STEREOSPECIFIC, NICKEL-CATALYZED CROSS-COUPLINGS OF AMINE AND ALCOHOL DERIVED SUBSTRATES

by

Kelsey M. Cobb

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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TABLE OF CONTENTS

LIST OF TABLES

LIST OF SCHEMES

ABSTRACT

This dissertation focuses on nickel-catalyzed cross-couplings of amine and alcohol derivatives to set stereogenic centers. Chapter 1 focuses on the cross-coupling of benzylic ammonium triflates with aryl, heteroaryl, and vinyl boronic acids. This method expands the scope of previous methods from our group, utilizing $Ni(cod)_2$ without any additional phosphine or N-heterocyclic carbene (NHC) ligands. This reaction allows for cross-coupling of both naphthyl and phenyl substituted ammonium salts. The mild conditions of this reaction displays excellent functional group tolerance.

Chapter 2 focuses on the cross-coupling of benzylic ammonium triflates with bis(pinacolato)diboron to afford secondary benzylic boronates with excellent chirality transfer, This reaction utilizes $Ni(cod)_2$ as a catalyst with either phosphine or NHC ligands. The reaction proceeds with mild reaction conditions and excellent functional group tolerance. It allows for the cross-coupling of both naphthyl and phenyl substituted ammonium salts. This is the first example of a Miyaura borylation of a non-allylic electrophile to deliver products in highly enantioenriched form.

Chapter 3 describes the development of the cross-coupling of tertiary benzylic acetates to form all-carbon quaternary stereocenters. This reaction prioritizes the use of an air-stable nickel(II) catalyst and environmentally friendly 2-Me-THF. The mild reaction conditions allow for excellent functional group tolerance. The reaction provides an efficient route to both di-aryl and tri-aryl quaternary stereocenters in high stereochemical fidelity. This method shows an expansion in transition metal catalysis to go beyond electrophiles adjacent to functional groups such as carbonyls and alkenes, and displays the possibility for tertiary benzylic electrophiles to under go transition metal catalysis.

Chapter 4 focuses on the cross-coupling of enantioenriched allylic pivalates with aryl and heteroaryl borxines to form allylic, all-carbon quaternary stereocenters. This utilizes an air-stable nickel (II) catalyst, and functional group tolerant boroxine coupling partners to afford these quaternary stereocenters with high stereochemical fidelity. This reaction provides a powerful way to readily access allylic quaternary stereocenters with substituted internal alkenes and a variety of functional groups and heteroatoms in high yield and enantioenrichment

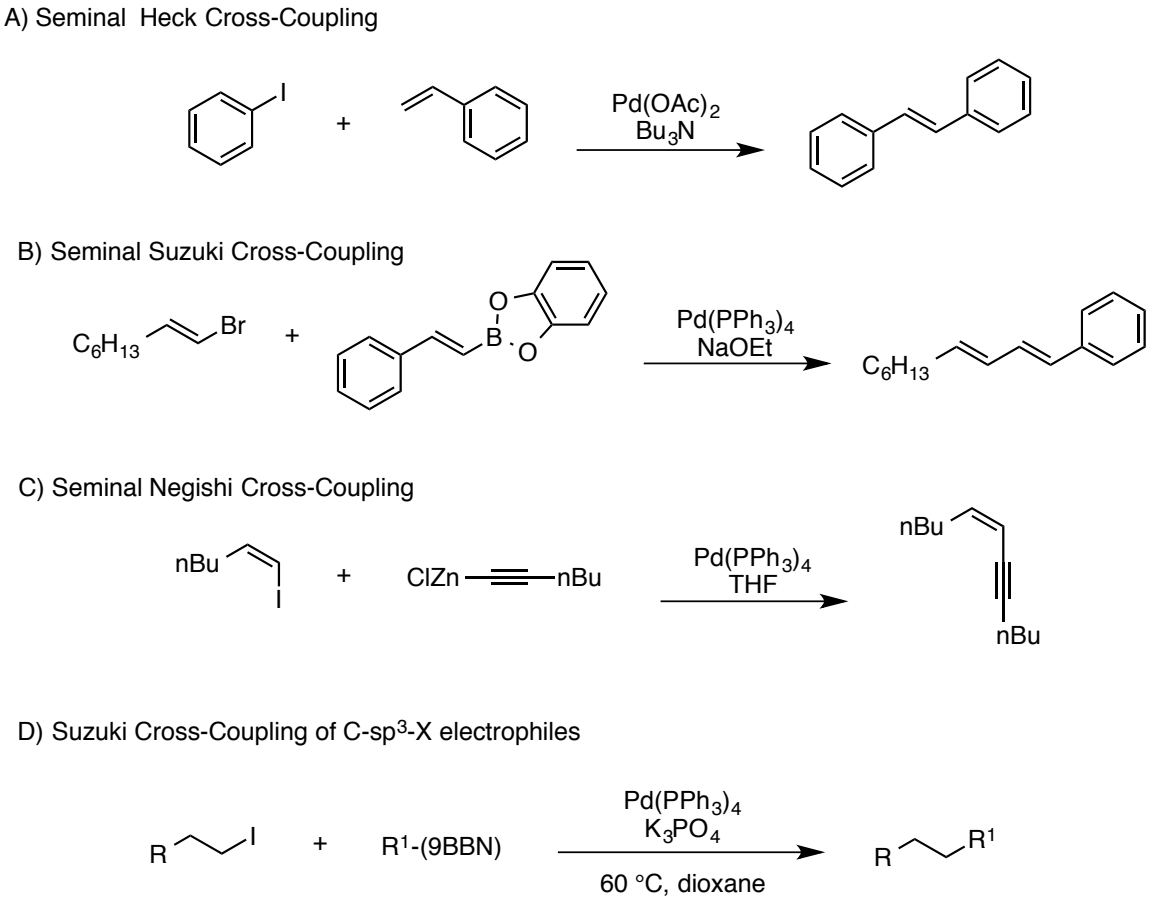
Chapter 1

A GENERAL, SIMPLE CATALYST FOR ENANTIOSPECIFIC CROSS-COUPLINGS OF BENZYLIC AMMONIUM TRIFLATES AND BORONIC ACIDS: NO PHOSPHINE LIGAND REQUIRED

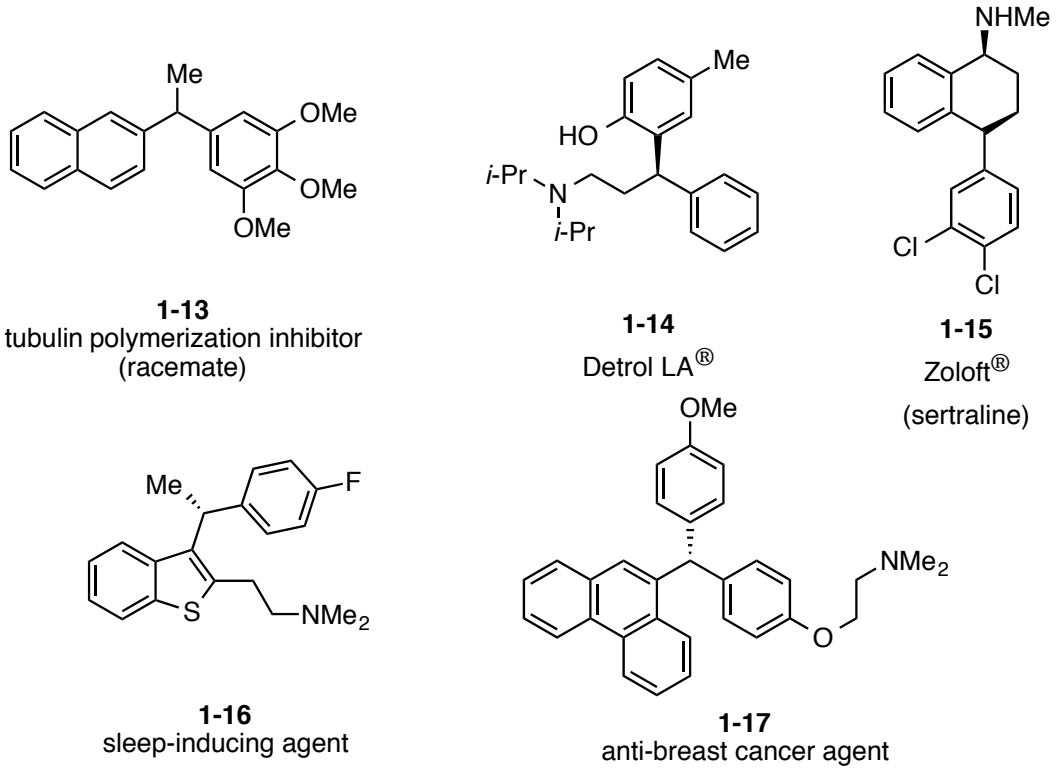
1.1 Introduction

Throughout this thesis my work has focused on utilizing non-traditional electrophiles in transition metal-catalyzed cross-couplings. The power of transition metal-catalyzed cross-coupling reactions has been recognized with the 2010 Nobel Prize in Chemistry awarded to Heck (Scheme 1-1A), Suzuki (Scheme 1-1B), and Negishi (Scheme 1-1C). [1] These reactions utilize a palladium catalyst in order to form new carbon-carbon bonds via activation of a Csp^2-X (X=I or Br) bond. The expansion of these methods to Csp^3-X allows for more complexity in the molecule, as well as the possibility of a stereocenter. Toward this goal Suzuki first showed the cross-coupling an alkyl iodide with alkyl 9-BBN reagents (Scheme 1-1D).[2] This work displays the powerful opportunities in transition metal-catalyzed cross-couplings of sp^3-hybridized electrophiles.

Scheme 1-1 Seminal Publications in Transition Metal-Catalyzed Cross-Couplings



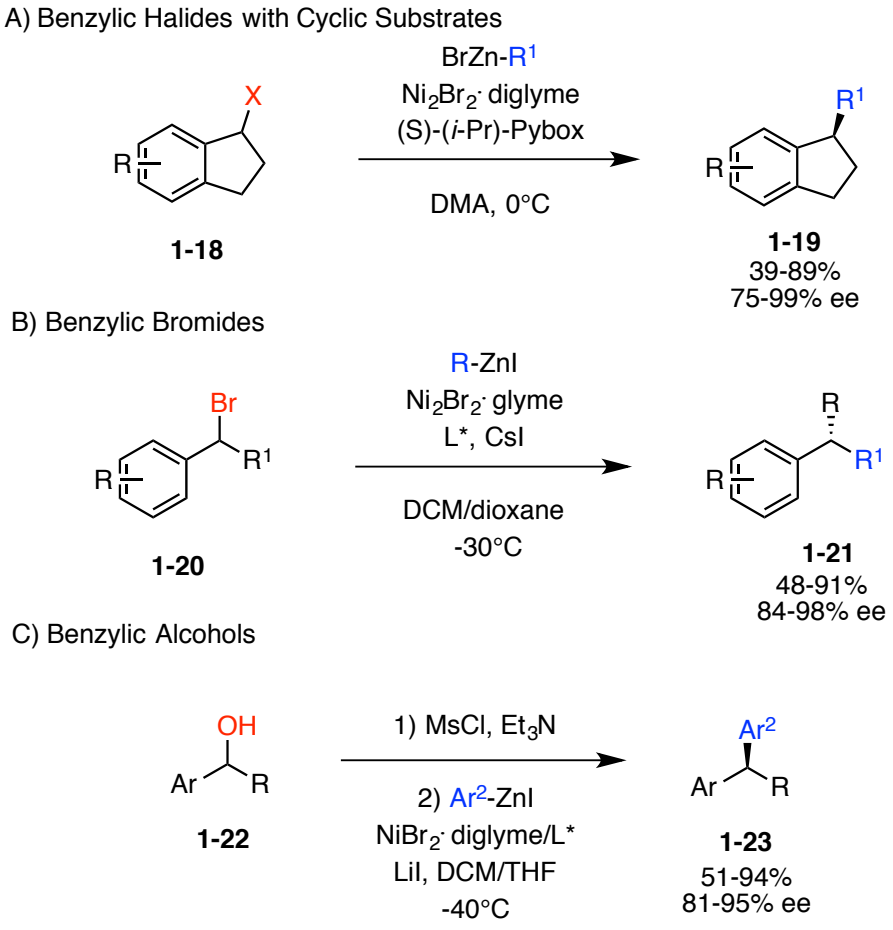
A powerful application of transition metal-catalyzed cross-couplings would be to produce diaryl and triaryl alkanes. Diaryl and triaryl alkanes are important motifs in molecules with potential applications in both pharmaceutical and materials science (Figure 1-1). Previously, there have been a variety of methods for cross-coupling of benzylic substrates in both enantioselective and enantiospecific transformations.



Scheme 1-2 Examples of Bioactive Diaryl and Triaryl Alkanes

Fu has demonstrated enantioselective nickel-catalyzed cross-couplings of either benzylic halides (Scheme 1-2A and 1-2B) or alcohols (Scheme 1-2C) with organozinc nucleophiles.[3] In the case of the reaction with benzylic alcohols, the mesylate is formed in situ and LiI (4.0 equiv) is necessary in order to go through a benzylic iodide intermediate. These reactions rely on chiral oxazoline ligands to afford the tertiary benzylic stereocenters in high yield and enantioenrichment. However this chemistry is limited in functional group compatibility due to the highly reactive nature of zinc nucleophiles.

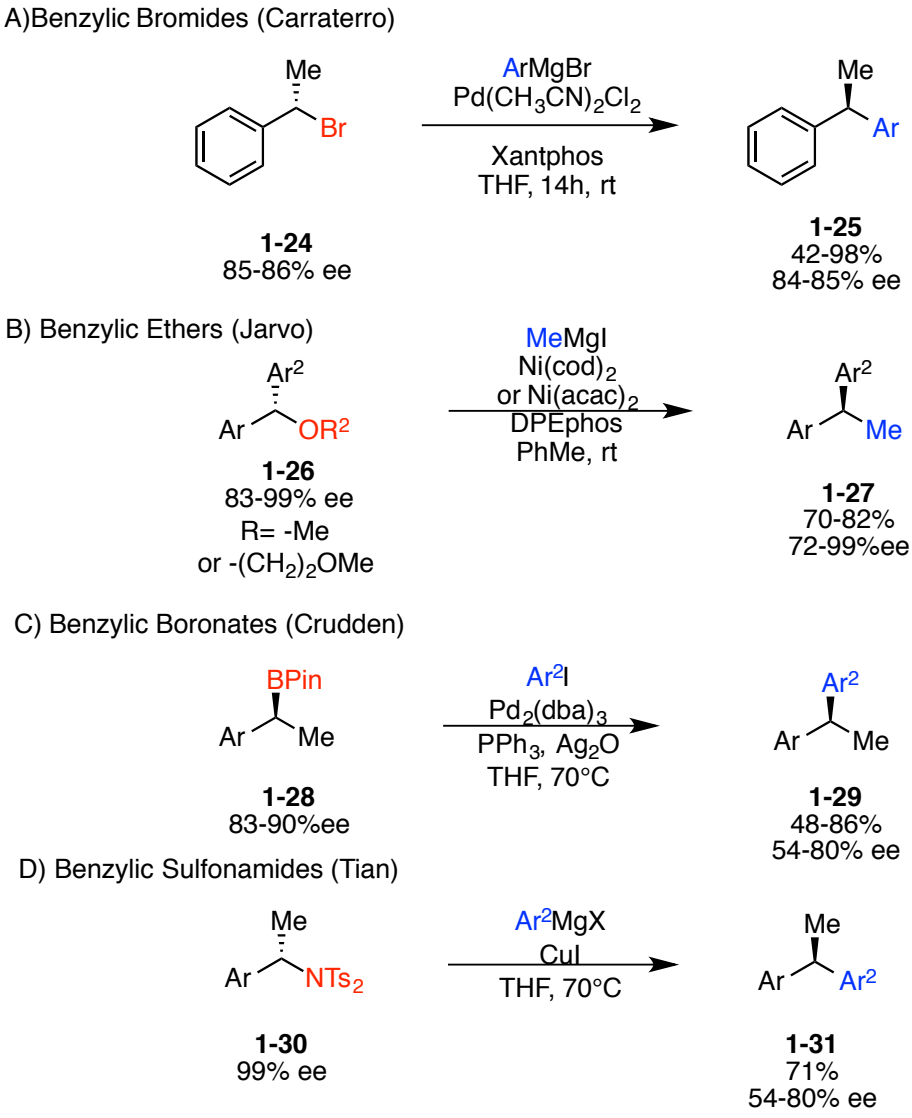
Scheme 1-3. Prior Art in Enantioselective Transition Metal-Catalyzed Cross-Couplings to Form Tertiary Stereocenters



With respect to enantiospecific cross-couplings, a number of substrates have been utilized. The Carratero group has shown that they can transform benzylic bromides into enantioenriched diaryl alkanes with a palladium catalyst and Grignard nucleophiles (Scheme 1-4A).[4] However, this chemistry is limited due to the high reactivity of their bromide starting materials. This high reactivity makes them readily decompose, which makes poor candidates for late-stage transformations. In order to circumvent the difficulty of using benzylic halides, the Jarvo group has developed methods that utilize benzylic alcohol derivatives (Scheme 1-4B).[5] These reactions

allow for late-stage transformations with alcohols that are readily accessible in highly enanantioenriched fashion. However, this chemistry is still limited in its functional group tolerance due to the use of harsh nucleophiles such as Grignard reagents as the coupling partner. The Crudden group has shown that the umpolung approach can be used with enantioenriched secondary boronic esters and aryl halides (Scheme 1-4C).[6] However, this chemistry suffers from a lack of efficient ways to form enantioenriched boronic esters. Inspiration for our group came from prior work from the Tian group (Scheme 1-4D). They demonstrated a copper-catalyzed cross-coupling of benzylic sulfonamides to form diaryl alkane products. However, they only show one example of an enantioenriched benzylic sulfonamide, and its reaction provided the product with very low stereochemical fidelity. However, this result did inspire us to use benzylic amines as electrophiles for a Suzuki cross-coupling due to the fact that they are readily accessible in high enantioenrichment.

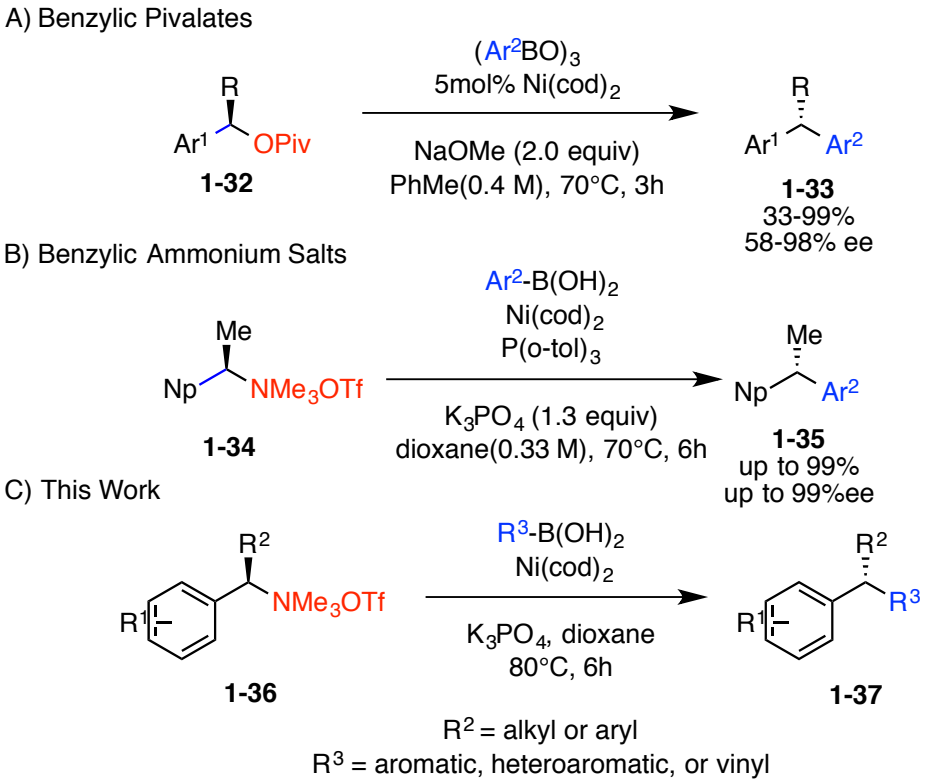
Scheme 1-4. Prior Art in Enantiospecific Transition-Metal Catalyzed Cross-Couplings to Form Tertiary Stereocenters



Previously the Watson group has developed Suzuki cross-coupling conditions that utilized either benzylic ammonium triflates (Scheme 1-5B)[7] or pivalates[8] (Scheme 1-5A) with arylboron reagents as a convenient, functional group tolerant, and highly stereospecific method to form diaryl and triaryl alkanes. These reactions represented some of the first cross-couplings of benzylic electrophiles with aryl

boronic reagents. However, significant limitations were observed, particularly in the aryl substituent of the benzylic electrophile; high yields were only observed with extended aromatic substituents, such as naphthyl. In addition, for benzylic ammonium salts, only methyl substitution was examined at the benzylic position. The substrate scope is also limited in terms of vinyl or heteroaromatic boronic acids as cross-coupling partners.

Scheme 1-5 Previous Stereospecific Suzuki Cross-Couplings from Our Group



In order to overcome these limitations, I collaborated with my colleague Danielle Shacklady McAtee. We have developed a second-generation catalyst system for the enantiospecific nickel-catalyzed Suzuki cross-coupling of benzylic ammonium triflates. This second-generation catalyst expands the scope to include non-extended

π-substituents on the benzylic ammonium salt, a variety of substituents (R^2) at the benzylic position, and vinyl and heteroaromatic boronic acids as coupling partners.

1.2 Results and Discussion

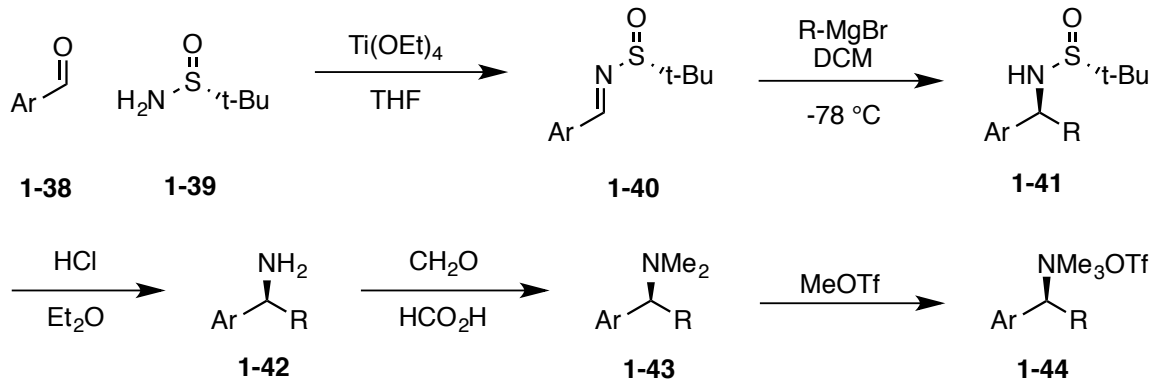
Synthesis of Benzylic Ammonium Salts

Enantioenriched benzylic ammonium triflates were prepared in one of two ways; either from commercially available primary amines or from the corresponding aldehyde. For amines that were not commercially available, the synthesis began with the condensation of (*R)*-2-methyl-2-propanesulfonamine and the appropriate aldehyde with titanium tetraethoxide as Lewis acid (Scheme 1-6). With the sulfimine **1-40** in hand, a Grignard reagent was added slowly to maximize the diastereoselectivity of the reaction. The diastereomers were separated via column chromatography to give a single diastereomer of **1-41,** as judged by ^{1}H NMR. Due to the absence of the minor diastereomer by ^{1}H NMR, I estimated the dr to be at least 95:5. Deprotection of the amine then afforded primary benzylic amine **1-42** in 95% ee. From this point, the synthesis of both commercially available and synthesized primary amines was the same. Using Eschenweiler-Clark conditions, the primary amines were heated with formic acid and formaldehyde to afford tertiary amines 1-**43**. These products were then purified via silica gel chromatography or distillation.

Subsequent methylation was achieved via slow addition of methyl triflate at 0 °C. In most cases, trimethyl ammonium triflate **1-44** would precipitate as a white solid that could be isolated by filtration and then washed with diethyl ether and hexanes. The salt was then dried under vacuum and used without further purification. In the cases where the trimethyl ammonium triflate did not precipitate immediately, the solvent was decanted. The remaining oil was washed repeatedly with diethyl ether and hexanes, and then dried under vacuum until a solid or foam formed. All ammonium salts were used without further purification. Notably, salts have been

observed to decompose in solution over the course of one week, but can be stored indefinitely in the solid form.

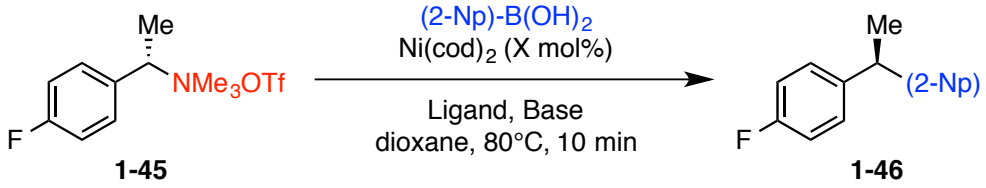
Scheme 1-6 Synthesis of Benzylic Ammonium Triflates



Optimization and Scope of 2nd Generation Cross-Coupling

I selected p-fluorophenyl substrate **1-45** as my model substrate because it gave the lowest yield under the first-generation catalyst system. There was excellent stereochemical fidelity, but the yield of this transformation was poor (Table 1-1 entry 1). Switching to different phosphine ligands or different bases that traditionally help this transformation did not give any significant improvement (Table 1-1 entries 2-3). However, by leaving out any additional ligand I observed a dramatic increase in yield. Slightly increasing the equivalence of base and boronic acid further improved yield, without much loss in stereochemical fidelity (entry 5).

Table 1-1 **Optimization of non-napthyl ammonium salts**



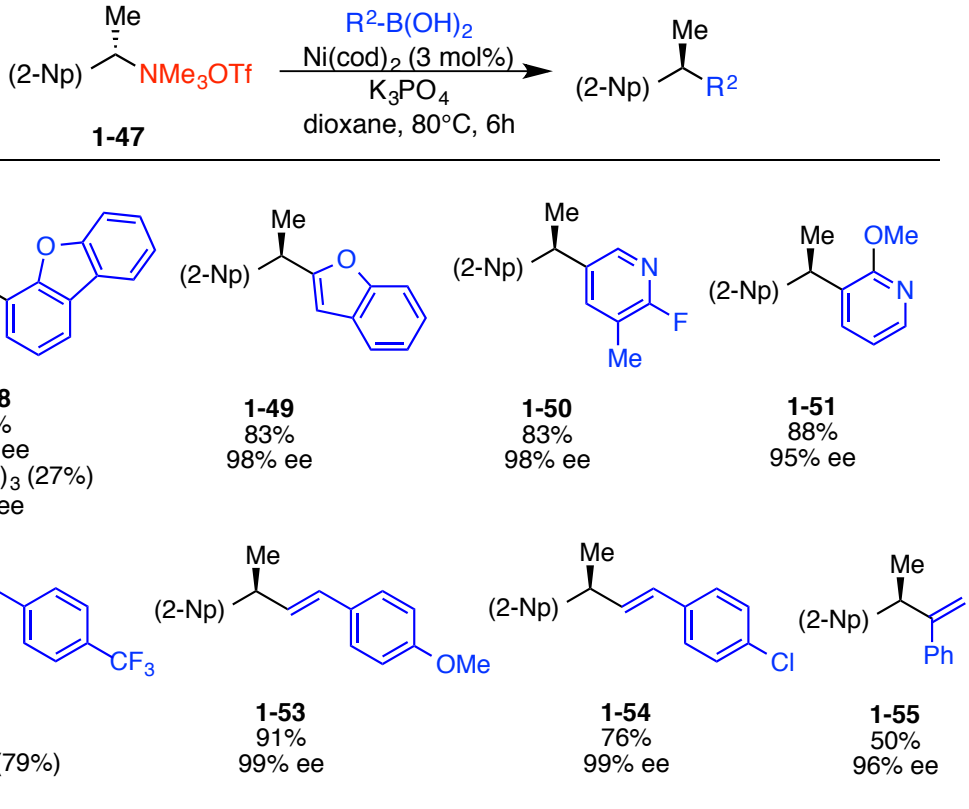
Entry	Ligand (mol %)	Base (equiv)	$NpB(OH)_2$ (equiv)	Yield (%)[b]	ee (%)[c]
1	t-BuXantphos (12)	K_3PO_4 (1.3)	1.2	37	99
2	$P(o\text{-}Tol)_3$ (22)	K_3PO_4 (1.3)	1.2	38	ND
3	$P(o\text{-}Tol)_3$ (22)	CsF (1.3)	1.2	26	ND
4	none	K_3PO_4 (1.3)	1.2	61	91
5	none	K_3PO_4 (1.5)	1.5	75	92

[a]Conditions: ammonium triflate **1** (0.1 mmol, 1.0 equiv), boronic acid, $Ni(cod)_2$, base, dioxane (0.33 M), 80°C, 6h. [b] Determined by ^1H NMR using 1,3,5-trimethoxybenzene as internal standard. [c] Determined by chiral HPLC analysis using chiral stationary phase. [d] ND = not determined.

Having identified a successful second-generation catalyst, I explored the scope with respect to the boronic acid coupling partner. These studies were performed in collaboration with Danielle Shacklady-McAtee, Corey H. Basch, and Yegeun Song. Under the optimized reaction conditions, a number of aryl, vinyl, and heteroaromatic boronic acids afforded enantioenriched products in high yields. Interestingly, in some cases my "ligandless" conditions were crucial for reactivity as displayed in Scheme 1-7. For example, the use of $P(o\text{-}Tol)_3$ furnished product **1-48** in only 27% yield, but my ligand-less conditions resulted in 80% yield. In other cases, the use of ligand made little to no difference as seen in entry **1-52**. However, my 2nd generation conditions are still advantageous because of lower costs, and ease of purification when reactions were performed without the addition of phosphine ligand.

Oxygen-containing heterocyclic boronic acids such as benzofuran and dibenzofuran coupled with high yields and high stereochemical fidelity (**1-48** and **1-49**). Unsubstituted pyridyl boronic acids were unreactive under these reaction conditions. This lack of reactivity could be due to the coordination of the pyridyl nitrogen to the catalyst, forming an unreactive nickel catalyst. For this reason, we explored pyridines with substitution in the 2-position (**1-50** and **1-51**), which efficiently provided the desired diaryl alkanes. With respect to vinyl boronic acids, we were pleased to see that electron-rich (**1-53**), electron-poor (**1-52**), halide-containing (**1-54**) vinyl groups could be installed. Aryl chlorides such as **1-54** are particularly attractive for further functionalization of the products. We were also excited to see that the sterically encumbered 1,1-disubstituted vinyl boronic acids reacted well affording product **1-55** in synthetically useful yields.

Scheme 1-7 Scope of Boronic Acids[a]

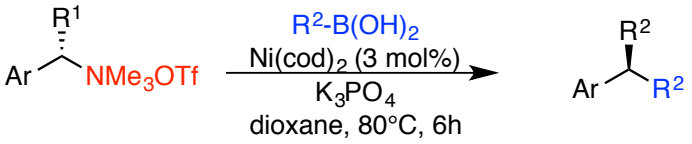


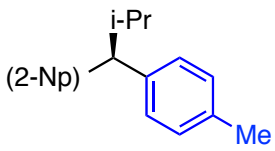
[a] Conditions: ammonium triflate (0.20 mmol, 1.0 equiv), Boronic acid (1.5 equiv), K_3PO_4 (1.5 equiv), $Ni(cod)_2$, dioxane (0.33 M), 80°C, 6h. Isolated yields are an average of duplicate experiments (±5%).

Average ee's from duplicate runs determined by chiral HPLC analysis using a chiral stationary phase (±1%). [b] Yields in parentheses determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard. [c] 10 mol% $Ni(cod)_2$ was used in this reaction. [d] $P(o\text{-}tol)_3$ (7 mol%) was used in this reaction.

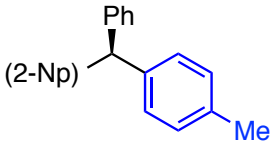
With respect to the ammonium triflate coupling partner, non-napthyl substituents and groups other than methyl at the benzylic position were explored. Isopropyl (**1-56)** and phenyl (**1-57**) substituents at the benzylic position were well tolerated, although with slightly lower stereochemical fidelity. With respect to the ammonium salt with simple aryl substituents, the model *p*-fluoro substrate worked very well (**1-59).** Both electron withdrawing *m*-methoxyphenyl (**1-60**) and electron donating *p*-methoxy (**1-61**) substituents were also well tolerated.

Scheme 1-8 Scope of Benzylic Ammonium Salts

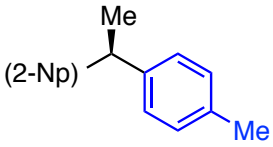




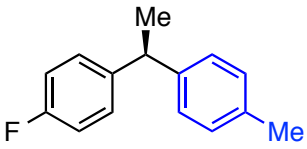
1-56[c]
55%
86% ee



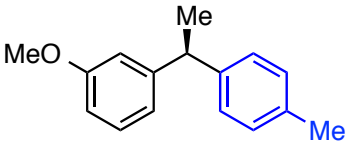
1-57[d]
58%
52% ee



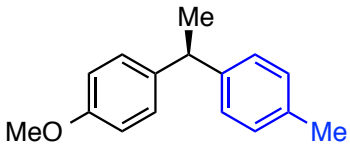
1-58[c]
82%
>99% ee[a]



1-59[c]
75%
92% ee



1-60[c]
71%
83% ee

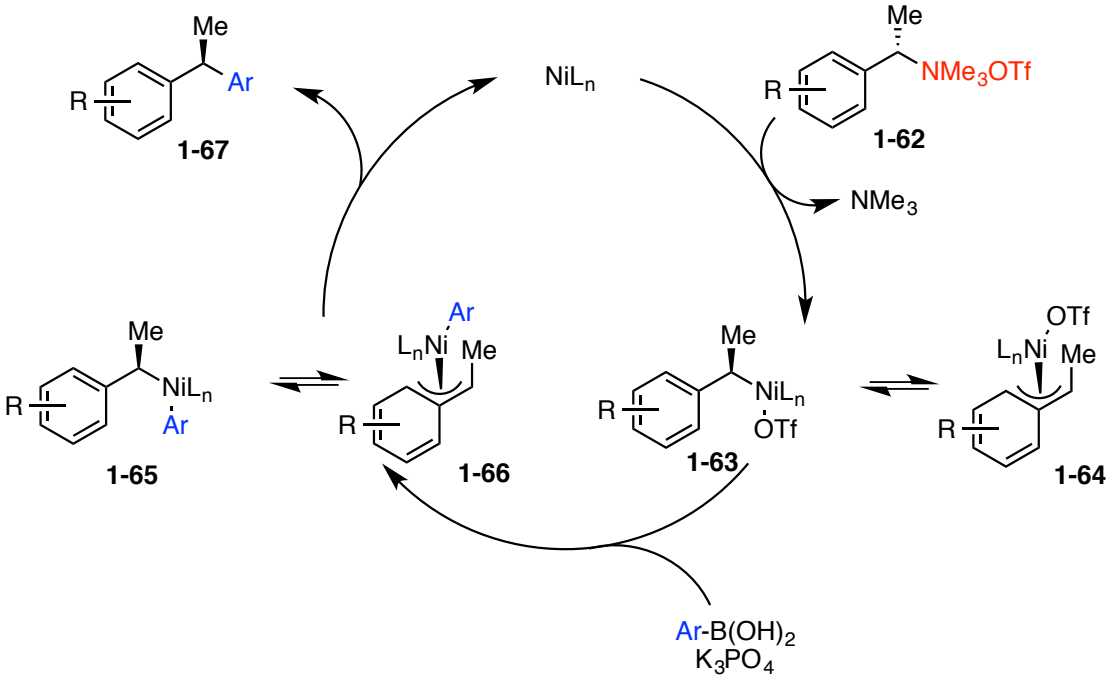


1-61[c]
53%
80% ee

[a] Conditions: ammonium triflate (0.20 mmol, 1.0 equiv), Boronic acid (1.5 equiv), K_3PO_4 (1.5 equiv), $Ni(cod)_2$, dioxane (0.33 M), 80°C, 6h. Isolated yields are an average of duplicate experiments (±5%). Average ee's from duplicate runs determined by chiral HPLC analysis using a chiral stationary phase (±1%). [b] Yields in parenthesis determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard. [c] 10 mol% $Ni(cod)_2$ was used in this reaction. [d] 5 mol% $Ni(cod)_2$ was used in this reaction.

In order to determine the absolute configuration of the products under these reaction conditions, the optical rotation and HPLC trace of compound **1-57** was compared to those of the same compound that had previously been synthesized in our laboratory. With this in mind, it was determined that the reaction was going through a net inversion of configuration at the benzylic stereocenter. Thus, the mechanism proposed for this reaction is an S_N2 or S_N2' type oxidative addition of the nickel(0) catalyst with inversion of configuration at the benzylic stereocenter to produce either an η^1- or η^3- π-benzyl nickel(II) complex (**1-63** or **1-64**). Subsequent transmetallation with the aryl boronic acid and reductive elimination with retention of configuration provides the products with overall inversion of the benzylic stereocenter. This type of mechanism has been previously proposed for stereospecific cross-couplings of other benzylic electrophiles. [9]

Scheme 1-9 Proposed Reaction Mechanism



1.3 Conclusion

In conclusion, I developed a highly stereospecific Suzuki cross-coupling of benzylic ammonium salts to afford tertiary benzylic stereocenters. My new catalyst system expanded the scope of heteroaromatic and vinyl boronic acids. It has also addressed challenges with electrophiles with non-extended π-substituents. This reaction utilizes an inexpensive nickel catalyst with commercially available, air-stable, and functional group tolerant boronic acids. The substrates are readily accessible in high enantioenrichment from benzylic amines or using classical methods. This reaction provides a powerful way to readily access tertiary benzylic stereocenters in high yield with high enantioenrichment.

Scheme 1-10 A general, simple catalyst for enantiospecific cross-couplings of benzylic ammonium triflates and boronic acids: no phosphine ligand required

1.4 Experimental Section

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. Select compounds were purified by flash chromatography on silica gel (5-20 μm) as needed. 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. [10]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 stored in a N_2-atmosphere glovebox. MeOTf was purchased from TCI America, and used as received. $CDCl_3$ 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; $(CD_3)_2CO$ = 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 77.07; $(CD_3)_2CO$ = 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 1 dm path length. Melting points were taken on a Stuart SMP10 instrument.

Dimethyl benzyl amines were prepared either from the benzyl amines using Escheweiler–Clarke conditions or via reductive amination of the benzaldehyde or acetophenone derivative. [11] It has been reported that epimerization does not occur under the Escheweiler–Clarke conditions. For amines that were not commercially available, the synthesis utilized Ellman's auxiliary to afford the enantioenriched primary amines. [12] Precursors for racemic ammonium triflates were synthesized via reductive amination of the corresponding acetophenone derivatives. [11]

General Procedure for Enantiospecific Cross-Coupling

In a N_2-atmosphere glovebox, $Ni(cod)_2$ (either 5.5 mg, 0.020 mmol, 10 mol % or 1.6 mg, 0.006 mmol, 3 mol %) and K_3PO_4 (64.0 mg, 0.30 mmol, 1.5 equiv) were weighed into a 1-dram vial. Benzyl ammonium triflate (0.20 mmol, 1.0 equiv) and boronic acid (0.30 mmol, 1.5 equiv) were added, followed by dioxane (0.6 mL, 0.33 M). The vial was capped with a Teflon-lined cap and removed from the glovebox.

The mixture was stirred for 6 h at 80 °C. After cooling to room temperature, the reaction mixture was then diluted with Et_2O (1.5 mL) and filtered through a short 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 cross-coupled product.

*4.2.1 (R)-4-(1-(naphthalen-2-yl)ethyl)dibenzo[b,d]furan (**1-48**)*. General procedure was followed using 3 mol % $Ni(cod)_2$. The crude material was purified by silica gel chromatography (100% hexanes) to give compound **1-48** (51 mg, 80%) as a white solid (mp 98–101 ºC). The enantiomeric excess was determined to be 99% ee by chiral HPLC analysis (CHIRALPAK IB, 1.0 mL/min, 0.2% *i*-PrOH/hexane, λ=254 nm); t_R(major)=7.996 min, t_R(minor)=10.60 min. $[\alpha]_D^{24}$ = +124.5° (c 1.11, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.7 Hz, 2H), 7.85 – 7.71 (m, 5H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.49 – 7.38 (m, 4H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 4.5 Hz, 1H), 5.01 (q, *J* = 7.2 Hz, 1H), 1.90 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1, 154.3, 142.7, 133.6, 132.3, 130.5, 128.0, 127.9, 127.7, 127.1, 127.0, 126.0, 125.7, 125.6, 125.5, 124.6, 124.2, 123.0, 122.7, 120.8, 118.7, 111.9, 39.0, 20.9; FTIR (NaCl/thin film) 3054, 2968, 1451, 1421, 1184, 751 cm^{-1}; HRMS (EI+) [M]+ calculated for $C_{24}H_{18}O$: 322.1358, found: 322.1342.

*4.2.2 (R)-2-(1-(naphthalen-2-yl)ethyl)benzofuran (**1-49**)*. General procedure was followed using 3 mol % $Ni(cod)_2$. The crude material was purified by silica gel chromatography (100% hexanes) to give compound **1-49** (45.0 mg, 83%) as a white solid (mp 97–100 ºC). The enantiomeric excess was determined to be 98% ee by chiral HPLC analysis (CHIRALPAK IC, 1.0 mL/min, 0.2% *i*-PrOH/hexane, λ=254 nm); t_R(minor)=6.26 min, t_R(major)=6.84 min. $[\alpha]_D^{24}$ = –38.3° (c 1.46, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.91 (m, 3H), 7.86 (s, 1H), 7.67 – 7.46 (m, 5H), 7.38 – 7.25 (m, 2H), 6.61 (s, 1H), 4.55 (q, *J* = 7.2 Hz, 1H), 1.91 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.1, 155.0, 140.8, 133.7, 132.6, 128.8, 128.4, 127.9, 127.8, 126.2, 126.1, 126.0, 125.8, 123.6, 122.6, 120.6, 111.1, 102.4, 39.9, 20.4; FTIR (NaCl/thin film) 3053, 2973, 1455, 1255 cm^{-1}; HRMS (EI+) [M]+ calculated for $C_{20}H_{16}O$: 272.1201, found: 272.1186.

*4.2.3 (R)-2-fluoro-3-methyl-5-(1-(naphthalen-2-yl)ethyl)pyridine (**1-50**)*. General procedure was followed using 3 mol % $Ni(cod)_2$. The crude material was purified by

silica gel chromatography (5% EtOAc/1% Et_3N/hexanes) to give compound 1-**50** (37 mg, 70%) as a pale yellow oil. The enantiomeric excess was determined to be 75% ee by chiral HPLC analysis (CHIRALPAK IB, 1.0 mL/min, 5.0% *i*-PrOH/hexane, λ=254 nm); t_R(minor)=5.99 min, t_R(major)=7.18 min. $[\alpha]_D^{24}$ = –89.6° (c 0.73, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 – 8.11 (m, 1H), 7.86 – 7.70 (m, 3H), 7.61 – 7.51 (m, 1H), 7.52 – 7.37 (m, 2H), 7.33 – 7.22 (m, 1H), 6.79 – 6.67 (m, 1H), 4.39 (q, J = 7.1 Hz, 1H), 2.21 (s, 3H), 1.74 (d, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7 (d, $J_{C–F}$ = 238.4 Hz), 151.8 (d, $J_{C–F}$ = 8.1 Hz), 145.7 (d, $J_{C–F}$ = 15.15 Hz), 142.3, 136.9 (d, $J_{C–F}$ = 5.1 Hz), 133.6, 132.2, 128.5, 127.7 (d, $J_{C–F}$ = 4.0 Hz), 126.3, 125.8, 125.6, 110.7, 110.4, 39.6, 22.0, 19.8 (d, $J_{C–F}$ = 3.0 Hz); ^{13}C NMR (101 MHz, $(CD_3)_2CO$) δ162.6 (d, $J_{C–F}$ = 232.3 Hz), 151.9 (d, $J_{C–F}$ = 8.1 Hz), 145.6 (d, $J_{C–F}$ = 16.2 Hz), 142.6, 137.4 (d, $J_{C–F}$ = 4.0 Hz), 133.7, 132.3, 128.2, 127.7, 126.1, 126.4, 126.1, 125.6, 125.5, 109.9 (d, $J_{C–F}$ = 19.2 Hz), 39.0, 21.2, 18.6 (d, $J_{C–F}$ = 3.0 Hz); FTIR (NaCl/thin film) 3053, 2968, 1608, 1485, 1373, 962 cm^{-1}; HRMS (EI+) [M]+ calculated for $C_{18}H_{16}FN$: 265.1267, found:265.1252. Please note: Although two ^{13}C NMR peaks are coincident when $CDCl_3$ is used as solvent, all 18 ^{13}C NMR peaks are seen when $(CD_3)_2CO$ is used as solvent.

*4.2.4 (R)-2-methoxy-3-(1-(naphthalen-2-yl)ethyl)pyridine (**1-51**)*. General procedure was followed using 3 mol % $Ni(cod)_2$. The crude material was purified by silica gel chromatography (5% EtOAc/1% EtN_3/hexanes) to give compound **1-51** (47 mg, 88%) as an oil. The enantiomeric excess was determined to be 95% ee by chiral SFC analysis (OJ-H, 3.0 mL/min, 40% *i*-PrOH(0.1% DEA)/CO_2, λ=254 and 220nm); t_R(major)=2.46 min, t_R(minor)=3.07 min. $[\alpha]_D^{24}$ = +58.4° (c 1.73, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.02 (m, 1H), 7.85 – 7.74 (m, 3H), 7.73 – 7.67 (m, 1H), 7.52 – 7.31 (m, 4H), 6.88 – 6.78 (m, 1H), 4.61 (q, J = 7.1, 6.0 Hz, 1H), 3.95 (s, 3H), 1.68 (d, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.6, 144.4, 142.7, 136.1, 133.6, 132.2, 129.1, 127.9, 127.8, 127.7, 127.1, 126.0, 125.6, 125.5, 116.9, 53.5, 37.9, 20.5; FTIR (NaCl/thin film) 3055, 2969, 2948, 1589, 1507, 1463, 1409, 1321, 1253, 1020 cm^{-1}; HRMS (EI+) [M]+ calculated for $C_{18}H_{17}NO$: 263.1310, found: 263.1297.

*4.2.5 (S,E)-2-(4-(4-(trifluoromethyl)phenyl)but-3-en-2-yl)naphthalene (**1-52**)*. General procedure was followed using 3 mol % $Ni(cod)_2$. The crude material was

purified by silica gel chromatography (100% hexanes) to give compound **1-52** (53.0 mg, 81%) as a white solid (mp 70–73 ºC). The enantiomeric excess was determined to be 98% ee by chiral HPLC analysis (CHIRALPAK IB, 0.8 mL/min, 100% hexane, λ=254 nm); t_R(major)=24.21 min, t_R(minor)=30.68 min. $[\alpha]_D^{24}$ = –30.5° (c 1.18, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.76 (m, 3H), 7.76 – 7.64 (m, 1H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.51 – 7.37 (m, 5H), 6.63 – 6.43 (m, 2H), 3.99 – 3.69 (m, 1H), 1.58 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 141.13, 141.11, 138.0, 133.8, 132.4, 129.0 (q, $J_{C–F}$ = 32.3 Hz), 128.3, 127.78, 127.76, 126.4, 126.3, 126.2, 125.64, 125.57 (q, $J_{C–F}$ = 4.0 Hz), 125.5, 124.4 (q, $J_{C–F}$ = 272.7 Hz), 42.8, 21.1; FTIR (NaCl/thin film) 3053, 2967, 1615, 1325, 1164, 1121, 1067 cm^{-1}; HRMS (EI+) [M]+ calculated for $C_{21}H_{17}F_3$: 326.1282, found:326.1284.

*4.2.6 (S,E)-2-(4-(4-chlorophenyl)but-3-en-2-yl)naphthalene (**1-53**).* General procedure was followed using 3 mol % $Ni(cod)_2$. The crude material was purified by silica gel chromatography (100% hexanes) to give **1-53** (44.0 mg, 76%) as a white solid (mp 68–71 ºC). The enantiomeric excess was determined to be 99% ee by chiral HPLC analysis (CHIRALPAK IB, 1.0 mL/min, 100% hexane, λ=254 nm); t_R(major)=22.47 min, t_R(minor)=28.85 min. $[\alpha]_D^{24}$ = –40.8° (c 1.42, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.82 (m, 3H), 7.77 (s, 1H), 7.63 – 7.43 (m, 3H), 7.43 – 7.25 (m, 4H), 6.59 – 6.38 (m, 2H), 3.98 – 3.80 (m, 1H), 1.63 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 141.0, 141.0, 137.9, 133.7, 132.3, 128.2, 127.69, 127.66, 126.3, 126.2, 126.1, 125.6, 125.4, 42.7, 21.0; ^{13}C NMR (101 MHz, $(CD_3)_2CO$) δ 143.8, 137.2, 136.8, 134.5, 133.1, 132.7, 129.2, 128.7, 128.4, 128.3, 128.2, 128.1, 126.9, 126.6, 126.1, 125.8, 43.4, 21.4; FTIR (NaCl/thin film) 3052, 2965, 1490, 1091, 966 cm^{-1}; HRMS (EI+) [M]+ calculated for C20H17Cl: 292.1019, found: 292.0993. Please note: Although two ^{13}C NMR peaks are coincident when $CDCl_3$ is used as solvent, all 18 ^{13}C NMR peaks are seen when $(CD_3)_2CO$ is used as solvent.

*4.2.7 (S,E)-2-(4-(4-methoxyphenyl)but-3-en-2-yl)naphthalene (**1-54**).* General procedure was followed using 3 mol % $Ni(cod)_2$. The crude material was purified by silica gel chromatography (100% hexanes) to give compound **1-54** (53.0 mg, 91%) as a white solid (mp 78–80 ºC). The enantiomeric excess was determined to be 99% ee

by chiral HPLC analysis (CHIRALPAK IA, 0.6 mL/min, 1% EtOAc/hexane, λ=254 nm); t_R(major)=27.88 min, t_R(minor)=30.19 min. $[\alpha]_D^{24}$ = –35.7° (c 1.43, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.77 (m, 3H), 7.72 – 7.68 (m, 1H), 7.50 – 7.38 (m, 3H), 7.34 – 7.28 (m, 2H), 6.90 – 6.80 (m, 2H), 6.48 – 6.26 (m, 2H), 3.81-3.78 (m, 4H), 1.55 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 143.4, 133.7, 133.1, 132.3, 130.4, 128.3, 128.1, 127.8, 127.7, 127.4, 126.5, 126.0, 125.4, 125.3, 114.0, 55.4, 42.7, 21.4; FTIR (NaCl/thin film) 2962, 1607, 1511, 1250, 1175, 1034 cm^{-1}; HRMS (EI+) [M]+ calculated for $C_{21}H_{20}O$: 288.1514, found: 288.1517.

*4.2.8 (R)-2-(3-phenylbut-3-en-2-yl)naphthalene (**1-55**)*. General procedure was followed using 3 mol % $Ni(cod)_2$. The crude material was purified by silica gel chromatography (100% hexane) to give compound **1-55** (26 mg, 50%) as a white solid (mp 64-65 ºC). The enantiomeric excess was determined to be 96% ee by chiral HPLC analysis (CHIRALCEL OD-H, 0.8 mL/min, 1% *i*-PrOH/hexane, λ=254 nm); t_R(minor)=6.33 min, t_R(major)=6.73 min. $[\alpha]_D^{24}$ = –64.0° (c 0.64, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.76 (m, 3H), 7.76 – 7.70 (m, 1H), 7.53 – 7.42 (m, 3H), 7.42 – 7.33 (m, 2H), 7.33 – 7.16 (m, 3H), 5.53 (s, 1H), 5.27 (t, *J* = 1.3 Hz, 1H), 4.24 (q, *J* = 7.0 Hz, 1H), 1.60 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, CDCl3) δ 152.5, 142.7, 142.2, 133.7, 132.3, 128.2, 128.2, 127.8, 127.7, 127.3, 126.8, 126.6, 125.9, 125.4, 113.5, 44.4, 21.8; ^{13}C NMR (101 MHz, $(CD_3)_2CO$) δ 152.6, 142.8, 142.1, 133.7, 132.2, 128.0, 127.9, 127.5, 127.5, 127.2, 126.6, 126.4, 125.82, 125.79, 125.3, 112.5, 43.7, 21.2; FTIR (NaCl/thin film) 3053, 2967, 2930, 2361, 2337, 1624, 1599, 1506 cm^{-1}; HRMS (EI+) [M]+ calculated for $C_{20}H_{18}$: 258.1409, found: 258.1422. Please note: Although two ^{13}C NMR peaks are coincident when $CDCl_3$ is used as solvent, all 18 ^{13}C NMR peaks are seen when $(CD_3)_2CO$ is used as solvent.

*4.2.9 (S)-2-(1-p-tolylethyl)naphthalene (**1-56**)*. General procedure was followed using 10 mol % $Ni(cod)_2$ and benzylic ammonium triflate prepared in 99.6% ee. The crude material was purified by silica gel chromatography (100% hexanes) to give compound **1-56** (40 mg, 82%) as a white solid. The enantiomeric excess was determined to be >99% ee by chiral HPLC analysis (CHIRALPAK IB, 0.4 mL/min, 100% hexane, λ =254 nm); t_R(major)=21.65; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.66 (m, 4H), 7.52 – 7.36 (m, 2H), 7.31 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.21 – 7.06 (m,

4H), 4.29 (q, *J* = 7.2 Hz, 1H), 2.32 (s, 3H), 1.72 (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, 128.0, 127.8, 127.7, 127.6, 126.9, 126.0, 125.4, 125.3, 44.5, 21.9, 21.1. The spectral data for this compound matches that reported in the literature.[7] Comparison of the HPLC spectrum of this product to that previously obtained in our laboratory confirmed that the absolute configuration of this product is *S*.[7]

*4.2.10 (S)-2-(2-methyl-1-p-tolylpropyl)naphthalene (**1-57**).* General procedure was followed using 10 mol % $Ni(cod)_2$ and benzylic ammonium triflate prepared in >95% ee. The crude material was purified by silica gel chromatography (100% hexanes) to give compound **1-57** (30 mg, 55%) as a white solid (mp 77–78 ºC). The enantiomeric excess was determined to be 87% ee by chiral HPLC analysis (CHIRALPAK IB, 0.8 mL/min, 100% hexane, λ =254 nm); t_R(major)=8.24 min, t_R(minor)=8.93 min. $[\alpha]_D^{24} = -33.5°$ (c 0.864, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.61 (m, 4H), 7.49 – 7.31 (m, 3H), 7.31 – 7.16 (m, 2H), 7.05 (d, *J* = 7.8 Hz, 2H), 3.53 (d, *J* = 10.8 Hz, 1H), 2.67 – 2.47 (m, 1H), 2.25 (s, 3H), 0.89 (dd, *J* = 14.4, 6.5 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7, 141.7, 135.5, 133.6, 132.1, 129.1, 128.0, 127.9, 127.6, 127.5, 126.5, 126.2, 125.8, 125.1, 60.5, 31.6, 22.0, 21.9, 21.0; FTIR (NaCl/thin film) 3053, 3019, 2955, 2922, 2868, 1508, 1457, 1385, 813, 760, 741 cm^{-1}; HRMS (EI+) [M]+ calculated for $C_{21}H_{22}$: 274.1722, found: 274.1724.

*4.2.11 (S)-2-(phenyl(p-tolyl)methyl)naphthalene (**1-58**).* General procedure was followed using 10 mol % $Ni(cod)_2$ and benzylic ammonium triflate prepared in >95% ee. The crude material was purified by silica gel chromatography (100% hexanes) to give compound **1-58** (36 mg, 58%) as an oil. The enantiomeric excess was determined to be 52% ee by chiral HPLC analysis (CHIRALCEL OD-H, 0.3 mL/min, 0.2% *i*-PrOH/pentane, λ =254 nm); t_R(major)=38.59 min, t_R(minor)=40.72 min. $[\alpha]_D^{24} = +37.6°$ (c 1.88, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.71 (m, 3H), 7.54 (s, 1H), 7.49 (dt, *J* = 6.1, 3.5 Hz, 2H), 7.40 – 7.33 (m, 3H), 7.33 – 7.26 (m, 1H), 7.26 – 7.20 (m, 2H), 7.20 – 7.09 (m, 4H), 5.74 (s, 1H), 2.40 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 141.7, 140.7, 135.9, 133.4, 132.1, 129.5, 129.4, 129.1, 128.3, 128.1, 127.9, 127.8, 127.7, 127.5, 126.3, 125.9, 125.6, 56.5, 21.1. The spectral data for this compound matches that reported in the literature.[13]

*4.2.12 (R)-2-(1-(4-fluorophenyl)ethyl)naphthalene (**1-59**)*. General procedure was followed using 10 mol % Ni(cod)2 and benzylic ammonium triflate prepared in 99% ee. The crude material was purified by silica gel chromatography (100% petroleum ether) to give compound **59** (38 mg, 75%) as an oil. The enantiomeric excess was determined to be 89% ee by chiral HPLC analysis (CHIRALCEL OD-H, 0.8 mL/min, 100% hexane, λ=254 nm); t_R(minor)=24.62 min, t_R(major)=31.78 min; ^{1}H NMR (400 MHz, CDCl3) δ 7.81 – 7.76 (m, 2H), 7.74 (d, J = 8.5 Hz, 1H), 7.68 – 7.64 (m, 1H), 7.49 – 7.37 (m, 2H), 7.29 – 7.23 (m, 1H), 7.23 – 7.16 (m, 2H), 7.01 – 6.91 (m, 2H), 4.29 (q, J = 7.2 Hz, 1H), 1.70 (d, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, CDCl3) δ 161.3 (d, $J_{C–F}$ = 245.4 Hz), 143.6, 141.9 (d, $J_{C–F}$ = 4.0Hz), 133.5, 132.1, 129.1 (d, $J_{C–F}$ = 7.1 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, 21.9. The spectral data for this compound matches that reported in the literature. [7]Comparison of the HPLC spectrum of this product to that previously obtained in our laboratory confirmed that the absolute configuration of this product is *R*. [7]

*4.2.13 (S)-1-methoxy-3-(1-p-tolylethyl)benzene (**1-60**)*. General procedure was followed using 10 mol % Ni(cod)$_2$ and benzylic ammonium triflate prepared in >99% ee. The crude material was purified by silica gel chromatography (0–1% Et_2O/hexanes) to give compound **1-60** (32 mg, 71%) as an oil. The enantiomeric excess was determined to be 83% ee by chiral HPLC analysis (CHIRALPAK IA, 10.8 mL/min, 1% *i*-PrOH/hexane, λ=254 nm); t_R(minor)=5.55 min, t_R(major)=5.81 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.21 (m, 1H), 7.20 – 7.08 (m, 4H), 6.92 – 6.82 (m, 2H), 6.77 (ddt, *J* = 8.1, 2.4, 1.4 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 1H), 3.82 (s, 3H), 2.36 (s, 3H), 1.66 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 148.4, 143.3, 135.6, 129.4, 129.2, 127.5, 120.2, 113.8, 110.9, 55.2, 44.5, 22.0, 21.1. The spectral data for this compound matches that reported in the literature. [7] Comparison of the HPLC spectrum of this product to that previously obtained in our laboratory confirmed that the absolute configuration of this product is *S*. [7]

*4.2.14 (S)-1-methoxy-4-(1-p-tolylethyl)benzene (**1-61**)*. General procedure was followed using 10 mol % Ni(cod)$_2$ and benzylic ammonium triflate prepared in 99.5% ee. The crude material was purified by silica gel chromatography (0–1% Et_2O/Hexane) to give compound **1-61** (24 mg, 53%) as an oil. The enantiomeric

excess was determined to be 81% ee by chiral HPLC analysis (CHIRALCEL OJ-H, 0.8 mL/min, 100% hexane, λ=254 nm); t_R(major)=45.54 min, t_R(minor)=55.21 min. $[\alpha]_D^{24}$ = –23.0° (c 1.02, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.07 (m, 6H), 6.90 – 6.79 (m, 2H), 4.09 (q, *J* = 7.2 Hz, 1H), 3.79 (s, 3H), 2.33 (s, 3H), 1.62 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 143.9, 138.9, 135.5, 129.2, 128.6, 127.5, 113.8, 55.4, 43.6, 22.3, 21.1. The spectral data for this compound matches that reported in the literature.[14]

Procedure for benzyl ammonium triflates

*4.3.1 (S)-N,N,N,2-tetramethyl-1-(naphthalen-2-yl)propan-1-aminiumtrifluoromethane sulfonate (**1-66**).* Dimethylbenzylamine (179 mg, 0.79 mmol, 1.0 equiv) was dissolved in Et_2O (0.17 mL, 4.0 M). MeOTf (0.17 mL, 1.0 mmol, 1.3 equiv) was added dropwise at 0 °C. White precipitate formed immediately. After complete addition the reaction mixture was stirred for an additional 15 minutes at 0 °C. In this case, a precipitate did not form upon addition of MeOTf. Instead, two distinct layers formed. The top layer was decanted off. The bottom layer was washed with Et_2O multiple times followed by rinsing with hexane. The oil was then dried under vacuum to give **1-66** (298 mg, 97%) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.96 – 7.86 (m, 2H), 7.86 – 7.80 (m, 1H), 7.58 – 7.44 (m, 3H), 4.61 (d, *J* = 5.2 Hz, 1H), 3.20 (s, 9H), 2.89 – 2.70 (m, 1H), 1.15 – 0.99 (m, 6H); ^{19}F NMR (565 MHz, $CDCl_3$) δ –78.4; FTIR (NaCl/thin film) 2975, 1490, 1278, 1166, 1030, 828, 638 cm^{-1}; LRMS (ESI) $[M–OTf]^+$ calculated for $[C_{17}H_{24}N]^+$: 242.2, found: 242. The ^{13}C NMR spectrum of **(1-66)** was complex due to the presence of rotamers.

*4.3.2 (S)-N,N,N-trimethyl-1-(naphthalen-2-yl)-1-phenylmethanaminiumtrifluoromethane sulfonate (**1-67**).* Dimethylbenzylamine (245 mg, 0.94 mmol, 1.0 equiv) was dissolved in Et_2O (0.24 mL, 4.0 M). MeOTf (0.13 mL, 1.2 mmol, 1.3 equiv) was added dropwise at 0 °C. White precipitate formed immediately. After complete addition the reaction mixture was stirred for an additional 15 minutes at 0 °C. In this case, a precipitate did not form upon addition of MeOTf. Instead, two distinct layers formed. The top layer was decanted off. The bottom layer was washed with washed with Et_2O multiple times followed by rinsing

with hexane. The oil was dried under vacuum to give salt **1-67** (225 mg, 57%) as a white fluffy solid (mp 61-63 °C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.98 – 7.76 (m, 6H), 7.58 – 7.39 (m, 5H), 6.12 (s, 1H), 3.25 (s, 9H); FTIR (NaCl/thin film) 3042, 1489, 1262, 1225, 1158, 1030, 735 cm^{-1}; ^{19}F NMR (565 MHz, $CDCl_3$) δ –78.3; LRMS (ESI) $[M–OTf]^+$ calculated for $[C_{20}H_{22}N]^+$: 276.2, found: 276. The ^{13}C NMR spectrum of **(1-67)** was complex due to the presence of rotamers.

*4.3.3(S)-1-(4-methoxyphenyl)-N,N,N-trimethylethanaminium trifluoromethanesulfonate (**1-68**).* Dimethylbenzylamine (426 mg, 2.4 mmol, 1.0 equiv) was dissolved in Et_2O (0.6 mL, 4.0 M). MeOTf (0.30 mL, 3.1 mmol, 1.3 equiv) was added dropwise at 0 °C. White precipitate formed immediately. After complete addition the reaction mixture was stirred for an additional 15 minutes at 0 °C. The precipitate was isolated by filtration and washed with Et_2O (2 x 5 mL). The resulting solid was dried under vacuum to give salt **1-68** (783 mg, 73%) as a white solid (mp 94–95 °C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.36 (m, 2H), 7.06 – 6.81 (m, 2H), 4.79 (q, J = 13.7, 6.8 Hz, 1H), 3.81 (s, 3H), 3.09 (s, 9H), 1.77 (d, J = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3, 131.8, 124.0, 120.7 (q, $J_{C–F}$ = 321.2 Hz), 114.6, 73.8, 55.5, 50.8, 15.0; ^{19}F NMR (565 MHz, $CDCl_3$) δ –78.3; FTIR (NaCl/thin film) 2967, 1611, 1518, 1258, 1157, 1029, 838 cm^{-1}; LRMS (ESI) $[M–OTf]^+$ calculated for $[C_{12}H_{30}NO]^+$: 194.2, found: 194.

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Chapter 2

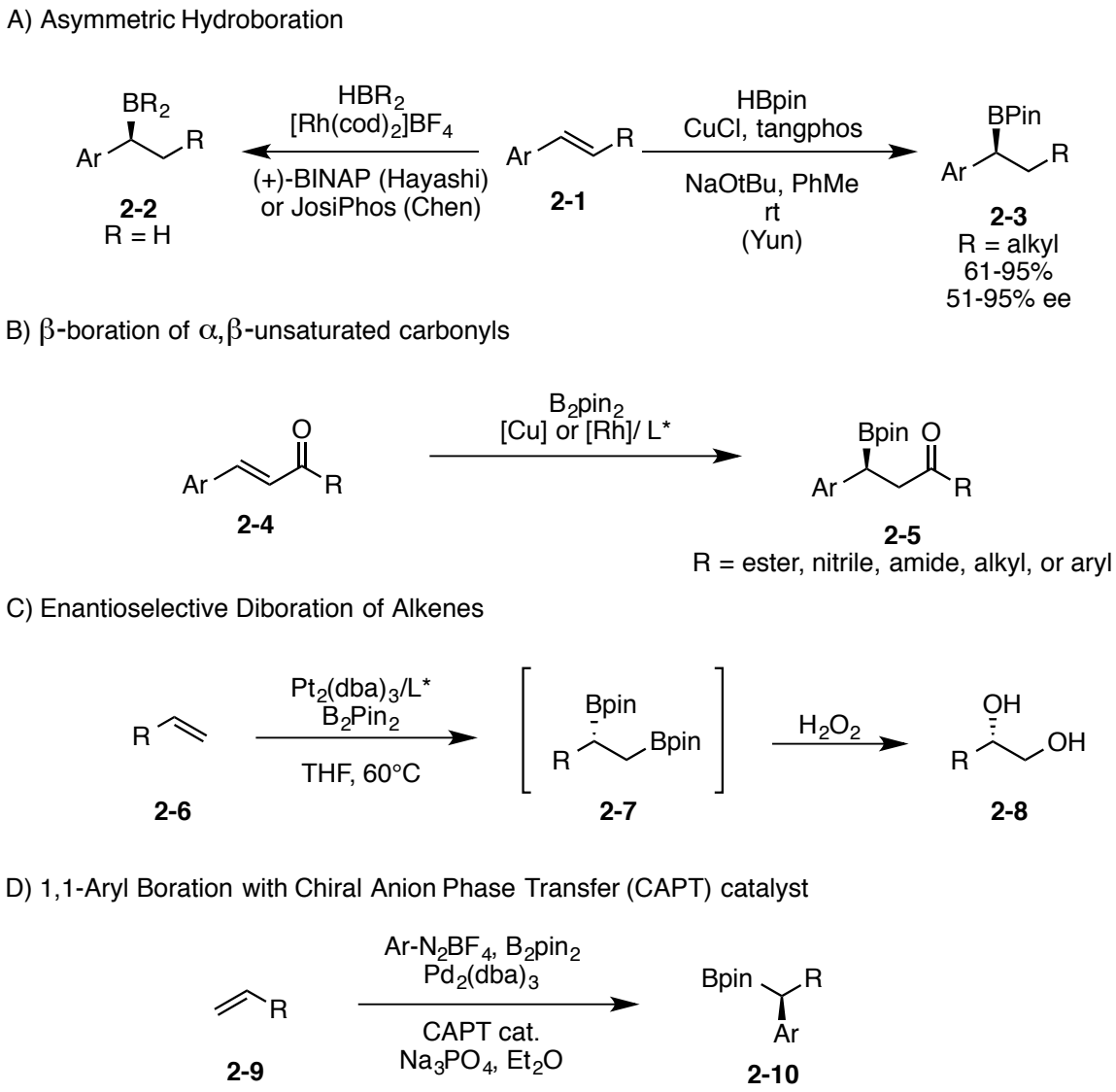
NICKEL-CATALYZED BORYLATION OF BENZYLIC AMMONIUM SALTS: STEREOSPECIFIC SYNTHESIS OF ENANTIOENRICHED BENZYLIC BORONATES

2.1 Introduction

Enantioenriched benzylic boronates are synthetically valuable intermediates due to their high reactivity. The carbon-boron (C-B) bond can easily be transformed enantiospecifically to form carbon-carbon or carbon-oxygen bonds. Oxidation of the carbon-boron bond will deliver an enantioenriched alcohol, while carbon-carbon bonds can be achieved through cross couplings or Matteson-type homologations. The utility of these benzylic boronates as synthetic intermediates has led to a number of ways to make them asymmetrically.

A variety of methods are known in order to make benzylic boronates enantioselectively from alkenes (Scheme 2-1). The most widely used method in these examples is the asymmetric hydroboration of alkenes (Scheme 2-1A).[1,2] The Hayashi group's seminal work in this field utilizes a rhodium catalyst with a chiral ligand in order to access enantioenriched benzylic boronates. [1a] However, this publication is limited to only methyl groups at the benzylic position from terminal styrenes (**2-2,** R=H**)**. The Yun group has shown that by using a chiral copper catalyst they can efficiently access the same scaffold in high yields and enantioenrichment. [3] This method can tolerate internal styrenes to deliver benzylic boronates substituted with linear alkyl chains **(2-3)**. However, they only report two such examples. Additional methods involving boration of alkenes include β-boration of α,β-unsaturated carbonyls (Scheme 2-1B) [2-4], diboration (Scheme 2-1C) [5], and 1,1-aryl borations (Scheme 2-1D). [6]

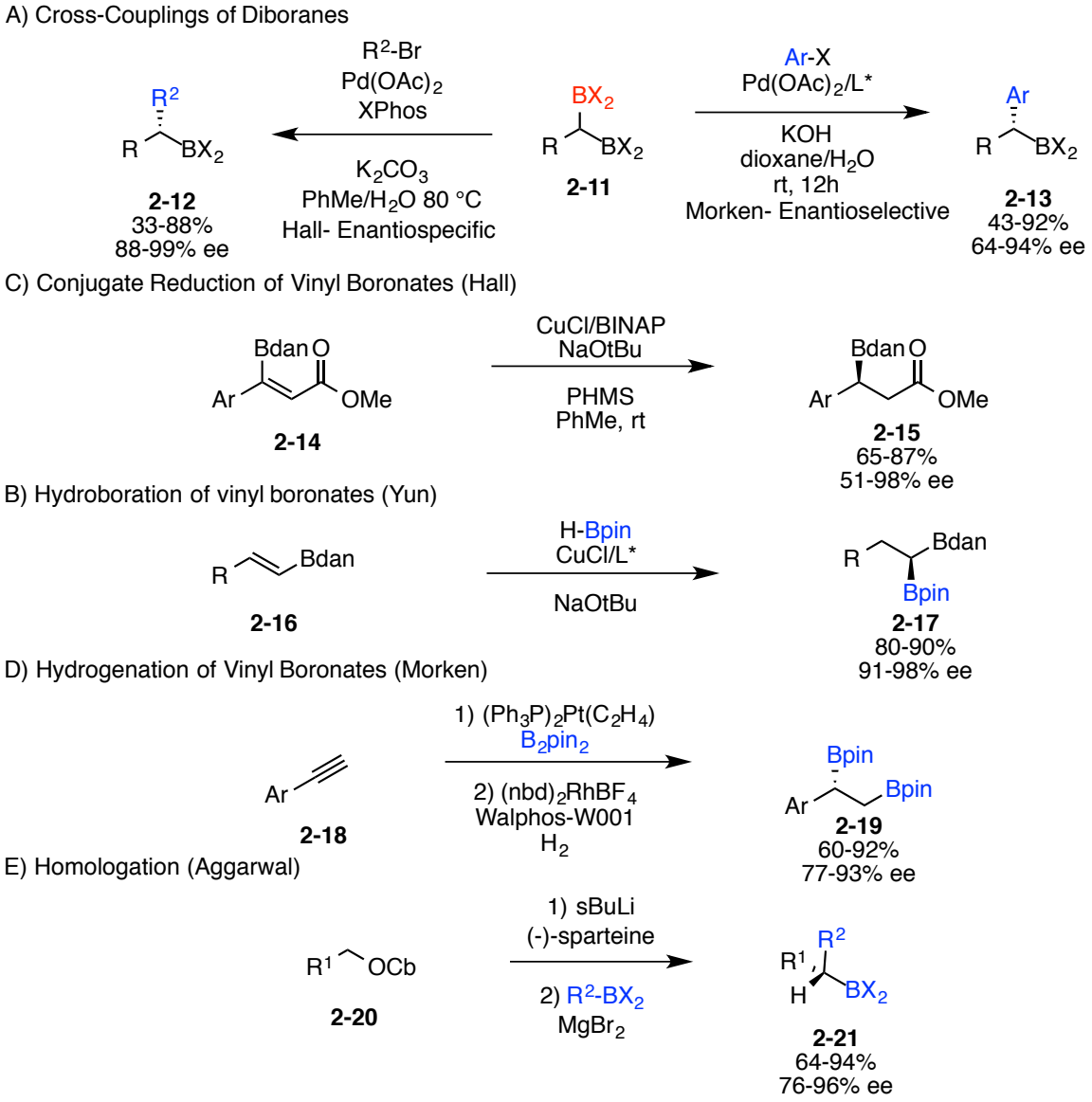
Scheme 2-1 Enantioselective Synthesis of Benzylic Boronates from Alkenes



Other strategies to access these products utilize starting materials already containing boron. For example, the Hall and Morken groups have independently shown that they can do a palladium-catalyzed cross-coupling of diboronates in order to afford the products in high yields and enantioenrichment (Scheme 2-2A). [5d,5b] The Hall group has done this

enantiospecifically by beginning with two distinct boron groups. The Morken group has done this enantioselectively beginning with two bispinacolborane groups, and utilizing a chiral TADDOL-based ligand. The Hall group has also shown that they can do an enantioselective, copper-catalyzed conjugate reduction of vinyl boronates(Scheme 2-2B). [6] The Yun and Morken groups have also shown that they can synthesize enantioenriched 1,1-or 1,2-diboronate compounds through either hydroboration (Scheme 2-2C) [5a] or 1,2 addition of a pinacoldiboron followed by asymmetric hydrogenation (Scheme 2-2D). [5c] Another powerful method in order to make these enantioenriched boronates has come from the Aggarwal group, where they have shown that they can do an enantioselective homologation of carbamates with boronates (Scheme 2-2E, Cb = $C_7H_{14}NO$). [7] However, this chemistry is limited due to the stoichiometric use of expensive (-)-sparteine as the chiral promoter as well as the harsh base *s*-BuLi, which limits functional group tolerance.

Scheme 2-2 Synthesis of Enantioenriched Benzylic Boronates From Boronate Precursors



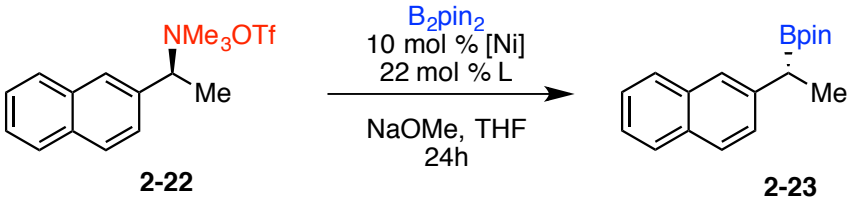
Building on our group's success in developing stereospecific Suzuki cross-couplings of enantioenriched benzylic ammonium salts in order to do a Suzuki cross-coupling[8], my colleague Corey Basch began to optimize a Miyaura borylation of

benzylic ammonium salts. This method utilizes derivatives of benzylic amines, which are readily available in high enantiomeric excess, commercially available and functional group tolerant diboranes as coupling partners, as well as an inexpensive nickel catalyst in low loadings. This method offers complementary scope to traditional methods such as hydroboration to make these benzylic boronates in high enantiomeric excess.

2.2 Results and Discussion

The borylation of ammonium salt **2-22** was chosen for reaction optimization. The primary amine precursor was commercially available in >99% ee, and was converted to ammonium salt **2-22** via a straightforward 2-step procedure that has been described in the previous chapter. Beginning with conditions that were optimal for the arylation of benzylic ammonium triflates, there was only 12% of product **2-23** observed (Table 2-1, entry 1). By switching the base from K_3PO_4 to NaOMe, the yield was increased to 78% with 95% ee (Table 2-1, entry 2). By dropping the temperature to room temperature, the enantiomeric excess was increased to 99%, and the yield increased to 84% (Table 2-1, entry 3). Exploring other monodentate phosphine ligands lead to the optimal PPh_3 providing a yield of 86% with 99% ee (Table 2-1, entry 4). Notably, this reaction proceeds well with the air stable $Ni(OAc)_2 \cdot 4H_2O$ (Table 2-1, entry 5) with only a slight decrease in yield. However, this was not consistent throughout the substrate scope, so $Ni(cod)_2$ was used in order to explore the scope of the reaction.

Table 2-1 Optimization of Miyura Borylation of Benzylic Ammonium Triflates



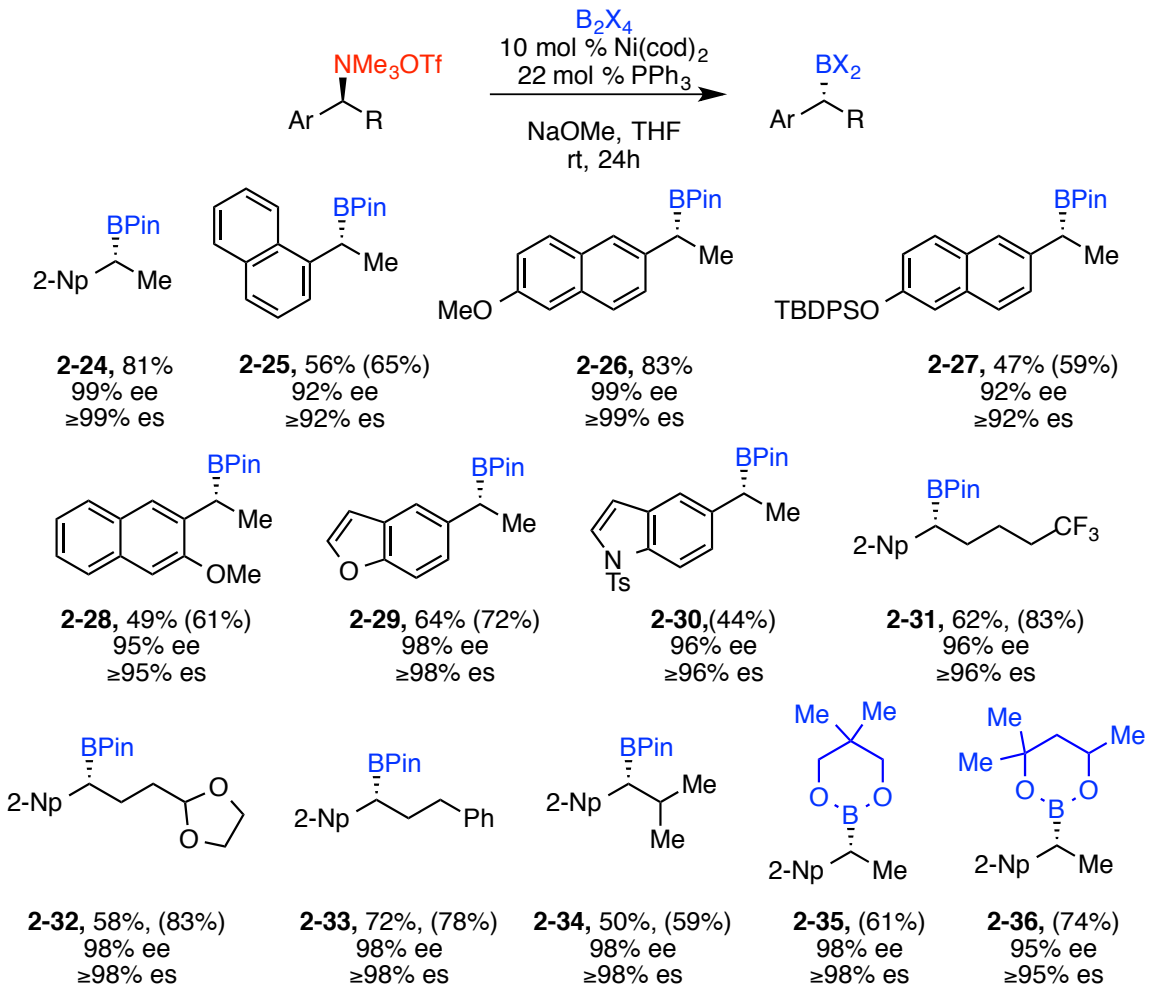
2-22 **2-23**

Entry	[Ni]	Ligand	temp (°C)	Yield (%)[b]	ee (%)[c]
1[d]	$Ni(cod)_2$	P(*o*-Tol)$_3$	70	12	n.d.[e]
2	$Ni(cod)_2$	P(*o*-Tol)$_3$	70	78	95
3	$Ni(cod)_2$	P(*o*-Tol)$_3$	rt	84	98
4	$Ni(cod)_2$	PPh_3	rt	86	99
5	$Ni(OAc)_2 \cdot 4H_2O$	PPh_3	rt	80	99

[a]Conditions: ammonium triflate **2-22** (>99% ee 0.1 mmol, 1.0 equiv), B_2Pin_2, [Ni], NaOMe(1.5 equiv), THF (0.2 M), 24h, unless otherwise noted. [b] Determined by ^1H NMR using 1,3,5-trimethoxybenzene as internal standard. [c] Ee's of the subsequent alcohol, formed via oxidation with H_2O_2 and NaOMe. Determined by chiral HPLC analysis using chiral stationary phase. [d] K_3PO_4 replaced NaOMe. [e]n.d. = not determined.

With these optimized conditions in hand, I joined the project in order to explore the substrate scope. As noted in Scheme 2-3, the model substrate afforded compound **2-24** in 81% yield and 99% ee. The more sterically encumbered 1-naphthyl product **2-25** still was formed in high yield and enantiomeric excess. Electron-rich methoxy (**2-26**) and siloxy (**2-27**) groups on the naphthyl substituent both resulted in high yields and stereochemical fidelity. Heterocycles such as benzofuran (**2-29**) and tosyl-protected indole (**2-30**) were also tolerated. Variations of the R substituent, including functionalized alkyl groups (eg. **2-31**-**2-33**) were also well tolerated. Notably, the reaction worked well with an isopropyl group at the benzylic position (**2-34**). This compound cannot be synthesized using popular asymmetric hydroboration methods. Other diboronates also reacted in high yields and stereochemical fidelity in this reaction (**2-35** and **2-36**).

Scheme 2-3 Scope of Miyura Borylation of Benzylic Ammoinum Salts

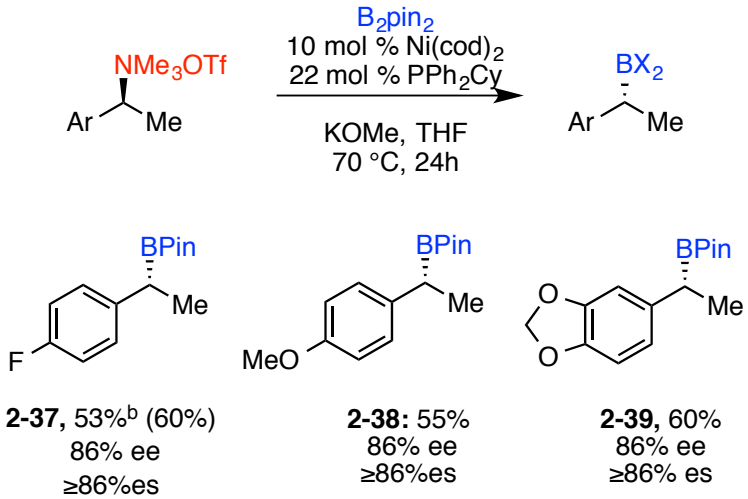


[a] Conditions: ammonium triflate (≥95% ee, 0.30 mmol, 1.0 equiv), B_2X_2 (1.5 equiv), $Ni(cod)_2$ (10 mol %), PPh_3 (22 mol %), NaOMe (1.5 equiv), THF (0.2 M), rt, 24 h, unless otherwise noted. Isolated yields. Yields in parentheses determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as internal standard. Ee's of the subsequent alcohol, formed via oxidation with H_2O_2 and NaOMe, determined by HPLC analysis using a chiral stationary phase. Enantiospecificity (es) = ee_{prod}/ee_{sm} X 100. [b] Opposite enantiomer of starting material used. [c] 50 °C.

Typically stereospecific cross-couplings of benzylic electrophiles tend to work better for naphthyl substituents due to an S_N2' type oxidative addition. When switching to simple phenyl systems, the energy barrier is much higher

than naphthyl due to a complete loss of aromaticity in the molecule if the oxidative addition still goes through the same pathway. This trend was condistent with respect to ammonium salts without an extended aryl substituent. Under the optimized conditions product **2-37** was only formed in 5% yield after 6 hours. By switching the ligand to 1,3-bis(cyclohexyl)imidazolium tetrafluoroborate (ICy·BF_4) or PPh_2Cy, the base to KOMe, and increasing the reaction temperature to 70 °C, the yield was improved to 53% with 86% ee. I hypothesize that these more electron-rich ligands accelerate the difficult oxidative addition. With these conditions, substrates with electron-donating groups on their phenyl substituent, such as *p*-methoxy (**2-38**) and acetal (**2-39**) were formed with good yields and ee's. These products show that this reaction can utilize benzylic electrophiles that are traditionally a challenge in stereospecific cross-couplings of benzylic electrophiles.

Scheme 2-4 Scope of Miyura Borylation of Non-Naphthyl Benzylic Ammonium Salts



2-37, 53%[b] (60%)
86% ee
≥86%es

2-38: 55%
86% ee
≥86%es

2-39, 60%
86% ee
≥86% es

[a] Conditions: ammonium triflate (≥95% ee, 0.30 mmol, 1.0 equiv), B_2X_2 (1.5 equiv), $Ni(cod)_2$ (10 mol %), PPh_2Cy (22 mol %), KOMe (1.7 equiv), THF (1.0 M), 70 °C, 24 h, unless otherwise noted. Isolated yields. Yields in parentheses determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as internal standard. Ee's of the subsequent alcohol, formed via oxidation with H_2O_2 and NaOMe, determined by HPLC analysis using a chiral stationary phase. Enantiospecificity (es) =

ee_{prod}/ee_{sm} X 100. [b] 0.5 mmol scale. ICy·HBF_4 (12 mol %) in place of PPh_2Cy. Result of a single experiment.

2.3 Conclusion

In conclusion, we have developed a highly stereospecific Miyaura borylation of benzylic ammonium salts to afford enantioenriched benzylic boronates.The reaction utilizes an inexpensive nickel catalyst with either phosphine or NHC ligands. This reaction delivers benzylic boronates with both extended aryl substituents and more challenging phenyl substituents. The substrates are readily accessible in high enantioenrichment from benzylic amines or using classical methods. This method delivers valuable enantioenriched benzylic boronate intermediates, and is the first example of a Miyaura borylation of a non-allylic electrophile to deliver products in high ee's.

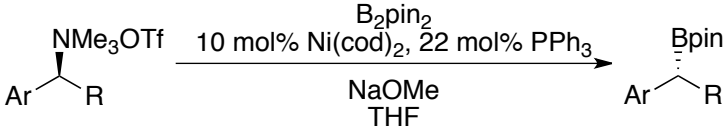
2.4 Experimental Section

Reactions were performed in oven-dried 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. 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: Bis(pinacolato)diboron, bis(neopentyl glycolato)diboron, and bis(hexylene glycolato)diboron were purchased from Sigma Aldrich and immediately placed in a N_2-atmosphere glovebox for storage. $Ni(OAc)_2 \cdot 4H_2O$ was purchased from Alfa Aesar and donated by AstraZeneca. Methyl trifluoromethanesulfonate (MeOTf) was purchased from TCI and used directly. 1,3-Bis(cyclohexyl)imidazolium tetrafluoroborate (ICy·HBF_4) was purchased from Sigma Aldrich and used as received.. THF was dried by passing through drying columns,

then degassed by sparging with N_2 and stored over activated 4Å MS in a N_2-atmosphere glovebox.[9] Commercially available enantioenriched amines were purchased from Alfa Aesar or Sigma Aldrich and used as received. Enantioenriched amines that were not commercially available were obtained through Grignard or hydride additions of Ellman's sulfinimines.[10] Dimethyl benzyl amines were prepared using Escheweiler-Clarke conditions or reductive amination of the corresponding primary benzyl amine with formaldehyde.[11] In some instances oven-dried potassium carbonate was added into $CDCl_3$ to remove trace amount of acid. Proton nuclear magnetic resonance (^{1}H NMR) spectra, carbon nuclear magnetic resonance (^{13}C NMR) spectra, fluorine nuclear magnetic resonance spectra (^{19}F NMR), and silicon nuclear magnetic resonance spectra (^{29}Si NMR) were recorded on both 400 MHz and 600 MHz spectrometers. Boron nuclear magnetic resonance spectra (^{11}B NMR) were recorded on a 600 MHz spectrometer. 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). 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). 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 KBr 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.

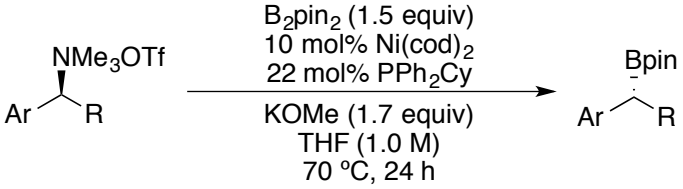
Stereospecific Borylation of Benzylic Ammonium Salts

General Procedure A: Borylation of Naphthyl-Substituted Benzylic Ammonium Salts



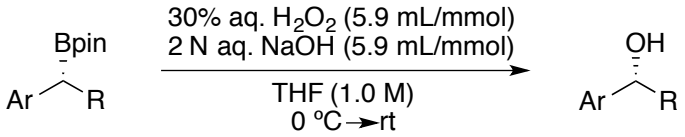
In a N_2-atmosphere glovebox, $Ni(cod)_2$ (8.3 mg, 0.030 mmol, 10 mol %), PPh_3 (4.4 mg, 0.066 mmol, 22 mol %), NaOMe (24 mg, 0.45 mmol, 1.5 equiv), B_2pin_2 (114 mg, 0.45 mmol, 1.5 equiv), and ammonium salt **1** (0.30 mmol, 1.0 equiv) were weighed into a 1-dram vial equipped with a magnetic stir bar. THF (1.5 mL, 0.2 M) was added, and the vial was capped with a Teflon-lined cap and removed from the glovebox. The mixture was stirred at room temperature for 24 h. The reaction mixture was then diluted with Et_2O (2.5 mL) and quickly filtered through a short plug of Celite®, which was then rinsed with Et_2O (~ 10 mL). The filtrate was concentrated and purified by silica gel chromatography to give the benzylic boronate product. The benzylic boronate was then converted to the corresponding benzylic alcohol via oxidation (see General Procedure C below) to determine the enantiomeric excess (ee).

General Procedure B: Borylation of Non-Naphthyl-Substituted Benzylic Ammonium Salts

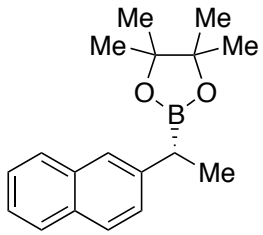


In a N_2-atmosphere glovebox, $Ni(cod)_2$ (8.3 mg, 0.030 mmol, 10 mol %), PPh_2Cy (18 mg, 0.066 mmol, 22 mol %), KOMe (38 mg, 0.45 mmol, 1.7 equiv), B_2pin_2 (114 mg, 0.45 mmol, 1.5 equiv), and ammonium salt **1** (0.30 mmol, 1.0 equiv) were weighed into a 1-dram vial equipped with a magnetic stir bar. THF (0.3 mL, 1.0 M) was added and the vial was capped with a Teflon-lined cap and removed from the glovebox. The mixture was stirred at 70 ºC for 24 h. The reaction mixture was then diluted with Et_2O (2.5 mL) and quickly filtered through a plug of Celite®, which was then rinsed with Et_2O (~ 10 mL). The filtrate was concentrated and then purified by silica gel chromatography to give the benzylic boronate product. The benzylic boronate was then converted to the corresponding benzylic alcohol via oxidation (see General Procedure C below) to determine the enantiomeric excess (ee).

General Procedure C: Oxidation of Benzylic Boronates to Benzylic Alcohols for Determination of Enantiomeric Excess (ee).

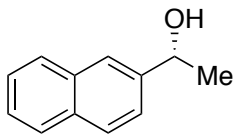


A solution of the benzylic boronate **2-23** (1.0 equiv) and Et_2O (0.017 M) was cooled to 0 ˚C. Aqueous NaOH (2 N, 5.9 mL/mmol of **2-23**) was added, followed by aq. H_2O_2 (30%, 5.9 mL/mmol of **2-23**). The mixture was stirred and allowed to warm slowly to room temperature overnight. The reaction mixture was diluted with H_2O and Et_2O, and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 20 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated. The crude mixture was purified via silica gel chromatography to afford benzylic alcohol **2-40** for ee determination. For duplicate experiments, alcohol **2-40** was isolated once via column chromatography (to verify high yield in the oxidation) and once via preparatory thin-layer chromatography under the same mobile-phase conditions.



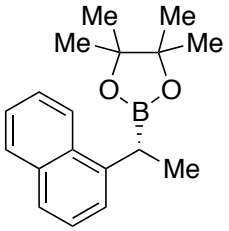
(*R*)-4,4,5,5-tetramethyl-2-(1-(naphthalen-2-yl)ethyl)-1,3,2-dioxaborolane (2-24). Prepared via General Procedure A using ammonium salt **2-22** (amine purchased in >99% ee). The crude mixture was purified by silica gel chromatography (5% EtOAc/hexanes) to give **2-24** (run 1: 69 mg, 82%; run 2: 79%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.75 (m, 3H), 7.67 (s, 1H), 7.48 – 7.37 (m, 3H), 2.64 (q, *J* = 7.4 Hz, 1H), 1.46 (d, *J* = 7.6 Hz, 3H), 1.23 (s, 6H), 1.22 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7, 134.0, 131.8, 127.8, 127.7, 127.6, 127.4, 125.8, 125.4, 124.9, 83.5, 24.8, 24.8, 17.0.[12] The spectral data match that previously reported in the literature.[2b]

Boronate **2-24** was oxidized to alcohol **2-40** via General Procedure C. The enantiomeric excess was determined to be 99% (run 1: 99% ee; run 2: 99% ee) by chiral HPLC analysis. See alcohol **2-40** below.



(*R*)-1-(naphthalen-2-yl)ethanol (2-40). Prepared via General Procedure C using benzylic boronate **2-24**. The crude mixture was purified by silica gel chromatography (20% EtOAc/hexanes) to give **2-40** (run 1 (66 mg of **2-24**): 38 mg, 95%) as a white solid. The enantiomeric excess was determined to be 99% (run 1: 99% ee; run 2: 99% ee) by chiral HPLC analysis (CHIRALPAK IA, 1.0 mL/min, 1% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 43.70 min, t_R(minor) = 45.74 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.79 (m, 4H), 7.56 – 7.42 (m, 3H), 5.06 (q, *J* = 6.2 Hz, 1H), 2.07 (s, 1H), 1.58 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 133.4, 133.0, 128.5, 128.1, 127.8, 126.3, 126.0, 123.97, 123.95 70.7, 25.3. The spectral data match that previously reported in the literature.[13]

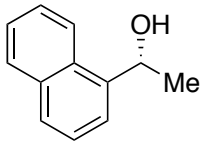
The absolute configuration of alcohol **2-40** was determined to be *R* by comparison of its HPLC trace to that of commercially available, enantioenriched **2-40**.



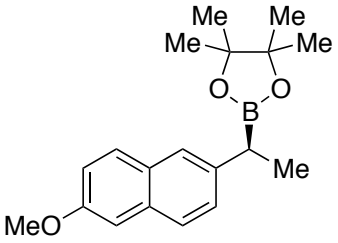
(*R*)-4,4,5,5-tetramethyl-2-(1-(naphthalen-1-yl)ethyl)-1,3,2-dioxaborolane ((*R*)-2-25). Prepared via General Procedure A using ammonium salt **2-22b** (amine purchased in >99% ee). The crude mixture was purified by silica gel chromatography (5% EtOAc/hexanes) to give **2-25** (run 1: 47 mg, 56%; run 2: 47 mg, 56%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.2 Hz, 1H), 7.88 – 7.83 (m, 1H),

7.69 (d, *J* = 7.5 Hz, 1H), 7.53 – 7.39 (m, 4H), 3.14 (q, *J* = 7.4 Hz, 1H), 1.52 (d, *J* = 7.5 Hz, 3H), 1.23 (s, 6H), 1.22 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 134.0, 132.1, 128.9, 126.0, 125.5, 125.4, 124.4, 124.2, 83.6, 24.8, 24.7, 16.6.[12] The spectral data matches that previously reported in the literature.[2b]

Boronate **2-25** was oxidized to alcohol **2-41** via General Procedure C. The enantiomeric excess was determined to be 92% (run 1: 92%, run 2: 91%) by chiral HPLC analysis. See alcohol **2-41** below.



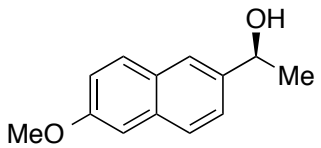
(*R*)-1-(naphthalen-1-yl)ethanol (2-41). Prepared via General Procedure C using benzylic boronate **2-25**. The crude mixture was purified by silica gel chromatography (20% EtOAc/hexanes) to give **2-41** (run 1 (47 mg of **2-25**): 21 mg, 72%) as a colorless oil. The enantiomeric excess was determined to be 92% (run 1: 92% ee; run 2: 91% ee) by chiral HPLC analysis (CHIRAPAK IC, 1.0 mL/min, 2% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 23.87 min, t_R(minor) = 18.43 min): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.69 (d, *J* = 7.1 Hz, 1H), 7.57 – 7.45 (m, 3H), 5.69 (q, *J* = 6.3 Hz, 1H), 1.96 (s, 1H), 1.68 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 133.9, 130.4, 129.1, 128.1, 126.2, 125.73, 125.70, 123.3, 122.1, 67.3, 24.5. The spectral data of this compound match that previously reported in the literature.[13]



(*S*)-2-(1-(6-methoxynaphthalen-2-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2-26). Prepared via General Procedure A using ammonium salt **2-22c** (amine prepared in ≥95% ee). The crude mixture was purified by silica gel

chromatography (5% EtOAc/hexanes) to give **2-26** (run 1: 78 mg, 83%; run 2: 78 mg, 83%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (t, *J* = 8.1 Hz, 2H), 7.60 (s, 1H), 7.38 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.12 (d, *J* = 8.1 Hz, 2H), 3.91 (s, 3H), 2.60 (q, *J* = 7.5 Hz, 1H), 1.44 (d, *J* = 7.5 Hz, 3H), 1.23 (s, 6H), 1.22 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 140.3, 132.7, 129.5, 129.1, 127.8, 126.7, 125.3, 118.5, 105.7, 83.5, 55.4, 24.8, 24.7, 17.1.[12] The spectral data match that previously reported in the literature.[1b]

Boronate **2-26** was oxidized to alcohol **2-42** via General Procedure C. The enantiomeric excess was determined to be 99% (run 1: 98% ee; run 2: 99% ee) by chiral HPLC analysis. See alcohol **2-42** below.



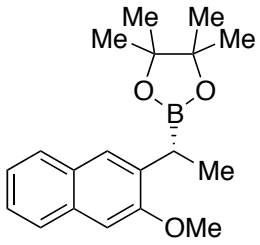
(*S*)-1-(6-methoxynaphthalen-2-yl)ethanol (2-42). Prepared via General Procedure C using benzylic boronate **2-26**. The crude mixture was purified by silica gel chromatography (20% EtOAc/hexanes) to give **2-42** (run 1 (67 mg of **2-26**): 31 mg, 72%) as a white solid; the enantiomeric excess was determined to be 99% (run 1: 98% ee; run 2: 99% ee) by chiral HPLC analysis (CHIRALPAK IB, 1.0 mL/min, 3% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 19.99 min, t_R(minor) = 25.84 min): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 – 7.69 (m, 3H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.18 – 7.11 (m, 2H), 5.02 (q, *J* = 6.5 Hz, 1H), 3.92 (s, 3H), 2.03 (s, 1H), 1.57 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.8, 141.1, 134.2, 129.6, 128.9, 127.3, 124.5, 123.9, 119.1, 105.9, 70.6, 55.5, 25.2. The spectral data match that previously reported in the literature.[14]

(*S*)-*tert*-butyldiphenyl((6-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)naphthalen-2-yl)oxy)silane (2-27). Prepared via General Procedure A using ammonium salt **2-22d** (amine prepared in ≥95% ee). The crude mixture was purified by silica gel chromatography (5% EtOAc/hexanes) to give **2-27** (76 mg, 47%) as a white solid (mp 84–86 ºC): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.78 (m, 4H), 7.62 – 7.53 (m, 2H), 7.49 – 7.37 (m, 7H), 7.29 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.10 – 7.03 (m, 2H), 2.57 (q, *J* = 7.4 Hz, 1H), 1.42 (d, *J* = 7.5 Hz, 3H), 1.25 (s, 6H), 1.23 (s, 6H), 1.18 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.8, 140.4, 135.7, 133.2, 132.7, 130.0, 129.6, 128.8, 128.0, 127.6, 126.8, 125.2, 121.5, 114.5, 83.5, 26.8, 24.82, 24.79, 19.7, 17.2;[12] ^{11}B NMR (193 MHz, $CDCl_3$) δ 33.6; ^{29}Si NMR (79 MHz, $CDCl_3$) δ –6.4; FTIR (neat) 2960, 2858, 1603, 1500, 1352, 1143, 975, 701 cm^{-1}; HRMS (LIFDI) calculated for $C_{34}H_{41}BO_3Si$: 536.2887, found: 536.2894.

Boronate **2-27** was oxidized to alcohol **2-43** via General Procedure C. The enantiomeric excess was determined to be 92% by chiral HPLC analysis. See alcohol **2-43** below.

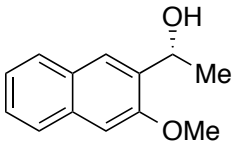
(*S*)-1-(6-((tert-butyldiphenylsilyl)oxy)naphthalen-2-yl)ethanol (2-43). Prepared via General Procedure C using benzylic boronate **2-27**. The crude mixture was purified by silica gel chromatography (20% EtOAc/hexanes) to give **2-43** (run 1 (71 mg of **2-27**): 54 mg, 95%) as a colorless semi-solid. The enantiomeric excess was determined to be 92% by chiral HPLC analysis (CHIRALPAK IA, 1.0 mL/min, 1% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 35.70 min, t_R(minor) = 33.76 min. $[\alpha]_D^{24}$ = –20.2º (c 2.2, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.75 (m, 4H), 7.67 (s, 1H), 7.63 – 7.59 (m, 1H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.47 – 7.34 (m, 7H), 7.12 – 7.05 (m, 2H), 4.98 (q, *J* = 6.4 Hz, 1H), 1.99 (bs, 1H), 1.54 (d, *J* = 6.5 Hz, 3H), 1.16 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6, 141.1, 135.7, 134.0, 133.0, 130.1, 129.3, 128.9, 128.0, 127.3, 124.2, 123.7, 122.0, 114.7, 70.6, 26.7, 25.2, 19.7; ^{29}Si NMR (119 MHz, $CDCl_3$) δ –5.9; FTIR (neat) 3347 (broad), 3051, 2931, 2858, 1606, 1482, 1263,

1175, 114, 76, 701, 504 cm^{-1}; HRMS (CI+) calculated for $C_{28}H_{30}BO_2Si$: 427.2093, found: 427.2090.



(*R*)-2-(1-(3-methoxynaphthalen-2-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2-28). Prepared via General Procedure A using ammonium salt **2-22e** (amine prepared in ≥95% ee). The crude mixture was purified by silica gel chromatography (5% EtOAc/hexanes) to give **2-28** (46 mg, 49%) as an opaque semi-solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.69 (m, 2H), 7.60 (s, 1H), 7.38 (ddd, *J* = 8.1, 6.8, 1.4 Hz, 1H), 7.31 (ddd, *J* = 8.1, 6.9, 1.3 Hz, 1H), 7.08 (s, 1H), 3.93 (s, 3H), 2.63 (q, *J* = 7.5 Hz, 1H), 1.43 (d, *J* = 7.5 Hz, 3H), 1.26 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 135.7, 133.1, 129.4, 127.3, 126.5, 126.3, 125.3, 123.5, 104.4, 83.2, 55.1, 24.80, 24.77, 14.8;[12] ^{11}B NMR (193 MHz, $CDCl_3$) δ 33.6; FTIR (neat) 2976, 1472, 1388, 1251, 1144, 847, 746 cm^{-1}; HRMS (LIFDI) calculated for $C_{19}H_{25}BO_3$: 312.1897, found: 312.1884.

Boronate **2-28** was oxidized to alcohol **3e** via General Procedure C. The enantiomeric excess was determined to be 95% by chiral HPLC analysis. See alcohol **2-44** below.



(*R*)-1-(3-methoxynaphthalen-2-yl)ethanol (2-44). Prepared via General Procedure C using benzylic boronate **2-28**. The crude mixture was purified by silica gel chromatography (20% EtOAc/hexanes) to give **2-44** (run 1 (46 mg of **2-28**): 25 mg, 83%) as a clear oil. The enantiomeric excess was determined to be 95% (CHIRALPAK IB, 1.0 mL/min, 5% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 22.47 min, t_R(minor) = 14.96 min. $[\alpha]_D^{24}$ = –35.7º (c 0.11, $CHCl_3$): ^{1}H NMR (600 MHz,

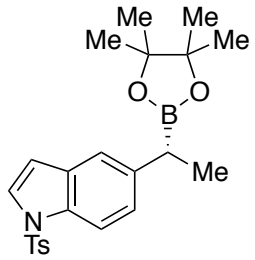
$CDCl_3$) δ 7.80 – 7.76 (m, 2H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.13 (s, 1H), 5.22 (q, *J* = 6.0 Hz, 1H), 3.97 (s, 3H), 2.77 (s, 1H), 1.61 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.6, 135.0, 133.9, 128.9, 127.9, 126.5, 126.4, 125.3, 124.1, 105.6, 67.0, 55.5, 23.1. The spectral data match that previously reported in the literature for the racemic compound.[15]

(*S*)-2-(1-(benzofuran-5-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2-29). Prepared via General Procedure A, except that the reaction temperature was 50 ºC, using ammonium salt **2-22f** (amine prepared in ≥95% ee). The crude mixture was purified by silica gel chromatography (5% EtOAc/hexanes) to give **2-29** (run 1: 48 mg, 59%; run 2: 55 mg, 67%) as a white solid (mp 58–59 ºC): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 2.2 Hz, 1H), 7.45 (d, *J* = 1.8 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 1H), 7.17 (dd, *J* = 8.6, 1.9 Hz, 1H), 6.71 (dd, *J* = 2.2, 1.0 Hz, 1H), 2.54 (q, *J* = 7.5 Hz, 1H), 1.39 (d, *J* = 7.5 Hz, 3H), 1.23 (s, 6H), 1.21 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.4, 144.9, 139.6, 127.7, 124.7, 119.8, 111.1, 106.7, 83.4, 24.79, 24.75, 17.9;[12] ^{11}B NMR (193 MHz, $CDCl_3$) δ 33.6; FTIR (neat) 2976, 1467, 1319, 1144, 843, 737 cm^{-1}; HRMS (LIFDI) calculated for $C_{16}H_{21}BO_3$: 272.1584, found: 272.1611.

Boronate **2-29** was oxidized to alcohol **2-45** via General Procedure C. The enantiomeric excess was determined to be 98% (run 1: 97% ee; run 2: 98% ee) by chiral HPLC analysis. See alcohol **2-45** below.

(*S*)-1-(benzofuran-5-yl)ethanol (2-45). Prepared via General Procedure C using benzylic boronate **2-29**. The crude mixture was purified by silica gel chromatography

(20% EtOAc/hexanes) to give **2-45** (run 1 (41 mg of **2-29**): 15 mg, 61%) as a clear oil. The enantiomeric excess was determined to be 98% (run 1: 97% ee; run 2: 98% ee) by chiral HPLC analysis (CHIRALPAK IC, 0.5 mL/min, 2% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 45.76 min, t_R(minor) = 43.97 min. $[\alpha]_D^{24}$ = –33.0º (c 0.79, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.57 (m, 2H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.32 (dd, *J* = 8.6, 1.8 Hz, 1H), 6.76 (d, *J* = 1.1 Hz, 1H), 5.01 (q, *J* = 6.4 Hz, 1H), 1.92 (bs, 1H), 1.54 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 145.6, 140.7, 127.6, 122.2, 118.1, 111.5, 106.8, 70.8, 25.7; FTIR (neat) 3344 (broad), 2921, 1444, 1261, 1129, 1072, 891, 813, 738 cm^{-1}; HRMS (CI+) calculated for $C_{10}H_{11}O_2$: 163.0759, found: 163.0756.

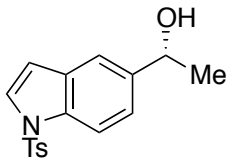


(*R*)-5-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-1-tosyl-1*H*-indole (2-30). Prepared via General Procedure A using ammonium salt **2-22g** (prepared in ≥95% ee). Instead of filtering through Celite®, the diluted mixture was filtered through a small plug of silica gel and then concentrated. 1,3,5-Trimethoxybenzene was added as internal standard, and the yield was determined by ^{1}H NMR to be 44% (run 1: 46%, run 2: 41%). The reaction mixture was complicated, preventing effective purification and isolation on scale. However, an analytical sample of **2-30** (contaminated with ~15% B_2pin_2) was purified by silica gel chromatography (prep TLC, 30% EtOAc/hexanes) to enable characterization: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.6 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 3.6 Hz, 1H), 7.34 (s, 1H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.17 (dd, *J* = 8.6, 1.3 Hz, 1H), 6.57 (d, *J* = 3.6 Hz, 1H), 2.48 (q, *J* = 7.5 Hz, 1H), 2.33 (s, 3H), 1.32 (d, *J* = 7.5 Hz, 3H), 1.20 (s, 6H), 1.18 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 140.2, 135.6, 133.1, 131.2, 130.0, 127.0, 126.3, 125.2, 120.0, 113.4, 109.3, 83.5, 24.79, 24.76, 21.7, 17.6;[12] ^{11}B (193 MHz,

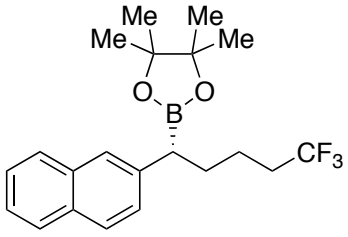
$CDCl_3$) δ 33.8; FTIR (neat, cm^{-1}) 2977, 2930, 1459, 1372, 1173, 676, 583; HRMS (CI) calculated for $C_{23}H_{28}BNO_4S$: 425.1832, found: 425.1840.

The sample was then concentrated and subjected to General Procedure C for oxidation and determination of enantiomeric excess.

Boronate **2-30** was oxidized to alcohol **2-46** via General Procedure C. The enantiomeric excess was determined to be 96% by chiral HPLC analysis. See alcohol **2-46** below.

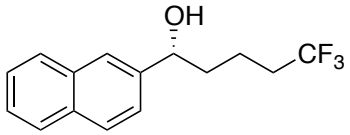


(*R*)-1-(1-tosyl-1*H*-indol-5-yl)ethanol (2-46). Prepared via General Procedure C using benzylic boronate **2-30**. The crude mixture was purified by silica gel chromatography (40% EtOAc/hexanes) to give **2-46** (run 1 (43 mg of **2-30**): 34 mg, 79%) as a pale yellow semi-solid. The enantiomeric excess was determined to be 96% (run 1: 96% ee; run 2: 95% ee) by chiral HPLC analysis (CHIRALPAK IA, 1.0 mL/min, 5% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 58.15 min, t_R(minor) = 53.38 min. $[\alpha]_D^{24}$ = -18.7º (c 0.165, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.6 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 3.6 Hz, 1H), 7.52 (s, 1H), 7.31 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.20 (d, *J* = 8.2 Hz, 2H), 6.62 (d, *J* = 3.6 Hz, 1H), 4.94 (q, *J* = 6.4 Hz, 1H), 2.32 (s, 3H), 1.99 (s, 1H), 1.49 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 141.2, 135.3, 134.3, 131.0, 130.0, 126.9, 126.9, 122.5, 118.2, 113.7, 109.2, 70.6, 25.5, 21.7; FTIR (neat) 3379 (broad), 2971, 1596, 1369, 1173, 1128, 676, 579 cm^{-1}; HRMS (CI+) $[M+H]^+$ calculated for $[C_{17}H_{18}NO_3S]^+$: 316.1007, found: 316.1017.



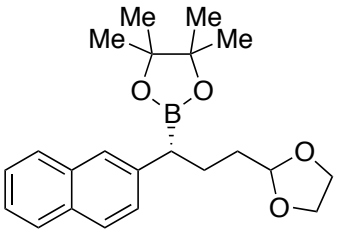
(*R*)-4,4,5,5-tetramethyl-2-(5,5,5-trifluoro-1-(naphthalen-2-yl)pentyl)-1,3,2-dioxaborolane (2-31). Prepared via General Procedure A using ammonium salt **1h** (amine prepared in ≥95% ee). The crude mixture was purified by silica gel chromatography (5% EtOAc/hexanes) to give **2-31** (run 1: 73 mg, 64%; run 2: 69 mg, 60%) as a white solid (mp 74–76 ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.74 (m, 3H), 7.65 (s, 1H), 7.50 – 7.33 (m, 3H), 2.50 (t, J = 7.9 Hz, 1H), 2.19 – 1.96 (m, 3H), 1.91 – 1.78 (m, 1H), 1.65 – 1.50 (m, 2H), 1.23 (s, 6H), 1.20 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.2, 134.0, 132.1, 128.1, 127.7, 127.6, 127.4 (q, $J_{C\text{-}F}$ = 276.4 Hz), 127.3, 126.5, 126.0, 125.2, 83.7, 33.9 (q, $J_{C\text{-}F}$ = 28.4 Hz), 31.6, 24.8, 24.7, 21.7 (q, $J_{C\text{-}F}$ = 2.7 Hz);[12] ^{11}B NMR (193 MHz, $CDCl_3$) δ 33.1; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ –66.3; FTIR (neat) 2978, 1361, 1259, 1141, 857, 749 cm^{-1}; HRMS (CI+) calculated for $C_{21}H_{26}BF_3O_2$: 379.2049, found: 379.2034.

Boronate **2-31** was oxidized to alcohol **2-47** via General Procedure C. The enantiomeric excess was determined to be 96% (run 1: 96% ee; run 2: 96% ee) by chiral HPLC analysis. See alcohol **3h** below.



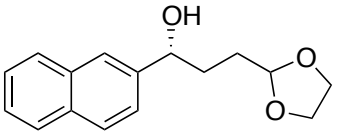
(*R*)-5,5,5-trifluoro-1-(naphthalen-2-yl)pentan-1-ol (2-47). Prepared via General Procedure C using benzylic boronate **2-31**. The crude mixture was purified by silica gel chromatography (20% EtOAc/hexanes) to give **2-47** (run 1 (61 mg of **2-31**): 40 mg, 93%) as a white solid (mp 48–50 ºC). The enantiomeric excess was determined to be 96% (run 1: 96% ee; run 2: 96% ee) by chiral HPLC analysis (CHIRALPAK IB, 1.0 mL/min, 3% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 28.25 min, t_R(minor) = 25.09 min. $[\alpha]_D^{24}$ = +38.4º (c 0.75, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.80 (m, 3H), 7.76 (s, 1H), 7.55 – 7.48 (m, 2H), 7.46 (dd, J = 8.6, 1.8 Hz, 1H), 4.87 – 4.79 (m, 1H), 2.20 – 2.02 (m, 3H), 1.99 – 1.67 (m, 3H), 1.68 – 1.52 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 133.4, 133.2, 128.7, 128.1, 127.9, 127.2 (q, $J_{C\text{-}F}$ = 277.5 Hz), 126.5, 126.2, 124.7, 123.9, 74.4, 37.8, 33.7 (q, $J_{C\text{-}F}$ = 28.6 Hz), 18.6 (q, $J_{C\text{-}F}$ = 3.0 Hz); ^{19}F NMR (376.5 Hz, $CDCl_3$) δ –66.3; FTIR (neat) 3350 (broad), 2947,

1391, 1259, 1134, 1028, 821, 749, 479 cm^{-1}; HRMS (CI+) calculated for $C_{15}H_{16}F_3O$: 269.1153, found: 269.1158.



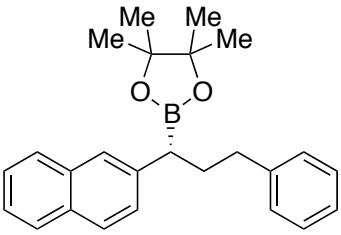
(*R*)-2-(3-(1,3-dioxolan-2-yl)-1-(naphthalen-2-yl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2-32). Prepared via General Procedure A using ammonium salt **2-22i** (amine prepared in ≥95% ee). The crude mixture was purified by silica gel chromatography (10% EtOAc/hexanes) to give **2-32** (64 mg, 58%) as a white solid (mp 82–84 ºC) (note: a 10:1 mixture of product to B_2pin_2 was observed): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.72 (m, 3H), 7.65 (s, 1H), 7.47 – 7.36 (m, 3H), 4.86 (t, *J* = 4.8 Hz, 1H), 3.98 – 3.77 (m, 4H), 2.51 (t, *J* = 8.0 Hz, 1H), 2.15 – 2.01 (m, 1H), 1.99 – 1.84 (m, 1H), 1.76 – 1.59 (m, 2H), 1.21 (s, 6H), 1.19 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 133.9, 131.9, 127.9, 127.63, 127.59 127.5, 126.5, 125.8, 125.0, 104.7, 83.5, 64.9, 33.5, 26.8, 24.8, 24.7; ^{11}B NMR (193 MHz, $CDCl_3$) δ 33.2; FTIR (neat) 2977, 2882, 1371, 1324, 1141, 857, 750 cm^{-1}; HRMS (LIFDI) calculated for $C_{22}H_{29}BO_4$: 368.2140, found: 368.2143.

Boronate **2-32** was oxidized to alcohol **2-48** via General Procedure C. The enantiomeric excess was determined to be 98% by chiral HPLC analysis. See alcohol **3i** below.



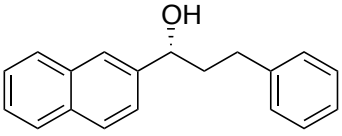
(*R*)-3-(1,3-dioxolan-2-yl)-1-(naphthalen-2-yl)propan-1-ol (2-48). Prepared via General Procedure C using benzylic boronate **2-32**. The crude mixture was purified by silica gel chromatography (40% EtOAc/hexanes) to give **2-38** (36 mg, 84%) as a white solid (mp 67–69 ºC). The enantiomeric excess was determined to be 98% by chiral HPLC analysis (CHIRALPAK IB, 1.0 mL/min, 5% *i*-PrOH/hexanes, λ=254

nm); t_R(major) = 31.06 min, t_R(minor) = 27.49 min. $[\alpha]_D^{24}$ = –18.4º (c 1.78, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.78 (m, 4H), 7.53 – 7.40 (m, 3H), 4.96 – 4.85 (m, 2H), 4.03 – 3.81 (m, 4H), 2.74 (d, *J* = 3.5 Hz, 1H), 2.05 – 1.92 (m, 2H), 1.91 – 1.73 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 133.4, 133.0, 128.4, 128.1, 127.8, 126.2, 125.9, 124.6, 124.2, 104.4, 74.3, 65.2, 65.1, 33.1, 30.1; FTIR (neat) 3434 (broad), 2882, 1409, 1139, 1031, 822, 751, 479 cm^{-1}; HRMS (CI+) calculated for $C_{16}H_{18}O_3$: 241.1229, found: 241.1225.



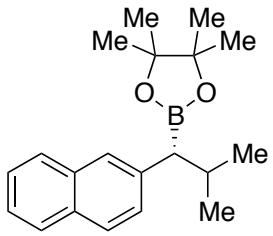
(*R*)-4,4,5,5-tetramethyl-2-(1-(naphthalen-2-yl)-3-phenylpropyl)-1,3,2-dioxaborolane (2-33). Prepared via General Procedure A using ammonium salt **2-22j** (amine prepared in ≥95% ee). The crude mixture was purified by silica gel chromatography (5% EtOAc/hexanes) to give **2-33** (80 mg, 72%) as a white solid (mp 77–79 ºC): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.79 (m, 3H), 7.71 (s, 1H), 7.52 – 7.41 (m, 3H), 7.34 – 7.28 (m, 2H), 7.24 – 7.18 (m, 3H), 2.65 (t, *J* = 7.9 Hz, 2H), 2.60 (t, *J* = 7.9 Hz, 1H), 2.37 – 2.26 (m, 1H), 2.21 – 2.10 (m, 1H), 1.25 (s, 6H), 1.23 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 140.6, 133.9, 131.9, 128.7, 128.4, 128.0, 127.7, 127.6, 127.5, 126.5, 125.84, 125.81, 125.0, 83.6, 35.6, 34.3, 24.84, 24.76;[12] ^{11}B NMR (193 MHz, $CDCl_3$) δ 33.7; FTIR (neat) 2977, 2930, 1323, 1141, 857, 748, 699 cm^{-1}; HRMS (LIFDI) calculated for $C_{25}H_{29}BO_2$: 372.2261, found: 372.2270.

Boronate **2-33** was oxidized to alcohol **2-48** via General Procedure C. The enantiomeric excess was determined to be 98% by chiral HPLC analysis. See alcohol **2-48** below.



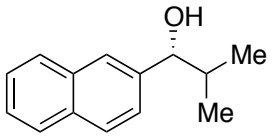
(*R*)-1-(naphthalen-2-yl)-3-phenylpropan-1-ol (2-48). Prepared via General Procedure C using benzylic boronate **2-33**. The crude mixture was purified by silica

gel chromatography (20% EtOAc/hexanes) to give **2-48** (43 mg, 94%) as a white solid (mp 85–86 ºC). The enantiomeric excess was determined to be 98% by chiral HPLC analysis (CHIRALPAK IA, 1.0 mL/min, 2% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 35.44 min, t_R(minor) = 38.33 min: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.81 (m, 3H), 7.79 (s, 1H), 7.55 – 7.44 (m, 3H), 7.34 – 7.27 (m, 2H), 7.25 – 7.16 (m, 3H), 4.87 (ddd, *J* = 8.1, 5.5, 2.9 Hz, 1H), 2.85 – 2.65 (m, 2H), 2.30 – 2.06 (m, 2H), 2.02 (d, *J* = 3.1 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.1, 141.9, 133.5, 133.2, 128.56, 128.59, 128.63, 128.1, 127.9, 126.4, 126.1, 126.0, 124.9, 124.2, 74.2, 40.5, 32.2. The spectral data match that of the literature.[16]

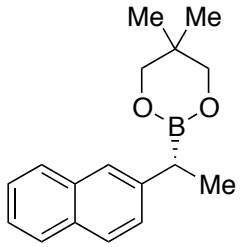


(*R*)-4,4,5,5-tetramethyl-2-(2-methyl-1-(naphthalen-2-yl)propyl)-1,3,2-dioxaborolane (2-34). Prepared via General Procedure A using ammonium salt **2-22k** (amine prepared in ≥95% ee). The crude mixture was purified by silica gel chromatography (5% EtOAc/hexanes) to give **2-34** (run 1: 46 mg, 49%; run 2: 47 mg, 50%) as a white solid (mp 85–86 ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.71 (m, 3H), 7.66 (s, 1H), 7.47 – 7.36 (m, 3H), 2.33 – 2.19 (m, 1H), 2.16 (d, *J* = 10.5 Hz, 1H), 1.21 (s, 6H), 1.18 (s, 6H), 1.10 (d, *J* = 6.4 Hz, 3H), 0.77 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.2, 133.9, 132.0, 128.1, 127.7, 127.6, 127.3, 125.7, 124.9, 83.4, 31.1, 24.8, 24.7, 23.4, 22.3;[12] ^{13}C NMR (151 MHz, $C(O)(CD_3)_2$) δ 141.2, 134.7, 132.9, 128.7, 128.3, 128.3, 128.2, 127.9, 126.6, 125.7, 83.9, 31.7, 25.0, 24.9, 23.5, 22.4;[4] ^{11}B NMR (193 MHz, $CDCl_3$) δ 33.2; FTIR (neat) 2922, 2850, 1382, 1323, 1143, 1103 cm^{-1}; HRMS (LIFDI) calculated for $C_{20}H_{27}BO_2$: 310.2104, found: 310.2126.

Boronate **2-34** was oxidized to alcohol **2-49** via General Procedure C. The enantiomeric excess was determined to be 98% (run 1: 97%, run 2: 98%) by chiral HPLC analysis. See alcohol **2-49** below.

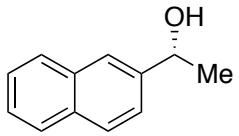


(*R*)-2-methyl-1-(naphthalen-2-yl)propan-1-ol (2-49). Prepared via General Procedure C using benzylic boronate **2-34**. The crude mixture was purified by silica gel chromatography (20% EtOAc/hexanes) to give **2-49** (run 1 (39 mg of **2-34**): 7 mg, 28%) as a clear oil. The enantiomeric excess was determined to be 98% (run 1: 97%, run 2: 98%) by chiral HPLC analysis (CHIRALPAK IC, 1.0 mL/min, 2% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 17.49 min, t_R(minor) = 16.15 min; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 – 7.80 (m, 3H), 7.76 (s, 1H), 7.51 – 7.44 (m, 3H), 4.54 (d, *J* = 6.9 Hz, 1H), 2.12 – 2.03 (m, *J* = 6.7 Hz, 1H), 1.93 (s, 1H), 1.05 (d, *J* = 6.7 Hz, 3H), 0.84 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2, 133.3, 133.1, 128.2, 128.1, 127.8, 126.2, 125.9, 125.6, 124.8, 80.4, 35.4, 19.3, 18.4. The spectral data match that previously reported in the literature.[17]

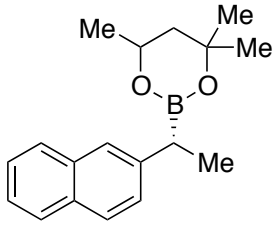


(*R*)-5,5-dimethyl-2-(1-(naphthalen-2-yl)ethyl)-1,3,2-dioxaborinane (2-35). Prepared via General Procedure A using ammonium salt **2-22a** (amine purchased in >99% ee) and bis(neopentyl glycolato)diboron (B_2neop_2) instead of B_2pin_2. Instead of filtering through Celite®, the diluted mixture was filtered through a small plug of silica gel and then concentrated. 1,3,5-Trimethoxybenzene was added as internal standard, and the yield of the reaction was determined by ^{1}H NMR analysis to be 61%. The sample was then concentrated and subjected to General Procedure C for oxidation and determination of enantiomeric excess.

Boronate **2-35** was oxidized to alcohol **2-40** via General Procedure C. The enantiomeric excess was determined to be 95% by chiral HPLC analysis. See alcohol **2-50** below.

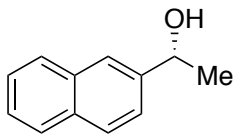


(*R*)-1-(naphthalen-2-yl)ethanol (2-50). Prepared via General Procedure C using benzylic boronate **2-35**. The crude mixture was purified by silica gel chromatography (20% EtOAc/hexanes) to give **2-40** (29 mg, 93%) as a white solid. The enantiomeric excess was determined to be 95% by chiral HPLC analysis (CHIRALPAK IA, 1.0 mL/min, 1% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 45.06 min, t_R(minor) = 47.29 min. The spectral data match that of alcohol **2-40** above.



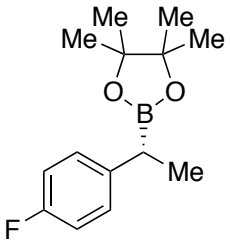
4,4,6-trimethyl-2-((*R*)-1-(naphthalen-2-yl)ethyl)-1,3,2-dioxaborinane (2-36). Prepared via General Procedure A using ammonium salt **2-22a** (amine purchased in >99% ee) and bis(hexylene glycolato)diboron (B_2hex_2) instead of B_2pin_2. Instead of filtering through Celite®, the diluted mixture was filtered through a small plug of silica gel and then concentrated. 1,3,5-Trimethoxybenzene was added as internal standard, and the yield of the reaction was determined by ^{1}H NMR analysis to be 74%. The sample was then concentrated and subjected to General Procedure C for oxidation and determination of enantiomeric excess.

Boronate **2-36** was oxidized to alcohol **2-40** via General Procedure C. The enantiomeric excess was determined to be 95% by chiral HPLC analysis. See alcohol **2-40** below.



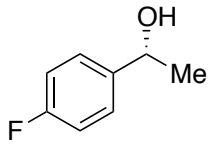
(*R*)-1-(naphthalen-2-yl)ethanol (2-40). Prepared via General Procedure C using benzylic boronate **2-36**. The crude mixture was purified by silica gel chromatography (20% EtOAc/hexanes) to give **2-40** (35 mg, quant.) as a white solid. The enantiomeric

excess was determined to be 95% by chiral HPLC analysis (CHIRALPAK IA, 1.0 mL/min, 1% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 44.64 min, t_R(minor) = 46.84 min. The spectral data match that of alcohol **2-40** above.



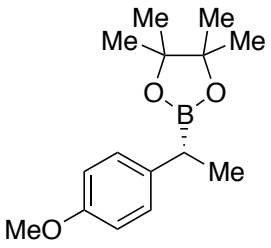
(*R*)-2-(1-(4-fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2-37). Prepared via General Procedure B on a 0.5-mmol scale using ammonium salt **2-22n** (amine purchased in >99% ee) and ICy·HBF_4 (19.2 mg, 0.060 mmol, 12 mol %) instead of PPh_2Cy. The crude mixture was purified by silica gel chromatography (5% EtOAc/hexanes) to give **2-37** (66 mg, 53%) as a clear oil (please note that **2-37** was not subjected to high vacuum due to its volatility): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.13 (m, 2H), 6.98 – 6.91 (m, 2H), 2.42 (q, J = 7.5 Hz, 1H), 1.31 (d, J = 7.5 Hz, 3H), 1.21 (s, 6H), 1.20 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0 (d, $J_{C\text{-}F}$ = 243.2 Hz), 140.7 (d, $J_{C\text{-}F}$ = 3.1 Hz), 129.1 (d, $J_{C\text{-}F}$ = 7.7 Hz), 115.1 (d, $J_{C\text{-}F}$ = 21.0 Hz), 83.5, 24.8, 17.4. The spectral data match that reported in the literature.[18] The sample was then concentrated and subjected to General Procedure C for oxidation and determination of enantiomeric excess.

Boronate **2-37** was oxidized to alcohol **2-50** via General Procedure C. The enantiomeric excess was determined to be 86% (run 1 from oxidation of isolated **2-37**: 87% ee; run 2 from oxidation of crude **2-37**: 85% ee) by chiral HPLC analysis. See alcohol **2-50** below.



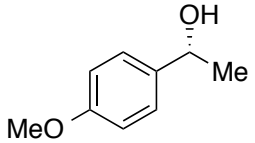
(*R*)-1-(4-fluorophenyl)ethanol (2-50). Prepared via General Procedure C using benzylic boronate **2-37**. The crude mixture was purified by silica gel chromatography

(20% EtOAc/hexanes) to give **2-50** (16 mg, 62%) as a clear oil. The enantiomeric excess was determined to be 86% (run 1 from oxidation of isolated **2-37**: 87% ee; run 2 from oxidation of crude **2-37**: 85% ee) by chiral HPLC analysis (CHIRALPAK IF, 1.0 mL/min, 2% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 16.25 min, t_R(minor) = 17.65 min: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 8.3, 5.6 Hz, 2H), 7.03 (t, *J* = 8.6 Hz, 2H), 4.89 (q, *J* = 6.4 Hz, 1H), 1.87 (s, 1H), 1.48 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.3 (d, J_{C-F} = 244.6 Hz), 141.7, 127.2 (d, J_{C-F} = 7.6 Hz), 115.4 (d, J_{C-F} = 22.7 Hz), 70.0, 25.5; ^{19}F NMR (565 MHz, $CDCl_3$) δ –115.4. The spectral data match that of the literature.[19]



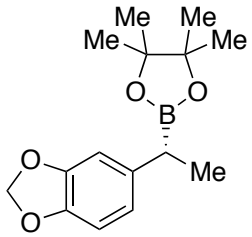
(*R*)-2-(1-(4-methoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2-38). Prepared via General Procedure B using ammonium salt **2-22o** (amine precursor purchased in >99% ee). The crude mixture was purified by silica gel chromatography (5% EtOAc/hexanes) to give **2-38** (run 1: 45 mg, 57%; run 2: 41 mg, 52%) as a clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 3.78 (s, 3H), 2.38 (q, *J* = 7.5 Hz, 1H), 1.30 (d, *J* = 7.6 Hz, 3H), 1.22 (s, 6H), 1.20 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 137.0, 128.6, 113.8, 83.2, 55.2, 24.7, 24.6, 17.4.[12] The spectral data matches that previously reported in the literature.[20]

Boronate **2-38** was oxidized to alcohol **2-51** via General Procedure C. The enantiomeric excess was determined to be 86% (run 1: 85% ee; run 2: 87% ee) by chiral HPLC analysis. See alcohol **2-51** below.



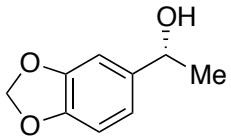
(*R*)-1-(4-methoxyphenyl)ethanol (2-51). Prepared via General Procedure C using benzylic boronate **2-38**. The crude mixture was purified by silica gel chromatography

(20% EtOAc/hexanes) to give **2-51** (run 1 (45 mg of **2-38**): 19 mg, 72%) as a clear oil. The enantiomeric excess was determined to be 86% (run 1: 85%, run 2: 87%) by chiral HPLC analysis (CHIRALPAK IB, 1.0 mL/min, 2% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 20.16 min, t_R(minor) = 22.24 min: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 4.86 (q, *J* = 6.4 Hz, 1H), 3.80 (s, 3H), 1.84 (bs, 1H), 1.48 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 138.1, 126.8, 114.0, 70.2, 55.5, 25.2. The spectral data match that previously reported in the literature.[21]



(*R*)-2-(1-(benzo[d][1,3]dioxol-5-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2-39). Prepared via General Procedure B using ammonium salt **2-22p** (amine prepared in ≥95% ee). The crude mixture was purified by silica gel chromatography (5% EtOAc/hexanes) to give **2-39** (run 1: 48 mg, 58%; run 2: 53 mg, 63%) as a clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74 (d, *J* = 1.7 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 6.65 (dd, *J* = 8.0, 1.7 Hz, 1H), 5.90 (s, 2H), 2.35 (q, *J* = 7.5 Hz, 1H), 1.28 (d, *J* = 7.5 Hz, 3H), 1.22 (s, 6H), 1.20 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 145.2, 139.0, 120.5, 108.6, 108.3, 100.8, 83.5, 24.8, 24.8, 17.7;[12] ^{11}B NMR (193 MHz, $CDCl_3$) δ 33.3; FTIR (neat) 2977, 1487, 1321, 1237, 1144, 1041, 938, 811 cm^{-1}; HRMS (CI) calculated for $C_{15}H_{21}BO_4$: 277.1611, found: 277.1609.

Boronate **2-39** was oxidized to alcohol **2-52** via General Procedure C. The enantiomeric excess was determined to be 85% (run 1: 84% ee; run 2: 85% ee) by chiral HPLC analysis. See alcohol **2-52** below.



(*R*)-1-(benzo[*d*][1,3]dioxol-5-yl)ethanol (2-52). Prepared via General Procedure C using benzylic boronate **2-29**. The crude mixture was purified by silica gel

chromatography (20% EtOAc/hexanes) to give **2-52** (run 1 (40 mg of **2-29**): 21 mg, 87%) as a clear oil. The enantiomeric excess was determined to be 85% (run 1: 85%, run 2: 84%) by chiral HPLC analysis (CHIRALPAK IA, 1.0 mL/min, 3% *i*-PrOH/hexanes, λ=210 nm); t_R(major) = 19.60 min, t_R(minor) = 22.01 min: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 – 6.88 (m, 1H), 6.85 – 6.75 (m, 2H), 5.95 (s, 2H), 4.82 (q, *J* = 6.4 Hz, 1H), 1.76 (bs, 1H), 1.46 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9, 147.0, 140.1, 118.9, 108.3, 106.2, 101.2, 70.5, 25.3. The spectral data match that previously reported in the literature.[21]

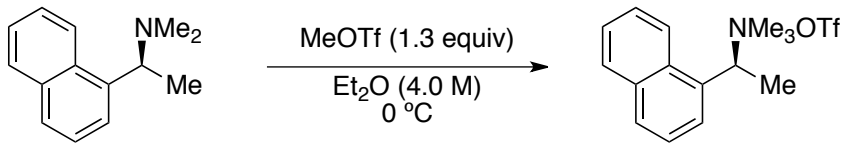
Preparation of Benzylic Ammonium Salts

Enantioenriched amines that were not commercially available were obtained through Grignard or hydride additions to Ellman's sulfinimines.[10] Via these reactions, a single diastereomer of each sulfinamine was isolated (as determined by ^{1}H NMR analysis). We thus assume ≥95% ee of the subsequent amine after removal of Ellman's auxiliary. Dimethyl benzyl amines were then prepared using Escheweiler-Clarke conditions or reductive amination of the corresponding primary benzyl amine with formaldehyde.[11] We assume no loss of ee in the formation of the trimethyl ammonium triflates from this intermediate. For enantioenriched amines that were commercially available, we also assume no loss of ee in the formation of the trimethyl ammonium triflates.

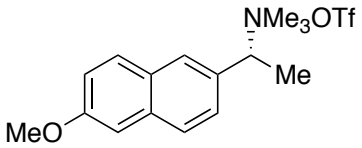
Ammonium triflates **2-22a**, **2-22b**, **2-22k**, **2-22n**, and **2-22o** have been previously prepared in our laboratory.[22]

Ammonium triflates prepared via these procedures were used as is in the stereospecific borylation reaction, without further purification. In some cases, impurities are present in the ammonium triflates.

General Procedure D: Preparation of (*S*)-*N*,*N*,*N*-trimethyl-1-(naphthalen-1-yl)ethanaminium trifluoromethanesulfonate (2-22b)



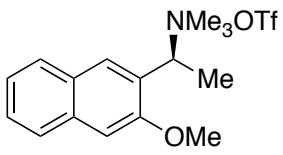
(*S*)-*N*,*N*-Dimethyl-1-(naphthalen-1-yl)ethanamine (0.806 g, 4.04 mmol, 1.0 equiv), which was prepared using Escheweiler-Clarke conditions[11a] from (*S*)-(-)-1-(1-naphthyl)ethylamine (purchased in >99% ee), was dissolved in Et_2O (1.01 mL, 4.0 M). MeOTf (0.58 mL, 5.25 mmol, 1.3 equiv) was added dropwise at 0 ºC. After complete addition, the mixture was allowed to stir for an additional 30 minutes at 0 ºC. The mixture was diluted with Et_2O (~ 2 mL), taken out of the ice bath, and allowed to warm to room temperature while stirring. The white precipitate was filtered and washed with Et_2O (3 x 15 mL). The solid was dried under high vacuum to afford salt **2-22b** (1.377 g, 94%) as a white solid, which was used directly in the benzylic borylation. This compound was previously prepared in our laboratory via this method.[15]



(*R*)-1-(6-methoxynaphthalen-2-yl)-*N*,*N*,*N*-trimethylethanaminium trifluoromethanesulfonate (2-22c). Prepared according to General Procedure D on a 5.64 mmol scale from (*R*)-1-(6-methoxynaphthalen-2-yl)-*N*,*N*-dimethylethanamine, which was prepared using Escheweiler-Clarke conditions[11a] from (*R*)-1-(6-methoxynaphthalen-2-yl)ethanamine (prepared using Ellman's auxiliary[10]), to afford salt **2-22c** (2.085 g, 94%) as a white solid (mp 109–111 ºC): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.84-7.74 (m, 2H), 7.49 (d, J = 8.3 Hz, 1H), 7.19 (dd, J = 9.0, 2.4 Hz, 1H), 7.13 (d, J = 2.1 Hz, 1H), 4.98 (q, J = 6.9 Hz, 1H), 3.92 (s, 3H), 3.15 (s, 9H), 1.88 (d, J = 6.8 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.3, 135.6, 130.2, 128.4, 128.1, 127.2, 121.0 (q, $J_{C\text{-}F}$ = 320.1 Hz), 120.4, 105.7, 74.5, 55.6, 51.2, 15.2; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ –78.4; FTIR (neat) 3043, 1608, 1488, 1270, 1160,

846, 639 cm^{-1}; LRMS (ESI+) $[M\text{-}OTf]^+$ calculated for $[C_{16}H_{22}NO^+]$: 244.2, found: 244.2.

(*R*)-1-(6-((*tert*-butyldiphenylsilyl)oxy)naphthalen-2-yl)-*N*,*N*,*N*-trimethylethanaminium trifluoromethanesulfonate (1d). Prepared according to General Procedure D on a 1.50 mmol scale from (*R*)-1-(6-((*tert*-butyldiphenylsilyl)oxy)naphthalen-2-yl)-*N*,*N*-dimethylethanamine, which was prepared by reductive amination[11b] from (*R*)-1-(6-((*tert*-butyldiphenylsilyl)oxy)naphthalen-2-yl)ethanamine (prepared using Ellman's auxiliary[10]). In this case, stirring ceased as a result of precipitate formation. The solution was diluted with Et_2O to 2.0 M and the stir bar was agitated with a spatula to resume stirring. The reaction afforded salt **1d** (0.698 g, 75%) as a white solid (mp 180–182 ºC): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.74 (d, *J* = 6.9 Hz, 4H), 7.69 (d, *J* = 8.9 Hz, 1H), 7.53 (d, *J* = 8.6 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.39 – 7.33 (m, 5H), 7.13 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.05 (d, *J* = 2.1 Hz, 1H), 4.92 (q, *J* = 6.9 Hz, 1H), 3.13 (s, 9H), 1.84 (d, *J* = 6.9 Hz, 3H), 1.13 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.3, 135.6, 135.4, 132.6, 130.3, 130.1, 128.5, 128.14, 128.09, 127.2, 123.3, 120.9 (q, $J_{C\text{-}F}$ = 320.1 Hz), 114.6, 74.6, 51.2, 26.7, 19.7, 15.2; ^{19}F NMR (565 MHz, $CDCl_3$) δ –78.4; ^{29}Si NMR (119 MHz, $CDCl_3$) δ –5.0; FTIR (neat) 3051, 2933, 2859, 1605, 1483, 1266, 1161, 1031, 879, 703, 639 cm^{-1}; LRMS (ESI+) $[M\text{-}OTf]^+$ calculated for $[C_{31}H_{38}NOSi^+]$: 468.3, found: 468.4.

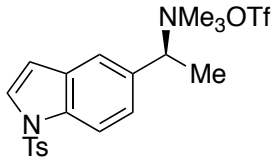


(*S*)-1-(3-methoxynaphthalen-2-yl)-*N*,*N*,*N*-trimethylethanaminium trifluoromethanesulfonate (2-22e) Prepared according to General Procedure D on a 1.45 mmol scale from (*S*)-1-(3-methoxynaphthalen-2-yl)-*N*,*N*-dimethylethanamine,

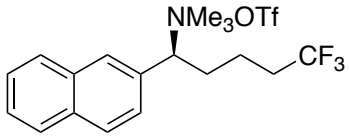
which was prepared using Escheweiler-Clarke conditions[11a] from (*S*)-1-(3-methoxynaphthalen-2-yl)ethanamine (prepared using Ellman's auxiliary[10]). In this case, a white precipitate did not form upon addition of MeOTf. Instead, two distinct layers formed. The top layer was decanted off. The bottom layer was washed with Et_2O (5 x 2 mL) and then hexanes (5 x 2 mL, HPLC grade) and then dried under high vacuum to give salt **2-22e** (0.359 g, 63%) as a clear viscous oil. By NMR, an ~8:1 mixture of rotamers was observed: ^{1}H NMR (600 MHz, $CDCl_3$, major rotamer) δ 7.97 (s, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.22 (s, 1H), 5.29 (q, *J* = 7.1 Hz, 1H), 3.98 (s, 3H), 3.11 (s, 9H), 1.85 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$, major rotamer) δ 154.8, 135.3, 130.7, 128.7, 128.5, 128.1, 126.6, 125.1, 122.5, 120.7 (q, $J_{C\text{-}F}$ = 320.0 Hz), 106.8, 65.9, 56.0, 51.09, 51.07, 51.05, 15.4;[23] ^{19}F NMR (376.5 MHz, $CDCl_3$) δ –78.4; FTIR (neat) 3048, 1634, 1474, 1260, 1163, 1031, 756, 639 cm^{-1}; LRMS (ESI+) $[M\text{-}OTf]^+$ calculated for $[C_{16}H_{22}NO^+]$: 244.2, found: 244.2.

(*R*)-1-(benzofuran-5-yl)-*N*,*N*,*N*-trimethylethanaminium trifluoromethanesulfonate (2-22f). Prepared according to General Procedure D on a 6.12 mmol scale from (*R*)-1-(benzofuran-5-yl)-*N*,*N*-dimethylethanamine, which was prepared using Escheweiler-Clarke conditions[11a] from (*R*)-1-(benzofuran-5-yl)ethanamine (prepared using Ellman's auxiliary[10]). In this case, a white precipitate did not form upon addition of MeOTf. Instead, two distinct layers formed. The top layer was decanted off. The bottom layer was washed with Et_2O (2 mL), which caused white precipitate to form. The precipitate was filtered and washed with Et_2O (3 x 15 mL) and dried under high vacuum to afford salt **2-22f** (2.076 g, 96%) as a white solid (mp 106–108 ºC): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.68 (d, *J* = 2.1 Hz, 1H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 1H), 6.85 – 6.81 (m, 1H), 4.98 (q, *J* = 7.0 Hz, 1H), 3.13 (s, 9H), 1.85 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.8, 146.9, 128.5, 127.1, 120.9 (q, $J_{C\text{-}F}$ = 320.1 Hz), 112.4, 107.0, 74.4,

51.18, 51.15, 51.1, 15.5;[23] ^{19}F NMR (565 MHz, $CDCl_3$) δ –78.4; FTIR (neat) 3042, 1472, 1263, 1158, 1030, 838, 750, 639, 518 cm^{-1}; LRMS (ESI+) $[M\text{-}OTf]^+$ calculated for $[C_{13}H_{18}NO^+]$: 204.1, found: 204.2.

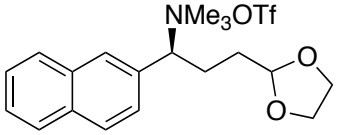


(*S*)-*N*,*N*,*N*-trimethyl-1-(1-tosyl-1*H*-indol-5-yl)ethanaminium trifluoromethanesulfonate (2-22g). Prepared according to General Procedure D on a 2.97 mmol scale from (*S*)-*N*,*N*-dimethyl-1-(1-tosyl-1*H*-indol-5-yl)ethanamine, which was prepared using Escheweiler-Clarke conditions[11a] from (*S*)-1-(1-tosyl-1*H*-indol-5-yl)ethanamine (prepared using Ellman's auxiliary[10]) to afford salt **2-22g** (1.277 g, 85%) as a white solid (mp 73-75 ºC); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, J = 8.6 Hz, 1H), 7.79 – 7.73 (m, 3H), 7.62 (d, J = 3.7 Hz, 1H), 7.42 (d, J = 8.6 Hz, 1H), 7.25 (s, 1H), 6.71 (d, J = 3.6 Hz, 1H), 4.91 (q, J = 6.9 Hz, 1H), 3.09 (s, 9H), 2.34 (s, 3H), 1.80 (d, J = 6.9 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.8, 135.6, 135.0, 131.3, 130.4, 128.0, 127.4, 127.1, 120.9 (q, $J_{C\text{-}F}$ = 320.12 Hz), 114.2, 109.1, 74.3, 51.2, 21.8, 15.4; ^{19}F NMR (565 MHz, $CDCl_3$) δ –78.4; FTIR (neat) 3051, 1464, 1373, 1273, 1175, 1031, 639, 581 cm^{-1}; LRMS (ESI+) $[M\text{-}OTf]^+$ calculated for $[C_{20}H_{25}N_2O_2S^+]$: 357.2, found: 357.3.



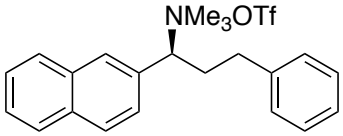
(*S*)-5,5,5-trifluoro-*N*,*N*,*N*-trimethyl-1-(naphthalen-2-yl)pentan-1-aminium trifluoromethanesulfonate (2-22h). Prepared according to General Procedure D on a 3.47 mmol scale from (*S*)-5,5,5-trifluoro-*N*,*N*-dimethyl-1-(naphthalen-2-yl)pentan-1-amine, which was prepared using Escheweiler-Clarke conditions[11a] from (*S*)-5,5,5-trifluoro-1-(naphthalen-2-yl)pentan-1-amine (prepared using Ellman's auxiliary[10]). In this case, a precipitate did not form upon addition of MeOTf. Instead, two distinct

layers were observed. The top layer was decanted. The bottom layer was washed with a 1:1 (v/v) solution of Et_2O/hexanes (5 x 4 mL) and dried under high vacuum at 50 ºC to afford salt **2-22h** (1.492 g, 94%) as a sticky solid: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 – 7.88 (m, 3H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.64 – 7.44 (m, 3H), 4.87 – 4.76 (m, 1H), 3.16 (s, 9H), 2.41 (s, 2H), 2.29 – 2.03 (m, 2H), 1.53 – 1.36 (m, 1H), 1.32 – 1.13 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.0, 134.1, 133.1, 130.0, 129.6, 128.7, 128.2, 127.9, 127.5, 126.9 (q, $J_{C\text{-}F}$ = 277.5 Hz), 122.9, 120.7 (q, $J_{C\text{-}F}$ = 320.1 Hz), 78.7, 51.8, 32.8 (q, $J_{C\text{-}F}$ = 29.0 Hz) 26.3, 19.2; ^{19}F NMR (565 MHz, $CDCl_3$) δ –78.4, –66.2; FTIR (neat) 3053, 2957, 1491, 1260, 1154, 1031, 831, 639 cm^{-1}; LRMS (ESI+) $[M\text{-}OTf]^+$ calculated for $[C_{18}H_{23}F_3N^+]$: 310.2, found: 310.4. Two-dimensonal NMR experiments were used to verify ^{1}H and ^{13}C assignments due to the complex nature of the spectra.



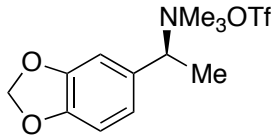
(*S*)-3-(1,3-dioxolan-2-yl)-*N*,*N*,*N*-trimethyl-1-(naphthalen-2-yl)propan-1-aminium trifluoromethanesulfonate (2-22i). Prepared according to General Procedure D on a 1.93 mmol scale from (*S*)-3-(1,3-dioxolan-2-yl)-*N*,*N*-dimethyl-1-(naphthalen-2-yl)propan-1-amine, which was prepared by reductive amination[11b] from (*S*)-3-(1,3-dioxolan-2-yl)-1-(naphthalen-2-yl)propan-1-amine (prepared using Ellman's auxiliary[10]). In this case, a white precipitate did not form upon addition of MeOTf. Instead, two distinct layers formed. The top layer was decanted off. The bottom layer was washed with Et_2O (5 x 2 mL) and then hexanes (5 x 2 mL, HPLC grade) and then dried under high vacuum to give salt **2-22i** (0.854 g, 98%) as a sticky white solid: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 – 7.89 (m, 3H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.63 – 7.41 (m, 3H), 4.89 – 4.83 (m, 1H), 4.81 (t, *J* = 4.0 Hz, 1H), 3.97 – 3.86 (m, 2H), 3.82 – 3.63 (m, 2H. Please note: this peak is contaminated with an unknown impurity. At 50 ºC the peak corresponding to the impurity shifts and an accurate integration of two protons is obtained), 3.17 (s, 9H), 2.50 – 2.29 (m, 2H), 1.60 – 1.24 (m, 2H); ^{1}H NMR (400 MHz, $CDCl_3$, 50 ºC) δ 8.14 – 7.99 (m, 1H), 7.99 – 7.90 (m, 2H), 7.90 – 7.82 (m,

1H), 7.62 – 7.46 (m, 3H), 4.97 – 4.74 (m, 2H), 4.00 – 3.67 (m, 4H), 3.18 (s, 9H), 2.59 – 2.26 (m, 2H), 1.61 – 1.29 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.2, 134.1, 133.1, 129.9, 129.5, 128.8, 128.1, 127.8, 127.4, 123.0, 120.8 (q, J_{C-F} = 321.1 Hz), 102.8, 78.9, 65.1, 65.0, 51.8, 30.0; ^{19}F NMR (565 MHz, $CDCl_3$) δ –78.3; FTIR (neat) 3054, 2890, 1489, 1264, 1159, 1031, 830, 639, 518 cm^{-1}; LRMS (ESI+) $[M\text{-}OTf]^+$ calculated for $[C_{19}H_{26}NO_2^+]$: 300.2, found: 300.3. Two-dimensonal NMR experiments were used to verify ^{1}H and ^{13}C assignments due to the complex nature of the spectra.

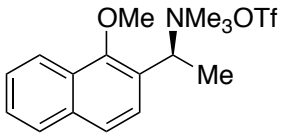


(*S*)-*N*,*N*,*N*-trimethyl-1-(naphthalen-2-yl)-3-phenylpropan-1-aminium trifluoromethanesulfonate (2-22j). Prepared according to General Procedure D on a 1.93 mmol scale from (*S*)-*N*,*N*-dimethyl-1-(naphthalen-2-yl)-3-phenylpropan-1-amine, which was prepared using Escheweiler-Clarke conditions[11a] from (*S*)-3-(1,3-dioxolan-2-yl)-1-(naphthalen-2-yl)propan-1-amine (prepared using Ellman's auxiliary[10]). In this case, a white precipitate did not form upon addition of MeOTf. Instead, two distinct layers formed. The top layer was decanted off. The bottom layer was washed with Et_2O (5 x 2 mL) and then hexanes (5 x 2 mL, HPLC grade) and then dried under high vacuum to give salt **1j** (0.854 g, 98%) as a beige solid that slowly turned yellow (mp 65–68ºC): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 – 7.92 (m, 3H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.64 – 7.56 (m, 2H), 7.53 (s, 1H), 7.22 (t, *J* = 7.5 Hz, 2H), 7.14 (t, *J* = 7.3 Hz, 1H), 7.05 (d, *J* = 7.3 Hz, 2H), 4.78 – 4.65 (m, 1H. Please note: this peak is contaminated with an unknown impurity; however at 50 ºC the peak corresponding to the impurity shifts and a more accurate integration is obtained.), 3.12 (s, 9H), 2.60 (d, *J* = 6.7 Hz, 2H), 2.49 – 2.27 (m, 2H); ^{1}H NMR (400 MHz, $CDCl_3$, 50 ºC) δ 8.05 (s, 1H), 8.02 – 7.93 (m, 2H), 7.93 – 7.87 (m, 1H), 7.64 – 7.55 (m, 2H), 7.55 – 7.50 (m, 1H), 7.25 – 7.18 (m, 2H), 7.17 – 7.11 (m, 1H), 7.08 – 7.02 (m, 2H), 4.77 – 4.60 (m, 1H), 3.13 (s, 9H), 2.66 – 2.55 (m, 2H), 2.51 – 2.33 (m, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.6, 135.1, 134.1, 133.1, 130.0, 129.5, 128.8, 128.4, 128.2, 127.9, 127.5, 127.3, 126.7, 123.0, 120.8 (q, $J_{C\text{-}F}$ = 320.9 Hz), 78.9, 51.7, 32.3, 29.3; ^{19}F NMR (565 MHz, $CDCl_3$) δ –78.3; FTIR (neat) 3058, 2969, 1490, 1262, 1160, 1030, 829, 638 cm^{-1}; LRMS (ESI+) $[M\text{-}OTf]^+$ calculated for $[C_{22}H_{26}N^+]$: 304.2, found: 304.3. Two-dimensonal NMR experiments were used to verify ^{1}H and ^{13}C assignments due to the complex nature of the spectra.



(*S*)-1-(benzo[d][1,3]dioxol-5-yl)-*N*,*N*,*N*-trimethylethanaminium trifluoromethanesulfonate (2-22p). Prepared according to General Procedure D on a 1.52 mmol scale from (*S*)-1-(benzo[d][1,3]dioxol-5-yl)-*N*,*N*-dimethylethanamine, which was prepared using Escheweiler-Clarke conditions[11a] from (*S*)-1-(benzo[d][1,3]dioxol-5-yl)ethanamine (prepared using Ellman's auxiliary[10]), to afford salt **2-22p** (0.471 g, 87%) as an off-white solid (mp 136–138 ºC); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.01 (d, J = 7.8 Hz, 1H), 6.95 (s, 1H), 6.85 (d, J = 8.0 Hz, 1H), 6.01 (s, 2H), 4.80 (q, J = 7.0 Hz, 1H), 3.11 (s, 9H), 1.76 (d, J = 6.9 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.8, 148.6, 125.9, 120.9 (q, $J_{C\text{-}F}$ = 320.1 Hz), 109.0, 102.1, 74.1, 51.13, 51.11, 51.08, 15.3;[23] ^{19}F NMR (565 MHz, $CDCl_3$) δ –78.5; FTIR (neat) 3045, 2909, 1493, 1256, 1159, 1031, 835, 639 cm^{-1}; LRMS (ESI+) $[M\text{-}OTf]^+$ calculated for $[C_{12}H_{18}NO_2^+]$: 208.1, found: 208.2.



(S)-1-(1-methoxynaphthalen-2-yl)-N,N,N-trimethylethanaminium trifluoromethanesulfonate (2-22q) Prepared according to General Procedure D on a 5.64 mmol scale from (*S*)-1-(1-methoxynaphthalen-2-yl)-*N*,*N*-dimethylethanamine, which was prepared using Escheweiler-Clarke conditions[11a] from (*S*)-1-(1-methoxynaphthalen-2-yl)ethanamine (prepared using Ellman's auxiliary[10]), to afford salt **2-22l** (2.085 g, 94%) as a white solid (mp 123–124 ºC); ^{1}H NMR (600 MHz,

$CDCl_3$) δ 8.14 – 8.09 (m, 1H), 7.91 – 7.86 (m, 1H), 7.74 (d, *J* = 8.7 Hz, 1H), 7.62 – 7.58 (m, 2H), 7.50 (d, *J* = 8.7 Hz, 1H), 5.30 (q, *J* = 7.1 Hz, 1H), 4.00 (s, 3H), 3.16 (s, 9H), 1.94 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.4, 135.9, 128.5, 128.3, 127.5, 127.4, 125.6, 124.4, 123.3, 120.94, 120.90 (q, J_{C-F} = 320.1 Hz), 67.1, 63.9, 51.38, 51.36 51.34, 15.4;[23] ^{19}F NMR (565 MHz, $CDCl_3$) δ –78.4; FTIR (neat) 3051, 1471, 1272, 1158, 1031, 827, 639 cm^{-1}; LRMS (ESI+) $[M\text{-}OTf]^+$ calculated for $[C_{16}H_{22}NO^+]$: 244.2, found: 244.2.

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12. quadrupole.
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23. rotation, h.

Chapter 3

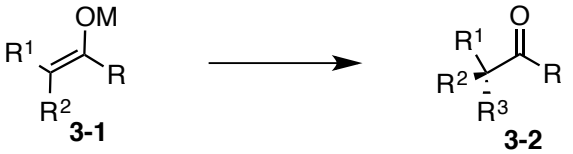
STEREOSPECIFIC CROSS-COUPLINGS TO SET BENZYLIC, ALL-CARBON QUATERNARY STEREOCENTERS IN HIGH ENANTIOPURITY

3.1 Introduction

Benzylic all-carbon quaternary stereocenters are an important scaffold in pharmaceutical, medicinal, natural products synthesis, and materials science. [1] Due to their prevalence in biologically active molecules, there are a variety of methods that have been developed in order to produce these compounds asymmetrically. Many of the advances in this field require a functional group in proximity to the quaternary center. These reactions include reactions at the α-ε carbon from a carbonyl, such as enolate allylations [1d, 2] or arylations [3] (Scheme 3-1A), conjugate additions [1b, 4] (Scheme 3-1B), and redox-relay Heck reactions [5] (Scheme 3-1C). Asymmetric synthesis of quaternary stereocenters α to an alkene can also be accomplished. Hydrovinylation of styrenes delivers this motif (Scheme 3-1D).[6] In addition, transition metal-catalyzed cross couplings of allylic phosphonate esters or halides provide these products (Scheme 3-1E).[7]

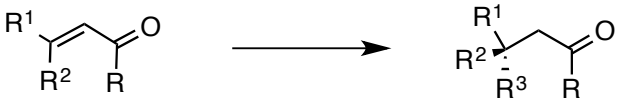
Scheme 3-1 Reactions to Deliver Quaternary Stereocenters Adjacent to sp^2-Hybridized Carbons

A) Enolate Allylations or Arylations



3-1 **3-2**

B) Conjugate Additions

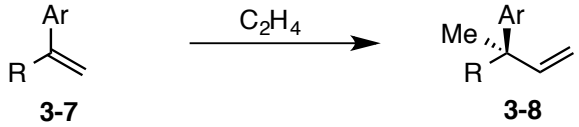


3-3 **3-4**

C) Redox-Relay Heck Reactions

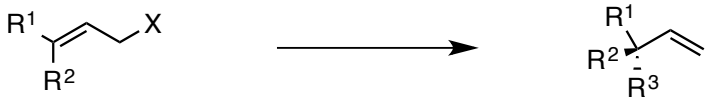
3-5 **3-6**

D) Hydrovinylations



3-7 **3-8**

E) Allylic Substitutions

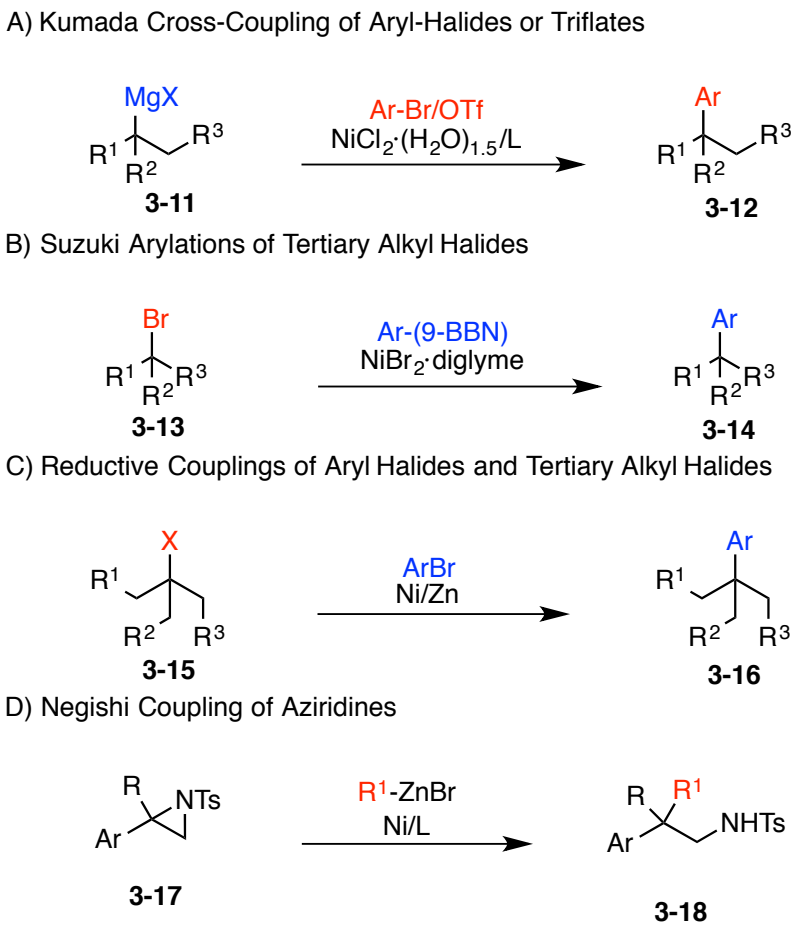


3-9 **3-10**

However, it still remains a challenge to form these quaternary stereocenter products isolated from either a carbonyl or vinyl group. Towards overcoming this limitation, transition-metal catalyzed cross-couplings have been developed. The Biscoe group has shown that they can form these products with a nickel-catalyzed

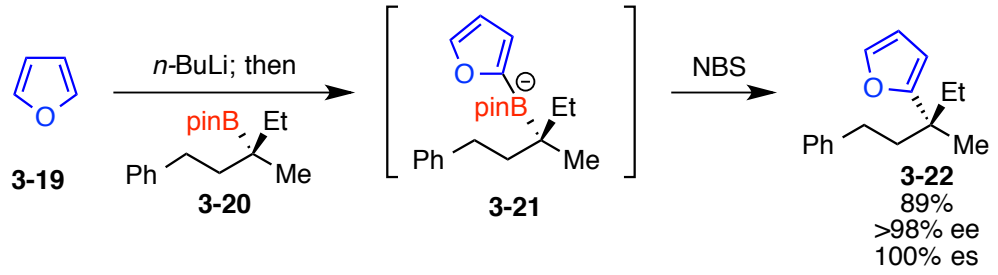
Kumada cross coupling of tertiary alkyl Grignard reagents and aryl bromides or triflates (Scheme 3-2A). [7] The Fu group has developed a nickel-catalyzed Suzuki cross-coupling of tertiary alkyl bromides and aryl boronic esters (Scheme 3-2B). [8] The Gong group has developed a reductive cross-coupling of tertiary alkyl halides and aryl bromides to afford these products (Scheme 3-2C). [9] While all of these examples are seminal publications in order to afford these challenging compounds, they all provide either achiral or racemic products. The only report of an enantioenriched product came from the Doyle group. Utilizing an aziridine as substrate, Doyle showed a single enantioselective example where they could make the product in good yields, but only 27% ee (Scheme 3-2D). [10]

Scheme 3-2 Transition Metal-Catalyzed Cross-Couplings to Form Achiral or Racemic Quaternary Stereocenters



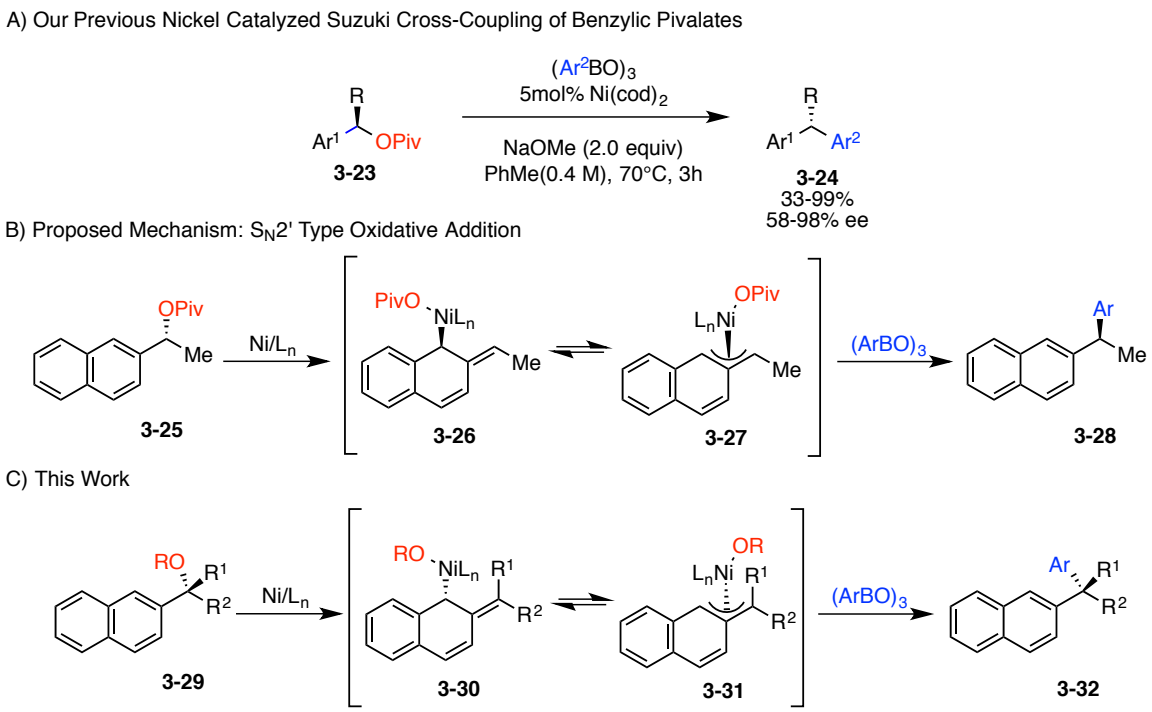
The state-of-the-art in asymmetric synthesis of all carbon quaternary stereocenters comes from the Aggarwal group. They have shown a transition metal-free coupling of enantioenriched tertiary boronic esters with aryl lithium reagents to stereospecifically form quaternary stereocenters in good yields and stereochemical fidelity (Scheme 3-3). [11] Although this is a powerful method to access these scaffolds, it is limited in functional group compatibility due to the harsh *n*-BuLi base.

Scheme 3-3 Transition Metal-Free Cross-Couplings of Tertiary Boronic Esters to Form Enantioenriched Quaternary Stereocenters



Previously, we have reported an enantiospecific nickel-catalyzed Suzuki cross-coupling of secondary benzylic pivalates in order to form tertiary stereocenters (Scheme 3-4A). [12] During this work, and consistent with other stereospecific cross-couplings[12-13, 13f{Maity, 2013 #38, 13g] we noticed that there is a preference for reactivity towards benzylic compounds with naphthyl substituents. It has been proposed that this is due to the mechanism of oxidative addition, which is believed to be S_N2' at the benzylic position (Scheme 3-4B). [13a 14] We hypothesized that with this type of oxidative addition, the increased steric hindrance of utilizing a tertiary carboxylate would be tolerated and allow us to do an enantiospecific nickel-catalyzed Suzuki cross-coupling to afford all-carbon benzylic quaternary stereocenters (Scheme 3-4C).

Scheme 3-4 Proposed S_N2' Type Oxidative Additions of Benzylic Carboxylates



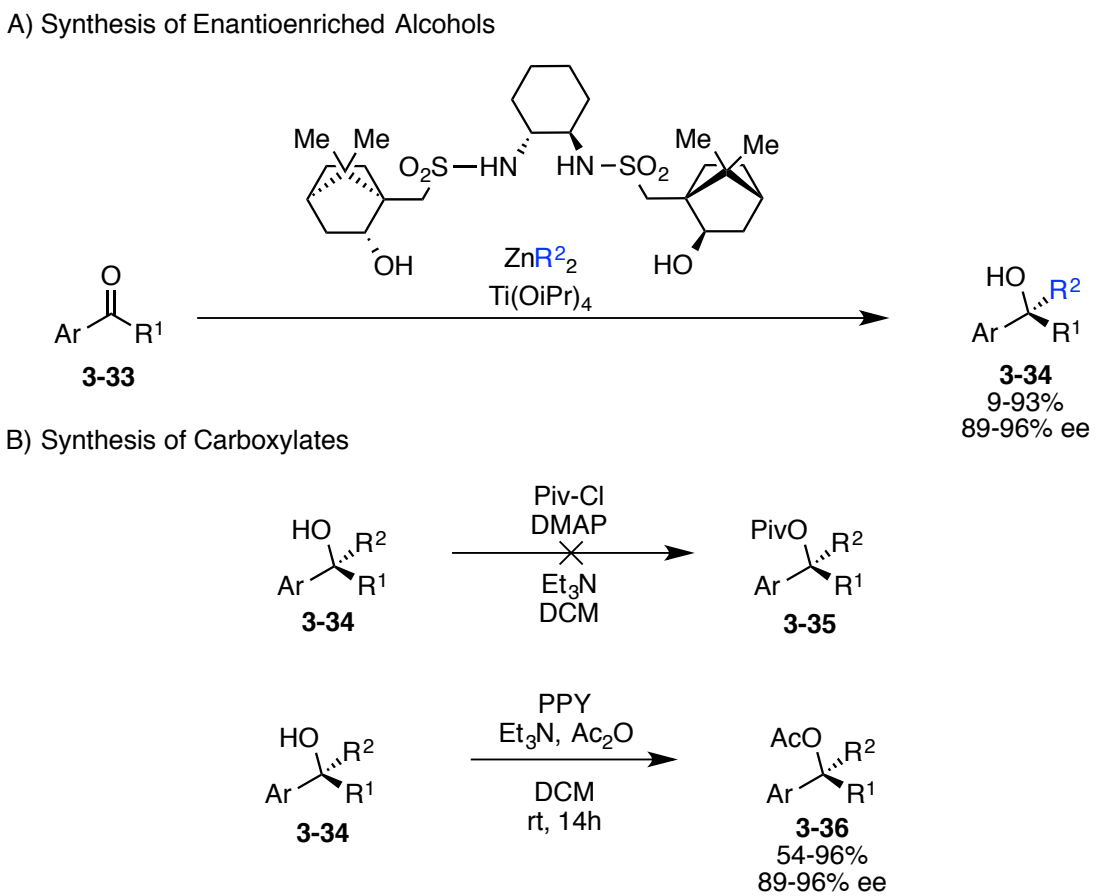
In order to develop this chemistry, my colleague Qi Zhou developed conditions in order to afford these quaternary stereocenters in high yields and enantioenrichment. This method utilizes acetates derived from enantioenriched benzylic alcohols, which are readily available through an asymmetric zinc addition.[15] It also has an air-stable nickel (II) pre-catalyst and air-stable and functional group tolerant aryl boronic esters. I came on this project in order to explore the scope of the reaction.

3.2 Results and Discussion

Synthesis of Enantioenriched Benzylic Acetates

The synthesis of enantioenriched benzylic substrates began with the corresponding ketone (**3-33,** Scheme 3-5A). Utilizing an asymmetric zinc addition to ketones developed by the Walsh lab[15], we were able to obtain enantioenriched benzylic alcohols (**3-34**) in high yields and enantioenrichment. With these in hand, we first attempted to make the benzylic pivalates, which were successful in our previous work to form tertiary stereocenters (Scheme 3-5B). However, due to the steric hinderance of the tertiary alcohols (**3-34**) we were unable to make these products (**3-35**) with our traditional methods. We instead opted for the smaller acetate, enabling synthesis of compounds **3-36** in high yield, with good stereochemical fidelity. The tertiary benzylic acetates (**3-36**) were stable for over 4 months when stored neat at —35°C in an N_2-atmosphere glovebox.

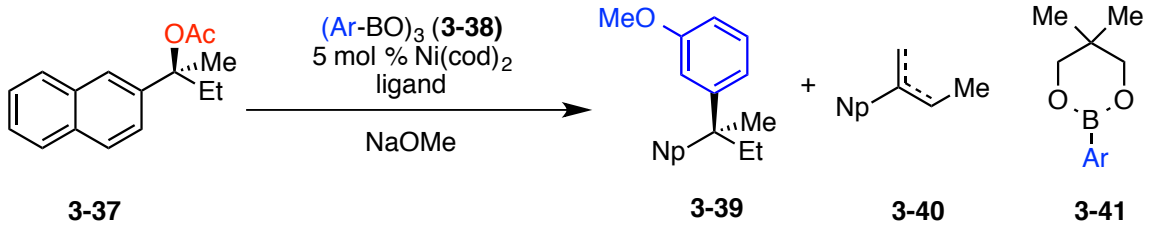
Scheme 3-5 Synthesis of Enantioenriched Benzylic Carboxylates



Optimization and Scope of Suzuki Cross-Coupling of Benzylic Acetates to Form All-Carbon Quaternary Stereocenters

My colleague Qi Zhou chose (*S*)-2-(naphthalen-2-yl)butan-2-yl acetate (**3-37**) for his preliminary investigation of this reaction. Under similar conditions as those for the Suzuki cross-couping of secondary carboxylates, he was excited to see very high yield of our desired quaternary stereocenter however with diminished enantioenrichment (Entry 1). By surveying different phosphine ligands such as $PhPCy_2$, the stereochemical fidelity was improved, but he saw an increase in elimination by-products **3-40** (Entry 2). Lower temperature (Entry 3) and using THF in place of toluene (Entry 4) improved the enantioenrichment even further, but did not aid in yield or suppression of byproduct formation. He proposed that if this byproduct was from β-hydride elimination, a bulky Buchwald ligand could suppress this pathway by blocking a coordination site on nickel. Fortunately, the use of CyJohnPhos gave **3-40** in only 5% yield, while giving the desired product in 81% with 96% ee (Entry 5). Transitioning to the more environmentally friendly 2-Me-THF and air-stable $NiCl_2 \cdot DME$, the desired product was obtained in 90% yield with 95% ee (Entry 6). Finally, by opting for the neopentyl aryl boronic ester instead of aryl boroxine **3-38**, product **3-39** was obtained in near quantitative yield with full stereochemical transfer of the starting material **3-37** (Entry 7). The improvement observed with the boronic ester is likely due to increased solubility.

Table 3-1: Optimization of Tertiary Benzylic Acetates to Form Quaternary Stereocenters



3-37 **3-39** **3-40** **3-41**

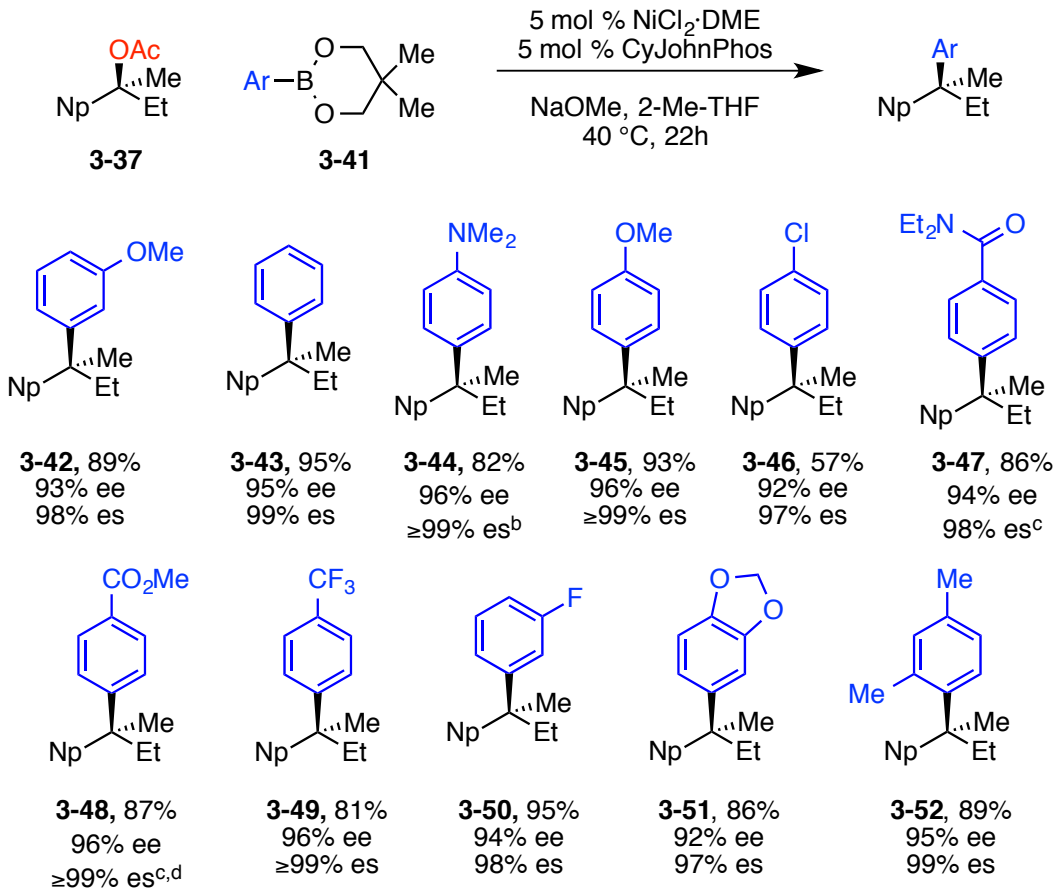
Entry	ligand (mol %)	temp (° C)	Solvent	yield (%)[b] **3-39** (ee, %)[c]	yield (%)[b] **3-40**	es (%)[d]
1	none	80	PhMe	93 (20)	2	21
2	$PhPCy_2$ (11)	80	PhMe	74 (87)	22	90
3	$PhPCy_2$ (11)	60	PhMe	72(90)	25	93
4	$PhPCy_2$ (11)	60	THF	63 (93)	24	96
5	CyJohnPhos (5)	40	THF	81 (96)	6	99
6[e]	CyJohnPhos (5)	40	2-Me-THF	90 (95)	6	98
7[e,f]	CyJohnPhos	40	2-Me-THF	99 (97)	≤3	>99

[a]Conditions: **3-37** (0.10 mmol), **3-38** (1.0 equiv), $Ni(cod)_2$ (5 mol %), ligand, NaOMe (2.0 equiv), solvent (0.4 M), unless otherwise noted. [b]Determined by ^1H NMR yields, using an internal standard. Total yields over 100% reflect the error of ^1H NMR yields, particularly for minor products. [c]Determined by HPLC using a chiral stationary phase. [d]es= enantiospecificity = $(ee_{product})/(ee_{starting\ material})$. [e]$NiCl_2 \cdot DME$ in place of $Ni(cod)_2$. [f]Boronate ester **3-41** (2.0 equiv) in place of boroxine **3-38**.

Having identified a successful catalyst for an enantiospecific Suzuki cross-coupling to afford benzylic quaternary stereocenters, I, along with Tianyu Tan, joined Qi Zhou in order to explore the substrate scope with respect to the boronic ester coupling partner. Both electron-rich boronic esters, such as amine (**3-44**) and ether (**3-45**), and electron-poor aryl boronic esters such as trifluoromethyl (**4-49**) and fluo (**3-50**) couple well under these reaction conditions. Functional groups such as amides (**3-47**) and esters (**3-48**) are also tolerated well under these mild conditions. Notably, a chloride-substituted aryl boronic ester (**3-46**) is tolerated, which would allows for further functionalization of these products. Gratifyingly, the sterically encumbered

2,4-dimethyl boronic ester (**3-52**) provided the quaternary center in high yield and excellent stereochemical fidelity.

Scheme 3-6 Scope of Aryl Boronate Esters

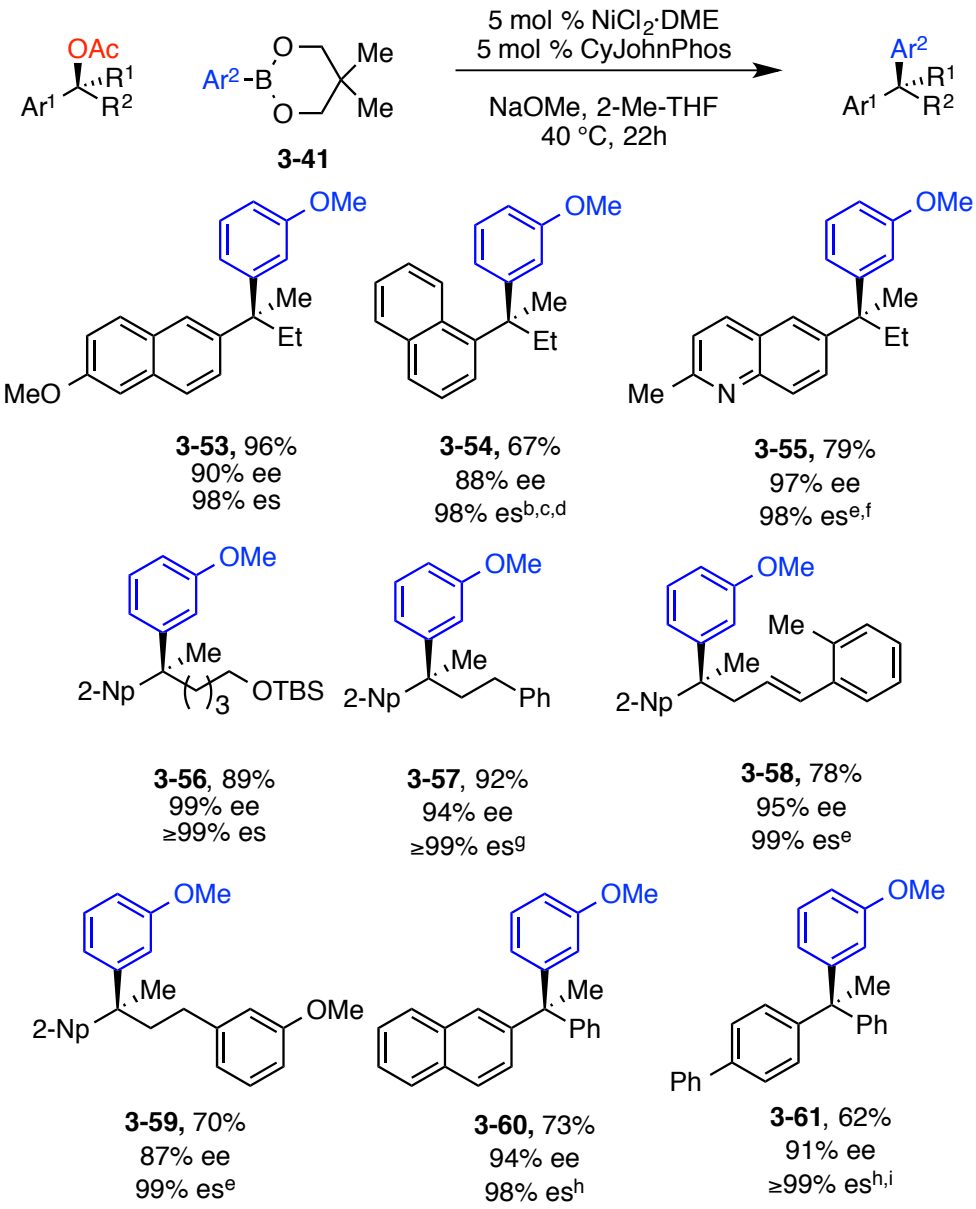


[a]Conditions: **3-37** (0.40 mmol), **3-41** (2.0 equiv), $NiCl_2$·DME (5 mol %), CyJohnPhos (5 mol %), NaOMe (2.0 equiv), 2-Me-THF (0.4 M), 40 °C, 22 h, unless noted. Average isolated yields (±9%) and ee's (±1%, determined by HPLC or SFC using a chiral stationary phase) of duplicate reactions, unless otherwise noted. [b]Single experiment. [c]60 °C, 12 h. [d]3.0 equiv of **3-41**.

With respect to the scope of tertiary acetates, the reaction tolerated electron-rich methoxy substitution (**3-53**), sterically encumbered 1-naphthyl (**3-54**), and

substituted quinoline (**3-55**) aromatic groups. Protected alcohols (**3-56**), aryl groups (**3-57 and 3-59**), and alkenes (**3-58**) on the alkyl chain all provide high yields and levels of stereochemical fidelity. Notably, these conditions can also be used in order to form triaryl quaternary stereocenters (**3-60** and **3-61**) in high yields and enantioenrichment. Compound **3-61** is significant as the only example of acetate without a naphthyl-like substituent.

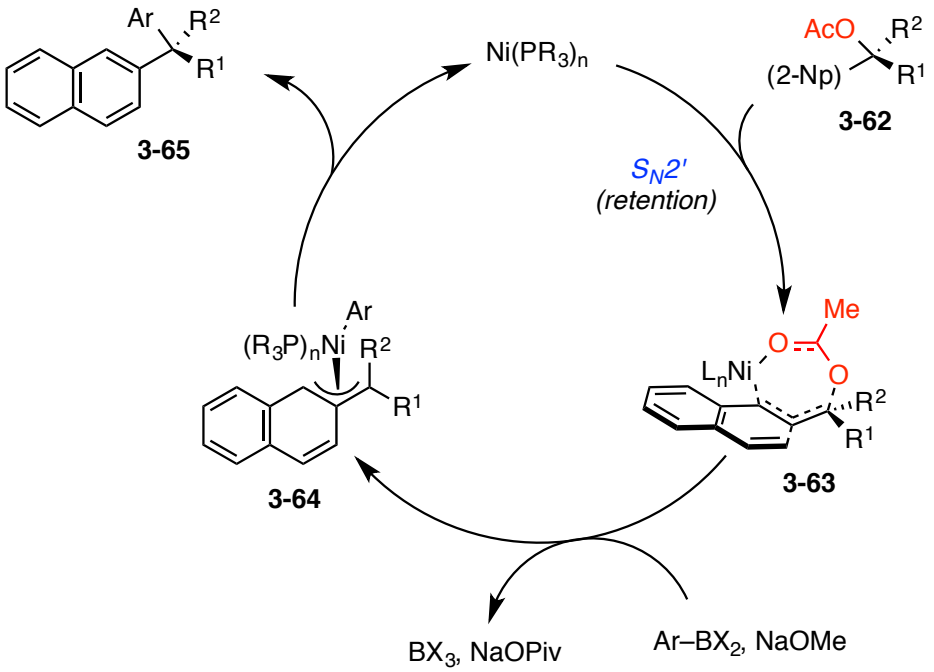
Scheme 3-7 Scope of Tertiary Acetates[a]



[a]Conditions: **3-37** (0.40 mmol), **3-41** (2.0 equiv), $NiCl_2$·DME (5 mol %), CyJohnPhos (5 mol %), NaOMe (2.0 equiv), 2-Me-THF (0.4 M), 40 °C, 22 h, unless noted. Average isolated yields (±9%) and ee's (±1%, determined by HPLC or SFC using a chiral stationary phase) of duplicate reactions, unless otherwise noted. [b]Single experiment. [c]78%, 83% ee, 99% es (84% ee of acetate) [d]0.3 mmol of acetate. [e]Aryl boroxine (0.83 equiv) in place of **3-41**. [f]60 °C. [g]48 h. [h]Opposite enantiomer of acetate used. [i]10 mol % $NiCl_2$·DME, 10 mol % CyJohnPhos, 60 °C, 48 h.

In order to determine the absolute stereochemistry of our starting materials and product, we were able to obtain a crystal of acetate **3-37** and benzylic quaternary stereocenter **3-47**. Through X-ray crystallography with a Cu Kα radiation, we were able to determine that the reaction was going through retention of configuration. As has been proposed for cross-couplings of benzylic and allylic electrophiles in the past, we believe that the reaction is going through a directed S_N2' type oxidative addition with the acetate coordinating the nickel catalyst. This is followed by a transmetallation (**3-64**) and reductive elimination which are known to go through retention of configuration to afford **3-65** with a net retention of the benzylic stereocenter.

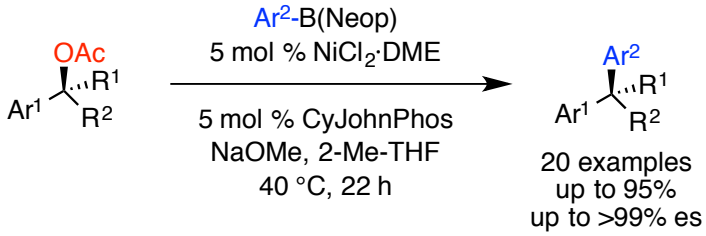
Scheme 3-8 Proposed Reaction Mechanism



3.3 Conclusion

In conclusion, we have developed a stereospecific nickel-catalyzed Suzuki cross-coupling of tertiary acetates to construct all-carbon benzylic quaternary stereocenters in high yield and enantiomeric excess. This reaction provides an efficient asymmetric synthesis to afford both di-aryl and tri-aryl quaternary stereocenters. This reaction utilizes enantioenriched tertiary benzylic alcohols, which are readily available in high enantioenrichment. It also uses air-stable nickel source and boronic ester nucleophiles that are functional group tolerant. This method shows an expansion in transition metal catalysis to go beyond electrophiles adjacent to functional groups such as carbonyls and alkenes, and displays the possibility for tertiary benzylic electrophiles to under go transition metal catalysis.

Scheme 3-9 Stereospecific Cross-Coupling to Set Benzylic, All-Carbon Quaternary Steroecenters in High Enantiopurity

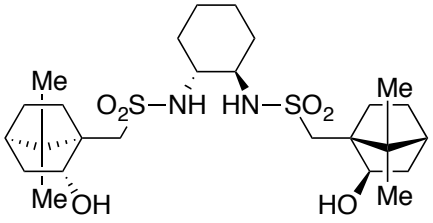


3.4 Experimental

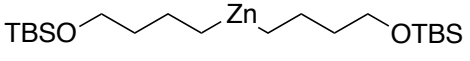
General Information

Reactions were performed in oven-dried vials with Teflon-lined caps or in oven-dried round-bottomed flasks unless otherwise noted. On occasions when a viscous mixture formed in the reaction vials, a higher speed of stirring or shaking was performed to guarantee sufficient mixing. 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, or 5-20 μm 60Å) unless otherwise noted. 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: sodium methoxide, anhydrous 2-methyltetrahydrofuran, diethyl zinc, dimethyl zinc (1.0 M in PhMe) were purchased from vendors and immediately placed in a N_2-atmosphere glovebox for storage. Acetic anhydride and Ti(O-*i*Pr)$_4$ were distilled before use and stored under N_2. Toluene, CH_2Cl_2, and THF were dried by passing through drying columns and stored over activated 4Å MS in a N_2-atmosphere glovebox.[i] (*R*,*R*)-Bis(sulfonamide) diol ligand **L1** was prepared according to reported literature procedure.[ii] Bis(4-((*tert*-butyldimethylsilyl)oxy)butyl)zinc was prepared according to reported literature procedure and used immediately.[iii] Oven-dried potassium carbonate was added into $CDCl_3$ to remove trace amount of acid. 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). 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). 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 and X-ray crystallography data were obtained at the University of Delaware facilities. 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. Enantiomeric excess (ee) was determined using chiral HPLC analysis at the University of Delaware or chiral SFC analysis at Lotus Separations, Inc.



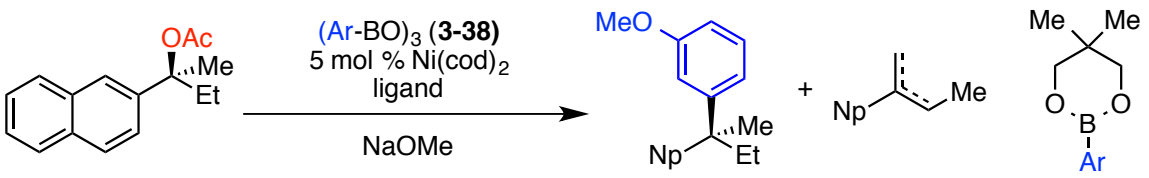
L1



bis(4-((*tert*-butyldimethylsilyl)oxy)butyl)zinc

Optimization of Benzylic Arylation

Detailed Optimization Table

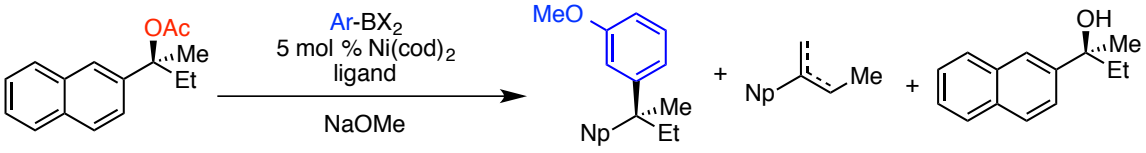


3-37 **3-39** **3-40** **3-41**

entry	[Ni]	ligand (mol %)	temp (° C)	solvent	time (h)	yield (%)[a] **3-39**	yield (%)[a] **3-40**	ee of **3-39** (%)[b]	es (%)[c]
1	$Ni(cod)_2$	none	80	PhMe	2	93	2	20	21
2	$Ni(cod)_2$	$PhPCy_2$ (11)	80	PhMe	2	74	22	87	90
3	$Ni(cod)_2$	$PhPCy_2$ (11)	60	PhMe	5	72	25	90	93
4	$Ni(cod)_2$	$PhPCy_2$ (11)	60	THF	5	63	24	93	96
5	$Ni(cod)_2$	CyJohnPhos (11)	40	THF	16	57	9	96	99
6	$Ni(cod)_2$	CyJohnPhos (5)	40	THF	16	81	6	96	99
7	$Ni(cod)_2$	CyJohnPhos (5)	40	1,4-dioxane	39	97	5	97	>99
8	$Ni(cod)_2$	CyJohnPhos (5)	40	2-Me-THF	22	92	8	96	99
9	$NiCl_2$·DME	CyJohnPhos (5)	40	2-Me-THF	22	90	6	95	98
10[d]	$NiCl_2$·DME	CyJohnPhos (5)	40	2-Me-THF	22	99	≤3	97	>99

Conditions: **1a** (0.10 mmol), **2a** (1.0 equiv), [Ni] (5 mol %), ligand, NaOMe (2.0 equiv), solvent (0.4 M), unless otherwise noted. [a] Determined by ^{1}H NMR analysis using an internal standard. Total yields over 100% reflect the inherent error bar of ^{1}H NMR yields, particularly for minor products. [b] Determined by HPLC analysis using a chiral stationary phase. [c] es = enantiospecificity = $(ee_{product})/(ee_{starting\ material})$. [d] Boronate ester **3a** used in place of boroxine **2a**.

Evaluation of Aryl Boronate Reagents



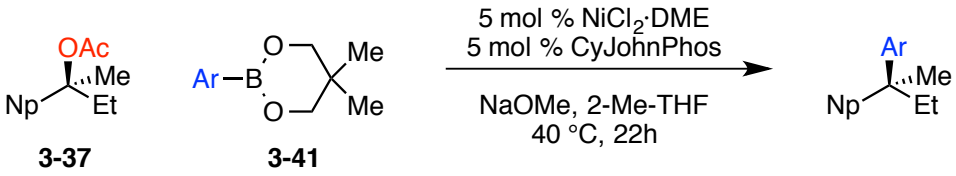
3-37 **3-39** **3-40** **3-34**

Entry	Ar–BX_2 (equiv)	yield (%)[a] **3-39**	yield (%)[a] **3-34**	ee of **3-34** (%)[b]	ee of **3-39** (%)[b]	es (%)[c]
1	$(ArBO)_3$ (**3-38**) (1.0)	90	—	97	95	98
2	**3-41** (2.0)	99	—	97	97	>99
3	Ar–$B(OH)_2$ (2.0)	86	5	94	92	98
4	Ar–Bpin (2.0)	80	0	94	92	98
5	Ar–BF_3K (2.0)	0	90	94	–	–

Conditions: **1a** (0.10 mmol), $ArBX_2$, $NiCl_2$·DME (5 mol %), CyJohnPhos (5 mol %), NaOMe (2.0 equiv), 2-Me-THF (0.4 M), 40 °C, 22 h. [a] Determined by ^{1}H NMR analysis using an internal standard. Total yields over 100% reflect the inherent error bar of ^{1}H NMR yields, particularly for minor products. [b] Determined by HPLC analysis using a chiral stationary phase. [c] es = enantiospecificity = $(ee_{product})/(ee_{starting\ material})$.

Stereospecific Arylation to Prepare Diaryl and Triarylalkanes

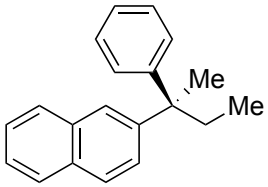
General Procedure A: Stereospecific Arylation of Tertiary Benzylic Acetates



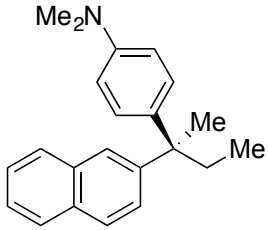
3-37 **3-41**

(*S*)-2-(2-(3-Methoxyphenyl)butan-2-yl)naphthalene (3-42). In a N_2-atmosphere glovebox, $NiCl_2$·DME (4.4 mg, 0.020 mmol, 5 mol %), CyJohnPhos (7.0 mg, 0.020 mmol, 5 mol %) and NaOMe (43 mg, 0.80 mmol, 2.0 equiv) were weighed into a 1-dram vial fitted with a magnetic stir bar. 2-(3-Methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (**3-41a**, 176 mg, 0.800 mmol, 2.0 equiv) and (*S*)-2-(naphthalen-2-yl)butan-2-yl acetate (**3-37a**, prepared in 95% ee, 97 mg, 0.40 mmol, 1.0 equiv) were added, followed by 2-Me-THF (1.0 mL, 0.4 M). The vial was capped with a Teflon-lined cap and removed from the glovebox. The mixture was stirred at 40 °C for 22 h. Please note that these reactions are heterogeneous and vigorous stirring is critical. The reaction mixture was then diluted with Et_2O (5 mL) and filtered through a plug of silica gel and Celite®, which was then rinsed with Et_2O (~ 15 mL). The filtrate was concentrated and then purified by silica gel chromatography (0−2% Et_2O/hexanes) to give the compound **3-42** (run 1: 100.3 mg, 86%; run 2: 105.7 mg, 91%) as a colorless sticky oil. The enantiomeric excess was determined to be 93% (run 1: 93% ee; run 2: 92% ee) by chiral HPLC analysis (CHIRALPAK IB, 0.6 mL/min, 0.1% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 12.058 min, t_R(minor) = 14.930 min. $[\alpha]_D^{24} = -10.2°$ (c 4.25, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 – 7.81 (m, 1H), 7.81 – 7.77 (m, 2H), 7.69 (d, J = 8.7 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.21 – 7.16 (m, 2H), 6.83 – 6.79 (m, 2H), 6.76 – 6.69 (m, 1H), 3.75 (s, 3H), 2.31– 2.20 (m,

2H), 1.70 (s, 3H), 0.77 (t, J = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.4, 151.5, 146.9, 133.3, 131.9, 128.9, 128.1, 127.6, 127.5, 127.2, 125.9, 125.5, 124.9, 120.4, 114.3, 110.3, 55.3, 46.8, 33.9, 26.9, 9.4; FTIR (NaCl/thin film) 3054, 2967, 2934, 2877, 1599, 1582, 1485, 1457, 1430, 1290, 1254, 1053, 819, 749, 703, 477 cm^{-1}; HRMS (CI+) $[M+H]^+$ calculated for $C_{21}H_{23}O$: 291.1749, found: 291.1773.

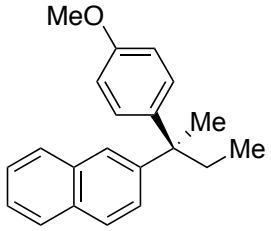


(*R*)-2-(2-Phenylbutan-2-yl)naphthalene (3-43). Prepared via General Procedure A using **3-37a** (prepared in 96% ee) as a colorless oil (run 1: 100 mg, 96%; run 2: 96.8 mg, 93%). The enantiomeric excess was determined to be 95% (run 1: 95% ee; run 2: 95% ee) by chiral SFC analysis (CHIRALCEL OJ-H (25 x 0.46 cm), 3.0 mL/min, 15% EtOH(0.1% diethylamine)/CO_2 (100 bar), λ=220 nm); t_R(major) = 6.25 min, t_R(minor) = 7.32 min. $[\alpha]_D^{24}$ = +13.3° (c 1.02, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.78 (m, 3H), 7.71 (d, J = 8.7 Hz, 1H), 7.53 – 7.43 (m, 2H), 7.33 – 7.18 (m, 6H), 2.36 – 2.22 (m, 2H), 1.73 (s, 3H), 0.79 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.7, 147.0, 133.2, 131.8, 128.10, 128.07, 127.63, 127.61, 127.5, 127.3, 126.0, 125.7, 125.6, 124.9, 46.8, 33.8, 26.9, 9.4; FTIR (NaCl/thin film) 3055, 2968, 2934, 2876, 1599, 1494, 1444, 1380, 1273, 1131, 1029, 948, 897, 770 cm^{-1}; HRMS (EI+) [M]+ calculated for $C_{20}H_{20}$: 260.1565, found: 260.1558.

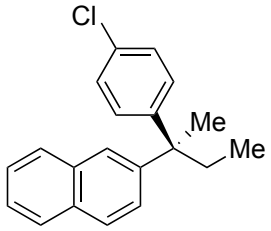


(*R*)-*N*,*N*-Dimethyl-4-(2-(naphthalen-2-yl)butan-2-yl)aniline (3-44). Prepared via General Procedure A using **3-37a** (prepared in 96% ee) as a white solid (mp 64–66 °C; 99 mg, 82%). The enantiomeric excess was determined to be 96% by chiral SFC analysis (CHIRALCEL OJ-H (25 x 0.46 cm), 3.5 mL/min, 55% MeOH(0.1% diethylamine)/CO_2 (100 bar), λ=220 nm); t_R(major) = 11.68 min, t_R(minor) = 17.76 min. $[\alpha]_D^{24}$ = +22.6° (c 3.8, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (dd, J = 8.0,

1.3 Hz, 1H), 7.79 – 7.74 (m, 2H), 7.67 (d, *J* = 8.7 Hz, 1H), 7.48 – 7.38 (m, 2H), 7.21 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.11 – 7.05 (m, 2H), 6.68 – 6.63 (m, 2H), 2.91 (s, 6H), 2.28 – 2.15 (m, 2H), 1.67 (s, 3H), 0.76 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.6, 147.6, 137.8, 133.3, 131.8, 128.2, 128.1, 127.50, 127.46, 127.4, 125.8, 125.4, 124.8, 112.3, 45.9, 40.8, 34.0, 27.0, 9.4; FTIR (NaCl/thin film) 3431, 3054, 2966, 2934, 2876, 1613, 1519, 1444, 1348, 1201, 1166, 948, 818, 746, 569, 476 cm^{-1}; HRMS (LIFDI) [M]+ calculated for $C_{22}H_{25}N$: 303.1987, found: 303.1966.

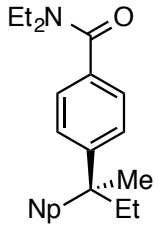


(*R*)-2-(2-(4-Methoxyphenyl)butan-2-yl)naphthalene (3-45). Prepared via General Procedure A using **3-37a** (prepared in 96% ee) as a colorless oil (run 1: 110 mg, 95%; run 2: 105.7 mg, 91%). The enantiomeric excess was determined to be 96% (run 1: 96% ee; run 2: 96% ee) by chiral SFC analysis (CHIRALCEL OJ-H (25 x 0.46 cm), 3.0 mL/min, 25% *i*-PrOH(0.1% diethylamine)/CO_2 (100 bar), λ=220 nm); t_R(major) = 4.89 min, t_R(minor) = 6.27 min. $[\alpha]_D^{24}$ = +12.4° (c 0.98, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.83 (m, 1H), 7.83 – 7.77 (m, 2H), 7.71 (d, *J* = 8.7 Hz, 1H), 7.54 – 7.43 (m, 2H), 7.23 – 7.13 (m, 3H), 6.87 – 6.80 (m, 2H), 3.81 (s, 3H), 2.35 – 2.16 (m, 2H), 1.71 (s, 3H), 0.79 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5, 147.2, 141.8, 133.2, 131.8, 128.6, 128.1, 127.6, 127.5, 127.3, 125.9, 125.5, 124.8, 113.3, 55.3, 46.1, 34.0, 27.1, 9.4; FTIR (NaCl/thin film) 3055, 2967, 2932, 2876, 1511, 1463, 1441, 1298, 1248, 1182, 1034, 852, 745 cm^{-1}; HRMS (CI+) $[M+H]^+$ calculated for $C_{21}H_{23}O$: 291.1749, found: 291.1768.



(*R*)-2-(2-(4-Chlorophenyl)butan-2-yl)naphthalene (3-46). Prepared via General Procedure A using **3-37a** (prepared in 95% ee) as a colorless oil (run 1: 62.1 mg,

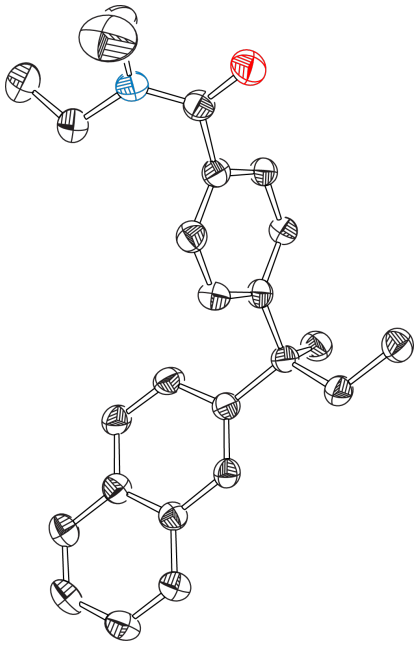
53%; run 2: 70.4 mg, 60%). The enantiomeric excess was determined to be 92% (run 1: 92% ee; run 2: 92% ee) by chiral SFC analysis (CHIRALCEL OJ-H (25 x 0.46 cm), 3.0 mL/min, 15% EtOH(0.1% diethylamine)/CO_2 (100 bar), λ=220 nm); t_R(major) = 6.18 min, t_R(minor) = 6.97 min. $[\alpha]_D^{24}$ = +10.8° (c 1.66, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.85 – 7.79 (m, 2H), 7.73 (d, *J* = 8.7 Hz, 1H), 7.55 – 7.45 (m, 2H), 7.31 – 7.25 (m, 2H), 7.20 – 7.13 (m, 3H), 2.35 – 2.19 (m, 2H), 1.72 (s, 3H), 0.80 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.3, 146.4, 133.3, 131.9, 131.6, 129.1, 128.2, 128.1, 127.8, 127.5, 127.0, 126.1, 125.7, 125.0, 46.6, 33.9, 26.9, 9.3; FTIR (NaCl/thin film) 3055, 2969, 2934, 2887, 1599, 1489, 1092, 1012, 817, 746, 477 cm^{-1}; HRMS (EI+) [M]+ calculated for $C_{20}H_{19}Cl$ 294.1775, found: 294.1189.

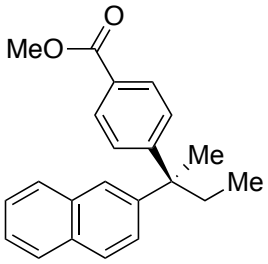


(*R*)-*N*,*N*-Diethyl-4-(2-(naphthalen-2-yl)butan-2-yl)benzamide (3-47). Prepared via General Procedure A using **3-37a** (prepared in 96% ee) except that the reaction mixture was heated at 60 °C for 12 h. Compound **3-47** was obtained as white solid (mp 96−100 °C; run 1: 125 mg, 87%; run 2: 122 mg, 85%). The enantiomeric excess was determined to be 94% (run 1: 94% ee, run 2: 94% ee) by chiral HPLC analysis (CHIRALPAK IA, 0.8 mL/min, 8% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 11.038 min, t_R(minor) = 10.179 min. $[\alpha]_D^{24}$ = +18.9° (c 1.16, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 1H), 7.80 – 7.76 (m, 2H), 7.69 (d, *J* = 8.7 Hz, 1H), 7.50 – 7.42 (m, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.15 (dd, *J* = 8.7, 1.9 Hz, 1H), 3.54 (br s, 2H), 3.28 (br s, 2H), 2.33 – 2.18 (m, *J* = 7.1 Hz, 2H), 1.70 (s, 3H), 1.23 (br s, 3H), 1.12 (br s, 3H), 0.77 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.5, 150.9, 146.5, 134.6, 133.2, 131.9, 128.1, 127.7, 127.6, 127.5, 127.2, 126.3, 126.0, 125.7, 125.1, 46.9, 43.4, 39.3, 33.8, 26.9, 14.4, 13.0, 9.3; FTIR (NaCl/thin film) 3053, 2970, 2934, 2876, 1630, 1457, 1424, 1288, 1098, 1019, 819, 748, 478 cm^{-1}; HRMS (CI+) $[M+H]^+$ calculated for $C_{25}H_{30}NO$: 360.2327, found: 360.2347.

X-ray quality crystals were obtained from slow evaporation of **3-47** in EtOAc. The crystal structure demonstrates that the absolute configuration is *R* (Figure S1). The enantiomeric excess of the crystal was determined to be 96% ee by chiral HPLC analysis, with the major enantiomer matching that of the bulk material isolated as described above.

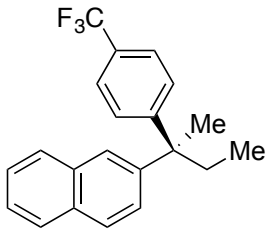
Figure S1. Molecular diagram of (*R*)-**3-47** with ellipsoids at 50% probability. H-atoms omitted for clarity. (CCDC 1424635)



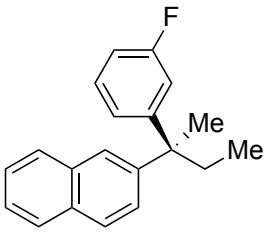


(*R*)-Methyl-4-(2-(naphthalen-2-yl)butan-2-yl)benzoate (3-48). Prepared via General Procedure A using **3-48** (prepared in 96% ee) except that 3.0 equiv of **3-41** were used and the reaction mixture was heated at 60 °C for 12 h. Compound **3-48** was obtained as a colorless oil (run 1: 114.5 mg, 90%; run 2: 105.6 mg, 83%). The

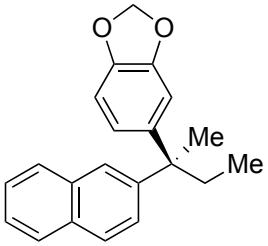
enantiomeric excess was determined to be 96% (run 1: 96% ee, run 2: 96% ee) by chiral HPLC analysis (CHIRALPAK IC, 0.6 mL/min, 1% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 30.604 min, t_R(minor) = 33.299 min. $[\alpha]_D^{24}$ = +8.1° (c 1.23, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 – 7.90 (m, 2H), 7.85 – 7.81 (m, 1H), 7.81 – 7.76 (m, 2H), 7.69 (d, *J* = 8.7 Hz, 1H), 7.51 – 7.41 (m, 2H), 7.34 – 7.28 (m, 2H), 7.12 (dd, *J* = 8.6, 1.9 Hz, 1H), 3.90 (s, 3H), 2.34 – 2.22 (m, 2H), 1.72 (s, 3H), 0.77 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.2, 155.1, 146.2, 133.3, 131.9, 129.4, 128.1, 127.84, 127.75, 127.7, 127.6, 127.0, 126.1, 125.8, 125.0, 52.1, 47.2, 33.8, 26.8, 9.3; FTIR (NaCl/thin film) 3055, 2969, 2878, 1718, 1608, 1435, 1279, 1188, 1115, 1018, 854, 819, 747, 477 cm^{-1}; HRMS (CI+) $[M+H]^+$ calculated for $C_{22}H_{23}O_2$: 319.1698, found: 319.1708.



(*R*)-2-(2-(4-(Trifluoromethyl)phenyl)butan-2-yl)naphthalene (3-49). Prepared via General Procedure A using **3-37a** (prepared in 96% ee) as a colorless oil (117 mg, 89%). The enantiomeric excess was determined to be 96% by chiral HPLC analysis (CHIRALPAK IB, 0.2 mL/min, 0% *i*-PrOH/hexane, λ=210 nm); t_R(major) = 39.173 min, t_R(minor) = 35.980 min. A second run using **3-37a** (prepared in 95% ee) gave **3-49** (95 mg, 72%) in 95% ee. $[\alpha]_D^{24}$ = +9.9° (c 1.1, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.84 (m, 1H), 7.84 – 7.79 (m, 2H), 7.73 (d, *J* = 8.6 Hz, 1H), 7.58 – 7.45 (m, 4H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.13 (dd, *J* = 8.7, 1.9 Hz, 1H), 2.38 – 2.21 (m, 2H), 1.74 (s, 3H), 0.79 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 145.9, 133.2, 131.9, 128.1, 128.02 (q, J_{C-F} = 32.9 Hz), 128.0, 127.9, 127.6, 126.9, 126.2, 125.8, 125.1, 125.0 (q, J_{C-F} = 3.8 Hz), 124.4 (q, J_{C-F} = 272.9 Hz), 47.0, 33.8, 26.8, 9.25; ^{19}F NMR (377 MHz, $CDCl_3$) δ –62.2; FTIR (NaCl/thin film) 3057, 2971, 2937, 2880, 1921, 1617, 1504, 1409, 1325, 1273, 1122, 1068, 1016, 948, 841, 748 cm^{-1}; HRMS (EI+) [M]+ calculated for $C_{21}H_{19}F_3$: 328.1439, found: 328.1447.

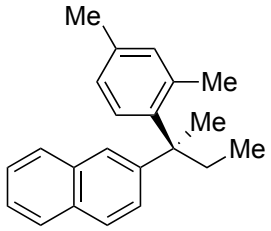


(*S*)-2-(2-(3-Fluorophenyl)butan-2-yl)naphthalene (3-50). Prepared via General Procedure A using **3-37a** (prepared in 96% ee) as a colorless oil (run 1: 103.5 mg, 93%; run 2: 106.4 mg, 96%). The enantiomeric excess was determined to be 94% (run 1: 94% ee; run 2: 94% ee) by chiral SFC analysis (CHIRALCEL OJ-H (25 x 0.46 cm), 3.0 mL/min, 8% EtOH(0.1% diethylamine)/CO_2 (100 bar), λ=220 nm); t_R(major) = 5.22 min, t_R(minor) = 5.57 min. $[\alpha]_D^{24}$ = +7.5° (c 1.19, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.9 Hz, 1H), 7.81 – 7.75 (m, 2H), 7.70 (d, *J* = 8.7 Hz, 1H), 7.52 – 7.41 (m, 2H), 7.21 (td, *J* = 8.0, 6.3 Hz, 1H), 7.15 (dd, *J* = 8.7, 1.9 Hz, 1H), 6.98 (dt, *J* = 8.0, 1.2 Hz, 1H), 6.95 (dt, *J* = 11.1, 2.2 Hz, 1H), 6.87 (td, *J* = 8.5, 2.7 Hz, 1H), 2.32 – 2.17 (m, 2H), 1.70 (s, 3H), 0.77 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.9 (d, J_{C-F} = 245 Hz), 152.6 (d, J_{C-F} = 6.4 Hz), 146.3, 133.3, 131.9, 129.4 (d, J_{C-F} = 8.2 Hz), 128.1, 127.8, 127.5, 127.0, 126.1, 125.7, 125.0, 123.4 (d, J_{C-F} = 2.7 Hz), 114.7 (d, J_{C-F} = 21.7 Hz), 112.7 (d, J_{C-F} = 21.2 Hz), 46.8 (d, J_{C-F} = 1.5 Hz), 33.8, 26.8, 9.3; ^{19}F NMR (565 MHz, $CDCl_3$) δ –113.6; FTIR (NaCl/thin film) 3056, 2970, 2878, 1612, 1585, 1485, 1433, 1243, 1163, 917, 818, 783, 477 cm^{-1}; HRMS (EI+) [M]+ calculated for $C_{20}H_{19}F$: 278.1471, found: 278.1479.

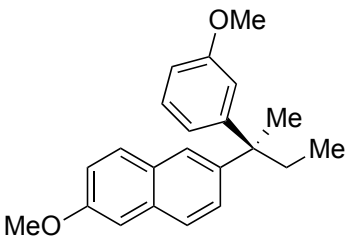


(*S*)-5-(2-(Naphthalen-2-yl)butan-2-yl)benzo-[1,3]-dioxole (3-51). Prepared via General Procedure A using **3-37a** (prepared in 95% ee) as a colorless oil (run 1: 110 mg, 90%; run 2: 100 mg, 82%). The enantiomeric excess was determined to be 92% (run 1: 92% ee; run 2: 92% ee) by chiral SFC analysis (CHIRALCEL OJ-H (25 x 0.46 cm), 3.0 mL/min, 30% EtOH(0.1% diethylamine)/CO_2 (100 bar), λ=220 nm); t_R(major) = 4.19 min, t_R(minor) = 4.93 min. $[\alpha]_D^{24}$ = +3.9° (c 4.57, $CHCl_3$): ^{1}H NMR

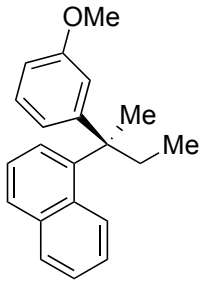
(600 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.81 – 7.77 (m, 2H), 7.70 (d, *J* = 8.7 Hz, 1H), 7.50 – 7.41 (m, 2H), 7.19 (dd, *J* = 8.7, 1.9 Hz, 1H), 6.74 (d, *J* = 1.3 Hz, 2H), 6.70 – 6.65 (m, 1H), 5.91 (s, 2H), 2.31 – 2.14 (m, 2H), 1.67 (s, 3H), 0.78 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.6, 147.1, 145.4, 143.8, 133.3, 131.9, 128.1, 127.7, 127.5, 127.1, 126.0, 125.6, 124.8, 120.4, 108.7, 107.6, 100.9, 46.6, 34.1, 27.1, 9.4; FTIR (NaCl/thin film) 3055, 2968, 2933, 2877, 1631, 1599, 1485, 1430, 1235, 1039, 938, 817, 746 cm^{-1}; HRMS (EI+) [M]+ calculated for $C_{21}H_{20}O$: 304.1463 found: 304.1482.



(*S*)-2-(2-(2,4-Dimethylphenyl)butan-2-yl)naphthalene (3-52). Prepared via General Procedure A using **3-37a** (prepared in 96% ee) as a colorless oil (run 1: 103.8 mg, 90%; run 2: 100.4 mg, 87%). The enantiomeric excess was determined to be 95% (run 1: 95% ee; run 2: 95% ee) by chiral SFC analysis (CHIRALCEL OJ-H (25 x 0.46 cm), 3.0 mL/min, 8% EtOH(0.1% diethylamine)/CO_2 (100 bar), λ=220 nm); t_R(major) = 7.83 min, t_R(minor) = 8.59 min. $[\alpha]_D^{24} = -16.3°$ (c 1.02, $CHCl_3$): ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.75 (m, 2H), 7.73 (d, *J* = 1.9 Hz, 1H), 7.67 (d, *J* = 8.6 Hz, 1H), 7.45 (dtd, *J* = 14.9, 7.5, 7.0, 5.4 Hz, 3H), 7.15 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.11 – 7.06 (m, 1H), 6.91 – 6.85 (m, 1H), 2.46 – 2.30 (m, 4H), 2.27 – 2.14 (m, 1H), 1.71 (s, 3H), 1.68 (s, 3H), 0.71 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2, 142.8, 137.2, 135.7, 133.5, 133.4, 131.7, 128.0, 127.7, 127.6, 127.5, 126.3, 126.1, 125.8, 125.3, 124.2, 46.9, 32.8, 28.0, 21.9, 20.9, 9.5; FTIR (NaCl/thin film) 3054, 2969, 2934, 2876 1630, 1598, 1502, 1455, 1376, 1265, 1130, 1040, 948, 894, 769, 476 cm^{-1}; HRMS (EI+) [M]+ calculated for $C_{22}H_{24}$: 288.1878, found: 288.1896.

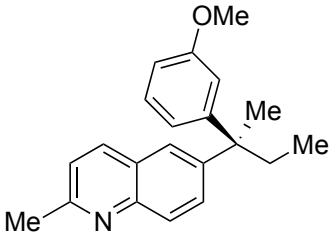


(*S*)-2-Methoxy-6-(2-(3-methoxyphenyl)butan-2-yl)naphthalene (3-53). Prepared via General Procedure A using **3-37b** (prepared in 92% ee) as a colorless sticky oil (run 1: 120 mg, 94%; run 2: 124.9 mg, 98%). The enantiomeric excess was determined to be 90% (run 1: 90% ee; run 2: 89% ee) by chiral HPLC analysis (CHIRALPAK IB, 0.6 mL/min, 0.1% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 16.688 min, t_R(minor) = 18.948 min. $[\alpha]_D^{24}$ = +7.7° (c 4.28, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 – 7.69 (m, 2H), 7.59 (d, *J* = 8.6 Hz, 1H), 7.21 – 7.12 (m, 3H), 7.10 (d, *J* = 2.5 Hz, 1H), 6.84 – 6.79 (m, 2H), 6.75 – 6.70 (m, 1H), 3.91 (s, 3H), 3.75 (s, 3H), 2.30 – 2.18 (m, 2H), 1.68 (s, 3H), 0.77 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.4, 157.6, 151.7, 144.6, 132.9, 129.6, 128.9, 128.7, 127.7, 126.6, 124.8, 120.4, 118.6, 114.3, 110.2, 105.7, 55.5, 55.2, 46.7, 33.9, 26.9, 9.4; FTIR (NaCl/thin film) 3057, 2967, 2936, 2834, 1609, 1488, 1456, 1388, 1264, 1198, 1032, 852, 779 cm^{-1}; HRMS (CI+) $[M+H]^+$ calculated for $C_{22}H_{25}O$: 321.1855, found: 321.1859.

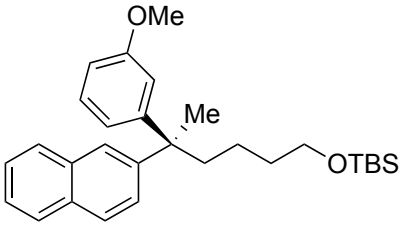


(*R*)-1-(2-(3-Methoxyphenyl)butan-2-yl)naphthalene (3-54). Prepared via General Procedure A using **3-37c** (prepared in 90% ee), except on a 0.30 mmol scale. Product **3-54** was isolated as a colorless sticky oil (58.6 mg, 67%). The enantiomeric excess was determined to be 88% by chiral HPLC analysis (CHIRALPAK IB, 0.6 mL/min, 0.1% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 11.227 min, t_R(minor) = 14.389 min. A duplicate run was performed via General Procedure A using **3-37c** (prepared in 84% ee), except on a 0.3 mmol scale, to give **3-54** as a colorless oil (70.1 mg, 80%) in 83% ee. $[\alpha]_D^{24}$ = +17.1° (c 3.09, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 – 7.77 (m, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.66 (dd, *J* = 7.3, 1.2 Hz, 1H), 7.56 (d, *J* = 8.8 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.30 (ddd, *J* = 8.0, 6.7, 1.1 Hz, 1H), 7.16 – 7.08 (m, 2H), 6.84 – 6.80 (m, 1H), 6.80 – 6.75 (m, 1H), 6.71 – 6.66 (m, 1H), 3.71 (s, 3H), 2.52 (dq, *J* = 14.6, 7.4 Hz, 1H), 2.25 (dq, *J* = 13.0, 7.3 Hz, 1H), 1.73 (s, 3H), 0.58 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.7, 153.1, 143.3, 135.0, 131.6, 129.3,

129.0, 127.9, 127.3, 125.3, 124.9, 124.8, 124.7, 119.4, 113.1, 110.0, 55.2, 47.5, 33.6, 29.4, 9.4; FTIR (NaCl/thin film) 3048, 2969, 2936, 2833, 1604, 1580, 1485, 1289, 1043, 877, 777, 705 cm^{-1}; HRMS (CI+) $[M+H]^+$ calculated for $C_{21}H_{23}O$: 291.1749, found: 291.1747.

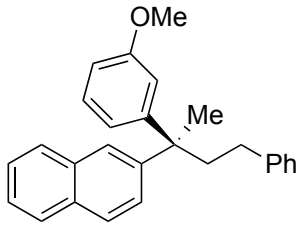


(*S*)-6-(2-(3-Methoxyphenyl)butan-2-yl)-2-methylquinoline (3-55). Prepared via General Procedure A using **3-37d** (prepared in 99% ee), except that **3-38** (133 mg, 0.332 mmol, 0.83 equiv) was used in place of **3a** and the reaction mixture was heated at 60 °C. Product **3-55** was isolated as a pale yellow oil (run 1: 91 mg, 74%; run 2: 102.9 mg, 84%). The enantiomeric excess was determined to be 97% (run 1: 97% ee; run 2: 97% ee) by chiral HPLC analysis (CHIRALPAK IA, 1.0 mL/min, 5% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 8.758 min, t_R(minor) = 9.969 min. $[\alpha]_D^{24}$ = +5.7° (c 3.68, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.68 (d, *J* = 2.1 Hz, 1H), 7.40 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.19 (t, *J* = 7.9 Hz, 1H), 6.82 – 6.76 (m, 2H), 6.75 – 6.69 (m, 1H), 3.74 (s, 3H), 2.73 (s, 3H), 2.30 – 2.16 (m, 2H), 1.68 (s, 3H), 0.76 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.5, 158.6, 151.1, 146.9, 146.6, 136.4, 130.7, 129.0, 128.3, 126.1, 124.5, 122.0, 120.3, 114.3, 110.4, 55.2, 46.8, 33.9, 26.9, 25.4, 9.3; FTIR (NaCl/thin film) 3053, 2968, 2936, 2833, 1599, 1488, 1431, 1291, 1254, 1173, 1052, 837, 703 cm^{-1}; HRMS (LIFDI) [M]+ calculated for $C_{21}H_{23}NO$: 305.1780, found: 305.1759.



(*S*)-*tert*-Butyl((5-(3-methoxyphenyl)-5-(naphthalen-2-yl)hexyl)oxy)dimethylsilane (3-56). Prepared via General Procedure A using **3-37e** (prepared in 99% ee) as a

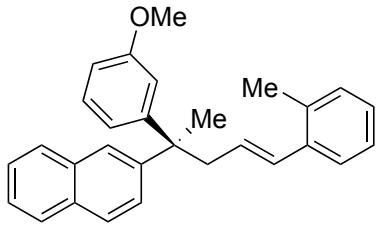
colorless sticky oil (159.8 mg, 89%). The enantiomeric excess was determined to be 99% by chiral HPLC analysis (CHIRALPAK IB, 0.4 mL/min, 100% hexane, λ=254 nm); t_R(major) = 33.672 min, t_R(minor) = 26.337 min. $[\alpha]_D^{24}$ = −11.0° (c 5.22, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 1H), 7.80 – 7.75 (m, 2H), 7.68 (d, *J* = 8.6 Hz, 1H), 7.45 (dddd, *J* = 19.3, 8.1, 6.8, 1.4 Hz, 2H), 7.21 – 7.15 (m, 2H), 6.83 – 6.78 (m, 2H), 6.75 – 6.70 (m, 1H), 3.75 (s, 3H), 3.55 (t, *J* = 6.6 Hz, 2H), 2.26 – 2.15 (m, 2H), 1.72 (s, 3H), 1.56 – 1.49 (m, 2H), 1.22 – 1.09 (m, 2H), 0.84 (s, 9H), –0.01 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.4, 151.6, 147.0, 133.3, 131.9, 129.0, 128.1, 127.7, 127.5, 127.1, 125.9, 125.5, 124.7, 120.3, 114.2, 110.3, 63.2, 55.2, 46.6, 41.4, 33.7, 27.6, 26.1, 21.3, 18.4, –5.1; FTIR (NaCl/thin film) 3055, 2934, 2856, 1606, 1470, 1255, 1099, 1046, 836, 775, 705, 476 cm^{-1}; HRMS (LIFDI) [M]+ calculated for $C_{29}H_{40}O_2Si$: 448.2798, found: 448.2790.



(*S*)-2-(2-(3-Methoxyphenyl)-4-phenylbutan-2-yl)naphthalene (3-57). Prepared via General Procedure A using **3-37f** (prepared in 94% ee), except that the reaction was run for 48 h. Product **3-57** was obtained as a colorless oil (run 1: 171.5 mg, 90%; run 2: 137.8 mg, 94%). The enantiomeric excess was determined to be 94% (run1: 94% ee; run 2: 94% ee) by chiral HPLC analysis (CHIRALPAK IB, 0.8 mL/min, 100% hexane, λ=210 nm); t_R(major) = 34.901 min, t_R(minor) = 31.785 min. $[\alpha]_D^{24}$ = −25.9° (c 4.54, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 − 7.83 (m, 2H), 7.81 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.73 (d, *J* = 8.7 Hz, 1H), 7.52 − 7.44 (m, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.25 – 7.17 (m, 3H), 7.17 – 7.13 (m, 2H), 6.88 – 6.85 (m, 2H), 6.76 (ddd, *J* = 8.3, 2.4, 1.0 Hz, 1H), 3.76 (s, 3H), 2.59 – 2.49 (m, 2H), 2.49 – 2.37 (m, 2H), 1.84 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.6, 151.1, 146.6, 143.0, 133.3, 132.0, 129.1, 128.51, 128.50, 128.2, 127.9, 127.5, 127.0, 126.1, 125.9, 125.7, 124.8, 120.2, 114.2, 110.5, 55.3, 46.7, 43.9, 31.5, 27.5; FTIR (NaCl/thin film) 3056, 3024, 2946, 2867,

1600, 1283, 1494, 1291, 1047, 908, 818, 760 cm^{-1}; HRMS (EI+) [M]+ calculated for $C_{27}H_{26}O$: 366.1984, found: 366.1967.

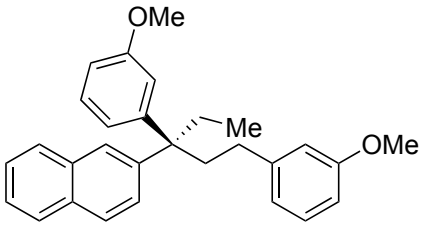
Please note: The absolute configuration of **3-57** is tentatively assigned. The absolute configuration resulting from the method used in the preparation of its alcohol precursor **3-71** has not been reported in the literature. Please see the experimental for **3-71** below.



***(E)*-2-(2-(3-Methoxyphenyl)-5-(*o*-tolyl)pent-4-en-2-yl)naphthalene (3-58).** Prepared via General Procedure A using **3-37g** (prepared in 96% ee), except that **3-38** (133 mg, 0.332 mmol, 0.83 equiv) was used in place of **3-41**. Product **3-58** was isolated as a colorless sticky oil (run 1: 125.6 mg, 80%; run 2: 119.7 mg, 76%). The enantiomeric excess was determined to be 95% (run 1: 95% ee; run 2: 94% ee) by chiral HPLC analysis (CHIRALPAK IC, 0.6 mL/min, 0.1% hexane, λ=210 nm); t_R(major) = 13.480 min, t_R(minor) = 15.096 min. $[\alpha]_D^{24}$ = +3.7° (c 4.84, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 – 7.81 (m, 2H), 7.81 – 7.76 (m, 1H), 7.71 (d, *J* = 8.6 Hz, 1H), 7.50 – 7.42 (m, 2H), 7.24 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.20 (t, *J* = 7.9 Hz, 1H), 7.17 (d, *J* = 7.3 Hz, 1H), 7.10 – 7.01 (m, 3H), 6.88 – 6.82 (m, 2H), 6.77 – 6.72 (m, 1H), 6.57 (d, *J* = 15.6 Hz, 1H), 5.76 (dt, *J* = 15.6, 7.2 Hz, 1H), 3.74 (s, 3H), 3.21 – 3.10 (m, 2H), 2.20 (s, 3H), 1.76 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.5, 151.0, 146.5, 137.1, 135.1, 133.3, 132.0, 131.1, 130.1, 129.1, 128.5, 128.2, 127.8, 127.5, 127.1, 127.0, 126.04, 126.02, 125.9, 125.7, 124.8, 120.3, 114.2, 110.6, 55.3, 46.8, 45.6, 27.7, 19.8; FTIR (NaCl/thin film) 3054, 2965, 2933, 1599, 1485, 1431, 1258, 1047, 967, 818, 754 cm^{-1}; HRMS (LIFDI) [M]+ calculated for $C_{29}H_{28}O$: 392.2140, found: 392.2137.

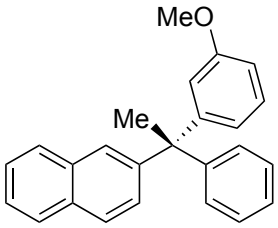
Please note: The absolute configuration of **3-58** is tentatively assigned. The absolute configuration resulting from the method used in the preparation of its acetate

precursor **3-37g** has not been reported in the literature. Please see the experimental for **3-37g** below.

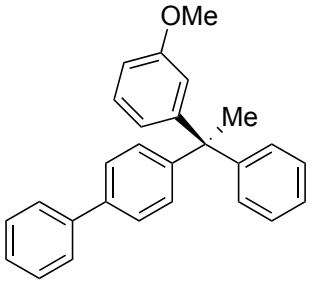


(*S*)-2-(1,3-Bis(3-methoxyphenyl)pentan-3-yl)naphthalene (3-59). Prepared via General Procedure A using **3-37h** (prepared in 89% ee), except that **3-38** (133 mg, 0.332 mmol, 0.83 equiv) was used in place of **3-41**. Product **3-59** was isolated as a colorless sticky oil (127 mg, 77%). The enantiomeric excess was determined to be 87% by chiral SFC analysis (CHIRALCEL OJ-H(25 x 0.46 cm), 3.0 mL/min, 20% MeOH(0.1% diethylamine)/CO_2 (100 bar), λ=220 nm); t_R(major) = 9.10 min, t_R(minor) = 7.81 min. A duplicate experiment was conducted with **1h** (prepared in 87% ee) to give **22** (103 mg, 63%) in 86% ee. $[\alpha]_D^{24} = -30.5°$ (c 3.04, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 – 7.81 (m, 2H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 8.7 Hz, 1H), 7.51 – 7.41 (m, 2H), 7.19 (td, *J* = 7.9, 4.1 Hz, 2H), 7.14 (dd, *J* = 8.7, 1.9 Hz, 1H), 6.86 – 6.81 (m, 2H), 6.77 – 6.67 (m, 3H), 6.65 – 6.61 (m, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 2.50 – 2.44 (m, 2H), 2.36 – 2.22 (m, 4H), 0.75 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.8, 159.4, 150.1, 145.7, 144.8, 133.2, 131.9, 129.5, 128.9, 128.2, 127.7, 127.51, 127.48, 126.0, 125.6, 125.5, 120.93, 120.92, 114.9, 114.4, 111.0, 110.4, 55.29, 55.28, 50.0, 38.9, 30.9, 29.5, 8.6; FTIR (NaCl/thin film) 3054, 2955, 2833, 1600, 1487, 1257, 1153, 1050, 908, 813, 782 cm^{-1}; HRMS (LIFDI) [M]+ calculated for $C_{29}H_{30}O_2$: 410.2246, found: 410.2238.

Please note: The absolute configuration of **3-59** is tentatively assigned. The absolute configuration resulting from the method used in the preparation of its alcohol precursor **3-72** has not been reported in the literature. Please see the experimental for **3-72** below.



(*R*)-2-(1-(3-Methoxyphenyl)-1-phenylethyl)naphthalene (3-6-). Prepared via General Procedure A using **3-37i** (prepared in 96% ee) as a colorless oil (run 1: 95 mg, 70%; run 2: 101 mg, 75%). The enantiomeric excess was determined to be 94% (run 1: 94%; run 2: 94%) by chiral HPLC analysis (CHIRALPAK IB, 0.2 mL/min, 0.1% hexane, λ=210 nm); t_R(major) = 49.084 min, t_R(minor) = 52.102 min. $[\alpha]_D^{24}$ = +15.0° (c 0.86, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 – 7.79 (m, 1H), 7.74 (d, *J* = 8.7 Hz, 1H), 7.72 – 7.67 (m, 1H), 7.49 – 7.41 (m, 3H), 7.32 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.28 (t, *J* = 7.4 Hz, 2H), 7.25 – 7.19 (m, 2H), 7.19 – 7.14 (m, 2H), 6.81 – 6.74 (m, 2H), 6.72 (t, *J* = 2.1 Hz, 1H), 3.72 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.4, 150.6, 148.8, 146.5, 133.2, 132.0, 130.6, 128.94, 128.91, 128.3, 128.1, 127.8, 127.5, 127.0, 126.2, 126.0, 125.9, 121.7, 115.6, 110.9, 55.3, 52.9, 30.6; FTIR (NaCl/thin film) 3055, 2978, 2934, 2833, 1597, 1487, 1256, 1044, 820, 745, 701 cm^{-1}; HRMS (CI+) $[M+H]^+$ calculated for $C_{25}H_{23}O$: 339.1749, found: 339.1742.

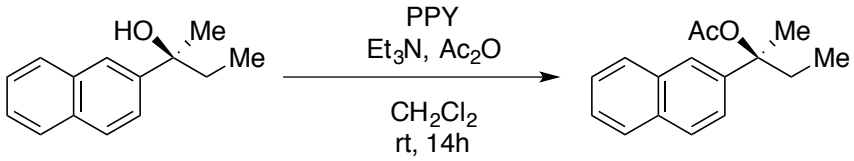


(*R*)-4-(1-(3-Methoxyphenyl)-1-phenylethyl)-1,1'-biphenyl (3-61). Prepared via General Procedure A using **3-37j** (prepared as 91% ee), except with 10 mol % $NiCl_2$·DME, 10 mol % CyJohnPhos, 60 °C, 48 h. Product **3-61** was isolated as a colorless oil (run 1: 84.4 mg, 58%; run 2: 96.2 mg, 66%). The 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% hexane, λ=254 nm); t_R(major) = 18.913 min, t_R(minor) = 18.288 min. $[\alpha]_D^{24}$ = +31.5° (c 1.68, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.54 – 7.48 (m, 2H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.35 –

7.31 (m, 1H), 7.29 (dd, J = 8.4, 6.9 Hz, 2H), 7.22 (td, J = 7.6, 4.0 Hz, 2H), 7.20 – 7.14 (m, 4H), 6.80 – 6.73 (m, 2H), 6.71 (t, J = 2.1 Hz, 1H), 3.74 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.4, 150.8, 149.0, 148.2, 140.9, 138.8, 129.3, 128.90, 128.86, 128.85, 128.0, 127.3, 127.1, 126.6, 126.2, 121.6, 115.6, 110.8, 55.3, 52.5, 30.6; FTIR (NaCl/thin film) 3055, 3028, 2979, 2833, 1598, 1486, 1290, 1254, 1040, 845, 735, 699 cm^{-1}; HRMS (CI+) $[M+H]^+$ calculated for $C_{27}H_{25}O$: 365.1905, found: 365.1907.

Preparation of Enantioenriched Tertiary Benzyl Acetates

General Procedure B: Preparation of (*S*)-2-(Naphthalen-2-yl)butan-2-yl Acetate (3-37a).

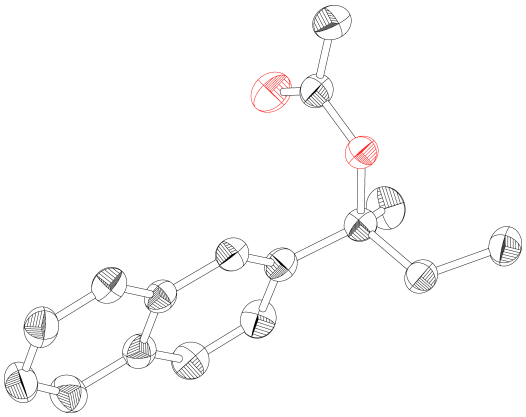


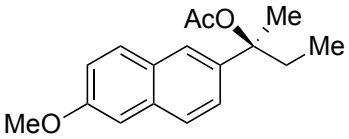
In an oven-dried 100-mL round-bottomed flask, was placed 2-(naphthalen-2-yl)butan-2-ol (**3-66**, prepared in 96% ee, 1.5 g, 7.5 mmol, 1.0 equiv), 4-pyrrolidinopyridine (PPY, 168 mg, 1.13 mmol, 0.150 equiv), and CH_2Cl_2 (25 mL, 0.3 M). Then flask was then placed in an ice/water bath. Et_3N (3.1 mL, 23 mmol, 3.0 equiv) was added, followed by acetic anhydride (1.4 mL, 15 mmol, 2.0 equiv). The solution was then stirred at room temperature for 14 h. Sat. $NaHCO_3$ (100 mL) was added, and the product was extracted with CH_2Cl_2 (3 x 25 mL). The combined organic layers were washed with sat. NaCl, dried (Na_2SO_4), filtered and concentrated. The crude mixture was purified by silica gel chromatography (0−20% EtOAc/hexanes) to give **3-37a** as a viscous oil (1.45 g, 80%). The enantiomeric excess was determined to be 96% by chiral HPLC analysis (CHIRALPAK IB, 1 mL/min, 1% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 8.234 min, t_R(minor) = 6.313 min. $[\alpha]_D^{24}$ = +5.0° (c 3.59, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 – 7.78 (m, 3H), 7.77 – 7.74 (m, 1H), 7.51 – 7.39 (m, 3H), 2.18 – 2.08 (m, 5H), 1.92 (s, 3H), 0.81 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.8, 142.4, 133.2, 132.5, 128.3, 128.1, 127.6, 126.2, 125.9, 123.6, 123.2, 84.6, 35.1, 24.5, 22.4, 8.3; FTIR (NaCl/thin film) 3057, 2977, 2938, 2880, 1734, 1458, 1366, 1246, 1128, 1017, 817, 747, 477 cm^{-1}; HRMS (EI+) [M]+ calculated for $C_{16}H_{18}O_2$: 242.1307, found: 242.1309.

This type of compound decomposed to olefins quickly in pure form at room temperature, but is relatively stable in cold solution. Our suggestion is to immediately dissolve in anhydrous 2-Me-THF and store in fridge under N_2.

A crystal suitable for X-ray diffraction analysis was obtained upon cooling the viscous oil isolated above neat at –35 °C. The crystal structure demonstrates that the absolute configuration is *S* (Figure S2).

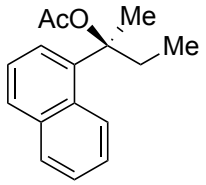
Figure S2. Molecular diagram of **3-37a** with ellipsoids at 50% probability, H-atoms omitted for clarity. (CCDC 1502353)



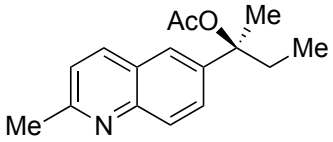


(*S*)-2-(6-Methoxynaphthalen-2-yl)butan-2-yl acetate (3-37b). Prepared via General Procedure B using **3-67** (prepared as 92% ee) as a colorless oil (75%). The enantiomeric excess was assumed to be 92% based on the starting material (**3-67**). $[\alpha]_D^{24}$ = +42° (c 1.5, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 – 7.66 (m, 3H), 7.40 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.14 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.11 (d, *J* = 2.5 Hz, 1H), 3.91 (s, 3H), 2.16 – 2.06 (m, 5H), 1.90 (s, 3H), 0.80 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.9, 157.8, 140.1, 133.6, 129.8, 128.7, 126.9, 123.8, 123.5, 119.0, 105.7, 84.7, 55.5, 35.1, 24.5, 22.4, 8.3; FTIR (NaCl/thin film) 2975, 2937, 1734,

1608, 1367, 1247, 1204, 1164, 1031, 850 cm^{-1}; HRMS (CI+) [M]+H calculated for $C_{17}H_{21}O_3$: 273.1491, found: 273.1501.

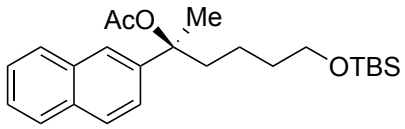


(*S*)-2-(Naphthalen-1-yl)butan-2-yl acetate (3-37c). Prepared via General Procedure B using **3-68** (90% ee) as a colorless oil (58%). The enantiomeric excess was determined to be 90% by chiral HPLC analysis (CHIRALPAK IA, 0.8 mL/min, 1.0% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 9.214 min, t_R(minor) = 8.322 min. $[\alpha]_D^{24}$ = +10.2° (c 0.88, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.55 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.87 (dd, *J* = 7.7, 1.9 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.52 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.50 – 7.41 (m, 3H), 2.48 (dq, *J* = 14.7, 7.5 Hz, 1H), 2.25 (dq, *J* = 14.6, 7.5 Hz, 1H), 2.04 (s, 3H), 2.02 (s, 3H), 0.87 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.5, 139.9, 134.9, 130.4, 129.7, 128.7, 125.6, 125.5, 125.1, 125.0, 124.3, 85.6, 34.0, 24.6, 21.8, 8.7; FTIR (NaCl/thin film) 2979, 2940, 1734, 1653, 1558, 1507, 1364, 1242, 1107, 1015, 804, 776 cm^{-1}; HRMS (EI+) [M]+ calculated for $C_{16}H_{18}O_2$: 242.1307, found: 242.1316.

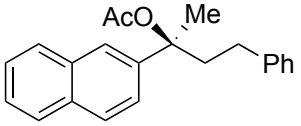


(*S*)-2-(2-Methylquinolin-6-yl)butan-2-yl acetate (3-37d). Prepared via General Procedure B using **3-69** (99% ee) as a yellow oil (87%). The enantiomeric excess was determined to be 99% by chiral HPLC analysis (CHIRLPAK IB, 1.0 mL/min, 6.0% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 13.331 min, t_R(minor) = 9.787 min. $[\alpha]_D^{24}$ = +7.8° (c 1.51, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.8 Hz, 1H), 7.67 (d, *J* = 2.1 Hz, 1H), 7.63 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.27 (s, 1H), 2.72 (s, 3H), 2.10 (s, 5H), 1.90 (s, 3H), 0.79 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.8, 159.0, 147.1, 142.2, 136.5, 128.7, 126.7, 126.1, 123.2, 122.3, 84.3, 35.1, 25.4, 24.4, 22.3, 8.3; FTIR (NaCl/thin film) 2977, 2938, 1739, 1601, 1368,

1247, 1136, 1078, 834 cm^{-1}; HRMS (CI+) [M]+H calculated for $C_{16}H_{20}NO_2$: 258.1494, found: 258.1488.

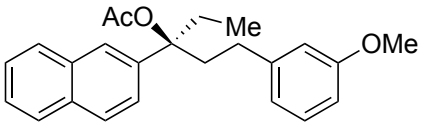


(*S*)-6-((tert-Butyldimethylsilyl)oxy)-2-(naphthalen-2-yl)hexan-2-yl acetate (3-37e). Prepared via General Procedure B using **3-70** (99% ee) as a colorless oil (75%). The enantiomeric excess was determined to be 99% by chiral HPLC analysis (CHIRLCEL OD-H, 1.0 mL/min, 0.5% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 21.535 min, t_R(minor) = 14.469 min. $[\alpha]_D^{24}$ = +15.4° (c 4.73, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 11.1, 8.5 Hz, 3H), 7.76 – 7.71 (m, 1H), 7.48 – 7.41 (m, 3H), 3.53 (t, *J* = 6.4 Hz, 2H), 2.14 – 2.03 (m, 5H), 1.93 (s, 3H), 1.46 (p, *J* = 7.0 Hz, 2H), 1.31 – 1.22 (m, 2H), 0.83 (s, 9H), –0.01 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 142.5, 133.2, 132.5, 128.3, 128.1, 127.6, 126.1, 125.9, 123.5, 123.1, 84.2, 63.0, 42.4, 33.0, 26.0, 24.8, 22.4, 20.3, 18.4, –5.2; FTIR (NaCl/thin film) 3058, 2952, 2929, 2857, 1739, 1366, 1248, 1101, 836, 775 cm^{-1}; HRMS (LIFDI) [M]+ calculated for $C_{24}H_{36}O_3Si$: 400.2434, found: 400.2435.



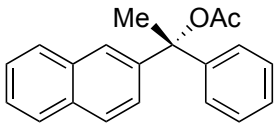
(*S*)-2-(Naphthalen-2-yl)-4-phenylbutan-2-yl acetate (3-37f). Prepared via General Procedure B as a colorless oil (96%). The enantiomeric excess was determine to be 94% by chiral HPLC analysis (CHIRALPAK IA, 1.0 mL/min, 0.5% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 11.227 min, t_R(minor) = 12.577 min. $[\alpha]_D^{24}$ = −74.8° (c 1.1, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.77 (m, 4H), 7.52 – 7.43 (m, 3H), 7.26 – 7.21 (m, 2H), 7.16 (d, *J* = 7.3 Hz, 1H), 7.13 – 7.07 (m, 2H), 2.58 – 2.34 (m, 4H), 2.12 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 142.2, 141.8, 133.2, 132.5, 128.49, 128.46, 128.4, 128.3, 127.6, 126.3, 126.01, 126.00, 123.6, 123.0, 84.0, 44.1, 30.4, 25.3, 22.4; FTIR (NaCl/thin film) 3059,3 025, 2937, 1734, 1717, 1652, 1558, 1506, 1244, 747 cm^{-1}; HRMS (LIFDI) [M]+ calculated for $C_{22}H_{22}O_2$: 318.1620, found: 318.1648.

Please note: The absolute configuration of **3-37f** is tentatively assigned. The absolute configuration resulting from the method used in the preparation of its alcohol precursor **3-71** has not been reported in the literature. Please see the experimental for **3-71** below.



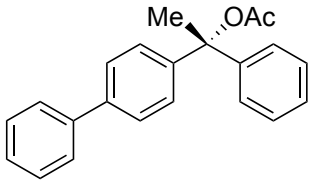
(*S*)-1-(3-Methoxyphenyl)-3-(naphthalen-2-yl)pentan-3-yl acetate (3-37h). Prepared via General Procedure B using **3-72**(89% ee) as a colorless oil (80%). The enantiomeric excess was assumed to be 89% based on the starting material. $[\alpha]_D^{24}$ = +30.5° (c 1.50, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 – 7.84 (m, 4H), 7.55 – 7.46 (m, 3H), 7.16 (t, *J* = 7.9 Hz, 1H), 6.70 (ddd, *J* = 13.7, 7.8, 2.0 Hz, 2H), 6.65 – 6.61 (m, 1H), 3.76 (s, 3H), 2.97 – 2.85 (m, 1H), 2.62 (dq, *J* = 14.6, 7.3 Hz, 1H), 2.51 – 2.41 (m, 2H), 2.39 – 2.29 (m, 1H), 2.27 – 2.16 (m, 4H), 0.74 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.7, 159.7, 143.6, 140.6, 133.2, 132.5, 129.4, 128.4, 128.2, 127.6, 126.3, 126.0, 124.5, 123.2, 120.9, 114.2, 111.3, 87.8, 55.2, 39.4, 30.9, 30.1, 22.2, 7.8; FTIR (NaCl/thin film) 3056, 2970, 2937, 1733, 1600, 1489, 1455, 1366, 1242, 1046, 1021, 819, 748 cm^{-1}; HRMS (LIFDI) [M]+ calculated for $C_{24}H_{26}O_3$: 362.1882, found: 362.1906.

Please note: The absolute configuration of **3-37h** is tentatively assigned. The absolute configuration resulting from the method used in the preparation of its alcohol precursor **3-72** has not been reported in the literature. Please see the experimental for **3-72** below.



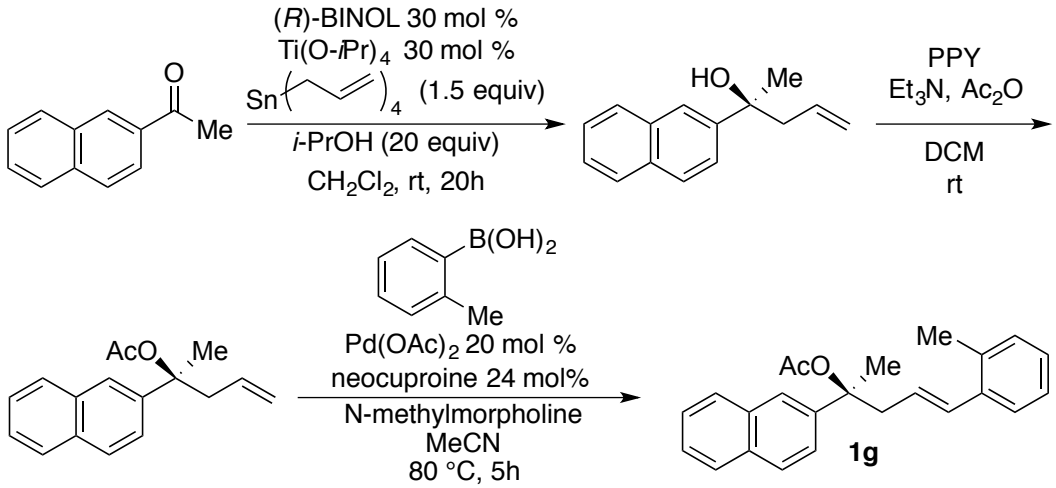
(*R*)-1-(Naphthalen-2-yl)-1-phenylethyl acetate (3-37i). Prepared via General Procedure B using **3-73** (96% ee) as a colorless sticky oil (54%). The enantiomeric excess was determined to be 96% by chiral HPLC analysis (CHIRLPAK IB, 1.0 mL/min, 1.0% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 8.923 min, t_R(minor) = 7.511

min. $[\alpha]_D^{24}$ = +15.3° (c 4.1, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 – 7.87 (m, 1H), 7.84 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.79 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.75 (d, *J* = 8.7 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.38 – 7.29 (m, 5H), 7.26 – 7.23 (m, 1H), 2.30 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.4, 145.6, 142.9, 133.0, 132.6, 128.5, 128.3, 128.1, 127.7, 127.3, 126.3, 126.2, 126.1, 124.6, 124.5, 84.8, 27.0, 22.6; FTIR (NaCl/thin film) 3056, 3024, 2981, 1739, 1368, 1241, 1188, 749, 699 cm^{-1}; HRMS (LIFDI) [M]+ calculated for $C_{20}H_{18}O_2$: 290.1307, found: 290.1328.



(*R*)-1-([1,1'-Biphenyl]-4-yl)-1-phenylethyl acetate (3-37j). Prepared via General Procedure B using **3-74** (91% ee) as a colorless oil (61%). The enantiomeric excess was assumed to be 91% based on the starting material. $[\alpha]_D^{24}$ = −17.8° (c 0.84, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 – 7.57 (m, 2H), 7.57 – 7.53 (m, 2H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.42 – 7.32 (m, 7H), 7.29 – 7.26 (m, 1H), 2.25 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.4, 145.7, 144.8, 140.8, 140.1, 128.9, 128.3, 127.4, 127.3, 127.2, 127.0, 126.5, 126.0, 84.6, 27.0, 22.6; FTIR (NaCl/thin film) 3057, 3029, 2939, 1739, 1600, 1582, 1487, 1446, 1368, 1238, 1057, 875, 761 cm^{-1}; HRMS (LIFDI) [M]+ calculated for $C_{22}H_{20}O_2$: 316.1463, found: 316.1485.

Preparation of (*S*,*E*)-2-(Naphthalen-2-yl)-5-(*o*-tolyl)pent-4-en-2-yl acetate (3-37g).



2-(Naphthalen-2-yl)pent-4-en-2-ol. This procedure was adapted from that reported in the literature.[iv] In an oven-dried, 50-mL, round-bottomed flask was placed (*R*)-BINOL (312 mg, 1.09 mmol, 0.300 equiv) in CH_2Cl_2 (9.0 mL). Ti(O-*i*Pr)$_4$ (0.33 mL, 1.1 mmol, 0.30 equiv) was added at room temperature. The mixture was stirred for 10 min. Then *i*PrOH (5.6 mL, 73 mmol, 20 equiv) was added, followed by a solution of 2-acetonaphthone (618 mg, 3.63 mmol, 1.00 equiv) and CH_2Cl_2 (3.0 mL), and then tetraallyltin (0.96 mL, 4.0 mmol, 1.1 equiv). The orange solution was stirred at room temperature for 22 h and quenched with sat. $NaHCO_3$ (40 mL). To remove solids, the mixture was filtered through Celite®, which was then washed with CH_2Cl_2. The layers were separated, and the organic layer was washed with sat. NaCl, dried (Na_2SO_4), filtered, and concentrated. The crude mixture was purified on silica gel chromatography (0−20% EtOAc/hexanes) to give a 2-(naphthalen-2-yl)pent-4-en-2-ol as a clear oil (634.2 mg, 82%). The enantiomeric excess was determined to be 96% by chiral HPLC analysis (CHIRALPAK IC, 1 mL/min, 3% i-PrOH/hexane, λ=254 nm); t_R(major) = 12.164 min, t_R(minor) = 10.175 min. The spectral data of this compound matches of that reported in the literature.[v]

Please note: The absolute configuration of 2-(naphthalene-2-yl)pent-4-en-2-ol is tentatively assigned. The absolute configuration resulting from this allylation procedure has not been reported in the literature.[REF: Walsh ACIE 2002]

2-(Naphthalen-2-yl)pent-4-en-2-yl acetate. Using General Procedure B, 2-(naphthalen-2-yl)pent-4-en-2-yl acetate was obtained as a colorless oil (632.5 mg, 86%) from 2-(naphthalen-2-yl)pent-4-en-2-ol (611 mg, 2.88 mmol, 96% ee): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 – 7.80 (m, 3H), 7.79 – 7.72 (m, 1H), 7.46 (dtd, *J* = 9.2, 6.9, 5.4 Hz, 3H), 5.63 (ddt, *J* = 17.3, 10.2, 7.2 Hz, 1H), 5.11 – 4.95 (m, 2H), 2.94 (dd, *J* = 14.0, 7.1 Hz, 1H), 2.85 (dd, *J* = 14.0, 7.3 Hz, 1H), 2.09 (s, 3H), 1.91 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.8, 142.2, 133.2, 133.0, 132.6, 128.4, 128.2, 127.6, 126.2, 126.0, 123.6, 123.1, 118.8, 83.4, 46.4, 25.1, 22.4.

(*S,E*)-2-(Naphthalen-2-yl)-5-(*o*-tolyl)pent-4-en-2-yl acetate (3-37g). The procedure was adapted from reported literature.[vi] In 25-mL, round-bottomed flask was placed 2-(naphthalen-2-yl)pent-4-en-2-yl acetate (632 mg, 2.49 mmol, 1.00 equiv), 2-methylphenyl boronic acid (677 mg, 5.00 mmol, 2.00 equiv), *N*-methylmorpholine (0.55 mL, 5.0 mmol, 2.0 equiv), and MeCN (10 mL). The flask was exposed to open air. $Pd(OAc)_2$ (335 mg, 0.498 mmol, 20 mol %) and neocuproine (125 mg, 0.598 mmol, 24 mol %) were added. The mixture was heated at 80 °C for 22 h. The mixture was cooled to room temperature and diluted with CH_2Cl_2 (30 mL). The solid was removed by filtration through a pad of Celite®, and the organic layer was concentrated. The crude mixture was purified via silica gel chromatography (0−15% EtOAc/hexanes) to give **3-37g** as a colorless oil (351 mg, 41%). The enantiomeric excess was determined to be 96% by chiral HPLC analysis (CHIRALPAK IA, 0.8 mL/min, 1% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 15.924 min, t_R(minor) = 21.866 min. $[\alpha]_D^{24}$ = +10.7° (c 1.12, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 – 7.78 (m, 4H), 7.52 – 7.44 (m, 3H), 7.28 (dd, *J* = 7.4, 2.2 Hz, 1H), 7.14 – 7.07 (m, 3H), 6.62 – 6.56 (m, 1H), 5.87 (dt, *J* = 15.3, 7.4 Hz, 1H), 3.12 – 2.99 (m, 2H), 2.22 (s, 3H), 2.10 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.8, 142.2, 136.8, 135.3, 133.2, 132.6, 132.1, 130.2, 128.4, 128.2, 127.6, 127.3, 126.3, 126.1, 126.05, 126.03, 125.9, 123.6, 123.2, 83.8, 45.9, 25.3, 22.4, 19.8; FTIR (NaCl/thin film) 2955, 2921, 2850, 1713, 1464, 1364, 1232, 1076, 748 cm^{-1}; HRMS (LIFDI) [M]+ calculated for $C_{24}H_{24}O_2$: 344.1776, found: 344.1769.

Please note: The absolute configuration of **3-37g** is tentatively assigned. The absolute configuration resulting from the method used in the preparation of its alcohol precursor has not been reported in the literature, as discussed above.

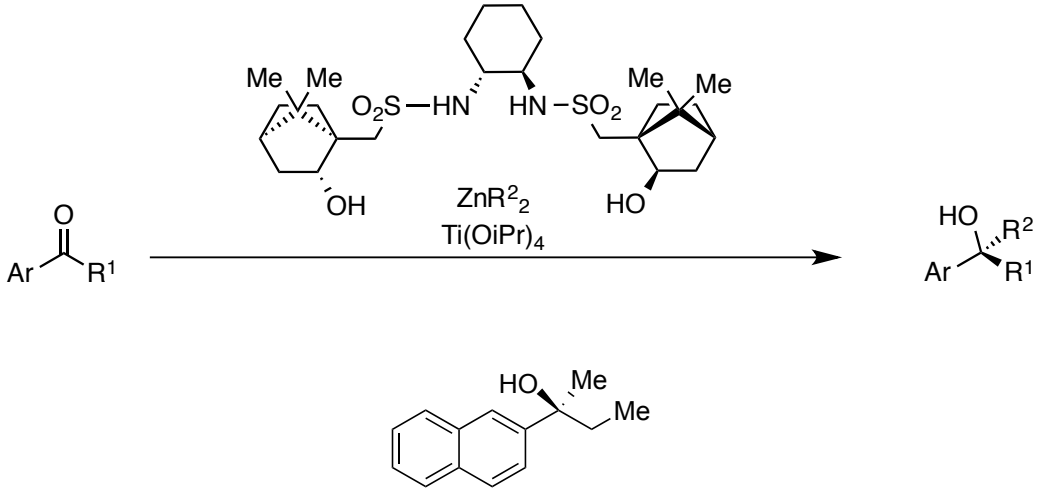
Preparation of Tertiary Benzyl Alcohols (3-66 – 3-XX)

In addition to the reactions described below, a number of other methods are available for the preparation of highly enantioenriched tertiary benzylic alcohols. Notable examples are described in the following references:

1) Jeon, S.-J., Li, H. & Walsh, P. J. A Green Chemistry Approach to a More Efficient Asymmetric Catalyst: Solvent-Free and Highly Concentrated Alkyl Additions to Ketones. *J. Am. Chem. Soc.* **127**, 16416-16425 (2005).
2) García, C., LaRochelle, L. K. & Walsh, P. J. A Practical Catalytic Asymmetric Addition of Alkyl Groups to Ketones. *J. Am. Chem. Soc.* **124**, 10970-10971 (2002).
3) Li, H. & Walsh, P. J. Catalytic Asymmetric Vinylation of Ketones. *J. Am. Chem. Soc.* **126**, 6538-6539 (2004).
4) García, C. & Walsh, P. J. Highly Enantioselective Catalytic Phenylation of Ketones with a Constrained Geometry Titanium Catalyst. *Org. Lett*. **5**, 3641-3644 (2003).
5) Waltz, K. M., Gavenonis, J. & Walsh, P. J. A Simple, Reliable, Catalytic Asymmetric Allylation of Ketones. *Angew. Chem., Int. Ed*. **41**, 3697-3699 (2002).
6) Watson, C. G. & Aggarwal, V. K. Asymmetric Synthesis of 1-Heteroaryl-1-arylalkyl Tertiary Alcohols and 1-Pyridyl-1-arylethanes by Lithiation–Borylation Methodology. *Org. Lett*. **15**, 1346-1349 (2013).
7) Cozzi, P. G. Enantioselective Alkynylation of Ketones Catalyzed by Zn(Salen) Complexes. *Angew. Chem., Int. Ed*. **42**, 2895-2898 (2003).

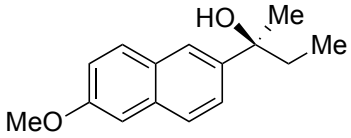
8) Zhou, Y., Wang, R., Xu, Z., Yan, W., Liu, L., Kang, Y. & Han, Z. Highly Enantioselective Phenylacetylene Additions to Ketones Catalyzed by (S)-BINOL–Ti Complex. *Org. Lett.* **6**, 4147-4149 (2004).

