γ-Selective Cross-Coupling of Allylic Silanolate Salts with Aromatic Bromides Using Trialkylphosphonium Tetrafluoroborate Salts Prepared Directly from Phosphine•Borane Adducts

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SUPPORTING INFORMATION

Table of Contents ***Page***

Detailed Experimental Procedures

General Experimental

All reactions were performed in oven (140 °C) and/or flame dried glassware under an atmosphere of dry argon unless otherwise noted. Reaction solvents tetrahydrofuran (Fisher, HPLC grade) and methylene chloride (Fisher, unstabilized HPLC grade) were dried by percolation through two columns packed with neutral alumina under a positive pressure of argon.

Reaction solvents hexanes (Fisher, OPTIMA grade) and toluene (Fisher, ACS grade) were dried by percolation through a column packed with neutral alumina and a column packed with Q5 reactant (supported copper catalyst for scavenging oxygen) under a positive pressure of argon. Solvents for filtration, transfers, and chromatography were certified ACS grade. “Brine” refers to a saturated solution of sodium chloride in water. All reaction temperatures correspond to internal temperatures measured with Teflon coated thermocouples unless otherwise noted.

^{1}H and ^{13}C NMR spectra were recorded on Varian Unity-500 MHz (126 MHz, ^{13}C) spectrometers. Spectra are referenced to residual chloroform (δ = 7.26 ppm, ^{1}H; 77.0 ppm, ^{13}C), residual benzene (δ = 7.15 ppm, ^{1}H; 128.0 ppm, ^{13}C), or residual methylene chloride (δ = 5.30 ppm, ^{1}H; 53.5 ppm, ^{13}C). Chemical shifts are reported in parts per million, multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), h (hextet), sext (sextet), m (multiplet), and br (broad). Coupling constants, *J*, are reported in Hertz, and integration is provided and assignments are indicated. Elemental analysis was performed by the University of Illinois Microanalysis Laboratory, or Robertson Microlit Laboratories. Mass spectrometry (MS) was performed by the University of Illinois Mass Spectrometry Laboratory. Electron Impact (EI) spectra were performed at 70 eV using methane as the carrier gas on a Finnagin-MAT C5 spectrometer. Chemical Ionization (CI) spectra were performed with methane reagent gas on a Micromass 70-VSE spectrometer. Electrospray Ionization (ESI) spectra were performed on a Micromass Q-Tof Ultima spectrometer. Data are reported in the form of m/z (intensity relative to the base peak = 100). Infrared spectra (IR) were recorded on a Perkin-Elmer FT-IR system and peaks are reported in cm^{-1} with indicated relative intensities: s (strong, 0–33% T); m (medium, 34–66% T), w (weak, 67–100% %), and br (broad). Melting points (mp) were determined on a Thomas-Hoover capillary melting point apparatus in sealed tubes and are corrected. Kugelrohr (bulb-to-bulb) distillations were performed on a Büchi GKR-50 apparatus with boiling points (bp) corresponding to uncorrected air bath temperatures (ABT).

Analytical thin-layer chromatography was performed on Merck silica gel 60 F_{254} or Merck silica gel 60 RP-18 F_{254s} plates. Visualization was accomplished with UV light and/or $KMnO_4$ solution. R_f values reported were measured using a 10 × 2 cm TLC plate in a developing chamber containing the solvent system described. Flash chromatography was performed using Merck silica gel 60 230–400 mesh (60–63 μ, 60 Å pore size).

Analytical gas chromatography (GC) was performed using a Hewlett-Packard 5890 Gas Chromatograph fitted with a flame ionization detector. GC Method 1 involved injections onto a Hewlett-Packard HP1 (30 m × 0.32 mm) capillary column. Injector temperature was 250 °C and the detector temperature was 300 °C with an N_2 carrier gas flow of 4.2 mL/min. The column temperature program was as follows: 50 °C for 2 min, 50 °C to 270 °C at 40 °C/min, then hold for 4.5 min for a total run time of 12 min. Retention times (t_R) were obtained using Agilent Chemstation software. Response factors were generated by triplicate runs of three molar ratios of analyte and mesitylene dissolved in ethyl acetate.

Commercial reagents were purified by distillation or recrystallization prior to use unless noted. 1-Bromonaphthylene (97%), 2-bromonaphthylene (99%), 2-bromoanisole (97%), 2-bromotoluene (99%), 4-bromoanisole (99%), and 4-bromobenzotrifluoride (99%), 4-bromodiphenyl ether (99%), 2-bromomesitylene (99%), 5-bromo-*m*-xylene (97%), and 4-bromo-*tert*-butylbenzene (98%) were purchased from Aldrich. 1,3-Butadiene (99%) and *tert*-Butyl lithium (1.7 M), 4-bromobenzoic acid (98%), and 5-bromoindole (99%), borane-tetrahydrofuran complex (1 M), tetrafluoroboric acid diethyl ether complex (54% w/w) were purchased from Aldrich and used as received. Ethylmagnesium bromide (3 M) was purchased from Aldrich and titrated by the method of Hoye[1] prior to use. Tri-*tert*-butylphosphine, tricyclohexylphosphine, and tetrakis(triphenylphosphine)palladium (99%) were purchased from Strem and used as received. 3-Bromoquinoline (99%) was purchased from Alfa-Aesar. Tetrafluoroboric acid (50% aq.) and 2-bromo-6-methoxynaphthalene (98%) was purchased from Alfa-Aesar and used as received. *trans*, *trans*-Dibenzylideneacetone was purchased from Acros and used as received. Palladium chloride was purchased from Pressure Chemical and used as received. Sodium hydride was purchased from Aldrich as a suspension in mineral oil, washed with hexanes and stored under dry argon.

Response Factors

Response factors for quantitative GC analysis were calculated using the following equation and data:

Response factor = (mmol analyte × rel. area mesitylene) ÷ (mmol mesitylene × rel. area analyte)

Response Factor for Determination of Conversion:

mmol mesitylene	rel. area mesitylene	mmol **2a**	rel. area **2a**	response factor
0.0835	76.627	0.0271	22.001	1.13
0.0835	76.607	0.0271	22.02	1.13
0.0835	76.562	0.0271	22.062	1.13
0.0627	62.442	0.0406	36.435	1.11
0.0627	62.425	0.0406	36.458	1.11
0.0627	62.432	0.0406	36.45	1.11
0.0418	45.721	0.0542	53.619	1.11
0.0418	45.662	0.0542	53.541	1.11
0.0418	45.583	0.0542	53.431	1.11
			Avg:	**1.12**

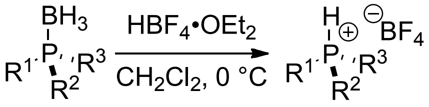
Response Factor for Determination of Yield:

mmol mesitylene	rel. area mesitylene	mmol **5a**	rel. area **5a**	response factor
0.0501	72.22	0.0143	26.129	0.787
0.0501	71.851	0.0143	26.099	0.784
0.0501	71.897	0.0143	26.18	0.782
0.0334	54.007	0.0214	44.235	0.782
0.0334	54.008	0.0214	44.271	0.781
0.0334	53.806	0.0214	44.196	0.780
0.0167	30.411	0.0285	67.448	0.770
0.0167	30.413	0.0285	67.501	0.769
0.0167	30.373	0.0285	67.482	0.769
			Avg:	**0.778**

Literature Preparations

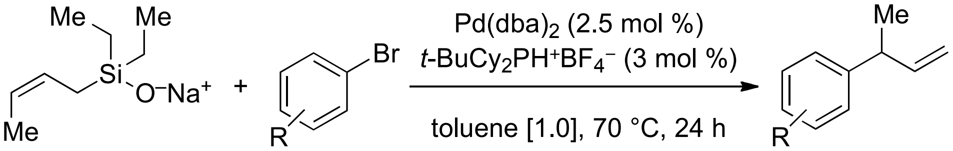
The following compounds were prepared by literature methods: Pd(dba)$_2$,[2] allylpalladium chloride dimer (APC),[3] 5-bromo-*N*-Boc-indole,[4] chlorodicyclohexylphosphine,[5] tricyclohexylphosphine trihydroboron,[6] tri-*tert*-butylphosphine trihydroboron.[6] (*Z*)-2-butenyltrichlorosilane,[7] (*E*)-2-butynol,[8] (*E*)-1-chloro-2-butene,[9] (*E*)-2-butenyltrichlorosilane,[7] sodium (*E*)-2-butenyldimethylsilanolate,[10] and sodium (*Z*)-2-butenyldimethylsilanolate.[10]

General Procedure I: Preparation of Trialkylphosphonium Tetrafluoroborate Salts



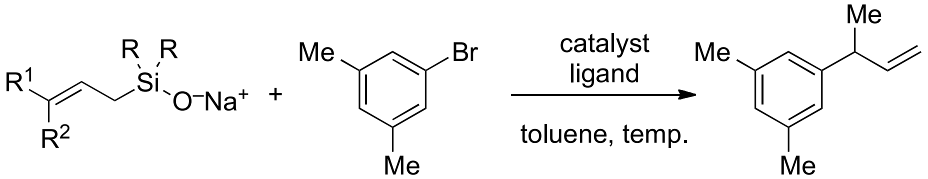
To a flame dried, 100-mL, single-neck, round-bottomed flask containing a magnetic stir bar, and equipped an argon inlet capped with a septum was added the phosphine•borane adduct (1.0 equiv). The flask was then evacuated and filled with argon. CH_2Cl_2 was then added by syringe and the resulting solution was cooled to 0 °C. While at 0 °C, HBF_4•OEt_2 (15 equiv) was added dropwise by syringe. The reaction mixture was stirred 30 min at 0 °C and then warmed to 22 °C by removal of the cooling bath. After 30 min at 22 °C, aq. tetrafluoroboric acid was added by pipette and the biphasic mixture was vigorously stirred an additional 30 min. The mixture was then diluted with CH_2Cl_2 and the aqueous phase was separated in a separatory funnel and was further extracted with CH_2Cl_2 (×2). The three separate organic extracts were combined, dried over $MgSO_4$ until flocculent, filtered, and concentrated (30 °C, 10 mm Hg) to a thick syrup. The syrup was then pipetted dropwise into an Erlenmeyer flask containing stirred ether. The resulting solid was harvested by filtration. Purification by recrystallization of a saturated solution (CH_2Cl_2) layered with ether (ether/CH_2Cl_2, ~10:1) afforded the product.

General Procedure II: Preparative Cross-Coupling Protocol



To a flame dried, 2-mL, Schlenk tube, containing a magnetic stir bar, equipped with a sidearm argon inlet and capped with a septum was added $Pd(dba)_2$ (14.4 mg, 0.025 mmol, 0.025 equiv) and *t*-$BuCy_2PH^+BF_4^-$ (10.3 mg, 0.03 mmol, 0.03 equiv). The flask was then sequentially evacuated and filled with argon three times. The aromatic bromide (1.0 equiv) was then added by syringe. Sodium (*Z*)-2-butenyldiethylsilanolate (270 mg, 1.5 mmol, 1.5 equiv), pre-weighed into a 10-mL, two-necked, round-bottomed flask in a dry-box, was then dissolved in toluene (1.0 mL) and added by syringe. The septum was replaced with a Teflon plug valve under an active flow of argon and the tube sealed. The mixture was then stirred at 22 °C for 5 min and then heated to 70 °C in a preheated oil bath. After 24 h, the mixture was cooled to 22 °C, filtered through silica gel (2 cm × 2 cm) in a glass-fritted filter (C, 2 cm × 5 cm) and the filter cake washed with ether (3 × 30 mL). The filtrate was concentrated (30 °C, 100 mm Hg) and to the residue was added sat. aq. KF (10 mL). The mixture was vigorously stirred for 1 h at 22 °C and then ether (15 mL) was added. The aqueous phase was separated in a 60-mL separatory funnel and was extracted with ether (2 × 15 mL). The three separate organic extracts were then sequentially washed with H_2O (2 × 15 mL) and brine (15 mL), then were combined, dried over $MgSO_4$ until flocculent, and filtered. Concentration of the filtrate (30 °C, 100 mm Hg) and purification by silica gel chromatography followed by Kugelrohr distillation afforded the product.

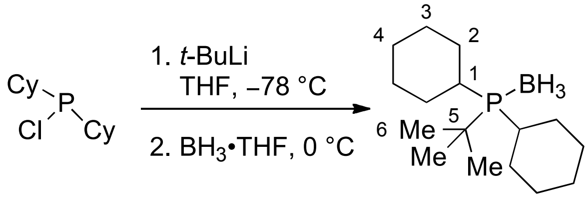
General Procedure III: Small Scale Cross-Coupling Protocol



In a dry box, the ligand was weighed into an oven dried, Dram vial containing a magnetic stir bar. The palladium catalyst was then weighed and added to the vial. A solution of the internal standard, aromatic bromide, and silanolate in the reaction solvent was then added to the vial via syringe. The vial was then capped with a Teflon lined screw cap and the seal wrapped with electrical tape. The vial was then removed from the dry box and heated in a preheated oil bath. After the allotted reaction time, an analytical aliquot (25 μL) was removed from the reaction mixture by syringe, quenched with 10% 2-(dimethylamino)ethanethiol hydrochloride solution (150 μL), and then was extracted with EtOAc (1.0 mL). The organic extract was then filtered through a small plug of silica gel in a pipette (0.5 cm × 1.0 cm) and the filter cake was washed with EtOAc (0.5 mL). The sample was then analyzed by GC.

Preparation of Phosphonium Tetrafluoroborate Salts

Preparation of Dicyclohexyl(1,1-dimethylethyl)phosphine-Trihydridoboron (6)



A flame dried, 50-mL, three-neck, round bottomed flask, containing a magnetic stir bar, equipped with a Teflon coated thermocouple, argon inlet, and septum was added THF (4 mL) and Cy_2PCl (1.1 mL, 5.0 mmol, 1.0 equiv). The flask was cooled to −78 °C and then *t*-BuLi (3.5 ml, 1.2 mmol, 1.2 equiv) was added dropwise via syringe. The mixture was then allowed to warm to 22 °C by removal of the cooling bath. After 2 h, the mixture was cooled to 0 °C and BH_3•THF (6.0 mL, 6.0 mmol, 1.2 equiv) was added slowly by syringe. The mixture was then warmed to 22 °C, stirred for 1 h, diluted with EtOAc (25 mL), and then poured onto 1 M HCl (50 mL) at 0 °C. The aqueous phase was separated in a 150-mL separatory funnel and then was extracted with EtOAc (2 × 25 mL). The three separate organic extracts were then sequentially washed with brine (50 mL), then were combined, dried over Na_2SO_4 until flocculent, and filtered. Concentration of the filtrate (30 °C, 10 mm Hg) and purification by recrystallization

(EtOAc) afforded 1.05 g (78%) of **6** as a white, crystalline solid.

Data for (**6**):

mp: 122–123 °C

^{1}H NMR: (500 MHz, $CDCl_3$)

2.02–1.95 (m, 6 H), 1.91 (tt, *J* = 11.5, 2.9, 2 H, HC(1)), 1.85–1.80 (m, 6 H), 1.72–1.69 (m, 3 H), 1.57–1.44 (m, 5 H), 1.25 (d, *J* = 12.2, 9 H HC(6)), 0.31 (dd, *J* = 189.5, 85.5, 3 H, HB).

^{13}C NMR: (126 MHz, $CDCl_3$)

32.5 (d, *J* = 27.9, C(1)), 30.8 (d, *J* = 27.5, C(5)), 28.7 (d, *J* = 1.5, C(2)), 28.5 (d, *J* = 0.7, C(6)), 28.2 (d, *J* = 1.5, C(2)), 27.5 (d, *J* = 4.2, C(3)), 27.4 (d, *J* = 4.2, C(3)), 26.0 (d, *J* = 1.1, C(4)).

^{31}P NMR: (162 MHz, $CDCl_3$)

38.8 (dd, *J* = 124, 49.7).

IR: (film)

2935 (s), 2855 (s), 2375 (m), 1477 (w), 1448 (m), 1398 (w), 1368 (w), 1273 (w), 1257 (w), 1189 (w), 1145 (w), 1071 (m), 1005 (w), 917 (w), 888 (w), 852 (w), 823 (w), 762 (s), 749 (s), 738 (s), 732 (s), 720 (s), 715 (m), 706 (s), 699 (m).

MS: (EI, 70 eV)

265 ($[M{-}3H]^+$, 18), 254 ($[M{-}BH_3]^+$, 100), 198 (26), 197 (18), 172 (75), 117 (32), 83 (20), 57 (37).

HRMS: $C_{16}H_{34}BP$ ($[M{-}H]^+$, ESI)

Calcd.: 267.2413

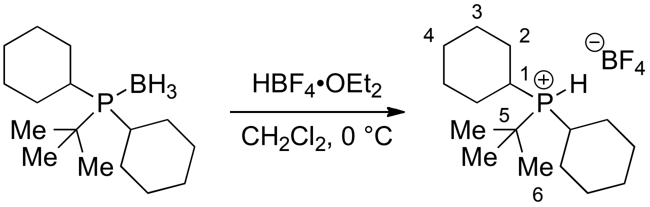
Found: 267.2414

TLC: R_f 0.54 (9:1 pentane/ether) [silica gel, aqueous $KMnO_4$]

Analysis: $C_{16}H_{34}BP$ (268.23)

Calcd.:	C, 71.65	H, 12.78
Found:	C, 71.83	H, 12.80

Preparation of Dicyclohexyl(1,1-dimethylethyl)phosphonium Tetrafluoroborate (3)



Following General Procedure I, **6** (500 mg, 1.86 mmol, 1.0 equiv), HBF_4•OEt_2 (3.4 mL, 28 mmol, 15 equiv), and CH_2Cl_2 (37 mL) were combined at 0 °C. After 30 min, the reaction mixture was warmed to 22 °C and aq. tetrafluoroboric acid (24 mL) was added. The aqueous phase was separated and the organic extract was dried over $MgSO_4$ until flocculent, filtered, and concentrated (30 °C, 10 mm Hg) to a thick syrup. The syrup was then pipetted dropwise into stirred ether and the resulting solid was harvested by filtration. Purification by recrystallization of a saturated solution (CH_2Cl_2) layered with ether (ether/CH_2Cl_2, ~10:1) afforded 573 mg (90%) of **3** as a white, crystalline solid.

Data for (**3**):

mp: 233–234 °C

^{1}H NMR: (500 MHz, CD_2Cl_2)

5.56 (d, *J* = 464.6, 1 H, HP), 2.55 (bq, *J* = 12.5, 2 H, HC(1)), 2.14–2.05 (m, 4 H), 1.96–1.88 (m, 4 H), 1.83–1.76 (m, 2 H), 1.75–1.63 (m, 4 H), 1.48 (d, *J* = 16.4, 9 H), 1.45–1.37 (m, 4 H), 1.36–1.25 (m, 2 H).

^{13}C NMR: (126 MHz, CD_2Cl_2)

32.4 (d, *J* = 36.1, C(1)), 31.0 (d, *J* = 35.7, C(5)), 29.9 (d, *J* = 3.8, C(2)), 28.9 (d, *J* = 3.8, C(2)), 27.4 (C(6)), 27.01 (d, *J* = 12.4, C(3)), 26.9 (d, *J* = 12.4, C(3)), 25.4 (d, *J* = 1.1, C(4)).

^{31}P NMR: (162 MHz, CD_2Cl_2)

40.7.

IR: (film)

3068 (w), 2943 (s), 2861 (m), 1467 (w), 1450 (m), 1406 (w), 1376 (w), 1298 (w), 1274 (w), 1266 (w), 1181 (w), 1060 (s), 932 (w), 876 (w), 820 (w).

MS: (EI, 70 eV)

254 ($[M{-}H]^+$, 52), 197 (48), 172 (95), 143 (22), 117 (100), 91 (17), 83 (78), 81 (36), 67 (11), 61 (10), 57 (85), 55 (63).

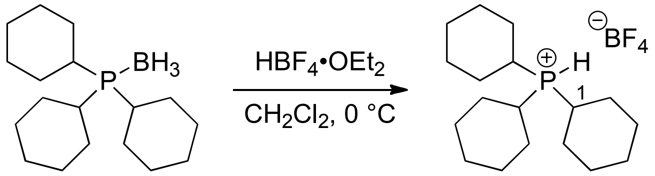
HRMS: $C_{16}H_{32}P$ (M^+, ESI)

Calcd.:	255.2242
Found:	255.2240

Analysis: $C_{16}H_{32}BF_4P$ (342.20)

Calcd.:	C, 56.16	H, 9.43	F, 22.21
Found:	C, 55.84	H, 9.71	F, 22.18

Preparation of Tricyclohexylphosphonium Tetrafluoroborate (10)



Following General Procedure I, **8** (294 mg, 1.0 mmol, 1.0 equiv), HBF_4•OEt_2 (1.8 mL, 15 mmol, 15 equiv), and CH_2Cl_2 (20 mL) were combined at 0 °C. After 30 min, the reaction mixture was warmed to 22 °C and aq. fluoroboric acid (13 mL) was added. The aqueous phase was separated and the organic extract was dried over $MgSO_4$ until flocculent, filtered, and concentrated (30 °C, 10 mm Hg) to a thick syrup. The syrup was then pipetted dropwise into stirred ether and the resulting solid was harvested by filtration. Purification by recrystallization of a saturated solution (CH_2Cl_2) layered with ether (ether/CH_2Cl_2, ~10:1) afforded 312 mg (85%) of **86** as a white, crystalline solid. Spectroscopic data matched those reported in the literature.[11]

Data for (**10**):

mp: 170–171 °C

^{1}H NMR: (500 MHz, CD_2Cl_2)

5.61 (dq, *J* = 466.3, 4.0, 1 H, HP), 2.52–2.42 (m, 3 H, HC(1)), 2.05–1.98 (m, 6 H), 1.96–1.90 (m, 6 H), 1.83–1.78 (m, 3 H), 1.65–1.54 (m, 6 H), 1.47–1.39 (m, 6 H), 1.38–1.27 (m, 3 H).

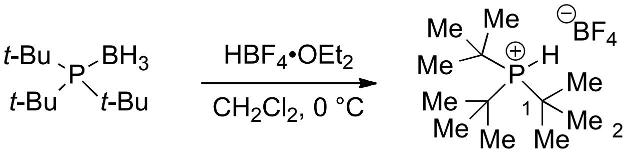
^{13}C NMR: (126 MHz, CD_2Cl_2)

28.5 (d, *J* = 39.3 C(1)), 28.3 (d, *J* = 3.6, C(2)), 26.6 (d, *J* = 12.8, C(3)), 25.4 (d, *J* = 1.1, C(4)).

^{31}P NMR: (162 MHz, CD_2Cl_2)

30.2

Preparation of Tri(1,1-dimethylethyl)phosphonium Tetrafluoroborate (9)



Following General Procedure I, **7** (216 mg, 1.0 mmol, 1.0 equiv), HBF_4•OEt_2 (1.8 mL, 15 mmol, 15 equiv), and CH_2Cl_2 (20 mL) were combined at 0 °C. After 30 min, the reaction mixture was warmed to 22 °C and aq. tetrafluoroboric acid (13 mL) was added. The aqueous phase was separated and the organic extract was dried over $MgSO_4$ until flocculent, filtered, and concentrated (30 °C, 10 mm Hg) to a thick syrup. The syrup was then pipetted dropwise into stirred ether and the resulting solid was harvested by filtration. Purification by recrystallization of a saturated solution (CH_2Cl_2) layered with ether (ether/CH_2Cl_2, ~10:1) afforded 262 mg (90%) of **9** as a white, crystalline solid. Spectroscopic data matched those reported in the literature.[12]

Data for (**9**):

mp: >250 °C (dec.)

^{1}H NMR: (500 MHz, CD_2Cl_2)

5.78 (d, *J* = 456.1, 1 H, HP), 1.64 (d, *J* = 15.4, 9 H, HC(2)).

^{13}C NMR: (126 MHz, CD_2Cl_2)

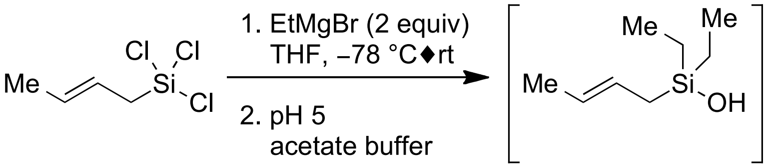
37.5 (d, *J* = 28.4, C(1)), 30.29 C(2).

^{31}P NMR: (162 MHz, CD_2Cl_2)

54.3.

Preparation of (*E*)-1b and (*Z*)-1b

Preparation of (*E*)-1,1-Diethyl-1-(2-buten-1-yl)silanol ((*E*)-1b')



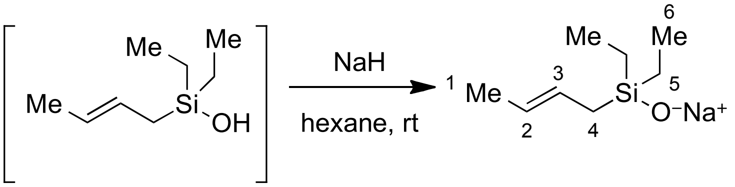
(*E*)-**1b'**

To a three-necked, 250 mL, round-bottom flask equipped with a magnetic stir bar, two septa, and an argon inlet was added THF (50 mL) and (*E*)-2-butenyltrichlorosilane (4.74 g, 25 mmol, 1.0 equiv). The solution was then cooled to −78 °C. EtMgBr (23 mL, 50 mmol, 2 equiv) was then added by cannula (~1.5 mL/min) over the course of 15 min. The resulting mixture was stirred 30 min at −78 °C and then warmed to 22 °C over the course of 1 h by removal of the cooling bath. The resulting suspension was then slowly poured into a 1-L Erlenmeyer flask containing vigorously stirred acetate buffer (165 mL, pH 5, 1 M) and ether (33 mL). After 5 min, the reaction mixture was then poured into a 1-L separatory funnel and the aqueous phase was separated and washed with ether (2 x 30 mL), The three separate organic extracts were then sequentially washed with H_2O (50 mL), and sat. aq. $NaHCO_3$ (50 mL). The pH of the resulting aqueous wash was checked with litmus paper to ensure alkalinity. The three separate organic extracts were then washed with H_2O (50 mL) and brine (50 mL), combined, dried over $NaSO_4$ until flocculent, filtered through a pad of silica gel (6 cm × 4 cm) and eluted with ether (2 x 100 mL), and concentrated (23 °C, 10 mm Hg). The residue was then purified by column chromatography (silica gel, 40 mm × 20 cm, pentane/ether, 4:1). Fractions were combined, concentrated to ~15 mL (23 °C, 10 mm Hg) and transferred to a dry box for conversion to its sodium salt.

Data for ((*E*)-**1b'**):

TLC: R_f 0.28 (pentane/Et_2O, 4:1) [silica gel, aqueous $KMnO_4$]

Preparation of Sodium (*E*)-1,1-Diethyl-1-(2-buten-1-yl)silanolate ((*E*)-1b)



(*E*)-**1b'** (*E*)-**1b**

In a dry box, NaH (750 mg, 31.2 mmol, 1.25 equiv) was weighed into a 50-mL, single-necked, round-bottomed flask containing a magnetic stir bar and suspended in hexane (10 mL). The silanol (*E*)-**1b'** in pentane/ether, 4:1 (~15 mL) and was added dropwise to the stirred suspension of NaH. After addition the reaction was aged 30 min with stirring, then was filtered through a fritted-glass funnel (M, 30 mL) into a 100-mL Schlenk flask and the filter cake was washed with hexane (10 mL). The colorless solution was then removed from the dry box and concentrated (23 °C, 0.5 mm Hg). After 3 h under vacuum the semisolid was dissolved in hexane (10 mL) and concentrated (23 °C, 0.5 mm Hg). After 12 h under vacuum (23 °C, 0.5 mm Hg), the resultant white solid was harvested to provide 3.1 g (69%) of (*E*)-**1b**. The silanolate (*E*)-**1b** was stable for months when stored in an anhydrous environment without change of reactivity or purity as determined by ^{1}H NMR analysis.

Data for ((*E*)-**1b**):

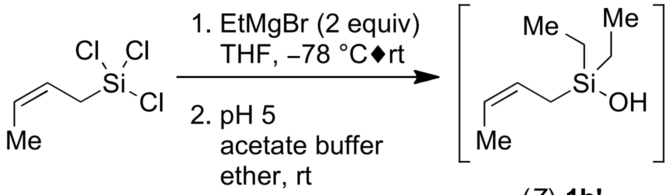
^{1}H NMR: (500 MHz, C_6D_6)

5.82–5.73 (m, 1 H, HC(2)), 5.44–5.35 (m, 1 H, HC(3)), 1.71 (dd, *J* = 6.3, 1.3, 3 H, HC(1)), 1.54 (d, *J* = 8.1, 2 H, HC(4)), 1.08 (t, *J* = 8.0, 6 H, HC(6)), 0.60–0.46 (m, 4 H, HC(5)).

^{13}<u>C NMR</u>: (126 MHz, C_6D_6)

133.4 C(2), 120.3 C(3), 24.8 C(4), 18.0 C(1), 9.8 C(6), 8.4 C(5).

Preparation of (*Z*)-1,1-Diethyl-1-(2-buten-1-yl)silanol ((*Z*)-1b')



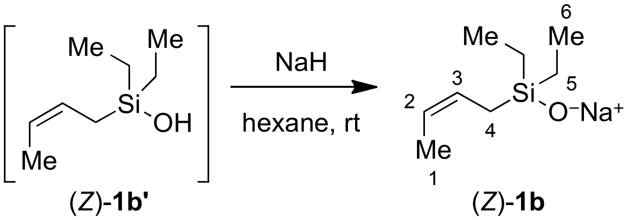
(*Z*)-**1b'**

To a three-necked, 500 mL, round-bottom flask equipped with a magnetic stir bar, two septa, and an argon inlet was added THF (102 mL) and (*Z*)-2-butenyltrichlorosilane (9.67 g, 51 mmol, 1.0 equiv). The solution was then cooled to −78 °C. EtMgBr (47 mL, 102 mmol, 2 equiv) was then added by cannula (~1.5 mL/min) over the course of 1 h. The resulting mixture was stirred 30 min at −78 °C and then warmed to 22 °C over the course of 1 h by removal of the cooling bath. The resulting suspension was then slowly poured into a 1-L Erlenmeyer flask containing vigorously stirred acetate buffer (337 mL, pH 5, 1 M) and ether (68 mL). After 5 min, the reaction mixture was then poured into a 1-L separatory funnel and the aqueous phase was separated and washed with ether (2 x 50 mL), The three separate organic extracts were then sequentially washed with H_2O (150 mL), and sat. aq. $NaHCO_3$ (150 mL). The pH of the resulting aqueous wash was checked with litmus paper to ensure alkalinity. The three separate organic extracts were then washed with H_2O (150 mL) and brine (150 mL), combined, dried over $NaSO_4$ until flocculent, filtered through a pad of silica gel (6 cm × 4 cm) and eluted with ether (2 x 100 mL), and concentrated (23 °C, 10 mm Hg). The residue was then purified by column chromatography (silica gel, 40 mm × 20 cm, pentane/ether, 4:1). Fractions were combined, concentrated to ~15 mL (23 °C, 10 mm Hg) and transferred to a dry box for conversion to its sodium salt.

