Supporting Information

Iridium-Catalyzed Diborylation of Benzylic C-H Bonds Directed by a Hydrosilyl Group: Synthesis of 1,1-Benzyldiboronate Esters

Seung Hwan Cho and John F. Hartwig*

Department of Chemistry, University of California, Berkeley, California 94720, United States

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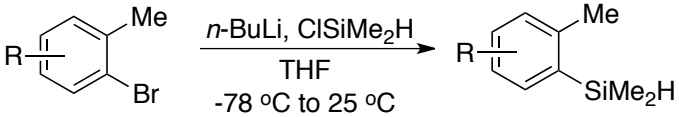
1. General experimental details

All borylation reactions were conducted under an atmosphere of argon in an Innovative Technologies glovebox. The THF used for the borylation reactions was degassed by purging with argon for 45 min and then dried with a solvent purification system comprising a 1 m column containing activated alumina. $[Ir(COD)OMe]_2$ was obtained from Johnson-Matthey and stored at -35 °C in the glovebox. 4,4'-Di-*tert*-butyl-2,2'-bipyridine (dtbpy) was purchased from Sigma-Aldrich and used as received. All reagents were purchased from commercial sources and used without further purification. Column chromatography was performed on Silicylce Siala-P silica gel. Borylation products were visualized on TLC plates by staining with potassium permanganate ($KMnO_4$). GC-MS data were obtained on an Agilent 6890-N GC system containing an Alltech EC-1 capillary column and an Agilent 5973 mass selective detector. NMR spectra were acquired on 400 MHz and 500 MHz Bruker instruments at the University of California, Berkeley NMR facility. Chemical shifts are reported in ppm relative to a residual solvent peak (CDCl3 = 7.26 ppm for ^1H and 77.16 ppm for ^{13}C). The resonances for the carbon atoms attached to boron were not observed due to the boron quadrupole. Mass spectrometric analyses were performed at the University of California, Berkeley Mass Spec Center.

2. General procedure of the preparation of starting materials



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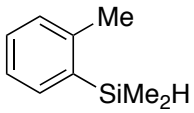
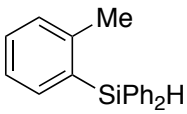
To a 50 mL round bottom flask containing a stirbar was added the 2-bromomethylbenzene derivative (5.00 mmol). The flask was sealed with a septum, and dry THF (15.0 mL) was added under N_2. The reaction mixture was cooled to –78 °C, at which time a solution of *n*-BuLi (4.69 mL, 7.50 mmol, 1.60 M in hexane) was added. The reaction was stirred for 30

minutes at -78 °C, and chlorodimethylsilane (710 mg, 7.50 mmol) was added in one portion at the same temperature. The reaction mixture was slowly warmed to room temperature and stirred for 24 h. The reaction was quenched with a saturated NH_4Cl solution (15.0 mL) and extracted with Et_2O (15.0 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to give 2-methylphenyl dimethylsilane derivatives (**1**).

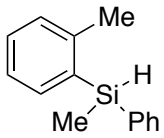


(*o*-Tolyl)dimethylsilane (1a): The reaction was performed according to the general procedure of the preparation of starting materials with 2-bromotoluene (856 mg, 5.00 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound **1a** as a colorless oil (677 mg, 90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.54 (m, 1H), 7.39 – 7.35 (m, 1H), 7.28 – 7.23 (m, 2H), 4.64 – 4.61 (m, 1H), 2.54 (s, 3H), 0.44 – 0.43 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.72, 136.15, 134.61, 129.56, 129.47, 125.08, 22.39, -3.52; HRMS (EI) calc'd for $C_9H_{14}Si$ (M^+) 150.0865, found 150.0869.

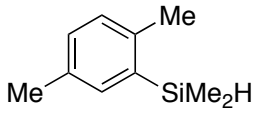


(*o*-Tolyl)diphenylsilane (1b): The reaction was performed according to the general procedure of the preparation of starting materials, except that chlorodiphenylsilane (1.20 g, 5.48 mmol) was used in place of chlorodimethylsilane, with 2-bromotoluene (856 mg, 5.00 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound **1b** as a colorless oil (1.09 g, 79%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.57 (m, 4H), 7.50 – 7.39 (m, 8H), 7.28 – 7.26 (d, J = 7.6 Hz, 1H), 7.23 – 7.19 (t, J = 7.3

Hz, 1H), 5.65 (s, 1H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.78, 136.97, 135.88, 133.30, 132.20, 130.26, 129.74, 129.70, 128.10, 125.15, 22.81; HRMS (EI) calc'd for $C_{19}H_{18}Si$ (M^+) 274.1178, found 274.1184.

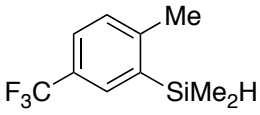


(*o*-Tolyl)methylphenylsilane (1c): The reaction was performed according to the general procedure of the preparation of starting materials, except that chloromethylphenylsilane (862 mg, 5.50 mmol) was used in place of chlorodimethylsilane, with 2-bromotoluene (856 mg, 5.00 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound **1c** as a colorless oil (882 mg, 83%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.57 (m, 2H), 7.55 – 7.53 (dd, J = 7.3, 1.6 Hz, 1H), 7.43 – 7.36 (m, 4H), 7.26 – 7.23 (m, 2H), 5.10 (m, 1H), 2.43 (s, 3H), 0.70 – 0.69 (d, J = 3.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.68, 136.17, 135.99, 135.22, 134.42, 130.40, 130.03, 129.83, 128.42, 125.55, 23.06, -4.37; HRMS (EI) calc'd for $C_{14}H_{16}Si$ (M^+) 212.1021, found 212.1025.

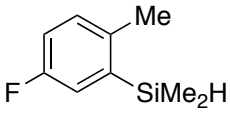


(2,5-Dimethylphenyl)dimethylsilane (1d): The reaction was performed according to the general procedure of the preparation of starting materials with 2-bromo-1,4-dimethylbenzene (926 mg, 5.00 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound **1d** as a colorless oil (780 mg, 95%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 1H), 7.21 – 7.16 (m, 2H), 4.65 – 4.61 (m, 1H), 2.52 (s, 3H), 2.42 (s, 3H), 0.47 – 0.46 (d, J = 3.8 Hz, 6H); ^{13}C NMR (101 MHz,

$CDCl_3$) δ 140.51, 135.90, 135.33, 134.22, 130.26, 129.46, 21.84, 21.05, -3.47; HRMS (EI) calc'd for $C_{10}H_{16}Si$ (M^+) 164.1021, found 164.1026.

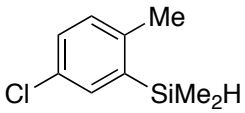


(2-Methyl-5-(trifluoromethyl)phenyl)dimethylsilane (1e): The reaction was performed according to the general procedure of the preparation of starting materials with 2-bromo-1-methyl-4-(trifluoromethyl)benzene (1.20 g, 5.02 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound **1e** as a colorless oil (887 mg, 81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.58 – 7.56 (d, J = 8.0 Hz, 1H), 7.32 – 7.30 (d, J = 8.0 Hz, 1H), 4.63 – 4.59 (m, 1H), 2.56 (s, 3H), 0.45 – 0.44 (d, J = 3.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.76, 137.36, 131.02 (q, $J_{C–F}$ = 3.6 Hz), 129.58, 126.19 (q, $J_{C–F}$ = 3.6 Hz), 127.4 (q, $J_{C–F}$ = 32.3 Hz), 124.58 (q, $J_{C–F}$ = 271 Hz), 22.33, -3.84; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.47; HRMS (EI) calc'd for $C_{10}H_{12}F_3Si$ ($[M–H]^+$) 217.0660, found 217.0664.

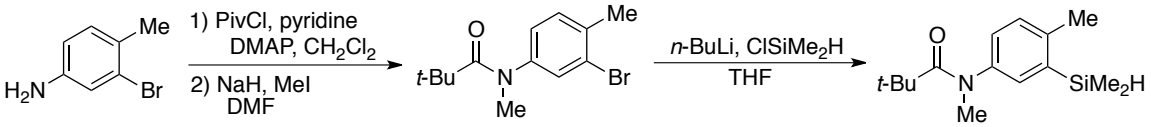


(5-Fluoro-2-methylphenyl)dimethylsilane (1f): The reaction was performed according to the general procedure of the preparation of starting materials with 2-bromo-4-fluoro-1-methylbenzene (945 mg, 5.00 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound **1f** as a colorless oil (588 mg, 70%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.12 (m, 2H), 6.99 – 6.94 (td, J = 8.5, 2.8 Hz, 1H), 4.55 – 4.51 (m, 1H), 2.44 (s, 3H), 0.39 – 0.38 (d, J = 3.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.78 (d, $J_{C–F}$ = 245 Hz), 138.93 (d, $J_{C–F}$ = 3.4 Hz), 138.62 (d, $J_{C–F}$ = 3.7 Hz), 130.88 (d, $J_{C–F}$ = 6.6 Hz), 120.66 (d, $J_{C–F}$ = 18.9 Hz), 116.00 (d, $J_{C–F}$ = 20.8 Hz),

21.37, -3.86; ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.12; HRMS (EI) calc'd for $C_9H_{13}FSi$ (M^+) 168.0771, found 168.0775.



(5-Chloro-2-methylphenyl)dimethylsilane (1g): The reaction was performed according to the general procedure of the preparation of starting materials, except that *tert*-BuLi (5.88 mL, 10.0 mmol, 1.70 M in pentane) was used in place of *n*-BuLi, with 2-bromo-4-chloro-1-methylbenzene (1.03 g, 5.01 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound **1g** as a colorless oil (730 mg, 79%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.26 – 7.24 (m, 1H), 7.11 – 7.09 (d, J = 8.1 Hz, 1H), 4.54 – 4.50 (m, 1H), 2.43 (s, 3H), 0.38 – 0.37 (d, J = 3.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.77, 138.64, 134.04, 131.18, 130.88, 129.23, 21.62, -3.83; HRMS (EI) calc'd for $C_9H_{13}{}^{35}ClSi$ (M^+) 184.0475, found 184.0475.



A **B** **1h**

***N*-(3-(Dimethylsilyl)-4-methylphenyl)-*N*-methylpivalamide (1h)**:

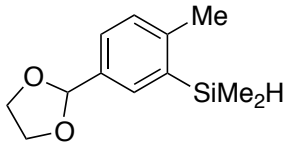
To a 100 mL round bottom flask containing a stirbar was added 3-bromo-4-methylaniline (930 mg, 5.00 mmol), DMAP (6.10 mg, 0.05 mmol), pyridine (1.01 g, 10.0 mmol) and dry CH_2Cl_2 (20.0 mL). The flask was sealed with a septum and cooled to 0 ^{o}C. To this mixture, pivaloyl chloride (724 mg, 6.00 mmol) was slowly added by syringe. The reaction mixture was warmed to room temperature and stirred for 3 h. The resulting mixture was quenched with a 1M HCl solution (10.0 mL) and extracted with CH_2Cl_2 (15.0 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give *N*-(3-bromo-4-methylphenyl)pivalamide **A**,

which was used without purification for the next step; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.79 (d, *J* = 2.1 Hz, 1H), 7.36 – 7.33 (m, 2H), 7.16 – 7.14 (d, *J* = 8.2 Hz, 1H), 2.34 (s, 3H), 1.30 (s, 9H).

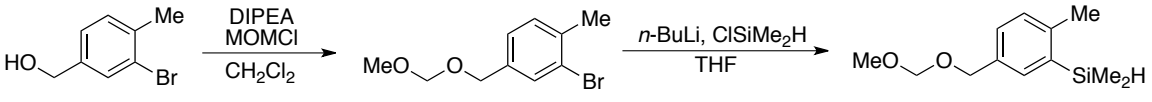
To a 50 mL round bottom flask containing a stirbar was added the above obtained *N*-(3-bromo-4-methylphenyl)pivalamide (**A**, ca. 5.00 mmol) and dry DMF (15.0 mL). The flask was cooled to 0 ^{o}C, and sodium hydride (300 mg, 7.50 mmol, 60% in mineral oil) was added in one portion. The flask was sealed with a septum and stirred for 30 min before the addition of MeI (1.42 g, 10.0 mmol) by syringe at 0 ^{o}C. The reaction mixture was warmed to room temperature and stirred for 4 h. The resulting mixture was quenched with a saturated NH_4Cl solution (10.0 mL) and extracted with EtOAc (15.0 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give *N*-(3-bromo-4-methylphenyl)-*N*-methylpivalamide (**B**), which was used without purification for the next step; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.41 (d, *J* = 2.2 Hz, 1H), 7.27 – 7.25 (d, *J* = 8.0 Hz, 1H), 7.09 – 7.07 (dd, *J* = 8.0, 2.2 Hz, 1H), 3.19 (s, 3H), 2.43 (s, 3H), 1.07 (s, 9H).

To a 50 mL round bottom flask containing a stirbar was added the above obtained *N*-(3-bromo-4-methylphenyl)-*N*-methylpivalamide (**B**, cat. 4.50 mmol). The flask was sealed with a septum, and dry THF (10.0 mL) was added under N_2. The reaction mixture was cooled to –78 ^{o}C, at which time a solution of *n*-BuLi (4.22 mL, 6.75 mmol, 1.6 M in hexane) was slowly added. The reaction was stirred for 30 minutes at -78 ^{o}C, and chlorodimethylsilane (640 mg, 6.76 mmol) was added in one portion at the same temperature. The reaction mixture was slowly warmed to room temperature and stirred for 24 h. The reaction was quenched with a saturated NH_4Cl solution (15.0 mL), and extracted with Et_2O (15.0 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude mixture was purified

by column chromatography on silica gel (hexanes:EtOAc, 85:15) to give compound **1h** as a light yellow oil (1.05 g, 80% over 3 steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.22 (d, J = 2.4 Hz, 1H), 7.15 – 7.13 (m, 1H), 7.09 – 7.07 (dd, J = 8.0, 2.4 Hz, 1H), 4.50 (m, 1H), 3.16 (s, 3H), 2.43 (s, 3H), 0.99 (s, 9H), 0.32 – 0.31 (d, J = 3.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.12, 143.16, 142.23, 137.45, 134.50, 130.23, 129.44, 41.32, 40.67, 29.45, 29.27, 26.33, 21.86, -3.80; HRMS (EI) calc'd for $C_{15}H_{25}NOSi$ (M^+) 263.1705, found 263.1710.



(5-(1,3-Dioxolan-2-yl)-2-methylphenyl)dimethylsilane (1i): 2-(3-Bromo-4-methylphenyl)-1,3-dioxolane was prepared by following a literature procedure.[1] The reaction was then performed according to the general procedure of the preparation of starting materials with 2-(3-bromo-4-methylphenyl)-1,3-dioxolane (1.22 g, 5.01 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 90:10) to give (5-(1,3-dioxolan-2-yl)-2-methylphenyl)dimethylsilane **1i** as a light yellow oil (990 mg, 89%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 2.0, 1H), 7.43 – 7.40 (dd, J = 7.8, 2.0 Hz, 1H), 7.22 – 7.20 (d, J = 7.8 Hz, 1H), 5.80 (s, 1H), 4.58 – 4.54 (m 1H), 4.18 – 4.16 (m, 2H), 4.09 – 4.03 (m, 2H), 2.48 (s, 3H), 0.39 – 0.38 (d, J = 3.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.85, 136.24, 134.20, 132.65, 129.43, 127.57, 103.91, 65.28, 22.15, -3.65; HRMS (EI) calc'd for $C_{12}H_{17}O_2Si$ ($[M–H]^+$) 221.0998, found 221.1004.



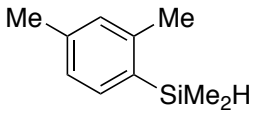
C **D** **1j**

(5-((Methoxymethoxy)methyl)-2-methylphenyl)dimethylsilane (1j):

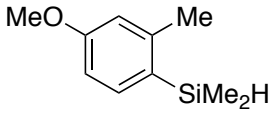
To a 50 mL round bottom flask containing a stirbar was added (3-bromo-4-methylphenyl)methanol (1.00 g, 5.00 mmol), *N*,*N*-diisopropylethylamine (1.42 g, 11.0 mmol) and dry CH_2Cl_2 (20.0 mL). The reaction mixture was cooled to 0 ^oC and chloromethyl methyl ether (641 mg, 7.50 mmol) was slowly added by syringe at 0 ^oC. The reaction mixture was warmed to room temperature and stirred for 12 h. The resulting mixture was quenched with a saturated NH_4Cl solution (10.0 mL) and extracted with CH_2Cl_2 (15.0 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 90:10) to give 2-bromo-4-((methoxymethoxy)methyl)-1-methylbenzene (**D**, 1.16 g, 95%).

To a 50 mL round bottom flask containing a stirbar was added the above obtained 2-bromo-4-((methoxymethoxy)methyl)-1-methylbenzene (**D**, 1.16 g, 4.75 mmol). The flask was sealed with a septum, and dry THF (10.0 mL) was added under N_2. The reaction mixture was cooled to –78 ^oC, at which time a solution of *n*-BuLi (4.45 mL, 7.13 mmol, 1.6 M in hexane) was slowly added. The reaction was stirred for 30 minutes at -78 ^oC, and chlorodimethylsilane (674 mg, 7.13 mmol) was added in one portion at the same temperature. The reaction mixture was slowly warmed to room temperature and stirred for 24 h. The reaction was quenched with a saturated NH_4Cl solution (15.0 mL), and extracted with Et_2O (15.0 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 90:10) to give compound **1j** as a light yellow oil (906 mg, 85%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.49 (d, J = 2.0 Hz, 1H), 7.34 – 7.32 (dd, J = 7.7, 2.0 Hz, 1H), 7.22 – 7.20 (d, J = 7.7 Hz, 1H), 4.75 (s, 2H), 4.61 (s, 2H), 4.60 – 4.56 (m, 1H), 3.47 (s, 3H), 2.50 (s, 3H), 0.42 – 0.41(d, J = 3.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.28, 136.33, 134.43, 134.24, 129.56, 129.38, 95.66,

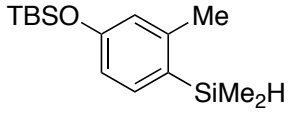
69.23, 55.35, 22.06, -3.56; HRMS (EI) calc'd for $C_{12}H_{20}O_2Si$ (M^+) 224.1233, found 224.1238.