Preparation of 3-66 – 3-69.

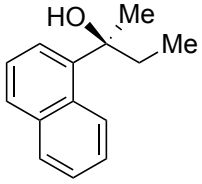


(*S*)-2-(Naphthalen-2-yl)butan-2-ol (3-66). This procedure was adapted from that reported in the literature.[vii a] In an oven-dried, 100-mL, round-bottomed flask was placed **L1** (33 mg, 0.060 mmol, 0.010 equiv) and Et_2Zn (0.73 mL, 7.2 mmol, 1.2 equiv). Ti(O-*i*Pr)$_4$ (2.1 mL, 7.2 mmol, 1.2 equiv) was added. The resulting greenish solution was stirred at room temperature for 5 min. 2-Acetonaphthalone (1.02 g, 6.00 mmol, 1.00 equiv) was added into the flask in one portion. The mixture was stirred at room temperature for 17 h. The resulting brown sticky oil was diluted with EtOAc (50 mL) and quenched with HCl (1 N). The product was extracted from the aqueous layer with EtOAc (25 mL x 2). The combined organic layers were washed with sat. NaCl, dried ($MgSO_4$), filtered, and concentrated. The residue was purified via silica gel chromatography (5−10% Et_2O/hexanes) to give **3-66** (470 mg, 39%) as a colorless oil. The enantiomeric excess was determined to be 97% by chiral HPLC analysis (CHIRLPAK IB, 1.0 mL/min, 3.0% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 10.269 min, t_R(minor) = 11.370 min. Based on the optical rotation, $[\alpha]_D^{24} = -9.5°$ (c 1.0, MeOH) (Literature data: $[\alpha]_D^{24} = +16.3°$ (c 1.0, MeOH) for *R* configuration), [7b] the

absolute configuration of **3-66** was assigned as *S*. The spectral data of this compound matched that reported in the literature.[7]

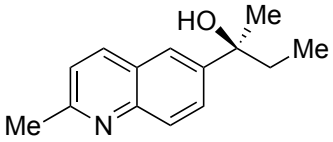


(*S*)-2-(6-Methoxynaphthalen-2-yl)butan-2-ol (3-67). Prepared via the procedure described above for preparation of **3-66** as a colorless oil (32%). The enantiomeric excess was determined to be 92% by chiral HPLC analysis (CHIRLPAK IC, 1.0 mL/min, 3.0% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 21.219 min, t_R(minor) = 16.516 min. $[\alpha]_D^{24}$ = +5.1° (c 3.02, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 1.9 Hz, 1H), 7.73 (dd, *J* = 12.2, 8.7 Hz, 2H), 7.50 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.16 – 7.11 (m, 2H), 3.92 (s, 3H), 1.99 – 1.85 (m, 2H), 1.79 (d, *J* = 3.6 Hz, 1H), 1.63 (s, 3H), 0.82 (td, *J* = 7.4, 1.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.7, 143.0, 133.4, 129.7, 128.8, 126.8, 124.4, 123.3, 118.9, 105.7, 75.2, 55.5, 36.7, 29.9, 8.5; FTIR (NaCl/thin film) 3447 (br s), 3059, 2969, 2935, 1634, 4606, 1504, 1485, 1462, 1388, 1265, 1199, 1033, 852, 810 cm^{-1}; HRMS (CI+) [M]+H calculated for $C_{15}H_{19}O_2$: 231.1385, found: 231.1400.



(*S*)-2-(Naphthalen-1-yl)butan-2-ol (3-68). Prepared via the procedure described above for preparation of **3-66** as a colorless oil (9%). The enantiomeric excess was determined as 90% by chiral HPLC analysis (CHIRLPAK IB, 0.7 mL/min, 2.0% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 15.085 min, t_R(minor) = 17.287 min. $[\alpha]_D^{24}$ = +33.7° (c 1.91, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.79 – 8.75 (m, 1H), 7.87 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.58 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.48 (pd, *J* = 6.8, 1.6 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 1H), 2.30 – 2.17 (m, 2H), 2.02 (s, 1H), 1.82 (s, 3H), 0.83 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.4, 135.0, 131.1, 129.3, 128.6, 127.1, 125.3, 125.2, 124.9, 124.0, 76.9, 35.4, 29.5, 9.0; FTIR (NaCl/thin

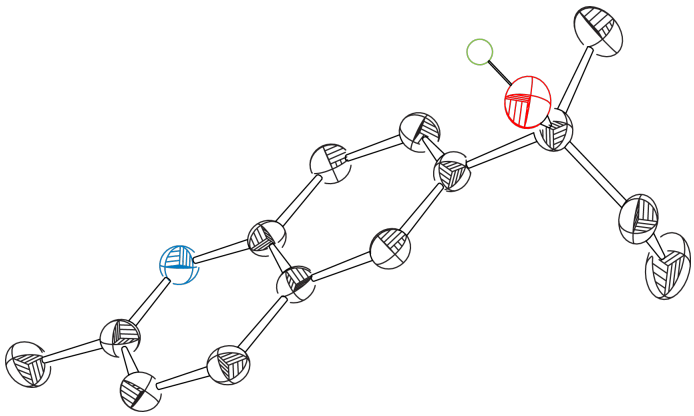
film) 3420 (brs), 3048, 2971, 2936, 2877, 1653, 1508, 1456, 1374, 1117, 804, 777 cm^{-1}; HRMS (EI+) [M]+H calculated for $C_{14}H_{16}O$: 200.1201, found: 200.1205.



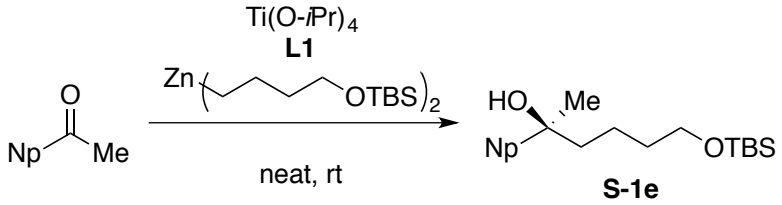
(*S*)-2-(2-Methylquinolin-6-yl)butan-2-ol (3-69). Prepared via the procedure described above for preparation of **3-66** as a pale yellow solid (mp 86–89°, 41%). The enantiomeric excess was determined as 99% by chiral HPLC analysis (CHIRLPAK IC, 1 mL/min, 8.0% *i*-PrOH/hexanes, λ=230 nm); t_R(major) = 23.228 min, t_R(minor) = 19.313 min. $[\alpha]_D^{24}$ = +33° (c 1.03, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.8 Hz, 1H), 7.85 (d, *J* = 2.1 Hz, 1H), 7.71 (dd, *J* = 8.9, 2.1 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 1H), 2.74 (s, 3H), 1.93 (ddt, *J* = 27.2, 14.1, 7.1 Hz, 2H), 1.64 (s, 3H), 0.81 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.9, 147.0, 145.1, 136.5, 128.6, 127.4, 126.2, 123.1, 122.3, 75.1, 36.7, 30.0, 25.5, 8.4; FTIR (NaCl/thin film) 3355 (brs), 2969, 2933, 2878, 1601, 1497, 1457, 1374, 1165, 1126, 837, 755 cm^{-1}; HRMS (CI+) [M]+H calculated for $C_{14}H_{18}NO$: 216.1388, found: 216.1398.

A crystal suitable for X-ray diffraction analysis was obtained via diffusion of hexanes into a solution of **3-69** in EtOAc at –18 °C. The crystal structure demonstrates that the absolute configuration is *S* (Figure S3).

Figure S3. Molecular diagram of **3-69** with ellipsoids at 50% probability, all non-oxygen bound H-atoms omitted for clarity. (CCDC 1424634)

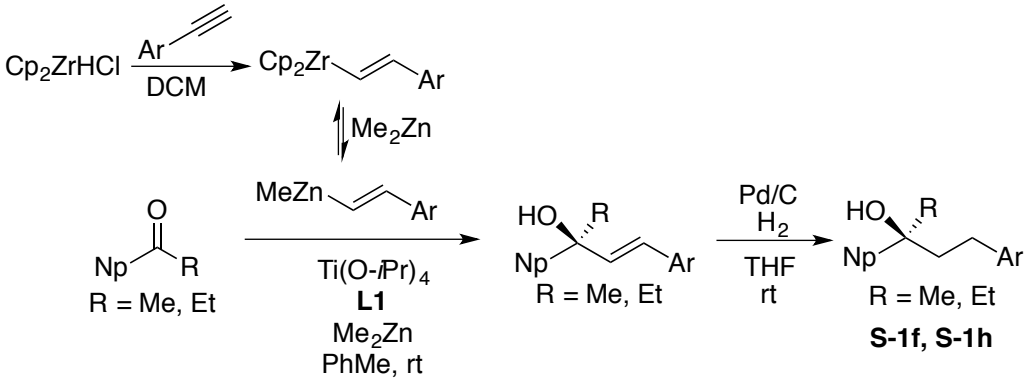


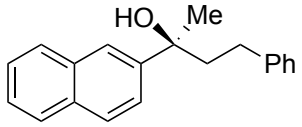
Preparation of 3-70.



(*S*)-6-((*tert*-Butyldimethylsilyl)oxy)-2-(4-nitrophenyl)hexan-2-ol 3-70). Prepared via the procedure described above for preparation of **3-66**, except that bis(4-((*tert*-butyldimethylsilyl)oxy)butyl)zinc was used instead of Et_2Zn, as a colorless oil (30%). The enantiomeric excess was determined to be 99% by chiral HPLC analysis (CHIRLPAK IA, 0.6 mL/min, 3.0% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 14.468 min, t_R(minor) = 13.695 min. $[\alpha]_D^{24}$ = +10.2° (c 2.63, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 – 7.89 (m, 1H), 7.86 – 7.79 (m, 3H), 7.52 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.50 – 7.42 (m, 2H), 3.54 (t, *J* = 6.5 Hz, 2H), 2.01 – 1.84 (m, 3H), 1.65 (s, 3H), 1.53 – 1.45 (m, 2H), 1.40 – 1.28 (m, 1H), 1.27 – 1.17 (m, 1H), 0.83 (s, 9H), –0.01 (d, *J* = 2.3 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.5, 133.3, 132.4, 128.3, 128.0, 127.6, 126.1, 125.8, 123.8, 123.3, 75.1, 63.1, 43.8, 33.1, 30.4, 26.1, 20.6, 18.4, –5.16, –5.17; FTIR (NaCl/thin film) 3432 (brs), 3056, 2952, 2929, 2857, 1471, 1254, 1101, 836, 775, 476 cm^{-1}; HRMS (LIFDI) [M]+ calculated for $C_{24}H_{26}O_3$: 358.2328, found: 358.2343.

Preparation of 3-71 and 3-72.



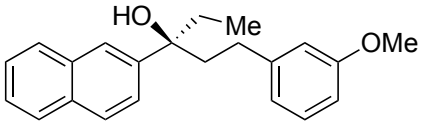


(*S*)-2-(naphthalen-2-yl)-4-phenylbutan-2-ol 3-71). The procedure for formation of the allylic alcohol was adapted from a reported procedure.[viii] For preparation the vinylzinc reagent, in an oven-dried, round-bottomed flask was placed Cp_2ZrHCl (346 mg, 1.20 mmol, 1.20 equiv) and CH_2Cl_2 (4.0 mL). At room temperature, phenylacetylene (0.13 mL, 1.2 mmol, 1.2 equiv) was added into the flask and stirred for 10 min. The solvent was removed, and the orange solid was dissolved in PhMe (4.0 mL). The solution was cooled to –78 °C, before Me_2Zn (1.0 mL, 1.2 mmol, 1.2 equiv, 1.2 M in PhMe) was added. The mixture was stirred at –78 °C for 10 min. The resulting solution was assumed to be the vinylzinc in PhMe solution. In a separate flask was placed **L1** (54.5 mg, 0.100 mmol, 0.100 equiv), Me_2Zn (0.33 mL, 0.40 mmol, 0.40 equiv, 1.2 M in PhMe), and PhMe (2.0 mL). To this mixture was added $Ti(O\text{-}iPr)_4$ (0.36 mL, 1.2 mmol, 1.2 equiv) at room temperature. The mixture was stirred at room temperature for 15 min, then the solution was added into the pre-formed vinylzinc solution at –78 °C via cannula. The combined solution was warmed to 0 °C, and treated with a solution of 2-acetylnaphthalone (170 mg, 1.0 mmol, 1.0 equiv) and PhMe (1.0 mL). The resulting reddish solution was stirred at room temperature for 16 h and then quenched with sat. $NaHCO_3$ aq. (20 mL). The solid was removed via filtration through a pad of Celite®. The product was extracted with EtOAc. The combined organic layers were washed with sat. NaCl, dried (Na_2SO_4), filtered, and concentrated. The residue was purified via silica gel chromatography (0–10% EtOAc/hexanes) to give (*E*)-2-(naphthalen-2-yl)-4-phenylbut-3-en-2-ol as a colorless oil (202 mg, 77%), which was used directly in next step.

Please note: We assume the same absolute configuration using these homemade vinylzinc reagents as when Et_2Zn is used. However, the absolute configuration obtained for this procedure has not been reported in the literature.[viii]

(*E*)-2-(Naphthalen-2-yl)-4-phenylbut-3-en-2-ol (202 mg, 0.736 mmol) was dissolved in THF (7 mL) at room temperature. Pd/C (39 mg, 0.037 mmol, 10% w) was added. The headspace of the flask was evacuated and refilled with H_2 three times.

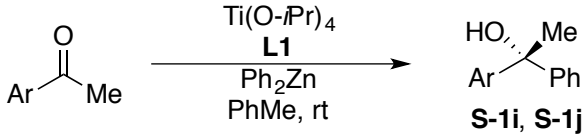
The mixture was then stirred at room temperature for 12 h under H_2 (1 atm). The solid was removed via filtration through a tight-packed pad of Celite®. The filtrate was concentrated and purified via silica gel chromatography (0–10% EtOAc/hexanes) to give **3-71** (189 mg, 93%) as a white solid (mp 76–79°). $[\alpha]_D^{24}$ = +43.6° (c 2.2, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 – 7.98 (m, 1H), 7.92 – 7.86 (m, 3H), 7.60 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.52 (pd, *J* = 6.8, 1.5 Hz, 2H), 7.29 – 7.21 (m, 2H), 7.21 – 7.16 (m, 1H), 7.16 – 7.13 (m, 2H), 2.69 (ddd, *J* = 13.7, 11.8, 5.6 Hz, 1H), 2.48 (ddd, *J* = 13.6, 11.8, 4.9 Hz, 1H), 2.33 – 2.20 (m, 2H), 1.93 (s, 1H), 1.73 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.0, 142.3, 133.4, 132.4, 128.51, 128.46, 128.3, 128.2, 127.6, 126.3, 125.90, 125.89, 123.7, 123.4, 75.1, 45.9, 30.8, 30.7; FTIR (NaCl/thin film) 3446 (brs), 3057, 3024, 2972, 2932, 1601, 1496, 1455, 819, 747, 700, 487 cm^{-1}; HRMS (EI+) [M]+ calculated for $C_{20}H_{20}O$: 276.1514, found: 276.1514.

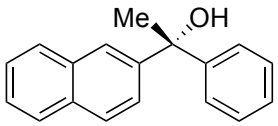


(*S*)-1-(3-methoxyphenyl)-3-(naphthalen-2-yl)pentan-3-ol 3-72). Following a similar procedure as for the preparation of **3-71** above, **3-72** was prepared as a colorless oil (40% overall yield from 1-(naphthalene-2-yl)propan-1-one). The enantiomeric excess was determined to be 89% ee by chiral HPLC analysis (CHIRLPAK IC, 1.0 mL/min, 5.0% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 9.989 min, t_R(minor) = 10.700 min. $[\alpha]_D^{24}$ = +41.3° (c 0.92, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 – 7.93 (m, 1H), 7.90 – 7.84 (m, 3H), 7.50 (dtd, *J* = 9.4, 7.0, 5.3 Hz, 3H), 7.17 (t, *J* = 7.9 Hz, 1H), 6.71 (dd, *J* = 8.0, 2.1 Hz, 2H), 6.66 (t, *J* = 2.0 Hz, 1H), 3.76 (s, 3H), 2.66 (ddd, *J* = 13.6, 11.7, 5.5 Hz, 1H), 2.35 (ddd, *J* = 13.6, 11.8, 4.7 Hz, 1H), 2.32 – 2.17 (m, 2H), 2.03 (dq, *J* = 14.9, 7.4 Hz, 1H), 1.95 (dq, *J* = 14.5, 7.4 Hz, 1H), 1.88 (s, 1H), 0.81 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.8, 144.2, 143.0, 133.3, 132.3, 129.5, 128.3, 128.1, 127.6, 126.2, 125.8, 124.4, 123.9, 120.8, 114.2, 111.2, 77.6, 55.2, 44.5, 35.9, 30.3, 7.9; FTIR (NaCl/thin film) 3486 (brs), 3054, 2964, 2936, 1680, 1489, 1455, 1258, 1152, 1048, 819, 748, 698, 477 cm^{-1}; HRMS (EI+) [M]+ calculated for $C_{22}H_{24}O_2$: 320.1776, found: 320.1753.

Please note: We assume the same absolute configuration using these homemade vinylzinc reagents as when Et_2Zn is used. However, the absolute configuration obtained for this procedure has not been reported in the literature.[viii]

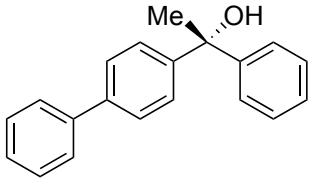
Preparation of 3-73, 3-74.





(*R*)-1-(naphthalen-2-yl)-1-phenylethan-1-ol (3-73). The procedure was adapted from that reported in the literature.[ix] In an oven-dried, 50-mL, round-bottomed flask was placed **L1** (54.5 mg, 0.100 mmol, 0.100 equiv), Ph_2Zn (351 mL, 1.60 mmol, 1.60 equiv), and PhMe (10 mL) at room temperature. Ti(O-*i*Pr)$_4$ (0.18 mL, 0.60 mmol, 0.60 equiv) was added. The mixture was stirred at room temperature for 15 min. A solution of 2-acetonaphthalone (170 mg, 1.0 mmol, 1.0 equiv) and PhMe (5 mL) was added into the flask. The mixture was stirred at room temperature for 17 h. The reaction was then quenched with sat. NH_4Cl aq. (20 mL). The solids were removed via filtration through a pad of Celite®. The mixture was extracted with EtOAc (25 mL x 2). The combined organic layers were washed with sat. NaCl, dried ($NaSO_4$), filtered, and concentrated. The residue was purified via silica gel chromatography (5−15% Et_2O/hexanes) to give **3-73** (203.7 mg, 82%) as a colorless oil. The enantiomeric excess was determined to be 95% by chiral HPLC analysis (CHIRLPAK IB, 1.0 mL/min, 4.0% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 13.183 min, t_R(minor) = 14.119 min. $[\alpha]_D^{24}$ = +10.7° (c 0.82, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 – 7.95 (m, 1H), 7.87 – 7.83 (m, 1H), 7.81 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.77 (d, *J* = 8.6 Hz, 1H), 7.52 – 7.44 (m, 4H), 7.42 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.33 (dd, *J* = 8.5, 7.0 Hz, 2H), 7.27 (d, *J* = 6.6 Hz, 1H), 2.29 (s, 1H), 2.06 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.9, 145.4, 133.1, 132.5, 128.40, 128.38, 128.1, 127.6, 127.2,

126.3, 126.10, 126.09, 125.1, 123.9, 76.5, 30.9; FTIR (NaCl/thin film) 3560 (brs), 3056, 2978, 2931, 1599, 1505, 1493, 14461, 1372, 1126, 1065, 909, 858 cm^{-1}; HRMS (EI+) [M]+ calculated for $C_{18}H_{16}BO$: 248.1201, found: 248.1193.

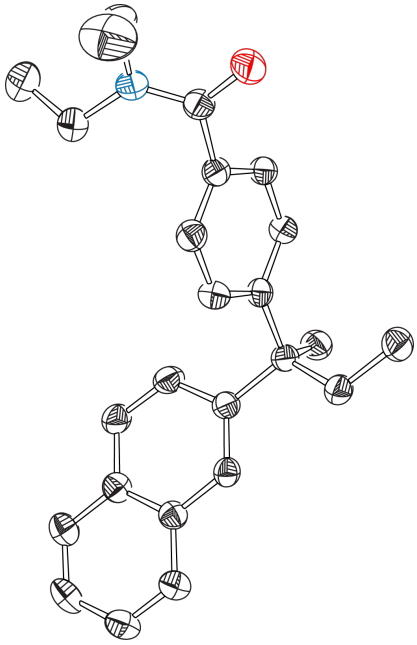


(*R*)-1-([1,1'-biphenyl]-4-yl)-1-phenylethan-1-ol (3-74). Following a similar procedure as described for **3-73** above, compound **3-73** was prepared as a white solid (mp 108–111 °C, 72%). The enantiomeric excess was determined to be 91% by chiral HPLC analysis (CHIRLPAK IB, 1.0 mL/min, 2.0% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 34.792 min, t_R(minor) = 18.929 min. $[\alpha]_D^{24}$ = +9.0° (c 1.0, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 – 7.57 (m, 2H), 7.57 – 7.54 (m, 2H), 7.51 – 7.46 (m, 4H), 7.43 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.38 – 7.32 (m, 3H), 7.29 – 7.26 (m, 1H), 2.22 (s, 1H), 2.00 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.0, 147.2, 140.9, 140.0, 128.9, 128.4, 127.4, 127.21, 127.17, 127.1, 126.4, 126.0, 76.3, 31.0; FTIR (NaCl/thin film) 3458 (brs), 3056, 3028, 2978, 1599, 1486, 1449, 1401, 1266, 1171, 1068, 907, 845 cm^{-1}; HRMS (CI+) [M]+H calculated for $C_{20}H_{19}O$: 275.1436, found: 275.1444.

Evidence for Stereoretention

As discussed above, the absolute configurations of **3-37a**, **3-47**, and **3-69** were determined by X-ray crystallography. The arylation of (S)-**3-37a** produced ®-**3-47**, demonstrating that this arylation proceeds with overall retention of absolute stereochemistry.

Crystal Structure Data for 3-47



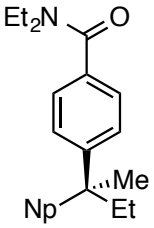


Table S1. Sample and crystal data for (*R*)-**10**.

Identification code	mary029	
Chemical formula	$C_{25}H_{29}NO$	
Formula weight	359.49	
Temperature	200(2) K	
Wavelength	1.54178 Å	
Crystal size	0.248 x 0.378 x 0.487 mm	
Crystal system	orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 8.1727(3) Å	α = 90°
	b = 12.9877(5) Å	β = 90°
	c = 19.1341(7) Å	γ = 90°
Volume	2030.98(13) $Å^3$	
Z	4	
Density (calculated)	1.176 g/cm^3	
Absorption coefficient	0.540 mm^{-1}	
F(000)	776	

Table S2. Data collection and structure refinement for (*R*)-**10**.

Theta range for data collection	4.11 to 59.90°	
Index ranges	-8<=h<=9, -14<=k<=13, -21<=l<=19	
Reflections collected	6276	
Independent reflections	2630 [R(int) = 0.0365]	
Coverage of independent reflections	95.1%	
Absorption correction	multi-scan	
Max. and min. transmission	0.8780 and 0.7080	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	2630 / 0 / 249	
Goodness-of-fit on F^2	0.860	
Final R indices	2423 data; I>2σ(I)	R1 = 0.0373, wR2 = 0.1046
	all data	R1 = 0.0407, wR2 = 0.1084
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.1000P)^2]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.0(3)	
Extinction coefficient	0.0058(9)	
Largest diff. peak and hole	0.135 and -0.151 eÅ^{-3}	
R.M.S. deviation from mean	0.037 eÅ^{-3}	

Table S3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for (*R*)-**10**.
U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	**y/b**	**z/c**	**U(eq)**
O1	0.4981(3)	0.50887(17)	0.01225(10)	0.0528(6)
N1	0.5202(3)	0.39117(18)	0.09868(13)	0.0412(6)
C1	0.6431(3)	0.61242(19)	0.24991(13)	0.0288(6)
C2	0.5755(3)	0.5641(2)	0.30982(14)	0.0311(7)
C3	0.4047(4)	0.5453(2)	0.31633(15)	0.0364(7)
C4	0.3434(4)	0.4997(2)	0.37492(16)	0.0445(8)
C5	0.4486(4)	0.4689(2)	0.42913(16)	0.0455(8)
C6	0.6129(4)	0.4850(2)	0.42429(15)	0.0403(7)
C7	0.6800(3)	0.5343(2)	0.36502(14)	0.0334(7)
C8	0.8496(3)	0.5562(2)	0.35893(14)	0.0377(7)
C9	0.9094(3)	0.6044(2)	0.30127(14)	0.0376(8)
C10	0.8070(3)	0.6340(2)	0.24435(13)	0.0305(6)
C11	0.8828(3)	0.6918(2)	0.18274(13)	0.0298(6)
C12	0.9236(4)	0.8013(2)	0.20884(16)	0.0396(7)
C13	0.7628(3)	0.6988(2)	0.12036(13)	0.0354(7)

C14	0.8307(4)	0.7444(2)	0.05339(14)	0.0435(8)
C15	0.0316(3)	0.5282(2)	0.14805(14)	0.0342(7)
C16	0.1636(3)	0.4742(2)	0.12206(14)	0.0355(7)
C17	0.3068(3)	0.5257(2)	0.10319(12)	0.0295(6)
C18	0.3106(3)	0.6315(2)	0.11035(13)	0.0305(6)
C19	0.1794(3)	0.6850(2)	0.13789(13)	0.0303(6)
C20	0.0364(3)	0.6345(2)	0.15721(13)	0.0290(6)
C21	0.4492(4)	0.4735(2)	0.06862(14)	0.0354(7)
C22	0.6428(4)	0.3346(3)	0.05765(18)	0.0536(9)
C23	0.5677(6)	0.2525(3)	0.0140(3)	0.0894(15)
C24	0.4761(4)	0.3501(2)	0.16769(16)	0.0459(8)
C25	0.6199(4)	0.3331(3)	0.21548(18)	0.0530(9)

Table S4. Bond lengths (Å) for (*R*)-**10**.

O1-C21	1.239(3)	N1-C21	1.345(4)
N1-C24	1.469(4)	N1-C22	1.470(4)
C1-C10	1.373(4)	C1-C2	1.419(4)
C1-H1	0.95	C2-C7	1.413(4)
C2-C3	1.422(4)	C3-C4	1.363(4)
C3-H3	0.95	C4-C5	1.406(4)
C4-H4	0.95	C5-C6	1.361(5)
C5-H5	0.95	C6-C7	1.414(4)
C6-H6	0.95	C7-C8	1.419(4)
C8-C9	1.359(4)	C8-H8	0.95
C9-C10	1.426(4)	C9-H9	0.95
C10-C11	1.529(4)	C11-C20	1.539(4)
C11-C12	1.543(4)	C11-C13	1.548(4)
C12-H12A	0.98	C12-H12B	0.98
C12-H12C	0.98	C13-C14	1.517(4)
C13-H13A	0.99	C13-H13B	0.99
C14-H14A	0.98	C14-H14B	0.98
C14-H14C	0.98	C15-C16	1.379(4)
C15-C20	1.393(4)	C15-H15	0.95
C16-C17	1.396(4)	C16-H16	0.95
C17-C18	1.381(4)	C17-C21	1.501(4)
C18-C19	1.382(4)	C18-H18	0.95
C19-C20	1.390(4)	C19-H19	0.95
C22-C23	1.487(5)	C22-H22A	0.99
C22-H22B	0.99	C23-H23A	0.98
C23-H23B	0.98	C23-H23C	0.98
C24-C25	1.506(5)	C24-H24A	0.99
C24-H24B	0.99	C25-H25A	0.98
C25-H25B	0.98	C25-H25C	0.98

Table S5. Bond angles (°) for (*R*)-**10**.

C21-N1-C24	124.5(2)	C21-N1-C22	117.6(2)
C24-N1-C22	117.8(2)	C10-C1-C2	122.2(2)
C10-C1-H1	118.9	C2-C1-H1	118.9
C7-C2-C1	119.3(2)	C7-C2-C3	118.8(3)
C1-C2-C3	121.9(3)	C4-C3-C2	120.5(3)
C4-C3-H3	119.8	C2-C3-H3	119.8
C3-C4-C5	120.4(3)	C3-C4-H4	119.8
C5-C4-H4	119.8	C6-C5-C4	120.6(3)
C6-C5-H5	119.7	C4-C5-H5	119.7
C5-C6-C7	120.5(3)	C5-C6-H6	119.8
C7-C6-H6	119.8	C2-C7-C6	119.3(3)
C2-C7-C8	118.3(2)	C6-C7-C8	122.4(3)
C9-C8-C7	120.7(3)	C9-C8-H8	119.7
C7-C8-H8	119.7	C8-C9-C10	122.2(3)
C8-C9-H9	118.9	C10-C9-H9	118.9
C1-C10-C9	117.3(2)	C1-C10-C11	123.7(2)
C9-C10-C11	118.9(2)	C10-C11-C20	109.7(2)
C10-C11-C12	106.9(2)	C20-C11-C12	111.8(2)
C10-C11-C13	111.5(2)	C20-C11-C13	107.5(2)
C12-C11-C13	109.4(2)	C11-C12-H12A	109.5
C11-C12-H12B	109.5	H12A-C12-H12B	109.5
C11-C12-H12C	109.5	H12A-C12-H12C	109.5
H12B-C12-H12C	109.5	C14-C13-C11	116.3(2)
C14-C13-H13A	108.2	C11-C13-H13A	108.2
C14-C13-H13B	108.2	C11-C13-H13B	108.2
H13A-C13-H13B	107.4	C13-C14-H14A	109.5
C13-C14-H14B	109.5	H14A-C14-H14B	109.5
C13-C14-H14C	109.5	H14A-C14-H14C	109.5
H14B-C14-H14C	109.5	C16-C15-C20	121.8(3)
C16-C15-H15	119.1	C20-C15-H15	119.1
C15-C16-C17	120.4(3)	C15-C16-H16	119.8
C17-C16-H16	119.8	C18-C17-C16	118.1(2)
C18-C17-C21	118.4(2)	C16-C17-C21	123.2(2)
C17-C18-C19	121.4(3)	C17-C18-H18	119.3
C19-C18-H18	119.3	C18-C19-C20	121.1(2)
C18-C19-H19	119.5	C20-C19-H19	119.5
C19-C20-C15	117.3(2)	C19-C20-C11	122.8(2)
C15-C20-C11	119.8(2)	O1-C21-N1	121.9(3)
O1-C21-C17	117.8(3)	N1-C21-C17	120.4(2)
N1-C22-C23	112.1(3)	N1-C22-H22A	109.2
C23-C22-H22A	109.2	N1-C22-H22B	109.2
C23-C22-H22B	109.2	H22A-C22-H22B	107.9
C22-C23-H23A	109.5	C22-C23-H23B	109.5
H23A-C23-H23B	109.5	C22-C23-H23C	109.5

H23A-C23-H23C	109.5	H23B-C23-H23C	109.5
N1-C24-C25	114.1(3)	N1-C24-H24A	108.7
C25-C24-H24A	108.7	N1-C24-H24B	108.7
C25-C24-H24B	108.7	H24A-C24-H24B	107.6
C24-C25-H25A	109.5	C24-C25-H25B	109.5
H25A-C25-H25B	109.5	C24-C25-H25C	109.5
H25A-C25-H25C	109.5	H25B-C25-H25C	109.5

Table S6. Torsion angles (°) for (*R*)-**10**.

C10-C1-C2-C7	-1.8(4)	C10-C1-C2-C3	177.7(3)
C7-C2-C3-C4	0.3(4)	C1-C2-C3-C4	-179.2(3)
C2-C3-C4-C5	-1.3(4)	C3-C4-C5-C6	0.7(5)
C4-C5-C6-C7	0.9(5)	C1-C2-C7-C6	-179.2(2)
C3-C2-C7-C6	1.3(4)	C1-C2-C7-C8	1.4(4)
C3-C2-C7-C8	-178.2(3)	C5-C6-C7-C2	-1.9(4)
C5-C6-C7-C8	177.5(3)	C2-C7-C8-C9	-0.2(4)
C6-C7-C8-C9	-179.6(3)	C7-C8-C9-C10	-0.7(5)
C2-C1-C10-C9	1.0(4)	C2-C1-C10-C11	-176.1(2)
C8-C9-C10-C1	0.3(4)	C8-C9-C10-C11	177.5(3)
C1-C10-C11-C20	-133.0(3)	C9-C10-C11-C20	50.0(3)
C1-C10-C11-C12	105.5(3)	C9-C10-C11-C12	-71.5(3)
C1-C10-C11-C13	-14.1(4)	C9-C10-C11-C13	168.9(2)
C10-C11-C13-C14	-173.7(2)	C20-C11-C13-C14	-53.4(3)
C12-C11-C13-C14	68.3(3)	C20-C15-C16-C17	-0.8(4)
C15-C16-C17-C18	-1.0(4)	C15-C16-C17-C21	-174.3(2)
C16-C17-C18-C19	2.5(4)	C21-C17-C18-C19	176.1(2)
C17-C18-C19-C20	-2.2(4)	C18-C19-C20-C15	0.4(4)
C18-C19-C20-C11	-175.2(2)	C16-C15-C20-C19	1.1(4)
C16-C15-C20-C11	176.8(2)	C10-C11-C20-C19	-138.7(3)
C12-C11-C20-C19	-20.3(4)	C13-C11-C20-C19	99.9(3)
C10-C11-C20-C15	45.9(3)	C12-C11-C20-C15	164.3(2)
C13-C11-C20-C15	-75.6(3)	C24-N1-C21-O1	175.3(3)
C22-N1-C21-O1	-8.8(4)	C24-N1-C21-C17	-4.5(4)
C22-N1-C21-C17	171.3(3)	C18-C17-C21-O1	-48.9(4)
C16-C17-C21-O1	124.4(3)	C18-C17-C21-N1	131.0(3)
C16-C17-C21-N1	-55.7(4)	C21-N1-C22-C23	-88.4(4)
C24-N1-C22-C23	87.7(4)	C21-N1-C24-C25	-129.8(3)
C22-N1-C24-C25	54.3(4)		

Table S7. Anisotropic atomic displacement parameters (Å^2) for (*R*)-**10**.
The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	0.0573(14)	0.0621(14)	0.0391(12)	0.0079(11)	0.0201(12)	0.0140(12)
N1	0.0358(14)	0.0424(14)	0.0453(14)	0.0030(12)	0.0100(12)	0.0097(12)
C1	0.0289(14)	0.0312(14)	0.0262(14)	0.0003(12)	-0.0029(12)	0.0033(11)
C2	0.0331(15)	0.0278(15)	0.0323(16)	-0.0029(12)	0.0014(13)	-0.0010(12)
C3	0.0313(15)	0.0395(17)	0.0384(17)	0.0019(14)	0.0009(14)	-0.0025(13)
C4	0.0386(17)	0.0449(18)	0.0499(19)	0.0010(16)	0.0045(15)	-0.0121(14)
C5	0.0537(19)	0.0443(18)	0.0385(18)	0.0054(14)	0.0095(15)	-0.0116(15)
C6	0.0464(18)	0.0413(17)	0.0332(16)	0.0040(13)	0.0004(15)	-0.0025(14)
C7	0.0356(15)	0.0325(15)	0.0319(15)	-0.0034(13)	-0.0005(13)	0.0001(12)
C8	0.0315(15)	0.0515(18)	0.0301(15)	0.0065(14)	-0.0023(14)	0.0056(13)
C9	0.0252(15)	0.0516(19)	0.0360(17)	0.0004(14)	-0.0015(13)	0.0014(13)
C10	0.0276(13)	0.0337(15)	0.0302(14)	0.0024(12)	0.0000(13)	0.0047(12)
C11	0.0230(13)	0.0367(15)	0.0295(14)	0.0017(12)	0.0004(12)	0.0030(11)
C12	0.0370(16)	0.0366(16)	0.0453(17)	-0.0011(14)	0.0076(14)	0.0029(13)
C13	0.0297(15)	0.0412(16)	0.0353(16)	0.0038(13)	0.0005(12)	0.0052(13)
C14	0.0436(19)	0.0510(17)	0.0359(15)	0.0077(15)	0.0006(15)	0.0077(15)
C15	0.0274(14)	0.0372(17)	0.0379(15)	0.0044(13)	0.0035(13)	-0.0020(12)
C16	0.0367(16)	0.0305(15)	0.0392(16)	-0.0013(13)	0.0041(13)	0.0014(13)
C17	0.0300(14)	0.0378(16)	0.0207(13)	0.0026(12)	0.0005(12)	0.0046(13)
C18	0.0255(13)	0.0392(16)	0.0269(13)	0.0054(12)	-0.0017(12)	-0.0016(12)
C19	0.0290(15)	0.0312(14)	0.0309(14)	0.0011(12)	0.0013(13)	0.0009(12)
C20	0.0278(14)	0.0329(16)	0.0262(14)	0.0039(12)	-0.0015(12)	0.0009(11)
C21	0.0330(15)	0.0413(17)	0.0319(16)	-0.0020(13)	0.0045(13)	0.0039(13)
C22	0.0482(19)	0.0486(19)	0.064(2)	-0.0055(18)	0.0122(18)	0.0142(16)
C23	0.092(3)	0.063(2)	0.113(4)	-0.035(3)	0.027(3)	-0.003(2)
C24	0.0411(17)	0.0452(18)	0.0513(18)	0.0145(15)	0.0062(16)	0.0087(14)
C25	0.051(2)	0.0470(19)	0.061(2)	0.0045(16)	-0.0059(18)	0.0073(16)

Table S8. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for (*R*)-**10**.

	x/a	**y/b**	**z/c**	**U(eq)**
H1	-0.4274	0.6304	0.2124	0.035
H3	-0.6672	0.5646	0.2796	0.044
H4	-0.7711	0.4887	0.3792	0.053
H5	-0.5952	0.4366	0.4695	0.055
H6	-0.3172	0.4629	0.4610	0.048
H8	-0.0780	0.5370	0.3955	0.045
H9	0.0232	0.6188	0.2988	0.045
H12A	-0.1767	0.8350	0.2251	0.059
H12B	-0.0286	0.8413	0.1705	0.059
H12C	0.0021	0.7970	0.2475	0.059
H13A	-0.2777	0.6285	0.1100	0.042
H13B	-0.3326	0.7405	0.1350	0.042

H14A	-0.1280	0.8139	0.0626	0.065
H14B	-0.2562	0.7477	0.0182	0.065
H14C	-0.0799	0.7010	0.0361	0.065
H15	-0.0653	0.4918	0.1600	0.041
H16	0.1570	0.4016	0.1170	0.043
H18	0.4054	0.6682	0.0960	0.037
H19	0.1871	0.7575	0.1437	0.036
H22A	0.7236	0.3032	0.0898	0.064
H22B	0.7019	0.3834	0.0270	0.064
H23A	0.5062	0.2051	0.0440	0.134
H23B	0.6538	0.2145	-0.0105	0.134
H23C	0.4934	0.2837	-0.0201	0.134
H24A	0.4182	0.2838	0.1613	0.055
H24B	0.3992	0.3985	0.1905	0.055
H25A	0.6849	0.2750	0.1984	0.079
H25B	0.5805	0.3181	0.2628	0.079
H25C	0.6879	0.3953	0.2164	0.079

Crystal Structure Data for 1a

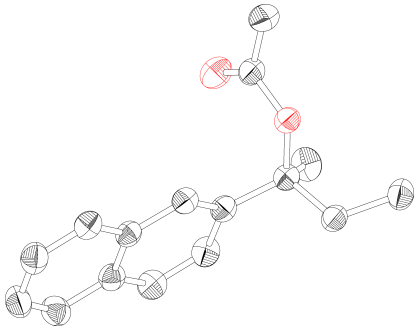


Table S9. Sample and crystal data for (*S*)-1a.

Identification code	mary035	
Chemical formula	$C_{16}H_{18}O_2$	
Formula weight	242.30 g/mol	
Temperature	200(2) K	
Wavelength	1.54178 Å	
Crystal size	0.144 x 0.196 x 0.269 mm	
Crystal system	monoclinic	
Space group	C 1 2 1	
Unit cell dimensions	a = 21.7695(7) Å	α = 90°
	b = 5.8807(2) Å	β = 97.282(2)°
	c = 10.4637(3) Å	γ = 90°
Volume	1328.76(7) $Å^3$	
Z	4	
Density (calculated)	1.211 g/cm^3	
Absorption coefficient	0.620 mm^{-1}	
F(000)	520	

Table S10. Data collection and structure refinement for (*S*)-1a.

Theta range for data collection	4.09 to 75.07°
Index ranges	-27<=h<=26, -7<=k<=7, -13<=l<=12

Reflections collected	13728
Independent reflections	2708 [R(int) = 0.0319]
Coverage of independent reflections	99.4%
Absorption correction	multi-scan
Max. and min. transmission	0.7539 and 0.6441
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick 2008)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	2708 / 1 / 166
Goodness-of-fit on F^2	1.035
Final R indices	2626 data; I>2σ(I) R1 = 0.0349, wR2 = 0.0937 all data R1 = 0.0359, wR2 = 0.0948
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0638P)^2+0.1971P]$ where $P=(F_o^2+2F_c^2)/3$
Absolute structure parameter	-0.1(1)
Largest diff. peak and hole	0.193 and -0.164 eÅ^{-3}
R.M.S. deviation from mean	0.034 eÅ^{-3}

Table S11. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for (*S*)-1a.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
O1	0.40605(5)	0.6779(2)	0.16441(11)	0.0352(3)
O2	0.32500(7)	0.4448(3)	0.10507(15)	0.0560(4)
C1	0.44069(7)	0.5057(3)	0.24545(16)	0.0324(4)
C2	0.45441(10)	0.3005(3)	0.1639(2)	0.0452(4)
C3	0.50055(7)	0.6315(3)	0.29722(16)	0.0353(4)
C4	0.54151(8)	0.6990(4)	0.19539(19)	0.0444(4)
C5	0.35048(8)	0.6252(4)	0.09814(17)	0.0407(4)
C6	0.32655(9)	0.8226(5)	0.0164(2)	0.0528(5)
C7	0.40667(7)	0.4437(3)	0.35920(16)	0.0324(4)
C8	0.42021(8)	0.2325(3)	0.42318(19)	0.0378(4)
C9	0.39467(8)	0.1768(3)	0.53140(18)	0.0398(4)
C10	0.35368(8)	0.3262(3)	0.58396(18)	0.0358(4)
C11	0.32657(9)	0.2747(4)	0.69691(19)	0.0445(4)
C12	0.28692(9)	0.4252(4)	0.74387(19)	0.0481(5)
C13	0.27174(9)	0.6322(4)	0.67982(19)	0.0453(5)
C14	0.29716(8)	0.6866(3)	0.57105(18)	0.0381(4)
C15	0.33914(7)	0.5370(3)	0.52055(17)	0.0325(4)
C16	0.36692(7)	0.5906(3)	0.40857(16)	0.0327(3)

Table S12. Bond lengths (Å) for (*S*)-1a.

O1-C5	1.352(2)	O1-C1	1.466(2)
O2-C5	1.204(3)	C1-C7	1.524(2)
C1-C2	1.529(2)	C1-C3	1.536(2)
C2-H2A	0.98	C2-H2B	0.98
C2-H2C	0.98	C3-C4	1.526(2)
C3-H3A	0.99	C3-H3B	0.99
C4-H4A	0.98	C4-H4B	0.98
C4-H4C	0.98	C5-C6	1.496(3)
C6-H6A	0.98	C6-H6B	0.98
C6-H6C	0.98	C7-C16	1.369(2)
C7-C8	1.424(2)	C8-C9	1.363(3)
C8-H8	0.95	C9-C10	1.413(3)
C9-H9	0.95	C10-C11	1.419(3)
C10-C15	1.423(2)	C11-C12	1.370(3)
C11-H11	0.95	C12-C13	1.409(3)
C12-H12	0.95	C13-C14	1.365(3)
C13-H13	0.95	C14-C15	1.418(2)
C14-H14	0.95	C15-C16	1.420(2)
C16-H16	0.95		

Table S13. Bond angles (°) for (*S*)-1a.

C5-O1-C1	119.98(14)	O1-C1-C7	110.59(12)
O1-C1-C2	110.15(14)	C7-C1-C2	113.31(15)
O1-C1-C3	102.86(13)	C7-C1-C3	108.33(13)
C2-C1-C3	111.09(14)	C1-C2-H2A	109.5
C1-C2-H2B	109.5	H2A-C2-H2B	109.5
C1-C2-H2C	109.5	H2A-C2-H2C	109.5
H2B-C2-H2C	109.5	C4-C3-C1	115.06(14)
C4-C3-H3A	108.5	C1-C3-H3A	108.5
C4-C3-H3B	108.5	C1-C3-H3B	108.5
H3A-C3-H3B	107.5	C3-C4-H4A	109.5
C3-C4-H4B	109.5	H4A-C4-H4B	109.5
C3-C4-H4C	109.5	H4A-C4-H4C	109.5
H4B-C4-H4C	109.5	O2-C5-O1	124.07(19)
O2-C5-C6	126.06(18)	O1-C5-C6	109.87(17)
C5-C6-H6A	109.5	C5-C6-H6B	109.5
H6A-C6-H6B	109.5	C5-C6-H6C	109.5
H6A-C6-H6C	109.5	H6B-C6-H6C	109.5
C16-C7-C8	118.41(16)	C16-C7-C1	122.46(15)
C8-C7-C1	118.95(15)	C9-C8-C7	121.23(17)
C9-C8-H8	119.4	C7-C8-H8	119.4
C8-C9-C10	121.20(17)	C8-C9-H9	119.4
C10-C9-H9	119.4	C9-C10-C11	122.78(17)
C9-C10-C15	118.34(16)	C11-C10-C15	118.88(16)
C12-C11-C10	120.54(19)	C12-C11-H11	119.7

C10-C11-H11	119.7	C11-C12-C13	120.54(18)
C11-C12-H12	119.7	C13-C12-H12	119.7
C14-C13-C12	120.26(19)	C14-C13-H13	119.9
C12-C13-H13	119.9	C13-C14-C15	120.91(18)
C13-C14-H14	119.5	C15-C14-H14	119.5
C14-C15-C16	122.12(16)	C14-C15-C10	118.86(16)
C16-C15-C10	119.02(15)	C7-C16-C15	121.79(16)
C7-C16-H16	119.1	C15-C16-H16	119.1

Table S14. Torsion angles (°) for (*S*)-1a.

C5-O1-C1-C7	-66.62(18)	C5-O1-C1-C2	59.41(19)
C5-O1-C1-C3	177.89(14)	O1-C1-C3-C4	-64.92(17)
C7-C1-C3-C4	177.97(16)	C2-C1-C3-C4	52.9(2)
C1-O1-C5-O2	3.6(3)	C1-O1-C5-C6	-176.21(14)
O1-C1-C7-C16	-26.1(2)	C2-C1-C7-C16	-150.35(16)
C3-C1-C7-C16	85.91(18)	O1-C1-C7-C8	158.93(14)
C2-C1-C7-C8	34.7(2)	C3-C1-C7-C8	-89.05(18)
C16-C7-C8-C9	-0.3(3)	C1-C7-C8-C9	174.88(16)
C7-C8-C9-C10	0.2(3)	C8-C9-C10-C11	-179.53(18)
C8-C9-C10-C15	0.5(3)	C9-C10-C11-C12	-179.82(18)
C15-C10-C11-C12	0.2(3)	C10-C11-C12-C13	0.9(3)
C11-C12-C13-C14	-1.0(3)	C12-C13-C14-C15	0.0(3)
C13-C14-C15-C16	-179.14(16)	C13-C14-C15-C10	1.1(3)
C9-C10-C15-C14	178.85(16)	C11-C10-C15-C14	-1.2(2)
C9-C10-C15-C16	-0.9(2)	C11-C10-C15-C16	179.06(16)
C8-C7-C16-C15	-0.2(2)	C1-C7-C16-C15	-175.20(14)
C14-C15-C16-C7	-178.95(15)	C10-C15-C16-C7	0.8(2)

Table S15. Anisotropic atomic displacement parameters (Å^2) for (*S*)-1a.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

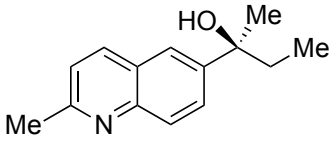
	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	0.0306(6)	0.0377(6)	0.0366(6)	0.0034(5)	0.0016(4)	-0.0007(5)
O2	0.0427(7)	0.0672(10)	0.0555(8)	-0.0023(8)	-0.0033(6)	-0.0155(8)
C1	0.0318(7)	0.0301(8)	0.0353(8)	-0.0008(7)	0.0035(6)	0.0007(6)
C2	0.0510(11)	0.0386(10)	0.0478(10)	-0.0099(8)	0.0134(8)	-0.0023(8)
C3	0.0299(8)	0.0387(9)	0.0368(8)	-0.0010(7)	0.0029(6)	-0.0005(7)
C4	0.0357(9)	0.0512(11)	0.0472(10)	-0.0004(9)	0.0085(7)	-0.0061(8)
C5	0.0320(8)	0.0560(12)	0.0341(8)	-0.0024(8)	0.0037(6)	-0.0019(8)
C6	0.0387(9)	0.0745(15)	0.0443(10)	0.0088(10)	0.0016(8)	0.0103(10)
C7	0.0308(7)	0.0296(8)	0.0363(8)	-0.0022(7)	0.0025(6)	-0.0018(6)
C8	0.0376(8)	0.0283(8)	0.0479(10)	-0.0003(7)	0.0071(7)	0.0030(7)
C9	0.0420(9)	0.0291(8)	0.0478(10)	0.0037(8)	0.0036(7)	0.0002(7)
C10	0.0334(8)	0.0342(8)	0.0391(8)	0.0004(7)	0.0025(6)	-0.0048(7)

C11	0.0469(10)	0.0434(10)	0.0432(10)	0.0055(8)	0.0059(8)	-0.0062(8)
C12	0.0482(10)	0.0577(12)	0.0407(9)	-0.0002(9)	0.0146(8)	-0.0094(9)
C13	0.0395(9)	0.0528(12)	0.0448(10)	-0.0086(8)	0.0100(7)	-0.0004(8)
C14	0.0337(8)	0.0379(9)	0.0425(9)	-0.0033(8)	0.0036(6)	0.0010(7)
C15	0.0287(7)	0.0307(8)	0.0374(8)	-0.0006(6)	0.0013(6)	-0.0029(6)
C16	0.0320(7)	0.0282(8)	0.0374(8)	0.0006(6)	0.0024(6)	-0.0005(6)

Table S16. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for (*S*)-1a.

	x/a	y/b	z/c	U(eq)
H2A	0.4184	0.1992	0.1532	0.068
H2B	0.4904	0.2184	0.2070	0.068
H2C	0.4633	0.3526	0.0791	0.068
H3A	0.4894	0.7708	0.3422	0.042
H3B	0.5249	0.5333	0.3617	0.042
H4A	0.5574	0.5617	0.1577	0.067
H4B	0.5763	0.7908	0.2354	0.067
H4C	0.5172	0.7877	0.1276	0.067
H6A	0.3521	0.8435	-0.0533	0.079
H6B	0.3282	0.9605	0.0693	0.079
H6C	0.2836	0.7932	-0.0204	0.079
H8	0.4476	0.1286	0.3898	0.045
H9	0.4046	0.0348	0.5722	0.048
H11	0.3360	0.1347	0.7403	0.053
H12	0.2695	0.3896	0.8202	0.058
H13	0.2437	0.7343	0.7124	0.054
H14	0.2866	0.8267	0.5286	0.046
H16	0.3577	0.7322	0.3668	0.039

Crystal Structure Data for S-1d



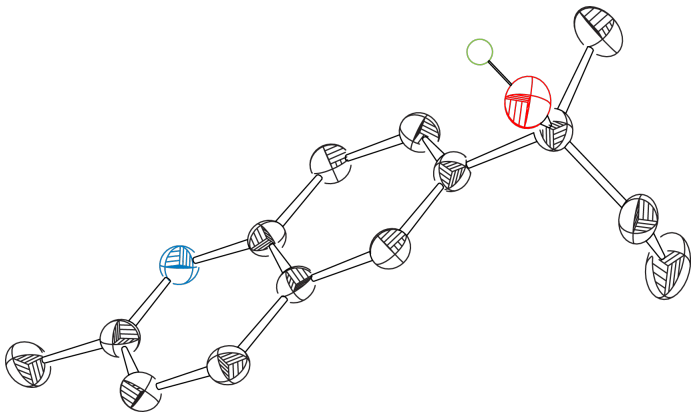


Table S17. Sample and crystal data for **S-1d**.

Identification code	mary026	
Chemical formula	$C_{14}H_{17}NO$	
Formula weight	215.28	
Temperature	200(2) K	
Wavelength	1.54178 Å	
Crystal size	0.216 x 0.425 x 0.545 mm	
Crystal system	orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 5.9000(2) Å	α = 90°
	b = 8.4404(3) Å	β = 90°
	c = 23.7442(10) Å	γ = 90°
Volume	1182.42(8) $Å^3$	
Z	4	
Density (calculated)	1.209 g/cm^3	
Absorption coefficient	0.591 mm^{-1}	
F(000)	464	

Table S18. Data collection and structure refinement for **S-1d**.

Theta range for data collection	3.72 to 74.70°
Index ranges	-7<=h<=7, -10<=k<=10, -29<=l<=29
Reflections collected	19673

Independent reflections	2415 [R(int) = 0.0388]	
Max. and min. transmission	0.8830 and 0.7390	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	2415 / 0 / 150	
Goodness-of-fit on F^2	1.020	
Δ/σ_{max}	0.001	
Final R indices	2389 data; I>2σ(I)	R1 = 0.0333, wR2 = 0.0953
	all data	R1 = 0.0337, wR2 = 0.0976
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0716P)^2+0.1296P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	-0.1(1)	
Extinction coefficient	0.0143(18)	
Largest diff. peak and hole	0.213 and -0.198 eÅ^{-3}	
R.M.S. deviation from mean	0.044 eÅ^{-3}	

Table S19. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for **S-1d**.
U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
N1	0.7994(2)	0.02782(15)	0.06577(6)	0.0283(3)
O1	0.37311(19)	0.72139(14)	0.84869(5)	0.0341(3)
C1	0.7123(4)	0.1740(2)	0.15036(7)	0.0426(4)
C2	0.6518(3)	0.12030(18)	0.09177(6)	0.0297(3)
C3	0.4435(3)	0.16671(18)	0.06700(7)	0.0309(4)
C4	0.3886(3)	0.11487(18)	0.01428(6)	0.0275(3)
C5	0.5437(3)	0.01707(16)	0.98464(6)	0.0244(3)
C6	0.5001(2)	0.95546(17)	0.93022(6)	0.0256(3)
C7	0.6555(3)	0.86111(17)	0.90266(6)	0.0254(3)
C8	0.8641(3)	0.82844(17)	0.92987(6)	0.0275(3)
C9	0.9091(2)	0.88311(18)	0.98318(6)	0.0275(3)
C10	0.7501(3)	0.97764(16)	0.01203(6)	0.0243(3)
C11	0.5951(3)	0.79050(17)	0.84508(6)	0.0273(3)
C12	0.7606(3)	0.6636(2)	0.82559(7)	0.0408(4)
C13	0.5692(3)	0.9218(2)	0.80068(7)	0.0376(4)
C14	0.7760(5)	0.0252(3)	0.79252(8)	0.0610(7)

Table S20. Bond lengths (Å) for **S-1d**.

N1-C2	1.322(2)	N1-C10	1.376(2)

O1-C11	1.4365(19)	O1-H1	0.84
C1-C2	1.506(2)	C1-H1A	0.98
C1-H1B	0.98	C1-H1C	0.98
C2-C3	1.418(2)	C3-C4	1.365(2)
C3-H3	0.95	C4-C5	1.419(2)
C4-H4	0.95	C5-C6	1.416(2)
C5-C10	1.420(2)	C6-C7	1.379(2)
C6-H6	0.95	C7-C8	1.417(2)
C7-C11	1.5335(19)	C8-C9	1.373(2)
C8-H8	0.95	C9-C10	1.409(2)
C9-H9	0.95	C11-C12	1.522(2)
C11-C13	1.537(2)	C12-H12A	0.98
C12-H12B	0.98	C12-H12C	0.98
C13-C14	1.512(3)	C13-H13A	0.99
C13-H13B	0.99	C14-H14A	0.98
C14-H14B	0.98	C14-H14C	0.98

Table S21. Bond angles (°) for **S-1d**.

C2-N1-C10	118.39(14)	C11-O1-H1	109.5
C2-C1-H1A	109.5	C2-C1-H1B	109.5
H1A-C1-H1B	109.5	C2-C1-H1C	109.5
H1A-C1-H1C	109.5	H1B-C1-H1C	109.5
N1-C2-C3	122.71(14)	N1-C2-C1	116.91(15)
C3-C2-C1	120.37(15)	C4-C3-C2	119.84(14)
C4-C3-H3	120.1	C2-C3-H3	120.1
C3-C4-C5	119.22(14)	C3-C4-H4	120.4
C5-C4-H4	120.4	C6-C5-C4	123.29(14)
C6-C5-C10	119.17(13)	C4-C5-C10	117.53(13)
C7-C6-C5	121.61(13)	C7-C6-H6	119.2
C5-C6-H6	119.2	C6-C7-C8	118.24(13)
C6-C7-C11	119.53(13)	C8-C7-C11	122.19(13)
C9-C8-C7	121.53(14)	C9-C8-H8	119.2
C7-C8-H8	119.2	C8-C9-C10	120.62(14)
C8-C9-H9	119.7	C10-C9-H9	119.7
N1-C10-C9	118.97(14)	N1-C10-C5	122.28(14)
C9-C10-C5	118.75(13)	O1-C11-C12	108.50(13)
O1-C11-C7	108.45(11)	C12-C11-C7	113.30(13)
O1-C11-C13	104.08(12)	C12-C11-C13	111.28(14)
C7-C11-C13	110.75(12)	C11-C12-H12A	109.5
C11-C12-H12B	109.5	H12A-C12-H12B	109.5
C11-C12-H12C	109.5	H12A-C12-H12C	109.5
H12B-C12-H12C	109.5	C14-C13-C11	115.07(16)
C14-C13-H13A	108.5	C11-C13-H13A	108.5
C14-C13-H13B	108.5	C11-C13-H13B	108.5

H13A-C13-H13B	107.5	C13-C14-H14A	109.5
C13-C14-H14B	109.5	H14A-C14-H14B	109.5
C13-C14-H14C	109.5	H14A-C14-H14C	109.5
H14B-C14-H14C	109.5		

Table S22. Torsion angles (°) for **S-1d**.

C10-N1-C2-C3	1.4(2)	C10-N1-C2-C1	-179.53(14)
N1-C2-C3-C4	0.3(2)	C1-C2-C3-C4	-178.76(15)
C2-C3-C4-C5	-1.1(2)	C3-C4-C5-C6	178.91(13)
C3-C4-C5-C10	0.2(2)	C4-C5-C6-C7	179.80(14)
C10-C5-C6-C7	-1.5(2)	C5-C6-C7-C8	-0.9(2)
C5-C6-C7-C11	176.90(12)	C6-C7-C8-C9	2.6(2)
C11-C7-C8-C9	-175.20(13)	C7-C8-C9-C10	-1.7(2)
C2-N1-C10-C9	178.04(13)	C2-N1-C10-C5	-2.3(2)
C8-C9-C10-N1	178.83(13)	C8-C9-C10-C5	-0.8(2)
C6-C5-C10-N1	-177.24(13)	C4-C5-C10-N1	1.5(2)
C6-C5-C10-C9	2.4(2)	C4-C5-C10-C9	-178.84(13)
C6-C7-C11-O1	-47.66(18)	C8-C7-C11-O1	130.09(14)
C6-C7-C11-C12	-168.19(14)	C8-C7-C11-C12	9.6(2)
C6-C7-C11-C13	65.96(18)	C8-C7-C11-C13	-116.29(16)
O1-C11-C13-C14	174.47(15)	C12-C11-C13-C14	-68.9(2)
C7-C11-C13-C14	58.1(2)		

Table S23. Anisotropic atomic displacement parameters (Å^2) for **S-1d**.
The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N1	0.0306(7)	0.0276(6)	0.0268(6)	-0.0002(5)	-0.0030(5)	0.0005(5)
O1	0.0311(6)	0.0391(6)	0.0321(6)	-0.0004(4)	-0.0023(4)	-0.0084(5)
C1	0.0553(11)	0.0413(9)	0.0311(8)	-0.0072(7)	-0.0055(8)	0.0079(8)
C2	0.0365(8)	0.0247(6)	0.0279(7)	0.0000(6)	-0.0006(6)	-0.0004(6)
C3	0.0348(8)	0.0276(7)	0.0301(7)	-0.0007(6)	0.0041(6)	0.0036(6)
C4	0.0253(7)	0.0265(6)	0.0308(7)	0.0018(6)	-0.0003(6)	0.0023(6)
C5	0.0242(7)	0.0225(6)	0.0264(7)	0.0033(5)	0.0005(5)	-0.0006(6)
C6	0.0230(7)	0.0270(7)	0.0268(7)	0.0021(5)	-0.0021(6)	-0.0004(6)
C7	0.0262(7)	0.0257(6)	0.0242(6)	0.0019(5)	0.0011(5)	-0.0031(6)
C8	0.0235(7)	0.0290(7)	0.0301(7)	-0.0010(6)	0.0016(6)	0.0023(6)
C9	0.0226(7)	0.0293(7)	0.0305(7)	0.0011(6)	-0.0028(5)	0.0006(6)
C10	0.0245(7)	0.0222(6)	0.0260(7)	0.0021(5)	-0.0016(5)	-0.0022(6)
C11	0.0278(7)	0.0293(7)	0.0249(7)	-0.0013(5)	-0.0009(5)	-0.0025(6)
C12	0.0406(9)	0.0441(9)	0.0377(8)	-0.0141(7)	-0.0021(7)	0.0055(8)
C13	0.0509(10)	0.0376(8)	0.0242(7)	0.0019(6)	-0.0016(7)	-0.0046(8)

C14	0.0884(17)	0.0595(12)	0.0351(9)	0.0044(8)	0.0028(11)	-0.0373(13)

Table S24. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for **S-1d**

	x/a	**y/b**	**z/c**	**U(eq)**
H1	0.3743	0.6477	0.8725	0.051
H1A	0.6046	1.1287	1.1773	0.064
H1B	0.7057	1.2898	1.1523	0.064
H1C	0.8659	1.1382	1.1596	0.064
H3	0.3423	1.2337	1.0870	0.037
H4	0.2483	1.1439	0.9976	0.033
H6	0.3605	0.9797	0.9123	0.031
H8	0.9754	0.7673	0.9108	0.033
H9	1.0488	0.8570	1.0008	0.033
H12A	0.7689	0.5794	0.8539	0.061
H12B	0.9111	0.7106	0.8205	0.061
H12C	0.7085	0.6189	0.7898	0.061
H13A	0.5308	0.8720	0.7642	0.045
H13B	0.4402	0.9903	0.8116	0.045
H14A	0.8085	1.0824	0.8275	0.091
H14B	0.7473	1.1013	0.7622	0.091
H14C	0.9062	0.9587	0.7825	0.091

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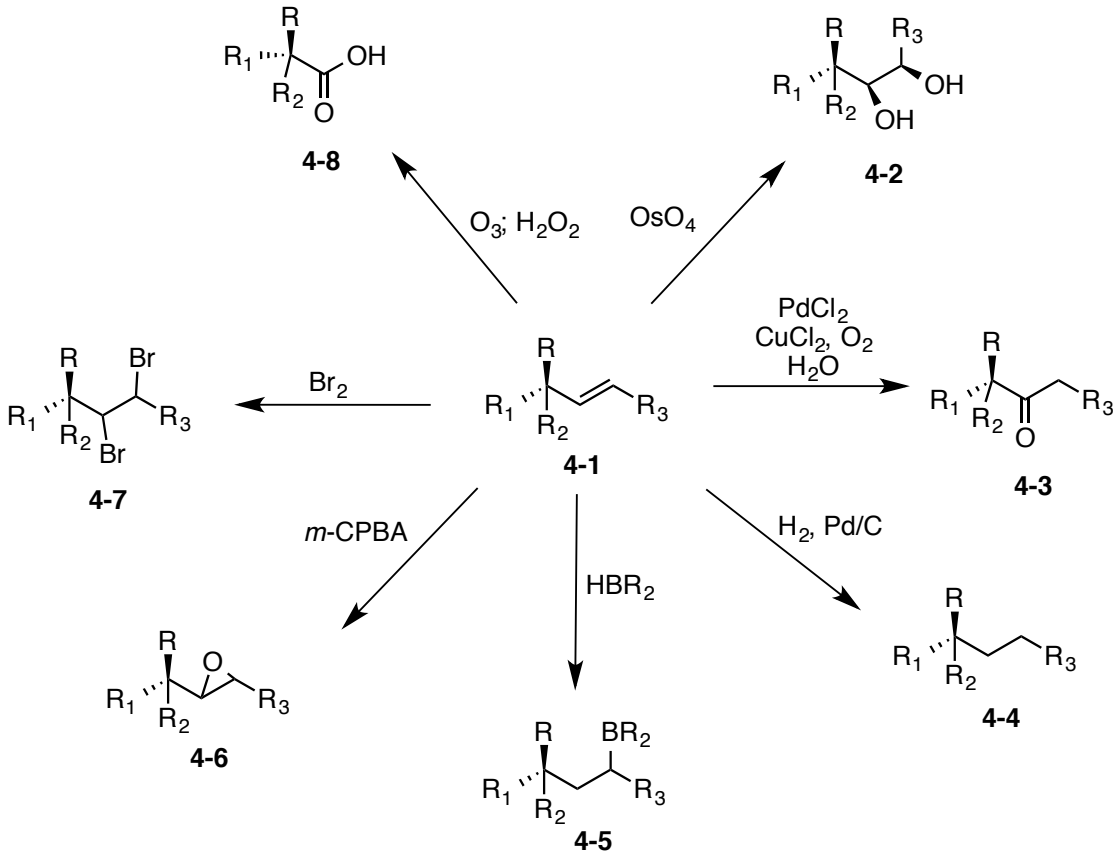
Chapter 4

STEREOSPECIFIC, NICKEL-CATALYZED CROSS-COUPLINGS OF ALLYLIC PIVALATES AND ARYL BOROXINES TO DELIVER QUATERNARY STEREOCENTERS

4.1 Introduction

All-carbon quaternary stereocenters are an important motif in biologically active molecules, pharmaceuticals, and materials applications.[1] One motif that is of particular interest is allylic quaternary stereocenters. These are particularly attractive because the alkene is a powerful functional group handle to further functionalize the molecule (Scheme 4-1). Some of these applications include dihydroxylation,[2] Wacker oxidation,[3] hydrogenations, hydroborations,[4] epoxidations,[5] brominations,[6] and oxidative cleavage of the alkene.[7] Due to these applications, and the variety of structures that can quickly be accessed via an alkene functional group handle, there are a number of synthetic methods that have been developed in order to access these types of molecules.

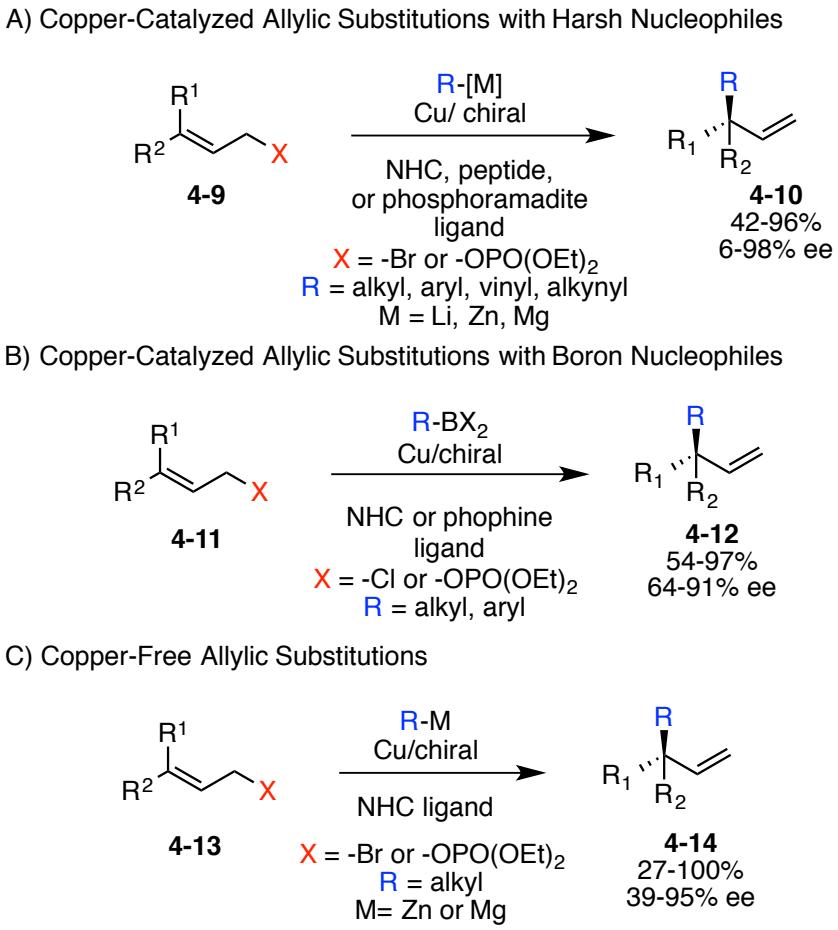
Scheme 4-1 Functionalization of Allylic Quaternary Stereocenters



One powerful method to access these scaffolds is asymmetric substitution of allylic electrophiles. There are a number of examples that enantioselectively form allylic quaternary stereocenters substituted with terminal alkenes. Using a copper catalyst and either bromide or phosphonate esters as leaving groups, these transformations can deliver alkyl,[8] aryl,[9] vinyl,[10] or alkynyl[11] groups with the use of harsh nucleophiles such as lithium, zinc, or Grignard reagents (Scheme 4-2A). The Sawamura and Hayashi groups have also demonstrated enantioselective cross-couplings with alkyl9-BBN[12] and aryl boronic esters[13] with a chiral copper catalyst (Scheme 4-2B). The Hoveyda and Alexakis groups have also

shown that these types of transformations can be done in the absence of a transition metal. They have used chiral N-heterocyclic carbene (NHC) ligands in order to do an asymmetric allylic substitution with either Grignard,[14] lithio, or zinc nucleophiles (Scheme 4-2C).

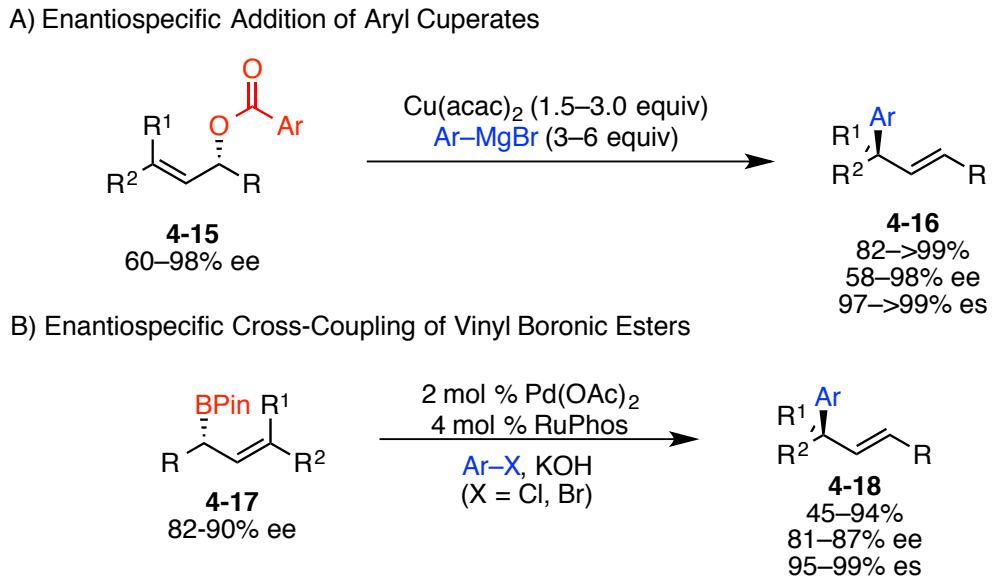
Scheme 4-2 Enantioselective Allylic Substitutions to Form Terminal Alkenes



While there are a number of methods that deliver allylic quaternary stereocenters with substituted terminal alkenes, there are only two previous examples where internal alkenes are formed. The Kobayashi group has shown that they can use enantioenriched allylic carboxylates along with aryl cuprates in order to

enantiospecifically form quaternary stereocenters with excellent stereochemical fidelity (Scheme 4-3A).[15] While this is a powerful approach to this motif, it is limited by the fact that it uses stoichiometric copper and harsh Grignard nucleophiles. The Morken group has used an umpolung approach in order to form these quaternary stereocenters stereospecifically (Scheme 4-3B).[16] Using chemistry previously developed in their group,[17] they can make enantiomerically enriched allylic boronates (**4-17**) that undergo a palladium-catalyzed cross-coupling with aryl halides to form quaternary stereocenters adjacent to an internal alkene (**4-18**). Although this approach displays excellent stereochemical fidelity, the starting materials suffer from lower enantioenrichment (82-90% ee) leading to products with 81-87% ee.

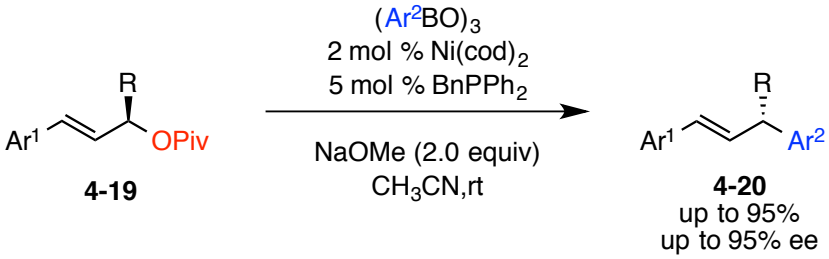
Scheme 4-3 Enantiospecific Allylic Substitution to Deliver Internal Alkenes



Forming allylic quaternary stereocenters with substituted internal alkenes in high enantioenrichment still remains a synthetic challenge. We believed that a powerful method to addressing this challenge would be a combination of these two approaches. The Kobayashi group has shown that allylic alcohols can be synthesized in high enantioenrichment, and can be good electrophiles for enantiospecific cross-

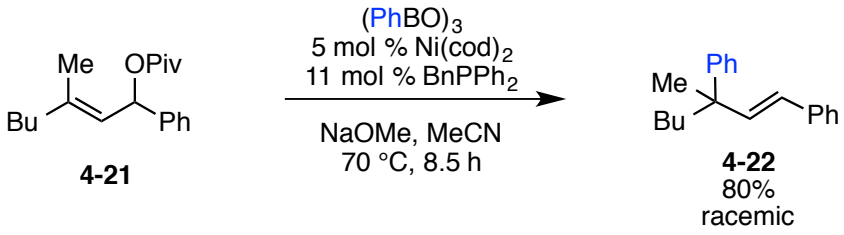
couplings. We also were intrigued by the catalytic cross-coupling and the use of an organoborane displayed by the Morken group. With both of these factors in mind, we also drew inspiration from chemistry previously developed in our group where we utilized secondary allylic pivalates (**4-19**) in order to do a stereospecific nickel-catalyzed Suzuki cross-coupling to form tertiary allylic stereocenters (Scheme 4-4).[18]

Scheme 4-4 Nickel-Catalyzed Suzuki Cross-Coupling to Form Tertiary Allylic Stereocenters



With this precedent in mind, my colleague Qi Zhou initially discovered the reaction on a racemic allylic pivalate under the same conditions that were used in forming tertiary allylic stereocenters (Scheme 4-5). This initial discovery proved that while there was high reactivity with these allylic pivalates, it remained uncertain if the reaction would be enantiospecific or stereooblative. I set out to find conditions that would provide both high yields and stereochemical fidelity in the Suzuki cross-coupling of allylic pivalates to form quaternary stereocenters. As described below, this method transforms readily available, highly enantioenriched allylic alcohol derivatives into products with all-carbon quaternary sterereocenters substituted with internal alkenes. It features low loadings of an inexpensive, air-stable nickel pre-catalyst and the use of commercially available, functional group tolerant aryl boronic esters. This is the first example of quaternary stereocenter formation to form internal substituted alkenes via allylic substitution with an aryl boronic nucleophile.

Scheme 4-5 Proof of Concept For Nickel-Catalyzed Suzuki Cross-Coupling to Form Quaternary Stereocenters

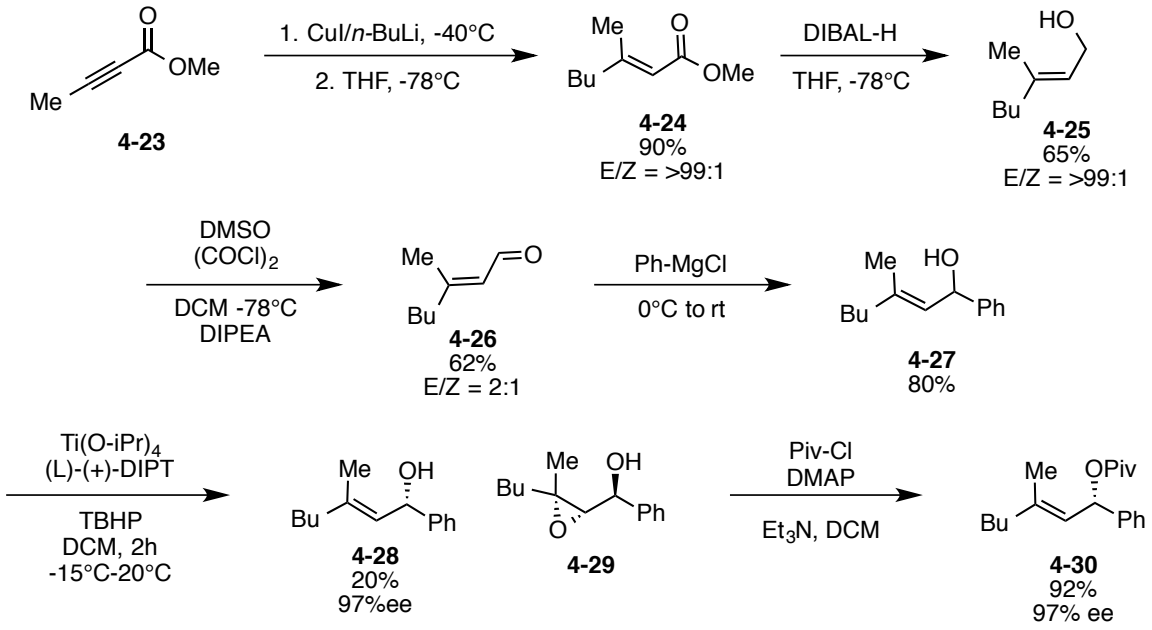


4.2 Results and Discussion

Synthesis of Enantioenriched Allylic Pivalates

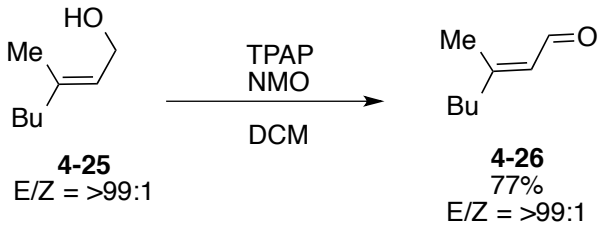
In order for this strategy to make allylic quaternary stereocenters to be useful, I needed to have an efficient synthesis in order to make enantioenriched allylic alcohols. I began my synthesis with methyl-2-butynoate (**4-23**), and did a Gilman cuprate addition across the alkene to afford trans-alkene **4-24**. The ester was then reduced to primary alcohol **4-25** with DIBAL-H. The primary alcohol was then oxidized to alkene **4-26** with a swern oxidation. Addition of phenyl Grignard then provided racemic alcohol **4-27**. A kinetic resolution using asymmetric sharpless epoxidation then provided enantioenriched alcohol **4-28** in 20% yield and 97% ee. Pivalation of the enantioenriched alcohol then proceeded in high yield (92%) without any loss of enantiomeric excess (ee).

Scheme 4-6 Initial Synthesis of Enantioenriched Allylic Pivalates



While this synthesis did provide the desired products in high ee, there were a few problems that I had discovered. The first issue with the synthesis was that the Swern oxidation was isomerizing the alkene in product **4-26**. In order to circumvent this problem, I switched to a TPAP oxidation, which provided product **4-26** without any isomerization, and in 77% yield (Scheme 4-7). The second issue was the kinetic resolution that afforded excellent enantioselectivity but with less than optimal yields. I envisioned that by accessing the ketone of substrate **4-26**, I could do a CBS-reduction to afford enantioenriched **4-28** in high yields and ee.

Scheme 4-7 Oxidation of Primary Alcohol Without Isomerization of Alkene Geometry

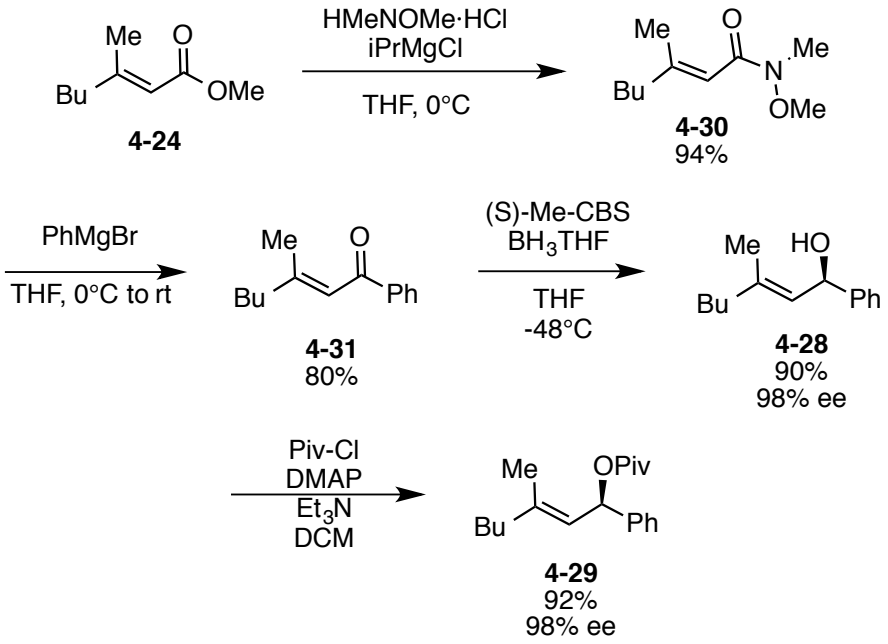


4-25
E/Z = >99:1

4-26
77%
E/Z = >99:1

In order to set up my substrate for a CBS-reduction, I had to revise my synthesis again. After the Gilman cuprate addition to form trans-alkene **4-24**, I made Weinreb amide **4-30**. An aryl Grignard was then added to the Weinreb amide in order to afford the ketone **4-31**. We were then able to do a CBS reduction on the ketone to afford the enantioenriched alcohol **4-28** in between 94-99% ee. The alcohol could then undergo pivalation to provide the starting material **4-29**. In most cases we were able to determine the ee via HPLC or SFC analysis with a chiral stationary phase. However, in some cases the pivalates proved to be unstable on the chiral columns, in which case we assume the pivalate was formed without any loss of enantioenrichment from the alcohol.

Scheme 4-8 Synthesis of Enantioenriched Allylic Alcohols



Optimization and Scope of Suzuki Cross-Coupling of Allylic Pivalates

I chose to begin my optimization with (*S*,*E*)-3-methyl-1-phenyl-2-hepten-yl pivalate (**4-29**). I began by testing conditions that worked well for the Suzuki cross-coupling of allylic pivalates to provide tertiary stereocenters[18]. Although the conditions provided high yields of the desired product **4-32**, the stereochemical fidelity was only 56% es (Table 4-1, Entry 1). By switching to a different phosphine ligand such as PCy_3, the yield and ee increased, but not significantly (Entry 2). Switching from air-sensitive $Ni(cod)_2$ to the air stable $Ni(OTf)_2$ decreased the yield, but there was an increase to 75% ee (Entry 3). Due to the air-stable and less expensive Ni(II) source, I proceeded with this in place of $Ni(cod)_2$.

Table 4-1 Optimization of Suzuki Cross-Coupling of Allylic Pivalates

4-29, 98% ee

4-32

entry	Ni (mol %)	ligand (mol %)	T (°C)	yield (%)[b]	ee (%)[c]	es (%)[d]
1	$Ni(cod)_2$ (5)	$BnPPh_2$	70	90	54	56
2	$Ni(cod)_2$ (5)	PCy_3	70	95	64	67
3[e]	$Ni(OTf)_2$ (5)	PCy_3	70	56	75	79
4[e]	$Ni(OTf)_2$ (5)	dppf	70	30	89	93
5[e]	$Ni(OTf)_2$ (5)	dppb	70	48	75	79
6[e,f]	$Ni(OTf)_2$ (5)	BISBI	70	87	90	95
7[f,g]	$NiCl_2$·DME (2)	BISBI	50	96	91	95
8[h]	$NiCl_2$·DME (2)	BISBI	rt	28	95	99

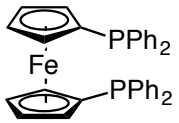
[a]Conditions: Allylic pivalate **4-29** (0.2 mmol, 1.0 equiv), Boroxine (1.0 equiv), NaOMe (2.0 equiv), MeCN (0.4 M), 3h, unless otherwise noted. [b]Determined by ^1H NMR using 1,3,5-trimethoxybenzene as internal standard. [c]Determined by chiral HPLC analysis using chiral stationary phase. [d] es = enantiospecificity = $(ee_{product})/(ee_{starting\ material})$ [e]KOMe used in place of NaOMe. [f]1.5 equiv of Boroxine and 3.0 equiv of base. [g]16h. [h]24 h.

In considering possible reasons for the low stereochemical fidelity, I speculated that the oxidative addition step of nickel-catalyzed cross couplings of allylic and benzylic pivalates can proceed via either open or closed transition states (see mechanism discussion and Scheme 4-15 below).[19] These different modes of oxidative addition lead to opposite enantiomers of product. In MeCN, previous cross couplings of allylic pivalates have led to inversion of stereochemistry, presumably via the open transition state. I anticipated that the major pathway in my reaction involved

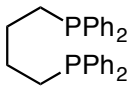
a similar open transition state, but that the closed transition state may be competitive, lowering stereochemical fidelity. In the closed, cyclic transition state, the nickel catalyst is coordinated by the pivalate leaving group. I hypothesized that a bidentate ligand may prevent this coordination, thereby shutting down the directed oxidative addition pathway.

Indeed, when I tried bidentate ligands such as dppf, there was a significant boost in ee to 89%, but the yield dropped to only 30% with a poor mass balance (Entry 4). I proposed that a ligand with a similar bite angle to dppf would keep the high stereochemical fidelity without decomposition of the starting material. I then tried dppb as the ligand which has a bite angle of 97° compared to that of dppf which is 99°.[20] This change did improve the yield to 48%, however the ee dropped to 75% (Entry 5). This drop is likely due to the more flexible backbone of dppb as compared to dppf. This is when I switched to the ligand BISBI, which has a natural bite angle of 113°. BISBI has also been shown to adapt to bite angles from 92° to 115° with less than 3 kcal/mol increase in energy.[20] Gratifyingly, this change raised the yield to 87% with 90% ee (Entry 6). By switching from $Ni(OTf)_2$ to $NiCl_2 \cdot DME$, I was able to drop the temperature to 50° C, and the catalyst loading from 5 mol % to 2 mol %. This combination increased the yield to 96% with a 91% ee (Entry 7). Lowering the temperature from 50 °C to room temperature did increase the stereochemical fidelity, however after 24 h the yield was still only 28% (Entry 8). For this reason, I continued with the conditions in Entry 7 as optimal in order to explore the substrate scope of this reaction.

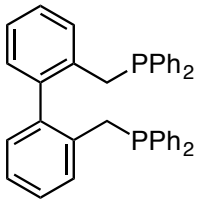
Scheme 4-9 Ligands With Wide Bite Angles



dppf
bite angle: 98.7°



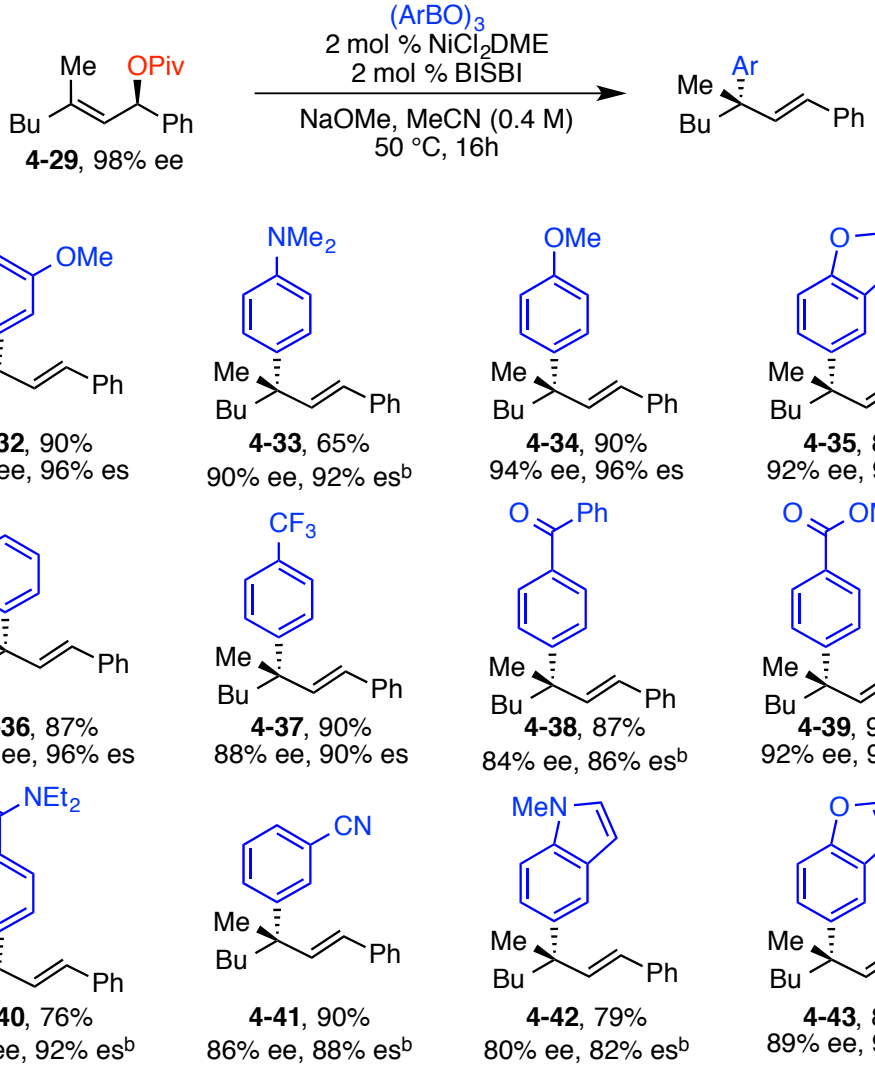
dppb
bite angle: 97.1°



BISBI
bite angle: 113°
(92°-155°)

Having identified a efficient catalyst to form these allylic quaternary stereocenters in high yields and stereochemical fidelity, I explored the scope of this reaction. For these studies I recruited graduate students Javon Rabb-Lynch and Megan Hoerrner, as well as undergraduate Alex Manders to join my team. Broad scope was demonstrated with respect to the aryl boroxine. Our model substrate **4-32** was isolated in 90% yield and 94% ee. Electron-rich aryl boroxines worked very well under these reaction conditions including those with dimethyl amino (**4-33**), methoxy (**4-34**), and dioxolane groups (**4-35)**. Cross-couplings with electron-neutral phenyl (**4-36**) as well as electron-poor trifluormethyl (**4-37**), also provided quaternary stereocenter in high yields and stereochemical fidelity. Aryl boronic esters with functional groups such as ketones (**4-38**), esters (**4-39**), and amides (**4-40**), and nitriles (**4-41**) were all well tolerated under these reaction conditions. However, the ketone (**4-38**), amide (**4-40**), and nitrile (**4-41**) substrates did require elevated temperatures for the reaction to go to completion. We were also pleased to see that heteroaromatic boronic esters such as N-methyl indole (**4-42**) and benzofuran (**4-43**) provided good yields and stereochemical fidelity.

Scheme 4-10 Scope of Aryl Boroxines

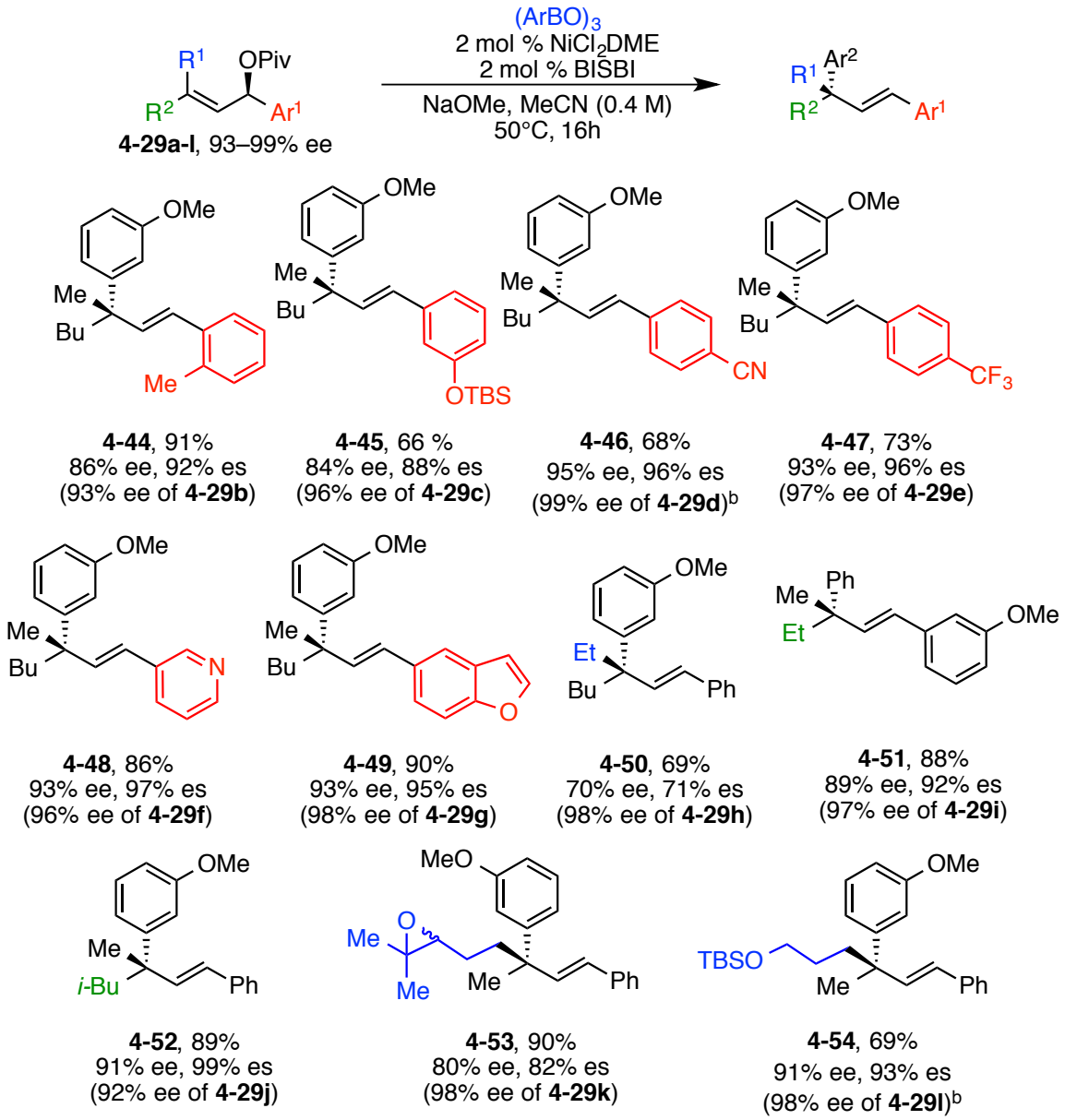


[a]Conditions: allylic pivalate (**4-29**) (0.4 mmol, 1.0 equiv), Boroxine (1.5 equiv), NaOMe (3.0 equiv), MeCN (0.4 M), 50 °C, 16h. Isolated yields are an average of duplicate experiments (±8%). Average ee's from duplicate runs determined by chiral HPLC analysis using a chiral stationary phase (±2%). [b] Reaction run at 70 °C.

With respect to the pivalate coupling partner, we explored the scope of the substituents on the alkene, as well as the aryl group. With respect to the aromatic group, increased steric hindrance of substitution at the ortho position (**4-44**) was well tolerated. Silyl-protected phenols were also undisturbed under these reaction conditions (**4-45**). Cross-couplings of pivalates with electron-poor aromatic groups provide the desired quaternary stereocenter in good yields and excellent stereochemical fidelity (**4-46** and **4-47**). Heteroaromatic groups such as pyridines (**4-48**) and benzofurans (**4-49**) are also well tolerated under these reaction conditions.

For substitution on the alkene, increased bulk of both ethyl (**4-48**) and *iso*-butyl (**4-50**) groups produce the quaternary stereocenter in high yields. Functional groups on the alkene such as an epoxide (**4-51**) and silyl-protected alcohols (**4-52**) were also unharmed under these mild reaction conditions.

Scheme 4-11 Scope of Allylic Pivalates



4-44, 91%
86% ee, 92% es
(93% ee of **4-29b**)

4-45, 66 %
84% ee, 88% es
(96% ee of **4-29c**)

4-46, 68%
95% ee, 96% es
(99% ee of **4-29d**)[b]

4-47, 73%
93% ee, 96% es
(97% ee of **4-29e**)

4-48, 86%
93% ee, 97% es
(96% ee of **4-29f**)

4-49, 90%
93% ee, 95% es
(98% ee of **4-29g**)

4-50, 69%
70% ee, 71% es
(98% ee of **4-29h**)

4-51, 88%
89% ee, 92% es
(97% ee of **4-29i**)

4-52, 89%
91% ee, 99% es
(92% ee of **4-29j**)

4-53, 90%
80% ee, 82% es
(98% ee of **4-29k**)

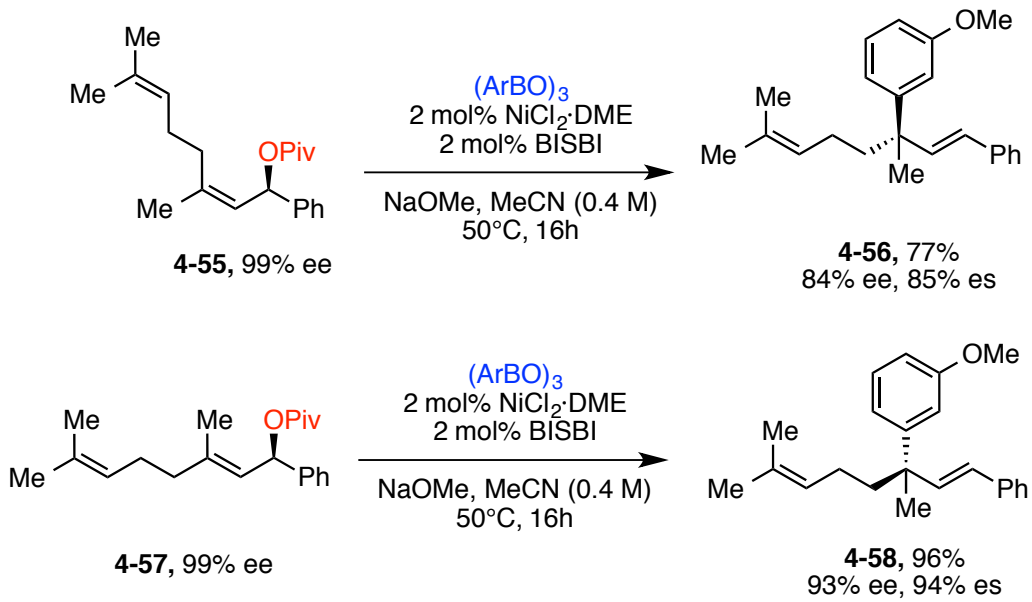
4-54, 69%
91% ee, 93% es
(98% ee of **4-29l**)[b]

[a]Conditions: allylic pivalate (**4-29a-l**) (0.4 mmol, 1.0 equiv), boroxine (1.5 equiv), NaOMe (3.0 equiv), MeCN (0.4 M), 50 °C, 16 h. Isolated yields are an average of duplicate experiments (±8%). Average ee's from duplicate runs determined by chiral HPLC analysis using a chiral stationary phase (±2%). [b] Single experiment.

In developing this chemistry, one question I had was if the alkene geometry of pivalates would have any influence on reactivity. In order to test this theory, I

synthesized enantioenriched allylic pivalates beginning from either geraniol (*E*-alkene isomer) or nerol (*Z*-alkene isomer). Under the same reaction conditions, they had similar reactivity however they produced the opposite enantiomer of product. Geraniol-derived pivalate (**4-53**) showed similar yields and stereochemical fidelity to the model substrate providing the product **4-54** in 96% yield and 93% ee. However, the nerol-derived pivalate (**4-55**) showed lower yields and ee of product **4-56**. This suggests that the reaction proceeds better with *E*-isomers of alkene, and for highly enantioenriched products it is essential to synthesize allylic pivalates with only one alkene isomer.

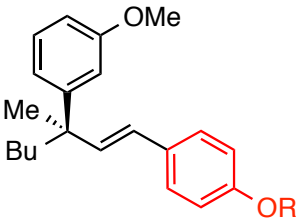
Scheme 4-12 Influence of Alkene Geometry



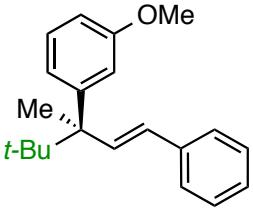
There are several limitations in the scope of this reaction. We found that pivalates with electron-rich aryl substituents such as *p*-methoxyphenyl (**4-57**) decomposed with minor amounts of the product formed. I hypothesized that this may be due to instability of the pivalate, and having an electron-withdrawing group on the phenol (e.g. a pivalate (**4-58**) would help stabilize the reactant). However, this led to further problems in decomposition. While there were a number of decomposition products, I hypothesized that this may be due to activation of both the allylic and aryl-

pivalate. [21] While we were excited to see that *iso*-butyl substitution on the alkene was tolerated (**4-50**), it seems to be the upper limit for size as both *tert*-butyl (**4-59**) and *sec*-butyl (**4-60**) both inhibit product formation. I also saw limitation in the size of boroxine coupling partner that was tolerated. Ortho-substitution on the boroxine also did not provide any of the desired product (**4-61**). Halogens on the boroxine (**4-62**) as well as pyridines (**4-63 to 4-65**) were also unsuccessful. I believe that aryl-halogens may also be activated by the catalyst, providing product other than the desired quaternary stereocenters. I hypothesize that pyridyl boronic acids are unreactive due to possible coordination of the nitrogen to the nickel, forming an unreactive catalyst. For this reason, I also tried boroxines with substitution adjacent to the nitrogen atom. However, they still remained unreactive.

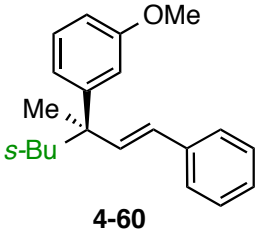
Scheme 4-13 Unsuccessful Substrates



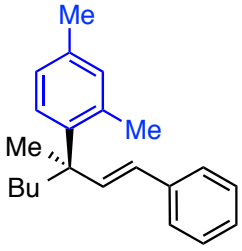
4-57: R = Me
4-58: R = Piv



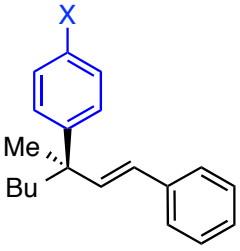
4-59



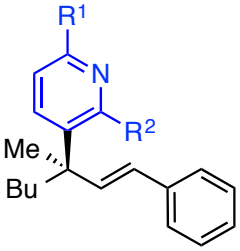
4-60



4-61



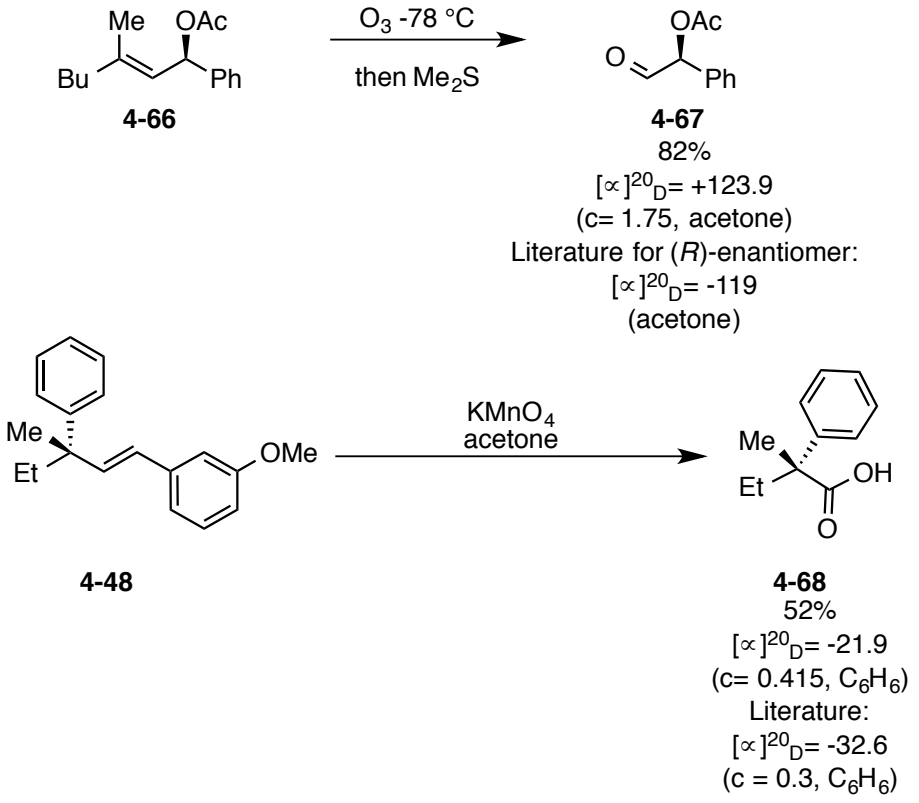
4-62
X= Br or Cl



4-63: R^1= F, R^2= H
4-64: R^1= Me, R^2= H
4-65: R^1= H, R^2= Me

In order to determine the absolute stereochemistry of our starting materials, I was able to acylate alcohol **4-28**, to obtain **4-66**. Oxidative cleavage of **4-66** using ozone provided aldehyde **4-67**. By comparing the optical rotation of **4-67** to that reported in the literature,[22] I have determined that the allylic pivalates we are forming are the *(R*)-enantiomer. This is in agreement with the literature report from the Grubbs group that is used to make these allylic alcohols.[23] In order to determine the absolute stereochemistry of the products, I did an oxidative cleavage of the alkene in compound **4-48**, to obtain carboxylic acid **4-68** (Scheme 4-14). By comparing the optical rotation of **4-68** to that reported in the literature,[24] I have determined that the allylic quaternary stereocenters we are forming are the (*S*)-enantiomer. I am currently working to define the absolute stereochemistry of the alcohols and pivalates. This result means that we are going through inversion of stereochemistry.

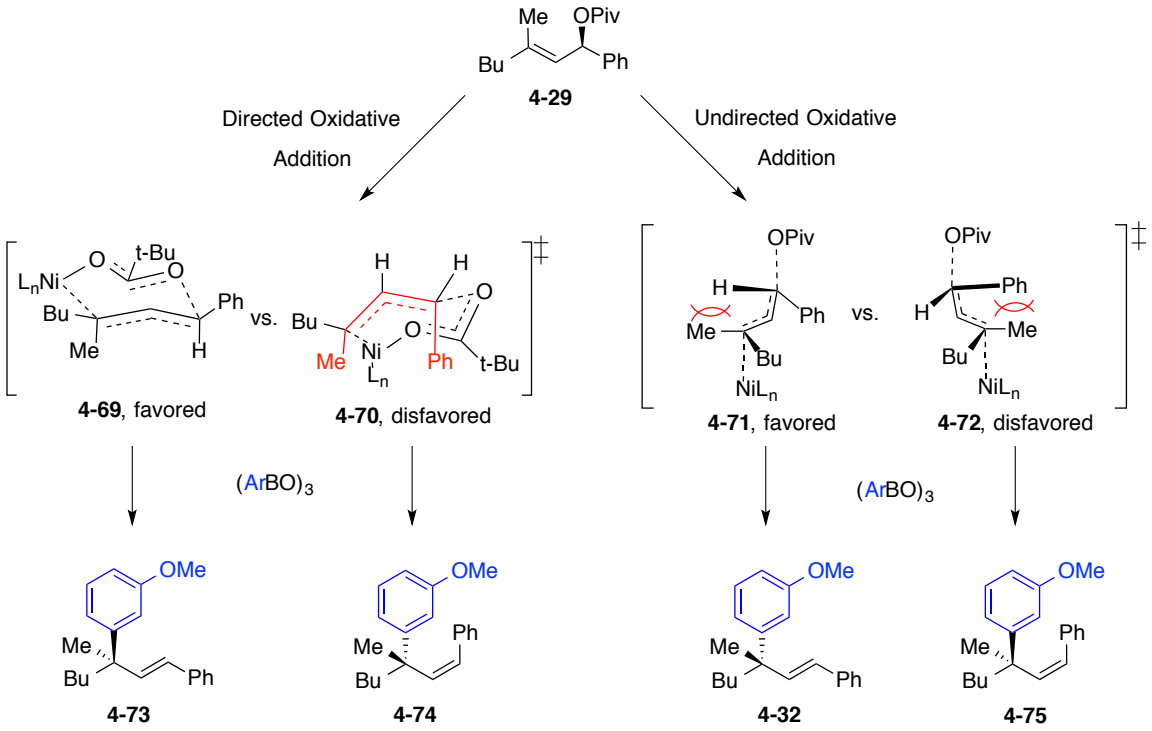
Scheme 4-14 Determination of Absolute Configuration



When considering the possible mechanistic pathways possible for this reaction, we have considered four possibilities. These come from open or closed transition states of the oxidative addition step that have previously been reported for nickel-catalyzed cross couplings of allylic and benzylic pivalates.[19] Retention of configuration occurs through either transition state **4-69** or **4-70**. The alternative option is an open transition state where the pivalate is not coordinated to the nickel (**4-71** or **4-72**). Both transition states **4-70** and **4-72** are disfavored due to a developing A(1,3) strain between the methyl and phenyl substituents. In transition states **4-69** and **4-71**, these steric interactions are minimized with an interaction instead between methyl and hydrogen. We also have confirmation that the reaction does not go through transition state **4-70** and **4-72**, because this would result in formation of (*Z*)-**4-74** and (*Z*)-**4-74**. The large coupling constant characteristic of a cis-olefin vinyl protons (J = 16.3 Hz) rules this out. We anticipate that this reaction

would go through the open transition state **4-71** because the optimal solvent is MeCN, which can coordinate the nickel catalyst and suppress coordination of the pivalate. [19a, 25] Also, large bidentate ligands have been proposed to block the coordination of pivalates which would also favor the open transition states.[19b] This hypothesis was supported through the synthesis of **4-68**, and **4-67** showing that we have made the (*R*)-enantiomer of our alcohols, and the (*S*)-enantiomer of our products (Scheme 4-14). After the undirected oxidative addition, we believe the reaction then undergoes transmetallation with the aryl boroxine and reductive elimination, which are well precedented to proceed with stereoretention.[26]

Scheme 4-15 Proposed Transition State for Retention of Configuration



4.3 Conclusion

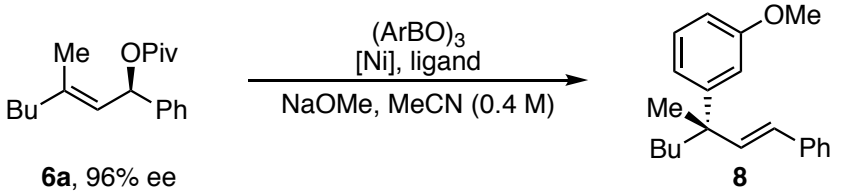
In conclusion, I have developed a highly stereospecific Suzuki cross-coupling of allylic pivalates to afford allylic all-carbon quaternary stereocenters. This reaction utilizes an inexpensive nickel catalyst with air-stable and functional group tolerant boroxines. The allylic alcohols are readily accessible in high enantioenrichment from the corresponding ketone via a classical CBS-reduction. This reaction provides a powerful way to readily access allylic quaternary stereocenters with substituted internal alkenes and a variety of functional groups and heteroatoms in high yield and enantioenrichment.

4.4 Experimental Section

Reactions were performed in oven-dried 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. Commercial reagents were purchased from Sigma Aldrich, Acros, Fisher, Strem, TCI, Combi Blocks, Alfa Aesar, Oakwood Chemicals, or Cambridge Isotopes Laboratories and used as received with the following exceptions: Sodium methoxide was purchased from Sigma Aldrich and immediately placed in a N_2-atmosphere glovebox for storage. PhMe, CH_2Cl_2, MeCN, and THF were dried by passing through drying columns. PhMe and MeCN were then degassed by sparging with N_2 and stored over activated 4Å MS in a N_2-atmosphere glovebox. Enantioenriched allylic alcohols are obtained via CBS reduction of ketones according to the procedure reported in the literature.[23] Oven-dried potassium carbonate was added into $CDCl_3$ to remove trace amount of acid. 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). 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). Chemical shifts for fluorine were externally referenced to $CFCl_3$ in $CDCl_3$ ($CFCl_3$ = δ 0). Chemical shifts for silicon were externally referenced to tetramethylsilane in $CDCl_3$ (tetramethylsilane = δ 0). 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.

Optimization Studies



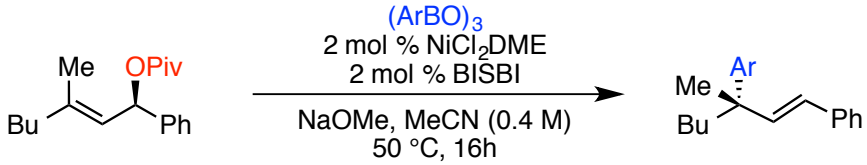
6a, 96% ee **8**

General Optimization Procedure. In a N_2-atmosphere glovebox, nickel, ligand, and base were weighed into a 1-dram vial fitted with a stir bar. Allylic pivalate (0.20 mmol, 1.0 equiv) and boroxine 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 the temperature described below for 3h, unless otherwise stated. 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, 1,3,5-trimethoxybenzene (internal standard) and $CDCl_3$ were added and the yield was determined by ^1H NMR. An analytical sample of product **32** was prepared via preparatory thin layer chromatography, and the ee of this sample was determined by HPLC using a chiral stationary phase. Changes to this general procedure are noted in the table below.

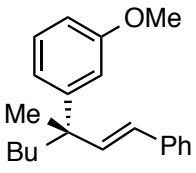
Entry	[Ni] (mol%)	Ligand (mol %)	T (°C)	time (h)	Base (equiv)	Equiv $(ArBO)_3$	% pdt	% ee	% es
1	$Ni(cod)_2$ (5)	$BnPPh_2$ (11)	70	3	NaOMe (2.0)	1.0	90	54	56
2	$Ni(cod)_2$ (5)	PCy_3 (11)	70	3	NaOMe (2.0)	1.0	95	64	67
3	$Ni(OTf)_2$ (5)	PCy_3 (11)	70	3	KOMe (2.0)	1.0	56	75	79
4	$Ni(OTf)_2$ (5)	DPPF (5)	70	3	KOMe (2.0)	1.0	30	89	93
5	$Ni(OTf)_2$ (5)	dppb (5)	70	3	KOMe (2.0)	1.0	48	75	79
6	$Ni(OTf)_2$ (5)	BISBI (5)	70	3	KOMe (3.0)	1.5	87	90	95
7	$NiCl_2$·DME (2)	BISBI (2)	50	16	NaOMe (3.0)	1.5	96	91	95
8	None	None	70	3	NaOMe (3.0)	1.5	0	-	-
9	None	BISBI (2)	70	3	NaOMe (3.0)	1.5	0	-	-

Stereospecific, Nickel-Catalyzed Cross Coupling of Allylic Pivalates

General Procedure A: Stereospecific, Nickel-Catalyzed Coupling of Allylic Pivalates with Boroxines

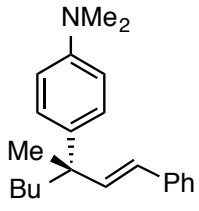


In a N_2-atmosphere glovebox, $NiCl_2$·DME (1.8 mg, 0.008 mmol, 2 mol %), BISBI (4.4 mg, 0.008 mmol, 2 mol %), and NaOMe (64.8 mg, 1.2 mmol, 3.0 equiv) were weighed into a 1-dram vial fitted with a stir bar. Allylic pivalate (0.40 mmol, 1.0 equiv) and boroxine (0.30 mmol, 1.5 equiv) were added, followed by acetonitrile (1.0 mL, 0.4 M). The vial was capped with a Teflon-lined cap and removed from the glovebox. The mixture was stirred at 50 °C for 16 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 then purified by silica gel chromatography to give the arylated product.

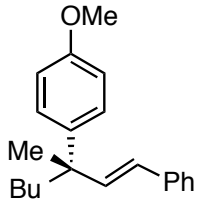


((*S*,*E*)-3-(*m*-Methoxyphenyl)-3-methyl-1-phenyl-1-heptene (32). Prepared via General Procedure A using pivalate **4-29a** (prepared in 98% ee). The crude material was purified by silica gel chromatography (1–2% Et_2O/hexanes) to give compound **8** (run 1: 112.4 mg, 94%; run 2: 100.0 mg, 85%) as colorless oil. The enantiomeric excess was determined to be 93% (run 1: 92% ee; run 2: 94% ee) by chiral HPLC analysis (CHIRACEL IC, 0.4 mL/min, 100% hexane λ=254 nm); t_R(major)= 23.73 min, t_R(minor)= 20.68 min. $[\alpha]_D^{24}$ = –17.7 (c 1.52, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 2H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.24 – 7.18 (m, 2H), 6.99 – 6.94 (m, 1H), 6.92 (t, *J* = 2.2 Hz, 1H), 6.75 (dd, *J* = 8.1, 2.6 Hz, 1H), 6.43 (d, *J* = 16.2 Hz, 1H), 6.38 (d, *J* = 16.3 Hz, 1H), 3.80 (s, 3H), 1.84 (dddd, *J* = 38.7, 13.2, 11.8, 4.6 Hz, 2H), 1.47 (s, 3H), 1.36 – 1.27 (m, 2H), 1.27 – 1.20 (m, 1H), 1.20 – 1.10 (m, 1H), 0.87 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.6, 150.0, 139.5, 138.0, 129.2, 128.7, 127.2, 127.1, 126.4, 119.5, 113.6, 110.5, 55.4, 44.2,

41.5, 27.0, 25.8, 23.6, 14.3; FTIR (NaCl/thin film) 2957, 2860, 1599, 1252,1050, 693 cm^{-1}; HRMS (ESI+) $[M+H]^+$ calculated for $C_{21}H_{27}O$: 295.1984, found: 295.2056.

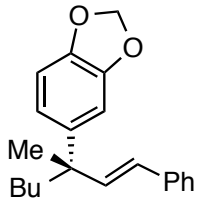


***N*,*N*-Dimethyl{*p*-[(*S*,*E*)-1-butyl-1-methyl-3-phenyl-2-propenyl]phenyl}amine (33).** Prepared via General Procedure A using pivalate **4-29a** (prepared in 98% ee). The reaction was stirred at 50 °C for 16 h. The crude material was purified by silica gel chromatography (2–5% EtOAc/hexanes) to give compound **33** (run 1: 79.9 mg, 65%; run 2: 76.2 mg, 62%) as a yellow oil. The enantiomeric excess was determined to be 90% (run 1: 90% ee; run 2: 90% ee) by chiral HPLC analysis (CHIRALPAK IC, 0.4 mL/min, 100% hexanes, λ=254 nm); t_R(major)=43.77 min, t_R(minor)=39.09 min. $[\alpha]_D^{24} = -11.0$ (c 1.50, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.21 (dd, *J* = 13.5, 8.1 Hz, 3H), 6.71 (d, *J* = 8.8 Hz, 2H), 6.42 (d, *J* = 16.3 Hz, 1H), 6.35 (d, *J* = 16.3 Hz, 1H), 2.93 (s, 6H), 1.89 – 1.73 (m, 2H), 1.44 (s, 3H), 1.29 (m, *J* = 7.6 Hz, 2H), 1.26 – 1.20 (m, 1H), 1.20 – 1.13 (m, 1H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.9, 140.4, 138.3, 136.1, 128.6, 127.5, 126.9, 126.4, 126.3, 112.7, 43.2, 41.6, 40.9, 27.1, 25.9, 23.7, 14.3; FTIR (NaCl/thin film) 2929, 2859, 1613, 1519, 748 cm^{-1}; HRMS (ESI+) $[M+H]^+$ calculated for $C_{22}H_{30}N$: 308.2300, found: 308.2362.

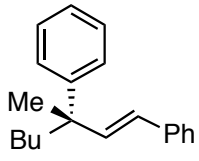


(*S*,*E*)-3-(*p*-Methoxyphenyl)-3-methyl-1-phenyl-1-heptene (34). Prepared via General Procedure A using pivalate **4-29a** (prepared in 98% ee).The crude material was purified by silica gel chromatography (1–2% Et_2O in hexanes) to give compound **34** (run 1: 95.5 mg, 80%; run 2: 110.3 mg, 94%) as a colorless oil.

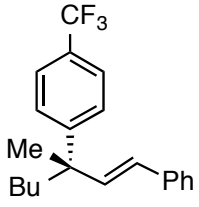
The enantiomeric excess was determined to be 93% (run 1: 94% ee; run 2: 91% ee) by chiral HPLC analysis (CHIRALPAK IB, 0.4 mL/min, 100% hexanes, λ=254 nm); t_R(major)=26.67 min, t_R(minor)=24.13 min. $[\alpha]_D^{24}$ = –16.1 (c 1.40, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.8 Hz, 2H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.27 (d, *J* = 8.9 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.42 (d, *J* = 16.3 Hz, 1H), 6.36 (d, *J* = 16.3 Hz, 1H), 3.80 (s, 3H), 1.93 – 1.73 (m, 2H), 1.45 (s, 3H), 1.36 – 1.26 (m, 2H), 1.26 – 1.19 (m, 1H), 1.19 – 1.10 (m, 1H), 0.88 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.8, 140.2, 140.0, 138.1, 128.7, 127.9, 127.1, 126.8, 126.3, 113.6, 55.4, 43.5, 41.7, 27.0, 26.0, 23.6, 14.3; FTIR (NaCl/thin film) 2957, 2931, 1511, 1250, 1035, 828 cm^{-1}; HRMS (ESI+) $[M+H]^+$ calculated for $C_{21}H_{27}O$: 295.1984, found: 295.2058.



5-[(*S*,*E*)-1-Butyl-1-methyl-3-phenyl-2-propenyl]-2*H*-1,3-benzodioxole (35). Prepared via General Procedure A using pivalate **4-29a** (prepared in 98% ee).The crude material was purified by silica gel chromatography (1–2% Et_2O/hexanes) to give compound **35** (run 1: 114.9 mg, 93%; run 2: 104.8 mg, 85%) as a colorless oil. The enantiomeric excess was determined to be 92% (run 1: 93% ee; run 2: 90% ee) by chiral HPLC analysis (CHIRAlPAK IC, 0.4 mL/min, 100% hexanes, λ=254 nm); t_R(major)=28.55 min, t_R(minor)=25.79 min. $[\alpha]_D^{24}$ = –15.0 (c 0.71, $CHCl_3$): ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 7.8 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.21 (t, *J* = 6.9 Hz, 1H), 6.86 (s, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 6.75 (d, *J* = 8.1 Hz, 1H), 6.37 (s, 2H), 5.93 (d, *J* = 1.5 Hz, 2H), 1.88 – 1.72 (m, 2H), 1.43 (d, *J* = 1.7 Hz, 3H), 1.34 – 1.26 (m, 2H), 1.26 – 1.18 (m, 1H), 1.18 – 1.11 (m, 1H), 0.88 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.7, 145.6, 142.3, 139.7, 138.0, 128.7, 127.2, 126.9, 126.3, 119.8, 107.9, 107.8, 101.0, 44.0, 41.7, 27.0, 26.1, 23.6, 14.3; FTIR (NaCl/thin film) 2958, 2870, 1486,1241, 1040 811, 693 cm^{-1}; HRMS (ESI+) $[M]^+$ calculated for $C_{21}H_{24}O_2$: 308.1776, found: 308.1771.

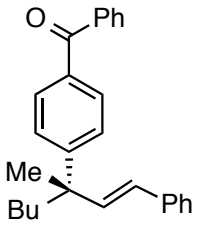


(*S*,*E*)-3-Methyl-1,3-diphenyl-1-heptene (36). Prepared via General Procedure A using pivalate **4-29a** (prepared in 98% ee).The crude material was purified by silica gel chromatography (0–1% Et_2O/hexanes) to give compound **36** (run 1: 94.7 mg, 90%; run 2: 89.4 mg, 84%) as a colorless oil. The enantiomeric excess was determined to be 94% (run 1: 94% ee; run 2: 93% ee) by chiral HPLC analysis (CHIRAlPAK OJ-3R, 1.0 mL/min, 50–66% MeCN in H_2O, λ=254 nm); t_R(major)=19.11 min, t_R(minor)=20.22 min. $[\alpha]_D^{24}$ = –17.2 (c 1.54, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.9, 1.5 Hz, 2H), 7.36 (d, 2H), 7.31 (t, *J* = 8.1, 7.7, 1.8 Hz, 4H), 7.21 (m, 2H), 6.45 (d, *J* = 16.3 Hz, 1H), 6.39 (d, *J* = 16.3 Hz, 1H), 1.97 – 1.77 (m, 2H), 1.48 (s, 3H), 1.34 – 1.27 (m, 2H), 1.27 – 1.19 (m, 1H), 1.19 – 1.08 (m, 1H), 0.87 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.2, 139.7, 138.1, 128.7, 128.3, 127.2, 127.1, 126.9, 126.4, 126.0, 44.1, 41.6, 27.0, 25.8, 23.6, 14.3; FTIR (NaCl/thin film) 3057, 2931, 2361, 1494, 607 cm^{-1}; HRMS (ESI+) $[M]^+$ calculated for $C_{20}H_{24}$: 264.1878, found: 264.1869.

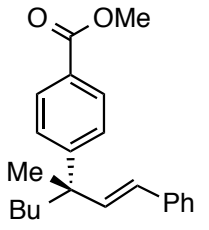


(*S*,*E*)-3-Methyl-1-phenyl-3-[*p*-(trifluoromethyl)phenyl]-1-heptene (37 Prepared via General Procedure A using pivalate **4-29a** (prepared in 98% ee).The crude material was purified by silica gel chromatography (0–1% Et_2O/hexanes) to give compound **37** (run 1: 123.2 mg, 93%; run 2: 115.6 mg, 87%) as a colorless oil. The enantiomeric excess was determined to be 88% (run 1: 88% ee; run 2: 88% ee) by chiral HPLC analysis (CHIRALPAK OJ-3R, 1.0 mL/min, 50-100% MeCN in H_2O, λ=280 nm); t_R(major)=13.01 min, t_R(minor)=12.06 min. $[\alpha]_D^{24}$ = –8.35 (c 1.15, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.43 – 7.36 (m, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.23 (s, 1H), 6.39 (s, 2H), 1.96 – 1.76 (m, 2H), 1.49 (s, 3H), 1.37 – 1.25 (m, 2H), 1.25 – 1.16 (m, 1H), 1.16 – 1.05 (m, 1H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ; 152.3,

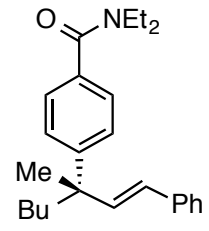
138.6, 137.7, 128.8, 128.8, 128.4 (q, $J_{C\text{-}F}$ = 32.3 Hz), 128.2, 127.9, 127.5, 127.3, 126.4, 125.4 (q, $J_{C\text{-}F}$ = 271.8 Hz)z, 125.3 (q, $J_{C\text{-}F}$ = 2.7 Hz), 125.3, 125.2, 125.2, 125.2, 123.6, 44.4, 41.5, 27.0, 25.8, 23.6, 14.2;^{19}F NMR (376 MHz, $CDCl_3$) δ –62.3; FTIR (NaCl/thin film) 2959, 1617, 1327, 1123, 692 cm^{-1}; HRMS (EI+) [M]+ calculated for $C_{21}H_{23}F_3$: 332.1752, found: 332.1742.



{*p*-[(*S*,*E*)-1-Butyl-1-methyl-3-phenyl-2-propenyl]phenyl} phenylformaldehyde (38). Prepared via General Procedure A using pivalate **4-29a** (prepared in 98% ee), except that the reaction mixture was heated at 70 °C for 16 h. The crude material was purified by silica gel chromatography (3–5% EtOAc/hexanes) to give compound **38** (run 1: 123.3 mg, 84%; run 2: 131.2 mg, 89%) as a colorless oil. The enantiomeric excess was determined to be 81% (run 1: 81% ee; run 2: 80% ee) by chiral HPLC analysis (CHIRALPAK OJ-3R, 1.0 mL/min, 50–100% MeCN in H_2O, λ=280 nm); t_R(major)=15.71 min, t_R(minor)=18.06 min. $[\alpha]_D^{24}$ = –8.42 (c 1.94, $CHCl_3$):^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 – 7.80 (m, 2H), 7.80 – 7.76 (m, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.50 – 7.45 (m, 5H), 7.40 (d, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 6.45 (d, *J* = 16.3 Hz, 1H), 6.41 (d, *J* = 16.3 Hz, 1H), 1.98 – 1.80 (m, 2H), 1.53 (s, 3H), 1.36 – 1.28 (m, 2H), 1.28 – 1.22 (m, 1H), 1.21 – 1.12 (m, 1H), 0.89 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.6, 153.3, 138.8, 138.1, 137.8, 135.4, 132.4, 130.3, 130.2, 128.8, 128.4, 127.8, 127.4, 126.9, 126.4, 44.5, 41.6, 27.0, 25.7, 23.6, 14.2; FTIR (NaCl/thin film) 2931, 1658, 1277, 701 cm^{-1}; HRMS (ESI+) $[M+H]^+$ calculated for $C_{27}H_{29}O$: 369.214, found: 369.2182.

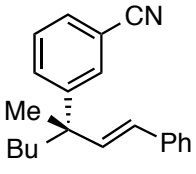


Methyl *p*-[(*S*,*E*)-1-butyl-1-methyl-3-phenyl-2-propenyl]benzoate (39). Prepared via General Procedure A using pivalate **4-29a** (prepared in 98% ee). The crude material was purified by silica gel chromatography (1–2% Et_2O/hexanes) to give compound **39** (run 1: 115.6 mg, 87%; run 2: 107.3 mg, 95%) 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, 1.0 mL/min, 0.1% isopropanol/hexanes, λ=254 nm); t_R(major)=12.04 min, t_R(minor)=10.62 min. $[\alpha]_D^{24} = -19.1$ (c 1.04, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 7.6 Hz, 2H), 7.24 (t, J = 7.6 Hz, 2H), 7.15 (t, J = 7.3 Hz, 1H), 6.33 (dd, 2H), 3.83 (s, 3H), 1.87 – 1.79 (m, 1H), 1.79 – 1.72 (m, 1H), 1.42 (s, 3H), 1.26 – 1.17 (m, 2H), 1.17 – 1.09 (m, 1H), 1.09 – 0.99 (m, 1H), 0.79 (t, J = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.3, 153.6, 138.8, 137.8, 129.7, 128.8, 128.0, 127.7, 127.4, 127.0, 126.4, 52.2, 44.5, 41.5, 27.0, 25.7, 23.6, 14.2; FTIR (NaCl/thin film) 2955, 2362, 1723, 1279, 1017, 755 cm^{-1}; HRMS (ESI+) $[M+H]^+$ calculated for $C_{22}H_{27}O_2$: 323.1933, found: 323.2000.

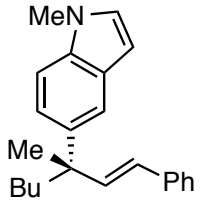


{*p*-[(*S*,*E*)-1-Butyl-1-methyl-3-phenyl-2-propenyl]phenyl}(diethylamino)formaldehyde (40). Prepared via General Procedure A using pivalate **4-29a** (prepared in 98% ee).The crude material was purified by silica gel chromatography (20–25% EtOAc/hexanes) to give compound **40** (run 1: 104.4 mg, 72%; run 2: 116.0 mg, 80%) as a colorless oil. The enantiomeric excess was determined to be 90% (run 1: 91% ee; run 2: 88% ee) by chiral HPLC analysis (CHIRALPAK IB, 1.0 mL/min, 5% isopropanol/hexanes, λ=254 nm); t_R(major)=9.77 min, t_R(minor)=8.67 min. $[\alpha]_D^{24} = -16.9$ (c 2.42, $CHCl_3$): ^{1}H NMR (600 MHz,

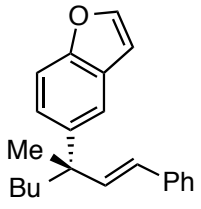
$CDCl_3$) δ7.40 – 7.38 (m, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 7.31 (dd, *J* = 8.2, 6.7 Hz, 4H), 7.23 – 7.20 (m, 1H), 6.42 (d, *J* = 16.3 Hz, 1H), 6.38 (d, *J* = 16.3 Hz, 1H), 3.54 (s, 2H), 3.29 (s, 2H), 1.91 – 1.76 (m, 2H), 1.47 (s, 3H), 1.32 – 1.27 (m, 2H), 1.27 – 1.20 (m, 5H), 1.18 – 1.08 (m, 4H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 149.3, 139.2, 137.8, 134.8, 128.7, 128.6, 127.3, 126.9, 126.4, 126.3, 44.2, 43.5, 41.5, 39.4, 26.9, 25.7, 23.6, 14.5, 14.3, 13.1; FTIR (NaCl/thin film) 2963, 2870, 1631, 1425, 1095 972, 694 cm^{-1}; HRMS (ESI+) $[M+H]^+$ calculated for $C_{25}H_{34}NO$: 364.2562, found: 364.2635.



***p*-[(*S*,*E*)-1-Butyl-1-methyl-3-phenyl-2-propenyl]benzonitrile (41).** Prepared via General Procedure A using pivalate **4-29a** (prepared in 98% ee), except that the reaction mixture was heated at 70 °C for 16 h. The crude material was purified by silica gel chromatography (3–5% EtOAc/hexanes) to give compound **41** (run 1: 104.9 mg, 90%; run 2: 103.0 mg, 89%) as a colorless oil. The enantiomeric excess was determined to be 86% (run 1: 88% ee; run 2: 84% ee) by chiral HPLC analysis (CHIRALPAK IB, 0.4 mL/min, 100% hexanes, λ=254 nm); t_R(major)=40.85 min, t_R(minor)=45.27 min. $[\alpha]_D^{24} = -19.3$ (c 1.02, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.44 – 7.36 (m, 3H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.21 (m, 1H), 6.39 (d, *J* = 16.3 Hz, 1H), 6.35 (d, *J* = 16.3 Hz, 1H), 1.92 – 1.78 (m, 2H), 1.48 (s, 3H), 1.36 – 1.27 (m, 2H), 1.25 – 1.17 (m, 1H), 1.15 – 1.06 (m, 1H), 0.88 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.8, 137.9, 137.4, 131.7, 130.7, 129.8, 129.1, 128.8, 128.3, 127.6, 126.4, 119.5, 112.4, 44.2, 41.4, 26.9, 25.6, 23.5, 14.2; FTIR (NaCl/thin film) 2956, 2860, 2228, 1598, 972, 749, 693 cm^{-1}; HRMS (ESI+) $[M+H]^+$ calculated for $C_{21}H_{24}N$: 290.1830, found: 290.1903.

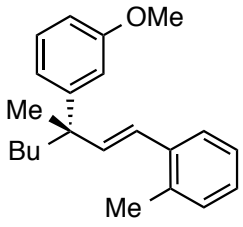


5-[(*S*,*E*)-1-Butyl-1-methyl-3-phenyl-2-propenyl]-1-methyl-1*H*-indole (42). Prepared via General Procedure A using pivalate **4-29a** (prepared in 98% ee), except that the reaction mixture was heated at 70 °C for 16 h. The crude material was purified by silica gel chromatography (3–5% EtOAc/hexanes) to give compound **42** (run 1: 99.6 mg, 78%; run 2: 101.6 mg, 80%) as a pale yellow oil. 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, 100% hexanes, λ =254 nm); t_R(major)=29.82 min, t_R(minor)=18.83 min. $[\alpha]_D^{24} = -23.1$ (c 1.35, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (t, J = 1.2 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.31 (t, J = 7.7 Hz, 2H), 7.29 – 7.23 (m, 3H), 7.23 – 7.18 (m, 1H), 7.03 (d, J = 3.0 Hz, 1H), 6.52 (d, J = 16.3 Hz, 1H), 6.45 (d, J = 3.1 Hz, 1H), 6.41 (d, J = 16.2 Hz, 1H), 3.78 (s, 3H), 2.01 – 1.92 (m, 1H), 1.92 – 1.85 (m, 1H), 1.54 (s, 4H), 1.35 – 1.21 (m, 3H), 1.21 – 1.12 (m, 1H), 0.87 (t, J = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.8, 139.0, 138.3, 135.3, 129.0, 128.7, 128.5, 127.0, 126.4, 126.3, 121.3, 118.6, 108.9, 101.1, 44.0, 41.9, 33.0, 27.1, 26.4, 23.7, 14.3; sFTIR (NaCl/thin film) 2957, 869, 1489, 1249, 971, 747, 694 cm^{-1}; HRMS (ESI+) $[M+H]^+$ calculated for $C_{23}H_{28}N$: 317.2143, found: 318.2214.

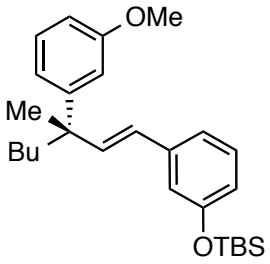


5-[(*S*,*E*)-1-Butyl-1-methyl-3-phenyl-2-propenyl]-1-benzofuran (43). Prepared via General Procedure A using pivalate **4-29a** (prepared in 98% ee). The crude material was purified by silica gel chromatography (0–1% Et_2O/hexanes) to give compound **43** (run 1: 90.6 mg, 74%; run 2: 111.0 mg, 91%) as a colorless oil. The enantiomeric excess was determined to be 89% (run 1: 89% ee; run 2: 89% ee) by chiral HPLC analysis (CHIRALPAK ID, 0.4 mL/min, 100% hexanes, λ=254 nm);

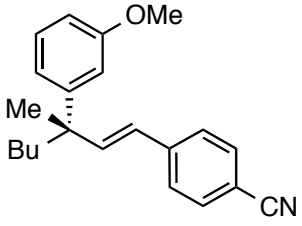
t_R(major)=28.12 min, t_R(minor)=25.16 min. $[\alpha]_D^{24}$ = –20.1 (c 2.33, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 16.0, 2.0 Hz, 2H), 7.45 – 7.38 (m, 3H), 7.35 – 7.28 (m, 3H), 7.24 – 7.18 (m, 1H), 6.73 (dd, *J* = 2.2, 1.0 Hz, 1H), 6.49 (d, *J* = 16.3 Hz, 1H), 6.40 (d, *J* = 16.2 Hz, 1H), 1.98 – 1.83 (m, 2H), 1.53 (d, *J* = 1.9 Hz, 3H), 1.35 – 1.27 (m, 2H), 1.27 – 1.20 (m, 1H), 1.20 – 1.11 (m, 1H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.5, 145.2, 142.7, 140.1, 138.0, 128.7, 127.3, 127.2, 126.8, 126.3, 123.7, 119.1, 111.0, 106.9, 44.1, 41.9, 27.1, 26.3, 23.6, 14.3; FTIR (NaCl/thin film) 2956, 2859, 1466, 1262, 1030, 737 cm^{-1}; HRMS (ESI+) $[M+H]^+$ calculated for $C_{22}H_{25}O$: 305.1827, found: 305.1890.



(*S*,*E*)-3-(*m*-Methoxyphenyl)-3-methyl-1-(*o*-tolyl)-1-heptene (44). Prepared via General Procedure A using pivalate **4-29b** (prepared in 98% ee), except that the reaction mixture was heated at 70 °C for 16 h. The crude material was purified by silica gel chromatography (3–5% EtOAc/hexanes) to give compound **44** (run 1: 113.2 mg, 92%; run 2: 111.2 mg, 90%) as a colorless oil. The enantiomeric excess was determined to be 86% (run 1: 86% ee; run 2: 86% ee) by chiral HPLC analysis (CHIRALPAK IB, 0.4 mL/min, 100% hexanes, λ =254 nm); t_R(major)=22.22 min, t_R(minor)=20.61 min. $[\alpha]_D^{24}$ = –9.0 (c 1.21, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 6.8 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 3H), 7.19 – 7.11 (m, 3H), 6.97 (d, *J* = 7.7 Hz, 1H), 6.94 (t, *J* = 2.2 Hz, 1H), 6.75 (dd, *J* = 8.2, 2.6 Hz, 1H), 6.59 (d, *J* = 16.1 Hz, 1H), 6.26 (d, *J* = 16.2 Hz, 1H), 3.81 (s, 3H), 2.35 (s, 3H), 1.84 (dddd, *J* = 36.0, 13.3, 11.7, 4.7 Hz, 2H), 1.48 (s, 3H), 1.35 – 1.16 (m, 5H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.5, 150.0, 140.7, 137.2, 135.2, 130.1, 129.0, 126.9, 126.1, 125.6, 125.0, 119.3, 113.4, 110.4, 55.2, 44.3, 41.4, 26.9, 25.8, 23.5, 19.9, 14.1; FTIR (NaCl/thin film) 2956, 2860, 600, 1484, 1251, 748 cm^{-1}; HRMS (ESI+) $[M+H]^+$ calculated for $C_{22}H_{29}O$: 309.2140, found: 309.2213.

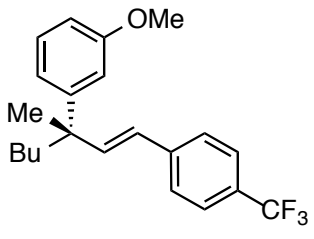


(S,E)-*tert*-Butyl(3-(3-(3-methoxyphenyl)-3-methylhept-1-en-1-yl)phenoxy)dimethylsilane (45). Prepared via General Procedure A using pivalate **4-29c** (prepared in 96% ee). The crude material was purified by silica gel chromatography (1–2% Et_2O/hexanes) to give compound **45** (run 1: 103.5 mg, 61%; run 2: 118.6, 70%) as a colorless oil. The enantiomeric excess was determined to be 84% (run 1: 86% ee; run 2: 82% ee) by chiral HPLC analysis (CHIRALPAK IC, 0.2 mL/min, 100% hexanes, λ=254 nm); t_R(major)=38.04 min, t_R(minor)=35.60 min. $[\alpha]_D^{24}$ = –11.7 (c 2.03, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 7.9 Hz, 1H), 6.99 (d, *J* = 7.7 Hz, 1H), 6.95 (d, *J* = 7.8 Hz, 1H), 6.93 – 6.89 (m, 1H), 6.86 – 6.83 (m, 1H), 6.75 (dd, *J* = 8.1, 2.3 Hz, 1H), 6.69 (dd, *J* = 8.0, 1.8 Hz, 1H), 6.38 (d, *J* = 16.2 Hz, 1H), 6.31 (d, *J* = 16.3 Hz, 1H), 3.80 (s, 3H), 1.91 – 1.75 (m, 2H), 1.45 (s, 3H), 1.35 – 1.25 (m, 2H), 1.25 – 1.18 (m, 1H), 1.18 – 1.11 (m, 1H), 0.99 (s, 9H), 0.87 (t, *J* = 7.3 Hz, 3H), 0.20 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 156.0, 150.0, 139.51, 139.48, 129.5, 129.2, 126.9, 119.5, 119.4, 118.8, 118.1, 113.5, 110.5, 55.3, 44.1, 41.5, 27.0, 25.9, 25.8, 23.6, 18.4, 14.3, –4.2; ^{29}Si NMR (119 MHz, $CDCl_3$) δ 20.56; FTIR (NaCl/thin film) 2930, 2858, 1598, 1485, 1280, 856, 780 cm^{-1}; HRMS (ESI+) $[M+H]^+$ calculated for $C_{27}H_{41}O_2Si$: 425.2798, found: 425.2828.



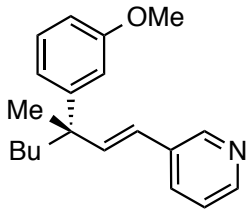
***p*-[(*S*,*E*)-3-(*m*-Methoxyphenyl)-3-methyl-1-heptenyl]benzonitrile (46).** Prepared via General Procedure A using pivalate **4-29d** (prepared in 99% ee). The crude material was purified by silica gel chromatography (3–5% Et_2O/hexanes) to give compound **46** (86.5 mg, 68%) as a colorless oil. The enantiomeric excess was determined to be 95% by chiral HPLC analysis

(CHIRALPAK IB, 1.0 mL/min, 1% isopropanol/hexanes, λ=254 nm); t_R(major)= 11.75 min, t_R(minor)=15.31 min. $[\alpha]_D^{24}$ = –23.2 (c 1.33, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.30 – 7.22 (m, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.90 – 6.86 (m, 1H), 6.77 (dd, *J* = 8.1, 2.3 Hz, 1H), 6.55 (d, *J* = 16.3 Hz, 1H), 6.38 (d, *J* = 16.2 Hz, 1H), 3.81 (s, 3H), 1.96 – 1.75 (m, 2H), 1.48 (s, 3H), 1.30 (p, *J* = 6.7 Hz, 2H), 1.24 – 1.07 (m, 2H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 149.0, 143.7, 142.5, 132.5, 129.4, 126.8, 125.7, 119.31, 119.28, 113.7, 110.5, 110.3, 55.3, 44.4, 41.2, 26.9, 25.3, 23.5, 14.2; FTIR (NaCl/thin film) 2932, 2224, 1603, 1290, 1043, 701 cm^{-1}; HRMS (ESI+) $[M+H]^+$ calculated for $C_{22}H_{26}NO$: 320.1936, found: 320.1984.

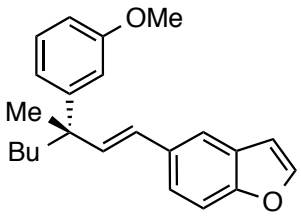


(*S*,*E*)-3-(*m*-Methoxyphenyl)-3-methyl-1-[*p*-(trifluoromethyl)phenyl]-1-heptene (47). Prepared via General Procedure A using pivalate **4-29e** (prepared in 97% ee). The crude material was purified by silica gel chromatography (1–2% Et_2O/hexanes) to give compound **47** (run 1: 106.4 mg, 74%; run 2: 96 mg, 66%) as a colorless oil. There was a 4% impurity of the S_N2 product observed in this reaction. The enantiomeric excess was determined to be 93% (run 1: 93% ee; run 2: 93%) by chiral HPLC analysis (CHIRALPAK IC, 0.2 mL/min, 100% hexanes, λ=254 nm); t_R(major)=36.59 min, t_R(minor)=34.08 min. $[\alpha]_D^{24}$ = –16.4 (c 2.19, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 7.9 Hz, 1H), 6.97 –z 6.91 (m, 1H), 6.89 (t, *J* = 2.2 Hz, 1H), 6.79 – 6.73 (m, 1H), 6.51 (d, *J* = 16.3 Hz, 1H), 6.40 (d, *J* = 16.2 Hz, 1H), 3.80 (s, 3H), 1.95 – 1.74 (m, 2H), 1.47 (s, 3H), 1.36 – 1.25 (m, 2H), 1.25 – 1.06 (m, 2H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.5, 149.2, 142.2, 141.3, 129.1, 128.8 (q, *J*= 32.6 Hz), 126.3, 125.8, 125.5 (q, *J*= 3.5 Hz), 124.3 (q, *J*= 271.5 Hz), 119.2, 113.5, 110.4, 55.2, 44.2, 41.2, 26.8, 25.4, 23.4, 14.1; ^{19}F NMR (376 MHZ,

$CDCl_3$) δ –62.36 FTIR (NaCl/thin film) 2958, 1607, 1324, 1123 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{22}H_{24}F_3O$: 362.1858, found: 362.1872.

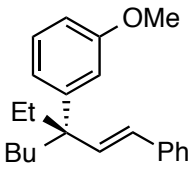


3-[(*S*,*E*)-3-(*m*-Methoxyphenyl)-3-methyl-1-heptenyl]pyridine (48). Prepared via General Procedure A using pivalate **4-29f** (prepared in 96% ee). The crude material was purified by silica gel chromatography (40% EtOAc/hexanes with 5% Et_3N) to give compound **48** (run 1: 103.3 mg, 87%; run 2: 98.8 mg, 84%) as a colorless 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, 1% isopropanol/hexanes, λ=220 nm); t_R(major)=32.69 min, t_R(minor)=23.16 min. $[\alpha]_D^{24}$ = +13.4 (c 1.86, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.59 (d, *J* = 2.2 Hz, 1H), 8.46 – 8.41 (m, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.25 (m, *J* = 7.9 Hz, 1H), 7.22 (dd, *J* = 8.0, 4.8 Hz, 1H), 6.96 – 6.91 (m, 1H), 6.89 (t, *J* = 2.2 Hz, 1H), 6.78 – 6.74 (m, 1H), 6.48 (d, *J* = 16.3 Hz, 1H), 6.35 (d, *J* = 16.3 Hz, 1H), 3.80 (s, 3H), 1.92 – 1.84 (m, 1H), 1.84 – 1.75 (m, 1H), 1.47 (s, 3H), 1.35 – 1.26 (m, 2H), 1.26 – 1.18 (m, 1H), 1.18 – 1.08 (m, 1H), 0.87 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.7, 149.3, 148.5, 148.3, 142.0, 133.5, 132.7, 129.3, 123.6, 123.5, 119.4, 113.6, 110.6, 55.4, 44.4, 41.4, 27.0, 25.5, 23.6, 14.2; FTIR (NaCl/thin film) 2956, 2869, 1605, 1484, 1252, 1044, 702 cm^{-1}; HRMS (ESI+) $[M+H]^+$ calculated for $C_{20}H_{26}NO$: 296.1936, found: 296.2009.

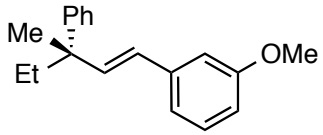


5-[(*S*,*E*)-3-(*m*-Methoxyphenyl)-3-methyl-1-heptenyl]-1-benzofuran (49). Prepared via General Procedure A using pivalate **4-29g** (prepared in 98% ee). The crude material was purified by silica gel chromatography (1–2%

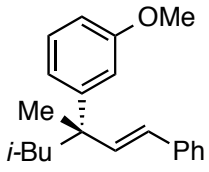
Et_2O/hexanes) to give compound **49** (run 1: 120.2 mg, 90%; run 2: 120.3 mg, 90%) as a colorless oil. The enantiomeric excess was determined to be 93% (run 1: 93% ee; run 2: 93% ee) by chiral HPLC analysis (CHIRALPAK IC, 1.0 mL/min, 0.1% isopropanol/hexanes, λ=254 nm); t_R(major)=7.87 min, t_R(minor)=6.90 min. $[\alpha]_D^{24}$ = –23.9 (c 1.20, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (t, *J* = 1.8 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 1H), 7.35 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 6.99 – 6.95 (m, 1H), 6.94 – 6.90 (m, 1H), 6.77 – 6.71 (m, 2H), 6.47 (d, *J* = 16.3 Hz, 1H), 6.39 (d, *J* = 16.2 Hz, 1H), 3.80 (s, 3H), 1.91 – 1.77 (m, 2H), 1.48 (s, 3H), 1.35 – 1.27 (m, 2H), 1.27 – 1.21 (m, 1H), 1.21 – 1.12 (m, 1H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.5, 154.4, 150.0, 145.4, 138.3, 133.0, 129.0, 127.7, 127.0, 122.8, 119.3, 118.6, 113.4, 111.3, 110.3, 106.6, 55.2, 44.0, 41.5, 26.9, 25.7, 23.5, 14.1; FTIR (NaCl/thin film) 2956, 2931, 1606, 1465, 1262, 1031, 765, 701 cm^{-1}; HRMS (ESI+) $[M+H]^+$ calculated for $C_{23}H_{27}O_2$: 335.1933, found: 335.2001.



(*S*,*E*)-3-Ethyl-3-(*m*-methoxyphenyl)-1-phenyl-1-heptene (50). Prepared via General Procedure A using pivalate **4-29h** (prepared in 98% ee). The crude material was purified by silica gel chromatography (1–2% Et_2O/hexanes) to give compound **50** (run 1: 82 mg, 67%; run 2: 89 mg, 70%) as a colorless oil. The enantiomeric excess was determined to be 68% (run 1: 68% ee run 2: 68% ee) by chiral HPLC analysis (CHIRALPAK IF, 0.2 mL/min, 100% pentane, λ=254 nm); t_R(major)=56.76 min, t_R(minor)=53.61 min. $[\alpha]_D^{24}$ = +4.1 (c 1.91, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.35 (m, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.25 – 7.17 (m, 2H), 6.97 – 6.91 (m, 1H), 6.91 – 6.87 (m, 1H), 6.79 – 6.70 (m, 1H), 6.42 (d, *J* = 16.4 Hz, 1H), 6.32 (d, *J* = 16.4 Hz, 1H), 3.80 (s, 3H), 2.00 – 1.76 (m, 4H), 1.28 (p, *J* = 7.0 Hz, 2H), 1.22 – 1.05 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H), 0.77 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.5, 148.5, 138.4, 138.2, 128.9, 128.7, 127.9, 127.1, 126.3, 120.3, 114.4, 110.4, 55.3, 47.7, 37.3, 30.5, 26.5, 23.7, 14.3, 8.8; FTIR (NaCl/thin film) 2957, 2932, 1599, 1485, 1247, 1052, 775, 693 cm^{-1}; HRMS (ESI+) $[M+H]^+$ calculated for $C_{22}H_{29}O$: 309.2140, found: 309.2205.

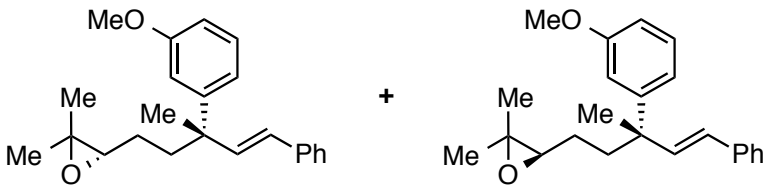


(*S*,*E*)-1-(*m*-Methoxyphenyl)-3-methyl-3-phenyl-1-pentene (51). Prepared via General Procedure A using pivalate **4-29i** (prepared in 97% ee). The crude material was purified by silica gel chromatography (1–2% Et_2O/hexanes) to give compound **51** (run 1: 96.3 mg, 90%; run 2: 91.6 mg, 86%) as a colorless oil. The enantiomeric excess was determined to be 89% (run 1: 89% ee; run 2: 88% ee) by chiral HPLC analysis (CHIRALPAK IA, 0.4 mL/min, 100% hexanes, λ=254 nm); t_R(major)=26.11 min, t_R(minor)=22.57 min. $[\alpha]_D^{24}$ = –16.6 (c 2.02, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.24 – 7.17 (m, 2H), 6.99 (dt, *J* = 7.7, 1.2 Hz, 1H), 6.93 (t, *J* = 2.1 Hz, 1H), 6.77 (dd, *J* = 8.1, 3.0 Hz, 1H), 6.43 (d, *J* = 16.3 Hz, 1H), 6.36 (d, *J* = 16.2 Hz, 1H), 3.81 (s, 3H), 1.99 – 1.82 (m, 2H), 1.46 (s, 3H), 0.82 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.9, 147.6, 139.5, 139.4, 129.5, 128.1, 127.0, 126.8, 125.8, 118.9, 112.7, 111.4, 55.2, 44.2, 33.9, 25.0, 9.1; FTIR (NaCl/thin film) 3852, 2964, 2361, 1578, 1156, 699 cm^{-1}; HRMS (ESI+) $[M+H]^+$ calculated for $C_{19}H_{23}O$: 267.1671, found: 267.1739.

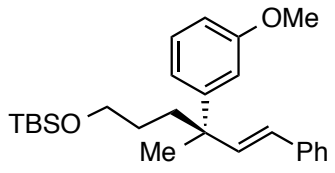


(*S*,*E*)-3-(*m*-methoxyphenyl)-3,5-dimethyl-1-phenyl-1-hexene (52). Prepared via General Procedure A using pivalate **4-29j** (prepared in 92% ee). The crude material was purified by silica gel chromatography (1–2% Et_2O/hexanes) to give compound **52** (run 1: 97.9 mg, 83%; run 2: 100.6 mg, 85%) as a colorless oil. The enantiomeric excess was determined to be 91% (run 1: 90% ee; run 2: 91% ee) by chiral HPLC analysis (CHIRALPAK IC, 0.4 mL/min, 100% hexanes, λ=254 nm); t_R(major)=22.80 min, t_R(minor)=19.57 min. $[\alpha]_D^{24}$ = –7.05 (c 2.05, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.31 (dd, *J* = 8.5, 6.9 Hz, 2H), 7.25 – 7.18 (m, 2H), 6.99 – 6.95 (m, 1H), 6.93 (t, *J* = 2.2 Hz, 1H), 6.76 – 6.72 (m, 1H), 6.45 (d, *J* = 16.3 Hz, 1H), 6.38 (d, *J* = 16.3 Hz, 1H), 3.80 (s, 3H), 1.86 – 1.75 (m, 2H), 1.70 – 1.62 (m, 1H), 1.50 (s, 3H), 0.87 (d, *J* = 6.7 Hz, 3H), 0.80 (d, *J* = 6.6 Hz, 3H); ^{13}C

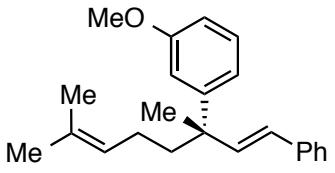
NMR (101 MHz, $CDCl_3$) δ 159.5, 150.3, 139.7, 138.0, 129.1, 128.7, 127.1, 126.8, 126.3, 119.5, 113.6, 110.5, 55.4, 50.8, 44.6, 26.1, 25.3, 25.2, 25.0; FTIR (NaCl/thin film) 2953, 1599, 1485, 1247, 693 cm^{-1}; HRMS (ESI+) $[M+H]^+$ calculated for $C_{21}H_{27}O$: 295.1198, found: 295.2056.



3-[(*S*,*E*)-3-(*m*-Methoxyphenyl)-3-methyl-5-phenyl-4-pentenyl]-2,2-dimethyloxirane (53). Prepared via General Procedure A using pivalate **4-29k** (prepared in 81% ee, 1:1 mixture of diastereomers). The crude material was purified by silica gel chromatography (10–15% Et_2O in hexanes) to give compound **53** (run 1: 121.7 mg, 91%; run 2: 118.2 mg, 88%) as a colorless oil. The enantiomeric excess of each diastereomer was determined to be 81% (run 1: 81% ee; run 2: 81% ee) by chiral HPLC analysis (CHIRALPAK IB, 1.0 mL/min, 0.8% isopropanol/hexanes, λ=254 nm); t_R(major for diastereomer 1)=12.96 min, t_R(minor for diastereomer 1)=11.43 min, t_R(major for diastereomer 2)=18.46 min, t_R(minor for diastereomer 2)=16.35 min. $[\alpha]_D^{24}$ = –8.0 (c 1.15, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$, both diastereomers) δ 7.42 – 7.34 (m, 2H), 7.30 (td, *J* = 7.6, 1.9 Hz, 2H), 7.25 – 7.17 (m, 2H), 6.95 (d, *J* = 7.8 Hz, 1H), 6.91 (d, *J* = 2.2 Hz, 1H), 6.79 – 6.71 (m, 1H), 6.41 (d, *J* = 1.6 Hz, 2H), 3.80 (s, 3H), 2.70 (t, *J* = 6.3 Hz, 1H), 2.19 – 1.99 (m, 1H), 1.99 – 1.81 (m, 1H), 1.56 – 1.41 (m, 5H), 1.41 – 1.32 (m, 1H), 1.28 (d, *J* = 1.2 Hz, 3H), 1.20 (s, 2H), 1.17 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 149.3, 149.0, 138.8, 138.4, 137.7, 137.7, 129.4, 129.4, 128.8, 128.7, 127.7, 127.4, 127.4, 127.3, 126.4, 119.4, 119.3, 113.6, 113.5, 110.8, 110.7, 64.8, 58.7, 58.6, 55.4, 44.0, 43.9, 38.0, 37.9, 25.7, 25.5, 25.1, 24.6, 24.6, 18.8, 18.8; FTIR (NaCl/thin film) 2963, 2361, 1599, 1486, 1251, 749, 694 cm^{-1}; HRMS (ESI+) $[M+H]^+$ calculated for $C_{23}H_{29}O_2$: 337.2089, found: 337.2155.

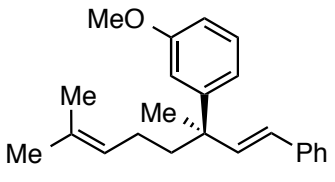


(*S,E*)-*tert*-Butyl((4-(3-methoxyphenyl)-4-methyl-6-phenylhex-5-en-1-yl)oxy)dimethylsilane (54). Prepared via General Procedure A using pivalate **4-29l** (prepared in >99% ee). The crude material was purified by silica gel chromatography (1–2% Et_2O/hexanes) to give compound **54** (109.1 mg, 69%) as acolorless oil. The enantiomeric excess was determined to be 89% by chiral HPLC analysis (CHIRALPAK IC, 0.2 mL/min, 100% hexanes, λ=254 nm); t_R(major)=46.40 min, t_R(minor)=43.28 min. $[\alpha]_D^{24}$ = –8.5 (c 1.31, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 2H), 7.30 (dd, *J* = 8.5, 6.9 Hz, 2H), 7.25 – 7.18 (m, 2H), 6.96 (dd, *J* = 7.8, 1.8, 0.9 Hz, 1H), 6.91 (t, *J* = 2.1 Hz, 1H), 6.74 (dd, *J* = 8.1, 2.6, 0.9 Hz, 1H), 6.40 (s, 2H), 3.79 (s, 3H), 3.58 (t, *J* = 6.4 Hz, 2H), 1.95 – 1.83 (m, 2H), 1.47 (s, 4H), 1.41 (dtd, *J* = 11.8, 6.5, 1.6 Hz, 1H), 0.89 (s, 9H), 0.03 (d, *J* = 1.0 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.7, 149.7, 139.2, 138.0, 129.2, 128.7, 127.23, 127.18, 126.4, 119.5, 113.6, 110.7, 63.8, 55.3, 43.9, 37.7, 28.3, 26.2, 25.9, 18.6, –5.1; ^{29}Si NMR (119 MHz, $CDCl_3$) δ 18.5; FTIR (NaCl/thin film) 1952, 2856,1599,1255, 1095, 835 cm^{-1}; HRMS (ESI+) $[M+H]^+$ calculated for $C_{26}H_{39}O_2Si$: 411.2641, found: 411.2680.



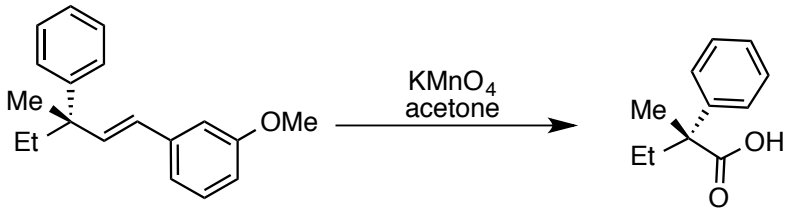
(*S*,1*E*)-3-(*m*-Methoxyphenyl)-3,7-dimethyl-1-phenyl-1,6-octadiene (56). Prepared via General Procedure A using pivalate **4-29m** (prepared in 98% ee). The crude material was purified by silica gel chromatography (1–2% Et_2O/hexanes) to give compound **56** (run 1: 119.0 mg, 93%, run 2: 125.2 mg, 98%) as a colorless oil. The enantiomeric excess was determined to be 93% ee (run 1: 93% ee, run 2: 93% ee) by chiral HPLC analysis (CHIRALPAK IC, 0.4 mL/min, 100% hexanes, λ=254 nm); t_R(major)=26.31 min, t_R(minor)=23.16 min. $[\alpha]_D^{24}$ = –4.09 (c 2.10, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.25 – 7.18 (m, 2H), 6.96 (dt, *J* = 7.8, 0.9 Hz, 1H), 6.93 – 6.90 (m, 1H), 6.78 –

6.72 (m, 1H), 6.41 (d, J = 1.7 Hz, 2H), 5.11 (ddd, J = 4.9, 3.6, 2.1 Hz, 1H), 3.80 (s, 3H), 1.96 – 1.78 (m, 4H), 1.66 (d, J = 1.4 Hz, 3H), 1.53 (d, J = 1.3 Hz, 3H), 1.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 149.7, 139.1, 138.0, 131.7, 129.2, 128.7, 127.2, 126.3, 124.8, 119.4, 113.5, 110.6, 55.4, 44.2, 41.7, 25.9, 25.7, 23.6, 17.8; FTIR (NaCl/thin film) 2965, 2927, 1599, 1485, 1290, 1049, 693 cm^{-1}; HRMS (EI+) $[M+H]^+$ calculated for $C_{23}H_{29}O$: 321.2140, found: 321.2208.



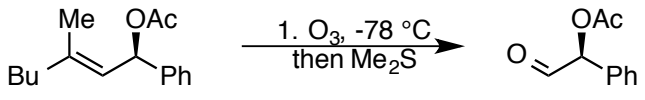
(*R*,1*E*)-3-(*m*-Methoxyphenyl)-3,7-dimethyl-1-phenyl-1,6-octadiene (58). Prepared via General Procedure A using pivalate **4-29n** (prepared in 98% ee). The crude material was purified by silica gel chromatography (1–2% Et_2O/hexanes) to give compound **58** (run 1: 95.6 mg, 75%, run 2: 101.6 mg, 79%) as a colorless oil. The enantiomeric excess was determined to be 84% (run 1: 84% ee, run 2: 84% ee) by chiral HPLC analysis (CHIRALPAK IC, 0.4 mL/min, 100% hexanes, λ=254 nm); t_R(major)=21.94 min, t_R(minor)=25.79 min. $[\alpha]_D^{24}$ = +3.43 (c 2.17, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H), 7.30 (t, J = 7.7 Hz, 2H), 7.28 – 7.18 (m, 8H), 6.96 (dd, J = 8.0, 1.9 Hz, 1H), 6.92 (s, 1H), 6.75 (dd, J = 8.1, 2.5 Hz, 1H), 6.42 (s, 1H), 6.41 (s, 1H), 5.11 (t, J = 5.9 Hz, 1H), 3.80 (s, 3H), 1.97 – 1.87 (m, 2H), 1.87 – 1.80 (m, 2H), 1.67 (s, 3H), 1.53 (s, 3H), 1.49 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.7, 149.7, 139.2, 138.1, 131.6, 129.2, 128.7, 127.3, 127.2, 126.4, 124.9, 119.5, 113.6, 110.7, 55.4, 44.3, 41.8, 25.9, 25.7, 23.7, 17.8. . The spectral data for this compound matches that of (*S*)-**31** reported above.

Determination of Absolute Configuration



S1 S2

(*R*)-2-Methyl-2-phenylhexanoic acid (32). The following synthesis was adapted from a literature procedure.[27] (*S*,*E*)-1-(*m*-Methoxyphenyl)-3-methyl-3-phenyl-1-pentene (**27**) (90 mg, 0.34 mmol, 1.0 equiv) was dissolved in acetone (1.6 mL, 0.22 M). $KMnO_4$ (0.46 g, 2.9 mmol, 8.7 equiv) was then added to the solution, which was then stirred overnight at room temperature. The mixture was then cooled to 0 °C, and EtOH (0.4 mL) was added dropwise. The mixture was then stirred for an additional hour at room temperature. The mixture was filtered through a pad of Celite, and the Celite bed was washed with water (2 x 2 mL) and acetone (2 x 2 mL). HCl (1 M, 3 mL) was added to the solution, and the aqueous layer was extracted with PhMe (2 x 10 mL). The combined organic fractions were then extracted with 1 M NaOH (1 x 15 mL). The aqueous layer was then made acidic with 1 M HCl, and extracted with PhMe (3 x 30 mL). The combined organic fractions were then washed with sat. aq. NaCl (1 x 60 mL), dried with $MgSO_4$, and concentrated. The resulting residue was then purified via silica gel chromatography (20% EtOAc/Hexane) to give compound **32** as a white solid. The spectral data matched that reported in the literature.[16] $[\alpha]_D^{24}$ = 21.9 (c 0.42, C_6H_6). The absolute configuration assigned by comparing the optical rotation with a reported literature value for *(R)*-**32**, $[\alpha]_D^{20}$ = 32.6 (c 0.3, C_6H_6). [24]



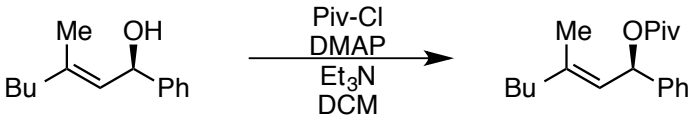
S3 S4

(*S*)-Formylphenylmethyl acetate (33) (*R*,*E*)-3-Methyl-1-phenyl-2-heptenyl acetate (1.9 mmol, 1.0 equiv) was dissolved in anhydrous DCM (76 mL, 0.025 M) and the solution was cooled to -78 °C. Ozone was then apassed through the

solution until there was a persistent blue color. Dimethyl sulfide (3.8 mmol, 2.0 equiv) was then added dropwise to the solution at -78 °C. The solution was allowed to stir and slowly warm to room temperature over a period of 3h. The solution was then concentrated, and purified via silica gel chromatography (30% EtOAc/Hex) to give compound **33** as a pale yellow oil. The spectral data matched that reported in the literature. $[\alpha]_D^{24}$ = +123.9 (c 2.17, acetone). The absolute configuration was assigned by comparing the optical rotation with a reported literature value for *(R)*-**33**, $[\alpha]_D^{24}$ = 119 (acetone). [22]

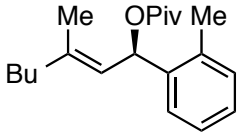
Preparation of Allylic Pivalates

General Procedure B: Preparation of Allylic Pivalates (4-29a-4-29i)

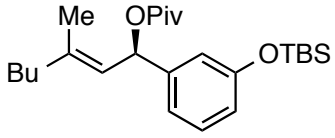


(*R*,*E*)-3-Methyl-1-(*phenyl*)-2-heptenyl pivalate (4-29a). (*R*,*E*)-3-methyl-1-phenyl-2-hepten-1-ol (1.26 g, 12.2 mmol, 1.0 equiv, 98% ee) and DMAP (75 mg, 0.62 mmol, 0.10 equiv) were dissolved in CH_2Cl_2 (25 mL, 0.25 M). Et_3N (1.72 mL, 12.3 mmol, 2.0 equiv) and pivaloyl chloride (0.91 mL, 7.39 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. NaOH (2.0 M, 40 mL), dried ($MgSO_4$), filtered, and concentrated. The resulting residue was purified by silica gel chromatography (column wet-packed with 1:1 Et_3N:hexanes; then run using 2% Et_2O/hexanes) to give compound **4-29a** (1.46 g, 82%) as a pale yellow oil. The enantiomeric excess was assumed to be 98%, because that is the ee of the allylic alcohol precursor. $[\alpha]_D^{24}$ = –31.3 (c 1.22, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (d, *J* = 5.8 Hz, 4H), 7.29 – 7.23 (m, 1H), 6.48 (d, *J* = 9.0 Hz, 1H), 5.33 (dd, *J* = 9.0, 1.3 Hz, 1H), 2.07 – 1.97 (m, 2H), 1.81 (d, *J* = 1.4 Hz, 3H), 1.44 – 1.35 (m, 2H), 1.34 – 1.24 (m, 3H), 1.22 (s, 9H), 0.88 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.5, 141.1, 140.8, 128.4, 127.4, 126.2, 123.2, 72.4, 39.2, 38.8, 29.7, 27.1,

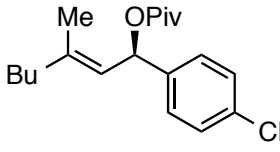
22.2, 16.8, 13.9; FTIR (NaCl/thin film) 2958, 2931, 1728, 1151, 697 cm^{-1}; HRMS (ESI) $[M+H]^+$ calculated for $C_{19}H_{29}O$: 289.2084, found: 289.1252.



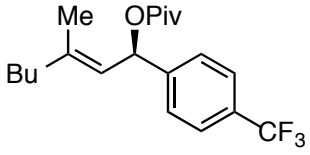
(*R*,*E*)-3-Methyl-1-(*o*-tolyl)-2-heptenyl pivalate (4-29b). Prepared according to General Procedure B on a 2.75 mmol scale to give **4-29b** (607 mg, 83%) as a yellow oil. The enantiomeric excess was determined to be 93% because that is the ee of the allylic alcohol precursor. $[\alpha]_D^{24}$ = –43.4 (c 1.54, $CHCl_3$): ^1H NMR (600 MHz, $CDCl_3$) δ 7.27 (s, 2H), 7.19 (s, 2H), 6.42 (d, *J* = 9.1 Hz, 1H), 5.27 (d, *J* = 9.1 Hz, 1H), 1.96 (t, *J* = 7.5 Hz, 2H), 1.75 (s, 3H), 1.39 – 1.27 (m, 2H), 1.25 – 1.17 (m, 2H), 1.15 (s, 9H), 0.81 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.6, 141.5, 139.6, 135.4, 130.6, 127.5, 126.3, 126.1, 123.0, 70.3, 39.4, 39.0, 30.0, 27.3, 22.4, 19.5, 17.0, 14.1; FTIR (NaCl/thin film) 2957, 1726, 1280, 1153, 752 cm^{-1}; HRMS (ESI+) $[M]^+$ calculated for $C_{20}H_{30}O_2$: 302.2246, found: 302.2232.



(*R*,*E*)-1-(3-((*tert*-Butyldimethylsilyl)oxy)phenyl)-3-methylhept-2-en-1-yl pivalate (4-29c). Prepared according to General Procedure B on a 4.12 mmol scale to give **4-29c** (1.24 g, 72%) as a clear oil. The enantiomeric excess was determined to be 96%, because that is the ee of the allylic alcohol precursor. $[\alpha]_D^{24}$ = –28.5 (c 1.59, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 4H), 7.29 – 7.22 (m, 4H), 6.47 (d, *J* = 9.0 Hz, 1H), 5.36 (dd, *J* = 9.2, 1.3 Hz, 1H), 3.56 (t, *J* = 6.5 Hz, 2H), 2.11 – 2.04 (m, 2H), 1.82 (d, *J* = 1.3 Hz, 3H), 1.66 – 1.59 (m, 2H), 1.21 (s, 9H), 0.88 (s, 9H), 0.02 (d, *J* = 3.0 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.7, 155.9, 142.7, 140.9, 129.5, 123.4, 119.33, 119.31, 118.0, 72.3, 39.4, 39.0, 29.9, 27.3, 25.9, 22.4, 18.4, 17.0, 14.1, –4.2; ^{29}Si NMR (119 MHz, $CDCl_3$) δ 20.8; FTIR (NaCl/thin film) 2957, 2859, 1731, 1278, 1153, 840, 781 cm^{-1}; HRMS (ESI+) $[M\text{-OPiv}]^+$ calculated for $C_{20}H_{33}OSi$: 317.2295, found: 317.2290.

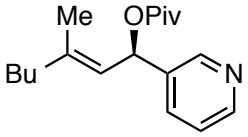


(*R*,*E*)-1-(p-Cyanophenyl)-3-methyl-2-heptenyl pivalate (4-29d). Prepared according to General Procedure B on a 0.72 mmol scale to give **4-29d** (202 mg, 89%) as a yellow oil. The enantiomeric excess was determined to be >99% by chiral SFC analysis (CHIRALPAK IF, 2.5 mL/min, 5% MeOH in CO_2, λ=210 nm); t_R(major)=1.97 min, t_R(minor)=2.47 min. $[\alpha]_D^{24}$ = –50.6 (c 2.62, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 6.48 (d, *J* = 9.1 Hz, 1H), 5.29 – 5.22 (m, 1H), 2.08 – 1.98 (m, 2H), 1.82 (d, *J* = 1.3 Hz, 3H), 1.45 – 1.32 (m, 2H), 1.31 – 1.23 (m, 2H), 1.22 (s, 9H), 0.87 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.6, 146.6, 142.7, 132.6, 126.9, 122.2, 119.0, 111.4, 71.8, 39.3, 39.0, 29.8, 27.3, 22.3, 17.1, 14.1; FTIR (NaCl/thin film) 2958, 2229, 1732, 1148, 824 cm^{-1}; HRMS (ESI+) $[M–OPiv]^+$ calculated for $C_{15}H_{18}N$: 212.1434, found: 212.1430.

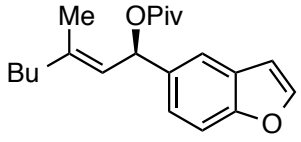


(*R*,*E*)-3-Methyl-1-[*p*-(trifluoromethyl)phenyl]-2-heptenyl pivalate (4-29e). Prepared according to General Procedure B on a 2.74 mmol scale to give **4-29e** (895 mg, 92%) as a yellow oil. The enantiomeric excess was determined to be 97% by chiral HPLC analysis (CHIRALPAK IC, 1.0 mL/min, 100% hexane, λ=210 nm); t_R(major)=14.47 min, t_R(minor)=16.64 min. $[\alpha]_D^{24}$ = –32.0 (c 2.27, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 6.50 (d, *J* = 9.1 Hz, 1H), 5.29 (dd, *J* = 9.2, 1.3 Hz, 1H), 2.03 (t, *J* = 7.5 Hz, 2H), 1.82 (d, *J* = 1.3 Hz, 3H), 1.45 – 1.35 (m, 2H), 1.31 – 1.24 (m, 2H), 1.23 (s, 9H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.6, 145.3f, 142.1, 129.8 (q, *J*=32.5 Hz), 126.6, 125.6 (q, *J*=3.7 Hz), 124.3 (q, J=272.9 Hz),122.7, 72.0, 39.4, 39.0, 29.8, 27.3, 22.4, 17.0, 14.1; ^{19}F NMR (376 MHz $CDCl_3$) δ –62.5; FTIR (NaCl/thin

film) 2960, 1732, 1325, 1149, 1067 cm^{-1}; HRMS (ESI+) $[M–OPiv]^+$ calculated for $C_{15}H_{18}F_3$: 255.1355, found: 225.1348.

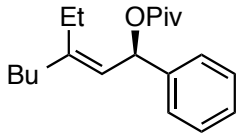


(*R*,*E*)-3-Methyl-1-(3-pyridyl)-2-heptenyl pivalate (4-29f). Prepared according to General Procedure B on a 1.44 mmol scale to give **4-29f** (367 mg, 88%) as a yellow oil. The enantiomeric excess was determined to be 96% by chiral HPLC analysis (CHIRALPAK IA, 1.0 mL/min, 3% isopropanol/hexane, λ=210 nm); t_R(major)=10.90 min, t_R(minor)=7.82 min. $[\alpha]_D^{24}$ = –38.3 (c 1.50, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 2.2 Hz, 1H), 8.52 (dd, *J* = 4.8, 1.7 Hz, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.31 – 7.23 (m, 1H), 6.50 (d, *J* = 9.0 Hz, 1H), 5.32 (dd, *J* = 9.1, 1.3 Hz, 1H), 2.07 – 2.00 (m, 2H), 1.81 (d, *J* = 1.3 Hz, 3H), 1.46 – 1.34 (m, 2H), 1.31 – 1.23 (m, 2H), 1.22 (s, 9H), 0.88 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.7, 149.0, 148.3, 142.3, 136.7, 134.0, 123.5, 122.3, 70.6, 39.3, 39.0, 29.8, 27.3, 22.4, 17.1, 14.1; FTIR (NaCl/thin film) 2958, 1729,1478, 1149, 712 cm^{-1}; HRMS (ESI+) $[M+H]^+$ calculated for $C_{18}H_{28}NO_2$: 290.2042, found: 290.2088.

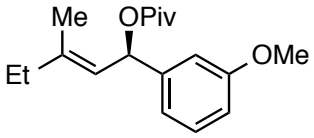


(*R*,*E*)-1-(1-Benzofuran-5-yl)-3-methyl-2-heptenyl pivalate (4-29g). Prepared according to General Procedure B on a 4.51 mmol scale to give **4-29g** (1.36 g, 92%) as a clear oil. The enantiomeric excess was determined to be 92% by chiral HPLC analysis (CHIRALPAK IA, 0.4 mL/min, 1% isopropanol/hexane, λ=210 nm); t_R(major)=11.47 min, t_R(minor)=12.99 min. $[\alpha]_D^{24}$ = –17.8 (c 1.06, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 2.2 Hz, 1H), 7.58 (d, *J* = 1.7 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.29 (d, *J* = 1.8 Hz, 1H), 6.75 (dd, *J* = 2.2, 1.0 Hz, 1H), 6.57 (d, *J* = 8.9 Hz, 1H), 5.41 (dd, *J* = 9.0, 1.3 Hz, 1H), 2.07 – 1.99 (m, 2H), 1.81 (d, *J* = 1.3 Hz, 3H), 1.47 – 1.31 (m, 2H), 1.31 – 1.24 (m, 2H), 1.21 (s, 9H), 0.88 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 154.5, 145.6, 140.7, 136.0, 127.6,

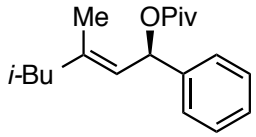
123.7, 123.1, 119.2, 111.5, 106.9, 72.9, 39.4, 39.0, 29.9, 27.3, 22.4, 17.0, 14.1; FTIR (NaCl/thin film) 2958, 2931, 1726, 1155, 737 cm^{-1}; HRMS (ESI+) $[M–OPiv]^+$ calculated for $C_{16}H_{19}O$: 227.1430, found: 227.1426.



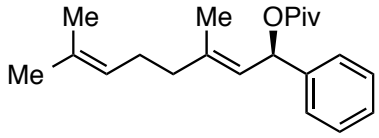
(*R*,*E*)-3-Ethyl-1-phenyl-2-heptenyl pivalate (4-29h). Prepared according to General Procedure B on a 1.72 mmol scale to give **4-29h** as a clear oil. The enantiomeric excess was assumed to be 98%, because that is the ee of the allylic alcohol precursor. $[\alpha]_D^{24}$ = -31.05 (c 1.13, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 4.3 Hz, 4H), 7.30 – 7.22 (m, 1H), 6.51 (d, *J* = 9.3 Hz, 1H), 5.29 (d, *J* = 9.4 Hz, 1H), 2.40 – 2.27 (m, 1H), 2.23 – 2.11 (m, 1H), 2.08 – 2.00 (m, 2H), 1.44 – 1.33 (m, 2H), 1.33 – 1.23 (m, 2H), 1.21 (s, 9H), 1.01 (t, *J* = 7.6 Hz, 3H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.7, 146.8, 141.4, 128.6, 127.6, 126.5, 122.7, 72.2, 38.9, 36.1, 30.1, 27.3, 23.9, 22.5, 14.2, 13.5; FTIR (NaCl/thin film) 2962, 2931, 1728, 1151, 697 cm^{-1}; HRMS (ESI+) $[M]^+$ calculated for $C_{20}H_{30}O_2$: 302.2240, found: 302.2232.



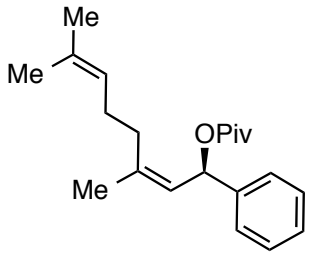
(*R*,*E*)-1-(*m*-Methoxyphenyl)-3-methyl-2-pentenyl pivalate (4-29i). Prepared according to General Procedure B on a 1.9 mmol scale to give **4-29i** (412 mg, 74%) as a clear oil. The enantiomeric excess was assumed to be 97%, because that is the ee of the allylic alcohol precursor. $[\alpha]_D^{24}$ = –41.1 (c 1.55, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (t, *J* = 7.9 Hz, 1H), 6.94 – 6.89 (m, 1H), 6.88 (t, *J* = 2.1 Hz, 1H), 6.80 (dd, *J* = 8.3, 2.7, 0.9 Hz, 1H), 6.46 (d, *J* = 9.0 Hz, 1H), 5.31 (dd, *J* = 9.1, 1.3 Hz, 1H), 3.80 (s, 3H), 2.04 (q, *J* = 7.4 Hz, 2H), 1.82 (d, *J* = 1.3 Hz, 3H), 1.22 (s, 9H), 1.00 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.5, 159.6, 142.8, 142.4, 129.5, 122.0, 118.5, 112.7, 111.9, 72.3, 55.2, 38.8, 32.2, 27.2, 16.9, 12.3; FTIR (NaCl/thin film) 2967, 2361, 1727, 1487, 1279, 1152, 699 cm^{-1}; HRMS (ESI+) $[M]^+$ calculated for: $C_{18}H_{26}O_3$: 290.1882, found: 290.1872.



(*R*,*E*)-3,5-Dimethyl-1-phenyl-2-hexenyl pivalate (4-29j). Prepared according to General Procedure B on a 4.9 mmol scale to give **4-29j** (1.31 g, 93%) as a clear oil. The enantiomeric excess was determined to be 92% because that is the ee of the allylic alcohol precursor. $[\alpha]_D^{24}$ = –39.7 (c 1.58, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 4.4 Hz, 4H), 7.28 (d, *J* = 4.4 Hz, 1H), 6.49 (d, *J* = 9.1 Hz, 1H), 5.31 (d, *J* = 9.1 Hz, 1H), 1.89 (t, *J* = 7.1 Hz, 2H), 1.82 – 1.71 (m, 4H), 1.22 (s, 9H), 0.82 (dd, *J* = 6.5, 4.9 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.7, 141.1, 140.0, 128.6, 127.6, 126.3, 124.8, 72.5, 49.5, 39.0, 27.3, 26.1, 22.7, 22.3, 16.9; FTIR (NaCl/thin film) 2956, 2930, 1729, 1152, 697 cm^{-1}; HRMS (ESI+) $[M–OPiv]^+$ calculated for $C_{14}H_{19}$: 187.1481, found: 187.1478.

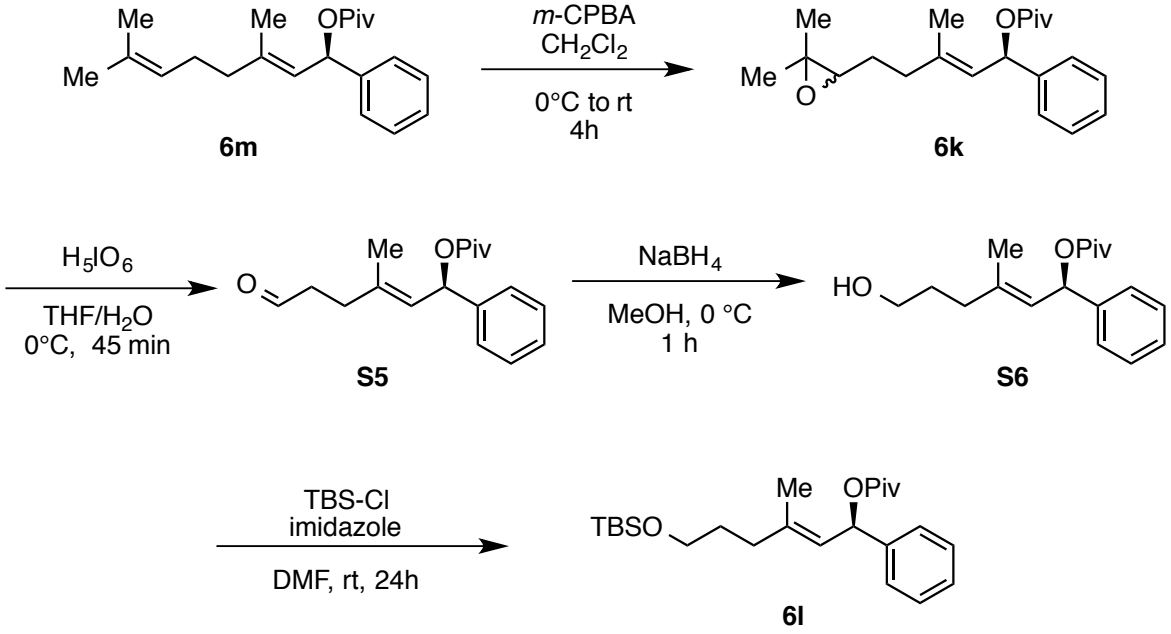


(*R*,2*E*)-3,7-Dimethyl-1-phenyl-2,6-octadienyl pivalate (4-29m). Prepared according to General Procedure B on a 3.7 mmol scale to give **4-29m** (1.09 g, 93%) as a clear oil. The enantiomeric excess was assumed to be 98%, because that is the ee of the allylic alcohol precursor. $[\alpha]_D^{24}$ = –55.0 (c 0.71, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 5.5 Hz, 3H), 7.30 – 7.23 (m, 2H), 6.48 (d, *J* = 9.1 Hz, 1H), 5.33 (dd, *J* = 9.1, 1.4 Hz, 1H), 5.04 (t, *J* = 6.6 Hz, 1H), 2.13 – 2.01 (m, 4H), 1.82 (d, *J* = 1.2 Hz, 3H), 1.65 (s, 3H), 1.57 (s, 3H), 1.22 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 141.2, 140.4, 131.9, 128.6, 127.6, 126.4, 123.9, 123.7, 72.5, 39.7, 39.0, 27.3, 26.3, 25.9, 17.9, 17.0; FTIR (NaCl/thin film) 2969, 1728, 1278, 1151, 697 cm^{-1}; HRMS (EI+) $[M–OPiv]^+$ calculated for $C_{16}H_{21}$: 212.1565, found: 212.1572.

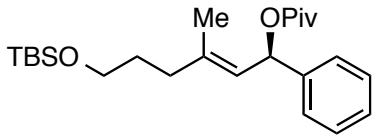


(*R*,2*Z*)-3,7-Dimethyl-1-phenyl-2,6-octadienyl pivalate (4-29n). Prepared according to General Procedure B on a 3.38 mmol scale to give **4-29n** (88.0 mg, 88%) as a clear oil. The enantiomeric excess was determined to be 98%, because that is the ee of the allylic alcohol precursor. $[\alpha]_D^{24} = -45.8$ (c 1.46, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (d, J = 4.4 Hz, 4H), 7.28 – 7.21 (m, 1H), 6.48 (d, J = 9.4 Hz, 1H), 5.38 (d, J = 9.4 Hz, 1H), 5.15 – 5.06 (m, 1H), 2.43 – 2.31 (m, 1H), 2.22 – 2.10 (m, 2H), 2.10 – 2.03 (m, 1H), 1.76 (s, 3H), 1.65 (s, 3H), 1.60 (s, 3H), 1.21 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 141.2, 140.4, 132.2, 128.6, 127.7, 126.5, 124.3, 124.0, 72.4, 39.0, 32.7, 27.3, 26.8, 25.9, 23.7, 17.9; FTIR (NaCl/thin film) 2969, 1728, 1278, 1151, 697 cm^{-1}; HRMS (EI+) $[M–OPiv]^+$ calculated for: $C_{16}H_{21}$: 212.1565, found: 212.1572.

Preparation of 6k and 6l



(*R,E*)-5-(3,3-Dimethyl-2-oxiranyl)-1-(*m*-methoxyphenyl)-3-methyl-2-pentenyl pivalate (4-29k). This procedure is adapted from a literature procedure. [28] Pivalate **4-29m** (1.24 g, 3.9 mmol, 1.0 equiv) was dissolved in anhydrous CH_2Cl_2 (28 mL, 0.14 M) and cooled to 0 °C. 3-Chloroperbenzoic acid (0.82 g, 3.9 mmol, 1.0 equiv) was then added to the solution, which was then stirred at rt for 4 h. To the resulting mixture was added sat. aq. $NaHCO_3$ (15 mL). The organic layer was then separated, and the aqueous layer was washed with CH_2Cl_2 (3 x 15 mL). The combined organic fractions were then washed with water (1 x 40 mL), sat. aq. $NaHCO_3$ (40 mL), and sat. aq. NaCl (40 mL). The organic layer was then dried ($MgSO_4$), filtered, and concentrated. The resulting residue was purified by silica gel chromatography (5% Et_2O/hexanes with 2% Et_3N) to give compound **4-29k** (911 mg, 94%) as a clear oil. The enantiomeric excess was assumed to be 98%, because that was the ee of compound **4-29m**. $[\alpha]_D^{24}$= –37.6 (c 1.19, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 5.7 Hz, 4H), 6.46 (dd, *J* = 9.0, 2.1 Hz, 1H), 5.42 – 5.36 (m, 1H), 2.66 (q, *J* = 6.1 Hz, 1H), 2.27 – 2.09 (m, 2H), 1.85 (t, *J* = 1.6 Hz, 3H), 1.72 – 1.59 (m, 2H), 1.25 (d, *J* = 4.6 Hz, 3H), 1.21 (d, *J* = 1.1 Hz, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 141.0, 141.0, 139.5, 128.7, 127.8, 127.8, 127.1, 126.4, 126.3, 124.4, 124.3, 72.6, 72.5, 64.1, 63.9, 58.7, 58.6, 39.0, 36.4, 27.3, 27.2, 27.1, 25.0, 24.9, 18.9, 18.9, 17.1, 17.0; FTIR (NaCl/thin film) 2965, 1728, 1152, 698 cm^{-1}; HRMS (EI+) [M–OPiv]+ calculated for $C_{16}H_{21}O$: 229.1592, found: 229.1592.



(*R,E*)-*tert*-Butyl((4-(3-methoxyphenyl)-4-methyl-6-phenylhex-5-en-1-yl)oxy)dimethylsilane (4-29l). This procedure is adapted from a literature procedure. [28] Pivalate (**4-29k**) (0.91 g, 2.75 mmol, 1.0 equiv) was dissolved in THF (4.6 mL, 0.6 M) and cooled to 0 °C. In a separate flask periodic acid (627 mg,

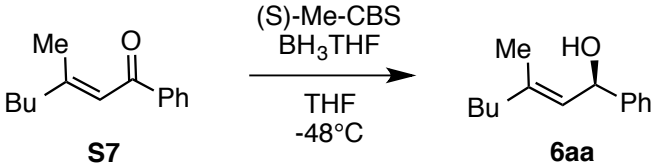
2.75 mmol, 1.0 equiv) was dissolved in water (2.8 mL, 1.0 M), and then added dropwise to the solution of pivalate (**4-29k**) and THF. The mixture was then stirred at 0 °C for an additional 45 min. Sat. aq. NaCl (5 mL) was then added. The aqueous layer was extracted with Et_2O (3 x 5 mL). The combined organic fractions were then washed with $NaHCO_3$ (2 x 20 mL) and sat. aq. NaCl (2 x 20 mL). The organic layer was then dried ($MgSO_4$), filtered, and concentrated. The resulting residue was purified via silica gel chromatography (10% Et_2O/hexanes with 2% Et_3N) to afford compound **S5** (460 mg, 54%). $[\alpha]_D^{24}$= –17.3 (c 1.31 , $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.75 (t, *J* = 1.5 Hz, 1H), 7.36 – 7.32 (m, 2H), 7.32 – 7.30 (m, 2H), 7.30 – 7.27 (m, 1H), 6.45 (d, *J* = 9.0 Hz, 1H), 5.37 (dd, *J* = 9.0, 1.4 Hz, 1H), 2.59 – 2.52 (m, 2H), 2.41 – 2.34 (m, 2H), 1.85 (d, *J* = 1.3 Hz, 3H), 1.21 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.9, 177.7, 140.7, 138.5, 128.7, 127.8, 126.3, 124.5, 72.3, 41.9, 39.0, 31.7, 27.3, 17.2 ; FTIR (NaCl/thin film) 2972, 1725, 1151, 698 cm^{-1}; HRMS (ESI+) [M–OPiv]+ calculated for $C_{13}H_{15}O$ 187.1117, found: 187.1111.

Compound **S5** (460 mg, 1.6 mmol, 1.0 equiv) was then dissolved in MeOH (18 mL, 0.09 M) and cooled to 0 °C. $NaBH_4$ (60 mg, 1.0 equiv) was then added, and the mixture was stirred for an additional hour at 0 °C. Acetone (3.0 mL) and water (9 mL) were added, and the mixture was warmed to room temperature. The aqueous layer was extracted with Et_2O (3 x 15 mL). The combined organic fractions were washed with sat. aq. NaCl (2 x 40 mL), dried ($MgSO_4$), filtered, and concentrated. The resulting residue was then purified via silica gel chromatography (20% EtOAc/hexanes with 2% Et_3N) to afford compound **S6** (336 mg, 73%) as a clear oil. $[\alpha]_D^{24}$= –27.9 (c 0.59, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 4H), 7.30 – 7.27 (m, 1H), 6.45 (d, *J* = 9.0 Hz, 1H), 5.38 (dd, *J* = 9.1, 1.3 Hz, 1H), 3.61 (t, *J* = 6.4 Hz, 2H), 2.17 (s, 1H), 2.16 – 2.08 (m, 2H), 1.85 (d, *J* = 1.3 Hz, 3H), 1.76 – 1.64 (m, 2H), 1.22 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 140.9, 140.2, 128.7, 127.7, 126.3, 124.1, 72.6, 62.7, 39.0, 36.1, 30.6, 27.3, 17.0; FTIR (NaCl/thin film) 3360, 2971, 1727, 1153, 698 cm^{-1}; HRMS (ESI+) [M–OPiv]+ calculated for $C_{13}H_{17}O$ calculated: 189.1274 found: 189.1267.

Compound **S6** (292 mg, 1.0 mmol, 1.0 equiv) and imidazole (272 mg, 4.0 mmol, 4.0 equiv) were then dissolved in DMF (13 mL, 0.08 M) at room temperature. TBS-Cl (166 mg, 1.1 mmol, 1.1 equiv) was then added to the solution, which was stirred for an additional 24 h at room temperature. Water (10 mL) was then added. The aqueous layer was extracted with Et_2O (3 x 15 mL). The combined organic fractions were then washed with water (2 x 40 mL) and sat. aq. NaCl (2 x 40 mL), dried ($MgSO_4$), filtered, and concentrated. The resulting residue was then purified via silica gel chromatography (column wet-packed with 1:1 Et_3N:hexanes; then run using 2% Et_2O/hexanes) to afford compound **4-29l** (211.4 mg, 52%) as a clear oil. The enantiomeric excess was assumed to be 98%, because that was the ee of compound **4-29m**. $[\alpha]_D^{24}$= –17.5 (c 0.54, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (d, *J* = 6.5 Hz, 4H), 7.28 – 7.24 (m, 1H), 6.47 (d, *J* = 9.0 Hz, 1H), 5.36 (dd, *J* = 9.2, 1.3 Hz, 1H), 3.56 (t, *J* = 6.5 Hz, 2H), 2.11 – 2.04 (m, 2H), 1.82 (d, *J* = 1.3 Hz, 3H), 1.67 – 1.58 (m, 2H), 1.21 (s, 9H), 0.88 (s, 9H), 0.02 (d, *J* = 3.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 141.2, 140.3, 128.6, 127.6, 126.3, 123.7, 72.6, 62.7, 39.0, 35.8, 30.9, 27.3, 26.1, 18.5, 17.1, –5.1; ^{29}Si NMR (119 MHz, $CDCl_3$) δ 18.6; FTIR (NaCl/thin film) 2955, 2857, 1729, 1151, 835, 697 cm^{-1}; HRMS (ESI+) [M–OPiv]+ calculated for $C_{19}H_{31}OSi$: 303.2139 found: 303.2132.

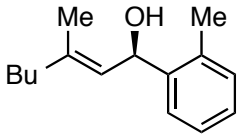
Preparation of Allylic Alcohols

General Procedure C: Preparation of (*R*,*E*)-3-Methyl-1-phenyl-2-hepten-1-ol (4-29aa) via CBS Reduction



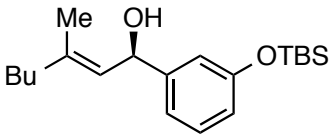
This procedure is adapted from a literature procedure.[23] (*S*)-Diphenyl prolinol (4.81 g, 9.5 mmol, 2.0 equiv) and methyl boronic acid (1.25 g, 20.9 mmol, 2.2 equiv) were dissolved in toluene (63.3 mL, 0.33 M). The flask was fitted with a Dean–Stark apparatus, and the mixture was refluxed for 4 h to form the CBS catalyst. The solution was then cooled to room temperature. In a separate oven-dried round-

bottomed flask purged with N_2, (*E*)-3-methyl-1-phenyl-2-hepten-1-one (1.92 g, 9.5 mmol, 1.0 equiv) was dissolved in anhydrous THF (47 mL, 0.2 M) with 4Å molecular sieves and stirred at rt for 2 h. The cooled solution of CBS catalyst was then added to the solution of (*E*)-3-methyl-1-phenyl-2-hepten-1-one and THF. The resulting mixture was cooled to –48 °C. BH_3·THF (1.0 M, 28.5 mL, 28.5 mmol, 3.0 equiv) was then added dropwise over 20 min using a syringe pump. The mixture was stirred at –48 °C for an additional 1.5 h. MeOH (25 mL) was then added at –48 °C, and the mixture was then allowed to warm to room temperature. The mixture was diluted with Et_2O (20 mL) and then washed with sat. aq. NH_4Cl (2 x 75 mL), sat. aq. $NaHCO_3$ (2 x 75 mL), and sat. aq. NaCl (2 x 75 mL). The organic layer was then dried ($MgSO_4$), filtered, and concentrated. The resulting residue was purified by silica gel chromatography (15% Et_2O/hexanes) to give compound **4-29aa** (1.82 g, 94%) as pale yellow oil. The enantiomeric excess was determined to be 98% by chiral HPLC analysis (CHIRALPAK IB, 1.0 mL/min, 0.8% *i*-PrOH/hexanes, λ=210 nm); t_R(major) = 33.62 min, t_R(minor) = 29.57 min. $[\alpha]_D^{24}$= –95.2 (c 1.01, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.23 (m, 2H), 5.49 (dd, *J* = 8.8, 3.5 Hz, 1H), 5.45 – 5.39 (m, 1H), 2.07 – 1.99 (m, 2H), 1.79 (s, 3H), 1.75 (d, *J* = 3.5 Hz, 1H), 1.45 – 1.36 (m, 2H), 1.36 – 1.23 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.5, 139.5, 128.6, 127.4, 127.3, 126.0, 70.9, 39.5, 30.0, 22.6, 16.9, 14.2; FTIR (NaCl/thin film) 3325, 2956, 2858, 1451, 1004, 698 cm^{-1}; HRMS (ESI+) $[M\text{-}OH]^+$ calculated for: $C_{14}H_{19}$: 187.1481, found: 187.1479.

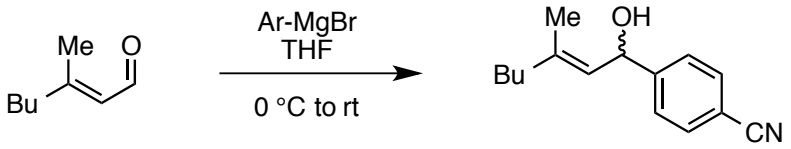


(*R*,*E*)-3-Methyl-1-(*o*-tolyl)-2-hepten-1-ol (4-29bb). Prepared according to General Procedure C on a 3.84 mmol scale to give **4-29bb** (602 mg, 72%) as a pale yellow oil. The enantiomeric excess was determined to be 94% by chiral HPLC analysis (CHIRALPAK IB, 1.0 mL/min, 0.8% isopropanol/hexane, λ=210 nm); t_R(major)=26.13 min, t_R(minor)=19.54 min. $[\alpha]_D^{24}$ = –79.9 (c 1.10,

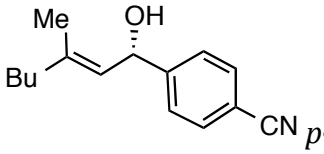
$CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.21 – 7.07 (m, 2H), 5.61 (dd, *J* = 8.9, 3.1 Hz, 1H), 5.33 (dd, *J* = 8.9, 1.3 Hz, 1H), 2.29 (s, 3H), 2.01 (t, *J* = 7.4 Hz, 2H), 1.82 (s, 3H), 1.66 (d, *J* = 3.1 Hz, 1H), 1.45 – 1.33 (m, 2H), 1.33 – 1.22 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 136.4, 135.7, 130.4, 127.4, 126.2, 125.8, 125.0, 73.7, 42.9, 28.6, 26.5, 23.3, 20.1, 14.3; FTIR (NaCl/thin film) 3319, 2929, 2858, 1461, 1002, 752 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{15}H_{22}O$: 218.1671, found: 218.1669.



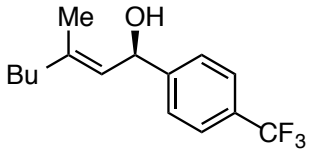
(*R*,*E*)-1-(*m*-Dimethyl, t-butyl-silyl phenol)-3-methyl-2-hepten-1-ol (4-29cc). Prepared according to General Procedure C on a 1.59 mmol scale to give **4-29cc** (270 mg, 51%) as a clear oil. The enantiomeric excess was determined to be 96% by chial HPLC analysis (CHIRALPAK IB, 1.0 mL/min, 0.5% isopropanol/hexane, λ=210 nm); t_R(major)=20.34 min, t_R(minor)=16.12 min. $[\alpha]_D^{24}$ = –79.8 (c 1.25, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.8 Hz, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.87 (s, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 5.42 (dd, *J* = 8.7, 3.4 Hz, 1H), 5.38 (d, *J* = 8.7 Hz, 1H), 2.02 (d, *J* = 15.2 Hz, 2H), 1.78 (s, 3H), 1.71 (d, *J* = 3.5 Hz, 1H), 1.45 – 1.35 (m, 2H), 1.28 (h, *J* = 7.3 Hz, 2H), 0.98 (s, 9H), 0.89 (t, *J* = 7.3 Hz, 3H), 0.19 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.0, 146.1, 139.4, 129.6, 127.3, 119.0, 118.9, 117.8, 70.7, 39.5, 30.1, 25.9, 22.6, 18.4, 16.9, 14.2, –4.2; ^{29}Si NMR (119 MHz, $CDCl_3$) δ 20.6; FTIR (NaCl/thin film) 2930, 2860, 1602, 1482, 1274, 957, 839 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{20}H_{34}O_2Si$: 318.2379, found: 318.2369.



S8 **(±)-6dd**

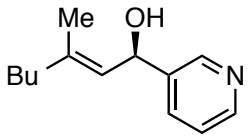


***p*-[(*S*,*E*)-1-hydroxy-3-methyl-2-heptenyl]benzonitrile (4-29dd).** Compound **S8** was added to an oven-dried round-bottomed flask, and dissolved in anhydrous THF (0.5 M). The reaction was then cooled to 0°C, and p-CN-PhMgBr (1.3 equiv) was added dropwise to the solution. The mixture was allowed to warm to room temperature, and stirred for an additional 3 h. The reaction was then quenched with sat. aq. NH_4Cl, and the aqueous layer was extracted with EtOAc (3x). The combined organic fractions were washed with sat. aq. NaCl, dried ($MgSO_4$), filtered, and concentrated. The resulting residue was purified via column chromatography (10% Et_2O/hexanes) to afford *p*-[(*E*)-1-hydroxy-3-methyl-2-heptenyl]benzonitrile (±)-**4-29dd)** .The enantiomers of (±)-**4-29dd** were then separated using preparatory SFC with a chiral stationary phase to give **4-29dd** in >99% ee. The absolute configuration of **4-29dd** was not determined. $[\alpha]_D^{24}$ = –150.2 (c 1.29, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 5.53 (dd, *J* = 8.9, 3.4 Hz, 1H), 5.36 – 5.25 (m, 1H), 2.08 – 1.99 (m, 2H), 1.82 (d, *J* = 1.4 Hz, 3H), 1.45 – 1.36 (m, 2H), 1.33 – 1.22 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 141.0, 132.3, 126.5, 126.2, 119.0, 110.8, 70.0, 39.3, 29.8, 22.4, 16.8, 14.0; FTIR (NaCl/thin film) 3428, 2929, 2228, 1607, 013, 820, 566 cm^{-1}; HRMS (ESI) $[M+H]^+$ calculated for $C_{15}H_{20}NO$: 230.1539, found: 230.1535.



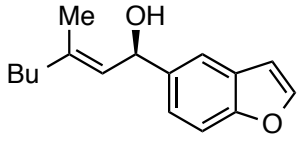
(*R*,*E*)-3-Methyl-1-[*p*-(trifluoromethyl)phenyl]-2-hepten-1-ol (4-29ee). Prepared according to General Procedure C on a 4.76 mmol scale to give **4-29ee** (800 mg, 62%) as a clear oil. The enantiomeric excess was determined to be 96% by chiral HPLC analysis (CHIRALPAK 1C, 1.0 mL/min, 1% isopropanol/hexane, λ=210 nm); t_R(major)=9.92 min, t_R(minor)=12.86 min; $[\alpha]_D^{24}$ = –79.8 (c 1.28, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.1 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 5.54 (dd, *J* = 8.9, 3.5 Hz, 1H), 5.35 (dd, *J* = 8.8, 1.3 Hz, 1H), 2.08

– 1.99 (m, 2H), 1.82 (d, J = 1.3 Hz, 3H), 1.79 (dd, J = 3.4, 2.3 Hz, 1H), 1.45 – 1.36 (m, 2H), 1.34 – 1.25 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.3, 140.5, 129.9, 129.6, 129.3, 129.0, 128.4, 126.7, 126.2, 125.7, 125.6, 125.5, 125.5, 125.4, 123.0, 120.3, 70.2, 39.4, 30.0, 22.5, 16.9, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.4; FTIR (NaCl/thin film) 3314, 2932, 2861, 1619, 1326, 1127, 1068, 824, 605 cm^{-1}; HRMS (ESI+) $[M–OH]^+$ calculated for $C_{15}H_{18}F_3$: 255.1355, found: 255.1350.

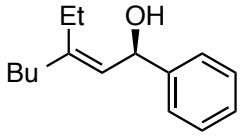


(*R*,*E*)-3-Methyl-1-(3-pyridyl)-2-hepten-1-ol (4-29ff). 3-Bromopyridine (1.2 equiv) was added to an oven-dried round-bottomed flask, dissolved in anhydrous THF (1.67 M), and cooled to 0 °C. *i* –PrMgCl•LiCl (1.32 equiv) was then added dropwise to the solution over 30 min with a syringe pump. The solution was stirred for an additional 1 hr at 0 °C. Compound **S8** (1.0 equiv) was added to a separate oven-dried round-bottomed flask, and dissolved in anhydrous THF (0.5 M). The reaction was then cooled to 0°C, and the prepared grignard reagent was added dropwise to the solution. The mixture was allowed to warm to room temperature, and stirred for an additional 3 h. The reaction was then quenched with sat. aq. NH_4Cl, and the aqueous layer was extracted with EtOAc (3x). The combined organic fractions were washed with sat. aq. NaCl, dried ($MgSO_4$), filtered, and concentrated. The resulting residue was purified via column chromatography (30% EtOAc/hexanes) to afford (*E*)-3-Methyl-1-(3-pyridyl)-2-hepten-1-ol **((±)-4-29ff)** The enantiomers of (±)-**4-29ff** were then separated using preparatory SFC with a chiral stationary phase to give **4-29ff**. The absolute configuration of **4-29ff** was not determined. The enantiomeric excess was determined to be 97% by chiral HPLC analysis using a chiral stationary phase; $[\alpha]_D^{24}$ = 82.2 (c 2.11, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 – 8.55 (m, 1H), 8.50 (dd, J = 4.7, 1.8 Hz, 1H), 7.73 (d, J = 7.9 Hz, 1H), 7.33 – 7.26 (m, 1H), 5.53 (d, J = 8.8 Hz, 1H), 5.39 (dd, J = 8.9, 1.3 Hz, 1H), 2.07 – 2.02 (m, 2H), 1.80 (d, J = 1.3 Hz, 3H), 1.46 – 1.33 (m, 2H), 1.33 – 1.20 (m, 2H), 0.89 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.3, 147.8, 140.1,

140.0, 133.9, 126.7, 123.6, 68.5, 39.4, 29.9, 22.5, 16.9, 14.1; FTIR (NaCl/thin film) 3211, 2928, 1423, 1018, 713 cm^{-1}; HRMS (ESI) $[M+H]^+$ calculated for $C_{13}H_{20}NO$: 206.1539, found: 206.1537.

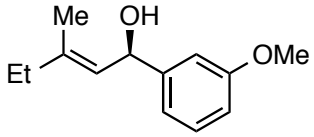


(*R*,*E*)-1-(1-Benzofuran-5-yl)-3-methyl-2-hepten-1-ol (4-29gg). Prepared according to General Procedure C on a 6.76 mmol scale to give **4-29gg** (1.27 g, 77%) as a pale yellow oil. The enantiomeric excess was determined to be 99% by chiral HPLC analysis (CHIRALPACK IC, 1.0 mL/min, 1% isopropanol/hexane, λ=210 nm); t_R(major)=52.02 min t_R(minor)=48.44 min; $[\alpha]_D^{24}$ = –109.2 (c 2.55, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 4.8, 1.9 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.32 (dd, *J* = 8.6, 1.7 Hz, 1H), 6.75 (d, *J* = 2.6 Hz, 1H), 5.58 (dd, *J* = 8.7, 2.4 Hz, 1H), 5.48 (dd, 1H), 2.07 – 1.98 (m, 2H), 1.86 (d, *J* = 2.7 Hz, 1H), 1.80 (d, *J* = 1.3 Hz, 3H), 1.46 – 1.36 (m, 2H), 1.35 – 1.23 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4, 145.5, 139.2, 139.1, 127.64, 127.62, 122.7, 118.5, 111.5, 106.9, 71.0, 39.5, 30.0, 22.6, 16.8, 14.2; FTIR (NaCl/thin film) 3325, 2928, 2858, 1467, 1262, 1032, 735 cm^{-1}; HRMS (ESI+) $[M–OH]^+$ calculated for $C_{16}H_{19}O$: 227.1430, found: 227.1427.

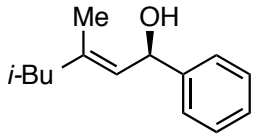


(*R*,*E*)-3-Ethyl-1-phenyl-2-hepten-1-ol (4-29hh). Prepared according to General Procedure C on a 2.13 mmol scale to give **4-29hh** (398 mg, 86%) as a pale yellow oil. The enantiomeric excess was determined to be 98% by chiral HPLC analysis (CHIRALPAK IB, 1.0 mL/min, 0.8% isopropanol/hexane, λ=210 nm); t_R(major)=19.10 min, t_R(minor)=16.86 min; $[\alpha]_D^{24}$ = –76.1 (c 1.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 8.3, 1.6 Hz, 2H), 7.35 (dd, *J* = 8.5, 6.7 Hz, 2H), 7.30 – 7.20 (m, 1H), 5.50 (dd, *J* = 9.0, 3.3 Hz, 1H), 5.37 (d, *J* = 9.0 Hz, 1H), 2.31 – 2.13 (m, 2H), 2.07 – 2.00 (m, 2H), 1.71 (d, *J* = 3.4 Hz, 1H), 1.45 z–1.35 (m, 2H), 1.35 – 1.24 (m, 2H), 1.04 (t, *J* = 7.6 Hz, 3H), 0.89 (t, *J* = 7.2 Hz, 3H);

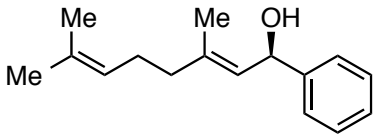
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 144.5, 128.6, 127.4, 126.6, 126.1, 70.4, 36.2, 30.3, 23.9, 22.7, 14.2, 13.8; FTIR (NaCl/thin film) 3330, 2961, 2872, 1432, 1006, 689 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{15}H_{22}O$: 218.1671, found: 218.1678.



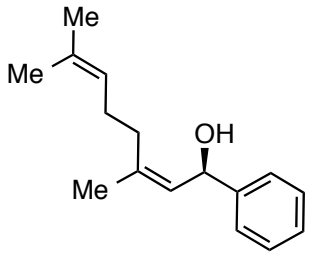
(*R*,*E*)-1-(*m*-Methoxyphenyl)-3-methyl-2-penten-1-ol (4-29ii). Prepared according to General Procedure C on a 2.3 mmol scale to give **4-29ii** (437.1 mg, 92%) as a pale yellow oil. The enantiomeric excess was determined to be 97% by chiral HPLC analysis (CHIRALPAK IB, 1.0 mL/min, 1% isopropanol/hexane, λ=210 nm); t_R(major)=46.15 min, t_R(minor)=32.69 min; $[\alpha]_D^{24}$ = –76.1 (c 1.50, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.22 (m, 1H), 6.99 – 6.93 (m, 2H), 6.84 – 6.77 (m, 1H), 5.47 (dd, *J* = 8.7, 3.4 Hz, 1H), 5.40 (dq, *J* = 8.7, 1.2 Hz, 1H), 3.82 (s, 3H), 2.05 (q, *J* = 7.8 Hz, 2H), 1.80 (d, *J* = 1.3 Hz, 3H), 1.76 (d, *J* = 3.5 Hz, 1H), 1.02 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.0, 146.2, 141.0, 129.7, 126.1, 118.4, 112.9, 111.6, 77.4, 70.8, 55.4, 32.4, 16.9, 12.5; FTIR (NaCl/thin film) 3330, 2961, 2872, 1432, 1006, 689 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{13}H_{18}O_2$: 206.1307, found: 206.1305.



(*R*,*E*)-3,5-Dimethyl-1-phenyl-2-hexen-1-ol (6jj). Prepared via General Procedure C on a 8.43 mmol scale to give **6jj** (1.54 g, 91%) as a clear oil. The enantiomeric excess was determined to be 98% by chiral HPLC analysis (CHIRALPAK IB 1 mL/min, 0.8% isopropanol/hexane, λ=210 nm); t_R(major)= 22.74 min, t_R(minor)= 19.41 min; $[\alpha]_D^{24}$ = –97.1 (c 1.67, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.31 (m, 4H), 7.26 (m, *J* = 14.1, 1.5 Hz, 1H), 5.49 (dd, *J* = 8.7, 3.6 Hz, 1H), 5.44 – 5.38 (m, 1H), 1.97 – 1.84 (m, 2H), 1.84 – 1.72 (m, 4H), 0.88 (d, *J* = 6.5 Hz, 3H), 0.82 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 138.3, 128.8, 128.6, 127.4, 126.0, 70.8, 49.5, 26.2, 22.8, 22.5, 16.8; FTIR (NaCl/thin film) 3320, 2953, 1451, 1006, 698 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{14}H_{20}O$: 204.1514, found: 204.1504.



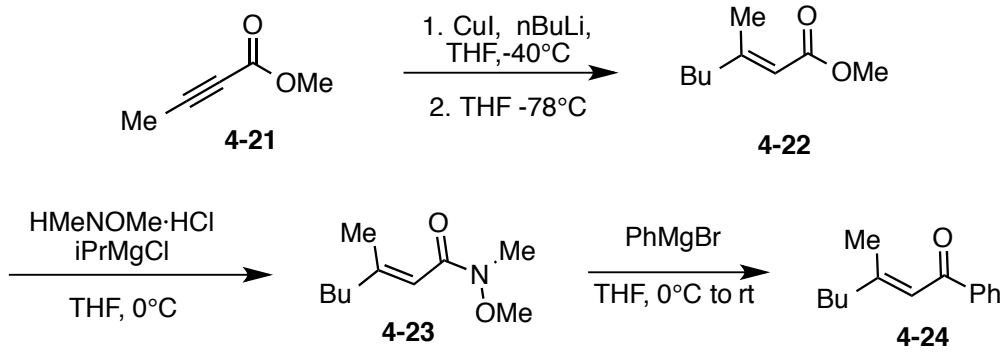
(*R*,2*E*)-3,7-Dimethyl-1-phenyl-2,6-octadien-1-ol (4-29mm). Prepared according to General Procedure C on a 4.1 mmol scale to give **4-29mm** (923 mg, 98%) as a clear oil. The enantiomeric excess was determined to be 98% by chiral HPLC analysis (CHIRALPAK IB, 1.0 mL/min, 0.8% isopropanol/hexane, λ=210 nm); t_R(major)=19.10 min, t_R(minor)=16.86 min; $[\alpha]_D^{24}$ = -76.1° (c 1.50, $CHCl_3$); The spectral data for this compound matches that previously reported in the literature. [29]



(*R*,2*Z*)-3,7-Dimethyl-1-phenyl-2,6-octadien-1-ol (4-29nn). Prepared according to General Procedure C on a 4.4 mmol scale to give **4-29nn** (780 mg, 78%) as a clear oil. The enantiomeric excess was determined to be 98% by chiral HPLC analysis (CHIRALPAK IB, 1.0 mL/min, 0.8% isopropanol/hexane, λ=210 nm); t_R(major)=19.10 min, t_R(minor)=16.86 min; $[\alpha]_D^{24}$ = -76.1° (c 1.50, $CHCl_3$); The spectral data for this compound matches that previously reported in the literature. [29]

Preparation of Enone Precurosrs

The synthesis of enone precursors generally was through the following 3-step synthesis.



The cuperate additions to form **4-22** were performed according to literature procedure.[30]

The formation of Weinreb amide **4-23** was performed according to literature procedure.[31]

(*E*)-1-(*N*-Methylmethoxyamino)-3-methyl-2-hepten-1-one **4-23** was added to an oven-dried round-bottomed flask, and dissolved in anhydrous THF (0.5 M). The reaction was then cooled to 0°C, and PhMgBr (1.3 equiv) was added dropwise to the solution. The mixture was allowed to warm to room temperature, and stirred for an additional 3 h. The reaction was then quenched with sat. aq. NH_4Cl, and the aqueous layer was extracted with EtOAc (3x). The combined organic fractions were washed with sat. aq. NaCl, dried ($MgSO_4$), filtered, and concentrated. The resulting residue was purified via column chromatography (10% Et_2O/hexanes) to afford (*E*)-3-methyl-1-phenyl-2-hepten-1-one (**4-24)**. The spectral data for this compound matched that reported in the literature.

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DMM4-236-2-CARBON2
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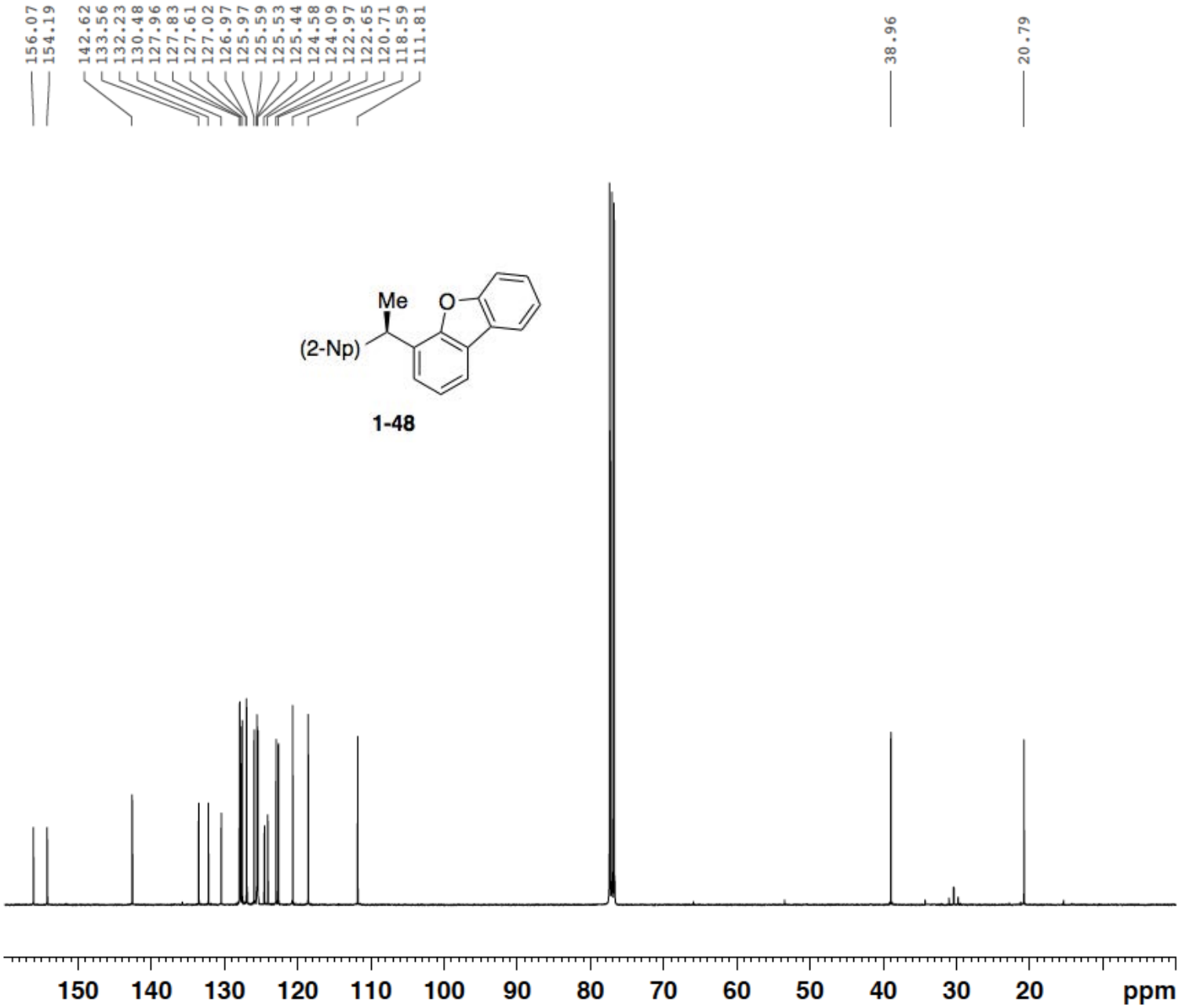

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PROCNO                     1

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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
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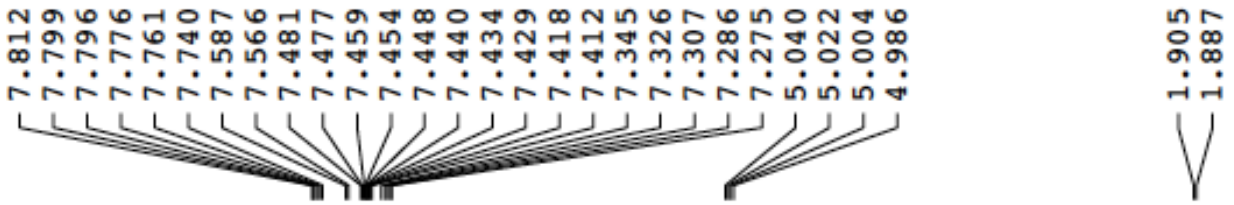
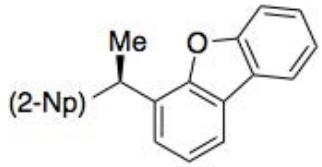
DMM4-362-2-PROTON 5
PROTON_16 CDCl3 /opt/topspin dmcatee 43





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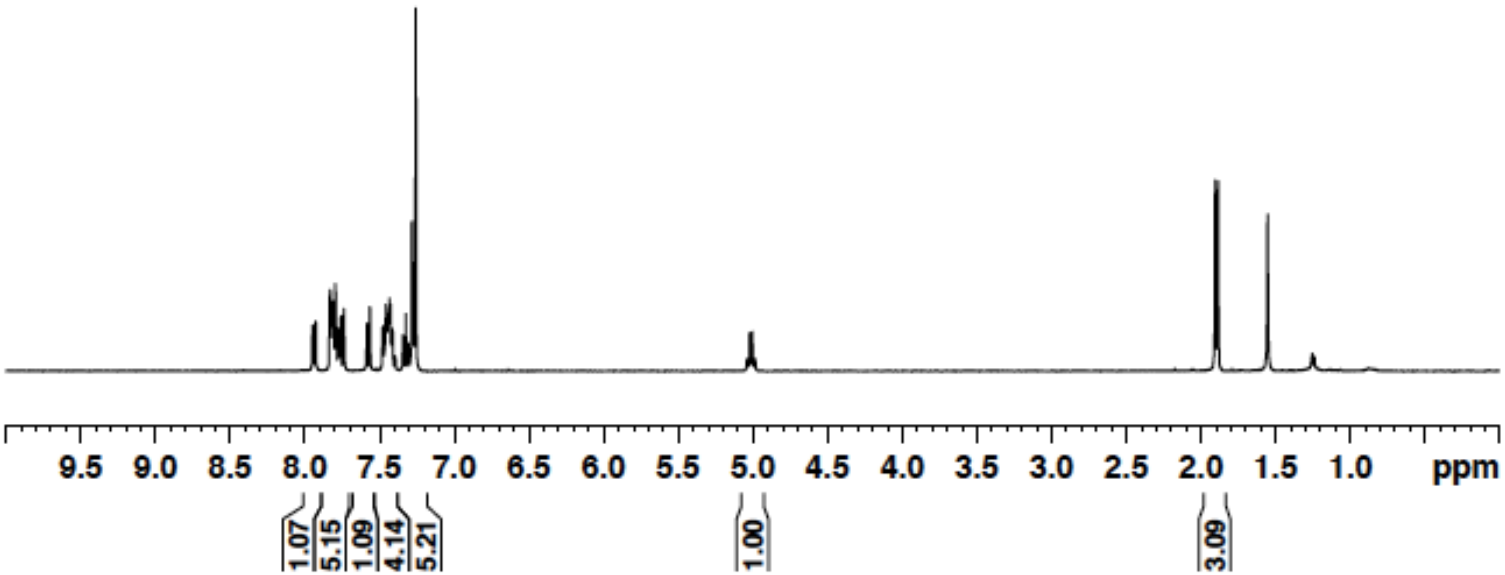


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TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH               8278.146 Hz
FIDRES            0.126314 Hz
AQ                3.9584243 sec
RG                      4
DW                 60.400 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           400.1300102 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                   1.00
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DMM4-234-4-CARBON
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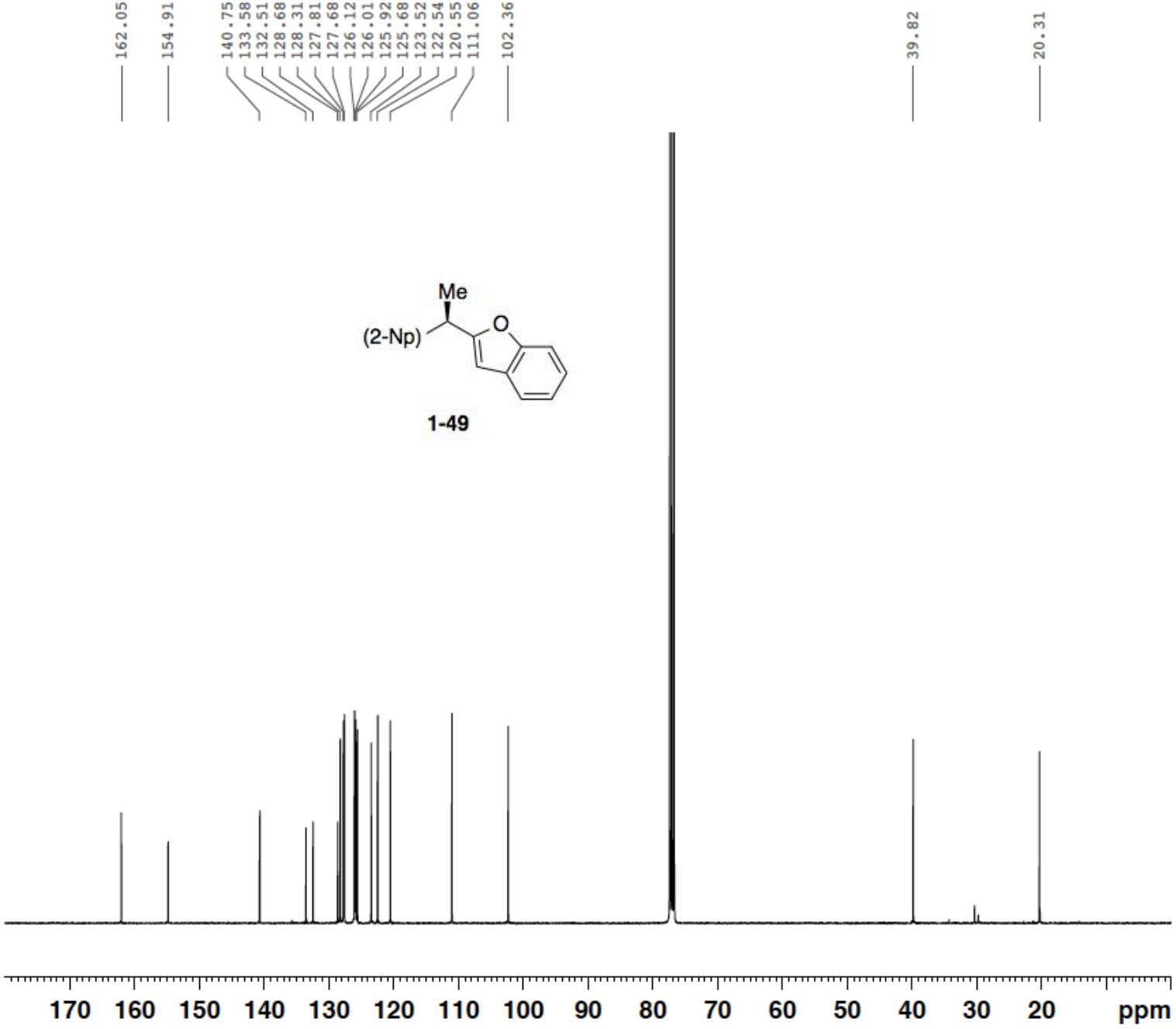


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EXPNO                    1
PROCNO                   1

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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
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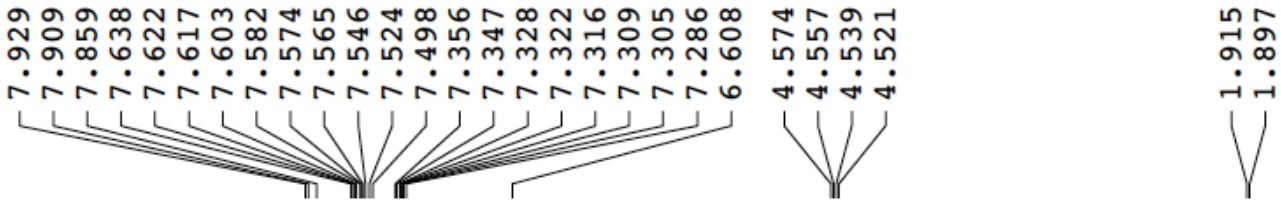
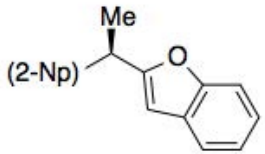
DMM4-234-4-PROTON
PROTON_16 CDCl3 /opt/topspin dmcatee 41





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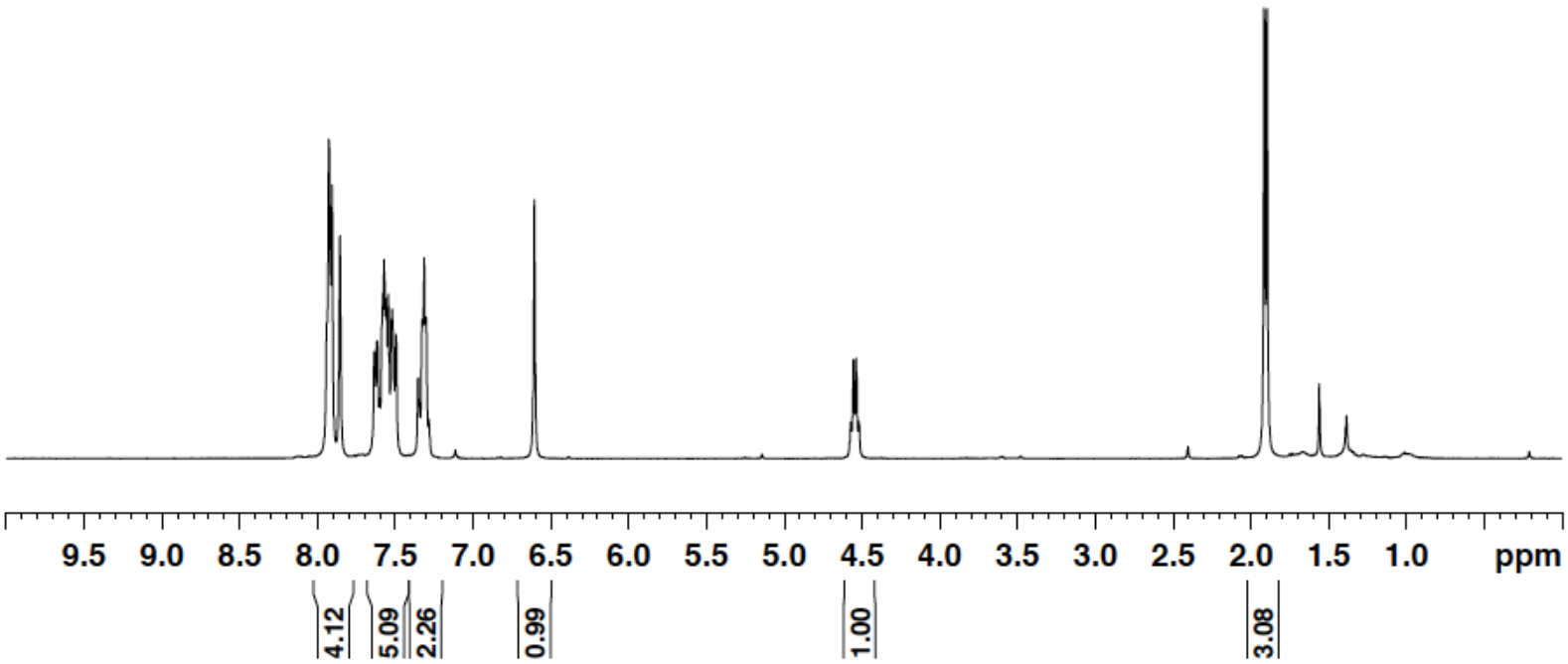


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PROCNO                   1

F2 - Acquisition Parameters
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Time                 18.13
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                      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            400.1299715 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
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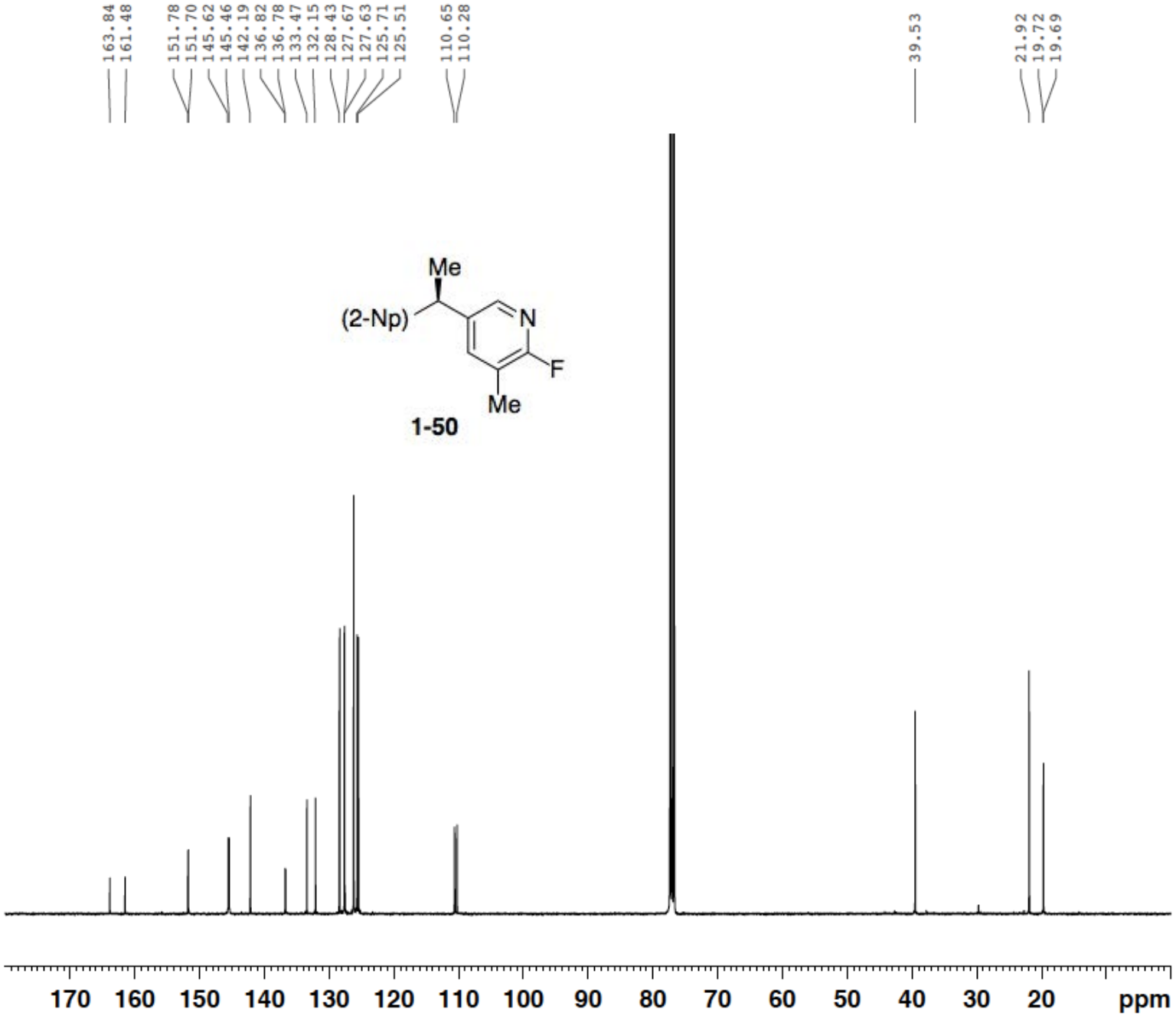
DMM4-242-3-CARBON-2
C13CPD1024 CDCl3 /opt/topspin dmcatee 27

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PROCNO                      1

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Time                   9.49
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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
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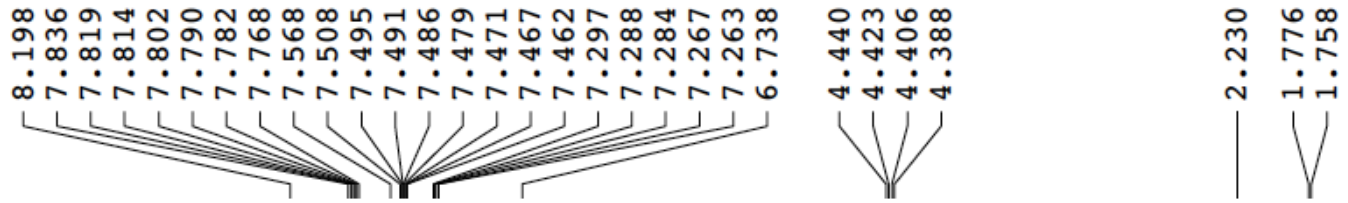
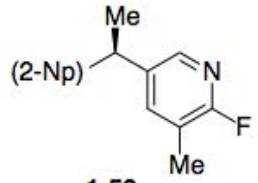
DMM4-242-3-PROTON-2
PROTON_16 CDCl3 /opt/topspin dmcatee 27





1-50

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Current Data Parameters
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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                        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
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WDW                      EM
SSB                       0
LB                    0.30 Hz
GB                        0
PC                     1.00
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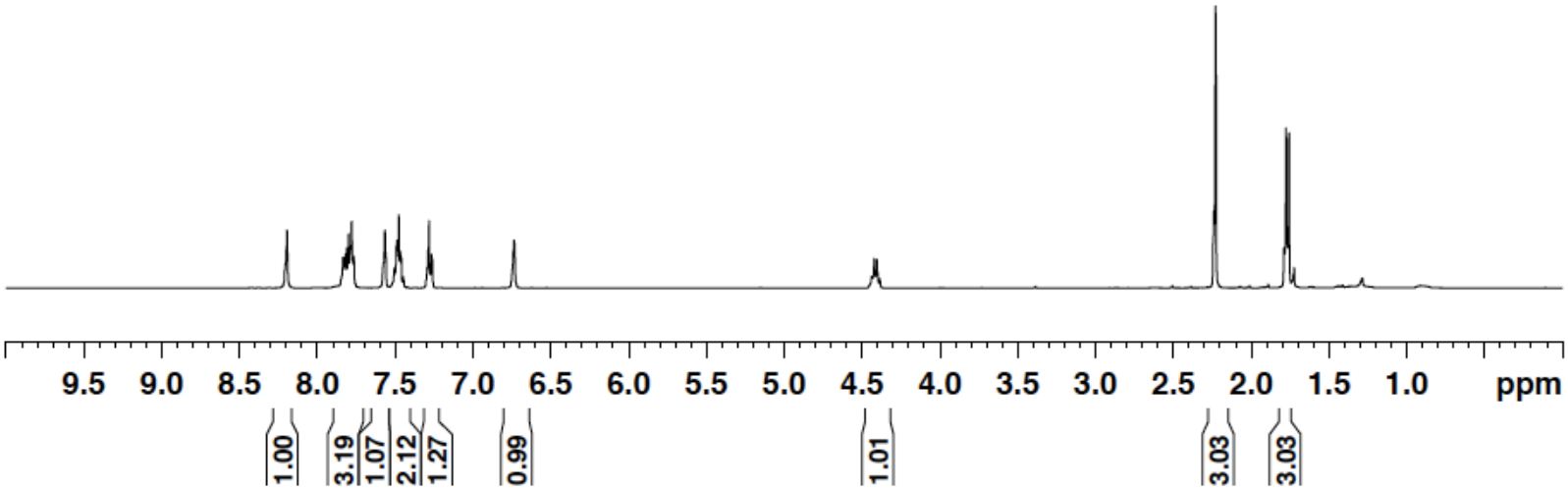
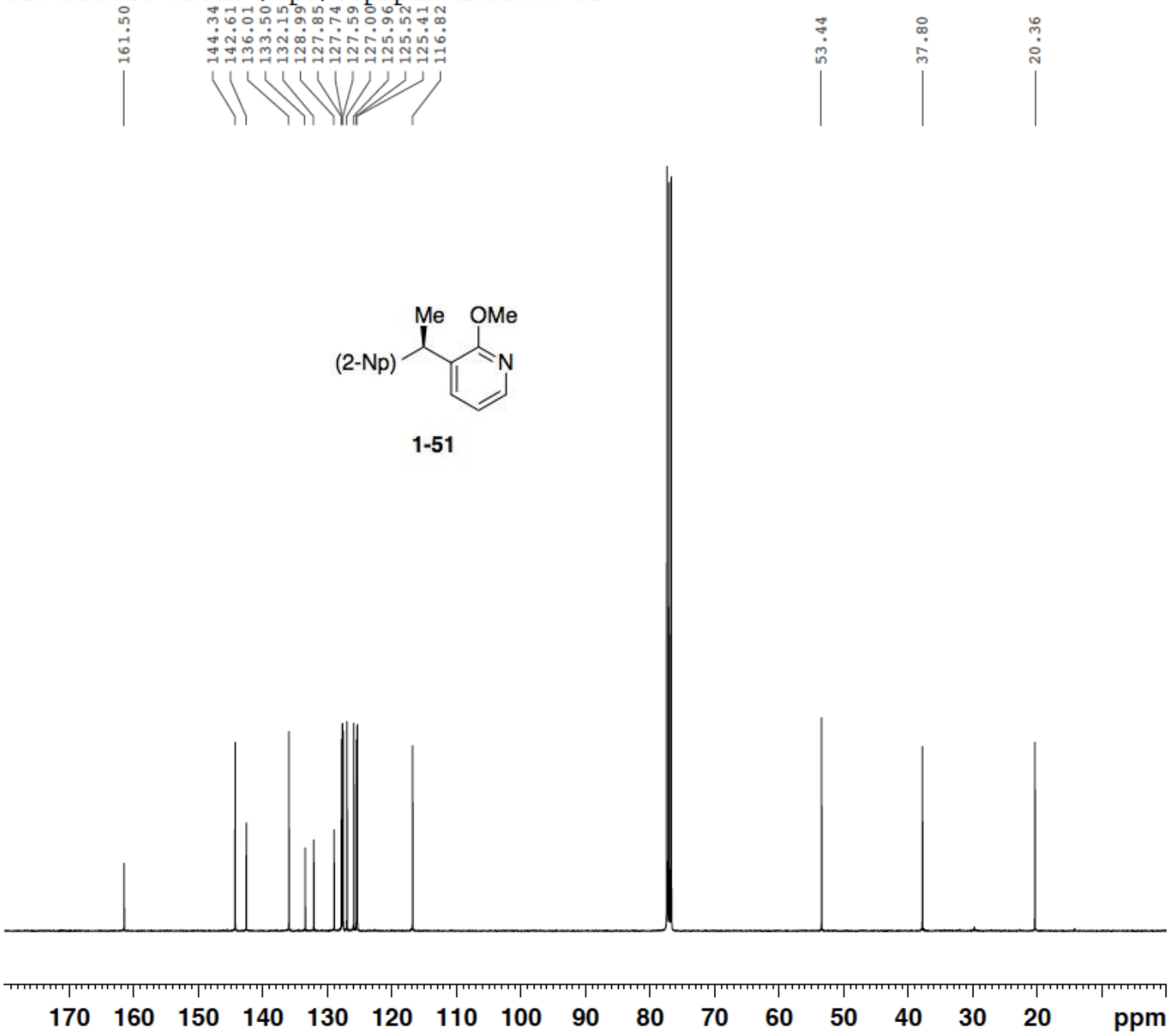


DMM4-250-1-CARBON2
C13CPD1024 CDCl3 /opt/topspin dmcatee 31

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PROCNO                     1

F2 - Acquisition Parameters
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Time                 21.05
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
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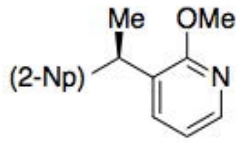
DMM4-250-1-PROTON2
PROTON_16 CDCl3 /opt/topspin dmcatee 31

8.061 8.053 8.049 8.041 8.036 7.817 7.813 7.799 7.795 7.783 7.771 7.762 7.749 7.695 7.484 7.470 7.467 7.455 7.452 7.436 7.433 7.419 7.415 7.405 7.401 7.387 7.383 7.360 7.351 7.348 7.339 7.330 7.327 7.258 6.849 6.844 6.836 6.831 6.818 4.636 4.620 4.602 4.584 3.949 1.687 1.669



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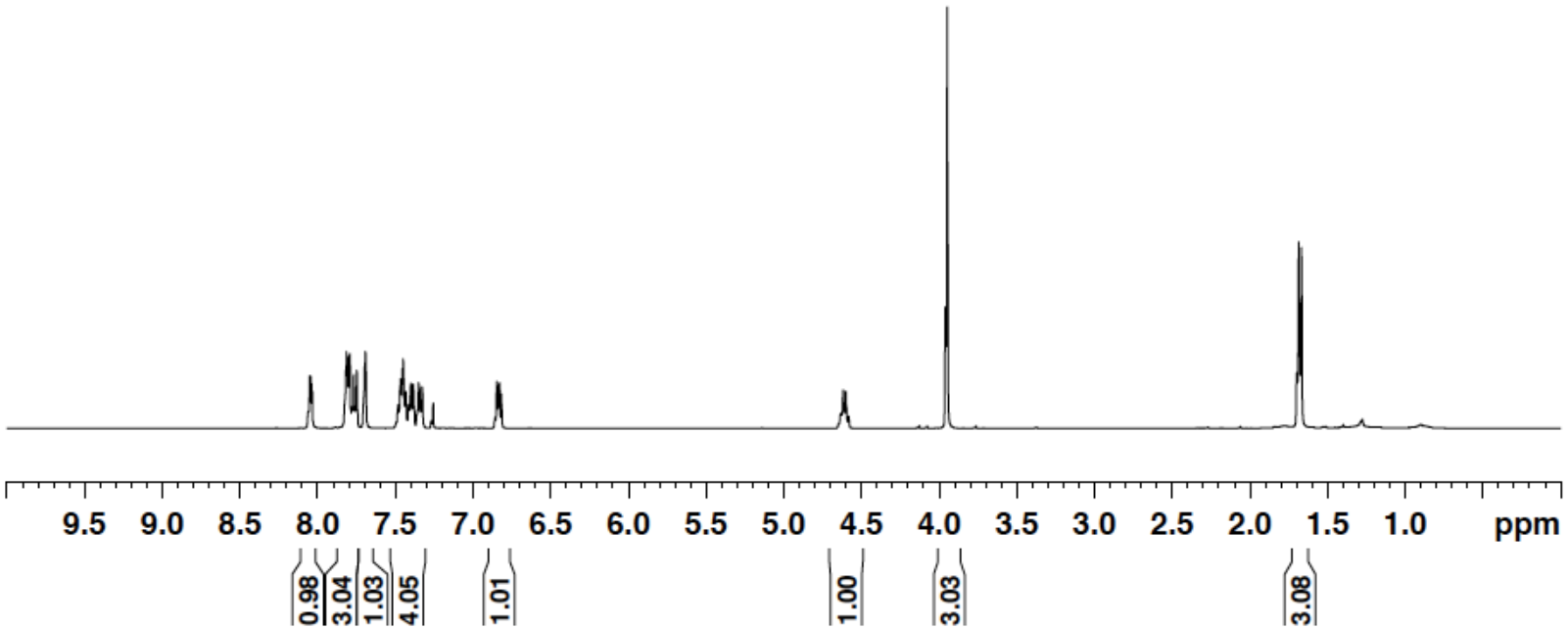


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TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8278.146 Hz
FIDRES             0.126314 Hz
AQ                 3.9584243 sec
RG                        9
DW                   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             400.1300101 MHz
WDW                      EM
SSB                       0
LB                    0.30 Hz
GB                        0
PC                     1.00
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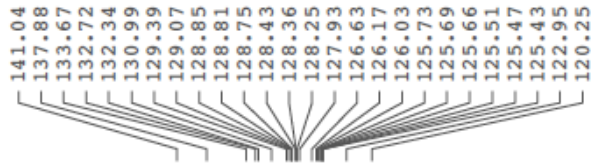
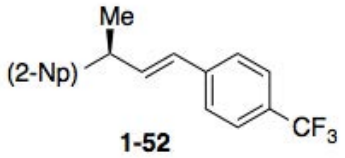
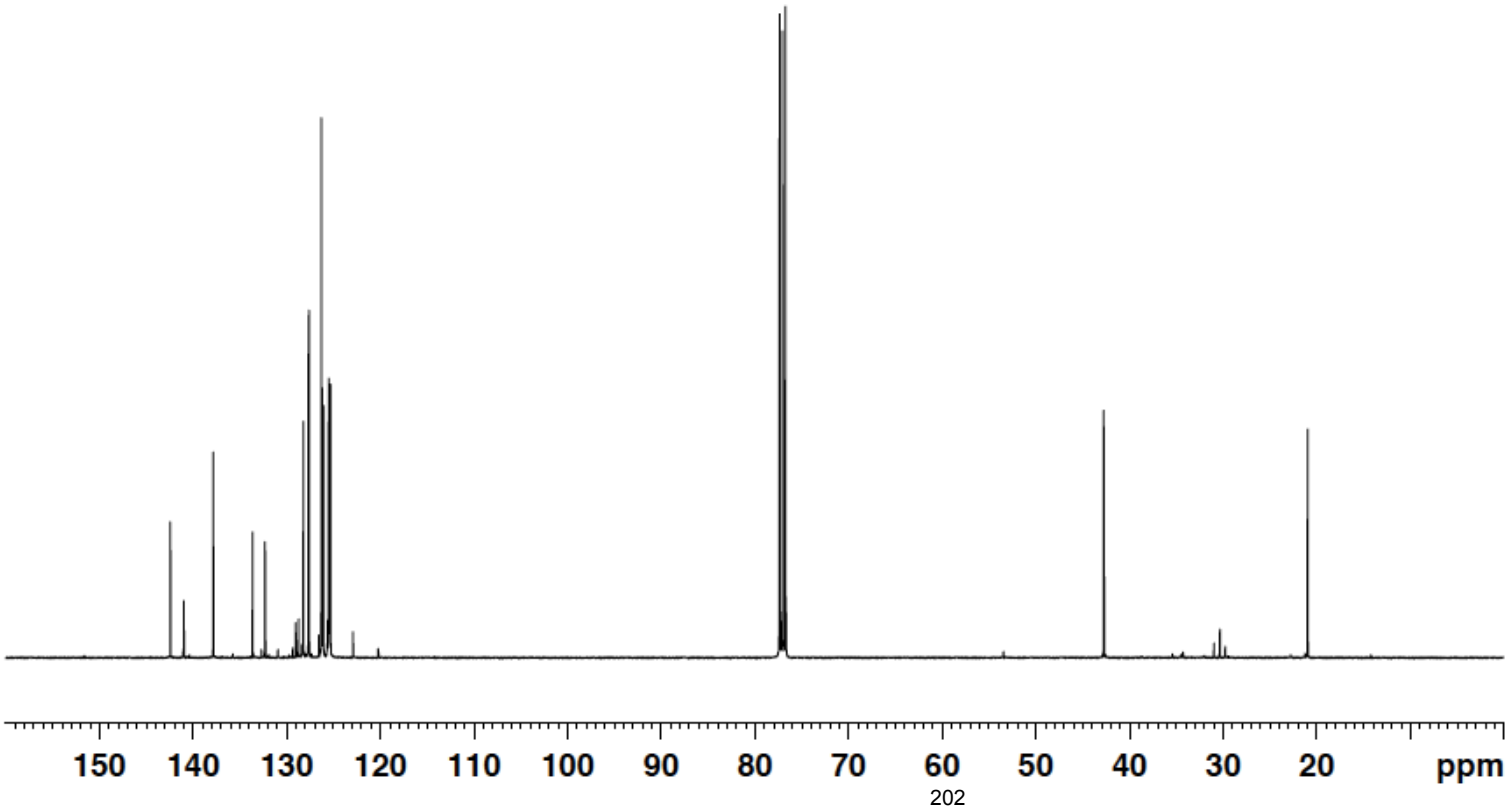
DMM4-234-1-CARBON2
C13CPD1024 CDCl3 /opt/topspin dmcatee 20



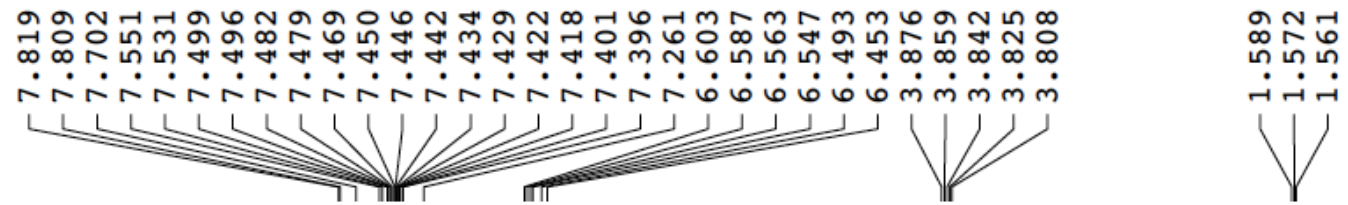


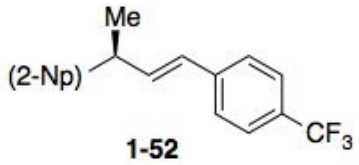
1-52



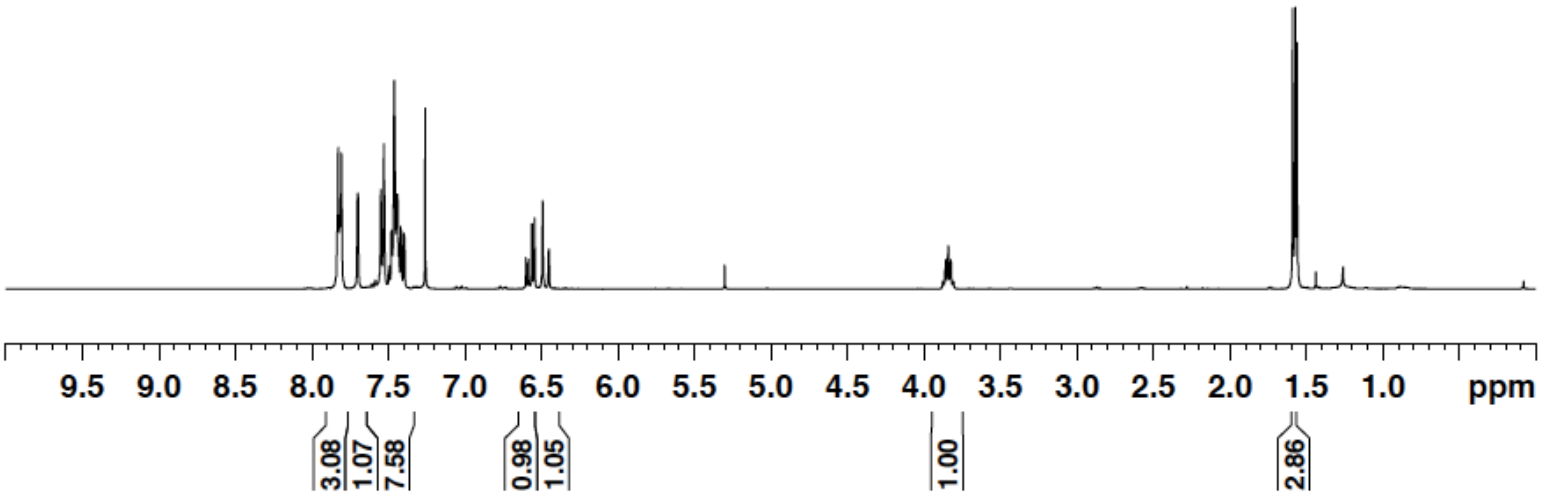

```
Current Data Parameters
NAME      DMM4-234-1-CARBON2
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_           20131220
Time                5.54
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
```

DMM4-234-1-PROTON-3
PROTON_16 CDCl3 /opt/topspin dmcatee 20



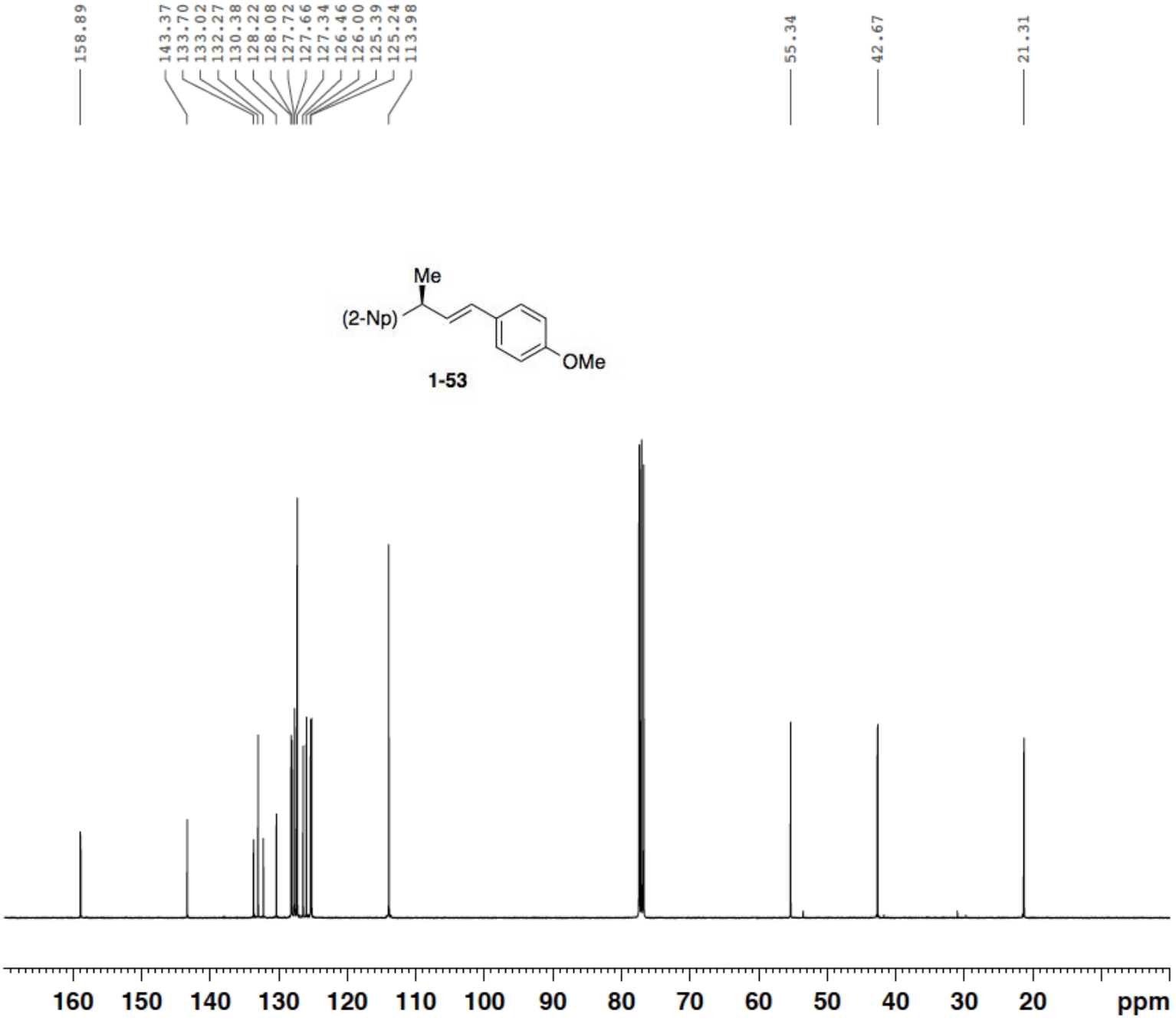


1-52



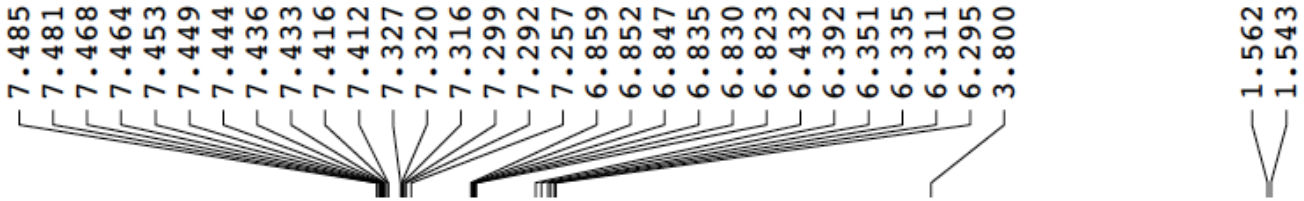

```
Current Data Parameters
NAME      DMM4-234-1-PROTON-3
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20131220
Time                  19.53
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                        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
```

