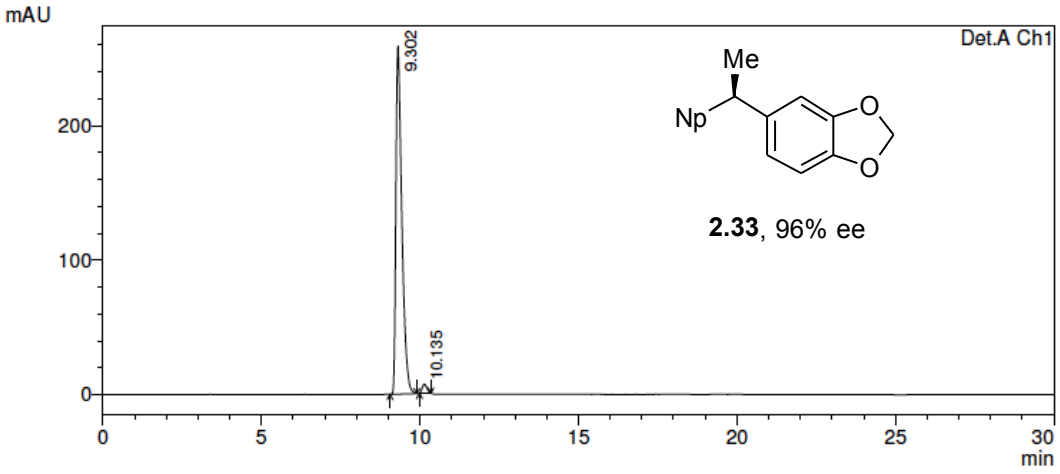
Compound 2.33, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.447	99369	8286	49.582	49.778
2	10.207	101046	8360	50.418	50.222
Total		200415	16646	100.000	100.000

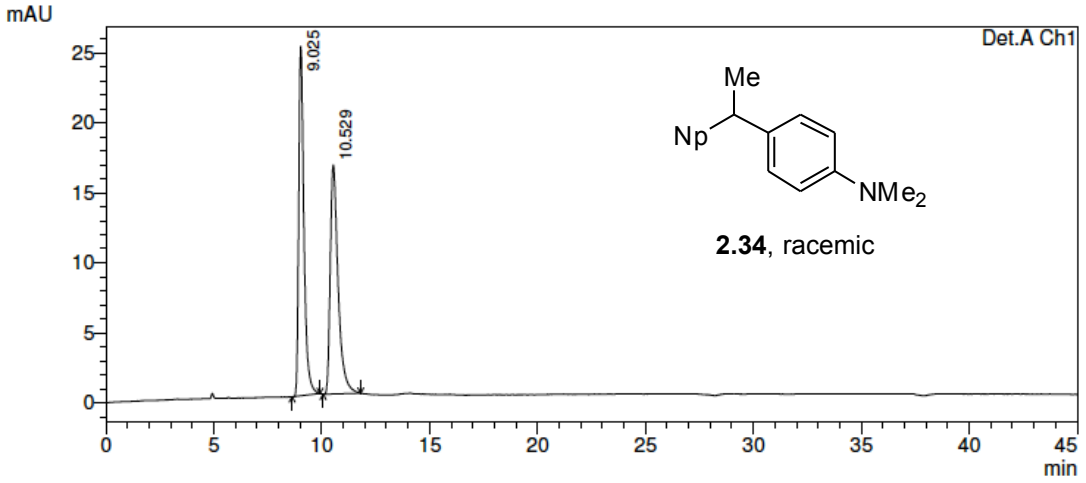
Compound 2.33, 96% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.302	3412628	258849	98.030	97.482
2	10.135	68590	6685	1.970	2.518
Total		3481218	265533	100.000	100.000

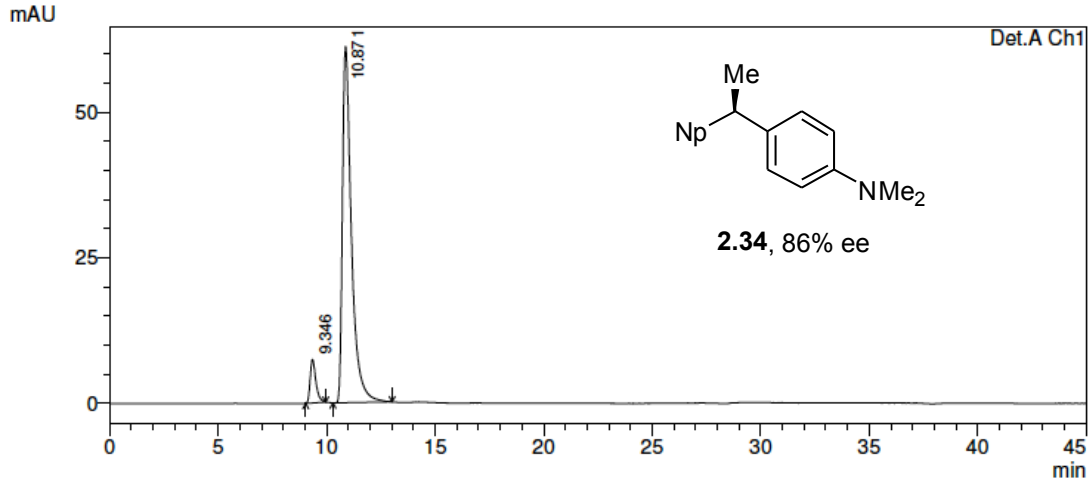
Compound 2.34, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.025	420349	24972	50.369	60.385
2	10.529	414192	16383	49.631	39.615
Total		834541	41355	100.000	100.000

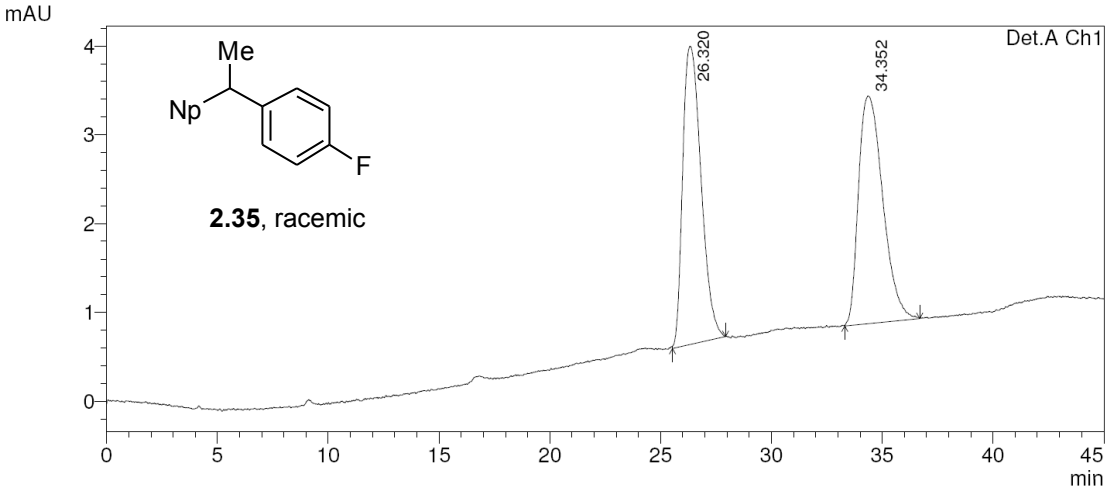
Compound 2.34, 86% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.346	136637	7475	7.169	10.895
2	10.871	1769349	61137	92.831	89.105
Total		1905986	68612	100.000	100.000

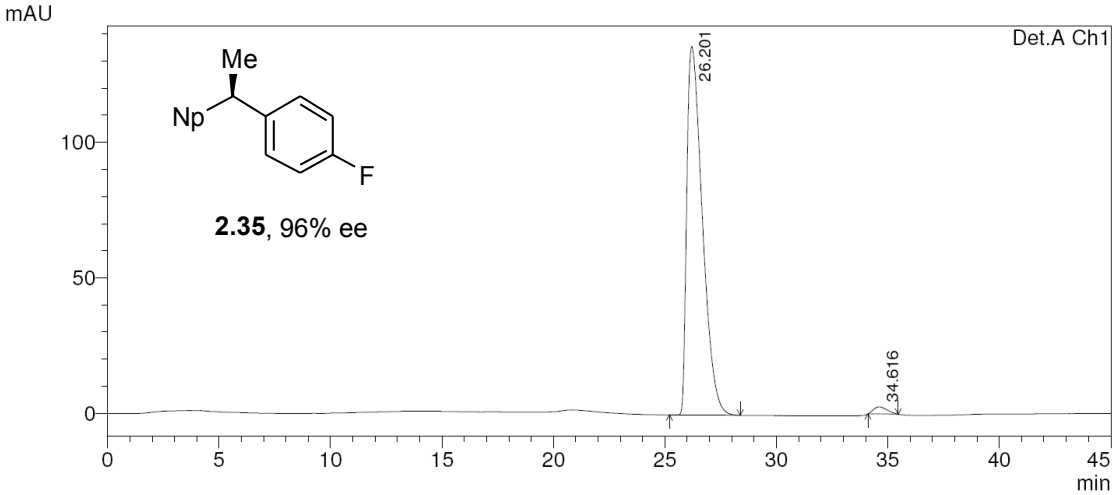
Compound 2.35, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.320	193738	3360	49.747	56.717
2	34.352	195710	2564	50.253	43.283
Total		389449	5925	100.000	100.000

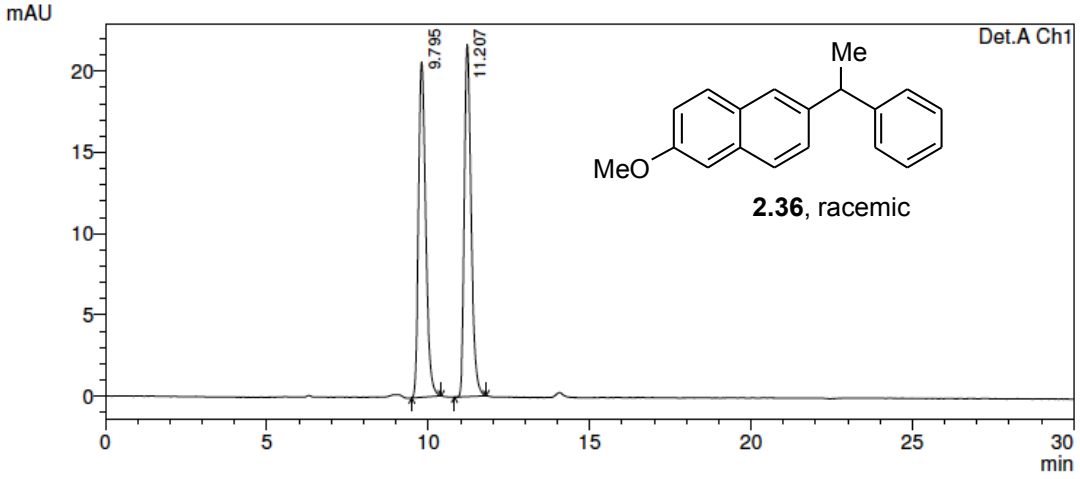
Compound 2.35, 96% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.201	6602080	135918	98.328	98.110
2	34.616	112284	2618	1.672	1.890
Total		6714364	138536	100.000	100.000

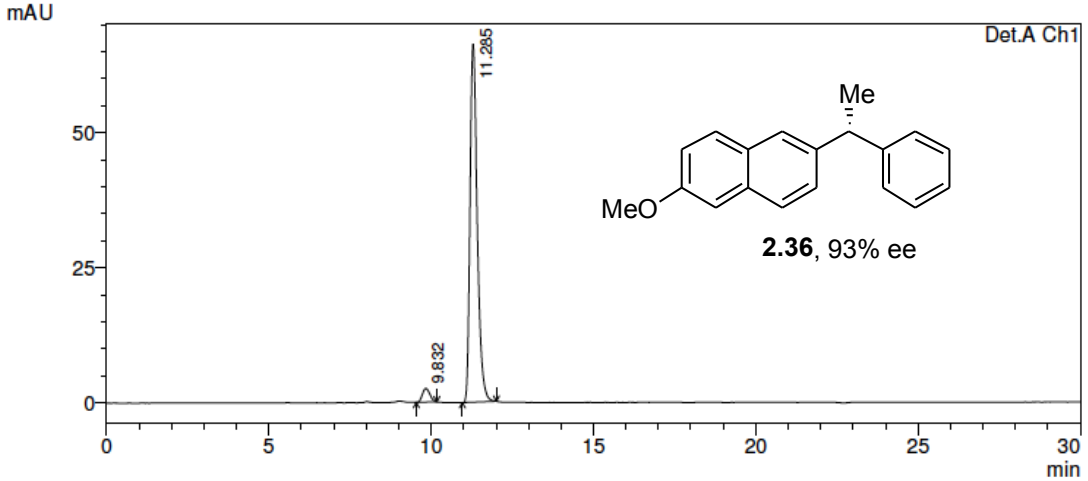
Compound 2.36, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.795	319664	20638	50.251	48.794
2	11.207	316471	21658	49.749	51.206
Total		636135	42296	100.000	100.000

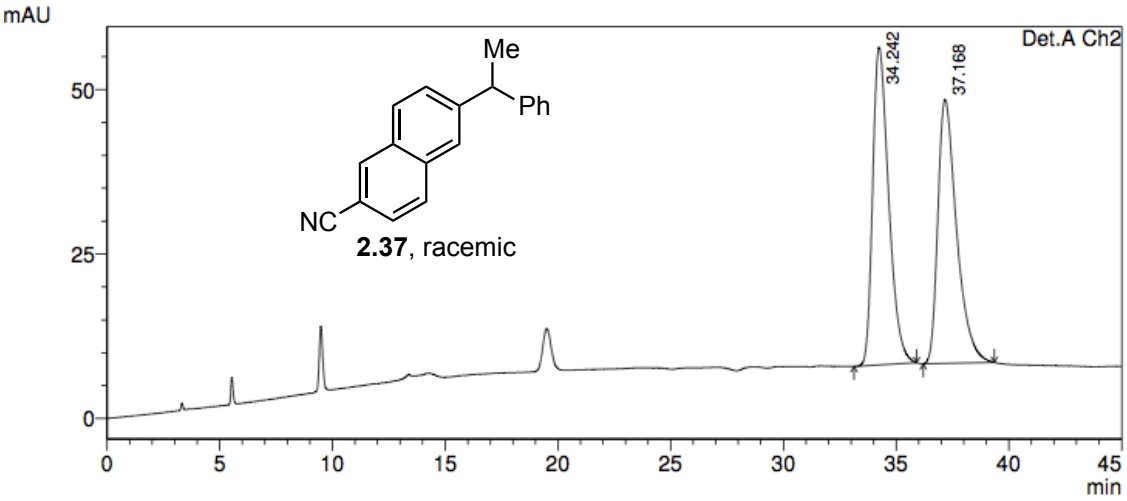
Compound 2.36, 93% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.832	40139	2543	3.773	3.694
2	11.285	1023789	66290	96.227	96.306
Total		1063928	68833	100.000	100.000

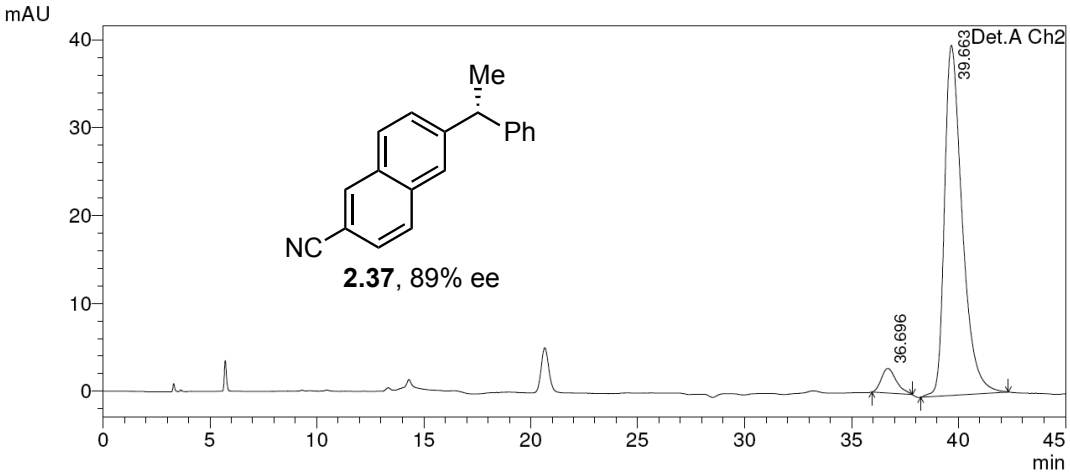
Compound 2.37, racemic



Detector A Ch2 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.242	2385648	48276	50.718	54.631
2	37.168	2318059	40092	49.282	45.369
Total		4703707	88368	100.000	100.000

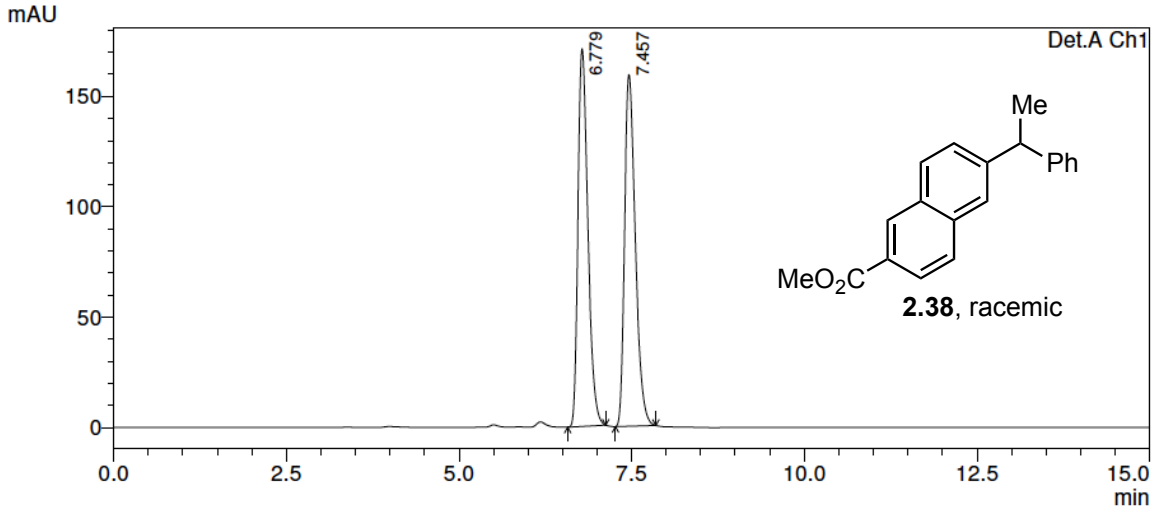
Compound 2.37, 89% ee



Detector A Ch2 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	32.051	57812	1412	5.285	6.564
2	34.791	1036032	20095	94.715	93.436
Total		1093843	21507	100.000	100.000

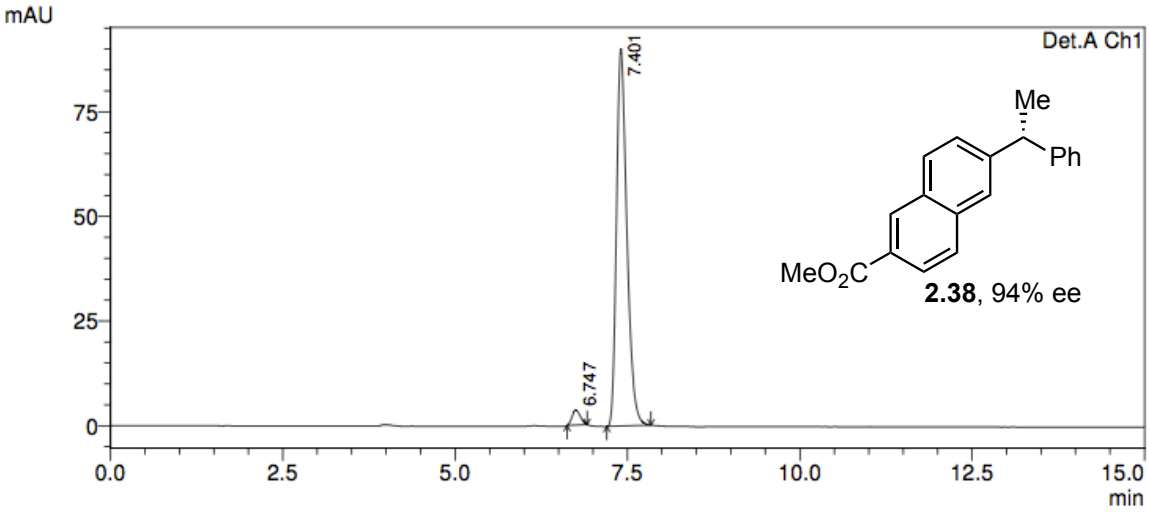
Compound 2.38, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.779	1705134	171182	49.744	51.809
2	7.457	1722698	159230	50.256	48.191
Total		3427831	330412	100.000	100.000

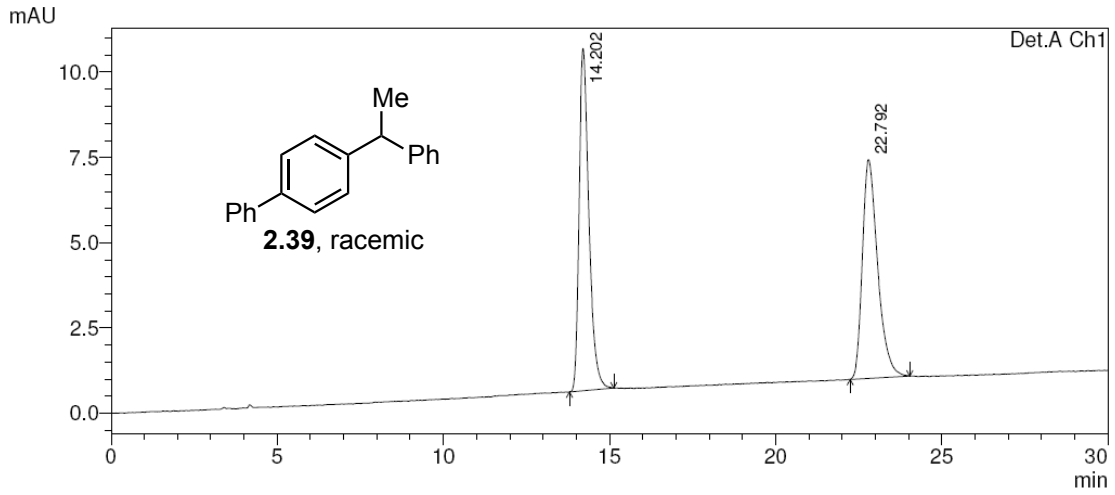
Compound 2.38, 94% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.747	30236	3609	3.099	3.847
2	7.401	945469	90198	96.901	96.153
Total		975705	93807	100.000	100.000

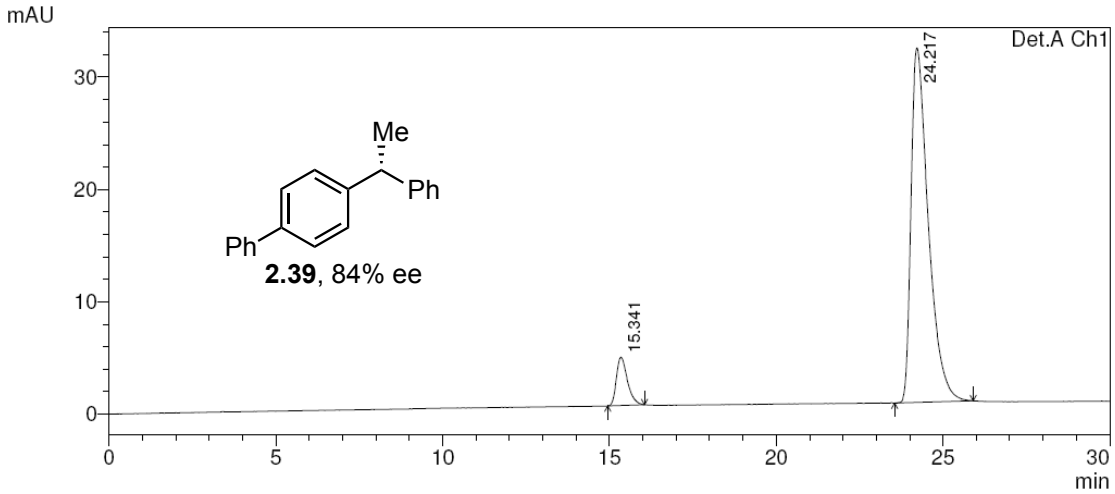
Compound 2.39, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.202	205998	10036	50.049	60.984
2	22.792	205596	6420	49.951	39.016
Total		411595	16456	100.000	100.000

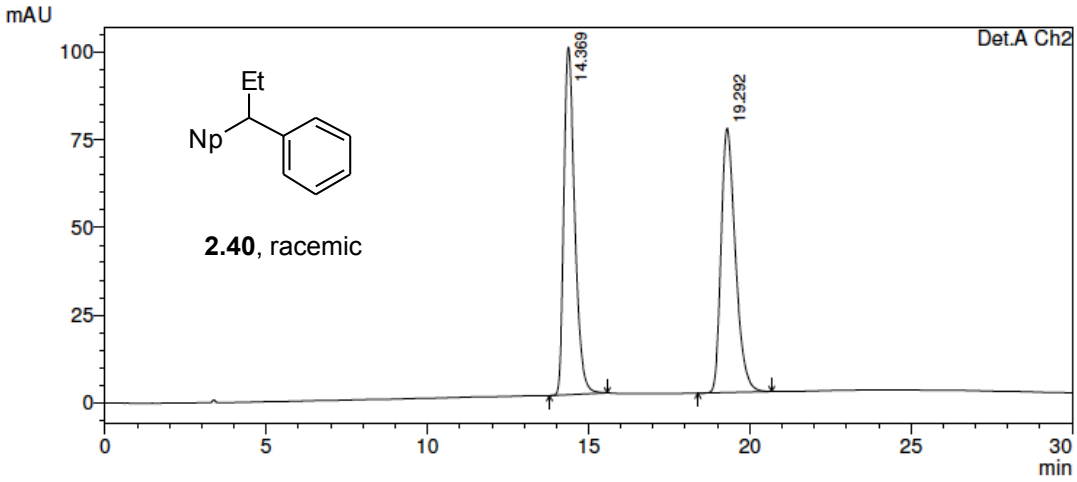
Compound 2.39, 84% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.341	98693	4298	7.974	11.991
2	24.217	1138964	31549	92.026	88.009
Total		1237657	35848	100.000	100.000

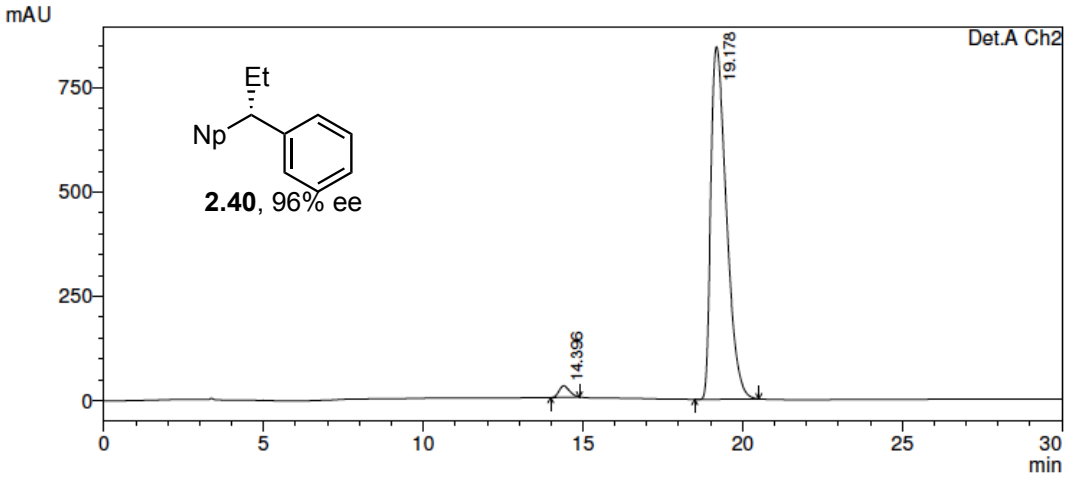
Compound 2.40, racemic



Detector A Ch2 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.369	2317727	98945	49.927	56.791
2	19.292	2324539	75281	50.073	43.209
Total		4642266	174226	100.000	100.000

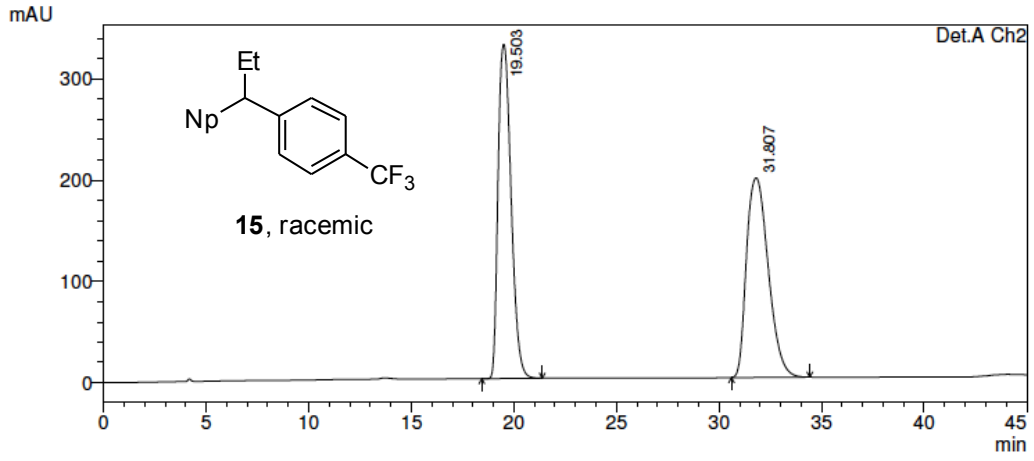
Compound 2.40, 96% ee



Detector A Ch2 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.396	619653	27486	2.118	3.152
2	19.178	28642737	844555	97.882	96.848
Total		29262391	872041	100.000	100.000

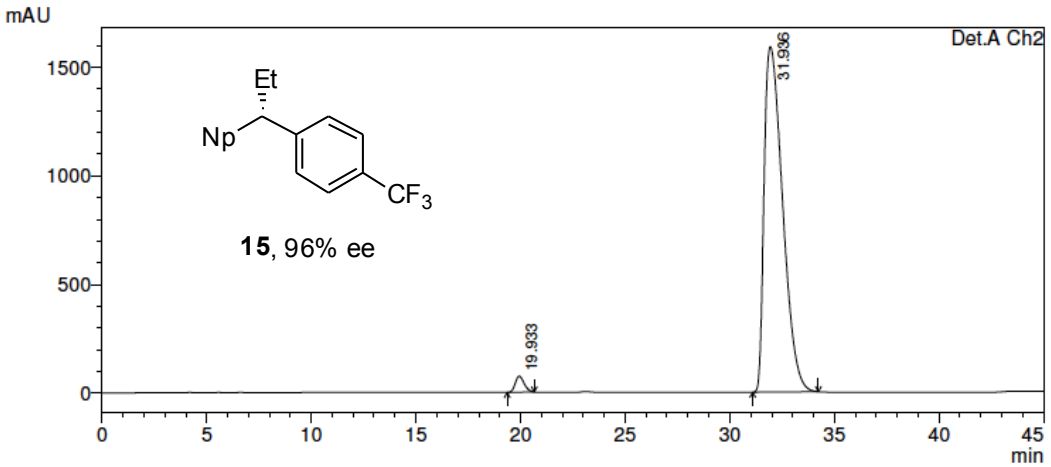
Compound 2.41, racemic



Detector A Ch2 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.503	14527364	330016	49.946	62.606
2	31.807	14558791	197114	50.054	37.394
Total		29086155	527130	100.000	100.000

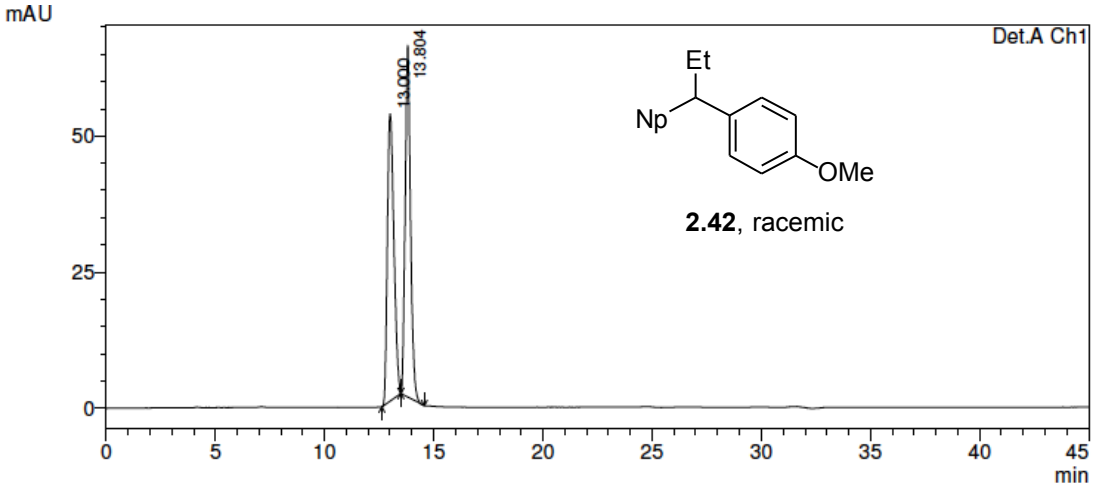
Compound 2.41, 96% ee



Detector A Ch2 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.933	2186019	73861	2.187	4.435
2	31.936	97776569	1591639	97.813	95.565
Total		99962589	1665500	100.000	100.000

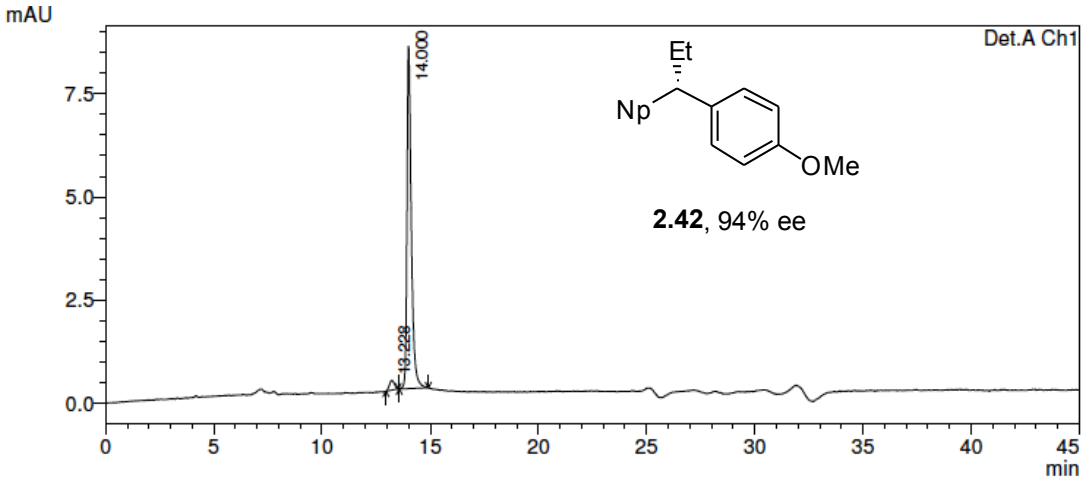
Compound 2.42, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.000	1095755	52759	49.972	44.969
2	13.804	1096990	64565	50.028	55.031
Total		2192745	117324	100.000	100.000

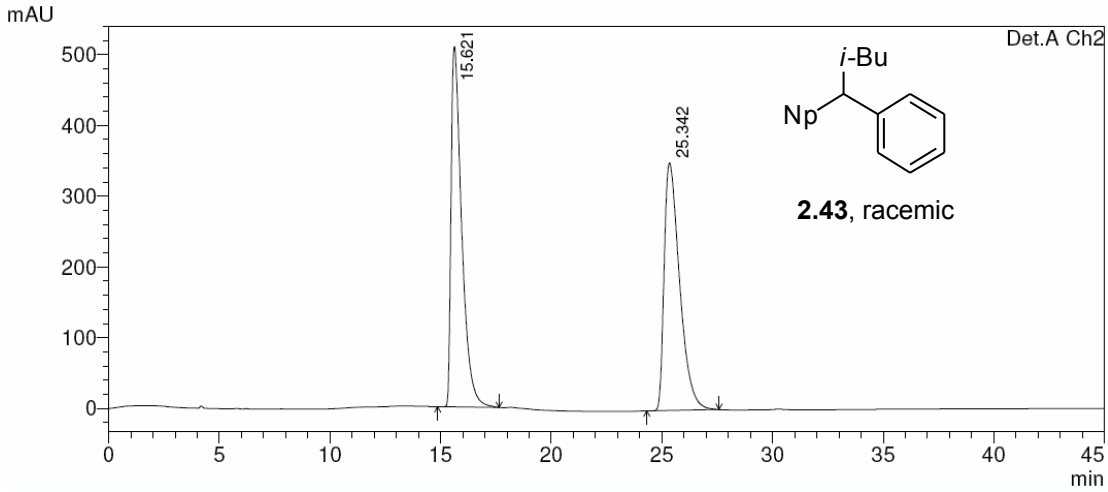
Compound 2.42, 94% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.228	3845	237	3.216	2.779
2	14.000	115716	8281	96.784	97.221
Total		119561	8518	100.000	100.000

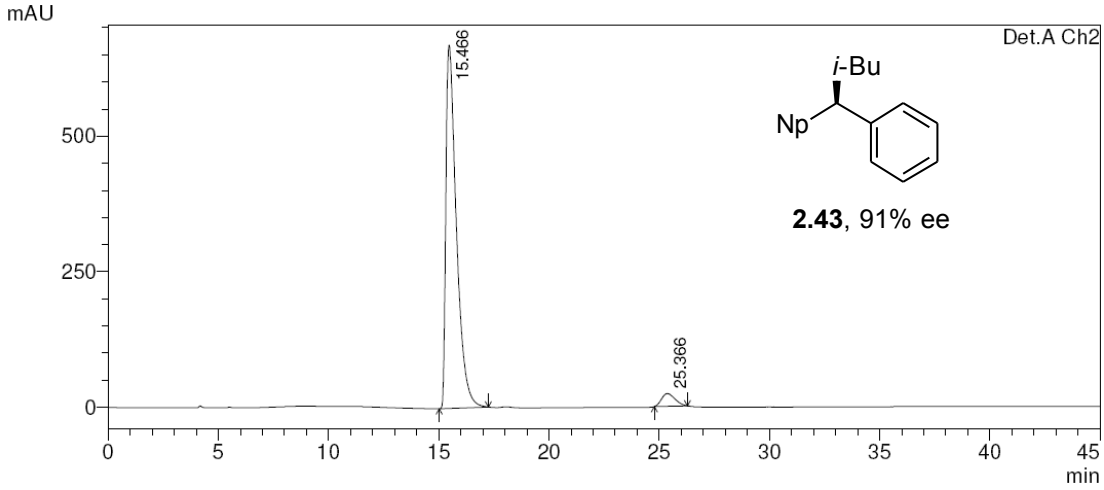
Compound 2.43, racemic



Detector A Ch2 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.621	16984566	509077	50.009	59.278
2	25.342	16978126	349718	49.991	40.722
Total		33962693	858795	100.000	100.000

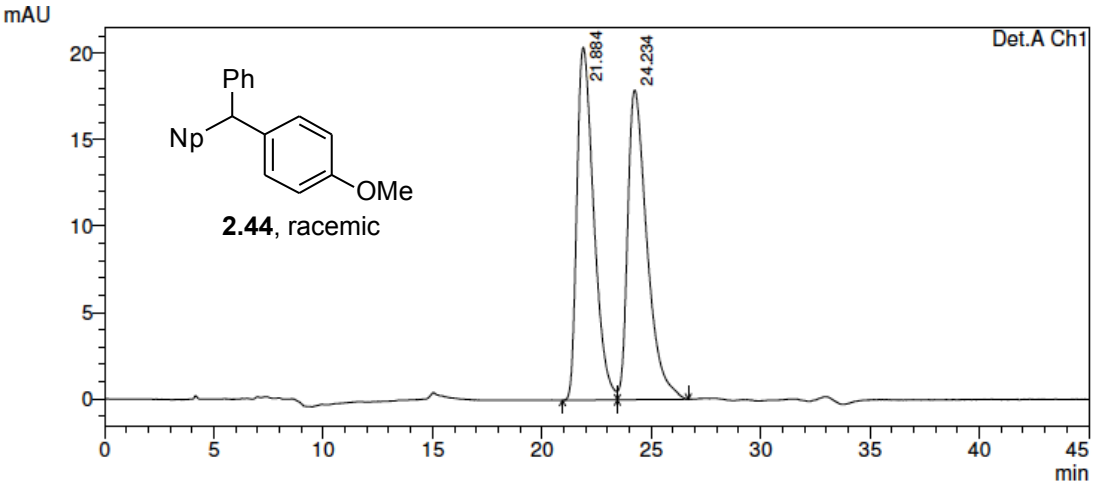
Compound 2.43, 91% ee



Detector A Ch2 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.466	22211081	670111	95.721	96.614
2	25.366	992790	23482	4.279	3.386
Total		23203871	693593	100.000	100.000

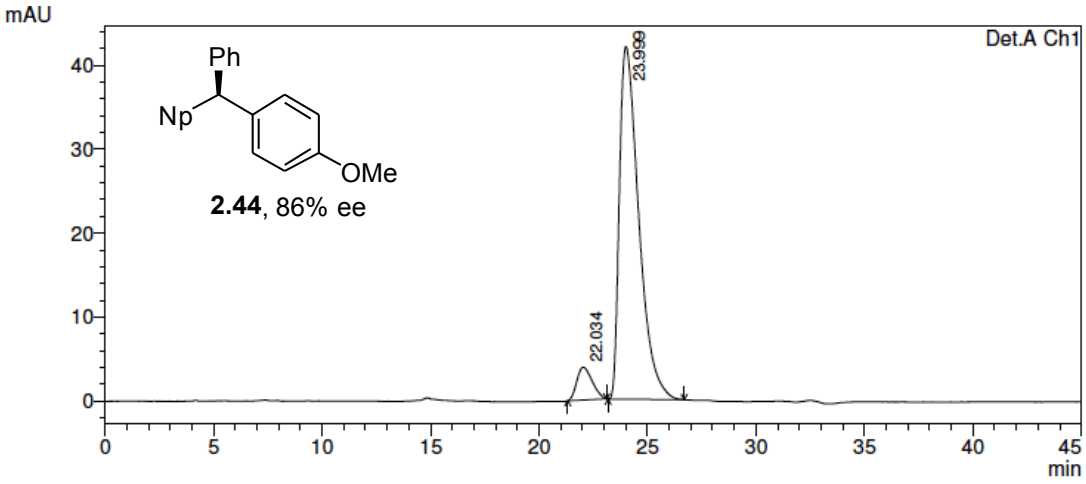
Compound 2.44, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.884	1094878	20418	49.887	53.263
2	24.234	1099828	17916	50.113	46.737
Total		2194707	38334	100.000	100.000

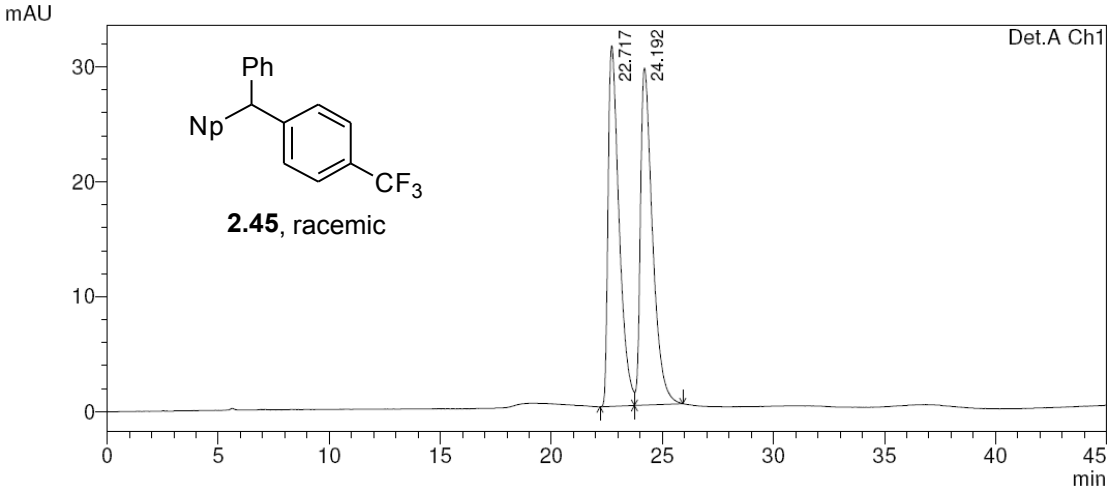
Compound 2.44, 86% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.034	191831	3896	6.858	8.490
2	23.999	2605492	41994	93.142	91.510
Total		2797324	45890	100.000	100.000

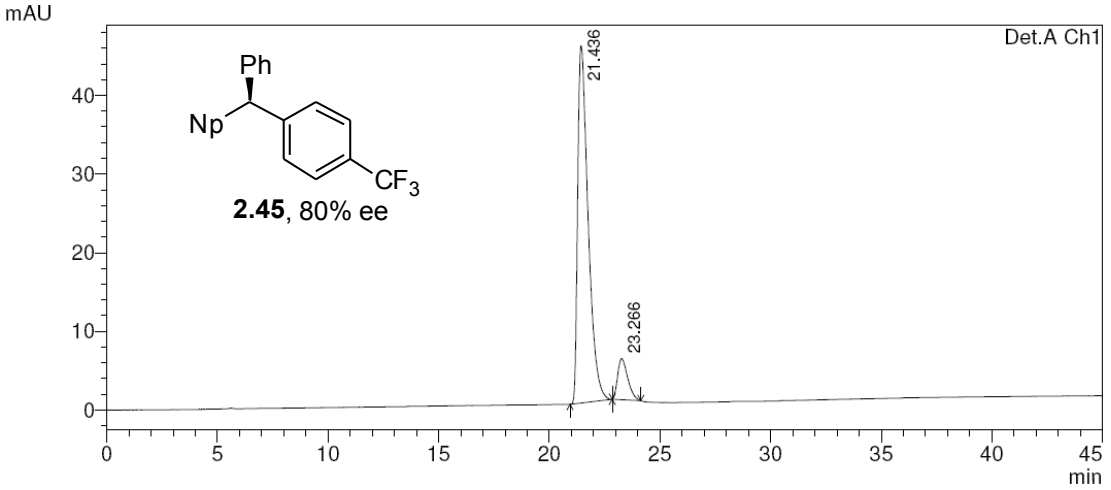
Compound 2.45, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.717	1082361	31364	49.305	51.676
2	24.192	1112865	29329	50.695	48.324
Total		2195226	60693	100.000	100.000

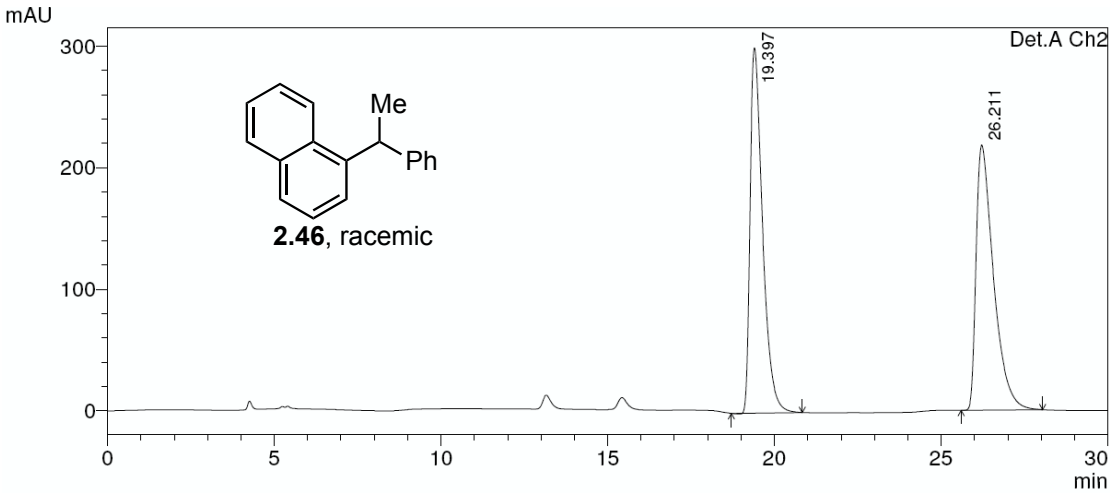
Compound 2.45, 80% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.436	1487789	45441	89.984	89.669
2	23.266	165603	5235	10.016	10.331
Total		1653392	50676	100.000	100.000

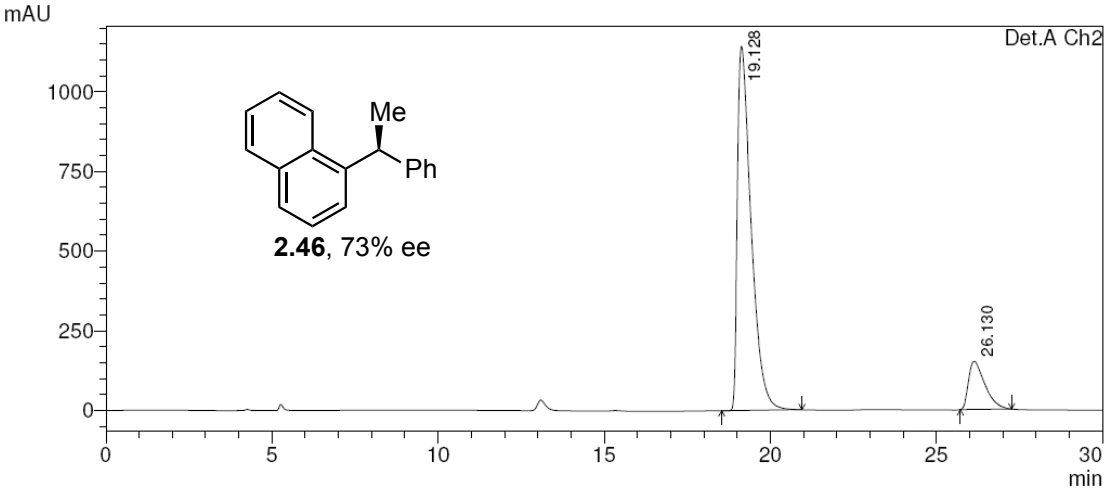
Compound 2.46, racemic



Detector A Ch2 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.397	7810522	300253	49.720	57.922
2	26.211	7898490	218125	50.280	42.078
Total		15709011	518378	100.000	100.000

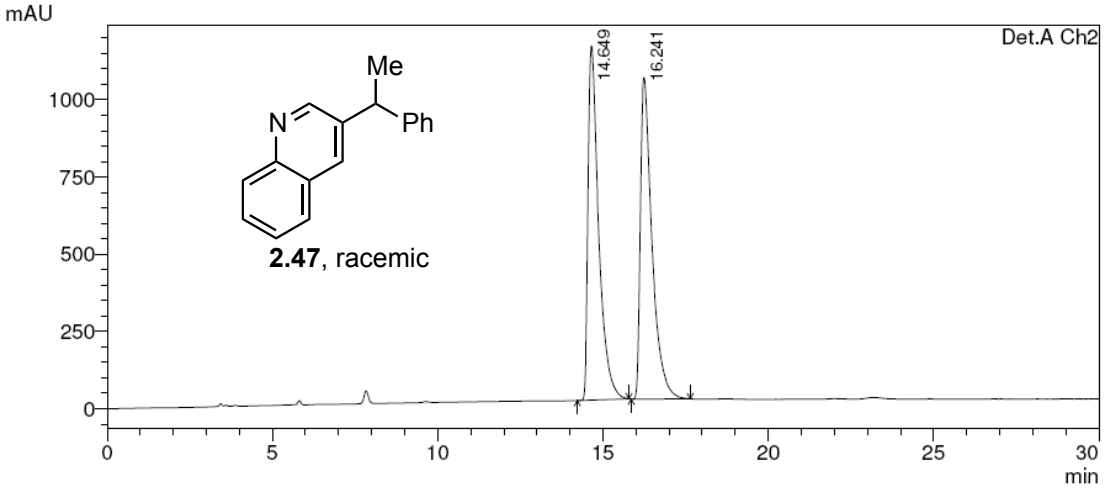
Compound 2.46, 73% ee



Detector A Ch2 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.128	32816995	1143059	86.387	88.309
2	26.130	5171503	151332	13.613	11.691
Total		37988498	1294391	100.000	100.000

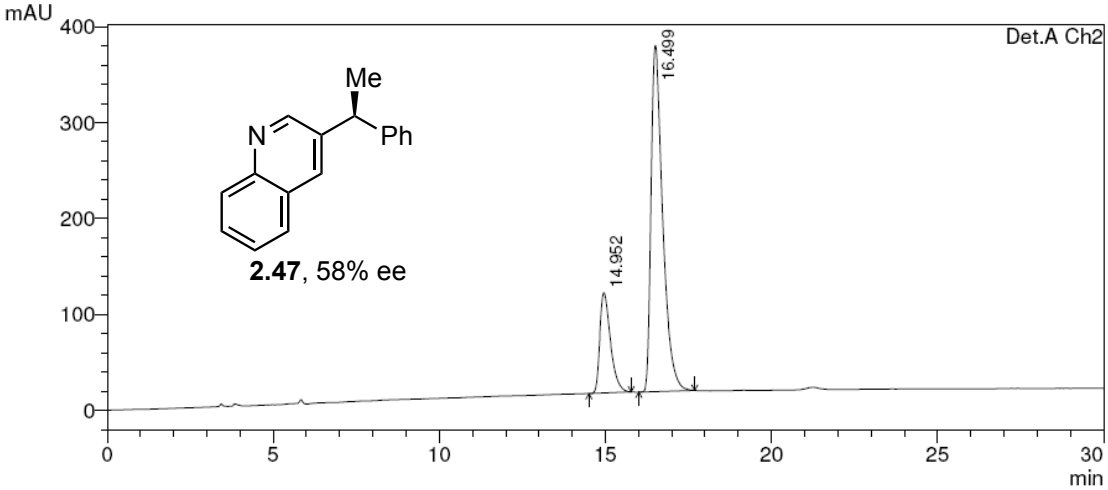
Compound 2.47, racemic



Detector A Ch2 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.649	25499869	1145829	50.011	52.413
2	16.241	25488158	1040344	49.989	47.587
Total		50988027	2186173	100.000	100.000

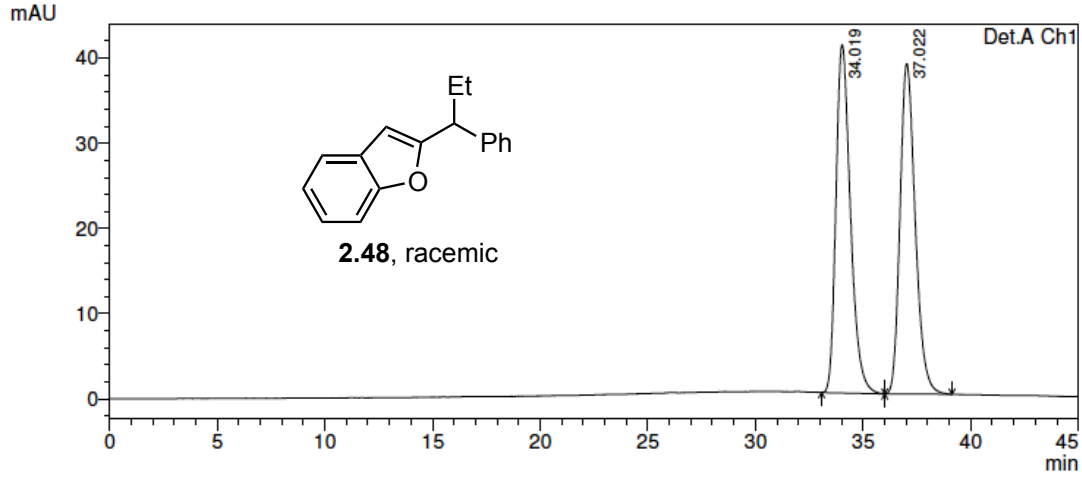
Compound 2.47, 58% ee



Detector A Ch2 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.952	2329178	104604	20.956	22.464
2	16.499	8785565	361045	79.044	77.536
Total		11114743	465649	100.000	100.000

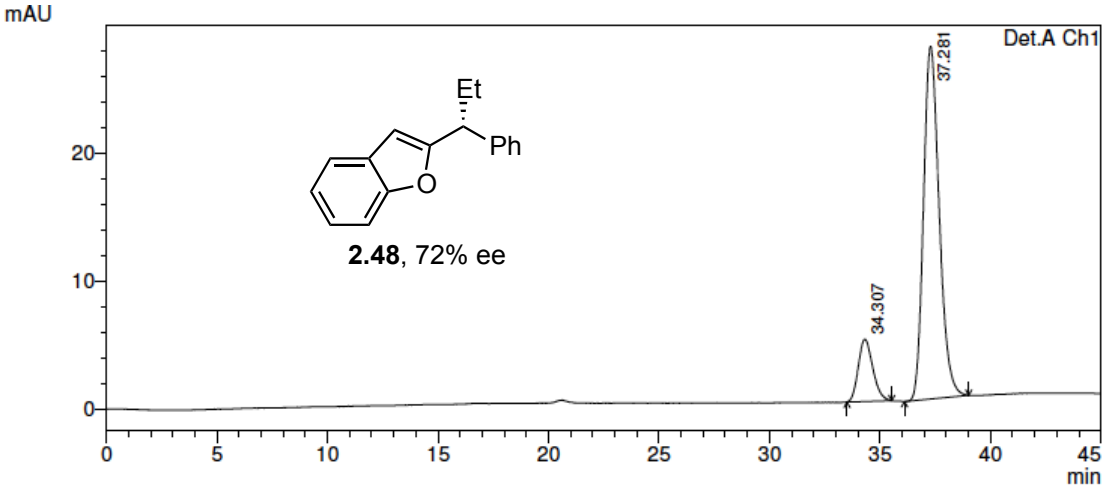
Compound 2.48, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.019	1909990	40855	50.048	51.323
2	37.022	1906321	38748	49.952	48.677
Total		3816311	79603	100.000	100.000

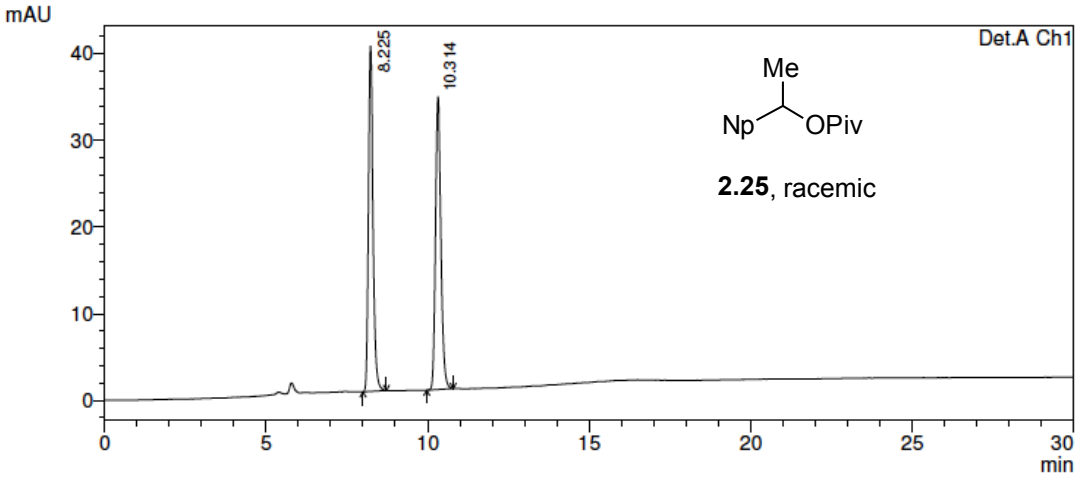
Compound 2.48, 72% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.307	221554	4844	14.011	14.963
2	37.281	1359765	27528	85.989	85.037
Total		1581318	32372	100.000	100.000

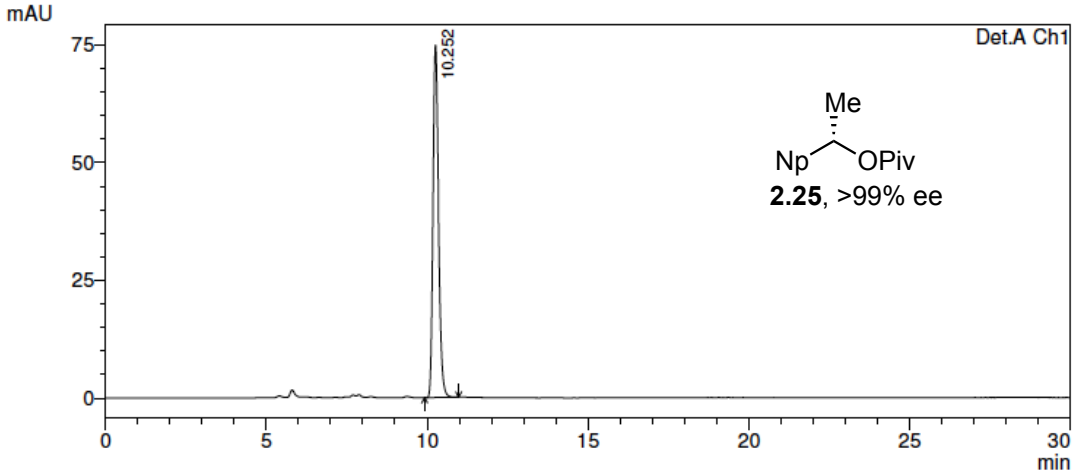
Compound 2.25, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.225	396397	39831	49.995	54.121
2	10.314	396480	33765	50.005	45.879
Total		792877	73597	100.000	100.000

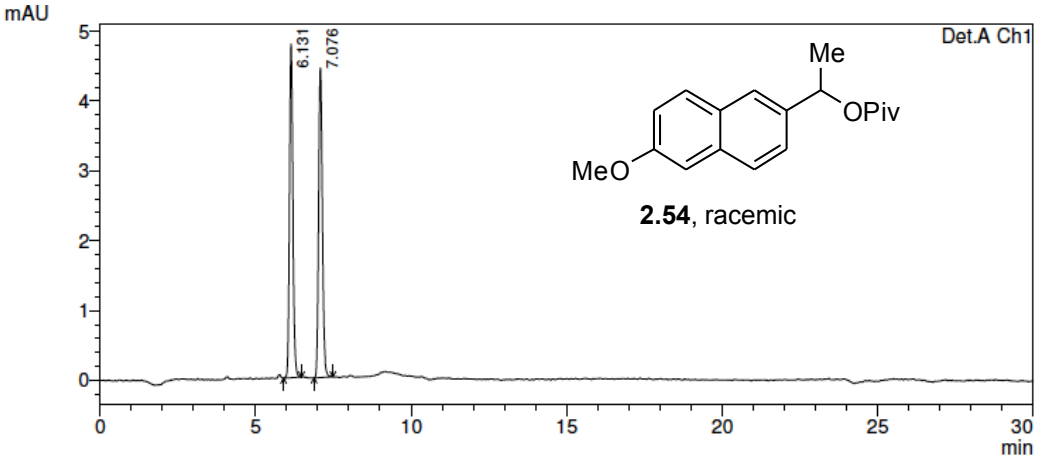
Compound 2.25, >99% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.252	897607	74803	100.000	100.000
Total		897607	74803	100.000	100.000

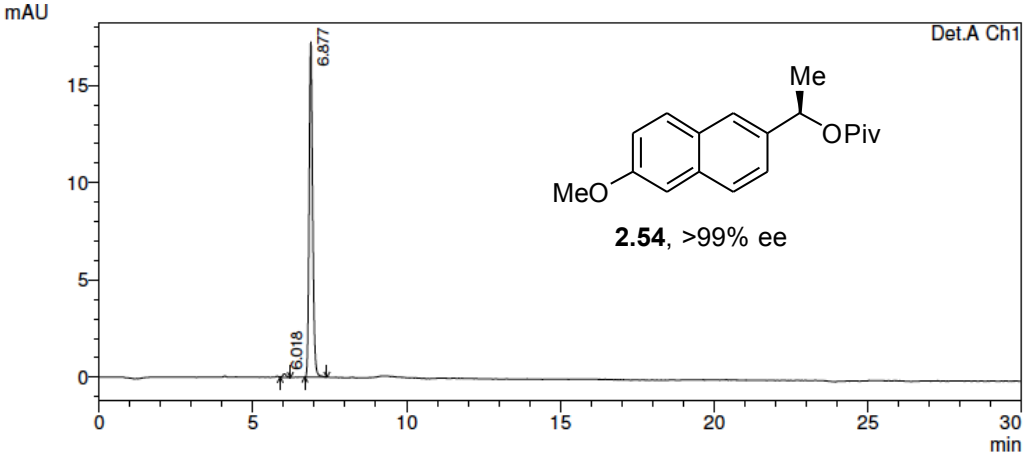
Compound 2.54, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.131	37054	4787	50.237	51.891
2	7.076	36705	4438	49.763	48.109
Total		73759	9224	100.000	100.000

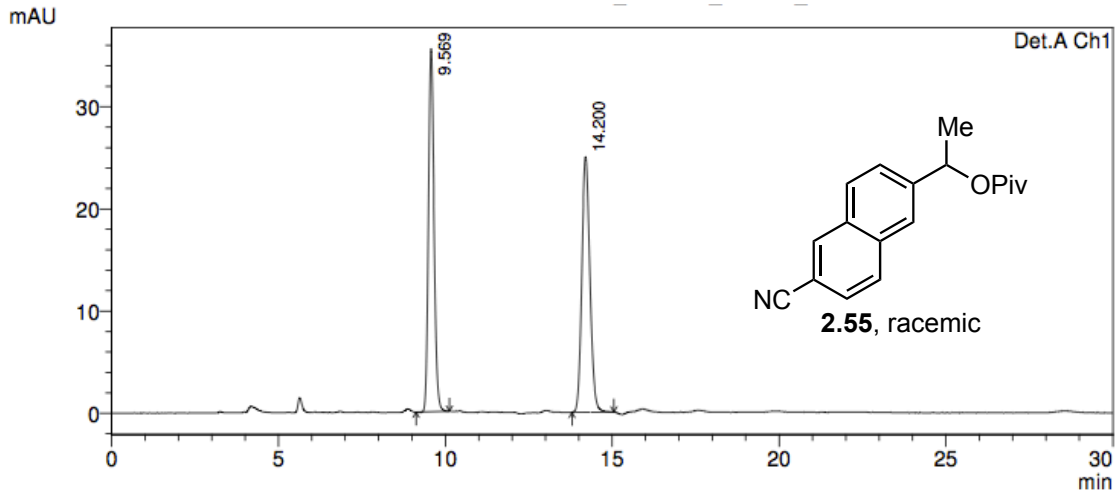
Compound 2.54, >99% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.018	1376	185	0.962	1.060
2	6.877	141653	17224	99.038	98.940
Total		143029	17409	100.000	100.000

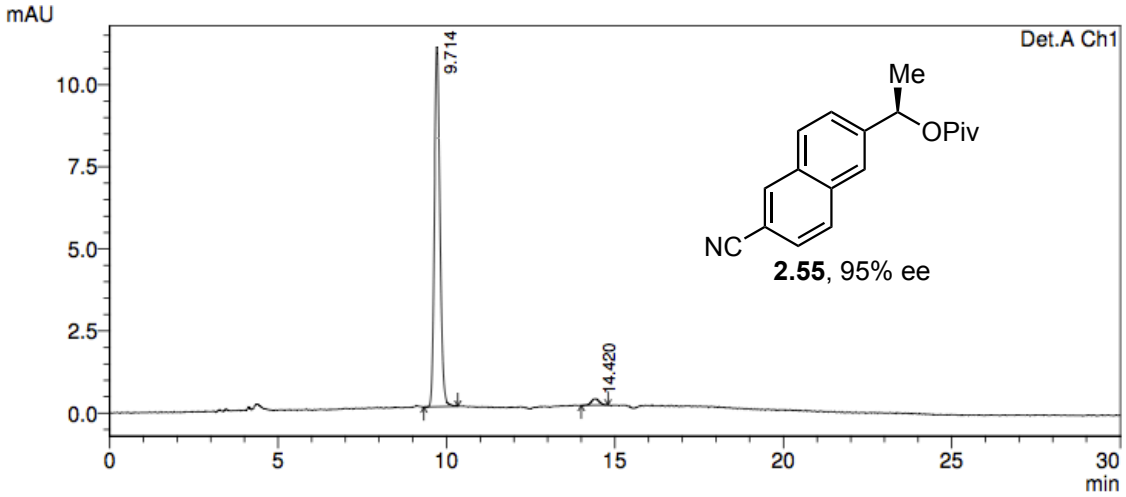
Compound 2.55, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.569	415129	35588	49.625	58.719
2	14.200	421402	25019	50.375	41.281
Total		836531	60608	100.000	100.000

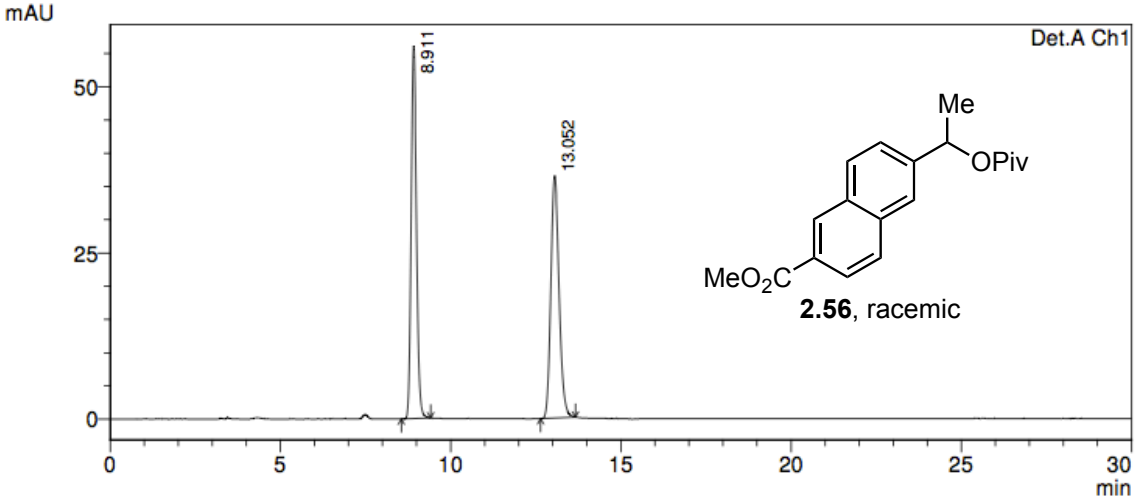
Compound 2.55, 95% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.714	126744	10973	97.412	98.176
2	14.420	3367	204	2.588	1.824
Total		130111	11177	100.000	100.000