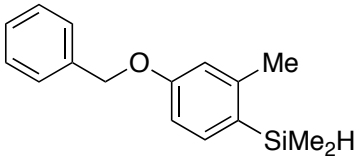
(2,4-Dimethylphenyl)dimethylsilane (1k): The reaction was performed according to the general procedure of the preparation of starting materials with 1-bromo-2,4-dimethylbenzene (926 mg, 5.00 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound **1k** as a colorless oil (764 mg, 93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.41 (d, J = 7.8 Hz, 1H), 7.07 – 7.05 (m, 2H), 4.59 – 4.55 (m, 1H), 2.48 (s, 3H), 2.37 (s, 3H), 0.41 – 0.40 (d, J = 3.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.67, 139.42, 134.70, 132.46, 130.44, 125.82, 22.23, 21.30, -3.46; HRMS (EI) calc'd for $C_{10}H_{16}Si$ (M^+) 164.1021, found 164.1025.



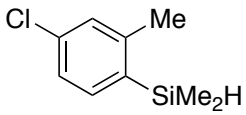
(4-Methoxy-2-methylphenyl)dimethylsilane (1l): The reaction was performed according to the general procedure of the preparation of starting materials, except that *tert*-BuLi (5.88 mL, 10.0 mmol, 1.70 M in pentane) was used in place of *n*-BuLi, with 1-bromo-4-methoxy-2-methylbenzene (1.00 g, 4.97 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound **1l** as a colorless oil (798 mg, 89%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.41 (d, J = 7.7 Hz, 1H), 6.78 – 6.76 (m, 2H), 4.55 – 4.52 (m, 1H), 3.83 (s, 3H), 2.47 (s, 3H), 0.38 – 0.37 (d, J = 3.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.76, 145.51, 136.02, 127.08, 115.53, 110.29, 54.95, 22.49, -3.35; HRMS (EI) calc'd for $C_{10}H_{16}OSi$ (M^+) 180.0970, found 180.0975.



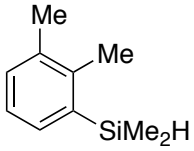
***tert*-Butyl(4-(dimethylsilyl)-3-methylphenoxy)dimethylsilane (1m)**: The reaction was performed according to the general procedure of the preparation of starting materials, except that *tert*-BuLi (5.88 mL, 10.0 mmol, 1.70 M in pentane) was used in place of *n*-BuLi, with 4-bromo-3-methylphenoxy-*tert*-butyl dimethylsilane (1.50 g, 5.00 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound **1m** as a colorless oil (1.23 g, 88%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.35 (d, J = 7.8 Hz, 1H), 6.72 – 6.69 (m, 2H), 4.55 – 4.52 (m, 1H), 2.44 (s, 3H), 1.04 (s, 9H), 0.38 – 0.37 (d, J = 3.8 Hz, 6H), 0.25 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.95, 145.47, 135.90, 127.71, 121.41, 116.56, 25.71, 22.35, 18.22, -3.32, -4.32; HRMS (EI) calc'd for $C_{15}H_{28}OSi_2$ (M^+) 280.1679, found 280.1683.



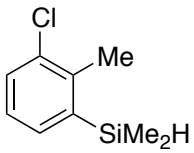
(4-(Benzyloxy)-2-methylphenyl)dimethylsilane (1n): The reaction was performed according to the general procedure of the preparation of starting materials, except that *tert*-BuLi (5.88 mL, 10.0 mmol, 1.70 M in pentane) was used in place of *n*-BuLi, with 1-bromo-4-(benzyloxy)-2-methylbenzene (1.38 g, 4.98 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound **1n** as a colorless oil (1.06 g, 83%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.38 (m, 6H), 6.89 – 6.84 (m, 2H), 5.11 (s, 2H), 4.57 – 4.54 (m, 1H), 2.49 (s, 3H), 0.40 – 0.39 (d, J = 3.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.07, 145.60, 137.08, 136.08, 128.61, 127.96, 127.49, 116.46, 111.16, 69.70, 22.54, -3.31; HRMS (EI) calc'd for $C_{16}H_{20}OSi$ (M^+) 256.1283, found 256.1283.



(4-Chloro-2-methylphenyl)dimethylsilane (1o): The reaction was performed according to the general procedure of the preparation of starting materials, except that *tert*-BuLi (5.88 mL, 10.0 mmol, 1.70 M in pentane) was used in place of *n*-BuLi, with 1-bromo-4-chloro-2-methylbenzene (1.03 g, 5.01 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound **1o** as a colorless oil (712 mg, 77%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.39 (dd, J = 7.4, 0.9 Hz, 1H), 7.19 – 7.17 (m, 2H), 4.53 (m, 1H), 2.46 (s, 3H), 0.38 – 0.37 (d, J = 3.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.53, 135.81, 135.51, 134.42, 129.37, 125.13, 22.11, -3.69; HRMS (EI) calc'd for $C_9H_{13}{}^{35}ClSi$ (M^+) 184.0475, found 184.0479.

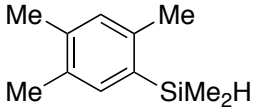


(2,3-Dimethylphenyl)dimethylsilane (1p): The reaction was performed according to the general procedure of the preparation of starting materials with 1-bromo-2,3-dimethylbenzene (926 mg, 5.00 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound **1p** as a colorless oil (748 mg, 91%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.40 (m, 1H), 7.35 – 7.33 (m, 1H), 7.29 – 7.25 (t, J = 7.4 Hz, 1H), 4.77 – 4.73 (m, 1H), 2.54 (s, 3H), 2.44 (s, 3H), 0.54 – 0.53 (d, J = 3.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.17, 136.36, 136.33, 132.57, 131.41, 125.39, 20.54, 19.44, -3.10; HRMS (EI) calc'd for $C_{10}H_{16}Si$ (M^+) 164.1021, found 164.1025.

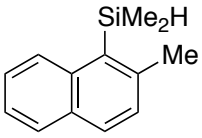


(3-Chloro-2-methylphenyl)dimethylsilane (1q): The reaction was performed according to the general procedure of the preparation of starting materials, except that *tert*-BuLi (5.88 mL, 10.0 mmol, 1.70 M in pentane) was used in place of *n*-BuLi, with 1-bromo-3-chloro-

2-methylbenzene (1.03 g, 5.01 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound **1q** as a colorless oil (767 mg, 83%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.37 (t, J = 7.4 Hz, 2H), 7.16 – 7.12 (t, J = 7.6 Hz, 1H), 4.57 (m, 1H), 2.52 (s, 3H), 0.40 – 0.39 (d, J = 3.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.86, 138.90, 134.91, 132.89, 130.36, 126.51, 19.71, -3.46; HRMS (EI) calc'd for $C_9H_{13}ClSi$ (M^+) 184.0475, found 184.0471.



(2,4,5-Trimethylphenyl)dimethylsilane (1r): The reaction was performed according to the general procedure of the preparation of starting materials with 1-bromo-2,4,5-trimethylbenzene (996 mg, 5.00 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound **1r** as a colorless oil (856 mg, 96%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 1H), 7.07 (s, 1H), 4.63 – 4.59 (m, 1H), 2.50 (s, 3H), 2.34 (s, 6H), 0.46 – 0.45 (d, J = 3.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.09, 138.01, 136.03, 132.99, 132.91, 131.07, 21.71, 19.63, 19.17, -3.38. HRMS (EI) calc'd for $C_{11}H_{18}Si$ (M^+) 178.1178, found 178.1178.

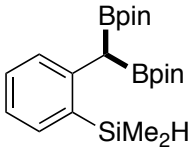


(2-Methylnaphthalen-1-yl)dimethylsilane (1s): The reaction was performed according to the general procedure of the preparation of starting materials with 1-bromo-2-methylnaphthalene (1.10 g, 4.97 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound **1s** a colorless oil (887 mg, 89%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 – 8.25 (d, J = 8.0 Hz, 1H), 7.84 – 7.82 (d, J = 8.0 Hz, 1H), 7.80 – 7.78 (d, J = 8.0 Hz, 1H), 7.52 – 7.50 (m, 1H), 7.48 – 7.42 (m, 1H), 7.33 – 7.31 (d, J = 8.0 Hz, 1H), 5.12 – 5.08 (m, 1H), 2.71 (s, 3H), 0.57 – 0.56 (d, J = 4.1 Hz,

6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.19, 137.55, 132.28, 131.71, 129.72, 129.19, 128.81, 127.49, 125.63, 124.42, 24.31, -2.03; HRMS (EI) calc'd for $C_{13}H_{16}Si$ (M^+) 200.1021, found 200.1023.

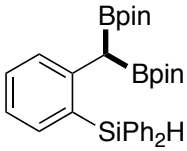
3. General procedure for the diborylation of benzylic C-H bonds

In a nitrogen-filled glovebox, the (2-methylphenyl)dimethylsilane derivative **1** (0.500 mmol) and B_2pin_2 (1.00 mmol) were added to a 4-mL vial with a stir bar. To this vial, freshly prepared stock solutions of $[Ir(COD)OMe]_2$ (2.50 μmol, 0.500 mol %) in THF (1.00 mL), and 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.00 μmol, 1.00 mol %) in THF (1.00 mL) were added. The vial was sealed with a Teflon-lined screw cap and then removed from the glovebox. The vial was placed in a pre-heated aluminum block at 50 °C and stirred for the indicated period of time. The reaction progress was monitored by GC analysis. After full conversion of the reactant, the solution was filtered through a pad of Celite and concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel to give pure 1,1-benzyldiboronate ester products **3**.

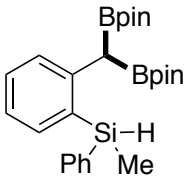


1,1-Benzyldiboronate ester 3a: The reaction was performed according to the general procedure for the diborylation of benzylic C-H bonds with **1a** (75.2 mg, 0.500 mmol), B_2pin_2 (254 mg, 1.00 mmol), $[Ir(COD)OMe]_2$ (2.50 μmol, 0.500 mol %) in THF (1.00 mL), and 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.00 μmol, 1.00 mol %) in THF (1.00 mL) at 50 °C for 4 h. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound **3a** as a white solid (175 mg, 87%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.47 (dd, J = 8.1, 1.3 Hz, 1H), 7.46 – 7.44 (dd, J = 7.3, 1.5 Hz, 1H), 7.35 – 7.31 (td, J = 7.6, 1.6 Hz, 1H), 7.15 – 7.13 (td, J = 7.3, 1.2 Hz, 1H), 4.59 – 4.55 (dt, J = 7.5, 3.8 Hz, 1H), 2.60 (s, 1H), 1.27 (s, 12H), 1.25 (s, 12H), 0.38 – 0.37

(d, J = 3.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.61, 135.35, 134.28, 129.38, 129.05, 123.64, 83.34, 24.65, 24.60, -3.19; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.80; HRMS (EI) calc'd for $C_{21}H_{36}{}^{11}B_2O_4Si$ (M^+) 402.2569, found 402.2578.

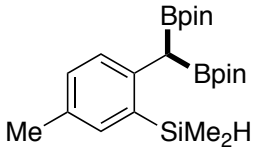


1,1-Benzyldiboronate ester 3b: The reaction was performed according to the general procedure for the diborylation of benzylic C-H bonds with **1b** (137 mg, 0.500 mmol), B_2pin_2 (254 mg, 1.00 mmol), and $[Ir(COD)OMe]_2$ (2.50 μmol, 0.500 mol %) in THF (1.00 mL), and 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.00 μmol, 1.00 mol %) in THF (1.00 mL) at 50 °C for 4 h. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound **3b** as a white solid (203 mg, 77%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.56 (m, 5H), 7.46 – 7.35 (m, 8H), 7.16 – 7.12 (dd, J = 7.9, 6.7 Hz, 1H), 5.69 (s, 1H), 2.72 (s, 1H), 1.21 (s, 24H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.06, 136.84, 136.11, 133.90, 131.21, 130.10, 129.81, 129.43, 127.93, 123.80, 83.35, 24.70, 24.62; ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.30; HRMS (EI) calc'd for $C_{31}H_{40}{}^{11}B_2O_4Si$ (M^+) 526.2882, found 526.2891.



1,1-Benzyldiboronate ester 3c: The reaction was performed according to the general procedure for the diborylation of benzylic C-H bonds with **1c** (106 mg, 0.500 mmol), B_2pin_2 (254 mg, 1.00 mmol), and $[Ir(COD)OMe]_2$ (2.50 μmol, 0.500 mol %) in THF (1.00 mL), and 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.00 μmol, 1.00 mol %) in THF (1.00 mL) at 50 °C for 4 h. The crude mixture was purified by column chromatography on silica gel

(hexanes:EtOAc, 100:0 to 95:5) to give compound **3c** as a white solid (197 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.54 (dd, *J* = 6.9, 2.8 Hz, 2H), 7.49 – 7.47 (d, *J* = 7.9 Hz, 1H), 7.43 – 7.42 (d, *J* = 7.4 Hz, 1H), 7.36 – 7.32 (m, 4H), 7.14 – 7.10 (t, *J* = 7.3 Hz, 1H), 5.09 – 5.06 (m, 1H), 2.60 (s, 1H), 1.20 (s, 12H), 1.18 (s, 12H), 0.65 – 0.64 (d, *J* = 3.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.32, 136.00, 135.62, 134.98, 133.10, 129.81, 129.46, 129.02, 127.77, 123.73, 83.32, 24.63, 24.61, 24.57, -4.34; ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.80; HRMS (EI) calc'd for $C_{26}H_{38}{}^{11}B_2O_4Si$ (M^+) 464.2725, found 464.2734.

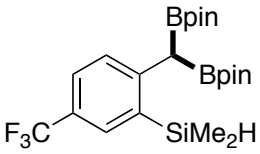


1,1-Benzyldiboronate ester 3d: The reaction was performed according to the general procedure for the diborylation of benzylic C-H bonds with **1d** (82.2 mg, 0.500 mmol), B_2pin_2 (254 mg, 1.00 mmol), and $[Ir(COD)OMe]_2$ (2.50 μmol, 0.500 mol %) in THF (1.00 mL), and 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.00 μmol, 1.00 mol %) in THF (1.00 mL) at 50 ^{o}C for 2 h. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound **3d** as a white solid (200 mg, 96%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.38 (d, *J* = 7.9 Hz, 1H), 7.27 (s, 1H), 7.18 – 7.16 (dd, *J* = 8.0, 2.1 Hz, 1H), 4.59 – 4.54 (m, 1H), 2.59 (s, 1H), 2.35 (s, 3H), 1.29 (s, 12H), 1.27 (s, 12H), 0.40 – 0.39 (d, *J* = 3.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.42, 135.15, 132.53, 130.05, 129.34, 83.35, 24.72, 24.70, 21.11, -3.04; ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.62; HRMS (EI) calc'd for $C_{22}H_{38}{}^{11}B_2O_4Si$ (M^+) 416.2725, found 416.2733.

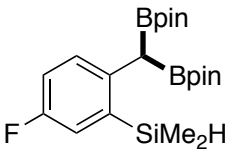
Scale up Reaction of 1d:

The reaction was performed according to the general procedure for the diborylation of benzylic C-H bonds with **1d** (822 mg, 5.00 mmol), B_2pin_2 (2.54 g, 10.0 mmol), and $[Ir(COD)OMe]_2$ (2.50 μmol, 0.500 mol %) in THF (10.0 mL), and 4,4'-di-*tert*-butyl-2,2'-

bipyridine (5.00 μmol, 1.00 mol %) in THF (100 mL) at 50 °C for 12 h. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound **3d** as a white solid (1.93 g, 93%), which gave spectral data identical to that obtained previously.

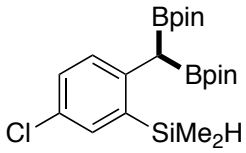


1,1-Benzyldiboronate ester 3e: The reaction was performed according to the general procedure for the diborylation of benzylic C-H bonds with **1e** (109 mg, 0.500 mmol), B_2pin_2 (254 mg, 1.00 mmol), and $[Ir(COD)OMe]_2$ (2.50 μmol, 0.500 mol %) in THF (1.00 mL), and 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.00 μmol, 1.00 mol %) in THF (1.00 mL) at 50 °C for 12 h. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound **3e** as a white solid (219 mg, 93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.55 – 7.50 (m, 2H), 4.56 – 4.52 (m, 1H), 2.64 (s, 1H), 1.24 (s, 12H), 1.26 (s, 12H), 0.38 – 0.37 (d, J = 3.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.17, 136.25, 130.89 (q, $J_{C–F}$ = 3.6 Hz), 129.60, 125.79 (q, $J_{C–F}$ = 3.6 Hz), 125.69 (q, $J_{C–F}$ = 24.2 Hz), 124.92 (q, $J_{C–F}$ = 272 Hz), 83.68, 24.65, 24.62, -3.41; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.15; ^{11}B NMR δ 32.4. HRMS (EI) calc'd for $C_{22}H_{34}{}^{11}B_2F_3O_4Si$ ($[M–H]^+$) 469.2365, found 469.2374.

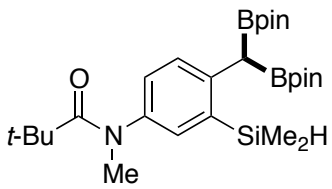


1,1-Benzyldiboronate ester 3f: The reaction was performed according to the general procedure for the diborylation of benzylic C-H bonds with **1f** (84.1 mg, 0.500 mmol), B_2pin_2 (254 mg, 1.00 mmol), and $[Ir(COD)OMe]_2$ (2.50 μmol, 0.500 mol %) in THF (1.00 mL), and 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.00 μmol, 1.00 mol %) in THF (1.00 mL) at

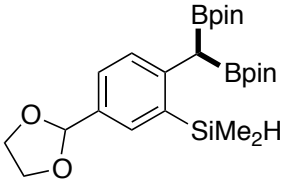
50 °C for 12 h. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound **3f** as a white solid (162 mg, 77%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.39 (dd, J = 8.6, 5.3 Hz, 1H), 7.09 – 7.06 (dd, J = 9.1, 2.9 Hz, 1H), 7.00 – 6.95 (td, J = 8.6, 2.9 Hz, 1H), 4.53 – 4.49 (m, 1H), 2.53 (s, 1H), 1.24 (s, 12H), 1.22 (s, 12H), 0.35 – 0.34 (d, J = 3.7 Hz, 6H);^{13}C NMR (101 MHz, $CDCl_3$) δ 160.01 (d, J_{C-F} = 244 Hz), 140.90 (d, J_{C-F} = 3.0 Hz), 137.63 (d, J_{C-F} = 3.3 Hz), 130.84 (d, J_{C-F} = 6.4 Hz), 120.20 (d, J_{C-F} = 18.4 Hz), 115.80 (d, J_{C-F} = 20.8 Hz), 83.43, 24.63, 24.58, -3.44; ^{11}B NMR δ 32.5; HRMS (EI) calc'd for $C_{21}H_{35}{}^{11}B_2FO_4Si$ (M^+) 420.2475, found 420.2484.