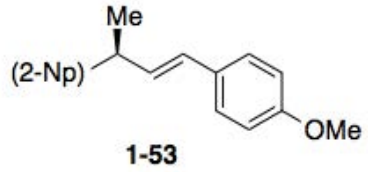
DMM4-234-2-CARBON
C13CPD1024 CDCl3 /opt/topspin dmcatee 21



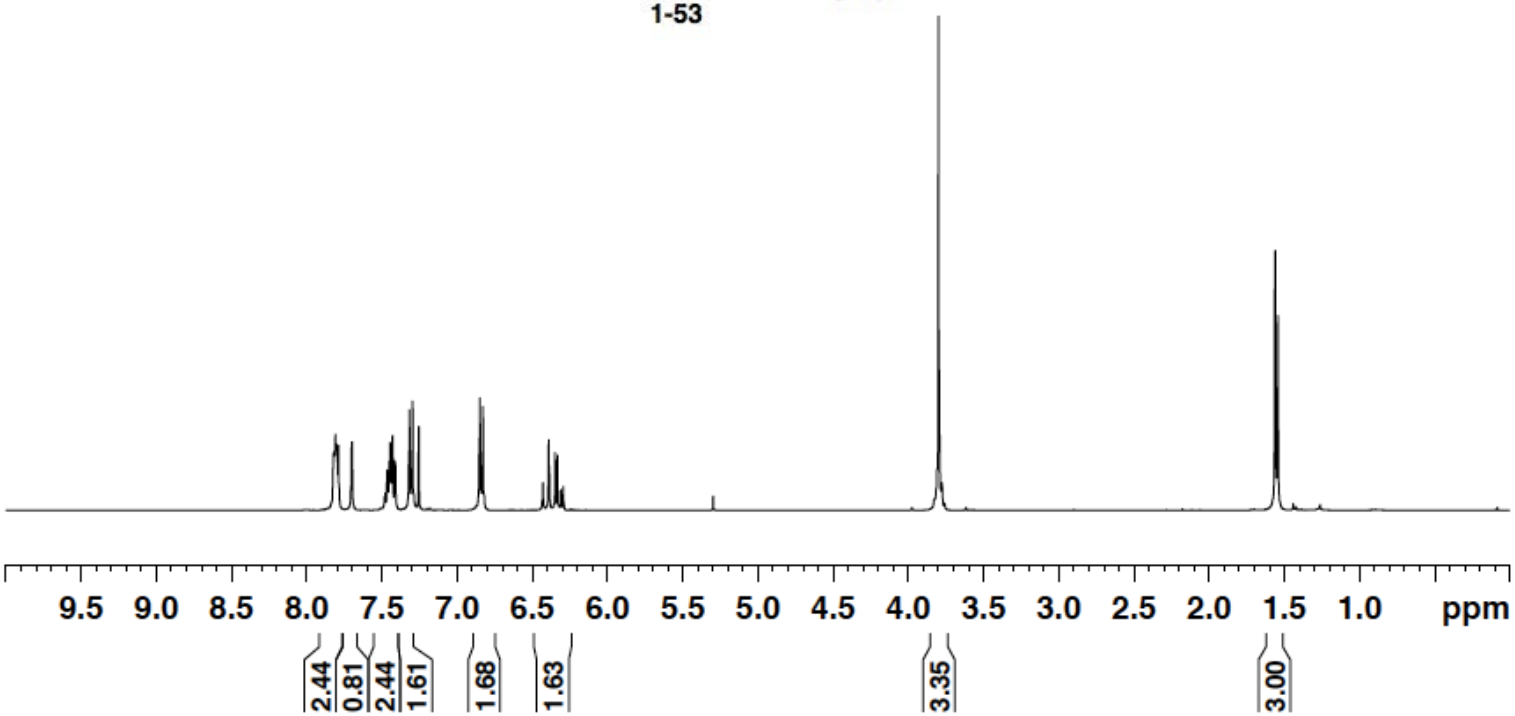

```
Current Data Parameters
NAME      DMM4-234-2-CARBON
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20131220
Time                 7.08
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           100.6127690 MHz
WDW                     EM
SSB                      0
LB                  1.00 Hz
GB                       0
PC                   1.40
```

DMM4-234-2-PROTON-3
PROTON_16 CDCl3 /opt/topspin dmcatee 21



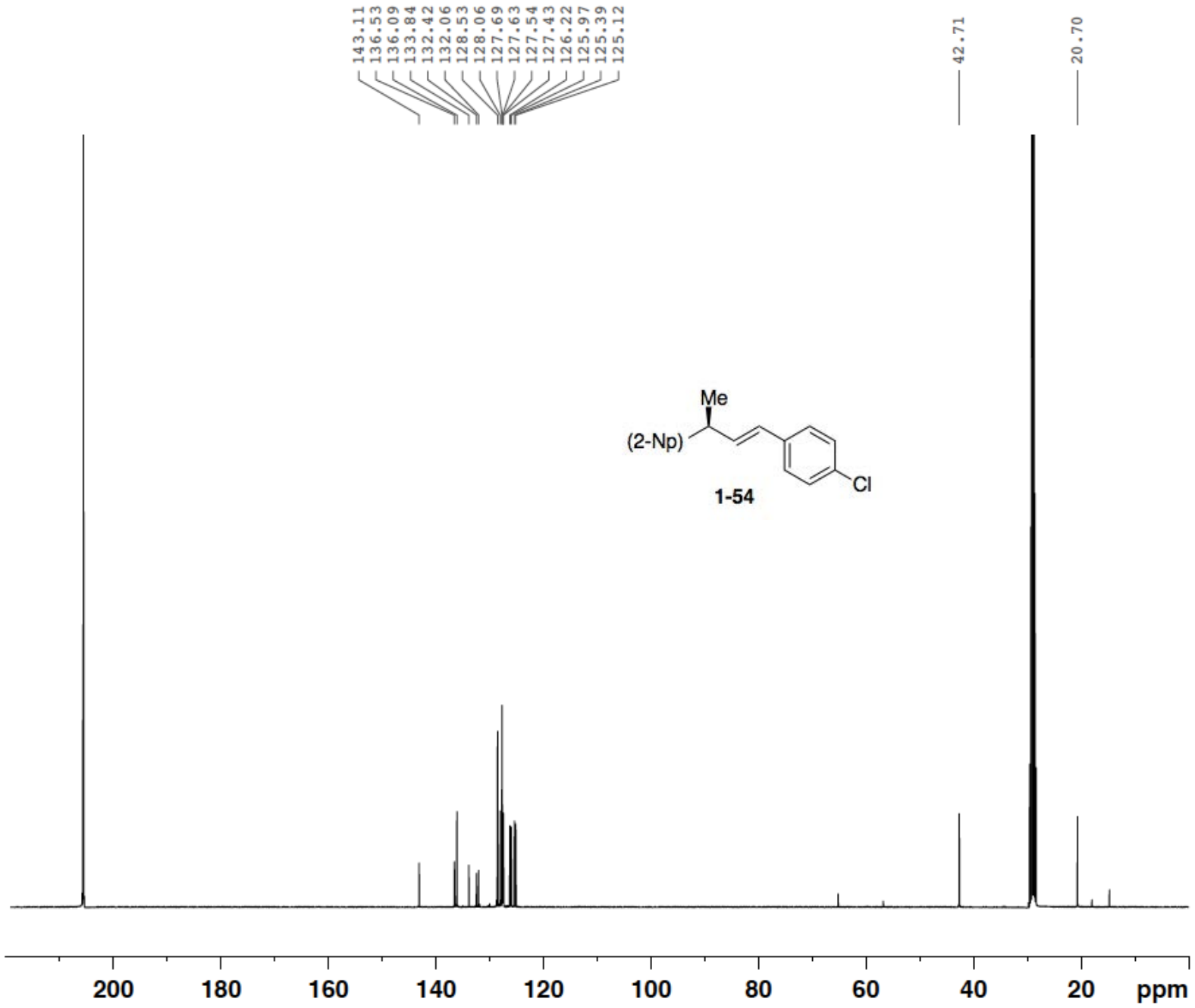


1-53



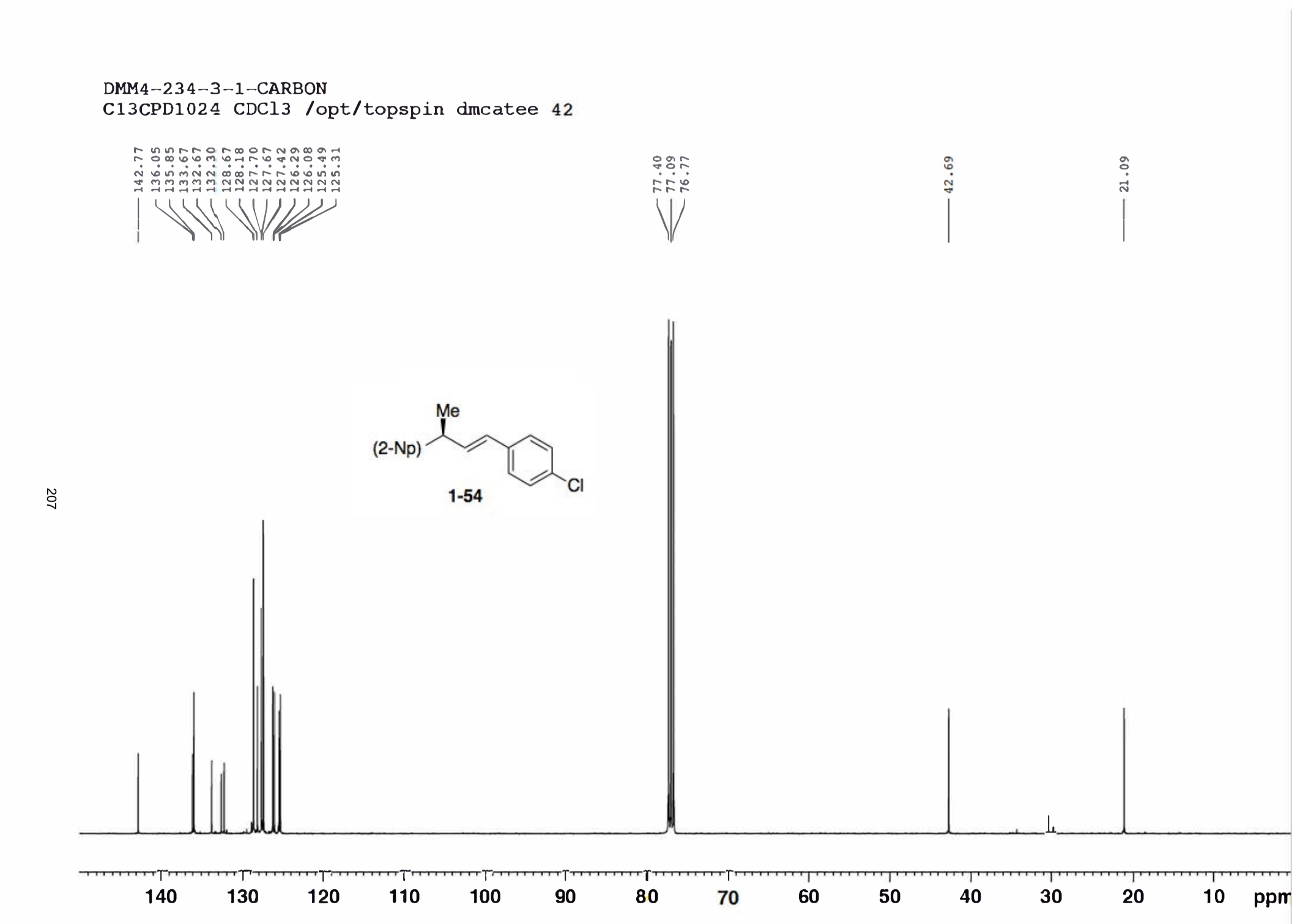

```
Current Data Parameters
NAME      DMM4-234-2-PROTON-3
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20131221
Time                   0.59
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            400.1300110 MHz
WDW                      EM
SSB                       0
LB                   0.30 Hz
GB                        0
PC                     1.00
```

DMM4-234-3-CARBON IN ACETONE
C13CPD1024 Acetone /opt/topspin dmcatee 47

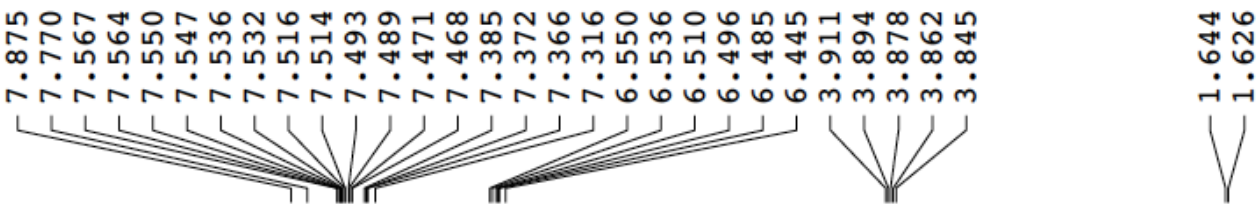


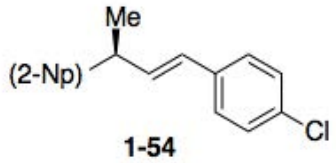

```
Current Data Parameters
NAME      DMM4-234-3-CARBON IN ACETONE
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20140101
Time              13.49
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
```

DMM4-234-3-1-CARBON
C13CPD1024 CDCl3 /opt/topspin dmcatee 42

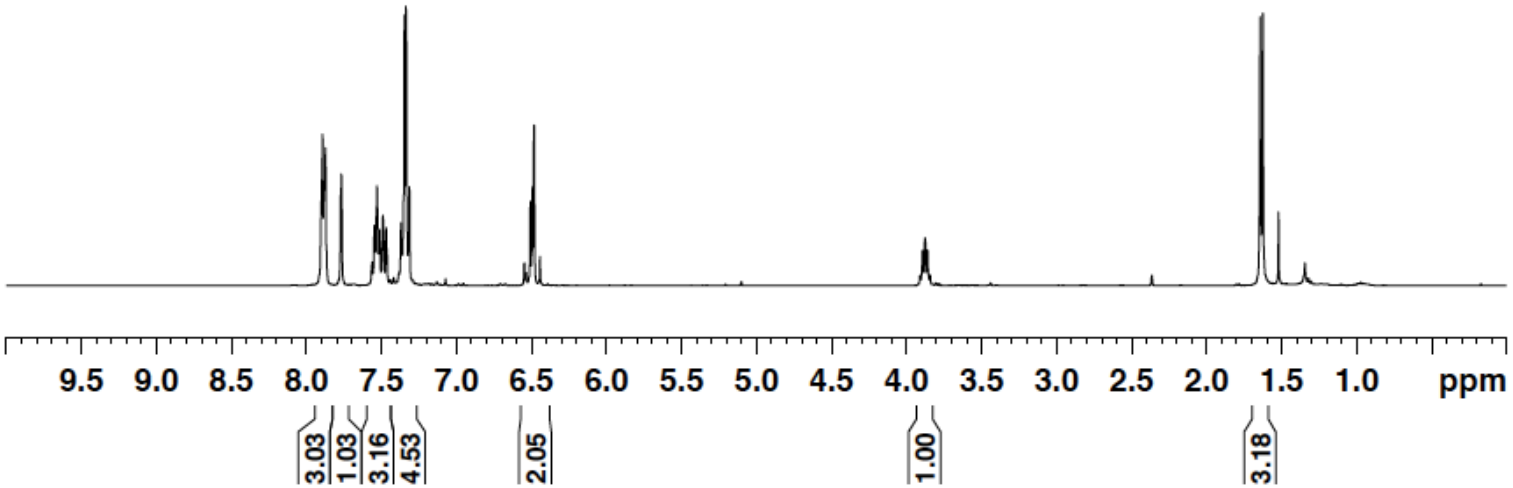


DMM4-234-3-1-PROTON
PROTON_16 CDCl3 /opt/topspin dmcatee 42



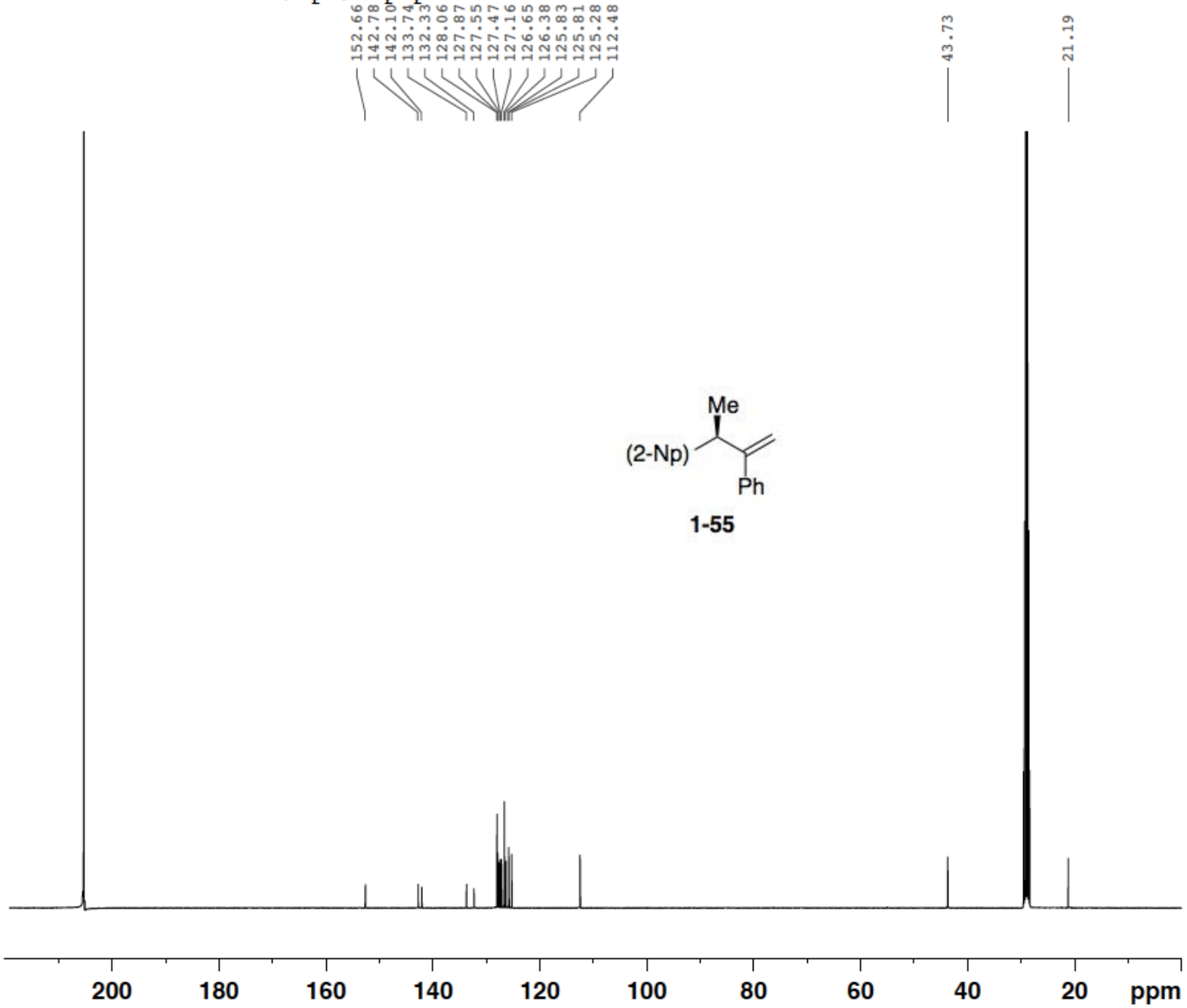


1-54



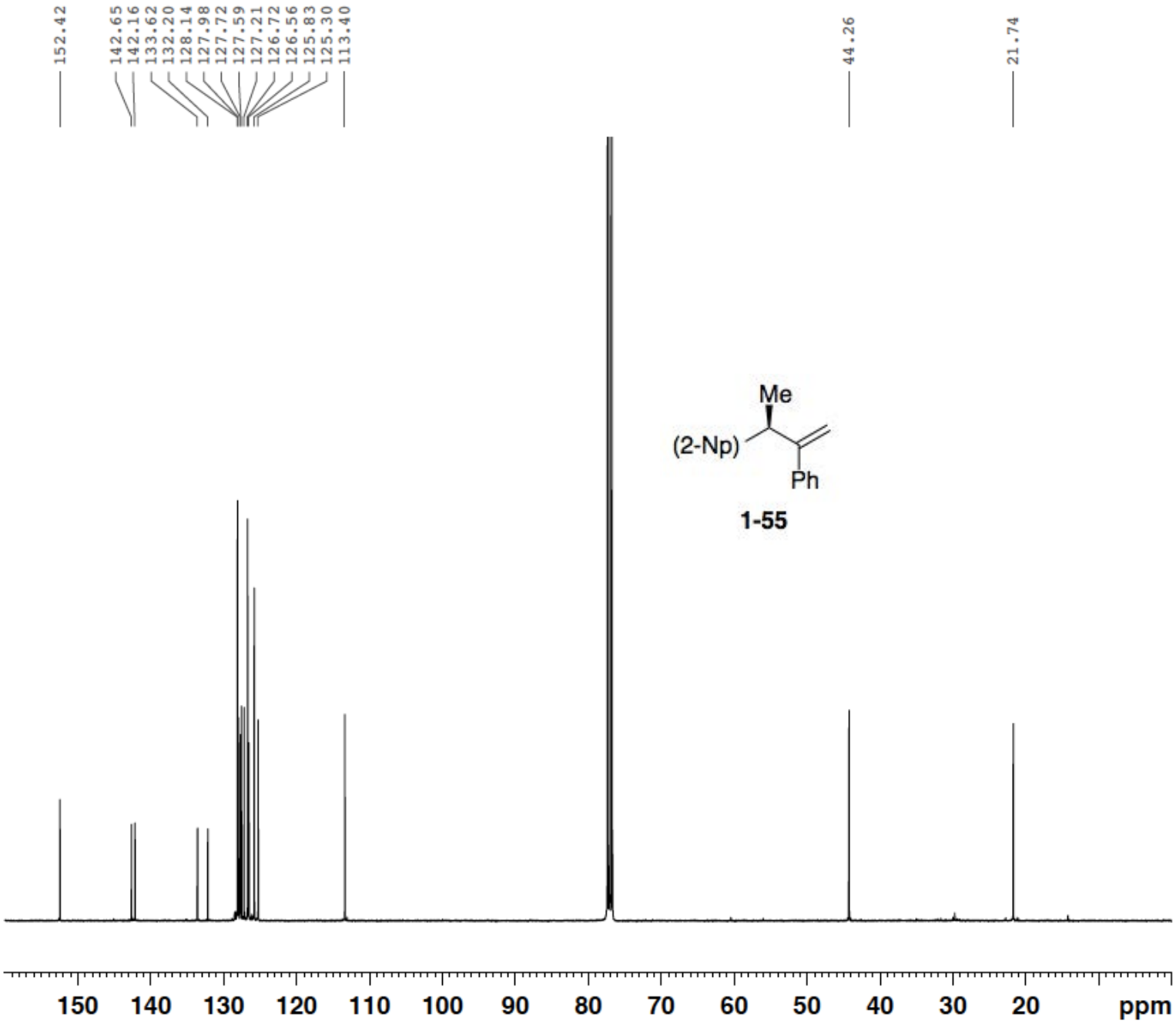

```
Current Data Parameters
NAME      DMM4-234-3-1-PROTON
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20131215
Time                  19.20
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            400.1299877 MHz
WDW                      EM
SSB                       0
LB                   0.30 Hz
GB                        0
PC                    1.00
```

DMM4-250-2-CARBON IN ACETONE2
C13CPD1024 Acetone /opt/topspin dmcatee 51



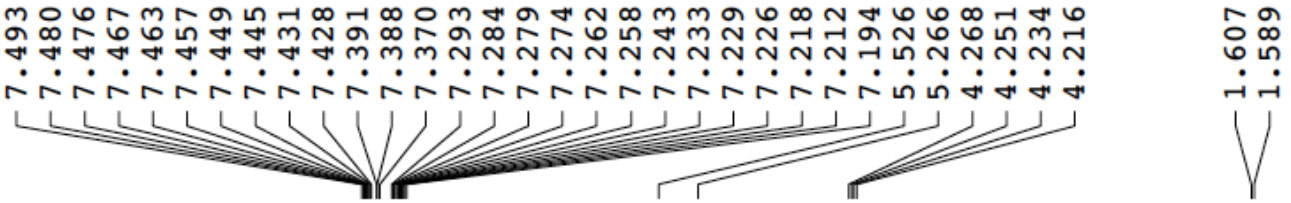

```
Current Data Parameters
NAME      DMM4-250-2-CARBON IN ACETONE2
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20140111
Time              16.55
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
```

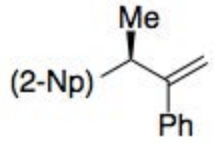
DMM4-250-2-CARBON1
C13CPD1024 CDCl3 /opt/topspin dmcatee 32



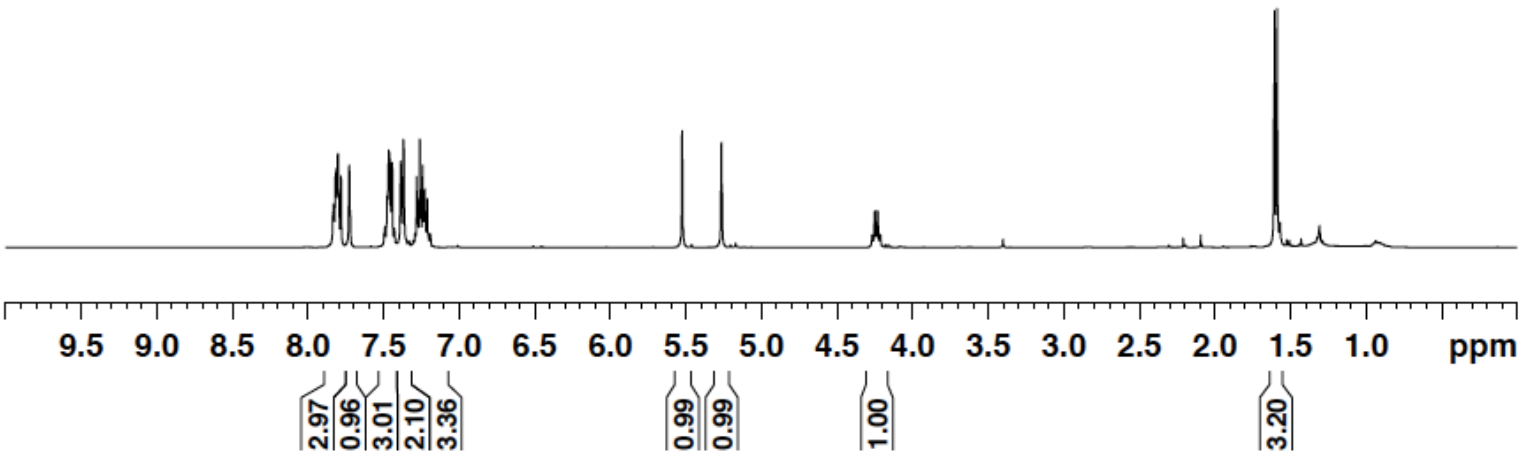

```
Current Data Parameters
NAME      DMM4-250-2-CARBON1
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20140109
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          100.6127690 MHz
WDW                     EM
SSB                      0
LB                  1.00 Hz
GB                       0
PC                   1.40
```

DMM4-250-2-PROTON1
PROTON_16 CDCl3 /opt/topspin dmcatee 32



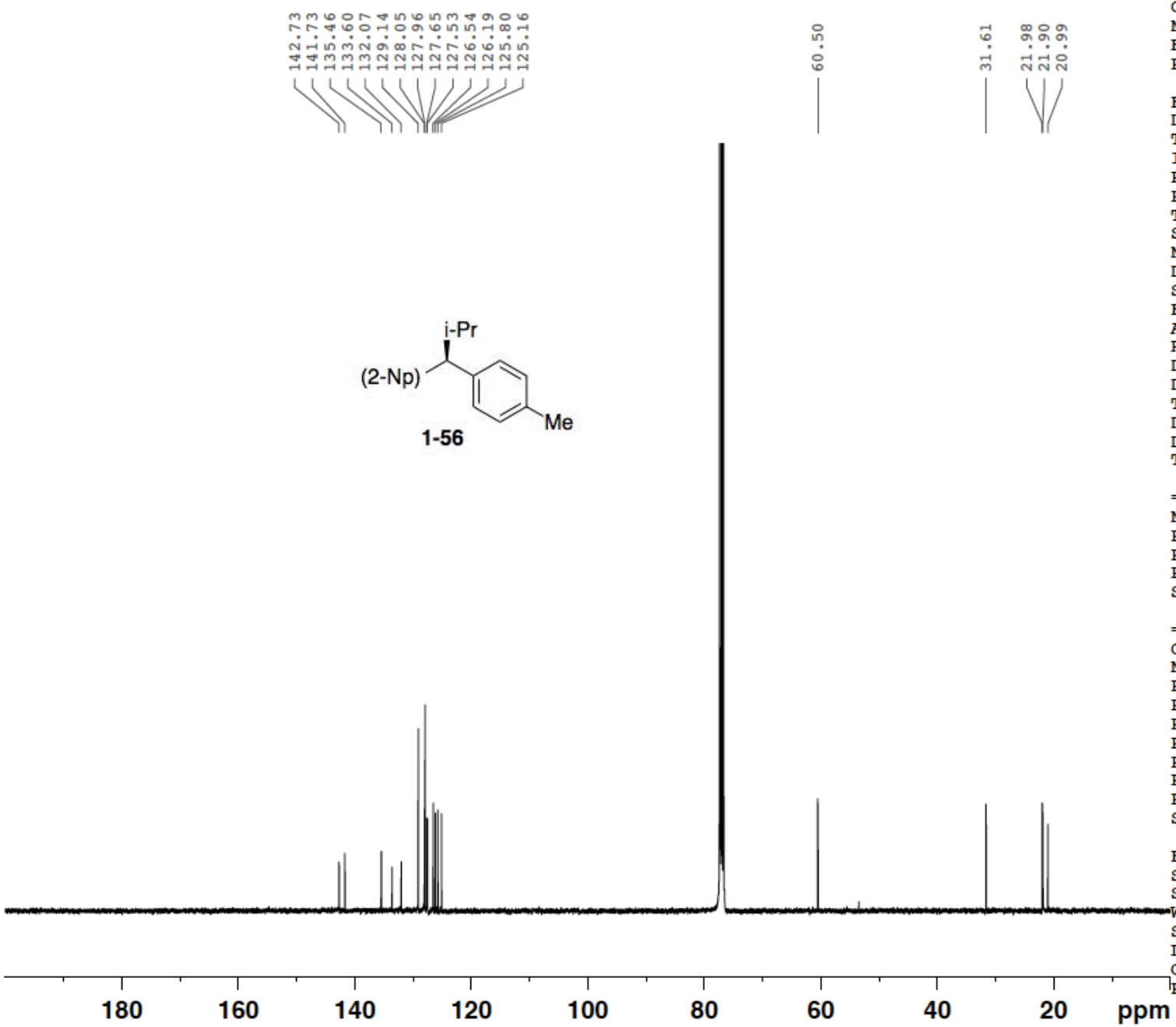


1-55



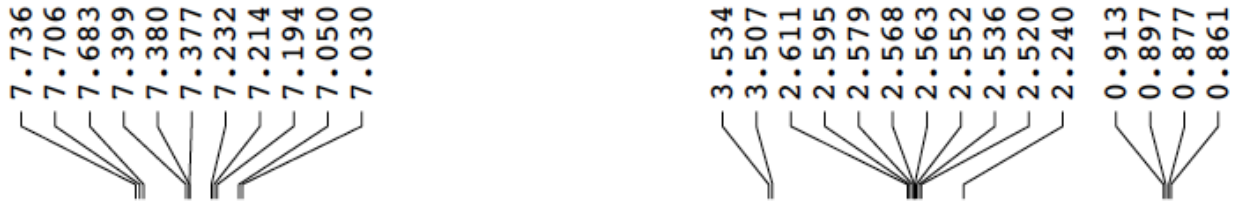

```
Current Data Parameters
NAME      DMM4-250-2-PROTON1
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20140109
Time                   5.40
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                     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
```

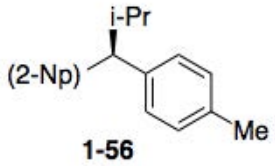
CHB1-240-carbon
C13CPD32 CDCl3 /opt/topspin kmrob 45



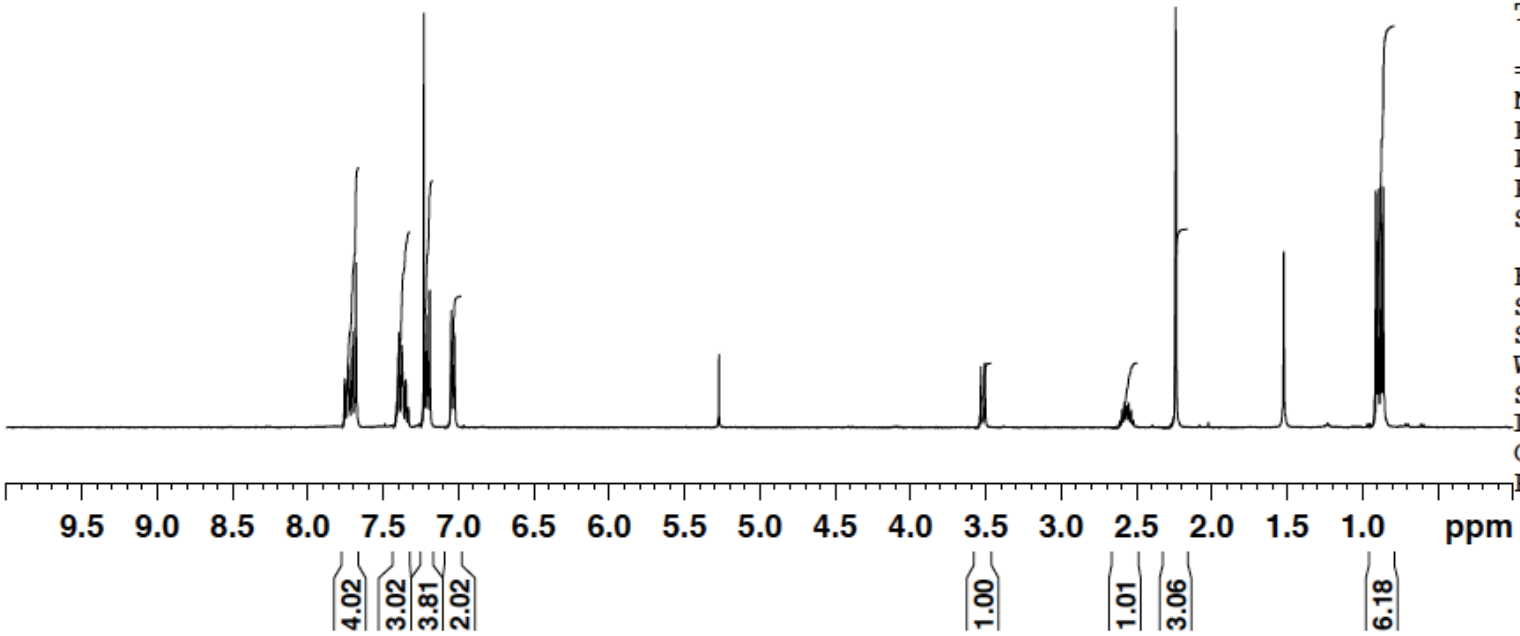

```
Current Data Parameters
NAME      CHB1-240-carbon
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20140113
Time                18.30
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
```

CHB1-240-proton
PROTON_16 CDCl3 /opt/topspin kmrob 45



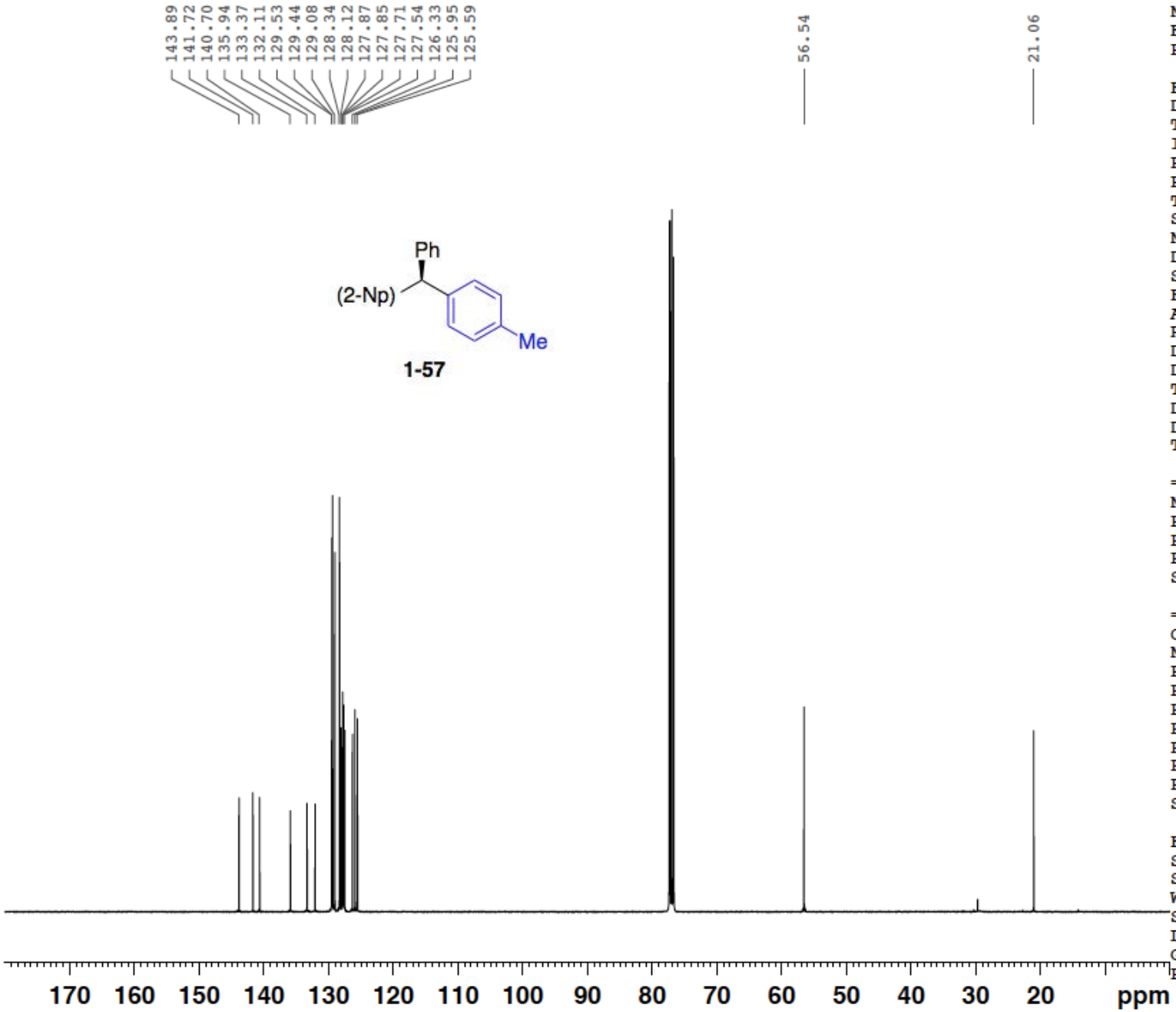


1-56



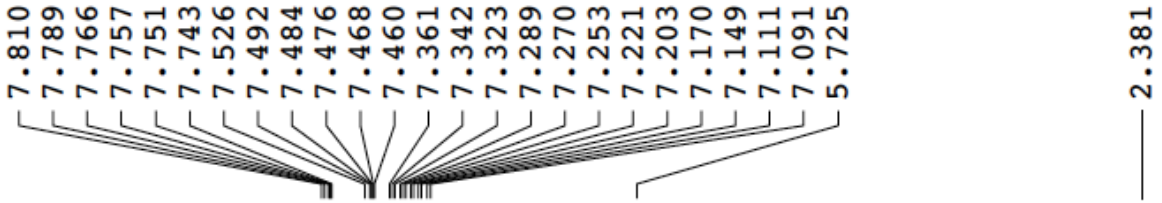

```
Current Data Parameters
NAME      CHB1-240-proton
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20140113
Time                17.30
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                   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          400.1300210 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

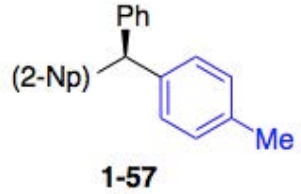
CHB1-230-carbon
C13CPD1024 CDCl3 /opt/topspin cbasch 40



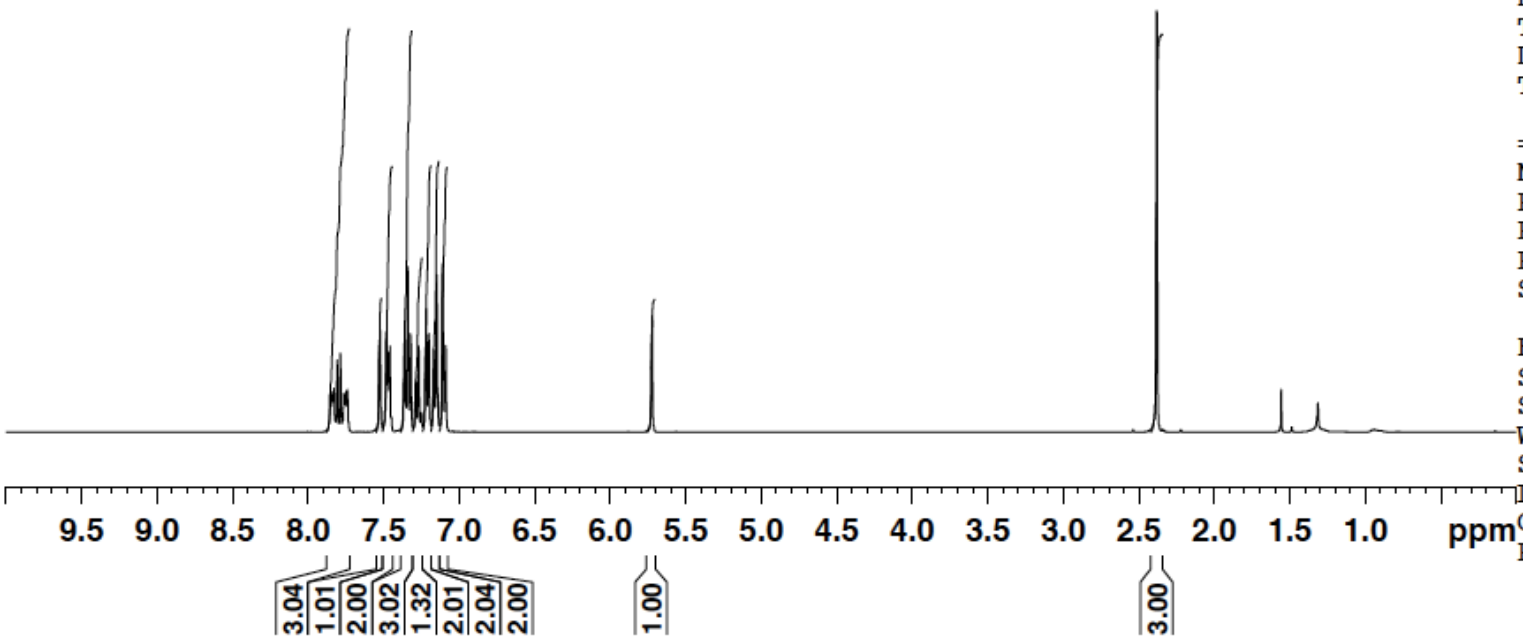

```
Current Data Parameters
NAME      CHB1-230-carbon
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20140105
Time                13.49
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         100.6127752 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                 1.40
```

CHB1-230-proton
PROTON_16 CDCl3 /opt/topspin cbasch 40



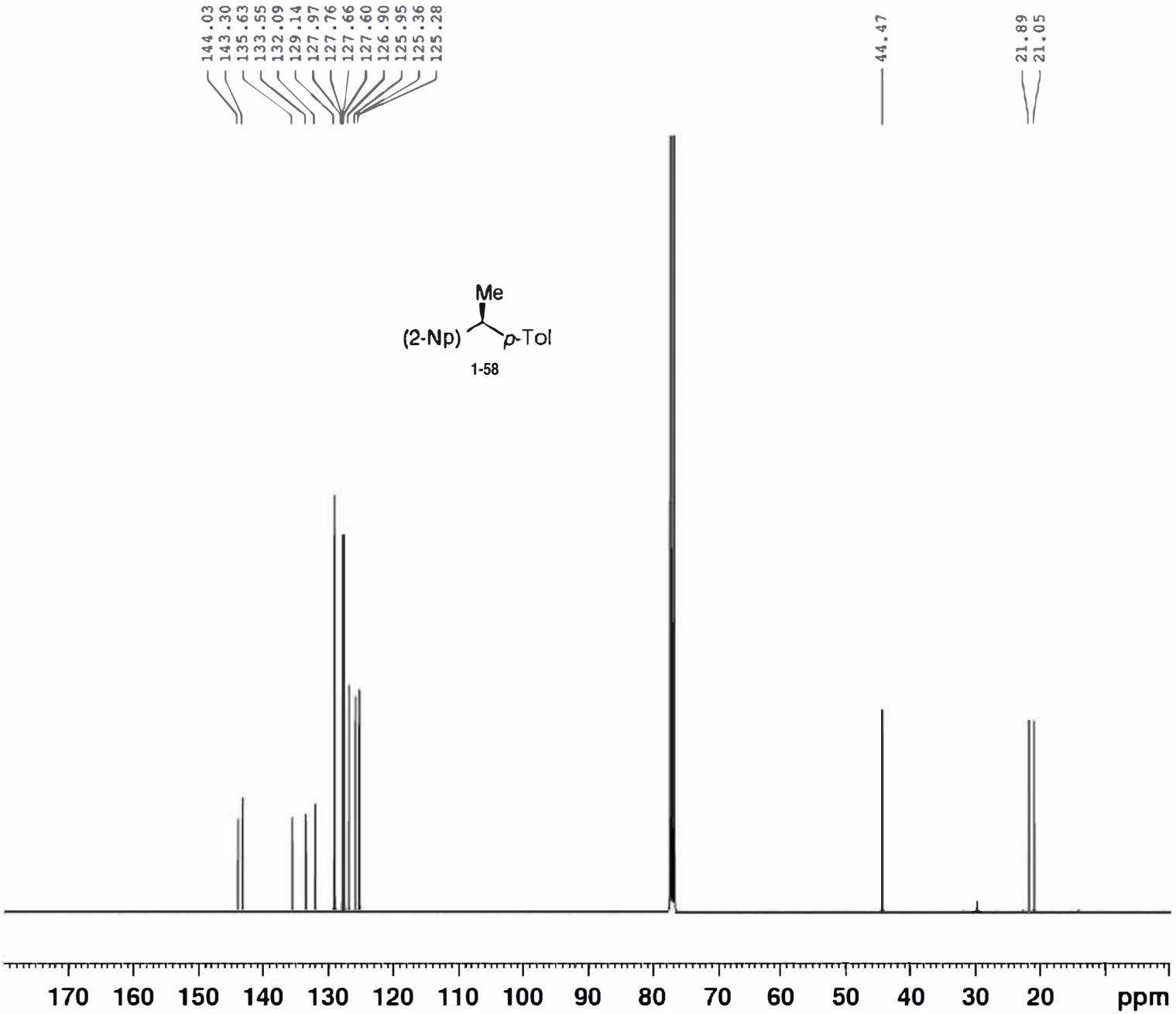


1-57




```
Current Data Parameters
NAME      CHB1-230-proton
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20140103
Time                14.07
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                     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          400.1300066 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                   1.00
```

KMR 1-231-CARBON
C13CPD32 CDCl3 /opt/topspin kmrob 2



Current Data Parameters

NAME	KMR 1-231-3-CARBON
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20140113
Time	16.57
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

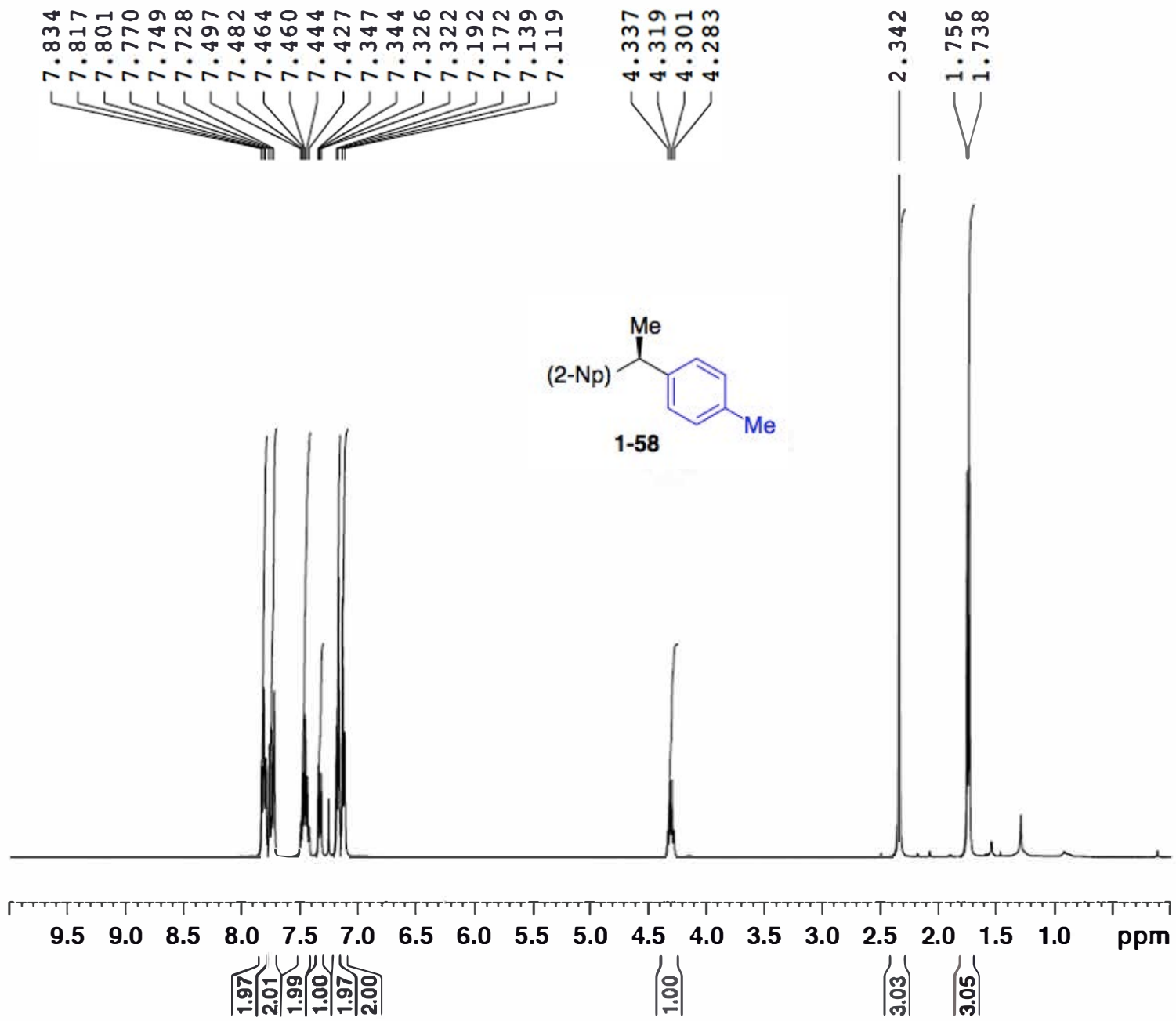
======== CHANNEL f2 ========

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

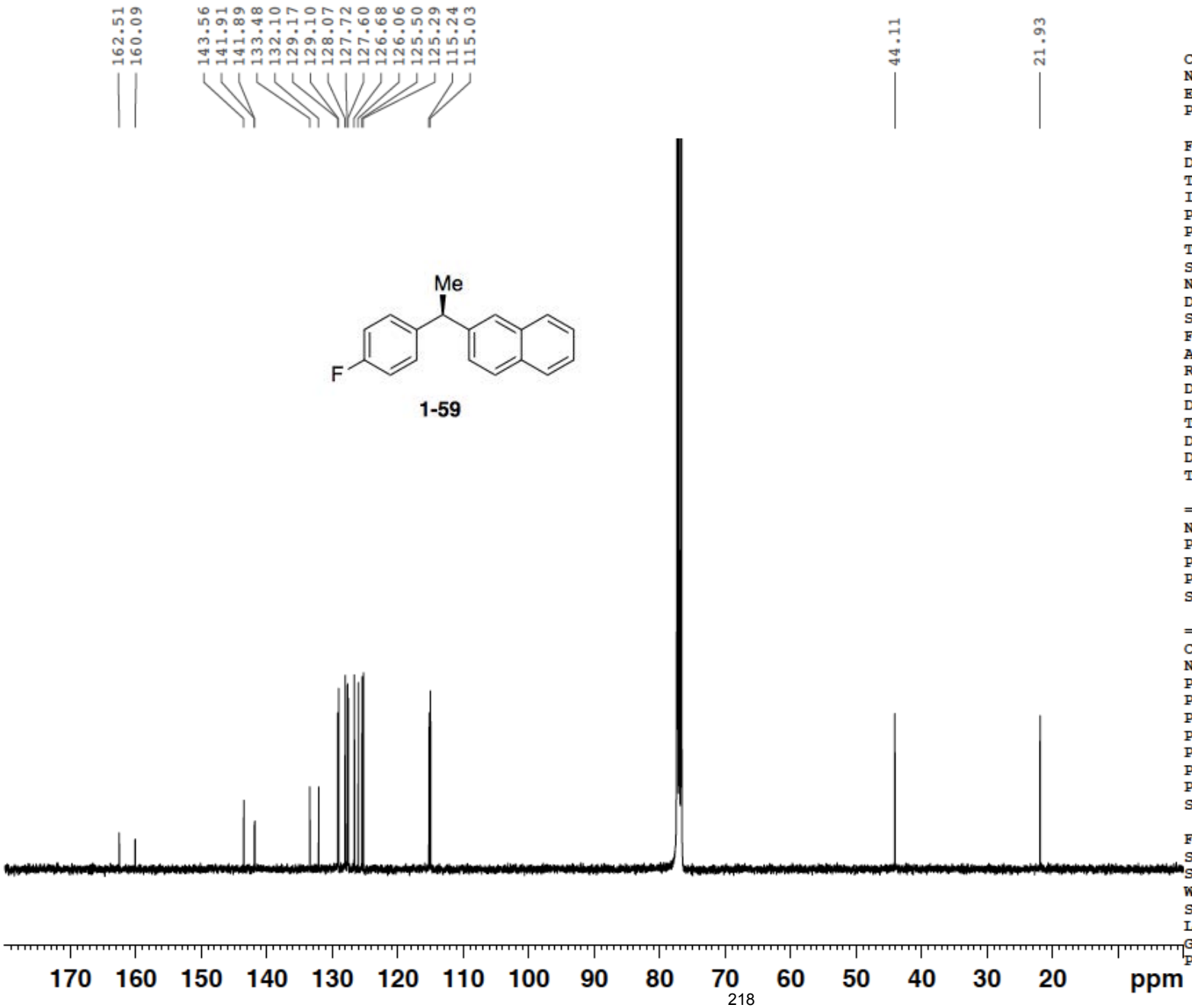
SI	32768
SF	100.6127690 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

KMR 1-231-3-PROTON
PROTON_16 CDCl3 /opt/topspin kmrob 4



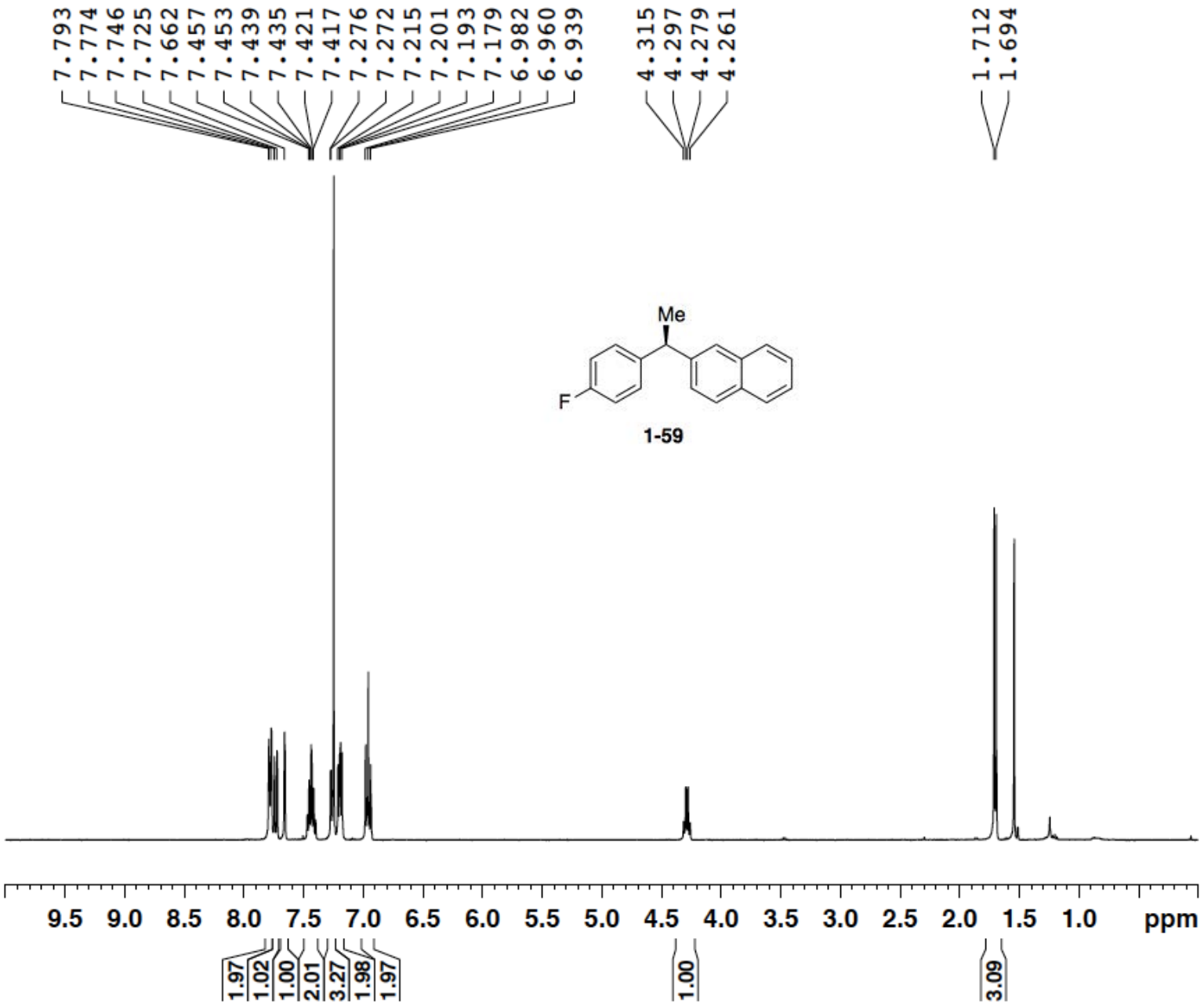

```
Current Data Parameters
NAME      KMR 1-231-3-PROTON
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20131231
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                       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            400.1300103 MHz
WDW                     EM
SSB                      0
LB                   0.30 Hz
GB                       0
PC                    1.00
```

KMR_01_240_2_YS_Carbon
C13CPD1024 CDCl3 /opt/topspin yegsong 20



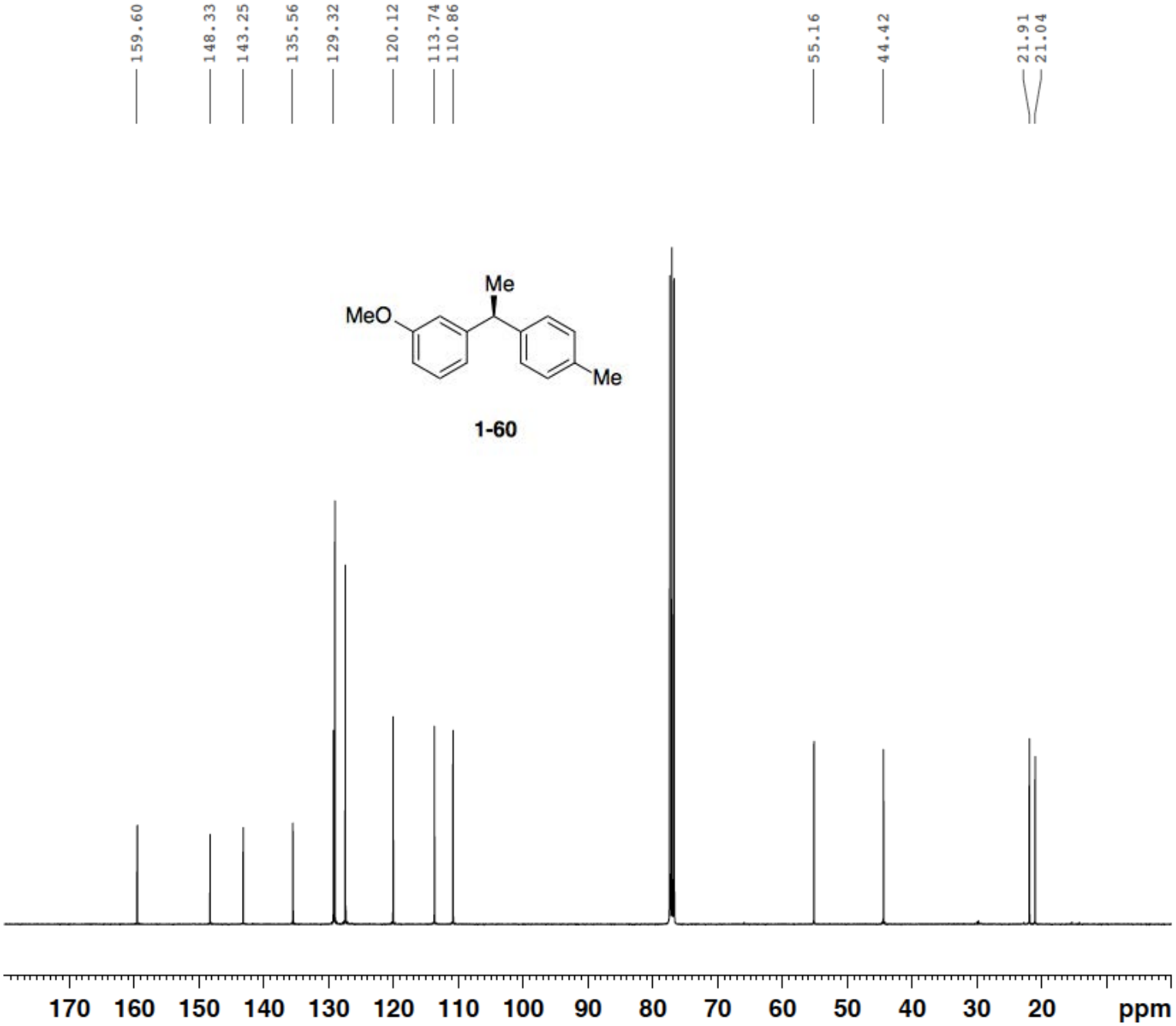

```
Current Data Parameters
NAME      KMR_01_240_2_YS_Carbon
EXPNO                          1
PROCNO                         1

F2 - Acquisition Parameters
Date_               20140112
Time                   23.26
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                    298.1 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
```

KMR_01_240_2_YS_Proton
PROTON_16 CDCl3 /opt/topspin yegsong 20



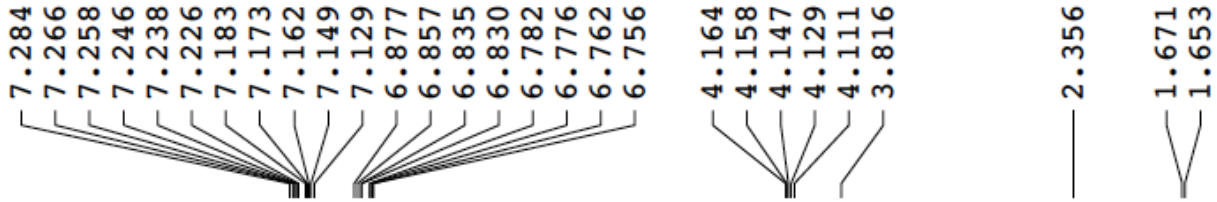

```
Current Data Parameters
NAME      KMR_01_240_2_YS_Proton
EXPNO                          1
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20140112
Time                       22.26
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                             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                 400.1300138 MHz
WDW                           EM
SSB                            0
LB                         0.30 Hz
GB                             0
PC                         1.00
```

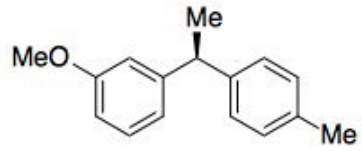
DMM4-252-2-CARBON1-AV400
C13CPD1024 CDCl3 /opt/topspin dmcatee 57



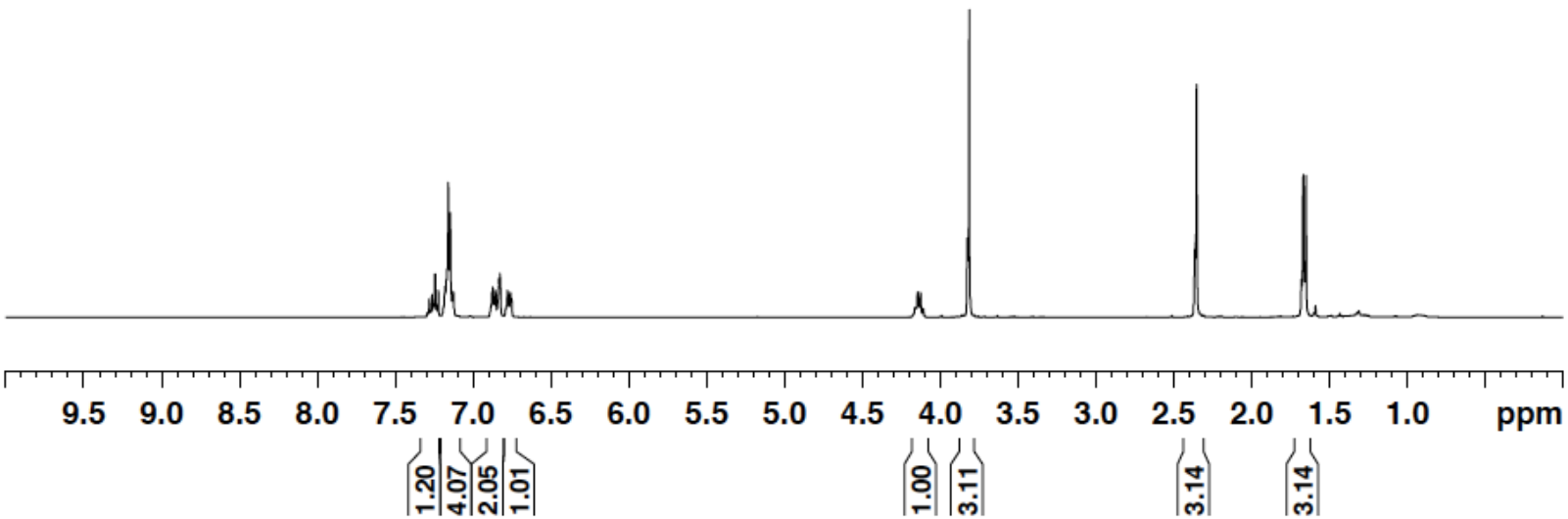

```
Current Data Parameters
NAME      DMM4-252-2-CARBON1-AV400
EXPNO                             1
PROCNO                            1

F2 - Acquisition Parameters
Date_                      20140110
Time                           2.57
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
```

DMM4-252-2-PROTON1-AV400
PROTON_16 CDCl3 /opt/topspin dmcatee 57



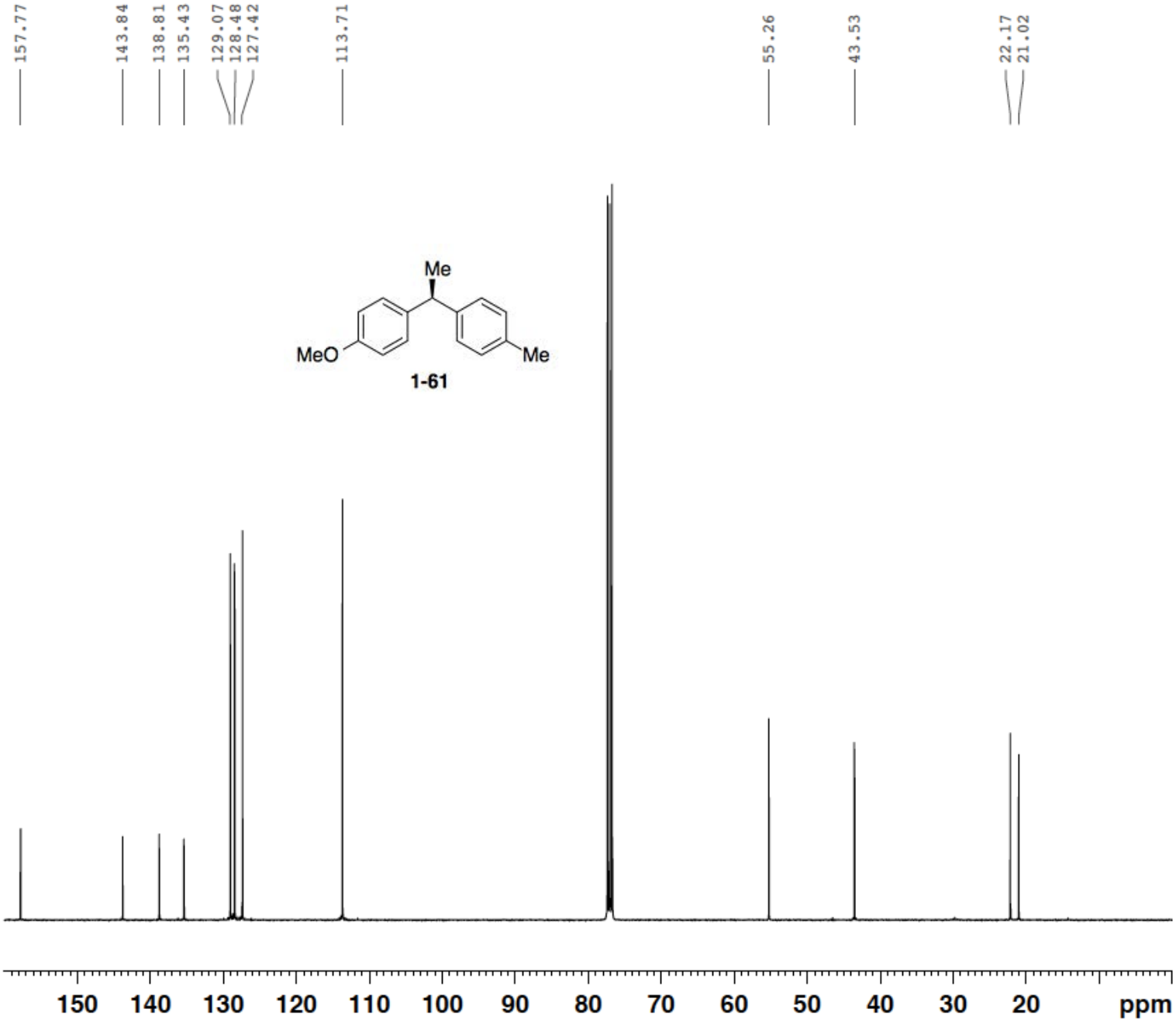


1-60



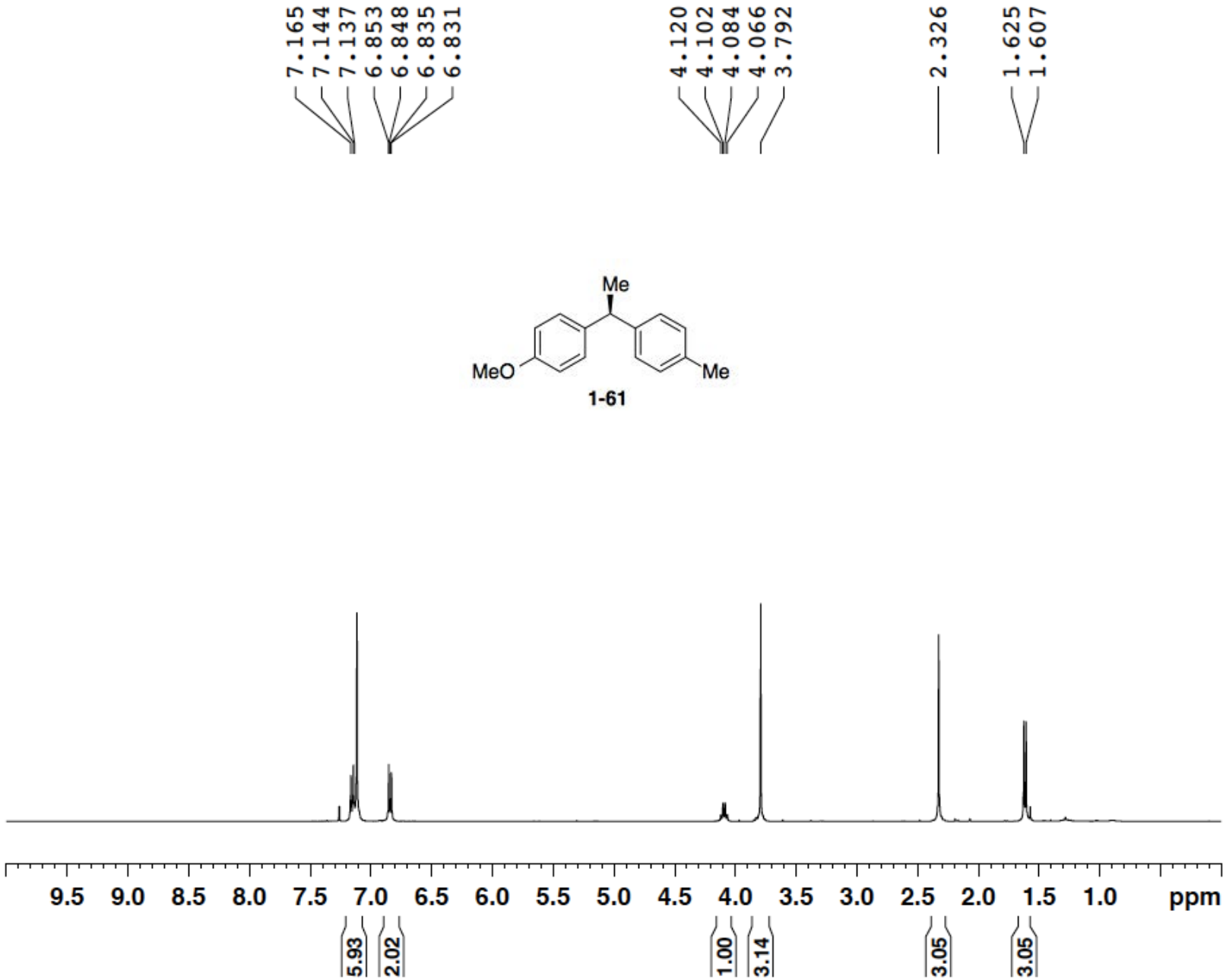

```
Current Data Parameters
NAME      DMM4-252-2-PROTON1-AV400
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140110
Time               6.57
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          400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

DMM4-252-1-CARBON1-AV400
C13CPD1024 CDCl3 /opt/topspin dmcatee 56



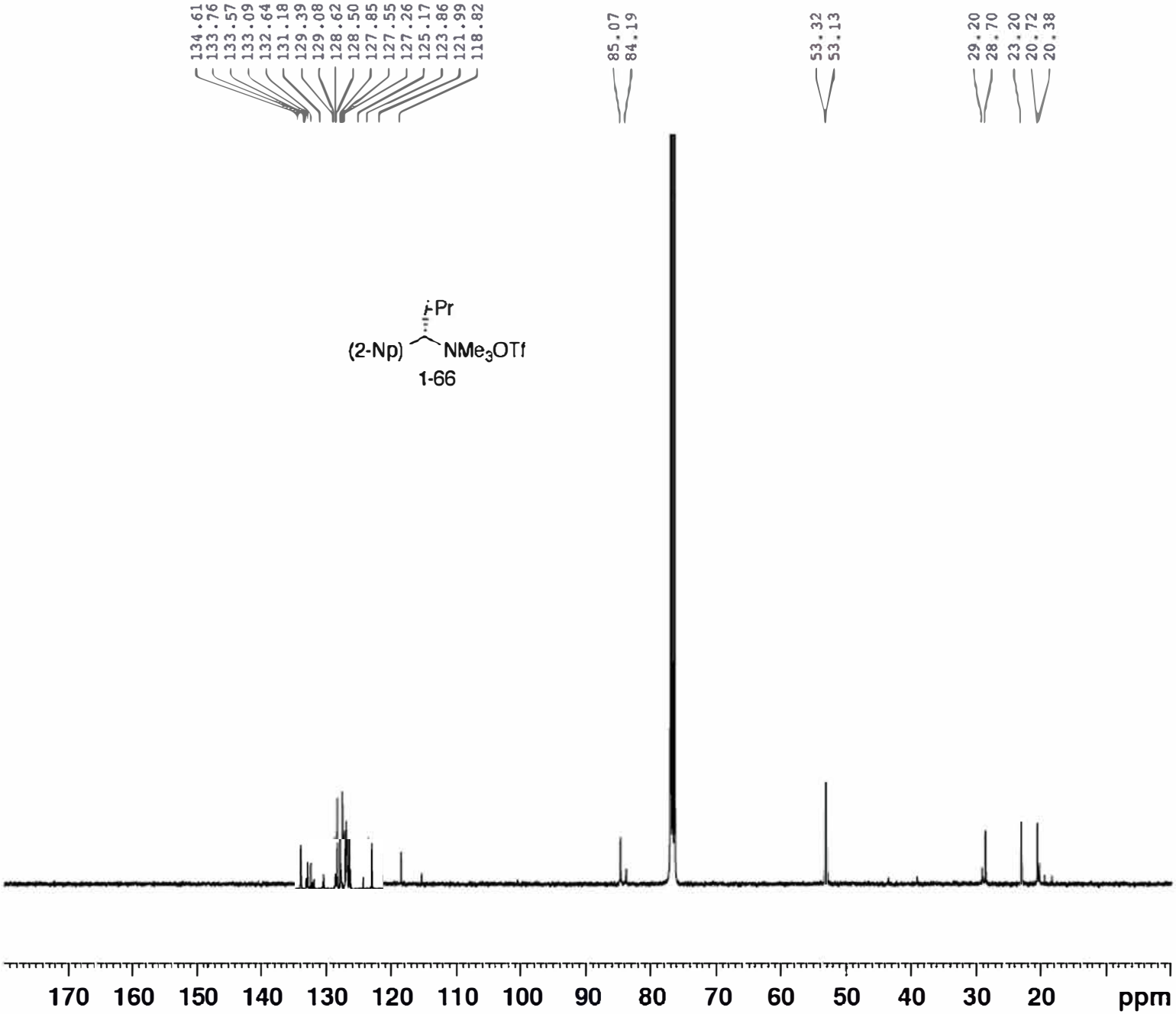

```
Current Data Parameters
NAME      DMM4-252-1-CARBON1-AV400
EXPNO                           1
PROCNO                          1

F2 - Acquisition Parameters
Date_                    20140110
Time                         1.51
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
```

DMM4-252-1-PROTON1-AV400
PROTON_16 CDCl3 /opt/topspin dmcatee 56




```
Current Data Parameters
NAME      DMM4-252-1-PROTON1-AV40
EXPNO                           1
PROCNO                          1

F2 - Acquisition Parameters
Date_                    20140110
Time                         5.51
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
```

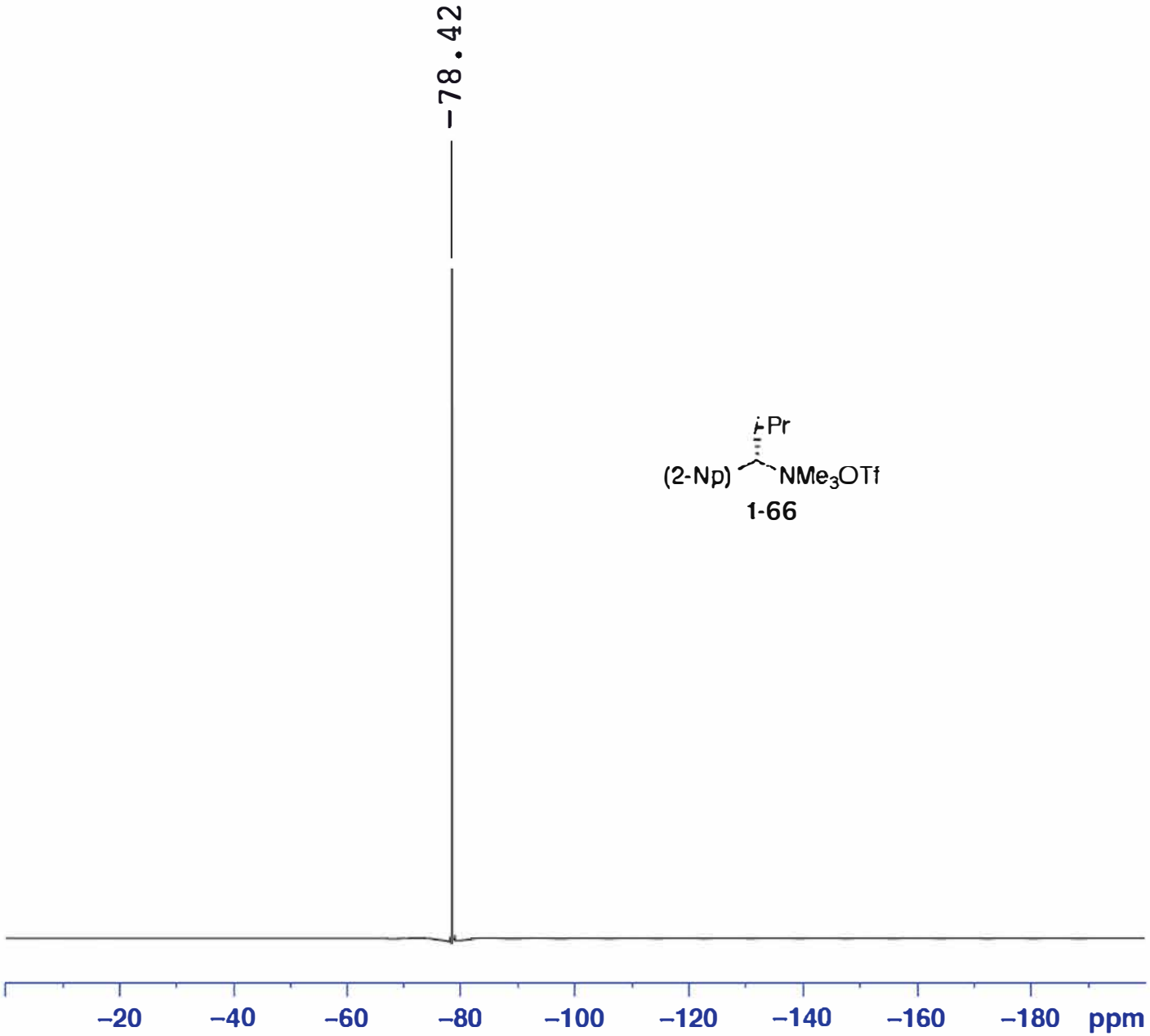
CHB1-233-carbon
C13CPD32 CDCl3 /opt/topspin kmrob 46




```
Current Data Parameters
NAME      CHB1-233-carbon
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140114
Time                20.29
INSTRUM             spect
PROBHD   5 mm CPQNP 1H/
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                   2048
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
```

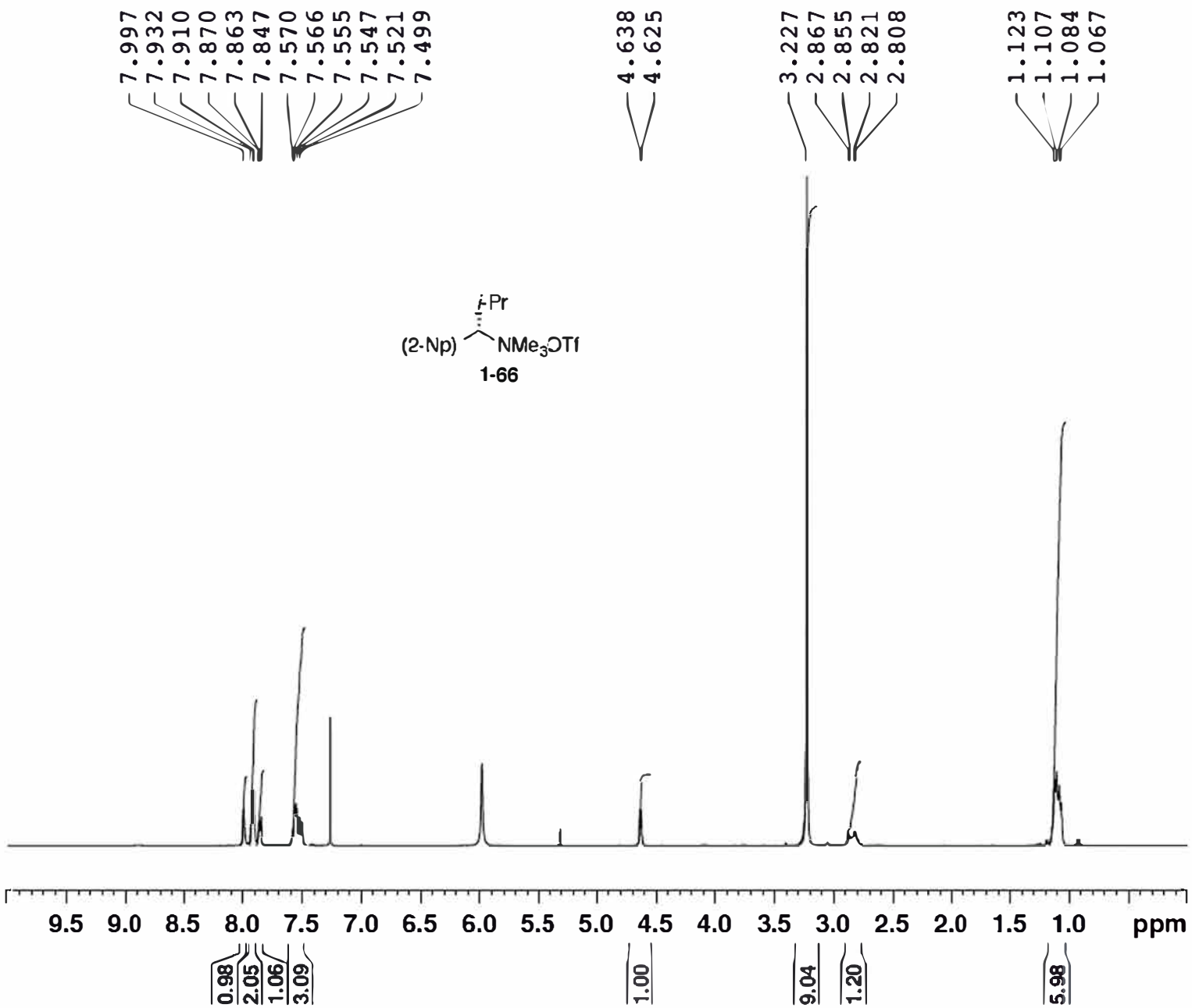
CHB1-233-fluorine

F19DEC 16 CDCl3 /opt/topspin kmroh 46



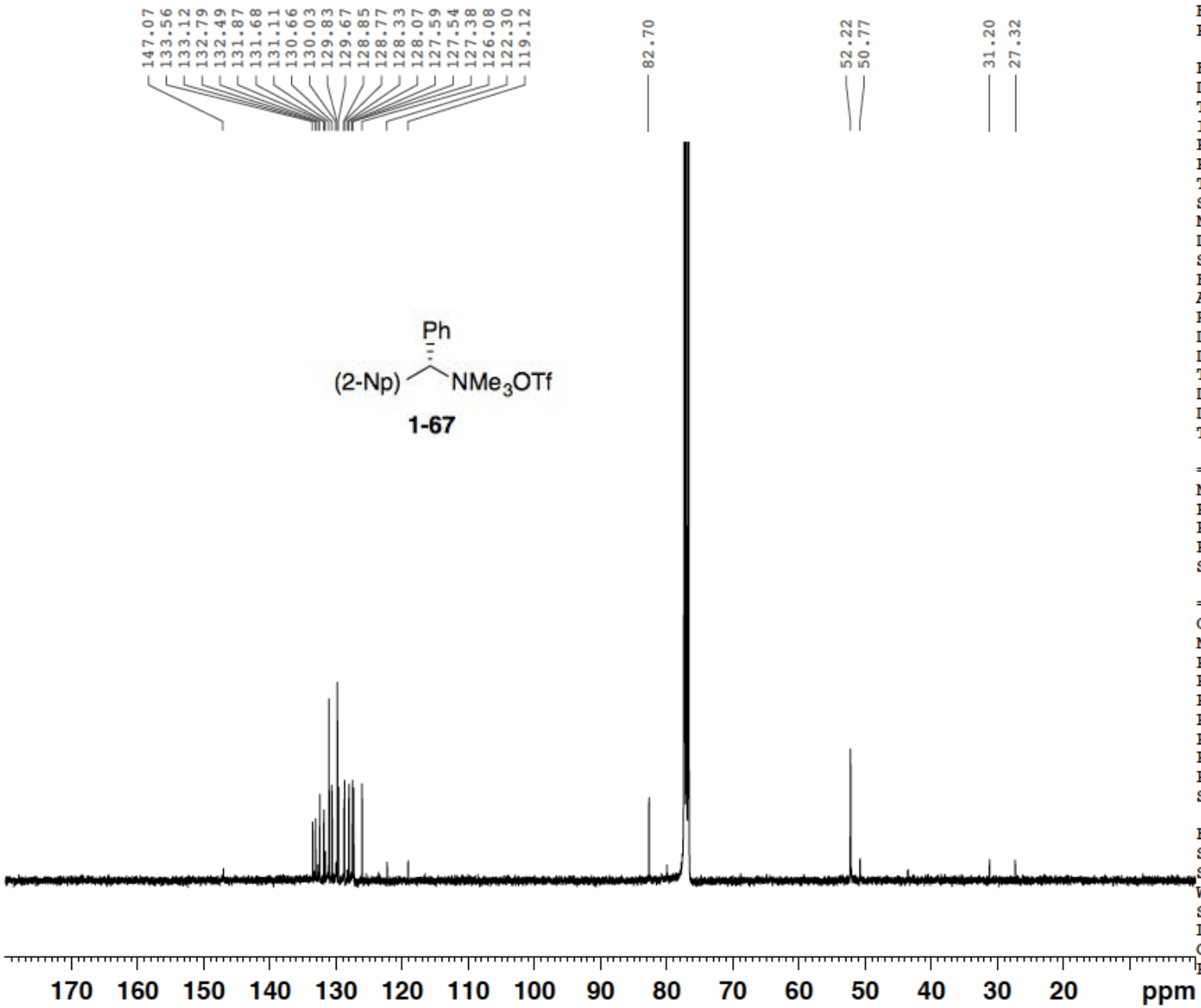

```
Current Data Parameters
NAME      CHB1-233-fluorine
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20140113
Time                 18.39
INSTRUM              spect
PROBHD    5 mm CPQNP 1H/
PULPROG              zgdc
TD                 131072
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              75187.969 Hz
FIDRES           0.573639 Hz
AQ               0.8716788 sec
RG                  1149.4
DW                   6.650 usec
DE                  20.00 usec
TE                  298.2 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   19F
P1                   15.03 usec
PL1                  -4.00 dB
PL1W         25.74305916 W
SFO1         376.4607164 MHz

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

F2 - Processing parameters
SI                 65536
SF           376.4983660 MHz
WDW                   EM
SSB                    0
LB                  2.00 Hz
GB                     0
PC                  1.00
```

CHB1-233-proton
PROTON_16 CDCl3 /opt/topspin kmrob 46




```
Current Data Parameters
NAME      CHB1-233-proton
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20140113
Time              18.36
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        400.1300077 MHz
WDW                EM
SSB                 0
LB               0.30 Hz
GB                  0
PC               1.00
```

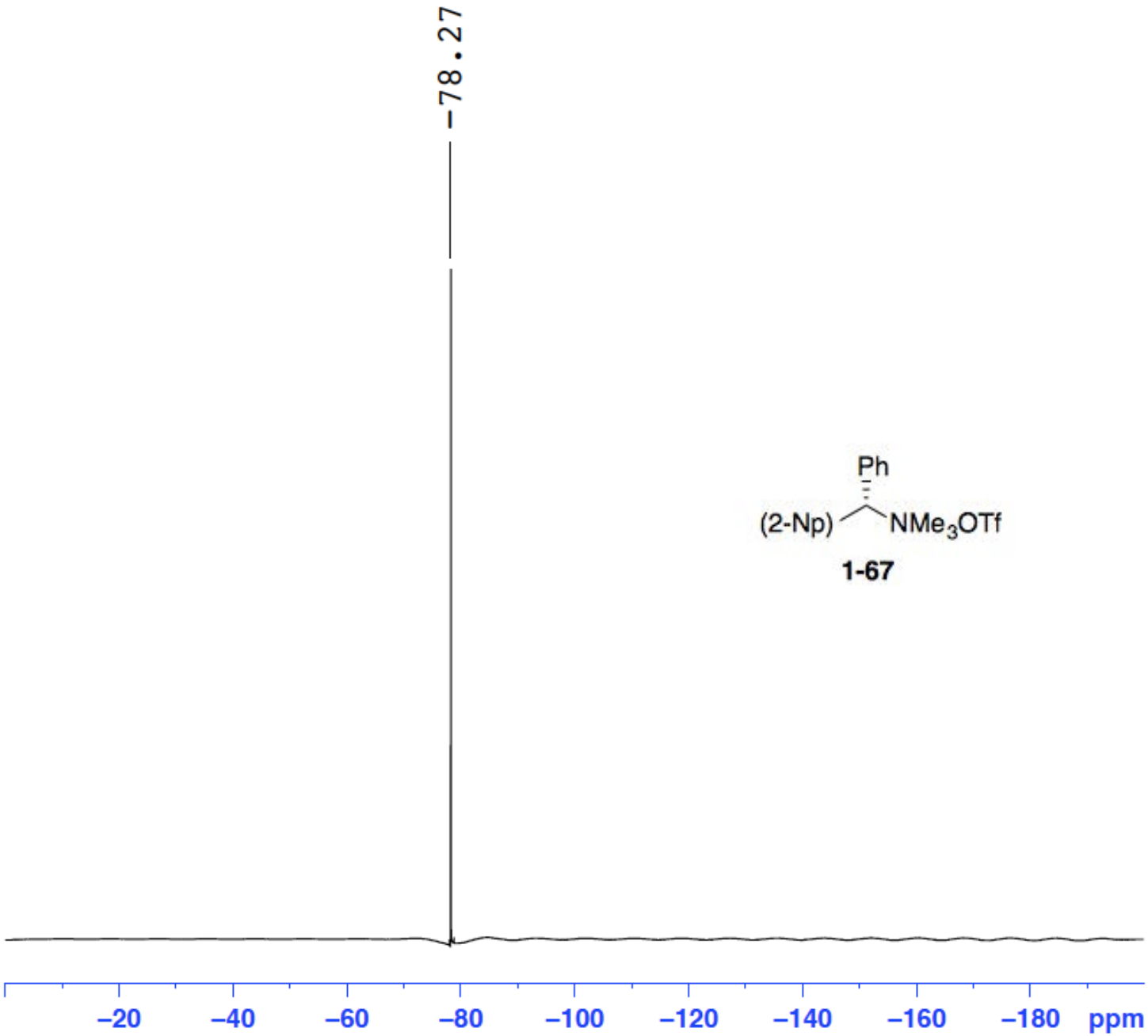
CHB1-221-carbon
C13CPD32 CDCl3 /opt/topspin kmrob 47




```
Current Data Parameters
NAME      CHB1-221-carbon
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20140114
Time                10.43
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                298.1 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
```

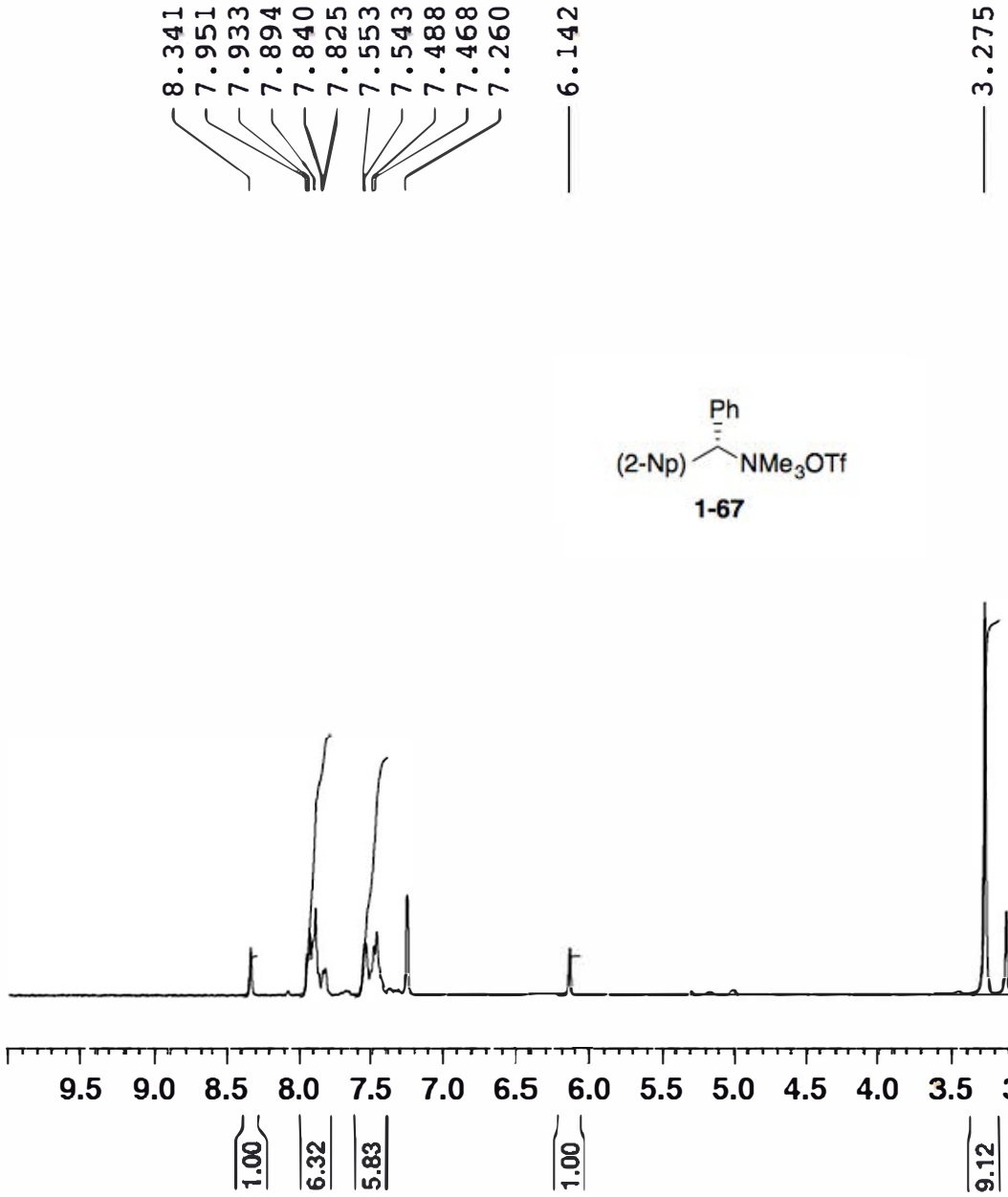
CHB1-221-fluorine

F19DEC 16 CDCl3 /opt/topspin kmrob 47




```
Current Data Parameters
NAME      CHB1-221-fluorine
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_           20140114
Time                9.43
INSTRUM            spect
PROBHD   5 mm CPQNP 1H/
PULPROG             zgdc
TD                131072
SOLVENT             CDCl3
NS                     16
DS                      2
SWH            75187.969 Hz
FIDRES          0.573639 Hz
AQ              0.8716788 sec
RG                 1625.5
DW                 6.650 usec
DE                20.00 usec
TE                298.2 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   19F
P1                 15.03 usec
PL1                -4.00 dB
PL1W         25.74305916 W
SFO1         376.4607164 MHz

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

F2 - Processing parameters
SI                 65536
SF           376.4983660 MHz
WDW                   EM
SSB                    0
LB                  2.00 Hz
GB                     0
PC                  1.00
```

CHB1-221-proton
PROTON_16 CDCl3 /opt/topspin kmrob 47



Current Data Parameters

NAME	CHB1-221-proton
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20140114
Time	9.40
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	4
DW	60.400 usec
DE	6.00 usec
TE	298.2 K
D1	1.00000000 sec
TD0	1

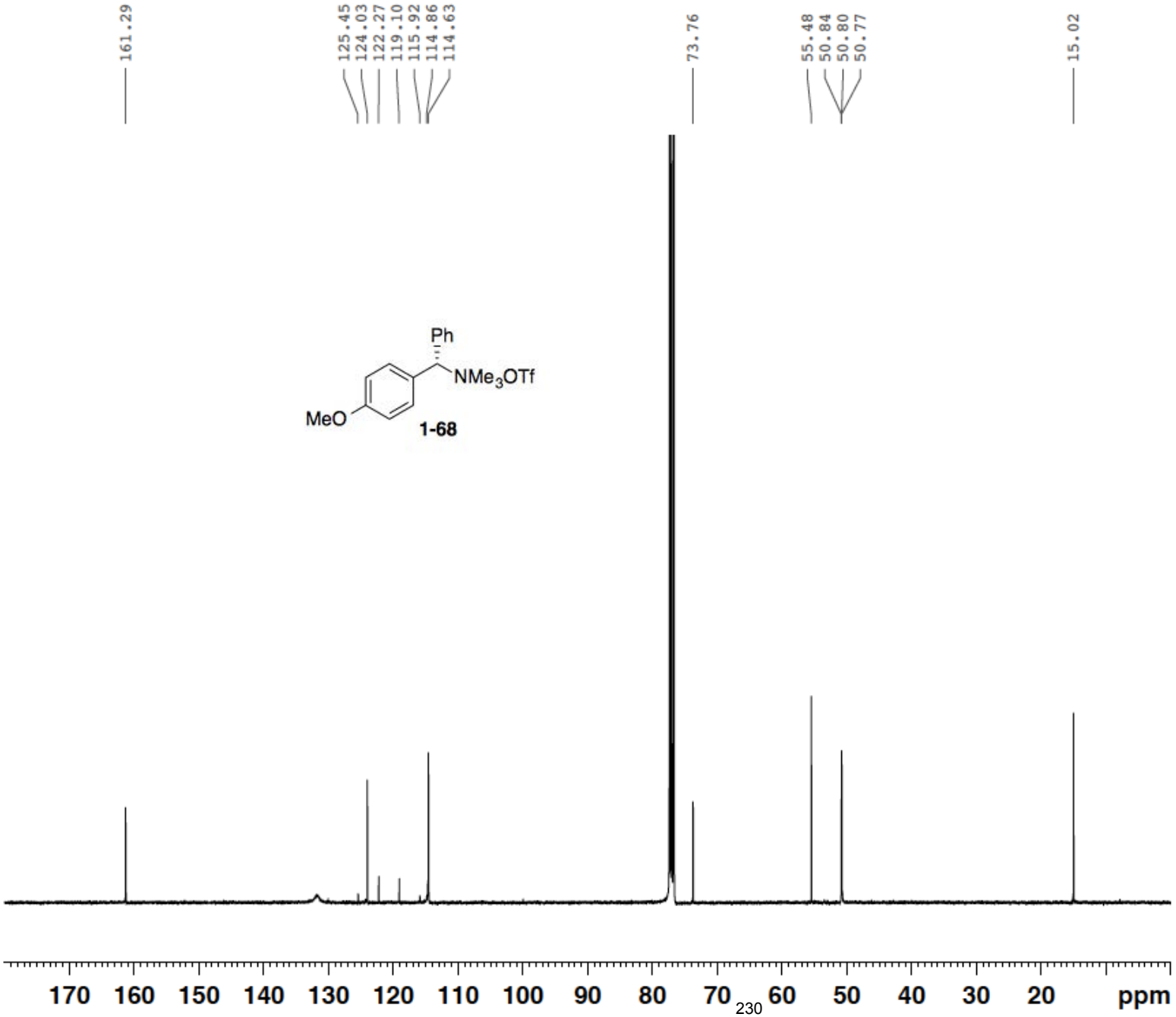
======== CHANNEL f1 ========

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

F2 - Processing parameters

SI	32768
SF	400.1300113 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

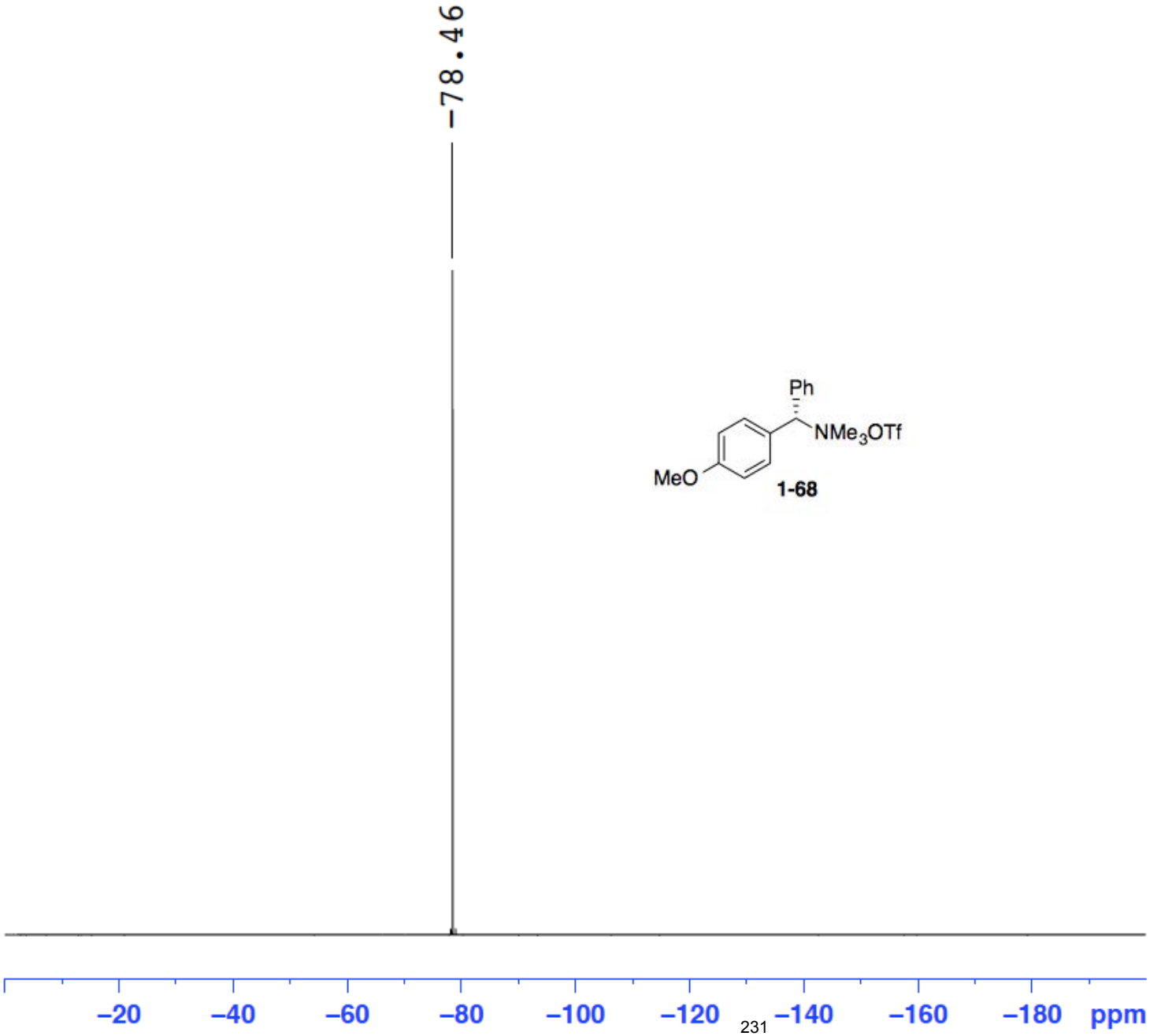
KMR 1-221-CARBON
C13CPD32 CDCl3 /opt/topspin kmrob 34




```
Current Data Parameters
NAME      KMR 1-221-CARBON
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20140113
Time                14.00
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
```

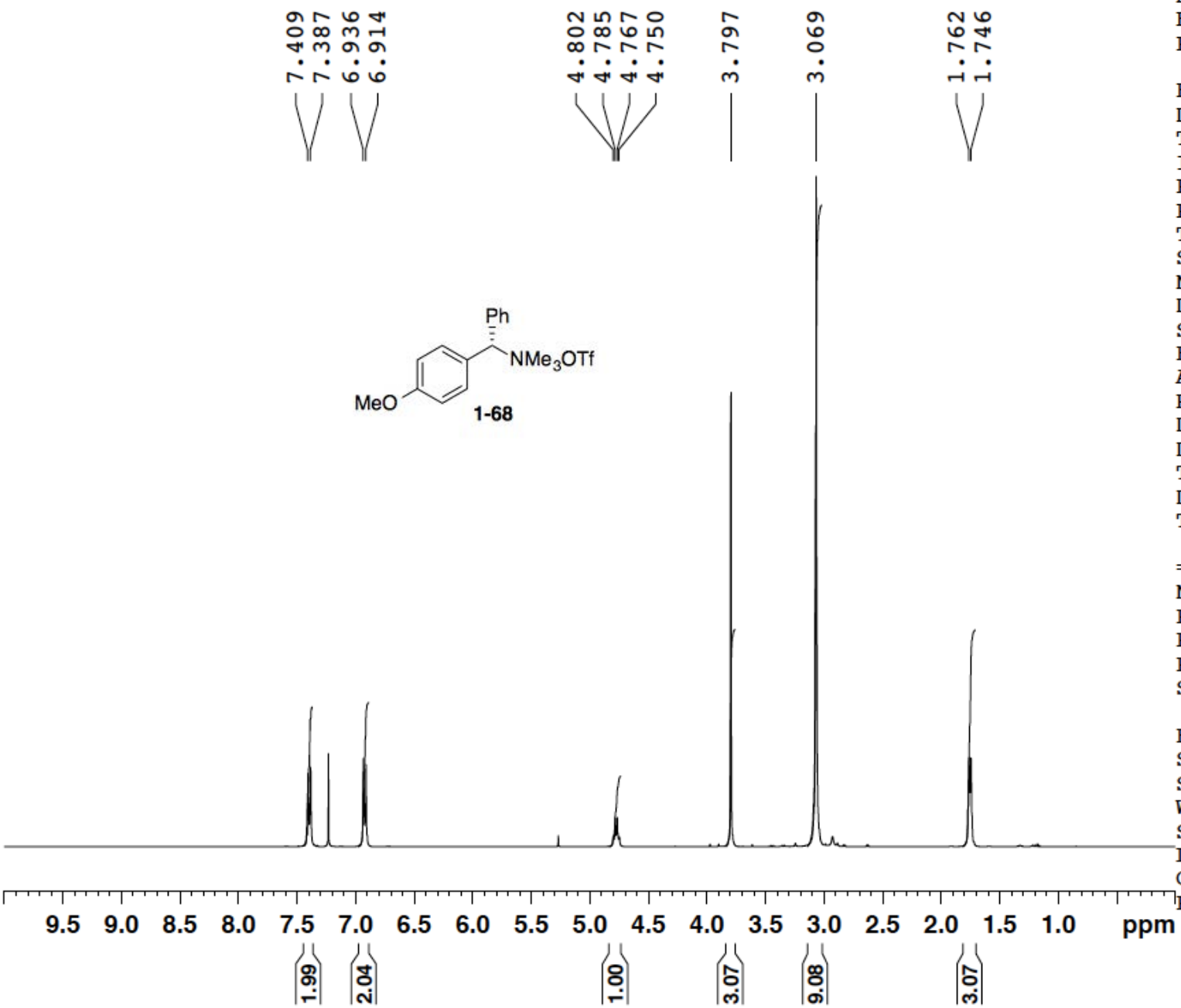
KMR 1-221-FLUORINE

F19CPD CDCl3 /opt/topspin kmrob 1



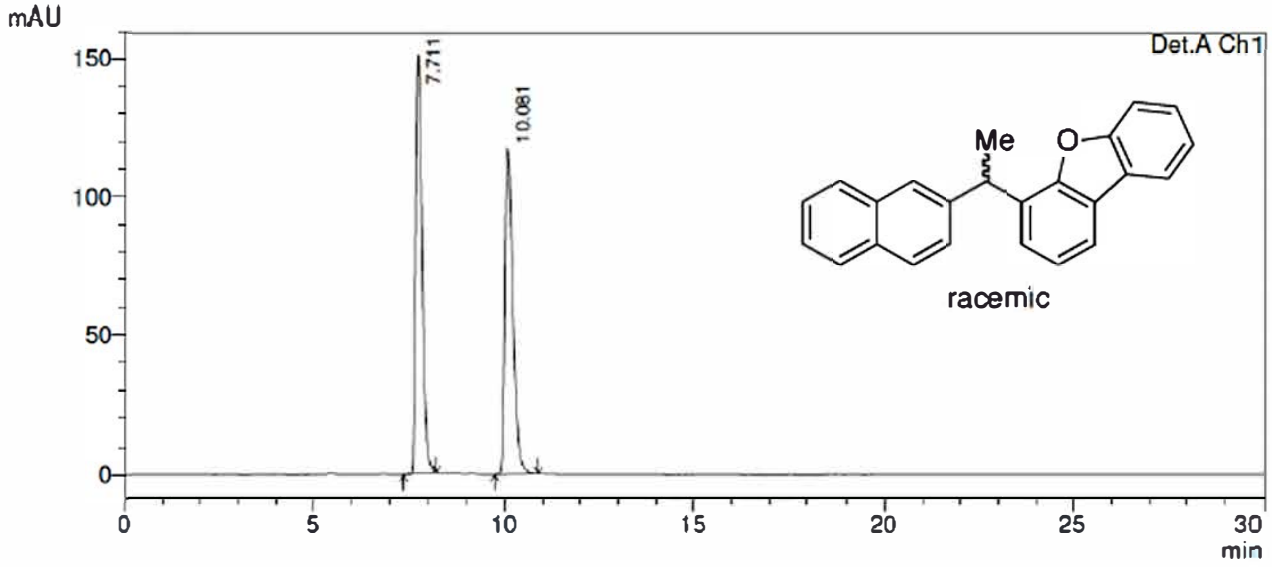

```
Current Data Parameters
NAME      KMR 1-221-FLUORINE
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_               20140112
Time                   16.19
INSTRUM                spect
PROBHD    5 mm CPQNP 1H/
PULPROG             zgfhigqn
TD                    131072
SOLVENT                CDCl3
NS                        16
DS                         4
SWH                75187.969 Hz
FIDRES              0.573639 Hz
AQ                  0.8716788 sec
RG                     2580.3
DW                      6.650 usec
DE                      6.50 usec
TE                     298.2 K
D1                1.00000000 sec
D11               0.03000000 sec
D12               0.00002000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      19F
P1                      15.03 usec
PL1                     -4.00 dB
PL1W             25.74305916 W
SFO1            376.4607164 MHz

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

F2 - Processing parameters
SI                     65536
SF              376.4983660 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```

KMR 1-221-PROTON
PROTON_16 CDCl3 /opt/topspin kmrob 34




```
Current Data Parameters
NAME      KMR 1-221-PROTON
EXPNO                    4
PROCNO                   1

F2 - Acquisition Parameters
Date_             20140113
Time                 14.03
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                      14.3
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           400.1300201 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

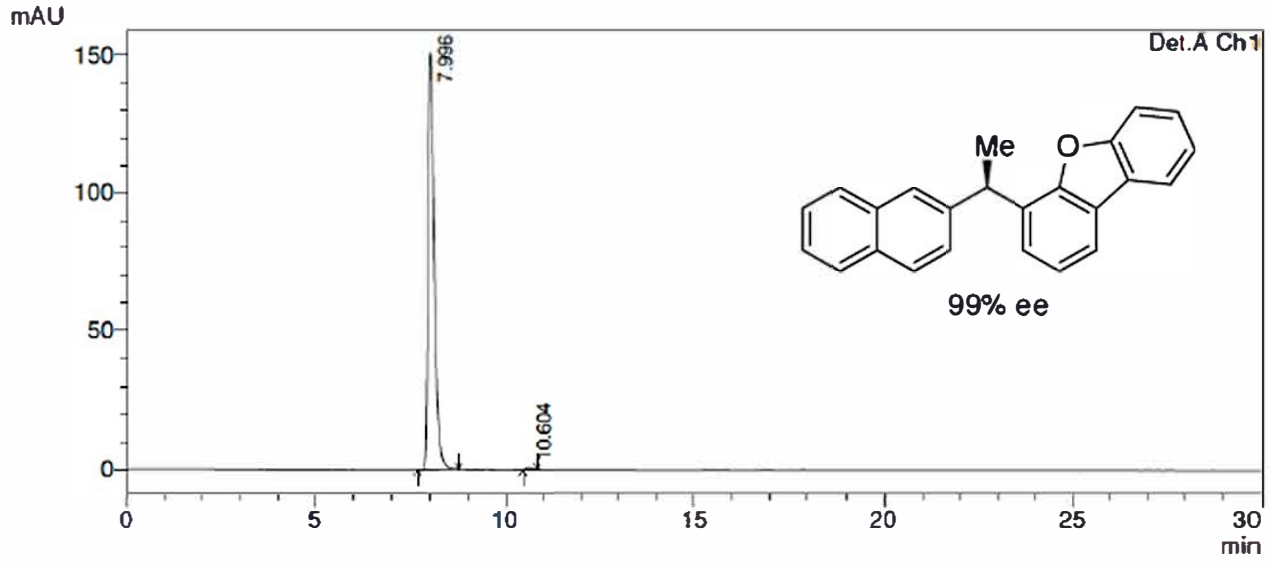
Compound 1-48, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.711	1656098	151316	49.649	56.269
2	10.081	1679516	117601	50.351	43.731
Total		3335614	268916	100.000	100.000

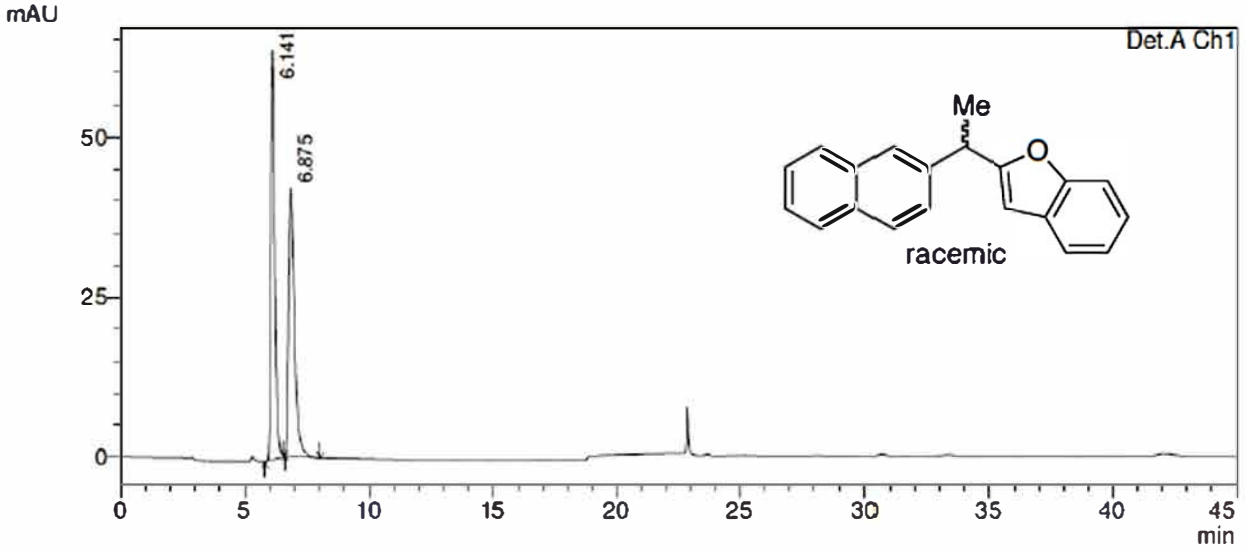
Compound 1-48, 99% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.996	1761412	151169	99.365	99.357
2	10.604	11252	978	0.635	0.643
Total		1772664	152147	100.000	100.000

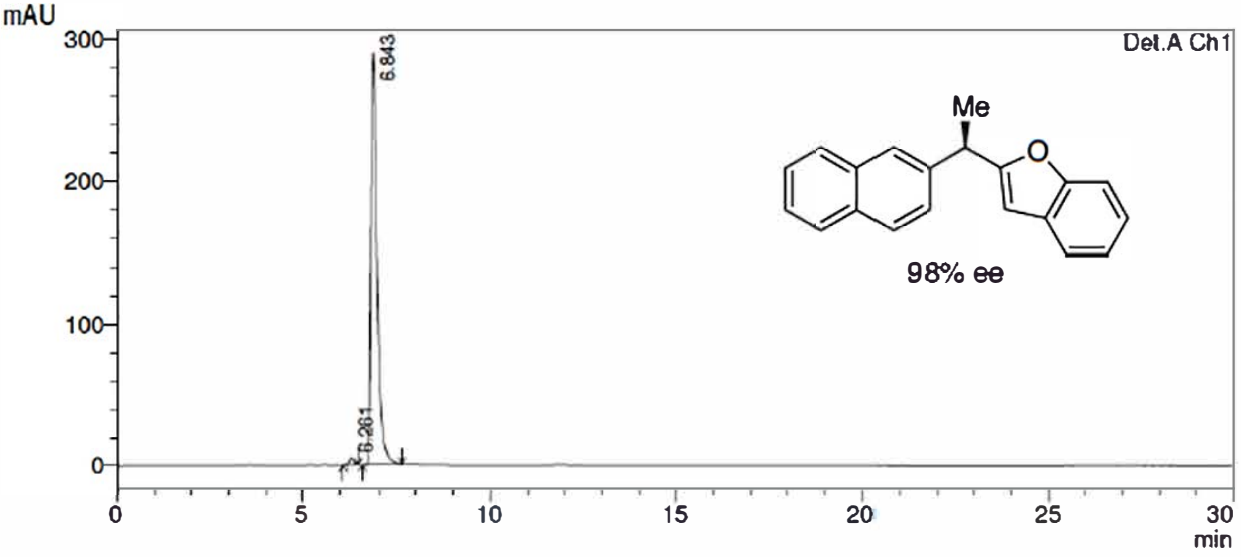
Compound 1-49, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.141	724449	63708	50.614	60.367
2	6.875	706862	41827	49.386	39.633
Total		1431312	105536	100.000	100.000

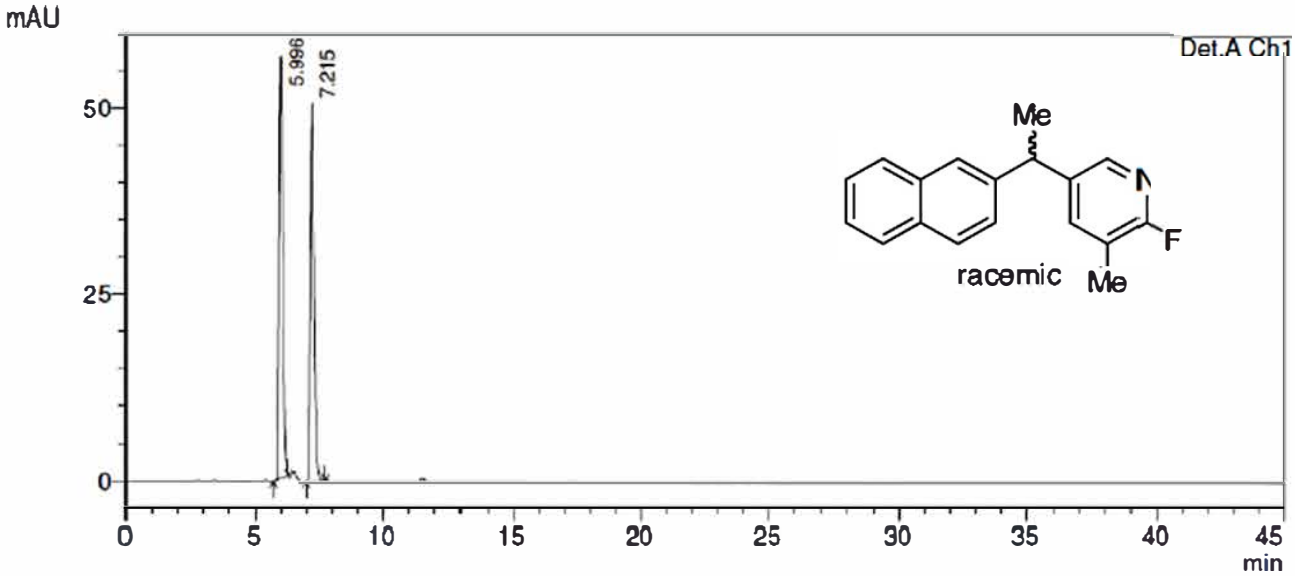
Compound 1-49, 98% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.261	40903	4730	1.159	1.601
2	6.843	3489421	290760	98.841	98.399
Total		3530324	295490	100.000	100.000

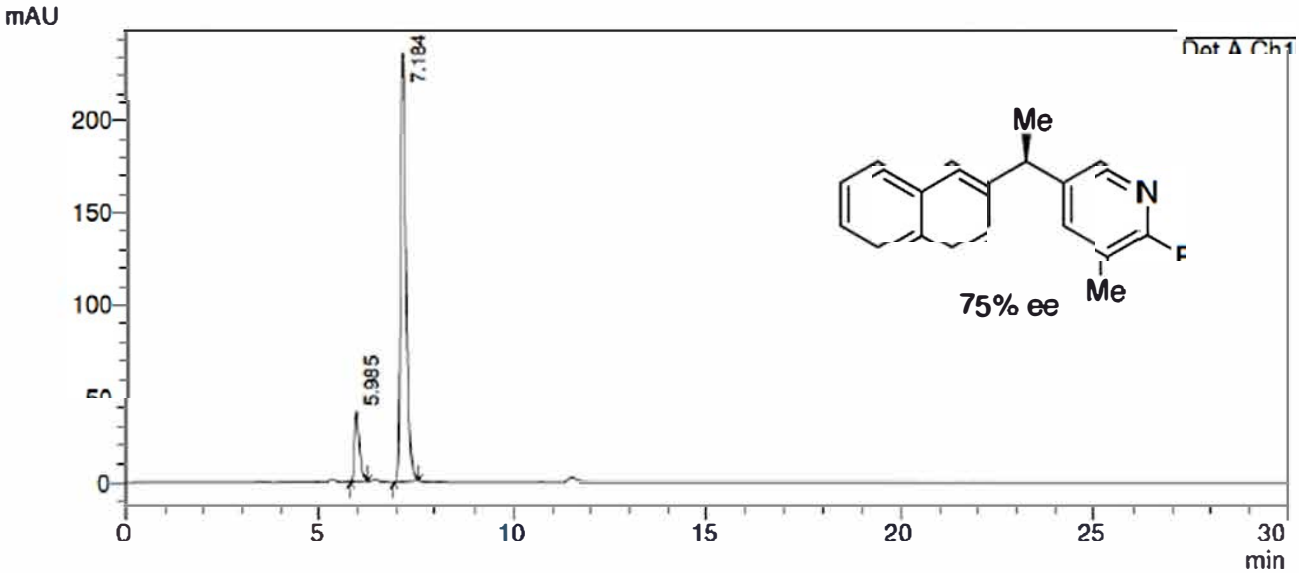
Compound 1-50, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.996	497654	56740	49.584	52.767
2	7.215	506004	50789	50.416	47.233
Total		1003657	107529	100.000	100.000

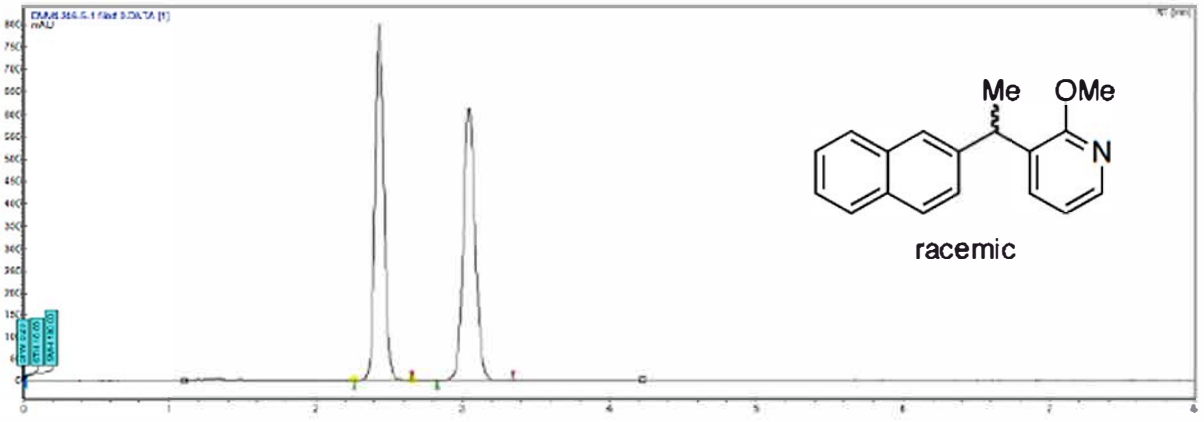
Compound 1-50, 75% ee



Detector A Ch1 254nm

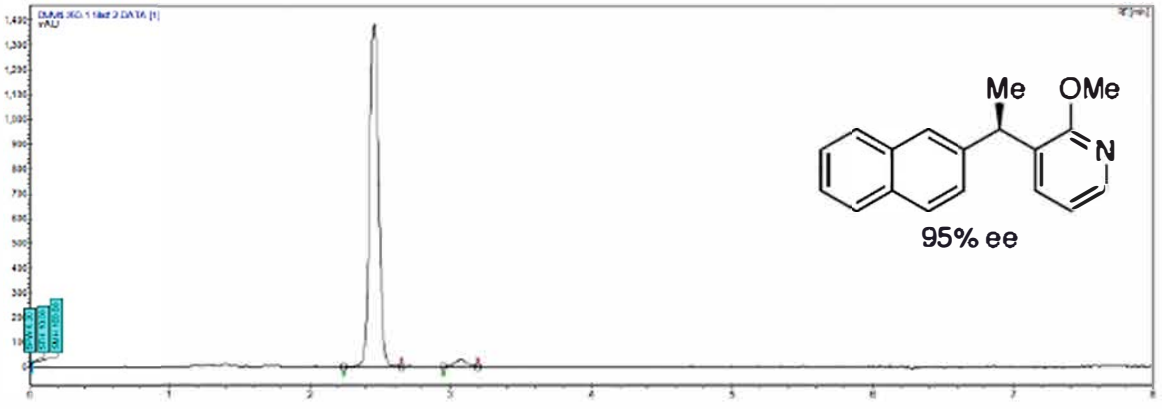
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.985	338641	37234	12.572	13.839
2	7.184	2355059	231805	87.428	86.161
Total		2693699	269038	100.000	100.000

Compound 1-51, racemic



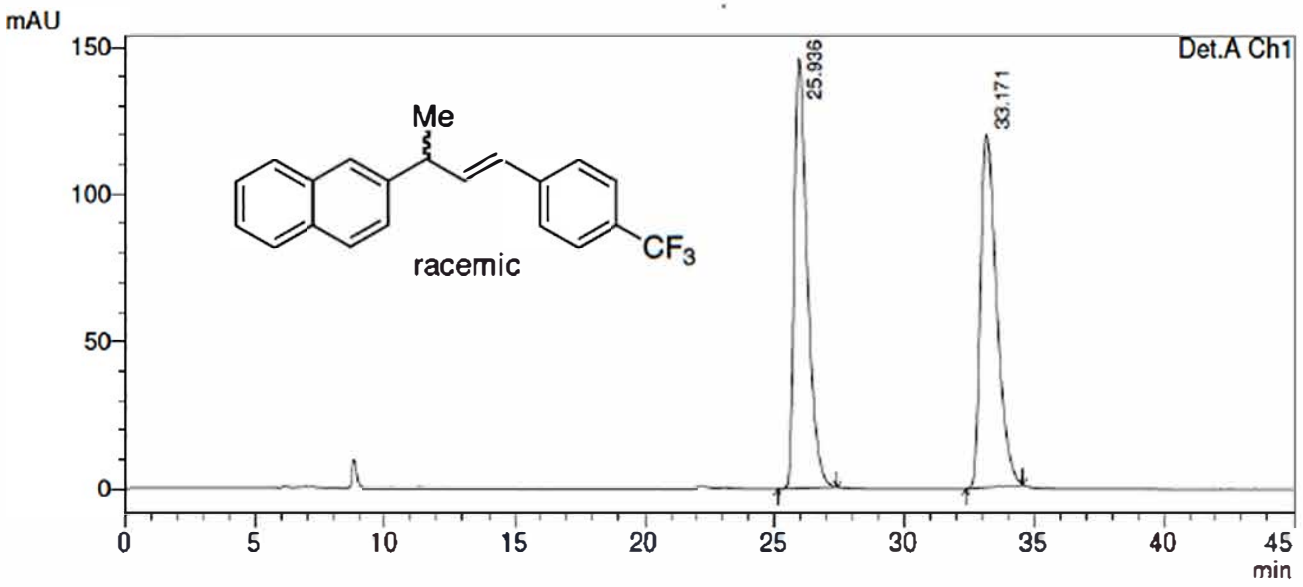
Index	Time	Width	Height	Res. HW	Selectivity	Area	Area
	[Min]	[Min]	[µV]			[µV.Min]	[%]
1	2.43	0.06	799.8	0.00	0.00	56.9	49.885
2	3.04	0.09	611.0	4.81	1.25	57.1	50.115
Total			1410.8			114.0	100.000

Compound 1-51, 95% ee



Index	Time (min)	Area (%)
Peak-1	2.46	97.553
Peak-2	3.07	2.447
Total		100.00

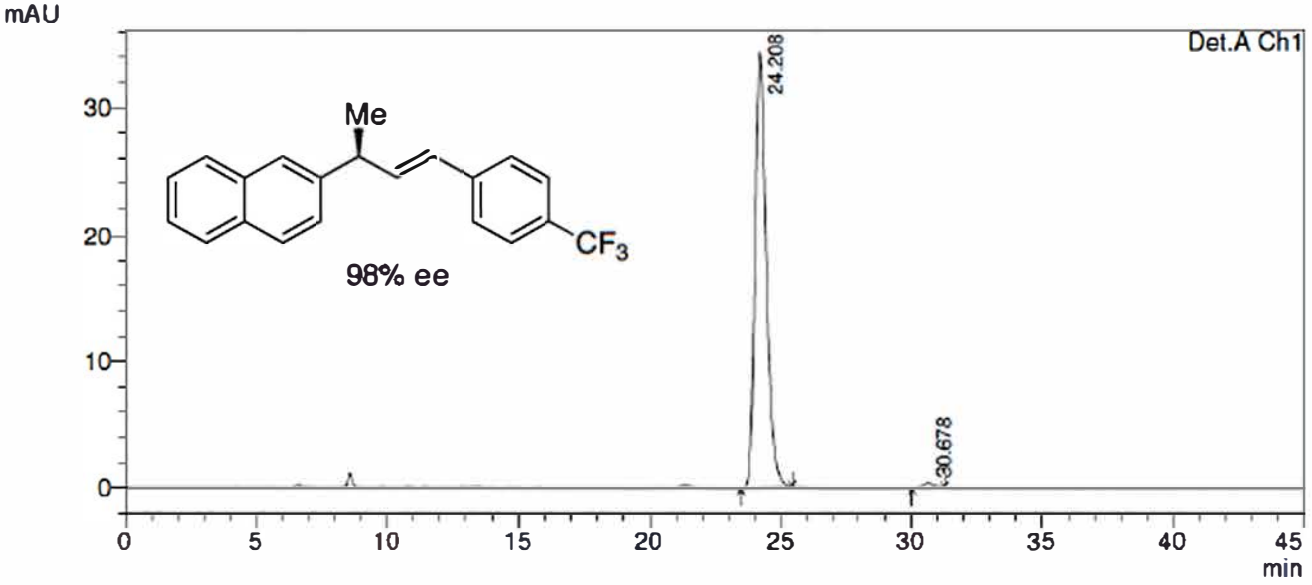
Compound 1-52, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.936	5203928	146301	50.289	54.908
2	33.171	5144076	120148	49.711	45.092
Total		10348004	266449	100.000	100.000

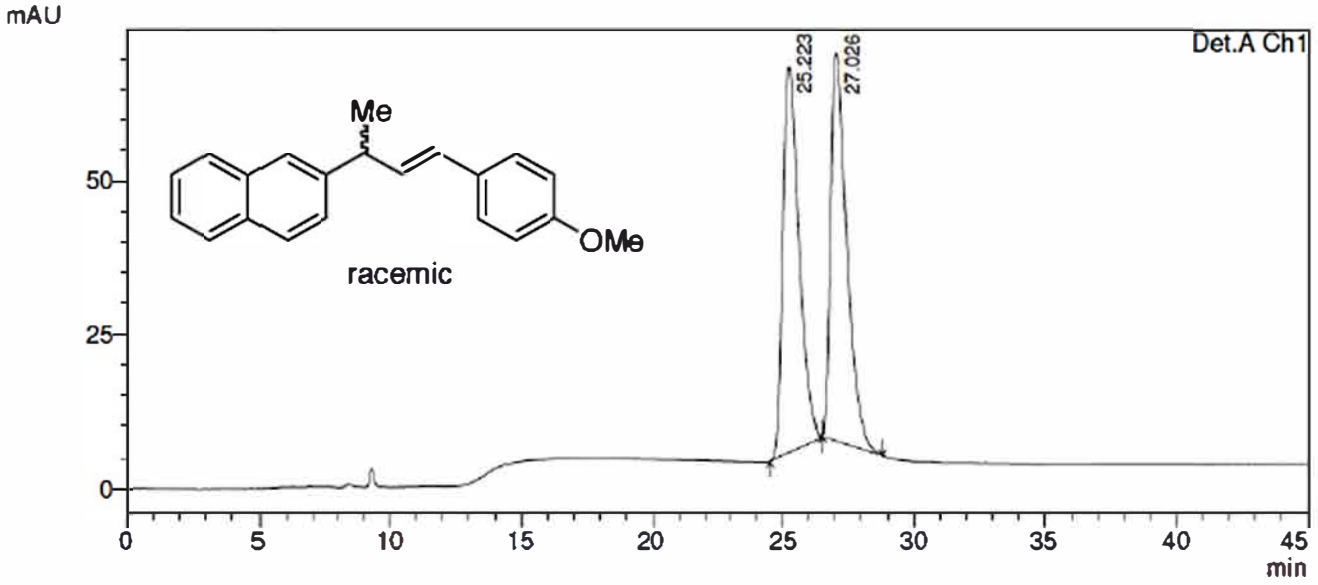
Compound 1-52, 98% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.208	1047966	34361	98.809	98.906
2	30.678	12628	380	1.191	1.094
Total		1060594	34741	100.000	100.000

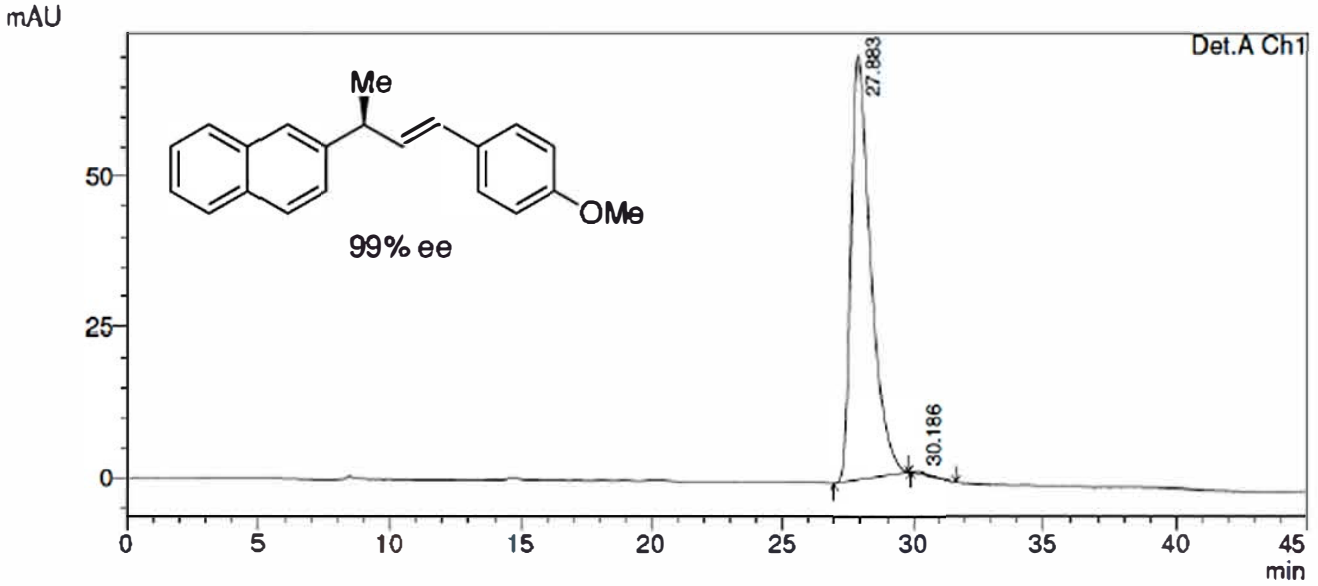
Compound 1-53, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.223	2654759	62771	49.692	49.803
2	27.026	2687689	63266	50.308	50.197
Total		5342448	126038	100.000	100.000

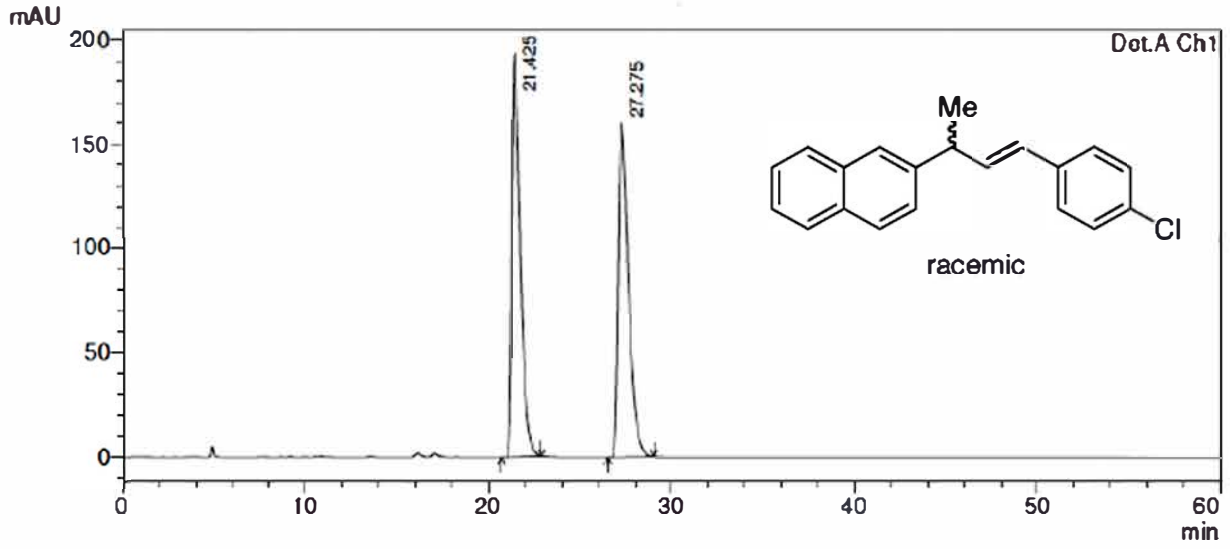
Compound 1-53, 99% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.883	3674930	70516	99.504	99.430
2	30.186	18306	404	0.496	0.570
Total		3693237	70920	100.000	100.000

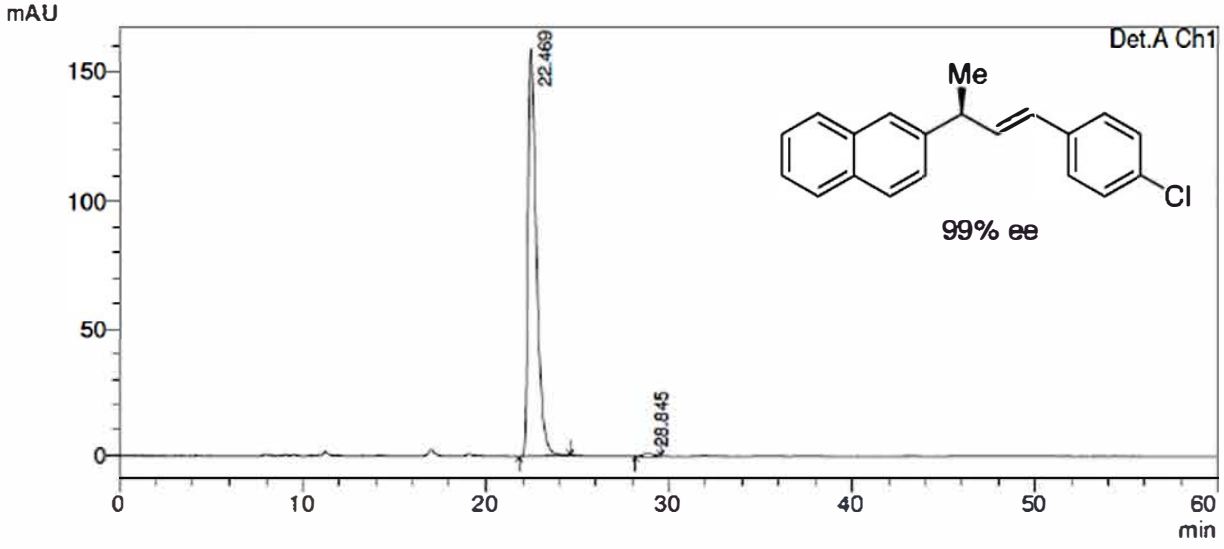
Compound 1-54, racemic



Det.A Ch1/254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.425	6187717	193804	49.926	54.757
2	27.275	6206154	160132	50.074	45.243
Total		12393871	353936	100.000	100.000

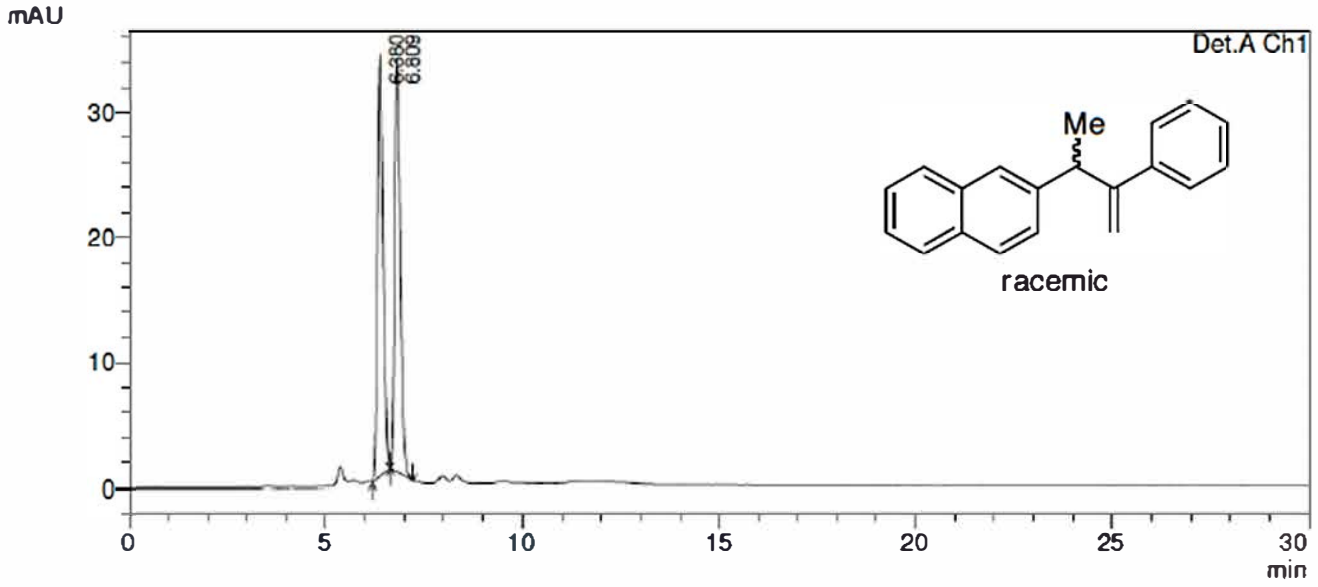
Compound 1-54, 99% ee



Det.A Ch1/254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.469	5156302	159225	99.359	99.400
2	28.845	33277	961	0.641	0.600
Total		5189578	160186	100.000	100.000

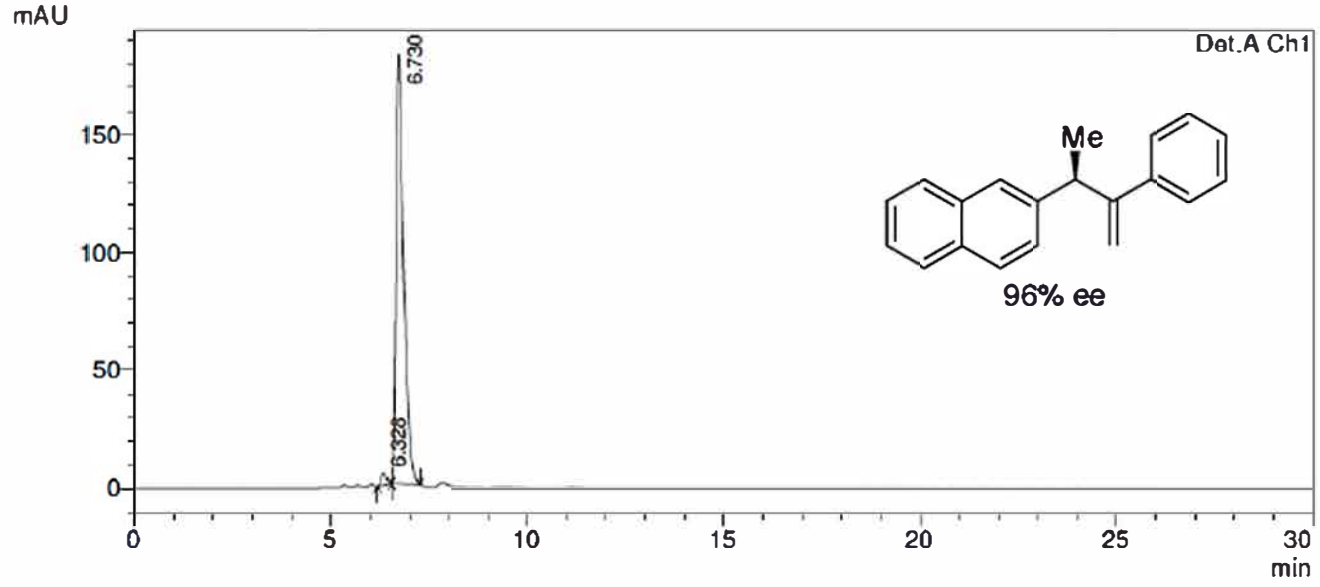
Compound 1-55, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.380	336440	33838	50.168	50.642
2	6.809	334192	32981	49.832	49.358
Total		670632	66819	100.000	100.000

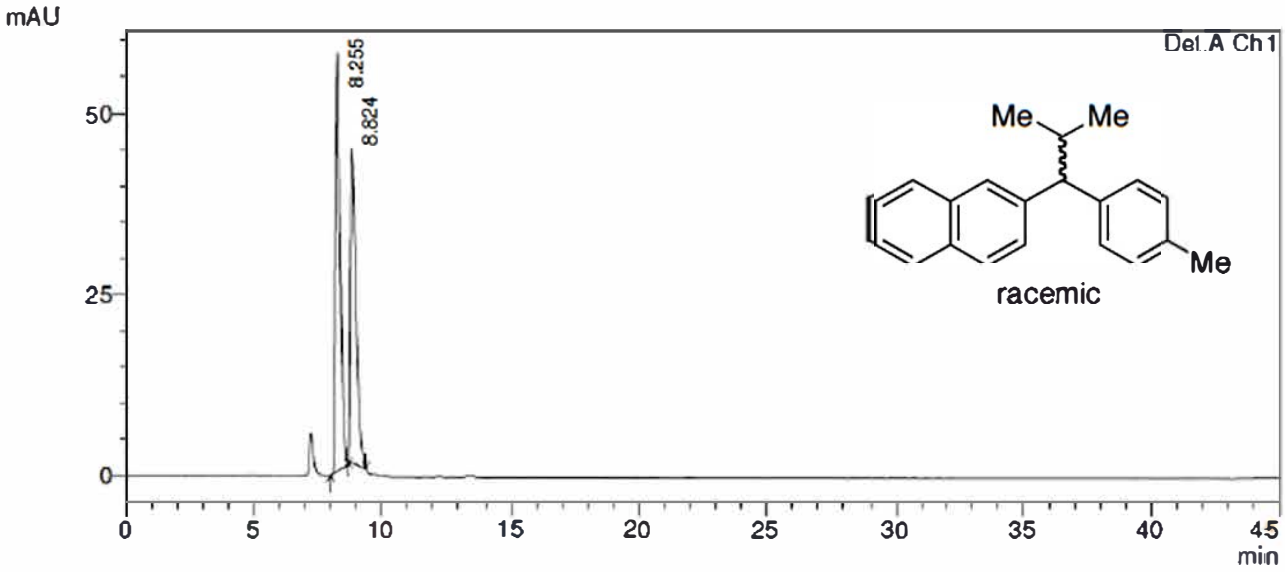
Compound 1-55, 96% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.328	48108	5104	2.009	2.725
2	6.730	2346770	182200	97.991	97.275
Total		2394878	187304	100.000	100.000

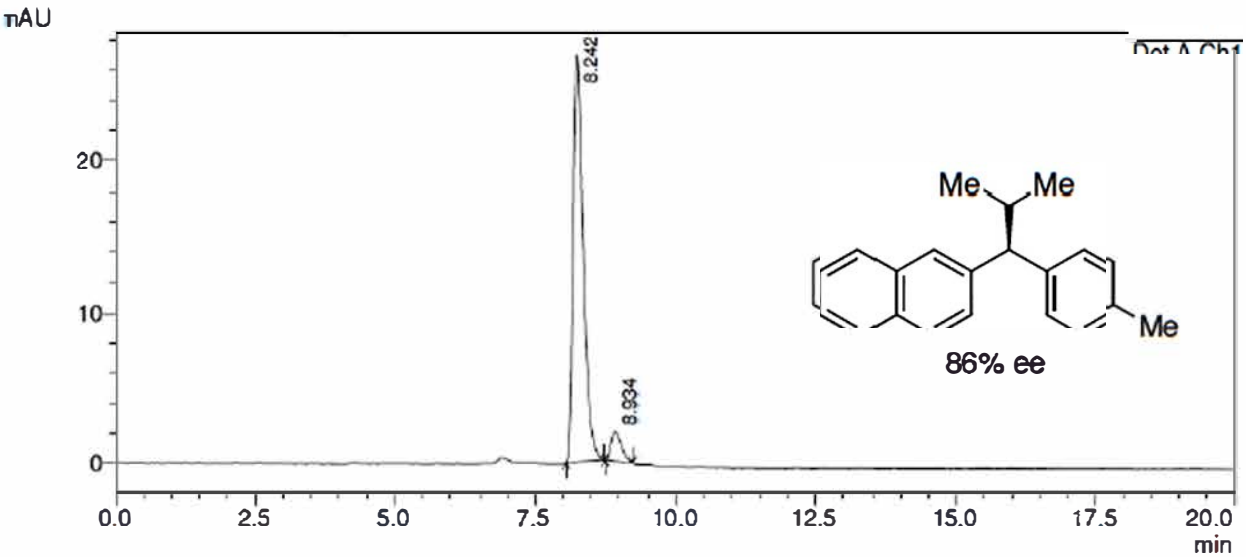
Compound 1-56, racemate



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.255	709002	57468	50.831	56.905
2	8.824	685811	43522	49.169	43.095
Total		1394812	100990	100.000	100.000

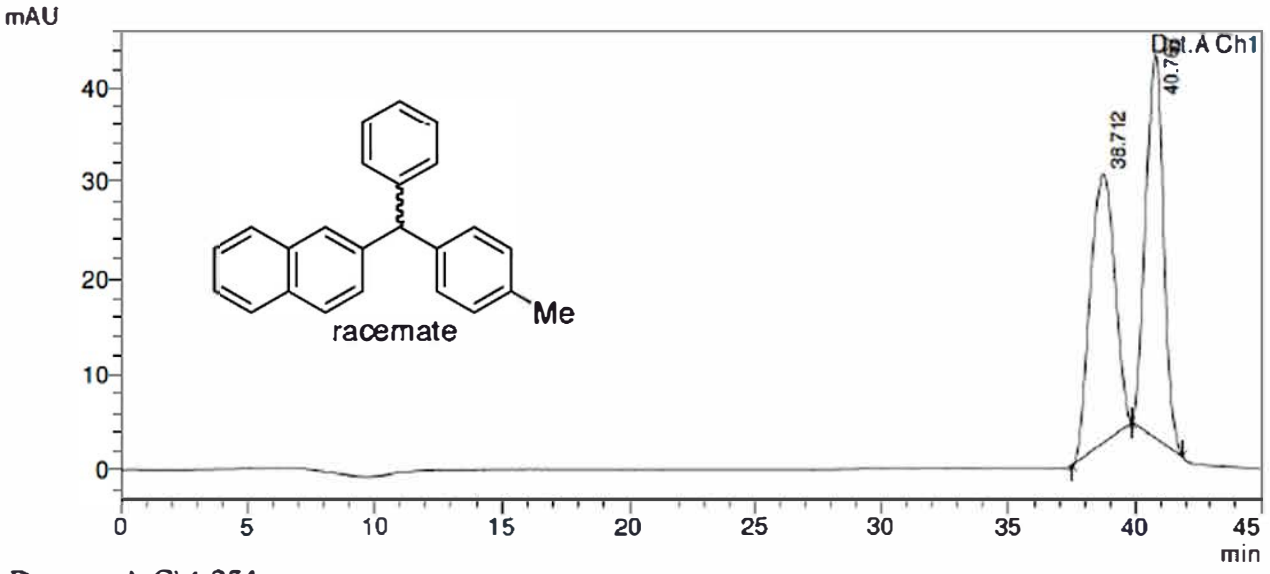
Compound 1-56, 86 % ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.242	342386	26925	93.176	93.236
2	8.934	25075	1954	6.824	6.764
Total		367462	28879	100.000	100.000

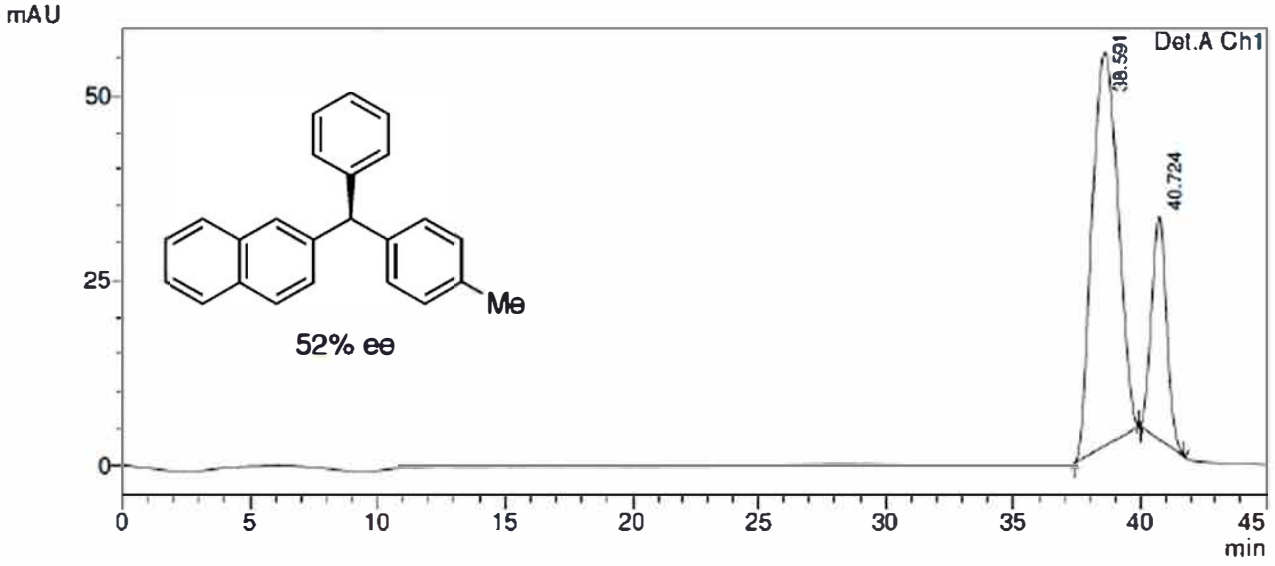
Compound 1-57, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	38.712	1882323	27993	49.000	41.014
2	40.767	1959118	40259	51.000	58.986
Total		3841441	68252	100.000	100.000

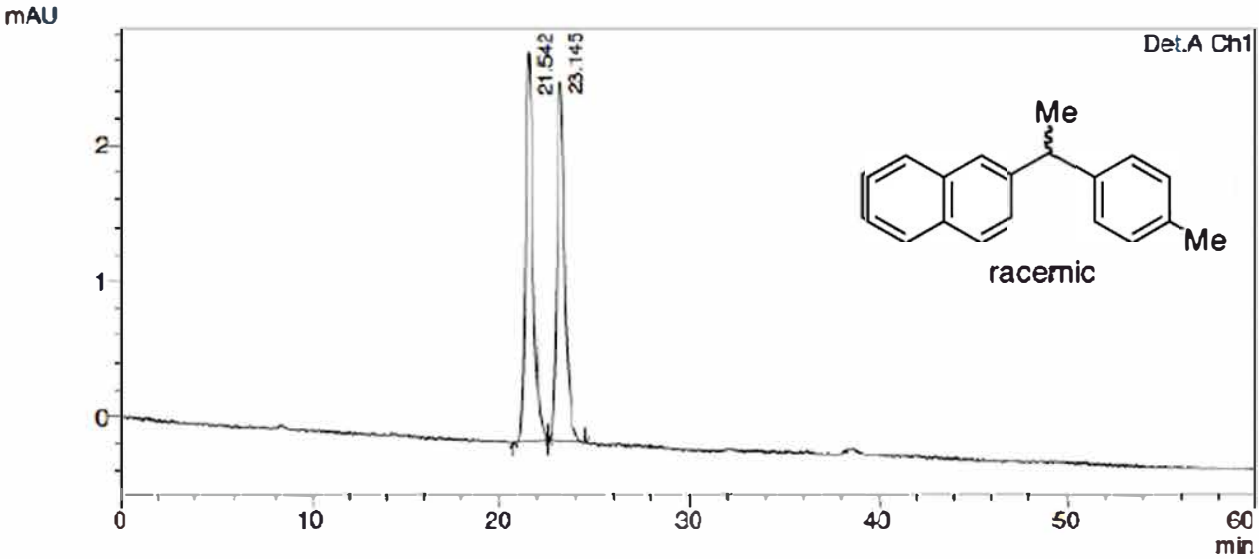
Compound 1-57, 52% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	38.591	3753096	53270	75.430	63.952
2	40.724	1222527	30027	24.570	36.048
Total		4975623	83297	100.000	100.000

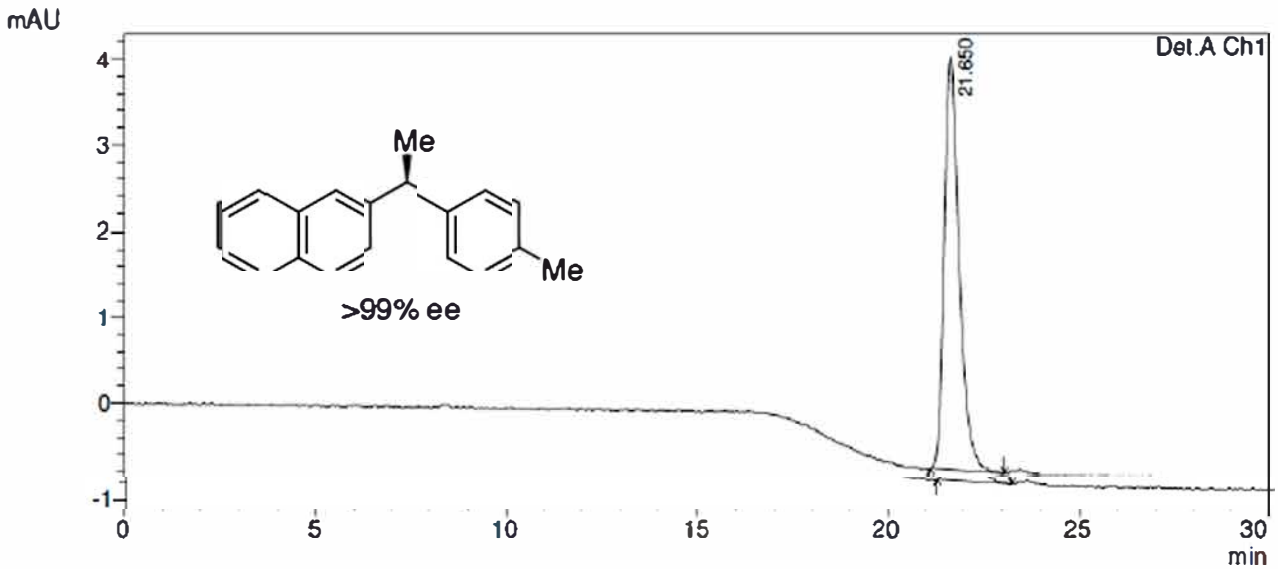
Compound 1-58, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.542	78839	2843	50.033	51.898
2	23.145	78735	2635	49.967	48.102
Total		157574	5478	100.000	100.000

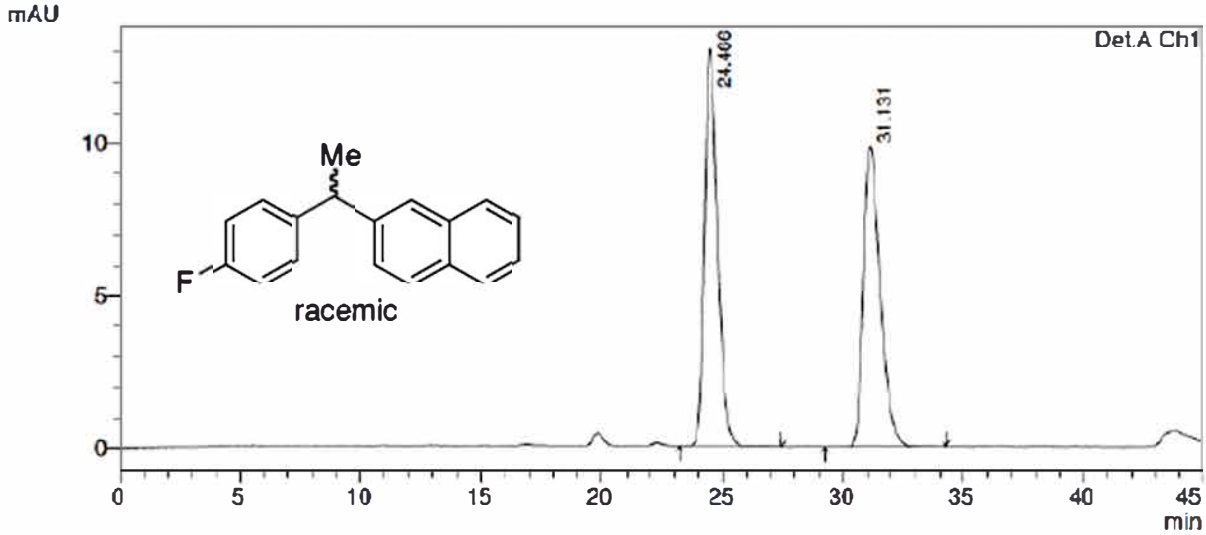
Compound 1-58, >99% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.650	132973	4798	100.000	100.000
Total		132973	4798	100.000	100.000

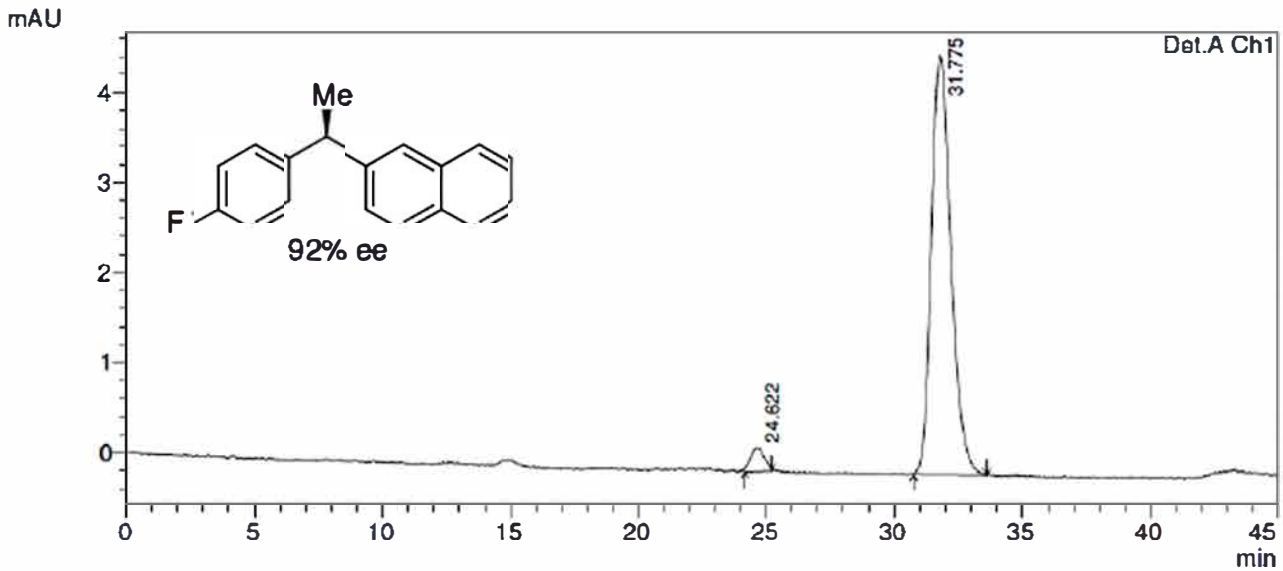
Compound 1-59, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.466	492703	13047	50.652	57.061
2	31.131	480018	9818	49.348	42.939
Total		972721	22865	100.000	100.000

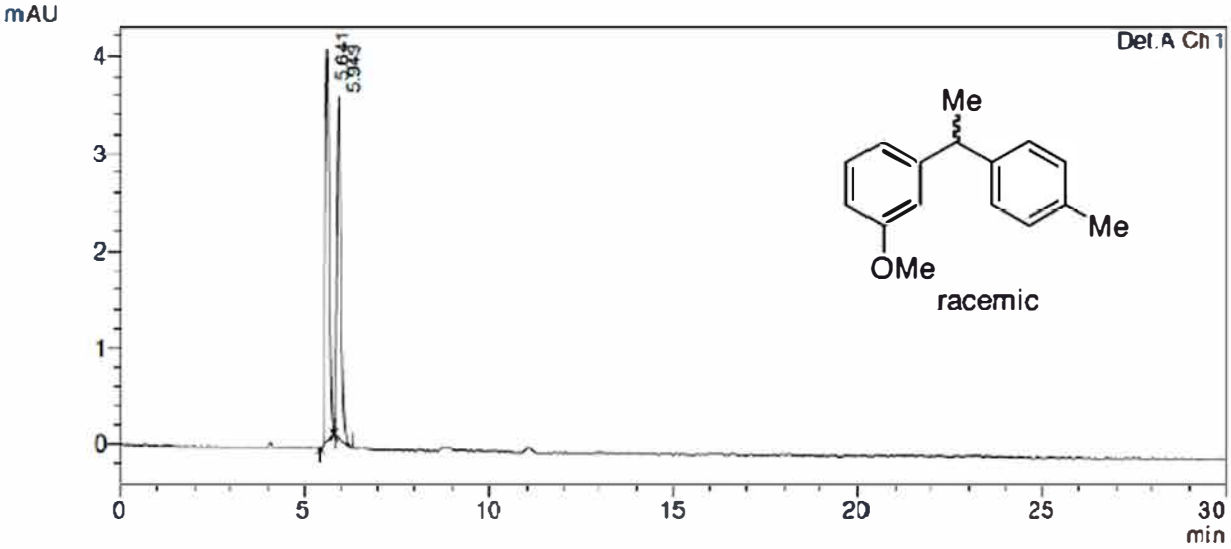
Compound 1-59, 92% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.622	9857	265	3.832	5.387
2	31.775	247379	4657	96.168	94.613
Total		257236	4923	100.000	100.000

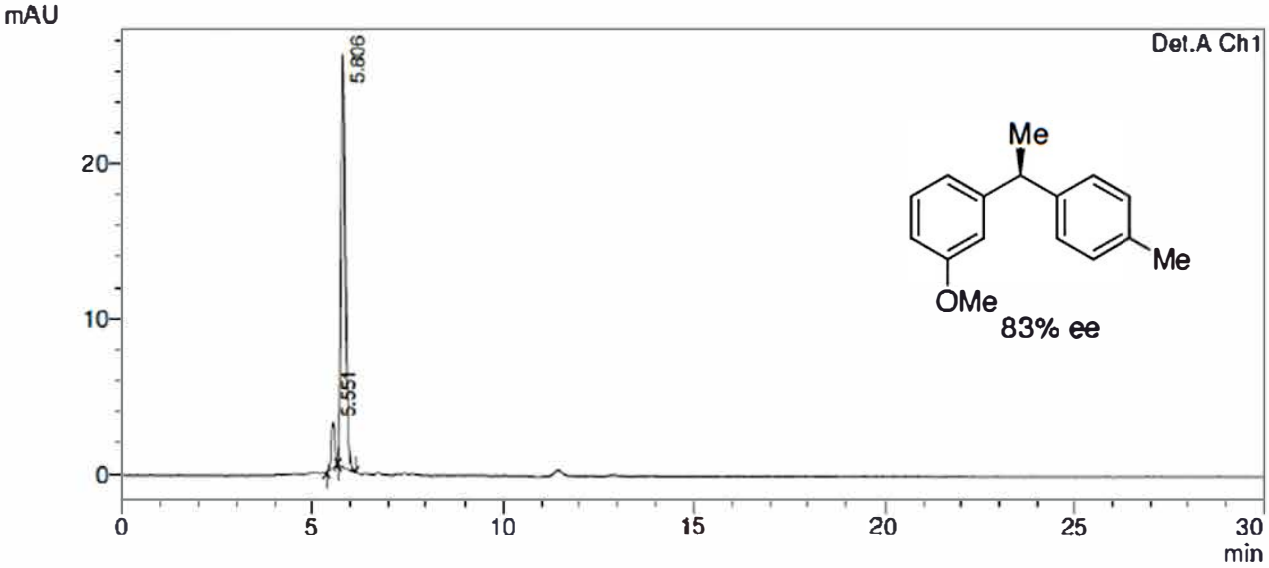
Compound 1-60, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.641	28336	4020	50.186	53.282
2	5.949	28127	3525	49.814	46.718
Total		56463	7545	100.000	100.000

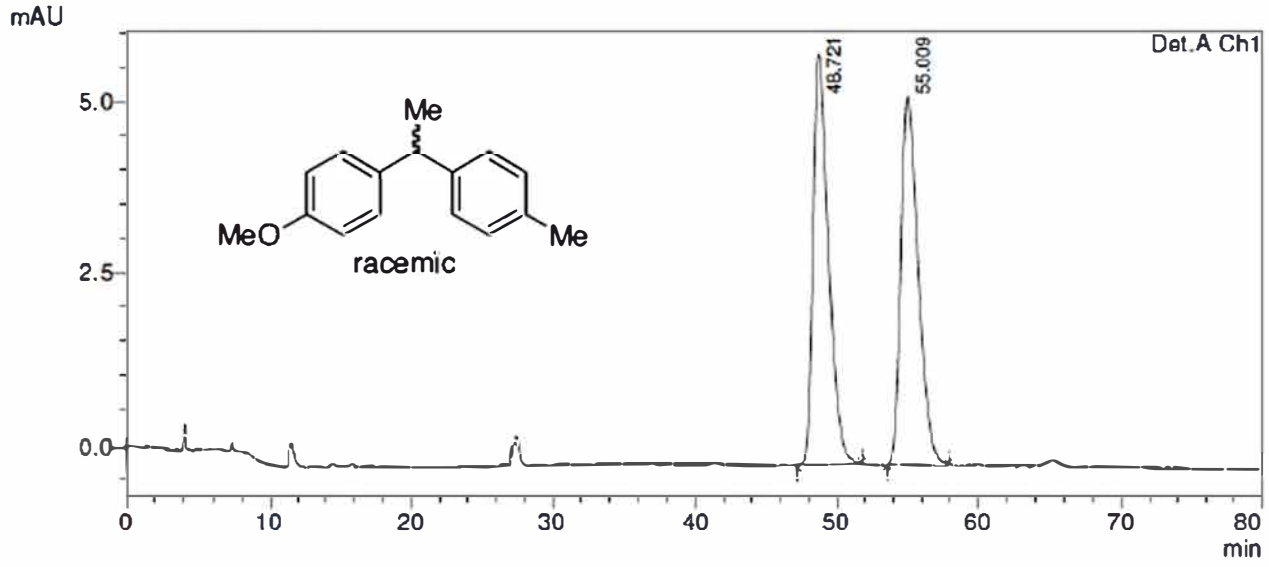
Compound 1-60, 83% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.551	19671	2814	8.659	9.580
2	5.806	207507	26561	91.341	90.420
Total		227178	29375	100.000	100.000

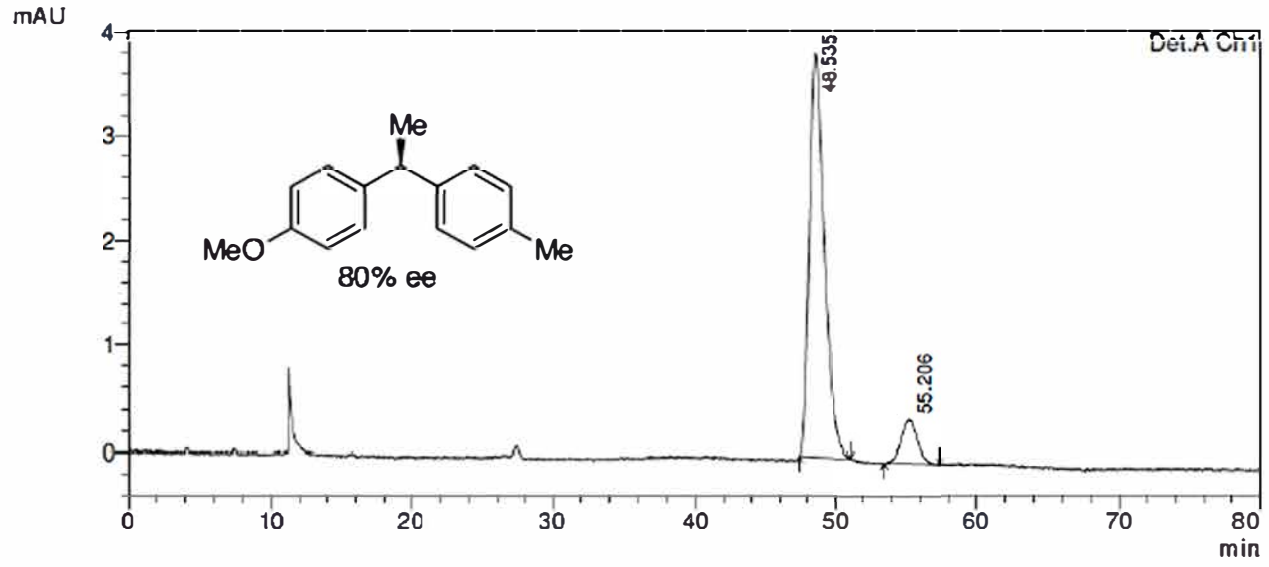
Compound 1-61, racemic



Detector A Ch1 254nm

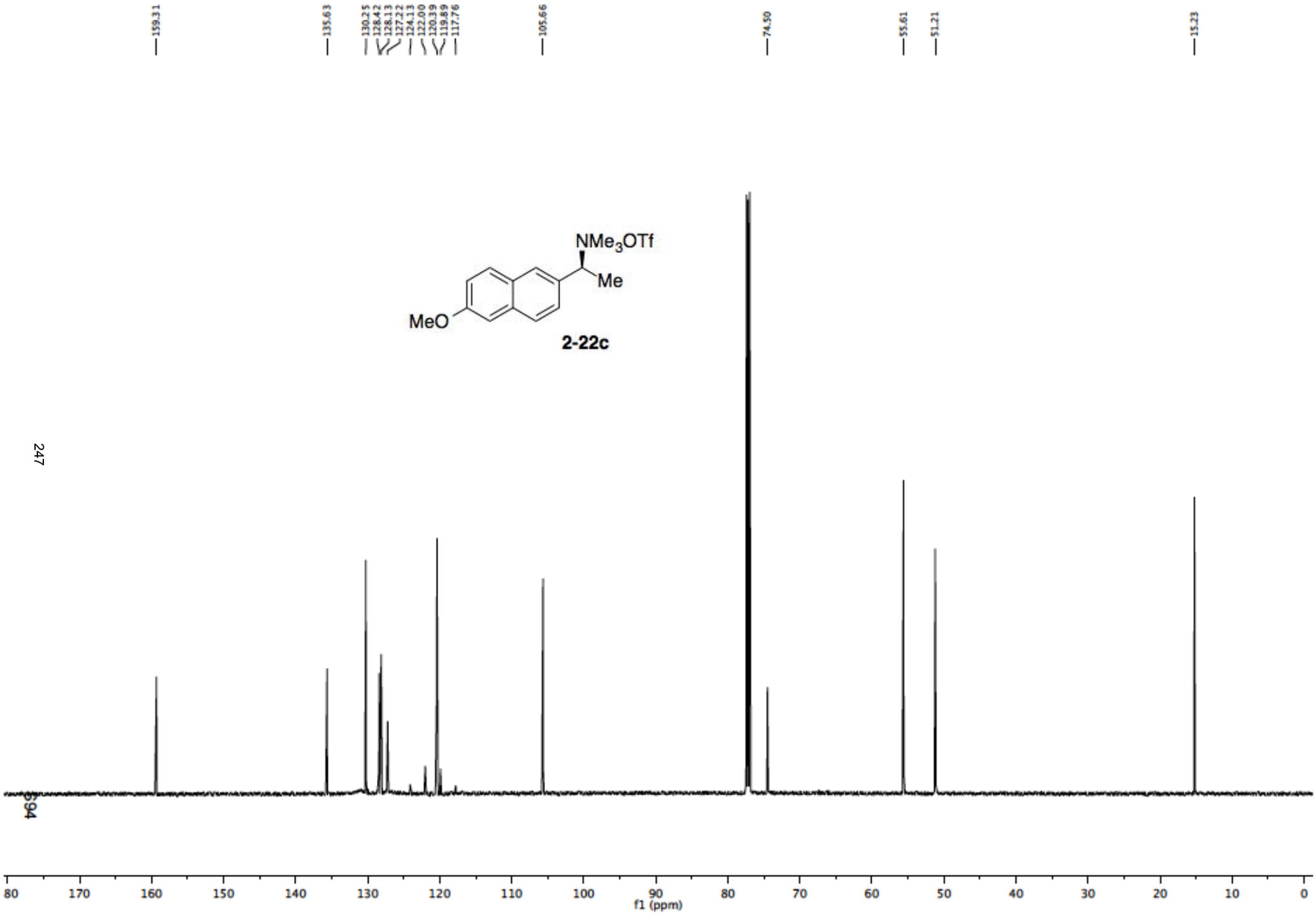
Peak#	Ret. Time	Area	Height	Area %	Height %
1	48.721	457545	5994	50.055	52.702
2	55.009	456533	5380	49.945	47.298
Total		914078	11374	100.000	100.000

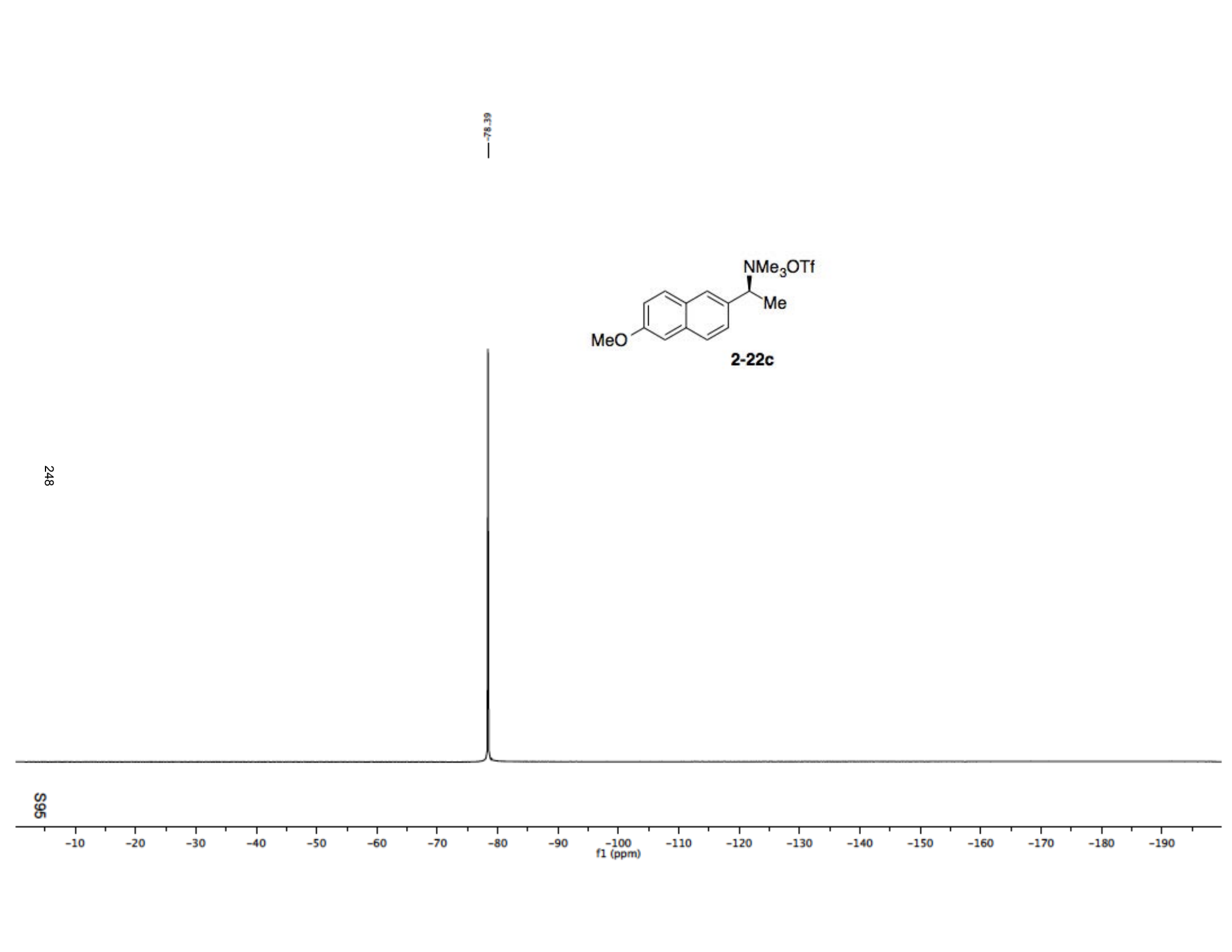
Compound 1-61, 80% ee

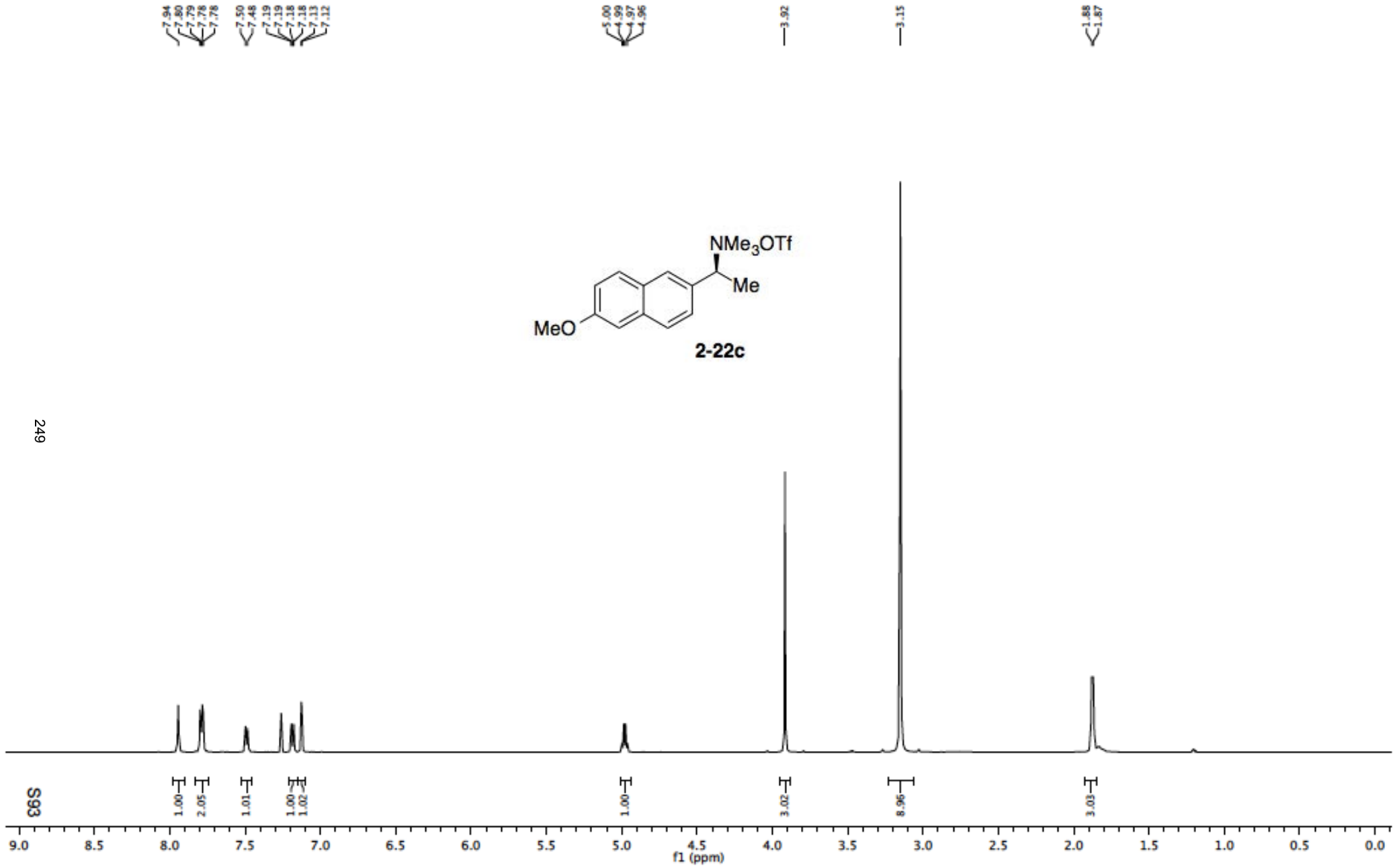


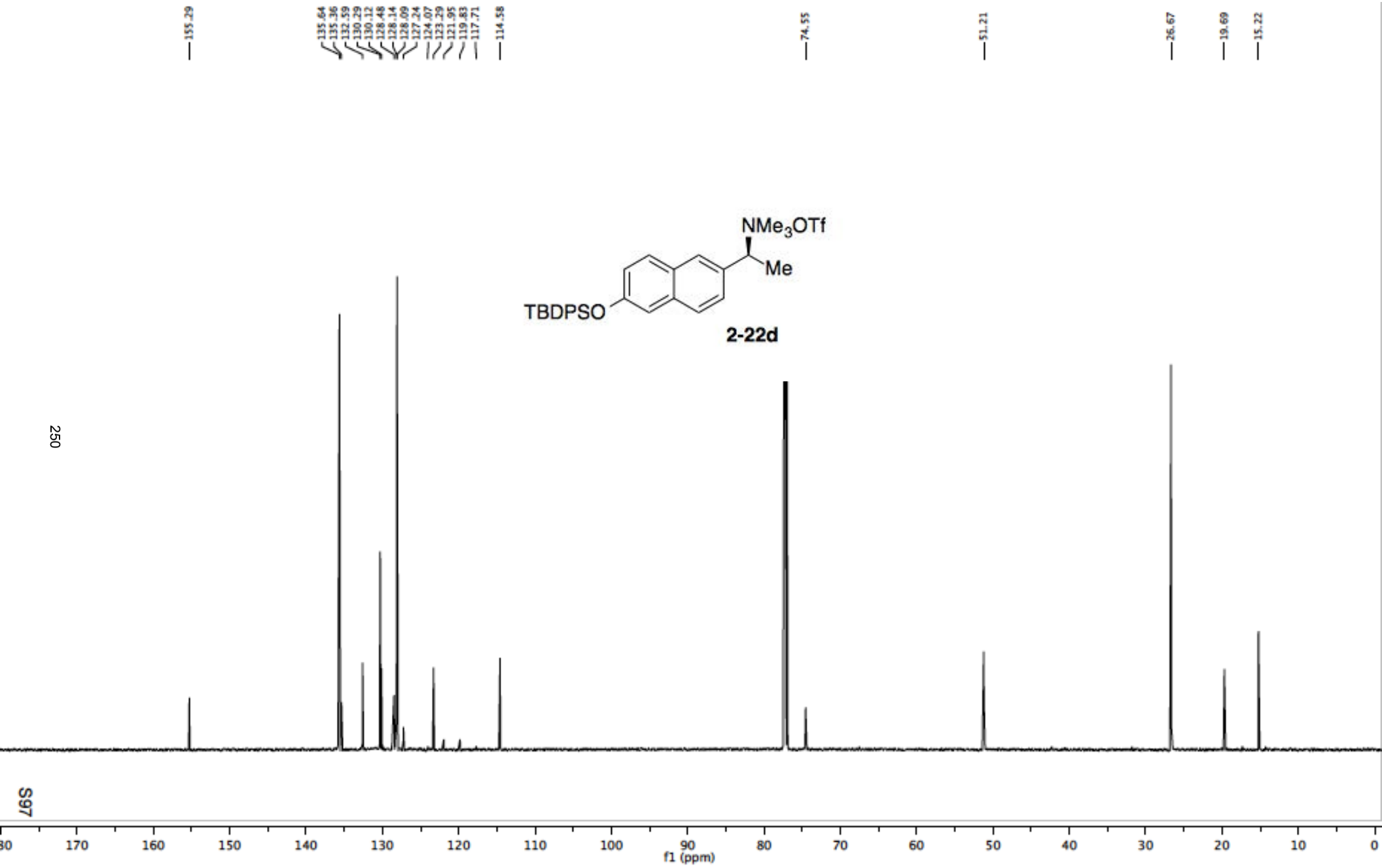
Detector A Ch1 254nm

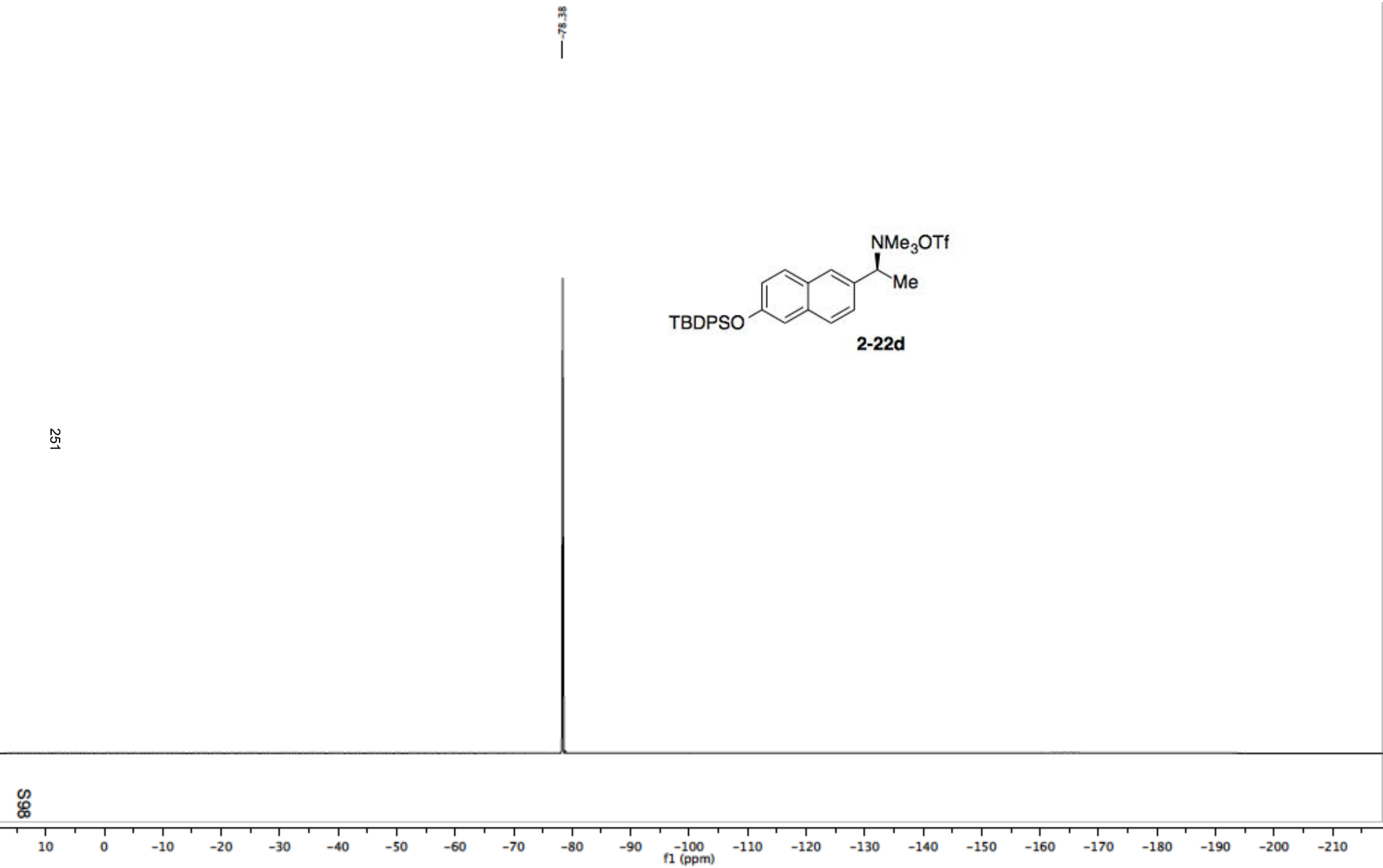
Peak#	Ret. Time	Area	Height	Area %	Height %
1	48.535	285395	3834	89.837	90.386
2	55.206	32285	408	10.163	9.614
Total		317680	4242	100.000	100.000

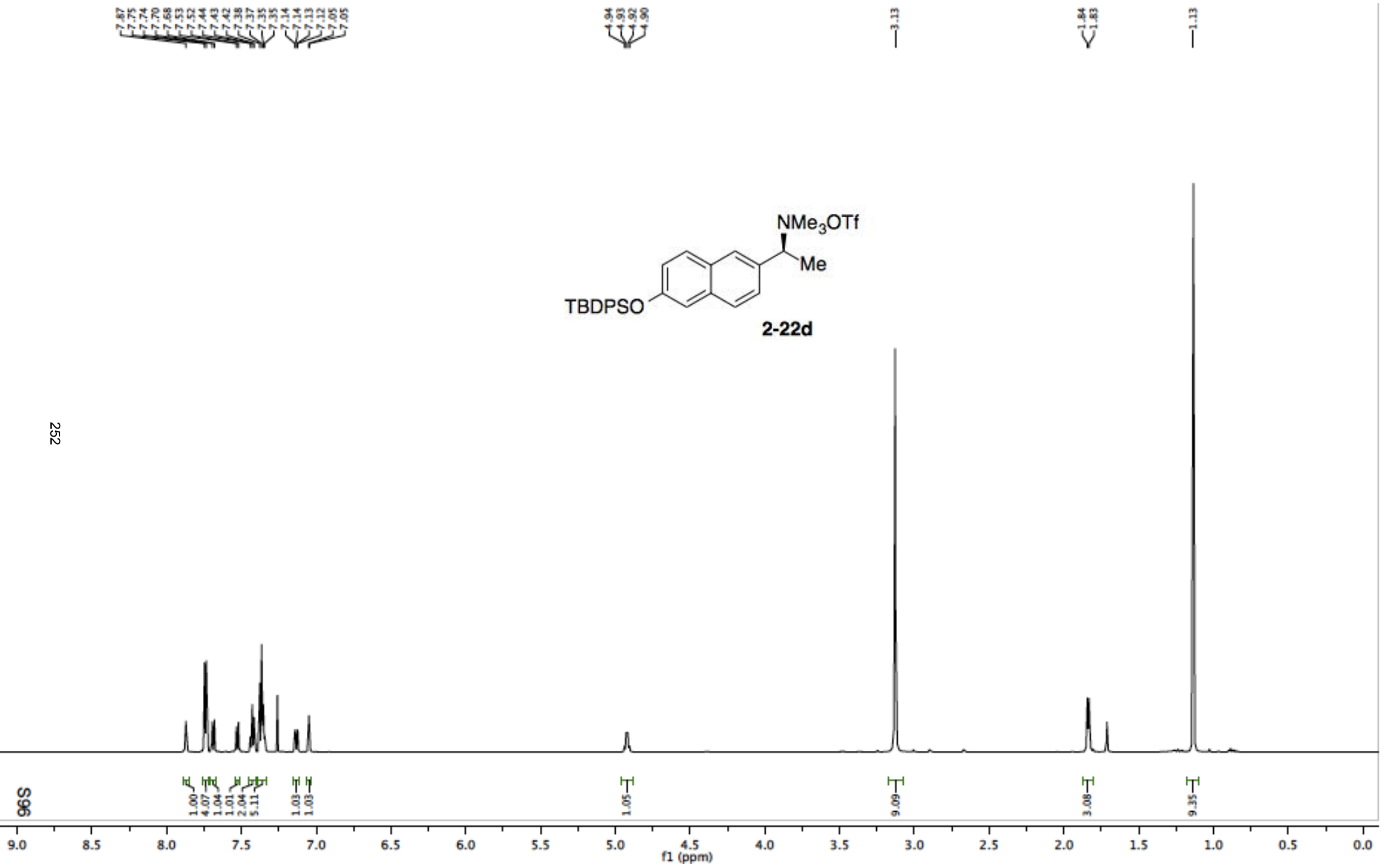

159.31
135.63
130.25
128.42
128.13
127.22
124.13
122.00
120.39
119.89
117.76
105.66
74.50
55.61
51.21
15.23
NMe3OTf
Me
MeO
2-22c
247
f1 (ppm)

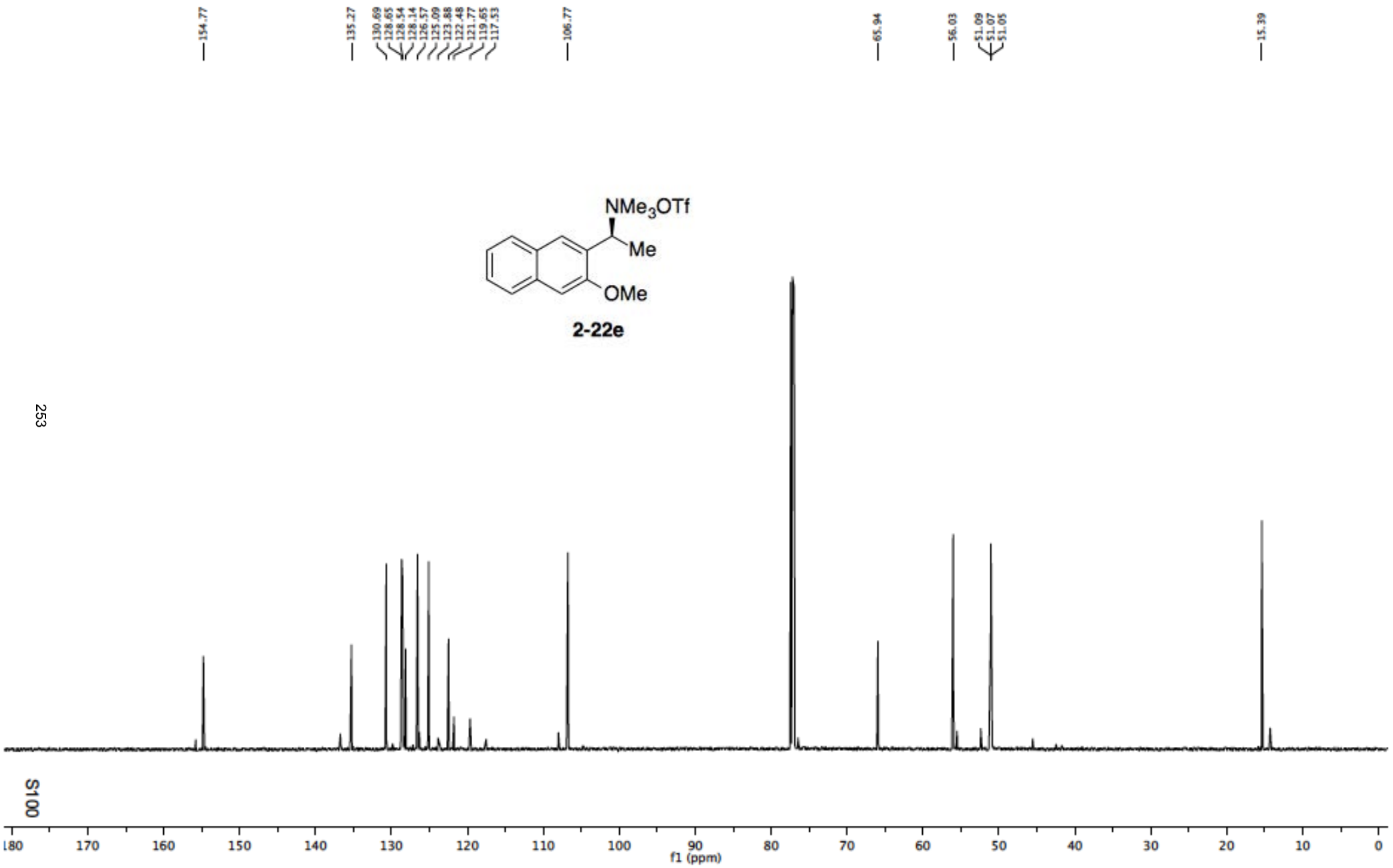

-78.39
NMe3OTf
Me
MeO
2-22c
248
S95
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

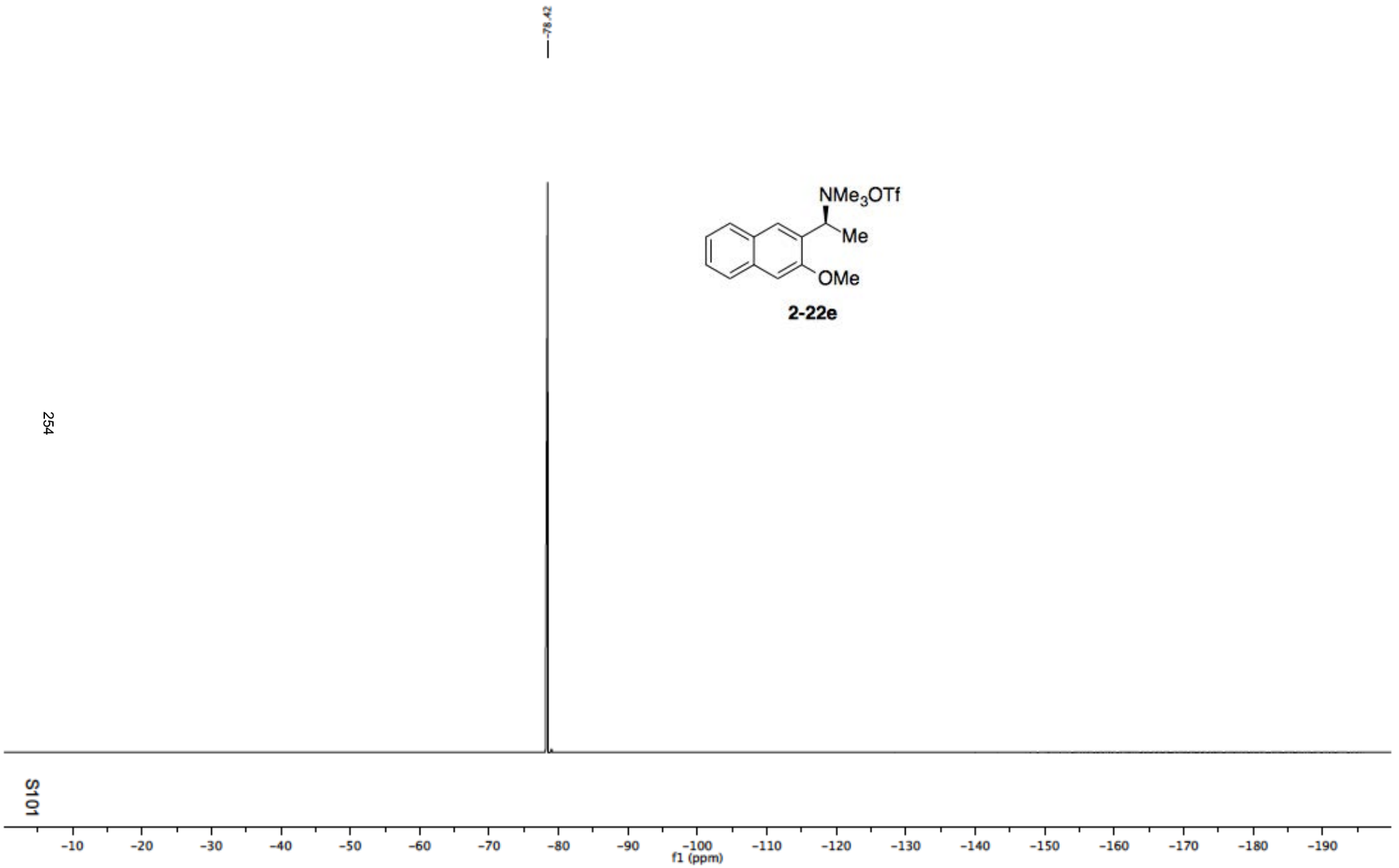

7.94
7.80
7.79
7.78
7.78
7.50
7.48
7.19
7.19
7.18
7.18
7.13
7.12
5.00
4.99
4.97
4.96
3.92
3.15
1.88
1.87
NMe3OTf
Me
MeO
2-22c
S93
1.00
2.05
1.01
1.00
1.02
1.00
3.02
8.96
3.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

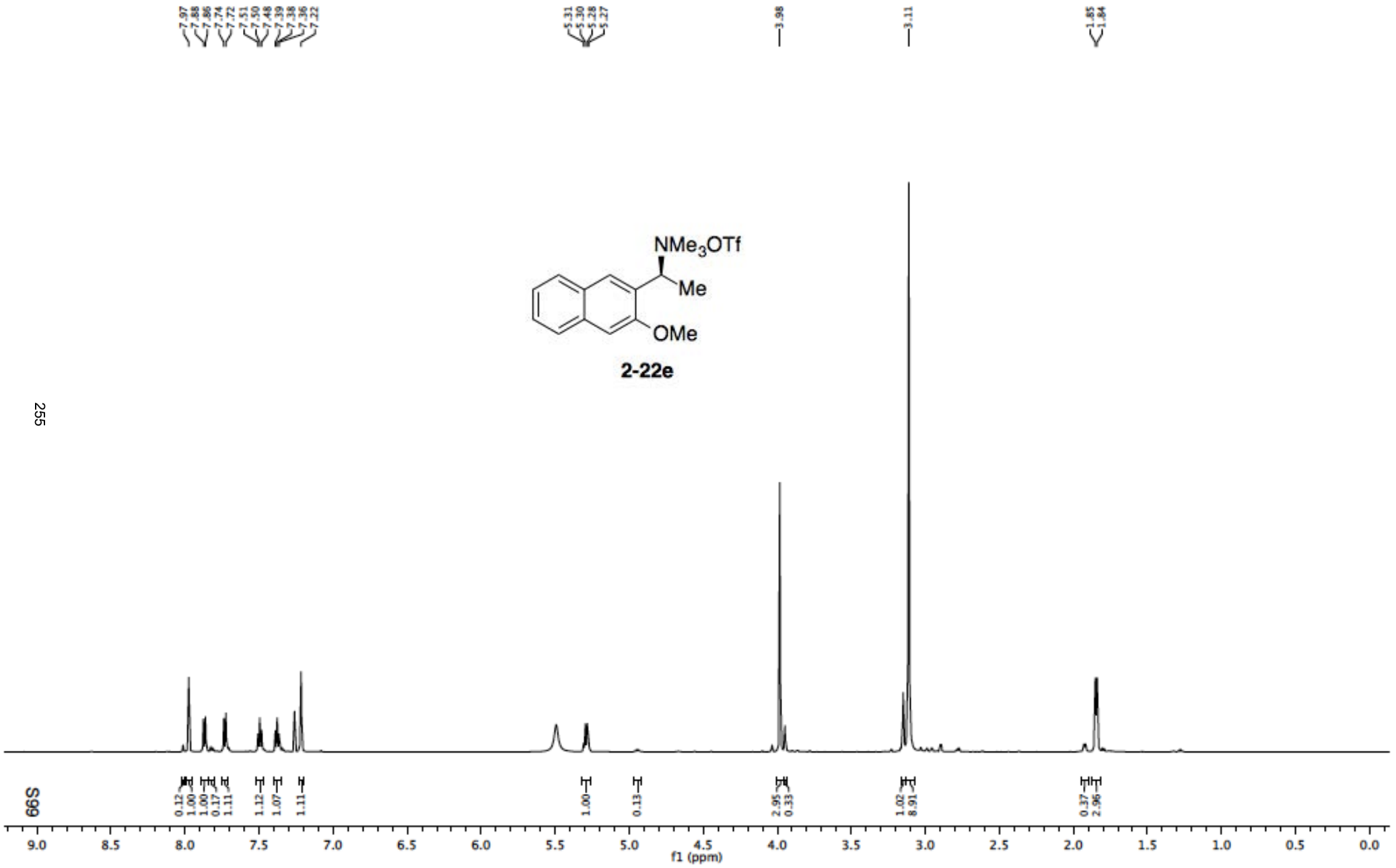

155.29
135.64
135.36
132.59
130.29
130.12
128.48
128.14
128.09
127.24
124.07
123.29
121.95
119.83
117.71
114.58
74.55
51.21
26.67
19.69
15.22
NMe3OTf
Me
TBDPSO
2-22d
250
f1 (ppm)

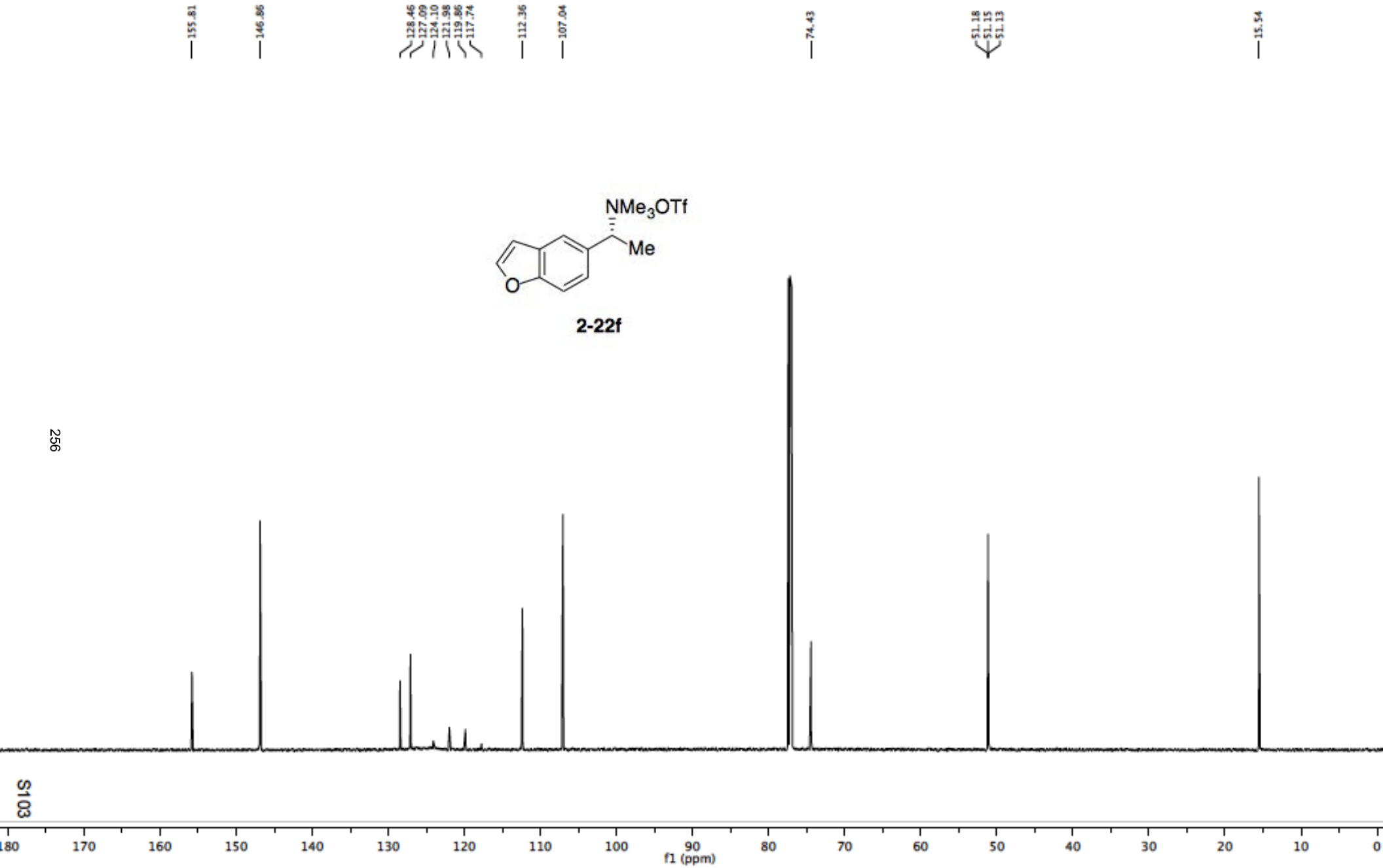

-78.38
NMe3OTf
Me
TBDPSO
2-22d
251
S98
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


7.87
7.75
7.74
7.70
7.68
7.53
7.52
7.44
7.43
7.42
7.38
7.37
7.35
7.35
7.14
7.14
7.13
7.12
7.05
7.05
4.94
4.93
4.92
4.90
3.13
1.84
1.83
1.13
NMe3OTf
Me
TBDPSO
2-22d
252
S96
1.00
4.07
1.04
1.01
2.04
5.11
1.03
1.03
1.05
9.09
3.08
9.35
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


154.77
135.27
130.69
128.65
128.54
128.14
126.57
125.09
123.88
122.48
121.77
119.65
117.53
106.77
65.94
56.03
51.09
51.07
51.05
15.39
NMe3OTf
Me
OMe
2-22e
253
S100
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-78.42
NMe3OTf
Me
OMe
2-22e
254
S101
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)


7.97
7.88
7.86
7.74
7.72
7.51
7.50
7.48
7.39
7.38
7.36
7.22
5.31
5.30
5.28
5.27
3.98
3.11
1.85
1.84
NMe3OTf
Me
OMe
2-22e
255
66S
0.12
1.00
1.00
0.17
1.11
1.12
1.07
1.11
1.00
0.13
2.95
0.33
1.02
8.91
0.37
2.96
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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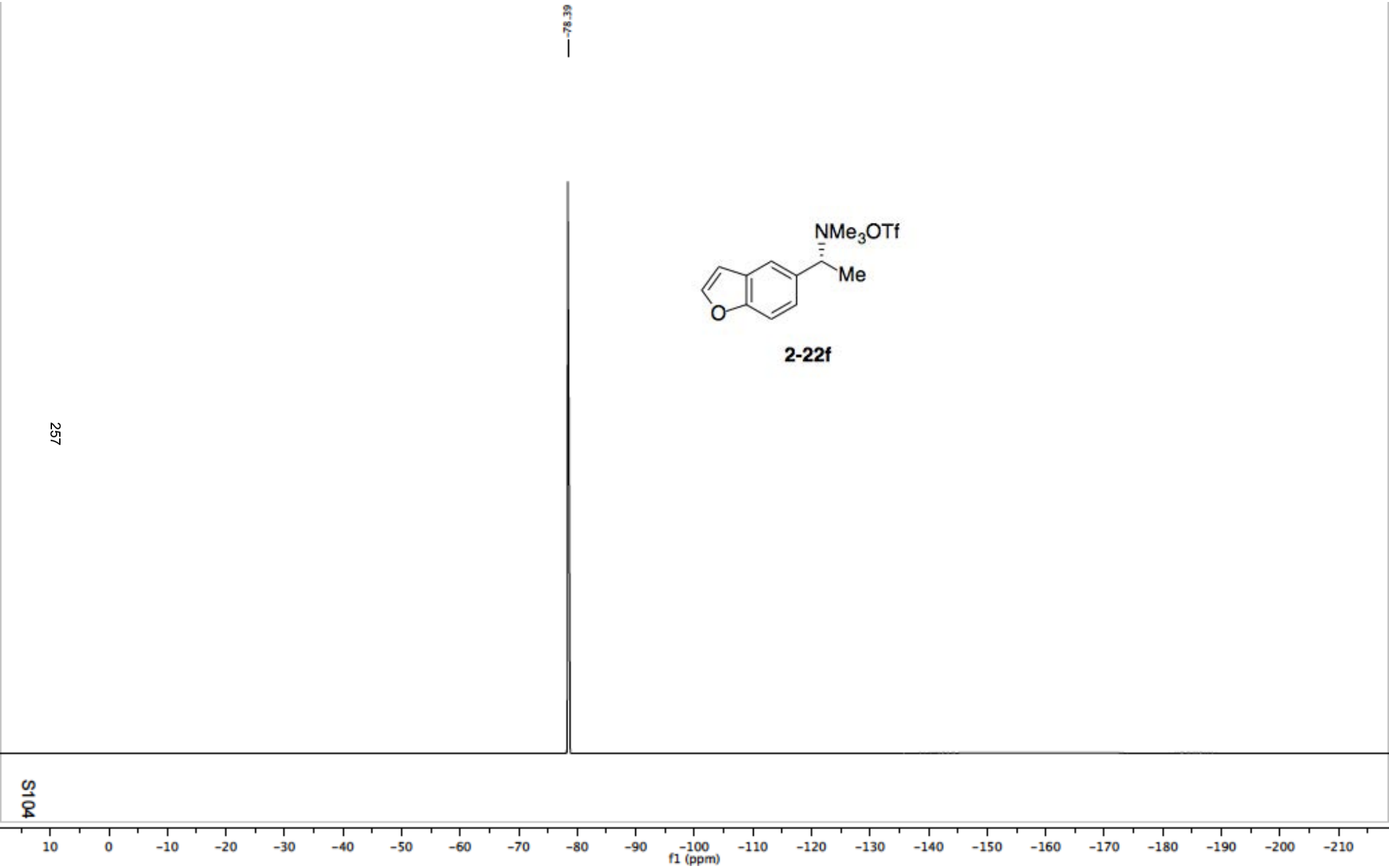
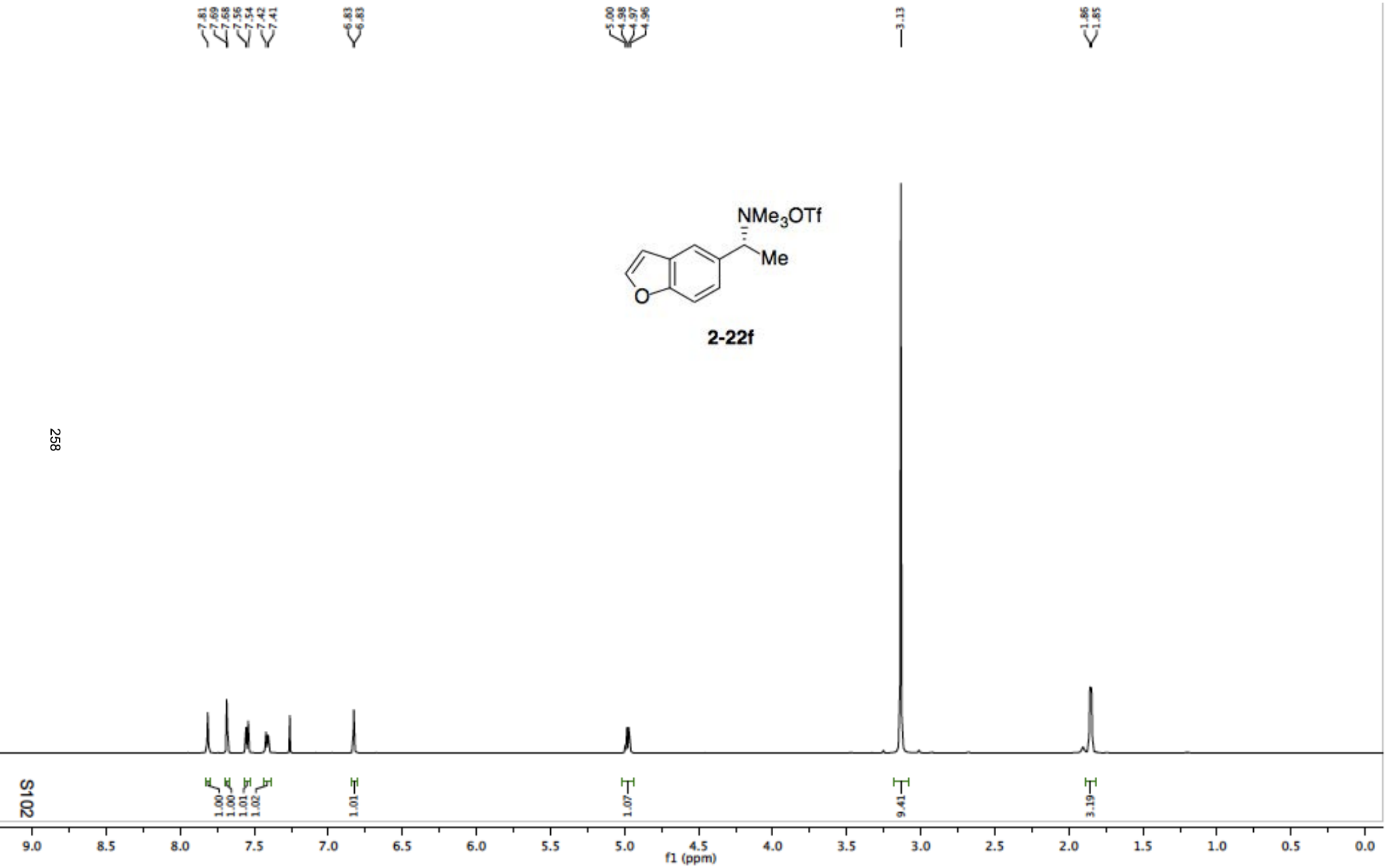
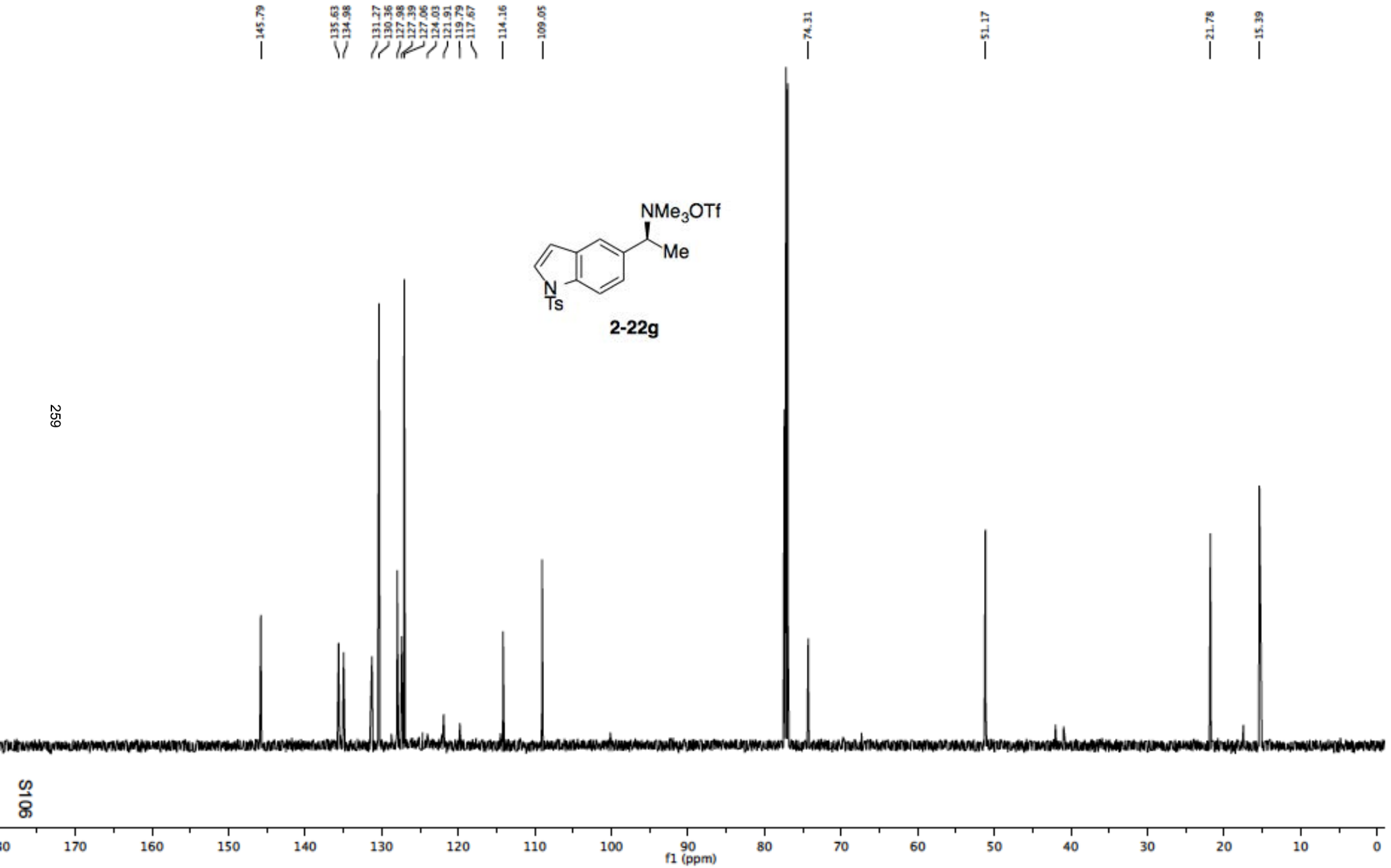
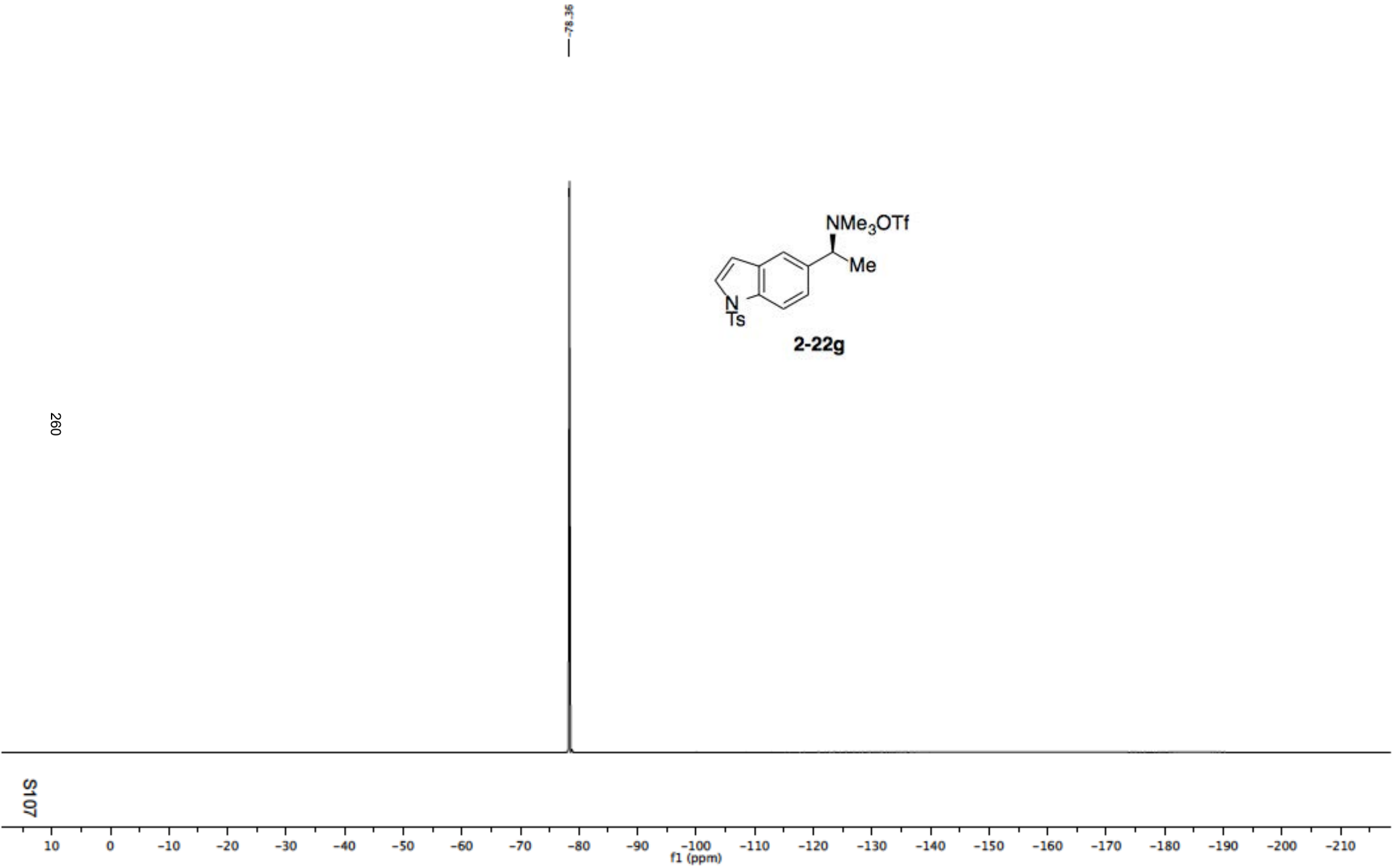
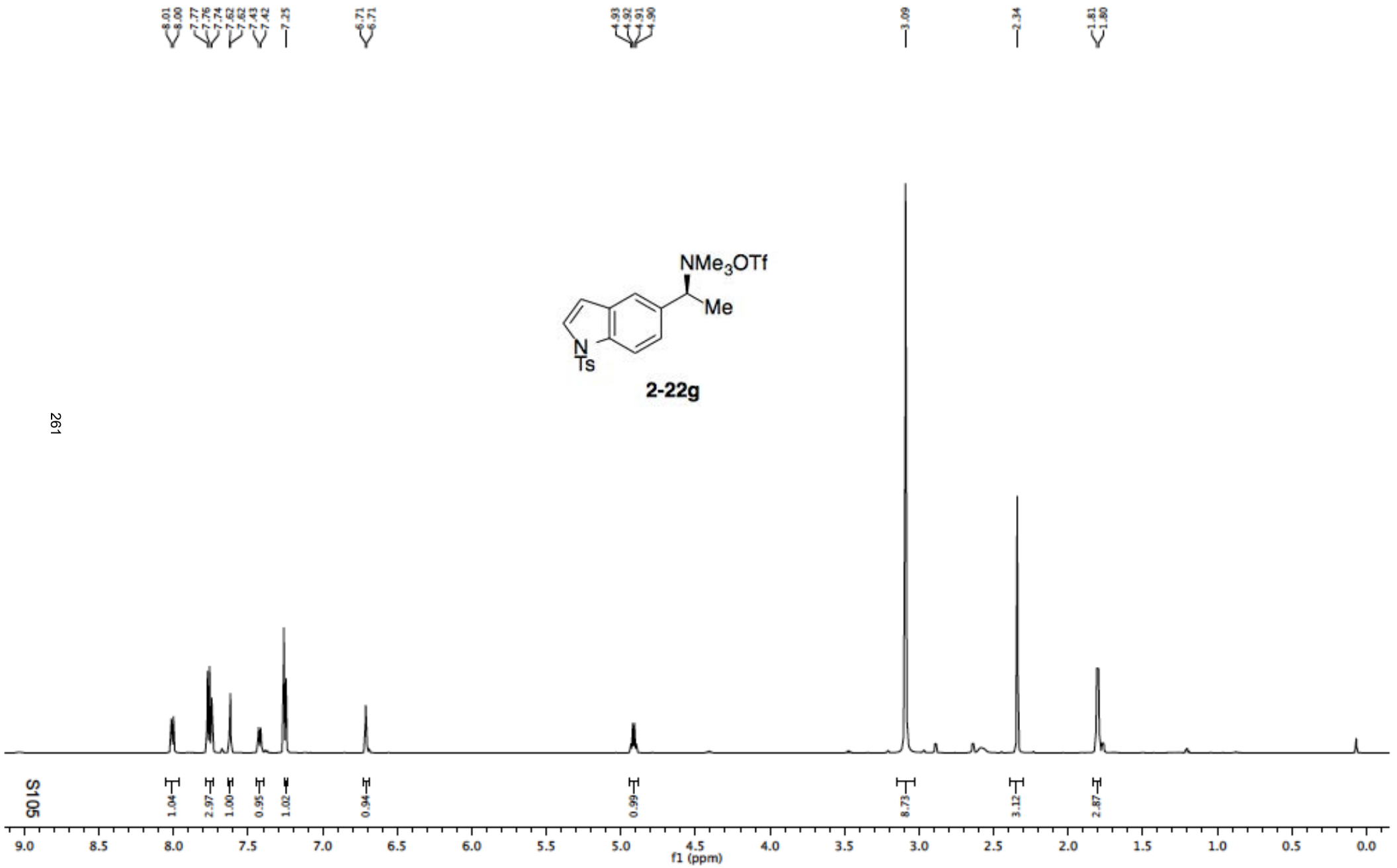
146.86
128.46
127.09
124.10
121.98
119.86
117.74
112.36
107.04
74.43
51.18
51.15
51.13
15.54
NMe3OTf
Me
O
2-22f
256
S103
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-78.39
NMe3OTf
Me
O
2-22f
257
S104
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

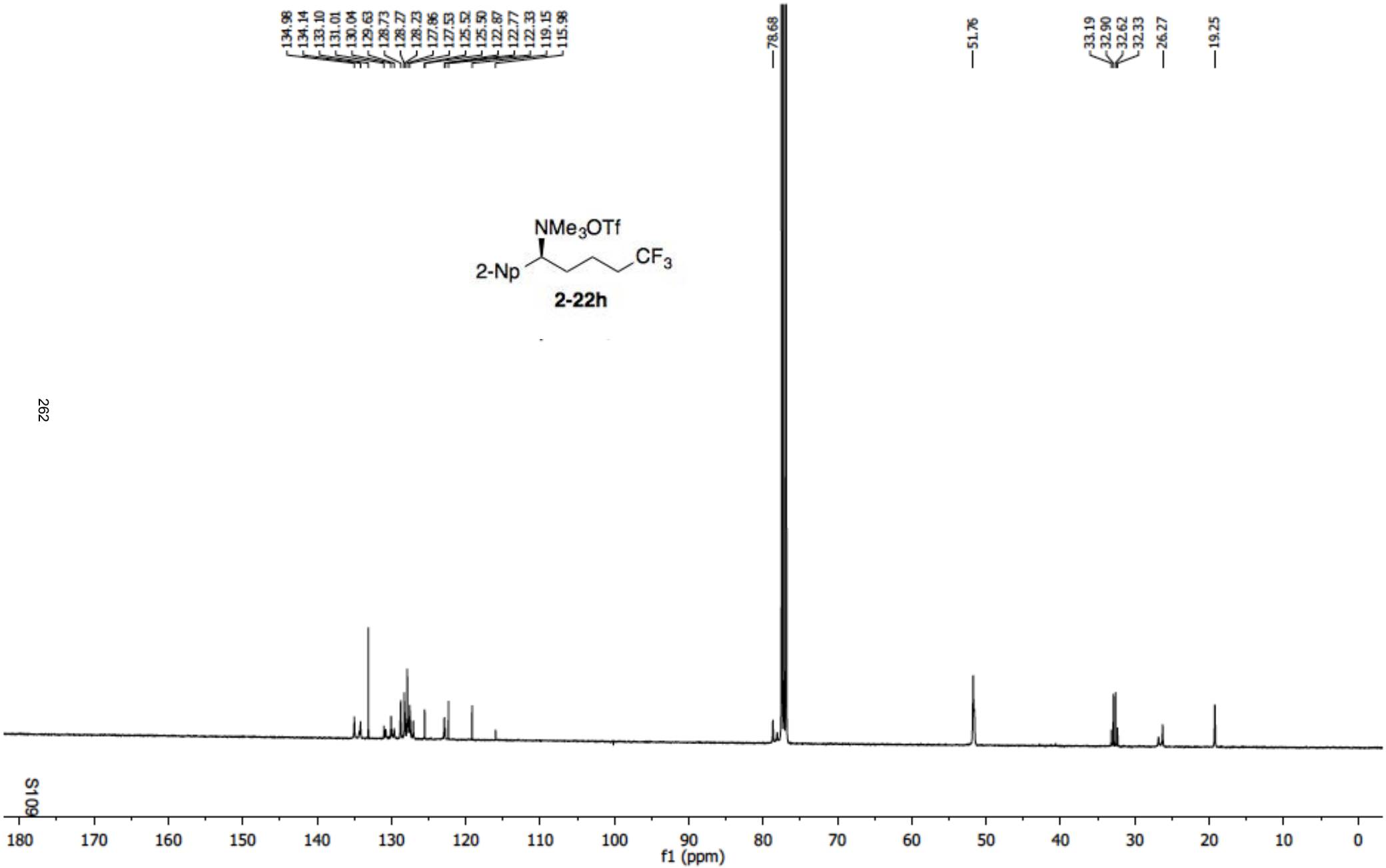

7.81
7.69
7.68
7.56
7.54
7.42
7.41
6.83
6.83
5.00
4.98
4.97
4.96
3.13
1.86
1.85
NMe3OTf
Me
O
2-22f
S102
1.00
1.00
1.01
1.02
1.01
1.07
9.41
3.19
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

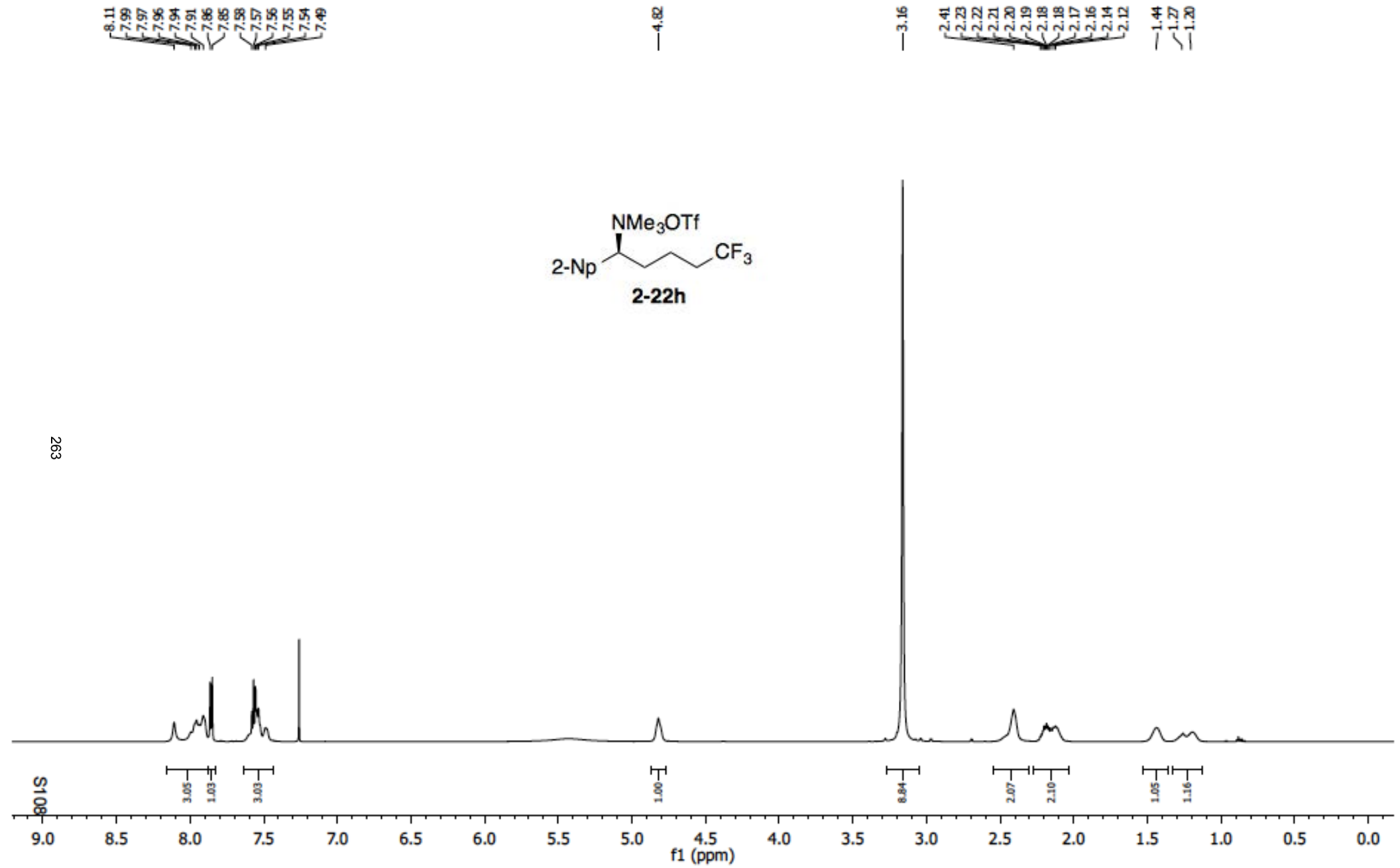

145.79
135.63
134.98
131.27
130.36
127.98
127.39
127.06
124.03
121.91
119.79
117.67
114.16
109.05
74.31
51.17
21.78
15.39
NMe3OTf
Me
N
Ts
2-22g
259
S106
f1 (ppm)

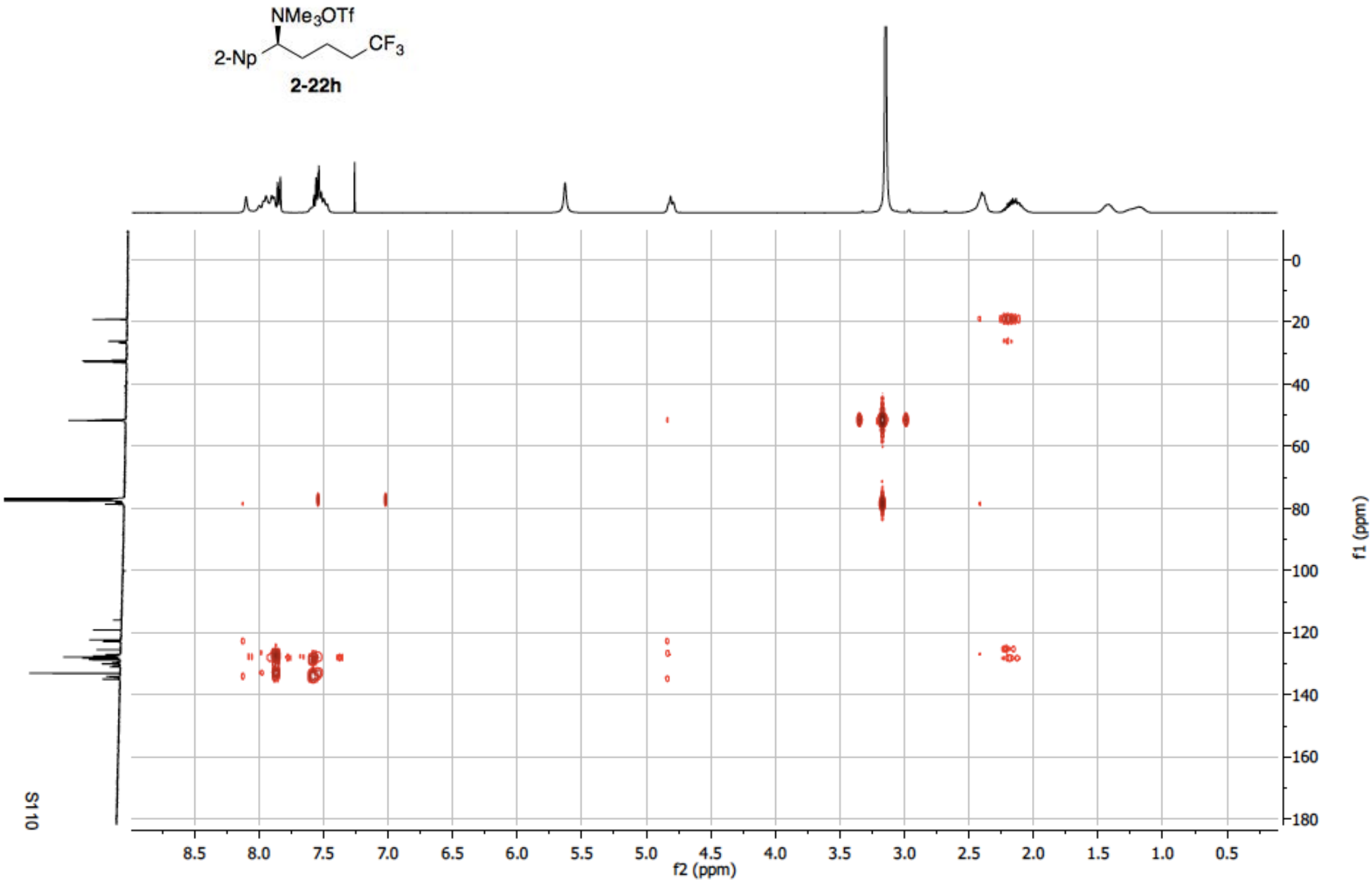

-78.36
NMe3OTf
Me
N
Ts
2-22g
260
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

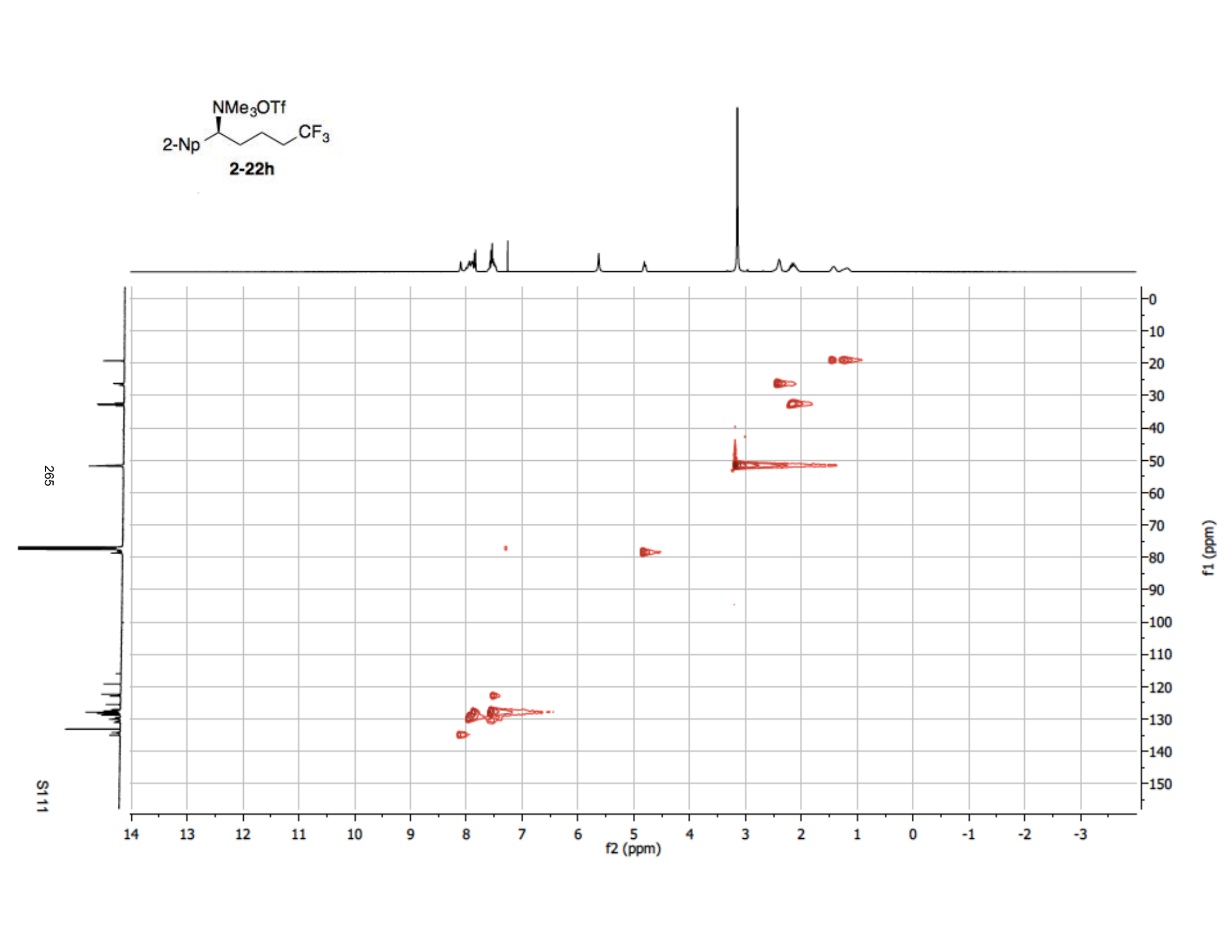

8.01
8.00
7.77
7.76
7.74
7.62
7.62
7.43
7.42
7.25
6.71
6.71
4.93
4.92
4.91
4.90
3.09
2.34
1.81
1.80
NMe3OTf
Me
N
Ts
2-22g
1.04
2.97
1.00
0.95
1.02
0.94
0.99
8.73
3.12
2.87
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

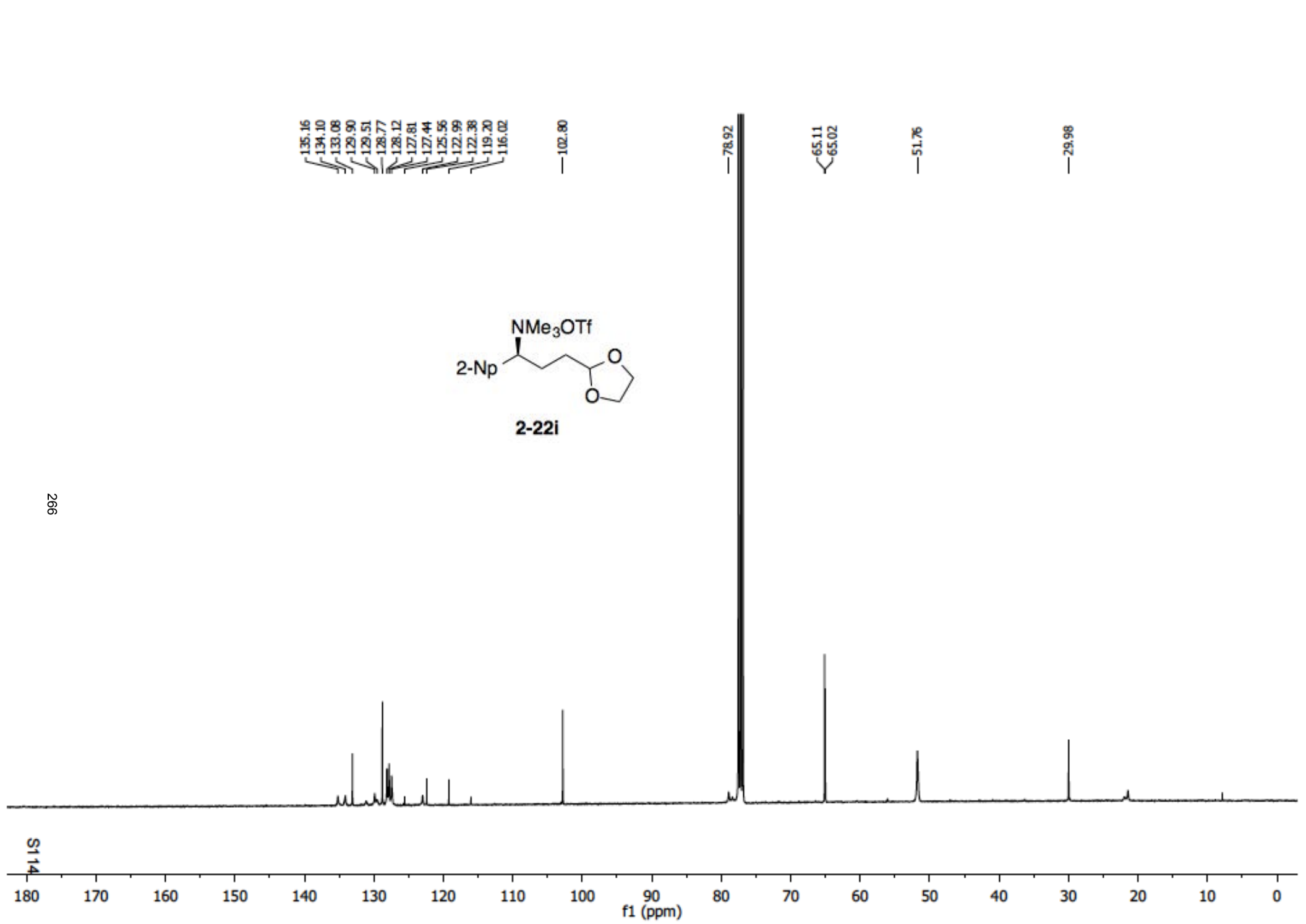
S105

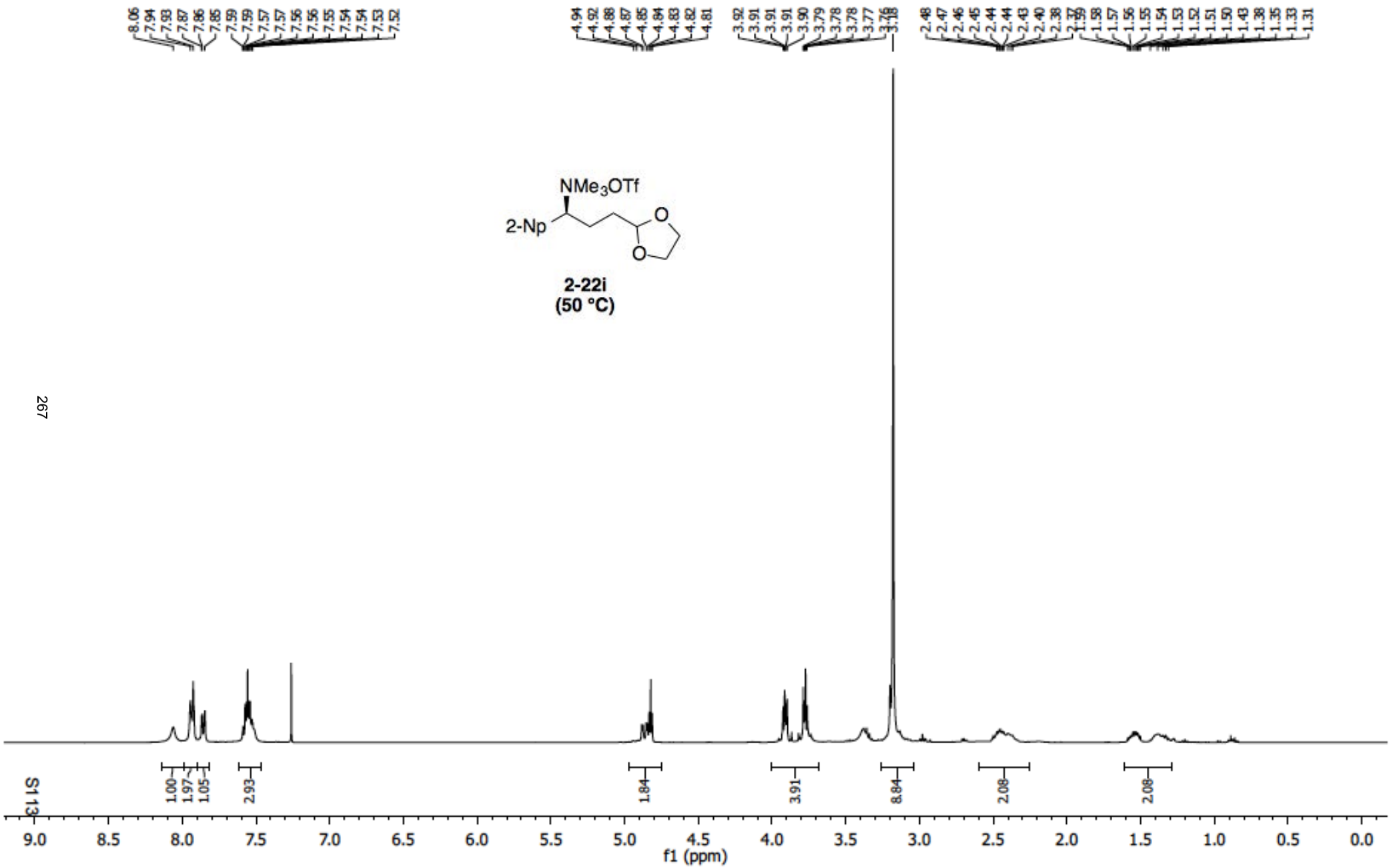

134.98
134.14
133.10
131.01
130.04
129.63
128.73
128.27
128.23
127.86
127.53
125.52
125.50
122.87
122.77
122.33
119.15
115.98
78.68
51.76
33.19
32.90
32.62
32.33
26.27
19.25
NMe3OTf
2-Np
CF3
2-22h
262
S109
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

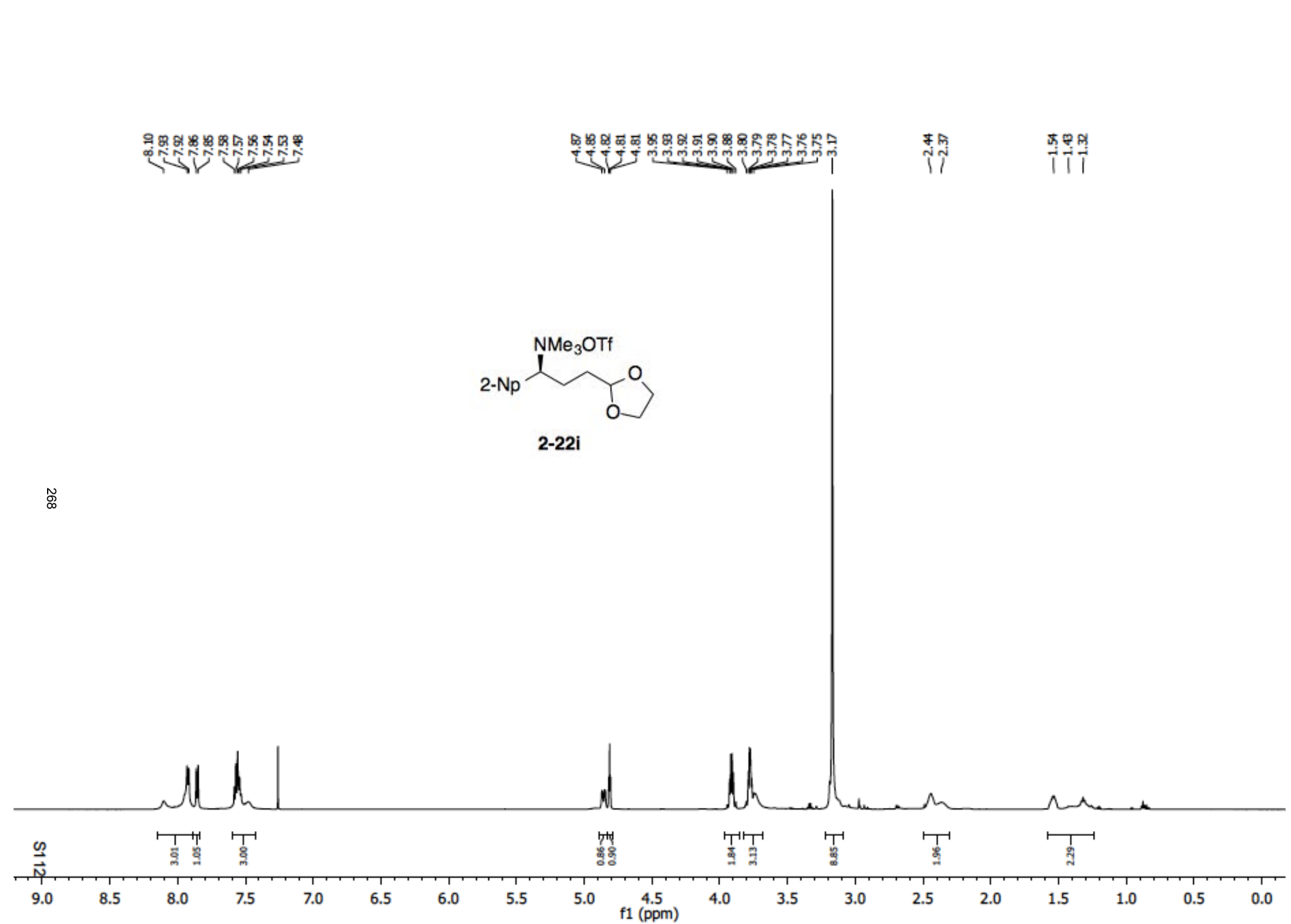

8.11
7.99
7.97
7.96
7.94
7.91
7.86
7.85
7.58
7.57
7.56
7.55
7.54
7.49
4.82
3.16
2.41
2.23
2.22
2.21
2.20
2.19
2.18
2.18
2.17
2.16
2.14
2.12
1.44
1.27
1.20
NMe3OTf
2-Np
CF3
2-22h
3.05
1.03
3.03
1.00
8.84
2.07
2.10
1.05
1.16
f1 (ppm)