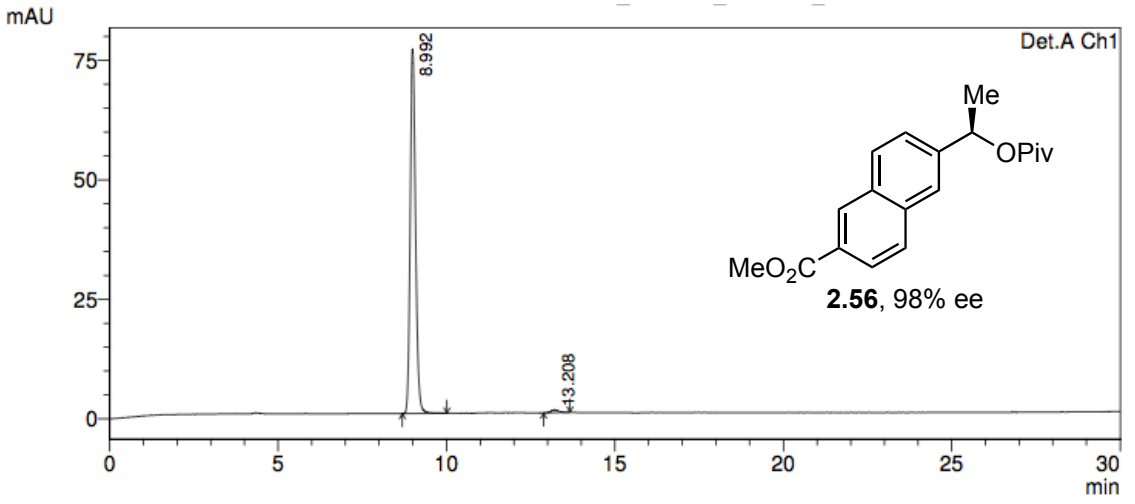
Compound 2.56, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.911	613049	56085	50.015	60.609
2	13.052	612685	36451	49.985	39.391
Total		1225734	92536	100.000	100.000

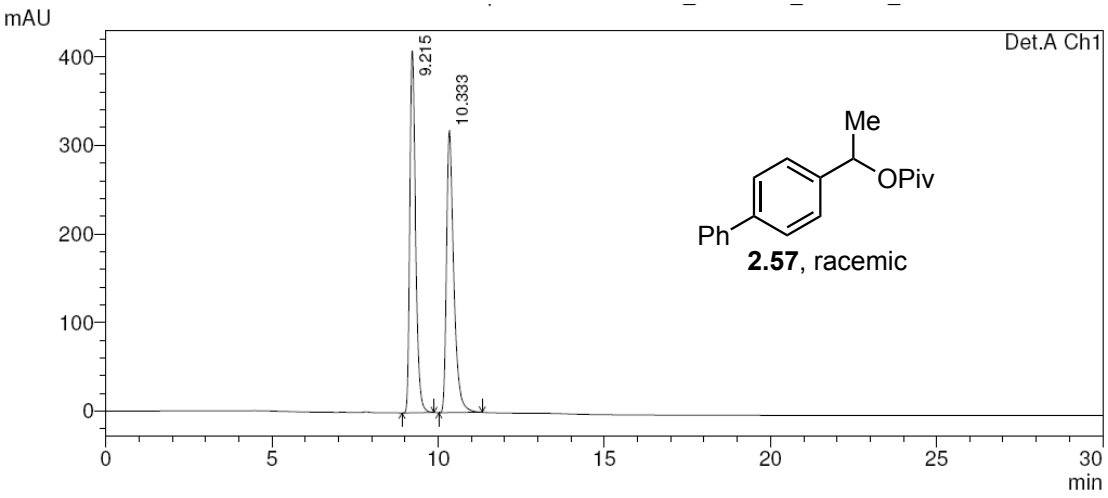
Compound 2.56, 98% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.992	851729	76272	99.004	99.274
2	13.208	8567	557	0.996	0.726
Total		860296	76830	100.000	100.000

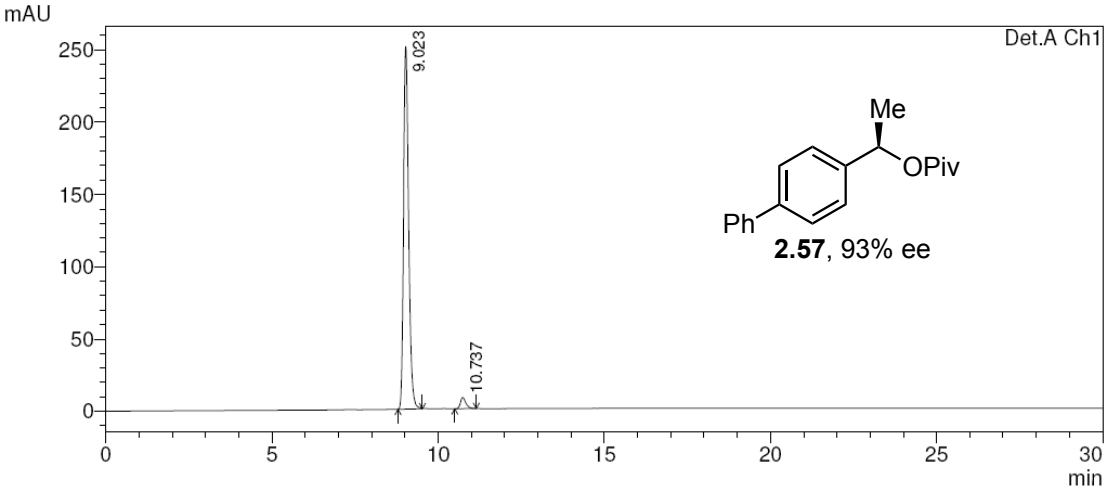
Compound 2.57, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.215	4946210	408528	50.233	56.198
2	10.333	4900271	318419	49.767	43.802
Total		9846481	726947	100.000	100.000

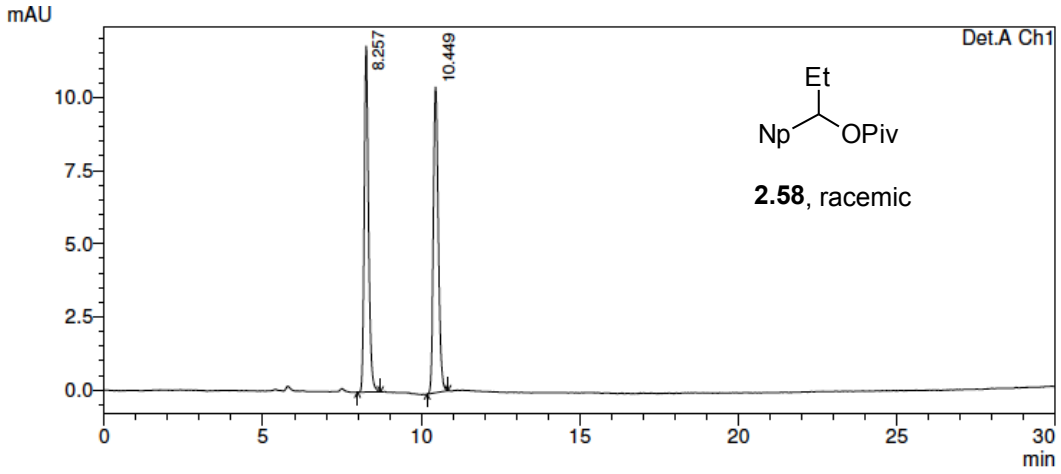
Compound 2.57, 93% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.023	2670459	250803	96.736	96.996
2	10.737	90112	7769	3.264	3.004
Total		2760571	258572	100.000	100.000

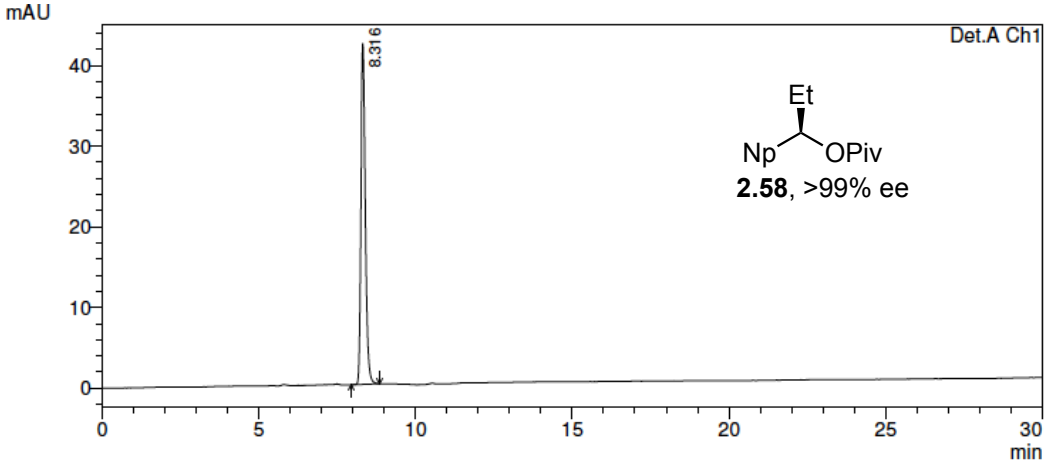
Compound 2.58, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.257	114388	11828	50.272	53.100
2	10.449	113152	10447	49.728	46.900
Total		227540	22276	100.000	100.000

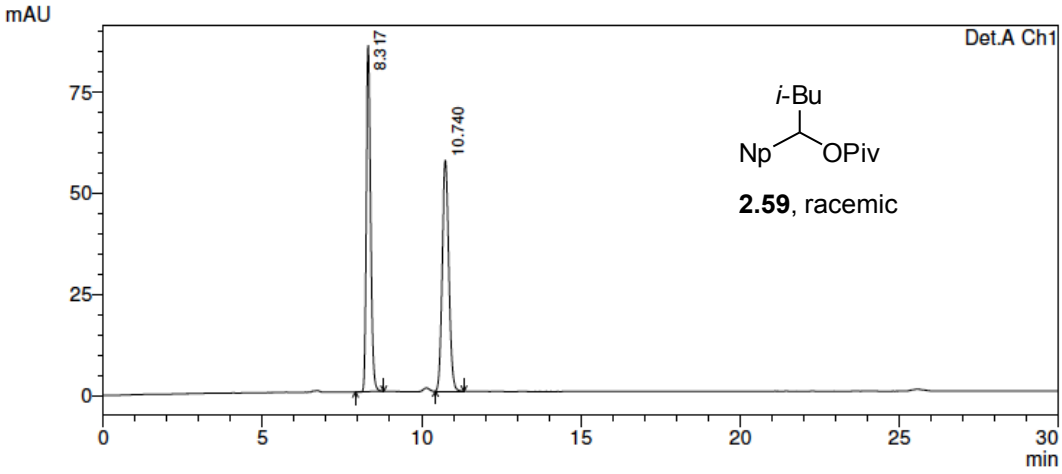
Compound 2.58, >99% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.316	415101	42242	100.000	100.000
Total		415101	42242	100.000	100.000

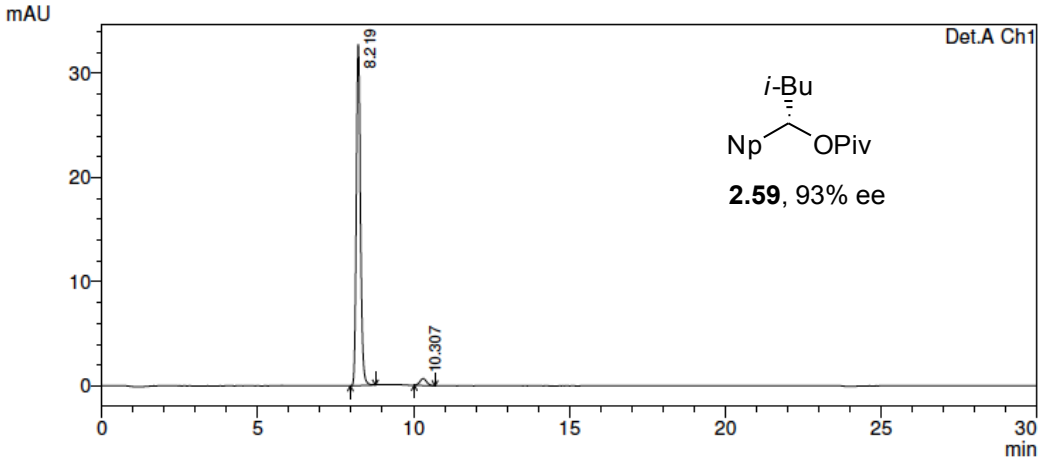
Compound 2.59, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.317	820067	85600	49.944	59.987
2	10.740	821921	57098	50.056	40.013
Total		1641989	142698	100.000	100.000

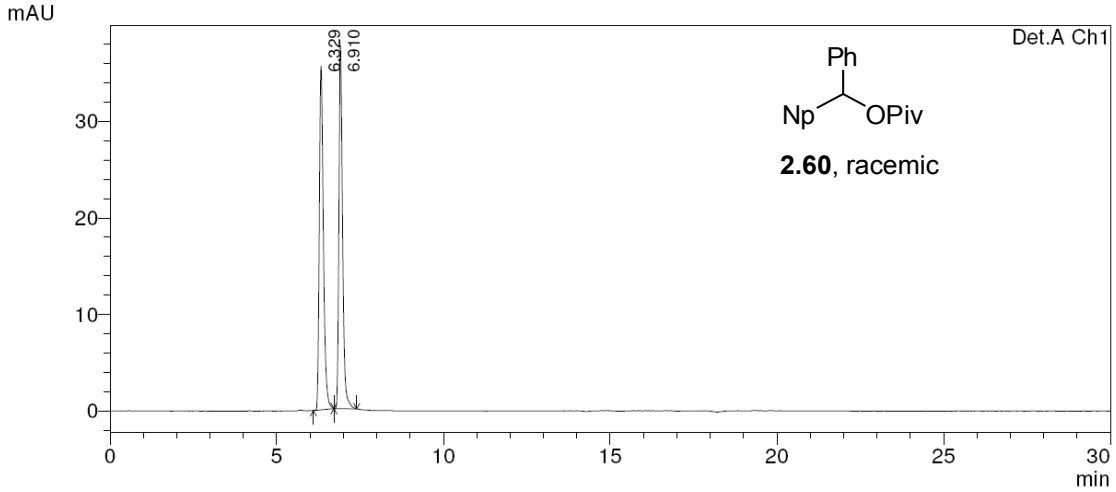
Compound 2.59, 93% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.219	308202	32752	96.654	97.974
2	10.307	10668	677	3.346	2.026
Total		318870	33429	100.000	100.000

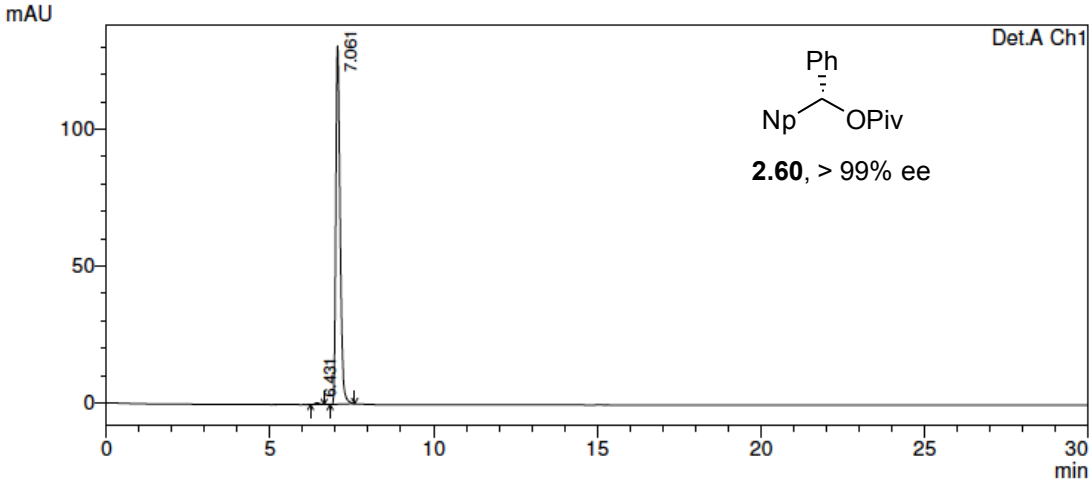
Compound 2.60, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.329	297105	35629	49.891	48.644
2	6.910	298408	37615	50.109	51.356
Total		595513	73244	100.000	100.000

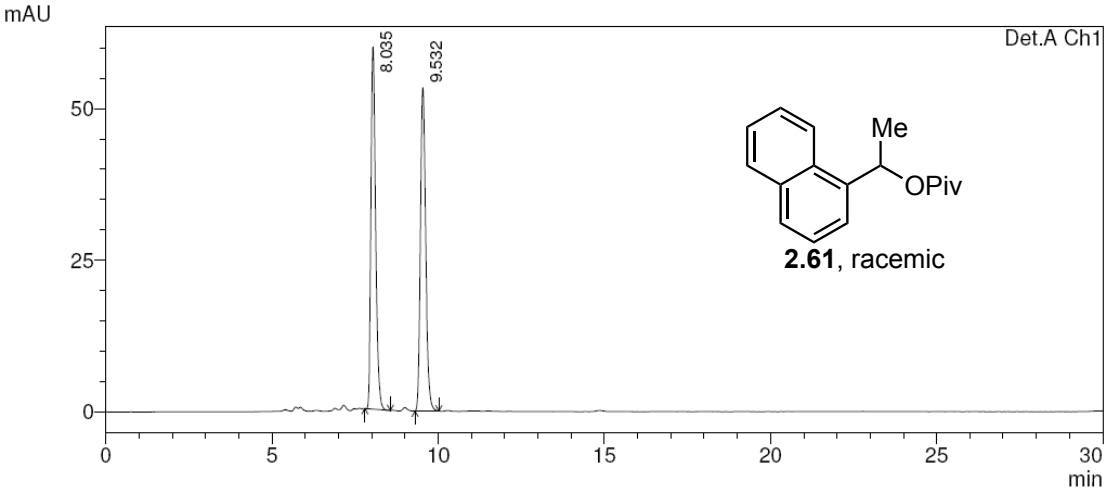
Compound 2.60, >99% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.431	5458	661	0.464	0.503
2	7.061	1171050	130897	99.536	99.497
Total		1176509	131558	100.000	100.000

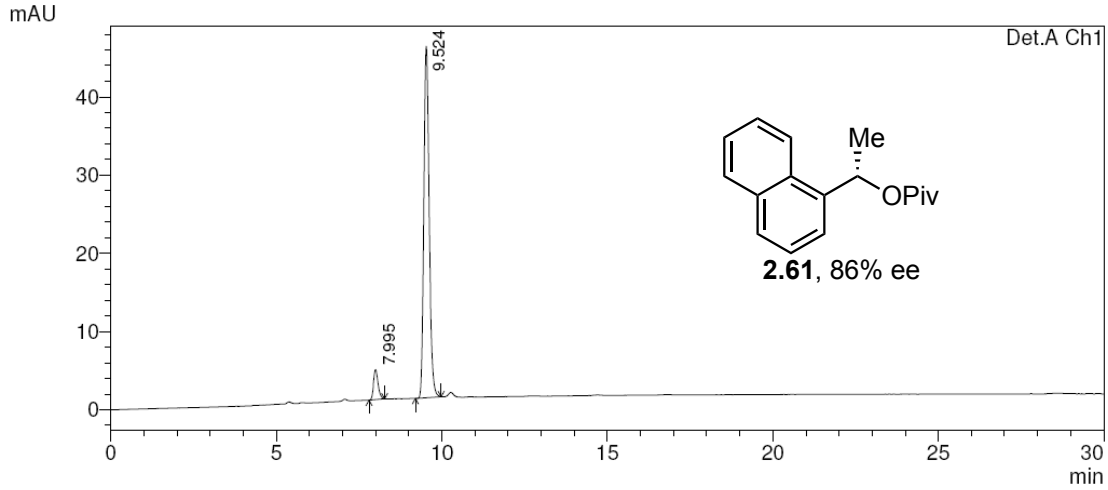
Compound 2.61, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.035	579672	59706	49.676	52.828
2	9.532	587238	53313	50.324	47.172
Total		1166910	113019	100.000	100.000

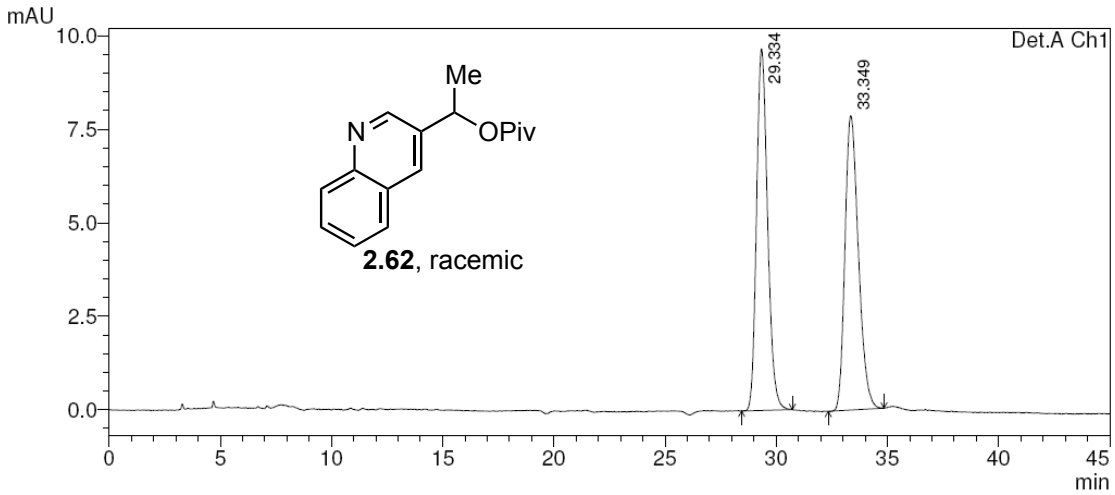
Compound2.61, 86% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.995	36367	3814	6.791	7.825
2	9.524	499160	44924	93.209	92.175
Total		535527	48738	100.000	100.000

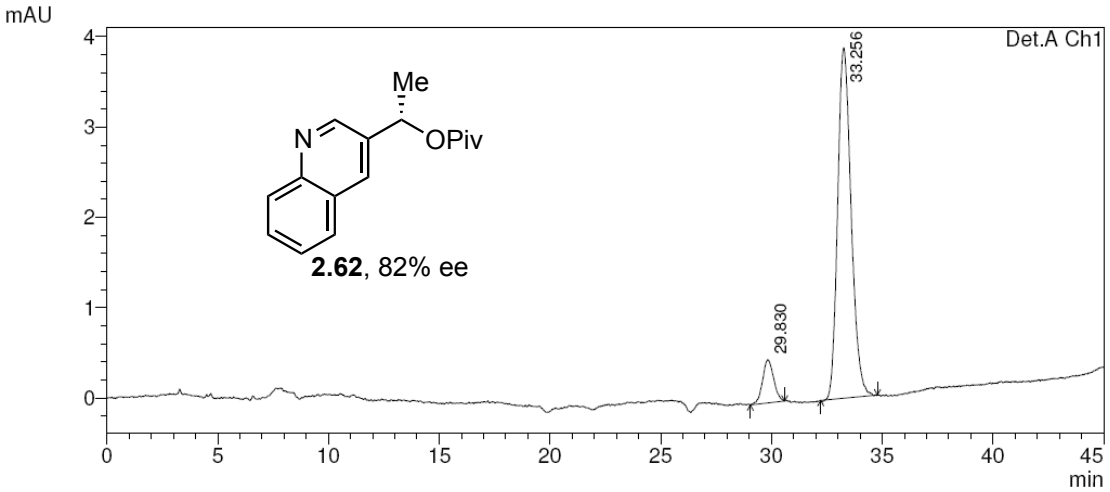
Compound 2.62, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.334	333054	9664	50.134	55.117
2	33.349	331269	7870	49.866	44.883
Total		664323	17534	100.000	100.000

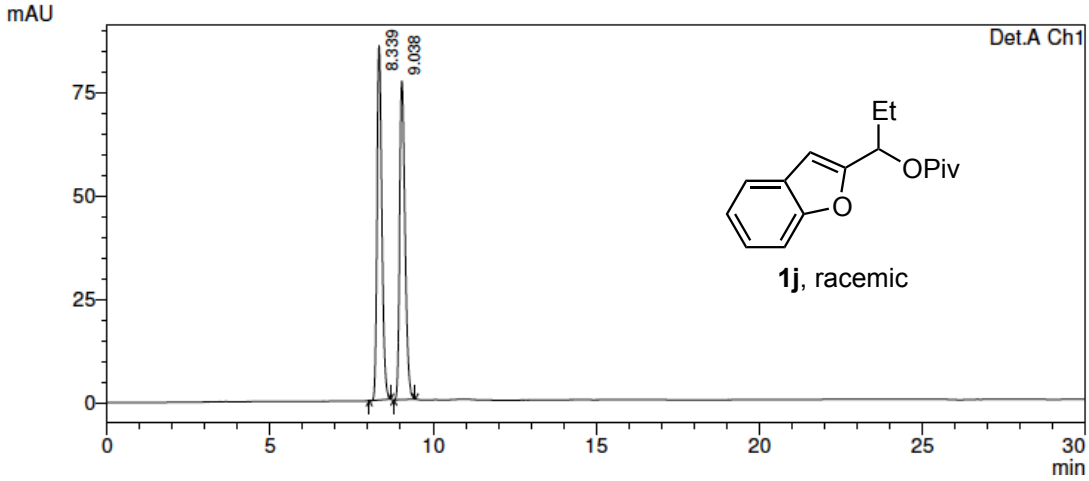
Compound 2.62, 82% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.830	16673	481	9.218	11.024
2	33.256	164207	3881	90.782	88.976
Total		180880	4362	100.000	100.000

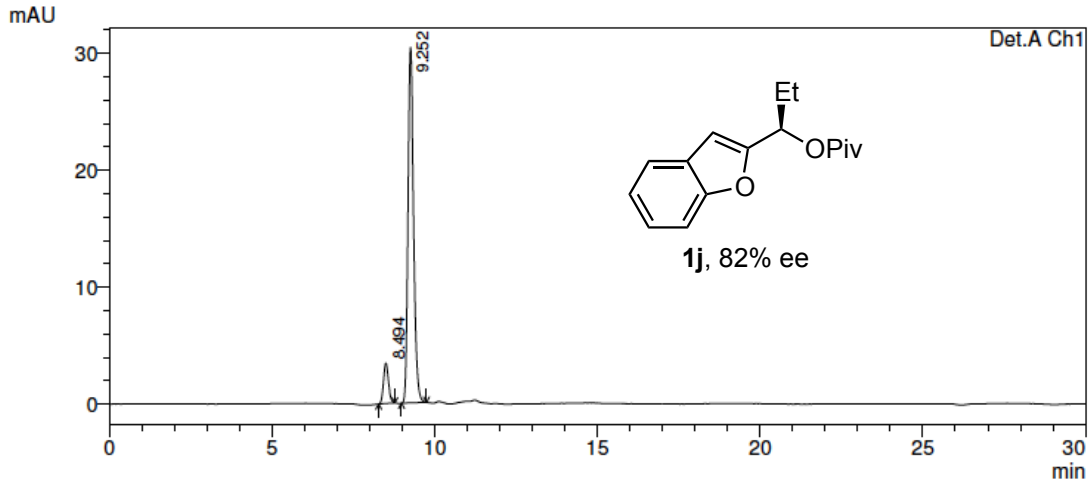
Compound 2.63, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.339	888842	85736	50.018	52.657
2	9.038	888188	77084	49.982	47.343
Total		1777030	162821	100.000	100.000

Compound 2.63, 82% ee

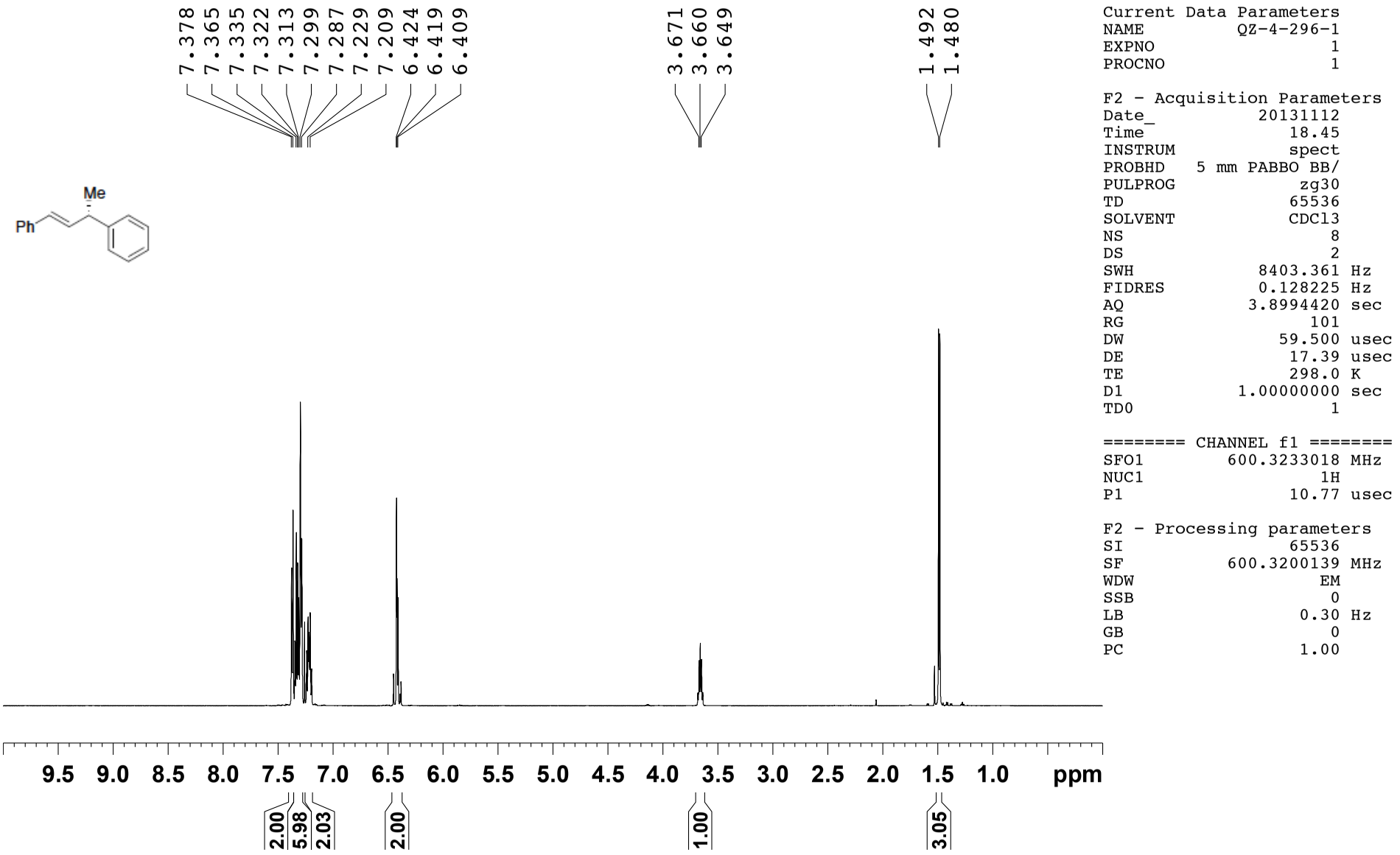


Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.494	36076	3440	9.012	10.169
2	9.252	364222	30391	90.988	89.831
Total		400298	33832	100.000	100.000

APPENDIX C
CHAPTER 3 SPECTRAL DATA

compound 3.11 1H NMR



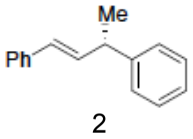

```
Current Data Parameters
NAME          QZ-4-296-1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20131112
Time              18.45
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8403.361 Hz
FIDRES         0.128225 Hz
AQ             3.8994420 sec
RG                  101
DW                59.500 usec
DE                17.39 usec
TE                298.0 K
D1             1.00000000 sec
TD0                   1

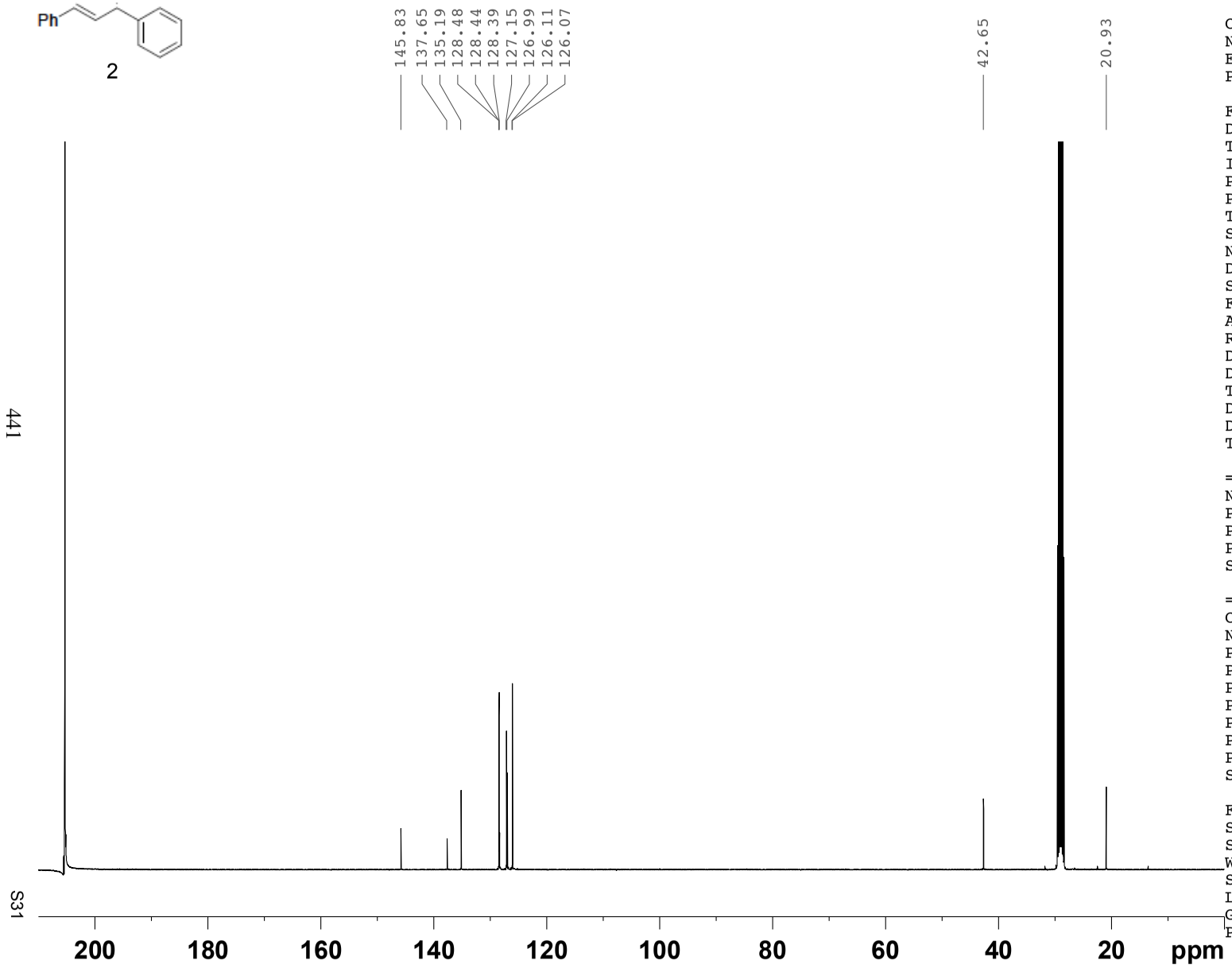
======== CHANNEL f1 ========
SFO1         600.3233018 MHz
NUC1                 1H
P1                10.77 usec

F2 - Processing parameters
SI                65536
SF           600.3200139 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

compound 3.11 13C NMR



2



Current Data Parameters
NAME QZ-3-244rs1
EXPNO 2
PROCNO 1

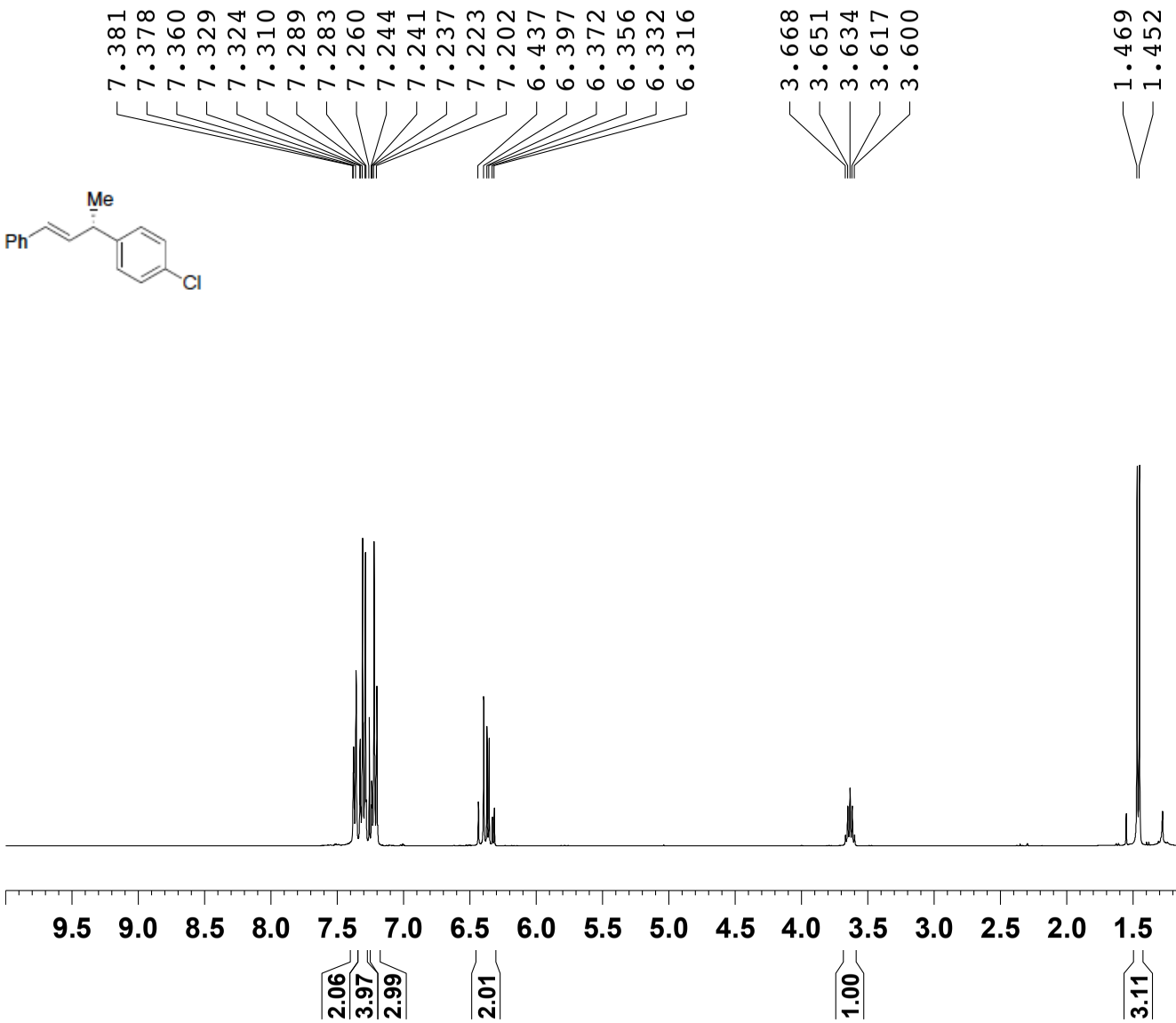
F2 - Acquisition Parameters
Date_ 20130524
Time 23.45
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 1024
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 512
DW 20.850 usec
DE 18.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.25 usec
PL1 0.55 dB
PL1W 35.18820572 W
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 4.90 dB
PL12 20.46 dB
PL13 21.00 dB
PL2W 3.30822015 W
PL12W 0.09195905 W
PL13W 0.08120718 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

compound 3.41 1H NMR



Current Data Parameters

NAME	HH-4-243
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20130413
Time	6.40
INSTRUM	spect
PROBHD	5 mm CPQNP 1H/
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	8
DW	60.400 usec
DE	6.00 usec
TE	298.1 K
D1	1.00000000 sec
TD0	1

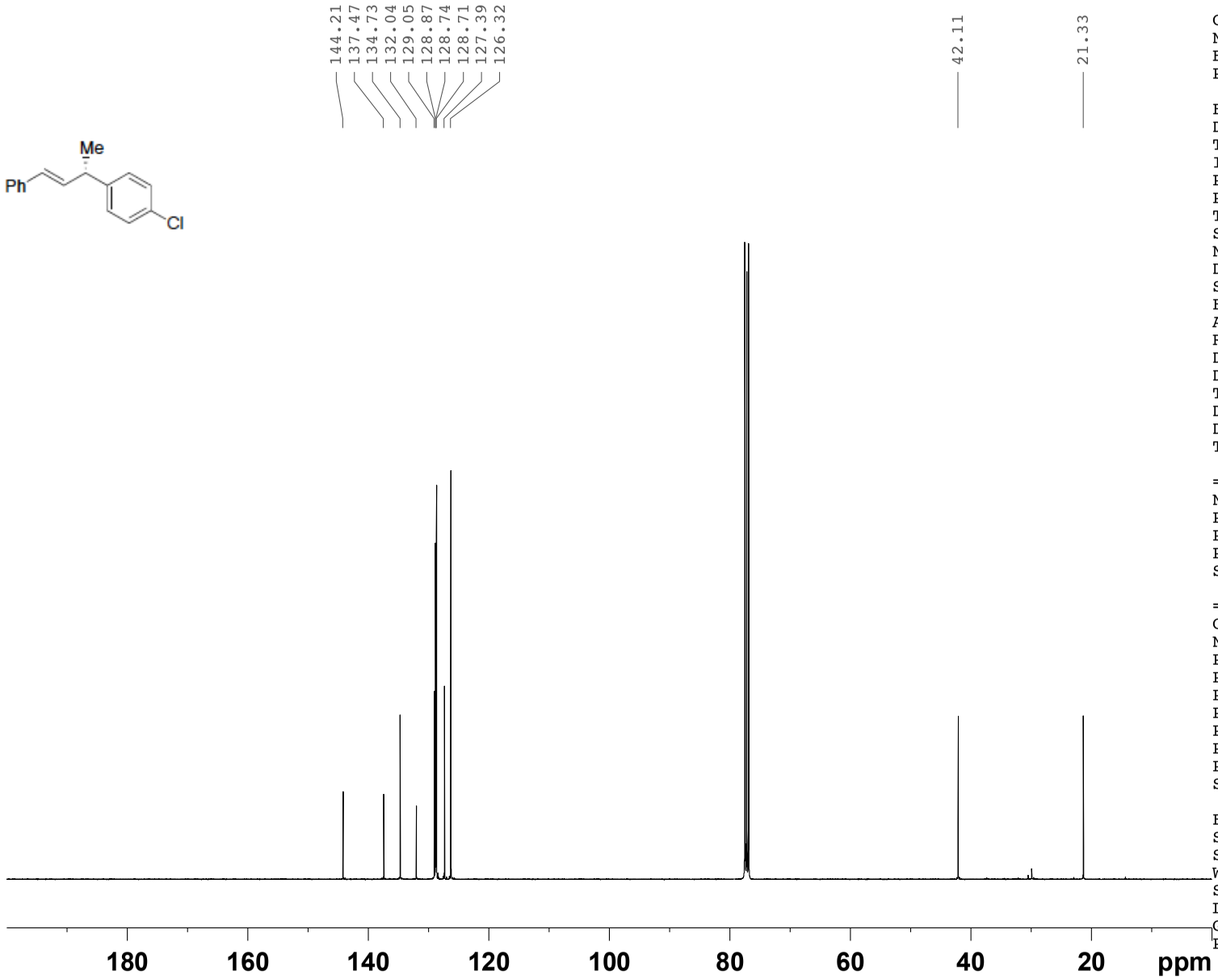
======== CHANNEL f1 ========

NUC1	1H
P1	15.00 usec
PL1	4.90 dB
PL1W	3.30822015 W
SFO1	400.1324710 MHz

F2 - Processing parameters

SI	32768
SF	400.1300097 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

compound 3.41 13C NMR




```
Current Data Parameters
NAME            HH-4-243
EXPNO                  2
PROCNO                 1

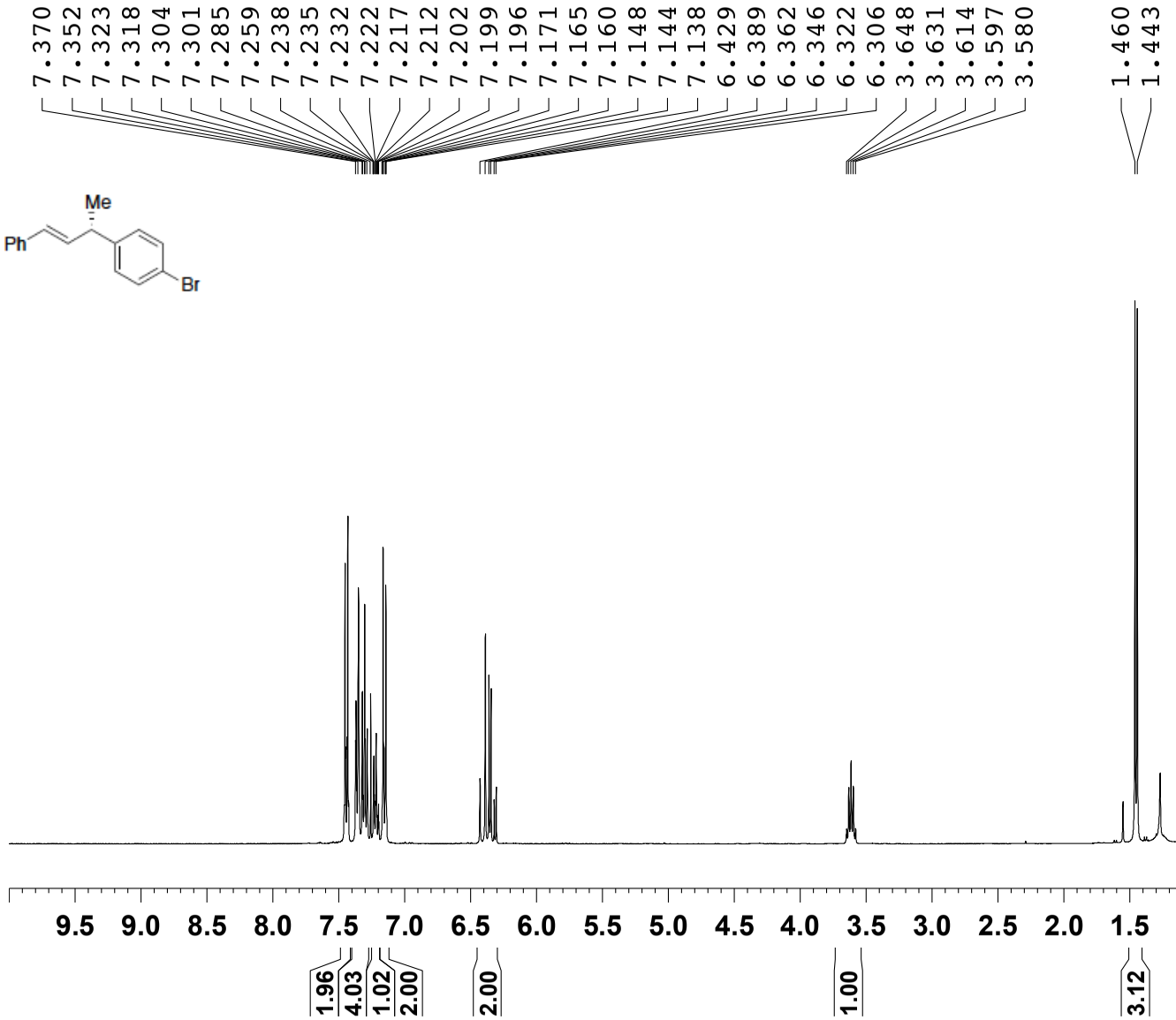
F2 - Acquisition Parameters
Date_           20130413
Time                7.40
INSTRUM            spect
PROBHD   5 mm CPQNP 1H/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ             1.3664756 sec
RG                   512
DW                20.850 usec
DE                18.00 usec
TE                298.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.25 usec
PL1                 0.55 dB
PL1W        35.18820572 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL2                 4.90 dB
PL12               20.46 dB
PL13               21.00 dB
PL2W         3.30822015 W
PL12W        0.09195905 W
PL13W        0.08120718 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127555 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

compound 3.42 1H NMR



Current Data Parameters

NAME	QZ-3-240(1)
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20130417
Time	17.29
INSTRUM	spect
PROBHD	5 mm CPQNP 1H/
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	9
DW	60.400 usec
DE	6.00 usec
TE	298.2 K
D1	1.00000000 sec
TD0	1

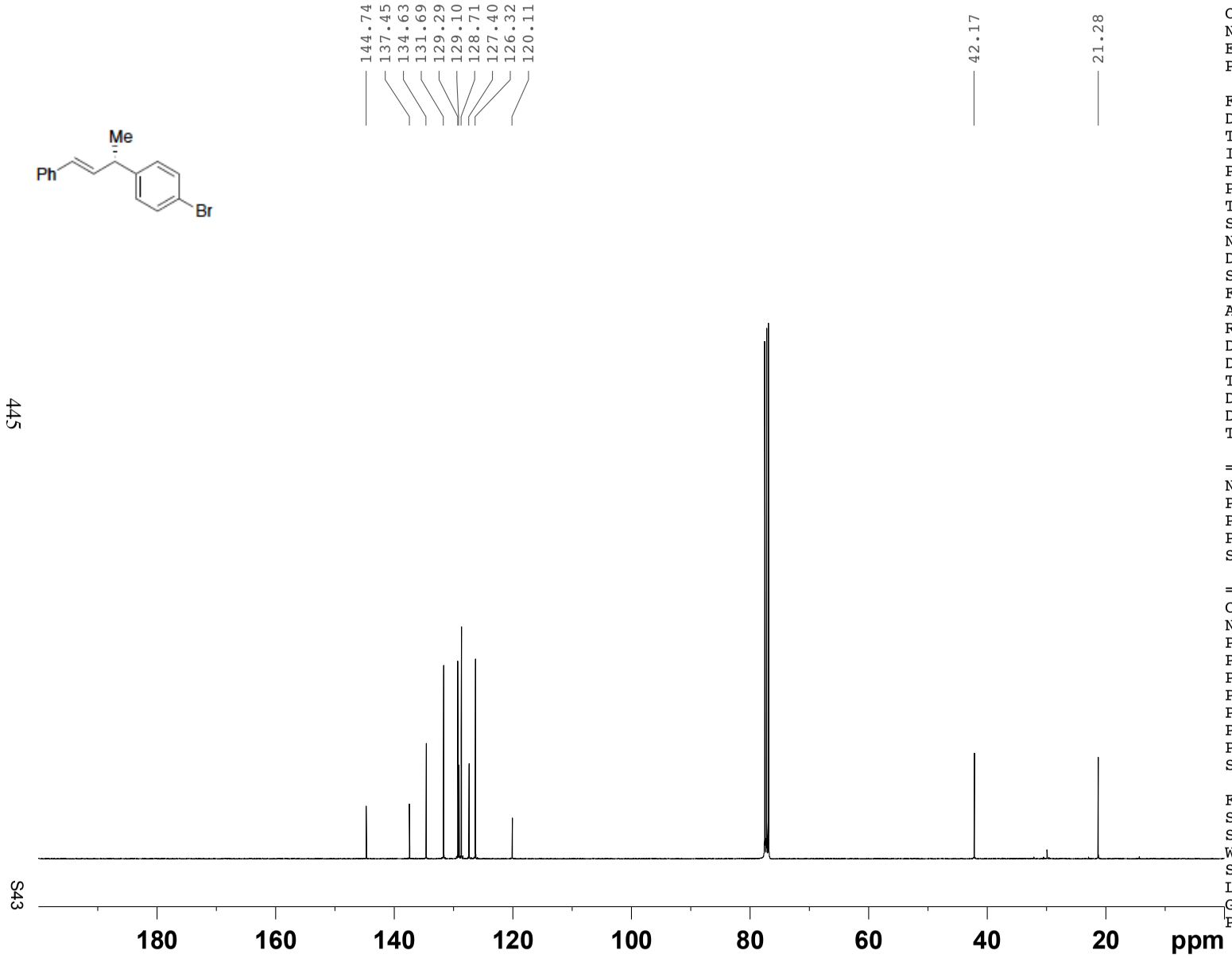
======== CHANNEL f1 ========

NUC1	1H
P1	15.00 usec
PL1	4.90 dB
PL1W	3.30822015 W
SFO1	400.1324710 MHz

F2 - Processing parameters

SI	32768
SF	400.1300099 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

compound 3.42 13 CNMR




```
Current Data Parameters
NAME         QZ-3-240(1)
EXPNO                  2
PROCNO                 1

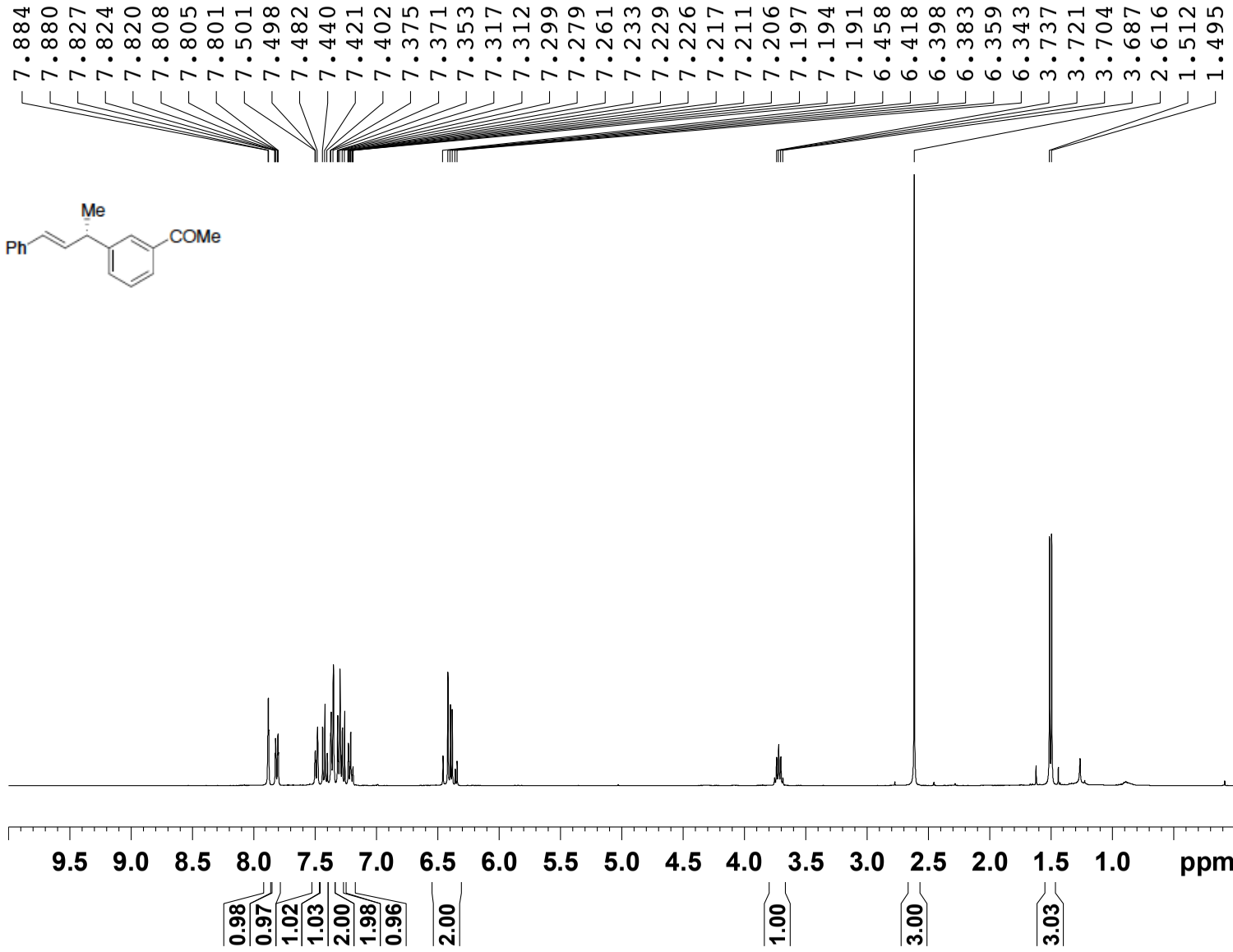
F2 - Acquisition Parameters
Date_           20130417
Time              23.11
INSTRUM           spect
PROBHD   5 mm CPQNP 1H/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ            1.3664756 sec
RG                  512
DW               20.850 usec
DE               18.00 usec
TE               298.1 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                9.25 usec
PL1               0.55 dB
PL1W       35.18820572 W
SFO1       100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2            90.00 usec
PL2               4.90 dB
PL12              20.46 dB
PL13              21.00 dB
PL2W        3.30822015 W
PL12W       0.09195905 W
PL13W       0.08120718 W
SFO2       400.1316005 MHz

F2 - Processing parameters
SI                32768
SF         100.6127551 MHz
WDW                EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

compound 3.43 1H NMR



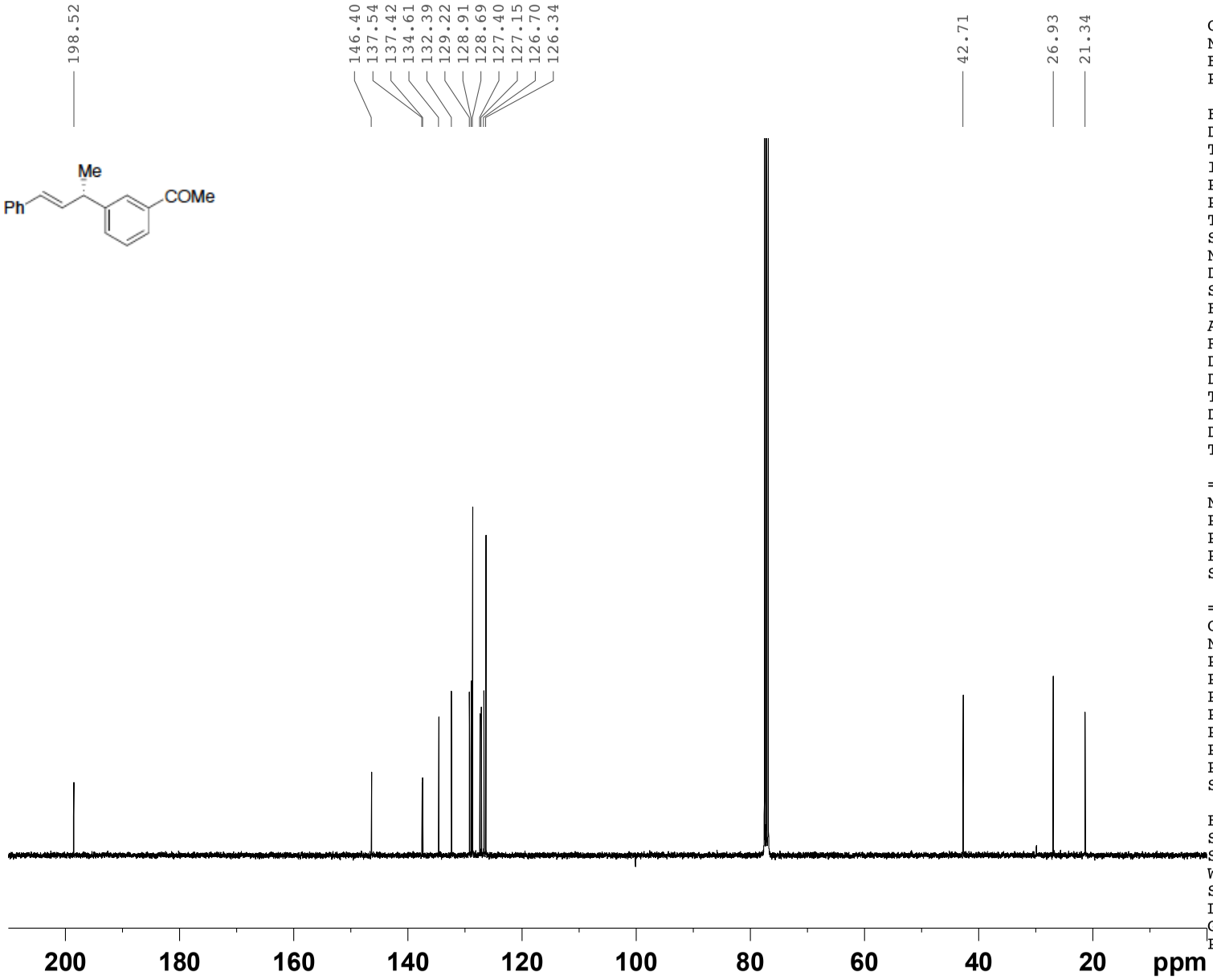

```
Current Data Parameters
NAME                  HH-4-262A
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20130517
Time                      18.28
INSTRUM                   spect
PROBHD    5 mm CPQNP 1H/
PULPROG                    zg30
TD                        65536
SOLVENT                   CDCl3
NS                           16
DS                            2
SWH                    8278.146 Hz
FIDRES                 0.126314 Hz
AQ                     3.9584243 sec
RG                            7.1
DW                        60.400 usec
DE                         6.00 usec
TE                        298.1 K
D1                    1.00000000 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                         1H
P1                        15.00 usec
PL1                        4.90 dB
PL1W                 3.30822015 W
SFO1               400.1324710 MHz

F2 - Processing parameters
SI                        32768
SF                 400.1300092 MHz
WDW                          EM
SSB                           0
LB                         0.30 Hz
GB                            0
PC                         1.00
```

compound 3.43 13 CNMR



Current Data Parameters

NAME	HH-4-262A
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20130517
Time	18.32
INSTRUM	spect
PROBHD	5 mm CPQNP 1H/
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	32
DS	4
SWH	23980.814 Hz
FIDRES	0.365918 Hz
AQ	1.3664756 sec
RG	512
DW	20.850 usec
DE	18.00 usec
TE	298.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1

======== CHANNEL f1 ========

NUC1	13C
P1	9.25 usec
PL1	0.55 dB
PL1W	35.18820572 W
SFO1	100.6228298 MHz

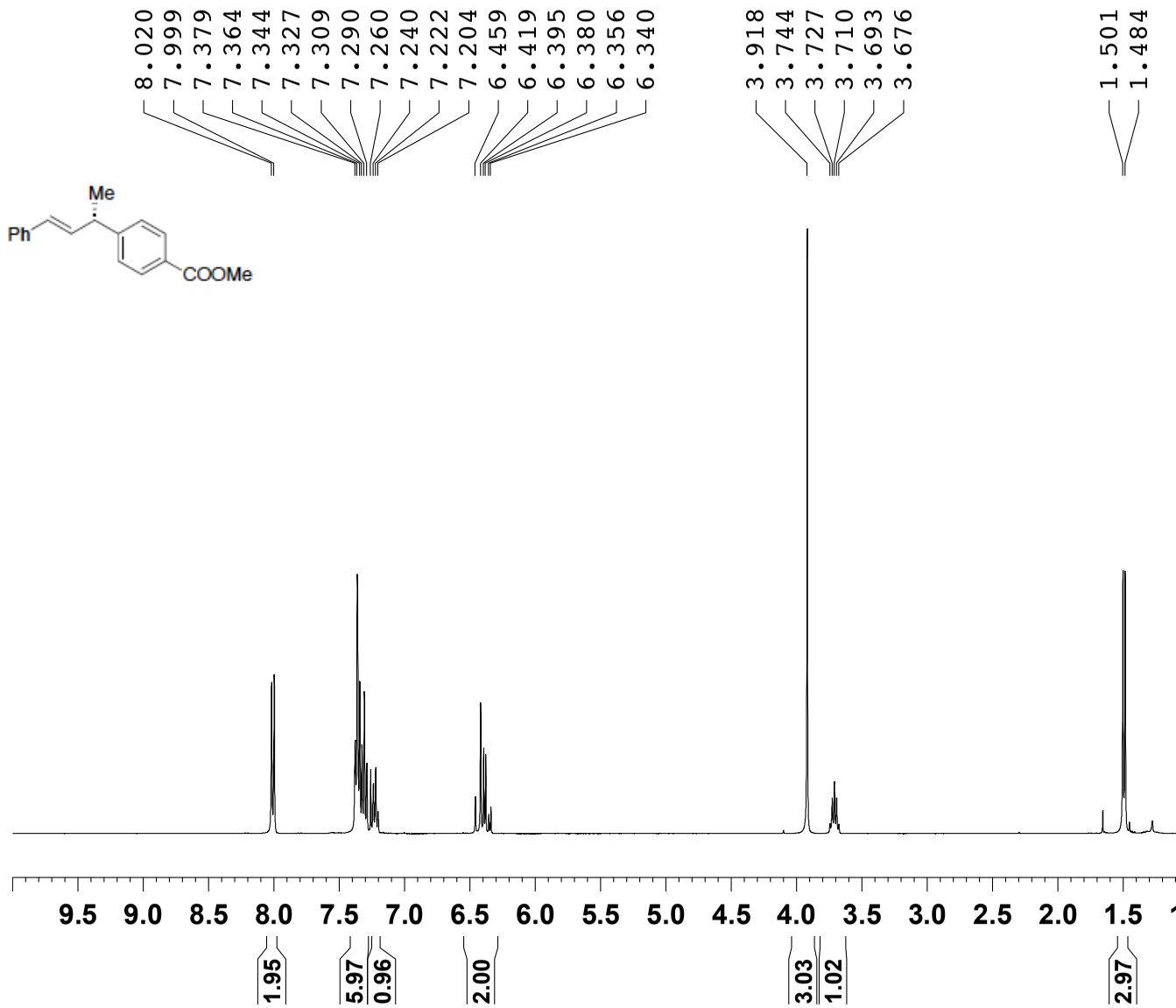
======== CHANNEL f2 ========

CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	4.90 dB
PL12	20.46 dB
PL13	21.00 dB
PL2W	3.30822015 W
PL12W	0.09195905 W
PL13W	0.08120718 W
SFO2	400.1316005 MHz

F2 - Processing parameters

SI	32768
SF	100.6127558 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

compound 3.44 1H NMR



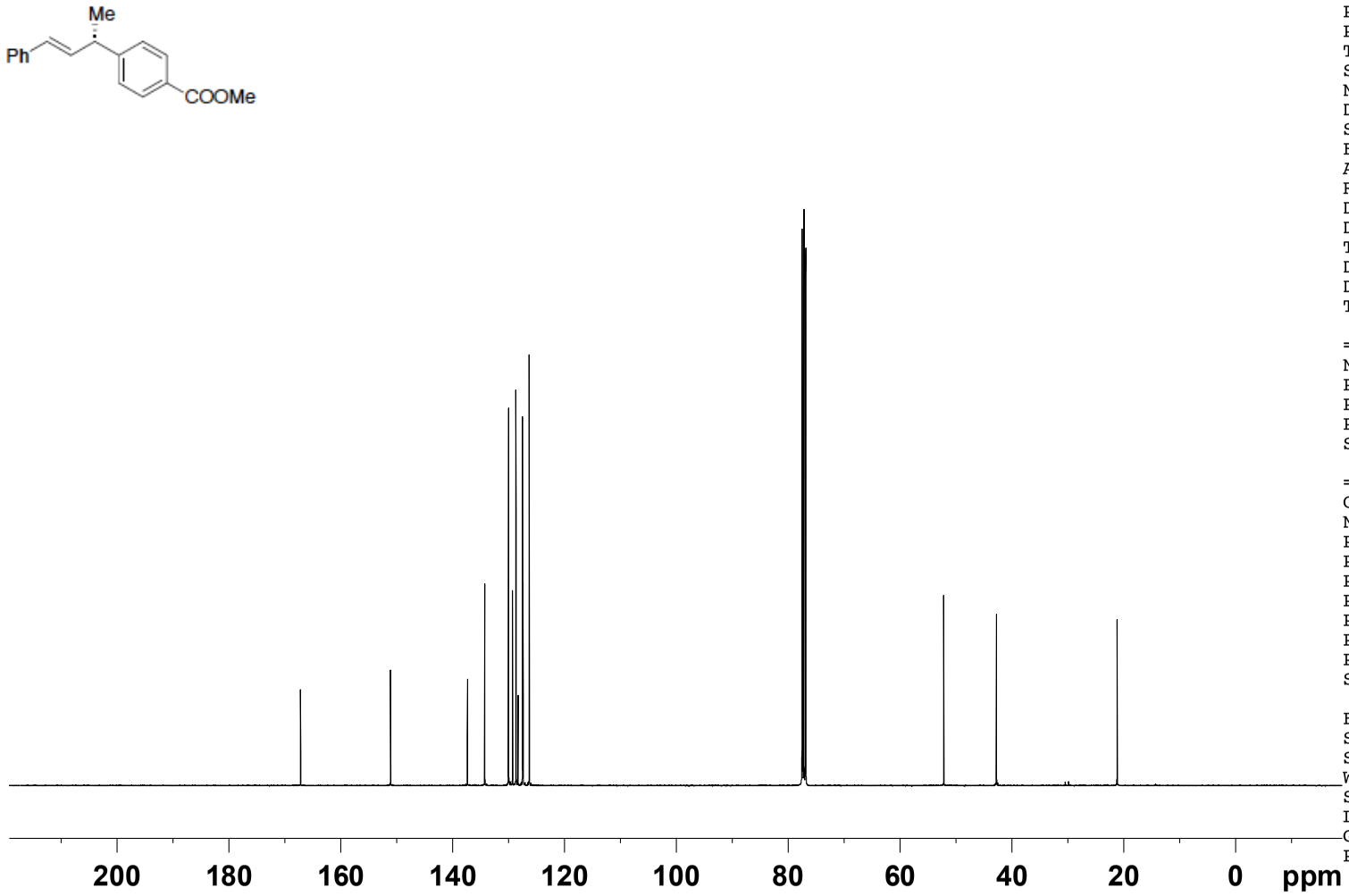