1,1-Benzyldiboronate ester 3g: The reaction was performed according to the general procedure for the diborylation of benzylic C-H bonds with **1g** (92.4 mg, 0.500 mmol), B_2pin_2 (254 mg, 1.00 mmol), and $[Ir(COD)OMe]_2$ (2.50 μmol, 0.500 mol %) in THF (1.00 mL), and 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.00 μmol, 1.00 mol %) in THF (1.00 mL) at 50 °C for 12 h. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound **3g** as a white solid (190 mg, 87%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.40 (dd, J = 8.4, 1.8 Hz, 1H), 7.37 – 7.35 (t, J = 2.2 Hz, 1H), 7.30 – 7.26 (m, 1H), 4.55 – 4.52 (m, 1H), 2.56 (s, 1H), 1.27 (s, 12H), 1.25 (s, 12H), 0.38 – 0.37 (d, J = 3.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.03, 137.91, 133.81, 131.00, 129.82, 129.05, 83.55, 24.68, 24.62, -3.37; ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.69; HRMS (EI) calc'd for $C_{21}H_{35}{}^{11}B_2{}^{35}ClO_4Si$ (M^+) 436.2179, found 436.2180.

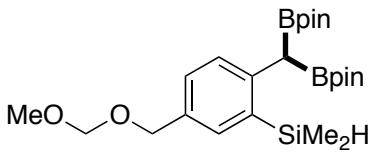


1,1-Benzyldiboronate ester 3h: The reaction was performed according to the general procedure for the diborylation of benzylic C-H bonds with **1h** (132 mg, 0.500 mmol), B_2pin_2 (254 mg, 1.00 mmol), and $[Ir(COD)OMe]_2$ (2.50 μmol, 0.500 mol %) in THF (1.00 mL), and 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.00 μmol, 1.00 mol %) in THF (1.00 mL) at 50 °C for 4 h. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 85:15) to give compound **3h** as a white solid (245 mg, 95%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.47 (d, J = 8.2 Hz, 1H), 7.20 – 7.10 (d, J = 2.5 Hz, 1H), 7.13 – 7.10 (dd, J = 8.2, 2.5 Hz, 1H), 4.58 – 4.52 (m, 1H), 3.24 (s, 3H), 2.62 (s, 1H), 1.29 (s, 3H), 1.25 (s, 12H), 1.22 (s, 12H), 1.01 (s, 9H), 0.35 – 0.34 (d, J = 3.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.39, 145.57, 140.66, 136.57, 134.12, 130.12, 129.15, 83.49, 41.12, 40.73, 29.48, 25.04, 24.71, 24.51, -3.32; ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.57; HRMS (EI) calc'd for $C_{27}H_{47}{}^{11}B_2NO_5Si$ (M^+) 515.3410, found 515.3421.

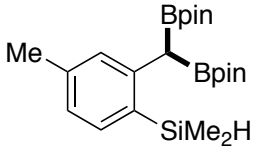


1,1-Benzyldiboronate ester 3i: The reaction was performed according to the general procedure for the diborylation of benzylic C-H bonds with **1i** (111 mg, 0.500 mmol), B_2pin_2 (254 mg, 1.00 mmol), and $[Ir(COD)OMe]_2$ (2.50 μmol, 0.500 mol %) in THF (1.00 mL), and 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.00 μmol, 1.00 mol %) in THF (1.00 mL) at 50 °C for 6 h. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 85:15) to give compound **3i** as a white solid (171 mg, 72%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.48 – 7.46 (d, J = 10.0 Hz, 1H), 7.42 – 7.40 (d, J = 10.0 Hz, 1H), 5.76 (s, 1H), 4.55 – 4.52 (m, 1H), 4.18 – 4.13 (m, 2H), 4.07 – 4.02 (m, 2H), 2.58 (s, 1H), 1.23 (s, 12H), 1.21 (s, 12H), 0.36 – 0.35 (d, J = 3.7 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.06, 135.39, 132.55, 132.32, 129.56, 127.28, 104.37, 83.50, 83.39,

65.31, 24.68, 24.63, -3.20; ^{11}B NMR δ 32.64. HRMS (EI) calc'd for $C_{24}H_{39}{}^{11}B_2O_6Si$ (M^+) 473.2702, found 473.2713.

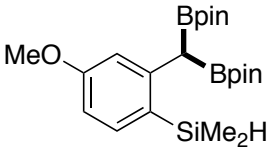


1,1-Benzyldiboronate ester 3j: The reaction was performed according to the general procedure for the diborylation of benzylic C-H bonds with **1j** (112 mg, 0.500 mmol), B_2pin_2 (254 mg, 1.00 mmol), and $[Ir(COD)OMe]_2$ (2.50 μmol, 0.500 mol %) in THF (1.00 mL), and 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.00 μmol, 1.00 mol %) in THF (1.00 mL) at 50 °C for 6 h. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 90:10) to give compound **3j** as a white solid (205 mg, 86%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.31 (d, J = 7.5 Hz, 1H), 7.26 (s, 1H), 6.95 – 6.93 (d, J = 7.4 Hz, 1H), 4.55 – 4.52 (m, 1H), 2.55 (s, 1H), 2.35 (s, 3H), 1.26 (s, 12H), 1.24 (s, 12H), 0.35 – 0.34 (d, J = 3.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.39, 135.49, 134.40, 132.44, 129.57, 129.26, 95.80, 83.39, 69.71, 55.28, 24.68, 24.65, -3.16; ^{11}B NMR δ 32.8; HRMS (EI) calc'd for $C_{24}H_{42}{}^{11}B_2O_6Si$ (M^+) 476.2937, found 476.2943.

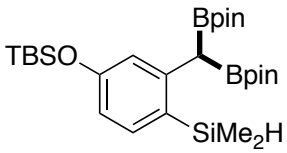


1,1-Benzyldiboronate ester 3k: The reaction was performed according to the general procedure for the diborylation of benzylic C-H bonds with **1k** (82.2 mg, 0.500 mmol), B_2pin_2 (254 mg, 1.00 mmol), and $[Ir(COD)OMe]_2$ (2.50 μmol, 0.500 mol %) in THF (1.00 mL), and 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.00 μmol, 1.00 mol %) in THF (1.00 mL) at 50 °C for 6 h. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound **3k** as a white solid (175 mg, 84%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.31 (d, J = 7.5 Hz, 1H), 7.26 (s, 1H), 6.95 – 6.93 (d, J =

7.4 Hz, 1H), 4.55 – 4.52 (m, 1H), 2.55 (s, 1H), 2.35 (s, 3H), 1.26 (s, 12H), 1.24 (s, 12H), 0.35 – 0.34 (d, J = 3.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.51, 138.61, 134.36, 132.02, 130.18, 124.75, 83.30, 24.72, 24.58, 21.58, -3.00; ^{11}B NMR δ 31.61; HRMS (EI) calc'd for $C_{22}H_{37}{}^{11}B_2O_4Si$ ($[M–H]^+$) 416.2647, found 416.2656.

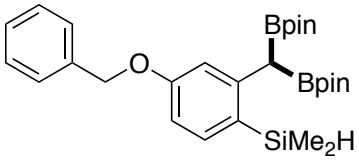


1,1-Benzyldiboronate ester 3l: The reaction was performed according to the general procedure for the diborylation of benzylic C-H bonds with **1l** (90.2 mg, 0.500 mmol), B_2pin_2 (254 mg, 1.00 mmol), and $[Ir(COD)OMe]_2$ (2.50 μmol, 0.500 mol %) in THF (1.00 mL), and 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.00 μmol, 1.00 mol %) in THF (1.00 mL) at 50 °C for 6 h. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 90:10) to give compound **3l** as a white solid (190 mg, 88%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.36 (d, J = 8.2 Hz, 1H), 7.12 – 7.1 (d, J = 2.5 Hz, 1H), 6.73 – 6.70 (dd, J = 8.2, 2.5 Hz, 1H), 4.57 – 4.53 (m, 1H), 3.85 (s, 3H), 2.60 (s, 1H), 1.28 (s, 12H), 1.27 (s, 12H), 0.37 – 0.36 (d, J = 3.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.40, 147.55, 135.57, 126.74, 115.62, 109.43, 83.40, 54.89, 24.73, 24.69, -2.91; ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.21; HRMS (EI) calc'd for $C_{22}H_{38}{}^{11}B_2O_5Si$ (M^+) 432.2675, found 432.2683.

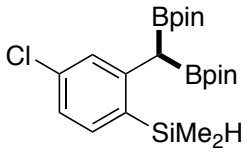


1,1-Benzyldiboronate ester 3m: The reaction was performed according to the general procedure for the diborylation of benzylic C-H bonds with **1m** (140 mg, 0.500 mmol), B_2pin_2 (254 mg, 1.00 mmol), and $[Ir(COD)OMe]_2$ (2.50 μmol, 0.500 mol %) in THF (1.00 mL), and 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.00 μmol, 1.00 mol %) in THF (1.00 mL) at

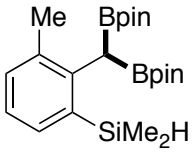
50 °C for 6 h. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 90:10) to give compound **3m** as a white solid (234 mg, 88%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.29 (d, *J* = 8.0 Hz, 1H), 7.09 – 7.08 (d, *J* = 2.4 Hz, 1H), 6.67 – 6.4 (dd, *J* = 8.0, 2.4 Hz, 1H), 4.56 – 4.52 (m, 1H), 2.60 (s, 1H), 1.29 (s, 12H), 1.26 (s, 12H), 1.07 (s, 9H), 0.38 – 0.37 (d, *J* = 3.7 Hz, 6H), 0.25 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.56, 147.23, 135.45, 126.77, 121.24, 115.84, 83.35, 25.89, 24.79, 24.64, 18.30, -2.96, -4.30; ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.30; HRMS (EI) calc'd for $C_{27}H_{50}{}^{11}B_2O_5Si_2$ (M^+) 532.3383, found 532.3371.



1,1-Benzyldiboronate ester 3n: The reaction was performed according to the general procedure for the diborylation of benzylic C-H bonds with **1n** (128 mg, 0.500 mmol), B_2pin_2 (254 mg, 1.00 mmol), and $[Ir(COD)OMe]_2$ (2.50 μmol, 0.500 mol %) in THF (1.00 mL), and 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.00 μmol, 1.00 mol %) in THF (1.00 mL) at 50 °C for 6 h. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 90:10) to give compound **3n** as a white solid (203 mg, 80%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.50 (d, *J* = 7.5 Hz, 2H), 7.44 – 7.41 (t, *J* = 7.6 Hz, 2H), 7.37 – 7.35 (m, 2H), 7.19 – 7.18 (d, *J* = 2.5 Hz, 1H), 6.79 – 6.77 (dd, *J* = 8.1, 2.5 Hz, 1H), 5.12 (s, 2H), 4.56 – 4.53 (m, 1H), 2.60 (s, 1H), 1.26 (s, 12H), 1.25 (s, 12H), 0.36 – 0.35 (d, *J* = 3.7 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.77, 147.60, 137.58, 135.58, 128.52, 127.80, 127.62, 127.06, 116.16, 110.65, 83.40, 69.64, 24.74, 24.69, -2.91; ^{11}B NMR (160 MHz, $CDCl_3$) δ 32.54; HRMS (EI) calc'd for $C_{28}H_{42}{}^{11}B_2O_5Si$ (M^+) 508.2988, found 508.2996.

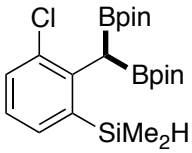


1,1-Benzyldiboronate ester 3o: The reaction was performed according to the general procedure for the diborylation of benzylic C-H bonds with **1o** (92.4 mg, 0.500 mmol), B_2pin_2 (254 mg, 1.00 mmol), and $[Ir(COD)OMe]_2$ (2.50 μmol, 0.500 mol %) in THF (1.00 mL), and 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.00 μmol, 1.00 mol %) in THF (1.00 mL) at 50 °C for 12 h. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound **3o** as a white solid (175 mg, 80%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.47 (d, J = 2.0 Hz, 1H), 7.36 – 7.34 (d, J = 8.0 Hz, 1H), 7.12 – 7.10 (dd, J = 7.9, 2.0 Hz, 1H), 4.56 – 4.52 (m, 1H), 2.58 (s, 1H), 1.28 (s, 12H), 1.26 (s, 12H), 0.37 – 0.36 (d, J = 3.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.82, 135.52, 135.22, 133.88, 129.37, 124.00, 83.61, 24.73, 24.60, -3.20; ^{11}B NMR (160 MHz, $CDCl_3$) δ 32.43; HRMS (EI) calc'd for $C_{21}H_{34}{}^{11}B_2{}^{35}ClO_4Si$ ($[M–H]^+$) 435.2101, found 435.2107.

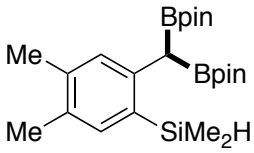


1,1-Benzyldiboronate ester 3p: The reaction was performed according to the general procedure for the diborylation of benzylic C-H bonds with **1p** (82.2 mg, 0.500 mmol), B_2pin_2 (254 mg, 1.00 mmol), and $[Ir(COD)OMe]_2$ (2.50 μmol, 0.500 mol %) in THF (1.00 mL), and 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.00 μmol, 1.00 mol %) in THF (1.00 mL) at 50 °C for 12 h. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound **3p** as a white solid (187 mg, 90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.33 (dd, J = 7.3, 1.7 Hz, 1H), 7.22 – 7.19 (dd, J = 7.5, 1.6 Hz, 1H), 7.12 – 7.08 (t, J = 7.4 Hz, 1H), 4.59 – 4.55 (m, 1H), 2.59 (s, 1H), 2.38 (s, 3H), 1.30 (12H), 1.27 (s, 12H), 0.40 – 0.39 (d, J = 3.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ

144.53, 136.84, 136.13, 132.25, 131.74, 124.23, 83.29, 25.07, 24.45, 21.30, -2.62; ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.49; HRMS (EI) calc'd for $C_{22}H_{37}{}^{11}B_2O_4Si$ ($[M–H]^+$) 416.2647, found 416.2658.

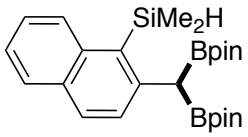


1,1-Benzyldiboronate ester 3q: The reaction was performed according to the general procedure for the diborylation of benzylic C-H bonds with **1a** (92.4 mg, 0.500 mmol), B_2pin_2 (254 mg, 1.00 mmol), and $[Ir(COD)OMe]_2$ (2.50 μmol, 0.500 mol %) in THF (1.00 mL), and 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.00 μmol, 1.00 mol %) in THF (1.00 mL) at 50 °C for 12 h. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound **3q** as a white solid (186 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.36 (m, 2H), 7.12 – 7.08 (m, 1H), 4.57 – 4.50 (m, 1H), 2.61 (s, 1H), 1.29 (s, 12H), 1.27 (s, 12H), 0.39 – 0.38 (d, J = 3.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.57, 138.88, 134.67, 132.91, 130.47, 125.42, 83.36, 25.13, 24.34, -2.95; ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.39; HRMS (EI) calc'd for $C_{21}H_{34}{}^{11}B_2{}^{35}ClO_4Si$ ($[M–H]^+$) 435.2101, found 435.2110.



1,1-Benzyldiboronate ester 3r: The reaction was performed according to the general procedure for the diborylation of benzylic C-H bonds with **1r** (89.2 mg, 0.500 mmol), B_2pin_2 (254 mg, 1.00 mmol), and $[Ir(COD)OMe]_2$ (2.50 μmol, 0.500 mol %) in THF (1.00 mL), and 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.00 μmol, 1.00 mol %) in THF (1.00 mL) at 50 °C for 12 h. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound **3r** as a white solid (181 mg, 84%); ^{1}H

NMR (400 MHz, $CDCl_3$) δ 7.23 (s, 1H), 7.21 (s, 1H), 4.57 – 4.54 (m, 1H), 2.53 (s, 1H), 2.31 (s, 3H), 2.27 (s, 3H), 1.30 (m, 12H), 1.28 (s, 12H), 0.38 – 0.37 (d, J = 3.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.93, 137.39, 135.88, 132.51, 131.52, 130.79, 83.32, 24.77, 24.66, 19.93, 19.31, -2.87; ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.17; HRMS (EI) calc'd for $C_{23}H_{40}{}^{11}B_2O_4Si$ (M^+) 430.2882, found 430.2888.



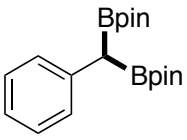
1,1-Benzyldiboronate ester 3s: The reaction was performed according to the general procedure for the diborylation of benzylic C-H bonds with **1s** (100 mg, 0.500 mmol), B_2pin_2 (254 mg, 1.00 mmol), and $[Ir(COD)OMe]_2$ (2.50 μmol, 0.500 mol %) in THF (1.00 mL), and 4,4'-di-*tert*-butyl-2,2'-bipyridine (5.00 μmol, 1.00 mol %) in THF (1.00 mL) at 80 °C for 12 h. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound **3s** as a light yellow solid (181 mg, 80%); ^1H NMR (400 MHz, $CDCl_3$) δ 8.32 – 8.30 (d, J = 8.5 Hz, 1H), 7.86 – 7.81 (m, 2H), 7.59 – 7.57 (d, J = 8.5 Hz, 1H), 7.49 – 7.46 (m, 1H), 7.44 – 7.42 (t, J = 7.3 Hz, 1H), 5.11 – 5.05 (m, 1H), 2.90 (s, 1H), 1.31 (s, 12H), 1.29 (s, 12H), 0.62 – 0.61 (d, J = 4.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.02, 137.89, 131.38, 129.59, 129.15, 128.78, 127.59, 125.11, 123.81, 83.47, 24.87, 24.55, -1.66; ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.54; HRMS (EI) calc'd for $C_{25}H_{38}{}^{11}B_2O_4Si$ (M^+) 452.2725, found 452.2734.