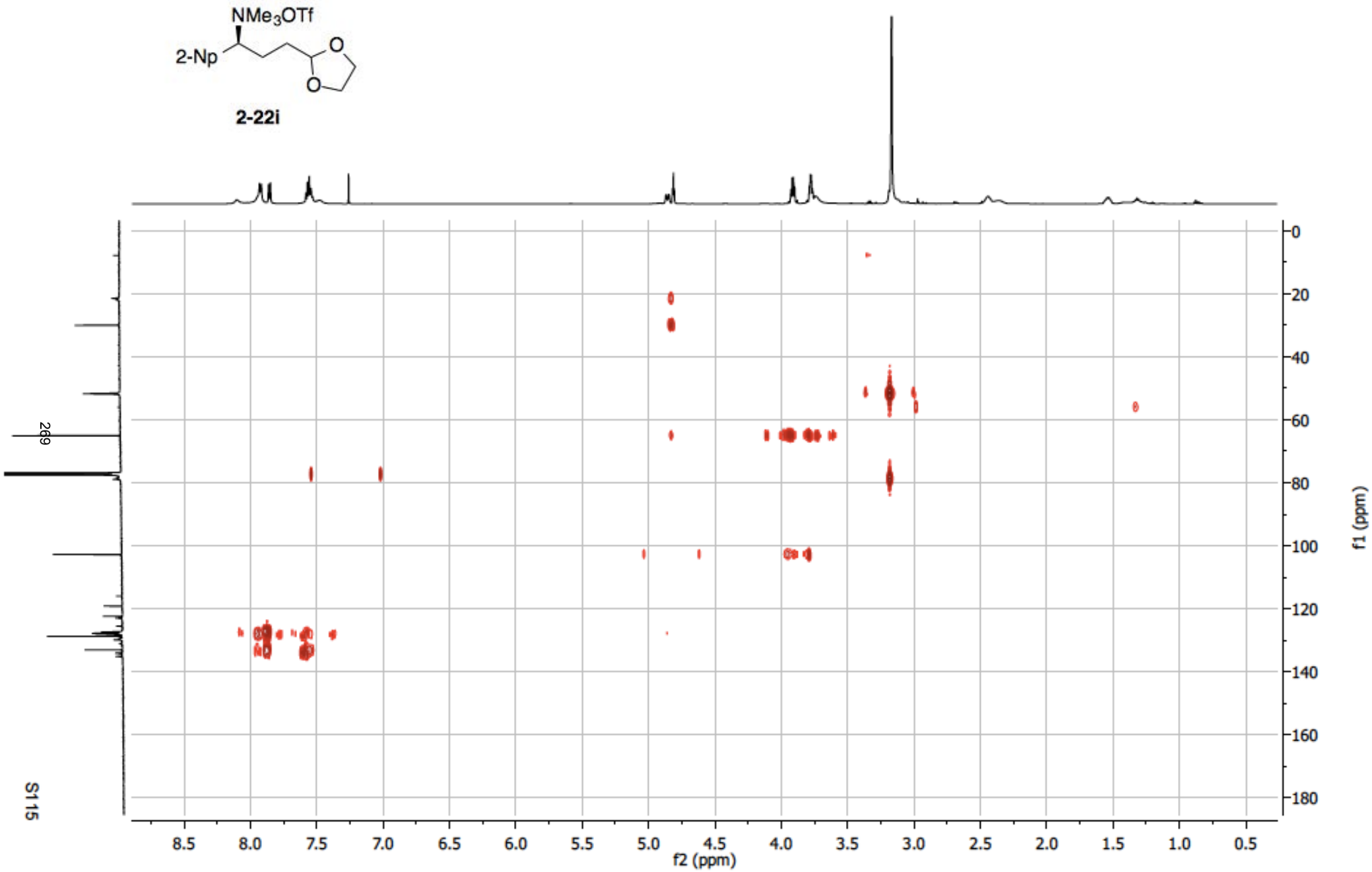

NMe3OTf
2-Np
CF3
2-22h
S110
f2 (ppm)
f1 (ppm)

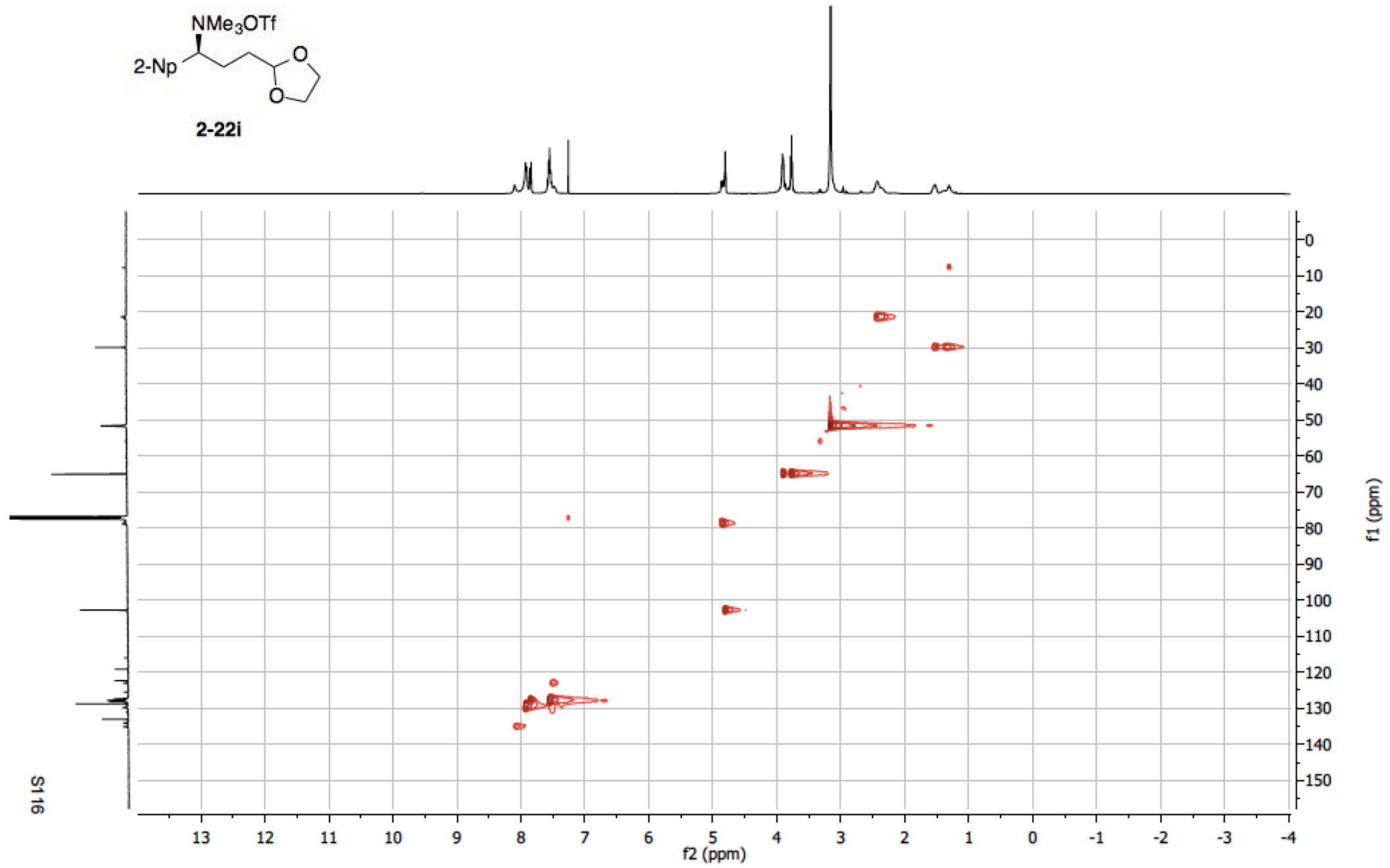

NMe3OTf
2-Np
CF3
2-22h
265
S111
f2 (ppm)
f1 (ppm)

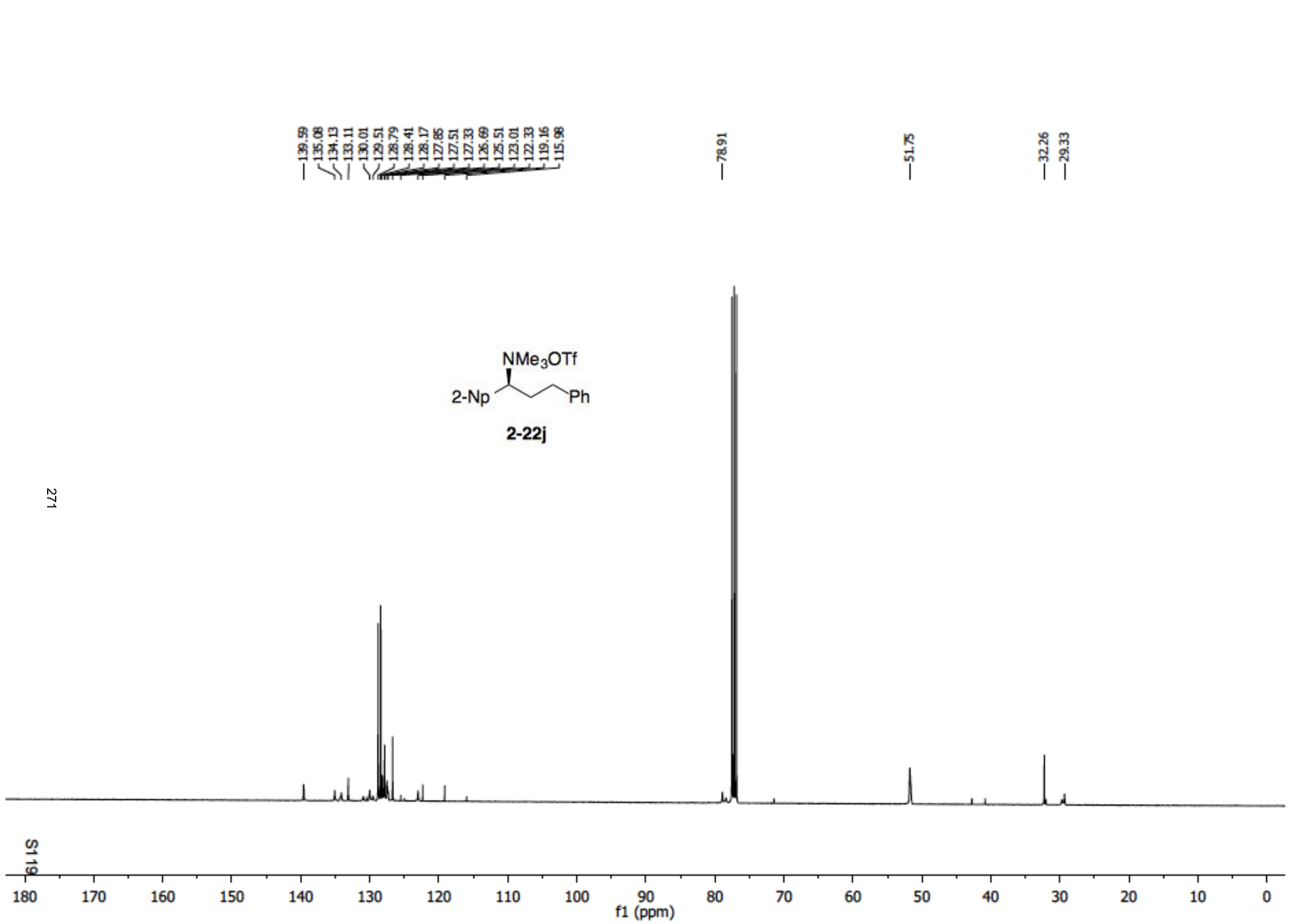

135.16
134.10
133.08
129.90
129.51
128.77
128.12
127.81
127.44
125.56
122.99
122.38
119.20
116.02
102.80
78.92
65.11
65.02
51.76
29.98
NMe3OTf
2-Np
O
O
2-22i
266
S114
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

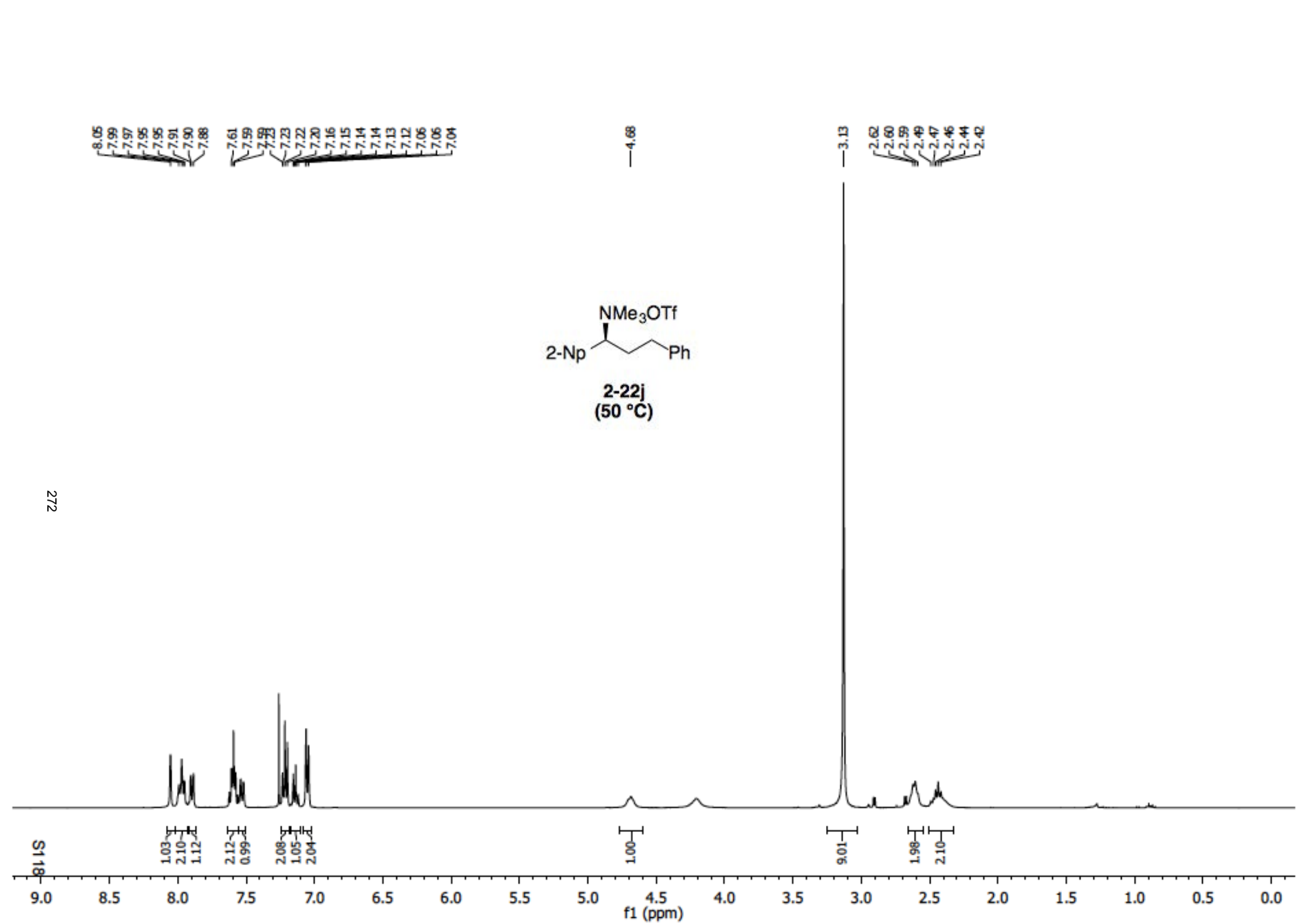

8.06
7.94
7.93
7.87
7.86
7.85
7.59
7.59
7.57
7.57
7.56
7.56
7.55
7.54
7.54
7.53
7.52
4.94
4.92
4.88
4.87
4.85
4.84
4.83
4.82
4.81
3.92
3.91
3.91
3.91
3.90
3.79
3.78
3.78
3.77
3.76
3.18
2.48
2.47
2.46
2.45
2.44
2.44
2.43
2.40
2.38
2.37
1.59
1.58
1.57
1.56
1.55
1.54
1.53
1.52
1.51
1.50
1.43
1.38
1.35
1.33
1.31
NMe3OTf
2-Np
O
O
2-22i
(50 °C)
1.00
1.97
1.05
2.93
1.84
3.91
8.84
2.08
2.08
S113
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

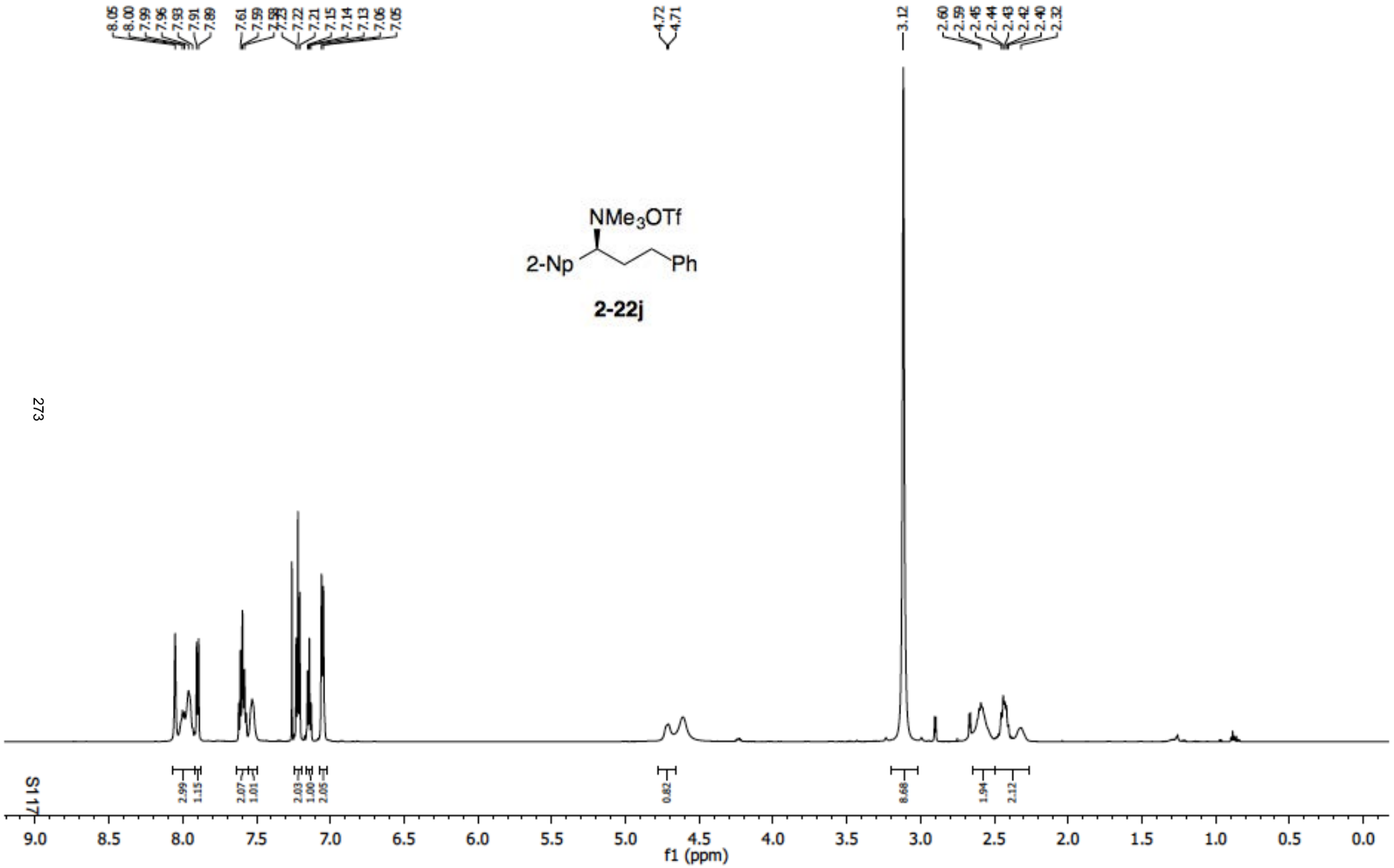

8.10
7.93
7.92
7.86
7.85
7.58
7.57
7.56
7.54
7.53
7.48
4.87
4.85
4.82
4.81
4.81
3.95
3.93
3.92
3.91
3.90
3.88
3.80
3.79
3.78
3.77
3.76
3.75
3.17
2.44
2.37
1.54
1.43
1.32
NMe3OTf
2-Np
O
O
2-22i
268
S11
3.01
1.05
3.00
0.86
0.90
1.84
3.13
8.85
1.96
2.29
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

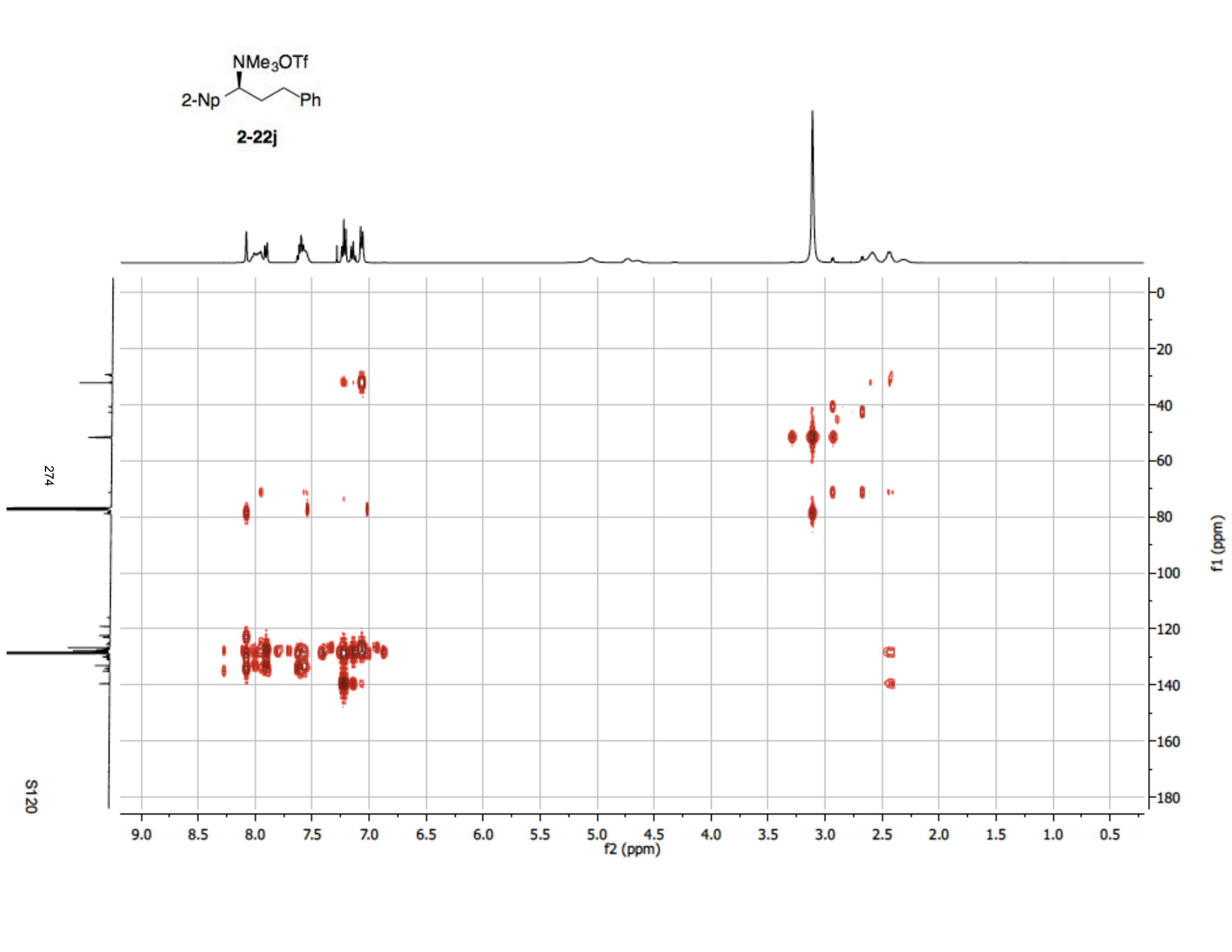

NMe3OTf
2-Np
O
O
2-22i
269
S115
f2 (ppm)
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
20
40
60
80
100
120
140
160
180

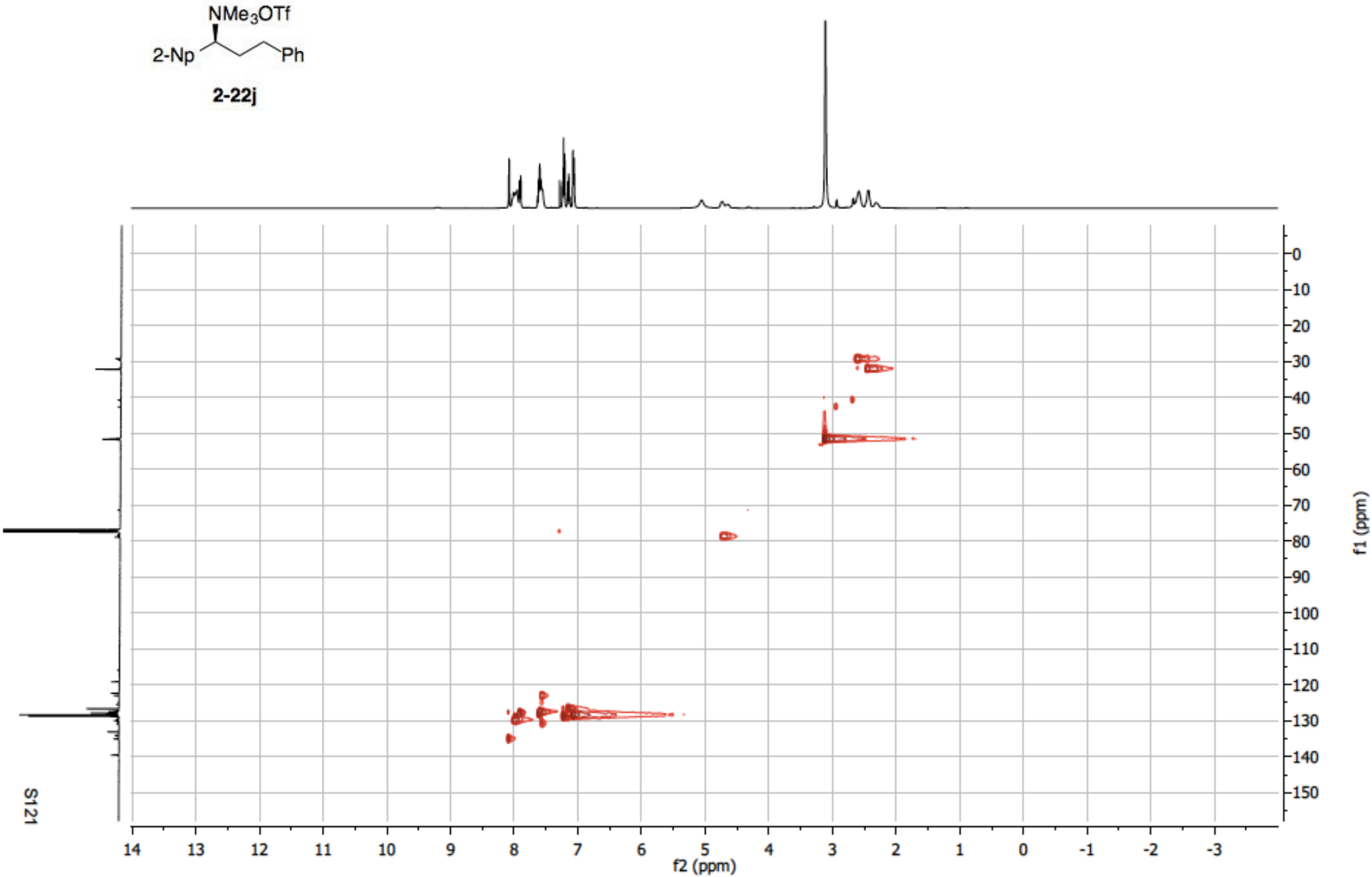

NMe3OTf
2-Np
O
O
2-22i
S116
f2 (ppm)
f1 (ppm)

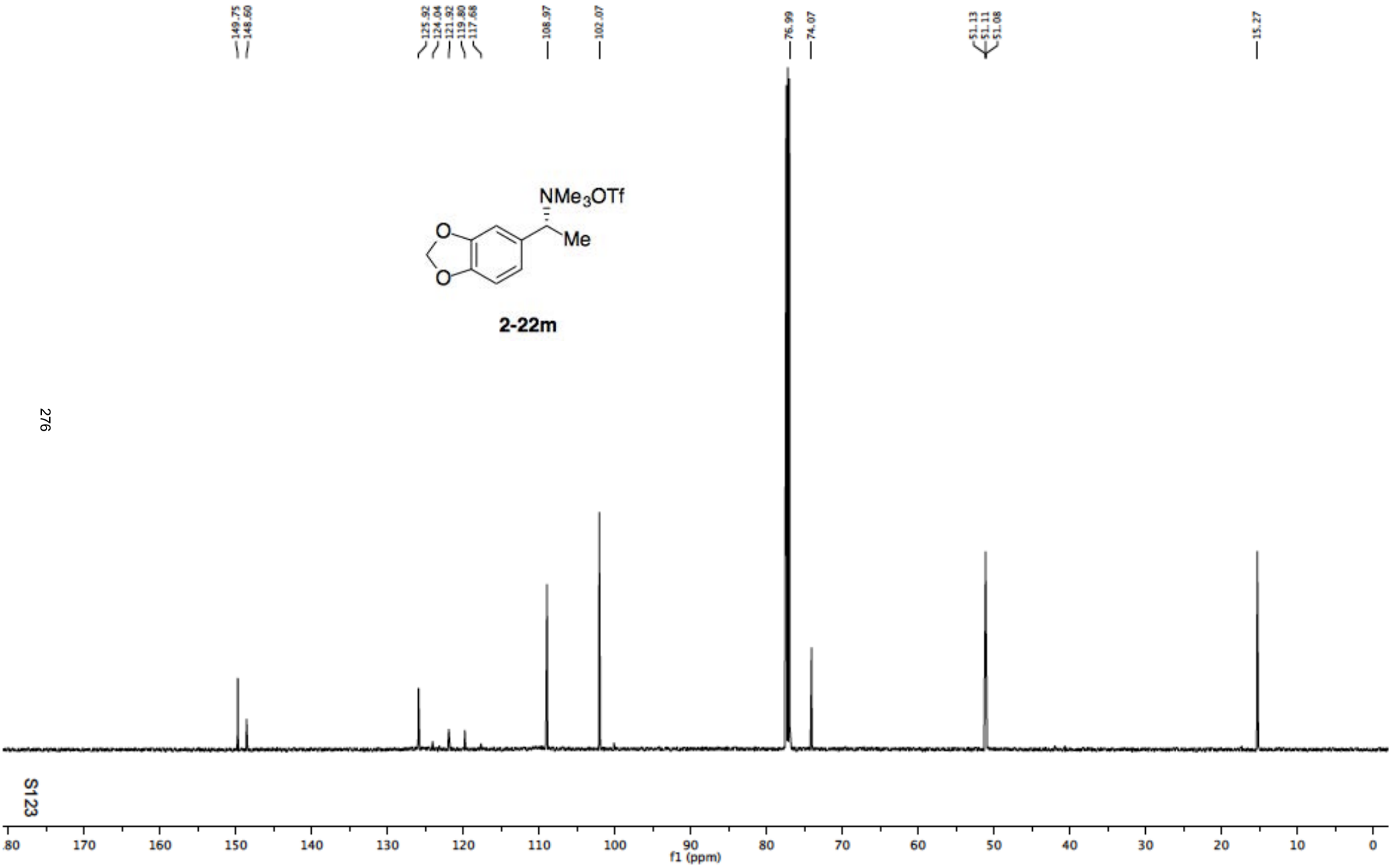

139.59
135.08
134.13
133.11
130.01
129.51
128.79
128.41
128.17
127.85
127.51
127.33
126.69
125.51
123.01
122.33
119.16
115.98
78.91
51.75
32.26
29.33
NMe3OTf
2-Np
Ph
2-22j
271
S116
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

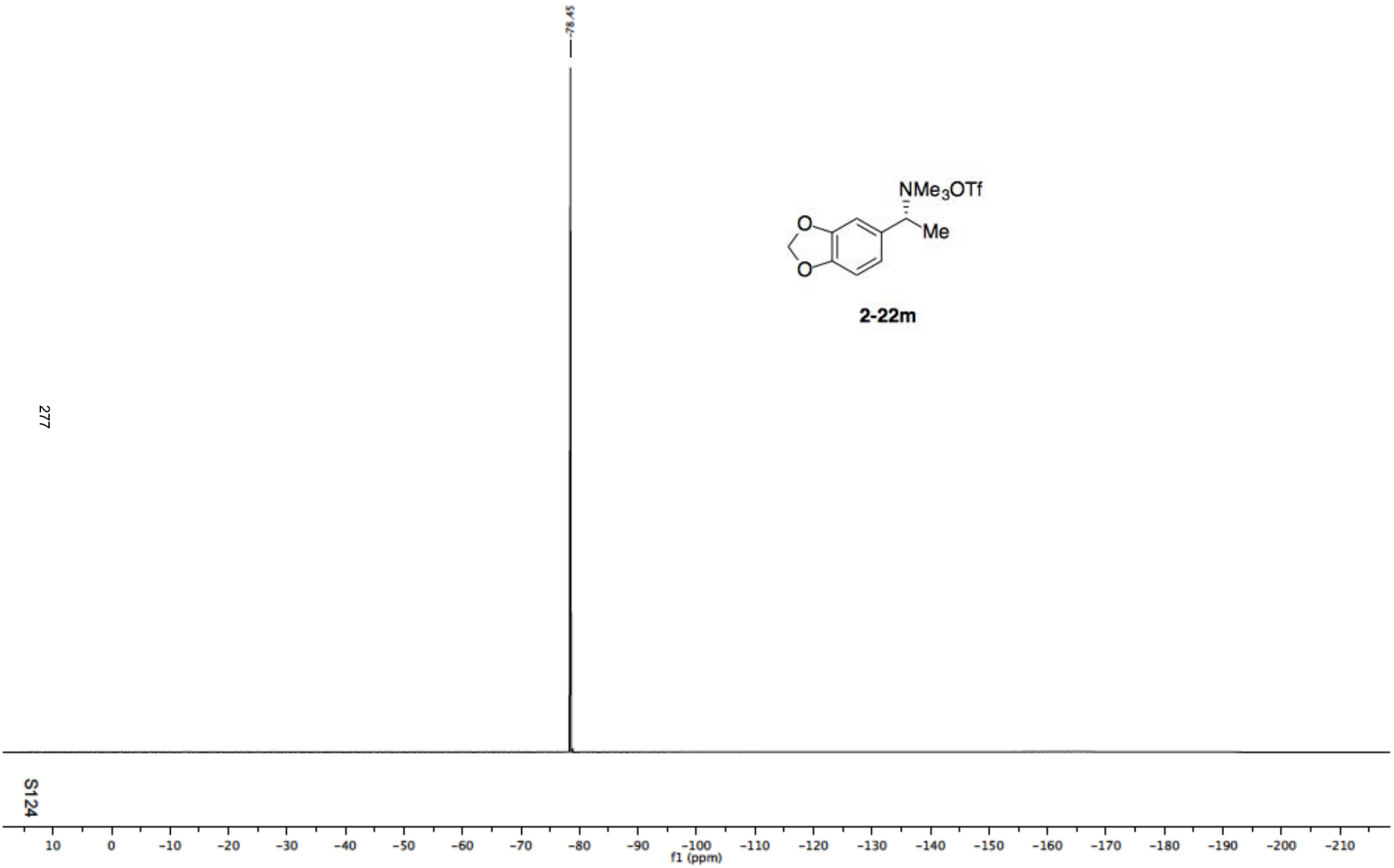

8.05
7.99
7.97
7.95
7.95
7.91
7.90
7.88
7.61
7.59
7.23
7.22
7.20
7.16
7.15
7.14
7.14
7.13
7.12
7.06
7.06
7.04
4.68
3.13
2.62
2.60
2.59
2.49
2.47
2.46
2.44
2.42
NMe3OTf
2-Np
Ph
2-22j
(50 °C)
272
S118
1.03
2.10
1.12
2.12
0.99
2.08
1.05
2.04
1.00
9.01
1.98
2.10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

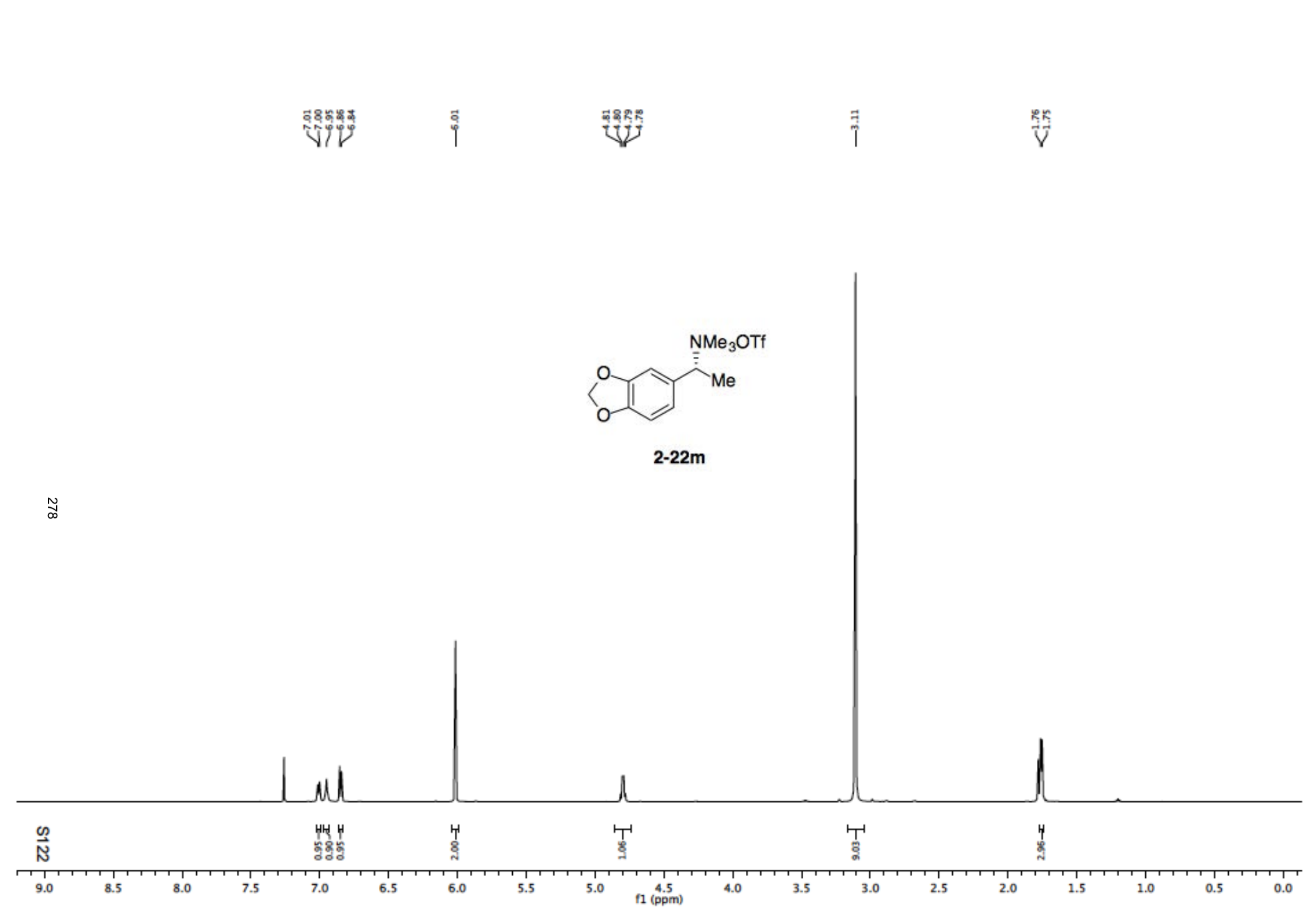

8.05
8.00
7.99
7.96
7.93
7.91
7.89
7.61
7.59
7.58
7.23
7.22
7.21
7.15
7.14
7.13
7.06
7.05
4.72
4.71
3.12
2.60
2.59
2.45
2.44
2.43
2.42
2.40
2.32
NMe3OTf
2-Np
Ph
2-22j
273
S117
2.99
1.15
2.07
1.01
2.03
1.00
2.05
0.82
8.68
1.94
2.12
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

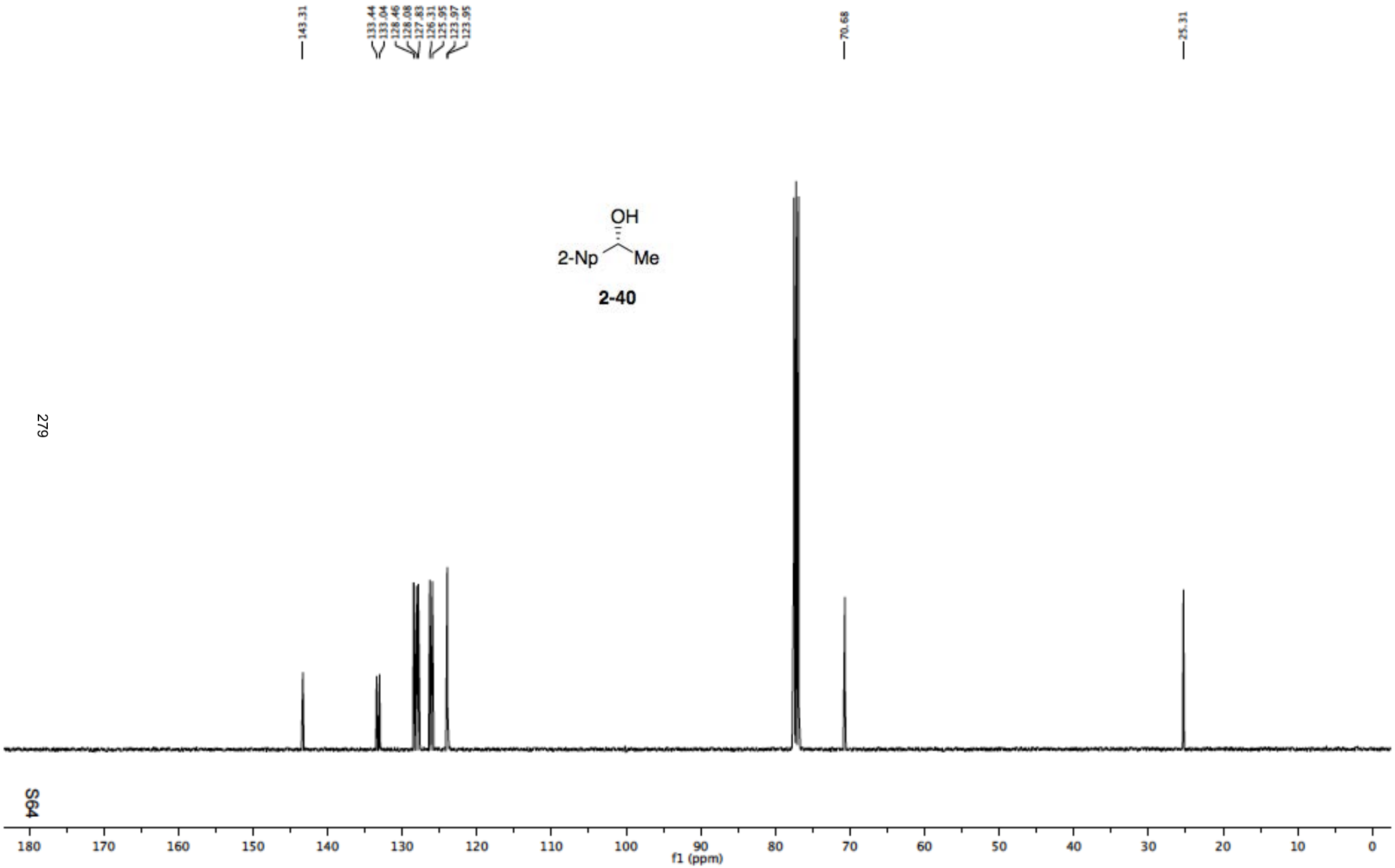

NMe3OTf
2-Np
Ph
2-22j
274
S120
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
0
20
40
60
80
100
120
140
160
180
f1 (ppm)

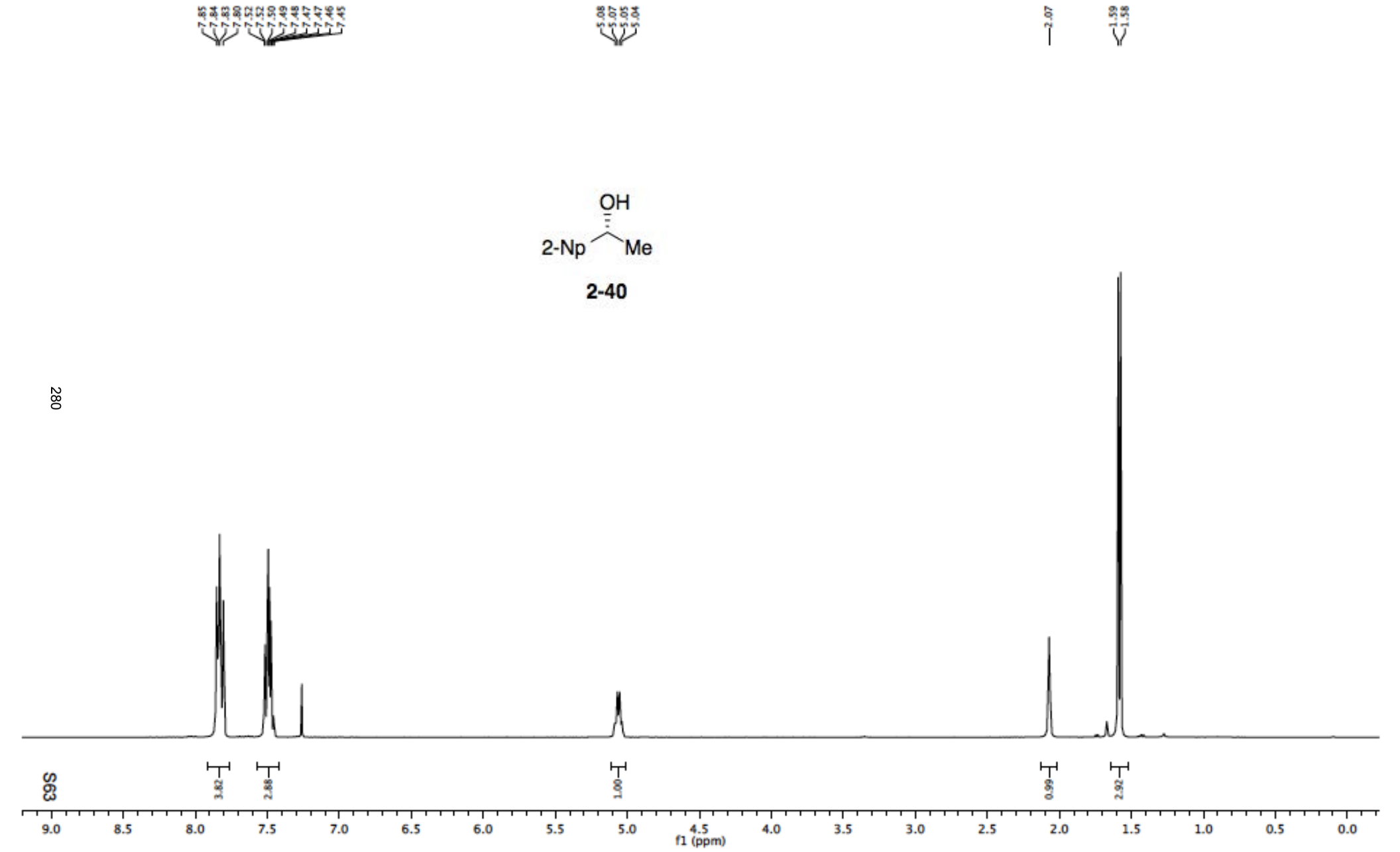

NMe3OTf
2-Np
Ph
2-22j
S121
f2 (ppm)
f1 (ppm)

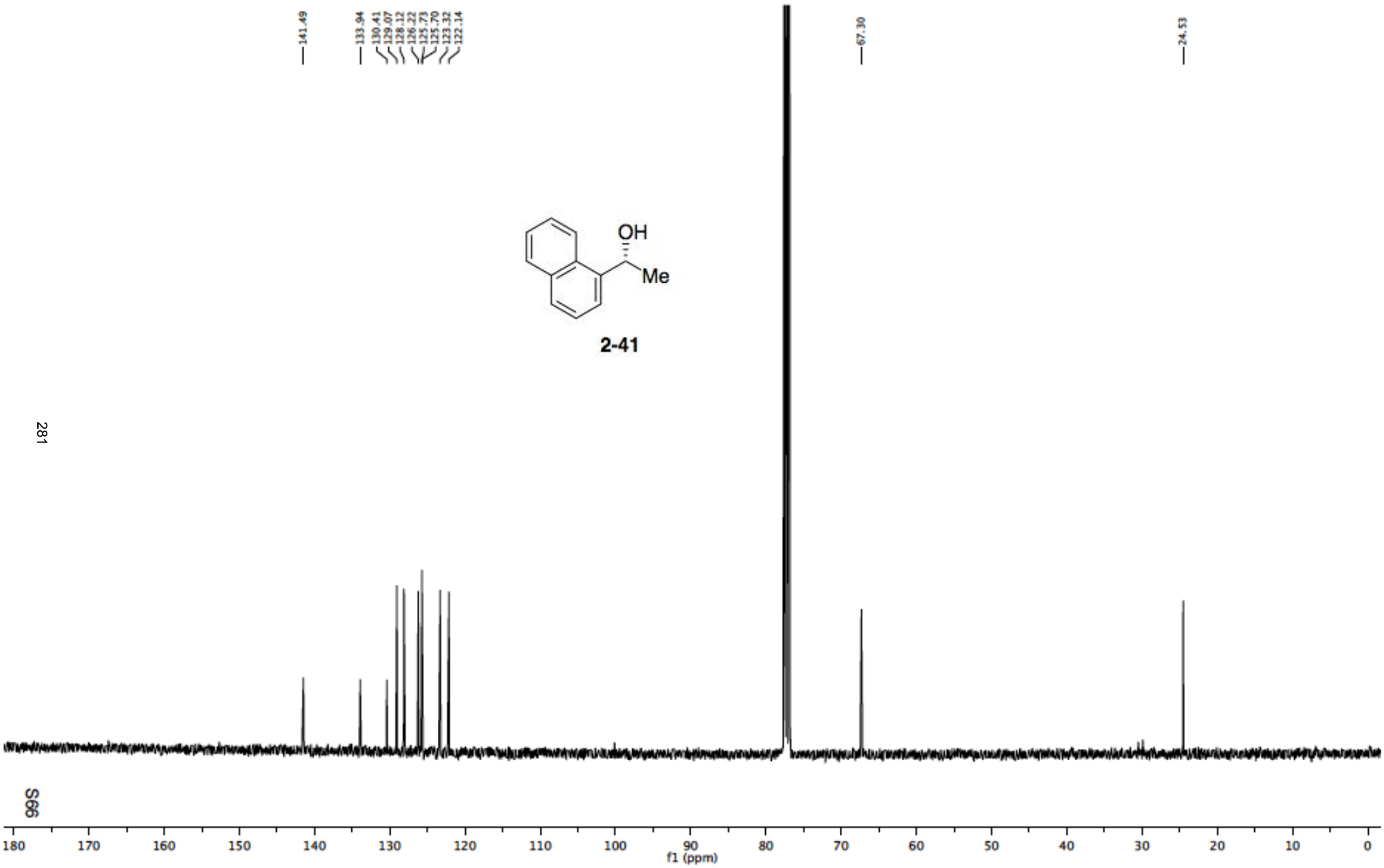

149.75
148.60
125.92
124.04
121.92
119.80
117.68
108.97
102.07
76.99
74.07
51.13
51.11
51.08
15.27
NMe3OTf
Me
O
O
2-22m
276
S123
f1 (ppm)

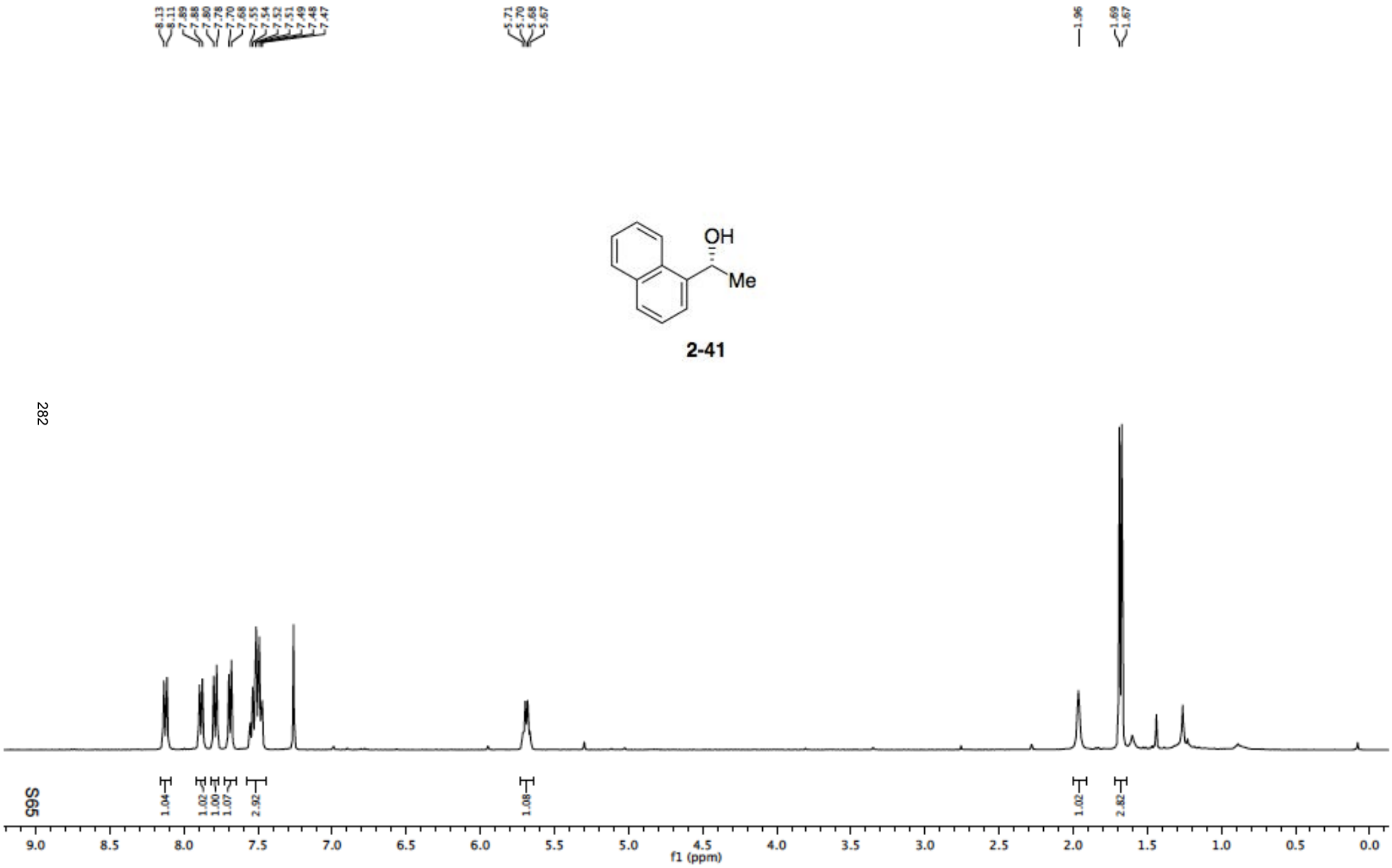

-78.45
NMe3OTf
Me
O
O
2-22m
277
S124
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

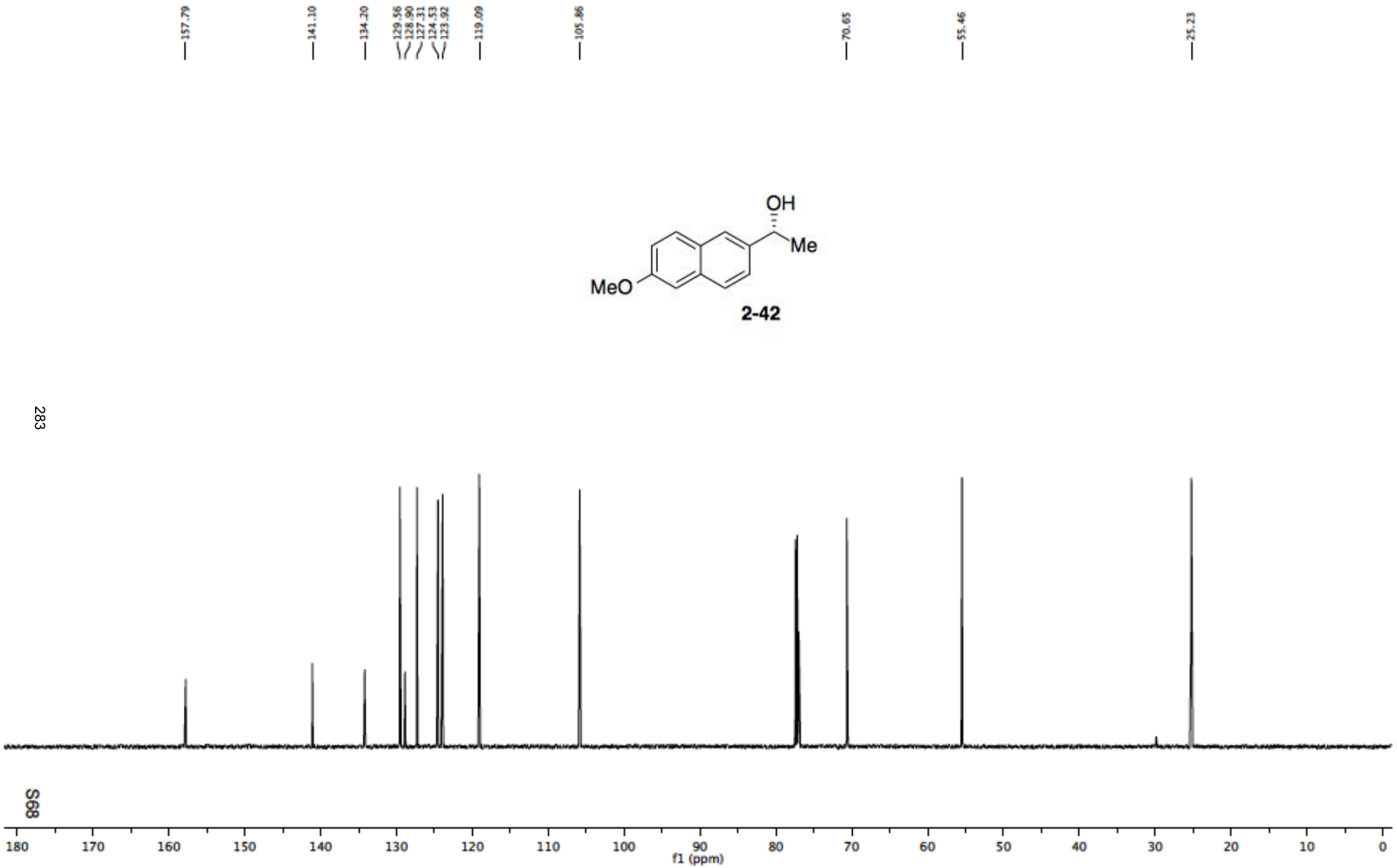

7.01
7.00
6.95
6.86
6.84
6.01
4.81
4.80
4.79
4.78
3.11
1.76
1.75
NMe3OTf
Me
O
O
2-22m
278
S122
0.95
0.90
0.95
2.00
1.06
9.03
2.96
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

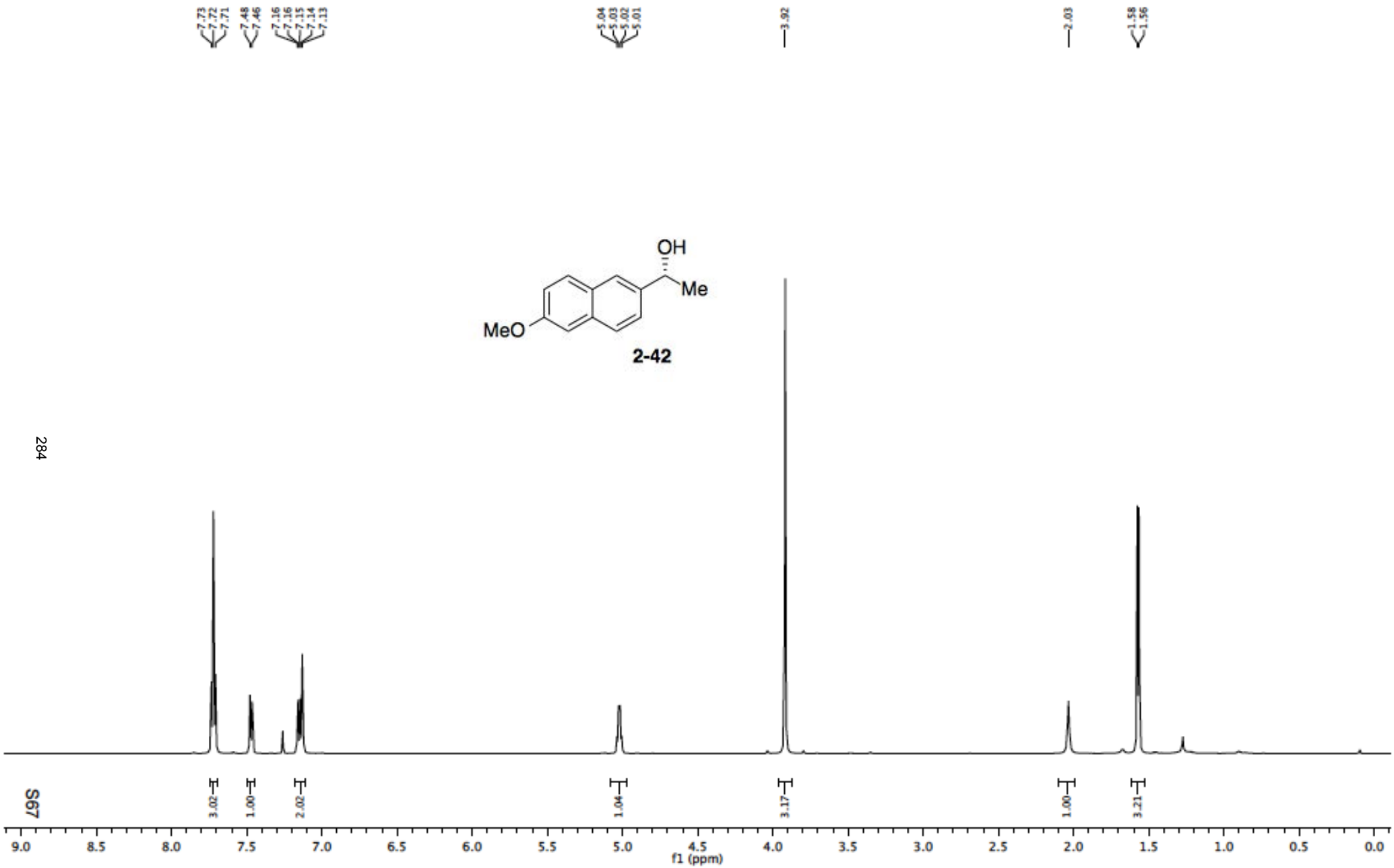

143.31
133.44
133.04
128.46
128.08
127.83
126.31
125.95
123.97
123.95
70.68
25.31
OH
2-Np
Me
2-40
279
S64
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

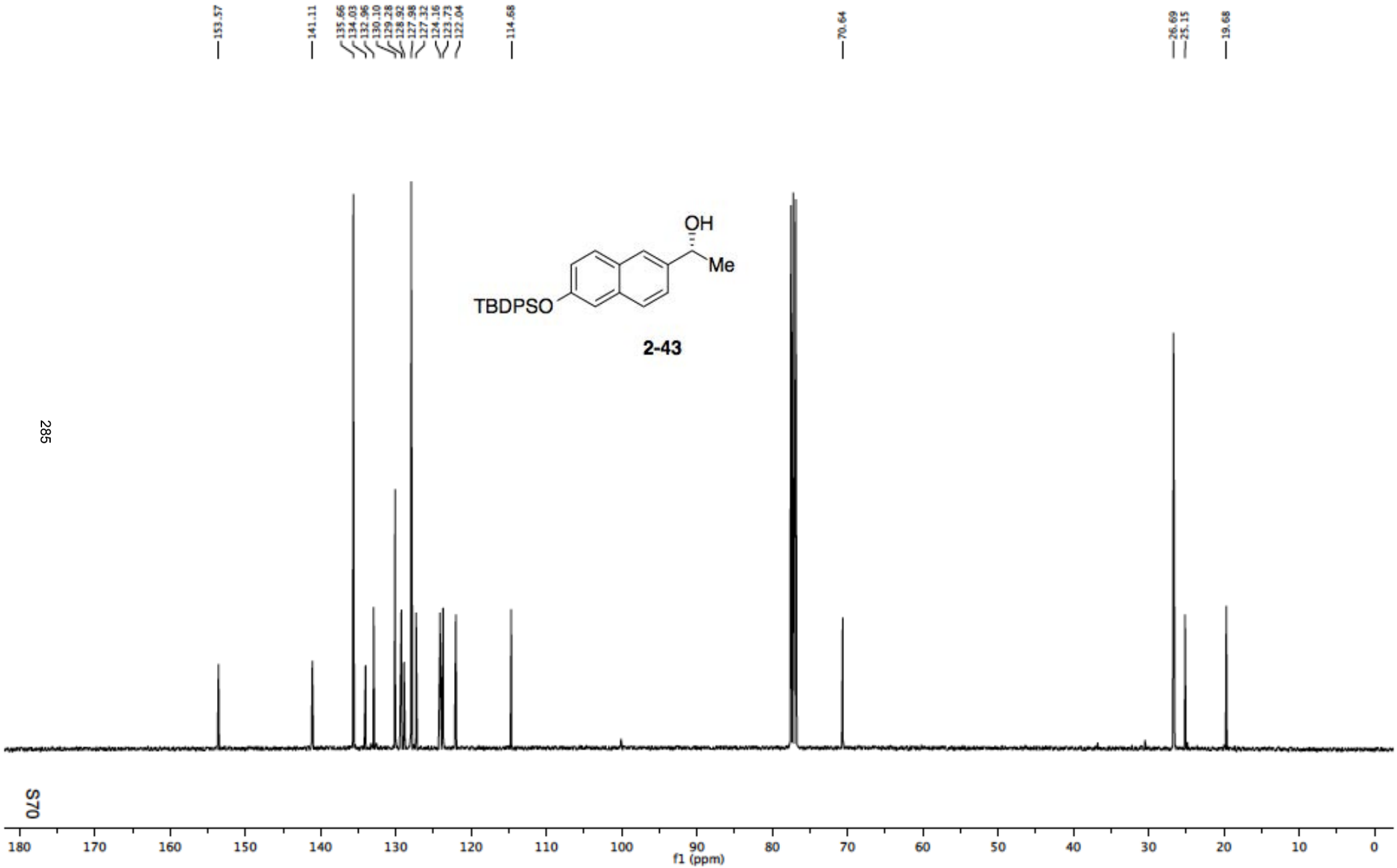

7.85
7.84
7.83
7.80
7.52
7.52
7.50
7.49
7.48
7.47
7.47
7.46
7.45
5.08
5.07
5.05
5.04
2.07
1.59
1.58
OH
2-Np
Me
2-40
280
S63
3.82
2.88
1.00
0.99
2.92
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

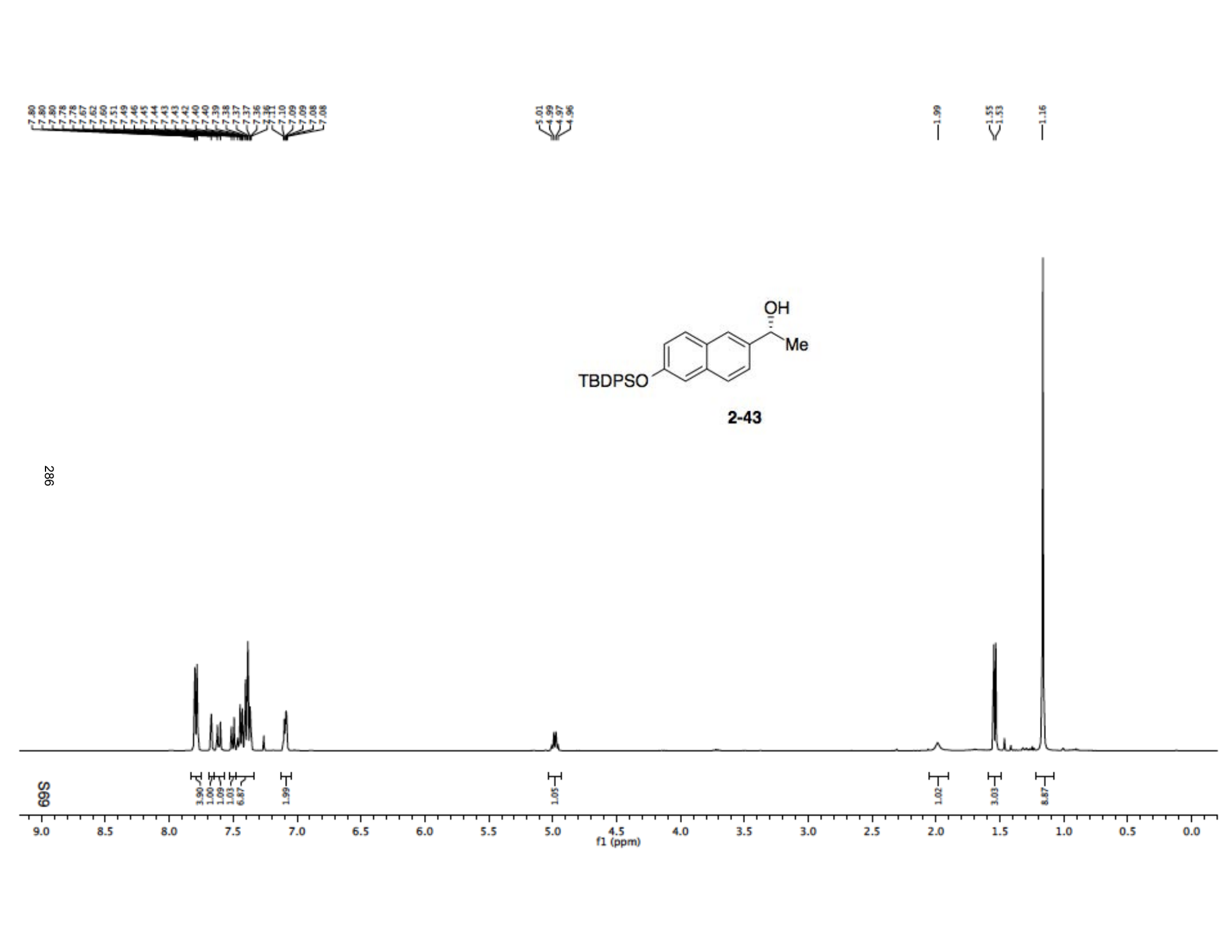

141.49
133.94
130.41
129.07
128.12
126.22
125.73
125.70
123.32
122.14
67.30
24.53
OH
Me
2-41
281
SS6
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

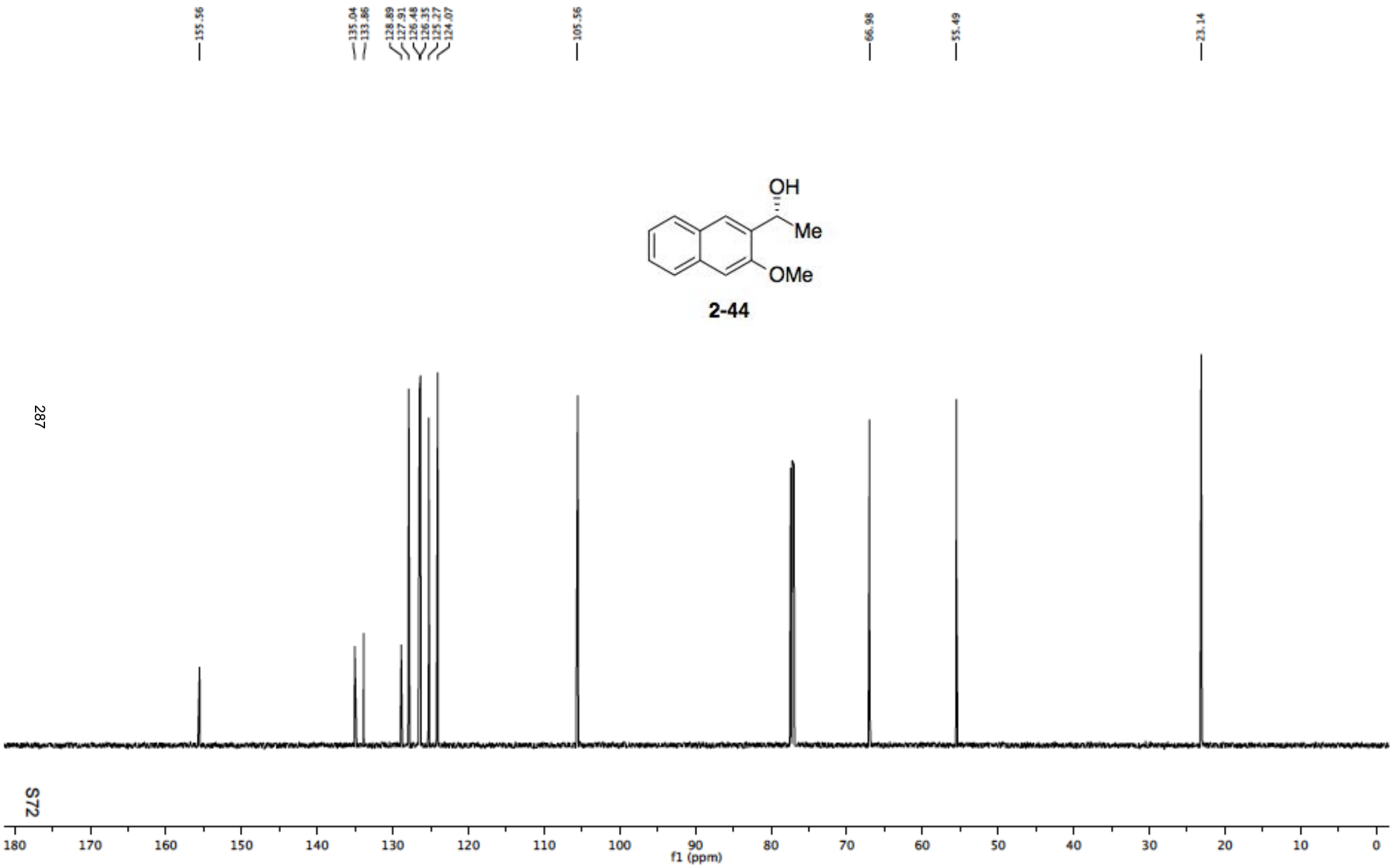

8.13
8.11
7.89
7.88
7.80
7.78
7.70
7.68
7.55
7.54
7.52
7.51
7.49
7.48
7.47
5.71
5.70
5.68
5.67
1.96
1.69
1.67
OH
Me
2-41
S65
1.04
1.02
1.00
1.07
2.92
1.08
1.02
2.82
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

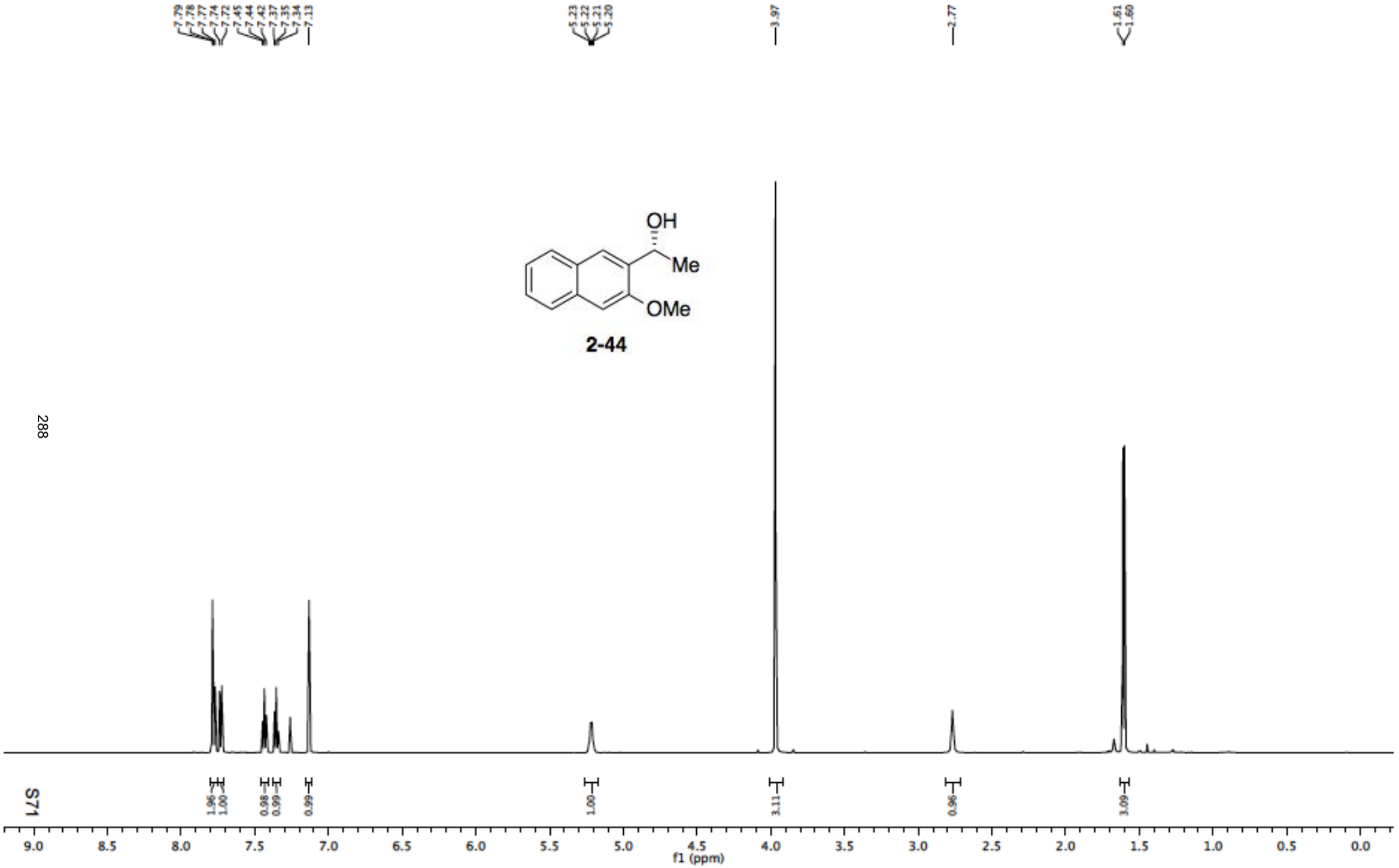

157.79
141.10
134.20
129.56
128.90
127.31
124.53
123.92
119.09
105.86
70.65
55.46
25.23
OH
Me
MeO
2-42
283
S68
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

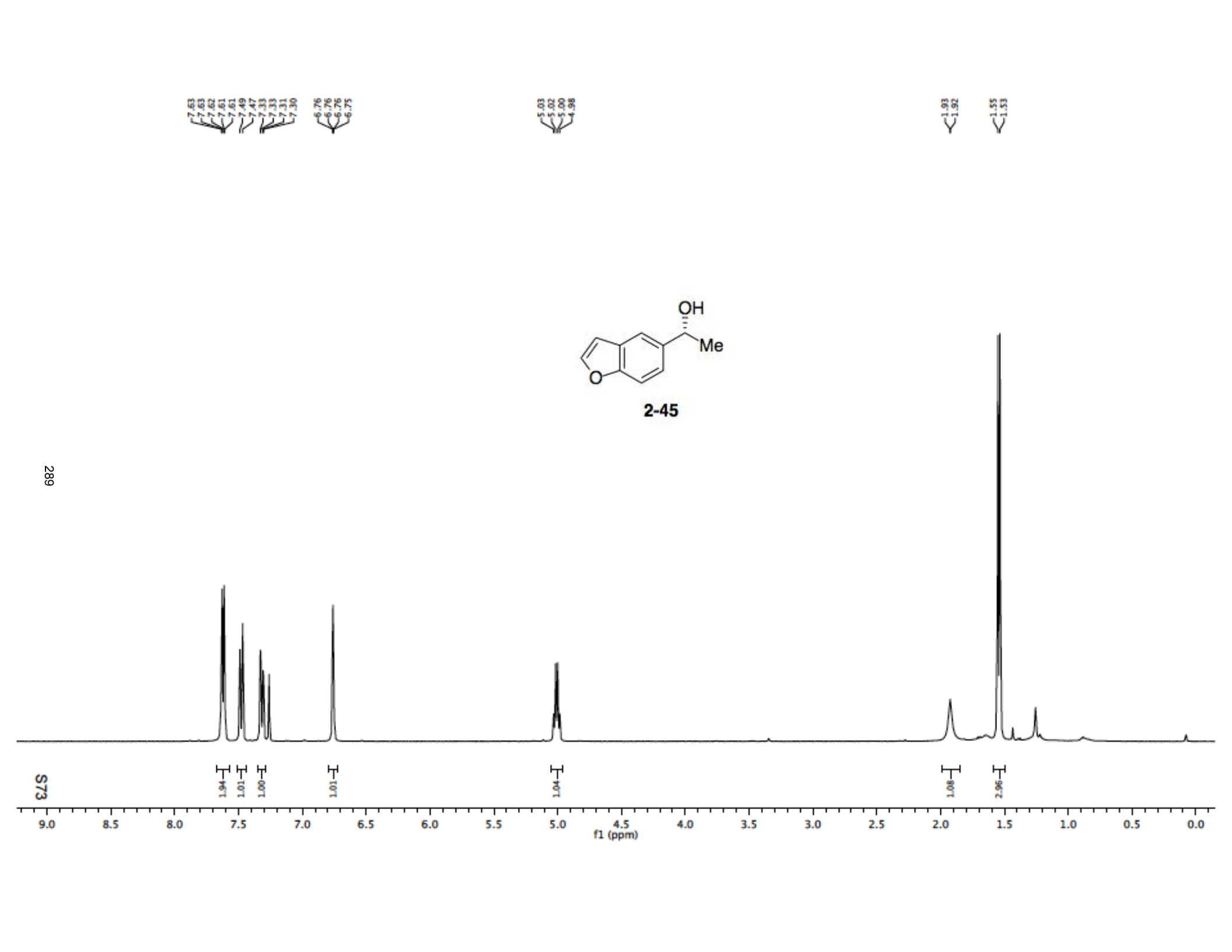

7.73
7.72
7.71
7.48
7.46
7.16
7.16
7.15
7.14
7.13
5.04
5.03
5.02
5.01
3.92
2.03
1.58
1.56
OH
Me
MeO
2-42
SS7
3.02
1.00
2.02
1.04
3.17
1.00
3.21
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


153.57
141.11
135.66
134.03
132.96
130.10
129.28
128.92
127.98
127.32
124.16
123.73
122.04
114.68
70.64
26.69
25.15
19.68
OH
Me
TBDPSO
2-43
285
S70
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.80
7.80
7.80
7.78
7.78
7.67
7.62
7.60
7.51
7.49
7.46
7.45
7.44
7.43
7.43
7.42
7.40
7.40
7.39
7.38
7.37
7.37
7.36
7.36
7.11
7.10
7.09
7.09
7.08
7.08
5.01
4.99
4.97
4.96
1.99
1.55
1.53
1.16
OH
Me
TBDPSO
2-43
286
S69
3.90
1.00
1.09
1.03
6.87
1.99
1.05
1.02
3.03
8.87
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


155.56
135.04
133.86
128.89
127.91
126.48
126.35
125.27
124.07
105.56
66.98
55.49
23.14
OH
Me
OMe
2-44
287
S72
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.79
7.78
7.77
7.74
7.72
7.45
7.44
7.42
7.37
7.35
7.34
7.13
5.23
5.22
5.21
5.20
3.97
2.77
1.61
1.60
OH
Me
OMe
2-44
1.96
1.00
0.98
0.99
0.99
1.00
3.11
0.96
3.09
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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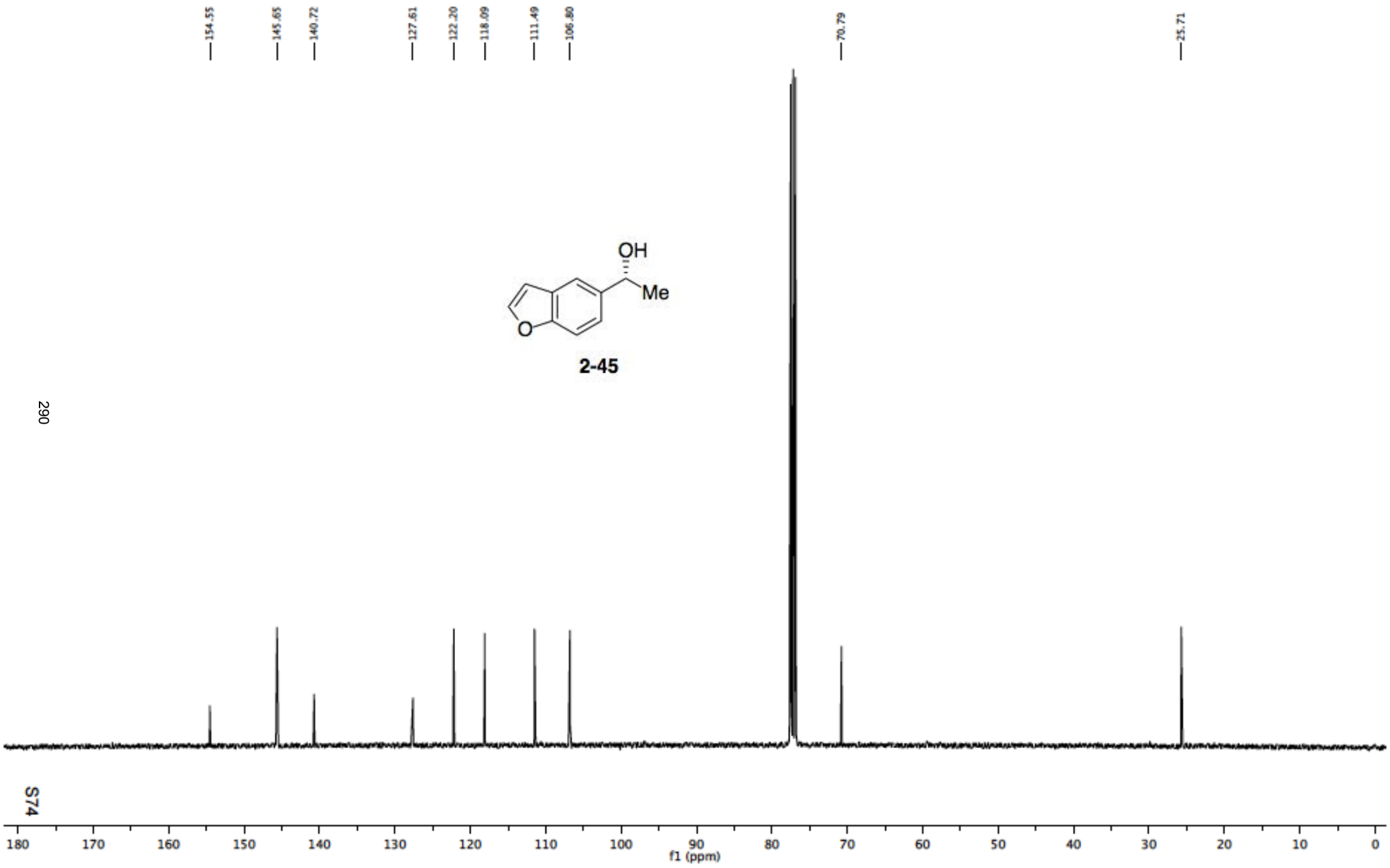
7.63
7.62
7.61
7.61
7.49
7.47
7.33
7.33
7.31
7.30
6.76
6.76
6.76
6.75
5.03
5.02
5.00
4.98
1.93
1.92
1.55
1.53
OH
Me
O
2-45
289
S73
1.94
1.01
1.00
1.01
1.04
1.08
2.96
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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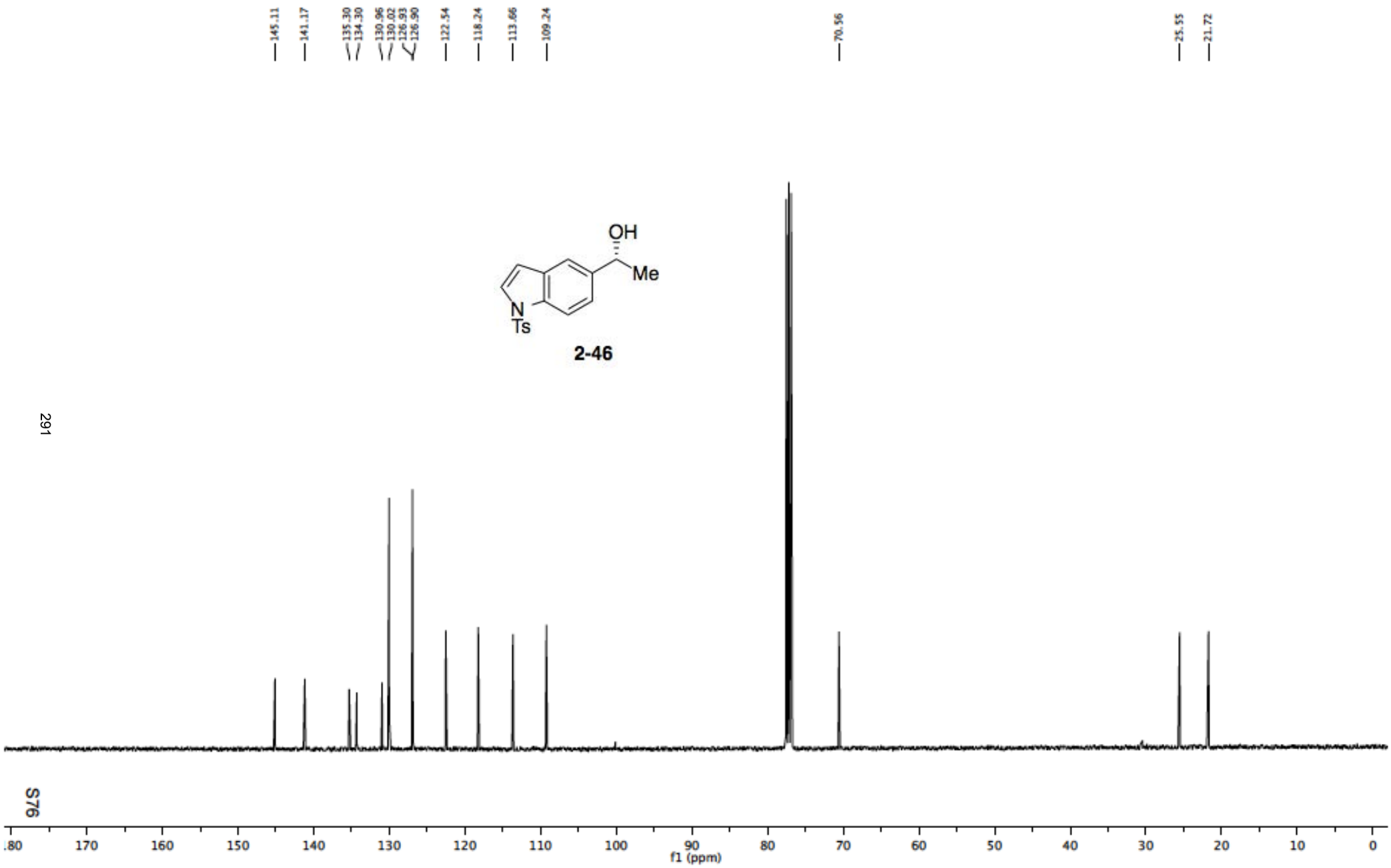
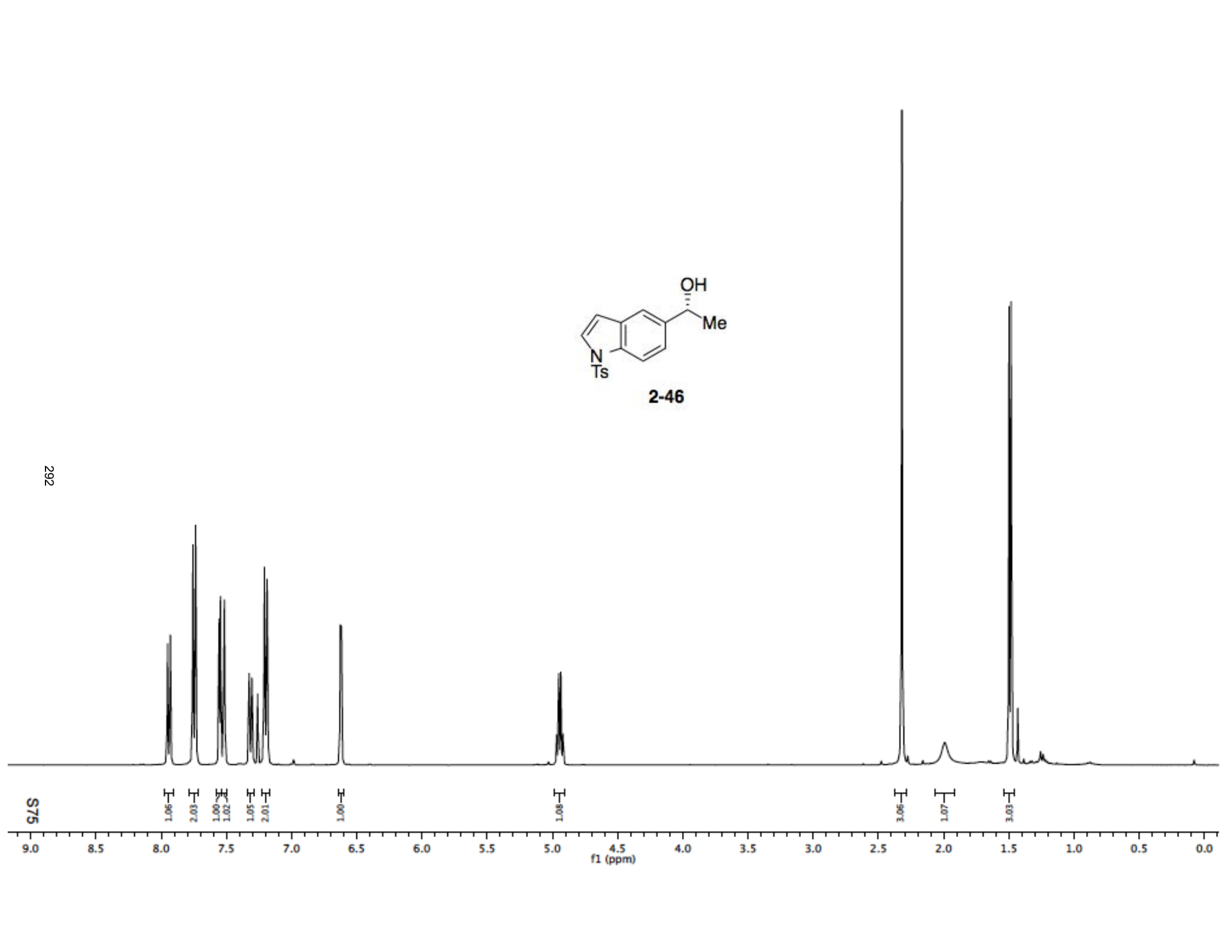
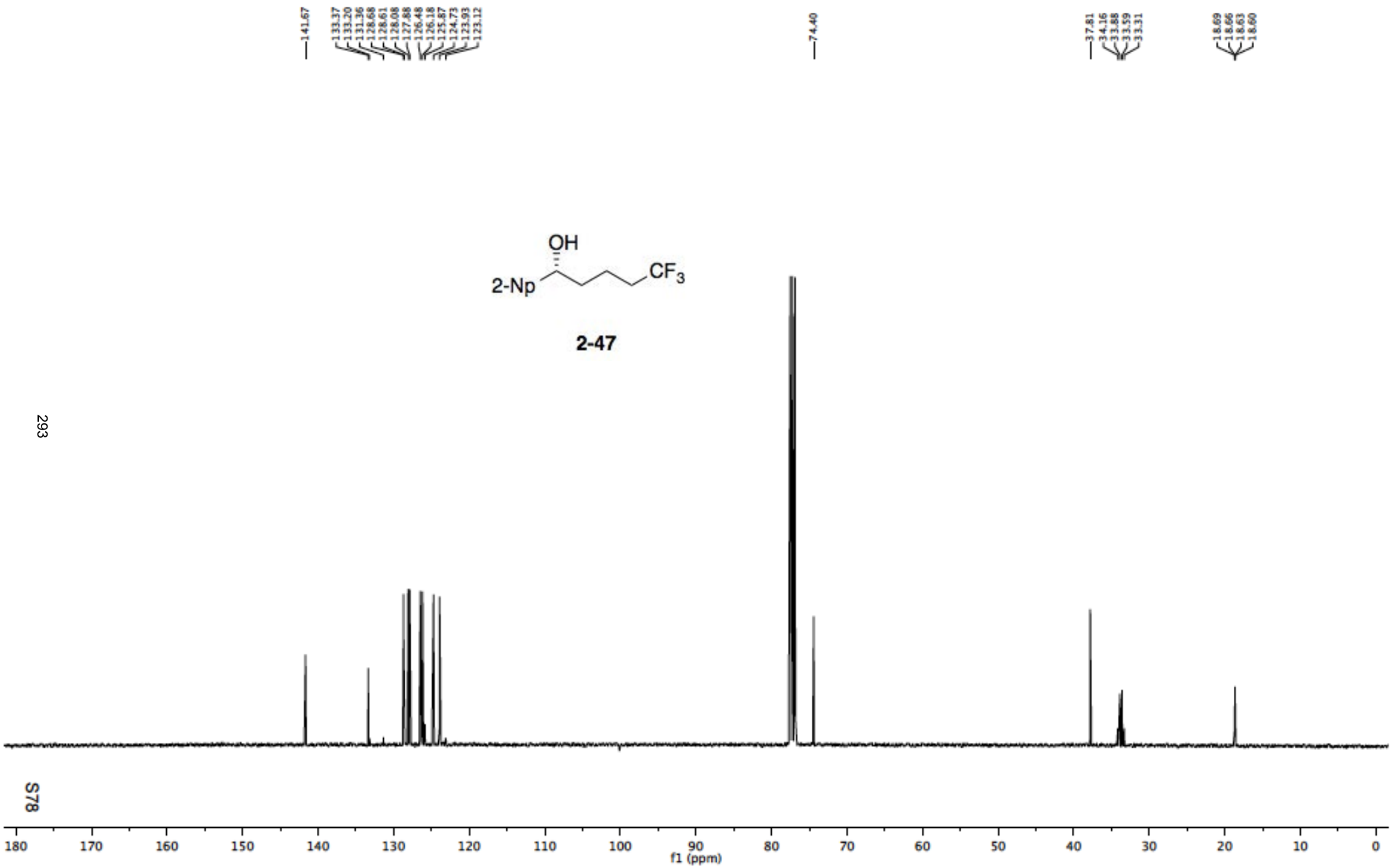
145.65
140.72
127.61
122.20
118.09
111.49
106.80
70.79
25.71
OH
Me
O
2-45
290
S74
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


145.11
141.17
135.30
134.30
130.96
130.02
126.93
126.90
122.54
118.24
113.66
109.24
70.56
25.55
21.72
OH
Me
N
Ts
2-46
291
S76
f1 (ppm)


OH
Me
N
Ts
2-46
292
S75
1.06
2.03
1.00
1.02
1.05
2.01
1.09
1.08
3.06
1.07
3.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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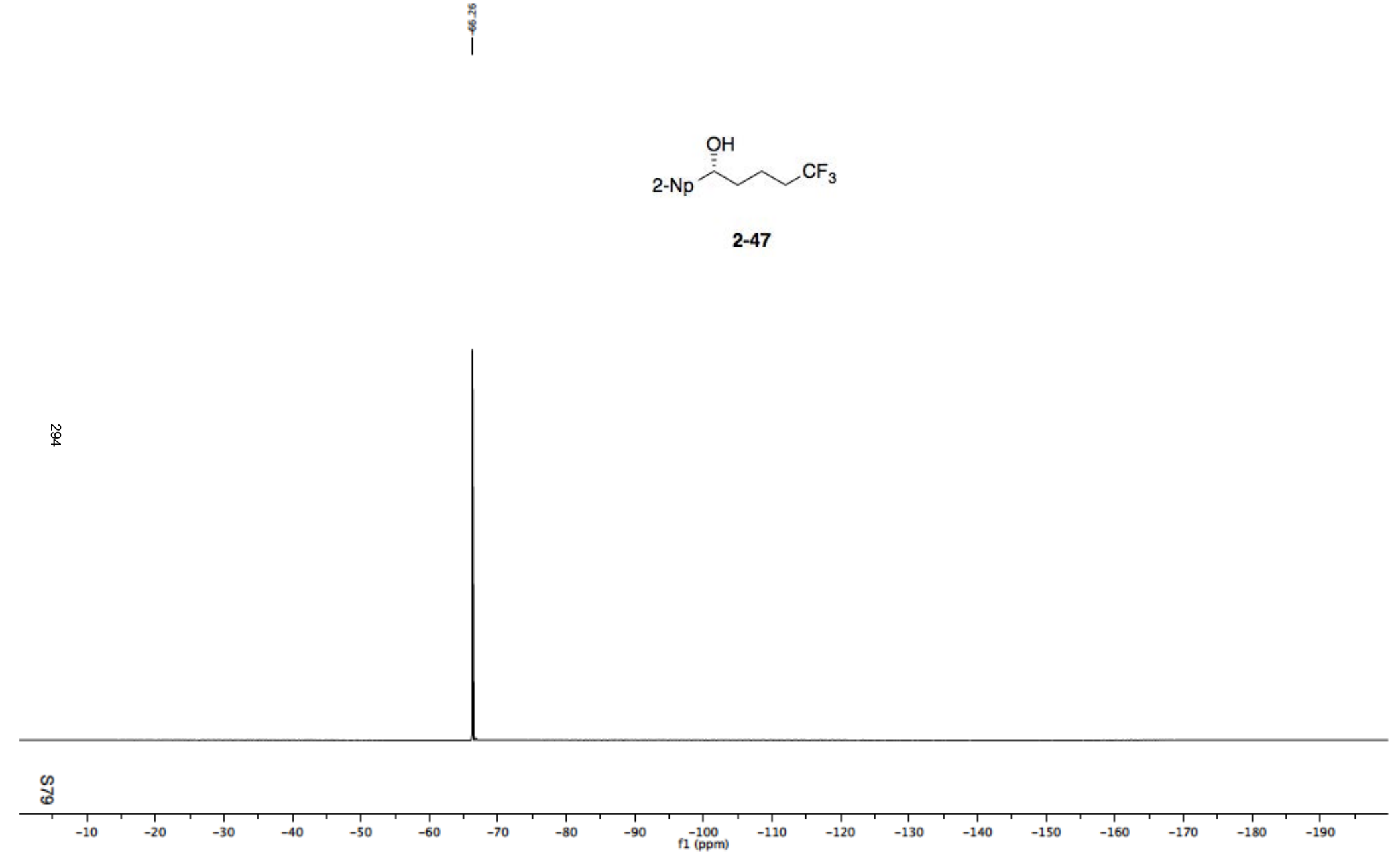
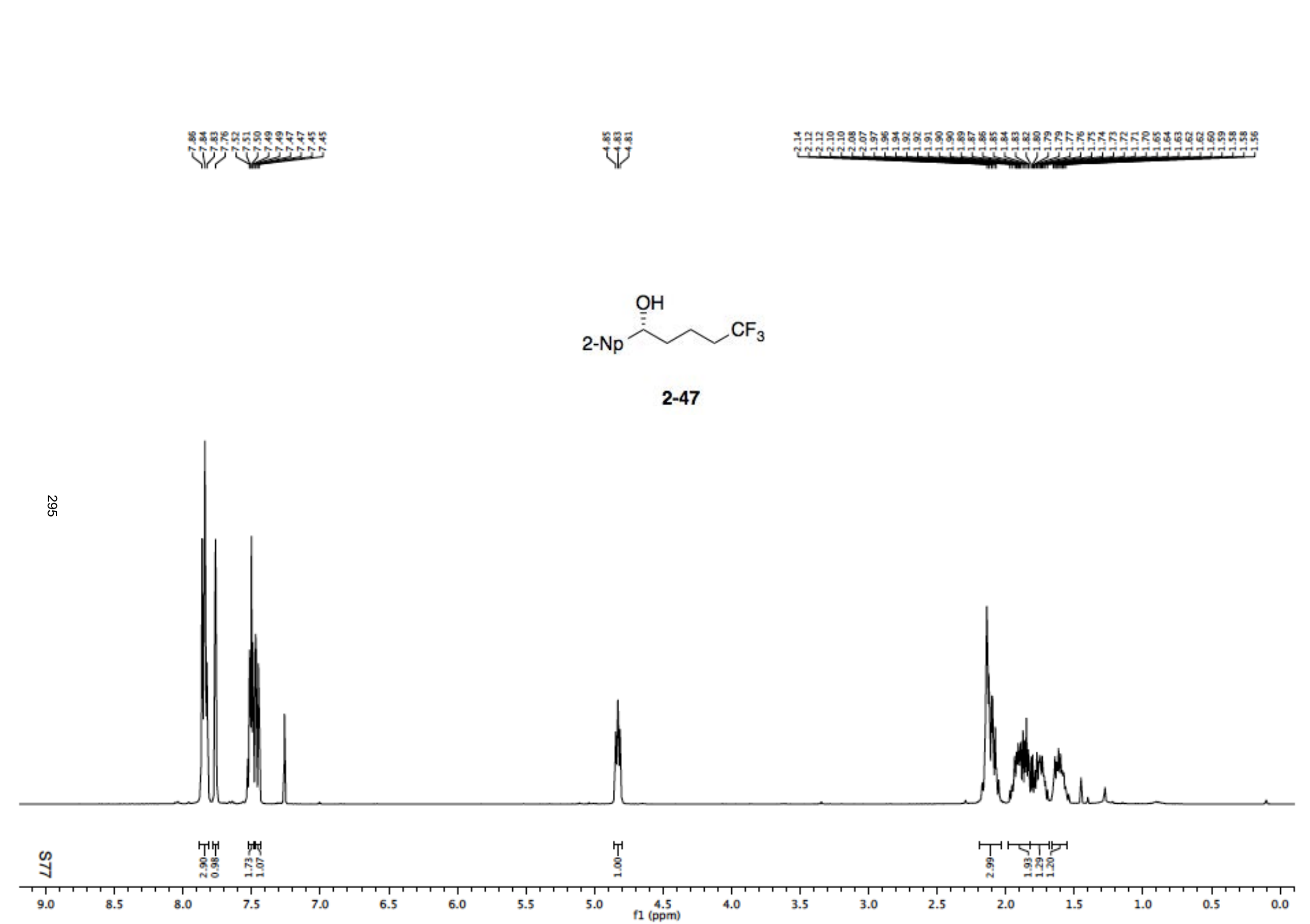
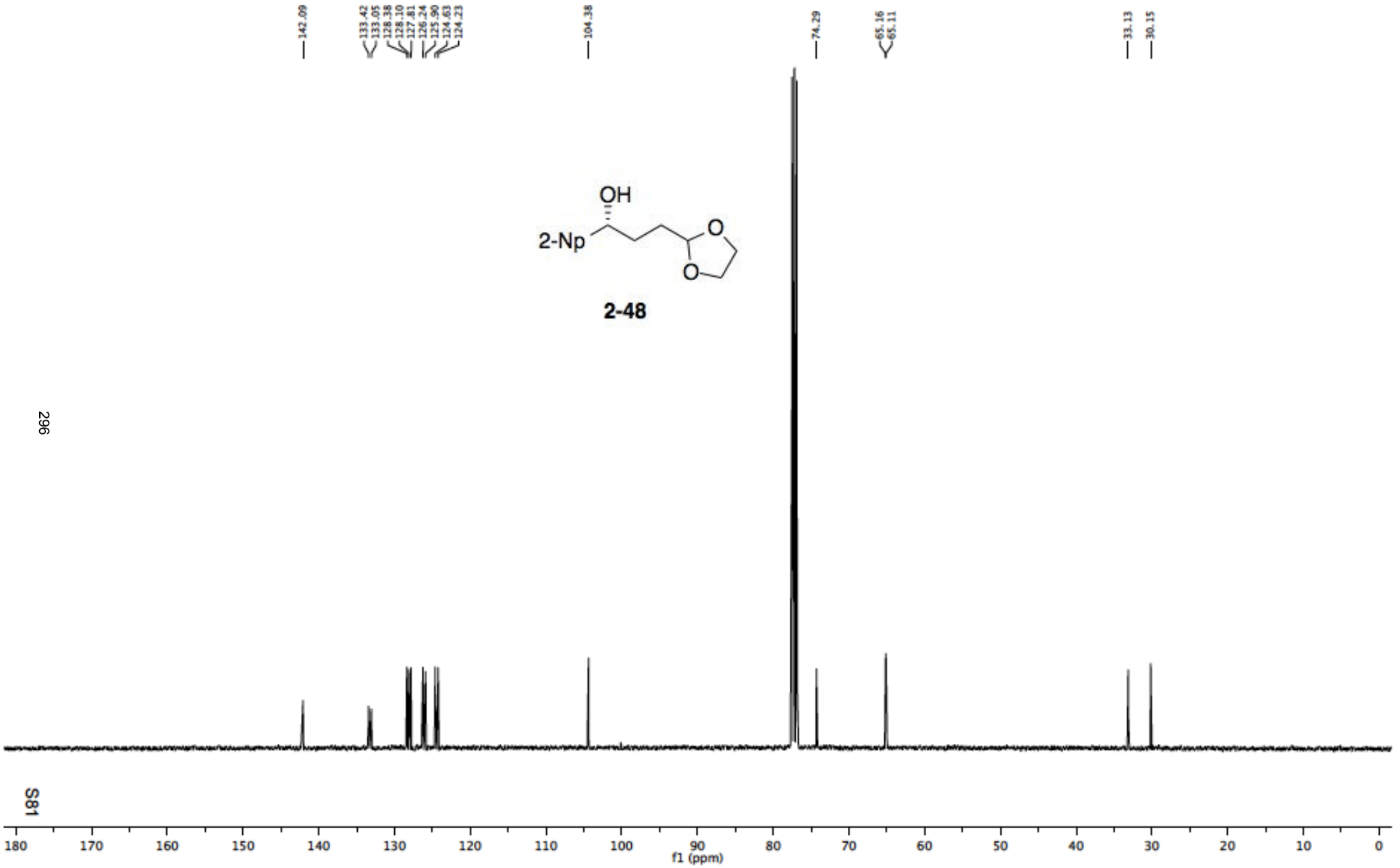
126.18
125.87
124.73
123.93
123.12
74.40
37.81
34.16
33.88
33.59
33.31
18.69
18.66
18.63
18.60
OH
2-Np
CF3
2-47
293
S78
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-66.26
OH
2-Np
CF3
2-47
294
S79
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)


7.86
7.84
7.83
7.76
7.52
7.51
7.50
7.49
7.49
7.47
7.47
7.45
7.45
4.85
4.83
4.81
2.14
2.12
2.12
2.10
2.10
2.08
2.07
1.97
1.96
1.94
1.92
1.92
1.91
1.90
1.90
1.89
1.87
1.86
1.85
1.84
1.83
1.82
1.80
1.79
1.79
1.77
1.76
1.75
1.74
1.73
1.72
1.71
1.70
1.65
1.64
1.63
1.62
1.62
1.60
1.59
1.58
1.58
1.56
OH
2-Np
CF3
2-47
295
S77
2.90
0.98
1.73
1.07
1.00
2.99
1.93
1.29
1.20
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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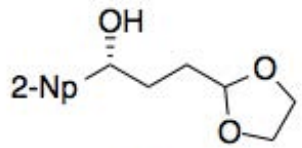
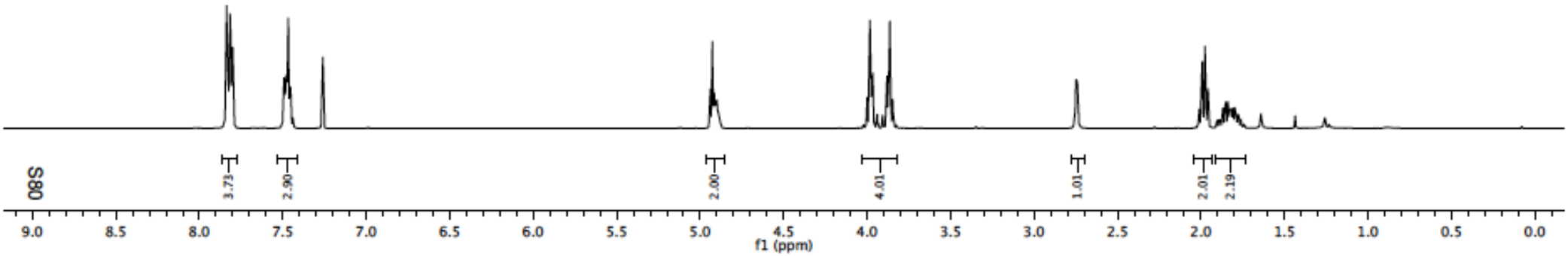
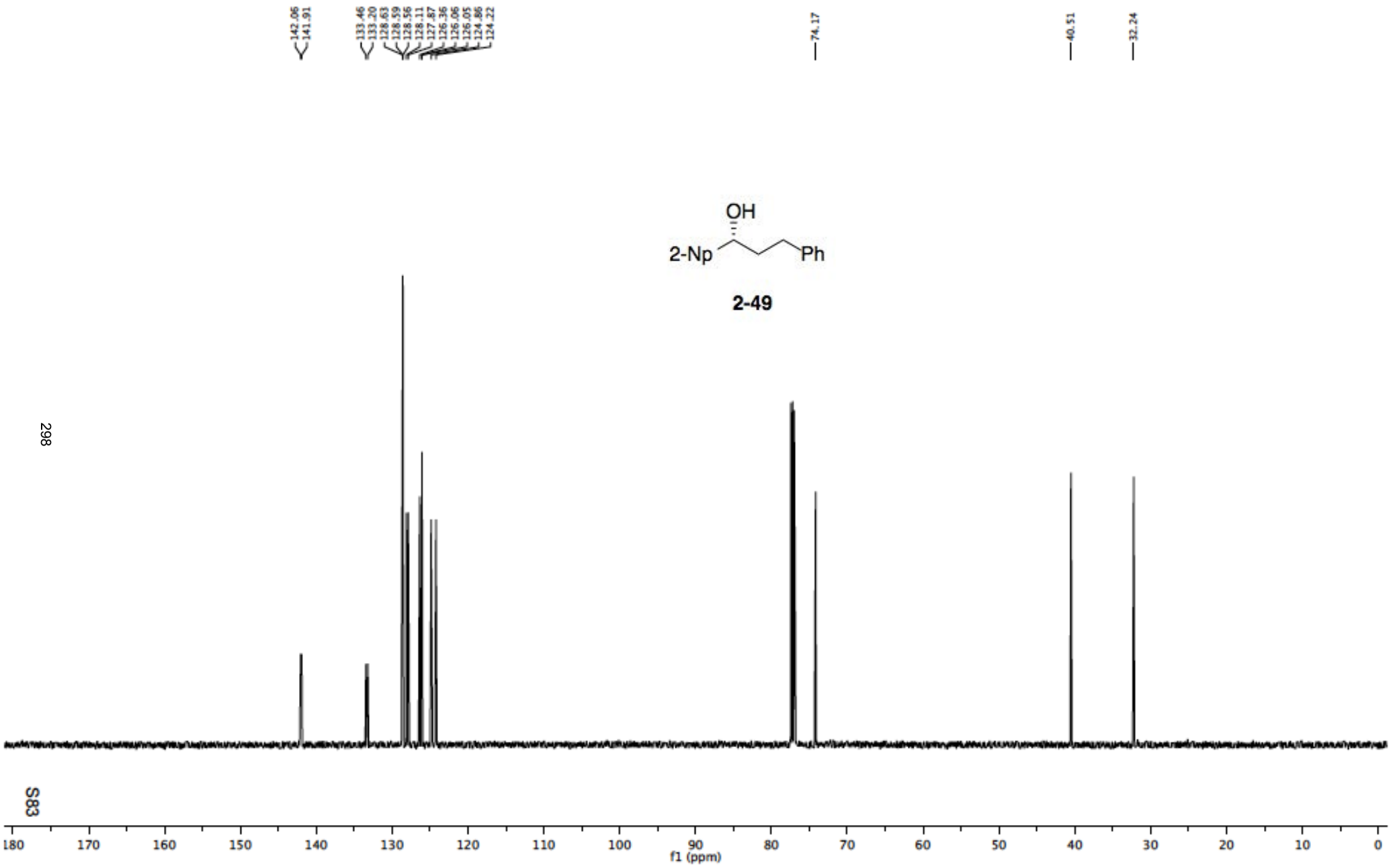
133.42
133.05
128.38
128.10
127.81
126.24
125.90
124.63
124.23
104.38
74.29
65.16
65.11
33.13
30.15
OH
2-Np
O
O
2-48
296
S81
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OH
2-Np
O
O

2-48


S80
3.73
2.90
2.00
4.01
1.01
2.01
2.19
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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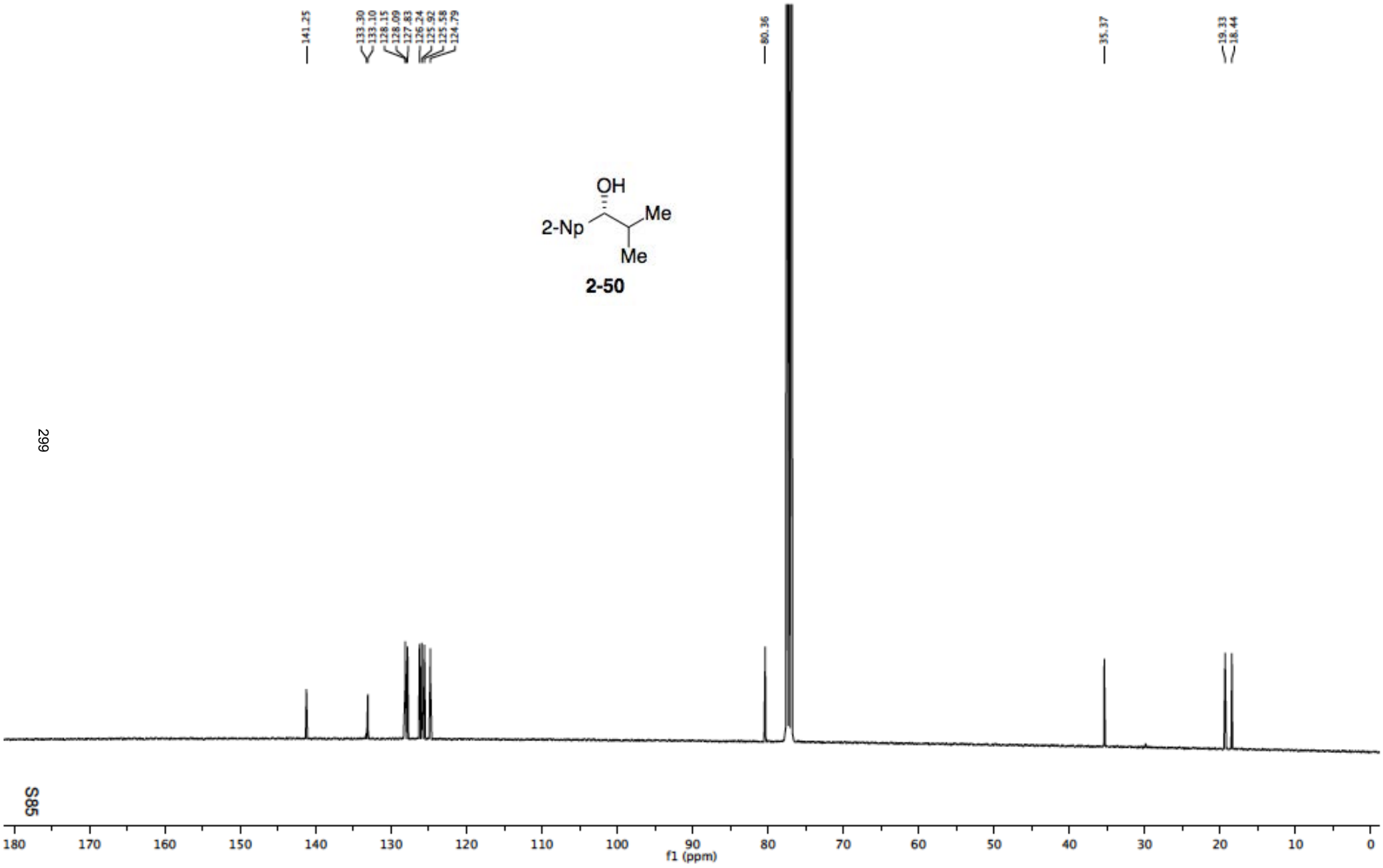
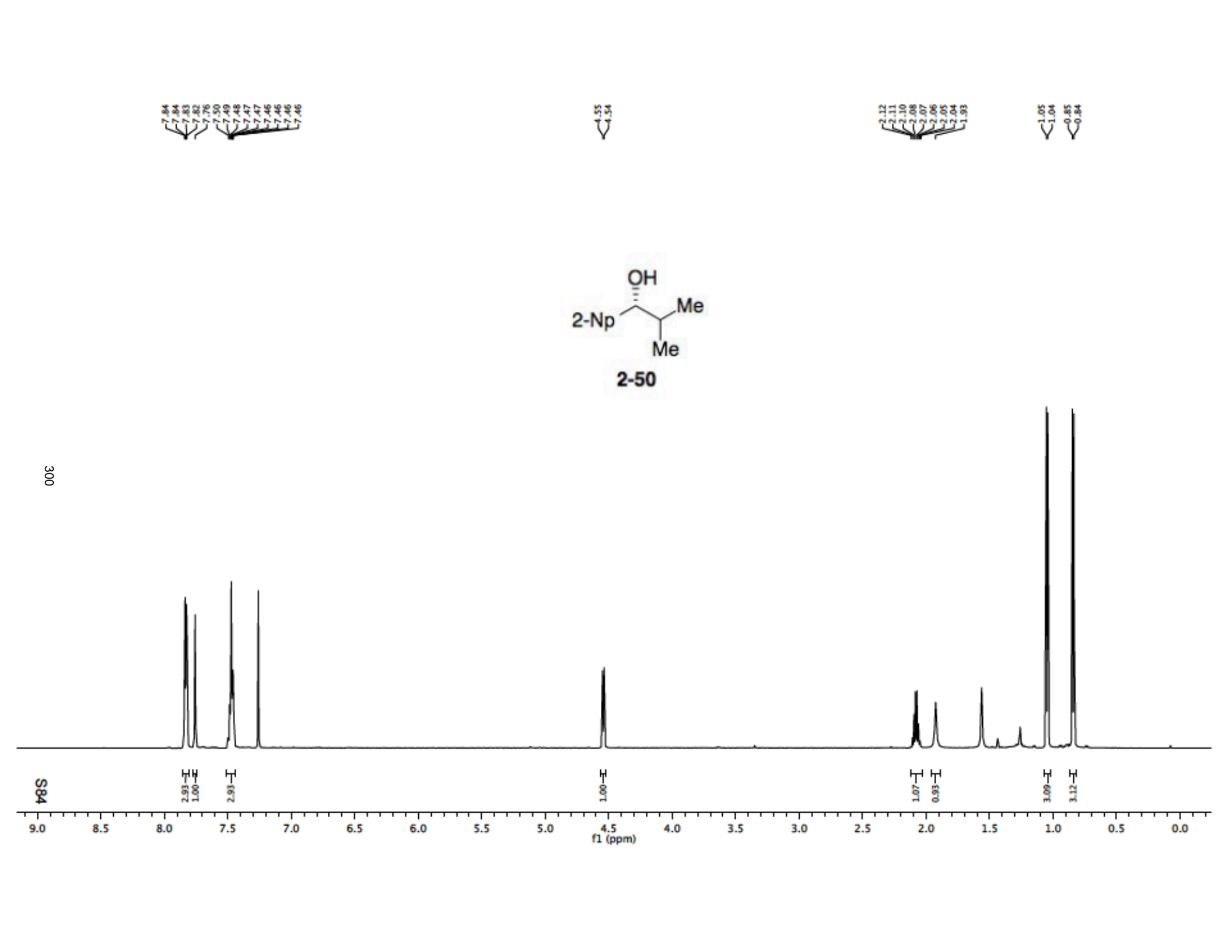
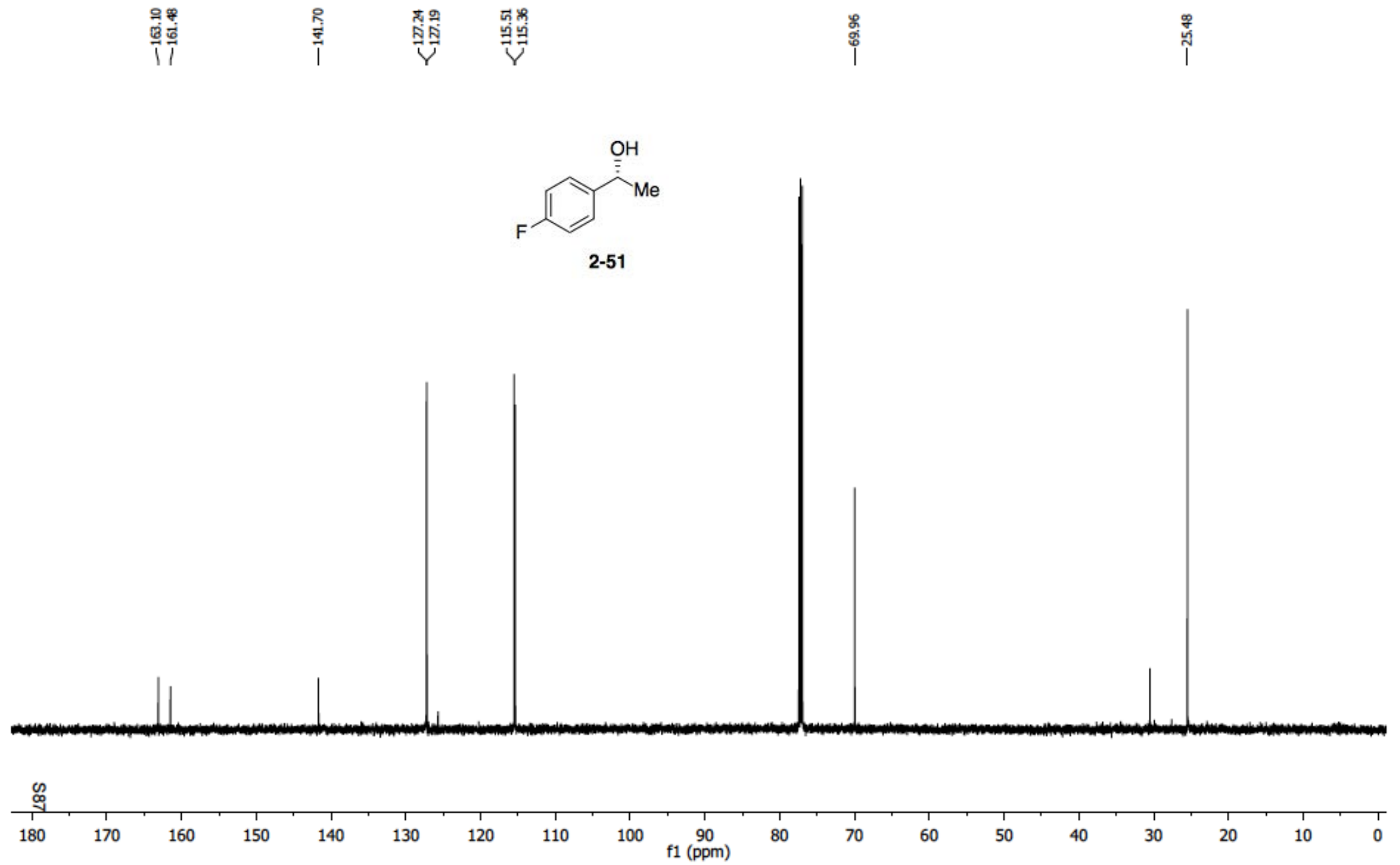
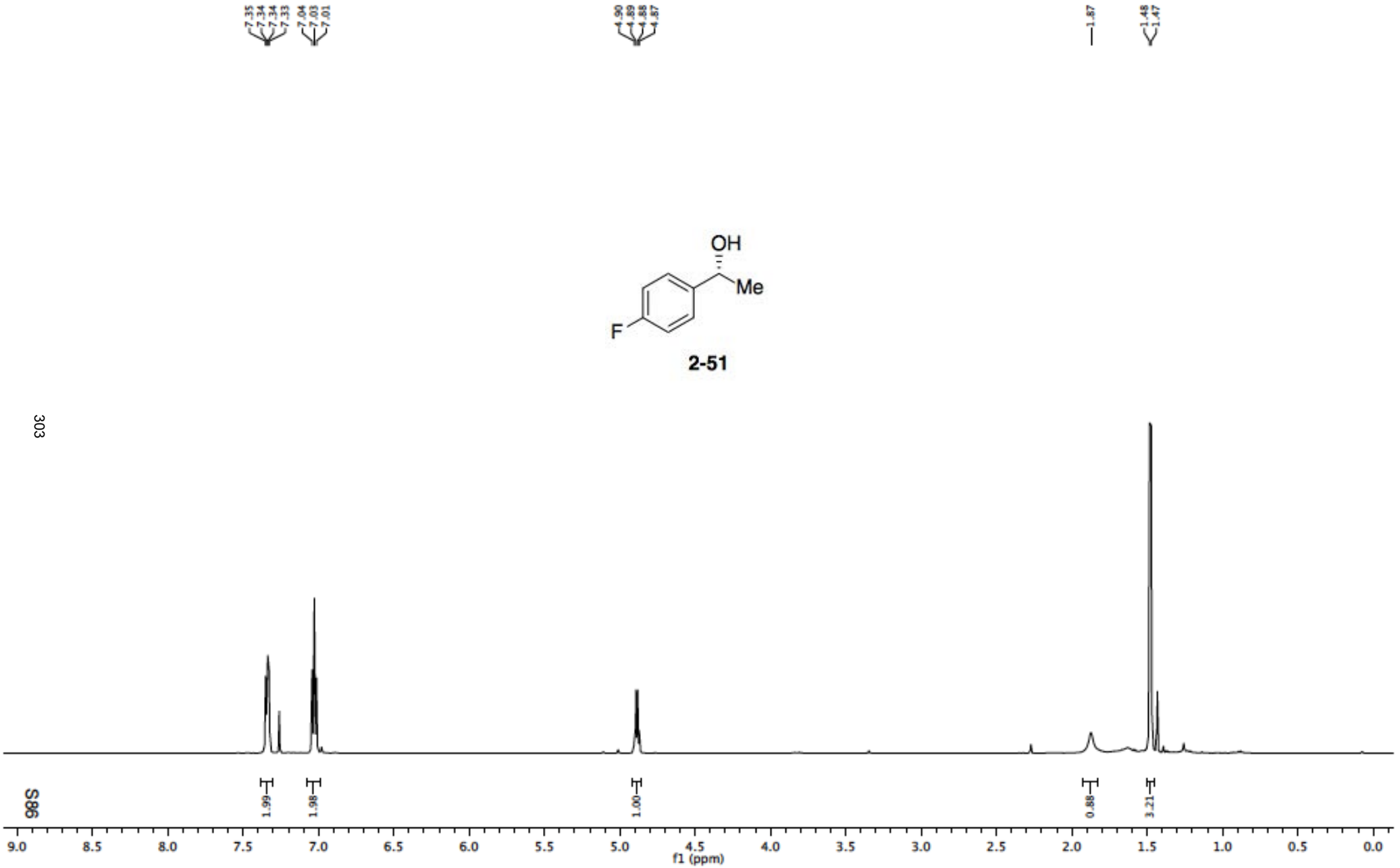
141.91
133.46
133.20
128.63
128.59
128.56
128.11
127.87
126.36
126.06
126.05
124.86
124.22
74.17
40.51
32.24
OH
2-Np
Ph
2-49
298
S83
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

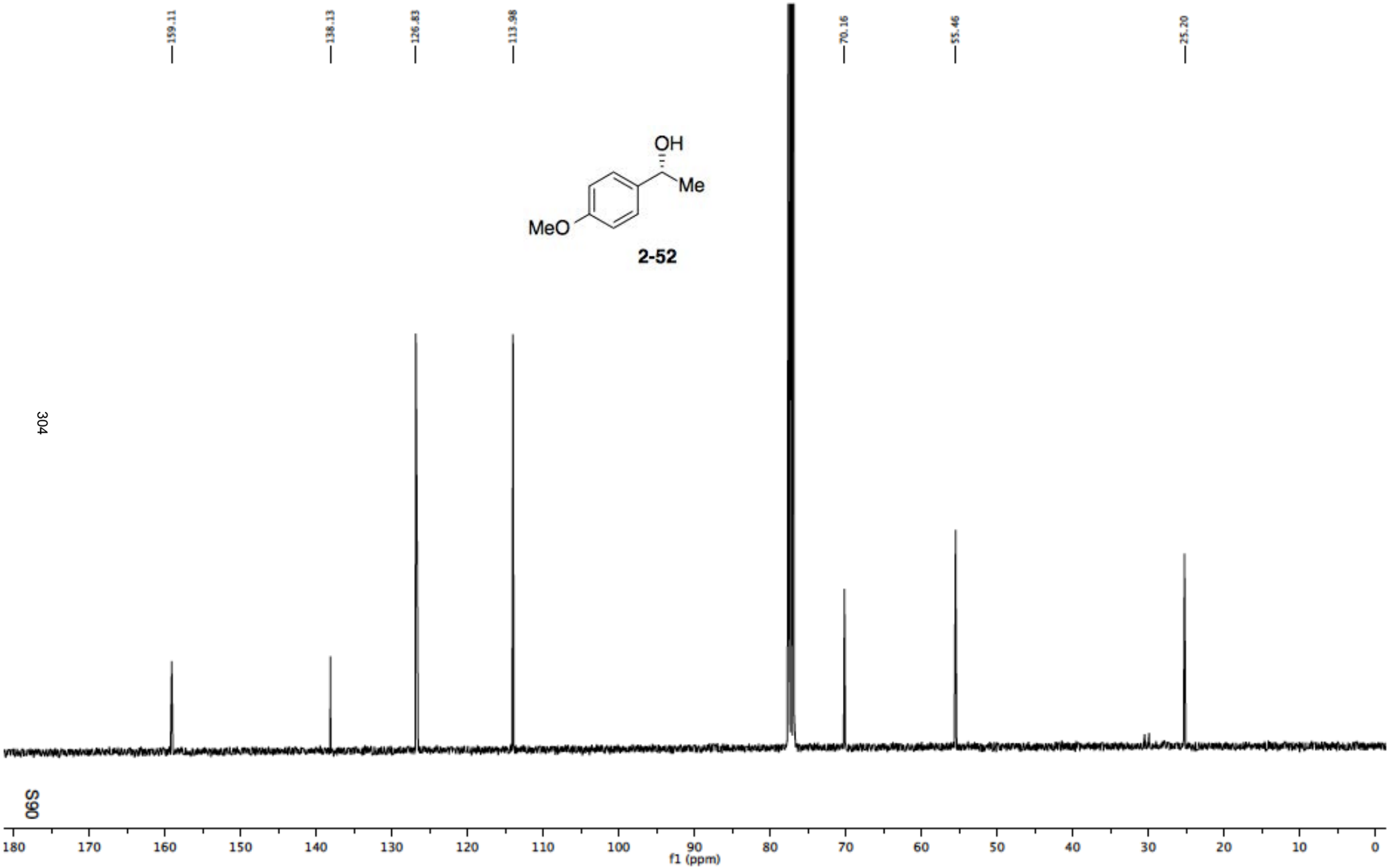

141.25
133.30
133.10
128.15
128.09
127.83
126.24
125.92
125.58
124.79
80.36
35.37
19.33
18.44
OH
2-Np
Me
Me
2-50
299
S85
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

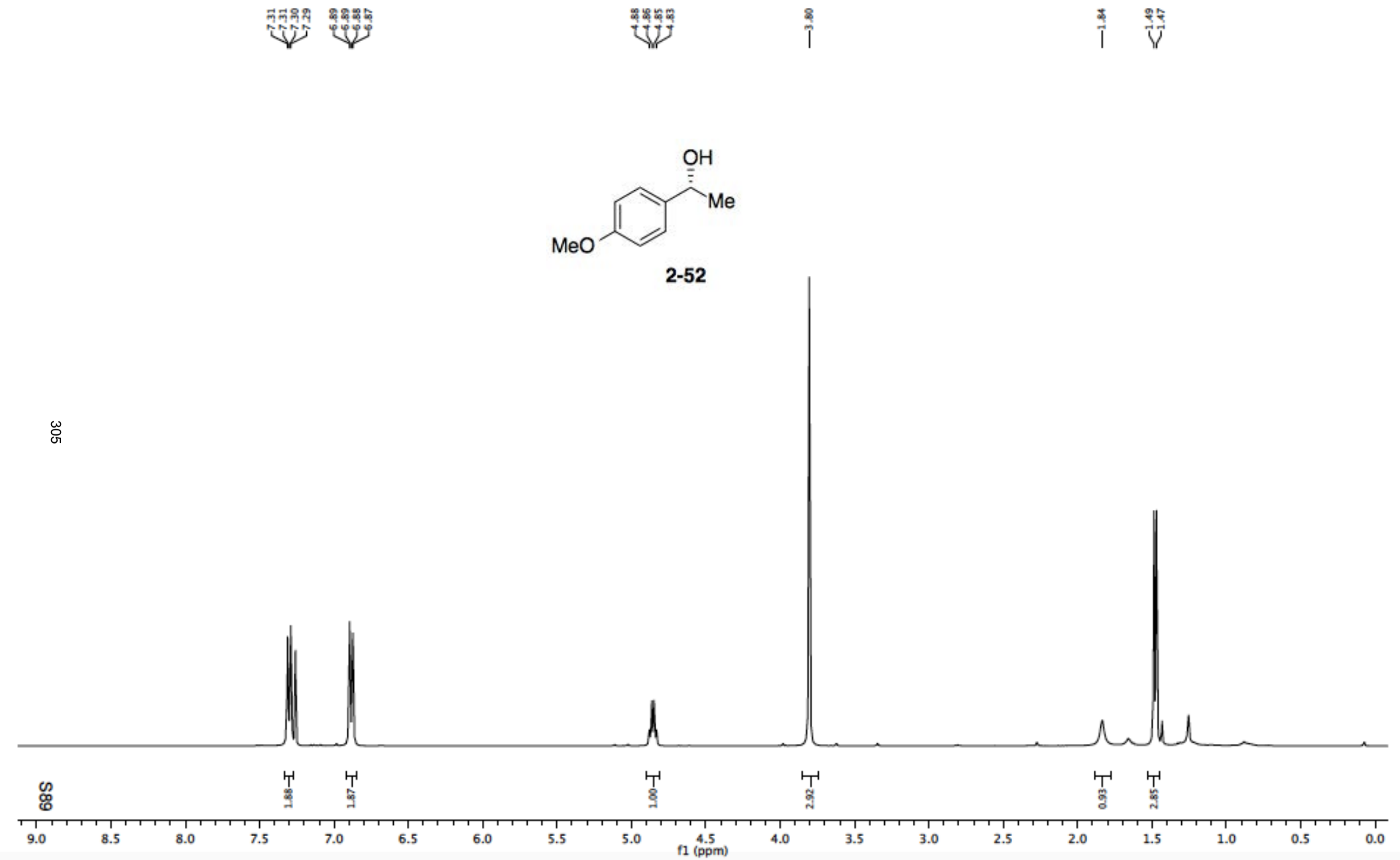

7.84
7.84
7.83
7.82
7.76
7.50
7.49
7.48
7.47
7.47
7.46
7.46
7.46
7.46
4.55
4.54
2.12
2.11
2.10
2.08
2.07
2.06
2.05
2.04
1.93
1.05
1.04
0.85
0.84
OH
2-Np
Me
Me
2-50
300
S84
2.93
1.00
2.93
1.00
1.07
0.93
3.09
3.12
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

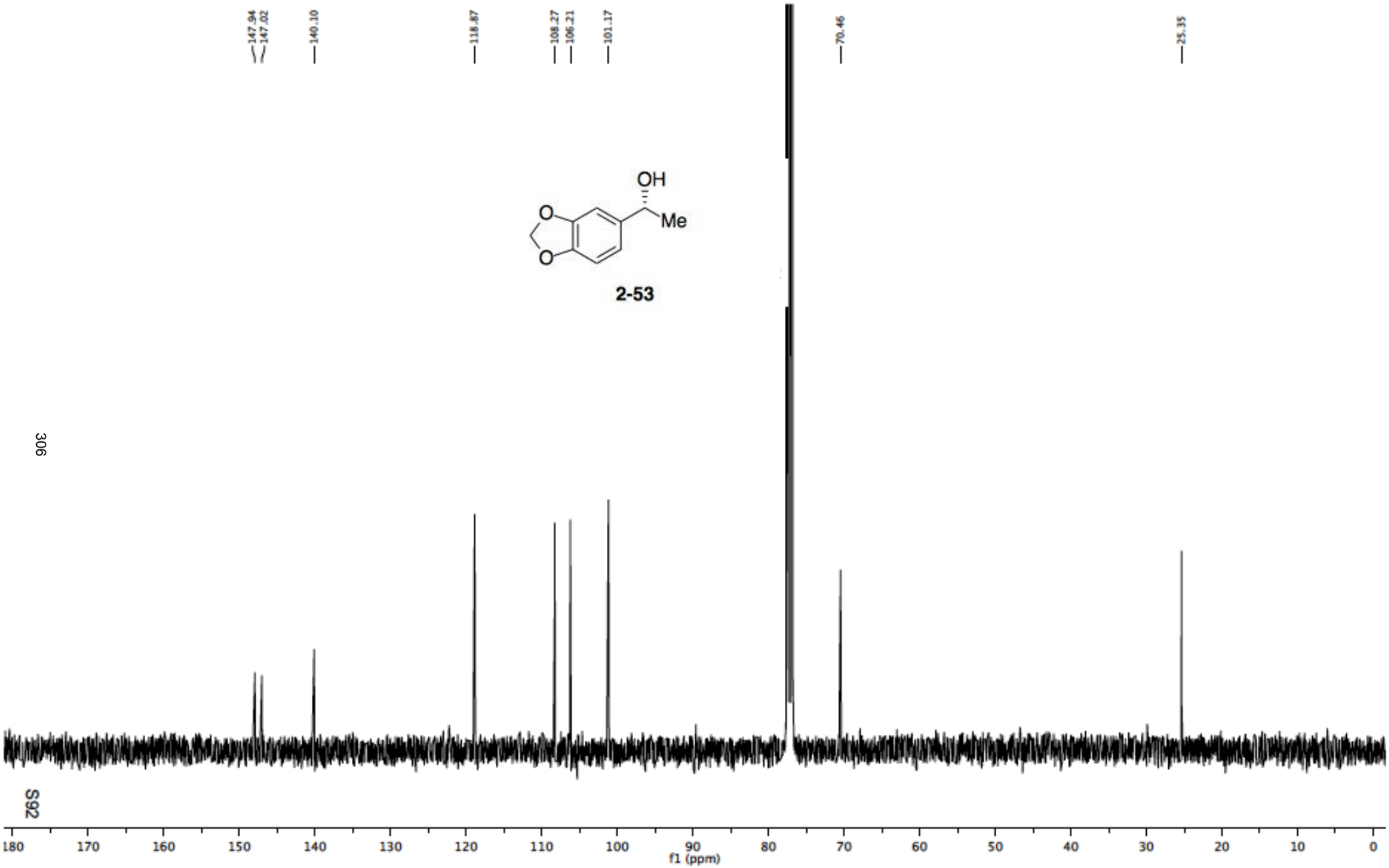

163.10
161.48
141.70
127.24
127.19
115.51
115.36
69.96
25.48
OH
Me
F
2-51
S87
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

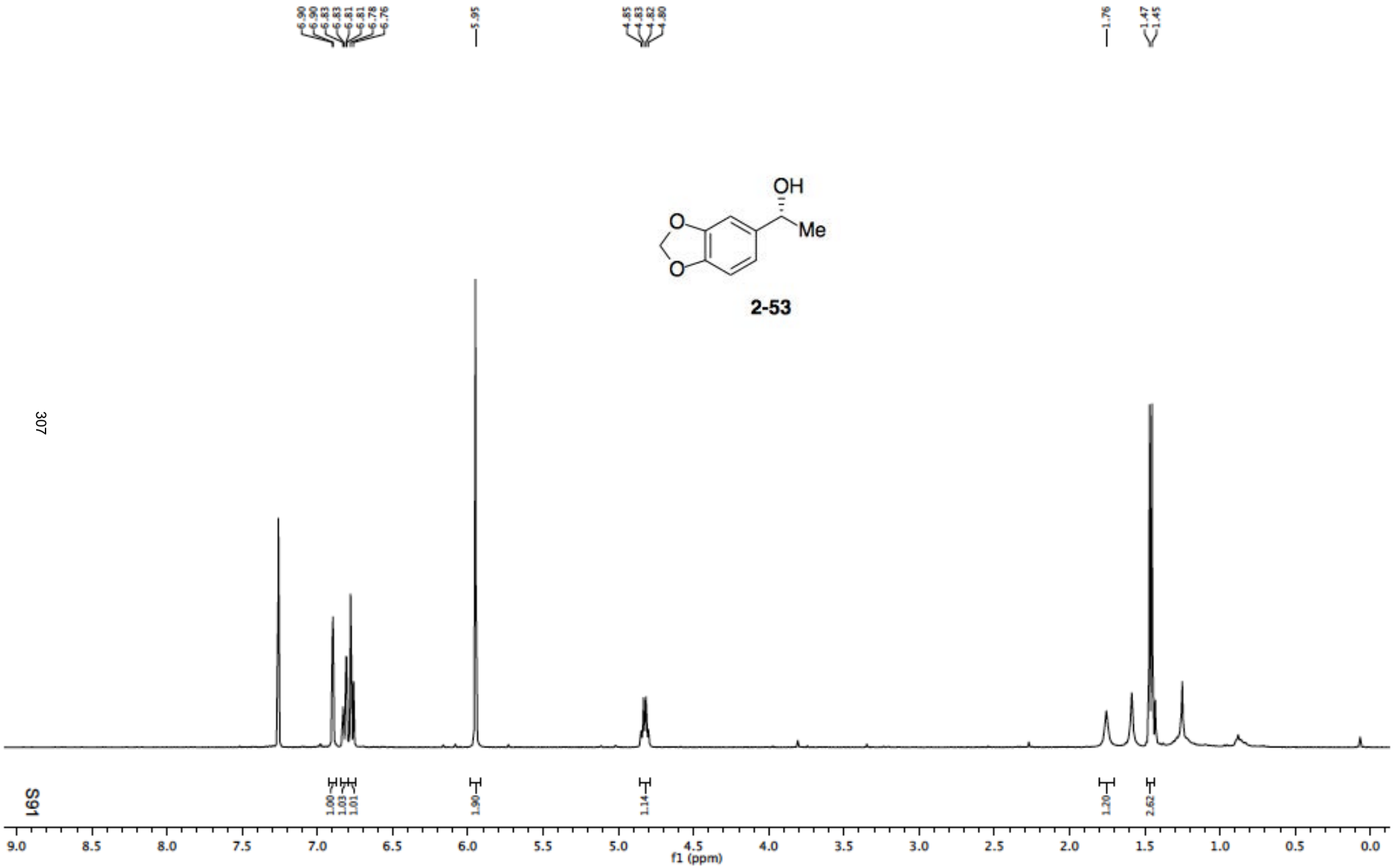

-115.36
OH
Me
F
2-51
88S
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

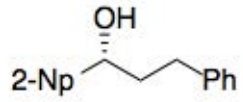

7.35
7.34
7.34
7.33
7.04
7.03
7.01
4.90
4.89
4.88
4.87
1.87
1.48
1.47
OH
Me
F
2-51
98S
1.99
1.98
1.00
0.88
3.21
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


159.11
138.13
126.83
113.98
70.16
55.46
25.20
OH
Me
MeO
2-52
304
S90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

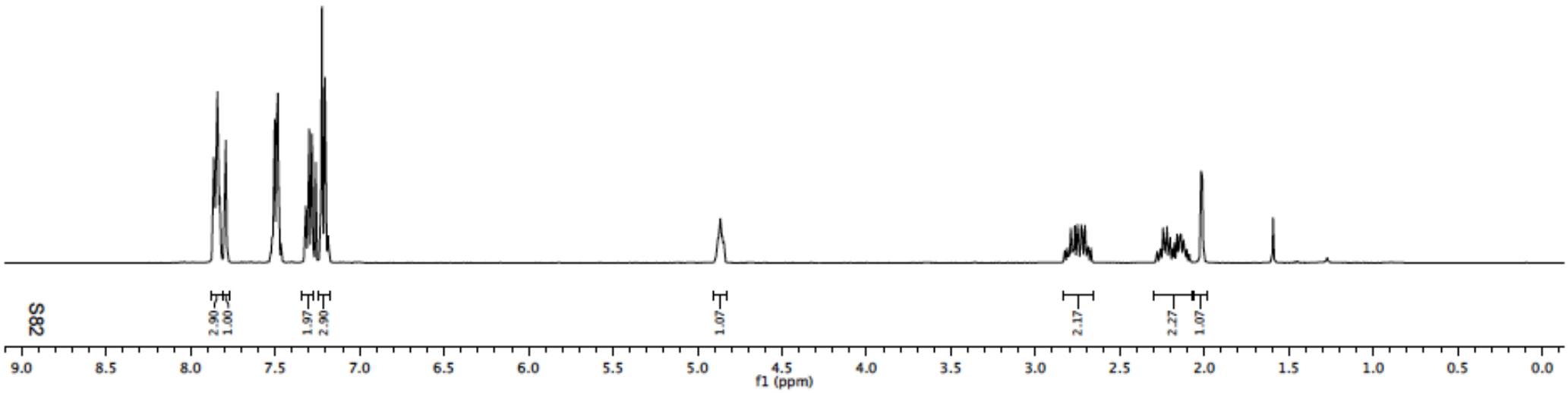

7.31
7.31
7.30
7.29
6.89
6.89
6.88
6.87
4.88
4.86
4.85
4.83
3.80
1.84
1.49
1.47
OH
Me
MeO
2-52
S69
1.88
1.87
1.00
2.92
0.93
2.85
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

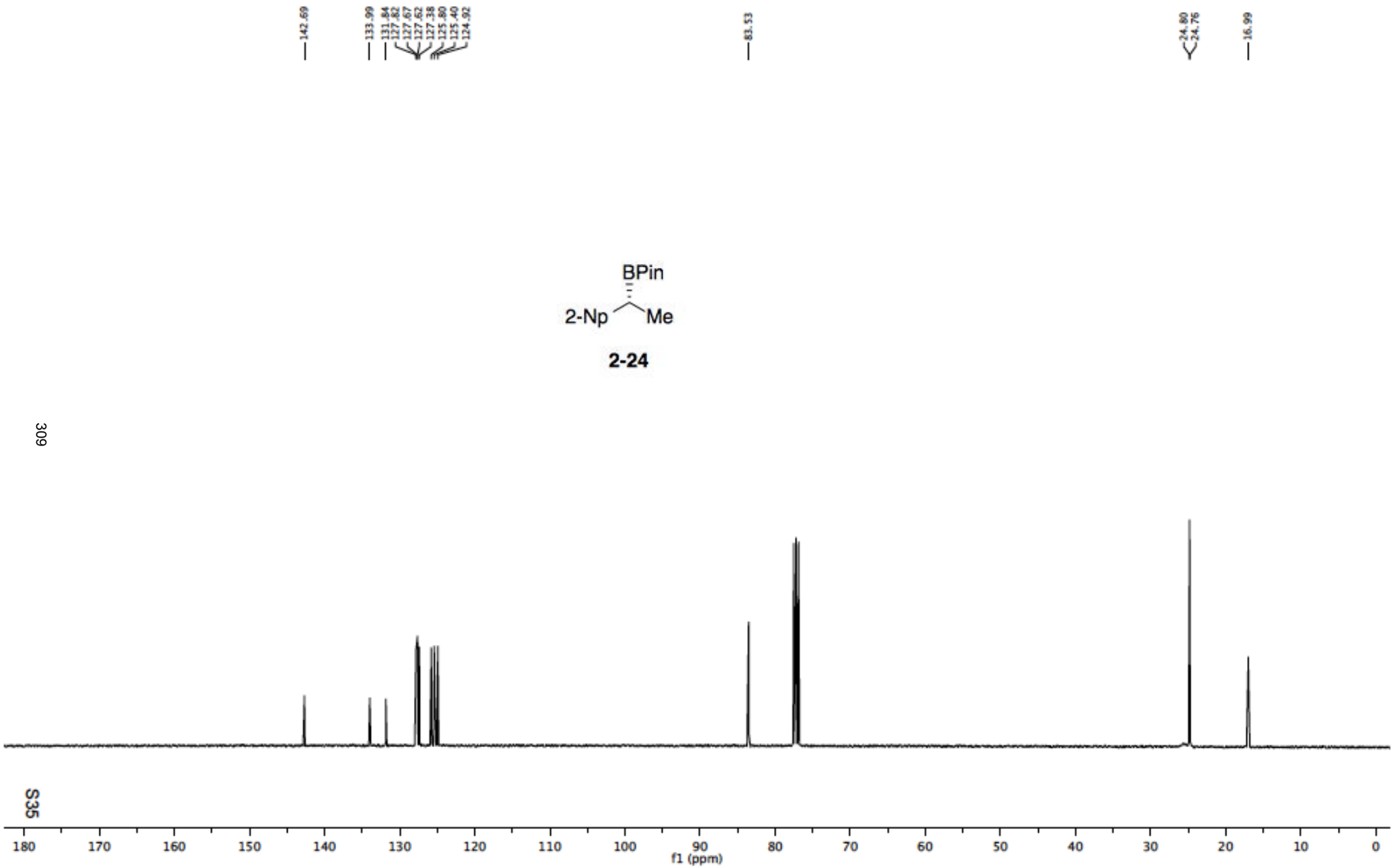

147.94
147.02
140.10
118.87
108.27
106.21
101.17
70.46
25.35
OH
Me
O
O
2-53
306
S92
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

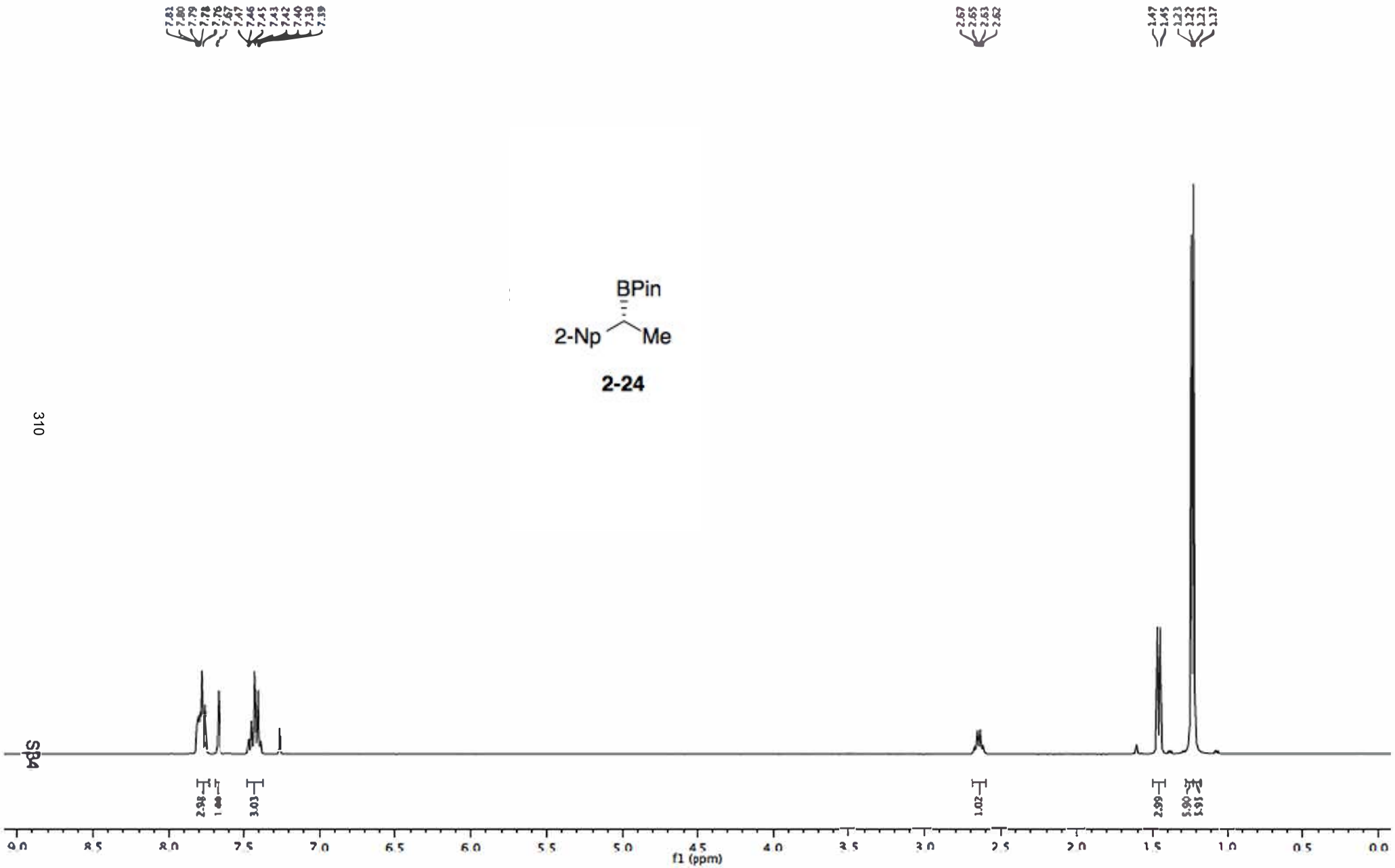

6.90
6.90
6.83
6.83
6.81
6.81
6.78
6.76
5.95
4.85
4.83
4.82
4.80
1.76
1.47
1.45
OH
Me
O
O
2-53
307
S91
1.00
1.03
1.01
1.90
1.14
1.20
2.62
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

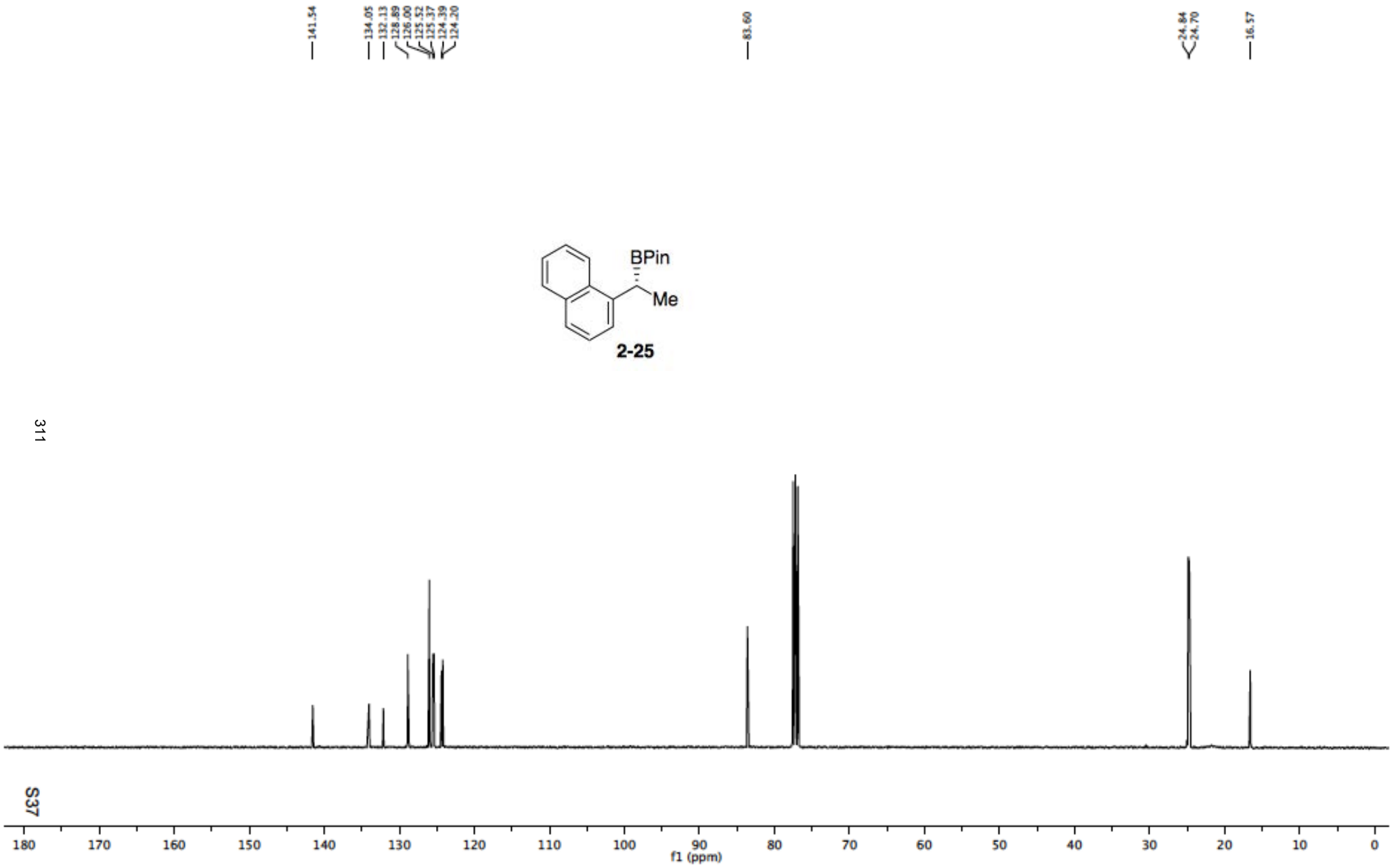

OH
2-Np
Ph

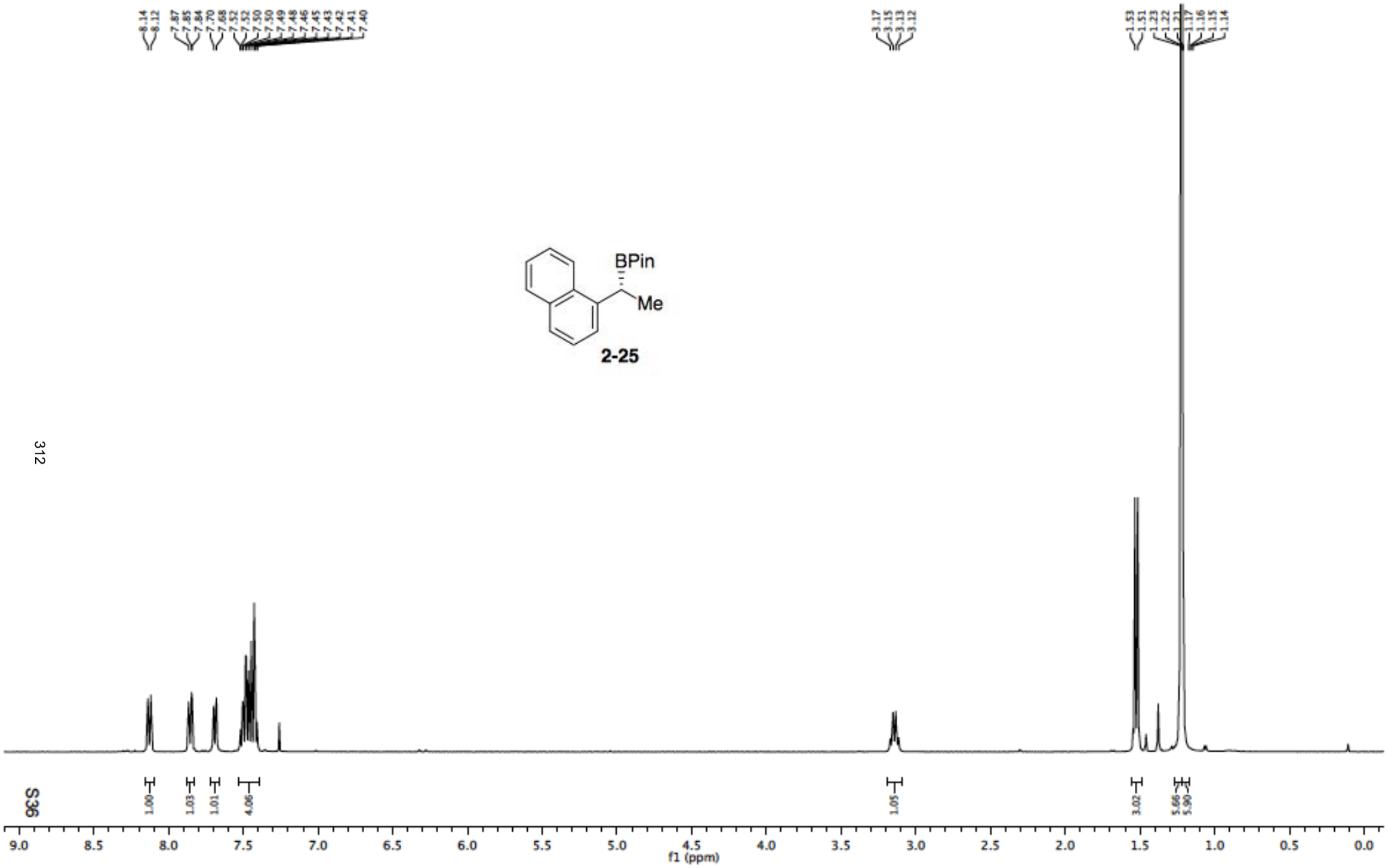
2-49


S82
2.90
1.00
1.97
2.90
1.07
2.17
2.27
1.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

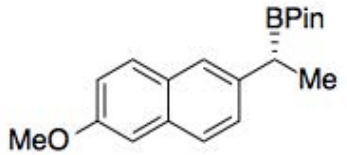

142.69
133.99
131.84
127.82
127.67
127.62
127.38
125.80
125.40
124.92
83.53
24.80
24.76
16.99
BPin
2-Np
Me
2-24
309
S35
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.81
7.80
7.79
7.78
7.76
7.67
7.47
7.46
7.45
7.43
7.42
7.40
7.39
7.39
2.67
2.65
2.63
2.62
1.47
1.45
1.23
1.22
1.21
1.17
BPin
2-Np
Me
2-24
SB4
2.98
1.00
3.03
1.02
2.99
5.90
1.91
f1 (ppm)


141.54
134.05
132.13
128.89
126.00
125.52
125.37
124.39
124.20
83.60
24.84
24.70
16.57
BPin
Me
2-25
311
S37
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.14
8.12
7.87
7.85
7.84
7.70
7.68
7.52
7.50
7.49
7.48
7.46
7.45
7.43
7.42
7.41
7.40
3.17
3.15
3.13
3.12
1.53
1.51
1.23
1.22
1.21
1.17
1.16
1.15
1.14
BPin
Me
2-25
1.00
1.03
1.01
4.06
1.05
3.02
5.66
5.90
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

157.03
140.29
132.75
129.46
129.10
127.82
126.74
125.31
118.52
105.68
83.46
55.40
24.78
24.74
17.08



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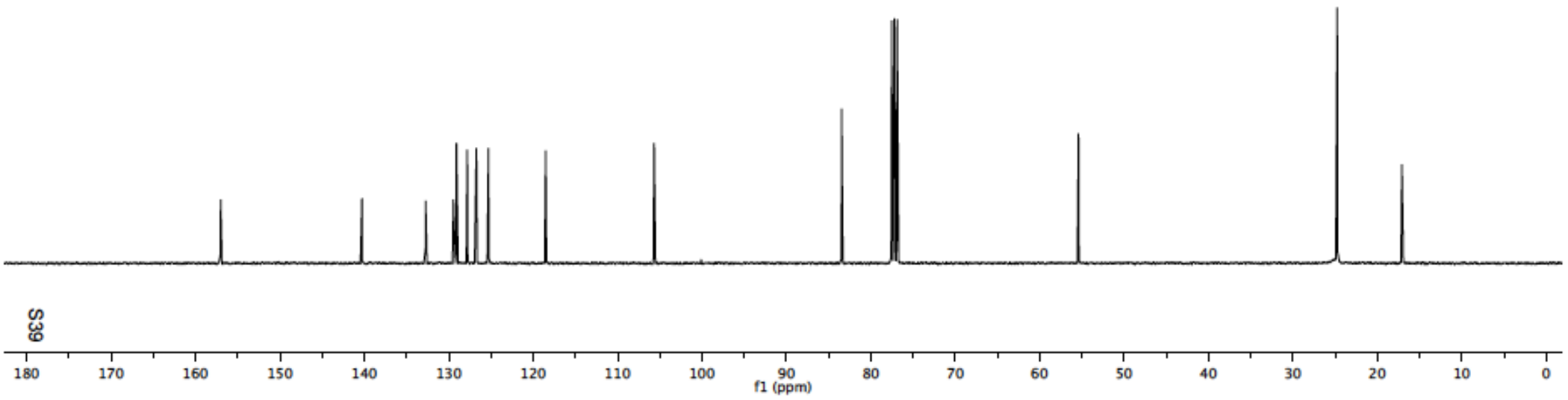
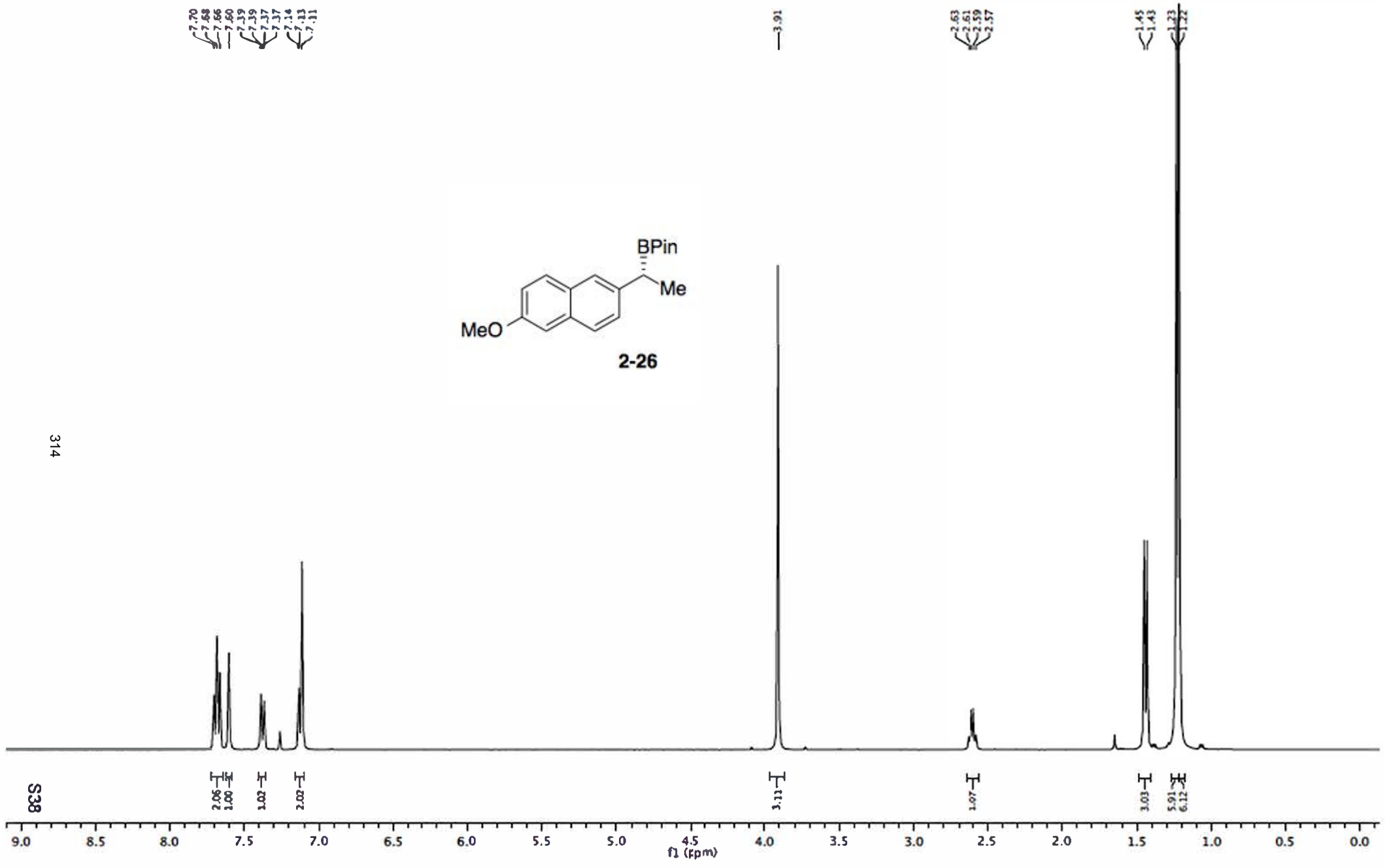
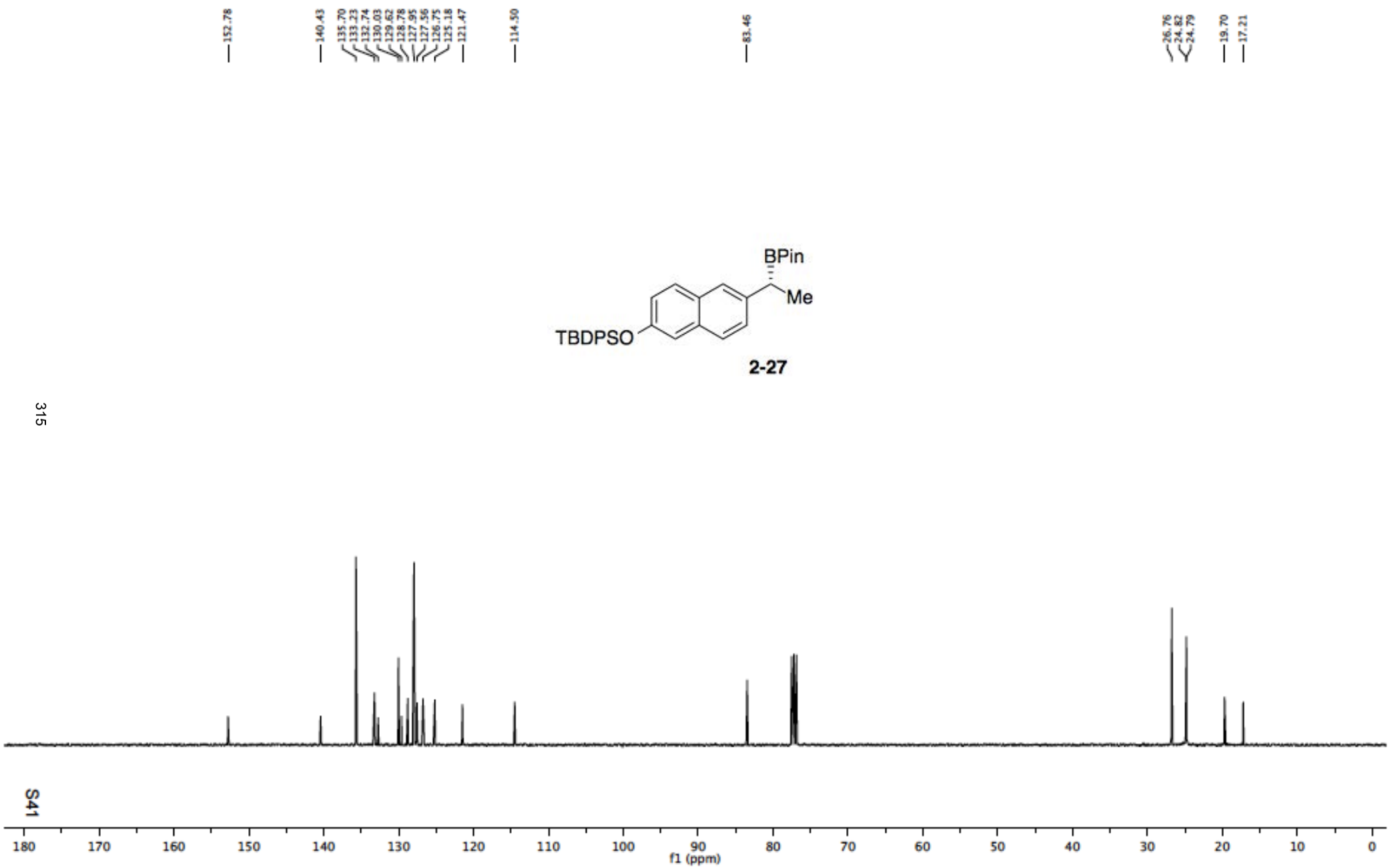
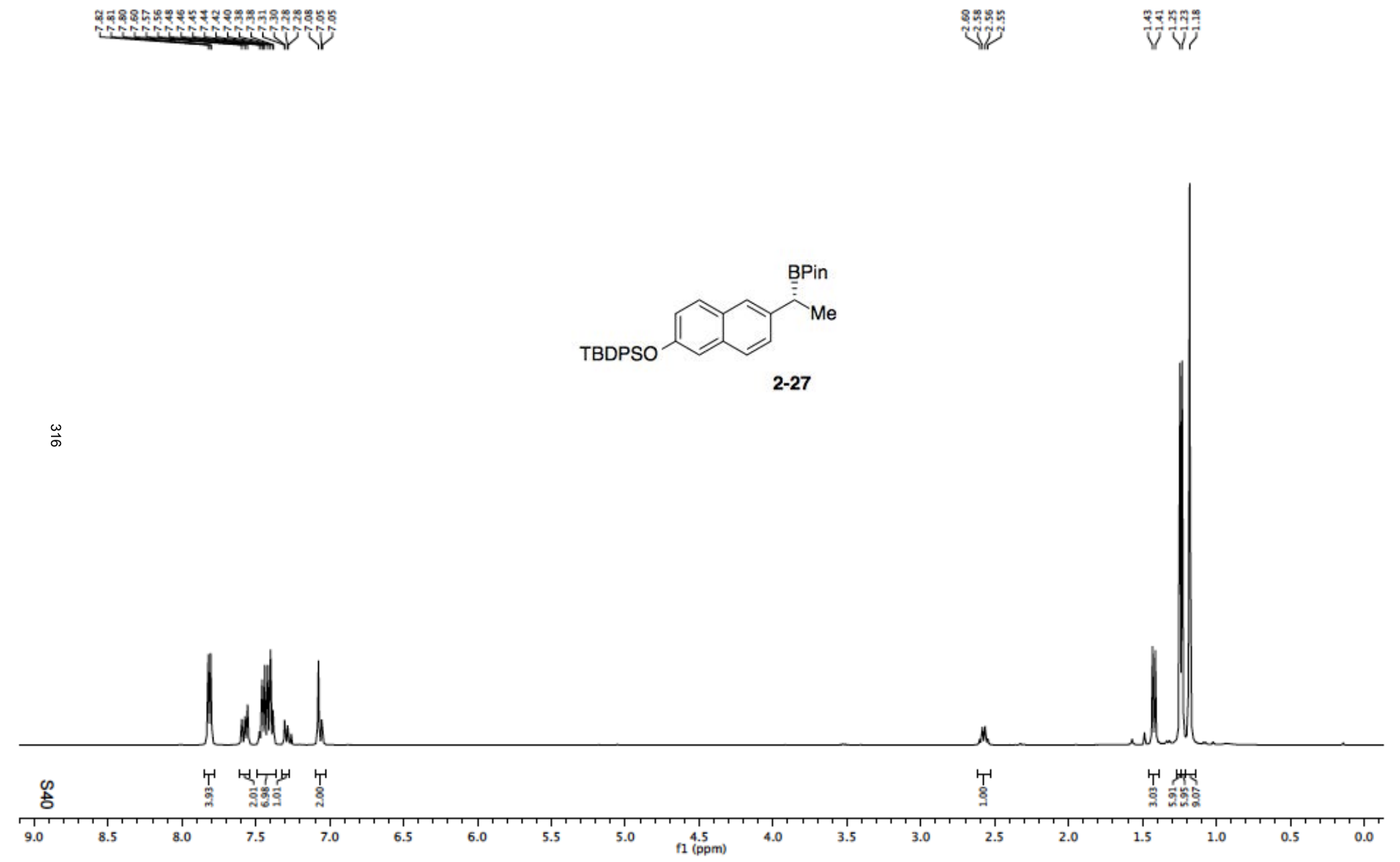
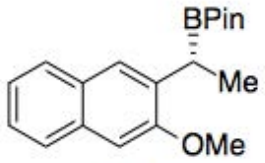



7.70
7.68
7.66
7.60
7.39
7.37
7.37
7.14
7.13
7.11
3.91
2.63
2.61
2.59
2.57
1.45
1.43
1.23
1.22
BPin
Me
MeO
2-26
2.06
1.00
1.02
2.02
3.11
1.07
3.03
5.91
6.12
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

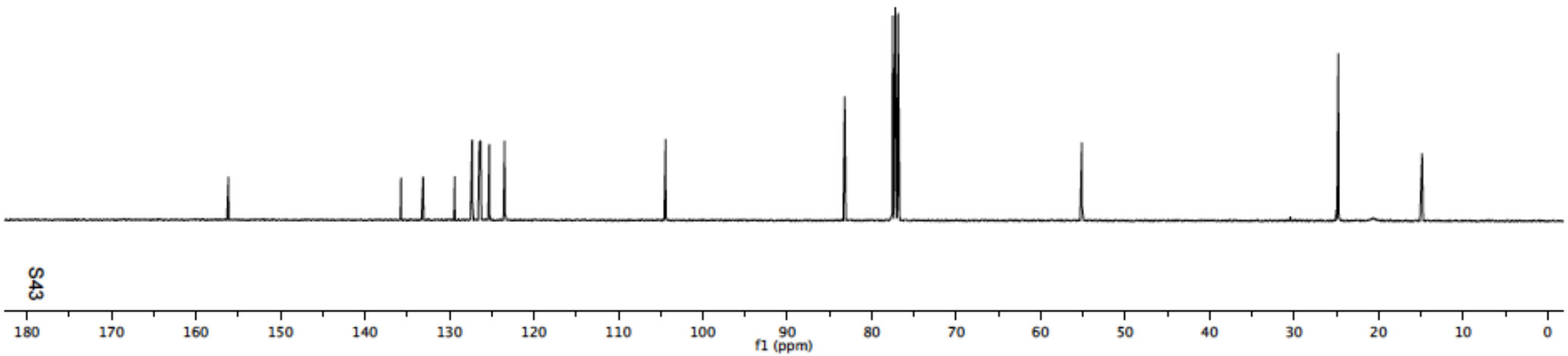

152.78
140.43
135.70
133.23
132.74
130.03
129.62
128.78
127.95
127.56
126.75
125.18
121.47
114.50
83.46
26.76
24.82
24.79
19.70
17.21
BPin
Me
TBDPSO
2-27
315
S41
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

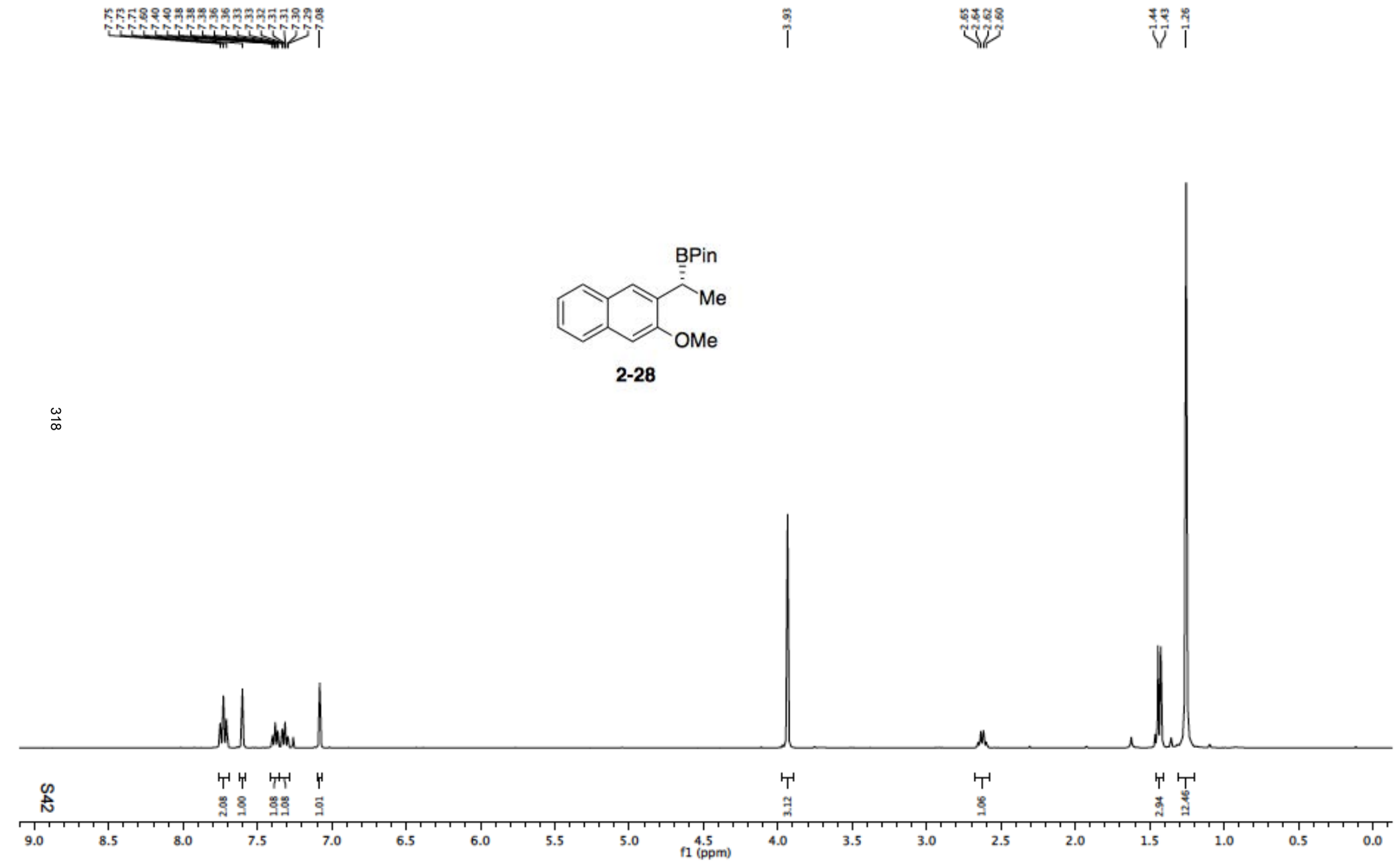

7.82
7.81
7.80
7.60
7.57
7.56
7.48
7.46
7.45
7.44
7.42
7.40
7.38
7.38
7.31
7.30
7.28
7.28
7.08
7.05
7.05
2.60
2.58
2.56
2.55
1.43
1.41
1.25
1.23
1.18
BPin
Me
TBDPSO
2-27
3.93
2.01
6.98
1.01
2.00
1.00
3.03
5.91
5.95
9.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

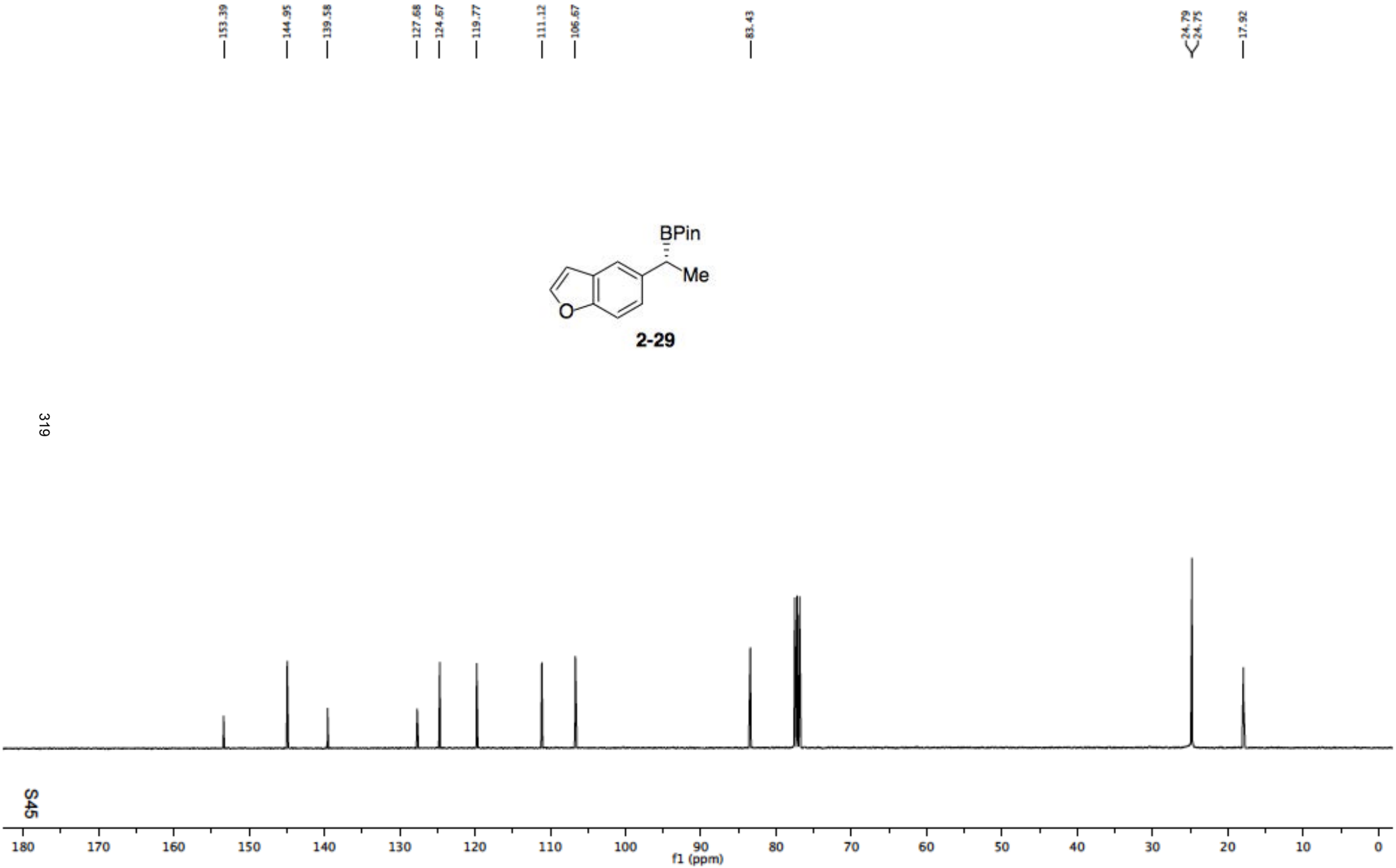

156.16
135.74
133.12
129.37
127.32
126.46
126.32
125.29
123.46
104.41
83.20
55.13
24.80
24.77
14.84

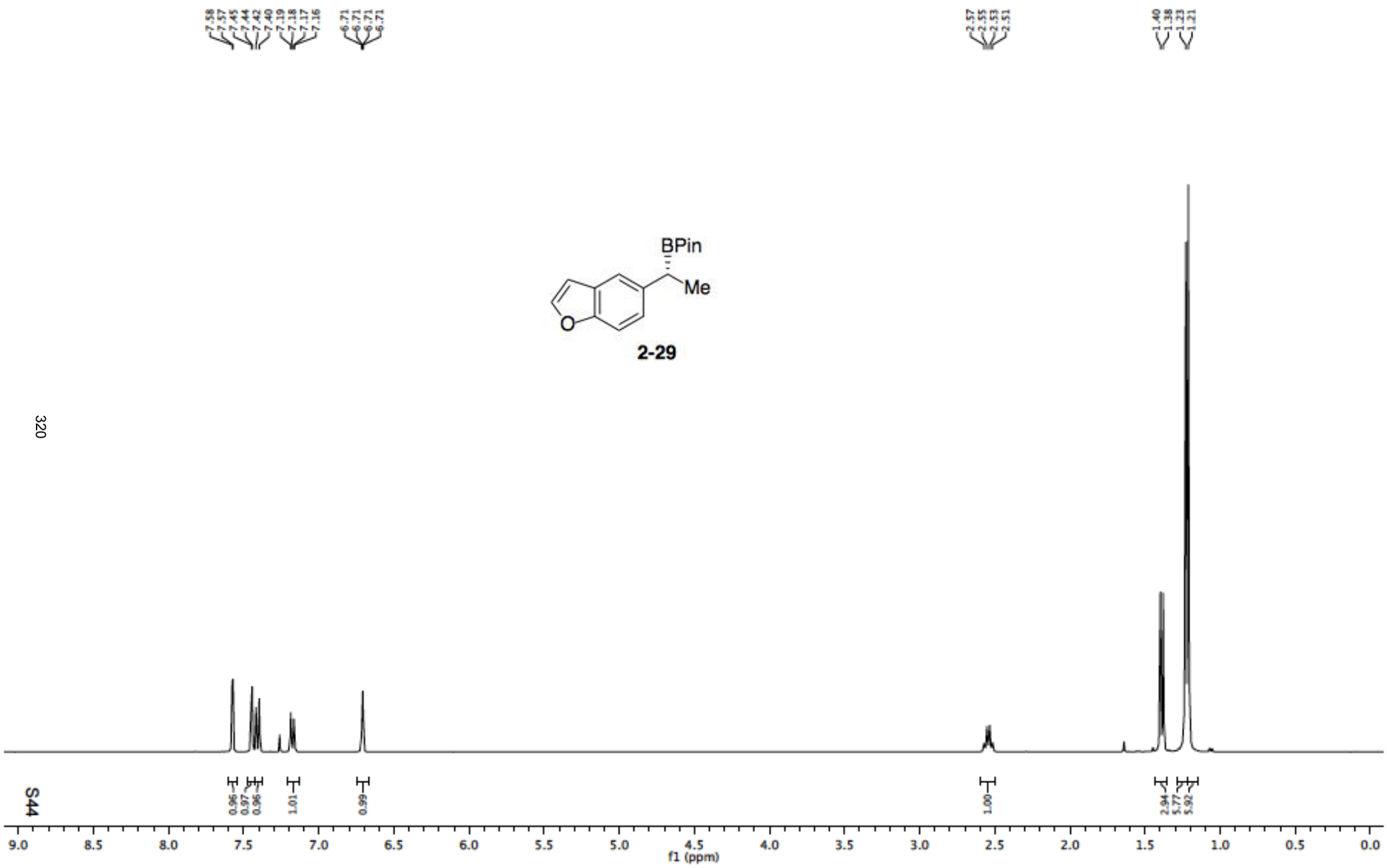

BPin
Me
OMe

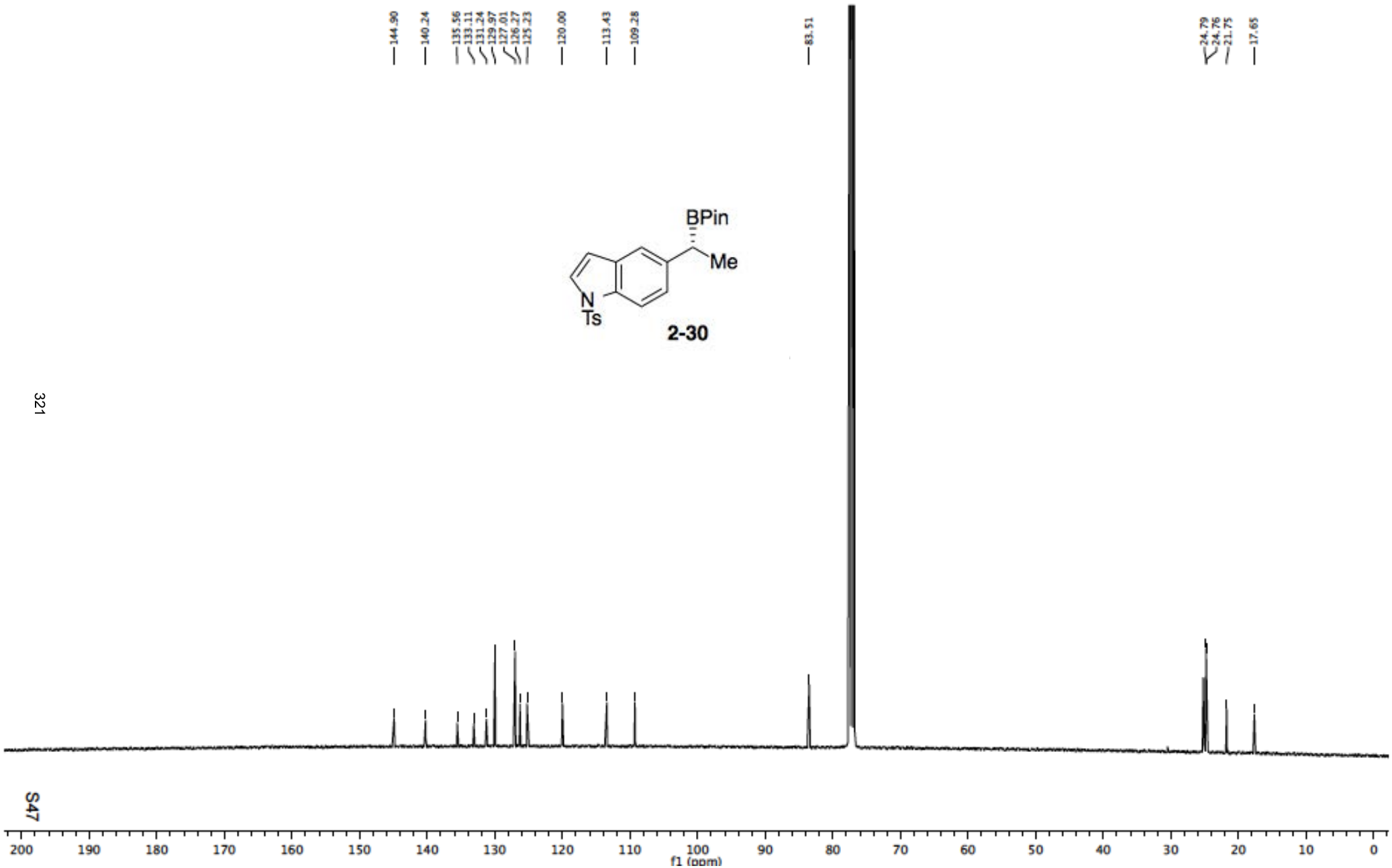
2-28

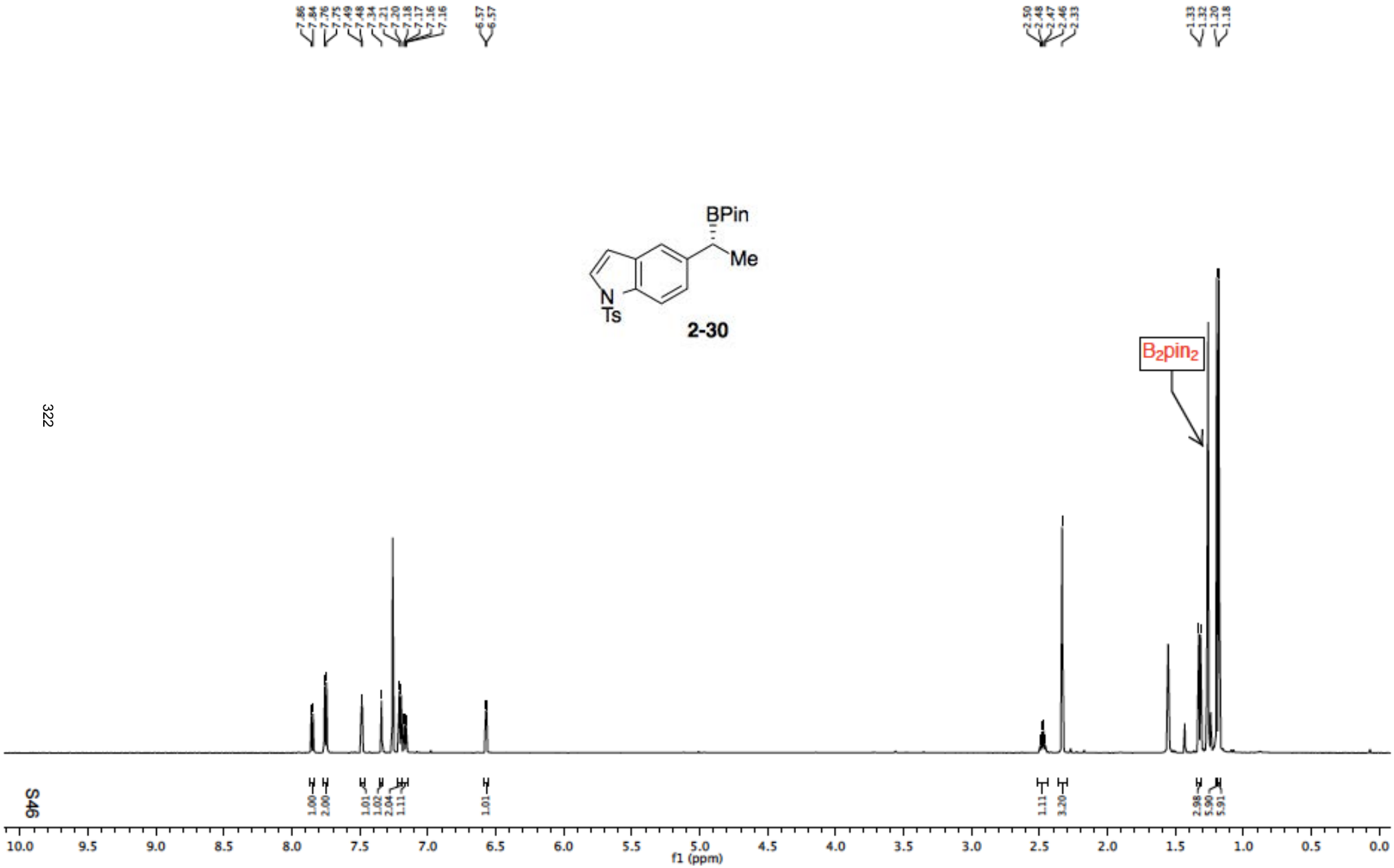

S43
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

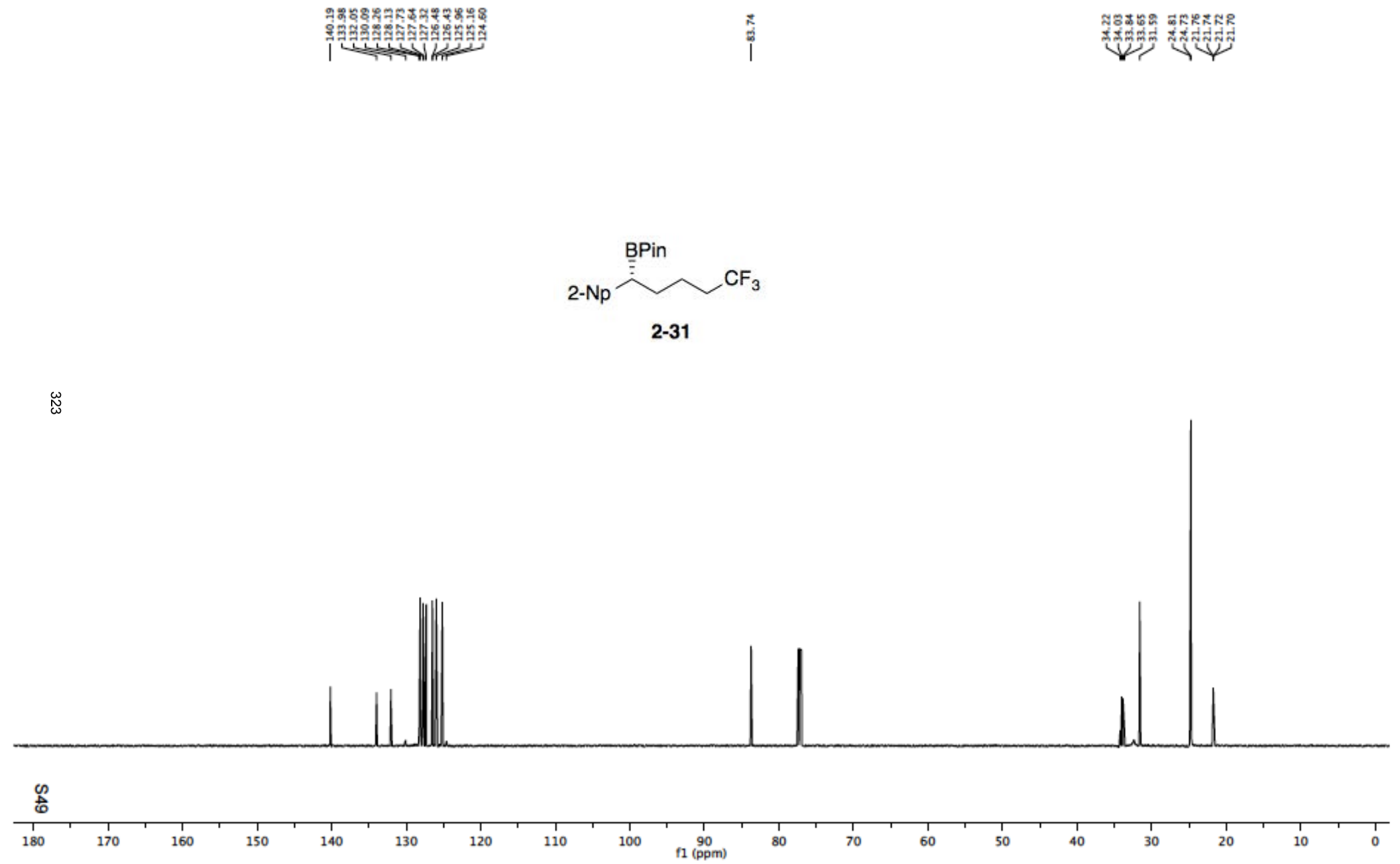

7.75
7.73
7.71
7.60
7.40
7.40
7.38
7.38
7.38
7.36
7.36
7.33
7.33
7.32
7.31
7.31
7.30
7.29
7.08
3.93
2.65
2.64
2.62
2.60
1.44
1.43
1.26
BPin
Me
OMe
2-28
2.08
1.00
1.08
1.08
1.01
3.12
1.06
2.94
12.46
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

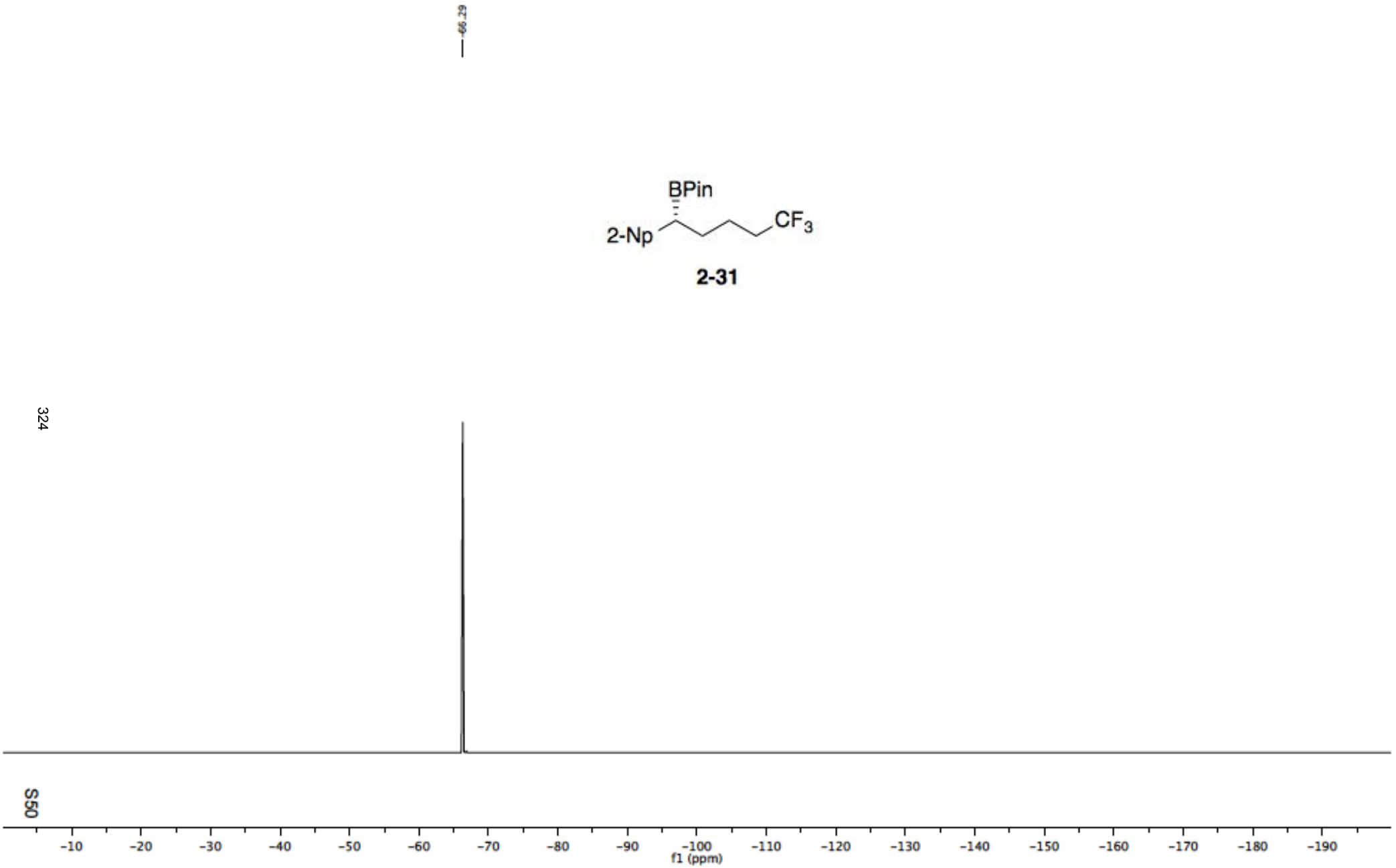

153.39
144.95
139.58
127.68
124.67
119.77
111.12
106.67
83.43
24.79
24.75
17.92
BPin
Me
O
2-29
319
S45
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

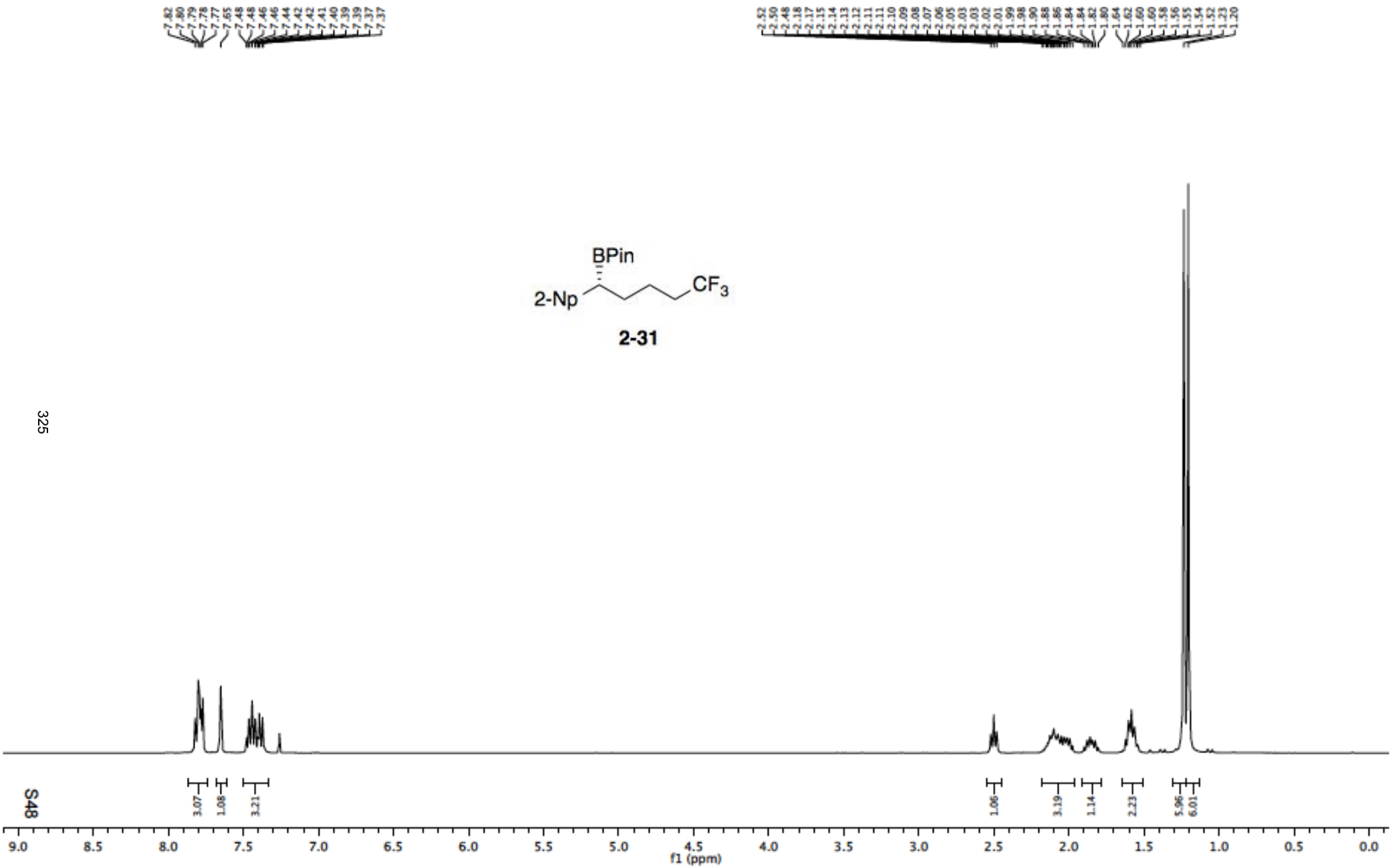

7.58
7.57
7.45
7.44
7.42
7.40
7.19
7.18
7.17
7.16
6.71
6.71
6.71
6.71
2.57
2.55
2.53
2.51
1.40
1.38
1.23
1.21
BPin
Me
O
2-29
0.96
0.97
0.96
1.01
0.99
1.00
2.94
5.77
5.92
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

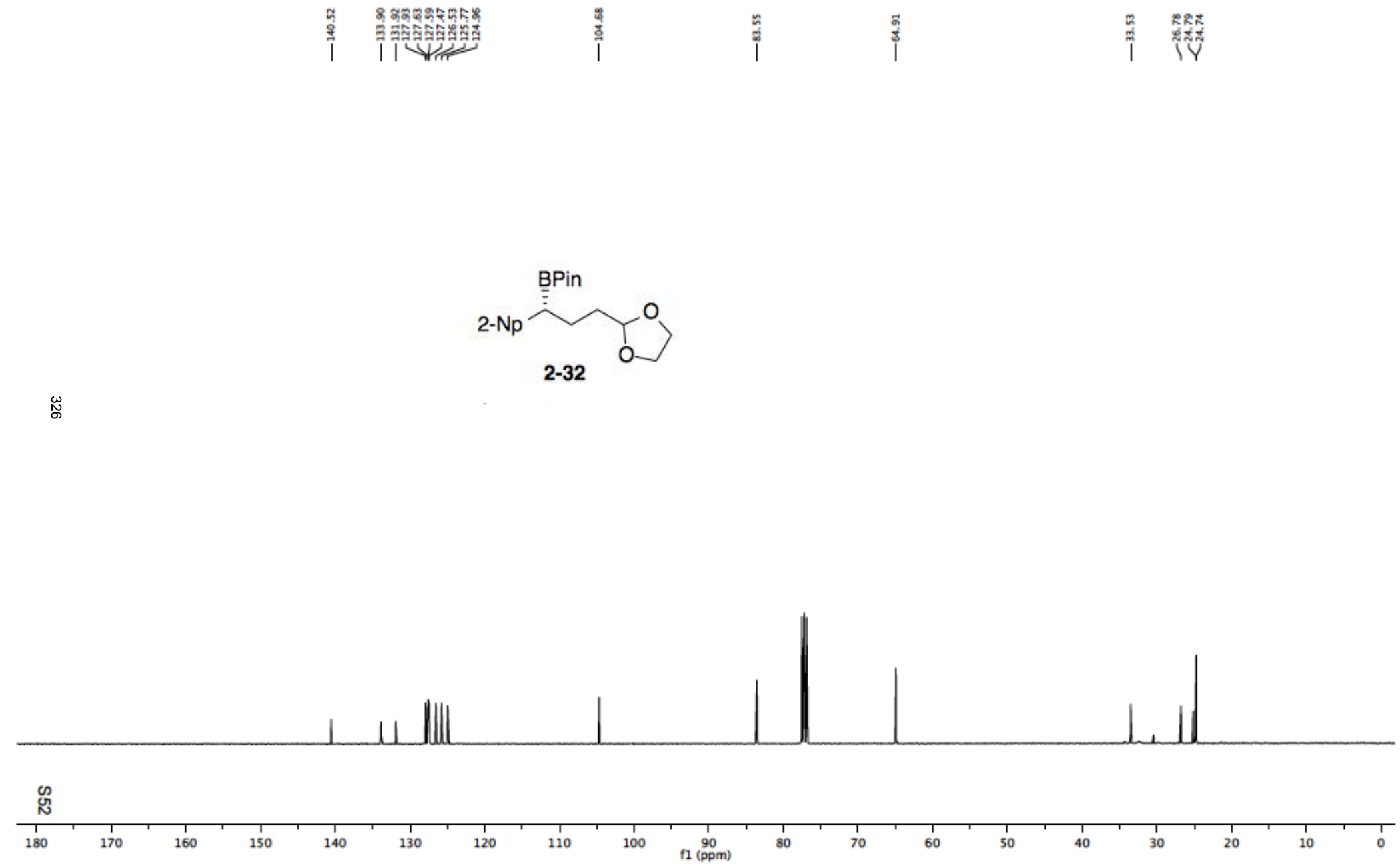

144.90
140.24
135.56
133.11
131.24
129.97
127.01
126.27
125.23
120.00
113.43
109.28
83.51
24.79
24.76
21.75
17.65
BPin
Me
N
Ts
2-30
321
S47
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

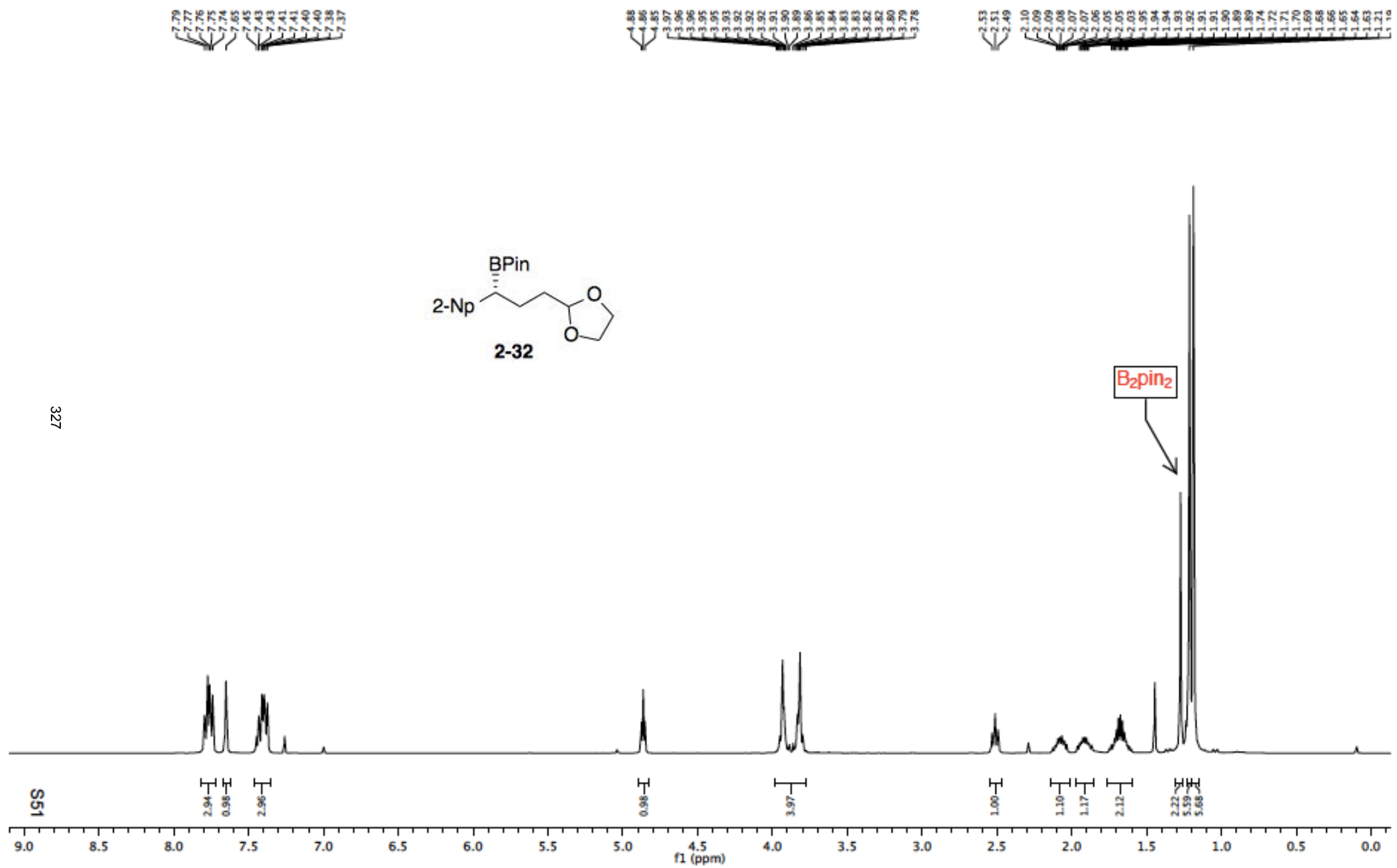

7.86
7.84
7.76
7.75
7.49
7.48
7.34
7.21
7.20
7.18
7.17
7.16
7.16
6.57
6.57
2.50
2.48
2.47
2.46
2.33
1.33
1.32
1.20
1.18
BPin
Me
N
Ts
2-30
B2pin2
1.00
2.00
1.01
1.02
2.04
1.11
1.01
1.11
3.20
2.98
5.90
5.91
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

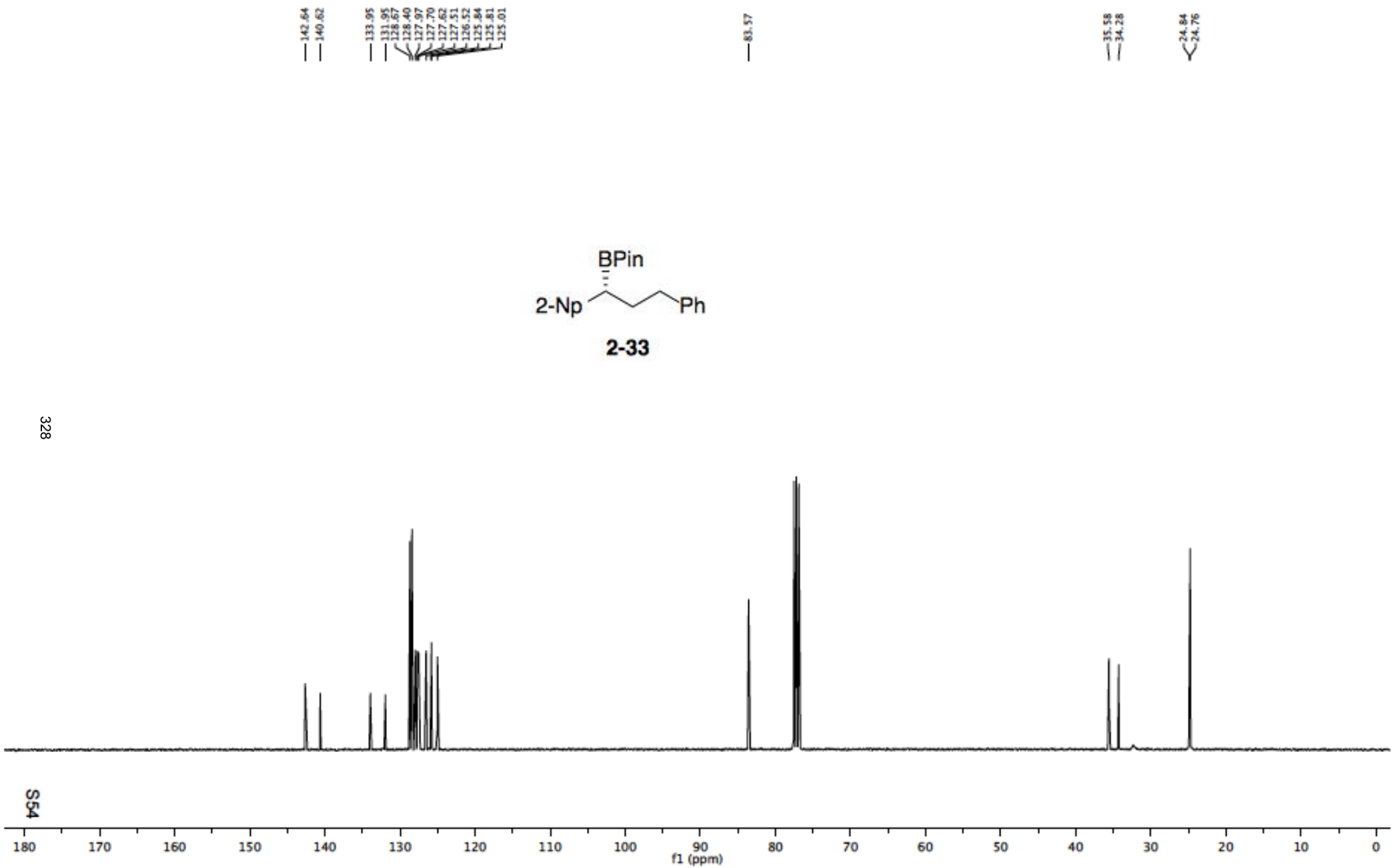

140.19
133.98
132.05
130.09
128.26
128.13
127.73
127.64
127.32
126.48
126.43
125.96
125.16
124.60
83.74
34.22
34.03
33.84
33.65
31.59
24.81
24.73
21.76
21.74
21.72
21.70
BPin
2-Np
CF3
2-31
f1 (ppm)

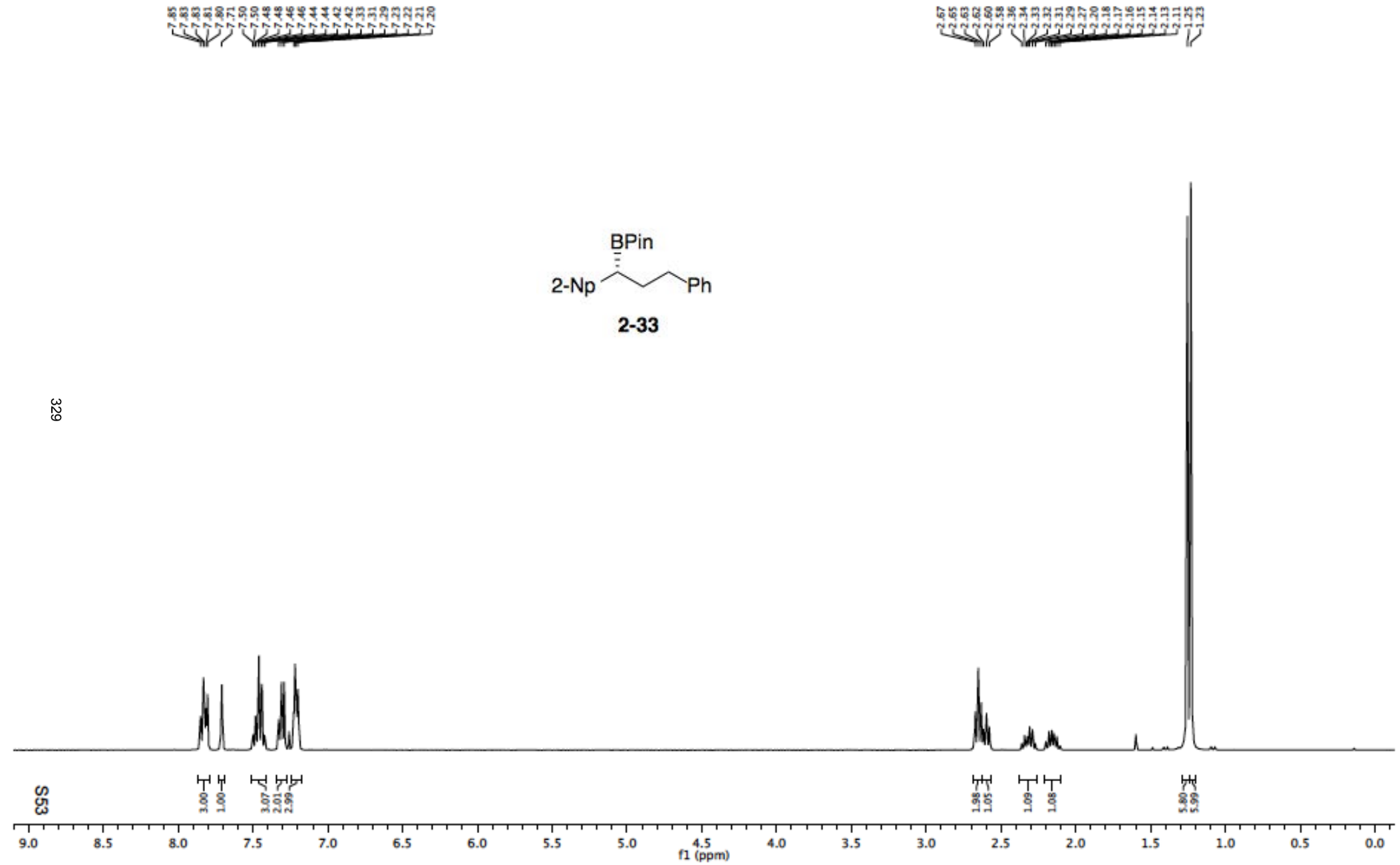

-66.29
BPin
2-Np
CF3
2-31
324
S50
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

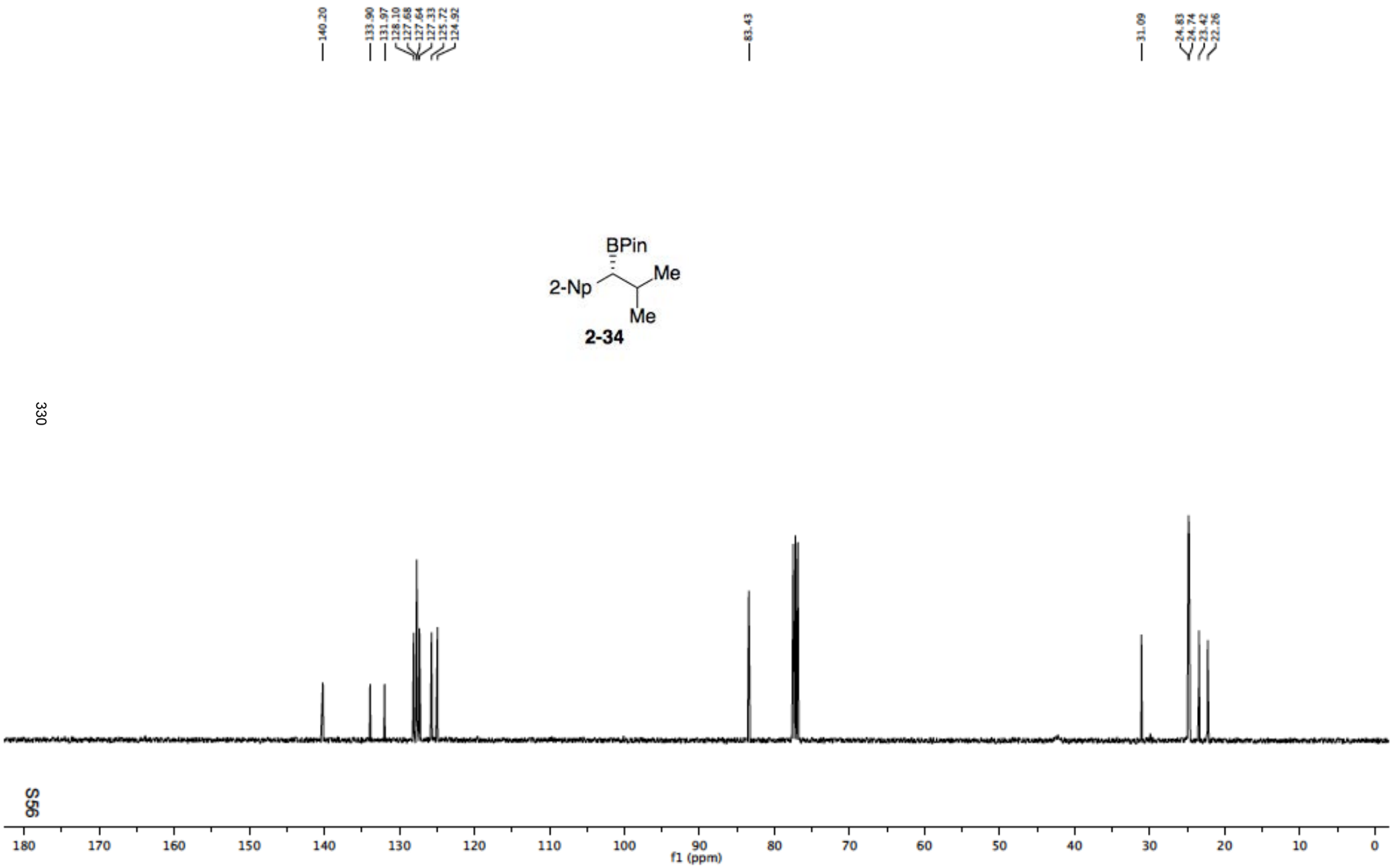

7.82
7.80
7.79
7.78
7.77
7.65
7.48
7.48
7.46
7.46
7.44
7.42
7.42
7.41
7.40
7.39
7.39
7.37
7.37
2.52
2.50
2.48
2.18
2.17
2.15
2.14
2.13
2.12
2.11
2.11
2.10
2.09
2.08
2.07
2.06
2.05
2.03
2.03
2.02
2.01
1.99
1.98
1.90
1.88
1.86
1.84
1.84
1.82
1.80
1.64
1.62
1.60
1.60
1.58
1.56
1.55
1.54
1.52
1.23
1.20
BPin
2-Np
CF3
2-31
3.07
1.08
3.21
1.06
3.19
1.14
2.23
5.96
6.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

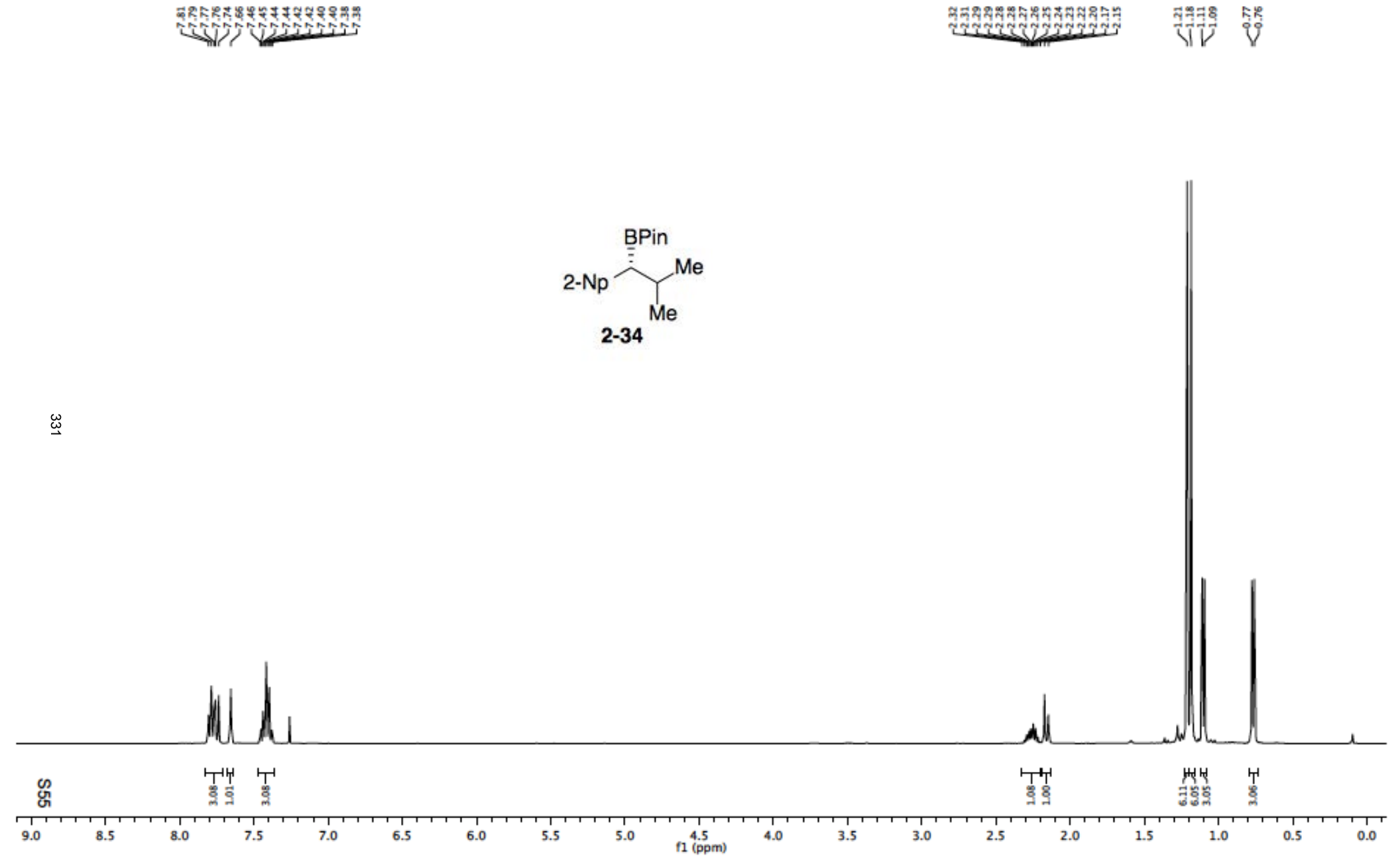

140.52
133.90
131.92
127.93
127.63
127.59
127.47
126.53
125.77
124.96
104.68
83.55
64.91
33.53
26.78
24.79
24.74
BPin
2-Np
O
O
2-32
S52
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

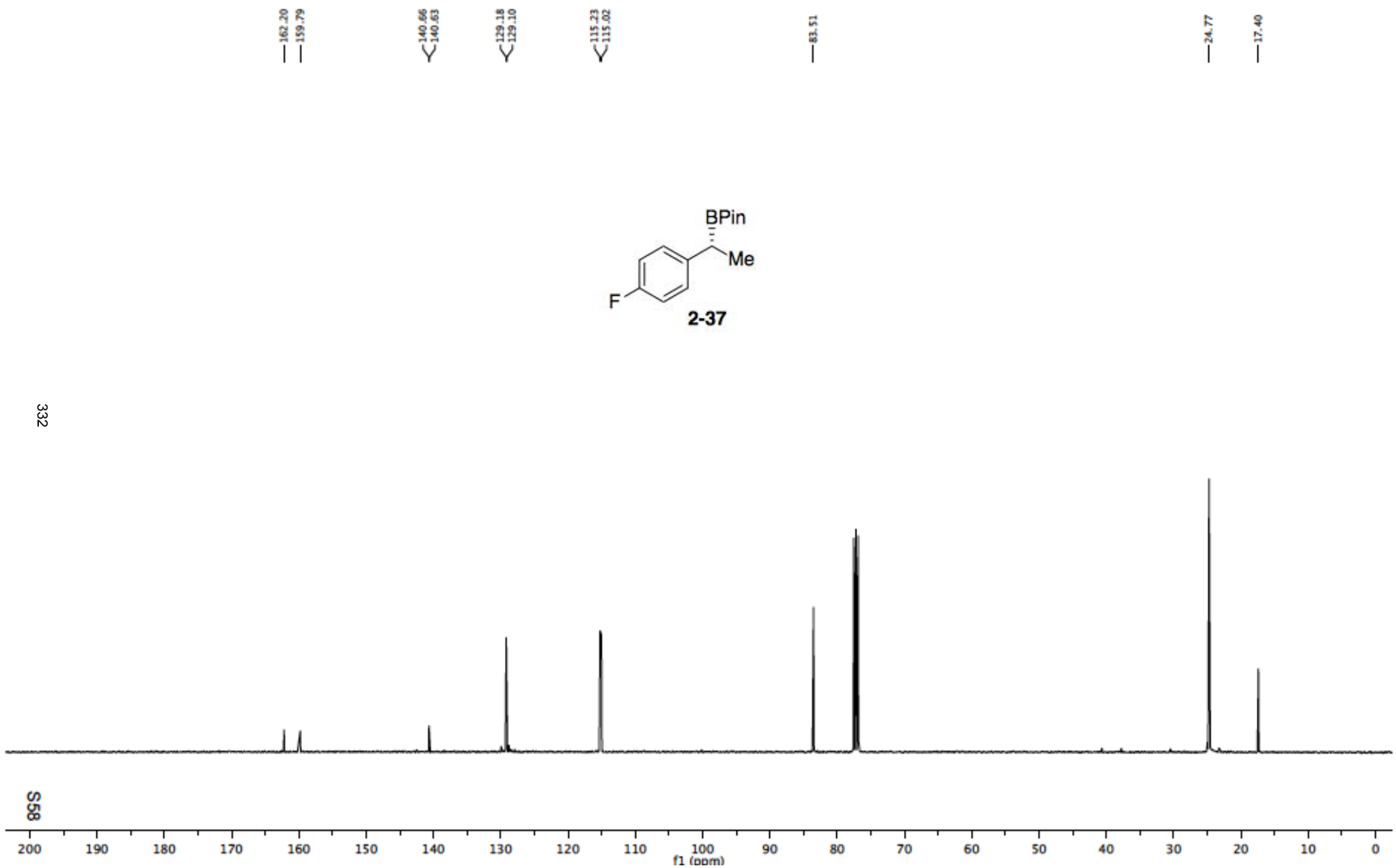

BPin
2-Np
O
O
2-32
B2pin2
S51
f1 (ppm)

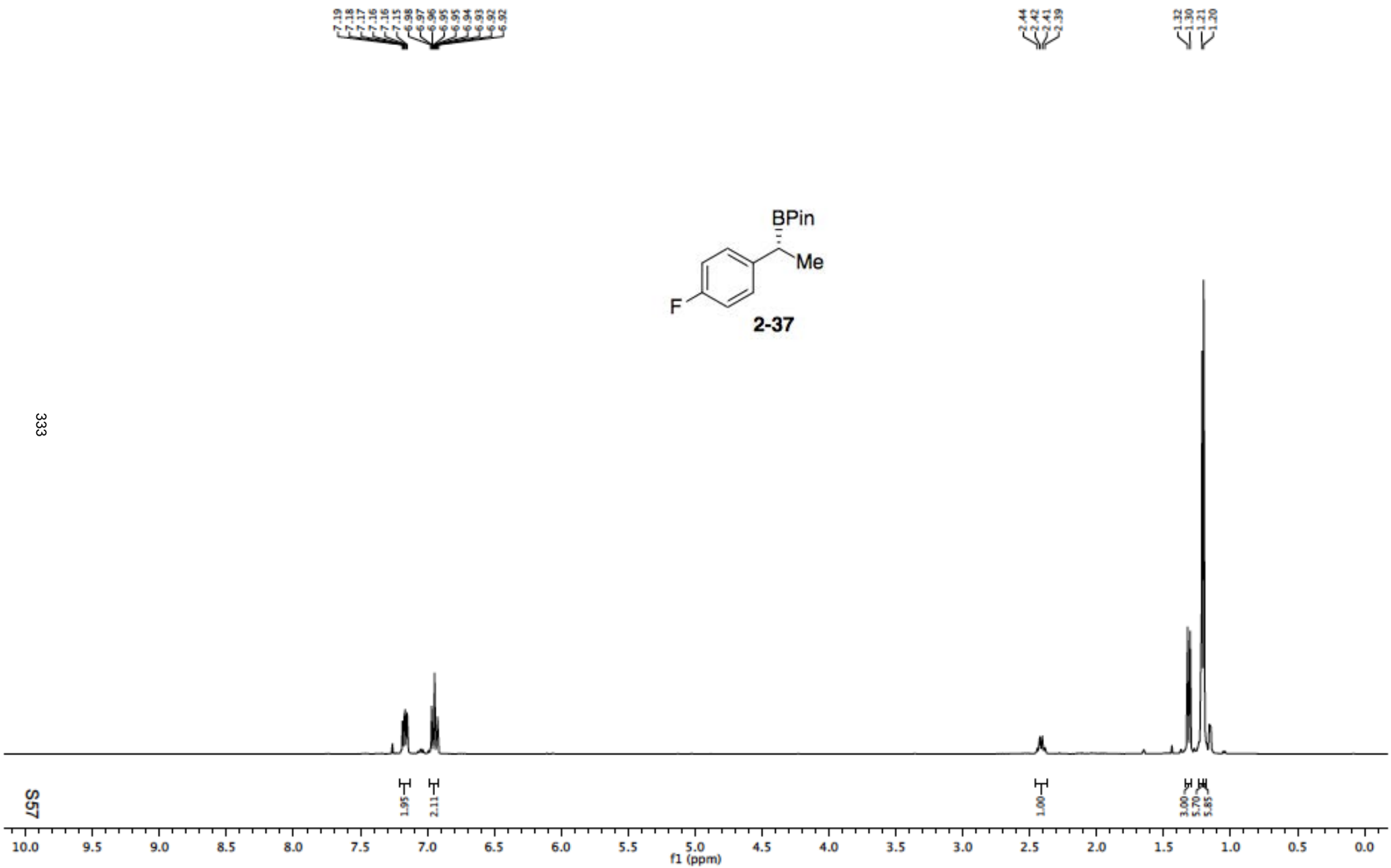

142.64
140.62
133.95
131.95
128.67
128.40
127.97
127.70
127.62
127.51
126.52
125.84
125.81
125.01
83.57
35.58
34.28
24.84
24.76
BPin
2-Np
Ph
2-33
328
S54
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.85
7.83
7.83
7.81
7.80
7.71
7.50
7.50
7.48
7.48
7.46
7.46
7.44
7.44
7.42
7.42
7.33
7.31
7.29
7.23
7.22
7.21
7.20
2.67
2.65
2.63
2.62
2.60
2.58
2.36
2.34
2.33
2.32
2.31
2.29
2.27
2.20
2.18
2.17
2.16
2.15
2.14
2.13
2.11
1.25
1.23
BPin
2-Np
Ph
2-33
329
S53
3.00
1.00
3.07
2.01
2.99
1.98
1.05
1.09
1.08
5.80
5.99
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


140.20
133.90
131.97
128.10
127.68
127.64
127.33
125.72
124.92
83.43
31.09
24.83
24.74
23.42
22.26
BPin
2-Np
Me
Me
2-34
330
S56
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.81
7.79
7.77
7.76
7.74
7.66
7.46
7.45
7.44
7.44
7.42
7.42
7.40
7.40
7.38
7.38
2.32
2.31
2.29
2.29
2.28
2.28
2.27
2.26
2.25
2.24
2.23
2.22
2.20
2.17
2.15
1.21
1.18
1.11
1.09
0.77
0.76
BPin
2-Np
Me
Me
2-34
SSS
3.08
1.01
3.08
1.08
1.00
6.11
6.05
3.05
3.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


162.20
159.79
140.66
140.63
129.18
129.10
115.23
115.02
83.51
24.77
17.40
BPin
Me
F
2-37
332
SS8
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.18
7.17
7.16
7.16
7.15
6.98
6.97
6.96
6.95
6.95
6.94
6.93
6.92
6.92
2.44
2.42
2.41
2.39
1.32
1.30
1.21
1.20
BPin
Me
F
2-37
S57
1.95
2.11
1.00
3.00
5.70
5.65
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.5
2.0
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1.0
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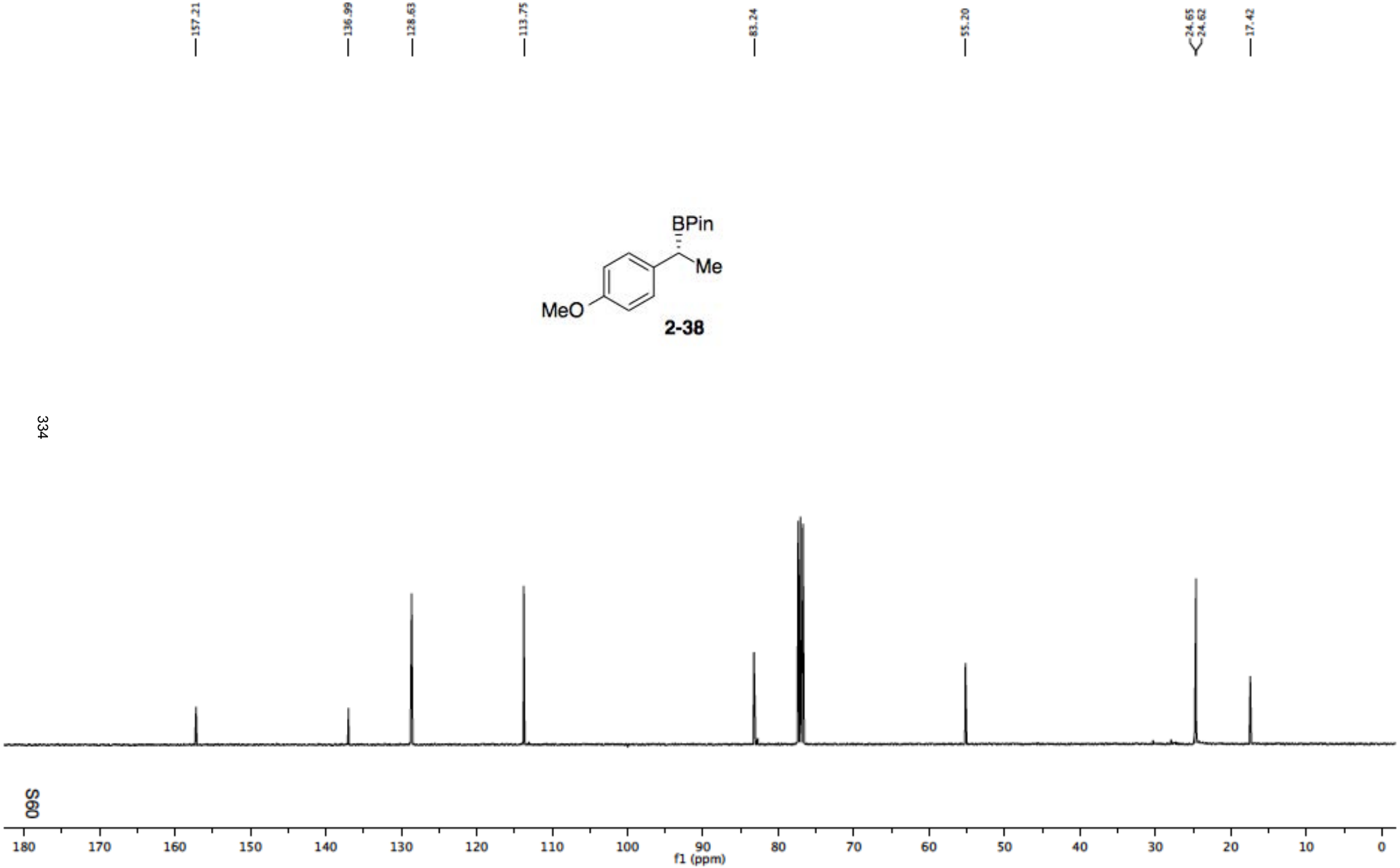
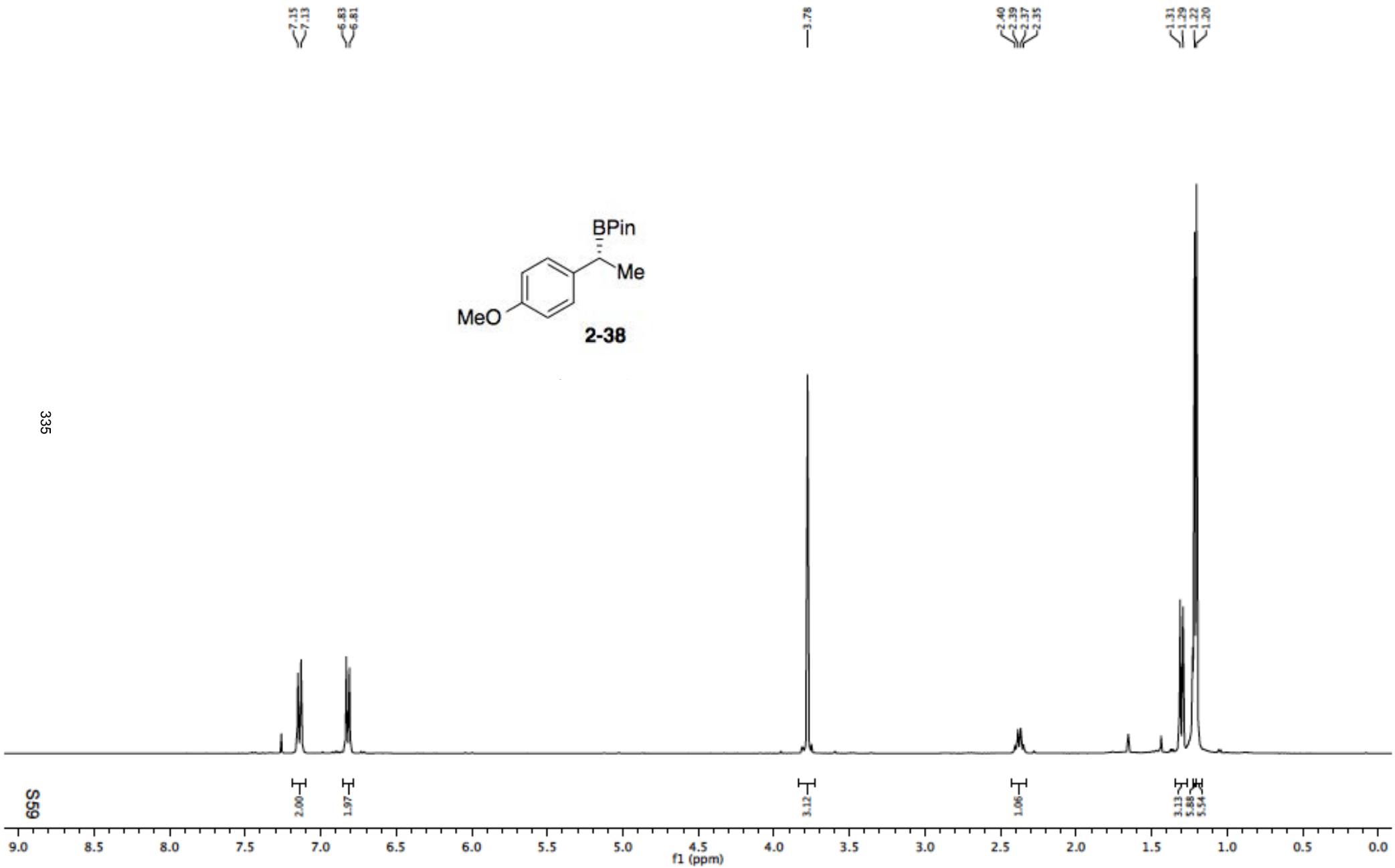
f1 (ppm)


157.21
136.99
128.63
113.75
83.24
55.20
24.65
24.62
17.42
BPin
Me
MeO
2-38
S60
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.15
7.13
6.83
6.81
3.78
2.40
2.39
2.37
2.35
1.31
1.29
1.22
1.20
BPin
Me
MeO
2-38
S59
2.00
1.97
3.12
1.06
3.13
5.88
5.94
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

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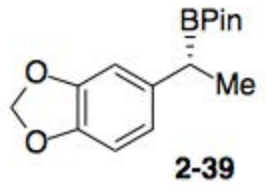
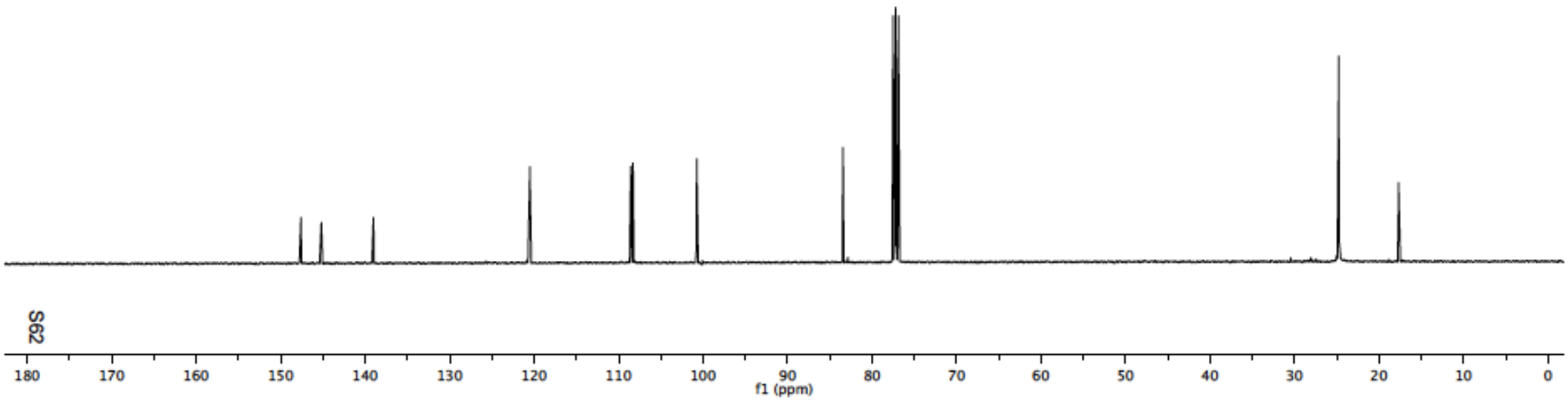
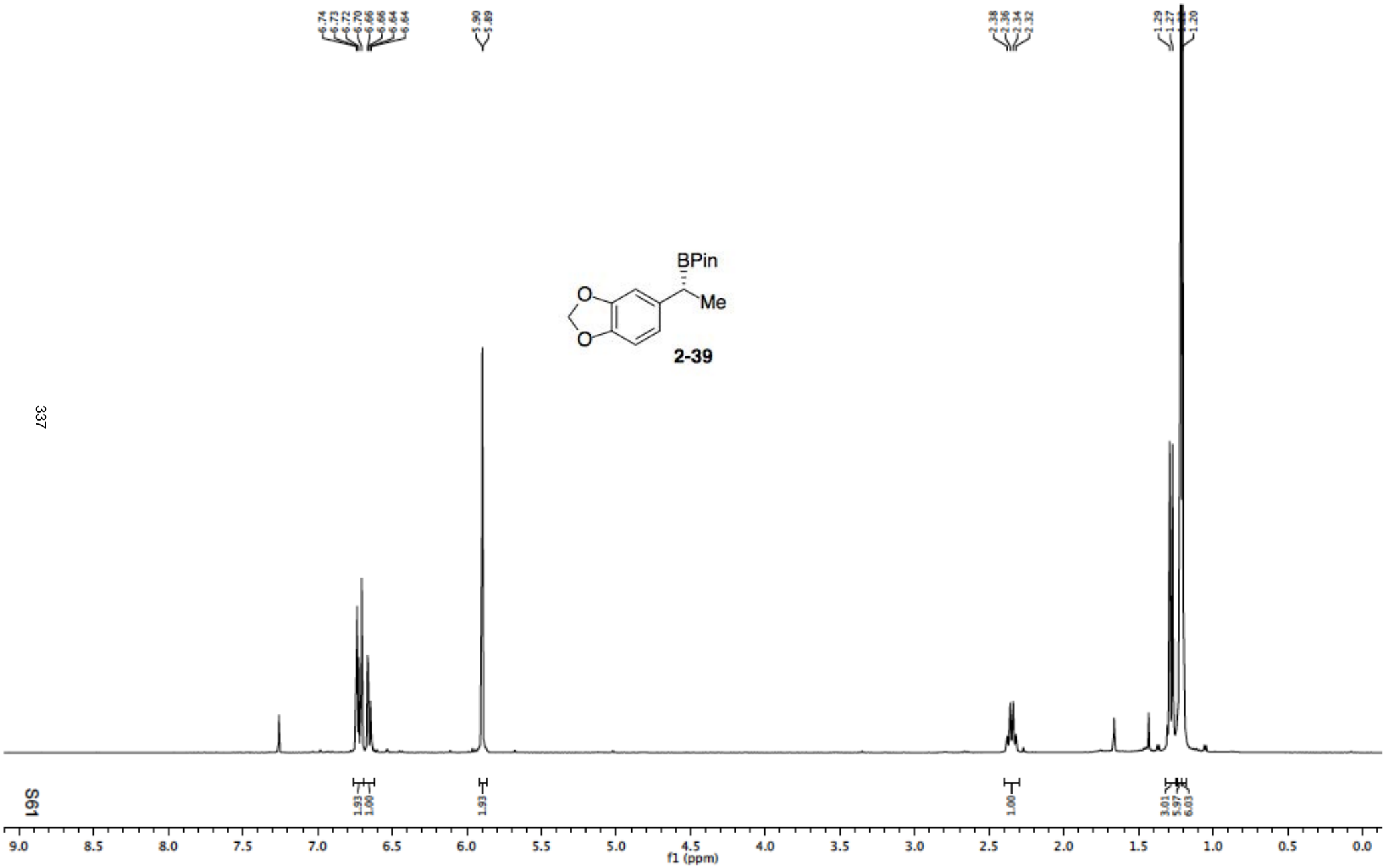
145.19
139.03
120.53
108.56
108.31
100.77
83.45
24.79
24.75
17.68



2-39

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6.70
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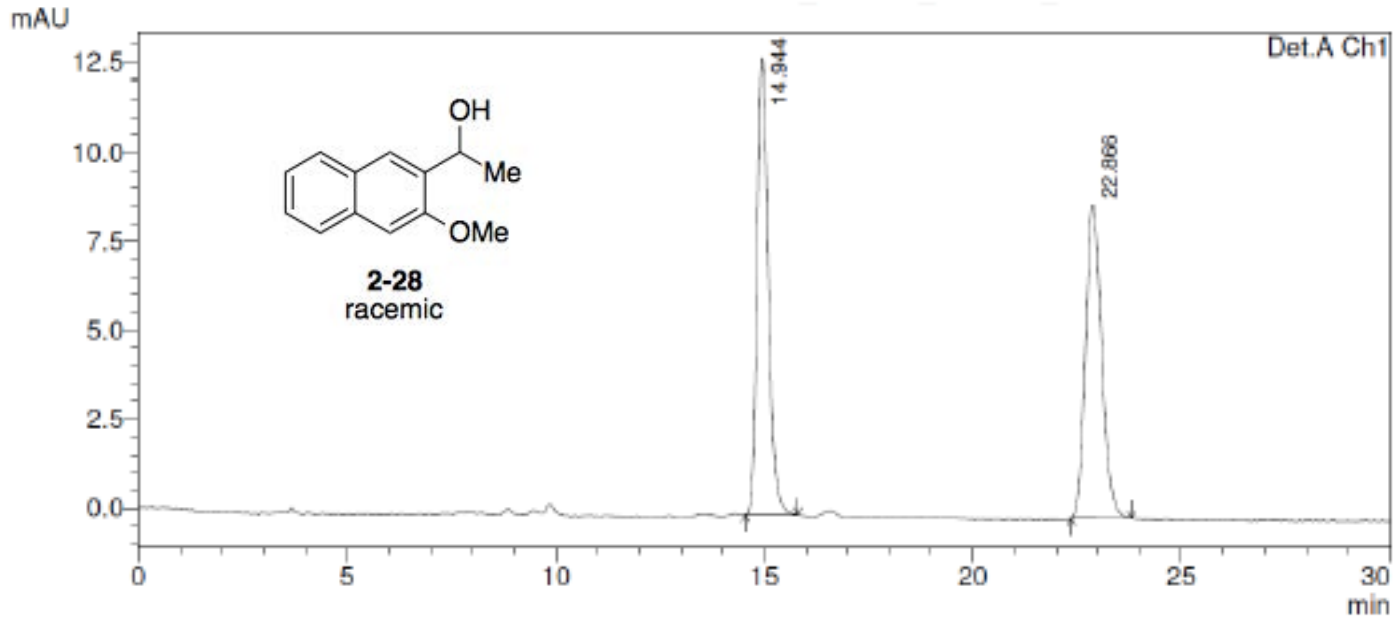
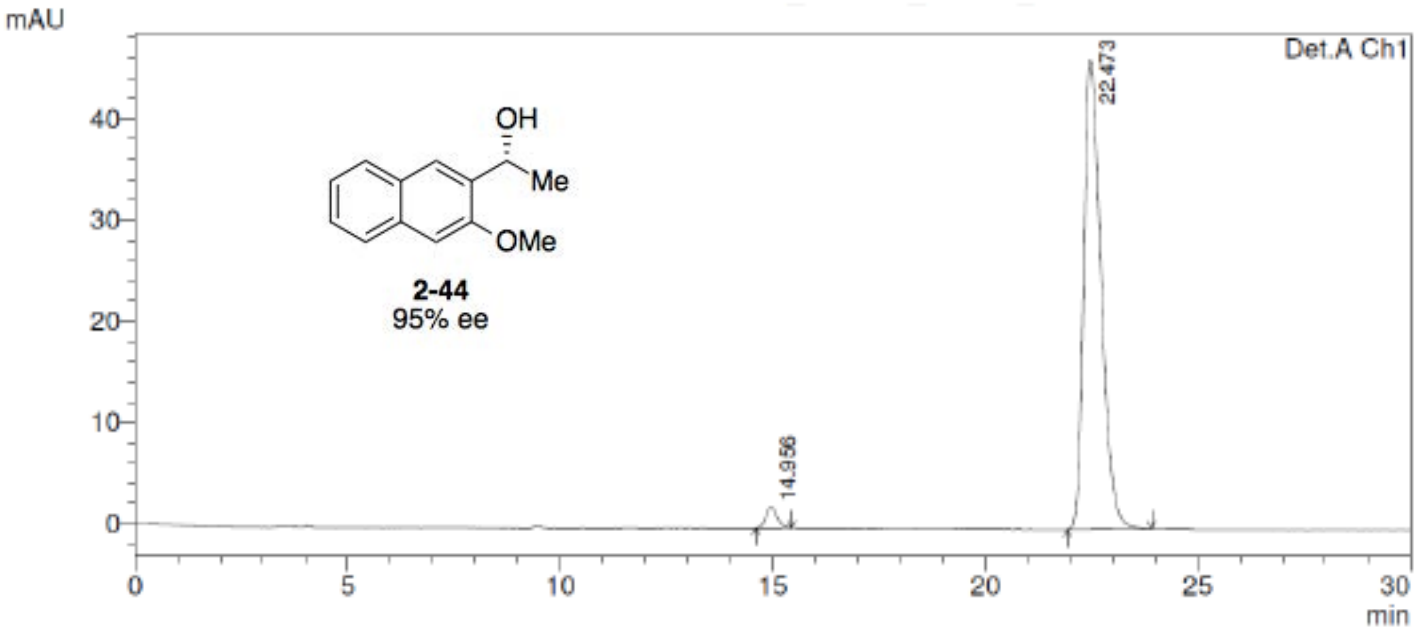
6.64
6.64
5.90
5.89
2.38
2.36
2.34
2.32
1.29
1.27
1.20
BPin
Me
O
O
2-39
S91
1.93
1.00
1.93
1.00
3.01
5.97
6.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

Compound 3e, racemic (254 nm)