```
Current Data Parameters
NAME                  HH-4-241A
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20130413
Time                       4.26
INSTRUM                   spect
PROBHD    5 mm CPQNP 1H/
PULPROG                   zg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                   8278.146 Hz
FIDRES                0.126314 Hz
AQ                    3.9584243 sec
RG                           5.7
DW                      60.400 usec
DE                       6.00 usec
TE                       298.1 K
D1                   1.00000000 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                         1H
P1                       15.00 usec
PL1                       4.90 dB
PL1W                 3.30822015 W
SFO1               400.1324710 MHz

F2 - Processing parameters
SI                           32768
SF                 400.1300093 MHz
WDW                             EM
SSB                              0
LB                            0.30 Hz
GB                               0
PC                            1.00
```

compound 3.44 13 CNMR



Current Data Parameters
NAME HH-4-241A
EXPNO 2
PROCNO 1

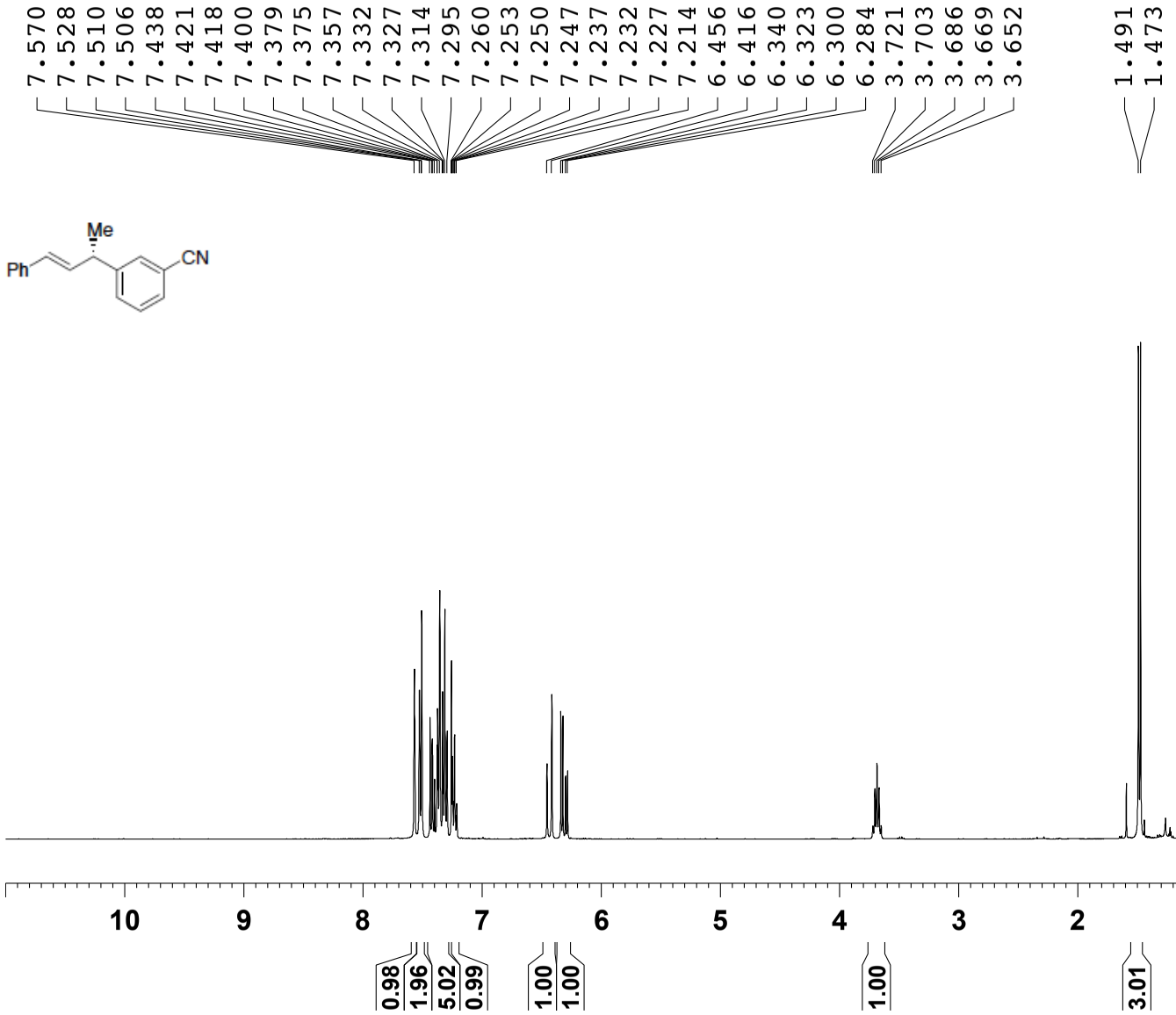
F2 - Acquisition Parameters
Date_ 20130413
Time 5.26
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 512
DW 20.850 usec
DE 18.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.25 usec
PL1 0.55 dB
PL1W 35.18820572 W
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 4.90 dB
PL12 20.46 dB
PL13 21.00 dB
PL2W 3.30822015 W
PL12W 0.09195905 W
PL13W 0.08120718 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127587 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

compound 3.45 1H NMR



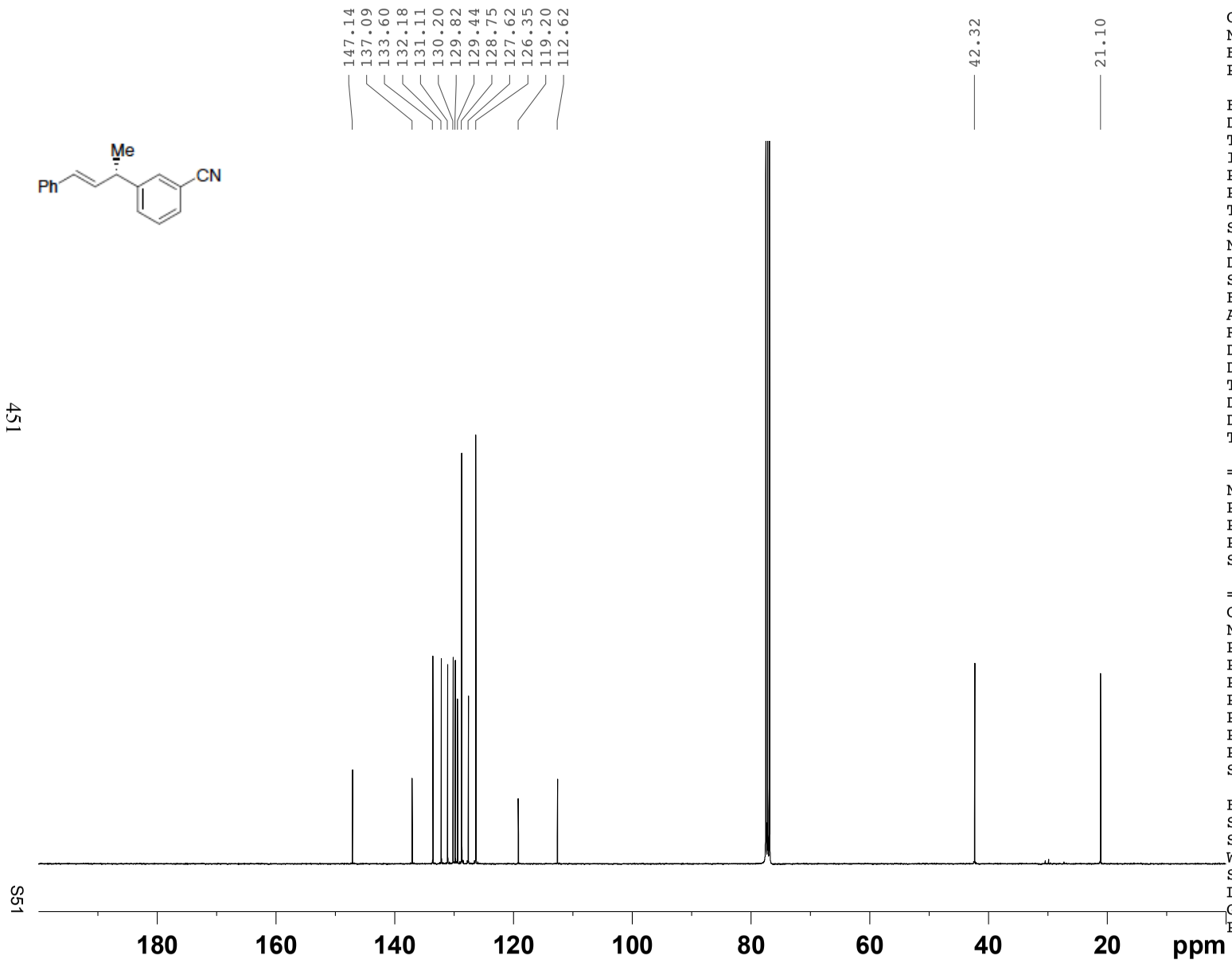

```
Current Data Parameters
NAME            HH-4-240
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130411
Time               18.37
INSTRUM            spect
PROBHD   5 mm CPQNP 1H/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ              3.9584243 sec
RG                  10.1
DW                60.400 usec
DE                 6.00 usec
TE                298.1 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                15.00 usec
PL1                4.90 dB
PL1W          3.30822015 W
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300097 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                 1.00
```

compound 3.45 13C NMR




```
Current Data Parameters
NAME            HH-4-240
EXPNO                  2
PROCNO                 1

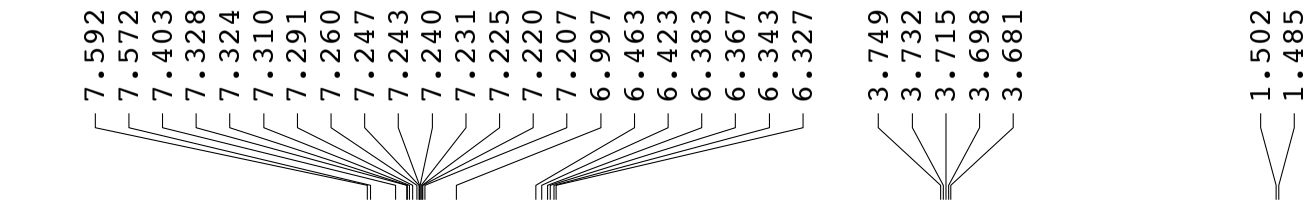
F2 - Acquisition Parameters
Date_           20130412
Time                4.48
INSTRUM            spect
PROBHD   5 mm CPQNP 1H/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ            1.3664756 sec
RG                   512
DW                20.850 usec
DE                18.00 usec
TE                298.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

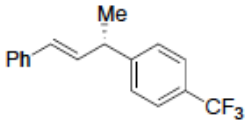
======== CHANNEL f1 ========
NUC1                 13C
P1                  9.25 usec
PL1                 0.55 dB
PL1W        35.18820572 W
SFO1       100.6228298 MHz

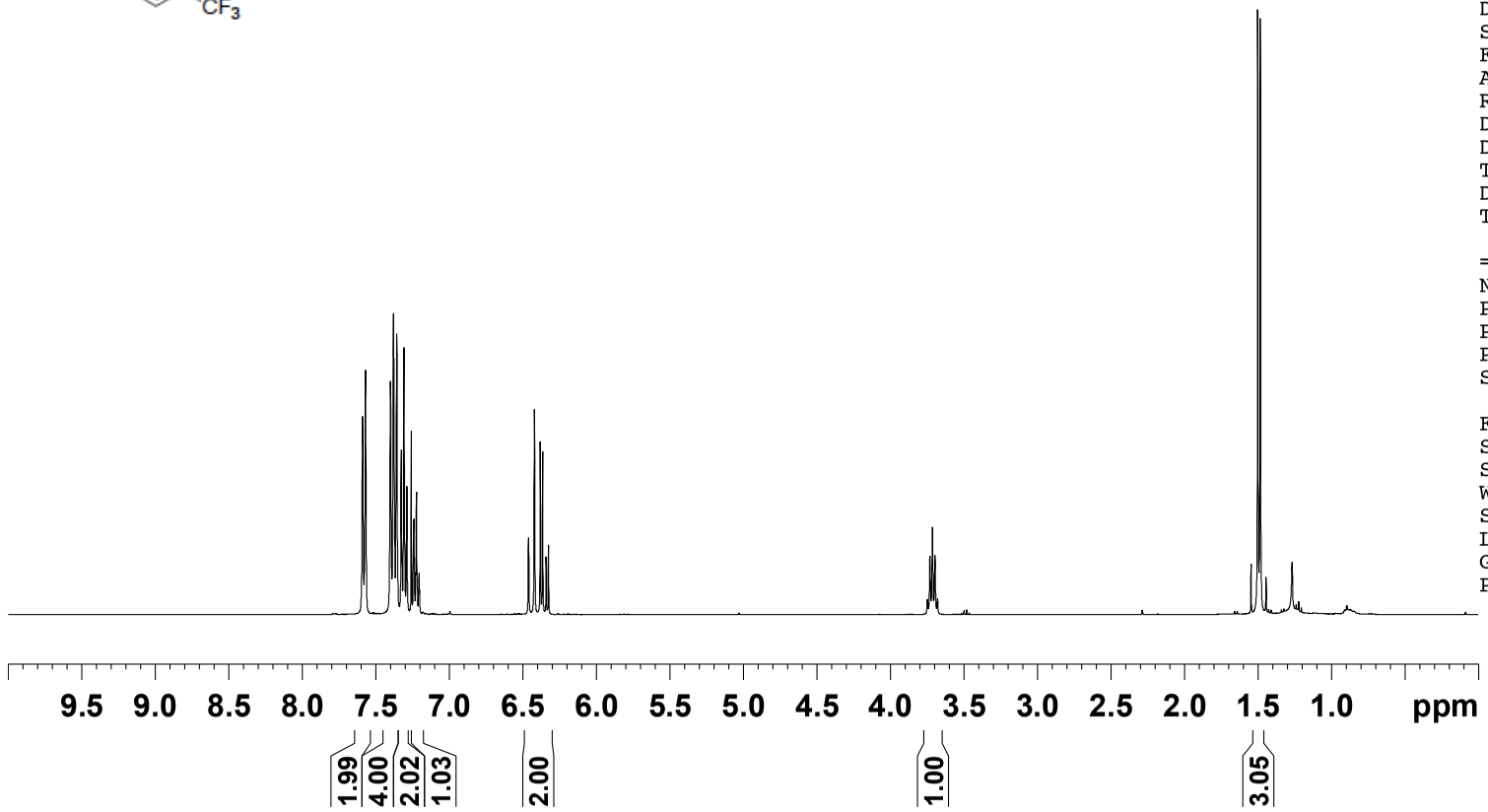
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL2                 4.90 dB
PL12               20.46 dB
PL13               21.00 dB
PL2W         3.30822015 W
PL12W        0.09195905 W
PL13W        0.08120718 W
SFO2       400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF         100.6127574 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

compound 3.46 1H NMR







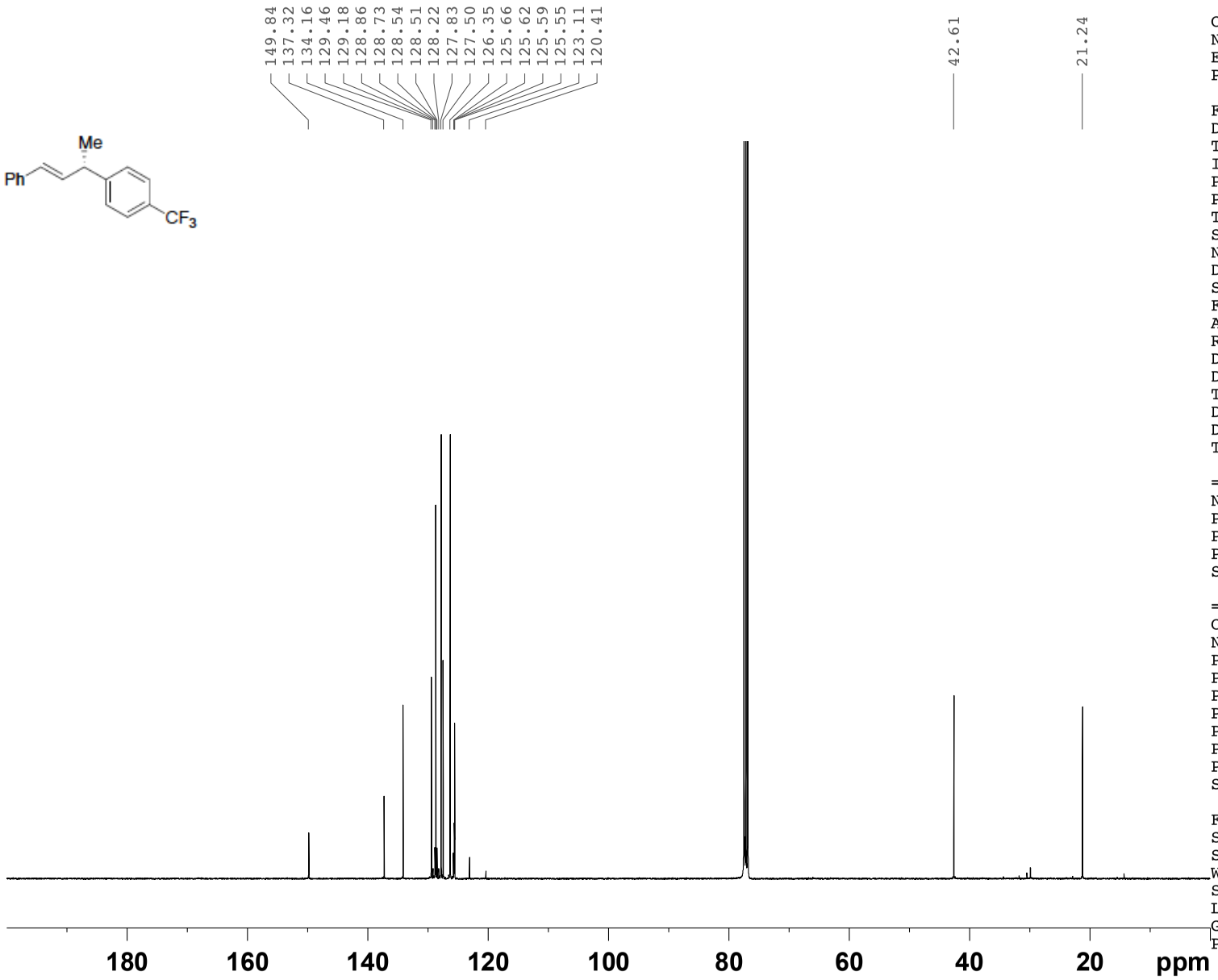

```
Current Data Parameters
NAME          HH-4-258A
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20130513
Time               12.30
INSTRUM            spect
PROBHD   5 mm CPQNP 1H/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ             3.9584243 sec
RG                    9
DW               60.400 usec
DE                6.00 usec
TE                298.2 K
D1            1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                15.00 usec
PL1                4.90 dB
PL1W         3.30822015 W
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300094 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

compound 3.46 13 NMR




```
Current Data Parameters
NAME          HH-4-258A
EXPNO                 2
PROCNO                1

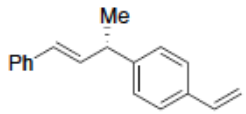
F2 - Acquisition Parameters
Date_          20130513
Time              22.23
INSTRUM           spect
PROBHD   5 mm CPQNP 1H/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ             1.3664756 sec
RG                  512
DW               20.850 usec
DE               18.00 usec
TE               298.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                9.25 usec
PL1               0.55 dB
PL1W       35.18820572 W
SFO1       100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2            90.00 usec
PL2               4.90 dB
PL12              20.46 dB
PL13              21.00 dB
PL2W        3.30822015 W
PL12W       0.09195905 W
PL13W       0.08120718 W
SFO2       400.1316005 MHz

F2 - Processing parameters
SI                32768
SF         100.6127547 MHz
WDW                EM
SSB                   0
LB                1.00 Hz
GB                    0
PC                1.40
```

compound 3.47 1H NMR



145.47
137.66
136.74
135.82
135.19
128.74
128.67
127.66
127.25
126.53
126.31
113.44
42.46
21.32

454

S37

180 160 140 120 100 80 60 40 20 ppm

```
Current Data Parameters
NAME          QZ-3-240a
EXPNO                 2
PROCNO                1

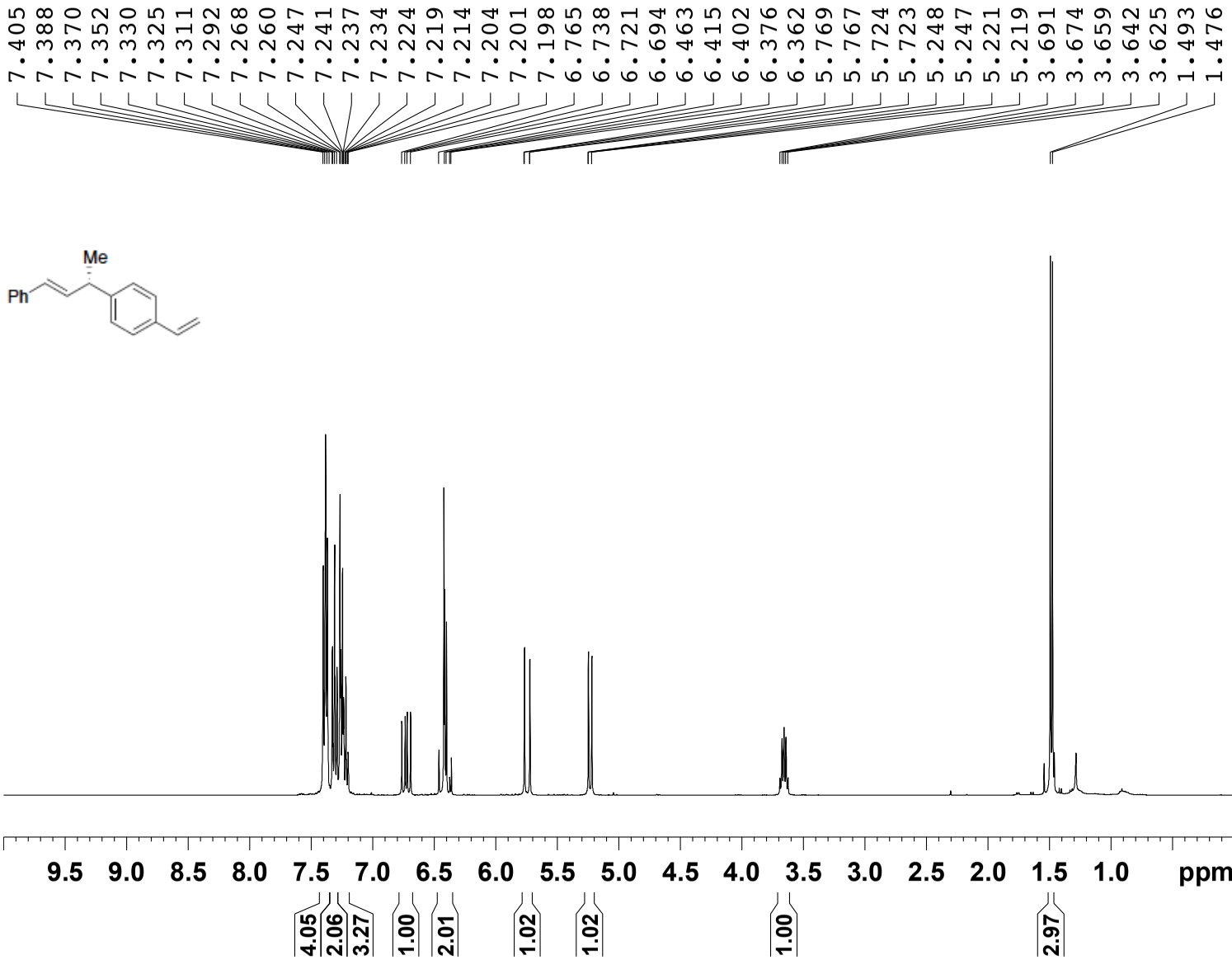
F2 - Acquisition Parameters
Date_          20130415
Time              22.07
INSTRUM           spect
PROBHD   5 mm CPQNP 1H/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ             1.3664756 sec
RG                  512
DW               20.850 usec
DE               18.00 usec
TE               298.1 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                9.25 usec
PL1               0.55 dB
PL1W        35.18820572 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2            90.00 usec
PL2               4.90 dB
PL12              20.46 dB
PL13              21.00 dB
PL2W         3.30822015 W
PL12W        0.09195905 W
PL13W        0.08120718 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127561 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC                1.40
```

compound 3.47 1H NMR



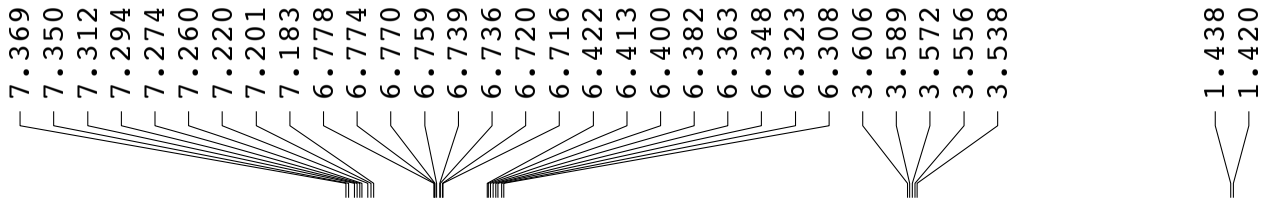

```
Current Data Parameters
NAME                 QZ-3-240a
EXPNO                        1
PROCNO                       1

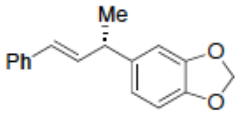
F2 - Acquisition Parameters
Date_                 20130415
Time                     15.55
INSTRUM                  spect
PROBHD    5 mm CPQNP 1H/
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                  8278.146 Hz
FIDRES               0.126314 Hz
AQ                   3.9584243 sec
RG                          8
DW                     60.400 usec
DE                      6.00 usec
TE                      298.2 K
D1                 1.00000000 sec
TD0                         1

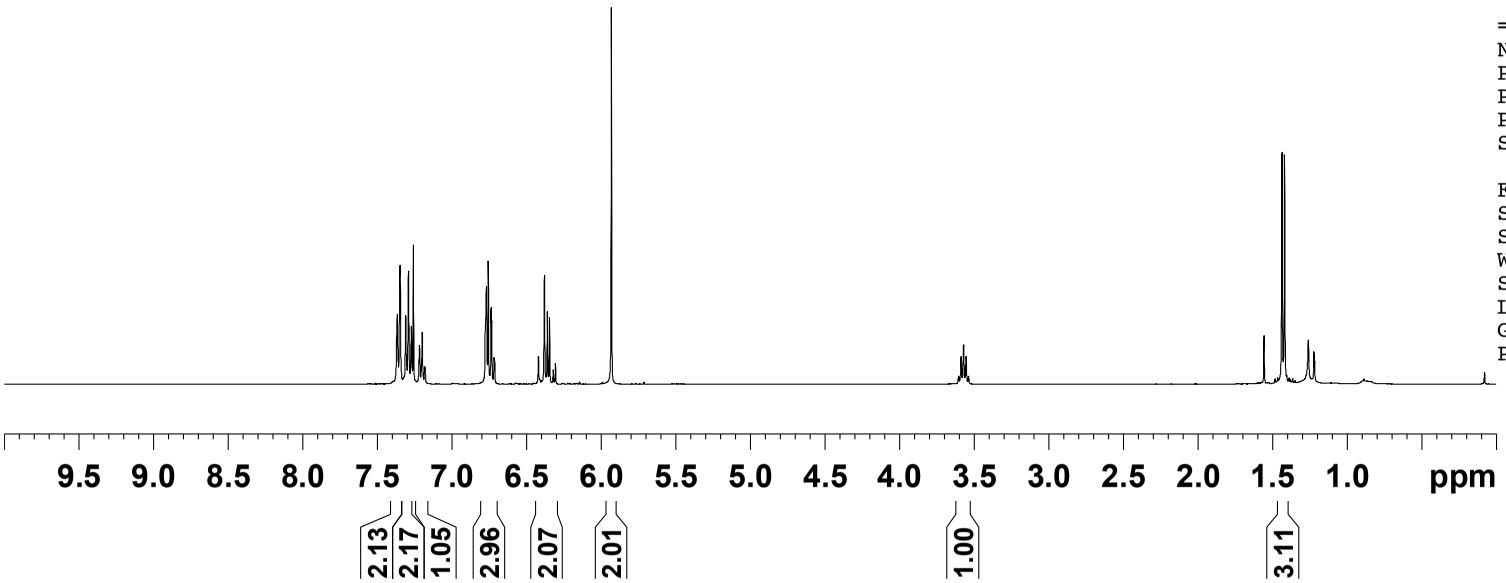
======== CHANNEL f1 ========
NUC1                       1H
P1                      15.00 usec
PL1                      4.90 dB
PL1W               3.30822015 W
SFO1             400.1324710 MHz

F2 - Processing parameters
SI                      32768
SF               400.1300096 MHz
WDW                        EM
SSB                         0
LB                      0.30 Hz
GB                          0
PC                      1.00
```

compound 3.48 1H NMR







Current Data Parameters

NAME	HH-4-249B
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20130429
Time	17.21
INSTRUM	spect
PROBHD	5 mm CPQNP 1H/
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	11.3
DW	60.400 usec
DE	6.00 usec
TE	298.1 K
D1	1.00000000 sec
TD0	1

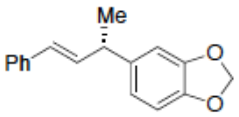
======== CHANNEL f1 ========

NUC1	1H
P1	15.00 usec
PL1	4.90 dB
PL1W	3.30822015 W
SFO1	400.1324710 MHz

F2 - Processing parameters

SI	32768
SF	400.1300095 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

compound 3.48 13C NMR



147.81
145.99
139.79
137.63
135.38
128.66
128.53
127.23
126.29
120.23
108.34
107.99
101.01
42.40
21.52

457

S53

200 180 160 140 120 100 80 60 40 20 0 ppm

```
Current Data Parameters
NAME          HH-4-249B
EXPNO                 2
PROCNO                1

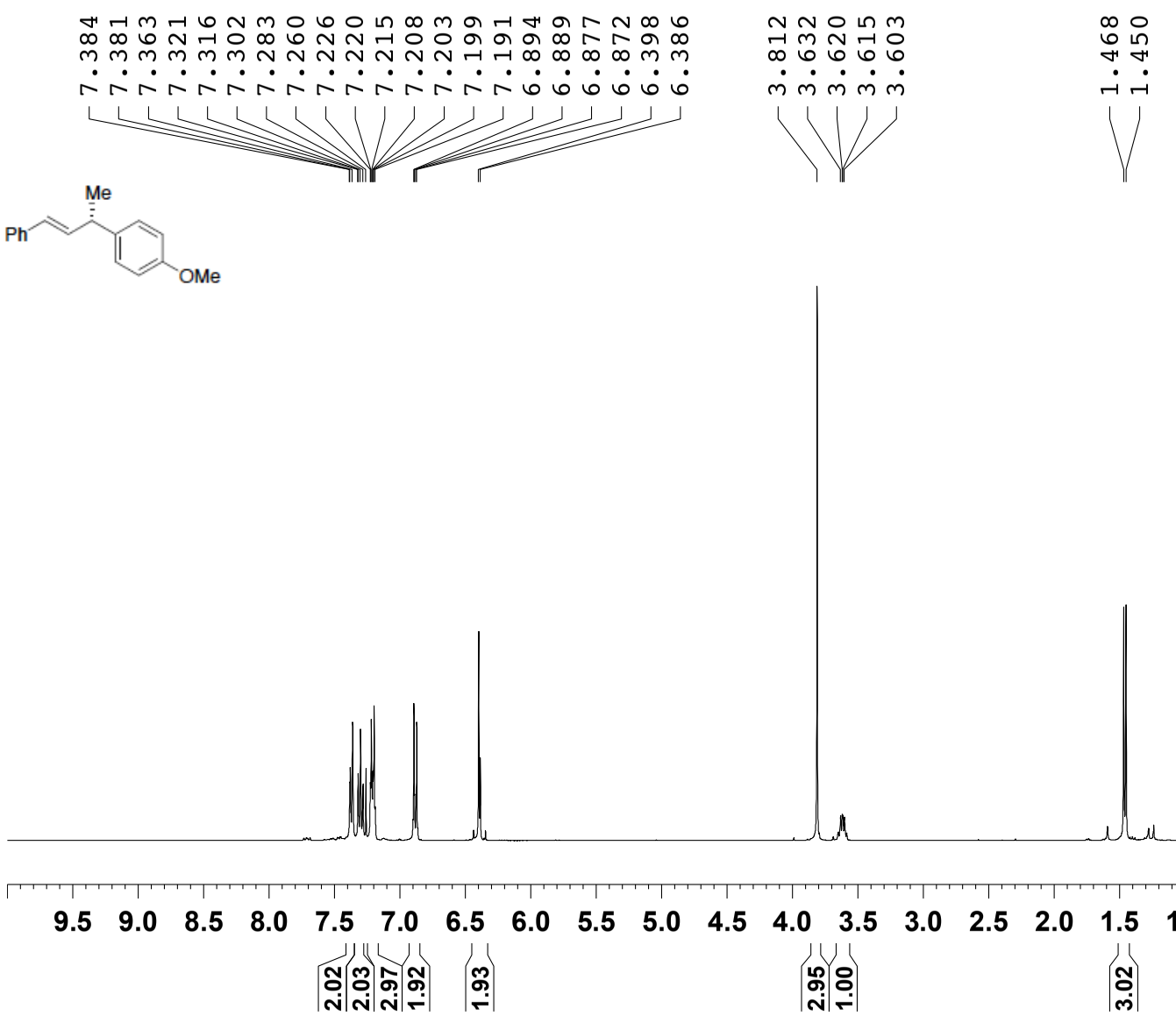
F2 - Acquisition Parameters
Date_          20130429
Time              17.24
INSTRUM           spect
PROBHD   5 mm CPQNP 1H/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ             1.3664756 sec
RG                  512
DW               20.850 usec
DE               18.00 usec
TE               298.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                9.25 usec
PL1               0.55 dB
PL1W        35.18820572 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2            90.00 usec
PL2               4.90 dB
PL12              20.46 dB
PL13              21.00 dB
PL2W         3.30822015 W
PL12W        0.09195905 W
PL13W        0.08120718 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127554 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

compound 3.49 1H NMR



Current Data Parameters

NAME	HH-4-250A
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20130429
Time	17.31
INSTRUM	spect
PROBHD	5 mm CPQNP 1H/
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	10.1
DW	60.400 usec
DE	6.00 usec
TE	298.2 K
D1	1.00000000 sec
TD0	1

======== CHANNEL f1 ========

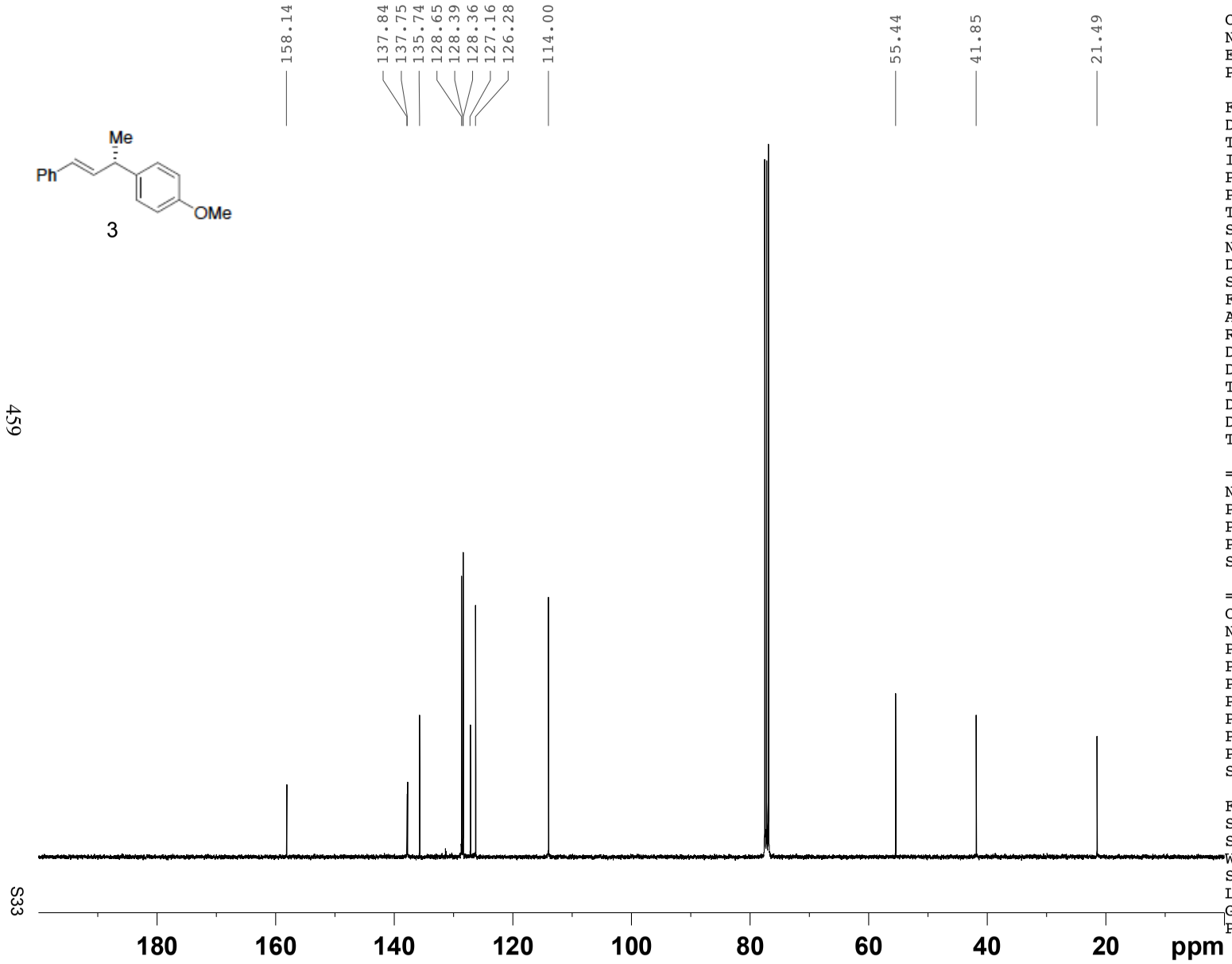
NUC1	1H
P1	15.00 usec
PL1	4.90 dB
PL1W	3.30822015 W
SFO1	400.1324710 MHz

F2 - Processing parameters

SI	32768
SF	400.1300093 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

compound 3.49 13C NMR

3




```
Current Data Parameters
NAME          HH-4-250A
EXPNO                 2
PROCNO                1

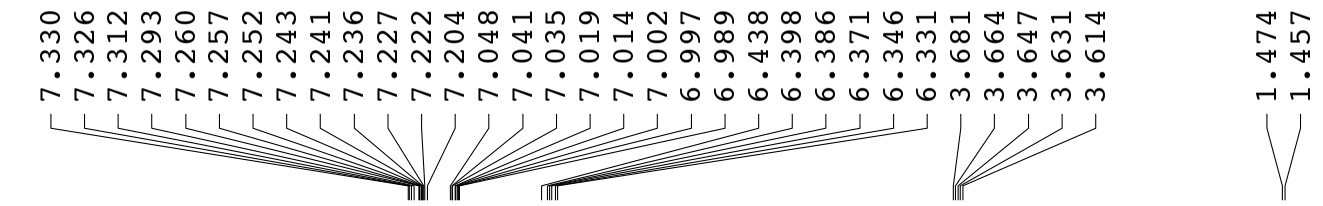
F2 - Acquisition Parameters
Date_          20130429
Time              17.34
INSTRUM           spect
PROBHD   5 mm CPQNP 1H/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ             1.3664756 sec
RG                  512
DW               20.850 usec
DE               18.00 usec
TE               298.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

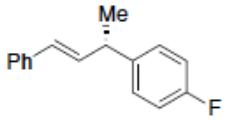
======== CHANNEL f1 ========
NUC1                 13C
P1                 9.25 usec
PL1                0.55 dB
PL1W        35.18820572 W
SFO1        100.6228298 MHz

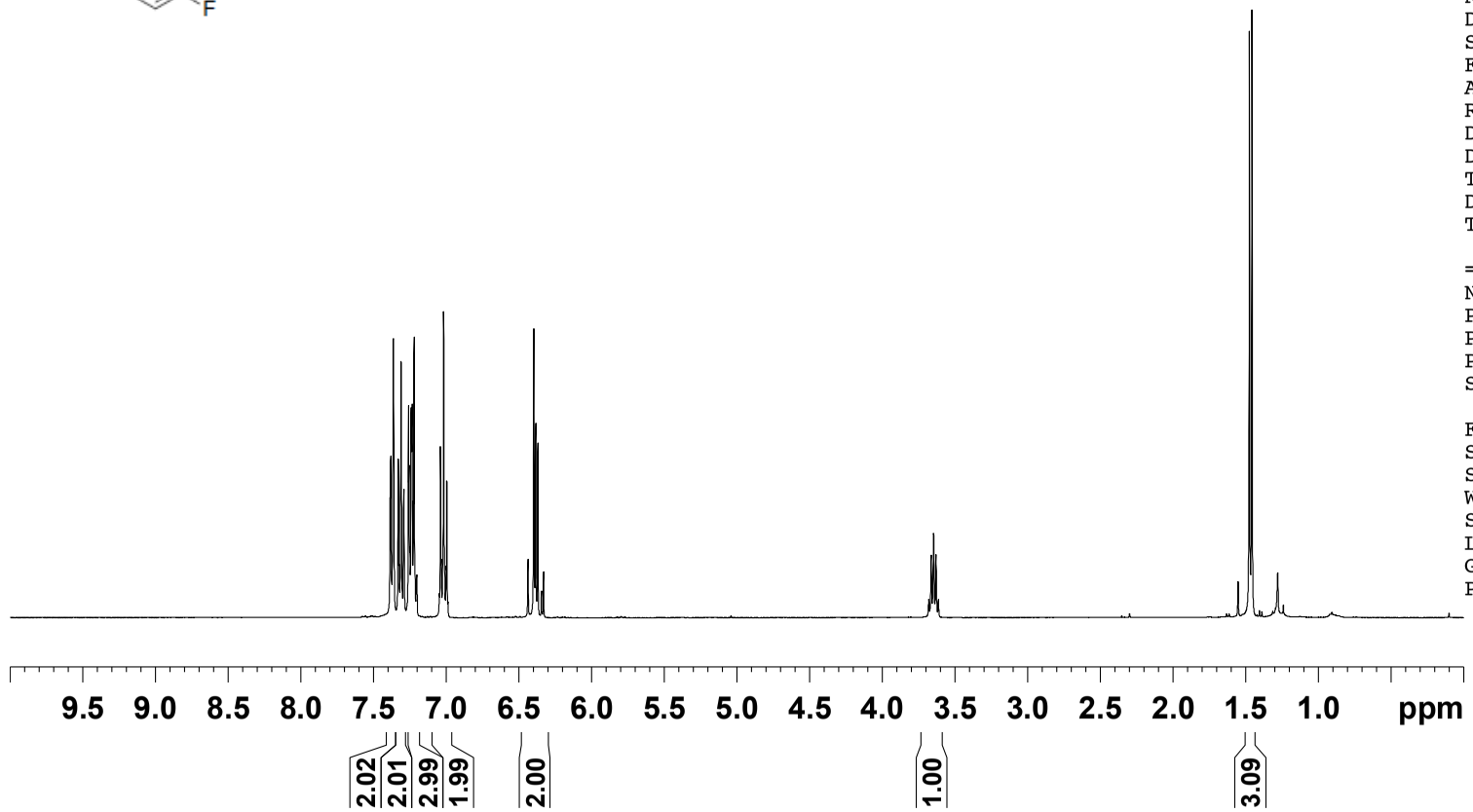
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             90.00 usec
PL2                4.90 dB
PL12              20.46 dB
PL13              21.00 dB
PL2W         3.30822015 W
PL12W        0.09195905 W
PL13W        0.08120718 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127559 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

compound 3.50 1H NMR







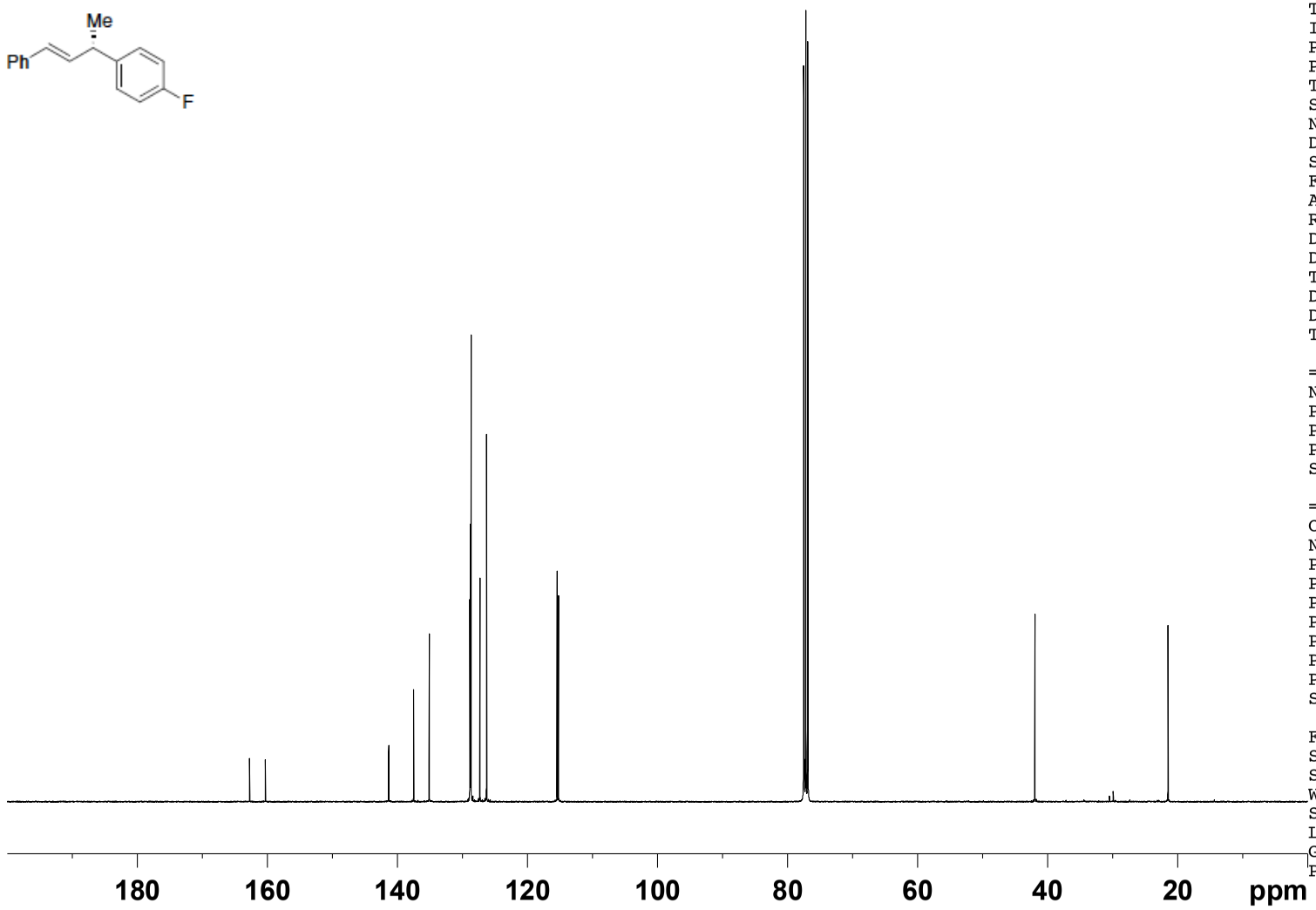

```
Current Data Parameters
NAME            HH-4-242
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130413
Time                5.33
INSTRUM            spect
PROBHD   5 mm CPQNP 1H/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ              3.9584243 sec
RG                     8
DW                60.400 usec
DE                 6.00 usec
TE                298.1 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 15.00 usec
PL1                 4.90 dB
PL1W          3.30822015 W
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300092 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

compound 3.50 13C NMR



461

S39

Current Data Parameters
NAME HH-4-242
EXPNO 2
PROCNO 1

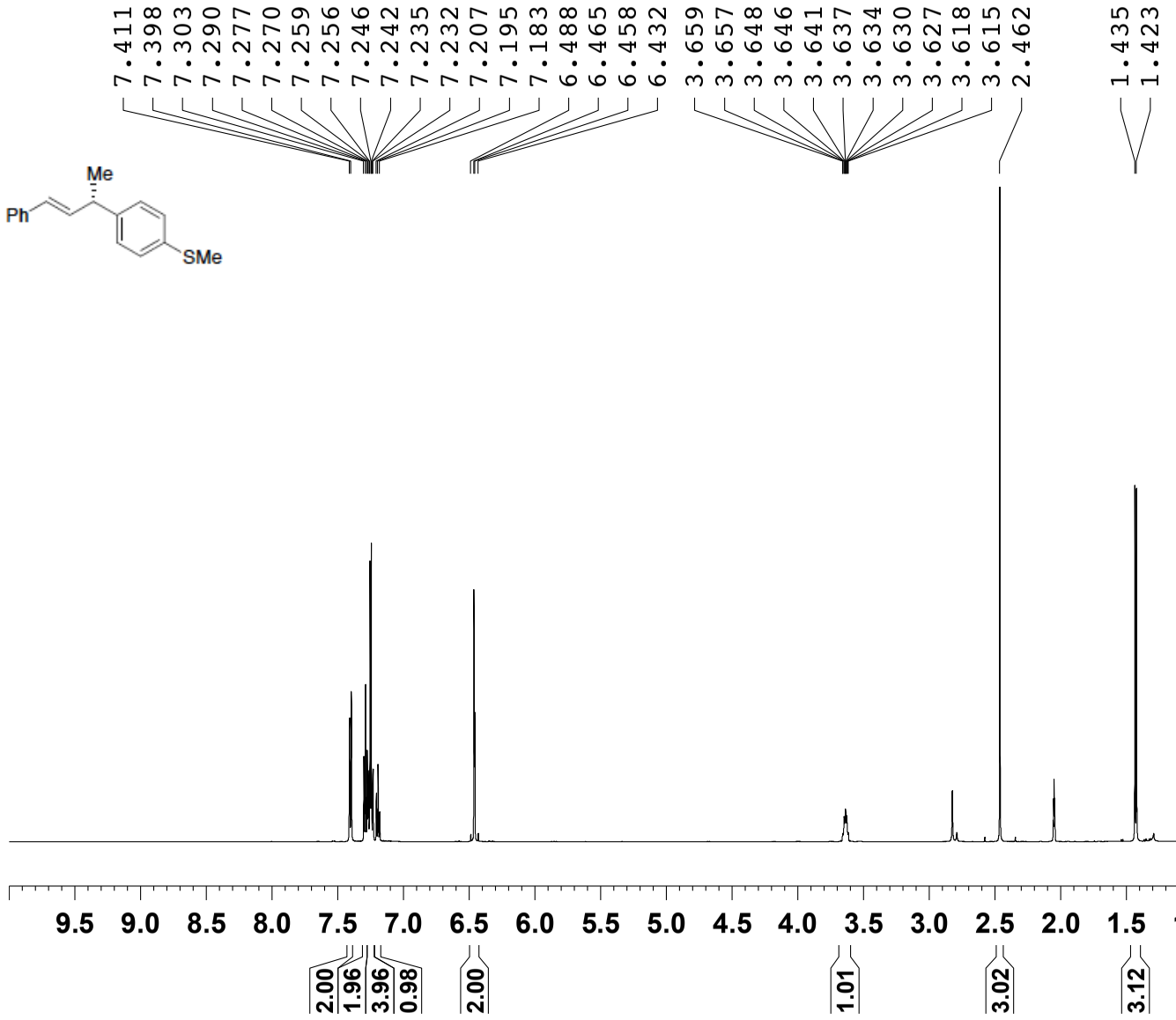
F2 - Acquisition Parameters
Date_ 20130413
Time 6.34
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 512
DW 20.850 usec
DE 18.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.25 usec
PL1 0.55 dB
PL1W 35.18820572 W
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 4.90 dB
PL12 20.46 dB
PL13 21.00 dB
PL2W 3.30822015 W
PL12W 0.09195905 W
PL13W 0.08120718 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127555 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

compound 3.51 1H NMR



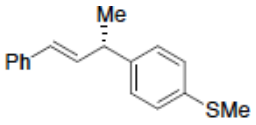
Current Data Parameters
NAME HH-4-247B-PURE
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130629
Time 13.04
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT Acetone
NS 8
DS 2
SWH 8403.361 Hz
FIDRES 0.128225 Hz
AQ 3.8994420 sec
RG 57
DW 59.500 usec
DE 17.39 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 600.3233018 MHz
NUC1 1H
P1 10.77 usec

F2 - Processing parameters
SI 65536
SF 600.3200119 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

compound 3.51 13 CNMR



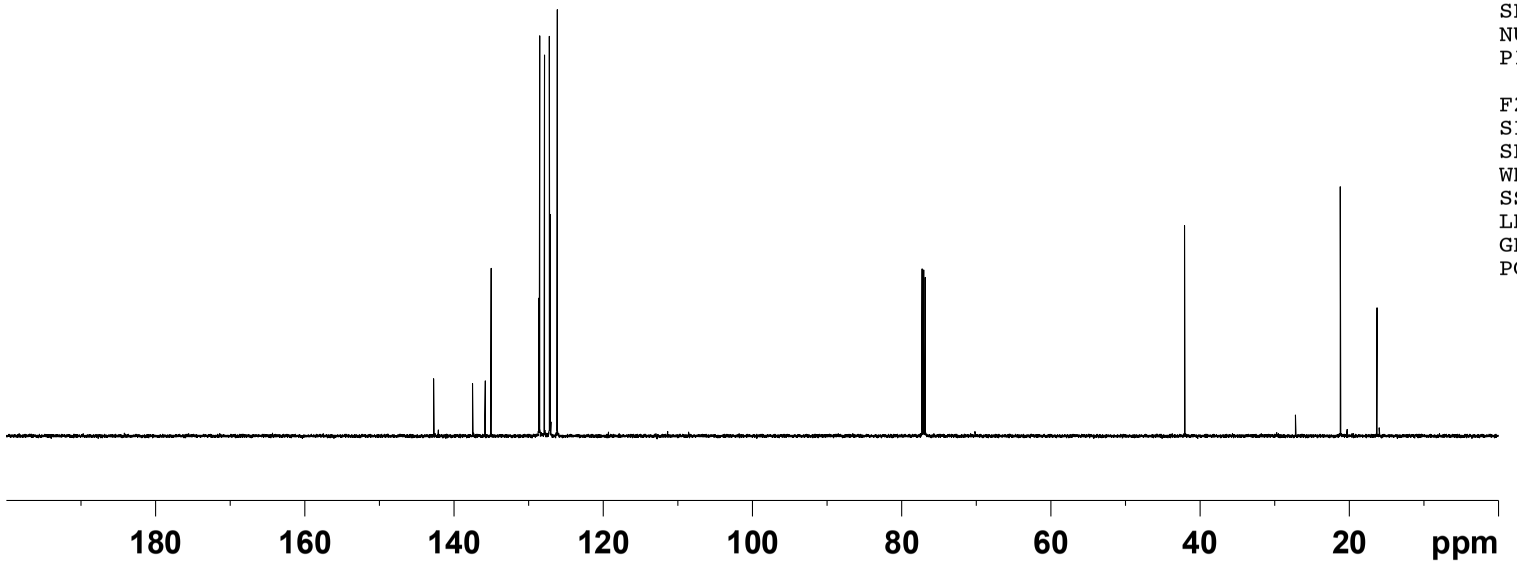
142.76
137.53
135.87
135.05
128.66
128.54
127.90
127.23
127.13
126.18

42.07

21.18

16.30

463



S35

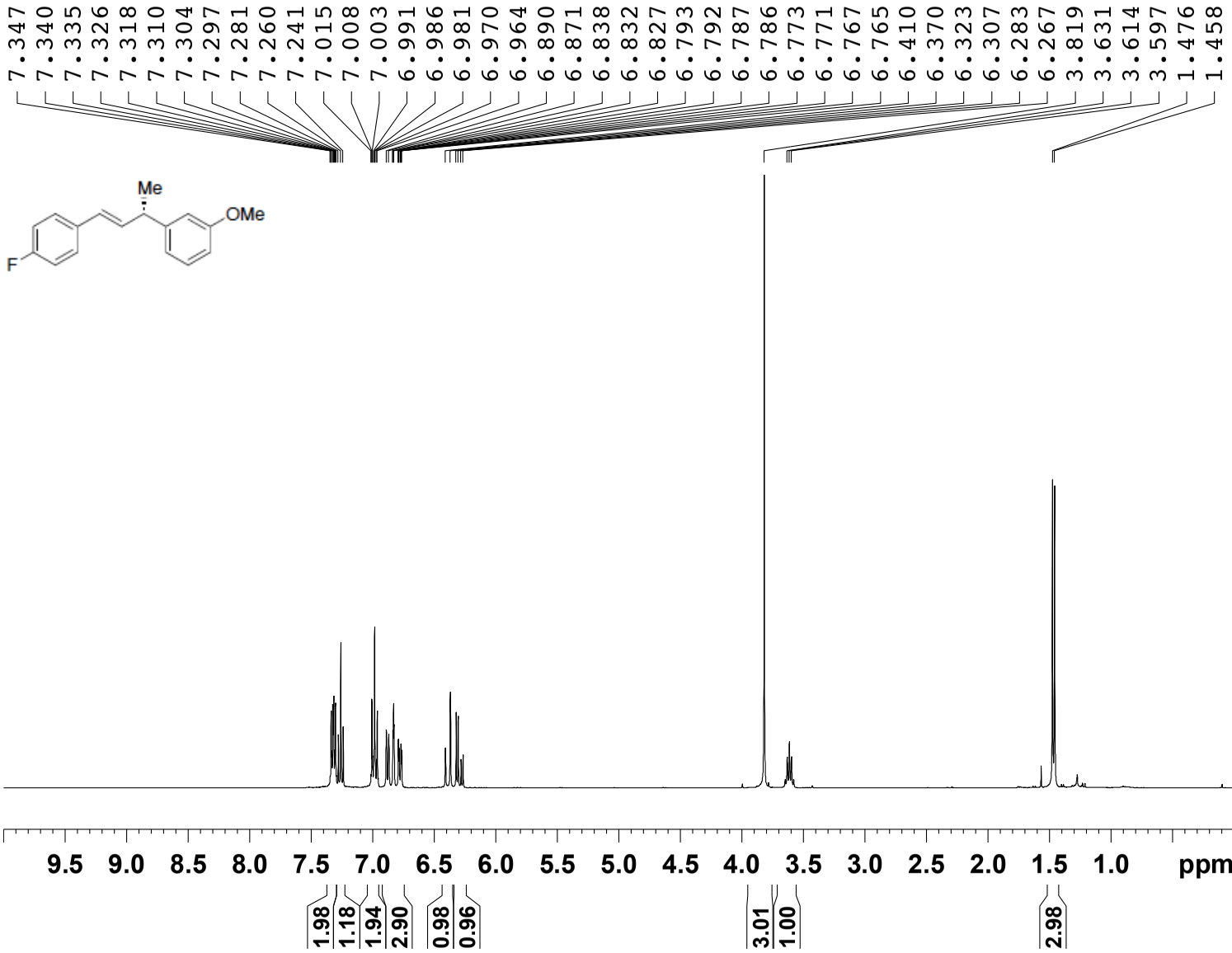
Current Data Parameters
NAME HH-4-247B
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130628
Time 16.39
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg55
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 34722.223 Hz
FIDRES 0.529819 Hz
AQ 0.9437684 sec
RG 2050
DW 14.400 usec
DE 19.34 usec
TE 298.0 K
D1 1.10000002 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 150.9656784 MHz
NUC1 13C
P1 10.63 usec

F2 - Processing parameters
SI 32768
SF 150.9505840 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

compound 3.52 1H NMR



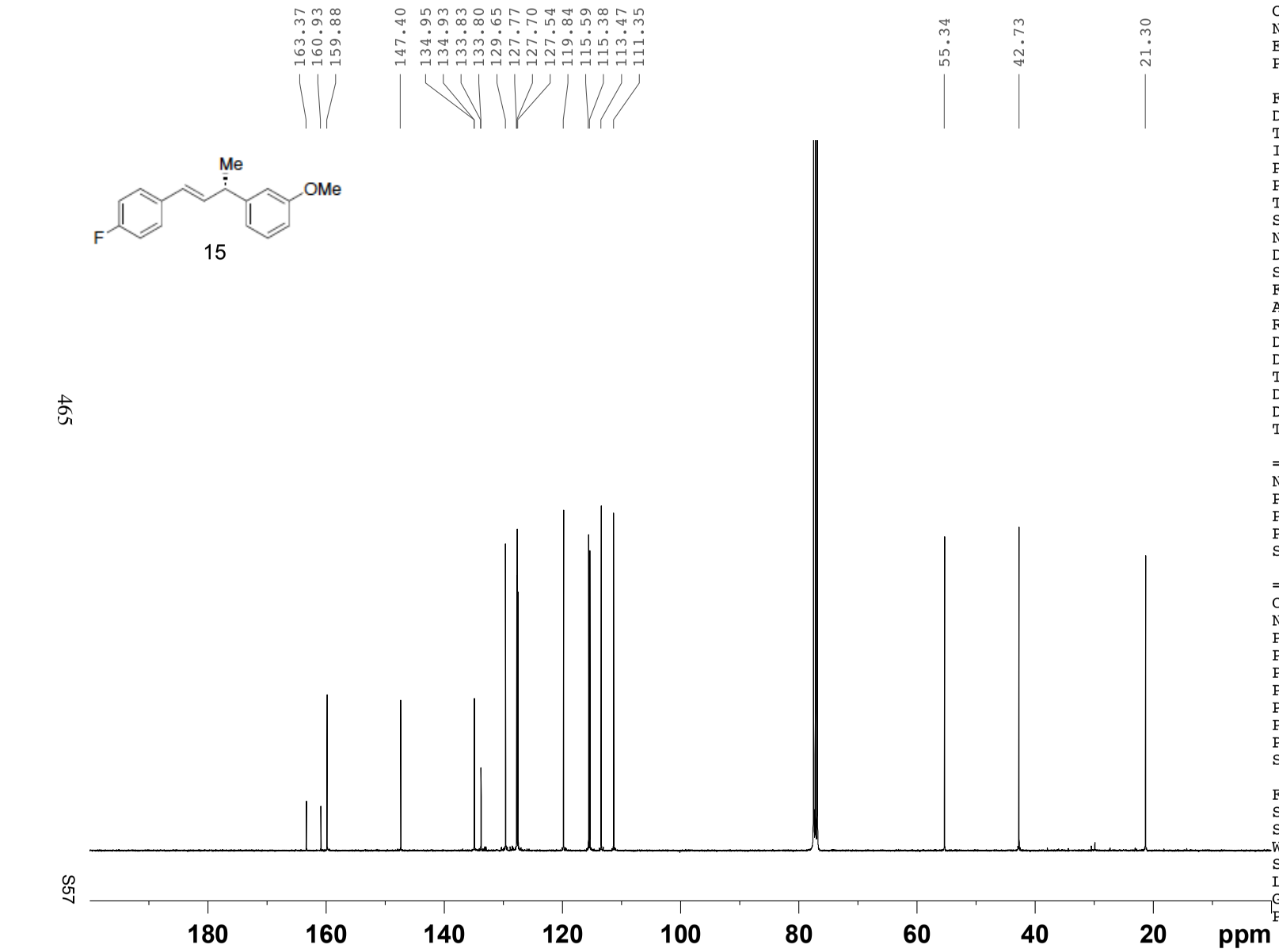
Current Data Parameters
NAME HH-4-252A
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130502
Time 17.32
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 8
DW 60.400 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 4.90 dB
PL1W 3.30822015 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300094 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

compound 3.52 13C NMR




```
Current Data Parameters
NAME          HH-4-252A
EXPNO                 2
PROCNO                1

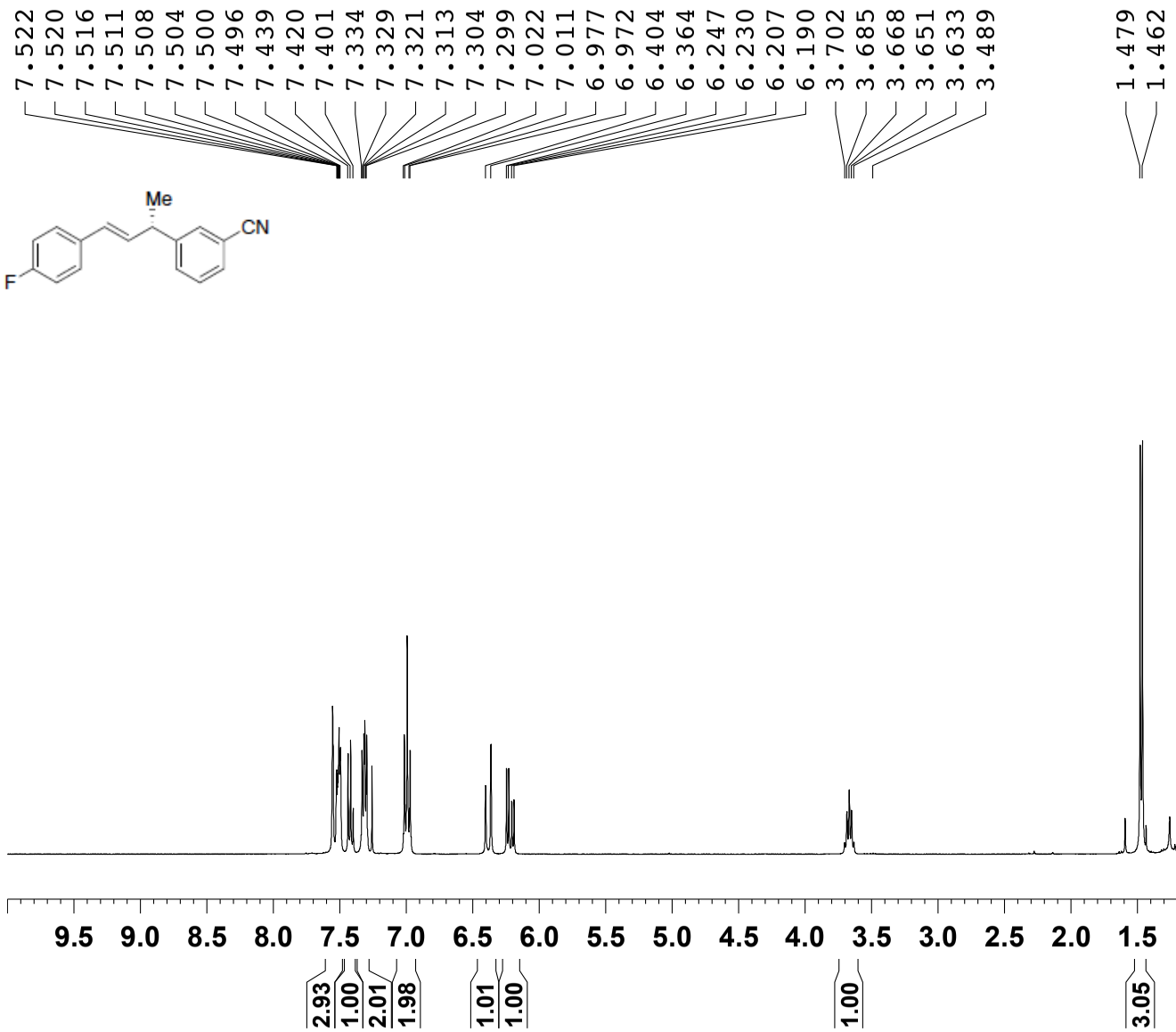
F2 - Acquisition Parameters
Date_          20130502
Time              22.12
INSTRUM           spect
PROBHD   5 mm CPQNP 1H/
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ             1.3664756 sec
RG                  512
DW               20.850 usec
DE               18.00 usec
TE               298.1 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                 9.25 usec
PL1                0.55 dB
PL1W        35.18820572 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             90.00 usec
PL2                4.90 dB
PL12              20.46 dB
PL13              21.00 dB
PL2W         3.30822015 W
PL12W        0.09195905 W
PL13W        0.08120718 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127562 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

compound 3.53 1H NMR



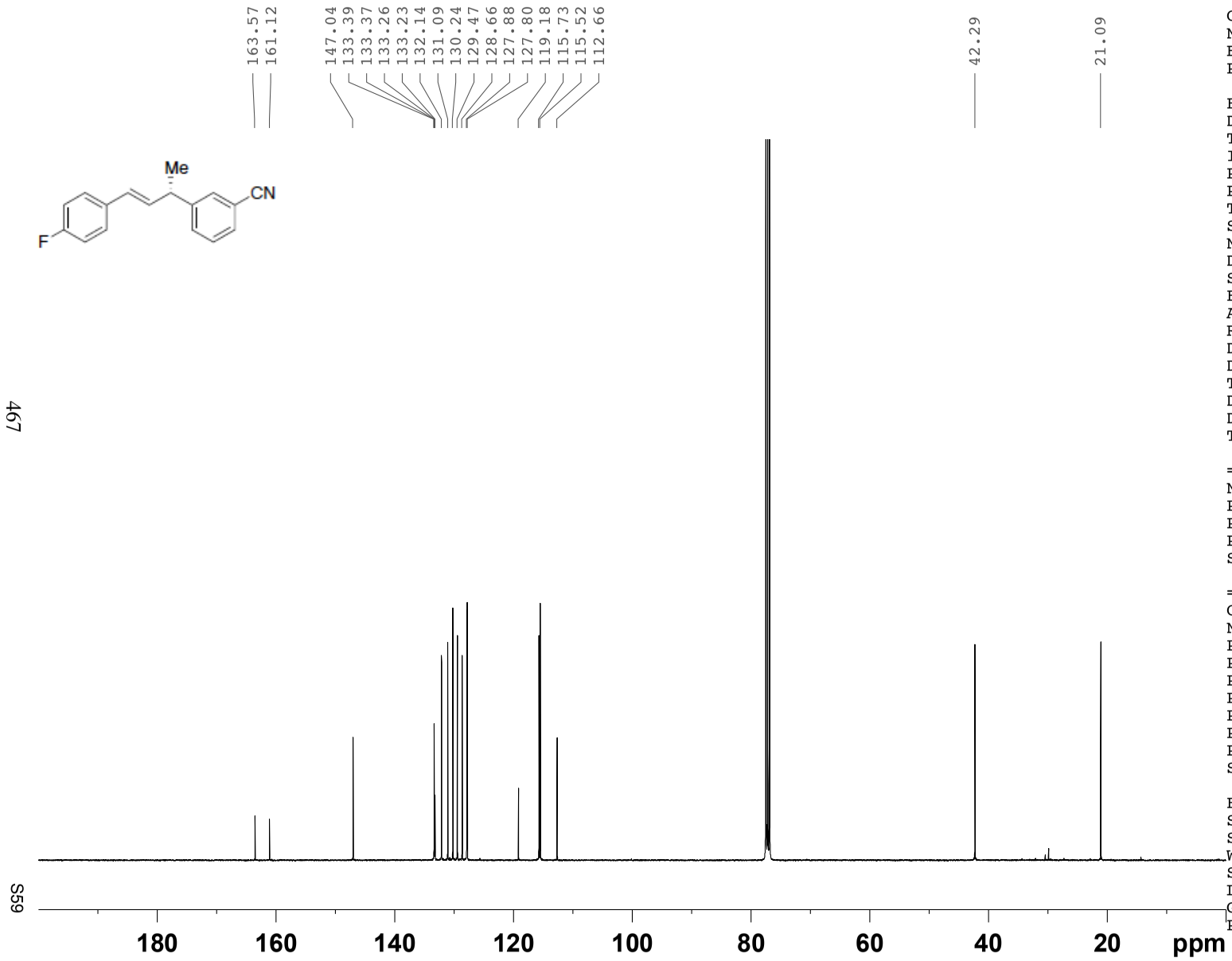
Current Data Parameters
NAME HH-4-246B
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130504
Time 8.06
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 4
DW 60.400 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 4.90 dB
PL1W 3.30822015 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300098 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

compound 3.53 13C NMR