Data for ((*Z*)-**1b'**):

TLC: R_f 0.29 (pentane/Et_2O, 4:1) [silica gel, aqueous $KMnO_4$]

Preparation of Sodium (*Z*)-1,1-Diethyl-1-(2-buten-1-yl)silanolate ((*Z*)-1b)



In a dry box, NaH (1.35 mg, 56 mmol, 1.1 equiv) was weighed into a 50-mL, single-necked, round-bottomed flask containing a magnetic stir bar and suspended in hexane (10 mL). The silanol (*Z*)-**1b'** in pentane/ether, 4:1 (~15 mL) and was added dropwise to the stirred suspension of NaH. After addition the reaction was aged 30 min with stirring, then was filtered through a fritted-glass funnel (M, 30 mL) into a 100-mL Schlenk flask and the filter cake was washed with hexane (10 mL). The colorless solution was then removed from the dry box and concentrated (23 °C, 0.5 mm Hg). After 3 h under vacuum the semisolid was dissolved in hexane (10 mL) and concentrated (23 °C, 0.5 mm Hg). After 12 h under vacuum (23 °C, 0.5 mm Hg), the resultant white solid was harvested to provide 6.67 g (72%) of (*Z*)-**1b**. The silanolate (*Z*)-**1b** was stable for months when stored in an anhydrous environment without change of reactivity or purity as determined by ^{1}H NMR analysis.

Data for ((*Z*)-**1b**):

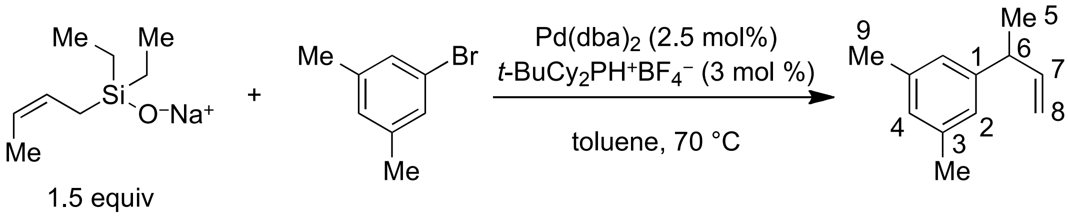
^{1}H NMR: (500 MHz, C_6D_6)

5.86–5.78 (m, 1 H, HC(2)), 5.47–5.39 (m, 1 H, HC(3)), 1.67 (d, *J* = 6.6, 3 H, HC(1)), 1.58 (d, *J* = 8.7, 2 H, HC(4)), 1.07 (t, *J* = 8.0, 6 H, HC(6)), 0.60–0.48 (m, 4 H, HC(5)).

^{13}C NMR: (126 MHz, C_6D_6)

132.2 C(2), 119.1 C(3), 19.2 C(4), 12.7 C(1), 10.2 C(6), 8.3 C(5).

Preparation of 1,3-Dimethyl-5-(1-Methyl-2-propenyl)benzene (5a)



Following General Procedure II, Pd(dba)$_2$ (14.4 mg, 0.025 mmol, 0.025 equiv), *t*-BuCy$_2$PH$^+$BF$_4^-$ (10.3 mg, 0.03 mmol, 0.03 equiv), **2a** (185 mg, 1.0 mmol, 1 equiv), (*Z*)-**1b** (270 mg, 1.5 mmol, 1.5 equiv) and toluene (1.0 mL) were combined and heated to 70 °C. After 24 h, the reaction mixture was cooled to 22 °C, filtered through silica gel (2 cm × 2 cm) and the filter cake washed with ether (3 × 30 mL). Purification by aqueous workup, silica gel chromatography (30 mm × 20 cm, pentane), and Kugelrohr distillation afforded 144 mg (91%) of **5a** as a clear, colorless oil. Spectroscopic data matched those reported in the literature.[10]

Data for (**5a**):

bp: 110 °C (9 mmHg, ABT)

^{1}H NMR: (500 MHz, $CDCl_3$)

6.86 (s, 1 H, HC(4)), 6.84 (s, 2 H, HC(2)), 6.01 (ddd, *J* = 17.0, 10.3, 6.5, 1 H, HC(7)), 5.05 (m, 2 H, HC(8)), 3.40 (ap, *J* = 7.0, 1 H, HC(5)), 2.31 (d, *J* = 0.5, 6 H, HC(9)), 1.35 (d, *J* = 7.0, 3 H, HC(5)).

^{13}C NMR: (126 MHz, $CDCl_3$)

145.6 C(1), 143.4 C(7), 137.9 C(3), 127.8 C(4), 125.0 C(2), 112.8 C(8), 43.1

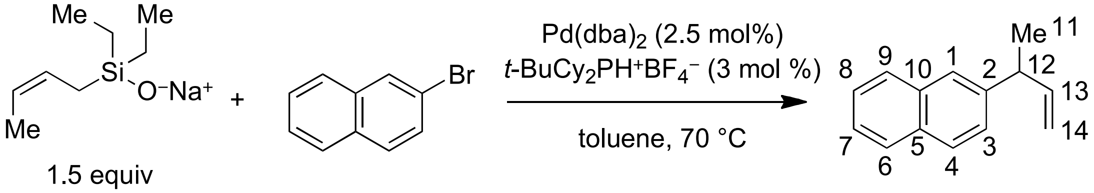
C(6), 21.3 C(9), 20.7 C(5).

TLC: R_f 0.39 (pentane) [silica gel, aqueous $KMnO_4$]

GC: γ-t_R: 5.29 min (>99:1 γ/α) (GC Method 1).

Cross-Coupling of (*Z*)-1b with 2a–2n

Preparation of 2-(1-Methyl-2-propen-1-yl)naphthalene (5b)



Following General Procedure II, $Pd(dba)_2$ (14.4 mg, 0.025 mmol, 0.025 equiv), *t*-$BuCy_2PH^+BF_4^-$ (10.3 mg, 0.03 mmol, 0.03 equiv), **2b** (207 mg, 1.0 mmol, 1 equiv), (*Z*)-**1b** (270 mg, 1.5 mmol, 1.5 equiv) and toluene (1.0 mL) were combined and heated to 70 °C. After 24 h, the reaction mixture was cooled to 22 °C, filtered through silica gel (2 cm × 2 cm) and the filter cake washed with ether (3 × 30 mL). Purification by aqueous workup, silica gel chromatography (30 mm × 20 cm, pentane), and Kugelrohr distillation afforded 168 mg (92%) of **5b** as a clear, colorless oil. Spectroscopic data matched those reported in the literature.[10]

Data for (**5b**):

bp: 110 °C (0.6 mmHg, ABT)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.83–7.79 (m, 3 H, HC(4), HC(6), HC(9)), 7.67 (d, *J* = 0.7, 1 H, HC(1)), 7.49–7.42 (m, 2 H, HC(7), HC(8)), 7.38 (dd, *J* = 8.5, 1.8, 1 H, HC(3)), 6.11 (ddd, *J* = 16.9, 10.2, 6.9, 1 H, HC(13)), 5.12 (m, 2 H, HC(14)), 3.66 (ap, *J* = 6.9, 1 H, HC(12)), 1.48 (d, , *J* = 6.9, 3 H, HC(11)).

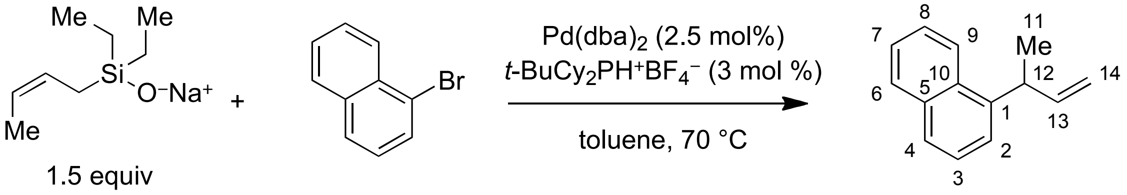
^{13}C NMR: (126 MHz, $CDCl_3$)

143.1 C(13), 143.0 C(2), 133.6 C(10), 132.2 C(5), 127.9 C(4), 127.62 C(9), 127.56 C(6), 126.2 C(1), 125.9 C(8), 125.3 C(7), 125.2 C(3), 113.4 C(14), 43.2 C(12), 20.6 C(11).

TLC: R_f 0.28 (pentane) [silica gel, aqueous $KMnO_4$]

GC: γ-t_R: 6.69 min (>99:1 γ/α) (GC Method 1)

Preparation of 1-(1-Methyl-2-propen-1-yl)naphthalene (5c)



Following General Procedure II, $Pd(dba)_2$ (14.4 mg, 0.025 mmol, 0.025 equiv), *t*-$BuCy_2PH^+BF_4^-$ (10.3 mg, 0.03 mmol, 0.03 equiv), **2c** (207 mg, 1.0 mmol, 1 equiv), *Z*)-**1b** (270 mg, 1.5 mmol, 1.5 equiv) and toluene (1.0 mL) were combined and heated to 70 °C. After 24 h, the reaction mixture was cooled to 22 °C, filtered through silica gel (2 cm × 2 cm) and the filter cake washed with ether (3 × 30 mL). Purification by aqueous workup, silica gel chromatography (30 mm × 20 cm, pentane), and Kugelrohr distillation afforded 162 mg (89%) of **5c** as a clear, colorless oil. Spectroscopic data matched those reported in the literature.[10]

Data for (**5c**):

bp: 110 °C (1 mmHg, ABT)

^{1}H NMR: (500 MHz, $CDCl_3$)

8.15 (d, *J* = 8.4, 1 H, HC(9)), 7.87 (d, *J* = 7.9, 1 H, HC(6)), 7.74 (d, *J* = 8.1, 1 H, HC(4)), 7.55–7.43 (m, 4 H, HC(2), HC(3), HC(7), HC(8)), 6.18 (ddd, *J* = 17.7, 10.0, 5.8, 1 H, HC(13)), 5.15 (m, 2 H, HC(14)), 4.32 (ap, *J* = 6.9, 1 H, HC(12)), 1.53 (d, *J* = 6.9, 3 H, HC(11)).

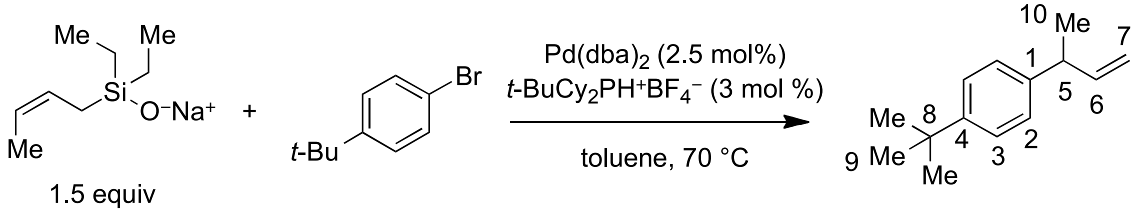
^{13}C NMR: (126 MHz, $CDCl_3$)

142.9 C(1), 141.4 C(13), 134.0 C(5), 131.4 C(10), 128.9 C(6), 126.8 C(4), 125.7 C(3), 125.6 C(2), 125.3 C(7), 123.6 C(8), 123.5 C(9), 113.6 C(14), 37.8 C(12), 20.2 C(11).

TLC: R_f 0.34 (pentane) [silica gel, aqueous $KMnO_4$]

GC: γ-t_R: 6.67 min (>99:1 γ/α) (GC Method 1)

Preparation of 1-(1,1-Dimethylethyl)4-(2-propen-1-yl)benzene (5d)



Following General Procedure II, $Pd(dba)_2$ (14.4 mg, 0.025 mmol, 0.025 equiv), *t*-$BuCy_2PH^+BF_4^-$ (10.3 mg, 0.03 mmol, 0.03 equiv), **2d** (213 mg, 1.0 mmol, 1 equiv), (*Z*)-**1b** (270 mg, 1.5 mmol, 1.5 equiv) and toluene (1.0 mL) were combined and heated to 70 °C. After 24 h, the reaction mixture was cooled to 22 °C, filtered through silica gel (2 cm × 2 cm) and the filter cake washed with ether (3 × 30 mL). Purification by aqueous workup, silica gel chromatography (30 mm × 20 cm, pentane), and Kugelrohr distillation afforded 176 mg (94%) of **5d** as a clear, colorless oil. Spectroscopic data matched those reported in the literature.[13]

Data for (**5d**):

bp: 150 °C (18 mmHg, ABT)

^{1}H NMR: (500 MHz, CDCl$_3$)

7.36–7.32 (m, 2 H, HC(2)), 7.19–7.15 (m, 2 H, HC(3)), 6.02 (ddd, *J* = 17.0, 10.3, 6.6, 1 H, HC(6)), 5.05 (m, 2 H, HC(7)), 3.46 (ap, *J* = 7.0, 1 H, HC(5)), 1.37 (d, *J* = 7.0, 3 H, HC(10)), 1.33 (s, 9 H, HC(9)).

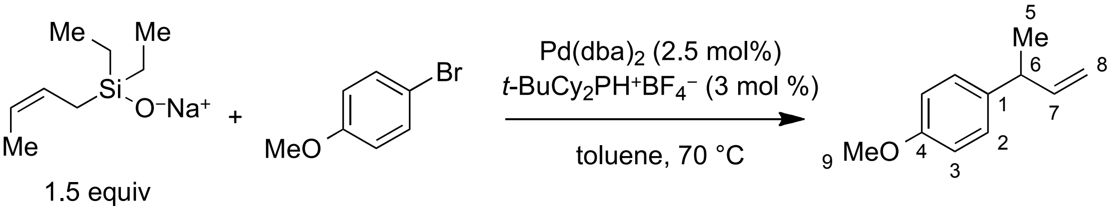
^{13}C NMR: (126 MHz, CDCl$_3$)

148.9 C(4), 143.5 C(7), 142.5 C(1), 126.8 C(3), 125.3 C(2), 112.9 C(7), 42.7 C(5), 34.3 C(8), 31.4 C(9), 20.7 C(10).

TLC: R_f 0.37 (pentane) [silica gel, aqueous KMnO$_4$]

GC: γ-t_R: 5.84 min (>99:1 γ/α) (GC Method 1)

Preparation of 1-Methoxy-4-(1-methyl-2-propen-1-yl)benzene (5e)



Following General Procedure II, Pd(dba)$_2$ (14.4 mg, 0.025 mmol, 0.025 equiv), *t*-BuCy$_2$PH$^+$BF$_4^-$ (10.3 mg, 0.03 mmol, 0.03 equiv), **2e** (187 mg, 1.0 mmol, 1 equiv), (*Z*)-**1b** (270 mg, 1.5 mmol, 1.5 equiv) and toluene (1.0 mL) were combined and heated to 70 °C. After 24 h, the reaction mixture was cooled to 22 °C, filtered through silica gel (2 cm × 2 cm) and the filter cake washed with ether (3 × 30 mL). Purification by aqueous workup, silica gel chromatography (30 mm × 20 cm, pentane→pentane/ether, 20:1), and Kugelrohr distillation afforded 138 mg (85%) of **5e** as a clear, colorless oil. Spectroscopic data matched those reported in the literature.[10]

Data for (**5e**):

bp: 110 °C (10 mmHg, ABT)

<u>^{1}H NMR</u>: (500 MHz, $CDCl_3$)

7.16–7.12 (m, 2 H, HC(2)), 6.87–6.84 (m, 2 H, HC(3)), 5.99 (ddd, *J* = 17.0, 10.3, 6.4, 1 H, HC(7)), 5.02 (m, 2 H, HC(8)), 3.80 (s, 3 H, HC(9)), 3.43 (ap, *J* = 7.0, 1 H, HC(6)), 1.35 (d, , *J* = 7.0, 3 H, HC(5)).

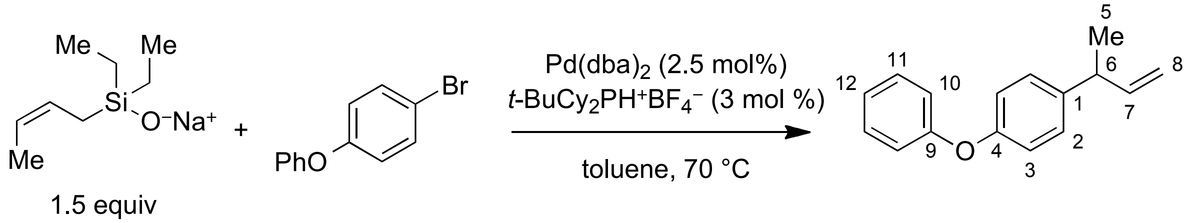
<u>^{13}C NMR</u>: (126 MHz, $CDCl_3$)

157.9 C(4), 143.6 C(7), 137.7 C(1), 128.1 C(2), 113.8 C(3), 112.8 C(8), 55.2 C(9), 42.3 C(6), 20.8 C(5).

<u>TLC</u>: R_f 0.51 (pentane/ether, 20:1) [silica gel, aqueous $KMnO_4$]

<u>GC</u>: γ-t_R: 5.55 min (>99:1 γ/α) (GC Method 1)

Preparation of 1-Phenoxy-4-(1-methyl-2-propen-1-yl)benzene (5f)



Following General Procedure II, $Pd(dba)_2$ (14.4 mg, 0.025 mmol, 0.025 equiv), *t*-$BuCy_2PH^+BF_4^-$ (10.3 mg, 0.03 mmol, 0.03 equiv), **2f** (249 mg, 1.0 mmol, 1 equiv), (*Z*)-**1b** (270 mg, 1.5 mmol, 1.5 equiv) and toluene (1.0 mL) were combined and heated to 70 °C. After 24 h, the reaction mixture was cooled to 22 °C, filtered through silica gel (2 cm × 2 cm) and the filter cake washed with ether (3 × 30 mL). Purification by aqueous workup, silica gel chromatography (30 mm × 20 cm, pentane/ether, 200:1→100:1), and Kugelrohr distillation afforded 188 mg (84%) of **5f** as a clear, colorless oil. Spectroscopic data matched those reported in the literature.[13]

<u>Data for (**5f**)</u>:

<u>bp</u>: 155 °C (1.8 mmHg, ABT)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.35–7.30 (m, 2 H, HC(11)), 7.20–7.16 (m, 2 H, HC(2)), 7.11–7.07 (m, 1 H, HC(12)), 7.02–6.99 (m, 2 H, HC(10)), 6.98–6.94 (m, 2 H, HC(3)), 6.01 (ddd, *J* = 16.9, 10.3, 6.5, 1 H, HC(7)), 5.05 (m, 2 H, HC(8)), 3.47 (ap, *J* = 7.0, 1 H, HC(6)), 1.37 (d, *J* = 7.0, 3 H, HC(5)).

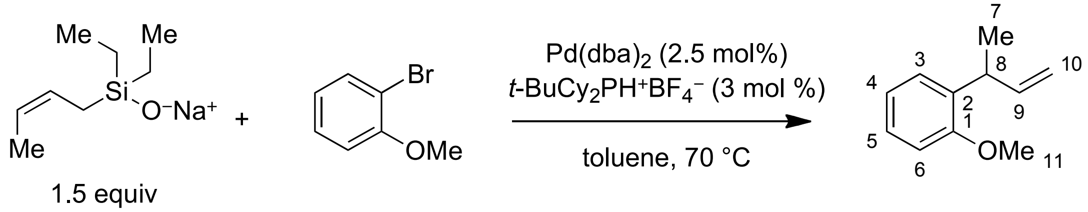
^{13}C NMR: (126 MHz, $CDCl_3$)

157.5 C(4), 157.3 C(9), 143.3 C(7), 140.5 C(1), 129.7 C(11), 128.4 C(2), 123.0 C(12), 118.9 C(3), 118.6 C(10), 113.1 C(8), 42.5 C(6), 20.8 C(5).

TLC: R_f 0.30 (pentane/ether, 200:1) [silica gel, aqueous $KMnO_4$]

GC: γ-t_R: 7.35 min (>99:1 γ/α) (GC Method 1)

Preparation of 2-(1-Methyl-2-propen-1-yl)-1-methoxybenzene (5g)



Following General Procedure II, $Pd(dba)_2$ (14.4 mg, 0.025 mmol, 0.025 equiv), *t*-$BuCy_2PH^+BF_4^-$ (10.3 mg, 0.03 mmol, 0.03 equiv), **2g** (187 mg, 1.0 mmol, 1 equiv), (*Z*)-**1b** (270 mg, 1.5 mmol, 1.5 equiv) and toluene (1.0 mL) were combined and heated to 70 °C. After 24 h, the reaction mixture was cooled to 22 °C, filtered through silica gel (2 cm × 2 cm) and the filter cake washed with ether (3 × 30 mL). Purification by aqueous workup, silica gel chromatography (30 mm × 20 cm, pentane→pentane/ether, 20:1), and Kugelrohr distillation afforded 138 mg (85%) of **5g** as a clear, colorless oil. Spectroscopic data matched those reported in the literature.[14]

Data for (**5g**):

bp: 100 °C (9.5 mmHg, ABT)

^{1}H NMR: (500 MHz, CDCl$_3$)

7.12–7.15 (m, 2 H, HC(3) and HC(5)), 6.93 (td, *J* = 7.5, 1.1, 1 H, HC(4)), 6.87 (dd, *J* = 8.1, 0.7, 1 H, HC(6)), 6.06 (ddd, *J* = 17.2, 10.4, 6.0, 1 H, HC(9)), 5.05 (m, 2 H, HC(10)), 3.93 (ap, *J* = 7.0, 1 H, HC(8)), 3.84 (s, 3 H, HC(11)), 1.32 (d, *J* = 7.0, 3 H, HC(7)).

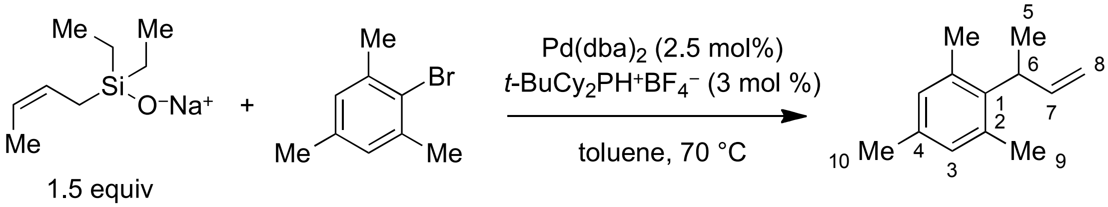
^{13}C NMR: (126 MHz, CDCl$_3$)

156.7 C(1), 142.8 C(9), 134.0 C(2), 127.4 C(3), 127.0 C(5), 120.6 C(4), 112.8 C(10), 110.5 C(6), 55.4 C(8), 35.5 C(4), 19.3 C(7).

TLC: R_f 0.61 (pentane/ether, 20:1) [silica gel, aqueous KMnO$_4$]

GC: γ-t_R: 5.36 min (>99:1 γ/α) (GC Method 1)

Preparation of 1,3,5-Trimethyl-2-(1-Methyl-2-propen-1-yl)benzene (5h)



Following General Procedure II, Pd(dba)$_2$ (14.4 mg, 0.025 mmol, 0.025 equiv), *t*-BuCy$_2$PH$^+$BF$_4^-$ (10.3 mg, 0.03 mmol, 0.03 equiv), **2h** (199 mg, 1.0 mmol, 1 equiv), (*Z*)-**1b** (270 mg, 1.5 mmol, 1.5 equiv) and toluene (1.0 mL) were combined and heated to 70 °C. After 24 h, the reaction mixture was cooled to 22 °C, filtered through silica gel (2 cm × 2 cm) and the filter cake washed with ether (3 × 30 mL). Purification by aqueous workup, silica gel chromatography (30 mm × 20 cm, pentane), and Kugelrohr distillation afforded 127 mg (73%) of **5h** as a clear, colorless oil.

Data for (**5h**):

bp: 145 °C (13 mmHg, ABT)

^{1}H NMR: (500 MHz, $CDCl_3$)

6.83 (s, 2 H, HC(3)), 6.11 (ddd, *J* = 17.4, 10.5, 4.1, 1 H, HC(7)), 5.05 (m, 2 H, HC(8)), 3.94 (m, 1 H, HC(6)), 2.31 (s, 6 H, HC(9), 2.25 (s, 3 H, HC(10)), 1.40 (d, *J* = 7.2, 3 H, HC(5)).

^{13}C NMR: (126 MHz, $CDCl_3$)

142.5 C(7), 138.5 C(1), 136.4 C(4), 135.3 C(2), 129.9 C(3), 112.6 C(8), 37.2 C(6), 21.1 C(9), 20.6 C(10), 17.0 C(5).

IR: (film)

3080 (w), 2966 (m), 2914 (m), 2866 (w), 1633 (w), 1611 (w), 1568 (w), 1483 (m), 1450 (m), 1412 (w), 1376 (w), 1068 (w), 1045 (w), 1024 (w), 1002 (w), 905 (m), 850 (m), 752 (w), 729 (w).

MS: (EI, 70eV)

174 (M^+, 31), 159 (100), 144 (27), 128 (16), 84 (12), 62 (36).

HRMS: $C_{13}H_{18}$ (M^+, EI, 70eV)

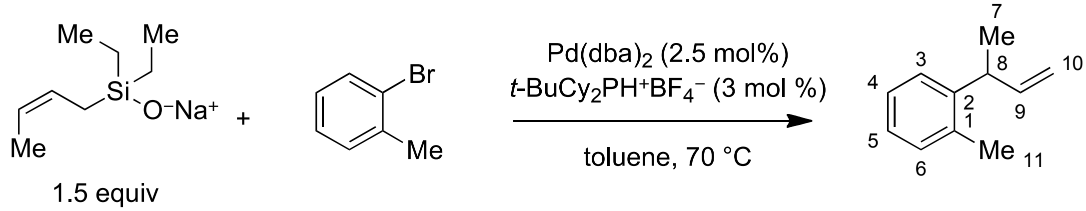
Calcd.: 174.1408

Found: 174.1423

TLC: R_f 0.31 (pentane) [silica gel, UV]

GC: t_R: 5.83 min (99.7%) (GC Method 1).

Preparation of 1-(1-Methyl-2-propen-1-yl)-2-methylbenzene (5i)



Following General Procedure II, Pd(dba)$_2$ (14.4 mg, 0.025 mmol, 0.025 equiv), *t*-BuCy$_2$PH$^+$BF$_4^-$ (10.3 mg, 0.03 mmol, 0.03 equiv), **2i** (171 mg, 1.0 mmol, 1 equiv), (*Z*)-**1b** (270 mg, 1.5 mmol, 1.5 equiv) and toluene (1.0 mL) were combined and heated to 70 °C. After 24 h, the reaction mixture was cooled to 22 °C, filtered through silica gel (2 cm × 2 cm) and the filter cake washed with ether (3 × 30 mL). Purification by aqueous workup, silica gel chromatography (30 mm × 20 cm, pentane), and Kugelrohr distillation afforded 108 mg (74%) of **5i** as a clear, colorless oil. Spectroscopic data matched those reported in the literature.[15]

Data for (**5i**):

bp: 90 °C (16 mmHg, ABT)

^{1}H NMR: (500 MHz, CDCl$_3$)

7.20–7.18 (m, 2 H, HC(4) and HC(5)), 7.17–7.14 (m, 1 H, HC(3)), 7.13–7.10 (m, 1 H, HC(6)), 5.99 (m, 1 H, HC(9)), 5.03 (m, 2 H, HC(10)), 3.70 (ap, *J* = 7.0, 1 H, HC(8)), 2.35 (s, 3 H, HC(11)), 1.35 (d, *J* = 7.0, 3 H, HC(7)).

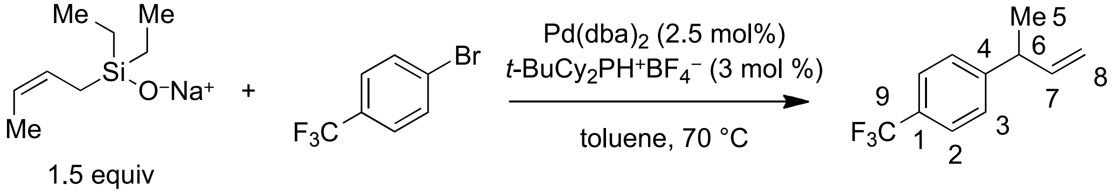
^{13}C NMR: (126 MHz, CDCl$_3$)

143.4 C(1), 142.7 C(9), 135.5 C(2), 130.3 C(3), 126.2 C(6), 126.1 C(4), 125.9 C(5), 113.0 C(10), 38.5 C(8), 19.9 C(7), 19.4 C(4).

TLC: R_f 0.36 (pentane) [silica gel, aqueous KMnO$_4$]

GC: γ-t_R: 4.93 min (>99:1 γ/α) (GC Method 1)

Preparation of 1-(1-Methyl-2-propen-1-yl)4-(trifluoromethyl)benzene (5j)



Following General Procedure II, $Pd(dba)_2$ (28.8 mg, 0.05 mmol, 0.05 equiv), *t*-$BuCy_2PH^+BF_4^-$ (20.6 mg, 0.06 mmol, 0.06 equiv), **2j** (225 mg, 1.0 mmol, 1 equiv), (*Z*)-**1b** (270 mg, 1.5 mmol, 1.5 equiv) and toluene (1.0 mL) were combined and heated to 70 °C. After 24 h, the reaction mixture was cooled to 22 °C, filtered through silica gel (2 cm × 2 cm) and the filter cake washed with ether (3 × 30 mL). Purification by aqueous workup, silica gel chromatography (30 mm × 20 cm, pentane), and Kugelrohr distillation afforded 165 mg (82%) of **5j** as a clear, colorless oil. Spectroscopic data matched those reported in the literature.[10]

Data for (**5j**):

bp: 95 °C (16 mmHg, ABT)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.55 (d, *J* = 8.2, 2 H, HC(3)), 7.32 (d, *J* = 8.2, HC(2)), 5.98 (ddd, *J* = 16.9, 10.7, 6.4, 1 H, HC(7)), 5.07 (m, 2 H, HC(8)), 3.53 (ap, *J* = 7.0, 1 H, HC(6)), 1.38 (d, *J* = 7.0, 3 H, HC(5)).

