Stereospecific, Nickel-Catalyzed Suzuki–Miyaura Cross-Coupling of Allylic Pivalates to Deliver Quaternary Stereocenters

Kelsey M. Cobb, Javon M. Rabb-Lynch, Megan E. Hoerrner, Alex Manders, Qi Zhou, Mary P. Watson*

Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716

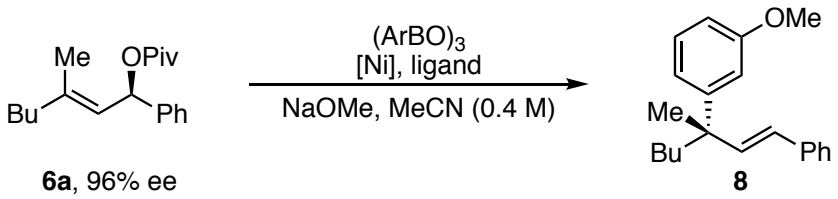
mpwatson@udel.edu

Supporting Information

General Information

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.[1] 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.[1] 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

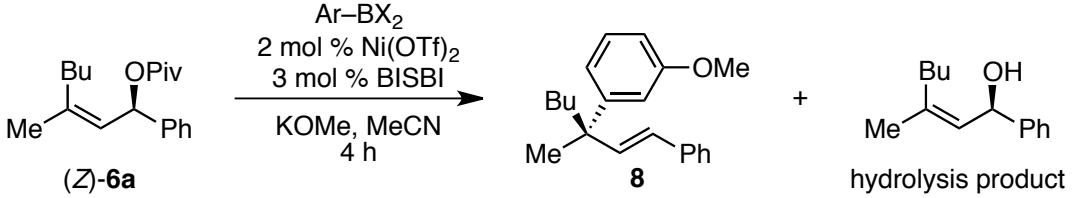
8

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 3 h, 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 analysis. An analytical sample of product **8** 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	-	-

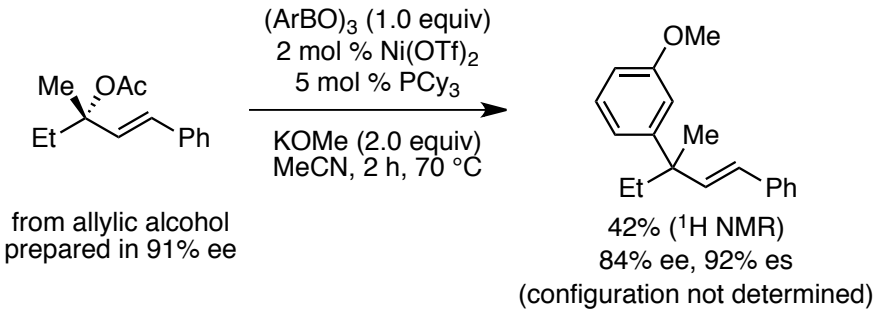
Effect of Boronic Reagent



Entry	$ArBX_2$ (equiv)	Temp (° C)	(*Z*)-**6a** (%)[a]	Hydrolysis product (%)[a]	**8** (%)[a]	es (%)[b]
1	$ArBF_3K$ (1.5)	70	0	83	Trace	n.d.[c]
2	ArBpin (1.5)	70	Trace	75	6	n.d.[c]
3	$ArB(OH)_2$ (2.0)	80	13	18	52	79
4	$(ArBO)_3$ (1.5)	80	12	0	81	81

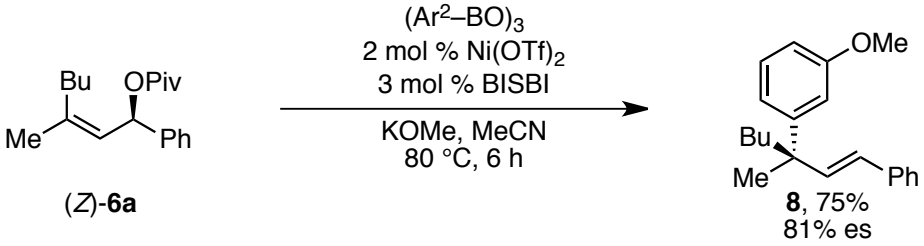
[a] Determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as internal standard. [b] es = $ee_{product}/ee_{starting\ material}$. Ee of **6a** and **8** determined by HPLC using a chiral stationary phase. [c] n.d. = not determined.

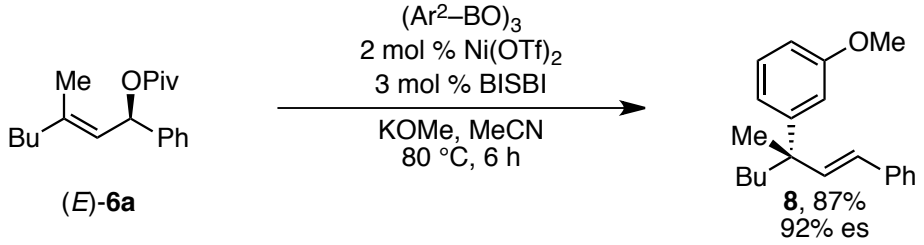
Effect of Starting Material Regiochemistry



Effect of Starting Material Alkene Geometry

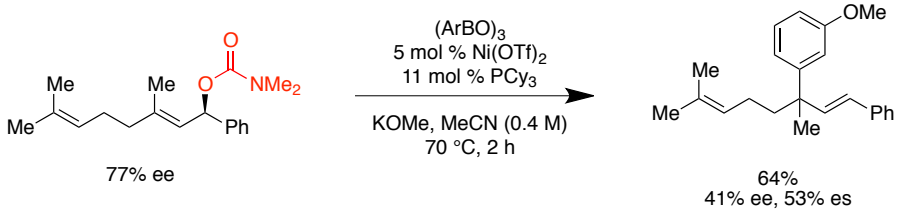
Please note: (*Z*)-**6a** contains <5% (*E*)-**6a**, as determined by ^{1}H NMR.

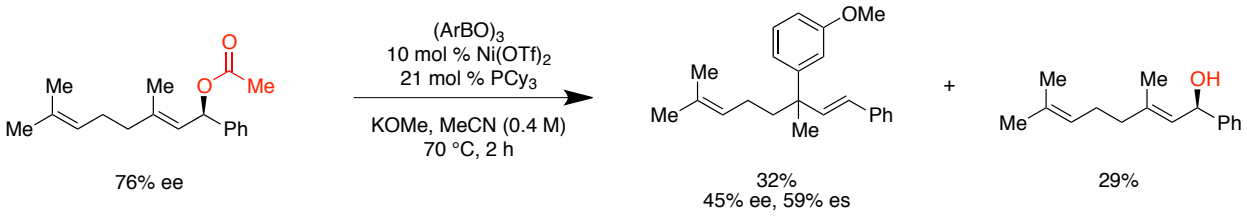


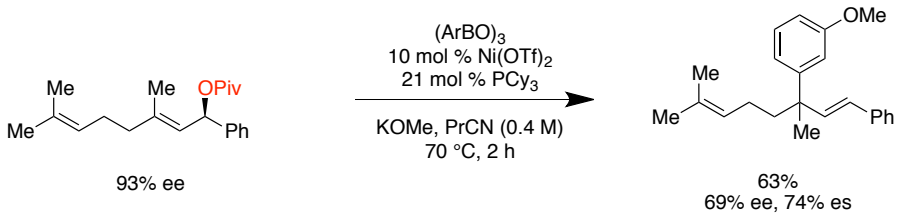


Effect of Leaving Group

Given the success we have previously observed with the pivalate leaving group, we briefly examined other leaving groups. Under similar conditions (please note that the pivalate reaction below uses PrCN instead of MeCN), lower stereochemical fidelity was observed with a carbamate and acetate. In addition, significant hydrolysis of the acetate was observed.

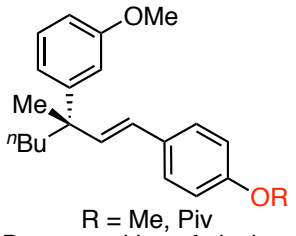






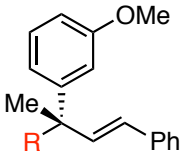
Limitations in Substrate Scope

electron-rich pivalates

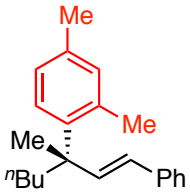


R = Me, Piv
Decomposition of pivalate and little desired product.

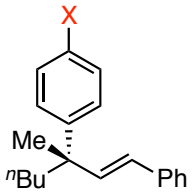
limits of steric hindrance



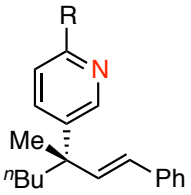
R = ^{t}Bu, ^{s}Bu



functional group & heteroaryl incompatibility



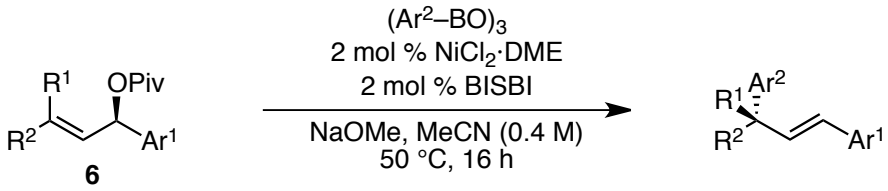
X = Br, Cl



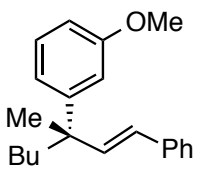
R = F, Me

Stereospecific Cross Coupling of Allylic Pivalates with Boroxines

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



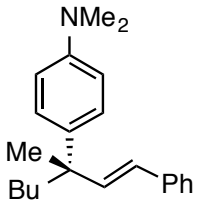
In a N_2-atmosphere glovebox, $NiCl_2$·DME (1.8 mg, 0.008 mmol, 2 mol %), BISBI (4.4 mg, 0.008 mmol, 2 mol %), and NaOMe (64.8 mg, 1.2 mmol, 3.0 equiv) were weighed into a 1-dram vial fitted with a stir bar. Allylic pivalate **6** (0.40 mmol, 1.0 equiv) and boroxine (0.30 mmol, 1.5 equiv) were added, 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 (8). Prepared via General Procedure A using pivalate **6a** (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:

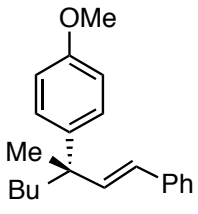
92% ee; run 2: 94% ee) by chiral HPLC analysis (CHIRACEL IC, 0.4 mL/min, 100% hexane λ=254 nm); t_R(major)= 23.73 min, t_R(minor)= 20.68 min. $[\alpha]_D^{24}$ = –17.7 (c 1.52, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 2H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.24 – 7.18 (m, 2H), 6.99 – 6.94 (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.

Product **8** was also prepared on a 1-mmol scale. In a N_2-atmosphere glovebox, $NiCl_2$·DME (4.4 mg, 0.020 mmol, 2 mol %), BISBI (11.0 mg, 0.020 mmol, 2 mol %), and NaOMe (162 mg, 3.0 mmol, 3.0 equiv) were weighed into a 2-dram vial fitted with a stir bar. Allylic pivalate **6a** (97% ee, 288 mg, 1.0 mmol, 1.0 equiv) and *m*-(methoxy)phenylboroxine (603mg, 1.5 mmol, 1.5 equiv) were added, followed by acetonitrile (2.5 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 (3 mL) and filtered through a plug of silica gel, which was rinsed with Et_2O (15 mL). The filtrate was concentrated and then purified by silica gel chromatography (2% Et_2O/hexanes) to give compound **8** (156 mg, 53%) as a pale yellow oil. The enantiomeric excess was determined to be 93% ee (96% es). The spectral data for this compound matches that of compound **8** above.

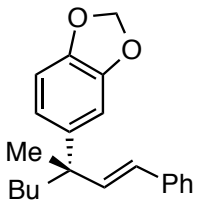


***N*,*N*-Dimethyl{*p*-[(*S*,*E*)-1-butyl-1-methyl-3-phenyl-2-propenyl]phenyl}amine (9).** Prepared via General Procedure A using pivalate **6a** (prepared in 98% ee), except that the reaction was stirred at 70 °C for 16 h. The crude material was purified by silica gel chromatography (2–5% EtOAc/hexanes) to give compound **9** (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.

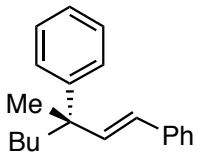


(*S*,*E*)-3-(*p*-Methoxyphenyl)-3-methyl-1-phenyl-1-heptene (10). Prepared via General Procedure A using pivalate **6a** (prepared in 98% ee). The crude material was purified by silica gel chromatography (1–2% Et_2O in hexanes) to give compound **10** (run 1: 95.5 mg, 80%; run 2: 110.3 mg, 94%) as a 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)=24.03 min, t_R(minor)=21.48 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.

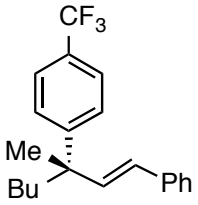


5-[(*S*,*E*)-1-Butyl-1-methyl-3-phenyl-2-propenyl]-2*H*-1,3-benzodioxole (11). Prepared via General Procedure A using pivalate **6a** (prepared in 98% ee). The crude material was purified by silica gel chromatography (1–2% Et_2O/hexanes) to give compound **11** (run 1:

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, $CDCl_3$) 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.

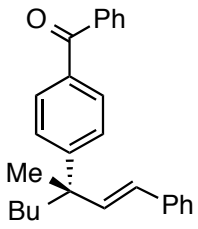


(*S*,*E*)-3-Methyl-1,3-diphenyl-1-heptene (12). Prepared via General Procedure A using pivalate **6a** (prepared in 98% ee). The crude material was purified by silica gel chromatography (0–1% Et_2O/hexanes) to give compound **12** (run 1: 94.7 mg, 90%; run 2: 89.4 mg, 84%) as a colorless oil. The enantiomeric 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.

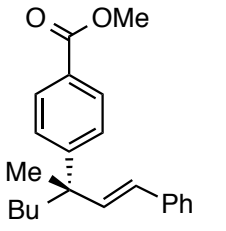


(*S*,*E*)-3-Methyl-1-phenyl-3-[*p*-(trifluoromethyl)phenyl]-1-heptene (13). Prepared via General Procedure A using pivalate **6a** (prepared in 98% ee).The crude material

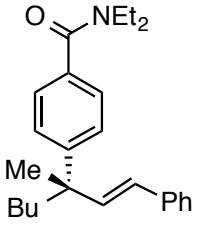
was purified by silica gel chromatography (0–1% Et_2O/hexanes) to give compound **13** (run 1: 123.2 mg, 93%; run 2: 115.6 mg, 87%) as a colorless oil. The enantiomeric excess was determined to be 88% (run 1: 88% ee; run 2: 88% ee) by chiral HPLC analysis (CHIRALPAK OJ-3R, 1.0 mL/min, 50-100% MeCN in 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 152.1, 138.4, 137.5, 128.6, 128.1 (q, $J_{C\text{-}F}$ = 32.3 Hz), 127.6, 127.3, 127.1, 126.2, 125.1 (q, $J_{C\text{-}F}$ = 3.7 Hz), 124.4 (q, $J_{C\text{-}F}$ = 272.7 Hz), 44.2, 41.3, 26.8, 25.6, 23.4, 14.1; ^{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 (14). Prepared via General Procedure A using pivalate **6a** (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 **14** (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.

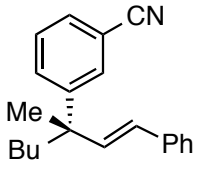


Methyl *p*-[(*S*,*E*)-1-butyl-1-methyl-3-phenyl-2-propenyl]benzoate (15). Prepared via General Procedure A using pivalate **6a** (prepared in 98% ee). The crude material was purified by silica gel chromatography (1–2% Et_2O/hexanes) to give compound **15** (run 1: 115.6 mg, 87%; run 2: 107.3 mg, 95%) 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.

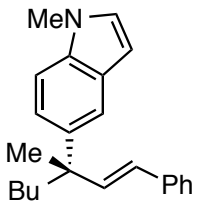


{*p*-[(*S*,*E*)-1-Butyl-1-methyl-3-phenyl-2-propenyl]phenyl} (diethylamino)formaldehyde (16). Prepared via General Procedure A using pivalate **6a** (prepared in 98% ee)), except that the reaction mixture was heated at 70 °C for 16 h.. The crude material was purified by silica gel chromatography (20–25% EtOAc/hexanes) to give compound **16** (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, $CDCl_3$) δ 7.40 – 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.

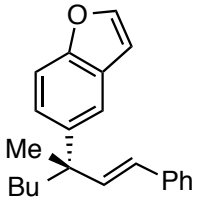


***p*-[(*S*,*E*)-1-Butyl-1-methyl-3-phenyl-2-propenyl]benzonitrile (17).** Prepared via General Procedure A using pivalate **6a** (prepared in 98% ee), except that the reaction mixture was heated at 70 °C for 16 h. The crude material was purified by silica gel chromatography (3–5% EtOAc/hexanes) to give compound **17** (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.

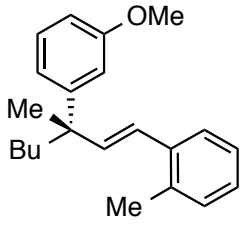


5-[(*S*,*E*)-1-Butyl-1-methyl-3-phenyl-2-propenyl]-1-methyl-1*H*-indole (18). Prepared via General Procedure A using pivalate **6a** (prepared in 98% ee), except that the reaction mixture was heated at 70 °C for 16 h. The crude material was purified by silica gel

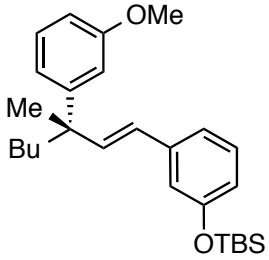
chromatography (3–5% EtOAc/hexanes) to give compound **18** (run 1: 99.6 mg, 78%; run 2: 101.6 mg, 80%) as a pale yellow oil. The enantiomeric excess was determined to be 89% (run 1: 89% ee; run 2: 88% ee) by chiral HPLC analysis (CHIRALPAK IC, 0.8 mL/min, 100% hexanes, λ=254 nm); t_R(major)=33.20 min, t_R(minor)=22.56 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; FTIR (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 (19). Prepared via General Procedure A using pivalate **6a** (prepared in 98% ee). The crude material was purified by silica gel chromatography (0–1% Et_2O/hexanes) to give compound **19** (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.

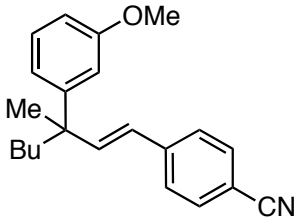


(*S*,*E*)-3-(*m*-Methoxyphenyl)-3-methyl-1-(*o*-tolyl)-1-heptene (20). Prepared via General Procedure A using pivalate **6b** (prepared in 98% ee), except that the reaction mixture was heated at 70 °C for 16 h. The crude material was purified by silica gel chromatography (3–5% EtOAc/hexanes) to give compound **20** (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, 1H), 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.

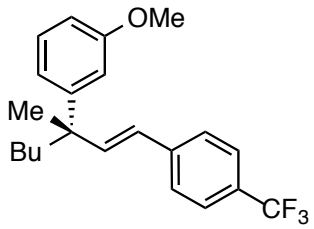


(S,E)-*tert*-Butyl(3-(3-(3-methoxyphenyl)-3-methylhept-1-en-1-yl)phenoxy)dimethylsilane (21). Prepared via General Procedure A using pivalate **6c** (prepared in 96% ee). The crude material was purified by silica gel chromatography (1–2% Et_2O/hexanes) to give compound **21** (run 1: 103.5 mg, 61%; run 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 –

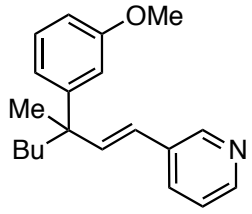
6.89 (m, 1H), 6.86 – 6.83 (m, 1H), 6.75 (dd, J = 8.1, 2.3 Hz, 1H), 6.69 (dd, J = 8.0, 1.8 Hz, 1H), 6.38 (d, J = 16.2 Hz, 1H), 6.31 (d, J = 16.3 Hz, 1H), 3.80 (s, 3H), 1.91 – 1.75 (m, 2H), 1.45 (s, 3H), 1.35 – 1.25 (m, 2H), 1.25 – 1.18 (m, 1H), 1.18 – 1.11 (m, 1H), 0.99 (s, 9H), 0.87 (t, J = 7.3 Hz, 3H), 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*-[(*E*)-3-(*m*-Methoxyphenyl)-3-methyl-1-heptenyl]benzonitrile (22).** Prepared via General Procedure A using pivalate **6d** (prepared in 98% ee, unknown absolute configuration). The crude material was purified by silica gel chromatography (3–5% Et_2O/hexanes) to give compound **22** (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. The absolute configuration is unknown, because the starting material configuration is unknown. $[\alpha]_D^{24}$ = –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.

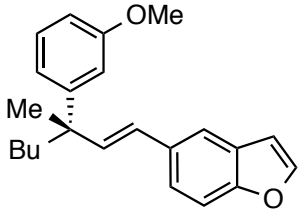


(*S*,*E*)-3-(*m*-Methoxyphenyl)-3-methyl-1-[*p*-(trifluoromethyl)phenyl]-1-heptene (23). Prepared via General Procedure A using pivalate **6e** (prepared in 97% ee). The crude material was purified by silica gel chromatography (1–2% Et_2O/hexanes) to give compound **23** (run 1: 106.4 mg, 74%; run 2: 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.

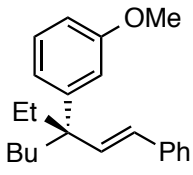


3-[(*E*)-3-(*m*-Methoxyphenyl)-3-methyl-1-heptenyl]pyridine (24). Prepared via General Procedure A using pivalate **6f** (prepared in 96% ee, unknown absolute configuration). The crude material was purified by silica gel chromatography (40% EtOAc/hexanes with 5% Et_3N) to give compound **24** (run 1: 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. The absolute configuration is unknown, because the starting material configuration is unknown. $[\alpha]_D^{24}$ = +13.4 (c 1.86, $CHCl_3$): ^{1}H NMR

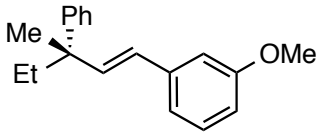
(600 MHz, $CDCl_3$) δ 8.59 (d, *J* = 2.2 Hz, 1H), 8.46 – 8.41 (m, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.25 (m, *J* = 7.9 Hz, 1H), 7.22 (dd, *J* = 8.0, 4.8 Hz, 1H), 6.96 – 6.91 (m, 1H), 6.89 (t, *J* = 2.2 Hz, 1H), 6.78 – 6.74 (m, 1H), 6.48 (d, *J* = 16.3 Hz, 1H), 6.35 (d, *J* = 16.3 Hz, 1H), 3.80 (s, 3H), 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.



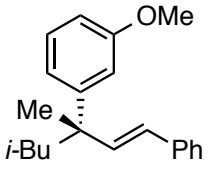
5-[(*S*,*E*)-3-(*m*-Methoxyphenyl)-3-methyl-1-heptenyl]-1-benzofuran (25). Prepared via General Procedure A using pivalate **6g** (prepared in 98% ee). The crude material was purified by silica gel chromatography (1–2% Et_2O/hexanes) to give compound **25** (run 1: 120.2 mg, 90%; run 2: 120.3 mg, 90%) 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, $CHCl_3$); ^1H 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.



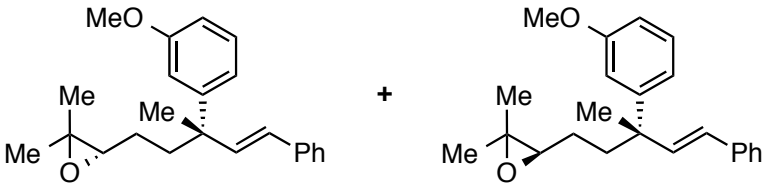
(*S*,*E*)-3-Ethyl-3-(*m*-methoxyphenyl)-1-phenyl-1-heptene (26). Prepared via General Procedure A using pivalate **6h** (prepared in 98% ee). The crude material was purified by silica gel chromatography (1–2% Et_2O/hexanes) to give compound **26** (run 1: 82 mg, 67%; run 2: 89 mg, 70%) as a colorless 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)=58.44 min, t_R(minor)=55.13 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 (27). Prepared via General Procedure A using pivalate **6i** (prepared in 97% ee). The crude material was purified by silica gel chromatography (1–2% Et_2O/hexanes) to give compound **27** (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.

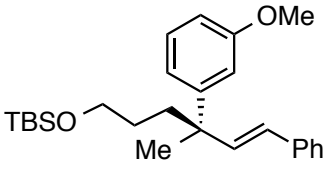


(*S*,*E*)-3-(*m*-Methoxyphenyl)-3,5-dimethyl-1-phenyl-1-hexene (28). Prepared via General Procedure A using pivalate **6j** (prepared in 98% ee). The crude material was purified by silica gel chromatography (1–2% Et_2O/hexanes) to give compound **28** (run 1: 97.9 mg, 83%; run 2: 100.6 mg, 85%) as a 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)=23.38 min, t_R(minor)=19.99 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.

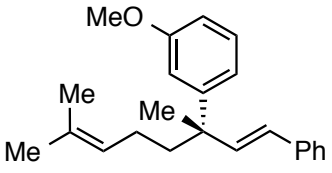


3-[(*S*,*E*)-3-(*m*-Methoxyphenyl)-3-methyl-5-phenyl-4-pentenyl]-2,2-dimethyloxirane (29). Prepared via General Procedure A using pivalate **6k** (1:1 mixture of diastereomers, each diastereomer prepared in 98% ee). The crude material was purified by silica gel chromatography (10–15% Et_2O in hexanes) to give compound **29** (run 1: 121.7 mg, 91%, 1:1 dr; run 2: 118.2 mg, 88%, 1:1 dr) as a colorless oil. The enantiomeric excess of diastereomer 1 was determined to be 82% (run 1: 83% ee; run 2: 81% ee), and the enantiomeric excess of diastereomer 2 was determined to be 83% (run 1: 84% ee; run 2: 81% ee), by chiral HPLC analysis of the mixture of diastereomers (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 7.41 – 7.35 (m, 4H), 7.35 – 7.28 (m, 4H), 7.26 – 7.15 (m, 8H), 6.95 (dd, *J* =

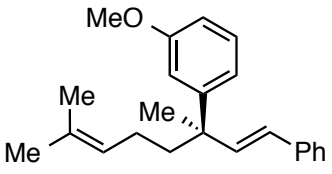
7.7, 2.1 Hz, 2H), 6.91 (q, *J* = 2.1 Hz, 2H), 6.79 – 6.72 (m, 2H), 6.41 (d, *J* = 1.6 Hz, 4H), 3.80 (s, 6H), 2.70 (t, *J* = 6.3 Hz, 2H), 2.21 – 1.99 (m, 2H), 1.99 – 1.79 (m, 2H), 1.56 – 1.41 (m, 10H), 1.34 (s, 2H), 1.28 (d, *J* = 1.2 Hz, 6H), 1.20 (s, 3H), 1.17 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, both diastereomers) δ 159.5, 149.1, 148.9, 138.6, 138.2, 137.6, 137.5, 129.20, 129.18, 128.56, 128.55, 127.5, 127.23, 127.17, 127.1, 126.2, 119.2, 119.1, 113.4, 113.3, 110.59, 110.56, 64.63, 64.62, 58.50, 58.47, 55.2, 43.79, 43.76, 37.9, 37.7, 25.5, 25.3, 24.9, 24.5, 24.4, 18.7, 18.6; 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. Please note that the ^{1}H and ^{13}C NMR spectra are complicated; some peaks of the diastereomers are coincident. Please see attached spectra.



(*S,E*)-*tert*-Butyl((4-(3-methoxyphenyl)-4-methyl-6-phenylhex-5-en-1-yl)oxy)dimethylsilane (30). Prepared via General Procedure A using pivalate **6l** (prepared in >99% ee). The crude material was purified by silica gel chromatography (1–2% Et_2O/hexanes) to give compound **30** (109.1 mg, 69%) as a colorless 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.



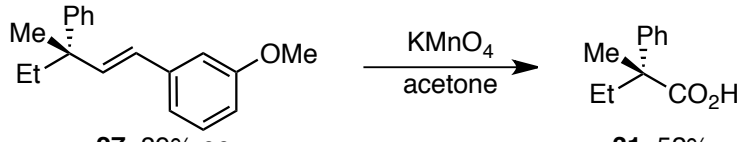
(*S*,1*E*)-3-(*m*-Methoxyphenyl)-3,7-dimethyl-1-phenyl-1,6-octadiene ((*S*)-32). Prepared via General Procedure A using pivalate (*E*)-**6m** (prepared in 98% ee). The crude material was purified by silica gel chromatography (1–2% Et_2O/hexanes) to give compound (*S*)-**32** (run 1: 119.0 mg, 93%, run 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 ((*R*)-32). Prepared via General Procedure A using pivalate (*Z*)-**6m** (prepared in 97% ee). The crude material was purified by silica gel chromatography (1–2% Et_2O/hexanes) to give compound (*R*)-**32** (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.

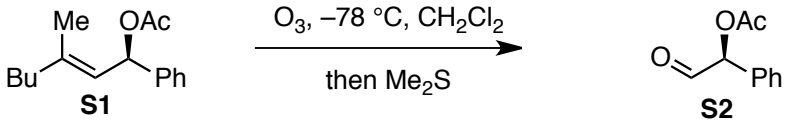
Determination of Absolute Configuration



27, 89% ee

31, 52%
$[\alpha]^D$ –21.9
literature: $[\alpha]^D$ –32.6

(*R*)-2-Methyl-2-phenylhexanoic acid (31). The following synthesis was adapted from a literature procedure.[2] (*S*,*E*)-1-(*m*-Methoxyphenyl)-3-methyl-3-phenyl-1-pentene (**27**) (90.6 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, 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 **31** as a white solid. The spectral data matched that reported in the literature.[3] $[\alpha]_D^{24}$ = 21.9 (c 0.42, C_6H_6). The absolute configuration assigned by comparing the optical rotation with a reported literature value for *(R)*-**31**, $[\alpha]_D^{20}$ = 32.6 (c 0.3, C_6H_6).[4]



S1

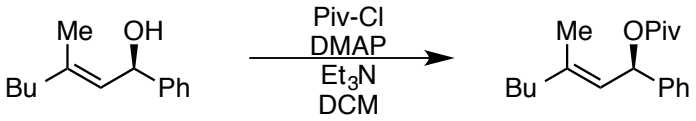
S2
$[\alpha]_D^{20}$ +123.9
literature: $[\alpha]_D^{20}$ +119

(*S*)-Formylphenylmethyl acetate (S2). (*R*,*E*)-3-Methyl-1-phenyl-2-heptenyl acetate (**S1**, 1.9 mmol, 1.0 equiv), prepared from allylic alcohol **6aa**, was dissolved in anhydrous CH_2Cl_2 (76

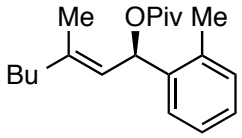
mL, 0.025 M). The solution was cooled to –78 °C. Ozone was then passed through the solution until there was a persistent blue color. Dimethyl sulfide (3.8 mmol, 2.0 equiv) was then added dropwise to the solution at –78 °C. The solution was allowed to stir and slowly warm to room temperature over a period of 3 h. The solution was then concentrated, and purified via silica gel chromatography (30% EtOAc/hexanes) to give compound **S2** 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)*-**S2**, $[\alpha]_D^{24}$ = 119 (acetone).[5]

Preparation of Pivalates

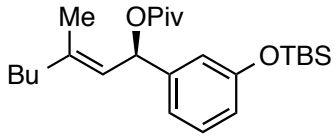
General Procedure B: Preparation of Allylic Pivalates (6a-6i)



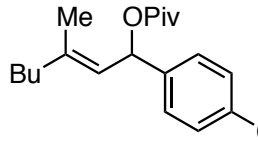
(*R*,*E*)-3-Methyl-1-(phenyl)-2-heptenyl pivalate (6a). (*R,E*)-3-methyl-1-phenyl-2-hepten-1-ol (**6aa**, 1.26 g, 12.2 mmol, 1.0 equiv, 98% ee) and DMAP (75 mg, 0.62 mmol, 0.10 equiv) were dissolved in CH_2Cl_2 (25 mL, 0.25 M). Et_3N (1.72 mL, 12.3 mmol, 2.0 equiv) and pivaloyl chloride (0.91 mL, 7.39 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 **6a** (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, 2H), 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 (6b). Prepared according to General Procedure B on a 2.75 mmol scale to give **6b** (607 mg, 83%) as a yellow oil. The enantiomeric excess was assumed to be 93%, because that is the ee of the allylic alcohol precursor. $[\alpha]_D^{24}$ = –43.4 (c 1.54, $CHCl_3$): ^{1}H 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.

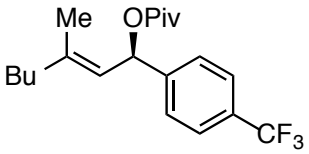


(*R*,*E*)-1-(3-((*tert*-Butyldimethylsilyl)oxy)phenyl)-3-methylhept-2-en-1-yl pivalate (6c). Prepared according to General Procedure B on a 4.12 mmol scale to give **6c** (1.24 g, 72%) as a clear oil. The enantiomeric excess was assumed to be 96%, because that is the ee of the allylic alcohol precursor. $[\alpha]_D^{24}$ = –28.5 (c 1.59, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.9 Hz, 1H), 6.90 (d, *J* = 7.7 Hz, 1H), 6.80 (d, *J* = 1.9 Hz, 1H), 6.73 (dd, *J* = 9.2, 1.9 Hz, 1H), 6.42 (d, *J* = 9.0 Hz, 1H), 5.29 (d, *J* = 7.8 Hz, 1H), 2.02 (t, *J* = 7.6 Hz, 2H), 1.80 (s, 3H), 1.44 – 1.34 (m, 2H), 1.26 (q, *J* = 7.3 Hz, 2H), 1.22 (s, 9H), 0.98 (s, 9H), 0.88 (t, *J* = 7.3 Hz, 3H), 0.19 (s, 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.

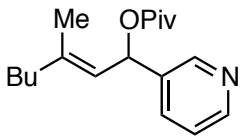


(*E*)-1-(p-Cyanophenyl)-3-methyl-2-heptenyl pivalate (6d). Prepared according to General Procedure B on a 0.72 mmol scale to give **6d** (202 mg, 89%) as a yellow oil. The enantiomeric excess was determined to be 98% by chiral HPLC analysis (CHIRALPAK

IA, 1.0 mL/min, 3% isopropanol/hexane, λ=254 nm); t_R(major)=4.38 min, t_R(minor)=5.28 min. The absolute configuration is unknown, because the starting material configuration is unknown. $[\alpha]_D^{24}$ = –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.

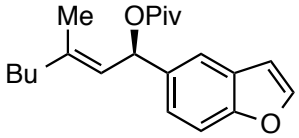


(*R*,*E*)-3-Methyl-1-[*p*-(trifluoromethyl)phenyl]-2-heptenyl pivalate (6e). Prepared according to General Procedure B on a 2.74 mmol scale to give **6e** (895 mg, 92%) as a yellow oil. The enantiomeric excess was determined to be 97% by chiral HPLC analysis (CHIRALPAK IC, 1.0 mL/min, 100% hexane, λ=210 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, 145.3, 142.1, 129.8 (q, $J_{C–F}$ = 32.5 Hz), 126.6, 125.6 (q, $J_{C–F}$ = 3.7 Hz), 124.3 (q, $J_{C–F}$ = 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.

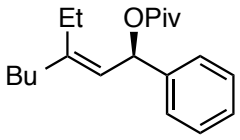


(*R*,*E*)-3-Methyl-1-(3-pyridyl)-2-heptenyl pivalate (6f). Prepared according to General Procedure B on a 1.44 mmol scale to give **6f** (367 mg, 88%) as a yellow oil. The enantiomeric excess was determined to be 96% by chiral HPLC analysis (CHIRALPAK IA, 1.0 mL/min, 3% isopropanol/hexane, λ=210 nm); t_R(major)=10.90 min, t_R(minor)=7.82 min. The absolute configuration is unknown, because the starting material configuration is unknown.

$[\alpha]_D^{24}$ = –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.

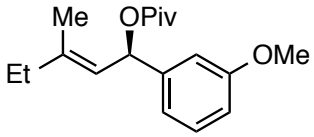


(*R*,*E*)-1-(1-Benzofuran-5-yl)-3-methyl-2-heptenyl pivalate (6g). Prepared according to General Procedure B on a 4.51 mmol scale to give **6g** (1.36 g, 92%) as a clear oil. The enantiomeric excess was determined to be 98% by chiral HPLC analysis (CHIRALPAK IA, 0.4 mL/min, 1% isopropanol/hexane, λ=210 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.

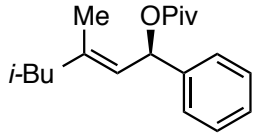


(*R*,*E*)-3-Ethyl-1-phenyl-2-heptenyl pivalate (6h). Prepared according to General Procedure B on a 1.72 mmol scale to give **6h** as a clear oil. The enantiomeric excess was assumed to be 98%, because that is the ee of the allylic alcohol precursor. $[\alpha]_D^{24}$ = –31.05 (c 1.13, $CHCl_3$): ^{1}H 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.

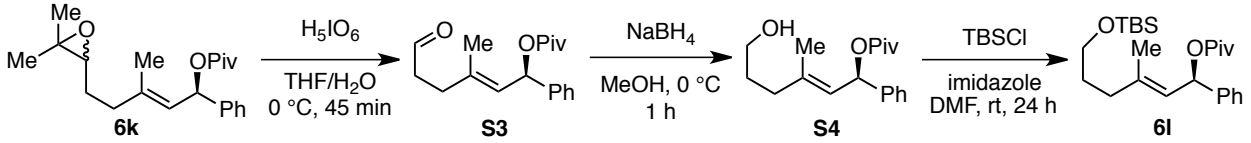


(*R*,*E*)-1-(*m*-Methoxyphenyl)-3-methyl-2-pentenyl pivalate (6i). Prepared according to General Procedure B on a 1.9 mmol scale to give **6i** (412 mg, 74%) as a clear oil. The enantiomeric excess was assumed to be 97%, because that is the ee of the allylic alcohol precursor. $[\alpha]_D^{24}$ = –41.1 (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 (6j). Prepared according to General Procedure B on a 4.9 mmol scale to give **6j** (1.31 g, 93%) as a clear oil. The enantiomeric excess was assumed to be 98%, because that is the ee of the allylic alcohol precursor. $[\alpha]_D^{24}$ = –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), 0.84 (d, J = 4.0 Hz, 3H), 0.82 (d, J = 6.5, 4.0 Hz, 3H); ^{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*,*E*)-5-(3,3-Dimethyl-2-oxiranyl)-1-(*m*-methoxyphenyl)-3-methyl-2-pentenyl pivalate (6k). This procedure is adapted from a literature procedure.[6] Pivalate (*E*)-**6m** (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 **6k** (911 mg, 94%, 1:1 dr) as a clear oil. The enantiomeric excess of each diastereomer was assumed to be 98%, because that was the ee of compound (*E*)-**6m**. $[\alpha]_D^{24}$= –37.6 (c 1.19, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, both diastereomers) δ 7.35 – 7.31 (m, 8H), 7.29–2.25 (m, 2H), 6.48 (d, *J* = 8.0 Hz, 2H), 5.33 (dd, *J* = 10, 2 Hz, 2H), 5.04 (t, *J* = 6 Hz, 2H), 2.12 – 2.03 (m, 8H), 1.82 (s, 6H), 1.65 (s, 6H), 1.57 (s, 6H), 1.22 (s, 9H); ^{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. Please note that the ^{1}H and ^{13}C NMR spectra are complicated; some peaks of the diastereomers are coincident. Please see attached spectra.



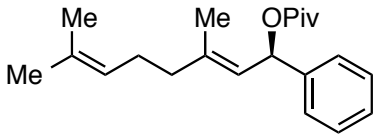
(*R*,*E*)-*tert*-Butyl((4-(3-methoxyphenyl)-4-methyl-6-phenylhex-5-en-1-yl)oxy)dimethylsilane (6l). This procedure is adapted from a literature procedure.[6] Pivalate **6k** (0.91 g, 2.75 mmol, 1.0 equiv) was dissolved in THF (4.6 mL, 0.6 M) and cooled to 0 °C. In a separate flask periodic acid (627 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 **6k** 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 **S3** (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.

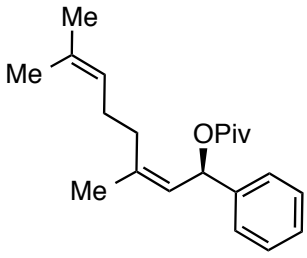
Compound **S3** (460 mg, 1.6 mmol, 1.0 equiv) was then dissolved in MeOH (18 mL, 0.09 M) and cooled to 0 °C. $NaBH_4$ (60 mg, 1.0 equiv) was then added, and the mixture was stirred for an additional hour at 0 °C. Acetone (3.0 mL) and water (9 mL) were added, and the mixture was warmed to room temperature. 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 **S4** (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 **S4** (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 **6l** (211.4 mg, 52%) as a clear oil. The enantiomeric excess was assumed to be 98%, because that was the ee of compound (*E*)-**6m**. $[\alpha]_D^{24}$= –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.



(*R*,2*E*)-3,7-Dimethyl-1-phenyl-2,6-octadienyl pivalate ((*E*)-6m). Prepared according to General Procedure B on a 3.7 mmol scale to give (*E*)-**6m** (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.

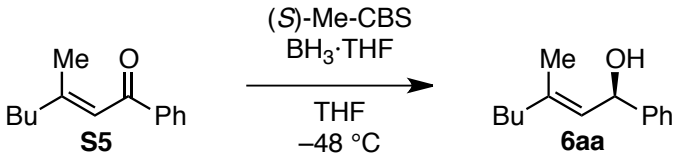


(*R*,2*Z*)-3,7-Dimethyl-1-phenyl-2,6-octadienyl pivalate ((*Z*)-6m). Prepared according to General Procedure B on a 3.38 mmol scale to give (*Z*)-**6m** (88.0 mg, 88%)

as a clear oil. The enantiomeric excess was assumed to be 97%, because that is the ee of the allylic alcohol precursor. $[\alpha]_D^{24} = -45.8$ (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.

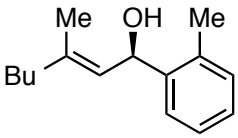
Preparation of Allylic Alcohols

General Procedure C: Preparation of (*R*,*E*)-3-Methyl-1-phenyl-2-hepten-1-ol (6aa) via CBS Reduction

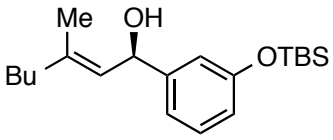


This procedure is adapted from a literature procedure.[1] (*S*)-Diphenyl prolinol (4.81 g, 9.5 mmol, 2.0 equiv) and methyl boronic acid (1.25 g, 20.9 mmol, 2.2 equiv) were dissolved in toluene (63.3 mL, 0.33 M). The flask was fitted with a Dean–Stark apparatus, and the mixture was refluxed for 4 h to 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 (**S5**, 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 (**S5**) 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 **6aa** (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, 1H), 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+) $[M–OH]^+$ calculated for: $C_{14}H_{19}$: 187.1481, found: 187.1479.

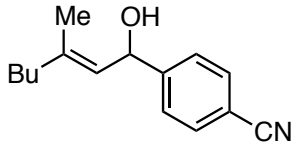


(*R*,*E*)-3-Methyl-1-(*o*-tolyl)-2-hepten-1-ol (6bb). Prepared according to General Procedure C on a 3.84 mmol scale to give **6bb** (602 mg, 72%) as a pale yellow oil. The enantiomeric excess was determined to be 94% by chiral HPLC analysis (CHIRALPAK IB, 1.0 mL/min, 0.8% isopropanol/hexane, λ=210 nm); 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.

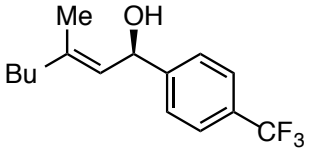


(*R*,*E*)-1-(*m*-Dimethyl, t-butyl-silyl phenol)-3-methyl-2-hepten-1-ol (6cc). Prepared according to General Procedure C on a 1.59 mmol scale to give **6cc** (270 mg, 51%) as a clear oil. The enantiomeric excess was determined to be 96% by chial HPLC analysis (CHIRALPAK IB, 1.0 mL/min, 0.5% isopropanol/hexane, 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

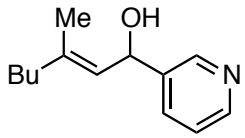
Hz, 1H), 5.38 (d, *J* = 8.7 Hz, 1H), 2.02 (d, *J* = 15.2 Hz, 2H), 1.78 (s, 3H), 1.71 (d, *J* = 3.5 Hz, 1H), 1.45 – 1.35 (m, 2H), 1.28 (h, *J* = 7.3 Hz, 2H), 0.98 (s, 9H), 0.89 (t, *J* = 7.3 Hz, 3H), 0.19 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.0, 146.1, 139.4, 129.6, 127.3, 119.0, 118.9, 117.8, 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.



***p*-[(*E*)-1-hydroxy-3-methyl-2-heptenyl]benzonitrile (6dd).** The following procedure was adapted from a literature report.[7] *p*-(Cyano)phenylMgBr (1.4 M, 8.0 mL, 11.2 mmol, 1.0 equiv) was prepared as described by Knochel. With the solution of Grignard reagent at 0 °C, (*E*)-3-methylhept-2-enal (1.41 g, 11.2 mmol, 1.0 equiv) was added via syringe. 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 (10 mL), and the aqueous layer was extracted with Et_2O (20 mL x 3). The combined organic fractions were washed with sat. aq. NaCl (30 mL), dried ($MgSO_4$), filtered, and concentrated. The resulting residue was purified by silica gel chromatography (10% Et_2O/hexanes) to afford *p*-[(*E*)-1-hydroxy-3-methyl-2-heptenyl]benzonitrile (±)-**6dd** (730 mg, 28%) as a yellow oil. The enantiomers of (±)-**6dd** were then separated using preparatory SFC with a chiral stationary phase to give **6dd** in >99% ee. 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. The absolute configuration of **6dd** 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.

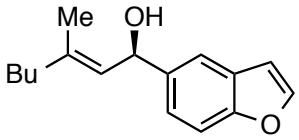


(*R*,*E*)-3-Methyl-1-[*p*-(trifluoromethyl)phenyl]-2-hepten-1-ol (6ee). Prepared according to General Procedure C on a 4.76 mmol scale to give **6ee** (800 mg, 62%) as a clear oil. The enantiomeric excess was determined to be 96% by chiral HPLC analysis (CHIRALPAK 1C, 1.0 mL/min, 1% isopropanol/hexane, 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, 129.3 (q, J_{C-F} = 32.4 Hz), 126.5, 126.1, 125.3 (q, J_{C-F} = 3.8 Hz), 124.2 (q, J_{C-F} = 272.8 Hz), 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.

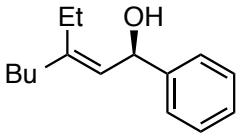


(*R*,*E*)-3-Methyl-1-(3-pyridyl)-2-hepten-1-ol (6ff). The following procedure was adapted from a literature report.[7] 3-PyridylMgBr (1.5 M, 9.0 mL, 14.0 mmol, 1.5 equiv) was prepared as described by Knochel. With the solution of Grignard reagent at 0 °C, (*E*)-3-methylhept-2-enal (1.18 g, 9.35 mmol, 1.0 equiv) was added via syringe. 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 (10 mL), and the aqueous layer was extracted with Et_2O (20 mL x 3). The combined organic fractions were washed with sat. aq. NaCl (30 mL), dried ($MgSO_4$), filtered, and concentrated. The resulting residue was purified by silica gel chromatography (50% Et_2O/hexanes) to afford (*E*)-3-methyl-1-(3-pyridyl)-2-hepten-1-ol (±)-**6ff** (917 mg, 51%) as a yellow oil. The enantiomers of (±)-**6ff** were then separated using preparatory SFC with a chiral stationary phase to give **6ff**. The absolute configuration of **6ff** was not determined. The enantiomeric excess was determined to be 97% by chiral HPLC analysis using a chiral stationary phase (CHIRALPAK 1B, 0.8 mL/min, 3% isopropanol/hexane, λ=254 nm); t_R(major)=51.38 min, t_R(minor)=59.71 min; $[\alpha]_D^{24} = 82.2$ (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.

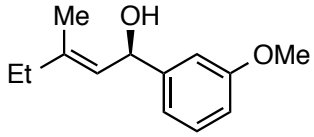


(*R*,*E*)-1-(1-Benzofuran-5-yl)-3-methyl-2-hepten-1-ol (6gg). Prepared according to General Procedure C on a 6.76 mmol scale to give **6gg** (1.27 g, 77%) as a pale yellow oil. The enantiomeric excess was determined to be 99% by chiral HPLC analysis (CHIRALPACK IC, 1.0 mL/min, 1% isopropanol/hexane, 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.

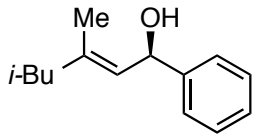


(*R*,*E*)-3-Ethyl-1-phenyl-2-hepten-1-ol (6hh). Prepared according to General Procedure C on a 2.13 mmol scale to give **6hh** (398 mg, 86%) as a pale yellow oil. The enantiomeric excess was determined to be 98% by chiral HPLC analysis (CHIRALPAK IB, 1.0 mL/min, 0.8% isopropanol/hexane, λ=210 nm); t_R(major)=19.10 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,

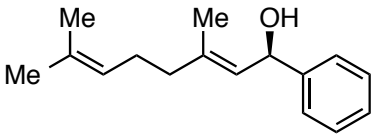
$CDCl_3$) δ 145.3, 144.5, 128.6, 127.4, 126.6, 126.1, 70.4, 36.2, 30.3, 23.9, 22.7, 14.2, 13.8; FTIR (NaCl/thin film) 3330, 2961, 2872, 1432, 1006, 689 cm^{-1}; HRMS (EI+) $[M]^+$ calculated for $C_{15}H_{22}O$: 218.1671, found: 218.1678.



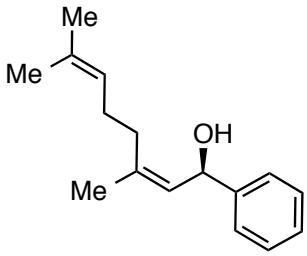
(*R*,*E*)-1-(*m*-Methoxyphenyl)-3-methyl-2-penten-1-ol (6ii). Prepared according to General Procedure C on a 2.3 mmol scale to give **6ii** (437.1 mg, 92%) as a pale yellow oil. The enantiomeric excess was determined to be 97% by chiral HPLC analysis (CHIRALPAK IB, 1.0 mL/min, 1% isopropanol/hexane, 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, 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), 7.29 – 7.23 (m, 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.



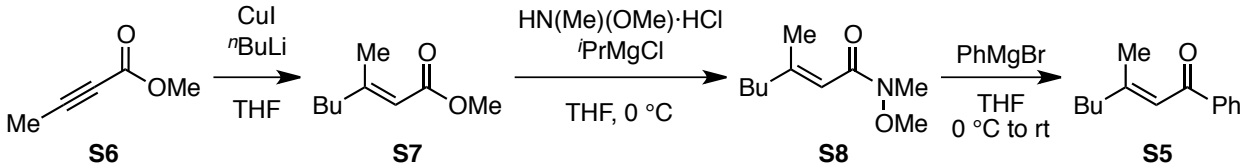
(*R*,2*E*)-3,7-Dimethyl-1-phenyl-2,6-octadien-1-ol ((*E*)-6mm). Prepared according to General Procedure C on a 4.1 mmol scale to give (*E*)-**6mm** (923 mg, 98%) as a clear oil. The enantiomeric excess was determined to be 98% by chiral HPLC analysis (CHIRALPAK IB, 1.0 mL/min, 0.8% isopropanol/hexane, λ=210 nm); t_R(major)=24.83 min, t_R(minor)=23.84 min; $[\alpha]_D^{24}$ = –89.4 (c 2.23, $CHCl_3$); The spectral data for this compound matches that previously reported in the literature.[8]



(*R*,2*Z*)-3,7-Dimethyl-1-phenyl-2,6-octadien-1-ol ((*Z*)-6mm). Prepared according to General Procedure C on a 4.4 mmol scale to give (*Z*)-**6mm** (780 mg, 78%) as a clear oil. The enantiomeric excess was determined to be 97% by chiral HPLC analysis (CHIRALPAK IA, 1.0 mL/min, 0.8% isopropanol/hexane, λ=230 nm); t_R(major)=27.87 min, t_R(minor)=29.326 min. The spectral data for this compound matches that previously reported in the literature.[8]

Preparation of Enone Precursors

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



S6 **S7** **S8** **S5**

The cuprate addition to form **S7** was performed according to literature procedure.[9]

The formation of Weinreb amide **S8** was performed according to literature procedure.[10]

(*E*)-1-(*N*-Methylmethoxyamino)-3-methyl-2-hepten-1-one **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 PhMgBr (1.5 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. 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 (**S5)**. The spectral data for this compound matched that reported in the literature.

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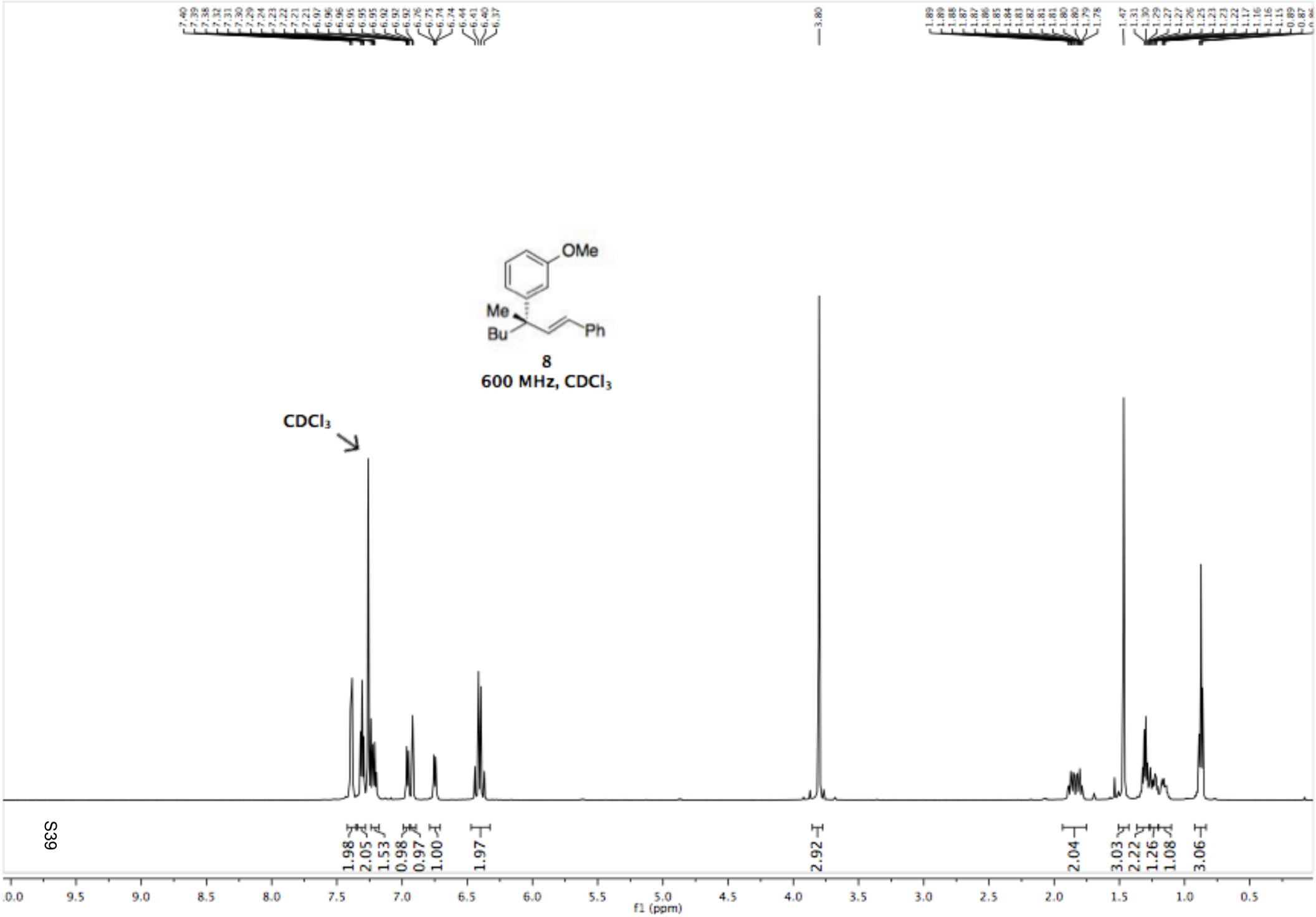
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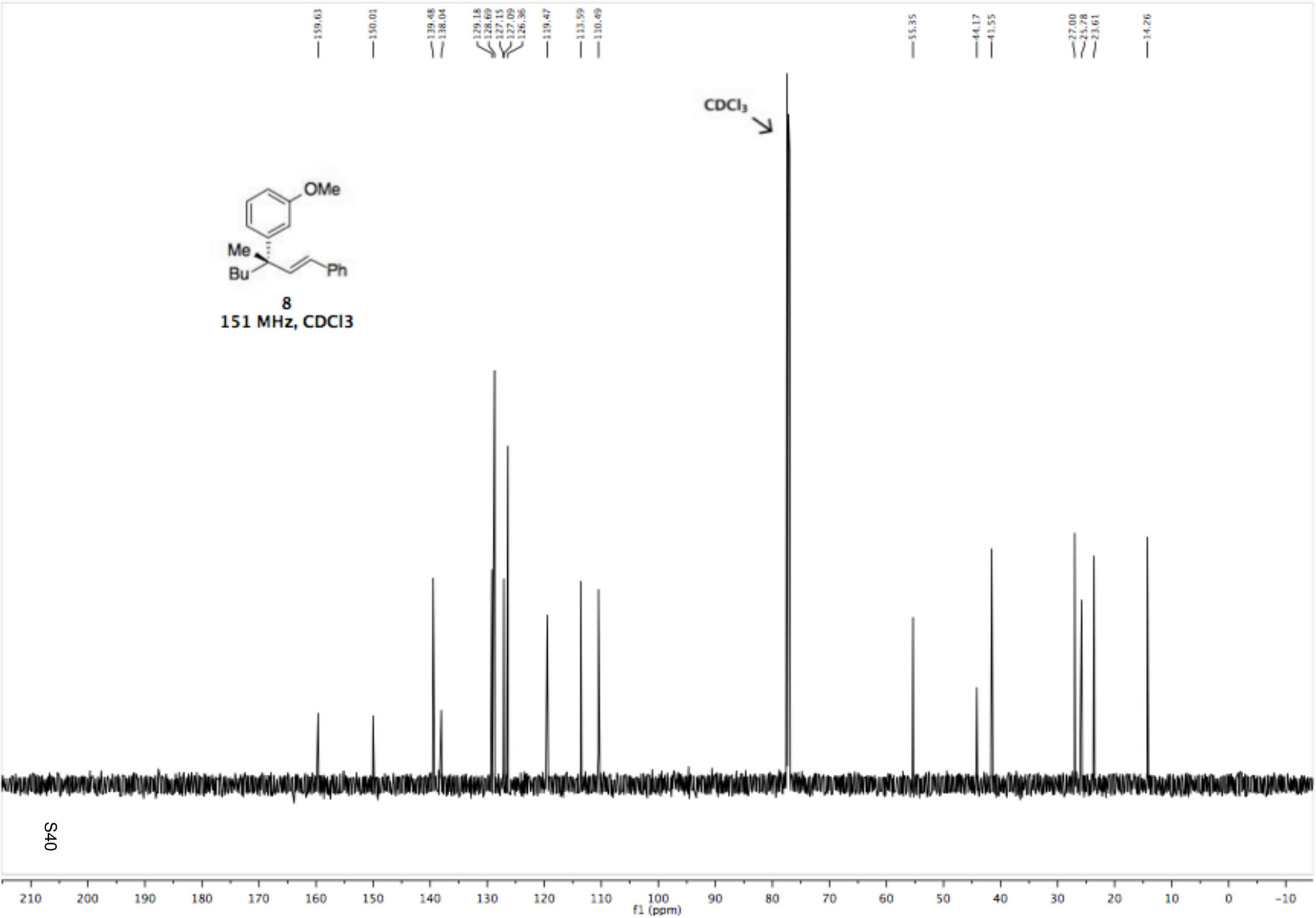
f1 (ppm)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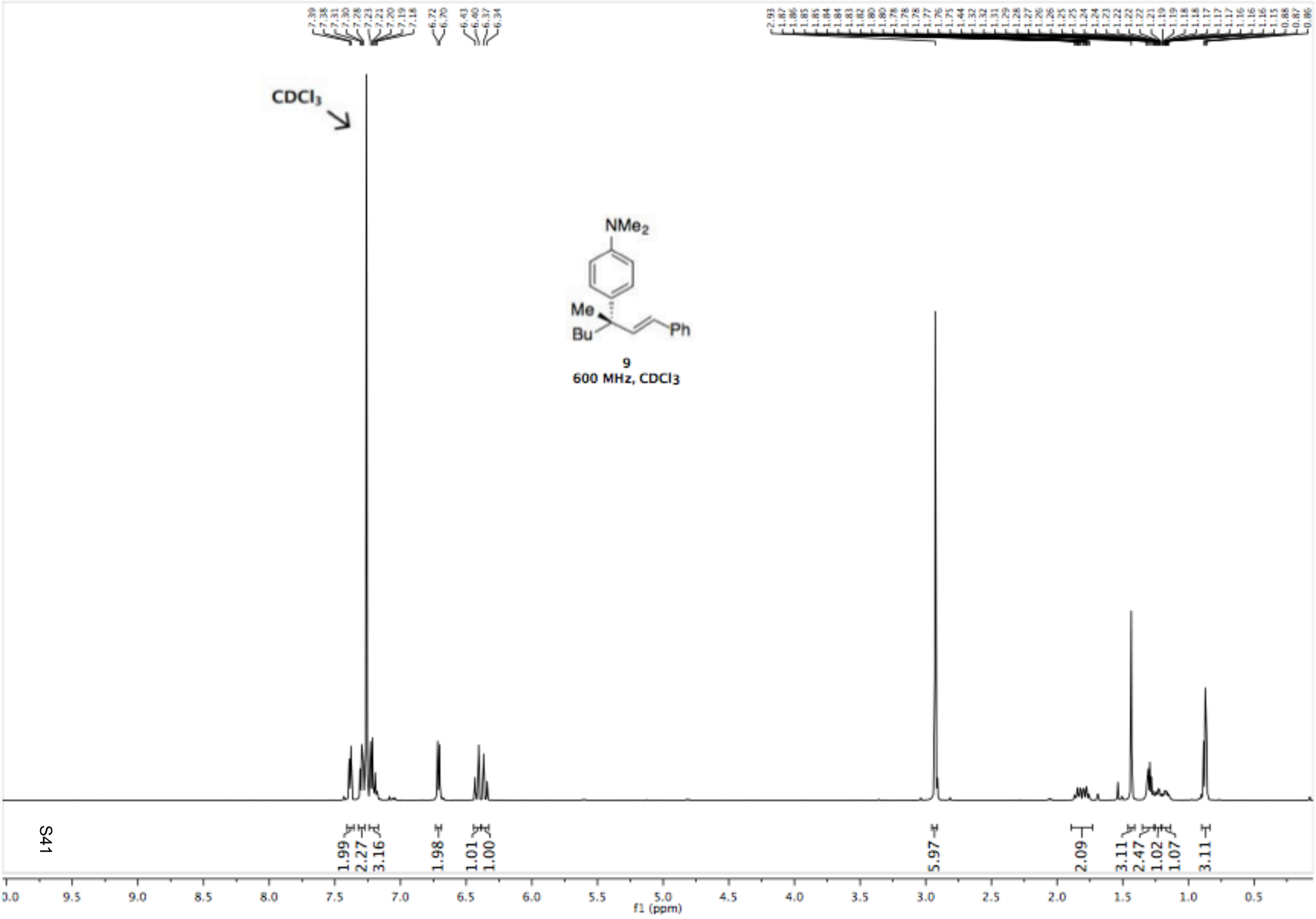
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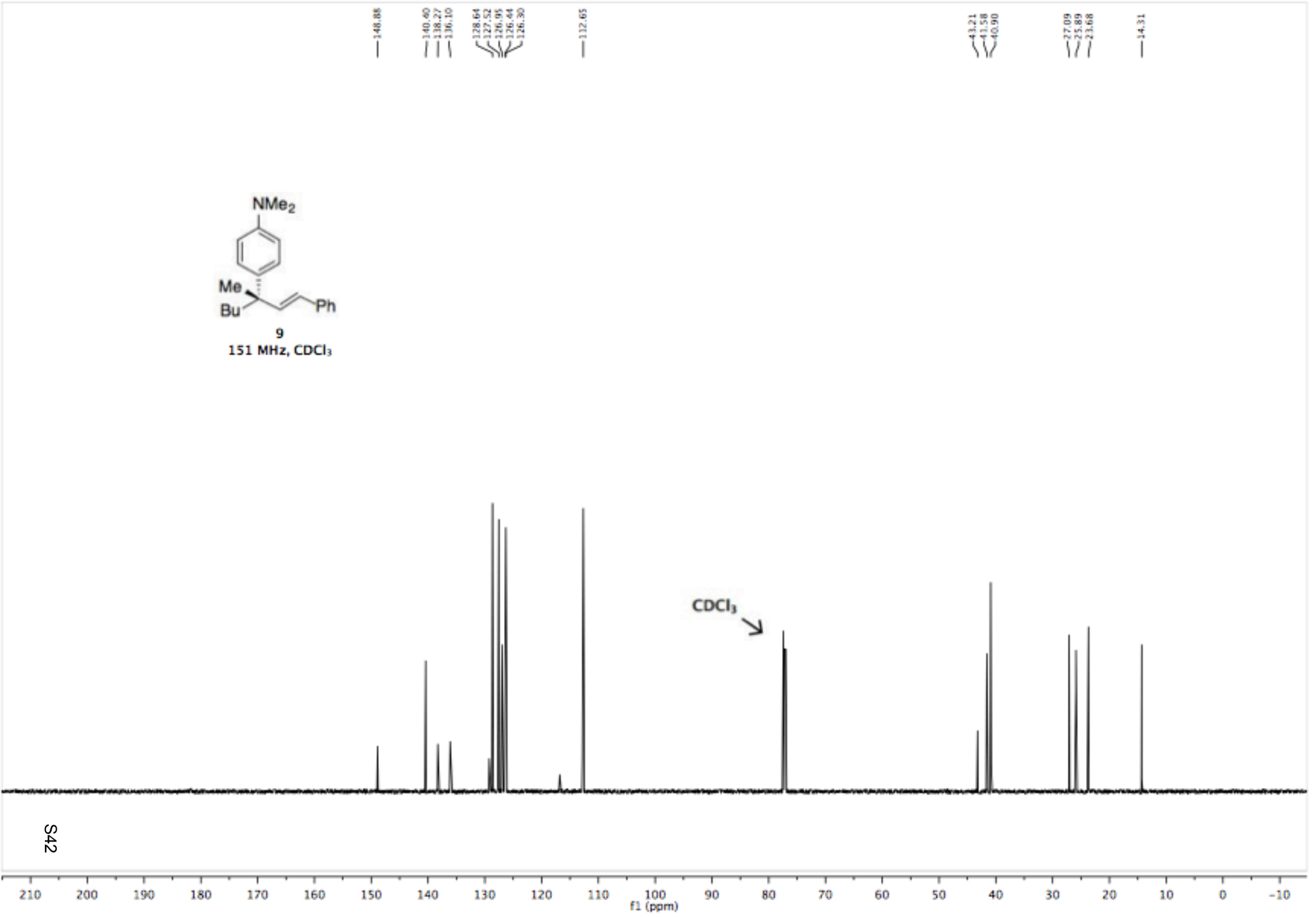
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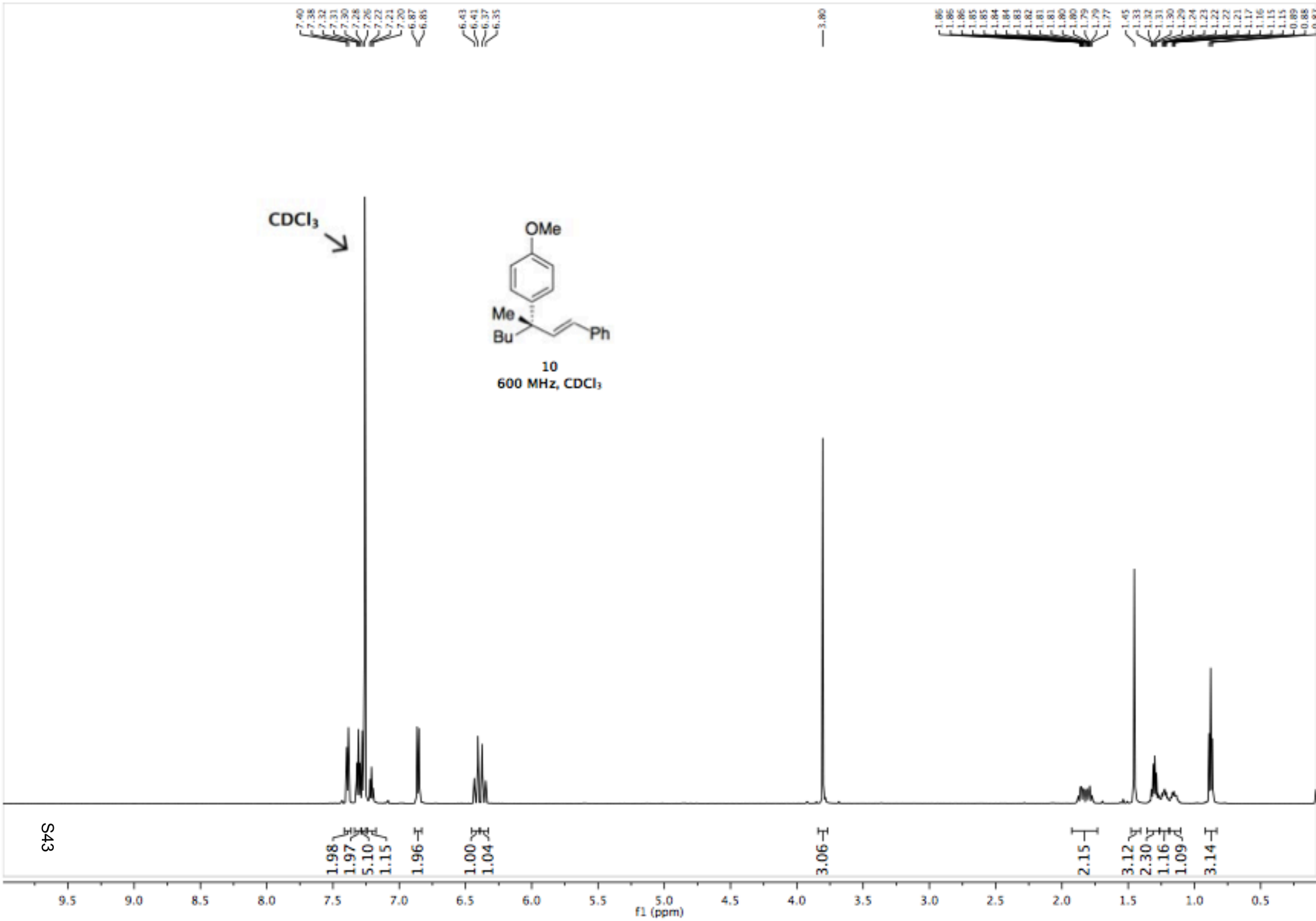
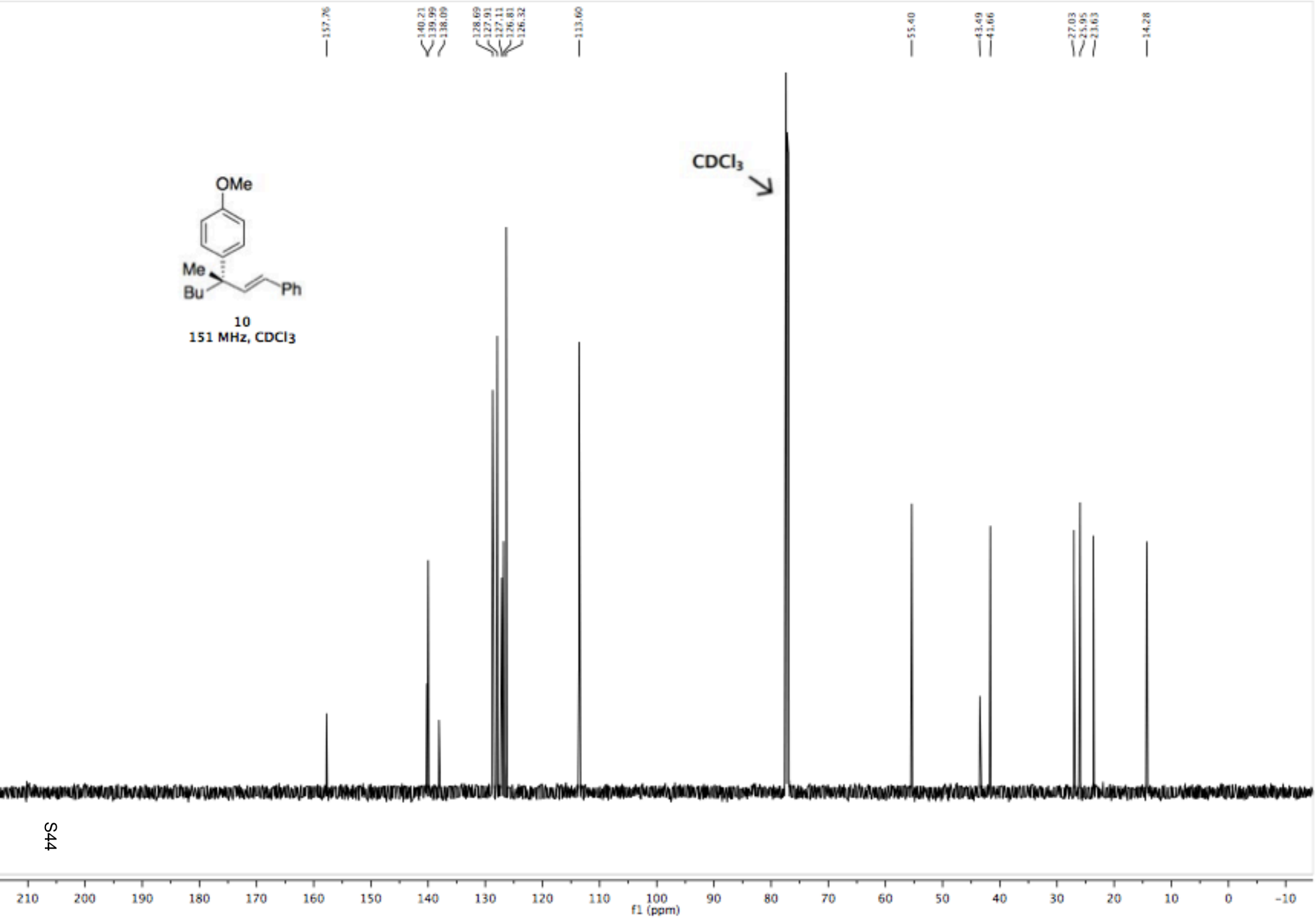
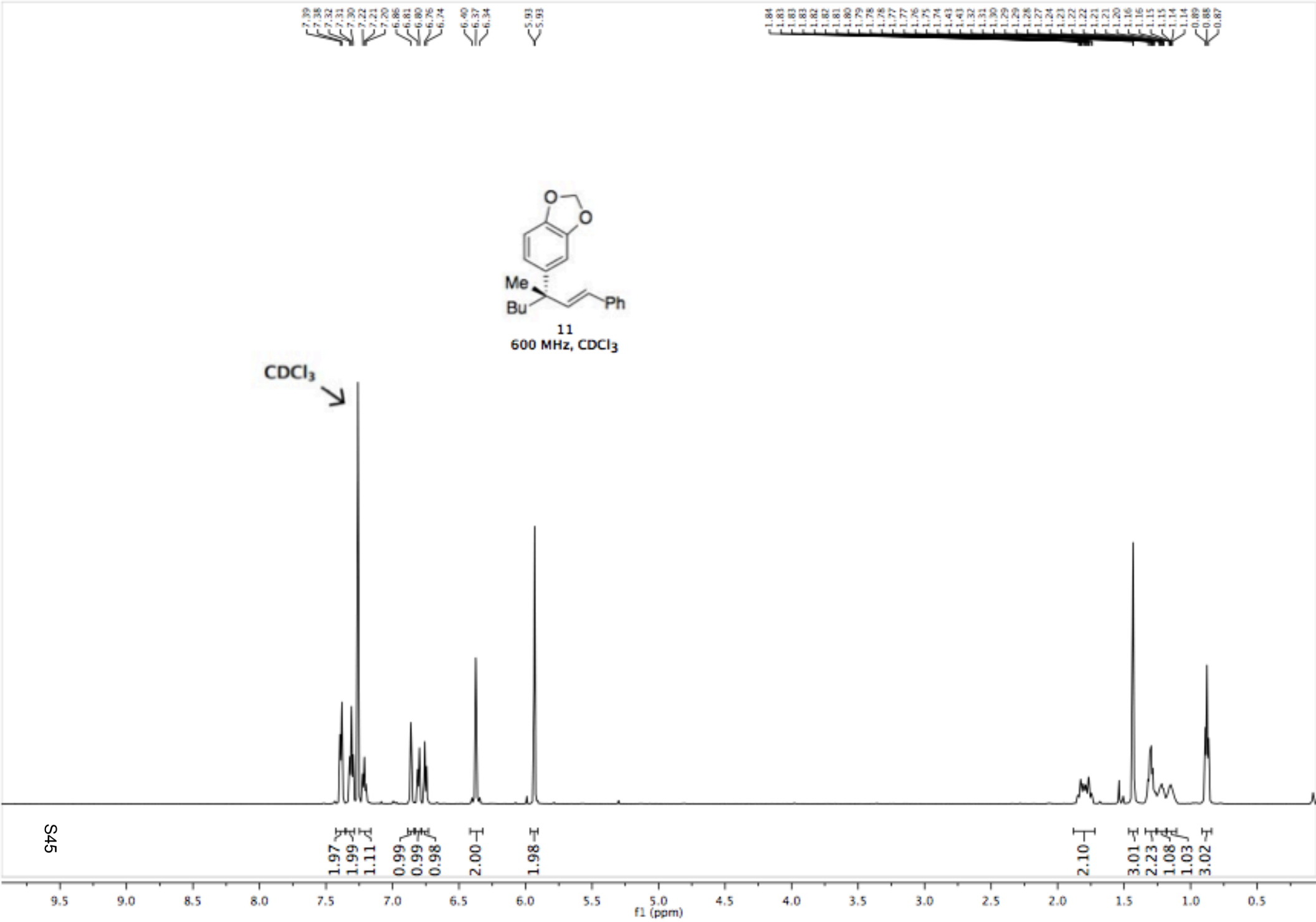
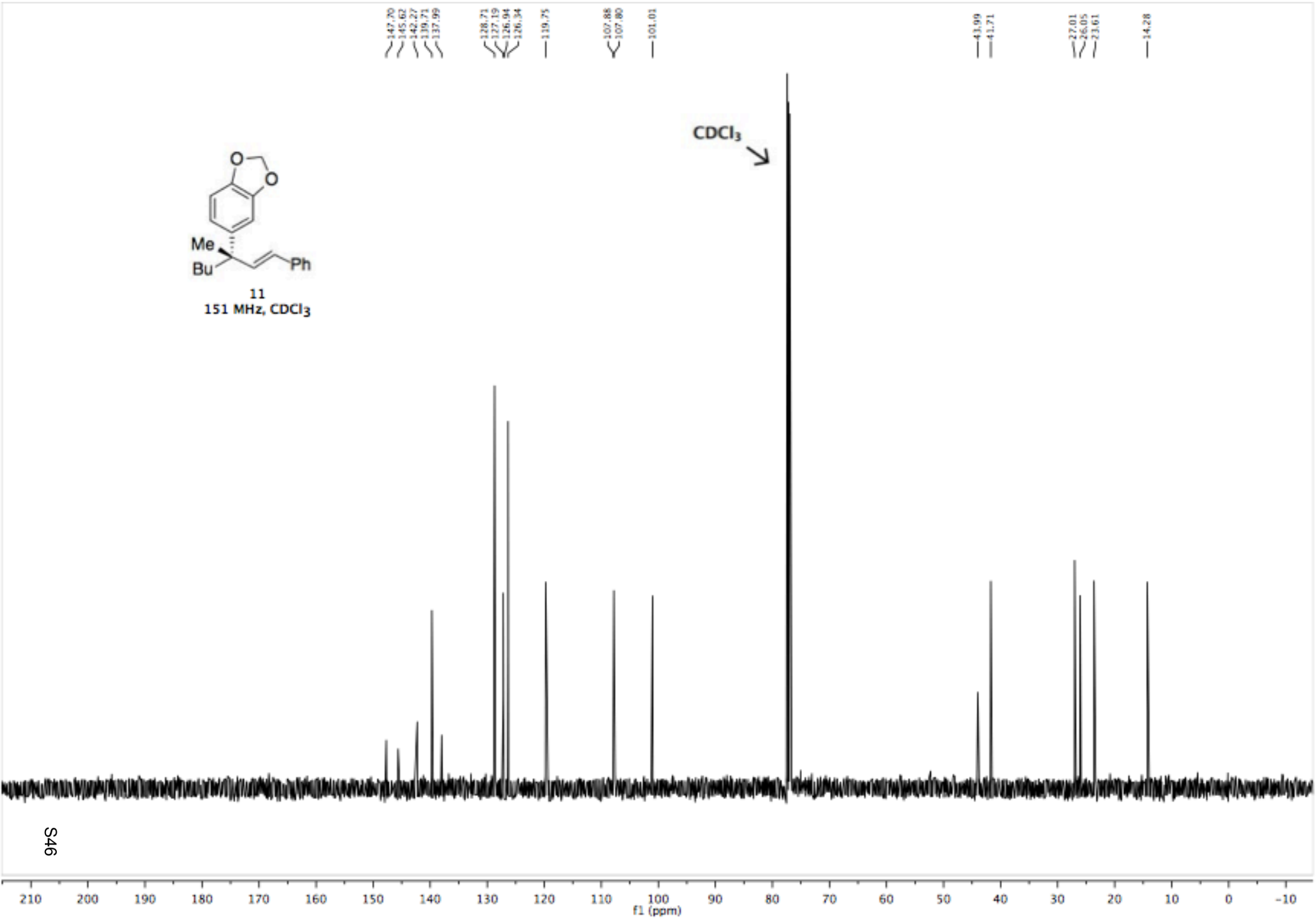
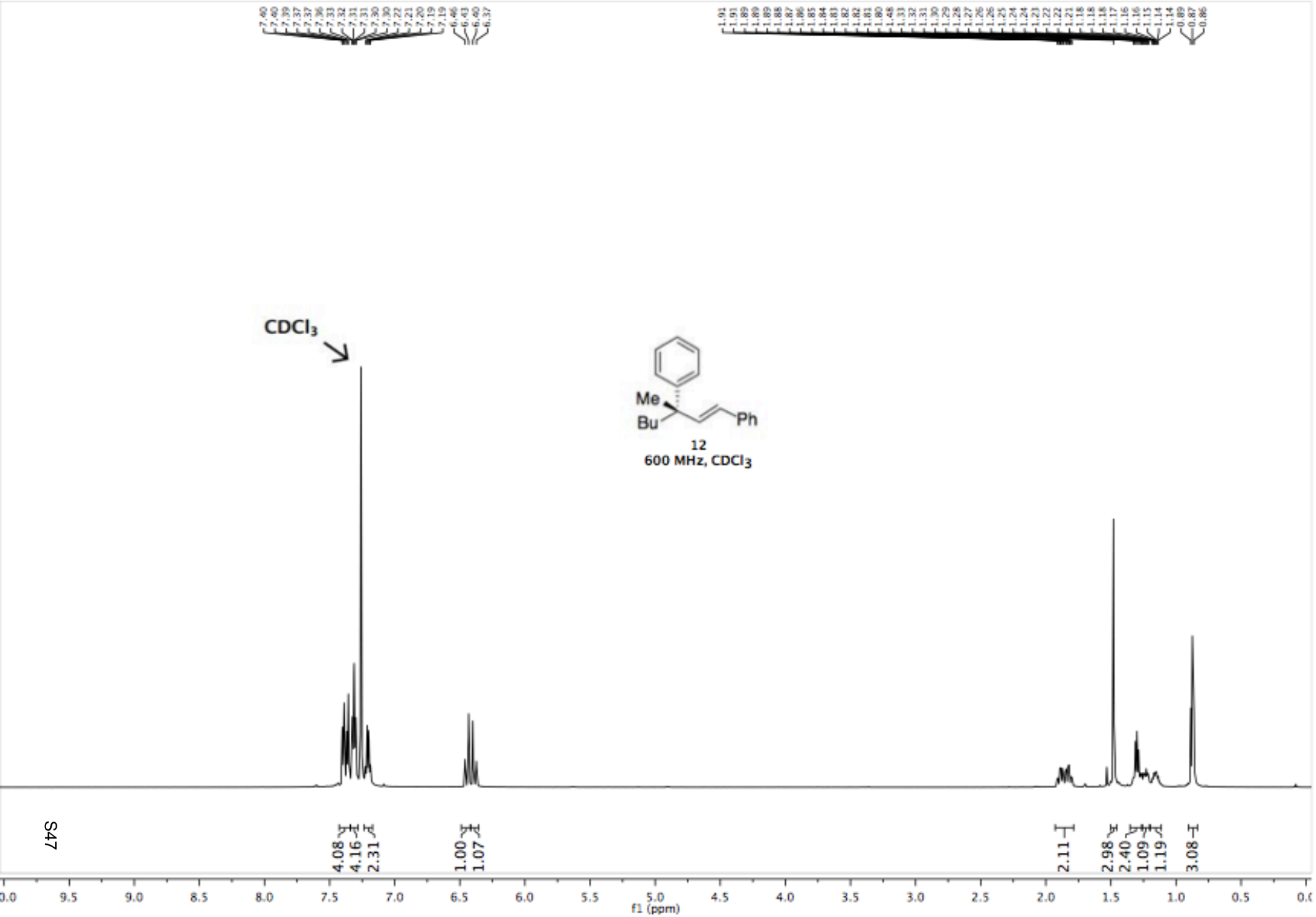
-10
f1 (ppm)