```
Current Data Parameters
NAME          HH-4-246B
EXPNO                 2
PROCNO                1

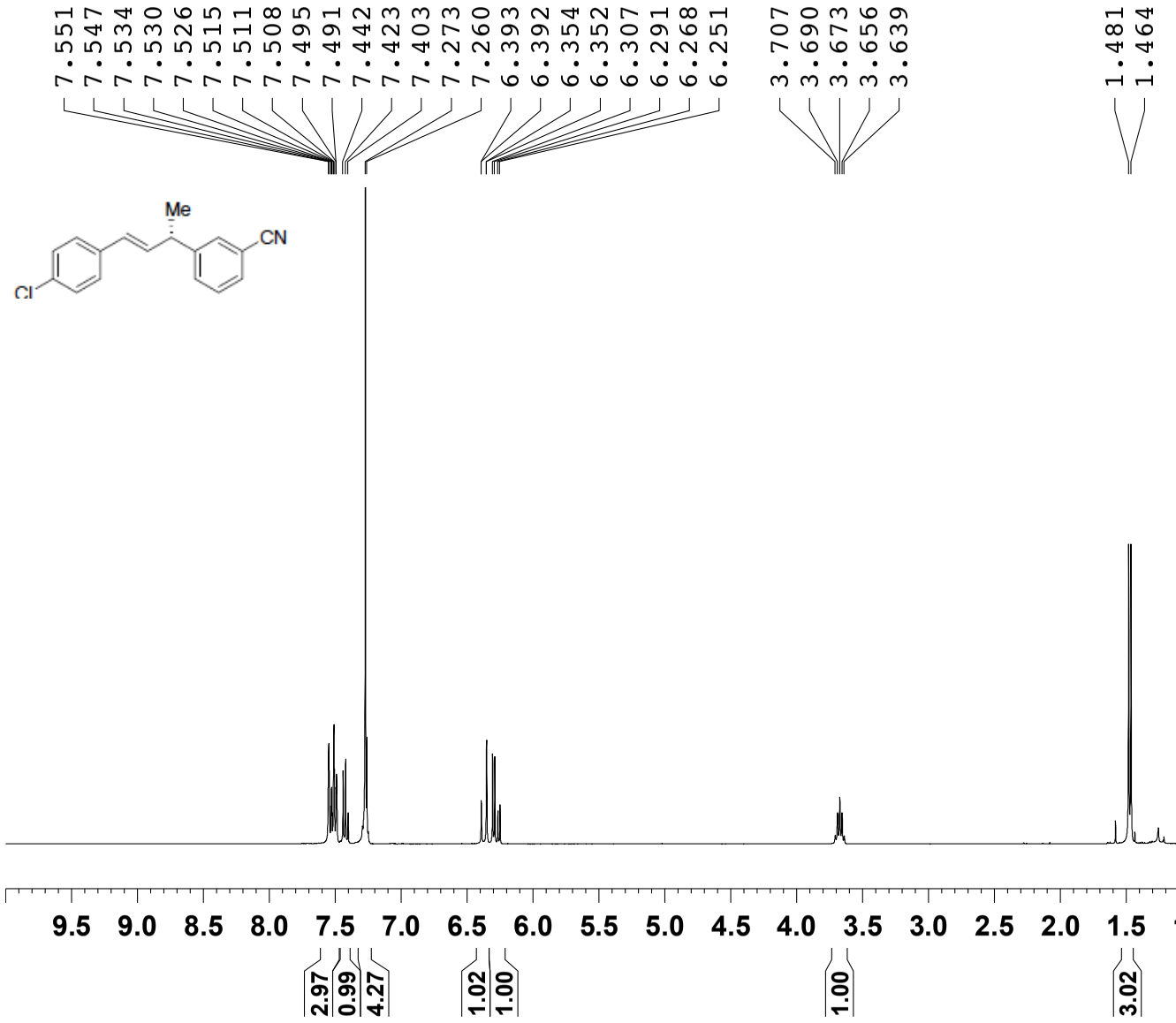
F2 - Acquisition Parameters
Date_          20130504
Time              21.03
INSTRUM           spect
PROBHD   5 mm CPQNP 1H/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ             1.3664756 sec
RG                  512
DW                20.850 usec
DE                18.00 usec
TE                298.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                 9.25 usec
PL1                0.55 dB
PL1W       35.18820572 W
SFO1       100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2              90.00 usec
PL2                 4.90 dB
PL12               20.46 dB
PL13               21.00 dB
PL2W        3.30822015 W
PL12W       0.09195905 W
PL13W       0.08120718 W
SFO2       400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF         100.6127567 MHz
WDW                   EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

compound 3.54 1H NMR



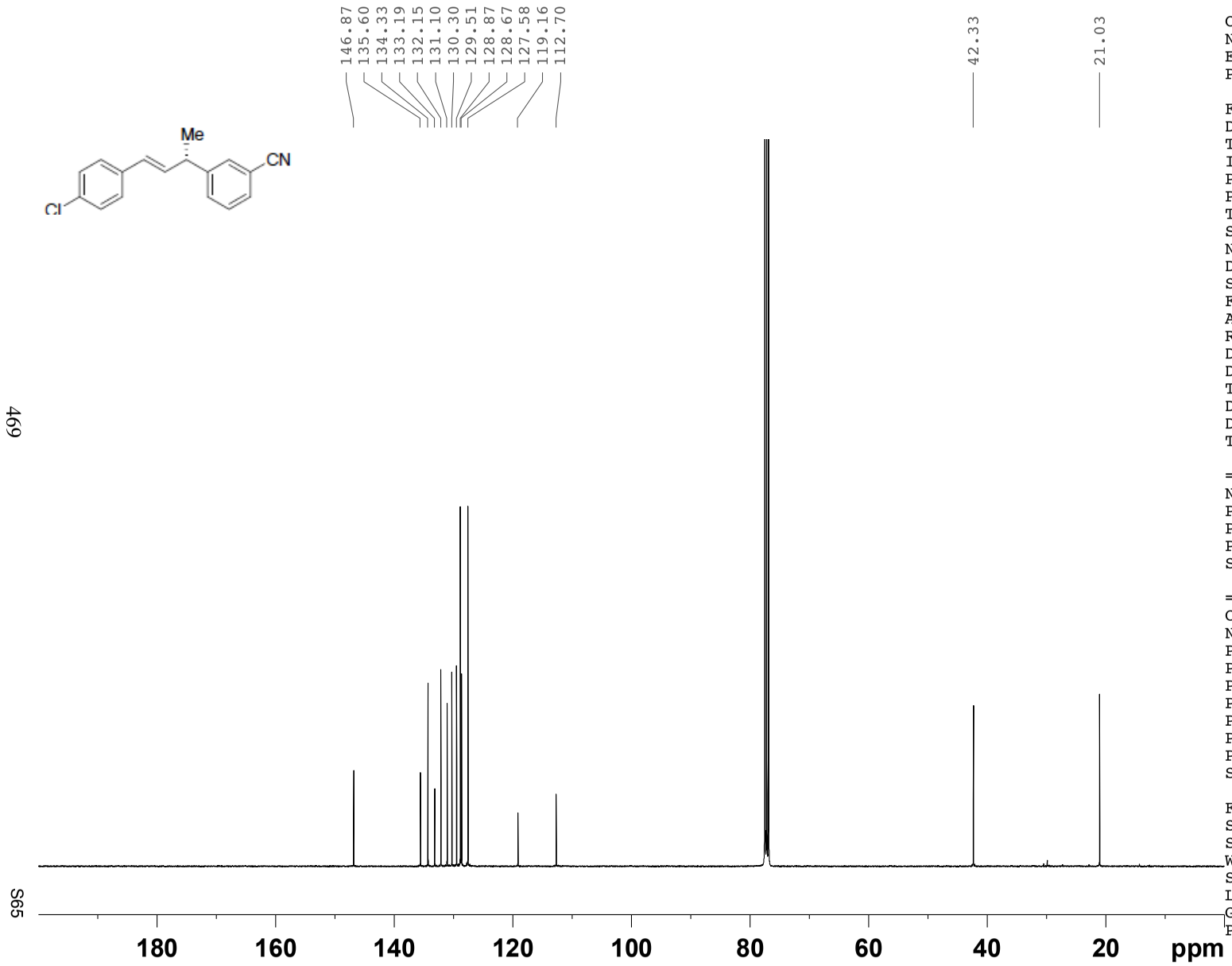

```
Current Data Parameters
NAME                  HH-4-256B
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20130513
Time                       1.28
INSTRUM                   spect
PROBHD    5 mm CPQNP 1H/
PULPROG                    zg30
TD                        65536
SOLVENT                   CDCl3
NS                           16
DS                            2
SWH                    8278.146 Hz
FIDRES                 0.126314 Hz
AQ                     3.9584243 sec
RG                           11.3
DW                        60.400 usec
DE                         6.00 usec
TE                        298.2 K
D1                    1.00000000 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                         1H
P1                        15.00 usec
PL1                        4.90 dB
PL1W                 3.30822015 W
SFO1                400.1324710 MHz

F2 - Processing parameters
SI                        32768
SF                  400.1300093 MHz
WDW                          EM
SSB                           0
LB                         0.30 Hz
GB                            0
PC                         1.00
```

compound 3.54 13 CNMR




```
Current Data Parameters
NAME          HH-4-256B
EXPNO                 2
PROCNO                1

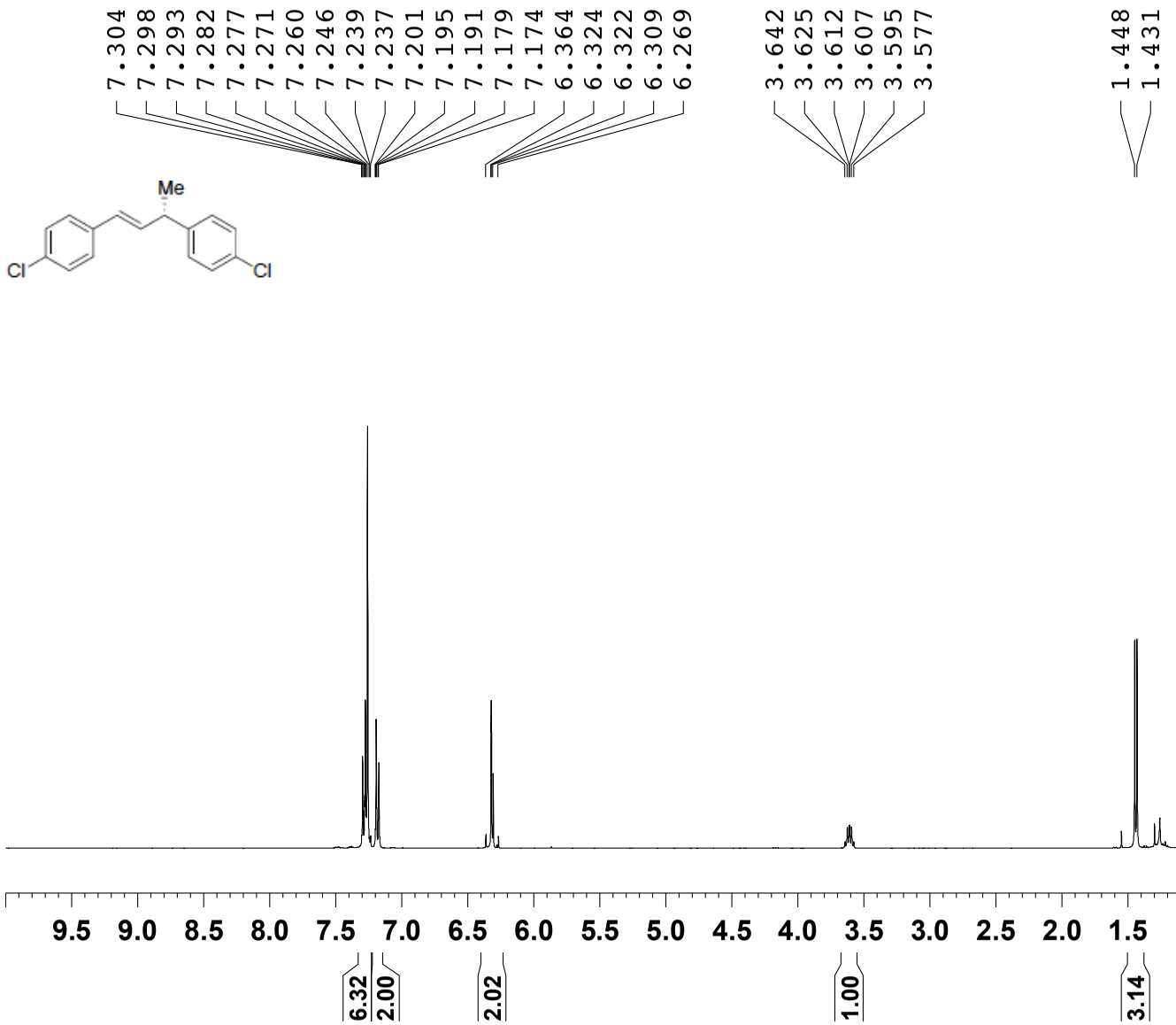
F2 - Acquisition Parameters
Date_          20130513
Time               2.28
INSTRUM           spect
PROBHD   5 mm CPQNP 1H/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ             1.3664756 sec
RG                  512
DW               20.850 usec
DE               18.00 usec
TE               298.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                 9.25 usec
PL1                0.55 dB
PL1W        35.18820572 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             90.00 usec
PL2                4.90 dB
PL12              20.46 dB
PL13              21.00 dB
PL2W         3.30822015 W
PL12W        0.09195905 W
PL13W        0.08120718 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127558 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

compound 3.55 1H NMR




```
Current Data Parameters
NAME          HH-4-257A
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20130513
Time               2.34
INSTRUM           spect
PROBHD   5 mm CPQNP 1H/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ             3.9584243 sec
RG                 11.3
DW               60.400 usec
DE                6.00 usec
TE                298.1 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                  1H
P1                15.00 usec
PL1                4.90 dB
PL1W         3.30822015 W
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300105 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

compound 3.55 13C NMR

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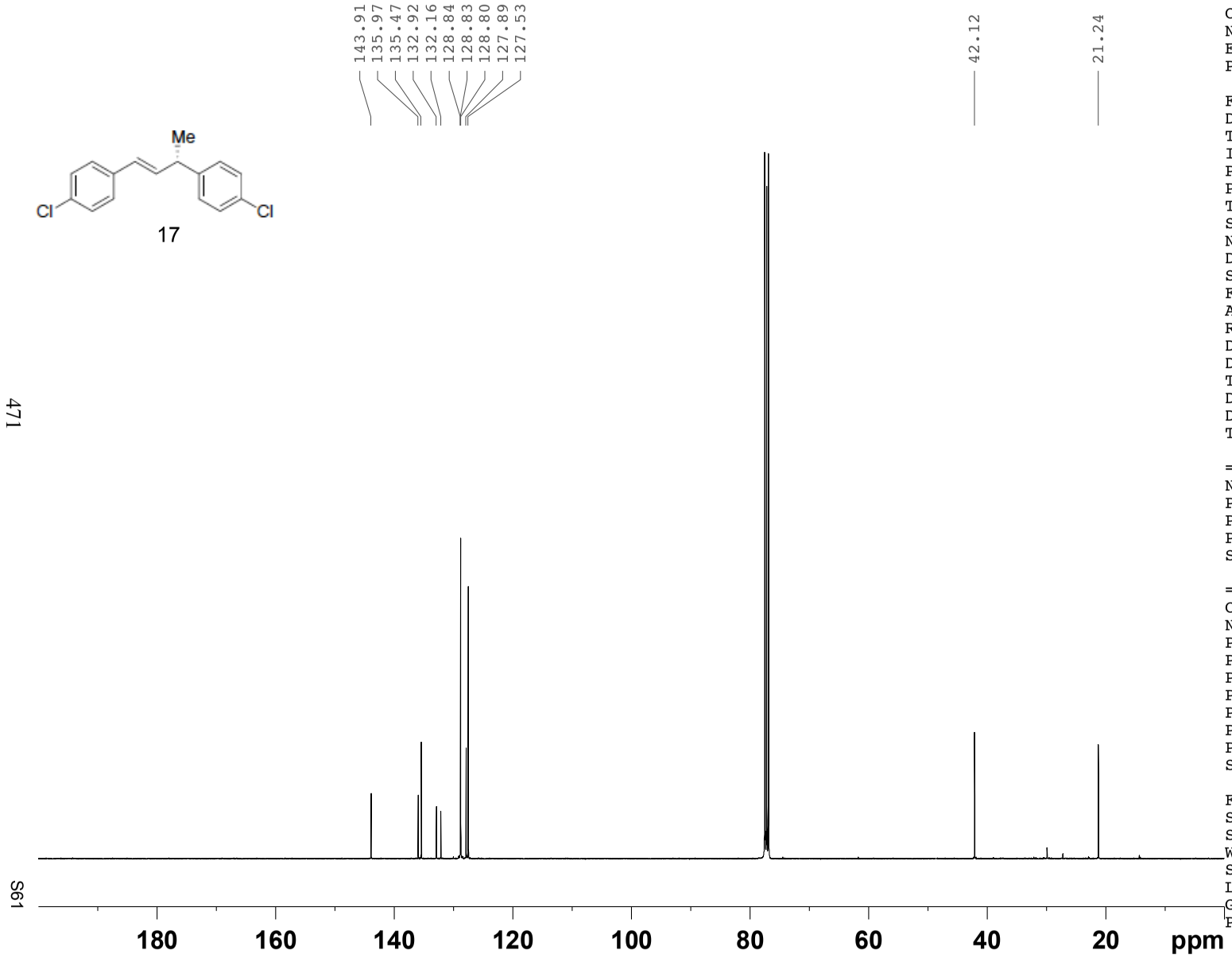



```
Current Data Parameters
NAME          HH-4-257A
EXPNO                 2
PROCNO                1

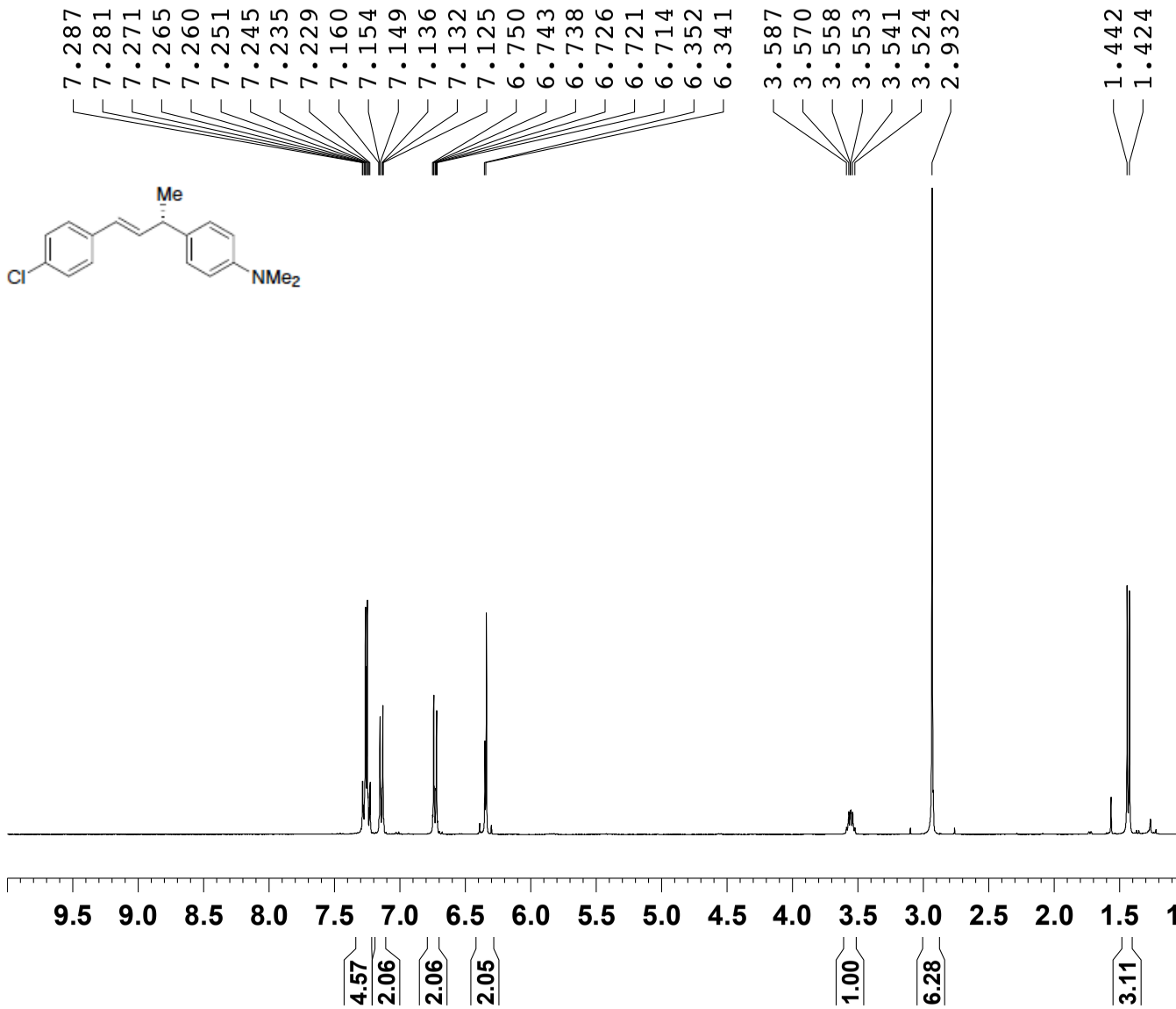
F2 - Acquisition Parameters
Date_          20130513
Time               3.34
INSTRUM           spect
PROBHD   5 mm CPQNP 1H/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ             1.3664756 sec
RG                  512
DW               20.850 usec
DE               18.00 usec
TE               298.1 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                 9.25 usec
PL1                0.55 dB
PL1W        35.18820572 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             90.00 usec
PL2                4.90 dB
PL12              20.46 dB
PL13              21.00 dB
PL2W         3.30822015 W
PL12W        0.09195905 W
PL13W        0.08120718 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127538 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

compound 3.56 1H NMR



Current Data Parameters

NAME	HH-4-276A
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20130531
Time	7.45
INSTRUM	spect
PROBHD	5 mm CPQNP 1H/
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	10.1
DW	60.400 usec
DE	6.00 usec
TE	298.2 K
D1	1.00000000 sec
TD0	1

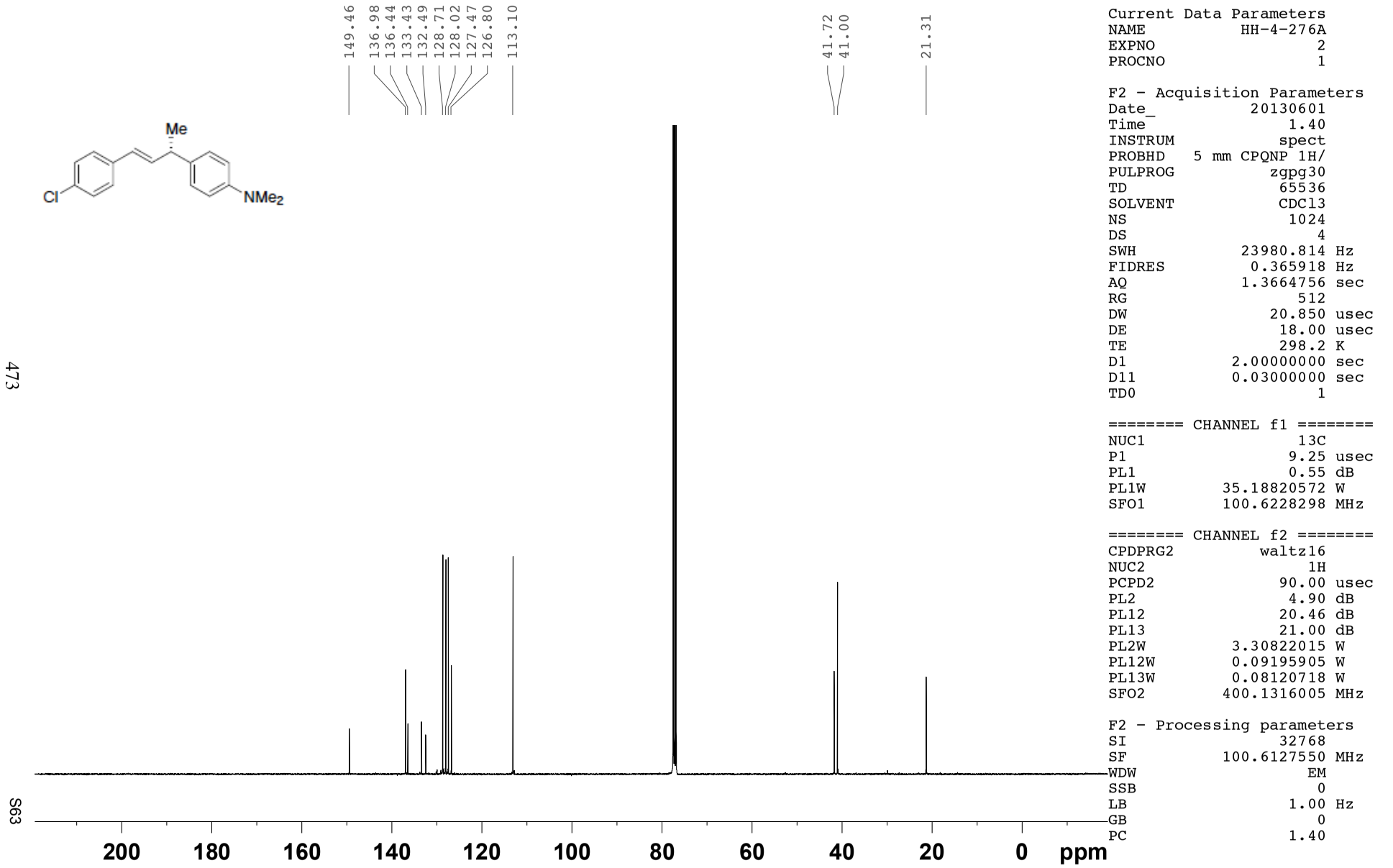
======== CHANNEL f1 ========

NUC1	1H
P1	15.00 usec
PL1	4.90 dB
PL1W	3.30822015 W
SFO1	400.1324710 MHz

F2 - Processing parameters

SI	32768
SF	400.1300095 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

compound 3.56 13C NMR




```
Current Data Parameters
NAME          HH-4-276A
EXPNO                 2
PROCNO                1

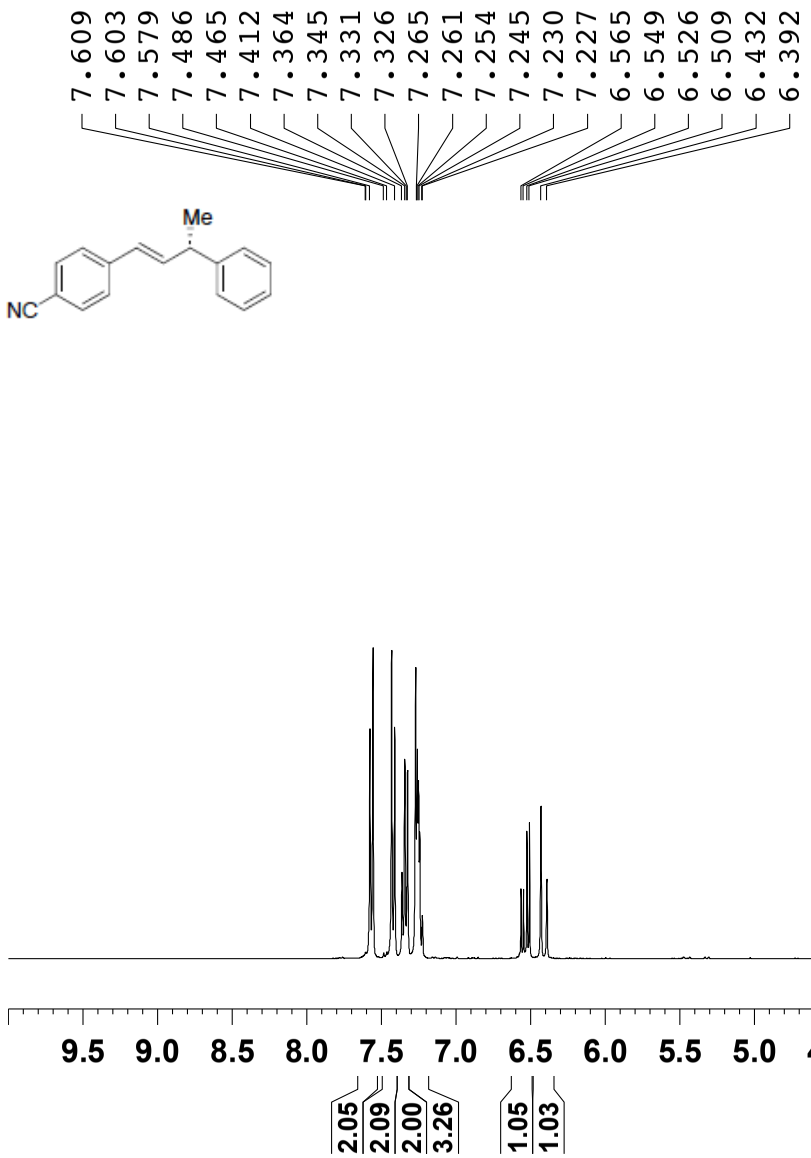
F2 - Acquisition Parameters
Date_          20130601
Time               1.40
INSTRUM           spect
PROBHD   5 mm CPQNP 1H/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ            1.3664756 sec
RG                  512
DW               20.850 usec
DE               18.00 usec
TE               298.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                9.25 usec
PL1               0.55 dB
PL1W       35.18820572 W
SFO1       100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2            90.00 usec
PL2               4.90 dB
PL12             20.46 dB
PL13             21.00 dB
PL2W        3.30822015 W
PL12W       0.09195905 W
PL13W       0.08120718 W
SFO2       400.1316005 MHz

F2 - Processing parameters
SI                32768
SF         100.6127550 MHz
WDW                EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

compound 3.57 1H NMR



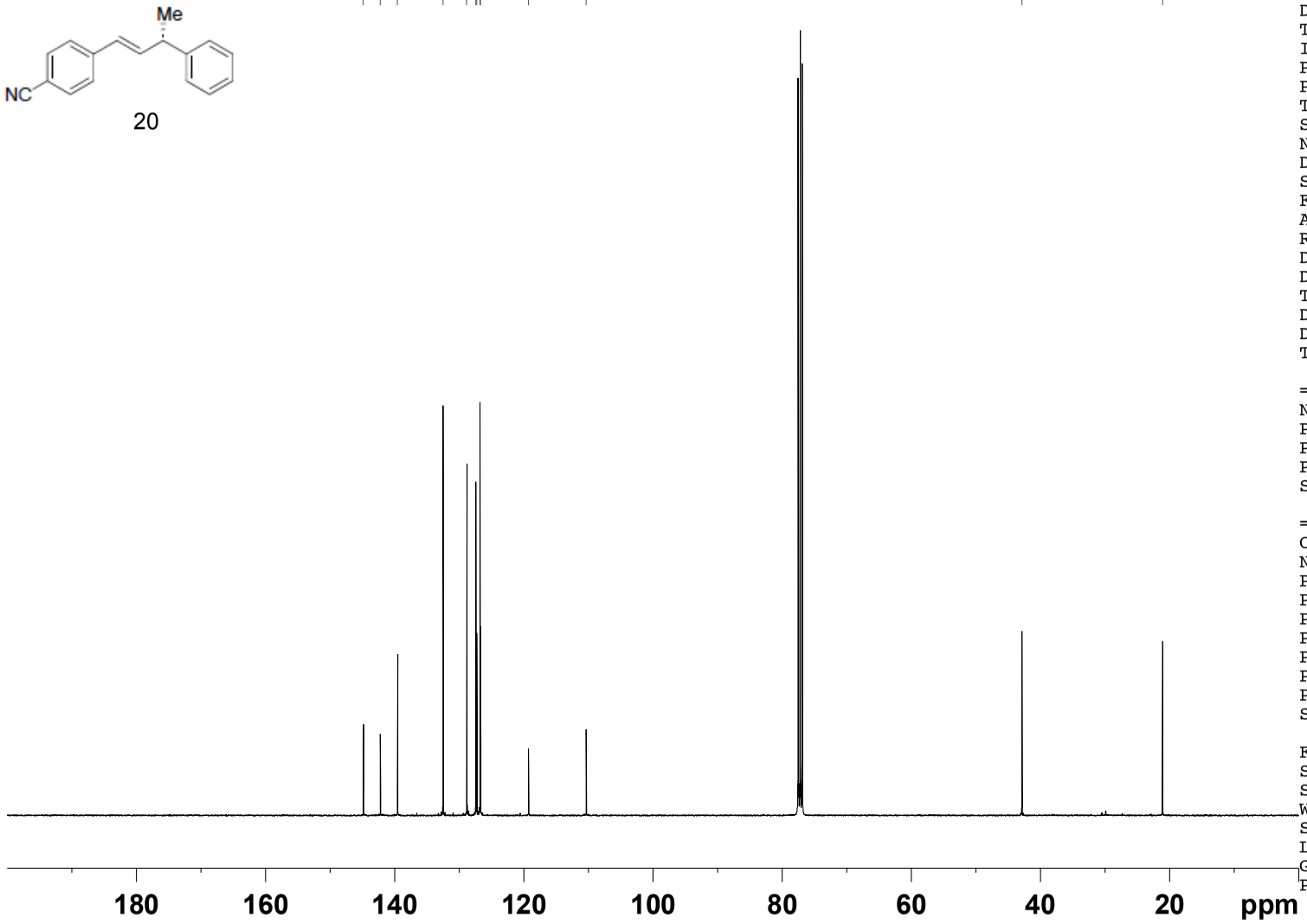

```
Current Data Parameters
NAME                  HH-4-263A
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20130518
Time                       1.11
INSTRUM                   spect
PROBHD    5 mm CPQNP 1H/
PULPROG                    zg30
TD                        65536
SOLVENT                   CDCl3
NS                           16
DS                            2
SWH                    8278.146 Hz
FIDRES                 0.126314 Hz
AQ                     3.9584243 sec
RG                           6.3
DW                        60.400 usec
DE                         6.00 usec
TE                        298.2 K
D1                     1.00000000 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                         1H
P1                        15.00 usec
PL1                        4.90 dB
PL1W                  3.30822015 W
SFO1                400.1324710 MHz

F2 - Processing parameters
SI                        32768
SF                  400.1300093 MHz
WDW                          EM
SSB                           0
LB                         0.30 Hz
GB                            0
PC                         1.00
```

compound 3.57 13C NMR




```
Current Data Parameters
NAME          HH-4-263A
EXPNO                 2
PROCNO                1

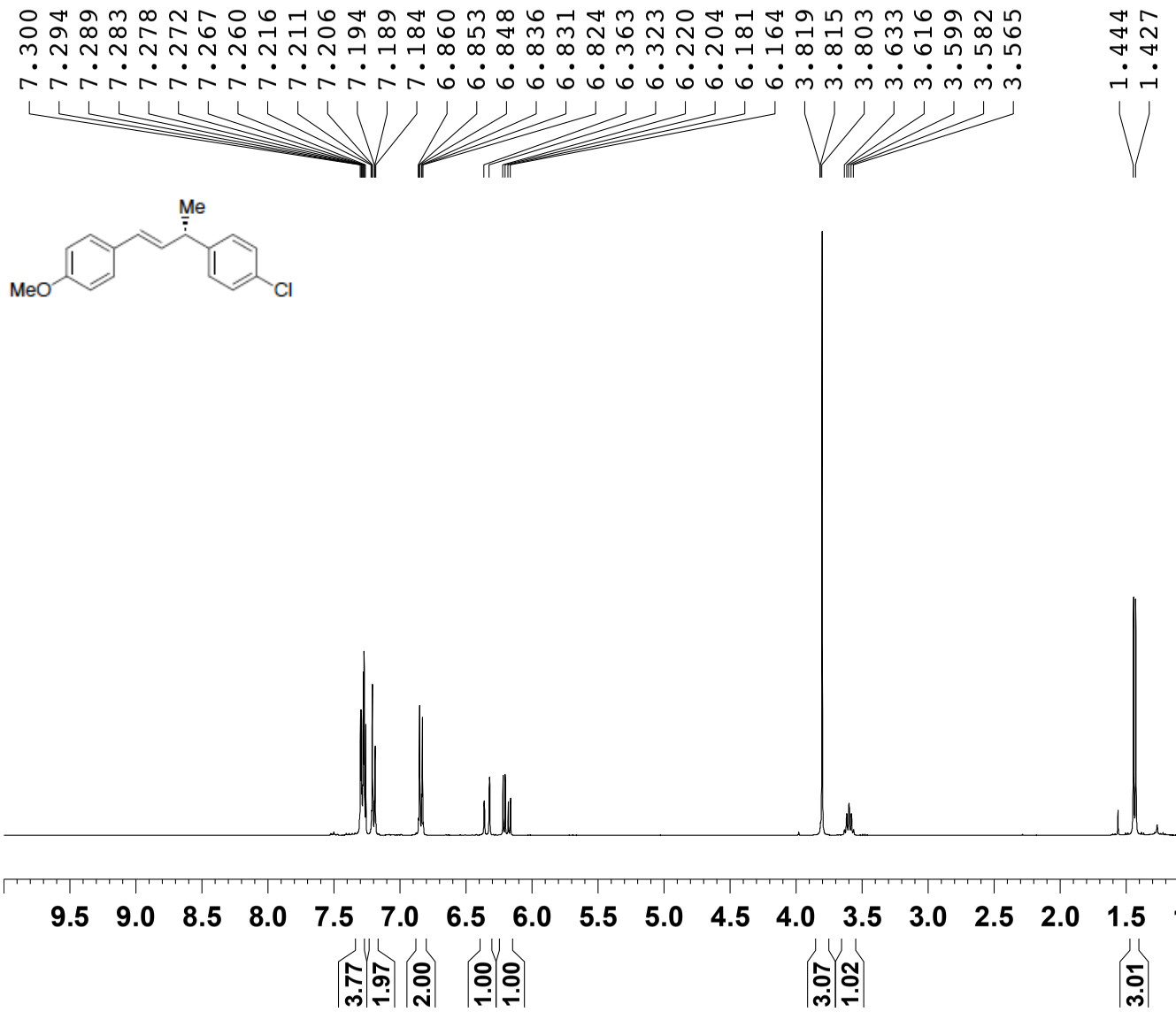
F2 - Acquisition Parameters
Date_          20130518
Time               2.11
INSTRUM           spect
PROBHD   5 mm CPQNP 1H/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ             1.3664756 sec
RG                  512
DW               20.850 usec
DE               18.00 usec
TE               298.1 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                 9.25 usec
PL1                0.55 dB
PL1W        35.18820572 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             90.00 usec
PL2                4.90 dB
PL12               20.46 dB
PL13               21.00 dB
PL2W         3.30822015 W
PL12W        0.09195905 W
PL13W        0.08120718 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127549 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

compound 3.58 1H NMR



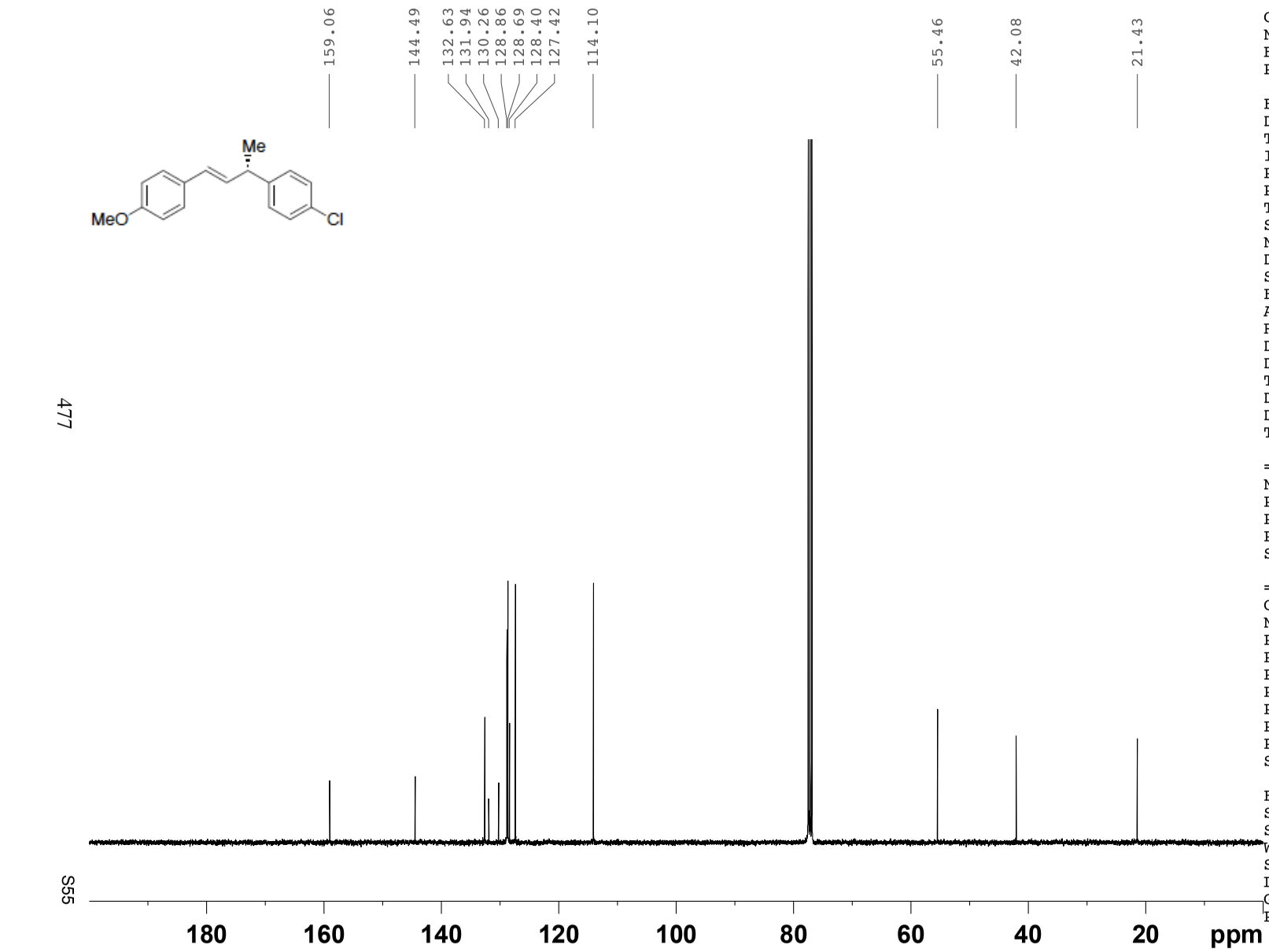
Current Data Parameters
NAME HH-4-264Brs
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130522
Time 13.42
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 8
DW 60.400 usec
DE 6.00 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 4.90 dB
PL1W 3.30822015 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300094 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

compound 3.58 13C NMR



Current Data Parameters
NAME HH-4-264Brs
EXPNO 2
PROCNO 1

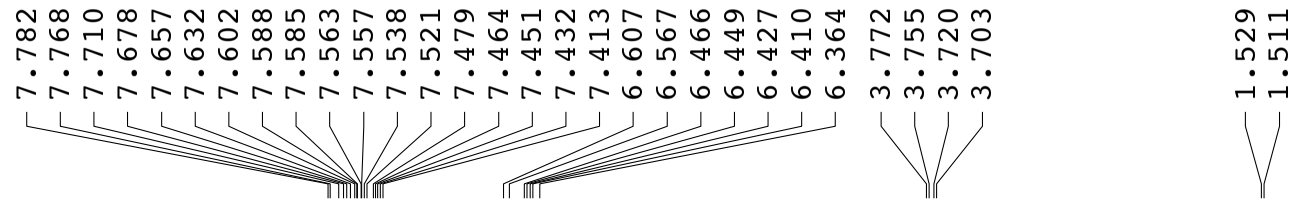
F2 - Acquisition Parameters
Date_ 20130522
Time 13.45
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 32
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 512
DW 20.850 usec
DE 18.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

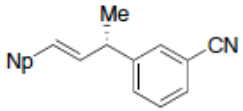
======== CHANNEL f1 ========
NUC1 13C
P1 9.25 usec
PL1 0.55 dB
PL1W 35.18820572 W
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 4.90 dB
PL12 20.46 dB
PL13 21.00 dB
PL2W 3.30822015 W
PL12W 0.09195905 W
PL13W 0.08120718 W
SFO2 400.1316005 MHz

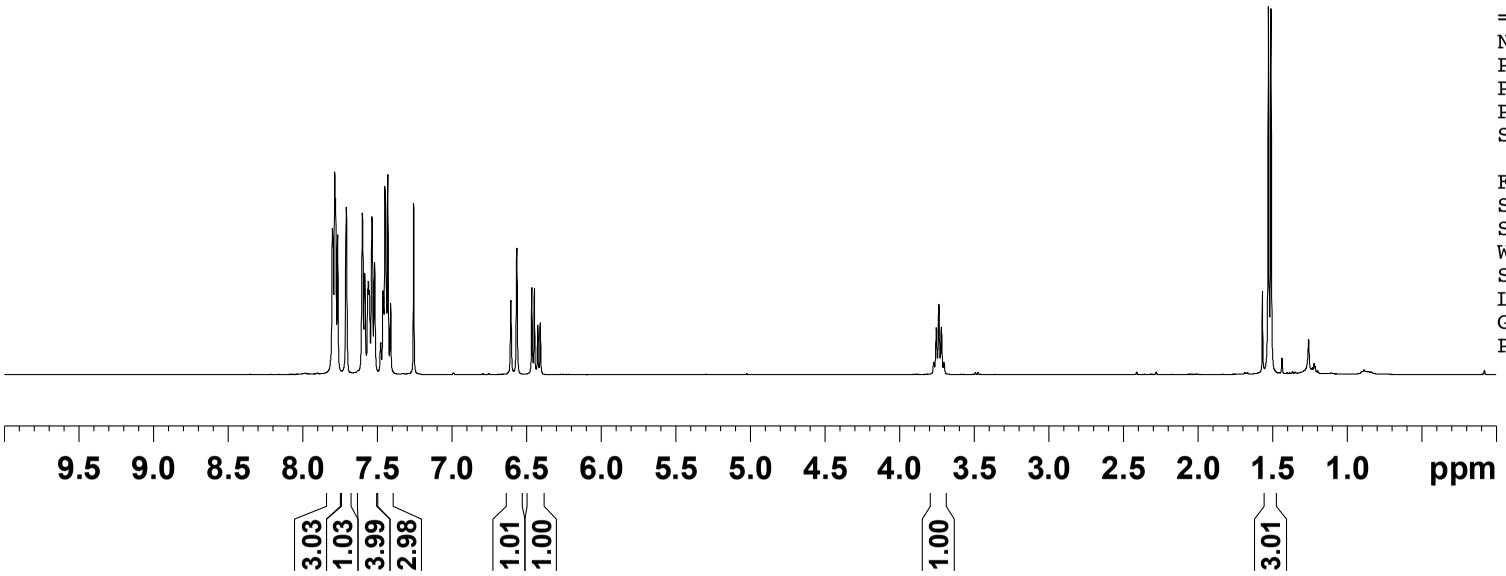
F2 - Processing parameters
SI 32768
SF 100.6127547 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

compound 3.59 1H NMR





478



S98

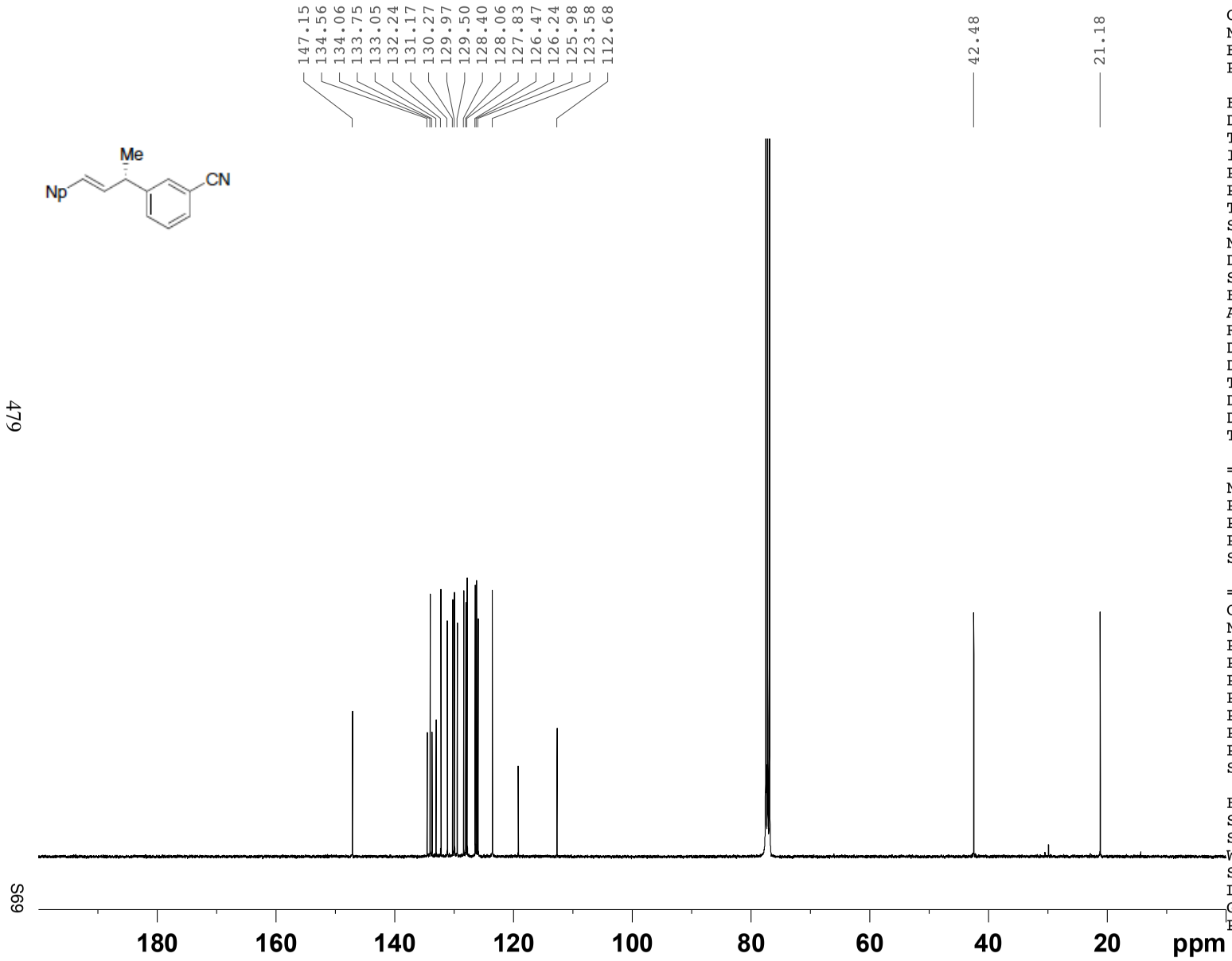
```
Current Data Parameters
NAME          HH-4-245A
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20130425
Time               7.04
INSTRUM           spect
PROBHD   5 mm CPQNP 1H/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ             3.9584243 sec
RG                 10.1
DW                60.400 usec
DE                 6.00 usec
TE                298.1 K
D1             1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                  1H
P1                15.00 usec
PL1                4.90 dB
PL1W         3.30822015 W
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300101 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

compound 3.59 13C NMR




```
Current Data Parameters
NAME          HH-4-245A
EXPNO                 2
PROCNO                1

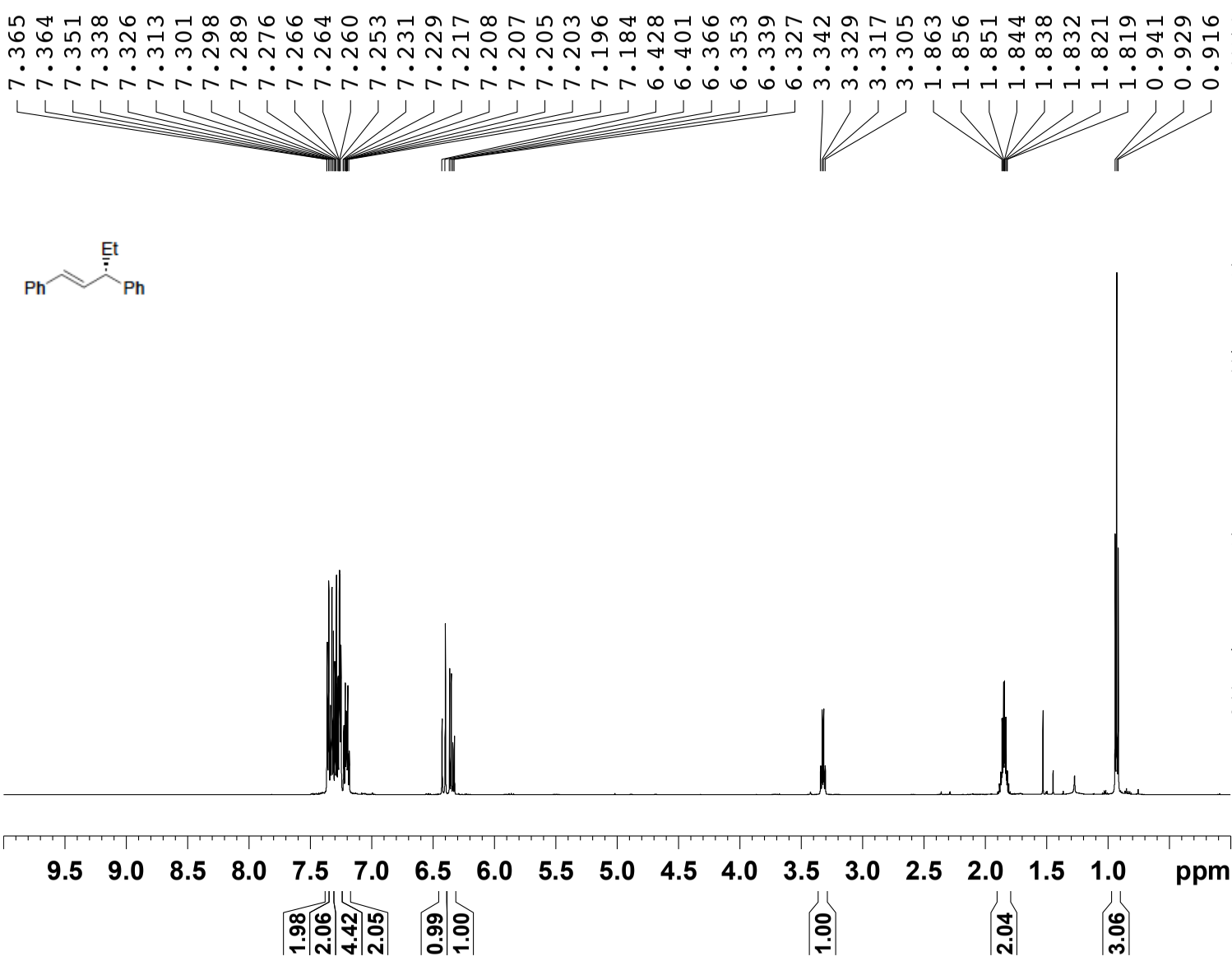
F2 - Acquisition Parameters
Date_          20130425
Time             21.08
INSTRUM          spect
PROBHD   5 mm CPQNP 1H/
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                1024
DS                   4
SWH          23980.814 Hz
FIDRES        0.365918 Hz
AQ           1.3664756 sec
RG                 512
DW              20.850 usec
DE              18.00 usec
TE              298.1 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1               9.25 usec
PL1              0.55 dB
PL1W       35.18820572 W
SFO1       100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2               1H
PCPD2           90.00 usec
PL2              4.90 dB
PL12            20.46 dB
PL13            21.00 dB
PL2W        3.30822015 W
PL12W       0.09195905 W
PL13W       0.08120718 W
SFO2       400.1316005 MHz

F2 - Processing parameters
SI                32768
SF         100.6127549 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC                1.40
```

compound 3.60 1H NMR




```
Current Data Parameters
NAME          QZ-4-022-2
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130617
Time               10.04
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8403.361 Hz
FIDRES          0.128225 Hz
AQ              3.8994420 sec
RG                   114
DW                59.500 usec
DE                17.39 usec
TE                298.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.3233018 MHz
NUC1                  1H
P1                10.77 usec

F2 - Processing parameters
SI                 65536
SF           600.3200161 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                1.00
```

compound 3.60 13C NMR

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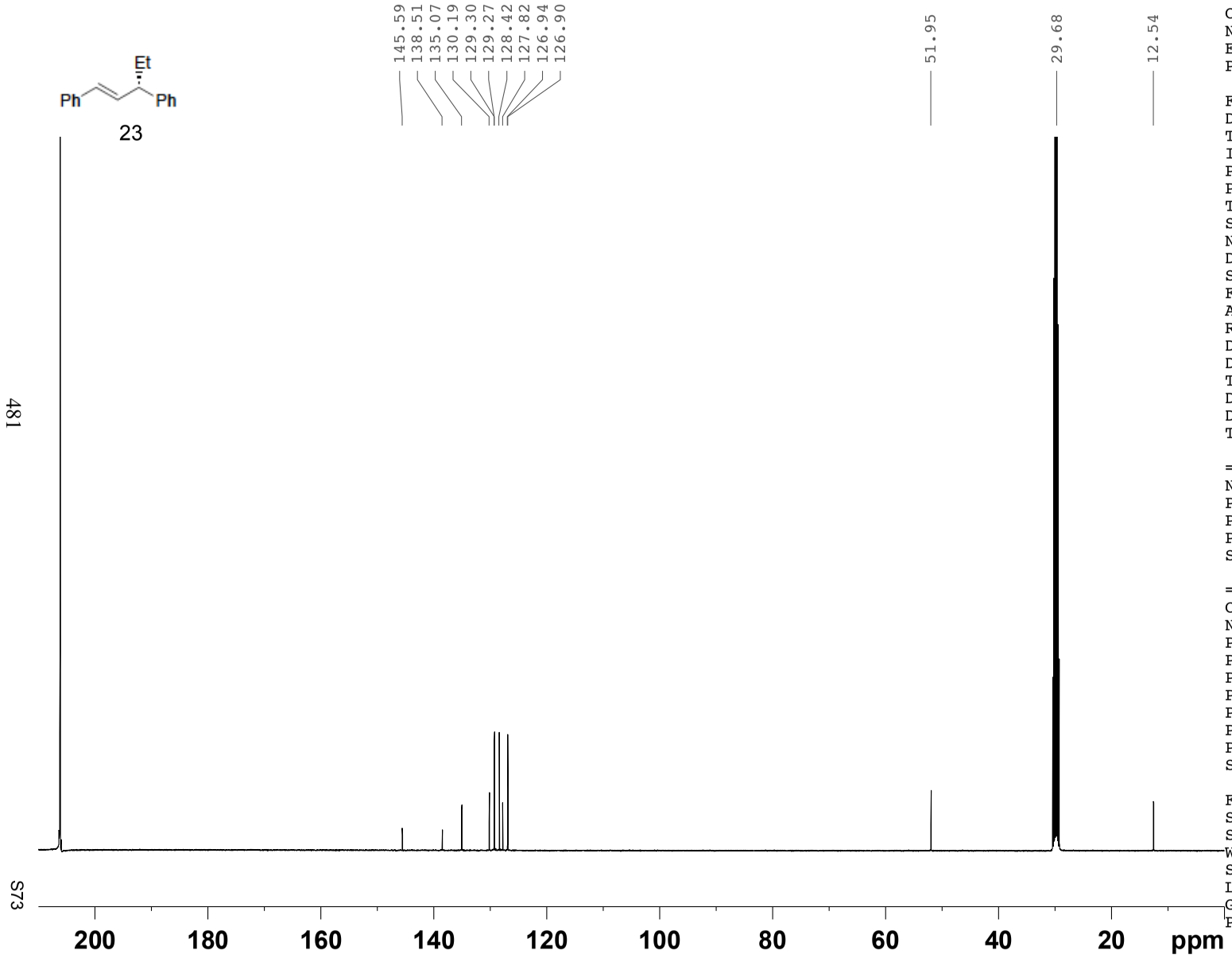



```
Current Data Parameters
NAME      QZ-4-022-2-Acetone
EXPNO                      2
PROCNO                     1

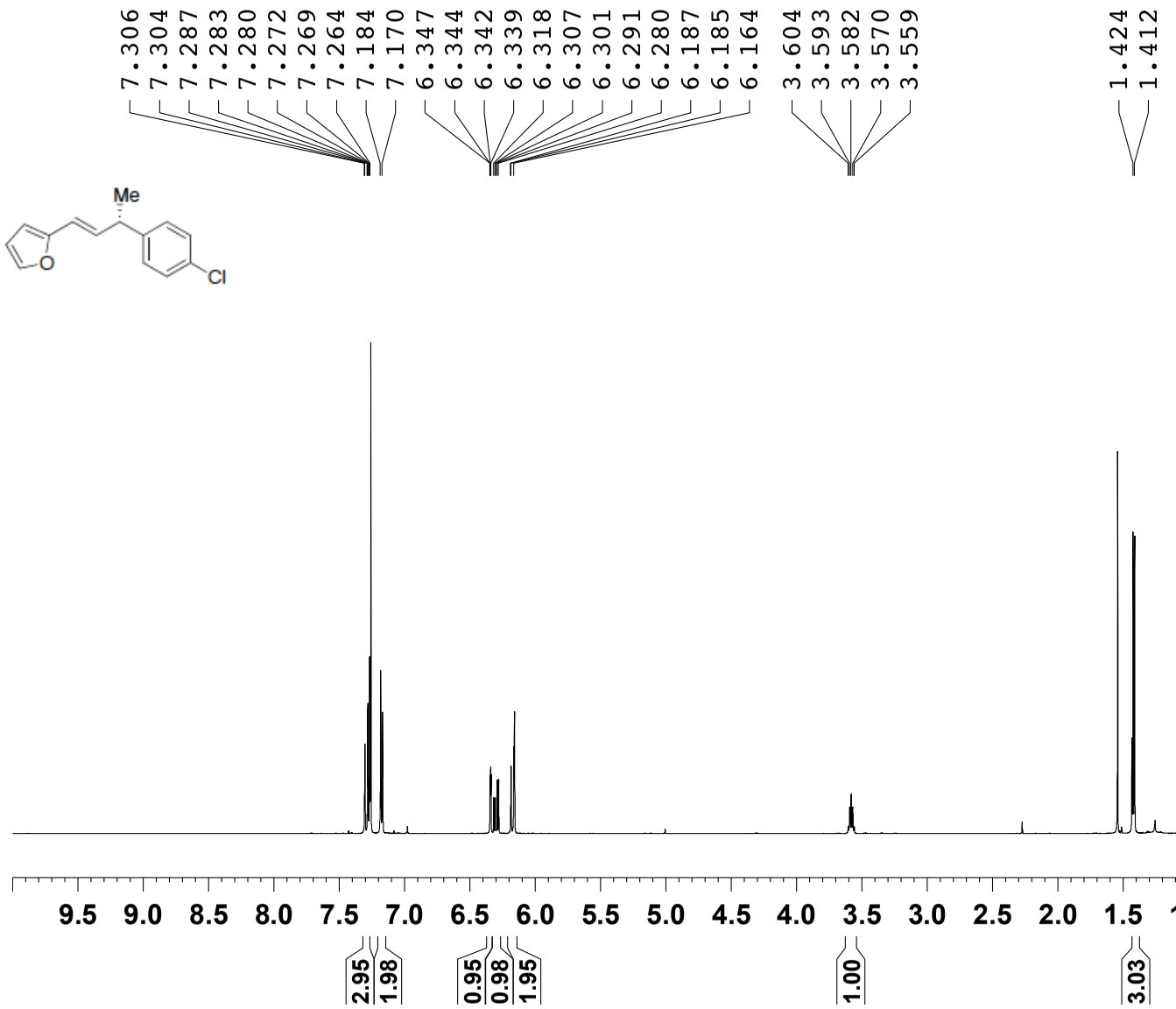
F2 - Acquisition Parameters
Date_              20130620
Time                 17.34
INSTRUM              spect
PROBHD   5 mm CPQNP 1H/
PULPROG             zgpg30
TD                   65536
SOLVENT            Acetone
NS                       256
DS                         4
SWH              23980.814 Hz
FIDRES            0.365918 Hz
AQ               1.3664756 sec
RG                       512
DW                  20.850 usec
DE                  18.00 usec
TE                  298.2 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                    13C
P1                   9.25 usec
PL1                  0.55 dB
PL1W          35.18820572 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                 4.90 dB
PL12                20.46 dB
PL13                21.00 dB
PL2W           3.30822015 W
PL12W          0.09195905 W
PL13W          0.08120718 W
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                    32768
SF           100.6126839 MHz
WDW                      EM
SSB                       0
LB                   1.00 Hz
GB                        0
PC                    1.40
```

compound 3.61 1H NMR



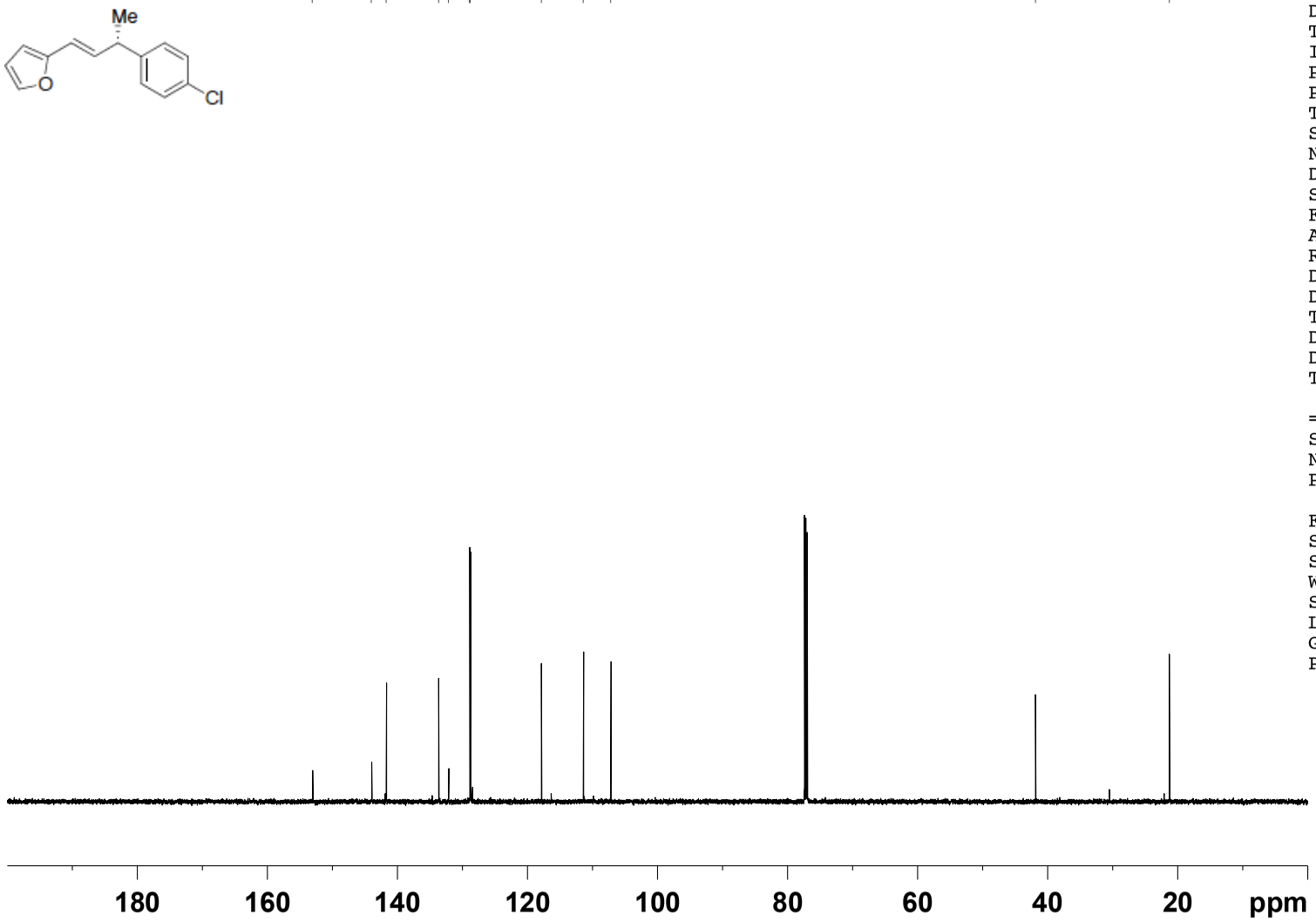

```
Current Data Parameters
NAME      QZ-4-038-PURE
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20130629
Time              13.01
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8403.361 Hz
FIDRES         0.128225 Hz
AQ             3.8994420 sec
RG                  228
DW                59.500 usec
DE                17.39 usec
TE                298.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        600.3233018 MHz
NUC1                1H
P1                10.77 usec

F2 - Processing parameters
SI                65536
SF          600.3200163 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

compound 3.61 13C NMR



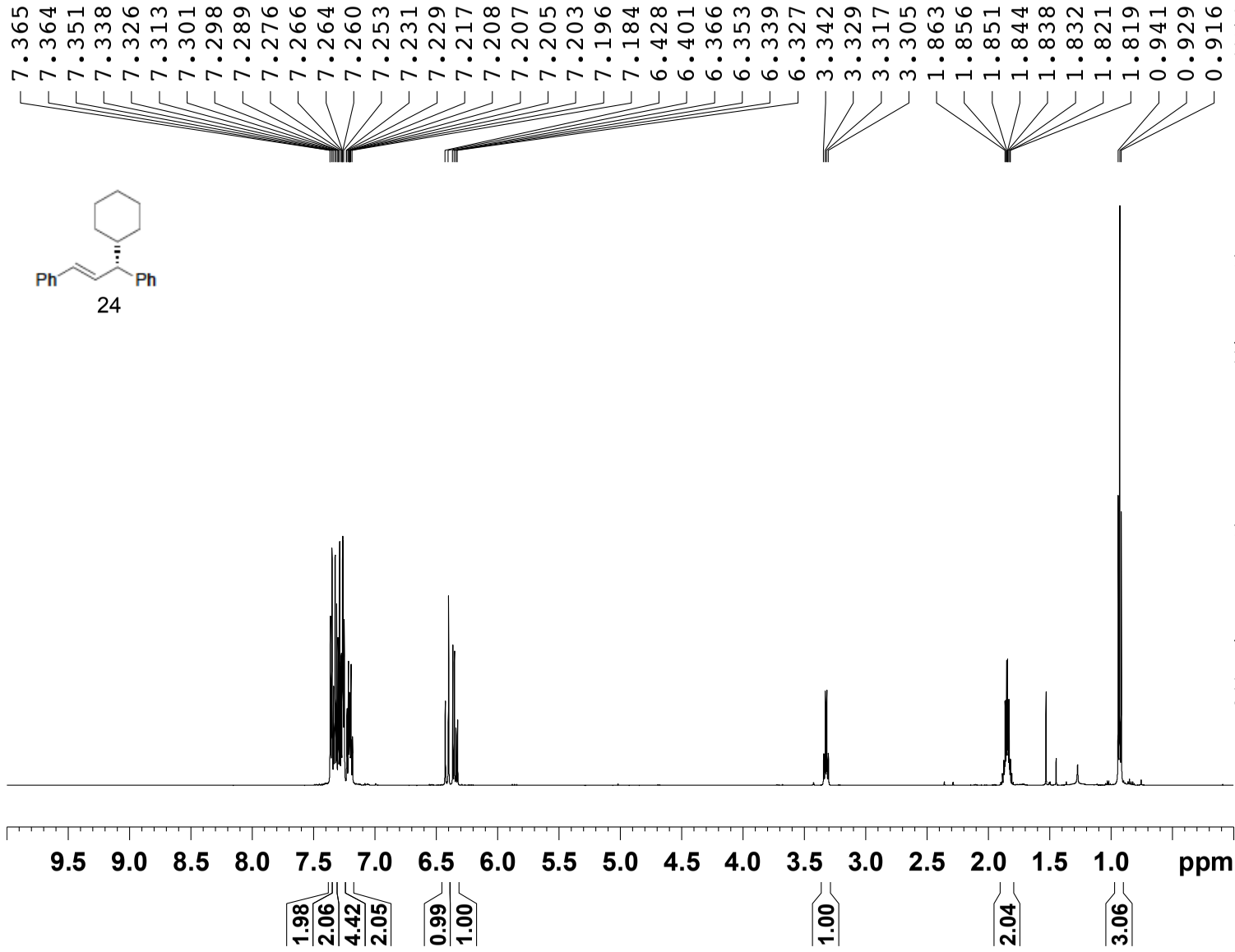
Current Data Parameters
NAME QZ-4-038
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130628
Time 16.10
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg55
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 34722.223 Hz
FIDRES 0.529819 Hz
AQ 0.9437684 sec
RG 2050
DW 14.400 usec
DE 19.34 usec
TE 298.0 K
D1 1.10000002 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 150.9656784 MHz
NUC1 13C
P1 10.63 usec

F2 - Processing parameters
SI 32768
SF 150.9505603 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

compound 3.62 1H NMR



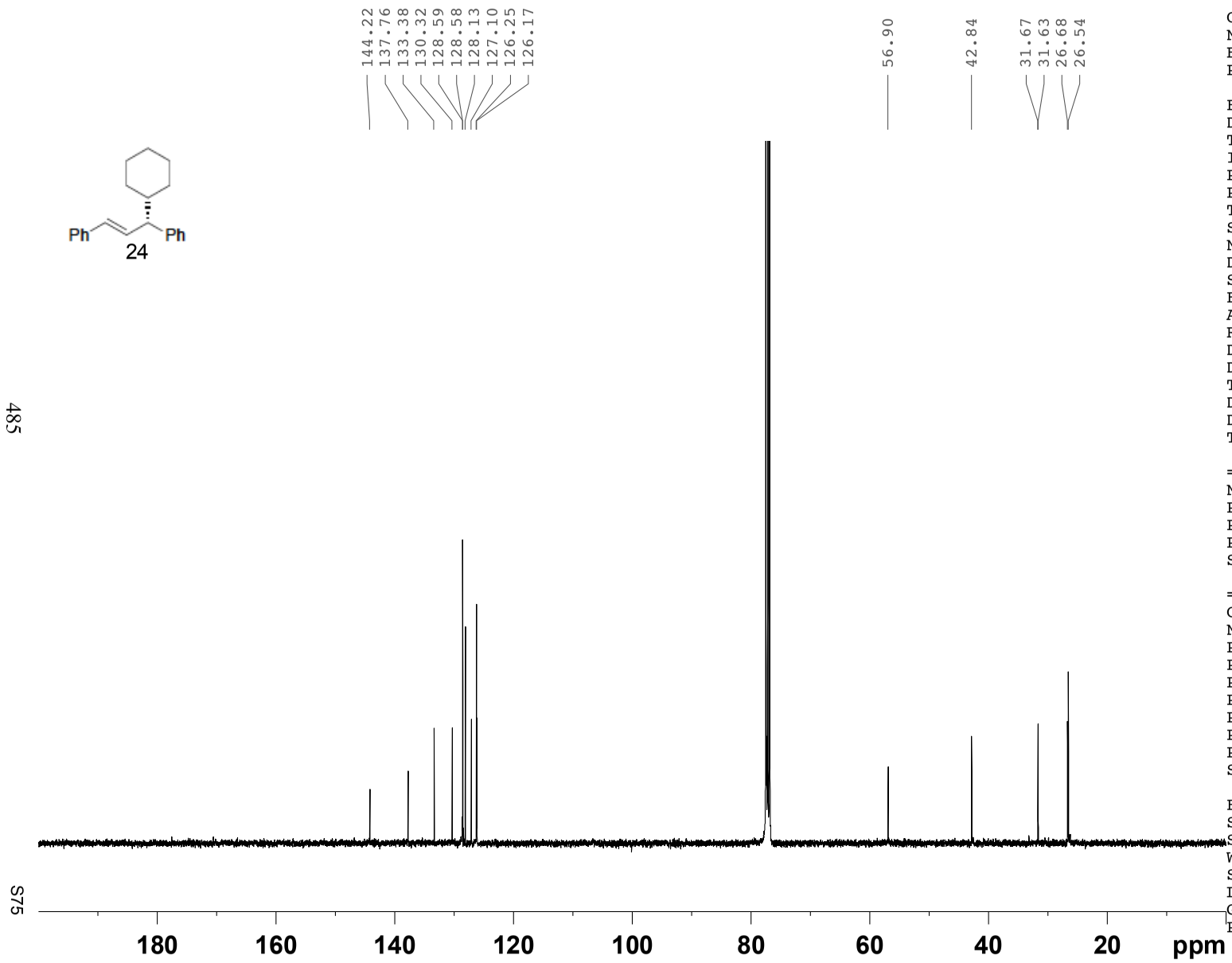