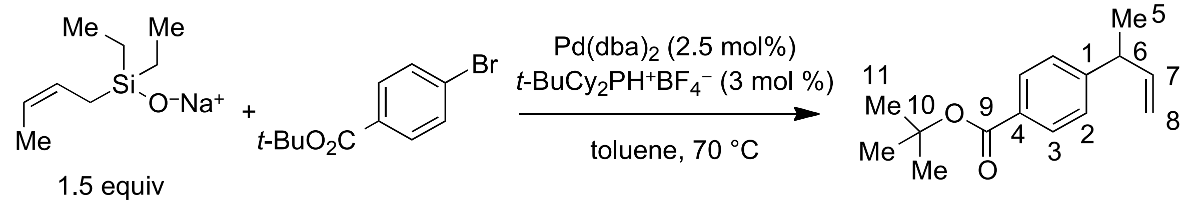
^{13}C NMR: (126 MHz, $CDCl_3$)

149.6 C(4), 142.2 C(7), 128.5 C(2), 127.6 C(8), 125.3 (q, *J* = 3.7, C(9)), 123.2 C(3), 114.0 C(1), 43.0 C(6), 20.6 C(5).

TLC: R_f 0.52 (pentane) [silica gel, aqueous $KMnO_4$]

GC: γ-t_R: 4.53 min (>99:1 γ/α) (GC Method 1)

Preparation of 4-(1-Methyl-2-propen-1-yl)benzoic Acid, 1,1-Dimethylethyl Ester (5k)



Following General Procedure II, Pd(dba)$_2$ (14.4 mg, 0.025 mmol, 0.025 equiv), *t*-BuCy$_2$PH$^+$BF$_4^-$ (10.3 mg, 0.03 mmol, 0.03 equiv), **2k** (257 mg, 1.0 mmol, 1 equiv), (*Z*)-**1b** (270 mg, 1.5 mmol, 1.5 equiv) and toluene (1.0 mL) were combined and heated to 70 °C. After 24 h, the reaction mixture was cooled to 22 °C, filtered through silica gel (2 cm × 2 cm) and the filter cake washed with ether (3 × 30 mL). Purification by aqueous workup, silica gel chromatography (30 mm × 20 cm, pentane→pentane/ether, 20:1), and Kugelrohr distillation afforded 211 mg (91%) of **5k** as a clear, colorless oil. Spectroscopic data matched those reported in the literature.[10]

Data for (**5k**):

bp: 140 °C (0.7 mmHg, ABT)

^{1}H NMR: (500 MHz, CDCl$_3$)

7.94–7.91 (m, 2 H, HC(3)), 7.27–7.24 (m, 2 H, HC(2)), 5.98 (ddd, *J* = 17.7, 9.8, 6.4, 1 H, HC(7)), 5.05 (m, 2 H, HC(8)), 3.51 (ap, *J* = 7.0 1 H, HC(6)), 1.58 (s, 9 H, HC(11)), 1.37 (d, *J* = 7.0, 3 H, HC(5)).

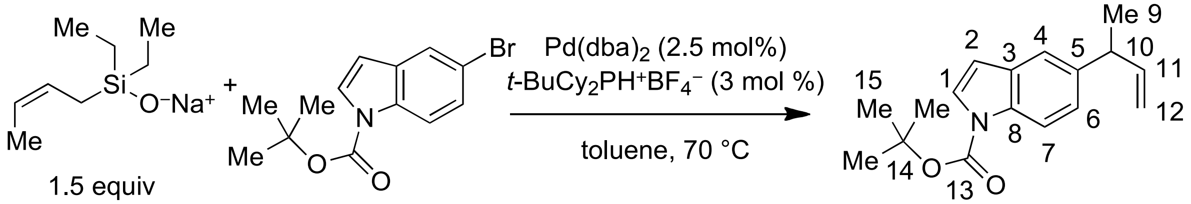
^{13}C NMR: (126 MHz, CDCl$_3$)

165.8 C(9), 150.4 C(1), 142.4 C(7), 130.0 C(4), 129.6 C(3), 127.1 C(2), 113.7 C(8), 80.7 C(10), 43.1 C(6), 28.2 C(11), 20.6 C(5).

TLC: R_f 0.51 (pentane/ether, 20:1) [silica gel, aqueous KMnO$_4$]

GC: γ-t_R: 6.84 min (>99:1 γ/α) (GC Method 1)

Preparation of 5-(1-Methyl-2-propen-1-yl)1H-indole-1-carboxylic Acid 1,1-Dimethylethyl Ester (5l)



Following General Procedure II, Pd(dba)$_2$ (14.4 mg, 0.025 mmol, 0.025 equiv), *t*-BuCy$_2$PH$^+$BF$_4^-$ (10.3 mg, 0.03 mmol, 0.03 equiv), **2l** (296 mg, 1.0 mmol, 1 equiv), (*Z*)-**1b** (270 mg, 1.5 mmol, 1.5 equiv) and toluene (1.0 mL) were combined and heated to 70 °C. After 24 h, the reaction mixture was cooled to 22 °C, filtered through silica gel (2 cm × 2 cm) and the filter cake washed with ether (3 × 30 mL). Purification by aqueous workup and silica gel chromatography (30 mm × 20 cm, hexane/EtOAc, 100:1→20:1) afforded 193 mg (91%) of **5l** as a clear, colorless oil. Spectroscopic data matched those reported in the literature.[10]

Data for (**5l**):

^{1}H NMR: (500 MHz, CDCl$_3$)

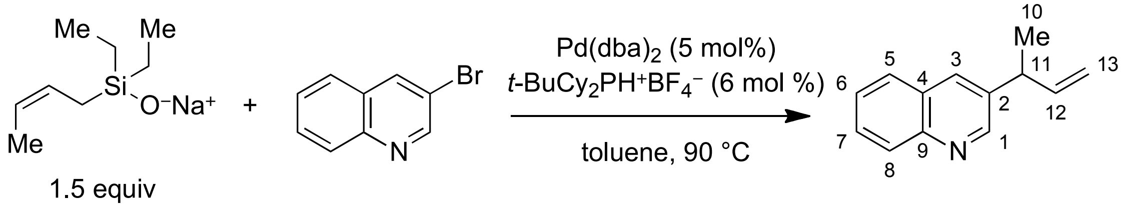
8.06 (d, *J* = 6.9, 1 H, HC(7)), 7.58 (d, *J* = 3.3, 1 H, HC(1)), 7.40 (d, *J* = 1.7, 1 H, HC(4)), 7.18 (m, 1 H, HC(6)), 6.53 (d, *J* = 3.3, 1 H, HC(2)), 6.07 (ddd, *J* = 16.9, 10.3, 6.3, 1 H, HC(11)), 5.06 (m, 2 H, HC(12)), 3.57 (ap, *J* = 7.0, 1 H, HC(10)), 1.67 (s, 9 H, HC(15)), 1.42 (d, *J* = 7.0, 3 H, HC(9)).

^{13}C NMR: (126 MHz, CDCl$_3$)

149.8 C(13), 143.7 C(11), 140.0 C(3), 133.7 C(5), 130.8 C(8), 126.0 C(1), 123.9 C(6), 119.1 C(4), 115.0 C(7), 112.8 C(12), 107.2 C(2), 83.5 C(14), 43.0 C(10), 28.2 C(15), 21.1 C(9).

TLC: R_f 0.39 (hexane/EtOAc, 20:1) [silica gel, UV]

Preparation of 3-(1-Methyl-2-propen-1-yl)quinoline (5m)



Following General Procedure II, Pd(dba)$_2$ (28.84 mg, 0.05 mmol, 0.05 equiv), *t*-BuCy$_2$PH$^+$BF$_4^-$ (20.6 mg, 0.06 mmol, 0.06 equiv), **2m** (208 mg, 1.0 mmol, 1 equiv), (*Z*)-**1b** (270 mg, 1.5 mmol, 1.5 equiv) and toluene (1.0 mL) were combined and heated to 90 °C. After 24 h, the reaction mixture was cooled to 22 °C, filtered through silica gel (2 cm × 2 cm) and the filter cake washed with ether (3 × 30 mL). Purification by aqueous workup, silica gel chromatography (30 mm × 20 cm, pentane/ether, 20:1→1:1), and Kugelrohr distillation afforded 150 mg (82%) of **5m** as a clear, colorless oil.

Data for (**5m**):

bp: 140 °C (1.0 mmHg, ABT)

^{1}H NMR: (500 MHz, CDCl$_3$)

8.81 (d, *J* = 2.2, 1 H, HC(1)), 8.10 (d, *J* = 8.2, 1 H, HC(8)), 7.94 (d, *J* = 2.2, 1 H, HC(3)), 7.79 (dd, *J* = 8.3, 1.1, 1 H, HC(5)), 7.67 (ddd, *J* = 8.3, 6.9, 1.1, 1 H, HC(6)), 7.53 (ddd, *J* = 8.2, 6.9, 1.1, 1 H, HC(7)), 6.07 (ddd, *J* = 16.9, 10.4, 6.3, 1 H, HC(12)), 5.14 (m, 2 H, HC(13)), 3.70 (m, 1 H, HC(11)), 1.49 (d, *J* = 7.1, 3 H, HC(10)).

^{13}C NMR: (126 MHz, CDCl$_3$)

151.3 C(1), 146.7 C(9), 141.8 C(12), 138.0 C(4), 133.1 C(3), 129.0 C(8), 128.8 C(6), 128.1 C(2), 127.5 C(5), 126.6 C(7), 114.5 C(13), 40.7 C(11), 20.5 C(10).

IR: (film)

3078 (w), 3064 (w), 3003 (w), 2968 (w), 2873 (w), 1636 (w), 1602 (w), 1571 (w), 1495 (w), 1455 (w), 1415 (w), 1380 (w), 1333 (w), 1259 (w), 1232 (w), 1194 (w), 1125 (w), 1068 (w), 1014 (w), 992 (w), 964 (w), 908 (w), 861 (w), 788 (w), 752 (m), 661 (w), 644 (w), 610 (w).

MS: (EI, 70eV)

183 (M^+, 62), 168 (100).

HRMS: $C_{13}H_{13}N$ (M^+, EI, 70eV)

Calcd.: 183.1066

Found: 183.1048

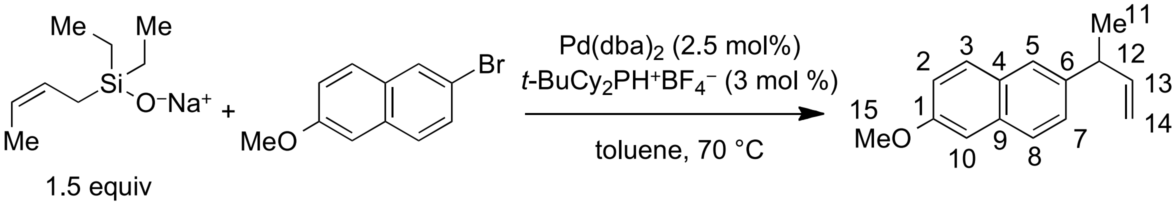
TLC: R_f 0.31 (pentane/ether, 1:1) [silica gel, UV]

GC: γ-t_R: 6.88 min, α-t_R: 7.08, 7.15 min (26:1 γ/α) (GC Method 1).

Analysis: $C_{13}H_{13}N$ (183.25)

Calcd.:	C, 85.21	H, 7.15	N, 7.64
Found:	C, 85.26	H, 7.26	N, 7.56

Preparation of 2-Methoxy-6-(1-methyl-2-propen-1-yl)naphthalene (5n)



Following General Procedure II, Pd(dba)$_2$ (14.4 mg, 0.025 mmol, 0.025 equiv), *t*-BuCy$_2$PH$^+$BF$_4^-$ (10.3 mg, 0.03 mmol, 0.03 equiv), **2n** (237 mg, 1.0 mmol, 1 equiv), (*Z*)-**1b** (270 mg, 1.5 mmol, 1.5 equiv) and toluene (1.0 mL) were combined and heated to 70 °C. After 24 h, the reaction mixture was cooled to 22 °C, filtered through silica gel (2 cm × 2 cm) and the filter cake washed with ether (3 × 30 mL). Purification by aqueous workup, silica gel chromatography (30 mm × 20 cm, pentane/ether/CH_2Cl_2, 99:0:1→97:2:1), and Kugelrohr distillation afforded 193 mg (91%) of **5n** as a clear, colorless oil that solidified upon standing. Spectroscopic data matched those reported in the literature.[10]

Data for (**5n**):

bp: 190 °C (0.6 mmHg, ABT)

mp: 30–31 °C

^{1}H NMR: (500 MHz, $CDCl_3$)

7.71–7.67 (m, 2 H, HC(3), HC(8)), 7.57 (d, *J* = 1.4, 1 H, HC(5)), 7.33 (dd, *J* = 8.5, 1.4, 1 H, HC(7)), 7.14–7.11 (m, 2 H, HC(2), HC(10)), 6.08 (ddd, *J* = 16.8,10.3, 6.4, 1 H, HC(13)), 5.08 (m, 2 H, HC(14)), 3.91 (s, 3 H, HC(15)), 3.60 (ap, *J* = 7.0, 1 H, HC(12)), 1.44 (d, *J* = 7.0, 3 H, HC(11)).

^{13}C NMR: (126 MHz, $CDCl_3$)

157.3 C(1), 143.3 C(13), 140.7 C(6), 133.2 C(9), 129.1 C(4), 129.0 C(3), 126.8 C(5), 126.7 C(8), 125.0 C(7), 118.6 C(2), 113.2 C(14), 105.6 C(10), 55.3 C(15), 43.0 C(12), 20.7 C(11).

TLC: R_f 0.40 (pentane/ether/CH_2Cl_2, 97:2:1) [silica gel, aqueous $KMnO_4$]

GC: γ-t_R: 7.53 min (>99:1 γ/α) (GC Method 1)

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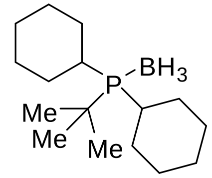
^{1}H NMR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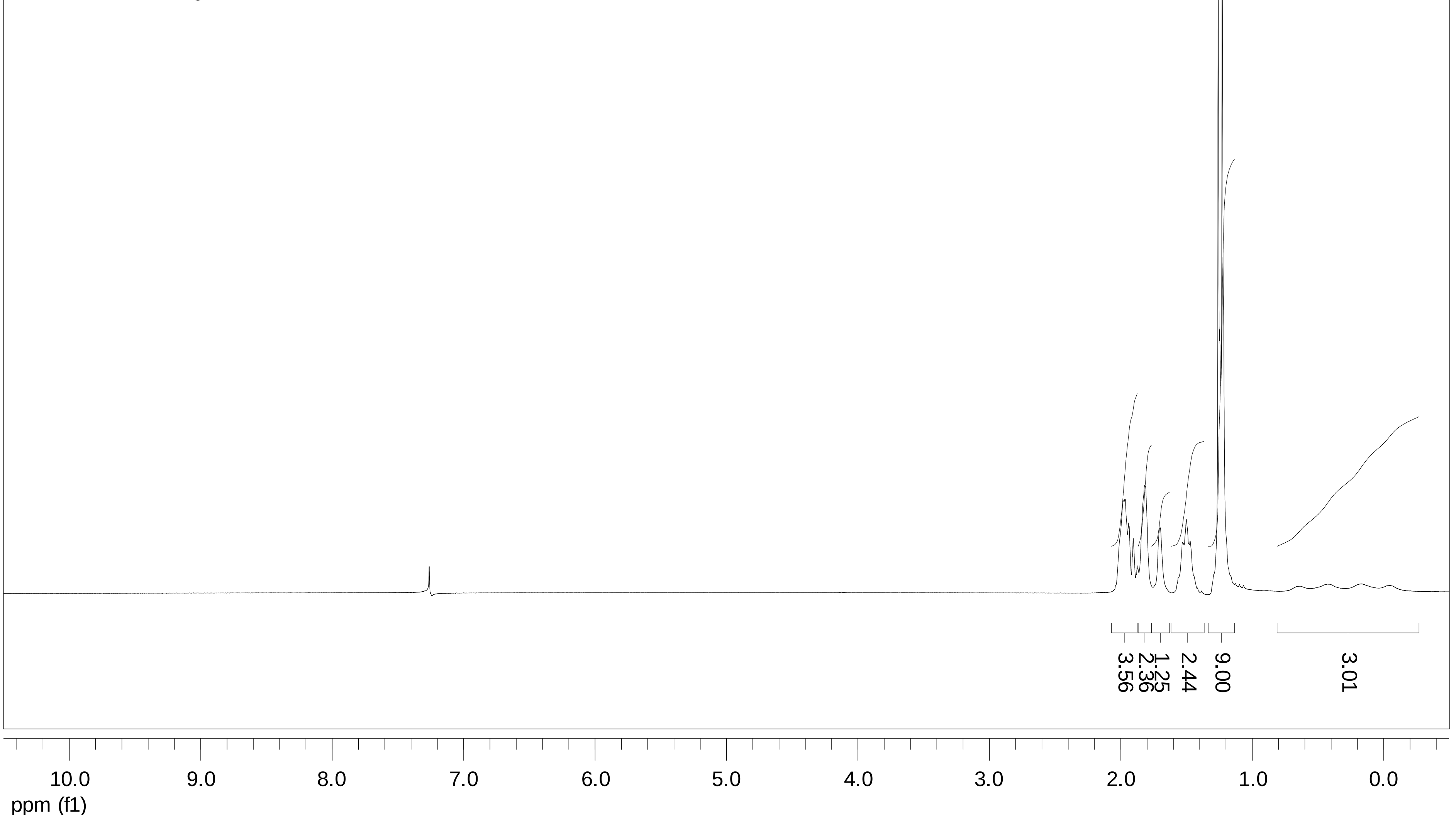
Me

6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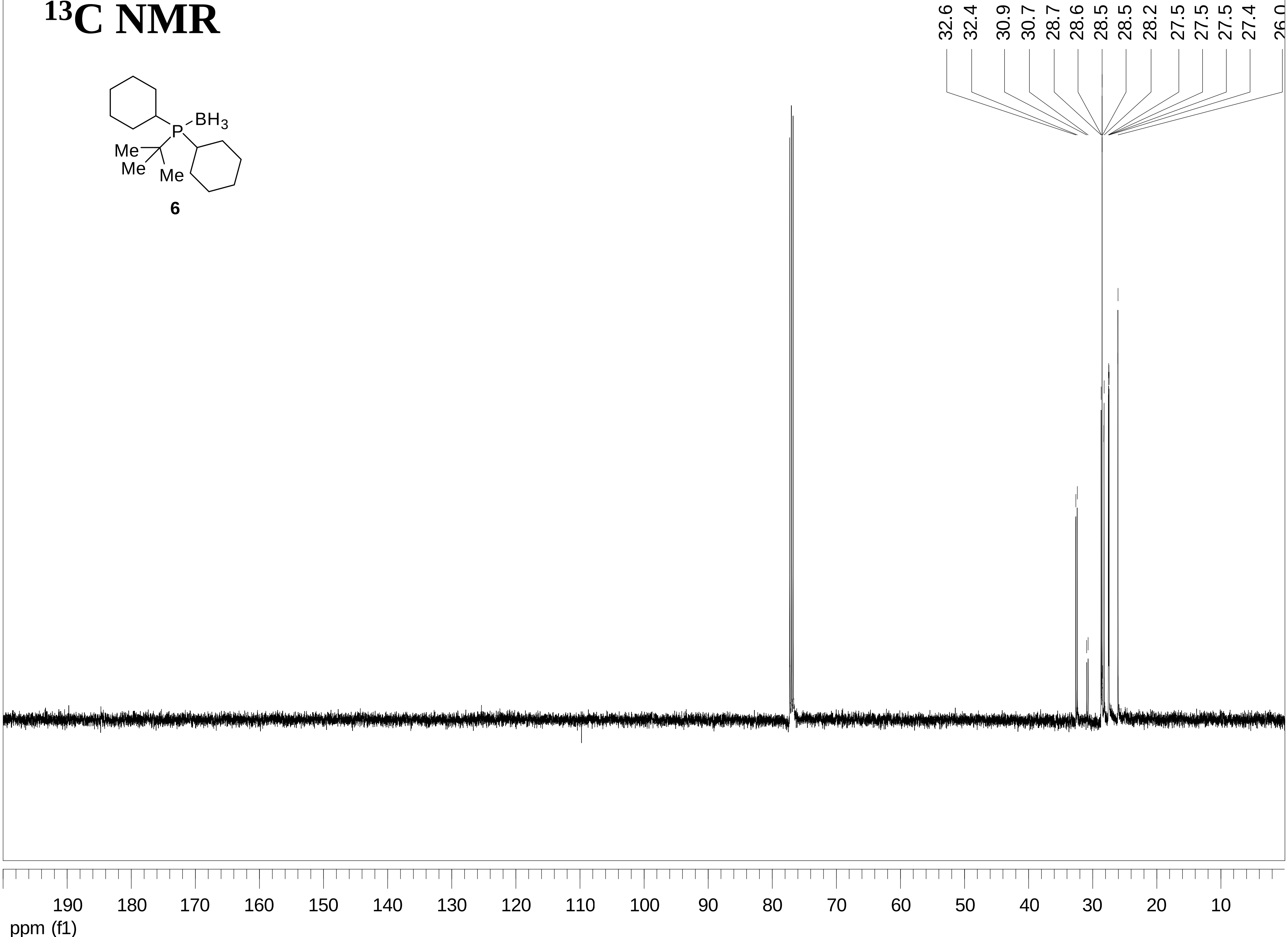
1.0
0.0
ppm (f1)

^{13}C NMR

BH3
P
Me
Me
Me

6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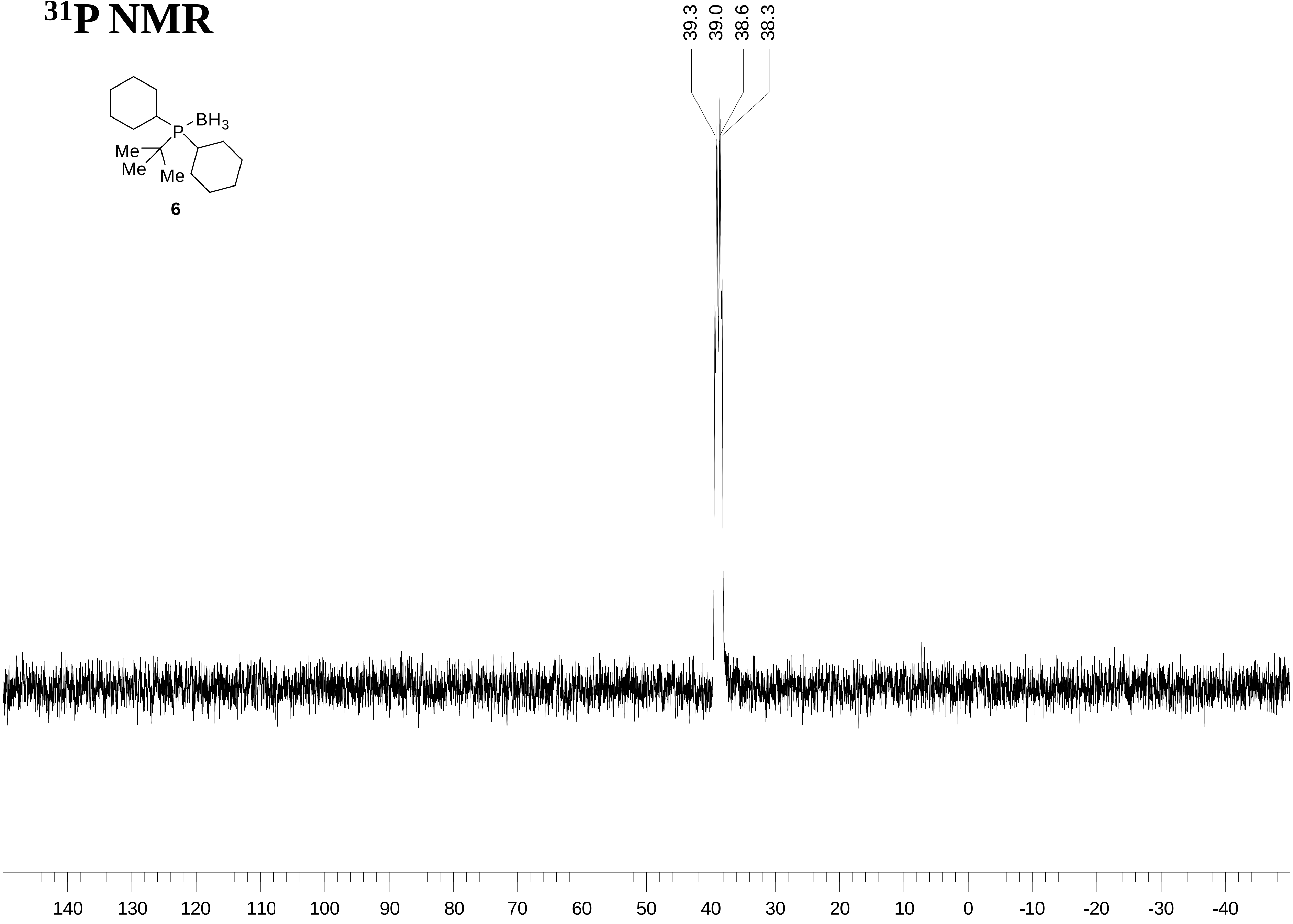
ppm (f1)

^{31}P NMR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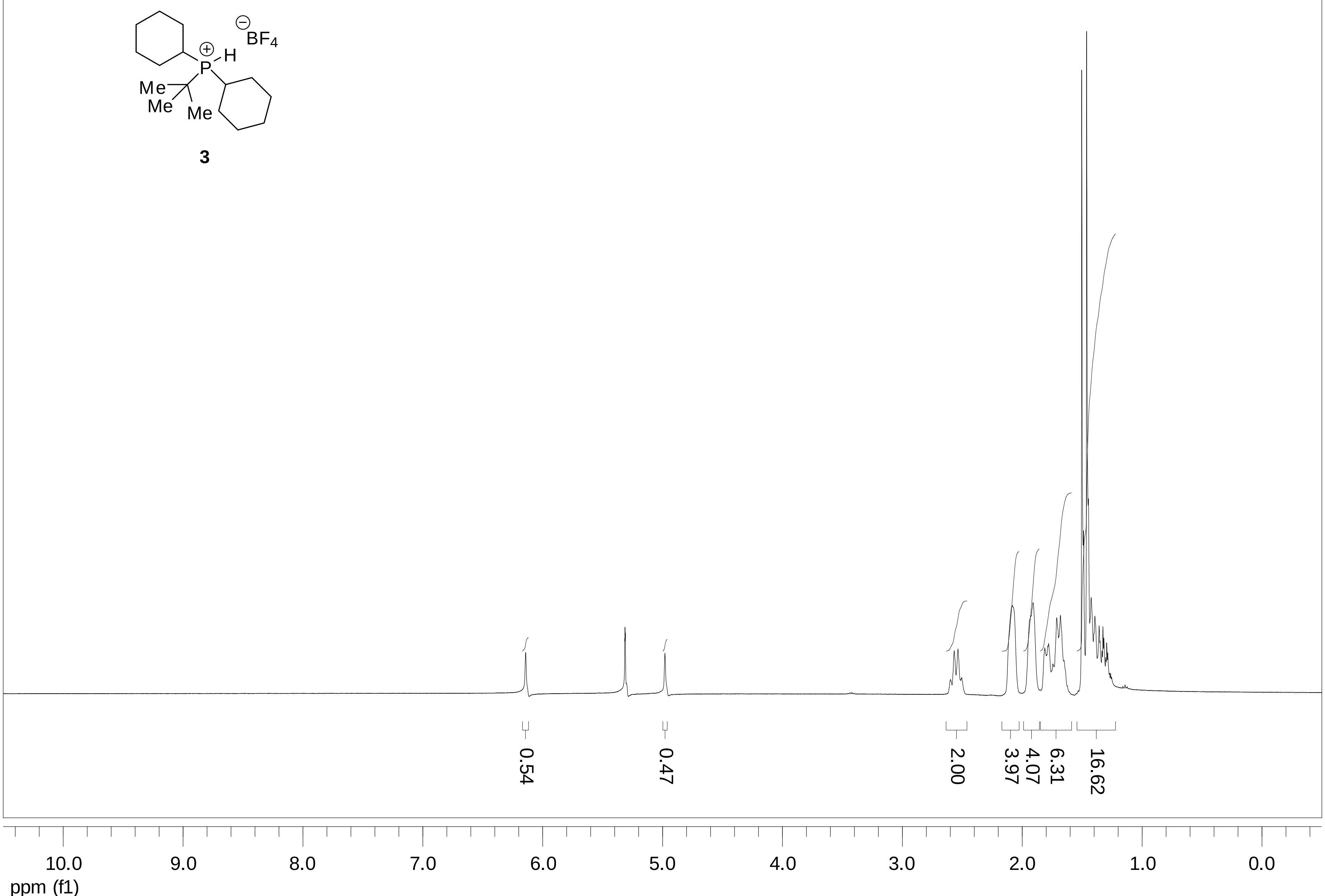