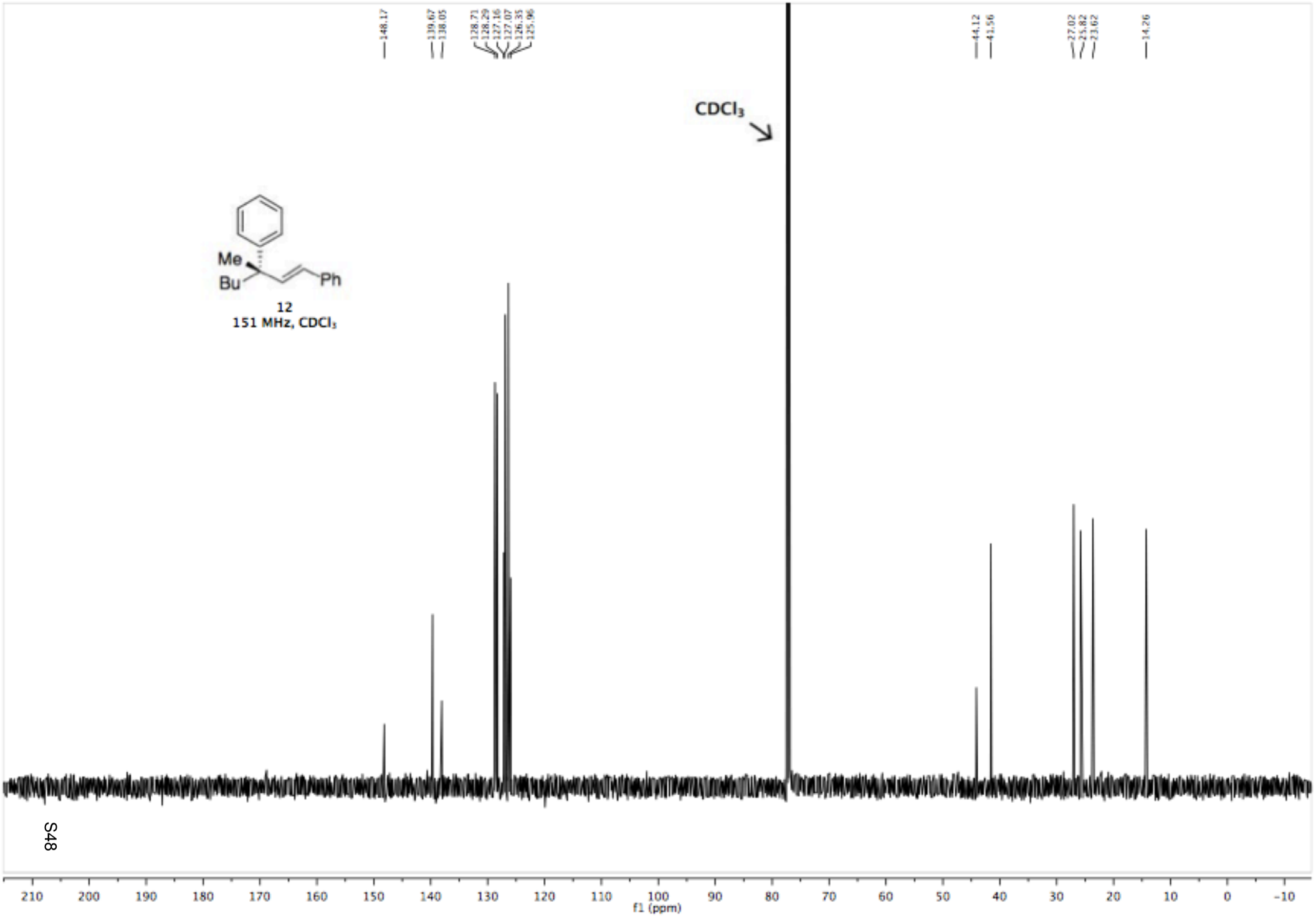

CDCl3
OMe
Me
Bu
Ph
10
600 MHz, CDCl3
f1 (ppm)

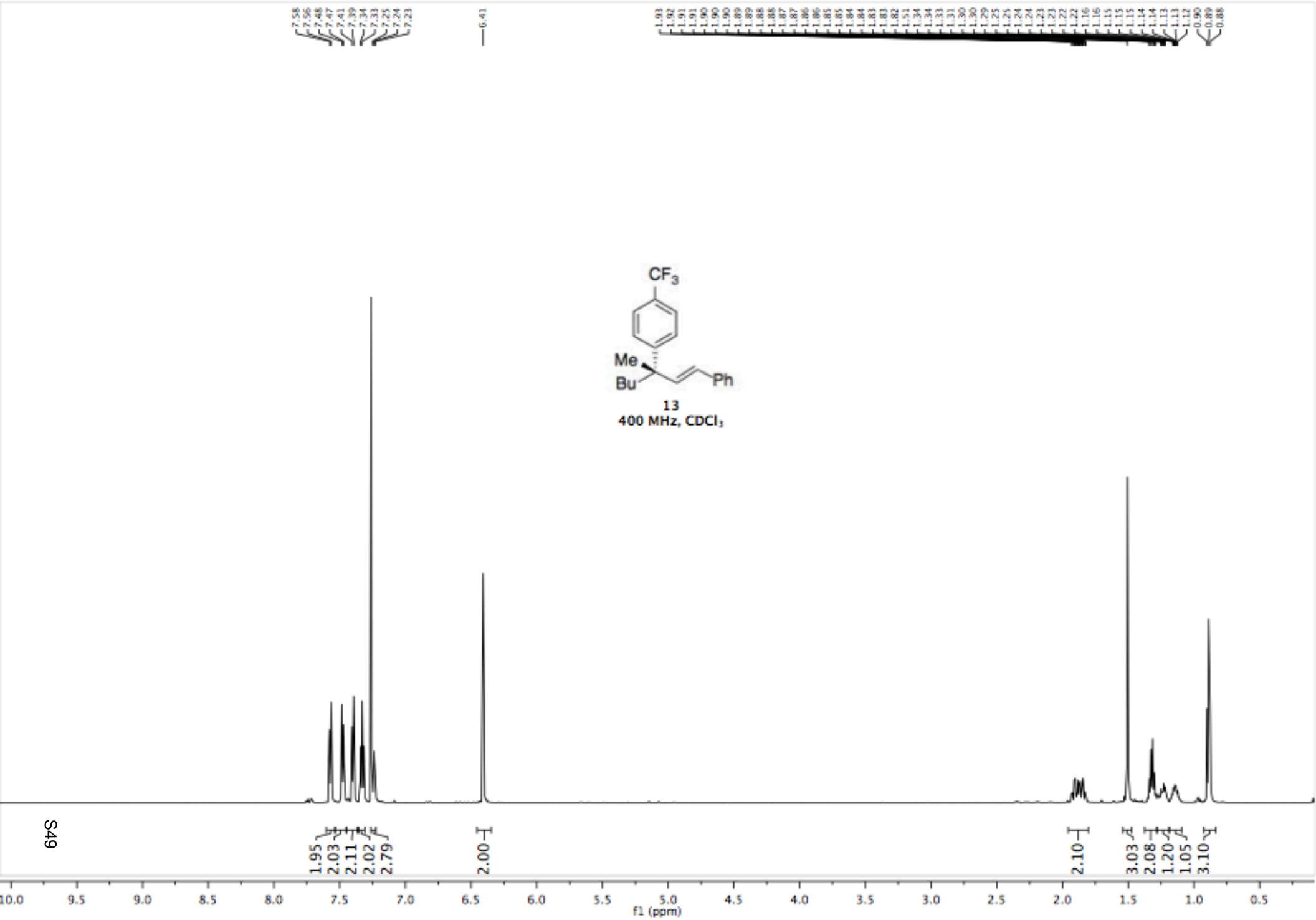

157.76
140.21
139.99
138.09
128.69
127.91
127.11
126.81
126.32
113.60
55.40
43.49
41.66
27.03
25.95
23.63
14.28
CDCl3
OMe
Me
Bu
Ph
10
151 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

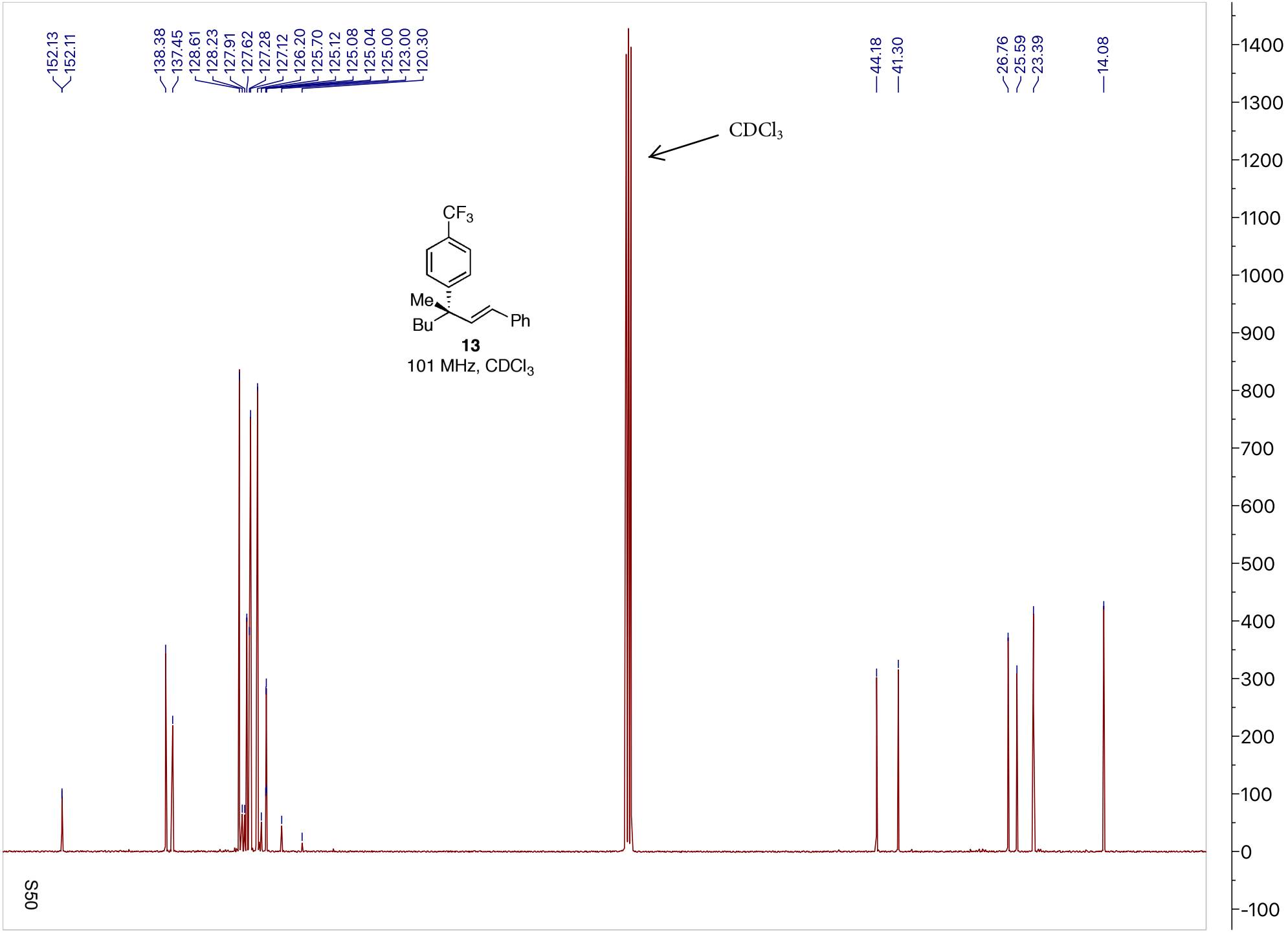

7.39
7.38
7.32
7.31
7.30
7.22
7.21
7.20
6.86
6.81
6.80
6.76
6.74
6.40
6.37
6.34
5.93
5.93
1.84
1.83
1.83
1.83
1.82
1.82
1.81
1.80
1.79
1.78
1.78
1.77
1.77
1.76
1.75
1.74
1.43
1.43
1.32
1.31
1.30
1.29
1.29
1.28
1.27
1.24
1.23
1.22
1.22
1.21
1.21
1.20
1.16
1.16
1.15
1.15
1.14
1.14
0.89
0.88
0.87
O
O
Me
Bu
Ph
11
600 MHz, CDCl3
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)

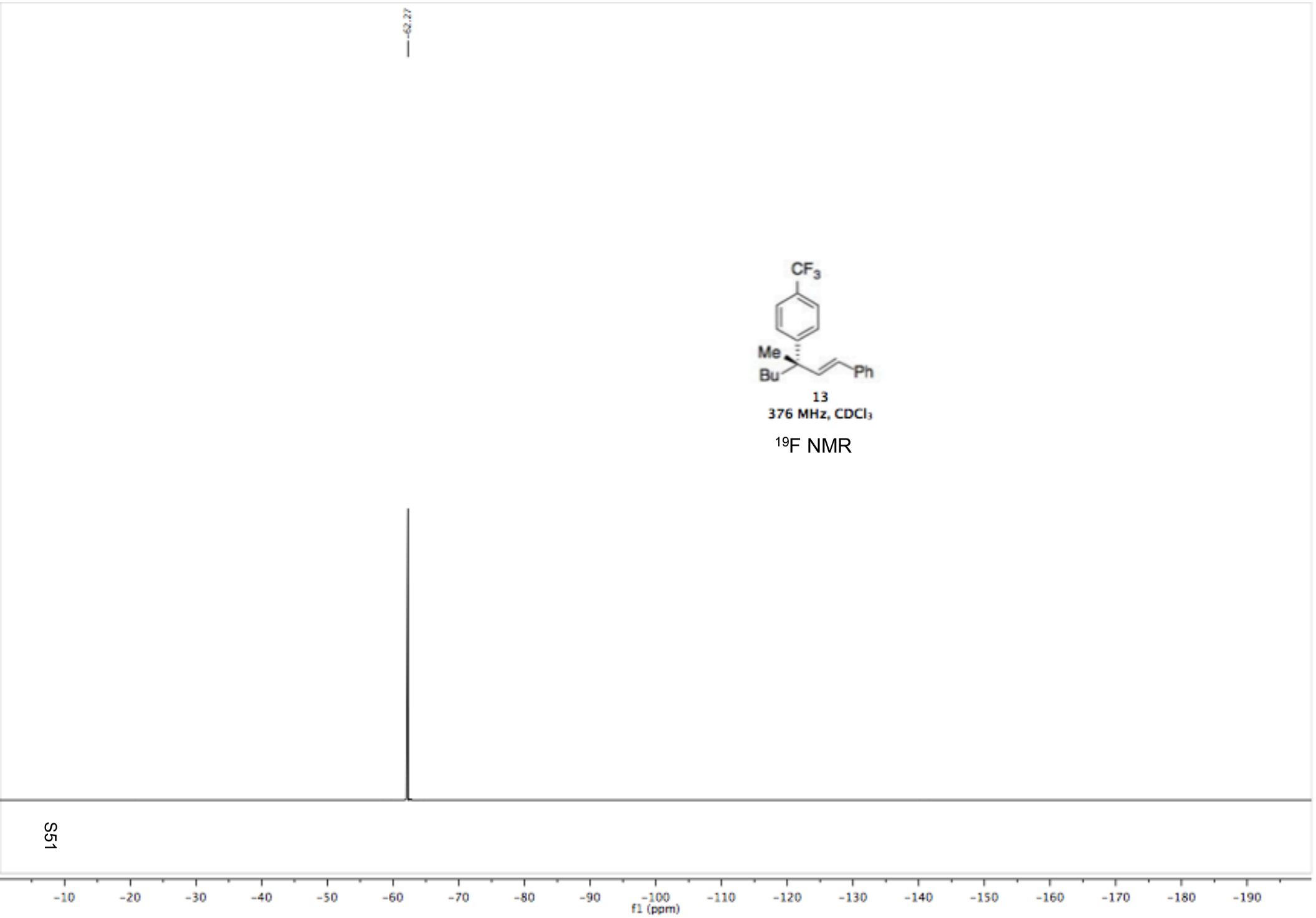

147.70
145.62
142.27
139.71
137.99
128.71
127.19
126.94
126.34
119.75
107.88
107.80
101.01
41.99
41.71
27.01
26.05
23.61
14.28
CDCl3
O
O
Me
Bu
Ph
11
151 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

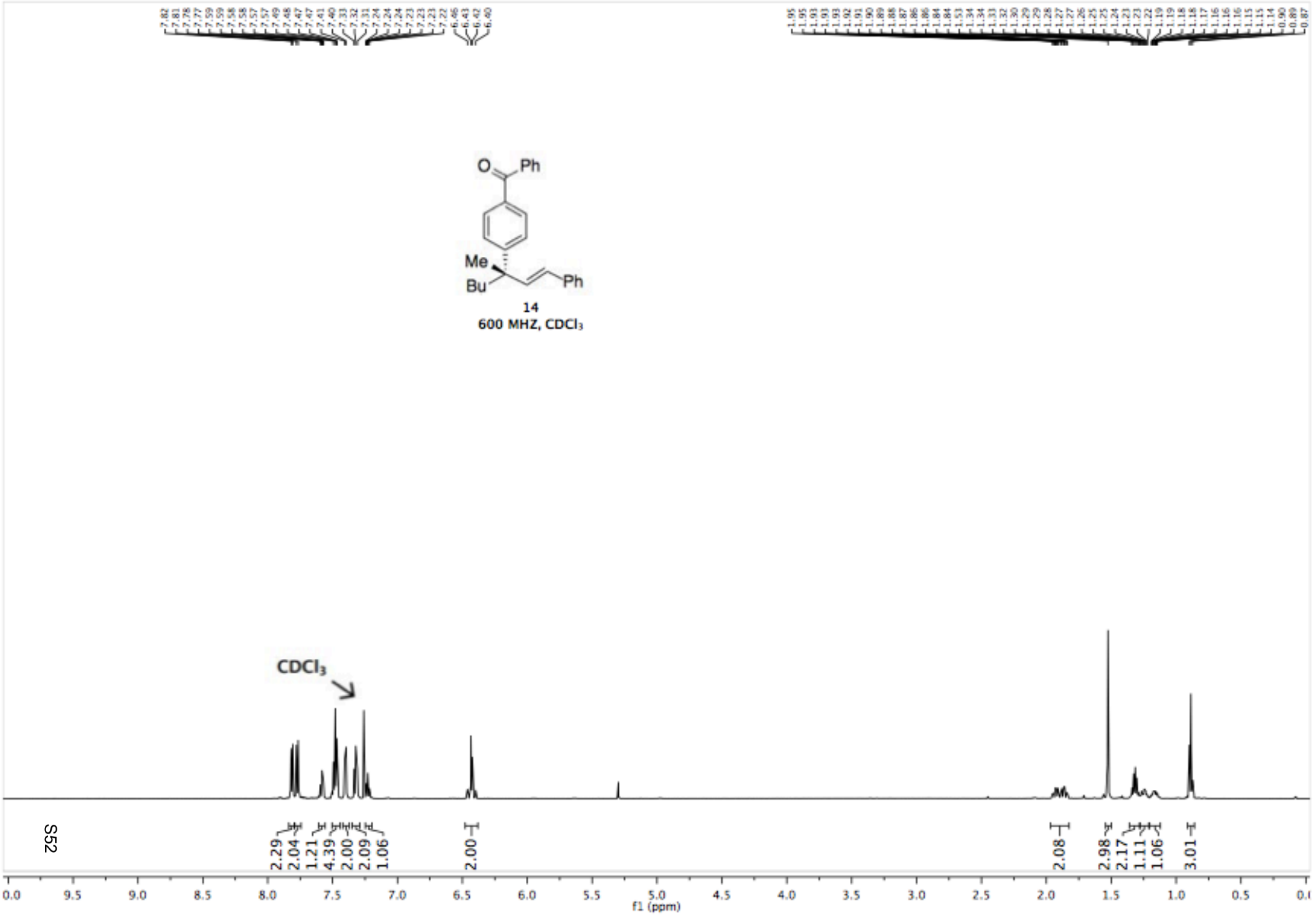

CDCl3
Me
Bu
Ph
12
600 MHz, CDCl3
4.08
4.16
2.31
1.00
1.07
2.11
2.98
2.40
1.09
1.19
3.08
f1 (ppm)

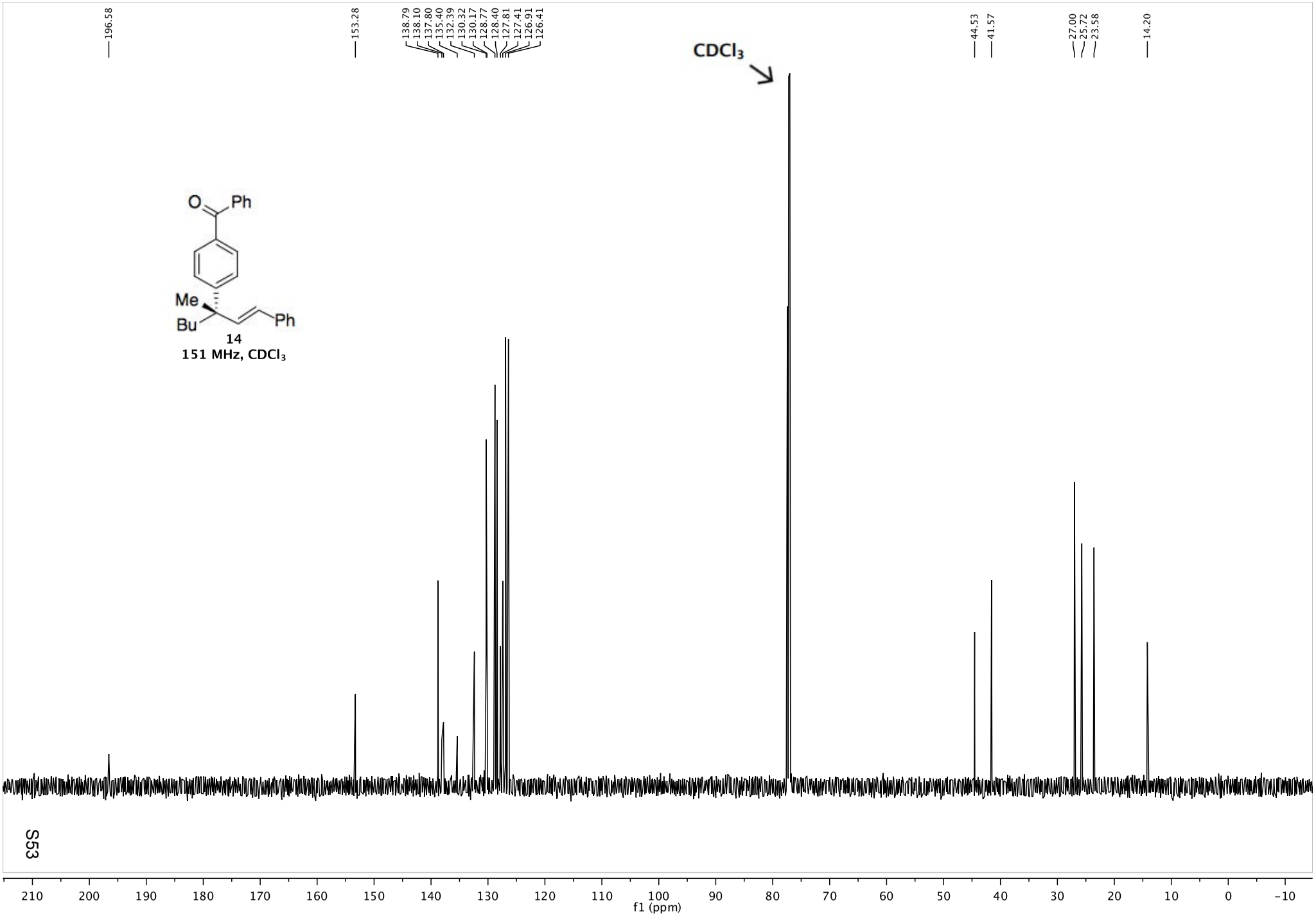

148.17
139.67
138.05
128.71
128.29
127.16
127.07
126.35
125.96
44.12
41.56
27.02
25.82
23.62
14.26
CDCl3
Me
Bu
Ph
12
151 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

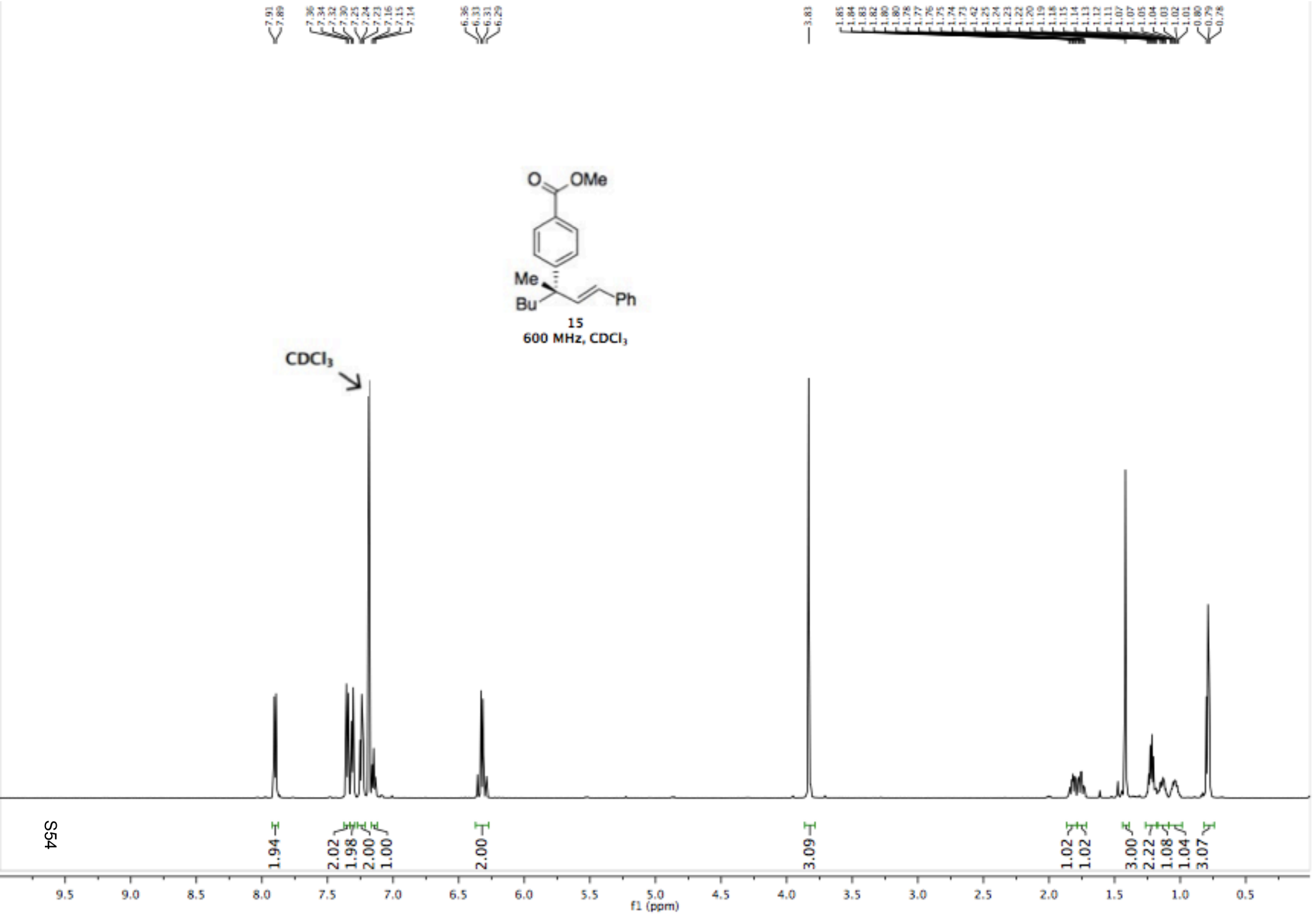

7.58
7.56
7.48
7.47
7.41
7.39
7.34
7.33
7.25
7.24
7.23
6.41
1.93
1.92
1.91
1.91
1.90
1.90
1.90
1.89
1.89
1.88
1.88
1.87
1.87
1.86
1.86
1.85
1.85
1.84
1.84
1.83
1.83
1.82
1.51
1.34
1.34
1.33
1.31
1.30
1.30
1.29
1.25
1.25
1.24
1.24
1.23
1.23
1.22
1.22
1.16
1.16
1.15
1.15
1.14
1.14
1.13
1.12
0.90
0.89
0.88
CF3
Me
Bu
Ph
13
400 MHz, CDCl3
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)

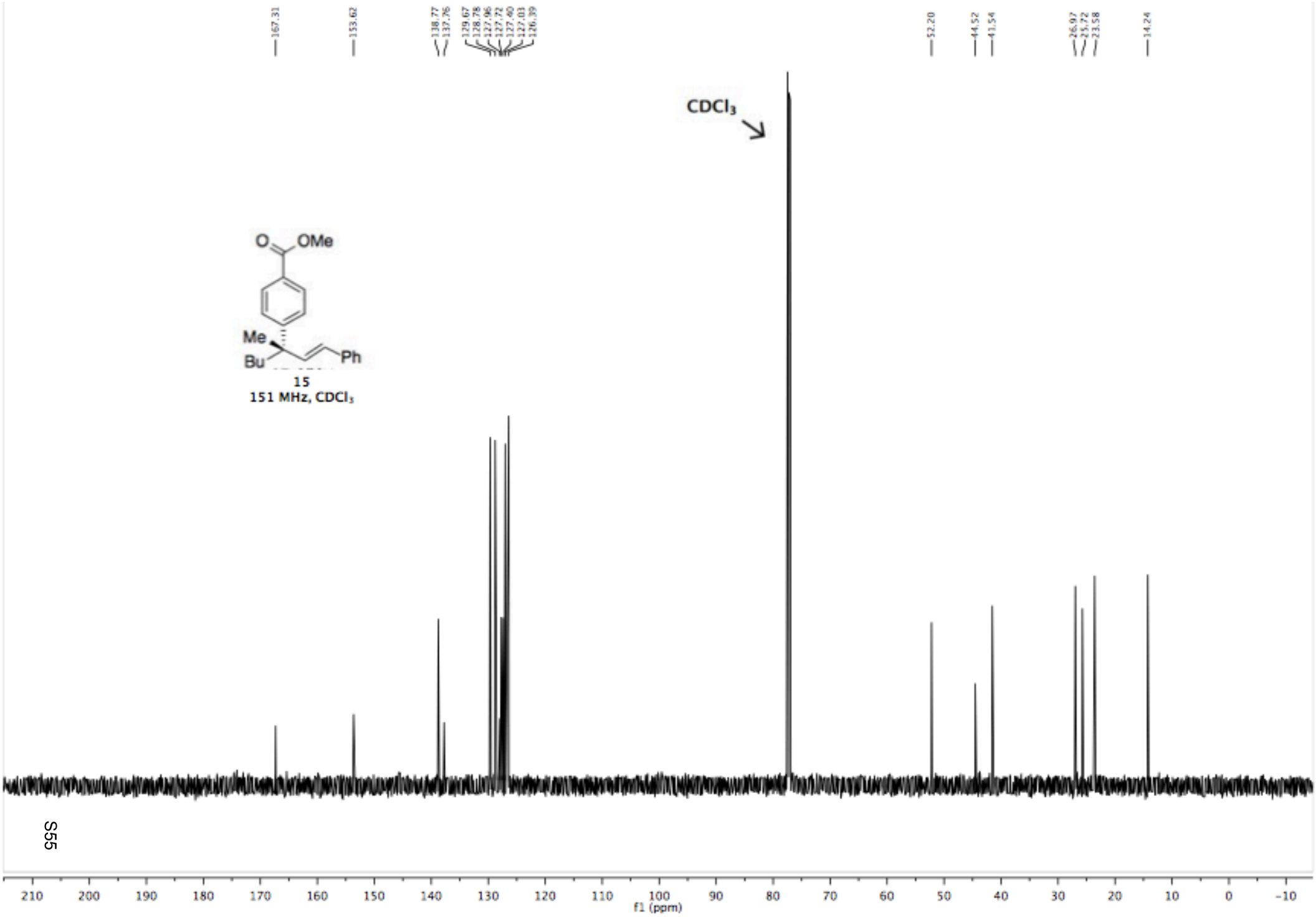

152.13
152.11
138.38
137.45
128.61
128.23
127.91
127.62
127.28
127.12
126.20
125.70
125.12
125.08
125.04
125.00
123.00
120.30
44.18
41.30
26.76
25.59
23.39
14.08
CDCl3
CF3
Me
Bu
Ph
13
101 MHz, CDCl3
S50
f1 (ppm)

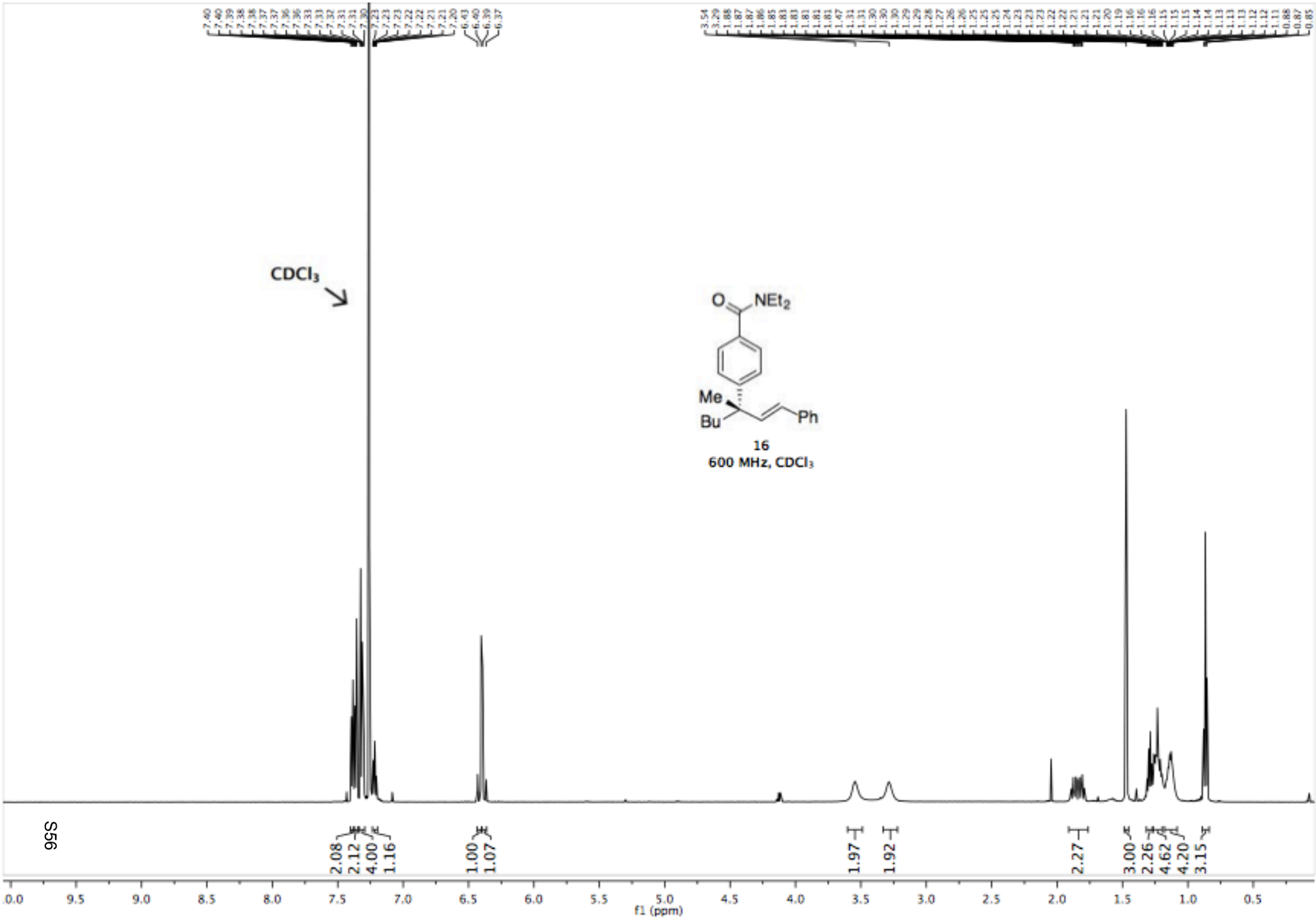

-62.27
CF3
Me
Bu
Ph
13
376 MHz, CDCl3
19F NMR
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

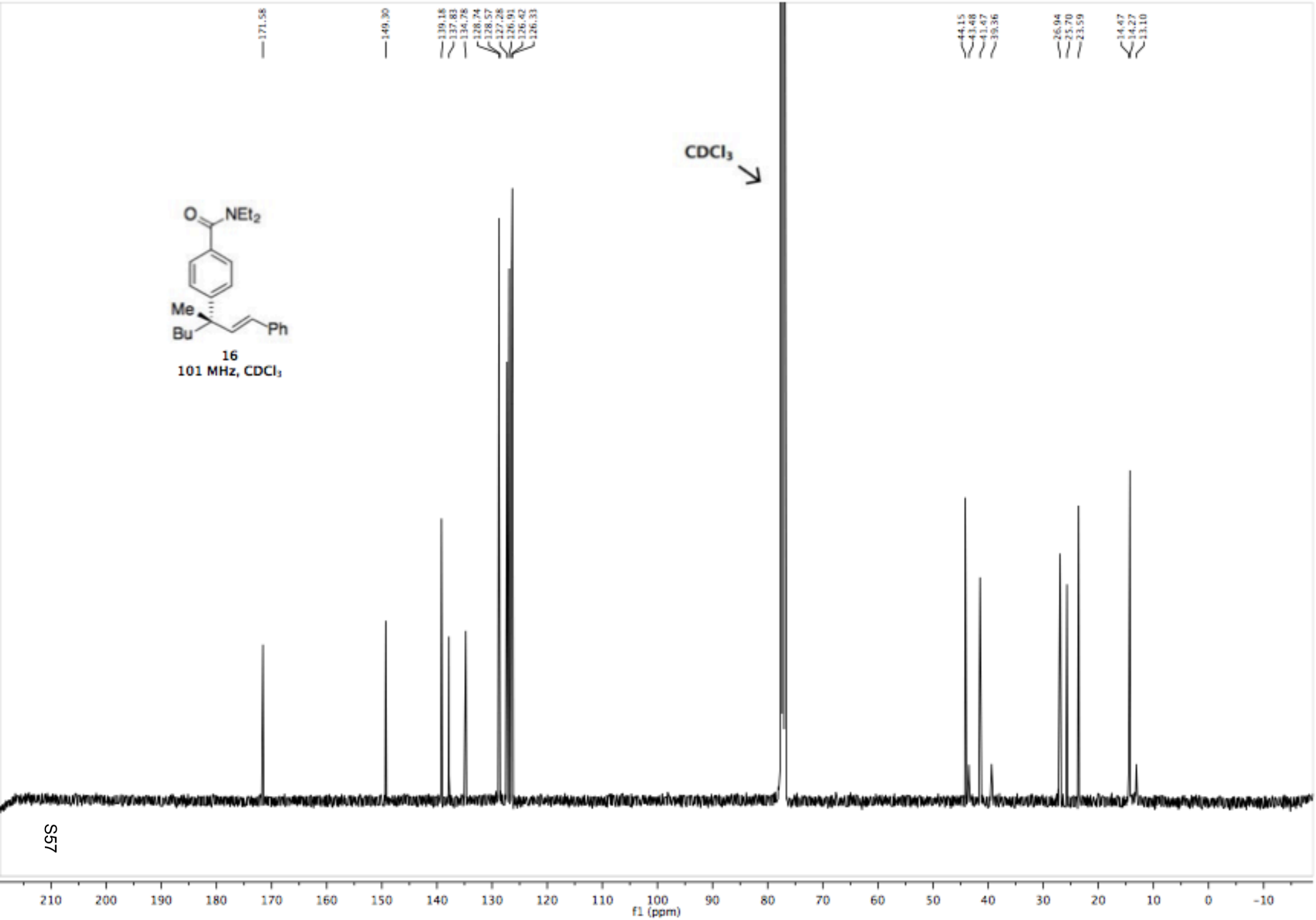

O
Ph
Me
Bu
Ph
14
600 MHZ, CDCl3
CDCl3
2.29
2.04
1.21
4.39
2.00
2.09
1.06
2.00
2.08
2.98
2.17
1.11
1.06
3.01
f1 (ppm)

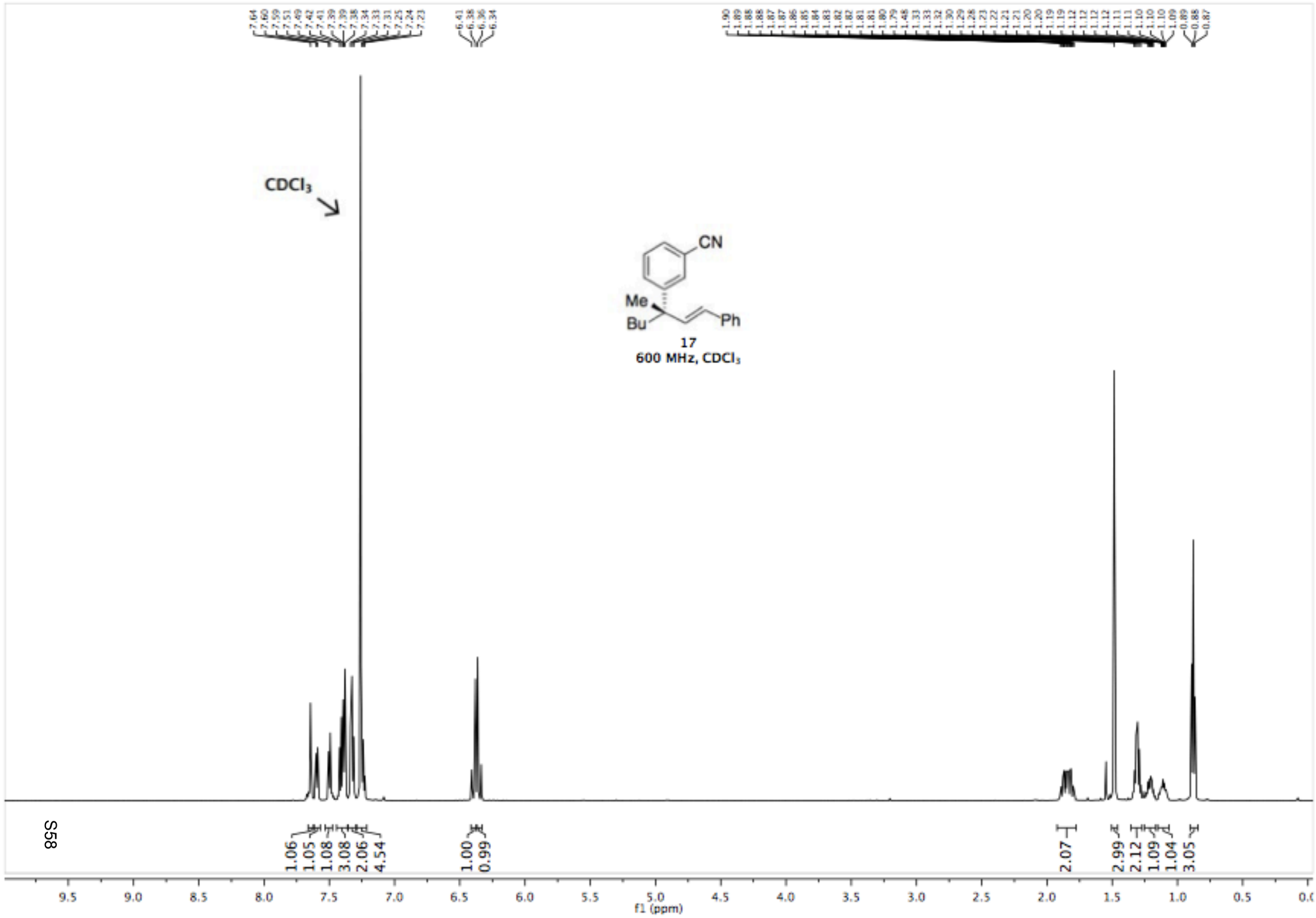

196.58
153.28
138.79
138.10
137.80
135.40
132.39
130.32
130.17
128.77
128.40
127.81
127.41
126.91
126.41
CDCl3
44.53
41.57
27.00
25.72
23.58
14.20
O
Ph
Me
Bu
Ph
14
151 MHz, CDCl3
S53
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

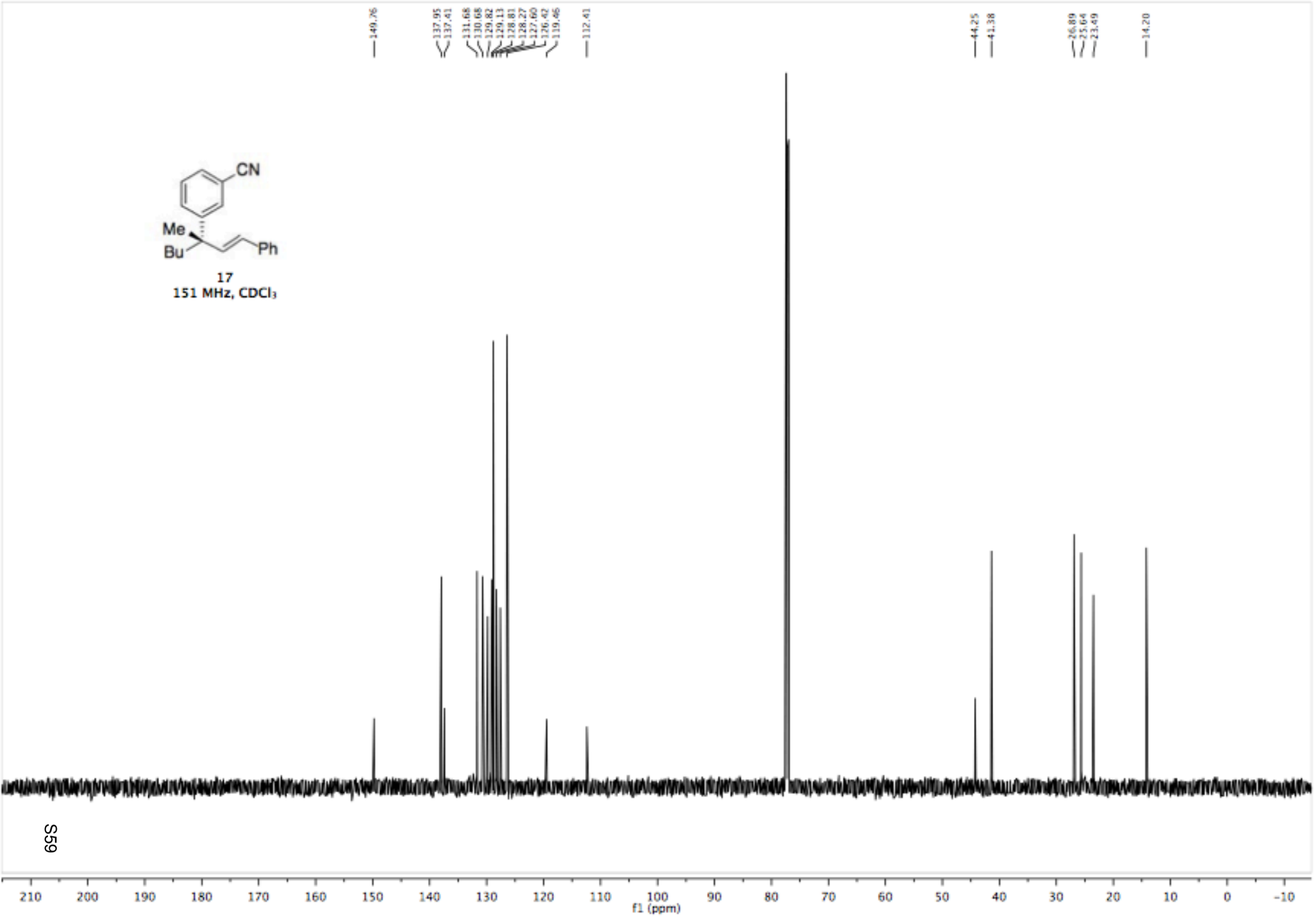

7.91
7.89
7.36
7.34
7.32
7.30
7.25
7.24
7.23
7.16
7.15
7.14
6.36
6.33
6.31
6.29
3.83
1.85
1.84
1.83
1.82
1.80
1.80
1.78
1.77
1.76
1.75
1.74
1.73
1.42
1.25
1.24
1.23
1.22
1.20
1.19
1.18
1.15
1.14
1.13
1.12
1.11
1.07
1.07
1.05
1.04
1.03
1.02
1.01
0.80
0.79
0.78
O
OMe
Me
Bu
Ph
15
600 MHz, CDCl3
CDCl3
1.94
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)

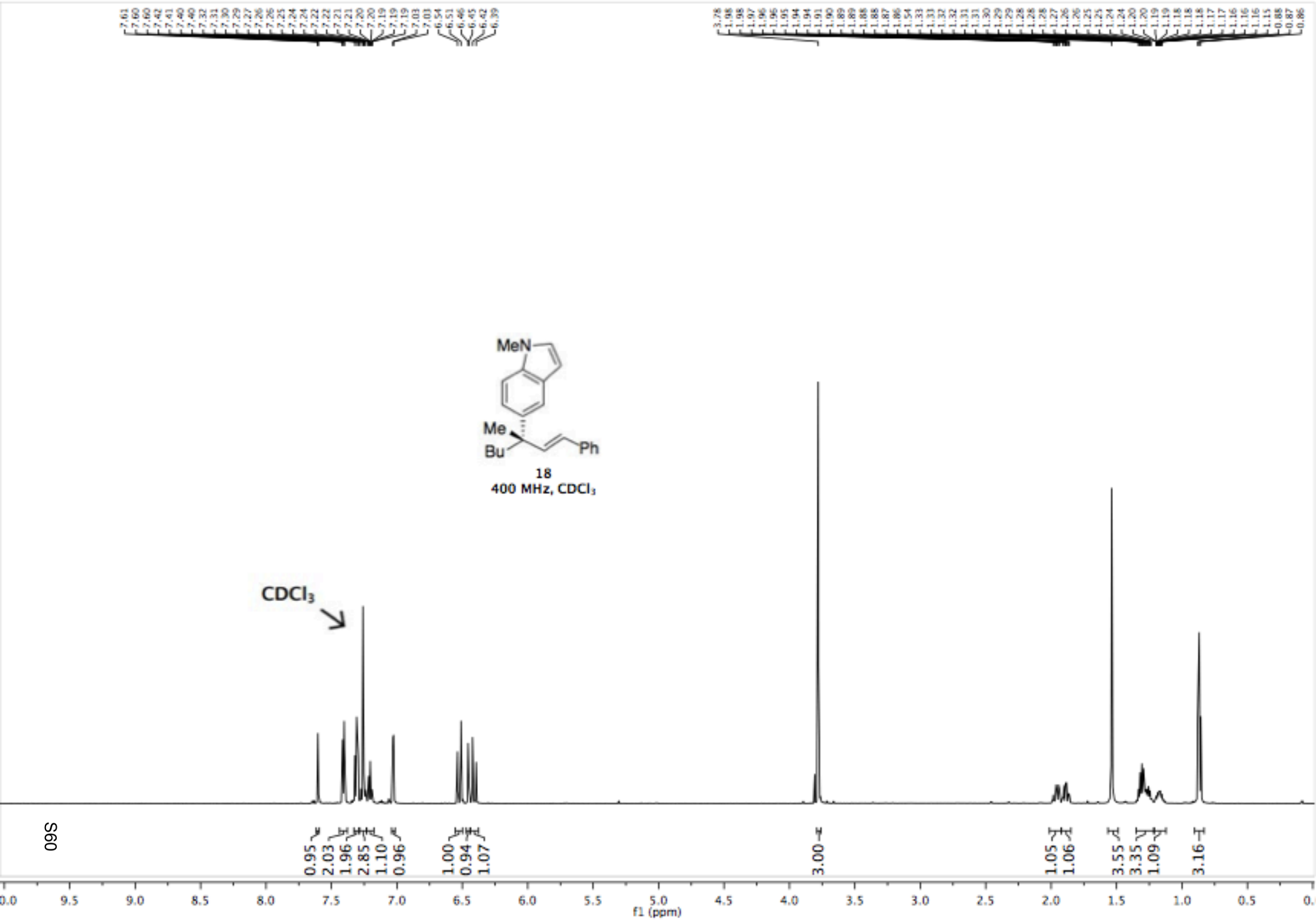

167.31
153.62
138.77
137.76
129.67
128.78
127.96
127.72
127.40
127.03
126.39
52.20
44.52
41.54
26.97
25.72
23.58
14.24
CDCl3
O
OMe
Me
Bu
Ph
15
151 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

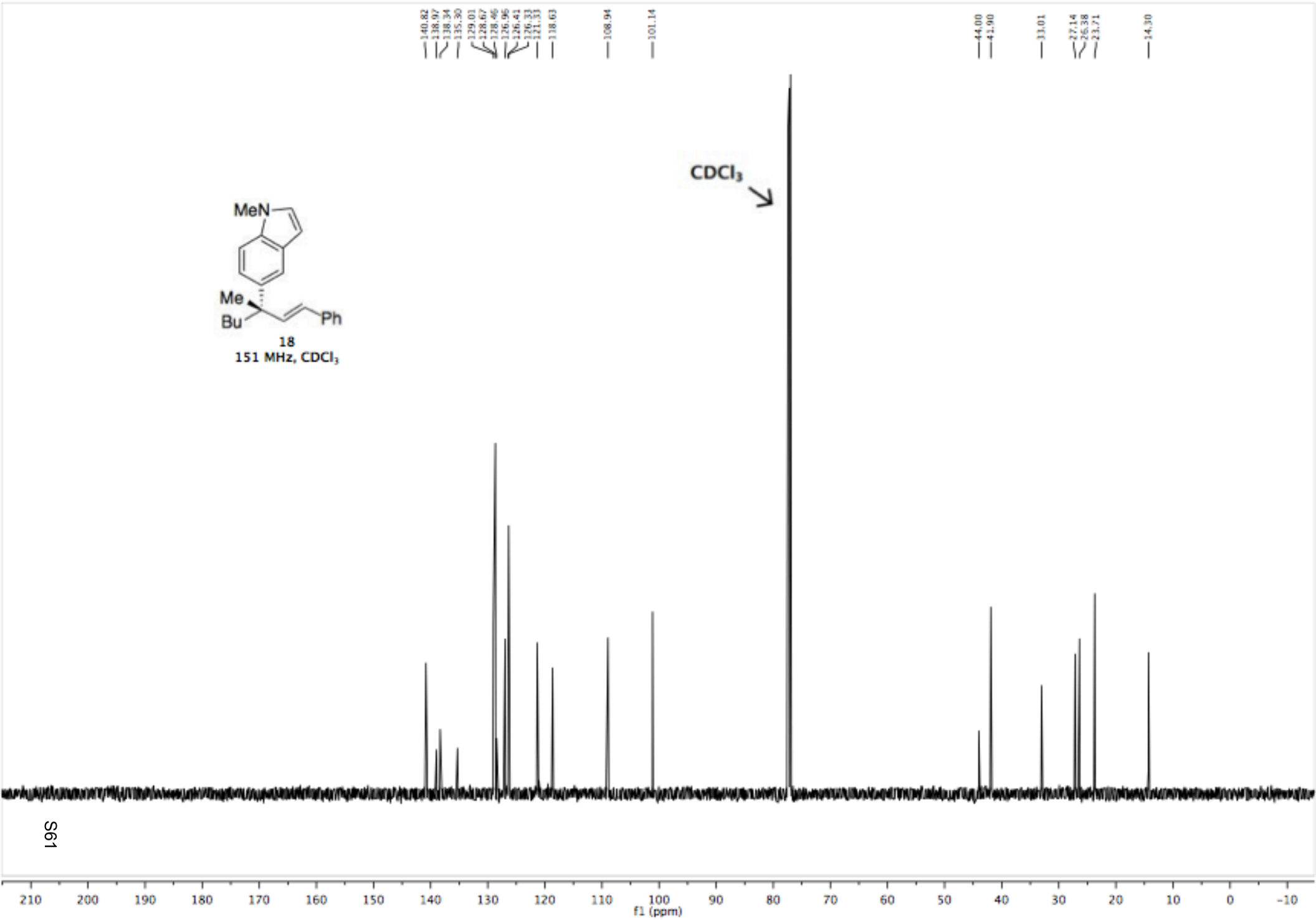

CDCl3
O
NEt2
Me
Bu
Ph
16
600 MHz, CDCl3
2.08
2.12
4.00
1.16
1.00
1.07
1.97
1.92
2.27
3.00
2.26
4.62
4.20
3.15
f1 (ppm)

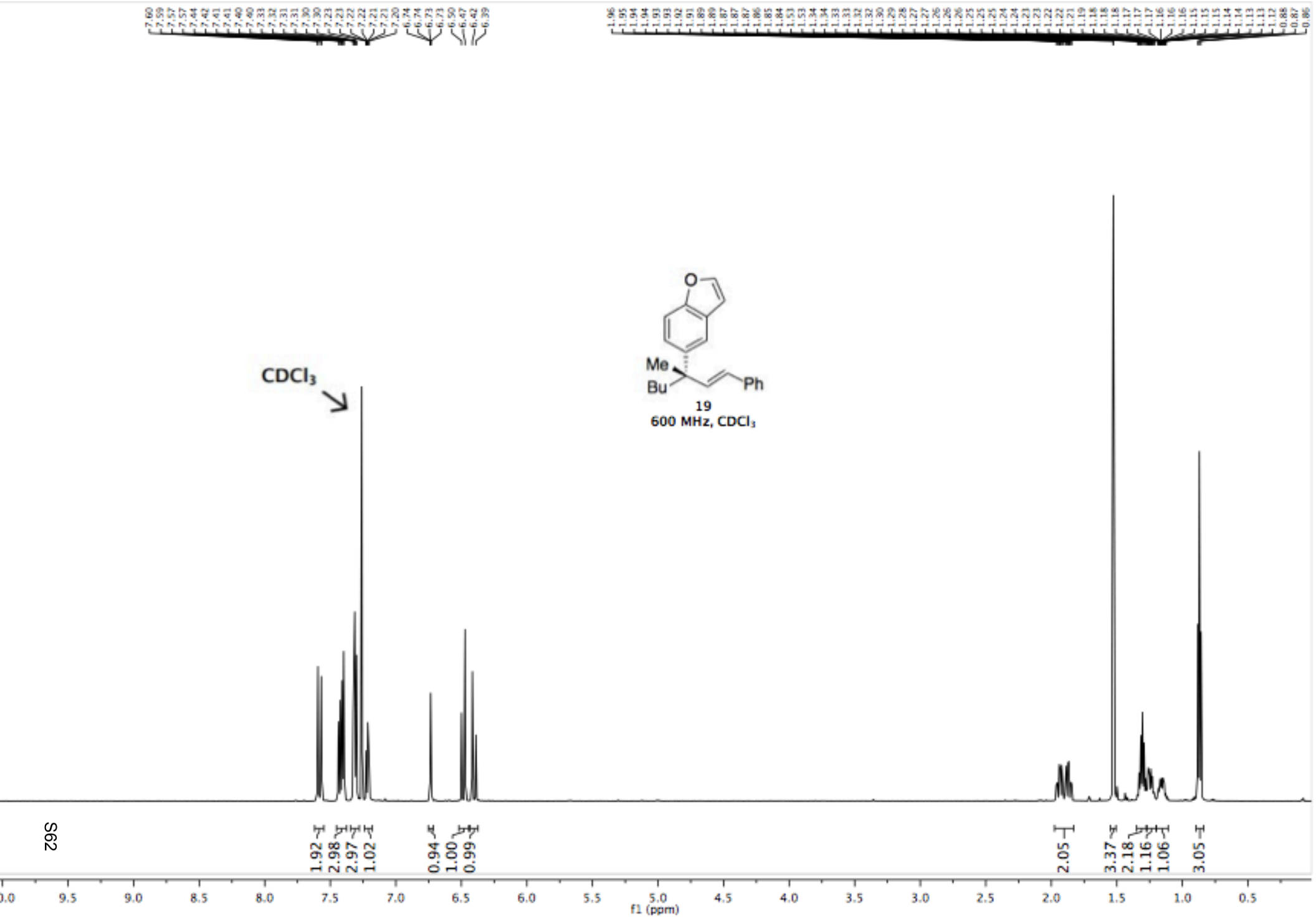

171.58
149.30
139.18
137.83
134.78
128.74
128.57
127.28
126.91
126.42
126.33
44.15
43.48
41.47
39.36
26.94
25.70
23.59
14.47
14.27
13.10
CDCl3
O
NEt2
Me
Bu
Ph
16
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

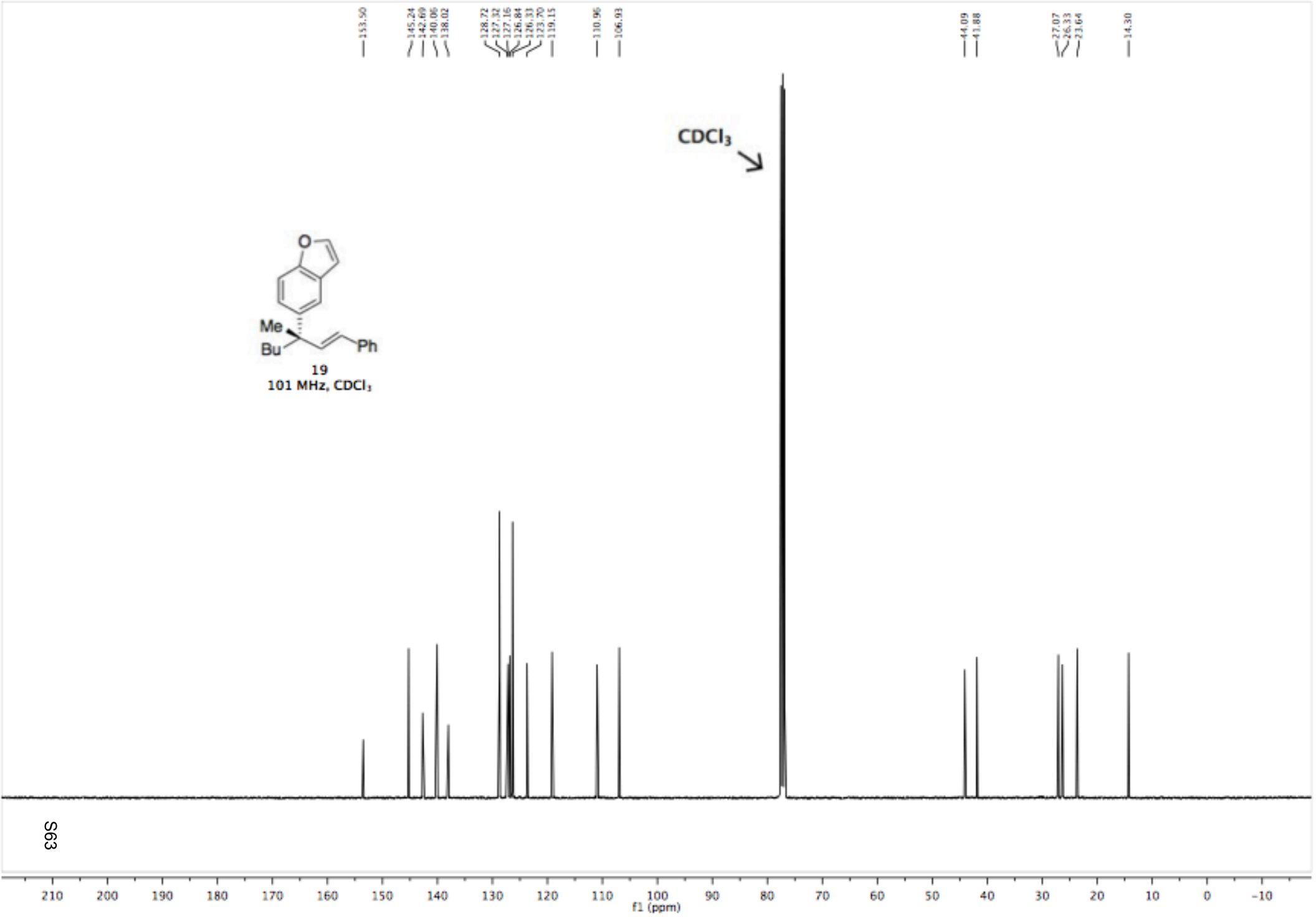

CDCl3
CN
Me
Bu
Ph
17
600 MHz, CDCl3
f1 (ppm)

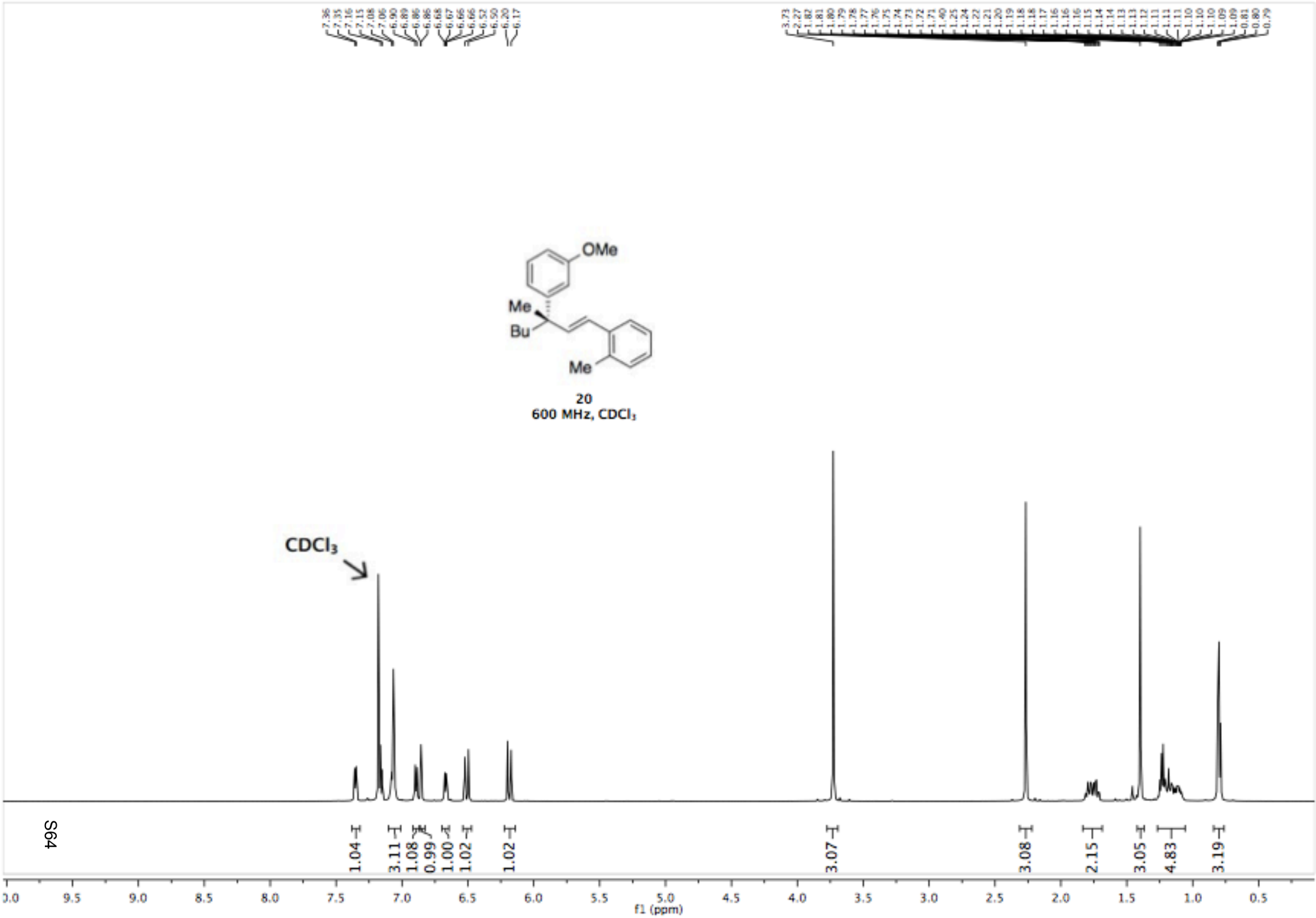

149.76
137.95
137.41
131.68
130.68
129.82
129.13
128.81
128.27
127.60
126.42
119.46
112.41
44.25
41.38
26.89
25.64
23.49
14.20
CN
Me
Bu
Ph
17
151 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

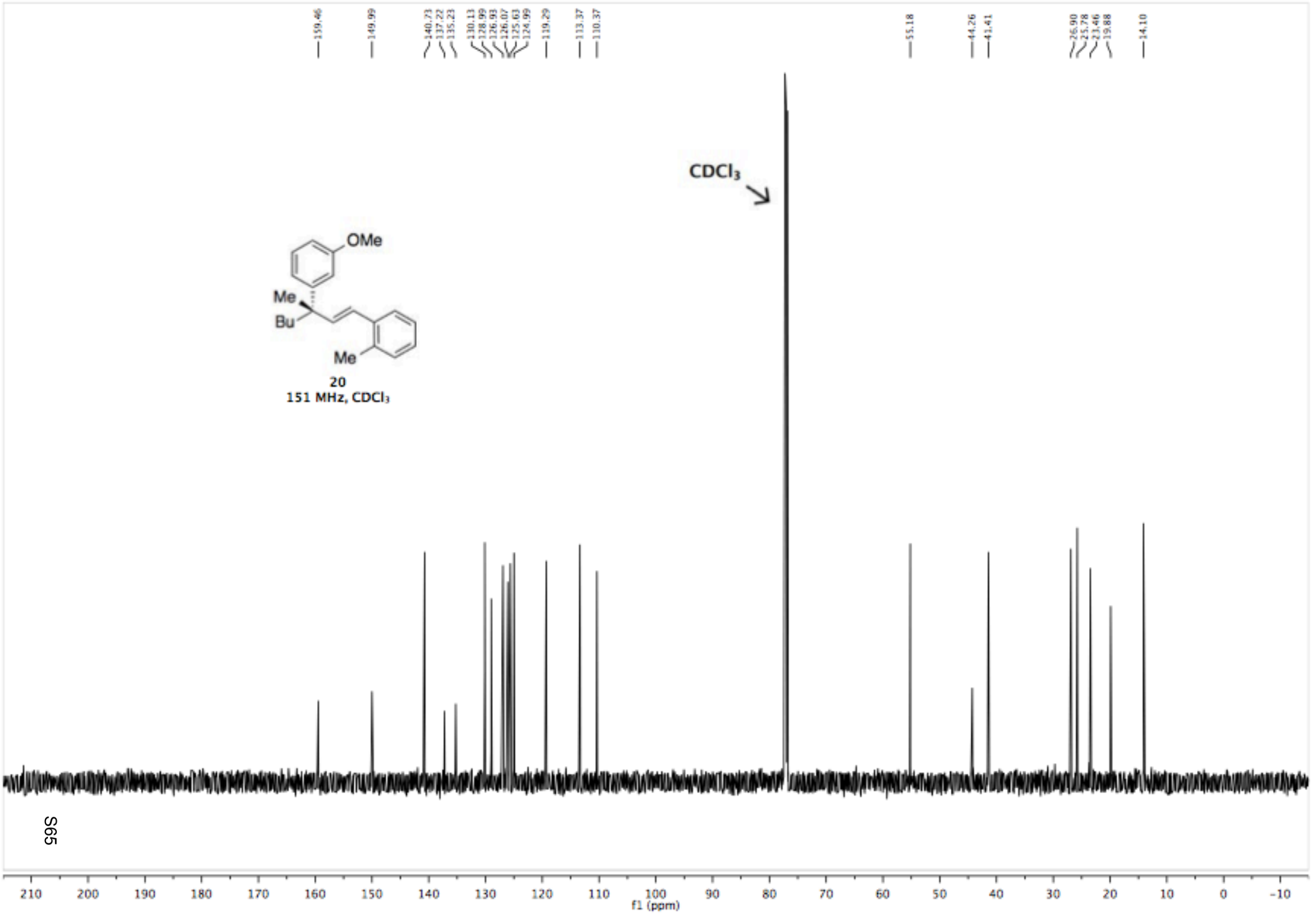

MeN
Me
Bu
Ph
18
400 MHz, CDCl3
CDCl3
0.95
2.03
1.96
2.85
1.10
0.96
1.00
0.94
1.07
3.00
1.05
1.06
3.55
3.35
1.09
3.16
f1 (ppm)

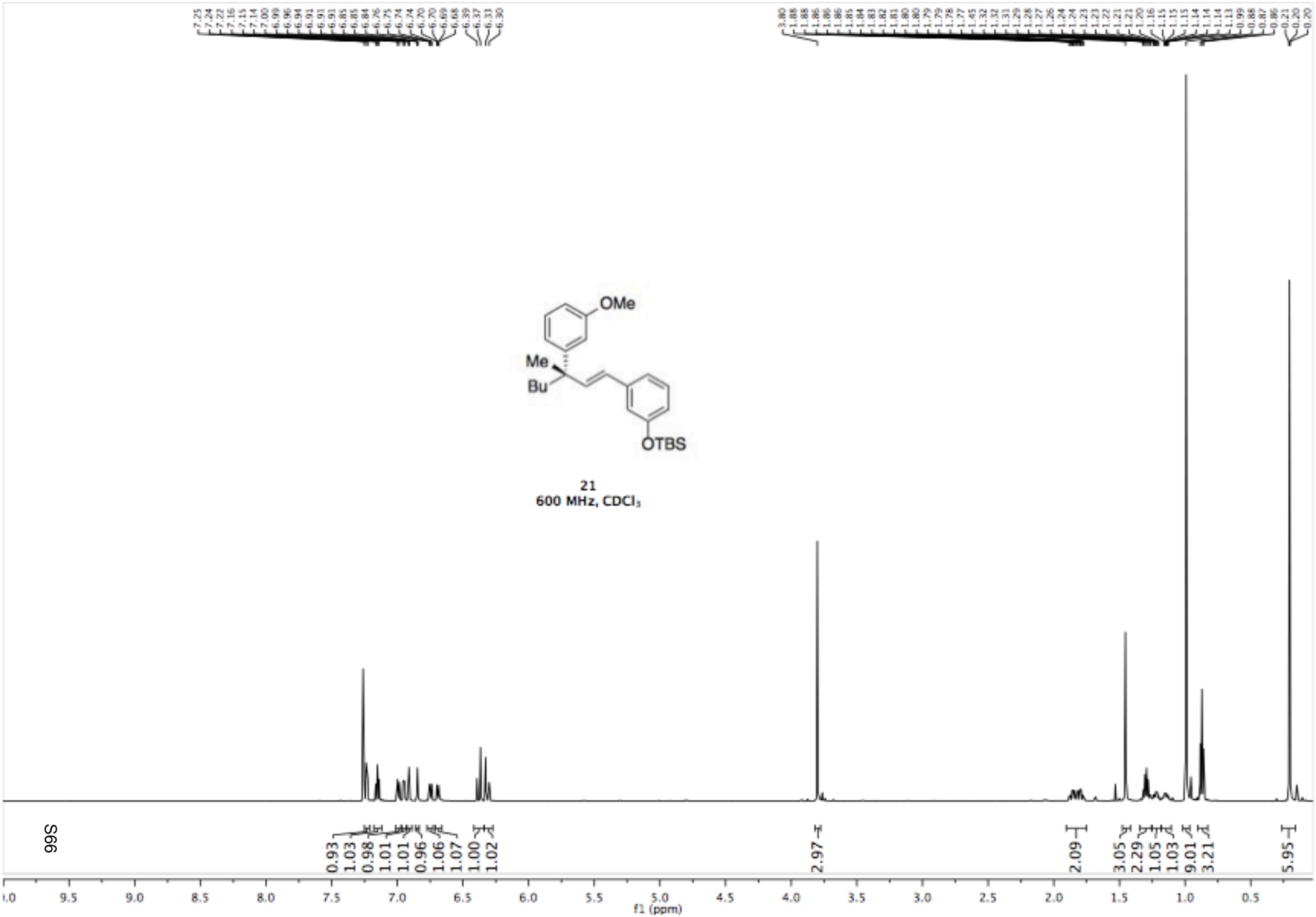

140.82
138.97
138.34
135.30
129.01
128.67
128.46
126.96
126.41
126.33
121.33
118.63
108.94
101.14
44.00
41.90
33.01
27.14
26.38
23.71
14.30
CDCl3
MeN
Me
Bu
Ph
18
151 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

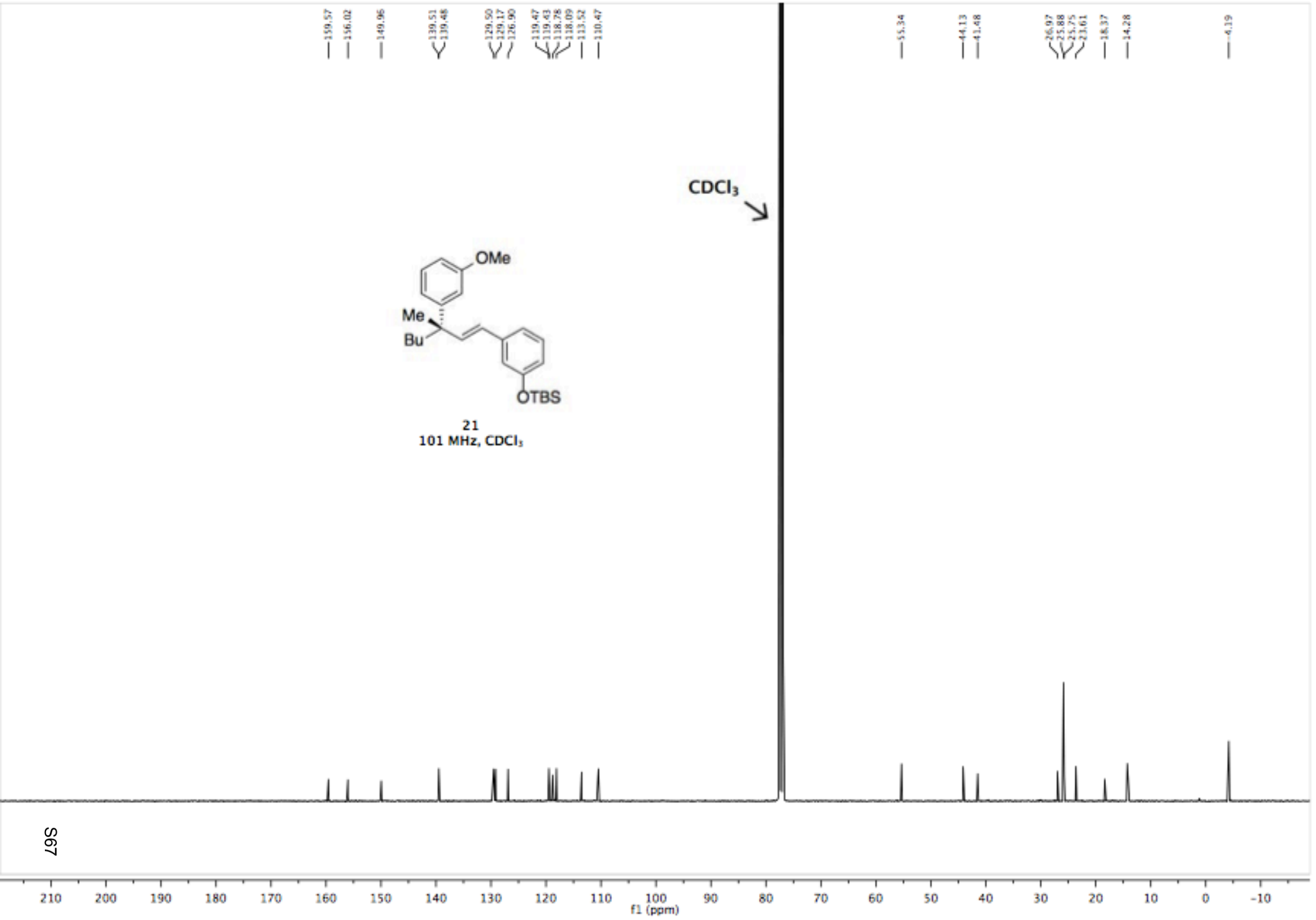

CDCl3
Me
Bu
Ph
19
600 MHz, CDCl3
1.92
2.98
2.97
1.02
0.94
1.00
0.99
2.05
3.37
2.18
1.16
1.06
3.05
f1 (ppm)

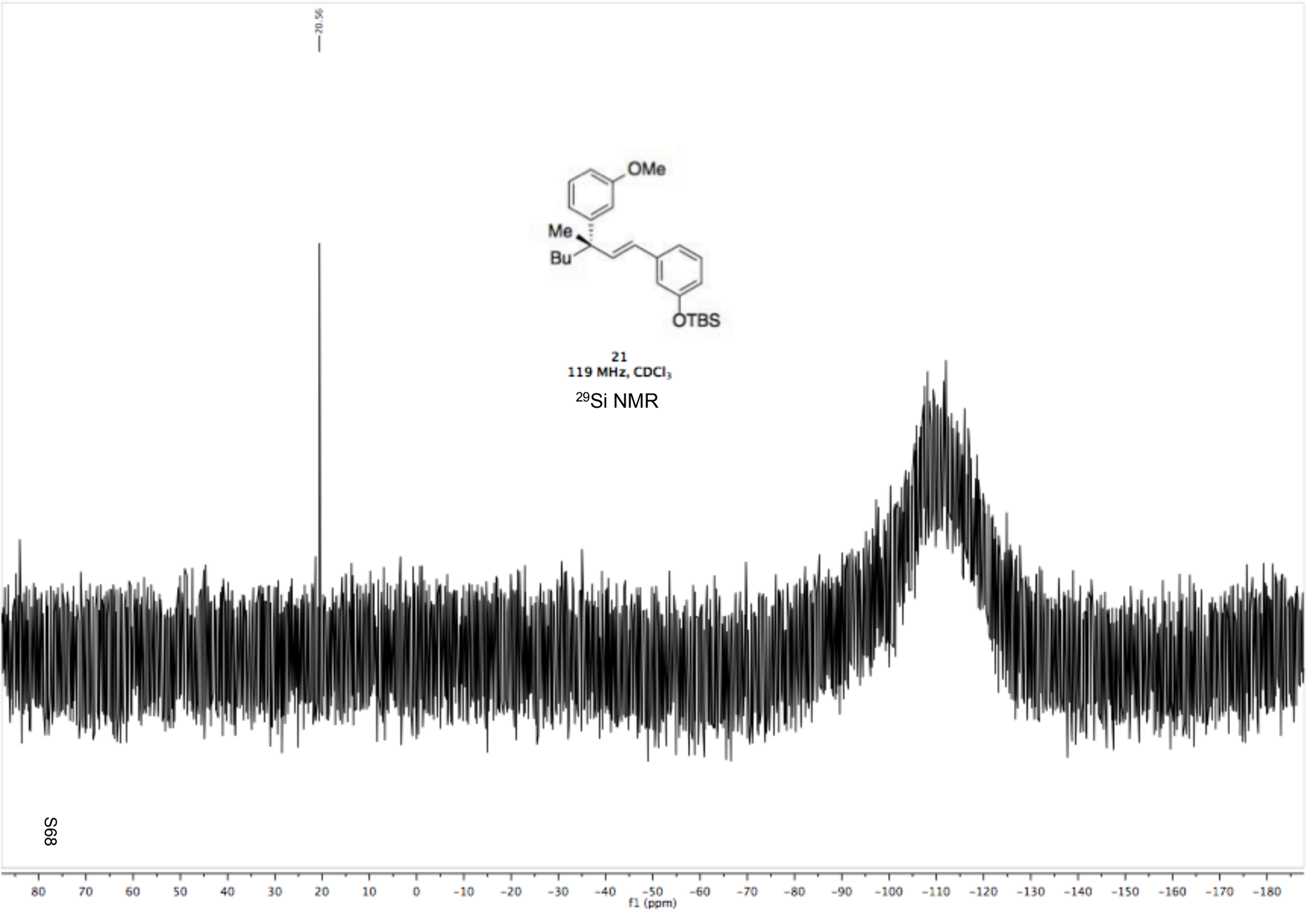

153.50
145.24
142.69
140.06
138.02
128.72
127.32
127.16
126.84
126.33
123.70
119.15
110.96
106.93
44.09
41.88
27.07
26.33
23.64
14.30
CDCl3
O
Me
Bu
Ph
19
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