4. General procedure for the conversion of a hydrosilyl group

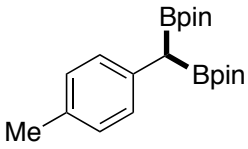
(1) Cleavage of a hydrosilyl group

A published procedure[2] for the cleavage of hydrosilyl group was followed with slight modifications. To a 4 mL vial containing a stir bar was added 1,1-benzyldiboronate ester **3** (1.00 equiv), KI (1.20 equiv), TMSCl (1.20 equiv), H_2O (1.20 equiv), and CH_3CN (0.100

M). The reaction was sealed with a Teflon-lined cap and stirred 2 h at room temperature. The mixture was filtered through a pad of SiO_2 and concentrated under reduced pressure. The crude mixture was purified by column chromatography to give the desilylated 1,1-benzyldiboronate ester **4**.

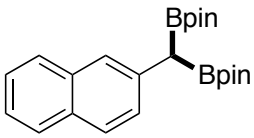


Desilylated 1,1-benzyldiboronate ester 4a: The reaction was performed according to the general procedure for the cleavage of hydrosilyl group with **3a** (2.01 g, 5.00 mmol), KI (996 mg, 6.00 mmol), TMSCl (652 mg, 6.00 mmol), H_2O (108 mg, 6.00 mmol) and CH_3CN (50.0 mL). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound **4a** as a white solid (1.65 g, 96%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.28 (m, 2H), 7.25 – 7.22 (t, J = 7.7 Hz, 2H), 7.12 – 7.08 (td, J = 7.2, 1.5 Hz, 1H), 2.33 (s, 1H), 1.26 (s, 12H), 1.24 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.50, 129.15, 127.95, 124.18, 83.37, 24.71, 24.62; ^{11}B NMR (160 MHz, $CDCl_3$) δ 32.78.



Desilylated 1,1-benzyldiboronate ester 4d: The reaction was performed according to the general procedure for the cleavage of hydrosilyl group with **3d** (167 mg, 0.400 mmol), KI (79.7 mg, 0.480 mmol), TMSCl (52.1 mg, 0.480 mmol), H_2O (8.70 mg, 0.480 mmol) and CH_3CN (4.00 mL). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound **4d** as a white solid (134 mg, 93%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 – 7.17 (dd, J = 8.1, 2.4 Hz, 2H), 7.06 – 7.04 (d, J = 7.5 Hz, 2H), 2.31 (s, 3H), 2.29 (s, 1H), 1.26 (s, 12H), 1.24 (s, 12H); ^{13}C NMR (126 MHz,

$CDCl_3$) δ 136.21, 133.32, 128.97, 128.72, 83.31, 24.70, 24.63, 21.00; ^{11}B NMR (160 MHz, $CDCl_3$) δ 32.70.

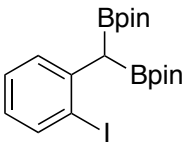


Desilylated 1,1-benzyldiboronate ester 4s: The reaction was performed according to the general procedure for the cleavage of hydrosilyl group with **3s** (181 mg, 0.400 mmol), KI (79.7 mg, 0.480 mmol), TMSCl (52.1 mg, 0.480 mmol), H_2O (8.70 mg, 0.480 mmol) and CH_3CN (4.00 mL). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound **4s** as a white solid (122 mg, 77%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 – 7.76 (t, J = 7.4 Hz, 2H), 7.74 – 7.72 (d, J = 8.5 Hz, 1H), 7.70 – 7.69 (m, 1H), 7.50 – 7.48 (dd, J = 8.4, 1.8 Hz, 1H), 7.43 – 7.40 (ddd, J = 8.2, 6.8, 1.4 Hz, 1H), 7.38 – 7.35 (ddd, J = 8.1, 6.8, 1.4 Hz, 1H), 2.50 (s, 1H), 1.26 (s, 12H), 1.24 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.31, 133.81, 131.24, 128.88, 127.45, 127.34, 127.20, 126.44, 125.33, 124.33, 83.47, 24.73, 24.61; ^{11}B NMR (160 MHz, $CDCl_3$) δ 33.02.

(2) Iodination of a hydrosilyl group

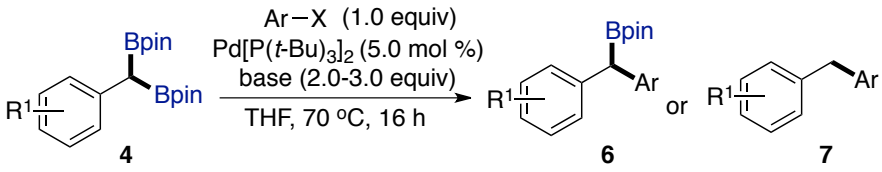
To a 4 mL vial, the boronate ester **3a** (103 mg, 0.299 mmol), [Ru(*p*-cymene)Cl]$_2$ (0.900 mg, 1.50 μmol, 0.50 mol %) and anhydrous 2-propanol (0.1 mL) were added with a stirbar. The reaction was sealed with a Teflon-lined cap and stirred at 25 ^{o}C for 4 h. The volatile materials were removed by placing the reaction mixture directly under high vacuum for 2 h. To this crude mixture, iodine monochloride (53.5 mg, 0.329 mmol) and dry CH_2Cl_2 were added. The reaction was sealed with a Teflon-lined cap, and stirred for 12 h at room temperature. The mixture was filtered through a pad of Celite and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography

(hexanes:EtOAc, 95:5) to give boronate ester **5a** as a pale oil (78% in 2 steps, 110 mg).



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.79 (d, J = 7.8 Hz, 1H), 7.59 – 7.57 (d, J = 7.8 Hz, 1H), 7.26 – 7.25 (d, J = 7.0 Hz, 1H), 6.81 – 6.78 (td, J = 7.5, 1.7 Hz, 1H), 2.72 (s, 1H), 1.27 (s, 12H), 1.26 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.42, 139.03, 129.31, 127.99, 126.19, 103.17, 83.59, 24.86, 24.84, 24.61, 24.59. ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.71.

5. General procedure for the chemoselective Suzuki-Miyaura cross-couplings

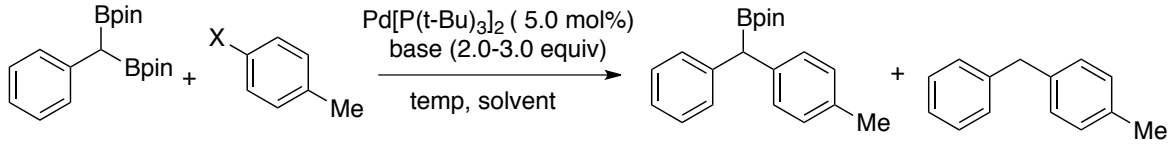


Method A: A published procedure[3] for the Suzuki-Miyaura cross-coupling reaction was followed with slight modifications. In a nitrogen-filled glovebox, aryl bromide (0.200 mmol), desilylated 1,1-benzyldiboronate ester **4** (1.50 equiv), base (2.00 equiv), and $Pd[P(t\text{-}Bu)_3]_2$ (5.00 mol %) were combined to a 4-mL vial containing a stirbar and THF (2.00 mL). The vial was sealed with a Teflon-lined screw cap and then removed from the glovebox. The vial was placed in a pre-heated aluminum block at 70 °C and stirred for 16 h. The mixture was filtered through a pad of SiO_2 and concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel to give compound **6**.

Method B: In a nitrogen-filled glovebox, aryl halide (0.200 mmol), desilylated 1,1-benzyldiboronate ester **4** (1.50 equiv), and $Pd[P(t\text{-}Bu)_3]_2$ (5.00 mol %) were combined to a 4-mL vial containing a stirbar and THF (2.00 mL). The reaction was sealed with a cap of septum and then removed from the glovebox. To this reaction mixture, an aqueous solution

of NaOH (3.00 equiv, 3.00 M) was added. The vial was placed in a pre-heated aluminum block at 70 °C and stirred for 16 h. The mixture was filtered through a pad of SiO_2 and concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel to give compound **7**.

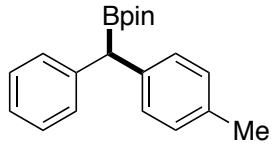
Table S1. Evaluation of the effect of base on the chemoselective Suzuki-Miyaura cross-coupling



4a **6a** **7a**

Entry	Method	X	Base (equiv)	Solvent	Temp (°C)	^{1}H NMR yield (%)	
						6a	**7a**
1	A	Br	NaOH (3.0)	THF	25	<1	27
2	B	Br	NaOH (3.0)	THF	70	<1	71
3	B	I	NaOH (3.0)	THF	70	<1	83(80)[a]
4	A	Br	K_2CO_3 (3.0)	THF	70	<1	<1
5	A	Br	K_3PO_4 (3.0)	THF	70	<1	<1
6	A	Br	NaO*t*Bu (3.0)	THF	70	16	15
7	A	Br	CsF (3.0)	THF	70	77	15
8	A	Br	CsF (2.0)	THF	70	88(81)[a]	<1
9	A	Br	CsF (2.0)	THF	25	21	<1

Method A: **4a** (0.300 mmol), 4-bromotoluene (0.200 mmol), Pd[P(*t*-Bu)$_3$]$_2$ (5.00 mol %), base (2.00 equiv), THF (2.00 mL) at indicated temperature for 16 h. *Method B*: **4a** (0.300 mmol), 4-iodotoluene (0.200 mmol), Pd[P(*t*-Bu)$_3$]$_2$ (5.00 mol %), NaOH (3.00 equiv), THF (2.00 mL) at indicated temperature for 16 h. [a] Isolated yield.

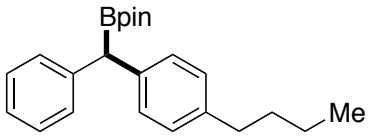


Boronate ester 6a: The reaction was performed according to the general procedure A for chemoselective Suzuki-Miyaura cross-coupling with **4a** (103 mg, 0.299 mmol), 4-bromotoluene (34.2 mg, 0.200 mmol), and CsF (60.7 mg, 0.400 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to

give compound **6a** as a white solid (50 mg, 81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.30 (m, 4H), 7.22 – 7.20 (m, 2H), 7.14 – 7.12 (m, 2H), 3.87 (s, 1H), 2.35 (s, 3H), 1.28 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.40, 138.96, 135.02, 129.15, 129.04, 128.38, 128.28, 125.52, 83.70, 24.76, 24.64, 21.03; ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.25; HRMS (EI) calc'd for $C_{20}H_{25}{}^{11}B\,O_2$ (M^+) 308.1948, found 308.1950.

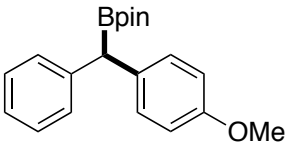
Tandem desilylation/Suzuki-Miyaura coupling of 3a

The desilylation was performed according to the general procedure for the cleavage of hydrosilyl group with **3a** (121 mg, 0.300 mmol), KI (60 mg, 0.360 mmol), TMSCl (39.1 mg, 0.360 mmol), H_2O (6.50 mg, 0.360 mmol) and CH_3CN (3.00 mL). The crude mixture was filtered through a pad of SiO_2 and concentrated under reduced pressure for 2 h. The crude **4a** (ca. 0.3 mmol), 4-bromotoluene (34.2 mg, 0.200 mmol), CsF (60.8 mg, 0.400 mmol), and $Pd[P(t\text{-}Bu)_3]_2$ (5.11 mg, 0.01 mmol, 5.00 mol %) were combined in a 4-mL vial containing a stirbar and THF (2.00 mL). The reaction was sealed with a Teflon-lined cap and stirred at 70 °C for 16 h. The mixture was filtered through a pad of SiO_2 and concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound **6a** as a white solid (47 mg, 76% in 2 steps), which gave spectral data identical to that obtained previously.

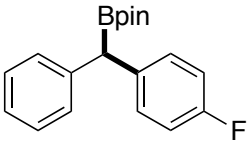


Boronate ester 6b: The reaction was performed according to the general procedure A for chemoselective Suzuki-Miyaura cross-coupling with **4a** (103 mg, 0.299 mmol), 1-bromo-4-butuylbenzene (42.6 mg, 0.200 mmol), and CsF (60.7 mg, 0.400 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound **6b** as a colorless oil (62 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ

7.33 – 7.29 (m, 4H), 7.27 – 7.20 (m, 3H), 7.16 – 7.14 (m, 2H), 3.90 (s, 1H), 2.65 – 2.61 (t, J = 7.8 Hz, 2H), 1.68 – 1.61 (m, 2H), 1.45 – 1.39 (m, 2H), 1.30 (s, 12H), 1.01 – 0.97 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.43, 140.07, 139.14, 129.11, 128.99, 128.48, 128.38, 125.53, 83.70, 35.28, 33.68, 24.66, 22.50, 14.04; ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.25; HRMS (EI) calc'd for $C_{23}H_{30}{}^{11}BO_2$ ($[M–H]^+$) 349.2339, found 349.2345.

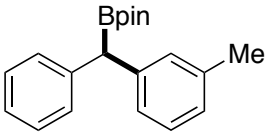


Boronate ester 6c: The reaction was performed according to the general procedure A for chemoselective Suzuki-Miyaura cross-coupling with **4a** (103 mg, 0.299 mmol), 4-bromoanisole (37.4 mg, 0.200 mmol), and CsF (60.7 mg, 0.400 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound **6c** as a white solid (50 mg, 77%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 4H), 7.26 – 7.22 (m, 2H), 7.22 – 7.17 (m, 1H), 6.92 – 6.82 (m, 2H), 3.85 (s, 1H), 3.82 (s, 3H), 1.28 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.63, 142.62, 134.05, 130.15, 128.94, 128.38, 125.50, 113.86, 83.70, 55.22, 24.64; ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.21; HRMS (EI) calc'd for $C_{20}H_{25}{}^{11}BO_3$ (M^+) 324.1897, found 324.1902.

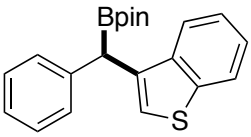


Boronate ester 6d: The reaction was performed according to the general procedure A for chemoselective Suzuki-Miyaura cross-coupling, except that 1,4-dioxane was used in place of THF as a solvent, with **4a** (103 mg, 0.299 mmol), 1-bromo-4-fluorobenzene (35.0 mg, 0.200 mmol), and CsF (60.7 mg, 0.400 mmol).. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound **6d** as a dark solid (41 mg, 65%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.16 (m, 7H), 7.01 – 6.97

(m, 2H), 3.87 (s, 1H), 1.26 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.18 (d, J_{C-F} = 196 Hz), 141.98, 137.71 (d, J = 3.3 Hz), 130.50 (d, J = 7.7 Hz), 128.99, 128.50, 125.75, 115.14 (d, J_{C-F} = 21.1 Hz), 83.84, 24.63, 24.61; ^{11}B NMR (160 MHz, $CDCl_3$) δ 33.10; HRMS (EI) calc'd for $C_{19}H_{22}{}^{11}BFO_2$ (M^+) 312.1697, found 312.1693.

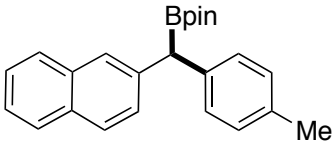


Boronate ester 6e: The reaction was performed according to the general procedure A for chemoselective Suzuki-Miyaura cross-coupling with **4a** (103 mg, 0.299 mmol), 3-bromotoluene (34.2 mg, 0.200 mmol), and CsF (60.7 mg, 0.400 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound **6e** as a white solid (43 mg, 70%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.28 (m, 4H), 7.20 – 7.19 (m, 2H), 7.13 – 7.10 (m, 2H), 7.02 – 7.00 (d, J = 7.4 Hz, 1H), 3.87 (s, 1H), 2.34 (s, 3H), 1.27 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.21, 141.90, 137.91, 129.98, 129.10, 128.38, 128.28, 126.43, 126.17, 125.56, 83.72, 24.64, 24.62, 21.54; ^{11}B NMR (160 MHz, $CDCl_3$) δ 33.09; HRMS (EI) calc'd for $C_{20}H_{25}{}^{11}BO_2$ (M^+) 308.1948, found 308.1950.

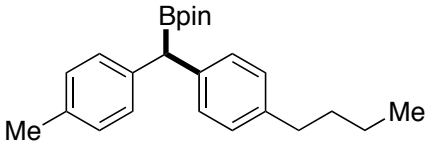


Boronate ester 6f: The reaction was performed according to the general procedure A for chemoselective Suzuki-Miyaura cross-coupling with **4a** (103 mg, 0.299 mmol), 3-bromobenzothiophene (42.6 mg, 0.200 mmol), and CsF (60.7 mg, 0.400 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound **6f** as a white solid (39.5 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.87 (m, 1H), 7.75 – 7.72 (m, 1H), 7.39 (s, 1H), 7.36 – 7.30 (m, 6H), 7.22 – 7.19 (m,

1H), 4.20 (s, 1H), 1.28 (s, 6H), 1.27 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.51, 140.41, 139.23, 135.88, 128.70, 128.48, 125.76, 124.07, 123.70, 123.00, 122.74, 122.22, 83.93, 24.65, 24.62; ^{11}B NMR (160 MHz, $CDCl_3$) δ 32.57; HRMS (EI) calc'd for $C_{21}H_{23}{}^{11}BO_2S$ (M^+) 350.1512, found 350.1513.

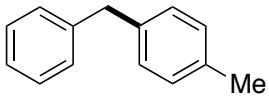


Boronate ester 6g: The reaction was performed according to the general procedure A for chemoselective Suzuki-Miyaura cross-coupling with **4s** (118 mg, 0.299 mmol), 4-bromotoluene (34.2 mg, 0.200 mmol), and CsF (60.7 mg, 0.400 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound **6g** as a white solid (62 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.81 (m, 3H), 7.76 (m, 1H), 7.50 – 7.46 (m, 3H), 7.29 – 7.27 (d, J = 7.8 Hz, 2H), 7.18 – 7.16 (d, J = 7.8 Hz, 2H), 4.08 (s, 1H), 2.39 (s, 3H), 1.32 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.01, 138.83, 135.16, 133.80, 131.90, 129.23, 129.17, 128.18, 127.89, 127.71, 127.55, 127.02, 125.73, 125.11, 83.82, 24.71, 24.68, 21.08; ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.73. ^{11}B NMR (160 MHz, $CDCl_3$) δ 32.57; HRMS (EI) calc'd for $C_{24}H_{27}{}^{11}BO_2$ (M^+) 358.2104, found 358.2111.