3

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8.0
7.0
6.0
5.0
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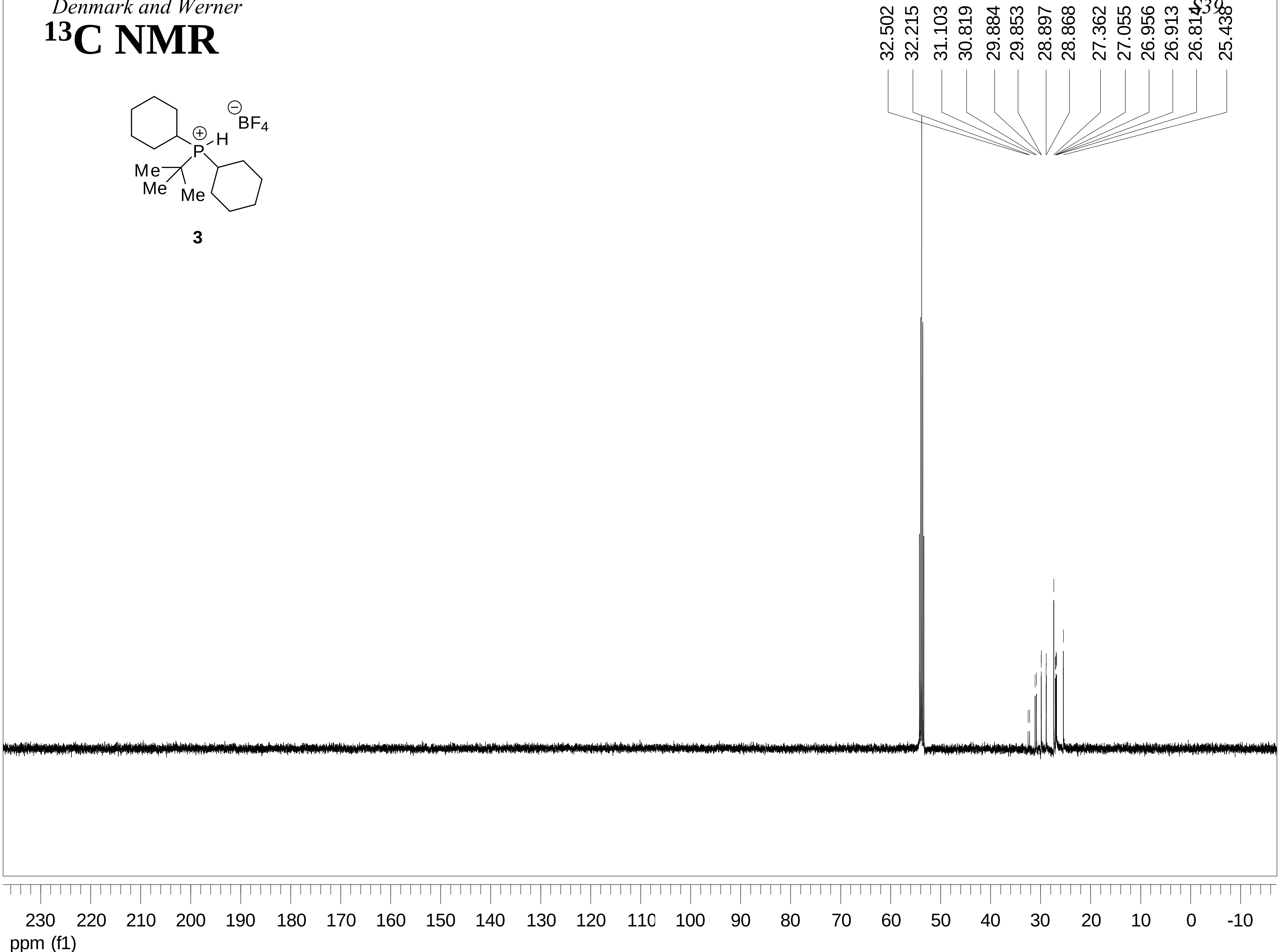
ppm (f1)

^{13}C NMR

BF4
H
P
Me
Me
Me

3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200
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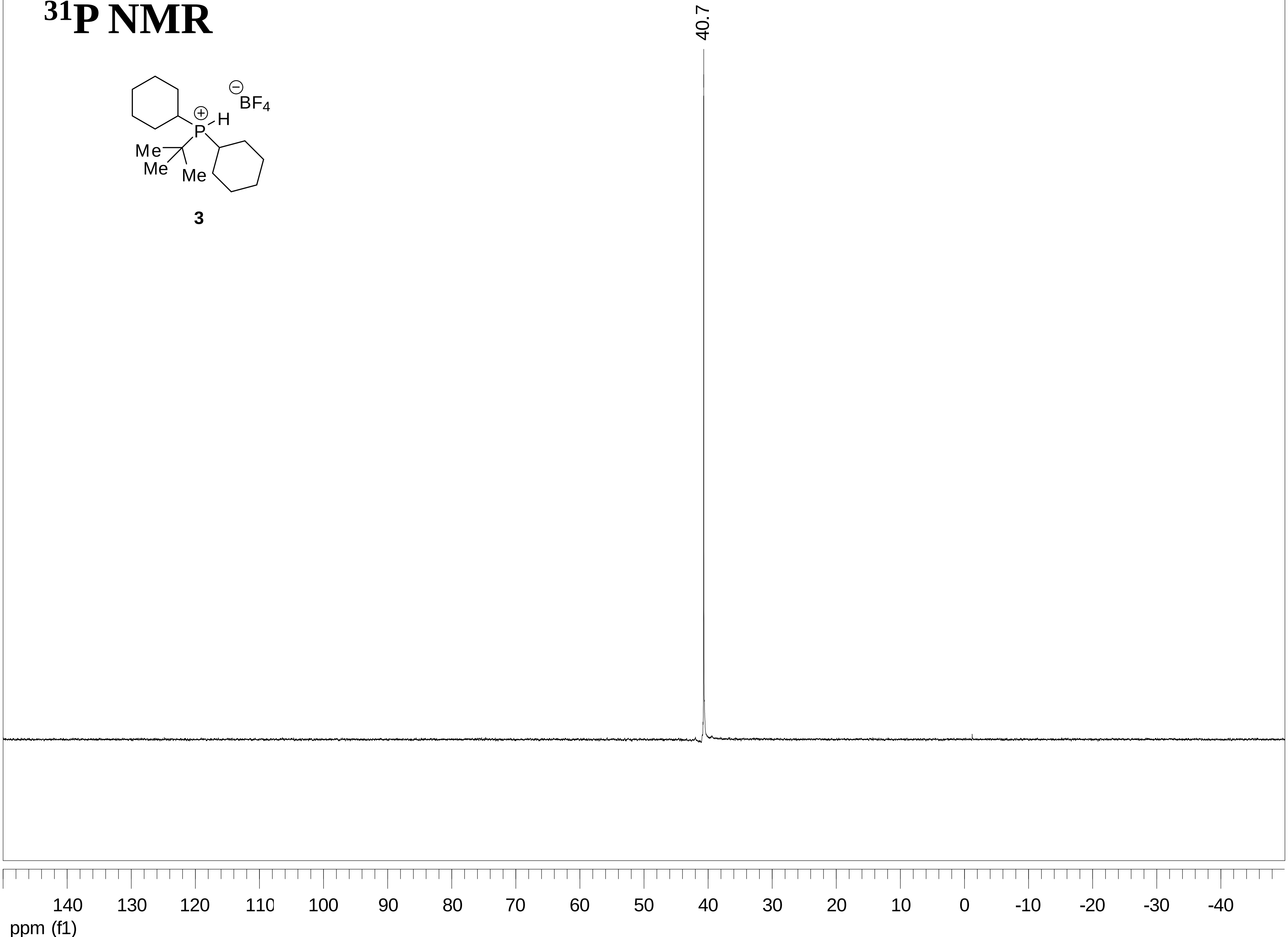
ppm (f1)

^{31}P NMR

3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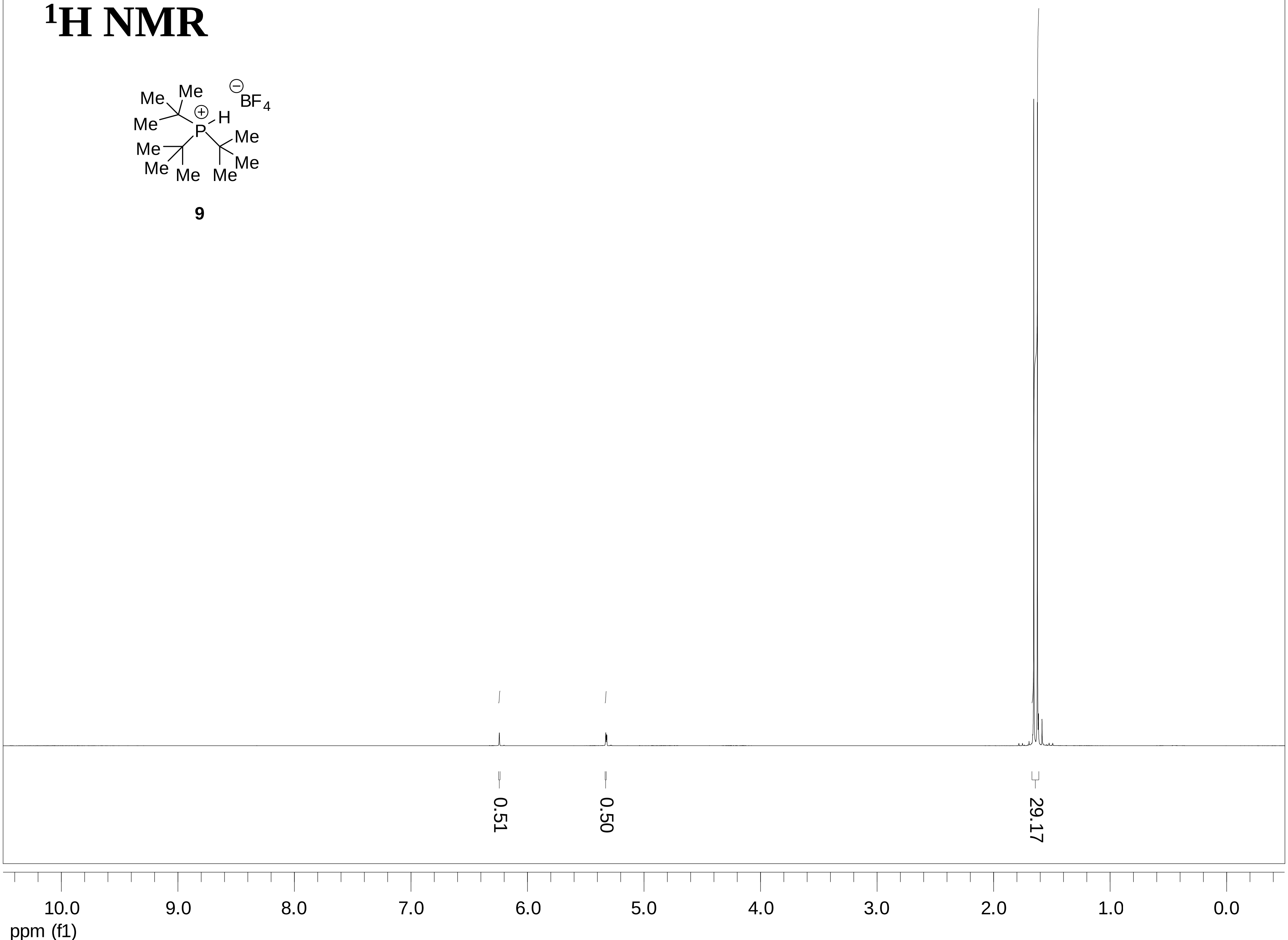
ppm (f1)

^{1}H NMR



9

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Me
Me
Me
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Me
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H
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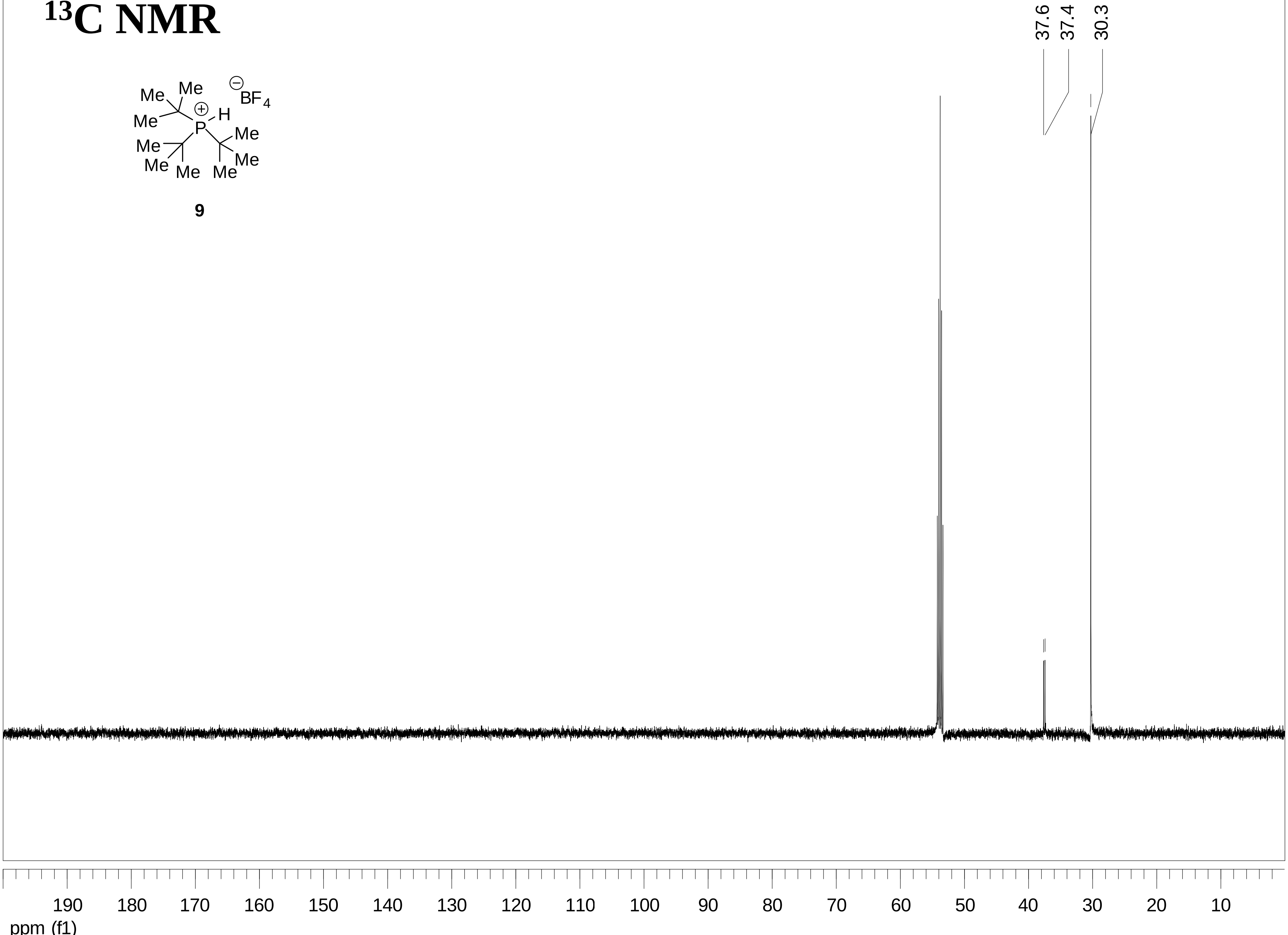
ppm (f1)

^{13}C NMR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Me
Me

9

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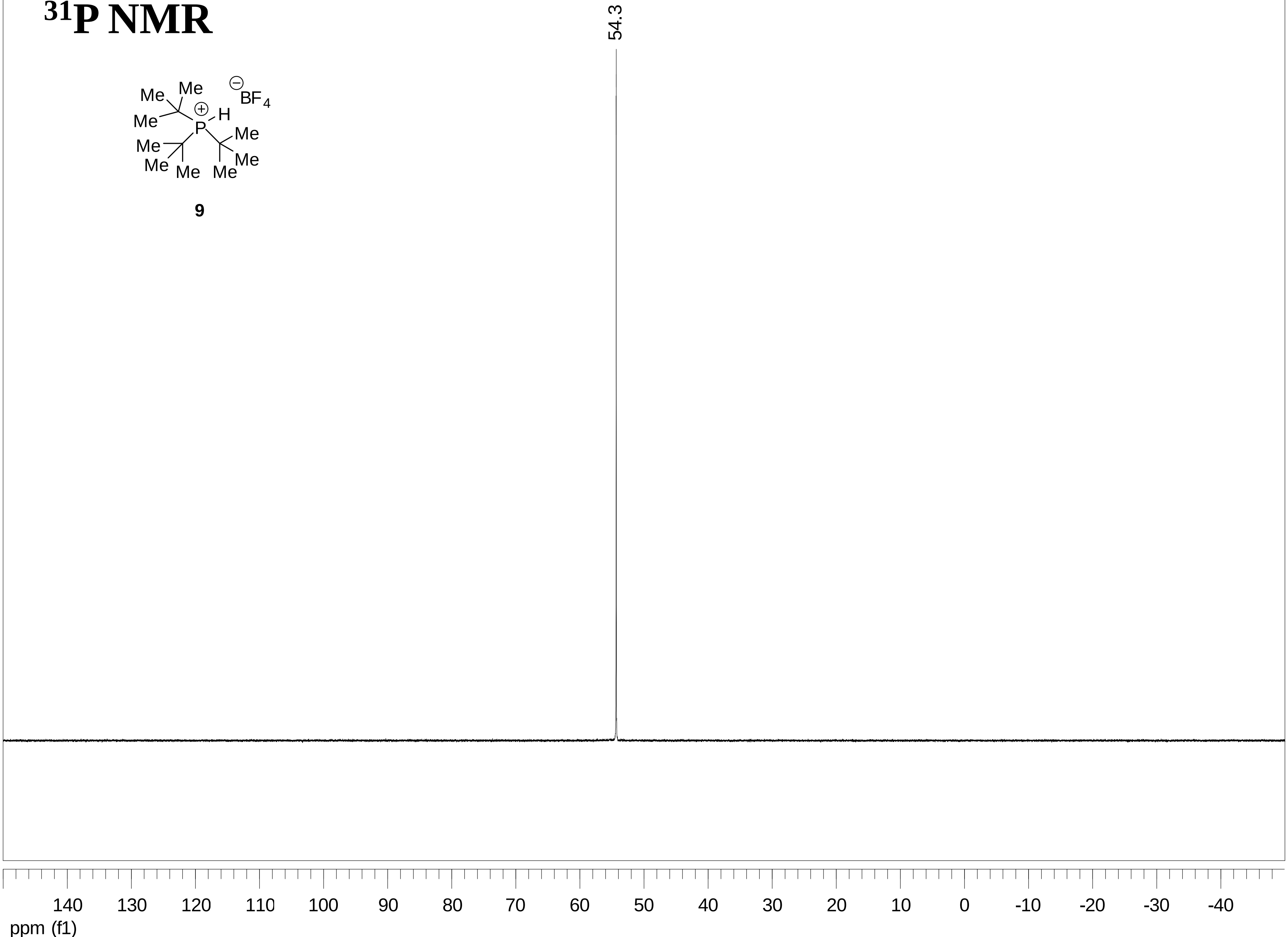
10
ppm (f1)

^{31}P NMR



9

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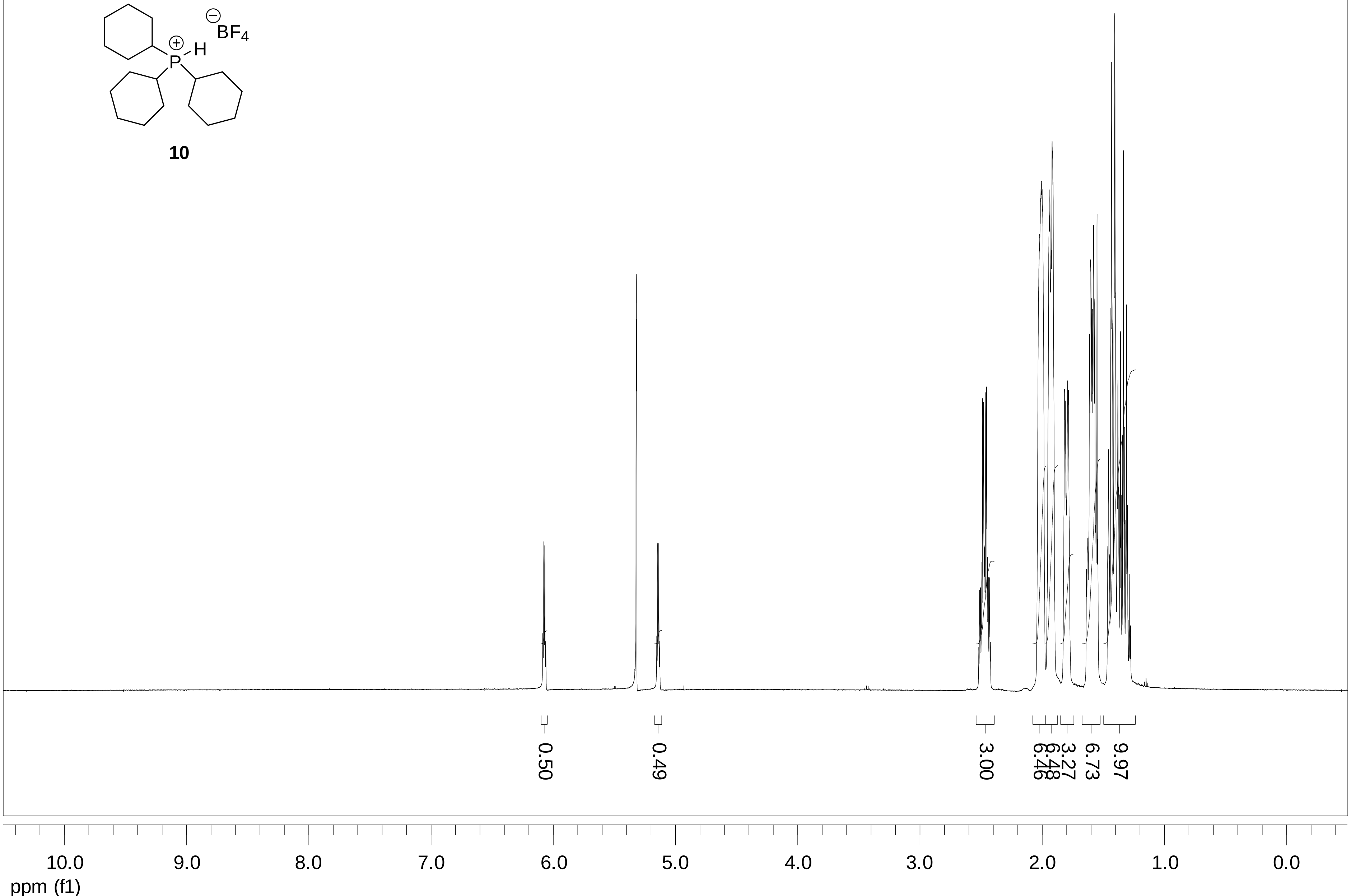
ppm (f1)

^{1}H NMR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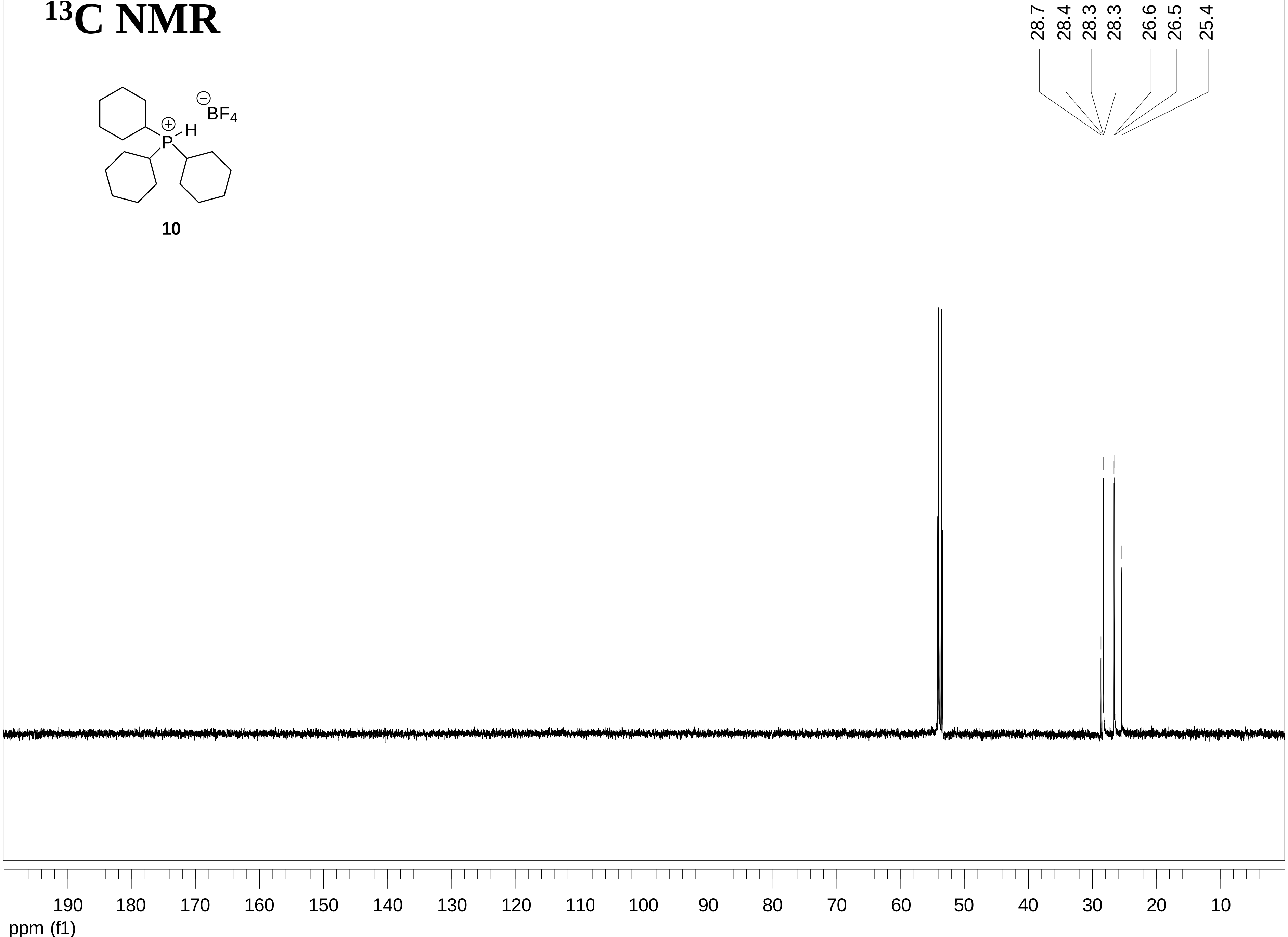
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

^{13}C NMR

$\ominus$
BF_4
$\oplus$
P
H

10



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28.3
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25.4
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110
100
90
80
70
60
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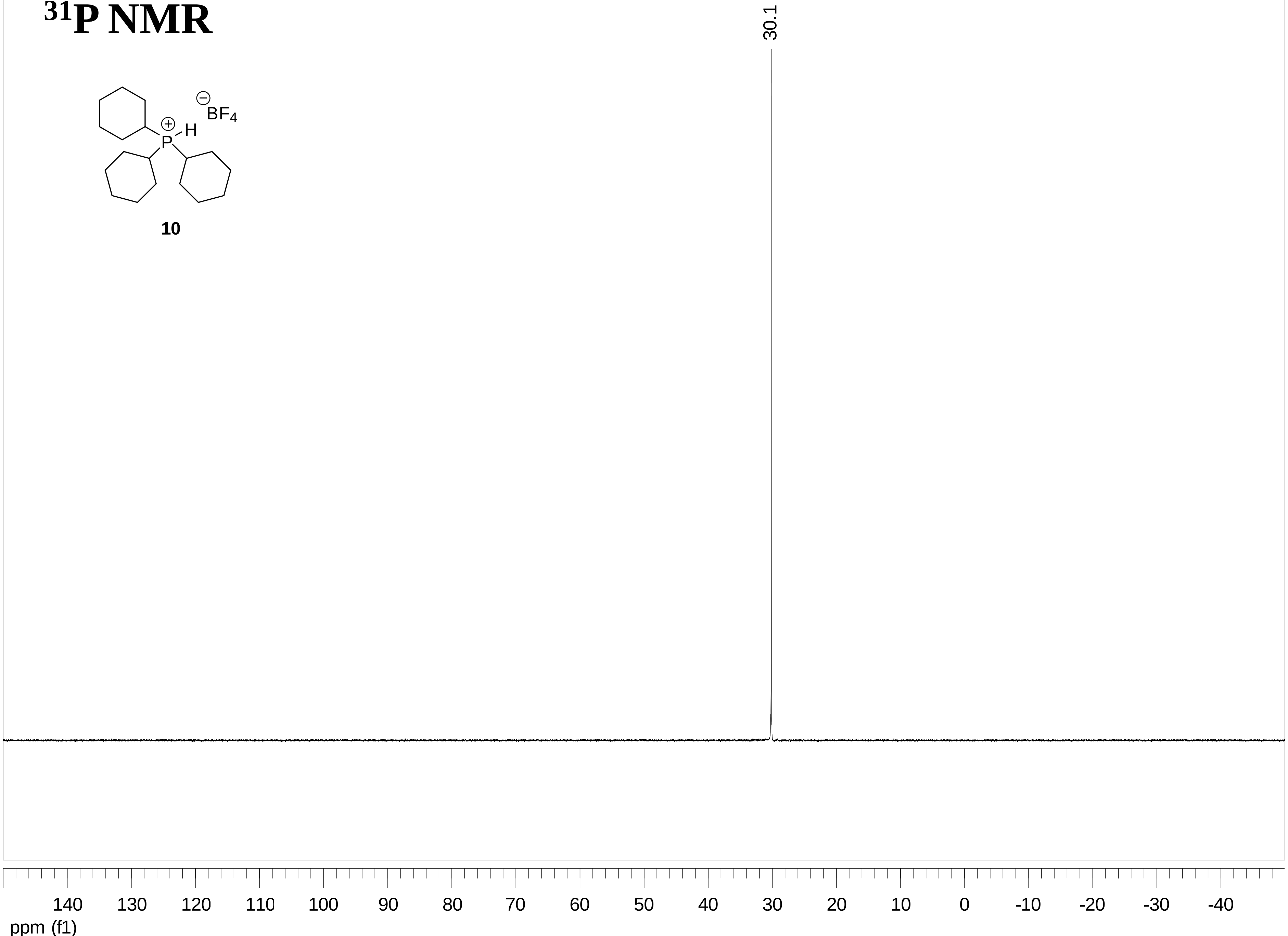
40
30
20
10
ppm (f1)