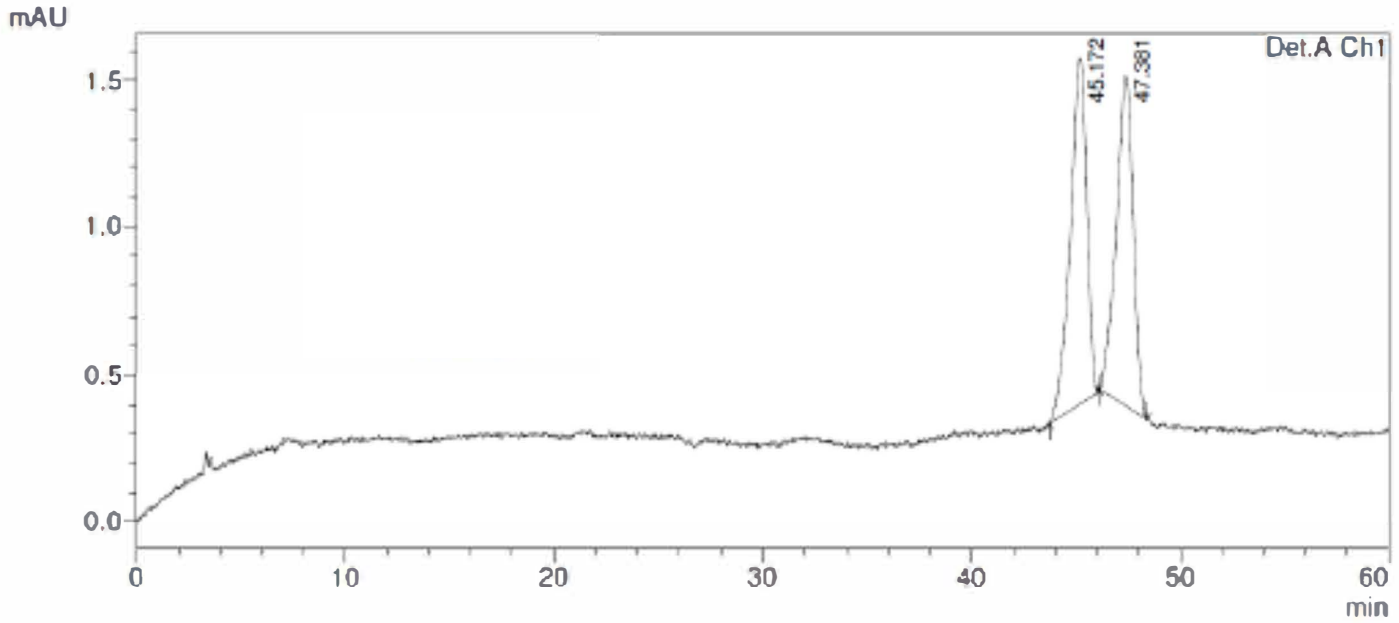
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.944	239370	12773	50.150	59.107
2	22.866	237935	8837	49.850	40.893
Total		477305	21610	100.000	100.000

Compound 3e, 95% ee (254 nm)



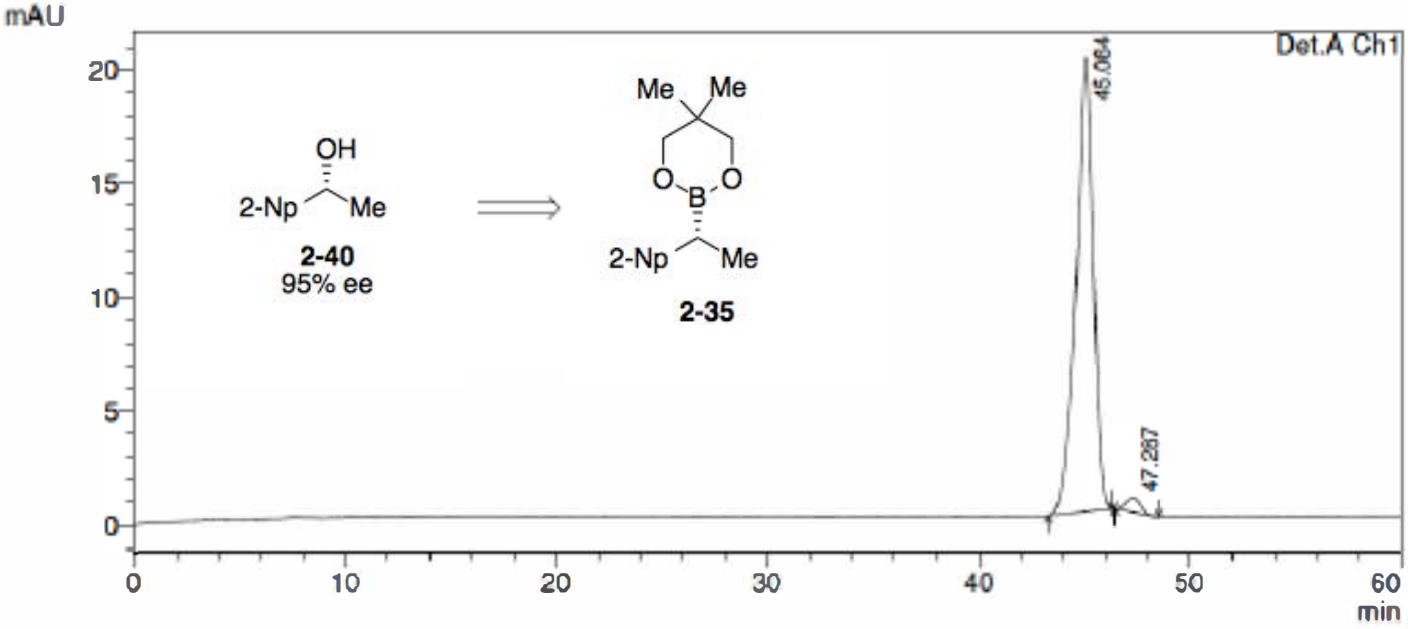
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.956	35963	1982	2.675	4.104
2	22.473	1308675	46315	97.325	95.896
Total		1344638	48297	100.000	100.000

Compound 2-40, racemic (254 nm)



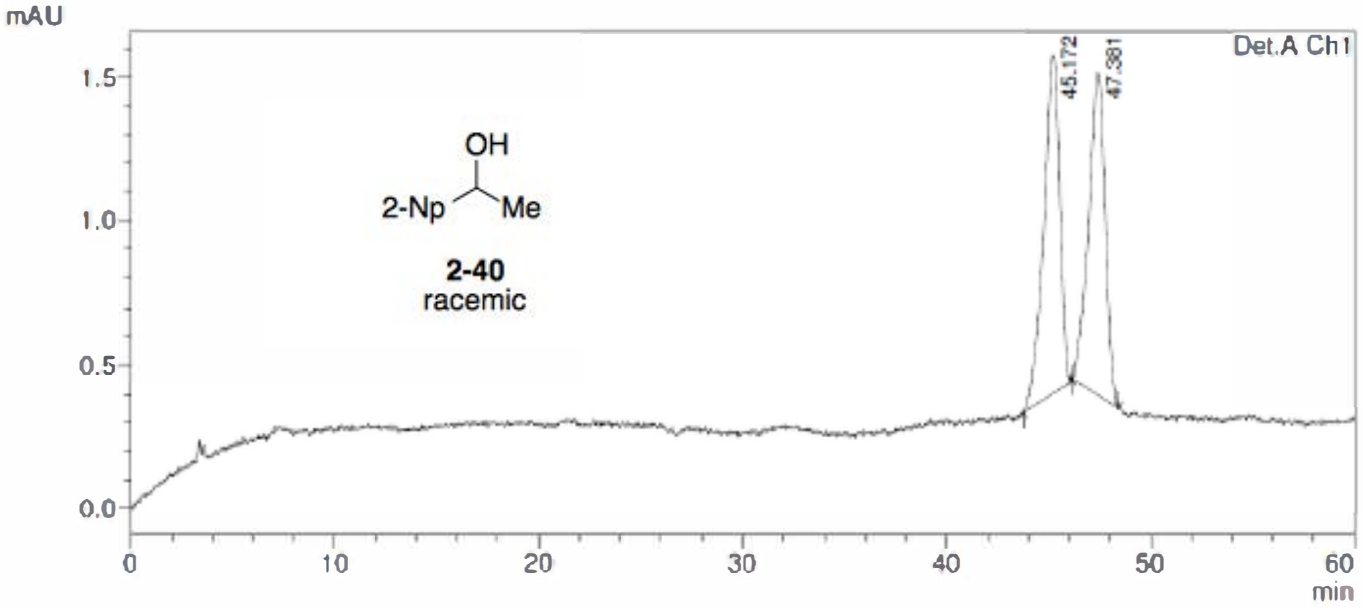
Peak#	Ret. Time	Area	Height	Area %	Height %
1	45.172	64627	1174	50.417	51.245
2	47.381	63558	1117	49.583	48.755
Total		128185	2292	100.000	100.000

Compound 2-40, 95% ee (254 nm)



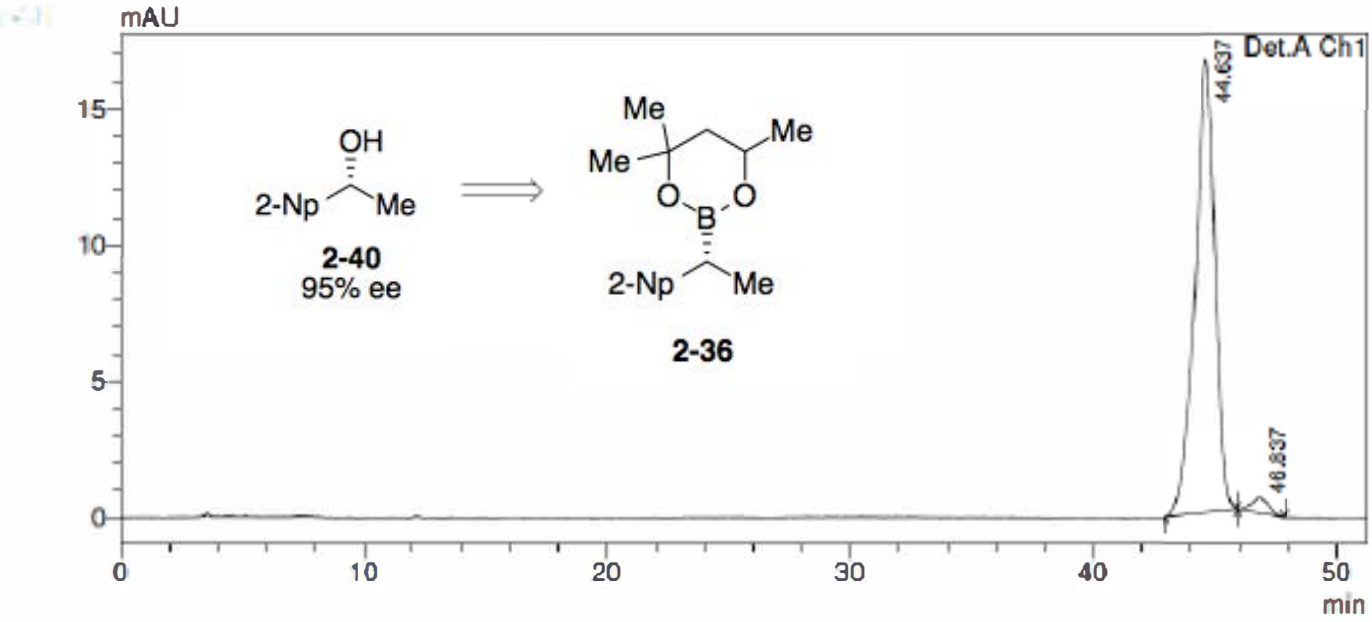
Peak#	Ret. Time	Area	Height	Area %	Height %
1	45.064	1159668	20005	97.571	97.019
2	47.287	28864	615	2.429	2.981
Total		1188532	20620	100.000	100.000

Compound 2-40, racemic (254 nm)



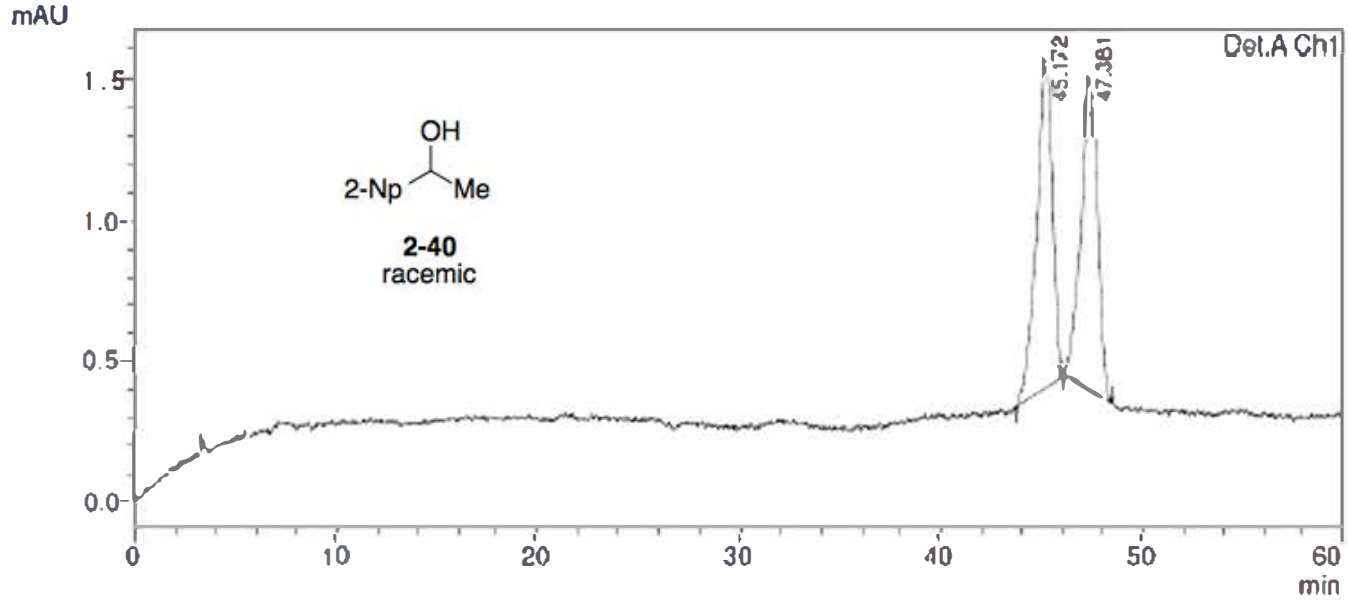
Peak#	Ret. Time	Area	Height	Area %	Height %
1	45.172	64627	1174	50.417	51.245
2	47.381	63558	1117	49.583	48.755
Total		128185	2292	100.000	100.000

Compound2-40,,95% ee (254nm)



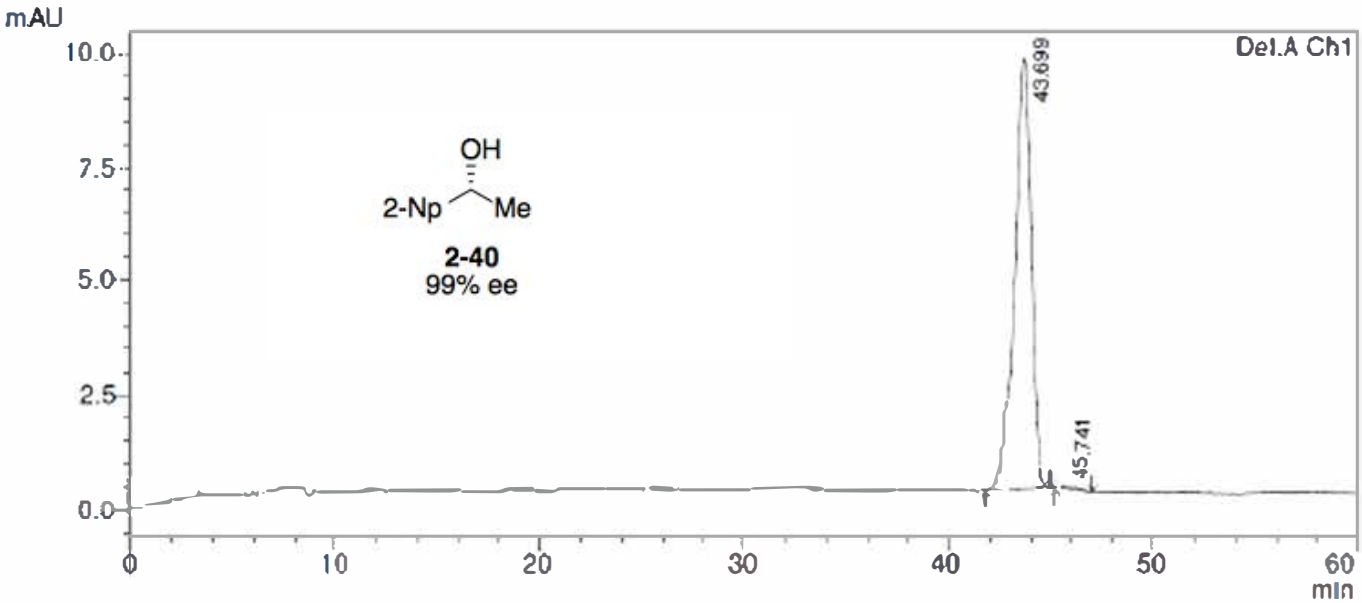
Peak#	Ret. Time	Area	Height	Area %	Height %
1	44.637	946536	16673	97.303	96.868
2	46.837	26234	539	2.697	3.132
Total		972770	17212	100.000	100.000

Compound 3a, racemic (254 nm)



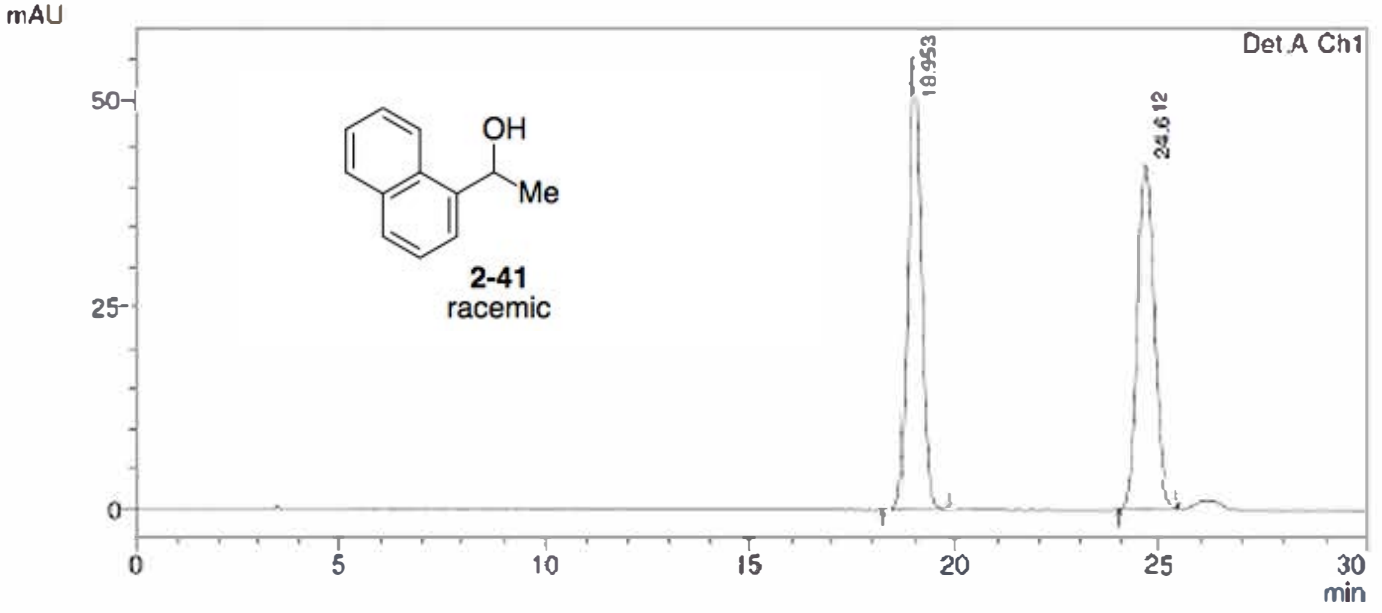
Peak#	Ret. Time	Area	Height	Area %	Height %
1	45.172	64627	1174	50.417	51.245
2	47.381	63558	1117	49.583	48.755
Total		128185	2292	100.000	100.000

Compound 3a, 99% ee (254 nm)



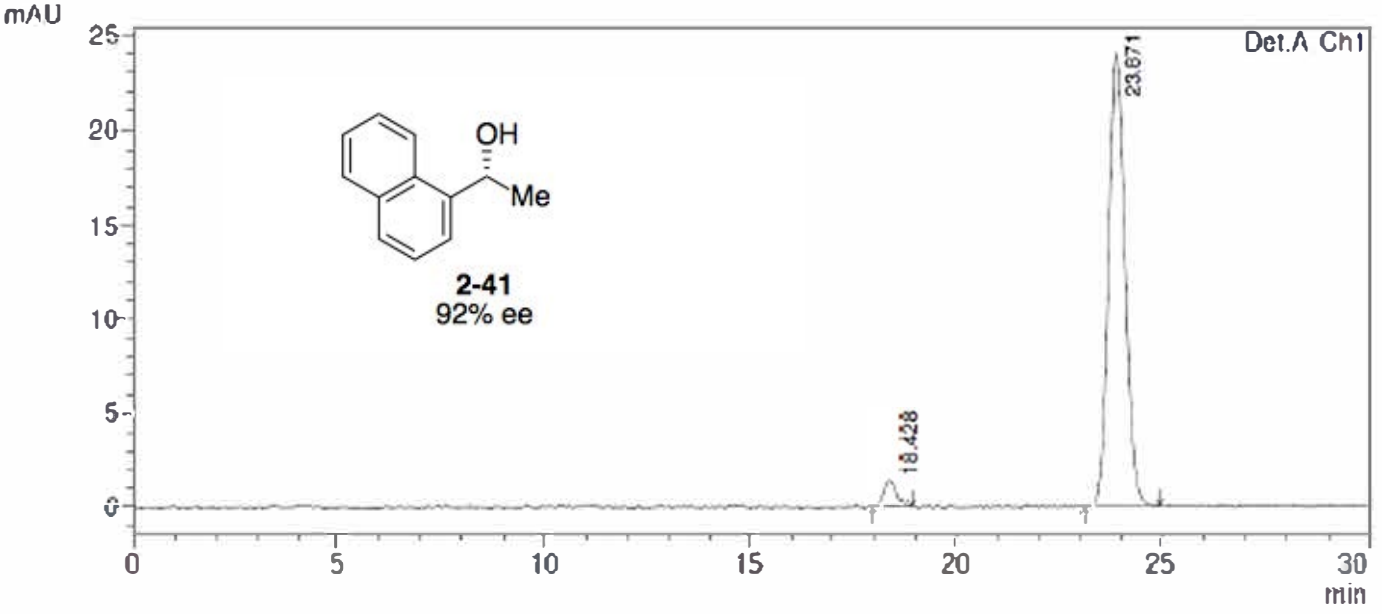
Peak#	Ret. Time	Area	Height	Area %	Height %
1	43.699	524955	9434	99.543	99.356
2	45.741	2408	61	0.457	0.644
Total		527362	9495	100.000	100.000

Compound 3b, racemic (254 nm)



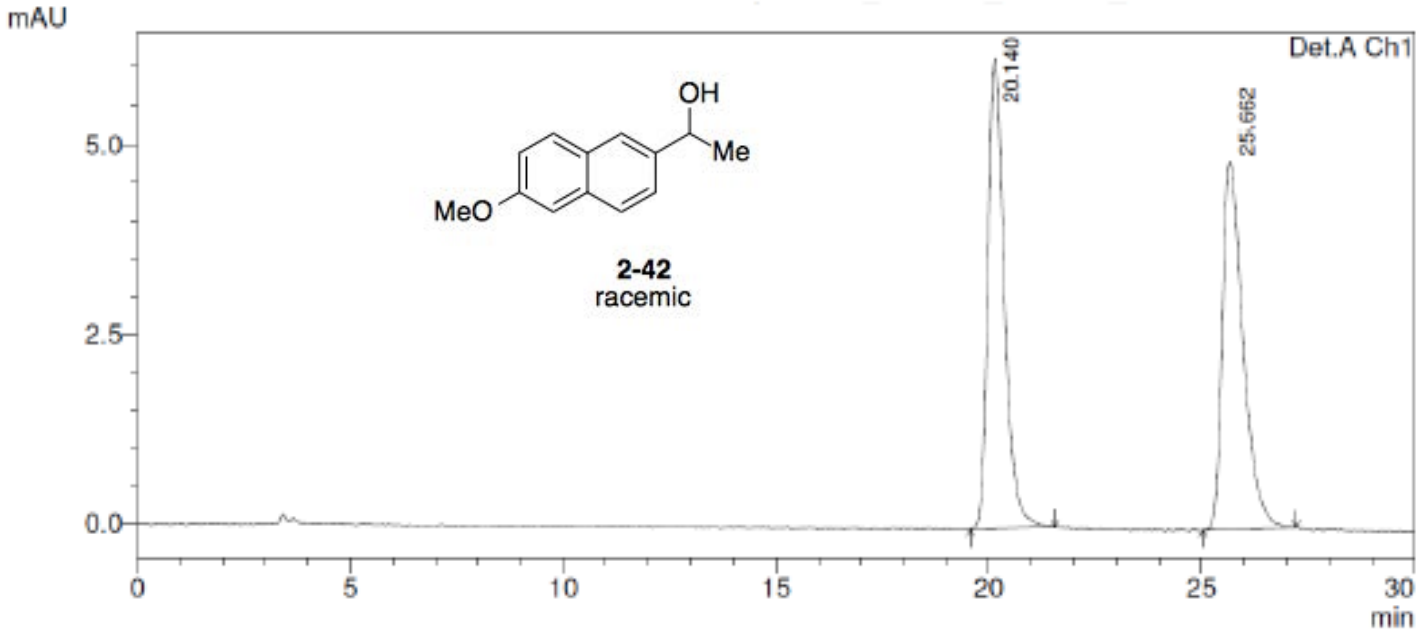
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.953	1239231	55611	50.146	56.632
2	24.612	1232017	42586	49.854	43.368
Total		2471248	98197	100.000	100.000

Compound 3b, 92% ee (254 nm)



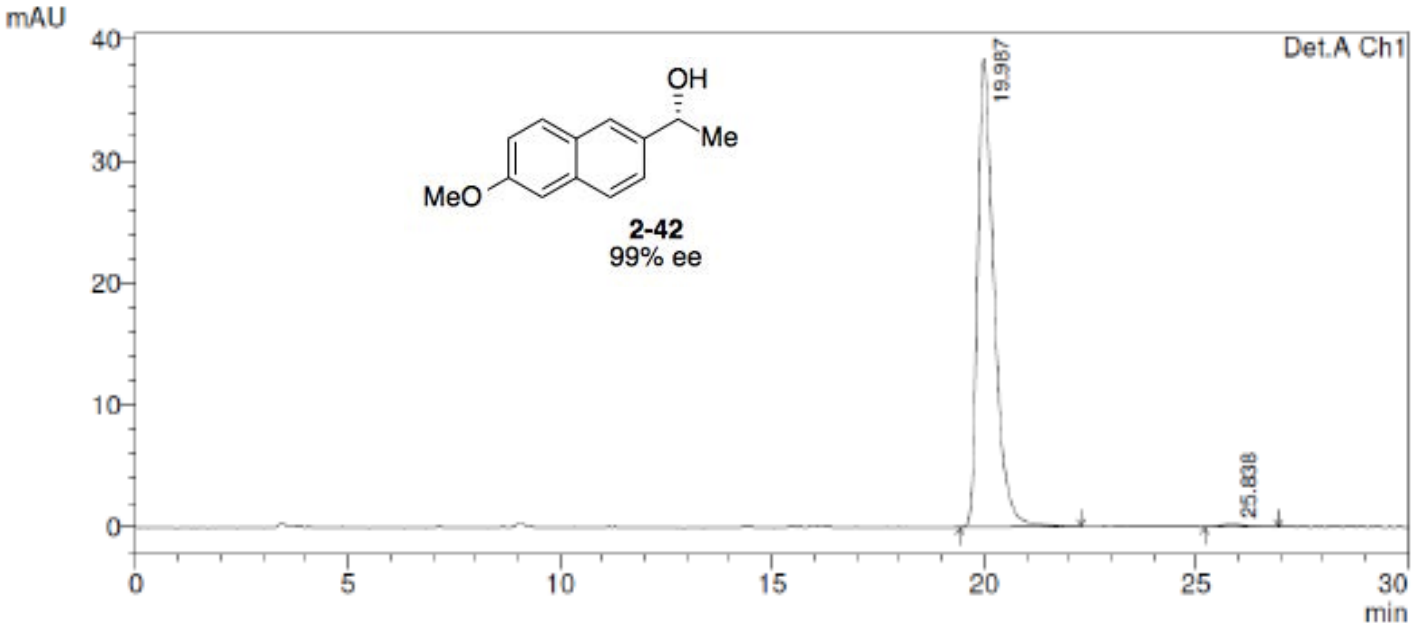
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.428	28226	1362	4.034	5.381
2	23.871	671567	23948	95.966	94.619
Total		699793	25310	100.000	100.000

Compound 3c, racemic (254 nm)



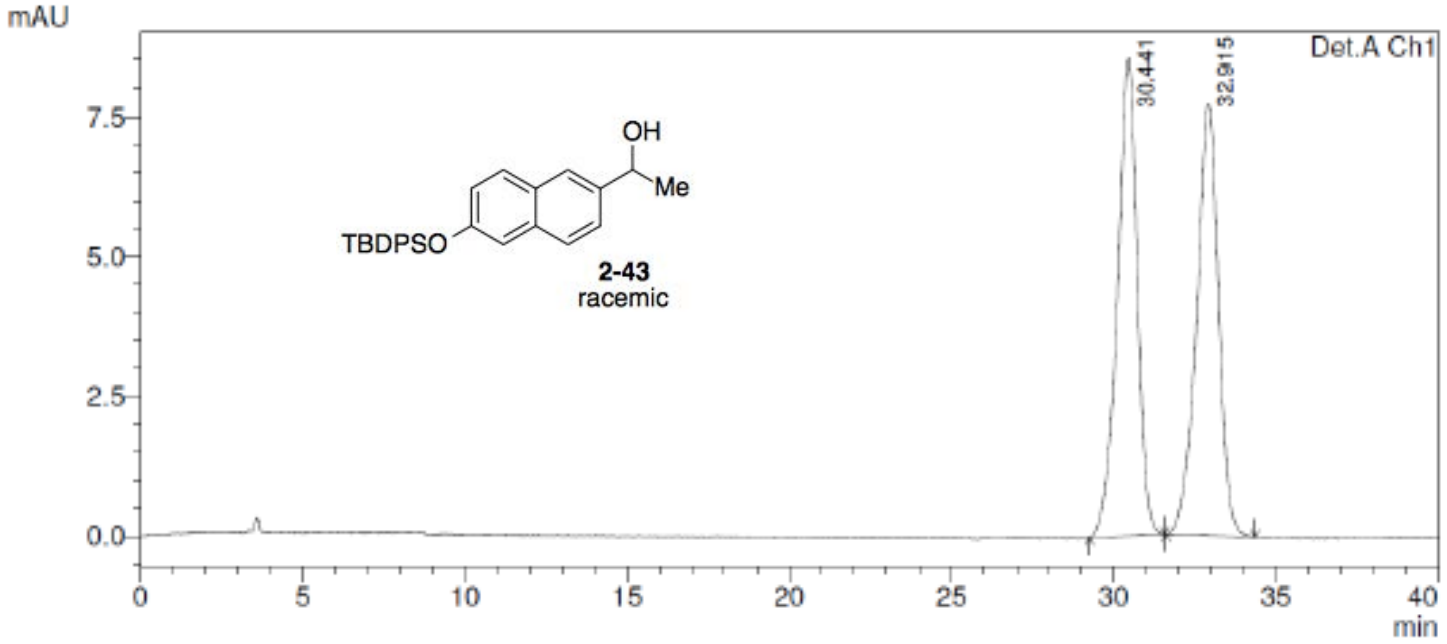
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.140	165137	6165	50.153	55.982
2	25.662	164128	4848	49.847	44.018
Total		329266	11013	100.000	100.000

Compound 3c, 99% ee (254 nm)



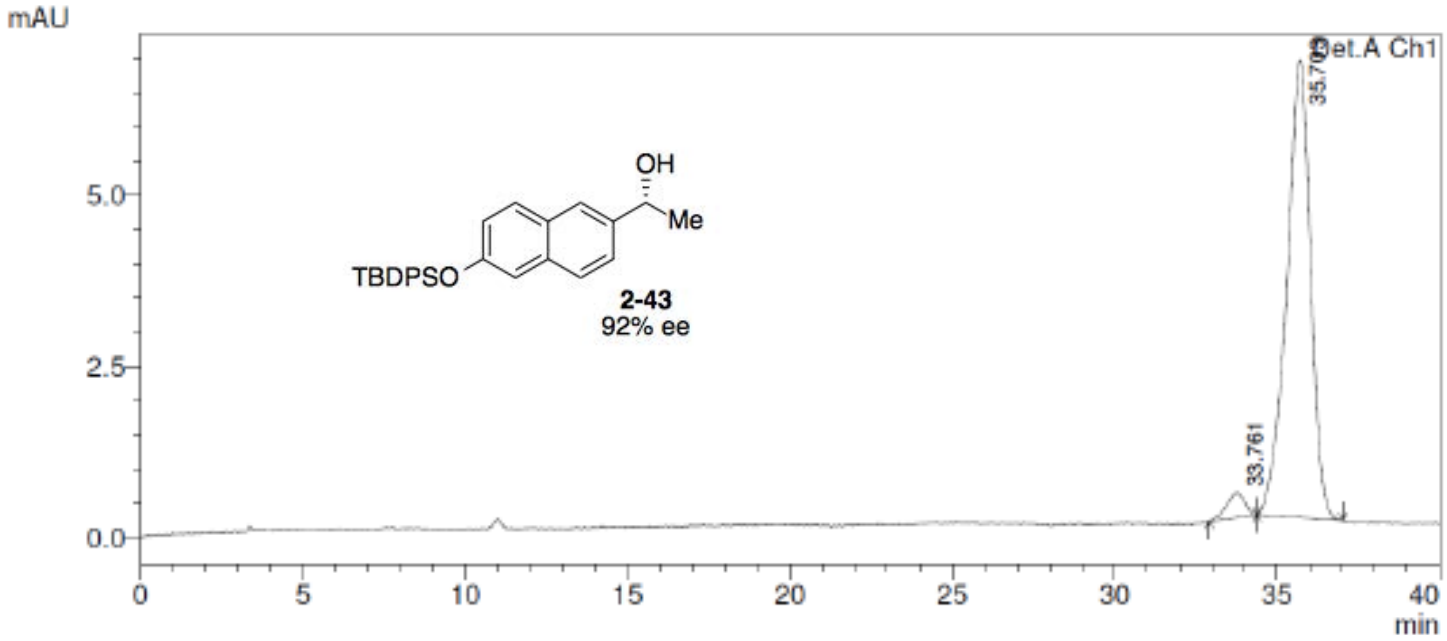
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.987	1037849	38360	99.309	99.372
2	25.838	7220	242	0.691	0.628
Total		1045069	38602	100.000	100.000

Compound 3d, racemic (254 nm)



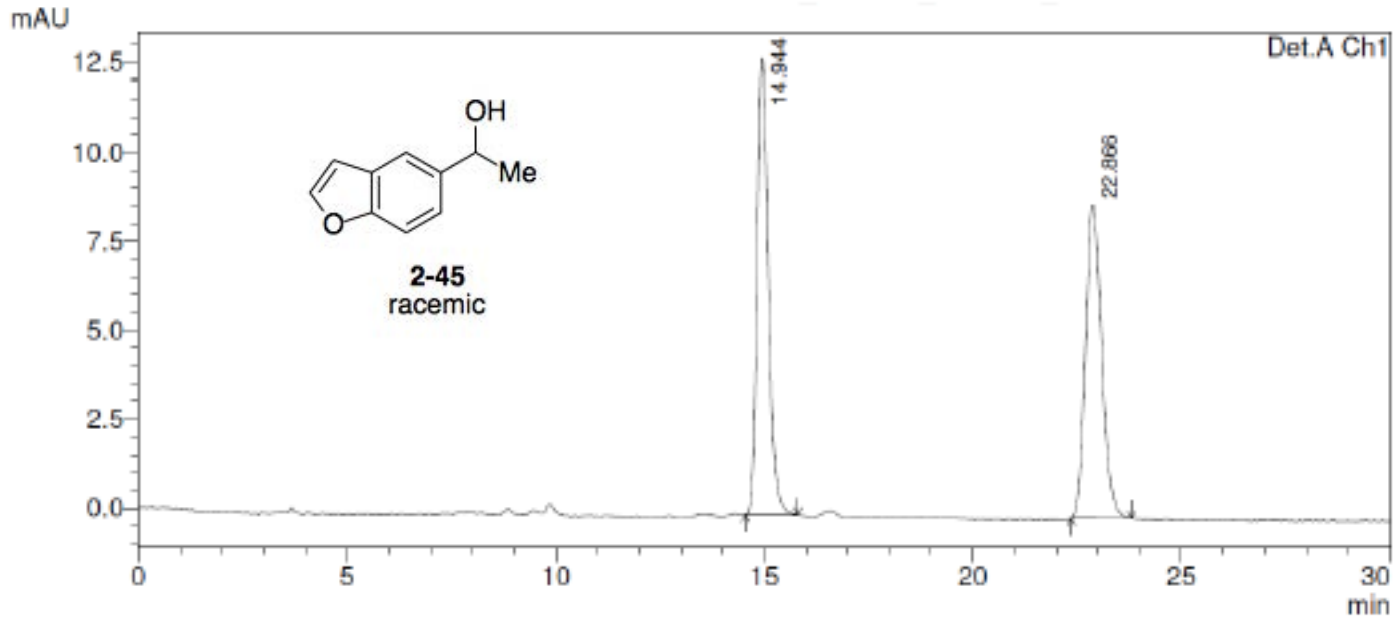
Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.441	364152	8496	49.958	52.369
2	32.915	364762	7727	50.042	47.631
Total		728913	16223	100.000	100.000

Compound 3d, 92% ee (254 nm)



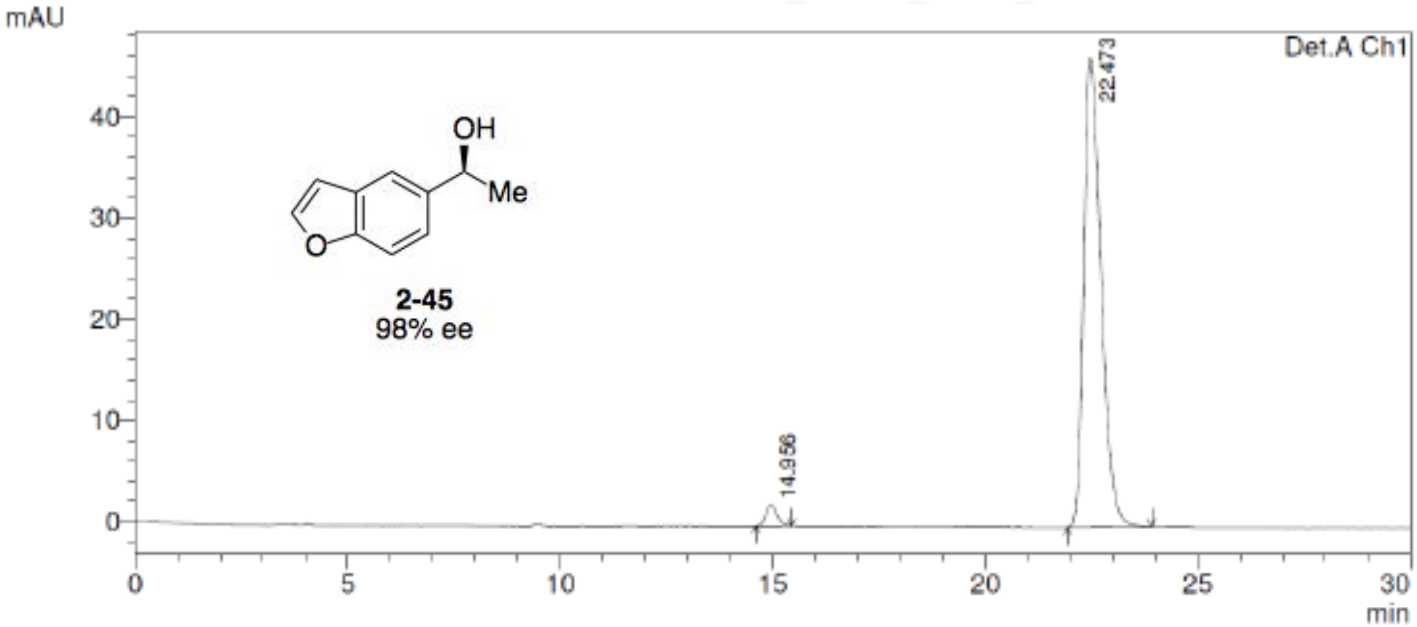
Peak#	Ret. Time	Area	Height	Area %	Height %
1	33.761	14125	358	3.958	5.084
2	35.703	342763	6682	96.042	94.916
Total		356888	7040	100.000	100.000

Compound 3e, racemic (254 nm)



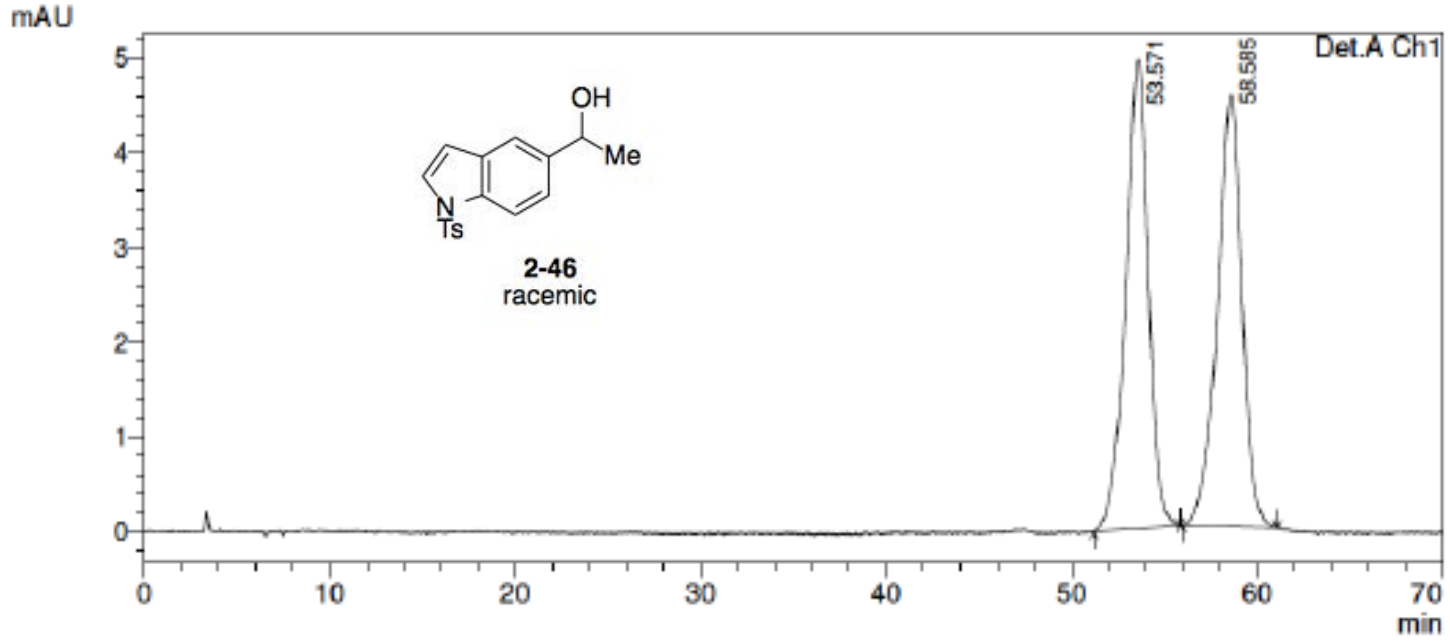
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.944	239370	12773	50.150	59.107
2	22.866	237935	8837	49.850	40.893
Total		477305	21610	100.000	100.000

Compound 3e, 95% ee (254 nm)



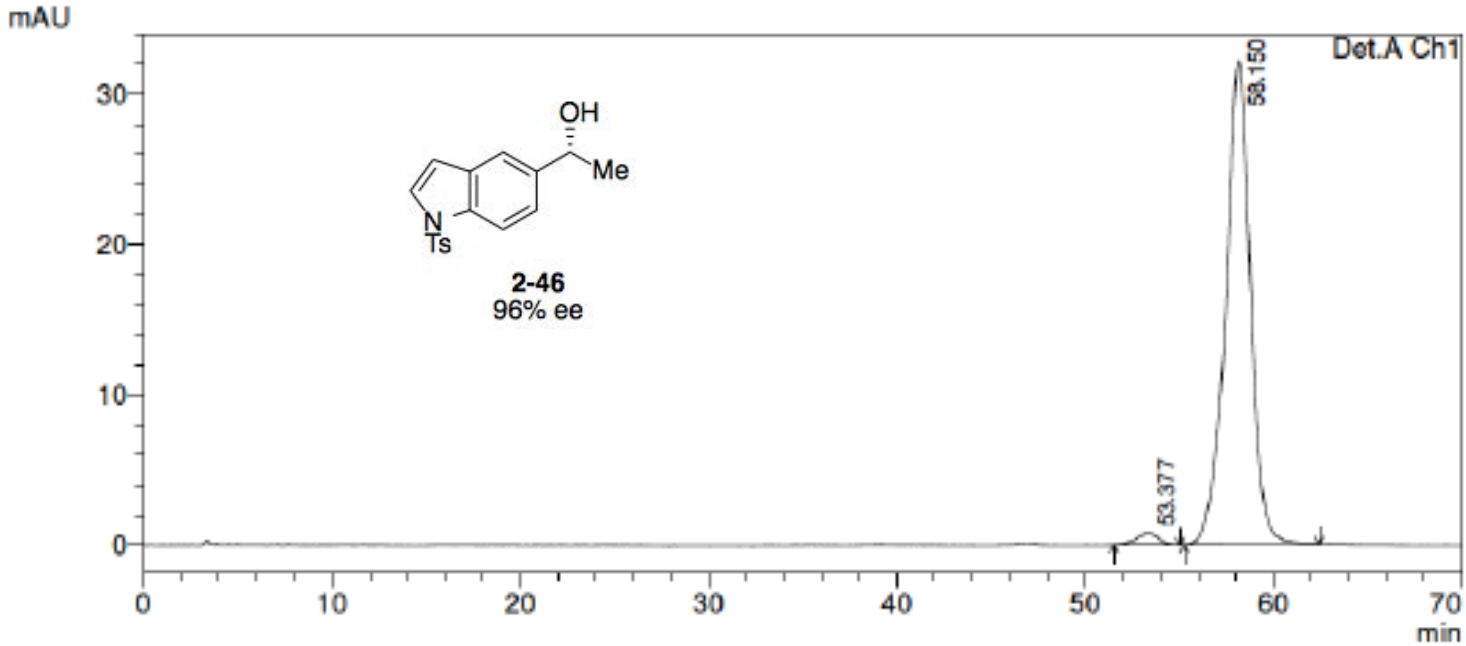
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.956	35963	1982	2.675	4.104
2	22.473	1308675	46315	97.325	95.896
Total		1344638	48297	100.000	100.000

Compound **3g**, racemic (254 nm)



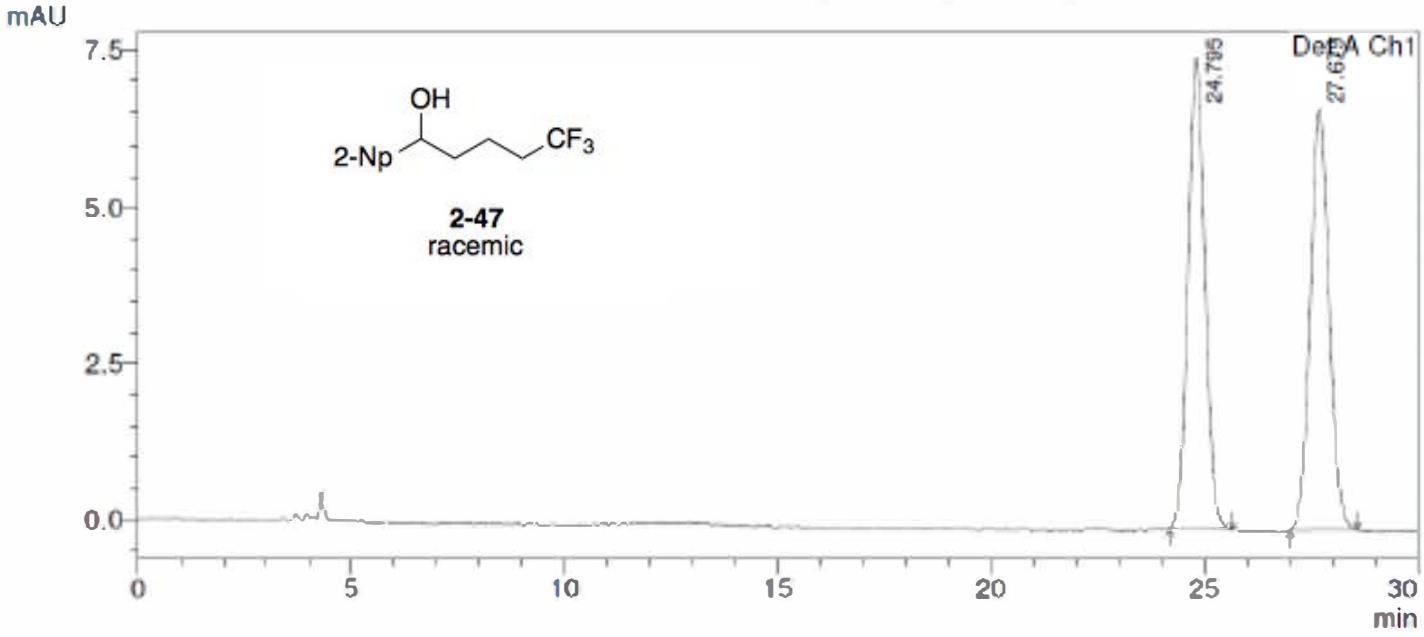
Peak#	Ret. Time	Area	Height	Area %	Height %
1	53.571	422898	4957	50.129	52.089
2	58.585	420722	4559	49.871	47.911
Total		843620	9516	100.000	100.000

Compound **3g**, 96% ee (254 nm)



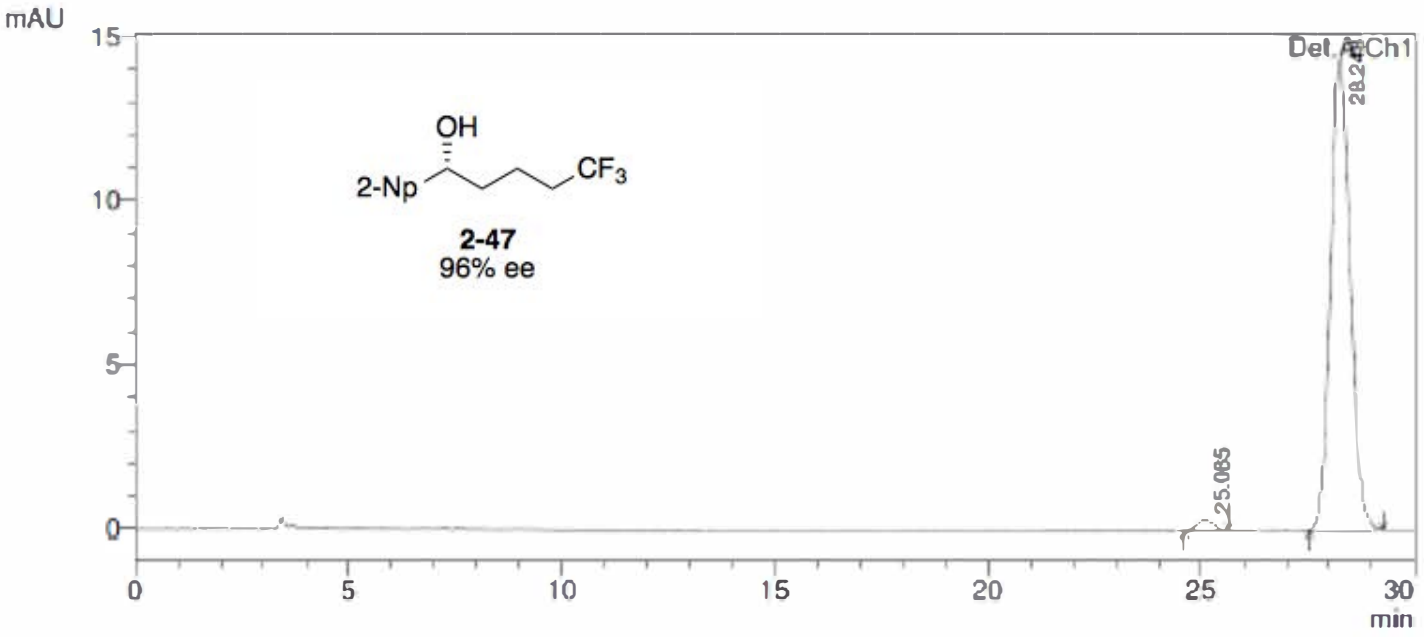
Peak#	Ret. Time	Area	Height	Area %	Height %
1	53.377	64936	808	2.149	2.450
2	58.150	2956179	32179	97.851	97.550
Total		3021114	32987	100.000	100.000

Compound 2-47, racemic (254 nm)



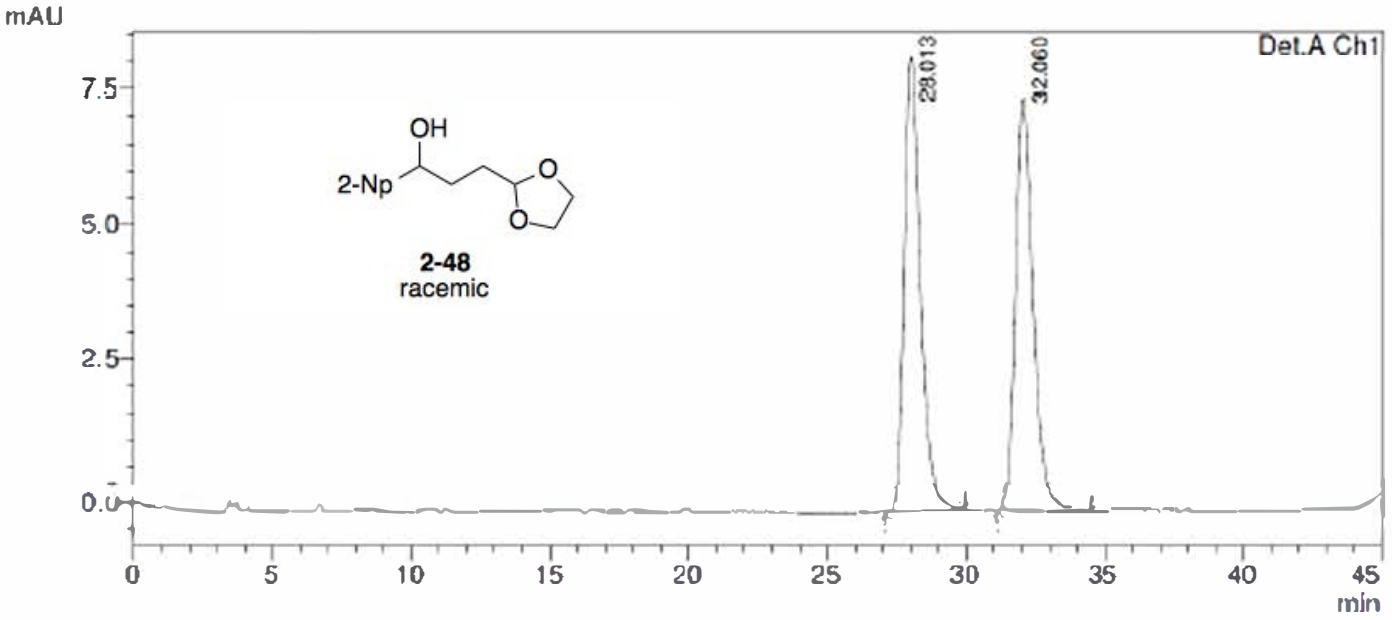
Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.795	210483	7521	50.324	52.855
2	27.679	207772	6708	49.676	47.145
Total		418255	14229	100.000	100.000

Compound 2-47, 96% ee (254 nm)



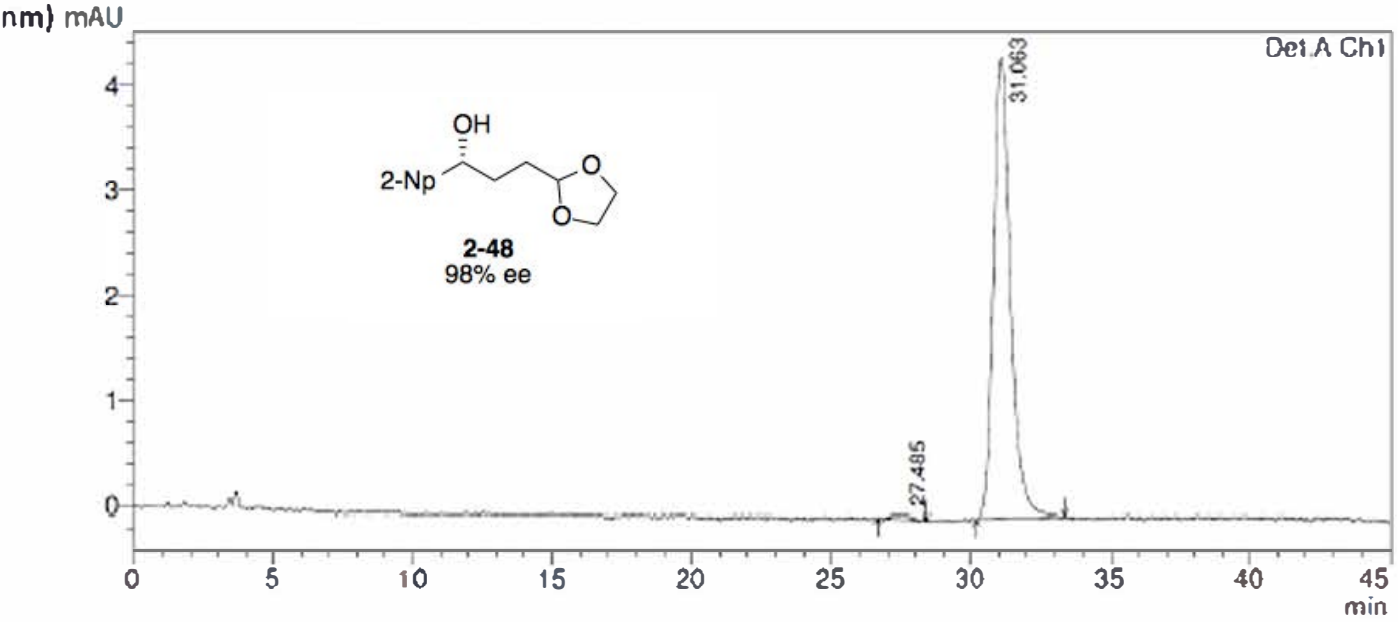
Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.085	8553	324	1.840	2.212
2	28.248	456259	14308	98.160	97.788
Total		464812	14632	100.000	100.000

Compound 2-48, racemic (254 nm)



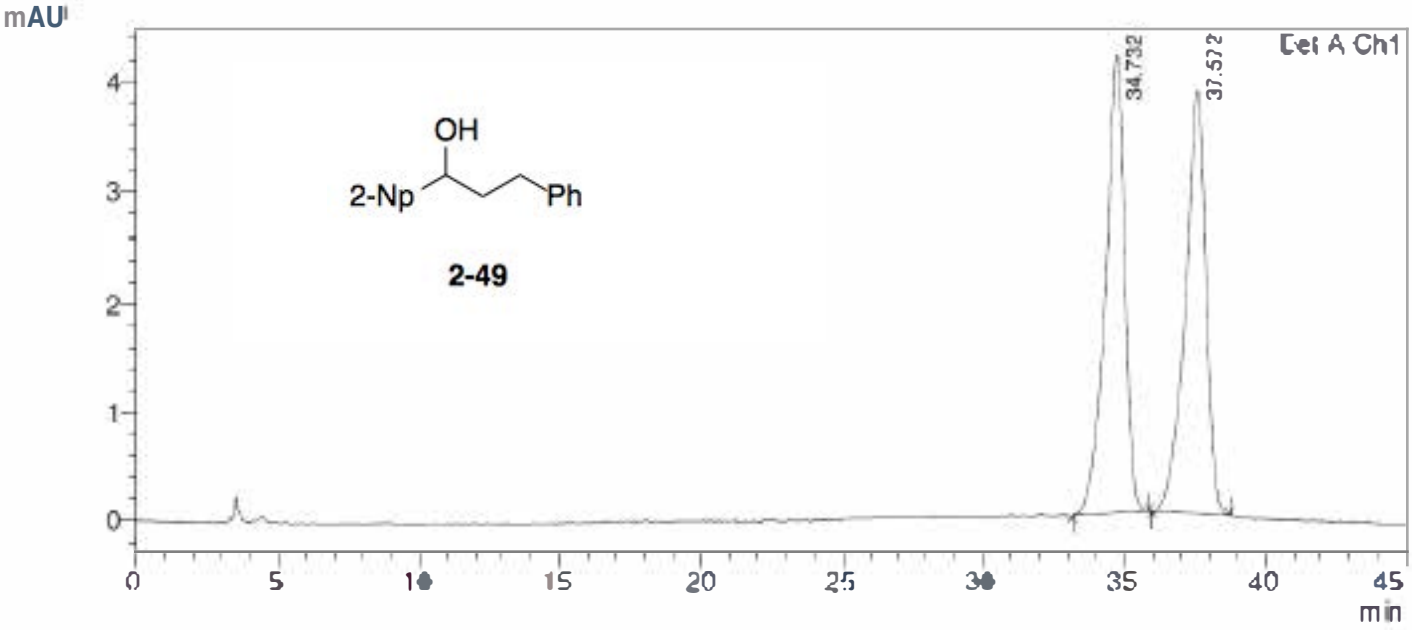
Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.013	346583	8466	49.977	52.224
2	32.060	346898	7745	50.023	47.776
Total		693481	16211	100.000	100.000

Compound 2-48, 98% ee (254 nm) mAU



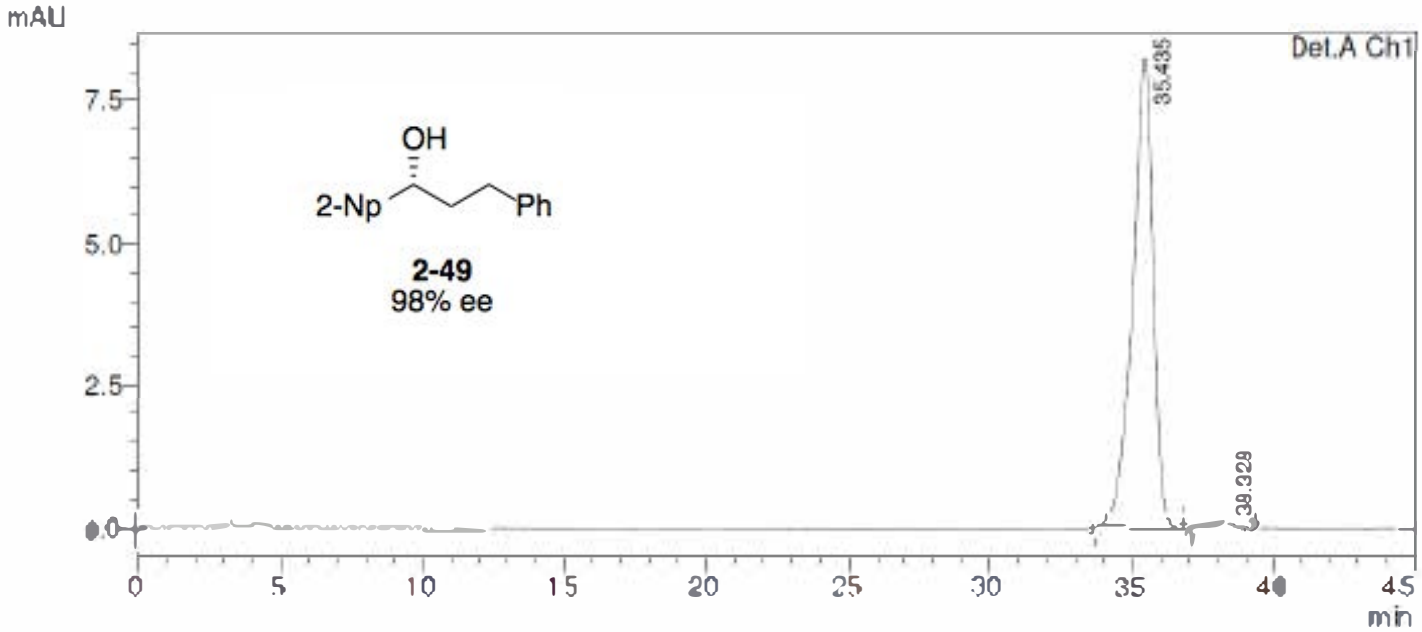
Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.485	1806	53	0.968	1.191
2	31.063	184751	4374	99.032	98.809
Total		186557	4426	100.000	100.000

Compound 2-49, racemic (254nm)



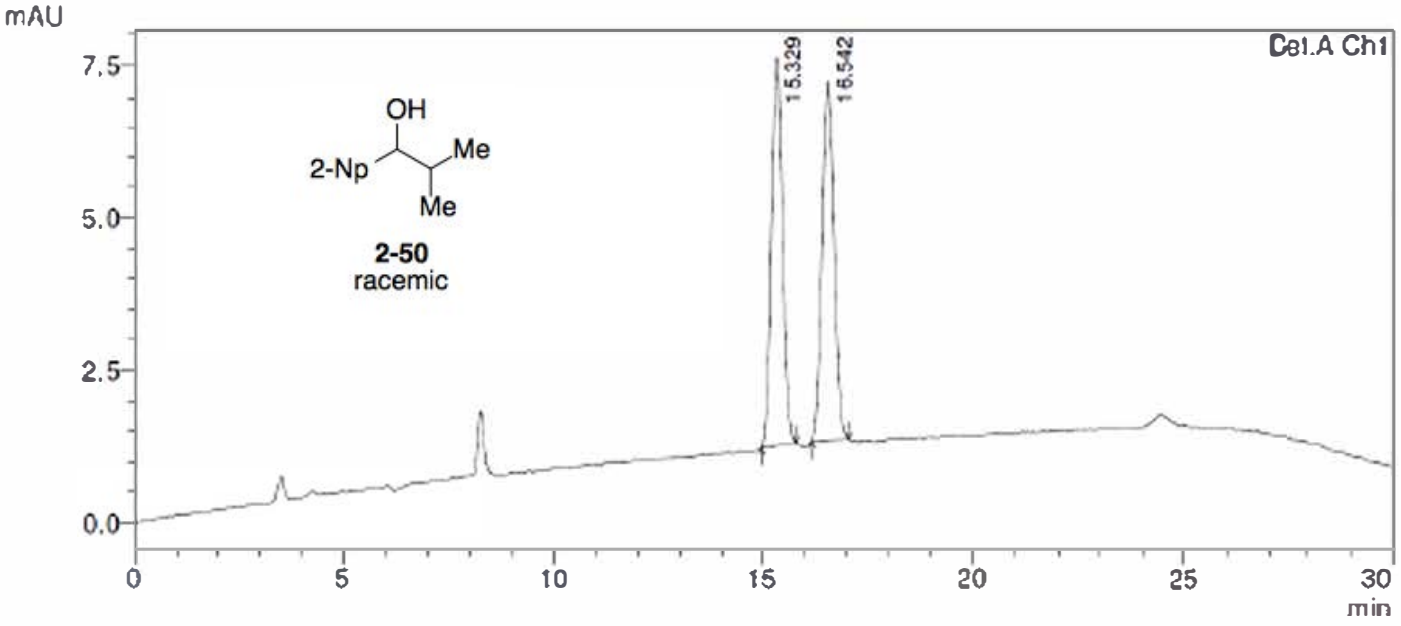
Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.732	198596	4170	50.141	51.978
2	37.572	197482	3853	49.859	48.022
Total		396078	8023	100.000	100.000

Compound 2-49, 98% ee (254nm)



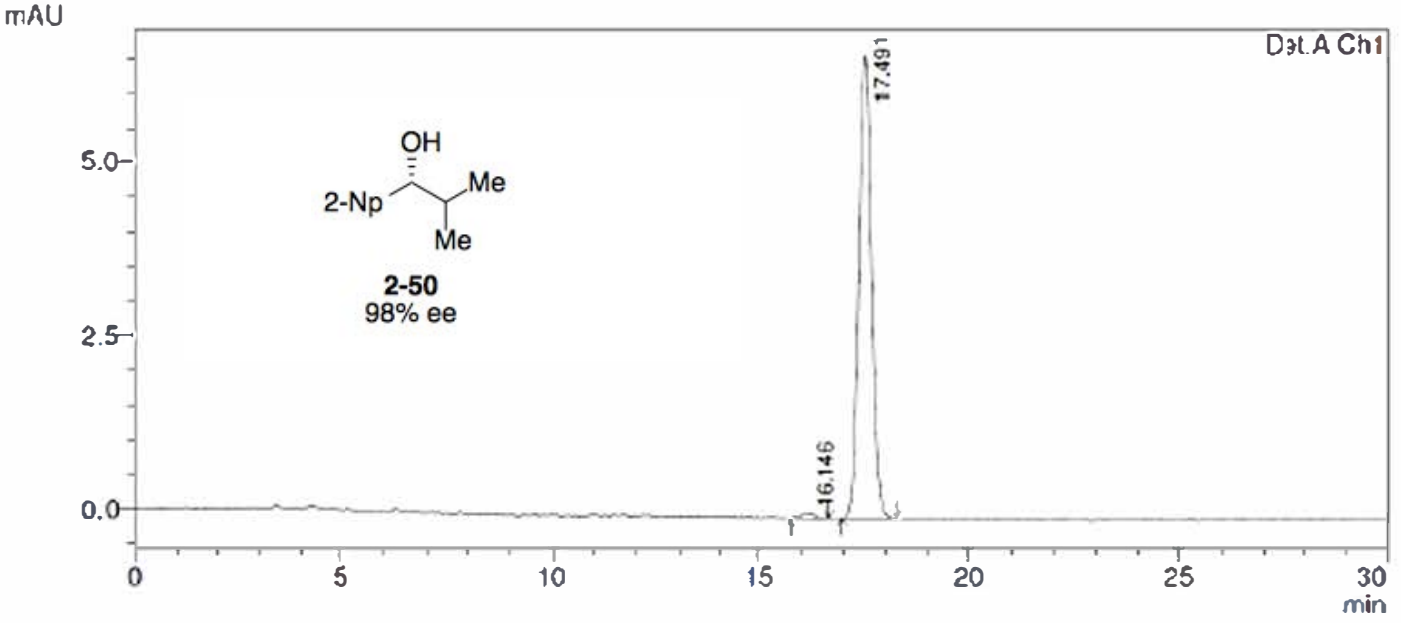
Peak#	Ret. Time	Area	Height	Area %	Height %
1	35.435	412336	8222	98.853	98.861
2	38.328	4783	95	1.147	1.139
Total		417119	8317	100.000	100.000

Compound 2-50, racemic (254 nm)



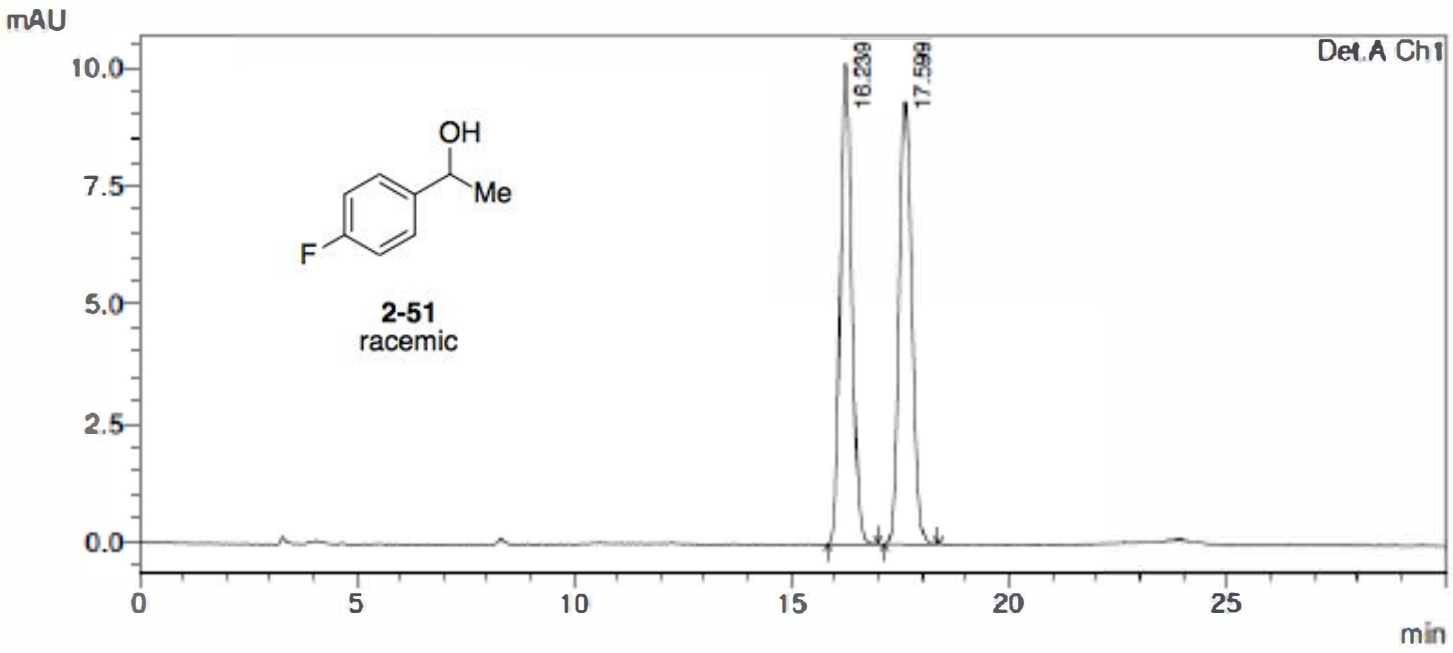
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.329	116684	6363	50.105	51.956
2	16.542	116193	5884	49.895	48.044
Total		232877	12246	100.000	100.000

Compound 2-50, 98% ee (254 nm)



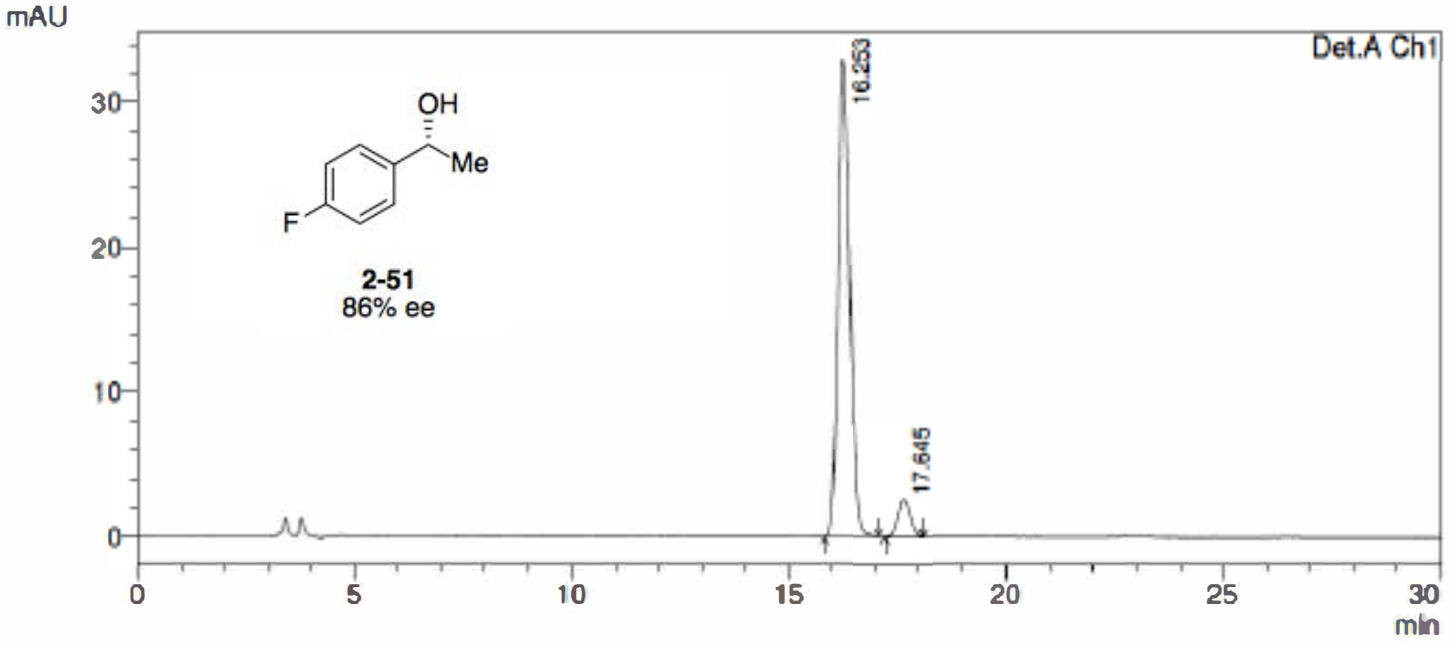
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.146	1594	70	1.126	1.034
2	17.491	140016	6657	98.874	98.966
Total		141610	6726	100.000	100.000

Compound 2-51, racemic (254 nm)



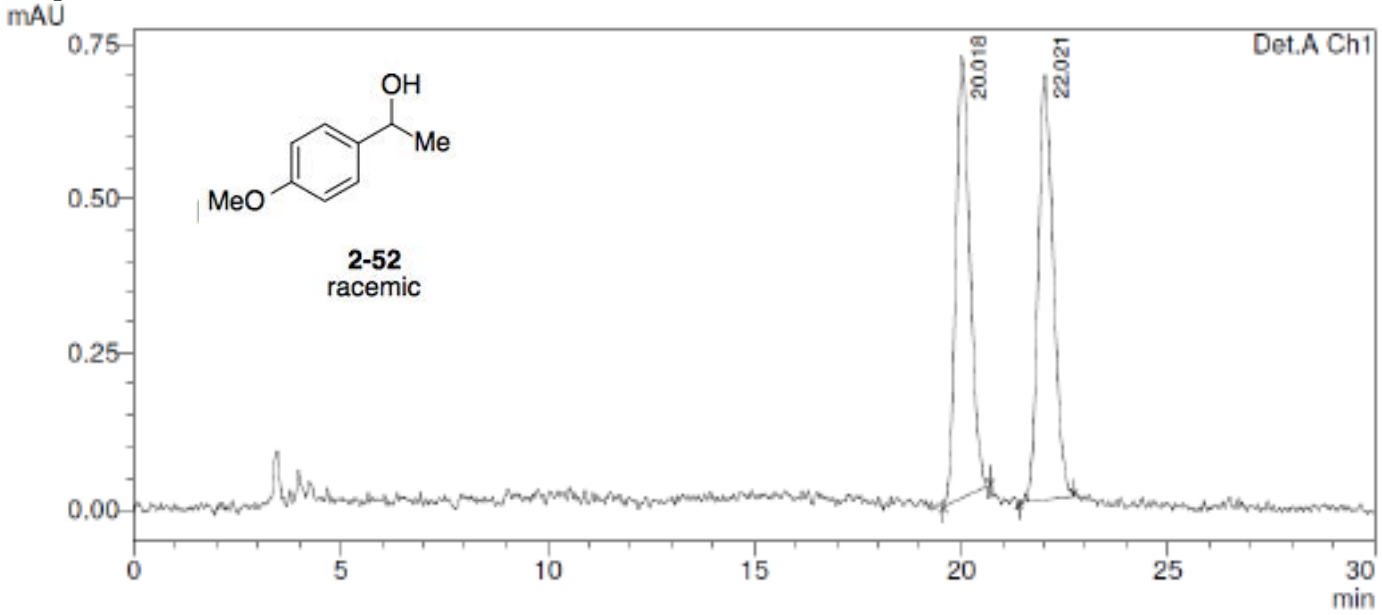
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.239	189291	10142	50.049	52.077
2	17.599	188917	9333	49.951	47.923
Total		378208	19476	100.000	100.000

Compound 2-51, 85% ee (254 nm)



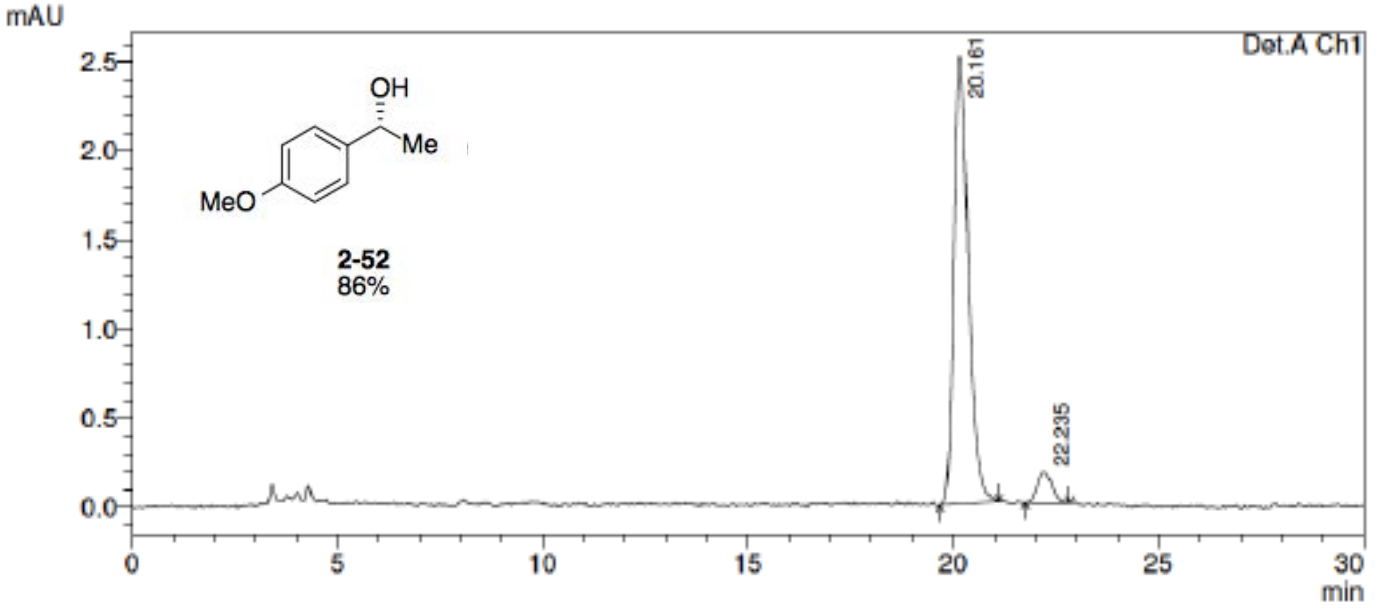
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.253	625785	33025	92.796	93.094
2	17.645	48585	2450	7.204	6.906
Total		674370	35475	100.000	100.000

Compound **2-52** racemic (254 nm)



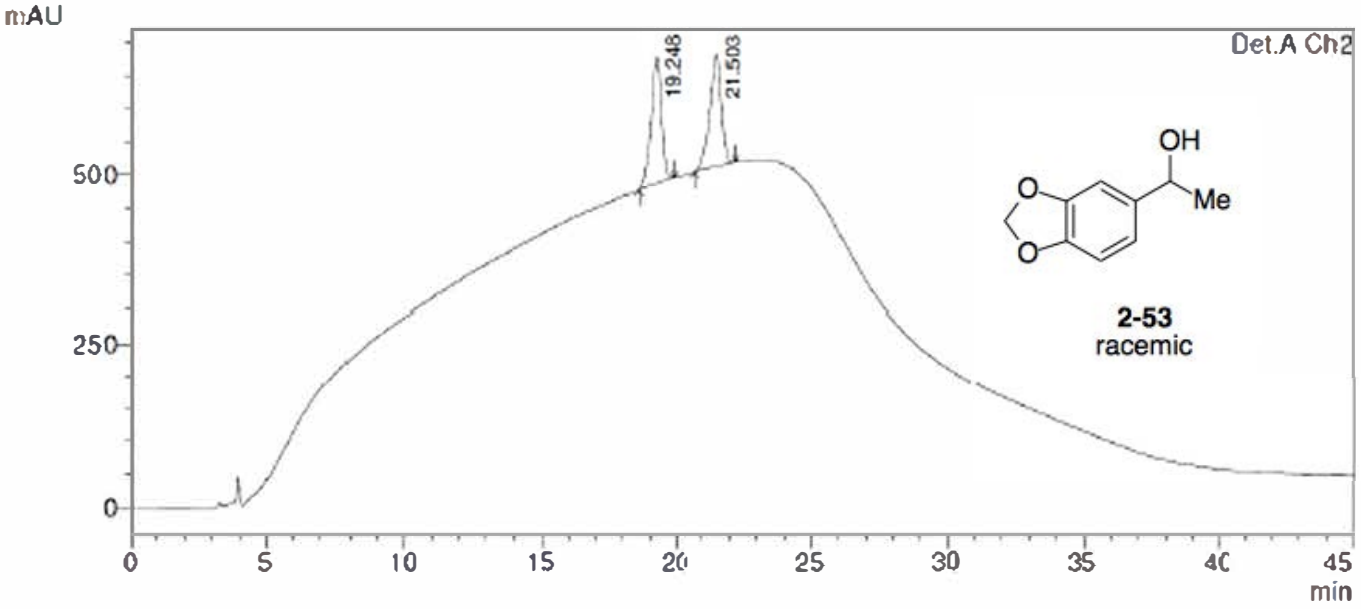
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.018	16955	713	49.424	51.024
2	22.021	17351	684	50.576	48.976
Total		34306	1397	100.000	100.000

Compound 2-52, 86% ee (254 nm)



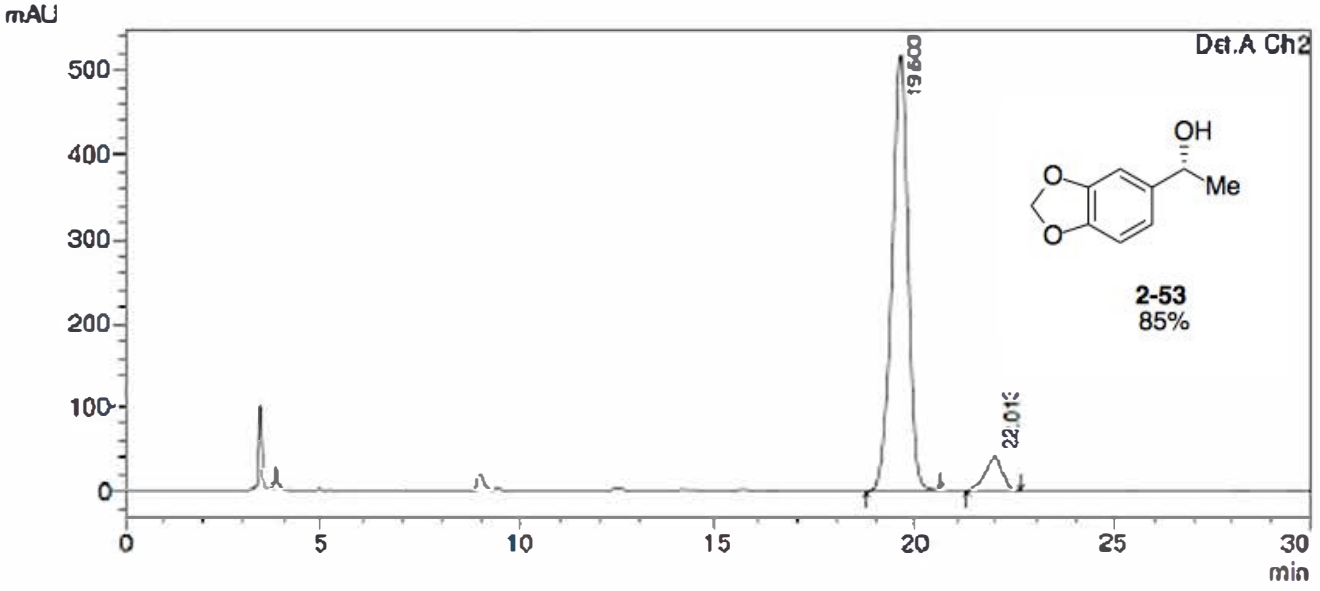
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.161	61611	2512	93.425	93.488
2	22.235	4336	175	6.575	6.512
Total		65947	2687	100.000	100.000

Compound 2-53, racemic (210 nm)

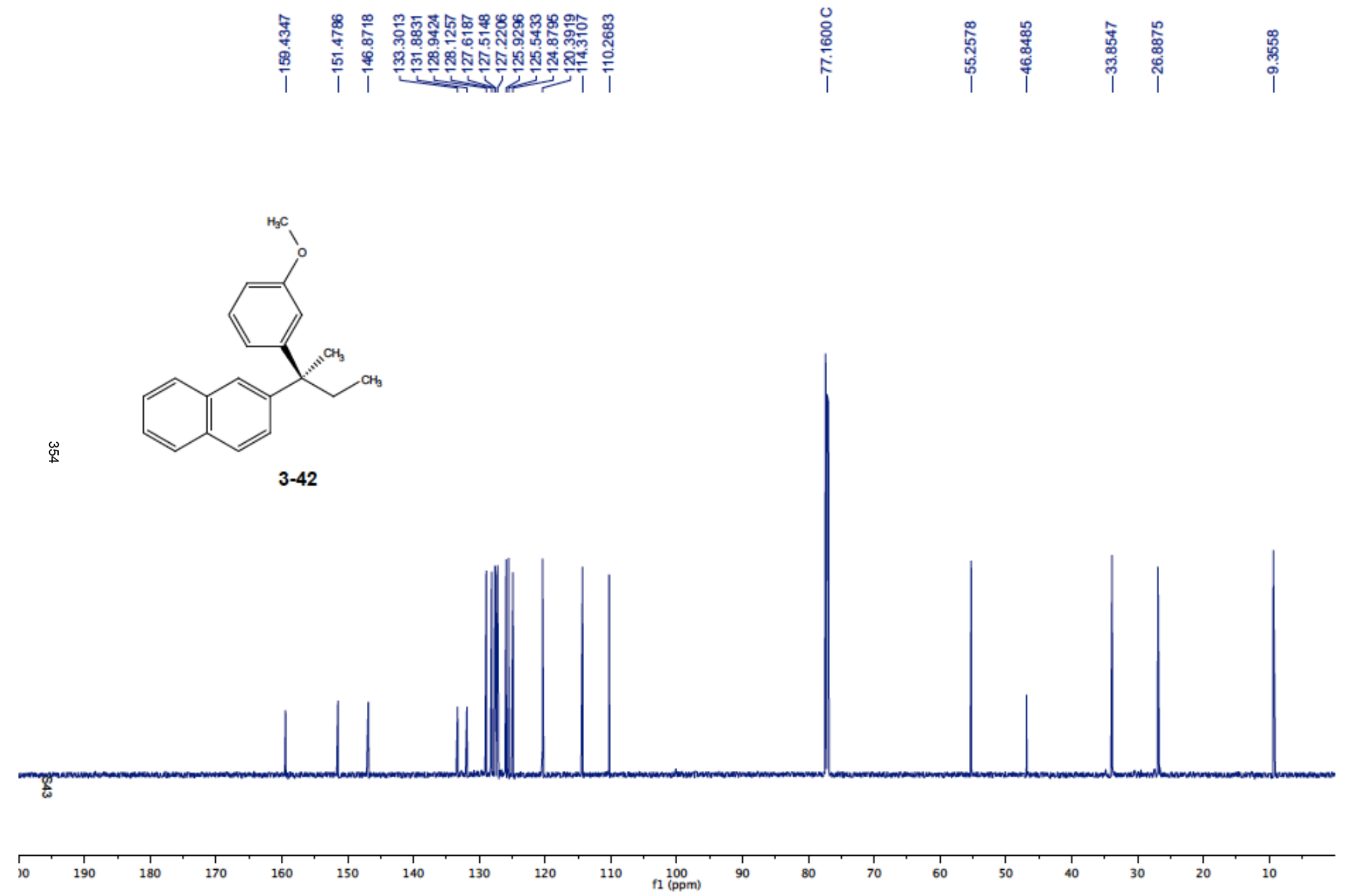


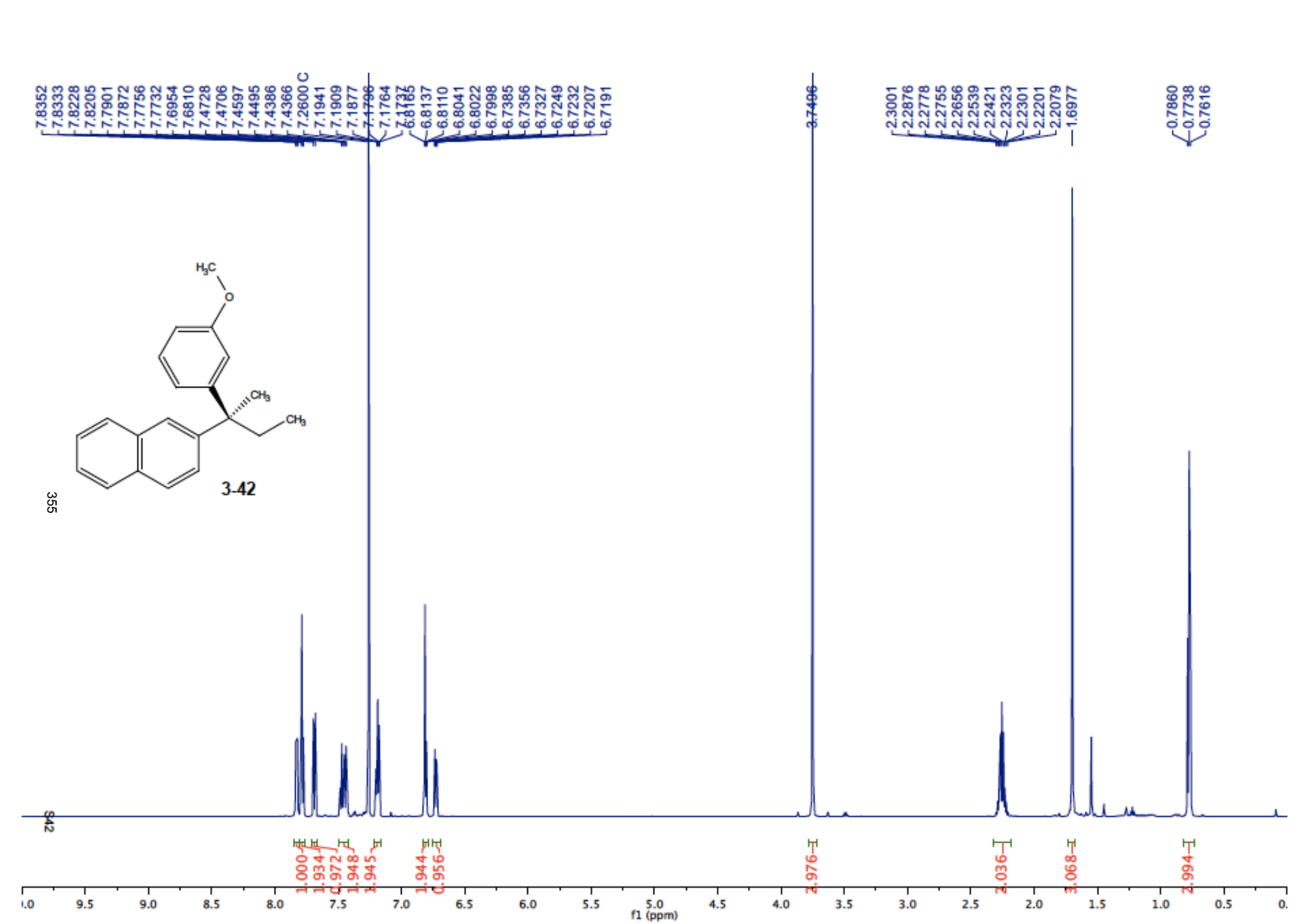
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.248	4853386	187177	49.816	52.913
2	21.503	4889175	166570	50.184	47.087
Total		9742560	353746	100.000	100.000

Compound 2-53, 85% *ee* (210 nm)



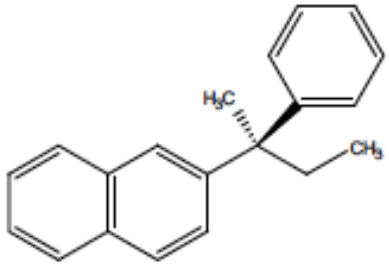
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.603	14324275	516565	92.465	92.804
2	22.013	1167262	40056	7.535	7.196
Total		15491537	556621	100.000	100.000


159.4347
151.4786
146.8718
133.3013
131.8831
128.9424
128.1257
127.6187
127.5148
127.2206
125.9296
125.5433
124.8795
120.3919
114.3107
110.2683
77.1600 C
55.2578
46.8485
33.8547
26.8875
9.3558
H3C
O
CH3
CH3
3-42
f1 (ppm)


7.8352
7.8333
7.8228
7.8205
7.7901
7.7872
7.7756
7.7732
7.6954
7.6810
7.4728
7.4706
7.4597
7.4495
7.4386
7.4366
7.2600 C
7.1941
7.1909
7.1877
7.1796
7.1764
6.8137
6.8110
6.8041
6.8022
6.7998
6.7385
6.7356
6.7327
6.7249
6.7232
6.7207
6.7191
3.7496
2.3001
2.2876
2.2778
2.2755
2.2656
2.2539
2.2421
2.2323
2.2301
2.2201
2.2079
1.6977
0.7860
0.7738
0.7616
H3C
O
CH3
CH3
3-42
355
S42
1.000
1.934
0.972
1.948
1.945
1.944
0.956
2.976
2.036
3.068
2.994
f1 (ppm)

QZ 8-173-2-C.1.fid
QZ 8-173-2-C
C13CPD32 CDCl3 /opt/topspin kmrob 11

149.6962
146.9841
133.2409
131.8088
128.0978
128.0670
127.6303
127.6114
127.5157
127.3059
125.9625
125.7368
125.5576
124.9309
77.1600 CDCl3
46.7828
33.8377
26.9303
9.3513

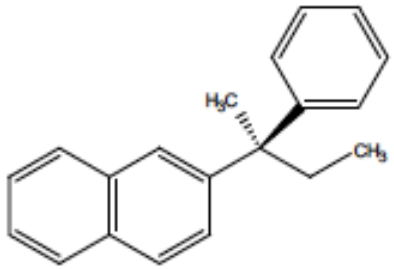


4-43

356

S45

f1 (ppm)

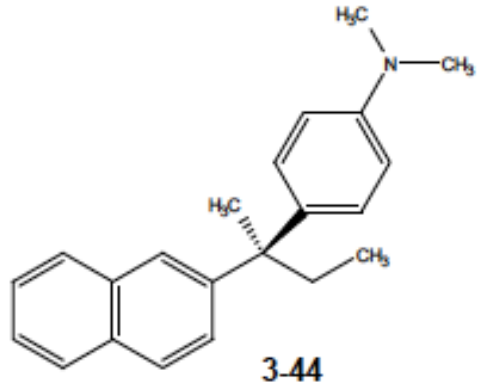

H3C
CH3

3-43

PROTON_16 CDCl3 /opt/topspin kmroh 54
S44
3.064
1.000
2.079
6.208
2.074
3.174
3.111
f1 (ppm)

QZ-8-067-1.2.fid
QZ-8-067-1
C13CPD2048 CDCl3 /opt/nmrdata.gzhou 59

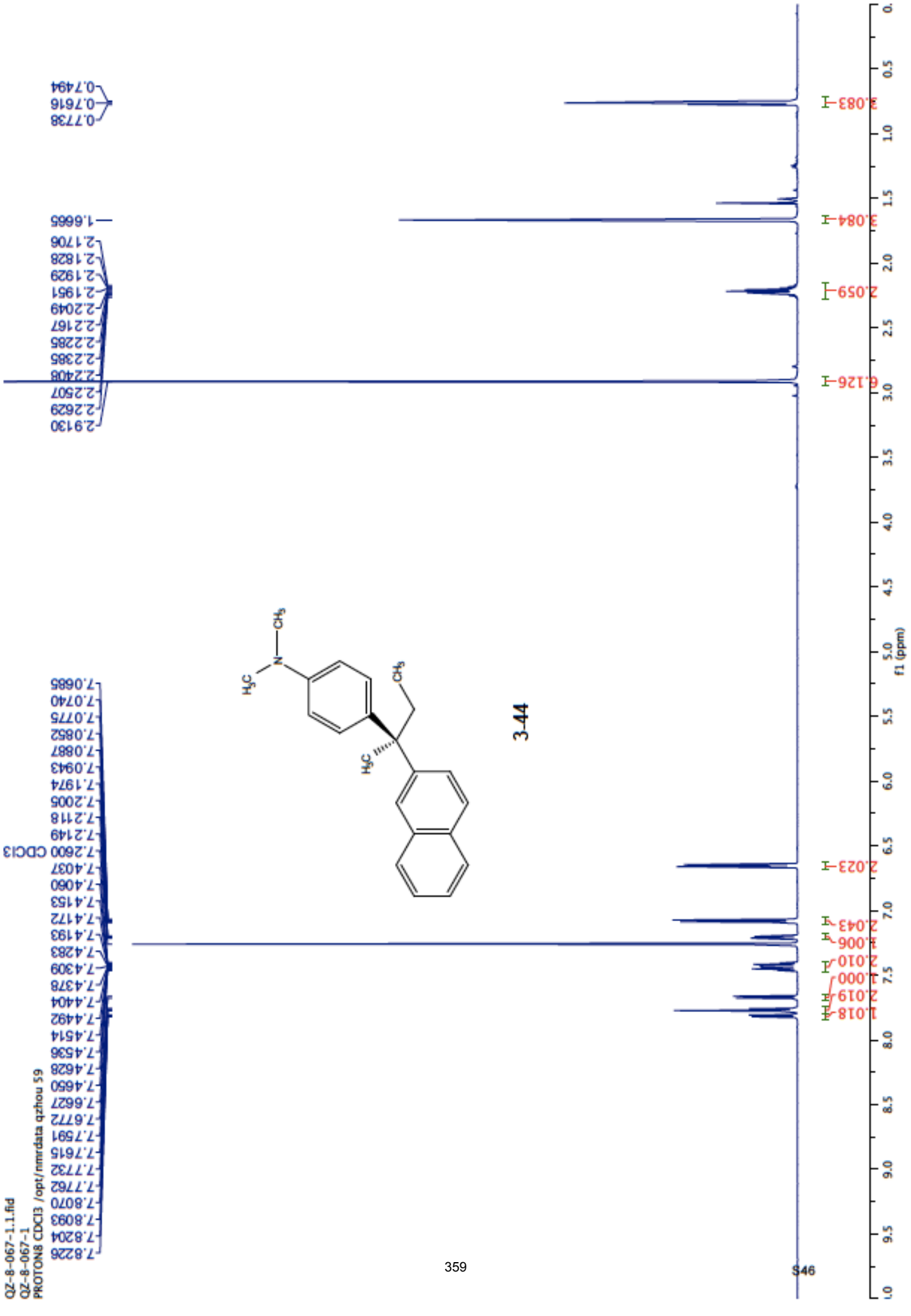
148.6150
147.6440
137.7713
133.3156
131.7962
128.2374
128.1021
127.4960
127.4619
127.4477
125.8200
125.3788
124.8220
112.3488
77.1600 CDCl3
45.8898
40.8040
34.0170
27.0495
9.4268



3-44

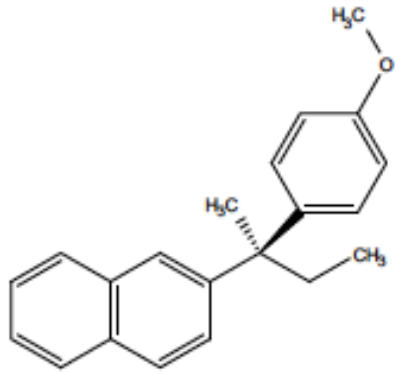
358

160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


3-44
CDCl3
f1 (ppm)
QZ-8-067-1.1.fid
QZ-8-067-1
PROTON8 CDCl3 /opt/nmrdata qzhou 59

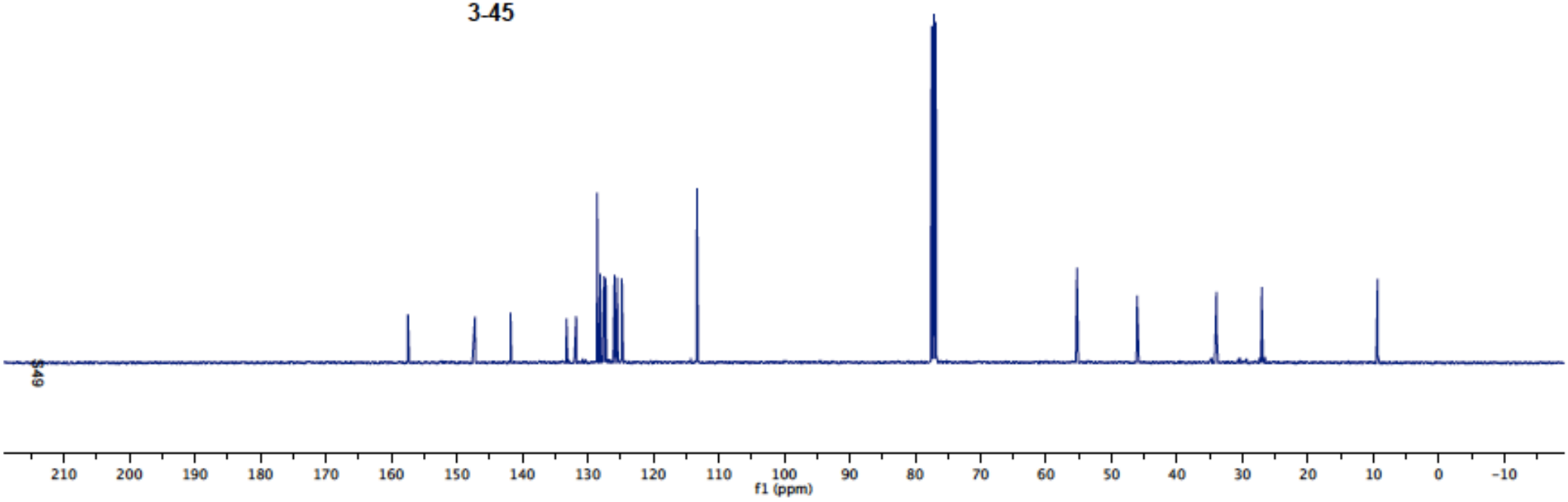
QZ 8-171-2-C.1.fid
QZ 8-171-2-C
C13CPD32 CDCl3 /opt/topspin kmrob 43

157.4747
147.2482
141.8057
133.2409
131.7806
128.5816
128.0816
127.5716
127.4988
127.2639
125.9328
125.5111
124.8029
113.3264
77.1600 CDCl3
55.2819
46.1091
33.9791
27.0590
9.3680



3-45

360

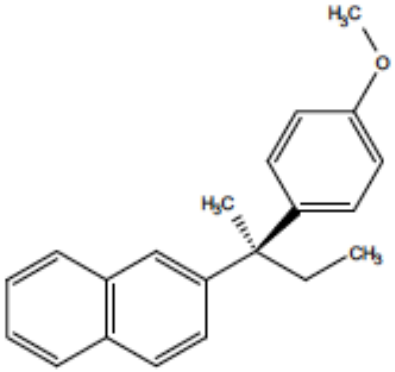


QZ 8-171-2-H.1.fid
QZ 8-171-2-H
PROTON_16 CDCl3 /opt/topspin kmrob 43

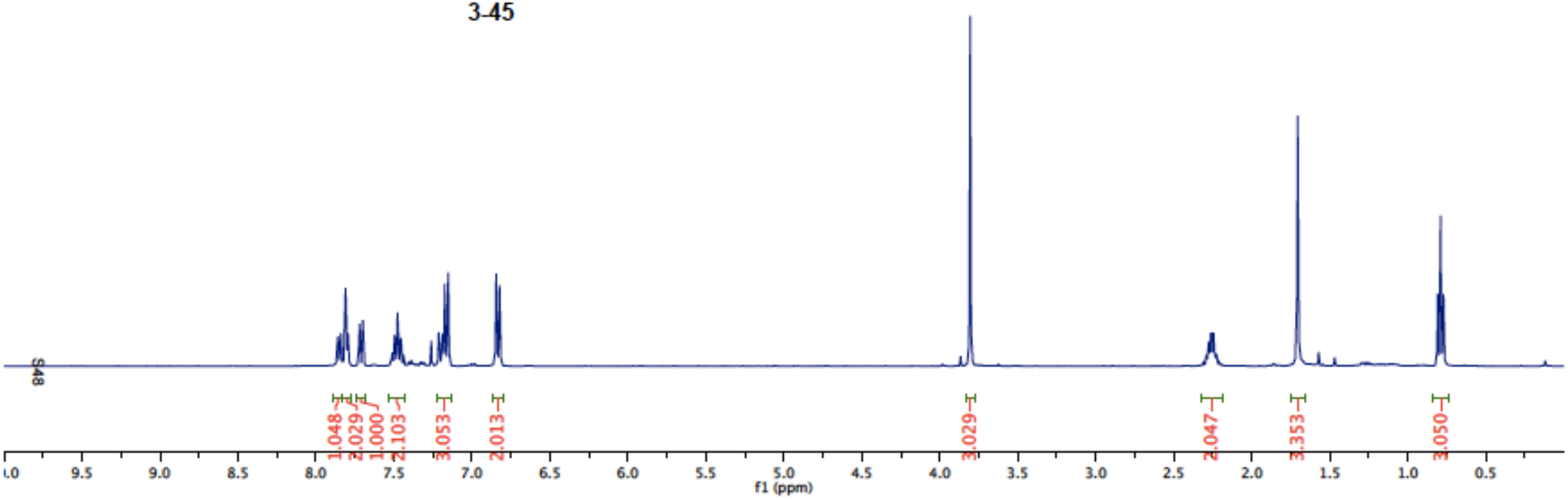
7.8602 7.8409 7.8385 7.8110 7.8058 7.7955 7.7912 7.7211 7.6994 7.4963 7.4925 7.4774 7.4724 7.4570 7.4535 7.2134 7.2086 7.1917 7.1869 7.1739 7.1686 7.1572 7.1518 6.8530 6.8447 6.8394 6.8279 6.8227 6.8144

3.8055 2.3258 2.3117 2.3072 2.2924 2.2888 2.2816 2.2738 2.2630 2.2553 2.2446 2.2367 2.2295 2.2262 2.2112 2.1930 1.7052

0.8073 0.7869 0.7706

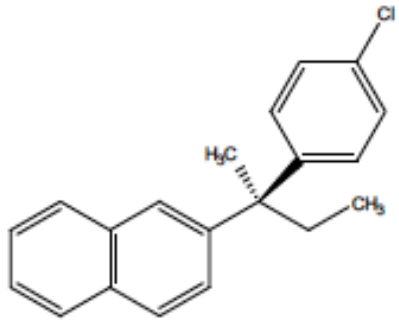


3-45



QZ-8-058-1

148.2688
146.4182
133.2653
131.9106
131.5563
129.0921
128.1838
128.1098
127.7987
127.5455
127.0017
126.1028
125.7289
124.9858
77.1600 CDCl3
46.5654
33.8643
26.9333
9.2883



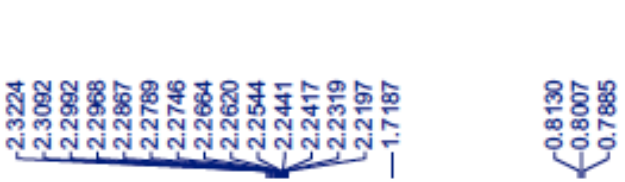
3-46

362

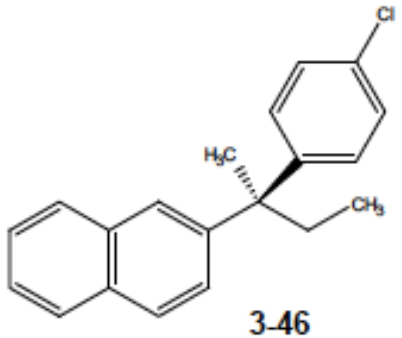
551

155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)

QZ-8-058-1



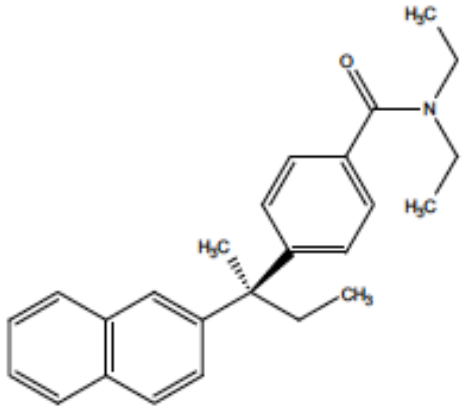
363



3-46

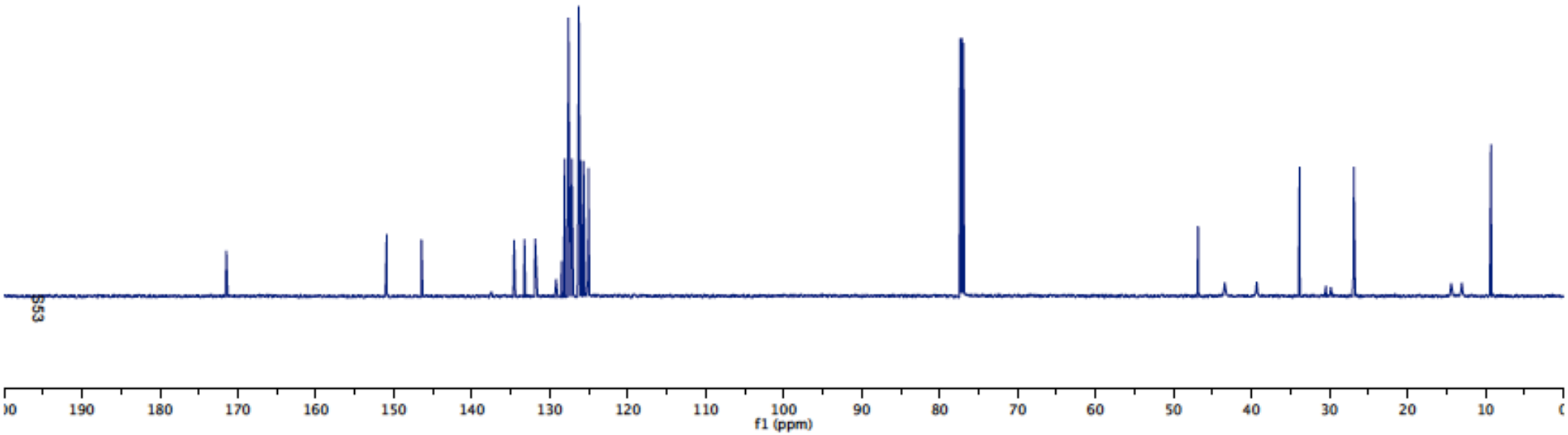
QZ-8-TYT-052-2
C13CPD256 CDCl3 /opt/nmrdata qzhou 10

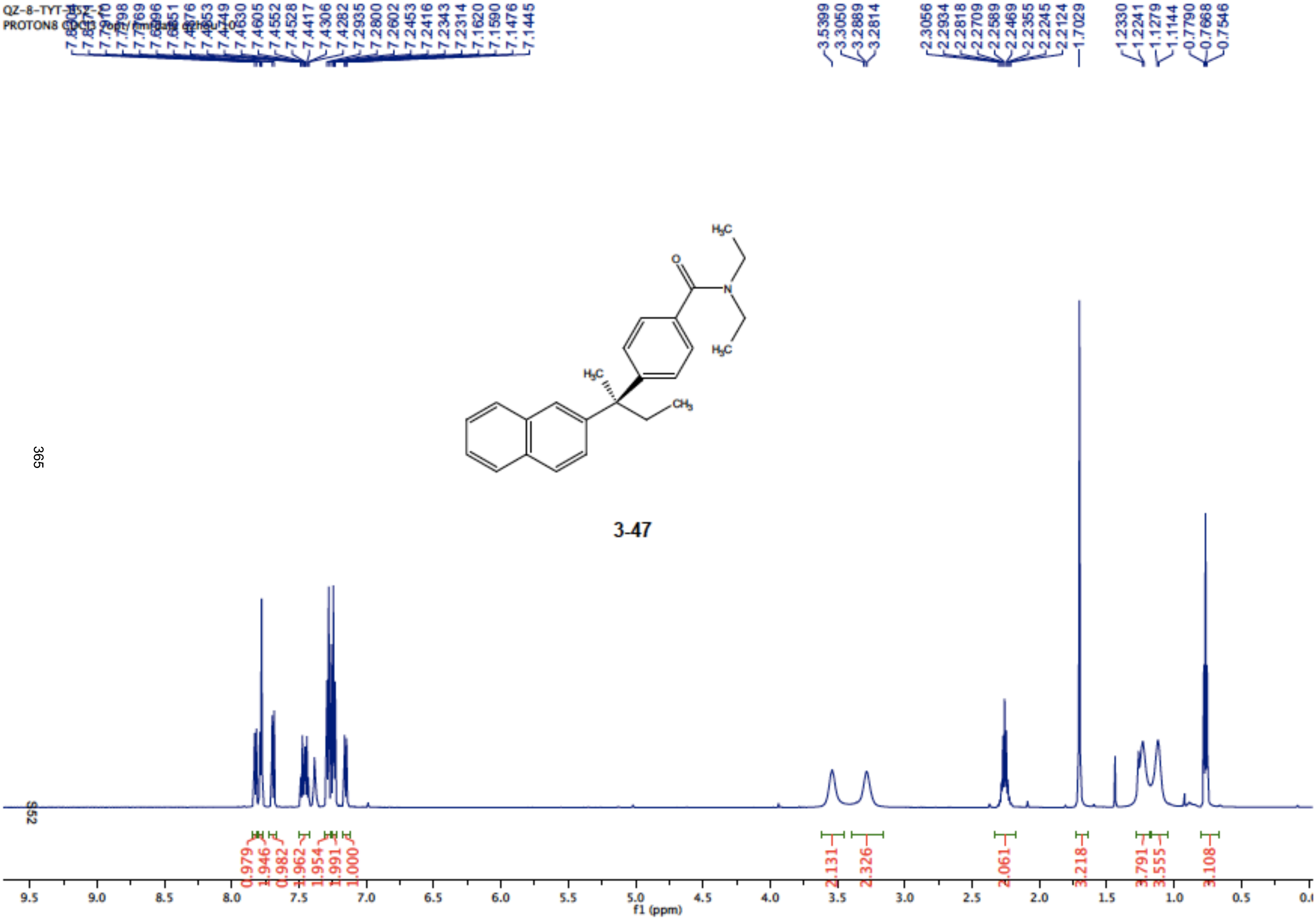
171.4812
150.9162
146.4565
134.5783
133.2420
131.8799
128.0922
127.6800
127.6085
127.5111
127.1704
126.2791
126.0286
125.6545
125.0523
77.1600 CDCl3
46.8535
43.4313
39.3409
33.8364
26.8962
14.3885
13.0286
9.2957



3-47

364

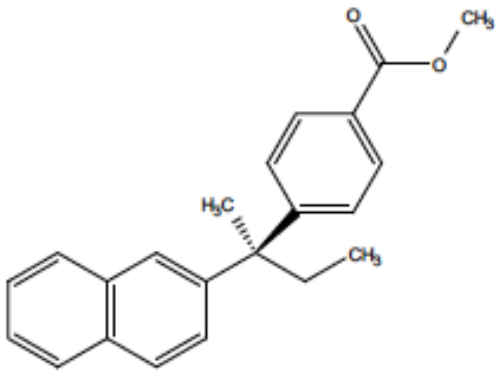



QZ-8-TYT-3-52-1
PROTON8 CDCl3 /opt/nmrdata qizheu 10
7.8304
7.8174
7.7910
7.7798
7.7769
7.6896
7.6851
7.4876
7.4853
7.4749
7.4630
7.4605
7.4552
7.4528
7.4417
7.4306
7.4282
7.2935
7.2800
7.2602
7.2453
7.2416
7.2343
7.2314
7.1620
7.1590
7.1476
7.1445
3.5399
3.3050
3.2889
3.2814
2.3056
2.2934
2.2818
2.2709
2.2589
2.2469
2.2355
2.2245
2.2124
1.7029
1.2330
1.2241
1.1279
1.1144
0.7790
0.7668
0.7546
H3C
O
N
H3C
H3C
CH3
S52
0.979
1.946
0.982
1.962
1.954
1.991
1.000
2.131
2.326
2.061
3.218
3.791
3.555
3.108
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3-47

QZ-P5-ESTER
C13CPD256 CDCl3 /opt/nmrdata qzhou 28

167.2292
155.1495
146.2048
133.2678
131.9357
129.4467
128.1170
127.8421
127.7519
127.7286
127.5516
126.9716
126.1294
125.7670
125.0479
77.1600 CDCl3
52.1169
47.1793
33.7852
26.7919
9.2566



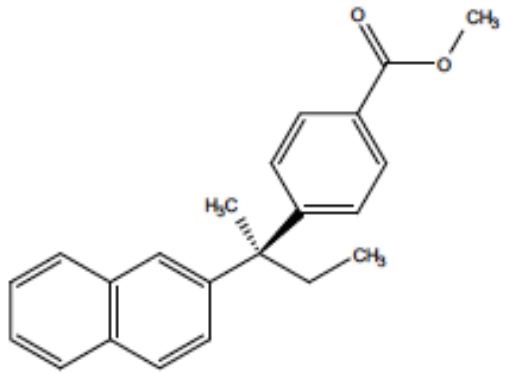
3-48

366

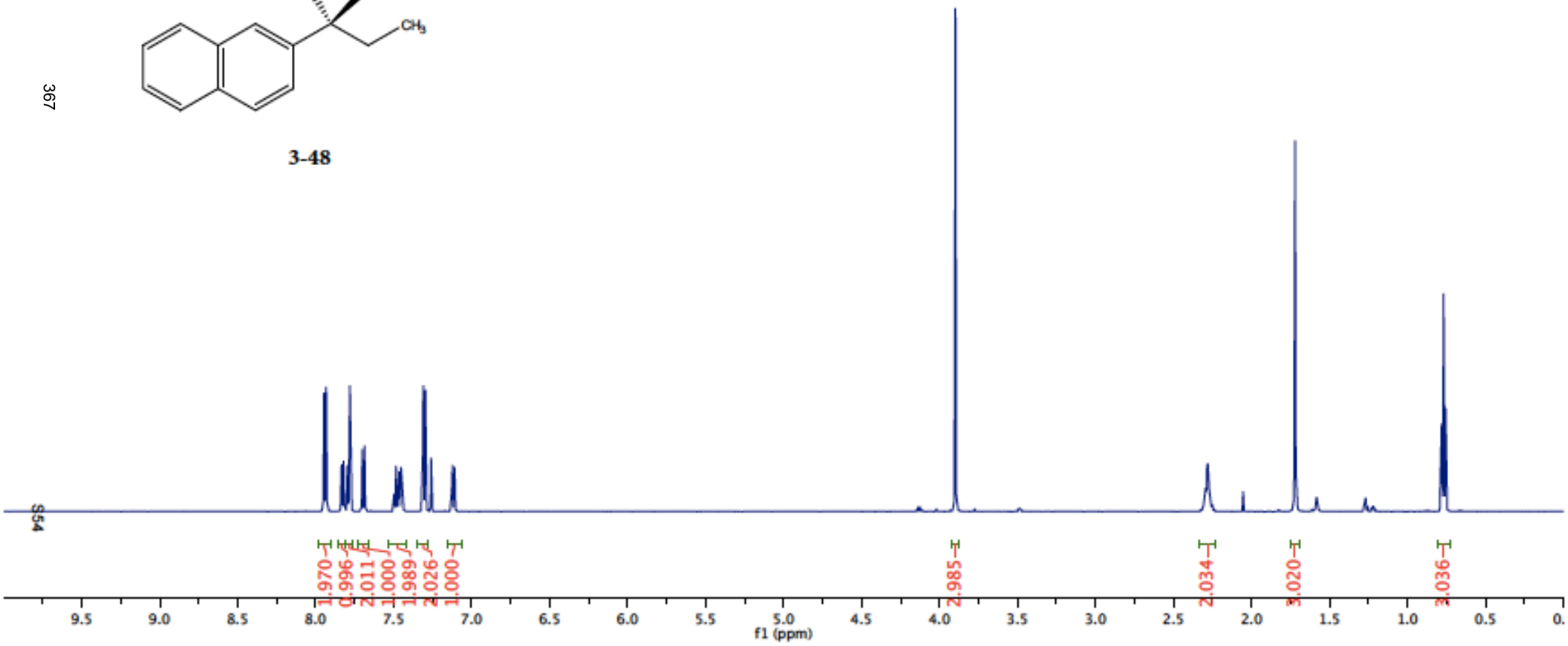
555

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

QZ-P5-ESTER
PROTON8 CDCl3 /opt/nmrdata qzhou 28

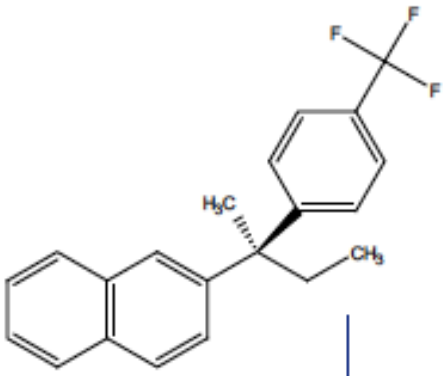


3-48



QZ 8-170-1-C.1.fid
QZ 8-170-1-C
C13CPD32 CDCl3 /opt/topspin kmrob 42

153.9134
145.9336
133.2344
131.9330
128.5075
128.1808
128.1204
127.9666
127.9255
127.8605
127.7670
127.5704
127.5375
126.9377
126.1948
125.8413
125.8102
125.0868
125.0506
125.0131
124.9756
123.1086
100.0797
77.4600 CDCl3
47.0277
33.7696
26.8342
9.2522

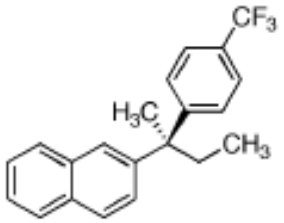


3-49

368

557

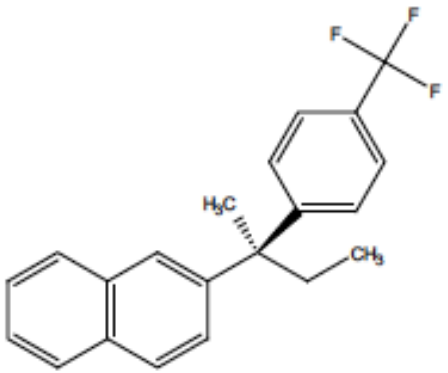
.80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


CF3
H3C
CH3

3-49

-62.21
-62.48
369
558
1.00
0.03
-40 -41 -42 -43 -44 -45 -46 -47 -48 -49 -50 -51 -52 -53 -54 -55 -56 -57 -58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74 -75 -76 -77 -78 -79
f1 (ppm)

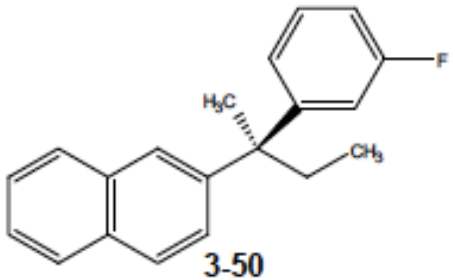
QZ 8-170-1-H.1.fid
QZ 8-170-1-H
PROTON_16 CDCl3 /opt/topspin kmrob 42



3-49

QZ-8-066-1A
C13CPD256 CDCl3 /opt/nmrdata qzhou 11

163.7318
162.1118
152.6313
152.5888
146.2849
133.2818
131.9363
129.4298
129.3751
128.1336
127.8054
127.5458
126.9837
126.0894
125.7314
124.9809
123.3933
123.3756
114.7691
114.6252
112.6972
112.5573
77.1600 CDCl3
46.8818
46.8716
33.8450
26.8301
9.2779



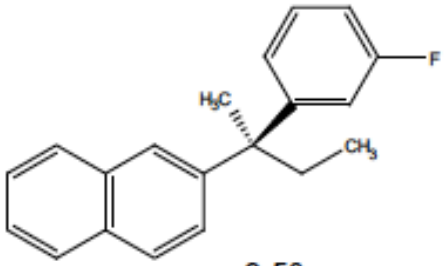
3-50

371

f1 (ppm)

QZ-8-066-1A
F19CPD16 CDCl3 /opt/nmrdata qzhou 11

-113.6002



3-50

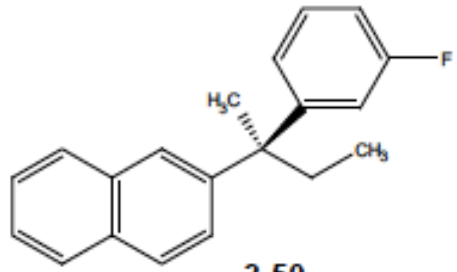
372

961

10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

f1 (ppm)

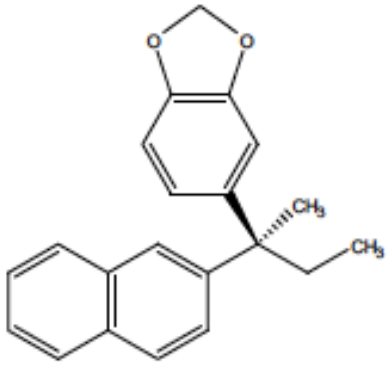
QZ-8-066-1A
PROTON8 CDCl3 /opt/nmrdata qzhou 11



3-50

QZ-P5-14
C13CPD256 CDCl3 /opt/nmrdata qzhou 34

147.5567
147.0948
145.4482
143.8385
133.2890
131.8654
128.1085
127.6611
127.5131
127.1468
125.9845
125.5874
124.7555
120.3690
108.6605
107.6091
100.9370
77.1600 CDCl3
46.6371
34.0513
27.1024
9.3576



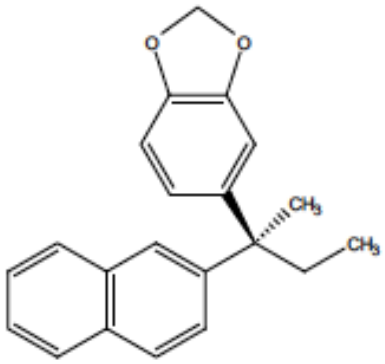
3-51

374

S63

f1 (ppm)

QZ-P5-14
PROTON8 CDCl3 /opt/nmrdata qzhou 34

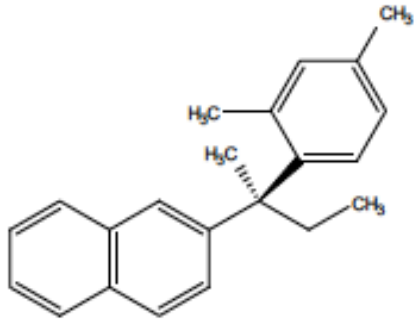


3-51

f1 (ppm)

QZ 8-172-1-C.1.fid
QZ 8-172-1-C
C13CPD32 CDCl3 /opt/topspin kmrob 9

148.1849
142.7814
137.1738
135.7482
133.4654
133.4343
131.7033
128.0126
127.7085
127.5507
127.4988
126.2825
126.0953
125.8306
125.2735
124.1825
77.1600 CDCl3
46.8538
32.8128
27.9761
21.8815
20.8726
9.5077



3-52

376

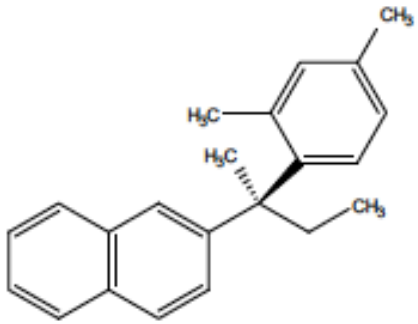
f1 (ppm)

QZ 8-172-1-H.1.fid
QZ 8-172-1-H
PROTON_16 CDCl3 /opt/topspin kmrob 52

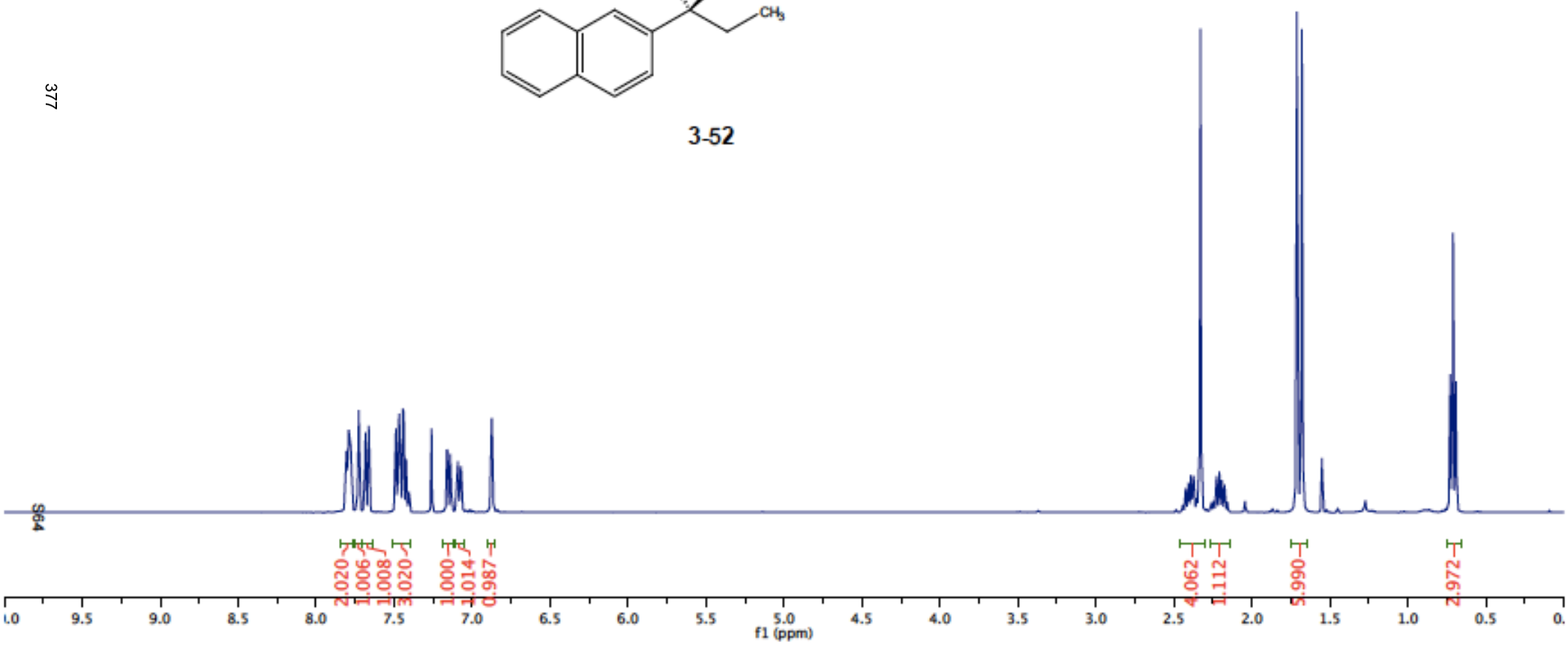
7.8090 7.8049 7.7975 7.7913 7.7853 7.7781 7.7738 7.7301 7.7253 7.6842 7.6627 7.4888 7.4791 7.4757 7.4688 7.4620 7.4581 7.4550 7.4434 7.4383 7.4266 7.4237 7.4200 7.4063 7.4028 CDCl3 7.1620 7.1572 7.1404 7.1356 7.0943 7.0914 7.0886 7.0744 7.0708 7.0679 6.8761 6.8728 6.8696

2.4247 2.4103 2.4062 2.3914 2.3805 2.3731 2.3546 2.3297 2.2602 2.2450 2.2267 2.2087 2.1936 2.1899 2.1751 2.1570 1.7110 1.6792

0.7283 0.7099 0.6915

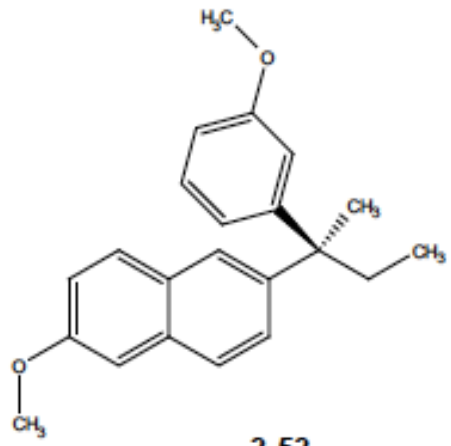


3-52



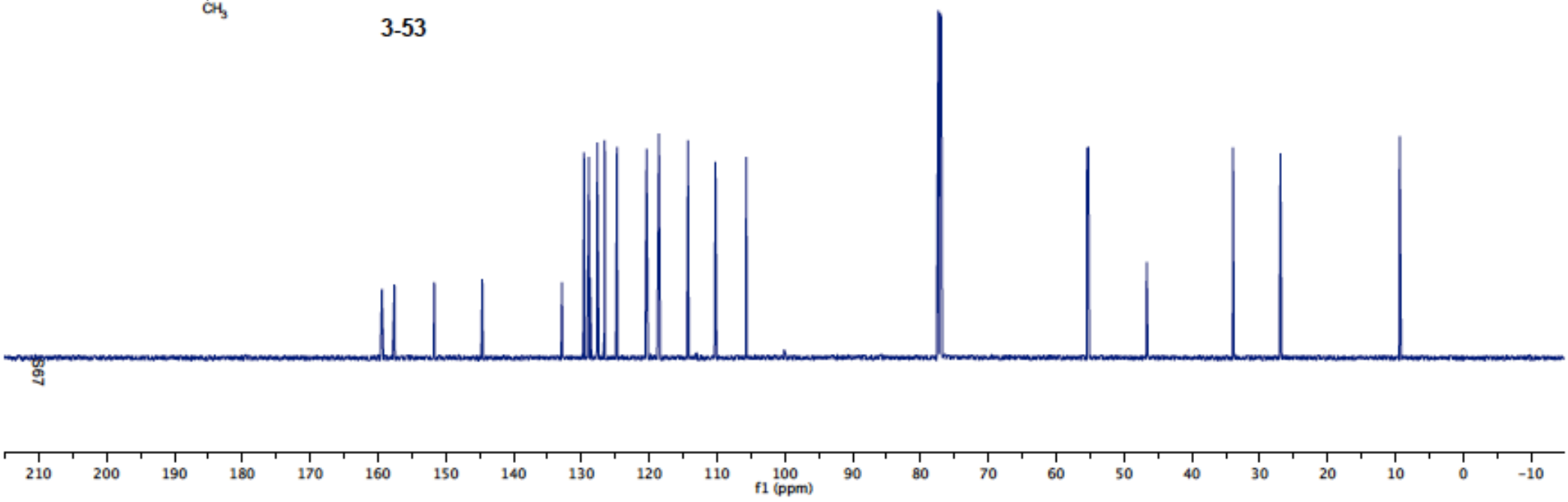
QZ-8-060-1.2.fid
QZ-8-060-1
C13CPD256 CDCl3 /opt/nmrdata qzhou 31

159.4226
157.5752
151.6911
144.6194
132.8664
129.6026
128.8975
128.7233
127.6773
126.5617
124.7679
120.3890
118.5771
114.2849
110.2401
105.7021
77.1600 CDCl3
55.4626
55.2498
46.6558
33.9275
26.9418
9.3619

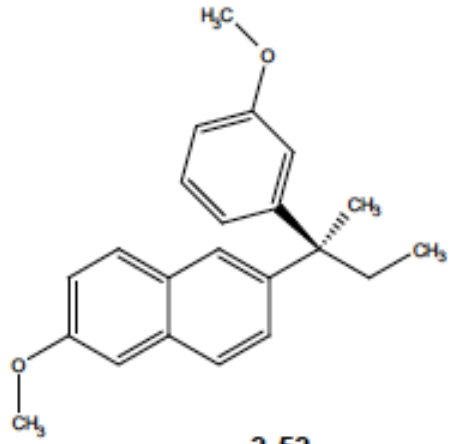


3-53

378



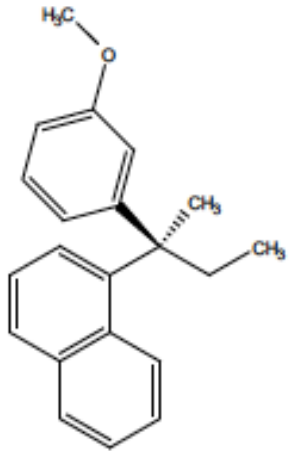
QZ-8-060-1.1.fid
QZ-8-060-1
PROTON8 CDCl3 /opt/nmrdata qzhou 31



3-53

QZ-P5-17
C13CPD256 CDCl3 /opt/nmrdata qzhou 36

159.6816
153.0956
143.2991
135.0391
131.5940
129.2766
129.0239
127.8726
127.2940
125.3149
124.8933
124.7691
124.6762
119.3869
113.1137
109.9678
77.1600 CDCl3
55.2120
47.4640
33.5703
29.4390
9.4348

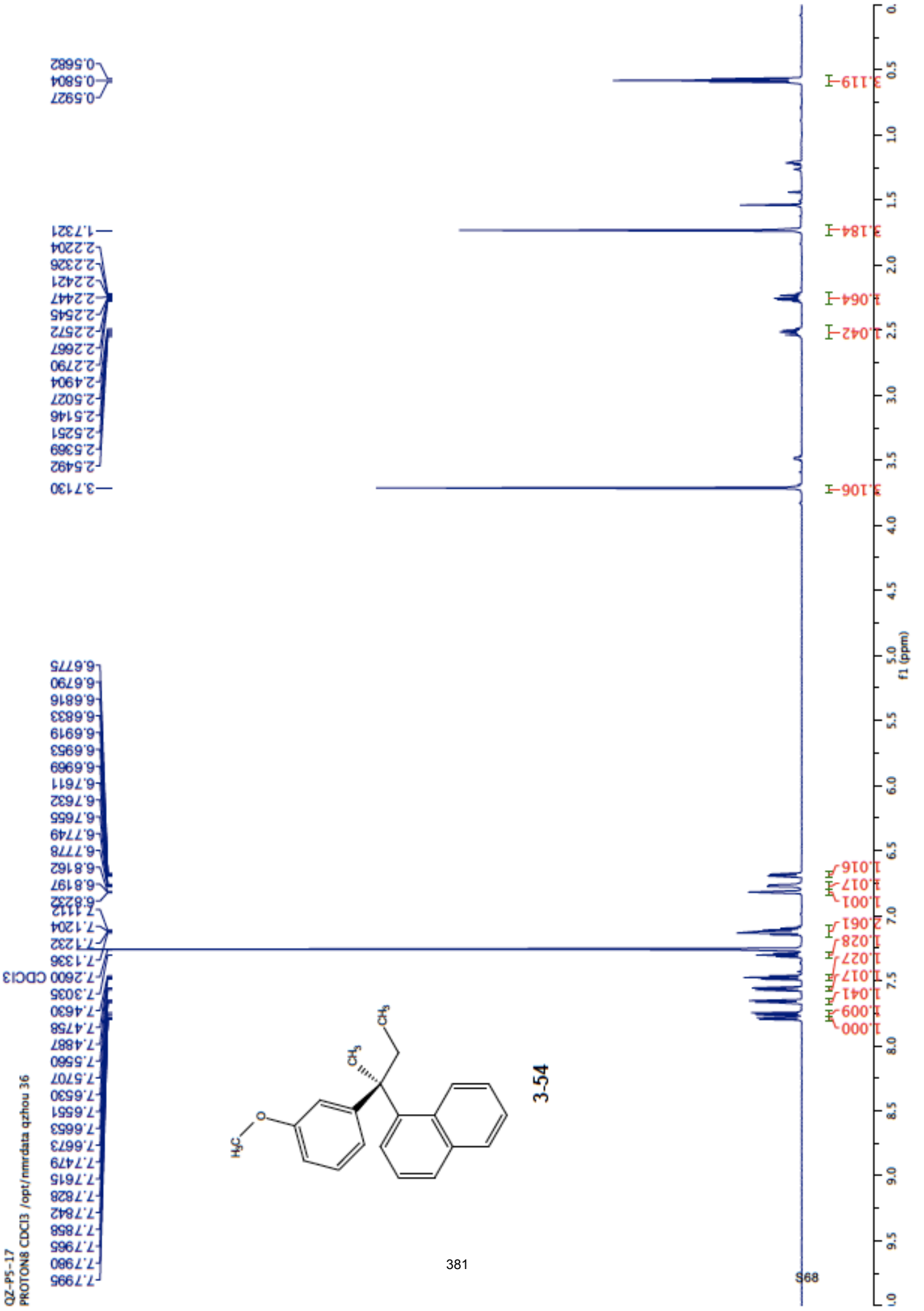


3-54

380

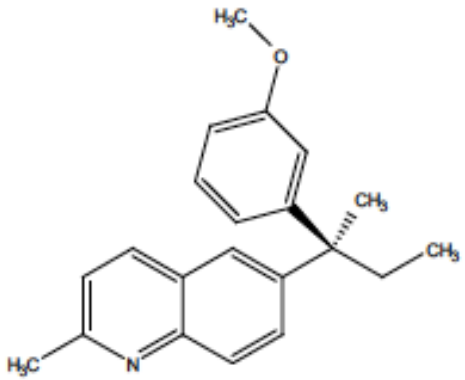
695

f1 (ppm)


QZ-PS-17
PROTON8 CDCl3 /opt/nmrdata qzhou 36
CDCl3
f1 (ppm)
3-54
S68

QZ-P5-18
C13CPD256 CDCl3 /opt/nmrdata qzhou 33

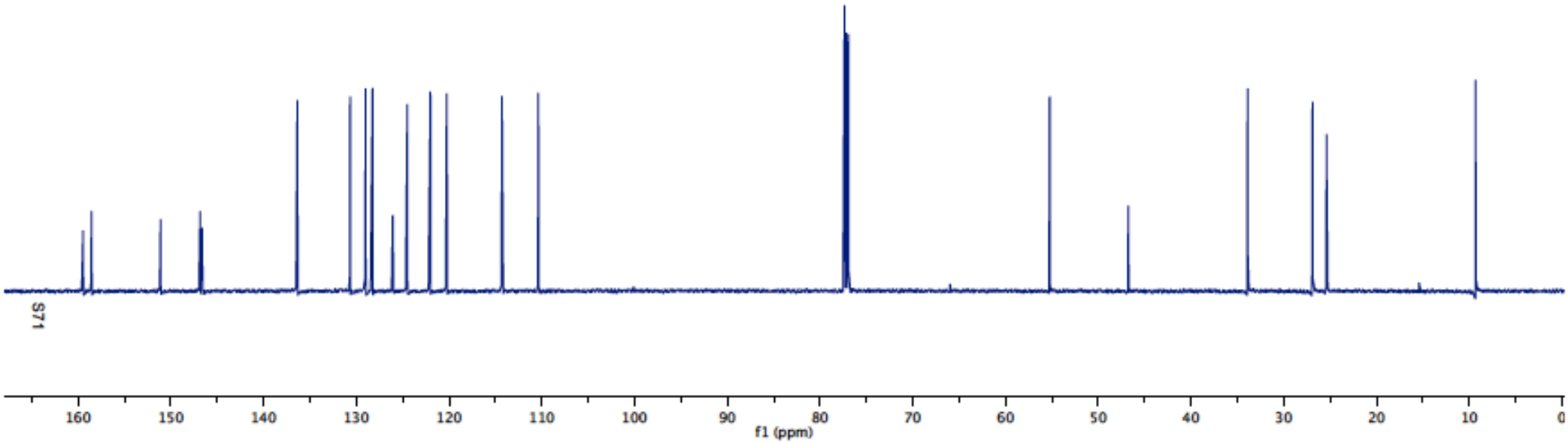
159.4628
158.5527
151.1139
146.8517
146.6337
136.3670
130.6775
129.0184
128.2582
126.0823
124.5082
122.0207
120.2642
114.2985
110.3769
77.1600 CDCl3
55.2386
46.7558
33.9032
26.8986
25.3959
9.3154

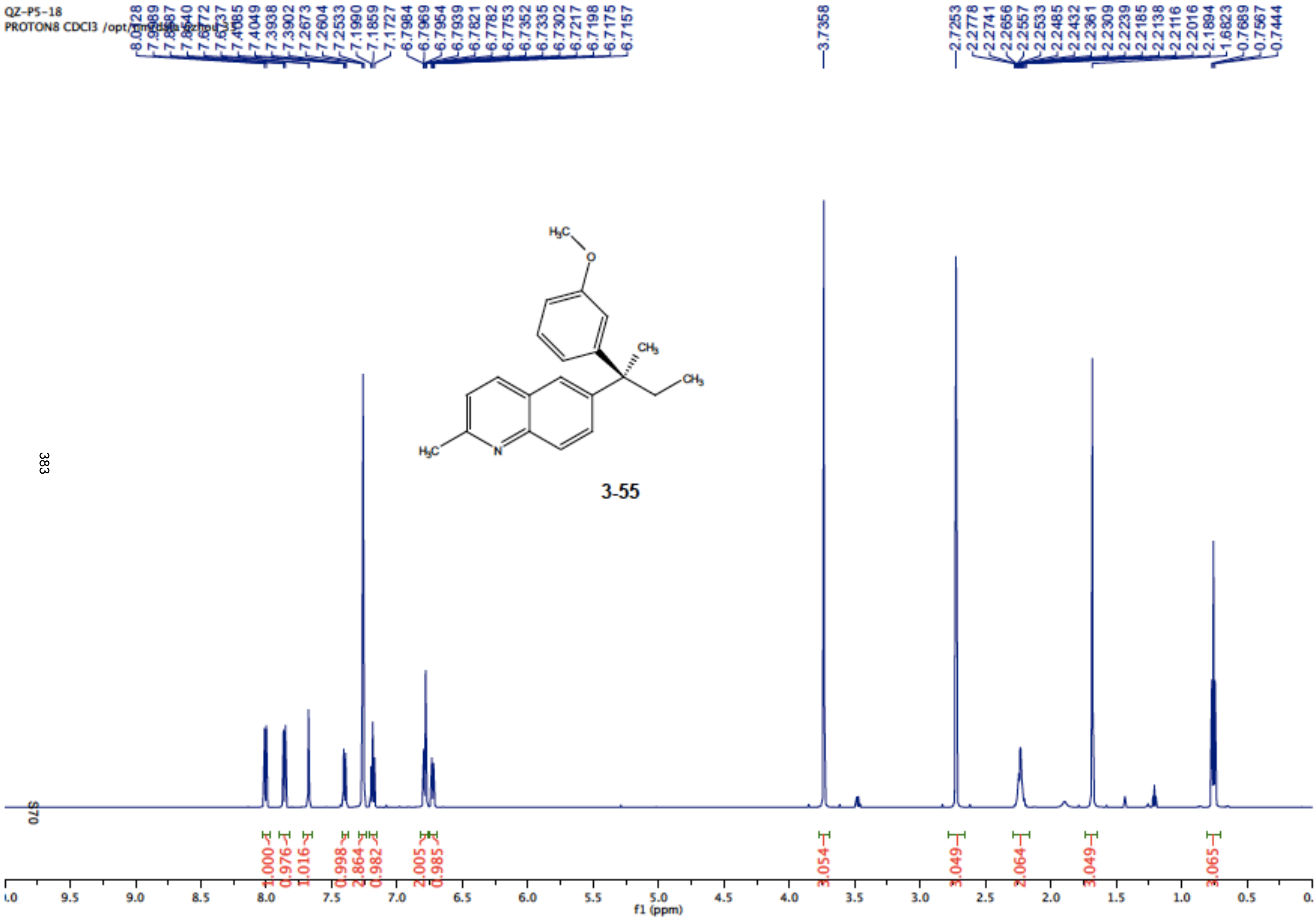


382

3-55

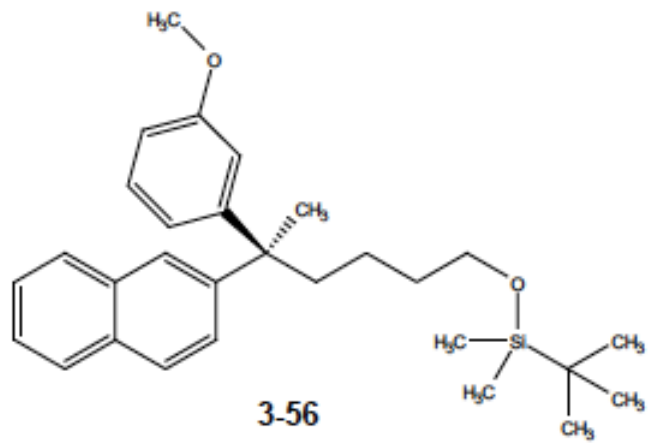
S71




QZ-P5-18
PROTON8 CDCl3 /opt/nmrdata/qzhou/3
8.0028
7.9989
7.8687
7.8640
7.6772
7.6737
7.4085
7.4049
7.3938
7.3902
7.2673
7.2604
7.2533
7.1990
7.1859
7.1727
6.7984
6.7969
6.7954
6.7939
6.7821
6.7782
6.7753
6.7352
6.7335
6.7302
6.7217
6.7198
6.7175
6.7157
3.7358
2.7253
2.2778
2.2741
2.2656
2.2557
2.2533
2.2485
2.2432
2.2361
2.2309
2.2239
2.2185
2.2138
2.2116
2.2016
2.1894
1.6823
0.7689
0.7567
0.7444
3-55
1.000
0.976
1.016
0.998
2.864
0.982
2.005
0.985
3.054
3.049
2.064
3.049
3.065
f1 (ppm)
S70

QZ-PS-19
C13CPD256 CDCl3 /opt/nmrdata qzhou 32

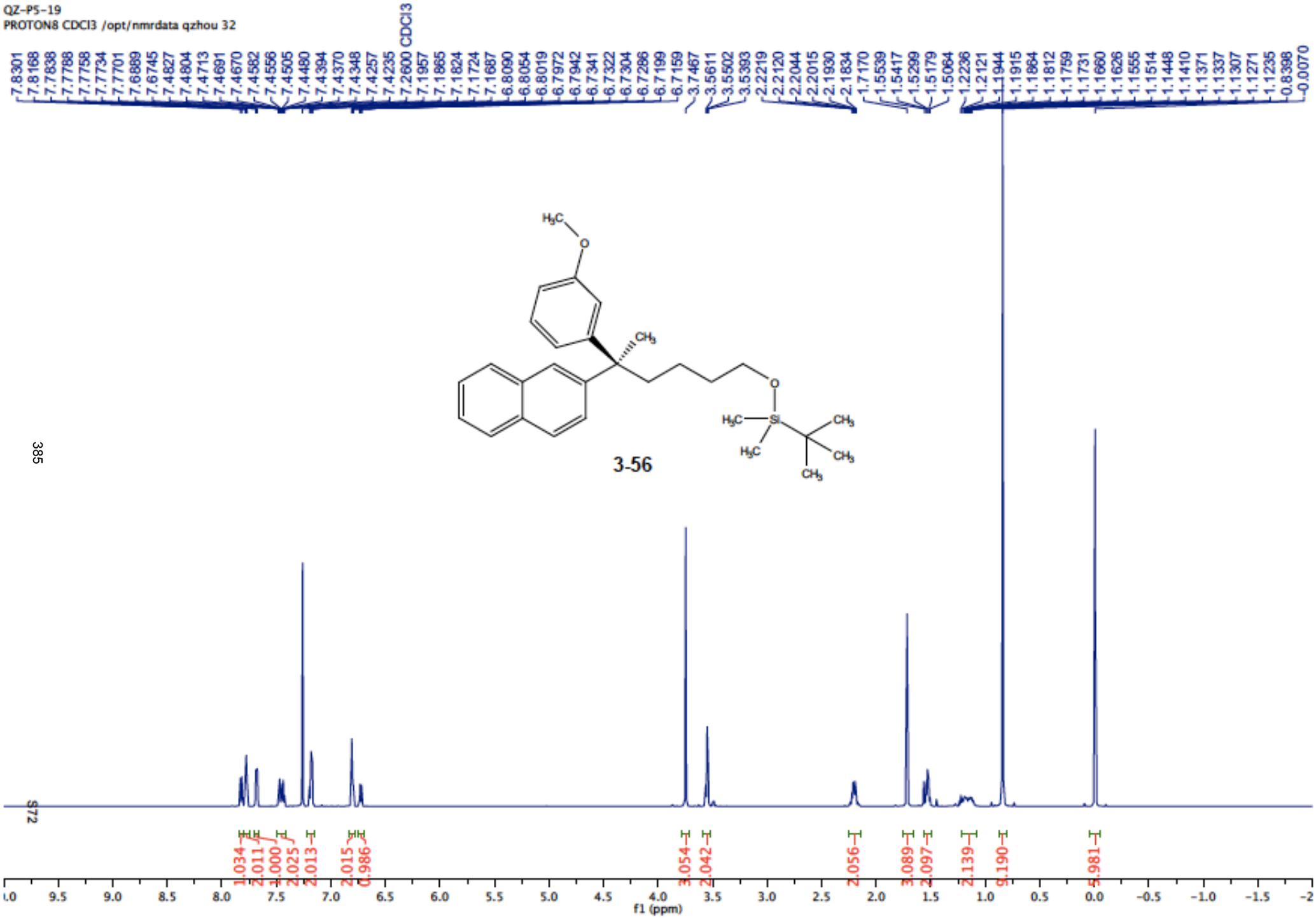
159.4446
151.5830
147.0107
133.3072
131.8969
128.9684
128.1329
127.6540
127.5043
127.1363
125.9212
125.5387
124.7416
120.2884
114.2137
110.2886
77.1600 CDCl3
63.1767
55.2449
46.6185
41.3942
33.6927
27.5744
26.0567
21.2801
18.4187
-5.1472



3-56

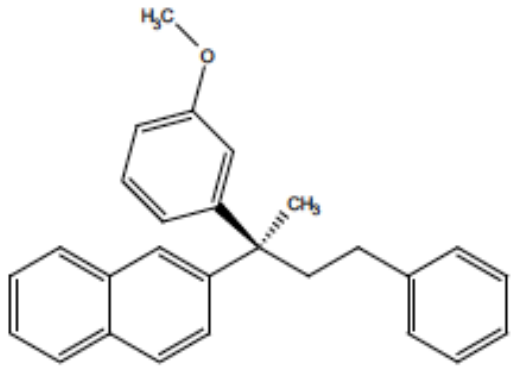
384

f1 (ppm)


QZ-P5-19
PROTON8 CDCl3 /opt/nmrdata qzhou 32
CDCl3
3-56
f1 (ppm)

QZ-P5-20
C13CPD256 CDCl3 /opt/nmrdata qzhou 38

159.5628
151.1202
146.6431
143.0156
133.3285
131.9583
129.1330
128.5063
128.5006
128.1528
127.8569
127.5406
127.0299
126.0500
125.8694
125.6794
124.7693
120.2469
114.2106
110.5092
77.1600 CDCl3
55.2968
46.7016
43.8754
31.5138
27.5307

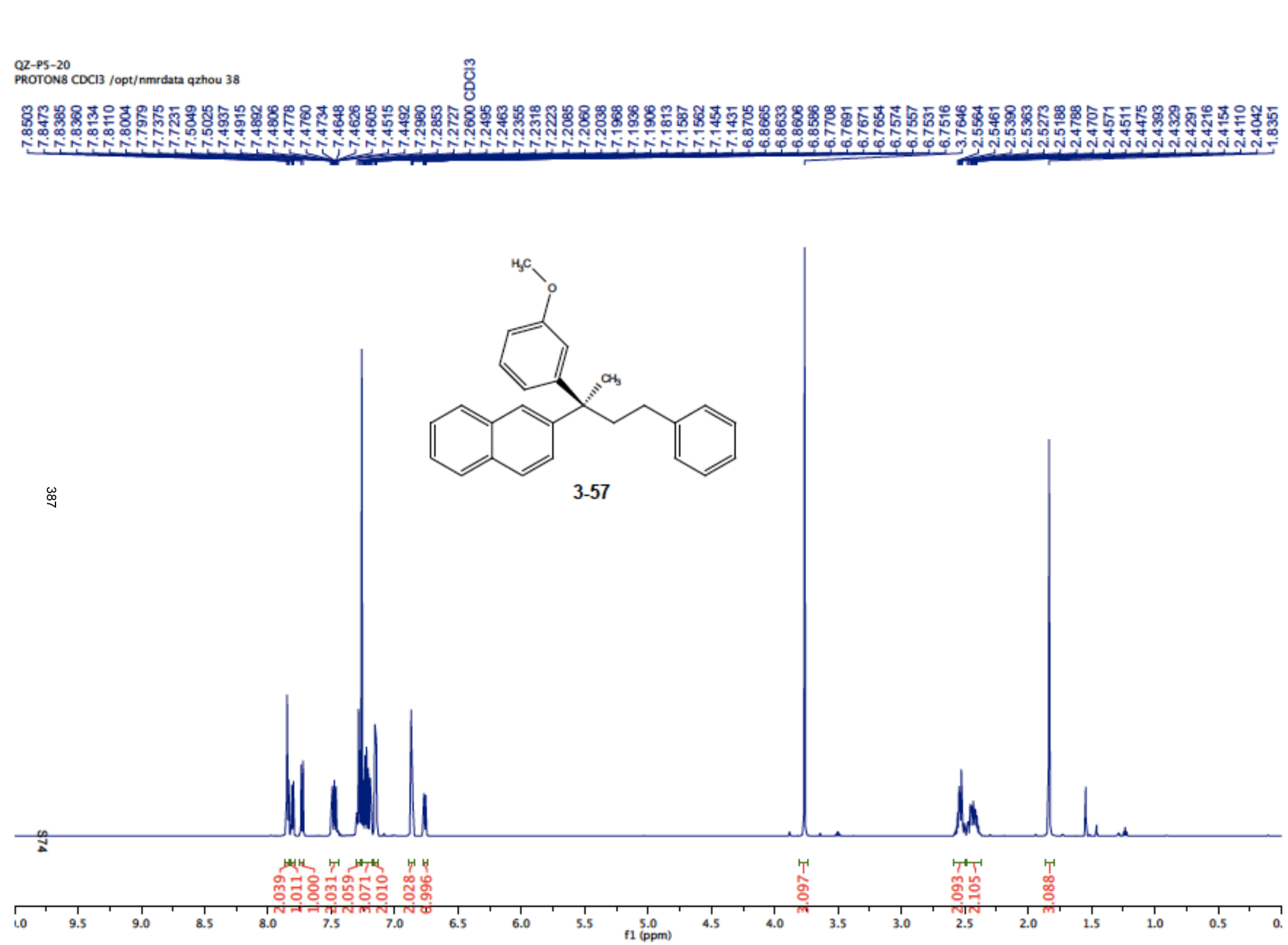


3-57

386

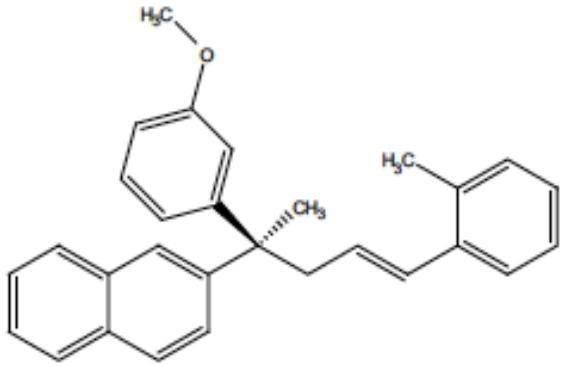
875

f1 (ppm)


QZ-P5-20
PROTON8 CDCl3 /opt/nmrdata qzhou 38
CDCl3
7.8503
7.8473
7.8385
7.8360
7.8134
7.8110
7.8004
7.7979
7.7375
7.7231
7.5049
7.5025
7.4937
7.4915
7.4892
7.4806
7.4778
7.4760
7.4734
7.4648
7.4626
7.4605
7.4515
7.4492
7.2960
7.2853
7.2727
7.2600
7.2495
7.2463
7.2355
7.2318
7.2223
7.2085
7.2060
7.2038
7.1968
7.1936
7.1906
7.1813
7.1587
7.1562
7.1454
7.1431
6.8705
6.8665
6.8633
6.8606
6.8586
6.7708
6.7691
6.7671
6.7654
6.7574
6.7557
6.7531
6.7516
3.7646
2.5564
2.5461
2.5390
2.5363
2.5273
2.5188
2.4788
2.4707
2.4571
2.4511
2.4475
2.4393
2.4329
2.4291
2.4216
2.4154
2.4110
2.4042
1.8351
H3C
O
CH3
3-57
387
374
2.039
1.011
1.000
2.031
2.059
3.071
2.010
2.028
6.996
3.097
2.093
2.105
3.088
f1 (ppm)

QZ-8-135-1
C13CPD256 CDCl3 /opt/nmrdata qzhou 23

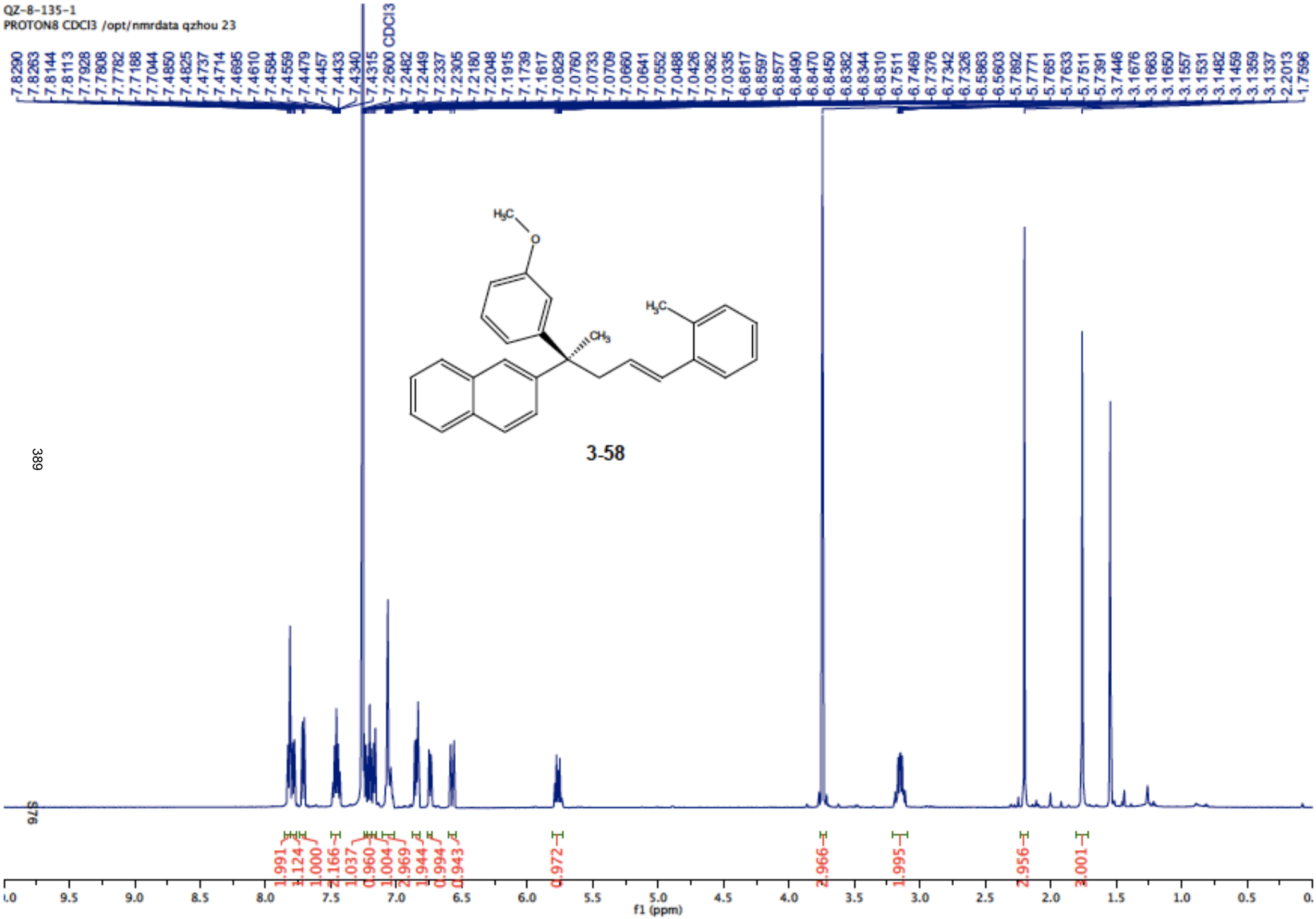
159.5317
150.9580
146.5152
137.0559
135.1024
133.3153
131.9894
131.1193
130.1365
129.0964
128.4942
128.1919
127.7801
127.5370
127.1005
127.0417
126.0446
126.0240
125.9076
125.6797
124.8267
120.2608
114.2293
110.6315
77.1600 CDCl3
55.3001
46.7860
45.6146
27.7164
19.8382



3-58

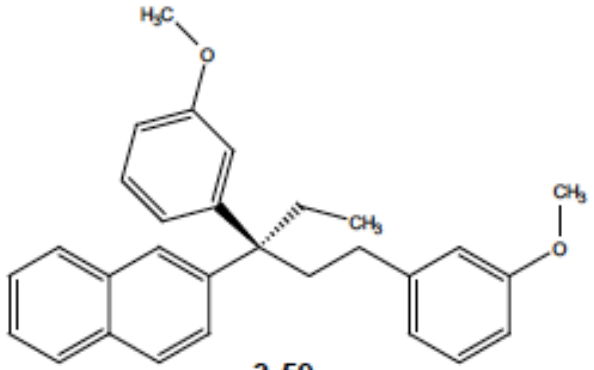
388

f1 (ppm)


QZ-8-135-1
PROTON8 CDCl3 /opt/nmrdata qzhou 23
CDCl3
7.8290
7.8263
7.8144
7.8113
7.7928
7.7808
7.7782
7.7188
7.7044
7.4850
7.4825
7.4737
7.4714
7.4695
7.4610
7.4584
7.4559
7.4479
7.4457
7.4433
7.4340
7.4315
7.2600
7.2482
7.2449
7.2337
7.2305
7.2180
7.2048
7.1915
7.1739
7.1617
7.0829
7.0760
7.0733
7.0709
7.0660
7.0641
7.0552
7.0488
7.0426
7.0362
7.0335
6.8617
6.8597
6.8577
6.8490
6.8470
6.8450
6.8382
6.8344
6.8310
6.7511
6.7469
6.7376
6.7342
6.7326
6.5863
6.5603
5.7892
5.7771
5.7651
5.7633
5.7511
5.7391
3.7446
3.1676
3.1663
3.1650
3.1557
3.1531
3.1482
3.1459
3.1359
3.1337
2.2013
1.7596
H3C
O
CH3
H3C
3-58
389
576
1.991
1.124
1.000
2.166
1.037
0.960
1.004
2.969
1.944
0.994
0.943
0.972
2.966
1.995
2.956
3.001
f1 (ppm)

QZ-8-119-1
C13CPD256 CDCl3 /opt/nmrdata qzhou 22

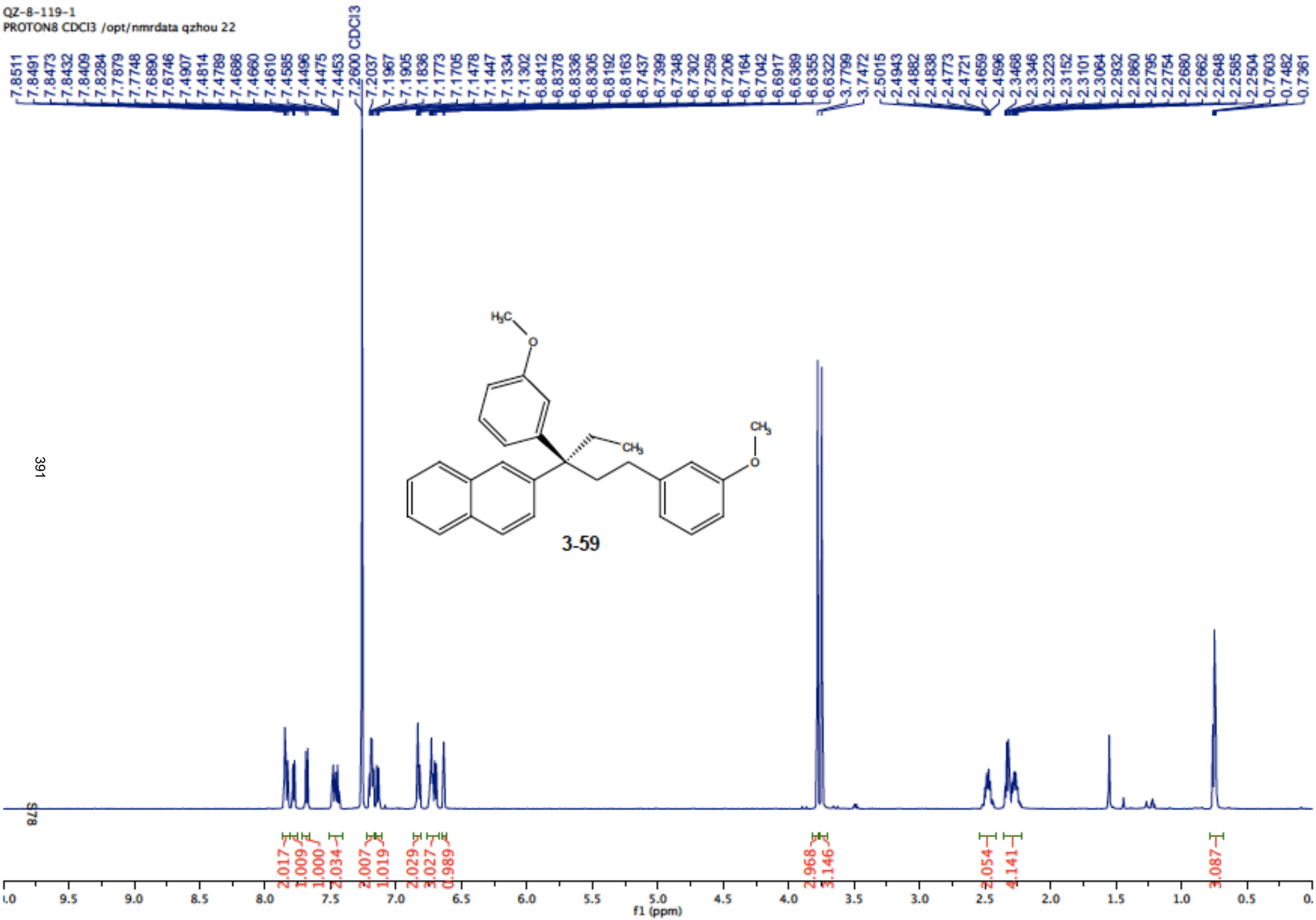
159.7617
159.4410
150.0731
145.7267
144.7897
133.1741
131.9308
129.4503
128.9078
128.1713
127.7341
127.5129
127.4844
125.9814
125.6379
125.4966
120.9337
120.9288
114.8705
114.4158
110.9810
110.3779
77.1600 CDCl3
55.2863
55.2829
49.9871
38.9310
30.8810
29.5236
8.6276



3-59

390

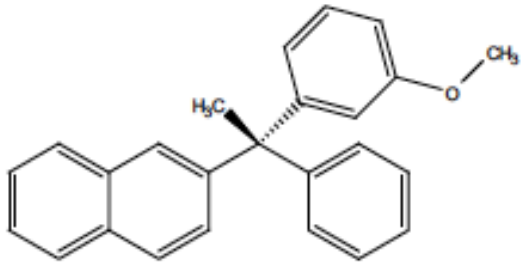
f1 (ppm)


QZ-8-119-1
PROTON8 CDCl3 /opt/nmrdata qzhou 22
CDCl3
7.8511
7.8491
7.8473
7.8432
7.8409
7.8284
7.7879
7.7748
7.6890
7.6746
7.4907
7.4814
7.4789
7.4686
7.4660
7.4610
7.4585
7.4496
7.4475
7.4453
7.2600
7.2037
7.1967
7.1905
7.1836
7.1773
7.1705
7.1478
7.1447
7.1334
7.1302
6.8412
6.8378
6.8336
6.8305
6.8192
6.8163
6.7437
6.7399
6.7348
6.7302
6.7259
6.7206
6.7164
6.7042
6.6917
6.6389
6.6355
6.6322
3.7799
3.7472
2.5015
2.4943
2.4882
2.4838
2.4773
2.4721
2.4659
2.4596
2.3468
2.3346
2.3223
2.3152
2.3101
2.3064
2.2932
2.2860
2.2795
2.2754
2.2680
2.2662
2.2648
2.2585
2.2504
0.7603
0.7482
0.7361
H3C
O
CH3
CH3
O
3-59
391
S78
2.017
1.009
1.000
2.034
2.007
1.019
2.029
3.027
0.989
2.968
3.146
2.054
4.141
3.087
f1 (ppm)

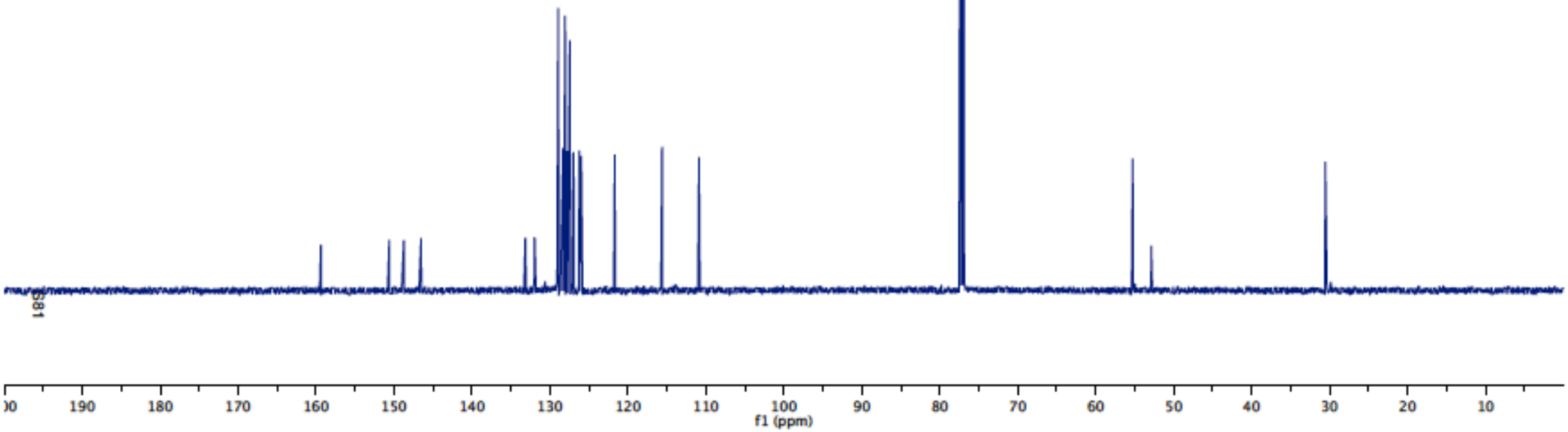
QZ-8-155-1
C13CPD256 CDCl3 /opt/nmrdata qzhou 13

159.3912
150.6256
148.7544
146.5370
133.1652
131.9677
130.6151
128.9438
128.9156
128.3354
128.0558
127.7844
127.4625
126.9718
126.2296
126.0031
125.8594
121.7021
115.6275
110.8911
77.1600 CDCl3
55.2607
52.8719
30.5566

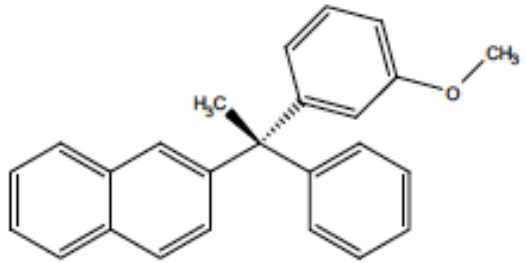
392



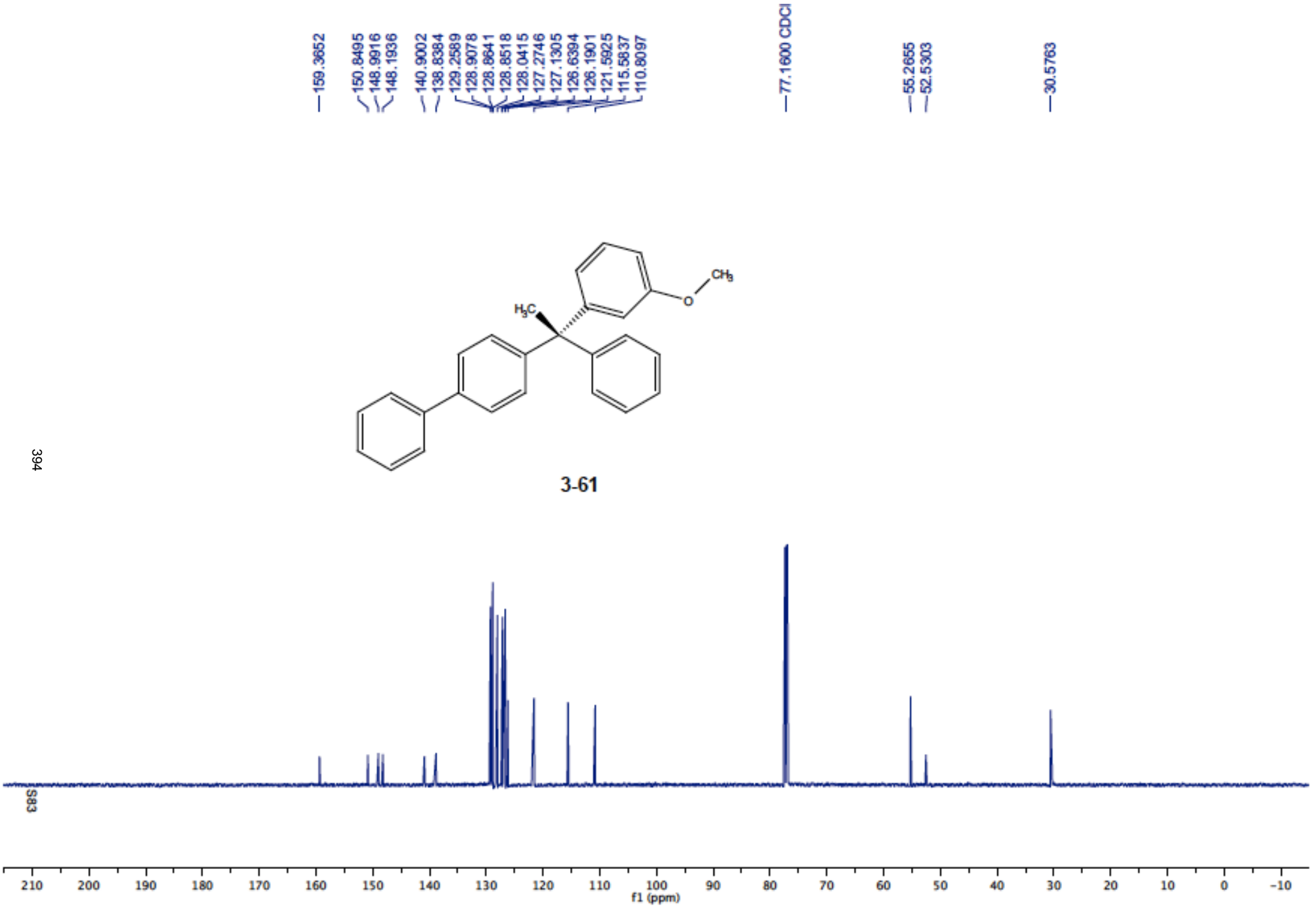
3-60

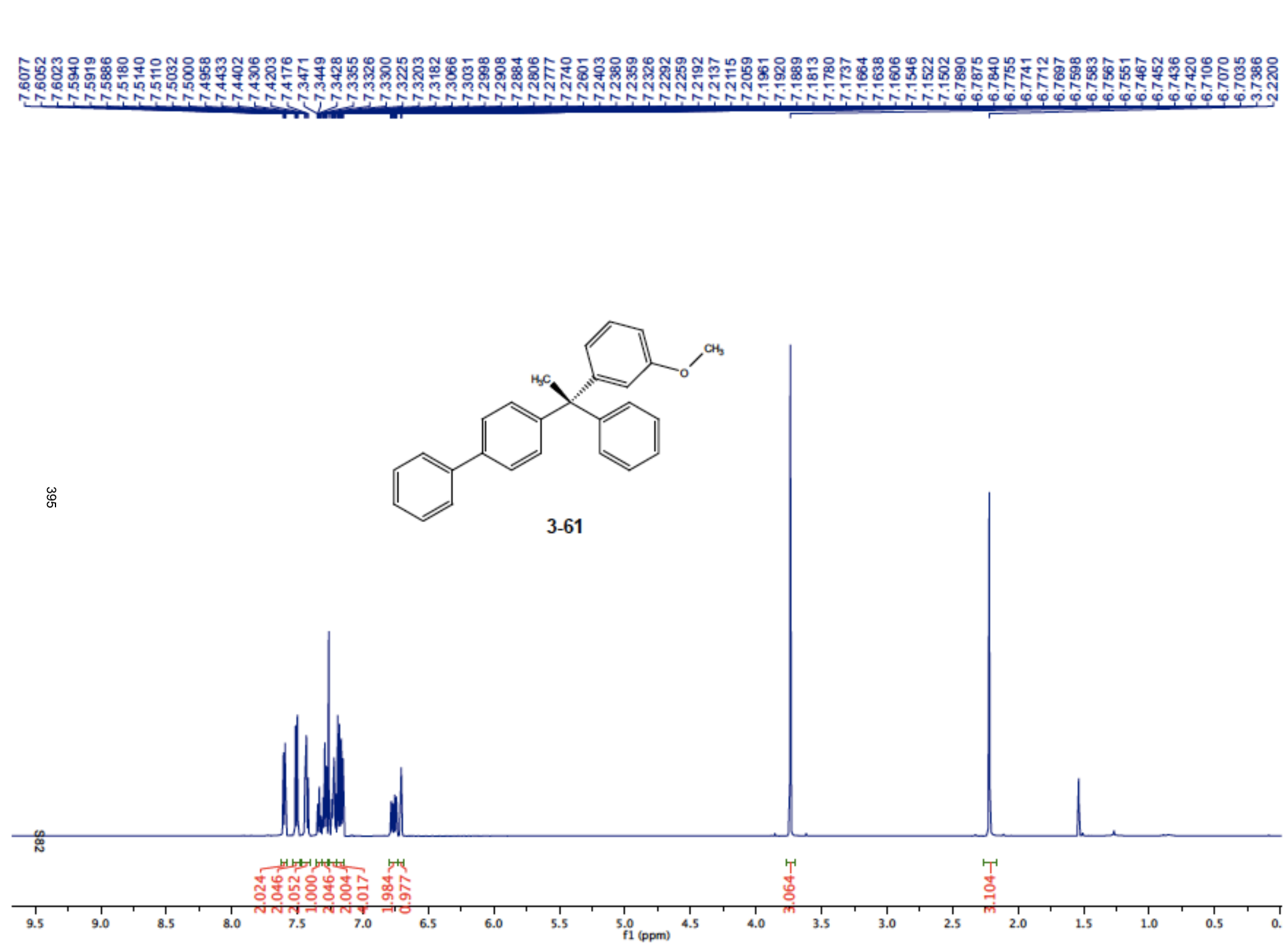


QZ-8-155-1
PROTON8 CDCl3 /opt/nmrdata qzhou 13



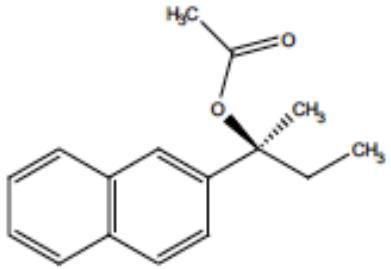
3-60


159.3652
150.8495
148.9916
148.1936
140.9002
138.8384
129.2589
128.9078
128.8641
128.8518
128.0415
127.2746
127.1305
126.6394
126.1901
121.5925
115.5837
110.8097
77.1600 CDCl
55.2655
52.5303
30.5763
CH3
O
H3C
3-61
S83
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.6077
7.6052
7.6023
7.5940
7.5919
7.5886
7.5180
7.5140
7.5110
7.5032
7.5000
7.4958
7.4433
7.4402
7.4306
7.4203
7.4176
7.3471
7.3449
7.3428
7.3355
7.3326
7.3300
7.3225
7.3203
7.3182
7.3066
7.3031
7.2998
7.2908
7.2884
7.2806
7.2777
7.2740
7.2601
7.2403
7.2380
7.2359
7.2326
7.2292
7.2259
7.2192
7.2137
7.2115
7.2059
7.1961
7.1920
7.1889
7.1813
7.1780
7.1737
7.1664
7.1638
7.1606
7.1546
7.1522
7.1502
6.7890
6.7875
6.7840
6.7755
6.7741
6.7712
6.7697
6.7598
6.7583
6.7567
6.7551
6.7467
6.7452
6.7436
6.7420
6.7106
6.7070
6.7035
3.7386
2.2200
H3C
O
CH3
3-61
395
S82
2.024
2.046
2.052
1.000
1.046
2.004
4.017
1.984
0.977
3.064
3.104
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

QZ-7-191-1.2.fid
QZ-7-191-1
C13CPD256 CDCl3 /opt/nmrdata qzhou 16

169.8367
142.3947
133.2393
132.5155
128.3367
128.0681
127.6227
126.1554
125.8861
123.6341
123.2258
84.6106
77.1600 CDCl3
35.0971
24.5124
22.3798
8.3254



3-37*a*

396

585

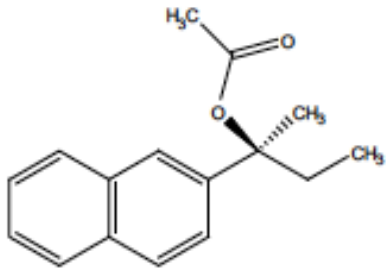
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

QZ-7-191-1.1.fid
QZ-7-191-1
PROTON8 CDCl3 /opt/nmrdata qzhou 16

7.8385 7.8366 7.8351 7.8237 7.8182 7.8042 7.8005 7.7588 7.7566 7.7548 7.4853 7.4828 7.4738 7.4712 7.4612 7.4579 7.4547 7.4513 7.4476 7.4452 7.4403 7.4368 7.4338 7.2600 CDCl3

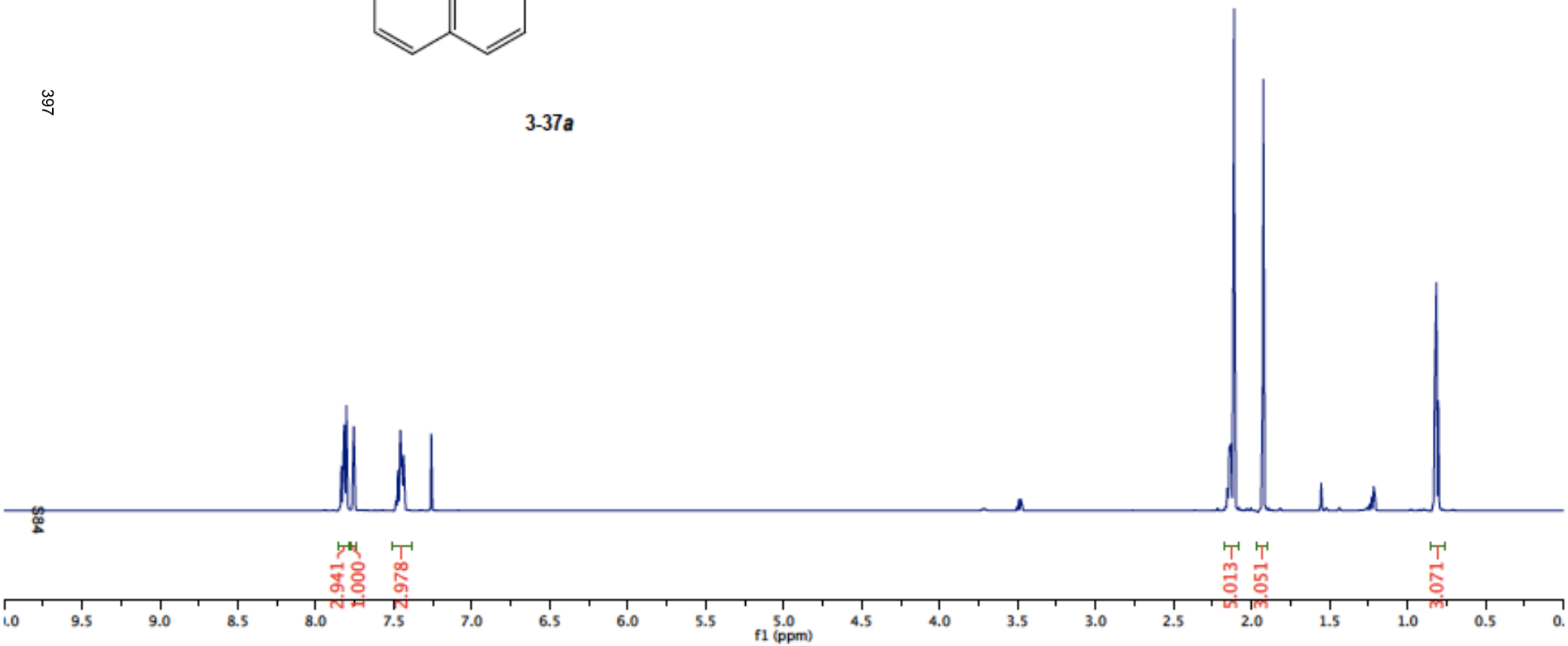
2.1562 2.1532 2.1436 2.1404 2.1313 2.1282 2.1188 2.1158 2.1122 1.9246

0.8269 0.8145 0.8021



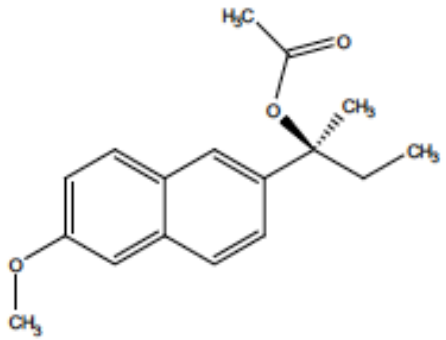
3-37*a*

397



QZ-8-055-1.2.fid
QZ-8-055-1
C13CPD256 CDCl3 /opt/nmrdata gzhou 9

169.8874
157.8034
140.1095
133.5910
129.8078
128.6806
126.9160
123.7663
123.4970
118.9521
105.6739
84.6747
77.1600 CDCl3
55.4686
35.0995
24.4920
22.4275
8.3489



3-37b

398

S87

f1 (ppm)

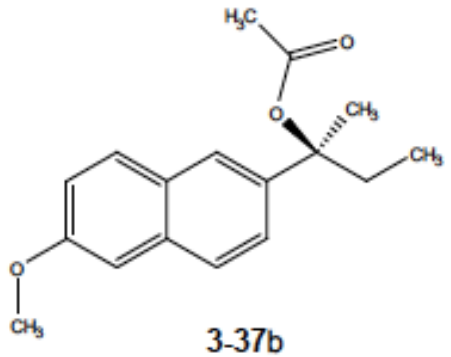
QZ-8-055-1.1.fid
QZ-8-055-1
PROTON8 CDCl3 /opt/nmrdata qzhou 9

7.7254
7.7104
7.7071
7.6927
7.6797
7.6765
7.4131
7.4099
7.3988
7.3955
7.2600 CDCl3
7.1464
7.1422
7.1317
7.1275
7.1107
7.1065

3.9120

2.1417
2.1371
2.1295
2.1245
2.1171
2.1122
2.1047
2.0961
2.0890
2.0837
1.9029

0.8128
0.8004
0.7881



3-37b

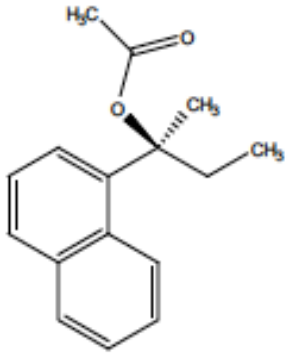
399

3.056
1.000
1.002
1.019
3.158
5.129
3.082
3.118

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

QZ-P5-1C-RERUN
C13CPD256 CDCl3 /opt/nmrdata qzhou 47

169.4549
139.8557
134.8647
130.4144
129.6911
128.7122
125.6416
125.4998
125.1200
124.9698
124.2951
85.6472
77.1600 CDCl3
33.9539
24.5636
21.8235
8.6762



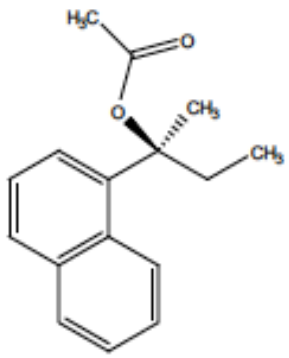
400

3-37c

689

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

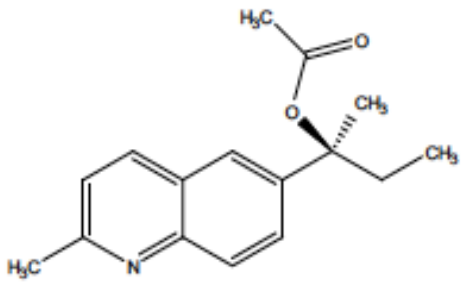
QZ-P5-1C-RERUN
PROTON8 CDCl3 /opt/nmrdata qzhou 47



3-37c

QZ-P5-1D
C13CPD256 CDCl3 /opt/nmrdata qzhou 31

169.8193
158.9881
147.0698
142.2440
136.5306
128.7441
126.7356
126.0862
123.2382
122.2677
84.2808
77.1600 CDCl3
35.1011
25.4306
24.4015
22.3340
8.2693

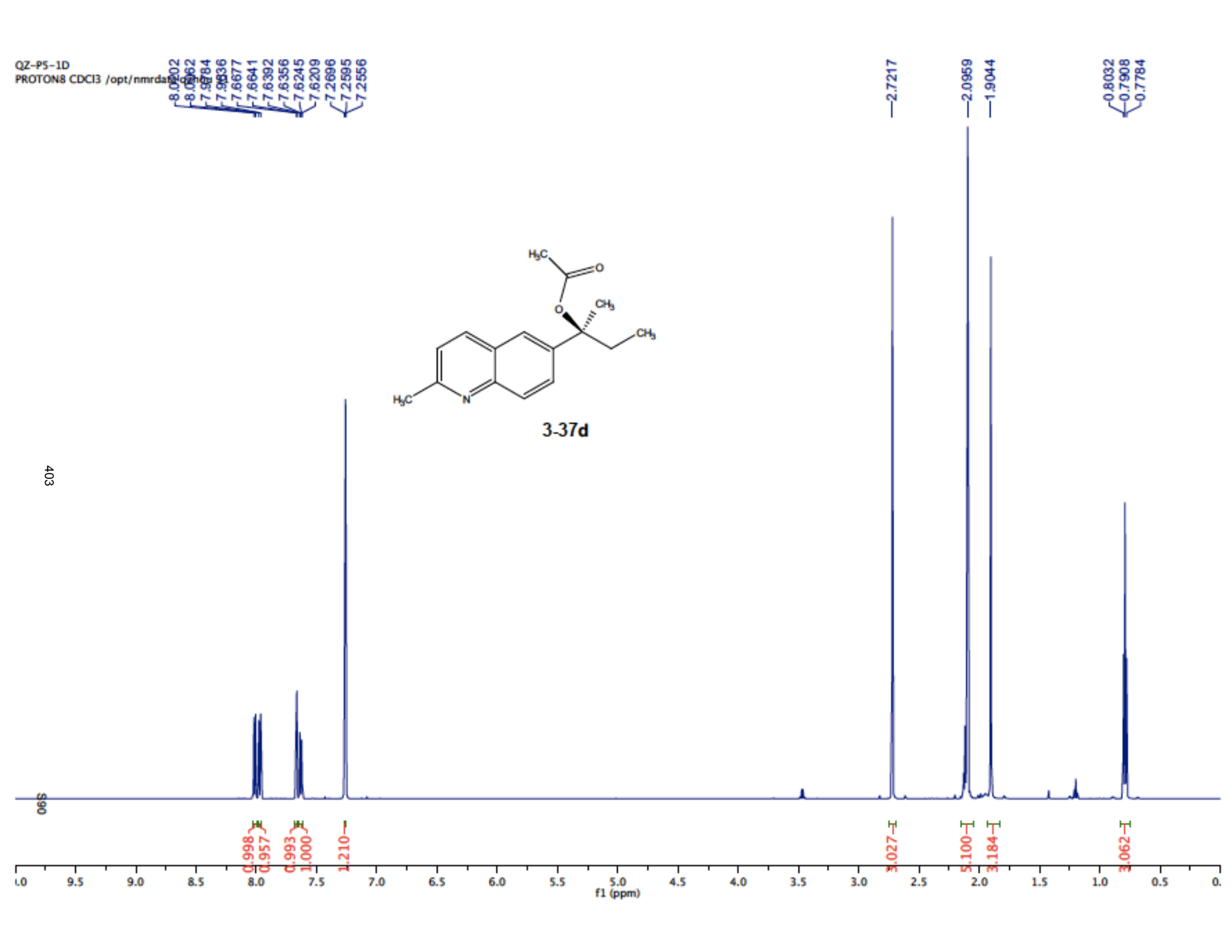


3-37d

402

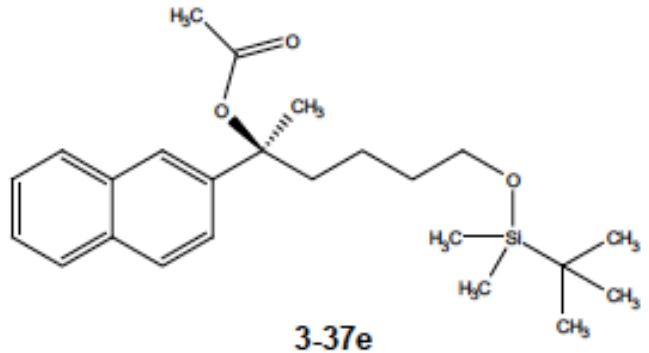
591

f1 (ppm)


QZ-P5-1D
PROTON8 CDCl3 /opt/nmrdata/qzhou
8.0202
8.0062
7.9784
7.9636
7.6677
7.6641
7.6392
7.6356
7.6245
7.6209
7.2696
7.2595
7.2556
2.7217
2.0959
1.9044
0.8032
0.7908
0.7784
H3C
O
O
CH3
CH3
H3C
N
3-37d
403
S90
0.998
0.957
0.993
1.000
1.210
3.027
5.100
3.184
3.062
f1 (ppm)

QZ-8-034-1.2.fid
QZ-8-034-1
C13CPD256 CDCl3 /opt/topspin gzhou 6

169.8888
142.5220
133.1848
132.4620
128.3226
128.1081
127.6023
126.1482
125.8737
123.4549
123.0939
84.2416
77.1600 CDCl3
62.9648
42.3906
32.9651
26.0198
24.8474
22.4388
20.2708
18.4139
-5.1782



3-37e

404

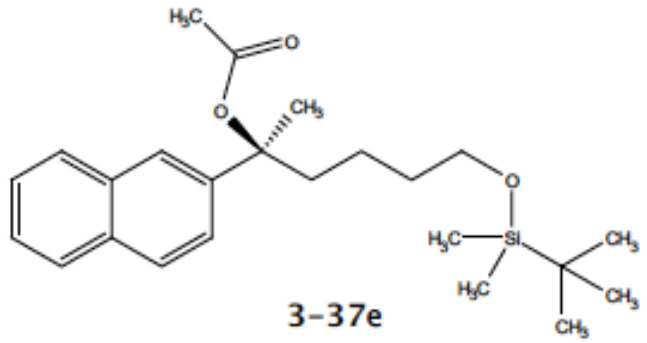
593

f1 (ppm)

QZ-8-052-1.1.fid
QZ-8-052-1
PROTON8 CDCl3 /opt/nmrdata qzhou 30

7.8223 7.8204 7.8187 7.8080 7.8037 7.7895 7.7398 7.7377 7.7357 7.4748 7.4723 7.4634 7.4607 7.4509 7.4477 7.4392 7.4362 7.4252 7.4219 7.2600 CDCl3

3.5407 3.5300 3.5193 2.1270 2.1174 2.1047 2.0955 2.0869 2.0818 2.0760 2.0694 2.0647 2.0512 2.0417 1.9348 1.4814 1.4697 1.4578 1.4461 1.4344 1.3182 1.3088 1.3058 1.2964 1.2889 1.2839 1.2795 1.2752 1.2683 1.2617 1.2559 1.2491 1.2442 1.2394 1.2354 1.2328 1.2272 1.2211 1.2172 0.8289 0.8238 -0.0148



3-37e

405

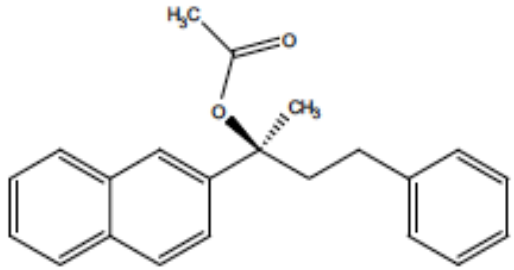
S92

3.060 1.000 3.048 2.072 5.248 2.954 2.101 2.165 9.310 5.980

f1 (ppm)

QZ-7-300-1.2.fid
C13CPD256 CDCl3 /opt/topspin qzhou 10

169.8930
142.2067
141.8434
133.2186
132.5238
128.4906
128.4629
128.3529
128.2884
127.6475
126.2734
126.0153
125.9682
123.5783
123.0261
84.0301
44.0798
30.4197
25.3116
22.4246

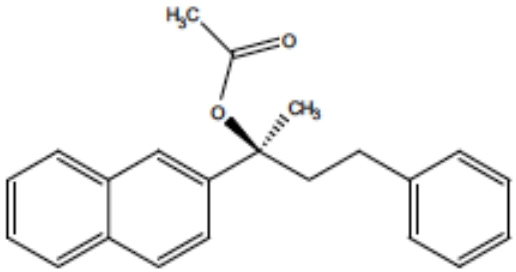


3-37f

406

f1 (ppm)

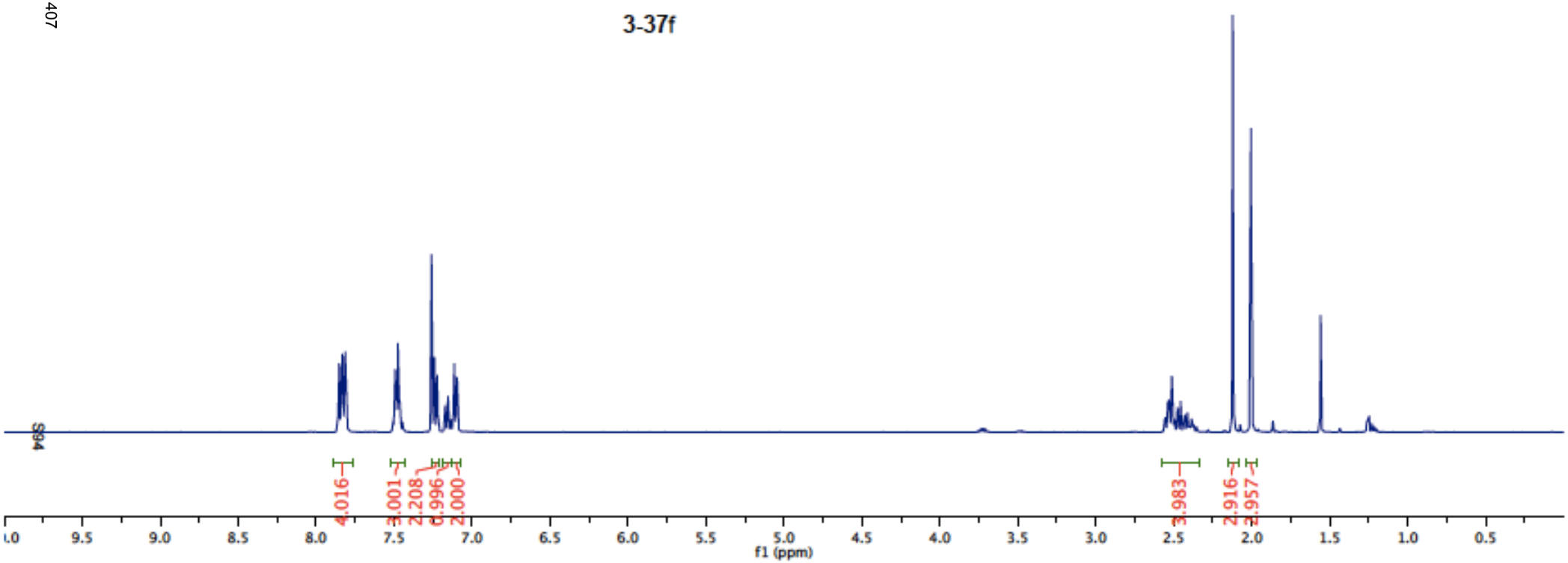
QZ-7-300-1.1.fid
PROTON_16 CDCl3 /opt/topspin qzhou 20



3-37f

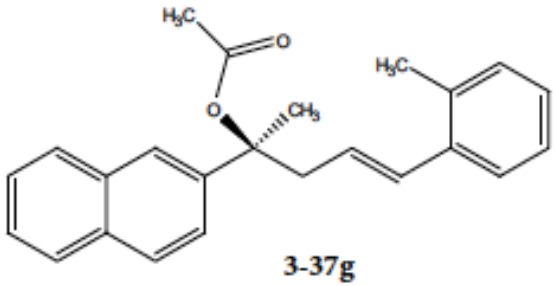
407

S94



QZ-8-113-1.2.fid
QZ-8-113-1
C13CPD2048 CDCl3 /opt/nmrdata qzhou 60

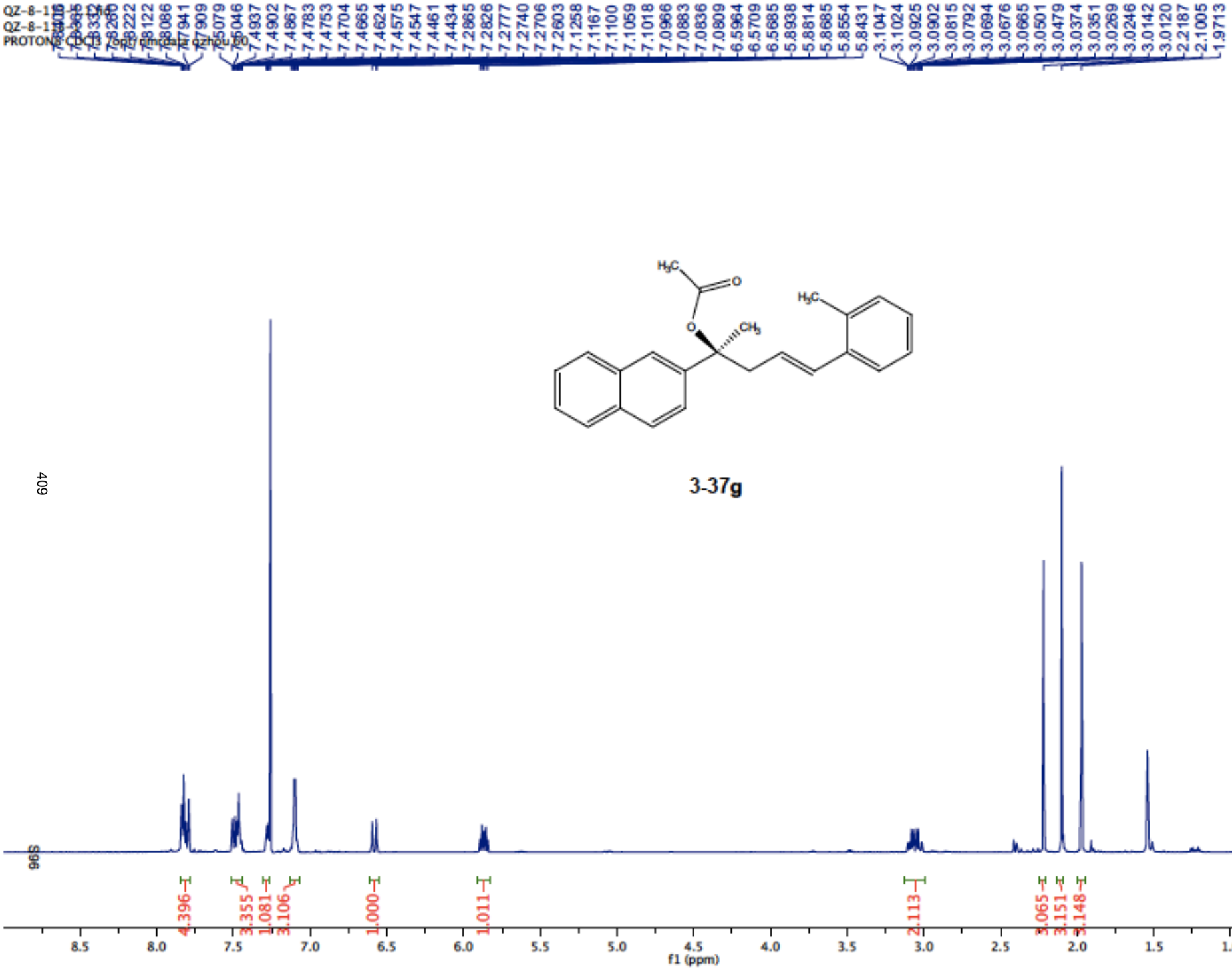
169.8246
142.1961
136.8149
135.2501
133.2451
132.6095
132.0588
130.2449
128.3980
128.2225
127.6466
127.3281
126.2502
126.1295
126.0473
126.0255
125.8767
123.6333
123.1565
83.7524
77.4000-CDCl3
45.9393
25.2512
22.4210
19.8190



3-37g

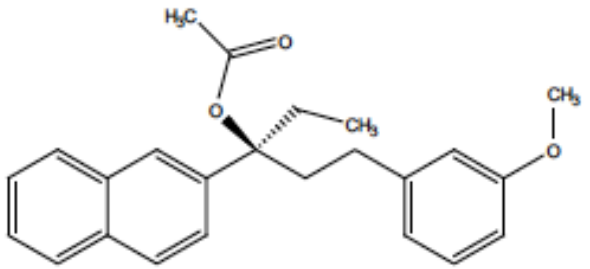
408

f1 (ppm)

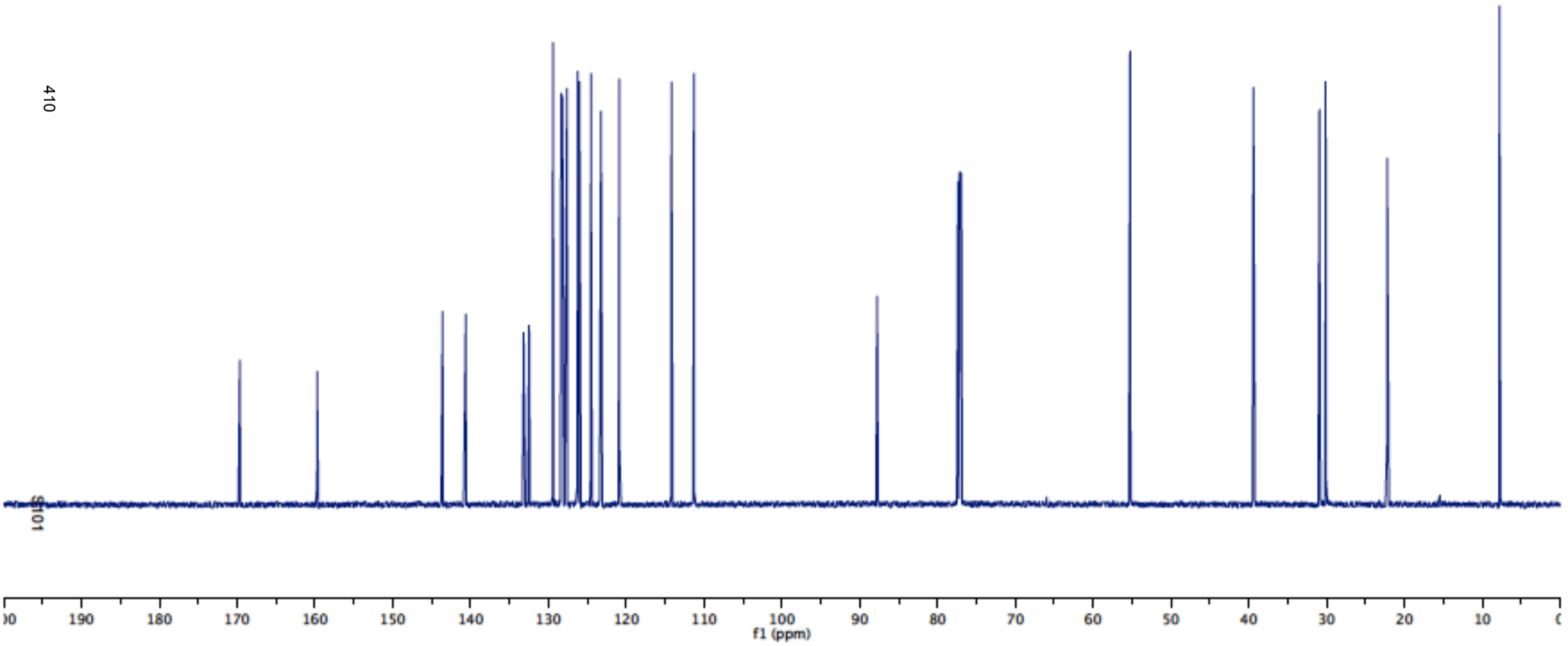

QZ-8-1
QZ-8-1
PROTON CDCl3 /opt/ mnodata qzhou 50
7.7941
7.7909
7.5079
7.5046
7.4937
7.4902
7.4867
7.4783
7.4753
7.4704
7.4665
7.4624
7.4575
7.4547
7.4461
7.4434
7.2865
7.2826
7.2777
7.2740
7.2706
7.2603
7.1258
7.1167
7.1100
7.1059
7.1018
7.0966
7.0883
7.0836
7.0809
6.5964
6.5709
6.5685
5.8938
5.8814
5.8685
5.8554
5.8431
3.1047
3.1024
3.0925
3.0902
3.0815
3.0792
3.0694
3.0676
3.0665
3.0501
3.0479
3.0374
3.0351
3.0269
3.0246
3.0142
3.0120
2.2187
2.1005
1.9713
H3C
O
O
CH3
H3C
3-37g
409
S96
4.396
3.355
1.081
3.106
1.000
1.011
2.113
3.065
3.151
3.148
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

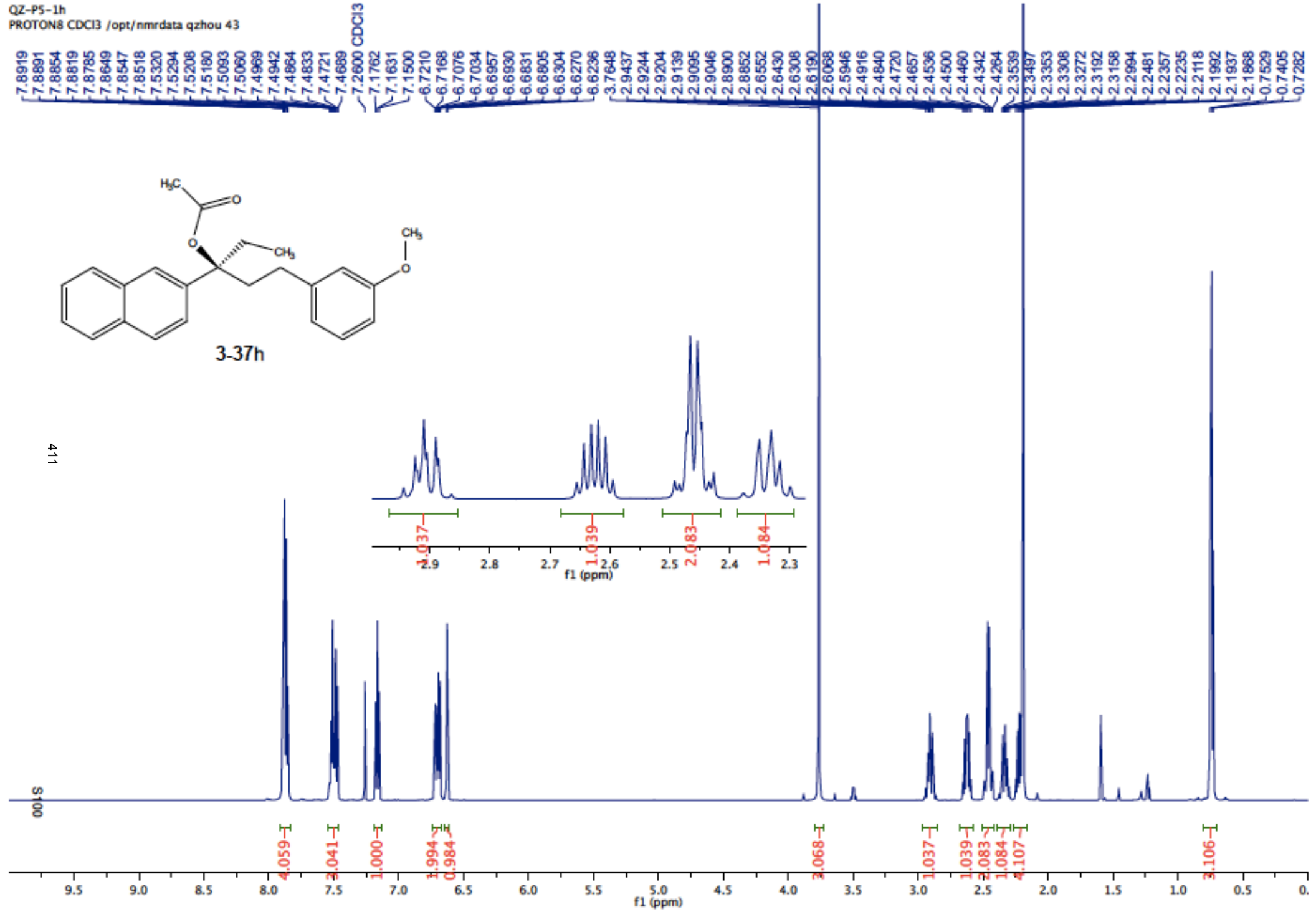
QZ-P5-1h
C13CPD256 CDCl3 /opt/nmrdata qzhou 43

169.6600
159.7248
143.5969
140.6155
133.1714
132.4838
129.4138
128.3731
128.1910
127.6216
126.2511
126.0125
124.5381
123.2455
120.8797
114.1867
111.3036
87.7645
77.1600 CDCl3
55.2489
39.4064
30.9258
30.1222
22.2182
7.7896



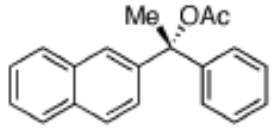
3-37h




QZ-P5-1h
PROTON8 CDCl3 /opt/nmrdata qzhou 43
CDCl3
3-37h
f1 (ppm)

QZ-P5-1i
C13CPD256 CDCl3 /opt/nmrdata qzhou 41

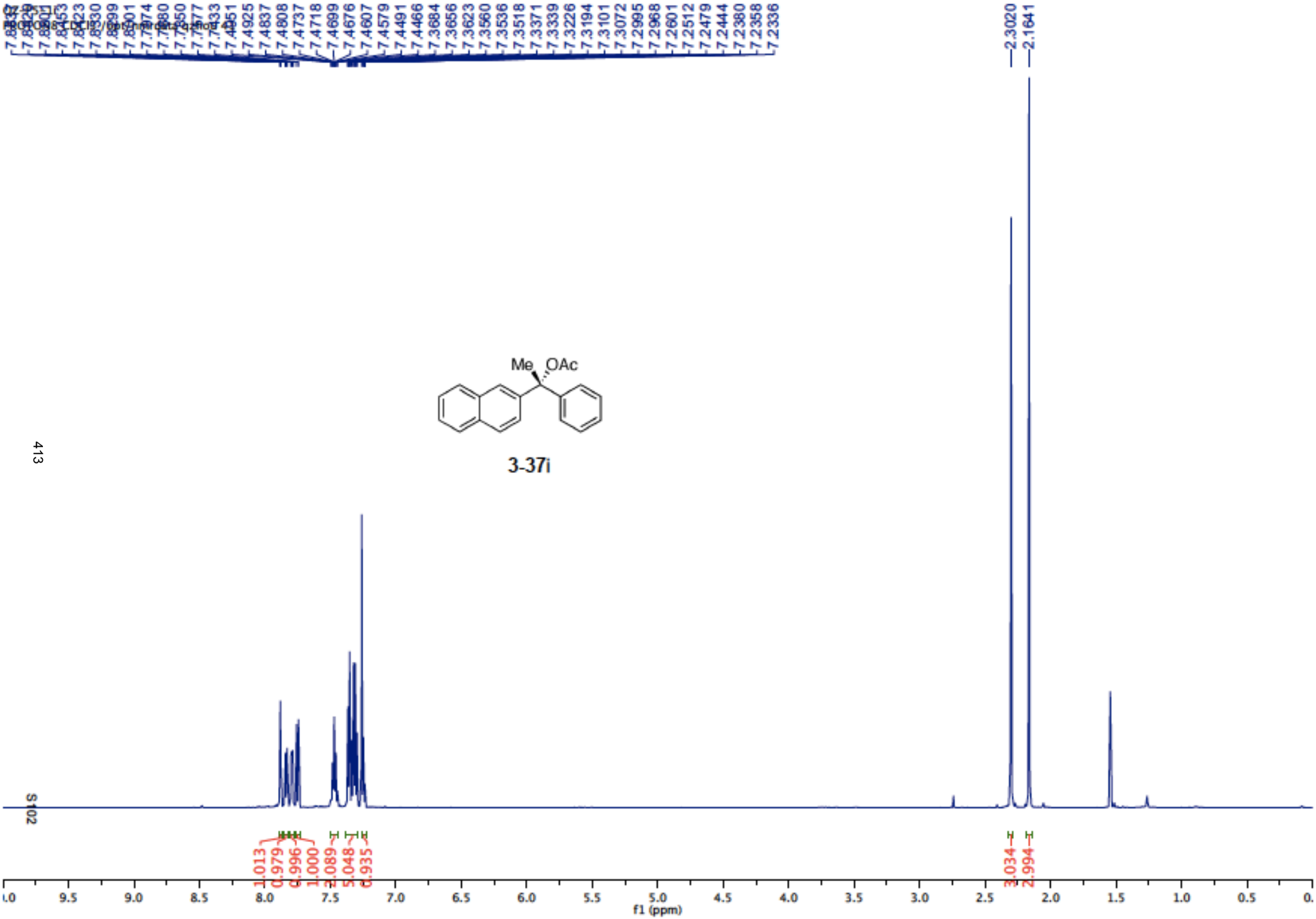
169.4174
145.6323
142.9140
133.0377
132.5715
128.4908
128.2891
128.1492
127.6567
127.3264
126.3001
126.2075
126.1208
124.5624
124.5227
84.8085
77.1600 CDCl3
26.9838
22.5707

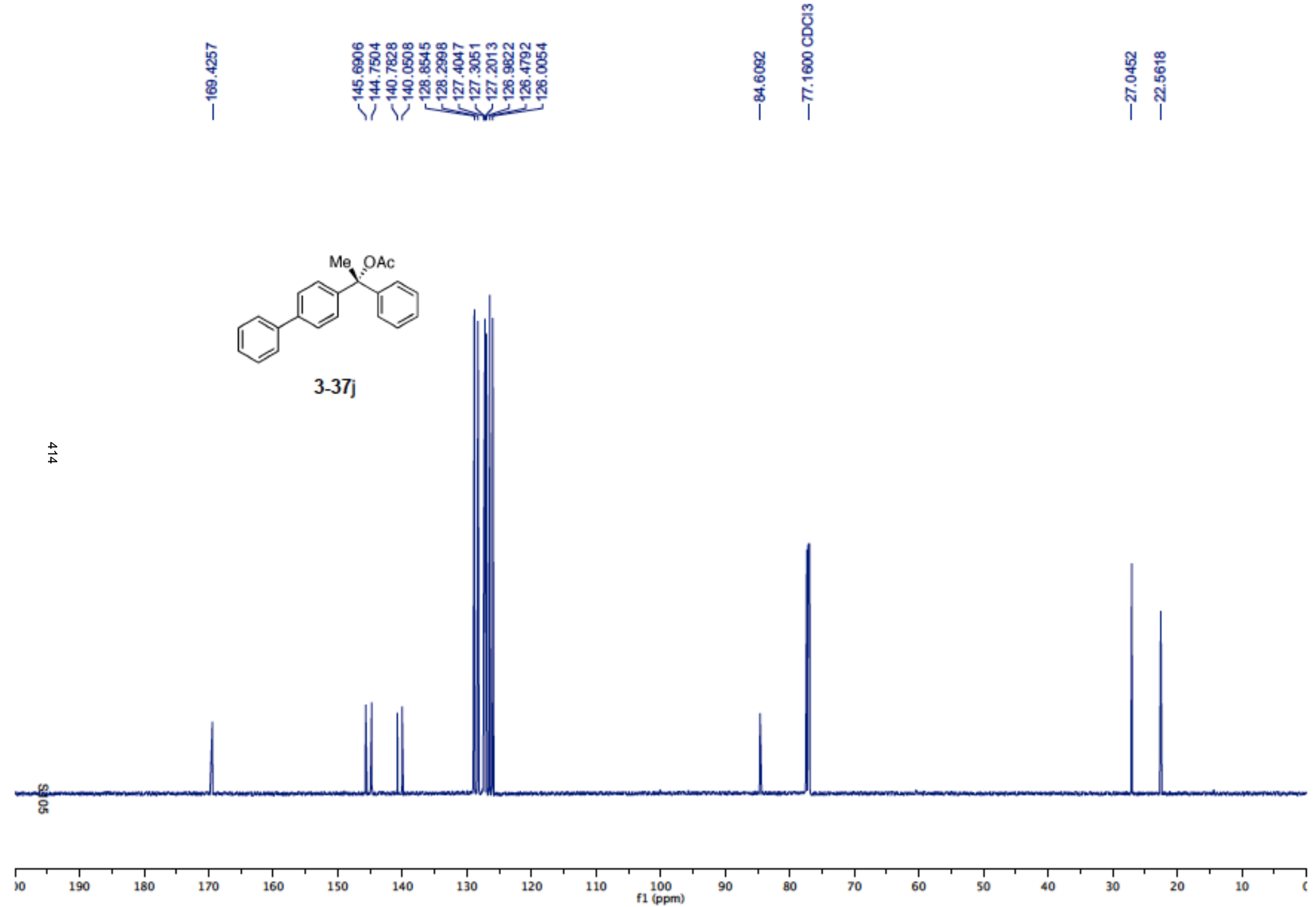


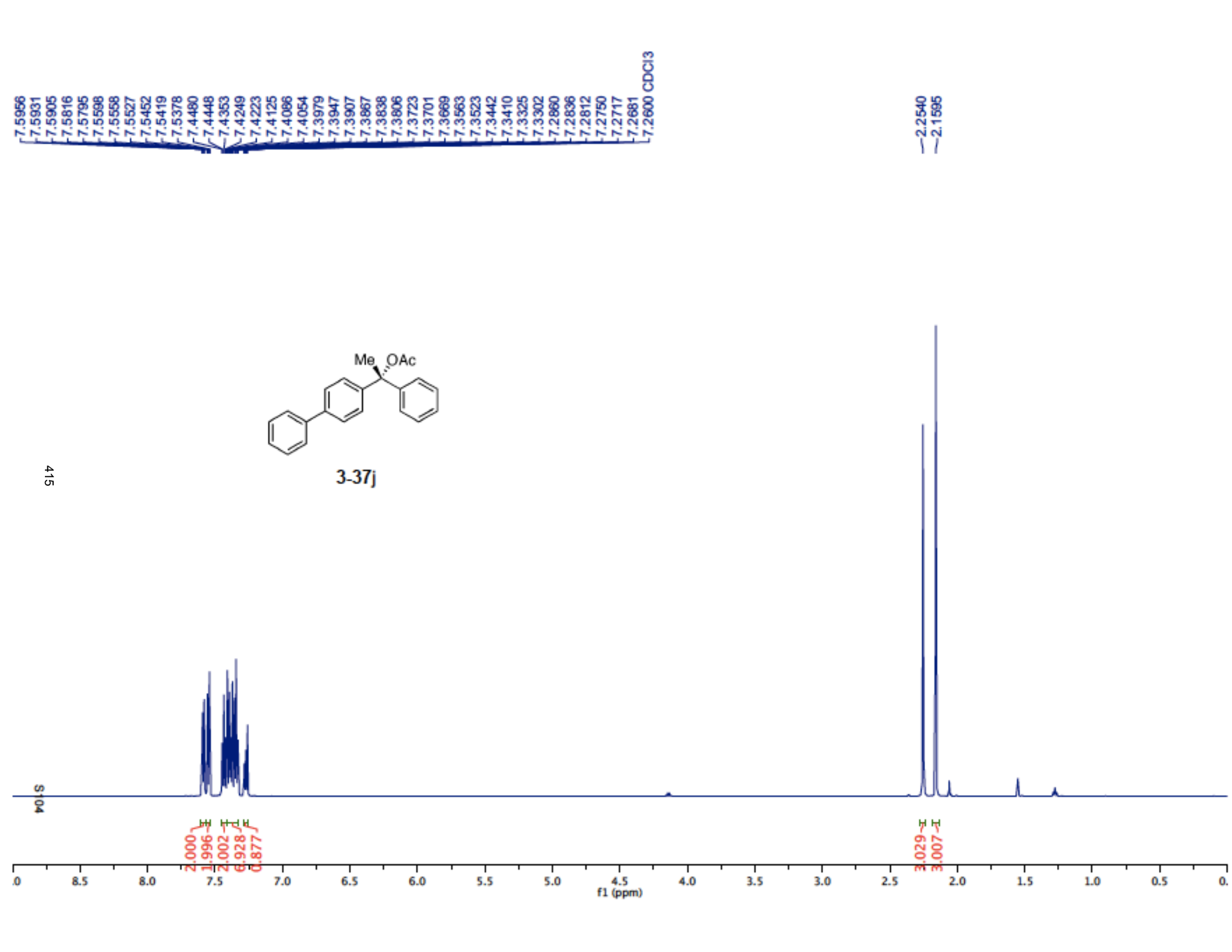
3-37i

412

f1 (ppm)

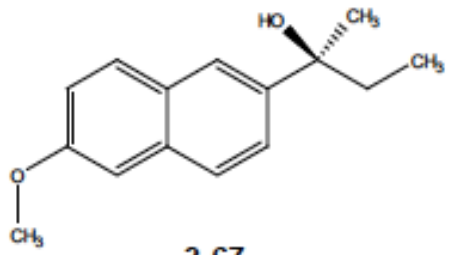

Me
OAc
3-37i
413
S102
f1 (ppm)


169.4257
145.6906
144.7504
140.7828
140.0508
128.8545
128.2998
127.4047
127.3051
127.2013
126.9822
126.4792
126.0054
84.6092
77.1600 CDCl3
27.0452
22.5618
Me
OAc
3-37j
414
SS05
f1 (ppm)


7.5956
7.5931
7.5905
7.5816
7.5795
7.5598
7.5558
7.5527
7.5452
7.5419
7.5378
7.4480
7.4448
7.4353
7.4249
7.4223
7.4125
7.4086
7.4054
7.3979
7.3947
7.3907
7.3867
7.3838
7.3806
7.3723
7.3701
7.3669
7.3563
7.3523
7.3442
7.3410
7.3325
7.3302
7.2860
7.2836
7.2812
7.2750
7.2717
7.2681
7.2600 CDCl3
2.2540
2.1595
Me
OAc
3-37j
415
S-104
2.000
1.996
2.002
6.928
0.877
3.029
3.007
f1 (ppm)

QZ-8-050-1-RERUN.2.fid
C13CPD256 CDCl3 /opt/nmrdata qzhou 1

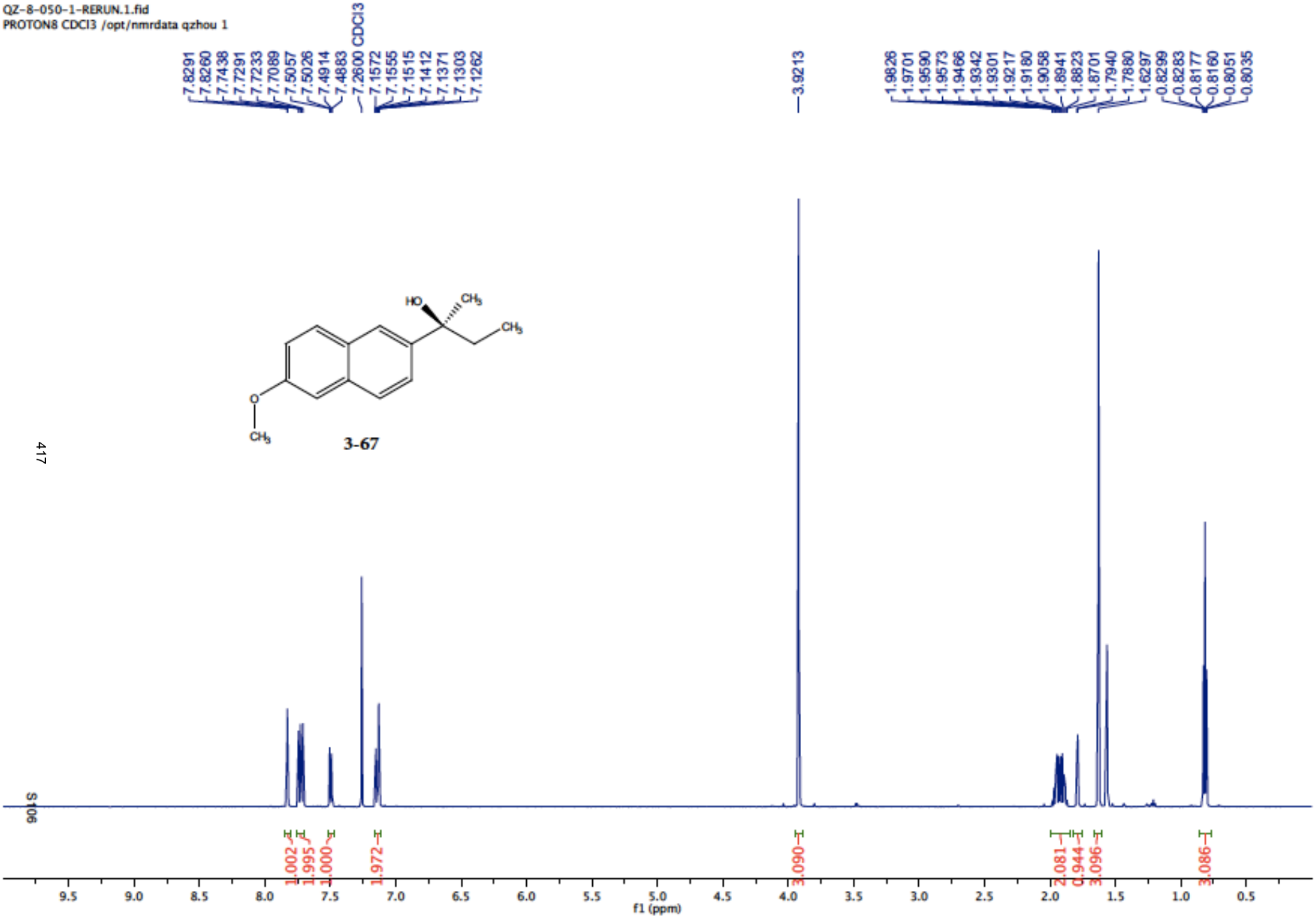
157.7226
142.9931
133.4354
129.7329
128.7678
126.8258
124.3844
123.2888
118.9297
105.6573
77.1600 CDCl3
75.1719
55.4721
36.6918
29.8643
8.5278



3-67

416

QZ-8-050-1-RERUN.1.fid
PROTON8 CDCl3 /opt/nmrdata qzhou 1

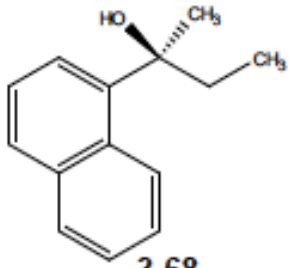


QZ-P5-S-1c
C13CPD256 CDCl3 /opt/nmrdata qzhou 30

142.4264
135.0227
131.0965
129.2640
128.5970
127.0880
125.3139
125.2173
124.8693
124.0180

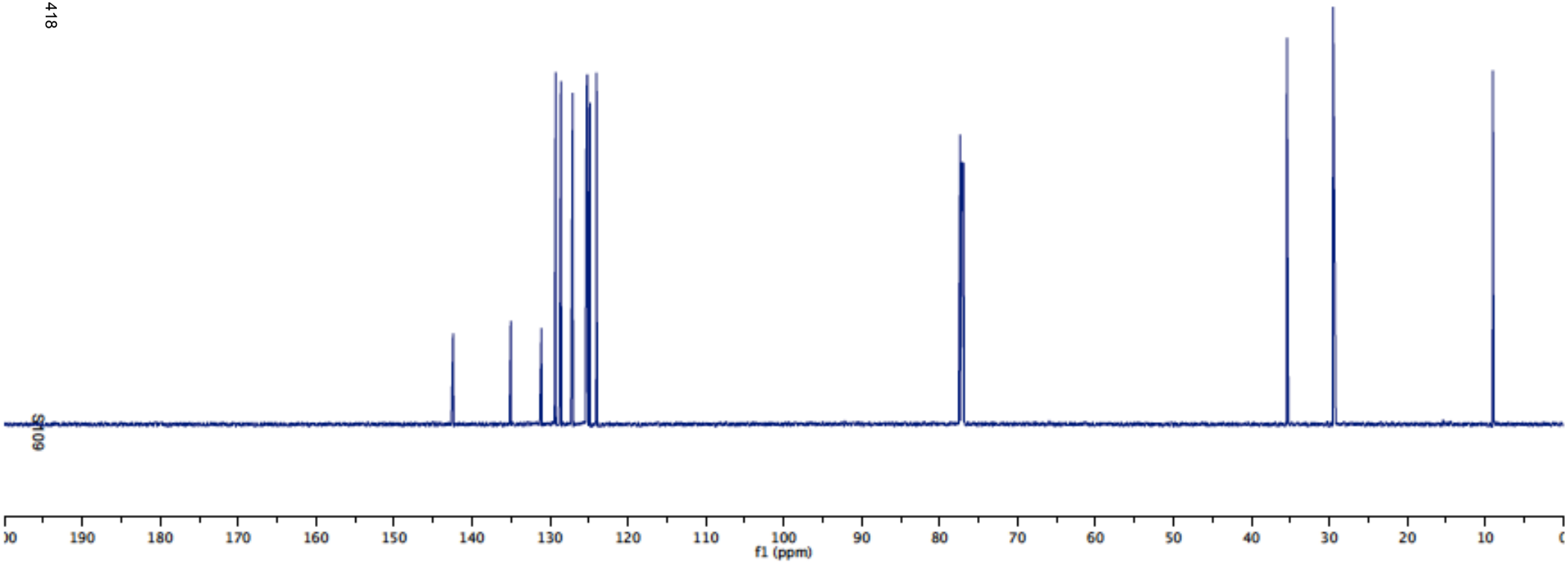
77.1600 CDCl3
76.8875

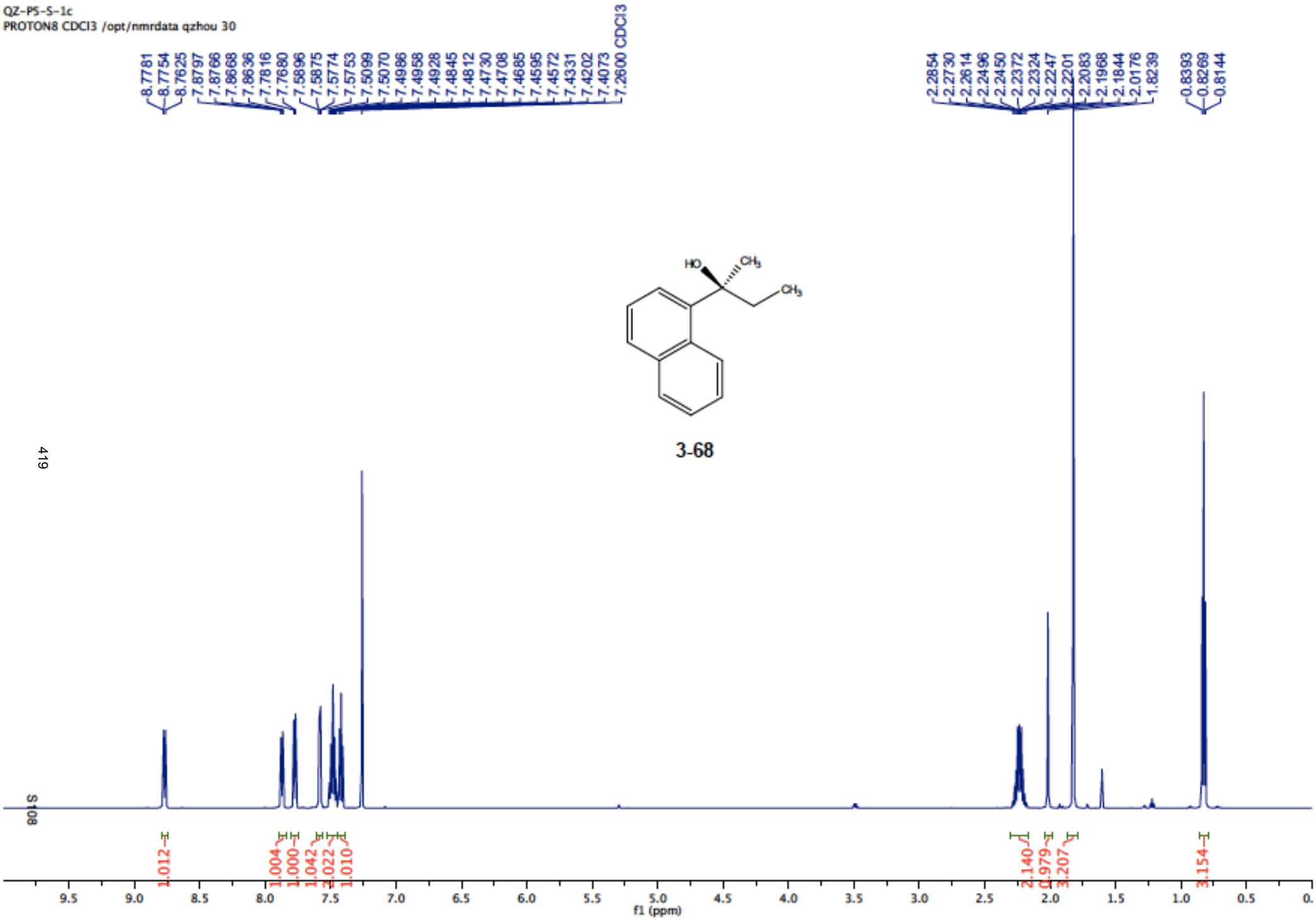
35.4490
29.5194
9.0241



3-68

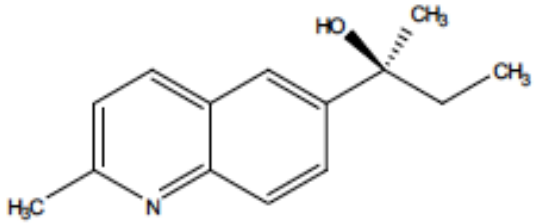
418




QZ-P5-S-1c
PROTON8 CDCl3 /opt/nmrdata qzhou 30
8.7781
8.7754
8.7625
7.8797
7.8766
7.8668
7.8636
7.7816
7.7680
7.5896
7.5875
7.5774
7.5753
7.5099
7.5070
7.4986
7.4958
7.4928
7.4845
7.4812
7.4730
7.4708
7.4685
7.4595
7.4572
7.4331
7.4202
7.4073
7.2600 CDCl3
2.2854
2.2730
2.2614
2.2496
2.2450
2.2372
2.2324
2.2247
2.2201
2.2083
2.1968
2.1844
2.0176
1.8239
0.8393
0.8269
0.8144
HO
CH3
CH3
3-68
419
S108
1.012
1.004
1.000
1.042
2.022
1.010
2.140
0.979
3.207
3.154
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

QZ-8-073-1.2.fid
QZ-8-073-1
C13CPD256 CDCl3 /opt/nmrdata qzhou 27

158.8913
147.0412
145.0936
136.5014
128.5678
127.4108
126.1728
123.1470
122.2522
77.1600 CDCl3
75.1398
36.7175
30.0053
25.4768
8.4412

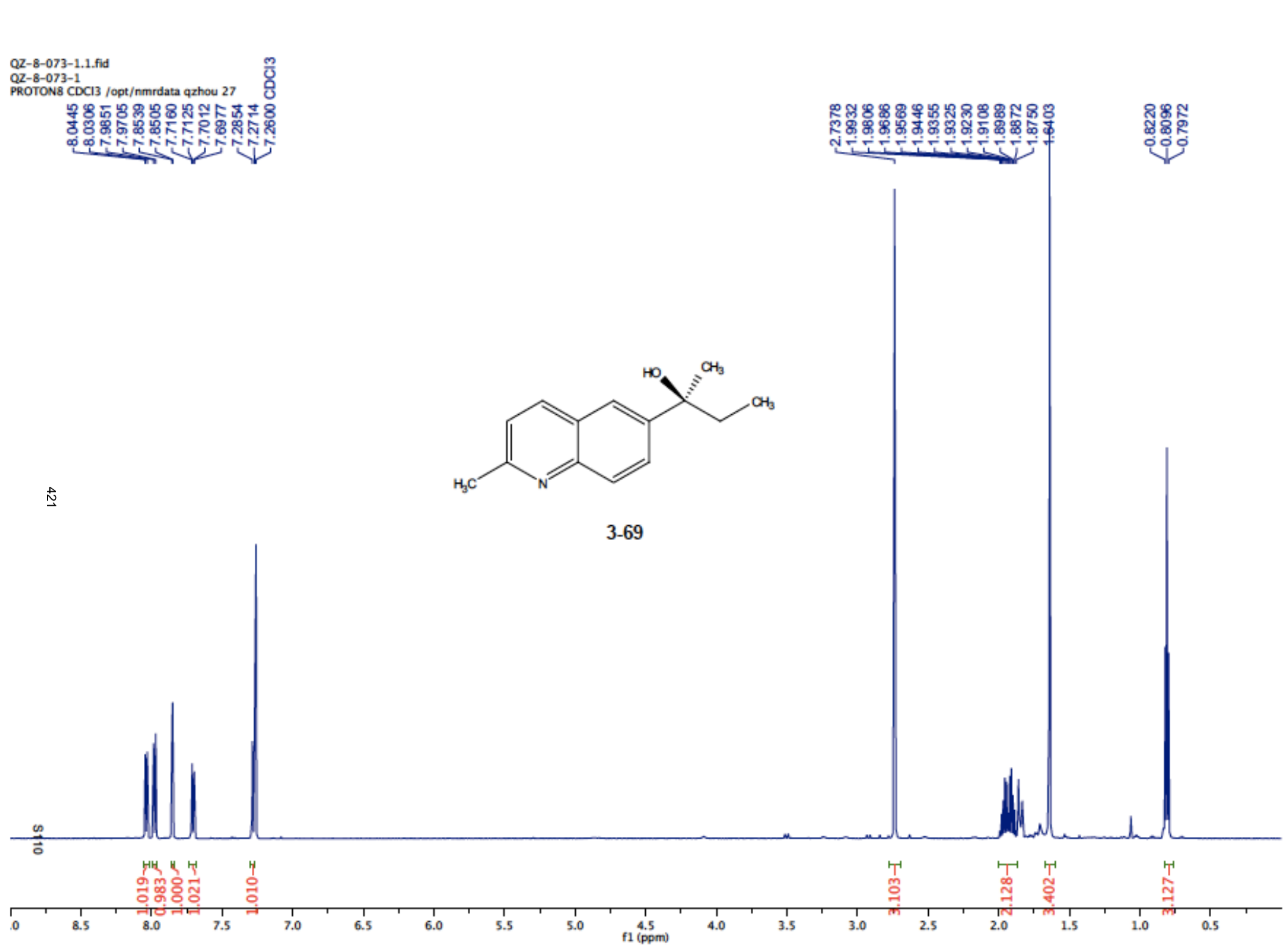


3-69

420

f1 (ppm)

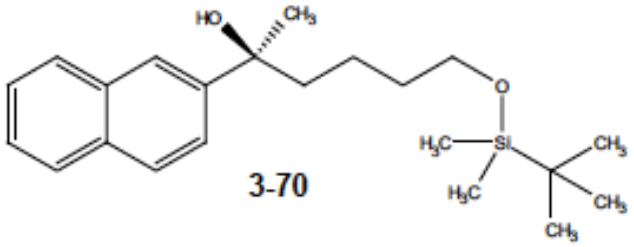
QZ-8-073-1.1.fid
QZ-8-073-1
PROTON8 CDCl3 /opt/nmrdata qzhou 27



3-69

QZ-8-016-OPTICALPURE.2.fid
QZ-8-016-OPTICALPURE
C13CPD256 CDCl3 /opt/nmrdata.gzhou 13

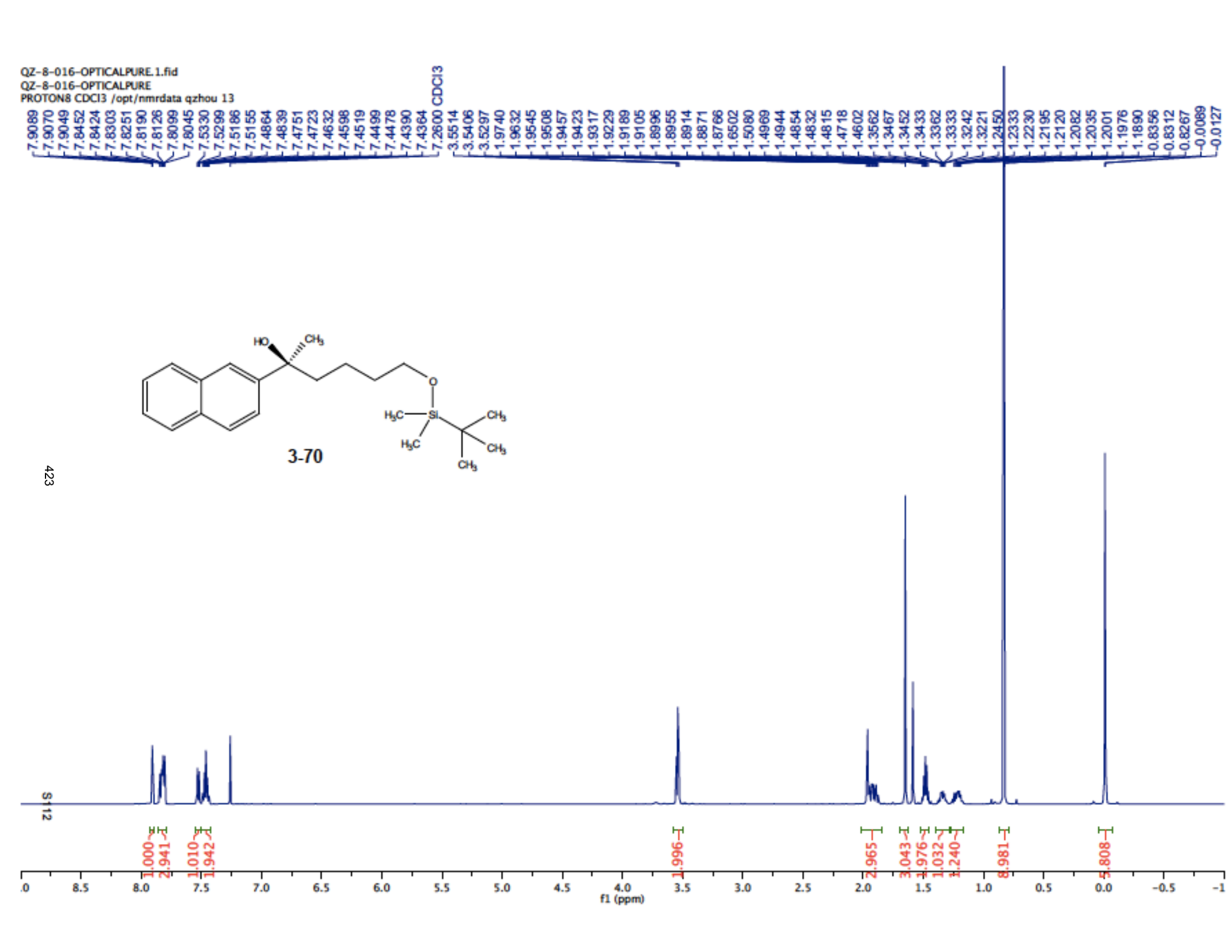
145.4855
133.3371
132.3813
128.2711
127.9678
127.5865
126.1199
125.7516
123.8208
123.2979
77.1600 CDCl3
75.0613
63.1386
43.8020
33.0962
30.3812
26.0614
20.5840
18.4401
-5.1578
-5.1695



3-70

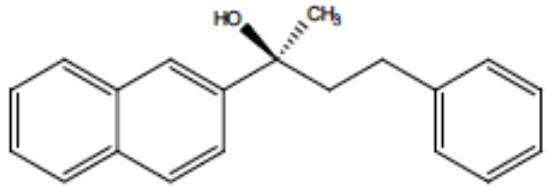
422

f1 (ppm)


QZ-8-016-OPTICALPURE.1.fid
QZ-8-016-OPTICALPURE
PROTON8 CDCl3 /opt/nmrdata qzhou 13
CDCl3
HO
CH3
O
H3C
Si
CH3
H3C
CH3
CH3
3-70
423
S+12
f1 (ppm)

QZ-8-080-1-RERUN.2.fid
QZ-8-080-1-RERUN
C13CPD256 CDCl3 /opt/nmrdata qzhou 55

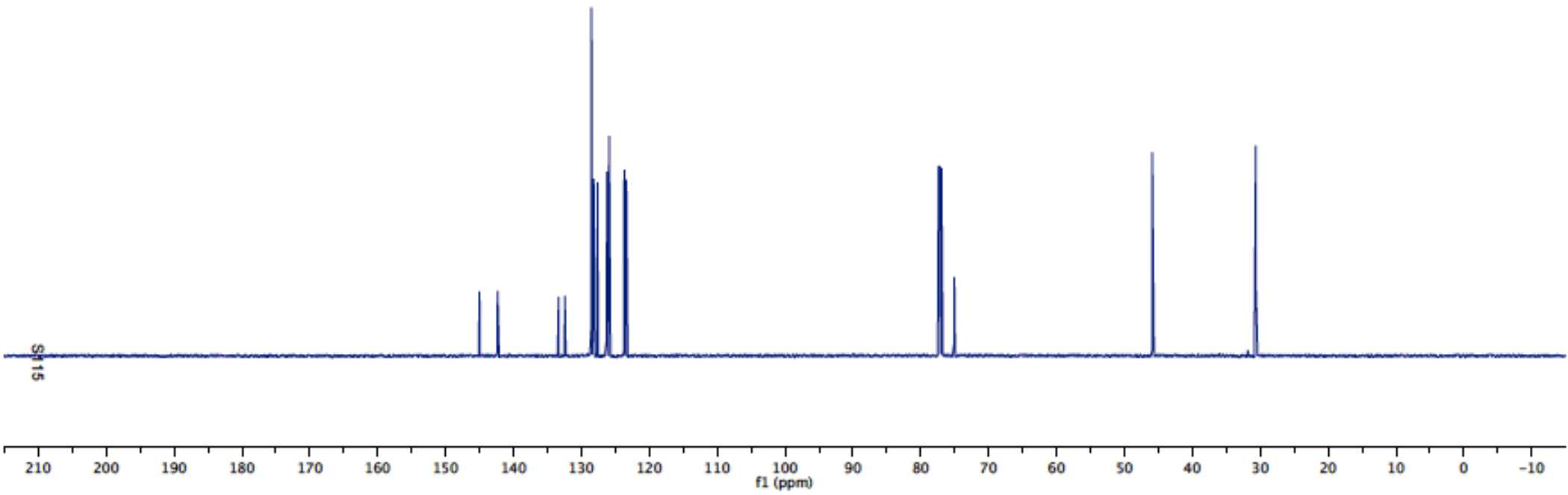
145.0119
142.3422
133.3507
132.4249
128.5138
128.4552
128.2894
128.1756
127.6304
126.2503
125.9013
125.8892
123.6814
123.3637
77.1600 CDCl3
75.0560
45.8996
30.7867
30.6530

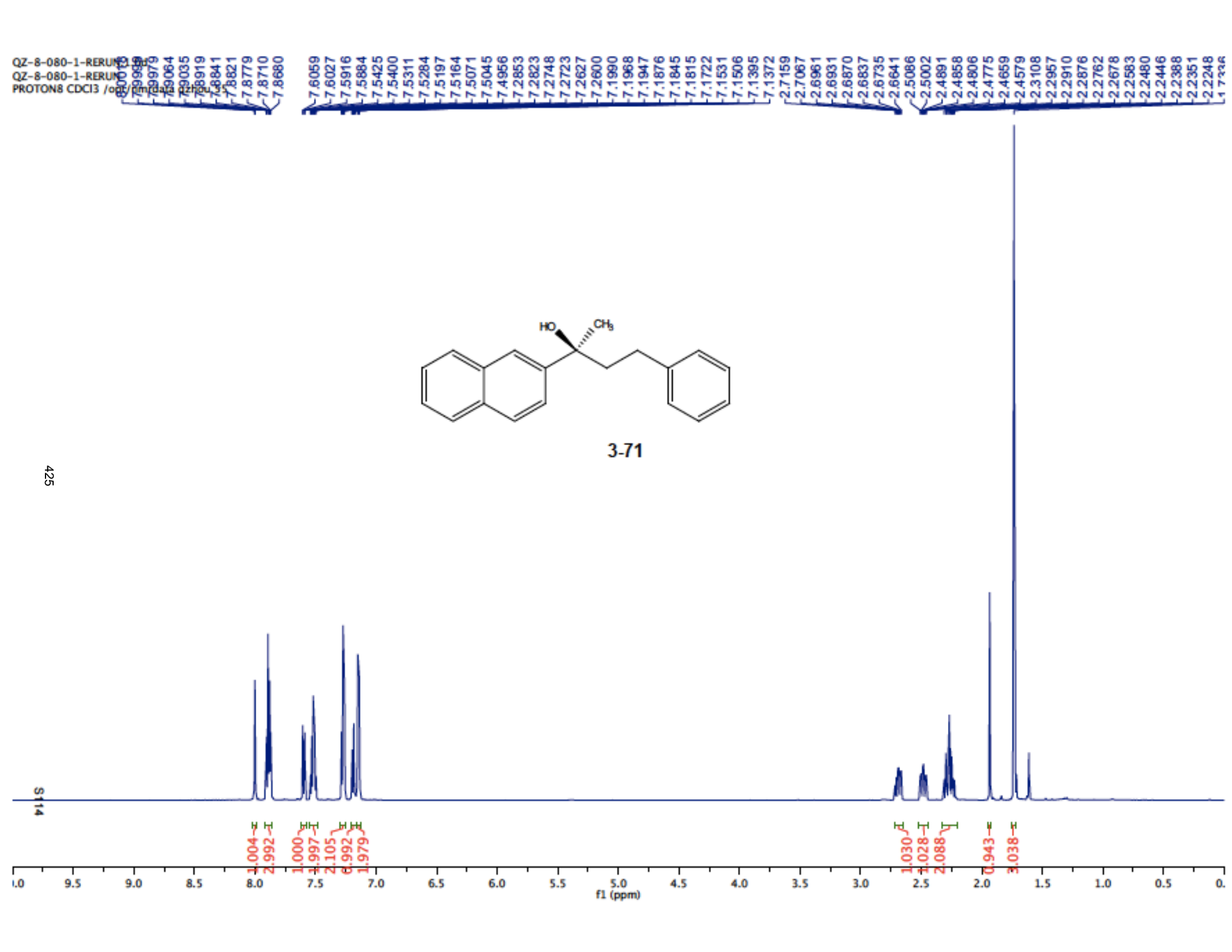


3-71

424

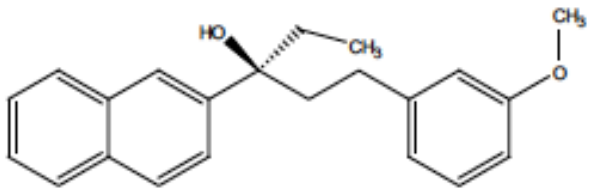
SH15




QZ-8-080-1-RERUN
QZ-8-080-1-RERUN
PROTON8 CDCl3
HO
CH3
3-71
425
S114
1.004
2.992
1.000
1.997
2.105
6.992
1.979
1.030
1.028
2.088
0.943
3.038
f1 (ppm)

QZ-P5-S-1H
C13CPD256 CDCl3 /opt/nmrdata qzhou 37

159.7648
144.1912
143.0353
133.3418
132.3443
129.4740
128.2615
128.0874
127.6145
126.1838
125.8092
124.3617
123.9259
120.8306
114.2035
111.2350
77.6311
77.1600 CDCl3
55.2394
44.4722
35.8806
30.3048
7.9054

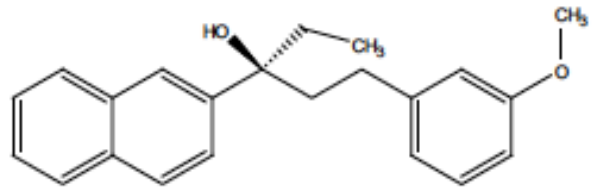


3-72

426
121

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

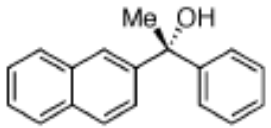
QZ-P5-S-1H
PROTON8 CDCl3 /opt/nmrdata qzhou 37



3-72

QZ-PS-S-1i
C13CPD256 CDCl3 /opt/nmrdata qzhou 44

147.8787
145.3900
133.1399
132.5306
128.3961
128.3754
128.1103
127.6384
127.2086
126.2788
126.0993
126.0939
125.0713
123.8730
77.1600 CDCl3
76.5164
30.8947