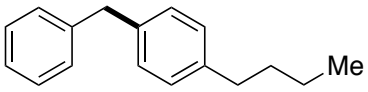


Boronate ester 6h: The reaction was performed according to the general procedure A for chemoselective Suzuki-Miyaura cross-coupling with **4d** (108 mg, 0.301 mmol), 1-bromo-4-butuylbenzene (42.6 mg, 0.200 mmol), and CsF (60.7 mg, 0.400 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound **6h** as a dark oil (51 mg, 70%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15

– 7.17 (m, 4H), 7.09 – 7.07 (m, 4H), 3.80 (s, 1H), 2.58 – 2.55 (t, *J* = 7.8 Hz, 2H), 2.31 (s, 3H), 1.61 – 1.55 (m, 2H), 1.40 – 1.34 (m, 2H), 1.25 (s, 12H), 0.94 – 0.92 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.93, 139.40, 139.25, 134.88, 129.09, 128.96, 128.84, 128.42, 83.62, 35.24, 33.65, 24.75, 24.63, 22.46, 21.02, 14.01; ^{11}B NMR (160 MHz, $CDCl_3$) δ 33.41; HRMS (EI) calc'd for $C_{24}H_{33}{}^{11}BO_2$ (M^+) 364.2574, found 364.2582.

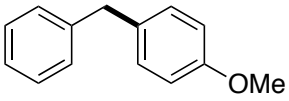


1-Benzyl-4-methylbenzene (7a)[4]: The reaction was performed according to the general procedure B for Suzuki-Miyaura cross-coupling with **4a** (103 mg, 0.299 mmol), 4-iodotoluene (43.6 mg, 0.200 mmol), and an aqueous solution of NaOH (0.200 mL, 0.600 mmol, 3.00 M). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound **7a** as a colorless oil (29 mg, 80%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.32 (m, 2H), 7.30 – 7.21 (m, 3H), 7.21 – 7.11 (m, 4H), 4.01 (s, 2H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.38, 138.05, 135.47, 129.11, 128.84, 128.79, 128.39, 125.94, 41.49, 20.96.

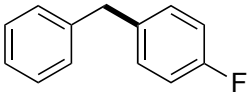


1-Benzyl-4-butylbenzene (7b): The reaction was performed according to the general procedure B for Suzuki-Miyaura cross-coupling with **4a** (103 mg, 0.299 mmol), 1-butyl-4-iodobenzene (52.0 mg, 0.200 mmol), and an aqueous solution of NaOH (0.200 mL, 0.600 mmol, 3.00 M). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound **7b** as a colorless oil (39 mg, 86%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.24 (m, 5H), 7.16 (s, 4H), 4.01 (s, 2H), 2.63 – 2.61 (t, *J* = 7.8 Hz, 2H), 1.66 – 1.62 (m, 2H), 1.44 – 1.38 (m, 2H), 1.00 – 0.96 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101

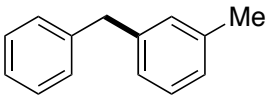
MHz, $CDCl_3$) δ 141.42, 140.65, 138.29, 128.95, 128.79, 128.52, 128.45, 126.00, 41.59, 35.29, 33.75, 22.45, 14.02.



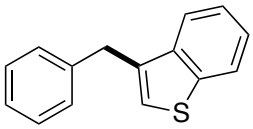
1-Benzyl-3-methoxybenzene (7c)[4]: The reaction was performed according to the general procedure B for Suzuki-Miyaura cross-coupling with **4a** (103 mg, 0.299 mmol), 4-iodoanisole (46.8 mg, 0.200 mmol), and an aqueous solution of NaOH (0.200 mL, 0.600 mmol, 3.00 M). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound **7c** as a colorless oil (32.5 mg, 82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 2H), 7.20 – 7.15 (m, 3H), 7.11 – 7.08 (m, 2H), 6.85 – 6.81 (d, J = 8.0 Hz, 2H), 3.93 (s, 2H), 3.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157. 96, 141.55, 133.24, 129.84, 128.79, 128.40, 125.94, 113.86, 55.23, 41.04.



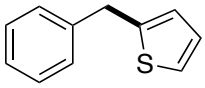
1-Benzyl-4-fluorobenzene (7d)[4]: The reaction was performed according to the general procedure B for chemoselective Suzuki-Miyaura cross-coupling with **4a** (103 mg, 0.299 mmol), 1-bromo-4-fluorobenzene (44.4 mg, 0.200 mmol), and an aqueous solution of NaOH (0.200 mL, 0.600 mmol, 3.00 M). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound **7d** as a colorless oil (33 mg, 88%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 2H), 7.30 – 7.13 (m, 5H), 7.07 – 6.95 (m, 2H), 4.00 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.41 (d, $J_{C–F}$ = 245.4 Hz), 140.91, 136.75 (d, $J_{C–F}$ = 3.0Hz), 130.25 (d, $J_{C–F}$ = 8.1 Hz), 128.66 (d, $J_{C–F}$ = 30.0 Hz), 126.18, 115.17 (d, $J_{C–F}$ = 21.2 Hz), 41.1.



1-Benzyl-3-methylbenzene (7e)[4]: The reaction was performed according to the general procedure B for chemoselective Suzuki-Miyaura cross-coupling with **4a** (103 mg, 0.299 mmol), 3-iodotoluene (43.6 mg, 0.200 mmol), and an aqueous solution of NaOH (0.200 mL, 0.600 mmol, 3.00 M). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound **7e** as a colorless oil (29.5 mg, 81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 2H), 7.19 – 7.17 (m, 4H), 7.16 – 6.97 (m, 3H), 3.92 (s, 2H), 2.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.23, 141.00, 137.98, 129.69, 128.89, 128.40, 128.32, 126.80, 125.98, 125.96, 41.88, 21.36.

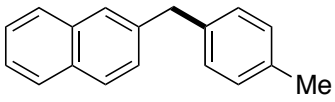


3-Benzylbenzothiophene (7f): The reaction was performed according to the general procedure B for chemoselective Suzuki-Miyaura cross-coupling with **4a** (103 mg, 0.299 mmol), 3-bromobenzothiophene (42.6 mg, 0.200 mmol), and an aqueous solution of NaOH (0.200 mL, 0.600 mmol, 3.00 M). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound **7f** as a colorless oil (42 mg, 93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.90 (m, 1H), 7.77 – 7.75 (m, 1H), 7.41 – 7.27 (m, 7H), 7.06 (s, 1H), 4.25 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.62, 139.37, 138.85, 135.63, 128.87, 128.56, 126.37, 124.28, 123.98, 123.12, 122.89, 122.00, 35.03.



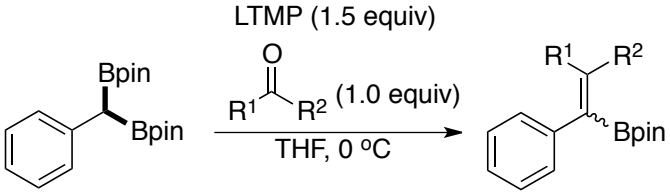
2-Benzylthiophene (7g)[4]: The reaction was performed according to the general procedure B for chemoselective Suzuki-Miyaura cross-coupling with **4a** (103 mg, 0.299 mmol), 2-bromothiophene (32.6 mg, 0.200 mmol), and an aqueous solution of NaOH (0.200 mL, 0.600 mmol, 3.00 M). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound **7g** as a colorless oil (27.5 mg, 93%); ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.31 – 7.21 (m, 5H), 7.13 – 7.11 (dd, *J* = 1.2, 5.0 Hz, 1H), 6.92 – 6.89 (dd, *J* = 3.2, 5.1 Hz), 6.79 – 6.77 (dd, *J* = 1.2, 3.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.01, 140.37, 125.8.56, 128.51, 126.79, 126.46, 125.13, 123.91, 36.01.



2-(4-Methylbenzyl)naphthalene (7h)[5]: The reaction was performed according to the general procedure B for chemoselective Suzuki-Miyaura cross-coupling with **4s** (118 mg, 0.299 mmol), 3-bromobenzothiophene (42.6 mg, 0.200 mmol), and an aqueous solution of NaOH (0.200 mL, 0.600 mmol, 3.00 M). The crude mixture was purified by column chromatography on silica gel (hexanes) to give compound **7h** as a colorless oil (42 mg, 90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.75 (m, 3H), 7.64 (s, 1H), 7.46 – 7.42 (m, 2H), 7.34 – 7.32 (m, 1H), 7.13 (m, 4H), 4.12 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.06, 138.09, 135.80, 133.79, 132.23, 129.35, 129.07, 128.20, 127.79, 127.15, 126.09, 125.44, 41.85, 21.18.

6. General procedure for the synthesis of tetrasubstituted alkenylboronate esters

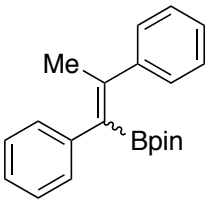


4a (1.5 equiv)

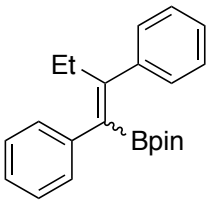
8a, R^1 = Me, R^2 = Ph, 93% (E/Z = 83/17)
8b, R^1 = Et, R^2 = Ph, 96% (E/Z = 91/9)
8c, R^1 = Me, R^2 = 1-Naphthyl, 90% (E/Z = 95/5)
8d, R^1 = R^2 = Ph, 97%

A published procedure[6] for the synthesis of tetrasubstituted alkenylboronate ester was followed with slight modifications. To a 25 mL vial containing stir bar was added boronate ester **4a** (103 mg, 0.299 mmol) and THF (0.500 mL). The reaction mixture was cooled to 0 °C, and LTMP (0.300 mmol. 0.400 M in THF) was slowly added. After 5 min, ketone (0.200 mmol) was added in one portion and stirred for 2 h at 0 °C. The reaction mixture

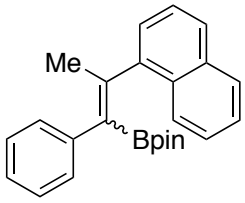
was filtered through a pad of SiO_2 and the filtrate was concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel to give compound **8**. The stereochemistry was determined by ^{1}H NMR analysis based on the literature.[7]



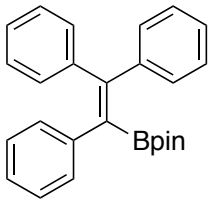
Boronate ester 8a: The reaction was performed according to the general procedure for the synthesis of tetrasubstituted alkenylboronate esters with acetophenone (24.0 mg, 0.200 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound **8a (**E/Z = 84/16) as a white solid (59.5 mg, 93%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.44 (m, 2H), 7.40 – 7.35 (m, 4H), 7.32 – 7.26 (m, 4H), 2.09 (s, 3H), 1.07 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.83, 145.47, 141.72, 128.78, 128.14, 128.03, 127.82, 127.18, 125.94, 83.36, 24.45, 21.51.



Boronate ester 8b: The reaction was performed according to the general procedure for the synthesis of tetrasubstituted alkenylboronate esters with propiophenone (26.8 mg, 0.200 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound **8b (**E/Z = 91/9) as a white solid (64 mg, 96%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 5H), 7.32 – 7.25 (m, 5H), 2.48 – 2.43 (q, J = 7.5 Hz, 1H), 1.03 (s, 12H), 0.90 – 0.87 (t, J = 7.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.81, 143.63, 141.52, 128.46, 128.43, 128.16, 127.90, 127.04, 125.92, 83.30, 27.16, 24.39, 13.31.

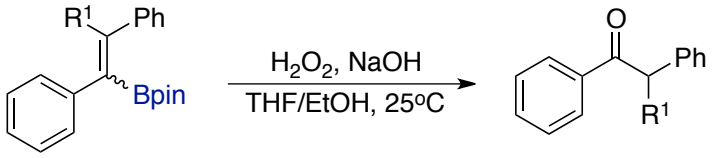


Boronate ester 8c: The reaction was performed according to the general procedure for the synthesis of tetrasubstituted alkenylboronate esters with 1-acetonaphthone (34.0 mg, 0.200 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100: 0 to 95:5) to give compound **8c** (E/Z = 95/5) as a white solid (67 mg, 90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 – 8.10 (d, J = 8.1 Hz, 1H), 7.87 – 7.86 (dd, J = 7.8, 1.7 Hz, 1H), 7.80 – 7.79 (d, J = 7.9 Hz, 1H), 7.53 – 7.42 (m, 8H), 7.30 – 7.28 (m, 1H), 2.20 (s, 3H), 0.77 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.62, 143.23, 141.13, 133.67, 131.65, 128.91, 128.15, 128.01, 126.95, 126.03, 126.00, 125.81, 125.52, 125.34, 125.21, 82.92, 24.00, 22.86.



Boronate ester 8d: The reaction was performed according to the general procedure for the synthesis of tetrasubstituted alkenylboronate esters with benzophenone (36.5 mg, 0.200 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound **8d** as a white solid (74 mg, 97%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.37 (m, 2H), 7.33 – 7.32 (m, 3H), 7.12 – 7.11 (m, 2H), 7.11 – 7.08 (m, 6H), 7.00 – 6.98 (m, 2H), 1.16 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.42, 144.67, 141.84, 141.70, 130.95, 129.73, 129.43, 128.01, 127.97, 127.60, 127.53, 126.79, 125.87, 83.71, 24.56; ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.42.

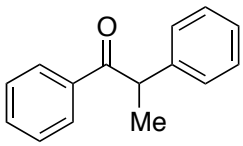
7. General procedure for the oxidation of tetrasubstituted alkenylboronate esters



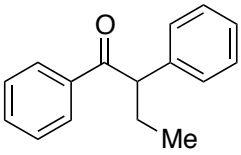
8a, R^1 = Me (E/Z = 83/17)
8b, R^1 = Et (E/Z = 91/9)

9a, R^1 = Me, 93%
9b, R^1 = Et, 97%

To a 25 mL vial containing a stir bar was added boronate ester **8** (0.150 mmol) and THF/EtOH (2/1, 3.00 mL). The reaction mixture was cooled to 0 °C, and an aqueous solution of NaOH (2.00 mL, 6.00 mmol, 3.00 M) and a solution of H_2O_2 (1.00 mL, 30 wt%) was added dropwise. The reaction was warmed to room temperature and stirred for 2 h. The reaction was quenched with a saturated NH_4Cl solution (5.00 mL), and the mixture was extracted with Et_2O (15.0 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel to give the desired ketone **9**.

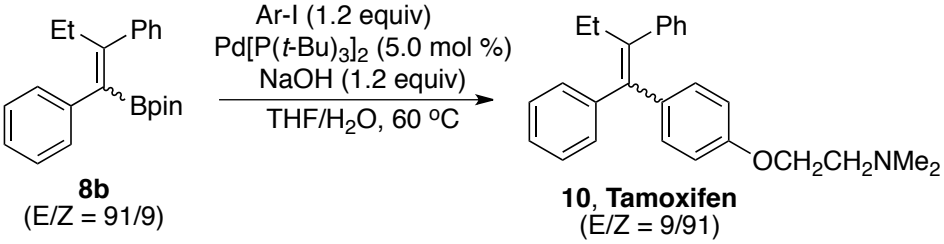


1,2-diphenylpropan-1-one (9a)[8]: The reaction was performed according to the general procedure for the oxidation of tetrasubstituted alkenylboronate esters with **8a** (48.1 mg, 0.150 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound **9a** as a colorless oil (29.5 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.96 (dt, J = 7.1, 1.4 Hz, 2H), 7.50 – 7.46 (m, 1H), 7.41 – 7.37 (m, 2H), 7.31 – 7.29 (m, 4H), 7.23 – 7.19 (m, 1H), 4.73 – 4.68 (q, J = 6.8 Hz, 1H), 1.56 – 1.54 (d, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.30, 141.43, 136.41, 132.76, 128.95, 128.74, 128.45, 127.73, 126.86, 47.86, 19.49.



1,2-diphenylbutan-1-one (9b)[8]: The reaction was performed according to the general procedure for the oxidation of tetrasubstituted alkenylboronate esters with **8b** (50.1 mg, 0.150 mmol). The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc, 100:0 to 95:5) to give compound **9b** as a colorless oil (33 mg, 97%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.99 (dd, J = 8.4, 1.4 Hz, 2H), 7.52 – 7.48 (m, 1H), 7.43 – 7.41 (m, 2H), 7.35 – 7.30 (m, 4H), 7.24 – 7.21 (m, 1H), 4.49 – 4.46 (t, J = 7.3 Hz, 1H), 2.29 – 2.18 (m, 1H), 1.94 – 1.85 (m, 1H), 0.95 – 0.92 (t, J = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.12, 139.65, 137.01, 132.81, 128.86, 128.67, 128.51, 128.28, 126.98, 55.47, 27.16, 12.35.

8. Synthesis of (*Z*)-Tamoxifen



8b
(E/Z = 91/9)

10, Tamoxifen
(E/Z = 9/91)

A published procedure[9] for the Suzuki-Miyaura cross-coupling was followed with slight modifications. To a 4 mL vial containing a stirbar was added **8b** (66.9 mg, 0.20 mmol), 2-(4-iodophenoxy)-*N*,*N*-dimethylethanamine[10] (69.8 mg, 0.240 mmol), Pd[P(*t*-Bu)$_3$]$_2$ (5.11 mg, 0.010 mmol, 5.00 mol %), NaOH (9.60 mg, 0.240 mmol), H_2O (4.32 mg, 0.240 mmol), and THF (0.20 mL). The reaction was sealed with a Teflon-lined cap and stirred at 60 °C for 24 h. After cooling the reaction mixture to room temperature, H_2O (3.00 mL) was added. The organic phase was separated and the aqueous phase was extracted with $CHCl_3$ (10.0 mL x 3). The combined organic layers were dried over Na_2SO4, filtered, and concentrated under reduced pressure. The crude mixture was purified by column

chromatography on silica gel ($CHCl_3$/MeOH/Et_3N, 100:10:1) to give compound **10** as a white solid (60 mg, 80%). The stereochemistry was determined by ^1H NMR analysis. ^1H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.36 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.28 (m, 3H), 7.20 – 7.18 (m, 2H), 7.16 – 7.14 (m, 3H), 6.81 – 6.78 (dd, *J* = 6.6, 2.1 Hz, 2H), 6.60 – 6.58 (d, *J* = 7.0 Hz, 2H), 3.97 – 3.95 (t, *J* = 5.8 Hz, 2H), 2.79 – 2.68 (t, *J* = 5.8 Hz, 2H), 2.55 – 2.47 (q, *J* = 7.5 Hz, 2H), 2.30 (s, 6H), 0.99 – 0.94 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.76, 143.83, 142.42, 141.31, 138.25, 135.54, 131.85, 129.71, 129.48, 128.10, 127.88, 126.52, 126.02, 113.38, 65.65, 58.31, 45.91, 29.03, 13.64.