^{31}P NMR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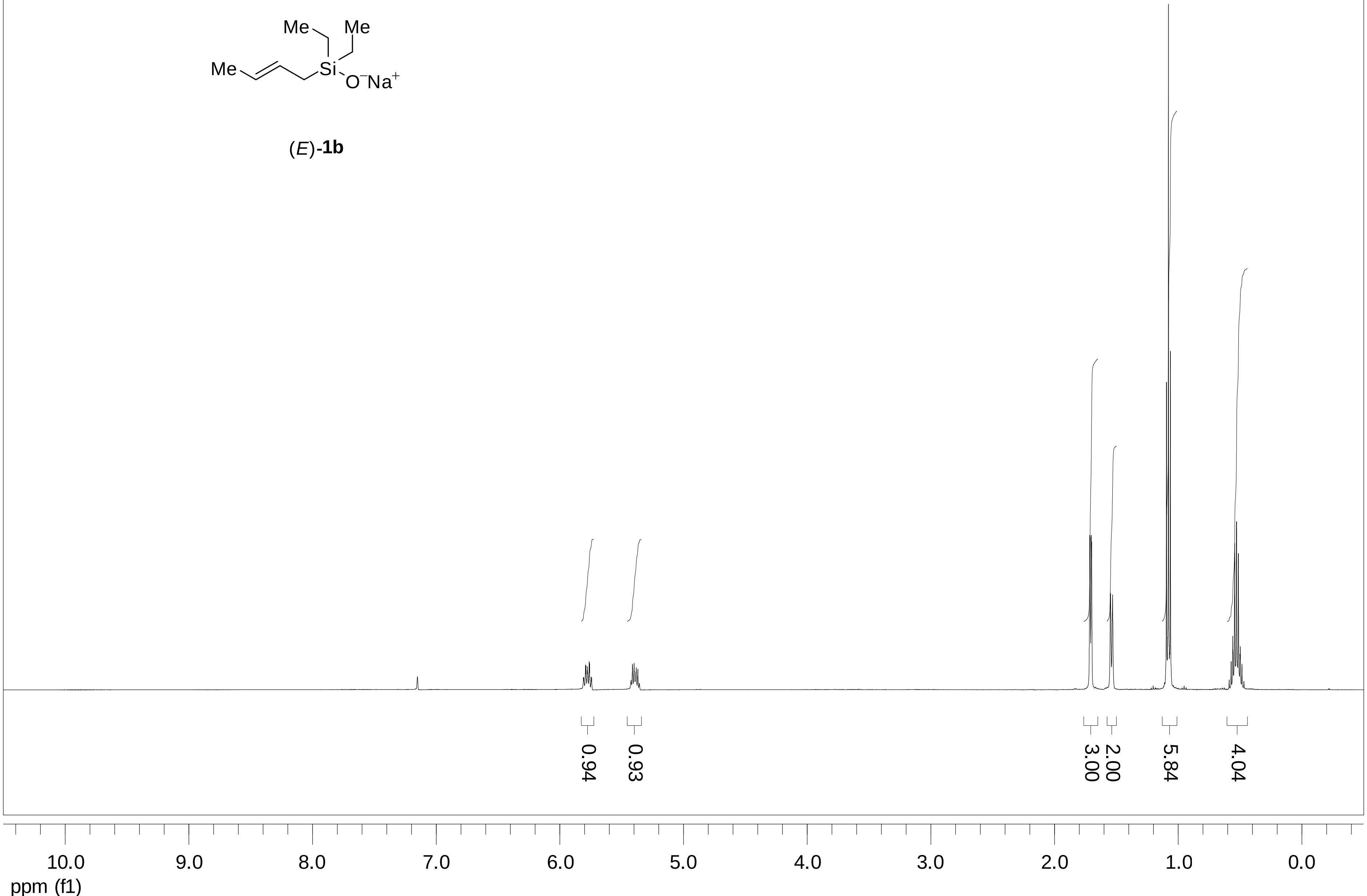
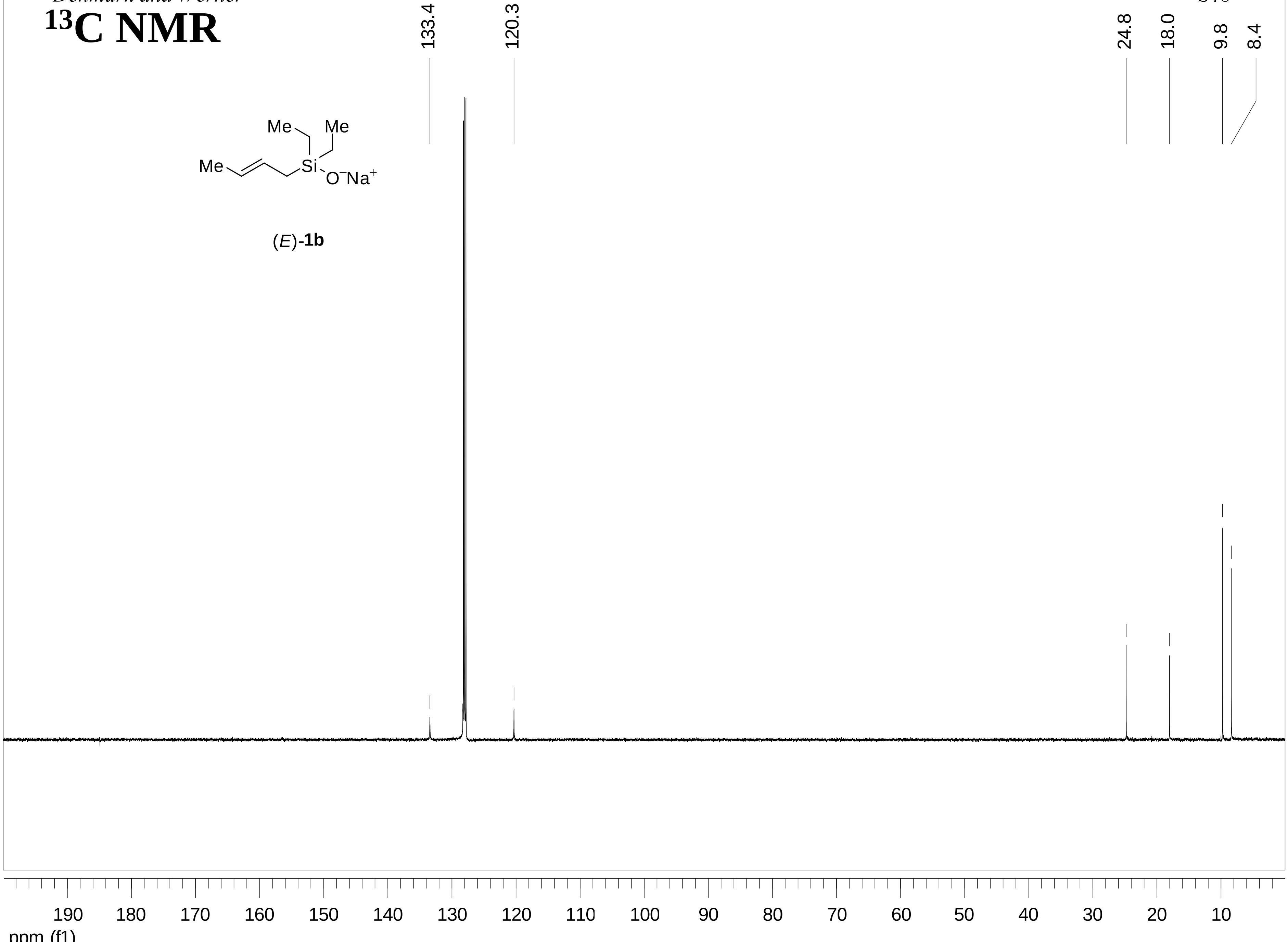


(*E*)-**1b**

^{13}C NMR



(*E*)-**1b**
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180
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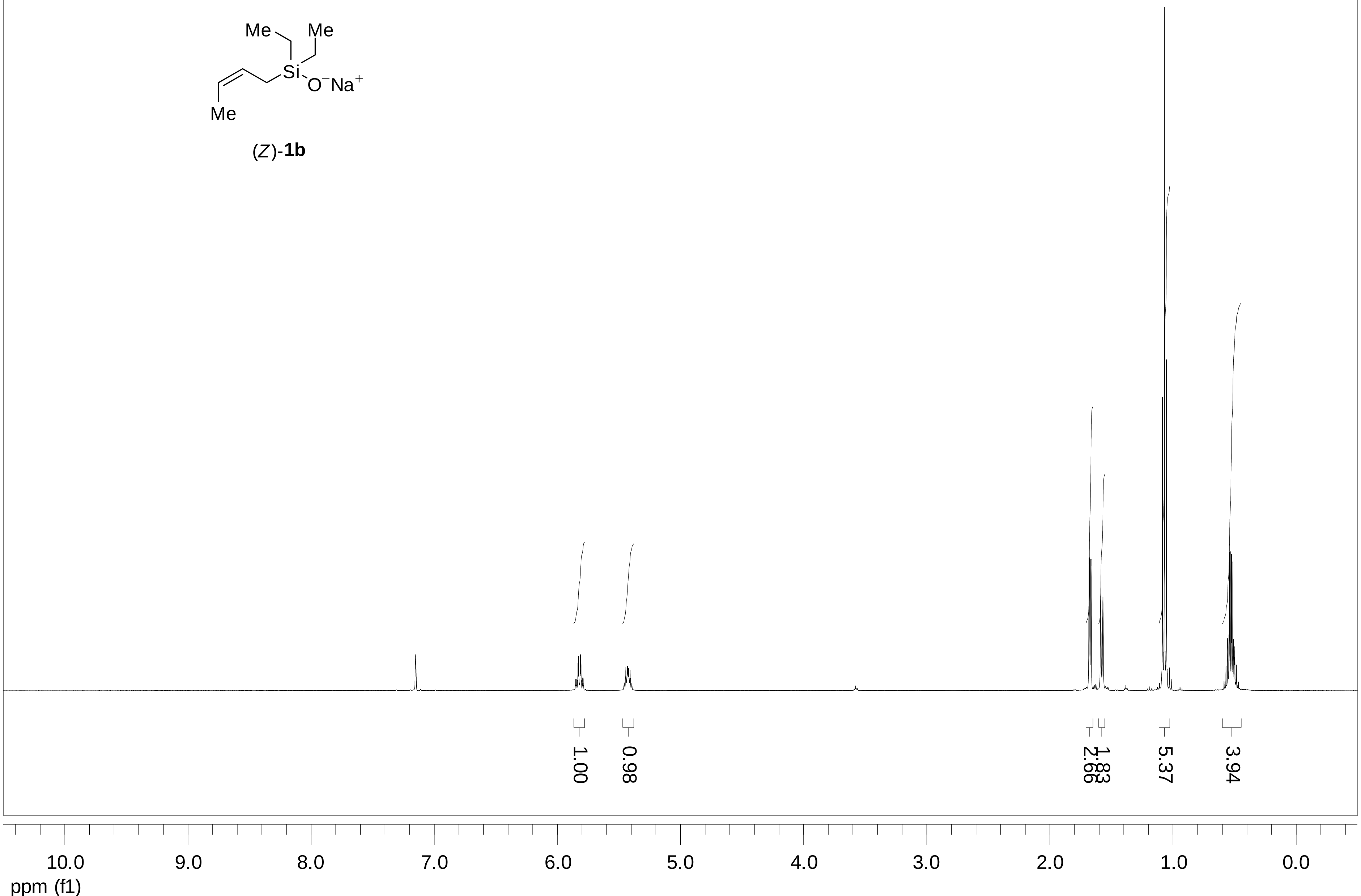
ppm (f1)

^{1}H NMR



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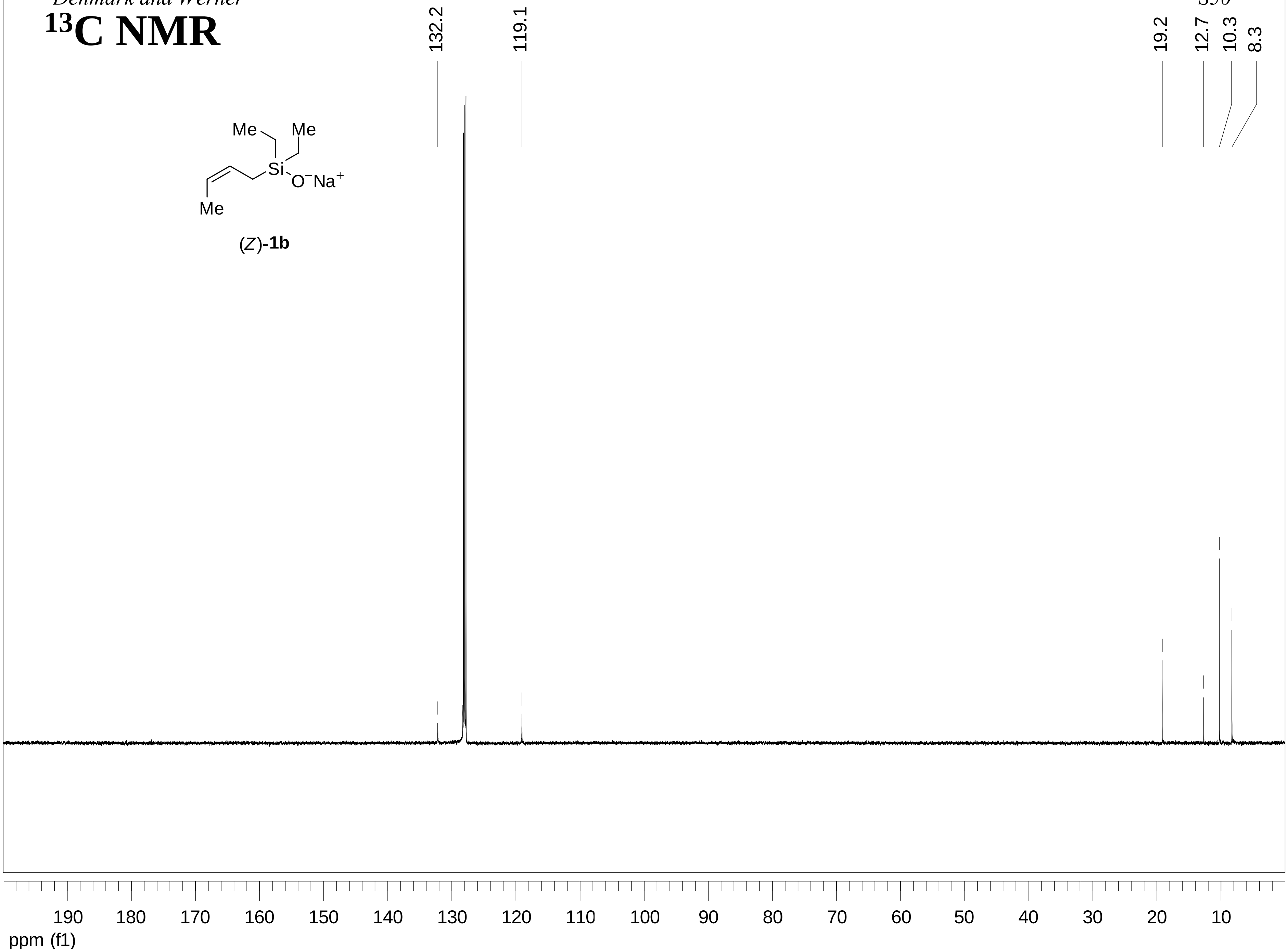
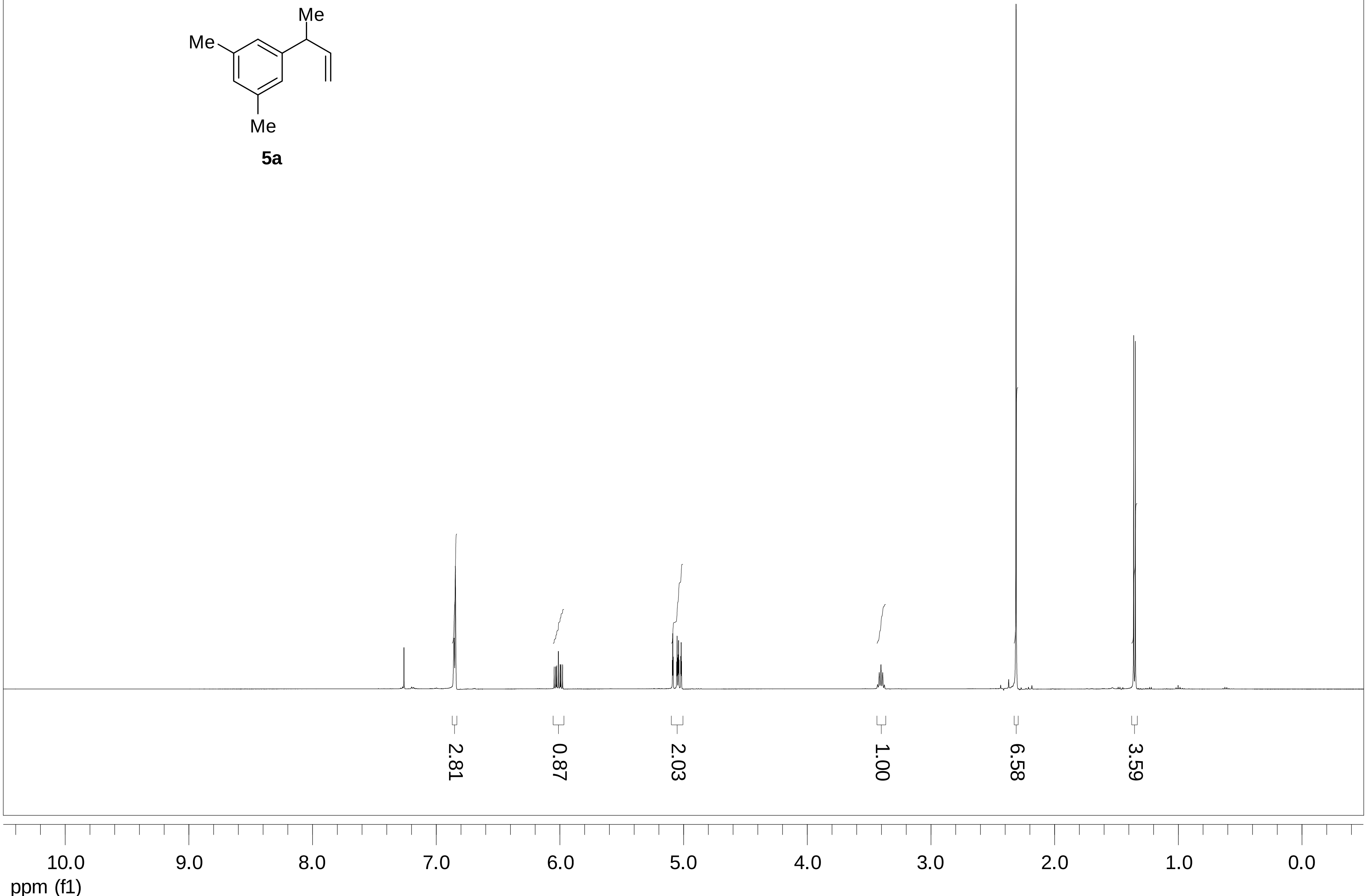
4.0
3.0
2.0
1.0
0.0
ppm (f1)

^{13}C NMR

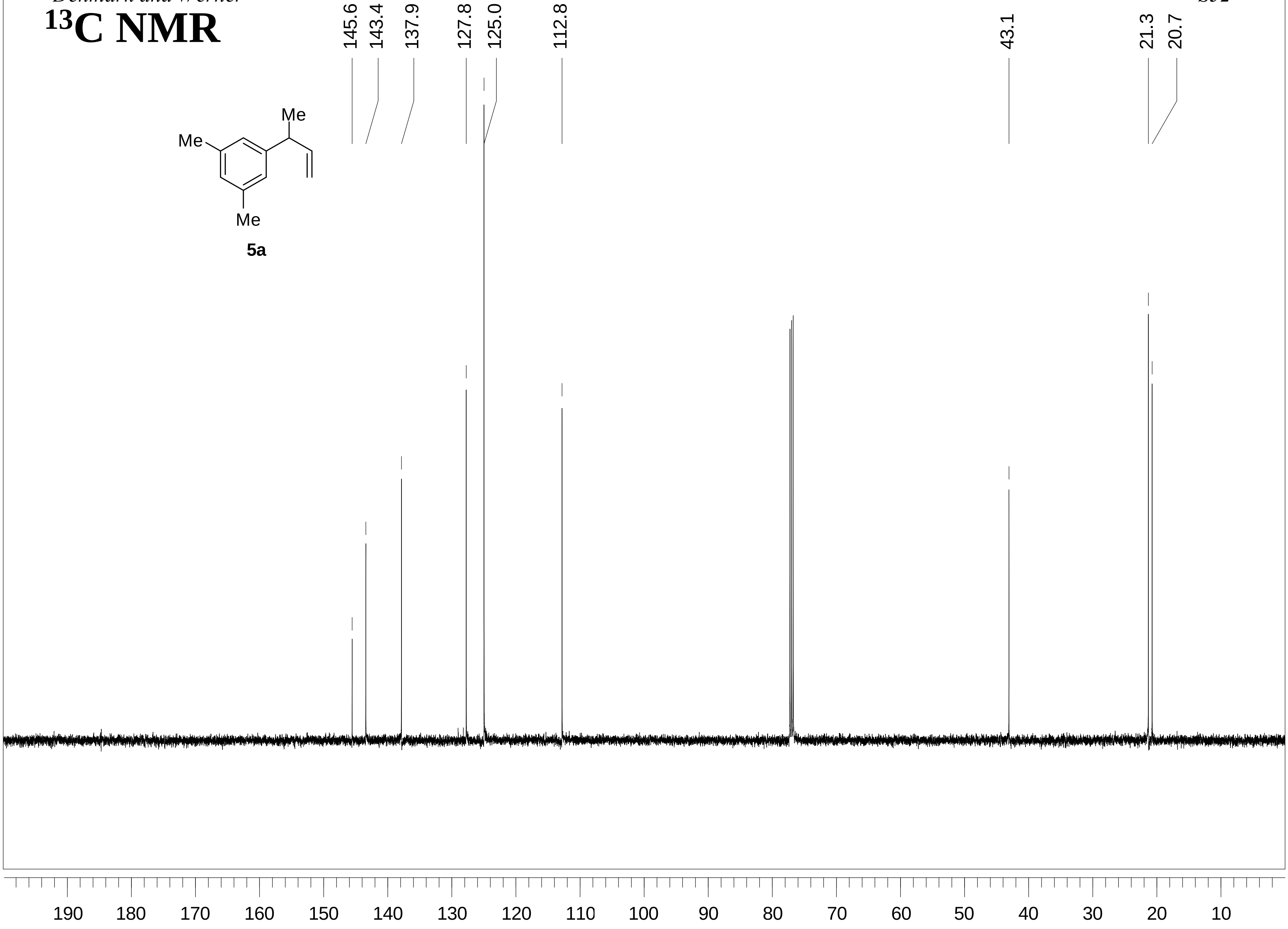

132.2
119.1
19.2
12.7
10.3
8.3
Me
Me
Si
O⁻Na⁺
Me
(Z)-1b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (f1)

^{1}H NMR


Me
Me
Me
2.81
0.87
2.03
1.00
6.58
3.59
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

5a

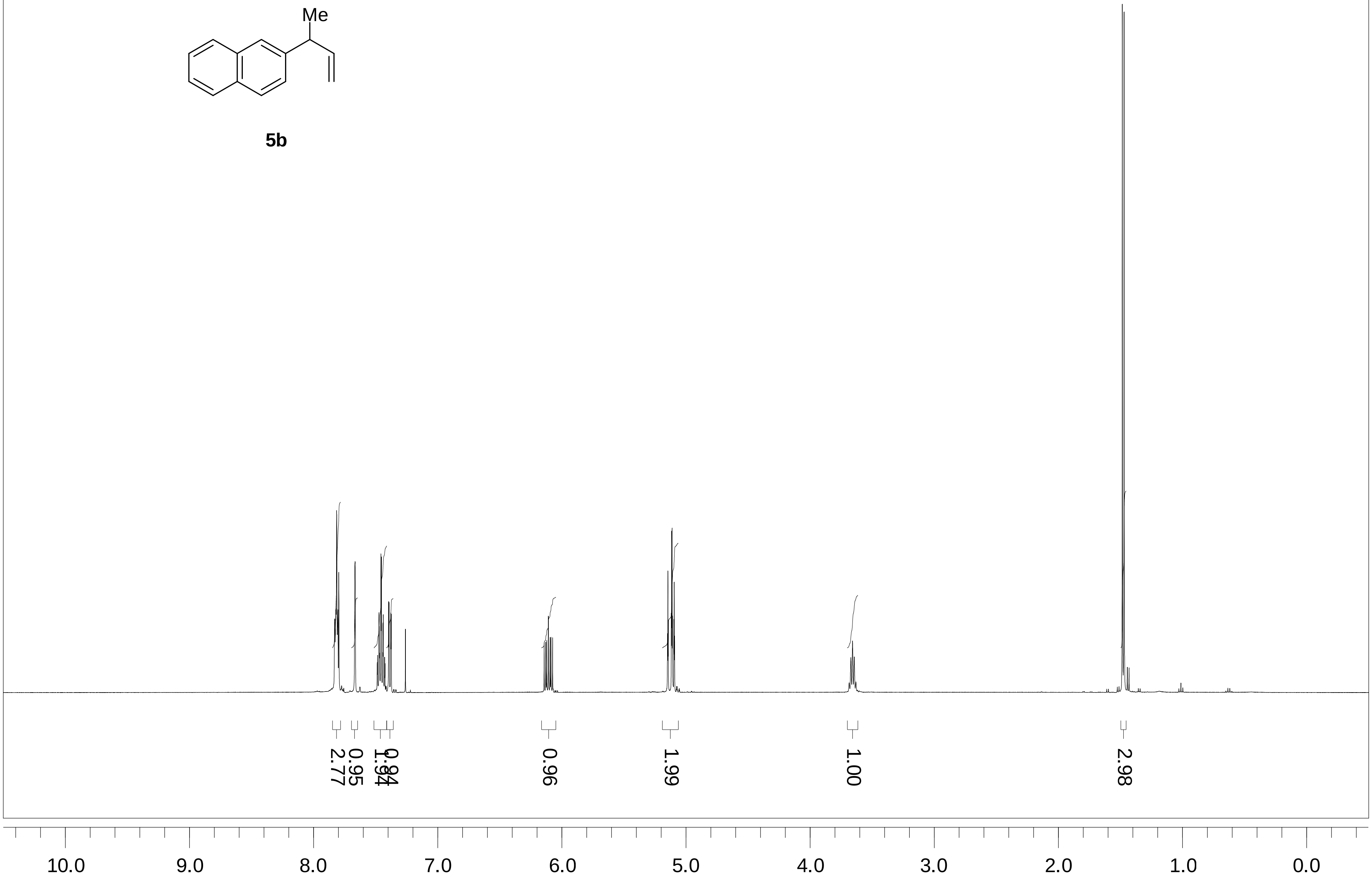
^{13}C NMR



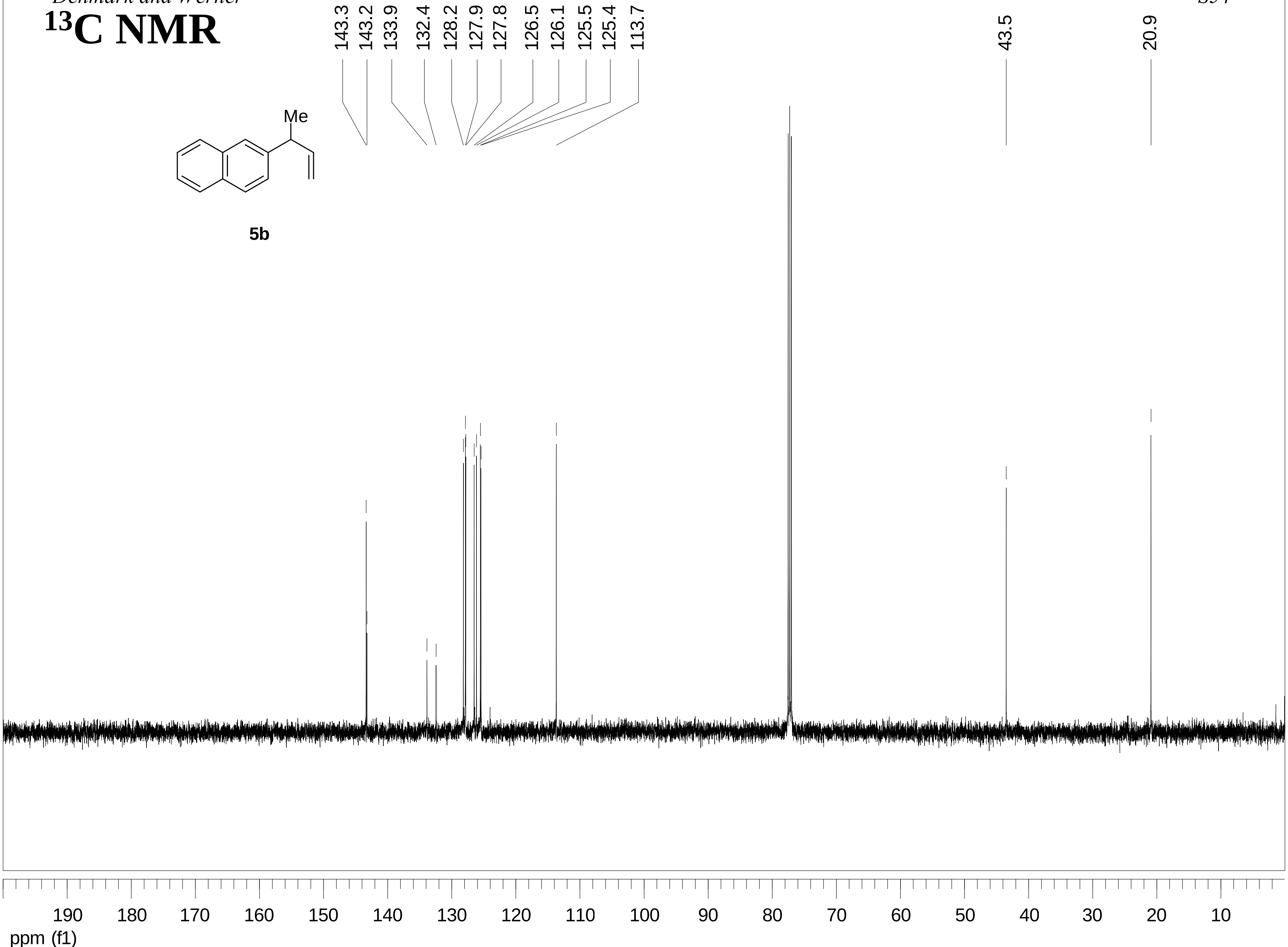
5a

145.6
143.4
137.9
127.8
125.0
112.8
43.1
21.3
20.7
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (f1)