```
Current Data Parameters
NAME          QZ-4-022-2
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130617
Time               10.04
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8403.361 Hz
FIDRES          0.128225 Hz
AQ              3.8994420 sec
RG                   114
DW                59.500 usec
DE                17.39 usec
TE                298.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.3233018 MHz
NUC1                   1H
P1                 10.77 usec

F2 - Processing parameters
SI                 65536
SF           600.3200161 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

compound 3.62 13C NMR




```
Current Data Parameters
NAME            QZ-4-017
EXPNO                  2
PROCNO                 1

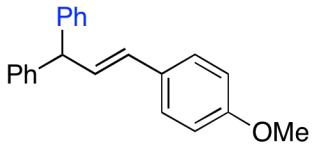
F2 - Acquisition Parameters
Date_           20130628
Time               10.50
INSTRUM            spect
PROBHD   5 mm CPQNP 1H/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ             1.3664756 sec
RG                  512
DW               20.850 usec
DE               18.00 usec
TE               298.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                13C
P1                9.25 usec
PL1               0.55 dB
PL1W        35.18820572 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2            90.00 usec
PL2               4.90 dB
PL12             20.46 dB
PL13             21.00 dB
PL2W         3.30822015 W
PL12W        0.09195905 W
PL13W        0.08120718 W
SFO2        400.1316005 MHz

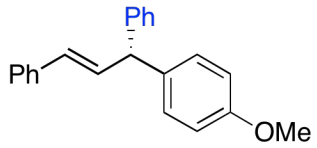
F2 - Processing parameters
SI                 32768
SF          100.6127549 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                 1.40
```

3.65 and enantioenriched **3.66**



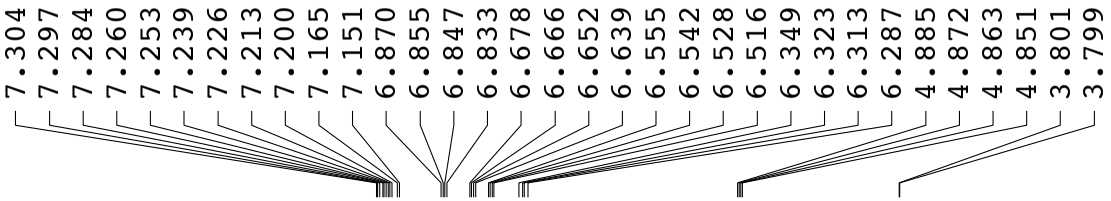
3.65

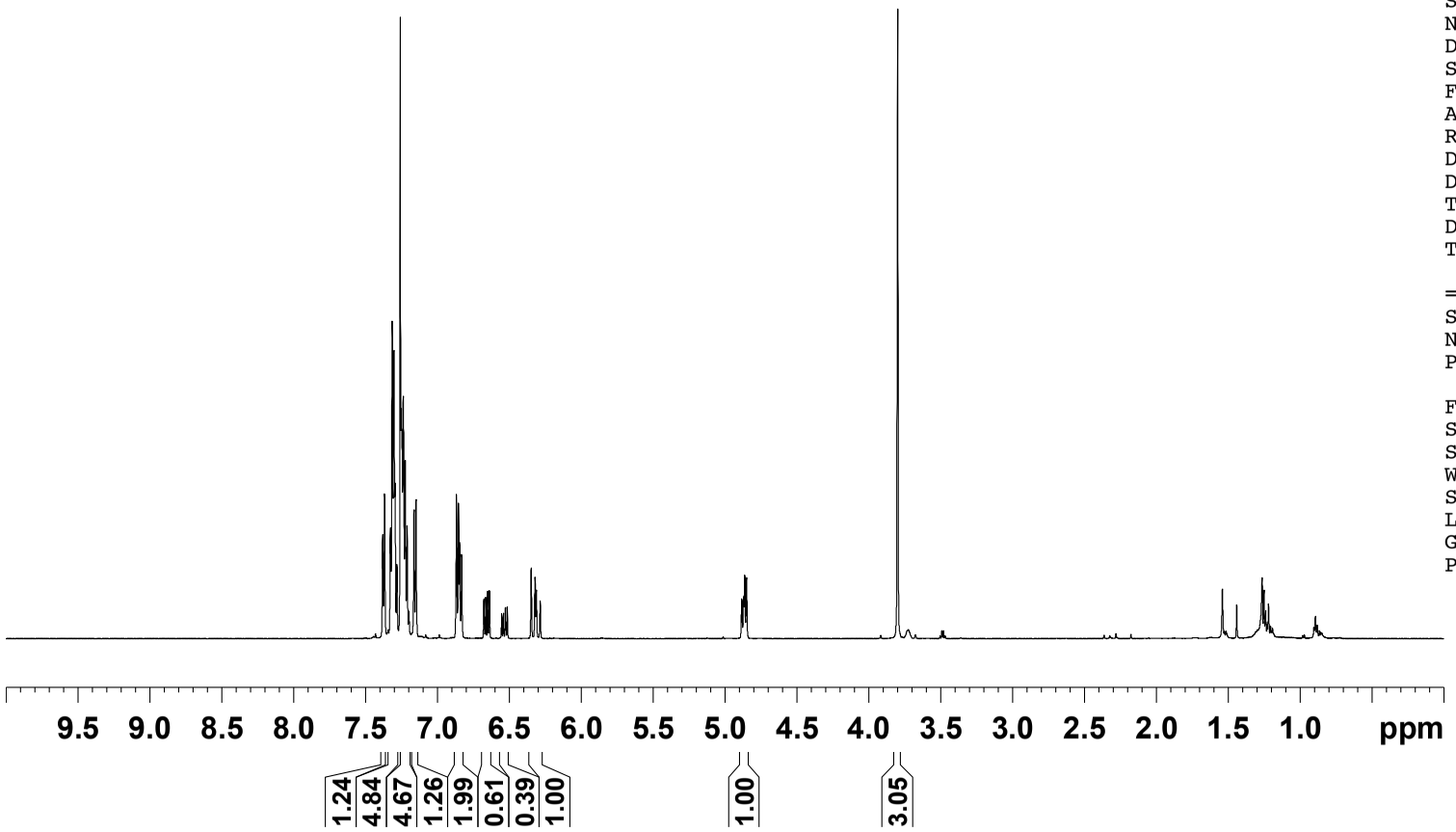
+



3.66

1: 1.5





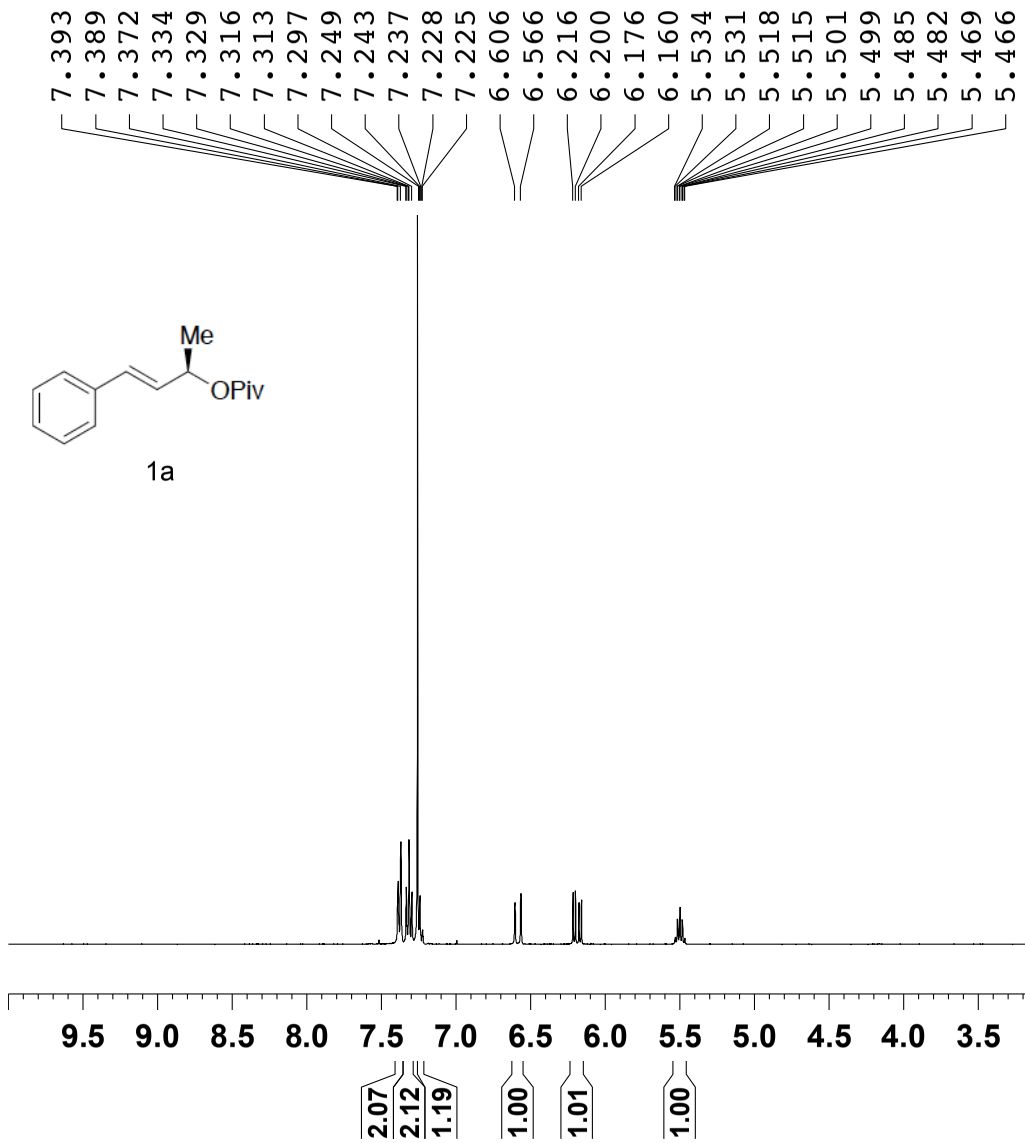

```
Current Data Parameters
NAME          QZ-5-123-2
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140214
Time               13.20
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8403.361 Hz
FIDRES          0.128225 Hz
AQ              3.8994420 sec
RG                   144
DW                59.500 usec
DE                17.39 usec
TE                298.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.3233018 MHz
NUC1                   1H
P1                 10.77 usec

F2 - Processing parameters
SI                 65536
SF           600.3200141 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                1.00
```

compound 3.37 1H NMR




```
Current Data Parameters
NAME                  HH-4-248
EXPNO                        3
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20130522
Time                      7.55
INSTRUM                  spect
PROBHD    5 mm CPQNP 1H/
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                  8278.146 Hz
FIDRES               0.126314 Hz
AQ                   3.9584243 sec
RG                          9
DW                     60.400 usec
DE                      6.00 usec
TE                      298.1 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      15.00 usec
PL1                      4.90 dB
PL1W               3.30822015 W
SFO1             400.1324710 MHz

F2 - Processing parameters
SI                      32768
SF               400.1300098 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00
```

compound 3.37 13C NMR


```
Current Data Parameters
NAME            HH-4-248
EXPNO                  2
PROCNO                 1

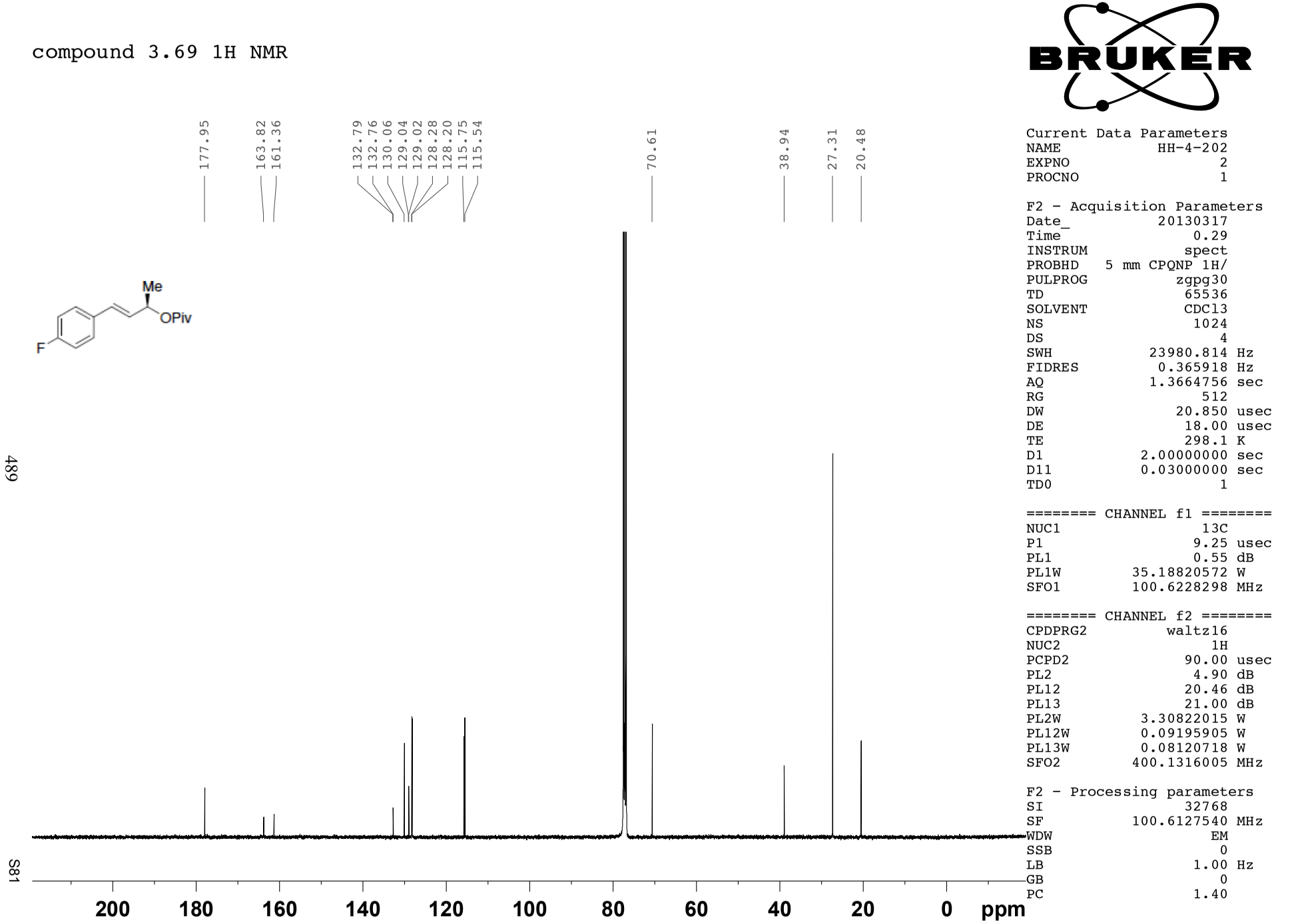
F2 - Acquisition Parameters
Date_           20130426
Time                0.18
INSTRUM            spect
PROBHD   5 mm CPQNP 1H/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ             1.3664756 sec
RG                   512
DW                20.850 usec
DE                18.00 usec
TE                298.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.25 usec
PL1                 0.55 dB
PL1W        35.18820572 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL2                 4.90 dB
PL12               20.46 dB
PL13               21.00 dB
PL2W         3.30822015 W
PL12W        0.09195905 W
PL13W        0.08120718 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127538 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

compound 3.69 1H NMR




```
Current Data Parameters
NAME            HH-4-202
EXPNO                  2
PROCNO                 1

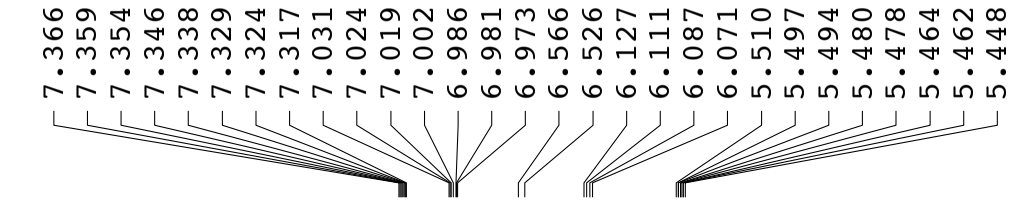
F2 - Acquisition Parameters
Date_           20130317
Time                0.29
INSTRUM            spect
PROBHD   5 mm CPQNP 1H/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ             1.3664756 sec
RG                   512
DW                20.850 usec
DE                18.00 usec
TE                298.1 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

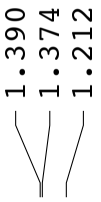
======== CHANNEL f1 ========
NUC1                 13C
P1                  9.25 usec
PL1                 0.55 dB
PL1W        35.18820572 W
SFO1        100.6228298 MHz

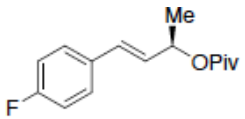
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL2                 4.90 dB
PL12               20.46 dB
PL13               21.00 dB
PL2W         3.30822015 W
PL12W        0.09195905 W
PL13W        0.08120718 W
SFO2        400.1316005 MHz

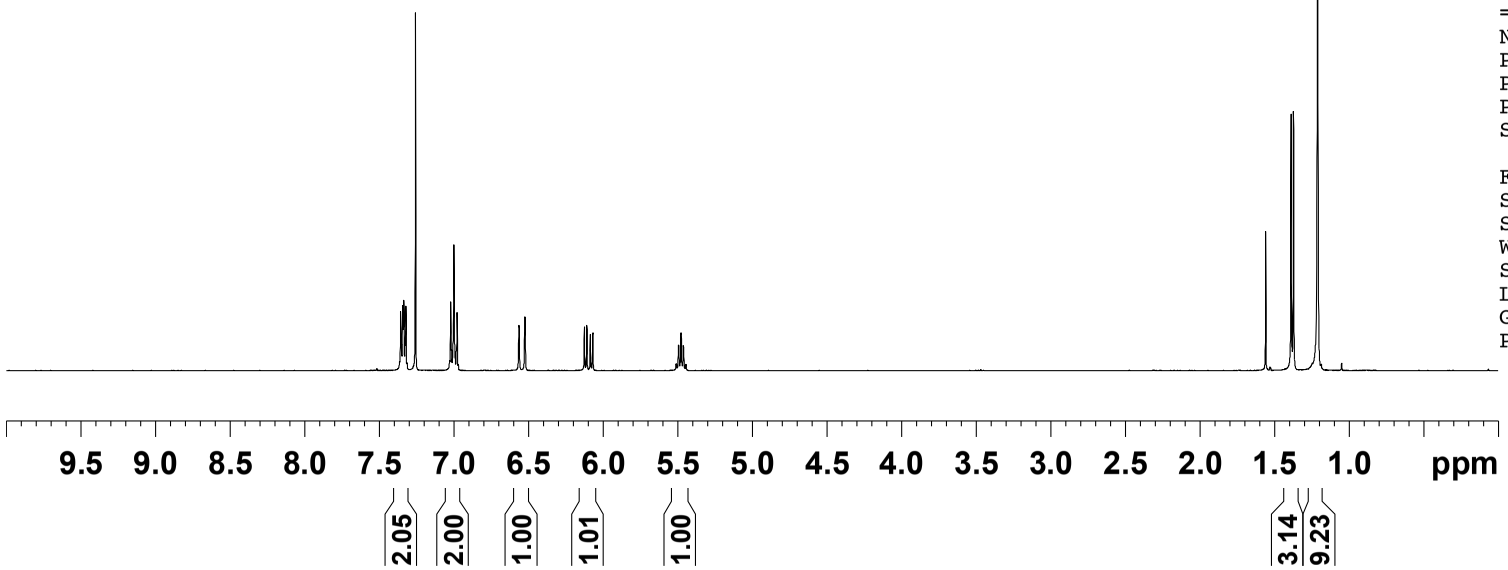
F2 - Processing parameters
SI                 32768
SF          100.6127540 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

compound 3.69 1H NMR









Current Data Parameters

NAME	HH-4-202
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20130316
Time	17.41
INSTRUM	spect
PROBHD	5 mm CPQNP 1H/
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	7.1
DW	60.400 usec
DE	6.00 usec
TE	298.2 K
D1	1.00000000 sec
TD0	1

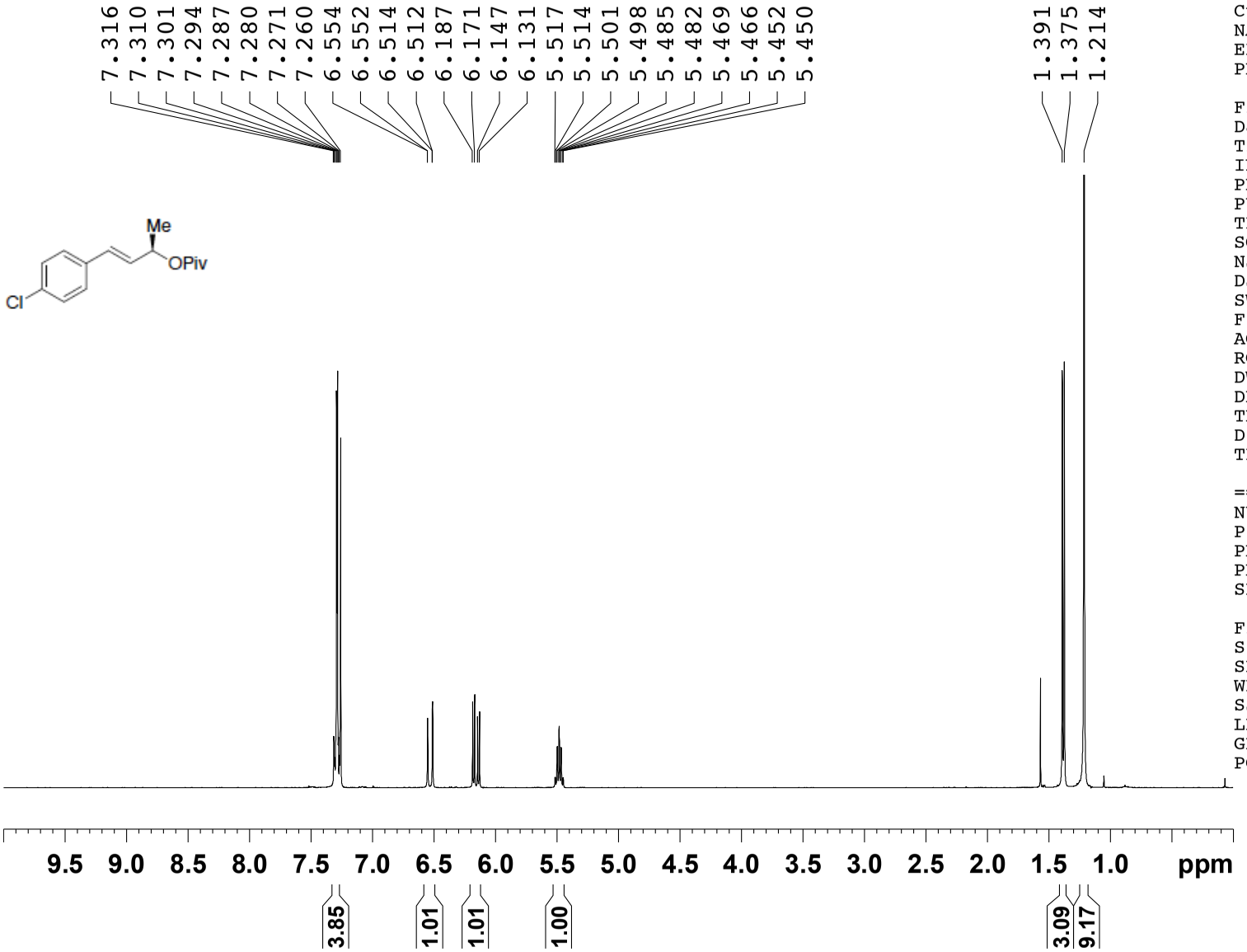
======== CHANNEL f1 ========

NUC1	1H
P1	15.00 usec
PL1	4.90 dB
PL1W	3.30822015 W
SFO1	400.1324710 MHz

F2 - Processing parameters

SI	32768
SF	400.1300099 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

compound 3.70 1H NMR



Current Data Parameters

NAME	HH-4-254
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20130522
Time	8.01
INSTRUM	spect
PROBHD	5 mm CPQNP 1H/
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	8
DW	60.400 usec
DE	6.00 usec
TE	298.1 K
D1	1.00000000 sec
TD0	1

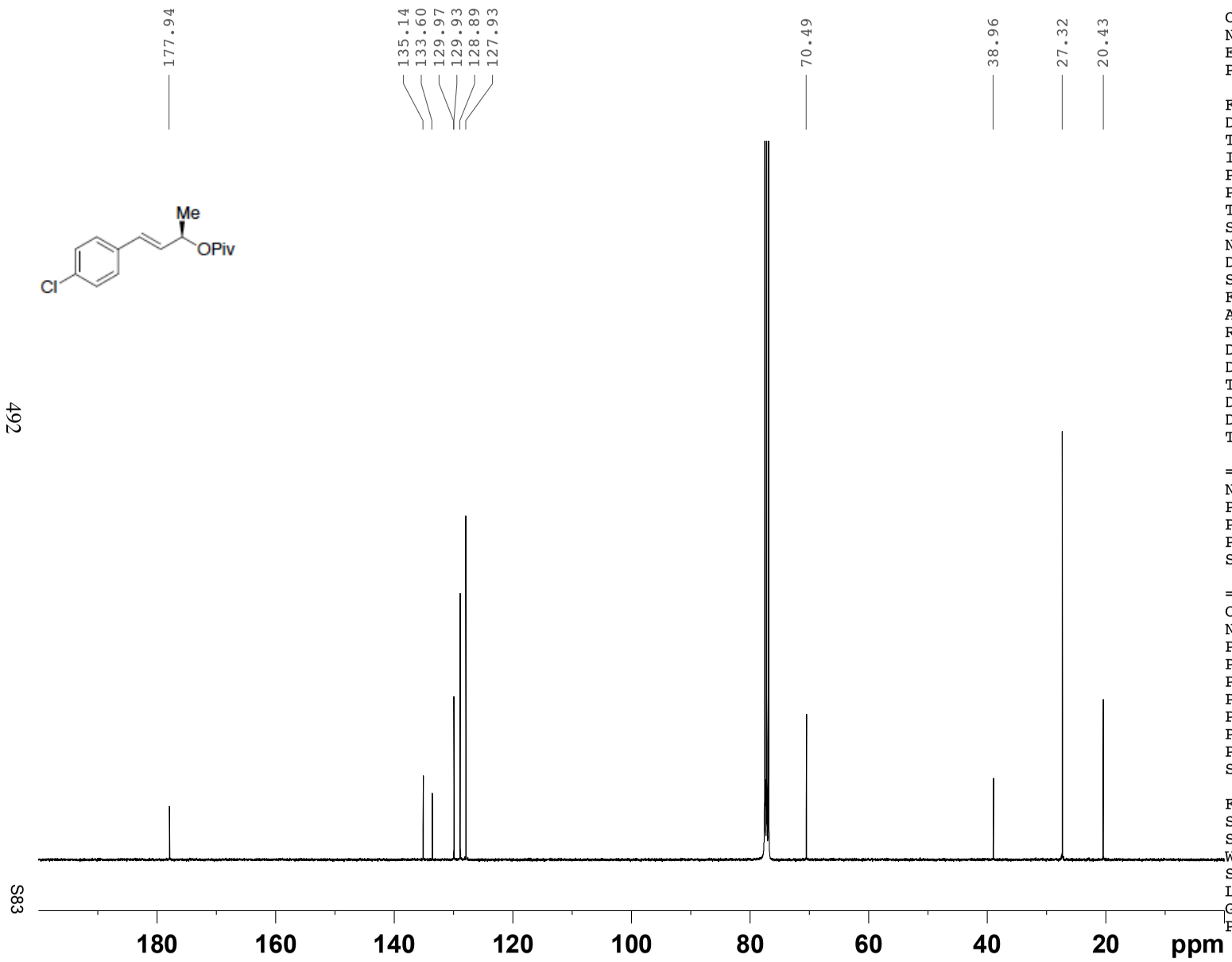
======== CHANNEL f1 ========

NUC1	1H
P1	15.00 usec
PL1	4.90 dB
PL1W	3.30822015 W
SFO1	400.1324710 MHz

F2 - Processing parameters

SI	32768
SF	400.1300094 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

compound 3.70 13C NMR




```
Current Data Parameters
NAME                  HH-4-254
EXPNO                        2
PROCNO                       1

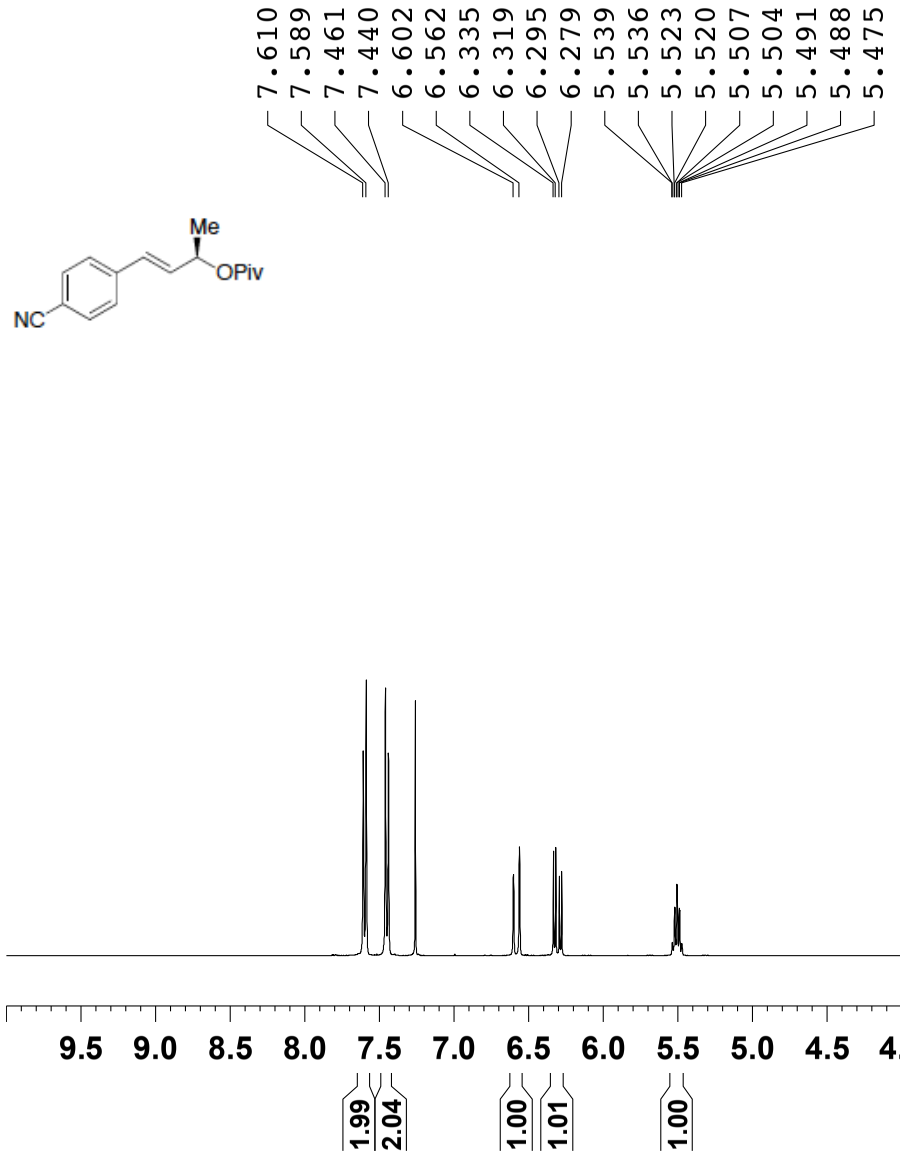
F2 - Acquisition Parameters
Date_                 20130522
Time                     22.06
INSTRUM                  spect
PROBHD    5 mm CPQNP 1H/
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                        1024
DS                           4
SWH                  23980.814 Hz
FIDRES                0.365918 Hz
AQ                    1.3664756 sec
RG                         512
DW                      20.850 usec
DE                      18.00 usec
TE                      298.1 K
D1                   2.00000000 sec
D11                  0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                        13C
P1                        9.25 usec
PL1                       0.55 dB
PL1W               35.18820572 W
SFO1              100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                        1H
PCPD2                    90.00 usec
PL2                       4.90 dB
PL12                     20.46 dB
PL13                     21.00 dB
PL2W                3.30822015 W
PL12W               0.09195905 W
PL13W               0.08120718 W
SFO2              400.1316005 MHz

F2 - Processing parameters
SI                         32768
SF                100.6127529 MHz
WDW                           EM
SSB                            0
LB                        1.00 Hz
GB                             0
PC                        1.40
```

compound 3.71 1H NMR



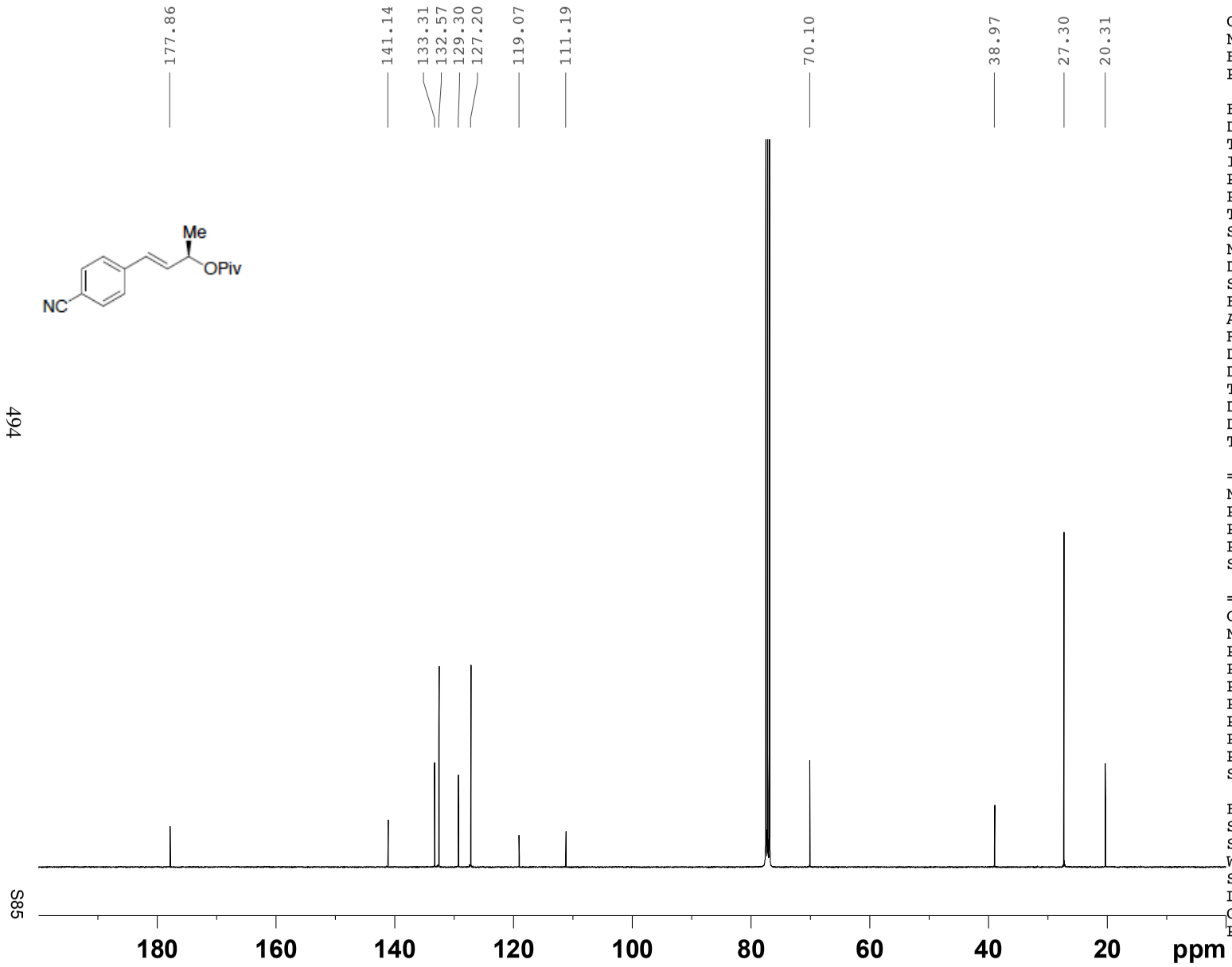
Current Data Parameters
NAME HH-4-227
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130522
Time 5.43
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 9
DW 60.400 usec
DE 6.00 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 4.90 dB
PL1W 3.30822015 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300094 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

compound 3.71 13C NMR




```
Current Data Parameters
NAME            HH-4-227
EXPNO                  2
PROCNO                 1

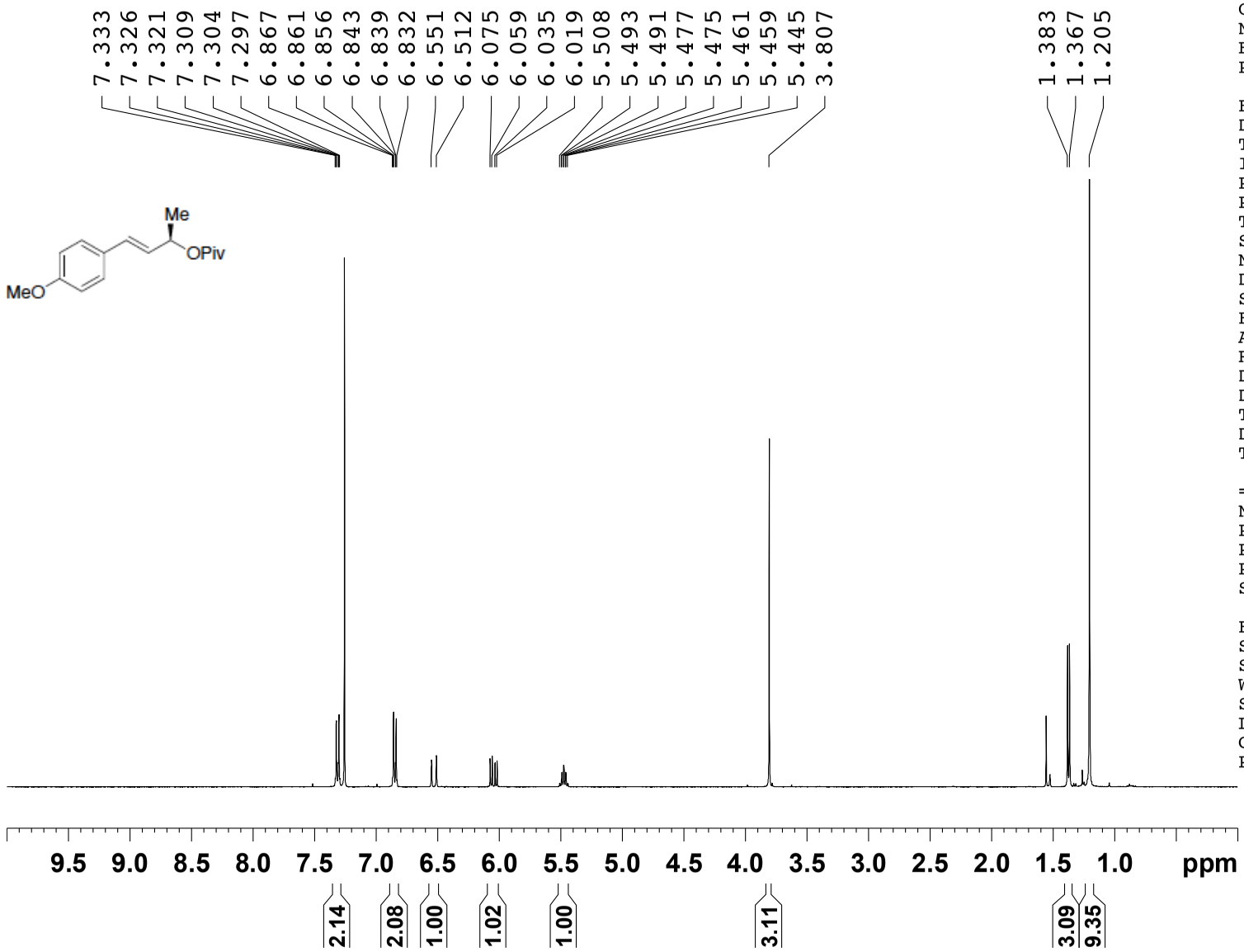
F2 - Acquisition Parameters
Date_           20130522
Time                6.43
INSTRUM            spect
PROBHD   5 mm CPQNP 1H/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ             1.3664756 sec
RG                   512
DW                20.850 usec
DE                18.00 usec
TE                298.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.25 usec
PL1                 0.55 dB
PL1W        35.18820572 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL2                 4.90 dB
PL12               20.46 dB
PL13               21.00 dB
PL2W         3.30822015 W
PL12W        0.09195905 W
PL13W        0.08120718 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127541 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

compound 3.72 1H NMR



Current Data Parameters

NAME	HH-4-148
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20130201
Time	2.32
INSTRUM	spect
PROBHD	5 mm CPQNP 1H/
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	11.3
DW	60.400 usec
DE	6.00 usec
TE	298.1 K
D1	1.00000000 sec
TD0	1

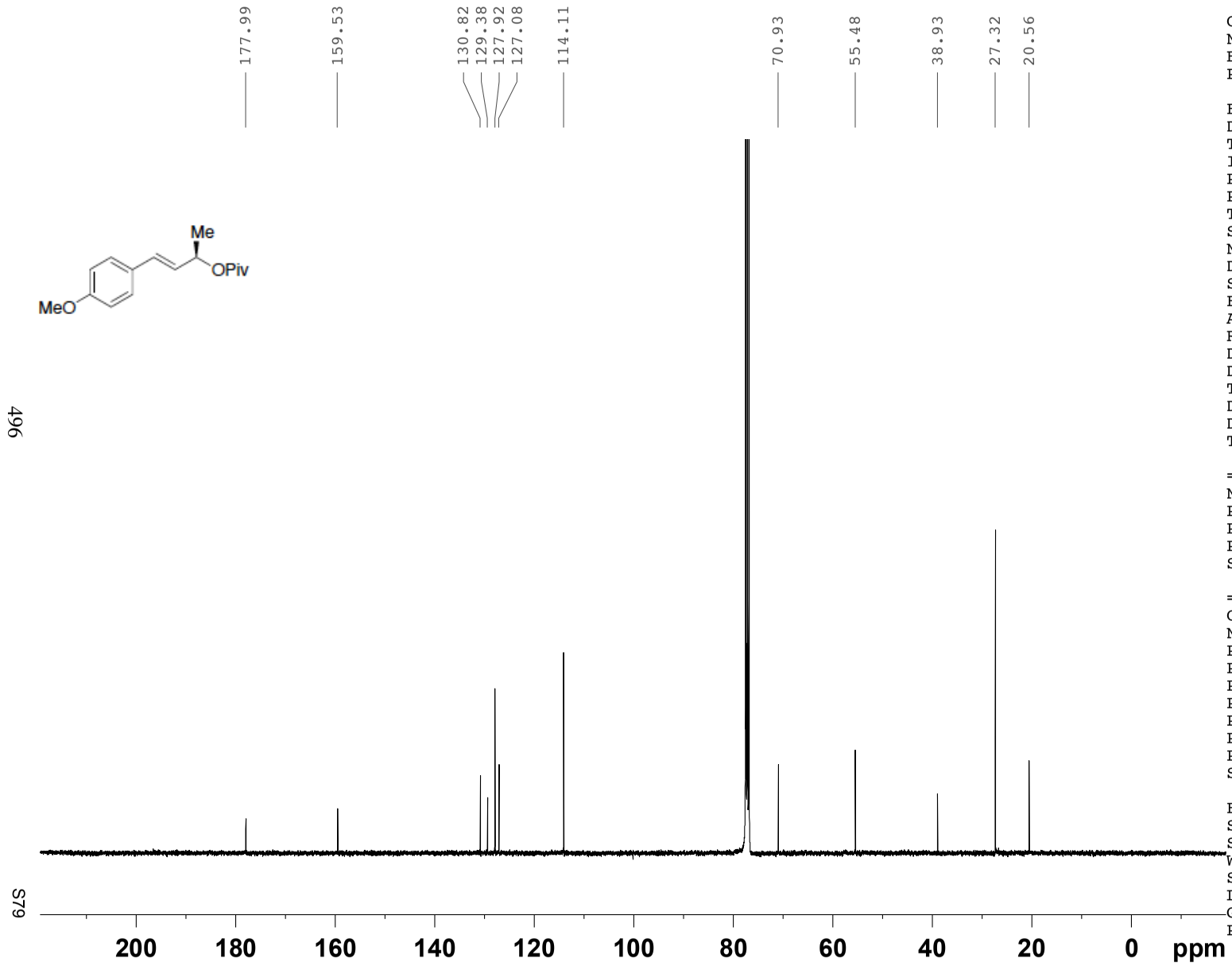
======== CHANNEL f1 ========

NUC1	1H
P1	15.00 usec
PL1	4.90 dB
PL1W	3.30822015 W
SFO1	400.1324710 MHz

F2 - Processing parameters

SI	32768
SF	400.1300107 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

compound 3.72 13C NMR




```
Current Data Parameters
NAME            HH-4-148
EXPNO                  2
PROCNO                 1

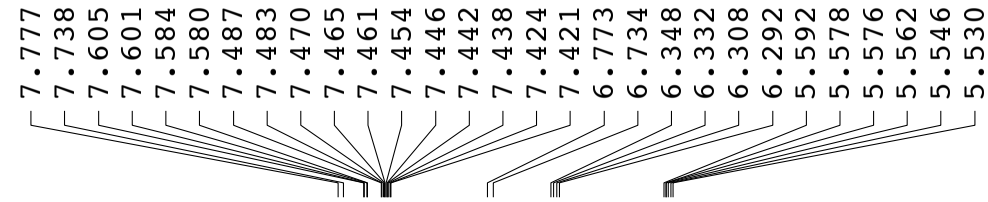
F2 - Acquisition Parameters
Date_           20130201
Time                3.32
INSTRUM            spect
PROBHD   5 mm CPQNP 1H/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG                   512
DW                20.850 usec
DE                18.00 usec
TE                298.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

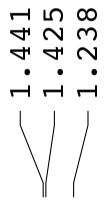
======== CHANNEL f1 ========
NUC1                 13C
P1                 9.25 usec
PL1                0.55 dB
PL1W        35.18820572 W
SFO1       100.6228298 MHz

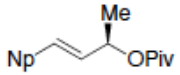
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             90.00 usec
PL2                4.90 dB
PL12               20.46 dB
PL13               21.00 dB
PL2W         3.30822015 W
PL12W        0.09195905 W
PL13W        0.08120718 W
SFO2       400.1316005 MHz

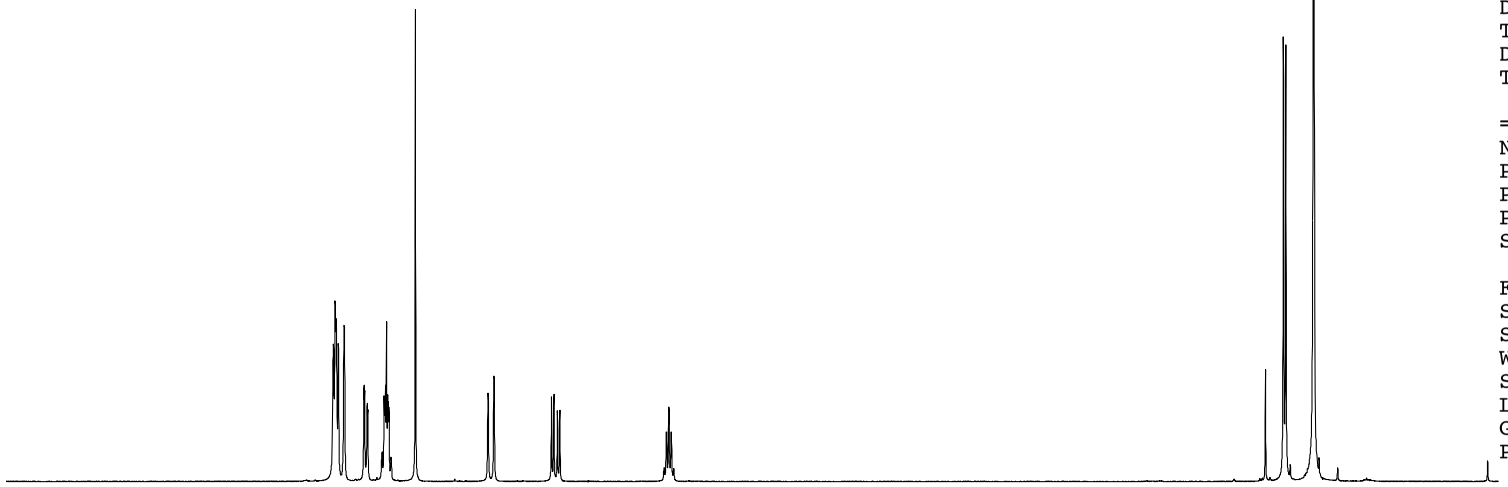
F2 - Processing parameters
SI                 32768
SF         100.6127536 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                 1.40
```

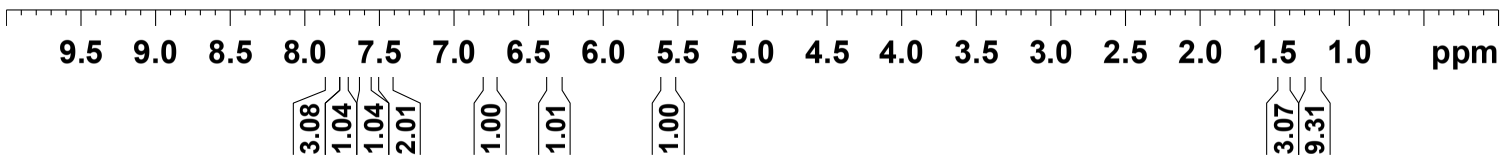
compound 3.73 1H NMR











Current Data Parameters
NAME HH-4-203rs
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130522
Time 4.37
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 8
DW 60.400 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1

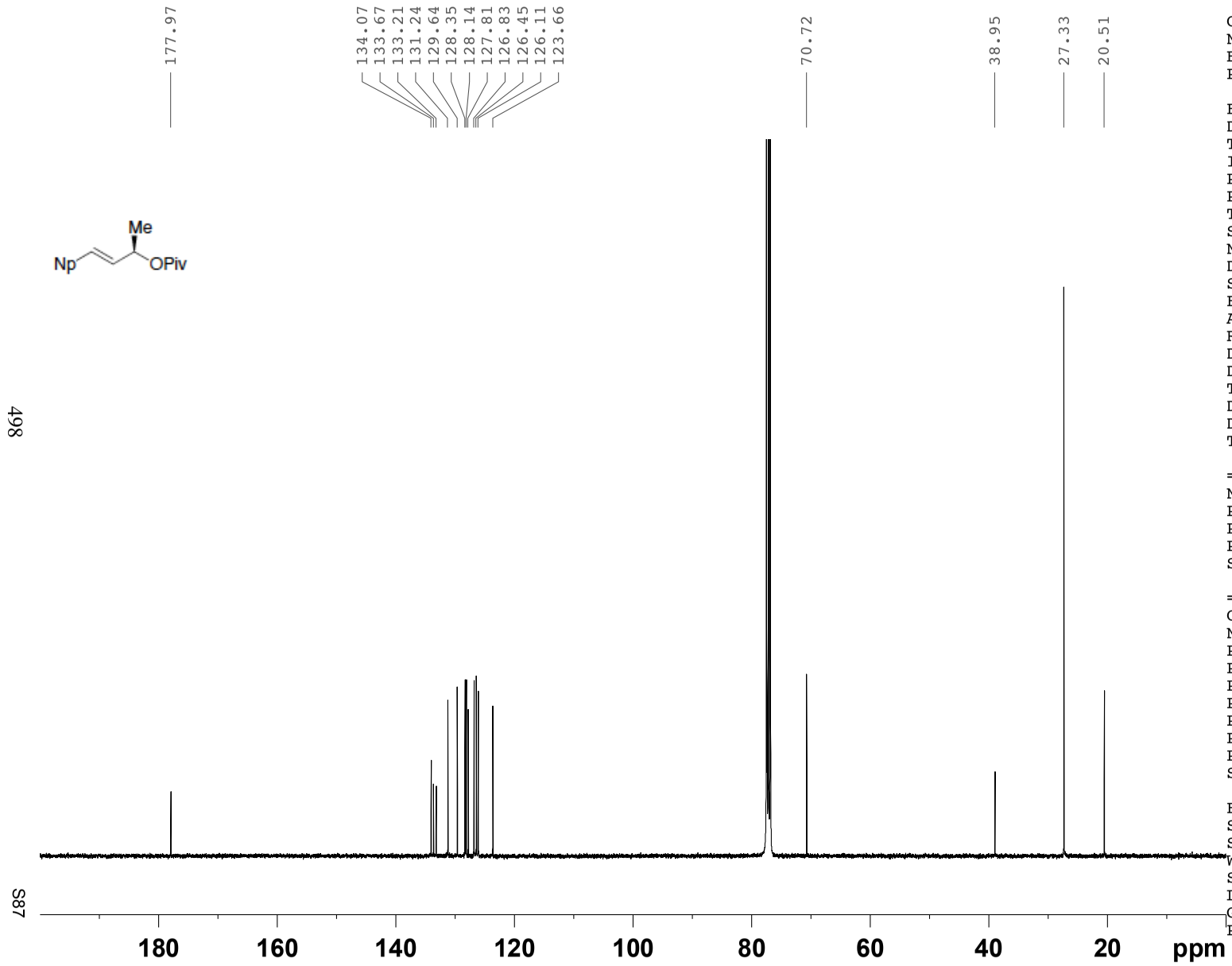
======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 4.90 dB
PL1W 3.30822015 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

497

S86

compound 3.73 13C NMR




```
Current Data Parameters
NAME          HH-4-203rs
EXPNO                  2
PROCNO                 1

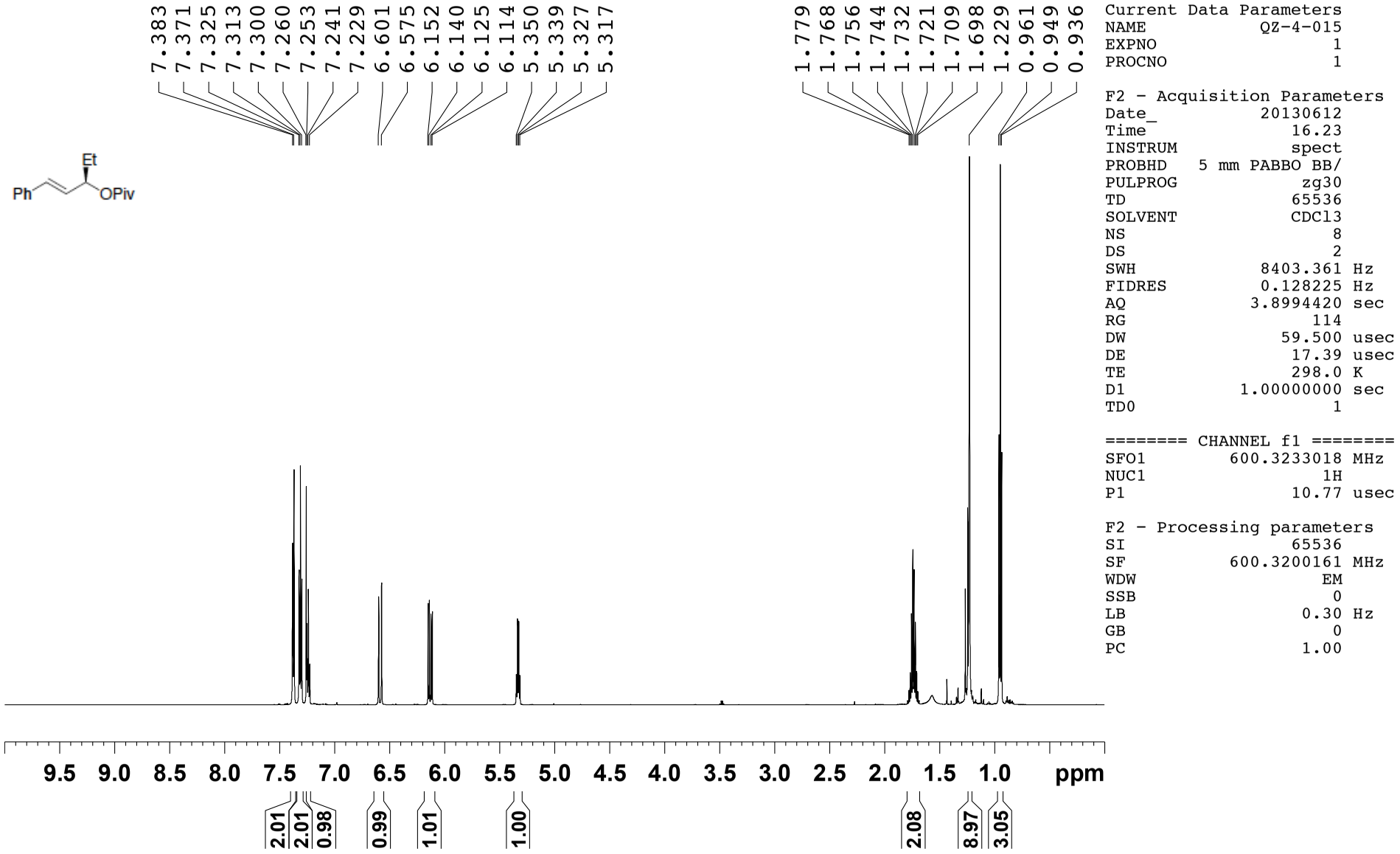
F2 - Acquisition Parameters
Date_           20130522
Time               5.37
INSTRUM           spect
PROBHD   5 mm CPQNP 1H/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ            1.3664756 sec
RG                  512
DW               20.850 usec
DE               18.00 usec
TE               298.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                 9.25 usec
PL1                0.55 dB
PL1W       35.18820572 W
SFO1       100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             90.00 usec
PL2                4.90 dB
PL12              20.46 dB
PL13              21.00 dB
PL2W        3.30822015 W
PL12W       0.09195905 W
PL13W       0.08120718 W
SFO2       400.1316005 MHz

F2 - Processing parameters
SI                32768
SF         100.6127560 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

compound 3.74 1H NMR



Current Data Parameters
NAME QZ-4-015
EXPNO 1
PROCNO 1

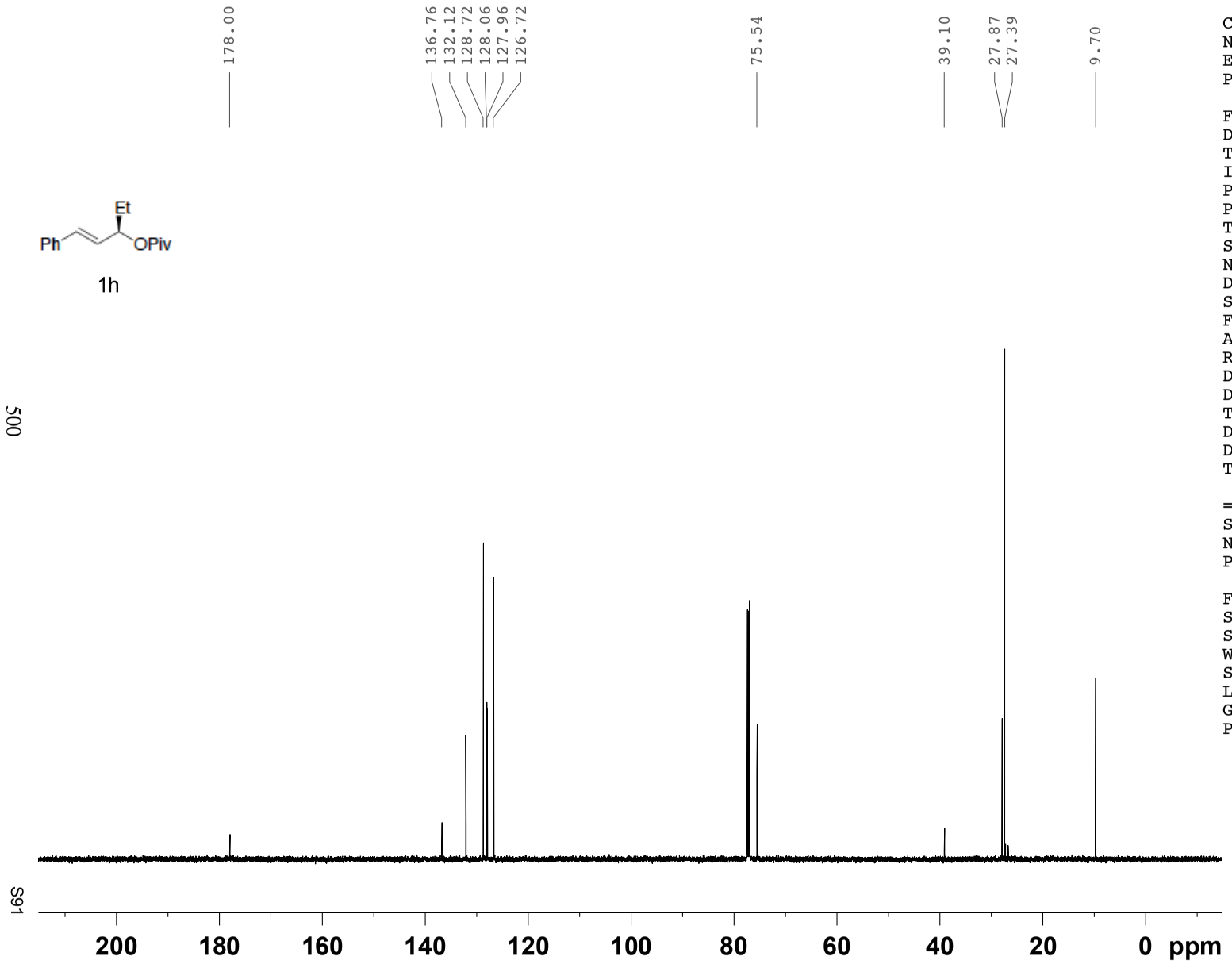
F2 - Acquisition Parameters
Date_ 20130612
Time 16.23
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8403.361 Hz
FIDRES 0.128225 Hz
AQ 3.8994420 sec
RG 114
DW 59.500 usec
DE 17.39 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 600.3233018 MHz
NUC1 1H
P1 10.77 usec