9. Reference

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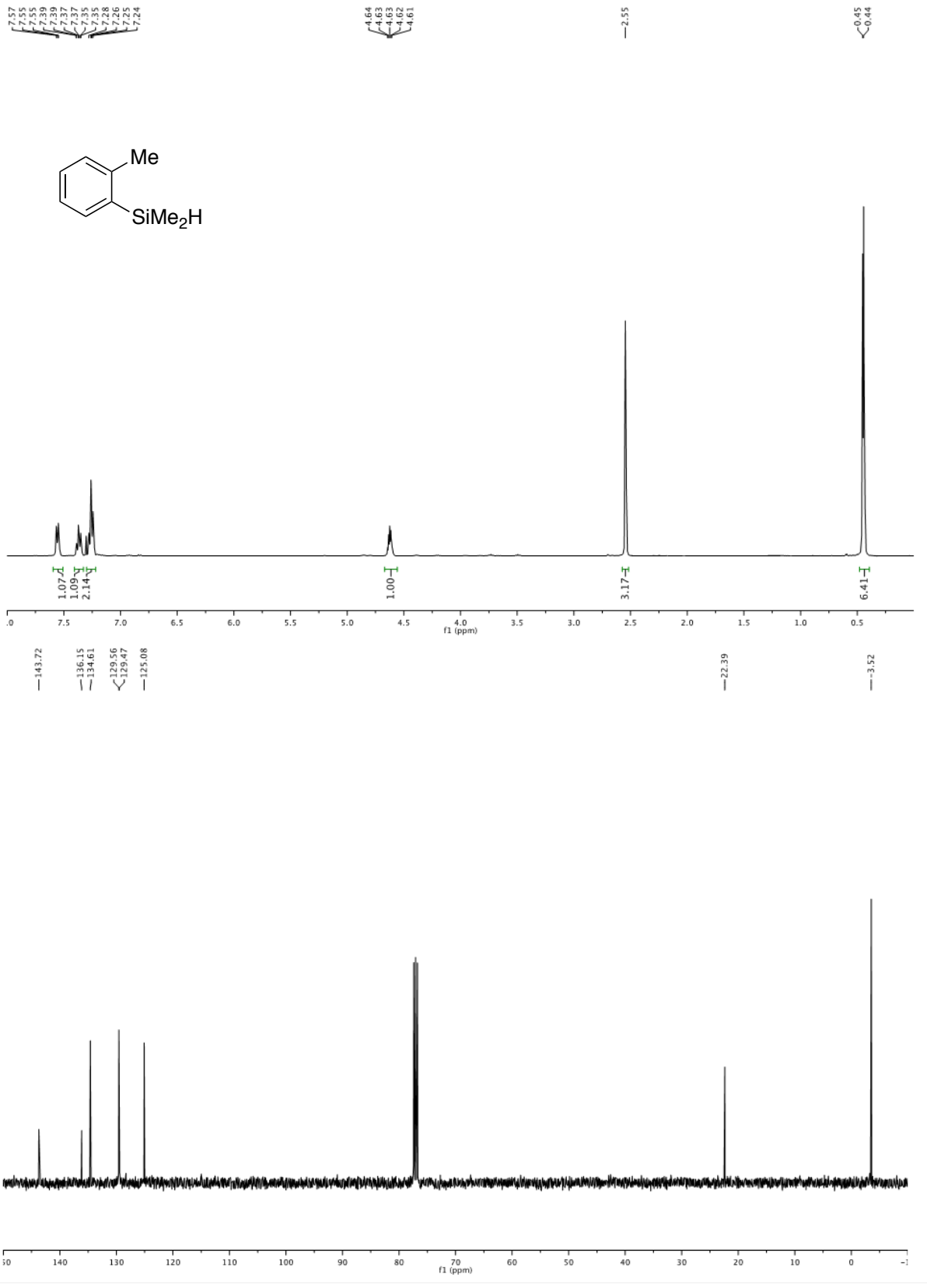
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7.24
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4.63
4.63
4.62
4.61
2.55
0.45
0.44
Me
SiMe2H
1.07
1.09
2.14
1.00
3.17
6.41
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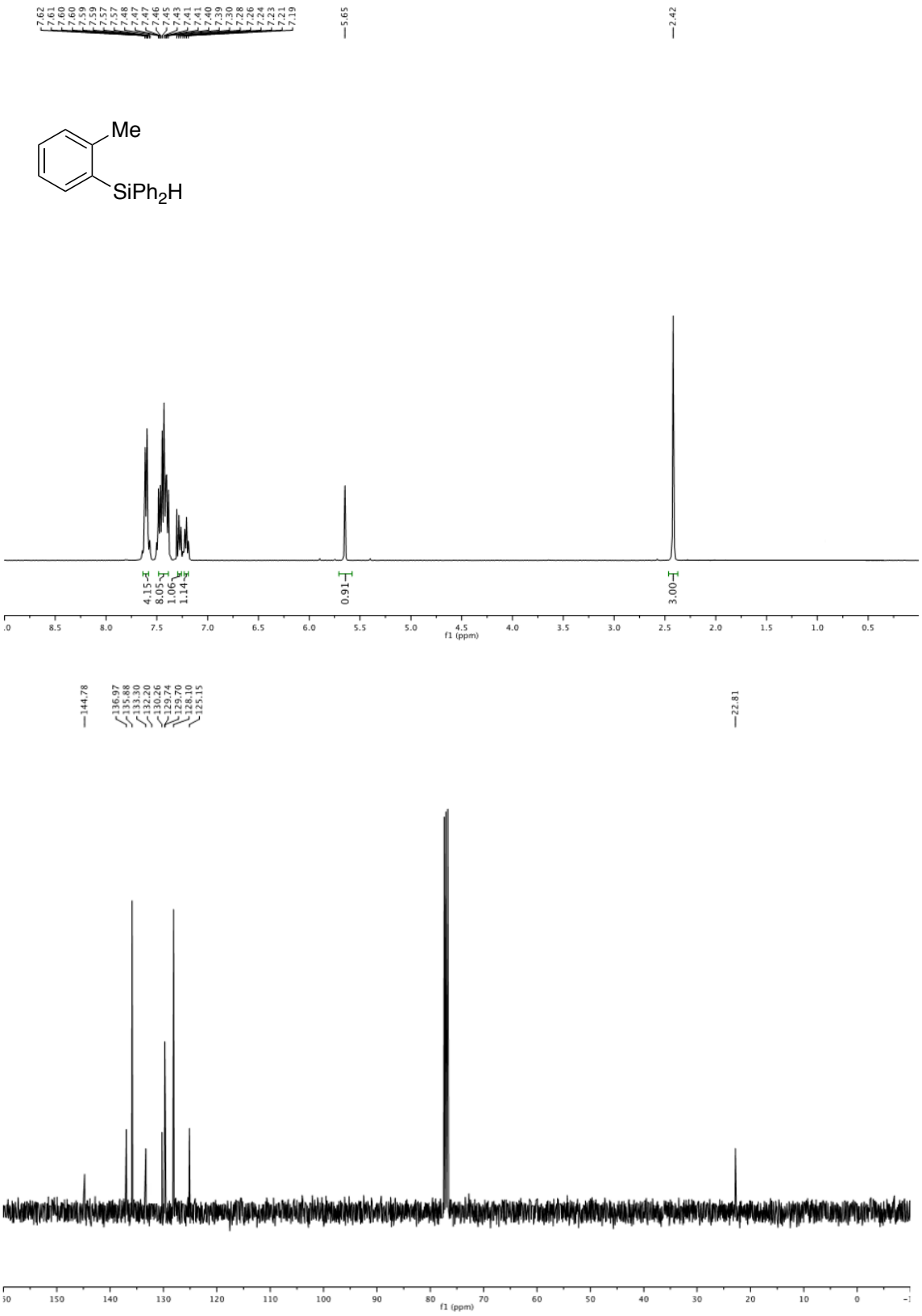
136.15
134.61
129.56
129.47
125.08
22.39
-3.52
f1 (ppm)