^{1}H NMR


Me
5b
2.77
0.95
1.94
0.94
0.96
1.99
1.00
2.98
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

^{13}C NMR



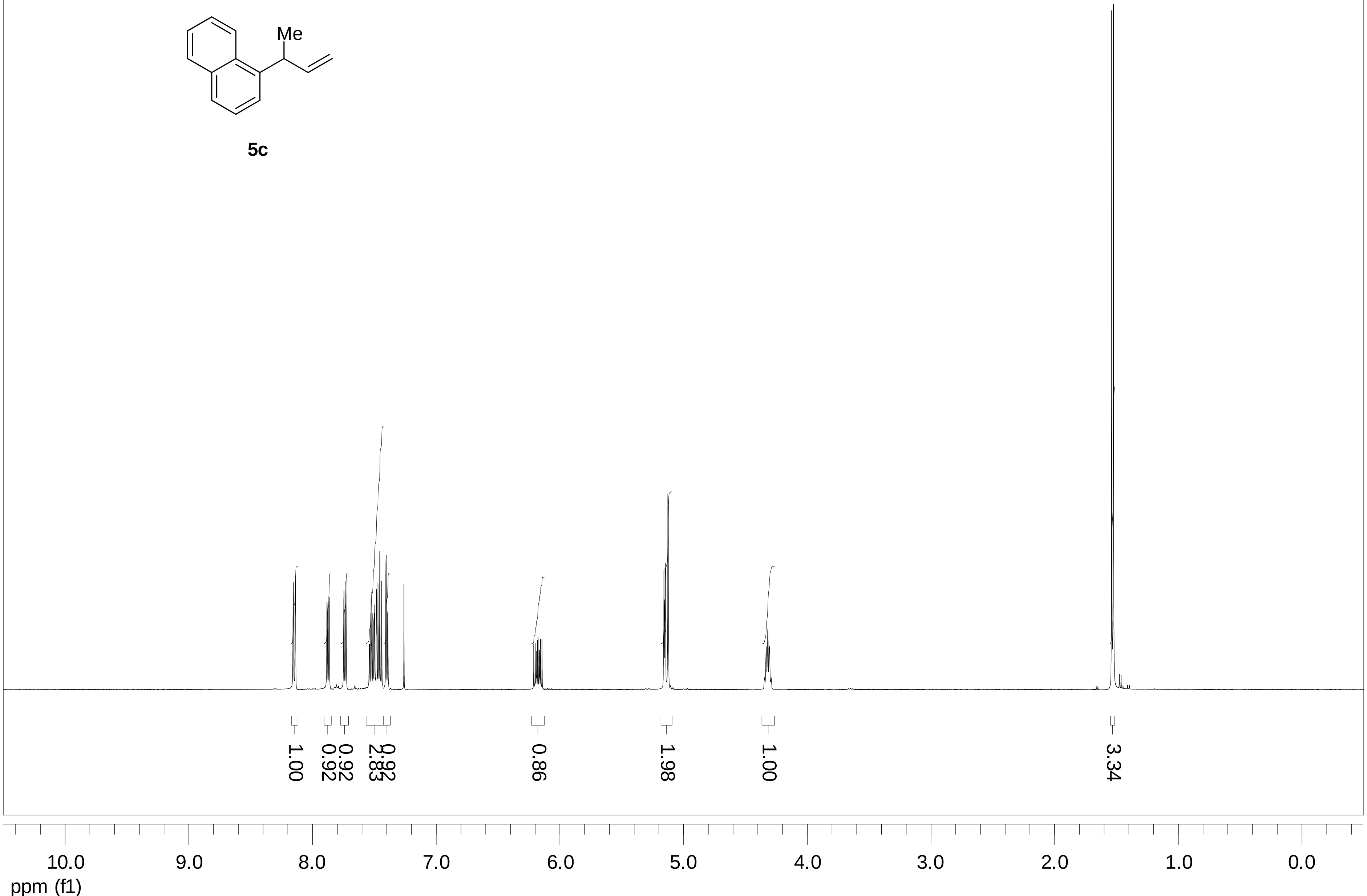
5b

143.3
143.2
133.9
132.4
128.2
127.9
127.8
126.5
126.1
125.5
125.4
113.7
43.5
20.9
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (f1)

^{1}H NMR

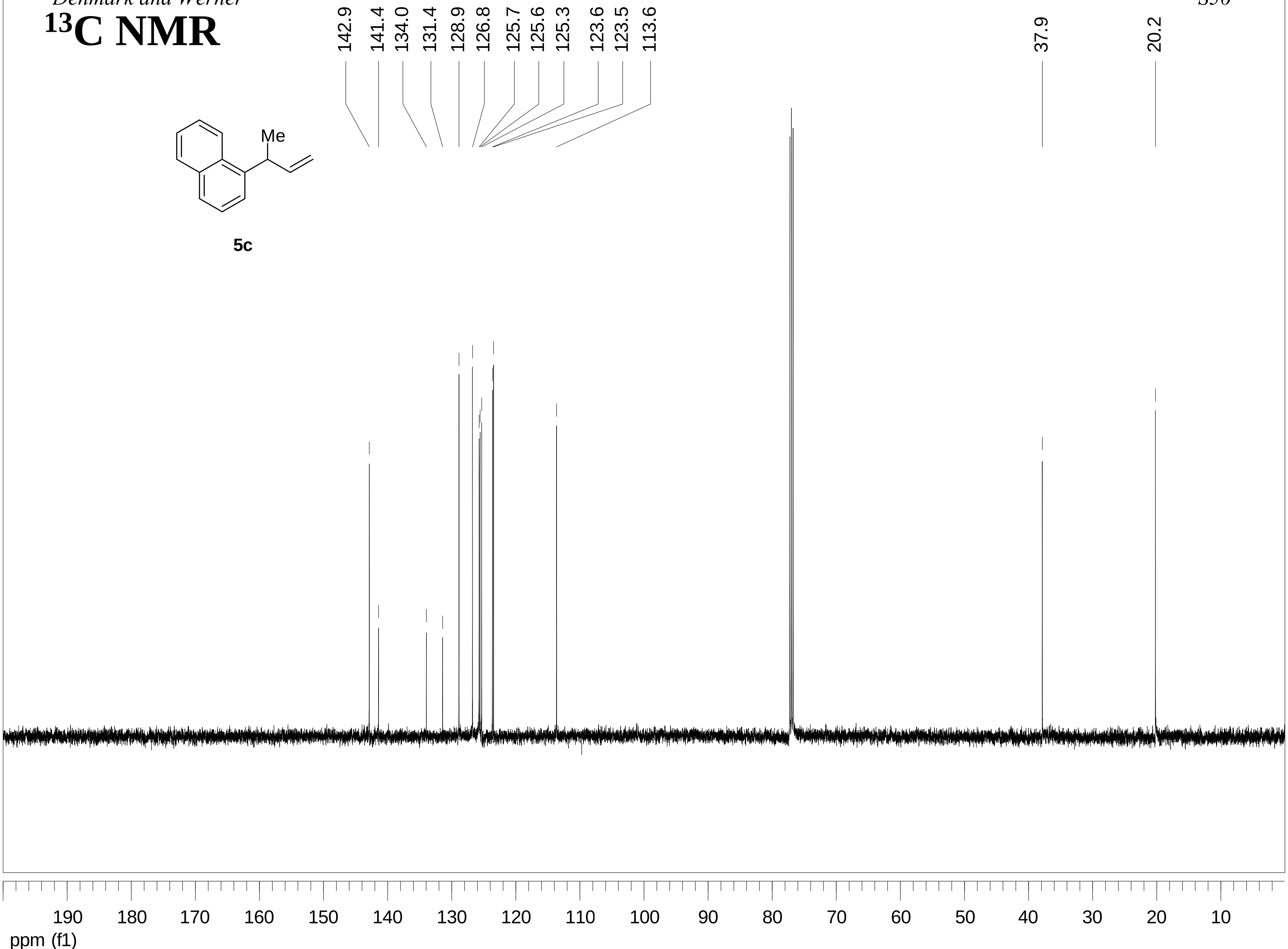
5c

Me



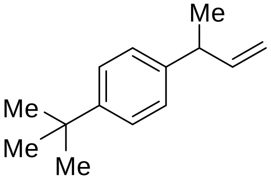
1.00
0.92
0.92
2.83
0.92
0.86
1.98
1.00
3.34
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

^{13}C NMR

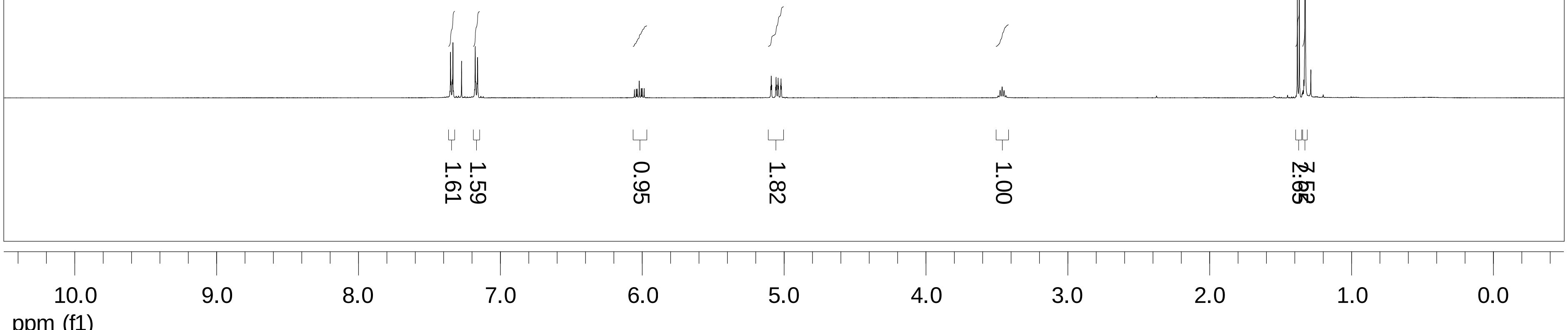


142.9
141.4
134.0
131.4
128.9
126.8
125.7
125.6
125.3
123.6
123.5
113.6
37.9
20.2
Me
5c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (f1)

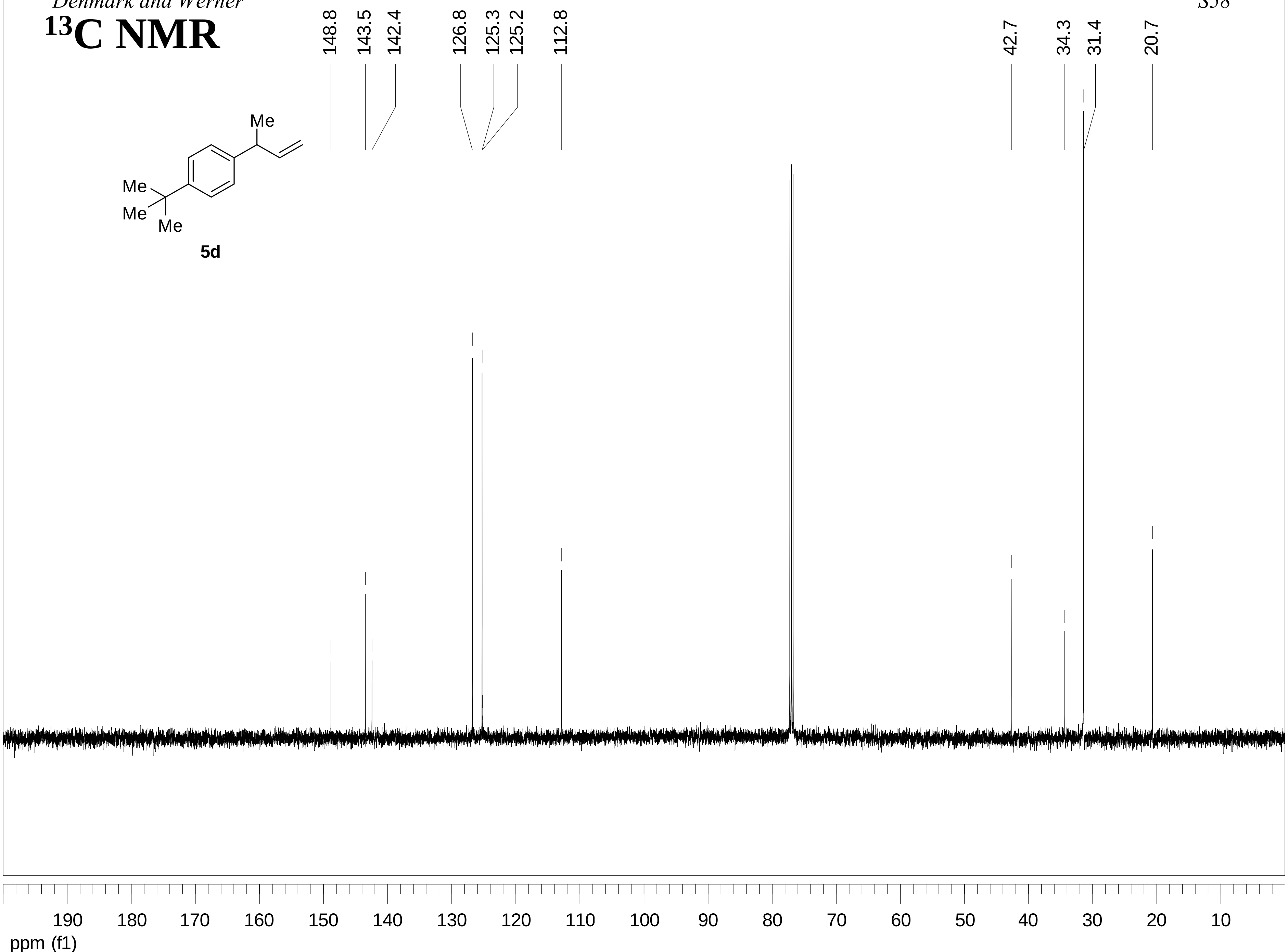
^{1}H NMR


Me
Me
Me
Me

5d


1.61
1.59
0.95
1.82
1.00
2.65
7.52
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

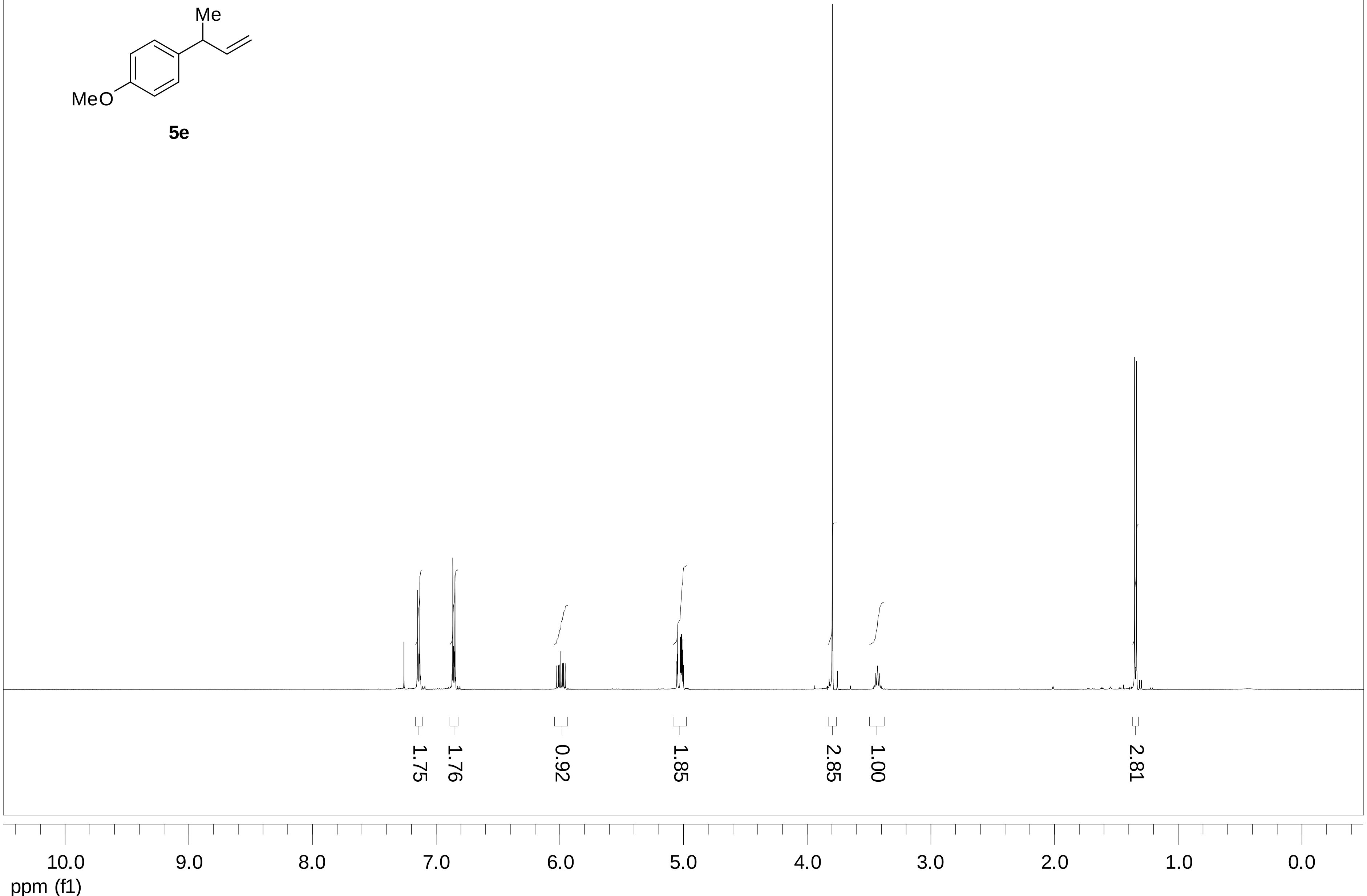
^{13}C NMR



5d

148.8
143.5
142.4
126.8
125.3
125.2
112.8
42.7
34.3
31.4
20.7
Me
Me
Me
Me
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (f1)

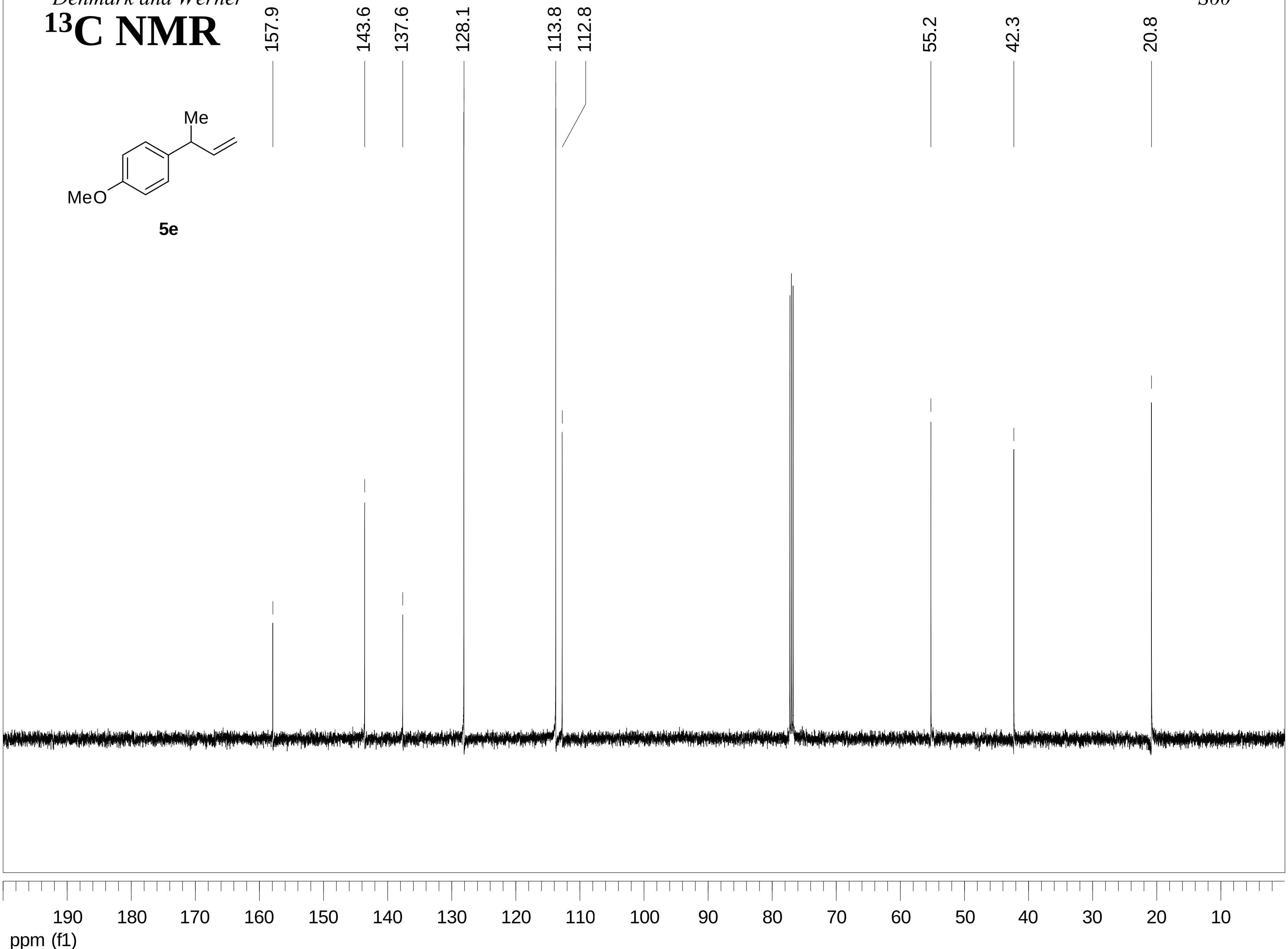
^{1}H NMR



5e

Me
MeO
1.75
1.76
0.92
1.85
2.85
1.00
2.81
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

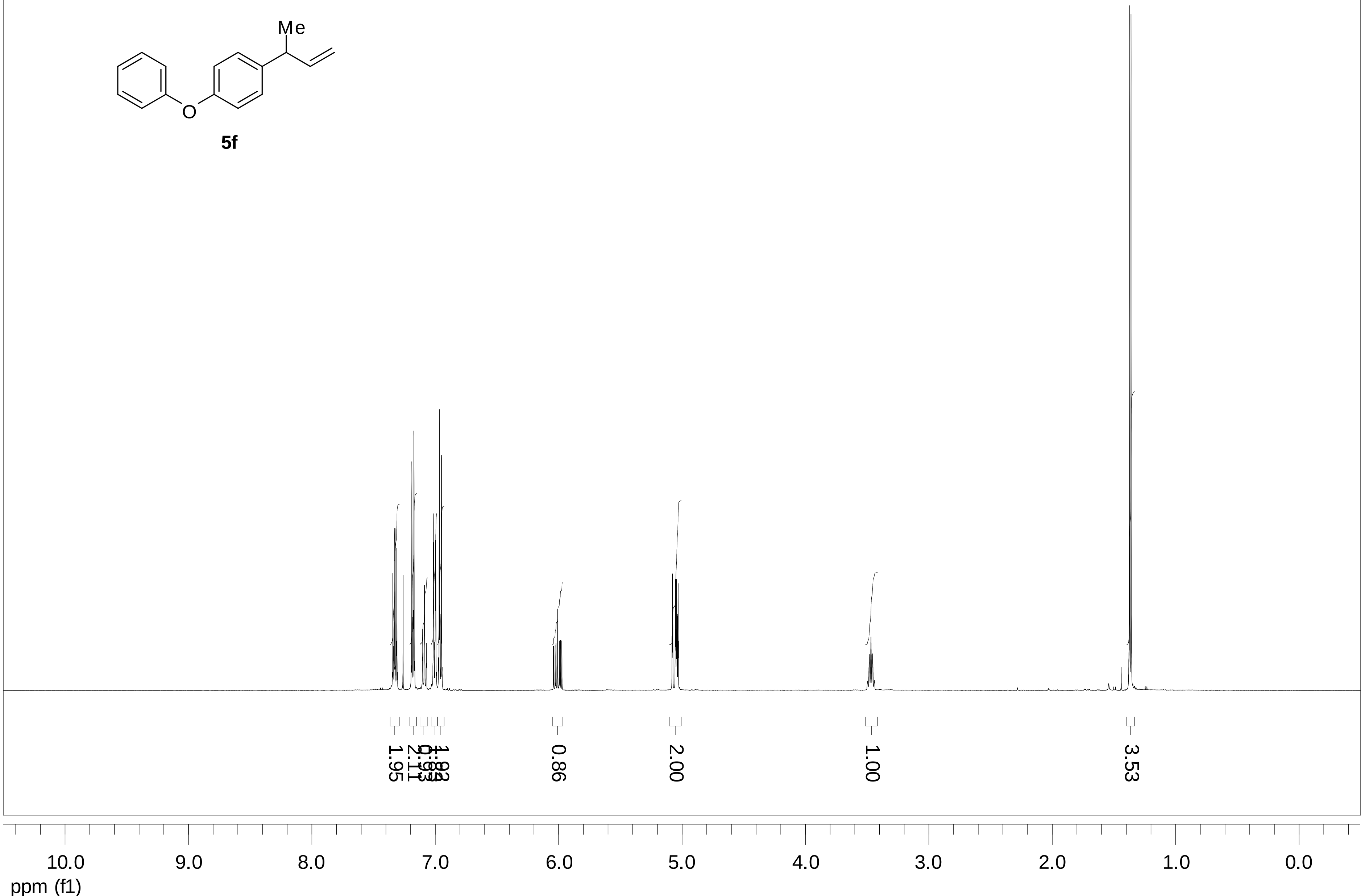
^{13}C NMR



5e

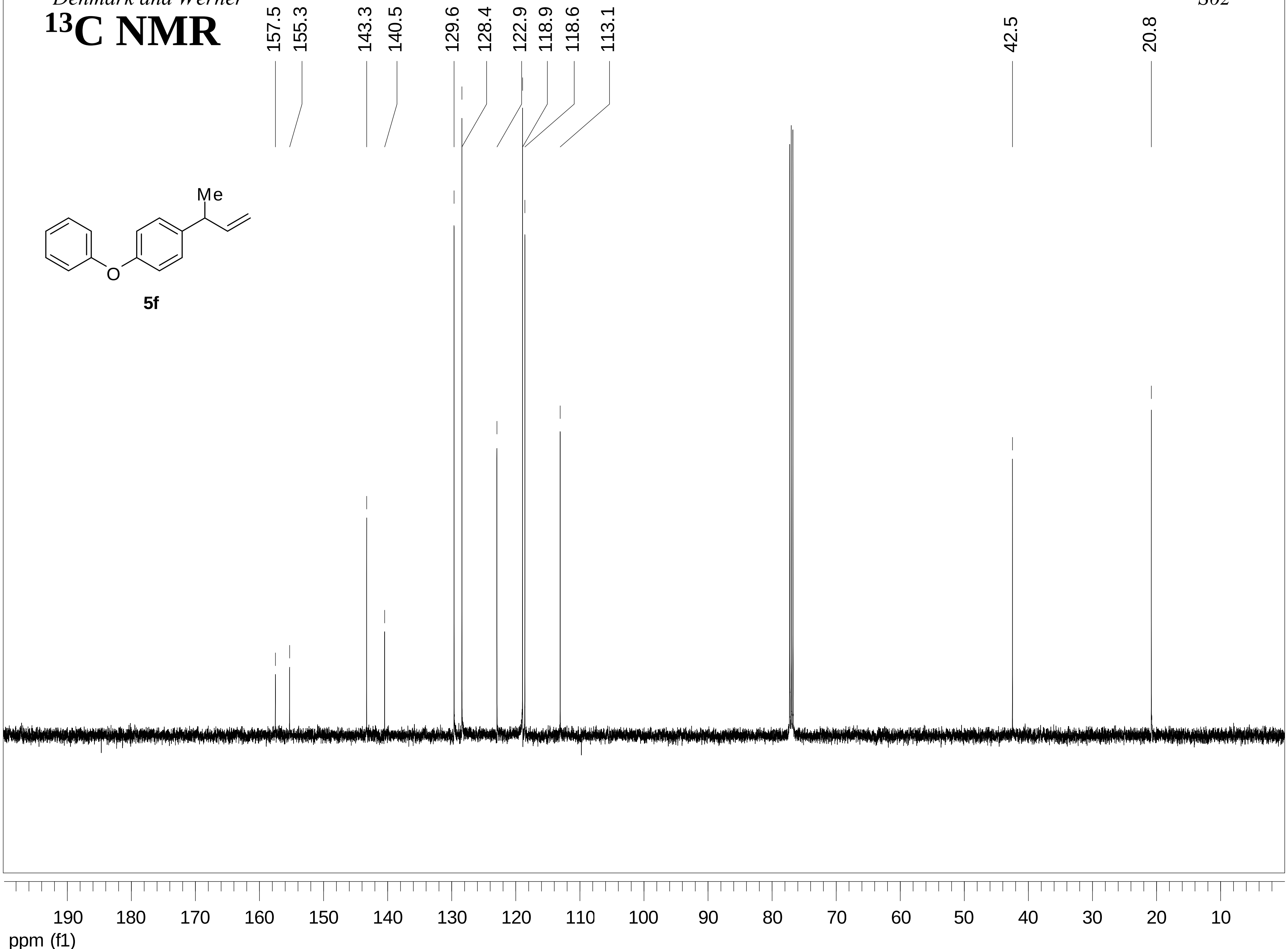
157.9
143.6
137.6
128.1
113.8
112.8
55.2
42.3
20.8
Me
MeO
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (f1)

^{1}H NMR


Me
O
1.95
2.11
0.93
1.83
1.82
0.86
2.00
1.00
3.53
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