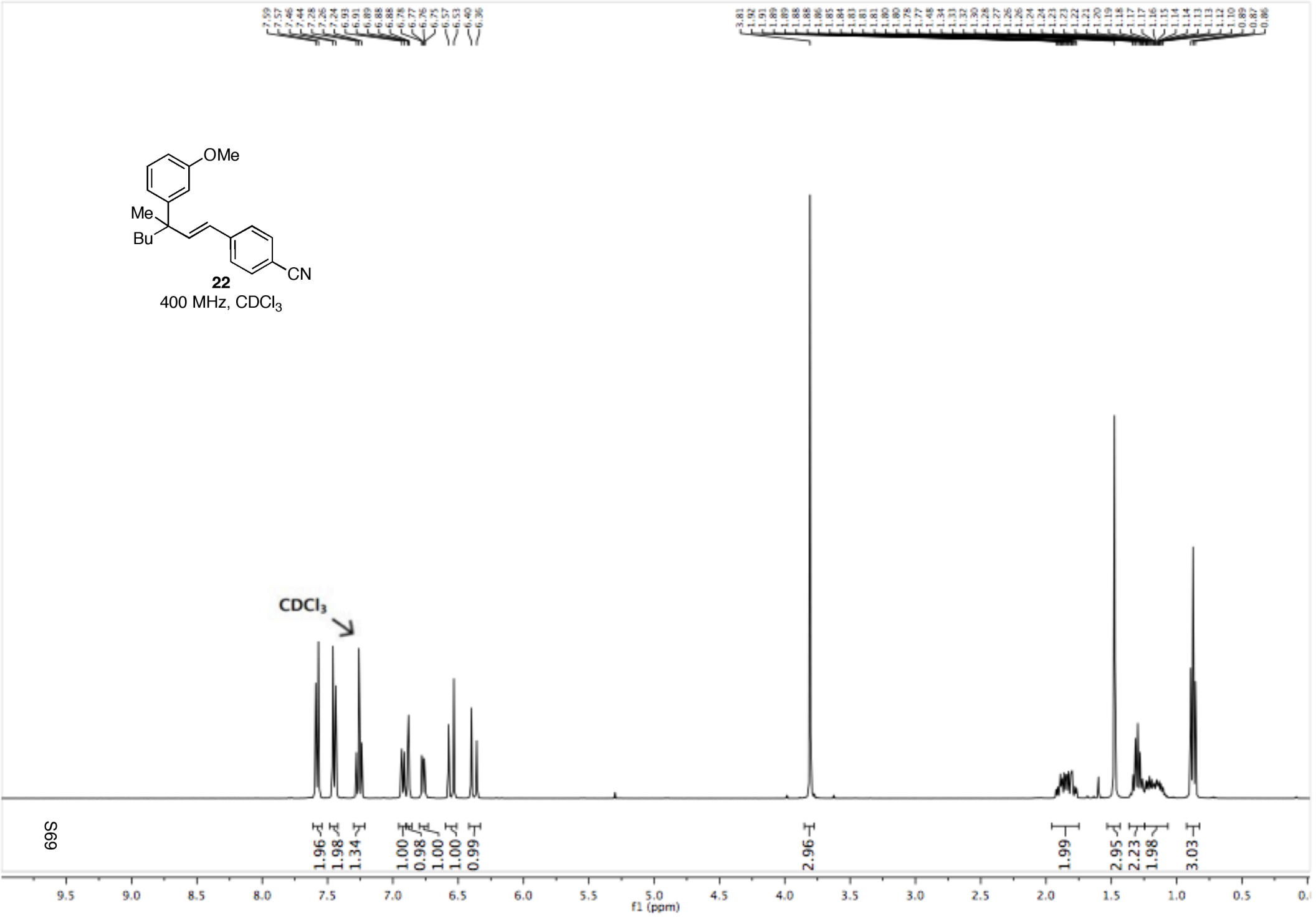

OMe
Me
Bu
Me
20
600 MHz, CDCl3
CDCl3
f1 (ppm)

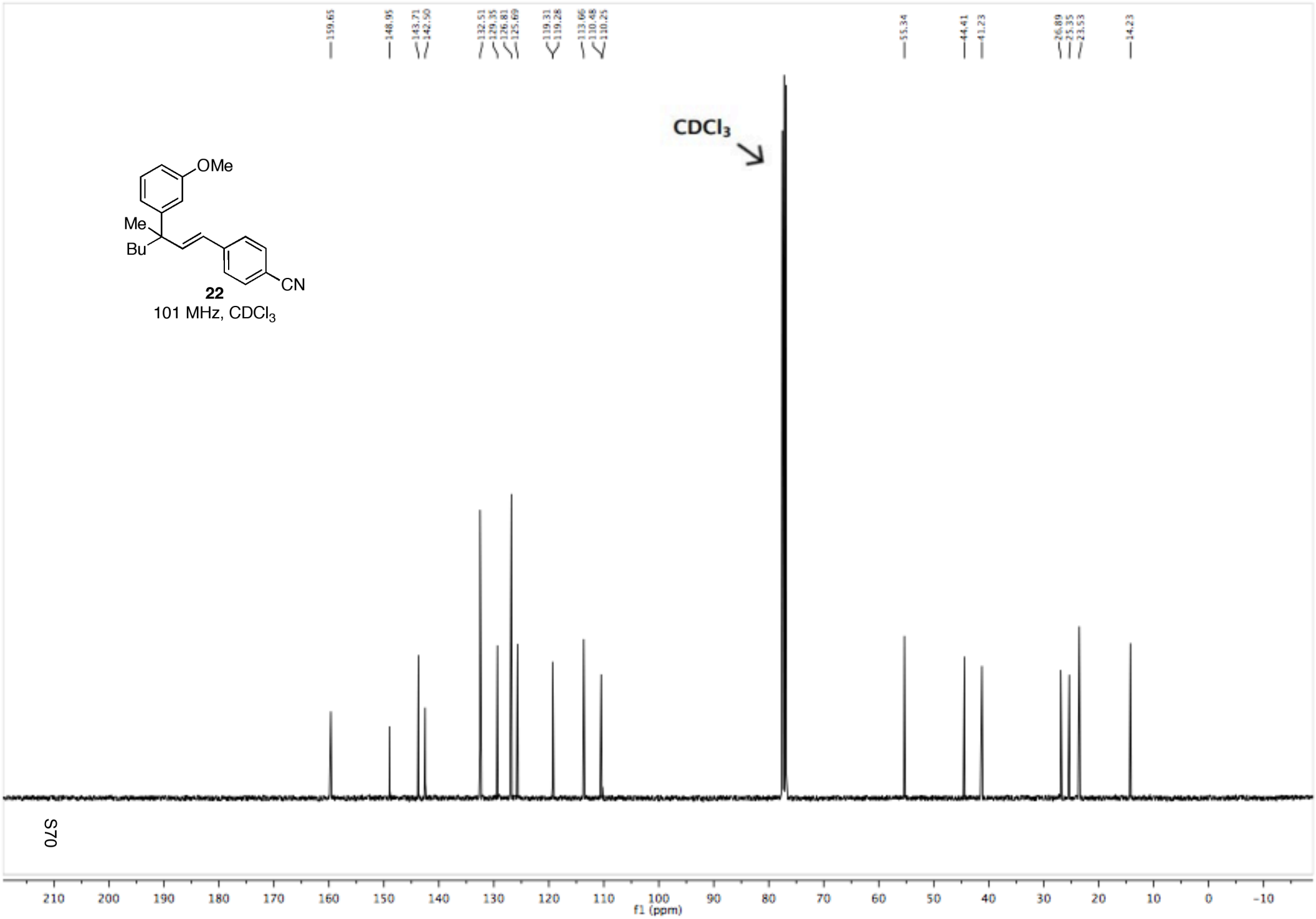

159.46
149.99
140.73
137.22
135.23
130.13
128.99
126.93
126.07
125.63
124.99
119.29
113.37
110.37
55.18
44.26
41.41
26.90
25.78
23.46
19.88
14.10
CDCl3
OMe
Me
Bu
Me
20
151 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

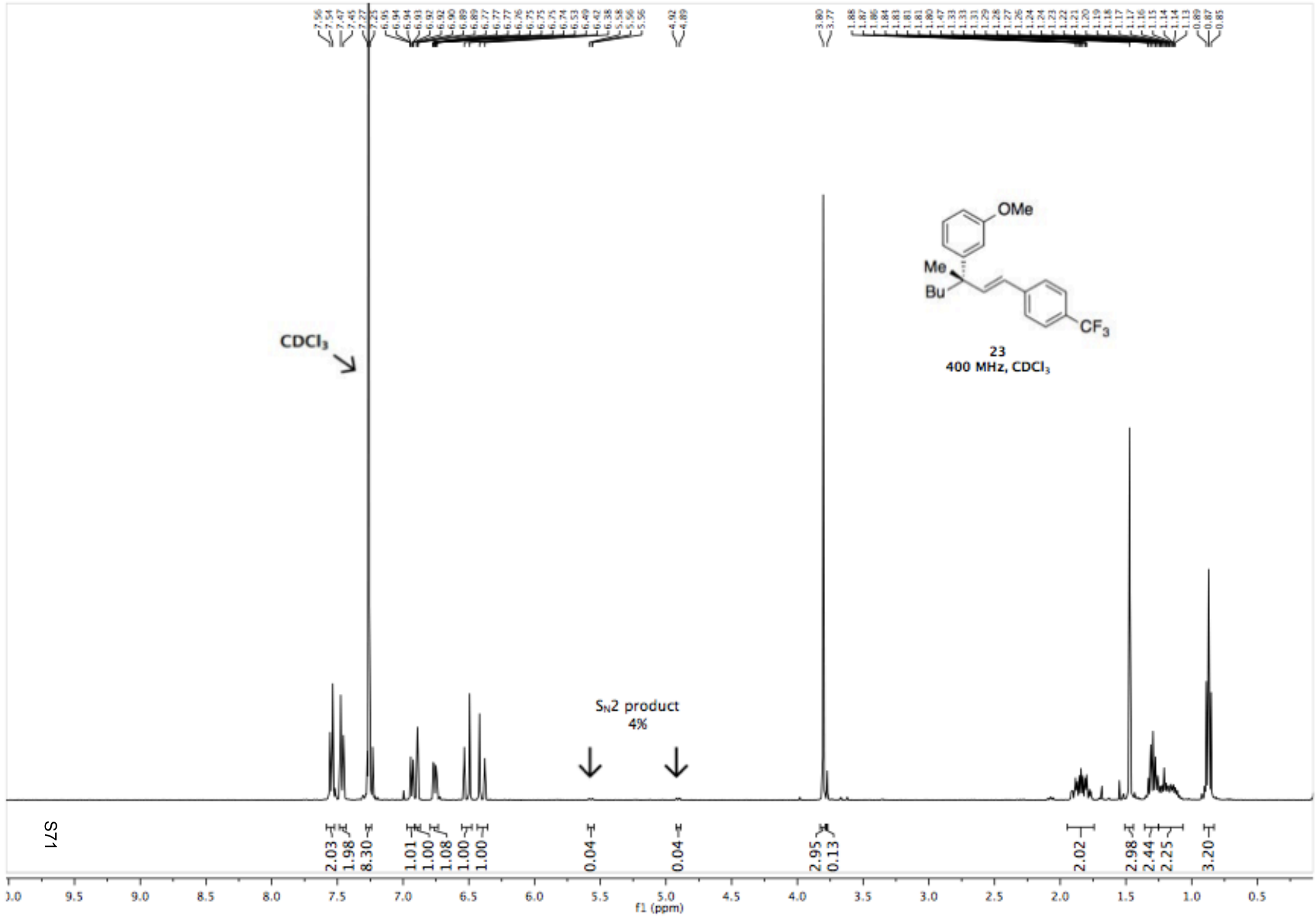

OMe
Me
Bu
OTBS
21
600 MHz, CDCl3
0.93
1.03
0.98
1.01
1.01
0.96
1.06
1.07
1.00
1.02
2.97
2.09
3.05
2.29
1.05
1.03
9.01
3.21
5.95
f1 (ppm)

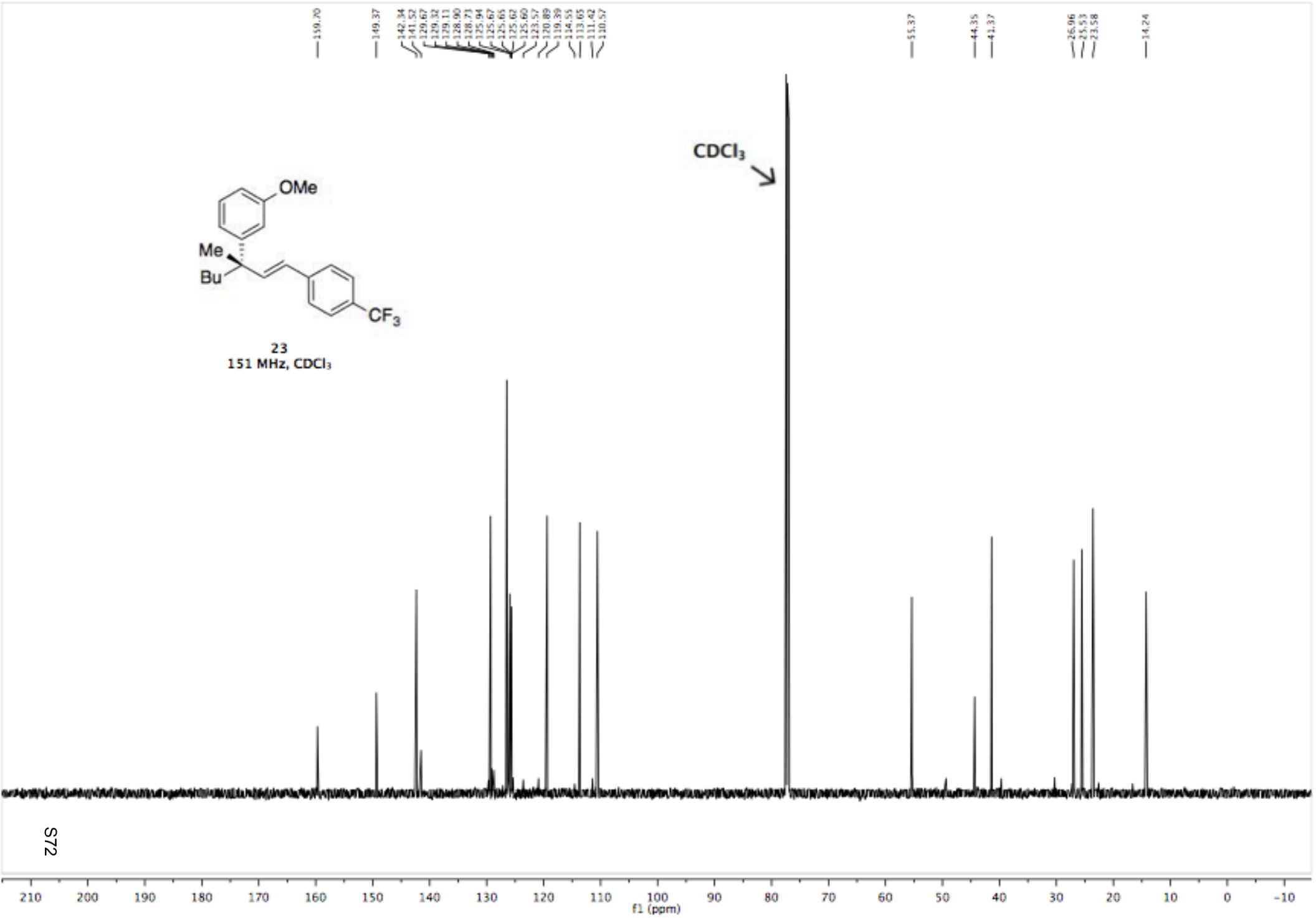

159.57
156.02
149.96
139.51
139.48
129.50
129.17
126.90
119.47
119.43
118.78
118.09
113.52
110.47
55.34
44.13
41.48
26.97
25.88
25.75
23.61
18.37
14.28
-4.19
CDCl3
OMe
Me
Bu
OTBS
21
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

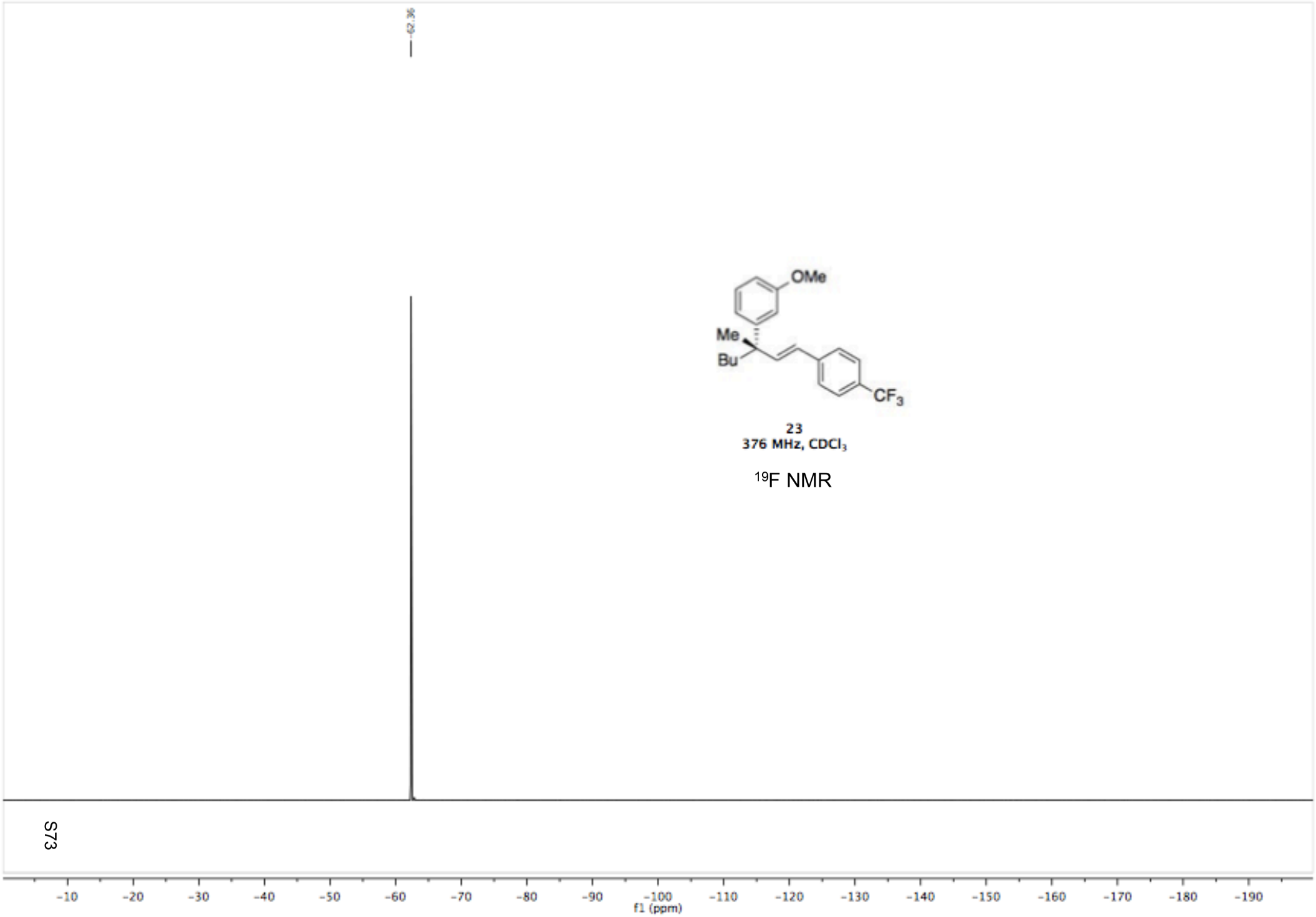

20.56
OMe
Me
Bu
OTBS
21
119 MHz, CDCl3
29Si NMR
80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180
f1 (ppm)

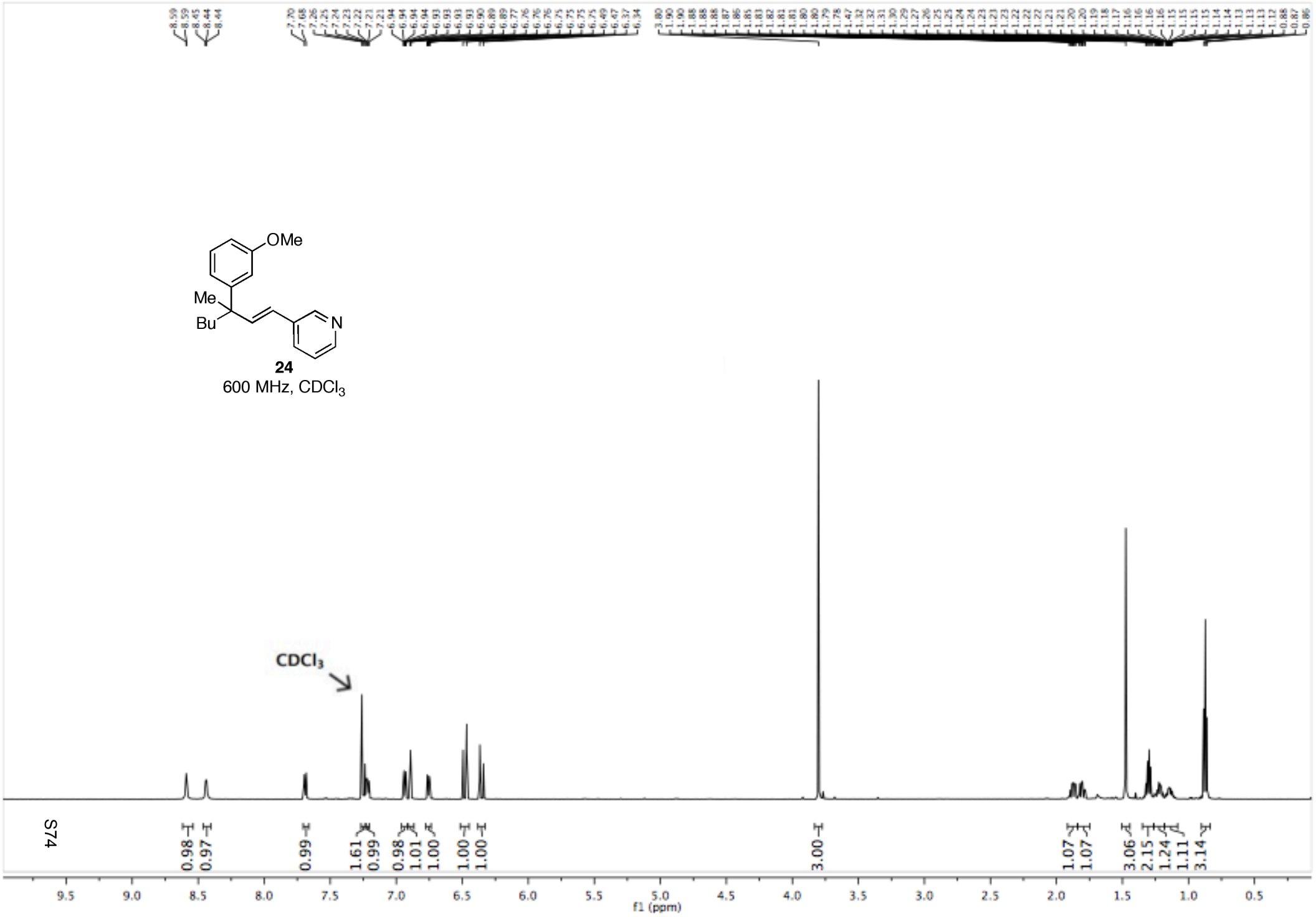

OMe
Me
Bu
CN
22
400 MHz, CDCl3
CDCl3
69S
f1 (ppm)

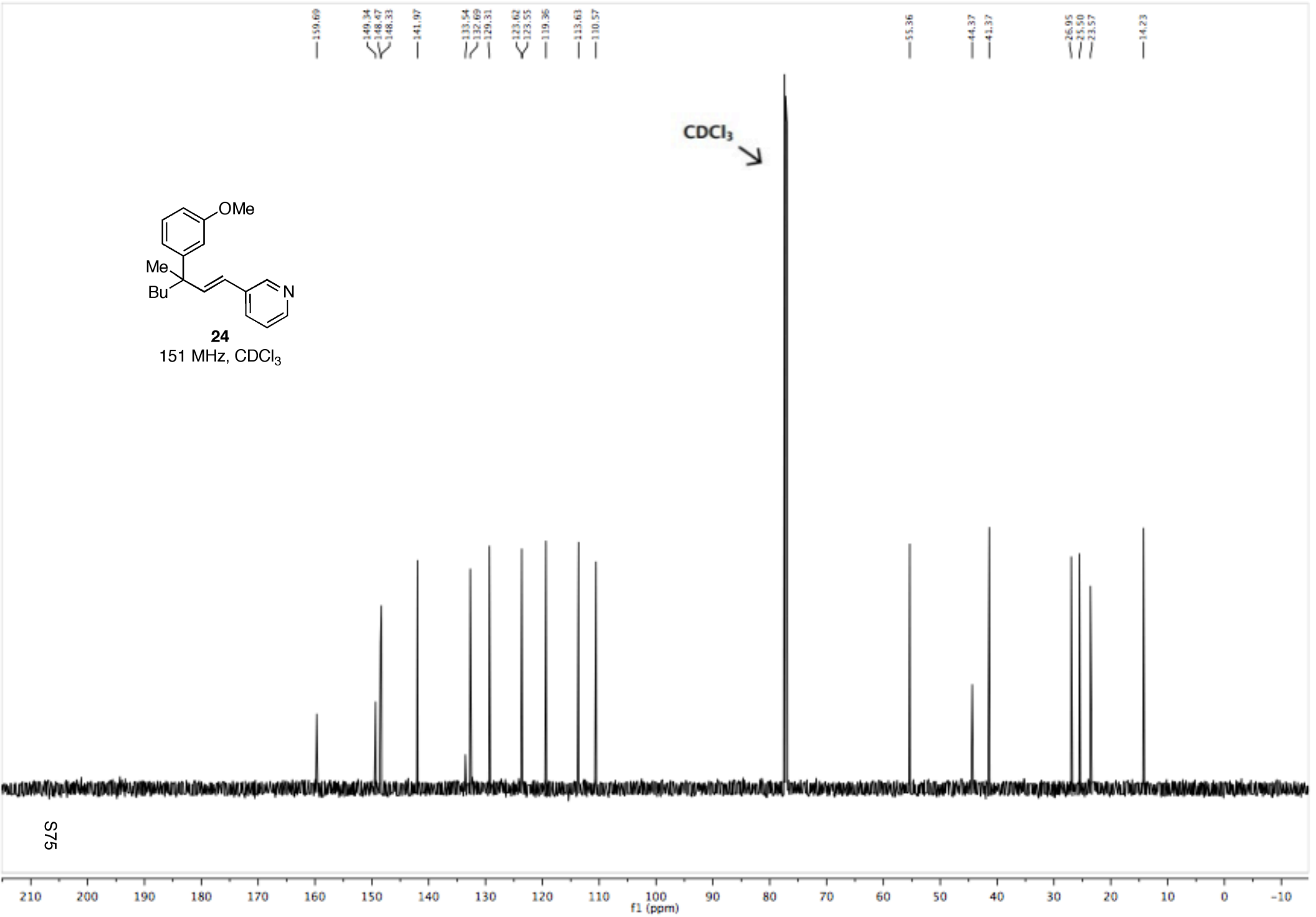

159.65
148.95
143.71
142.50
132.51
129.35
126.81
125.69
119.31
119.28
113.66
110.48
110.25
55.34
44.41
41.23
26.89
25.35
23.53
14.23
CDCl3
OMe
Me
Bu
CN
22
101 MHz, CDCl3
f1 (ppm)

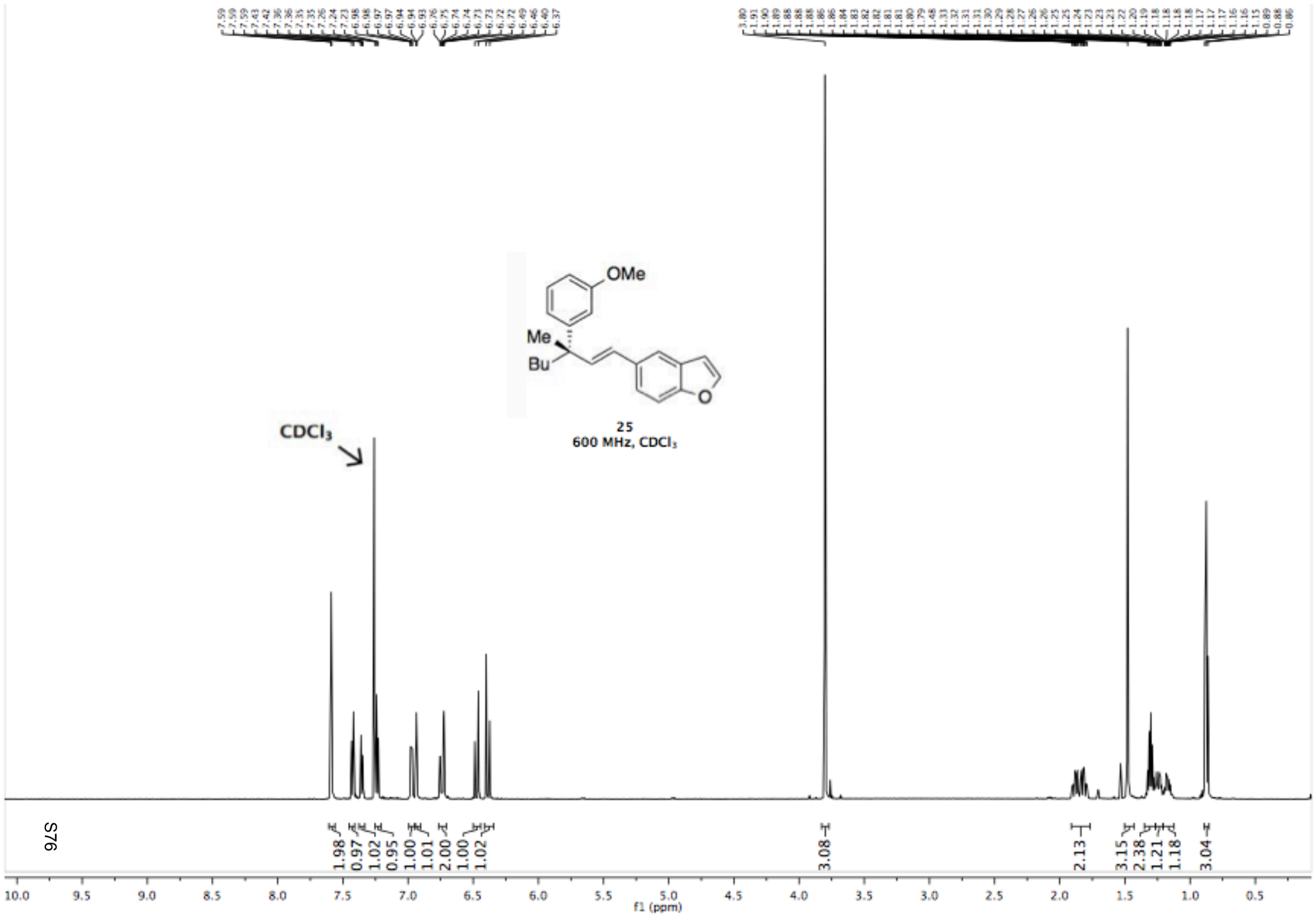

CDCl3
SN2 product
4%
OMe
Me
Bu
CF3
23
400 MHz, CDCl3
f1 (ppm)

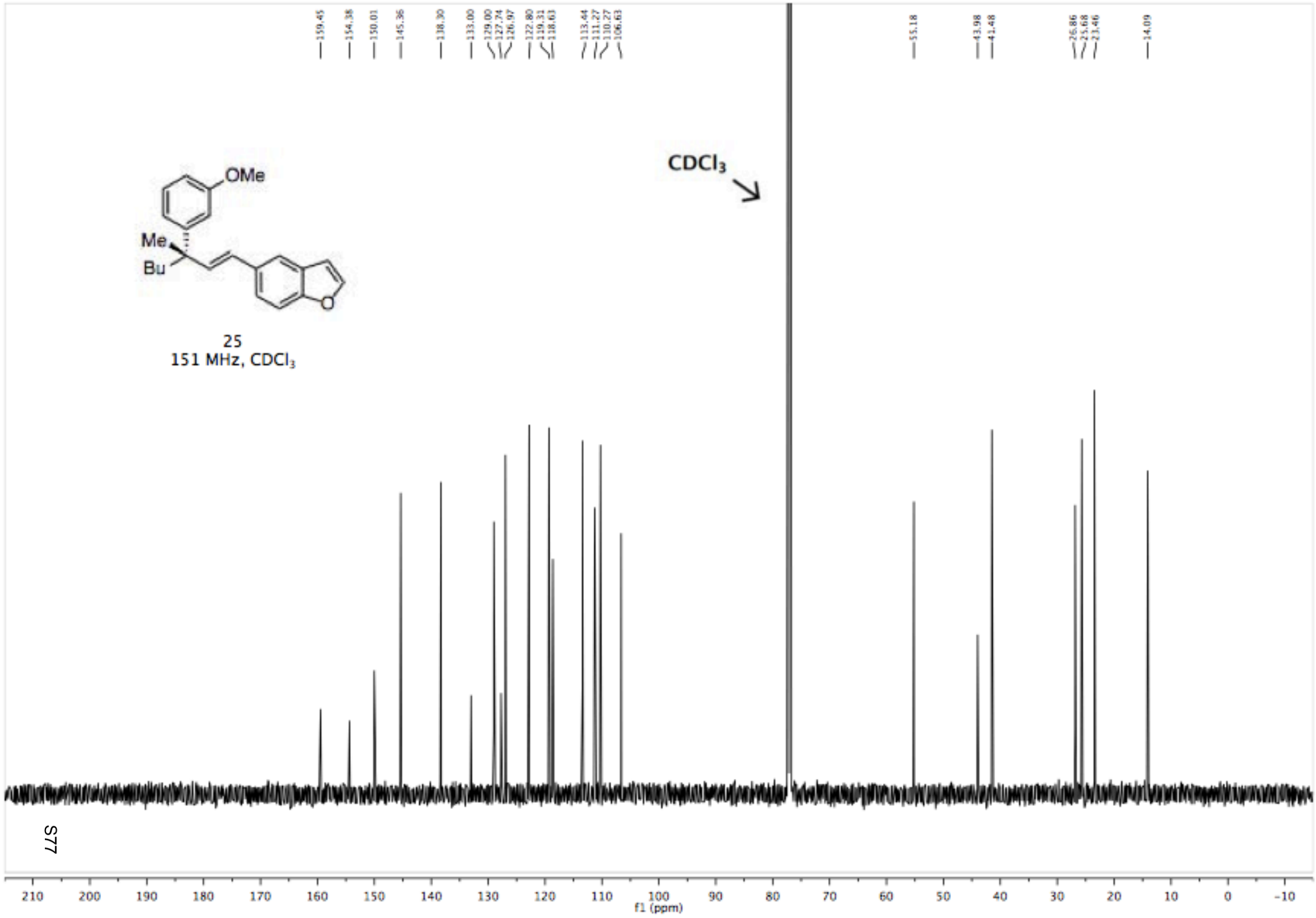

159.70
149.37
142.34
141.52
129.67
129.32
129.11
128.90
128.71
125.94
125.67
125.65
125.62
125.60
123.57
120.89
119.39
114.55
113.65
111.42
110.57
55.37
44.35
41.37
26.96
25.53
23.58
14.24
CDCl3
OMe
Me
Bu
CF3
23
151 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

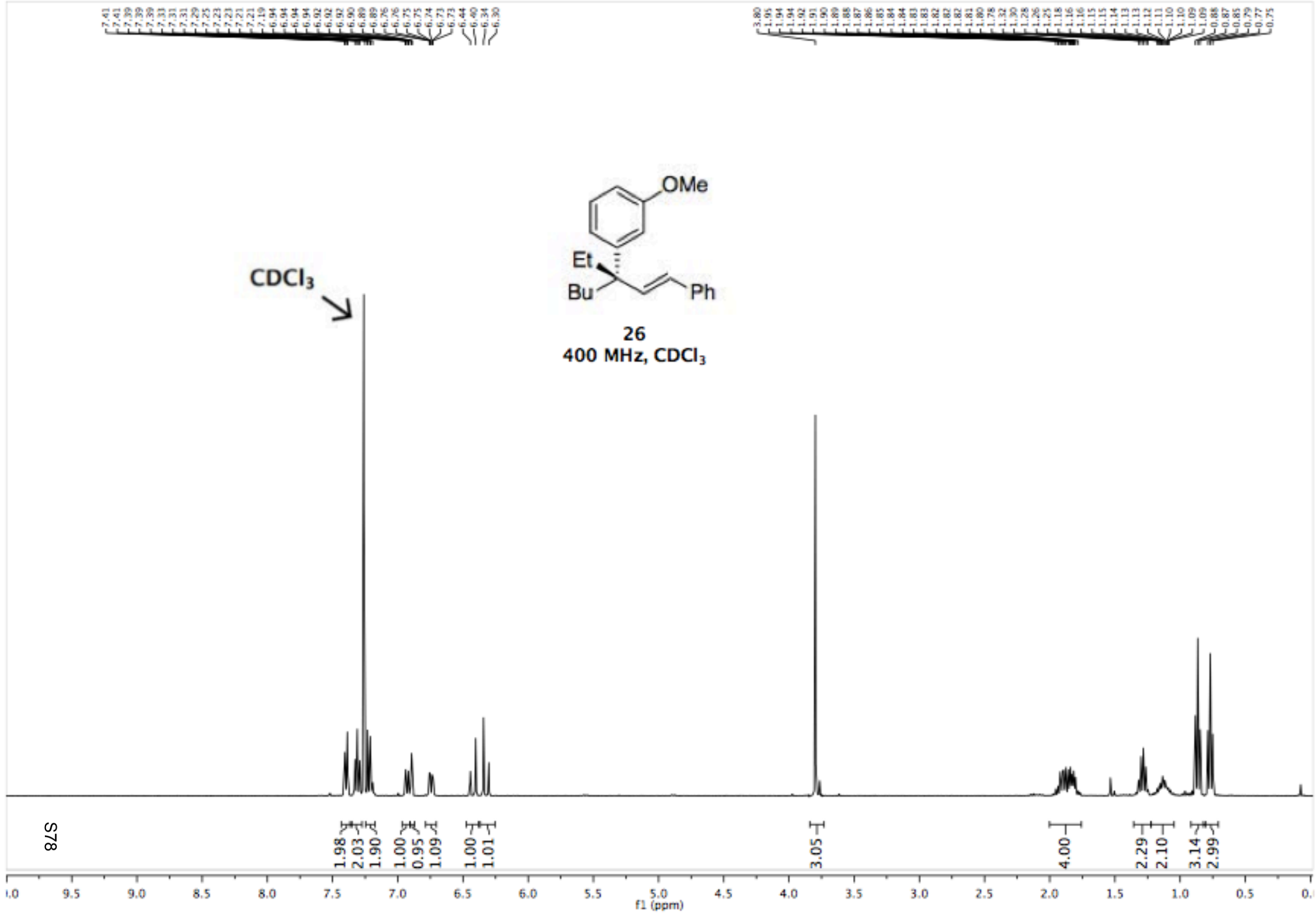

-62.36
OMe
Me
Bu
CF3
23
376 MHz, CDCl3
19F NMR
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

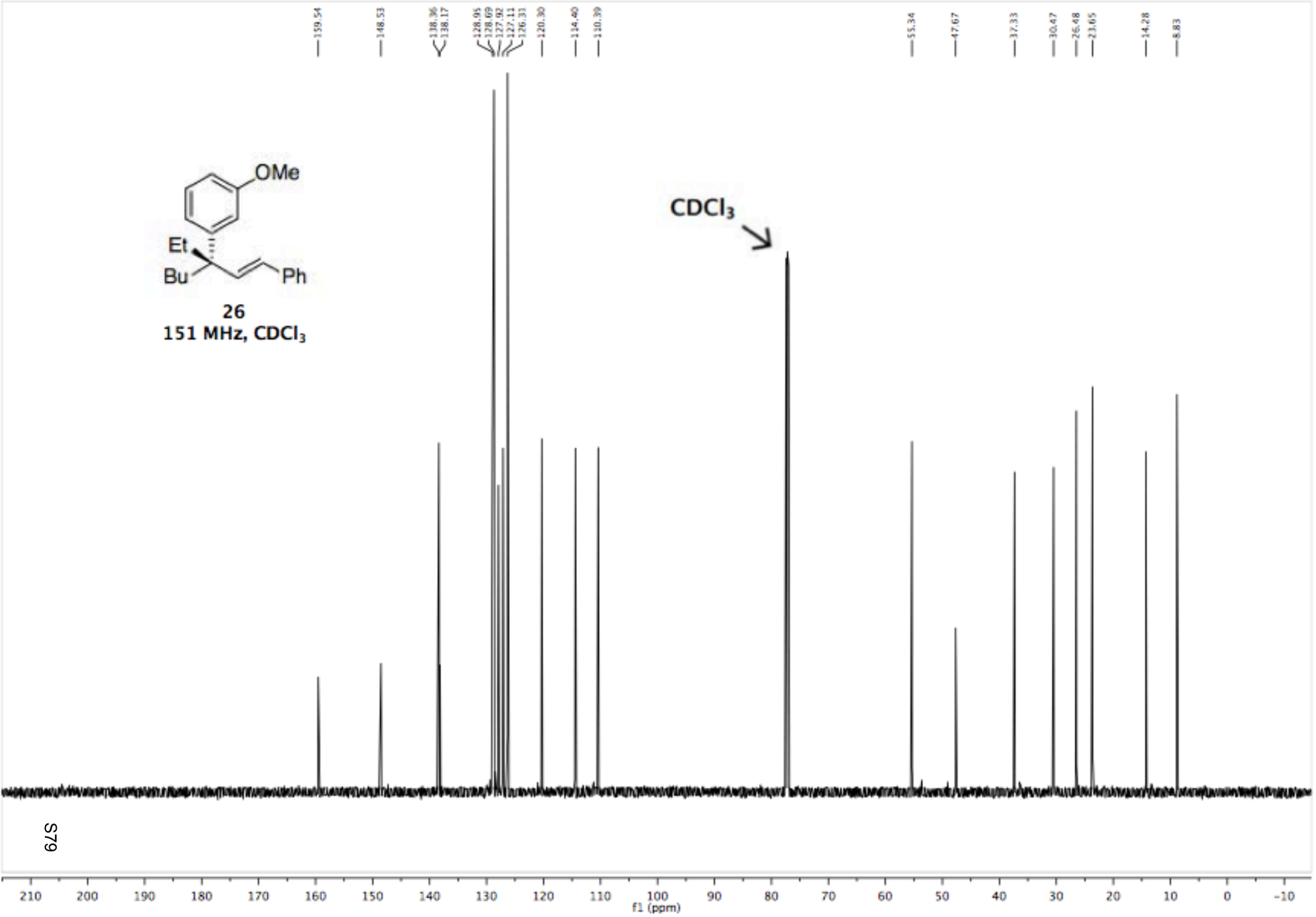

OMe
Me
Bu
N
24
600 MHz, CDCl3
CDCl3
0.98
0.97
0.99
1.61
0.99
0.98
1.01
1.00
1.00
1.00
3.00
1.07
1.07
3.06
2.15
1.24
1.11
3.14
f1 (ppm)

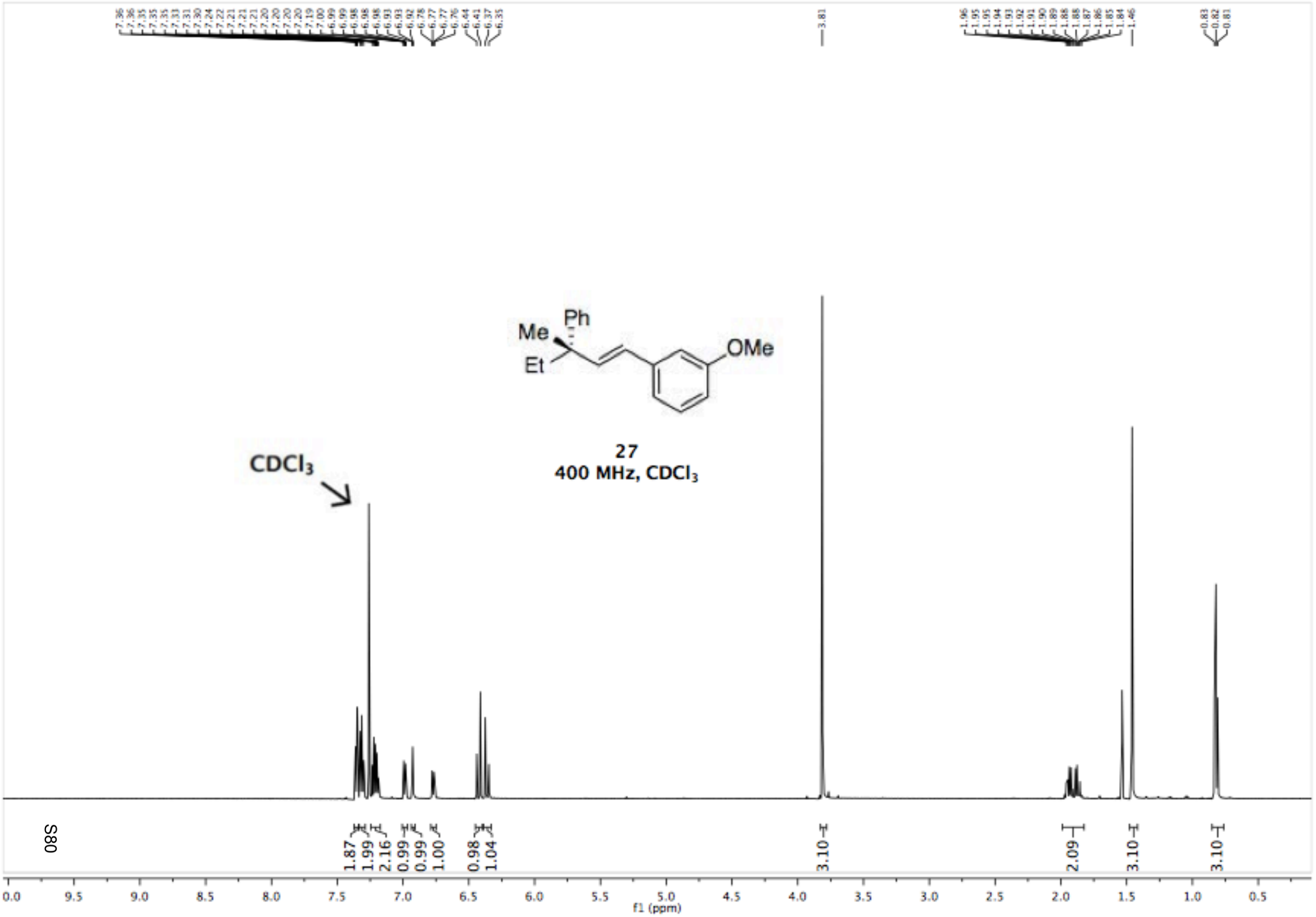

159.69
149.34
148.47
148.33
141.97
133.54
132.69
129.31
123.62
123.55
119.36
113.63
110.57
55.36
44.37
41.37
26.95
25.50
23.57
14.23
CDCl3
OMe
Me
Bu
N
24
151 MHz, CDCl3
f1 (ppm)

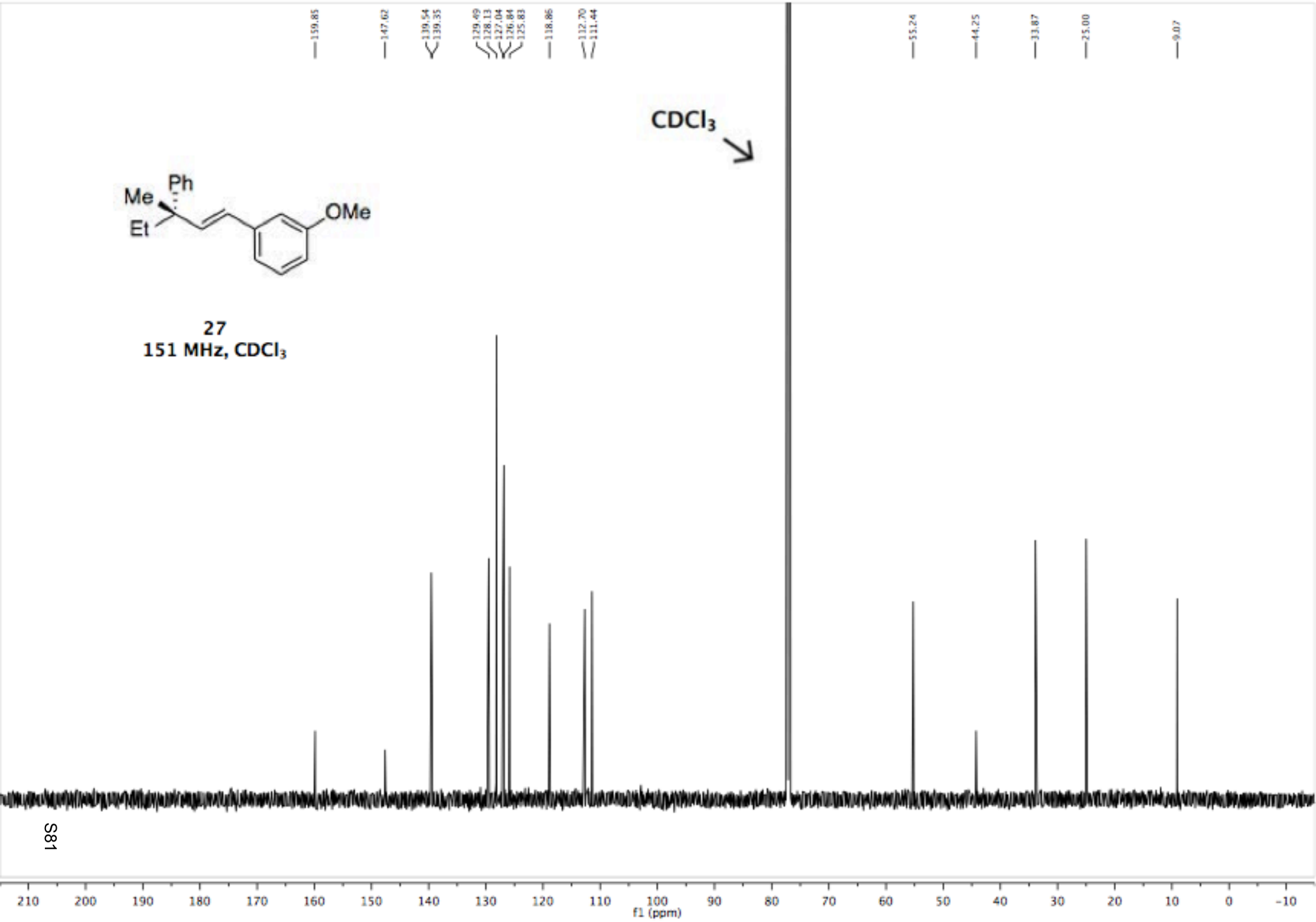

OMe
Me
Bu
O
25
600 MHz, CDCl3
CDCl3
1.98
0.97
1.02
0.95
1.00
1.01
2.00
1.00
1.02
3.08
2.13
3.15
2.38
1.21
1.18
3.04
f1 (ppm)

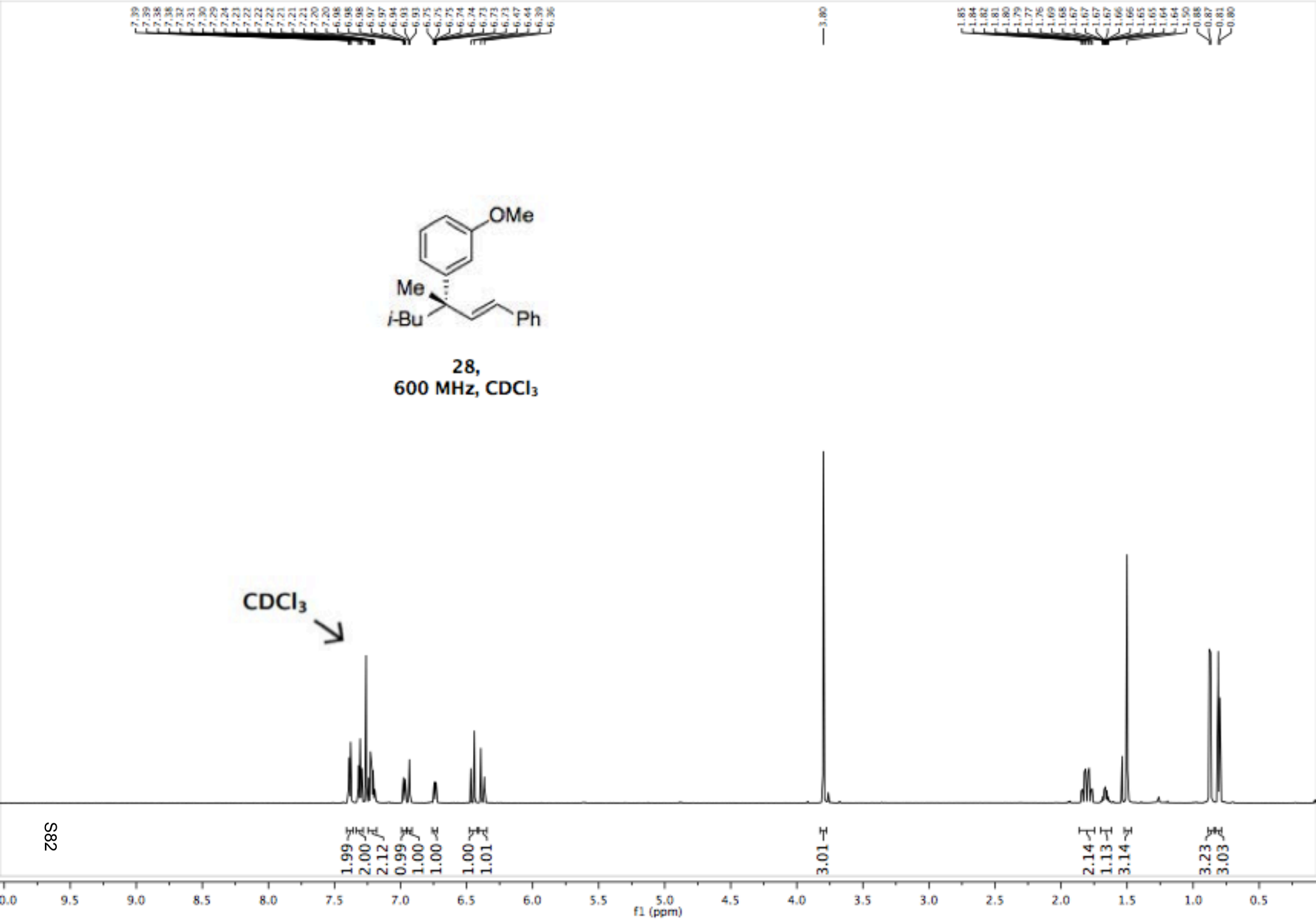

159.45
154.38
150.01
145.36
138.30
133.00
129.00
127.74
126.97
122.80
119.31
118.63
113.44
111.27
110.27
106.63
55.18
43.98
41.48
26.86
25.68
23.46
14.09
CDCl3
OMe
Me
Bu
O
25
151 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


OMe
Et
Bu
Ph
CDCl3
26
400 MHz, CDCl3
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)

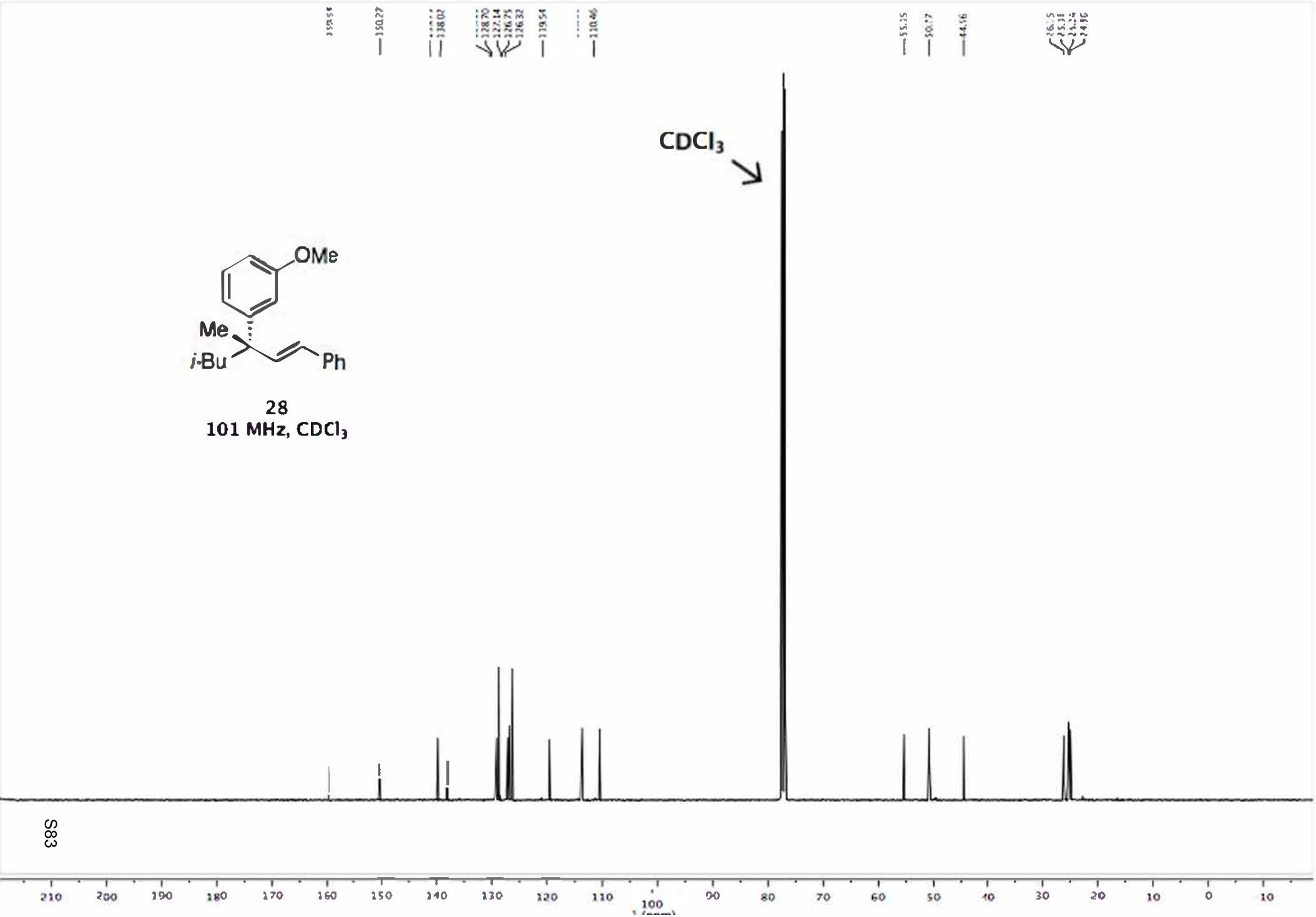

159.54
148.53
138.36
138.17
128.95
128.69
127.92
127.11
126.31
120.30
114.40
110.39
55.34
47.67
37.33
30.47
26.48
23.65
14.28
8.83
OMe
Et
Bu
Ph
CDCl3
26
151 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

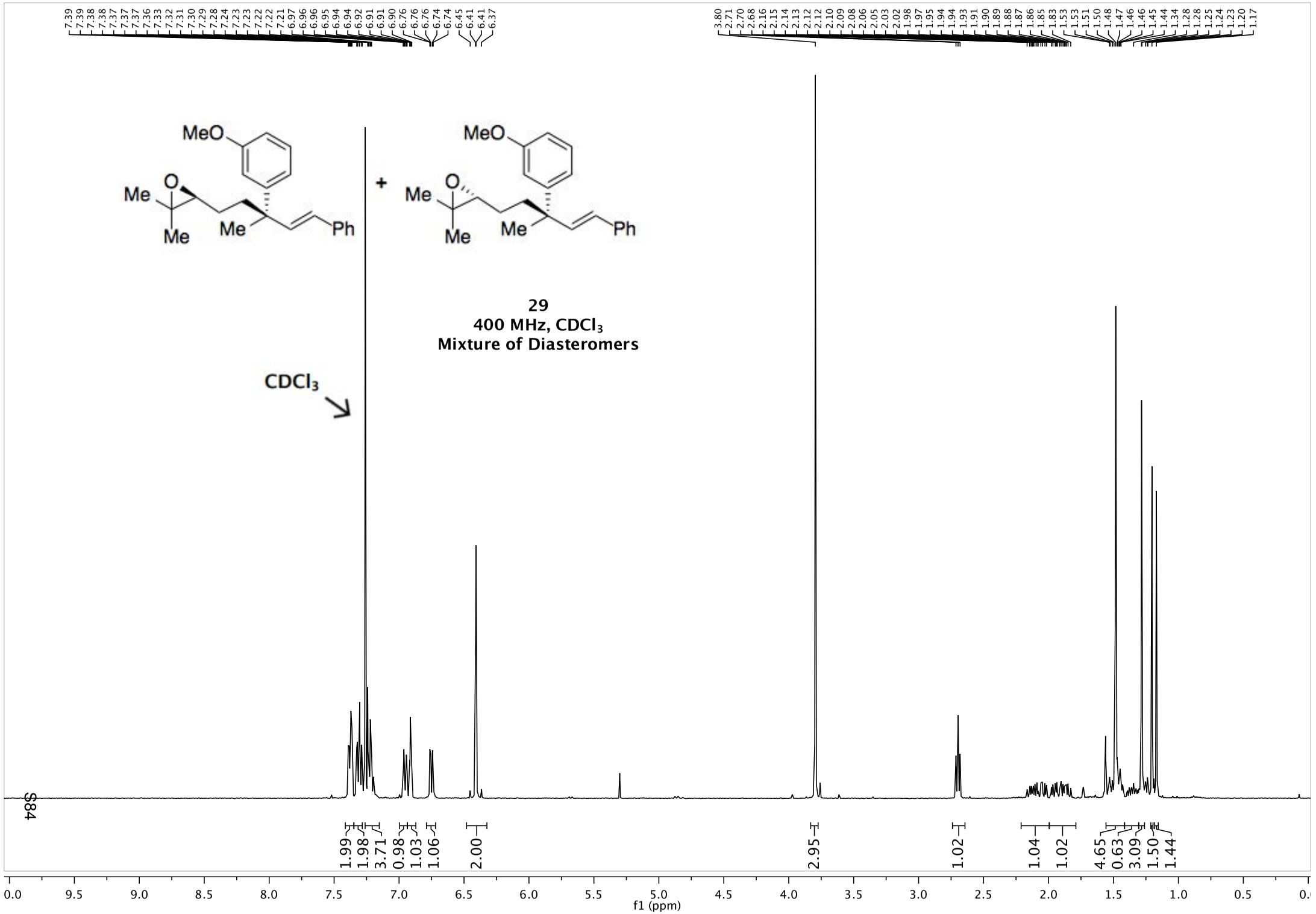

Ph
Me
Et
OMe
27
400 MHz, CDCl3
CDCl3
1.87
1.99
2.16
0.99
0.99
1.00
0.98
1.04
3.10
2.09
3.10
3.10
f1 (ppm)

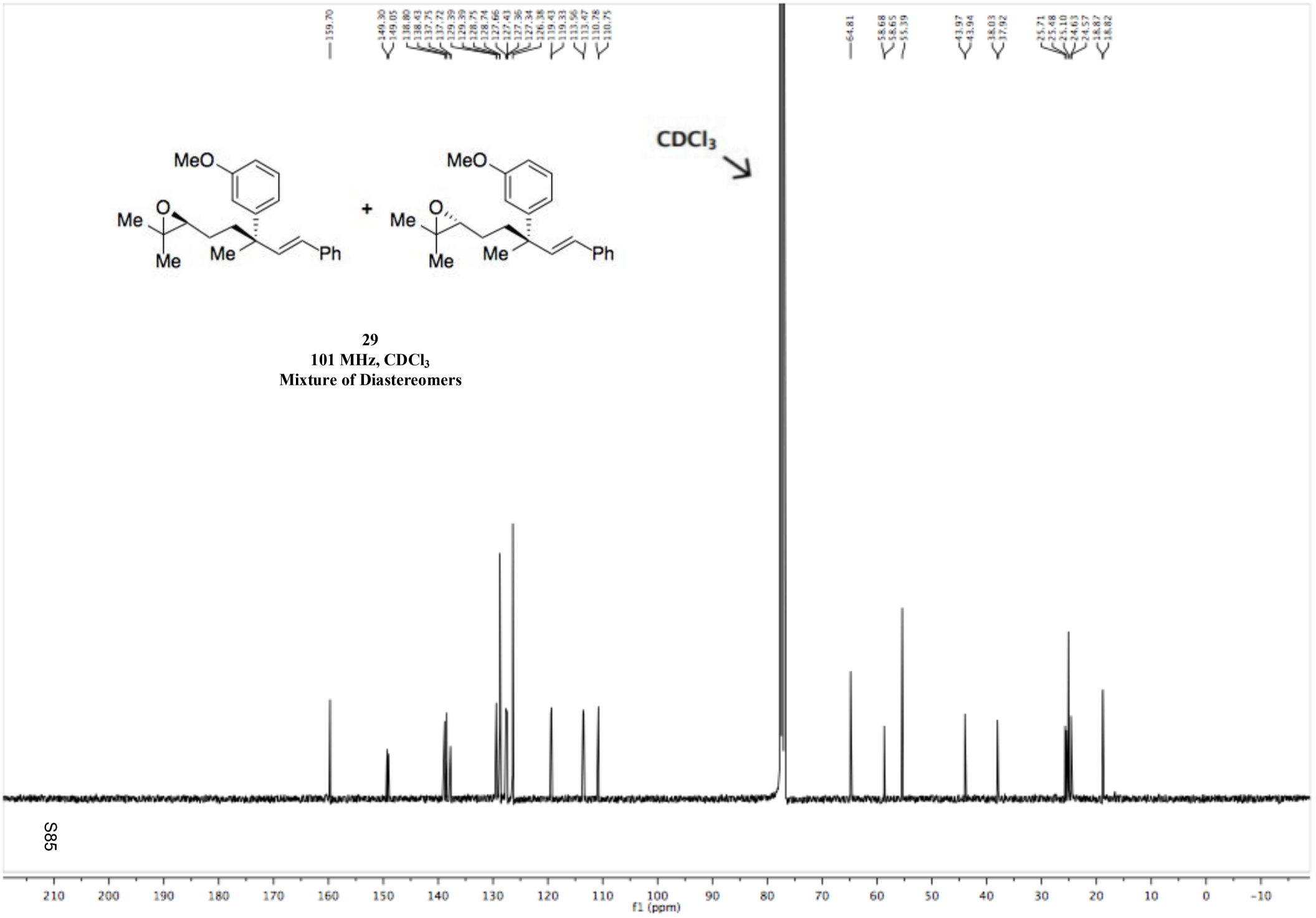

159.85
147.62
139.54
139.35
129.49
128.13
127.04
126.84
125.83
118.86
112.70
111.44
55.24
44.25
33.87
25.00
9.07
CDCl3
Me
Ph
Et
OMe
27
151 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



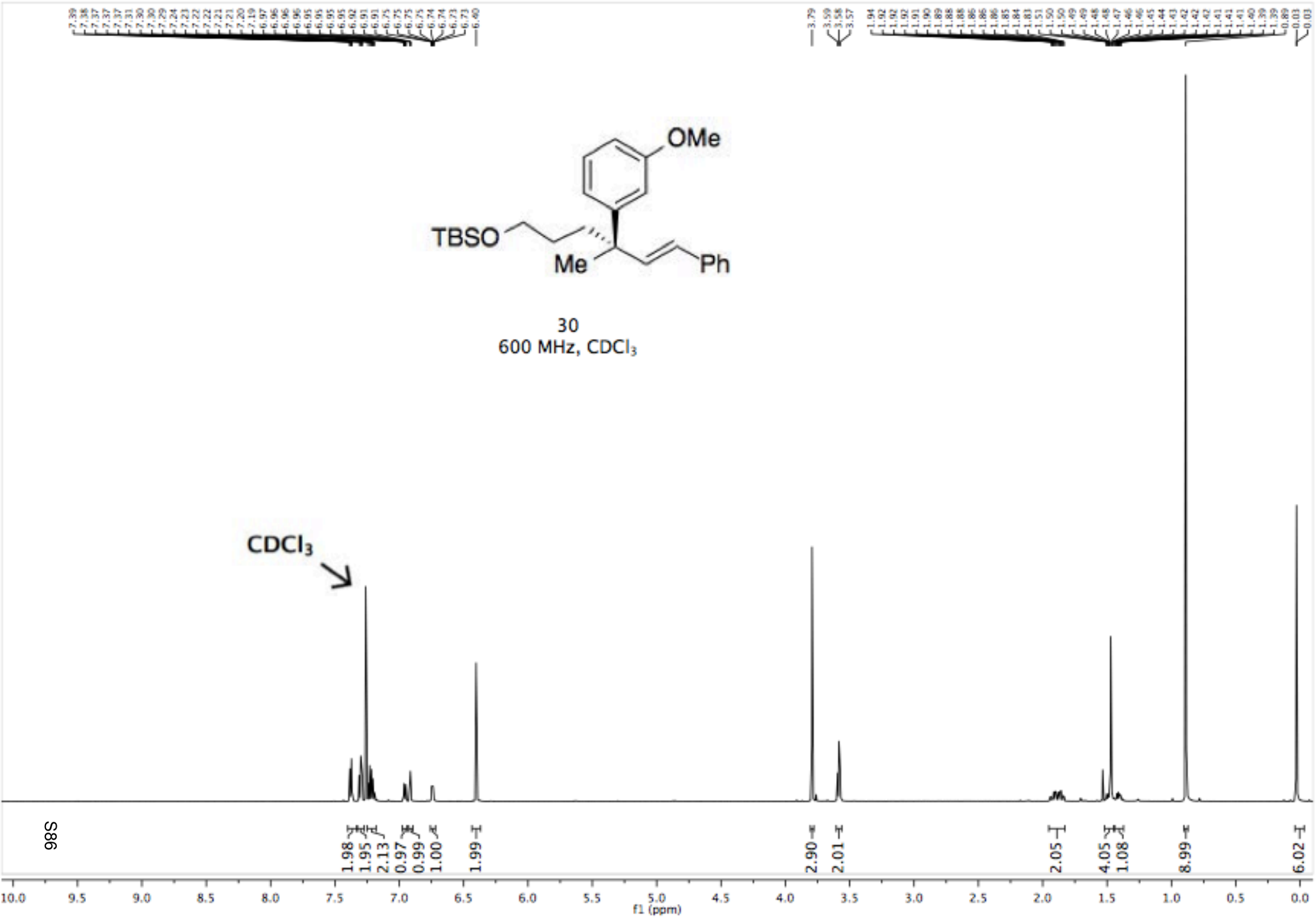
28,
600 MHz, $CDCl_3$

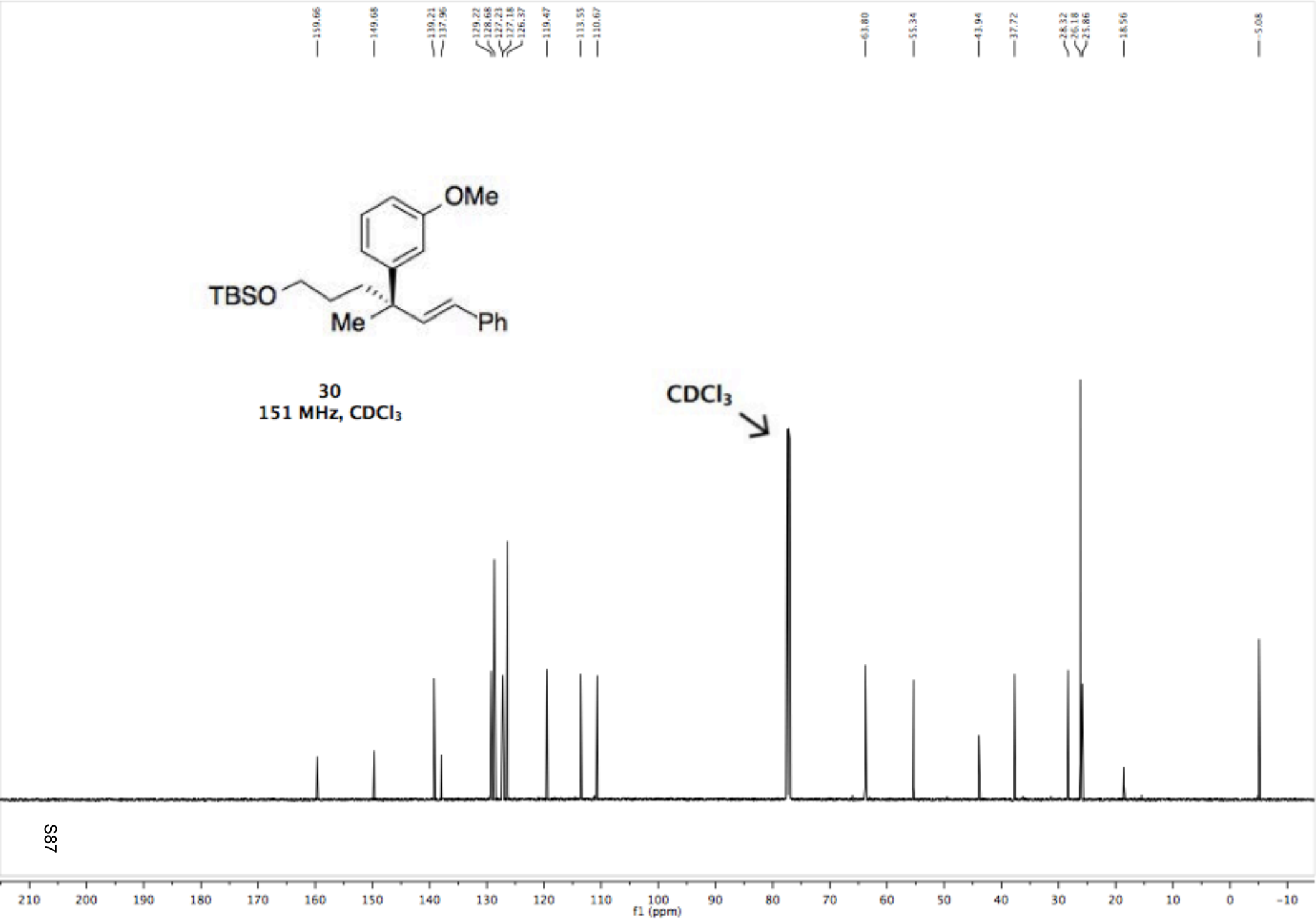

150.27
138.02
128.70
127.14
126.75
126.32
119.54
110.46
55.15
50.17
44.56
26.5
25.31
24.26
24.16
CDCl3
OMe
Me
i-Bu
Ph
28
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
10

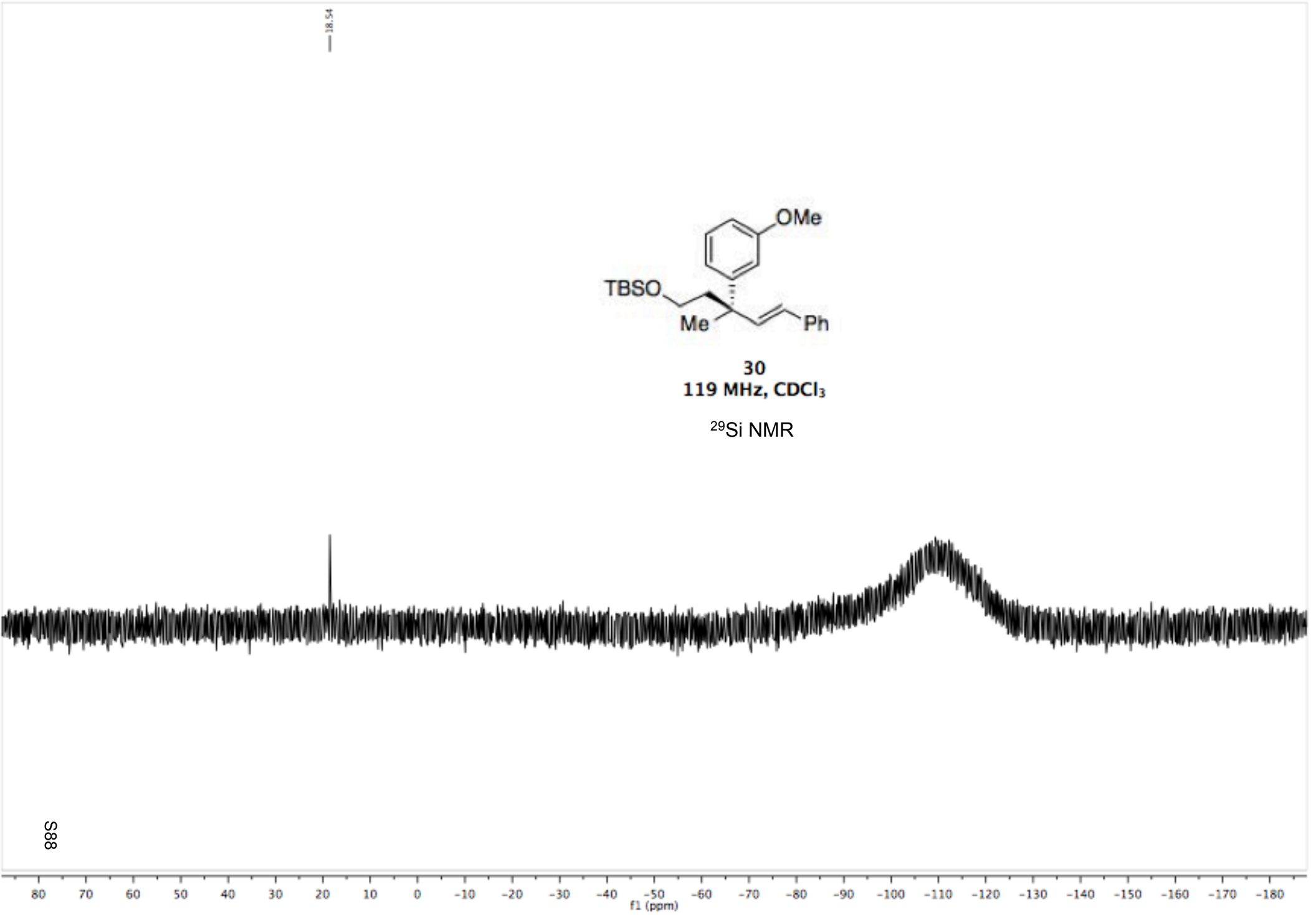

MeO
Me
O
Me
Me
Ph
+
MeO
Me
O
Me
Me
Ph
29
400 MHz, CDCl3
Mixture of Diasteromers
CDCl3
S84
1.99
1.98
3.71
0.98
1.03
1.06
2.00
2.95
1.02
1.04
1.02
4.65
0.63
3.09
1.50
1.44
f1 (ppm)

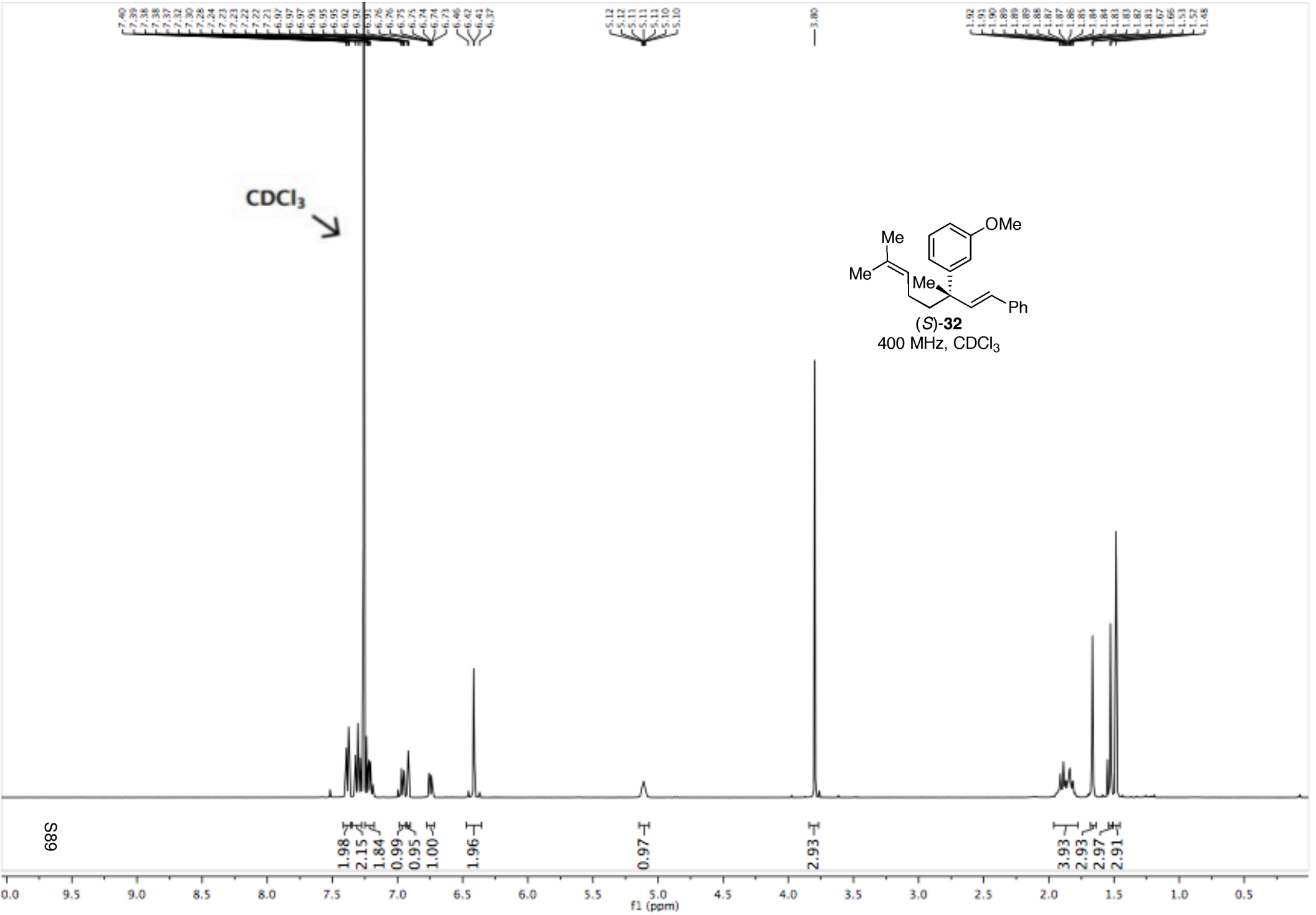


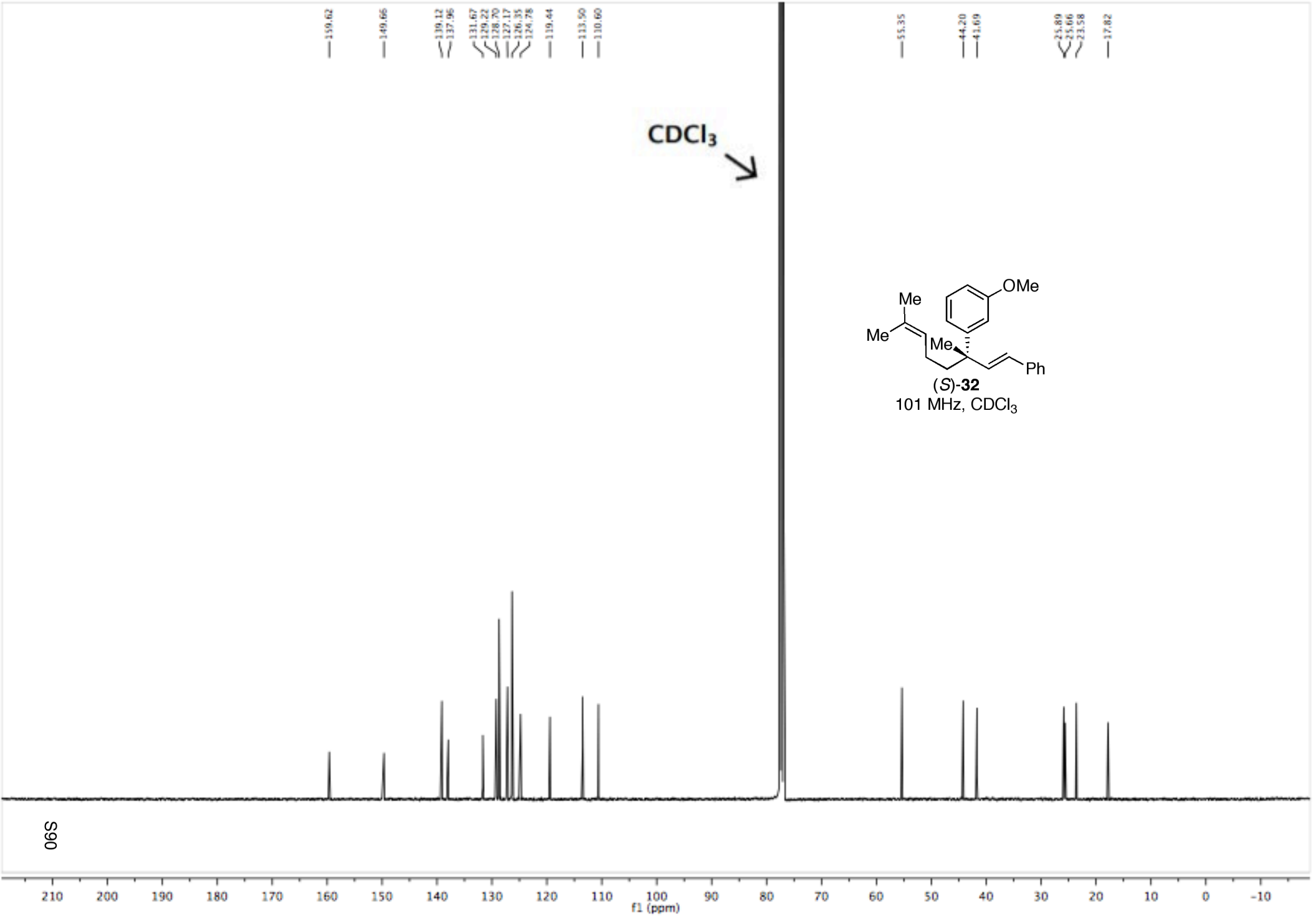
29
101 MHz, $CDCl_3$
Mixture of Diastereomers