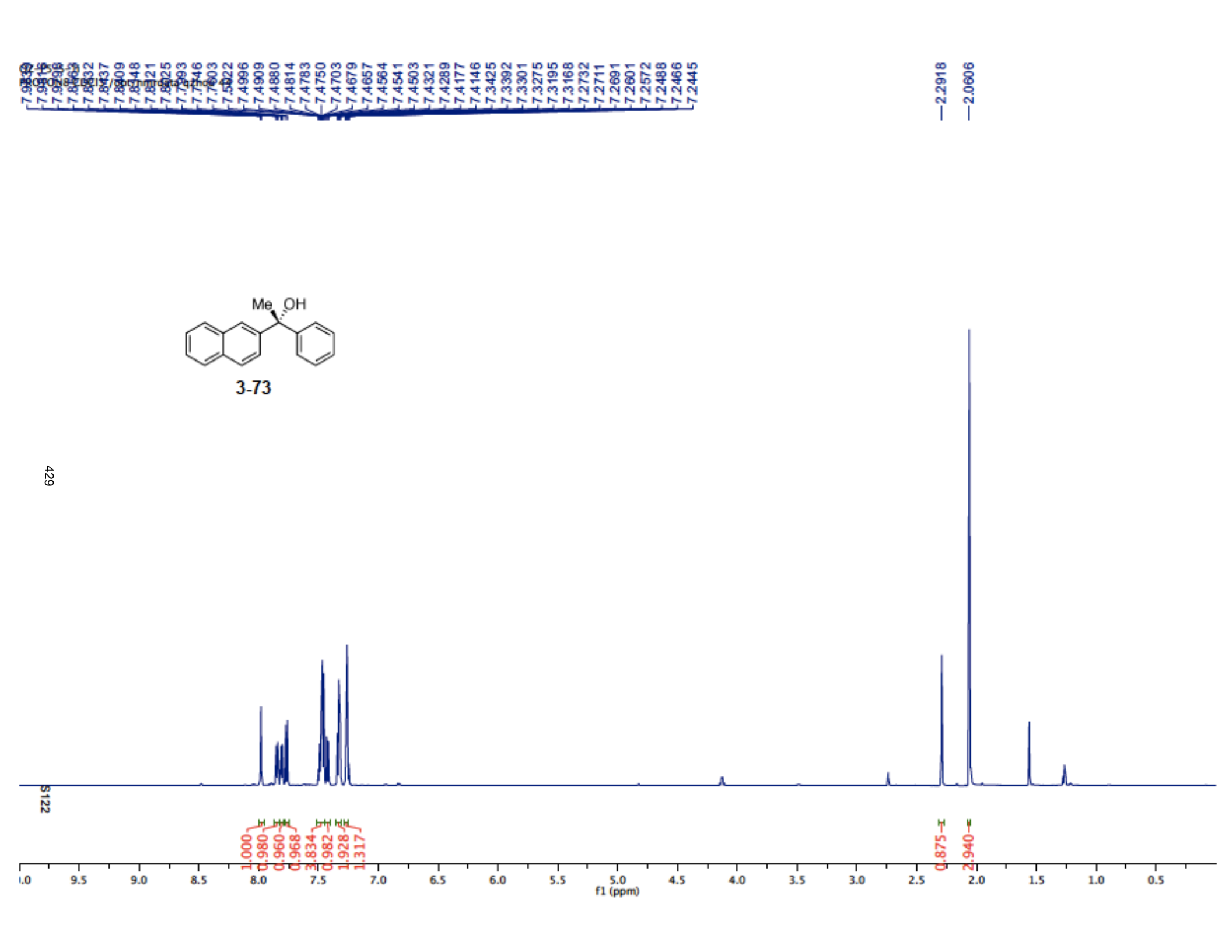


3-73

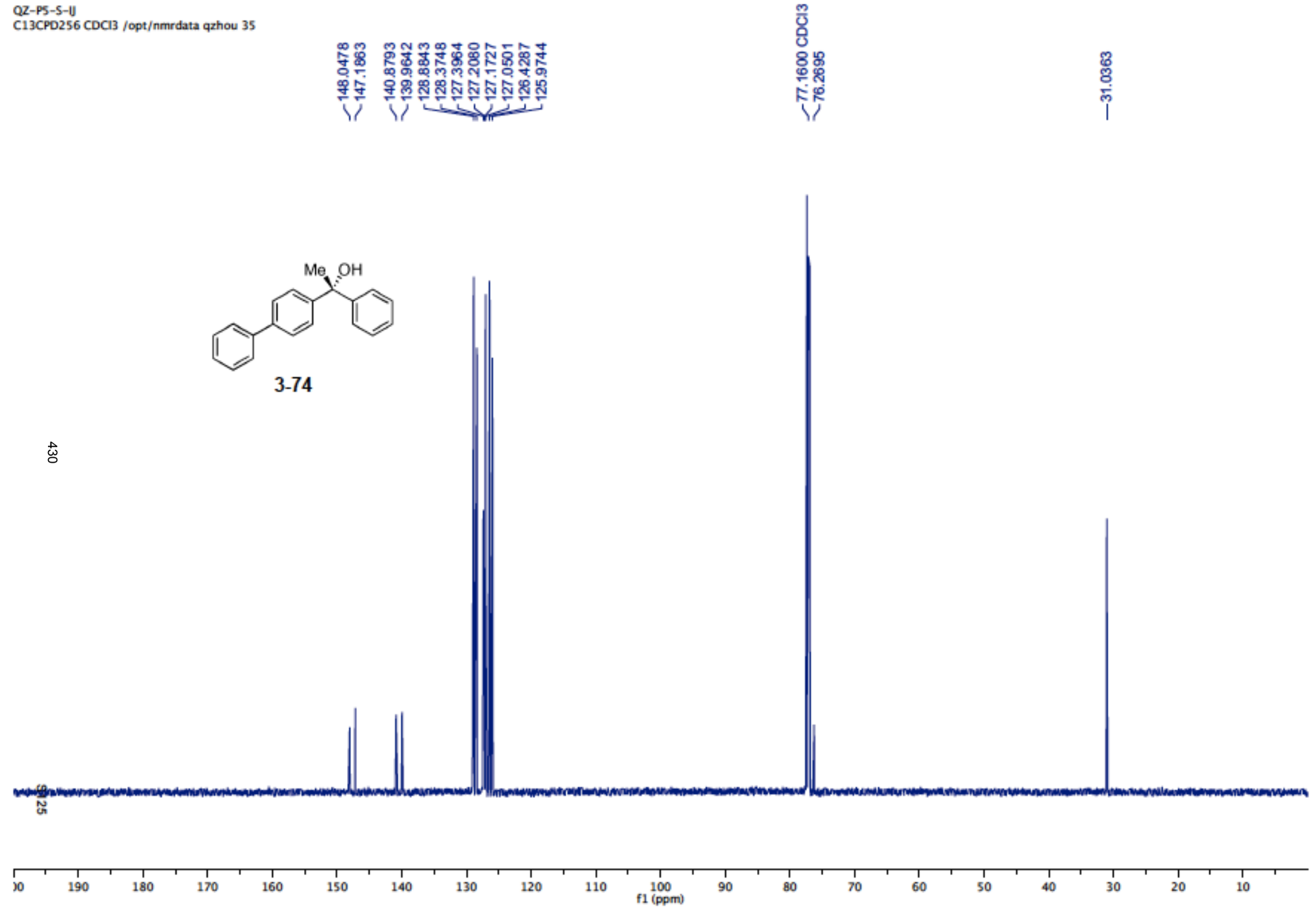
428

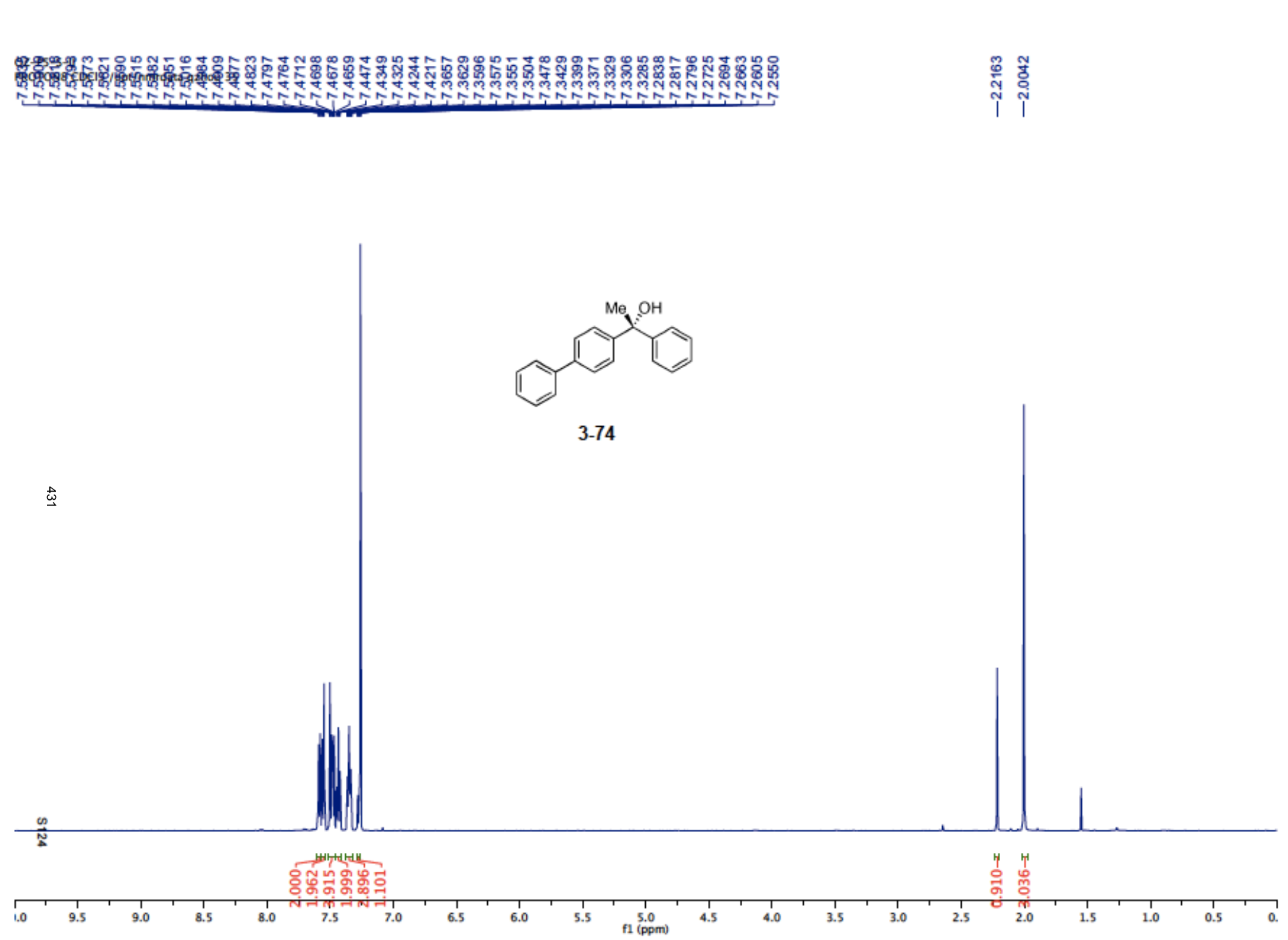
S123

155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25
f1 (ppm)

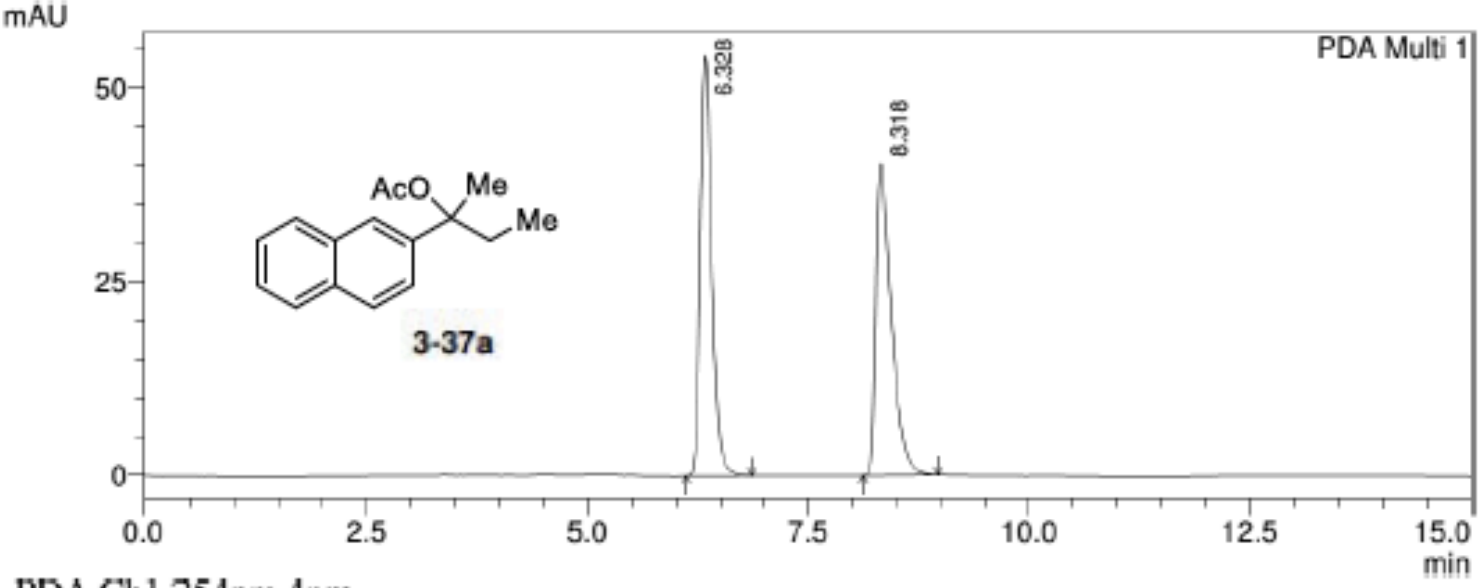

7.9339
7.9115
7.9038
7.8663
7.8632
7.8437
7.8409
7.8348
7.8321
7.8025
7.7993
7.7746
7.7603
7.5422
7.4996
7.4909
7.4880
7.4814
7.4783
7.4750
7.4703
7.4679
7.4657
7.4564
7.4541
7.4503
7.4321
7.4289
7.4177
7.4146
7.3425
7.3392
7.3301
7.3275
7.3195
7.3168
7.2732
7.2711
7.2691
7.2601
7.2572
7.2488
7.2466
7.2445
2.2918
2.0606
Me
OH
3-73
429
S122
1.000
0.980
0.960
0.968
3.834
0.982
1.928
1.317
0.875
2.940
f1 (ppm)

QZ-PS-S-IJ
C13CPD256 CDCl3 /opt/nmrdata qzhou 35




Me
OH
3-74
2.2163
2.0042
2.000
1.962
3.915
1.999
2.896
1.101
0.910
3.036
f1 (ppm)

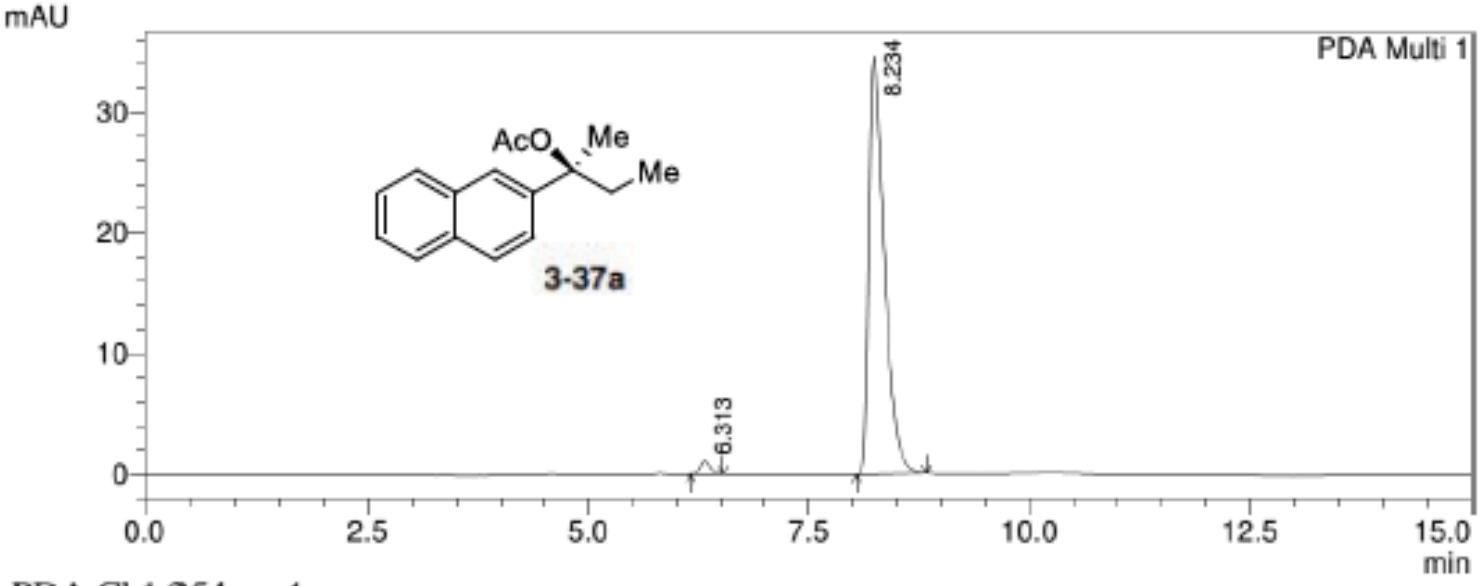
Racemic **3-37a**



PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.328	491674	54209	49.939	57.391
2	8.318	492882	40246	50.061	42.609
Total		984556	94456	100.000	100.000

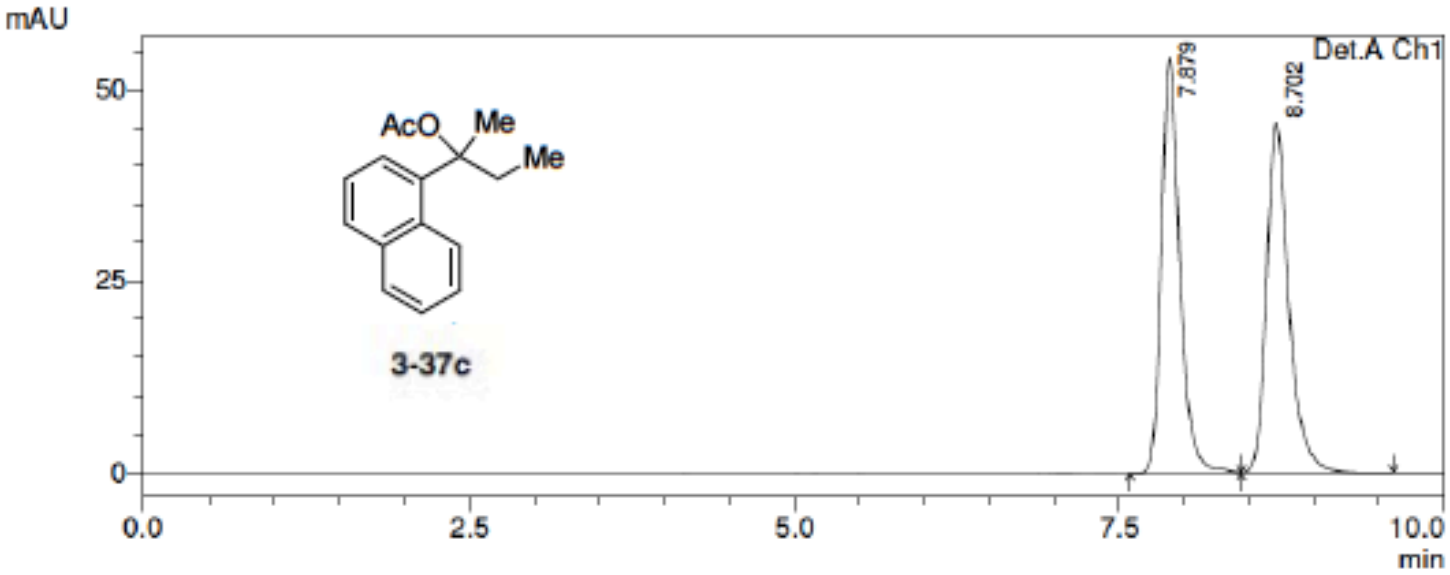
Enantioenriched **3-37a**, 96% ee



PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.313	8728	1084	2.011	3.036
2	8.234	425380	34633	97.989	96.964
Total		434108	35717	100.000	100.000

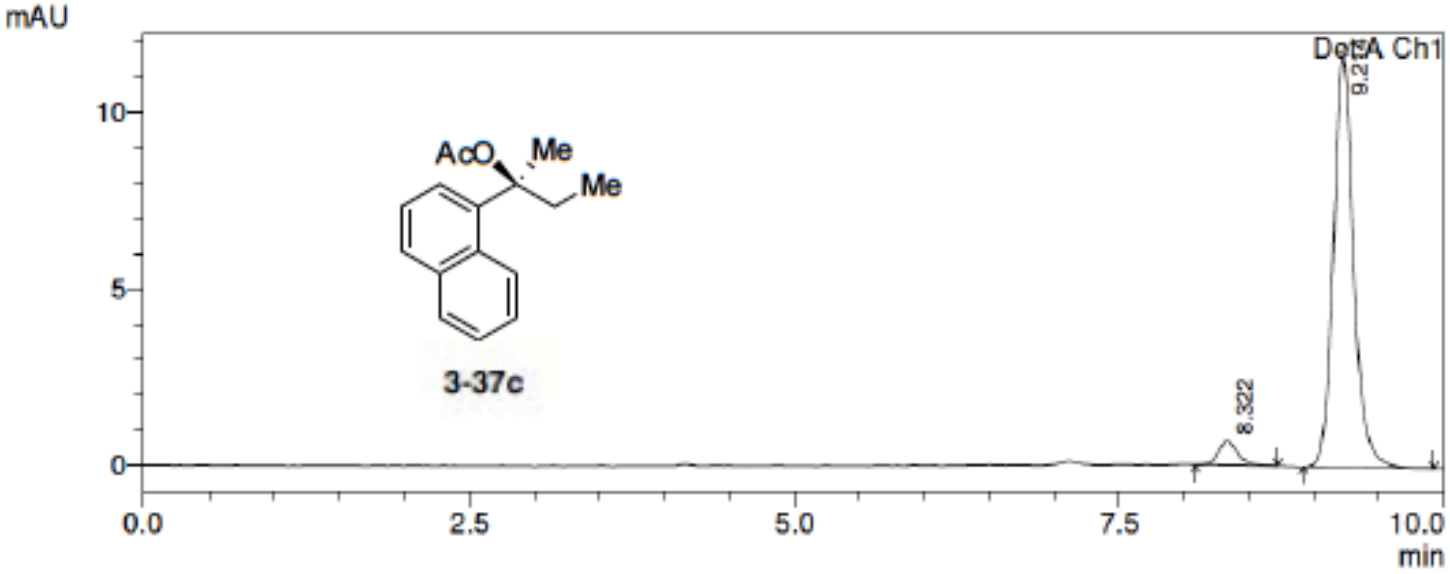
Racemic **3-37c**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.879	542497	54132	49.894	54.318
2	8.702	544812	45525	50.106	45.682
Total		1087309	99658	100.000	100.000

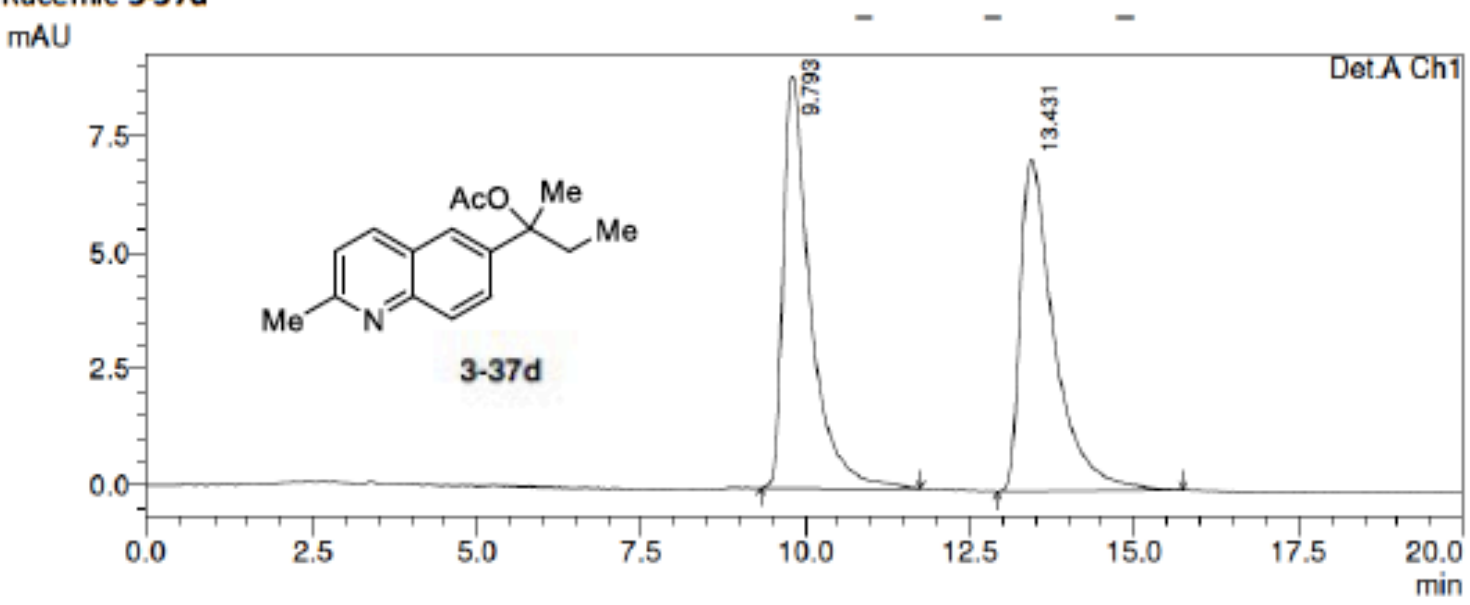
Enantioenriched **3-37c**, 90% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.322	6955	681	5.184	5.523
2	9.214	127204	11657	94.816	94.477
Total		134159	12338	100.000	100.000

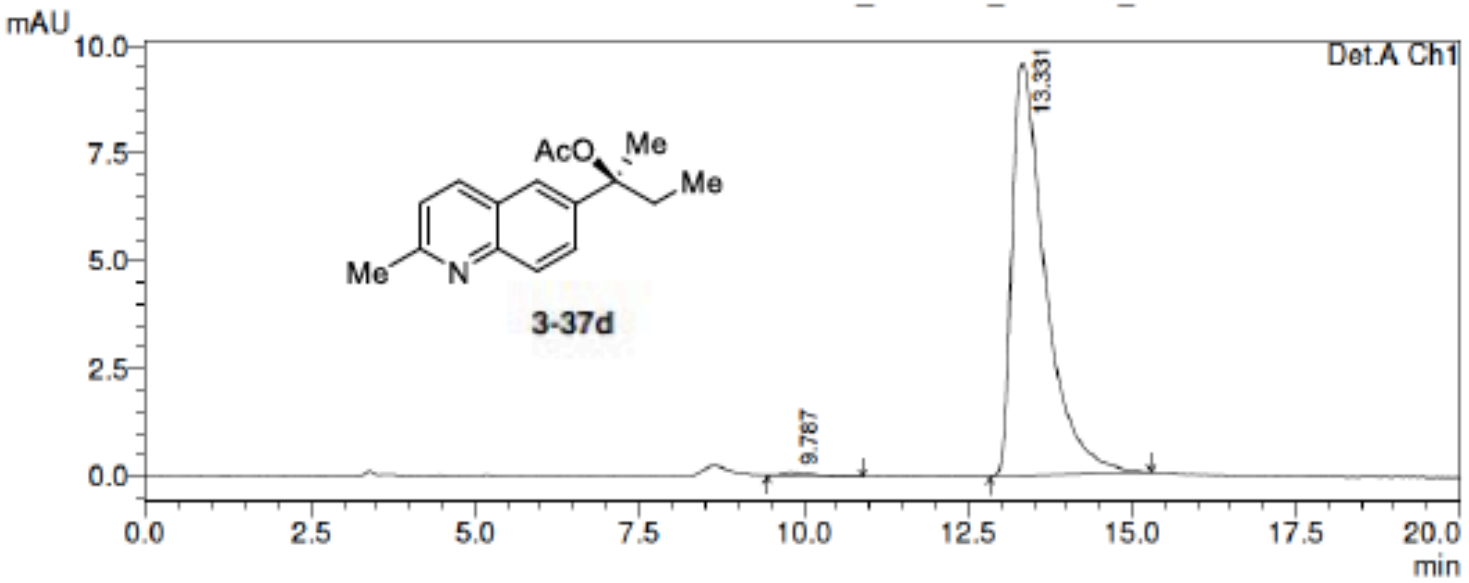
Racemic **3-37d**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.793	255341	8840	49.841	55.369
2	13.431	256972	7126	50.159	44.631
Total		512313	15966	100.000	100.000

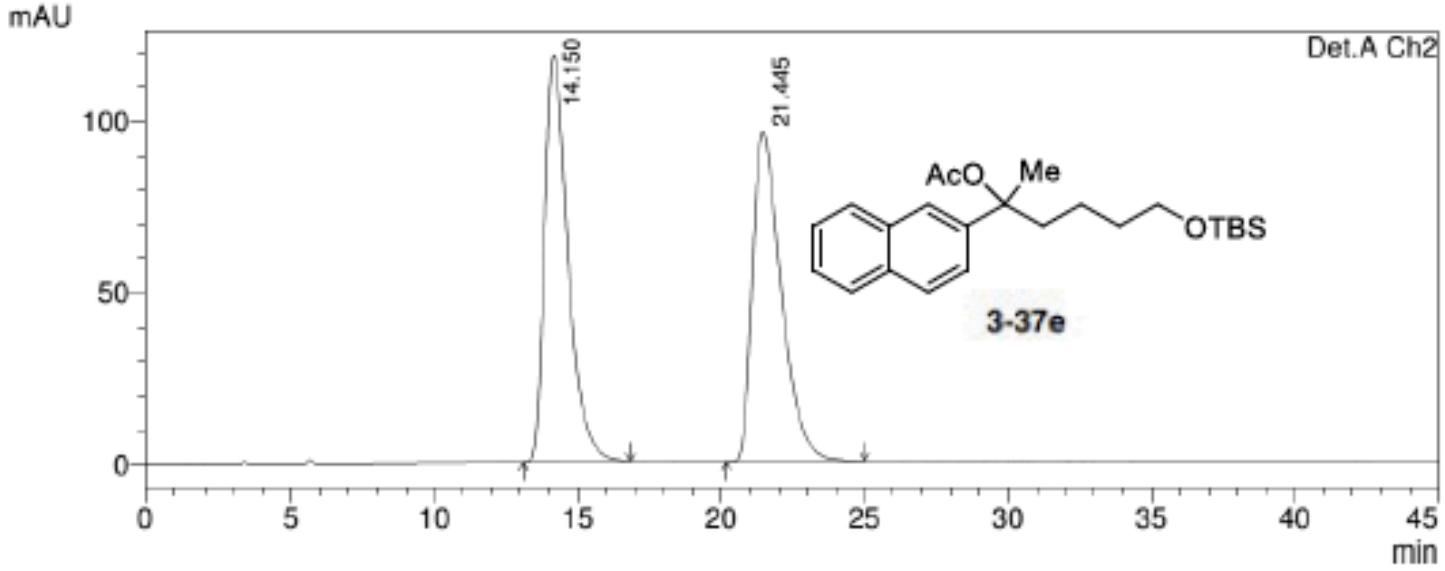
Enantioenriched **3-37d**, 99% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.787	2432	82	0.716	0.847
2	13.331	337293	9599	99.284	99.153
Total		339725	9681	100.000	100.000

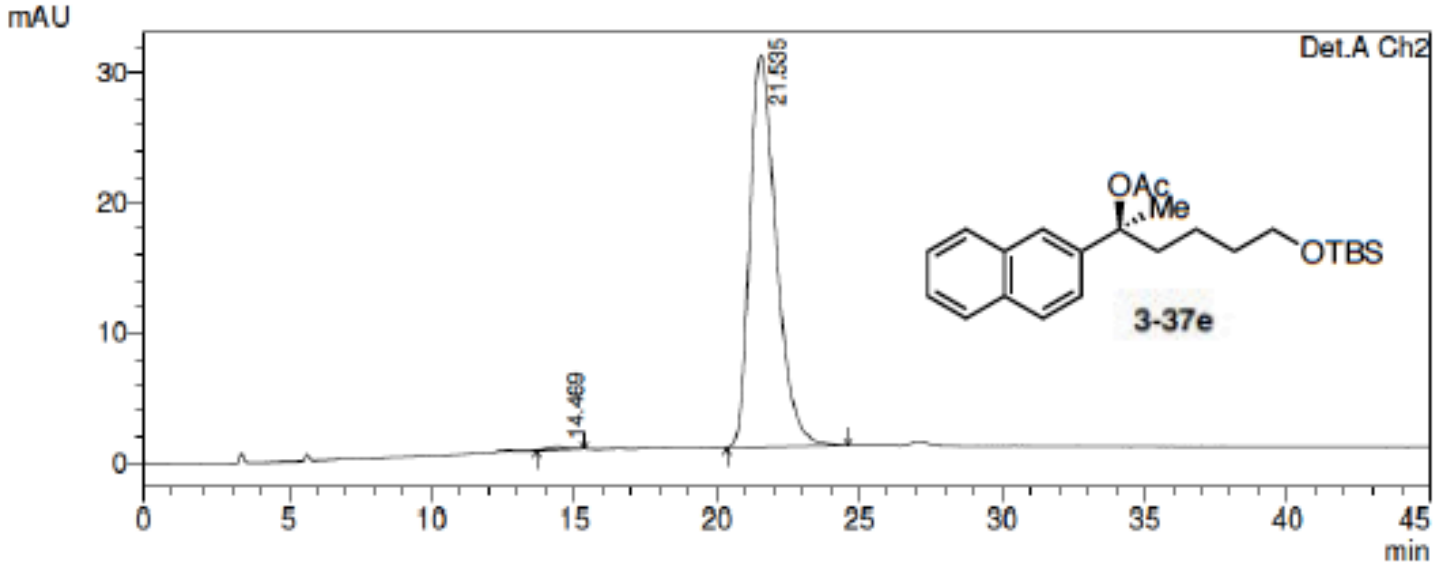
Racemic 3-37e



Detector A Ch2 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.150	6717068	118892	49.889	55.245
2	21.445	6746910	96316	50.111	44.755
Total		13463978	215209	100.000	100.000

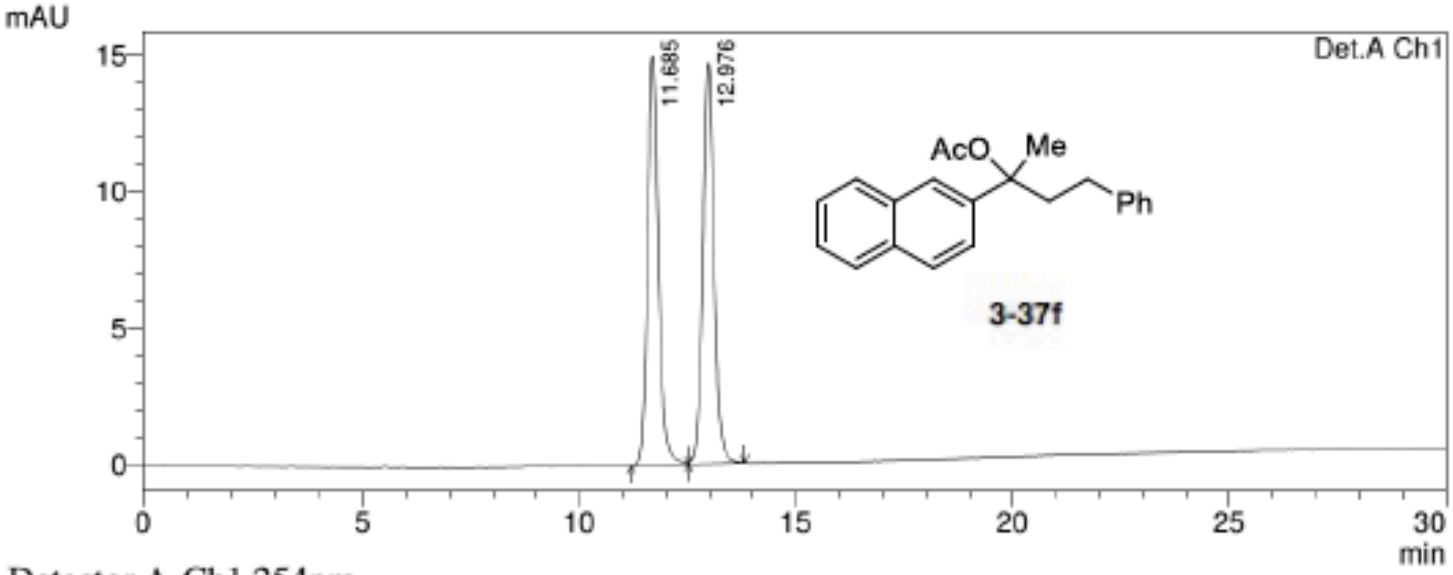
Enantioenriched 3-37e, 99% ee



Detector A Ch2 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.469	10257	216	0.521	0.711
2	21.535	1957089	30206	99.479	99.289
Total		1967346	30422	100.000	100.000

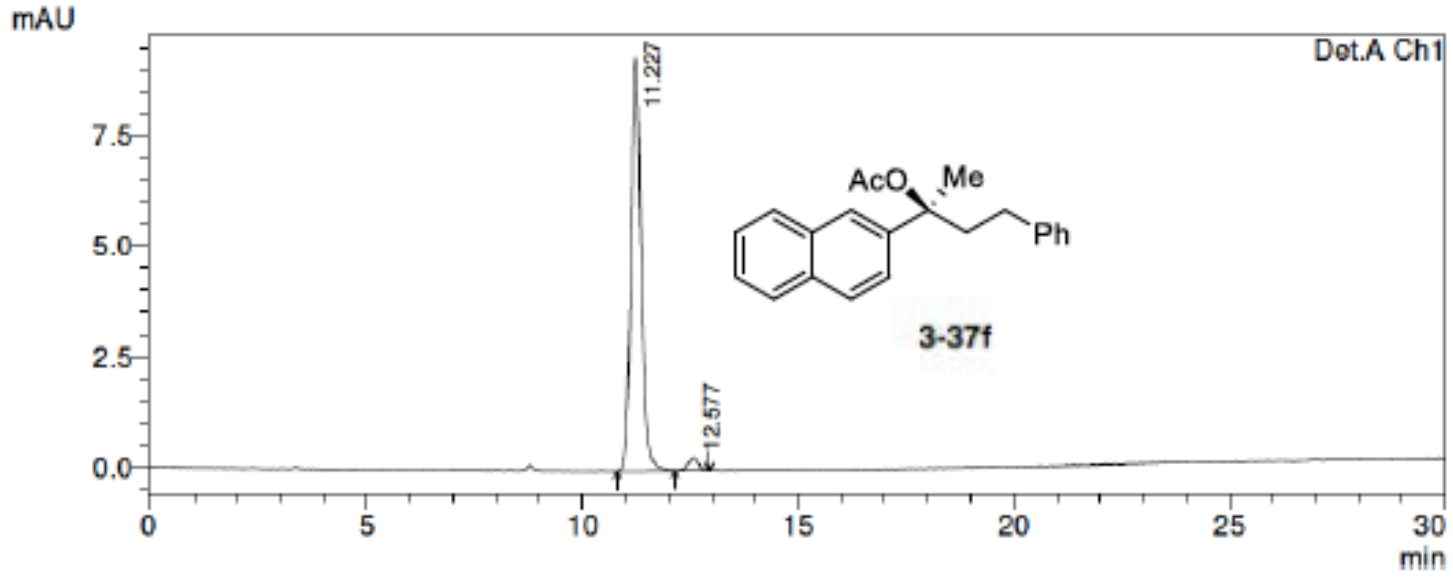
Racemic **3-37f**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.685	259259	14975	49.898	50.568
2	12.976	260324	14639	50.102	49.432
Total		519583	29614	100.000	100.000

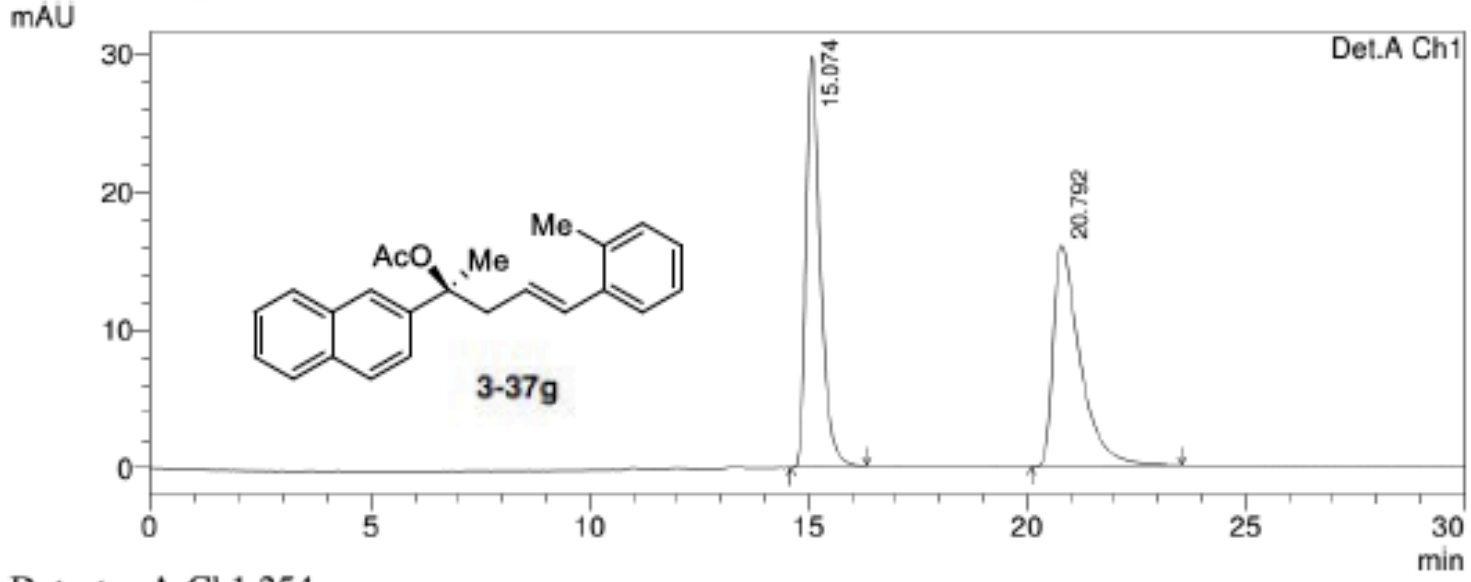
Enantioenriched **3-37f**, 94% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.227	154894	9370	97.078	96.964
2	12.577	4663	293	2.922	3.036
Total		159557	9664	100.000	100.000

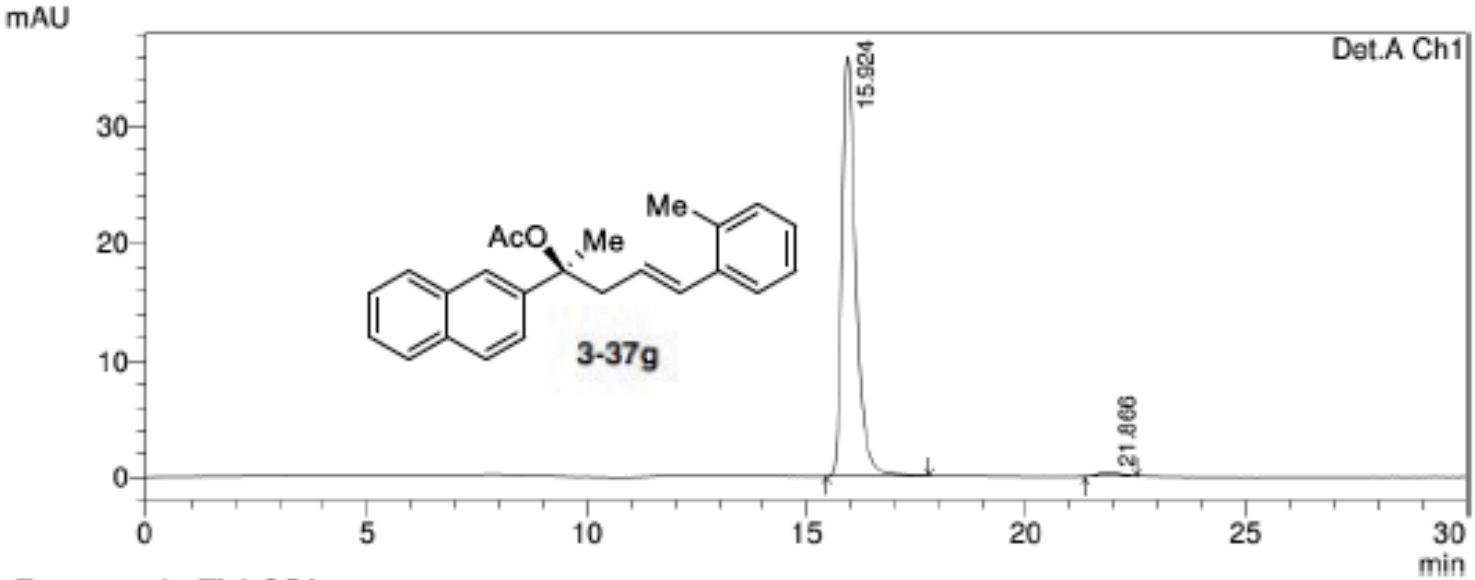
Racemic **3-37g**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.074	682100	29840	49.883	65.138
2	20.792	685307	15970	50.117	34.862
Total		1367408	45811	100.000	100.000

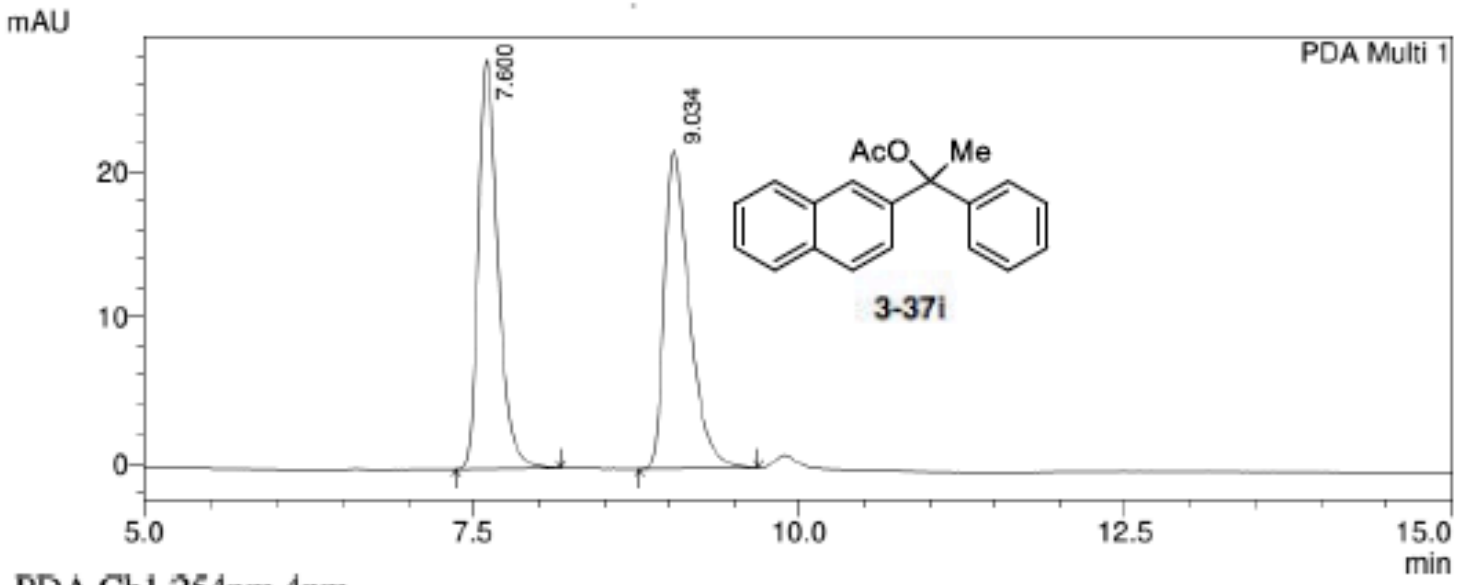
Enantioenriched **3-37g**, 96% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.924	789682	35965	98.270	99.044
2	21.866	13905	347	1.730	0.956
Total		803587	36312	100.000	100.000

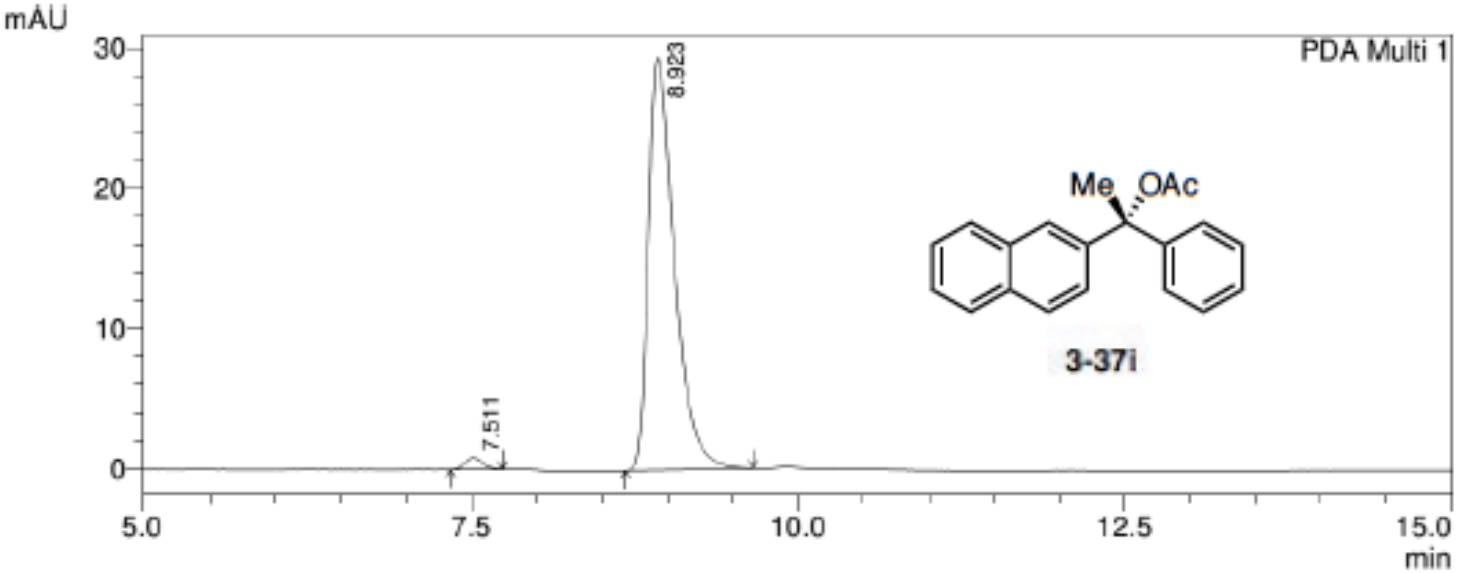
Racemic 3-37i



PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.600	291470	28014	50.165	56.265
2	9.034	289554	21776	49.835	43.735
Total		581024	49790	100.000	100.000

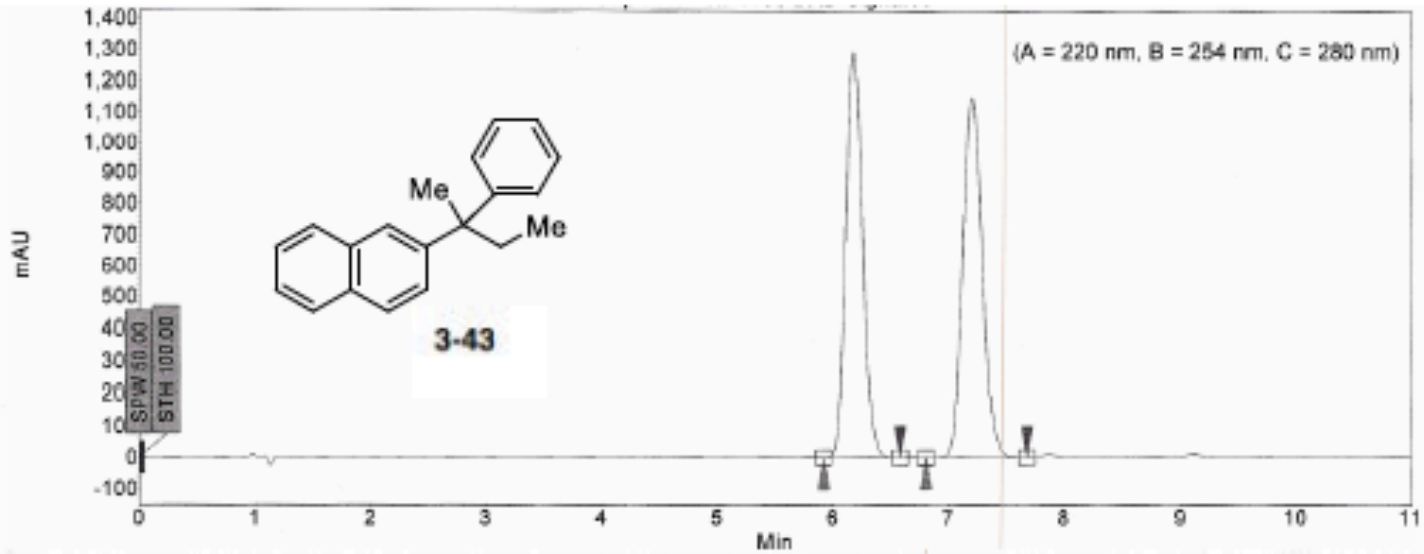
Enantioenriched 3-37i, 96% ee



PDA Ch1 254nm 4nm

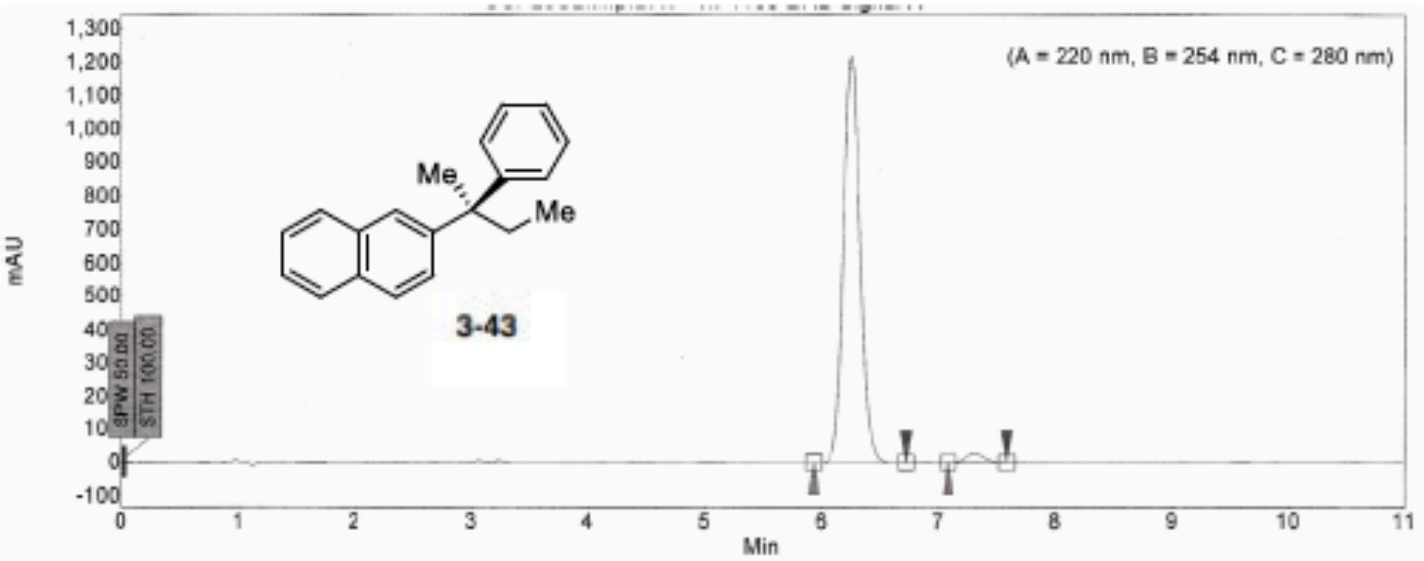
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.511	7964	824	1.915	2.731
2	8.923	407977	29359	98.085	97.269
Total		415942	30183	100.000	100.000

Racemic 3-43



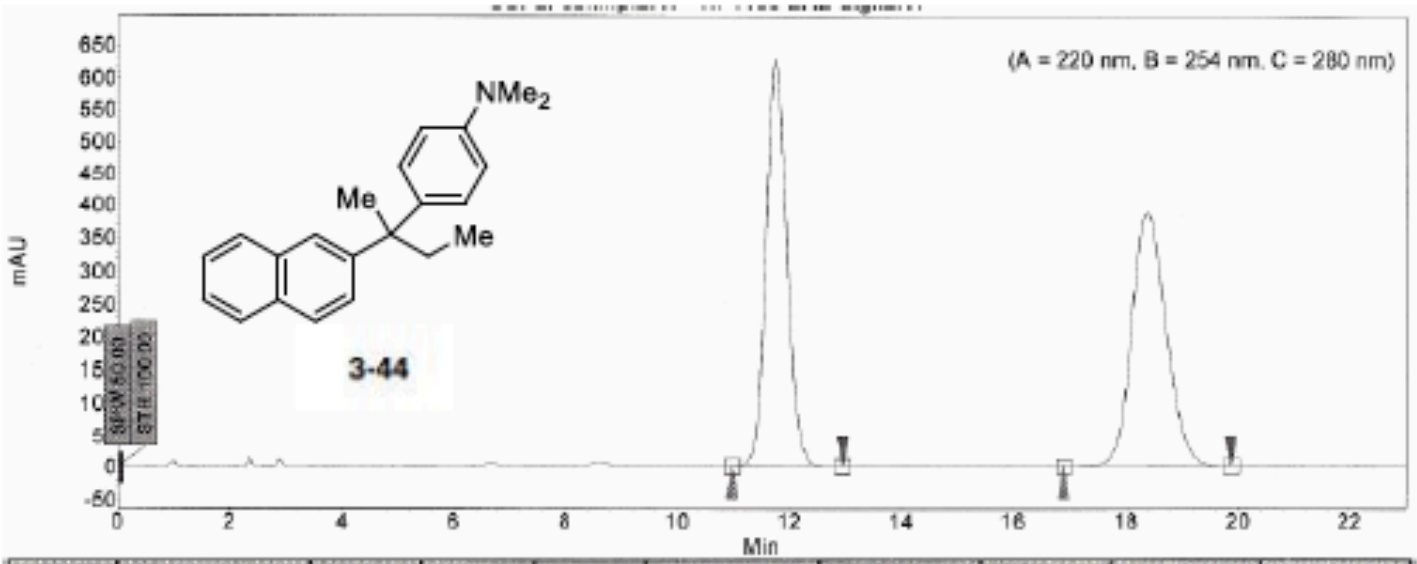
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	5.92	6.18	6.58	0.00	49.41	1292.6	217.5	49.413
2	UNKNOWN	6.81	7.21	7.68	0.00	50.59	1148.9	222.7	50.587
Total						100.00	2441.5	440.2	100.000

Enantioenriched 3-43, 95% ee



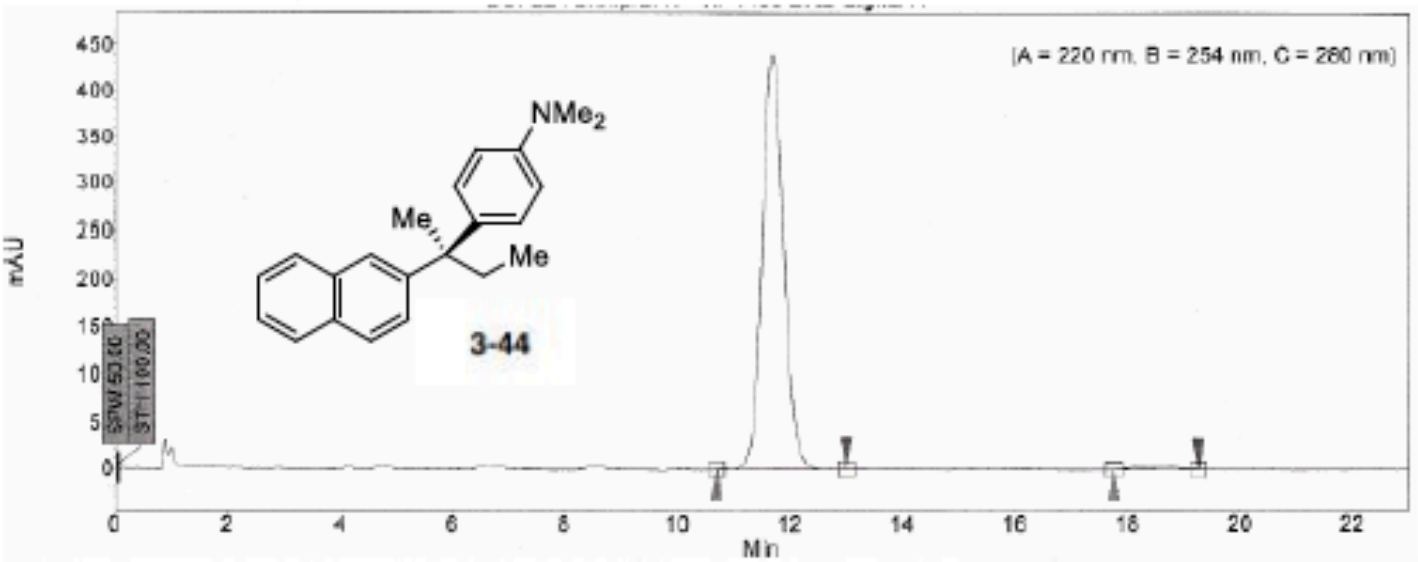
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
2	UNKNOWN	5.93	6.25	6.73	0.00	97.62	1220.1	202.1	97.625
1	UNKNOWN	7.09	7.32	7.59	0.00	2.38	27.5	4.9	2.375
Total						100.00	1247.6	207.0	100.000

Racemic 3-44



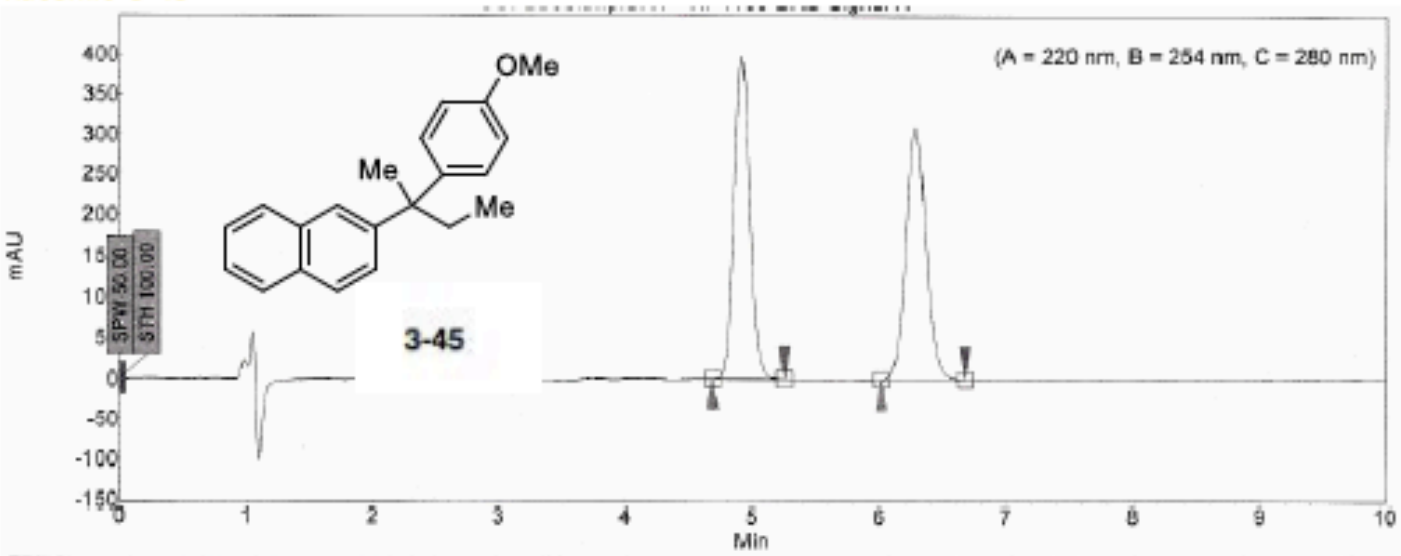
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	10.97	11.74	12.94	0.00	49.90	627.8	276.5	49.904
2	UNKNOWN	16.89	18.37	19.87	0.00	50.10	387.5	277.5	50.096
Total						100.00	1015.2	554.0	100.000

Enantioenriched 3-44, 96% ee



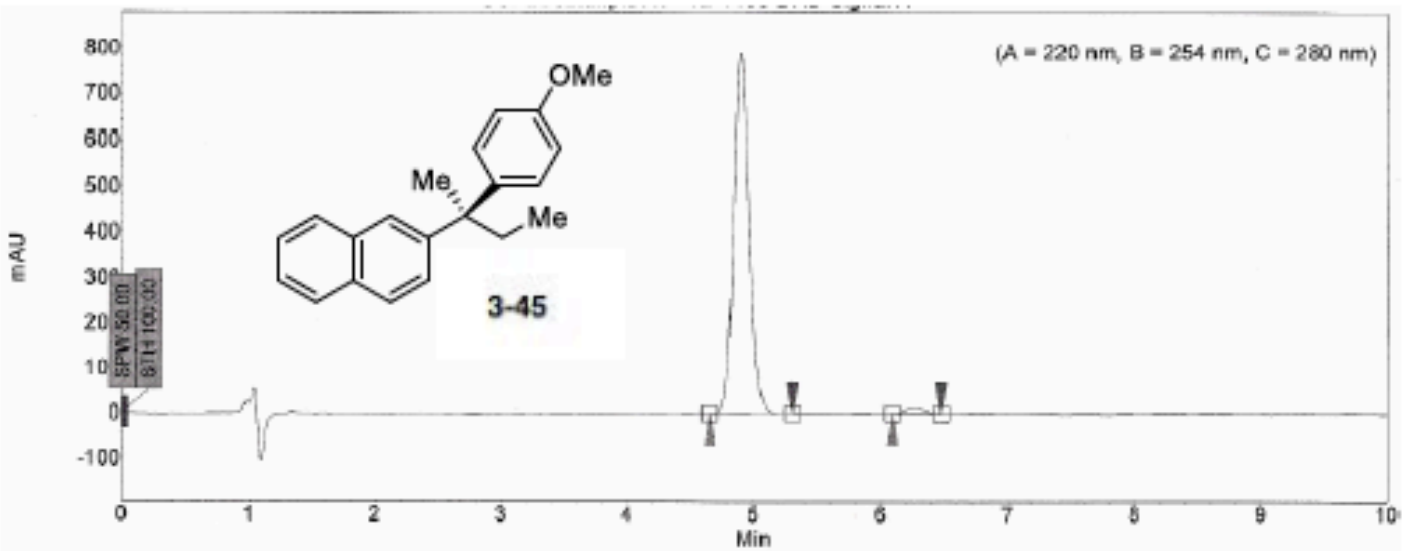
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	10.71	11.68	13.00	0.00	97.91	439.2	193.4	97.908
2	UNKNOWN	17.76	18.49	19.25	0.00	2.09	6.1	4.1	2.092
Total						100.00	445.4	197.5	100.000

Racemic 3-45



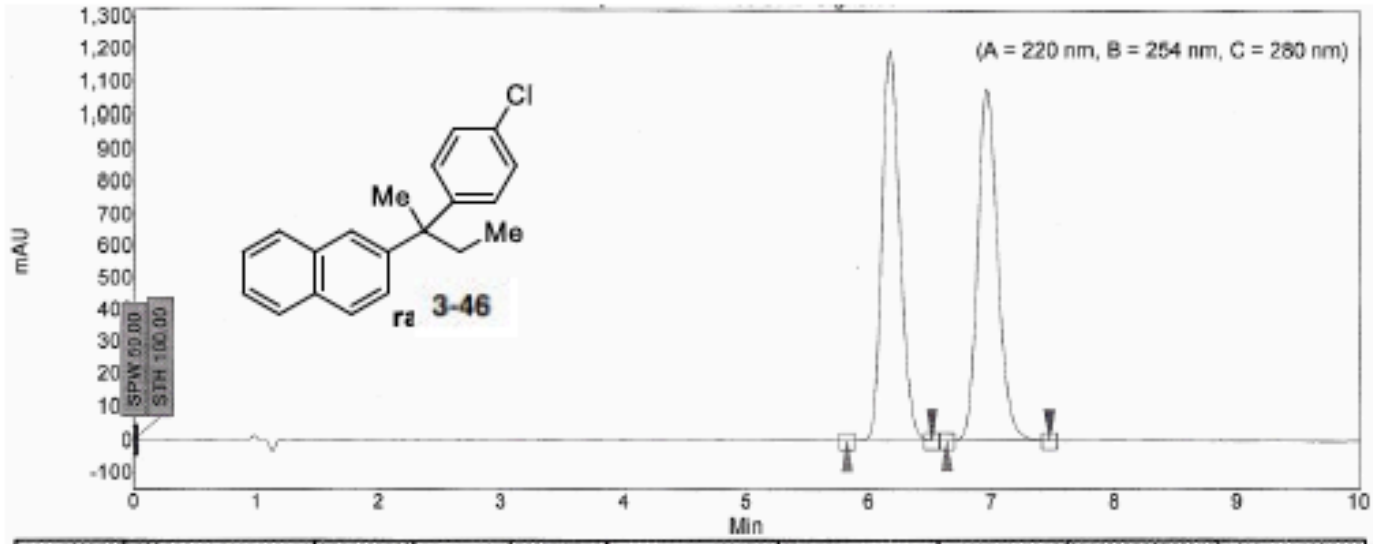
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	4.69	4.91	5.25	0.00	49.78	396.5	55.7	49.783
2	UNKNOWN	6.01	6.28	6.67	0.00	50.22	308.1	56.2	50.217
Total						100.00	704.6	112.0	100.000

Enantioenriched 3-45, 96% ee



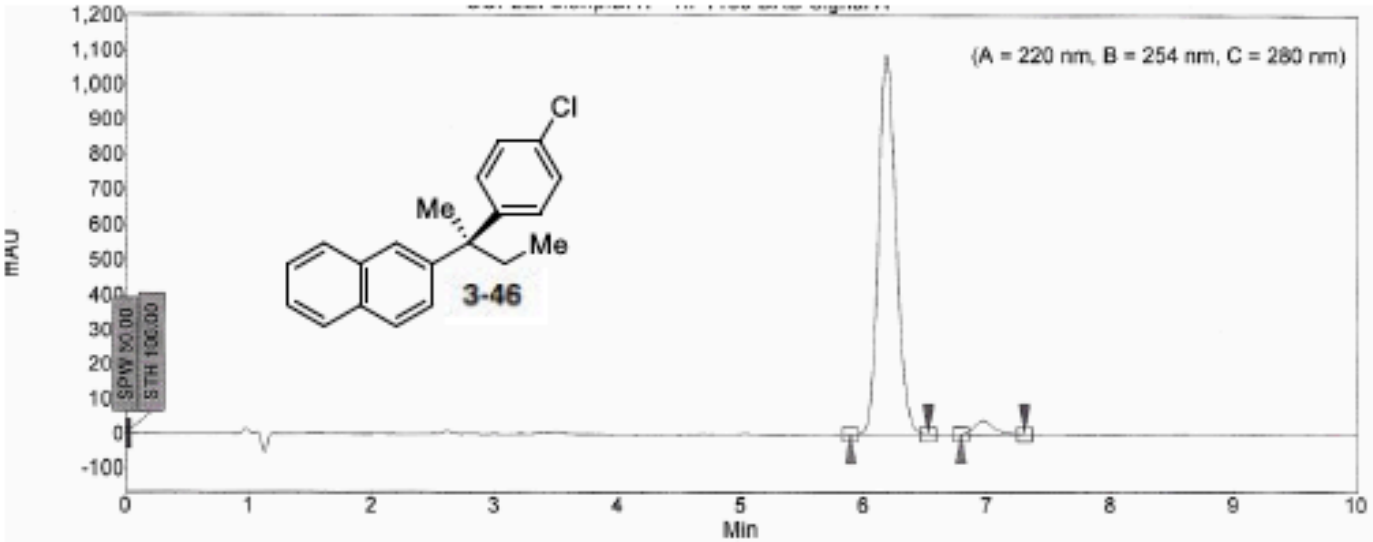
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
2	UNKNOWN	4.65	4.89	5.30	0.00	98.05	790.5	114.5	98.051
1	UNKNOWN	6.09	6.27	6.47	0.00	1.95	13.5	2.3	1.949
Total						100.00	804.0	116.8	100.000

Racemic 3-46



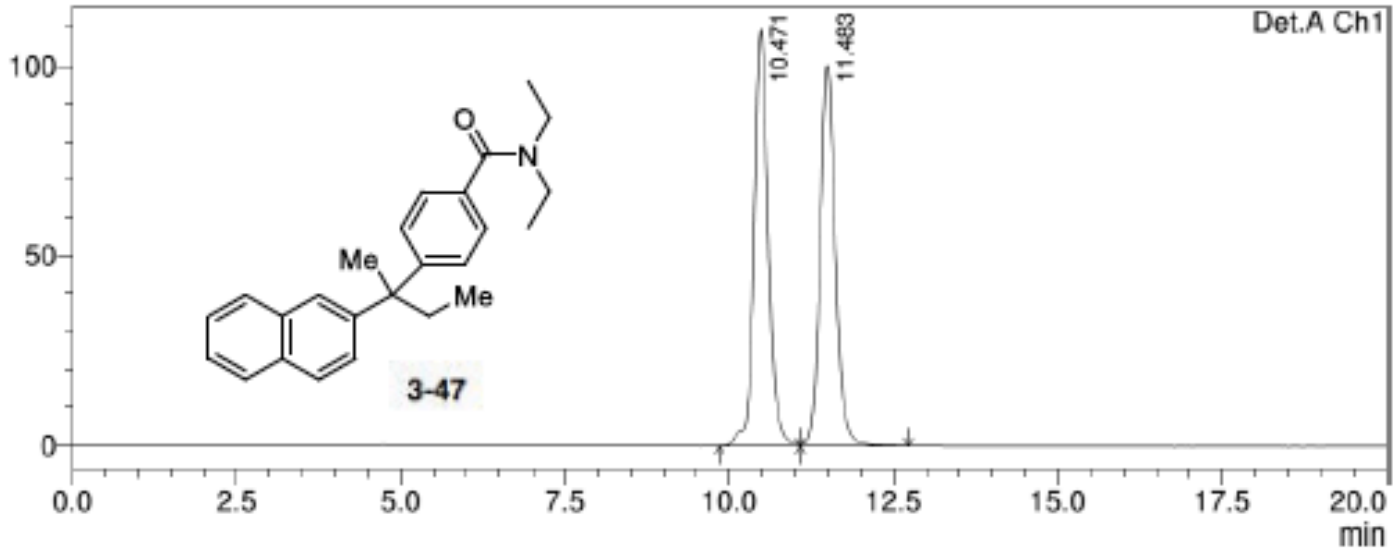
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	5.82	6.17	6.52	0.00	49.58	1197.4	201.8	49.580
2	UNKNOWN	6.64	6.96	7.47	0.00	50.42	1078.7	205.2	50.420
Total						100.00	2276.1	407.0	100.000

Enantioenriched 3-46, 92% ee



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	5.89	6.18	6.52	0.00	96.01	1087.1	180.0	96.009
2	UNKNOWN	6.79	6.97	7.30	0.00	3.99	41.2	7.5	3.991
Total						100.00	1128.3	187.4	100.000

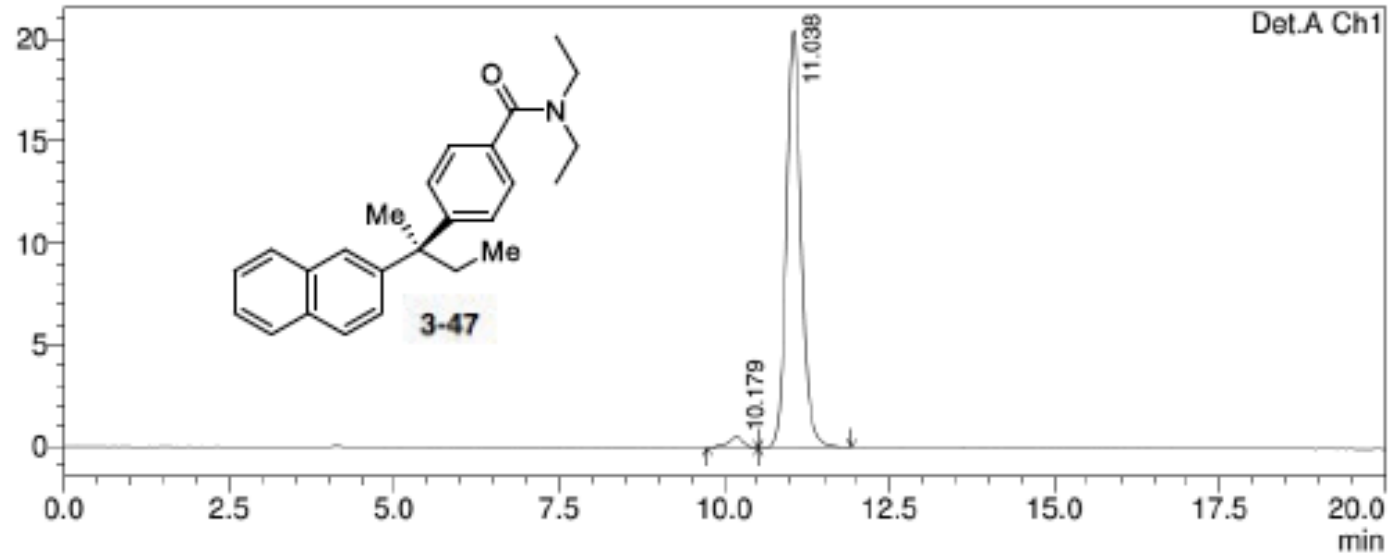
Racemic **3-47**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.471	1653101	109872	50.507	52.247
2	11.483	1619926	100424	49.493	47.753
Total		3273026	210296	100.000	100.000

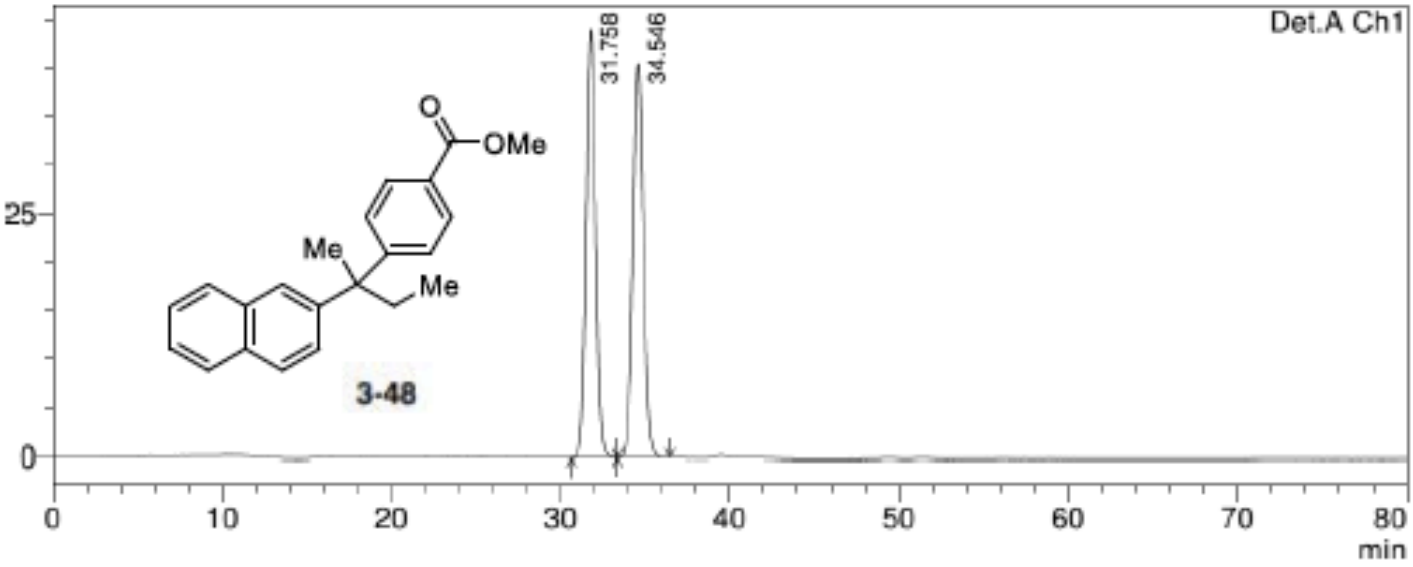
Enantioenriched **3-47**, 94% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.179	9333	548	2.832	2.609
2	11.038	320214	20472	97.168	97.391
Total		329548	21021	100.000	100.000

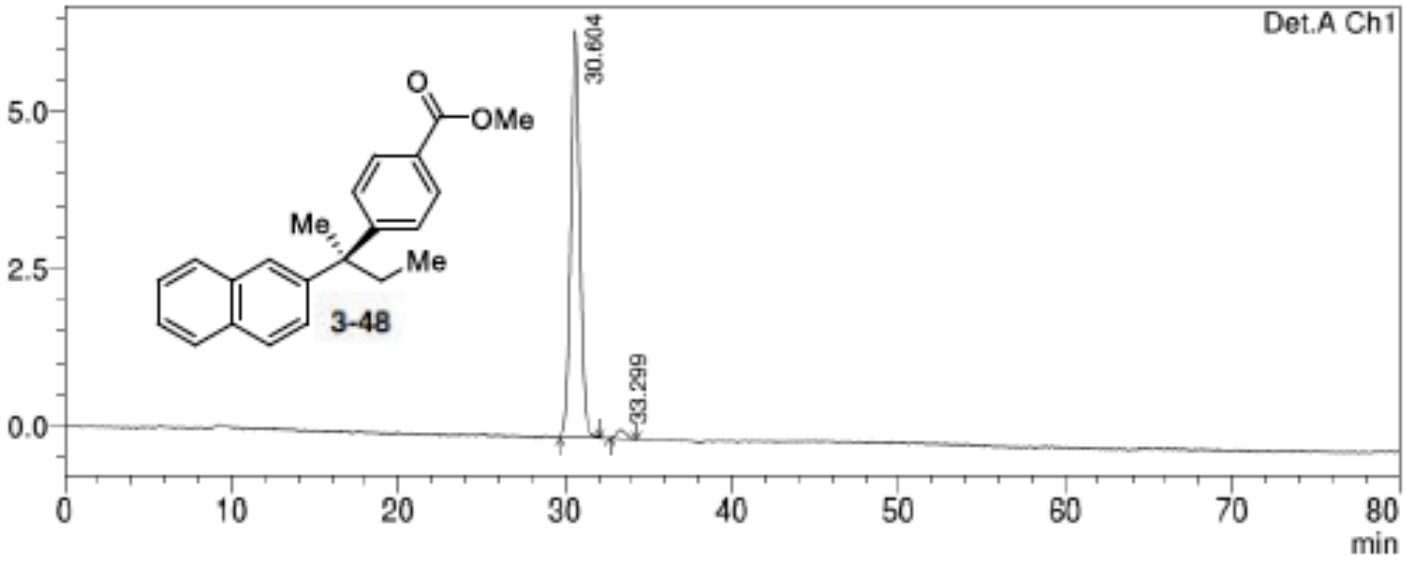
Racemic 3-48



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	31.758	1728236	44032	49.845	52.134
2	34.546	1738977	40427	50.155	47.866
Total		3467213	84459	100.000	100.000

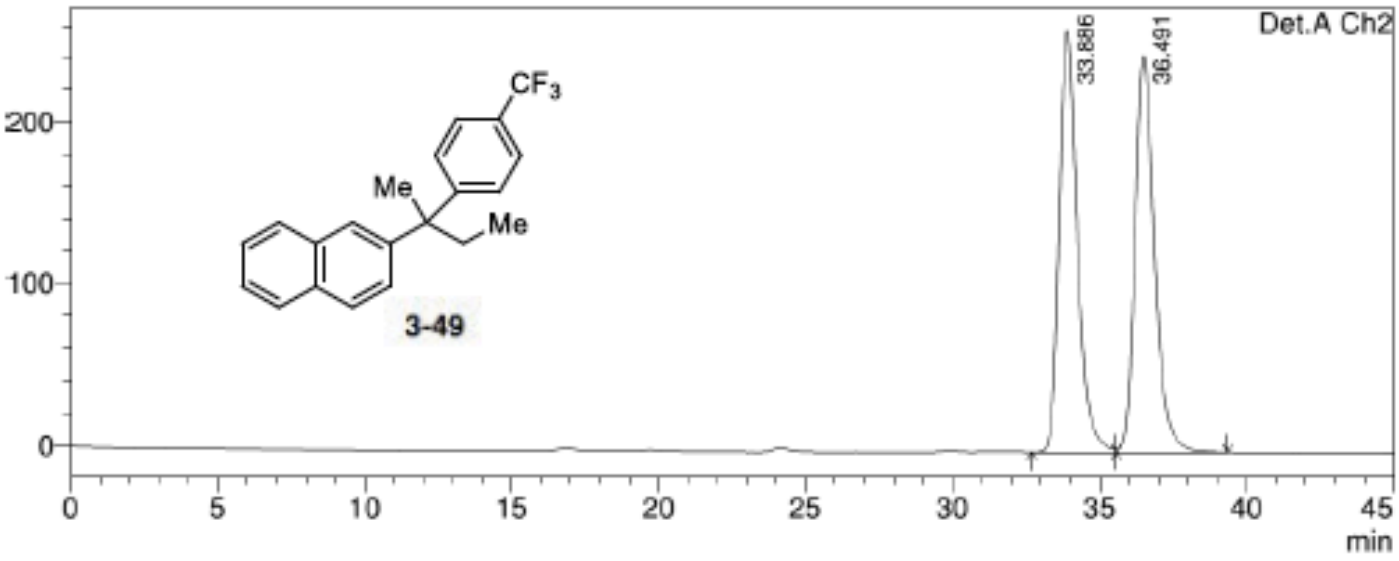
Enantioenriched 3-48, 96% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.604	251321	6477	97.885	98.017
2	33.299	5430	131	2.115	1.983
Total		256751	6608	100.000	100.000

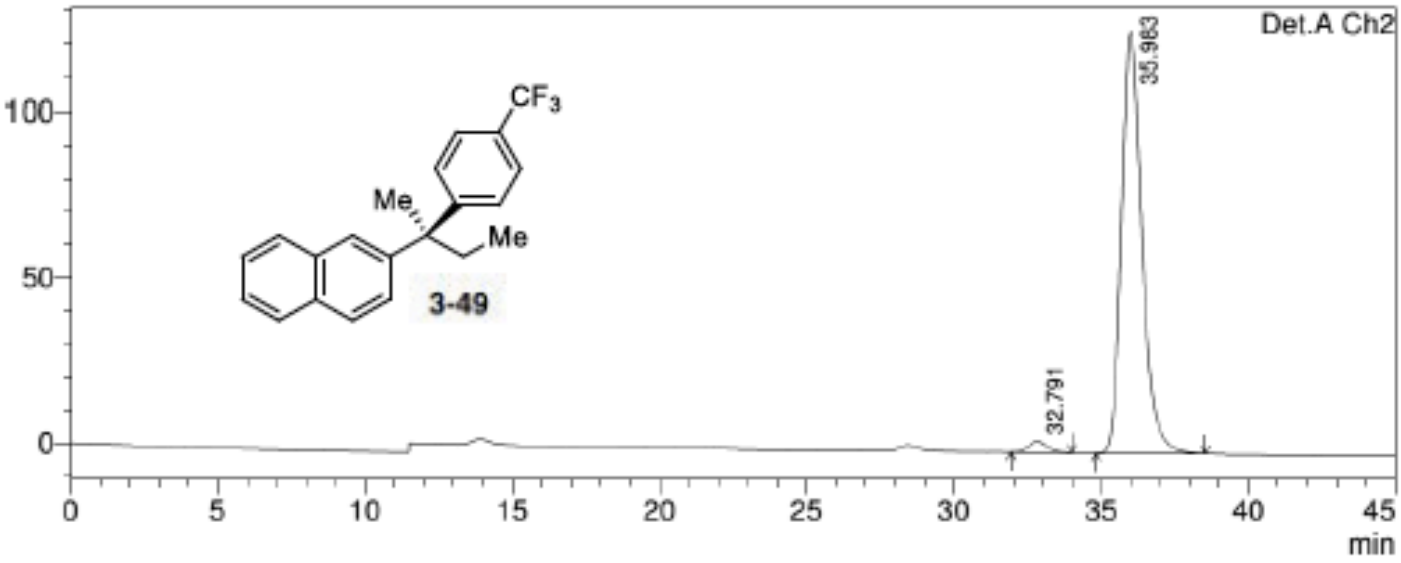
Racemic **3-49**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	33.885	1587788	36919	49.856	51.534
2	36.489	1596950	34721	50.144	48.466
Total		3184738	71640	100.000	100.000

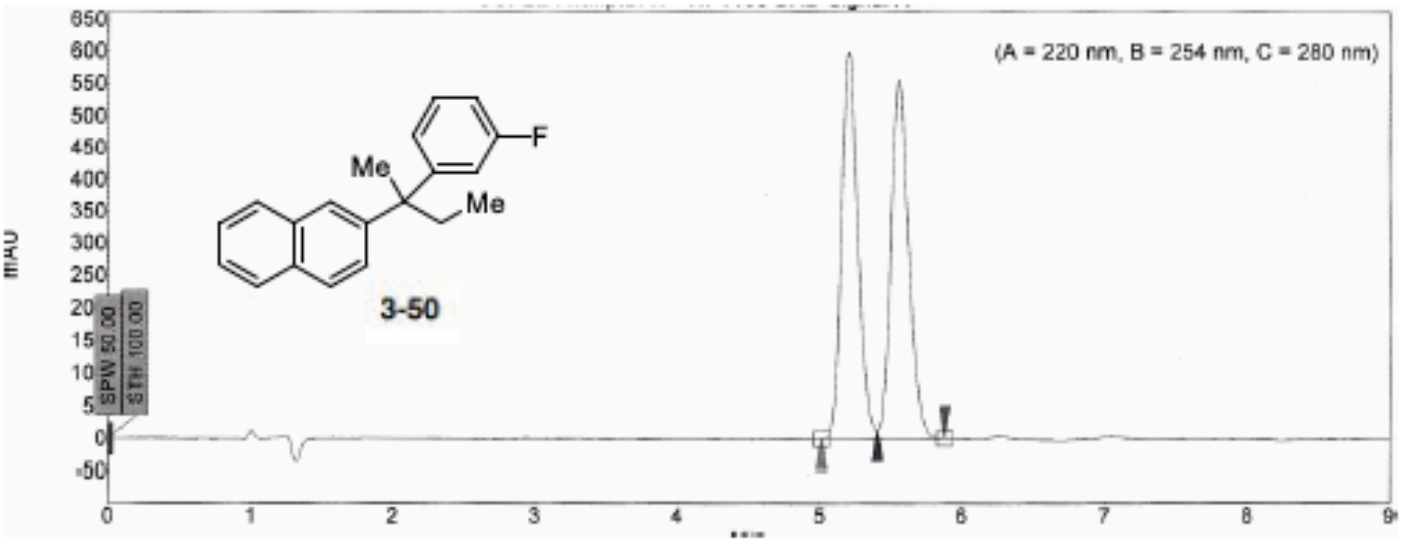
Enantioenriched **3-49**, 96% ee



Detector A Ch1 254nm

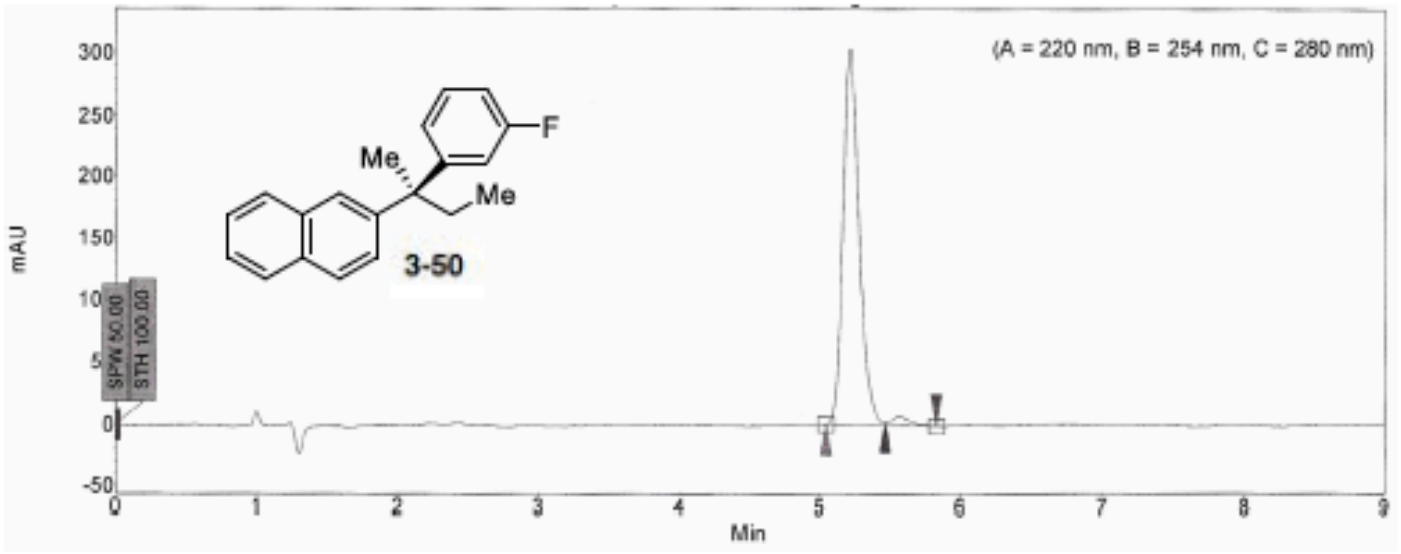
Peak#	Ret. Time	Area	Height	Area %	Height %
1	35.980	18779	442	2.148	2.424
2	39.173	855635	17798	97.852	97.576
Total		874414	18241	100.000	100.000

Racemic 3-50



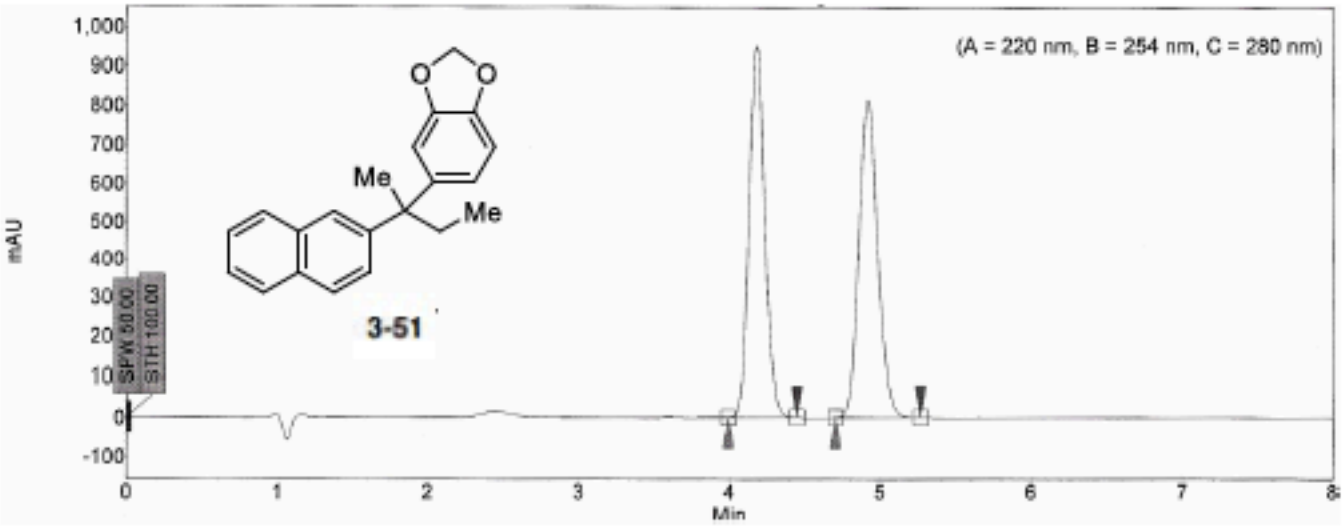
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	5.01	5.21	5.41	0.00	49.95	599.1	80.3	49.946
2	UNKNOWN	5.41	5.55	5.88	0.00	50.05	555.9	80.5	50.054
Total						100.00	1155.0	160.8	100.000

Enantioenriched 3-50, 94% ee



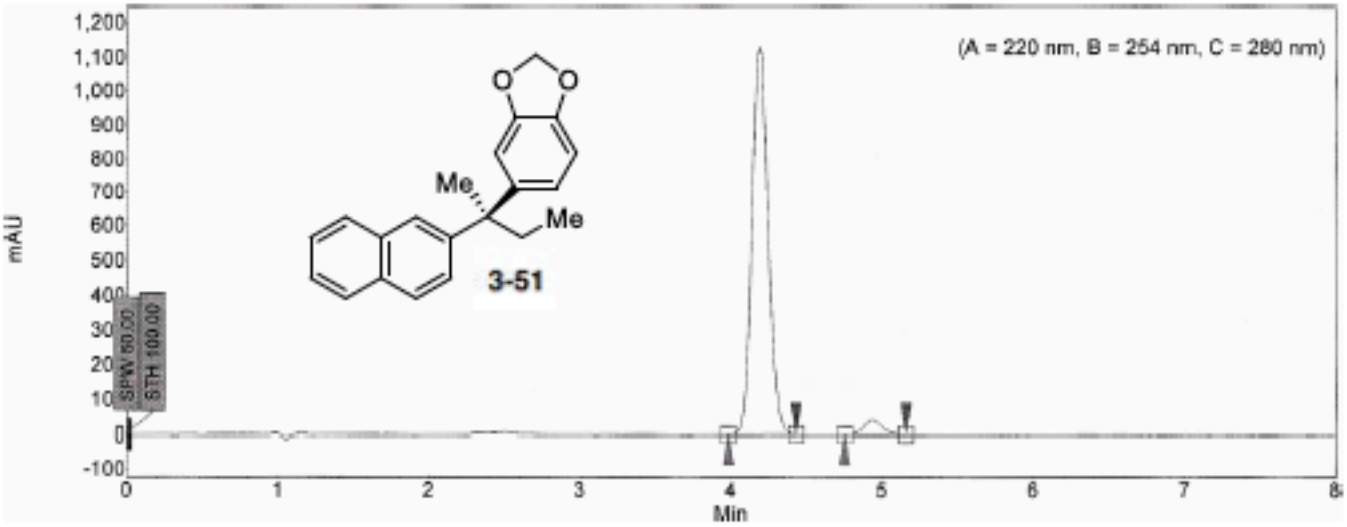
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	5.05	5.22	5.47	0.00	97.13	303.5	40.2	97.132
2	UNKNOWN	5.47	5.57	5.83	0.00	2.87	7.8	1.2	2.868
Total						100.00	311.3	41.4	100.000

Racemic 3-51



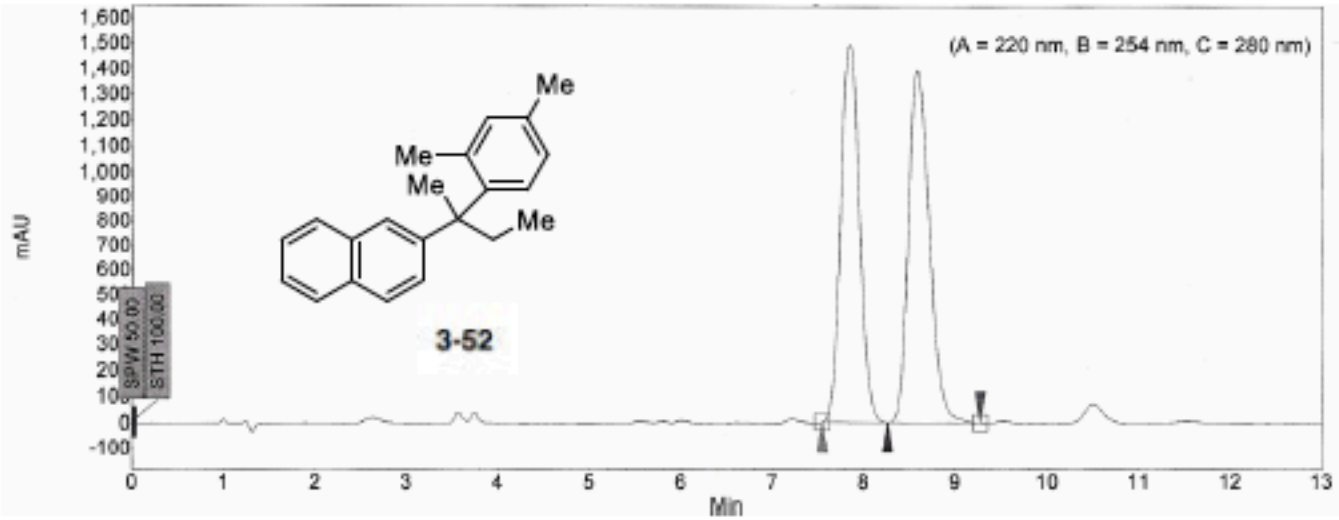
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	3.99	4.18	4.45	0.00	49.67	950.2	114.9	49.670
2	UNKNOWN	4.70	4.91	5.27	0.00	50.33	814.4	116.4	50.330
Total						100.00	1764.6	231.2	100.000

Enantioenriched 3-51, 92% ee



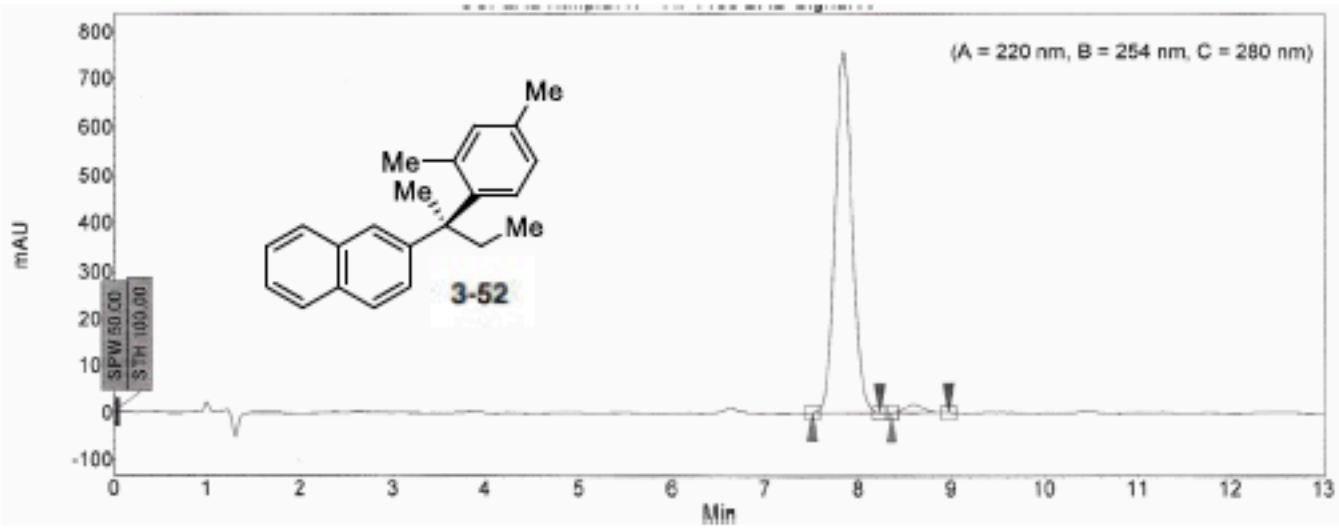
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	3.98	4.19	4.43	0.00	96.07	1130.0	139.5	96.066
2	UNKNOWN	4.75	4.93	5.16	0.00	3.93	41.1	5.7	3.934
Total						100.00	1171.2	145.2	100.000

Racemic 3-52



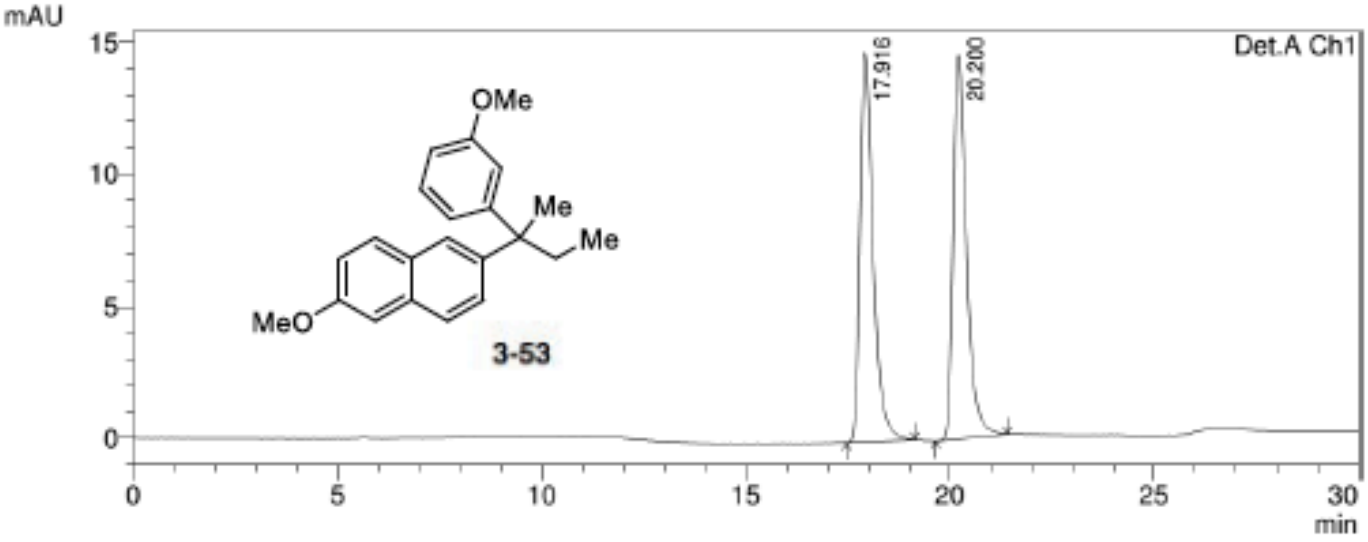
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	7.55	7.85	8.26	0.00	49.14	1491.2	352.2	49.145
2	UNKNOWN	8.26	8.59	9.27	0.00	50.86	1391.4	364.5	50.855
Total						100.00	2882.6	716.8	100.000

Enantioenriched 3-52, 95% ee



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	7.50	7.83	8.22	0.00	97.52	758.0	161.1	97.517
2	UNKNOWN	8.36	8.59	8.97	0.00	2.48	18.4	4.1	2.483
Total						100.00	776.4	165.2	100.000

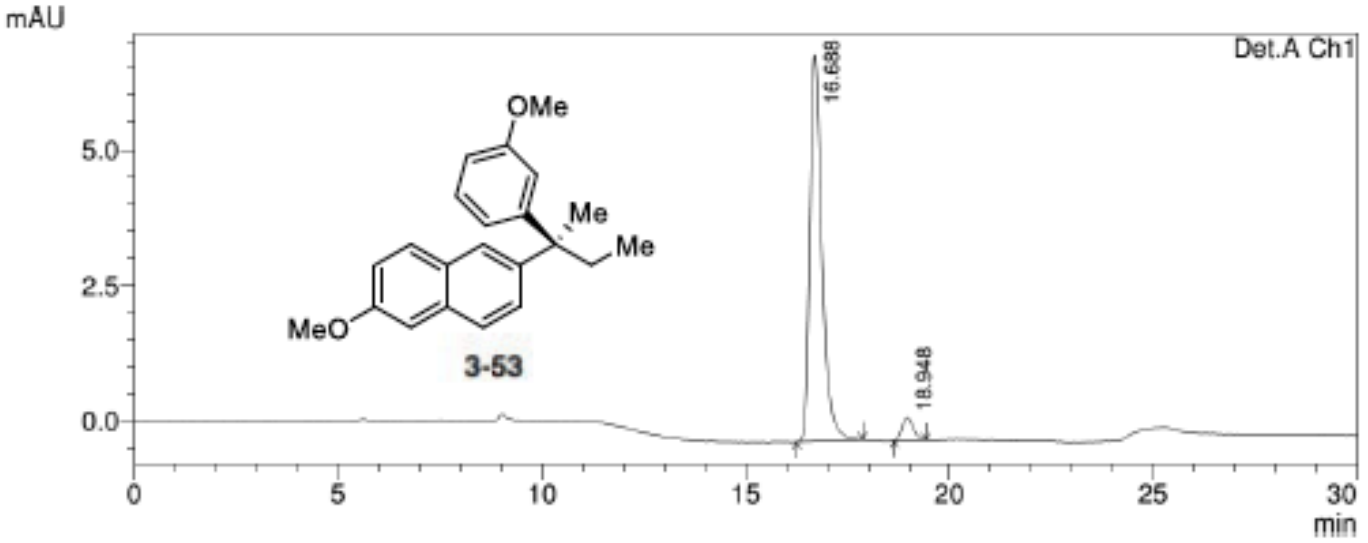
Racemic 3-53



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.916	330741	14782	49.859	50.395
2	20.200	332617	14550	50.141	49.605
Total		663357	29332	100.000	100.000

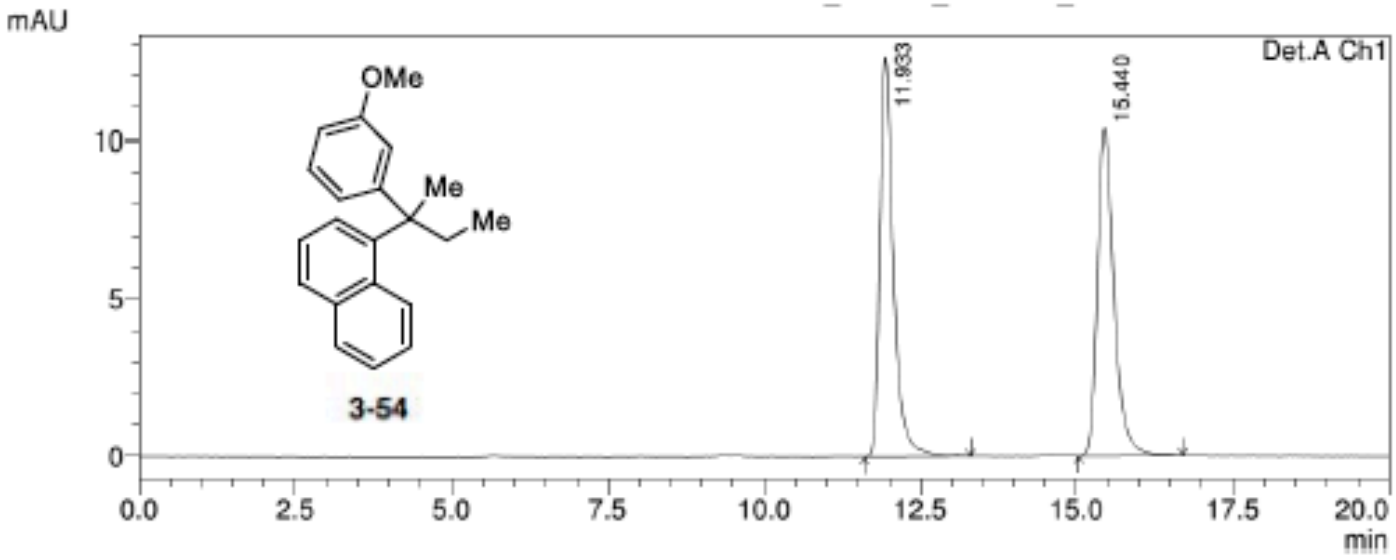
Enantioenriched 3-53, 90% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.688	147777	7132	94.789	94.386
2	18.948	8124	424	5.211	5.614
Total		155901	7556	100.000	100.000

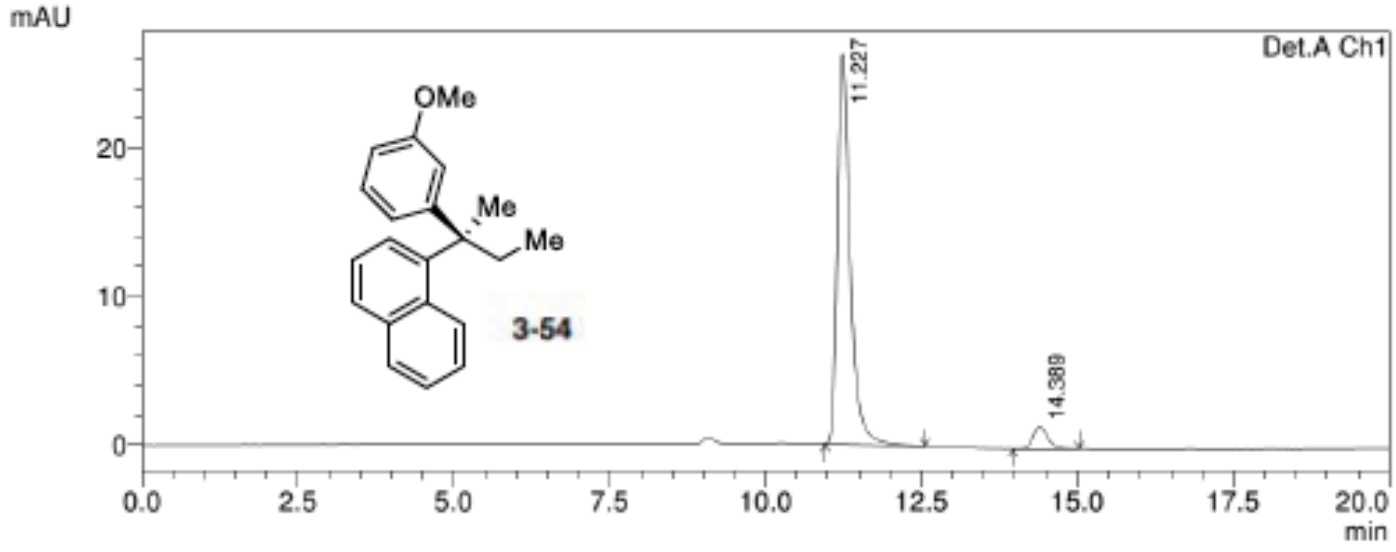
Racemic 3-54



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.933	192477	12599	50.018	54.934
2	15.440	192342	10336	49.982	45.066
Total		384819	22934	100.000	100.000

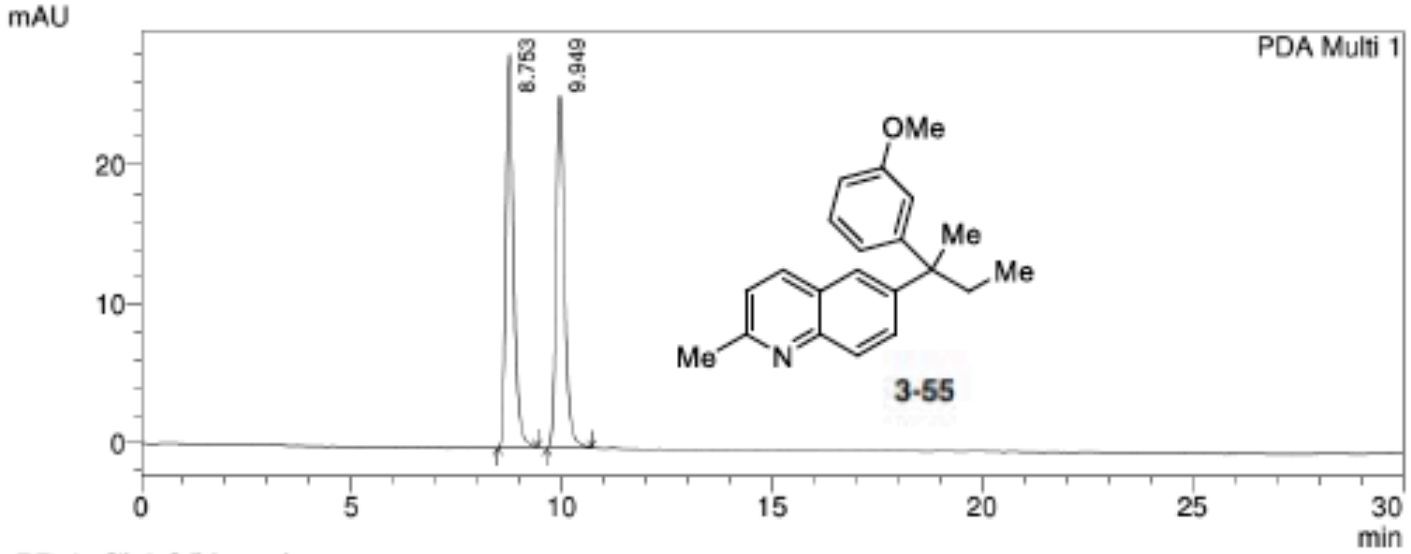
Enantioenriched 3-54, 88% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.227	378067	26292	93.832	94.517
2	14.389	24853	1525	6.168	5.483
Total		402920	27817	100.000	100.000

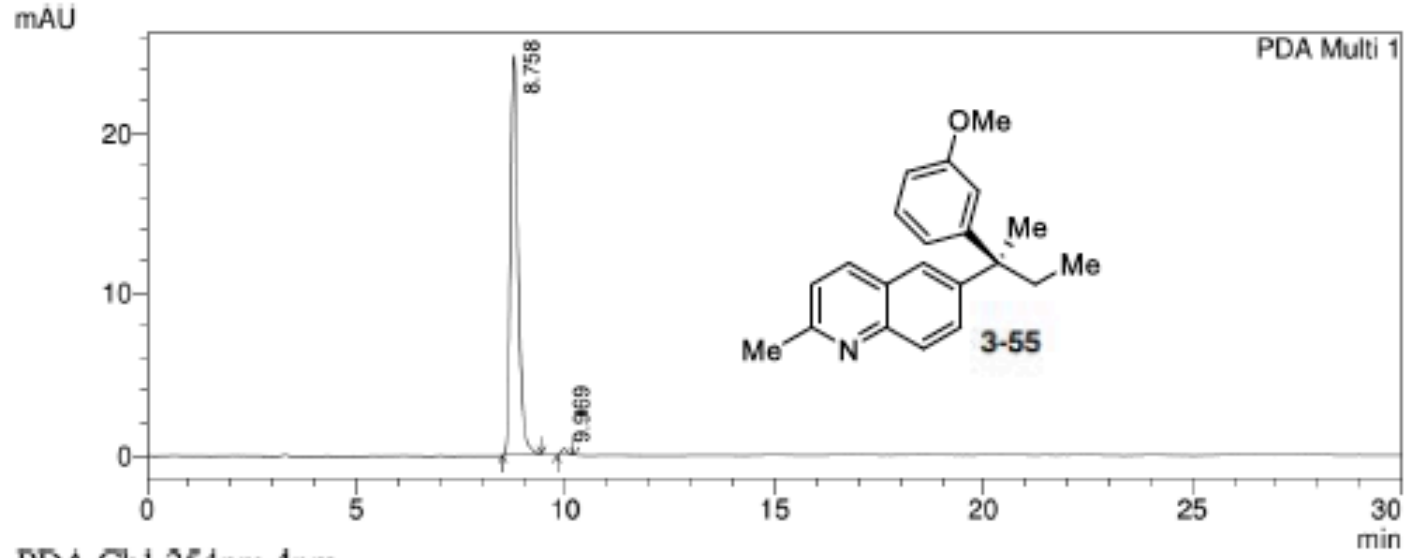
Racemic 3-55



PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.753	355326	28276	50.038	52.795
2	9.949	354785	25282	49.962	47.205
Total		710111	53557	100.000	100.000

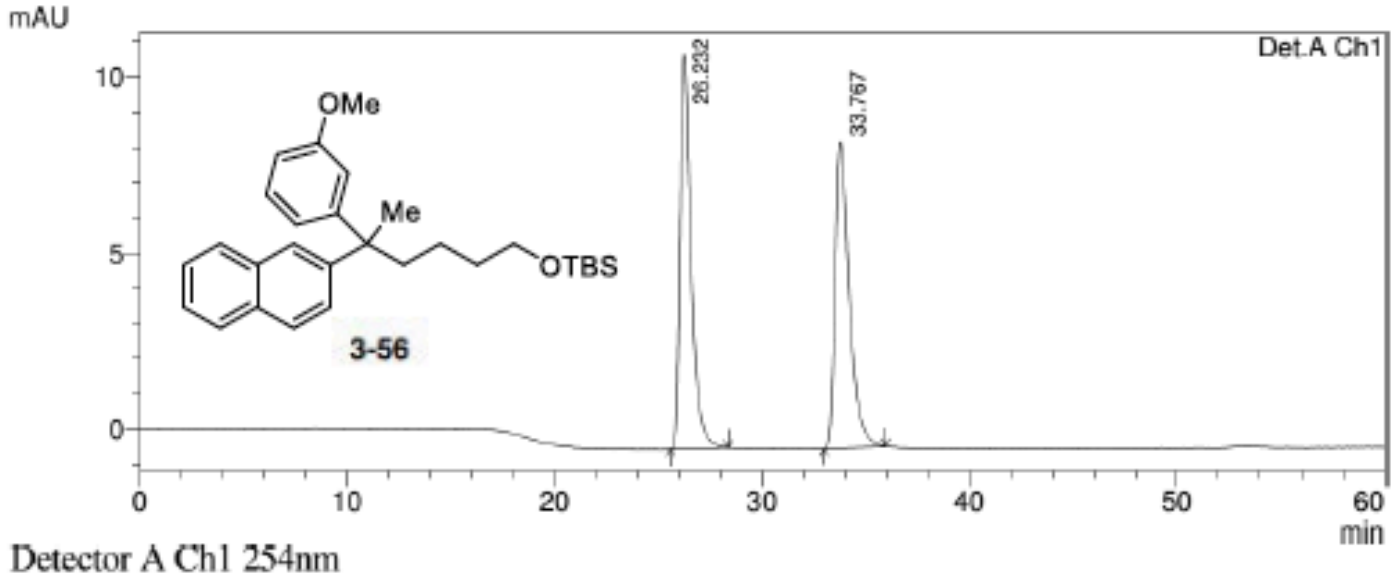
Enantioenriched 3-55, 97% ee



PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.758	310956	24796	98.496	98.455
2	9.969	4747	389	1.504	1.545
Total		315703	25185	100.000	100.000

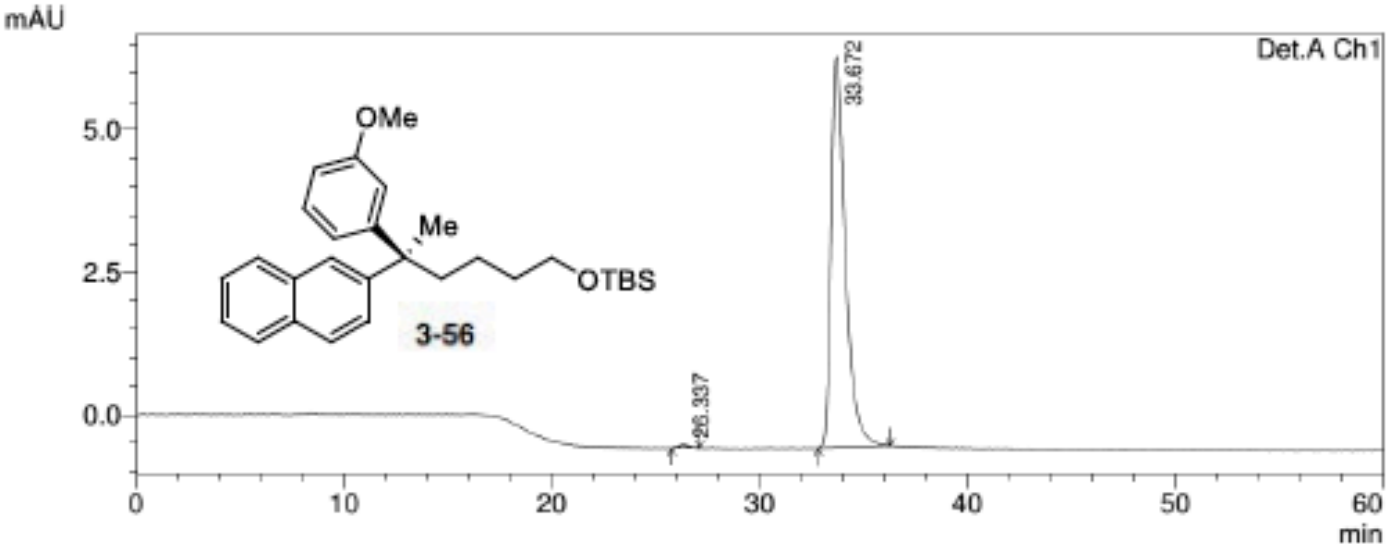
Racemic 3-56



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.232	416026	11202	50.139	56.329
2	33.767	413712	8684	49.861	43.671
Total		829738	19886	100.000	100.000

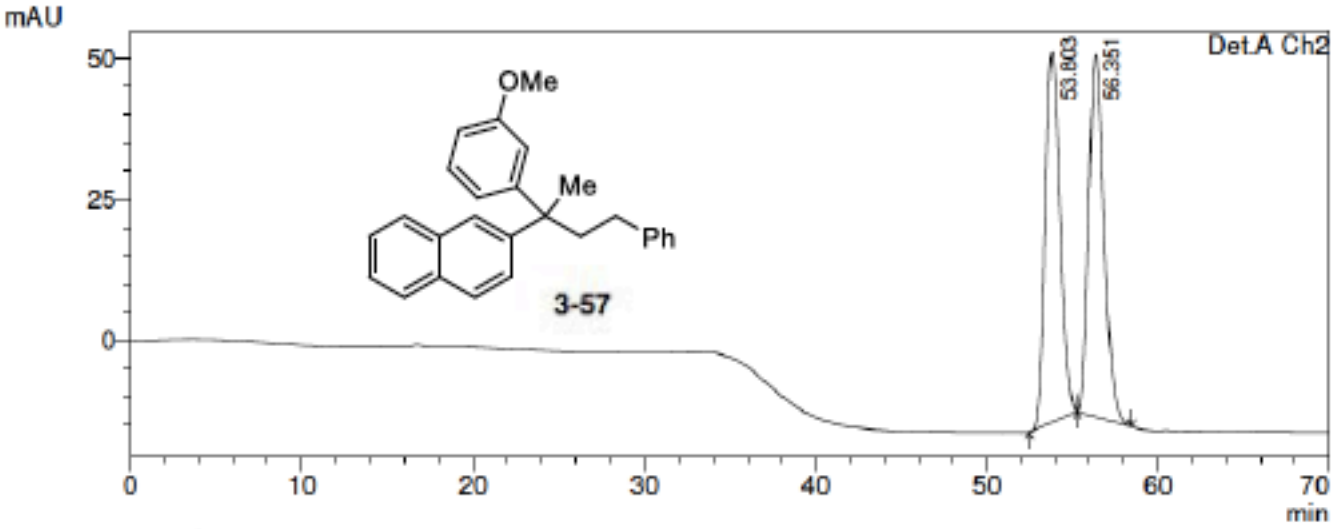
Enantioenriched 3-56, 99% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.337	2073	64	0.625	0.925
2	33.672	329423	6878	99.375	99.075
Total		331496	6942	100.000	100.000

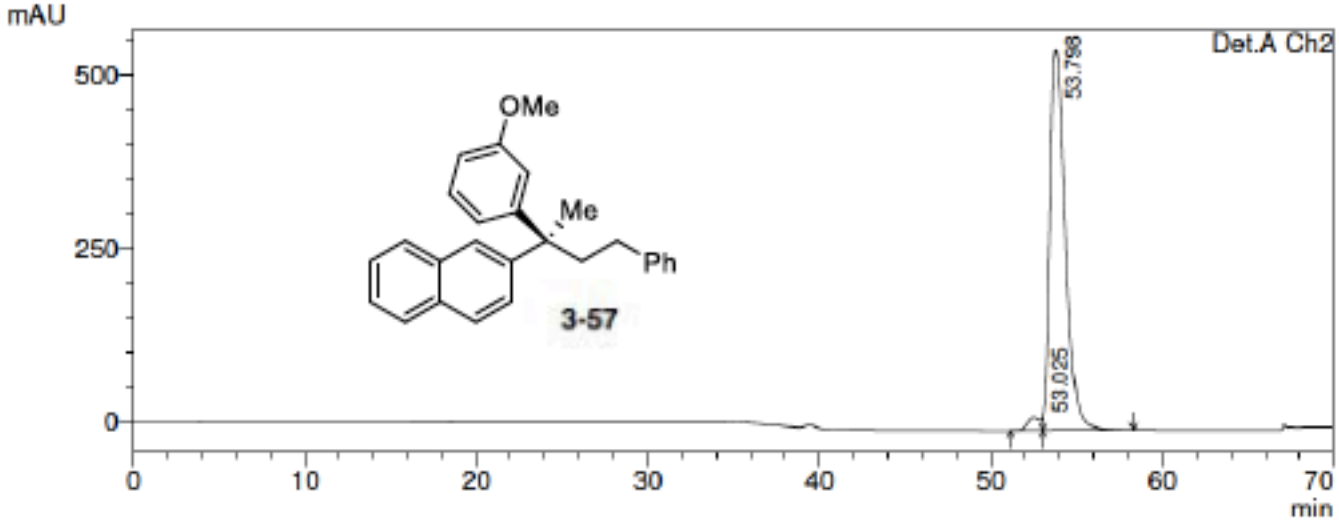
Racemic 3-57



Detector A Ch2 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	53.803	3938543	65377	49.786	50.537
2	56.351	3972469	63987	50.214	49.463
Total		7911011	129364	100.000	100.000

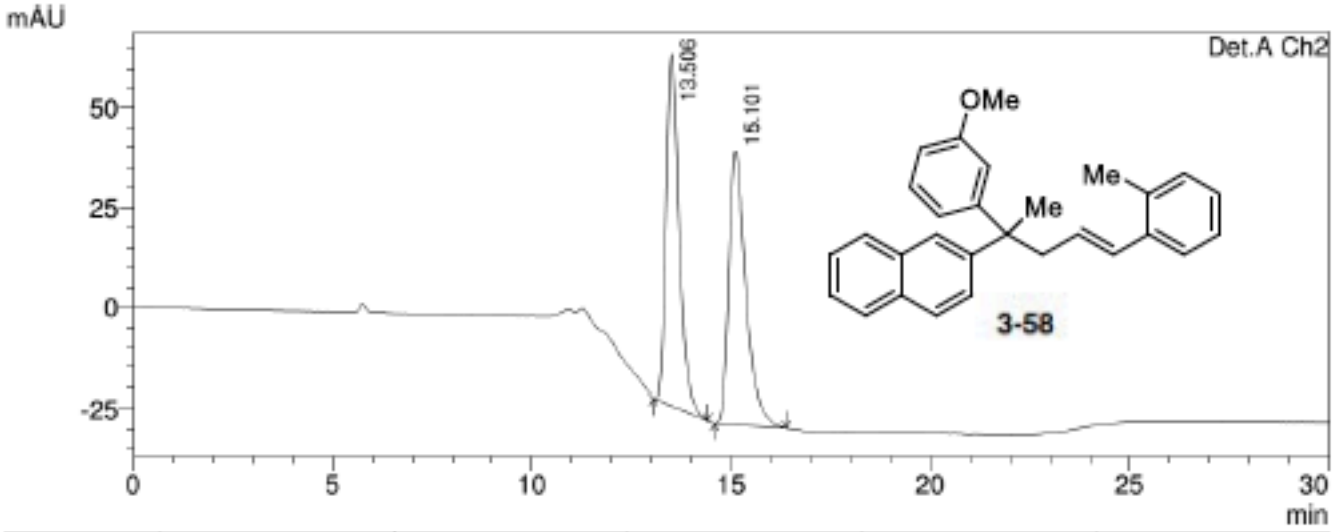
Enantioenriched 3-57, 94% ee



Detector A Ch2 220nm

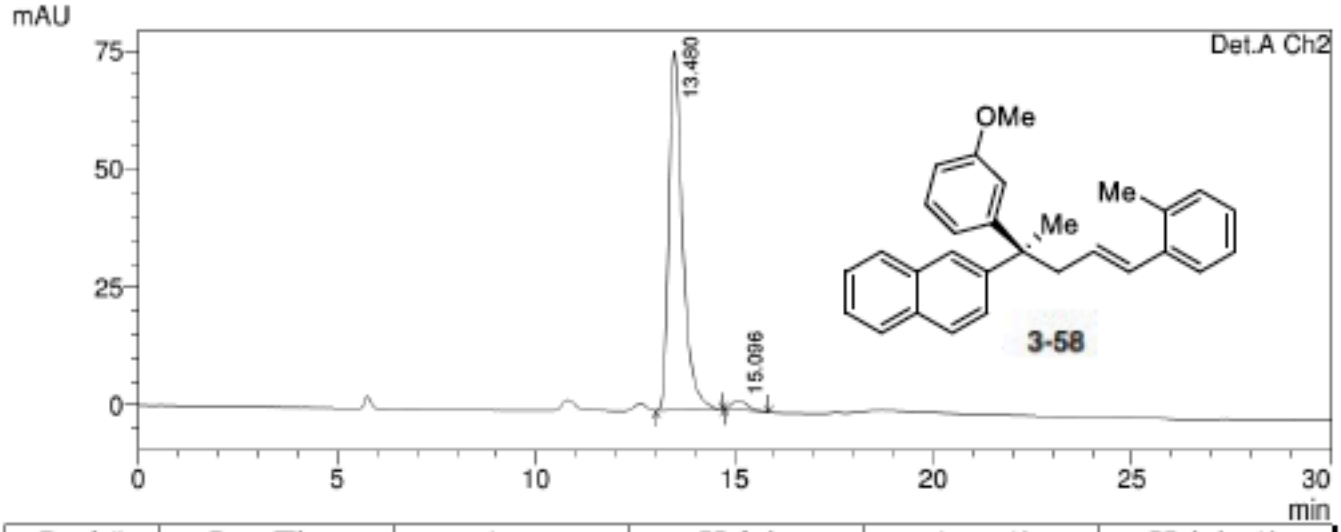
Peak#	Ret. Time	Area	Height	Area %	Height %
1	53.025	977426	19027	2.811	3.355
2	53.798	33790474	548101	97.189	96.645
Total		34767901	567128	100.000	100.000

Racemic **3-58**



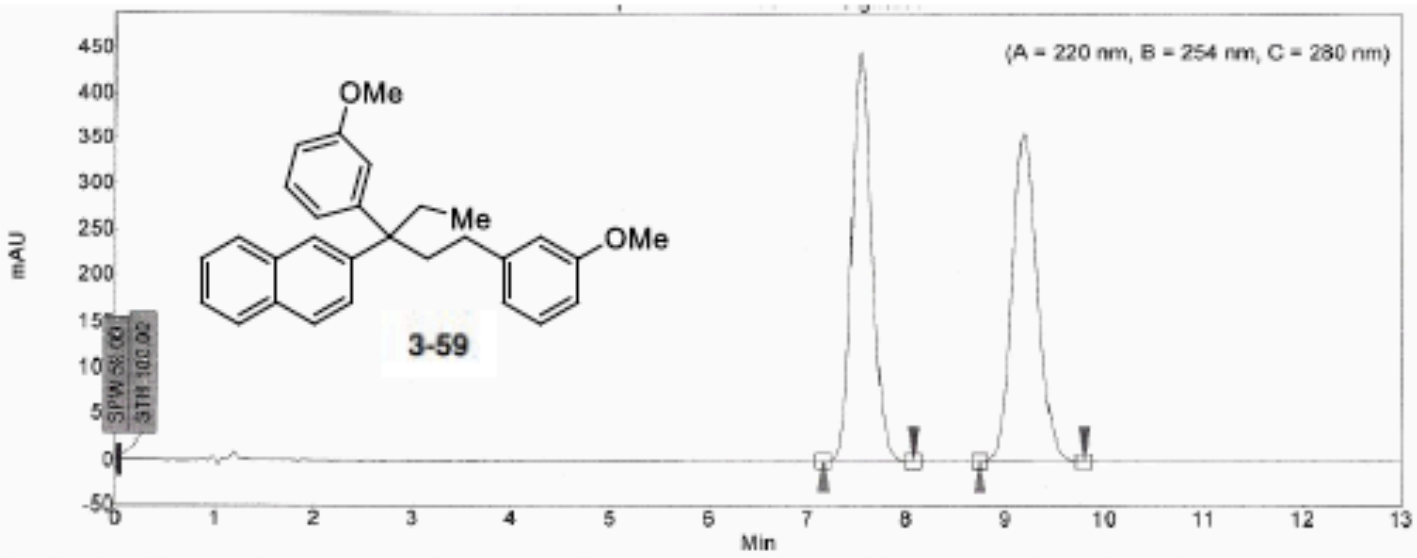
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.506	1981293	87791	49.645	56.359
2	15.101	2009656	67980	50.355	43.641
Total		3990949	155771	100.000	100.000

Enantioenriched **3-58**, 94% ee



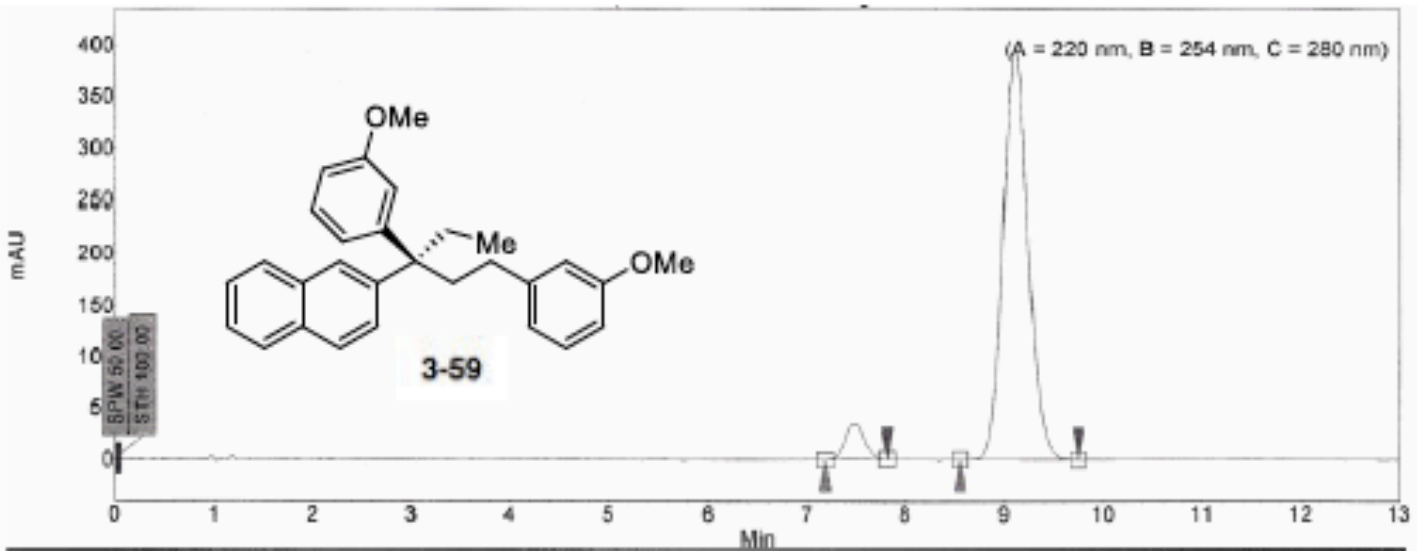
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.480	1845100	76078	97.047	97.444
2	15.096	56141	1996	2.953	2.556
Total		1901241	78073	100.000	100.000

Racemic 3-59



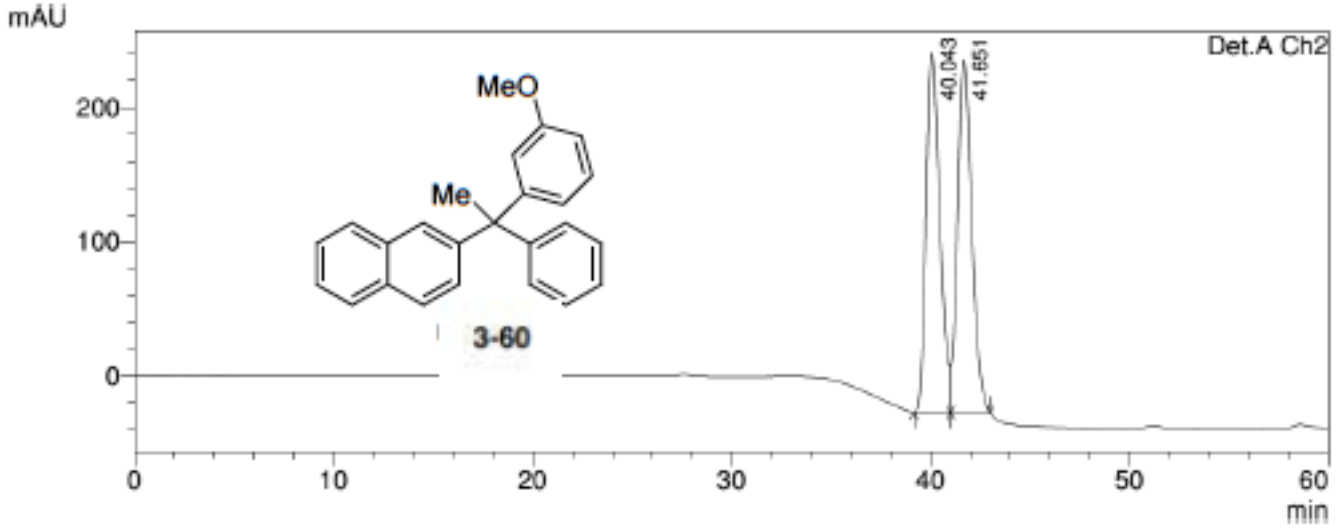
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	7.16	7.54	8.07	0.00	49.93	445.3	104.9	49.926
2	UNKNOWN	8.74	9.18	9.79	0.00	50.07	356.0	105.2	50.074
Total						100.00	801.3	210.1	100.000

Enantioenriched 3-59, 87% ee



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	7.18	7.48	7.81	0.00	6.28	34.8	7.8	6.282
2	UNKNOWN	8.55	9.10	9.75	0.00	93.72	396.5	116.7	93.718
Total						100.00	431.3	124.6	100.000

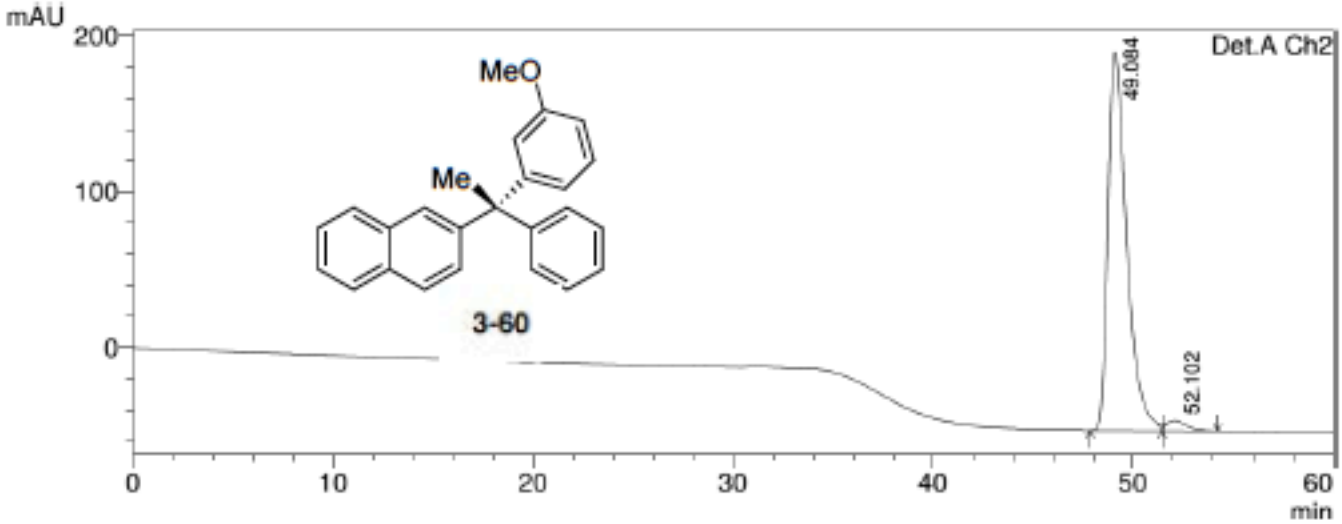
Racemic 3-60



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	40.045	1348999	27748	49.573	50.539
2	41.650	1372253	27157	50.427	49.461
Total		2721252	54905	100.000	100.000

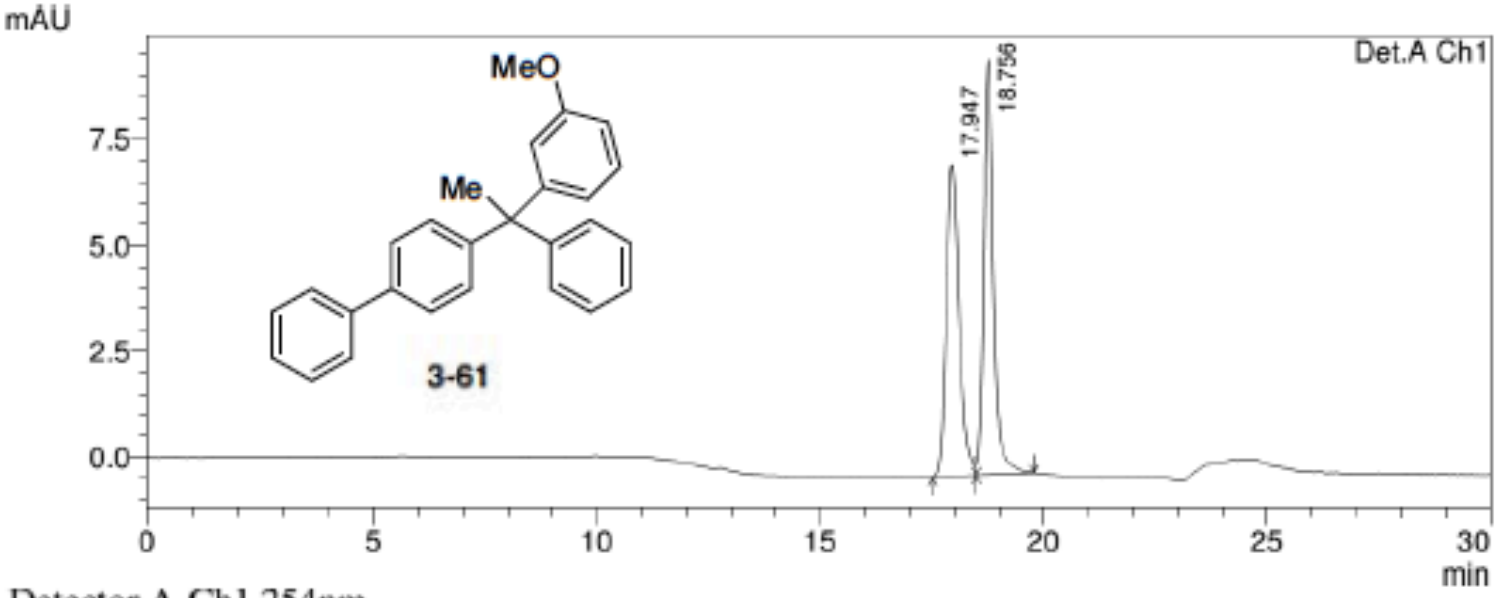
Enantioenriched 3-60, 94% ee



Detector A Ch2 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	49.084	15876695	242733	97.073	97.378
2	52.102	478750	6535	2.927	2.622
Total		16355444	249267	100.000	100.000

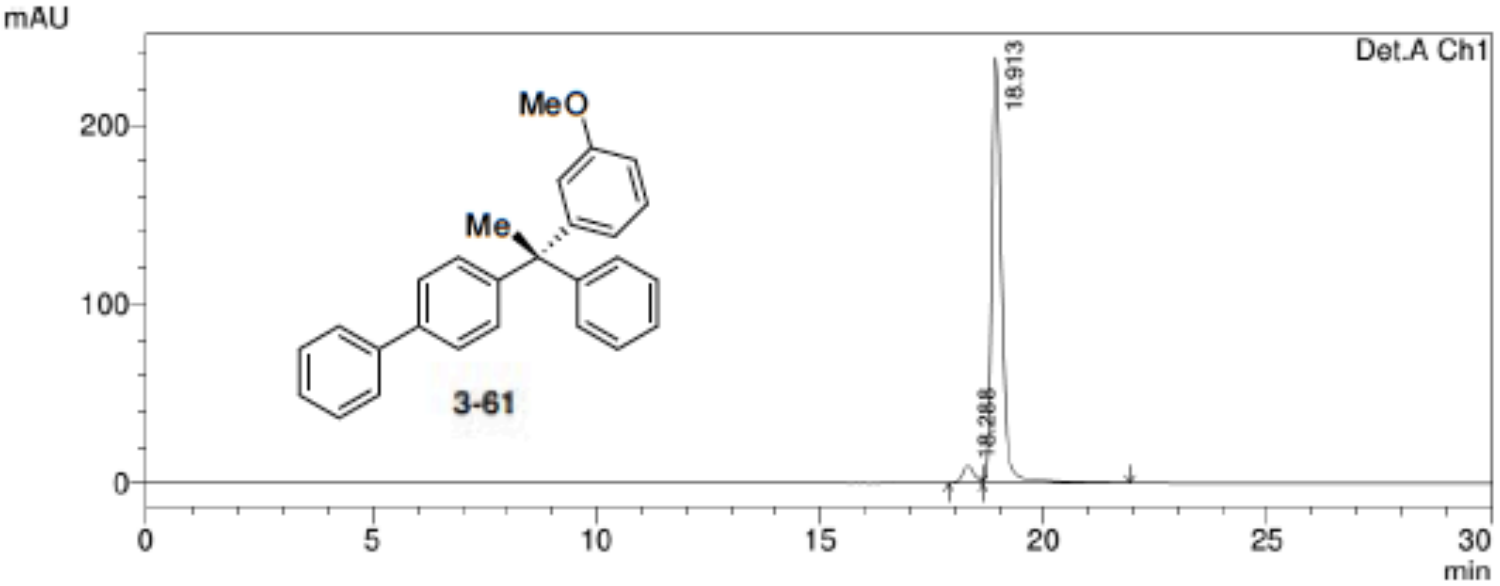
Racemic **3-61**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.947	146239	7340	49.779	42.872
2	18.756	147539	9781	50.221	57.128
Total		293778	17120	100.000	100.000

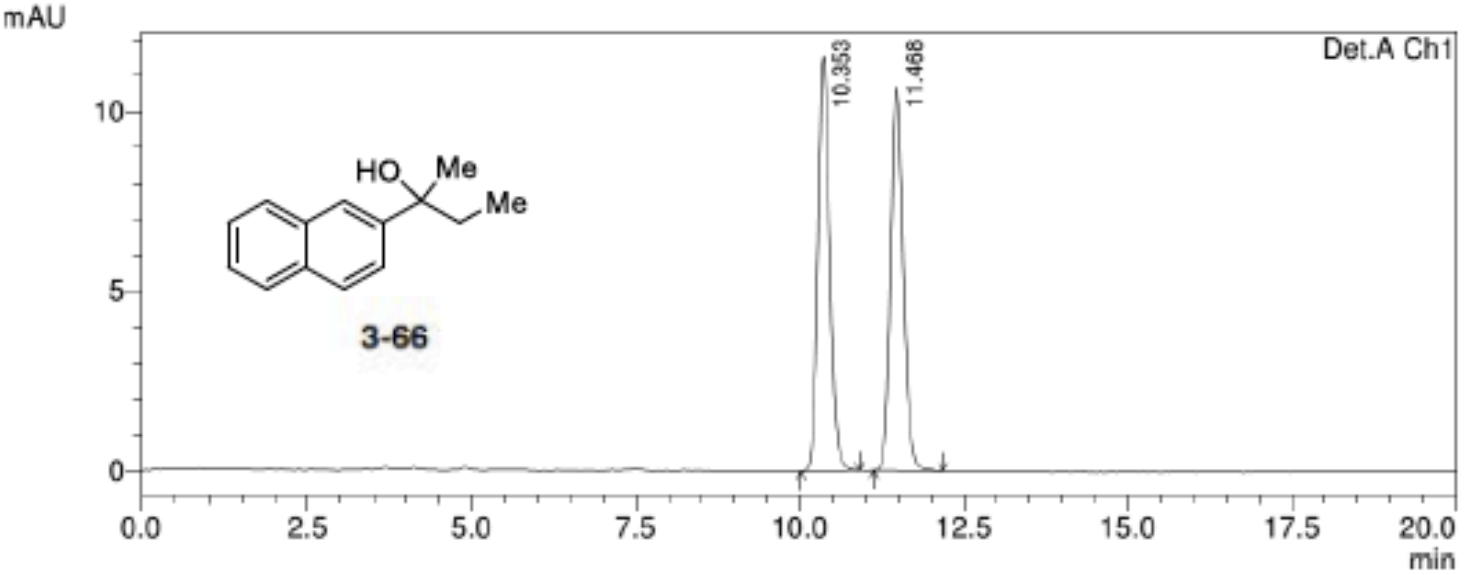
Enantioenriched **3-61**, 91% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.288	179299	9861	4.531	3.984
2	18.913	3777644	237657	95.469	96.016
Total		3956943	247518	100.000	100.000

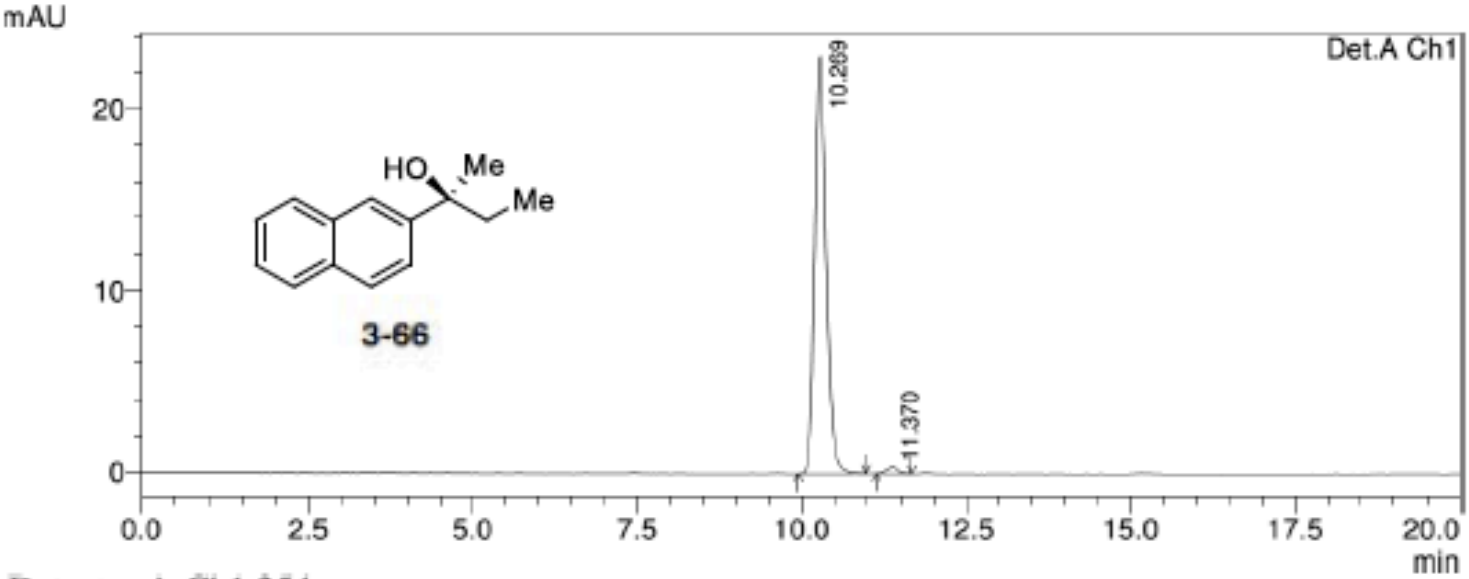
Racemic **3-66**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.353	144648	11554	49.962	51.955
2	11.468	144869	10684	50.038	48.045
Total		289518	22238	100.000	100.000

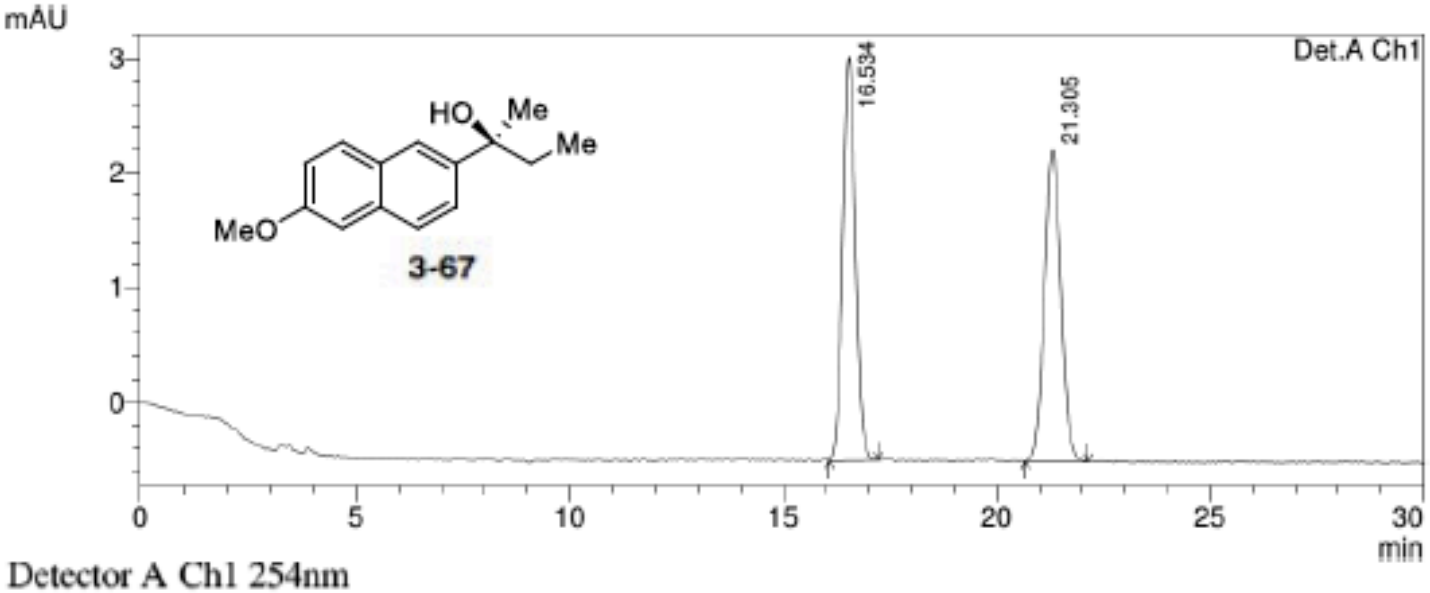
Enantioenriched **3-66**, 96% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.269	283433	22977	98.493	98.537
2	11.370	4338	341	1.507	1.463
Total		287771	23318	100.000	100.000

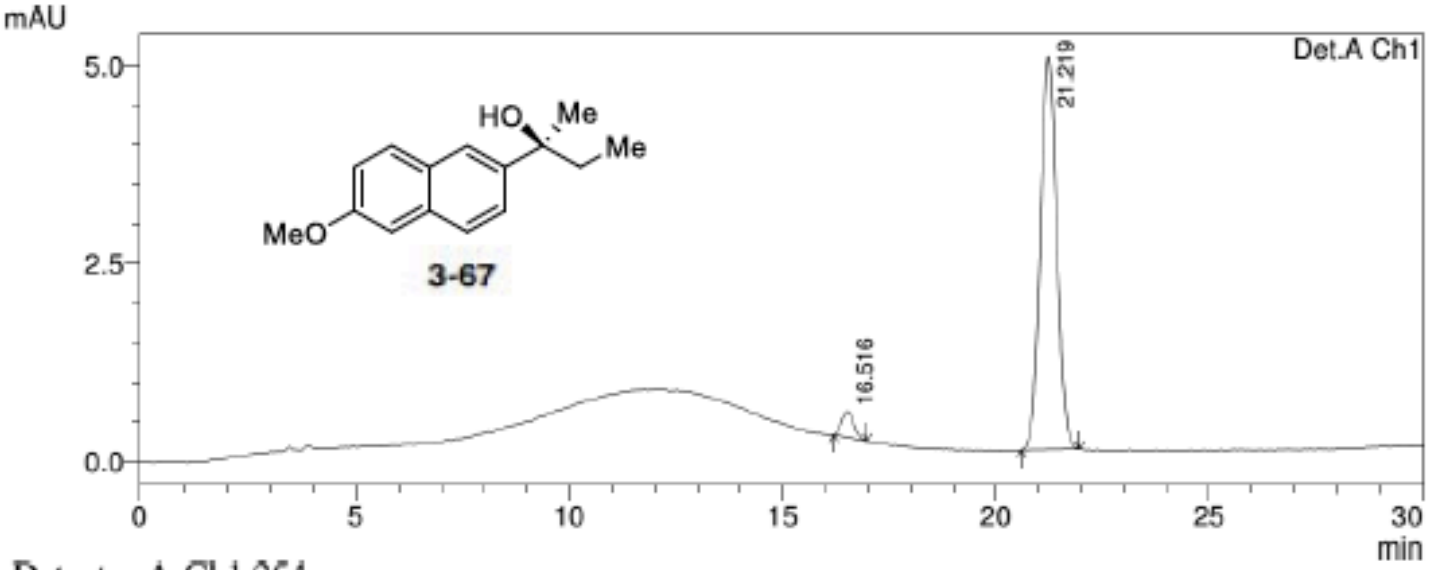
Racemic **3-67**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.534	73547	3522	50.022	56.460
2	21.305	73483	2716	49.978	43.540
Total		147031	6238	100.000	100.000

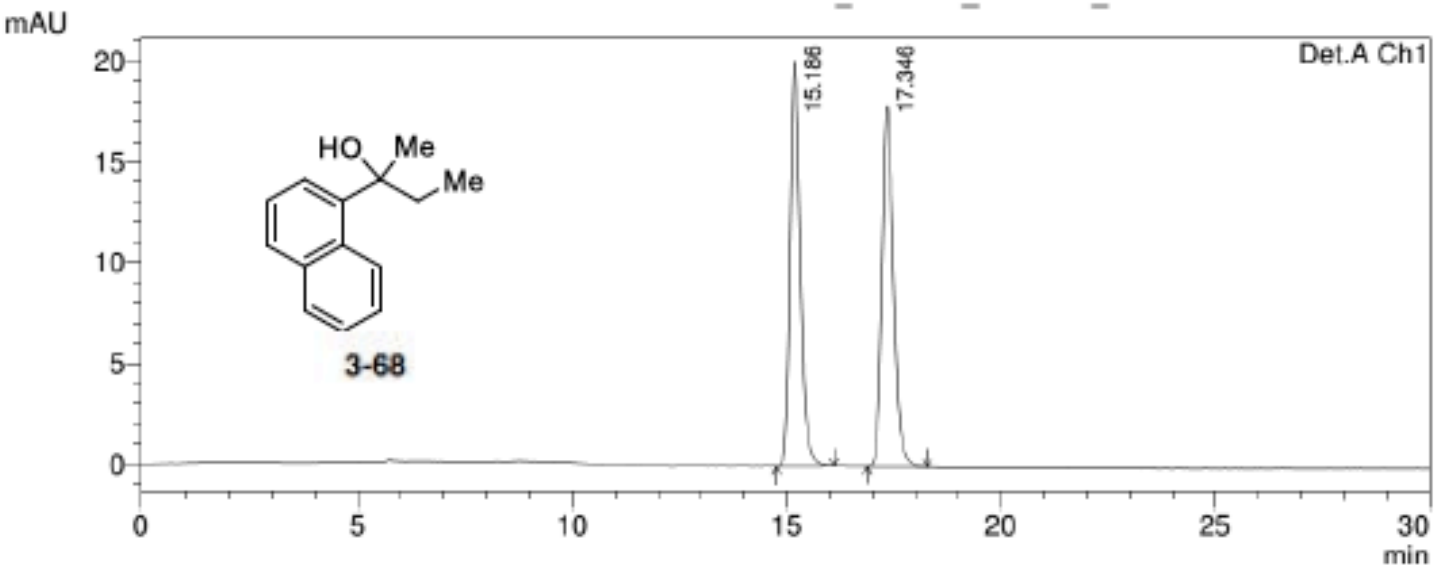
Enantioenriched **3-67**, 91% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.516	6536	328	4.672	6.201
2	21.219	133384	4962	95.328	93.799
Total		139920	5291	100.000	100.000

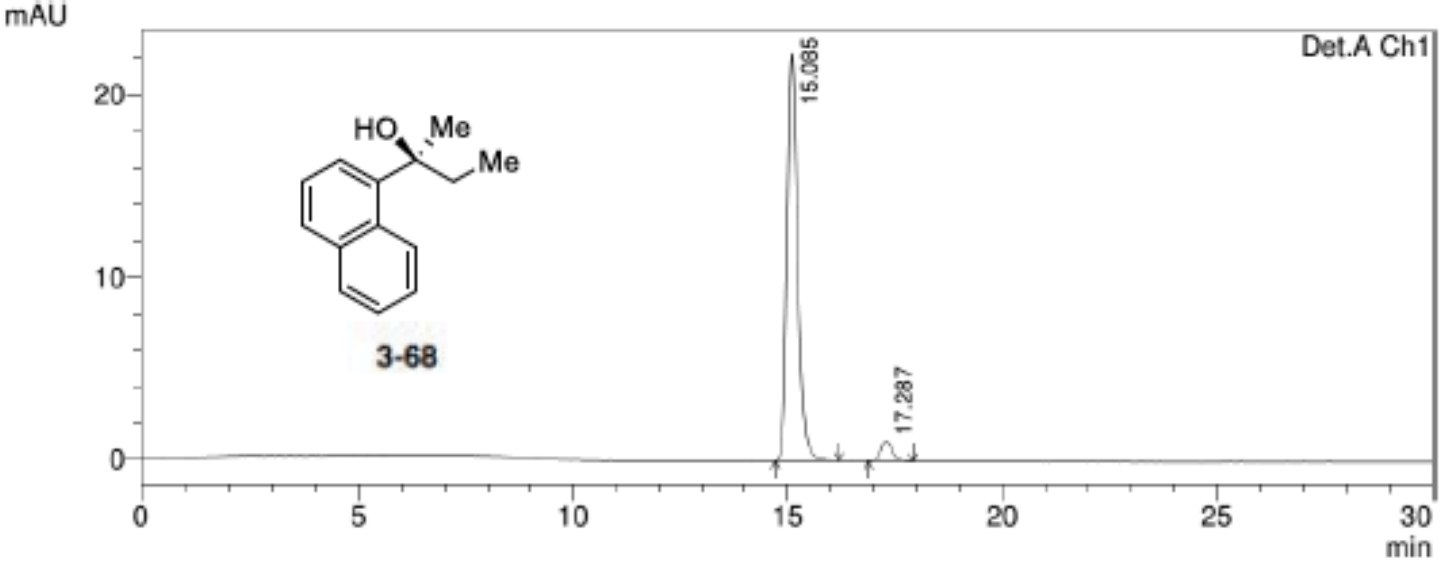
Racemic **3-68**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.186	337510	20102	49.967	52.913
2	17.346	337952	17889	50.033	47.087
Total		675461	37991	100.000	100.000

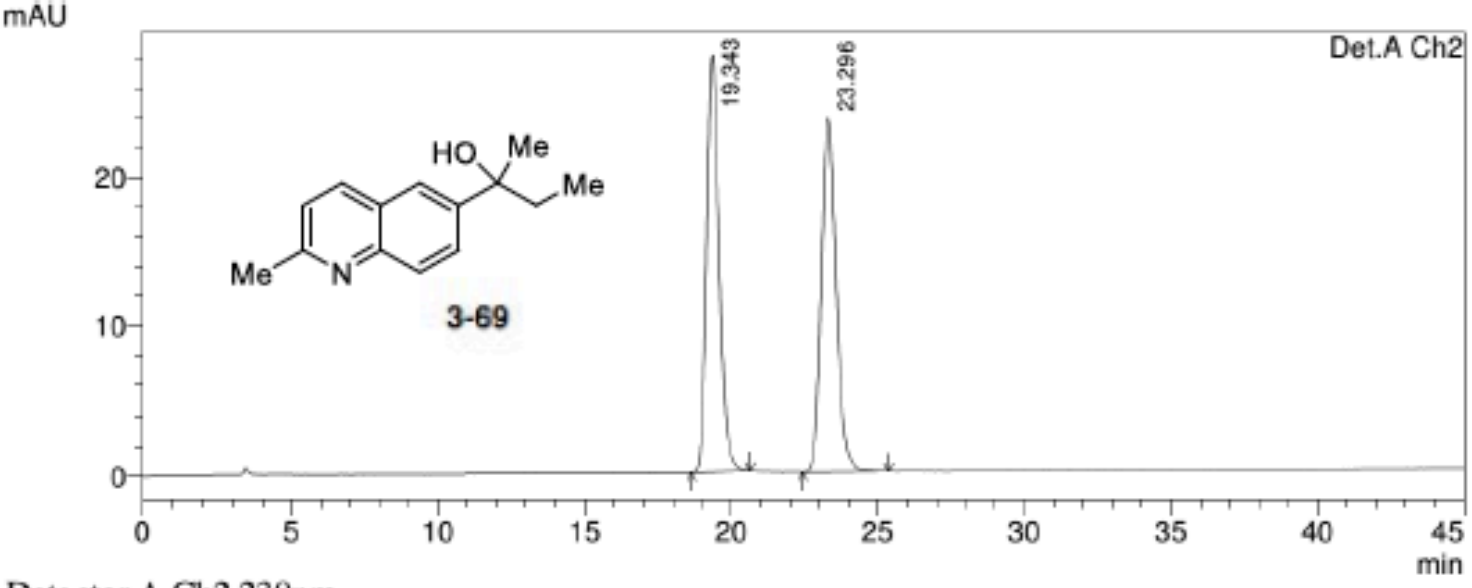
Enantioenriched **3-68**, 90% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.085	379069	22316	94.789	95.245
2	17.287	20837	1114	5.211	4.755
Total		399906	23430	100.000	100.000

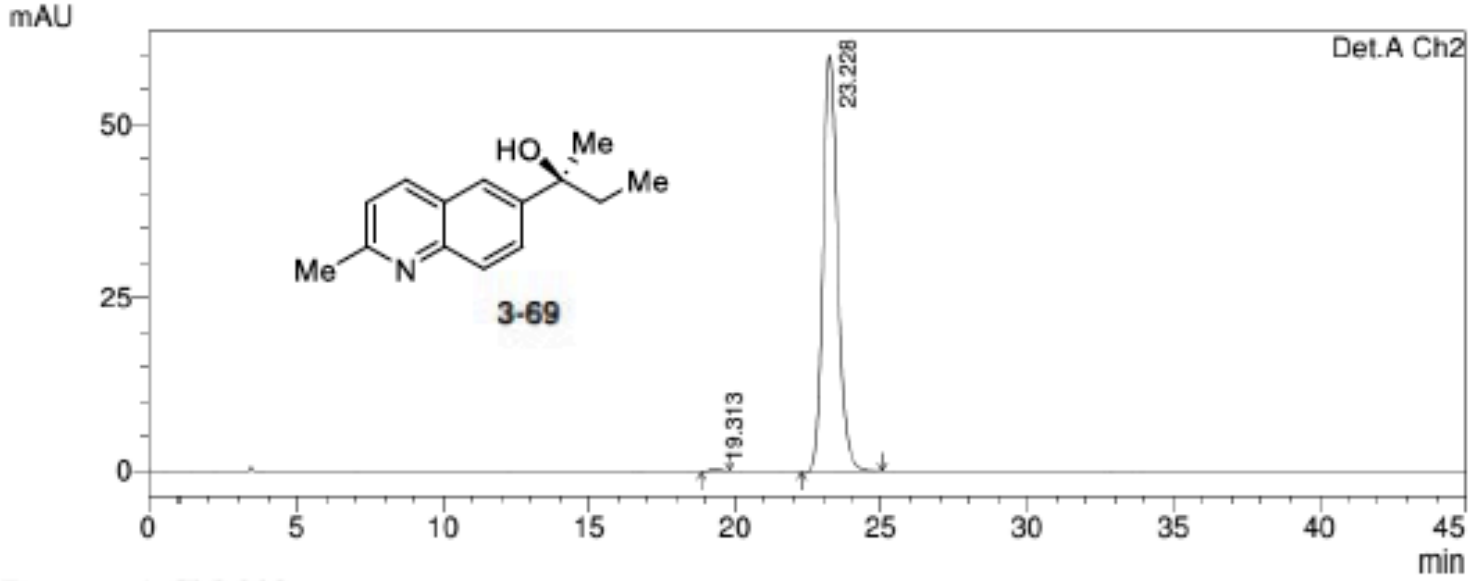
Racemic **3-69**



Detector A Ch2 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.343	830508	27995	49.756	54.100
2	23.296	838670	23752	50.244	45.900
Total		1669178	51747	100.000	100.000

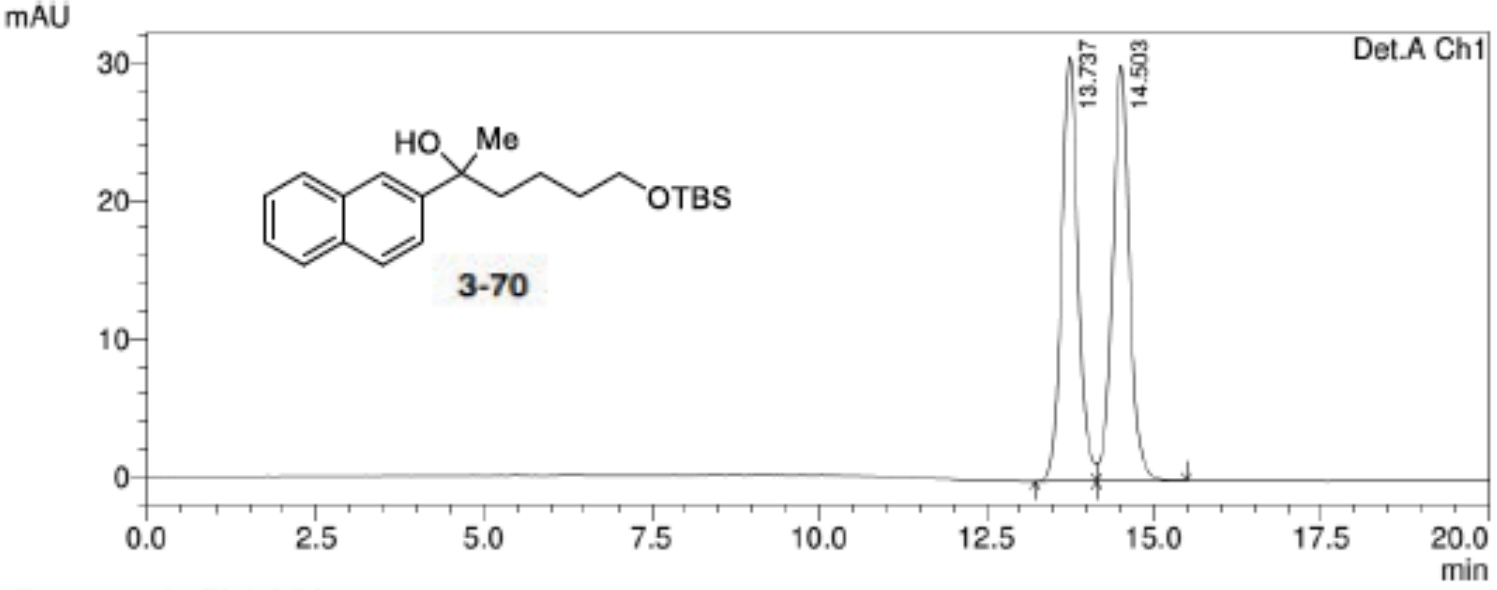
Enantioenriched **3-69**, 99% ee



Detector A Ch2 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.313	10754	429	0.510	0.708
2	23.228	2099723	60224	99.490	99.292
Total		2110477	60653	100.000	100.000

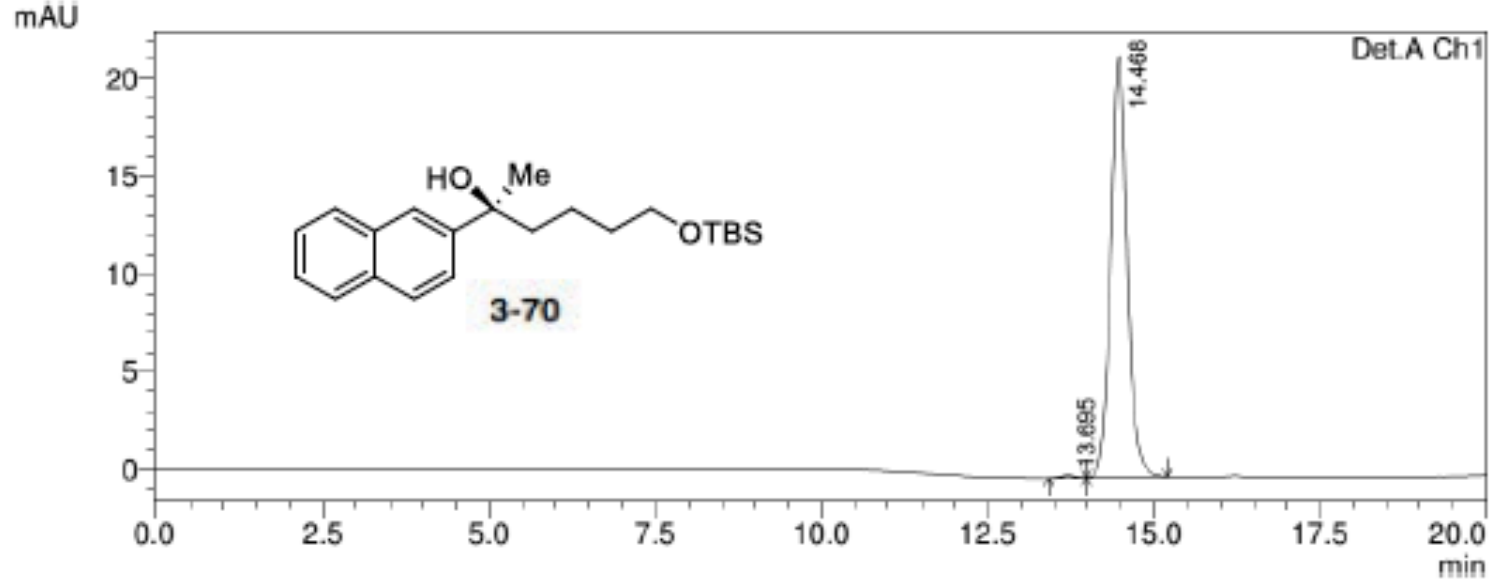
Racemic 3-70



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.737	525563	30811	49.594	50.552
2	14.503	534166	30139	50.406	49.448
Total		1059729	60950	100.000	100.000

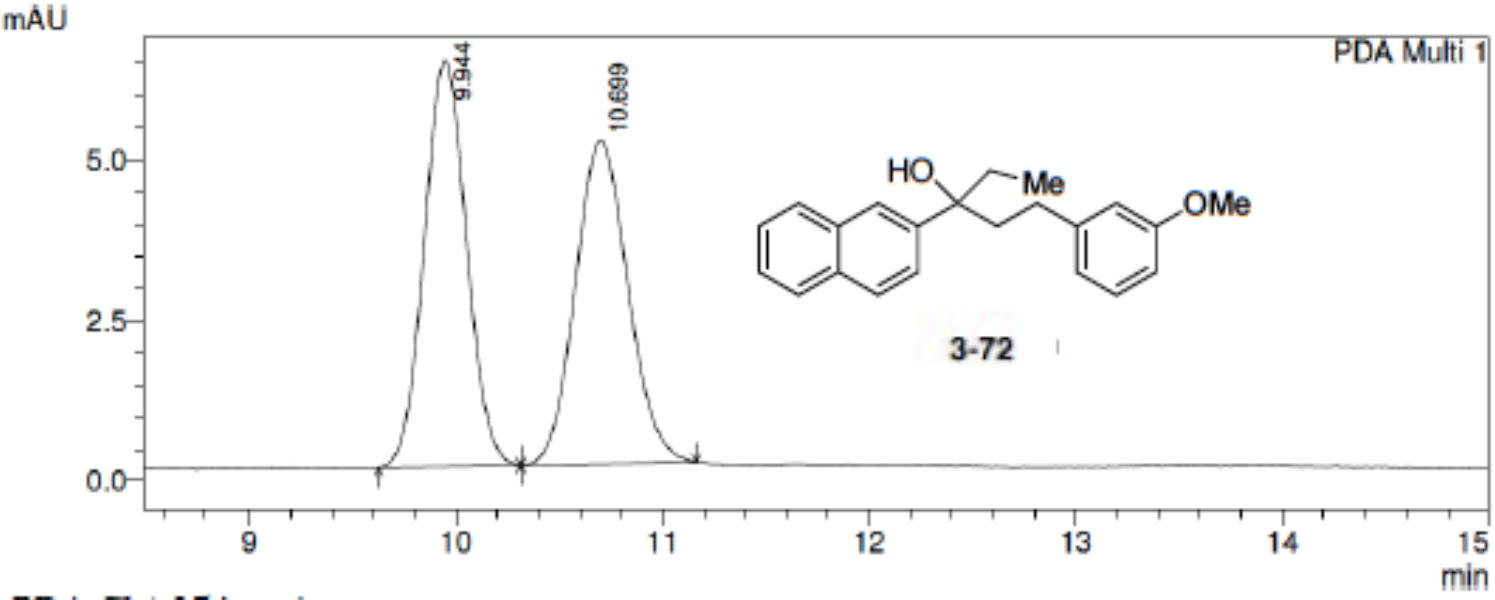
Enantioenriched 3-70, 99% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.695	2096	141	0.553	0.651
2	14.468	376900	21525	99.447	99.349
Total		378996	21666	100.000	100.000

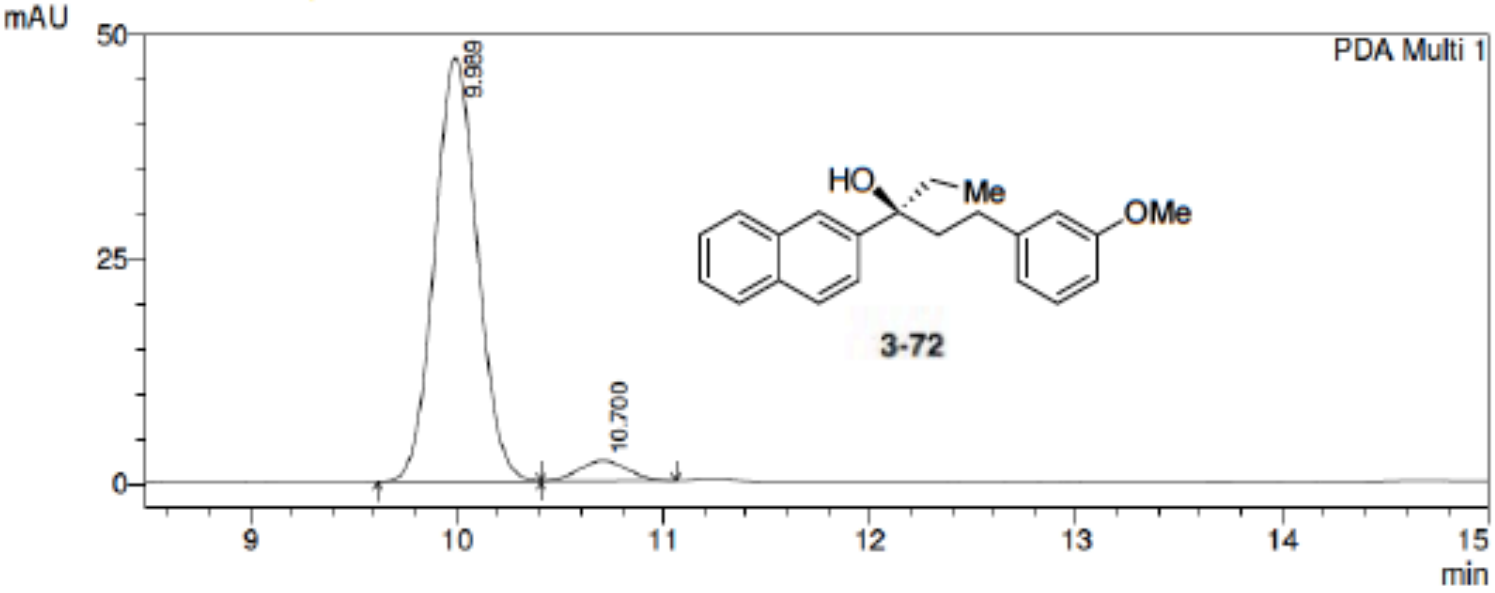
Racemic **3-72**



PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.944	89648	6313	50.174	55.701
2	10.699	89026	5021	49.826	44.299
Total		178674	11333	100.000	100.000

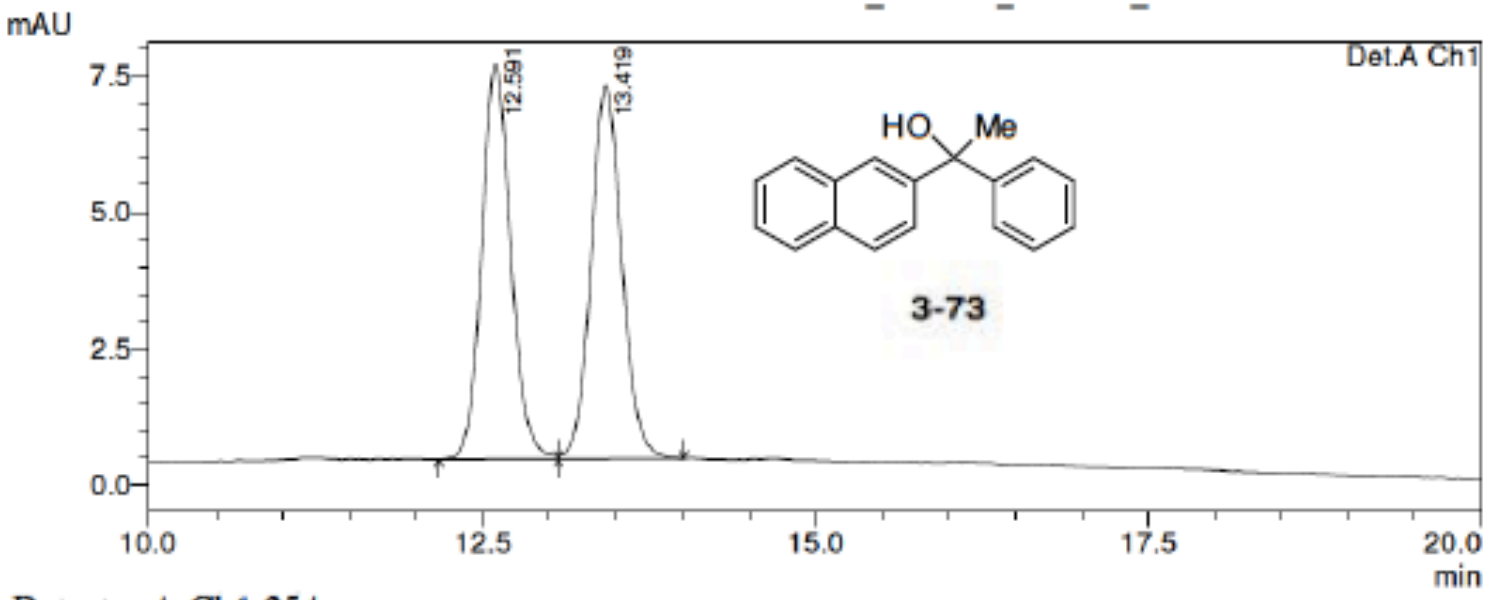
Enantioenriched **3-72**, 89% ee



PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.989	678937	47129	94.701	95.414
2	10.700	37992	2265	5.299	4.586
Total		716930	49394	100.000	100.000

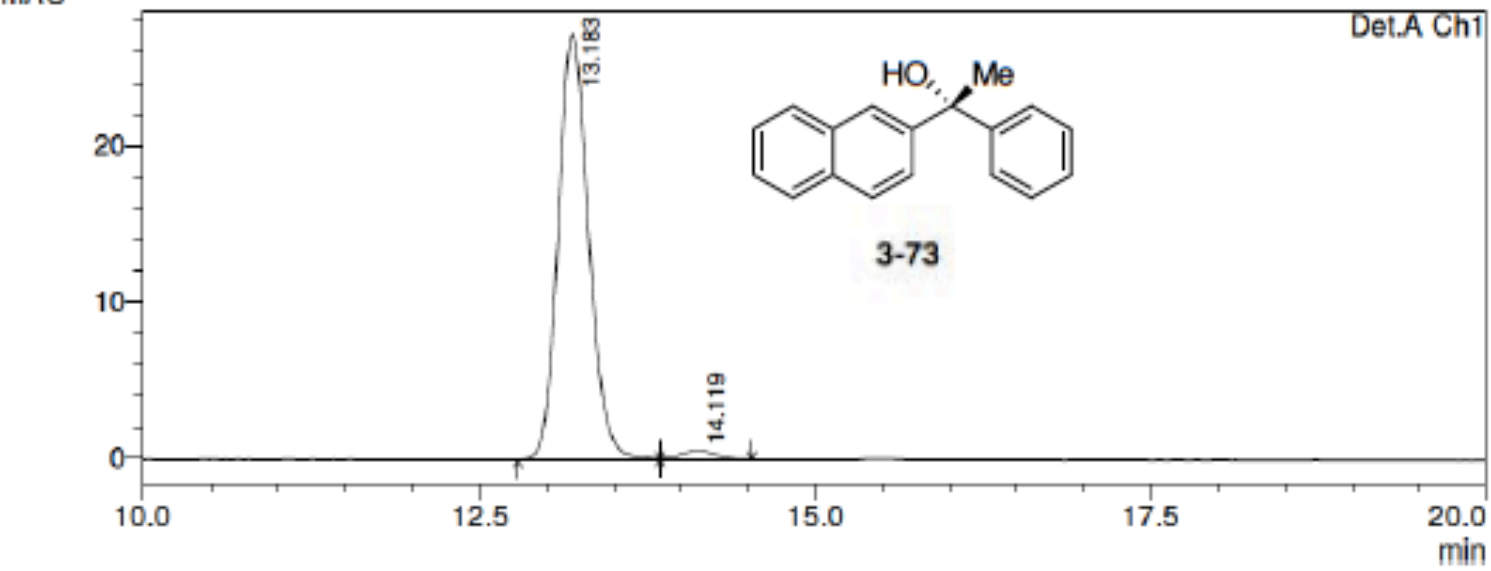
Racemic **3-73**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.591	110150	7219	50.024	51.378
2	13.419	110043	6832	49.976	48.622
Total		220194	14051	100.000	100.000

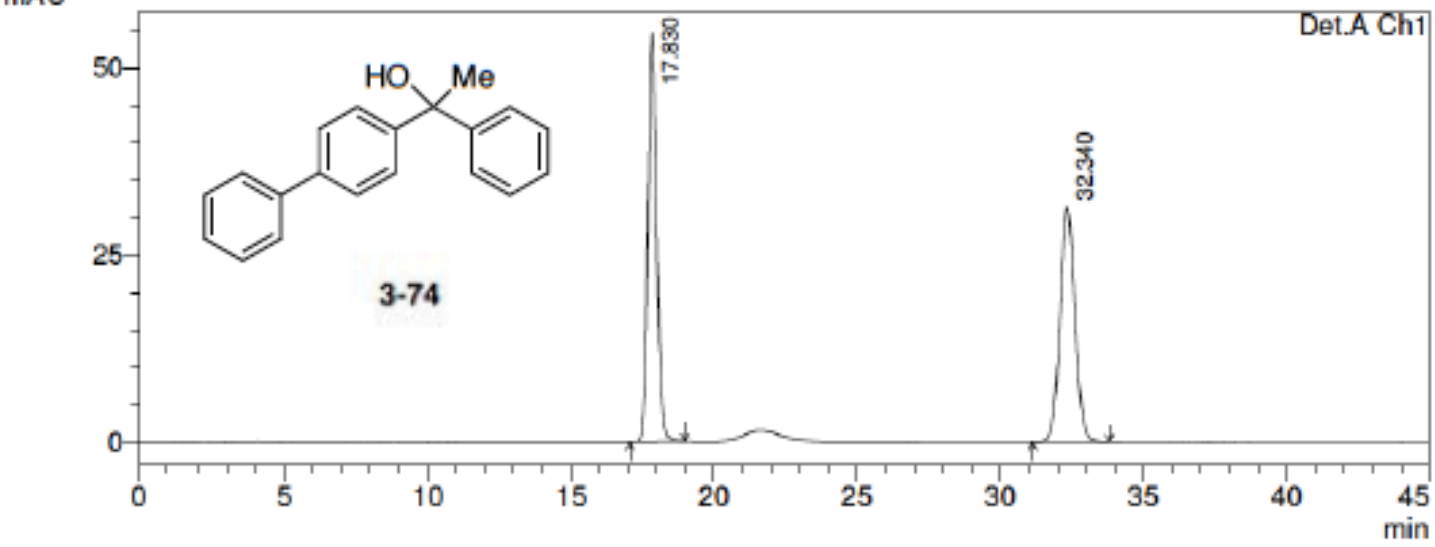
Enantioenriched **3-73**, 96% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.183	429320	27232	97.819	98.017
2	14.119	9571	551	2.181	1.983
Total		438890	27783	100.000	100.000

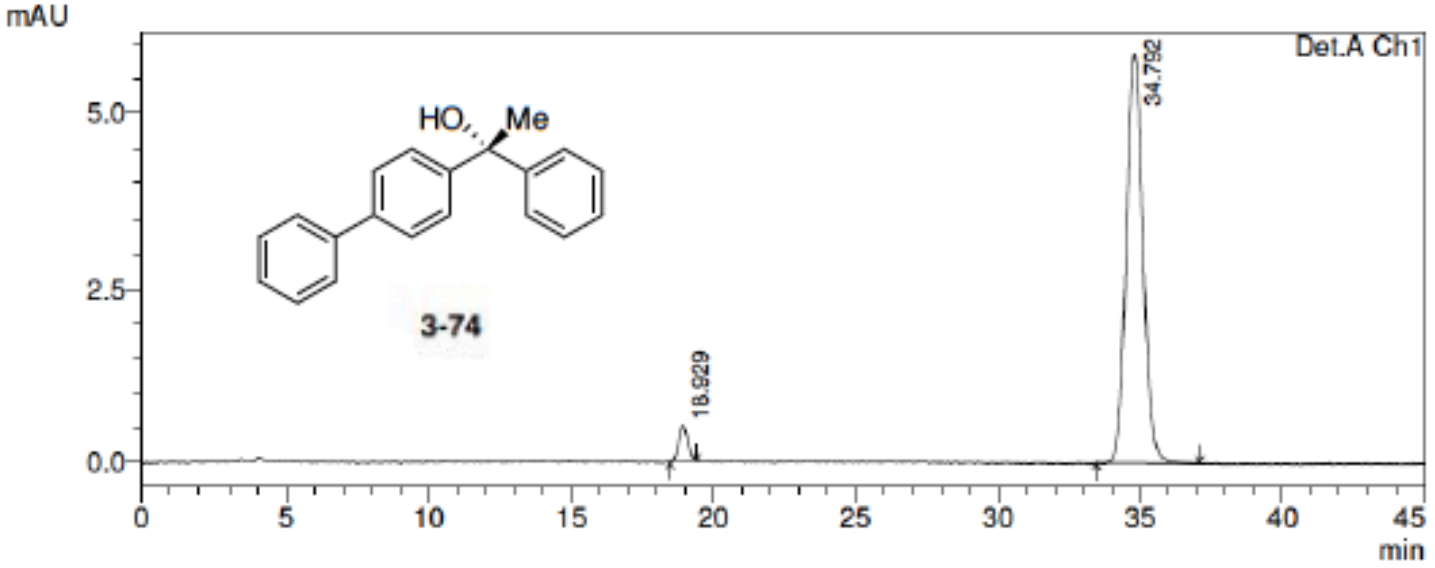
Racemic **3-74**



Detector A Ch1 254nm

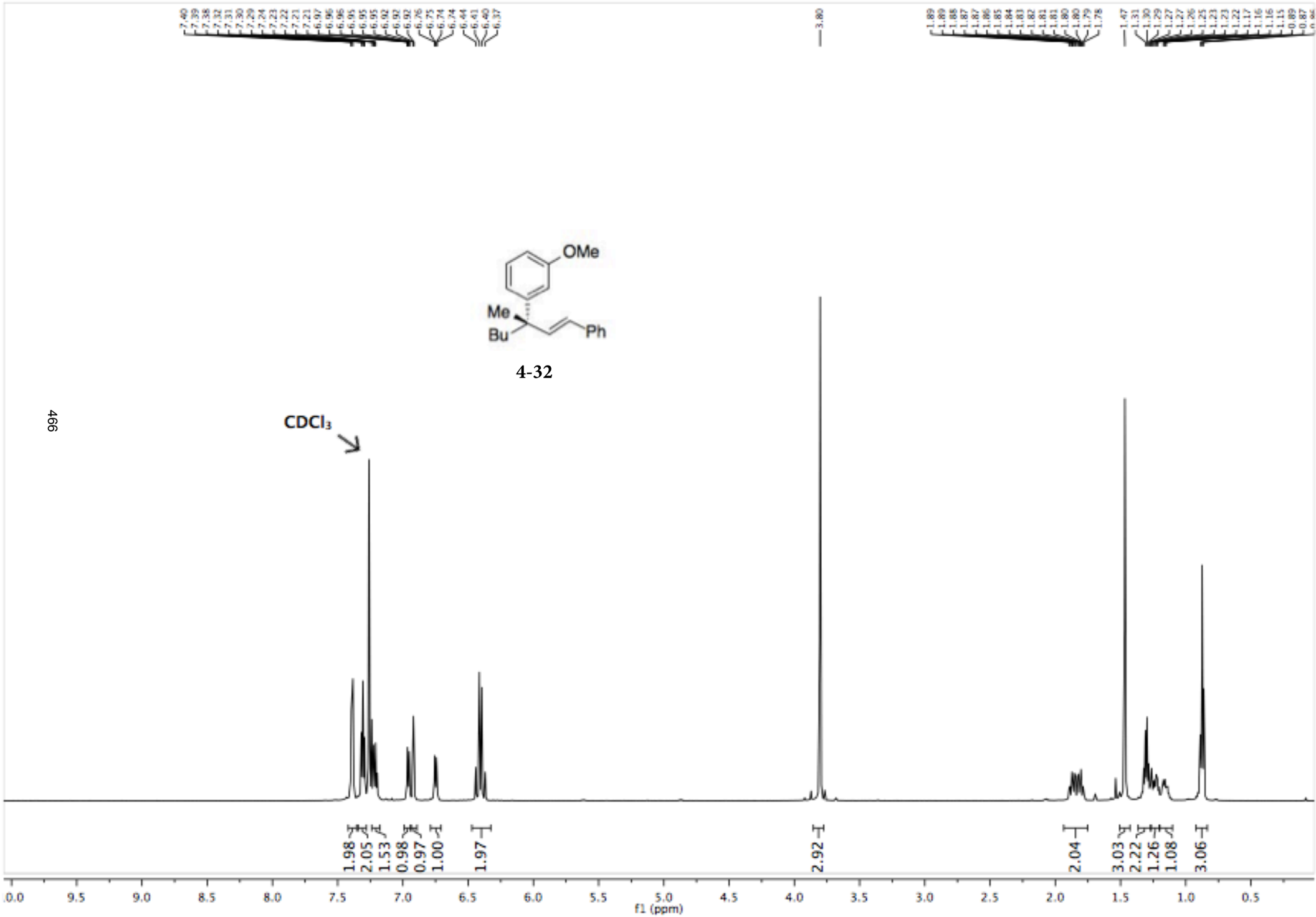
Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.830	1163647	54572	49.994	63.499
2	32.340	1163916	31370	50.006	36.501
Total		2327563	85942	100.000	100.000

Enantioenriched **3-74**, 91% ee

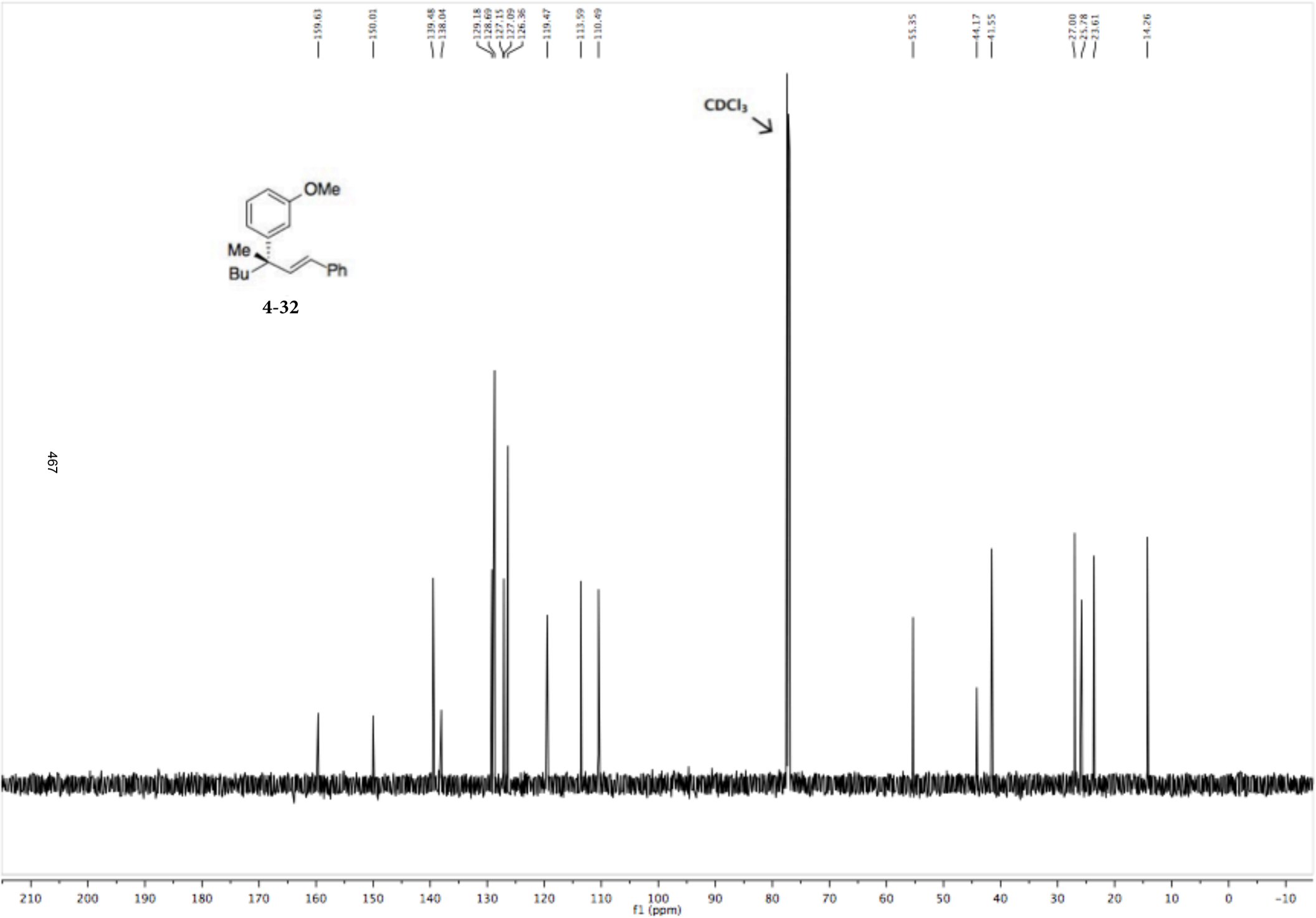


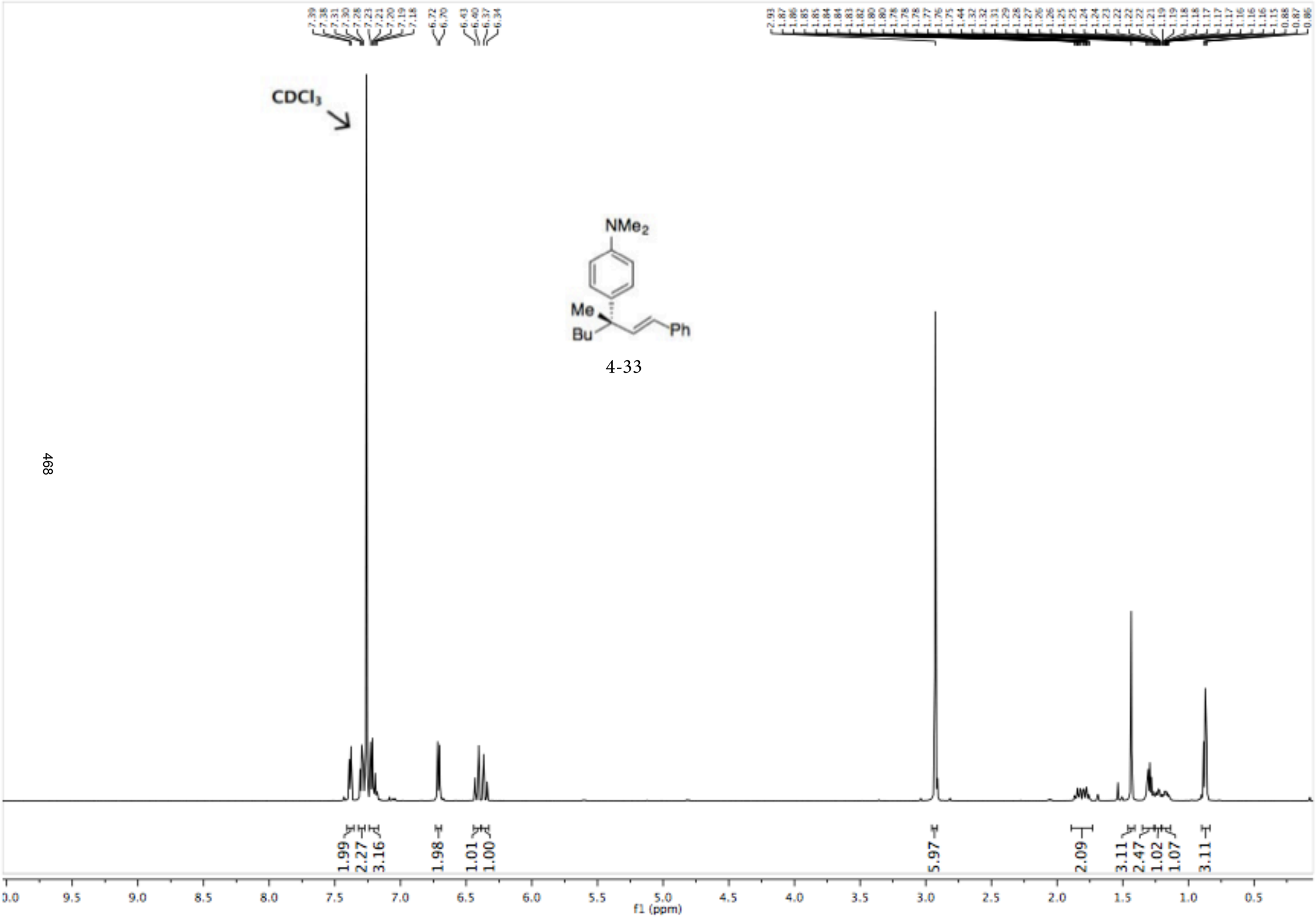
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.929	11129	512	4.454	8.053
2	34.792	238760	5845	95.546	91.947
Total		249889	6357	100.000	100.000

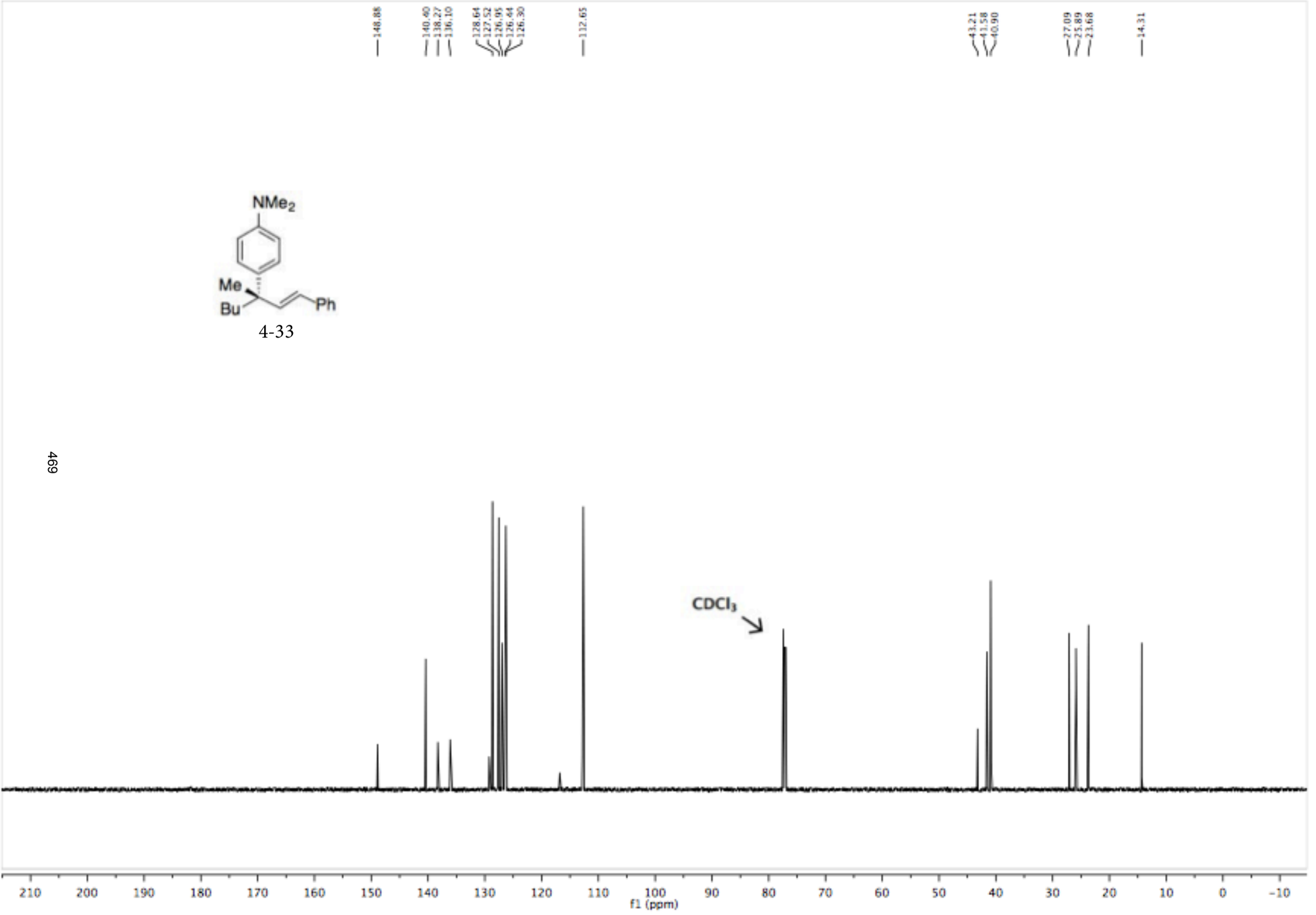

OMe
Me
Bu
Ph
CDCl3
1.98
2.05
1.53
0.98
0.97
1.00
1.97
2.92
2.04
3.03
2.22
1.26
1.08
3.06
f1 (ppm)

4-32

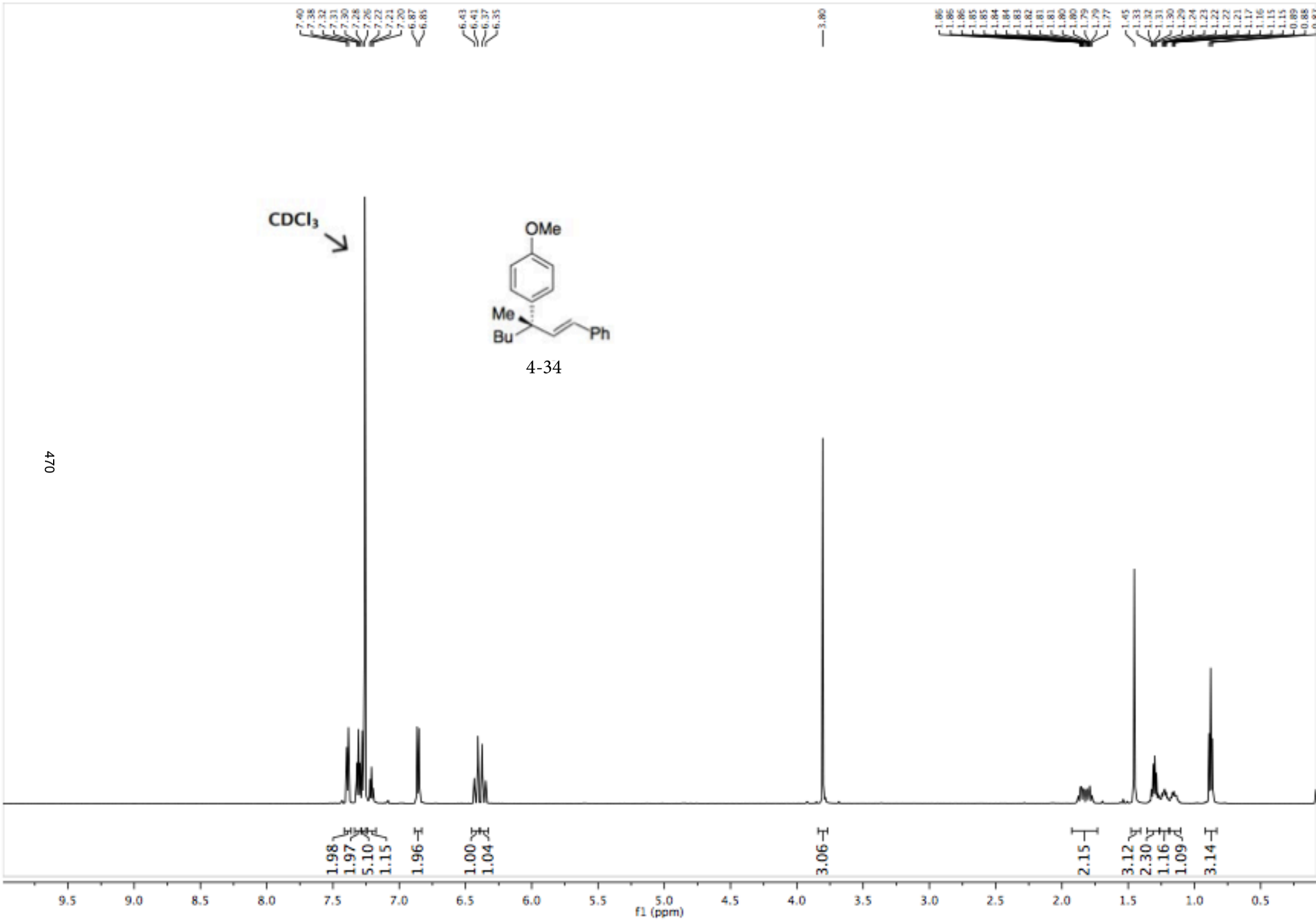

159.63
150.01
139.48
138.04
129.18
128.69
127.15
127.09
126.36
119.47
113.59
110.49
55.35
44.17
41.55
27.00
25.78
23.61
14.26
CDCl3
OMe
Me
Bu
Ph
4-32
467
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

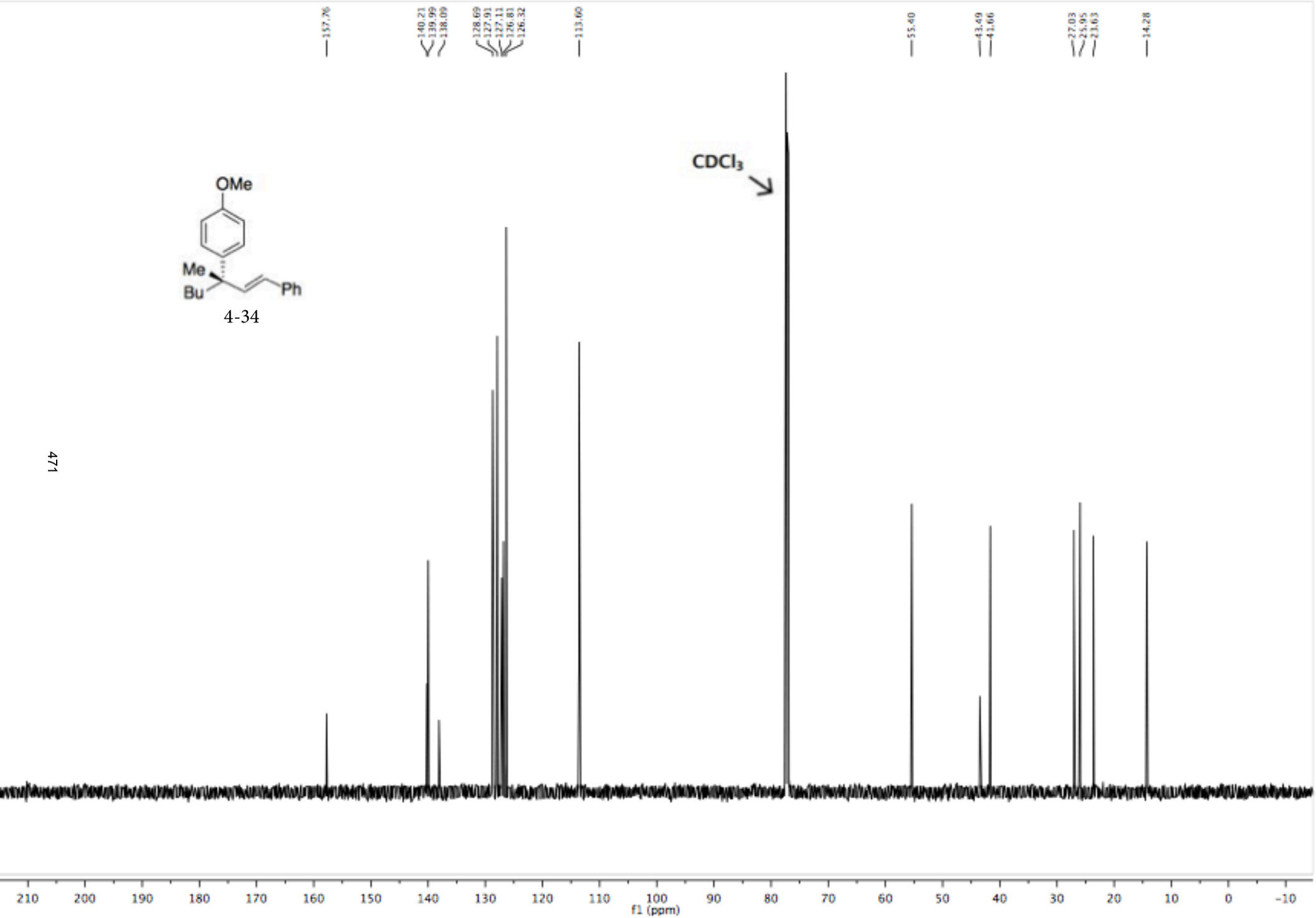


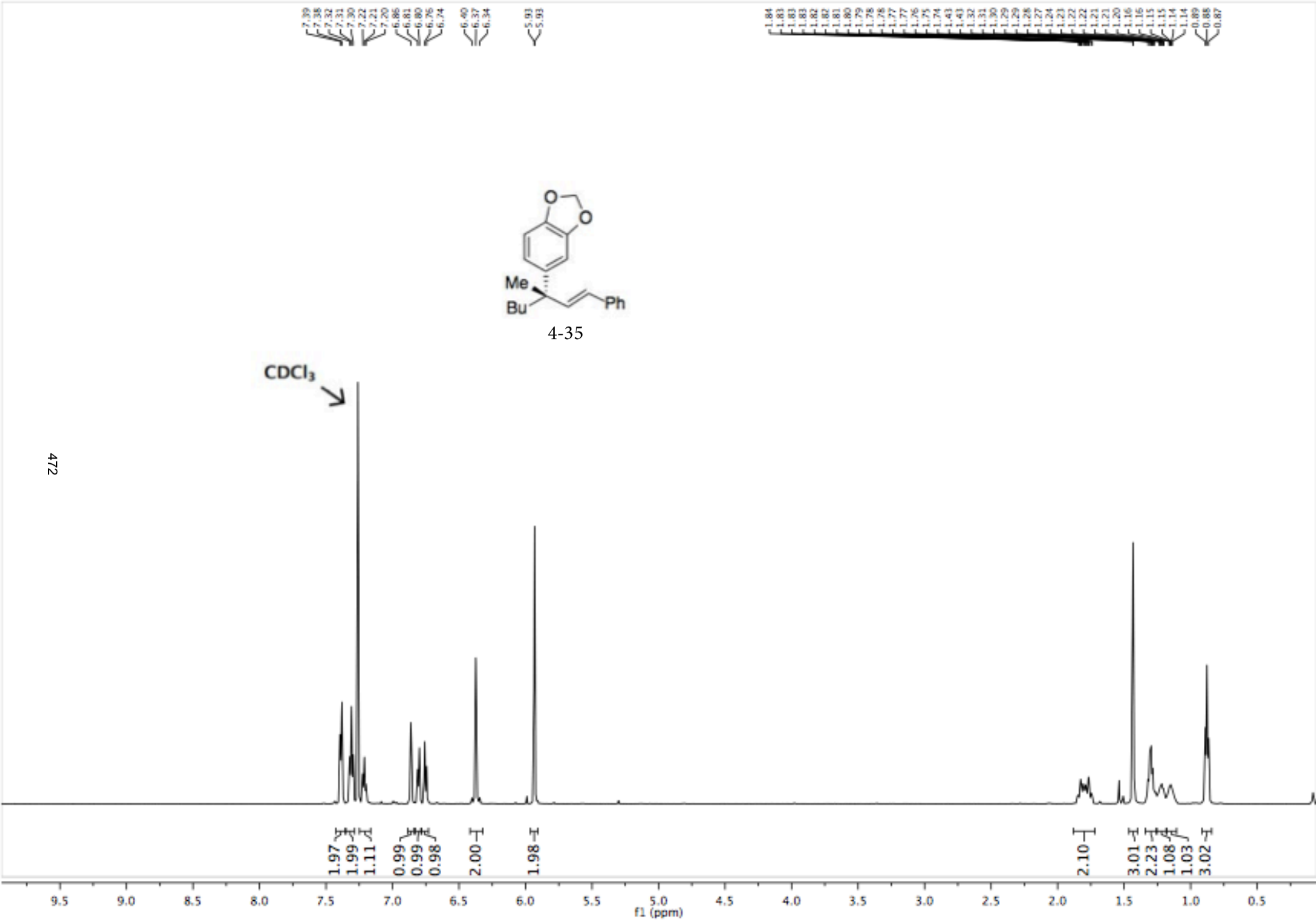
4-33


148.88
140.60
138.27
136.10
128.64
127.52
126.95
126.44
126.30
112.65
43.21
41.58
40.90
27.09
25.89
23.68
14.31
NMe2
Me
Bu
Ph
CDCl3
f1 (ppm)

4-33

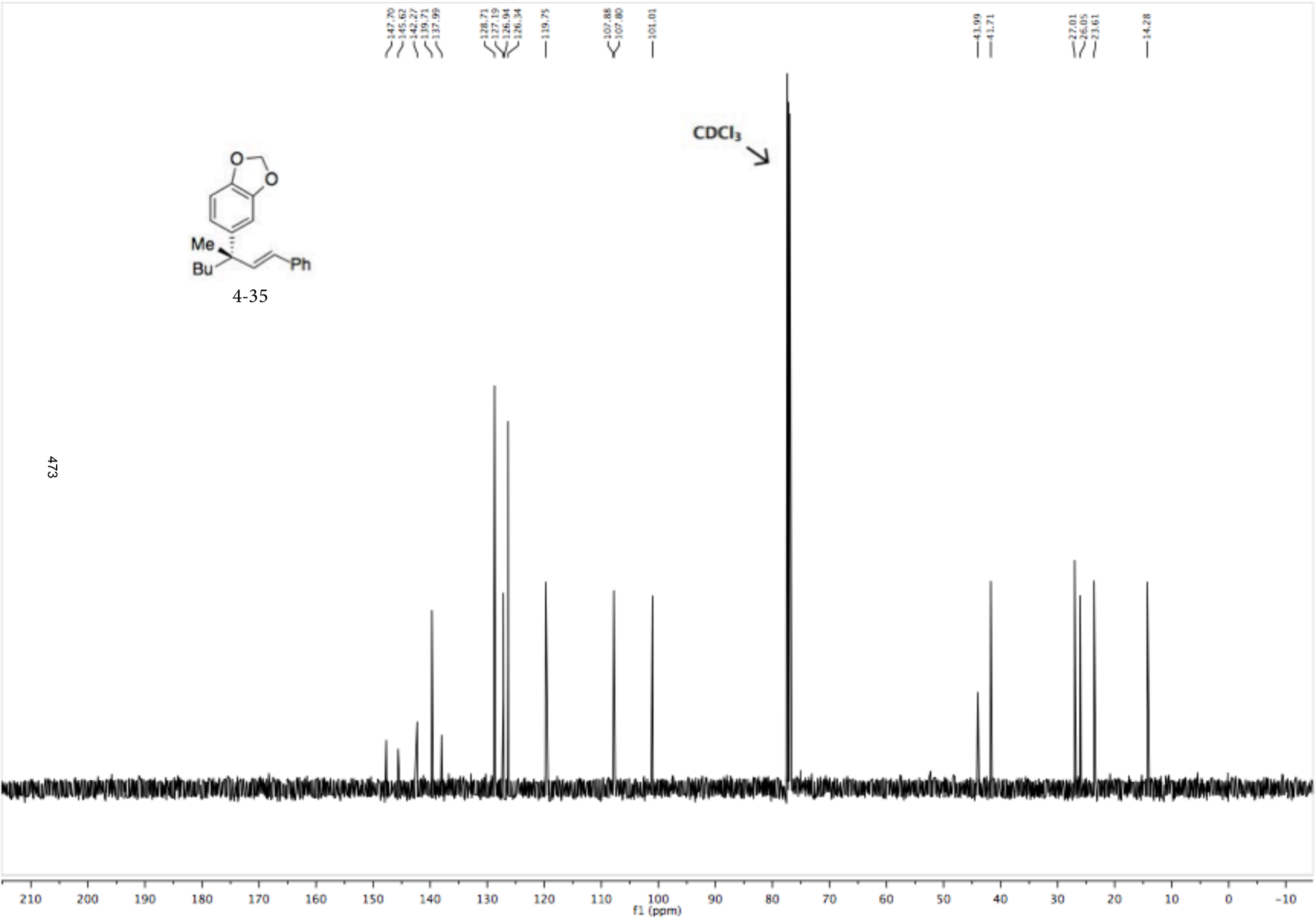

CDCl3
OMe
Me
Bu
Ph
4-34
f1 (ppm)


157.76
140.21
139.99
138.09
128.69
127.91
127.11
126.81
126.32
113.60
55.40
43.49
41.66
27.03
25.95
23.63
14.28
CDCl3
OMe
Me
Bu
Ph
4-34
f1 (ppm)

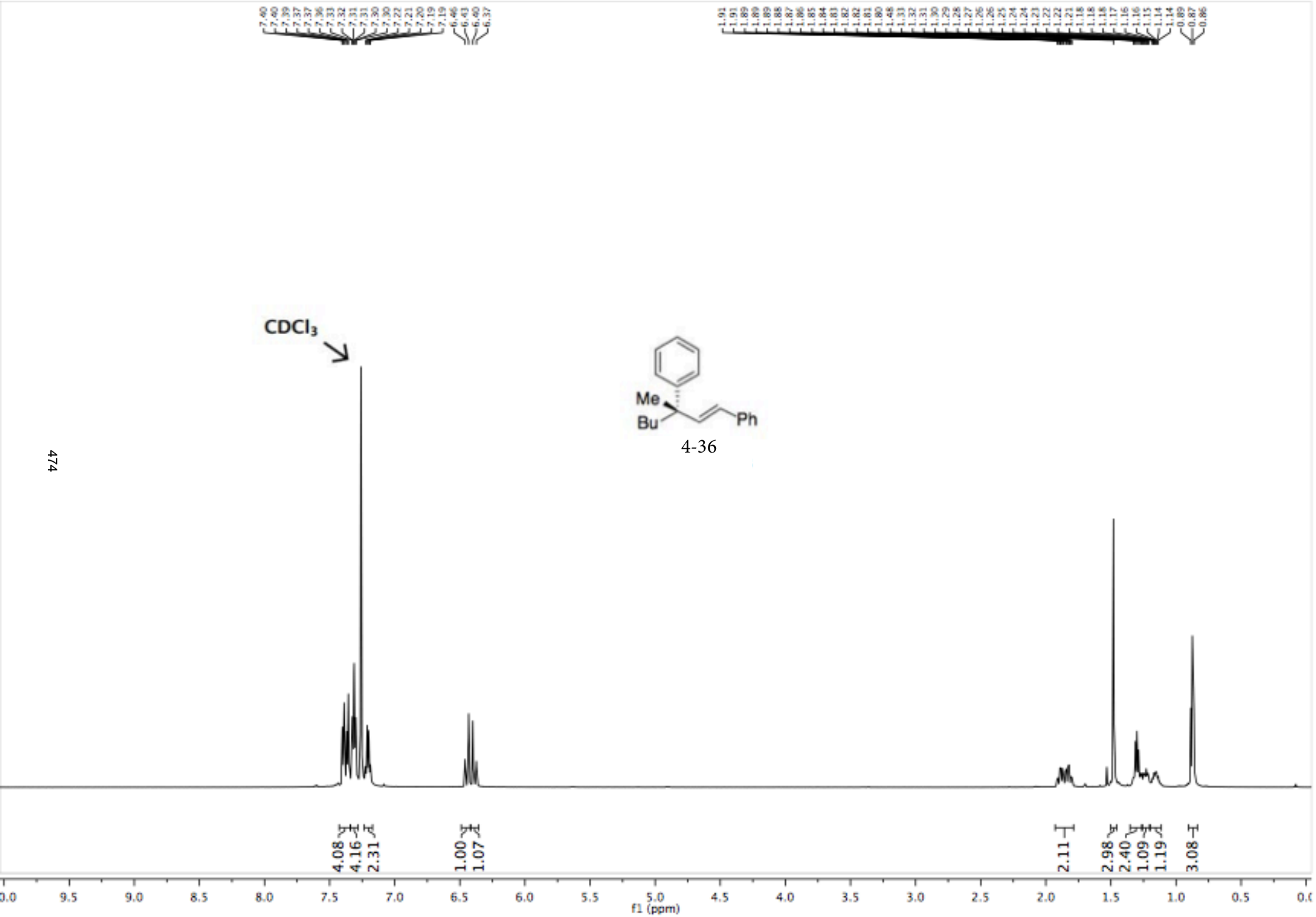

7.39
7.38
7.32
7.31
7.30
7.22
7.21
7.20
6.86
6.81
6.80
6.76
6.74
6.40
6.37
6.34
5.93
5.93
1.84
1.83
1.83
1.83
1.82
1.82
1.81
1.80
1.79
1.78
1.78
1.77
1.77
1.76
1.75
1.74
1.43
1.43
1.32
1.31
1.30
1.29
1.29
1.28
1.27
1.24
1.23
1.22
1.22
1.21
1.21
1.20
1.16
1.16
1.15
1.15
1.14
1.14
0.89
0.88
0.87
O
O
Me
Bu
Ph
CDCl3
1.97
1.99
1.11
0.99
0.99
0.98
2.00
1.98
2.10
3.01
2.23
1.08
1.03
3.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

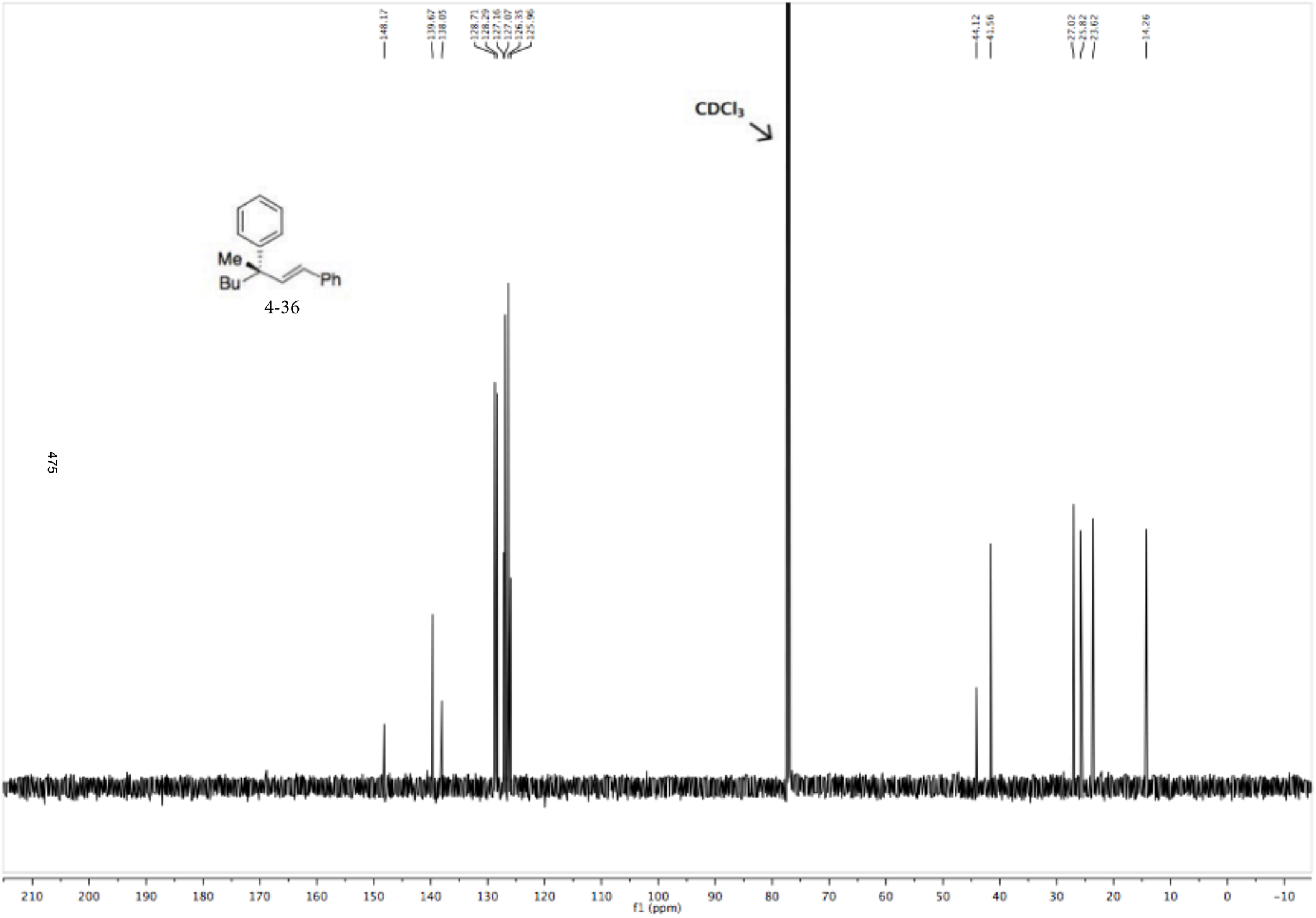
4-35

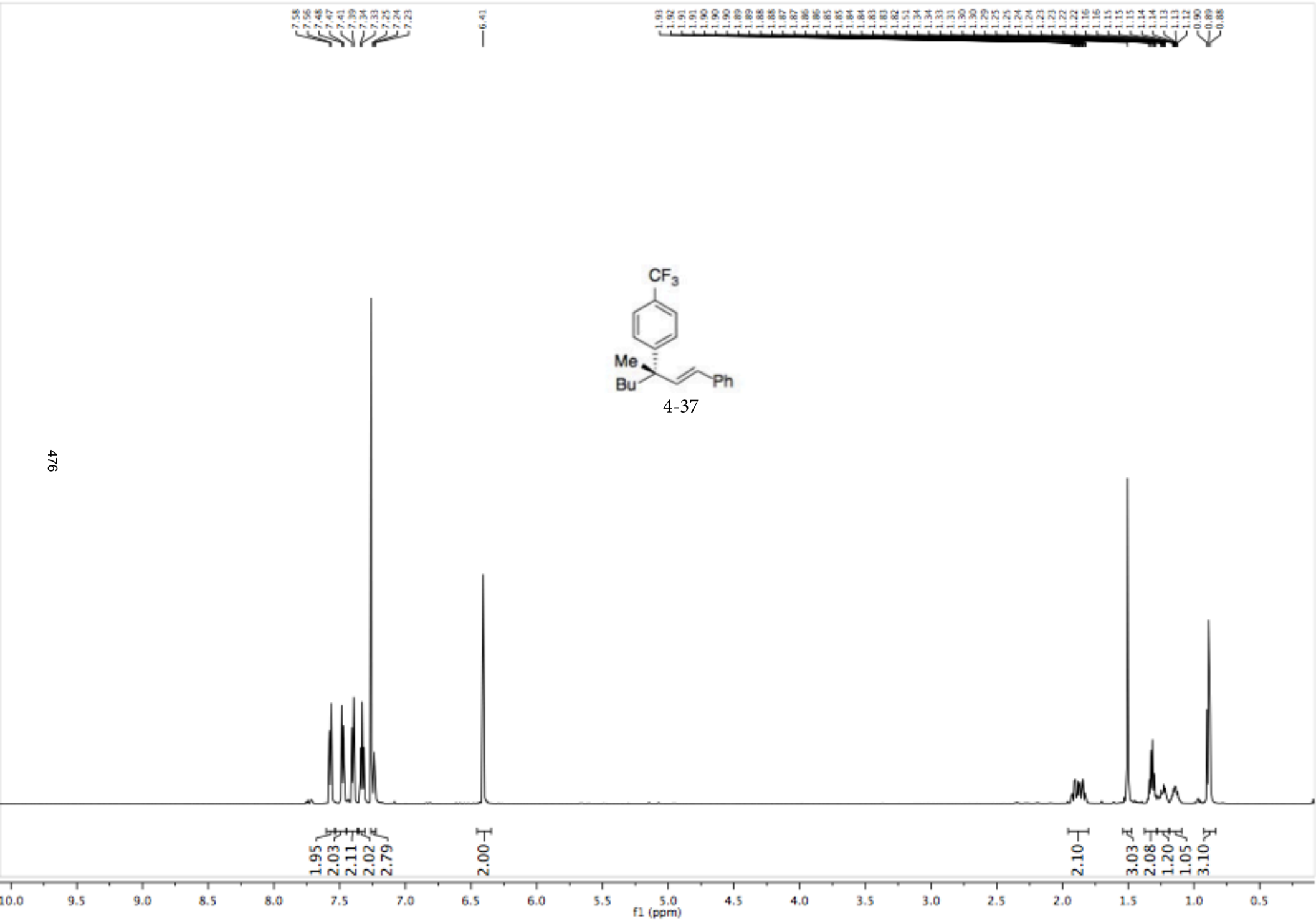
472


147.70
145.62
142.27
139.71
137.99
128.71
127.19
126.94
126.34
119.75
107.88
107.80
101.01
41.99
41.71
27.01
26.05
23.61
14.28
CDCl3
O
O
Me
Bu
Ph
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

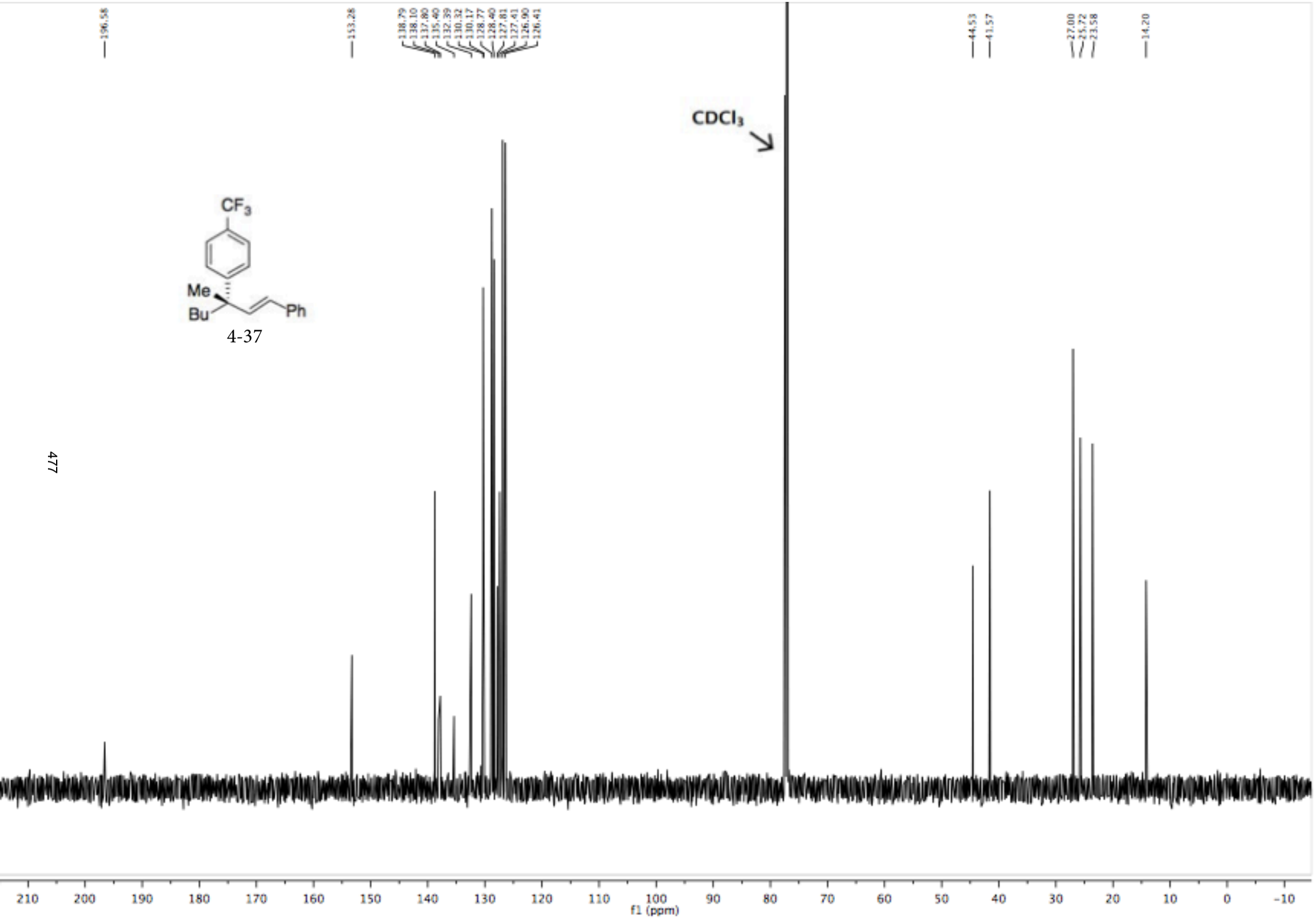
4-35

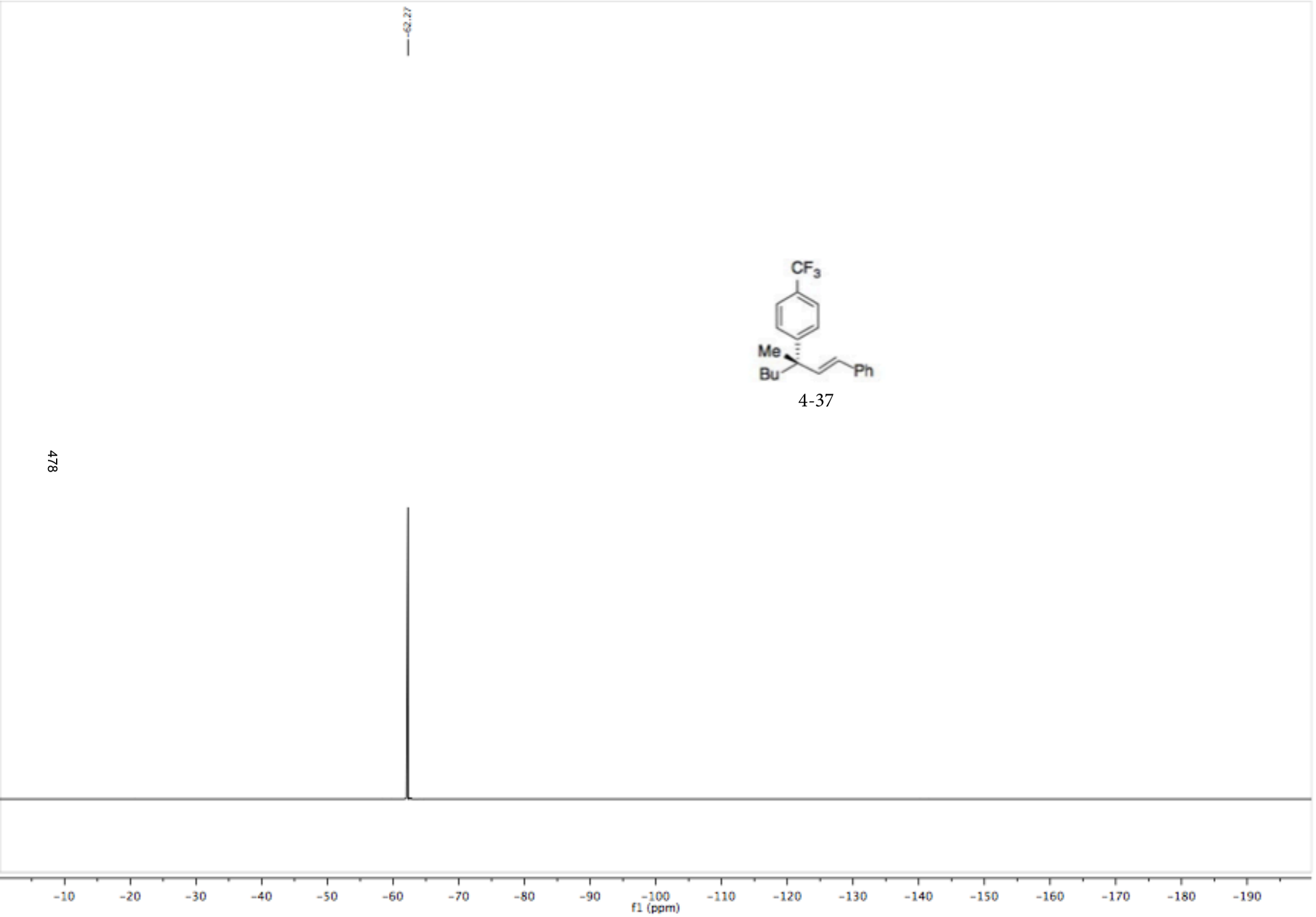

CDCl3
Me
Bu
Ph
4-36
f1 (ppm)


148.17
139.67
138.05
128.71
128.29
127.16
127.07
126.35
125.96
44.12
41.56
27.02
25.82
23.62
14.26
CDCl3
Me
Bu
Ph
4-36
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

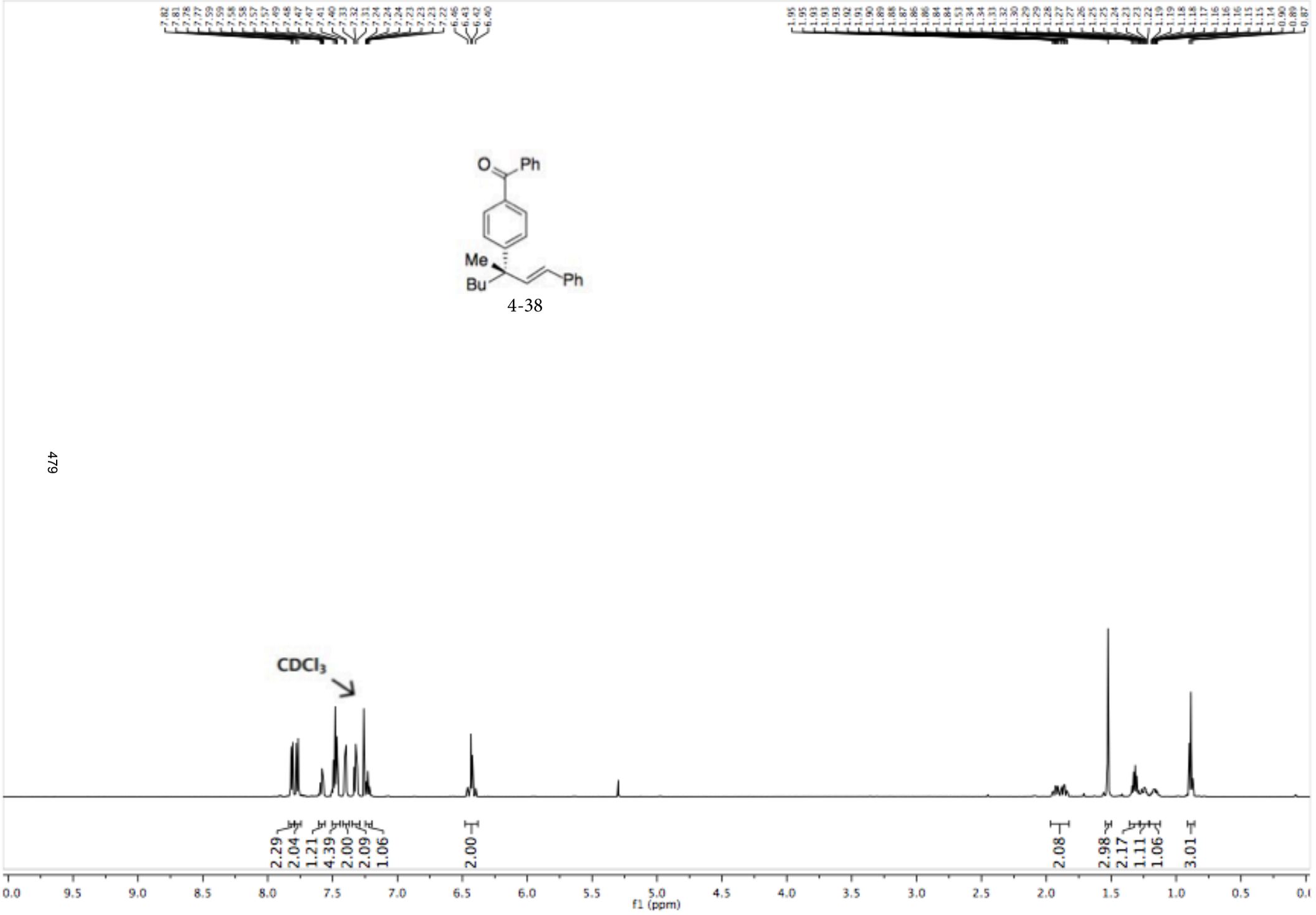

7.58
7.56
7.48
7.47
7.41
7.39
7.34
7.33
7.25
7.24
7.23
6.41
1.93
1.92
1.91
1.91
1.90
1.90
1.90
1.89
1.89
1.88
1.88
1.87
1.87
1.86
1.86
1.85
1.85
1.84
1.84
1.83
1.83
1.82
1.51
1.34
1.34
1.33
1.31
1.30
1.30
1.29
1.25
1.25
1.24
1.24
1.23
1.23
1.22
1.22
1.16
1.16
1.15
1.15
1.14
1.14
1.13
1.12
0.90
0.89
0.88
CF3
Me
Bu
Ph
1.95
2.03
2.11
2.02
2.79
2.00
2.10
3.03
2.08
1.20
1.05
3.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

4-37

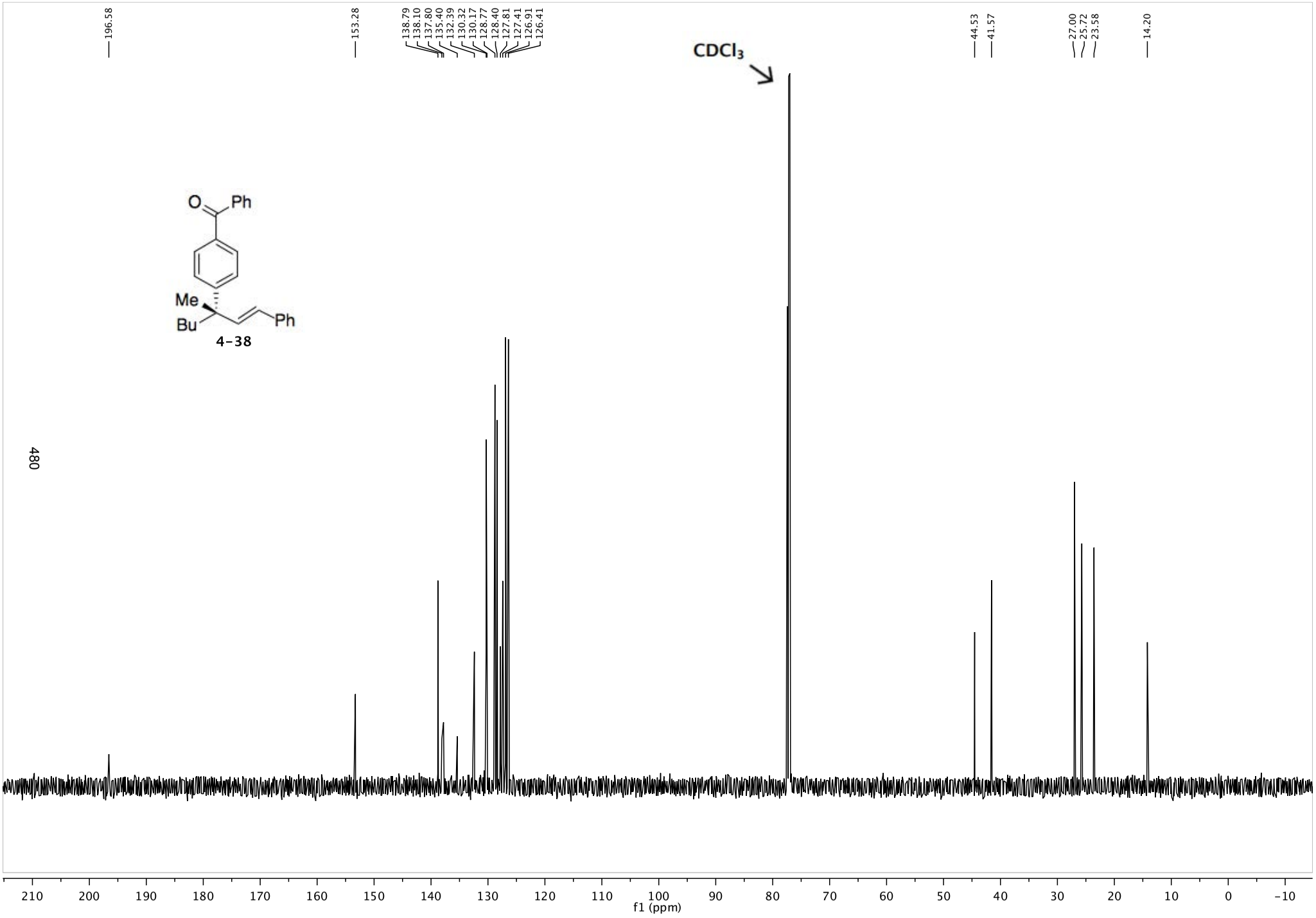

196.58
153.28
138.79
138.10
137.80
135.40
132.39
130.32
130.17
128.77
128.40
127.81
127.41
126.90
126.41
44.53
41.57
27.00
25.72
23.58
14.20
CDCl3
CF3
Me
Bu
Ph
4-37
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

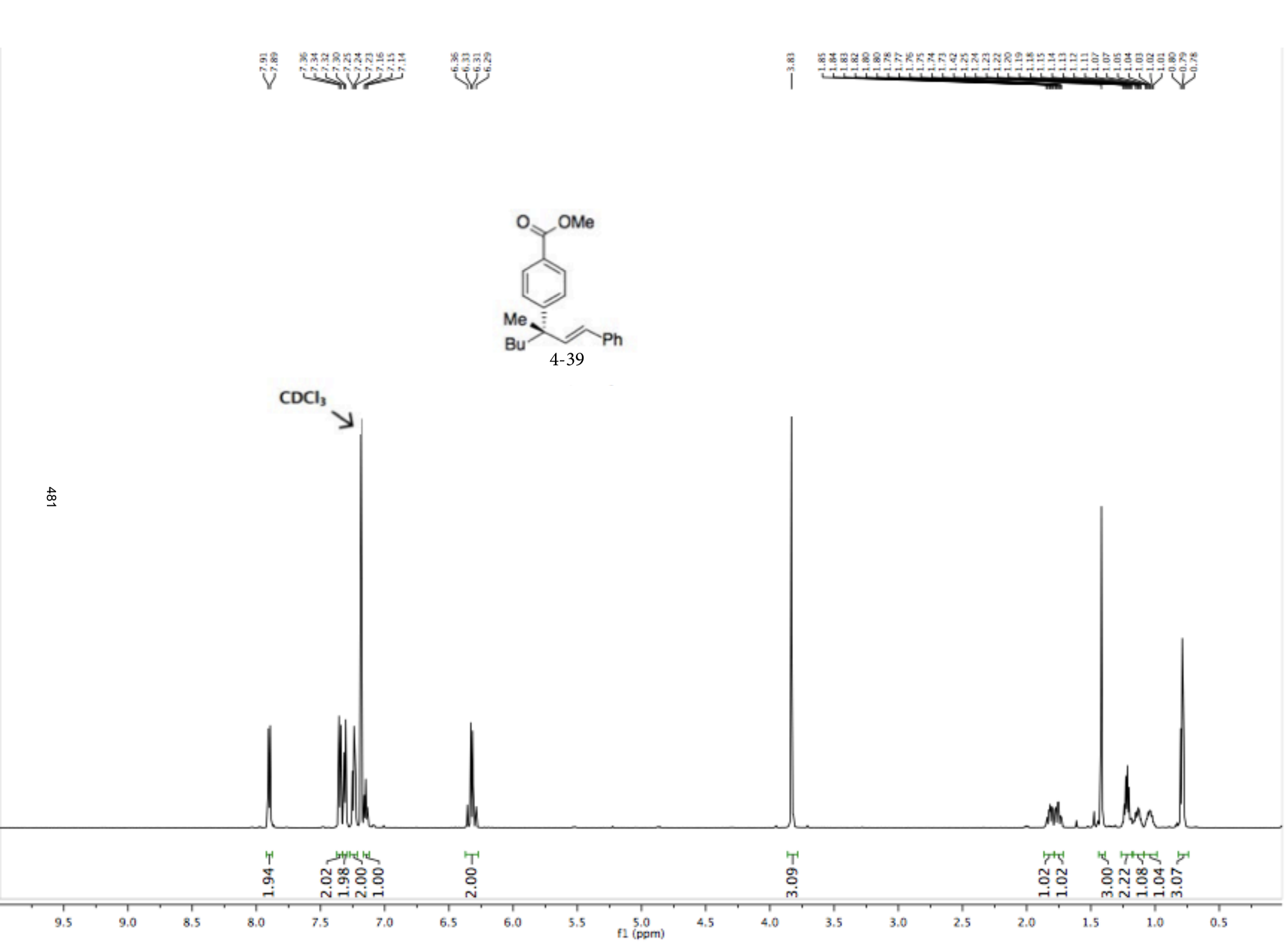

-62.27
CF3
Me
Bu
Ph
478
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

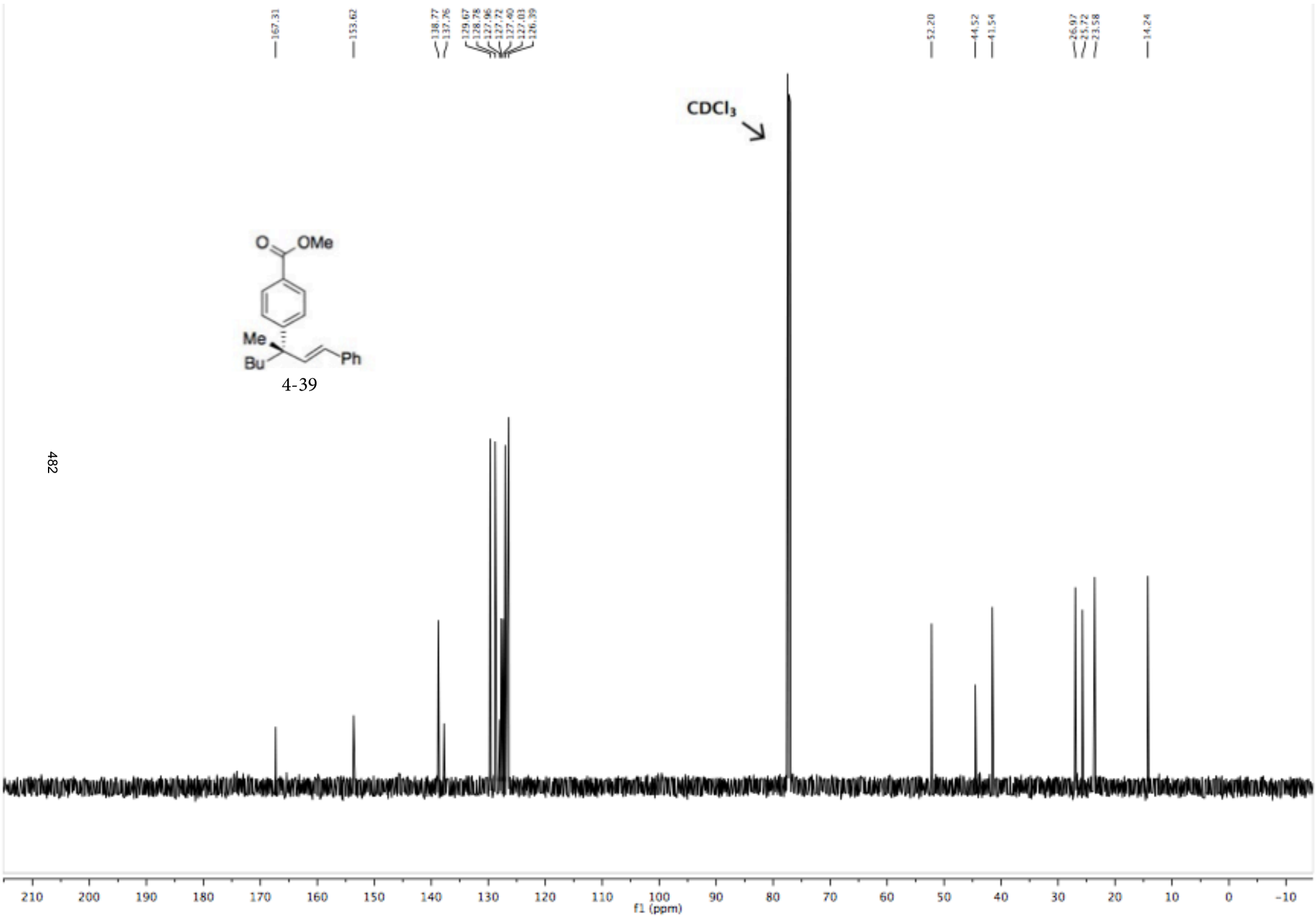
4-37


O
Ph
Me
Bu
Ph
CDCl3
2.29
2.04
1.21
4.39
2.00
2.09
1.06
2.00
2.08
2.98
2.17
1.11
1.06
3.01
f1 (ppm)

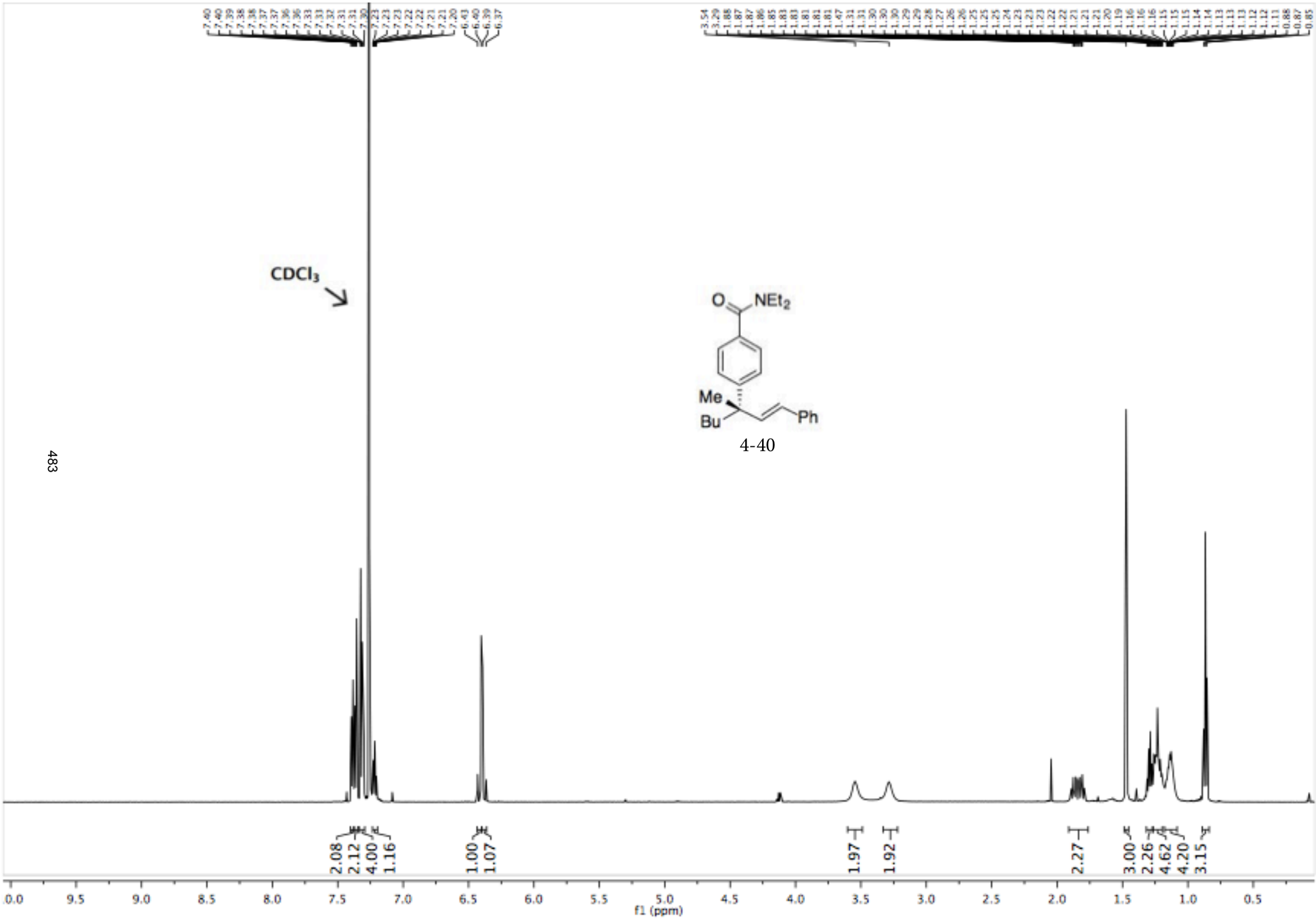
4-38

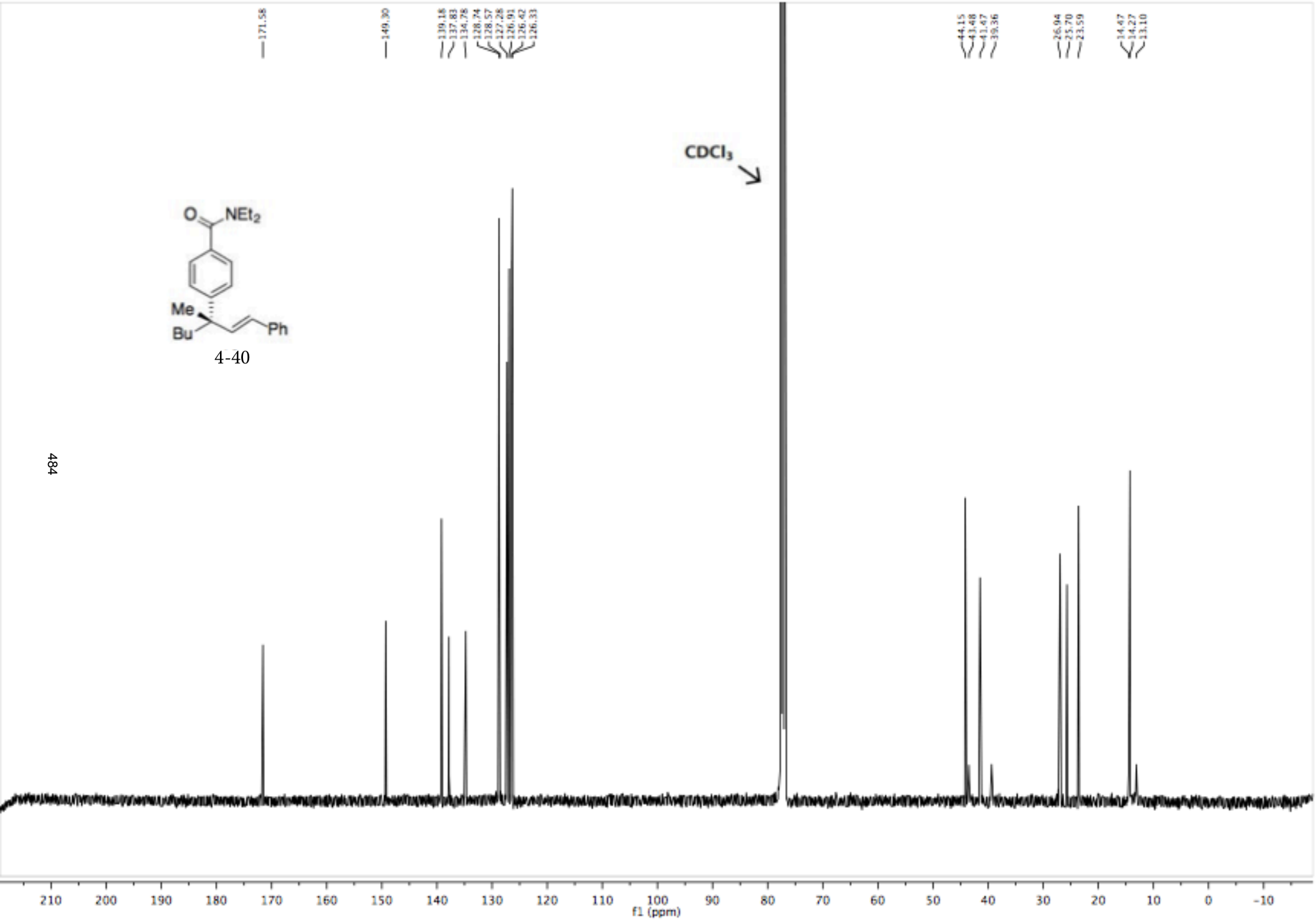

196.58
153.28
138.79
138.10
137.80
135.40
132.39
130.32
130.17
128.77
128.40
127.81
127.41
126.91
126.41
CDCl3
44.53
41.57
27.00
25.72
23.58
14.20
O
Ph
Me
Bu
Ph
4-38
480
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