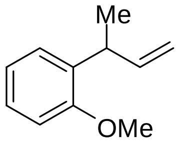
5f

^{13}C NMR

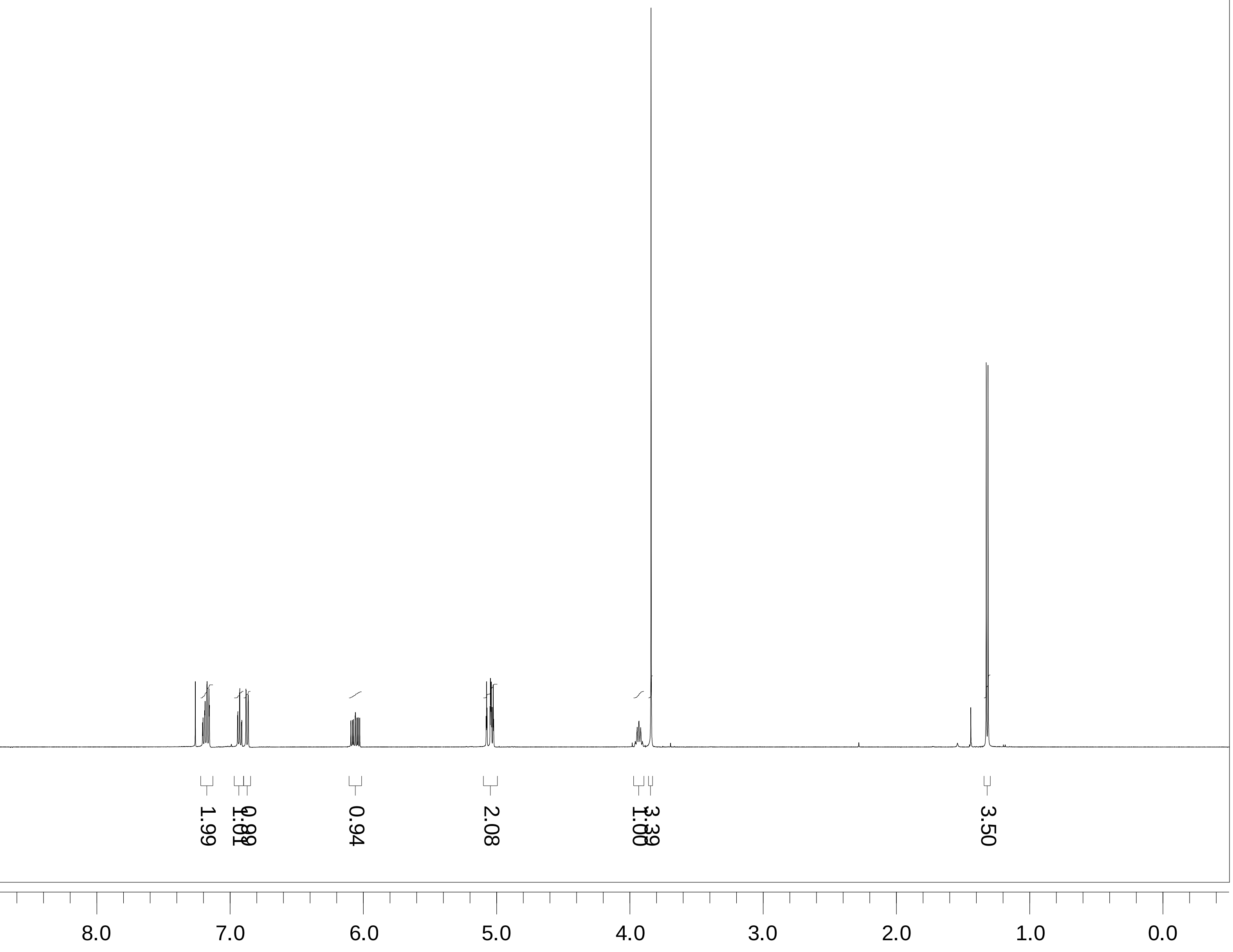

157.5
155.3
143.3
140.5
129.6
128.4
122.9
118.9
118.6
113.1
42.5
20.8
Me
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (f1)

5f

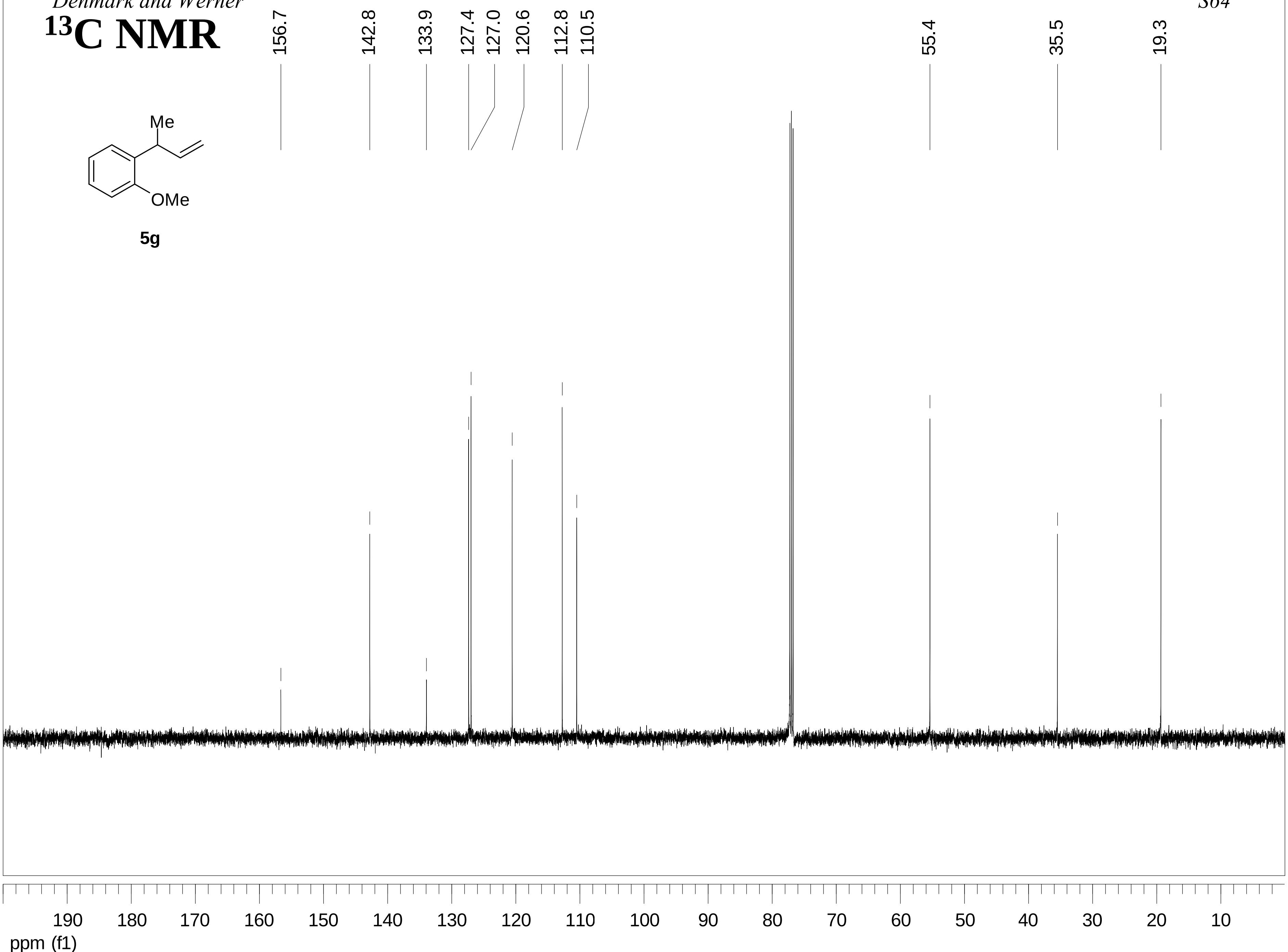
^{1}H NMR


Me
OMe

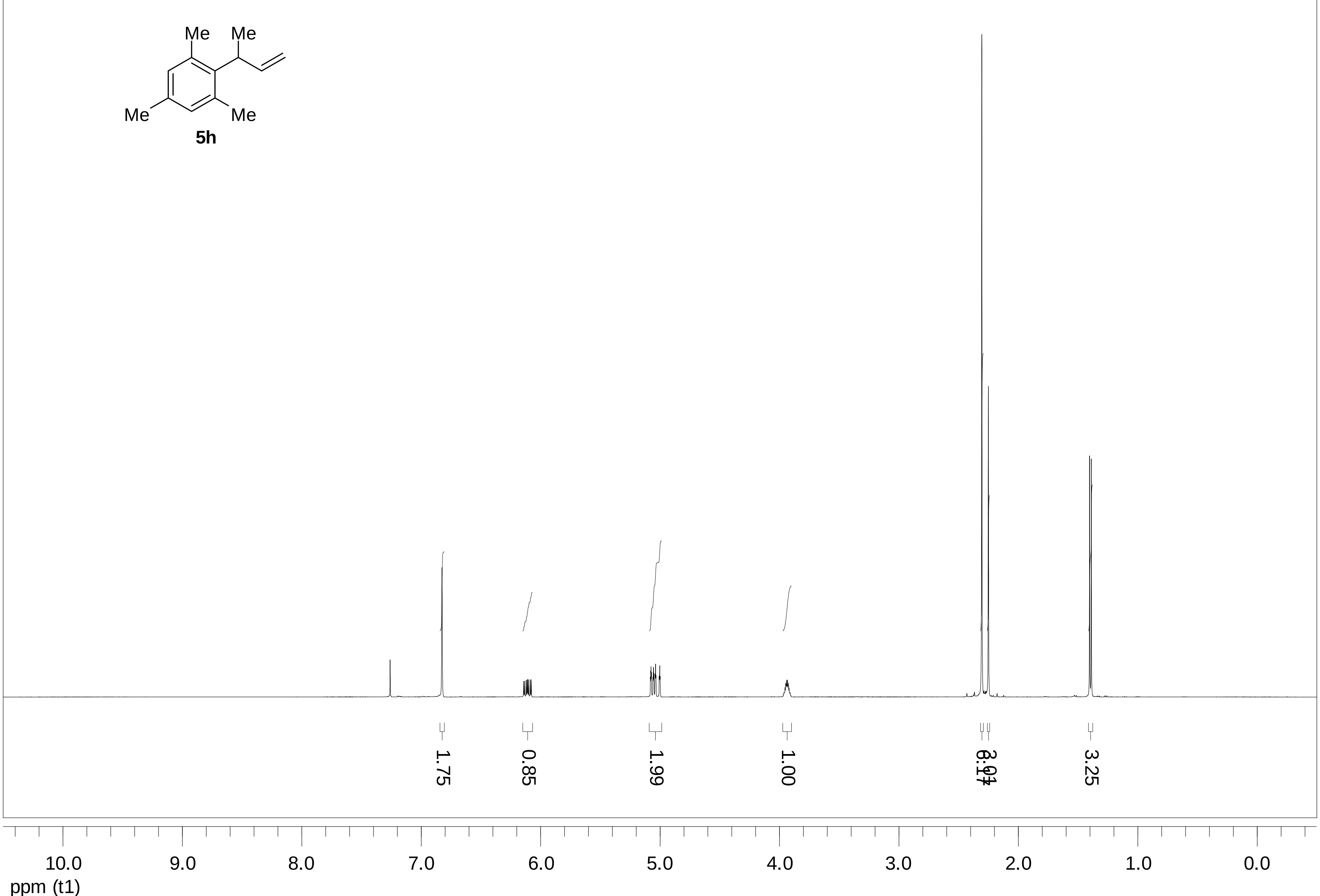
5g


1.99
1.01
0.89
0.94
2.08
1.00
3.39
3.50
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

^{13}C NMR

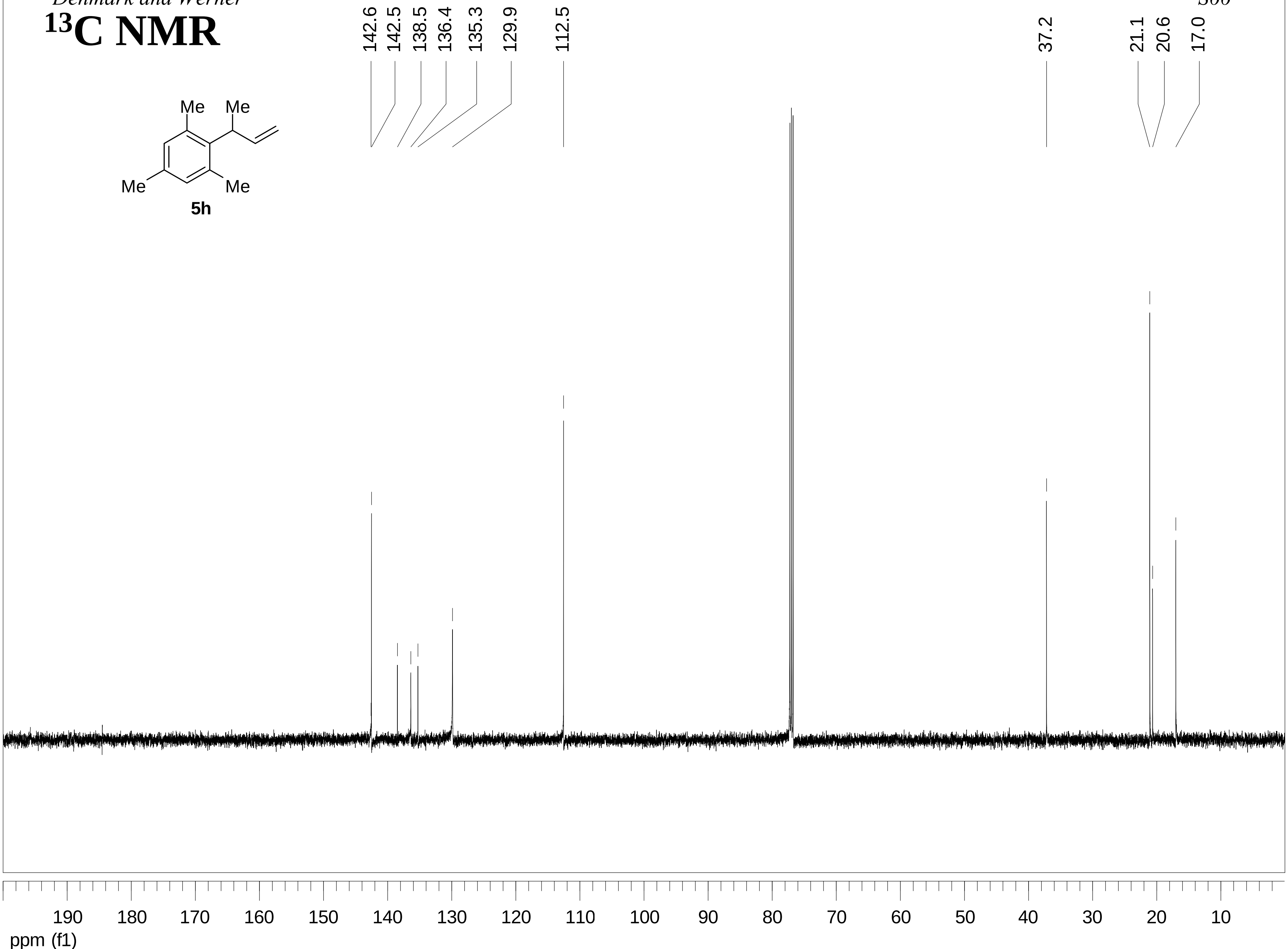

156.7
142.8
133.9
127.4
127.0
120.6
112.8
110.5
55.4
35.5
19.3
Me
OMe
5g
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (f1)

^{1}H NMR

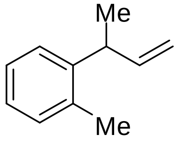

Me
Me
Me
Me
1.75
0.85
1.99
1.00
6.17
3.01
3.25
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

5h

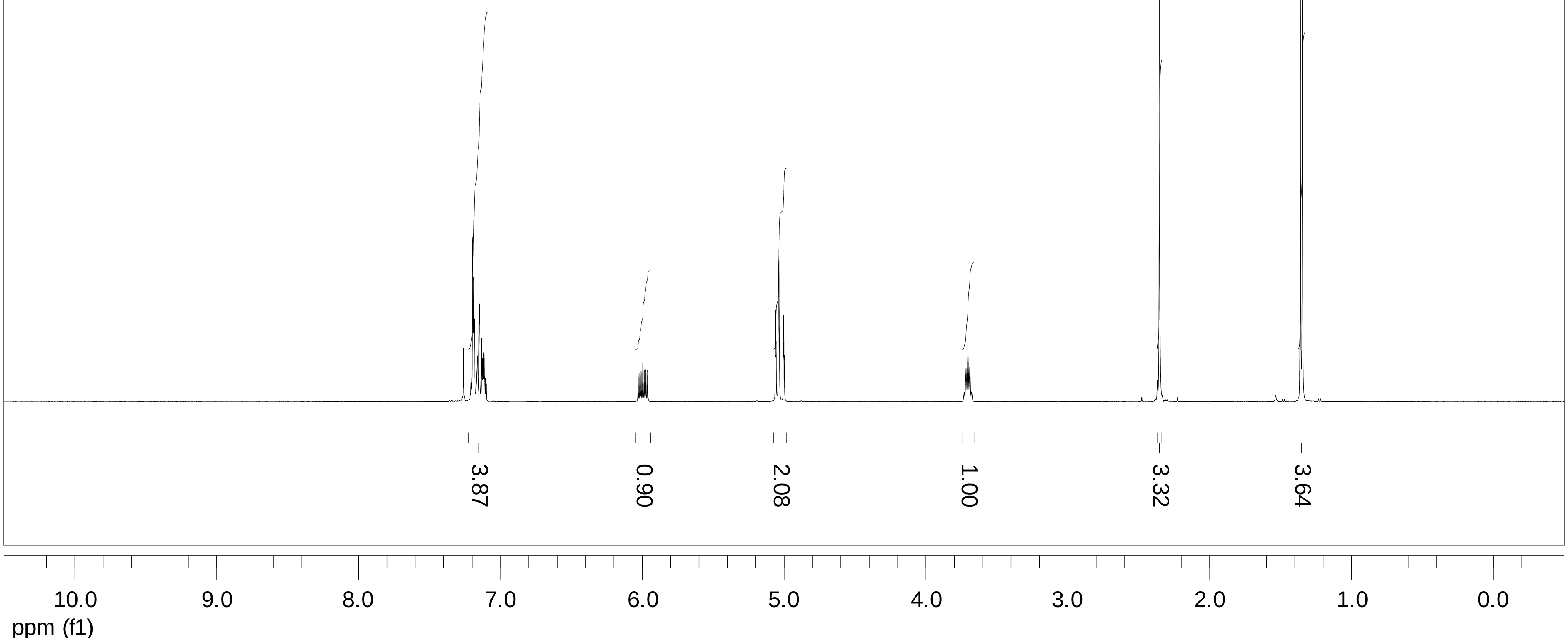
^{13}C NMR


142.6
142.5
138.5
136.4
135.3
129.9
112.5
37.2
21.1
20.6
17.0
Me
Me
Me
Me
5h
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (f1)

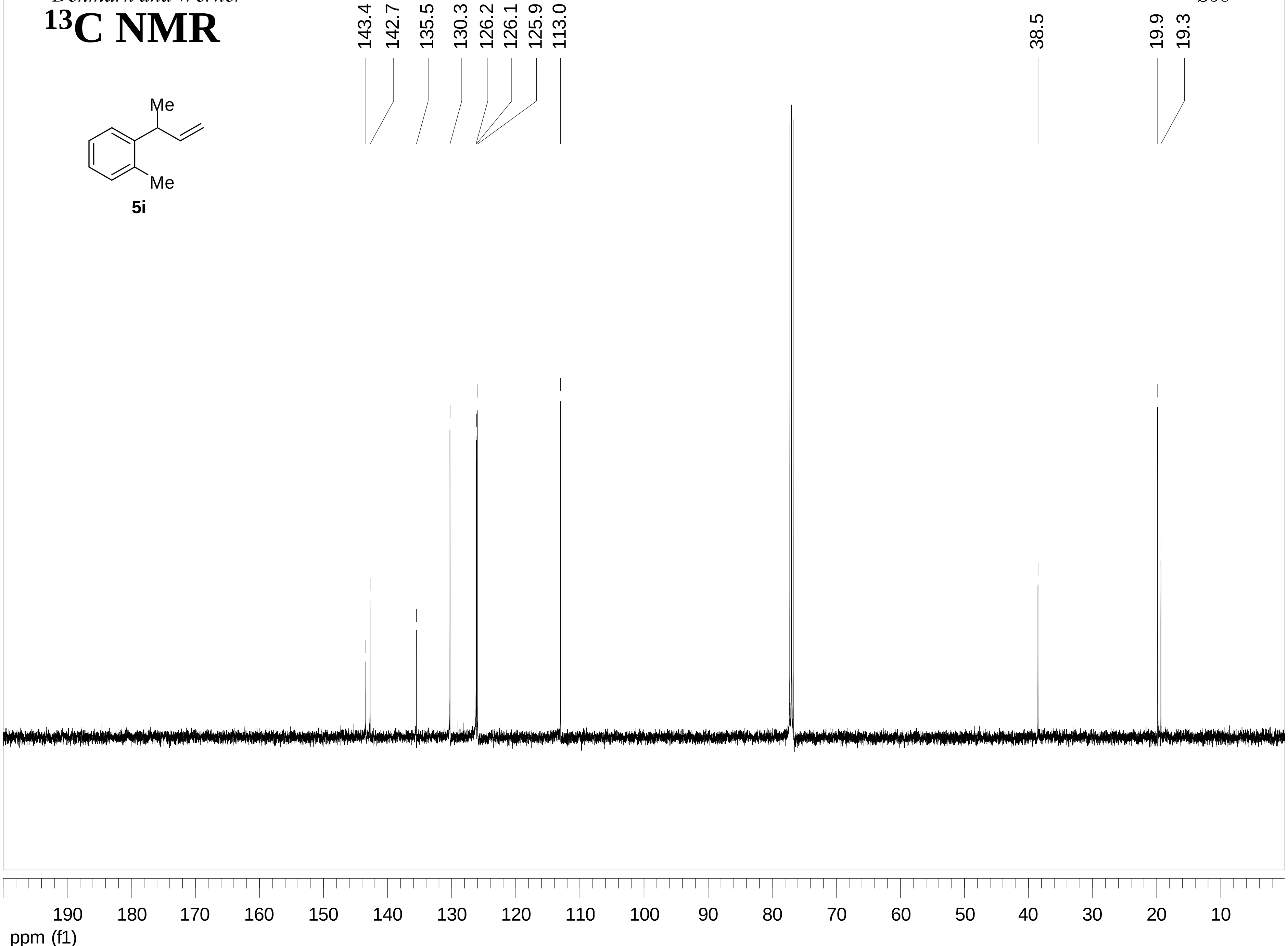
^{1}H NMR


Me
Me

5i


3.87
0.90
2.08
1.00
3.32
3.64
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

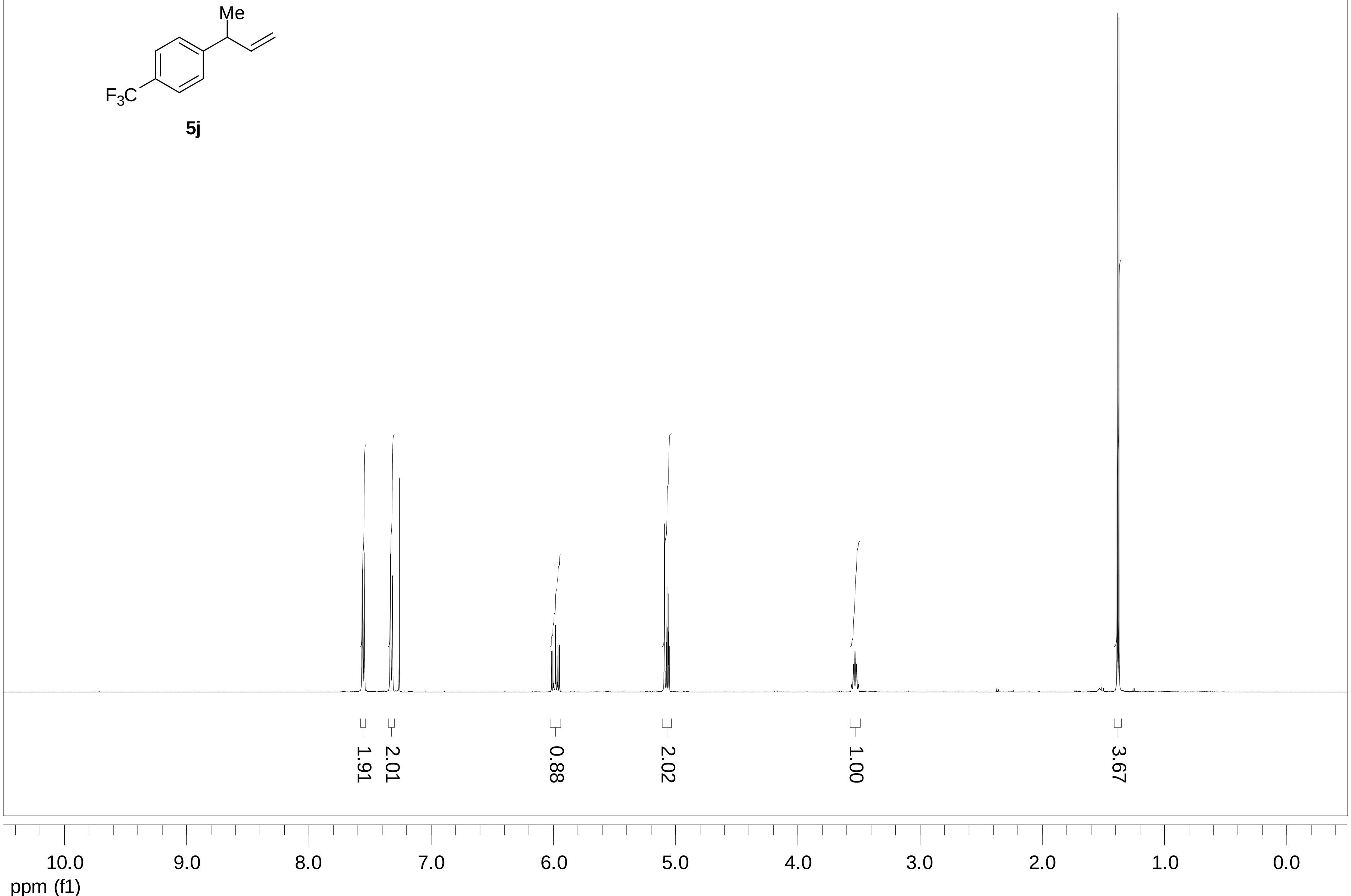
^{13}C NMR



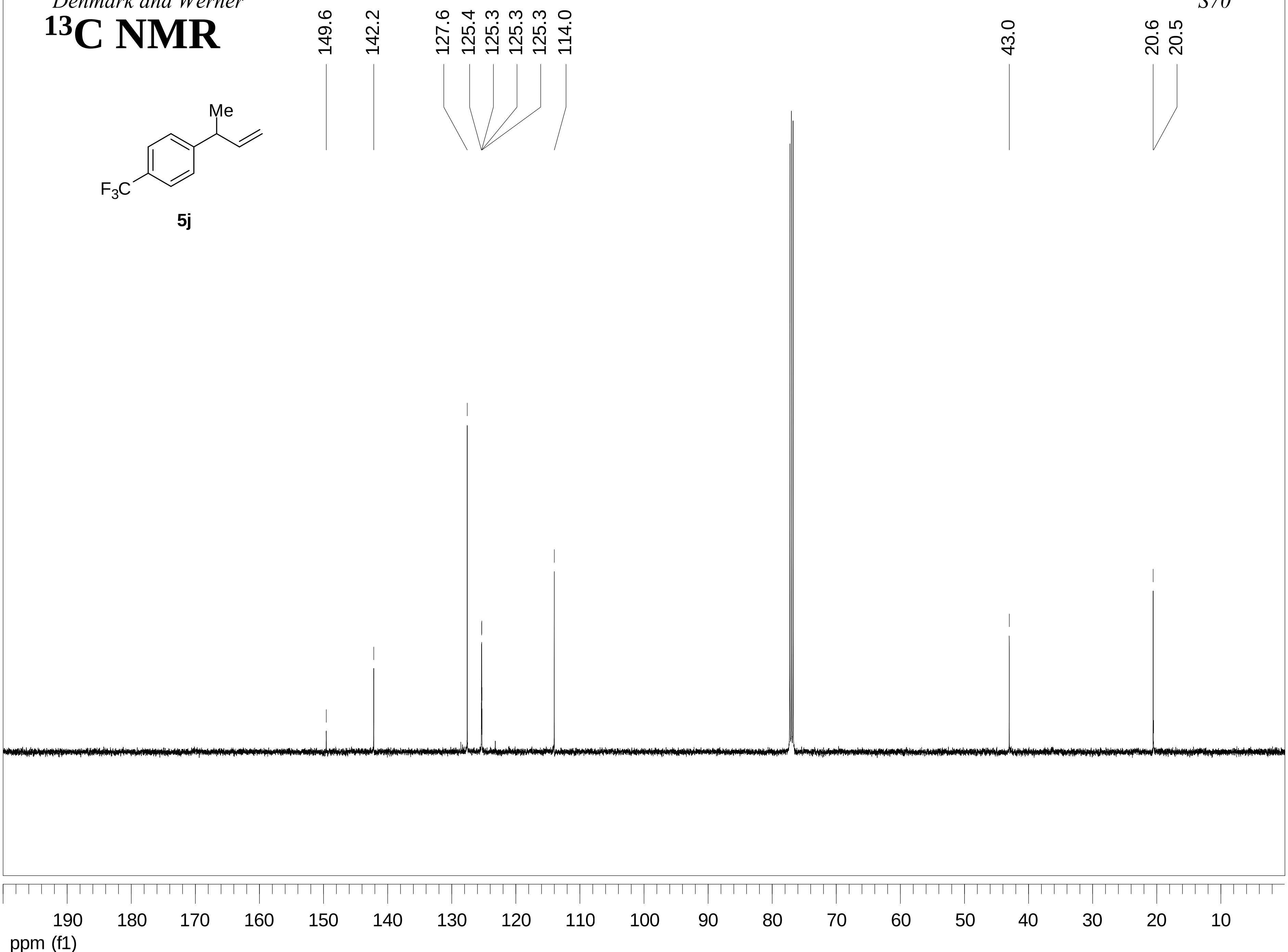
5i

Me
Me
143.4
142.7
135.5
130.3
126.2
126.1
125.9
113.0
38.5
19.9
19.3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (f1)

^{1}H NMR


Me
F3C
5j
1.91
2.01
0.88
2.02
1.00
3.67
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