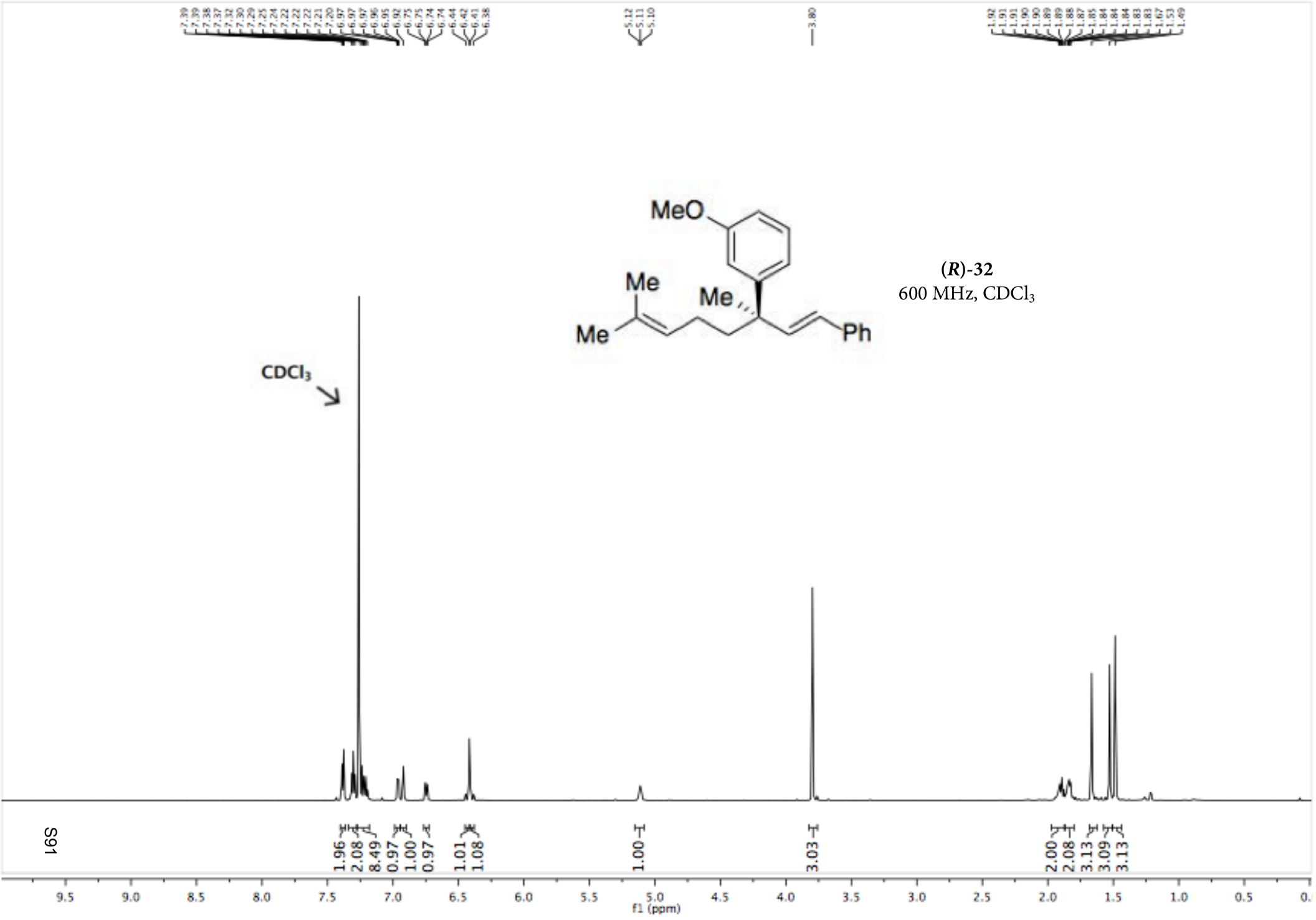

OMe
TBSO
Me
Ph
30
600 MHz, CDCl3
CDCl3
1.98
1.95
2.13
0.97
0.99
1.00
1.99
2.90
2.01
2.05
4.05
1.08
8.99
6.02
f1 (ppm)


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
30
151 MHz, CDCl3
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)

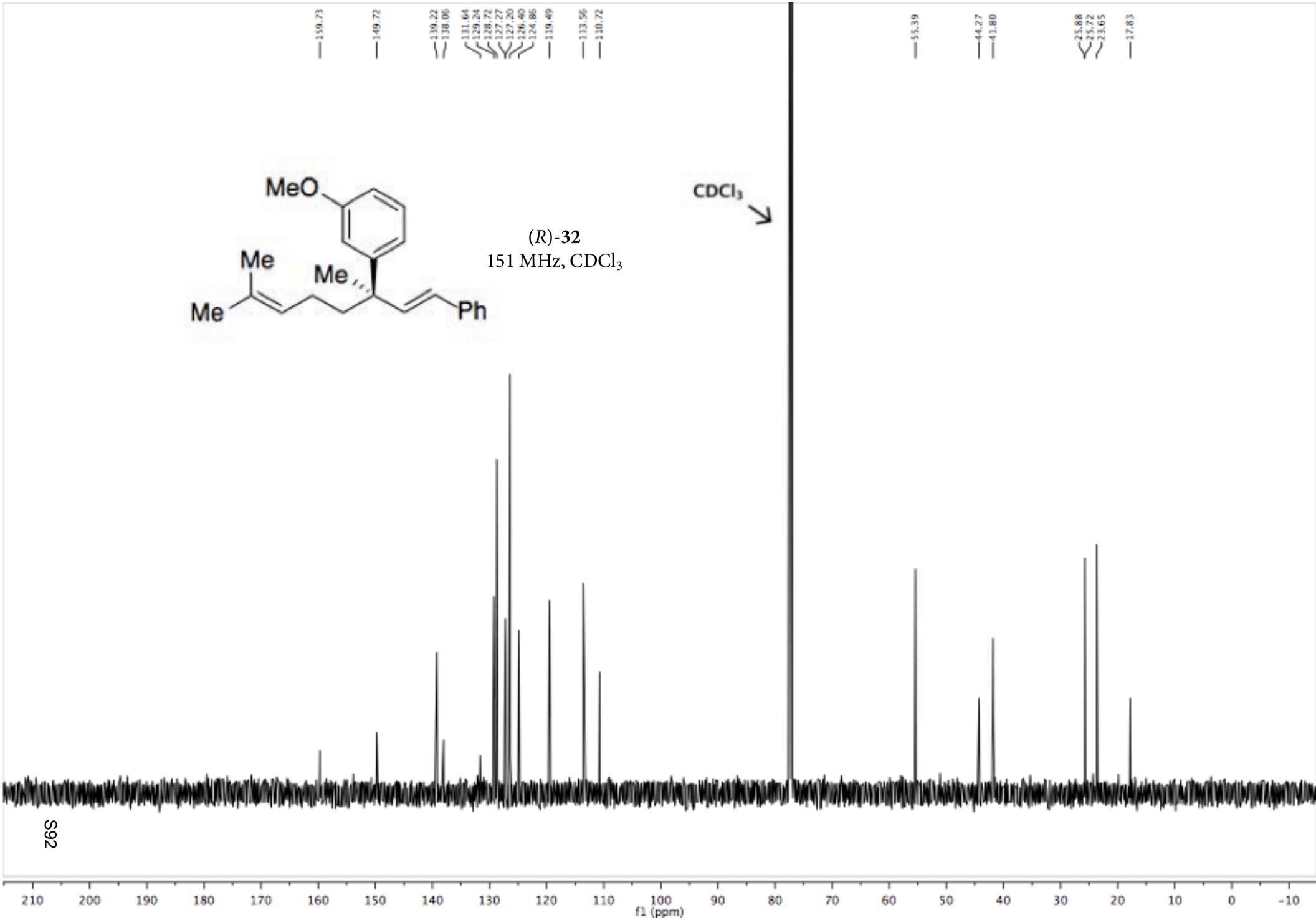

18.54
OMe
TBSO
Me
Ph
30
119 MHz, CDCl3
29Si NMR
S88
80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180
f1 (ppm)

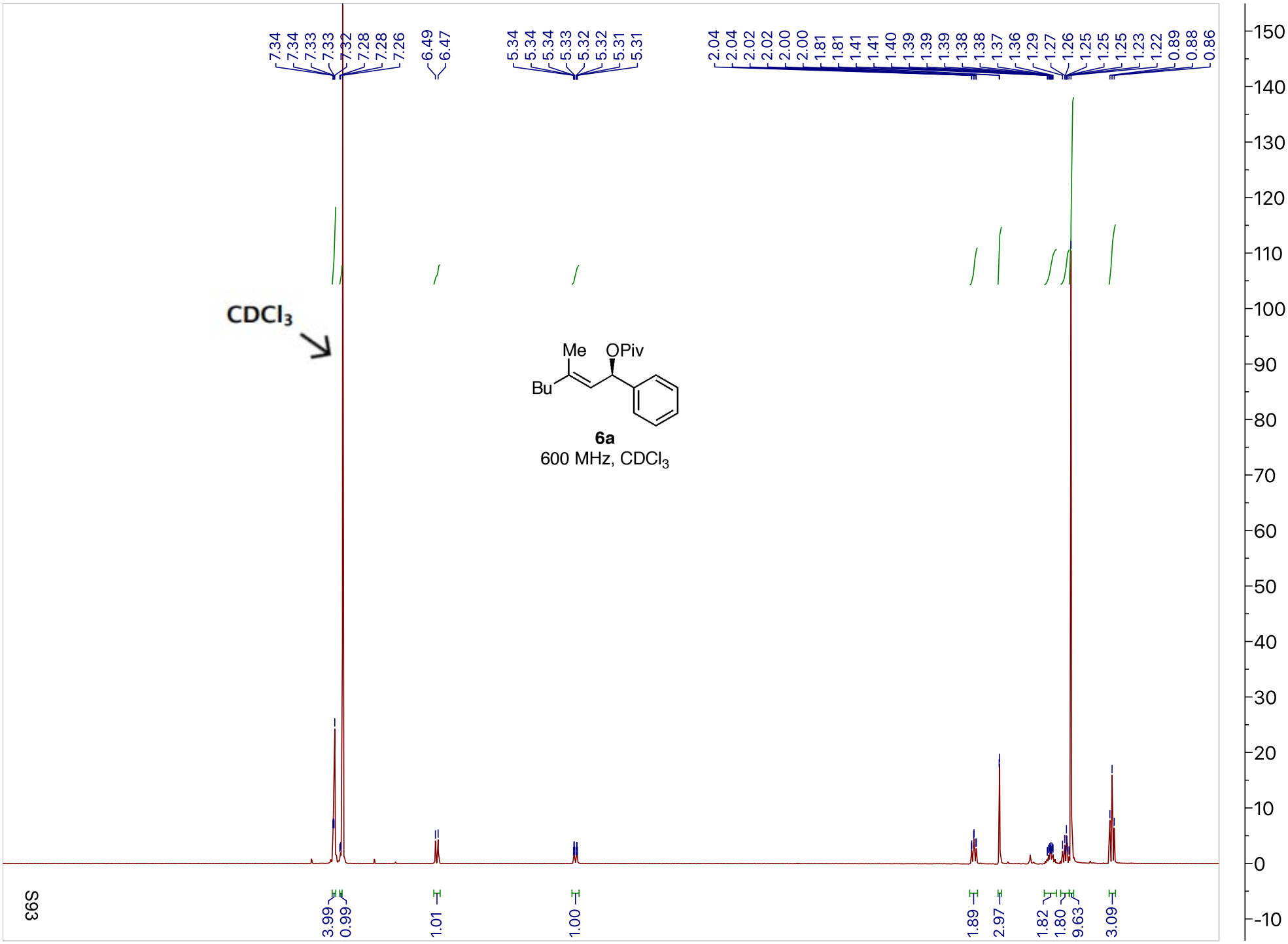

CDCl3
OMe
Me
Me
Me
Ph
(S)-32
400 MHz, CDCl3
1.98
2.15
1.84
0.99
0.95
1.00
1.96
0.97
2.93
3.93
2.93
2.97
2.91
f1 (ppm)

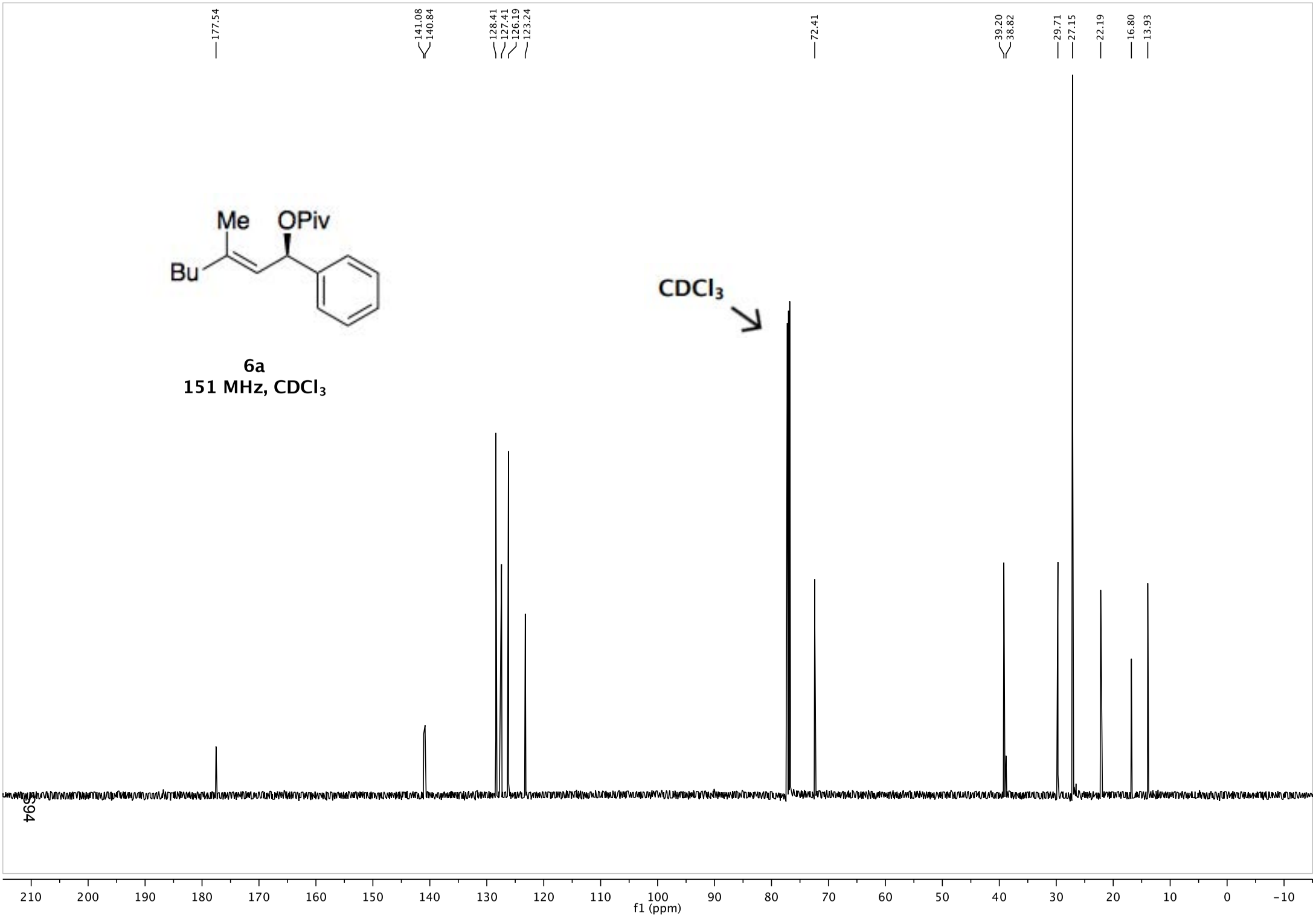

159.62
149.66
139.12
137.96
131.67
129.22
128.70
127.17
126.35
124.78
119.44
113.50
110.60
55.35
44.20
41.69
25.89
25.66
23.58
17.82
CDCl3
OMe
Me
Me
Me
Ph
(S)-32
101 MHz, CDCl3
S90
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

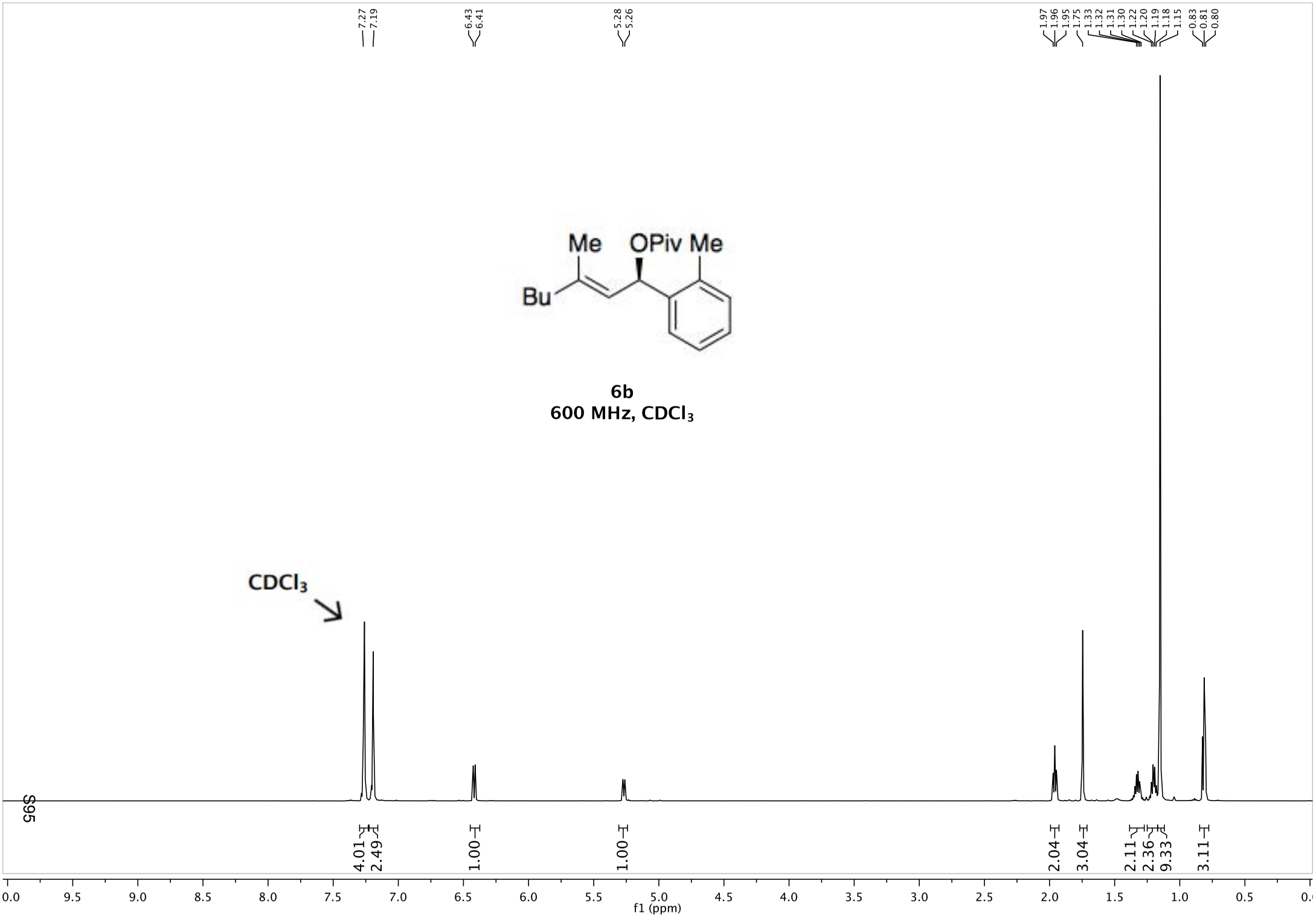


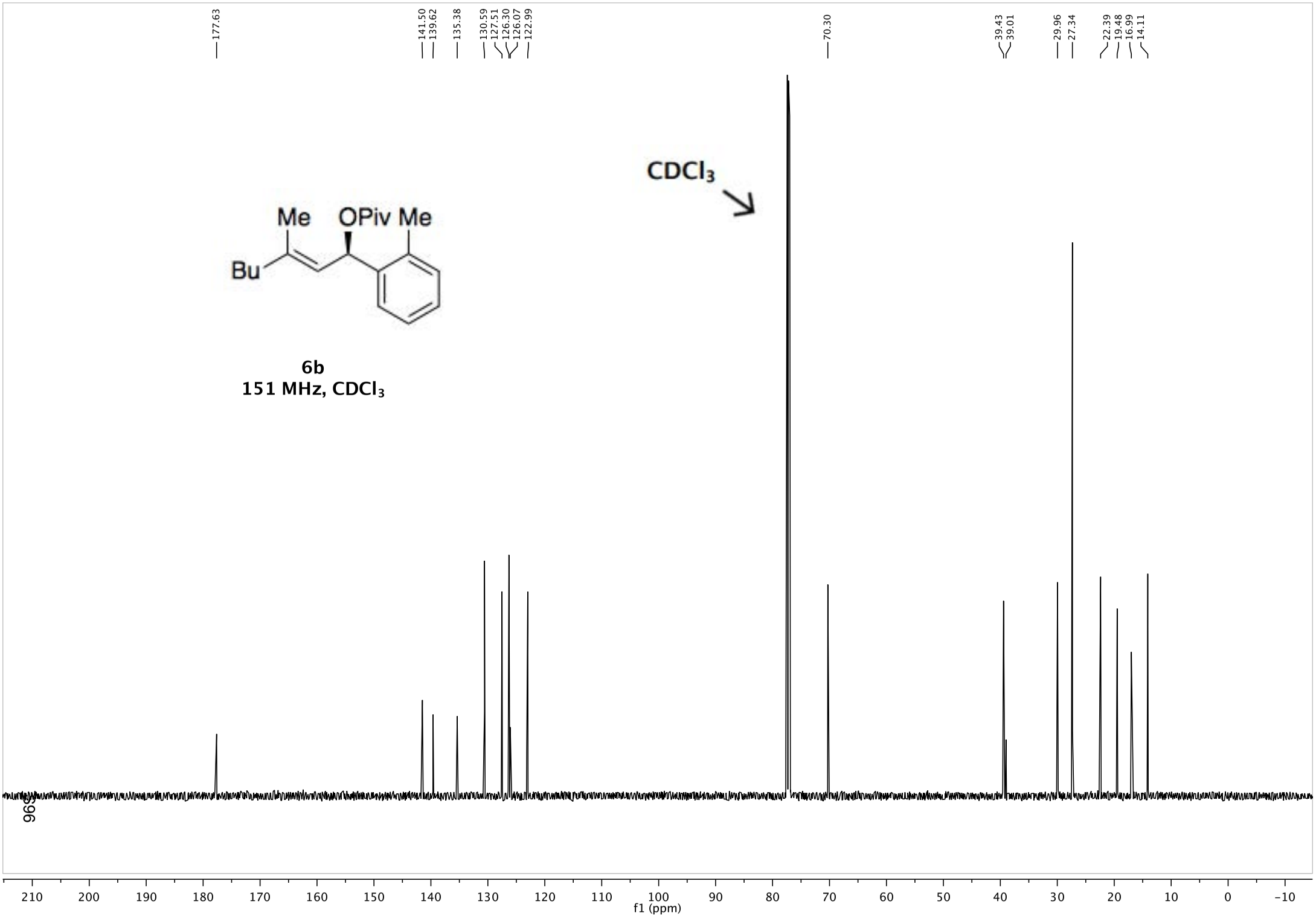
(*R*)-**32**
600 MHz, $CDCl_3$

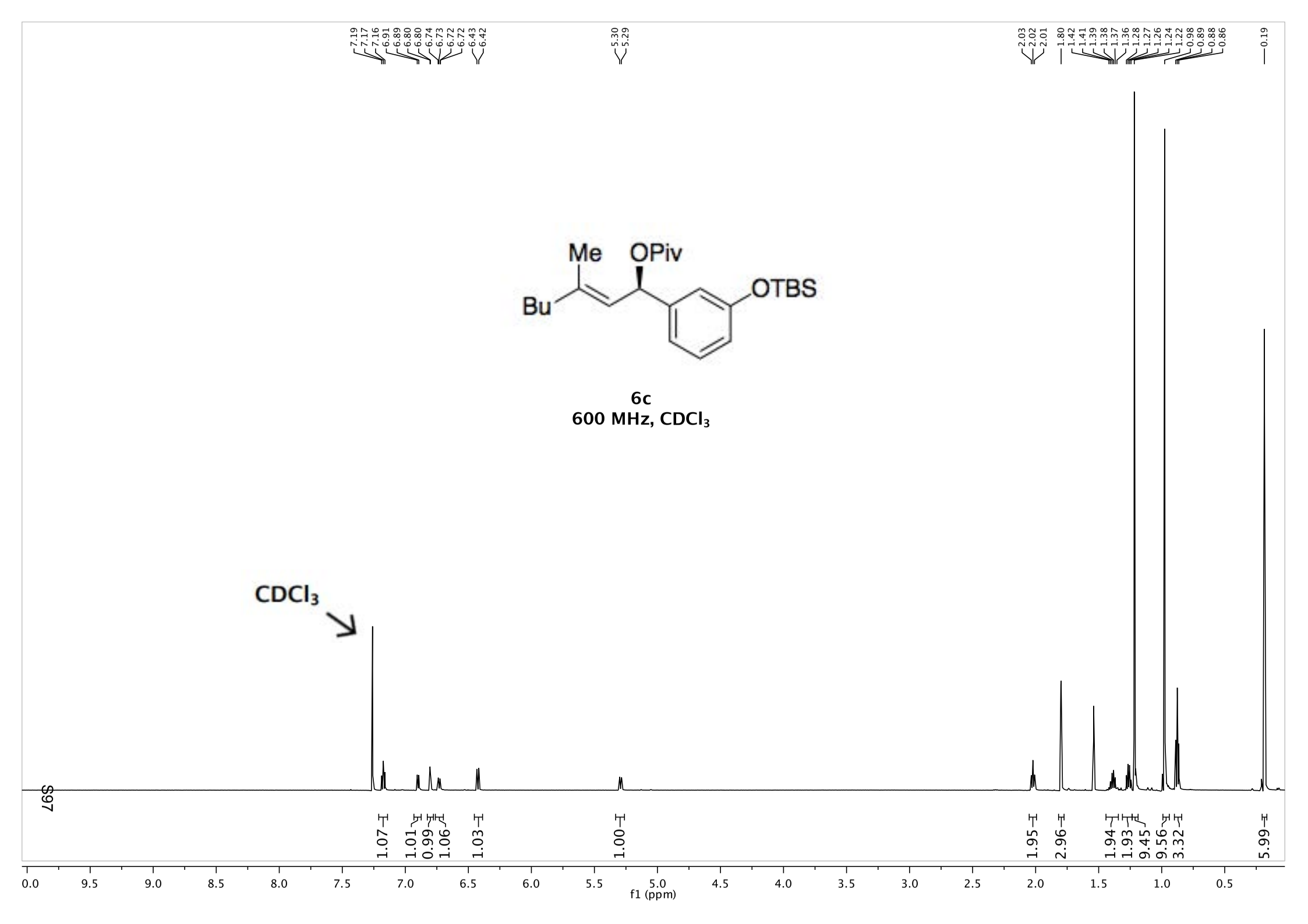

159.73
149.72
139.22
138.06
131.64
129.24
128.72
127.27
127.20
126.40
124.86
119.49
113.56
110.72
55.39
44.27
41.80
25.88
25.72
23.65
17.83
MeO
Me
Me
Me
Ph
CDCl3
(R)-32
151 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.34
7.34
7.33
7.33
7.32
7.28
7.28
7.26
6.49
6.47
5.34
5.34
5.34
5.33
5.32
5.32
5.31
5.31
2.04
2.04
2.02
2.02
2.00
2.00
1.81
1.81
1.41
1.41
1.40
1.39
1.39
1.39
1.38
1.38
1.37
1.36
1.29
1.27
1.26
1.25
1.25
1.25
1.23
1.22
0.89
0.88
0.86
CDCl3
Me
OPiv
Bu
6a
600 MHz, CDCl3
S93
3.99
0.99
1.01
1.00
1.89
2.97
1.82
1.80
9.63
3.09
f1 (ppm)


177.54
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
6a
151 MHz, CDCl3
694
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)


7.27
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
6b
600 MHz, CDCl3
CDCl3
S95
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)


177.63
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
6b
151 MHz, CDCl3
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
6c
600 MHz, CDCl3
CDCl3
S97
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
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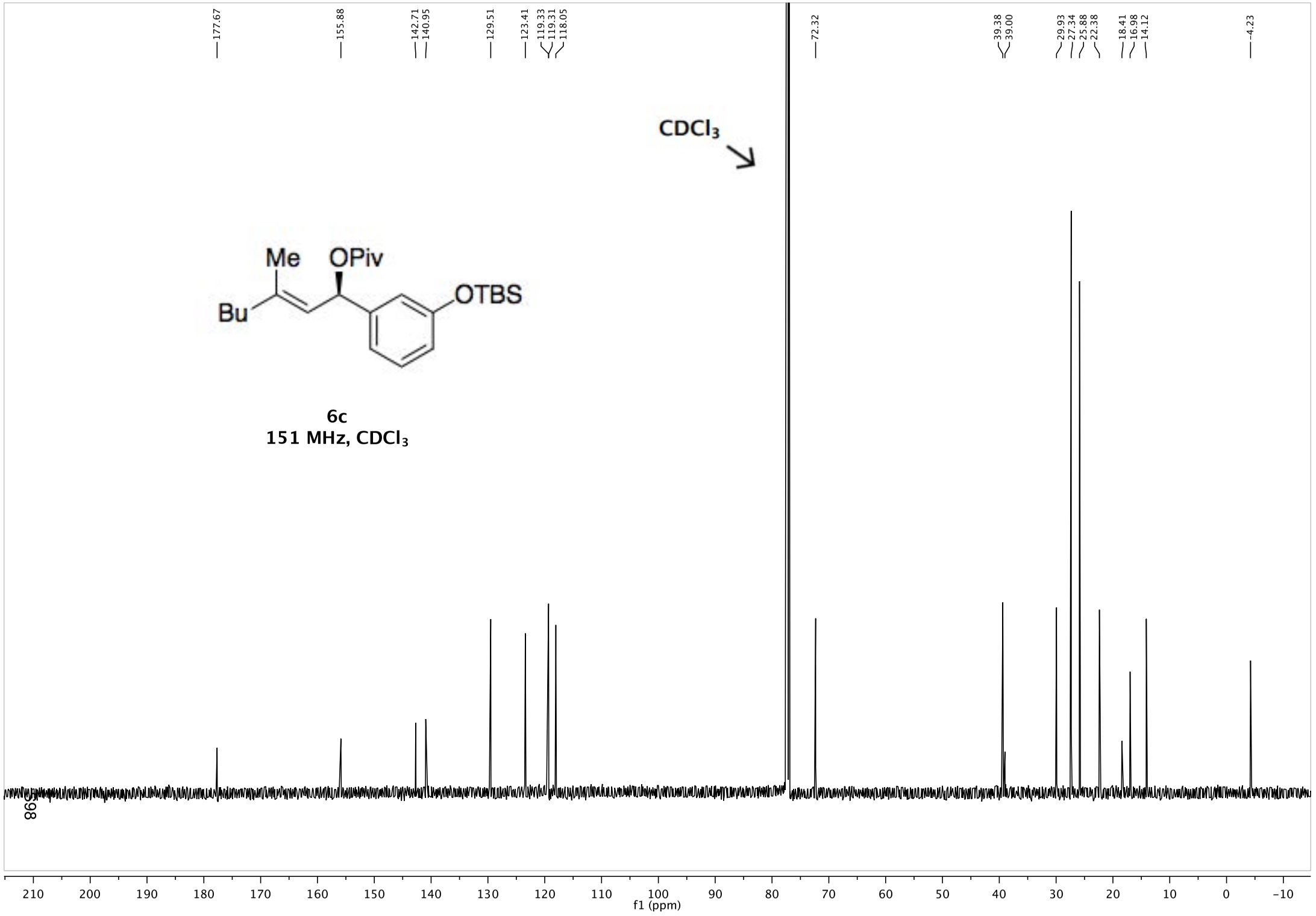
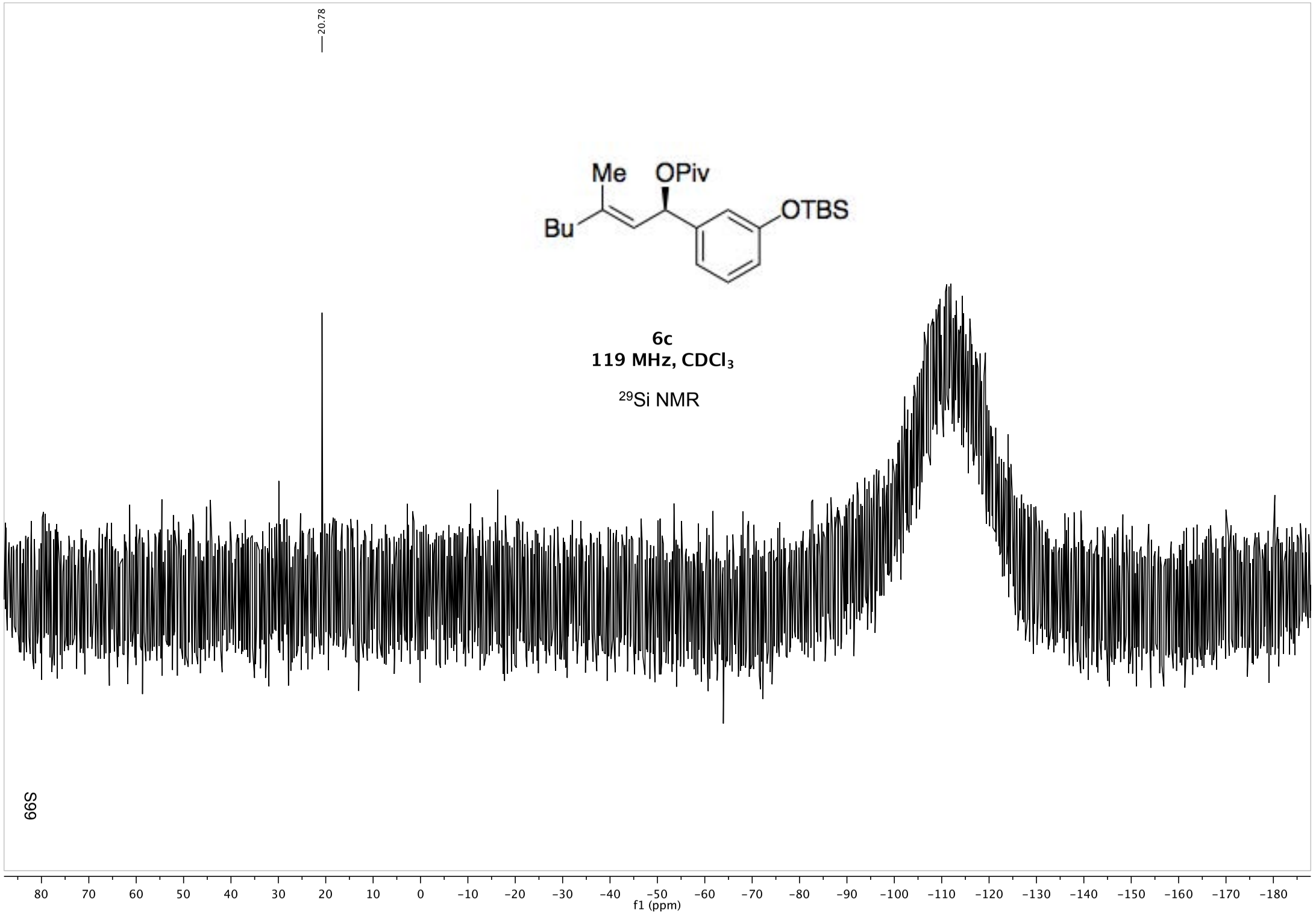
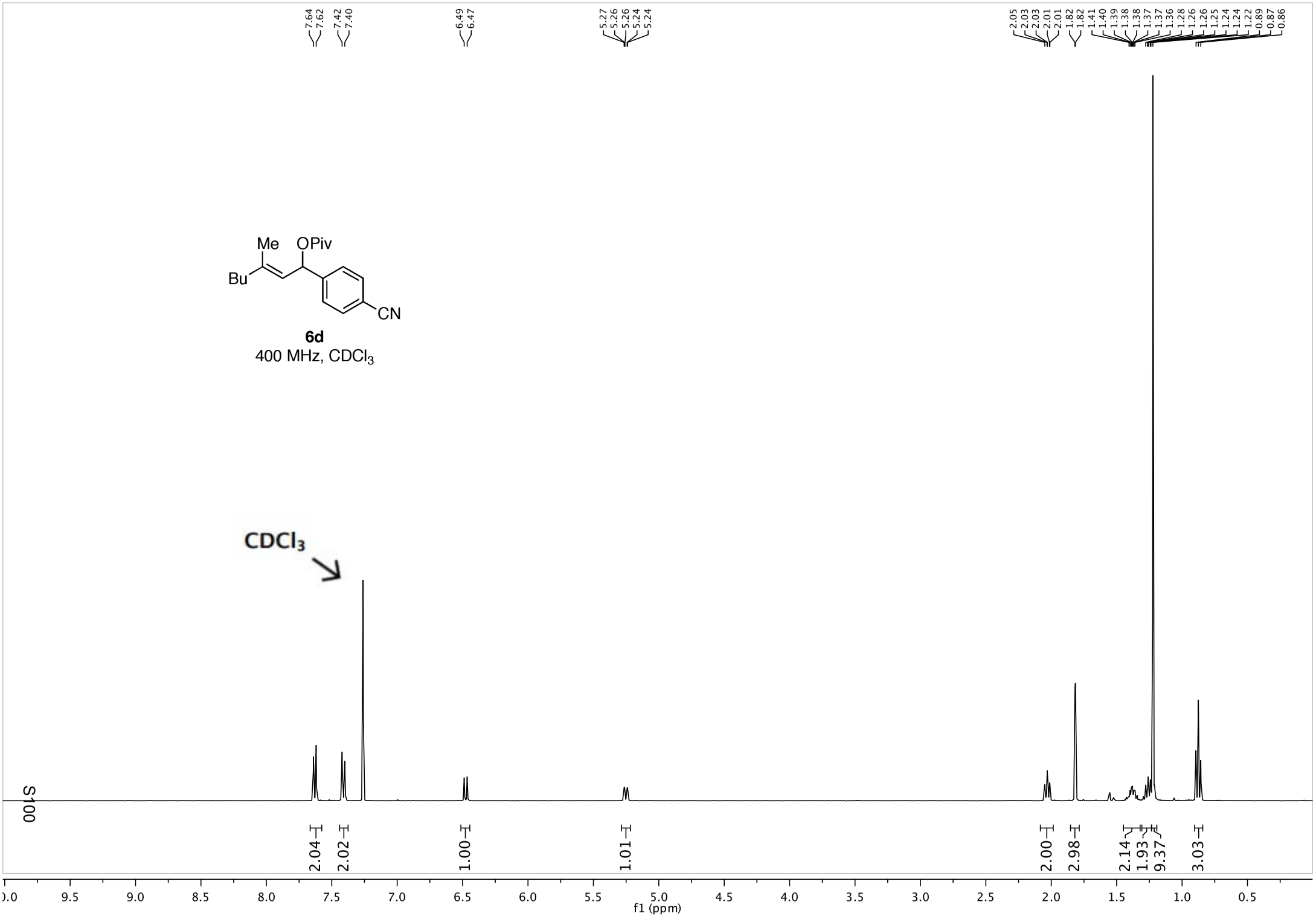
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


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
6c
151 MHz, CDCl3
f1 (ppm)


20.78
Me
OPiv
Bu
OTBS
6c
119 MHz, CDCl3
29Si NMR
66S
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)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7.62
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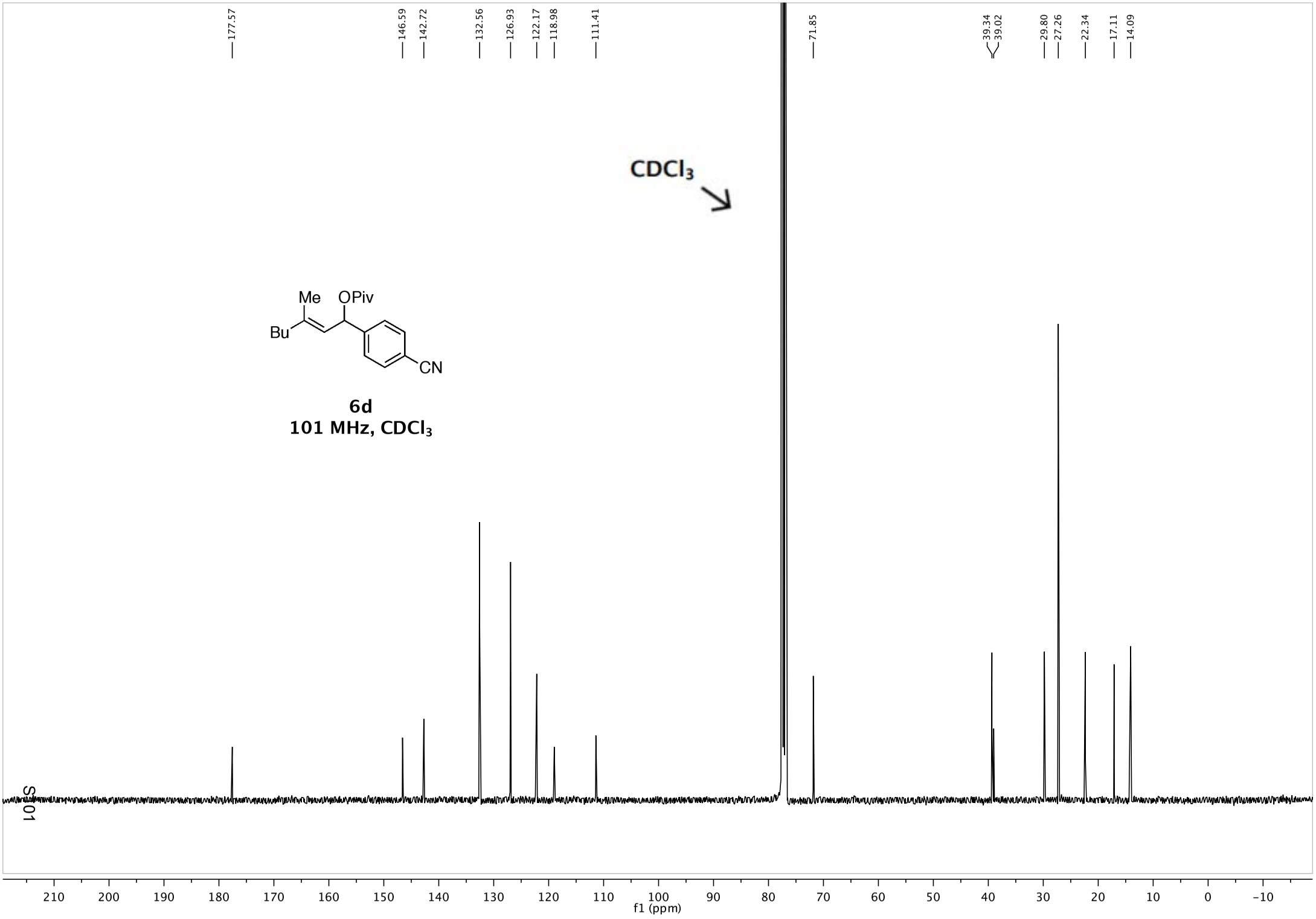
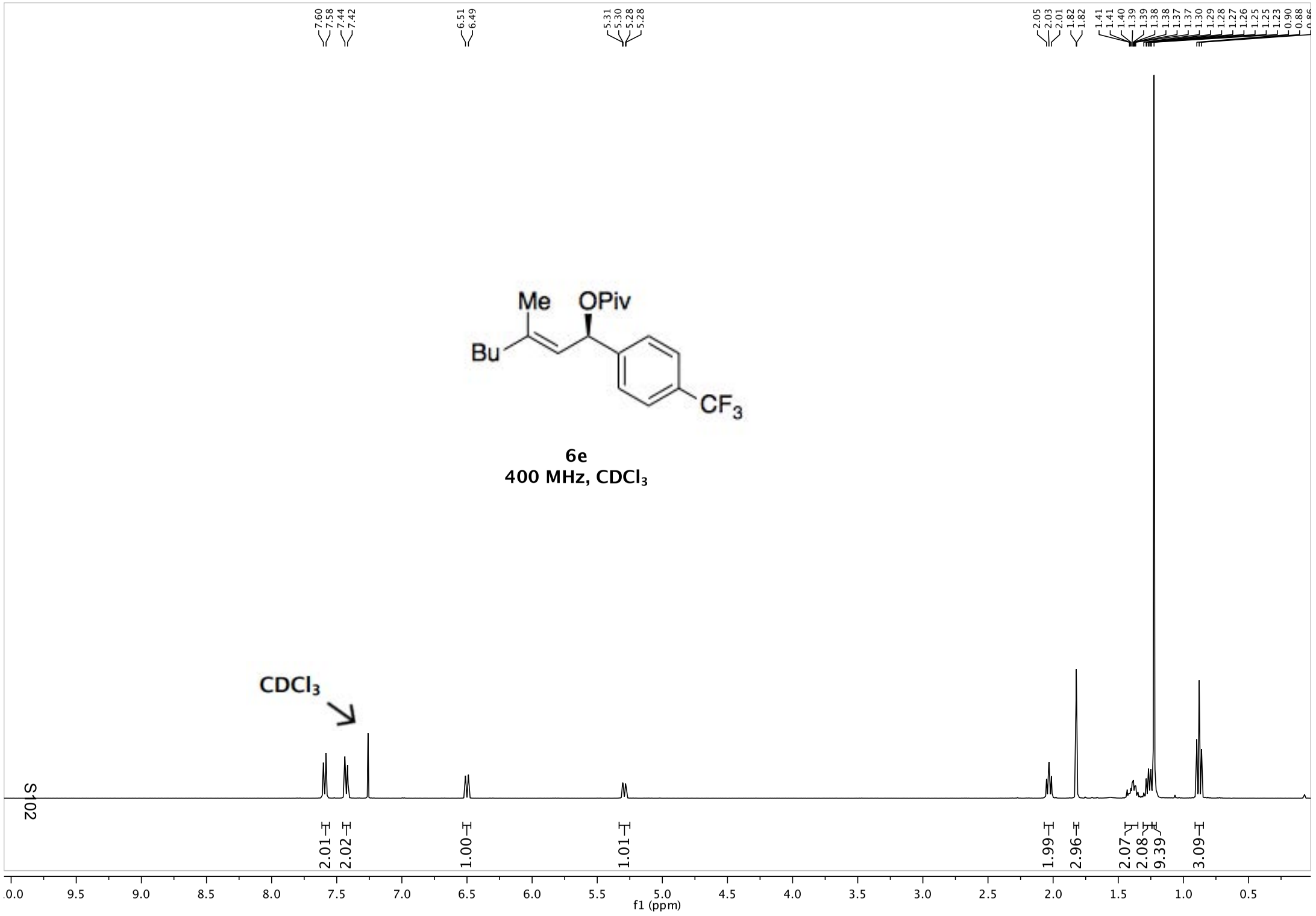
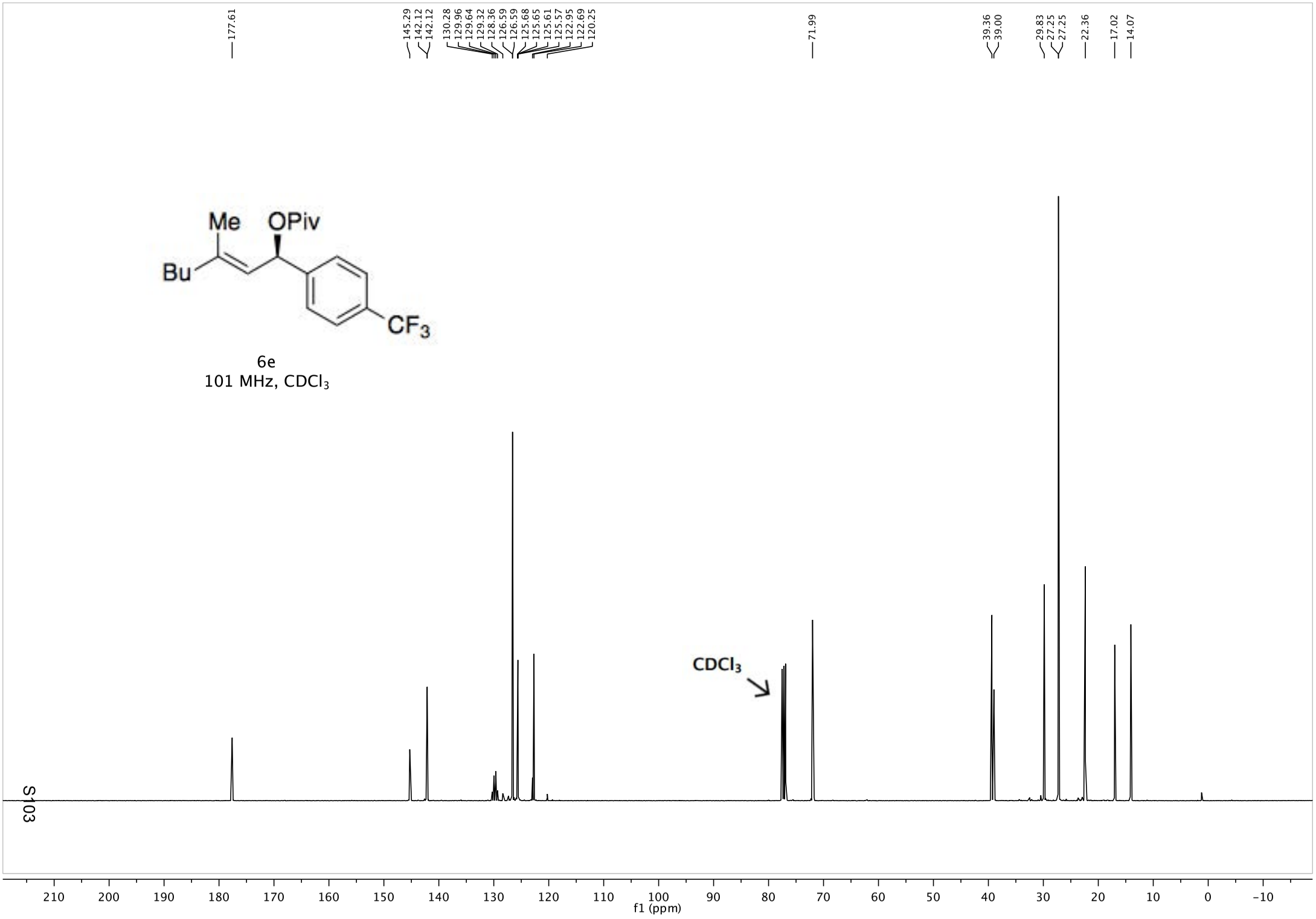
6.47
5.27
5.26
5.24
5.24
2.05
2.03
2.03
2.01
2.01
1.82
1.82
1.41
1.40
1.39
1.38
1.38
1.37
1.37
1.36
1.28
1.26
1.26
1.25
1.24
1.24
1.22
0.89
0.87
0.86
Me
OPiv
Bu
CN
6d
400 MHz, CDCl3
CDCl3
S100
2.04
2.02
1.00
1.01
2.00
2.98
2.14
1.93
9.37
3.03
f1 (ppm)


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
CN
6d
101 MHz, CDCl3
S101
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)


7.60
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
6e
400 MHz, CDCl3
CDCl3
S102
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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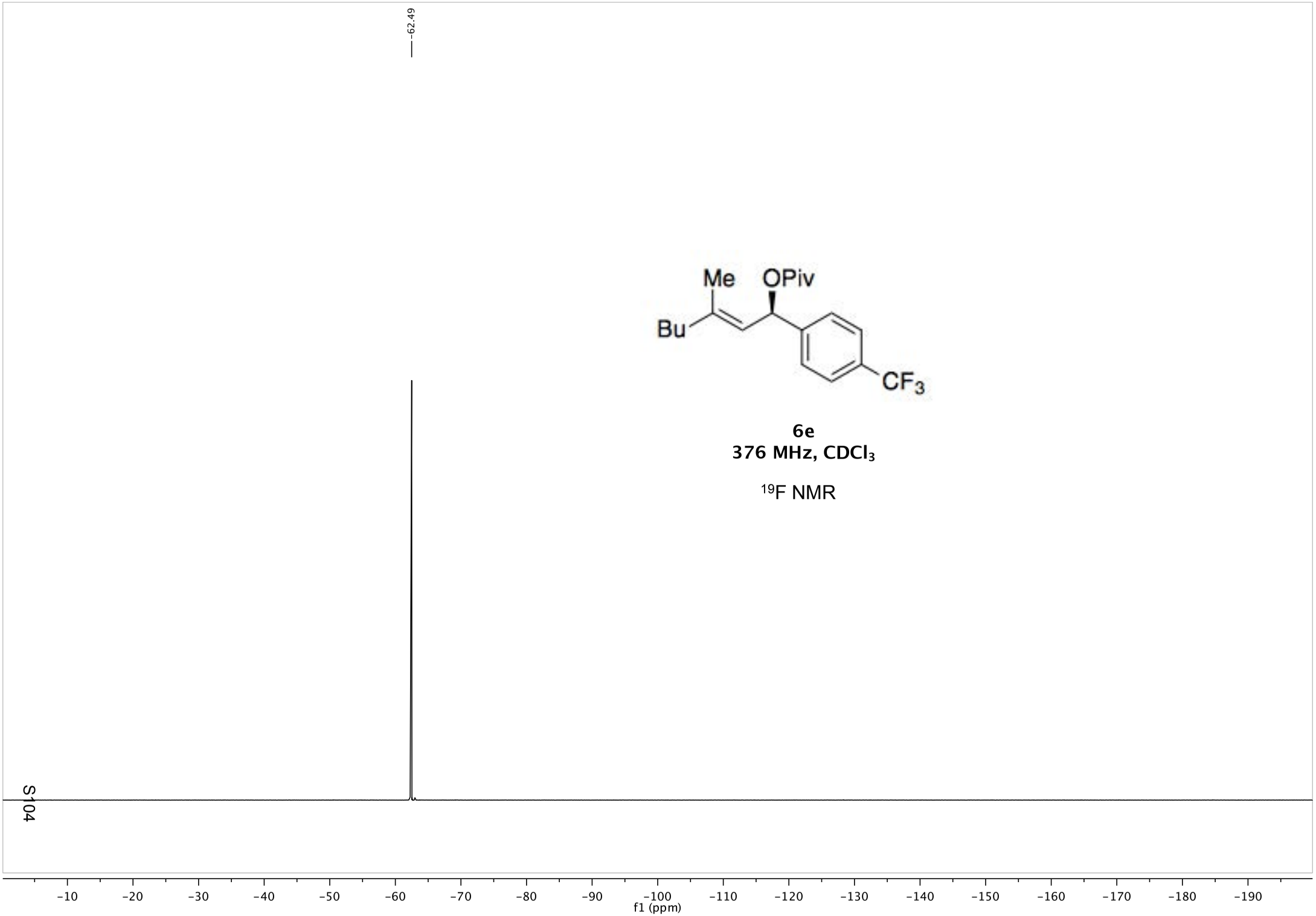
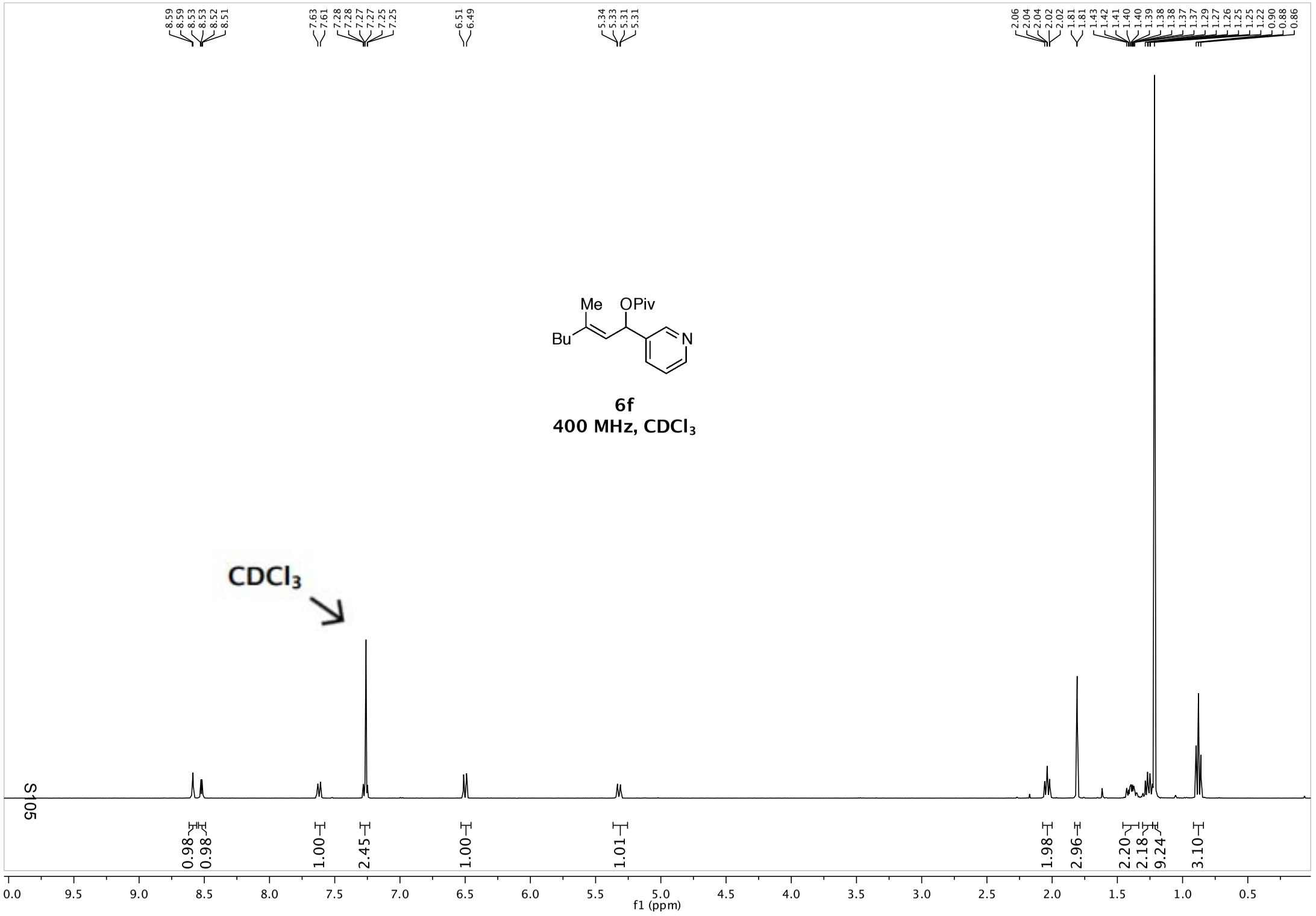
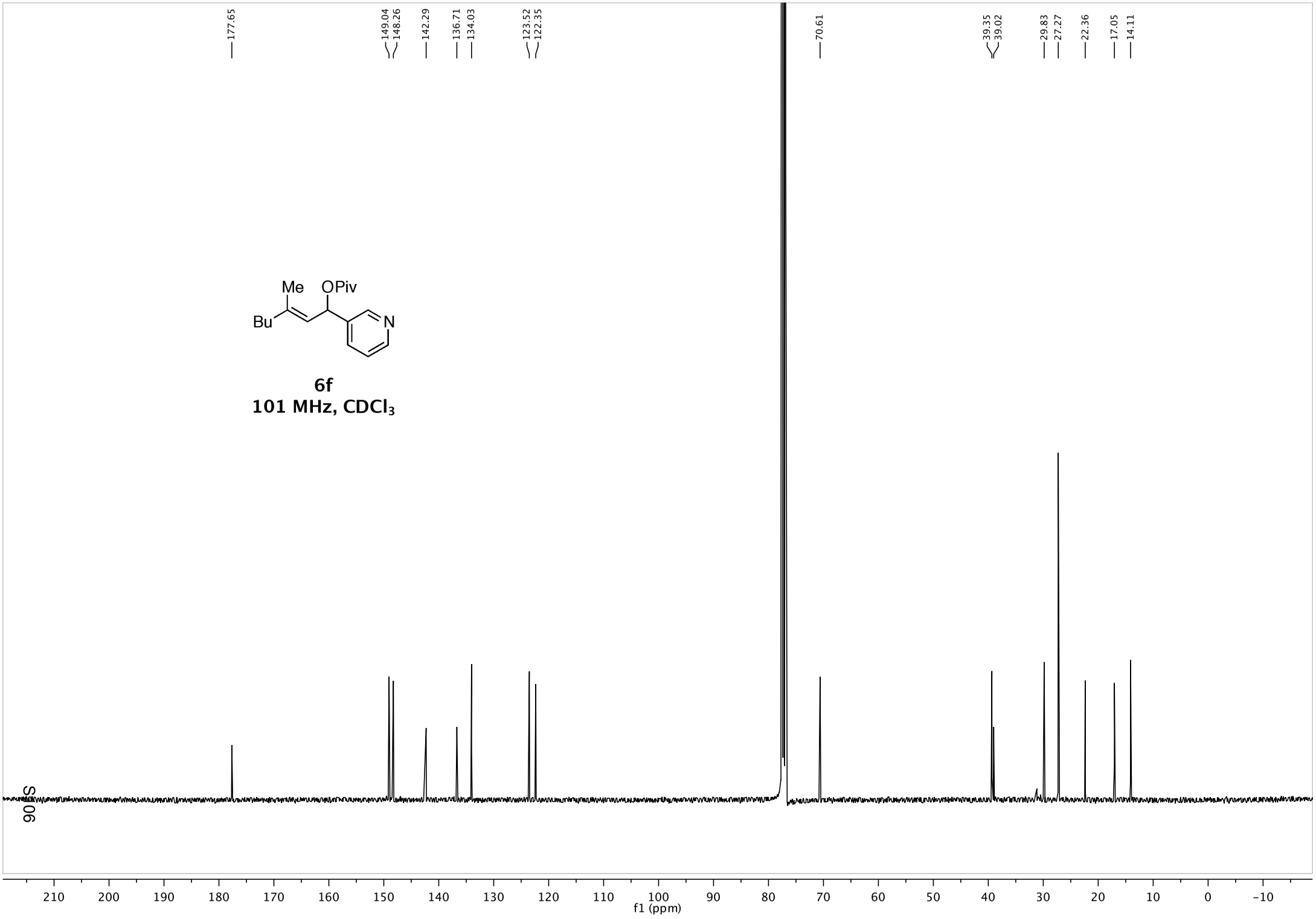
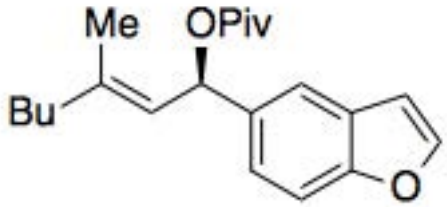
145.29
142.12
142.12
130.28
129.96
129.64
129.32
128.36
126.59
126.59
125.68
125.65
125.61
125.57
122.95
122.69
120.25
71.99
39.36
39.00
29.83
27.25
27.25
22.36
17.02
14.07
Me
OPiv
Bu
CF3
6e
101 MHz, CDCl3
CDCl3
S103
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

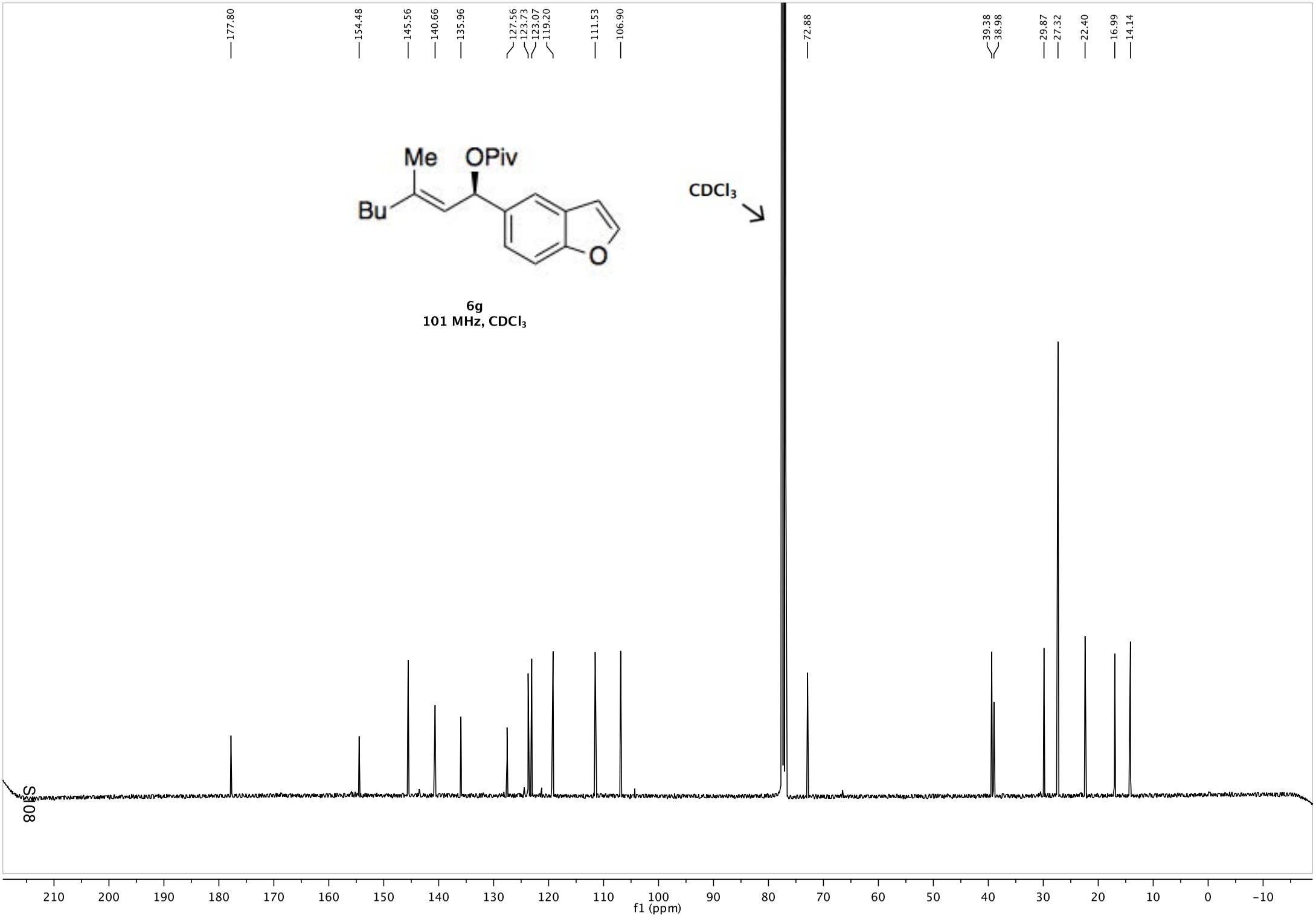

-62.49
Me
OPiv
Bu
CF3
6e
376 MHz, CDCl3
19F NMR
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

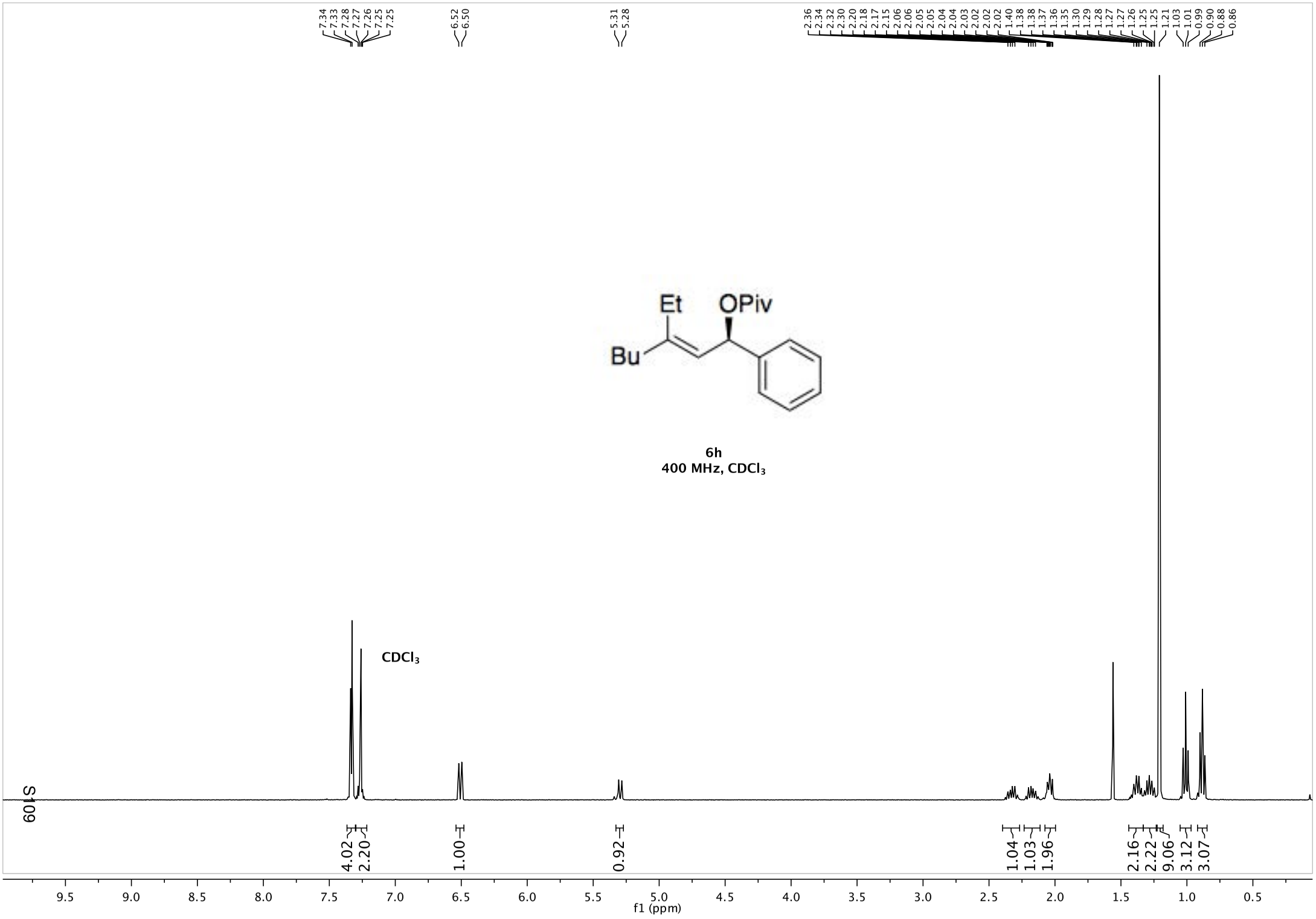

8.59
8.59
8.53
8.53
8.52
8.51
7.63
7.61
7.28
7.28
7.27
7.27
7.25
7.25
6.51
6.49
5.34
5.33
5.31
5.31
2.06
2.04
2.04
2.02
2.02
1.81
1.81
1.43
1.42
1.41
1.40
1.40
1.39
1.38
1.38
1.37
1.37
1.29
1.27
1.26
1.25
1.25
1.22
0.90
0.88
0.86
Me
OPiv
Bu
N
6f
400 MHz, CDCl3
CDCl3
S105
0.98
0.98
1.00
2.45
1.00
1.01
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)


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
6f
101 MHz, CDCl3
90
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)