F2 - Processing parameters
SI 65536
SF 600.3200161 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

compound 3.74 13C NMR

1h



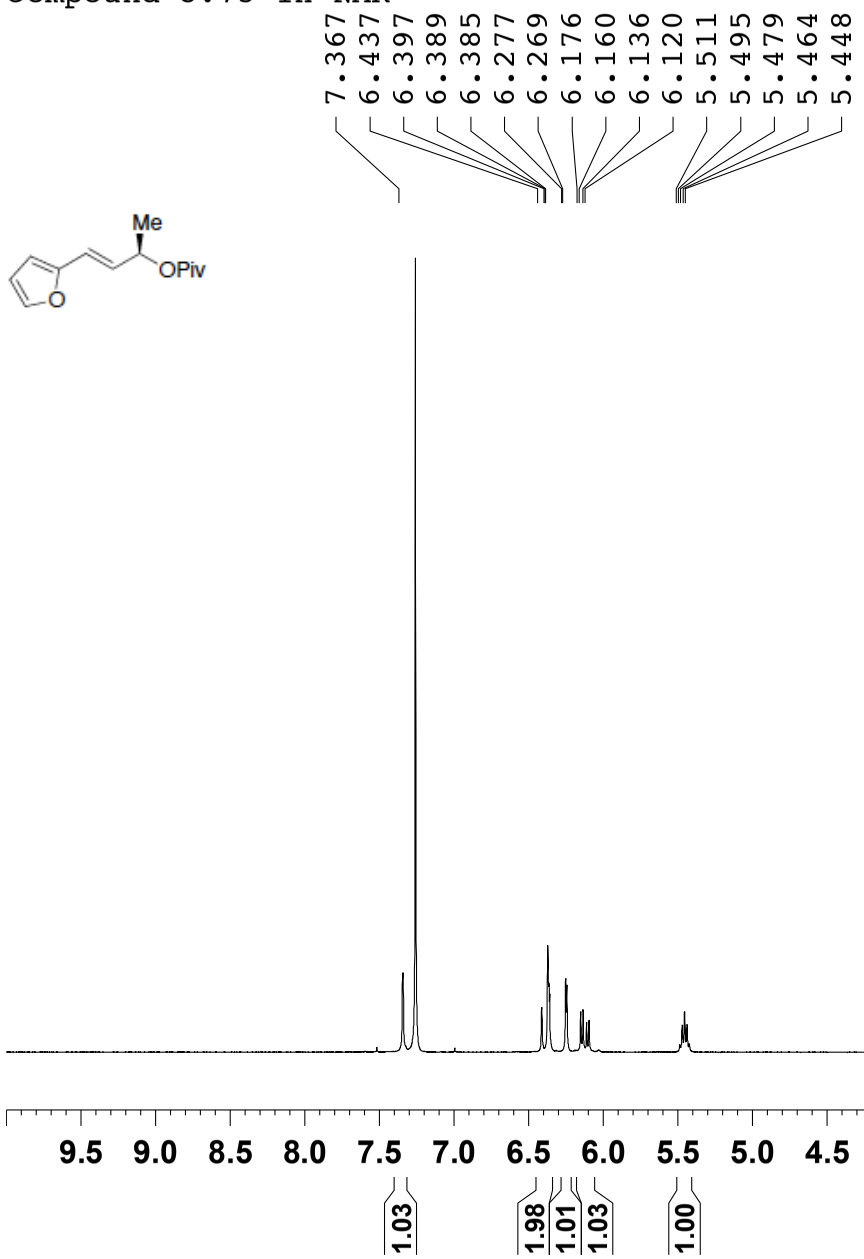

```
Current Data Parameters
NAME            QZ-4-015
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130612
Time               16.33
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg55
TD                 65536
SOLVENT            CDCl3
NS                   256
DS                     4
SWH           34722.223 Hz
FIDRES         0.529819 Hz
AQ            0.9437684 sec
RG                  2050
DW                14.400 usec
DE                19.34 usec
TE                298.0 K
D1           1.10000002 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        150.9656784 MHz
NUC1                  13C
P1                10.63 usec

F2 - Processing parameters
SI                 32768
SF          150.9505582 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

compound 3.75 1H NMR



BRUKER

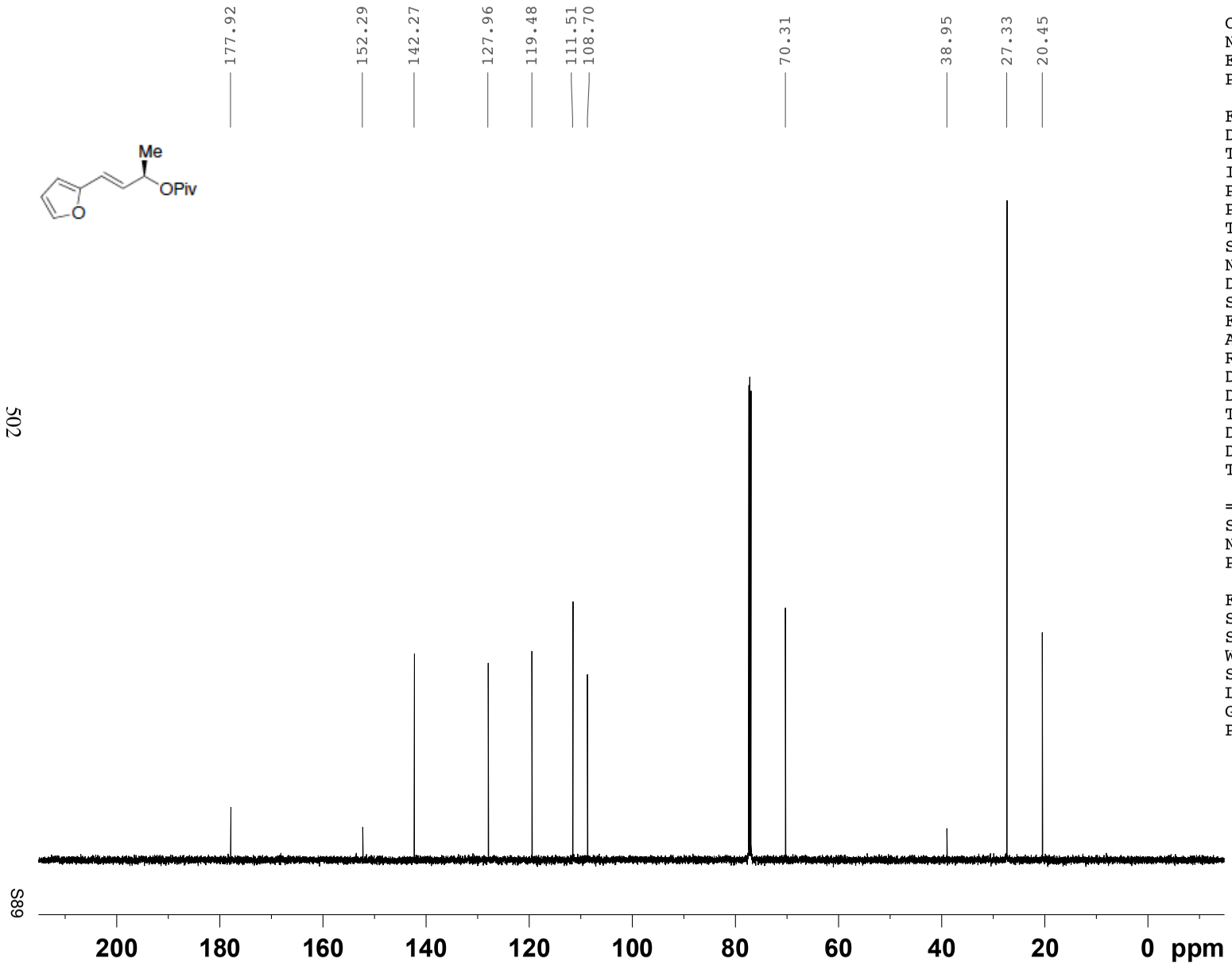
```
Current Data Parameters
NAME      QZ-3-242-1-RAC
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130422
Time              13.33
INSTRUM           spect
PROBHD   5 mm CPQNP 1H/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ             3.9584243 sec
RG                   5.7
DW                60.400 usec
DE                 6.00 usec
TE                298.2 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                15.00 usec
PL1                4.90 dB
PL1W         3.30822015 W
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300095 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

compound 3.75 13C NMR



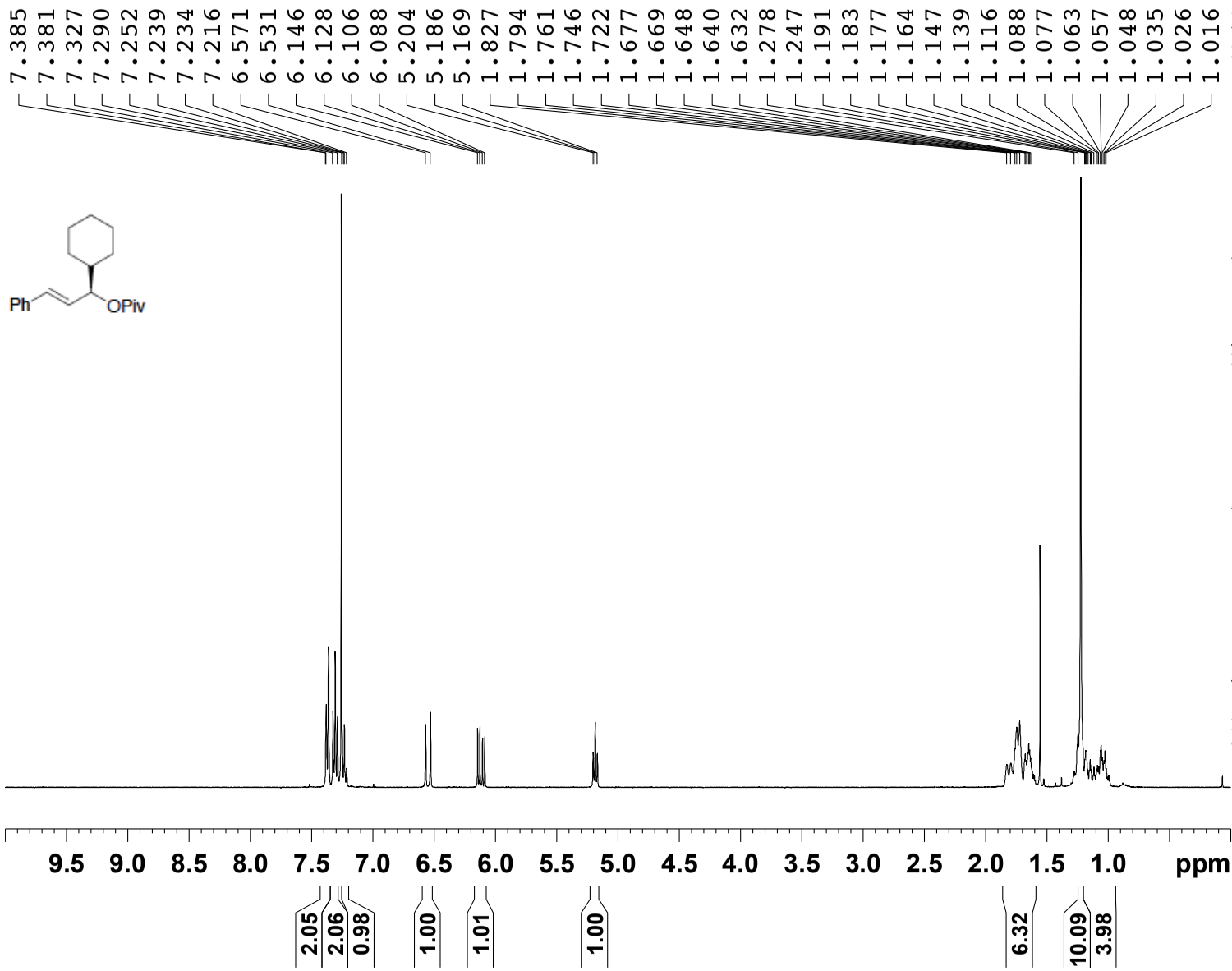
Current Data Parameters
NAME QZ-3-242-1
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130620
Time 15.33
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg55
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 34722.223 Hz
FIDRES 0.529819 Hz
AQ 0.9437684 sec
RG 2050
DW 14.400 usec
DE 19.34 usec
TE 298.0 K
D1 1.10000002 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 150.9656784 MHz
NUC1 13C
P1 10.63 usec

F2 - Processing parameters
SI 32768
SF 150.9505582 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

compound 3.76 1H NMR



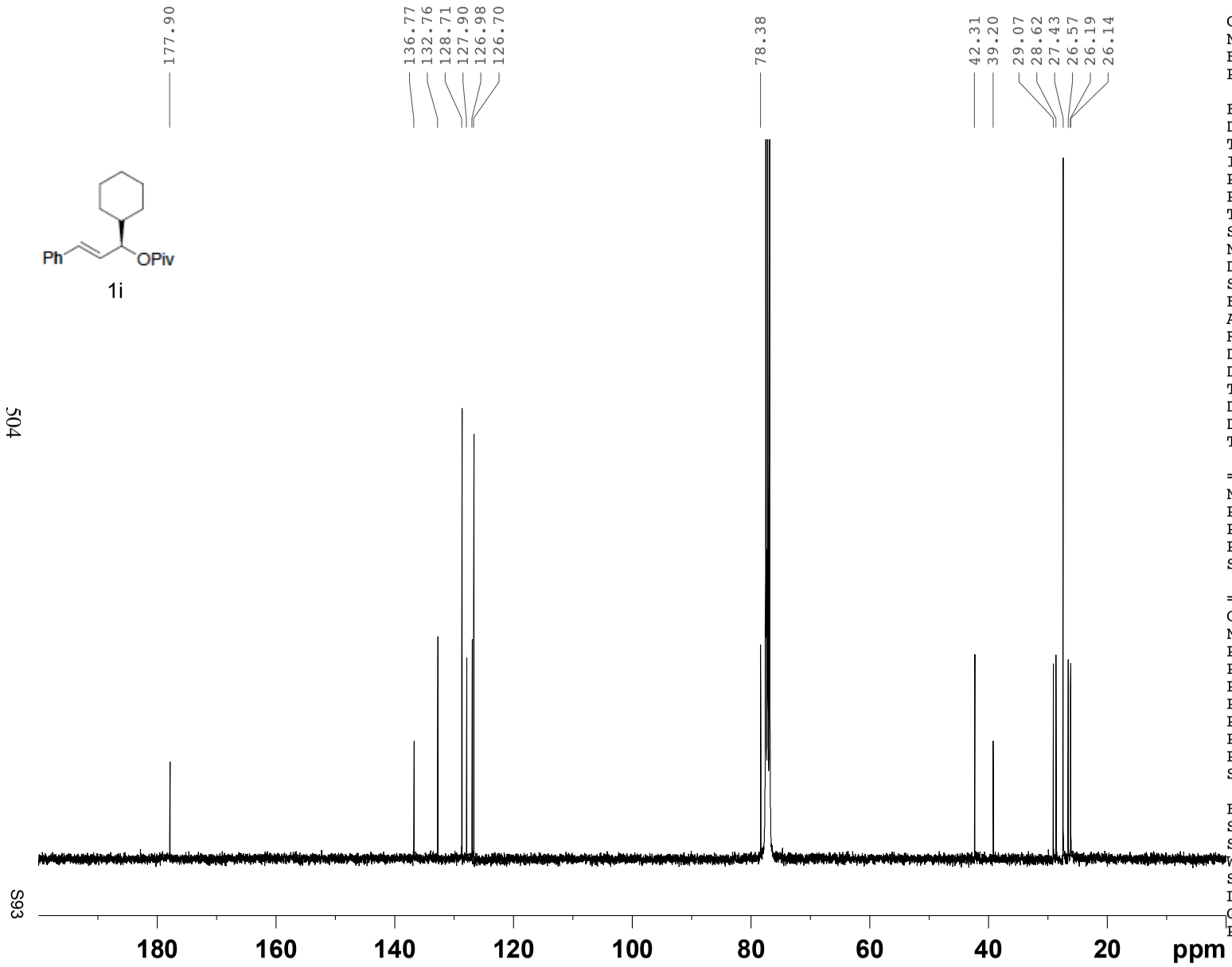

```
Current Data Parameters
NAME                  HH-4-291
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20130610
Time                     17.27
INSTRUM                  spect
PROBHD    5 mm CPQNP 1H/
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                  8278.146 Hz
FIDRES               0.126314 Hz
AQ                   3.9584243 sec
RG                         7.1
DW                    60.400 usec
DE                     6.00 usec
TE                     298.2 K
D1                1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                    15.00 usec
PL1                    4.90 dB
PL1W             3.30822015 W
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                         32768
SF               400.1300099 MHz
WDW                           EM
SSB                            0
LB                      0.30 Hz
GB                             0
PC                          1.00
```

compound 3.76 13C NMR




```
Current Data Parameters
NAME            HH-4-291
EXPNO                  2
PROCNO                 1

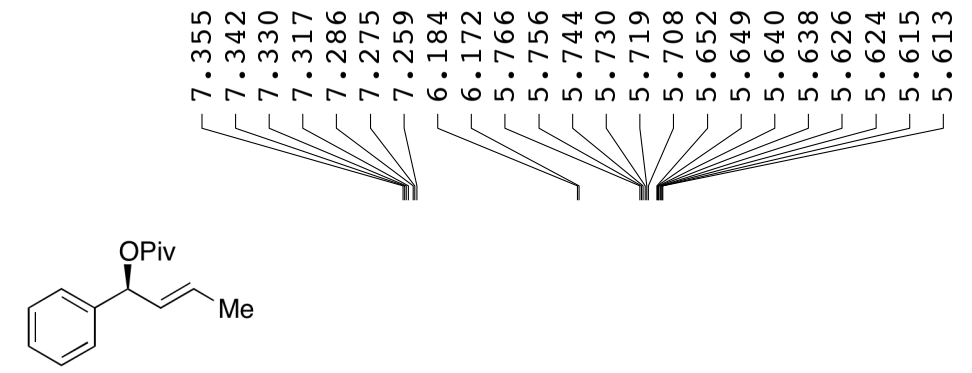
F2 - Acquisition Parameters
Date_           20130611
Time                0.35
INSTRUM            spect
PROBHD   5 mm CPQNP 1H/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ            1.3664756 sec
RG                   512
DW                20.850 usec
DE                18.00 usec
TE                298.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

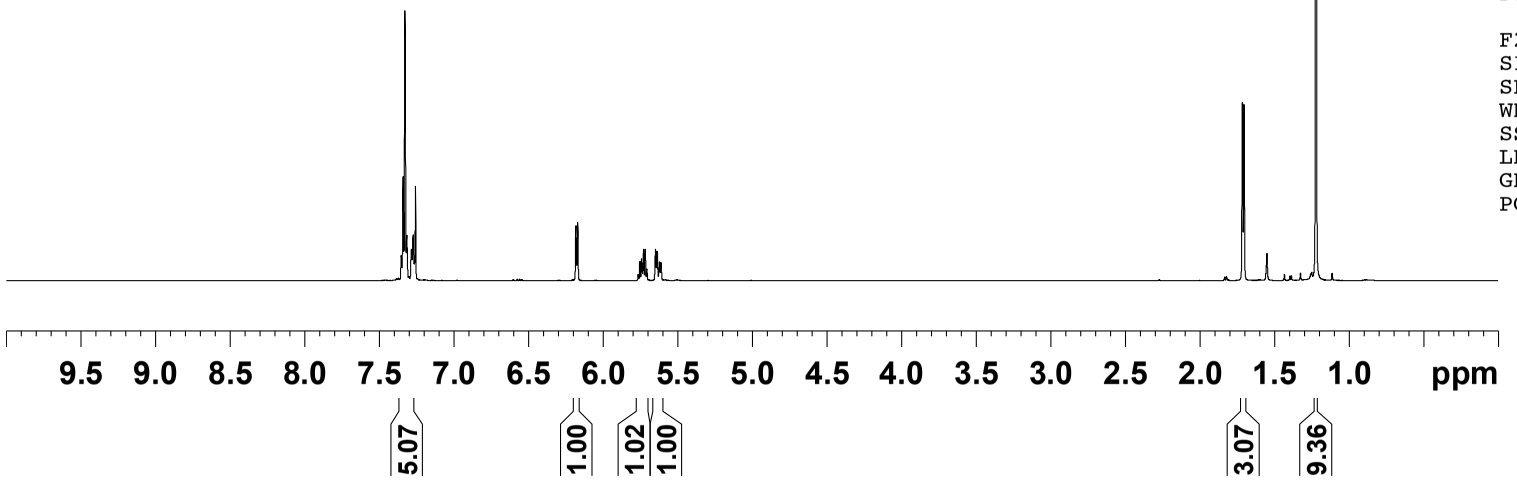
======== CHANNEL f1 ========
NUC1                 13C
P1                  9.25 usec
PL1                 0.55 dB
PL1W        35.18820572 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL2                 4.90 dB
PL12               20.46 dB
PL13               21.00 dB
PL2W         3.30822015 W
PL12W        0.09195905 W
PL13W        0.08120718 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127524 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

compound 3.63 1H NMR





505

S102

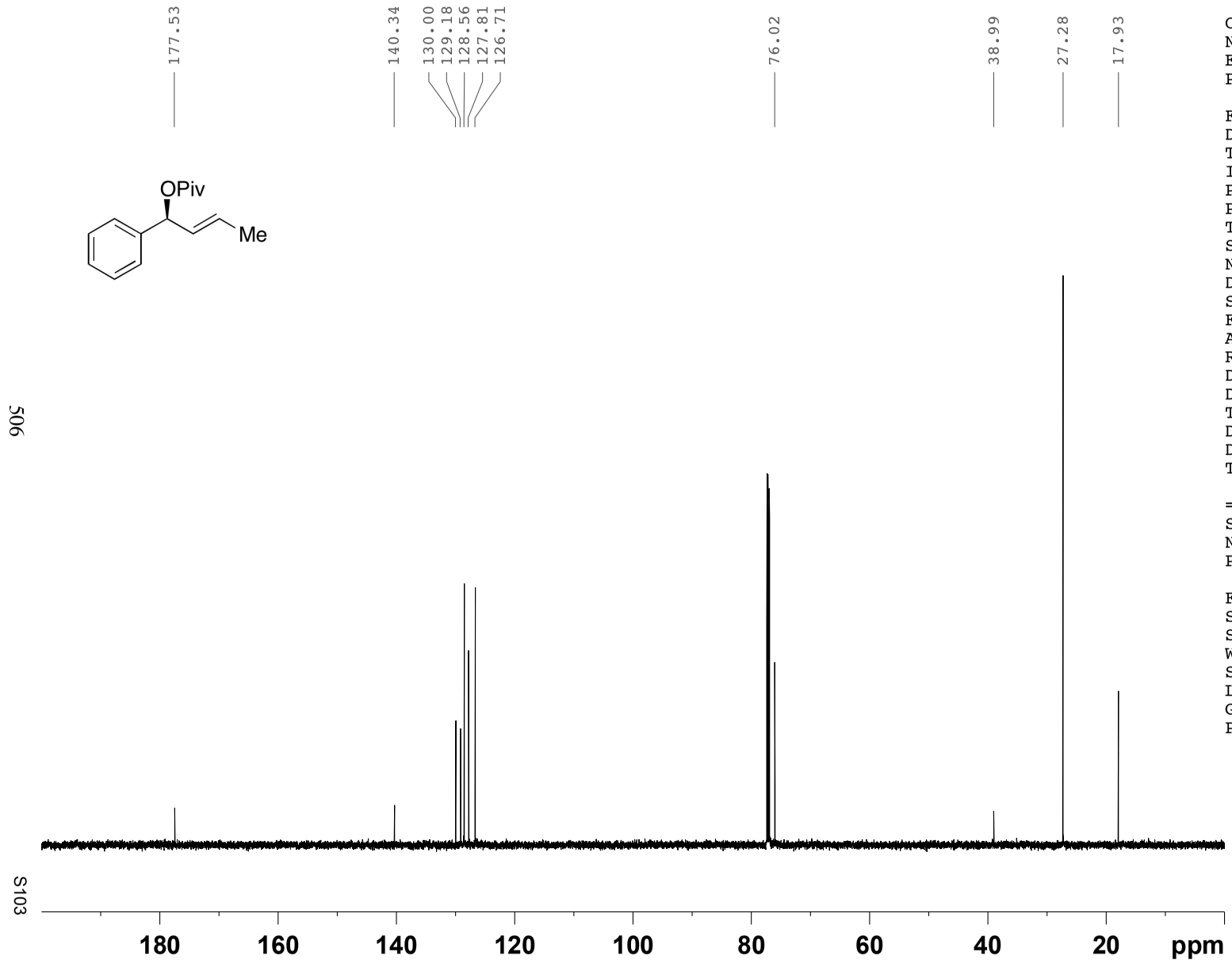
```
Current Data Parameters
NAME      QZ-3-239-1-NEW
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20140108
Time                12.21
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              8403.361 Hz
FIDRES           0.128225 Hz
AQ               3.8994420 sec
RG                    128
DW                 59.500 usec
DE                 17.39 usec
TE                 298.0 K
D1            1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         600.3233018 MHz
NUC1                   1H
P1                 10.77 usec

F2 - Processing parameters
SI                  65536
SF           600.3200150 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                   1.00
```

compound 3.63 13C NMR



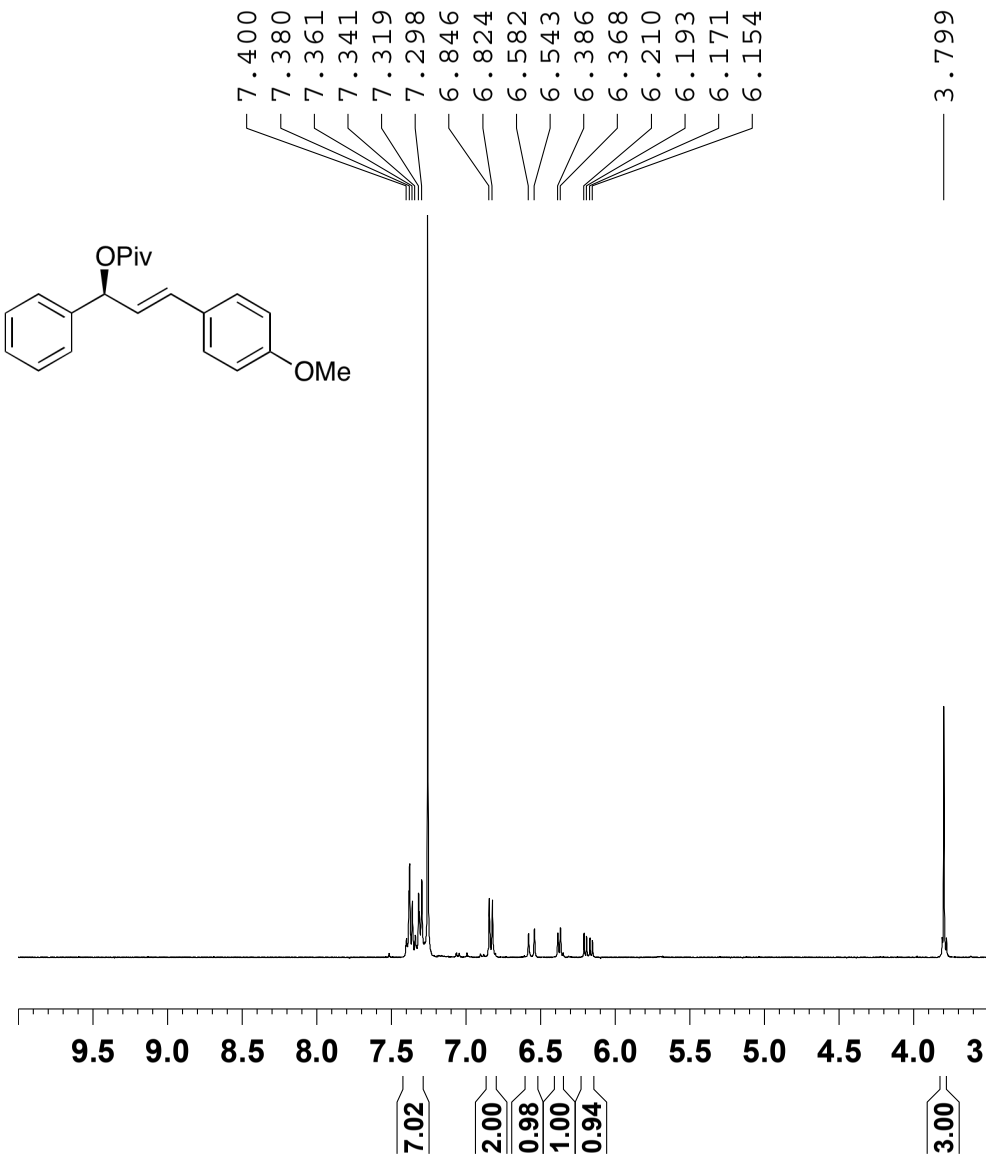
Current Data Parameters
NAME QZ-3-239-1-NEW
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140108
Time 12.32
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg55
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 34722.223 Hz
FIDRES 0.529819 Hz
AQ 0.9437684 sec
RG 2050
DW 14.400 usec
DE 19.34 usec
TE 298.0 K
D1 1.10000002 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 150.9656784 MHz
NUC1 13C
P1 10.63 usec

F2 - Processing parameters
SI 32768
SF 150.9505639 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

compound 3.64 1H NMR



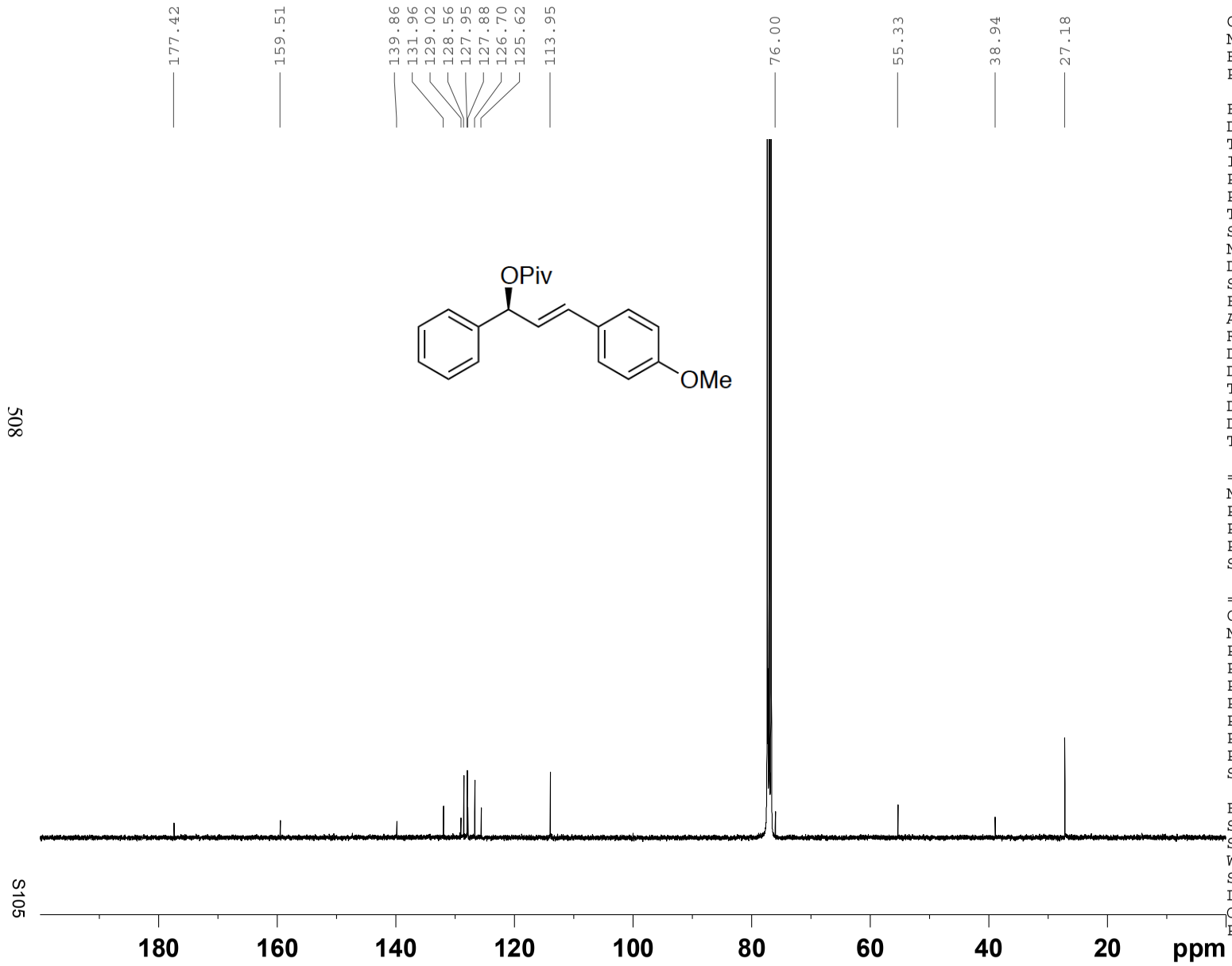
Current Data Parameters
NAME QZ-5-009fr1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20131121
Time 18.18
INSTRUM spect
PROBHD 5 mm CPQNP 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 8
DW 60.400 usec
DE 6.00 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 4.90 dB
PL1W 3.30822015 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300105 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

compound 3.64 13CNMR




```
Current Data Parameters
NAME         QZ-5-009fr1
EXPNO                  2
PROCNO                 1

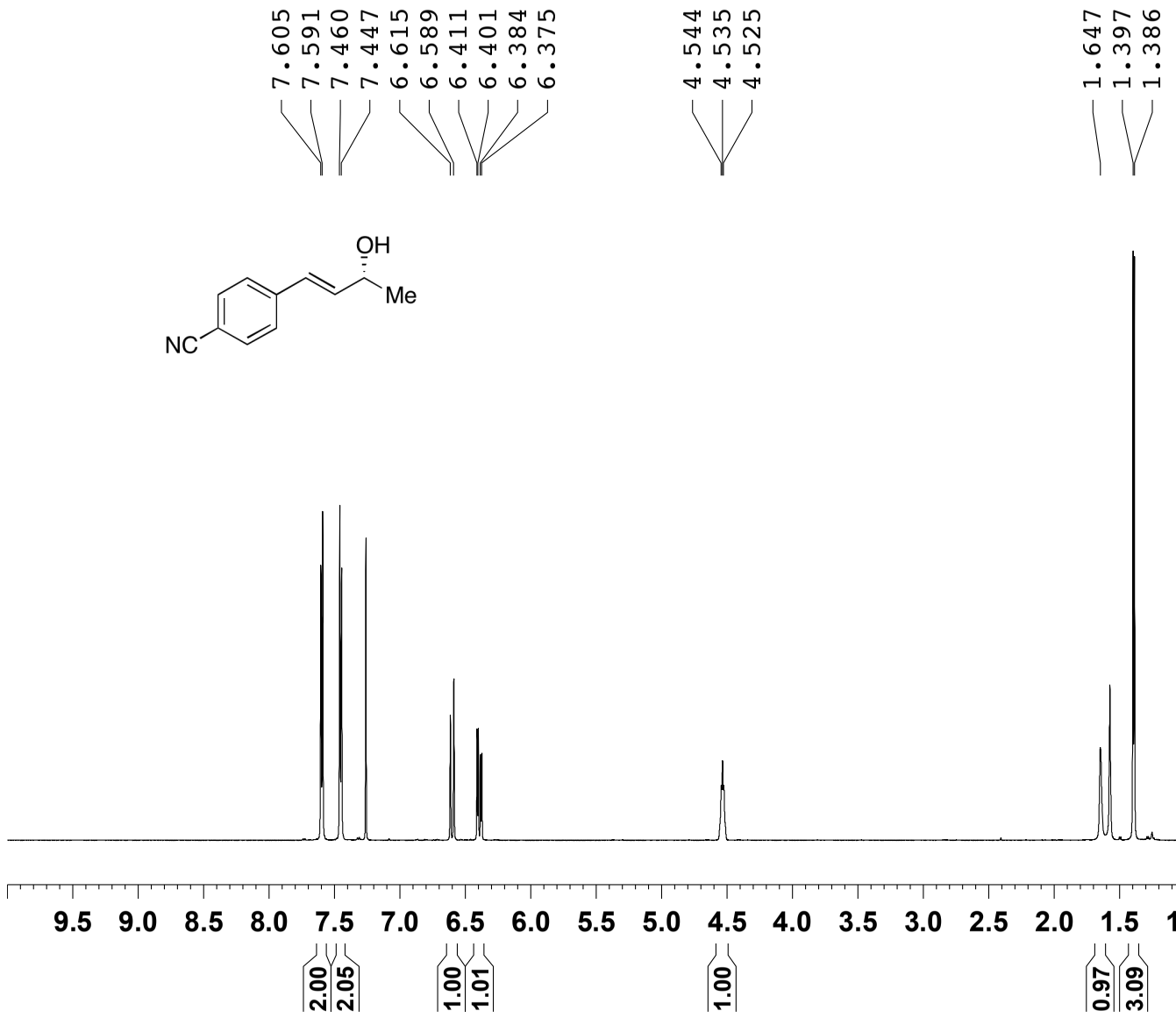
F2 - Acquisition Parameters
Date_           20131121
Time               22.06
INSTRUM            spect
PROBHD   5 mm CPQNP 1H/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ             1.3664756 sec
RG                  512
DW                20.850 usec
DE                18.00 usec
TE                298.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.25 usec
PL1                0.55 dB
PL1W        35.18820572 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2              90.00 usec
PL2                 4.90 dB
PL12               20.46 dB
PL13               21.00 dB
PL2W         3.30822015 W
PL12W        0.09195905 W
PL13W        0.08120718 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127690 MHz
WDW                   EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

compound 3.79 1HNMR



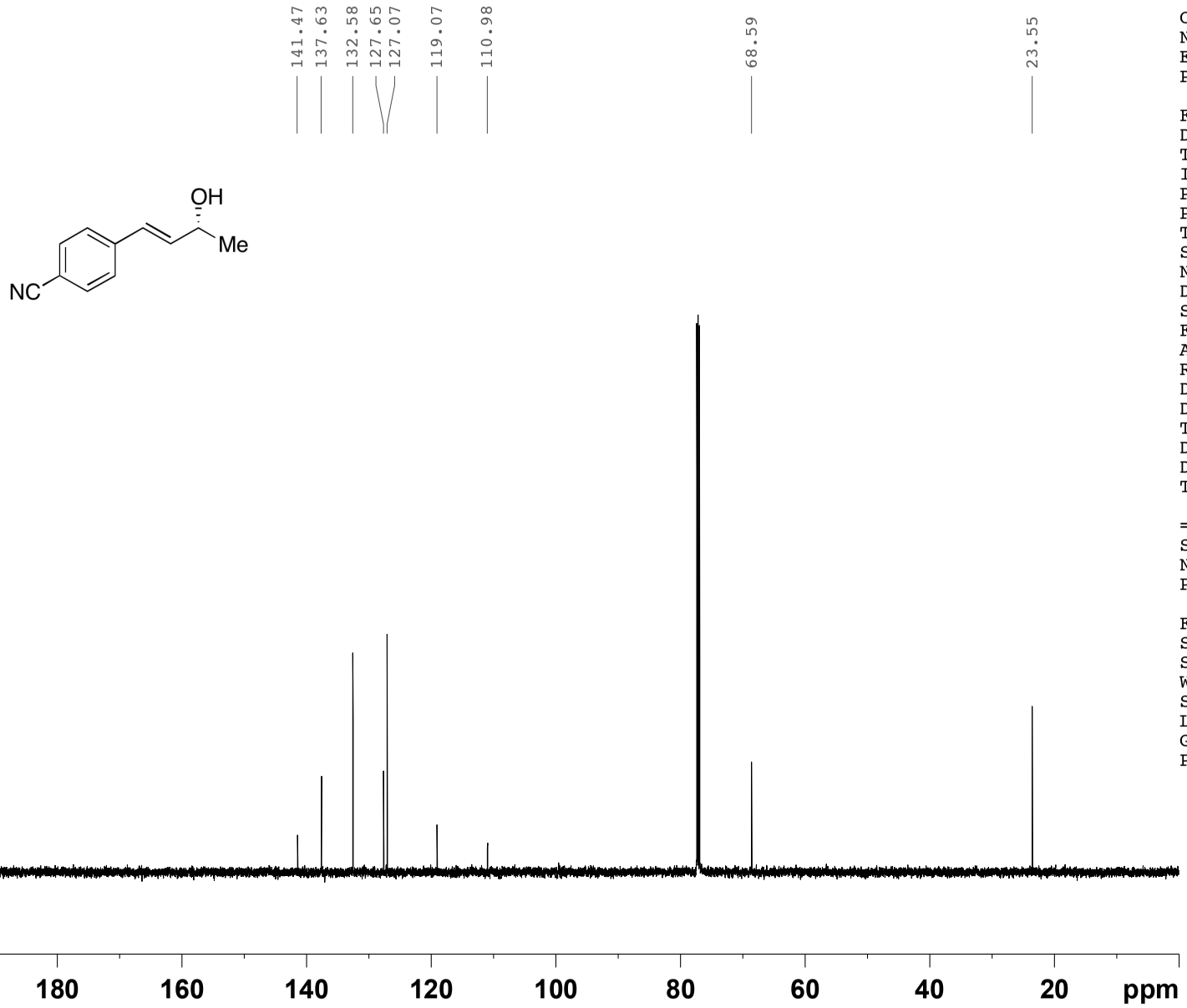

```
Current Data Parameters
NAME      QZ-HH-5-090-2
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20140220
Time              16.42
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8403.361 Hz
FIDRES         0.128225 Hz
AQ             3.8994420 sec
RG                  181
DW                59.500 usec
DE                17.39 usec
TE                298.0 K
D1            1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        600.3233018 MHz
NUC1                  1H
P1                10.77 usec

F2 - Processing parameters
SI                65536
SF          600.3200135 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

compound 3.79 13CNMR



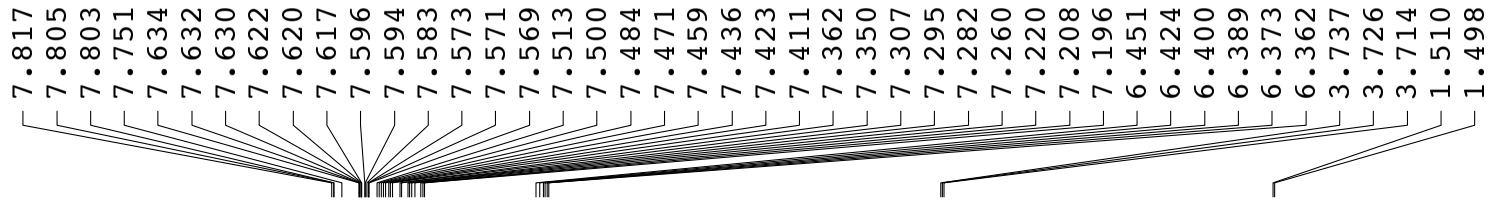

```
Current Data Parameters
NAME      QZ-HH-5-090-2
EXPNO                 2
PROCNO                1

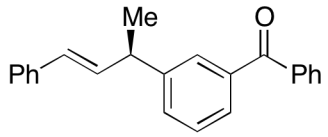
F2 - Acquisition Parameters
Date_          20140220
Time              17.00
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg55
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    4
SWH           34722.223 Hz
FIDRES         0.529819 Hz
AQ            0.9437684 sec
RG                 2050
DW               14.400 usec
DE               19.34 usec
TE               298.0 K
D1            1.10000002 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        150.9656784 MHz
NUC1                13C
P1                10.63 usec

F2 - Processing parameters
SI                32768
SF          150.9505634 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

compound 3.67 1HNMR





Current Data Parameters

NAME	QZ-5-132-1-2
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

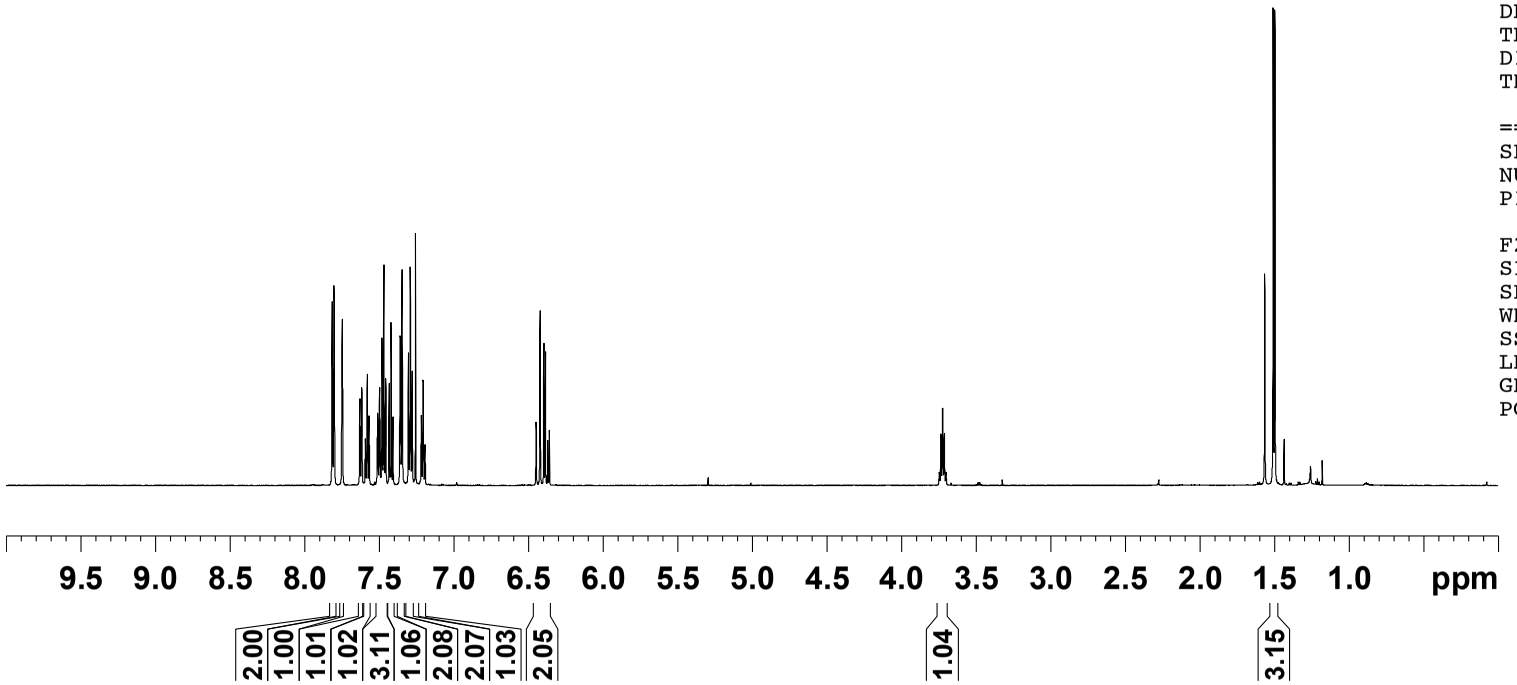
Date_	20140228
Time	17.17
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	2
SWH	12019.230 Hz
FIDRES	0.183399 Hz
AQ	2.7263477 sec
RG	128
DW	41.600 usec
DE	16.81 usec
TE	298.0 K
D1	1.00000000 sec
TD0	1

======== CHANNEL f1 ========

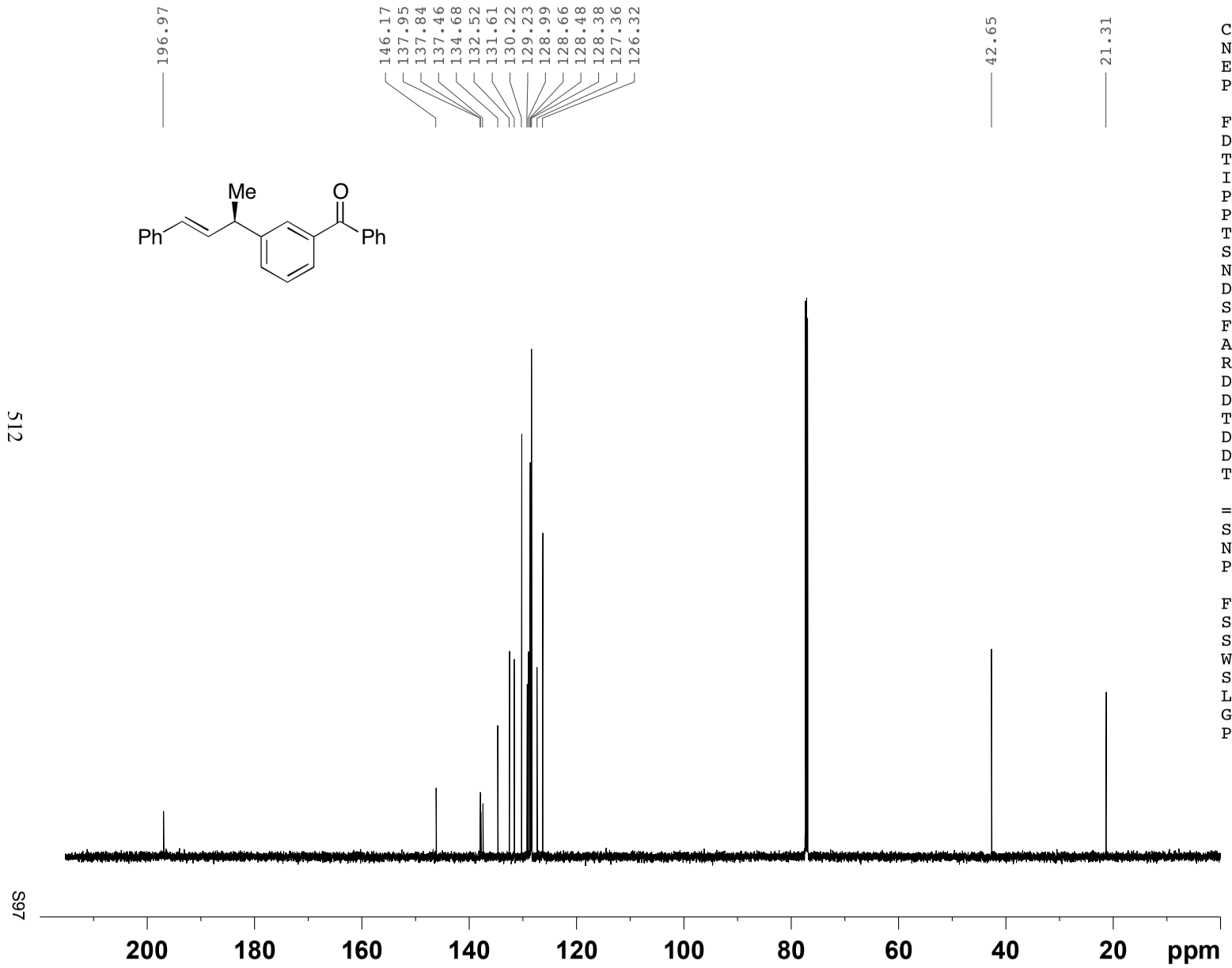
SFO1	600.3240221 MHz
NUC1	1H
P1	10.77 usec

F2 - Processing parameters

SI	65536
SF	600.3200143 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



compound 3.67 13CNMR



Current Data Parameters

NAME	QZ-5-132-1-2
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20140228
Time	17.27
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zgpg55
TD	65536
SOLVENT	CDCl3
NS	256
DS	4
SWH	34722.223 Hz
FIDRES	0.529819 Hz
AQ	0.9437684 sec
RG	2050
DW	14.400 usec
DE	19.34 usec
TE	298.0 K
D1	1.10000002 sec
D11	0.03000000 sec
TD0	1

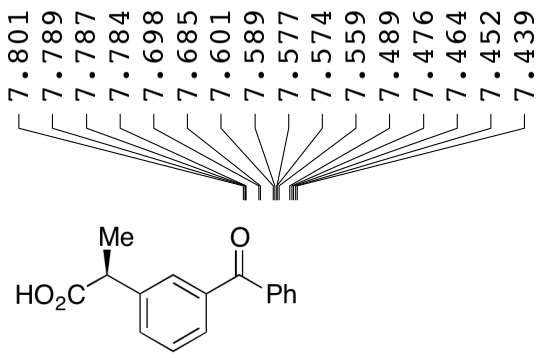
======== CHANNEL f1 ========

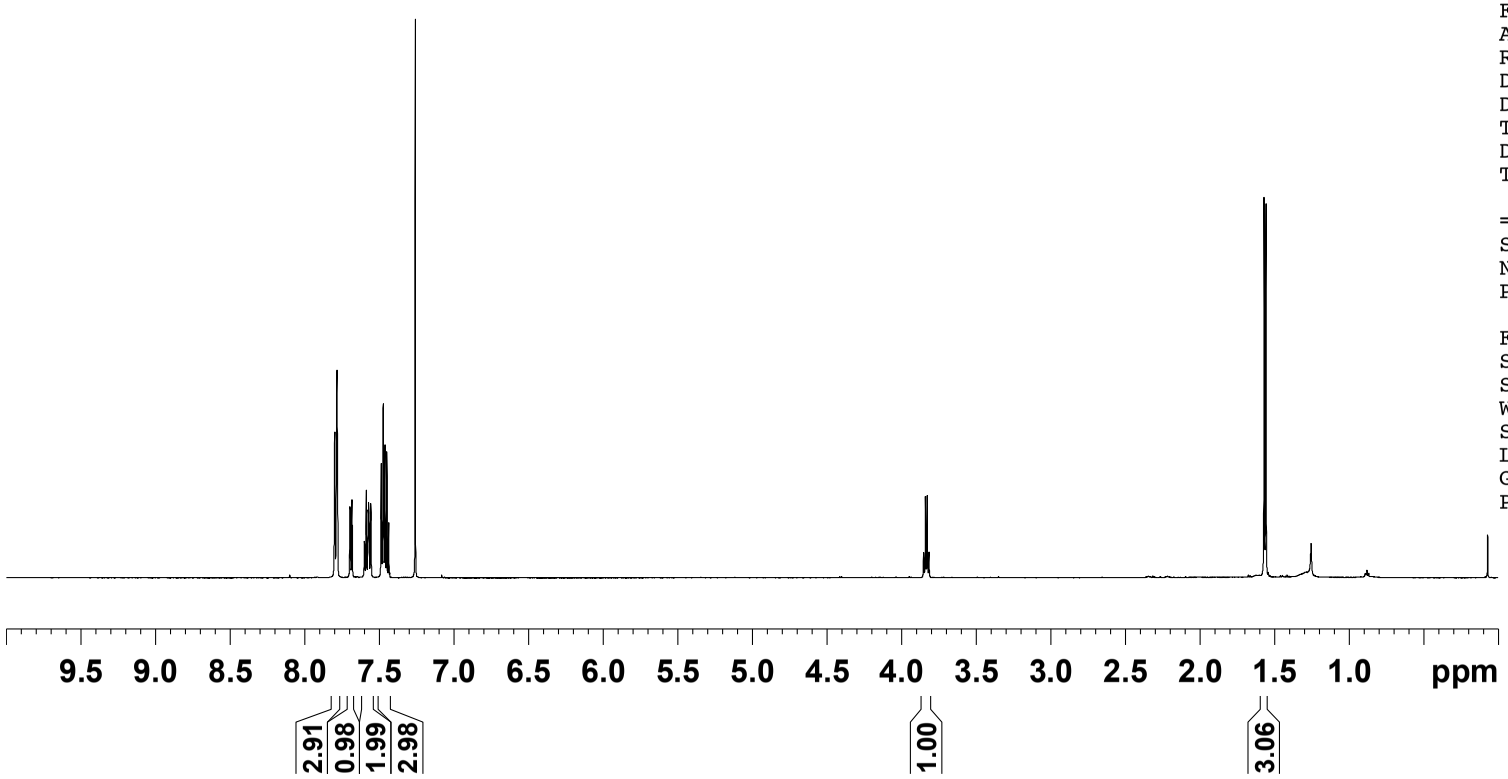
SFO1	150.9656784 MHz
NUC1	13C
P1	10.63 usec

F2 - Processing parameters

SI	32768
SF	150.9505662 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

compound 3.68 1HNMR (*S*)-ketoprofen





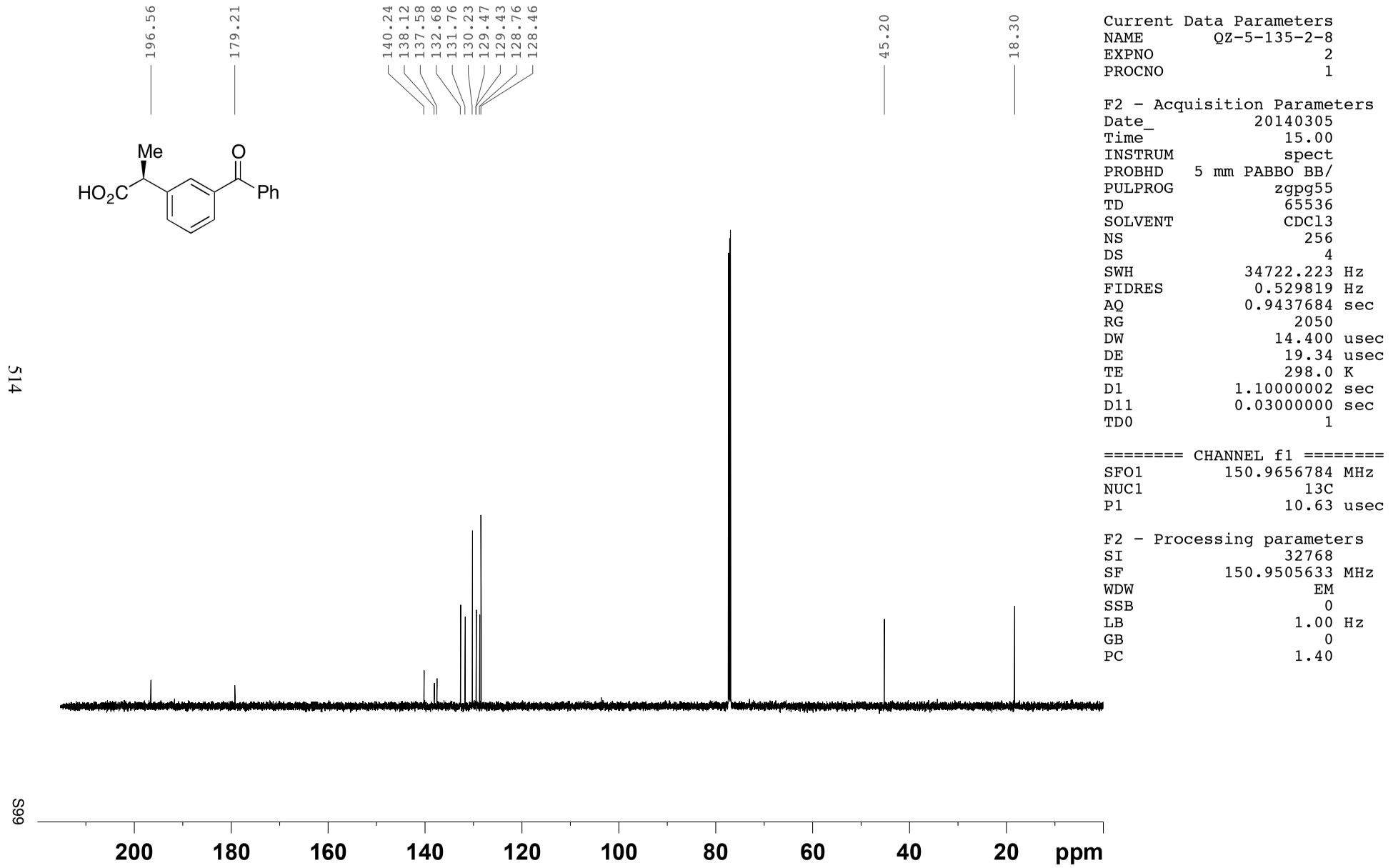

```
Current Data Parameters
NAME        QZ-5-135-2-8
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140305
Time               14.47
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH            12019.230 Hz
FIDRES          0.183399 Hz
AQ             2.7263477 sec
RG                   203
DW                41.600 usec
DE                16.81 usec
TE                298.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.3240221 MHz
NUC1                   1H
P1                 10.77 usec

F2 - Processing parameters
SI                 65536
SF           600.3200135 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                1.00
```

compound 3.68 13CNMR (*S*)-ketoprofen



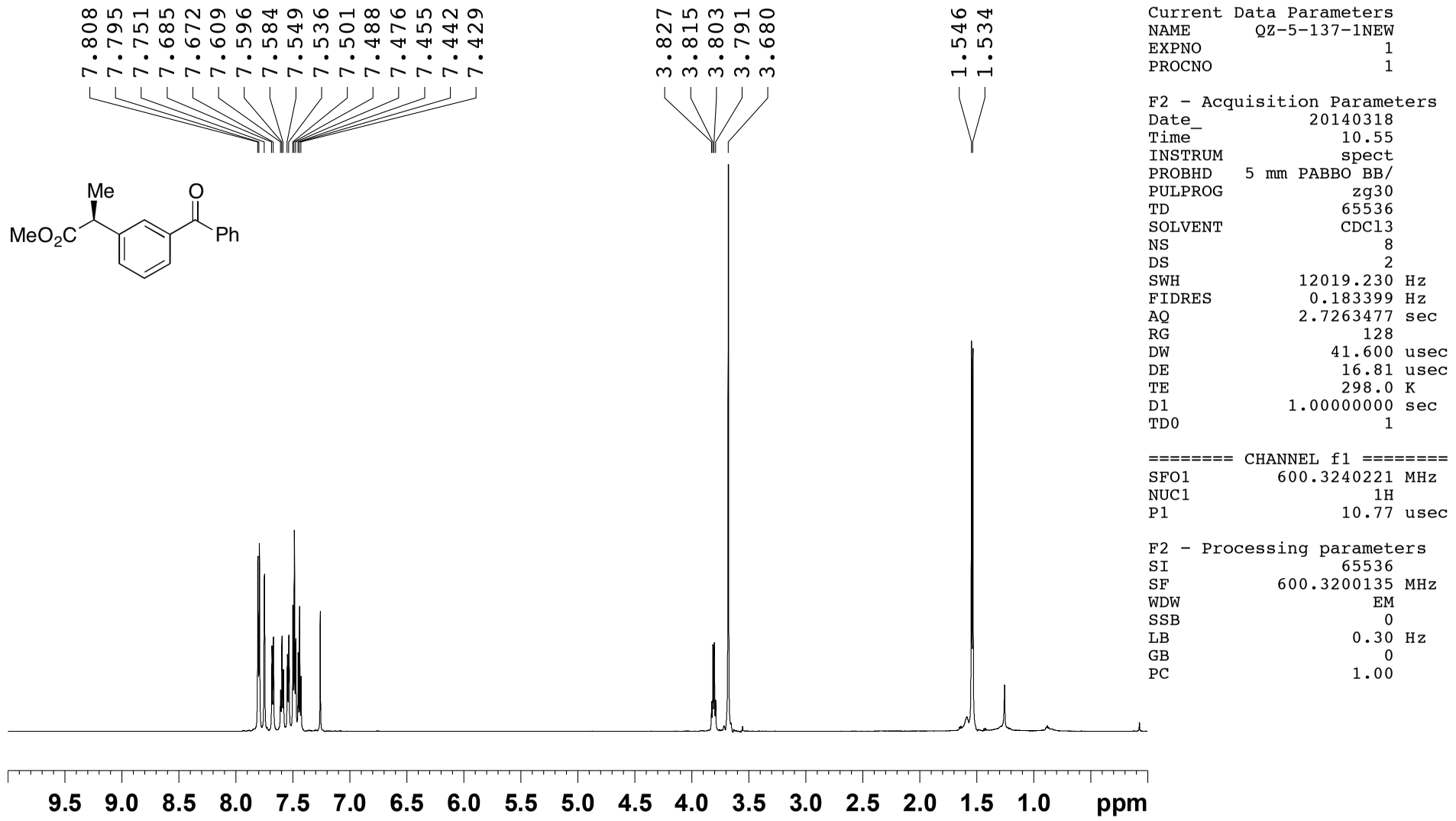

```
Current Data Parameters
NAME        QZ-5-135-2-8
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140305
Time               15.00
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg55
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    4
SWH           34722.223 Hz
FIDRES         0.529819 Hz
AQ            0.9437684 sec
RG                 2050
DW               14.400 usec
DE               19.34 usec
TE               298.0 K
D1            1.10000002 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        150.9656784 MHz
NUC1               13C
P1               10.63 usec

F2 - Processing parameters
SI                32768
SF          150.9505633 MHz
WDW                EM
SSB                0
LB              1.00 Hz
GB                 0
PC              1.40
```

compound 3.87 1HNMR



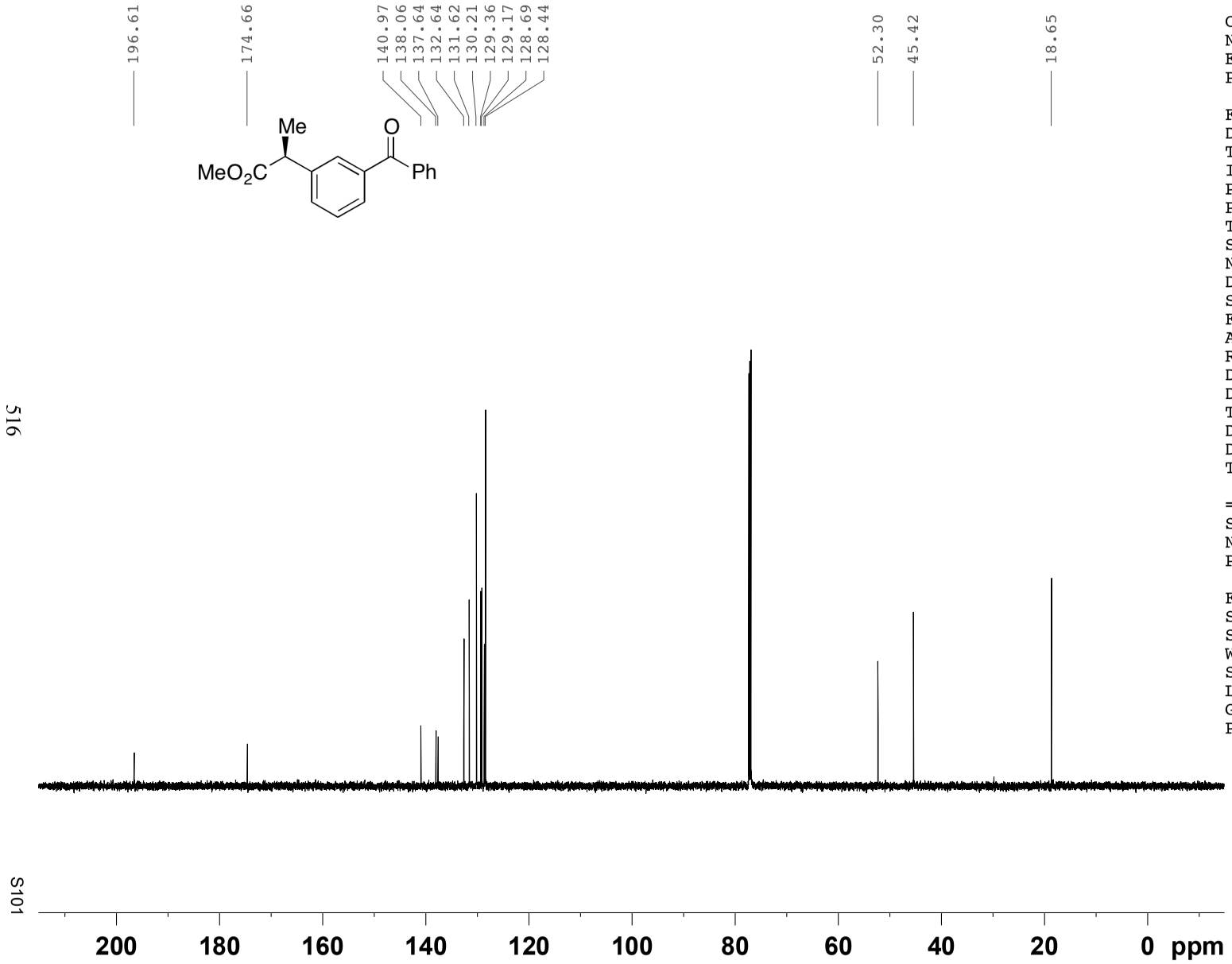

```
Current Data Parameters
NAME      QZ-5-137-1NEW
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20140318
Time               10.55
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH            12019.230 Hz
FIDRES          0.183399 Hz
AQ             2.7263477 sec
RG                   128
DW                41.600 usec
DE                16.81 usec
TE                298.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.3240221 MHz
NUC1                   1H
P1                 10.77 usec

F2 - Processing parameters
SI                 65536
SF           600.3200135 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

compound 3.87 13CNMR



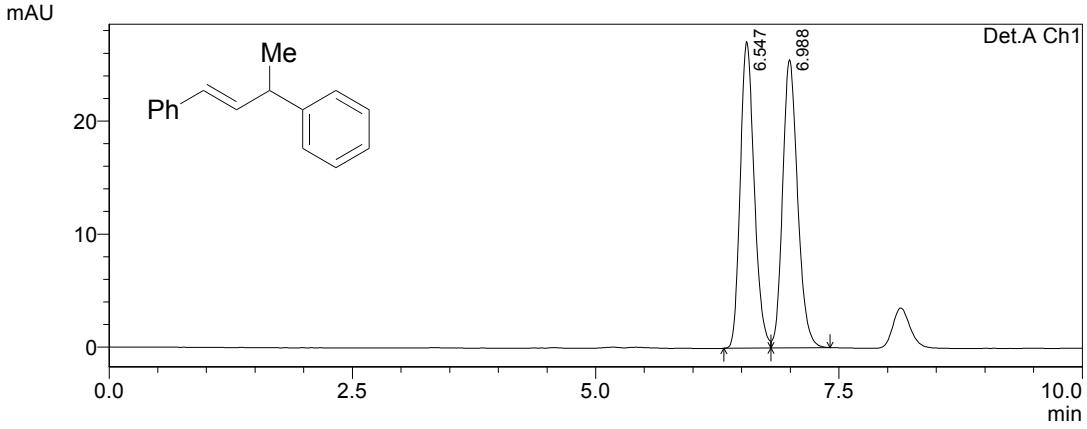