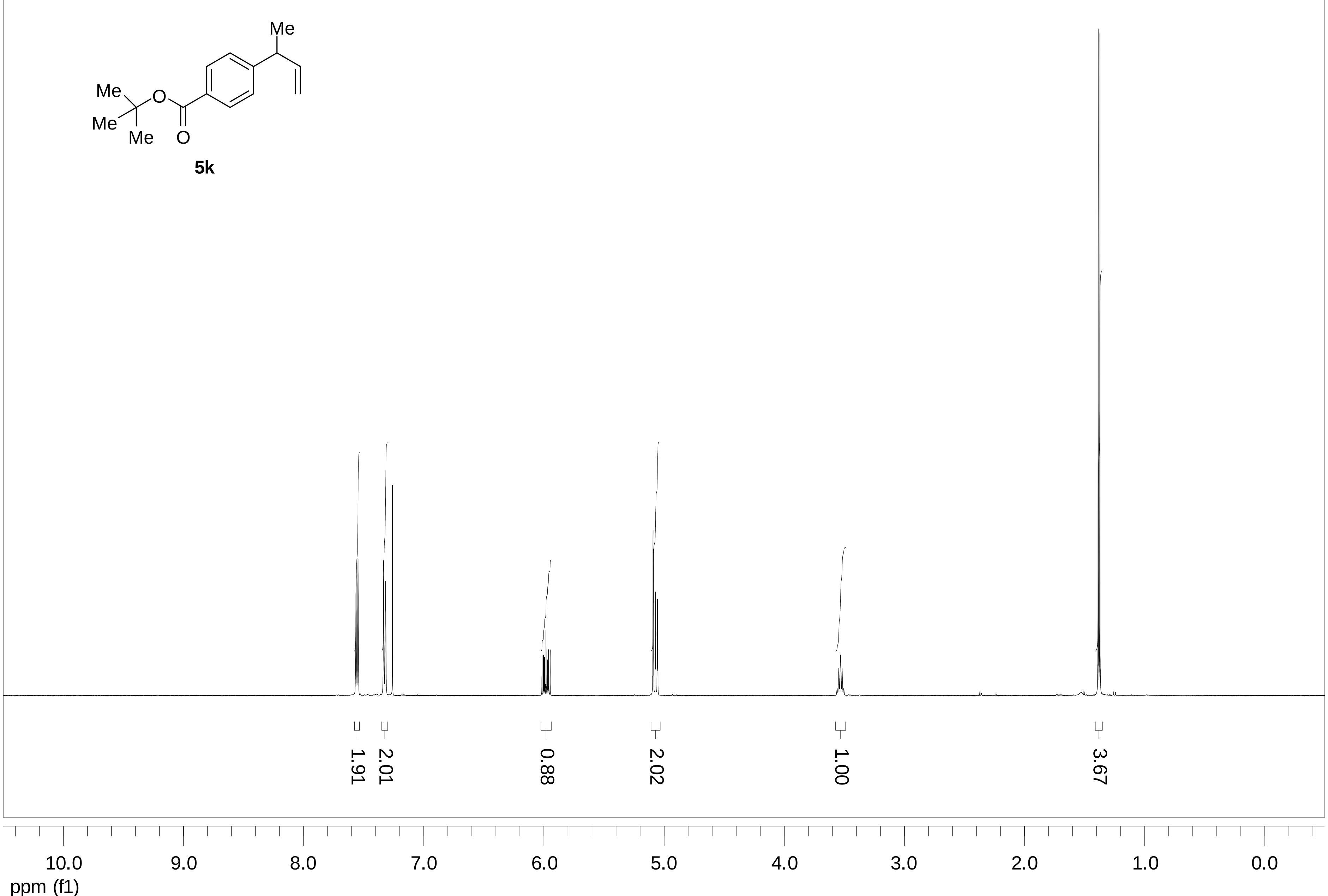
^{13}C NMR



5j

149.6
142.2
127.6
125.4
125.3
125.3
125.3
114.0
43.0
20.6
20.5
Me
F_3C
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (f1)

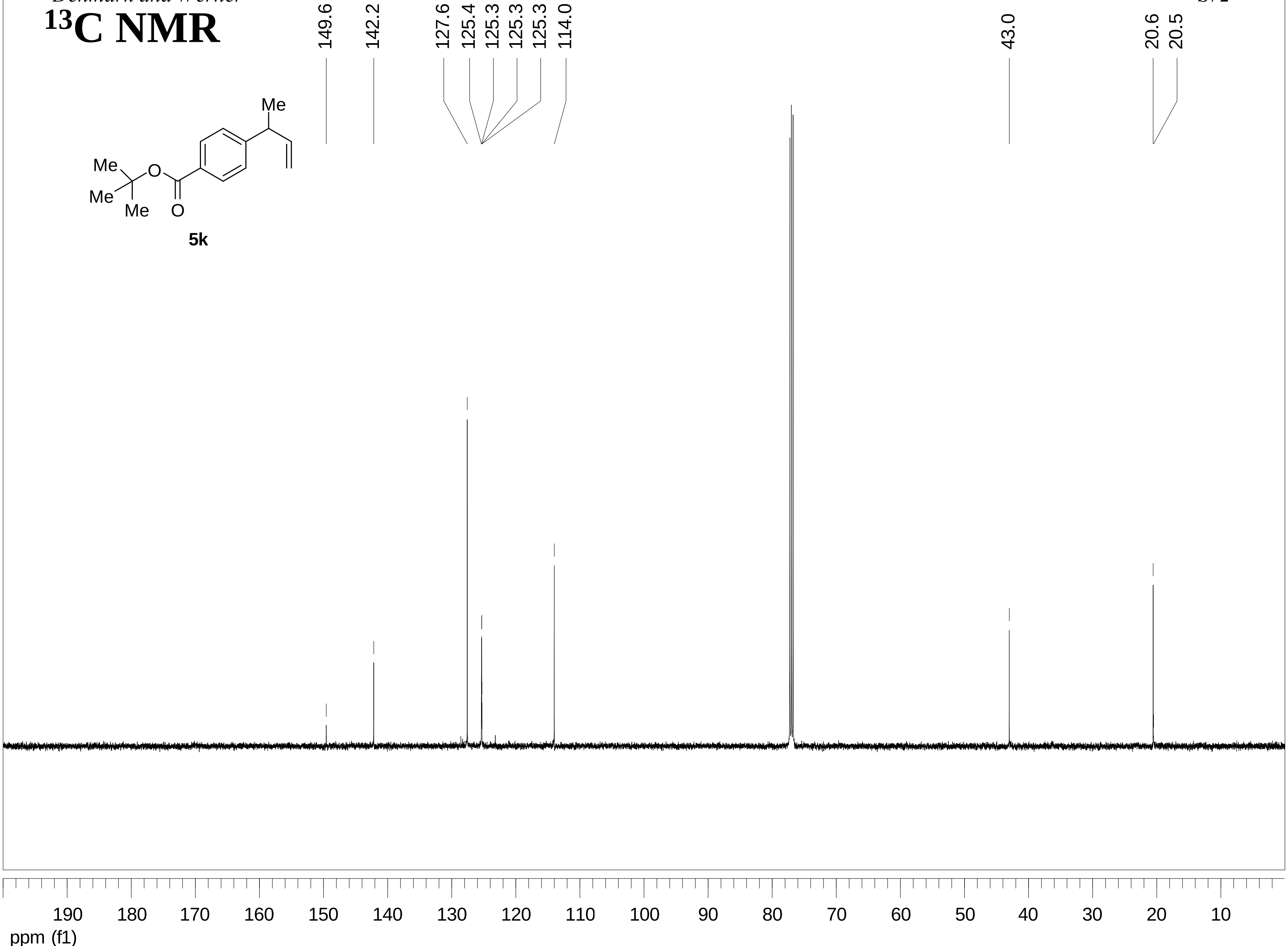
^{1}H NMR



5k

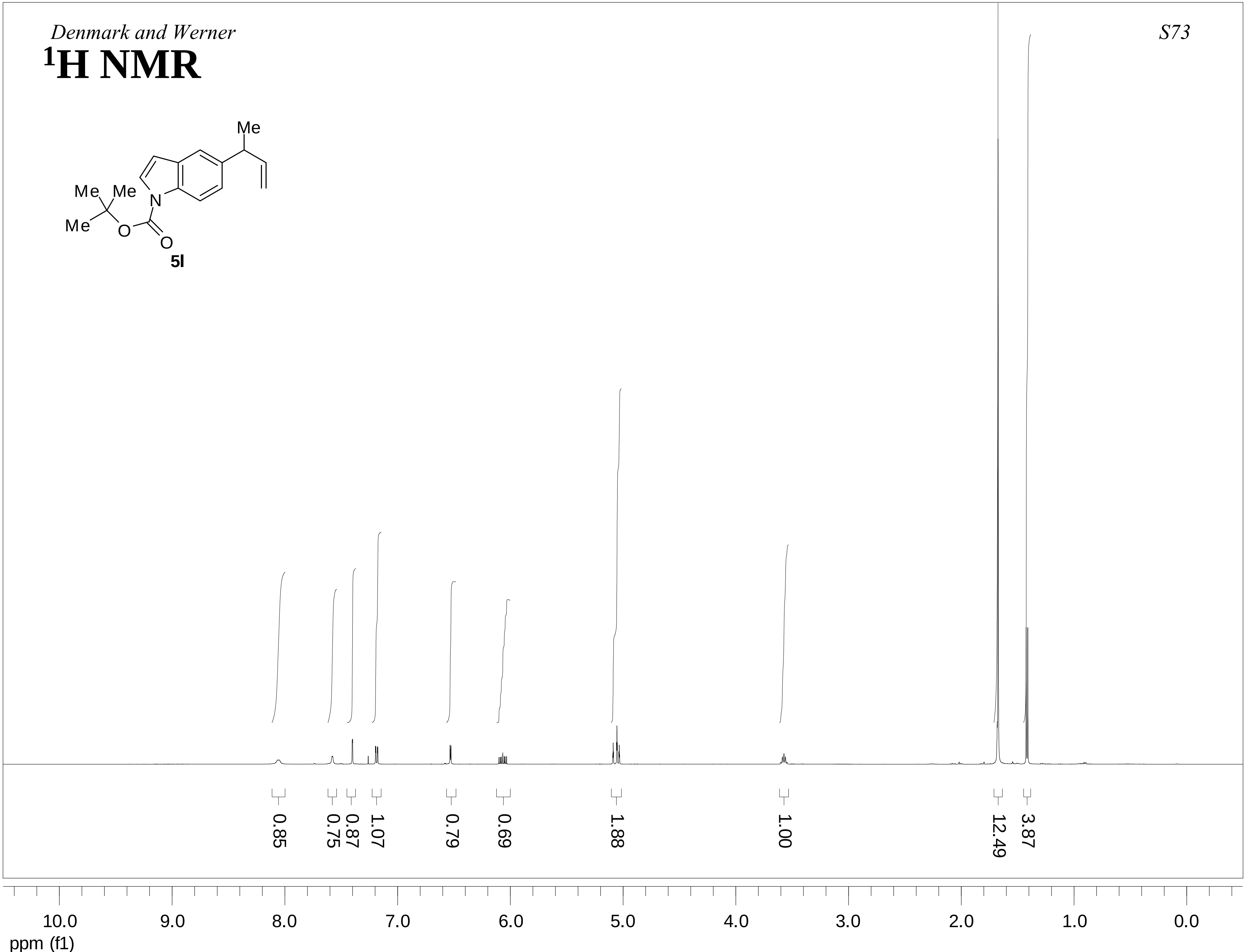
Me
Me
Me
Me
O
O
1.91
2.01
0.88
2.02
1.00
3.67
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

^{13}C NMR


149.6
142.2
127.6
125.4
125.3
125.3
125.3
114.0
43.0
20.6
20.5
Me
Me
O
Me
Me
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (f1)

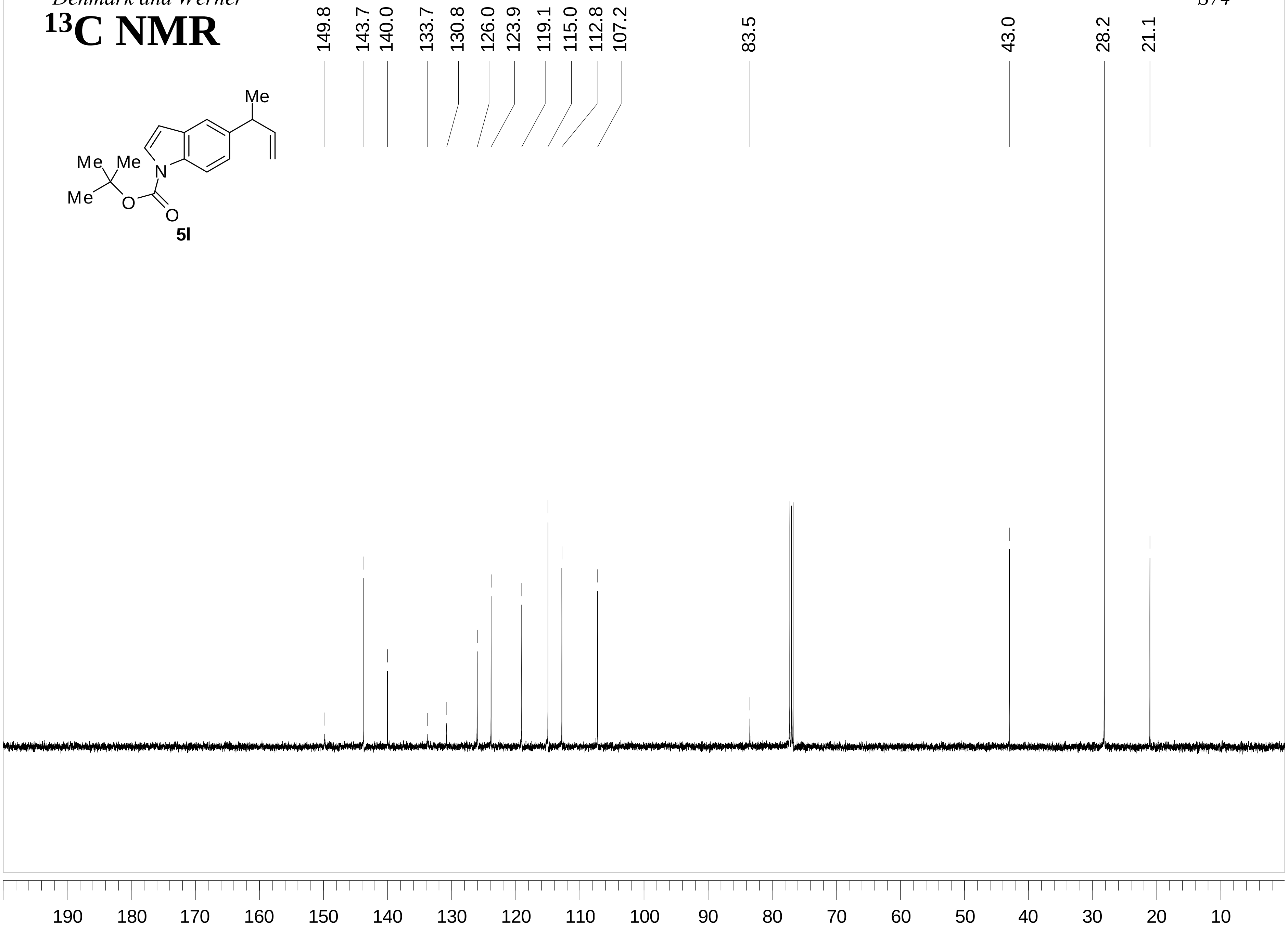
5k

^{1}H NMR

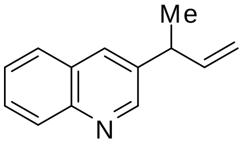

Me
Me
Me
Me
N
O
O
0.85
0.75
0.87
1.07
0.79
0.69
1.88
1.00
12.49
3.87
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

5l

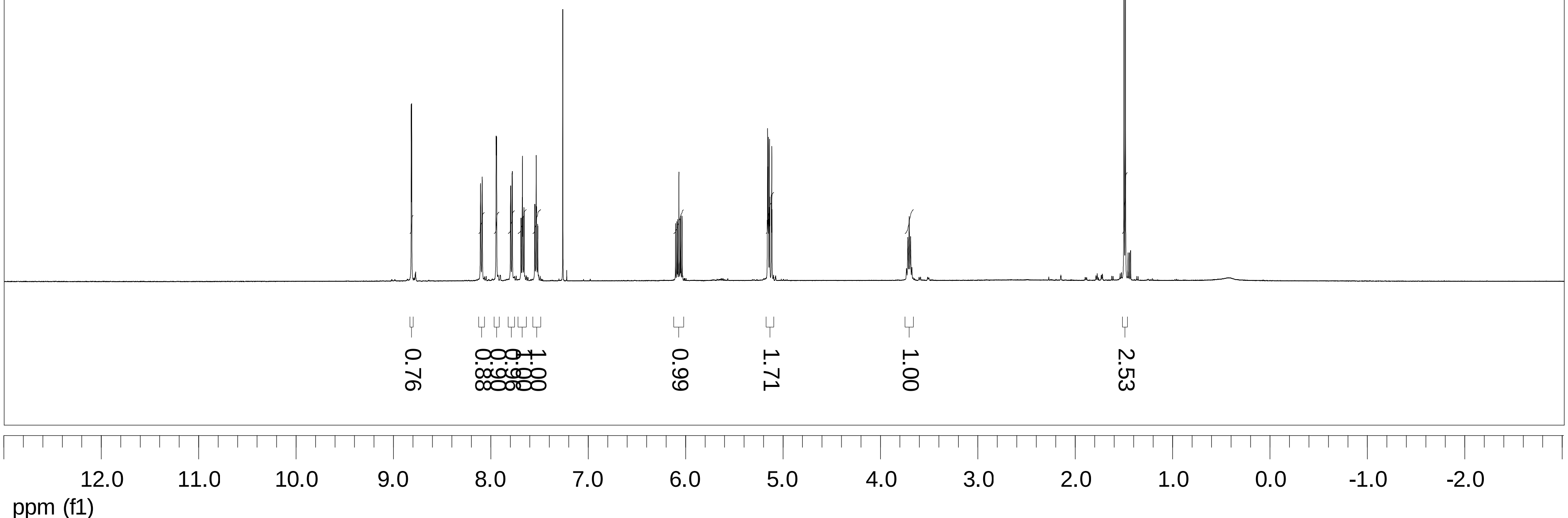
^{13}C NMR


Me
Me
Me
Me
N
O
O
5l
149.8
143.7
140.0
133.7
130.8
126.0
123.9
119.1
115.0
112.8
107.2
83.5
43.0
28.2
21.1
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (f1)

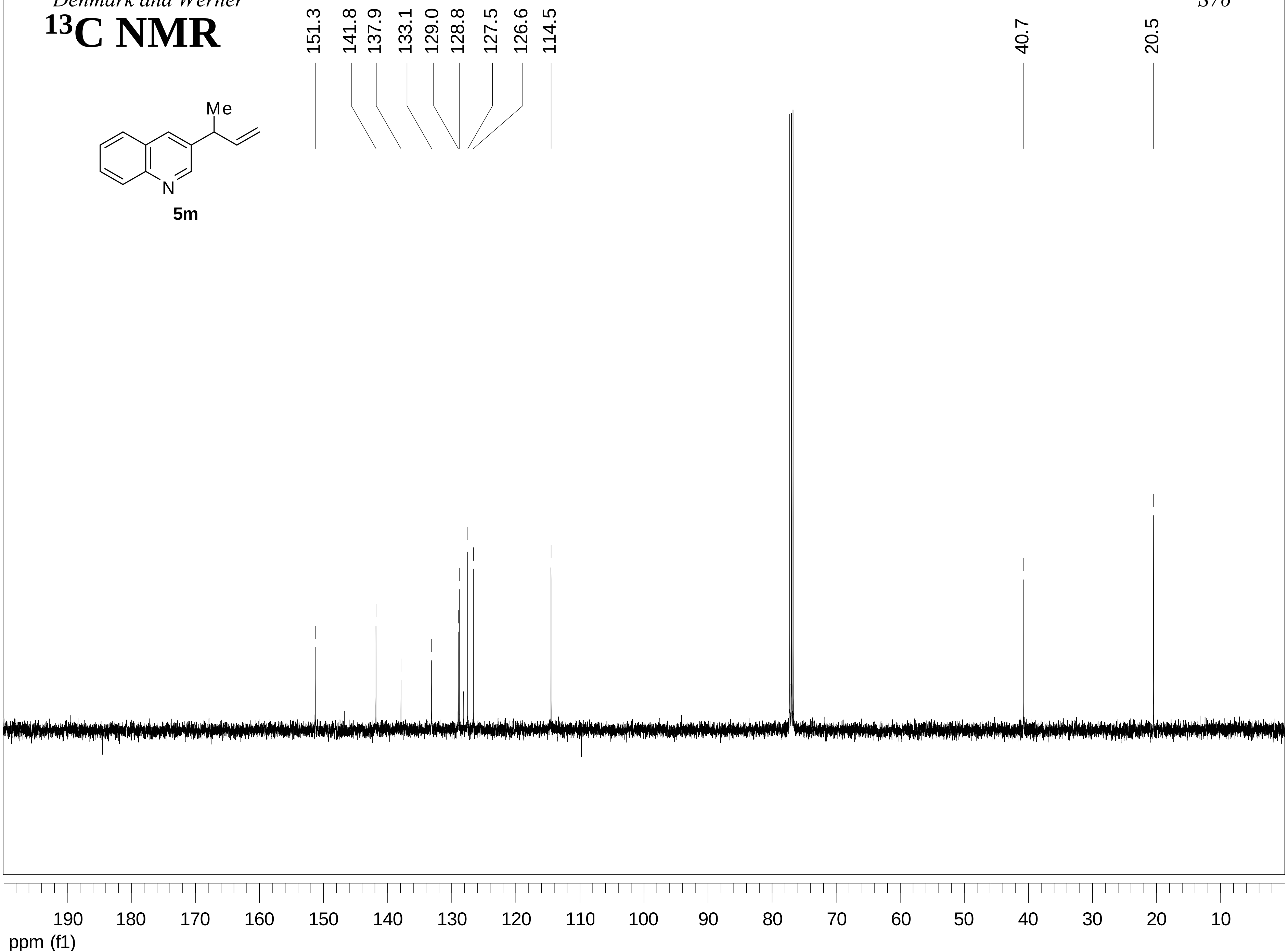
^{1}H NMR


Me
N

5m

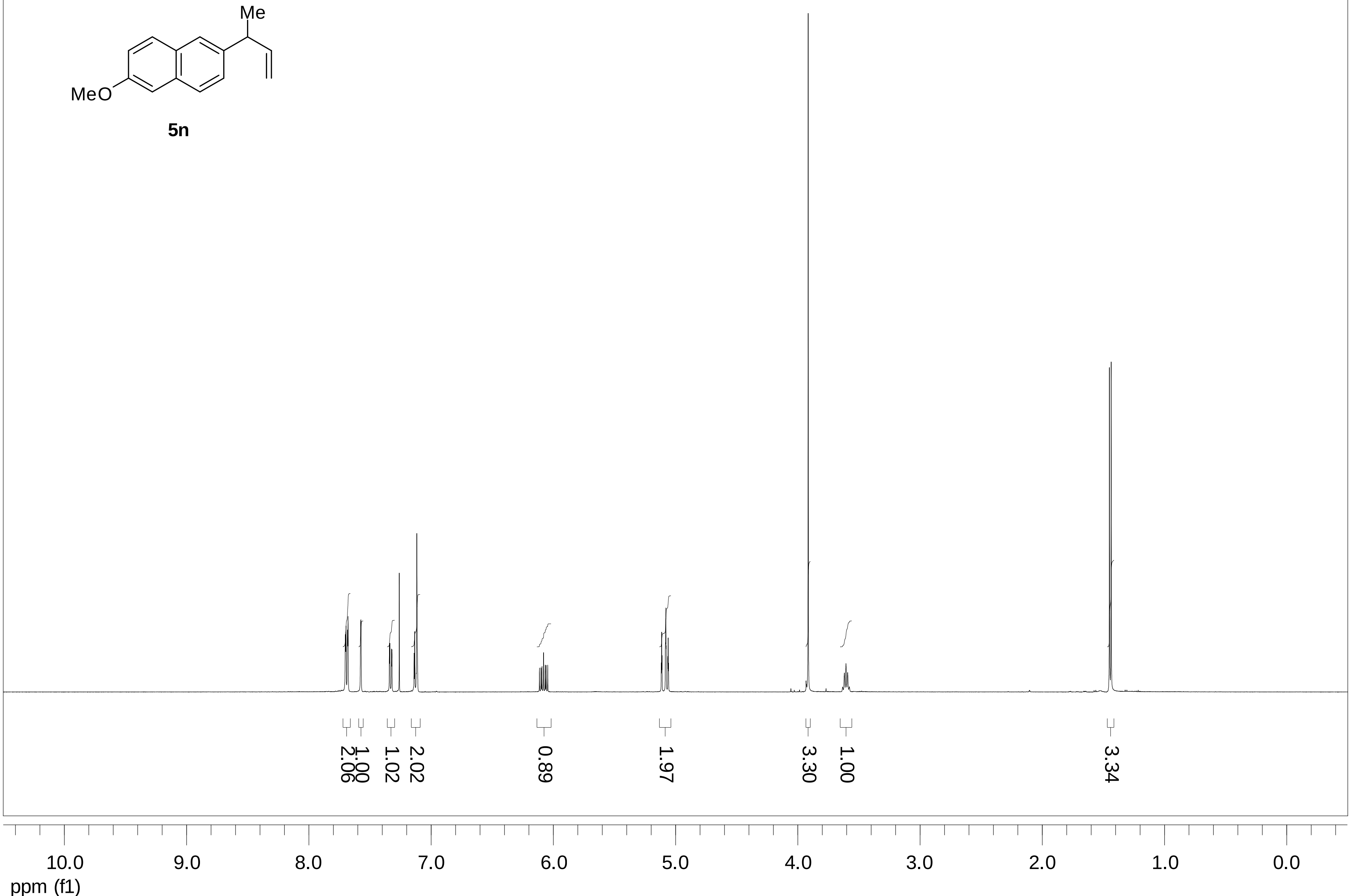

0.76
0.88
0.90
1.00
0.99
1.71
1.00
2.53
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
ppm (f1)

^{13}C NMR


151.3
141.8
137.9
133.1
129.0
128.8
127.5
126.6
114.5
40.7
20.5
Me
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (f1)

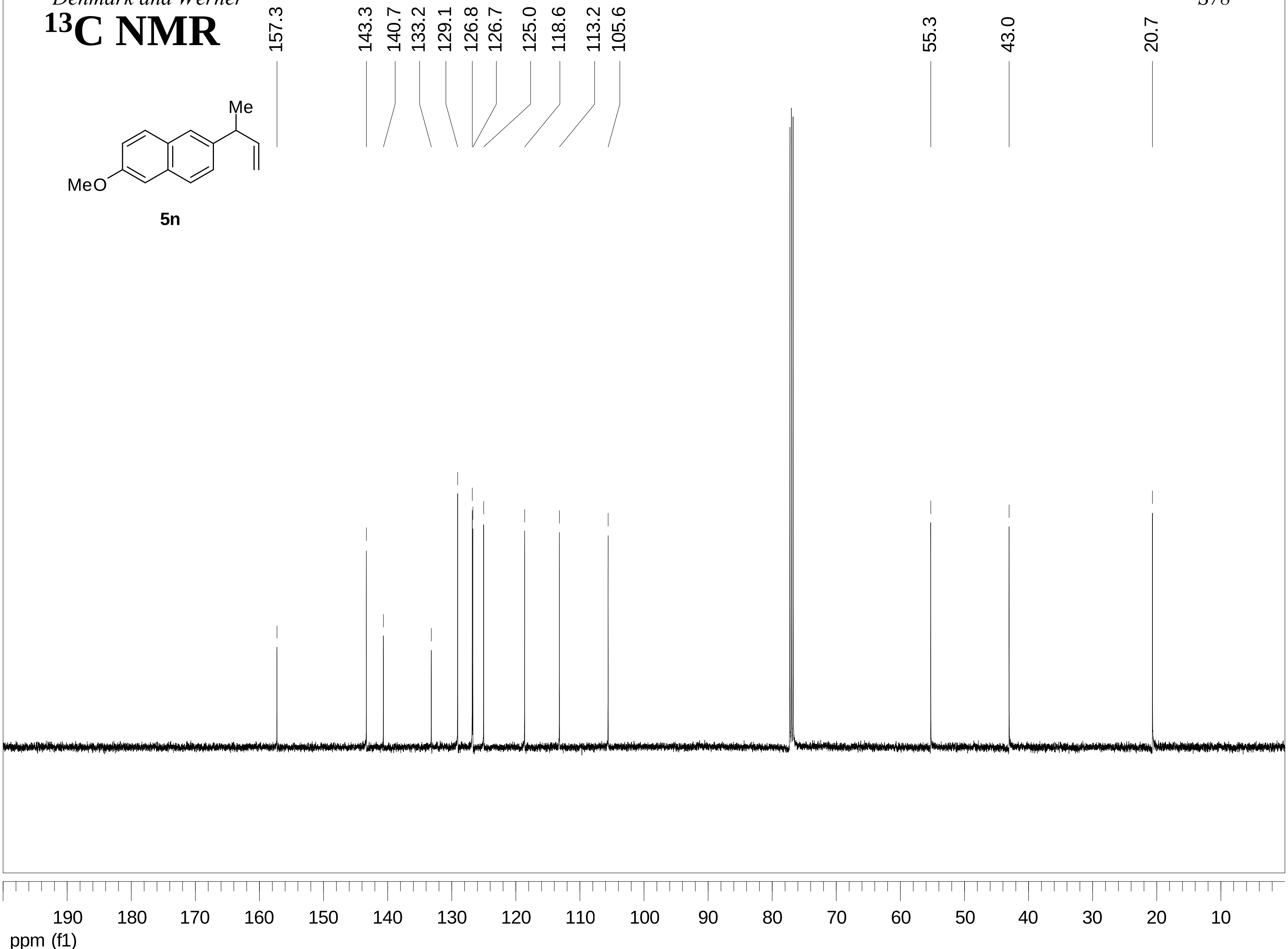
5m

^{1}H NMR


5n

Me
MeO
2.06
1.00
1.02
2.02
0.89
1.97
3.30
1.00
3.34
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

^{13}C NMR


157.3
143.3
140.7
133.2
129.1
126.8
126.7
125.0
118.6
113.2
105.6
55.3
43.0
20.7
Me
MeO
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (f1)

5n