6g
400 MHz, $CDCl_3$


177.80
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
6g
101 MHz, CDCl3
S108
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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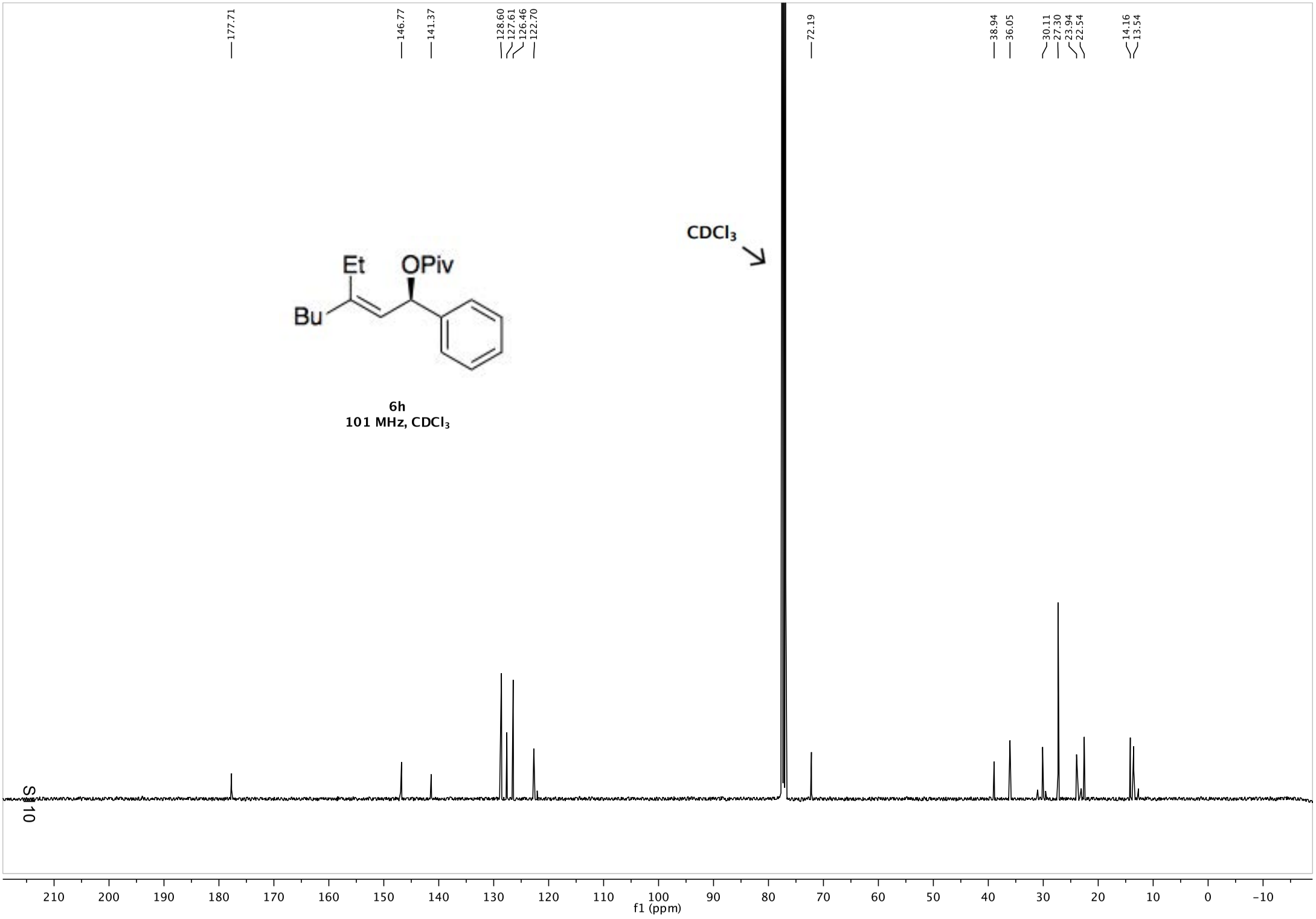
7.33
7.28
7.27
7.26
7.25
7.25
6.52
6.50
5.31
5.28
2.36
2.34
2.32
2.30
2.20
2.18
2.17
2.15
2.06
2.06
2.05
2.05
2.04
2.04
2.03
2.02
2.02
2.02
1.40
1.38
1.38
1.37
1.36
1.35
1.30
1.29
1.28
1.27
1.27
1.26
1.25
1.25
1.21
1.03
1.01
0.99
0.90
0.88
0.86
Et
OPiv
Bu
6h
400 MHz, CDCl3
CDCl3
S109
4.02
2.20
1.00
0.92
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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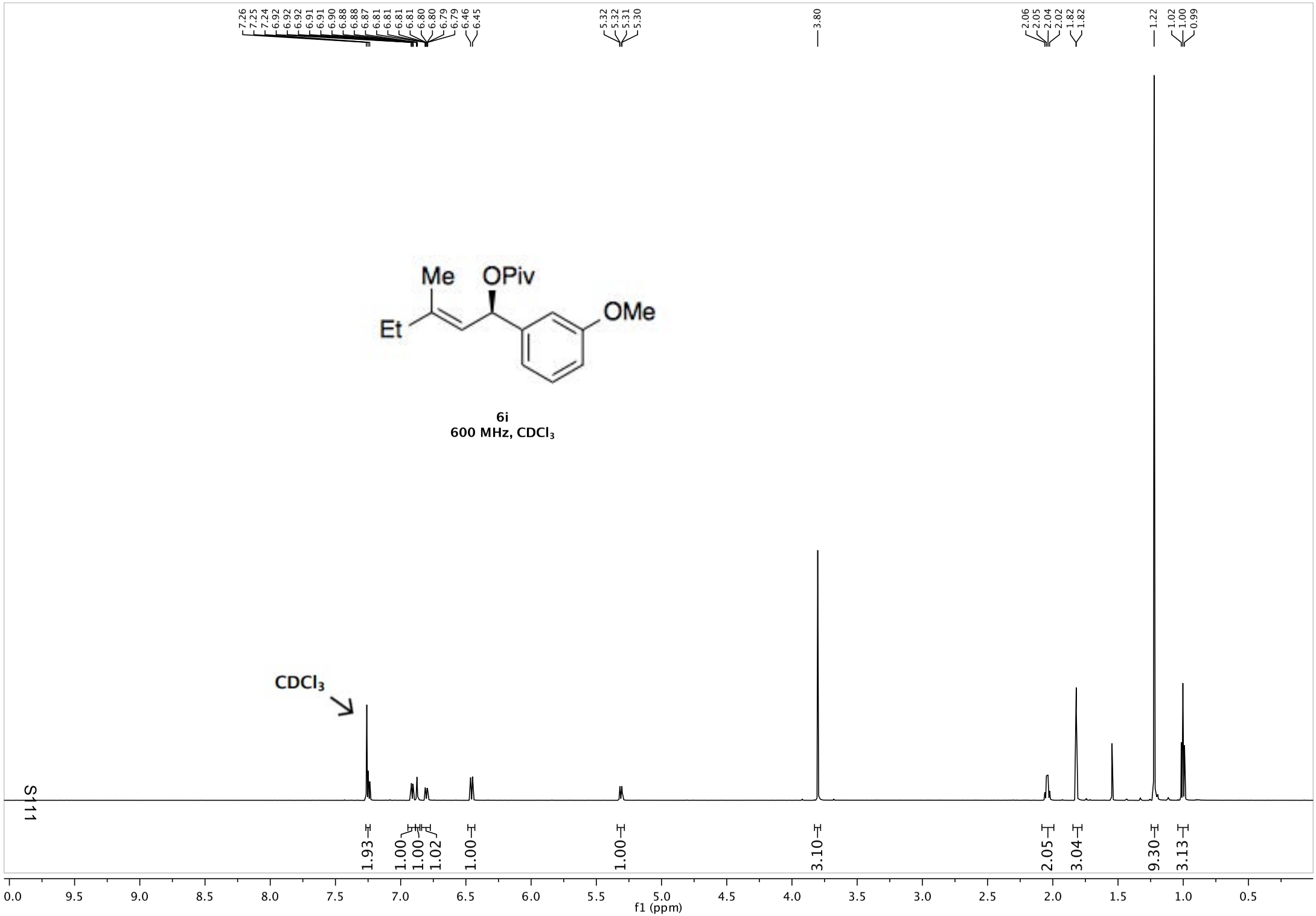
146.77
141.37
128.60
127.61
126.46
122.70
72.19
38.94
36.05
30.11
27.30
23.94
22.54
14.16
13.54
CDCl3
Et
OPiv
Bu
6h
101 MHz, CDCl3
S10
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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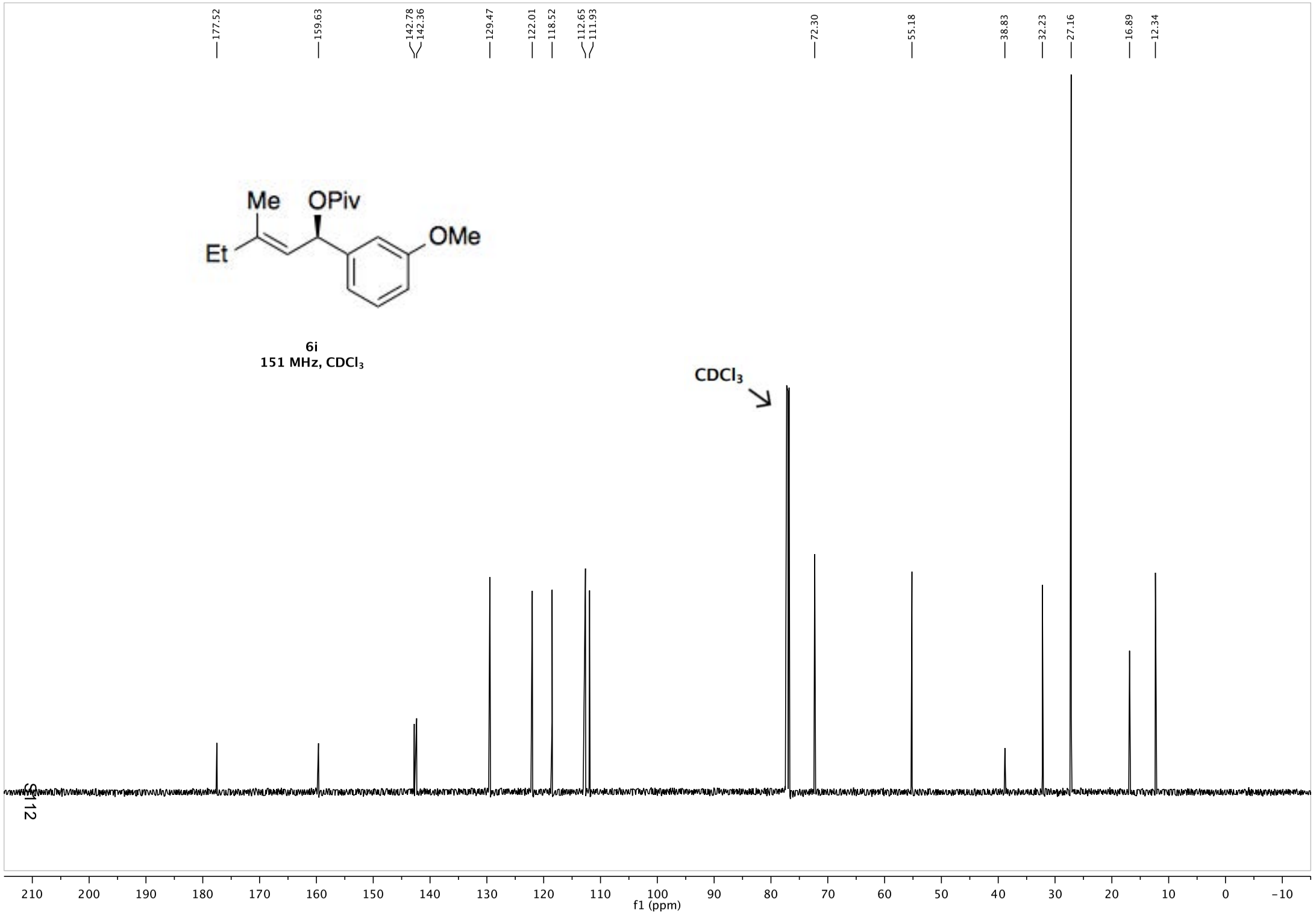
7.25
7.24
6.92
6.92
6.92
6.91
6.91
6.90
6.88
6.88
6.87
6.81
6.81
6.81
6.81
6.80
6.80
6.79
6.79
6.46
6.45
5.32
5.32
5.31
5.30
3.80
2.06
2.05
2.04
2.02
1.82
1.82
1.22
1.02
1.00
0.99
Me
OPiv
Et
OMe
6i
600 MHz, CDCl3
CDCl3
S111
1.93
1.00
1.00
1.02
1.00
1.00
3.10
2.05
3.04
9.30
3.13
0.0
9.5
9.0
8.5
8.0
7.5
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)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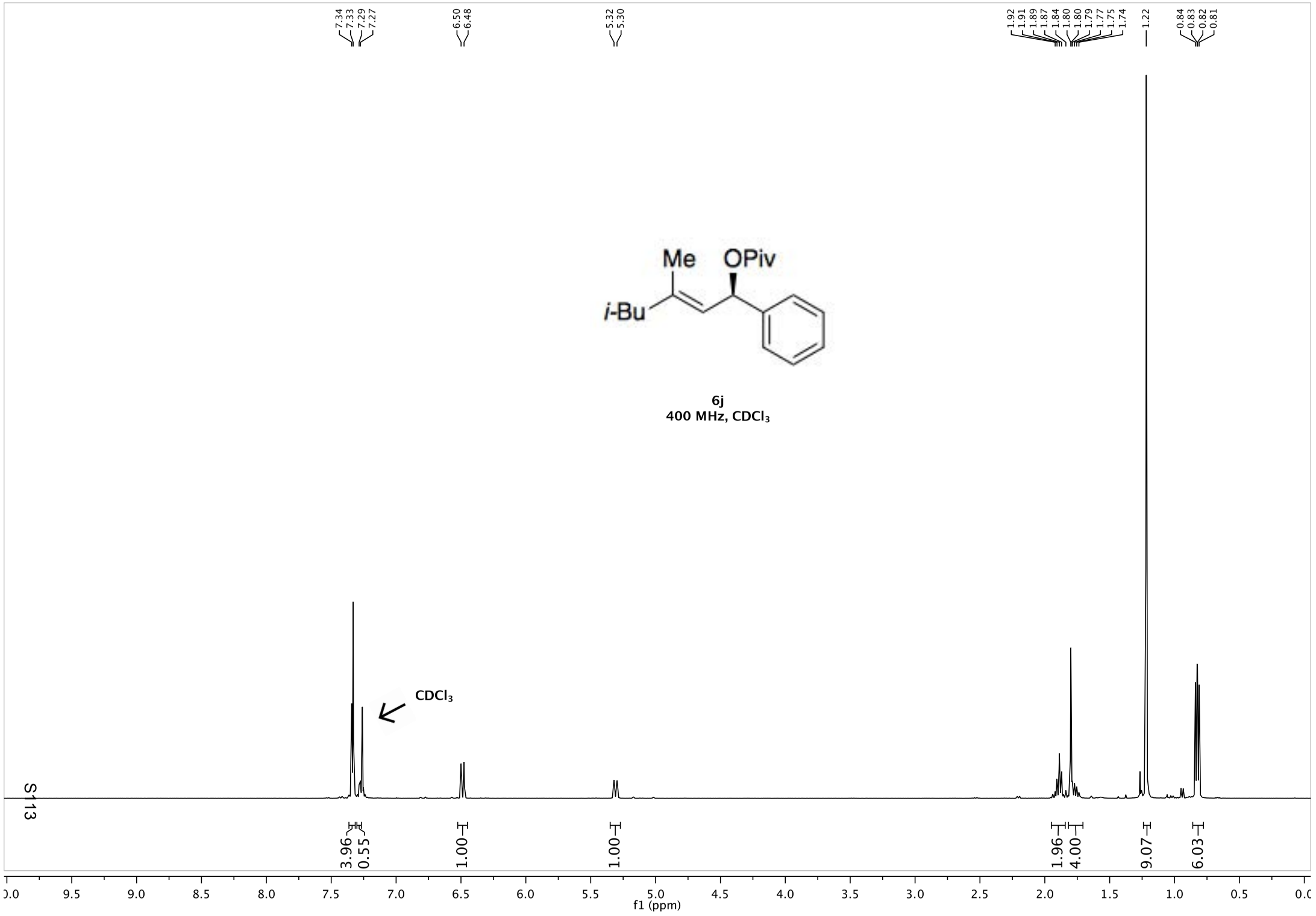
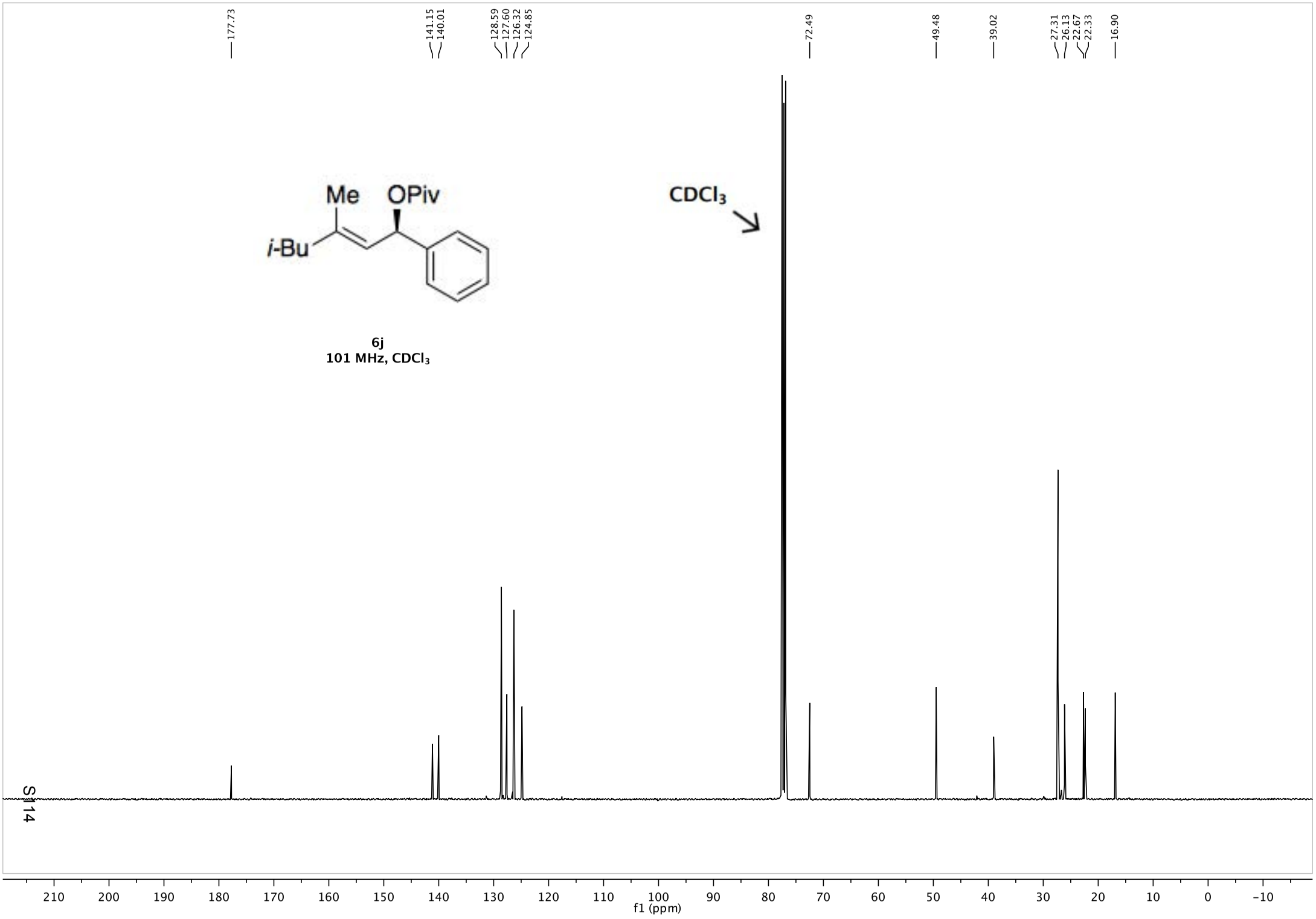
159.63
142.78
142.36
129.47
122.01
118.52
112.65
111.93
72.30
55.18
38.83
32.23
27.16
16.89
12.34
Me
OPiv
Et
OMe
6i
151 MHz, CDCl3
CDCl3
C112
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


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
6j
400 MHz, CDCl3
CDCl3
S113
3.96
0.55
1.00
1.00
1.96
4.00
9.07
6.03
f1 (ppm)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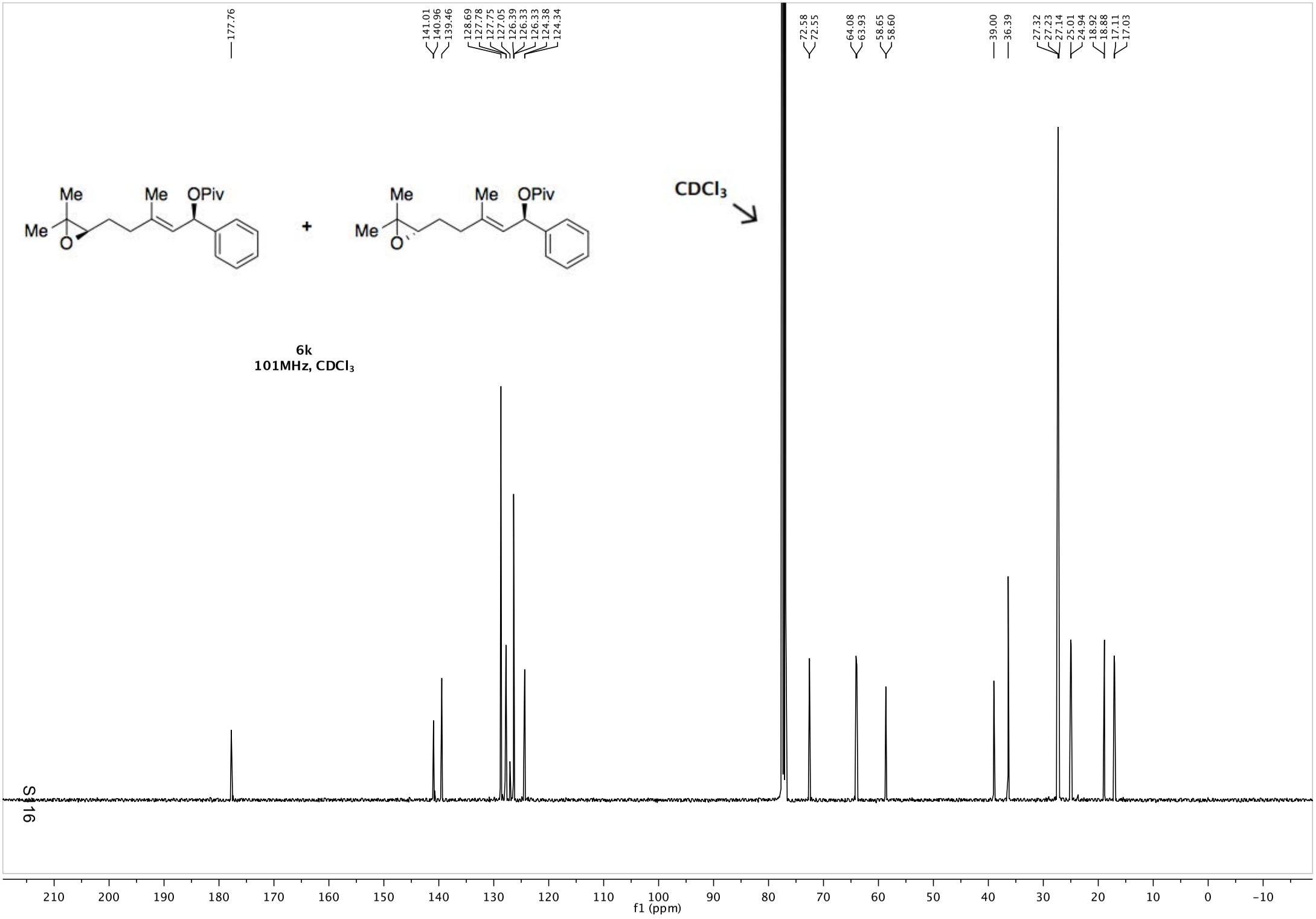
141.15
140.01
128.59
127.60
126.32
124.85
72.49
49.48
39.02
27.31
26.13
22.67
22.33
16.90
Me
OPiv
i-Bu
CDCl3
6j
101 MHz, CDCl3
f1 (ppm)


7.34
7.33
7.33
7.28
7.28
7.28
7.27
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
OPiv
Me
O
+
Me
Me
OPiv
Me
O
6k
400 MHz, CDCl3
CDCl3
S115
4.24
2.06
1.00
0.99
0.98
4.00
2.94
3.08
3.03
9.01
f1 (ppm)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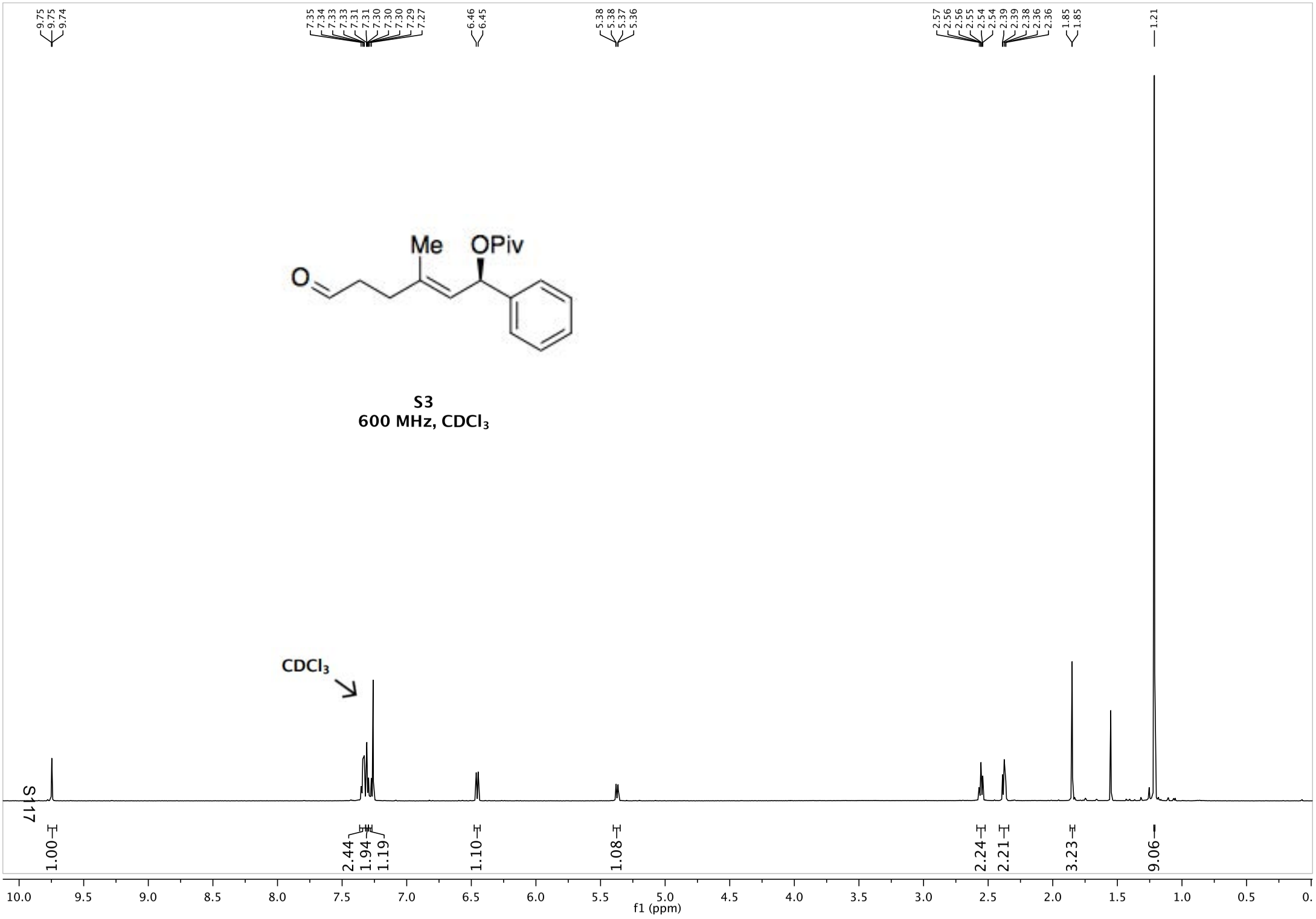
141.01
140.96
139.46
128.69
127.78
127.75
127.05
126.39
126.33
126.33
124.38
124.34
72.58
72.55
64.08
63.93
58.65
58.60
39.00
36.39
27.32
27.23
27.14
25.01
24.94
18.92
18.88
17.11
17.03
Me
Me
OPiv
O
+
Me
Me
OPiv
Me
O
CDCl3
6k
101MHz, CDCl3
S16
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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9.75
9.74
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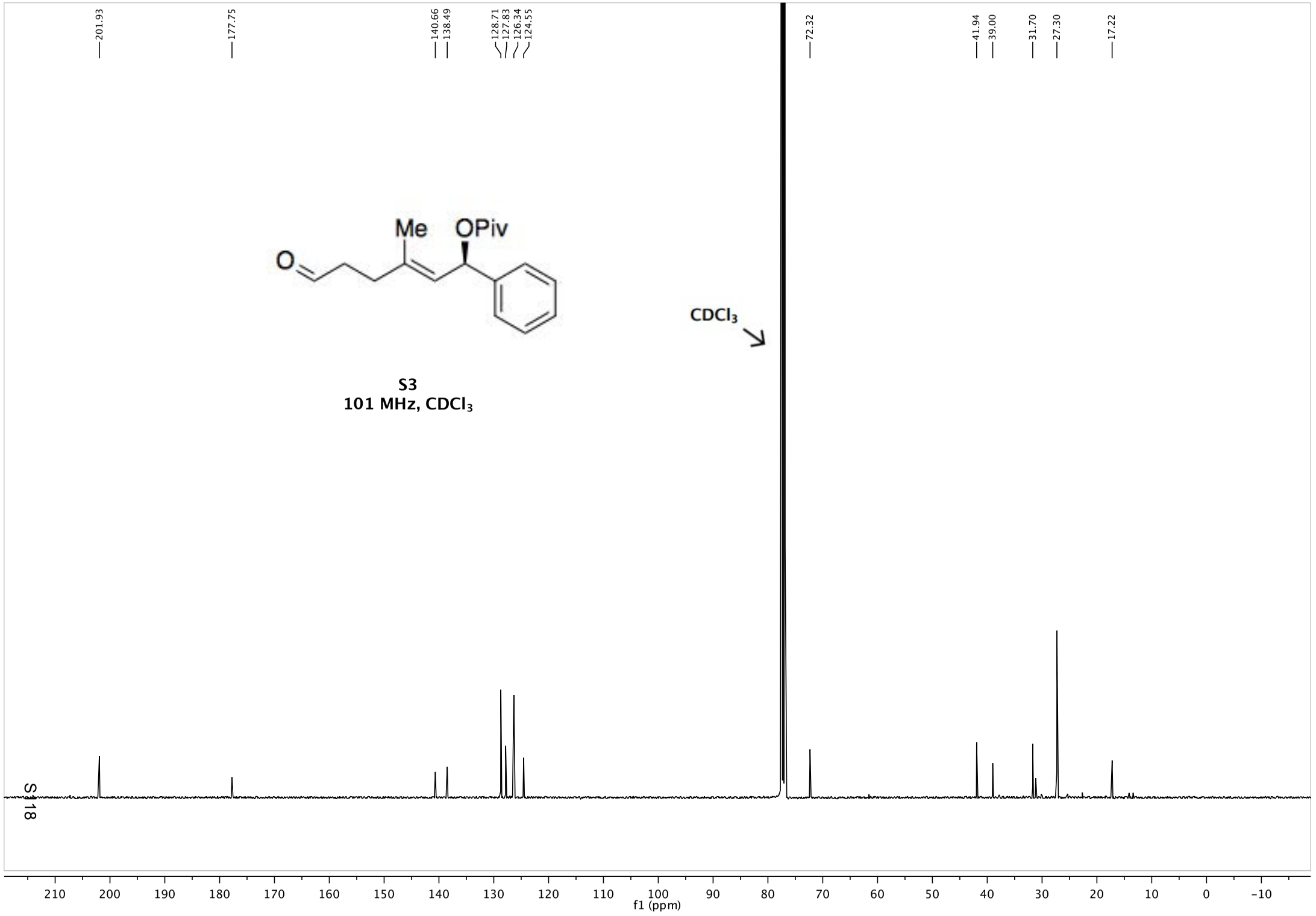
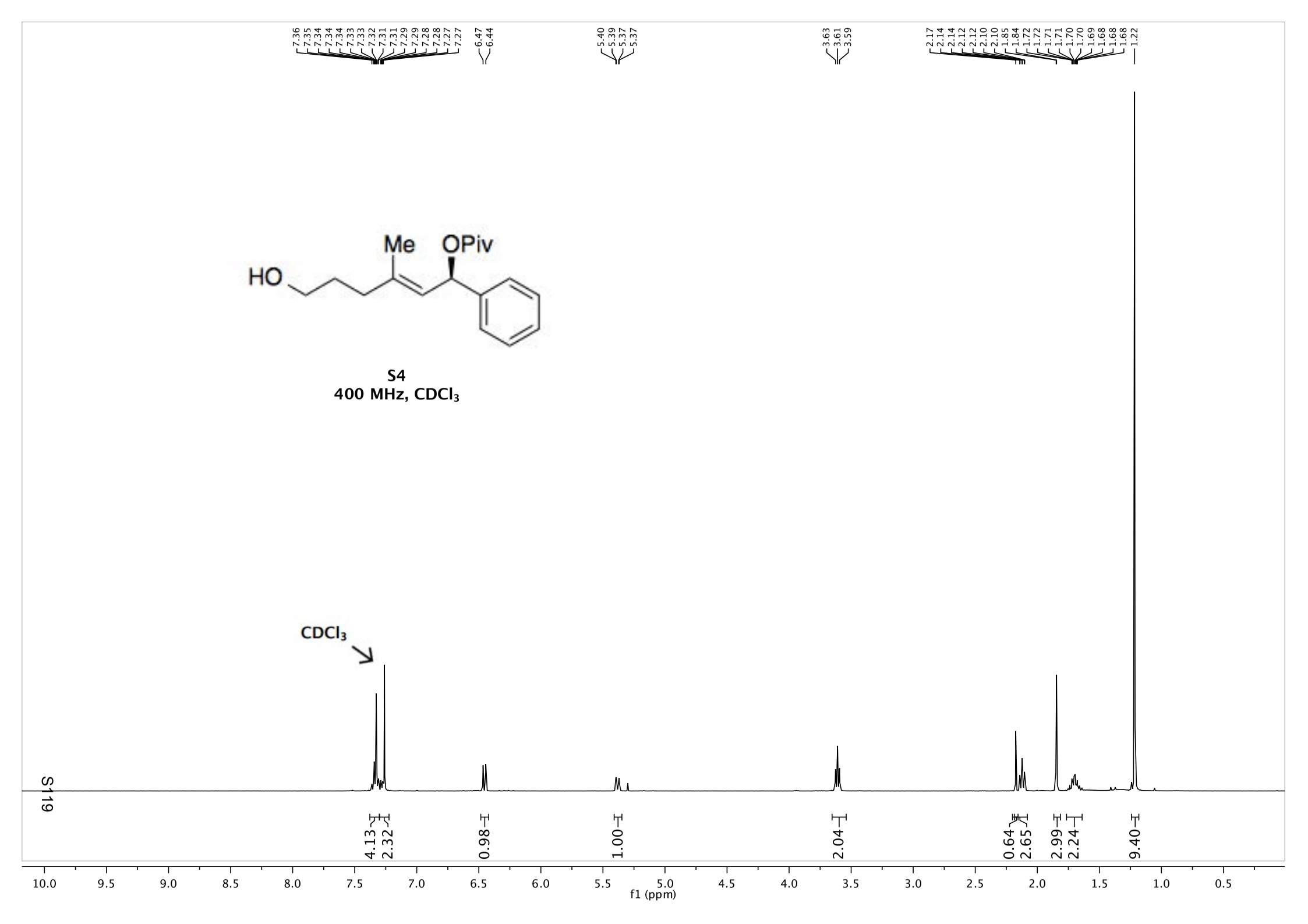
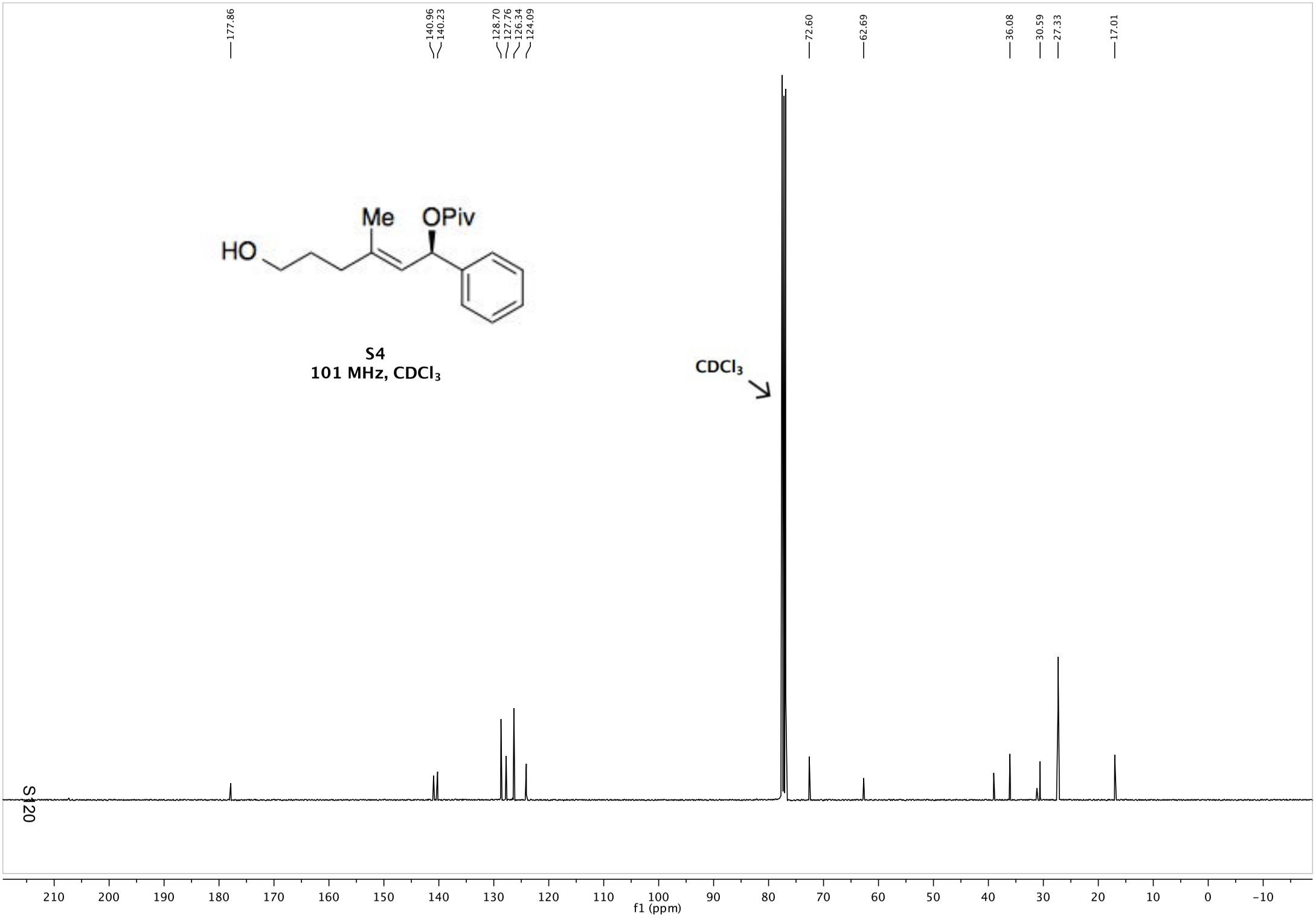
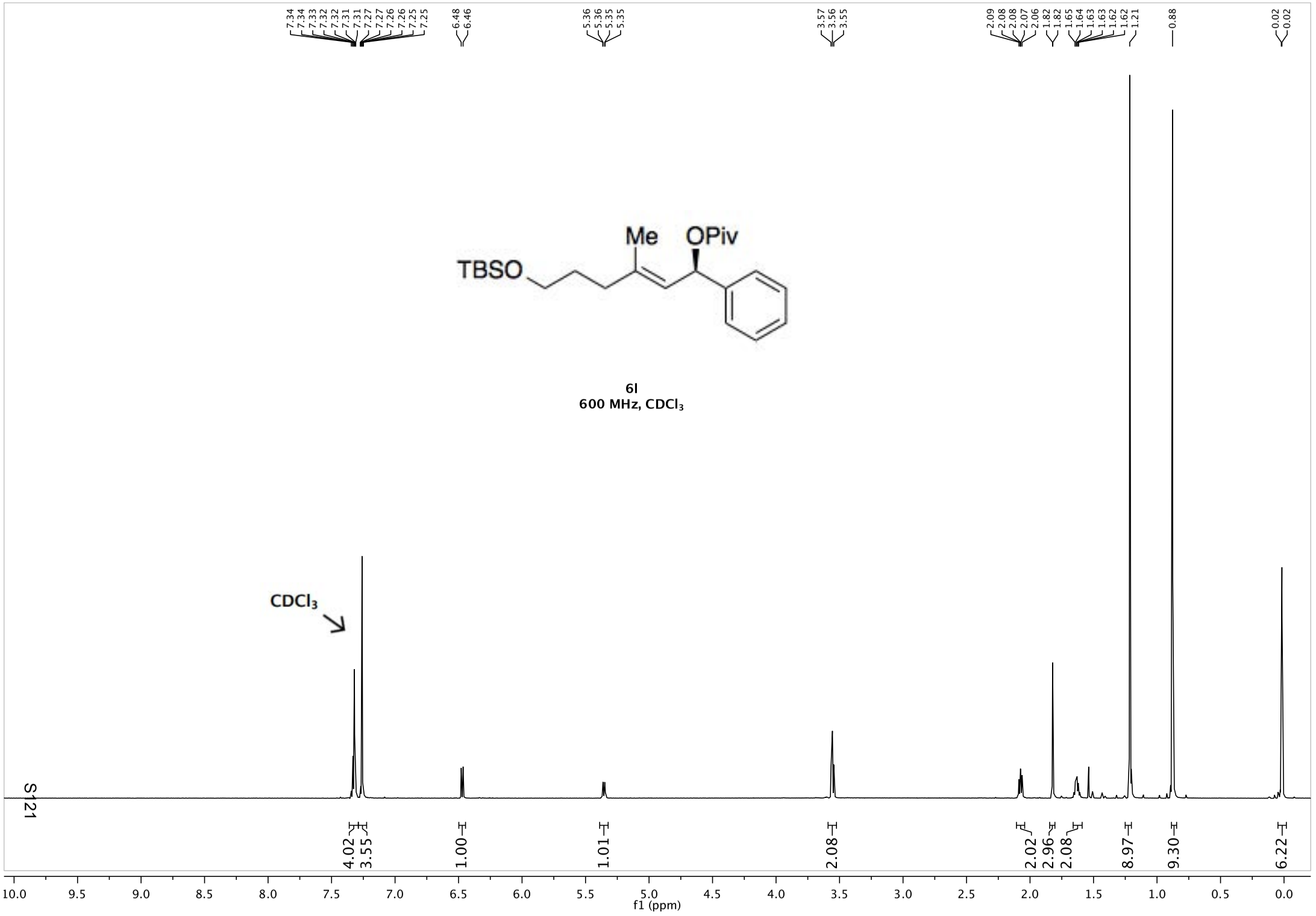
7.34
7.33
7.33
7.31
7.31
7.30
7.30
7.30
7.29
7.27
6.46
6.45
5.38
5.38
5.37
5.36
2.57
2.56
2.56
2.55
2.54
2.54
2.39
2.39
2.38
2.36
2.36
1.85
1.85
1.21
Me
OPiv
O
S3
600 MHz, CDCl3
CDCl3
S117
1.00
2.44
1.94
1.19
1.10
1.08
2.24
2.21
3.23
9.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

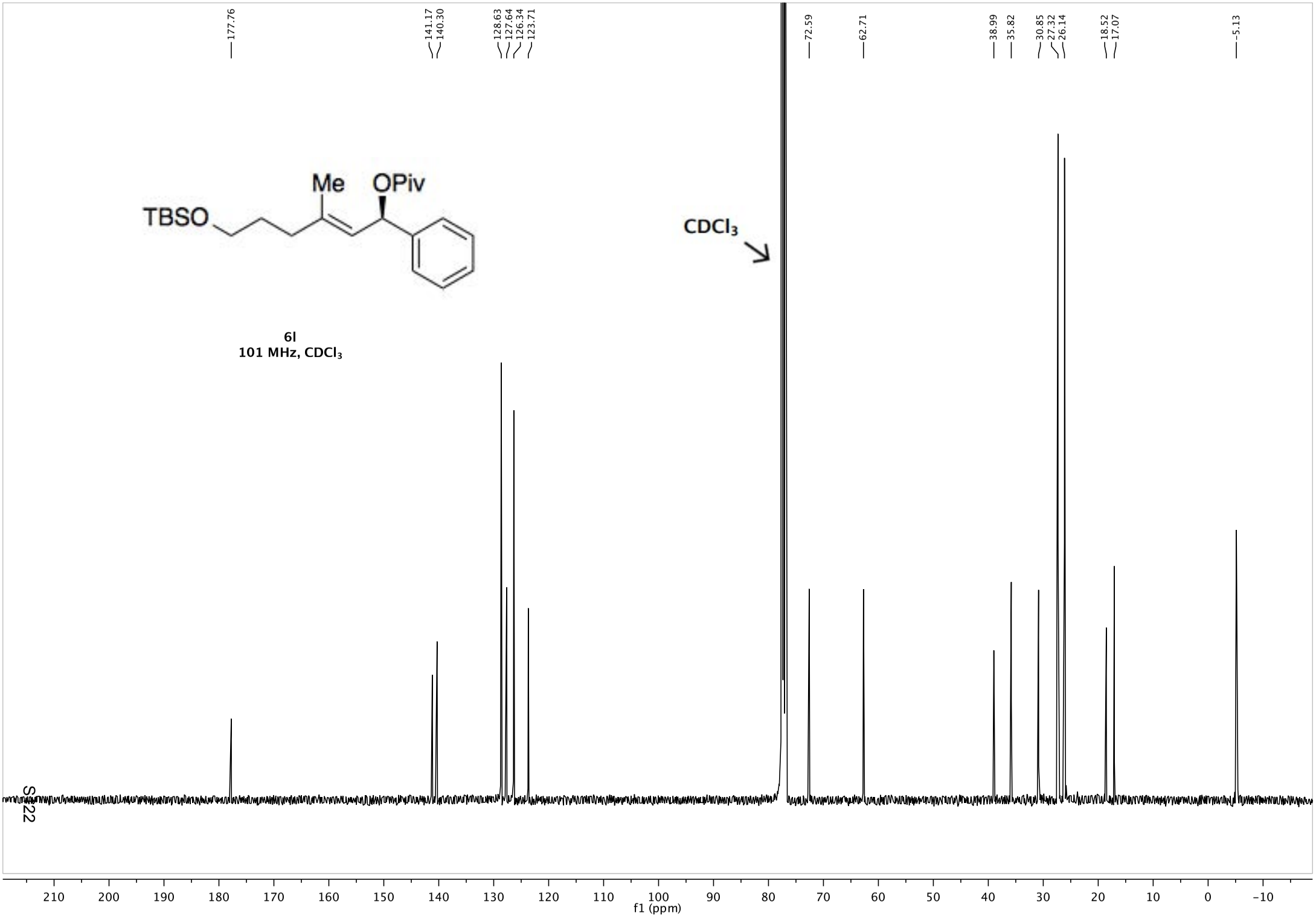

201.93
177.75
140.66
138.49
128.71
127.83
126.34
124.55
72.32
41.94
39.00
31.70
27.30
17.22
Me
OPiv
O
CDCl3
S3
101 MHz, CDCl3
S118
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

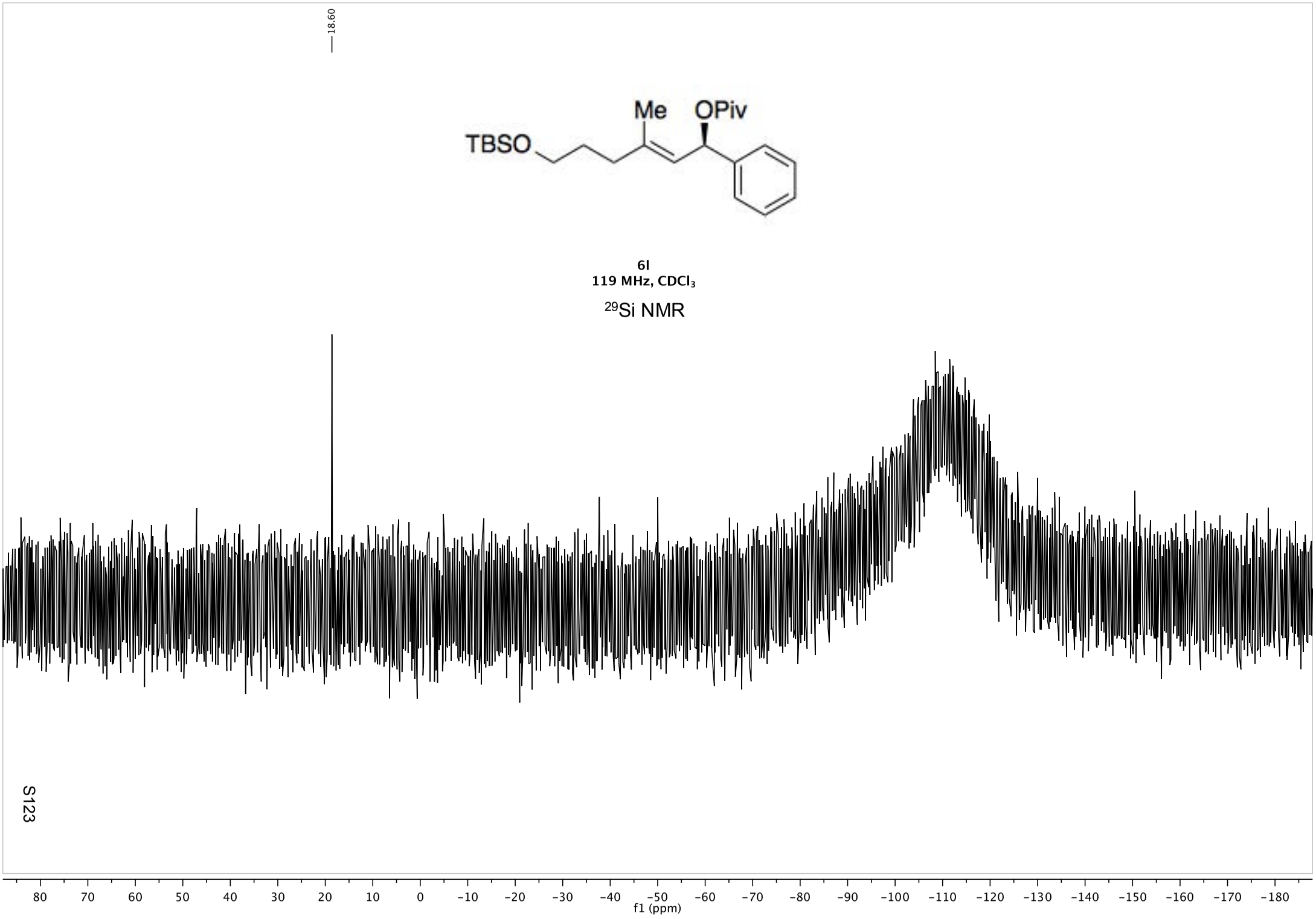


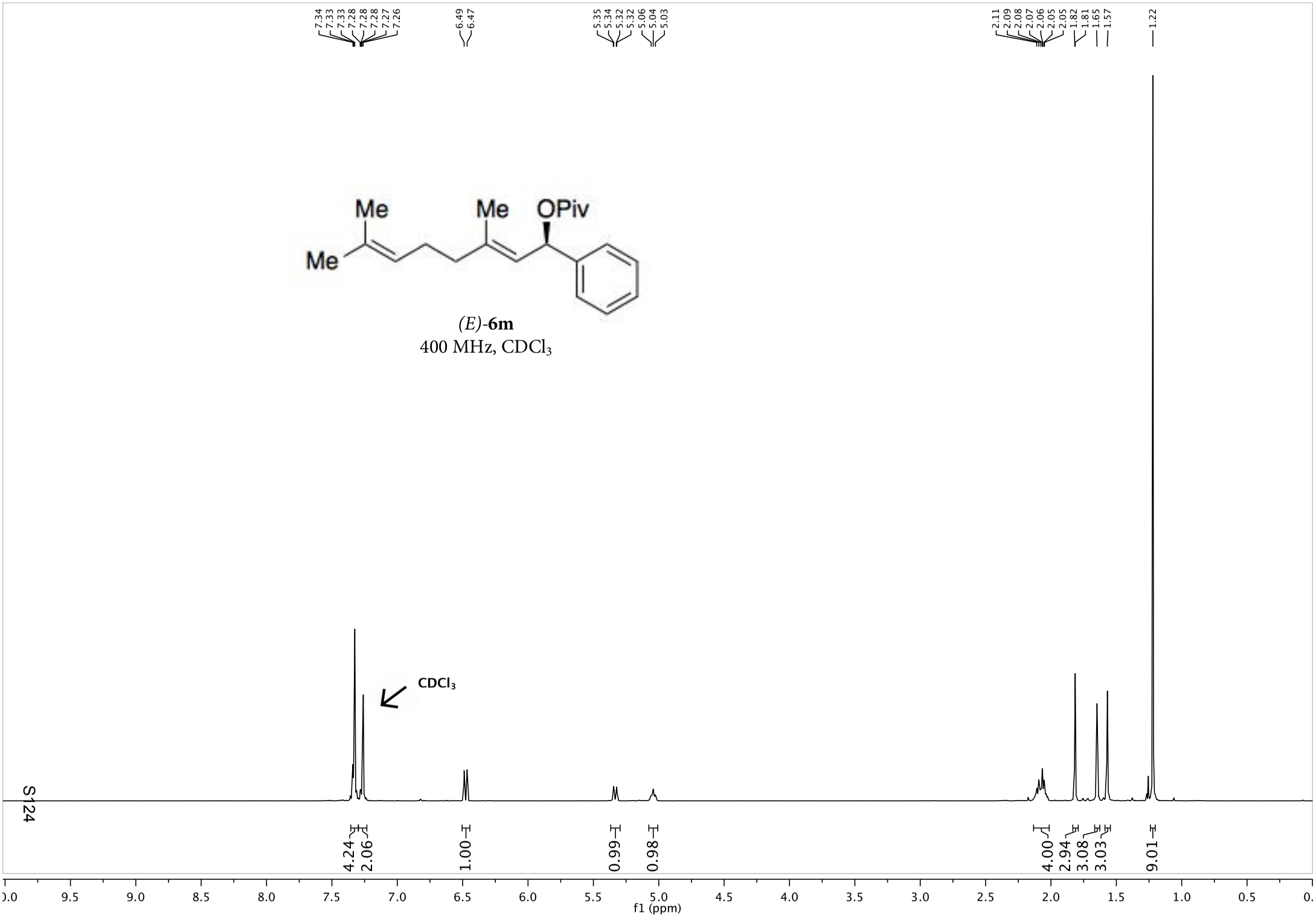
S4
400 MHz, $CDCl_3$


177.86
140.96
140.23
128.70
127.76
126.34
124.09
72.60
62.69
36.08
30.59
27.33
17.01
Me
OPiv
HO
S4
101 MHz, CDCl3
CDCl3
S120
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)

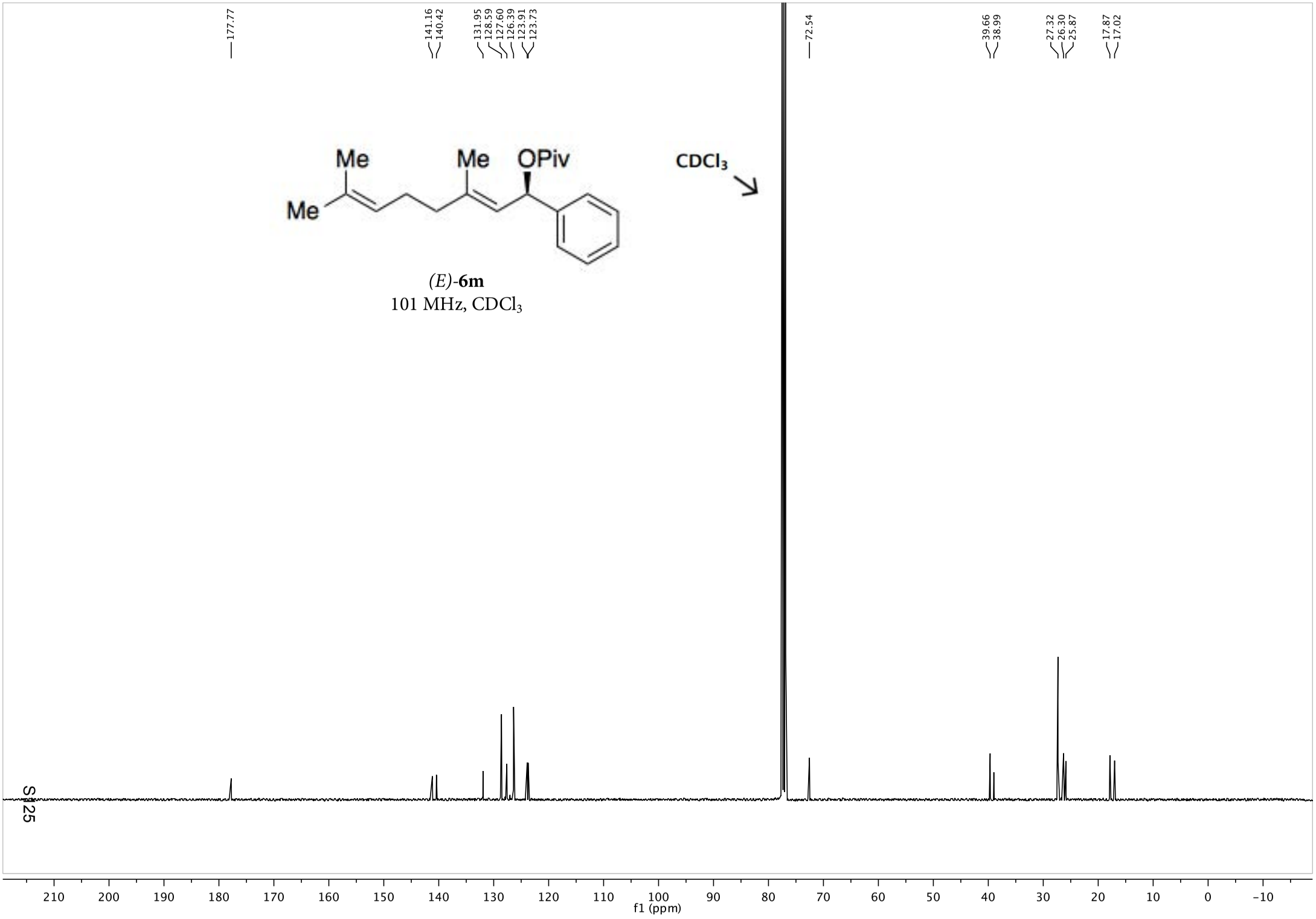

7.34
7.34
7.33
7.32
7.32
7.31
7.31
7.27
7.27
7.26
7.26
7.25
7.25
6.48
6.46
5.36
5.36
5.35
5.35
3.57
3.56
3.55
2.09
2.08
2.08
2.07
2.06
1.82
1.82
1.65
1.64
1.63
1.63
1.62
1.62
1.21
0.88
0.02
0.02
Me
OPiv
TBSO
6l
600 MHz, CDCl3
CDCl3
S121
4.02
3.55
1.00
1.01
2.08
2.02
2.96
2.08
8.97
9.30
6.22
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


177.76
141.17
140.30
128.63
127.64
126.34
123.71
72.59
62.71
38.99
35.82
30.85
27.32
26.14
18.52
17.07
-5.13
Me
OPiv
TBSO
CDCl3
6l
101 MHz, CDCl3
S22
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)

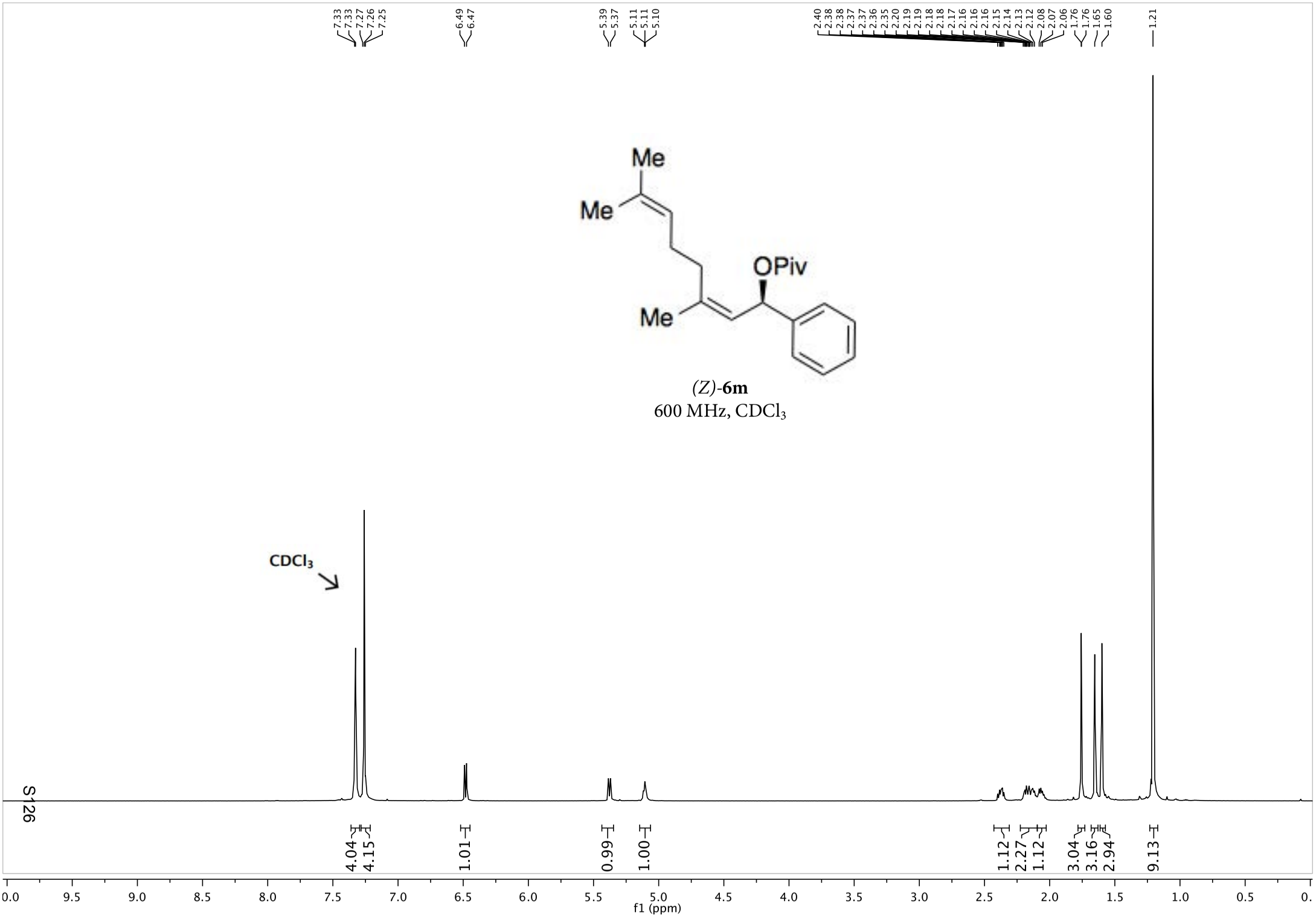

18.60
Me
OPiv
TBSO
6l
119 MHz, CDCl3
29Si NMR
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)



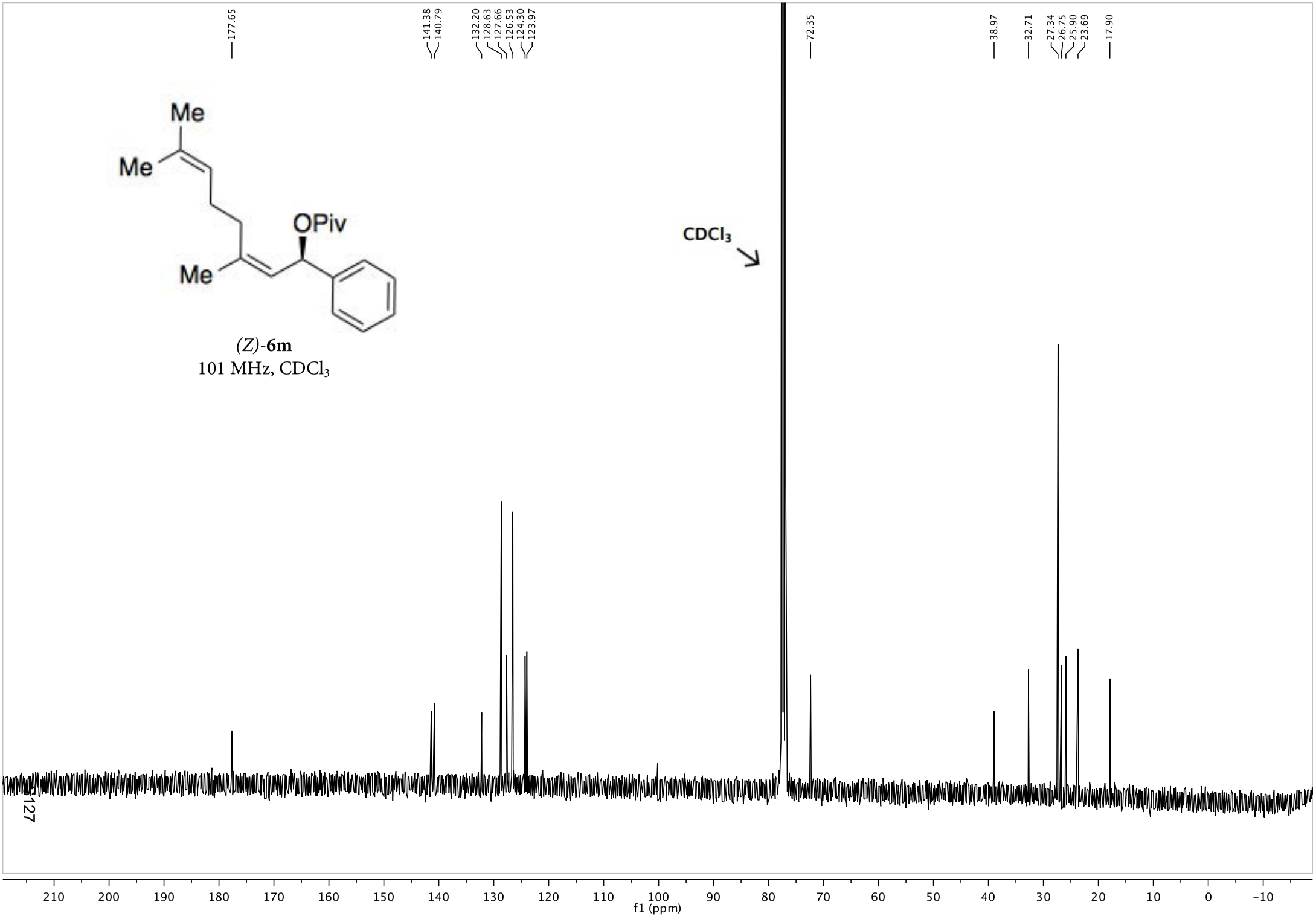
(E)-**6m**
400 MHz, $CDCl_3$

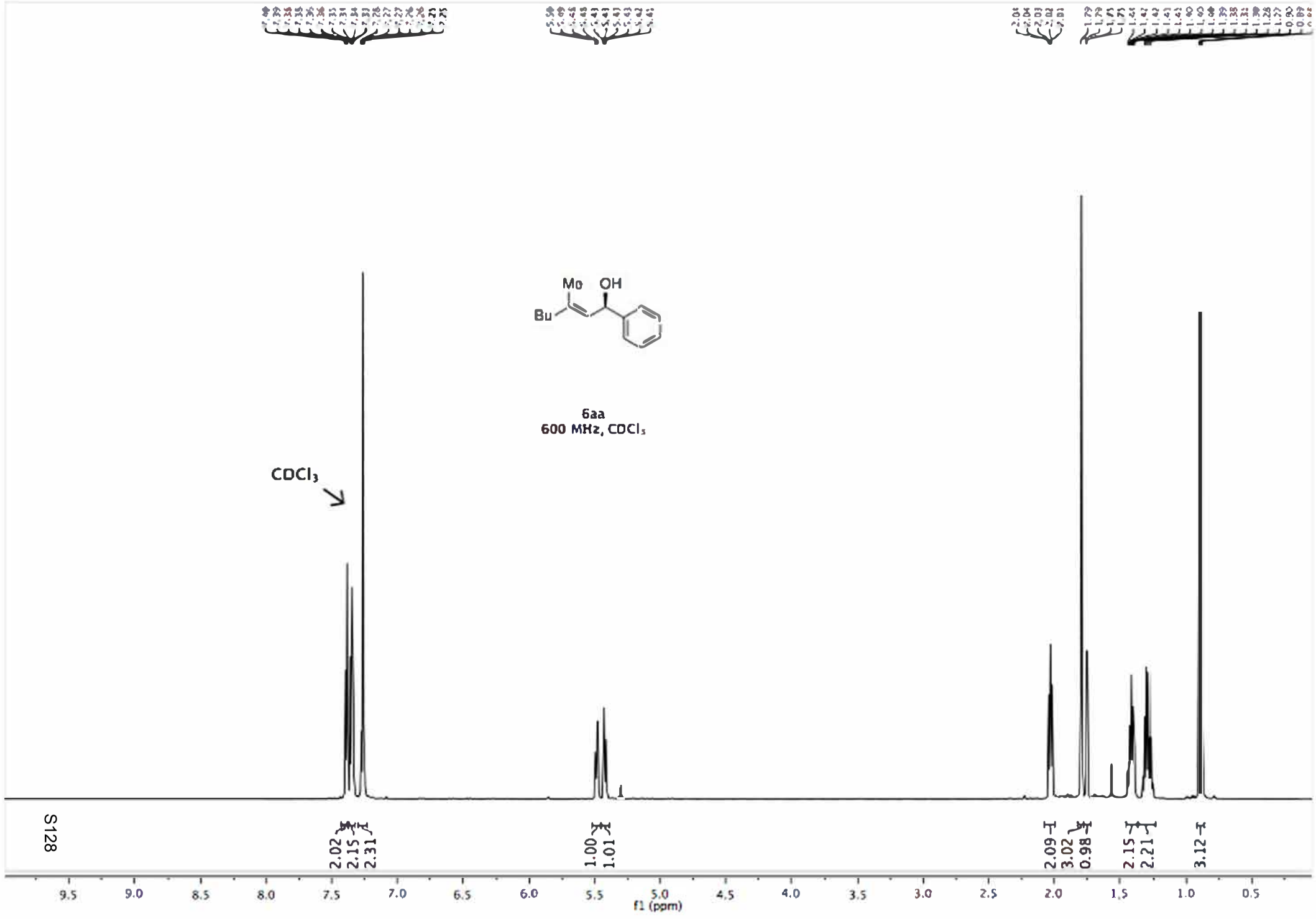


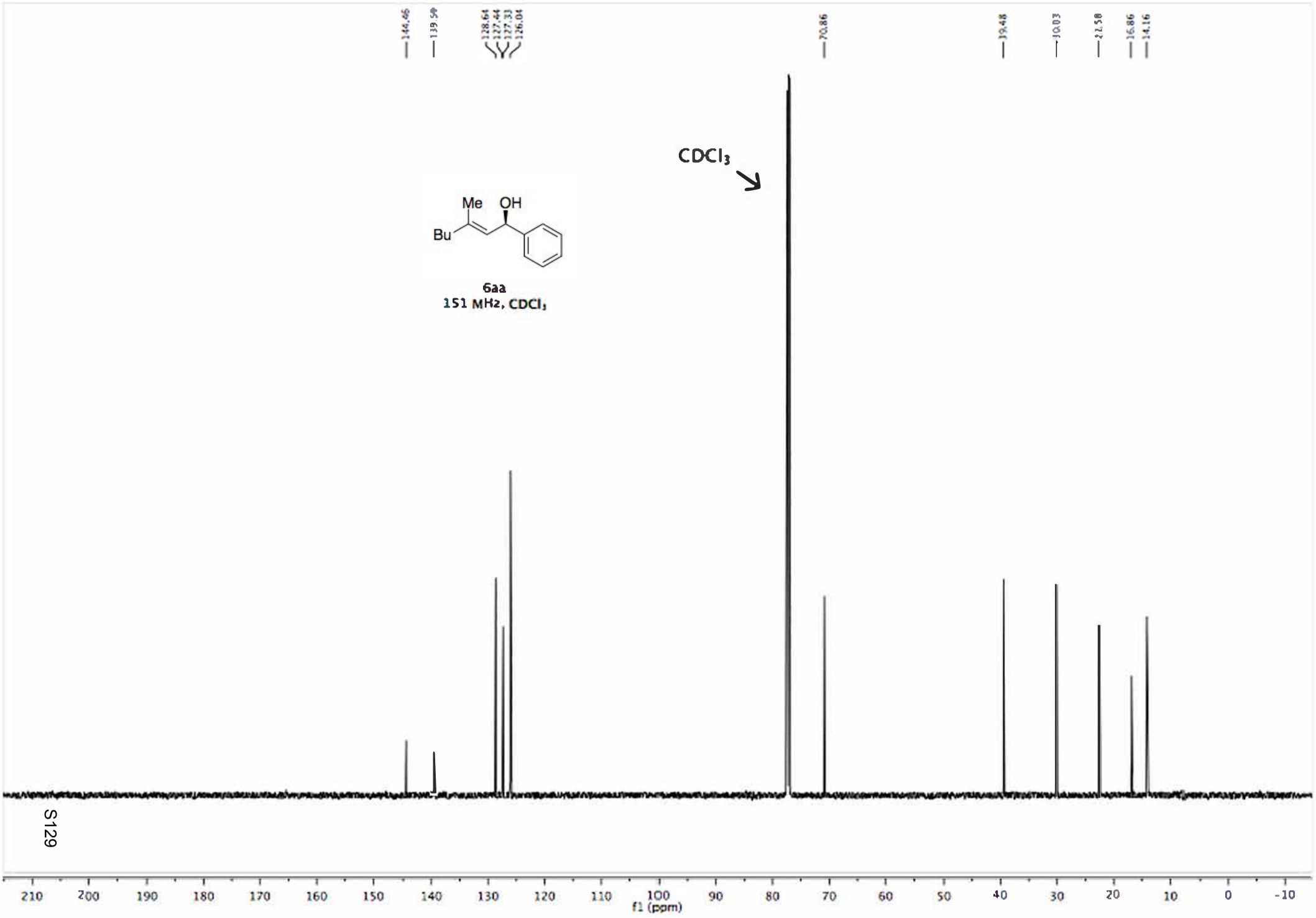
(E)-**6m**
101 MHz, $CDCl_3$

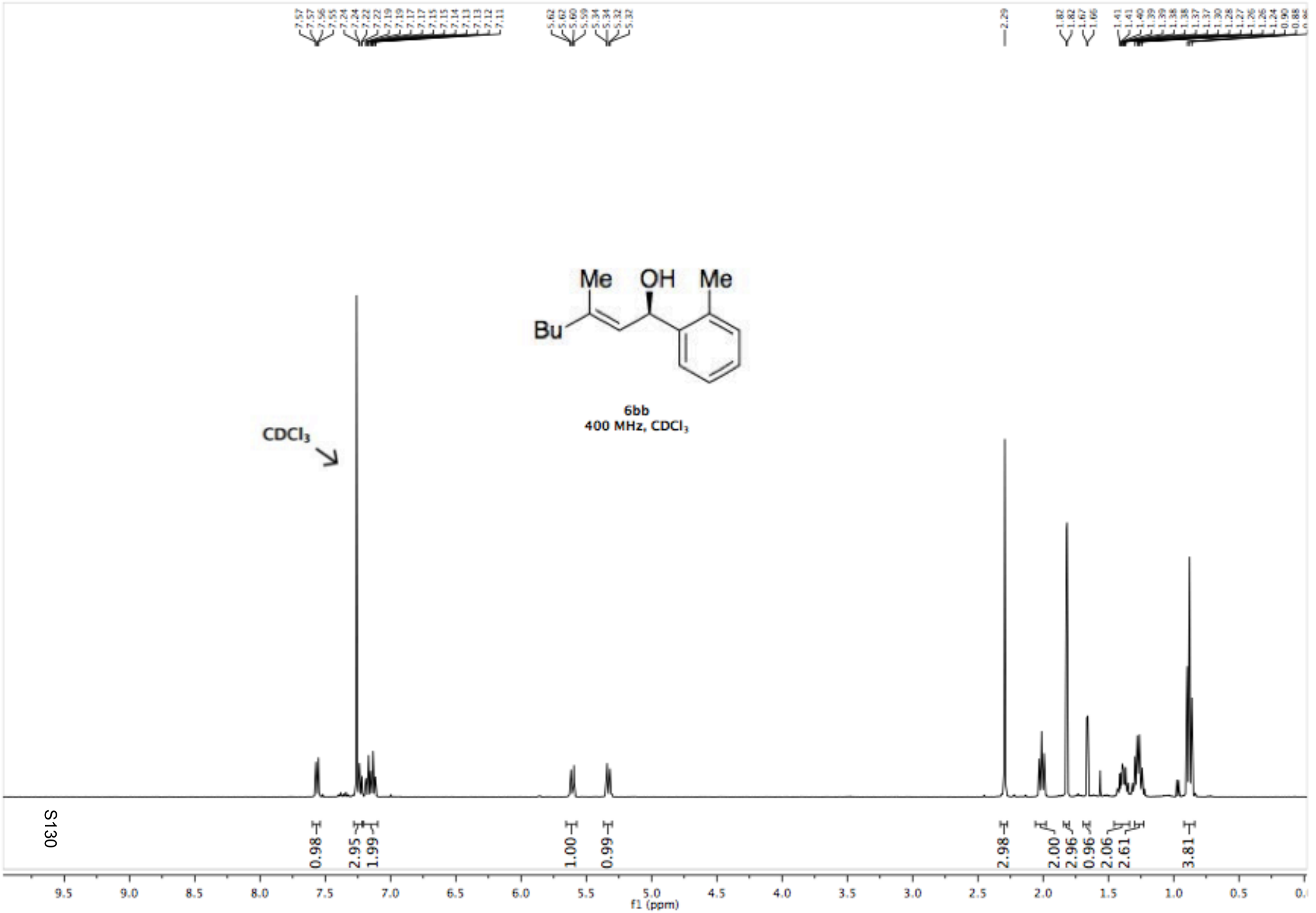


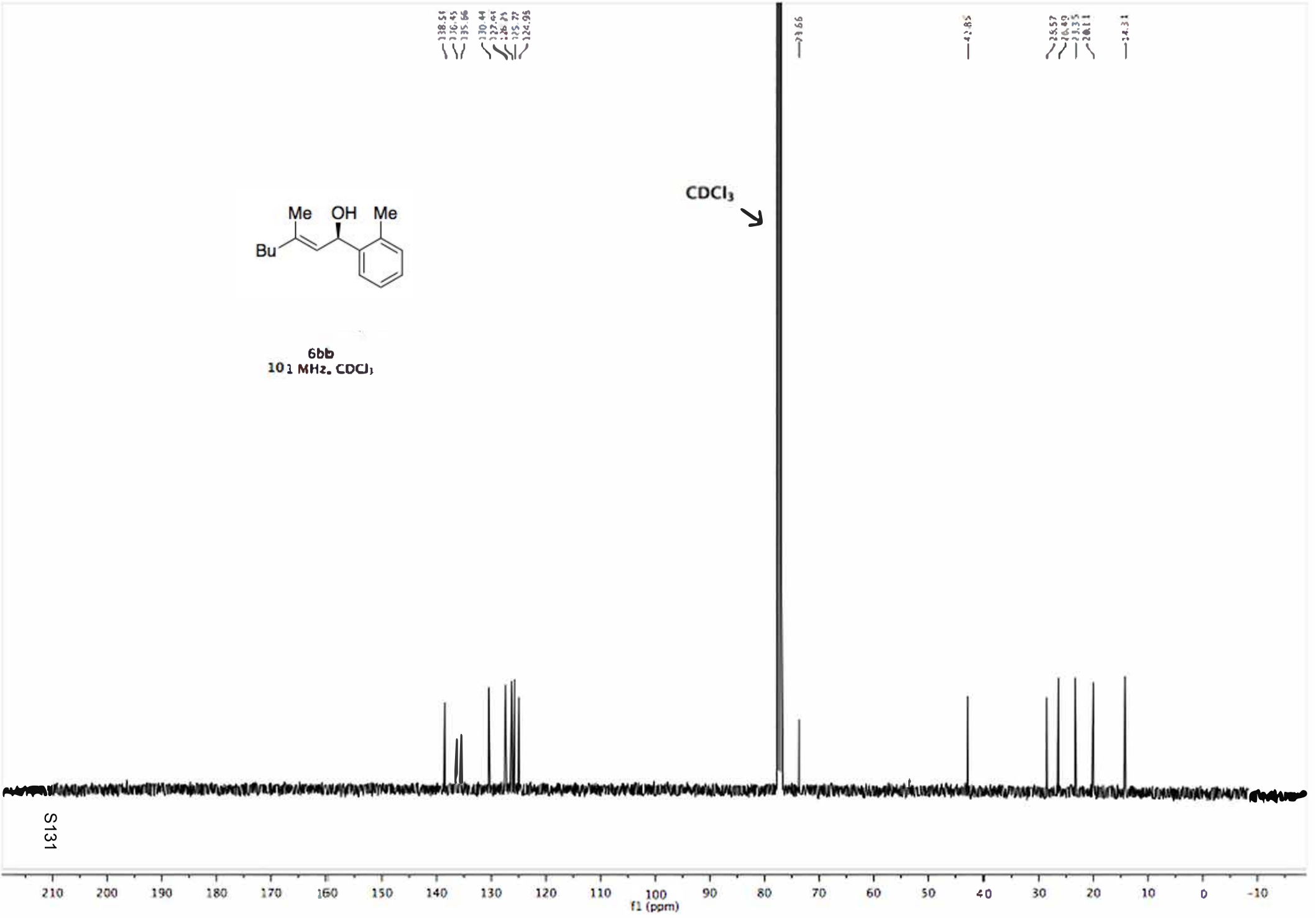
(Z)-**6m**
600 MHz, $CDCl_3$

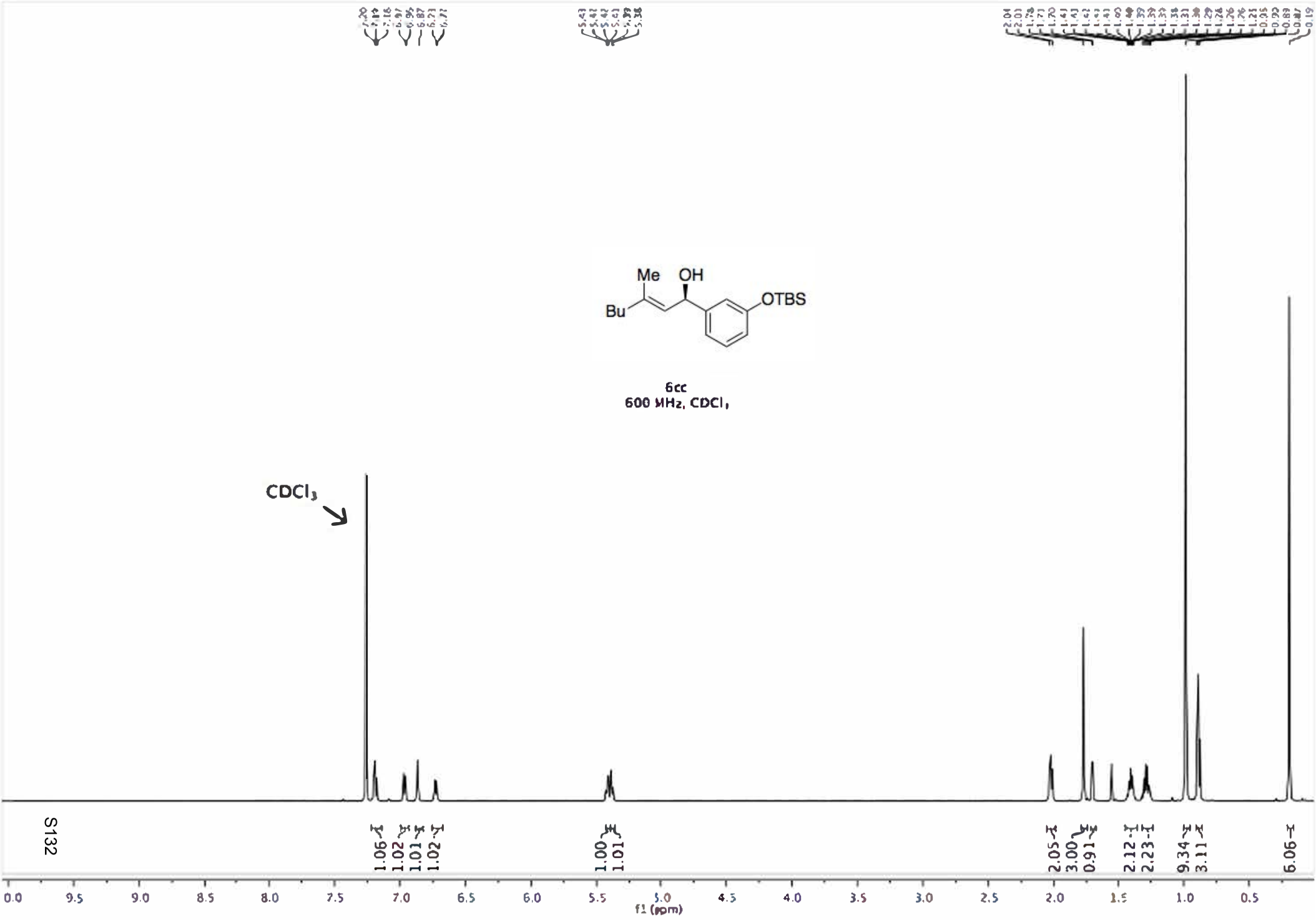

177.65
141.38
140.79
132.20
128.63
127.66
126.53
124.30
123.97
72.35
38.97
32.71
27.34
26.75
25.90
23.69
17.90
CDCl3
Me
Me
OPiv
Me
(Z)-6m
101 MHz, CDCl3
f1 (ppm)

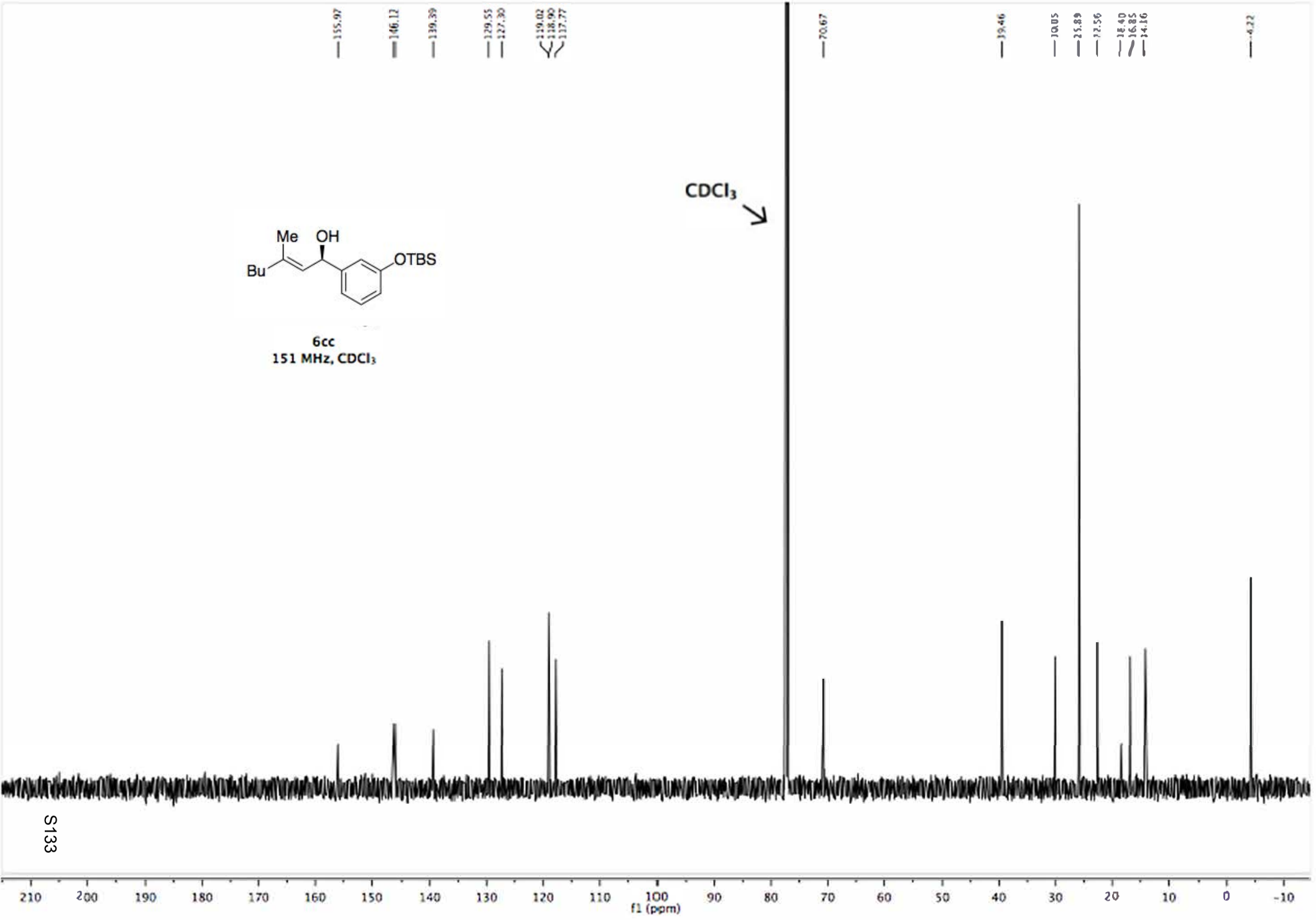

Mo
OH
Bu
6aa
600 MHz, CDCl3
CDCl3
2.02
2.15
2.31
1.00
1.01
2.09
3.02
0.98
2.15
2.21
3.12
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

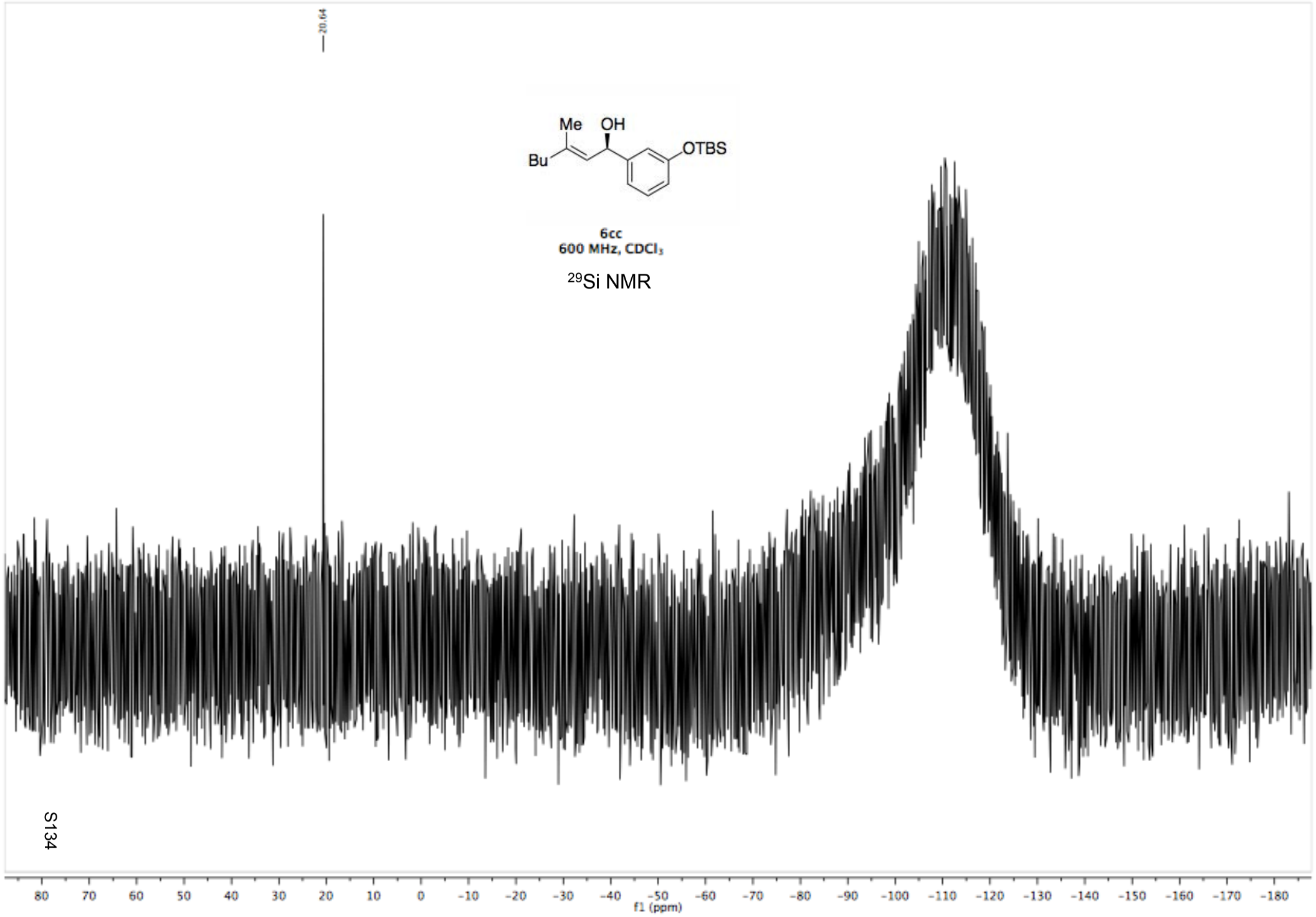

144.46
139.59
128.64
127.44
127.33
126.04
70.86
39.48
30.03
22.58
16.86
14.16
CDCl3
Me
OH
Bu
6aa
151 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