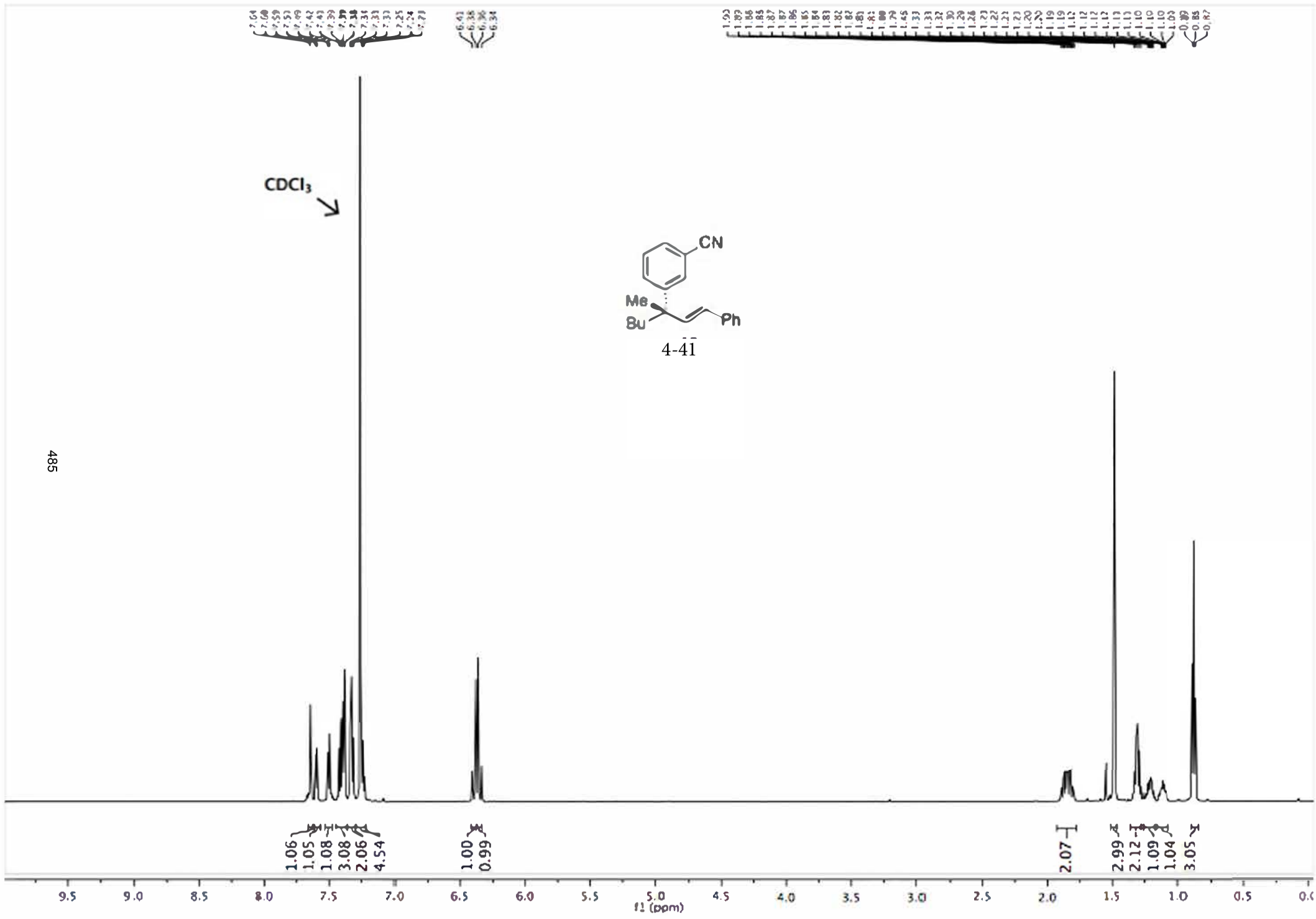

7.91
7.89
7.36
7.34
7.32
7.30
7.25
7.24
7.23
7.16
7.15
7.14
6.36
6.33
6.31
6.29
3.83
1.85
1.84
1.83
1.82
1.80
1.80
1.78
1.77
1.76
1.75
1.74
1.73
1.42
1.25
1.24
1.23
1.22
1.20
1.19
1.18
1.15
1.14
1.13
1.12
1.11
1.07
1.07
1.05
1.04
1.03
1.02
1.01
0.80
0.79
0.78
O
OMe
Me
Bu
Ph
4-39
CDCl3
481
1.94
2.02
1.98
2.00
1.00
2.00
3.09
1.02
1.02
3.00
2.22
1.08
1.04
3.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

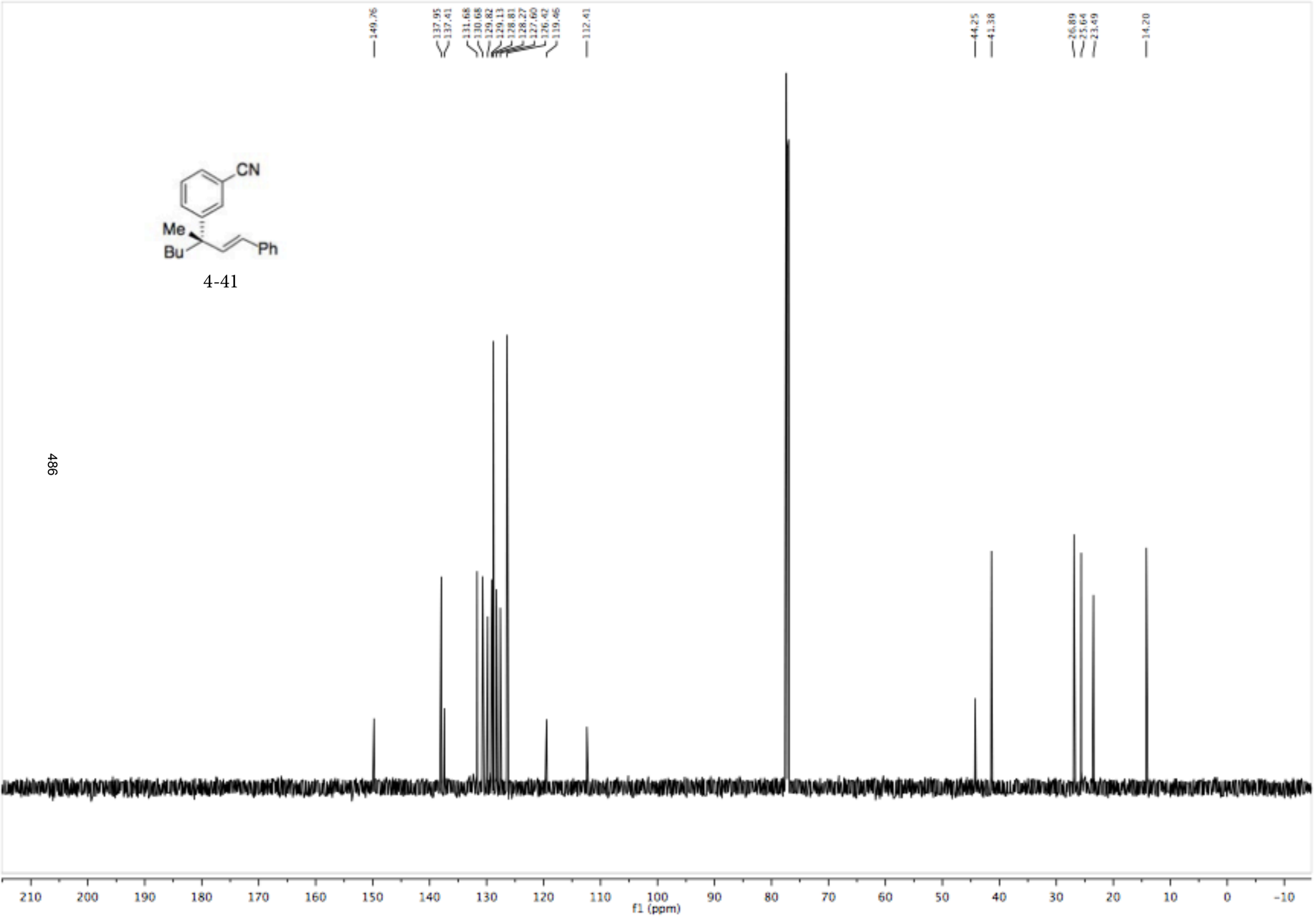

167.31
153.62
138.77
137.76
129.67
128.78
127.96
127.72
127.40
127.03
126.39
52.20
44.52
41.54
26.97
25.72
23.58
14.24
CDCl3
O
OMe
Me
Bu
Ph
f1 (ppm)

4-39

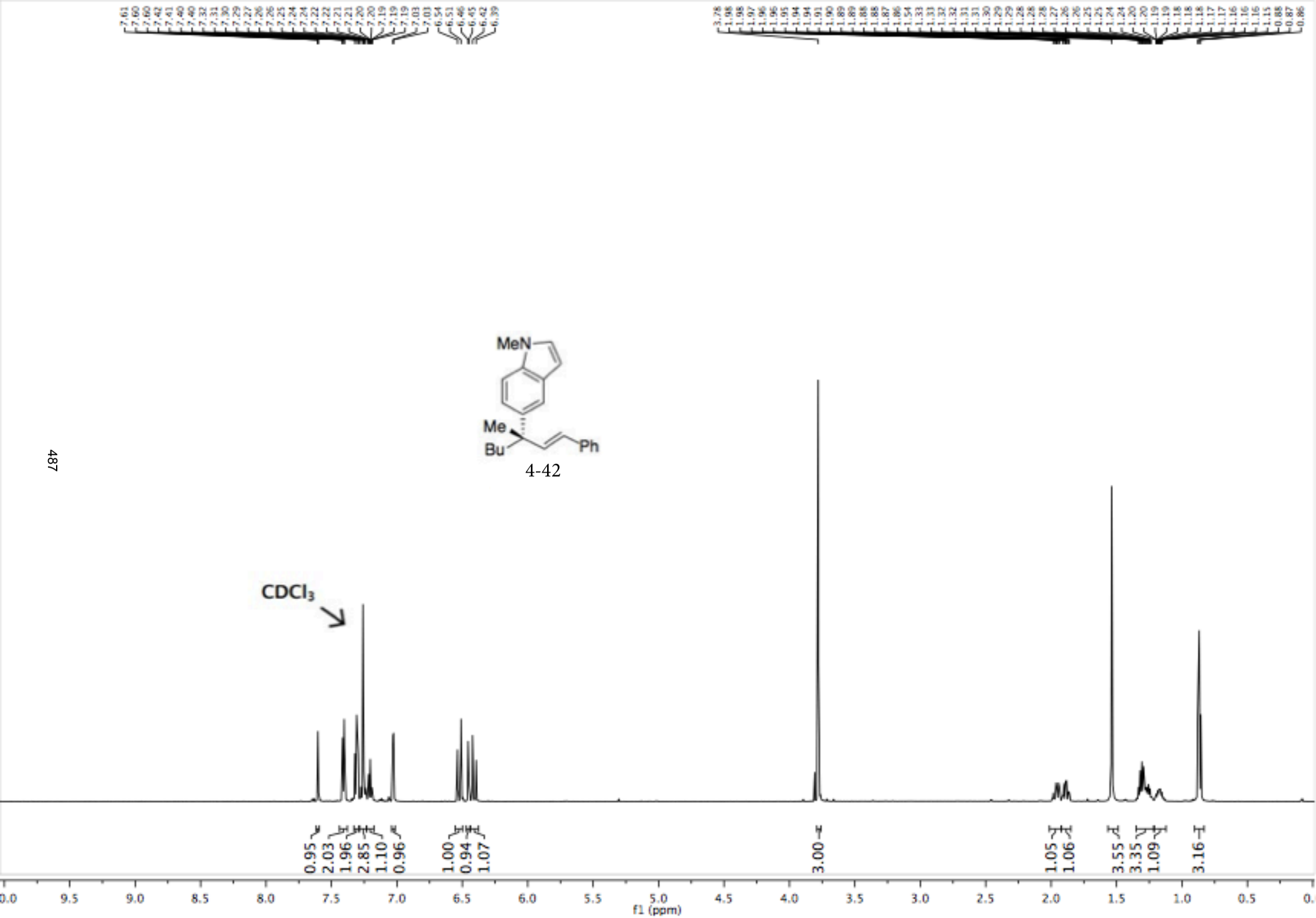

CDCl3
O
NEt2
Me
Bu
Ph
4-40
2.08
2.12
4.00
1.16
1.00
1.07
1.97
1.92
2.27
3.00
2.26
4.62
4.20
3.15
f1 (ppm)


171.58
149.30
139.18
137.83
134.78
128.74
128.57
127.28
126.91
126.42
126.33
44.15
43.48
41.47
39.36
26.94
25.70
23.59
14.47
14.27
13.10
CDCl3
O
NEt2
Me
Bu
Ph
4-40
484
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

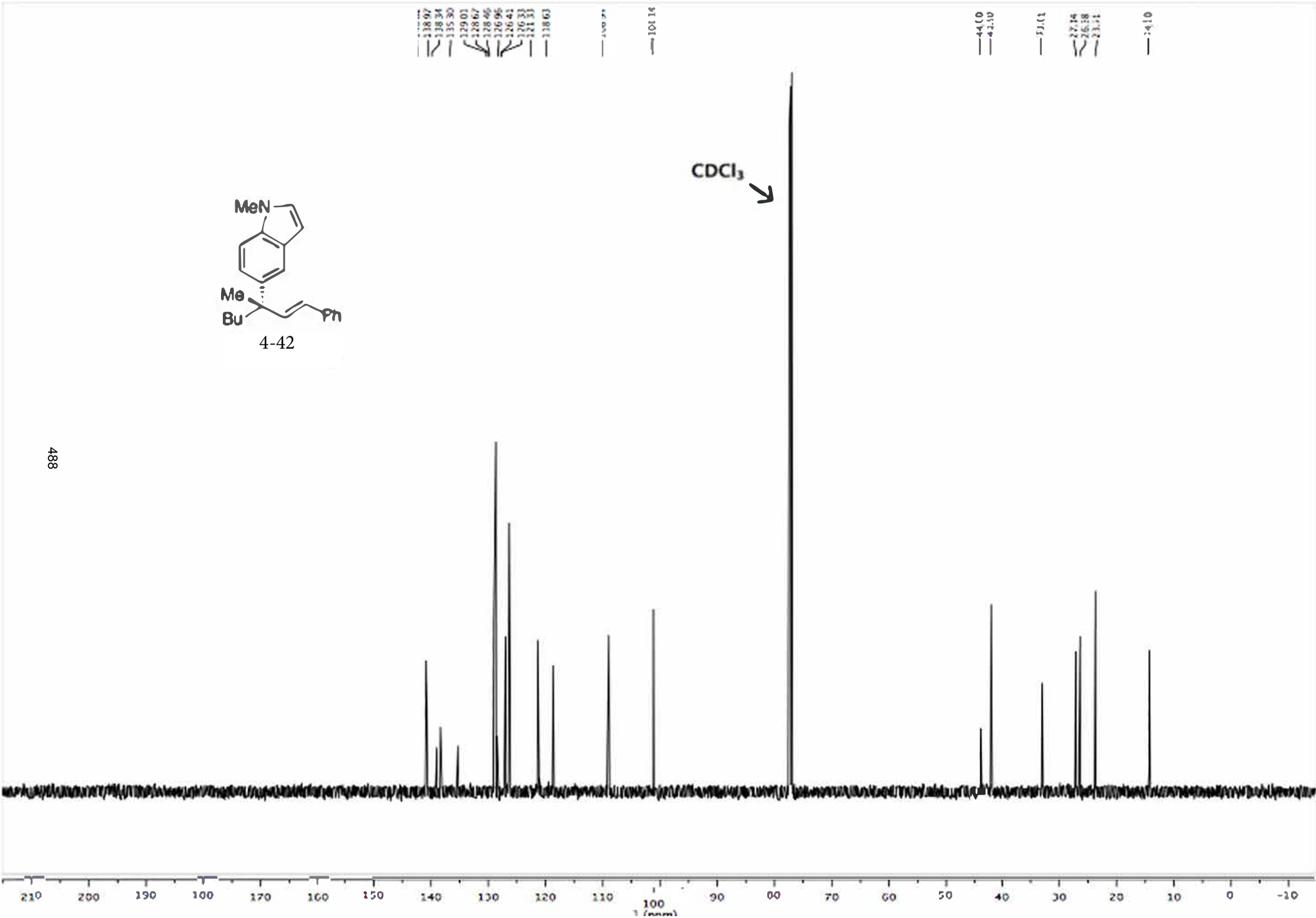

CDCl3
CN
Me
Bu
Ph
4-41
1.06
1.05
1.08
3.08
2.06
4.54
1.00
0.99
2.07
2.99
2.12
1.09
1.04
3.05
f1 (ppm)

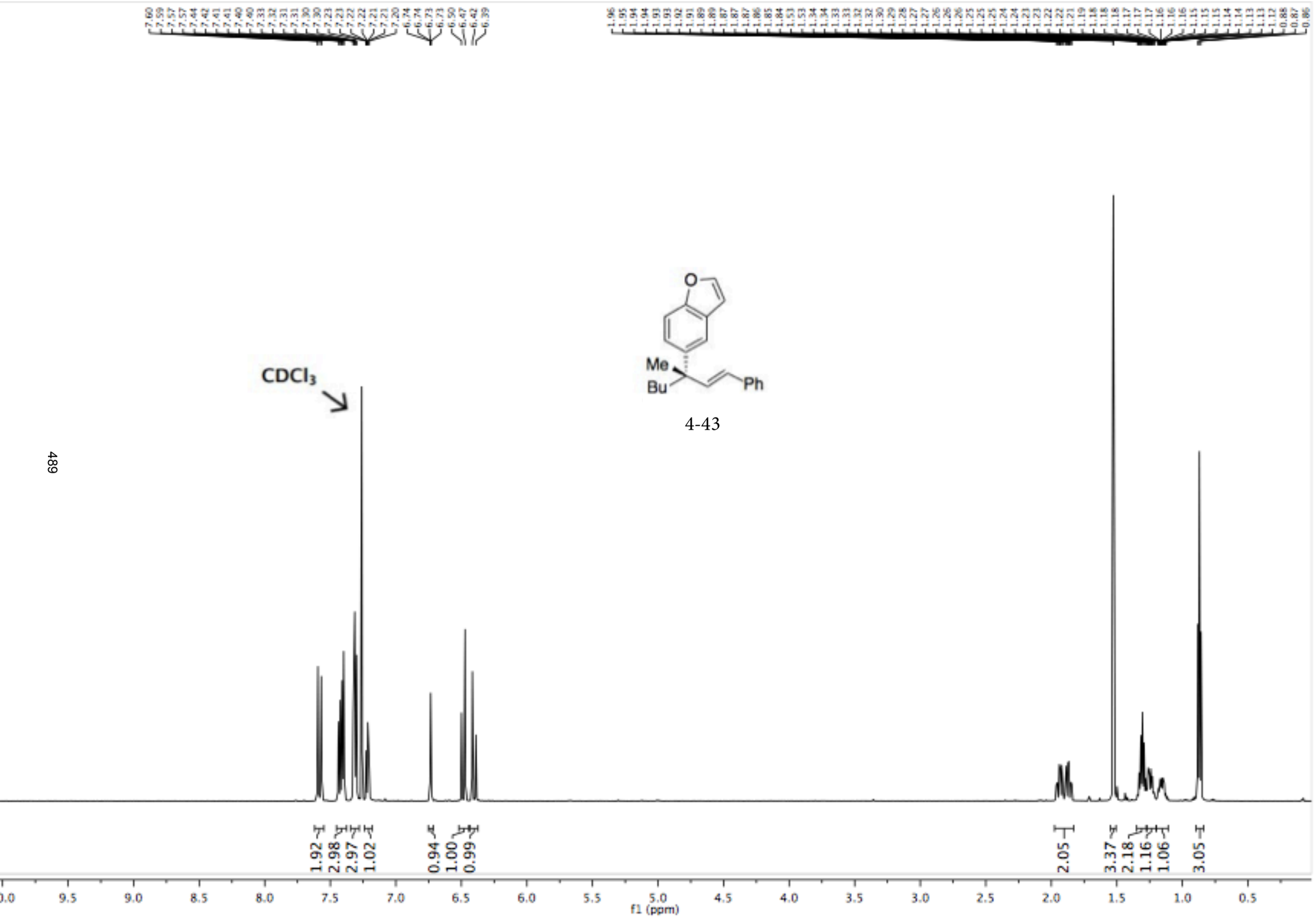

149.76
137.95
137.41
131.68
130.68
129.82
129.13
128.81
128.27
127.60
126.42
119.46
112.41
44.25
41.38
26.89
25.64
23.49
14.20
CN
Me
Bu
Ph
f1 (ppm)

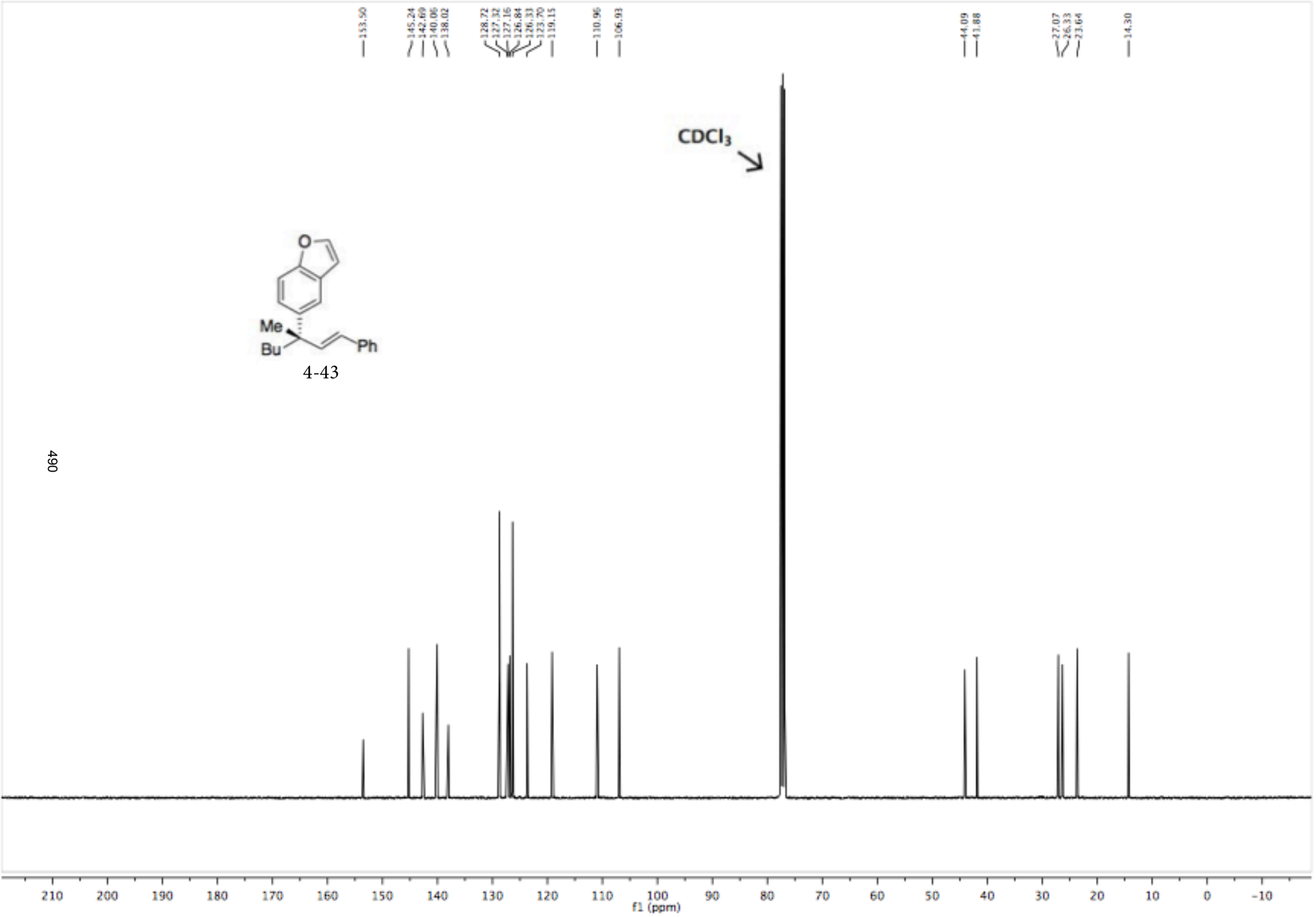
4-41

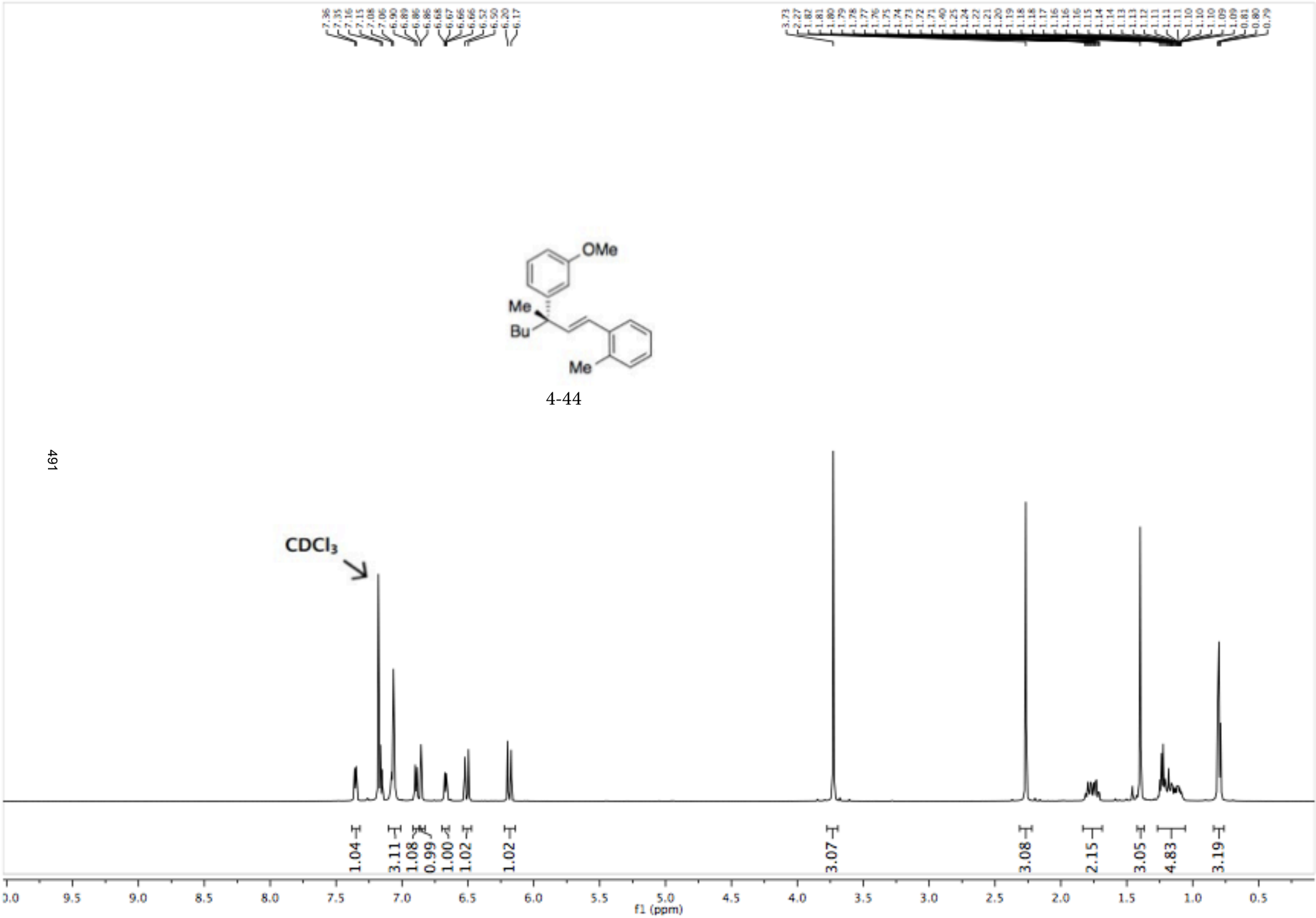

MeN
Me
Bu
Ph
CDCl3
0.95
2.03
1.96
2.85
1.10
0.96
1.00
0.94
1.07
3.00
1.05
1.06
3.55
3.35
1.09
3.16
f1 (ppm)

4-42

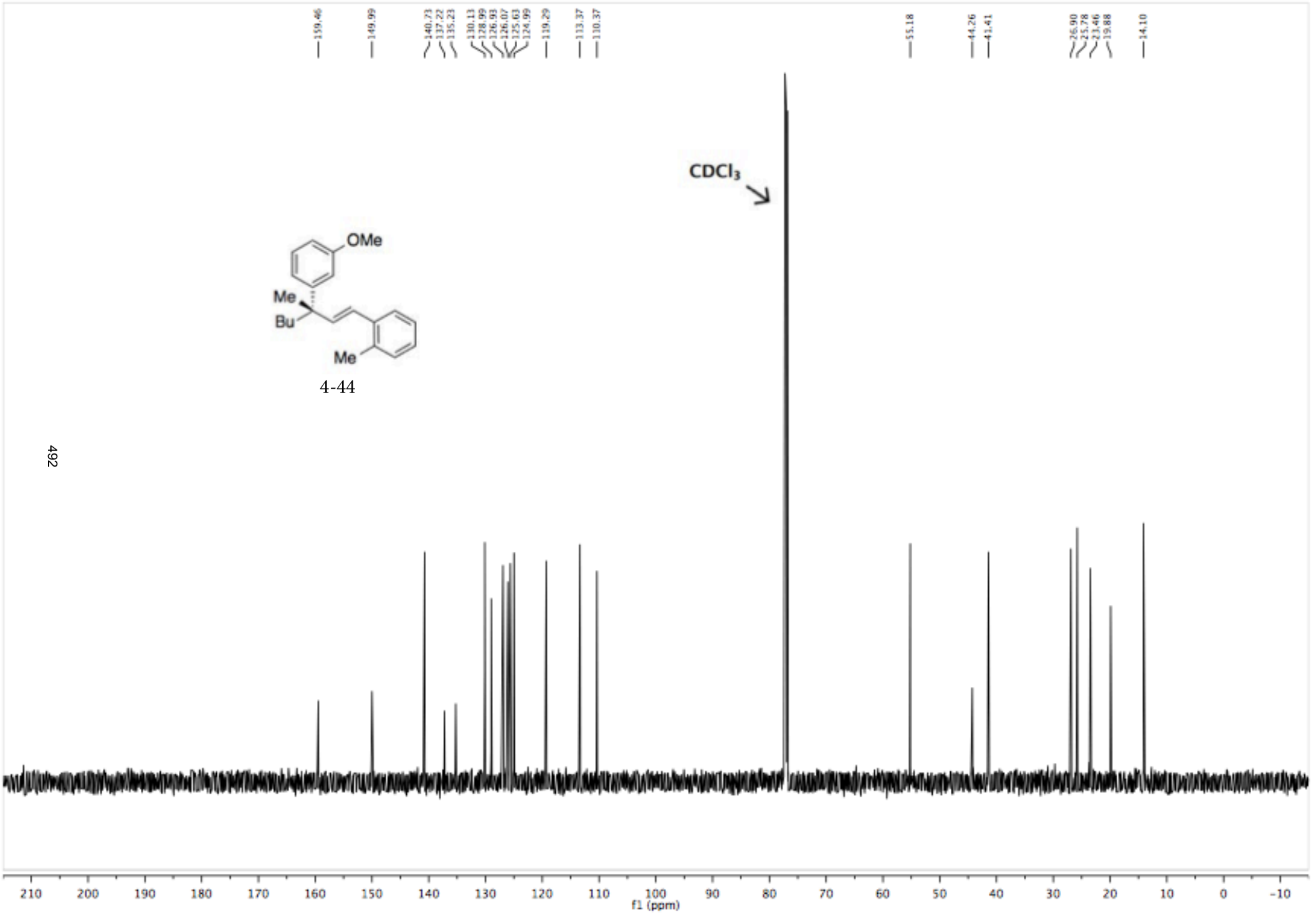

CDCl3
MeN
Me
Bu
Ph
4-42
488


CDCl3
Me
Bu
Ph
4-43
1.92
2.98
2.97
1.02
0.94
1.00
0.99
2.05
3.37
2.18
1.16
1.06
3.05
f1 (ppm)

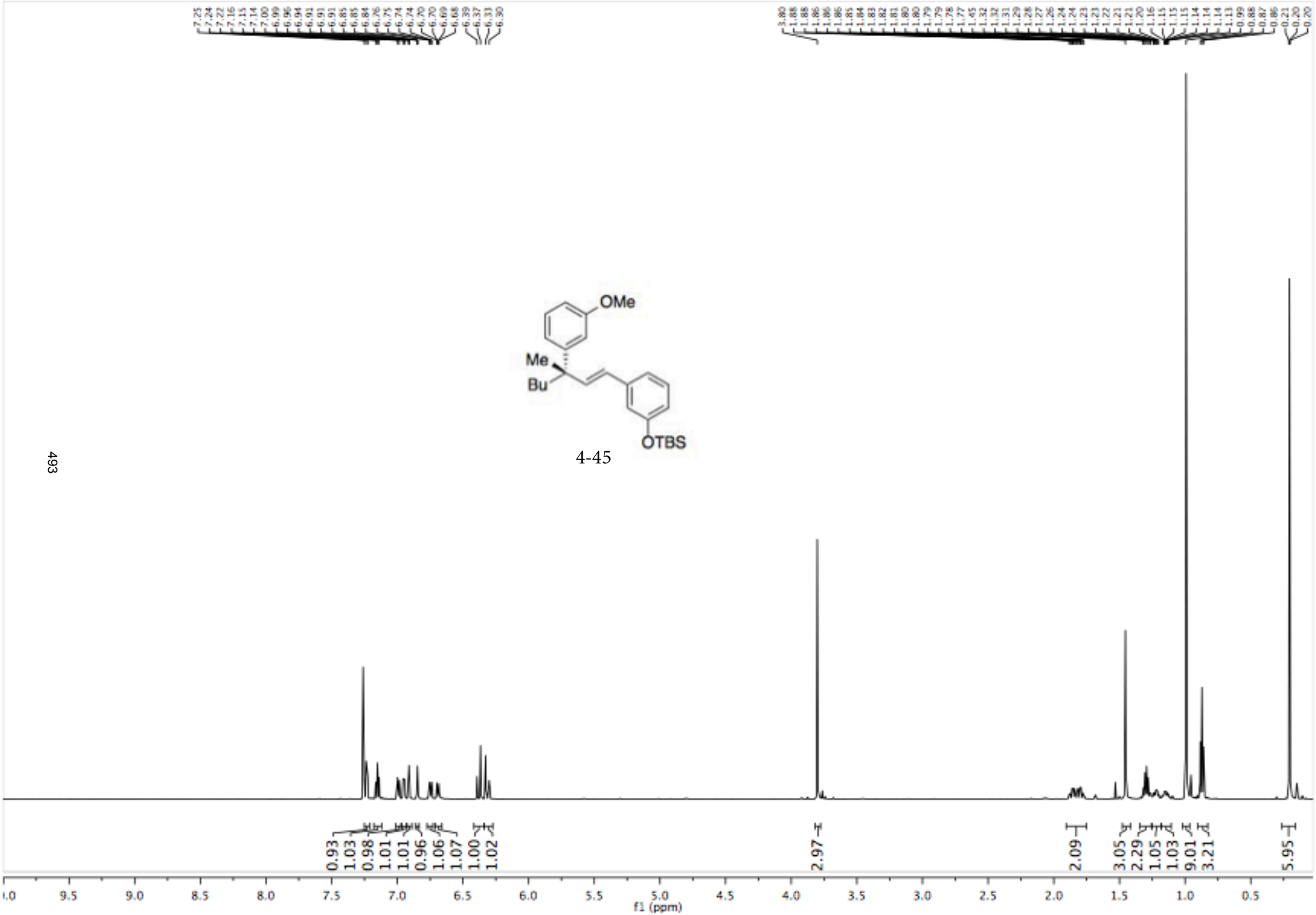

153.50
145.24
142.69
140.06
138.02
128.72
127.32
127.16
126.84
126.33
123.70
119.15
110.96
106.93
44.09
41.88
27.07
26.33
23.64
14.30
CDCl3
O
Me
Bu
Ph
4-43
490
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

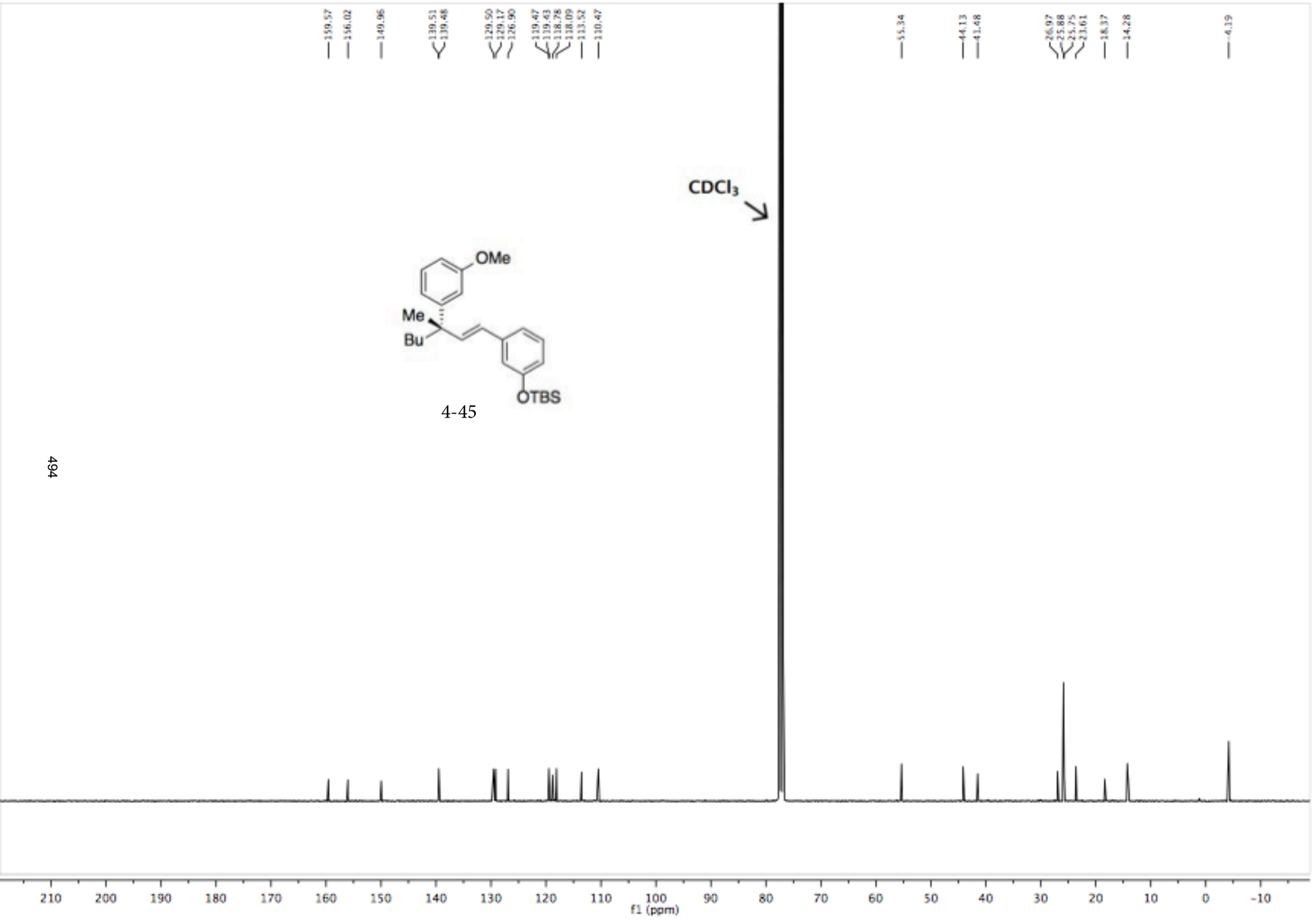

7.36
7.35
7.16
7.15
7.08
7.06
6.90
6.89
6.86
6.86
6.68
6.67
6.66
6.66
6.52
6.50
6.20
6.17
3.73
2.27
1.82
1.81
1.80
1.79
1.78
1.77
1.76
1.75
1.74
1.73
1.72
1.71
1.40
1.25
1.24
1.22
1.21
1.20
1.19
1.18
1.18
1.17
1.16
1.16
1.16
1.15
1.14
1.14
1.13
1.13
1.12
1.11
1.11
1.11
1.10
1.10
1.10
1.09
1.09
0.81
0.80
0.79
OMe
Me
Bu
Me
CDCl3
1.04
3.11
1.08
0.99
1.00
1.02
1.02
3.07
3.08
2.15
3.05
4.83
3.19
f1 (ppm)

4-44

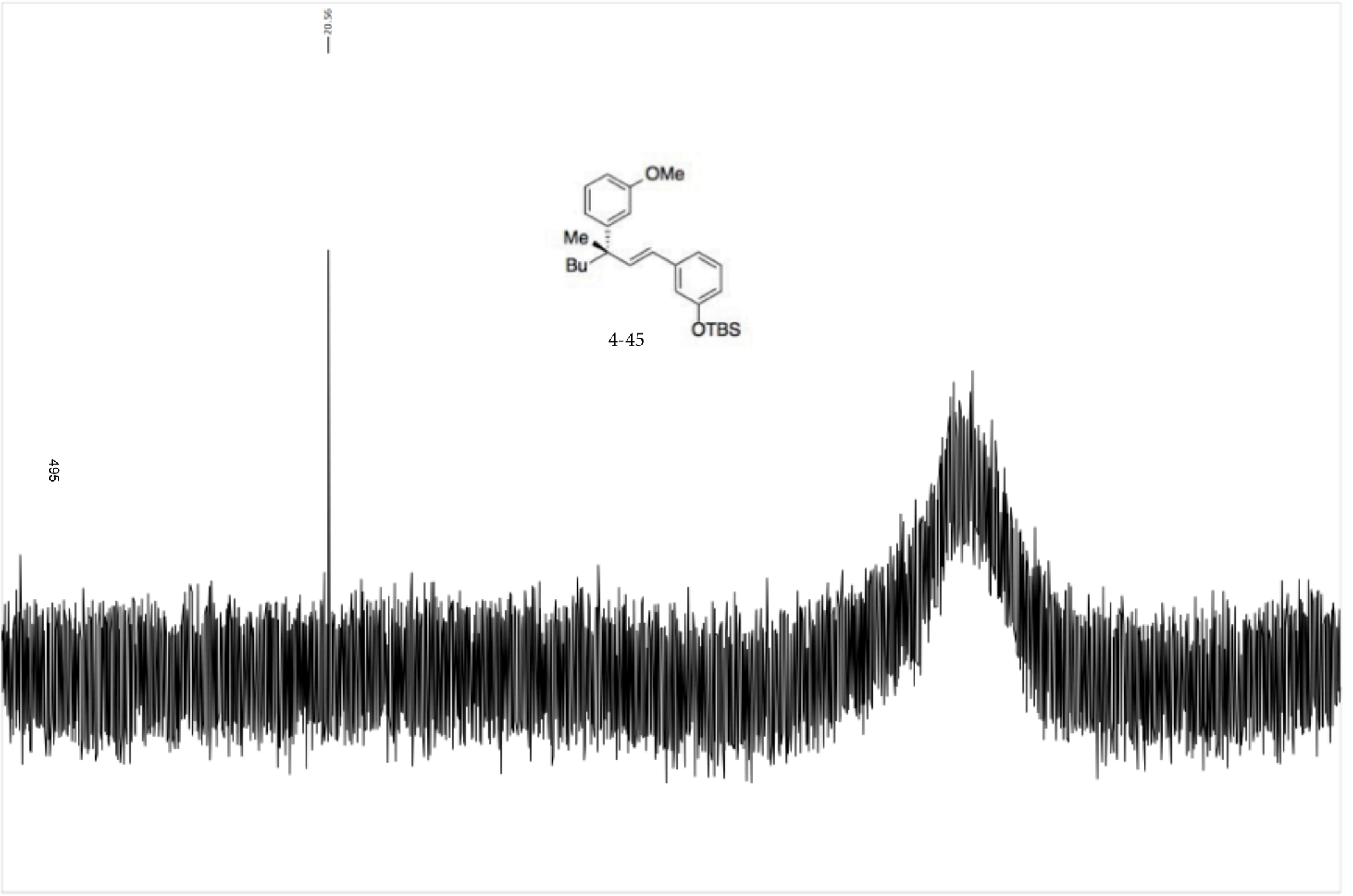

159.46
149.99
140.73
137.22
135.23
130.13
128.99
126.93
126.07
125.63
124.99
119.29
113.37
110.37
55.18
44.26
41.41
26.90
25.78
23.46
19.88
14.10
CDCl3
OMe
Me
Bu
Me
f1 (ppm)

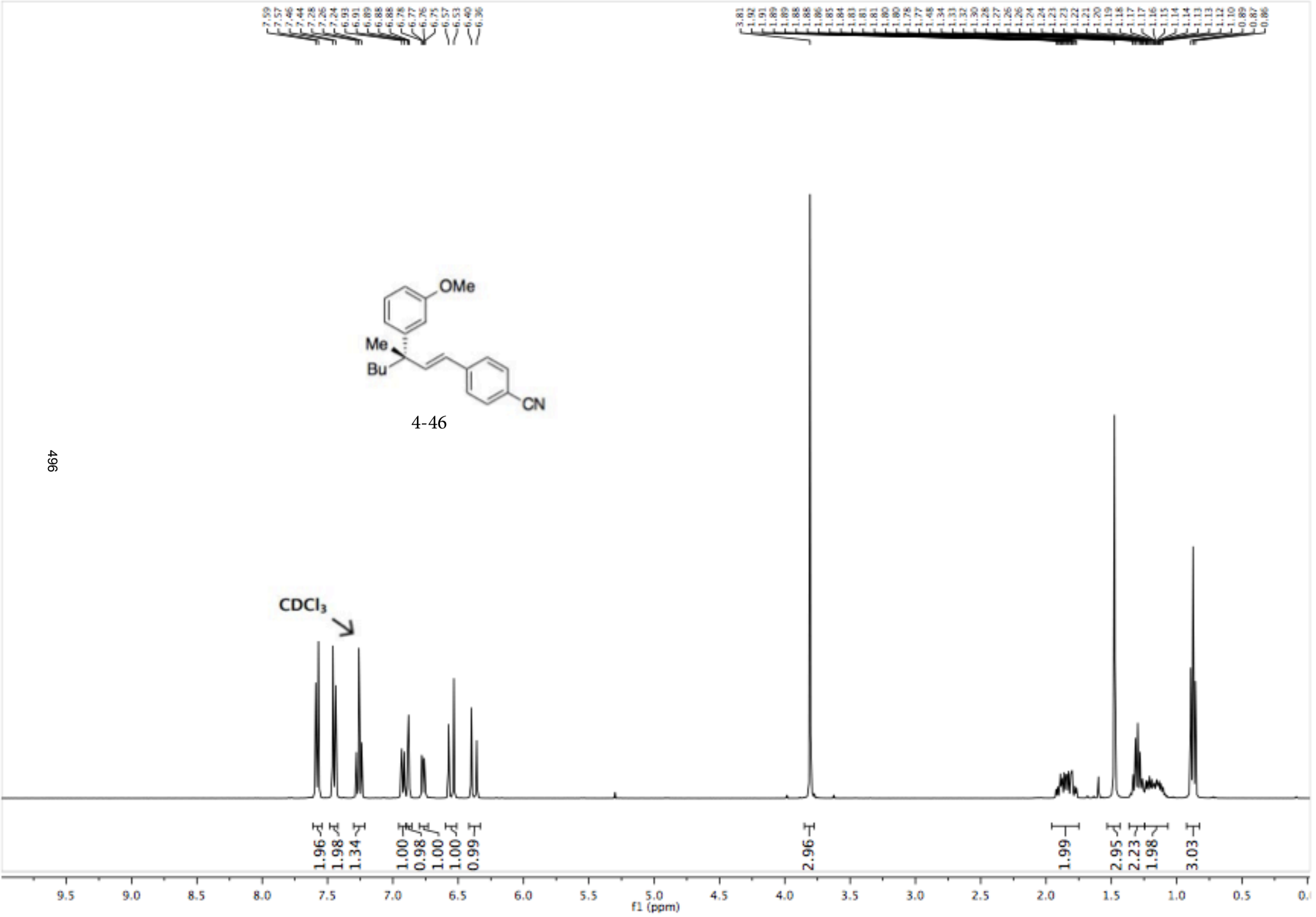
4-44


OMe
Me
Bu
OTBS
4-45
f1 (ppm)

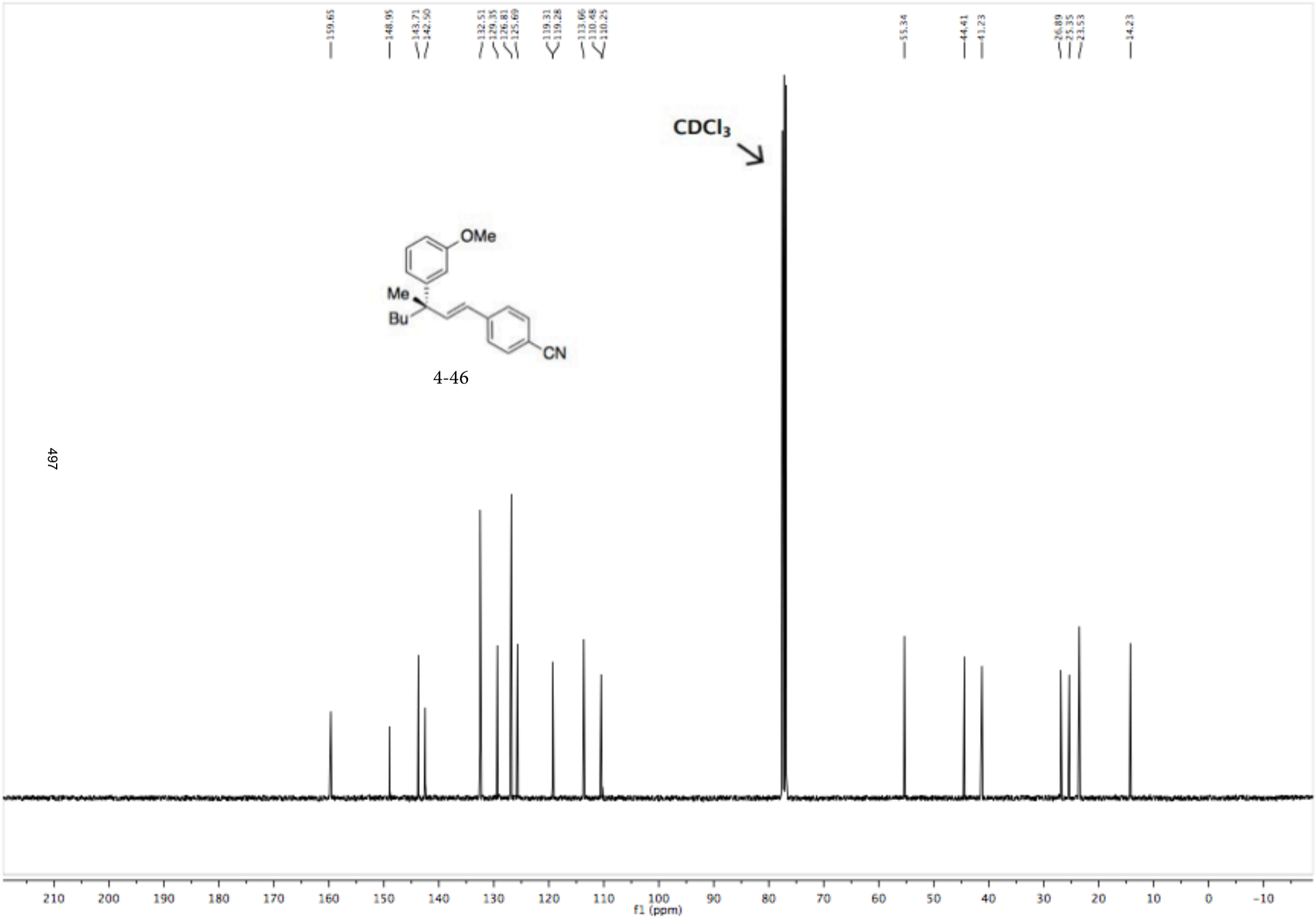

159.57
156.02
149.96
139.51
139.48
129.50
129.17
126.90
119.47
119.43
118.78
118.09
113.52
110.47
55.34
44.13
41.48
26.97
25.88
25.75
23.61
18.37
14.28
-4.19
CDCl3
OMe
Me
Bu
OTBS
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

4-45

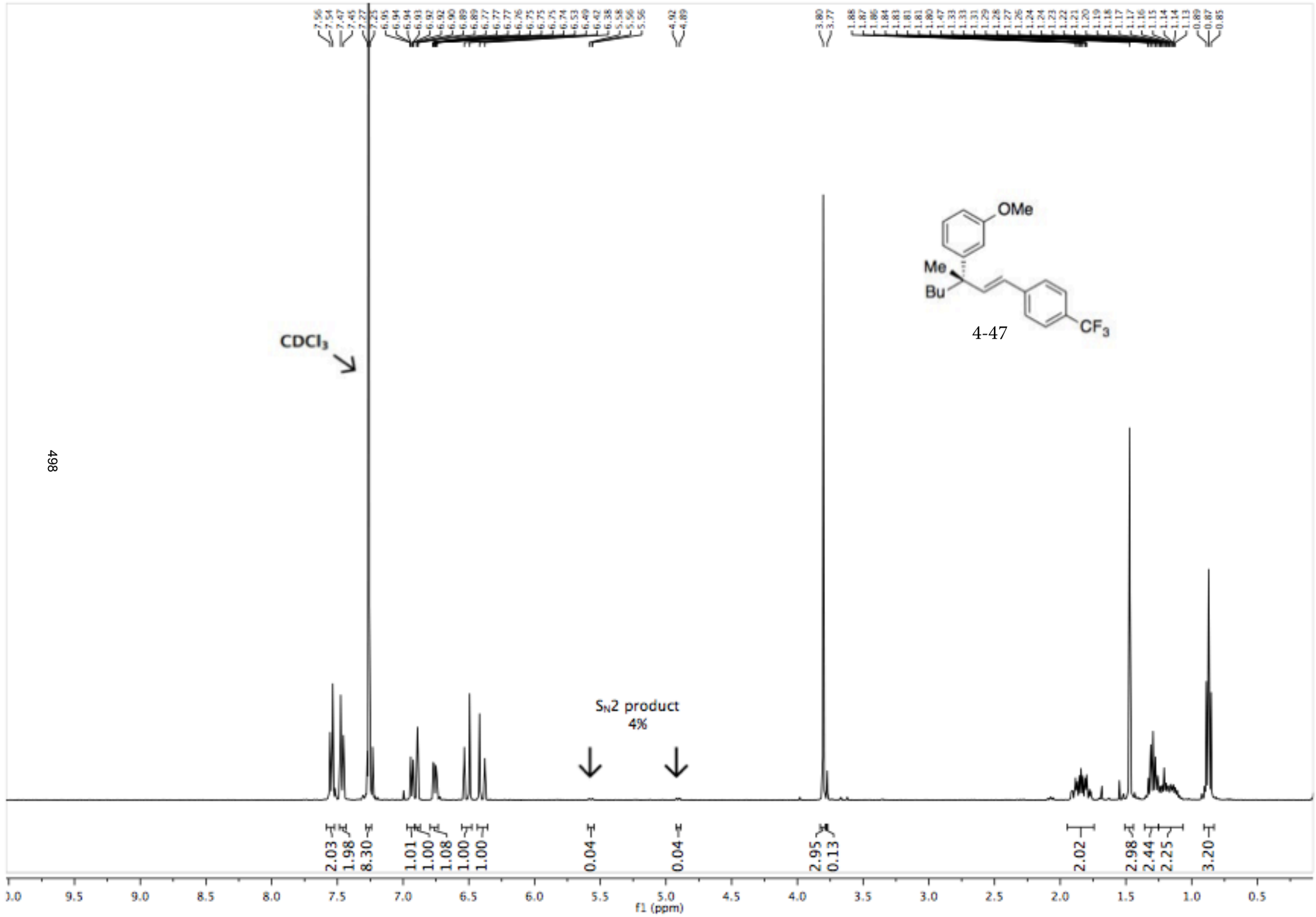

20.56
OMe
Me
Bu
OTBS
4-45
495
80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180
f1 (ppm)

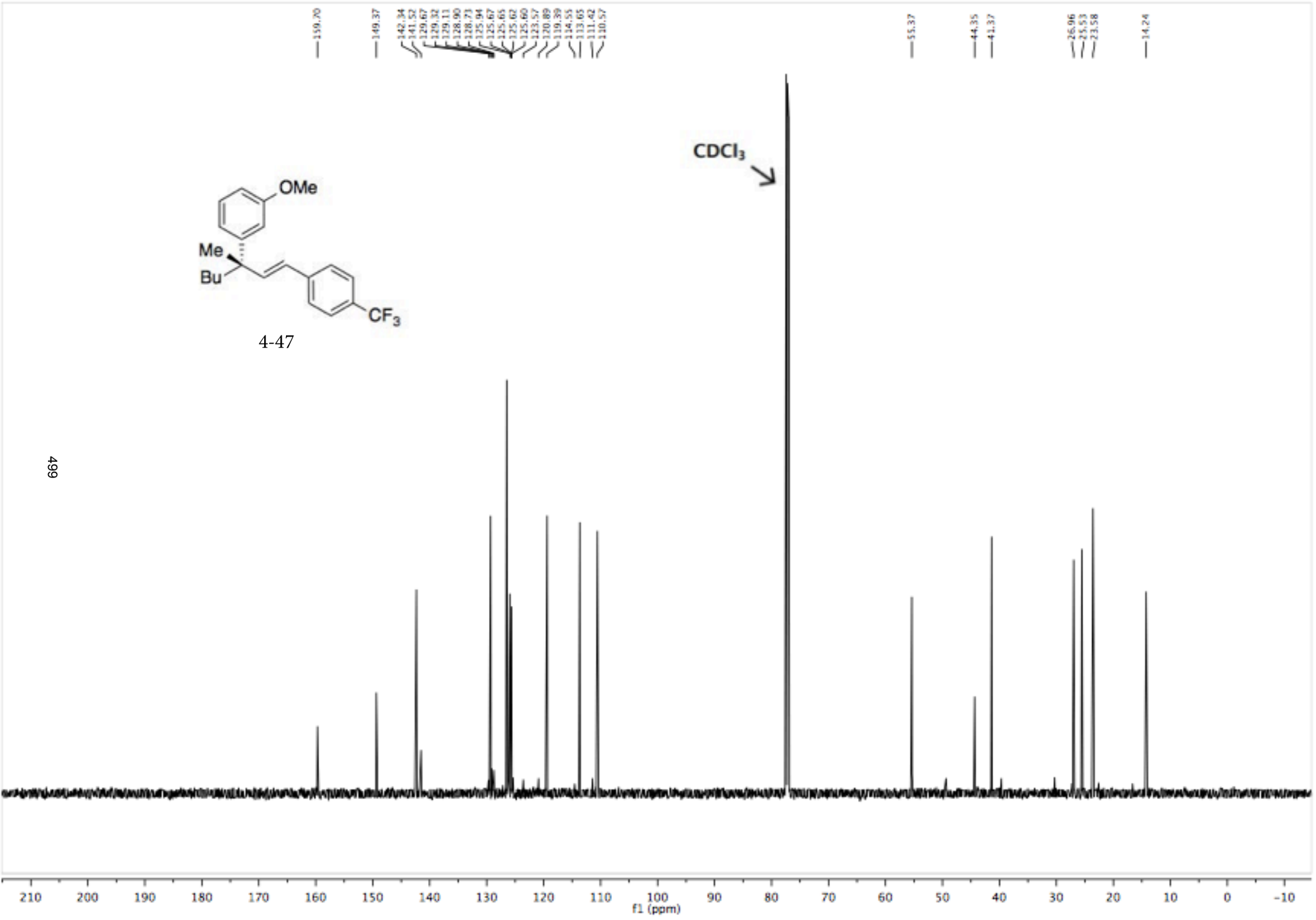

OMe
Me
Bu
CN
CDCl3
1.96
1.98
1.34
1.00
0.98
1.00
1.00
0.99
2.96
1.99
2.95
2.23
1.98
3.03
f1 (ppm)

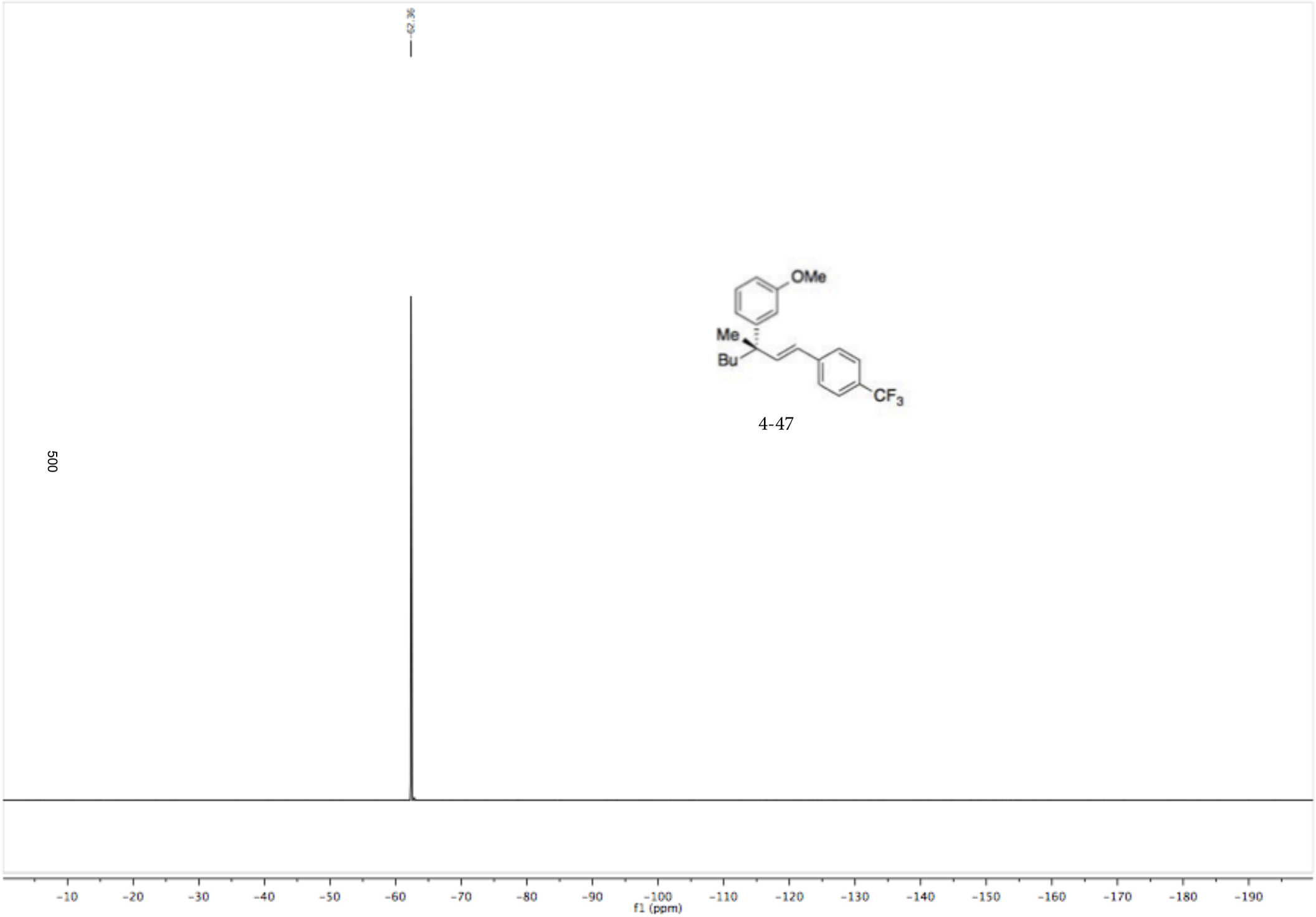
4-46


159.65
148.95
143.71
142.50
132.51
129.35
126.81
125.69
119.31
119.28
113.66
110.48
110.25
55.34
44.41
41.23
26.89
25.35
23.53
14.23
CDCl3
OMe
Me
Bu
CN
f1 (ppm)

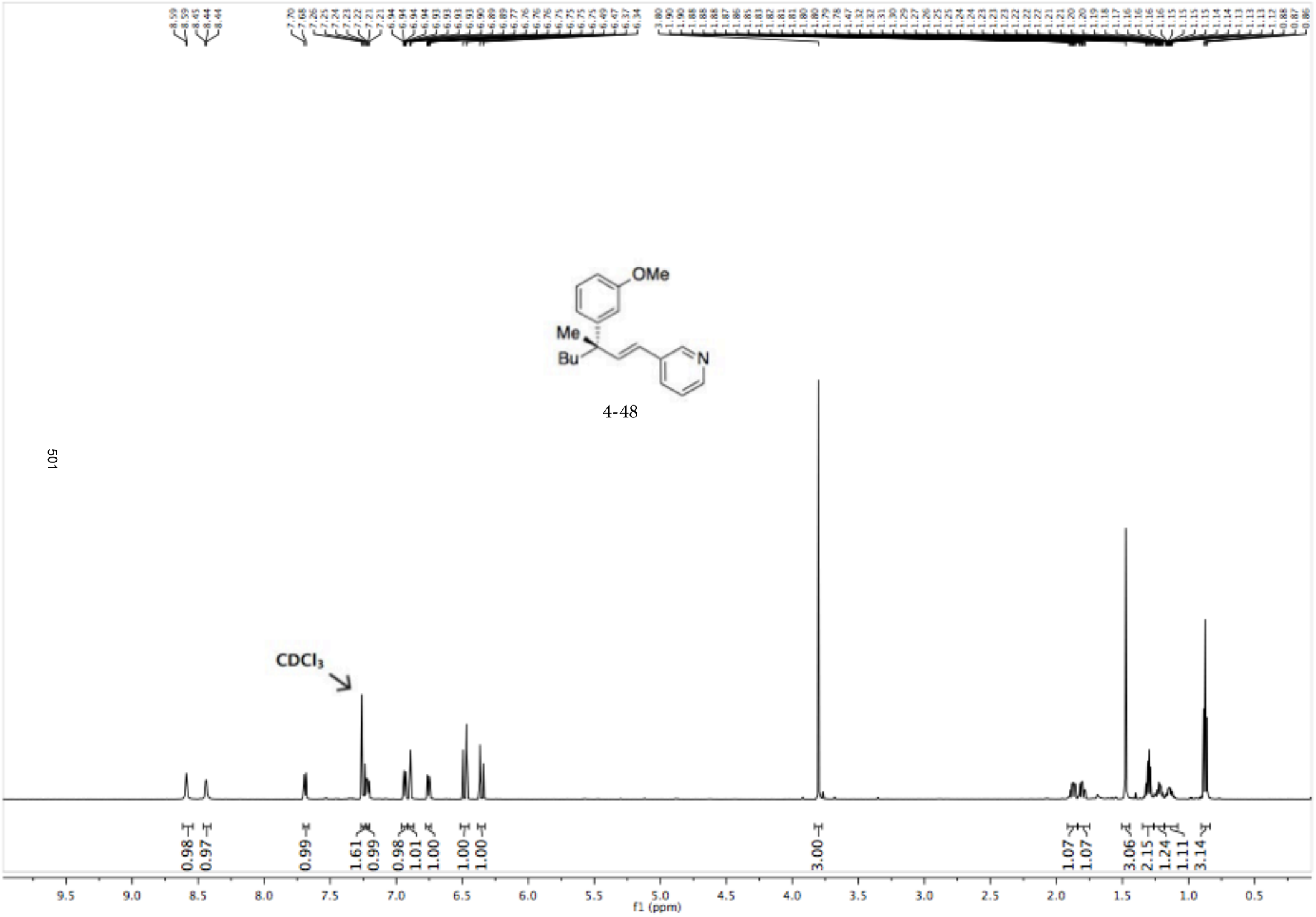
4-46

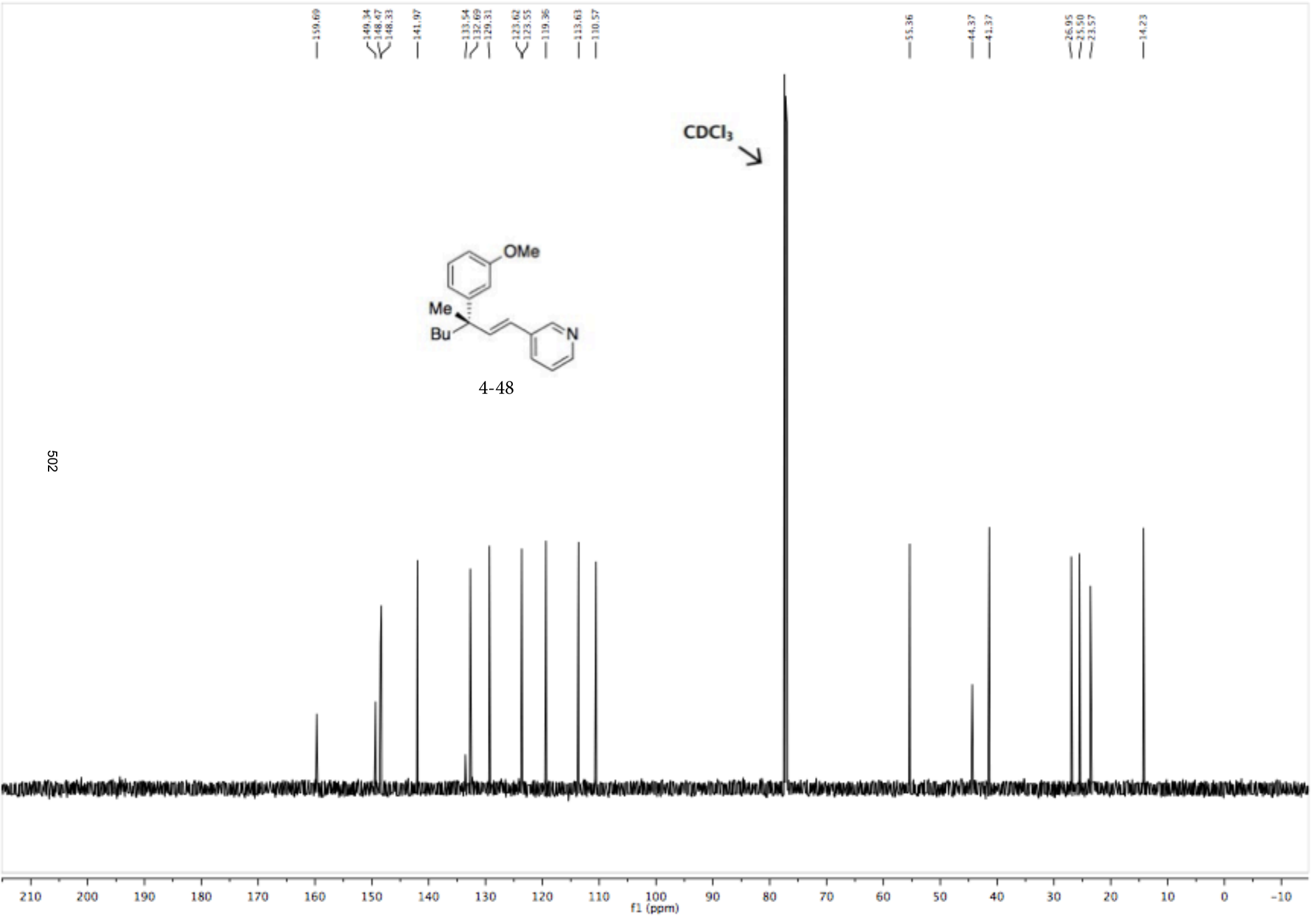

CDCl3
SN2 product
4%
OMe
Me
Bu
CF3
4-47
f1 (ppm)

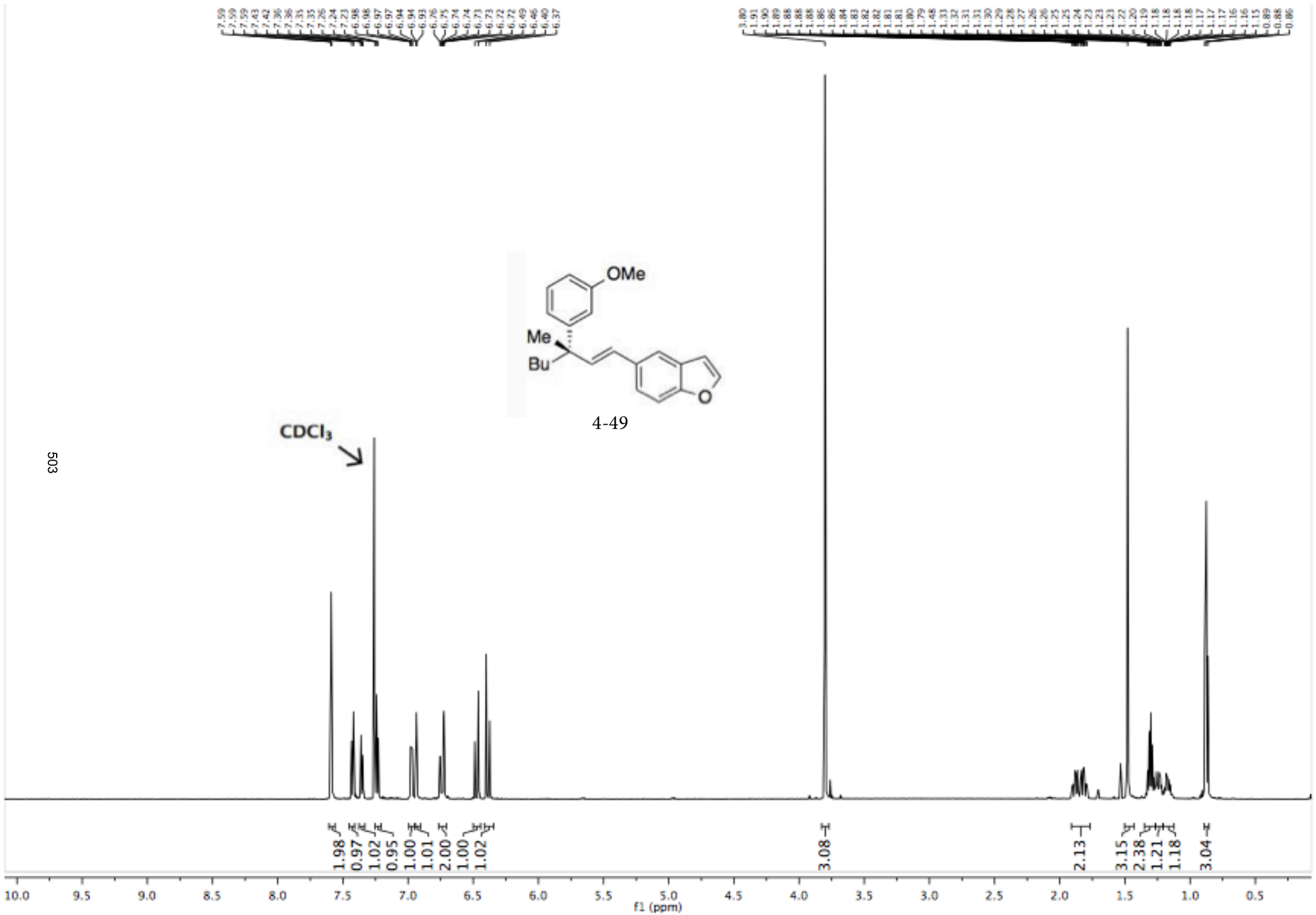

159.70
149.37
142.34
141.52
129.67
129.32
129.11
128.90
128.71
125.94
125.67
125.65
125.62
125.60
123.57
120.89
119.39
114.55
113.65
111.42
110.57
55.37
44.35
41.37
26.96
25.53
23.58
14.24
CDCl3
OMe
Me
Bu
CF3
4-47
499
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

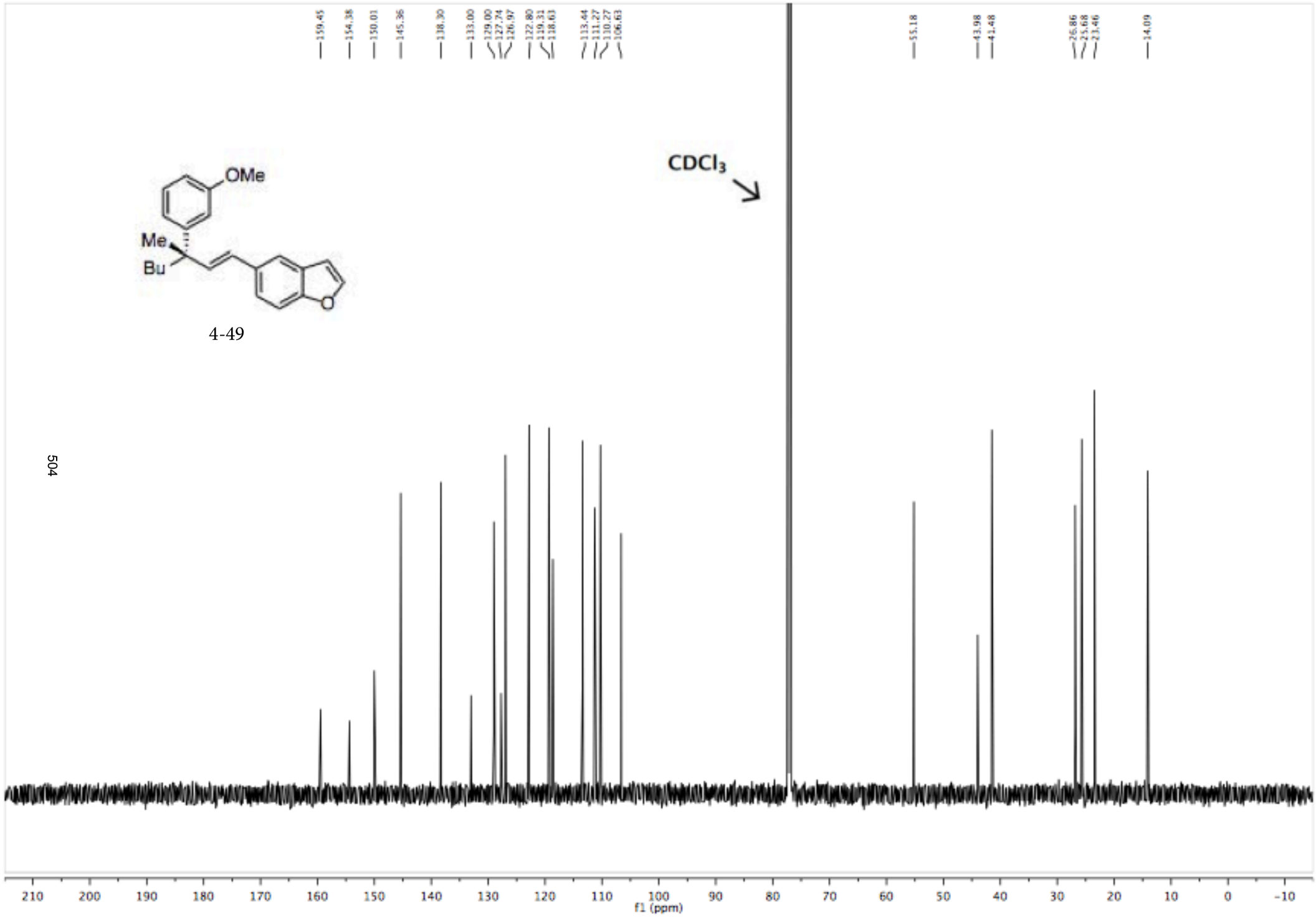

-62.36
OMe
Me
Bu
CF3
500
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

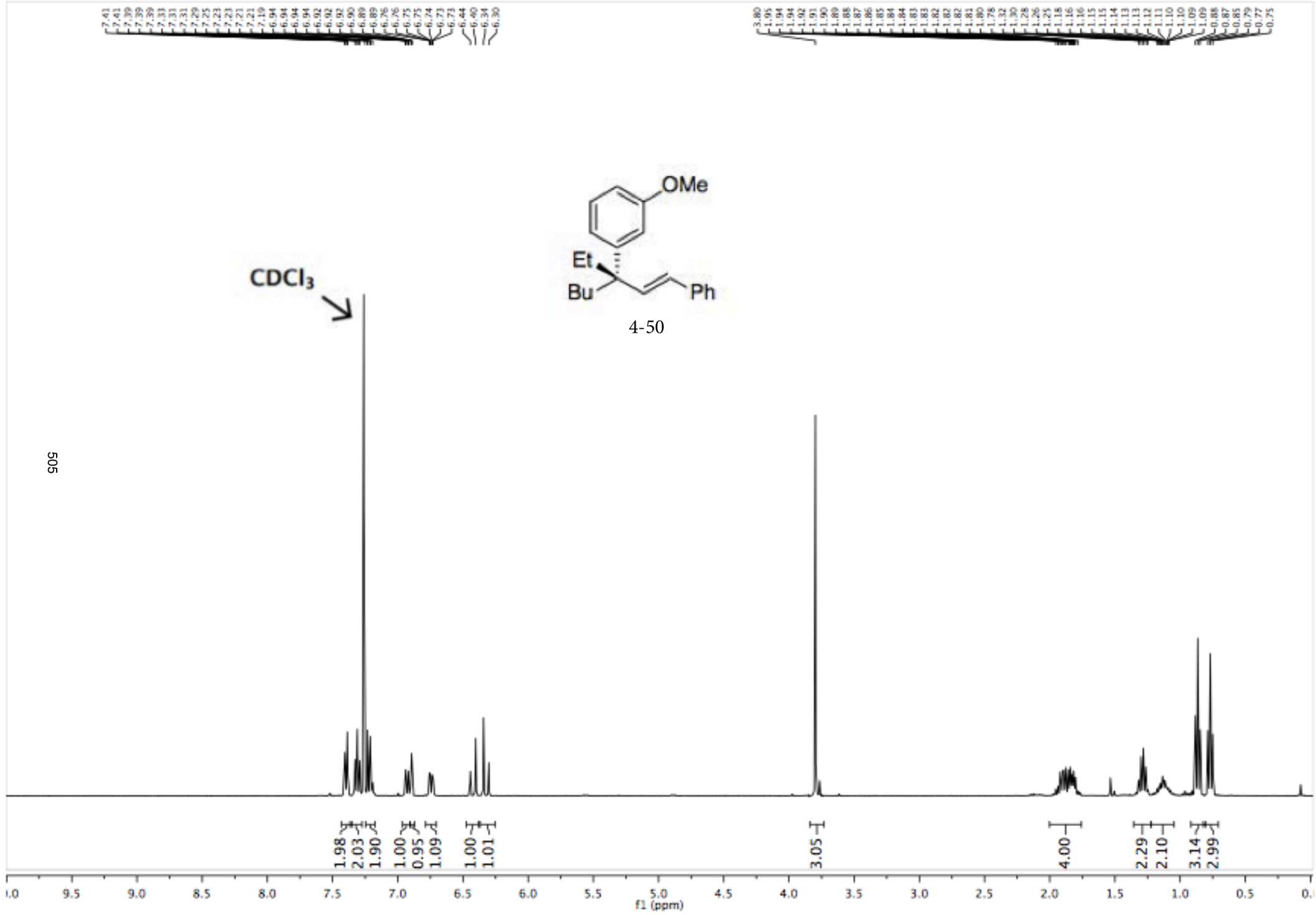
4-47


OMe
Me
Bu
N
4-48
501
CDCl3
0.98
0.97
0.99
1.61
0.99
0.98
1.01
1.00
1.00
1.00
3.00
1.07
1.07
3.06
2.15
1.24
1.11
3.14
f1 (ppm)

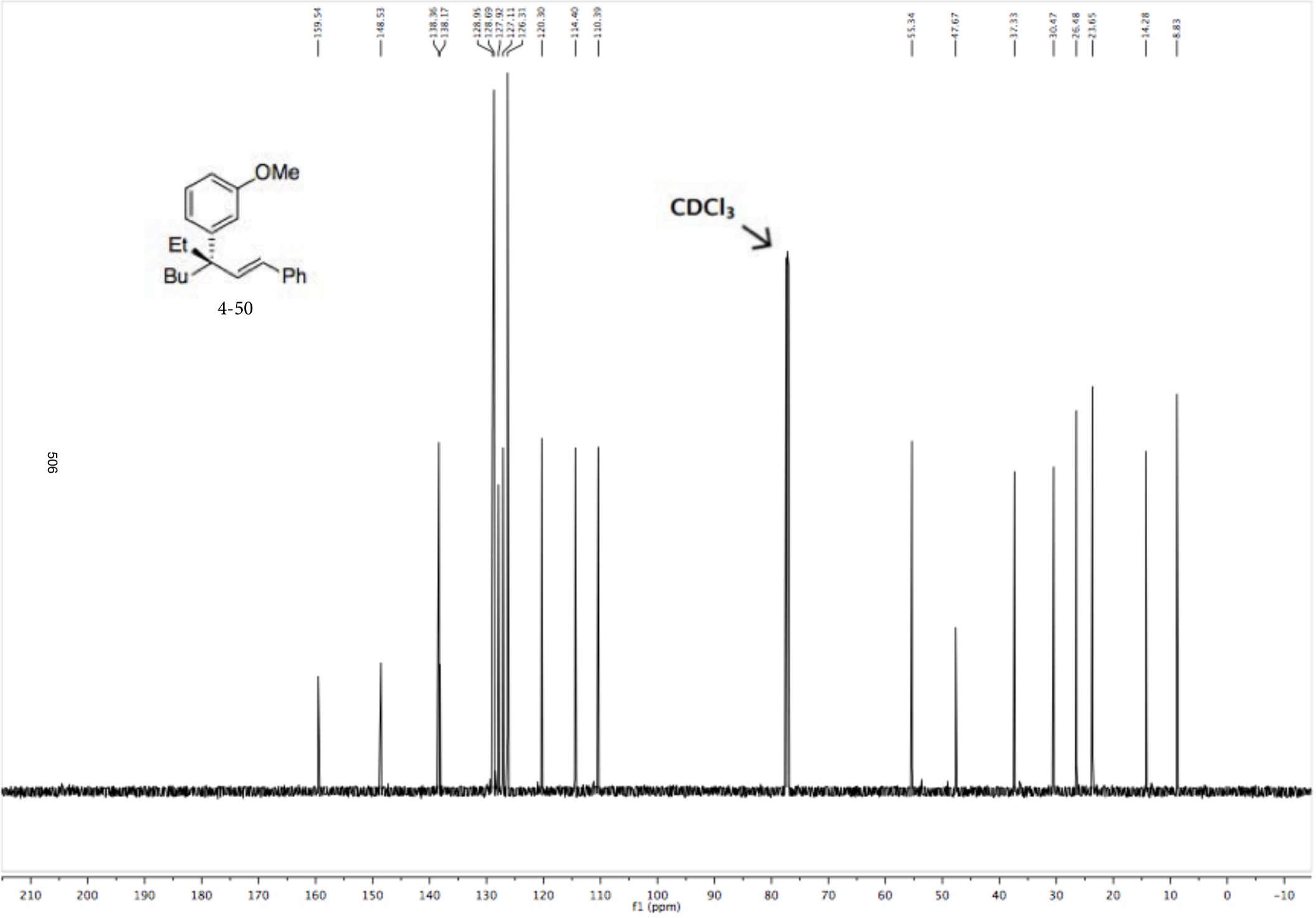

159.69
149.34
148.47
148.33
141.97
133.54
132.69
129.31
123.62
123.55
119.36
113.63
110.57
55.36
44.37
41.37
26.95
25.50
23.57
14.23
CDCl3
OMe
Me
Bu
N
4-48
502
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


OMe
Me
Bu
O
4-49
CDCl3
503
1.98
0.97
1.02
0.95
1.00
1.01
2.00
1.00
1.02
3.08
2.13
3.15
2.38
1.21
1.18
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

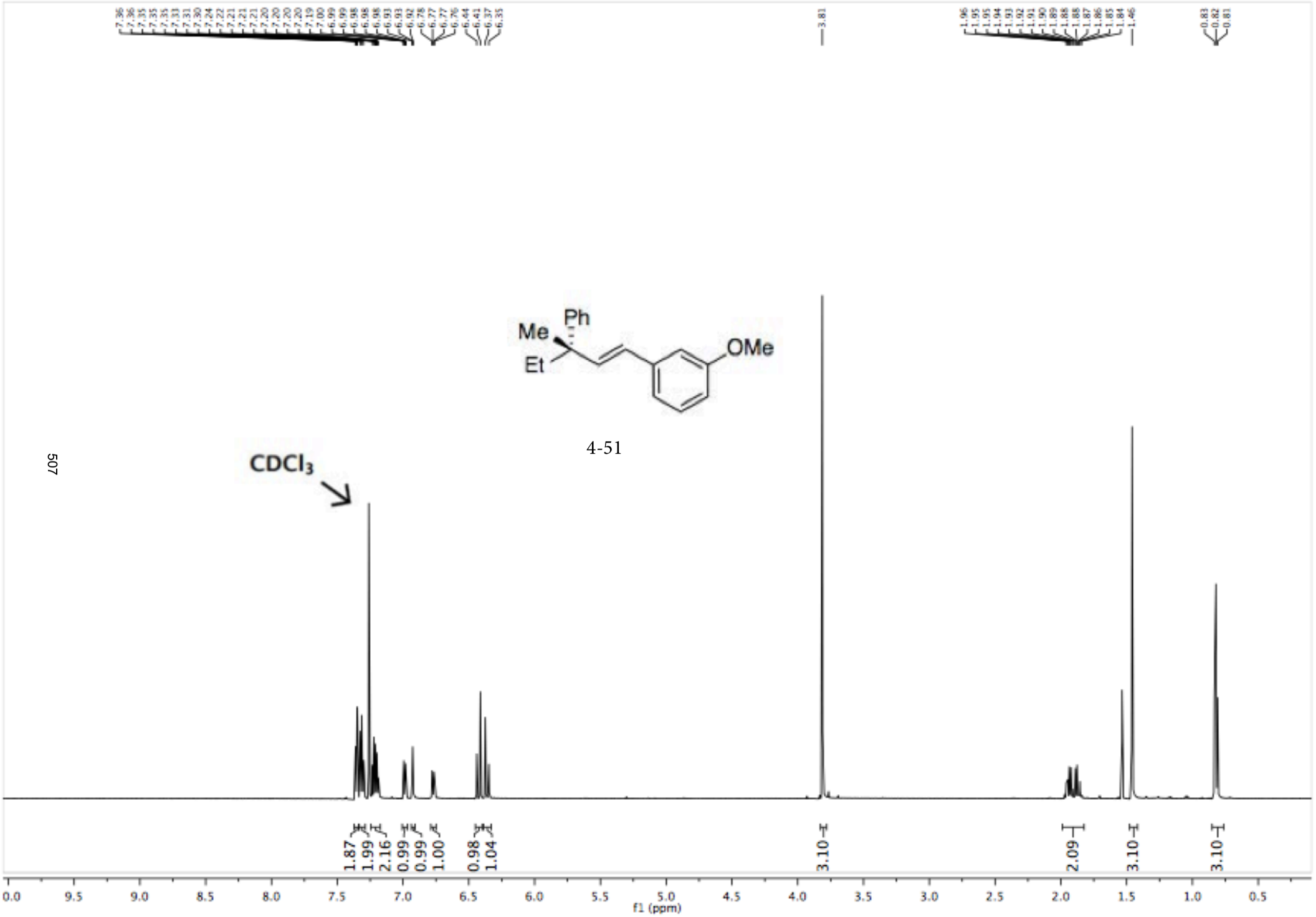

159.45
154.38
150.01
145.36
138.30
133.00
129.00
127.74
126.97
122.80
119.31
118.63
113.44
111.27
110.27
106.63
55.18
43.98
41.48
25.86
25.68
23.46
14.09
CDCl3
OMe
Me
Bu
O
4-49
504
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


OMe
Et
Bu
Ph
CDCl3
505
1.98
2.03
1.90
1.00
0.95
1.09
1.00
1.01
3.05
4.00
2.29
2.10
3.14
2.99
f1 (ppm)

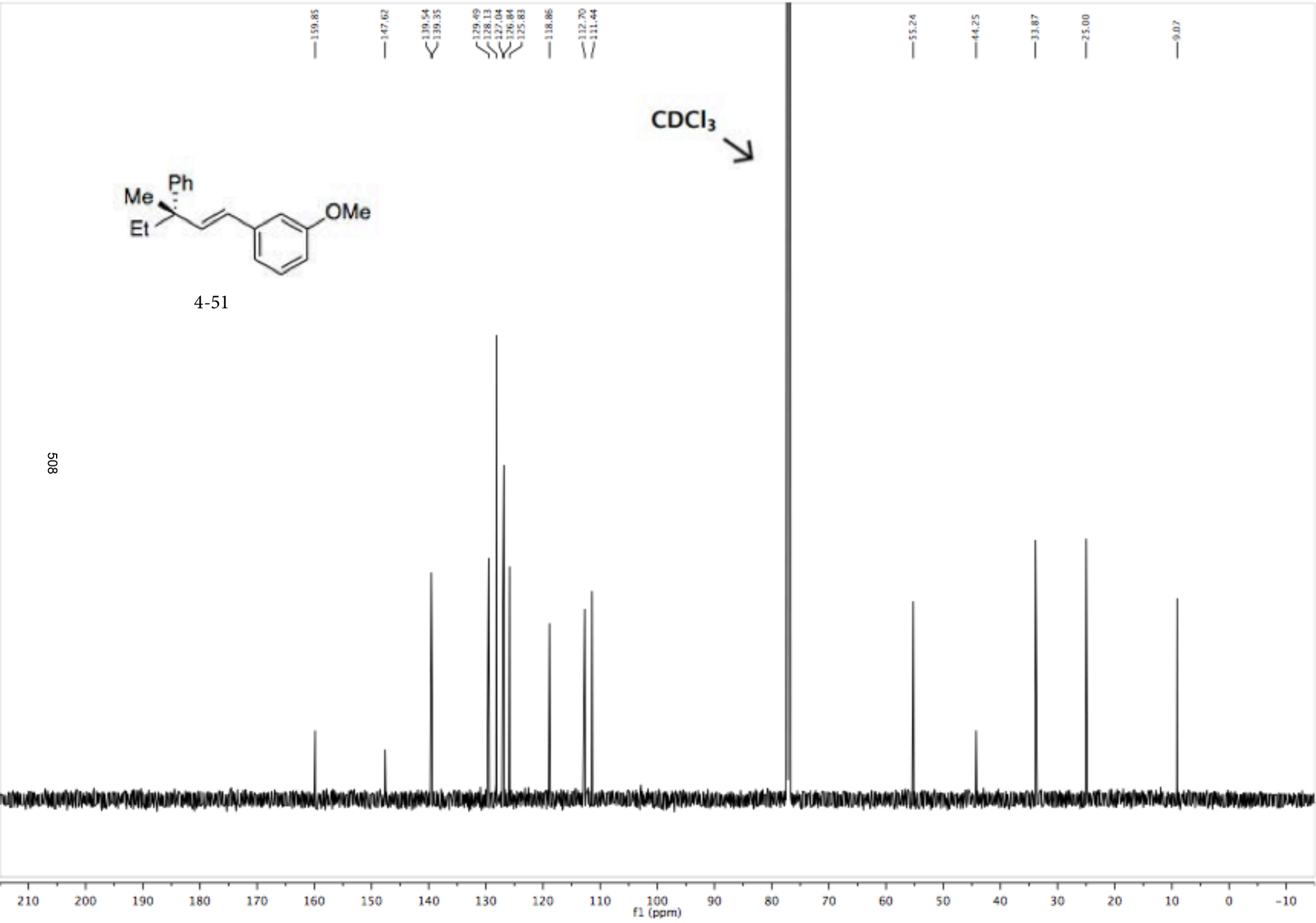
4-50


159.54
148.53
138.36
138.17
128.95
128.69
127.92
127.11
126.31
120.30
114.40
110.39
55.34
47.67
37.33
30.47
26.48
23.65
14.28
8.83
OMe
Et
Bu
Ph
CDCl3
506
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

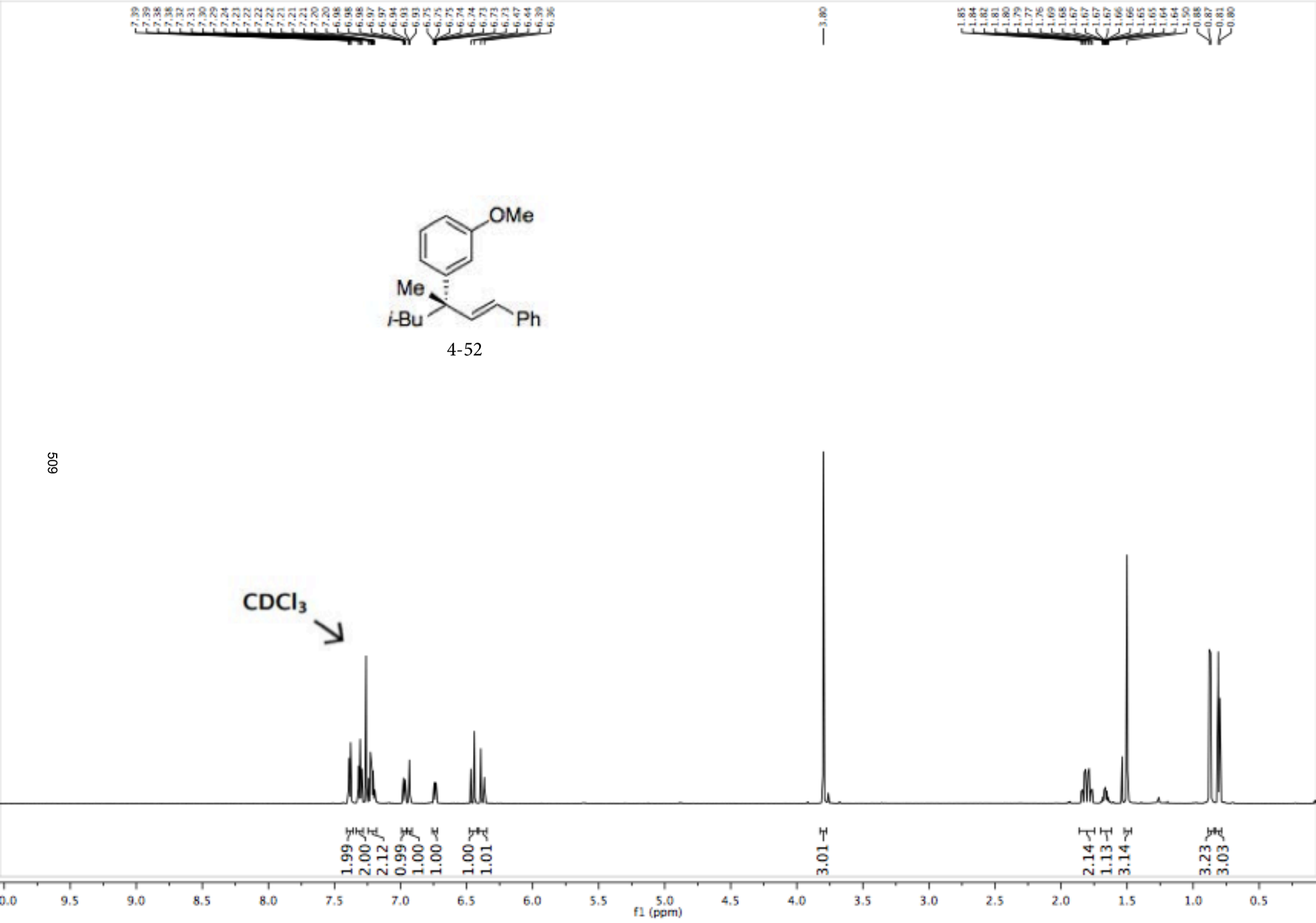
4-50


Ph
Me
Et
OMe
CDCl3
1.87
1.99
2.16
0.99
0.99
1.00
0.98
1.04
3.10
2.09
3.10
3.10
f1 (ppm)

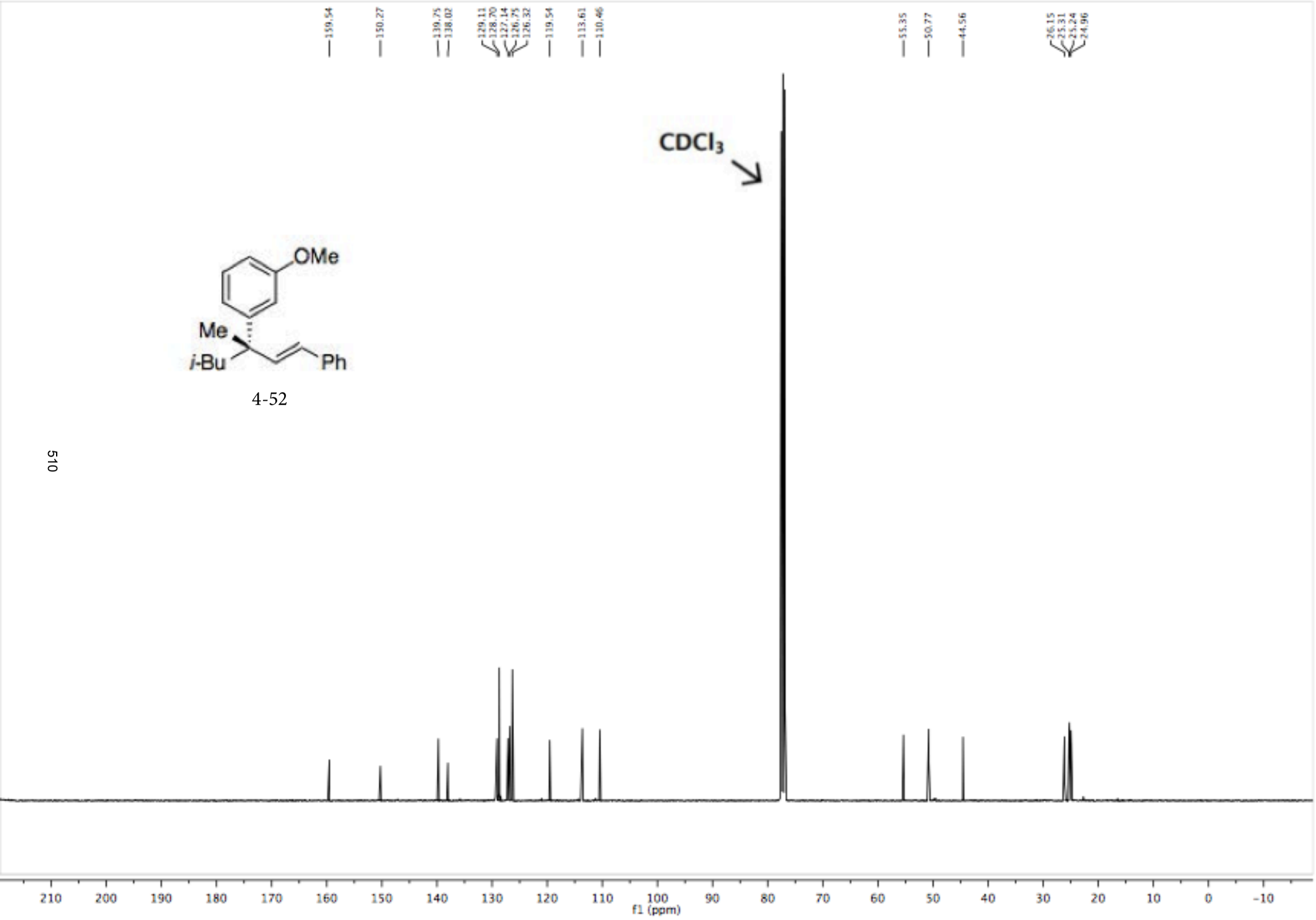
4-51


159.85
147.62
139.54
139.35
129.49
128.13
127.04
126.84
125.83
118.86
112.70
111.44
55.24
44.25
33.87
25.00
9.07
CDCl3
Ph
Me
Et
OMe
f1 (ppm)

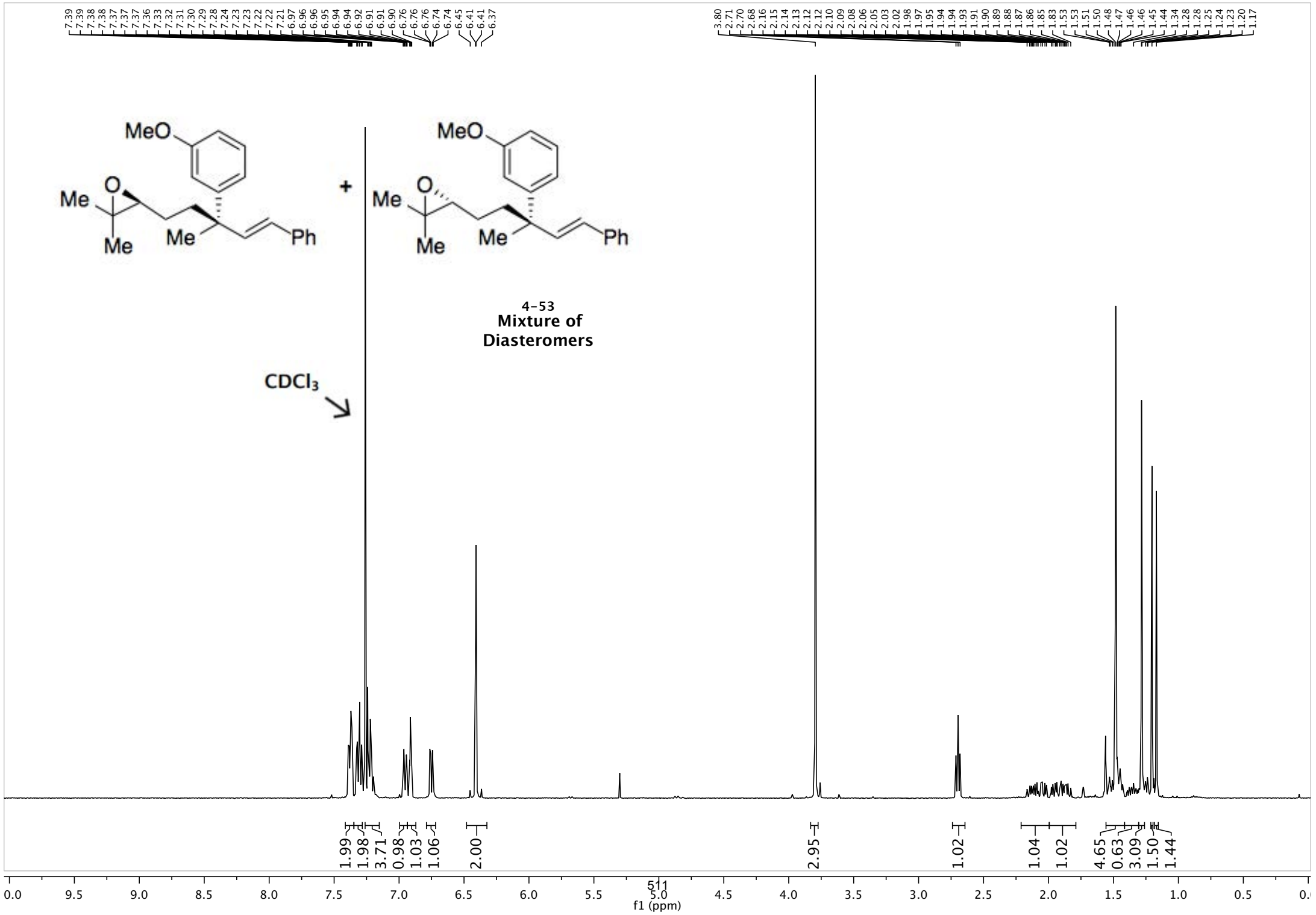
4-51

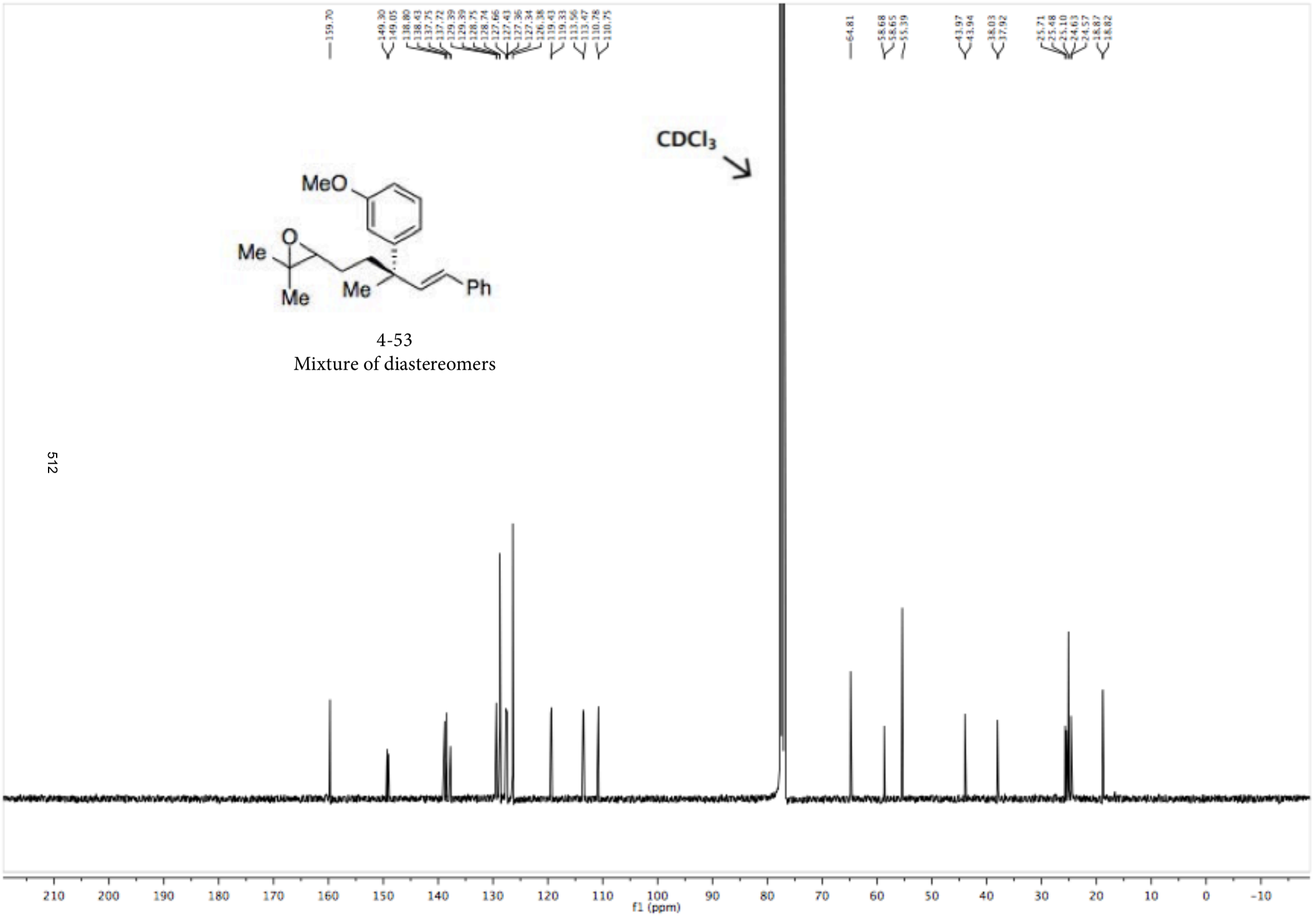


4-52

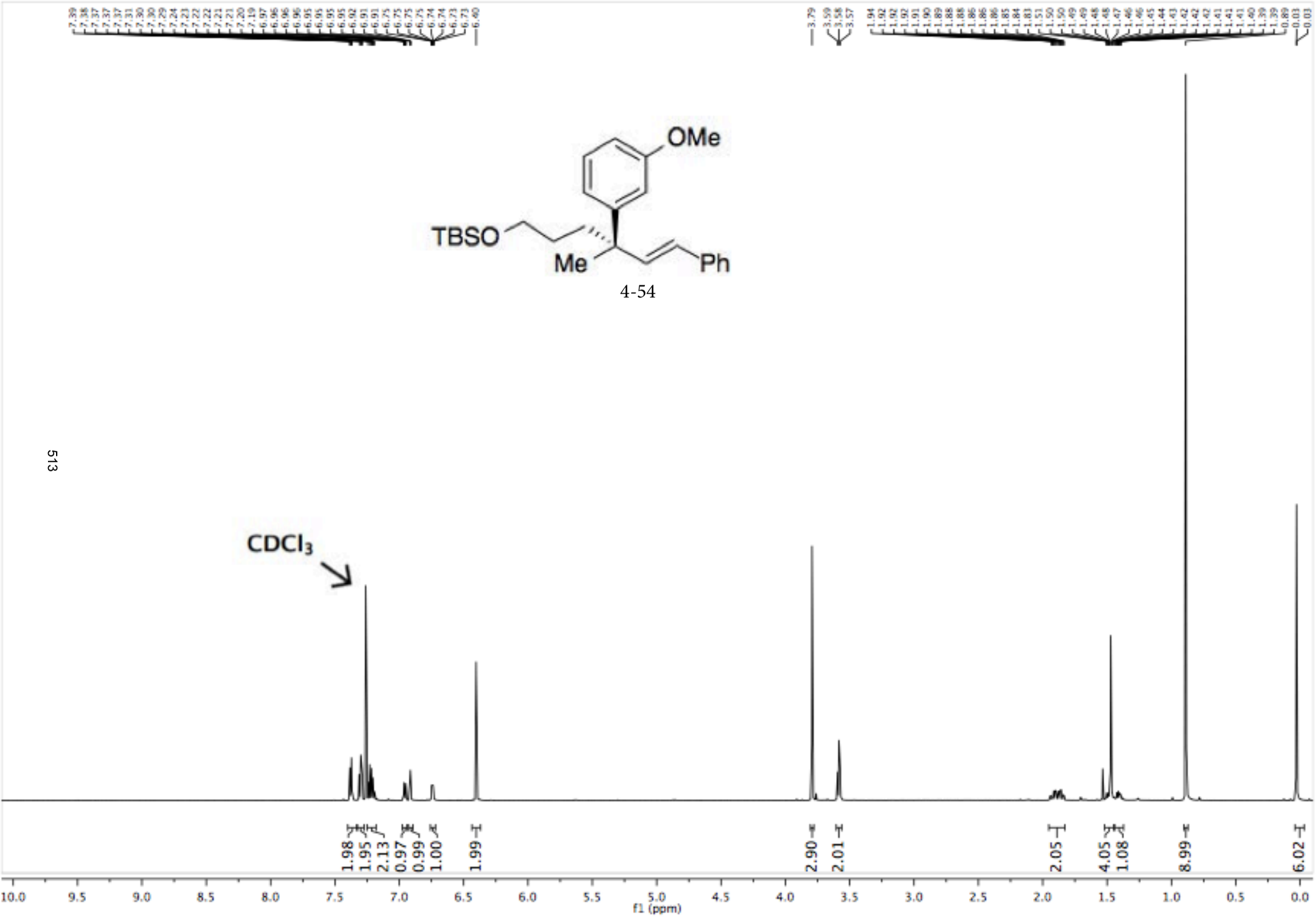

159.54
150.27
139.75
138.02
129.11
128.70
127.14
126.75
126.32
119.54
113.61
110.46
55.35
50.77
44.56
26.15
25.31
21.24
24.96
CDCl3
OMe
Me
i-Bu
Ph
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

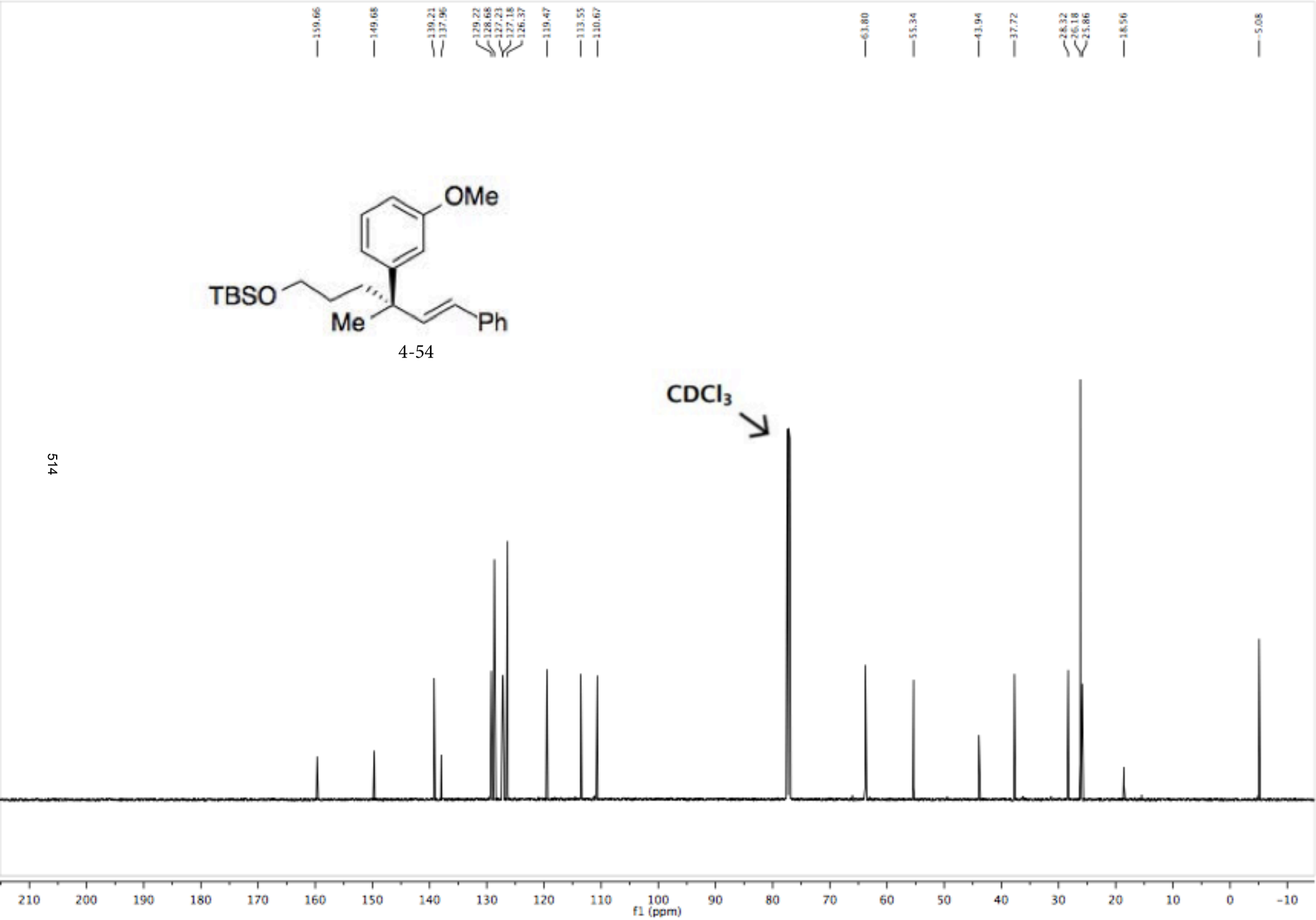
4-52


MeO
Me
O
Me
Me
Ph
+
MeO
Me
O
Me
Me
Ph
4-53
Mixture of
Diasteromers
CDCl3
1.99
1.98
3.71
0.98
1.03
1.06
2.00
2.95
1.02
1.04
1.02
4.65
0.63
3.09
1.50
1.44
f1 (ppm)

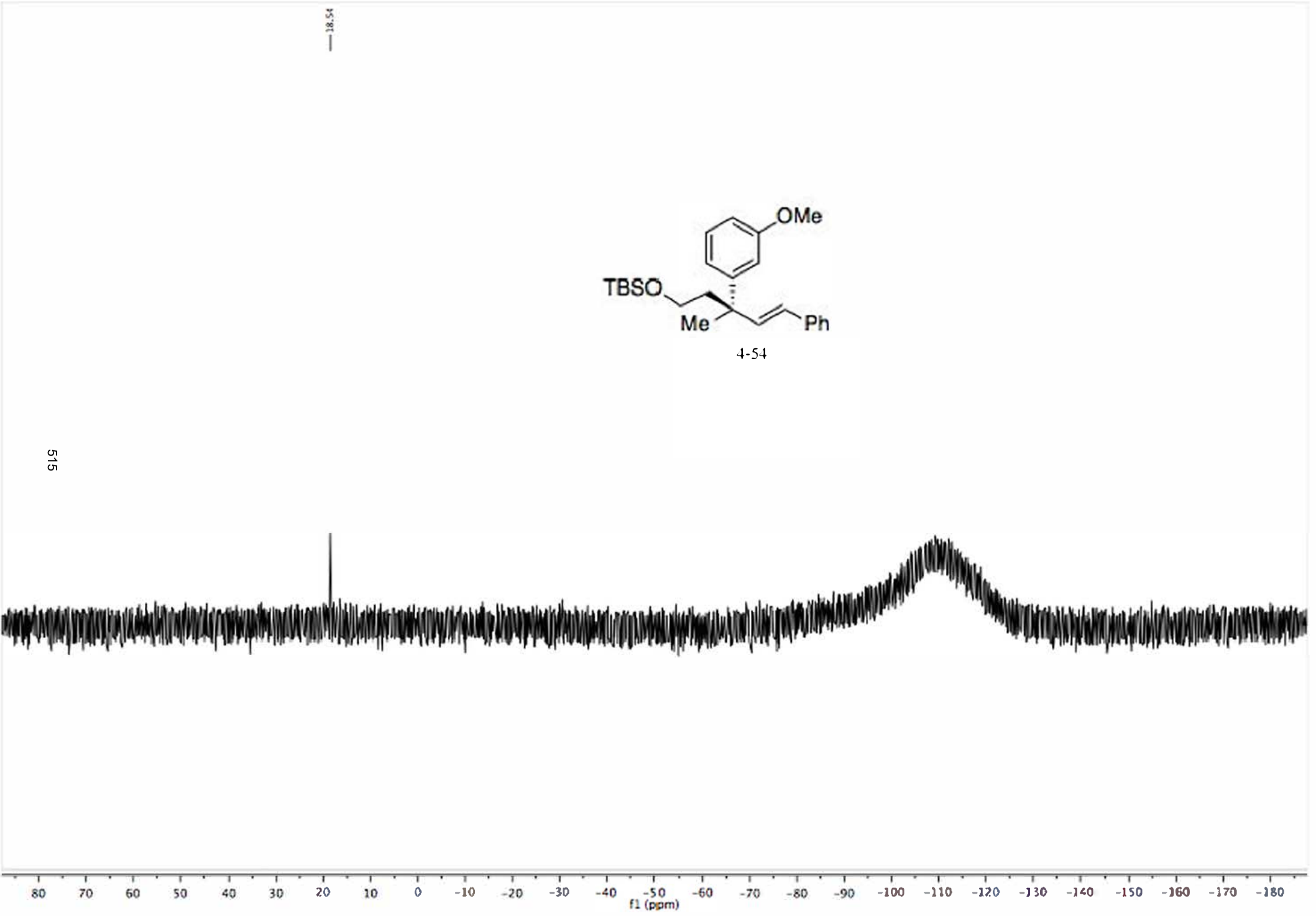


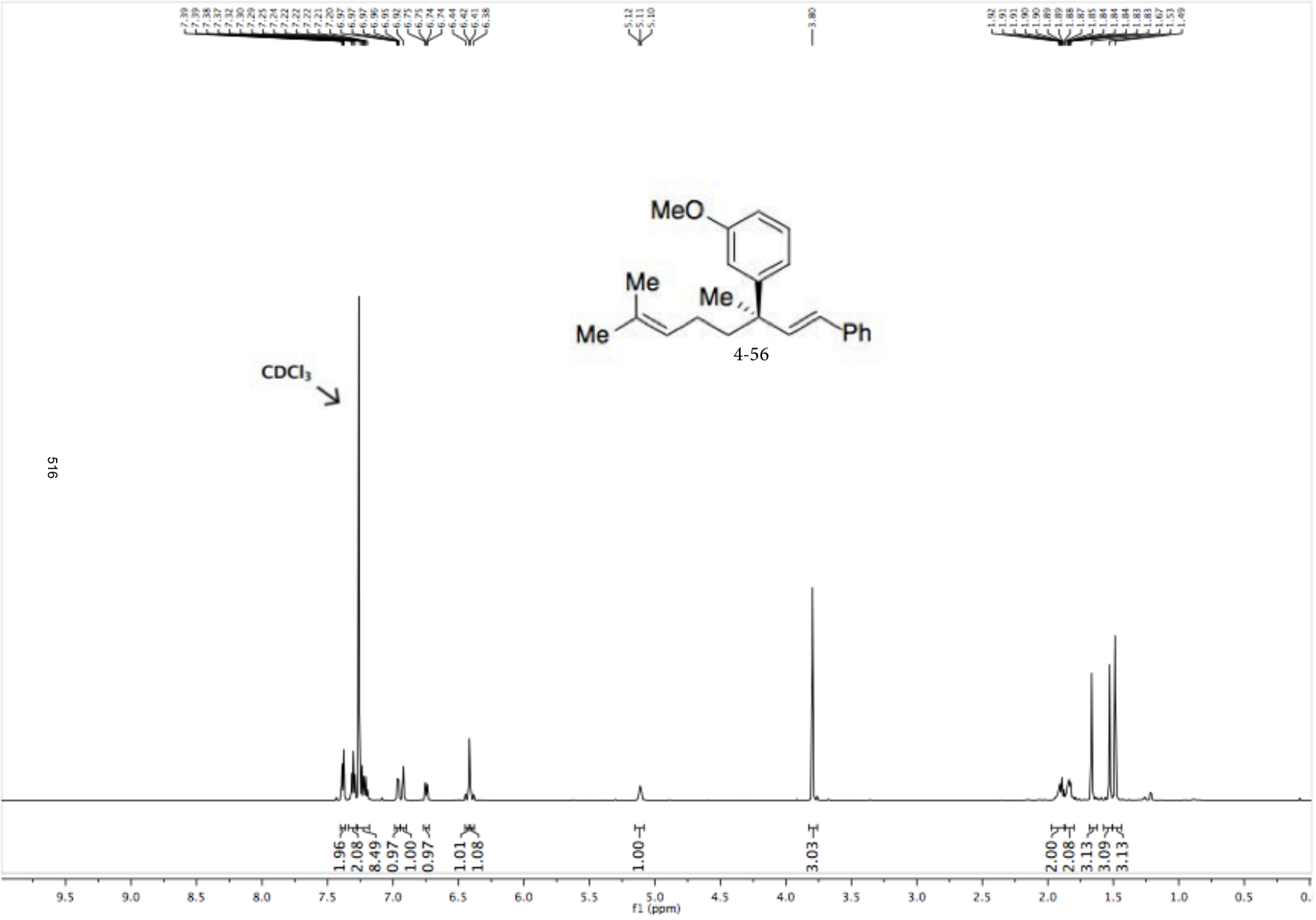
4-53
Mixture of diastereomers


OMe
TBSO
Me
Ph
4-54
513
CDCl3
1.98
1.95
2.13
0.97
0.99
1.00
1.99
2.90
2.01
2.05
4.05
1.08
8.99
6.02
f1 (ppm)

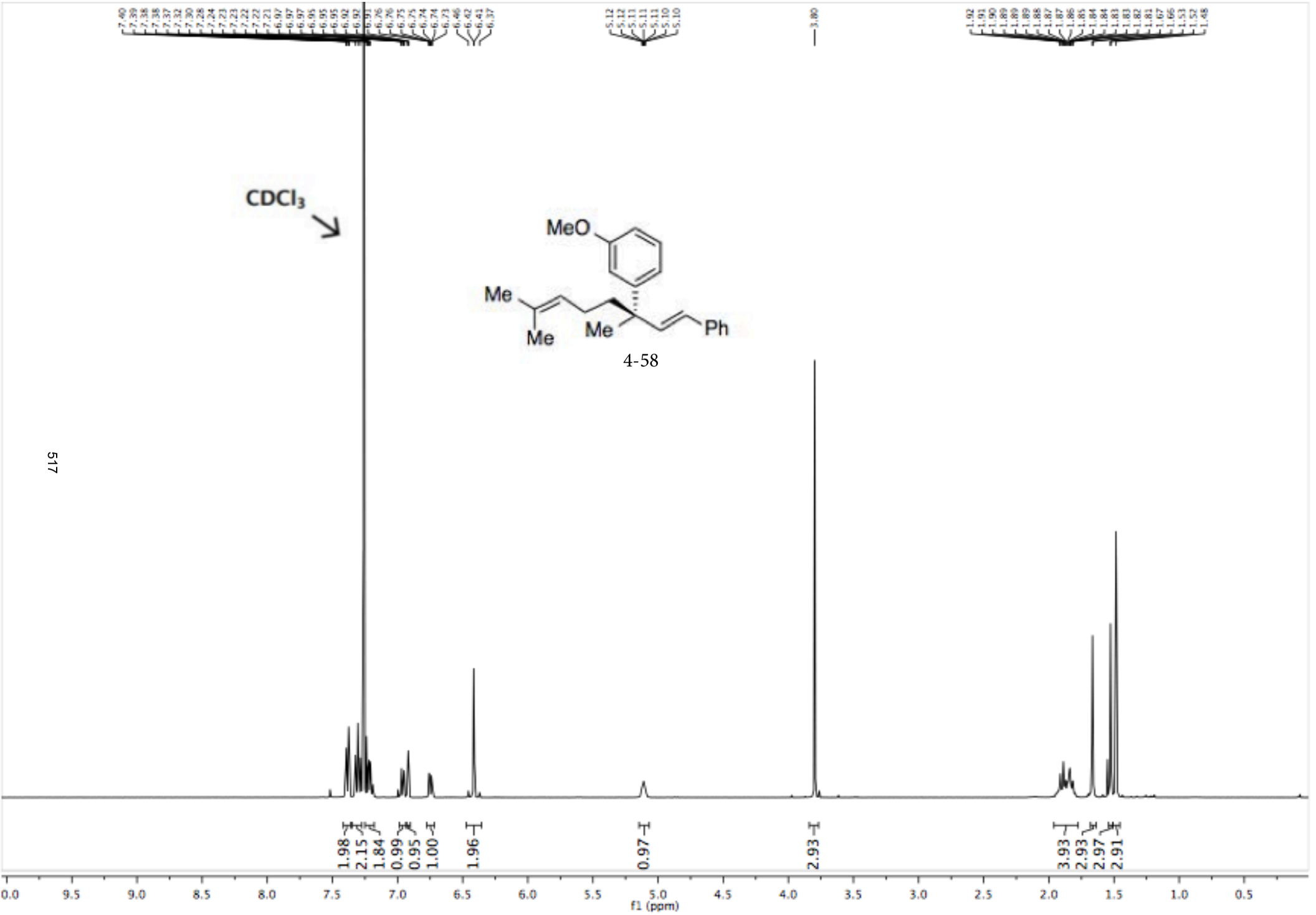

159.66
149.68
139.21
137.96
129.22
128.68
127.23
127.18
126.37
119.47
113.55
110.67
63.80
55.34
43.94
37.72
28.32
26.18
25.86
18.56
-5.08
OMe
TBSO
Me
Ph
CDCl3
514
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

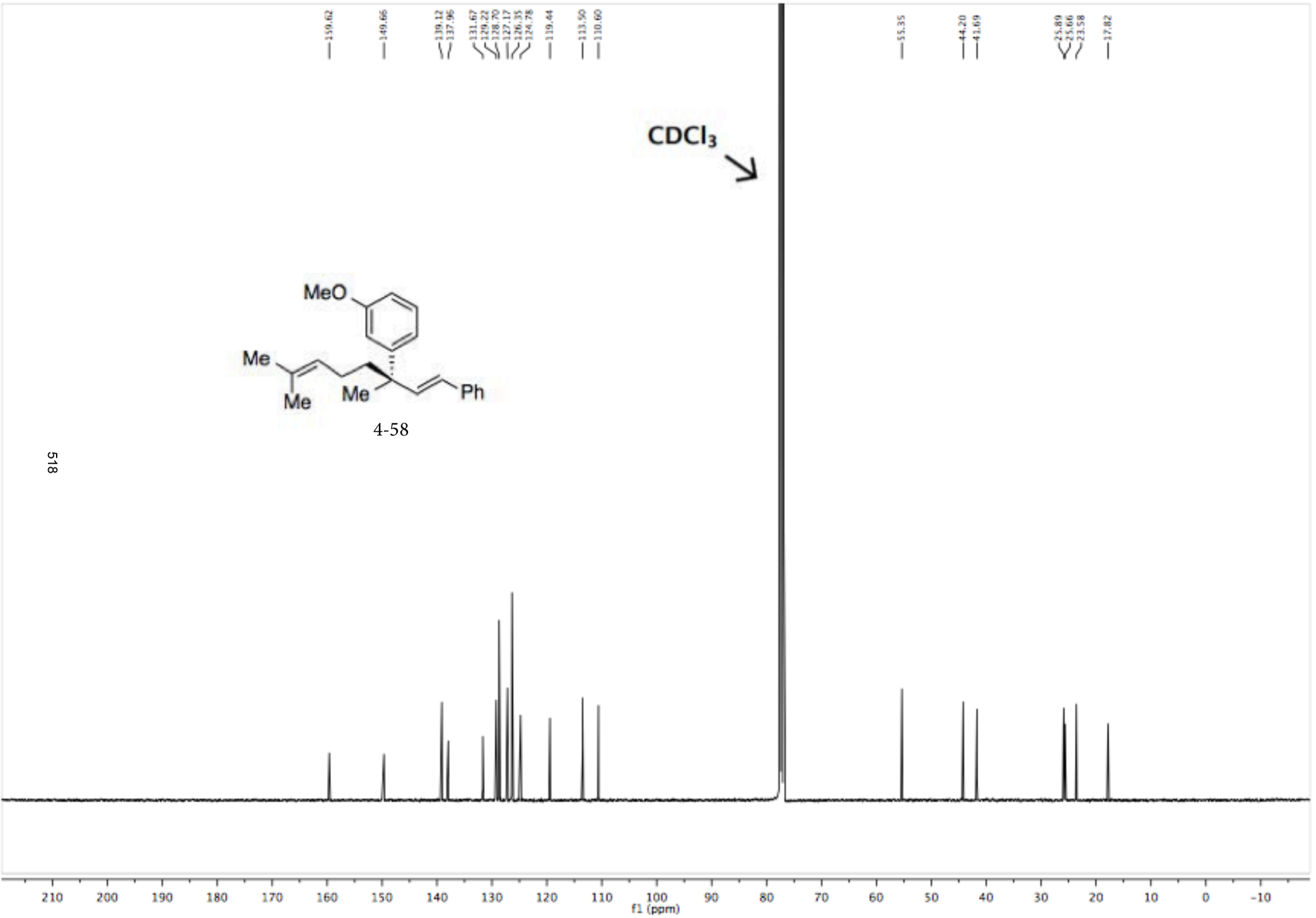
4-54

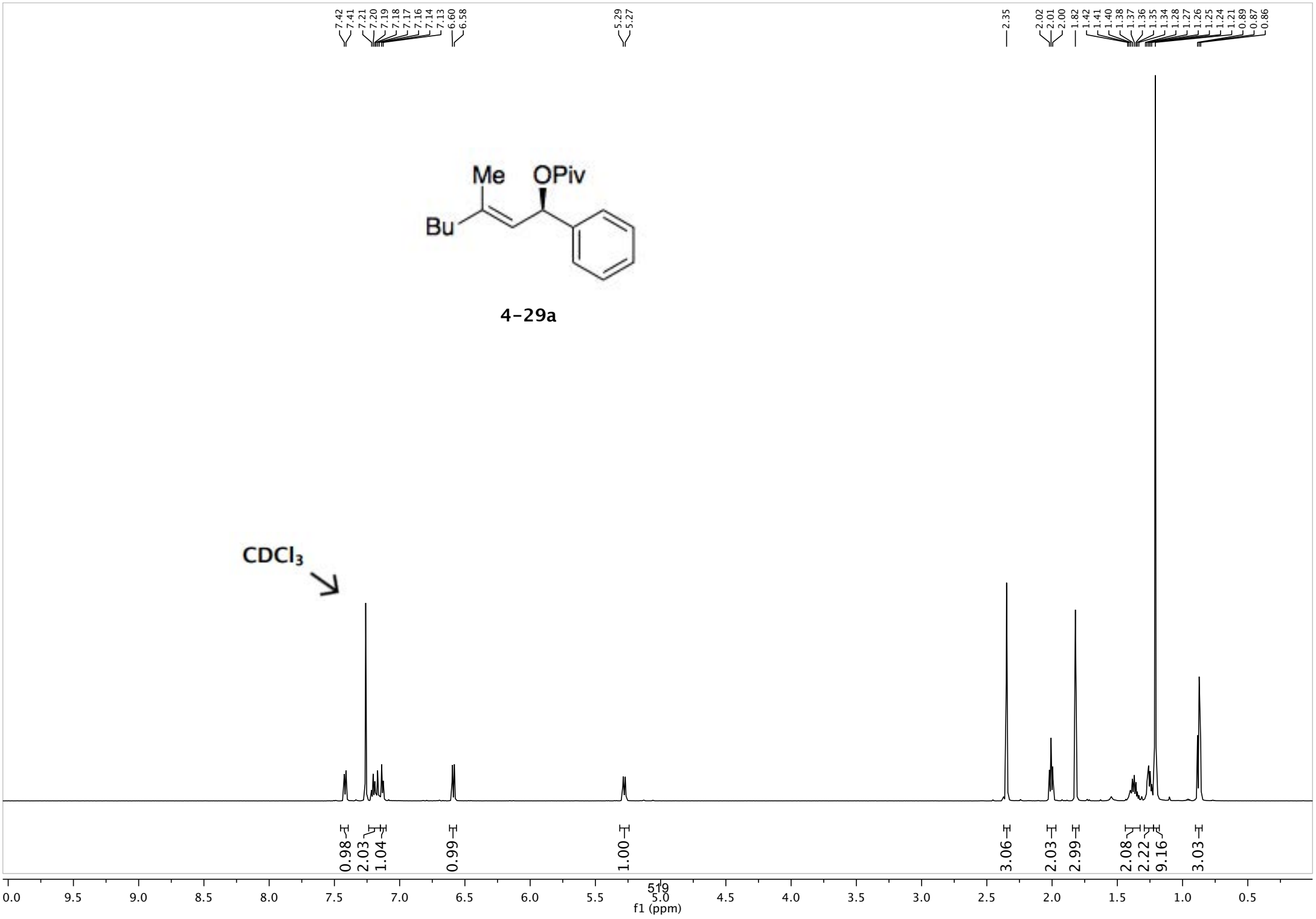

18.54
OMe
TBSO
Me
Ph
4-54
515
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)

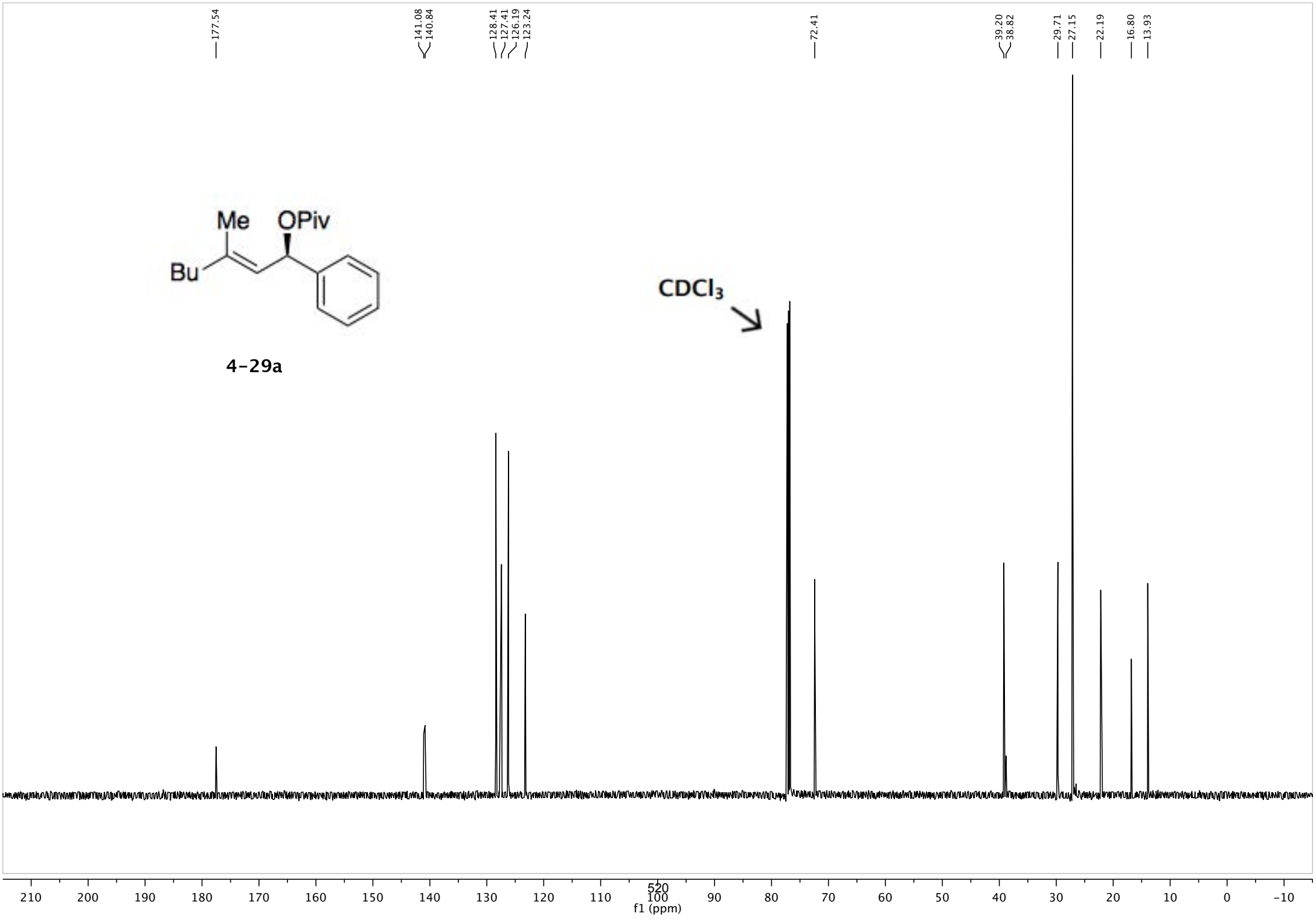


4-56


CDCl3
MeO
Me
Me
Me
Ph
4-58
f1 (ppm)


159.62
149.66
139.12
137.96
131.67
129.22
128.70
127.17
126.35
124.78
119.44
113.50
110.60
55.35
44.20
41.69
25.89
25.66
23.58
17.82
CDCl3
MeO
Me
Me
Me
Ph
4-58
518
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.42
7.41
7.21
7.20
7.19
7.18
7.17
7.16
7.14
7.13
6.60
6.58
5.29
5.27
2.35
2.02
2.01
2.00
1.82
1.42
1.41
1.40
1.38
1.37
1.36
1.35
1.34
1.28
1.27
1.26
1.25
1.24
1.21
0.89
0.87
0.86
Me
OPiv
Bu
4-29a
CDCl3
0.98
2.03
1.04
0.99
1.00
3.06
2.03
2.99
2.08
2.22
9.16
3.03
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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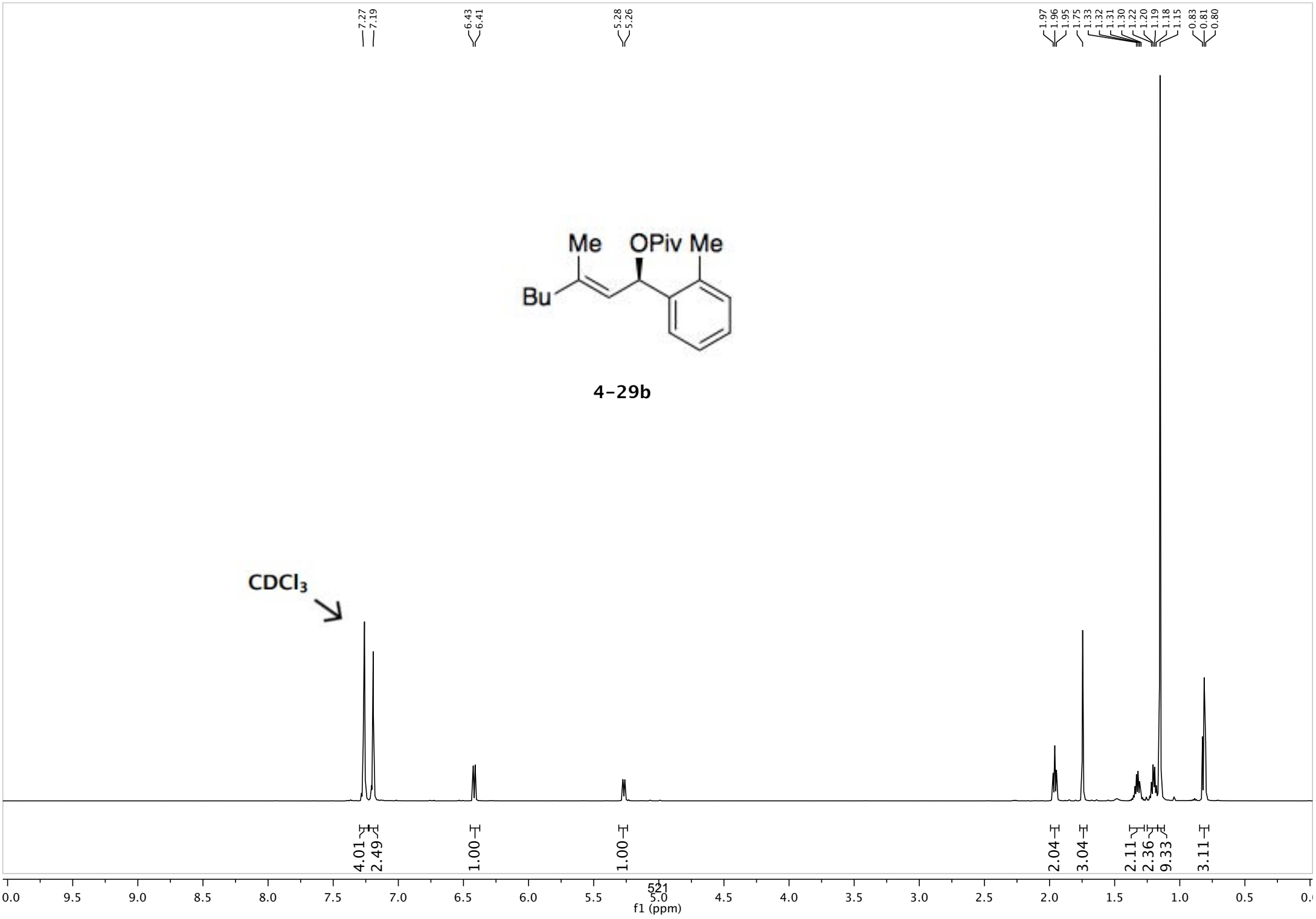
141.08
140.84
128.41
127.41
126.19
123.24
72.41
39.20
38.82
29.71
27.15
22.19
16.80
13.93
Me
OPiv
Bu
CDCl3
4-29a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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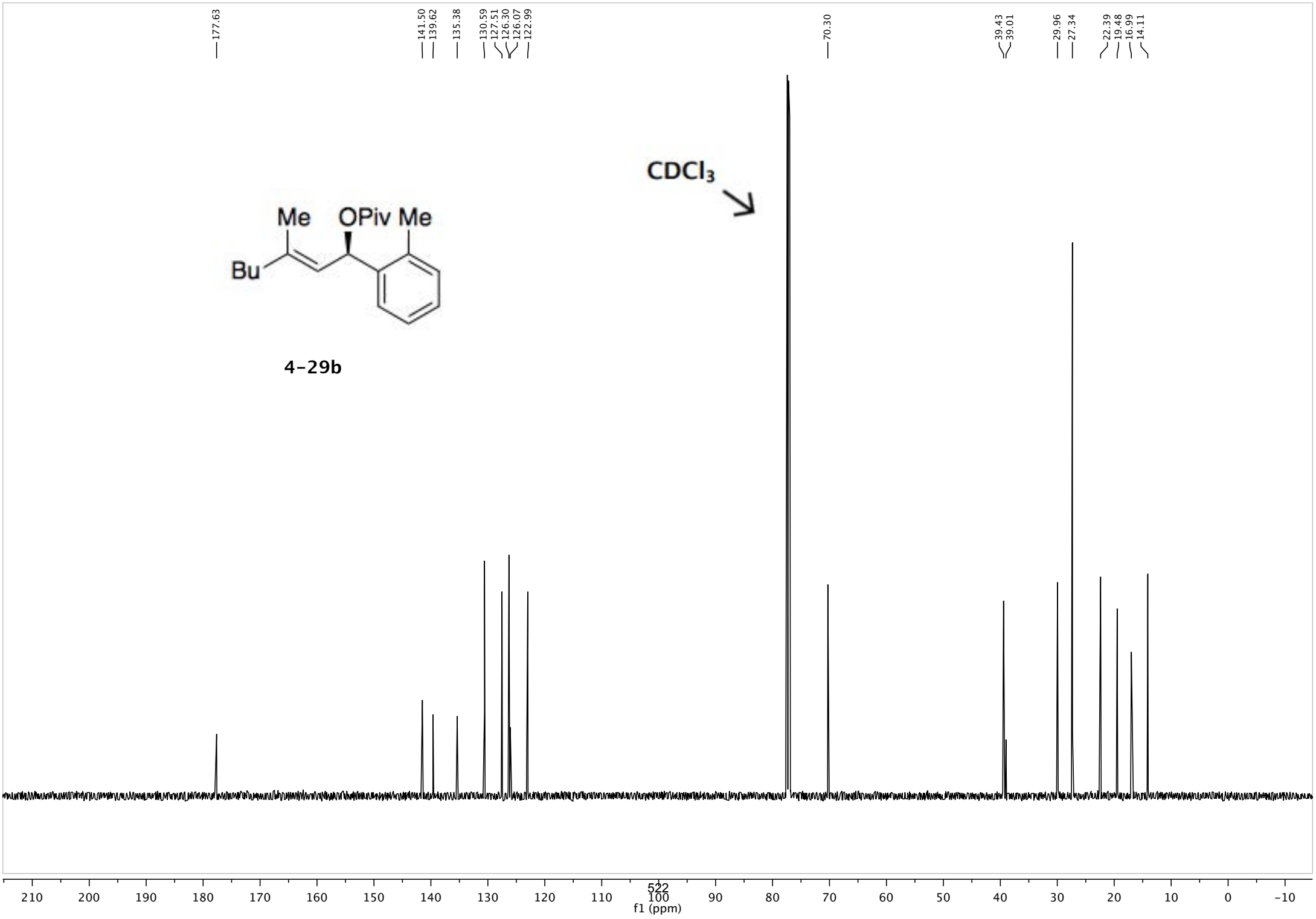
7.19
6.43
6.41
5.28
5.26
1.97
1.96
1.95
1.75
1.33
1.32
1.31
1.30
1.22
1.20
1.19
1.18
1.15
0.83
0.81
0.80
Me
OPiv
Me
Bu
CDCl3
4.01
2.49
1.00
1.00
2.04
3.04
2.11
2.36
9.33
3.11
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

4-29b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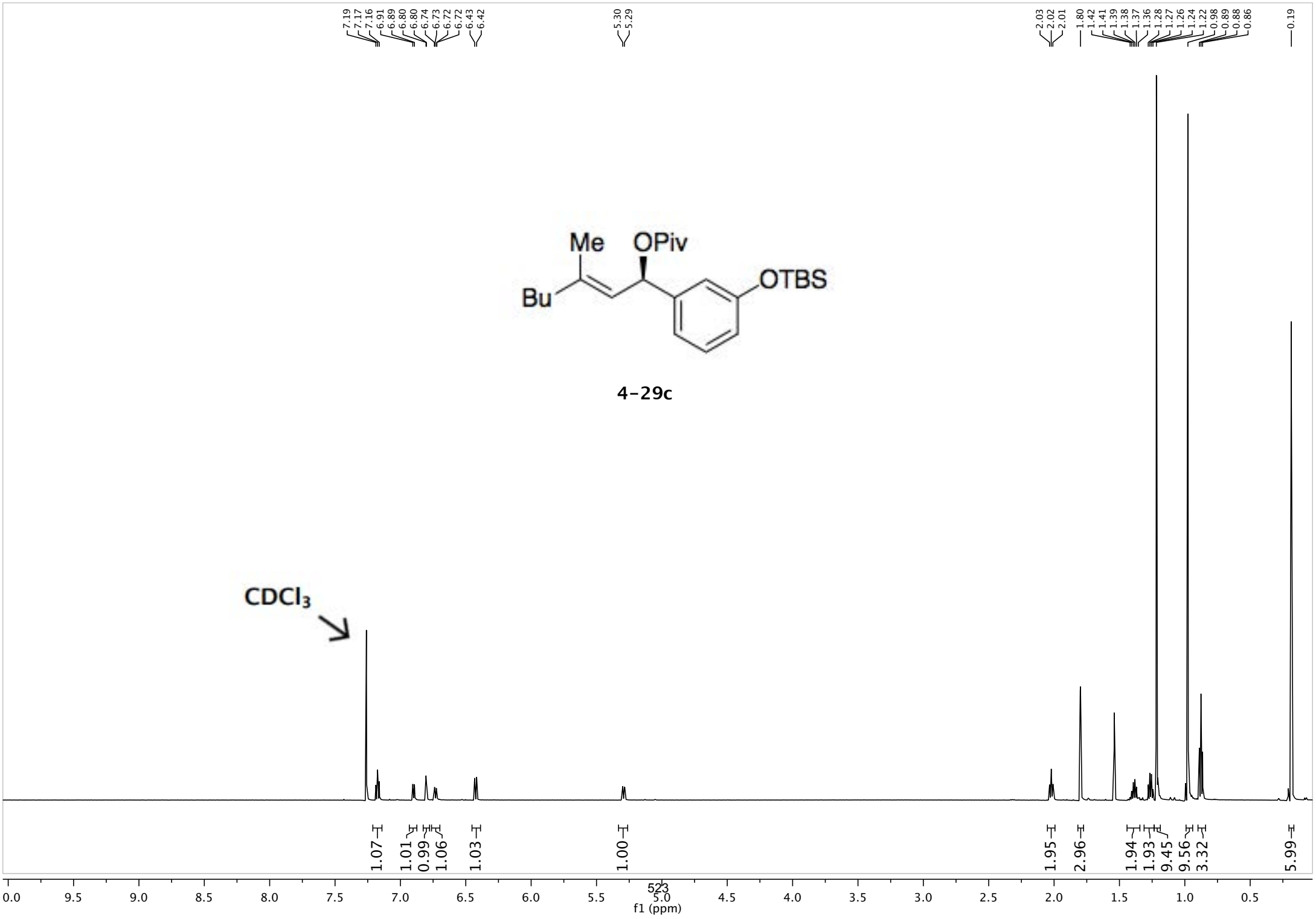
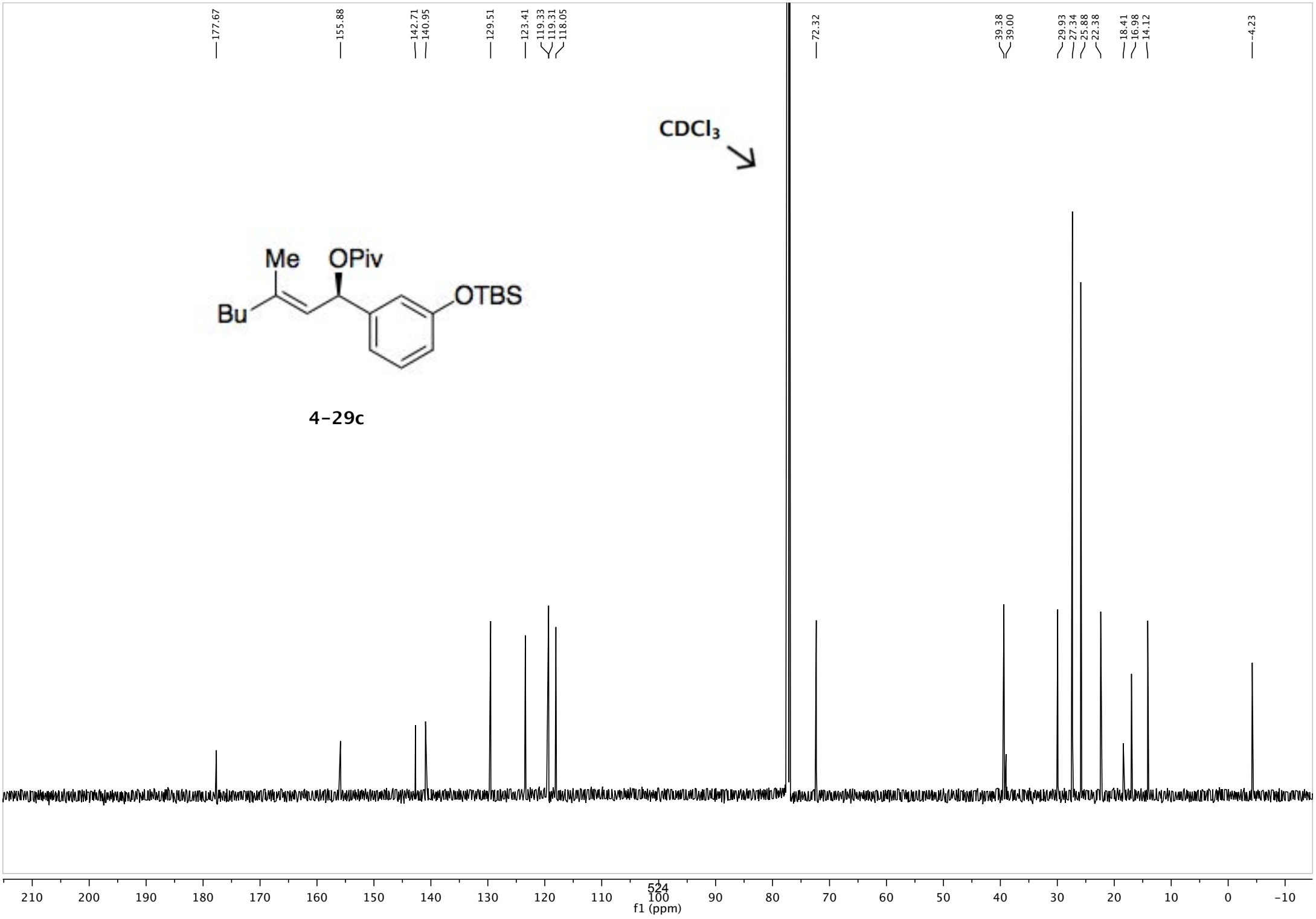
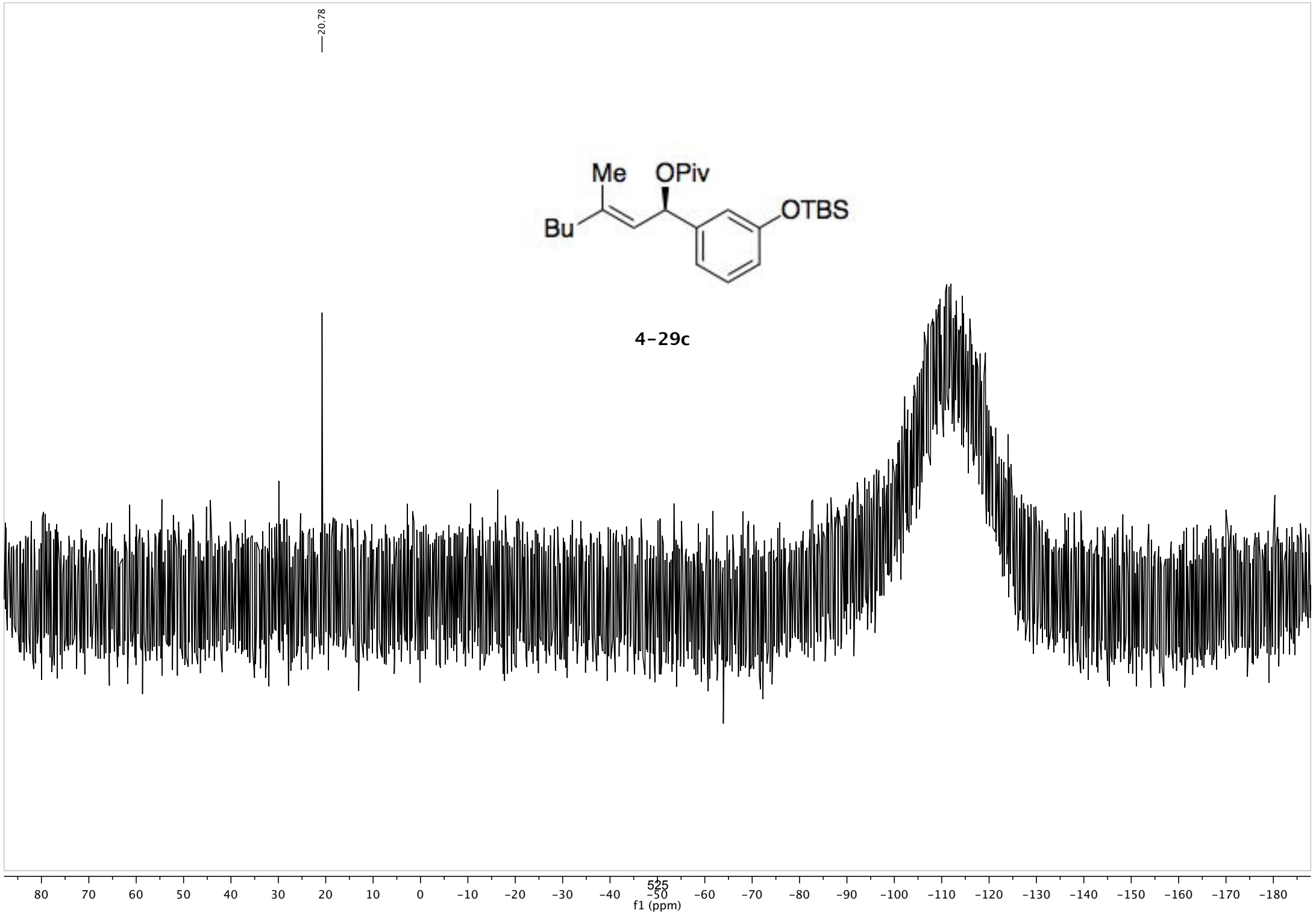
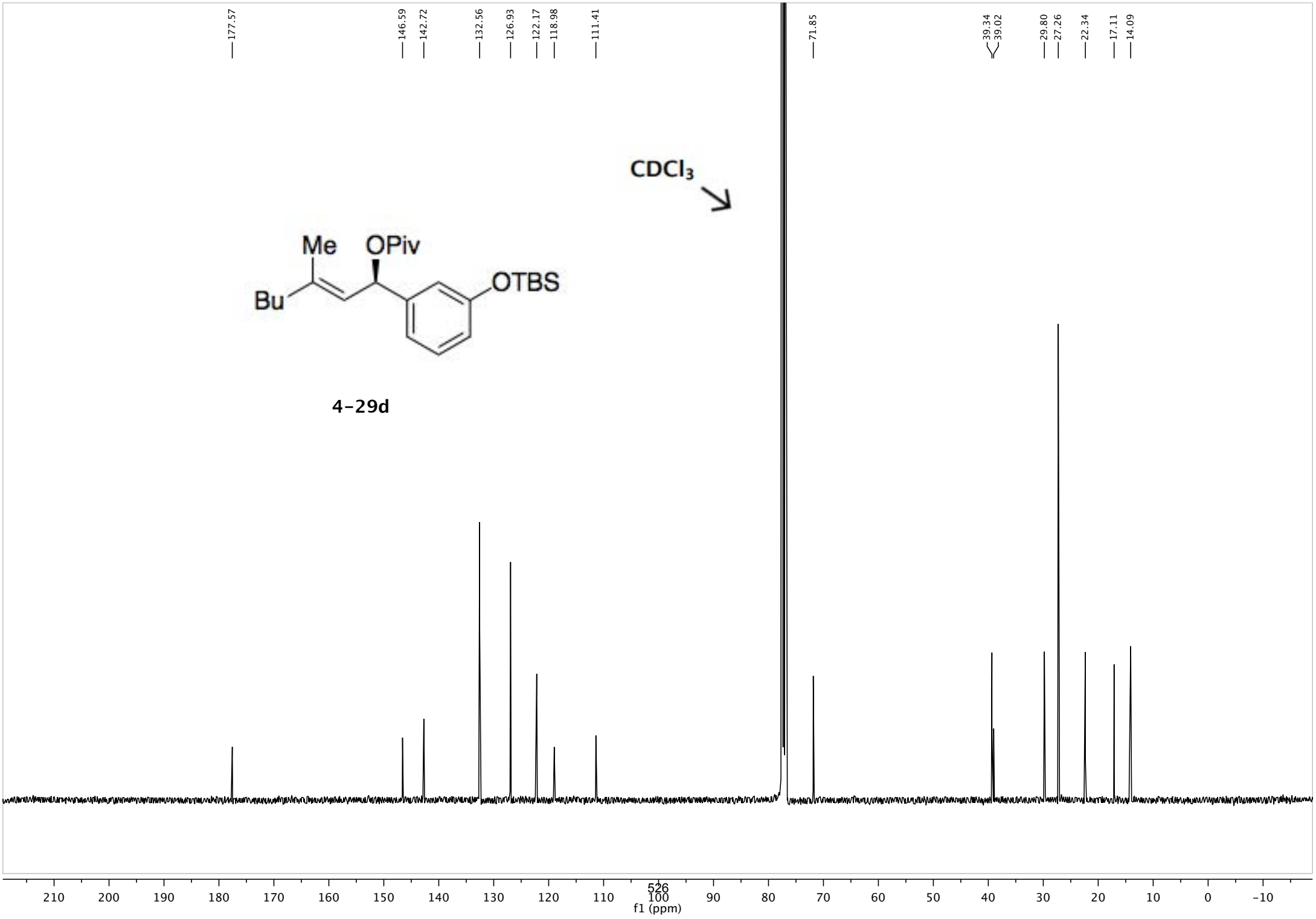
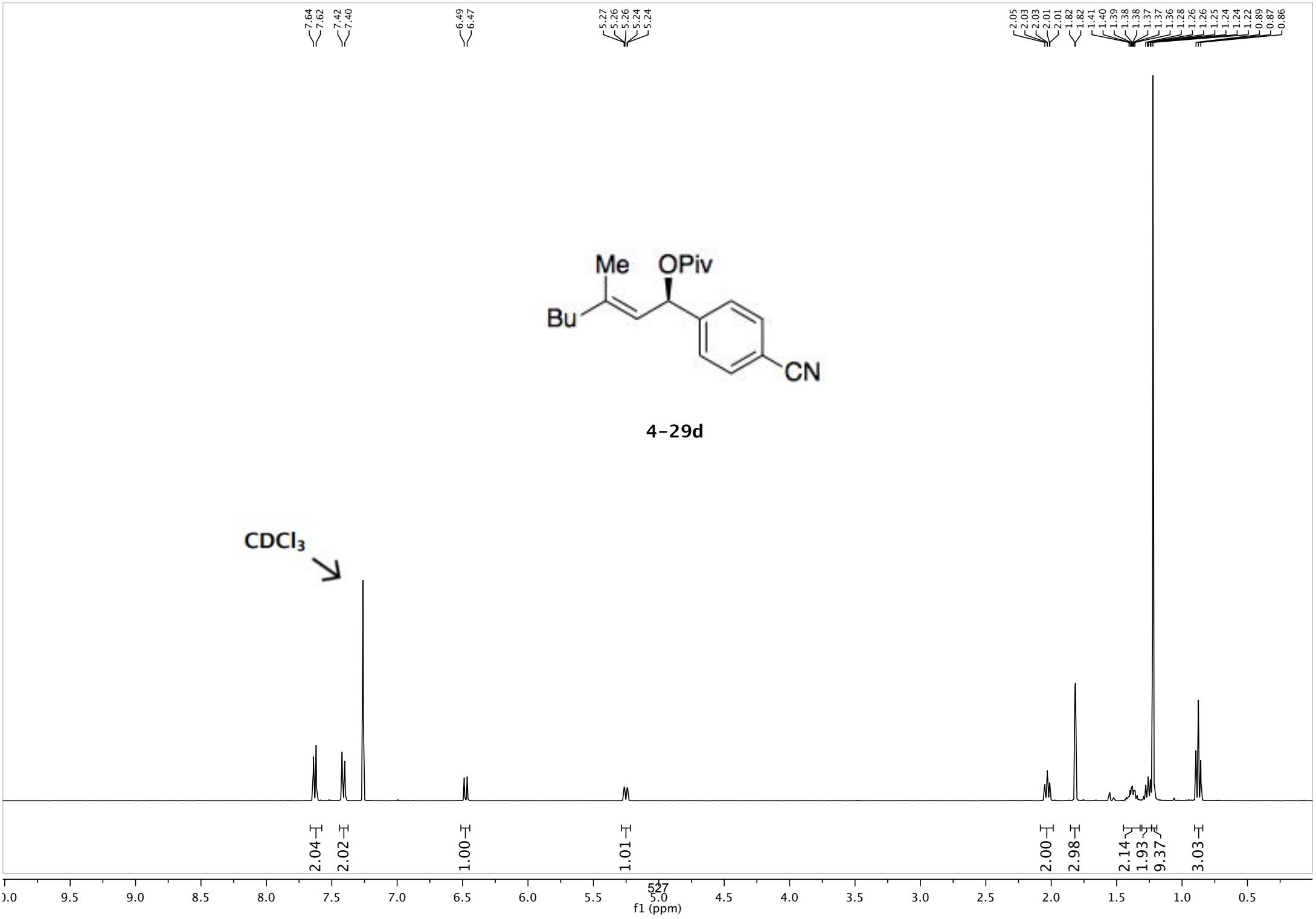
141.50
139.62
135.38
130.59
127.51
126.30
126.07
122.99
70.30
39.43
39.01
29.96
27.34
22.39
19.48
16.99
14.11
CDCl3
Me
OPiv
Me
Bu
4-29b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

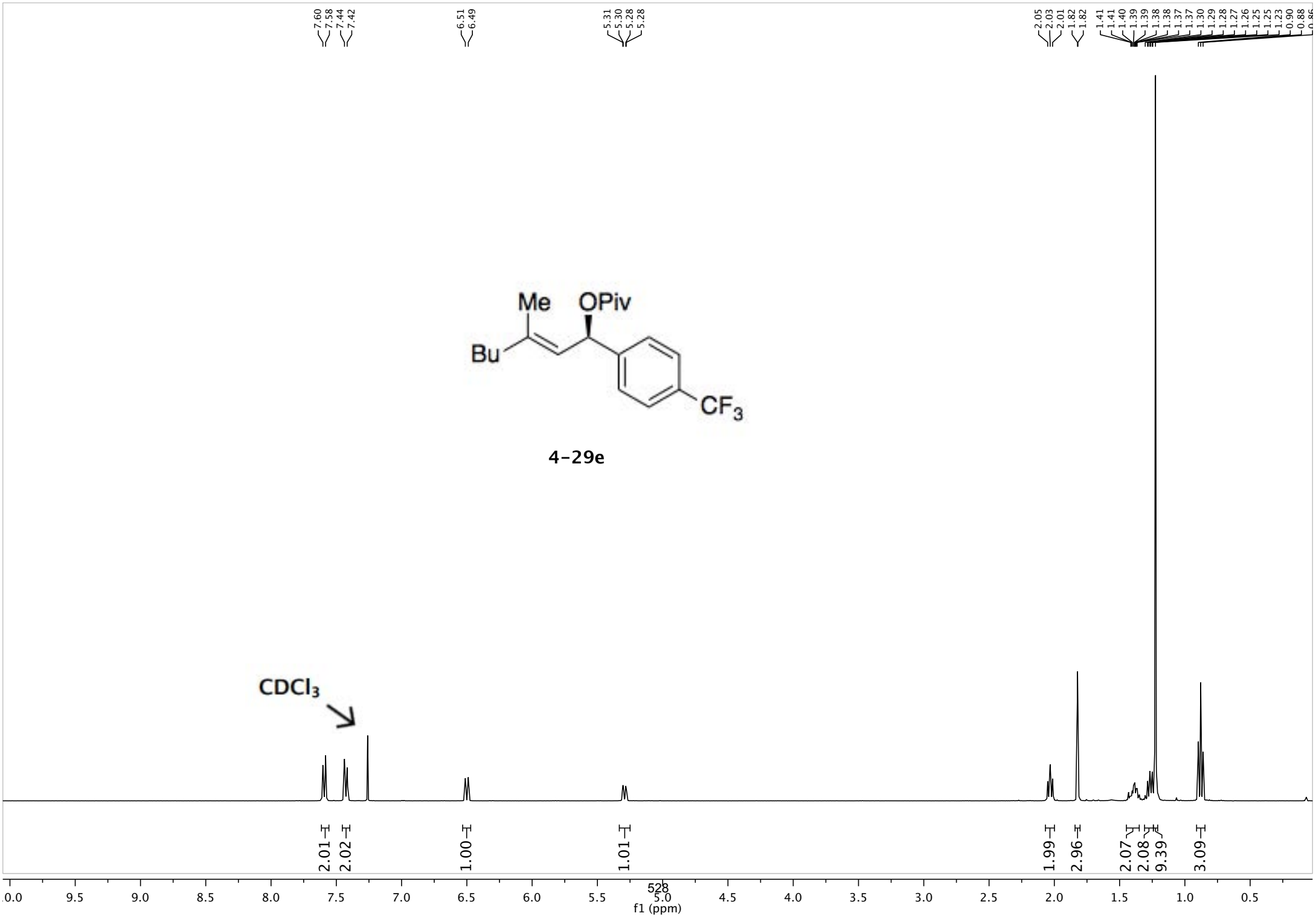

7.19
7.17
7.16
6.91
6.89
6.80
6.80
6.74
6.73
6.72
6.72
6.43
6.42
5.30
5.29
2.03
2.02
2.01
1.80
1.42
1.41
1.39
1.38
1.37
1.36
1.28
1.27
1.26
1.24
1.22
0.98
0.89
0.88
0.86
0.19
Me
OPiv
Bu
OTBS
4-29c
CDCl3
1.07
1.01
0.99
1.06
1.03
1.00
1.95
2.96
1.94
1.93
9.45
9.56
3.32
5.99
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

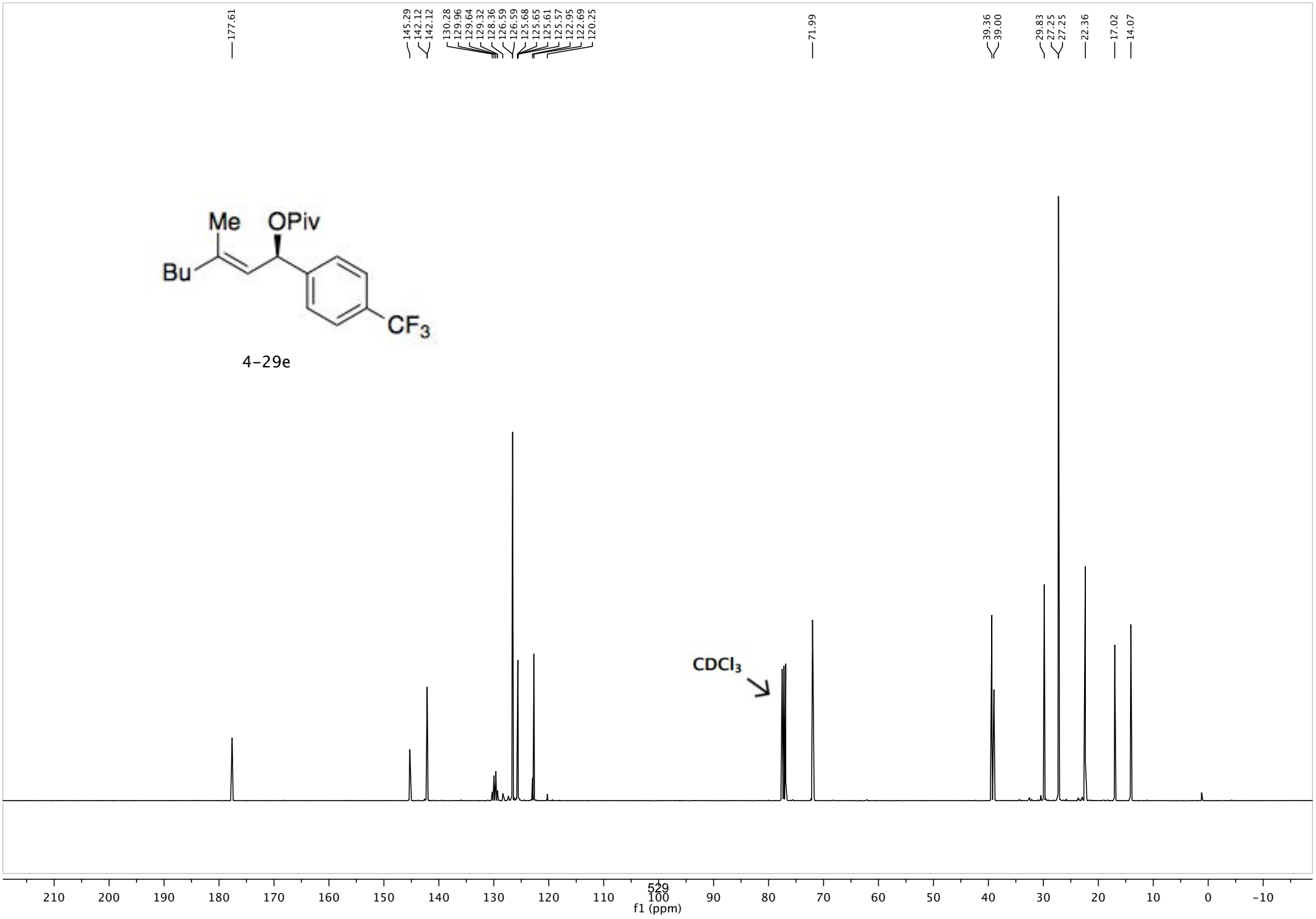

177.67
155.88
142.71
140.95
129.51
123.41
119.33
119.31
118.05
72.32
39.38
39.00
29.93
27.34
25.88
22.38
18.41
16.98
14.12
-4.23
CDCl3
Me
OPiv
Bu
OTBS
4-29c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


20.78
Me
OPiv
Bu
OTBS
4-29c
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)


177.57
146.59
142.72
132.56
126.93
122.17
118.98
111.41
71.85
39.34
39.02
29.80
27.26
22.34
17.11
14.09
CDCl3
Me
OPiv
Bu
OTBS
4-29d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.64
7.62
7.42
7.40
6.49
6.47
5.27
5.26
5.24
5.24
2.05
2.03
2.03
2.01
2.01
1.82
1.82
1.41
1.40
1.39
1.38
1.38
1.37
1.37
1.36
1.28
1.26
1.26
1.25
1.24
1.24
1.22
0.89
0.87
0.86
Me
OPiv
Bu
CN
4–29d
CDCl3
2.04
2.02
1.00
1.01
2.00
2.98
2.14
1.93
9.37
3.03
f1 (ppm)


7.60
7.58
7.44
7.42
6.51
6.49
5.31
5.30
5.28
5.28
2.05
2.03
2.01
1.82
1.82
1.41
1.41
1.40
1.39
1.39
1.38
1.38
1.37
1.37
1.30
1.29
1.28
1.27
1.26
1.25
1.25
1.23
0.90
0.88
Me
OPiv
Bu
CF3
4-29e
CDCl3
2.01
2.02
1.00
1.01
1.99
2.96
2.07
2.08
9.39
3.09
f1 (ppm)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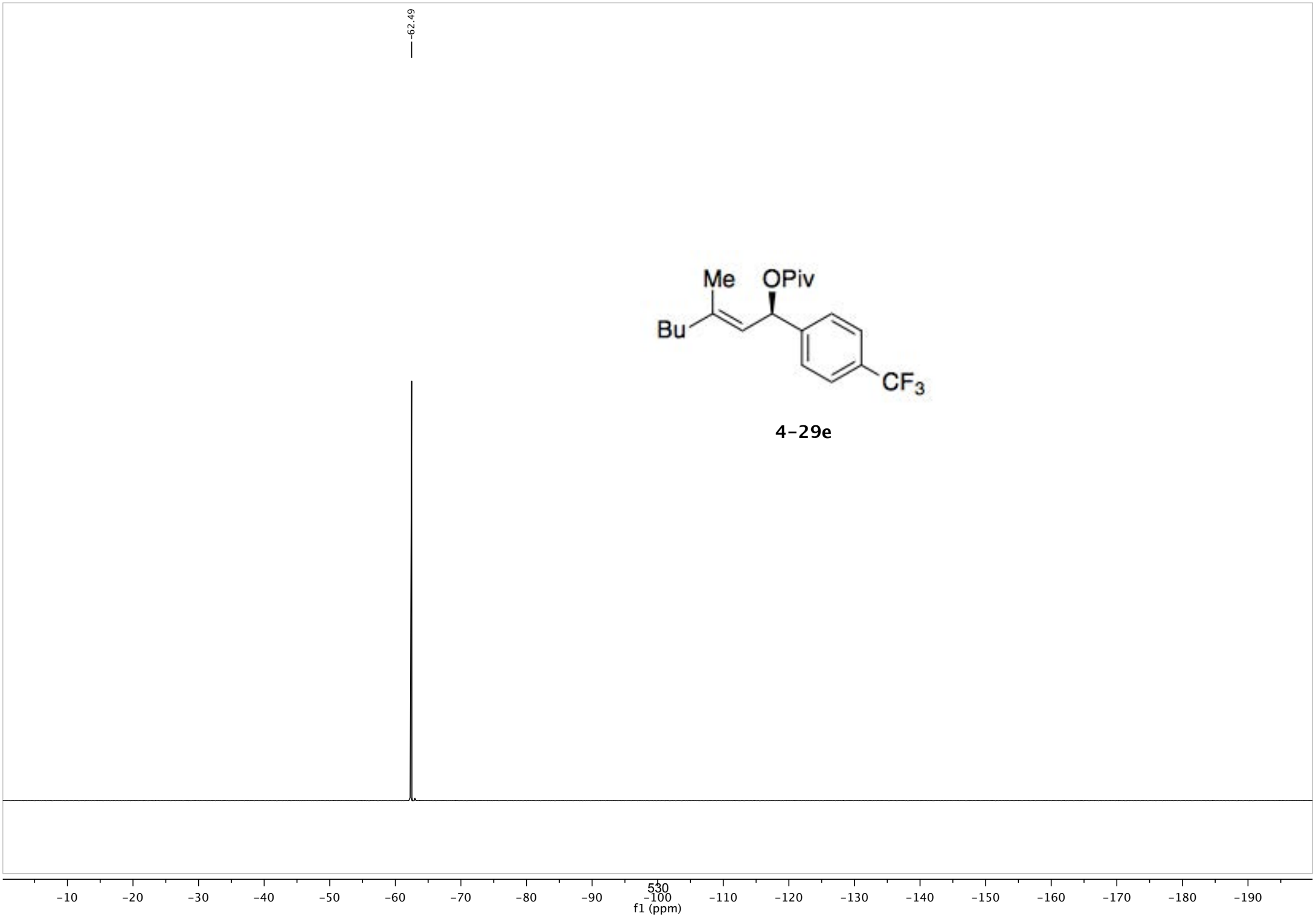
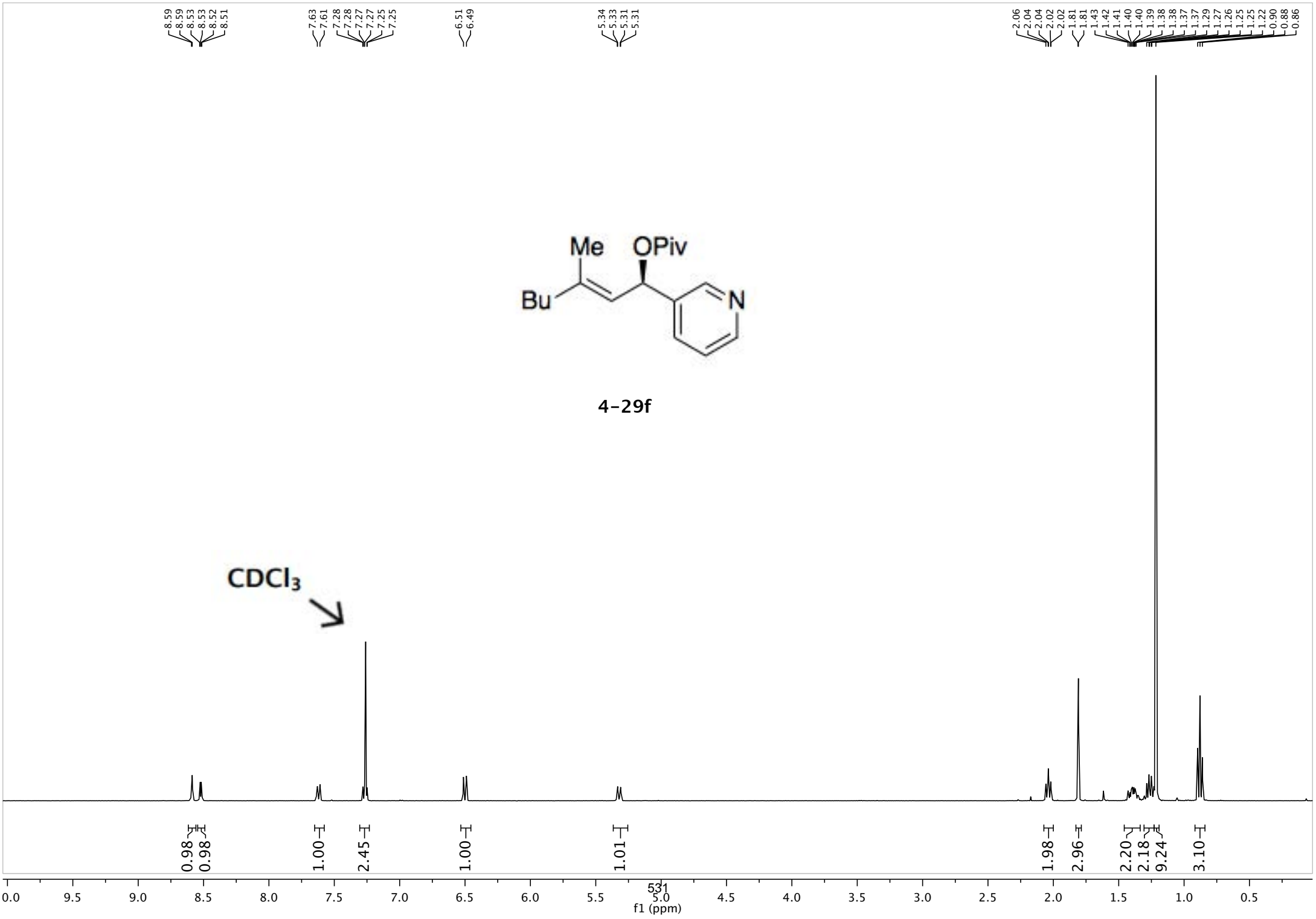
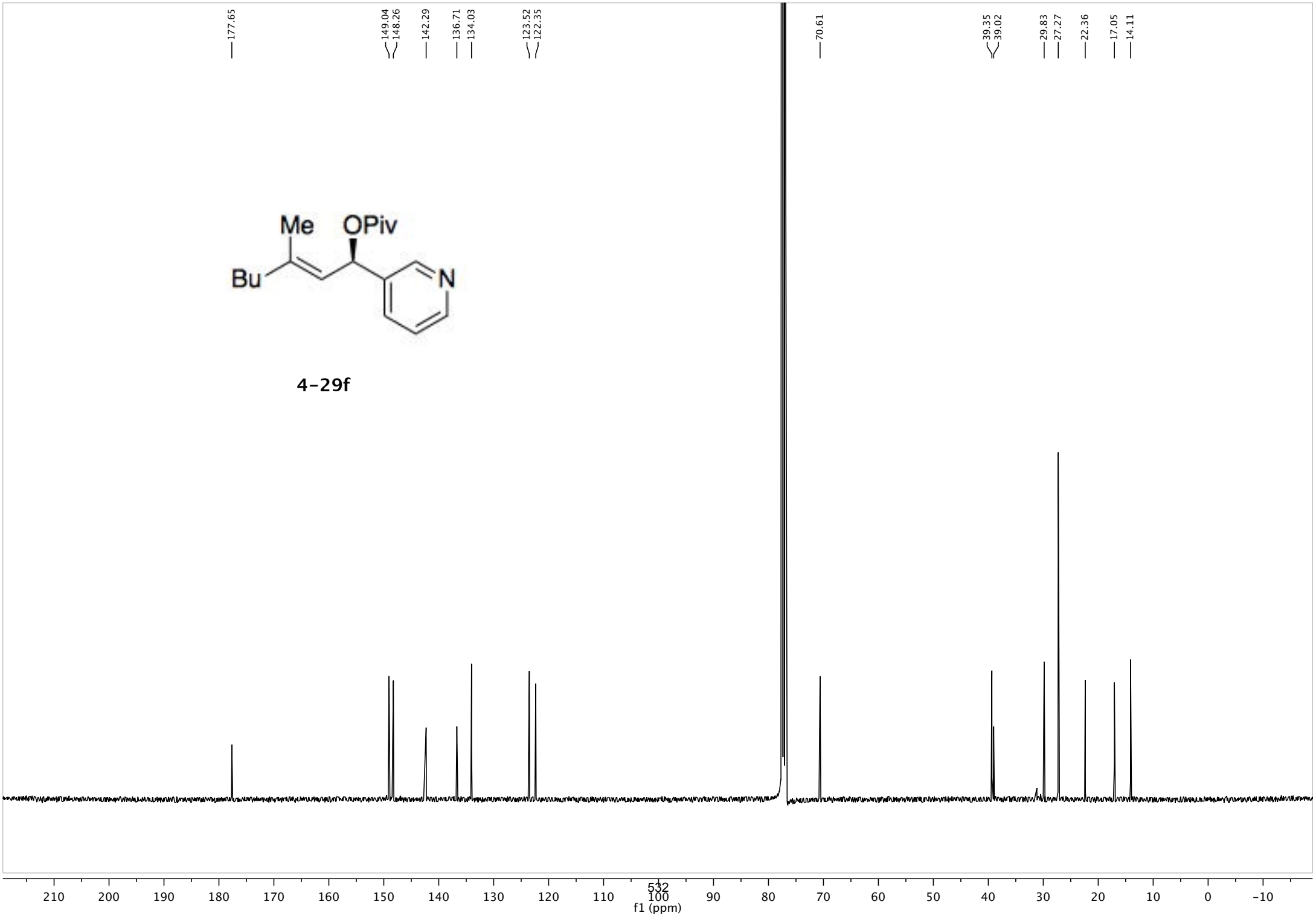
145.29
142.12
142.12
130.28
129.96
129.64
129.32
128.36
126.59
126.59
125.68
125.65
125.61
125.57
122.95
122.69
120.25
71.99
39.36
39.00
29.83
27.25
27.25
22.36
17.02
14.07
Me
OPiv
Bu
CF3
4-29e
CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

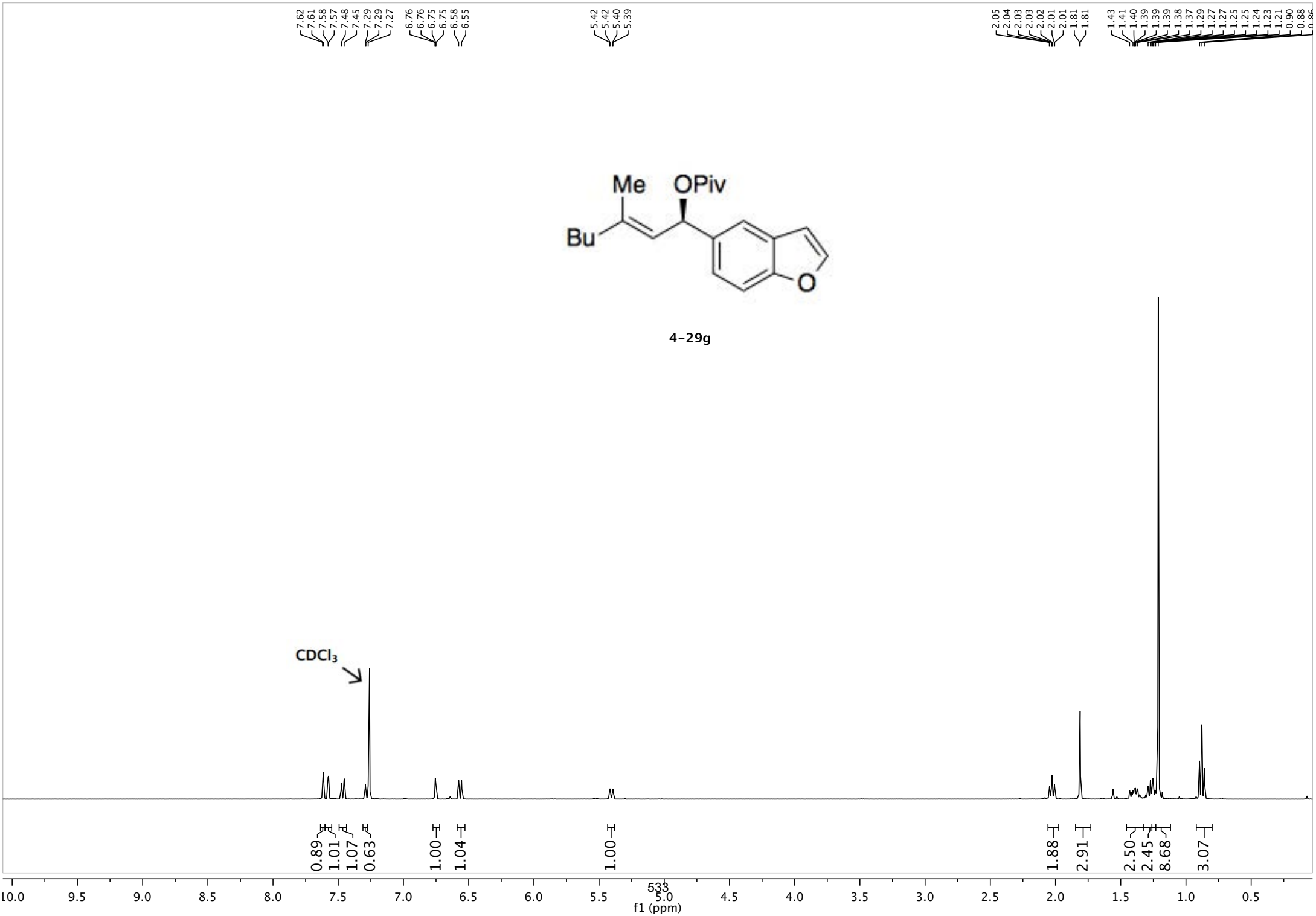

-62.49
Me
OPiv
Bu
CF3
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

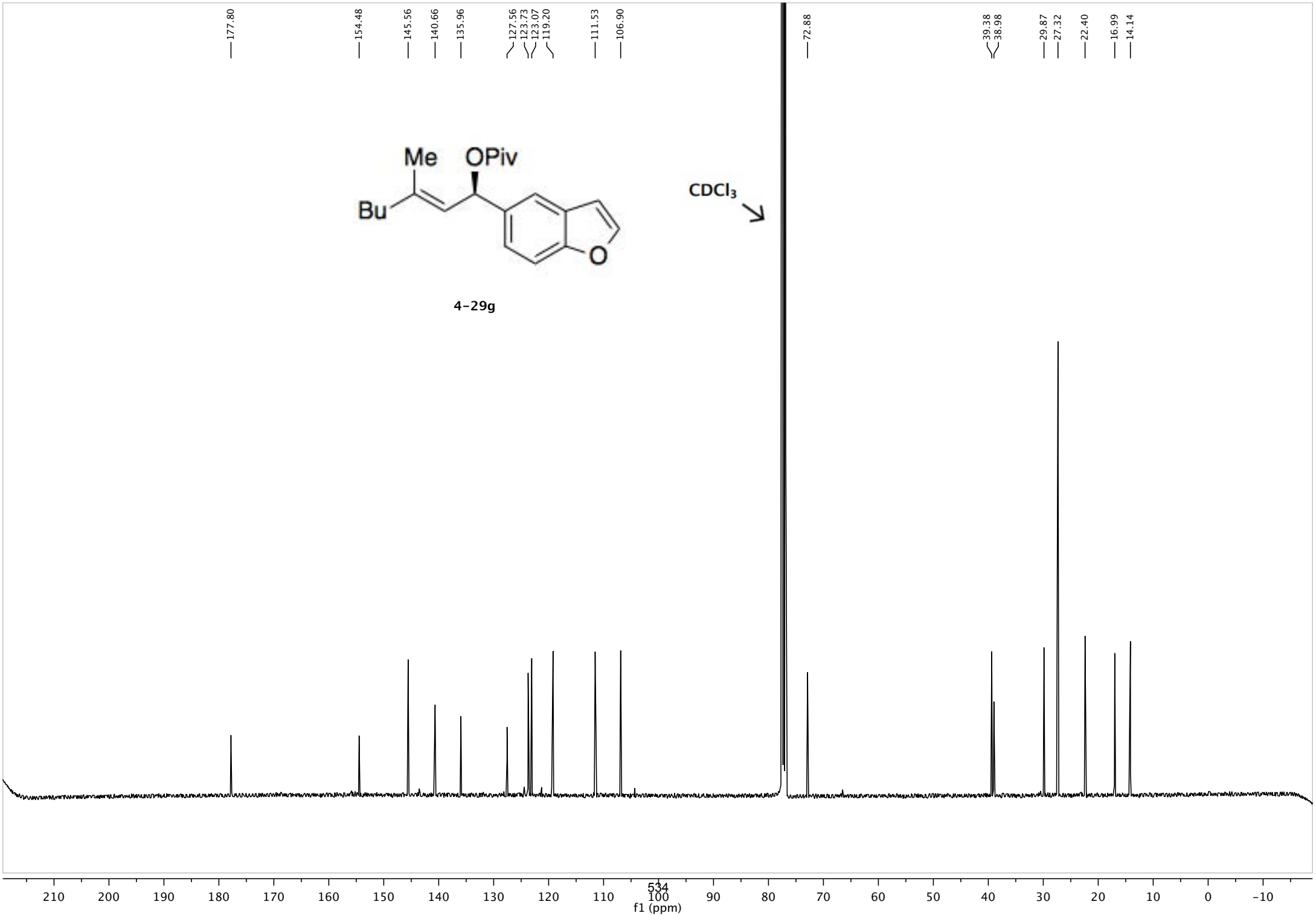
4-29e


8.59
8.59
8.53
8.53
8.52
8.51
7.63
7.61
7.28
7.28
7.27
7.27
7.25
7.25
6.51
6.49
5.34
5.33
5.31
5.31
2.06
2.04
2.04
2.02
2.02
1.81
1.81
1.43
1.42
1.41
1.40
1.40
1.39
1.38
1.38
1.37
1.37
1.29
1.27
1.26
1.25
1.25
1.22
0.90
0.88
0.86
Me
OPiv
Bu
N
CDCl3
0.98
0.98
1.00
2.45
1.00
1.01
1.98
2.96
2.20
2.18
9.24
3.10
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

4-29f


177.65
149.04
148.26
142.29
136.71
134.03
123.52
122.35
70.61
39.35
39.02
29.83
27.27
22.36
17.05
14.11
Me
OPiv
Bu
N
4-29f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Me
OPiv
Bu
O
4-29g
CDCl3
0.89
1.01
1.07
0.63
1.00
1.04
1.00
1.88
2.91
2.50
2.45
8.68
3.07
f1 (ppm)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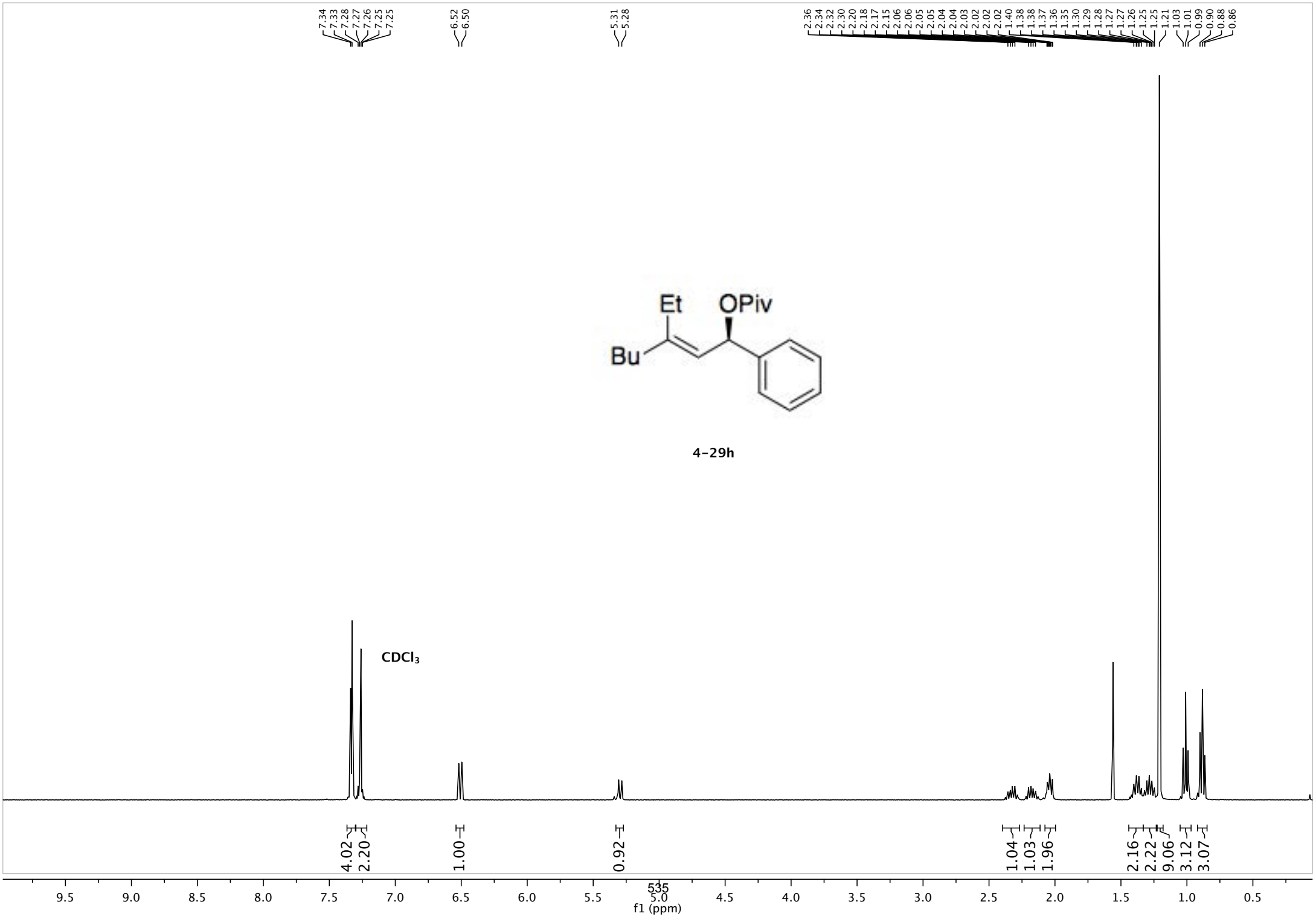
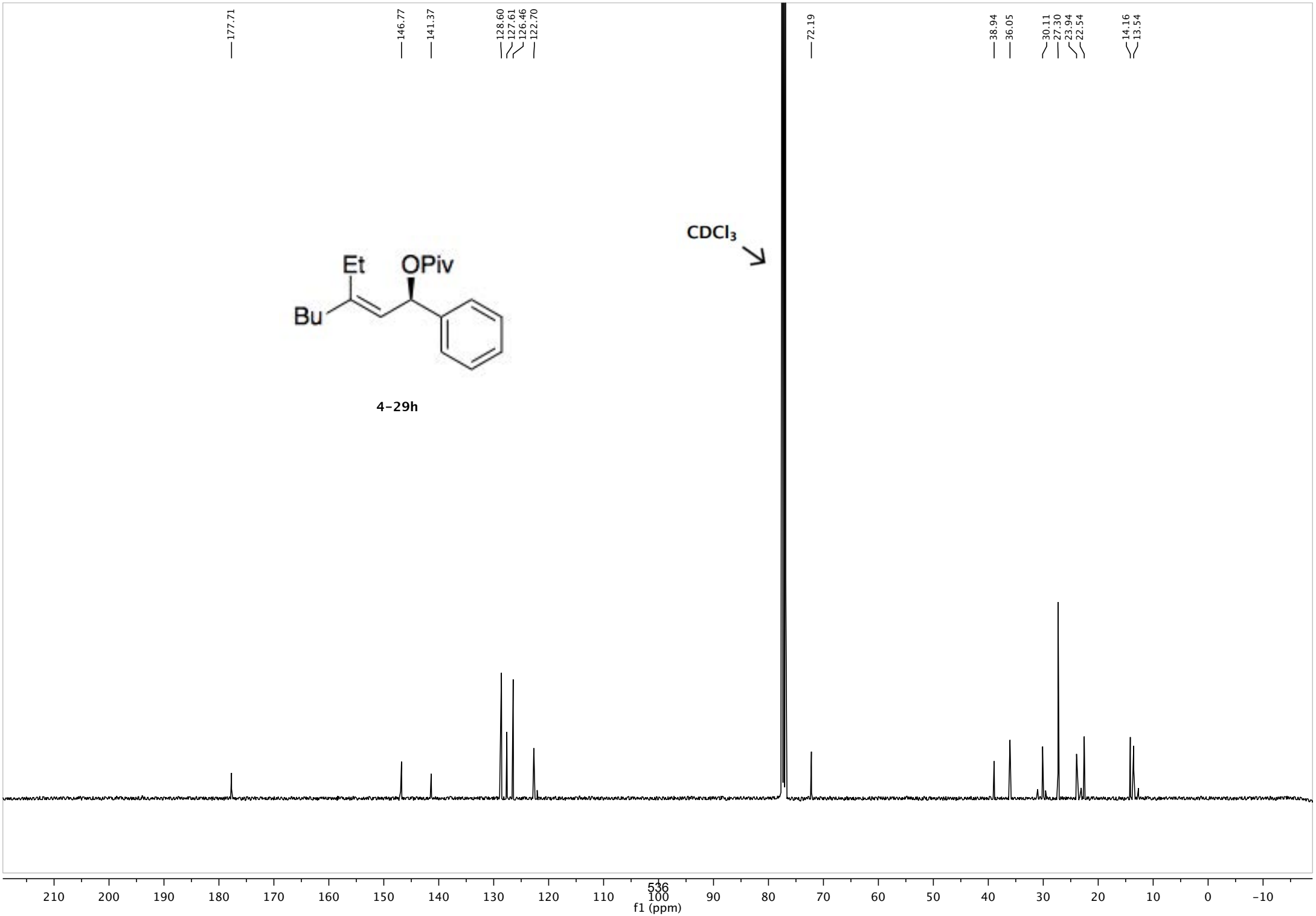
154.48
145.56
140.66
135.96
127.56
123.73
123.07
119.20
111.53
106.90
72.88
39.38
38.98
29.87
27.32
22.40
16.99
14.14
Me
OPiv
Bu
O
CDCl3
4-29g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.34
7.33
7.28
7.27
7.26
7.25
7.25
6.52
6.50
5.31
5.28
2.36
2.34
2.32
2.30
2.20
2.18
2.17
2.15
2.06
2.06
2.05
2.05
2.04
2.04
2.03
2.02
2.02
2.02
1.40
1.38
1.38
1.37
1.36
1.35
1.30
1.29
1.28
1.27
1.27
1.26
1.25
1.25
1.21
1.03
1.01
0.99
0.90
0.88
0.86
Et
OPiv
Bu
4-29h
CDCl3
4.02
2.20
1.00
0.92
1.04
1.03
1.96
2.16
2.22
9.06
3.12
3.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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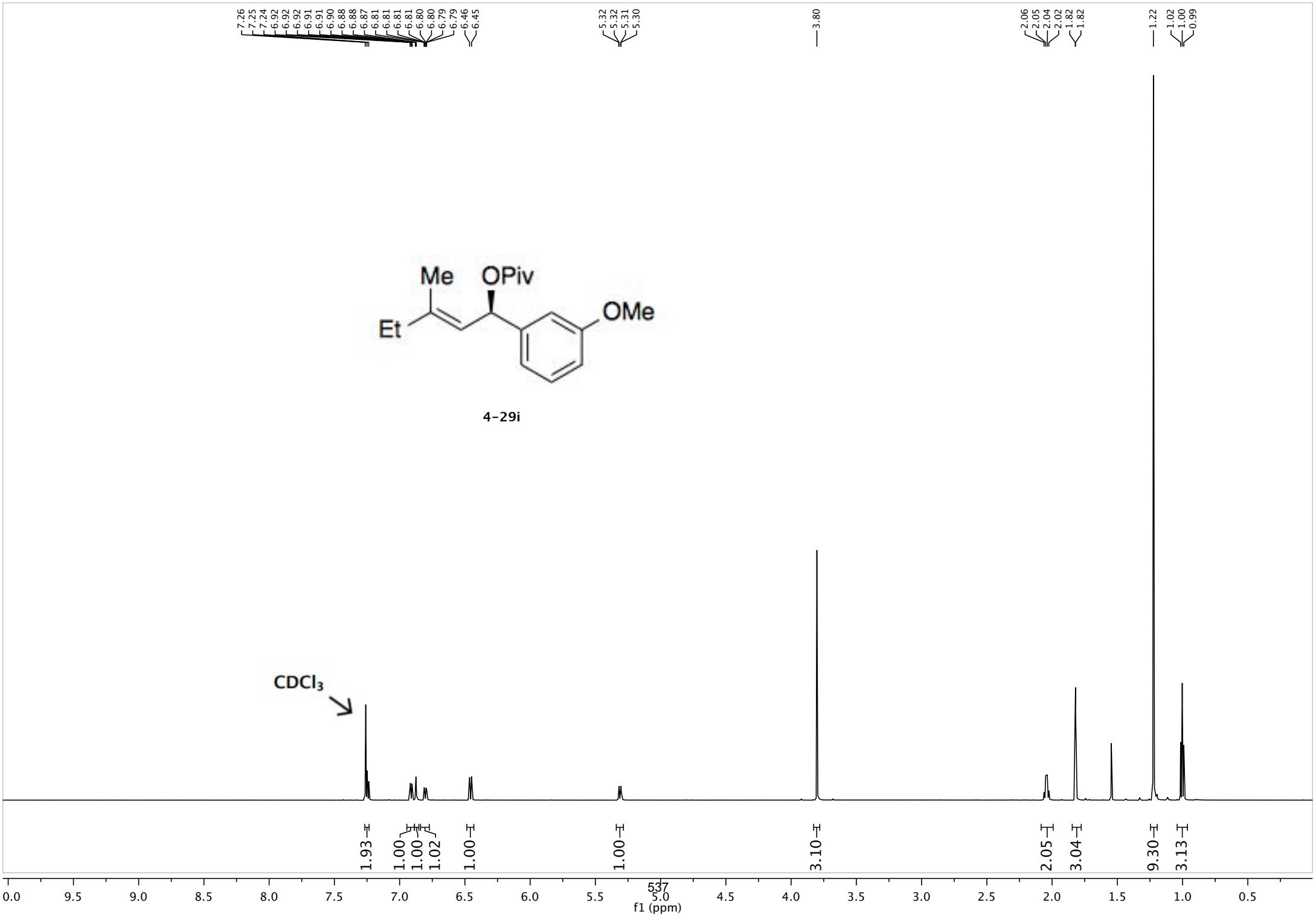
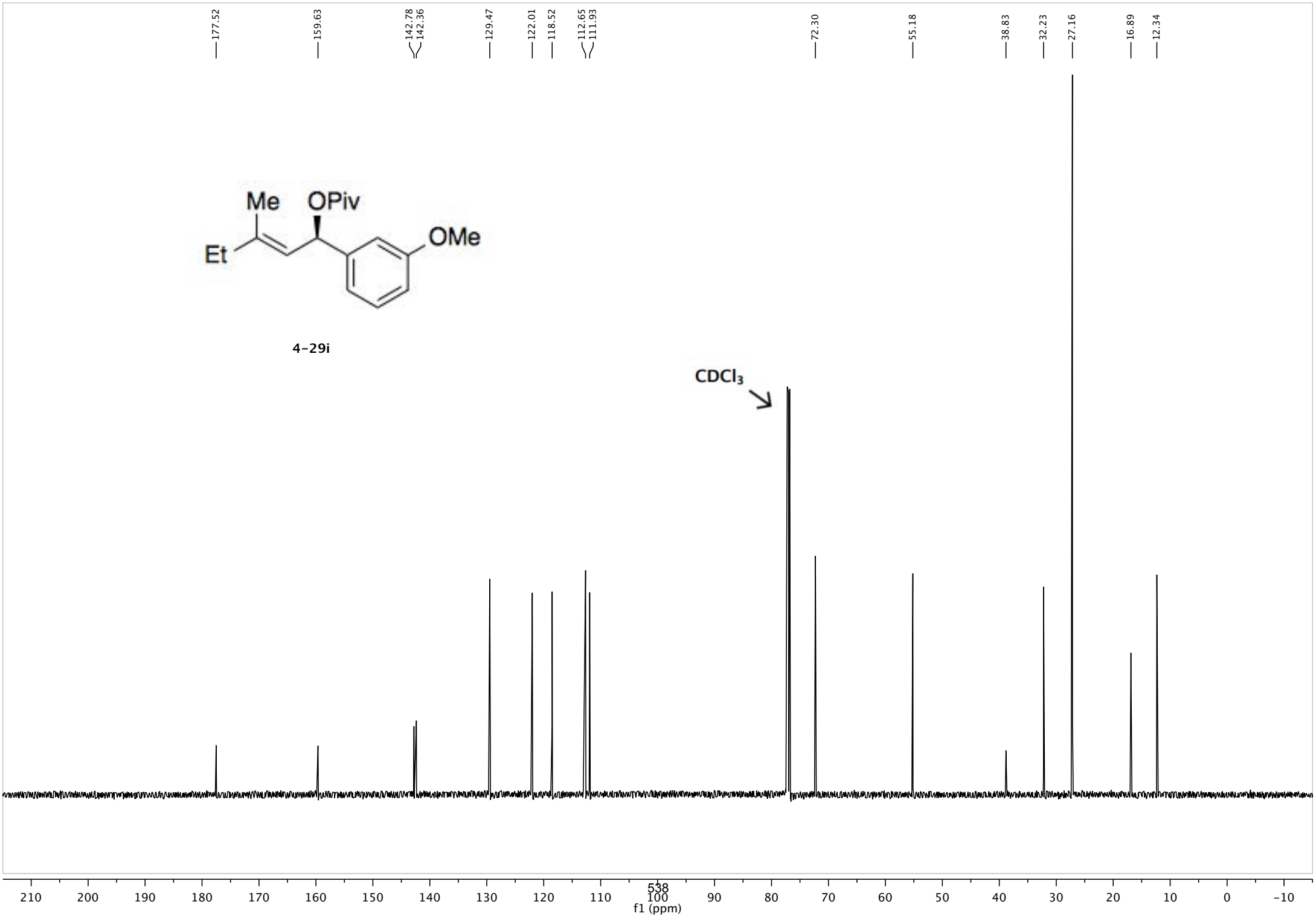
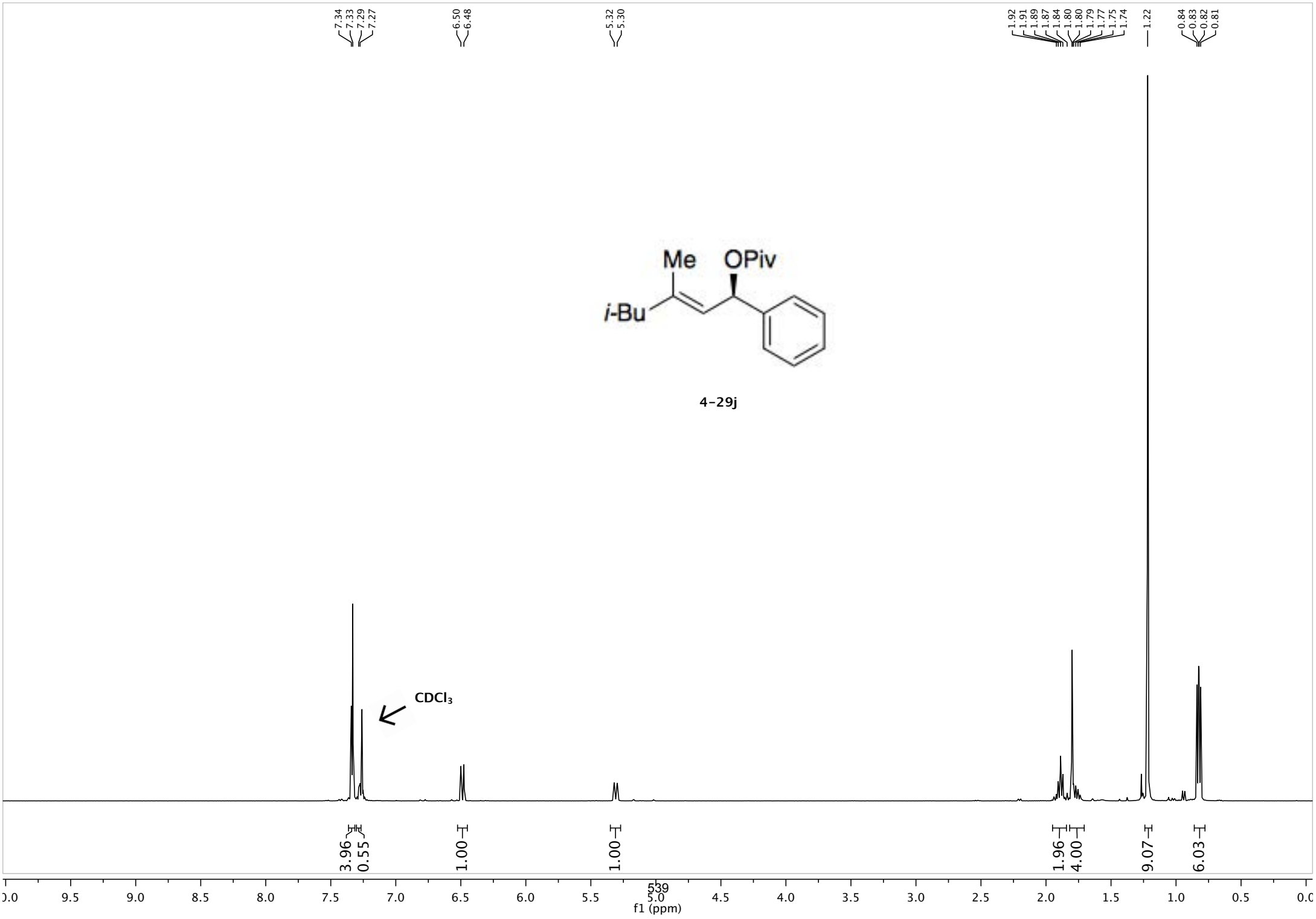
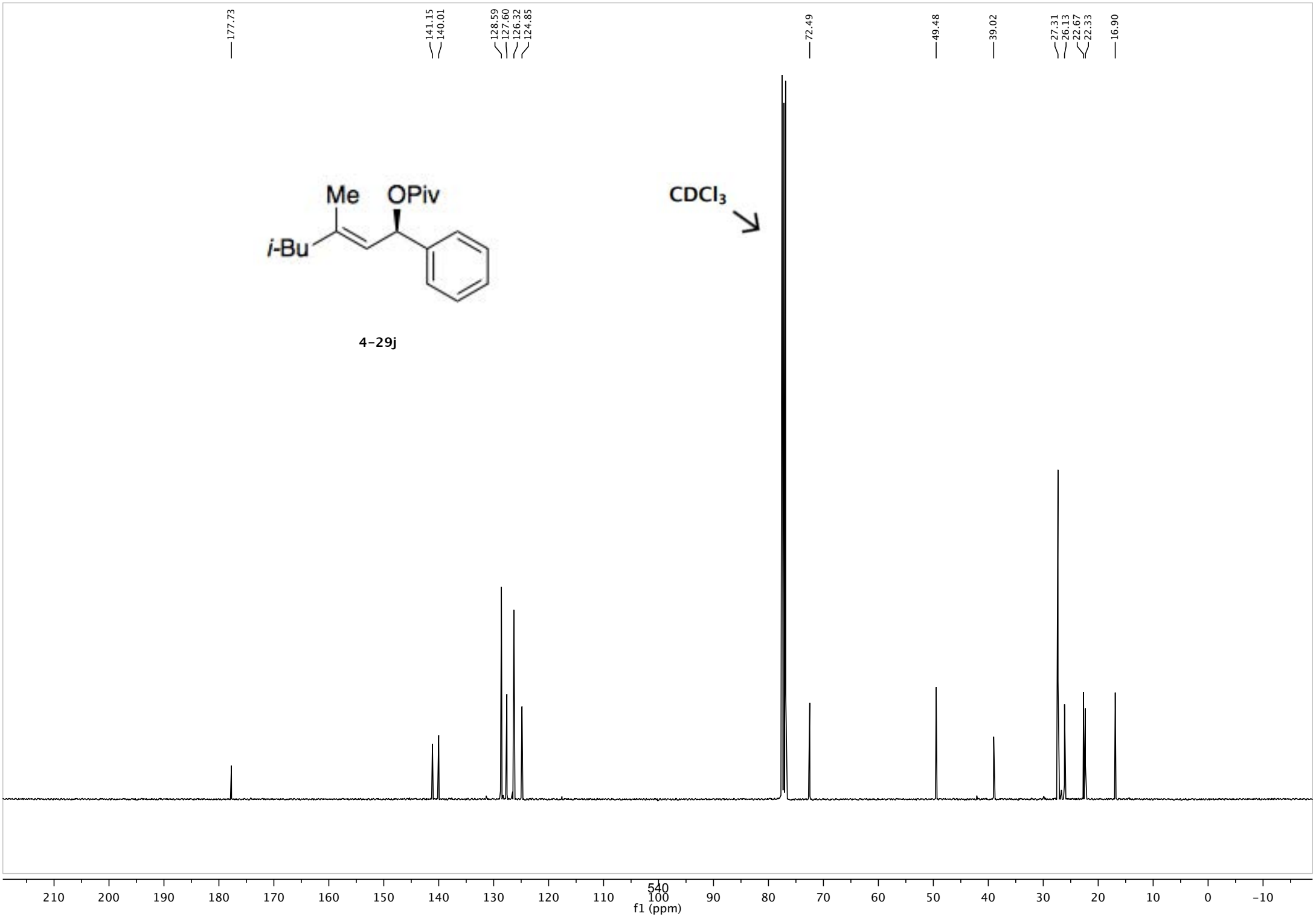
146.77
141.37
128.60
127.61
126.46
122.70
72.19
38.94
36.05
30.11
27.30
23.94
22.54
14.16
13.54
CDCl3
Et
OPiv
Bu
4-29h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.26
7.25
7.24
6.92
6.92
6.92
6.91
6.91
6.90
6.88
6.88
6.87
6.81
6.81
6.81
6.80
6.80
6.79
6.79
6.46
6.45
5.32
5.32
5.31
5.30
3.80
2.06
2.05
2.04
2.02
1.82
1.82
1.22
1.02
1.00
0.99
Me
OPiv
Et
OMe
4-29i
CDCl3
1.93
1.00
1.00
1.02
1.00
1.00
3.10
2.05
3.04
9.30
3.13
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


177.52
159.63
142.78
142.36
129.47
122.01
118.52
112.65
111.93
72.30
55.18
38.83
32.23
27.16
16.89
12.34
Me
OPiv
Et
OMe
4-29i
CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.34
7.33
7.29
7.27
6.50
6.48
5.32
5.30
1.92
1.91
1.89
1.87
1.84
1.80
1.80
1.79
1.77
1.75
1.74
1.22
0.84
0.83
0.82
0.81
Me
OPiv
i-Bu
4-29j
CDCl3
3.96
0.55
1.00
1.00
1.96
4.00
9.07
6.03
f1 (ppm)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124.85
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49.48
39.02
27.31
26.13
22.67
22.33
16.90
Me
OPiv
i-Bu
CDCl3
4-29j
210
200
190
180
170
160
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140
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120
110
100
90
80
70
60
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40
30
20
10
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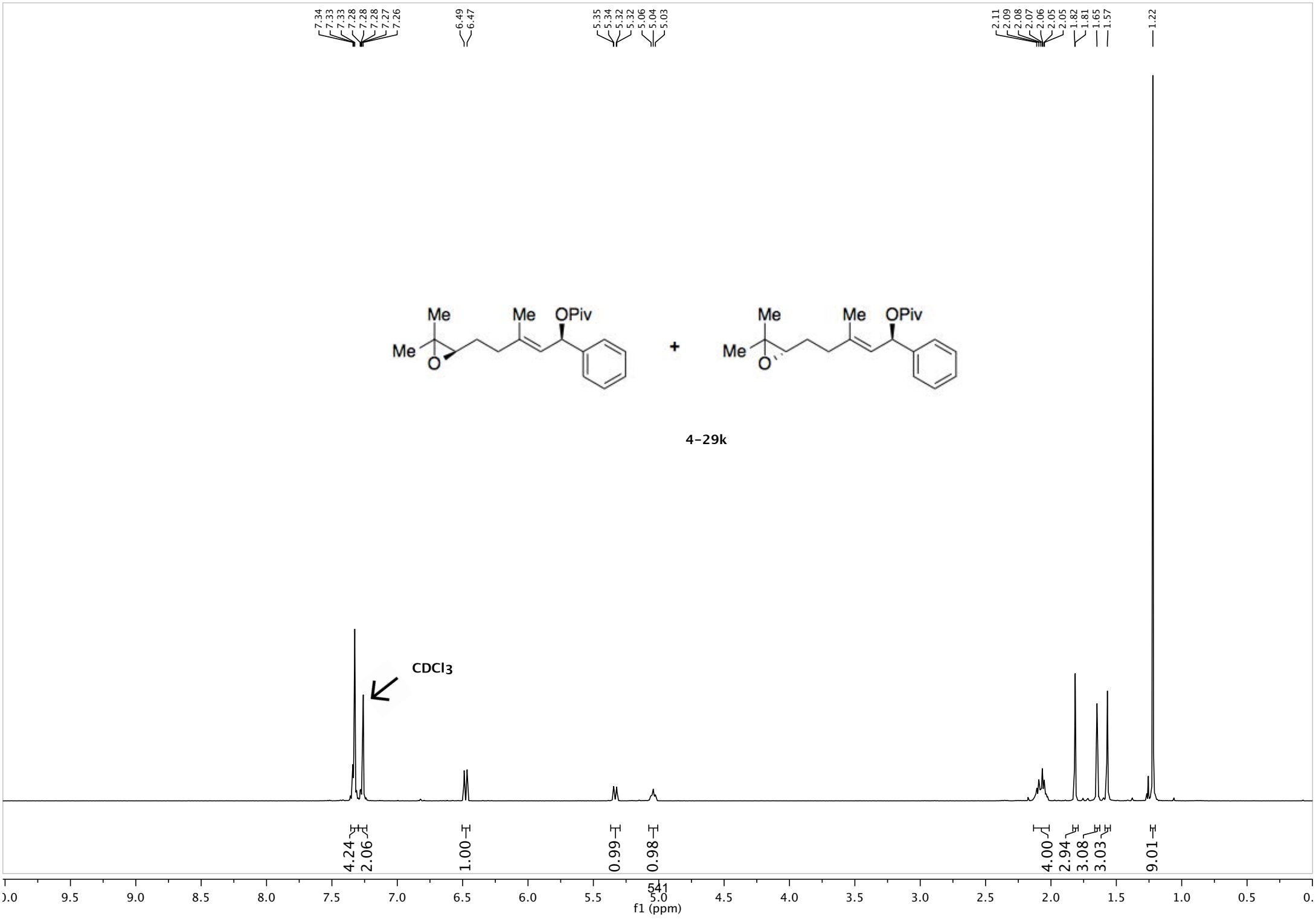
-10
f1 (ppm)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5.34
5.32
5.32
5.06
5.04
5.03
2.11
2.09
2.08
2.07
2.06
2.05
2.05
1.82
1.81
1.65
1.57
1.22
Me
Me
O
Me
OPiv
+
Me
Me
O
Me
OPiv
4-29k
CDCl3
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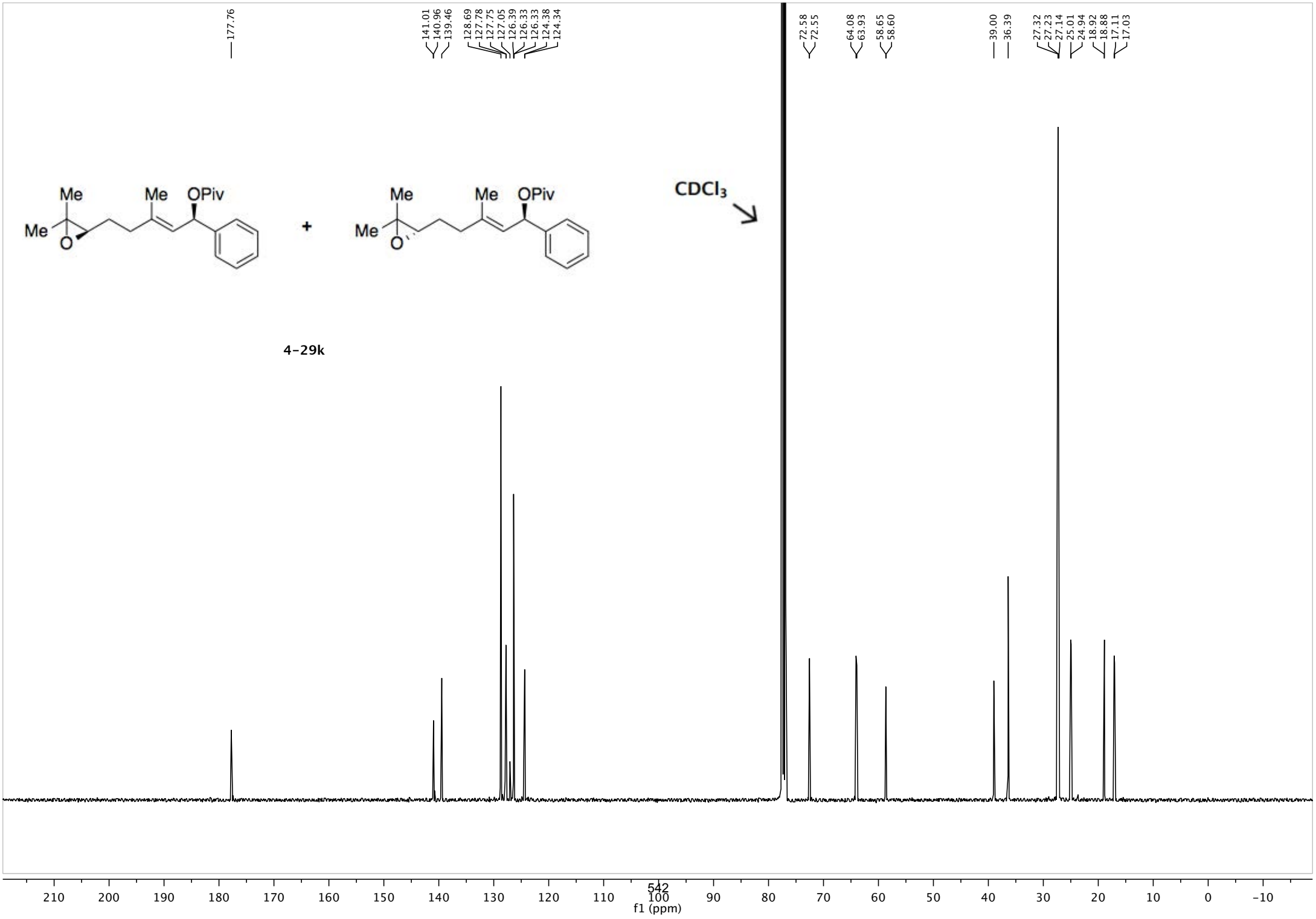
0.99
0.98
4.00
2.94
3.08
3.03
9.01
f1 (ppm)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124.38
124.34
72.58
72.55
64.08
63.93
58.65
58.60
39.00
36.39
27.32
27.23
27.14
25.01
24.94
18.92
18.88
17.11
17.03
Me
Me
OPiv
O
+
Me
Me
OPiv
Me
O
CDCl3
4-29k
210
200
190
180
170
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120
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100
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80
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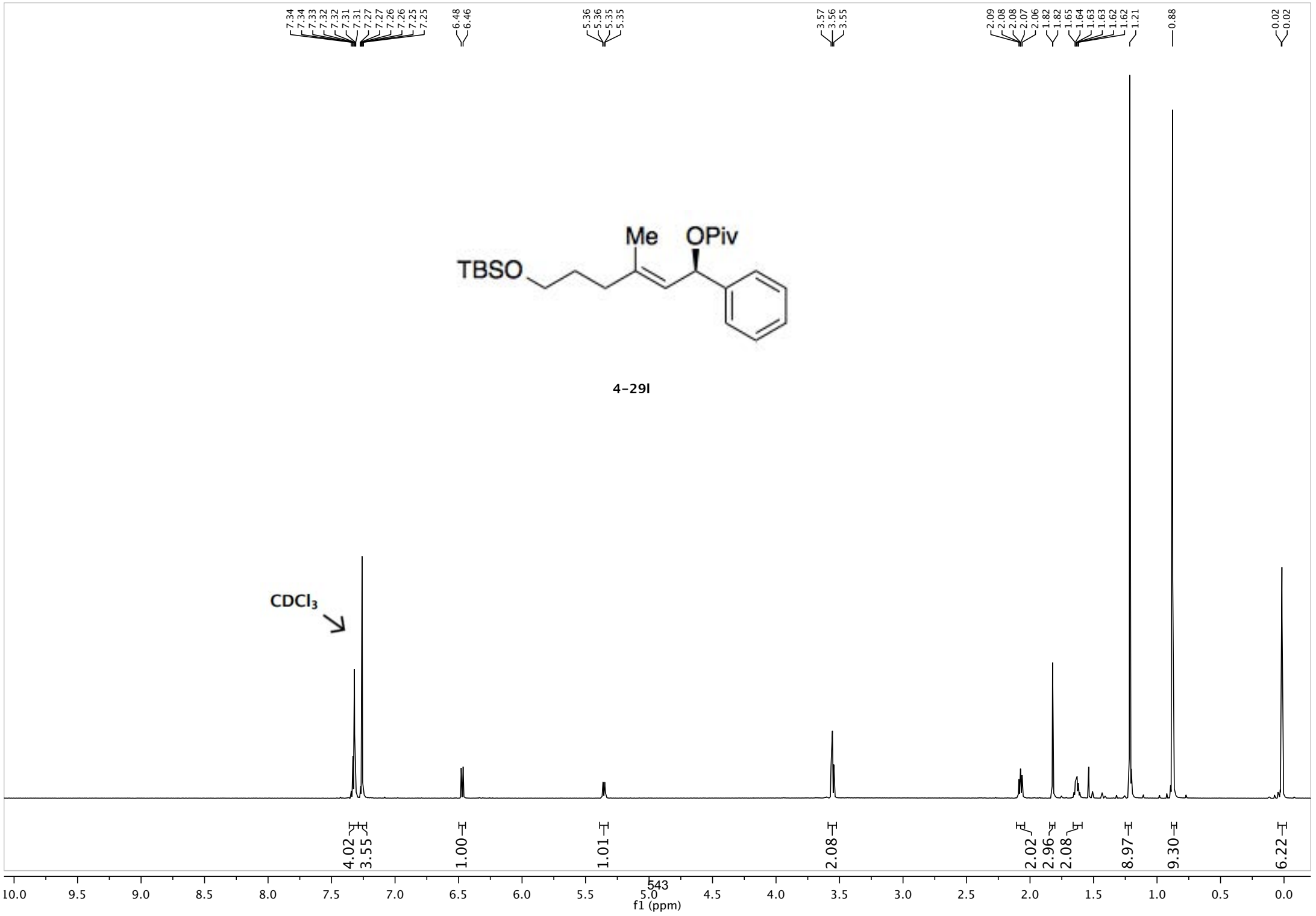
40
30
20
10
0
-10
f1 (ppm)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7.25
6.48
6.46
5.36
5.36
5.35
5.35
3.57
3.56
3.55
2.09
2.08
2.08
2.07
2.06
1.82
1.82
1.65
1.64
1.63
1.63
1.62
1.62
1.21
0.88
0.02
0.02
Me
OPiv
TBSO
4-29l
CDCl3
4.02
3.55
1.00
1.01
2.08
2.02
2.96
2.08
8.97
9.30
6.22
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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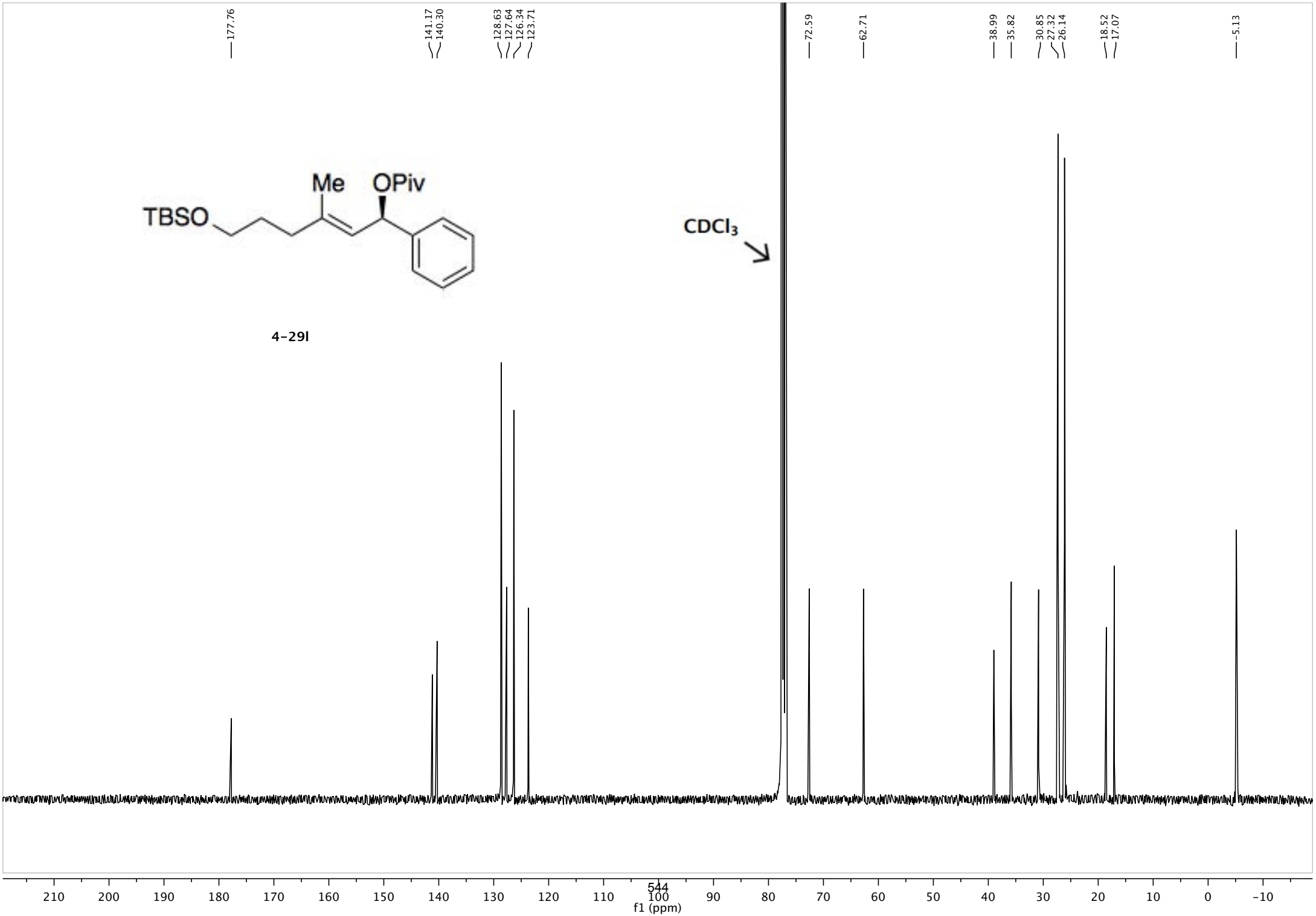
f1 (ppm)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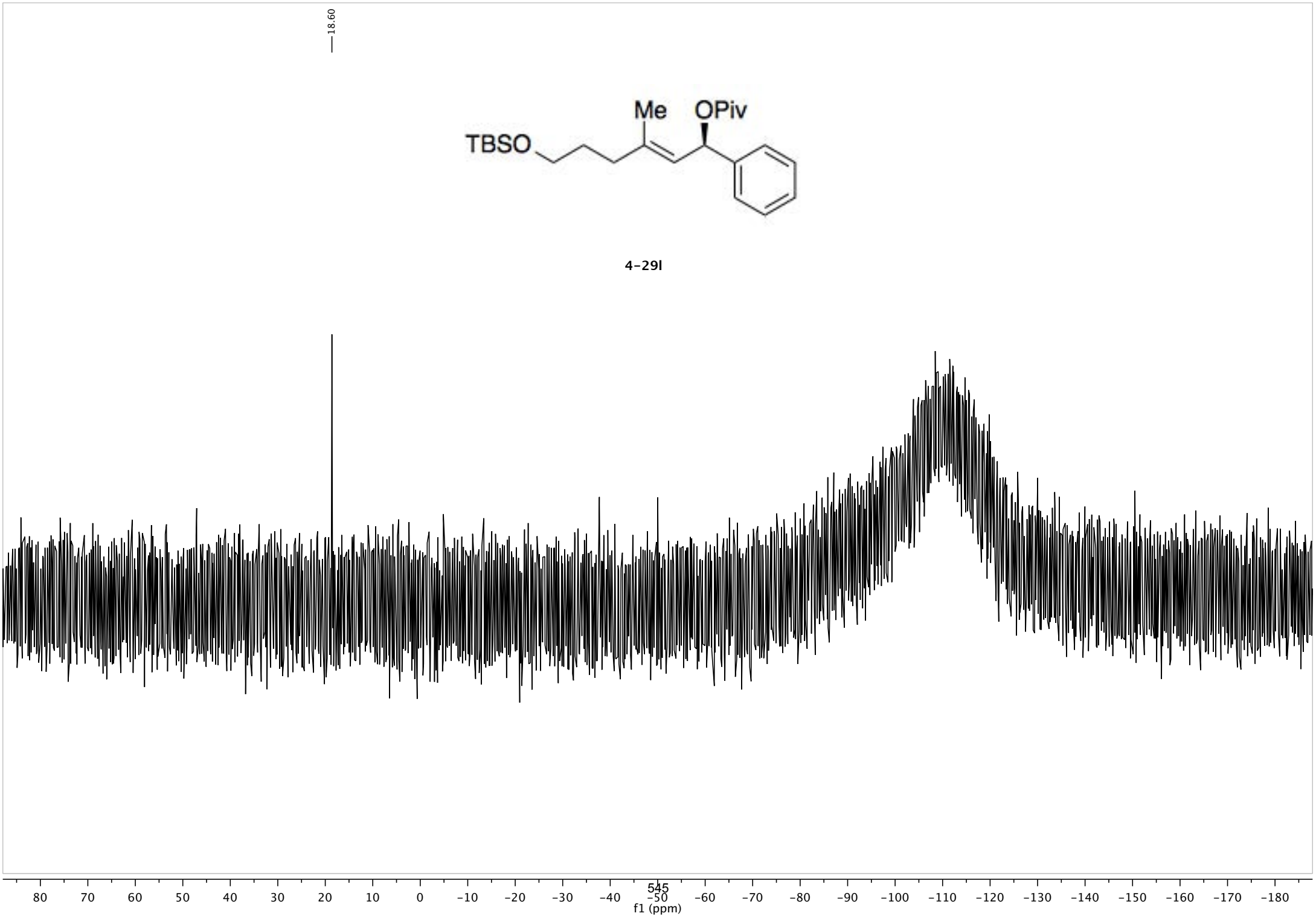
72.59
62.71
38.99
35.82
30.85
27.32
26.14
18.52
17.07
-5.13
Me
OPiv
TBSO
CDCl3
4-29l
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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Me
OPiv
TBSO
4-29l
80
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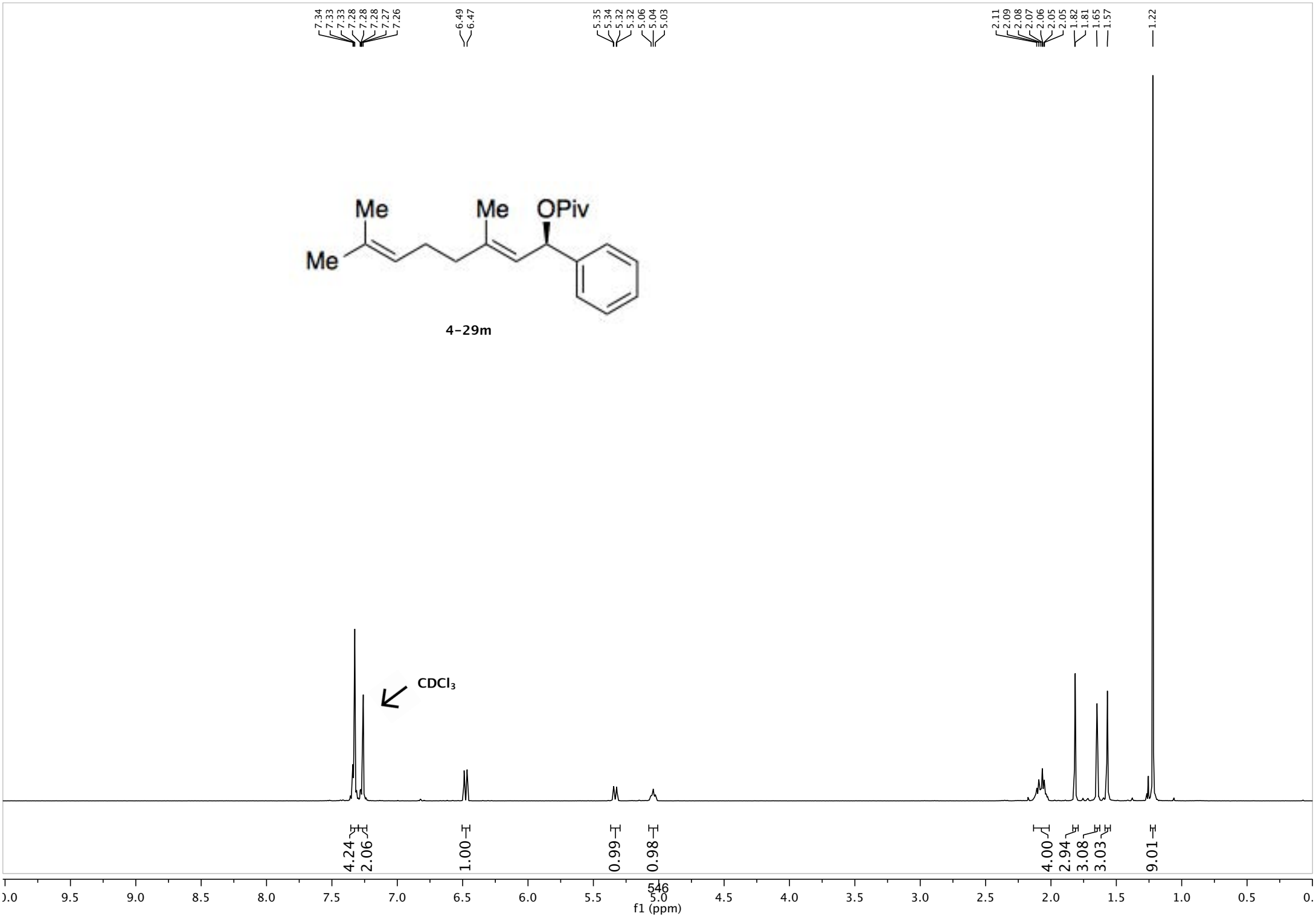
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)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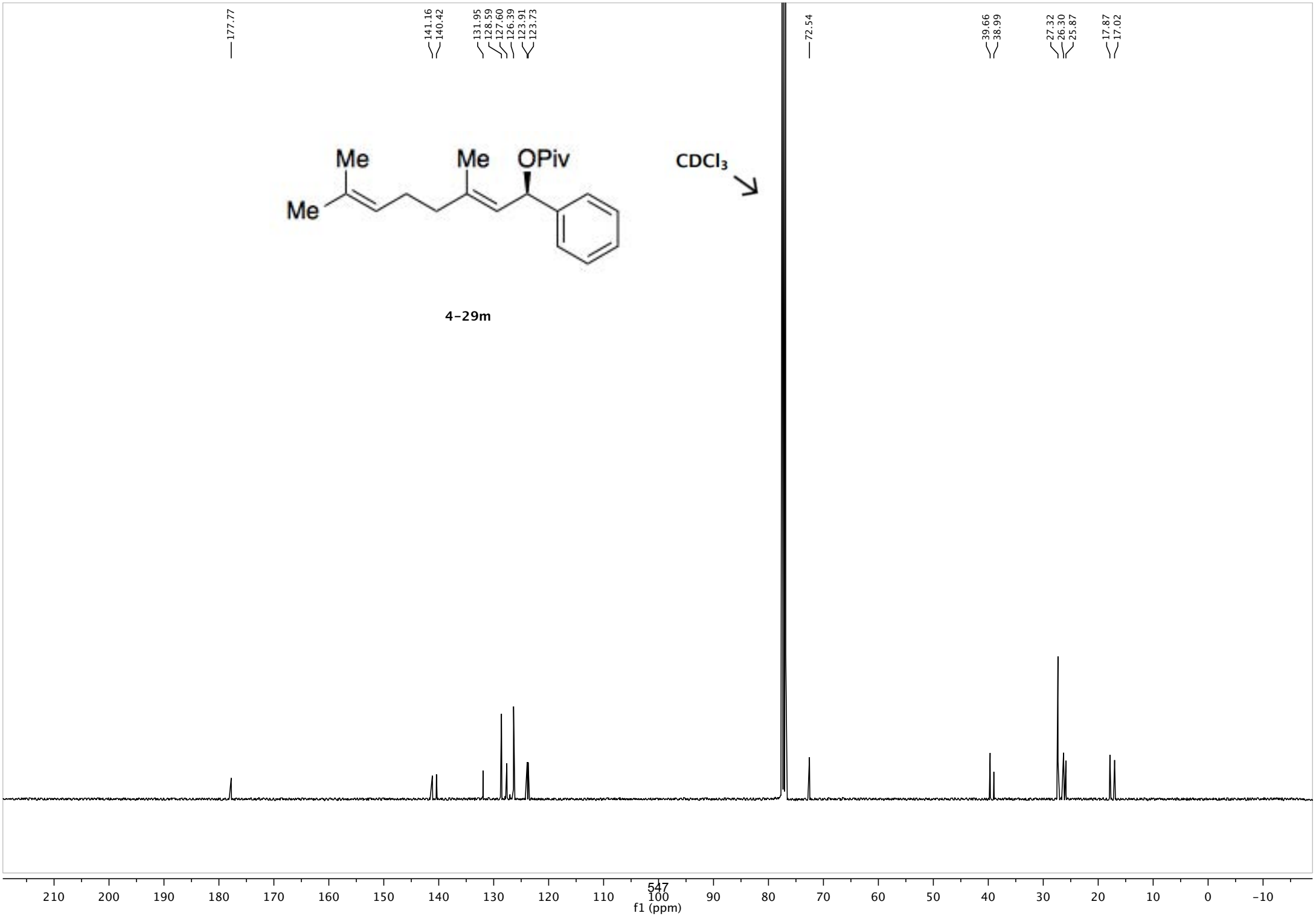
7.26
6.49
6.47
5.35
5.34
5.32
5.32
5.06
5.04
5.03
2.11
2.09
2.08
2.07
2.06
2.05
2.05
1.82
1.81
1.65
1.57
1.22
Me
Me
Me
OPiv
4-29m
CDCl3
4.24
2.06
1.00
0.99
0.98
4.00
2.94
3.08
3.03
9.01
546
f1 (ppm)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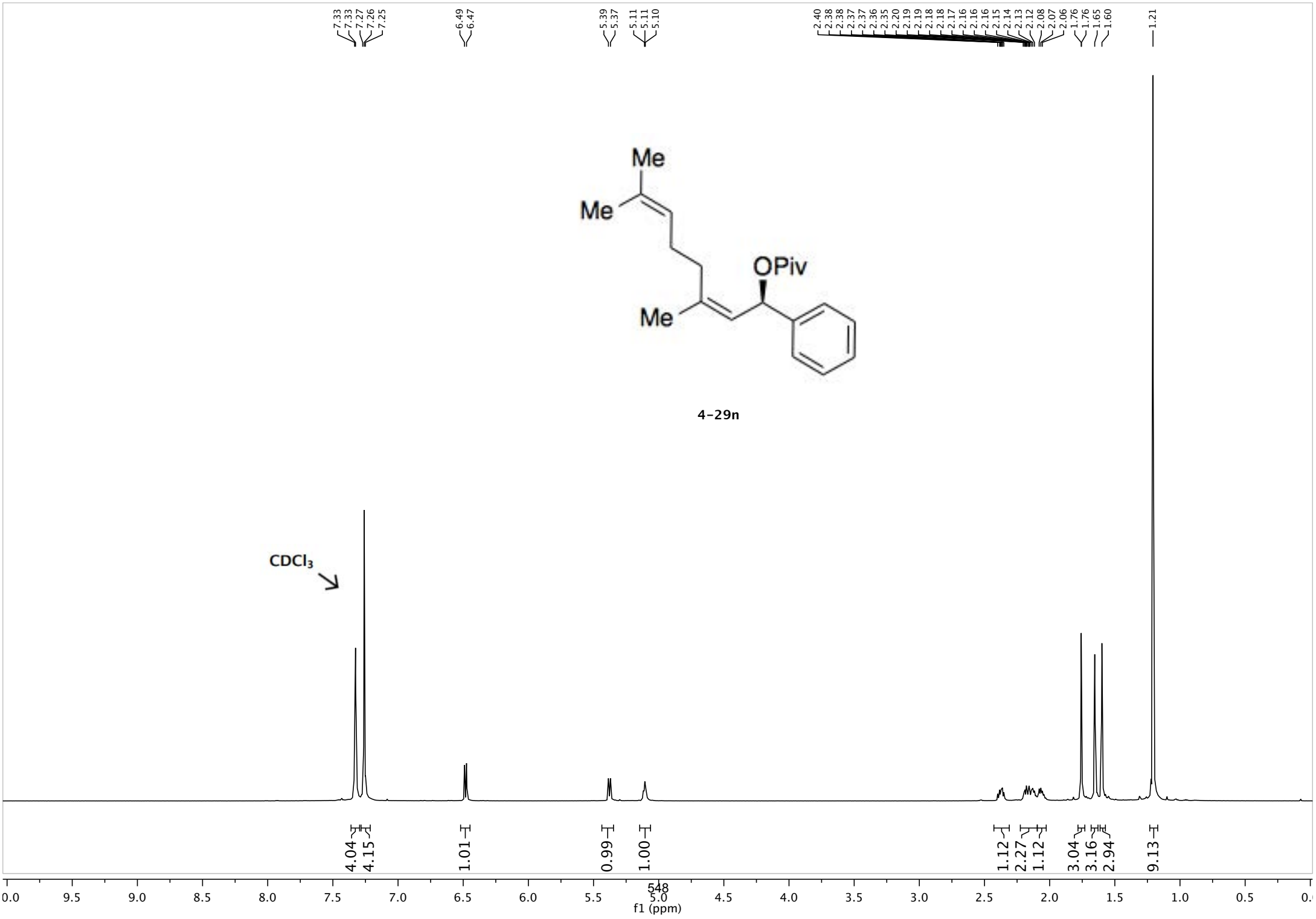
127.60
126.39
123.91
123.73
72.54
39.66
38.99
27.32
26.30
25.87
17.87
17.02
Me
Me
Me
OPiv
CDCl3
4-29m
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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6.49
6.47
5.39
5.37
5.11
5.11
5.10
2.40
2.38
2.38
2.37
2.37
2.36
2.35
2.20
2.19
2.19
2.18
2.18
2.17
2.16
2.16
2.16
2.15
2.14
2.13
2.12
2.08
2.07
2.06
1.76
1.76
1.65
1.60
1.21
Me
Me
OPiv
Me
CDCl3
4.04
4.15
1.01
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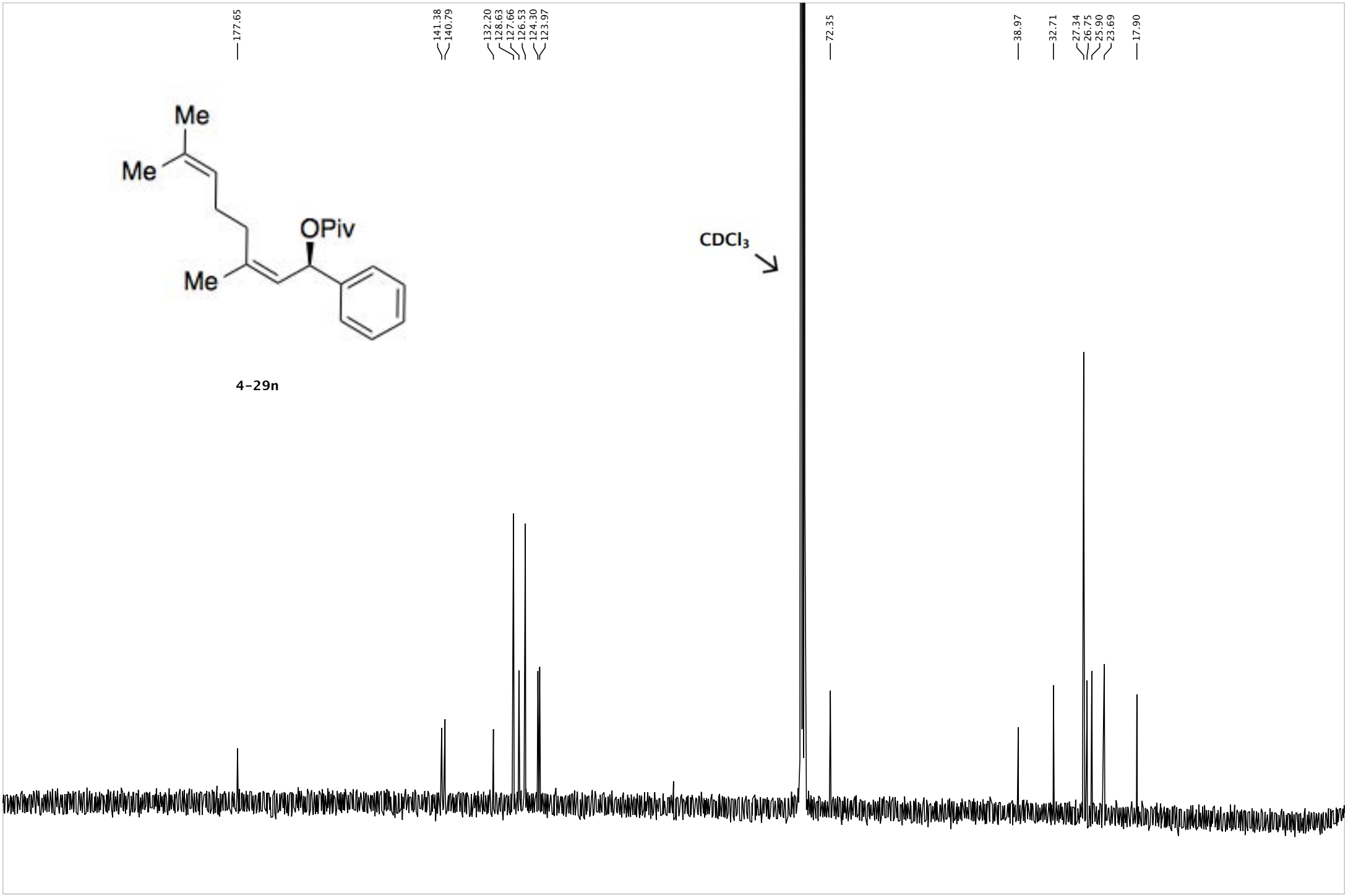
1.00
1.12
2.27
1.12
3.04
3.16
2.94
9.13
f1 (ppm)