```
Current Data Parameters
NAME      QZ-5-137-1NEW
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20140318
Time               11.05
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg55
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    4
SWH           34722.223 Hz
FIDRES         0.529819 Hz
AQ            0.9437684 sec
RG                 2050
DW               14.400 usec
DE               19.34 usec
TE               298.0 K
D1            1.10000002 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        150.9656784 MHz
NUC1                13C
P1                10.63 usec

F2 - Processing parameters
SI                32768
SF          150.9505656 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

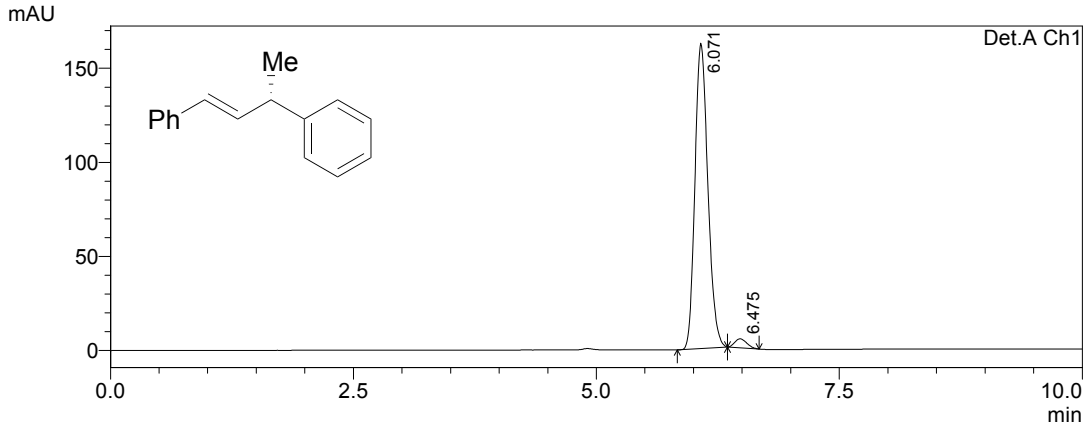
Racemic **3.11**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.547	270789	27126	49.766	51.556
2	6.988	273337	25488	50.234	48.444
Total		544126	52614	100.000	100.000

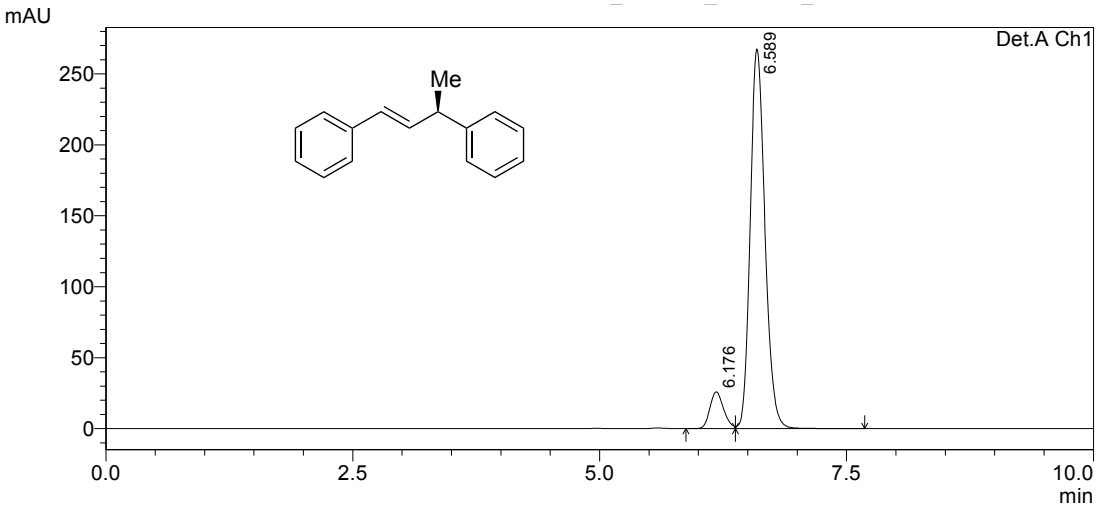
Enantioenriched **3.11**, ee = 95%



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.071	1497700	162221	97.383	97.181
2	6.475	40241	4706	2.617	2.819
Total		1537941	166928	100.000	100.000

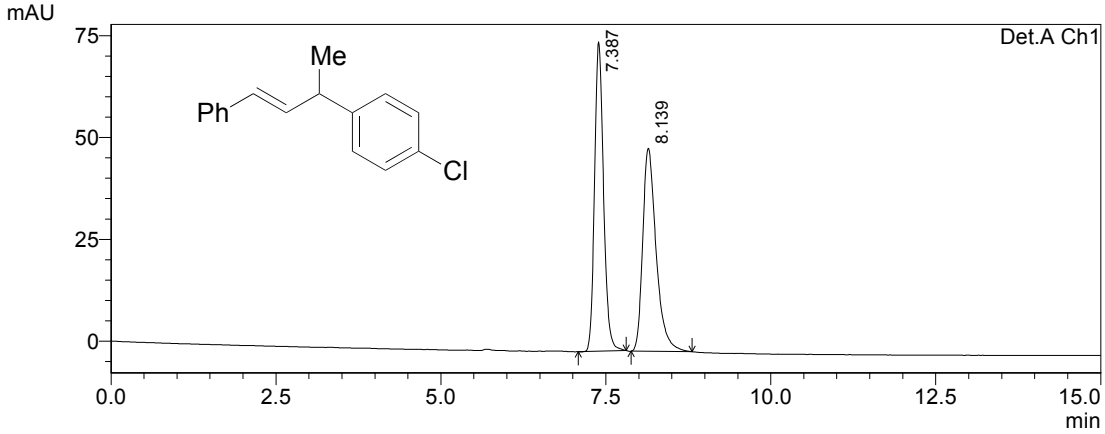
Enantioenriched *(R)*-**3.11**, prepared from **3.63**, as shown in Scheme 5, ee = 83%



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.176	249802	25887	8.275	8.818
2	6.589	2768940	267665	91.725	91.182
Total		3018741	293552	100.000	100.000

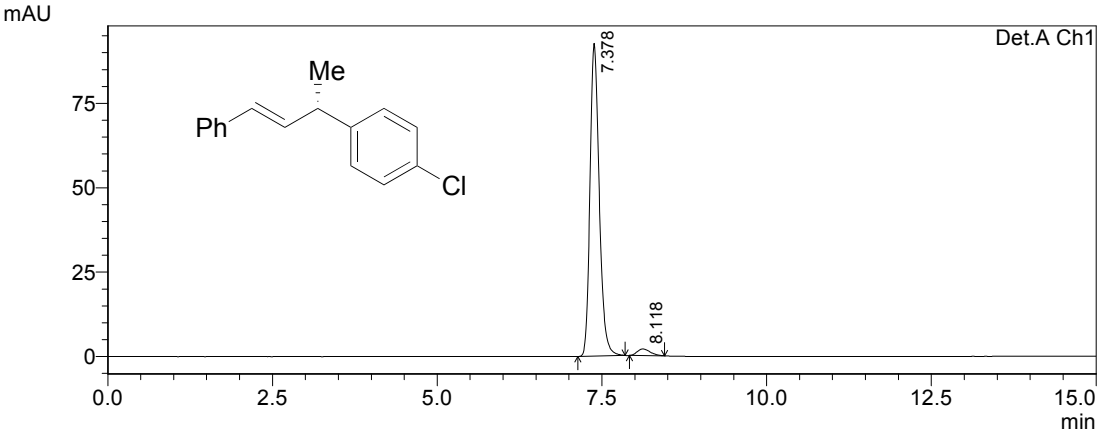
Racemic
3.41



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.387	719087	75904	50.501	60.370
2	8.139	704825	49826	49.499	39.630
Total		1423912	125730	100.000	100.000

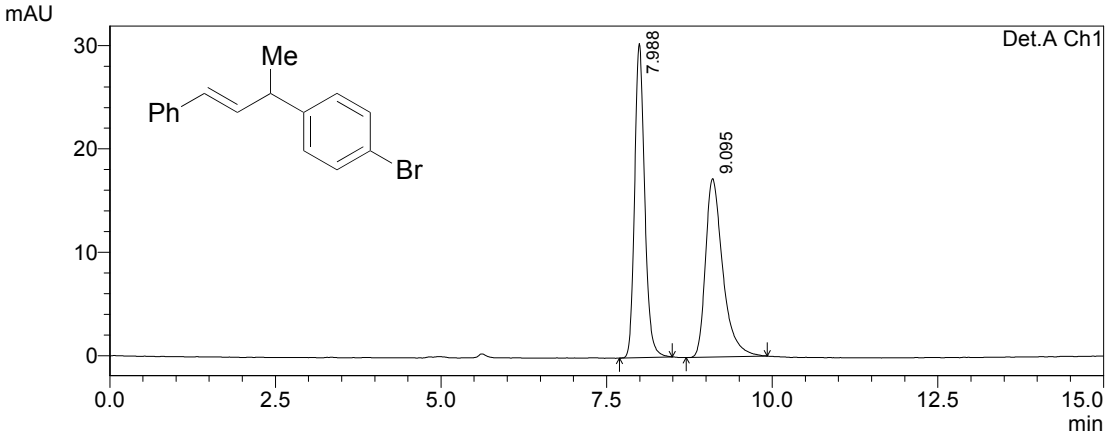
Enantioenriched **3.41**, ee = 94%



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.378	904758	92637	97.094	97.924
2	8.118	27077	1964	2.906	2.076
Total		931836	94601	100.000	100.000

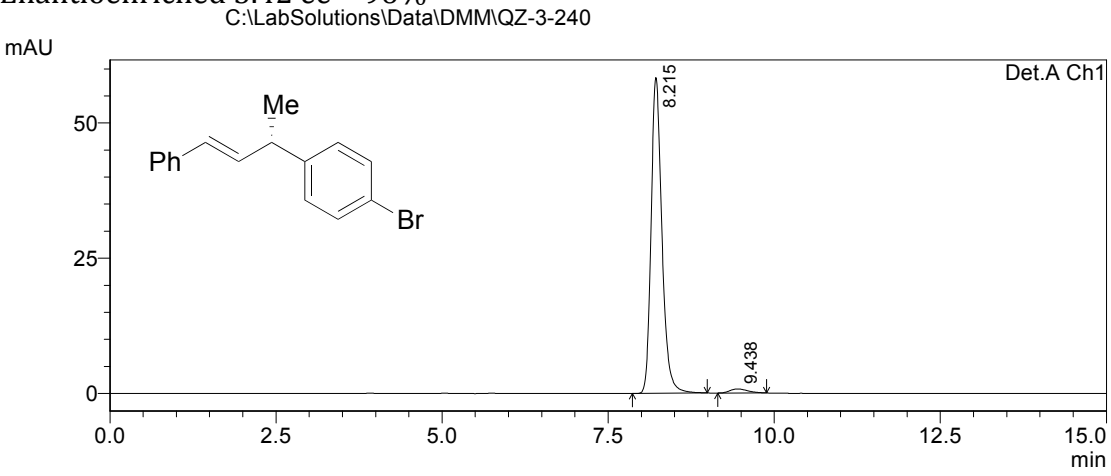
Racemic **3.42**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.988	320442	30359	50.720	63.778
2	9.095	311345	17242	49.280	36.222
Total		631787	47601	100.000	100.000

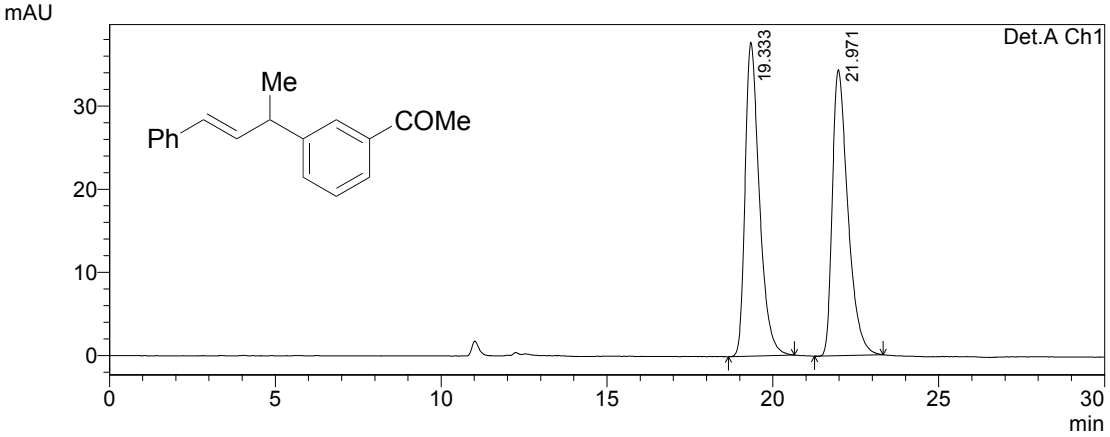
Enantioenriched 3.42 ee = 96%



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.215	661539	58358	97.938	98.732
2	9.438	13930	749	2.062	1.268
Total		675469	59108	100.000	100.000

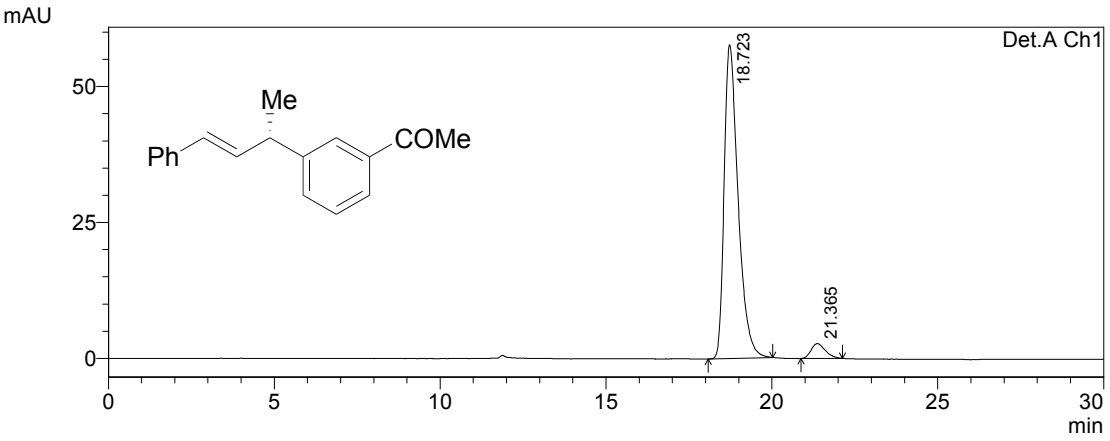
Racemic **3.43**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.333	1126904	37748	50.126	52.323
2	21.971	1121253	34396	49.874	47.677
Total		2248157	72144	100.000	100.000

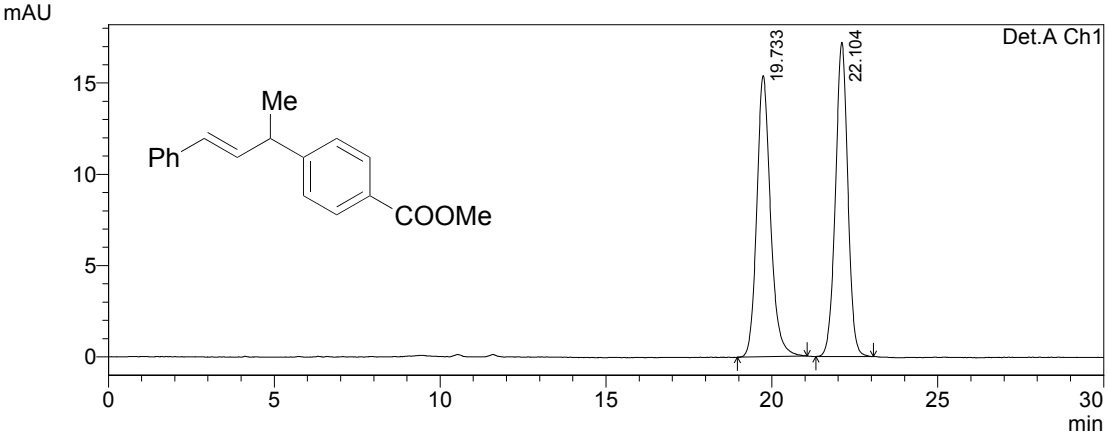
Enantioenriched **3.43**, ee = 91%



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.723	1683869	57676	95.364	95.458
2	21.365	81861	2744	4.636	4.542
Total		1765730	60420	100.000	100.000

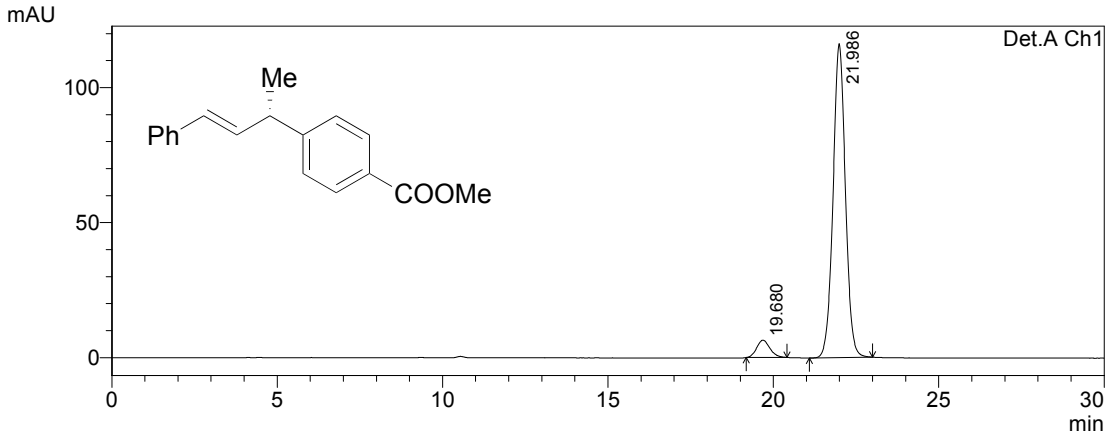
Racemic **3.44**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.733	444003	15399	49.901	47.223
2	22.104	445768	17211	50.099	52.777
Total		889771	32610	100.000	100.000

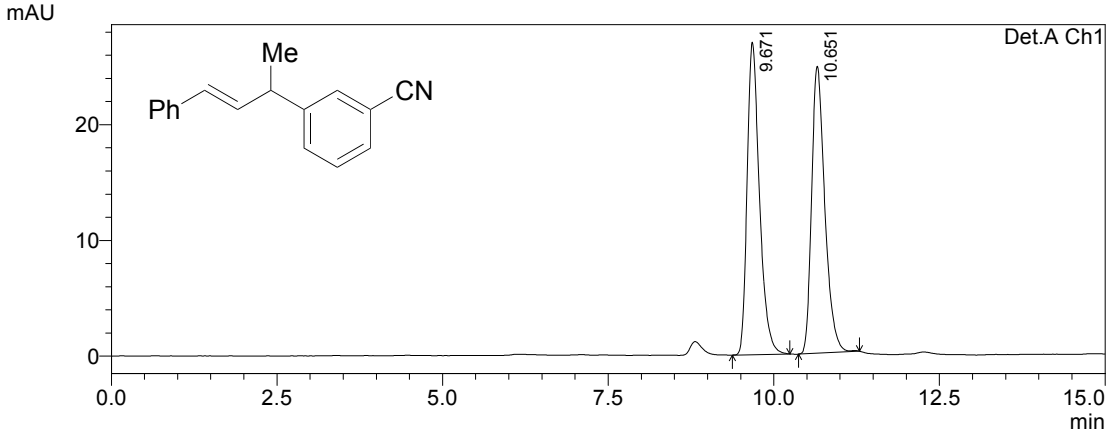
Enantioenriched **3.44**, 89%



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.680	178540	6440	5.592	5.249
2	21.986	3014453	116234	94.408	94.751
Total		3192993	122673	100.000	100.000

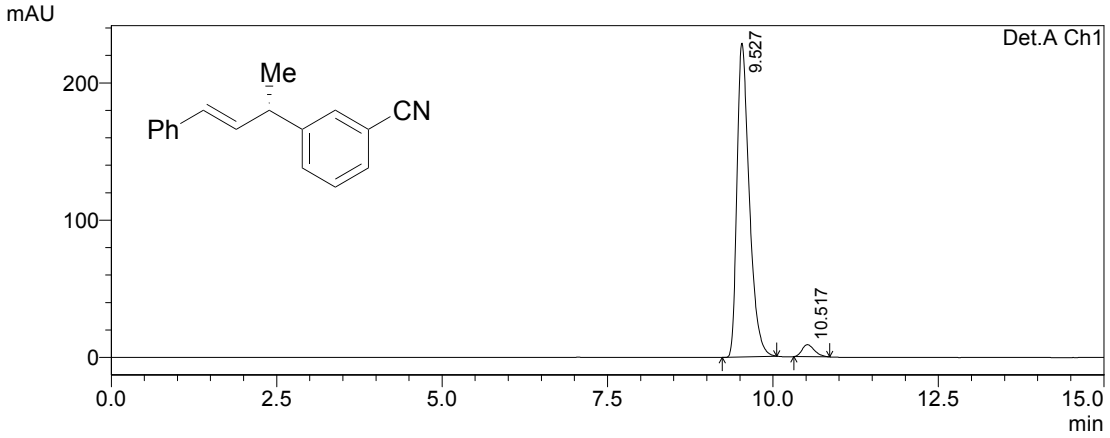
Racemic **3.45**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.671	349082	27005	50.386	52.117
2	10.651	343730	24810	49.614	47.883
Total		692812	51815	100.000	100.000

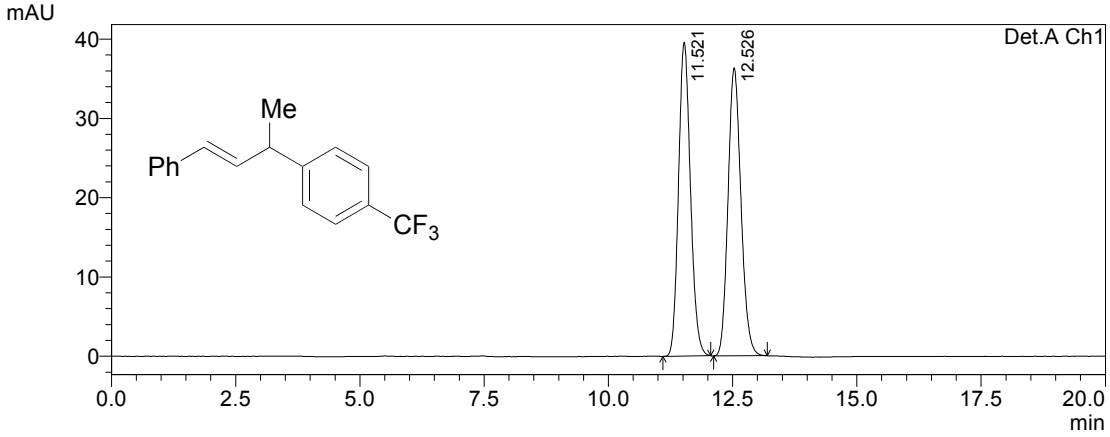
Enantioenriched **3.45**, ee = 93%



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.527	2955263	228575	96.263	96.292
2	10.517	114736	8801	3.737	3.708
Total		3069999	237376	100.000	100.000

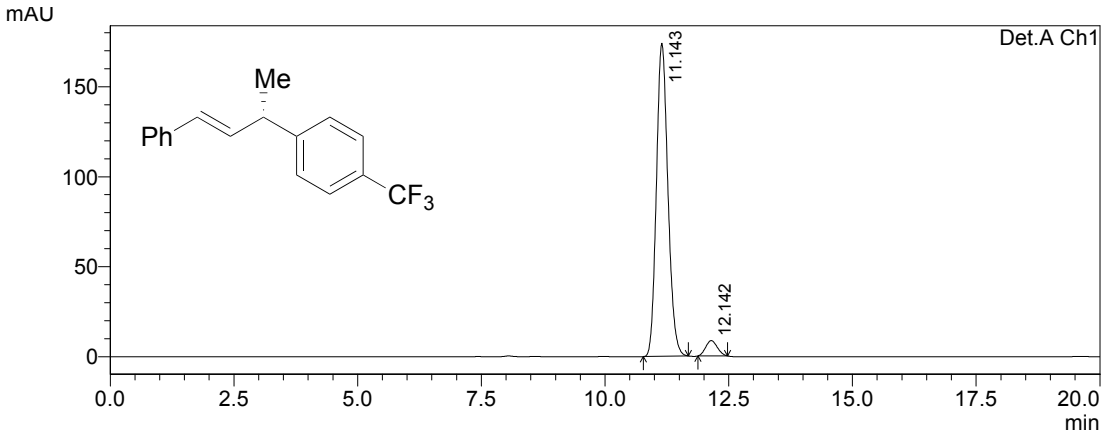
Racemic **3.46**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.521	660610	39588	50.006	52.136
2	12.526	660455	36345	49.994	47.864
Total		1321065	75933	100.000	100.000

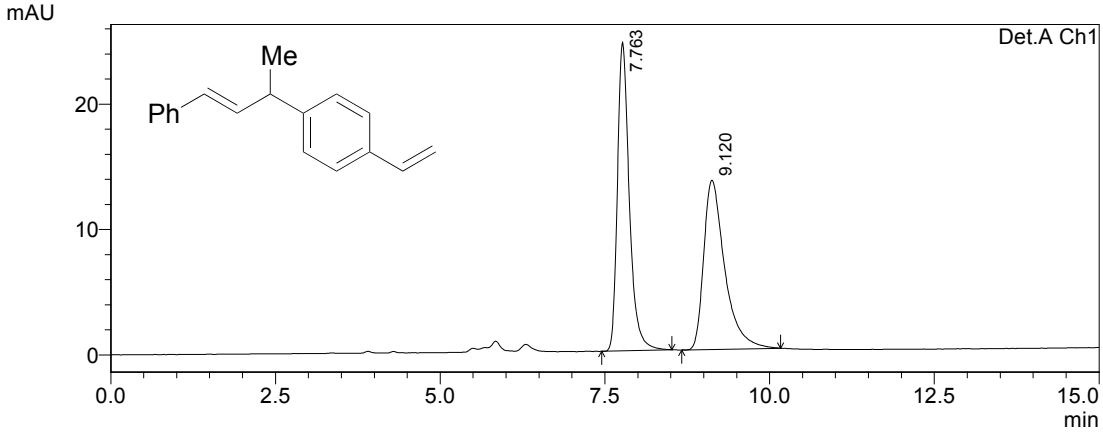
Enantioenriched **3.46**, ee = 91%



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.143	2817309	173908	95.290	95.325
2	12.142	139267	8530	4.710	4.675
Total		2956576	182438	100.000	100.000

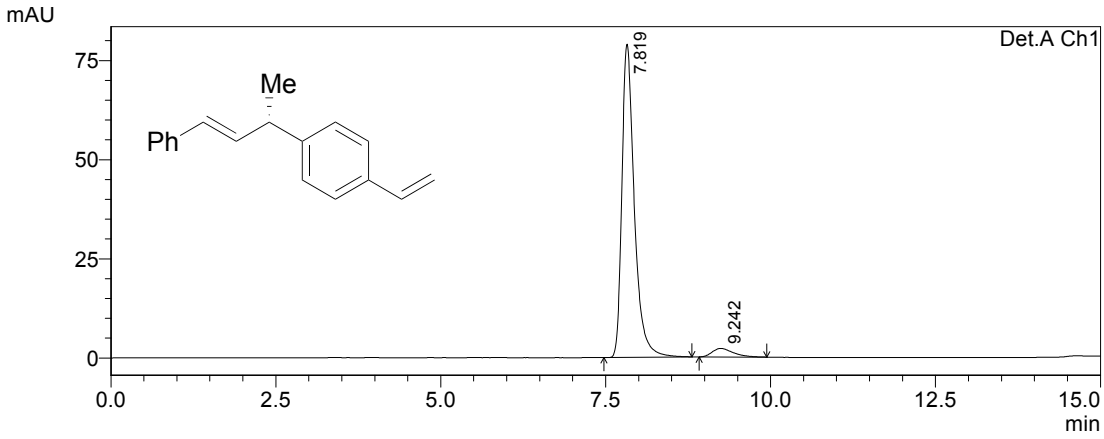
Racemic **3.47**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.763	309122	24632	50.797	64.592
2	9.120	299424	13503	49.203	35.408
Total		608545	38135	100.000	100.000

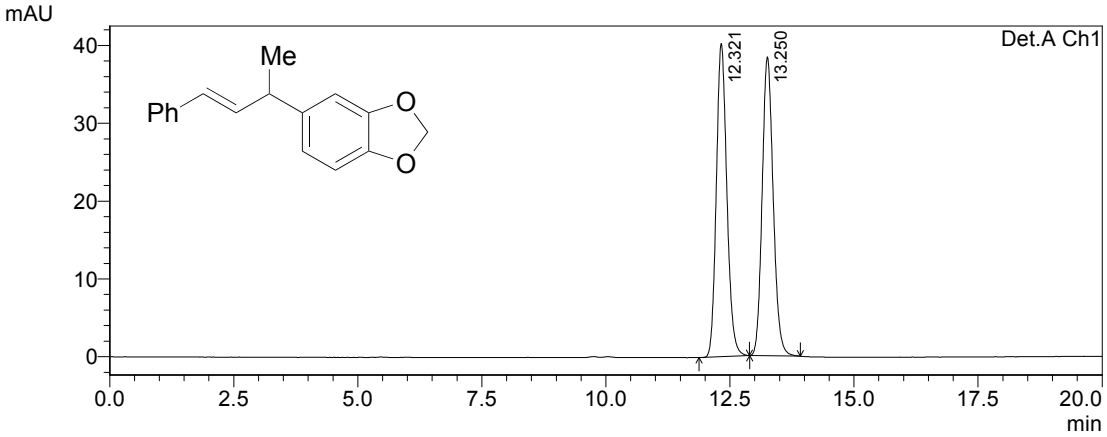
Enantioenriched **3.47**, ee = 1%



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.819	1036677	78979	95.516	97.324
2	9.242	48666	2171	4.484	2.676
Total		1085343	81150	100.000	100.000

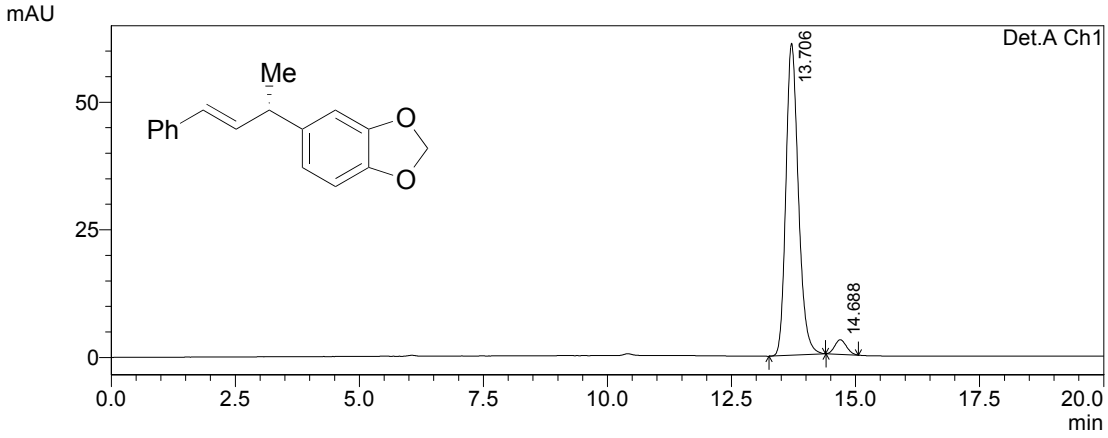
Racemic**3.48**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.321	594232	40220	49.983	51.167
2	13.250	594630	38386	50.017	48.833
Total		1188862	78605	100.000	100.000

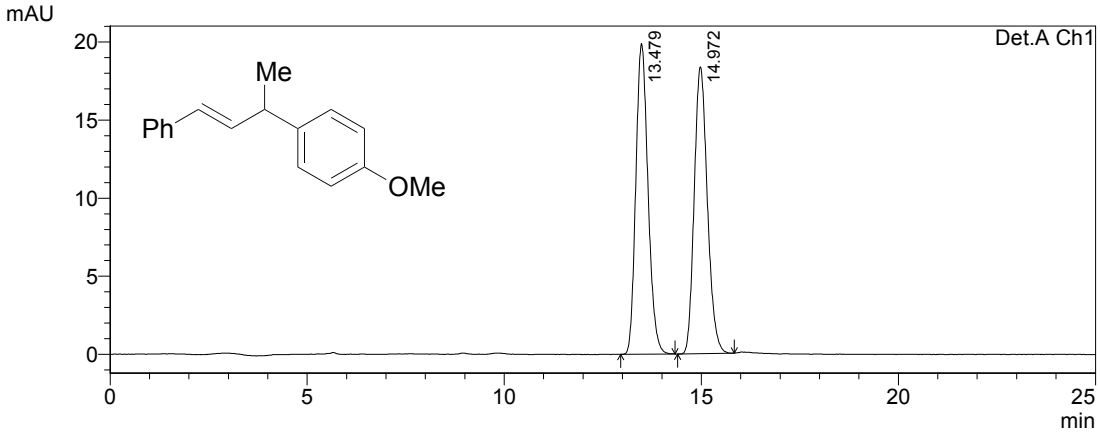
Enantioenriched **3.48**, ee = 92%



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.706	1067949	61099	95.807	95.549
2	14.688	46740	2846	4.193	4.451
Total		1114689	63945	100.000	100.000

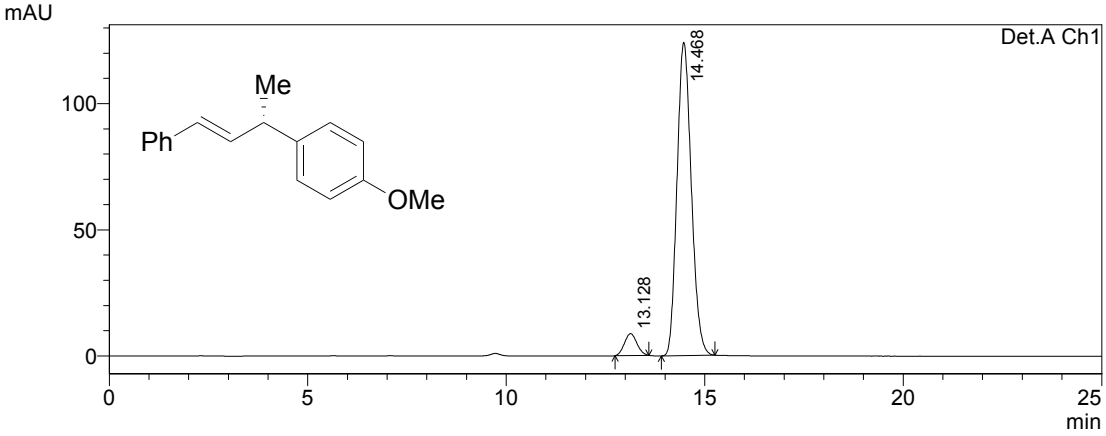
Racemic **3.49**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.479	427846	19884	50.127	51.998
2	14.972	425680	18356	49.873	48.002
Total		853526	38240	100.000	100.000

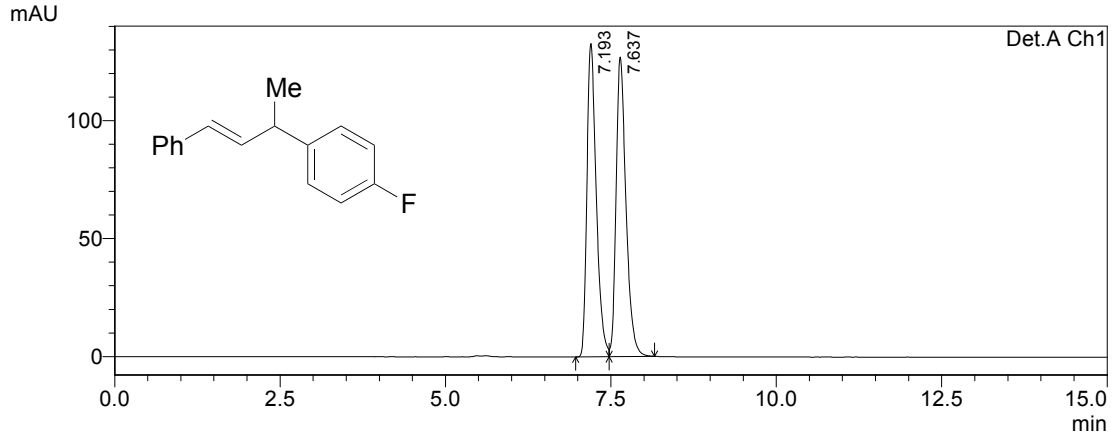
Enantioenriched **3.49**, ee = 89%



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.128	189418	8679	5.739	6.535
2	14.468	3111331	124131	94.261	93.465
Total		3300749	132811	100.000	100.000

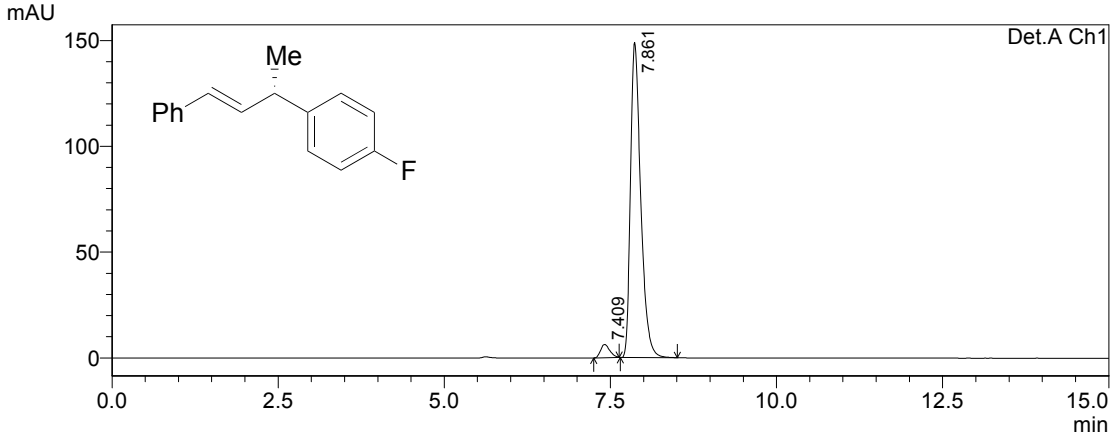
Racemic **3.50**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.193	1303841	132756	49.668	51.098
2	7.637	1321281	127053	50.332	48.902
Total		2625122	259810	100.000	100.000

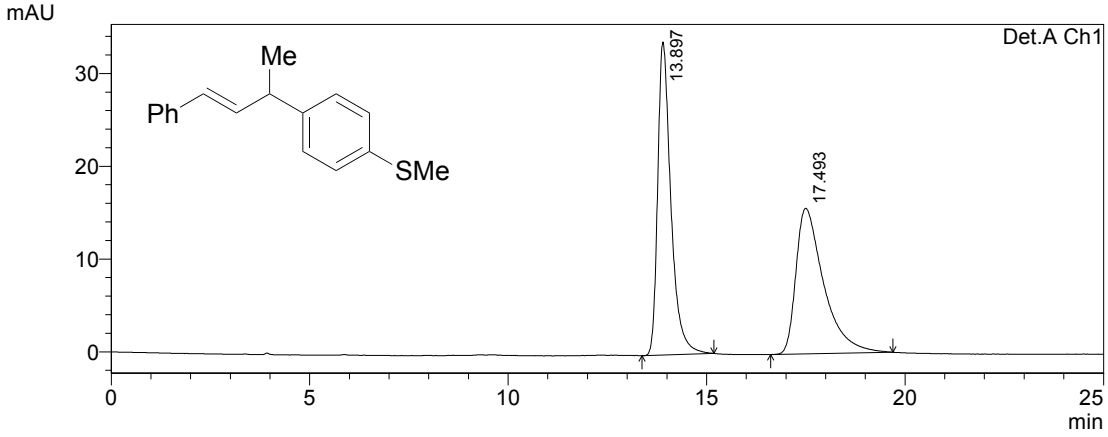
Enantioenriched **3.50**, ee = 93%



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.409	59690	6261	3.607	4.036
2	7.861	1595262	148864	96.393	95.964
Total		1654951	155125	100.000	100.000

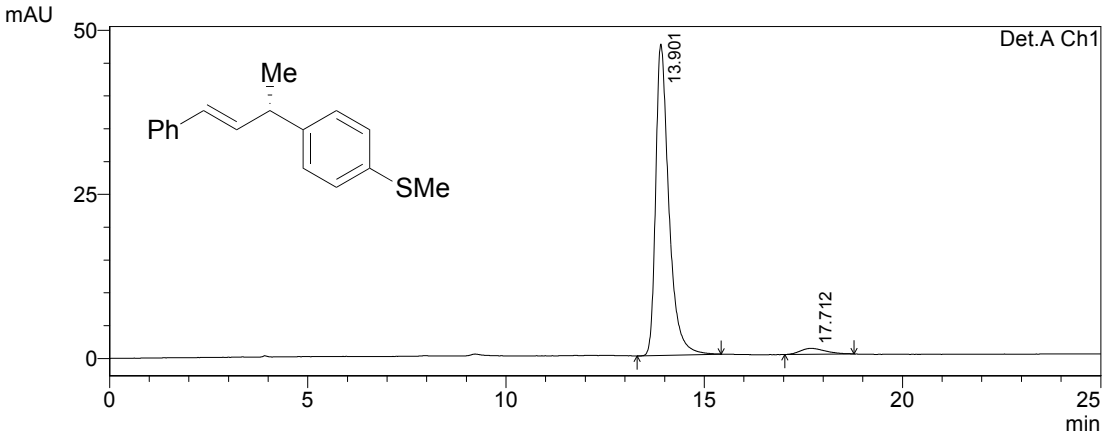
Racemic **3.51**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.897	780775	33745	50.587	68.263
2	17.493	762670	15688	49.413	31.737
Total		1543445	49433	100.000	100.000

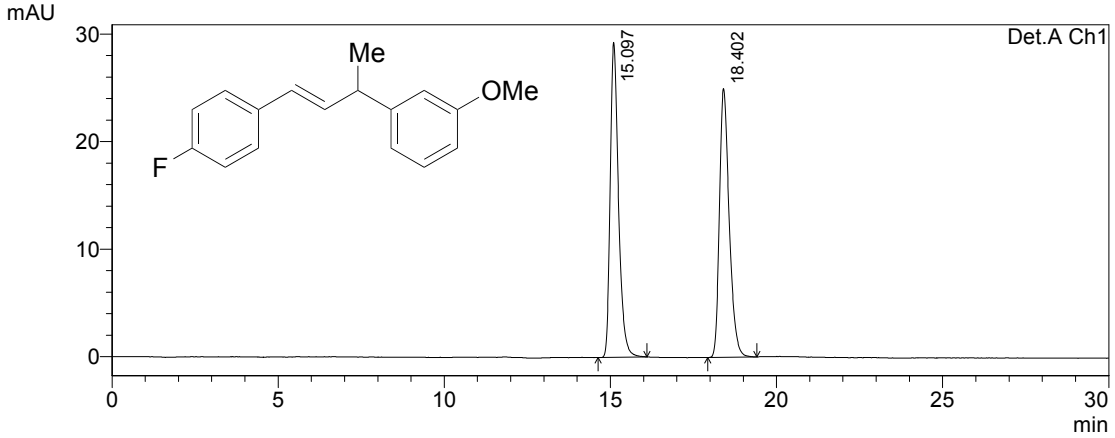
Enantioenriched **3.51**, ee = 93%



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.901	1093788	47430	96.408	98.119
2	17.712	40748	909	3.592	1.881
Total		1134537	48339	100.000	100.000

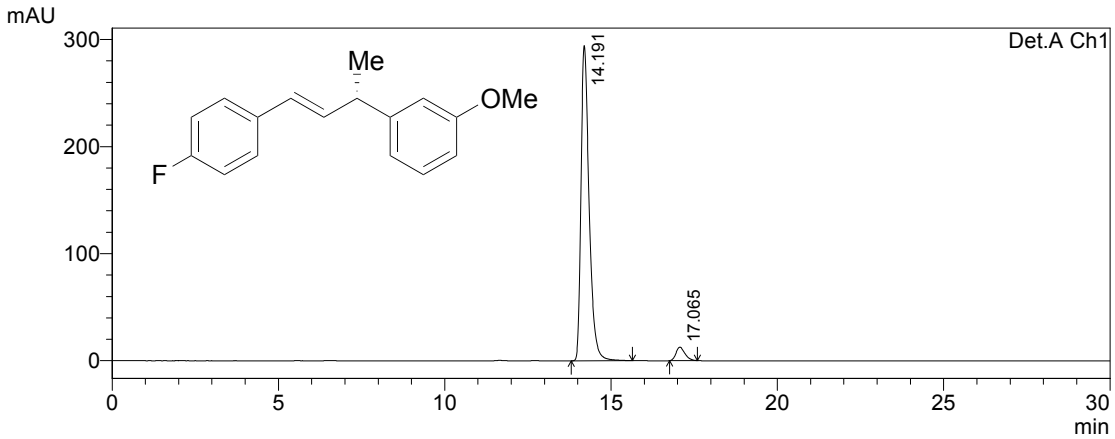
Racemic **3.52**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.097	508175	29289	49.940	53.947
2	18.402	509391	25003	50.060	46.053
Total		1017566	54292	100.000	100.000

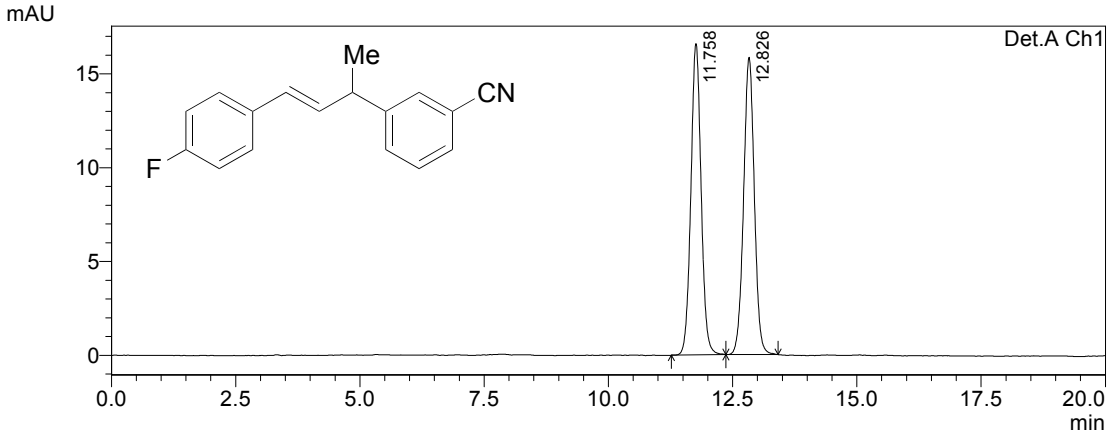
Enantioenriched **3.52**, 1%



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.191	5000569	294197	95.503	95.887
2	17.065	235491	12621	4.497	4.113
Total		5236060	306818	100.000	100.000

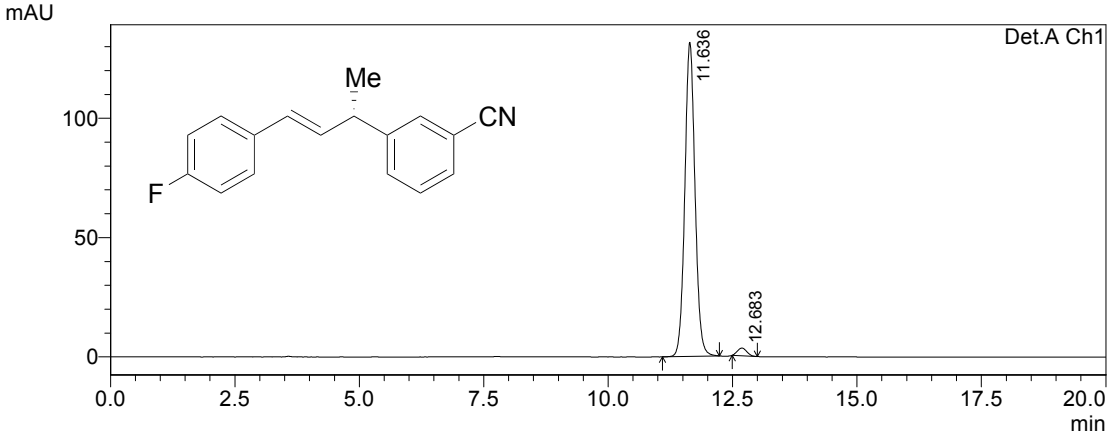
Racemic **3.53**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.758	237836	16587	49.983	51.145
2	12.826	237998	15845	50.017	48.855
Total		475834	32432	100.000	100.000

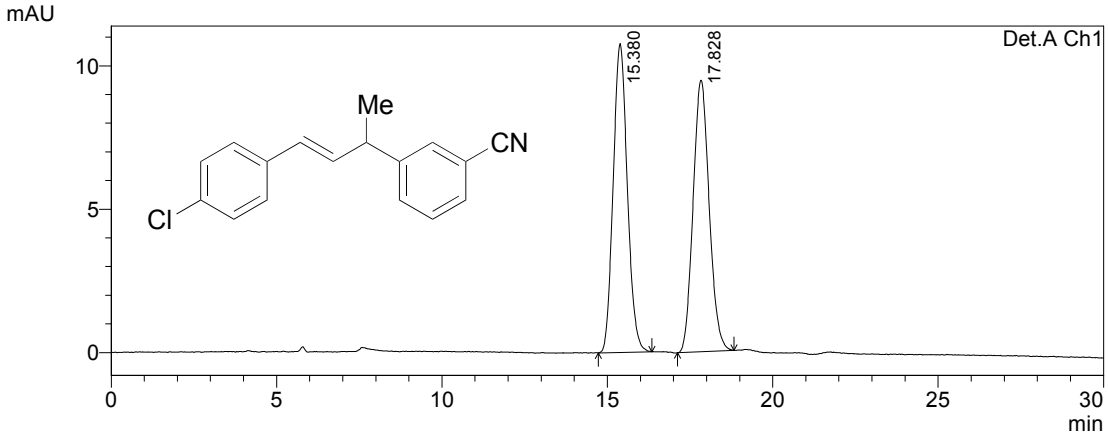
Enantioenriched **3.53**, ee = 96%



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.636	1878029	131646	97.804	97.592
2	12.683	42169	3248	2.196	2.408
Total		1920198	134894	100.000	100.000

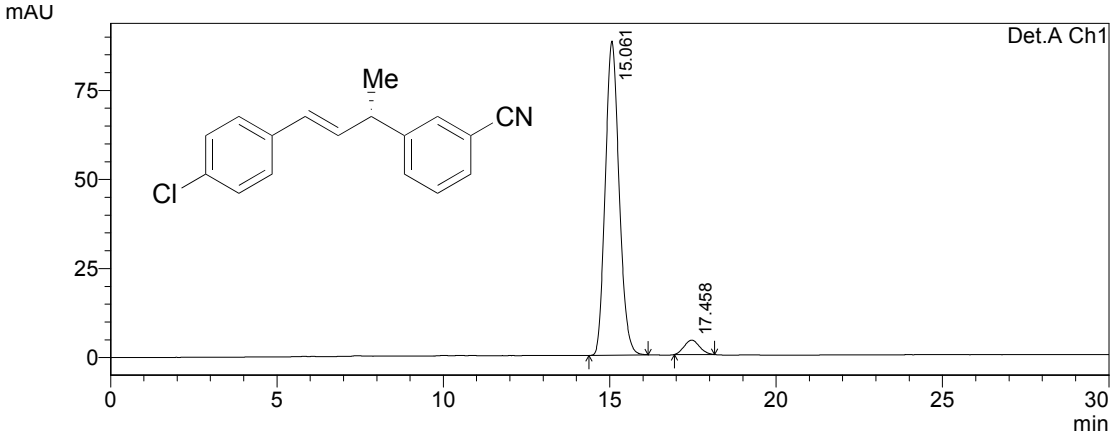
Racemic **3.54**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.380	320415	10768	50.063	53.201
2	17.828	319614	9472	49.937	46.799
Total		640029	20239	100.000	100.000

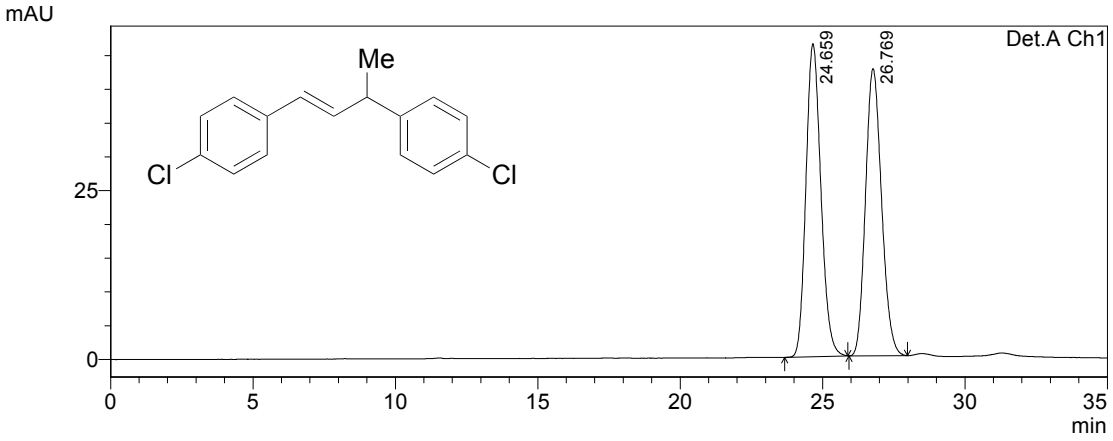
Enantioenriched **3.54** ee, 90%



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.061	2546825	88146	95.154	95.602
2	17.458	129704	4055	4.846	4.398
Total		2676529	92201	100.000	100.000

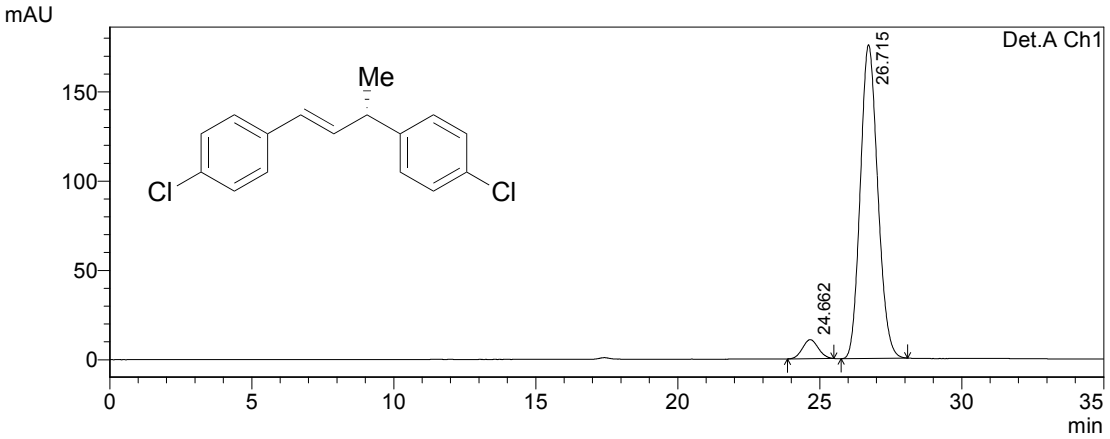
Racemic **3.55**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.659	1689765	46329	50.349	52.130
2	26.769	1666345	42543	49.651	47.870
Total		3356110	88872	100.000	100.000

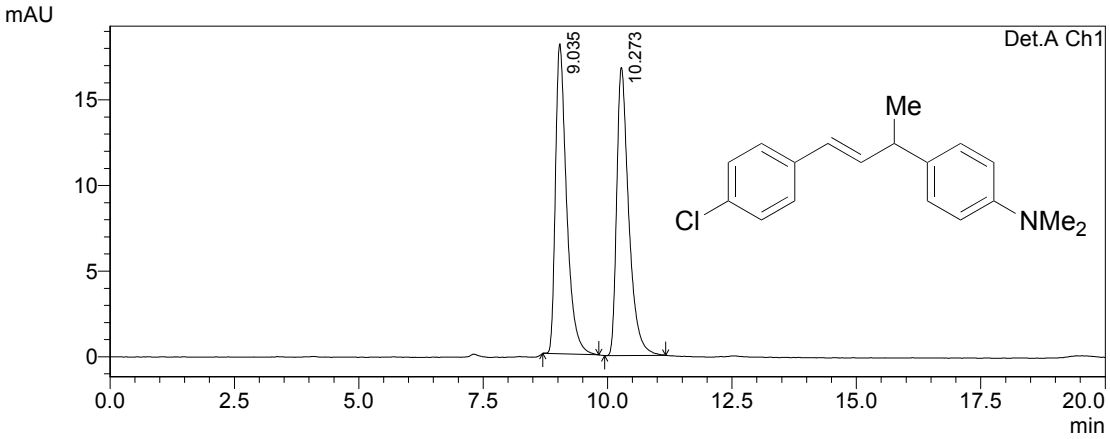
Enantioenriched **3.55**, ee = 90%



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.662	411573	10667	5.191	5.724
2	26.715	7516797	175693	94.809	94.276
Total		7928370	186360	100.000	100.000

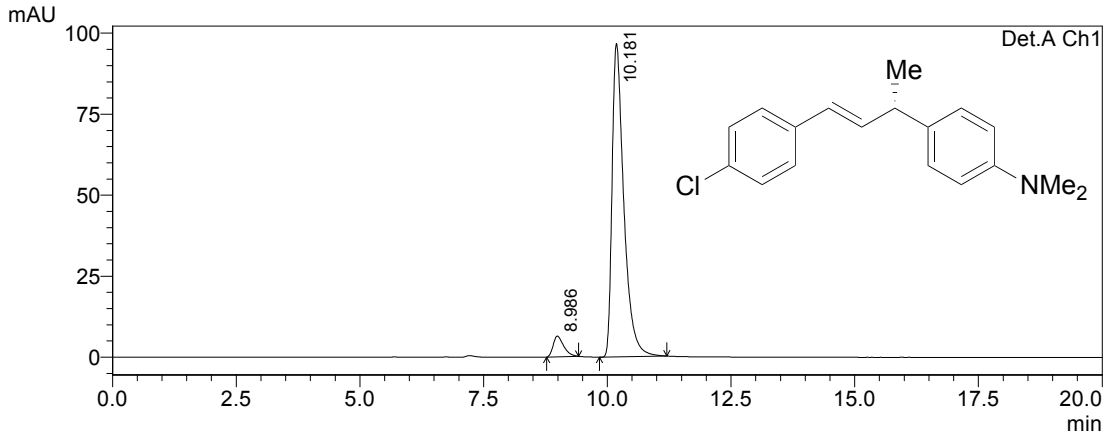
Racemic **3.56**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.035	281831	18100	49.870	51.821
2	10.273	283301	16828	50.130	48.179
Total		565132	34927	100.000	100.000

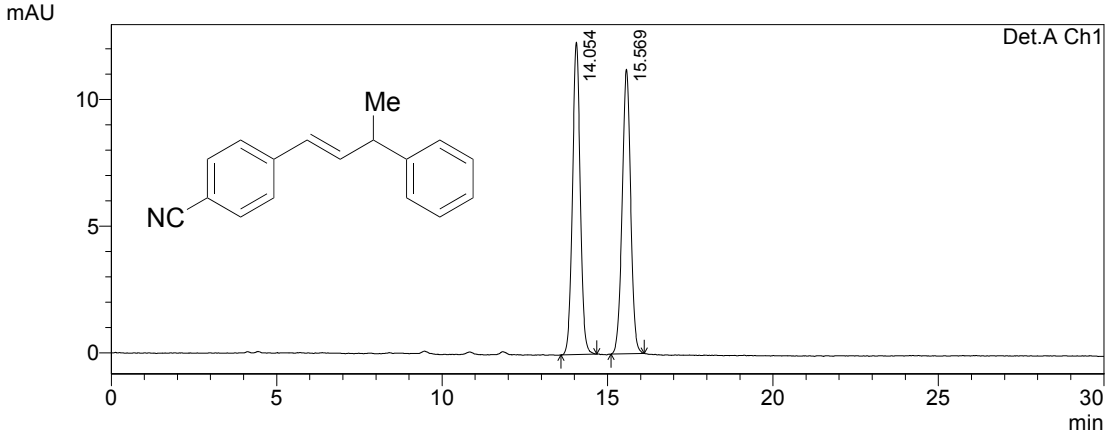
Enantioenriched **3.56**, 9%



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.986	94596	6406	5.584	6.214
2	10.181	1599390	96673	94.416	93.786
Total		1693986	103078	100.000	100.000

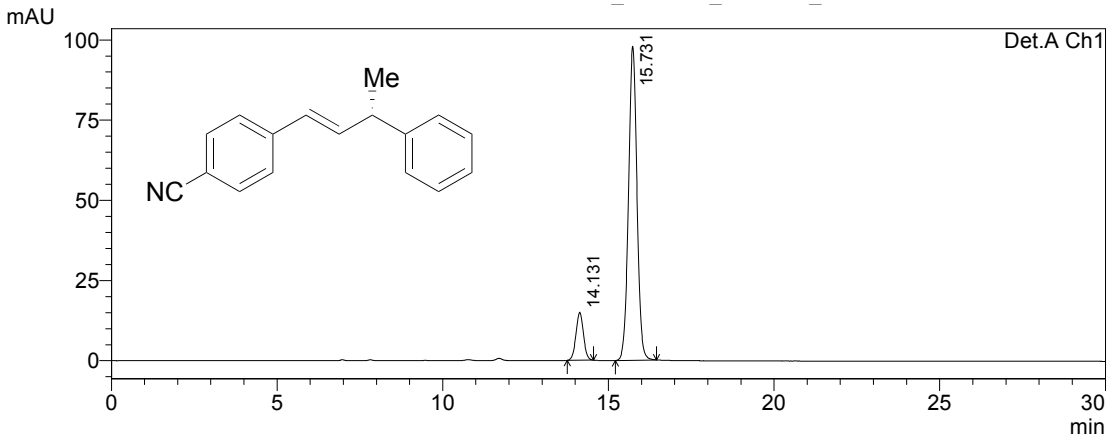
Racemic **3.57**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.054	200511	12325	50.027	52.327
2	15.569	200293	11229	49.973	47.673
Total		400804	23554	100.000	100.000

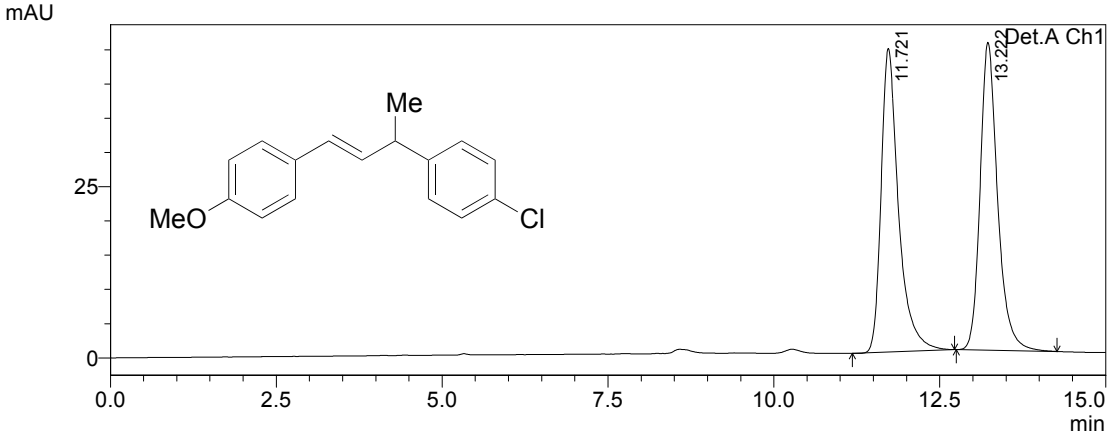
Enantioenriched **3.57** , ee =76%



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.131	235932	14981	11.961	13.275
2	15.731	1736595	97870	88.039	86.725
Total		1972527	112851	100.000	100.000

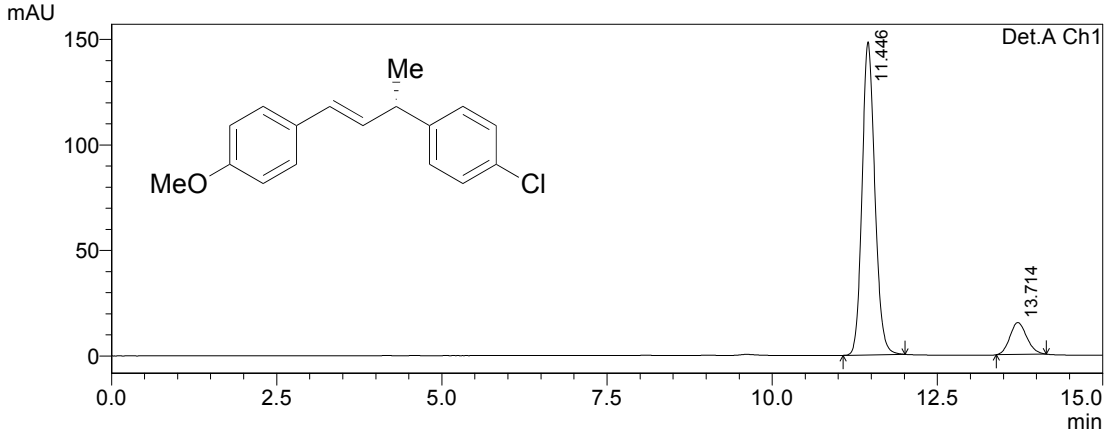
Racemic **3.58**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.721	807561	44373	49.506	49.663
2	13.222	823662	44976	50.494	50.337
Total		1631223	89349	100.000	100.000

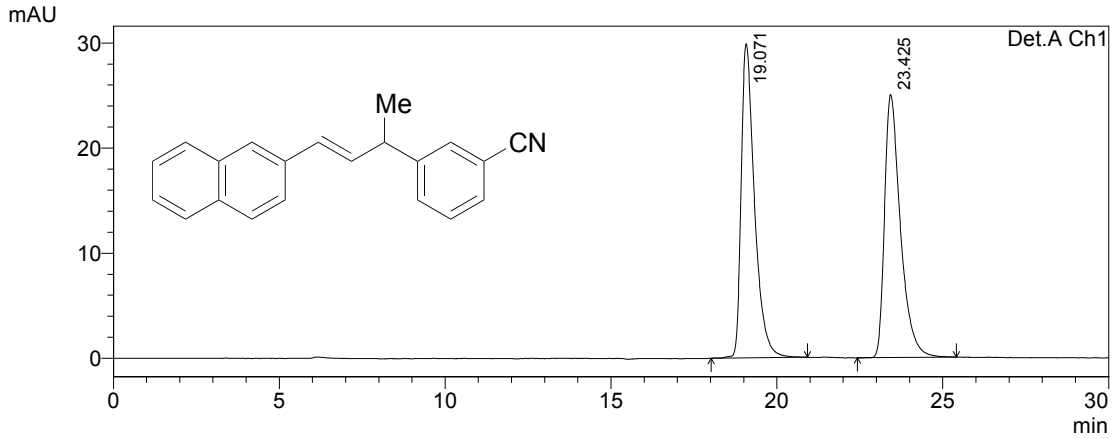
Enantioenriched **3.58** ee = 76%



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.446	1995853	148409	88.115	90.733
2	13.714	269209	15157	11.885	9.267
Total		2265062	163566	100.000	100.000

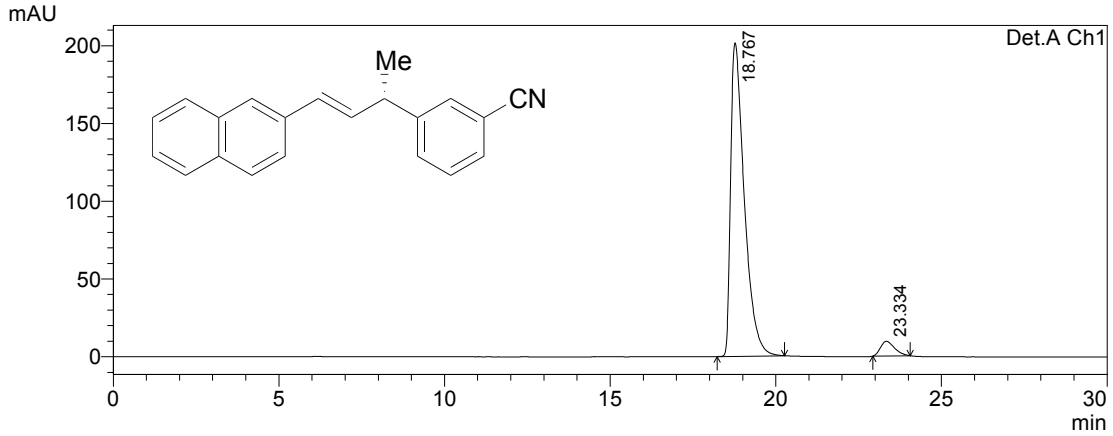
Racemic **3.59**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.071	835245	29879	50.109	54.427
2	23.425	831604	25018	49.891	45.573
Total		1666849	54897	100.000	100.000