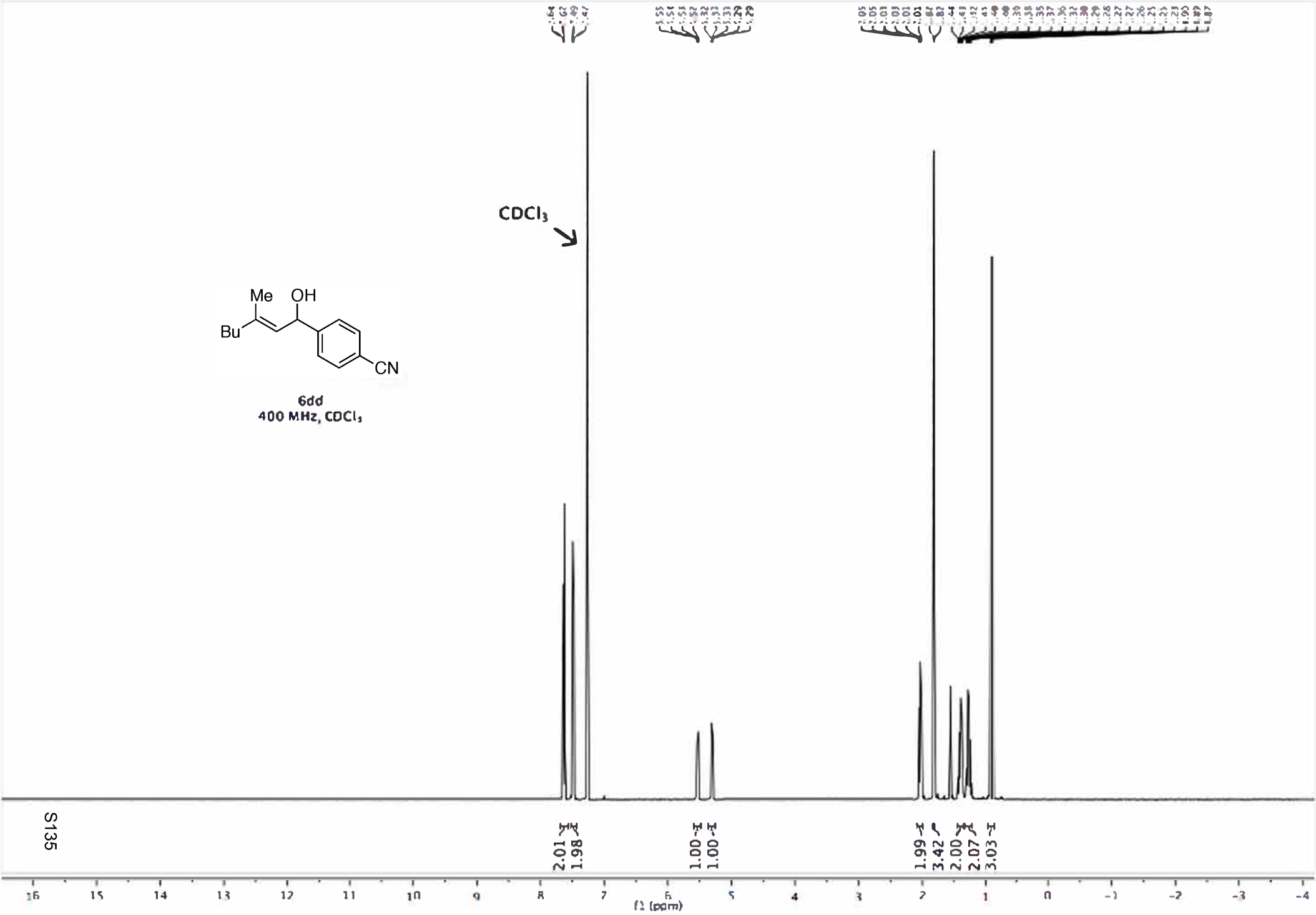

Me
OH
Me
Bu
6bb
400 MHz, CDCl3
CDCl3
f1 (ppm)

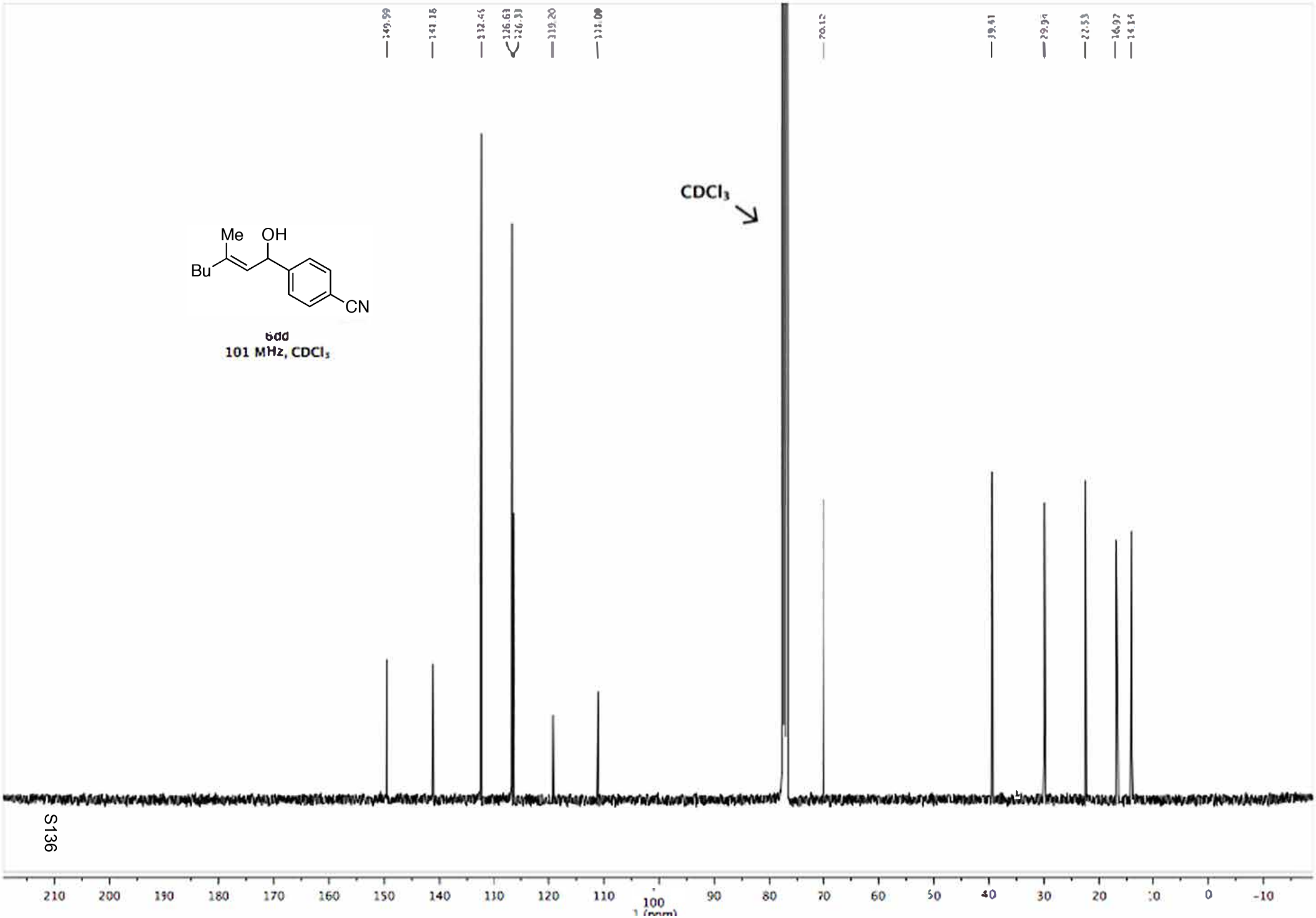

Me
OH
Me
Bu
CDCl3
6bb
101 MHz, CDCl3
f1 (ppm)


Me
OH
Bu
OTBS
6cc
600 MHz, CDCl3
CDCl3
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
f1 (ppm)

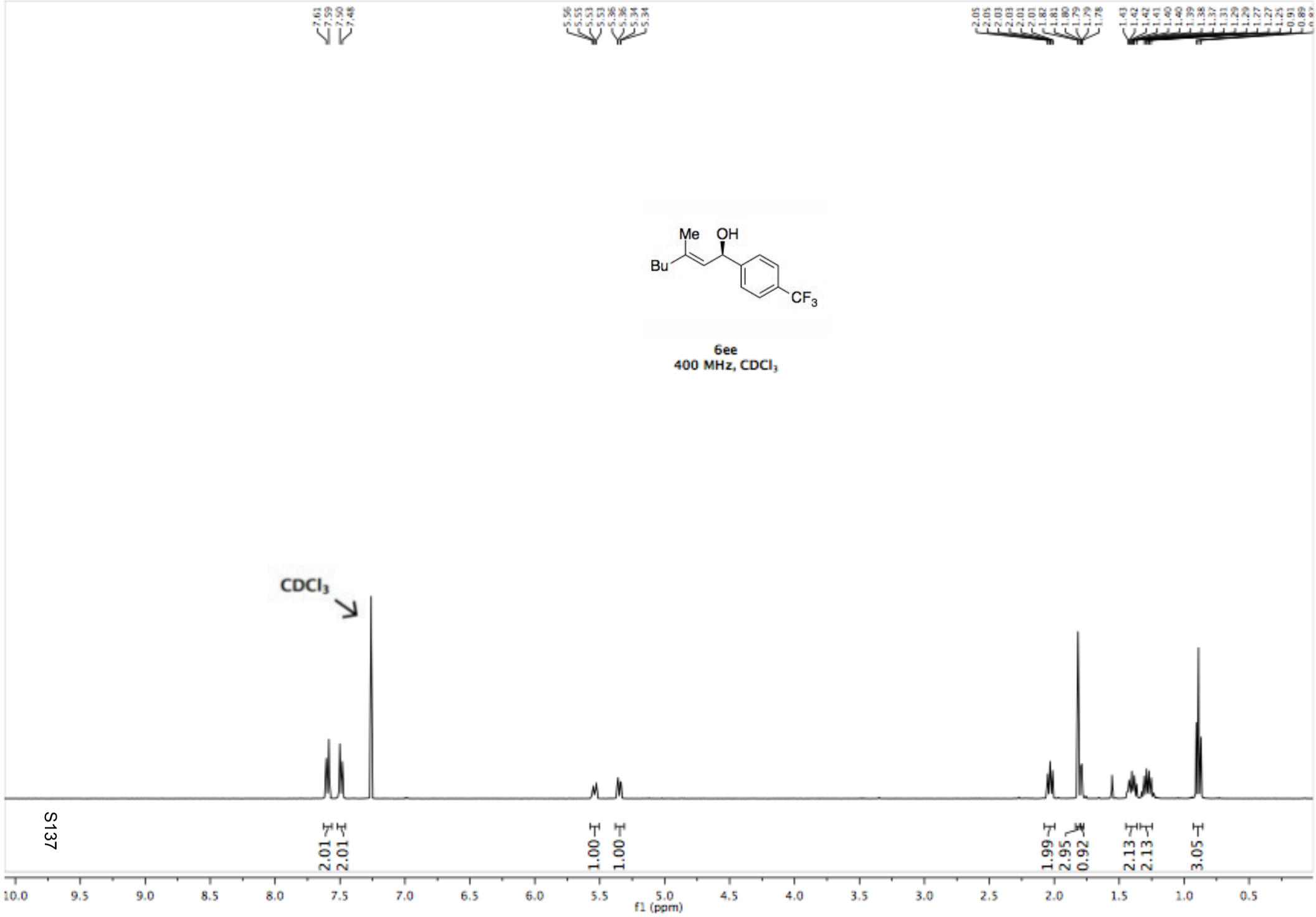

155.97
146.12
139.39
129.55
127.30
119.02
118.90
117.77
70.67
39.46
30.05
25.89
22.56
18.40
16.85
14.16
-4.22
CDCl3
Me
OH
Bu
OTBS
6cc
151 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

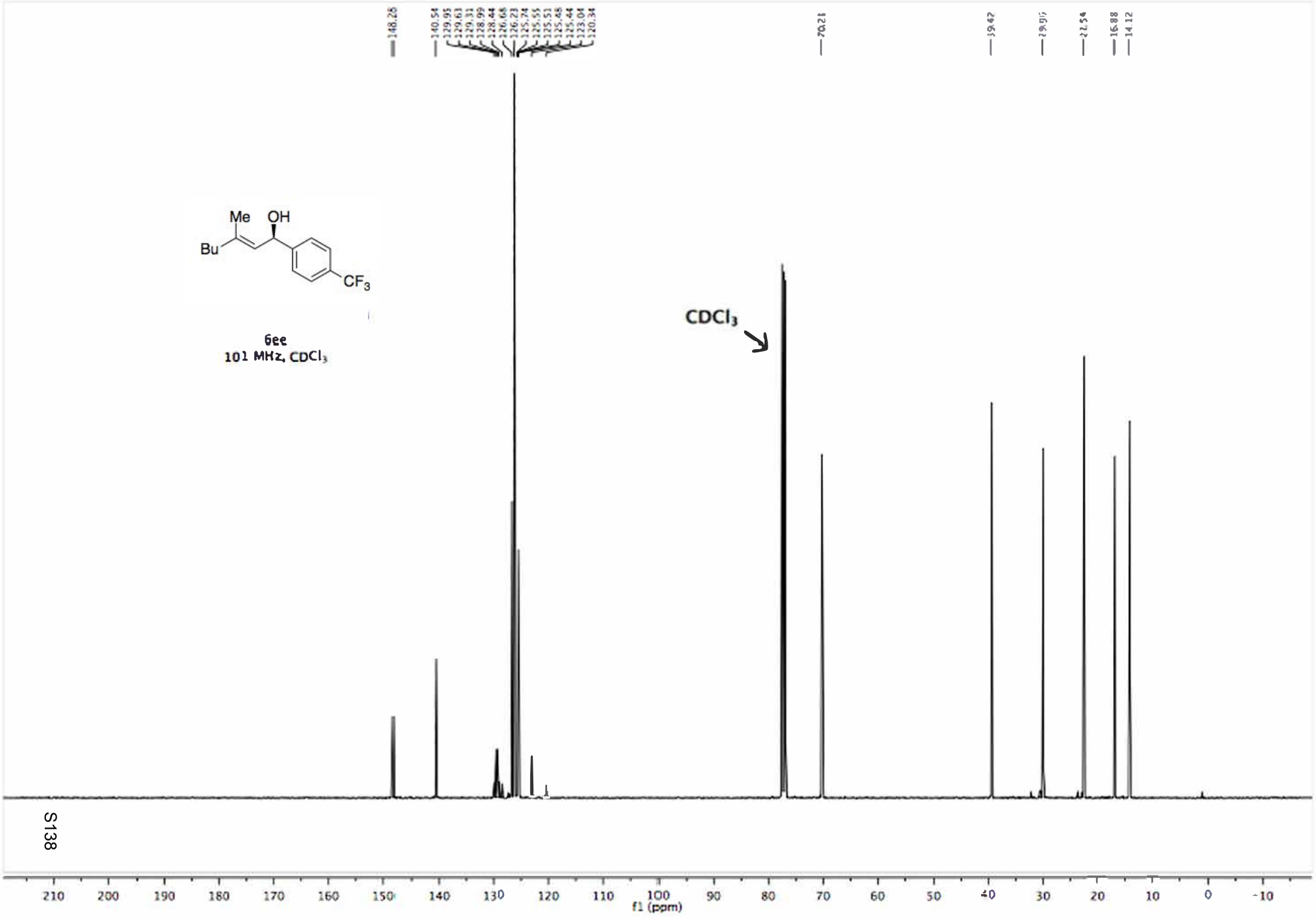

20.64
Me
OH
Bu
OTBS
6cc
600 MHz, CDCl3
29Si NMR
80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180
f1 (ppm)

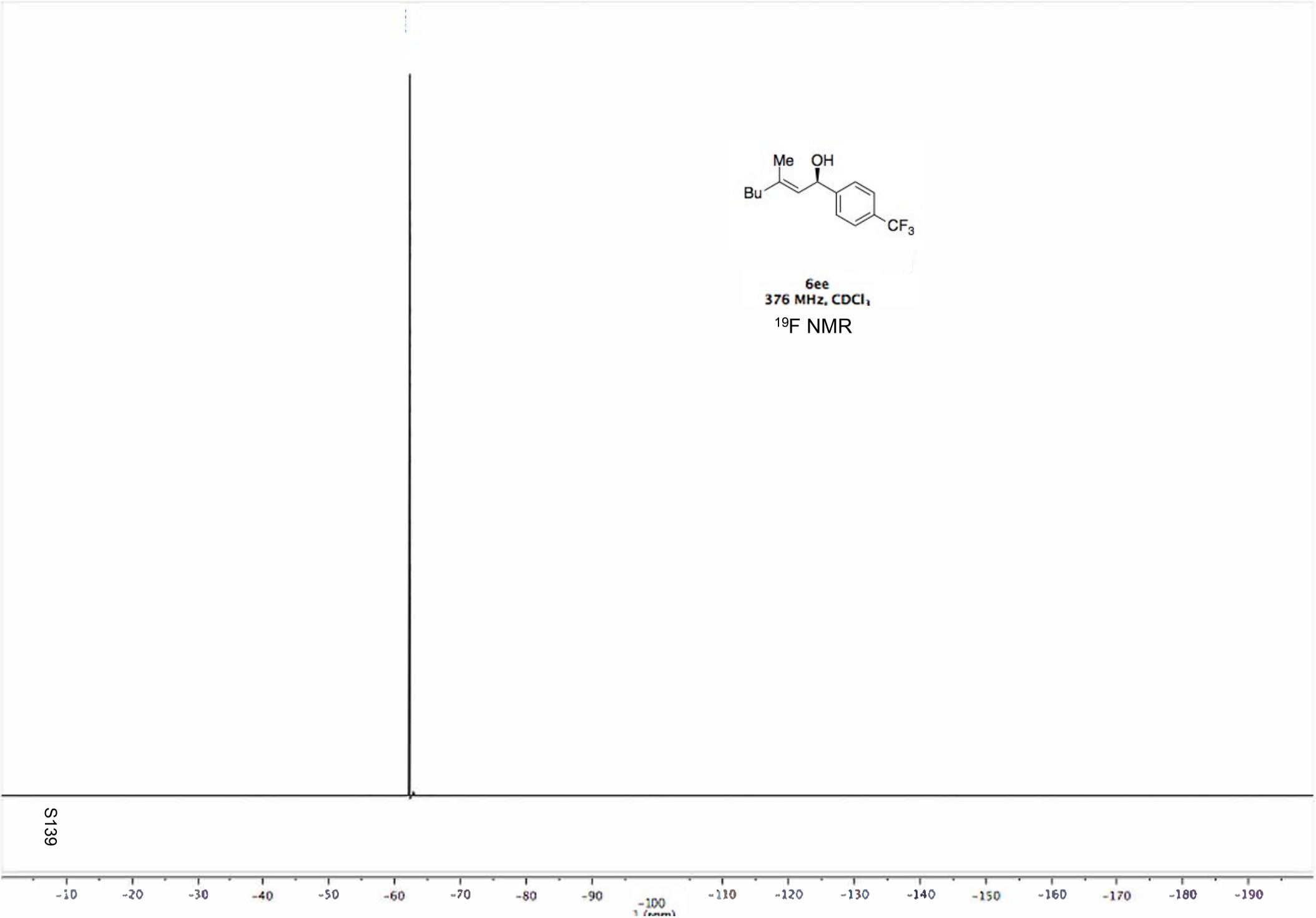

Me
OH
Bu
CN
6dd
400 MHz, CDCl3
CDCl3
2.01
1.98
1.00
1.00
1.99
3.42
2.00
2.07
3.03
f1 (ppm)



6dd
101 MHz, $CDCl_3$

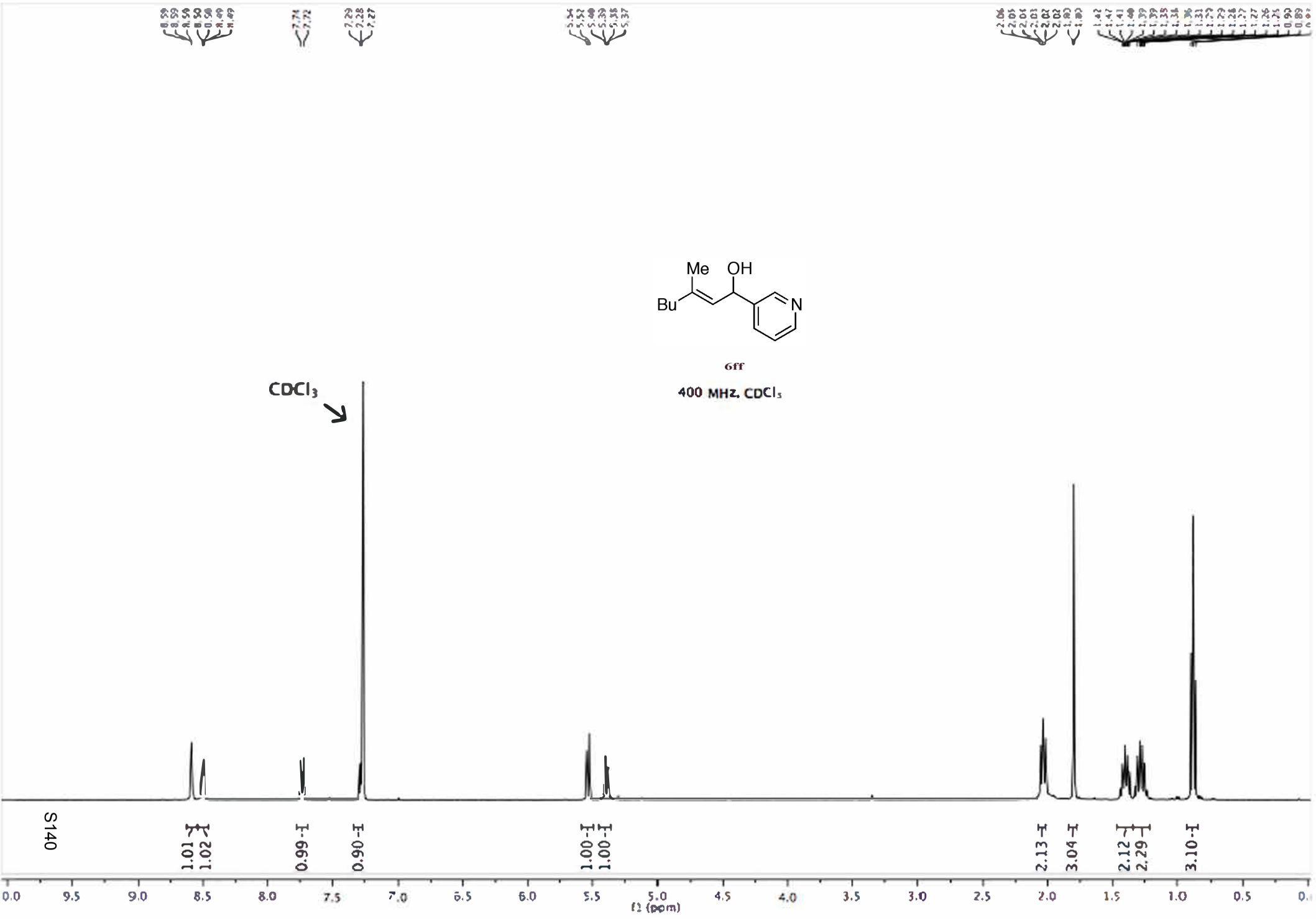

Me
OH
Bu
CF3
6ee
400 MHz, CDCl3
CDCl3
2.01
2.01
1.00
1.00
1.99
2.95
0.92
2.13
2.13
3.05
f1 (ppm)

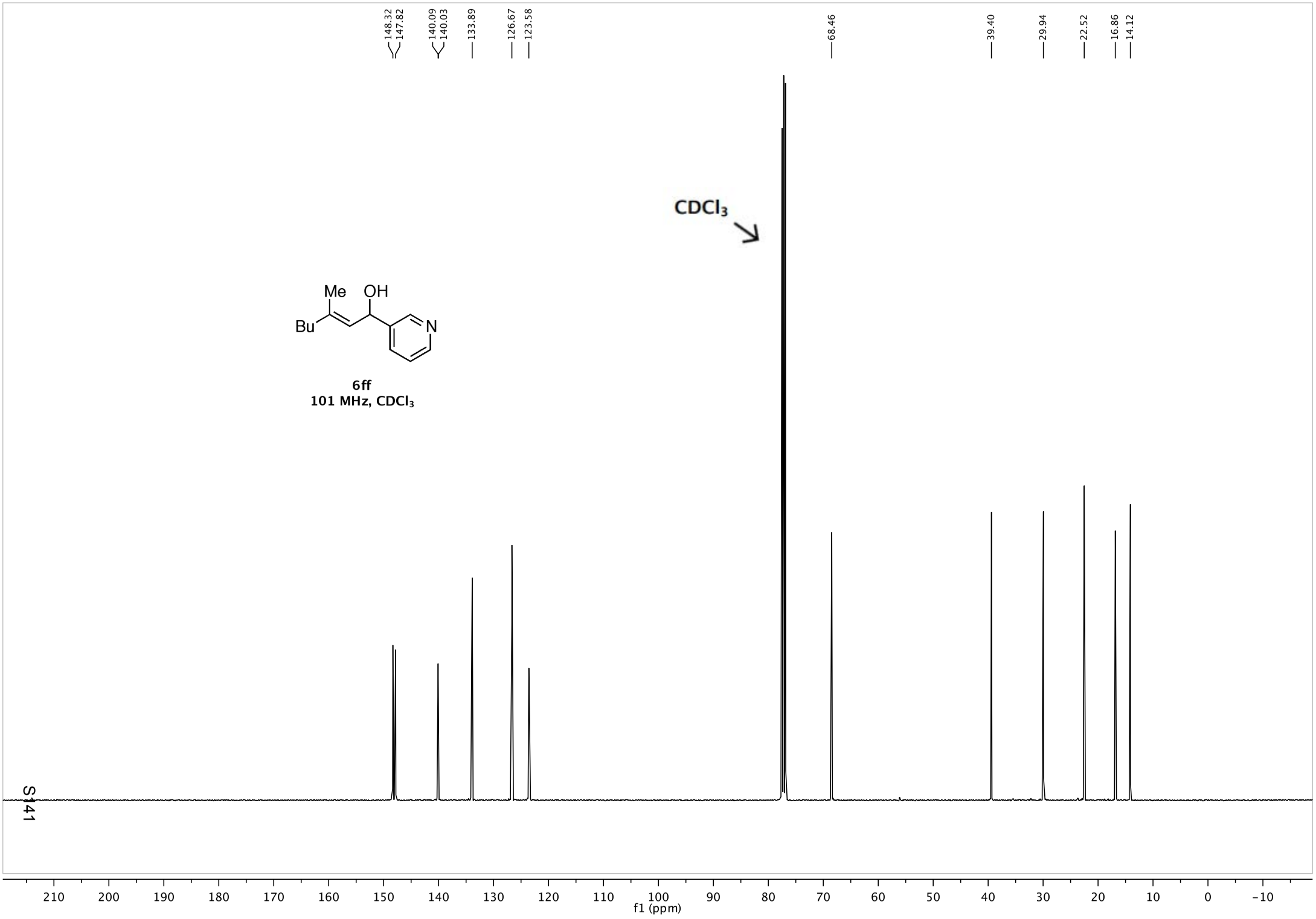

148.26
140.54
129.95
129.63
129.31
128.99
128.44
126.68
126.23
125.74
125.55
125.51
125.48
125.44
123.04
120.34
70.21
39.47
29.95
22.54
16.88
14.12
Me
OH
Bu
CF3
6ee
101 MHz, CDCl3
CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

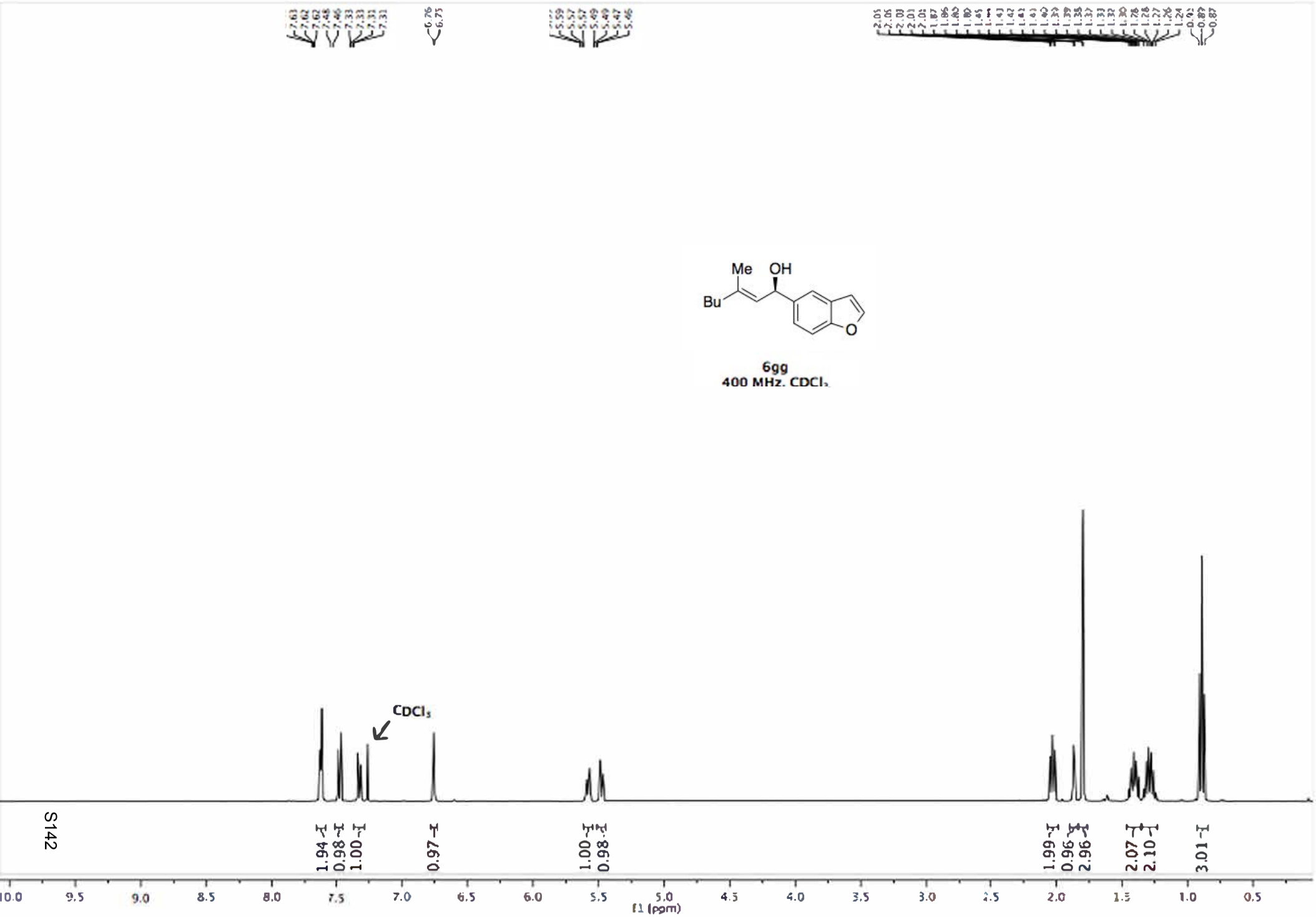


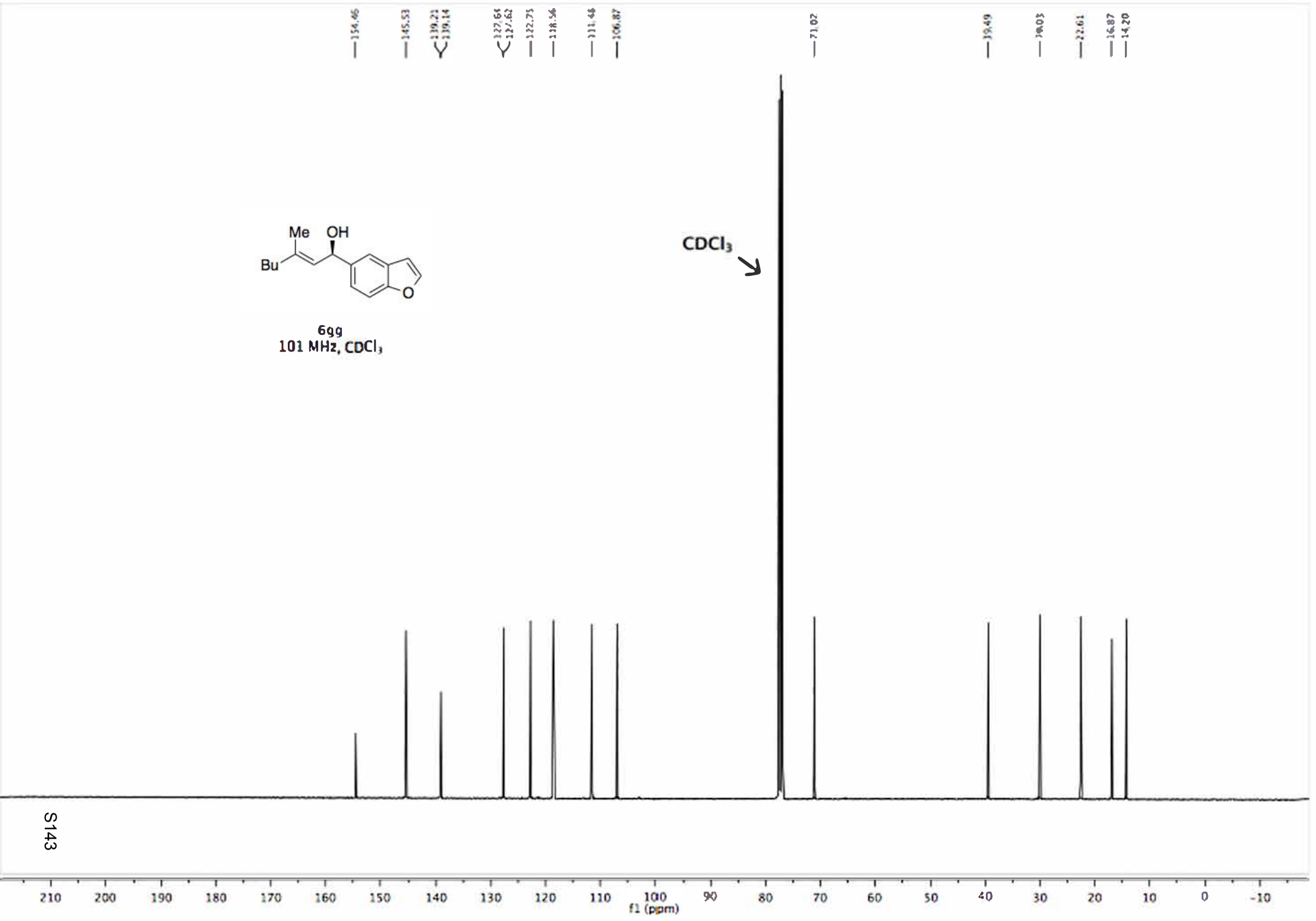
6ee
376 MHz, $CDCl_3$

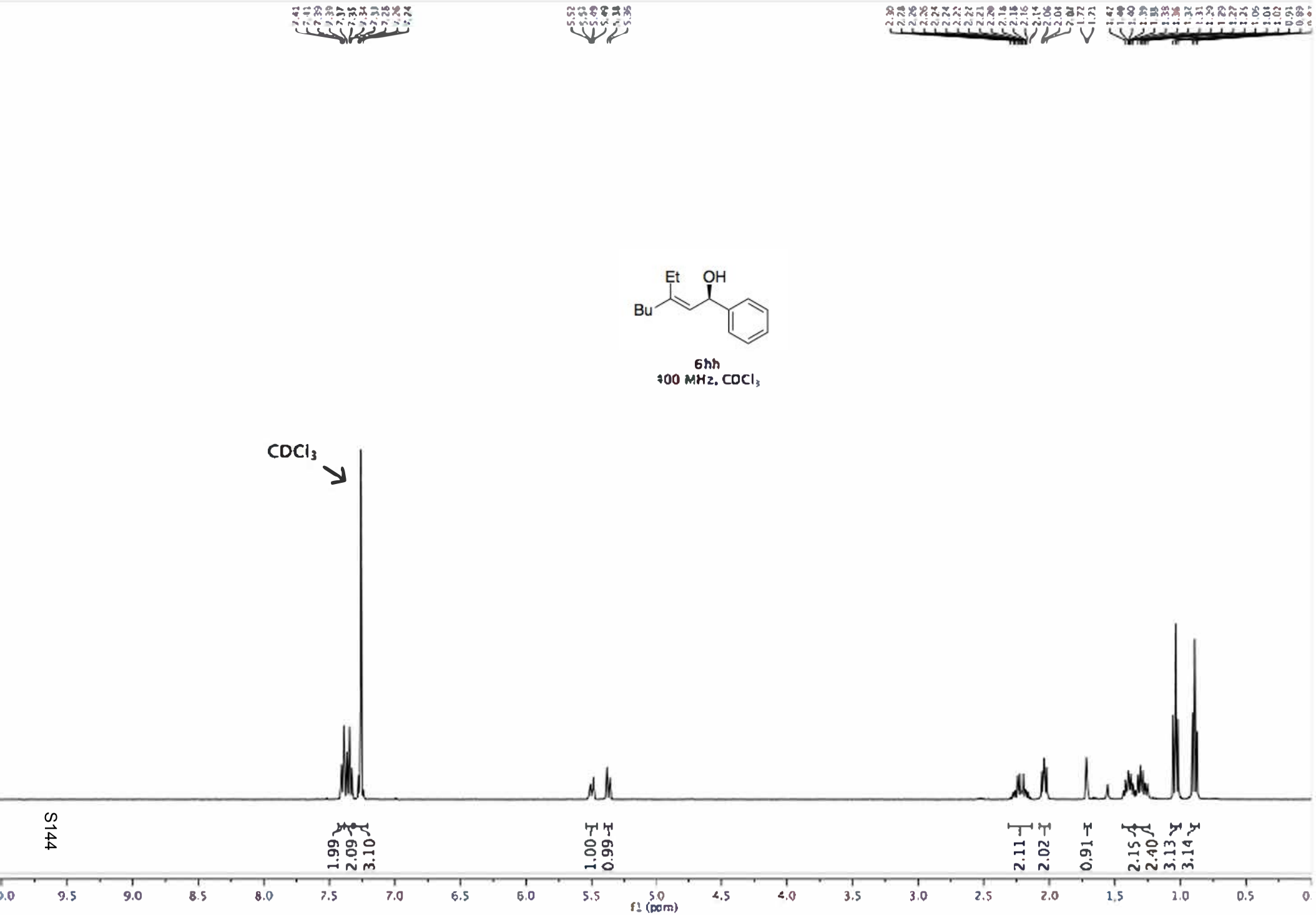
^{19}F NMR

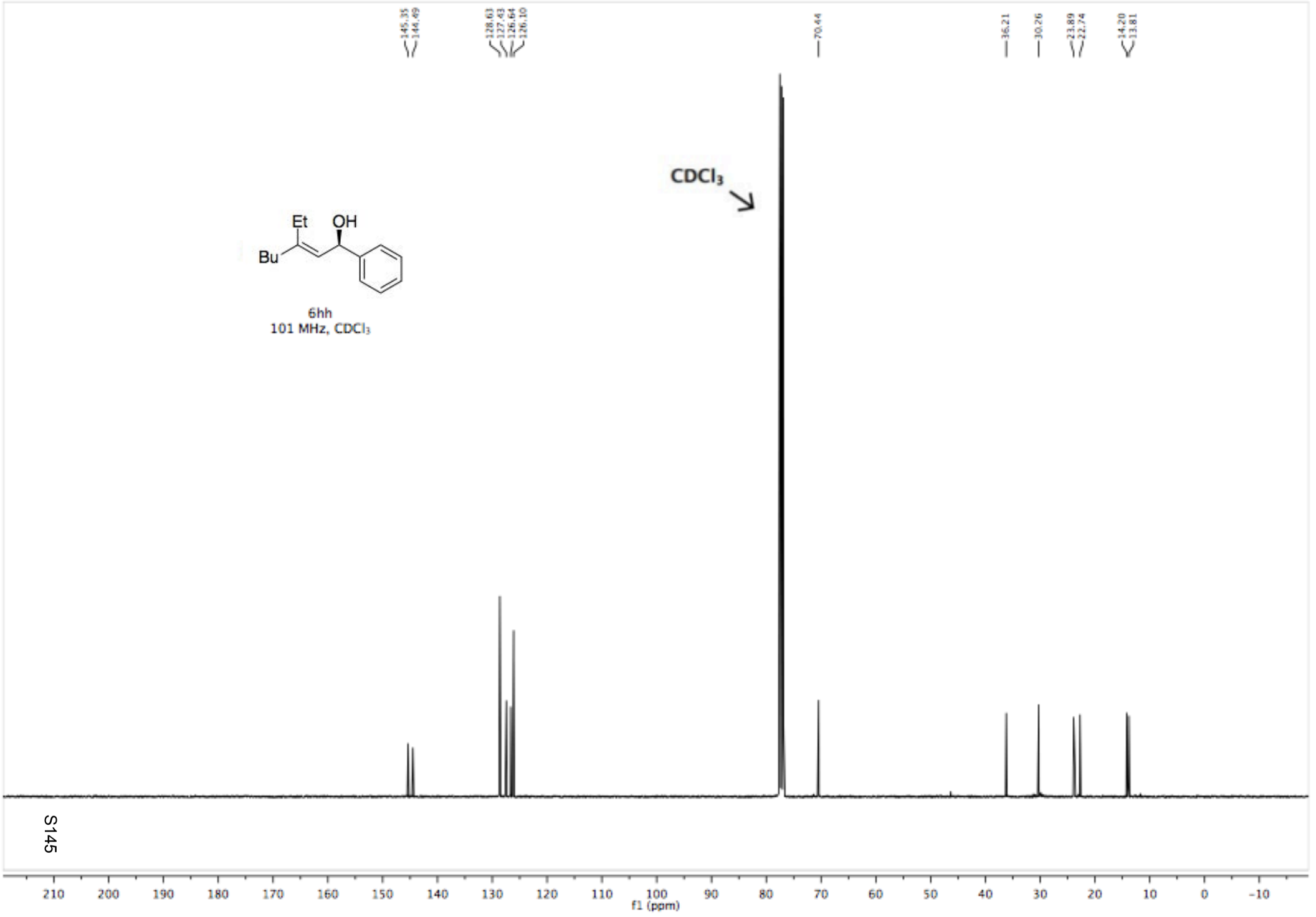

Me
OH
Bu
N
6ff
400 MHz, CDCl3
CDCl3
S140
1.01
1.02
0.99
0.90
1.00
1.00
2.13
3.04
2.12
2.29
3.10
f2 (ppm)

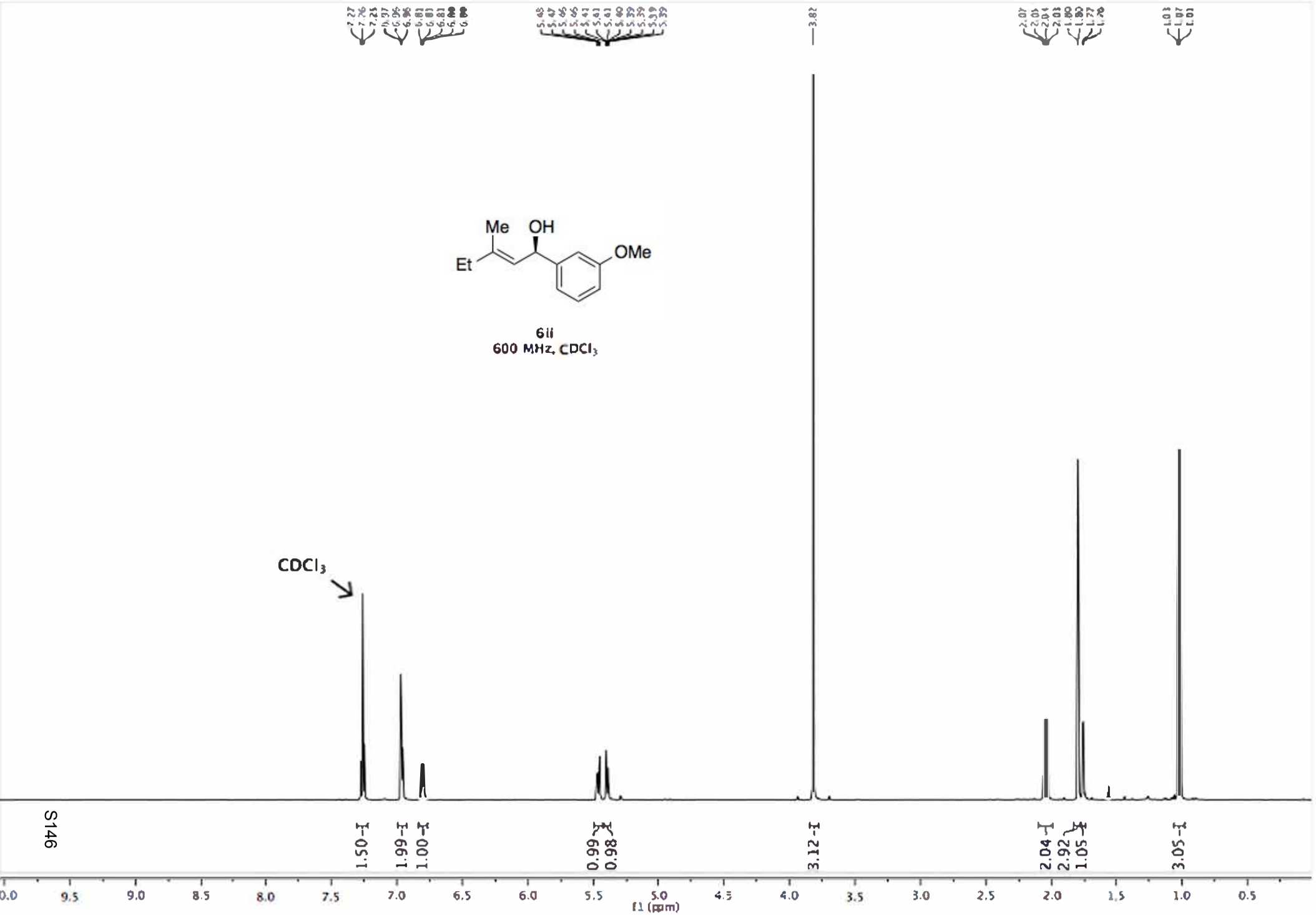

148.32
147.82
140.09
140.03
133.89
126.67
123.58
68.46
39.40
29.94
22.52
16.86
14.12
CDCl3
Me
OH
Bu
N
6ff
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

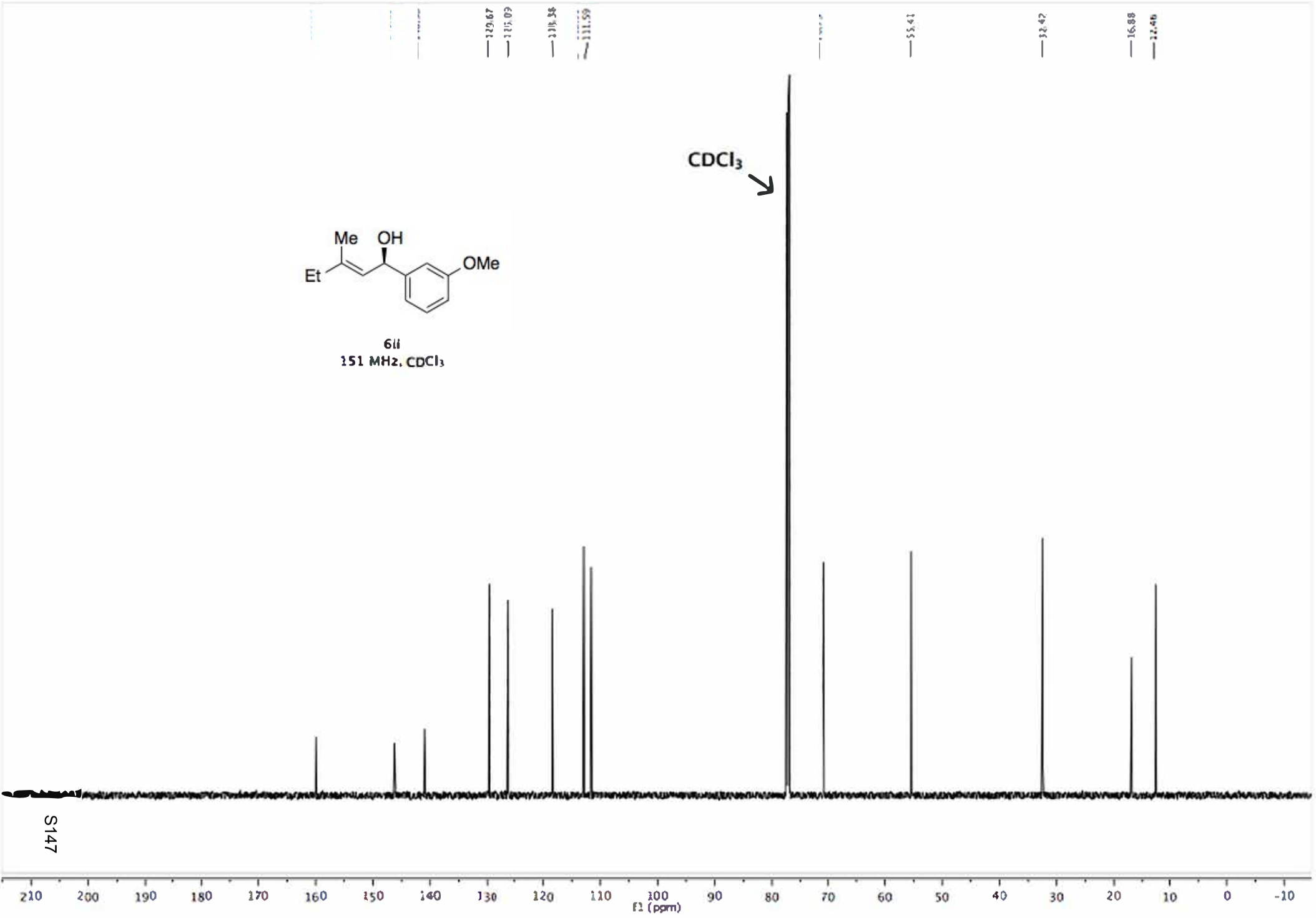

Me
OH
Bu
O
6gg
400 MHz, CDCl3
CDCl3
1.94
0.98
1.00
0.97
1.00
0.98
1.99
0.96
2.96
2.07
2.10
3.01
f1 (ppm)

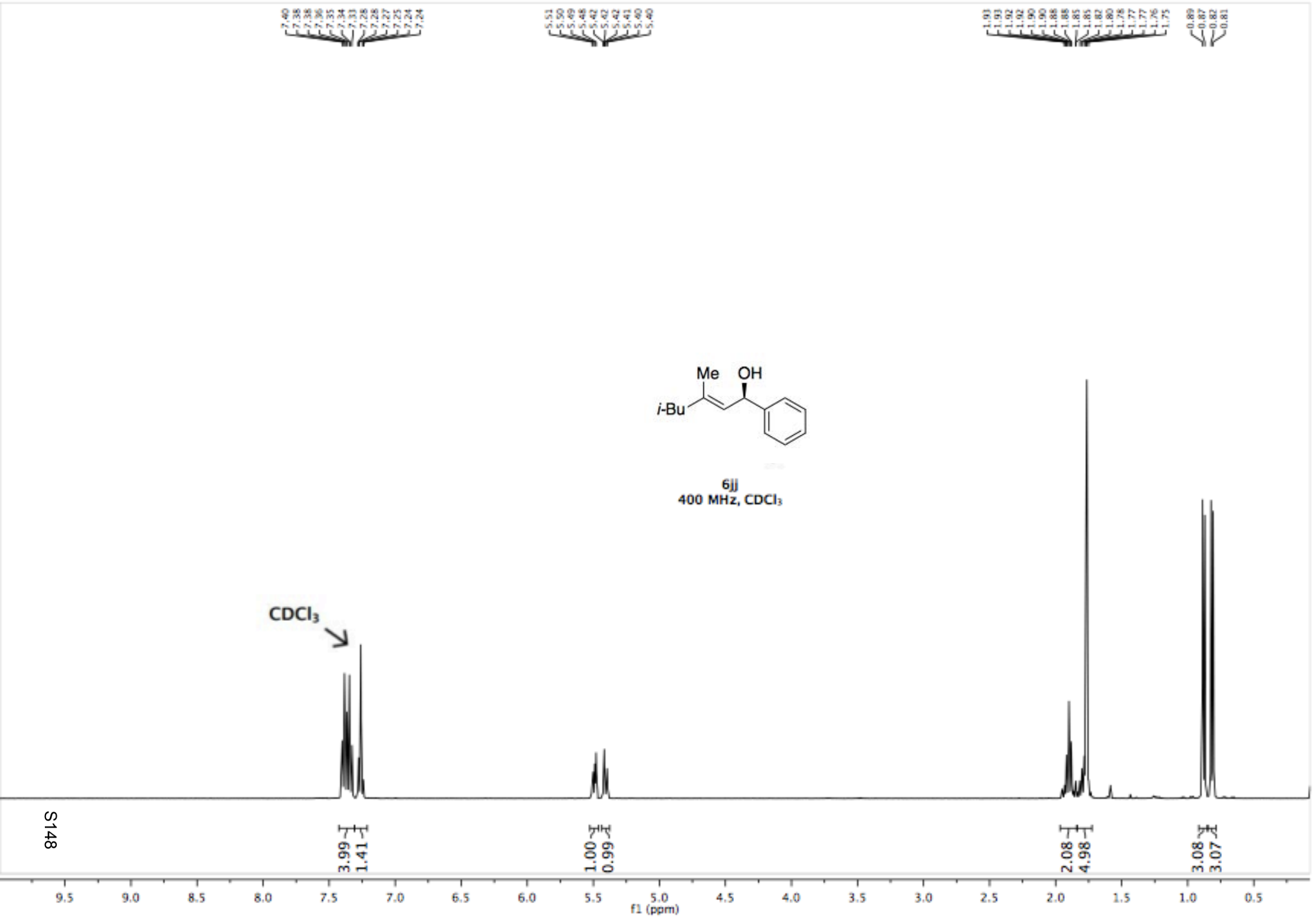

154.46
145.53
139.21
139.14
127.64
127.62
122.73
118.56
111.48
106.87
71.02
39.49
30.03
22.61
16.87
14.20
Me
OH
Bu
O
CDCl3
6gg
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

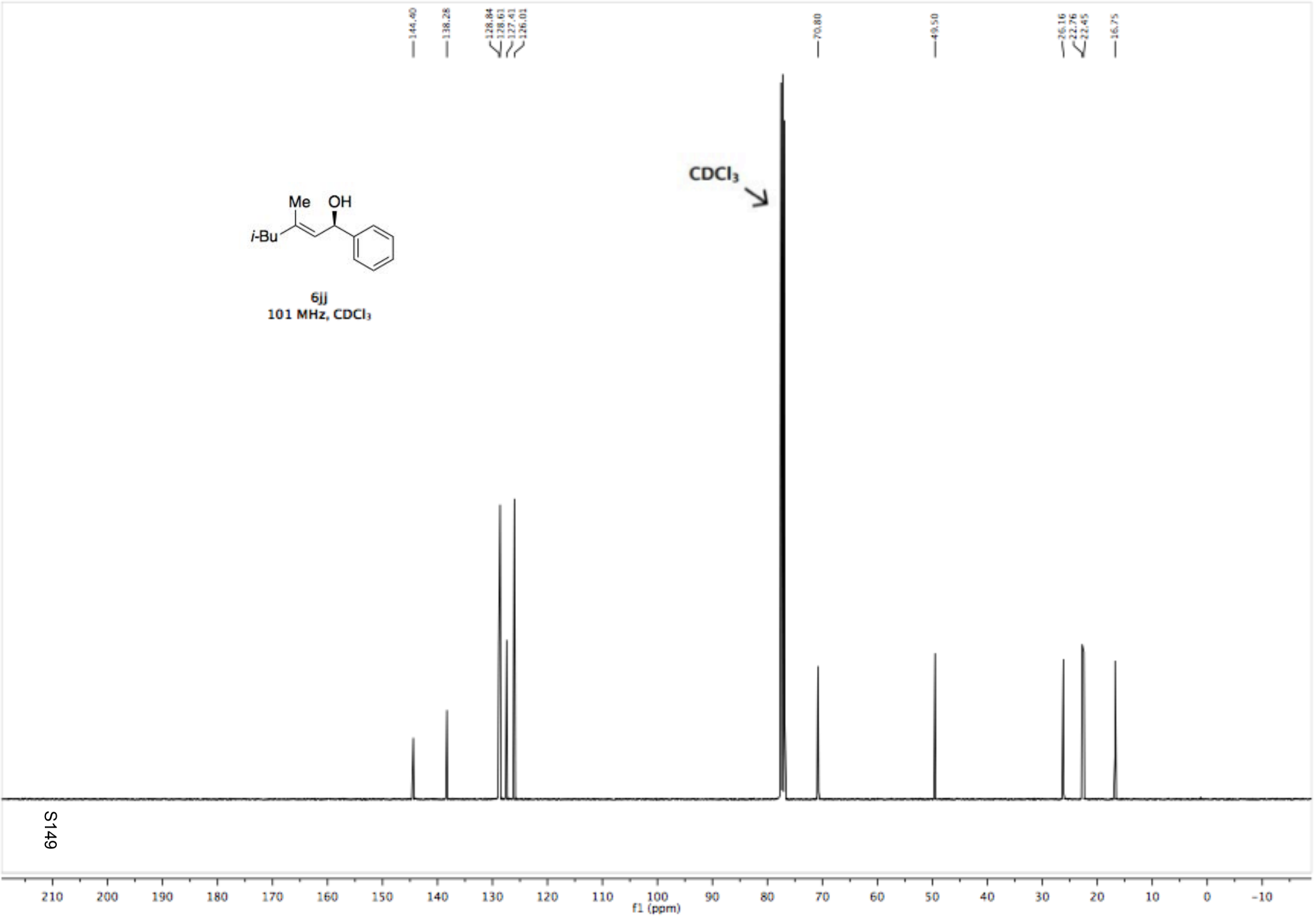

Et
OH
Bu
6hh
400 MHz, CDCl3
CDCl3
1.99
2.09
3.10
1.00
0.99
2.11
2.02
0.91
2.15
2.40
3.13
3.14
f1 (ppm)


145.35
144.49
128.63
127.43
126.64
126.10
70.44
36.21
30.26
23.89
22.74
14.20
13.81
CDCl3
Et
OH
Bu
6hh
101 MHz, 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)

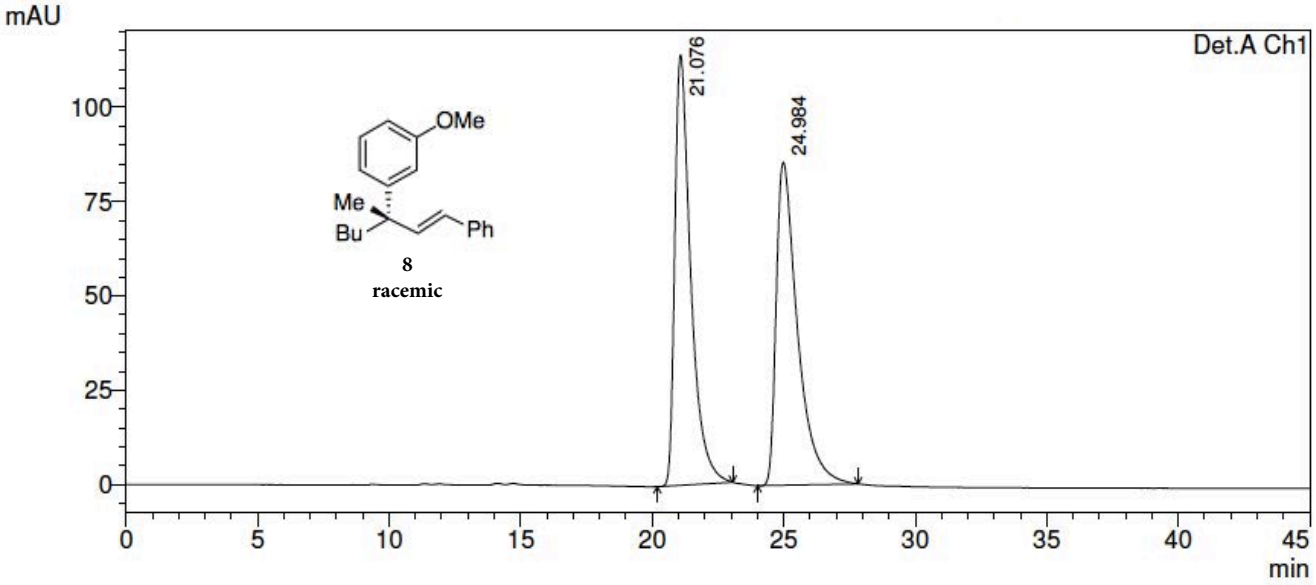

Me
OH
Et
OMe
6ii
600 MHz, CDCl3
CDCl3
1.50-I
1.99-I
1.00-I
0.99
0.98
3.12-I
2.04-I
2.92
1.05
3.05-I
f1 (ppm)


129.67
55.41
32.42
16.88
CDCl3
Me
OH
Et
OMe
6ll
151 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f2 (ppm)


7.40
7.38
7.38
7.36
7.35
7.34
7.33
7.28
7.28
7.27
7.25
7.24
7.24
5.51
5.50
5.49
5.48
5.42
5.42
5.42
5.41
5.40
5.40
1.93
1.93
1.92
1.92
1.90
1.90
1.88
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
OH
i-Bu
6jj
400 MHz, CDCl3
CDCl3
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
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

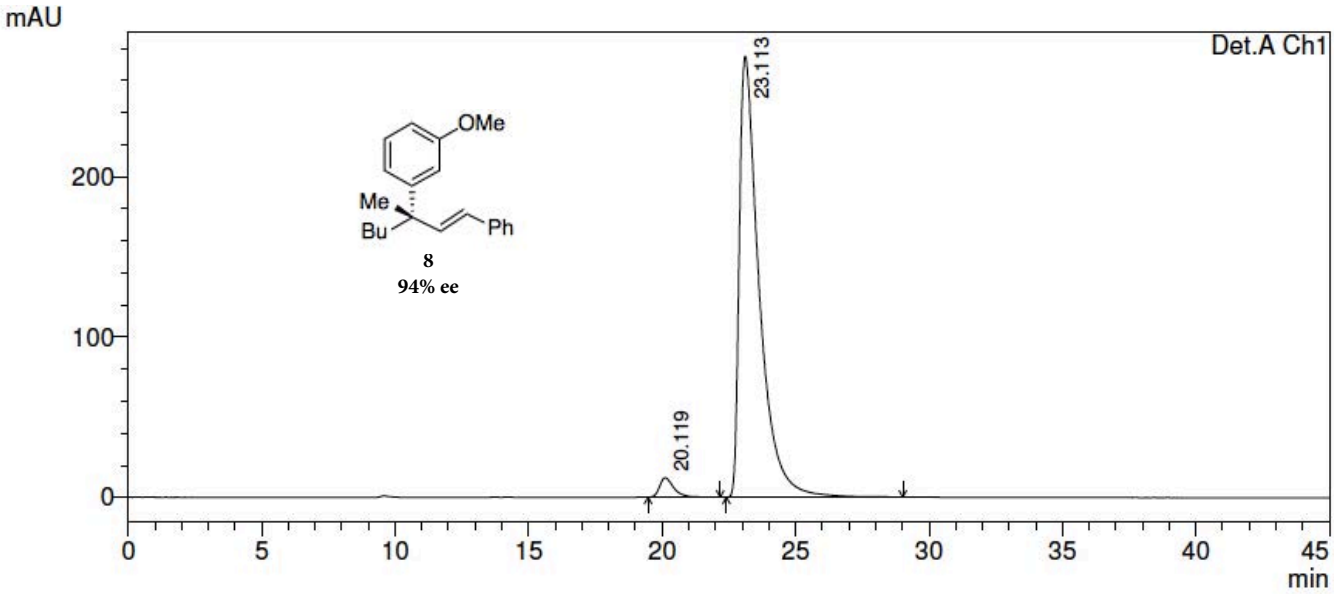

144.40
138.28
128.84
128.61
127.41
126.01
70.80
49.50
26.16
22.76
22.45
16.75
CDCl3
Me
OH
i-Bu
6jj
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

Compound 8, racemic



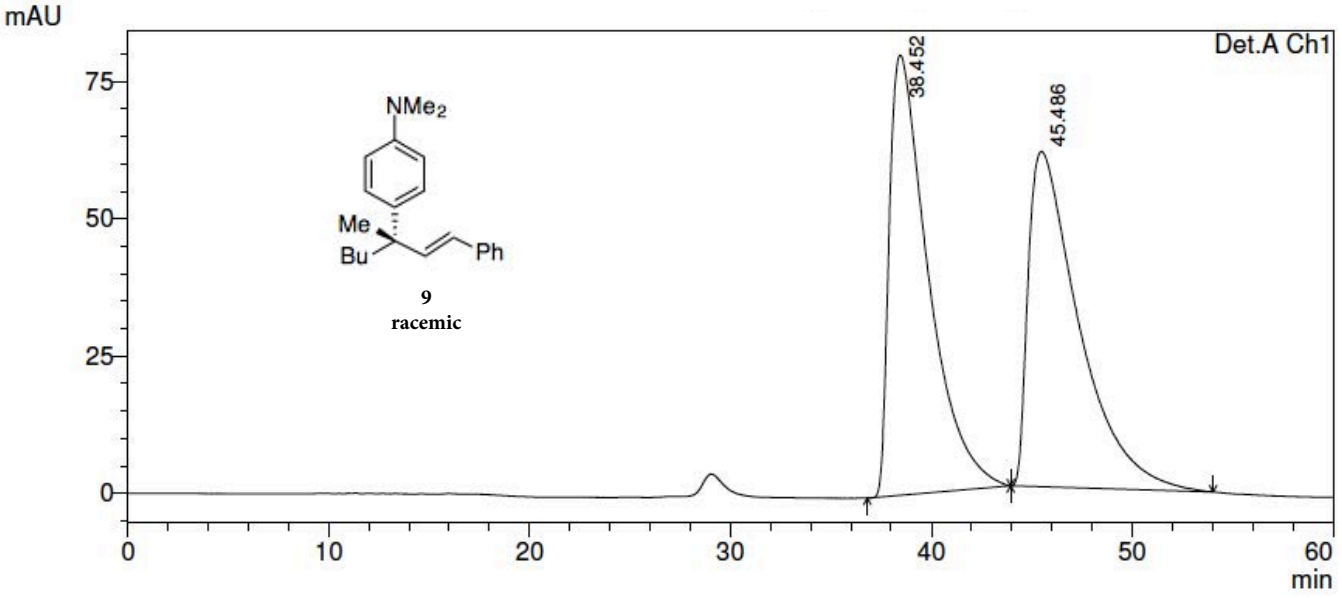
Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.076	4819547	114091	50.036	57.126
2	24.984	4812611	85626	49.964	42.874
Total		9632158	199717	100.000	100.000

Compound 8, 94% ee



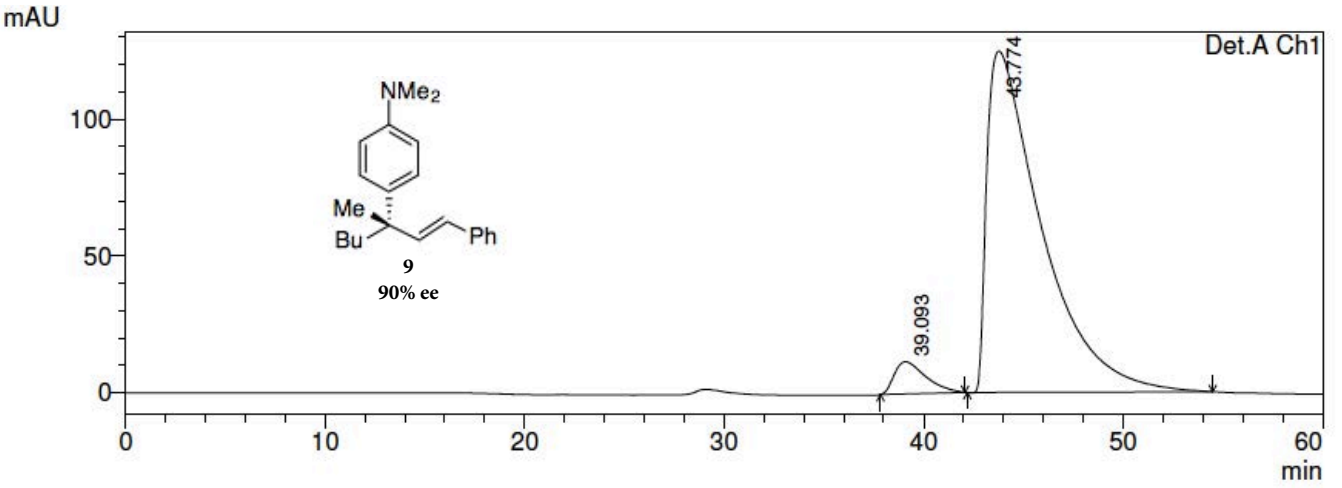
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.119	448026	12139	3.043	4.229
2	23.113	14275387	274912	96.957	95.771
Total		14723413	287051	100.000	100.000

Compound 9, 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

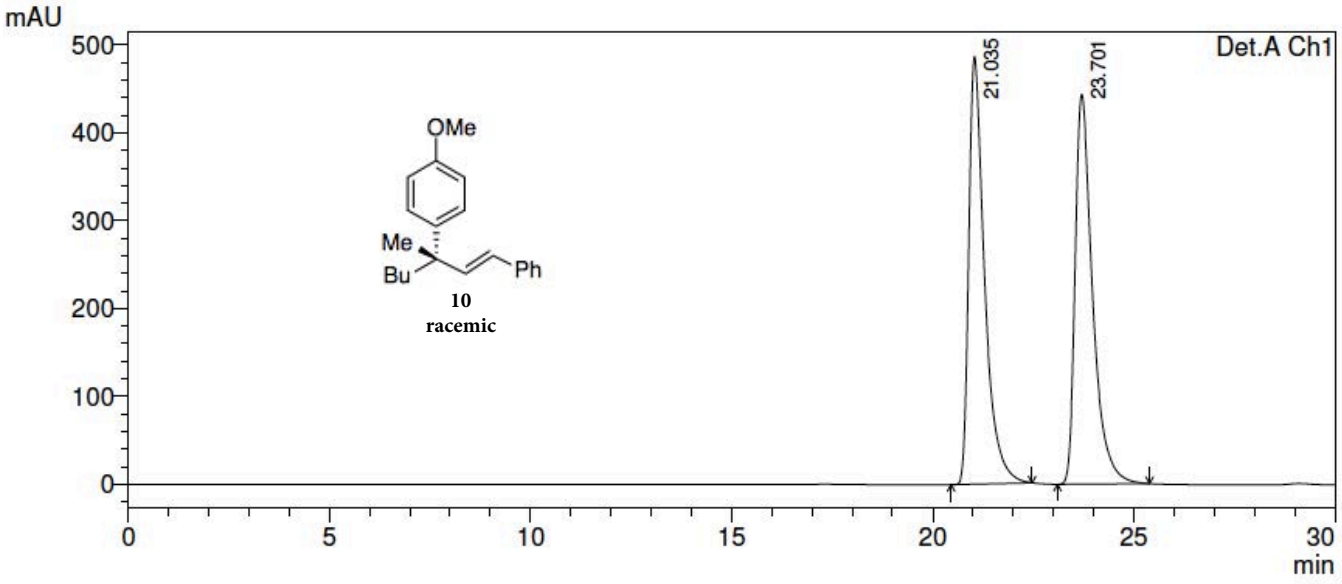
Compound 9, 90% ee



Detector A Ch1 254nm

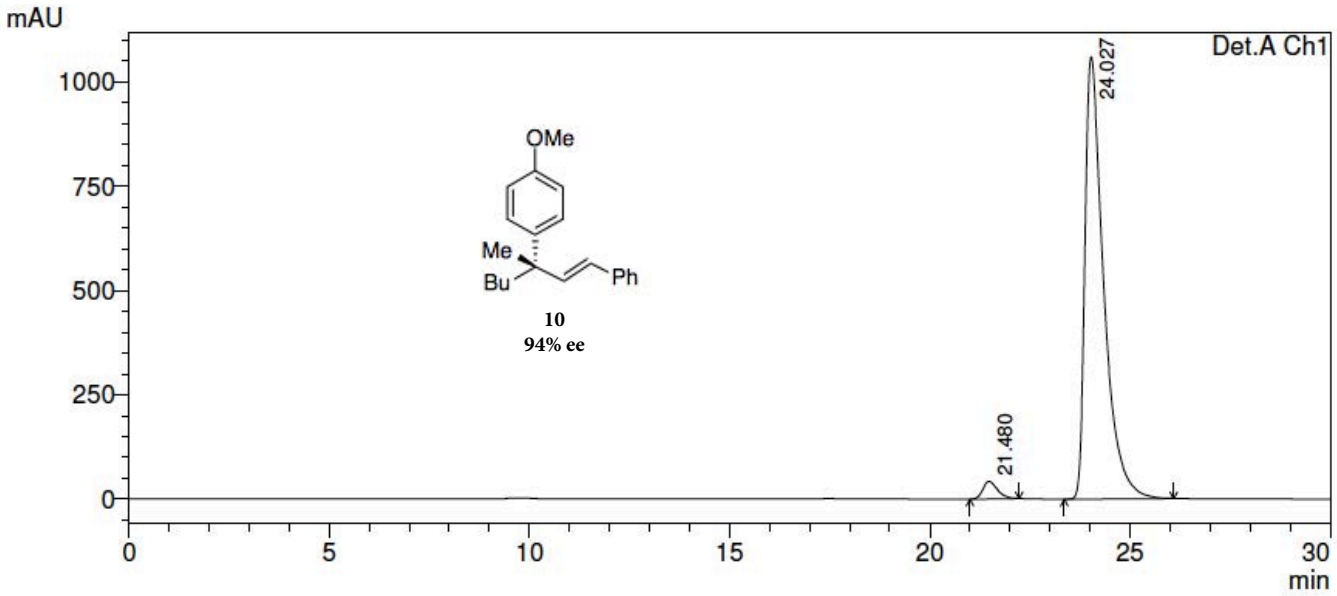
Peak#	Ret. Time	Area	Height	Area %	Height %
1	39.093	1294517	11782	5.156	8.625
2	43.774	23813212	124819	94.844	91.375
Total		25107729	136601	100.000	100.000

Compound 10, racemic



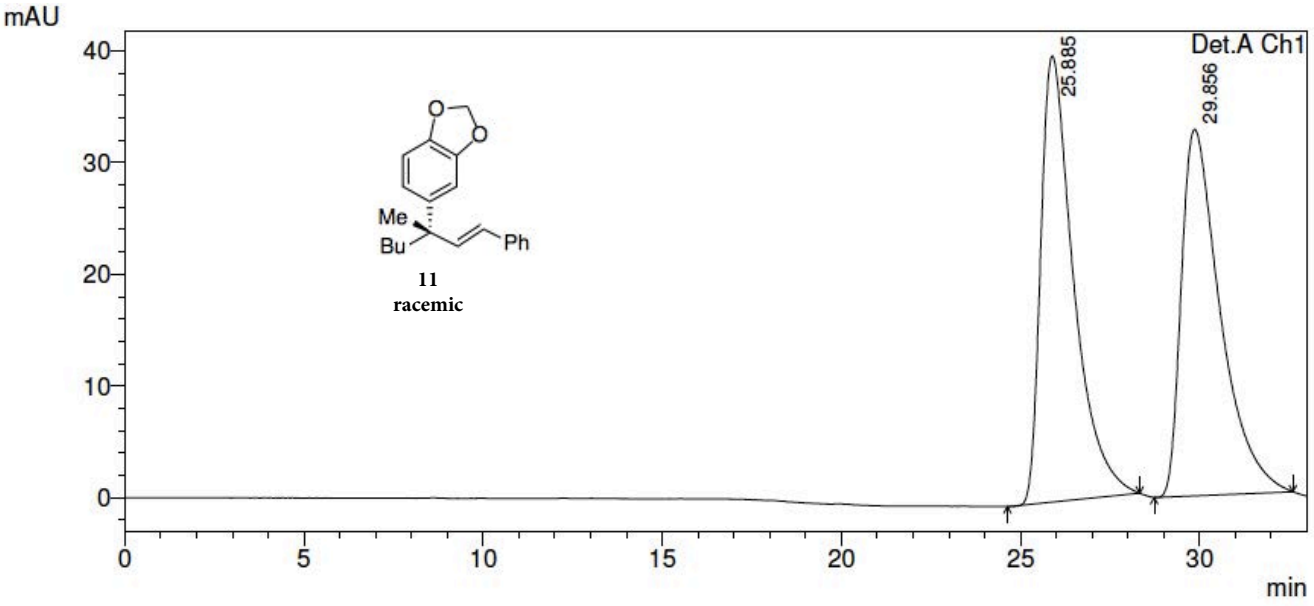
Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.035	13304169	487298	49.915	52.348
2	23.701	13349360	443582	50.085	47.652
Total		26653529	930881	100.000	100.000