4-29n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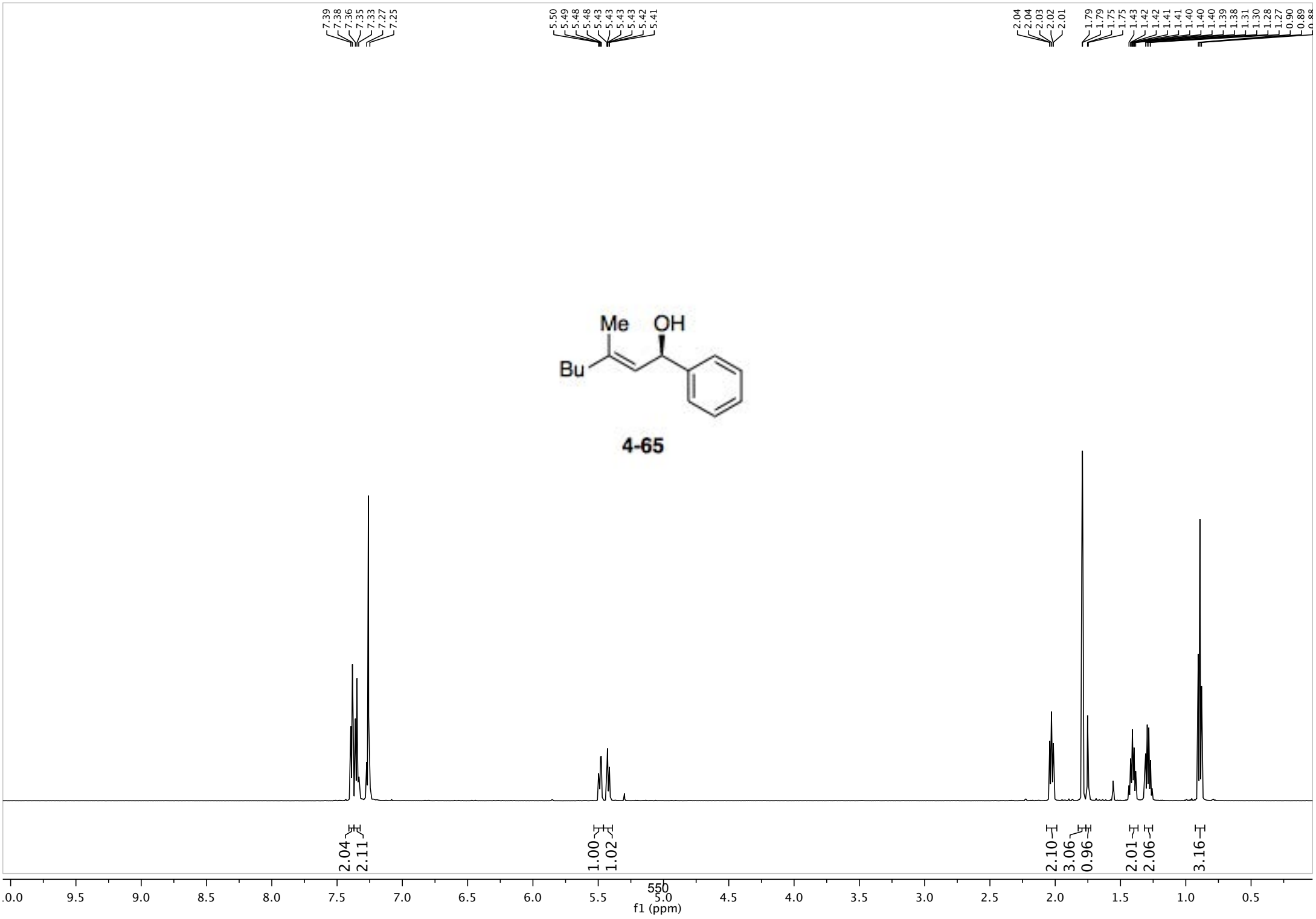
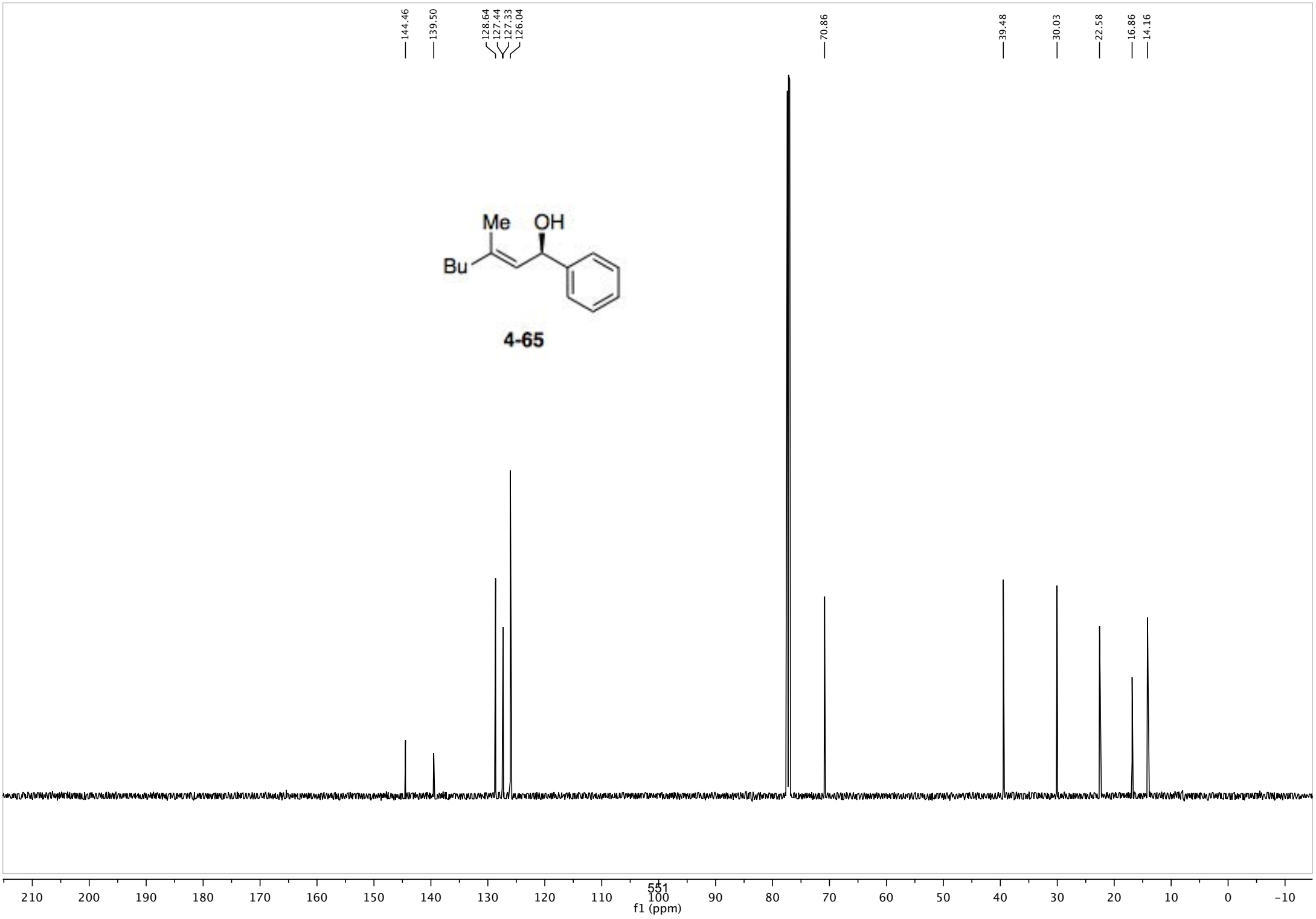
128.63
127.66
126.53
124.30
123.97
72.35
38.97
32.71
27.34
26.75
25.90
23.69
17.90
Me
Me
OPiv
Me
CDCl3
4-29n
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Me
OH
Bu
4-65
f1 (ppm)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30.03
22.58
16.86
14.16
Me
OH
Bu
4-65
210
200
190
180
170
160
150
140
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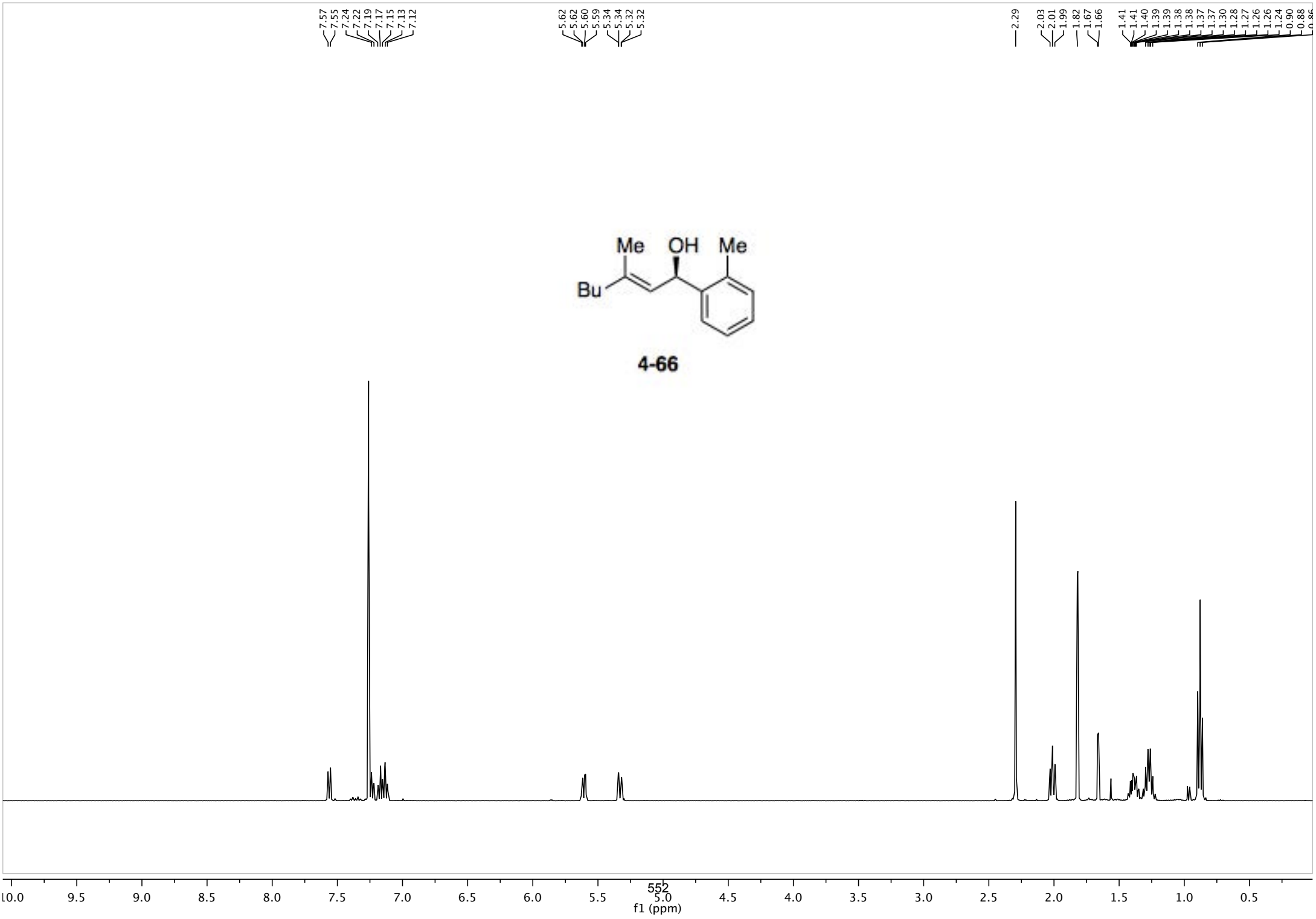
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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5.62
5.60
5.59
5.34
5.34
5.32
5.32
2.29
2.03
2.01
1.99
1.82
1.67
1.66
1.41
1.41
1.40
1.39
1.39
1.38
1.38
1.37
1.37
1.30
1.28
1.27
1.26
1.26
1.24
0.90
0.88
Me
OH
Me
Bu
4-66
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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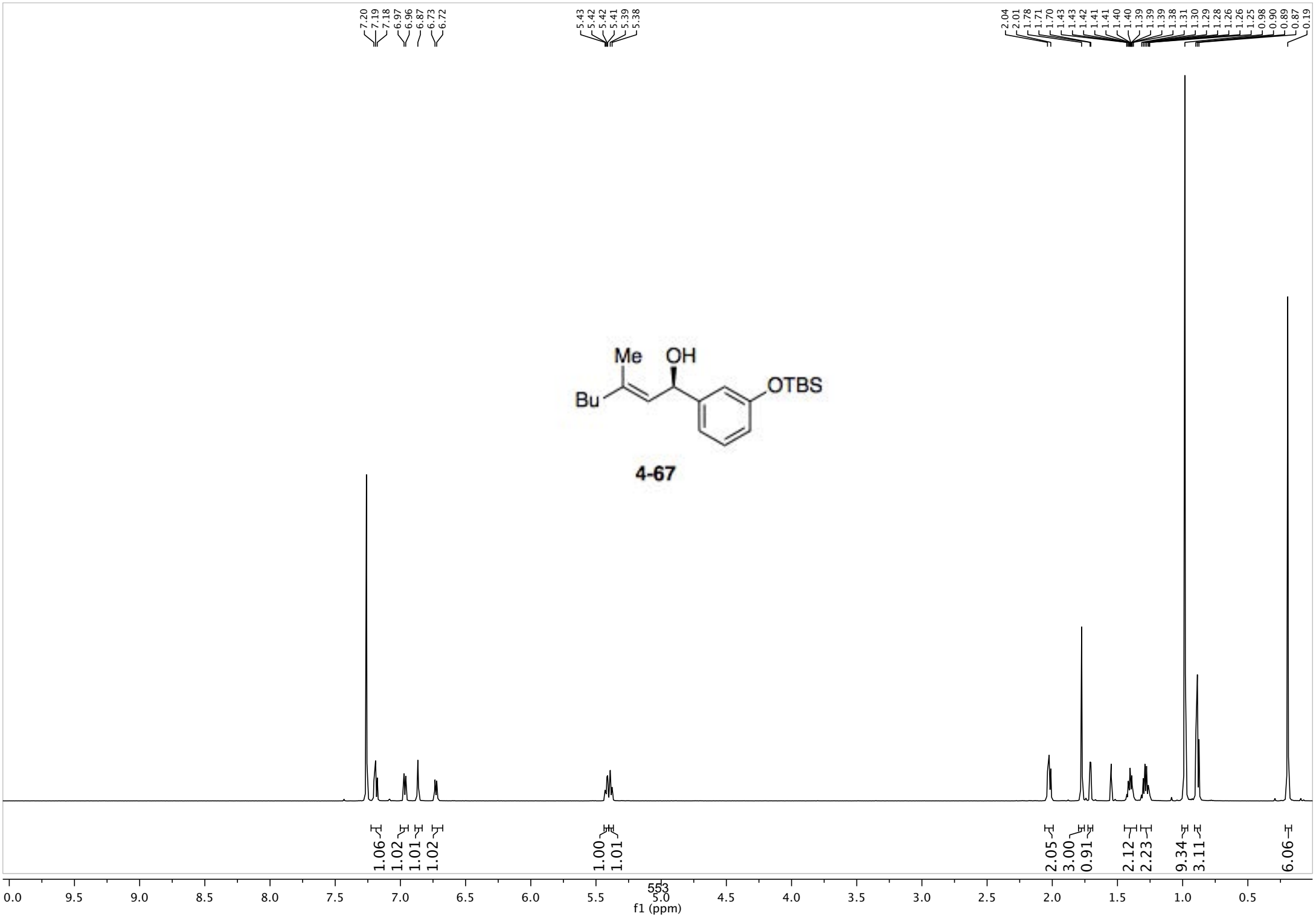
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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6.96
6.87
6.73
6.72
5.43
5.42
5.42
5.41
5.39
5.38
2.04
2.01
1.78
1.71
1.70
1.43
1.43
1.42
1.41
1.41
1.40
1.40
1.39
1.39
1.39
1.38
1.31
1.30
1.29
1.28
1.26
1.26
1.25
0.98
0.90
0.89
0.87
0.19
Me
OH
Bu
OTBS
4-67
1.06
1.02
1.01
1.02
1.00
1.01
2.05
3.00
0.91
2.12
2.23
9.34
3.11
6.06
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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5.0
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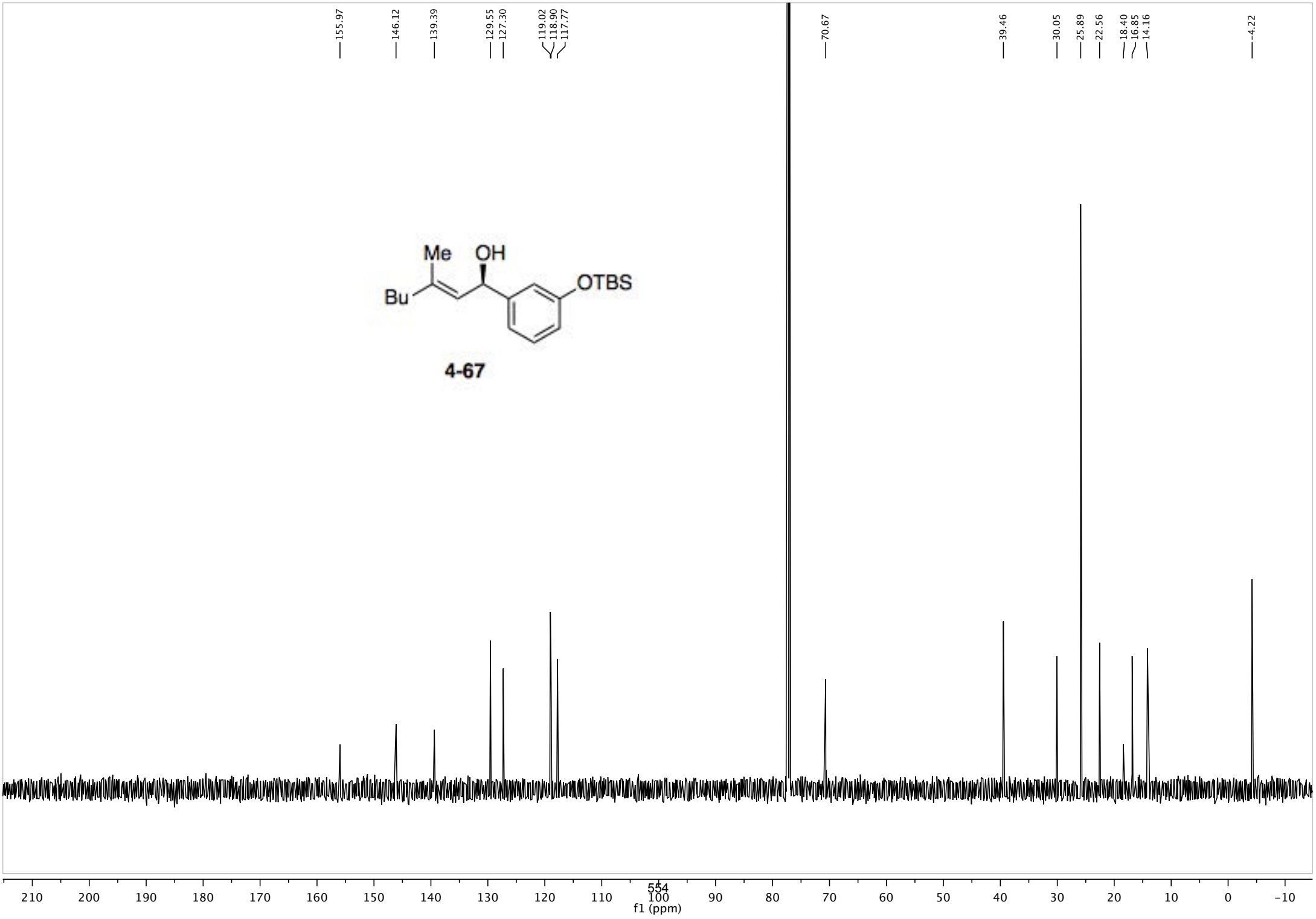
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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139.39
129.55
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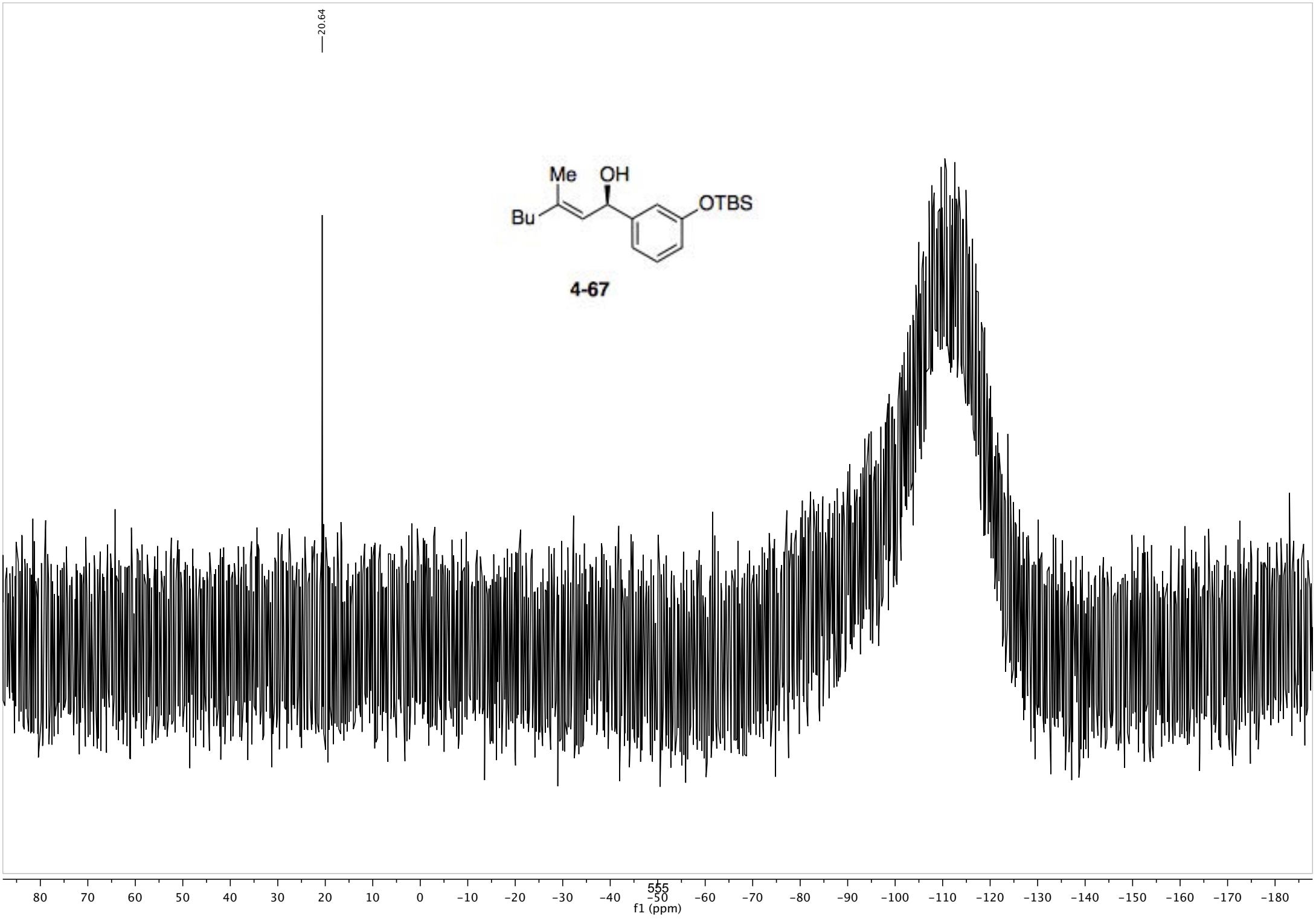
117.77
70.67
39.46
30.05
25.89
22.56
18.40
16.85
14.16
-4.22
Me
OH
Bu
OTBS
4-67
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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Me
OH
Bu
OTBS
4-67
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70
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50
40
30
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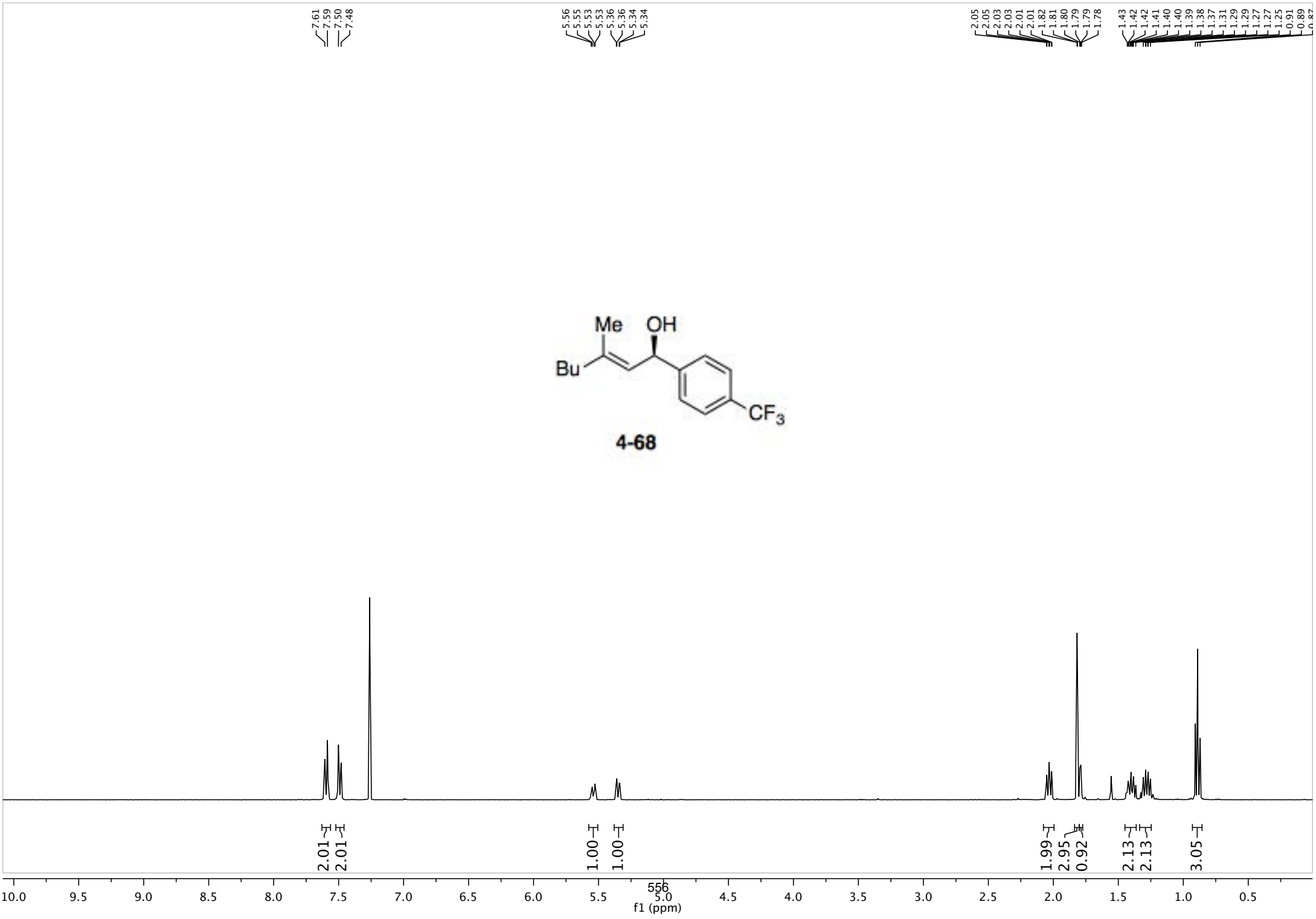
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
f1 (ppm)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5.34
5.34
2.05
2.05
2.03
2.03
2.01
2.01
1.82
1.81
1.80
1.79
1.79
1.78
1.43
1.42
1.42
1.41
1.40
1.39
1.38
1.37
1.31
1.29
1.29
1.27
1.27
1.25
0.91
0.89
Me
OH
Bu
CF3
4-68
2.01
2.01
1.00
1.00
1.99
2.95
0.92
2.13
2.13
3.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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3.0
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1.5
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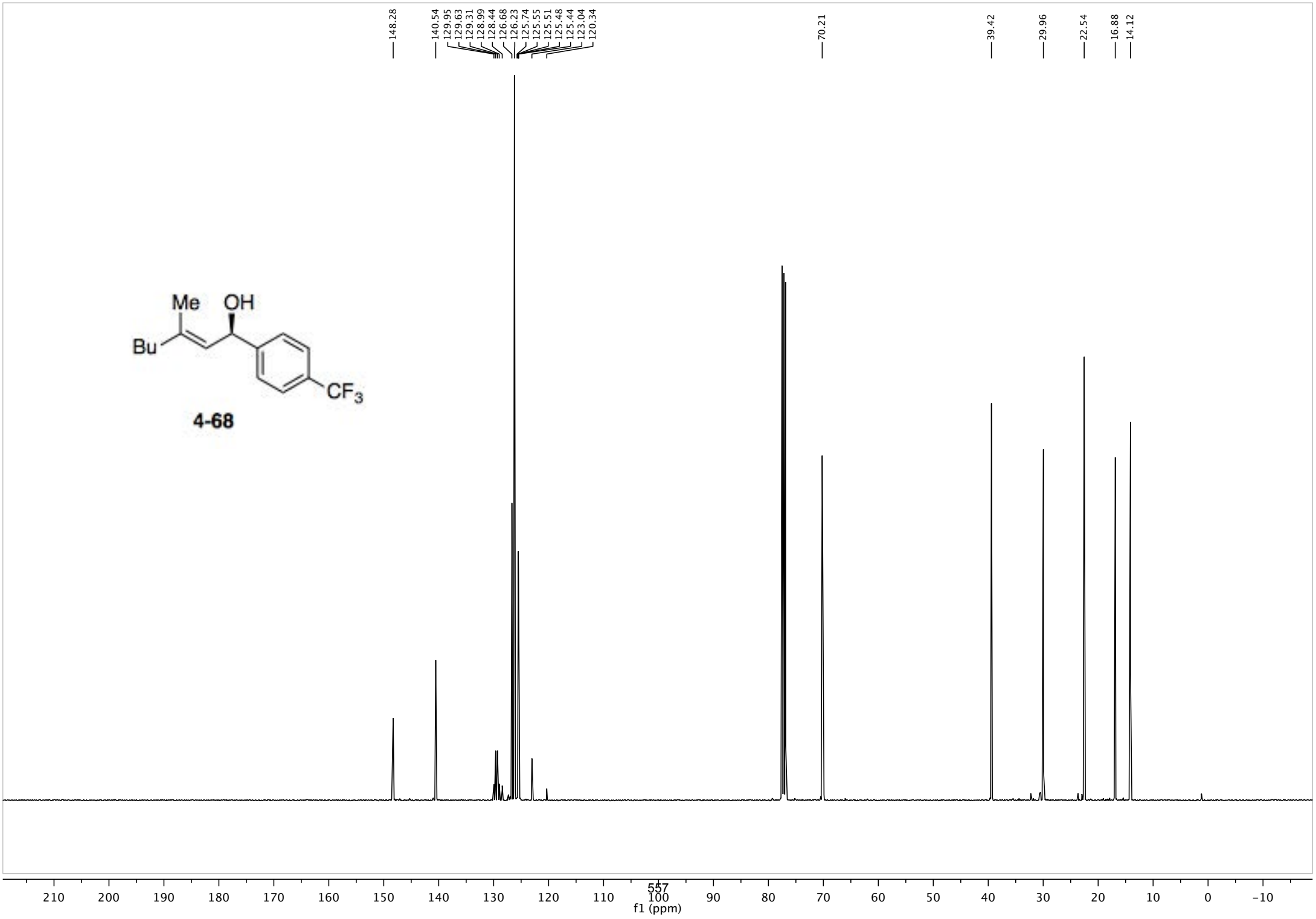
f1 (ppm)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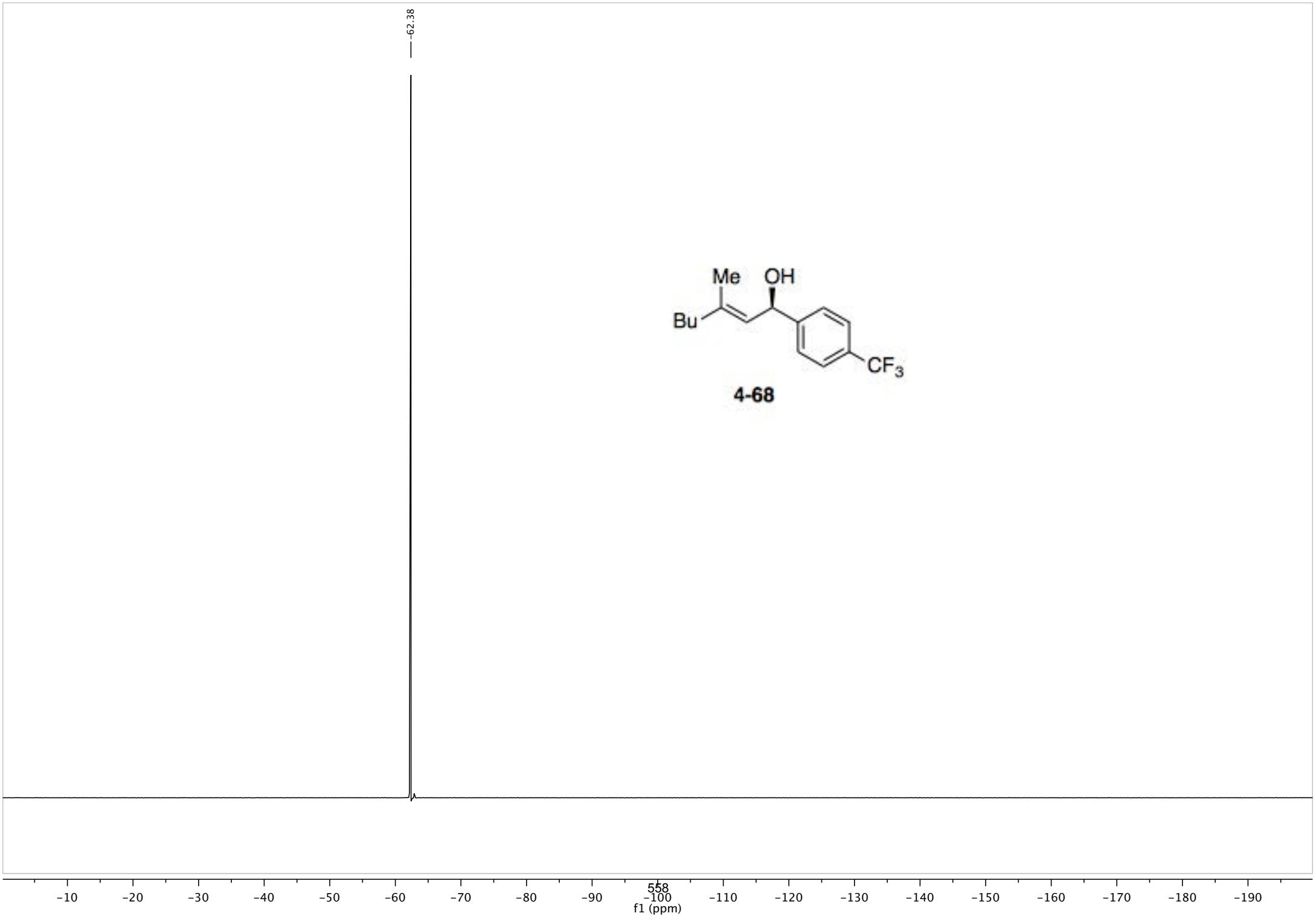
125.74
125.55
125.51
125.48
125.44
123.04
120.34
70.21
39.42
29.96
22.54
16.88
14.12
Me
OH
Bu
CF3
4-68
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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Bu
CF3
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-50
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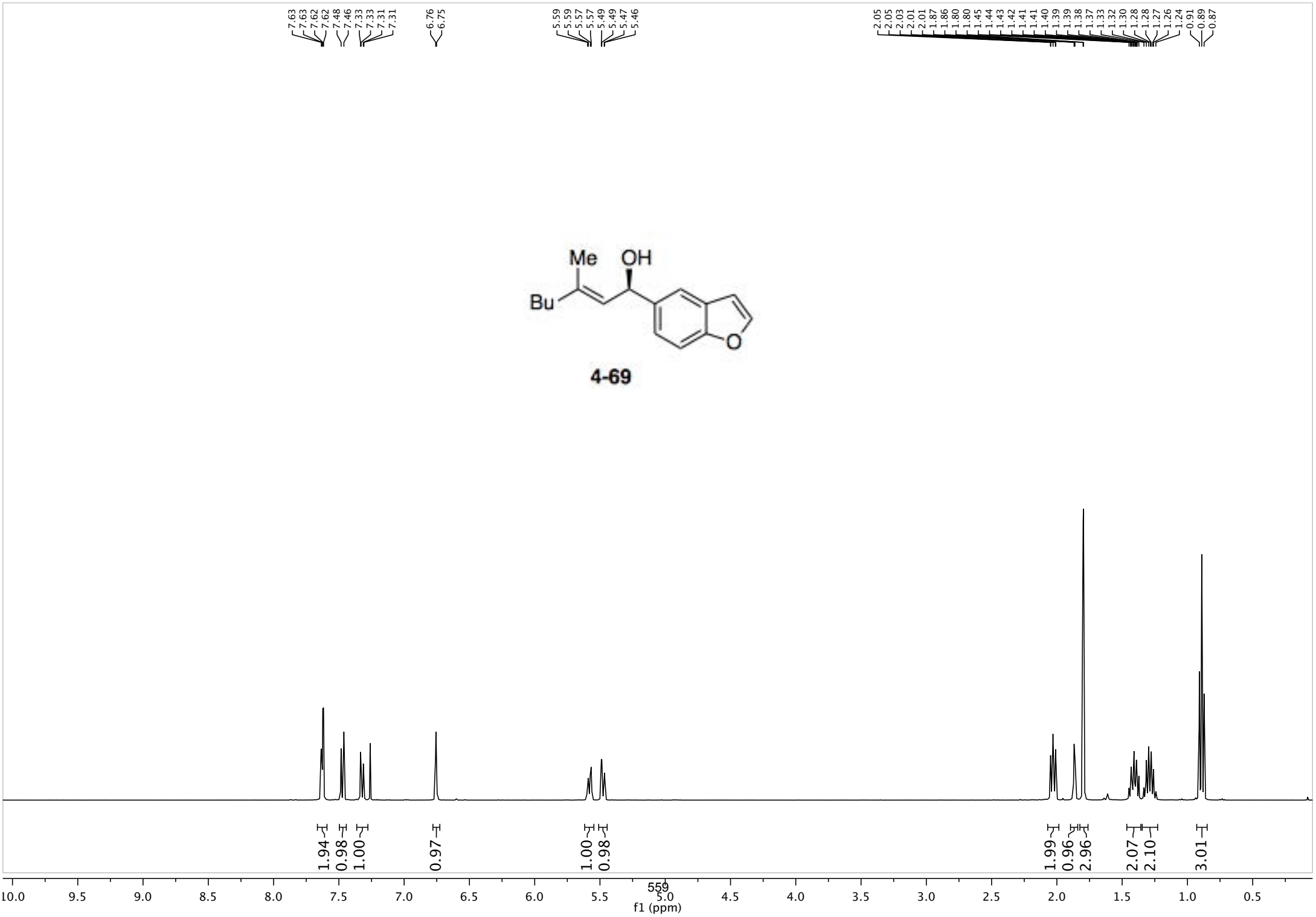
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)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6.76
6.75
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5.57
5.57
5.49
5.49
5.47
5.46
2.05
2.05
2.03
2.01
2.01
1.87
1.86
1.80
1.80
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1.43
1.42
1.41
1.41
1.40
1.39
1.39
1.38
1.37
1.33
1.32
1.30
1.28
1.28
1.27
1.26
1.24
0.91
0.89
0.87
Me
OH
Bu
O
4-69
1.94
0.98
1.00
0.97
1.00
0.98
1.99
0.96
2.96
2.07
2.10
3.01
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9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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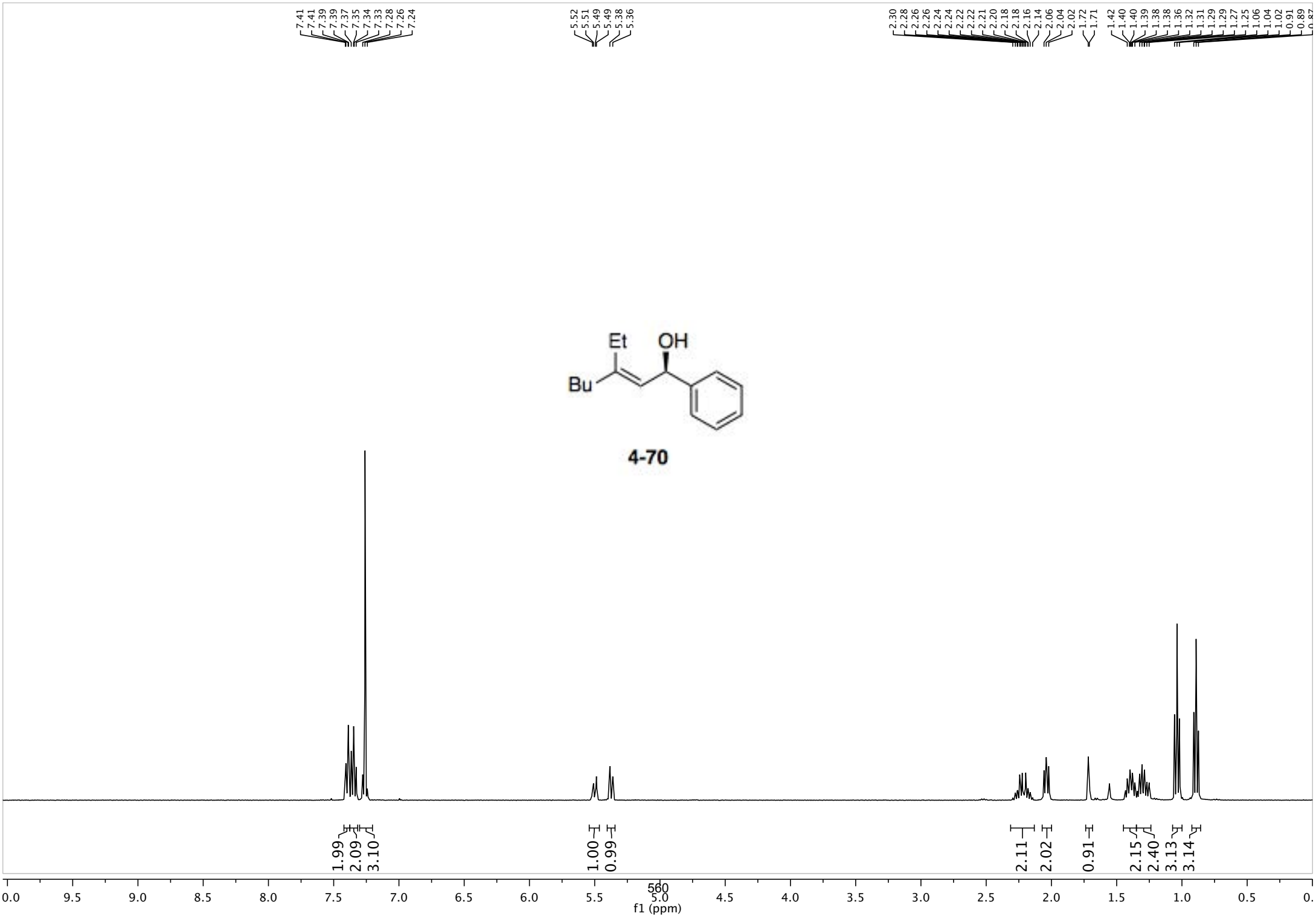
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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5.49
5.49
5.38
5.36
2.30
2.28
2.26
2.26
2.24
2.24
2.22
2.22
2.21
2.20
2.18
2.16
2.14
2.06
2.04
2.02
1.72
1.71
1.42
1.40
1.40
1.39
1.38
1.36
1.32
1.31
1.29
1.29
1.27
1.25
1.06
1.04
1.02
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Et
OH
Bu
4-70
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2.09
3.10
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2.40
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3.5
3.0
2.5
2.0
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1.0
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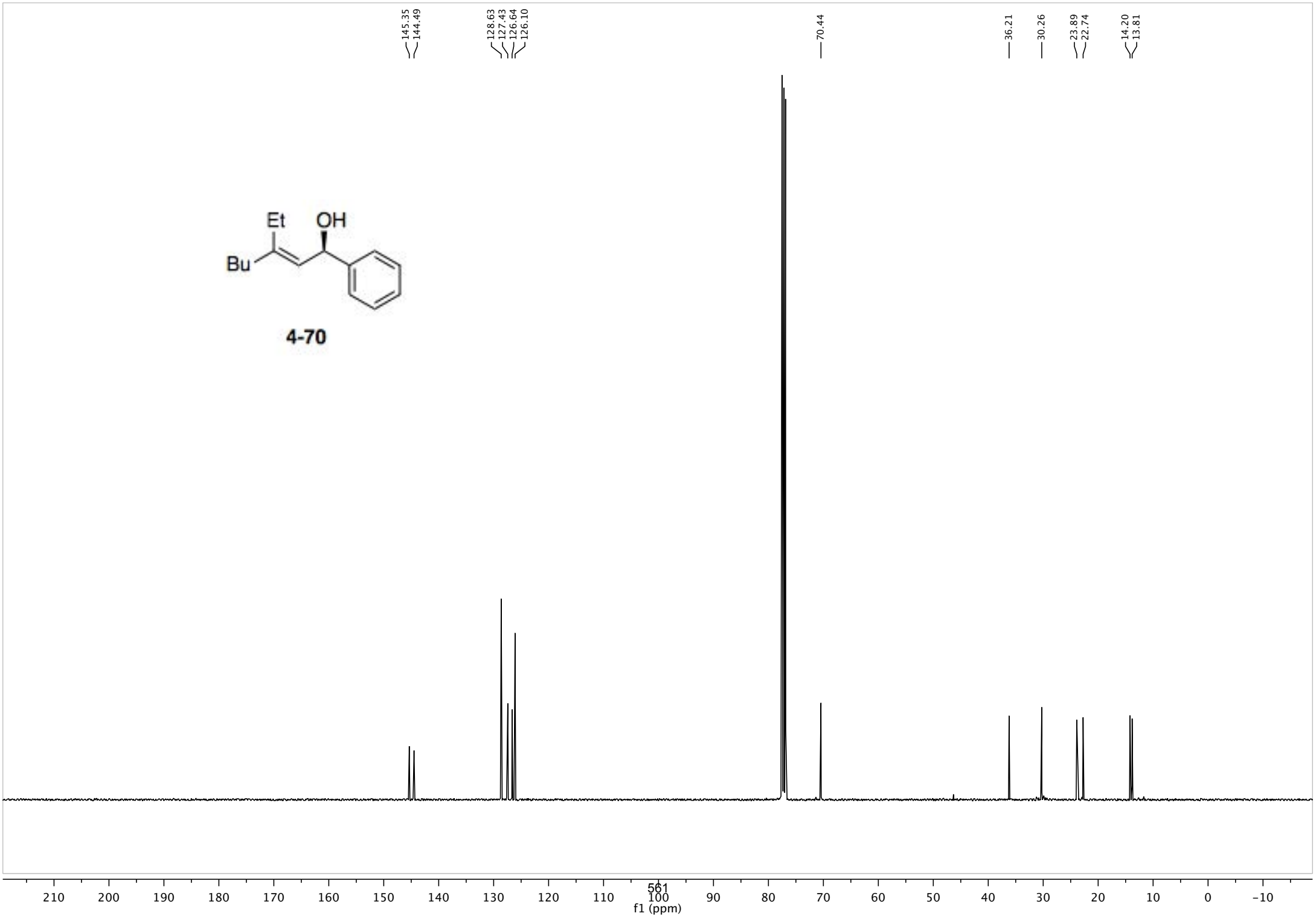
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127.43
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36.21
30.26
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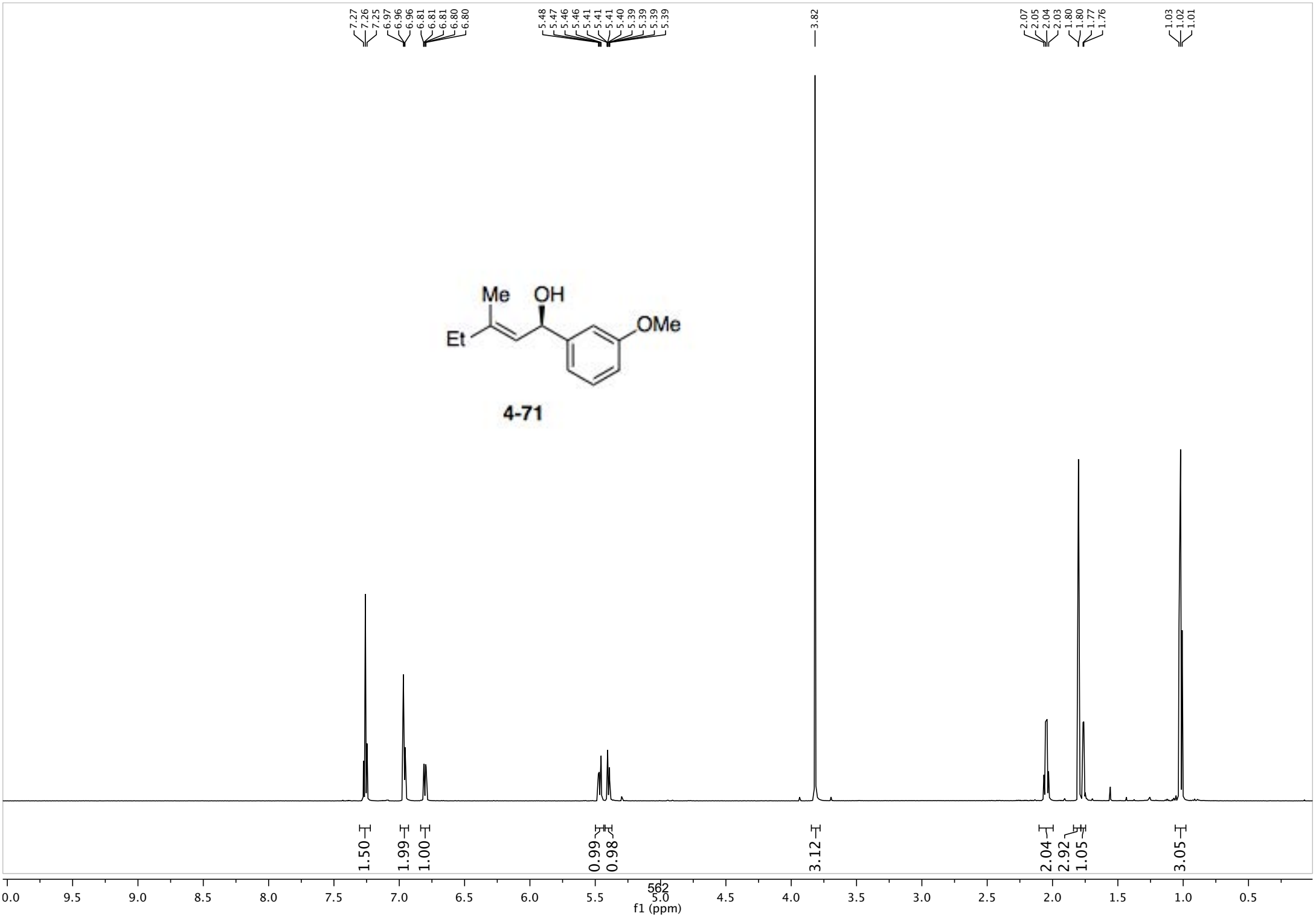
22.74
14.20
13.81
Et
OH
Bu
4-70
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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5.47
5.46
5.46
5.41
5.41
5.41
5.40
5.39
5.39
5.39
3.82
2.07
2.05
2.04
2.03
1.80
1.80
1.77
1.76
1.03
1.02
1.01
Me
OH
Et
OMe
4-71
1.50
1.99
1.00
0.99
0.98
3.12
2.04
2.92
1.05
3.05
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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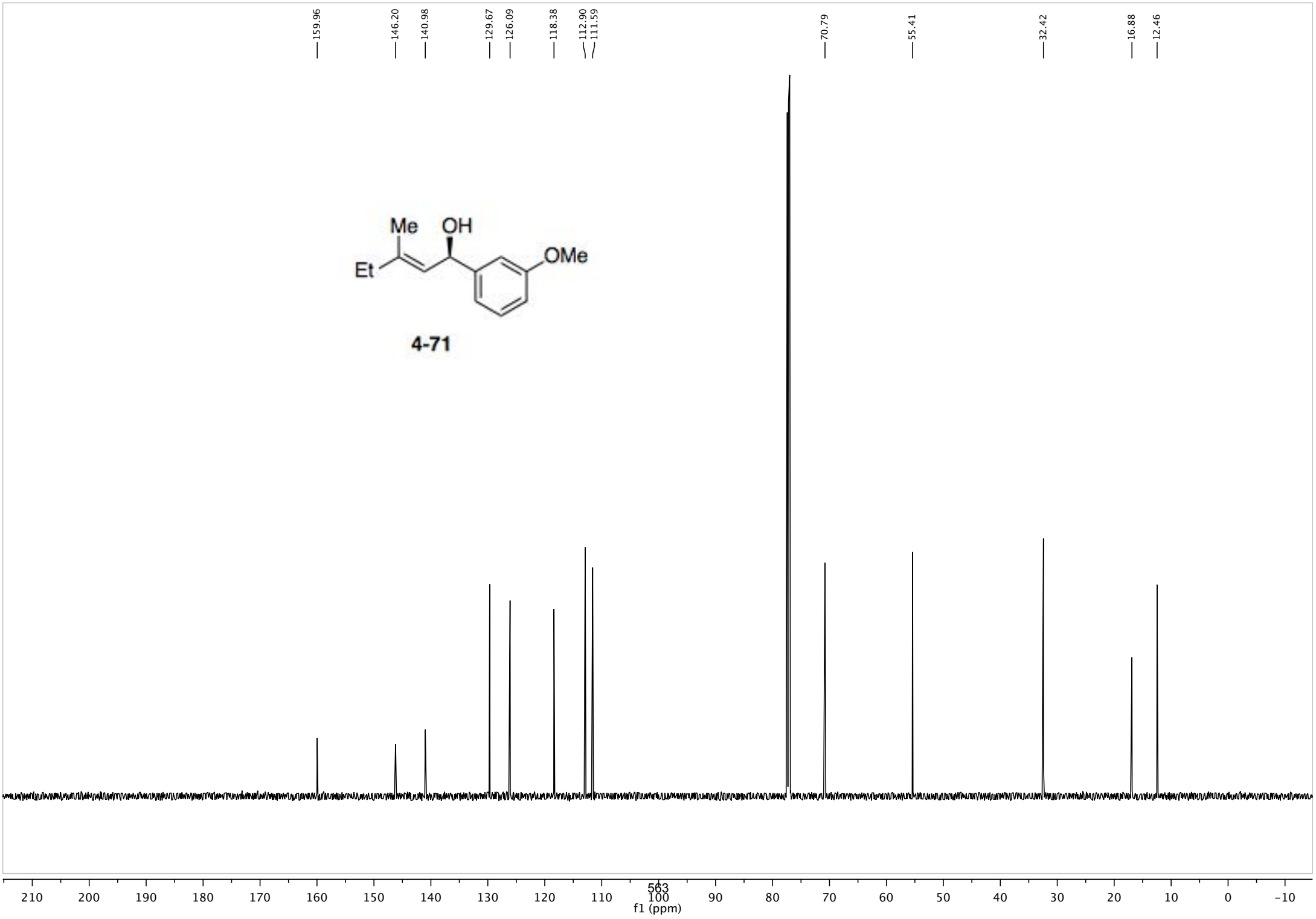
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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32.42
16.88
12.46
Me
OH
Et
OMe
4-71
210
200
190
180
170
160
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140
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120
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100
90
80
70
60
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40
30
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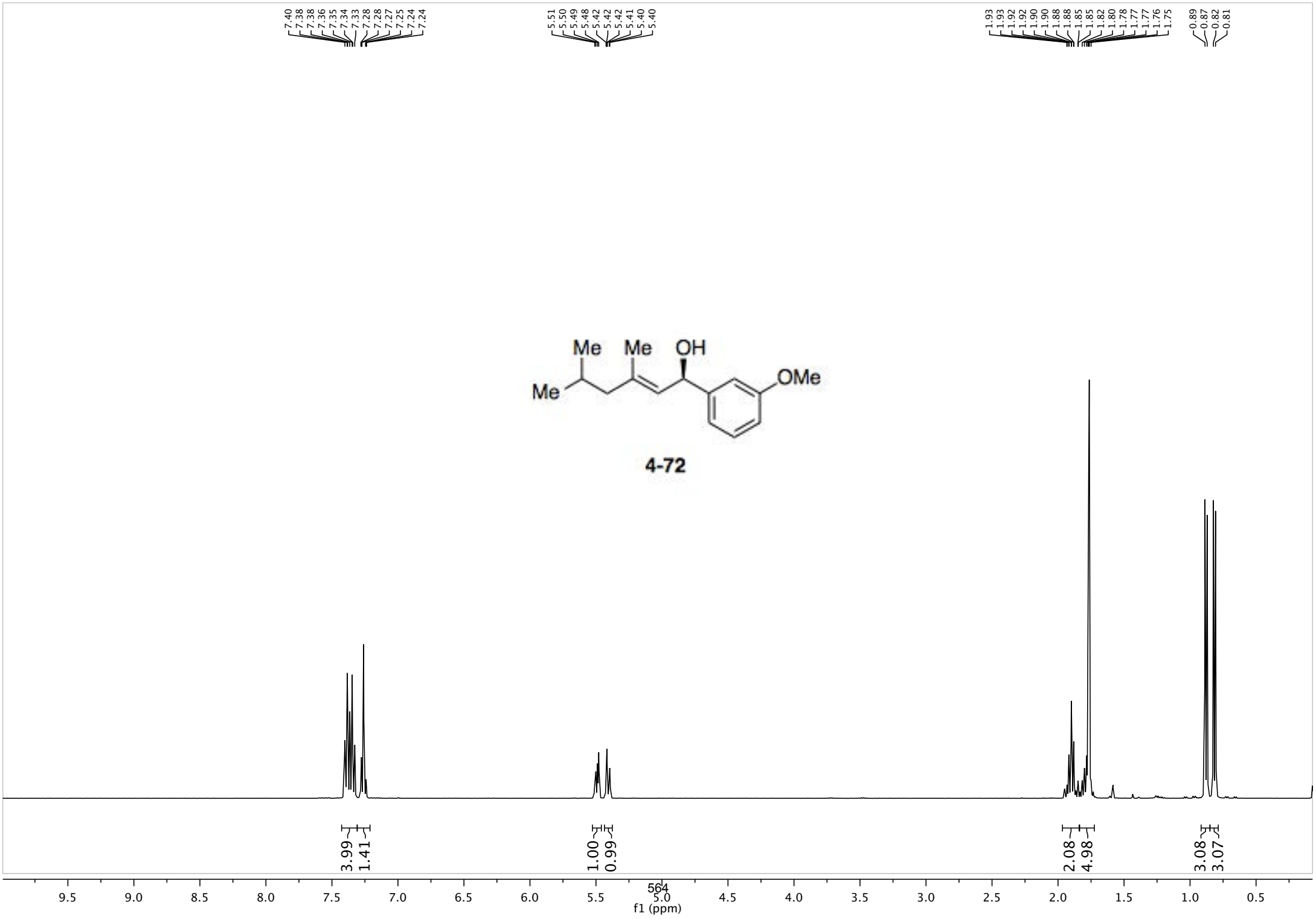
0
-10
f1 (ppm)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1.90
1.88
1.85
1.85
1.82
1.80
1.78
1.77
1.77
1.76
1.75
0.89
0.87
0.82
0.81
Me
Me
OH
Me
OMe
4-72
3.99
1.41
1.00
0.99
2.08
4.98
3.08
3.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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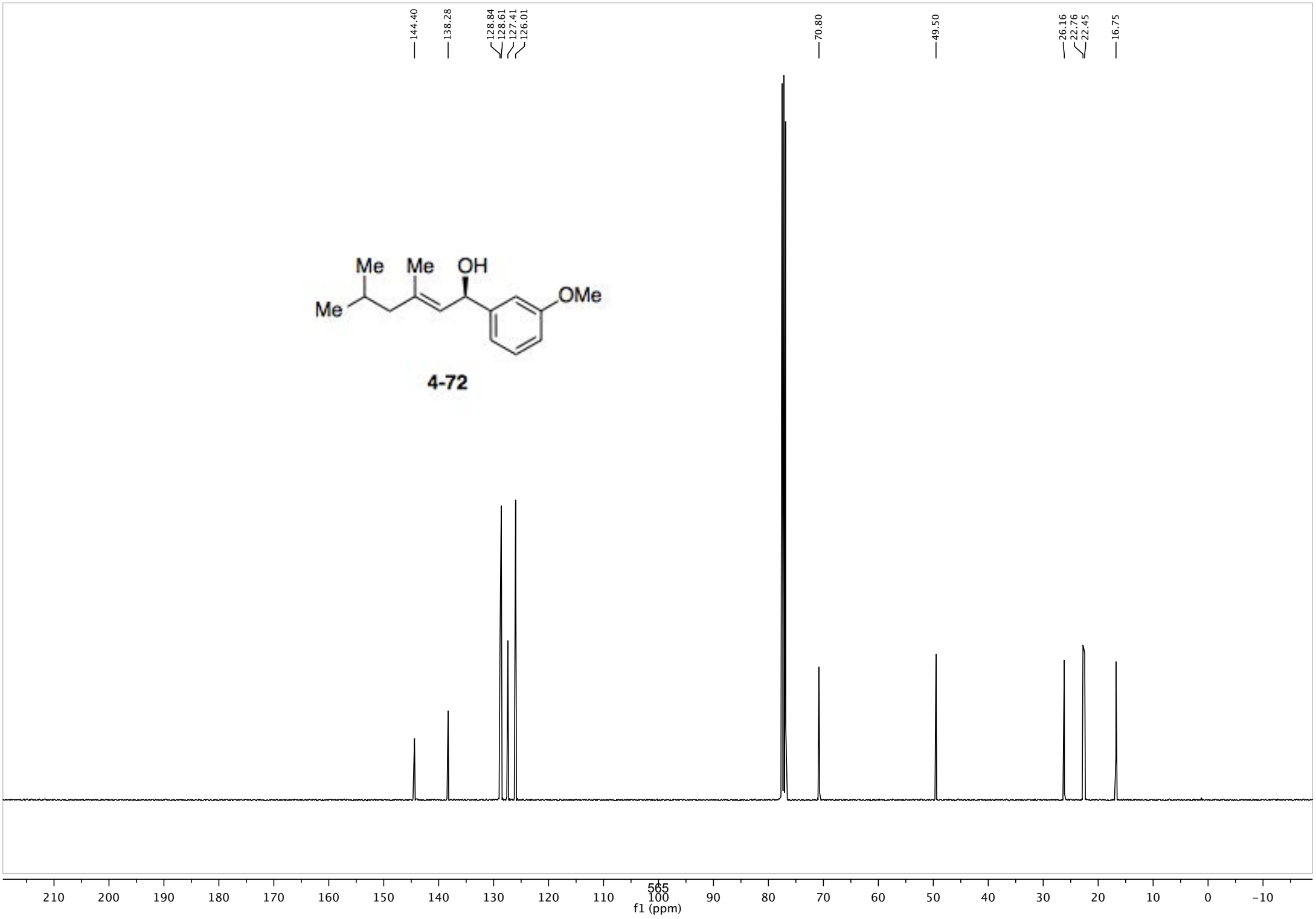
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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26.16
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22.45
16.75
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Me
OH
Me
OMe
4-72
210
200
190
180
170
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100
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80
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40
30
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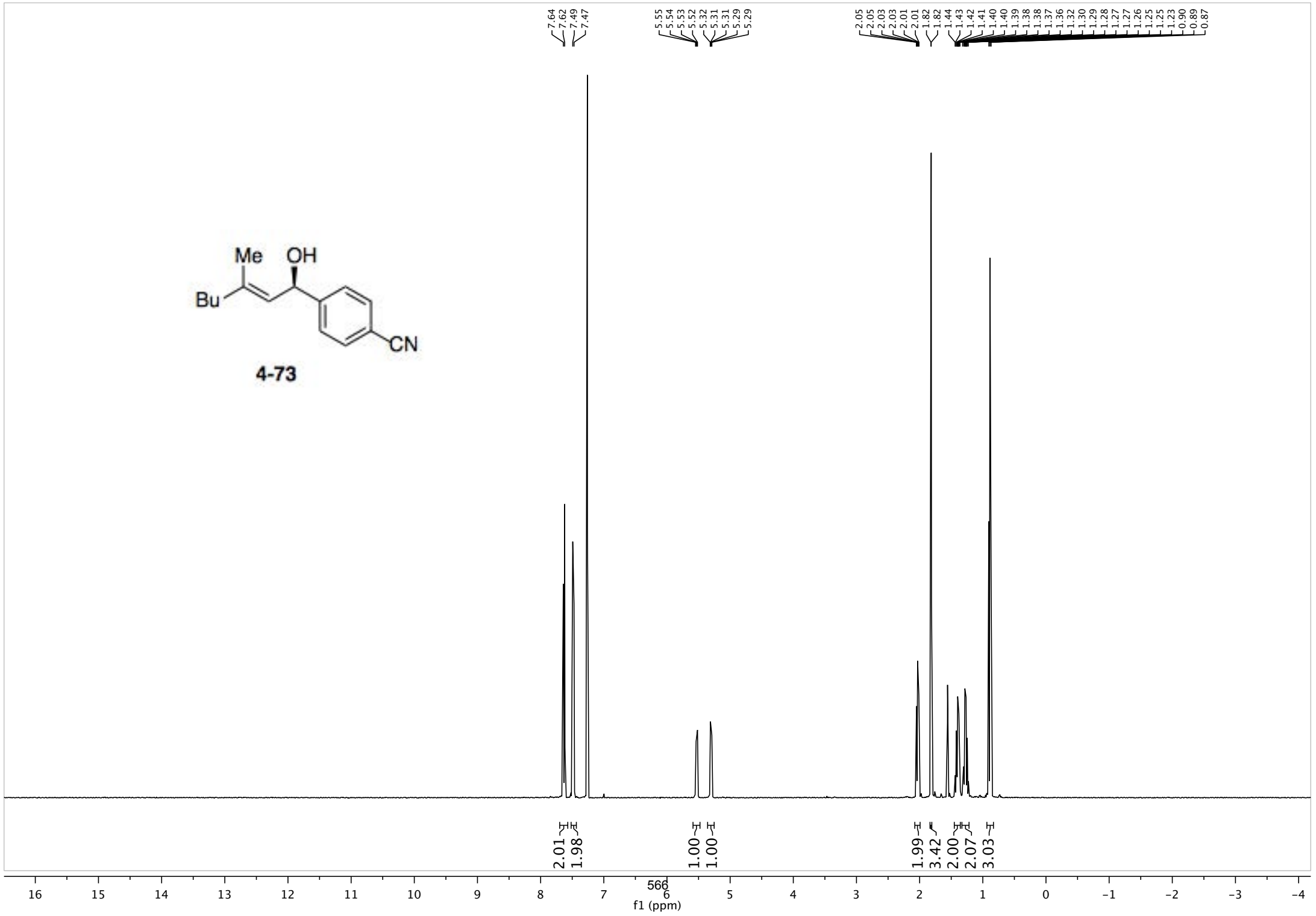
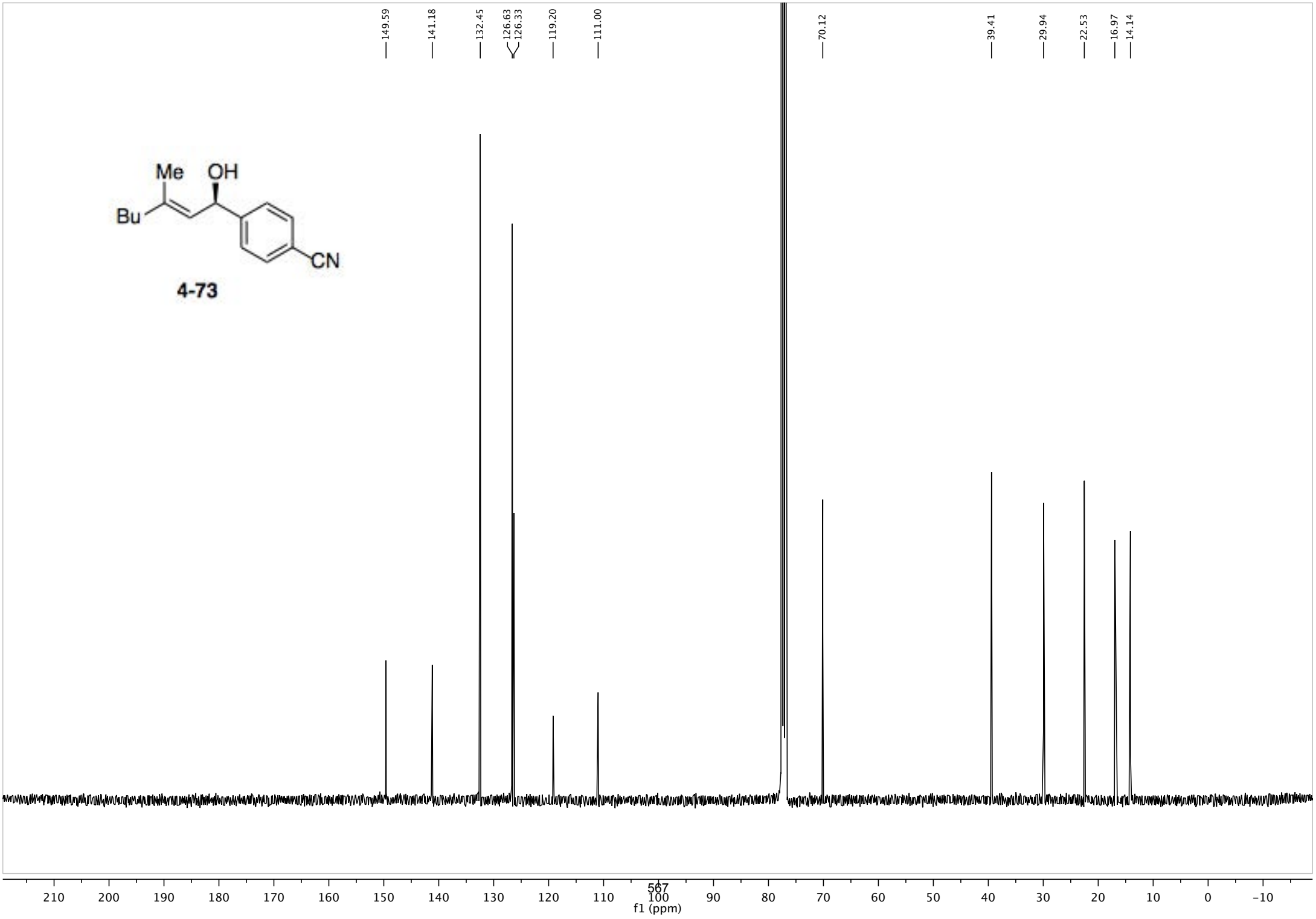
f1 (ppm)


Me
OH
Bu
CN
4-73
7.64
7.62
7.49
7.47
5.55
5.54
5.53
5.52
5.32
5.31
5.29
5.29
2.05
2.05
2.03
2.03
2.01
2.01
1.82
1.82
1.44
1.43
1.42
1.41
1.40
1.40
1.39
1.38
1.38
1.37
1.36
1.32
1.30
1.29
1.28
1.27
1.27
1.26
1.25
1.25
1.23
0.90
0.89
0.87
2.01
1.98
1.00
1.00
1.99
3.42
2.00
2.07
3.03
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
−4
f1 (ppm)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141.18
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126.33
119.20
111.00
70.12
39.41
29.94
22.53
16.97
14.14
Me
OH
Bu
CN
4-73
210
200
190
180
170
160
150
140
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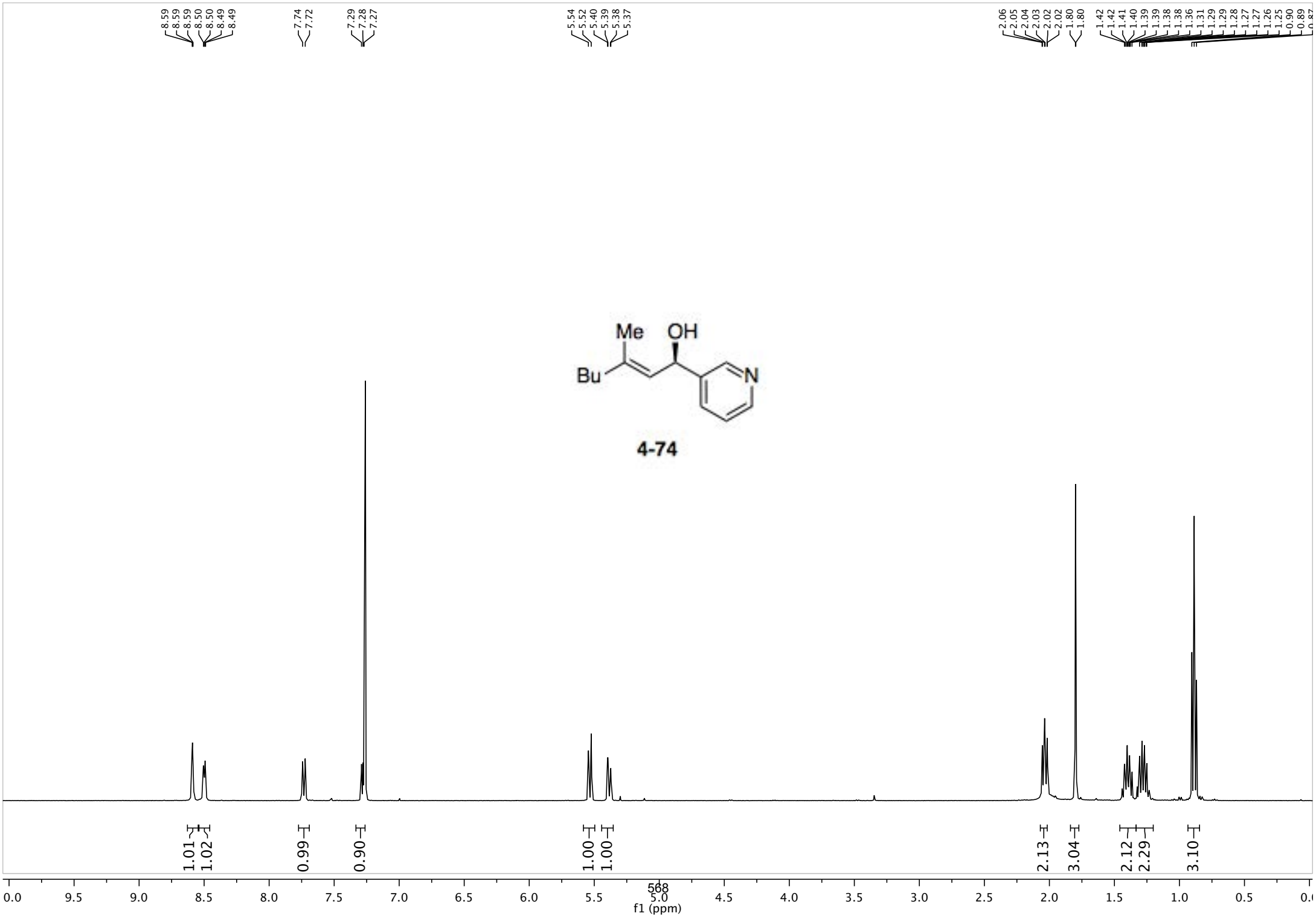
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


8.59
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8.59
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7.29
7.28
7.27
5.54
5.52
5.40
5.39
5.38
5.37
2.06
2.05
2.04
2.03
2.02
2.02
1.80
1.80
1.42
1.42
1.41
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1.39
1.38
1.38
1.36
1.31
1.29
1.29
1.28
1.27
1.27
1.26
1.25
0.90
0.89
Me
OH
Bu
N
4-74
1.01
1.02
0.99
0.90
1.00
1.00
2.13
3.04
2.12
2.29
3.10
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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5.0
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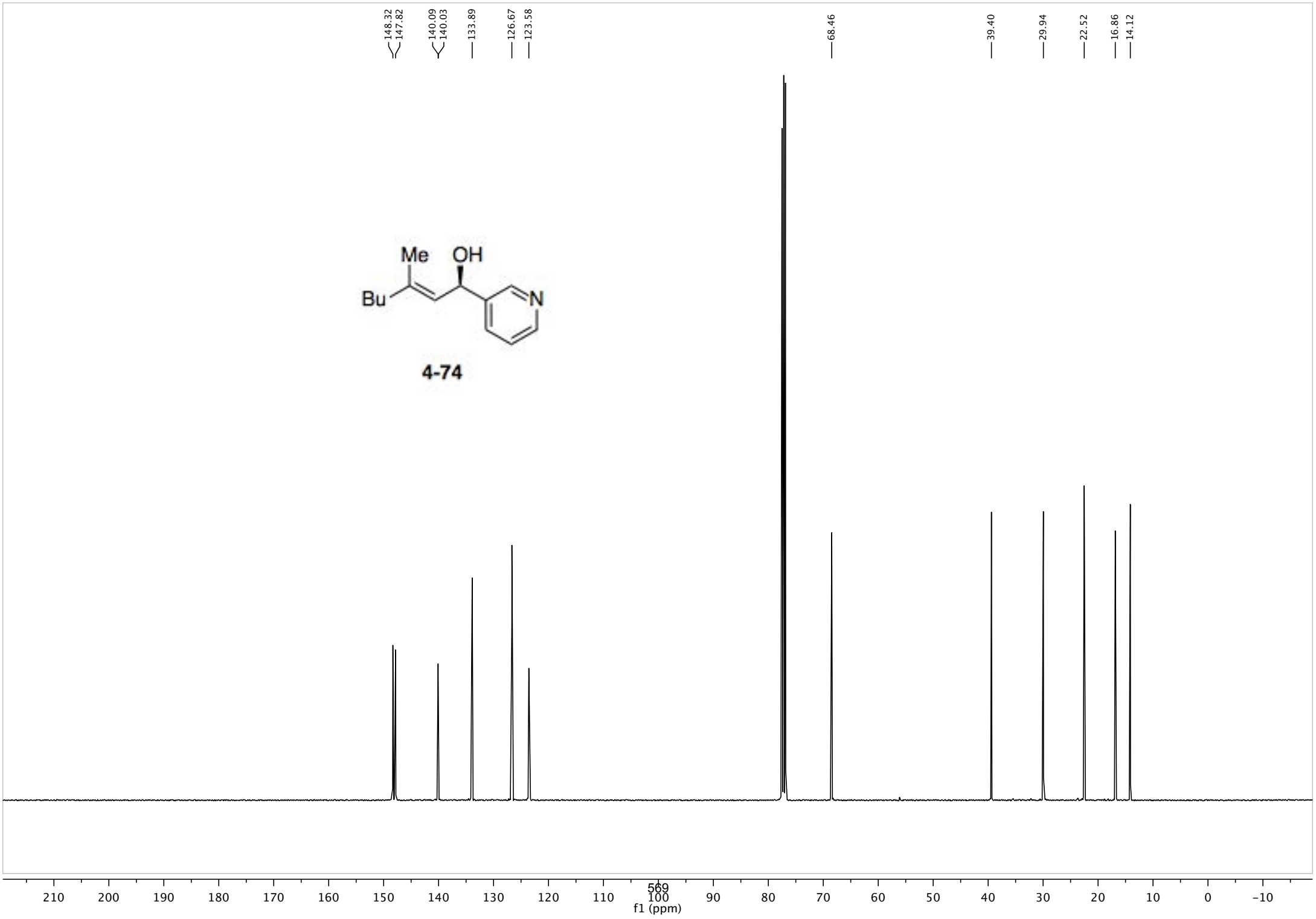
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


148.32
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140.03
133.89
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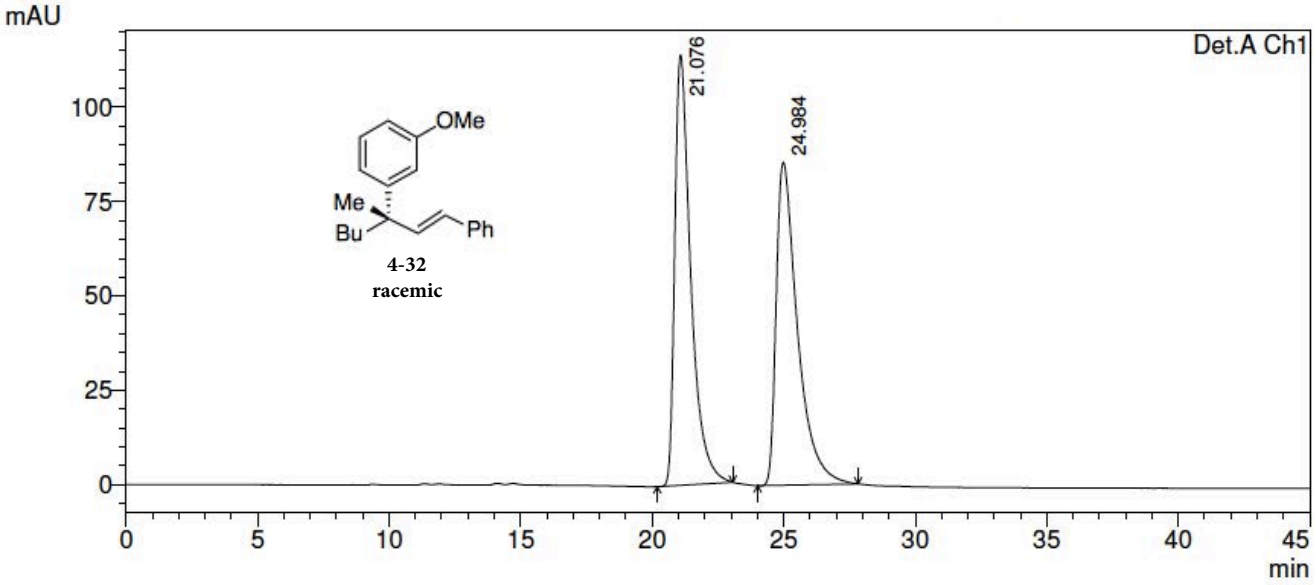
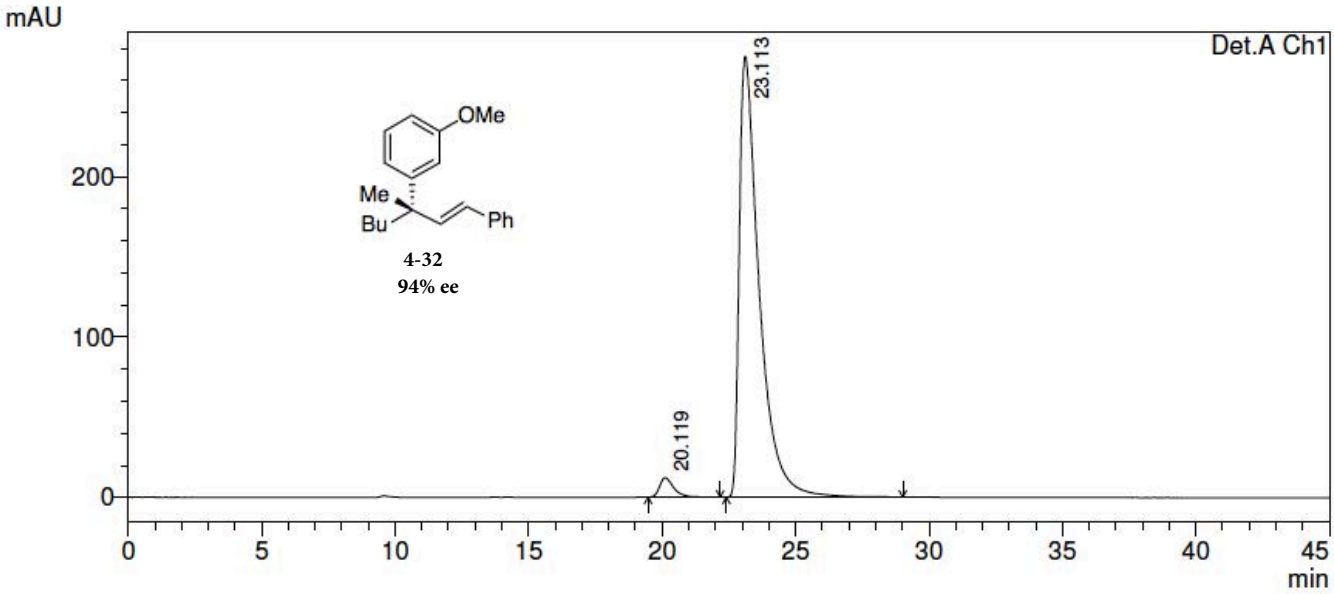
123.58
68.46
39.40
29.94
22.52
16.86
14.12
Me
OH
Bu
N
4-74
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

Compound 4-32, racemic



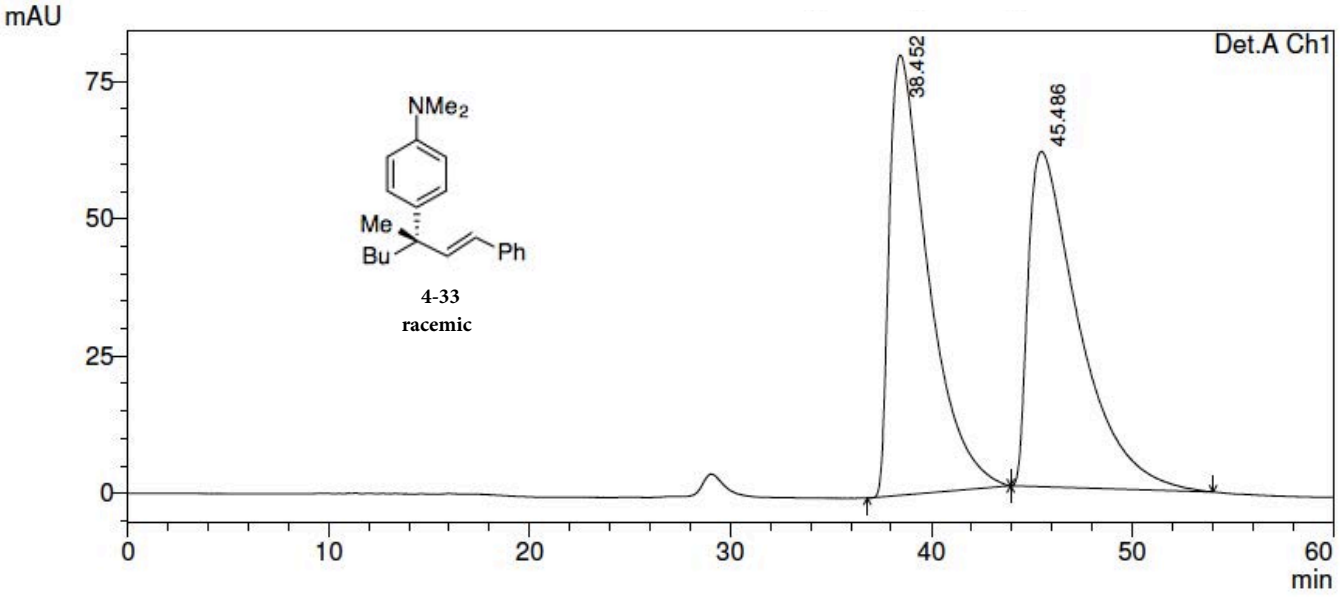
Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.076	4819547	114091	50.036	57.126
2	24.984	4812611	85626	49.964	42.874
Total		9632158	199717	100.000	100.000

Compound 4-32, 94% ee



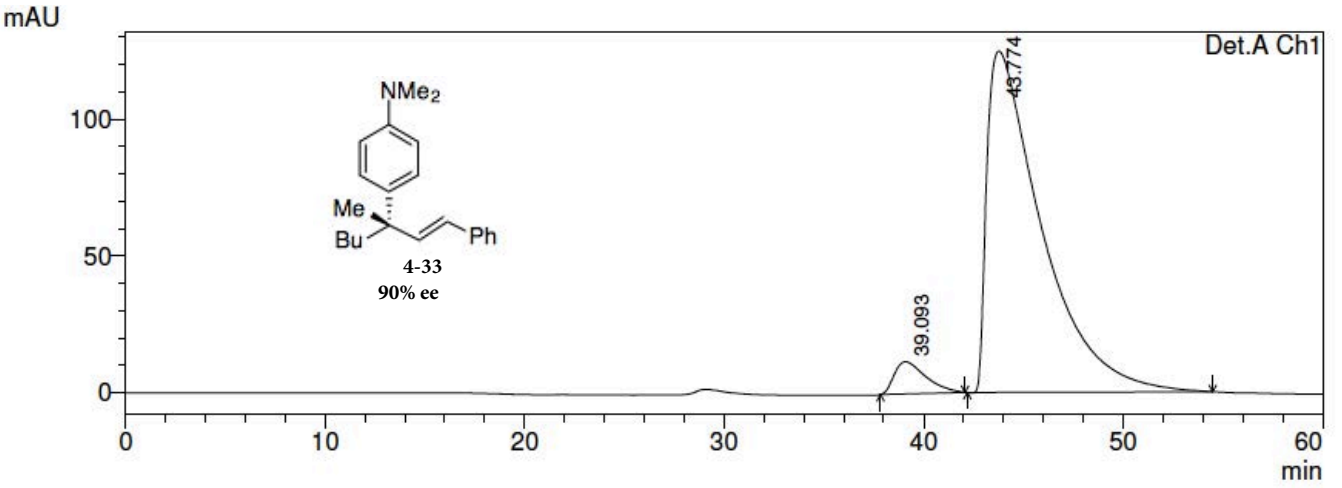
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.119	448026	12139	3.043	4.229
2	23.113	14275387	274912	96.957	95.771
Total		14723413	287051	100.000	100.000

Compound 4-33, racemic



Peak#	Ret. Time	Area	Height	Area %	Height %
1	38.452	10827966	80146	50.276	56.763
2	45.486	10708951	61050	49.724	43.237
Total		21536917	141196	100.000	100.000

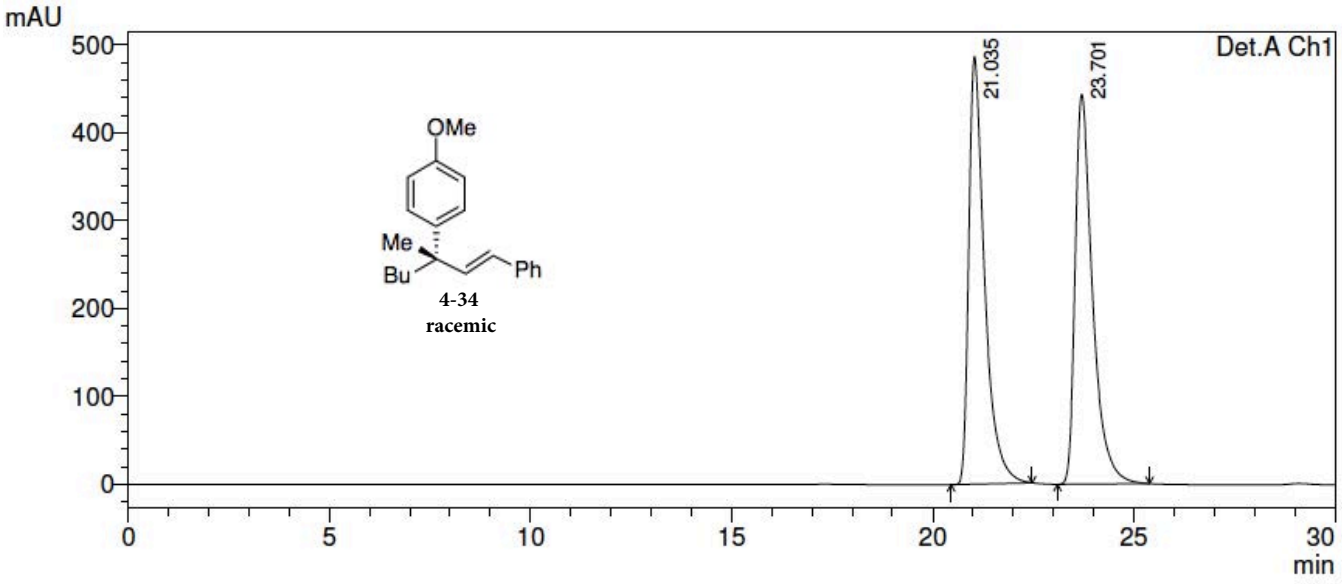
Compound 4-33, 90% ee



Detector A Ch1 254nm

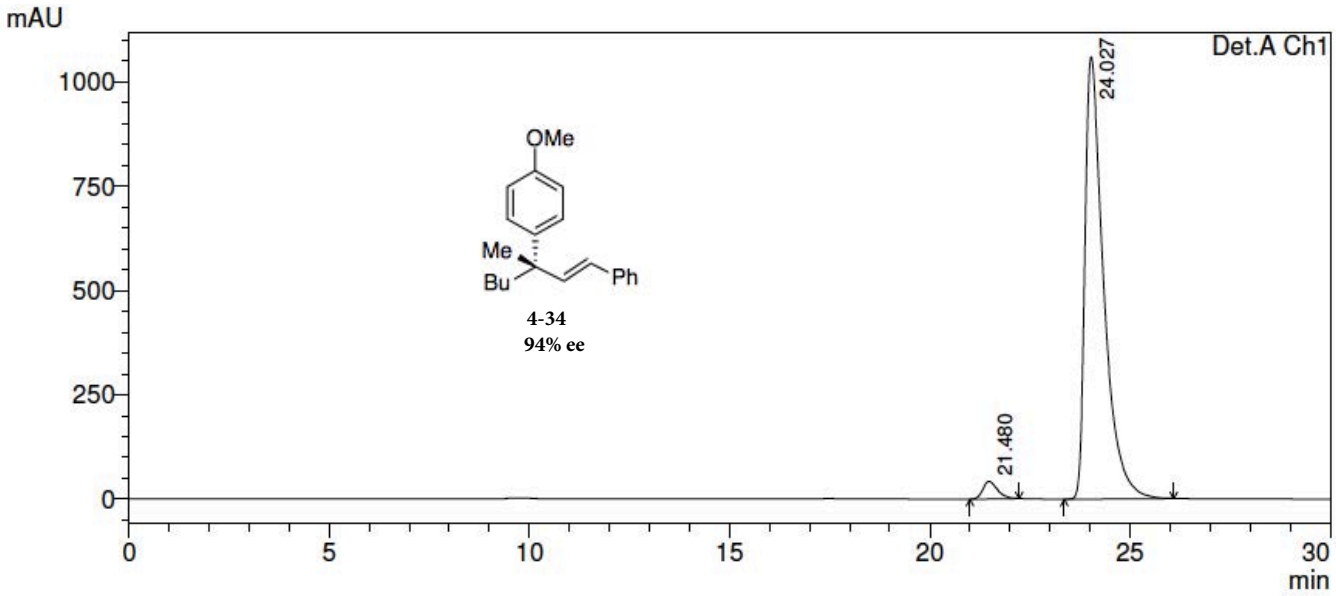
Peak#	Ret. Time	Area	Height	Area %	Height %
1	39.093	1294517	11782	5.156	8.625
2	43.774	23813212	124819	94.844	91.375
Total		25107729	136601	100.000	100.000

Compound 4-34, racemic



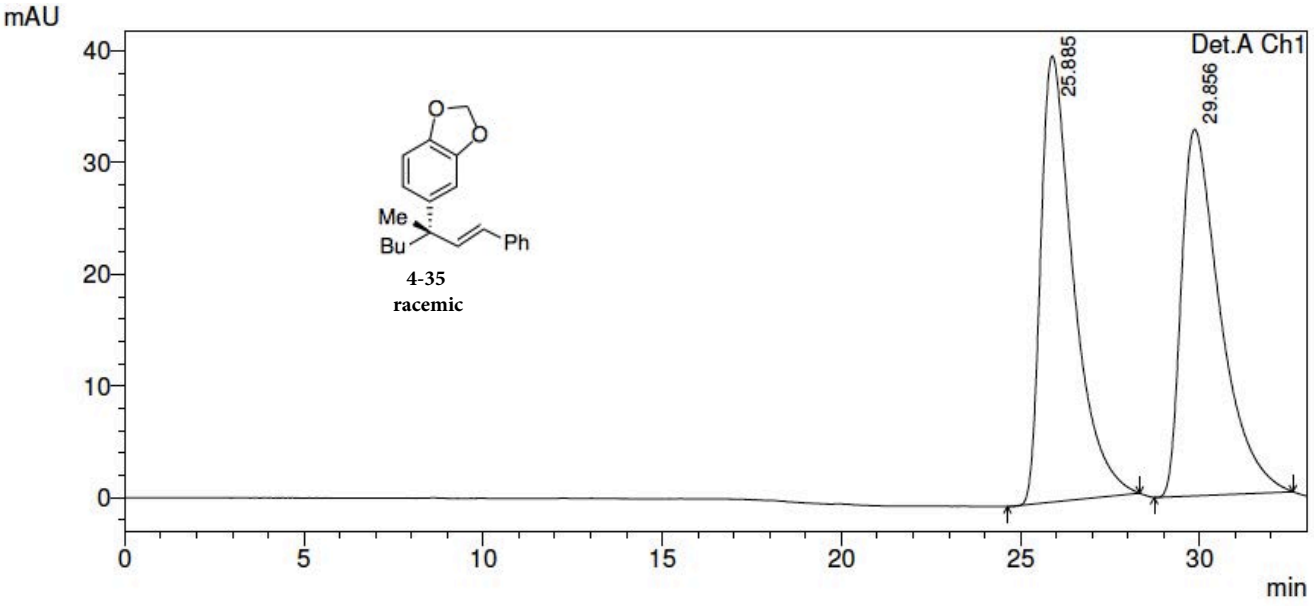
Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.035	13304169	487298	49.915	52.348
2	23.701	13349360	443582	50.085	47.652
Total		26653529	930881	100.000	100.000

Compound 4-34, 94% ee



Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.480	1076266	42140	3.038	3.824
2	24.027	34355565	1059798	96.962	96.176
Total		35431830	1101939	100.000	100.000

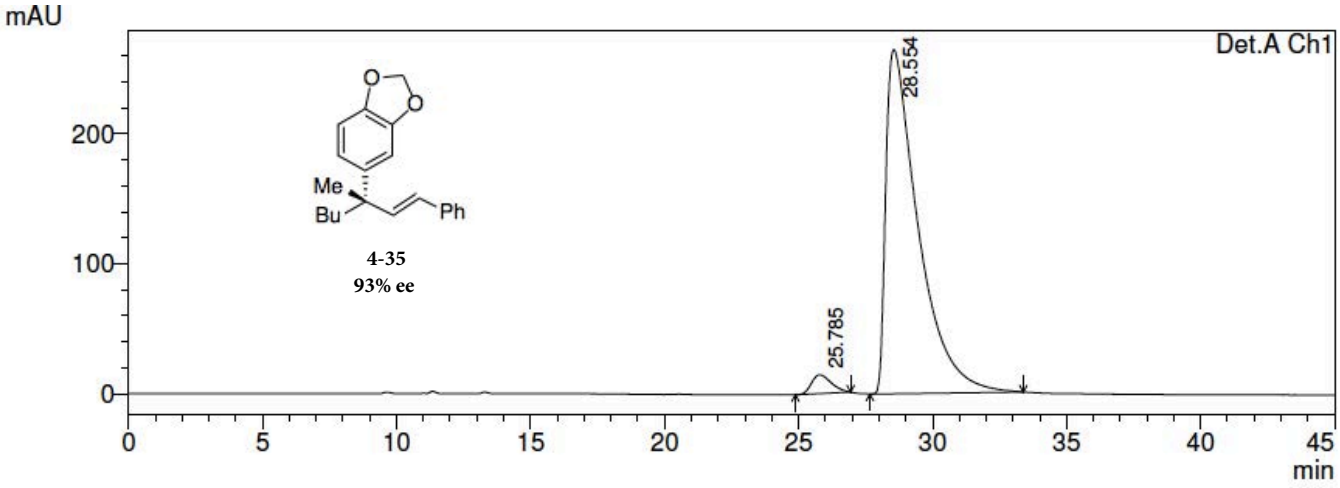
Compound 4-35, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.885	2547603	39950	50.655	54.898
2	29.856	2481675	32821	49.345	45.102
Total		5029278	72771	100.000	100.000

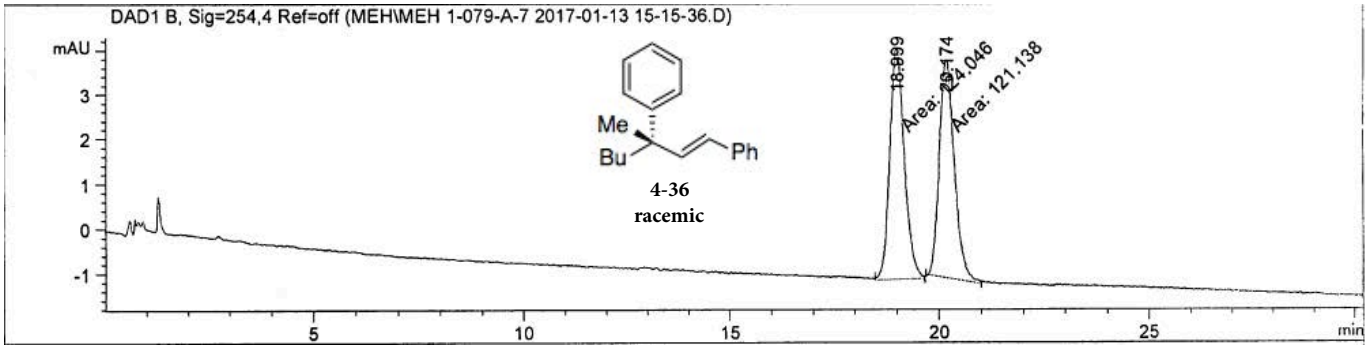
Compound 4-35, 93% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.785	746634	14550	3.248	5.208
2	28.554	22242277	264852	96.752	94.792
Total		22988911	279402	100.000	100.000

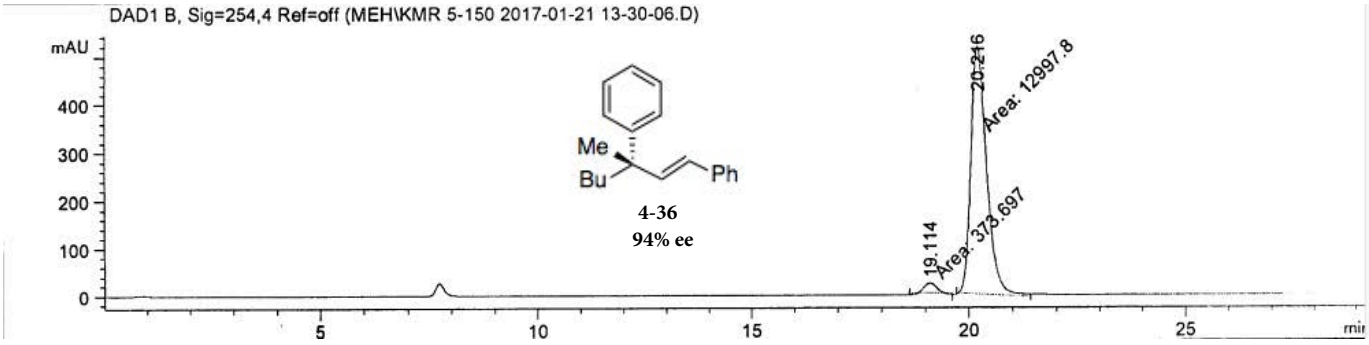
Compound 4-36, racemic



Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.999	MM	0.3994	124.04628	5.17638	50.5931
2	20.174	MM	0.4141	121.13783	4.87557	49.4069
Totals :				245.18410	10.05195	

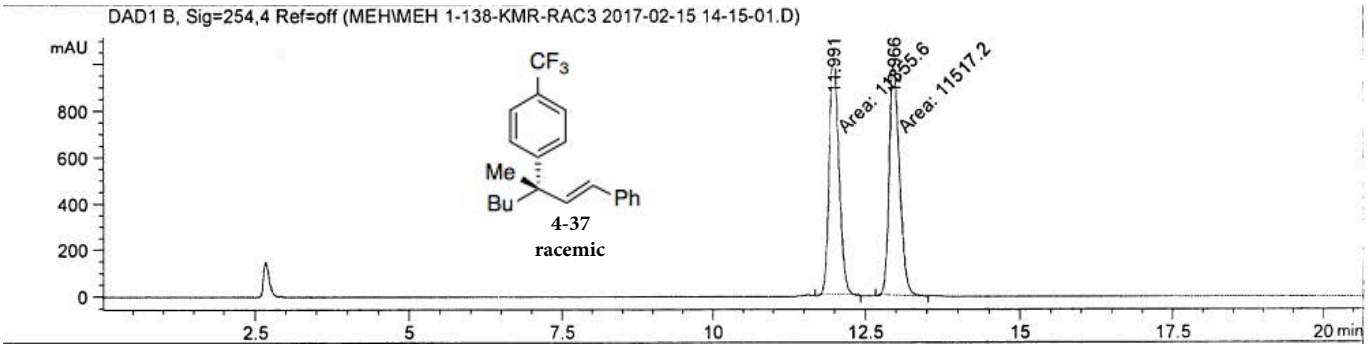
Compound 4-36, 94% ee



Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.114	MM	0.3064	373.69662	20.32554	2.7947
2	20.216	MM	0.4179	1.29978e4	518.40771	97.2053
Totals :				1.33715e4	538.73326	

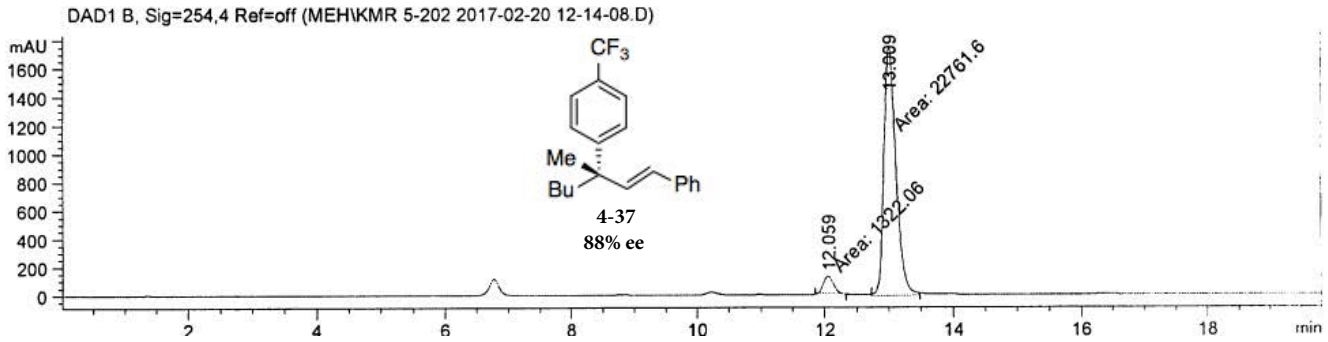
Compound 4-37, racemic



Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.991	MM	0.1791	1.13556e4	1056.96252	49.6468
2	12.966	MM	0.1928	1.15172e4	995.67889	50.3532
Totals :				2.28729e4	2052.64142	

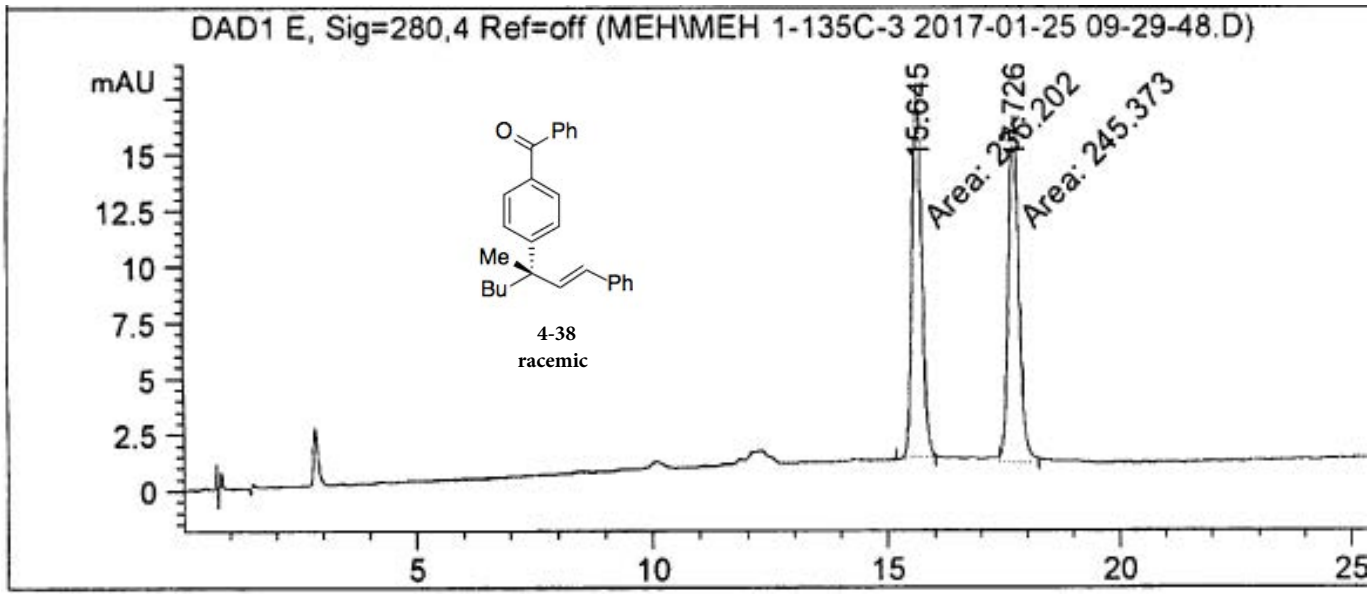
Compound 4-37, 88% ee



Signal 1: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.059	MM	0.1775	1322.05725	124.10520	5.4894
2	13.009	MM	0.2154	2.27616e4	1761.35901	94.5106
Totals :				2.40837e4	1885.46421	

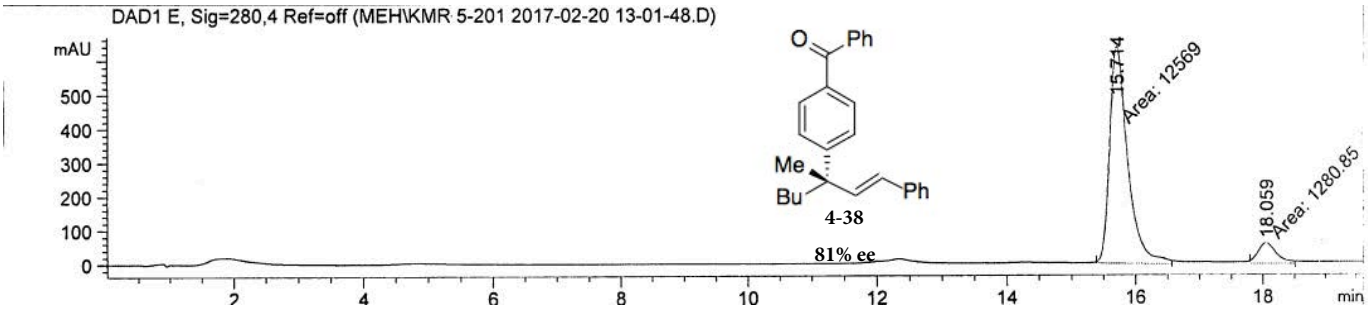
Compound 4-38, racemic



Signal 3: DAD1 E, Sig=280,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.645	MM	0.2342	235.20174	16.73850	48.9418
2	17.726	MM	0.2636	245.37256	15.51406	51.0582
Totals :				480.57430	32.25256	

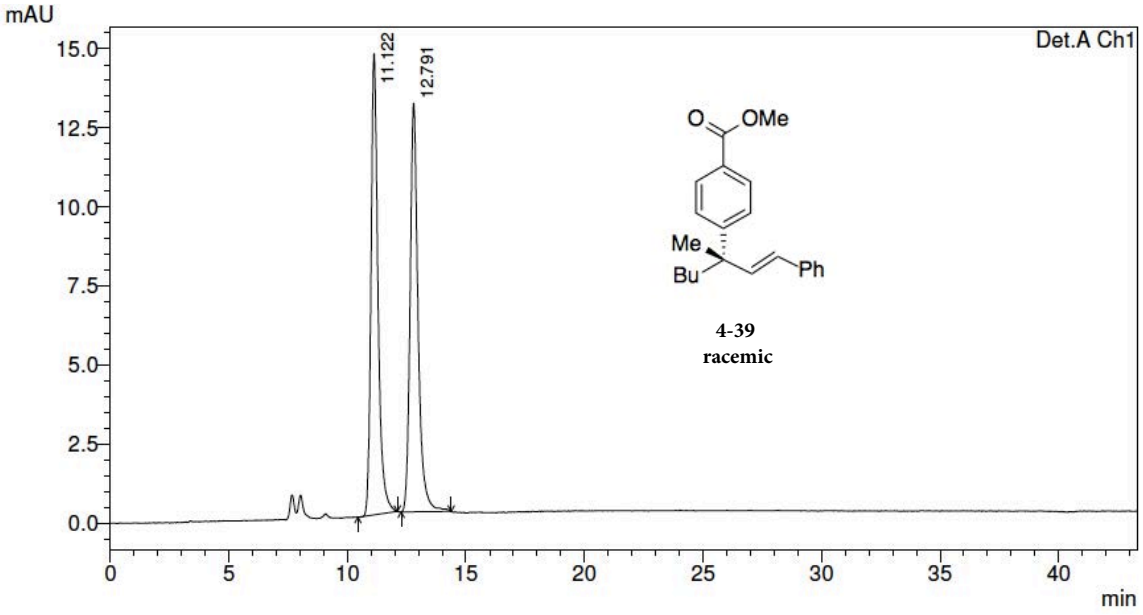
Compound 4-38, 81% ee



Signal 3: DAD1 E, Sig=280,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.714	MM	0.3276	1.25690e4	639.48132	90.7519
2	18.059	MM	0.3457	1280.85156	61.75790	9.2481
Totals :				1.38499e4	701.23922	

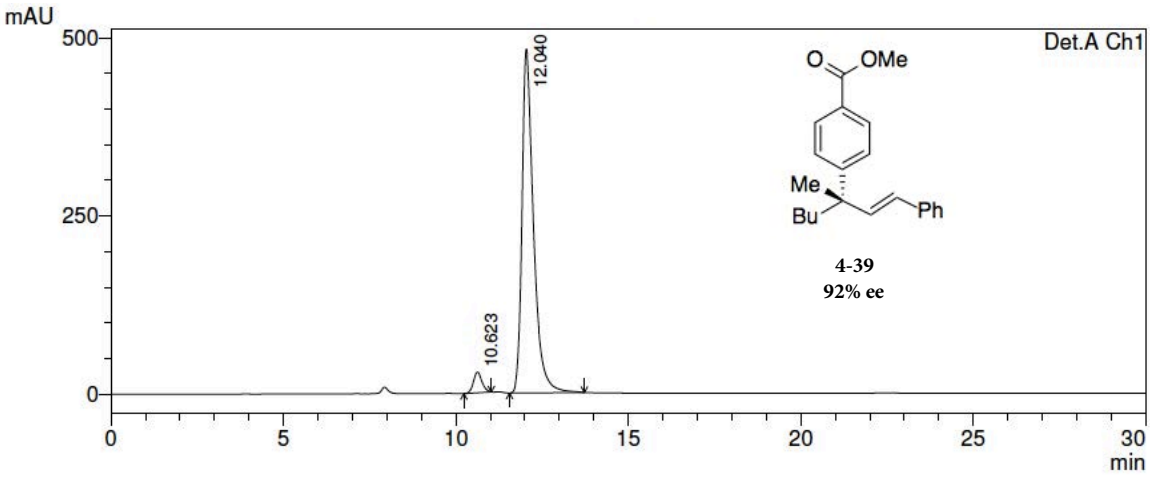
Compound 4-39, racemic



Detector A Ch1 254nm

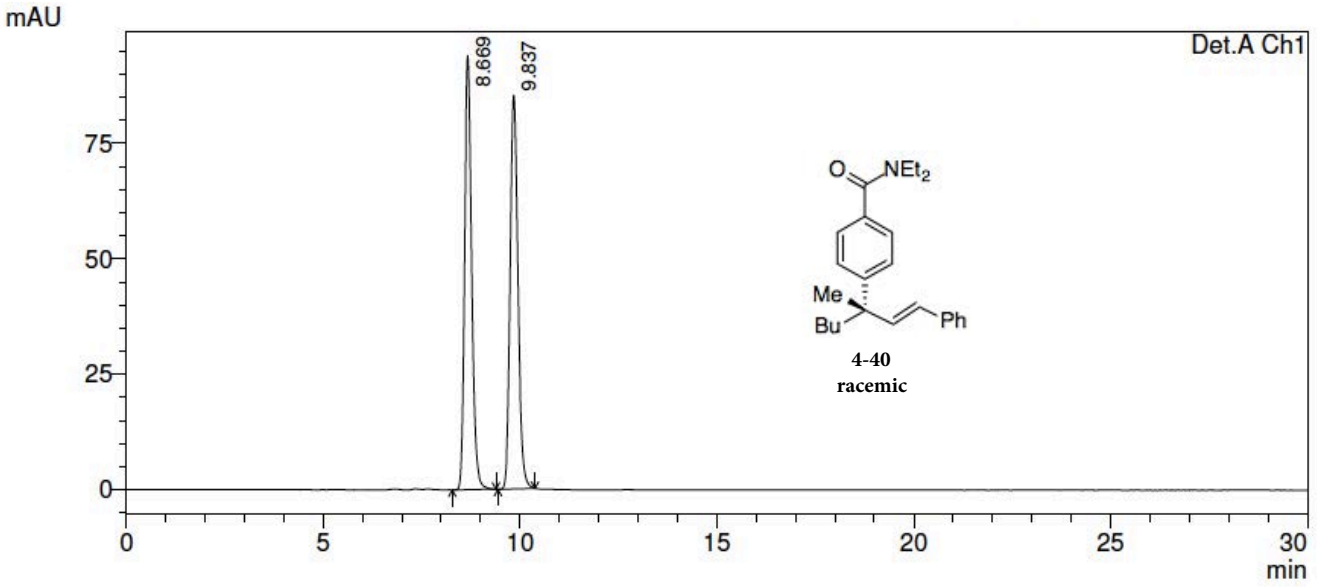
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.122	299350	14583	49.727	53.032
2	12.791	302638	12916	50.273	46.968
Total		601988	27499	100.000	100.000

Compound 4-39, 92% ee



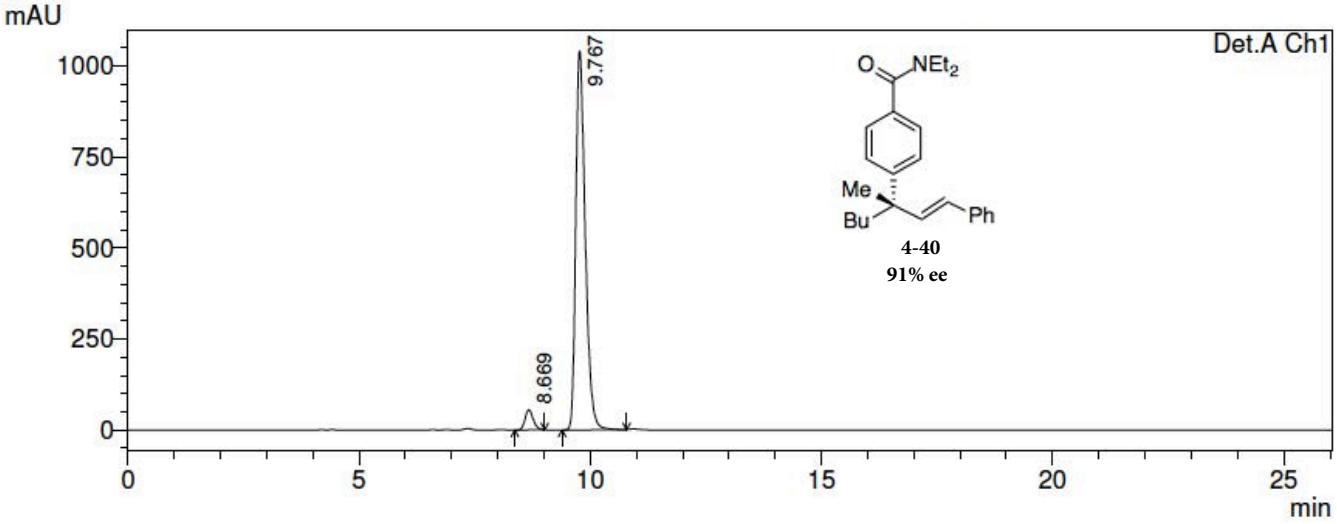
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.623	494765	29019	4.245	5.675
2	12.040	11159283	482281	95.755	94.325
Total		11654048	511299	100.000	100.000

Compound 4-40, racemic



Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.669	1179231	94071	50.182	52.444
2	9.837	1170671	85304	49.818	47.556
Total		2349903	179375	100.000	100.000

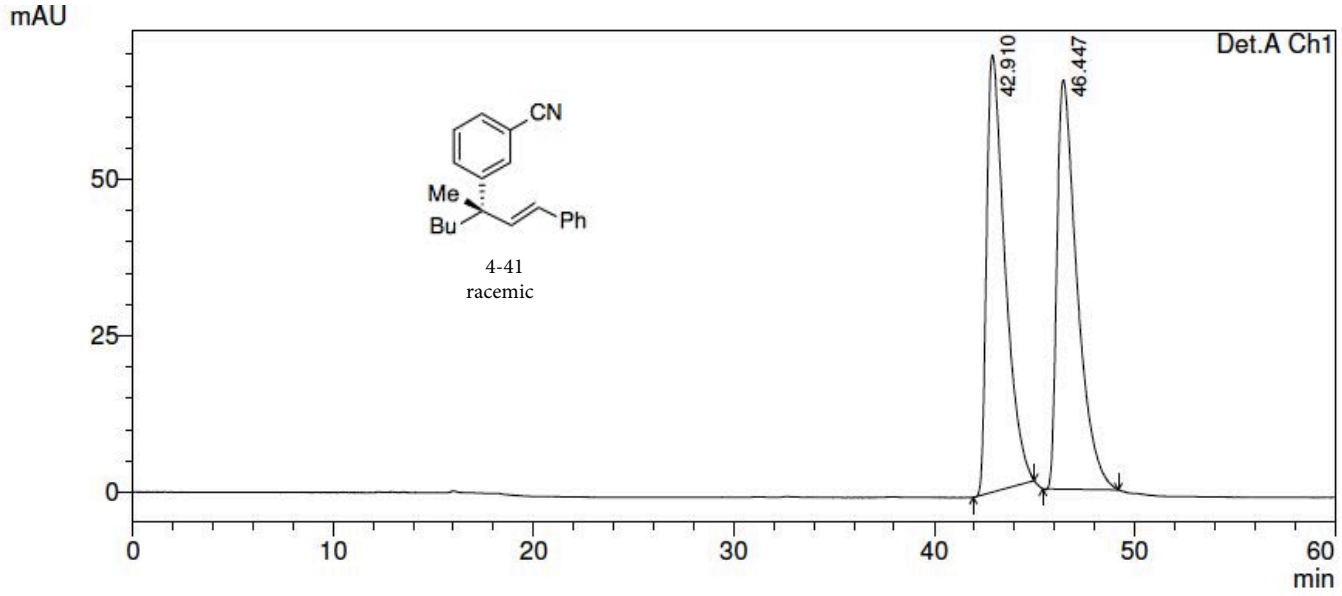
Compound 4-40, 91% ee



Detector A Ch1 254nm

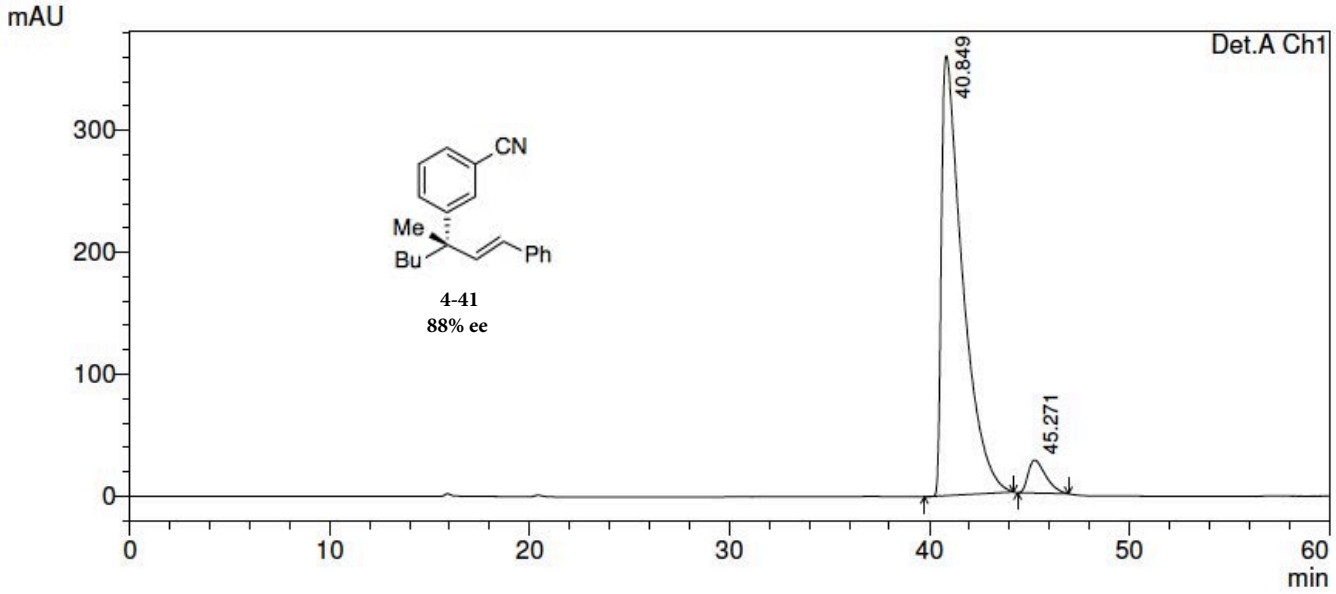
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.669	674026	55319	4.357	5.050
2	9.767	14797410	1040042	95.643	94.950
Total		15471436	1095361	100.000	100.000

Compound 4-41, racemic



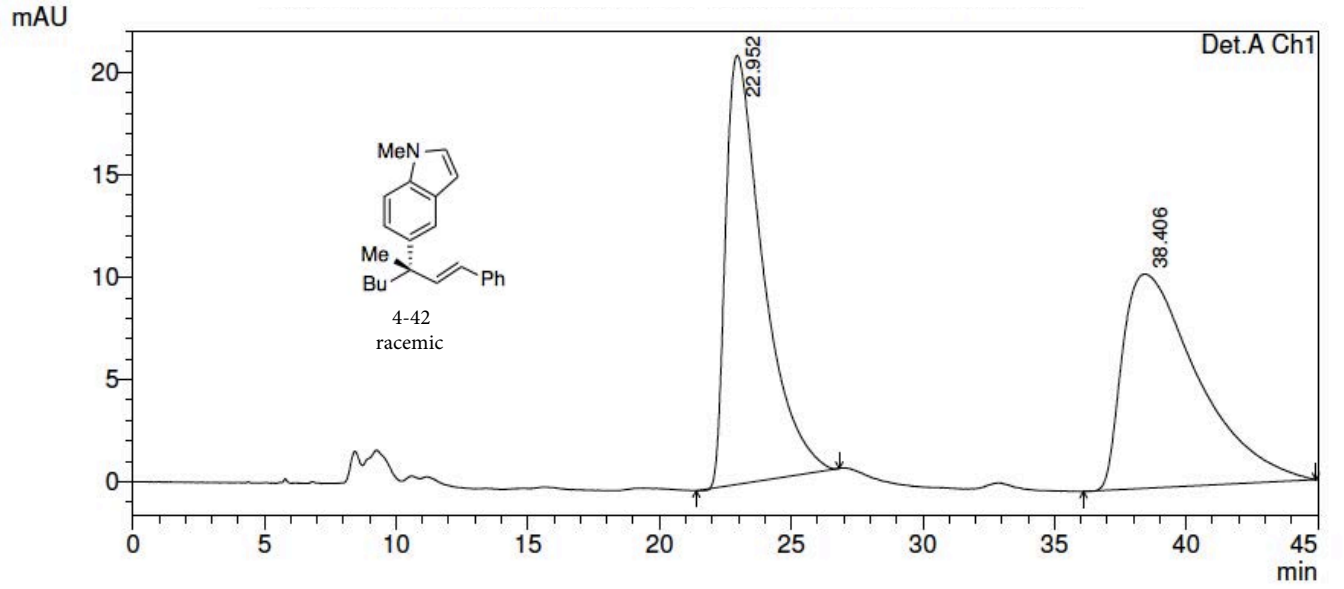
Peak#	Ret. Time	Area	Height	Area %	Height %
1	42.910	4486510	69917	49.505	51.658
2	46.447	4576267	65429	50.495	48.342
Total		9062777	135346	100.000	100.000

Compound 4-41, 88% ee



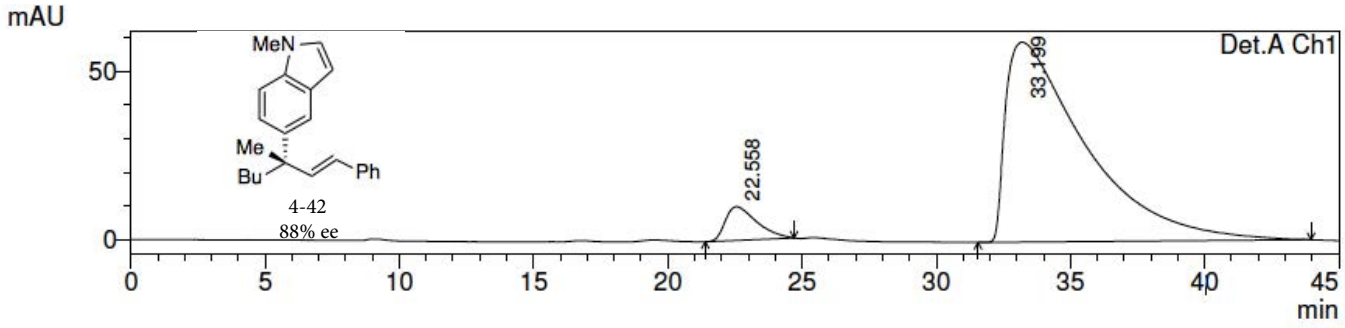
Peak#	Ret. Time	Area	Height	Area %	Height %
1	40.849	26586715	360699	94.130	93.030
2	45.271	1658039	27024	5.870	6.970
Total		28244754	387724	100.000	100.000

Compound 4-42, racemic



Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.952	2079164	20953	49.931	66.691
2	38.406	2084897	10465	50.069	33.309
Total		4164061	31418	100.000	100.000

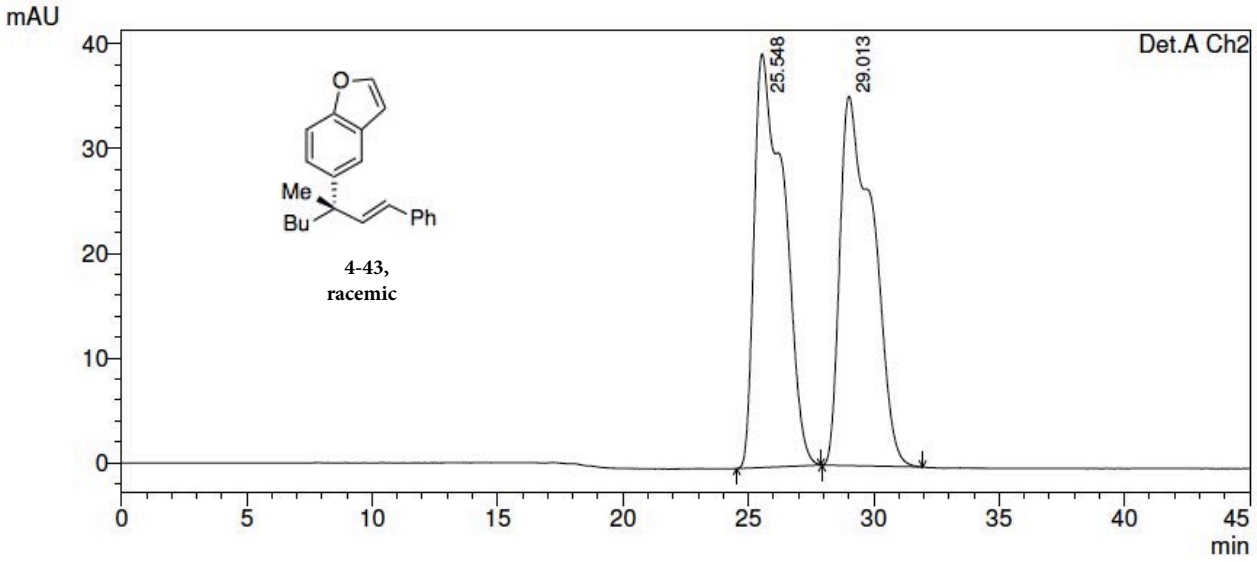
Compound 4-42, 88% ee



Detector A Ch1 254nm

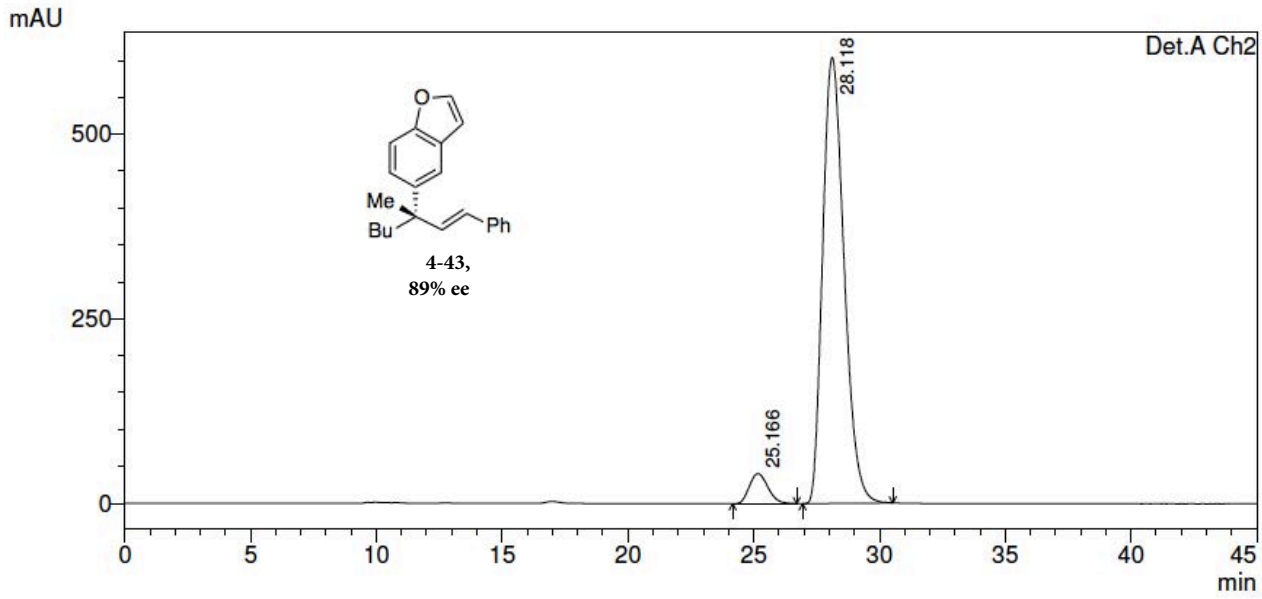
Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.558	809116	9988	6.153	14.383
2	33.199	12341591	59457	93.847	85.617
Total		13150707	69445	100.000	100.000

Compound 4-43, racemic



Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.547	4895877	59690	49.982	52.776
2	29.011	4899446	53411	50.018	47.224
Total		9795323	113101	100.000	100.000

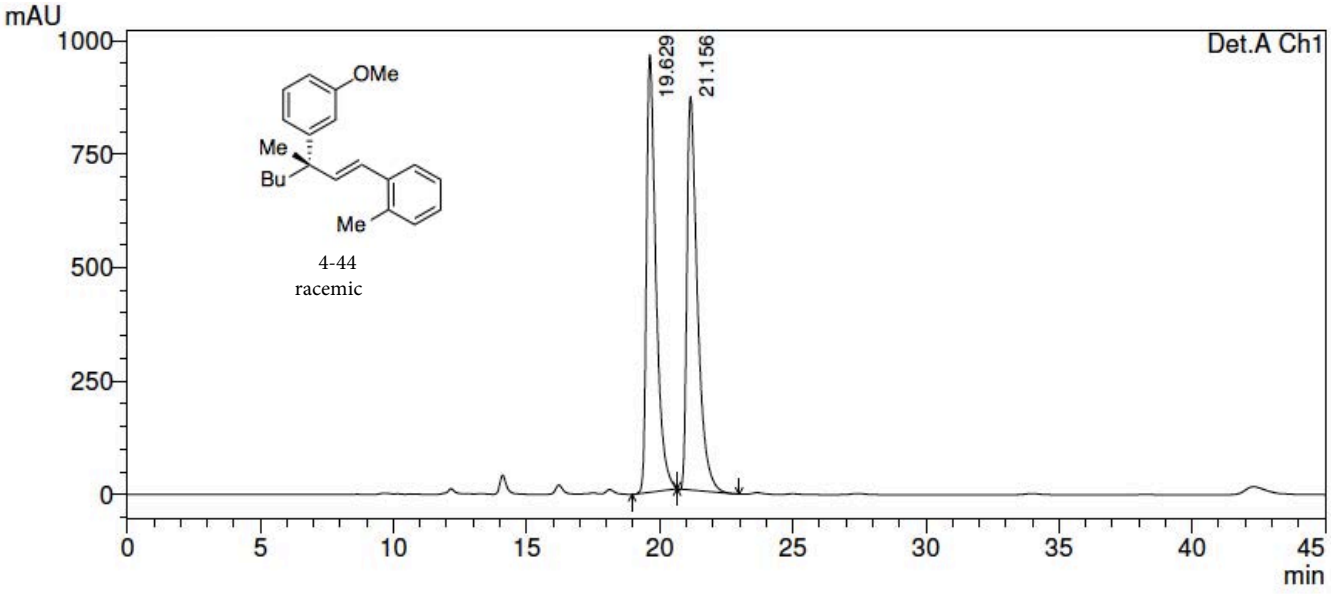
Compound 4-43, 89% ee



Detector A Ch2 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.166	2094816	40632	5.535	6.301
2	28.118	35754422	604196	94.465	93.699
Total		37849238	644828	100.000	100.000

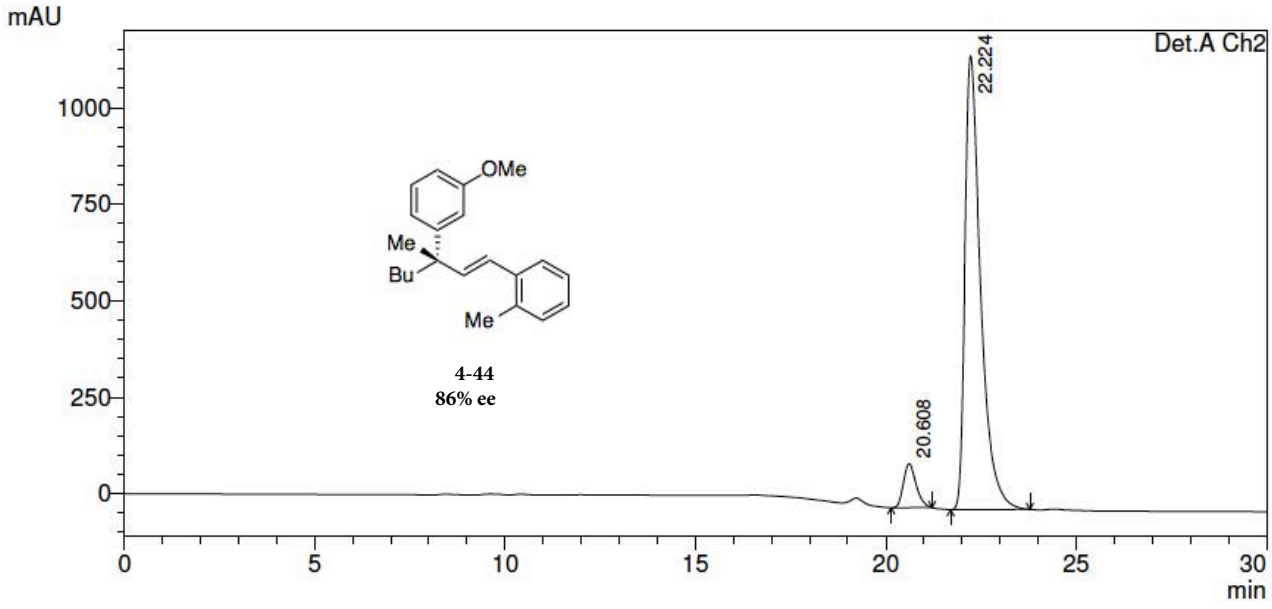
Compound 4-44, racemic



Detector A Ch2 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.632	49359832	1924806	49.693	52.126
2	21.158	49970465	1767807	50.307	47.874
Total		99330297	3692613	100.000	100.000

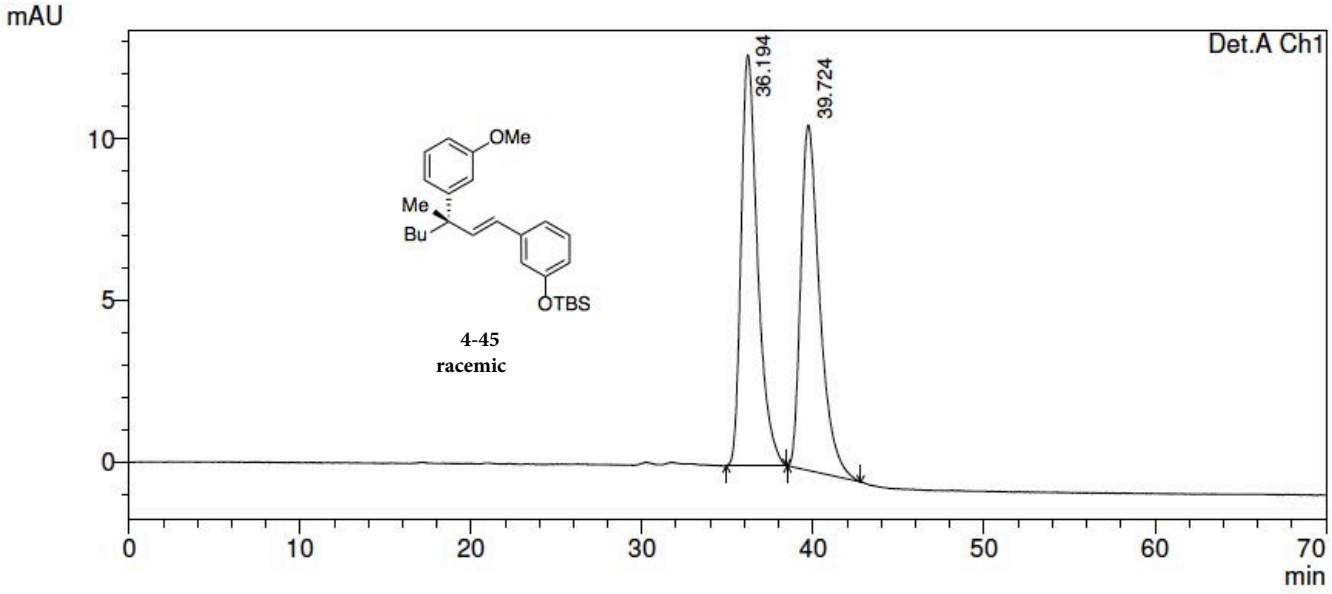
Compound 4-44, 86% ee



Detector A Ch2 210nm

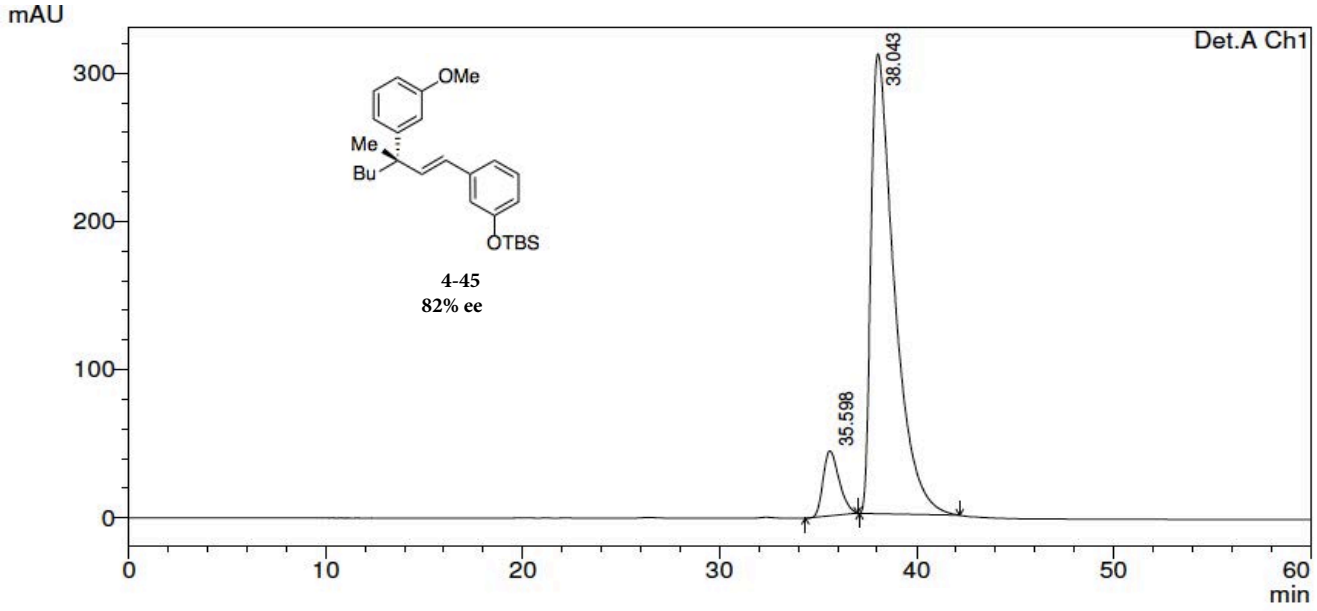
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.608	2633810	113975	7.253	8.838
2	22.224	33679787	1175606	92.747	91.162
Total		36313597	1289581	100.000	100.000

Compound 4-45, racemic



Peak#	Ret. Time	Area	Height	Area %	Height %
1	36.194	854860	12706	50.869	54.331
2	39.724	825650	10680	49.131	45.669
Total		1680510	23386	100.000	100.000

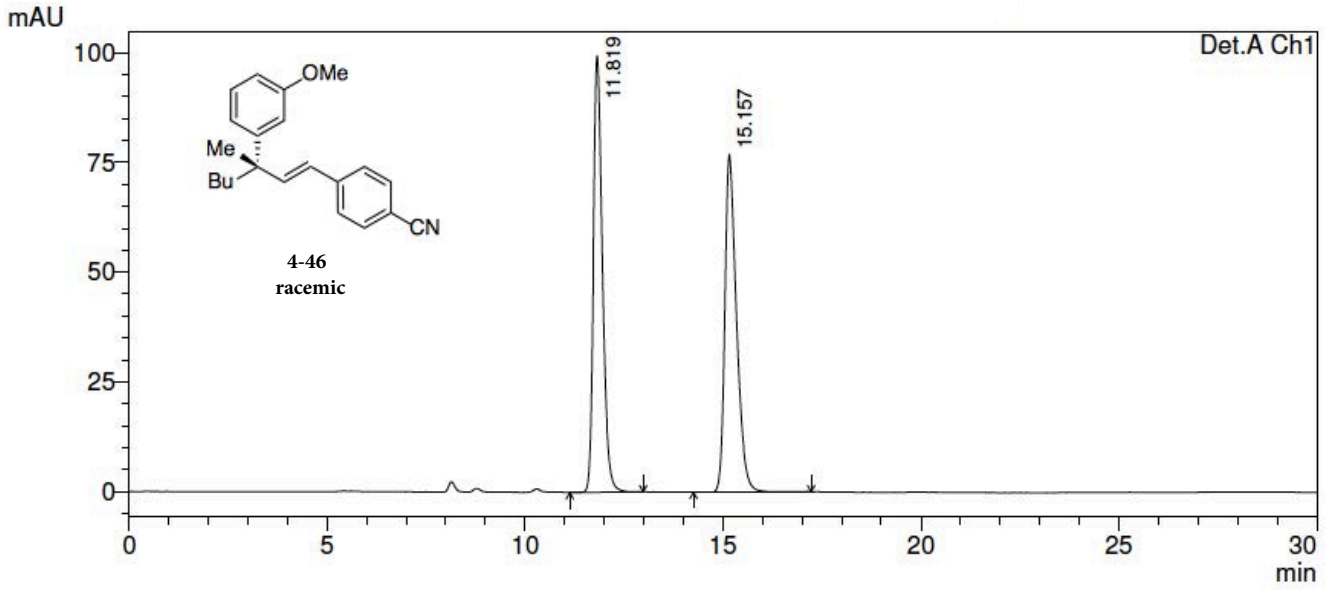
Compound 4-45, 82% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	35.598	2481988	43774	8.802	12.360
2	38.043	25716832	310393	91.198	87.640
Total		28198820	354167	100.000	100.000

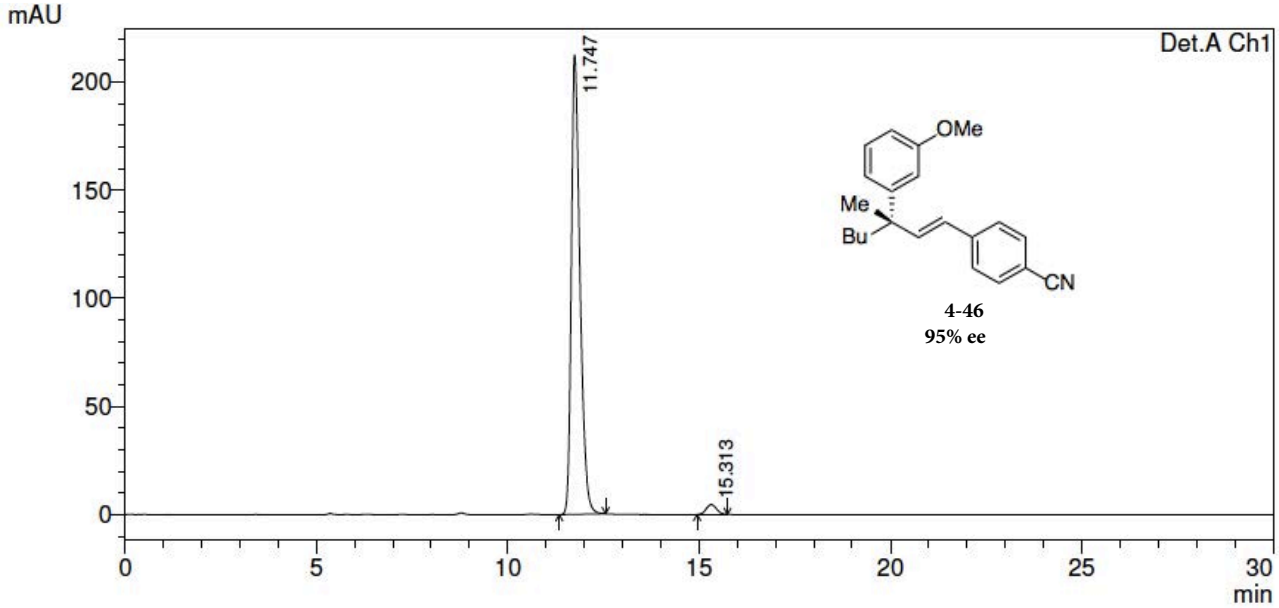
Compound 4-46, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.747	3371342	212472	97.531	97.910
2	15.313	85339	4536	2.469	2.090
Total		3456681	217008	100.000	100.000

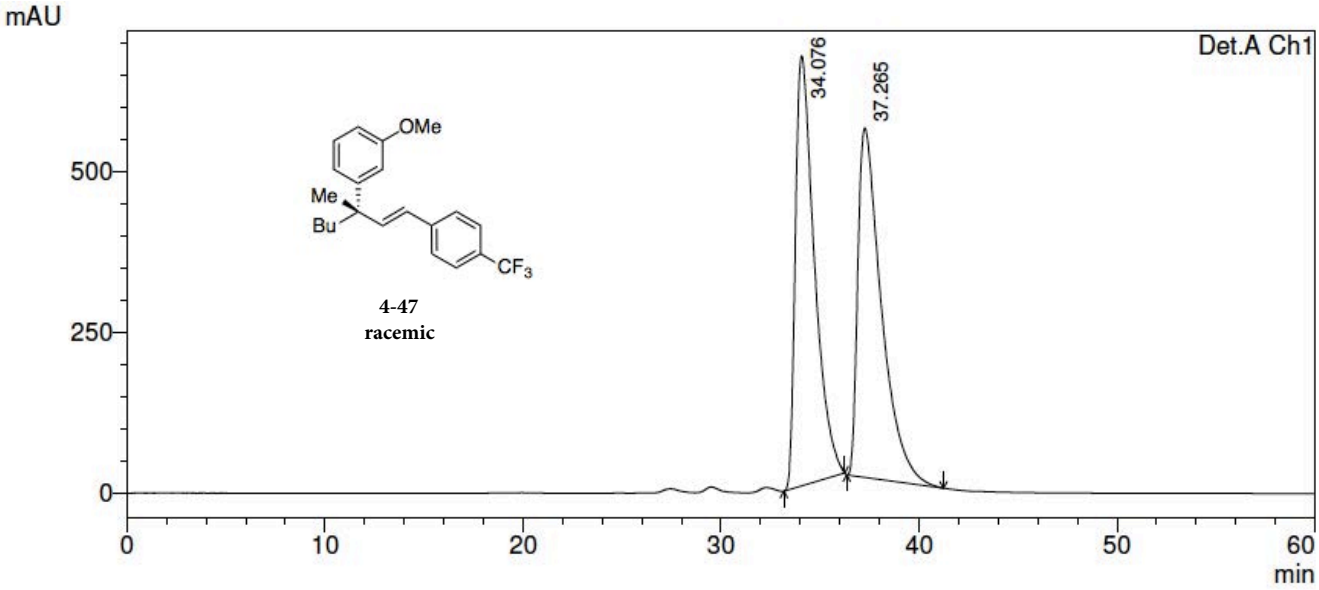
Compound 4-46, 95% ee



Detector A Ch1 254nm

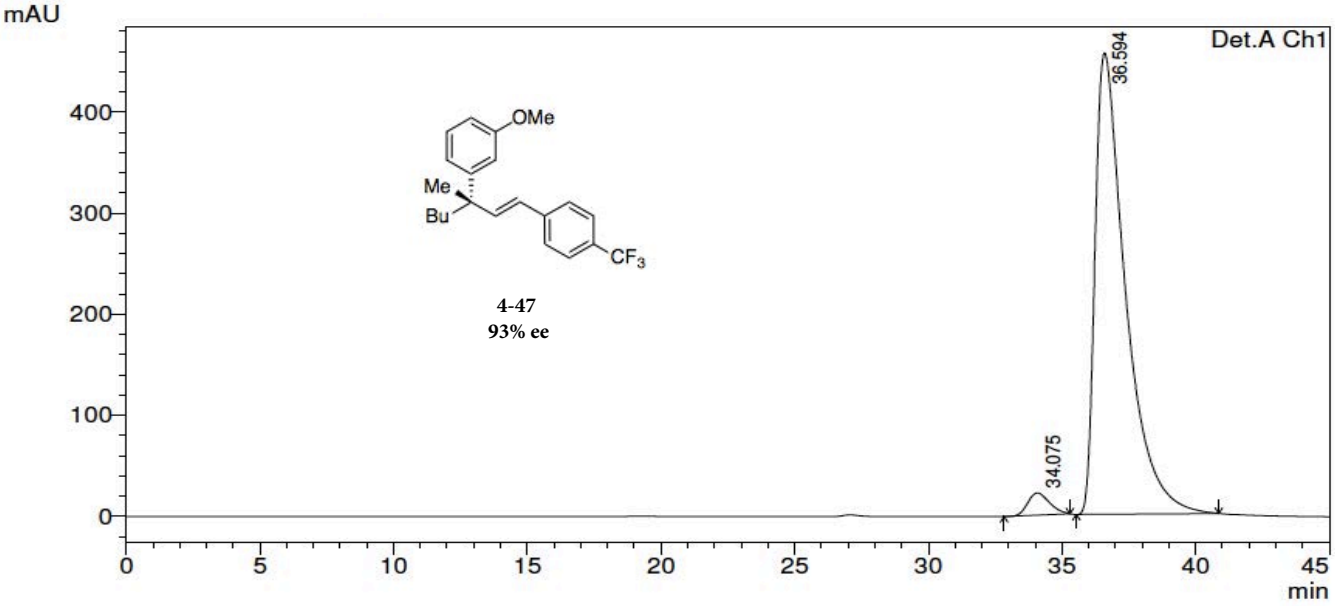
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.747	3371342	212472	97.531	97.910
2	15.313	85339	4536	2.469	2.090
Total		3456681	217008	100.000	100.000

Compound 4-47, racemic



Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.076	44757399	669031	49.909	55.164
2	37.265	44920381	543783	50.091	44.836
Total		89677780	1212814	100.000	100.000

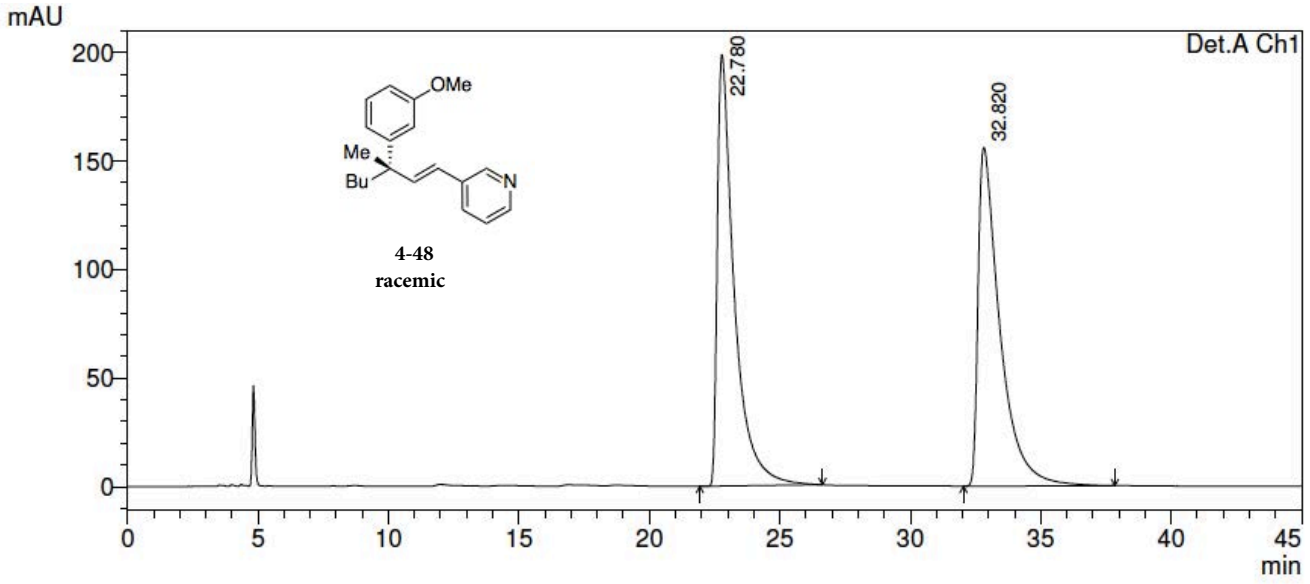
Compound 4-47, 93% ee



Detector A Ch1 254nm

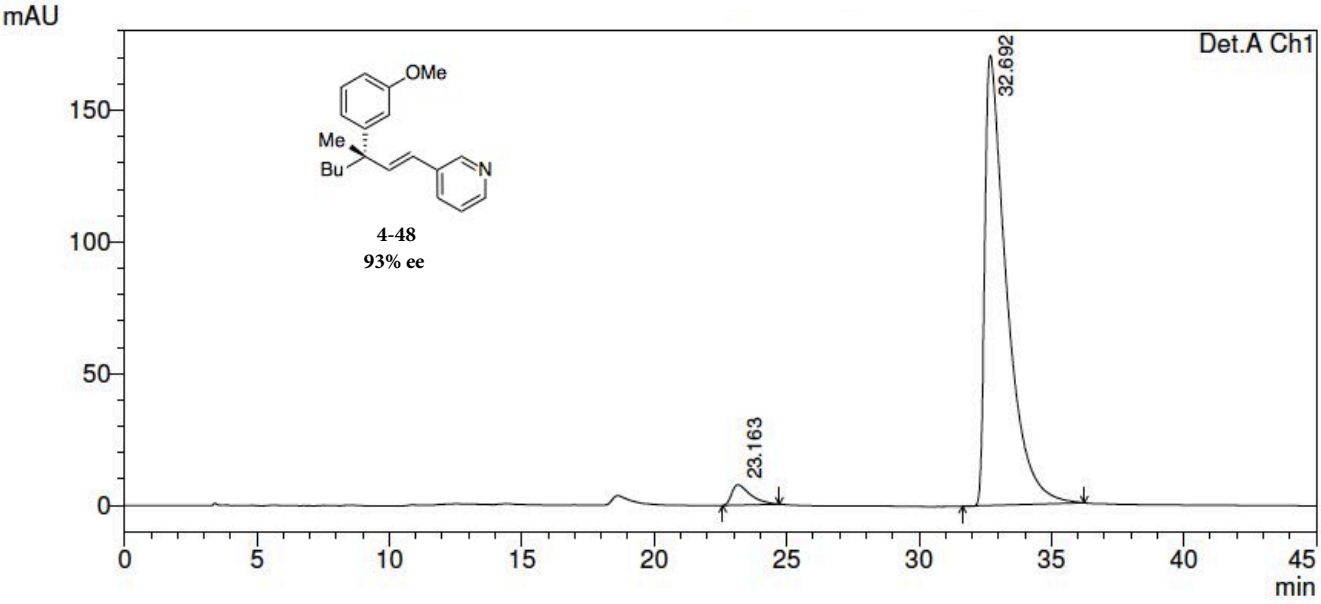
Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.075	1228232	21966	3.288	4.591
2	36.594	36124070	456463	96.712	95.409
Total		37352302	478429	100.000	100.000

Compound 4-48, racemic



Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.780	8997207	198863	49.799	56.034
2	32.820	9069729	156033	50.201	43.966
Total		18066936	354896	100.000	100.000

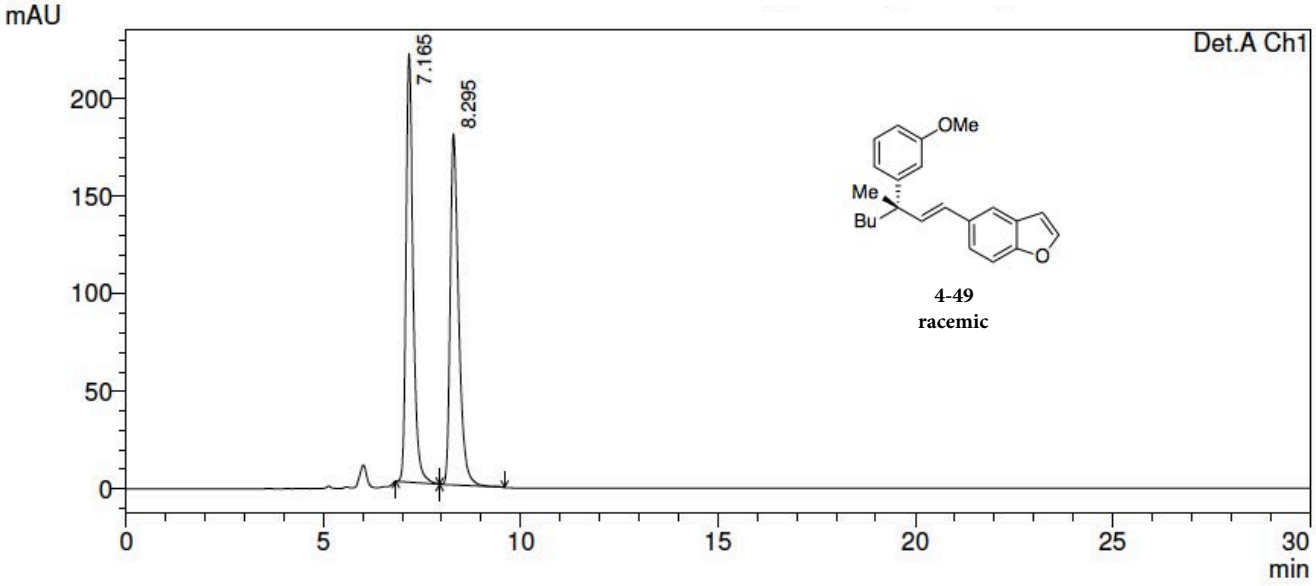
Compound 4-48, 93% ee



Detector A Ch1 220nm

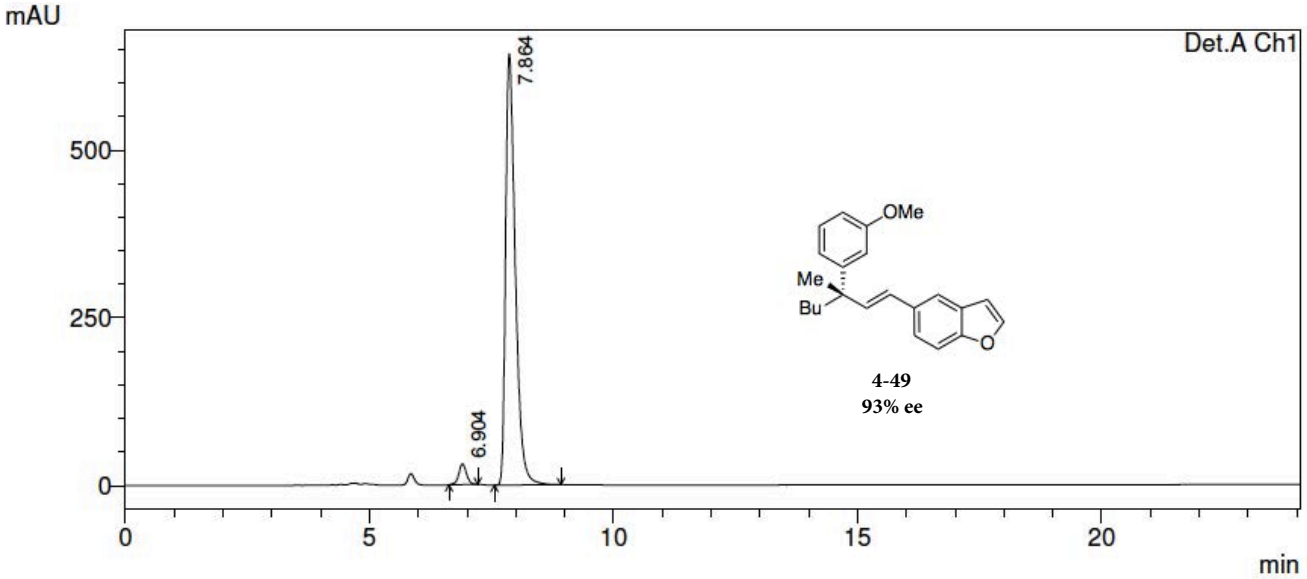
Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.163	381764	7705	3.753	4.316
2	32.692	9789515	170823	96.247	95.684
Total		10171279	178528	100.000	100.000

Compound 4-49, racemic



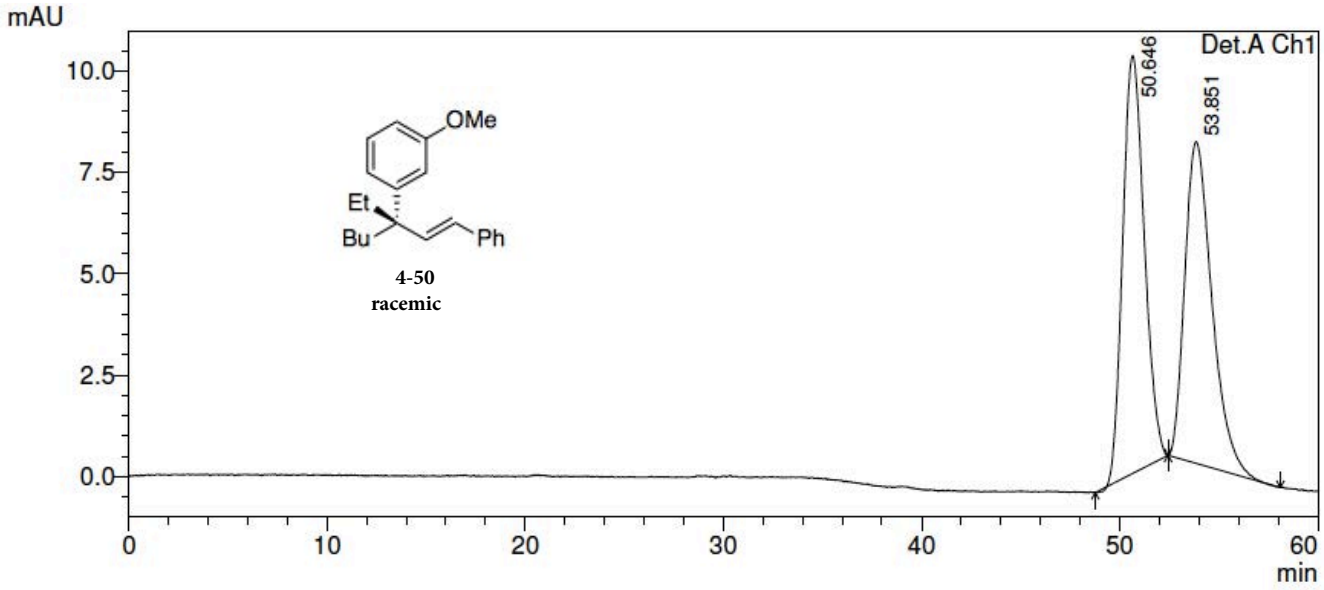
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.165	2737041	219557	50.187	54.963
2	8.295	2716668	179908	49.813	45.037
Total		5453709	399465	100.000	100.000

Compound 4-49, 93% ee



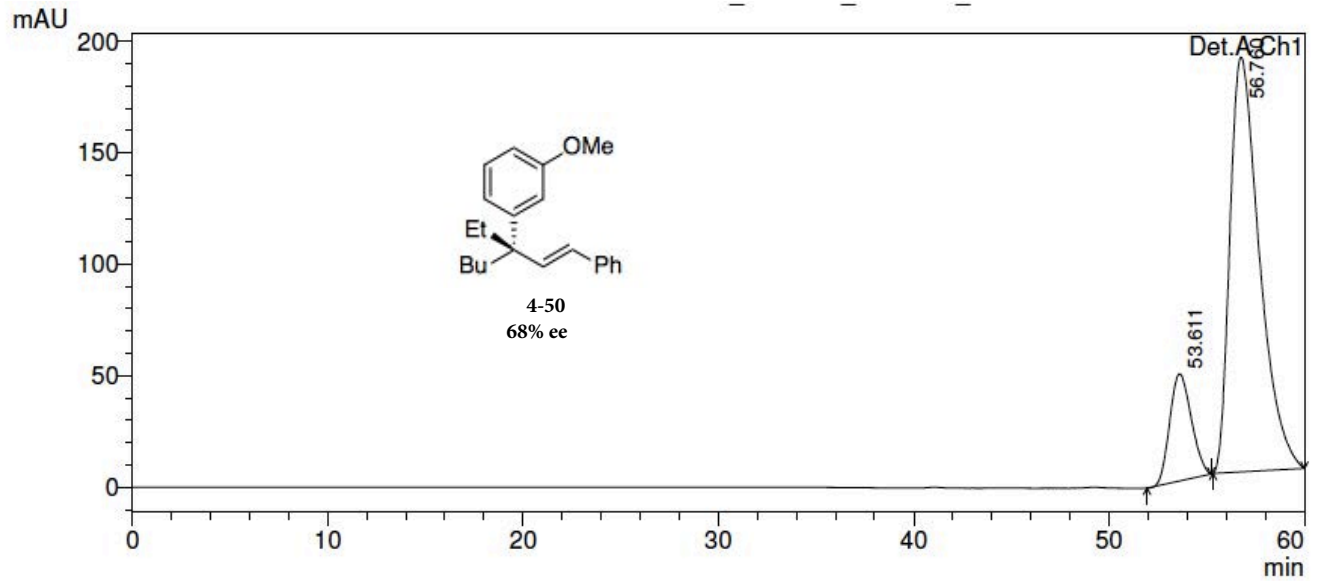
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.904	334768	30827	3.640	4.573
2	7.864	8861804	643275	96.360	95.427
Total		9196573	674102	100.000	100.000

Compound 4-50, racemic



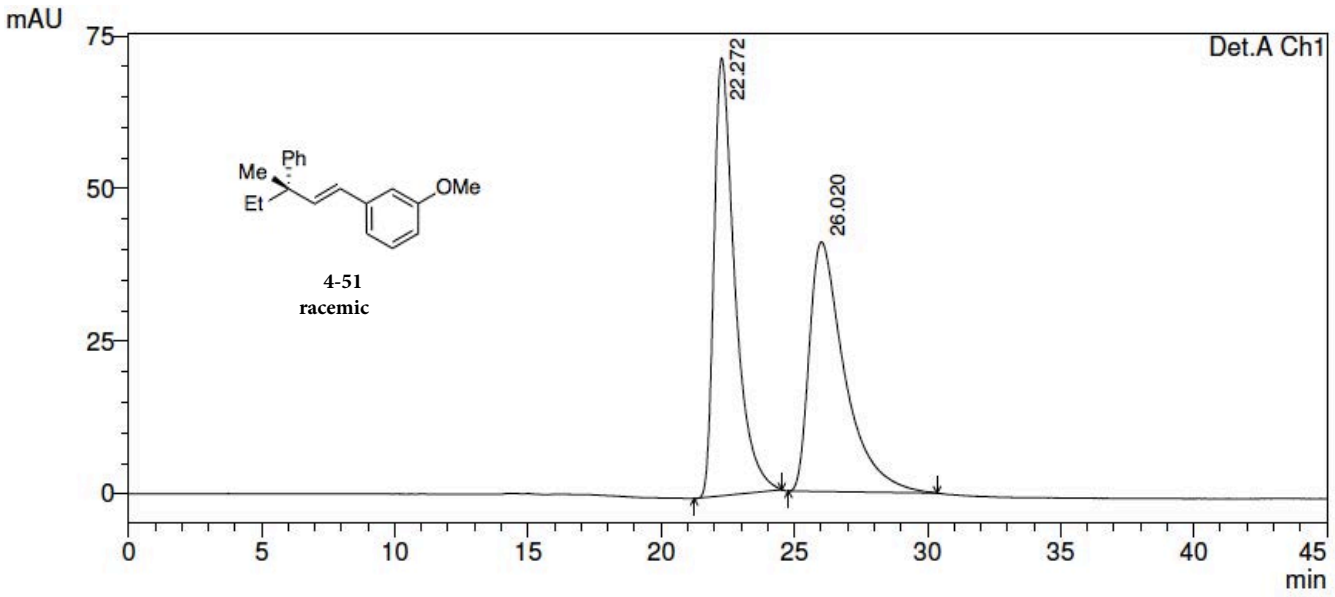
Peak#	Ret. Time	Area	Height	Area %	Height %
1	50.646	778238	10308	50.750	56.534
2	53.851	755237	7925	49.250	43.466
Total		1533475	18233	100.000	100.000

Compound 4-50, 68% ee



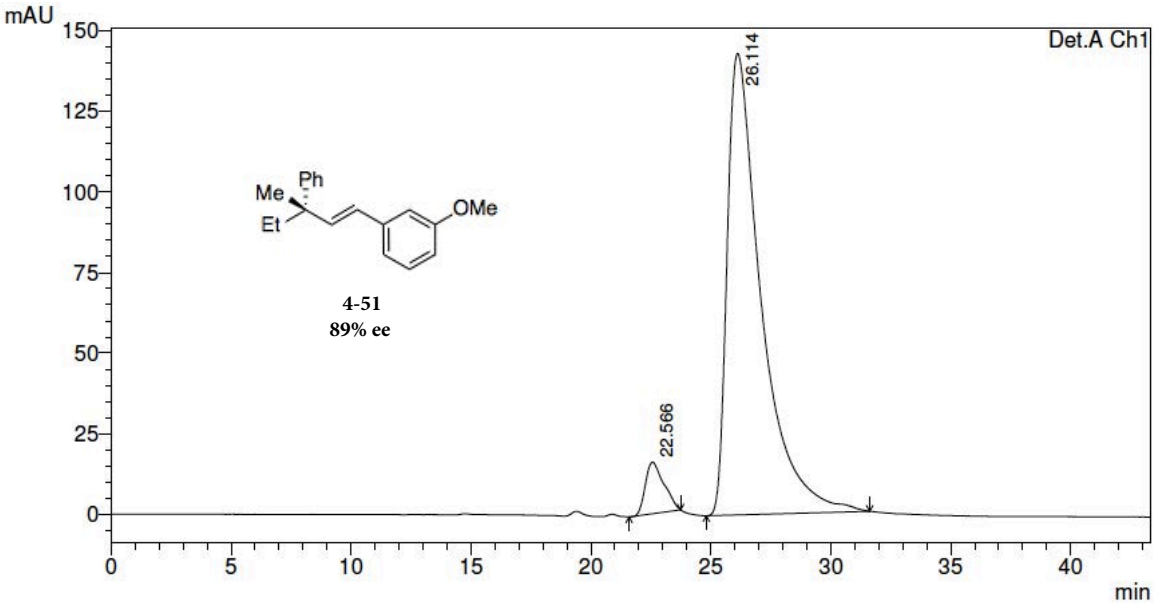
Peak#	Ret. Time	Area	Height	Area %	Height %
1	53.611	3691612	48030	15.874	20.526
2	56.760	19564760	185965	84.126	79.474
Total		23256371	233994	100.000	100.000

Compound 4-51, racemic



Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.272	3914722	71720	50.896	63.679
2	26.020	3776910	40907	49.104	36.321
Total		7691632	112627	100.000	100.000

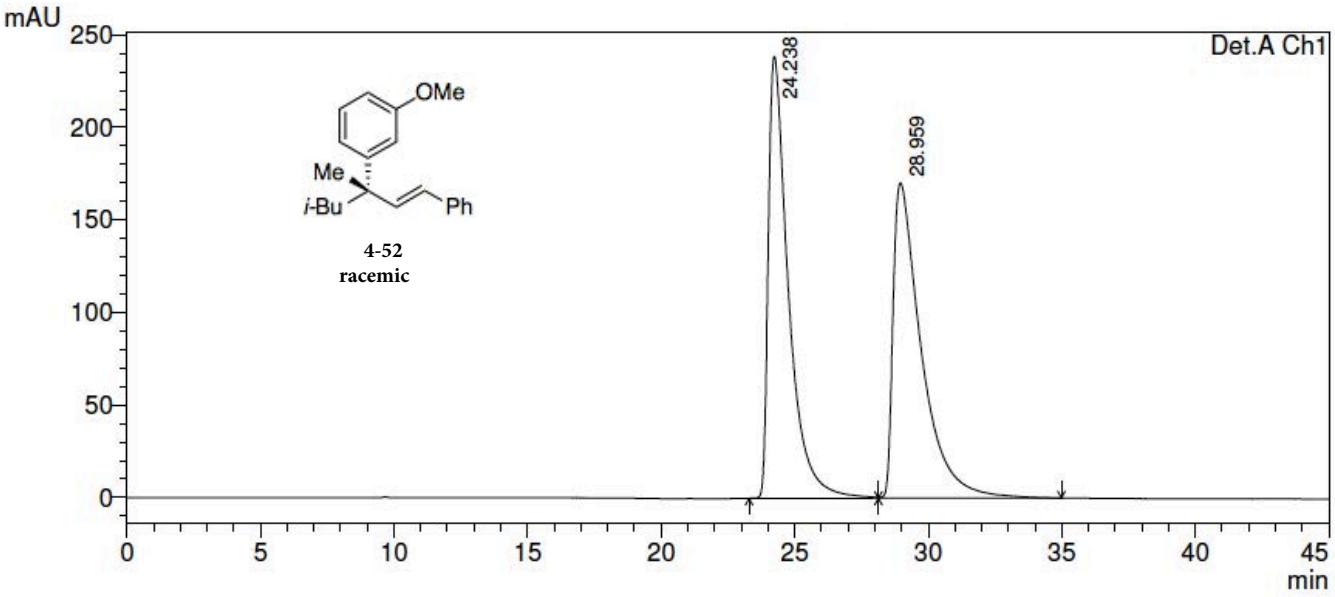
Compound 4-51, 89% ee



Detector A Ch1 254nm

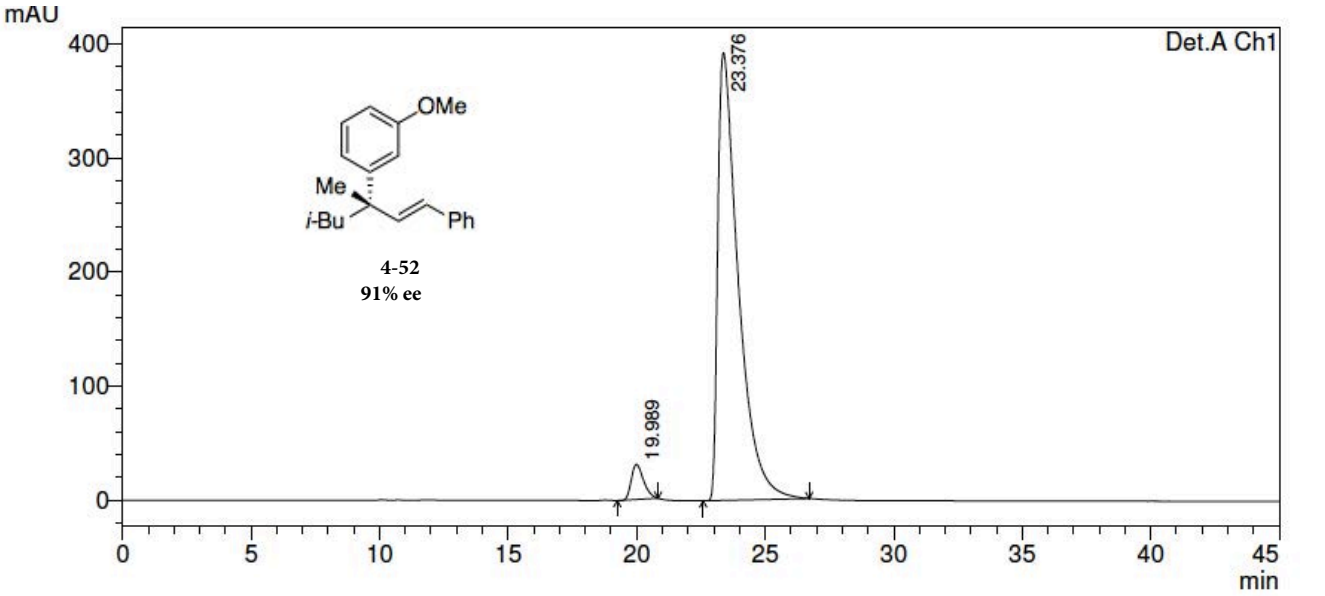
Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.566	854102	15960	5.711	10.027
2	26.114	14100842	143218	94.289	89.973
Total		14954944	159179	100.000	100.000

Compound 4-52, racemic



Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.238	12493360	238716	50.011	58.363
2	28.959	12487747	170307	49.989	41.637
Total		24981107	409023	100.000	100.000

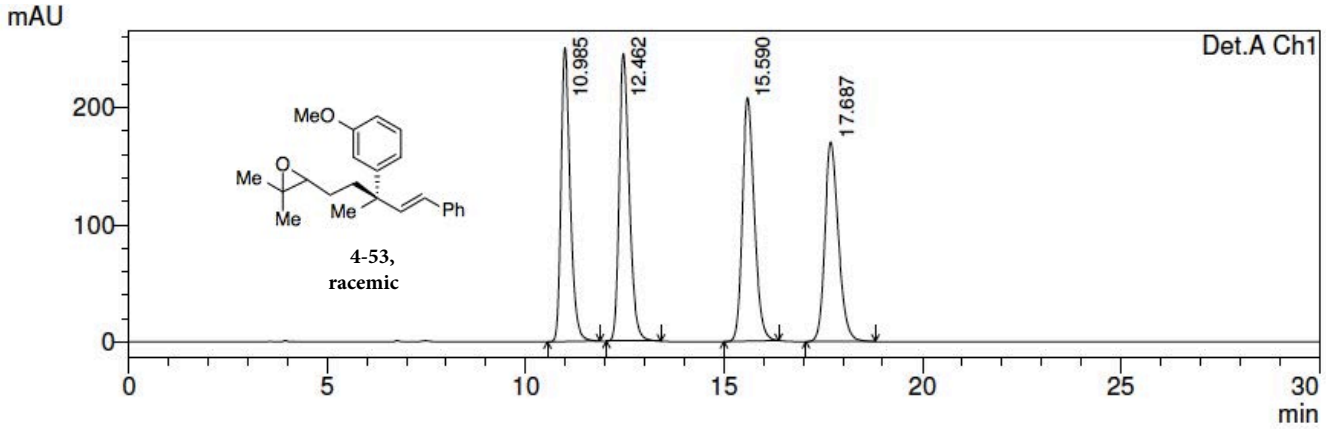
Compound 4-52, 91% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.989	1024179	30881	4.480	7.298
2	23.376	21834510	392246	95.520	92.702
Total		22858689	423127	100.000	100.000

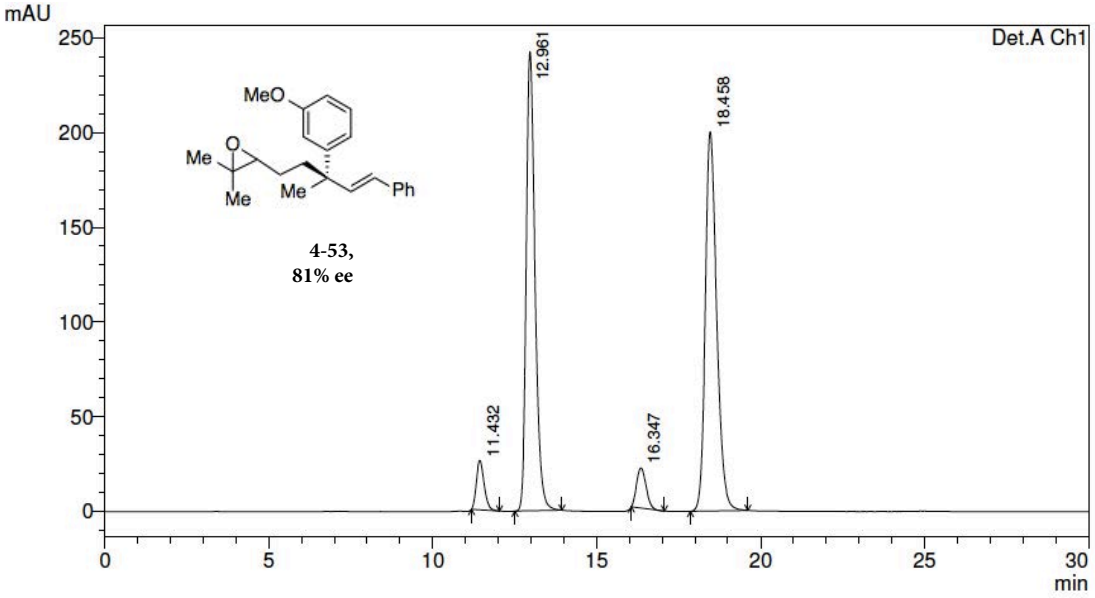
Compound 4-53, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.985	4036278	250999	24.036	28.679
2	12.462	4369575	245807	26.021	28.086
3	15.590	4346749	208055	25.885	23.772
4	17.687	4040175	170338	24.059	19.463
Total		16792778	875200	100.000	100.000

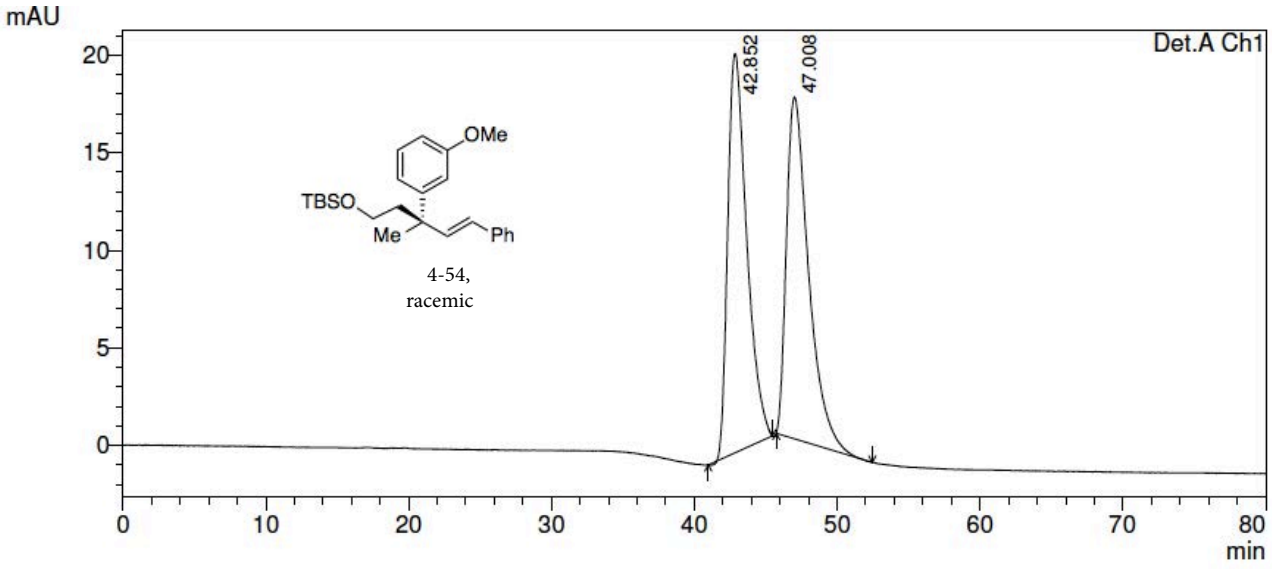
Compound 4-53, 81% ee



Detector A Ch1 254nm

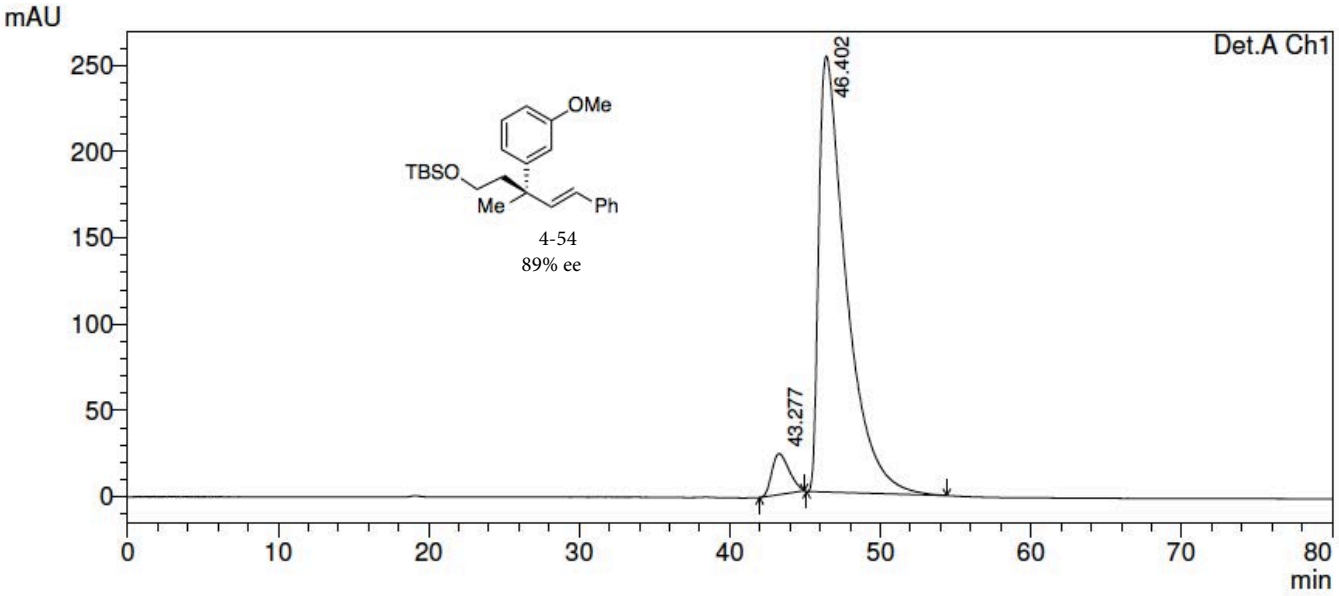
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.432	427501	26041	4.209	5.319
2	12.961	4491964	242351	44.225	49.498
3	16.347	421556	21115	4.150	4.312
4	18.458	4816061	200108	47.416	40.871
Total		10157082	489614	100.000	100.000

Compound 4-54, racemic



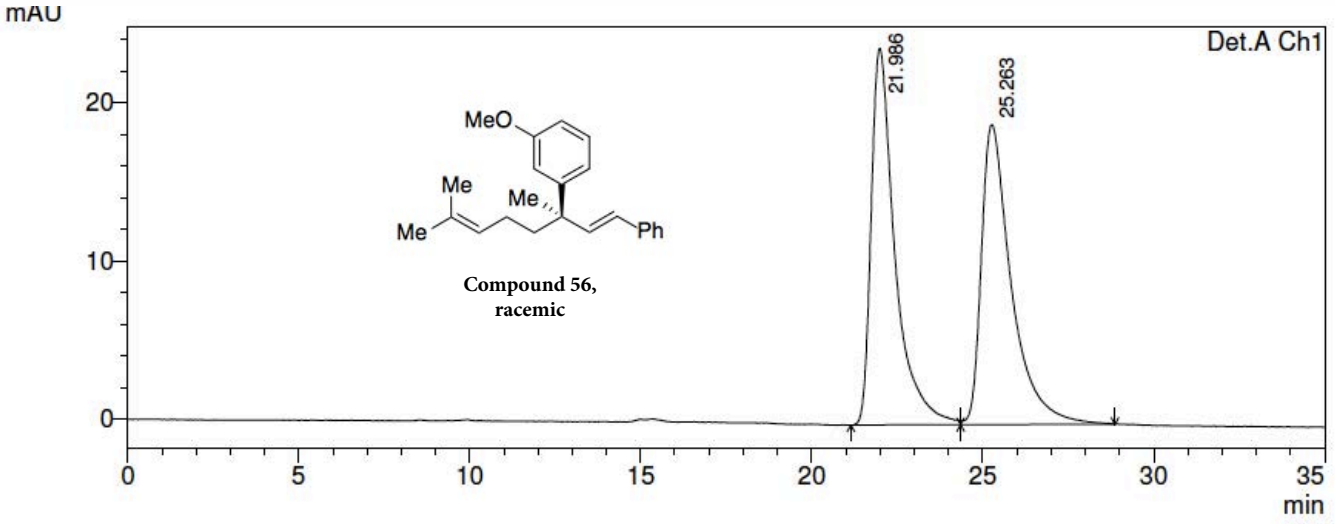
Peak#	Ret. Time	Area	Height	Area %	Height %
1	42.852	1890935	20471	50.054	53.872
2	47.008	1886834	17528	49.946	46.128
Total		3777769	37999	100.000	100.000

Compound 4-54, 89% ee



Peak#	Ret. Time	Area	Height	Area %	Height %
1	43.277	1878169	23616	5.540	8.548
2	46.402	32025864	252676	94.460	91.452
Total		33904033	276292	100.000	100.000

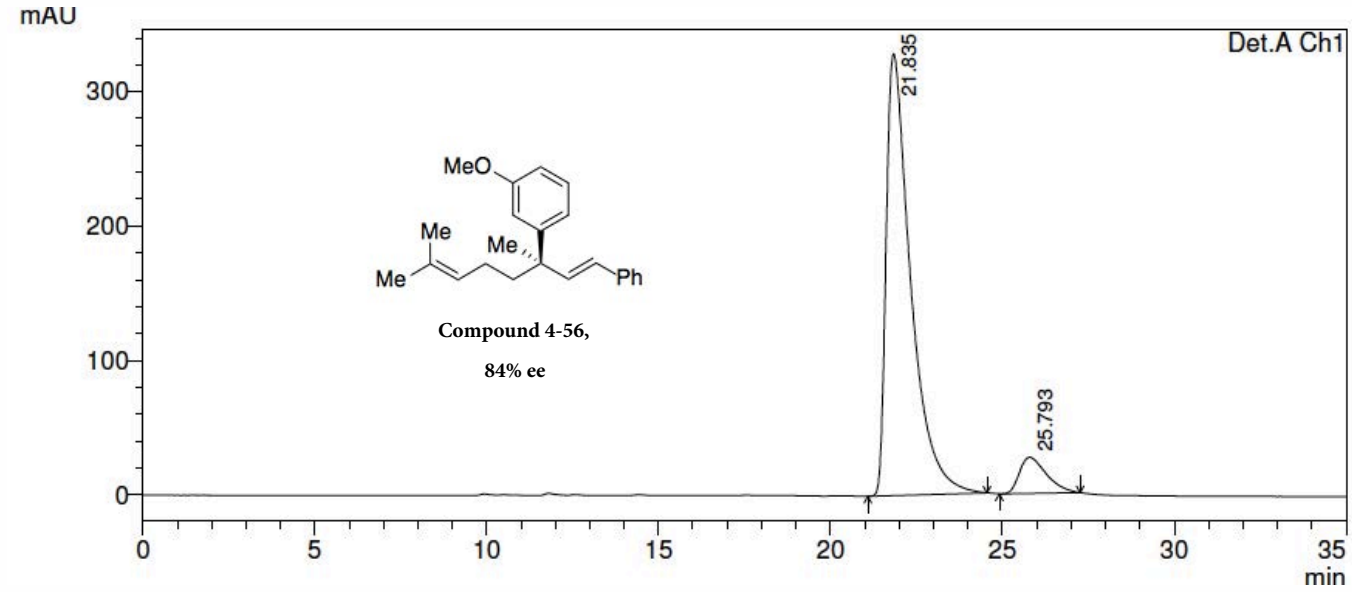
Compund 4-56, racemic



Detector A Ch1 254nm

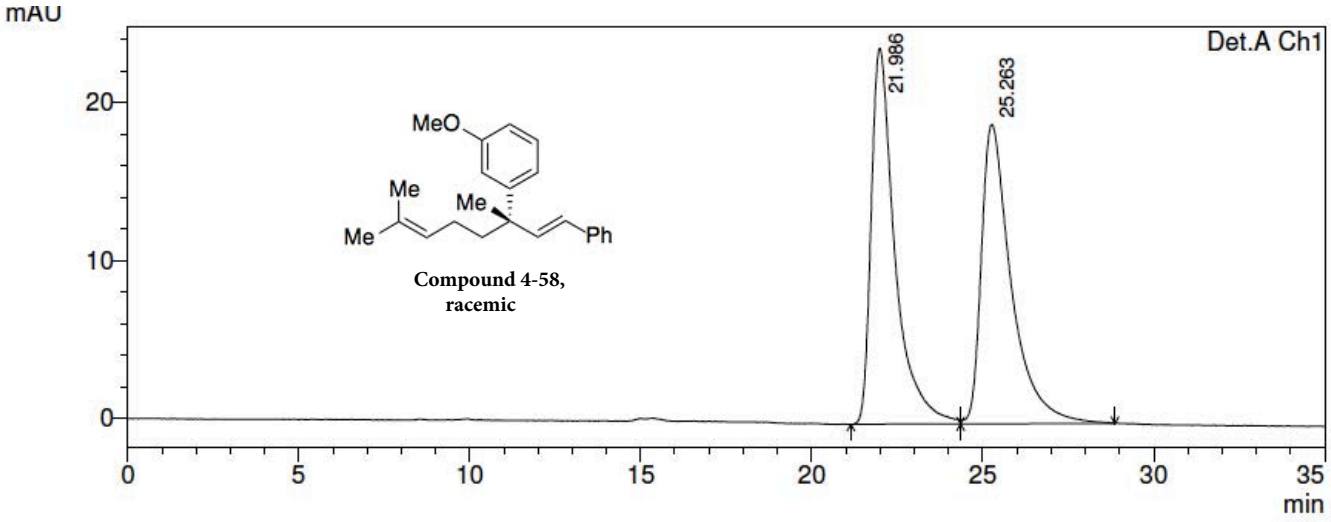
Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.986	1152996	23791	49.956	55.674
2	25.263	1155025	18942	50.044	44.326
Total		2308021	42733	100.000	100.000

Compund 4-56, 84% ee



Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.835	16305365	328410	91.760	92.448
2	25.793	1464266	26826	8.240	7.552
Total		17769631	355236	100.000	100.000

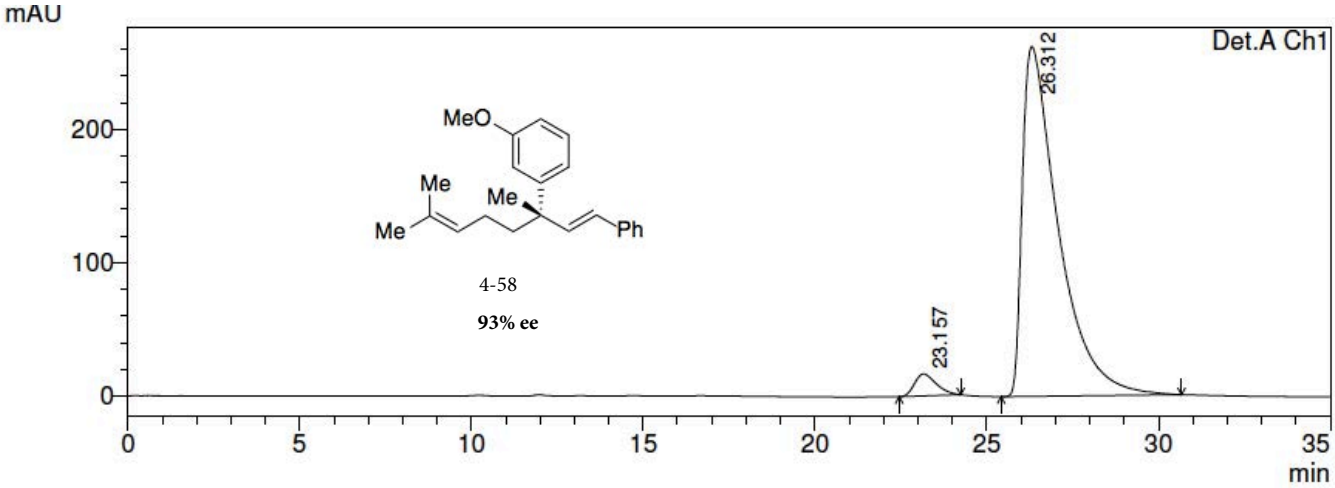
Compund 4-58, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.986	1152996	23791	49.956	55.674
2	25.263	1155025	18942	50.044	44.326
Total		2308021	42733	100.000	100.000

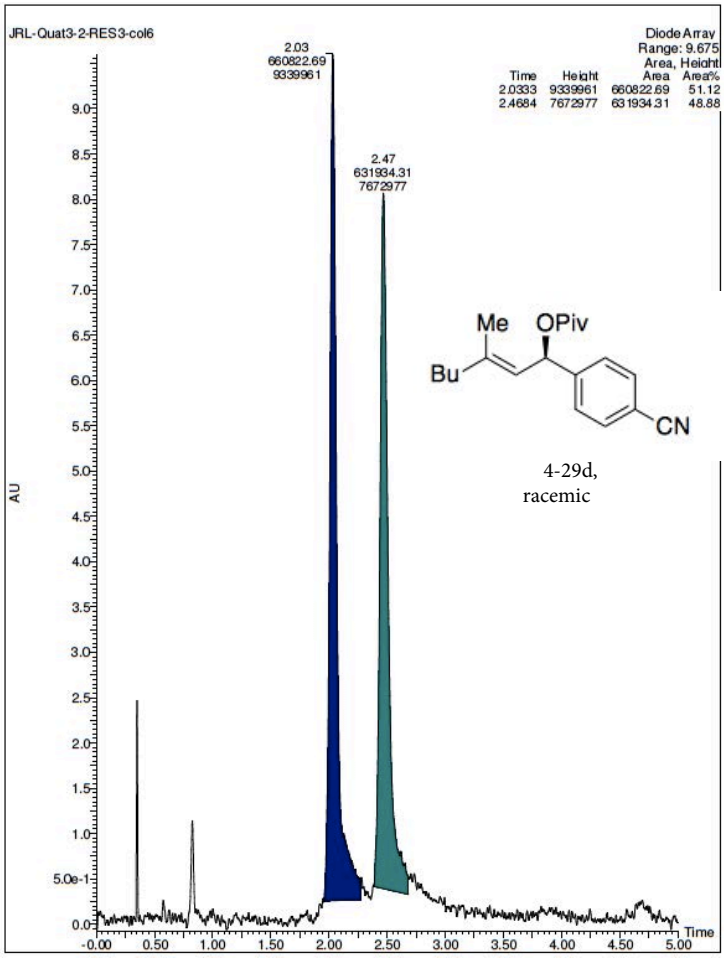
Compound 4-58, 93% ee



Detector A Ch1 254nm

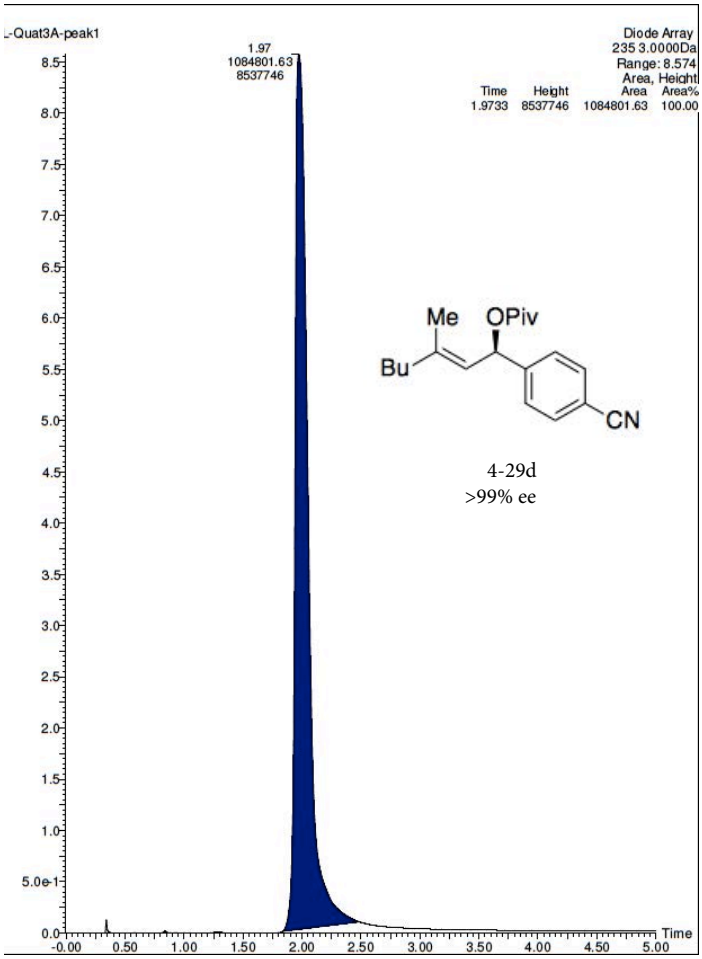
Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.157	731843	16501	3.689	5.915
2	26.312	19105750	262455	96.311	94.085
Total		19837593	278956	100.000	100.000

Compound 4-29d, racemic



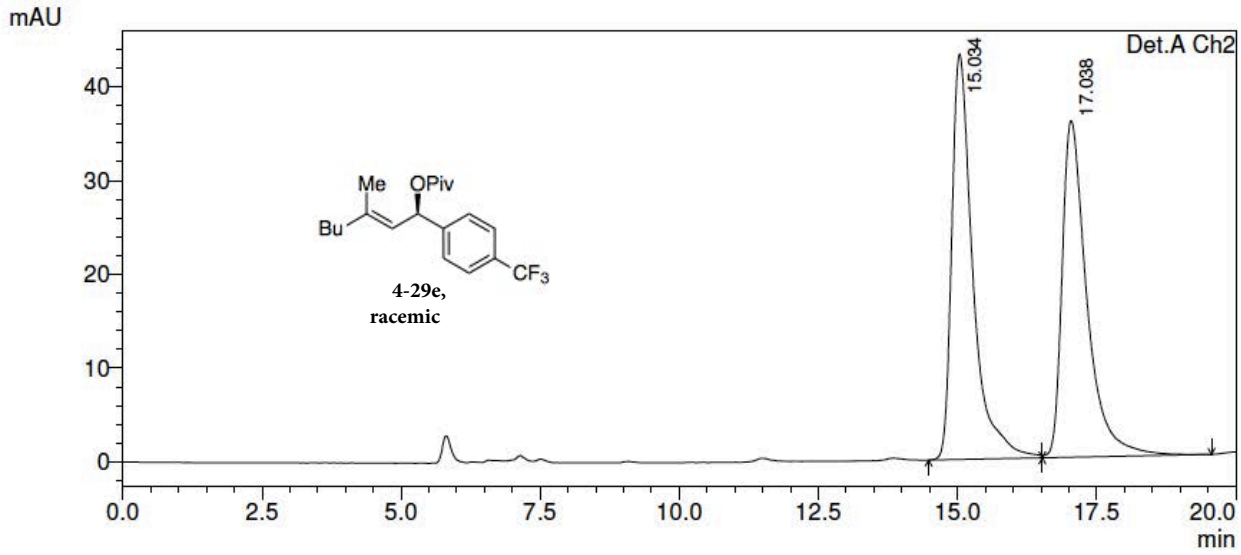
4-29d,
racemic

Compound 4-29d, >99% ee



4-29d
>99% ee

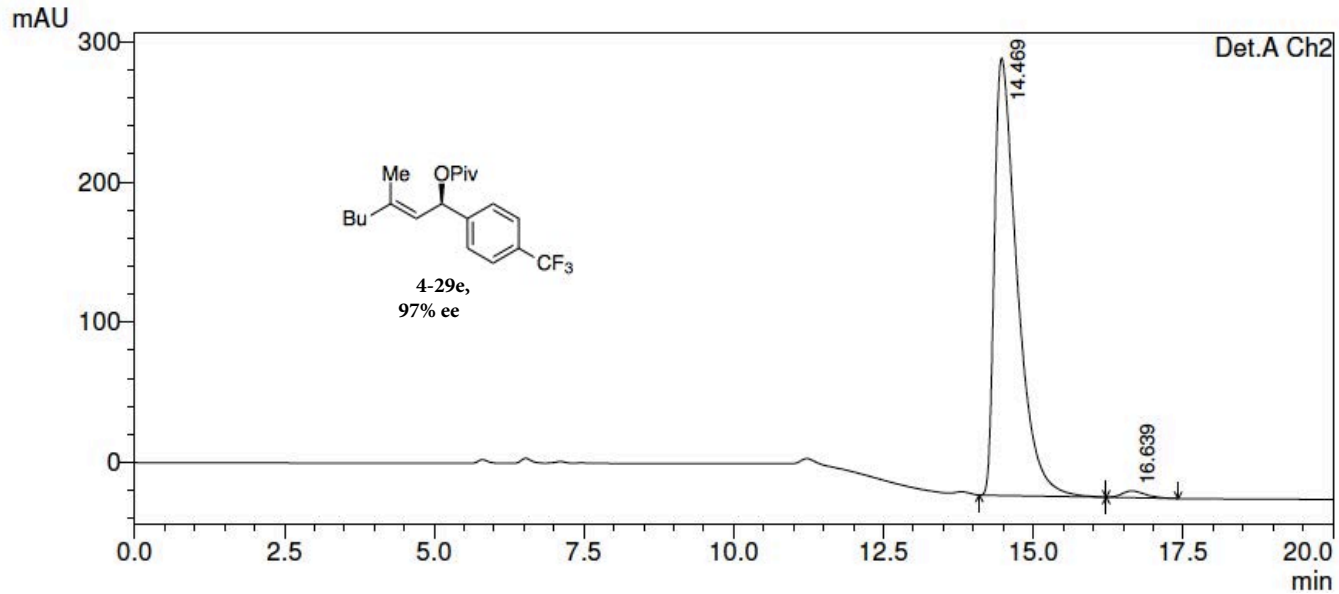
Compound 4-29e, racemic



Detector A Ch2 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.034	1143200	43216	50.678	54.626
2	17.038	1112611	35897	49.322	45.374
Total		2255811	79112	100.000	100.000

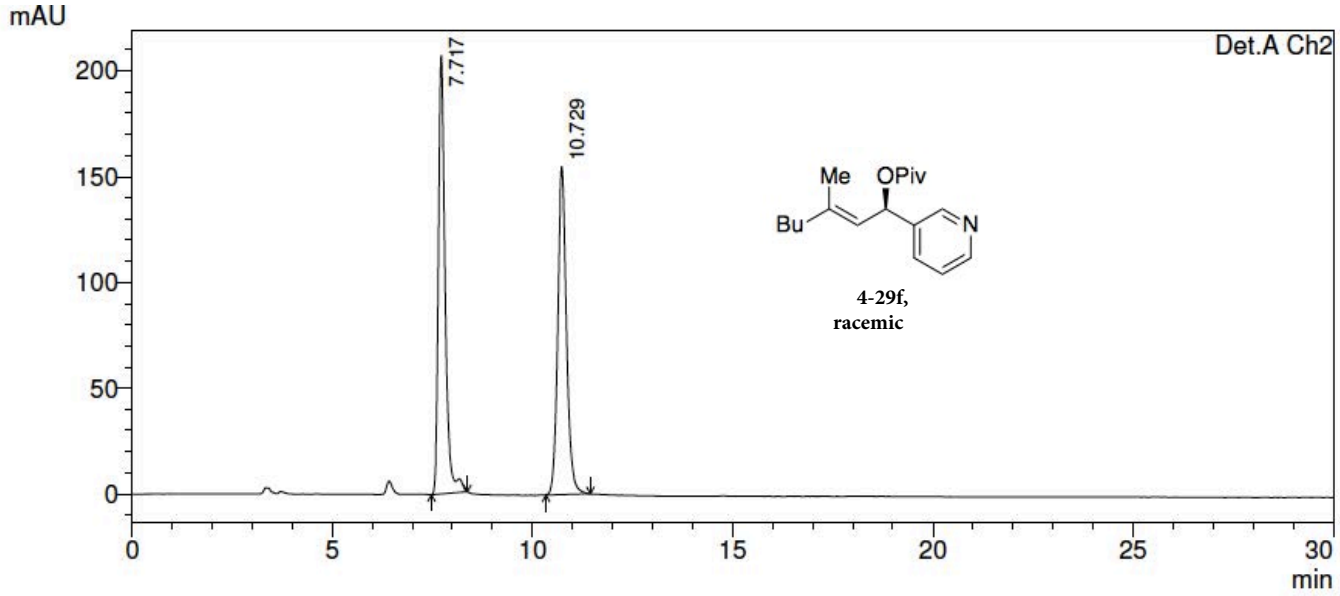
Compound 4-29e, 97% ee



Detector A Ch2 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.469	8246809	311990	98.462	98.479
2	16.639	128838	4819	1.538	1.521
Total		8375647	316809	100.000	100.000

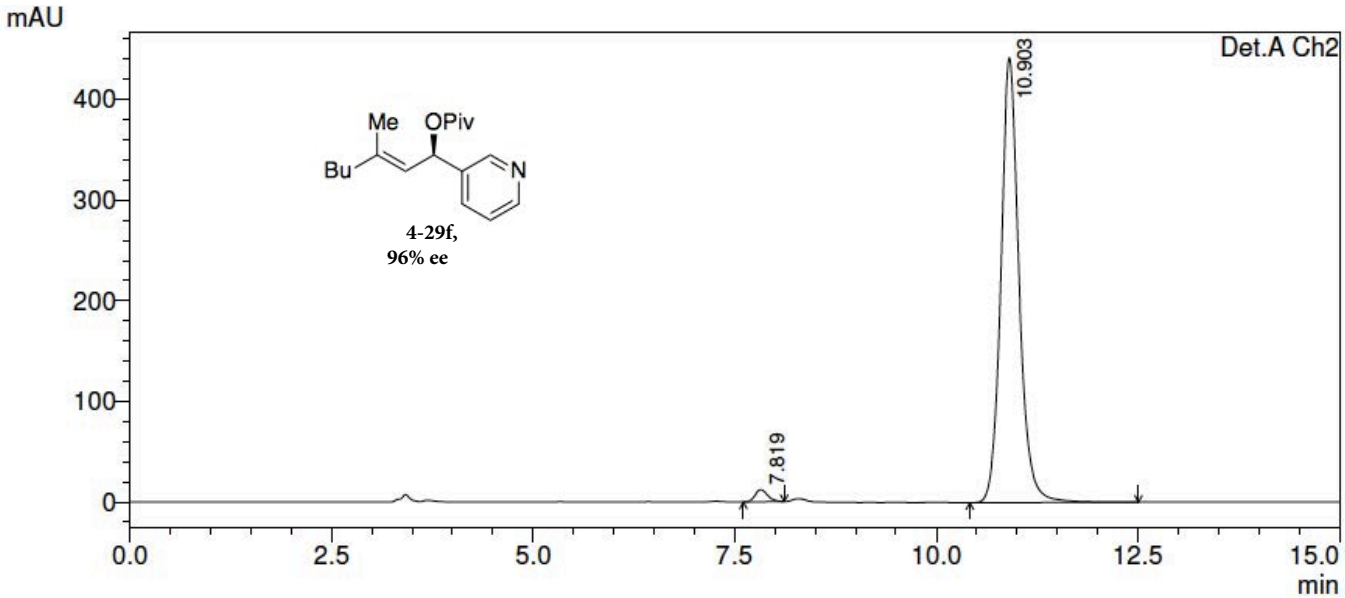
Compound 4-29f, racemic



Detector A Ch2 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.717	2393776	207135	50.452	57.192
2	10.729	2350902	155037	49.548	42.808
Total		4744678	362173	100.000	100.000

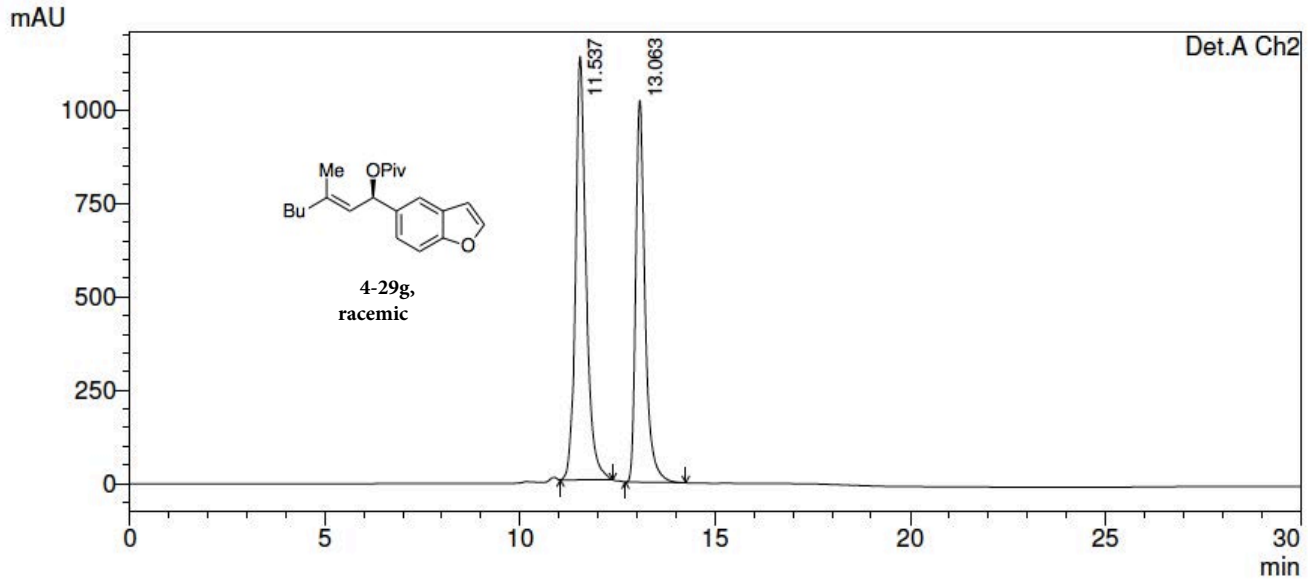
Compound 4-29f, 96% ee



Detector A Ch2 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.819	132363	12136	1.878	2.672
2	10.903	6914746	442105	98.122	97.328
Total		7047109	454242	100.000	100.000

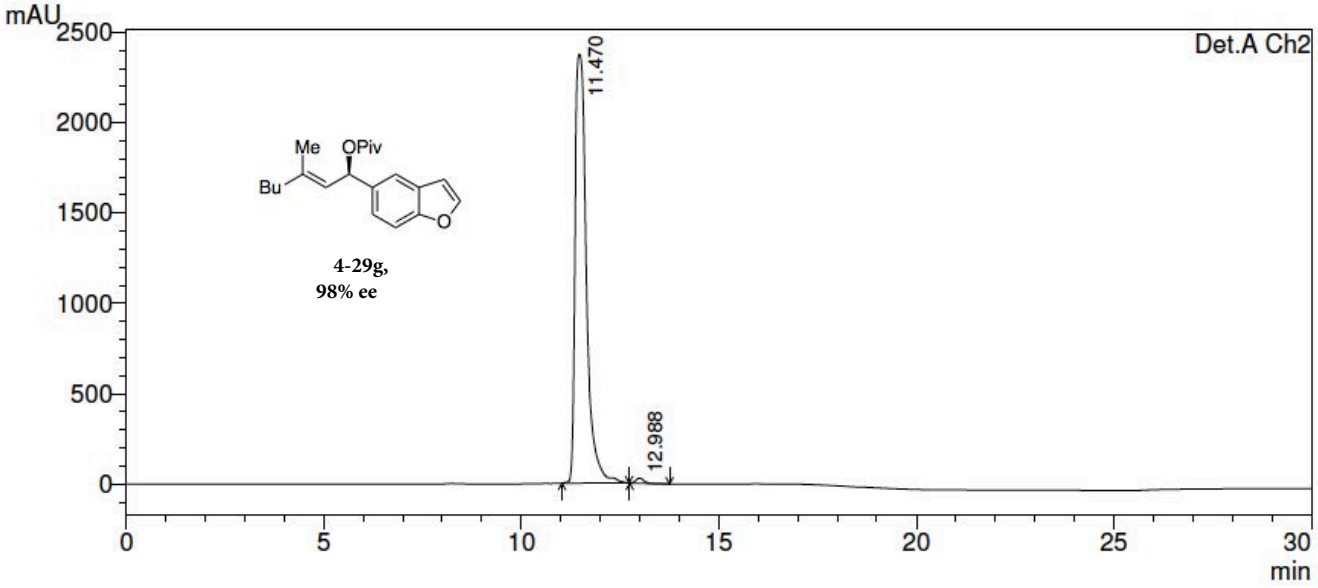
Compound 4-29g, racemic



Detector A Ch2 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.537	21254878	1133589	55.370	52.593
2	13.063	17132145	1021809	44.630	47.407
Total		38387023	2155398	100.000	100.000

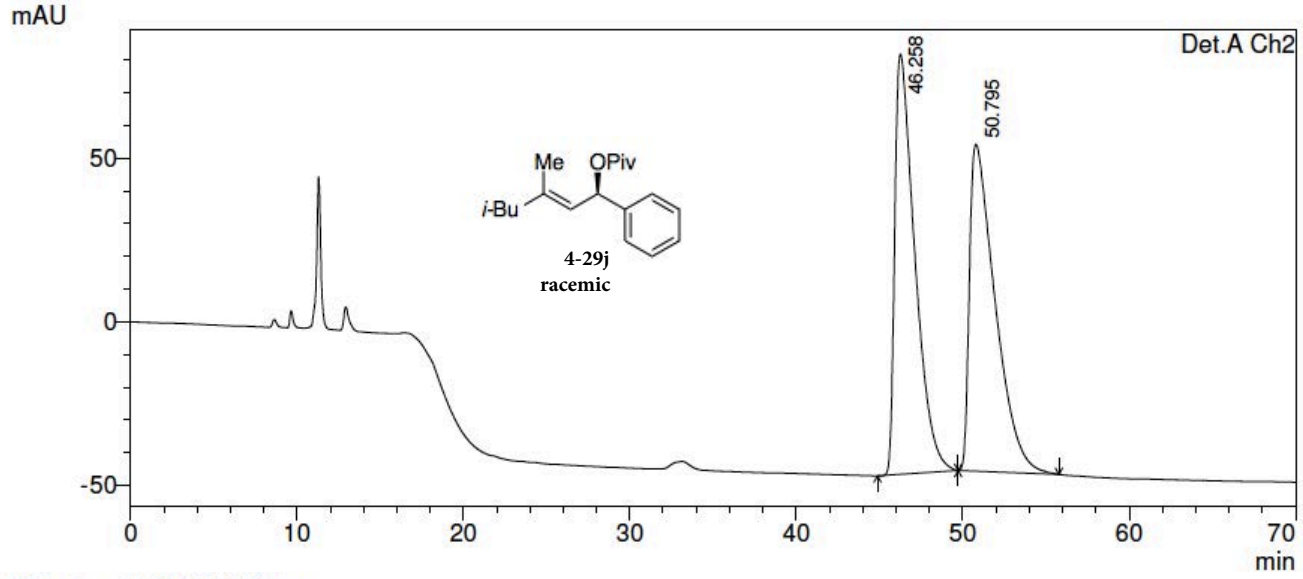
Compound 4-29g, 98% ee



Detector A Ch2 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.470	47294336	2372929	99.190	98.792
2	12.988	386123	29005	0.810	1.208
Total		47680459	2401934	100.000	100.000

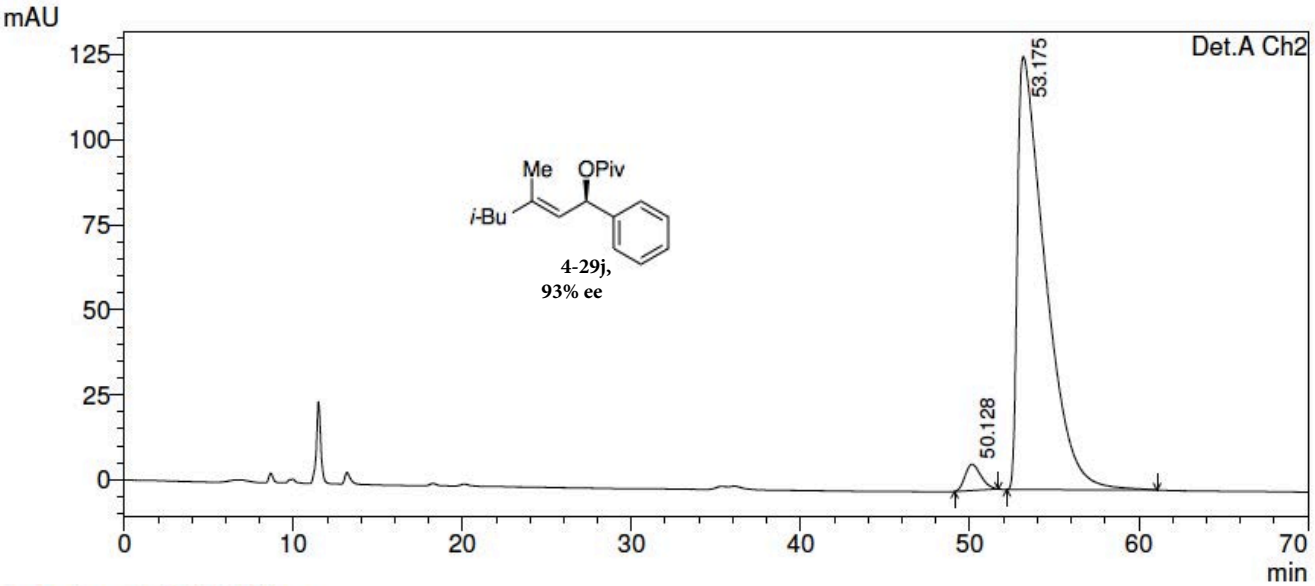
Compound 4-29j, racemic



Detector A Ch2 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	46.258	10788735	128556	50.175	56.243
2	50.795	10713561	100017	49.825	43.757
Total		21502296	228573	100.000	100.000

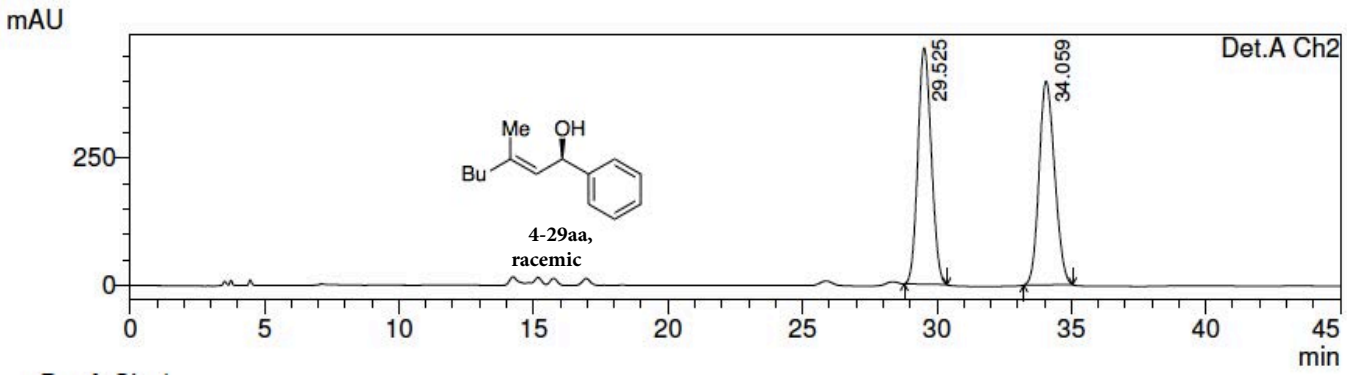
Compound 4-29j, 93% ee



Detector A Ch2 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	50.128	503325	7702	3.352	5.705
2	53.175	14514183	127308	96.648	94.295
Total		15017508	135010	100.000	100.000

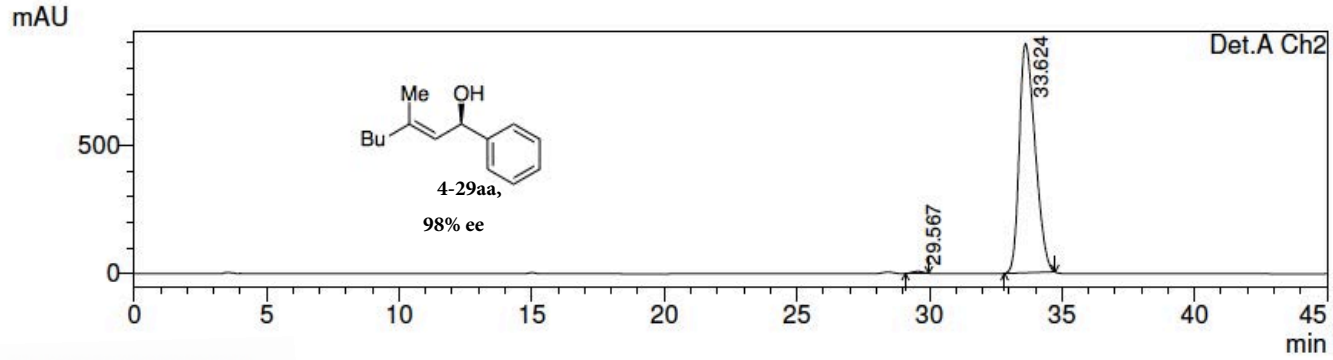
Compound 4-29aa, racemic



Detector A Ch2 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.525	16089450	463563	49.894	53.726
2	34.059	16158044	399258	50.106	46.274
Total		32247494	862821	100.000	100.000

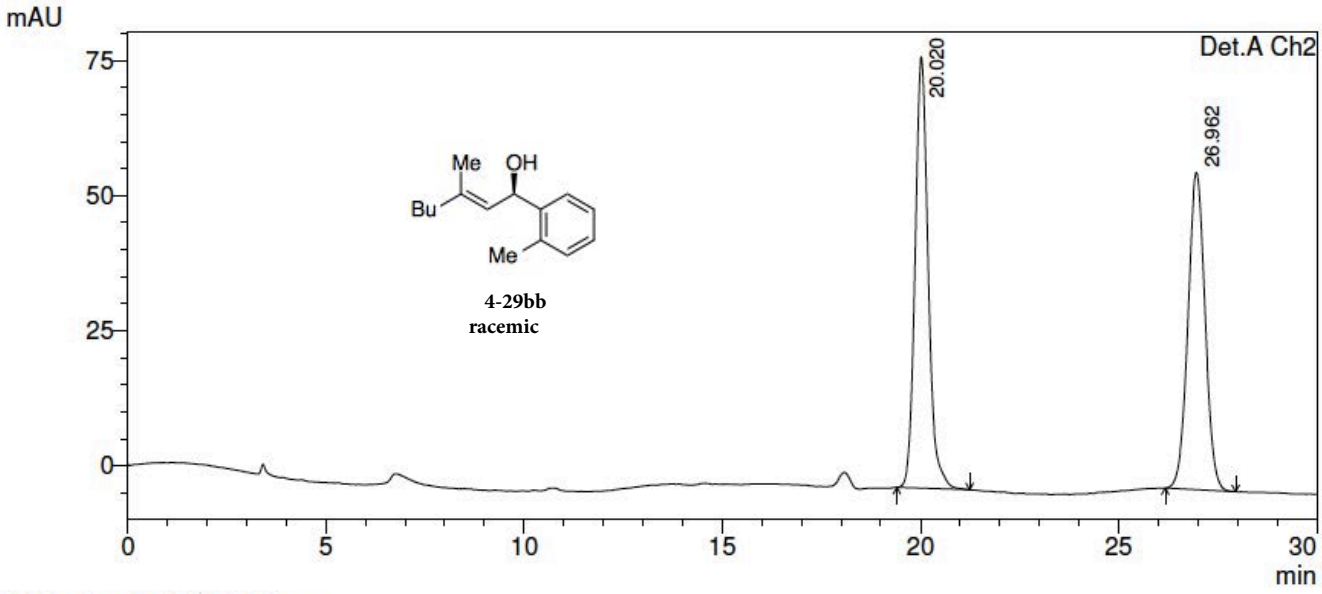
Compound 4-29aa, 98% ee



Detector A Ch2 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.567	199914	7224	0.537	0.804
2	33.624	37056909	891302	99.463	99.196
Total		37256823	898525	100.000	100.000

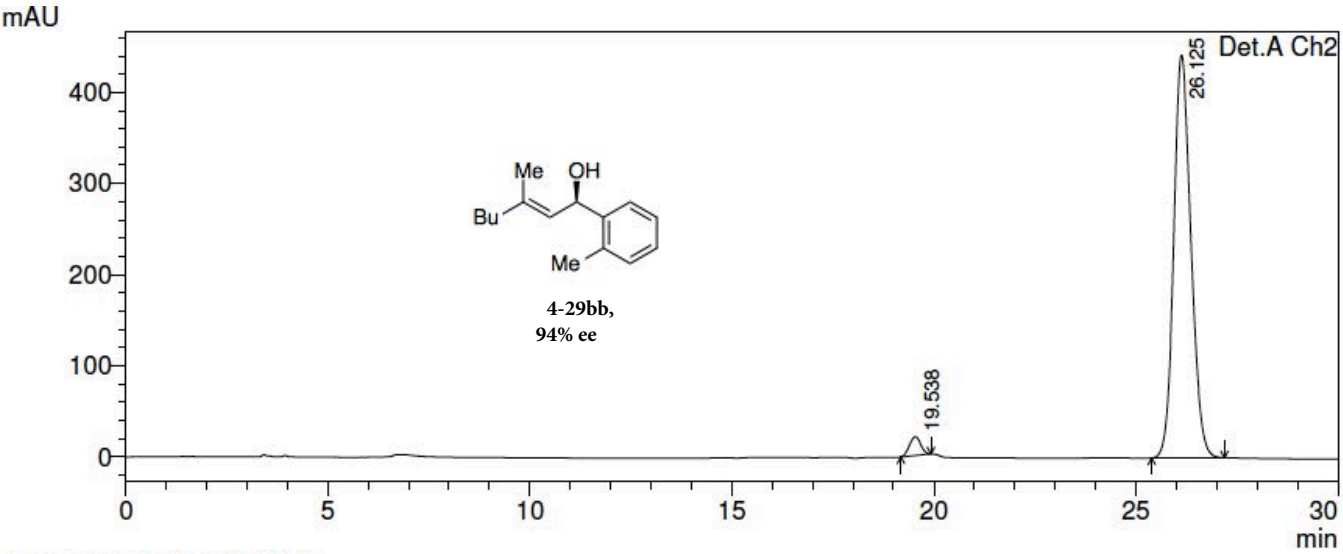
Compound 4-29bb, racemic



Detector A Ch2 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.020	1840078	79830	51.055	57.615
2	26.962	1764052	58727	48.945	42.385
Total		3604130	138556	100.000	100.000

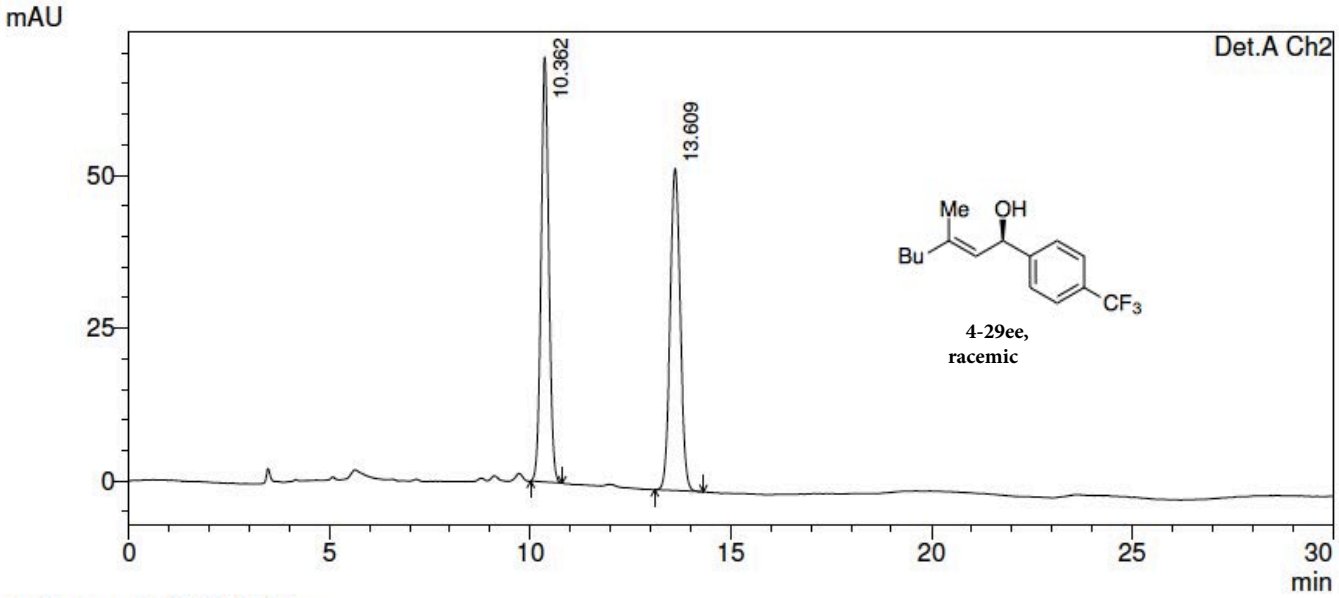
Compound 4-29bb, 94% ee



Detector A Ch2 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.538	394913	20531	2.935	4.436
2	26.125	13060249	442299	97.065	95.564
Total		13455162	462830	100.000	100.000

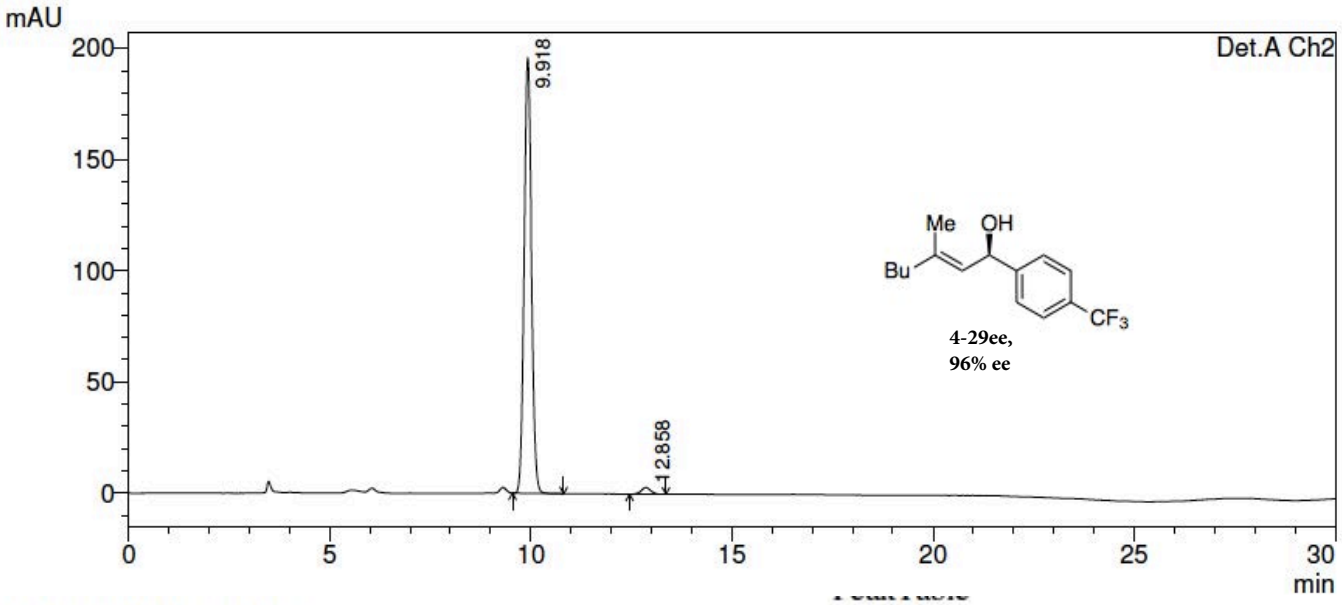
Compound 4-29ee, racemic



Detector A Ch2 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.362	938626	69546	50.404	56.893
2	13.609	923586	52693	49.596	43.107
Total		1862212	122239	100.000	100.000

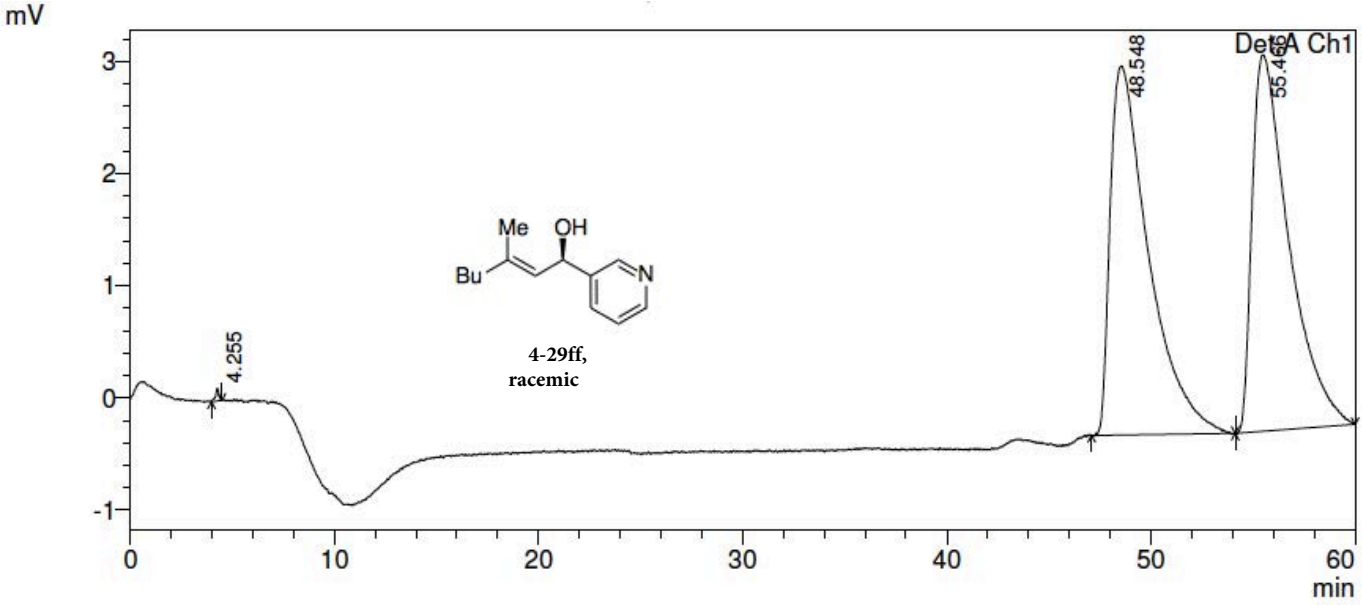
Compound 4-29ee, 96% ee



Detector A Ch2 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.918	2479272	195920	98.133	98.519
2	12.858	47159	2945	1.867	1.481
Total		2526432	198865	100.000	100.000

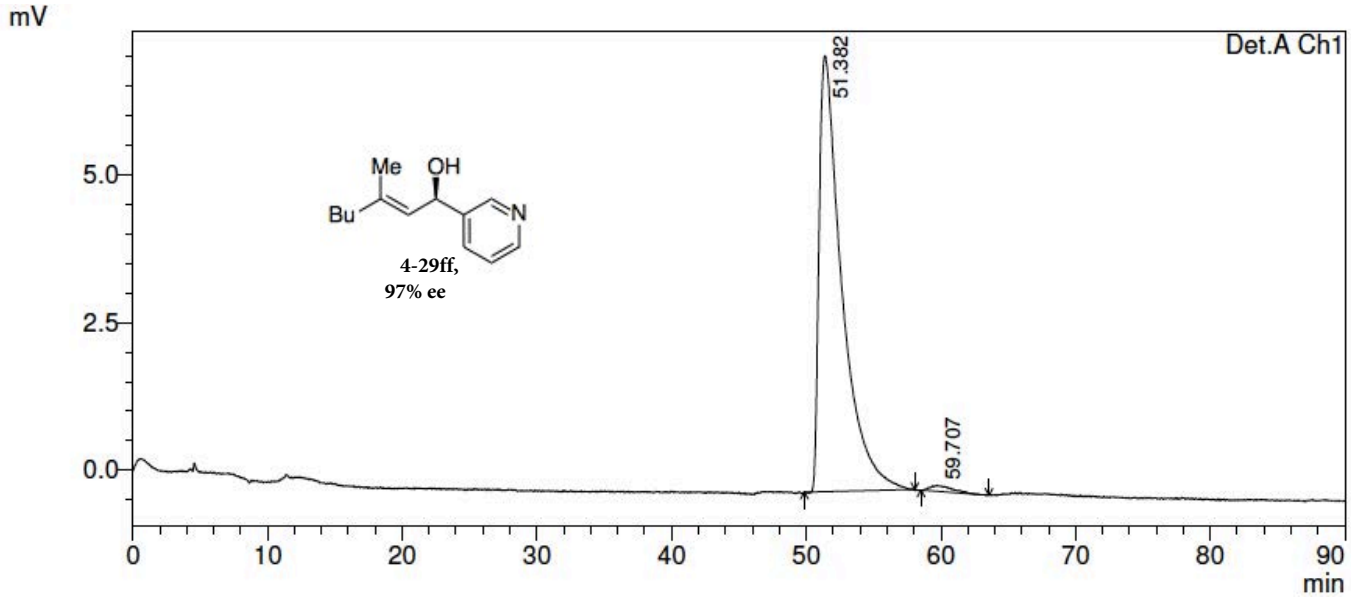
Compound 4-29ff, racemic



Detector A Ch2 254nm

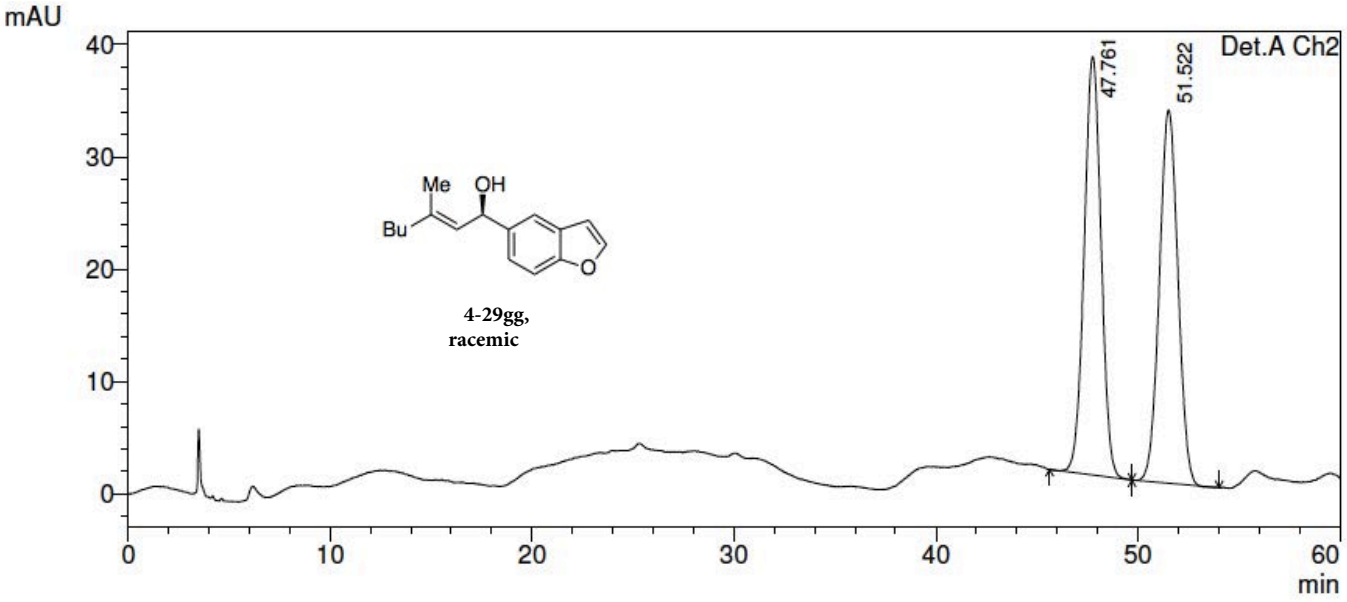
Peak#	Ret. Time	Area	Height	Area %	Height %
1	48.539	430843	3296	50.617	49.593
2	55.482	420331	3350	49.383	50.407
Total		851175	6646	100.000	100.000

Compound 4-29ff, 97% ee



Peak#	Ret. Time	Area	Height	Area %	Height %
1	51.382	865648	7381	98.645	98.613
2	59.707	11891	104	1.355	1.387
Total		877540	7485	100.000	100.000

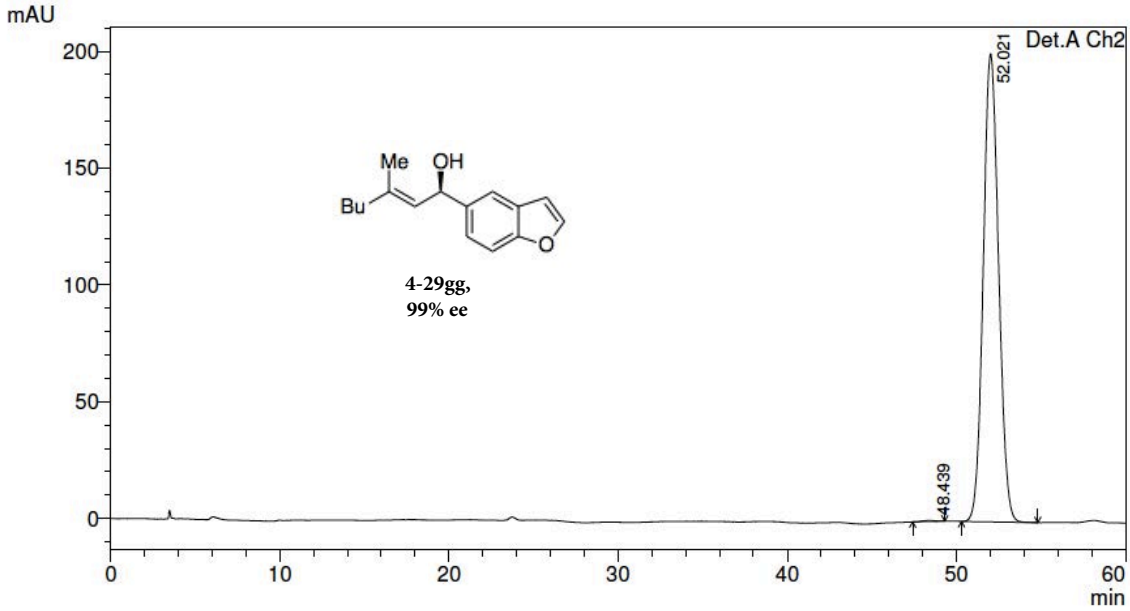
Compound 4-29gg, racemic



Detector A Ch2 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	47.761	2160552	37222	50.410	52.835
2	51.522	2125394	33227	49.590	47.165
Total		4285946	70449	100.000	100.000

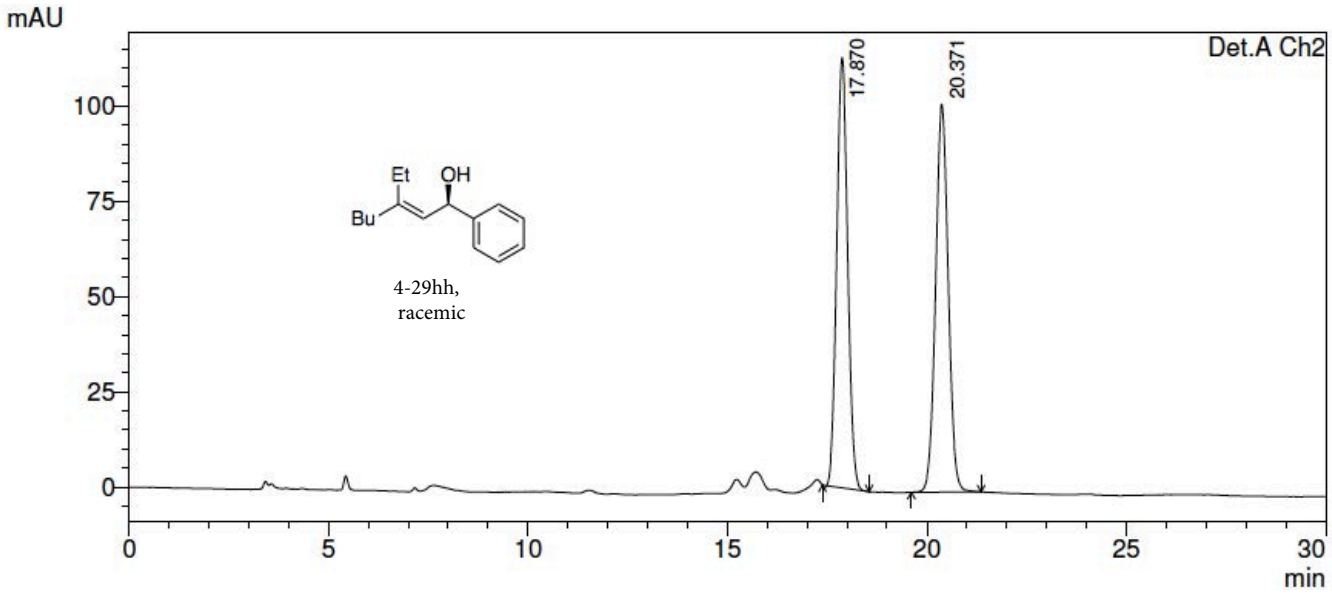
Compound 4-29gg, 99% ee



Detector A Ch2 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	48.439	20571	414	0.163	0.206
2	52.021	12622370	200325	99.837	99.794
Total		12642941	200738	100.000	100.000

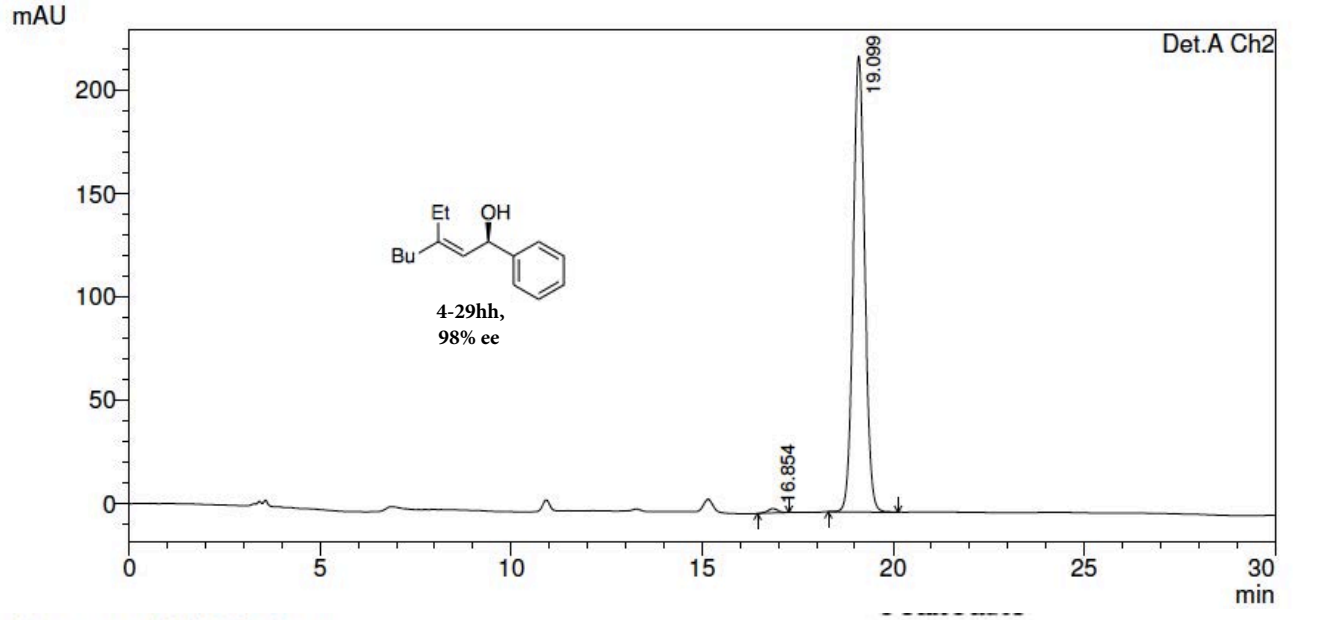
Compound 4-29hh, racemic



Detector A Ch2 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.870	2158660	112969	49.053	52.602
2	20.371	2241986	101793	50.947	47.398
Total		4400647	214762	100.000	100.000

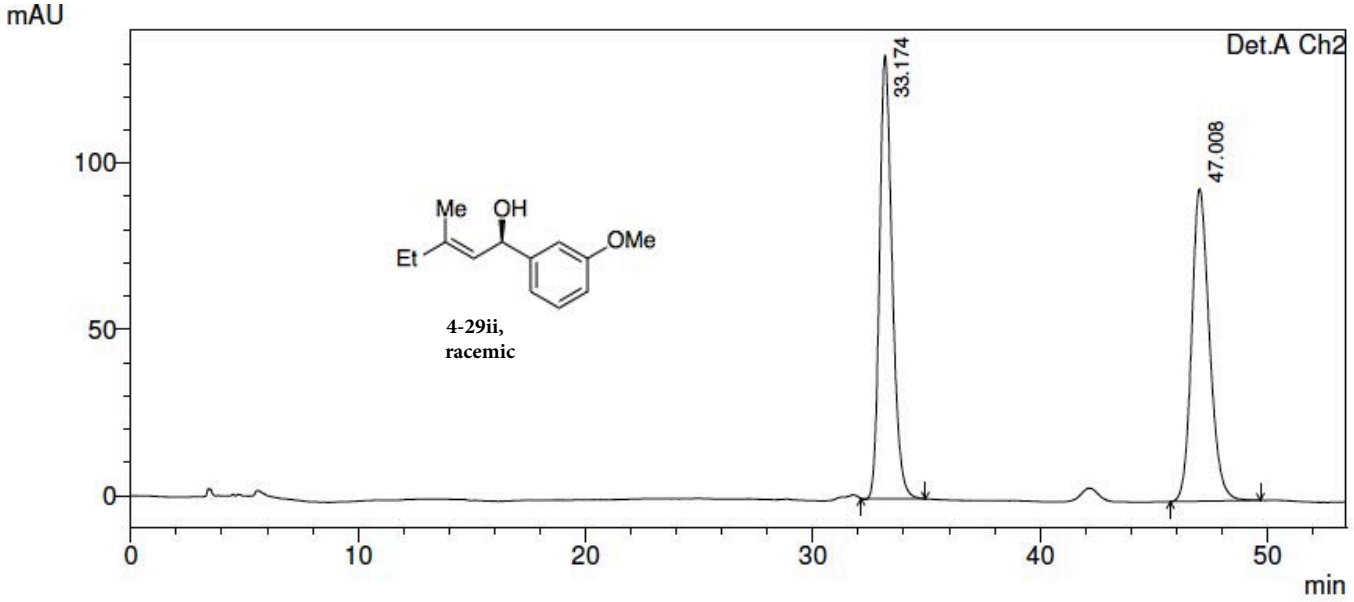
Compound 4-29hh, 98% ee



Detector A Ch2 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.854	38294	2073	0.819	0.931
2	19.099	4639023	220595	99.181	99.069
Total		4677317	222667	100.000	100.000

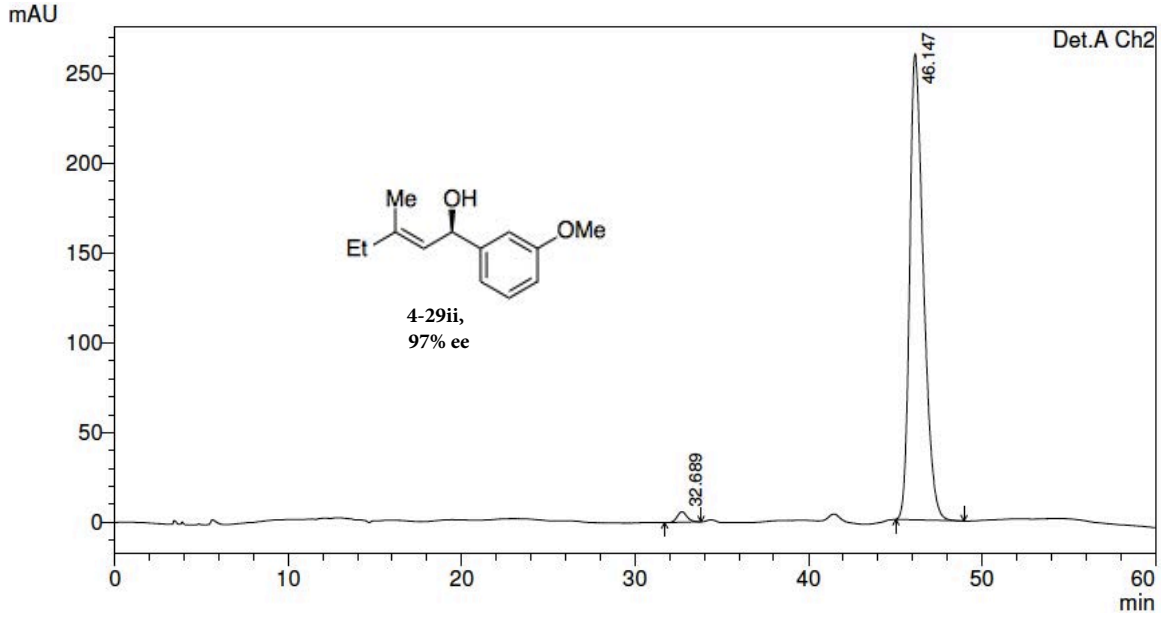
Compound 4-29ii, racemic



Detector A Ch2 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	33.174	5158905	133379	50.198	58.649
2	47.008	5118196	94041	49.802	41.351
Total		10277101	227420	100.000	100.000

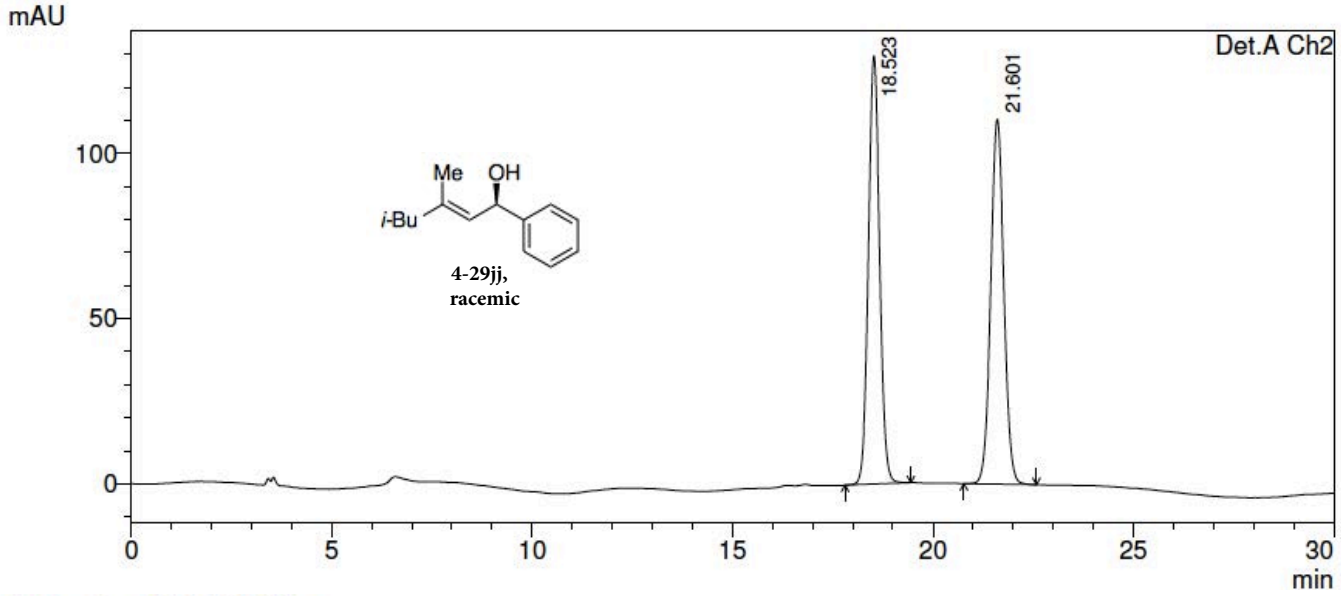
Compound 4-29ii, 97% ee



Detector A Ch2 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	32.689	225704	5805	1.545	2.186
2	46.147	14384665	259750	98.455	97.814
Total		14610369	265555	100.000	100.000

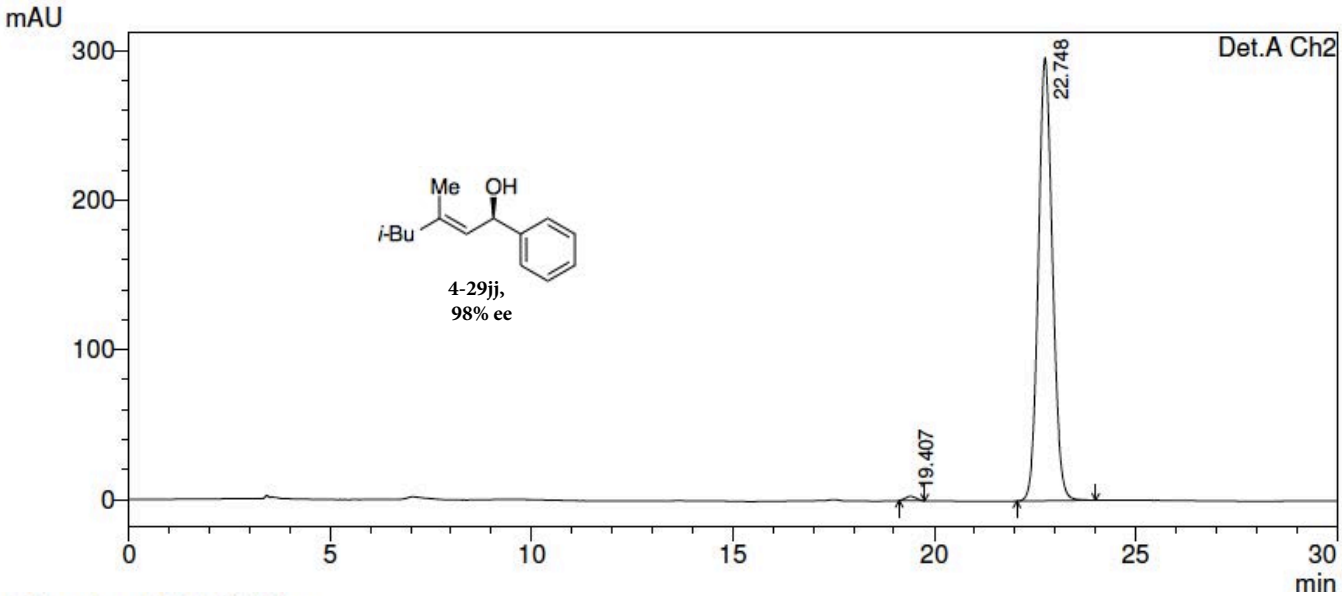
Compound 4-29jj, racemic



Detector A Ch2 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.523	2519318	129696	50.030	53.995
2	21.601	2516337	110503	49.970	46.005
Total		5035655	240199	100.000	100.000

Compound 4-29jj, 98% ee



Detector A Ch2 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.407	51562	2794	0.706	0.935
2	22.748	7252745	296151	99.294	99.065
Total		7304307	298945	100.000	100.000

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Author: Corey H. Basch, Kelsey M. Cobb, Mary P. Watson

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