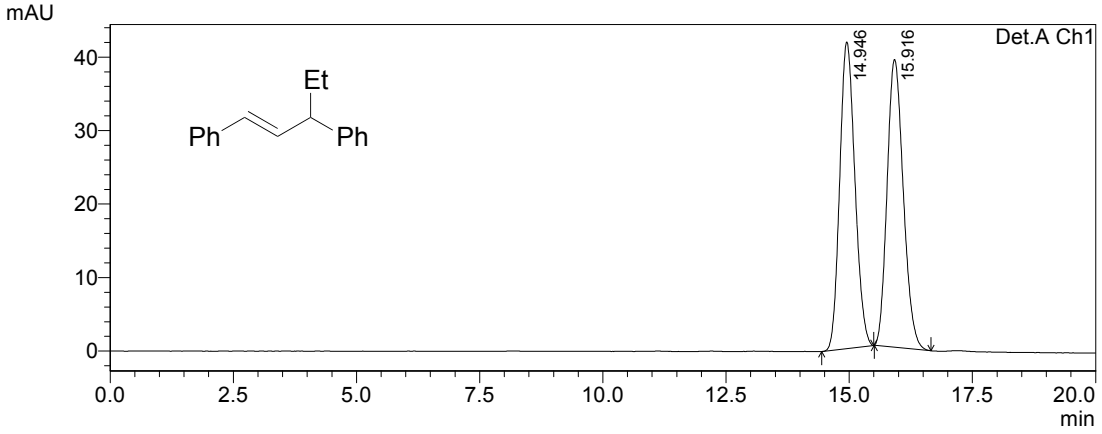
Enantioenriched 3.59 ee = 91%



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.767	5778302	201515	95.422	95.541
2	23.334	277193	9405	4.578	4.459
Total		6055496	210920	100.000	100.000

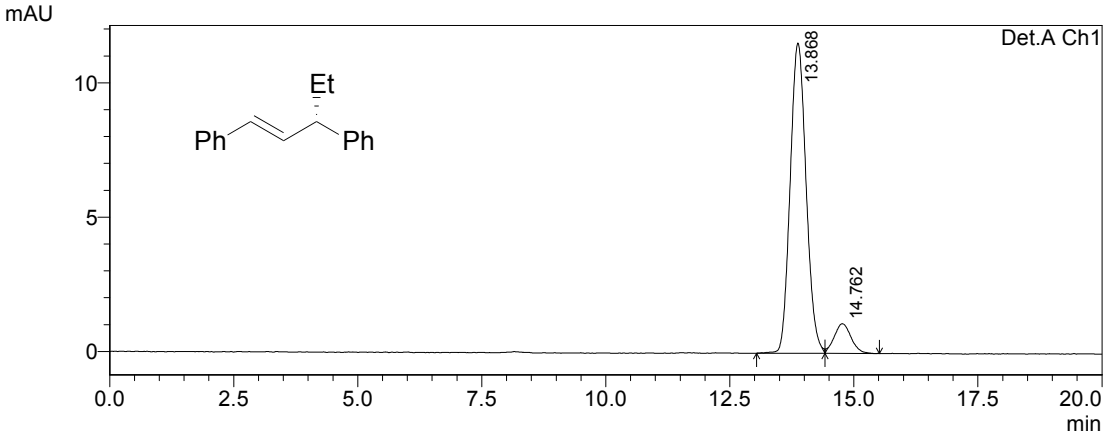
Racemic **3.60**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.946	895104	41713	49.972	51.580
2	15.916	896105	39157	50.028	48.420
Total		1791209	80870	100.000	100.000

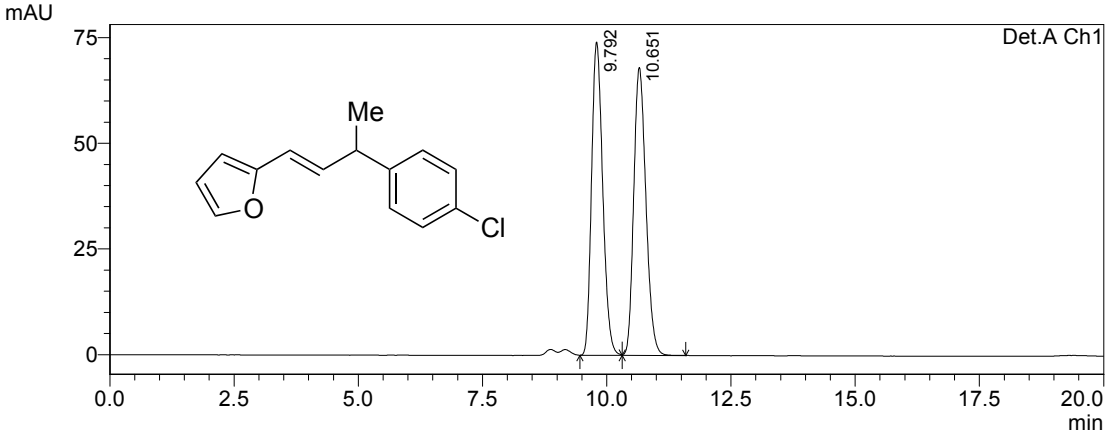
Enantioenriched **3.60**, ee = 82%



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.868	258330	11546	90.794	91.272
2	14.762	26194	1104	9.206	8.728
Total		284524	12650	100.000	100.000

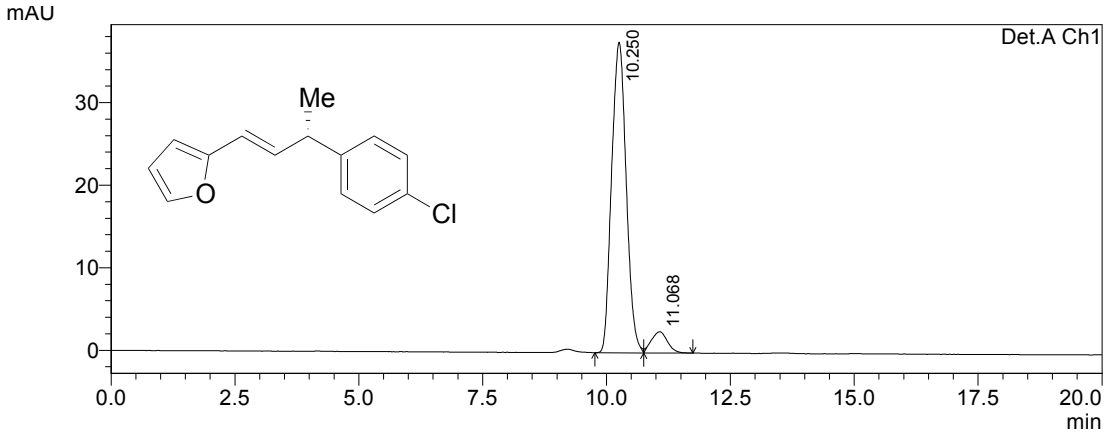
Racemic 3.61



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.792	1156522	74059	49.899	52.103
2	10.651	1161221	68081	50.101	47.897
Total		2317742	142140	100.000	100.000

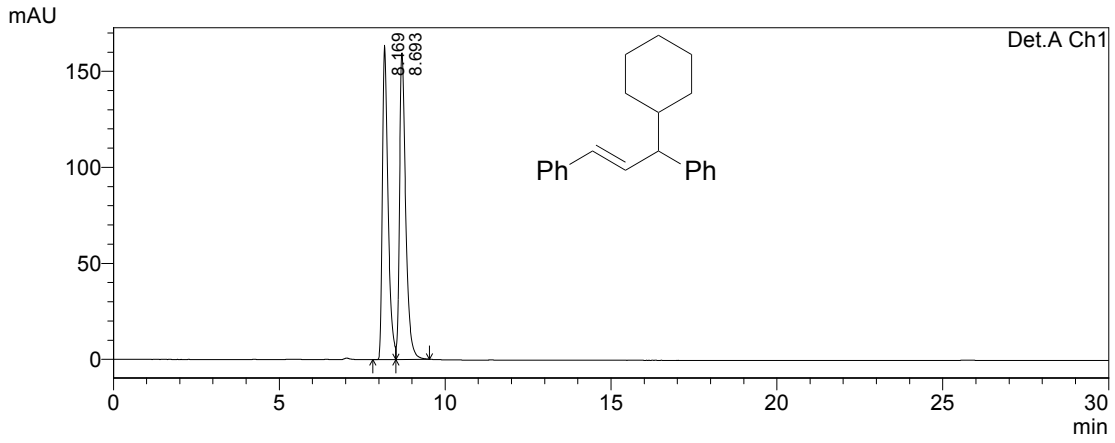
Enantioenriched **3.61** ee = 86%



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.250	771297	37625	92.947	93.597
2	11.068	58527	2574	7.053	6.403
Total		829824	40198	100.000	100.000

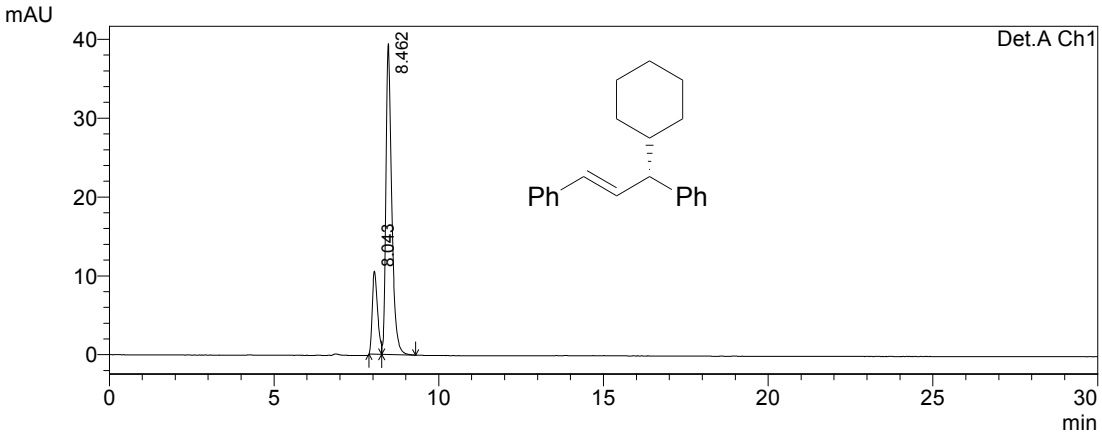
Racemic **3.62**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.169	1940959	163447	48.814	50.644
2	8.693	2035273	159293	51.186	49.356
Total		3976232	322740	100.000	100.000

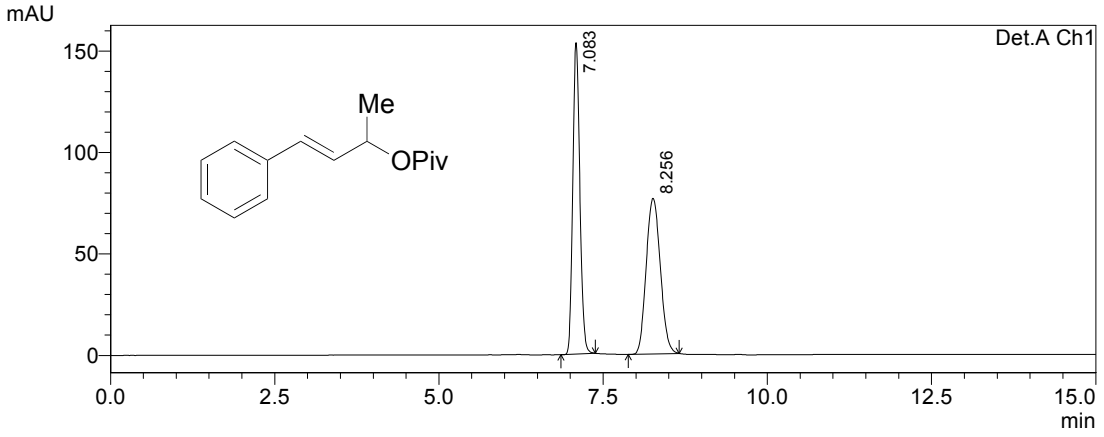
Enantioenriched **3.62** ee, 61%



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.043	116720	10518	19.377	21.073
2	8.462	485645	39394	80.623	78.927
Total		602365	49912	100.000	100.000

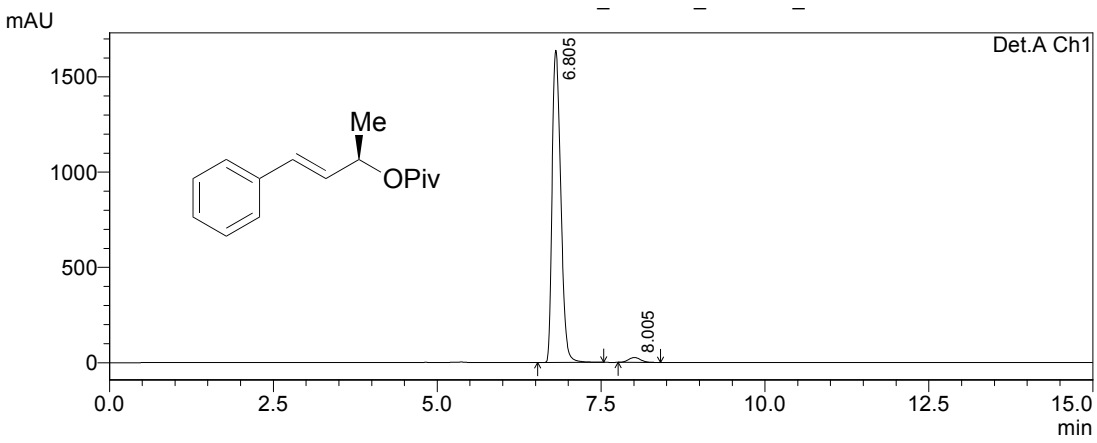
Racemic **3.37**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.083	1148930	153378	50.011	66.649
2	8.256	1148419	76750	49.989	33.351
Total		2297349	230128	100.000	100.000

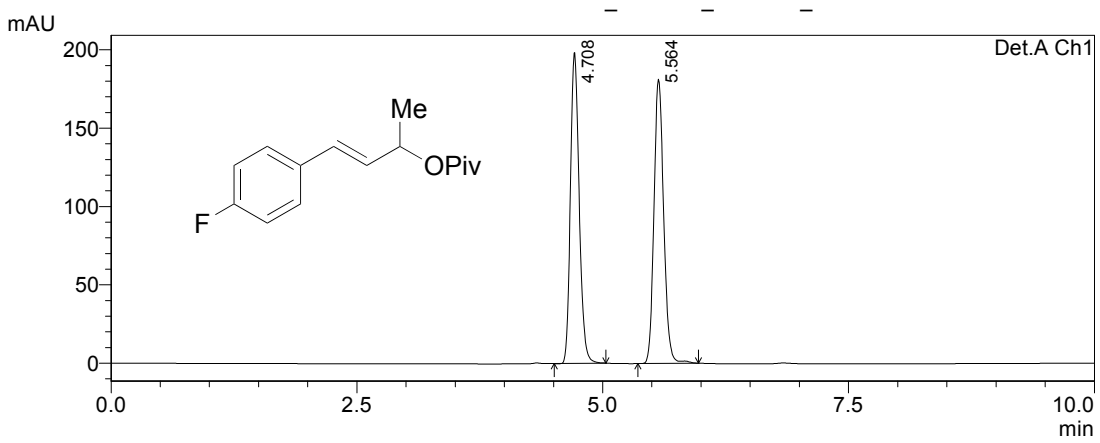
Enantioenriched **3.37**, ee 96 %



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.805	15085485	1638394	97.867	98.461
2	8.005	328742	25601	2.133	1.539
Total		15414227	1663995	100.000	100.000

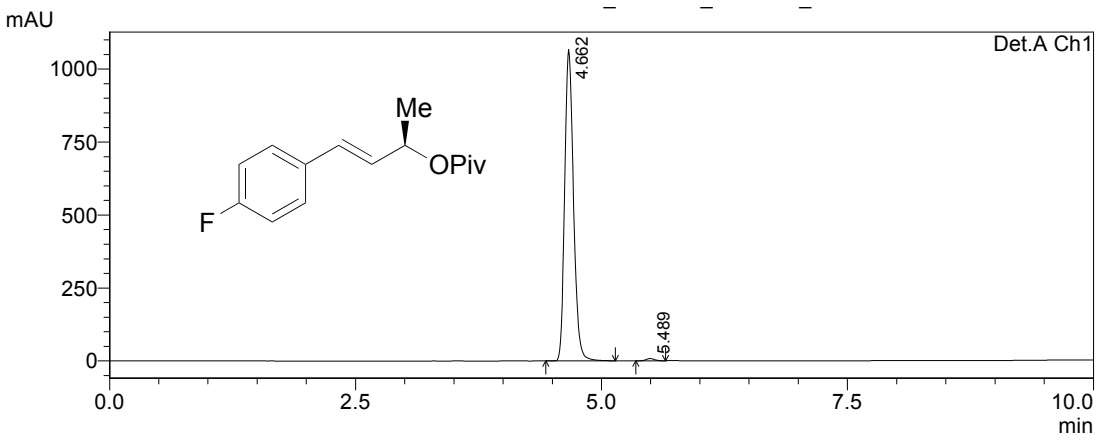
Racemic **3.69**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.708	1233223	198303	49.818	52.220
2	5.564	1242245	181443	50.182	47.780
Total		2475468	379746	100.000	100.000

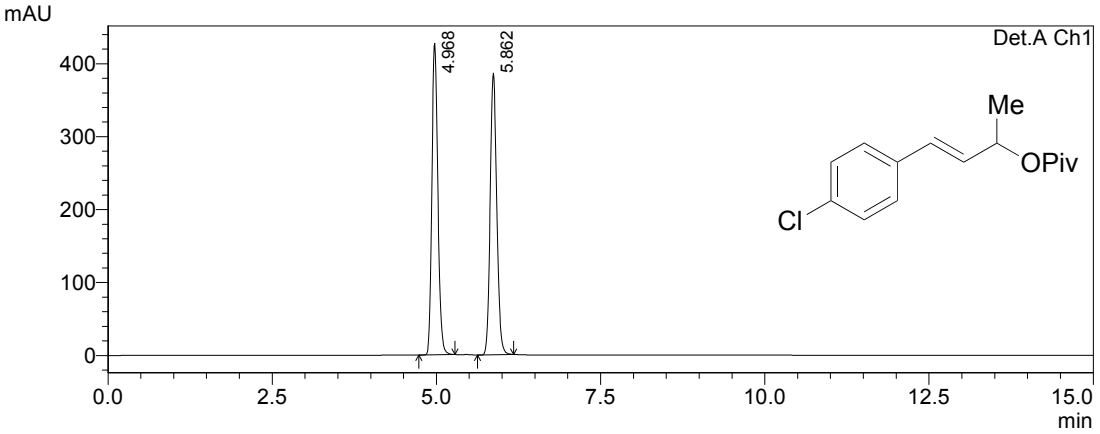
Enantioenriched **3.69**, e =98%



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.662	6650232	1066854	99.298	99.295
2	5.489	47028	7574	0.702	0.705
Total		6697260	1074428	100.000	100.000

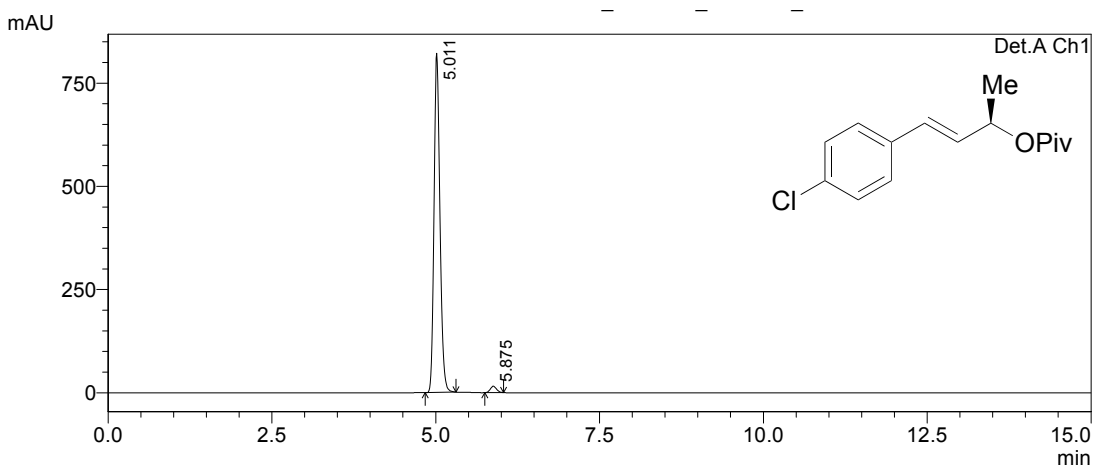
Racemic**3.70**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.968	2698912	427008	50.039	52.519
2	5.862	2694758	386051	49.961	47.481
Total		5393670	813059	100.000	100.000

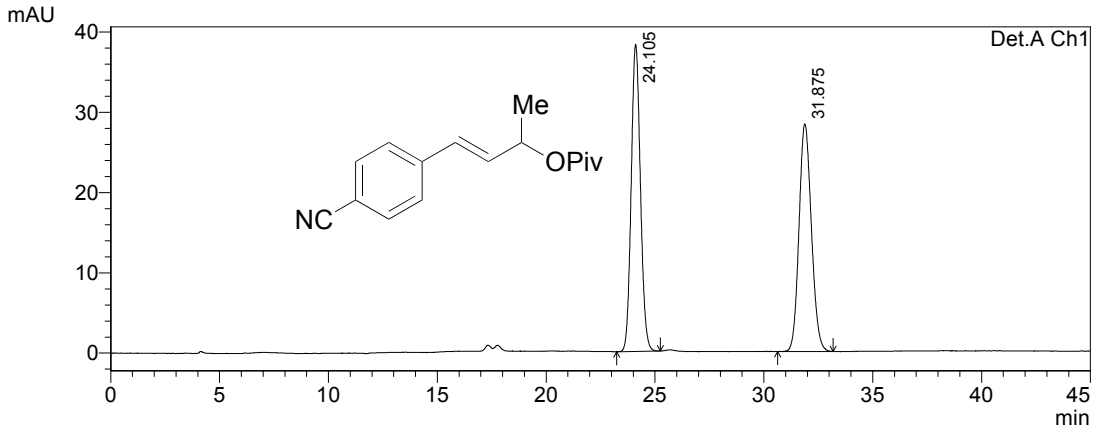
Enantioenriched **3.70**, ee = 96%



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.011	5220879	821541	98.026	98.146
2	5.875	105126	15518	1.974	1.854
Total		5326005	837059	100.000	100.000

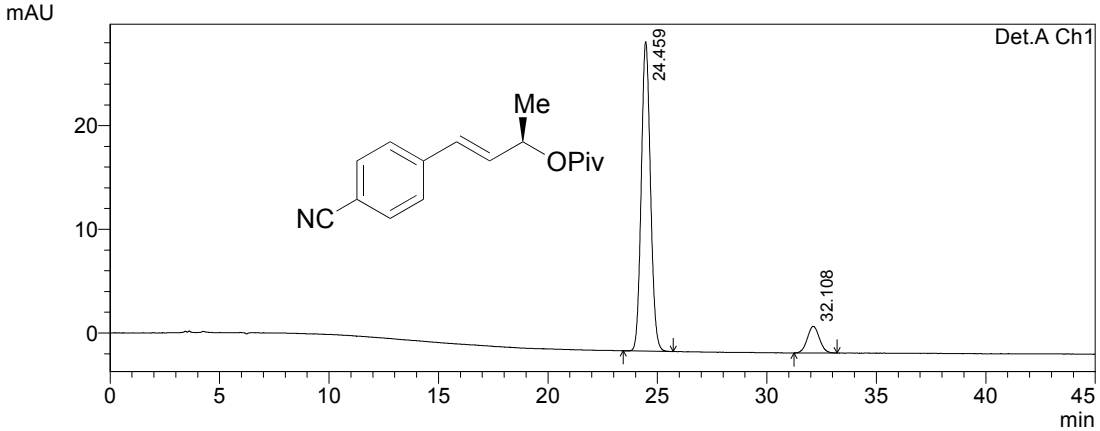
Racemic **3.71**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.105	1125881	38286	50.089	57.434
2	31.875	1121870	28374	49.911	42.566
Total		2247751	66661	100.000	100.000

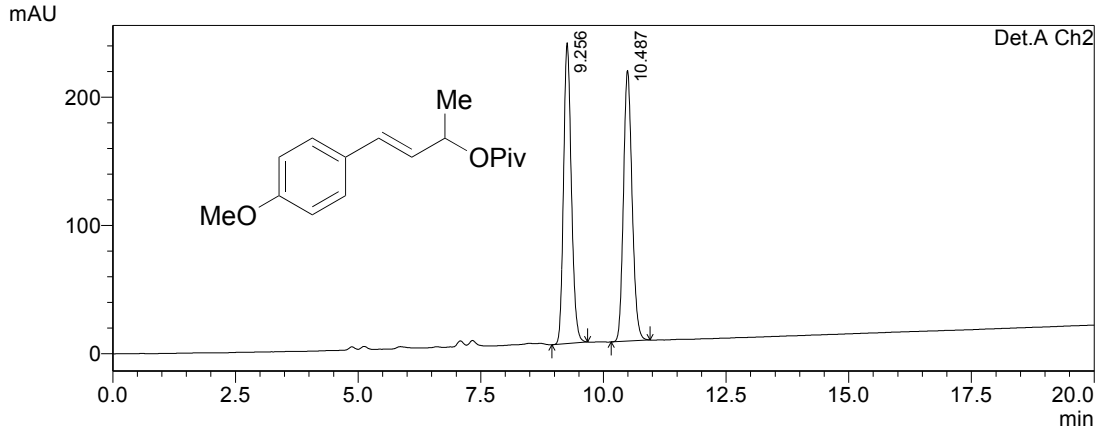
Enantioenriched **3.71** , ee = 80%



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.459	874057	29841	89.821	92.069
2	32.108	99056	2571	10.179	7.931
Total		973112	32411	100.000	100.000

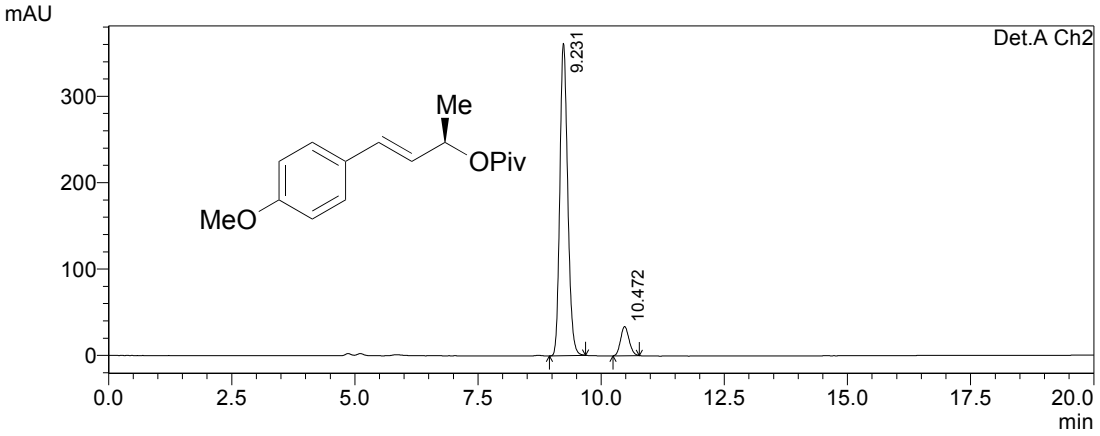
Racemic **3.72**



Detector A Ch2 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.256	2587105	234367	50.020	52.612
2	10.487	2585032	211095	49.980	47.388
Total		5172137	445462	100.000	100.000

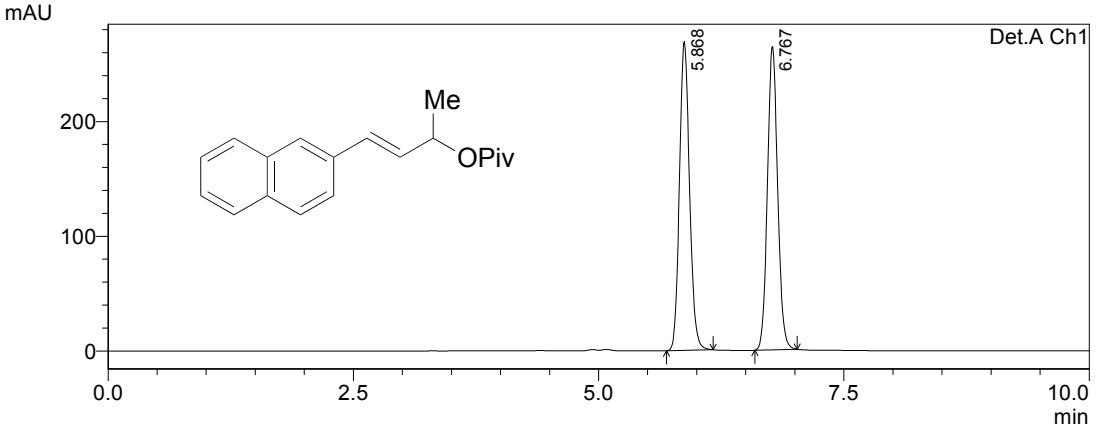
Enantioenriched **3.72** , ee = 82%



Detector A Ch2 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.231	4008739	361390	90.806	91.434
2	10.472	405887	33855	9.194	8.566
Total		4414626	395245	100.000	100.000

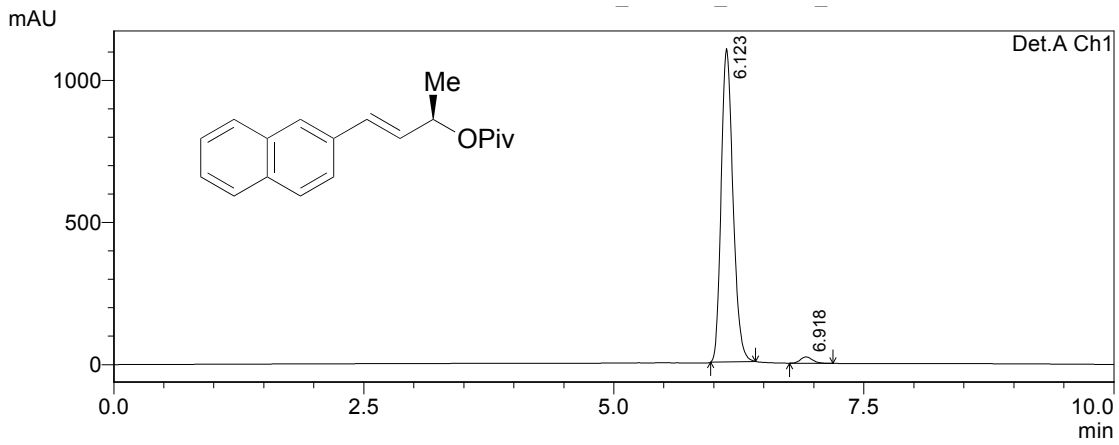
Racemic **3.73**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.868	1927376	269194	50.115	50.459
2	6.767	1918496	264295	49.885	49.541
Total		3845872	533490	100.000	100.000

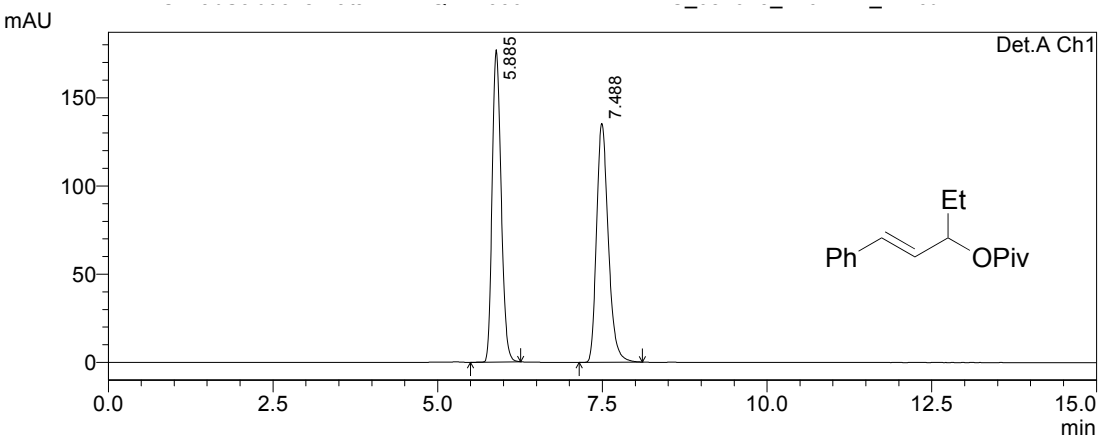
Enantioenriched **3.73**, = 96%



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.123	9044130	1102126	97.972	98.006
2	6.918	187203	22422	2.028	1.994
Total		9231333	1124548	100.000	100.000

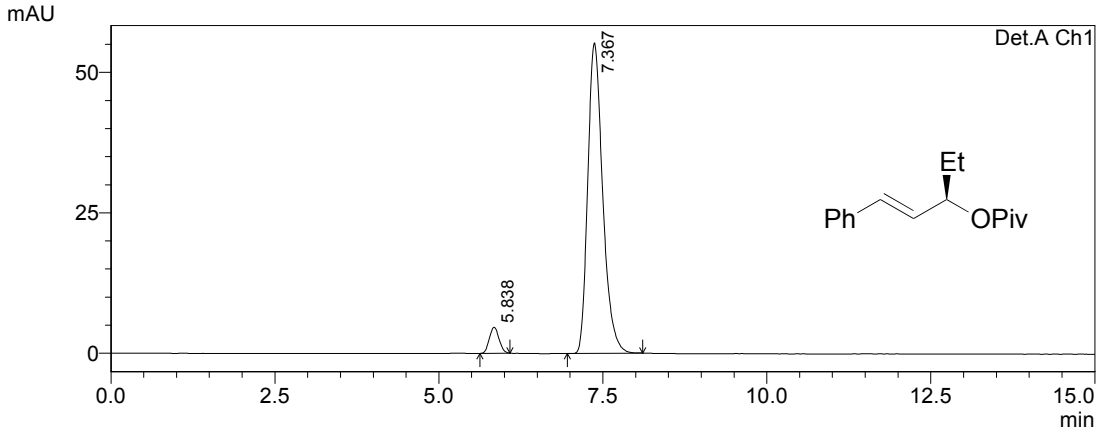
Racemic **3.74**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.885	1677000	176994	50.017	56.641
2	7.488	1675869	135488	49.983	43.359
Total		3352870	312481	100.000	100.000

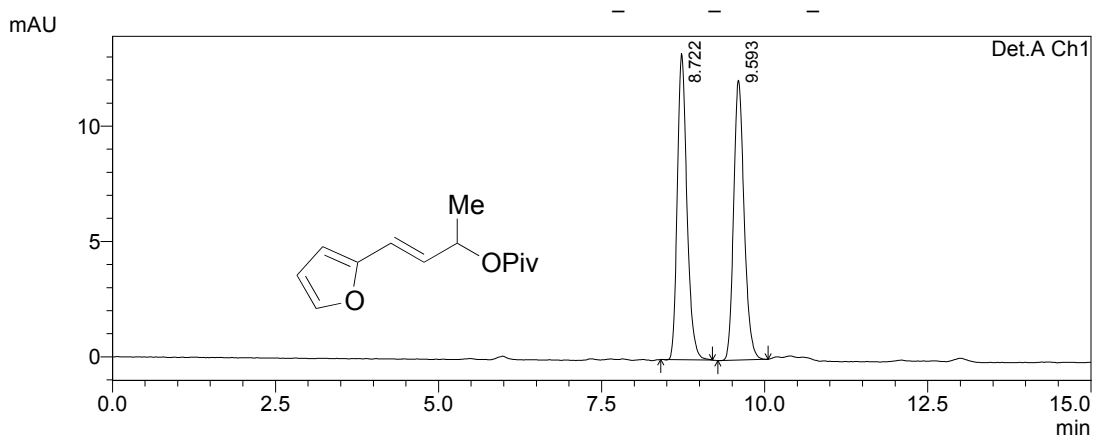
Enantioenriched **3.74**, ee = 90%



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.838	47604	4634	5.158	7.735
2	7.367	875250	55270	94.842	92.265
Total		922854	59903	100.000	100.000

Racemic **3.75**

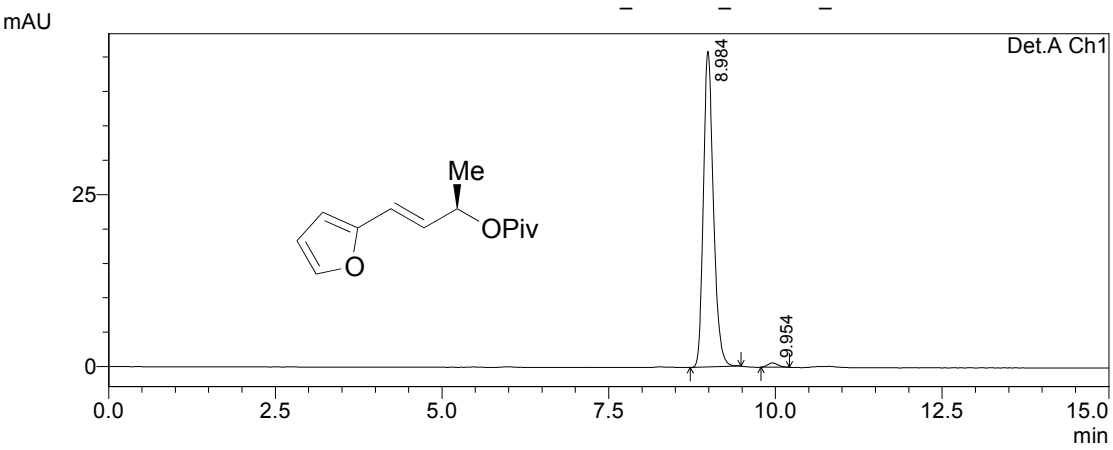


0

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.722	136201	13271	50.103	52.242
2	9.593	135642	12132	49.897	47.758
Total		271843	25403	100.000	100.000

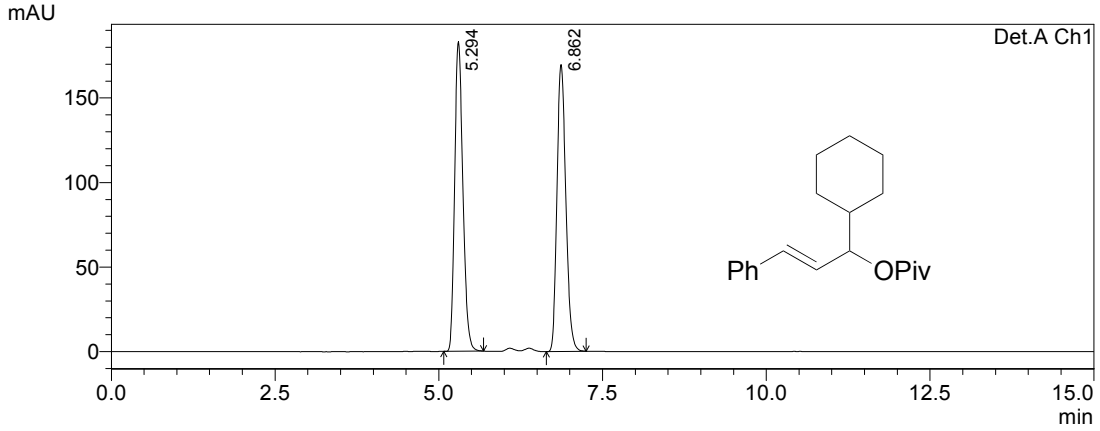
Enantioenriched **3.75** ee = 97%



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.984	480703	45863	98.617	98.634
2	9.954	6741	635	1.383	1.366
Total		487444	46498	100.000	100.000

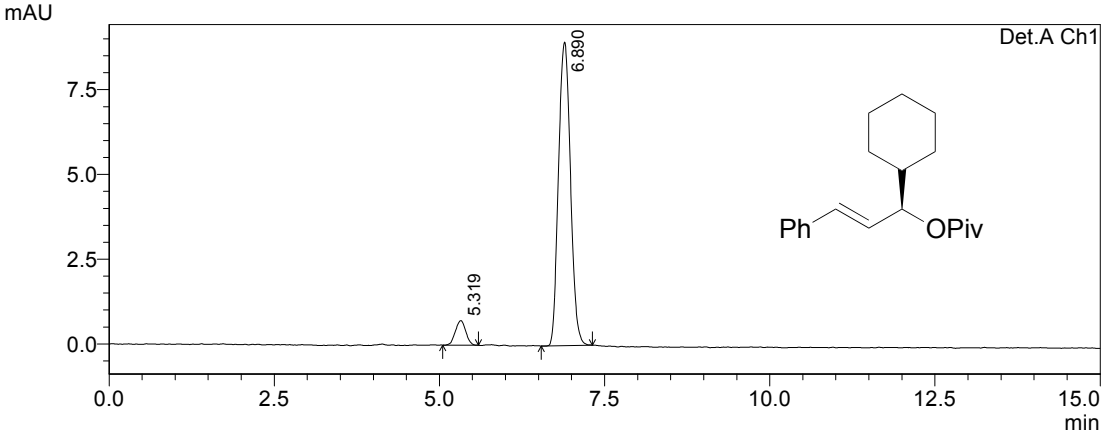
Racemic **3.76**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.294	1600071	183097	50.004	51.903
2	6.862	1599846	169669	49.996	48.097
Total		3199916	352766	100.000	100.000

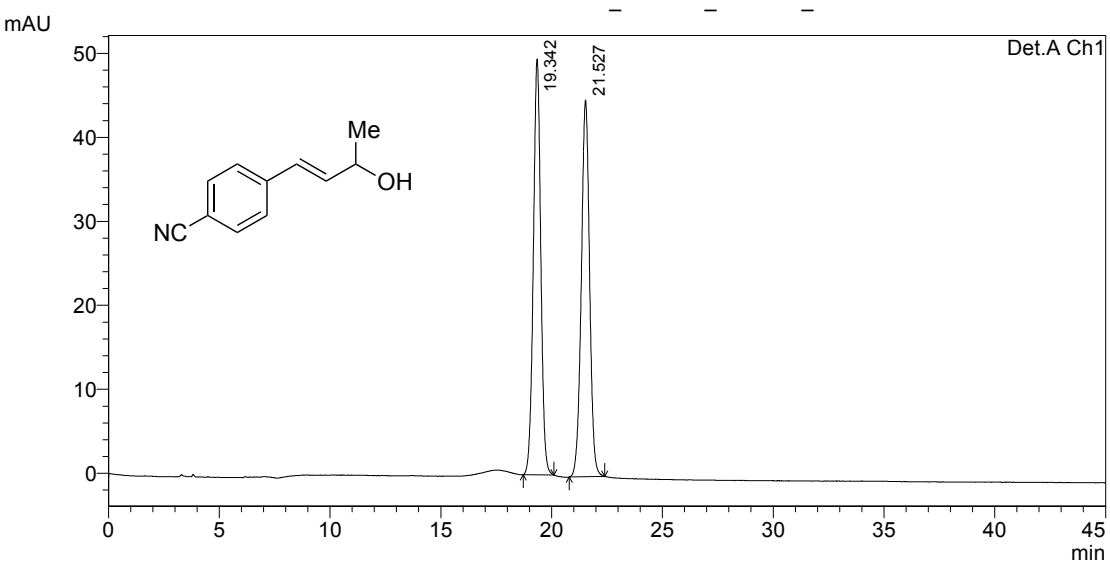
Enantioenriched **3.76**, = 87%



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.319	7957	726	6.585	7.505
2	6.890	112885	8953	93.415	92.495
Total		120842	9680	100.000	100.000

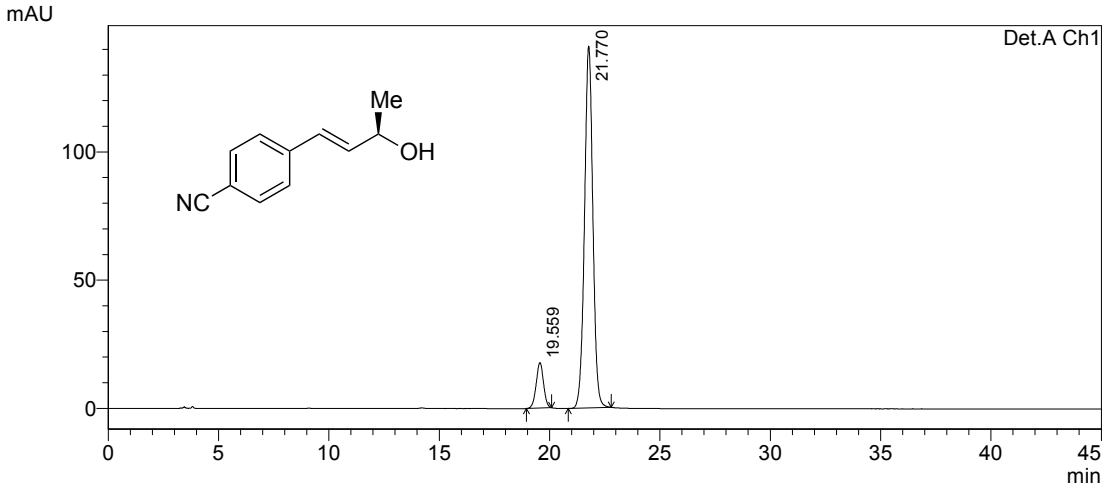
Racemic **3.79**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.342	1155111	49477	49.791	52.459
2	21.527	1164813	44838	50.209	47.541
Total		2319925	94314	100.000	100.000

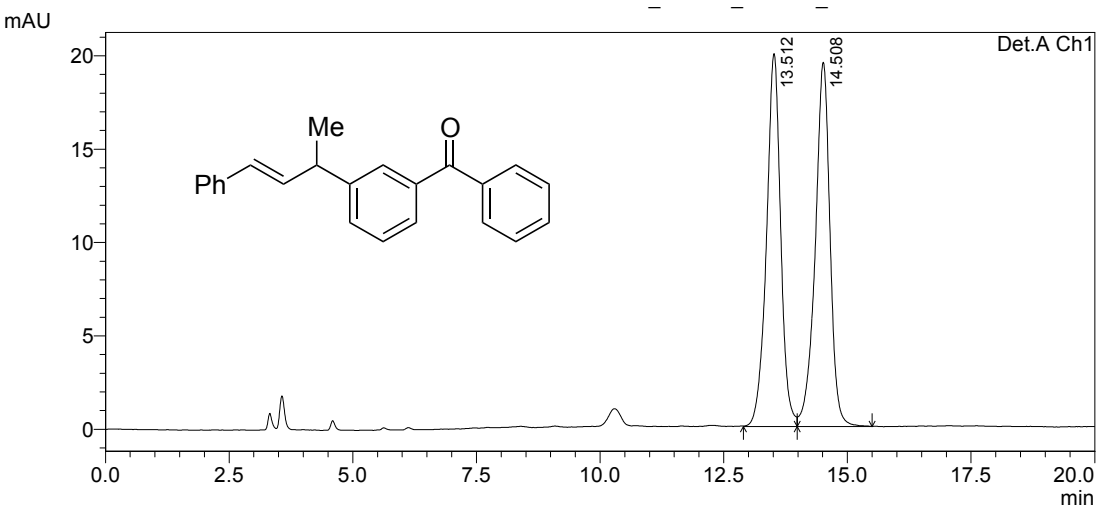
Enantioenriched **3.79**, 80% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.559	411243	17736	9.981	11.160
2	21.770	3708859	141186	90.019	88.840
Total		4120101	158922	100.000	100.000

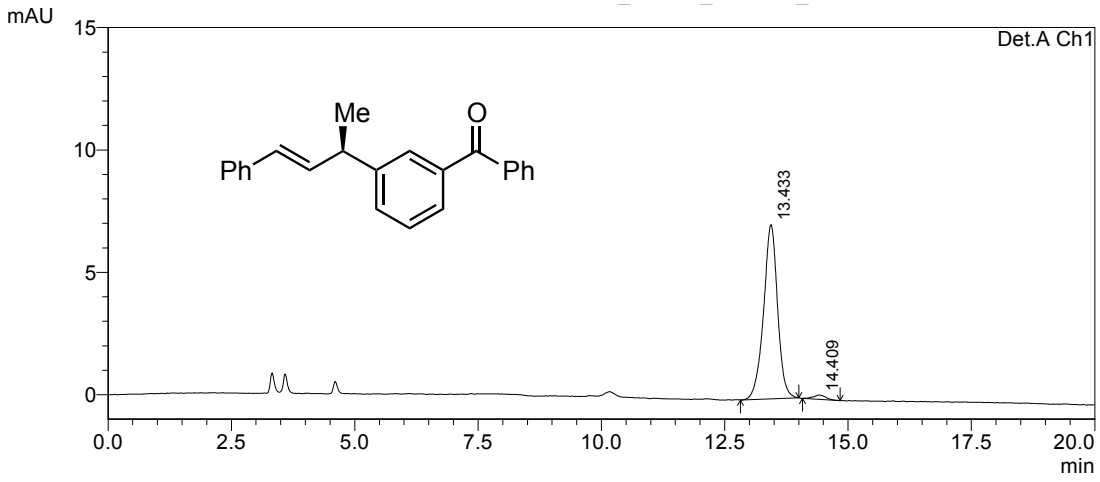
Racemic **3.67**



Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.512	399033	19975	49.585	50.590
2	14.508	405720	19509	50.415	49.410
Total		804753	39484	100.000	100.000

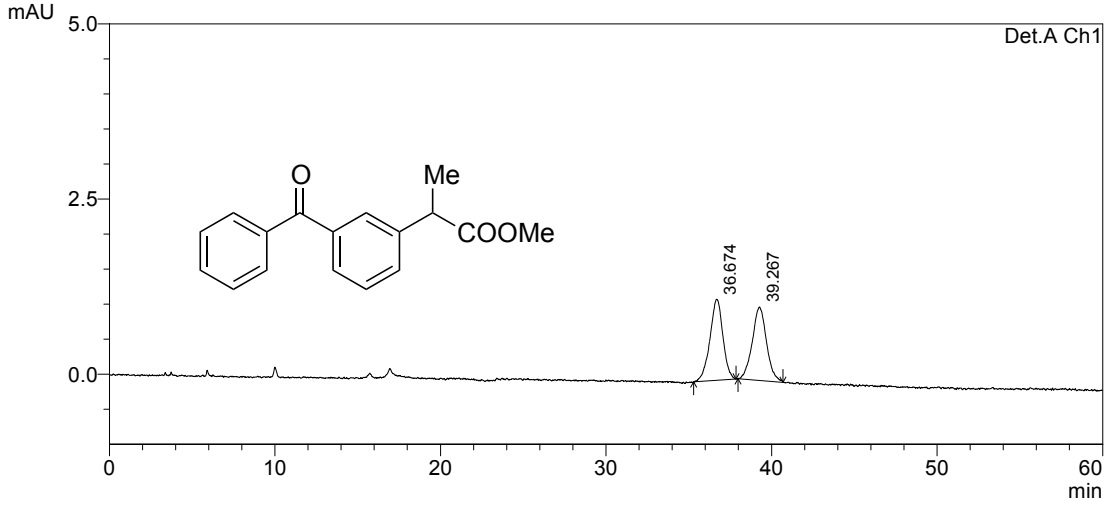
Enantioenriched **3.67**, 95%ee



Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.433	140135	7107	97.873	97.615
2	14.409	3045	174	2.127	2.385
Total		143180	7281	100.000	100.000

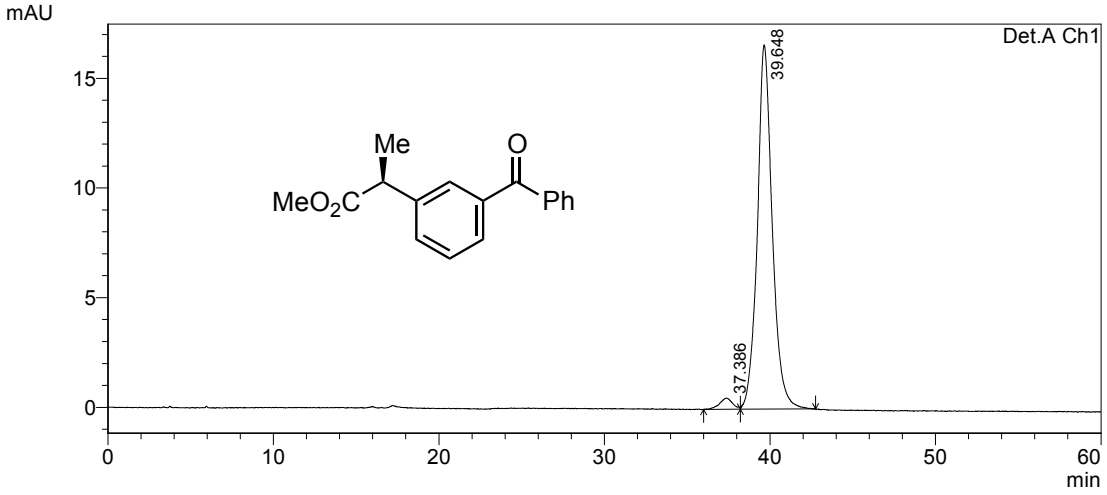
Racemic **3.87**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	36.674	62988	1156	50.223	52.472
2	39.267	62430	1047	49.777	47.528
Total		125418	2203	100.000	100.000

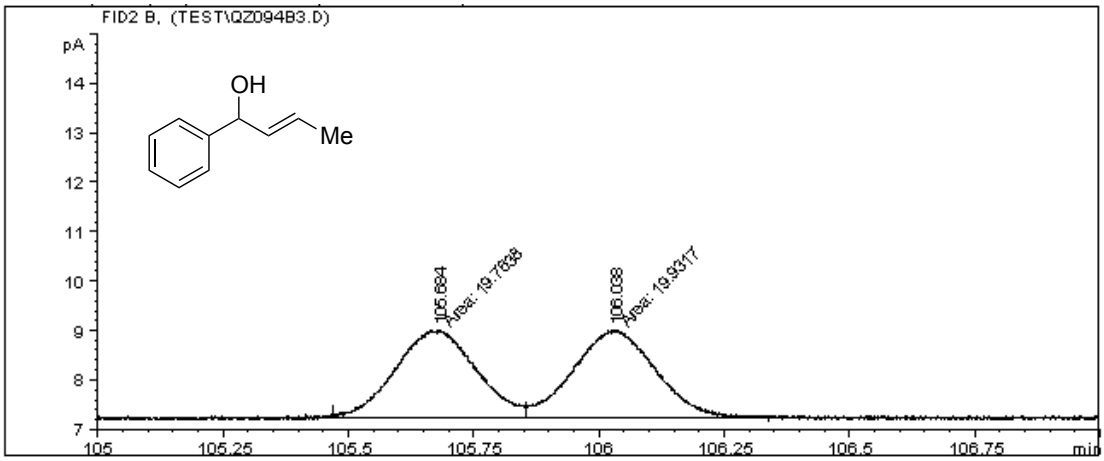
Enantioenriched **3.87** 95% ee



Detector A Ch1 254nm

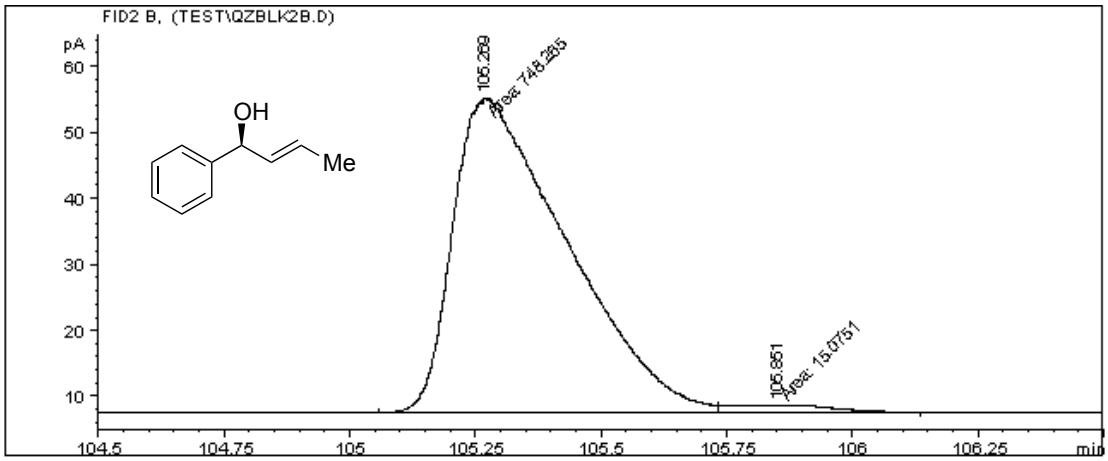
Peak#	Ret. Time	Area	Height	Area %	Height %
1	37.386	27762	513	2.592	2.995
2	39.648	1043427	16616	97.408	97.005
Total		1071188	17129	100.000	100.000

Racemic **3.85**



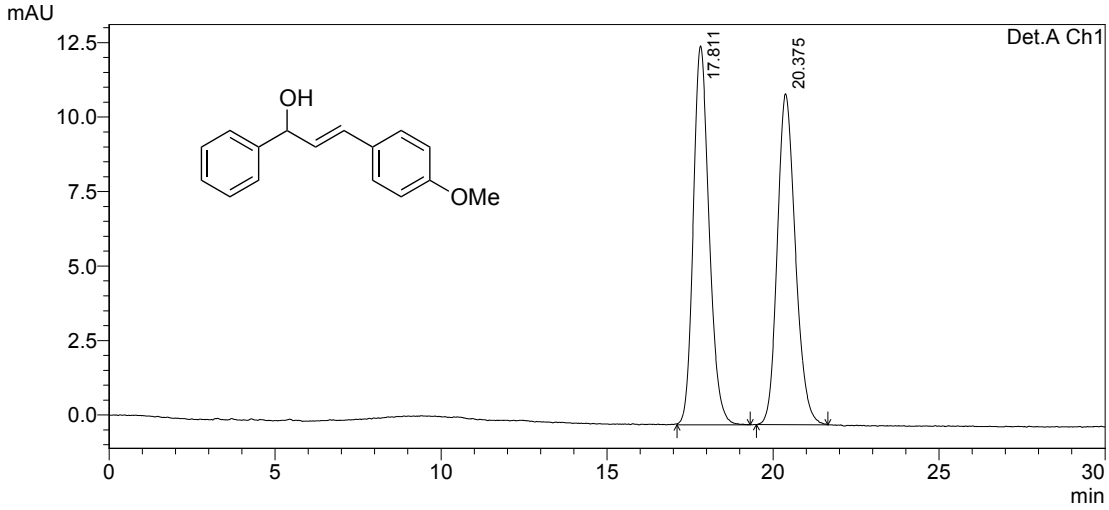
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	105.684	FM	0.1869	19.76379	1.76283	49.78847
2	106.038	FM	0.1888	19.93172	1.75918	50.21153
Totals :				39.69551	3.52201	

Enantioenriched **3.85**, 96% ee



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	105.269	MF	0.2624	748.26532	47.52031	98.02511
2	105.851	FM	0.2294	15.07510	1.09533	1.97489
Totals :				763.34042	48.61564	

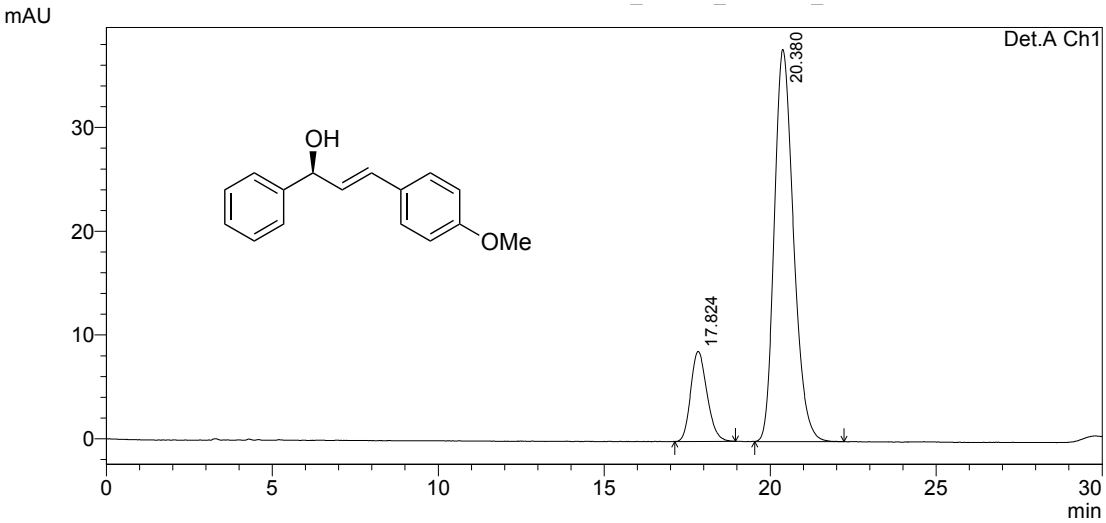
Racemic **3.86**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.811	421028	12719	50.067	53.386
2	20.375	419895	11106	49.933	46.614
Total		840923	23825	100.000	100.000

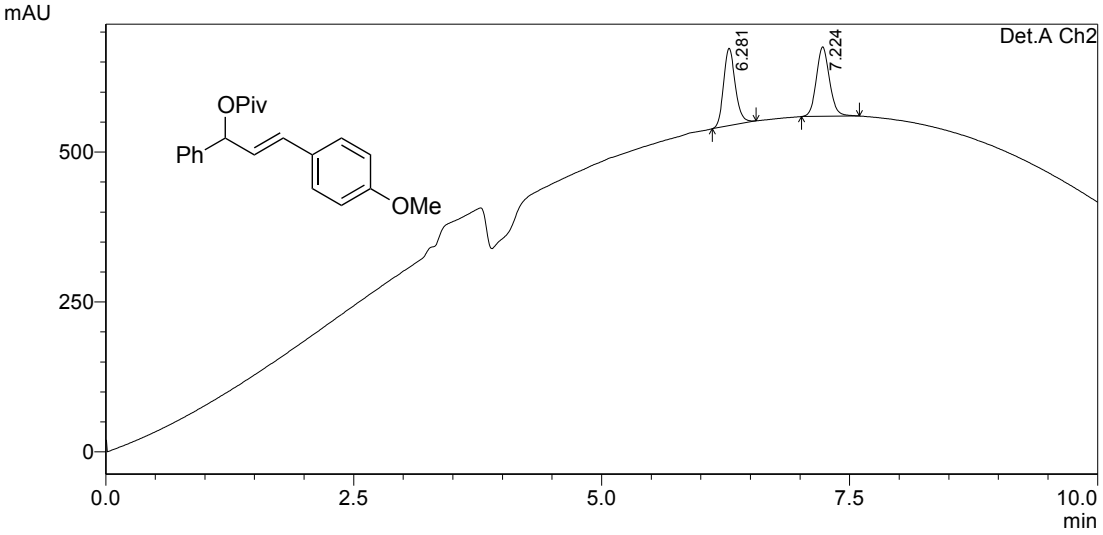
Enantioenriched **3.86** 67% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.824	297238	8687	16.342	18.689
2	20.380	1521674	37796	83.658	81.311
Total		1818913	46483	100.000	100.000

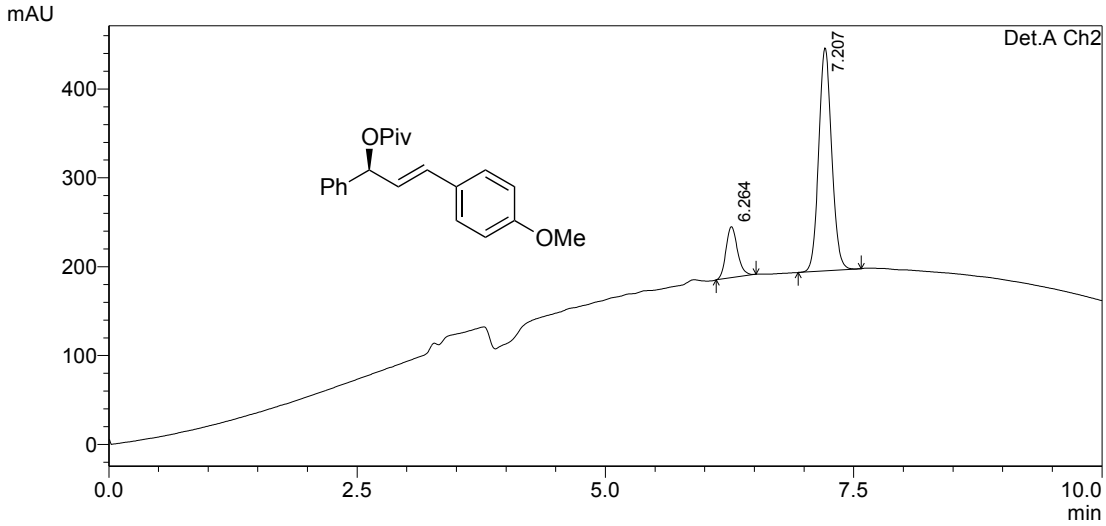
Racemic **3.64**



Detector A Ch2 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.281	1057077	129088	49.605	52.686
2	7.224	1073915	115925	50.395	47.314
Total		2130992	245013	100.000	100.000

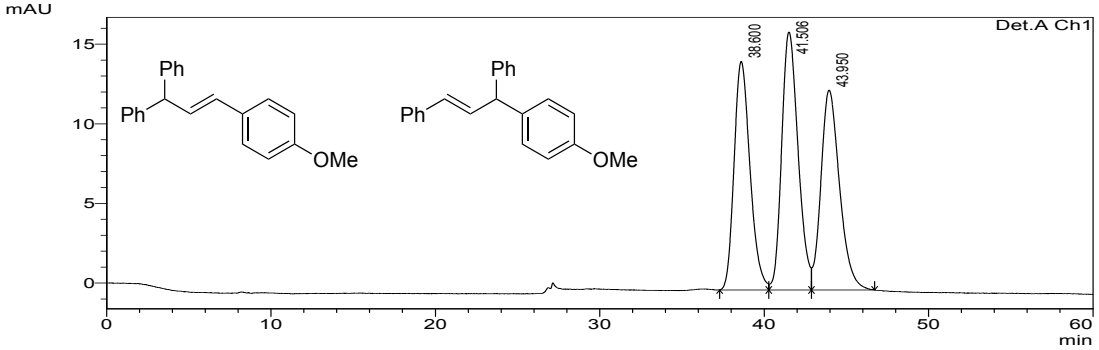
Enantioenriched **3.64**, 66% ee



Detector A Ch2 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.264	463024	57592	16.886	18.670
2	7.207	2279005	250877	83.114	81.330
Total		2742028	308469	100.000	100.000

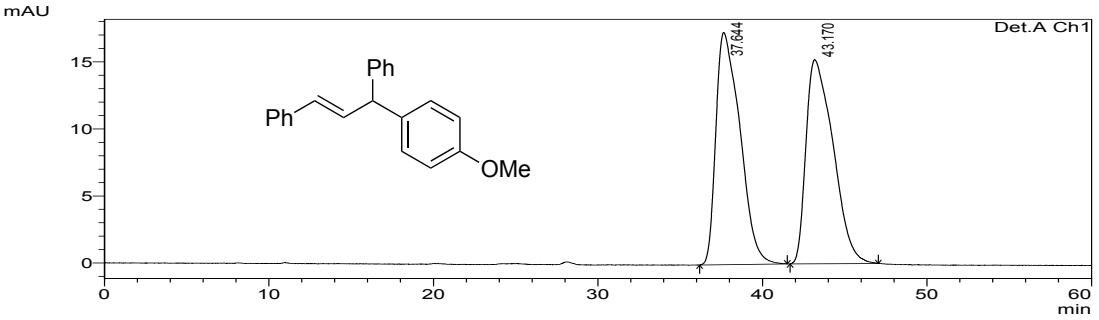
Mixture of **3.65** and Racemic **3.66**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	38.600	968147	14354	31.460	33.306
2	41.506	1121651	16195	36.449	37.578
3	43.950	987549	12548	32.091	29.116
Total		3077347	43098	100.000	100.000

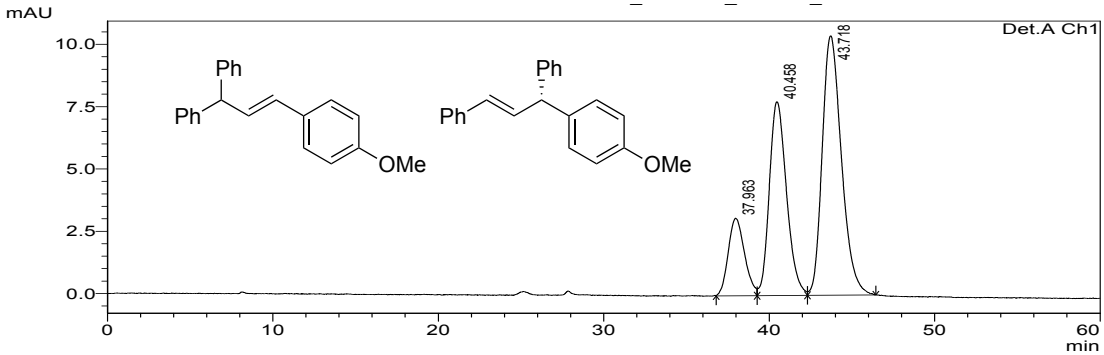
Racemic **3.66**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	37.644	1763496	17331	50.233	53.226
2	43.170	1747151	15230	49.767	46.774
Total		3510647	32562	100.000	100.000

Mixture of **3.65** and Enantioenriched **3.66** (60% ee)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	37.963	213435	3115	13.183	14.627
2	40.458	563166	7775	34.784	36.504
3	43.718	842453	10408	52.034	48.869
Total		1619054	21299	100.000	100.000

APPENDIX D

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Title: Copper-Catalyzed Enantioselective Additions to Oxocarbenium Ions: Alkynylation of Isochroman Acetals

Author: Prantik Maity, Harathi D. Srinivas, and Mary P. Watson

Publication: Journal of the American Chemical Society

Publisher: American Chemical Society

Date: Nov 1, 2011

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Title: Nickel-Catalyzed Cross-Couplings of Benzylic Pivalates with Arylboroxines: Stereospecific Formation of Diarylalkanes and Triarylmethanes

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Author: Qi Zhou, Harathi D. Srinivas, Srimoyee Dasgupta, and Mary P. Watson

Publication: Journal of the American Chemical Society

Publisher: American Chemical Society

Date: Mar 1, 2013

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Title: Enantiospecific, Nickel-Catalyzed Cross-Couplings of Allylic Pivalates and Arylboroxines

Author: Harathi D. Srinivas, Qi Zhou, and Mary P. Watson

Publication: Organic Letters

Publisher: American Chemical Society

Date: Jul 1, 2014

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