Compound 10, 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

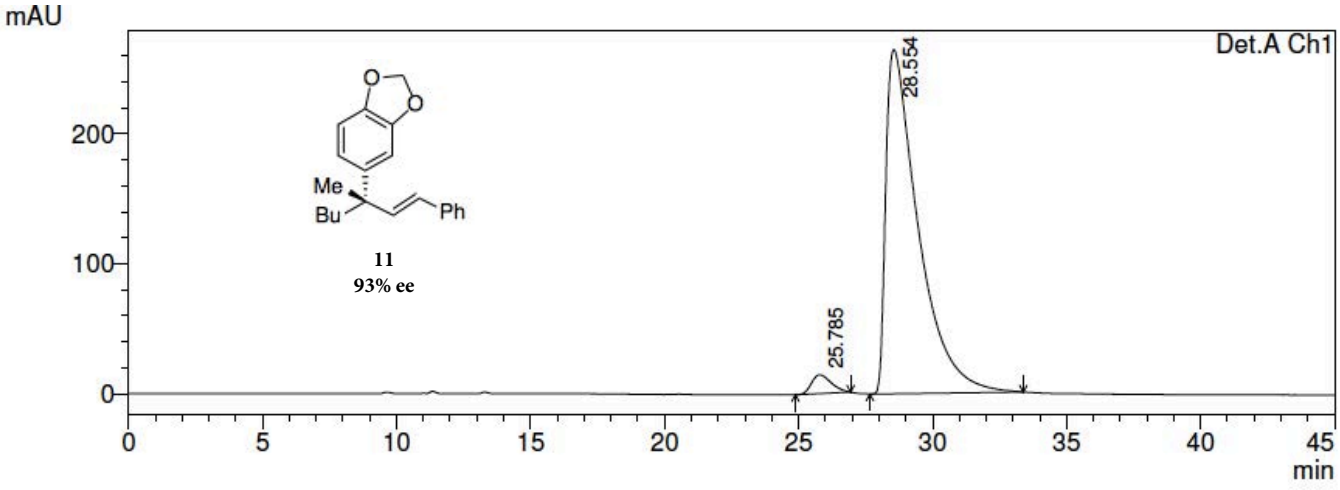
Compound 11, racemic



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

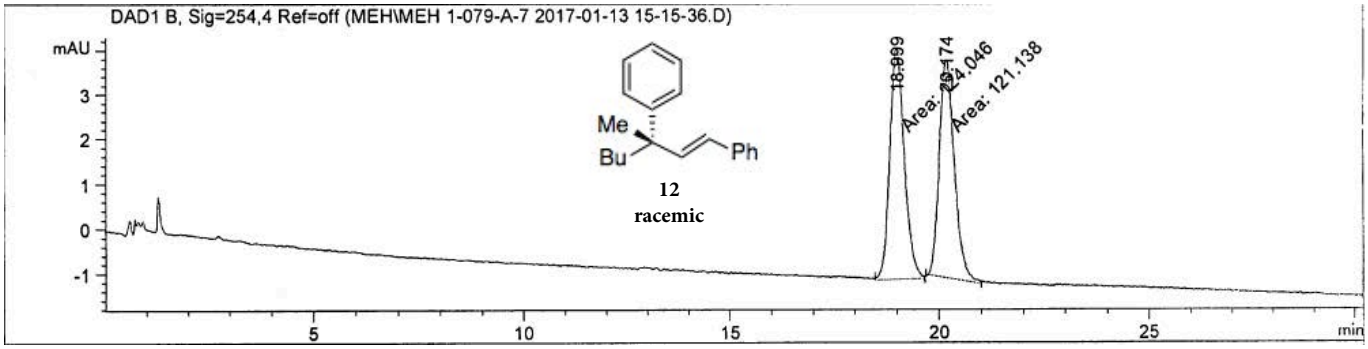
Compound 11, 93% ee



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

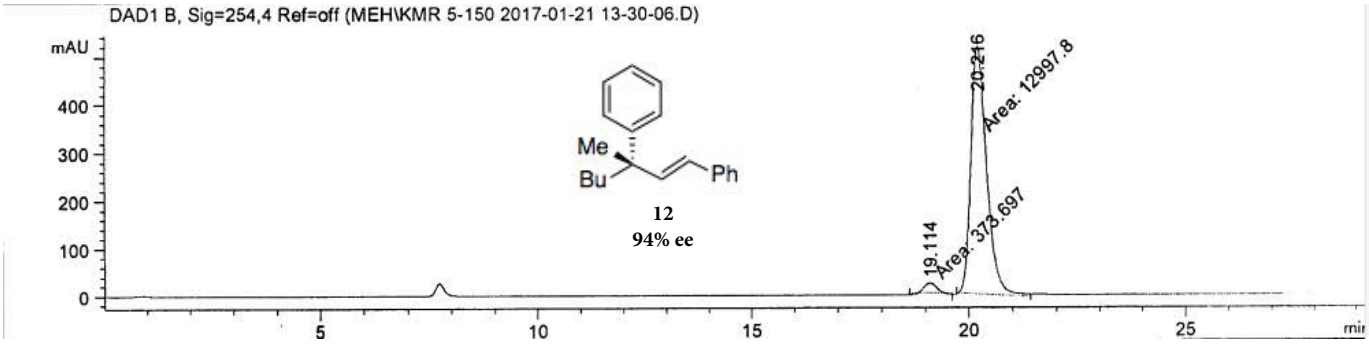
Compound 12, racemic



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	

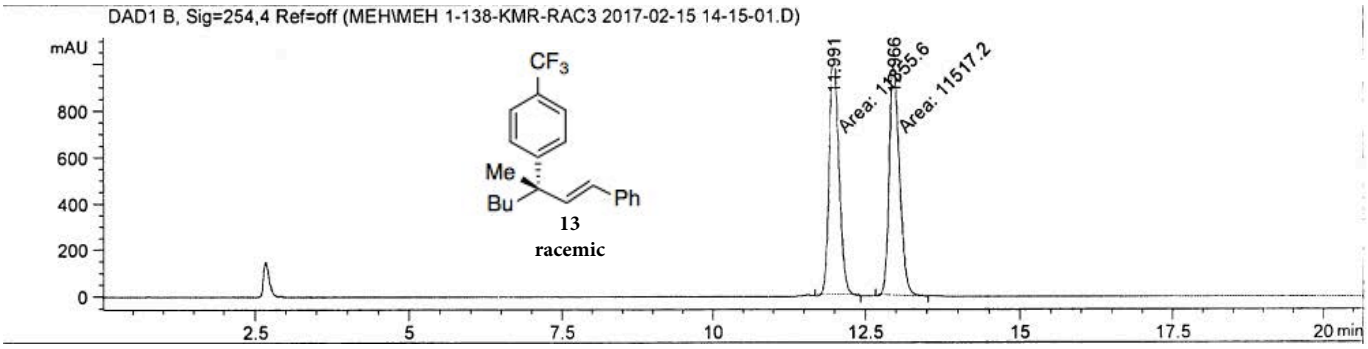
Compound 12, 94% ee



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	

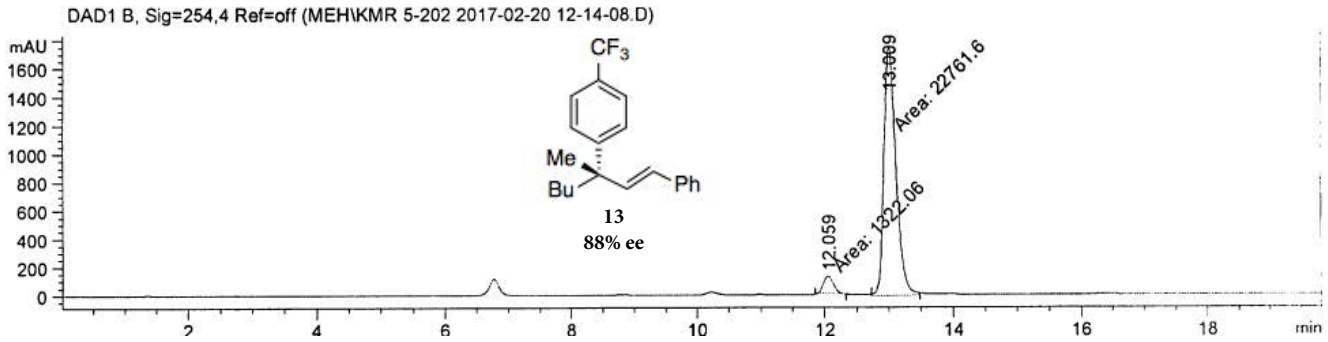
Compound 13, racemic



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	

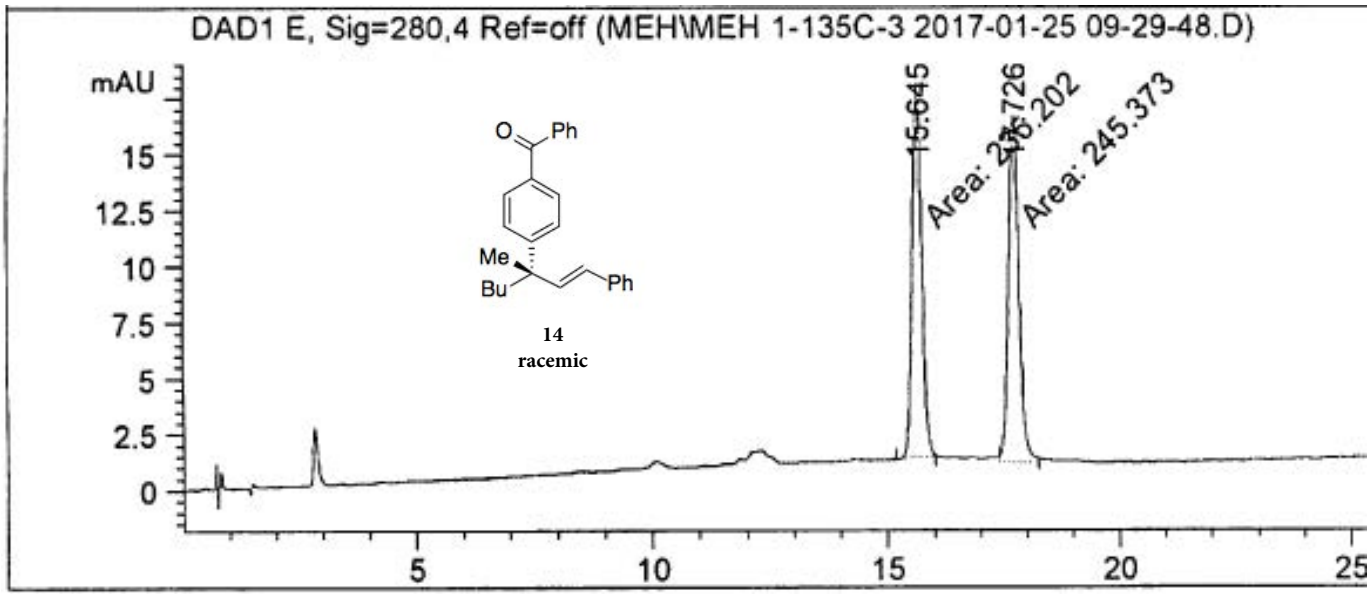
Compound 13, 88% ee



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	

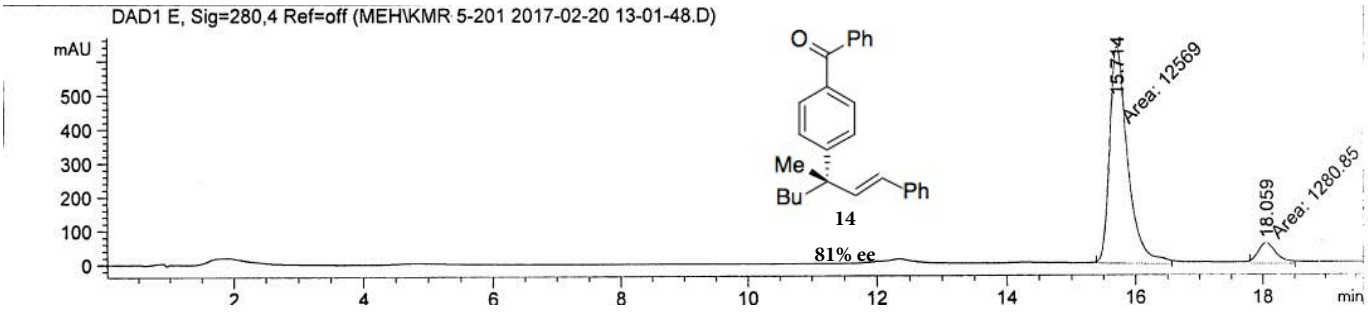
Compound 14, racemic



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	

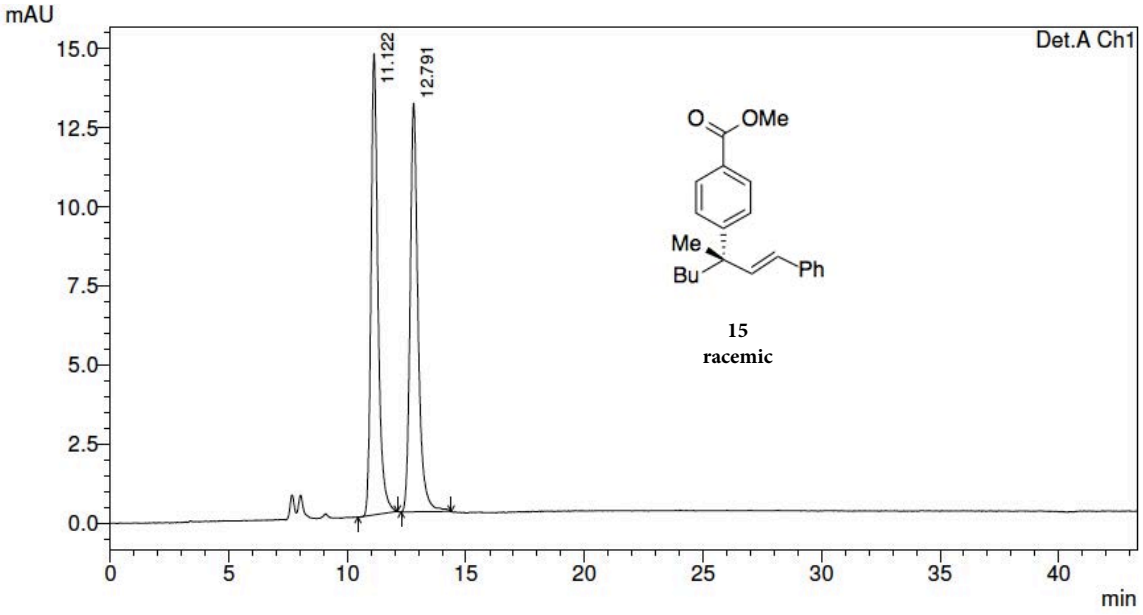
Compound 14, 81% ee



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	

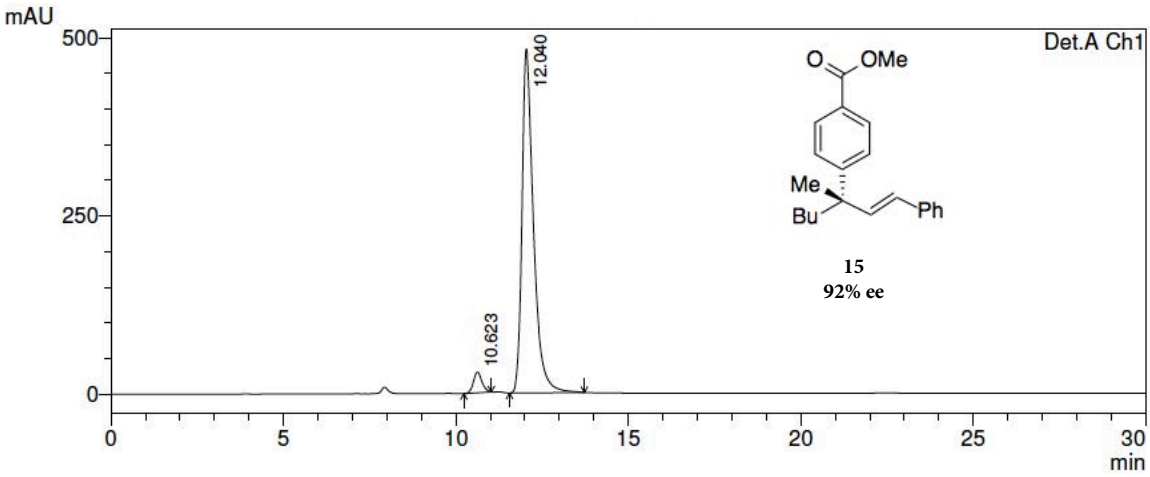
Compound 15, racemic



Detector A Ch1 254nm

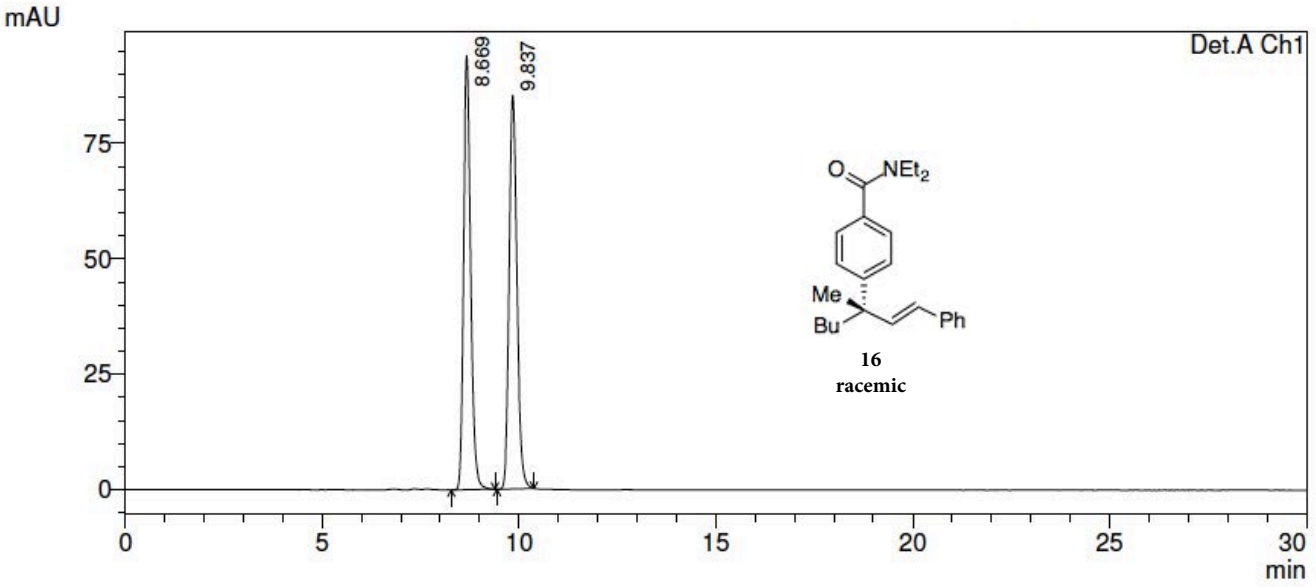
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.122	299350	14583	49.727	53.032
2	12.791	302638	12916	50.273	46.968
Total		601988	27499	100.000	100.000

Compound 15, 92% ee



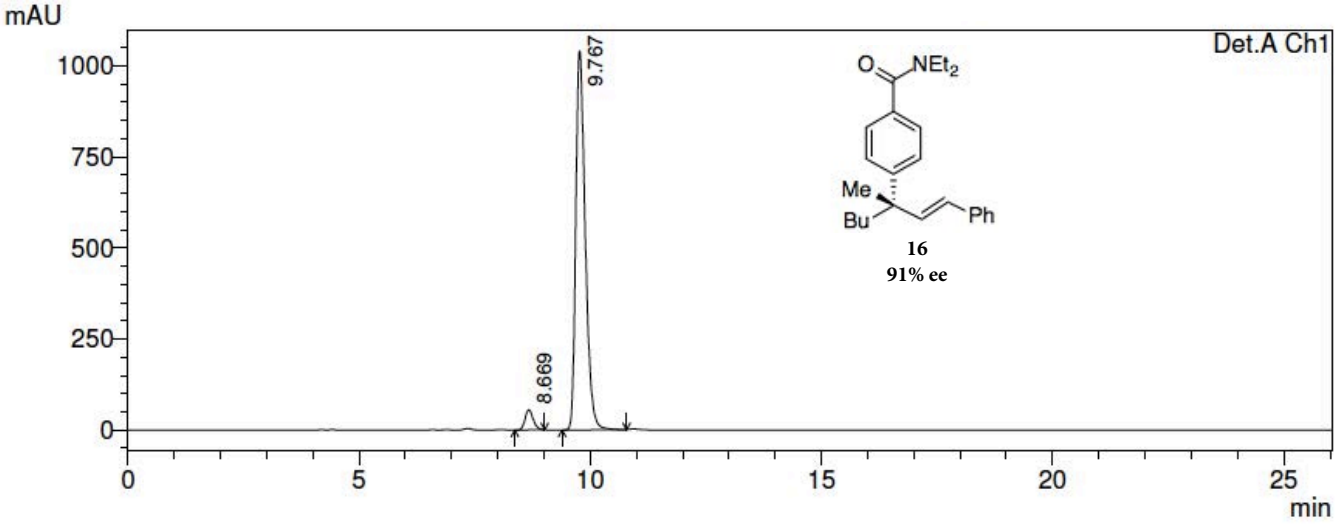
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.623	494765	29019	4.245	5.675
2	12.040	11159283	482281	95.755	94.325
Total		11654048	511299	100.000	100.000

Compound 16, 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

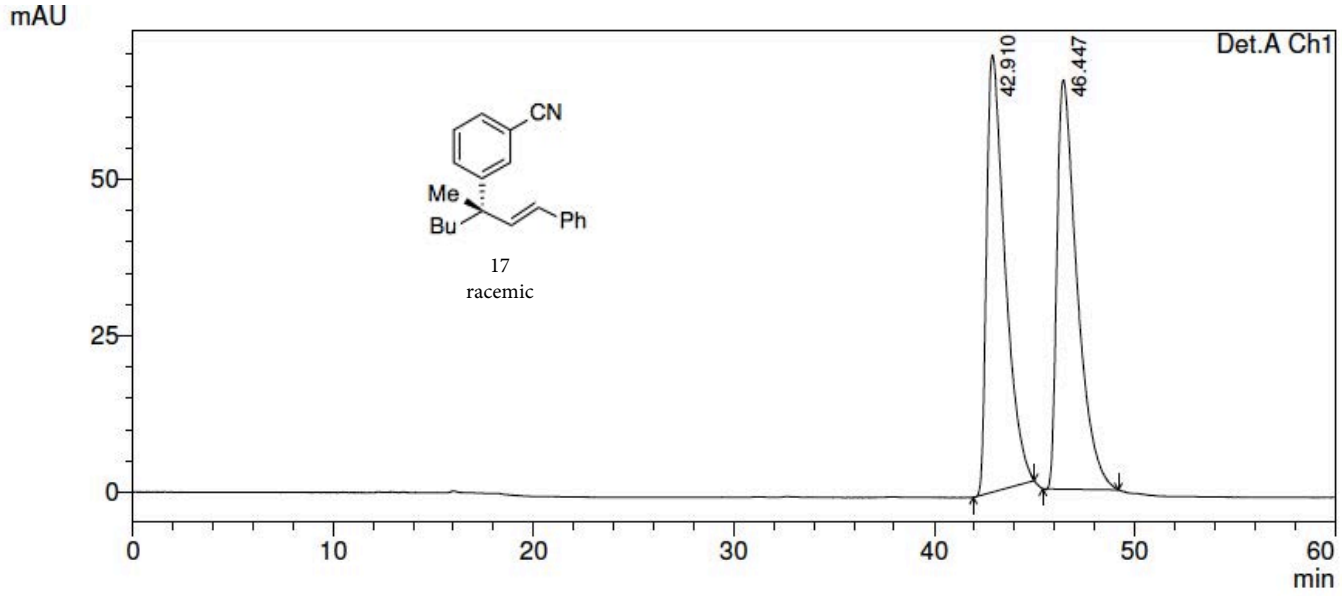
Compound 16, 91% ee



Detector A Ch1 254nm

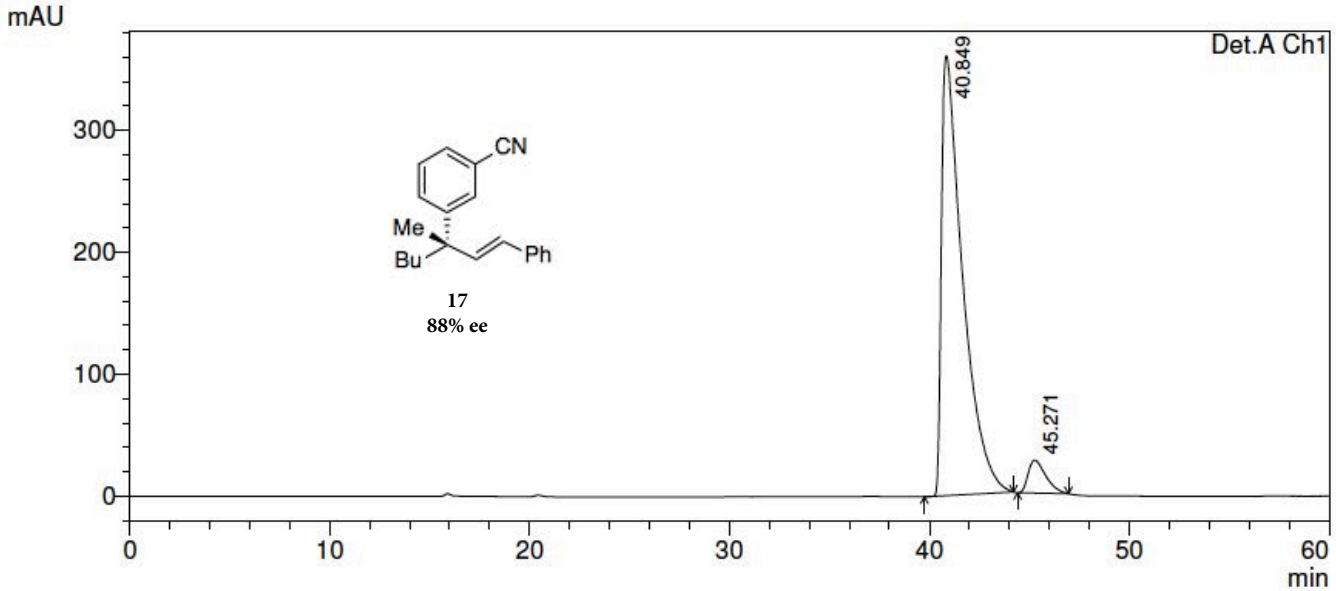
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.669	674026	55319	4.357	5.050
2	9.767	14797410	1040042	95.643	94.950
Total		15471436	1095361	100.000	100.000

Compound 17, racemic



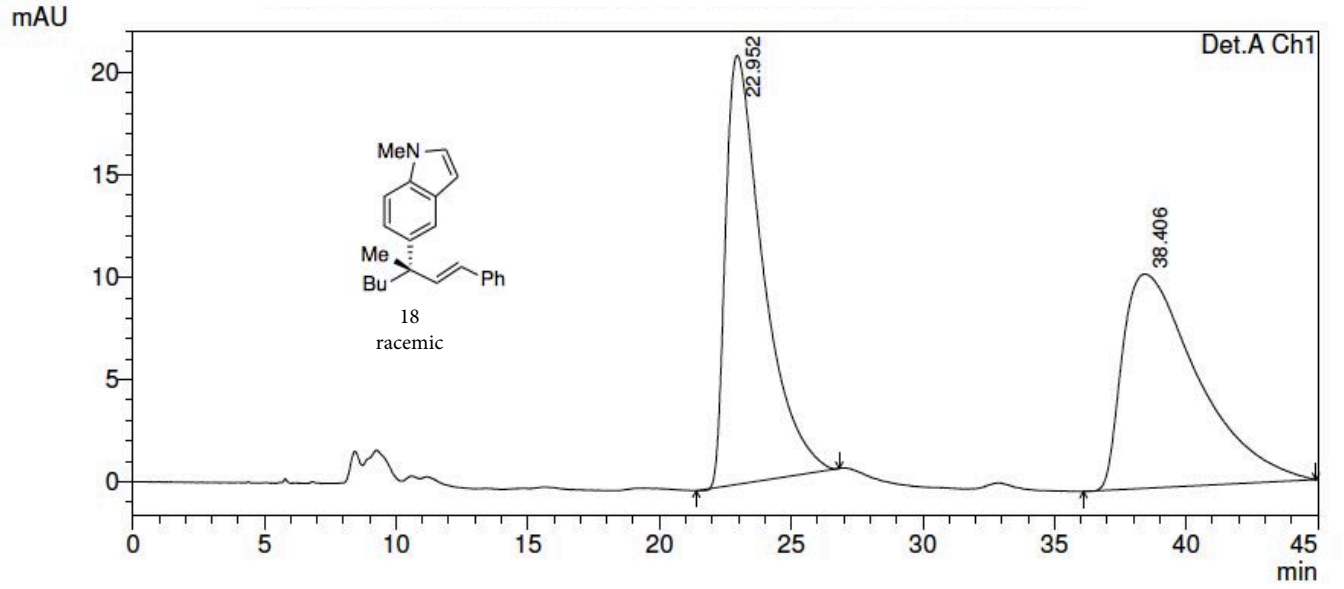
Peak#	Ret. Time	Area	Height	Area %	Height %
1	42.910	4486510	69917	49.505	51.658
2	46.447	4576267	65429	50.495	48.342
Total		9062777	135346	100.000	100.000

Compound 17, 88% ee



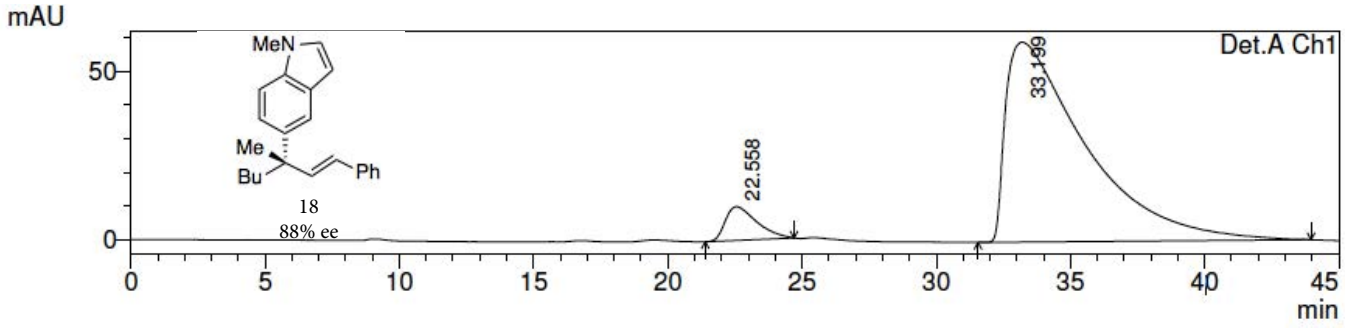
Peak#	Ret. Time	Area	Height	Area %	Height %
1	40.849	26586715	360699	94.130	93.030
2	45.271	1658039	27024	5.870	6.970
Total		28244754	387724	100.000	100.000

Compound 18, 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

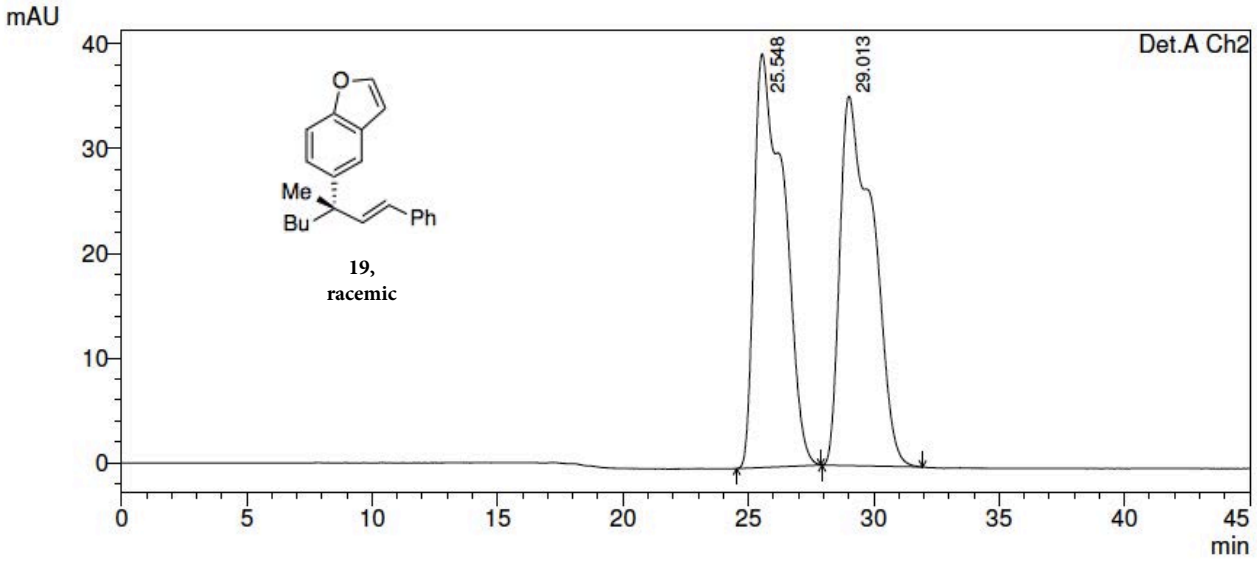
Compound 18, 88% ee



Detector A Ch1 254nm

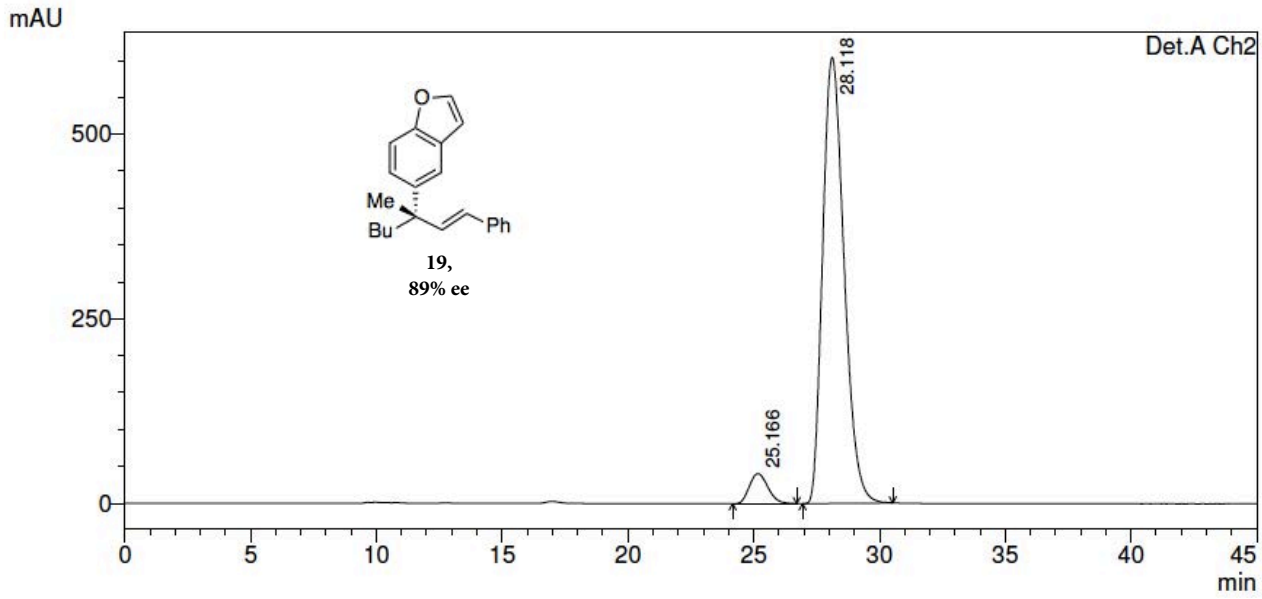
Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.558	809116	9988	6.153	14.383
2	33.199	12341591	59457	93.847	85.617
Total		13150707	69445	100.000	100.000

Compound 19, 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

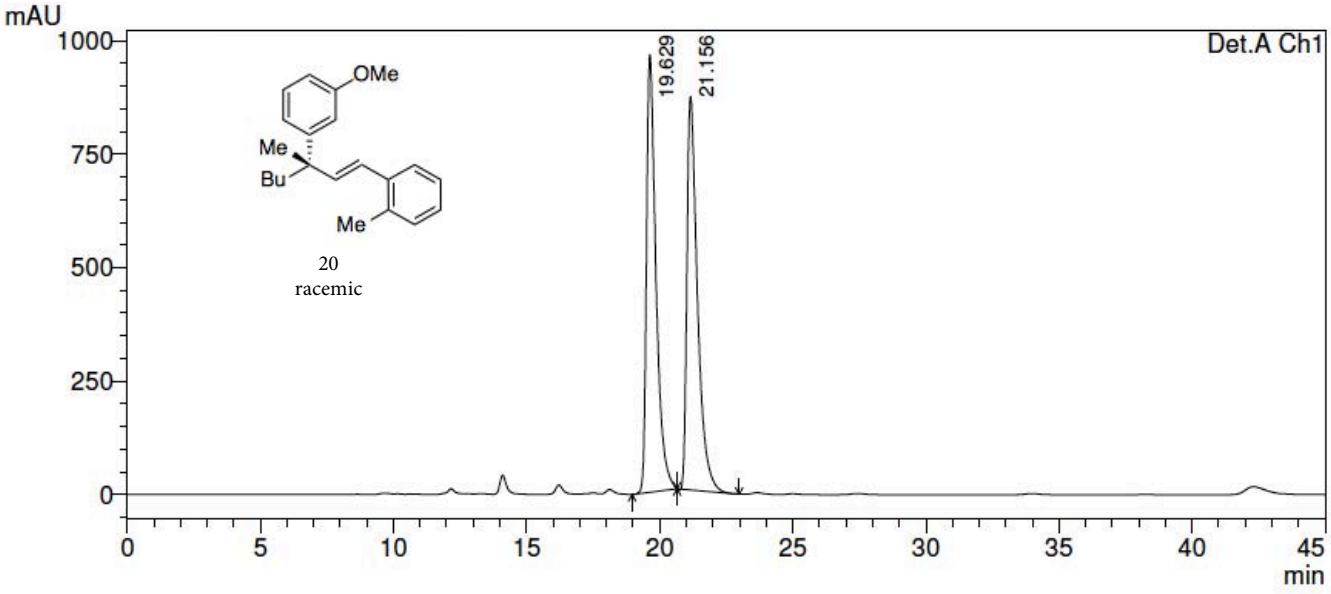
Compound 19, 89% ee



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 20, racemic

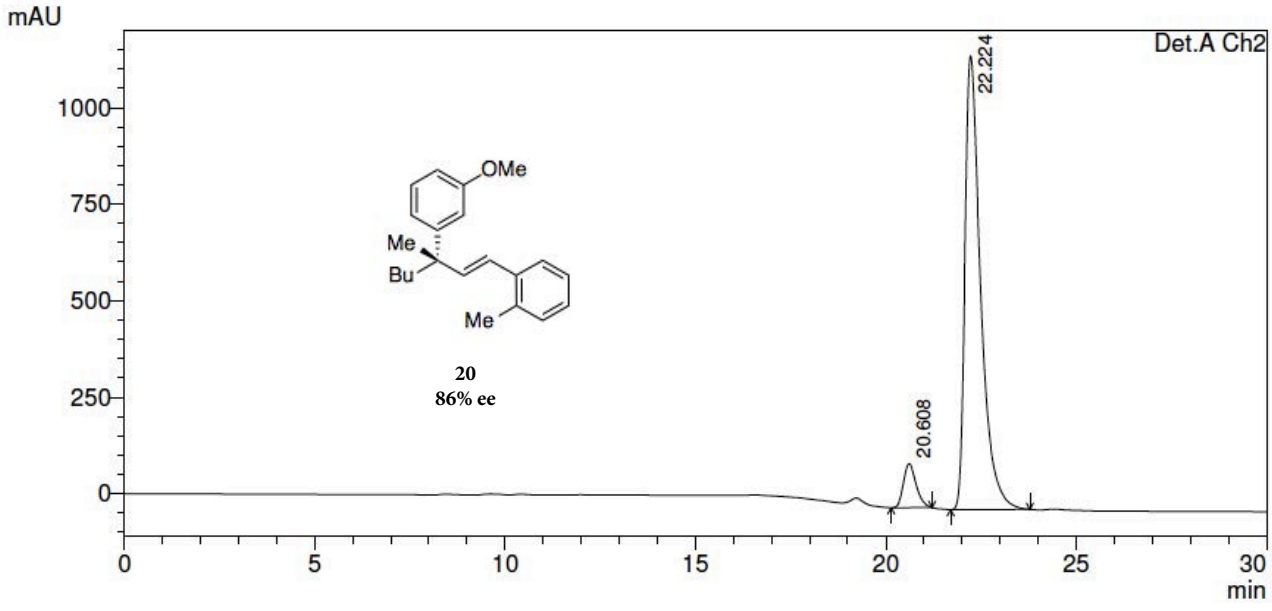


20
racemic

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 20, 86% ee



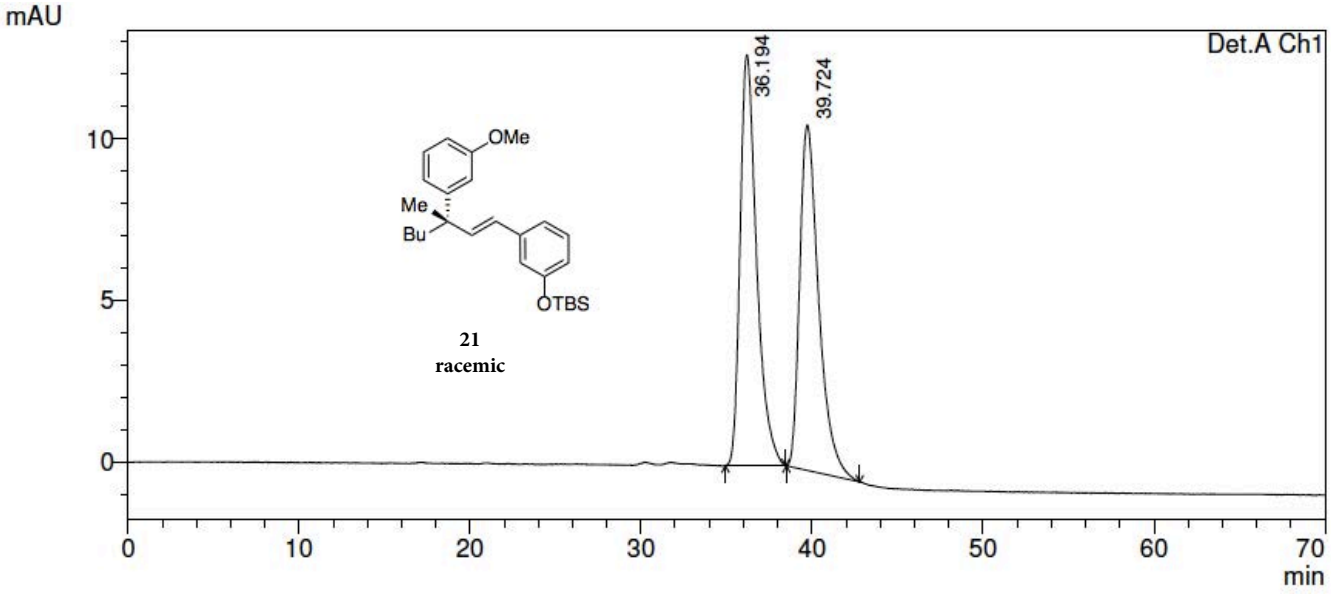
20
86% ee

Peak Table

Detector A Ch2 210nm

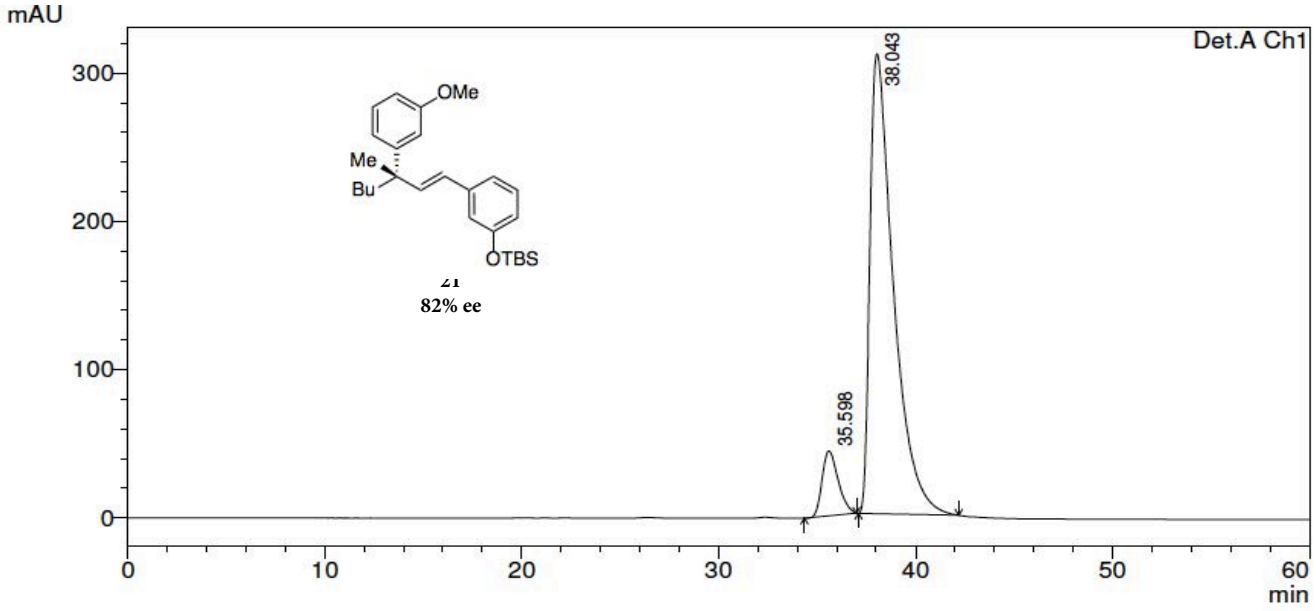
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.608	2633810	113975	7.253	8.838
2	22.224	33679787	1175606	92.747	91.162
Total		36313597	1289581	100.000	100.000

Compound 21, 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

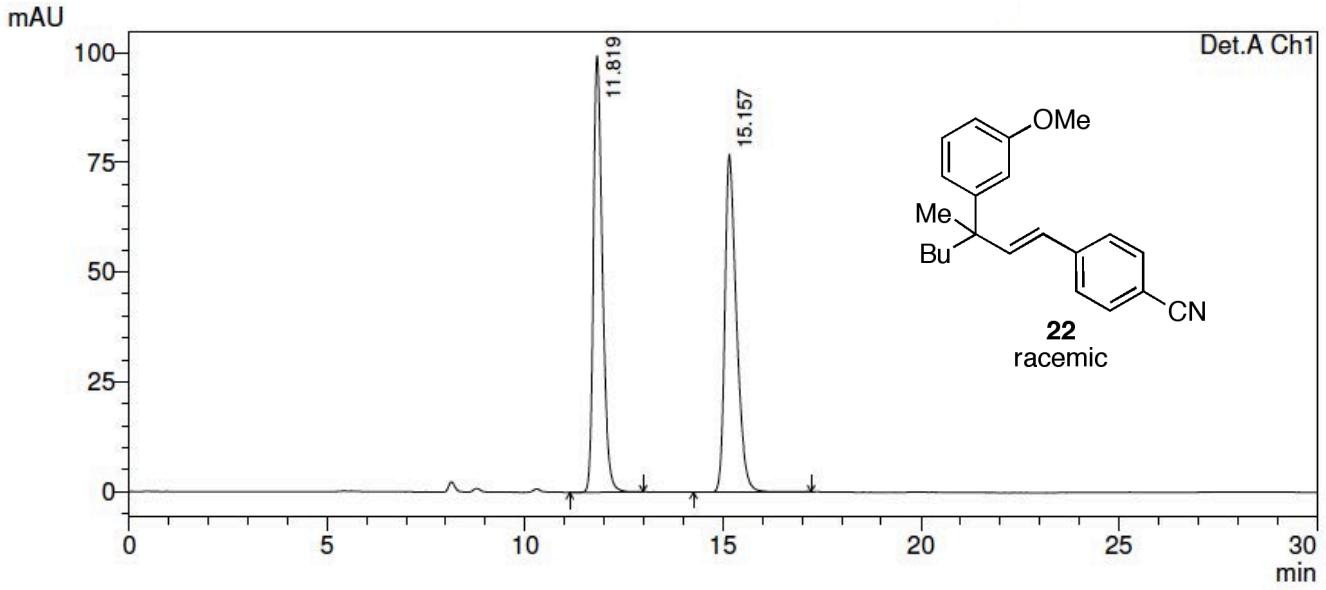
Compound 21, 82% ee



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

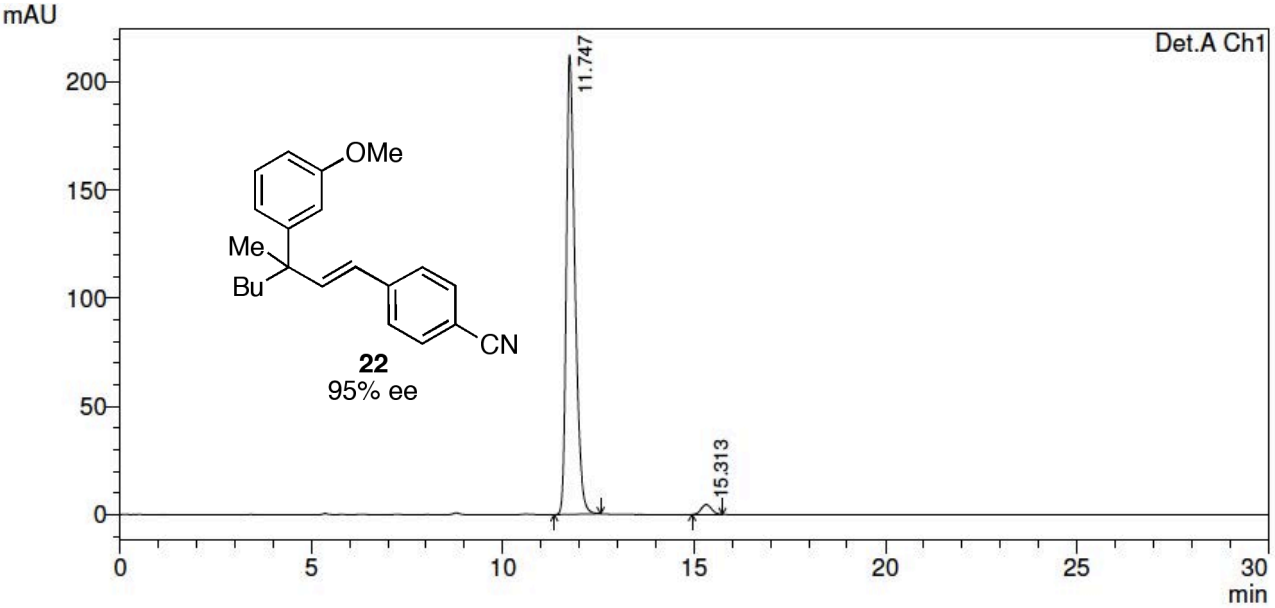
Compound 22, racemic



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

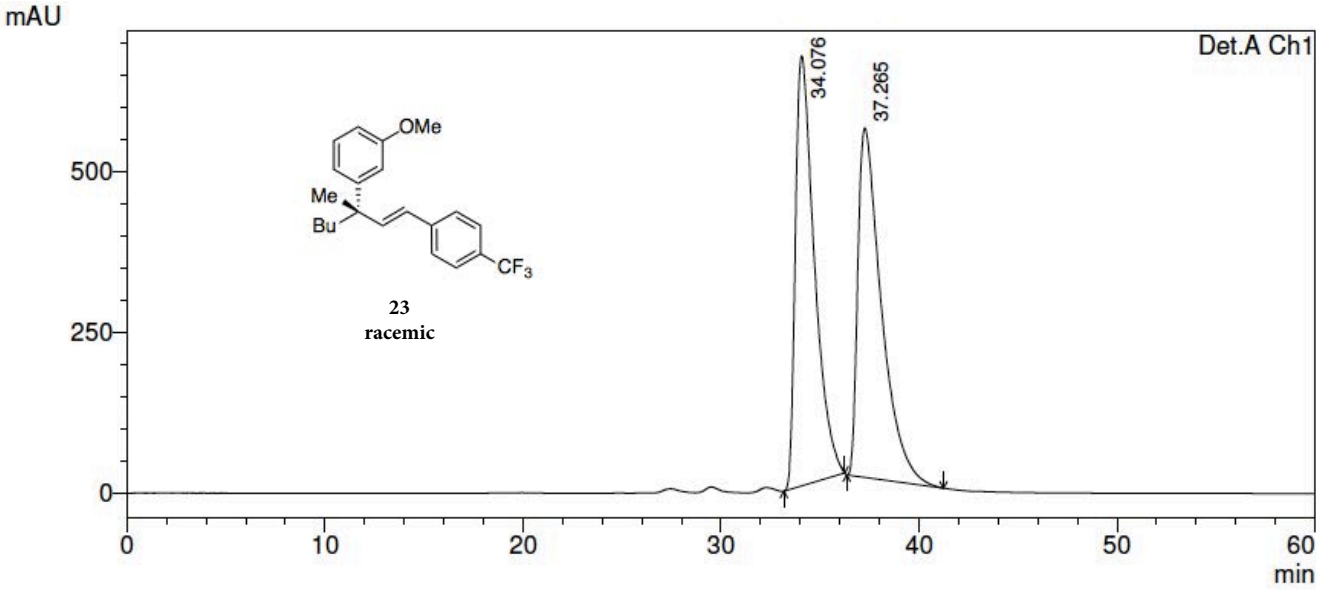
Compound 22, 95% ee



Detector A Ch1 254nm

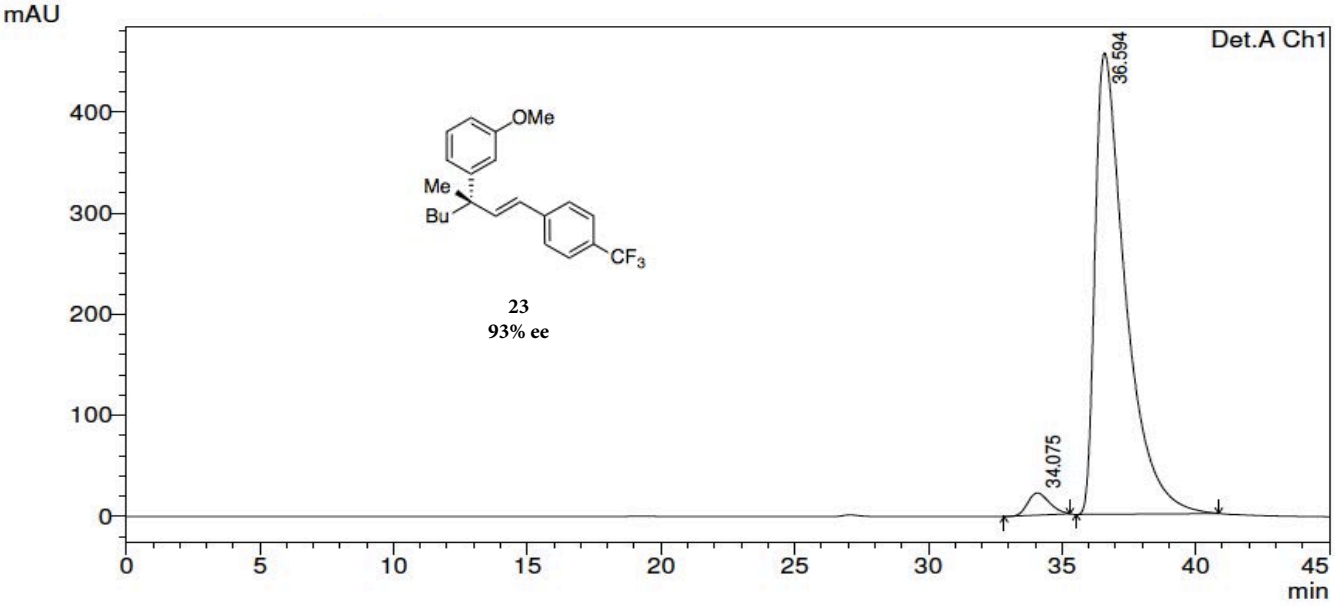
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.747	3371342	212472	97.531	97.910
2	15.313	85339	4536	2.469	2.090
Total		3456681	217008	100.000	100.000

Compound 23, 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

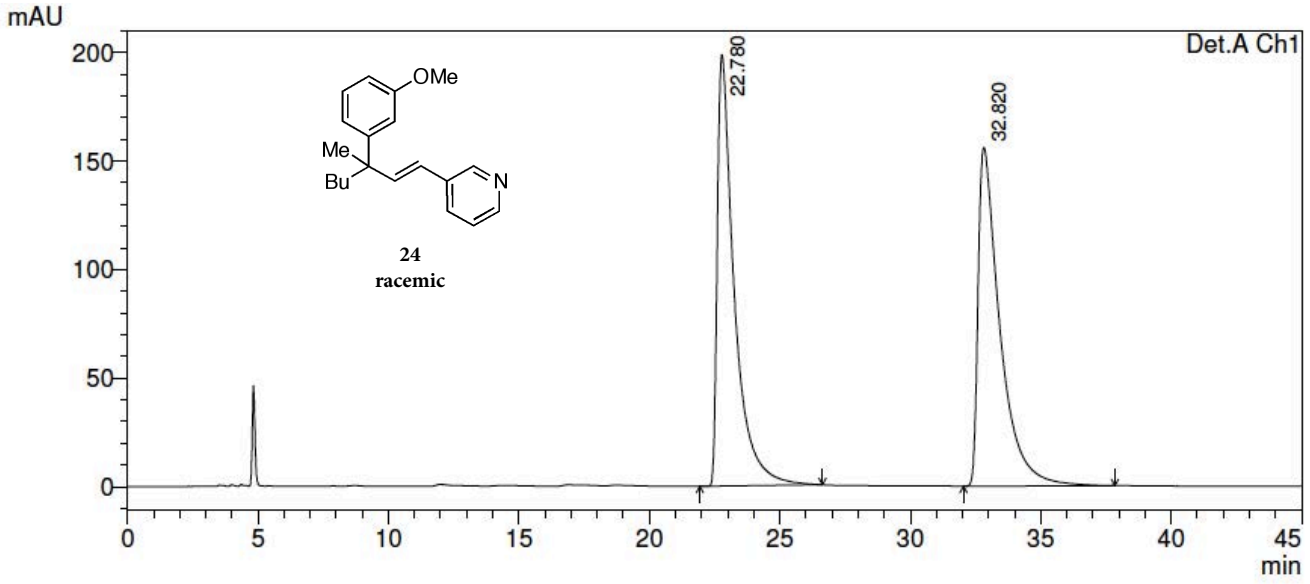
Compound 23, 93% ee



Detector A Ch1 254nm

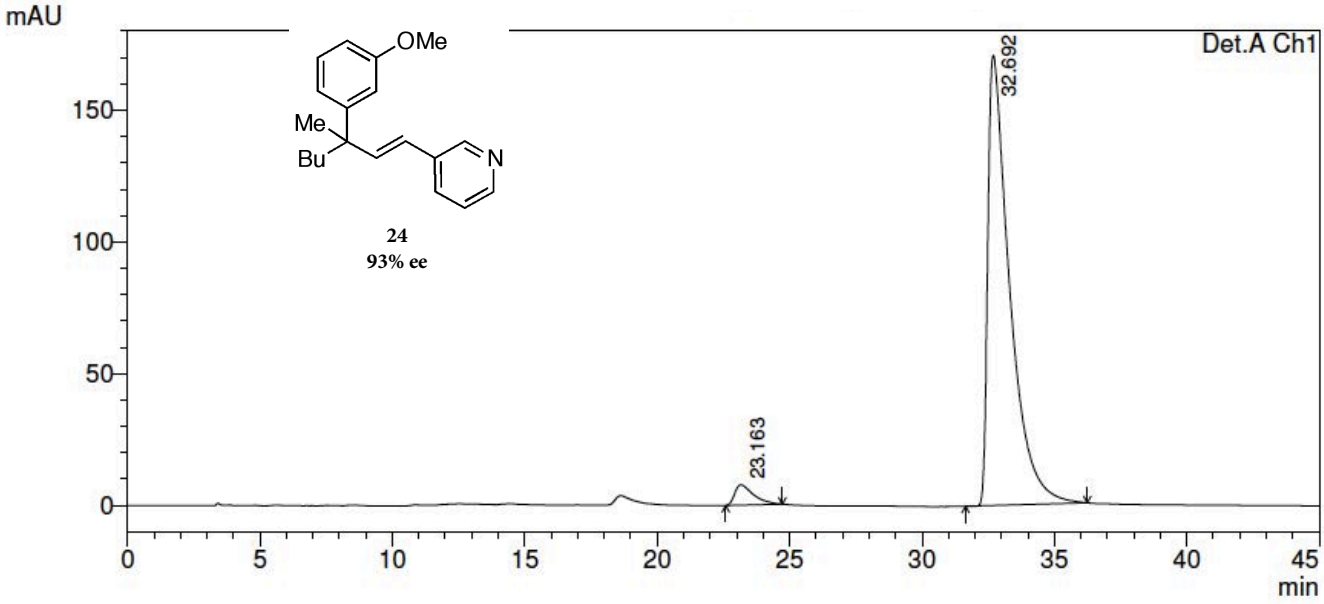
Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.075	1228232	21966	3.288	4.591
2	36.594	36124070	456463	96.712	95.409
Total		37352302	478429	100.000	100.000

Compound 24, 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

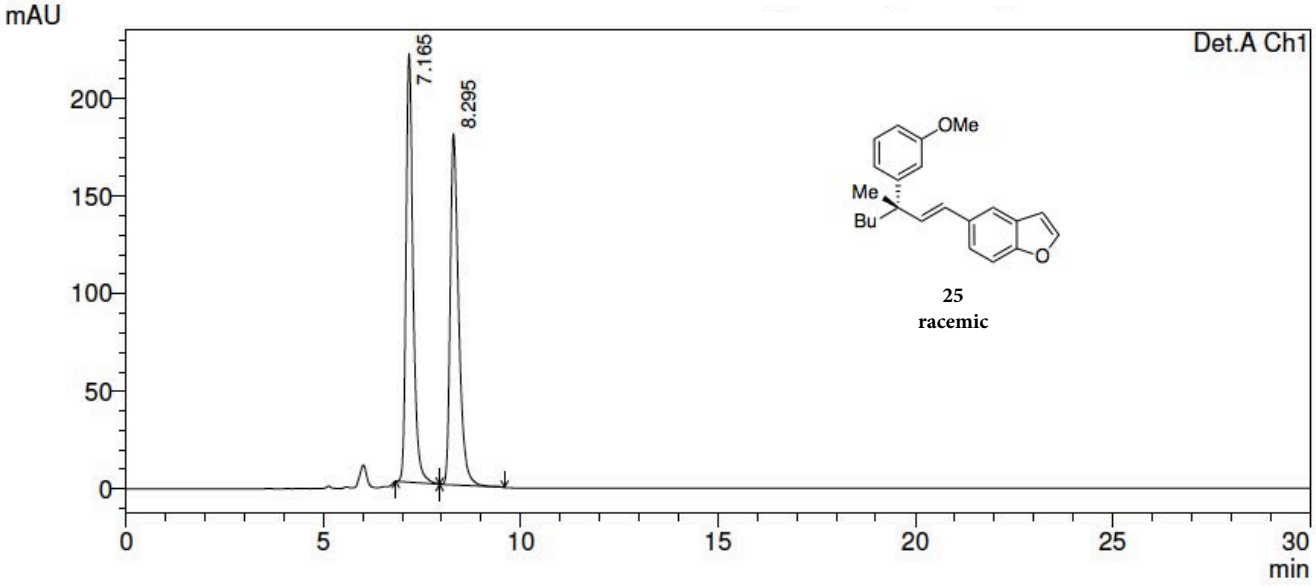
Compound 24, 93% ee



Detector A Ch1 220nm

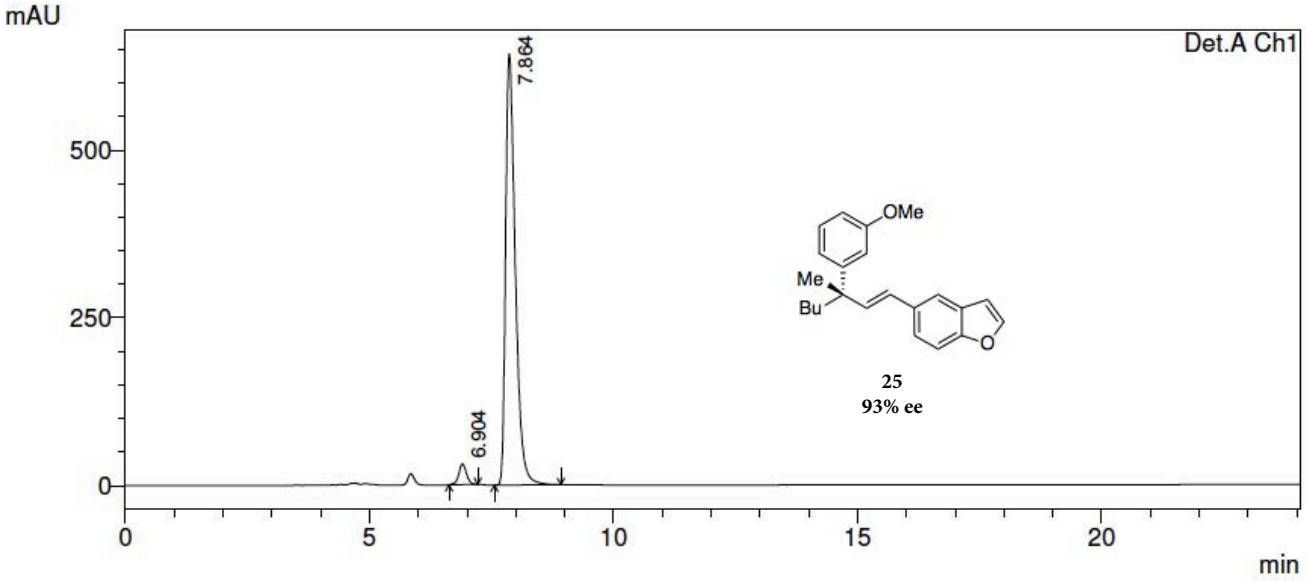
Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.163	381764	7705	3.753	4.316
2	32.692	9789515	170823	96.247	95.684
Total		10171279	178528	100.000	100.000

Compound 25, racemic



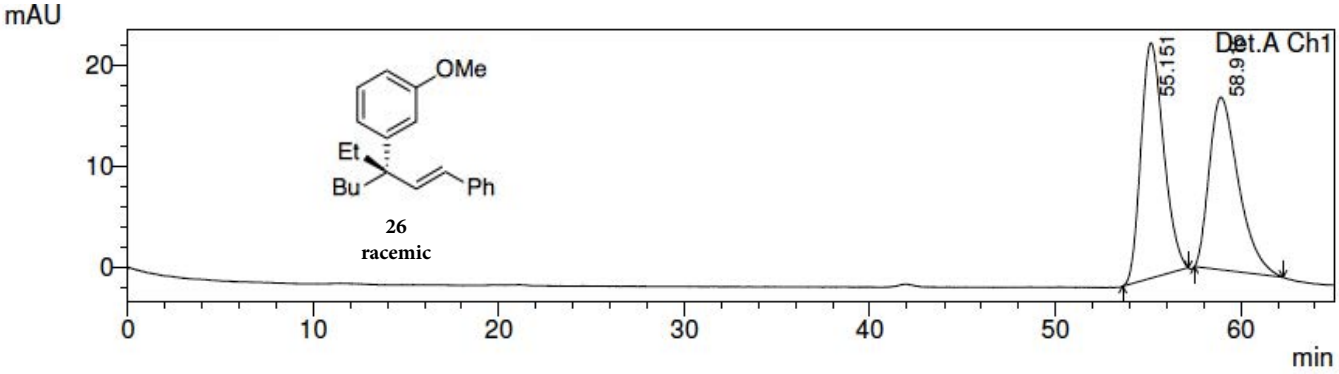
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.165	2737041	219557	50.187	54.963
2	8.295	2716668	179908	49.813	45.037
Total		5453709	399465	100.000	100.000

Compound 25, 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

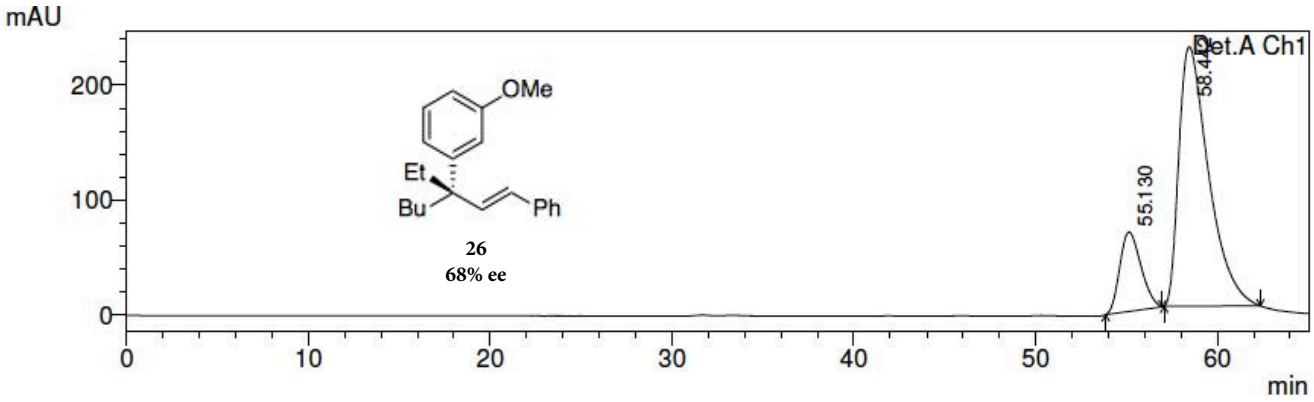
Compound 26, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	55.151	1984057	23289	51.489	57.701
2	58.915	1869299	17072	48.511	42.299
Total		3853356	40362	100.000	100.000

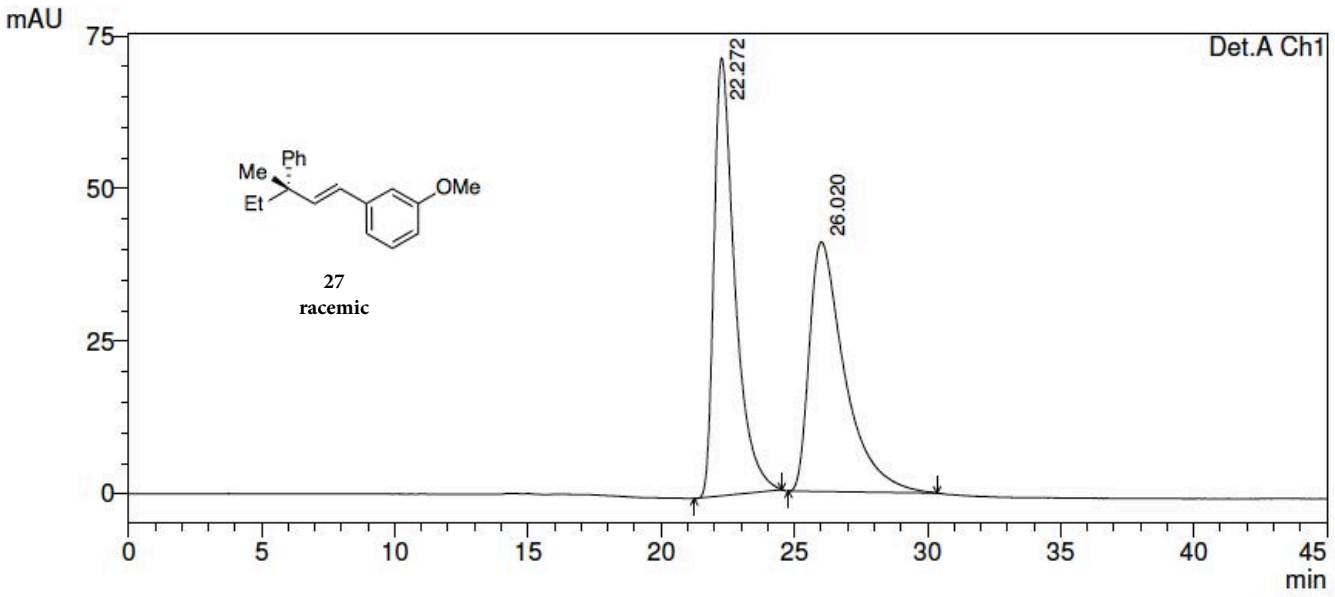
Compound 26, 68% ee



Detector A Ch1 254nm

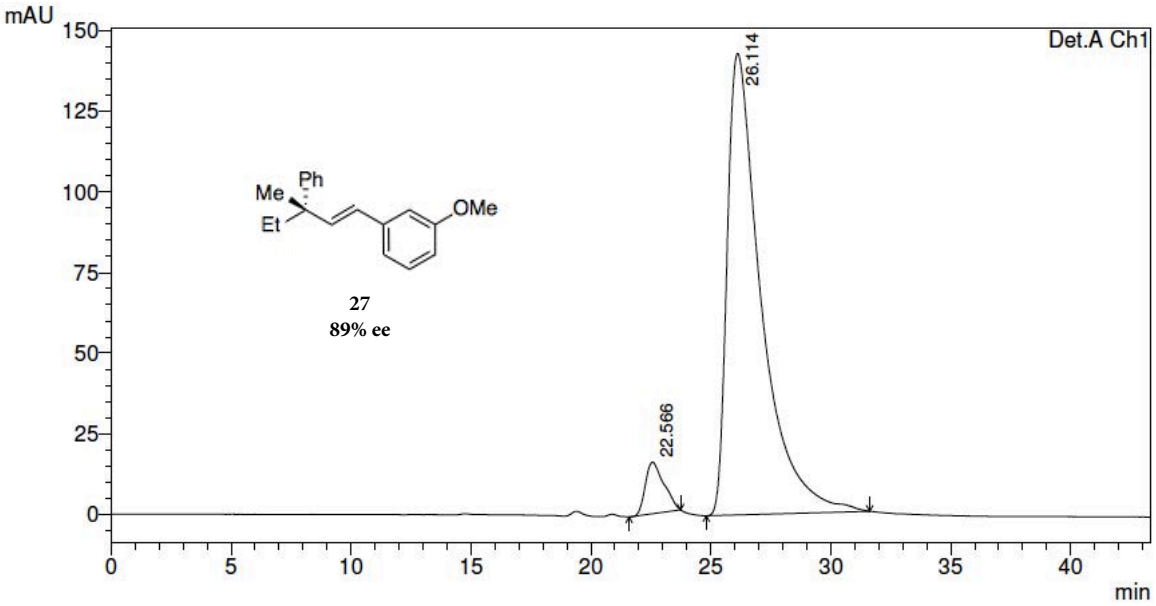
Peak#	Ret. Time	Area	Height	Area %	Height %
1	55.130	5586461	68871	17.876	23.403
2	58.442	25665149	225405	82.124	76.597
Total		31251610	294276	100.000	100.000

Compound 27, 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

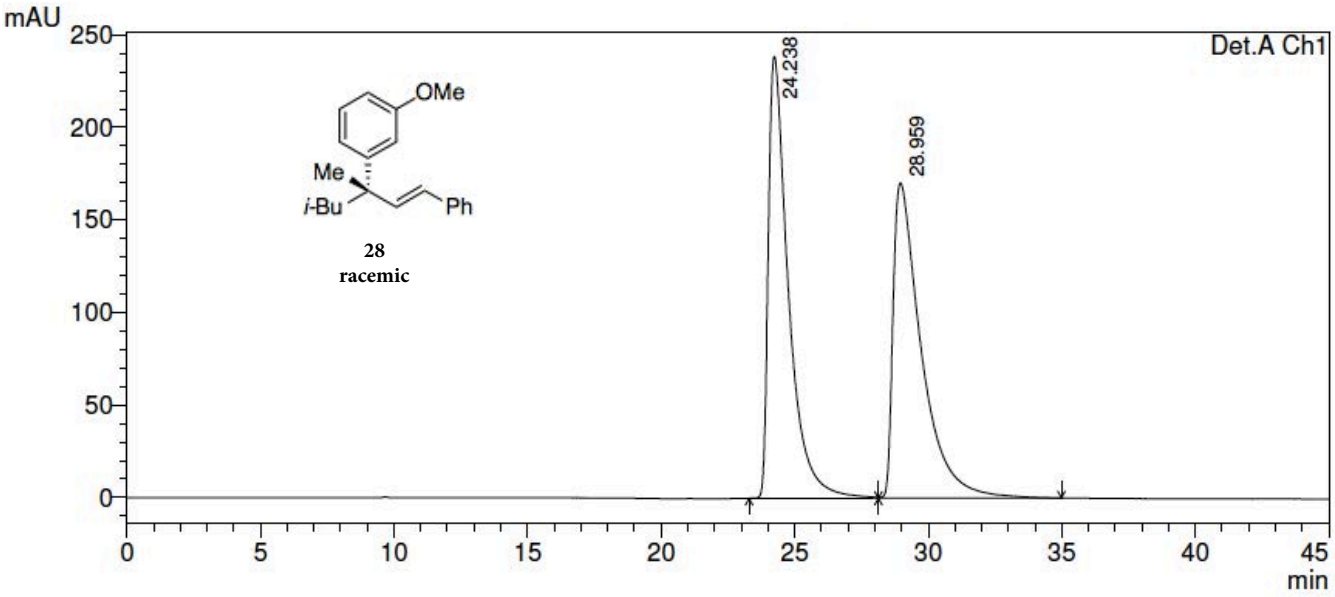
Compound 27, 89% ee



Detector A Ch1 254nm

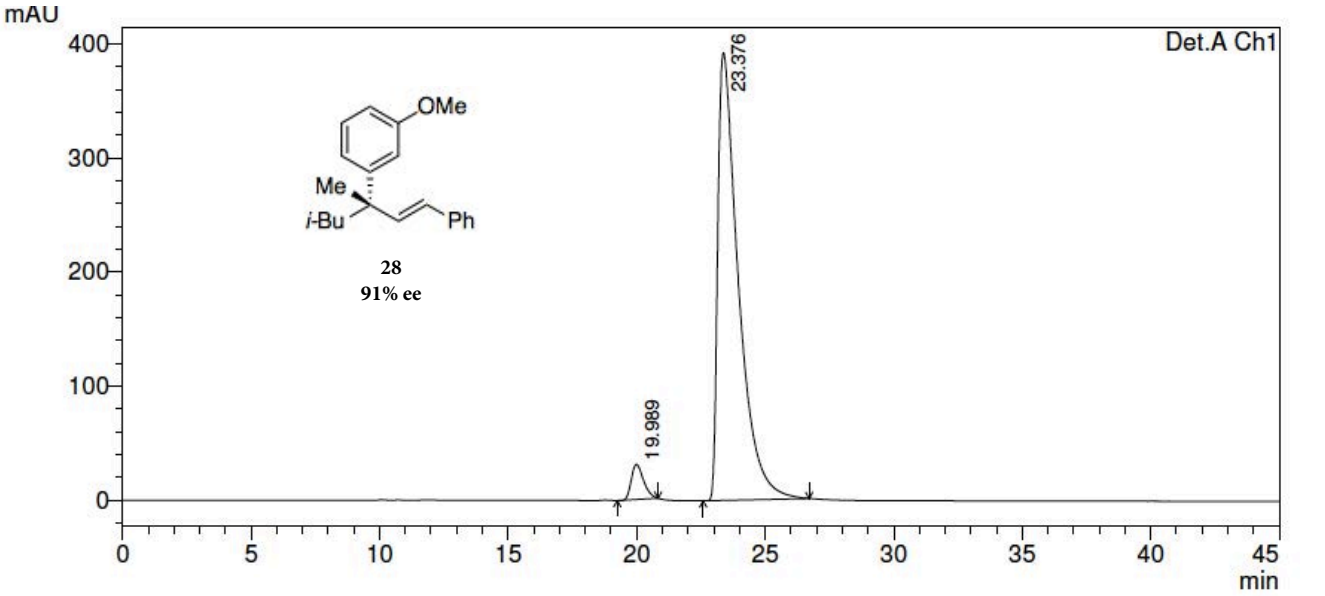
Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.566	854102	15960	5.711	10.027
2	26.114	14100842	143218	94.289	89.973
Total		14954944	159179	100.000	100.000

Compound 28, 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

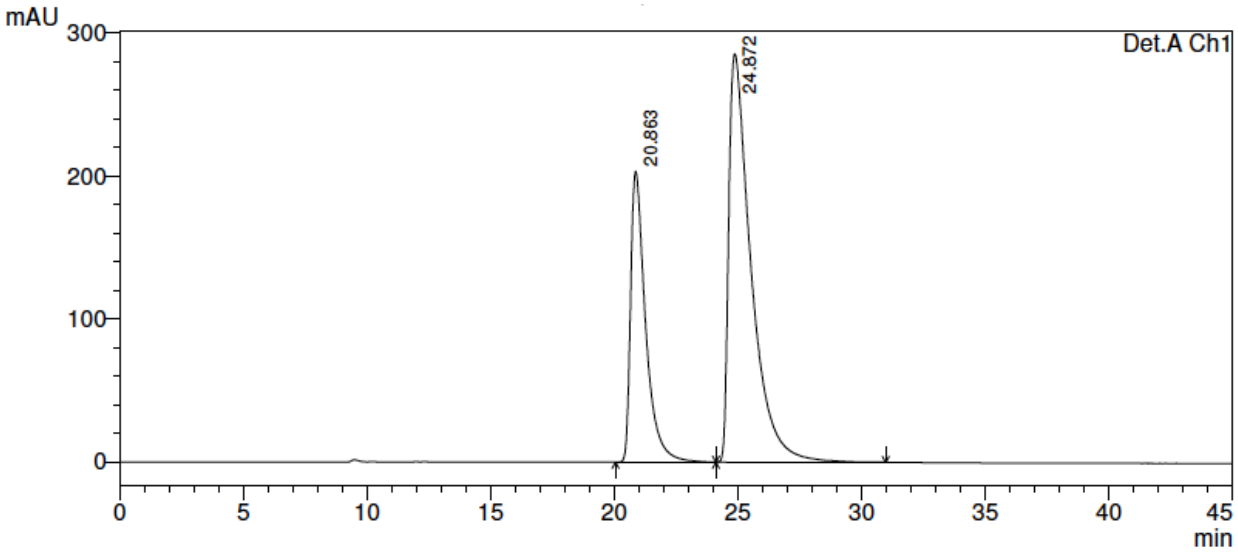
Compound 28, 91% ee



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

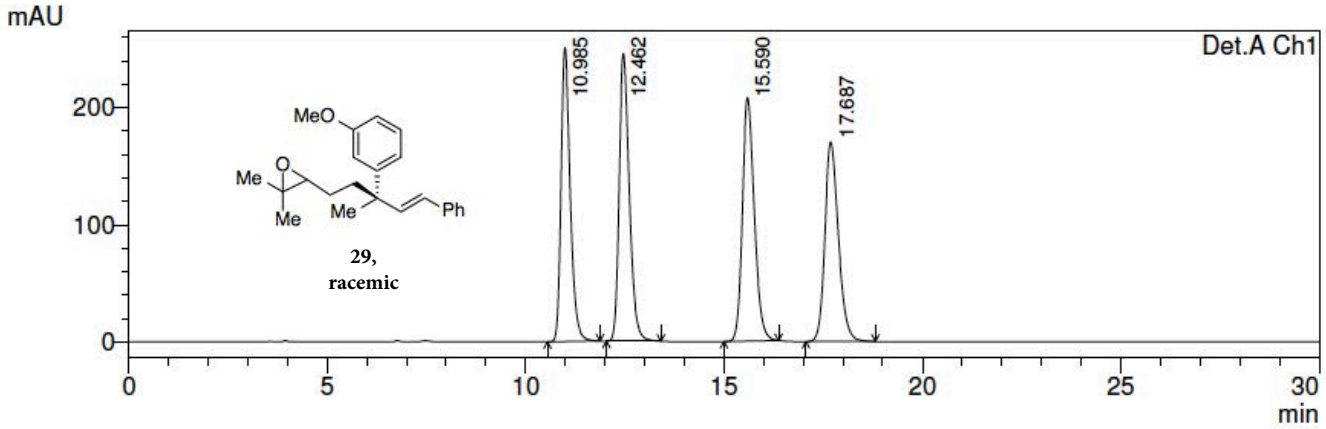
Compound **28**, co-injection of racemic and enantioenriched material



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.863	8605032	203562	32.422	41.591
2	24.872	17935748	285870	67.578	58.409
Total		26540780	489431	100.000	100.000

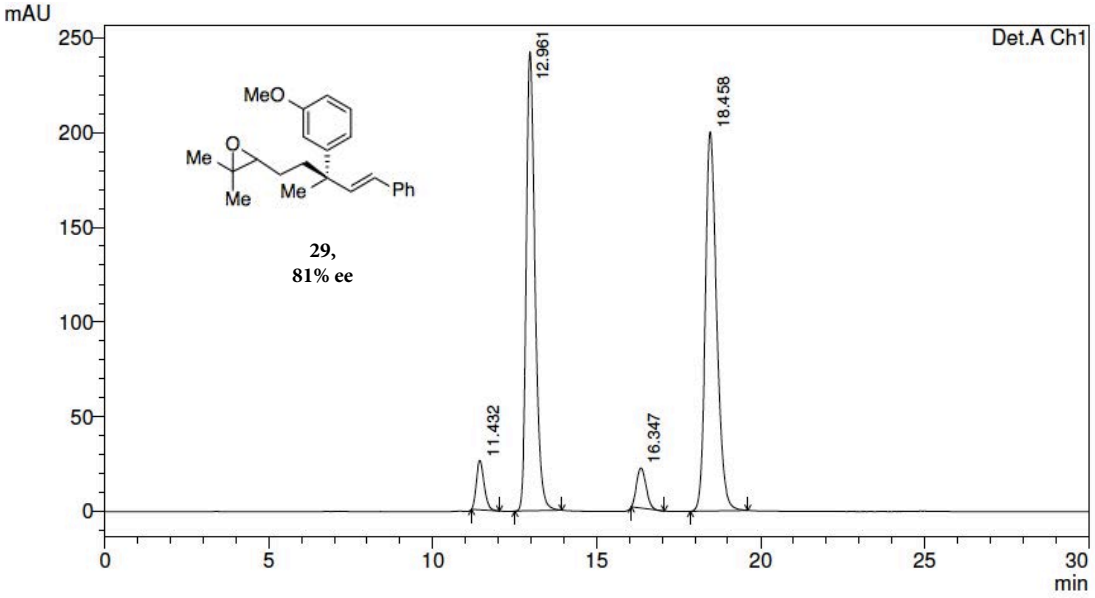
Compound 29, racemic



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

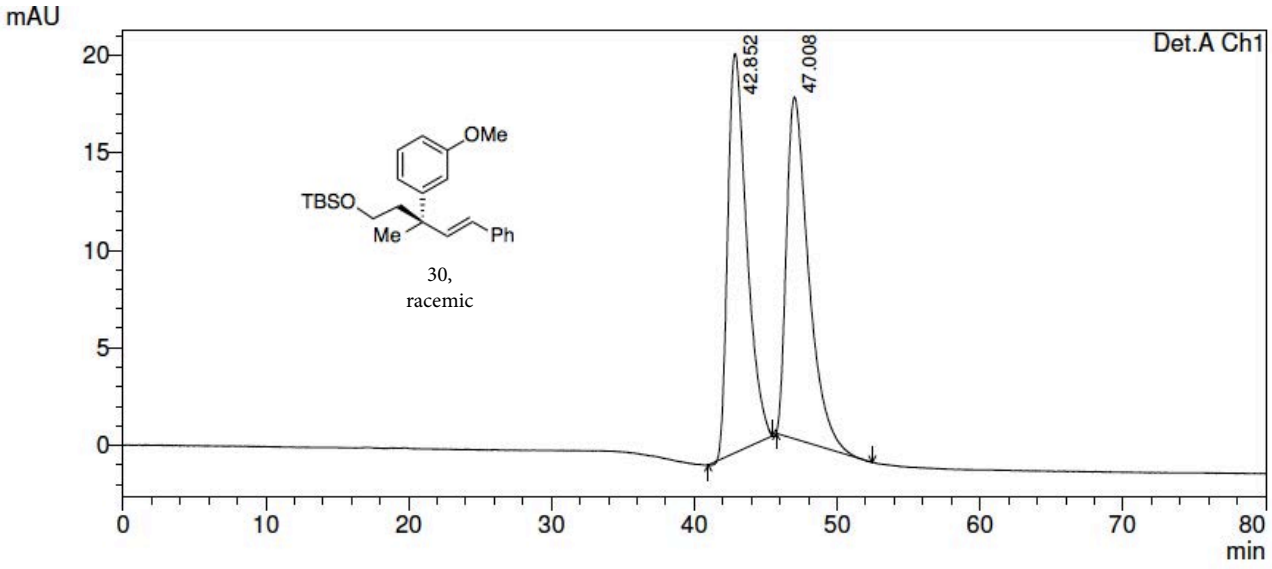
Compound 29, 81% ee



Detector A Ch1 254nm

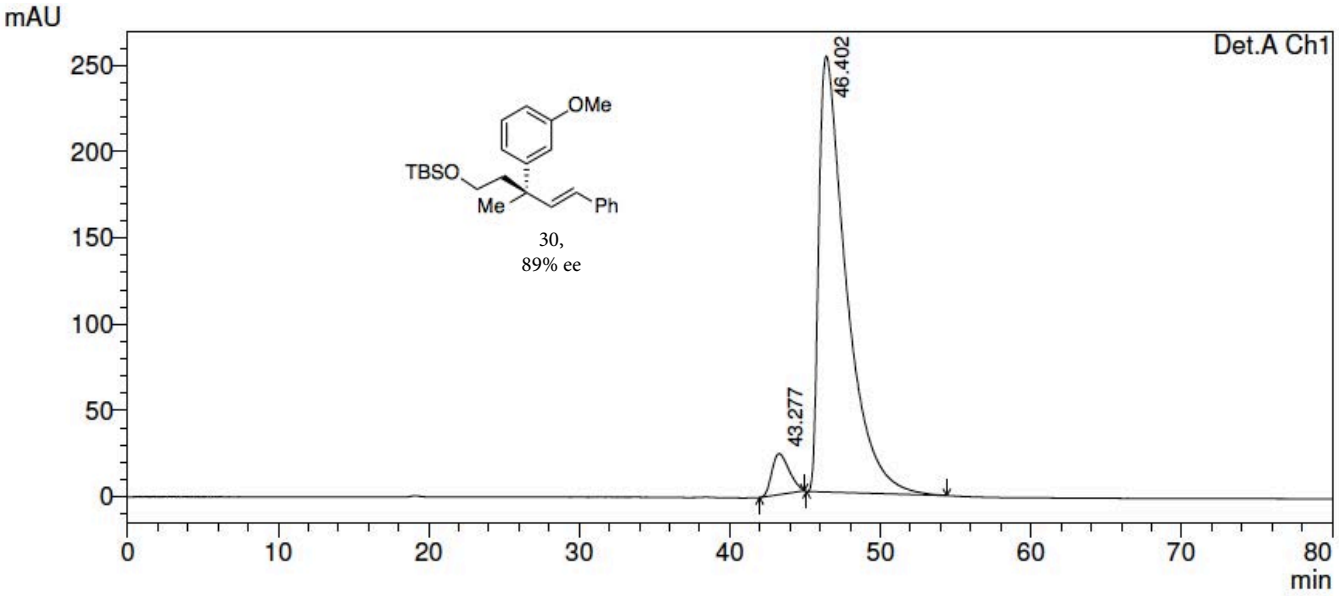
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.432	427501	26041	4.209	5.319
2	12.961	4491964	242351	44.225	49.498
3	16.347	421556	21115	4.150	4.312
4	18.458	4816061	200108	47.416	40.871
Total		10157082	489614	100.000	100.000