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7.47
7.45
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7.39
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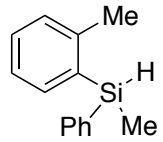
2.42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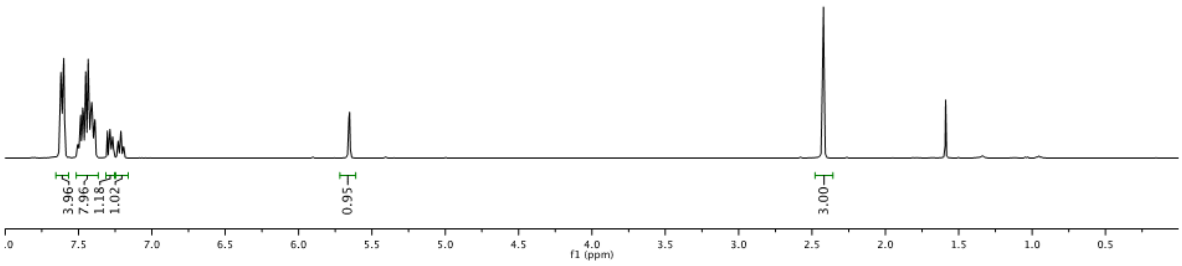
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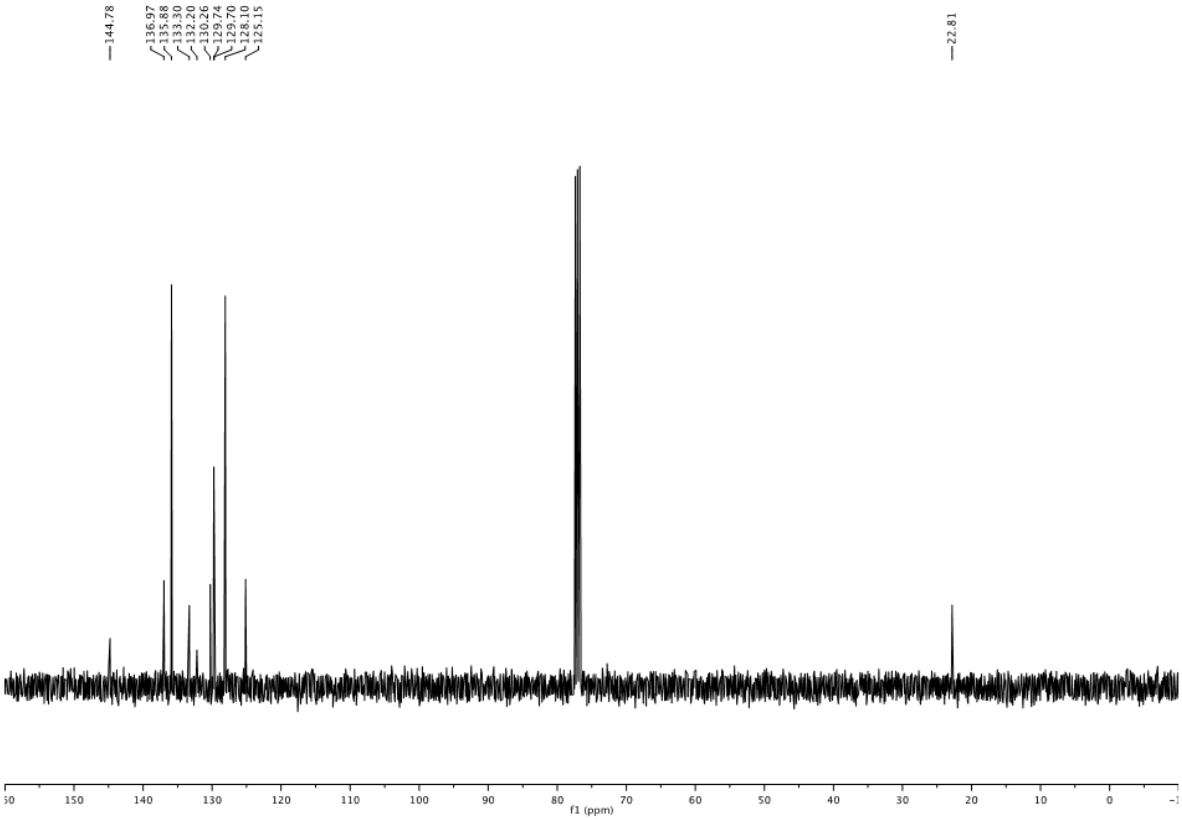
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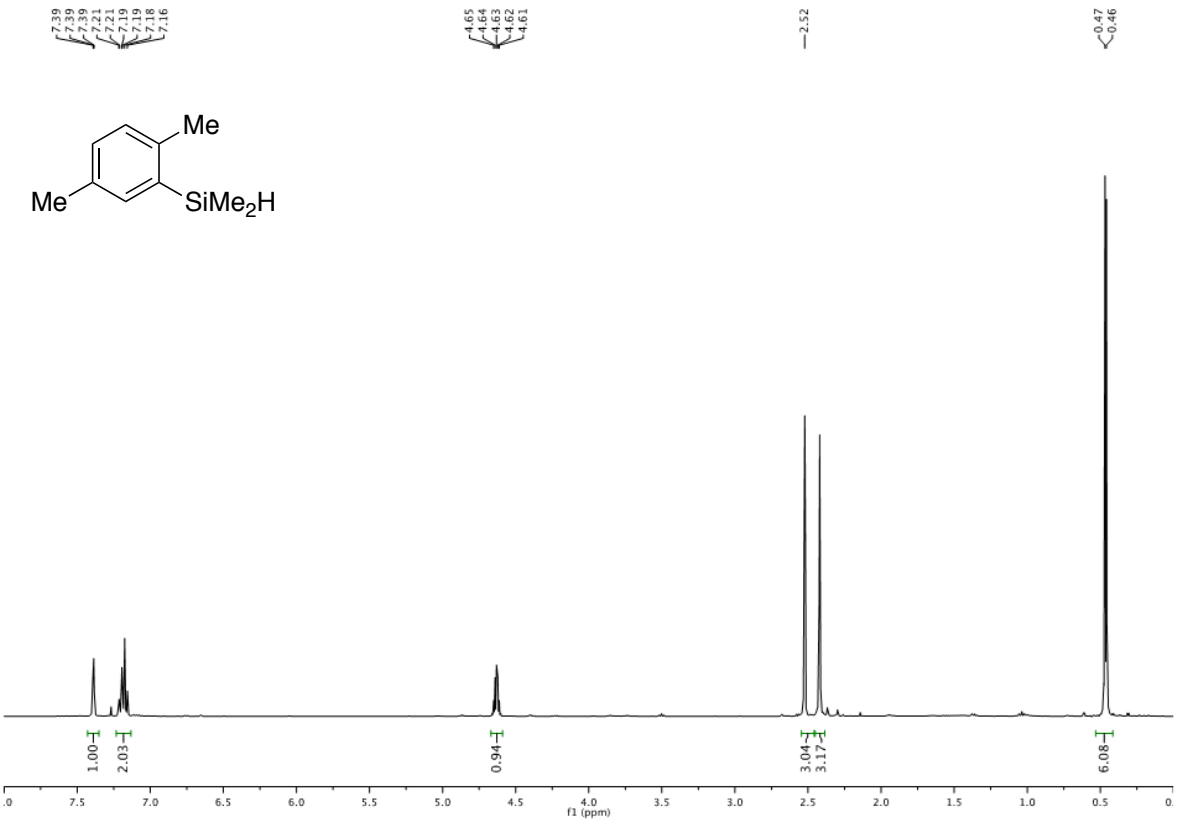
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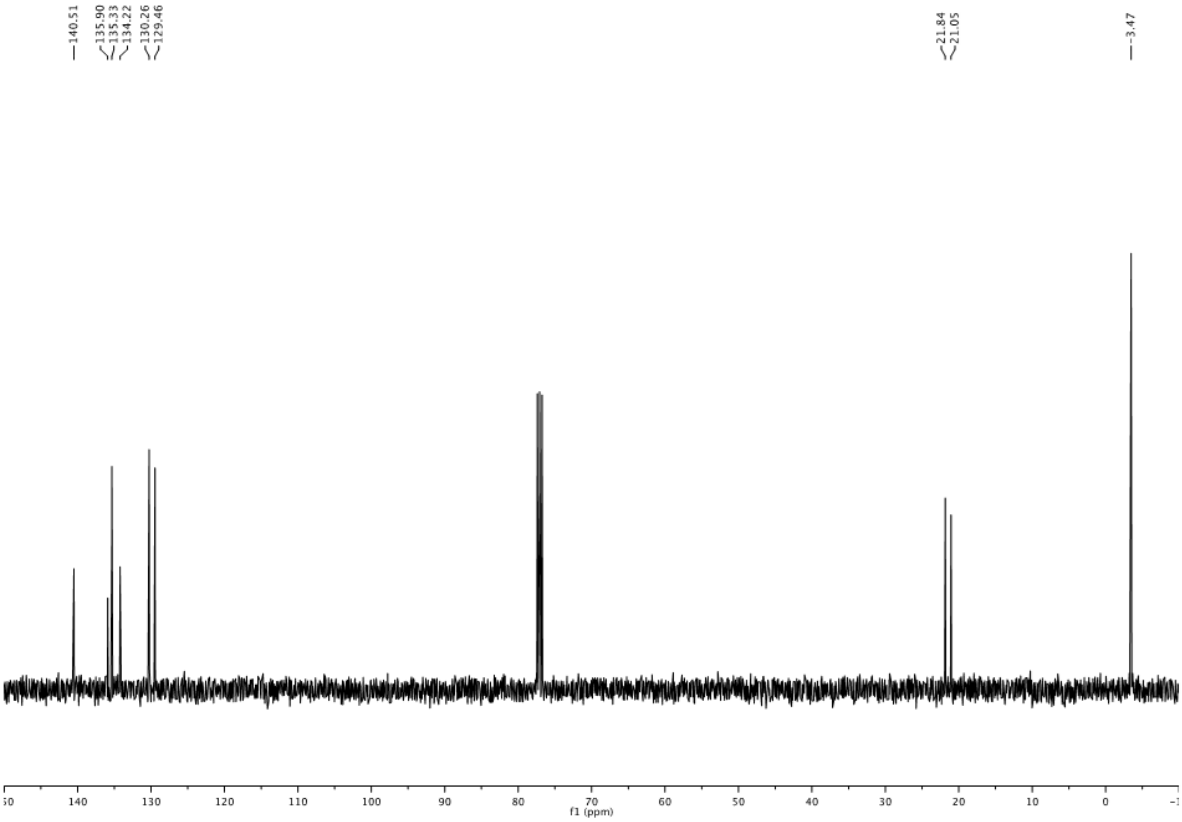
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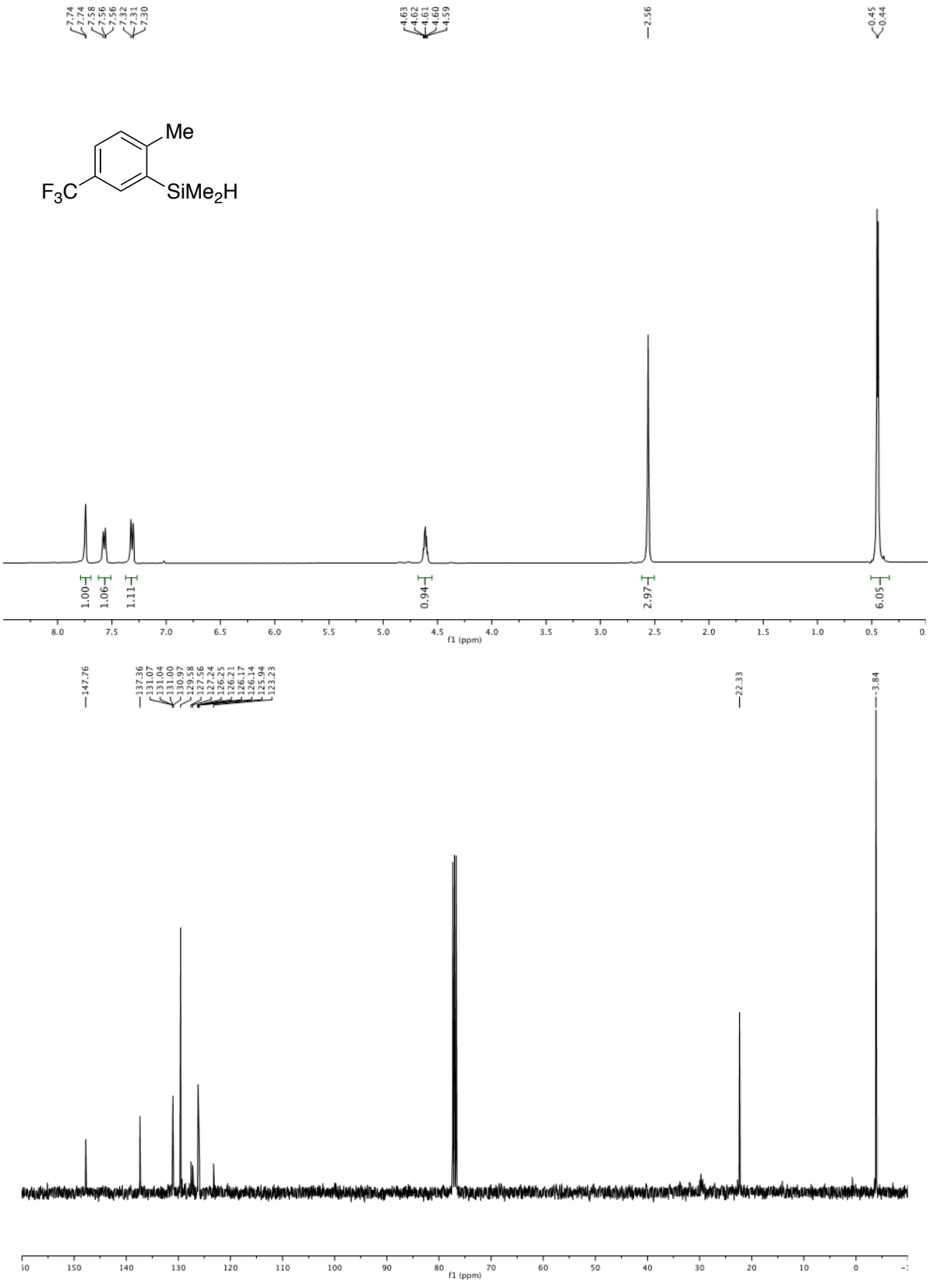
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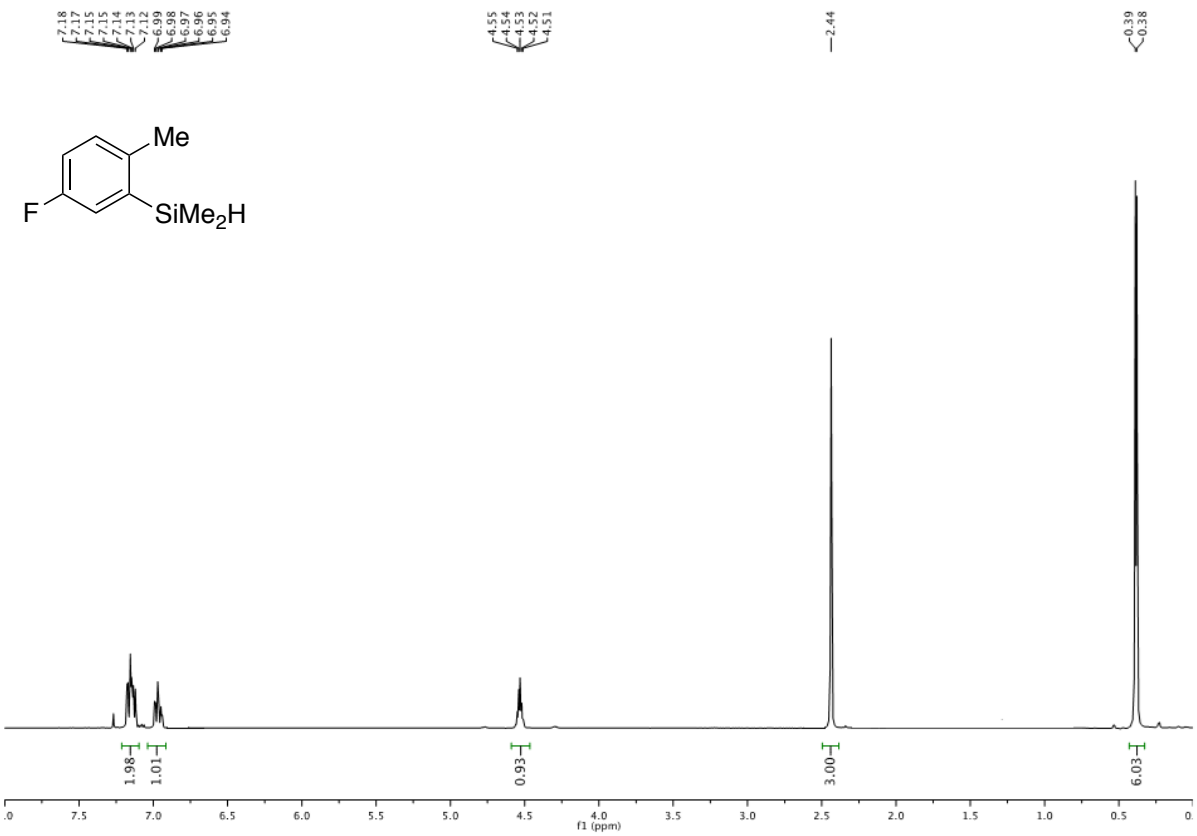
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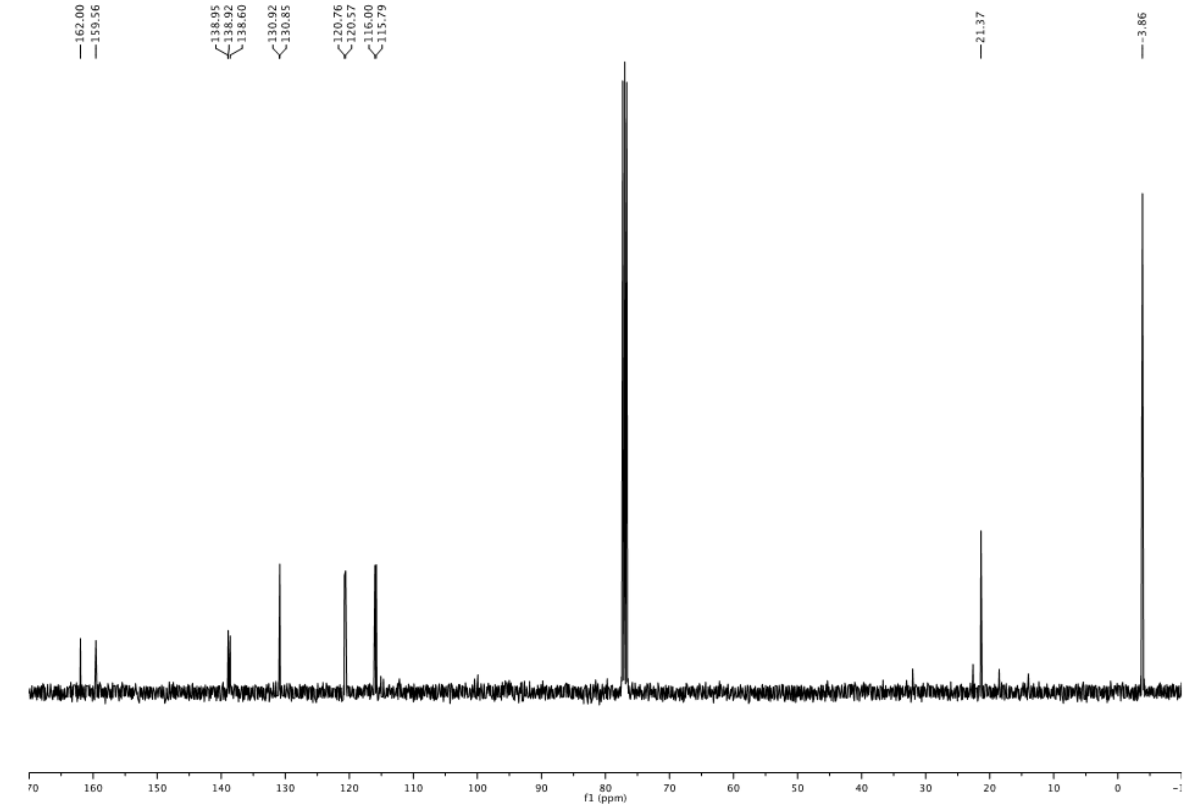
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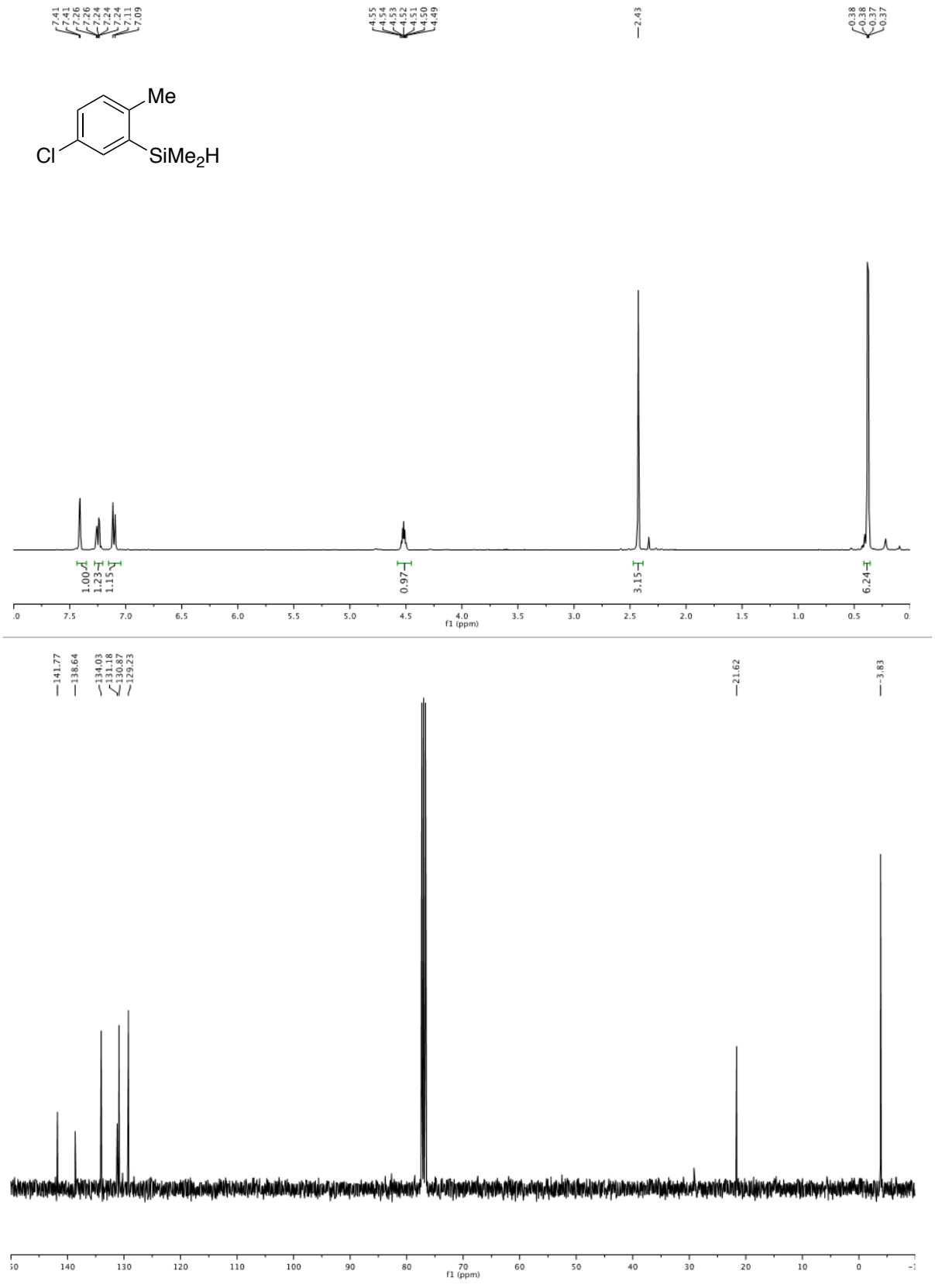