Compound 30, racemic



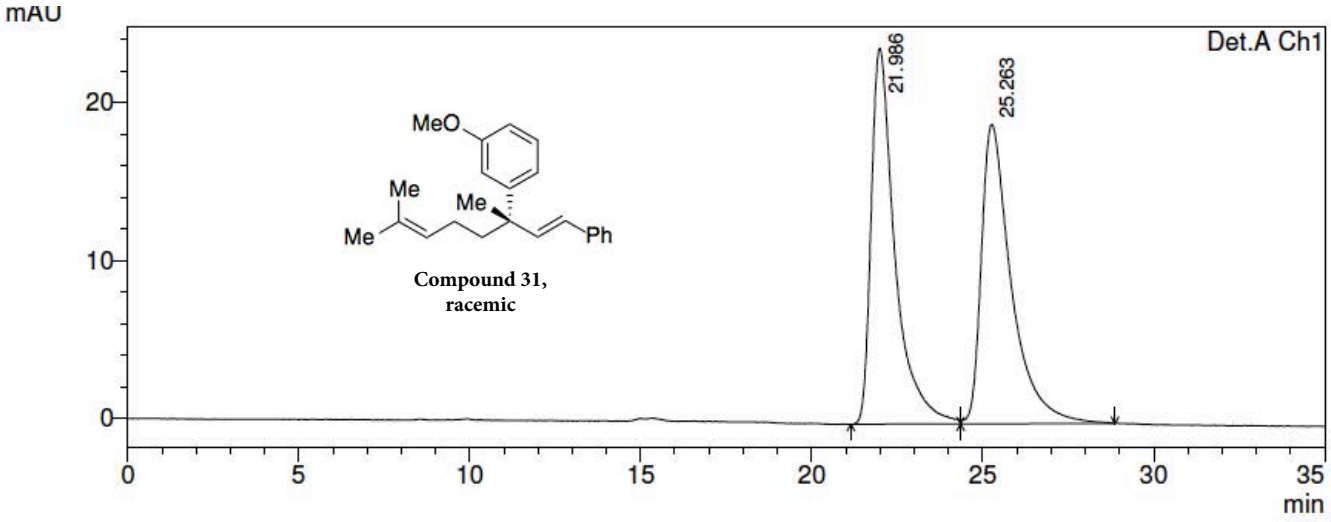
Peak#	Ret. Time	Area	Height	Area %	Height %
1	42.852	1890935	20471	50.054	53.872
2	47.008	1886834	17528	49.946	46.128
Total		3777769	37999	100.000	100.000

Compound 30, 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

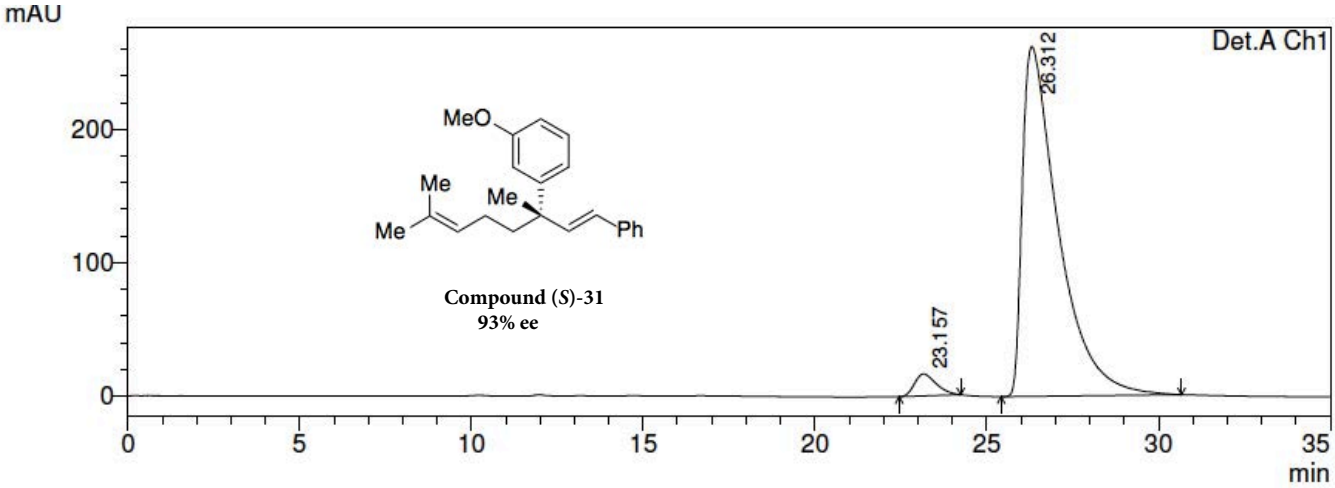
Compund 31, racemic



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

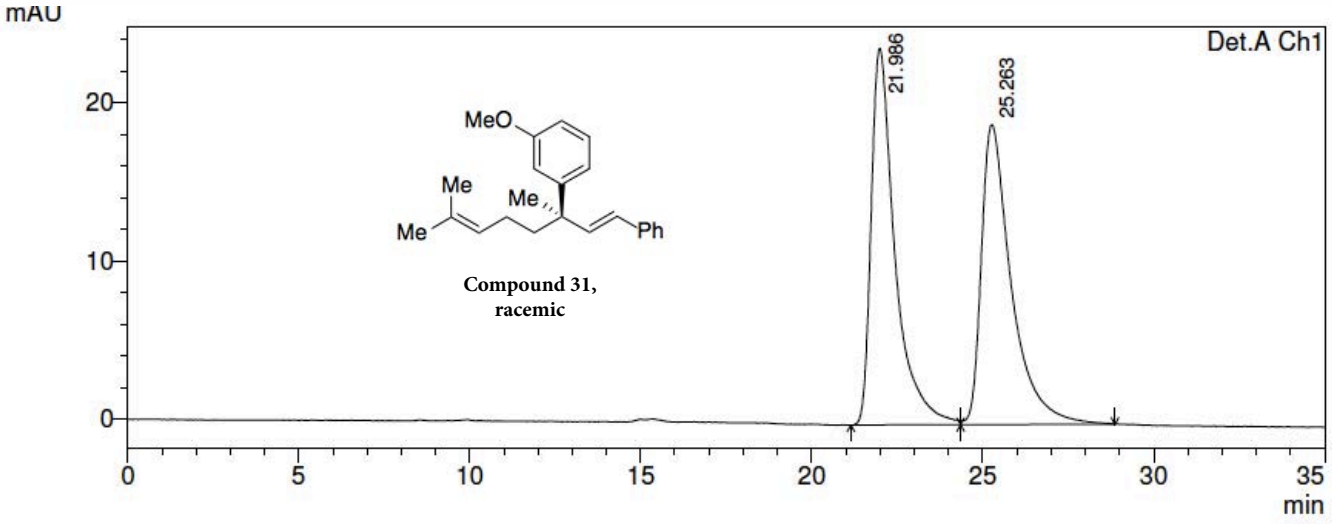
Compound (*S*)-31, 93% ee



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

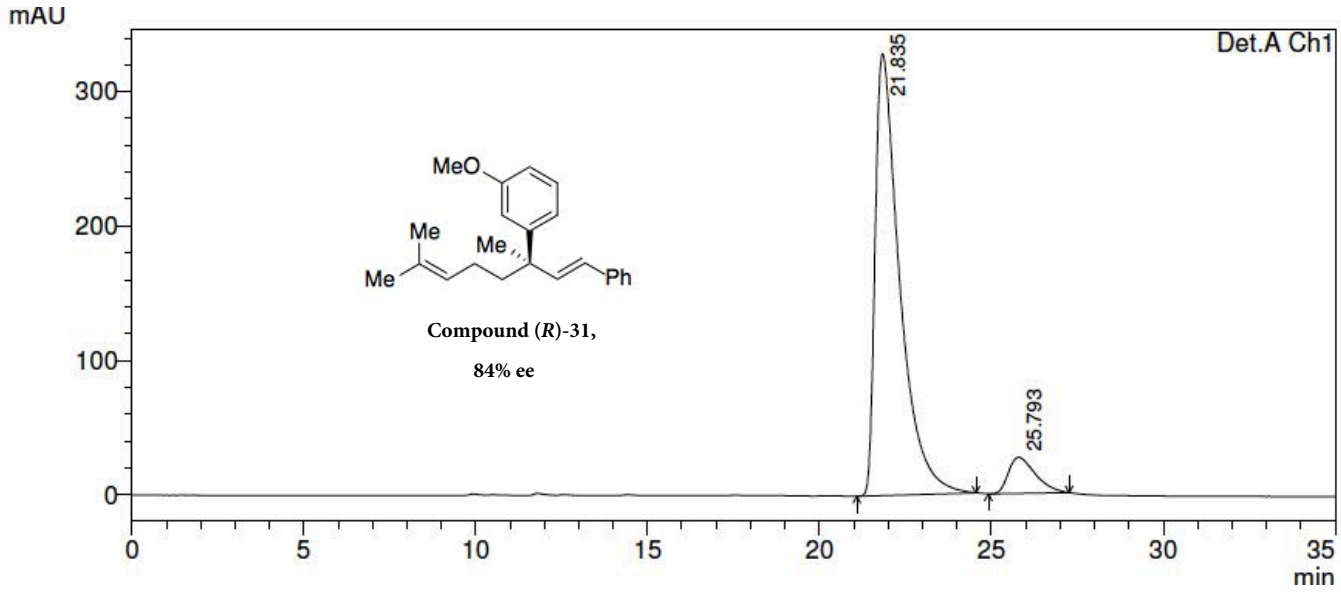
Compund 31, racemic



Detector A Ch1 254nm

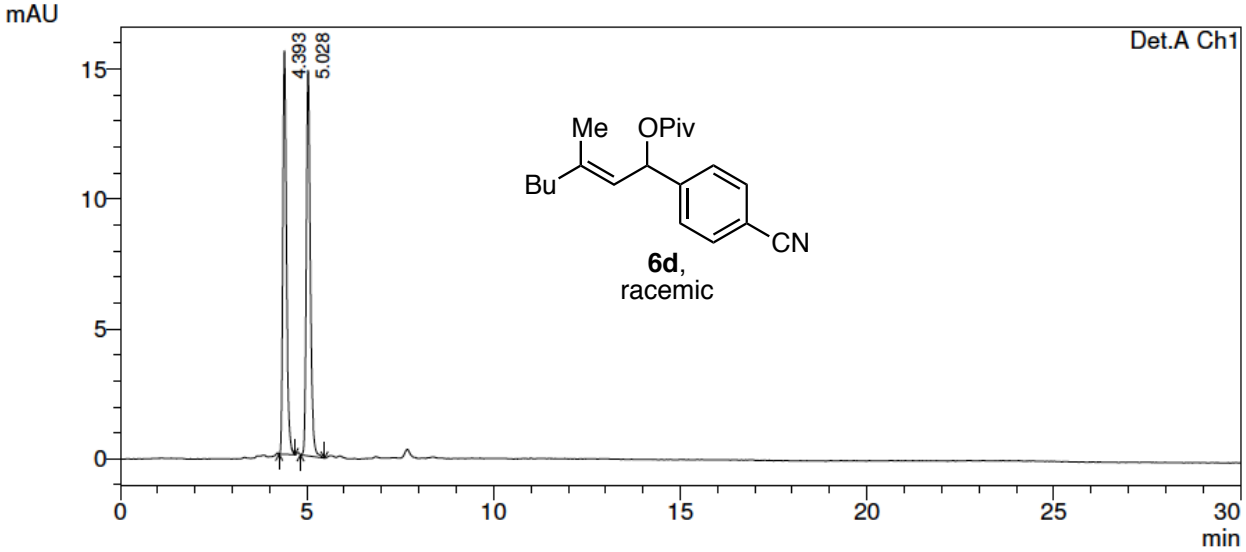
Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.986	1152996	23791	49.956	55.674
2	25.263	1155025	18942	50.044	44.326
Total		2308021	42733	100.000	100.000

Compund (*R*)-31, 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

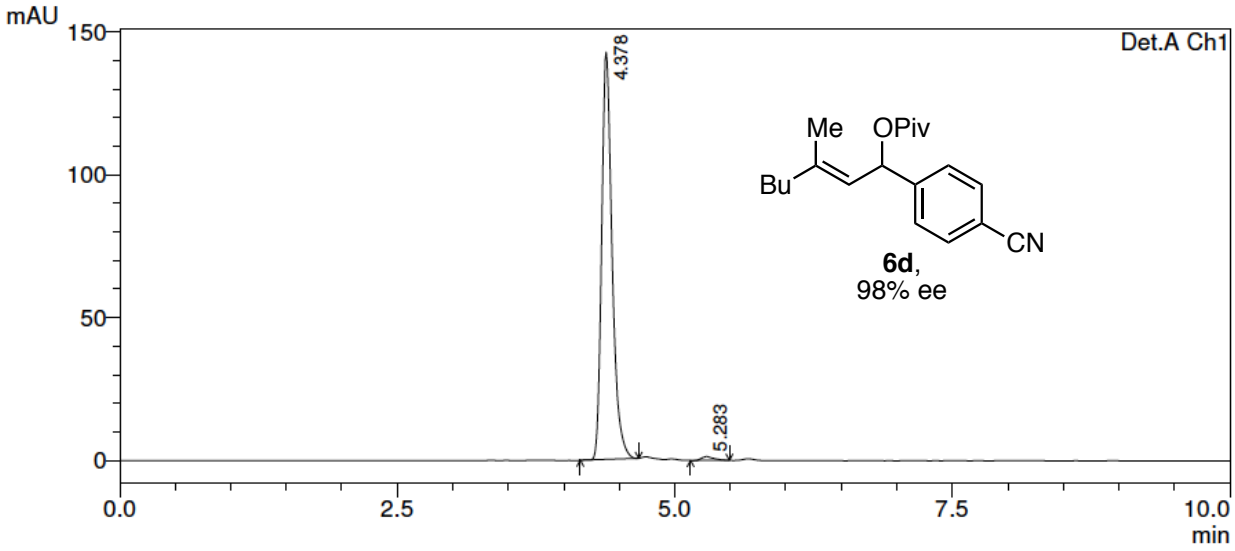
Compound **6d**, racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.393	105147	15528	49.078	51.156
2	5.028	109096	14827	50.922	48.844
Total		214243	30355	100.000	100.000

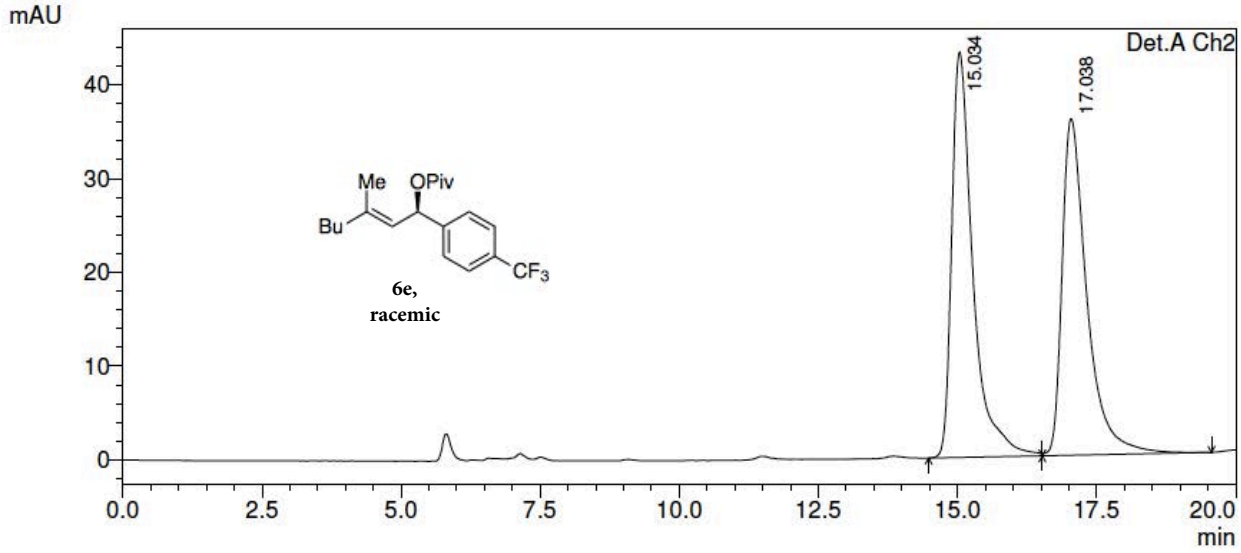
Compound **6d**, 98% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.378	937441	142512	98.946	99.069
2	5.283	9989	1340	1.054	0.931
Total		947430	143852	100.000	100.000

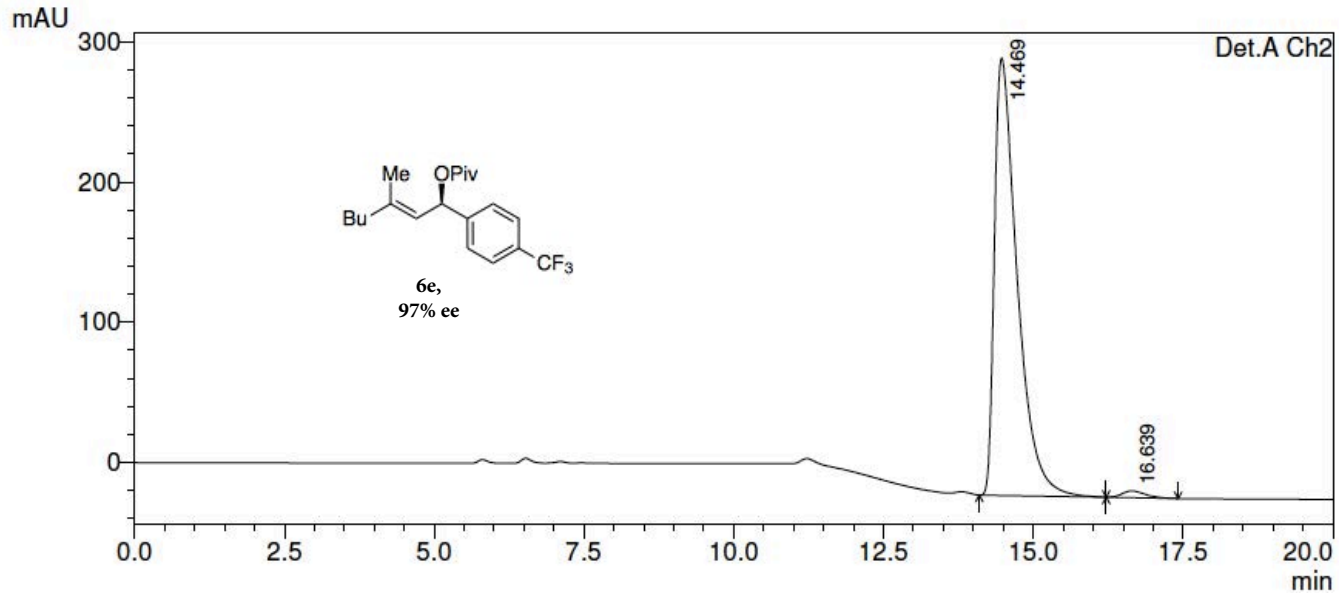
Compound 6e, racemic



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

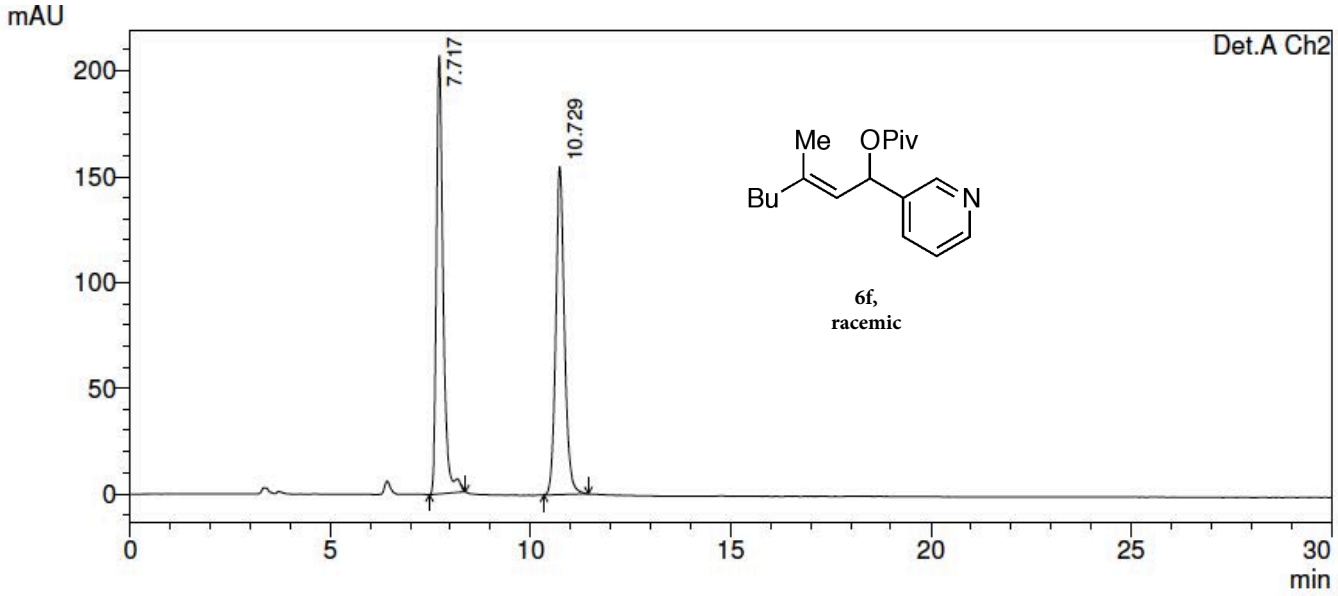
Compound 6e, 97% ee



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

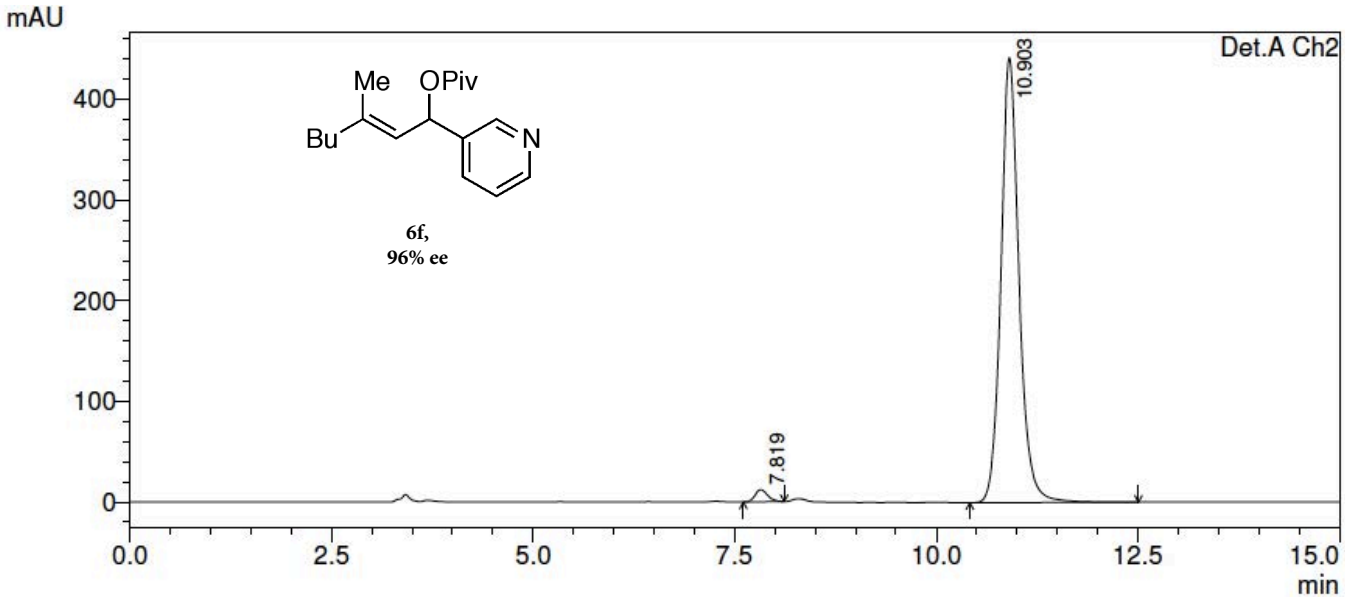
Compound 6f, racemic



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

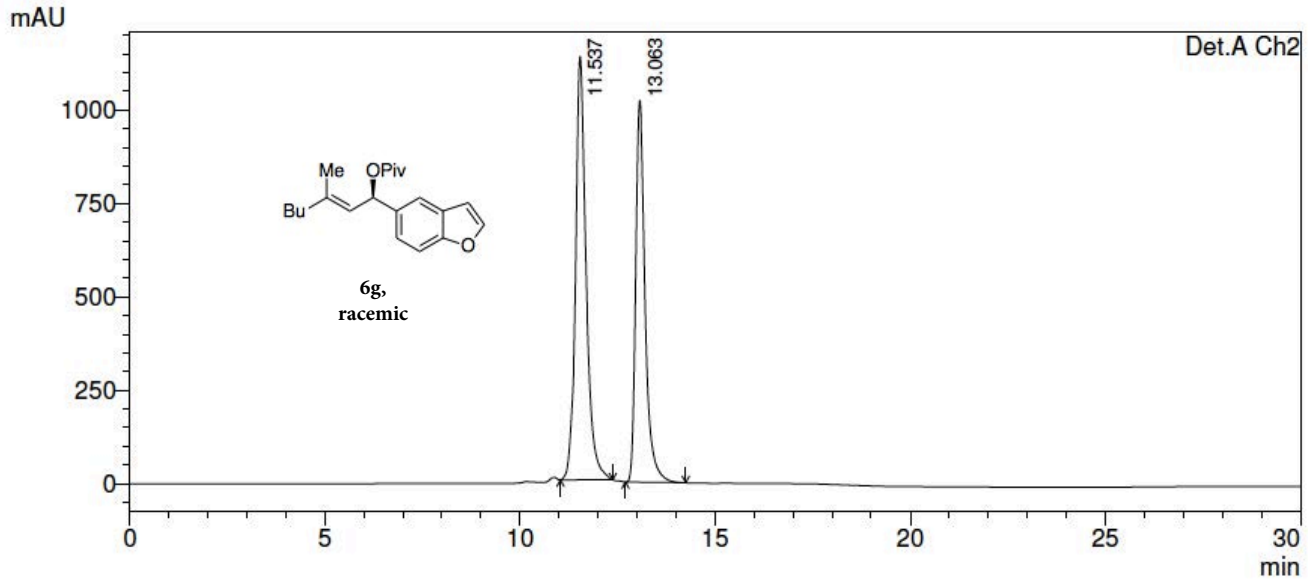
Compound 6f, 96% ee



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

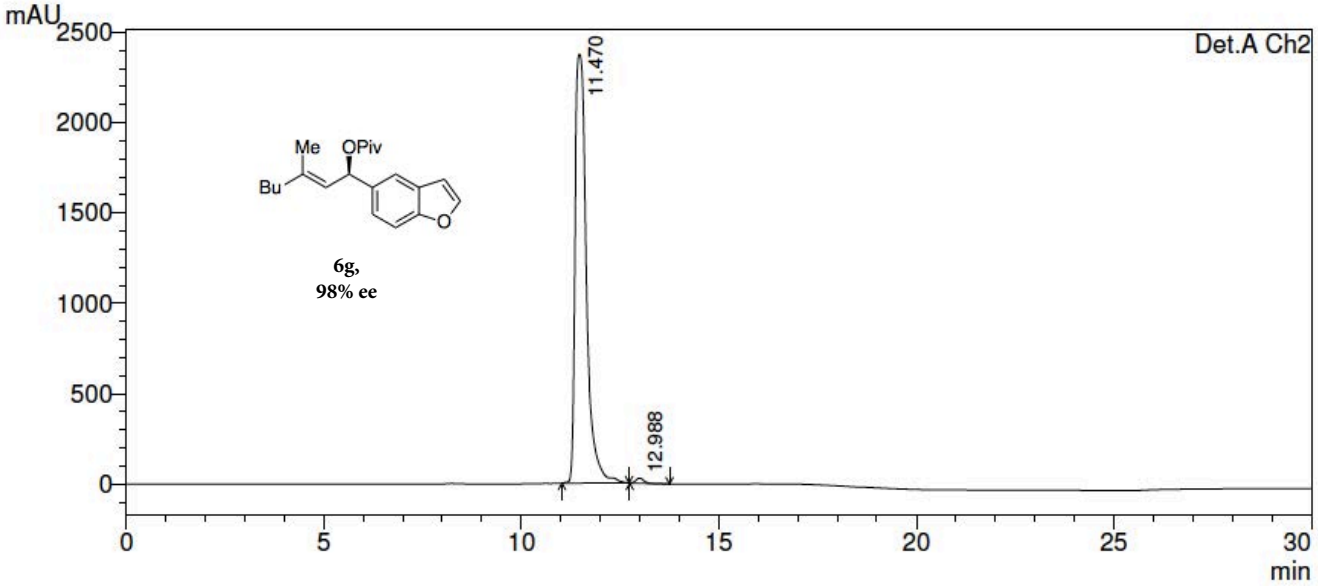
Compound 6g, racemic



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

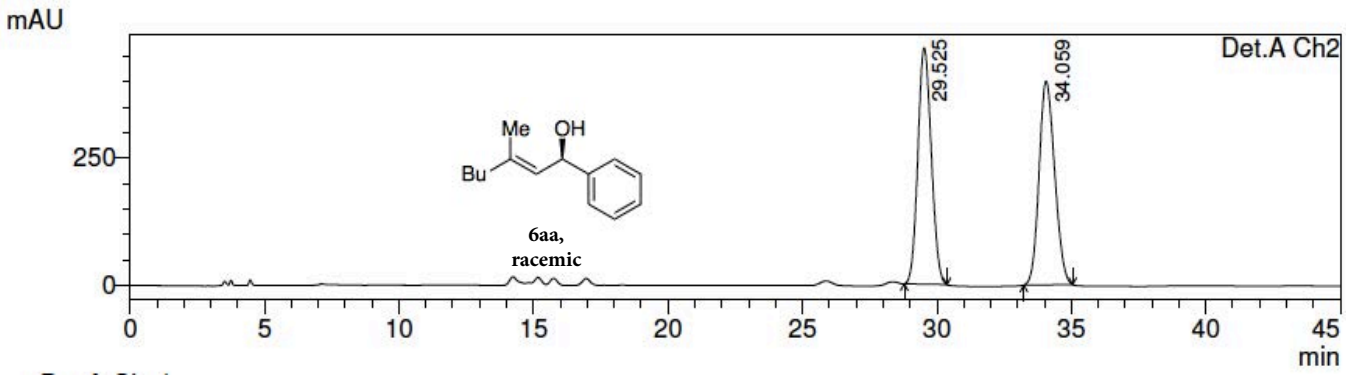
Compound 6g, 98% ee



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

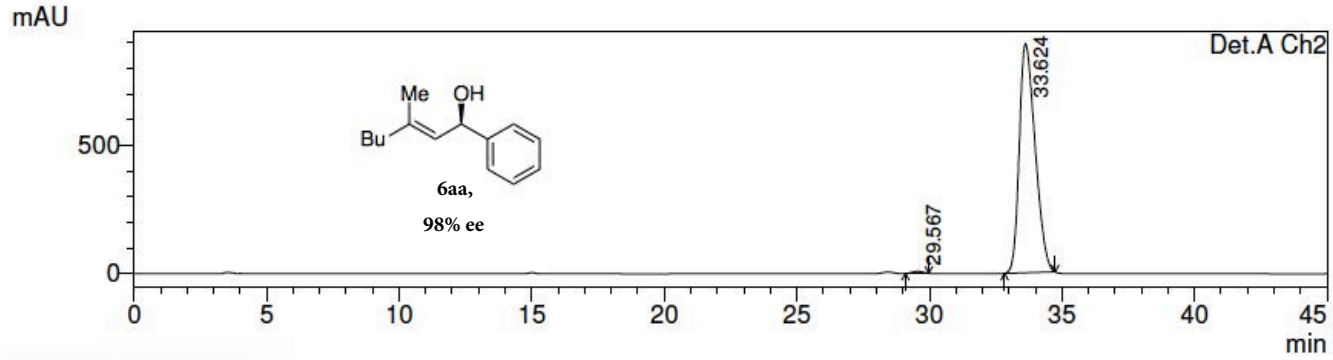
Compound 6aa, racemic



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

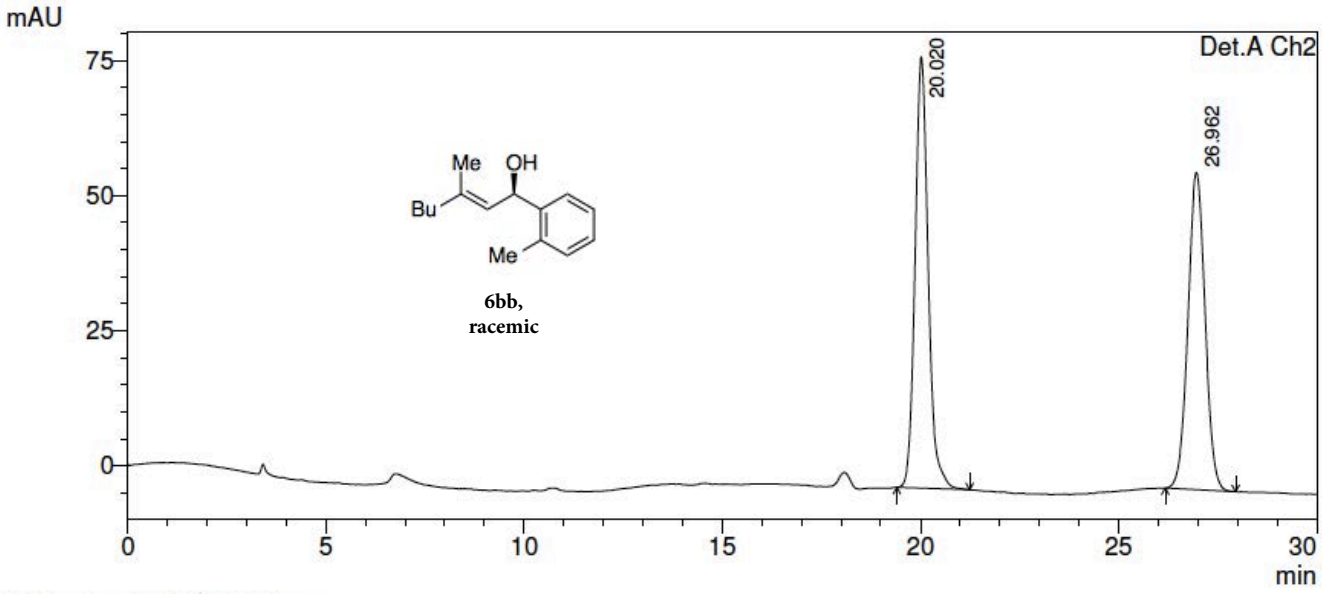
Compound 6aa, 98% ee



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

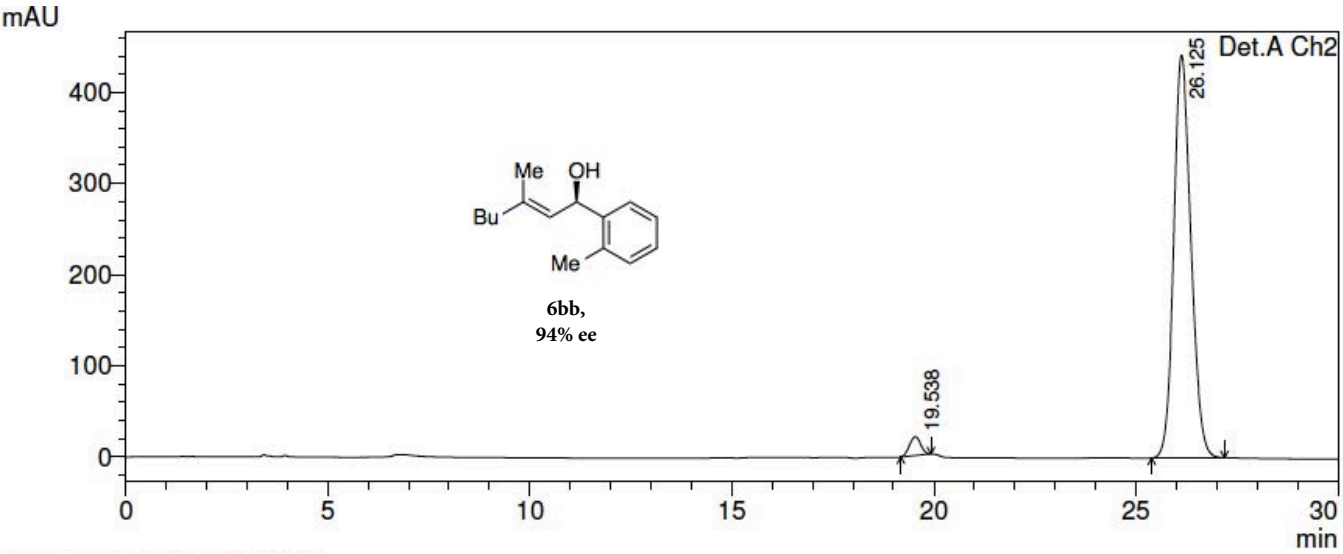
Compound 6bb, racemic



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

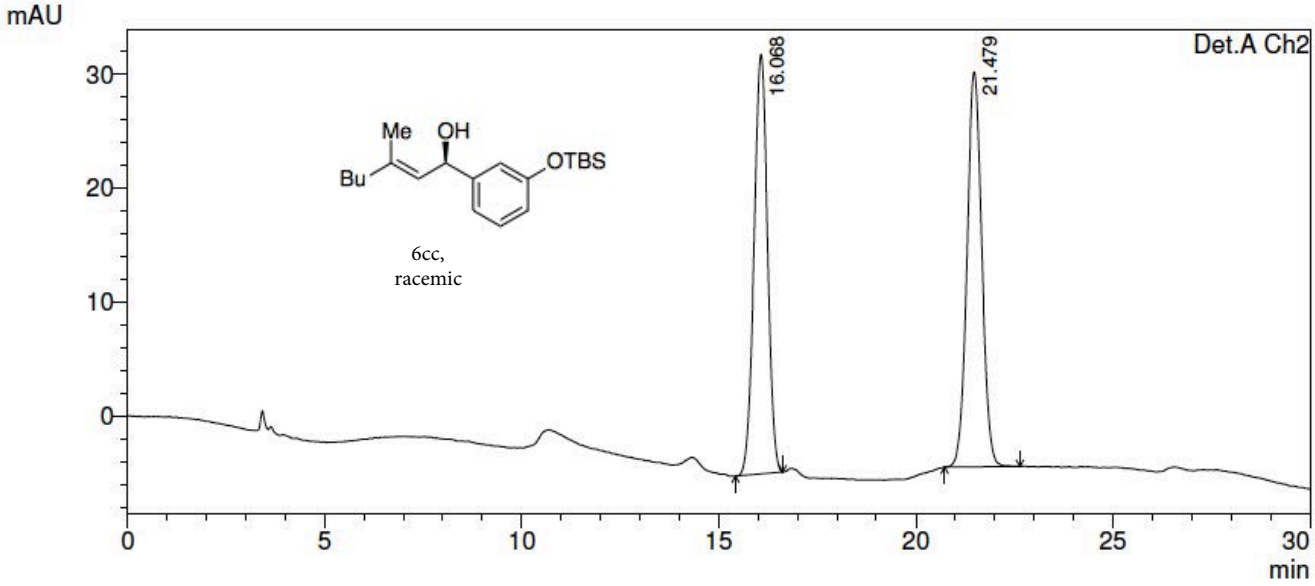
Compound 6bb, 94% ee



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

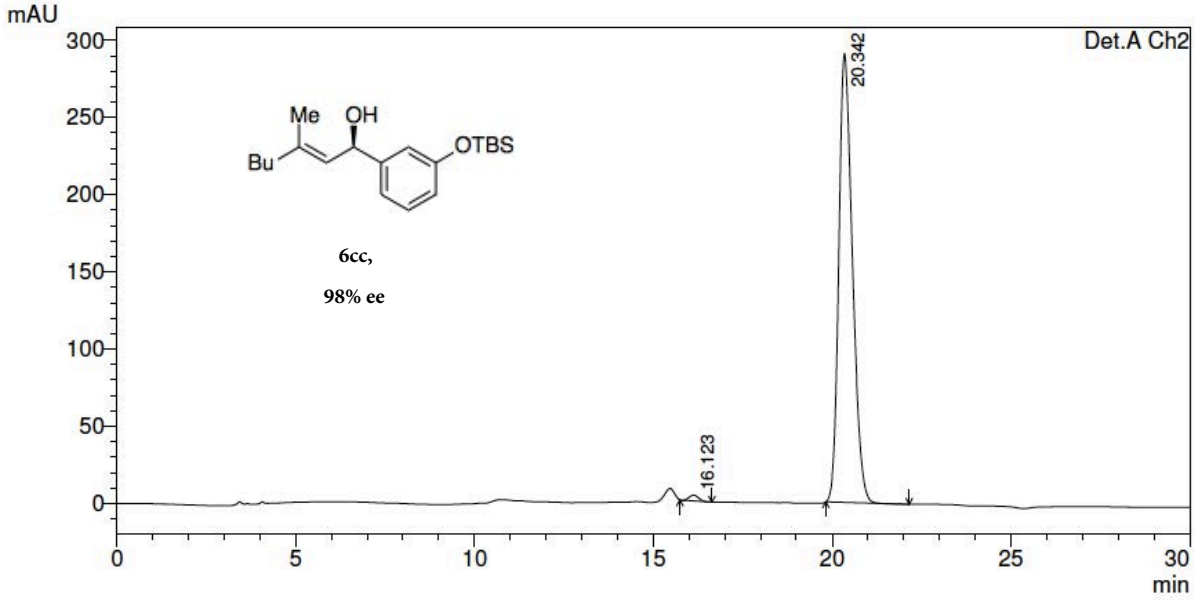
Compound 6cc, racemic



Detector A Ch2 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.068	872208	36832	49.089	51.493
2	21.479	904570	34696	50.911	48.507
Total		1776778	71528	100.000	100.000

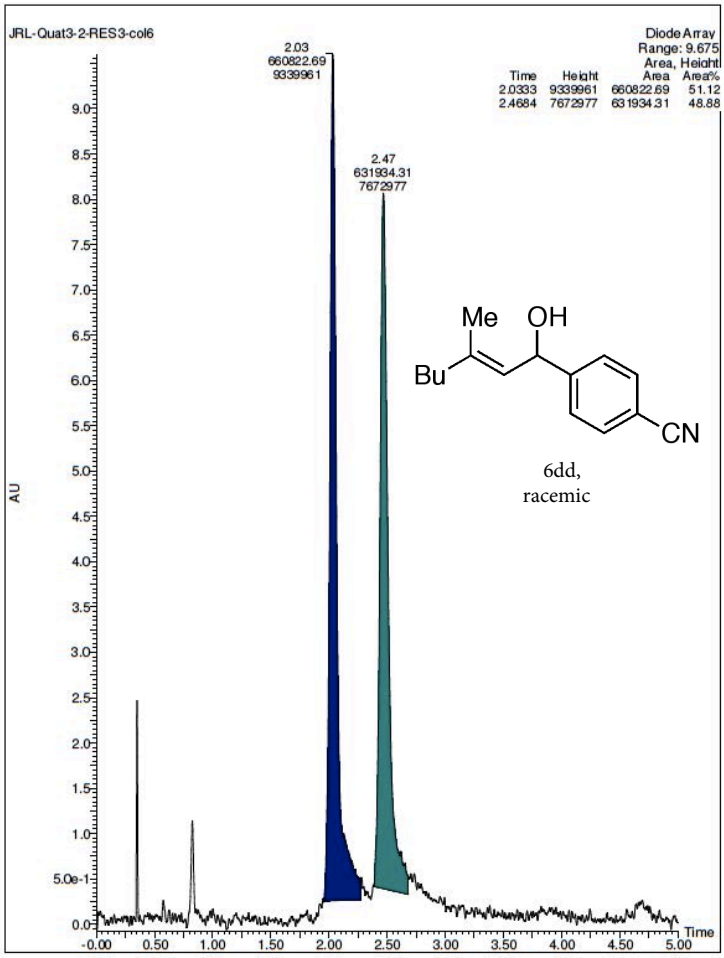
Compound 6cc, 98% ee



Detector A Ch2 210nm

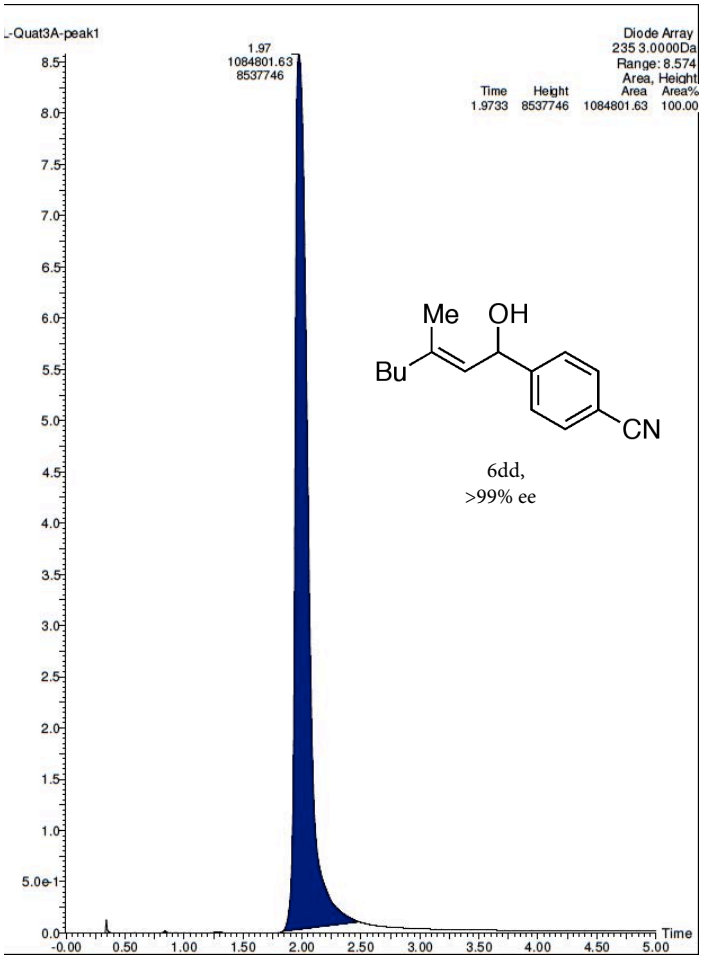
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.123	64591	3650	0.831	1.240
2	20.342	7705108	290709	99.169	98.760
Total		7769699	294359	100.000	100.000

Compound 6dd, racemic



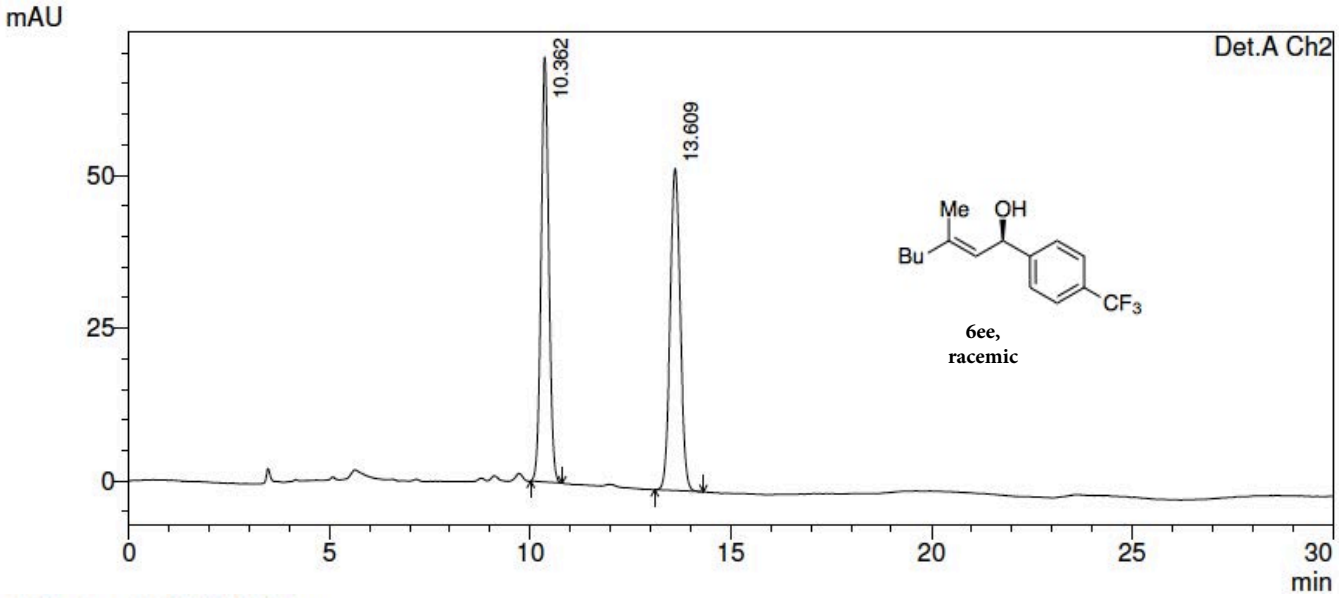
6dd,
racemic

Compound 6dd, >99% ee



6dd,
>99% ee

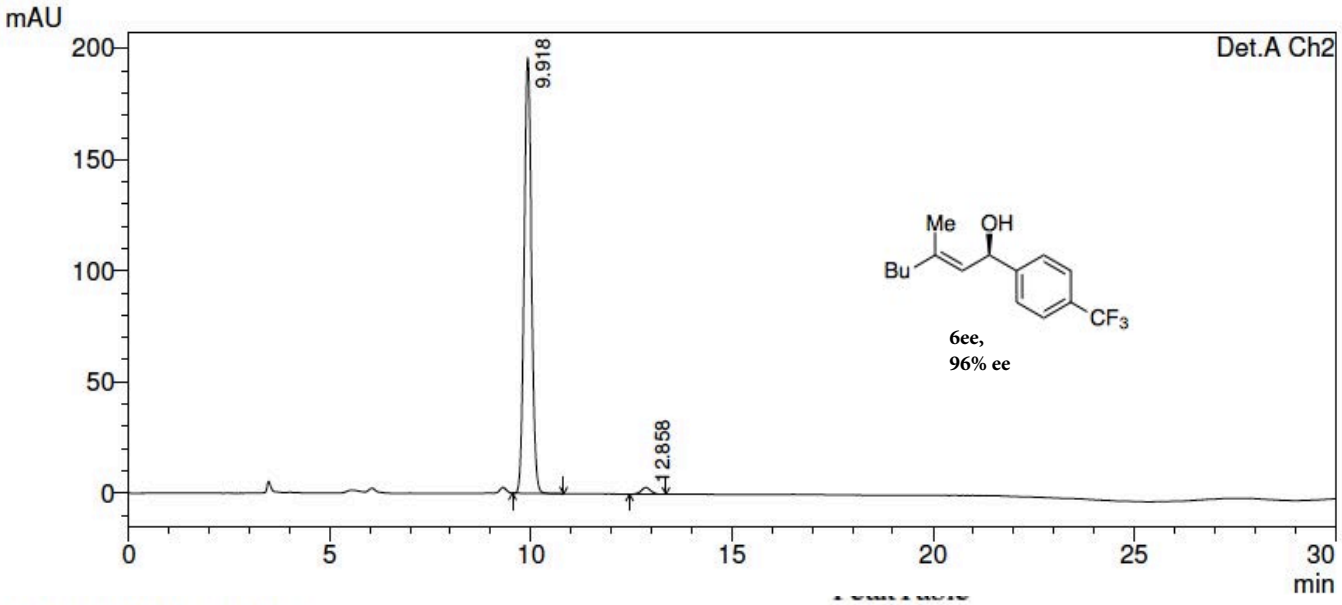
Compound 6ee, racemic



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

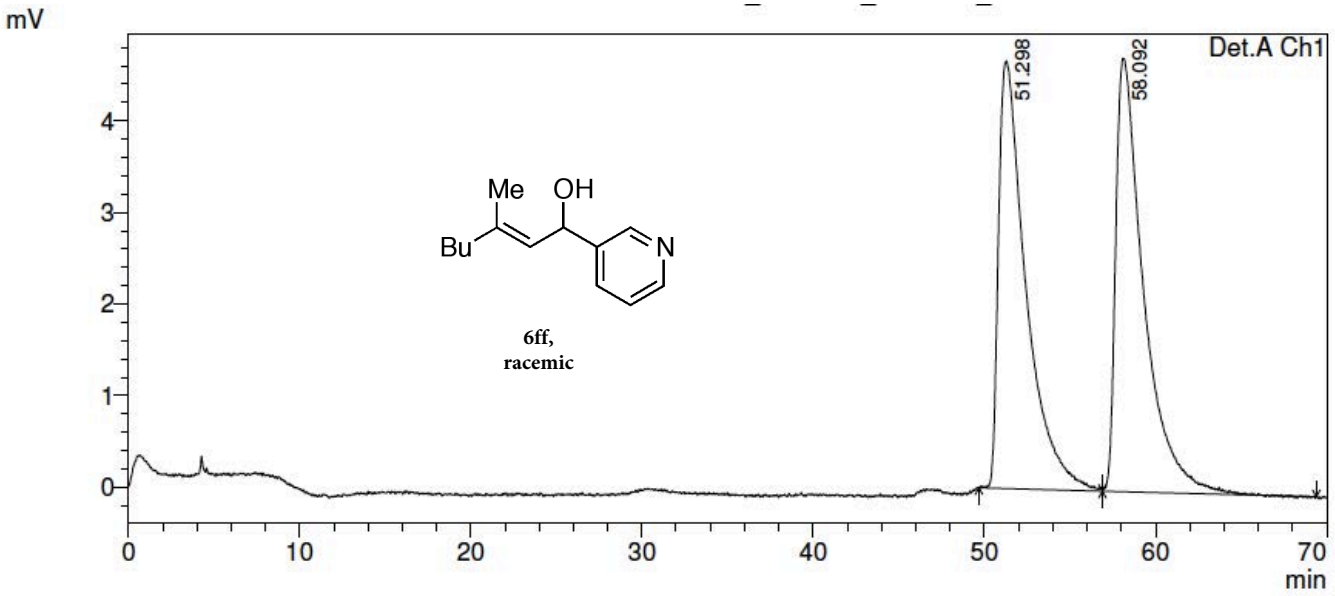
Compound 6ee, 96% ee



Detector A Ch2 210nm

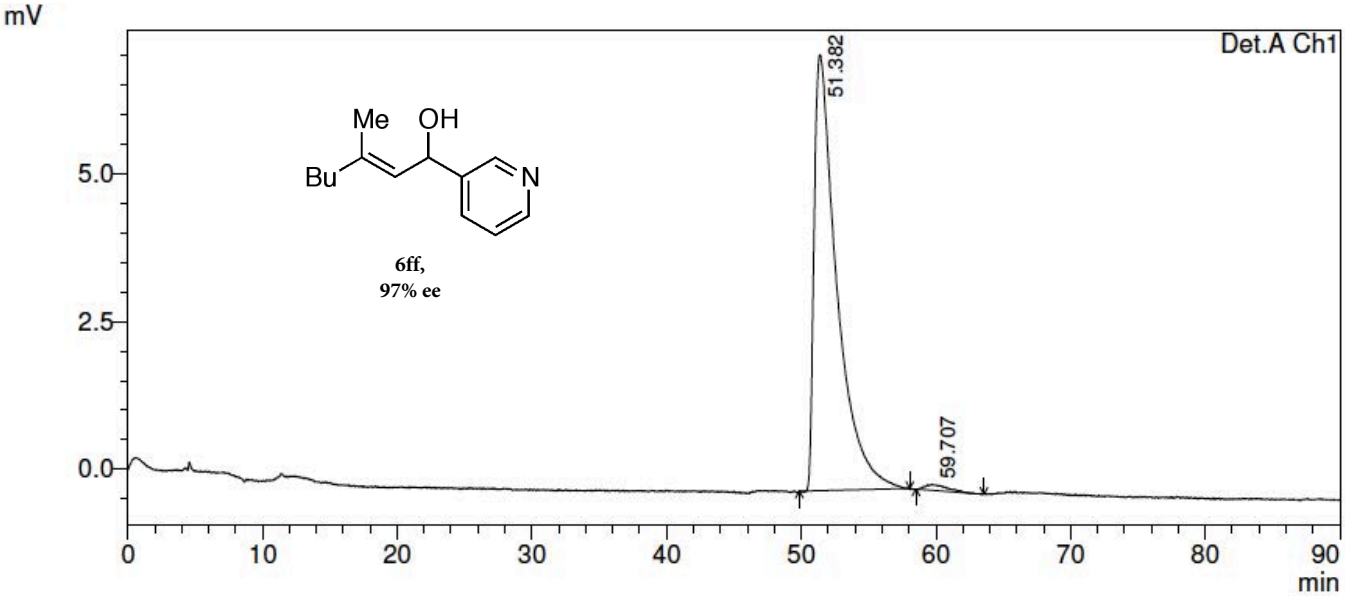
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.918	2479272	195920	98.133	98.519
2	12.858	47159	2945	1.867	1.481
Total		2526432	198865	100.000	100.000

Compound 6ff, racemic



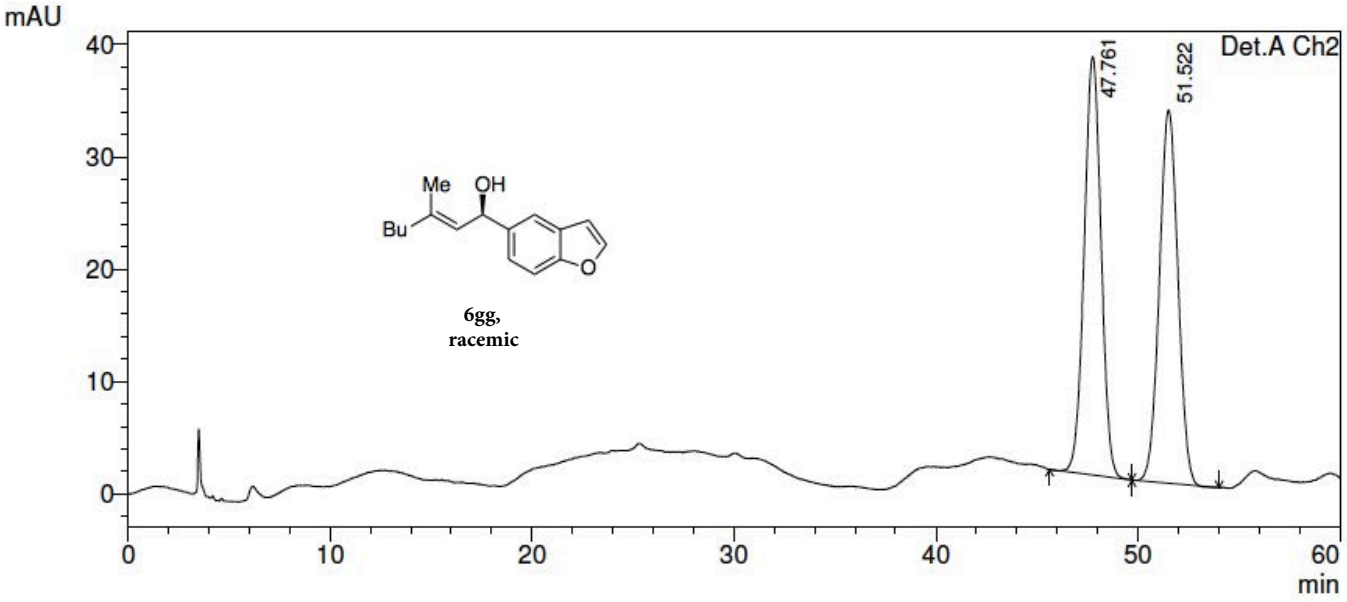
Peak#	Ret. Time	Area	Height	Area %	Height %
1	51.298	520059	4672	49.302	49.672
2	58.092	534794	4734	50.698	50.328
Total		1054853	9406	100.000	100.000

Compound 6ff, 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

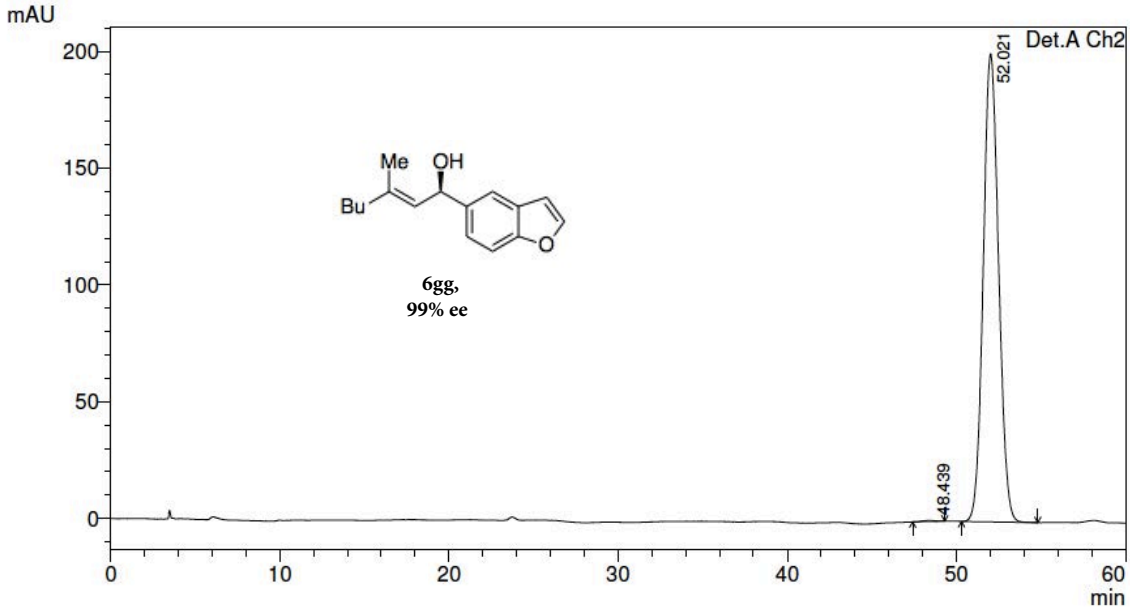
Compound 6gg, racemic



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

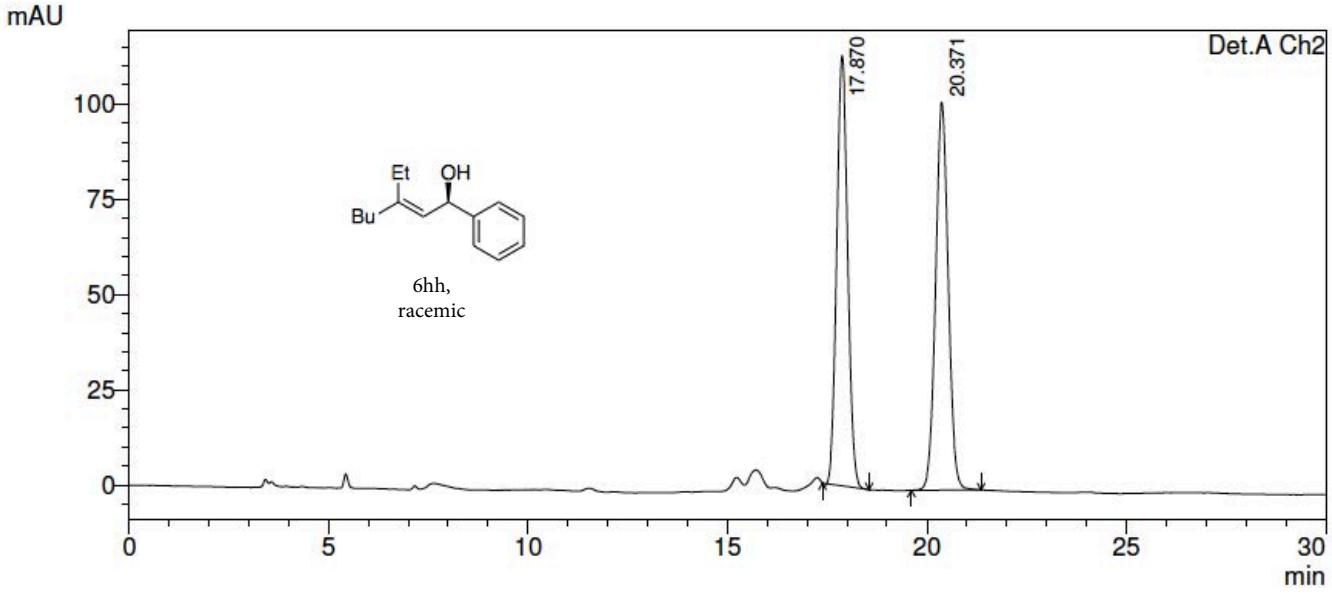
Compound 6gg, 99% ee



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

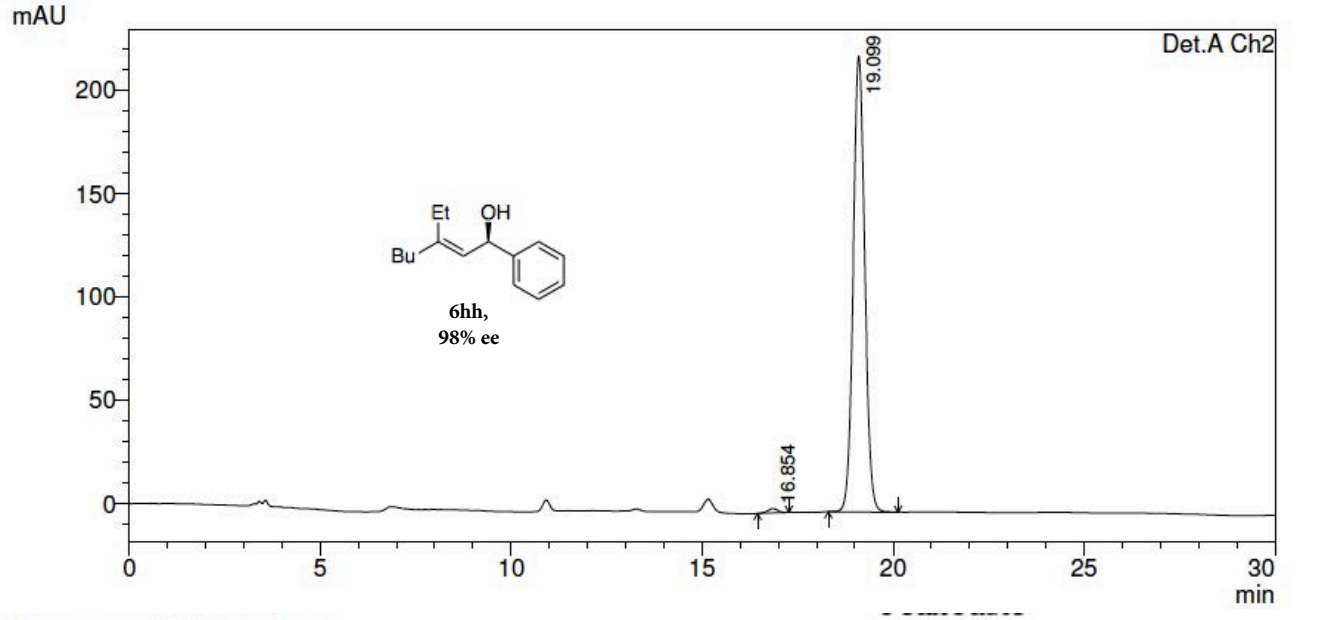
Compound 6hh, racemic



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

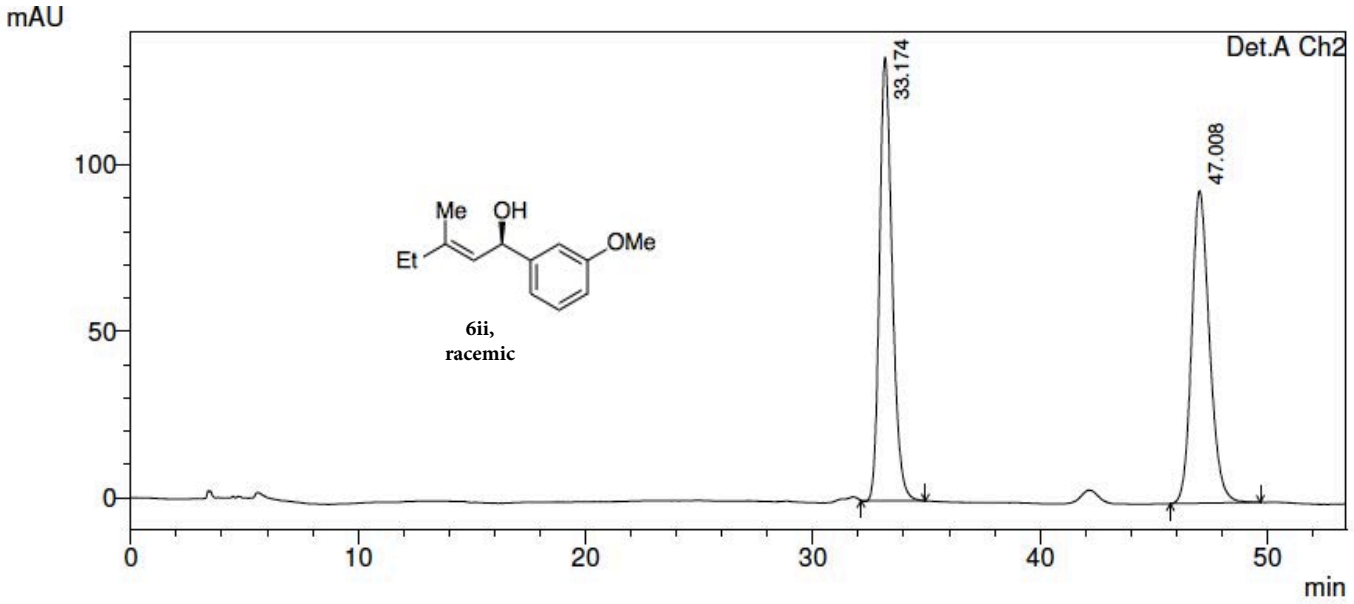
Compound 6hh, 98% ee



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

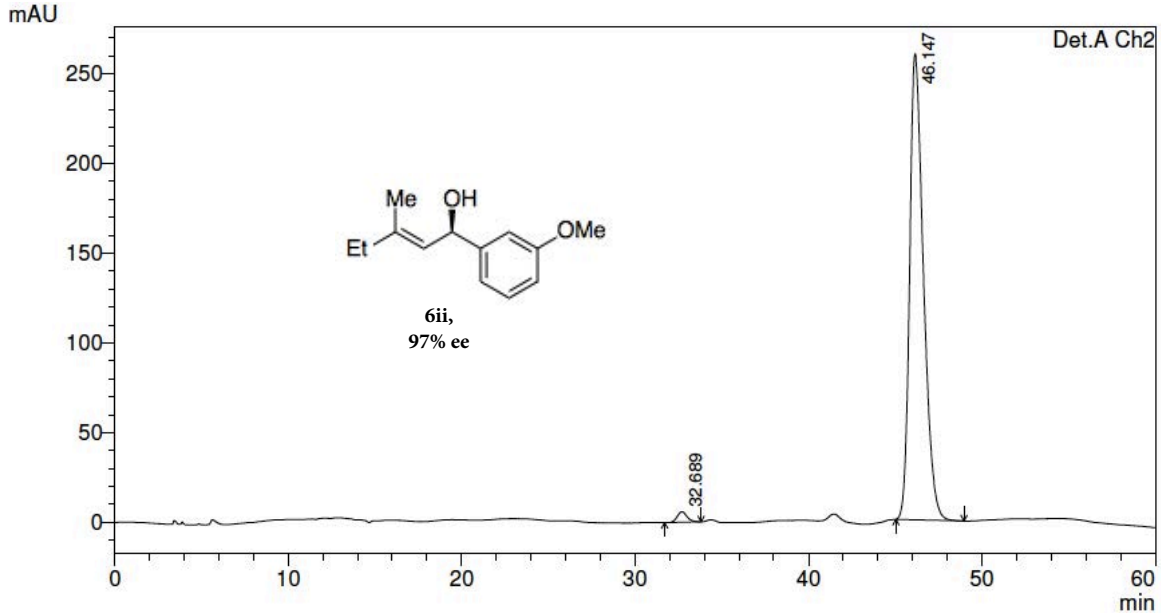
Compound 6ii, racemic



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

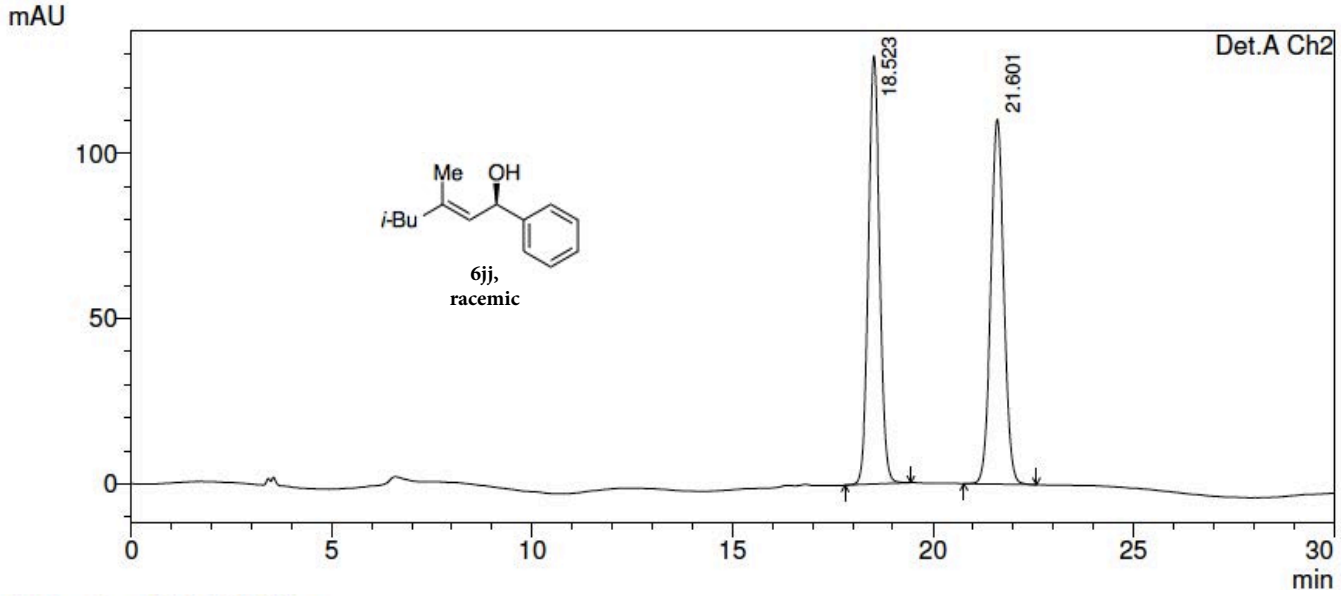
Compound 6ii, 97% ee



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

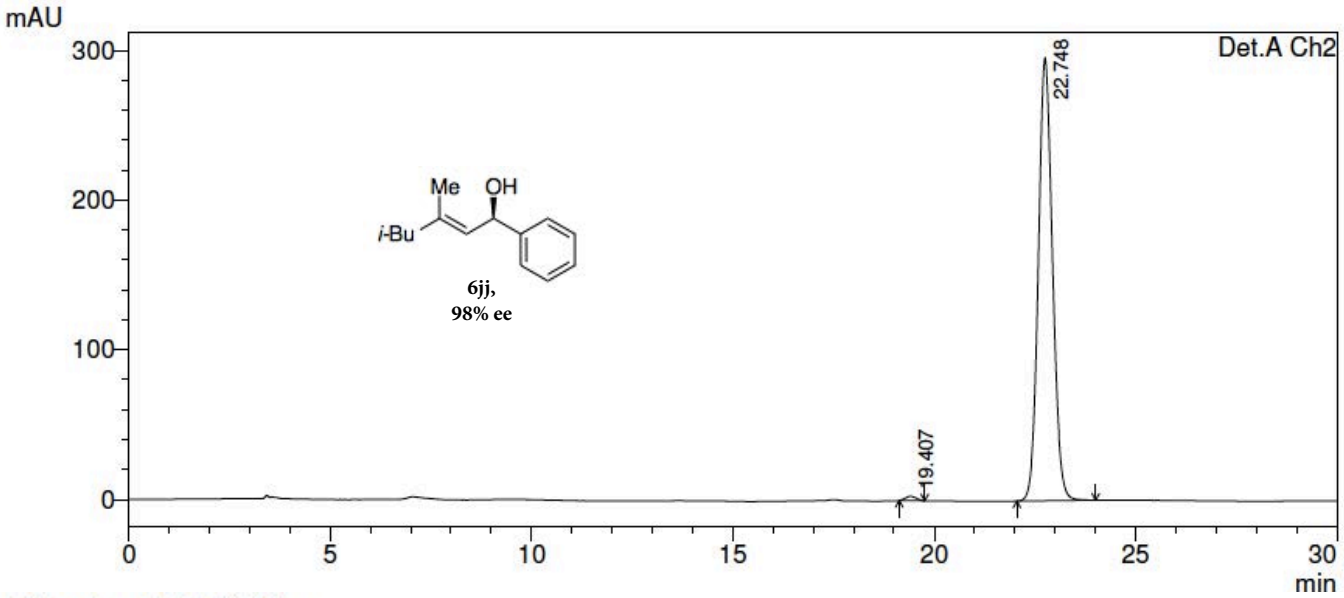
Compound 6jj, racemic



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

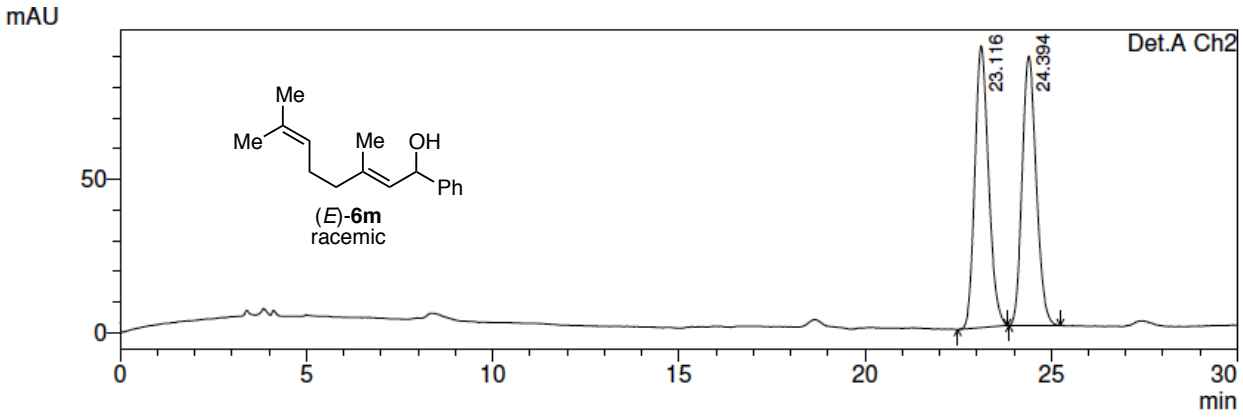
Compound 6jj, 98% ee



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

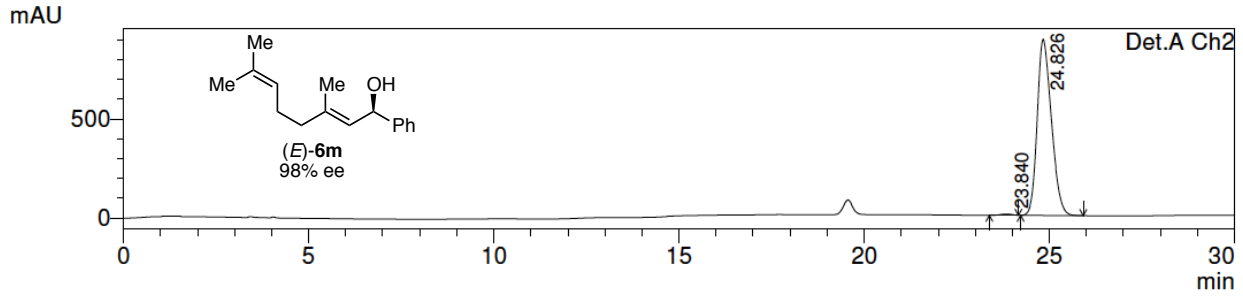
Compound (*E*)-**6mm**, racemic



Detector A Ch2 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.116	2360439	91725	50.551	51.151
2	24.394	2308992	87597	49.449	48.849
Total		4669430	179322	100.000	100.000

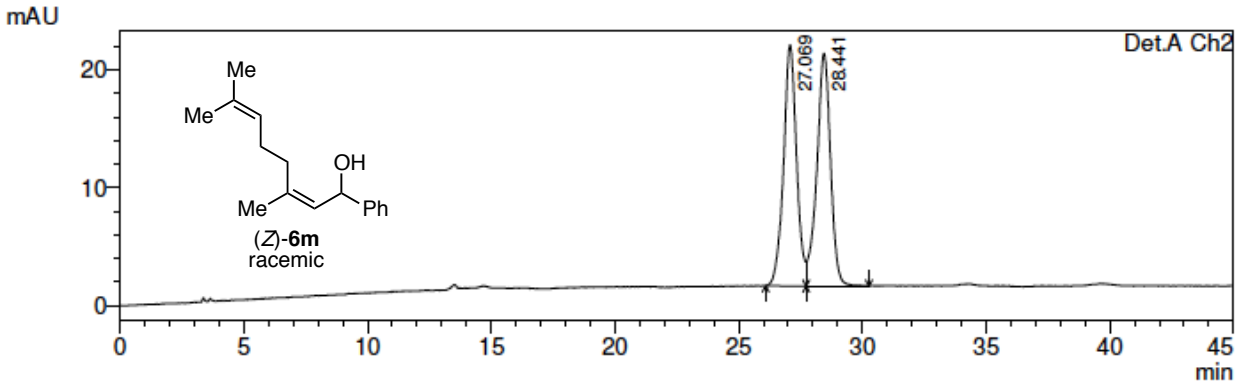
Compound (*E*)-**6mm**, 98% ee



Detector A Ch2 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.840	149095	7218	0.623	0.805
2	24.826	23775412	889683	99.377	99.195
Total		23924507	896900	100.000	100.000

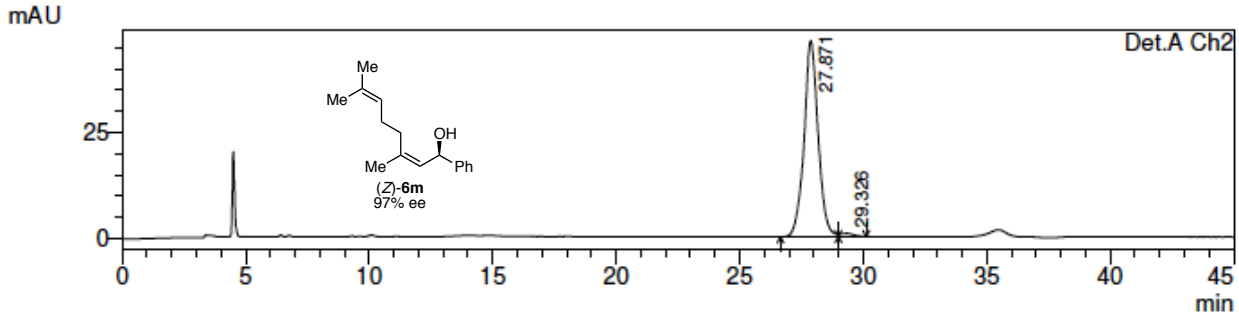
Compound (*Z*)-**6mm**, racemic



Detector A Ch2 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.069	746733	20459	49.506	50.884
2	28.441	761639	19748	50.494	49.116
Total		1508373	40208	100.000	100.000

Compound (*Z*)-**6mm**, 97% ee



Detector A Ch2 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.871	1821813	46039	98.403	98.313
2	29.326	29568	790	1.597	1.687
Total		1851381	46829	100.000	100.000