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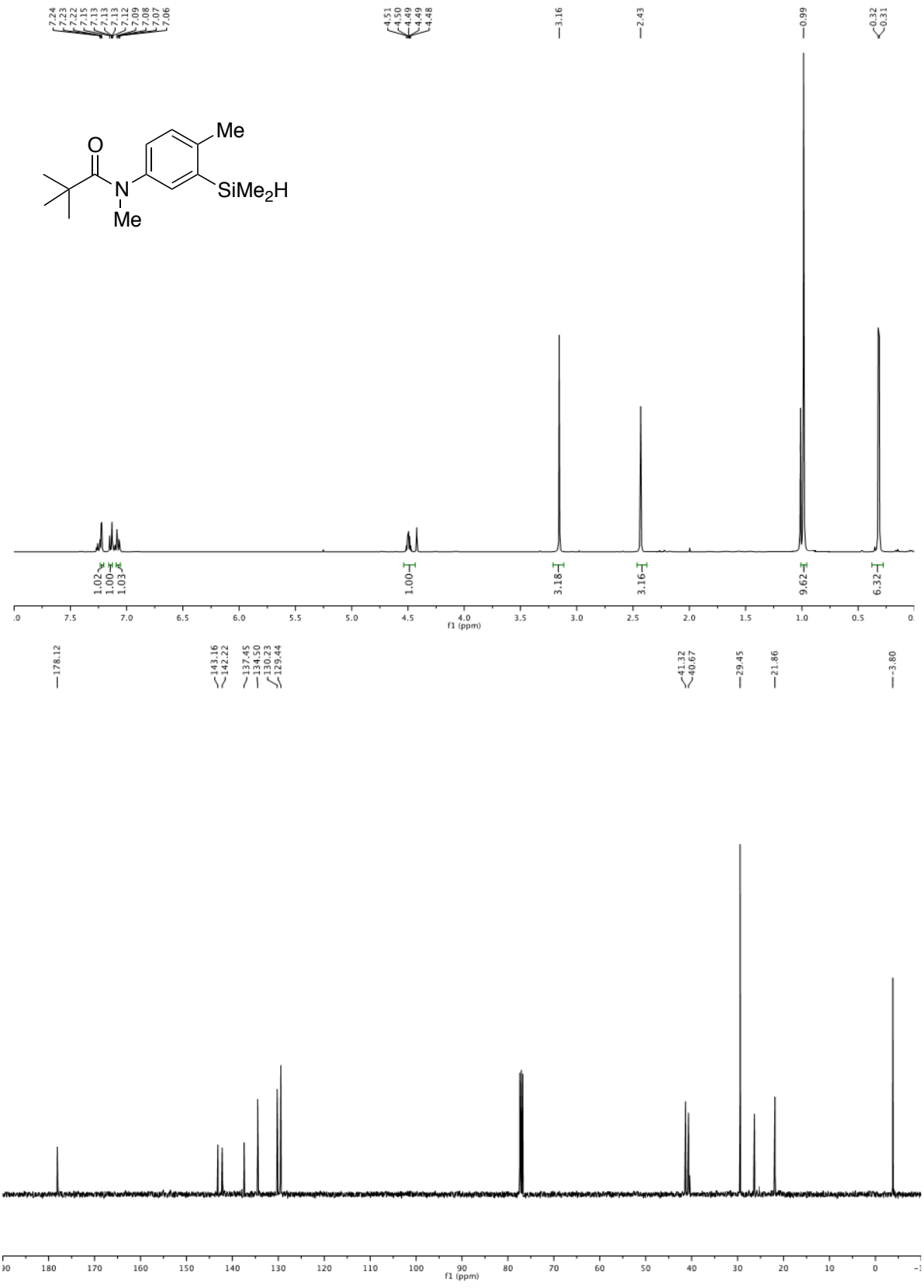
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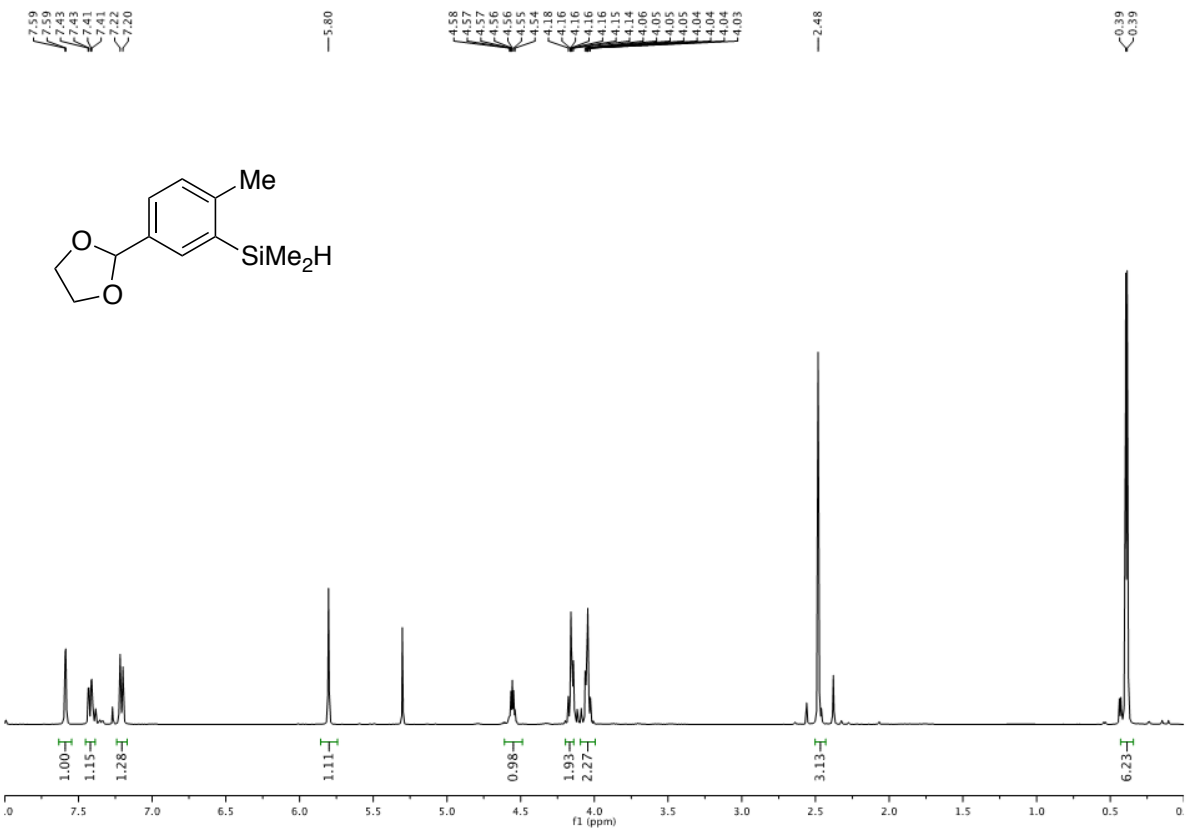
f1 (ppm)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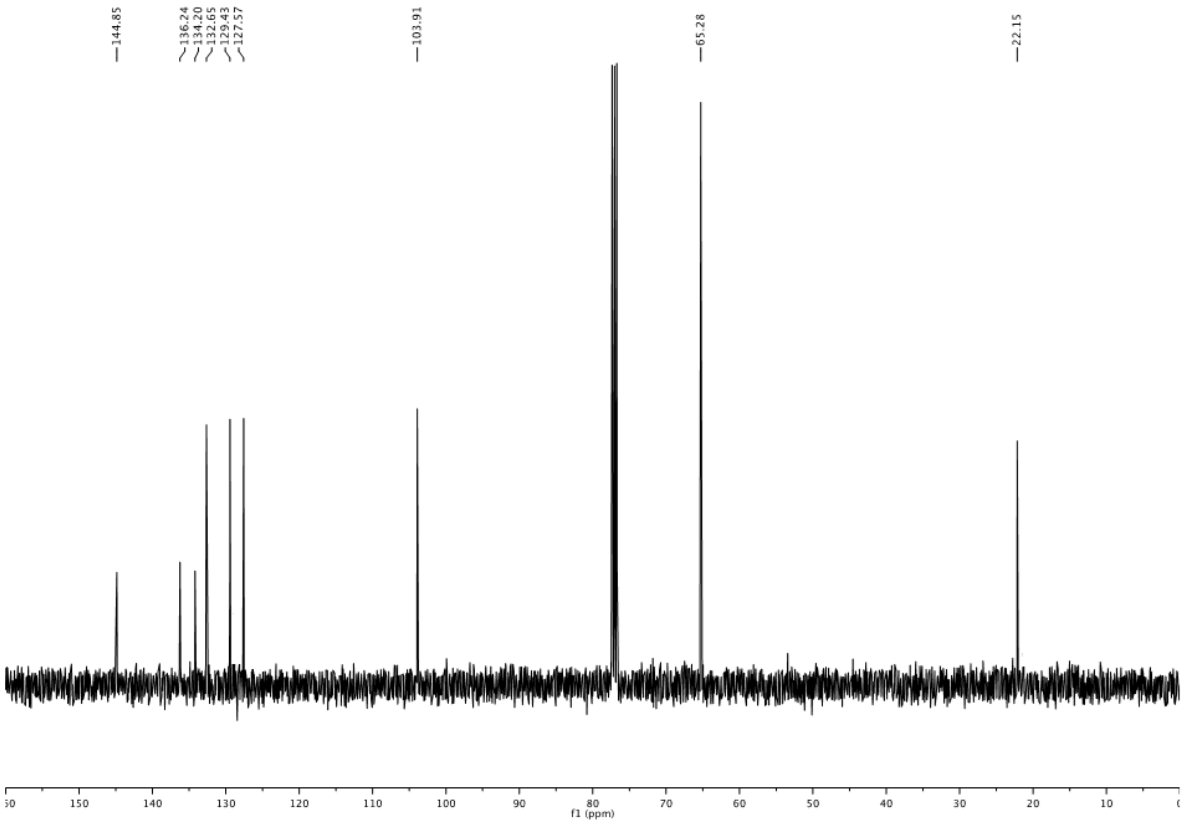
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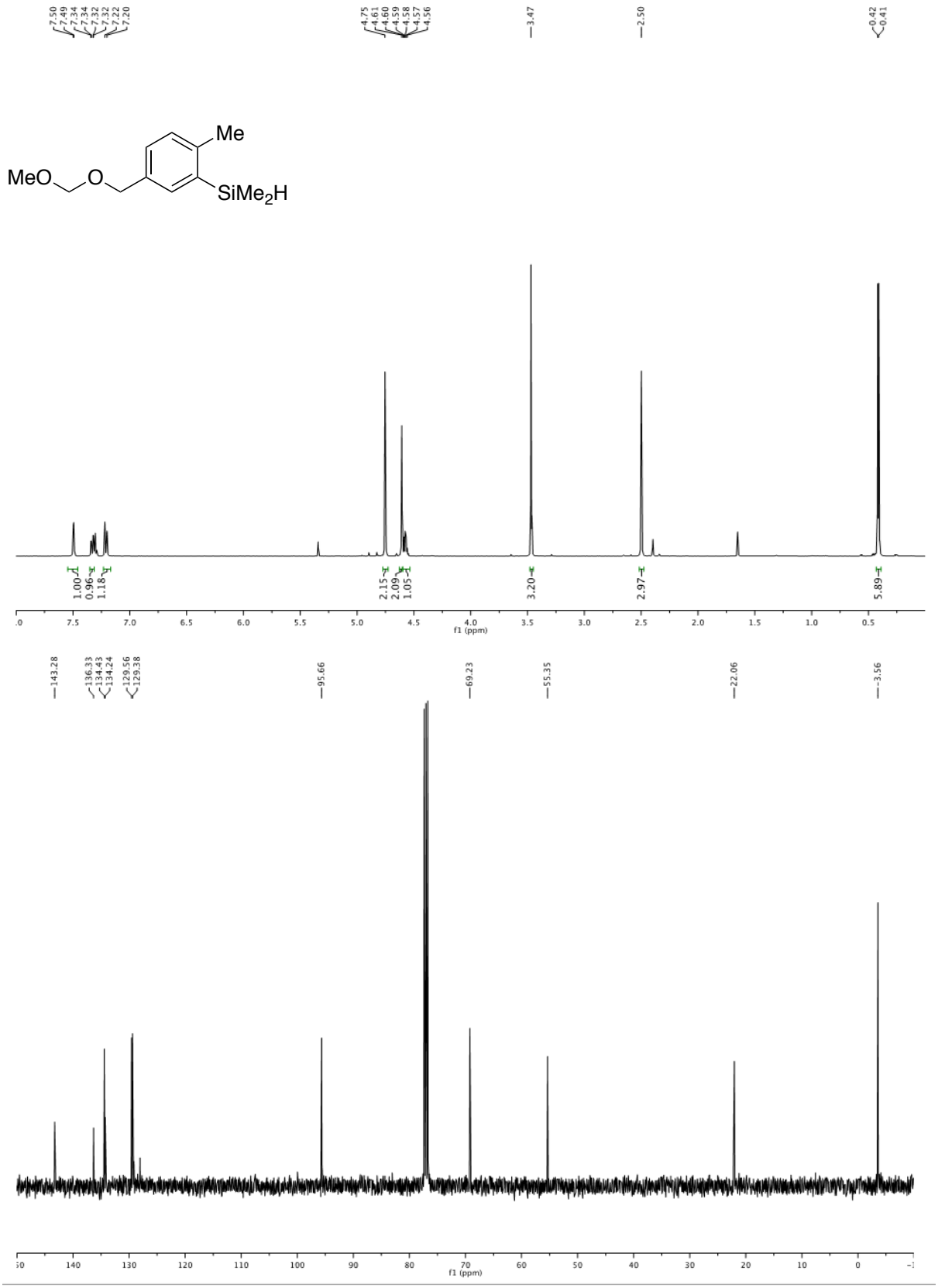
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4.57
4.56
3.47
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0.41
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MeO
O
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1.18
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2.09
1.05
3.20
2.97
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f1 (ppm)
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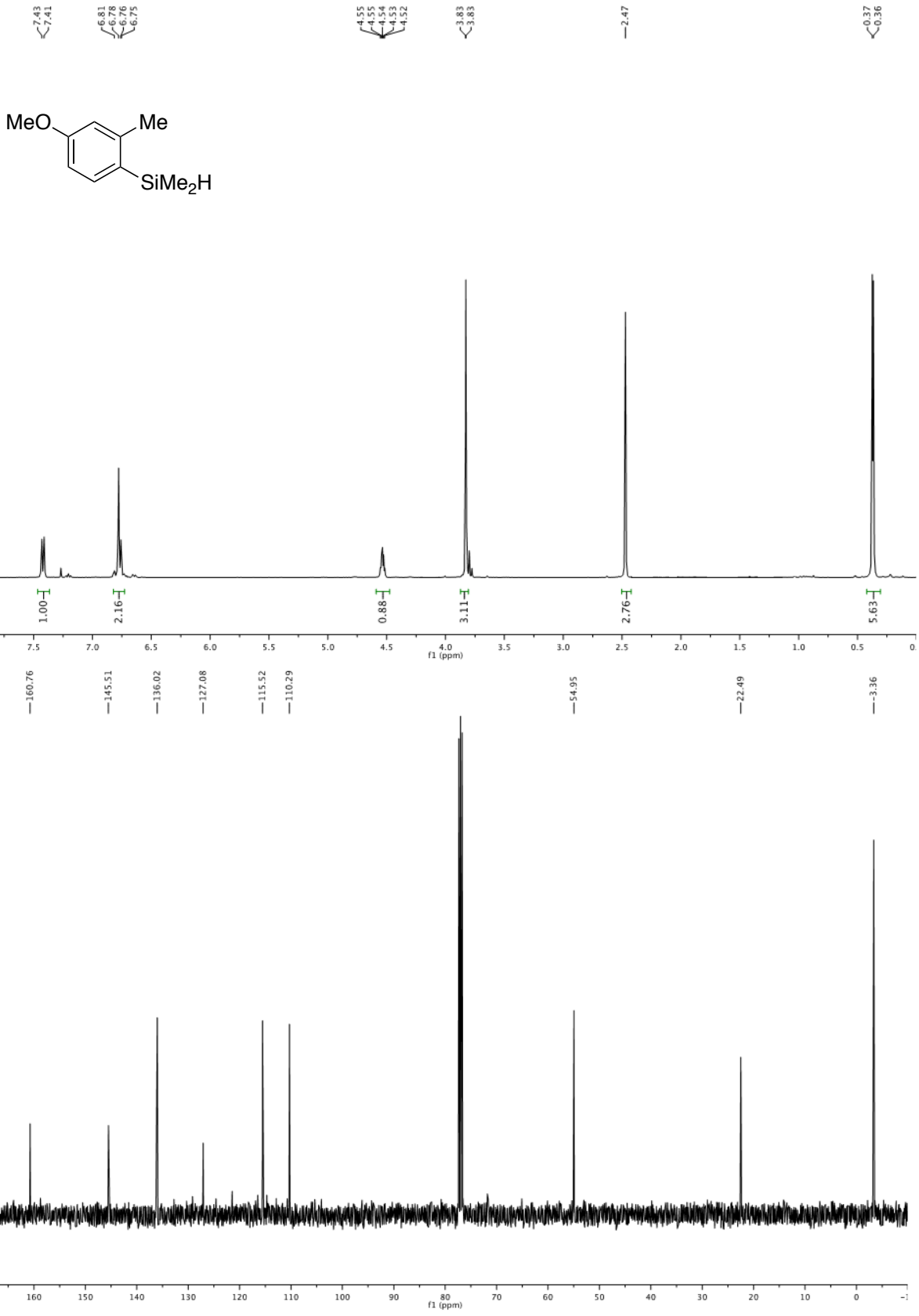
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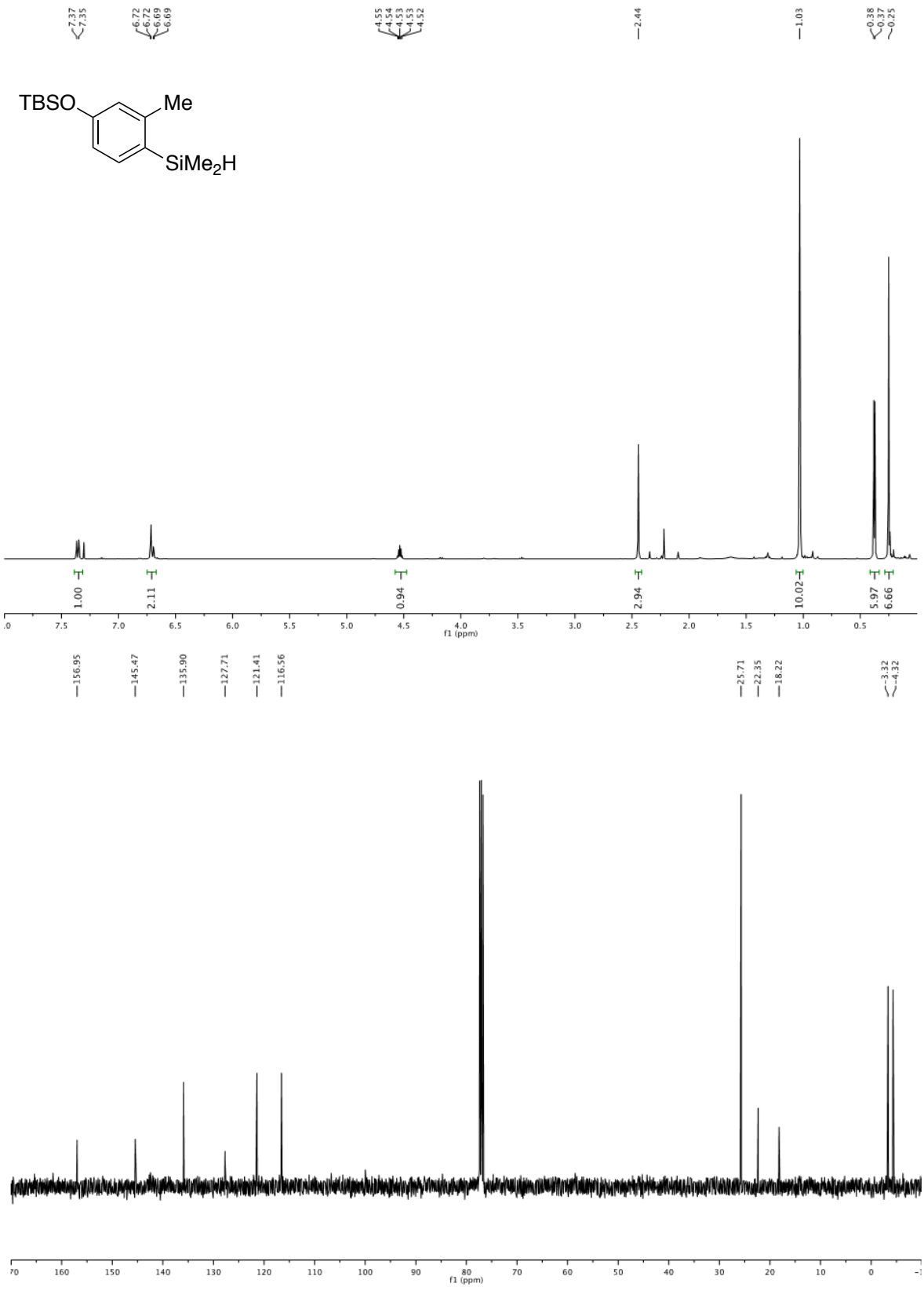
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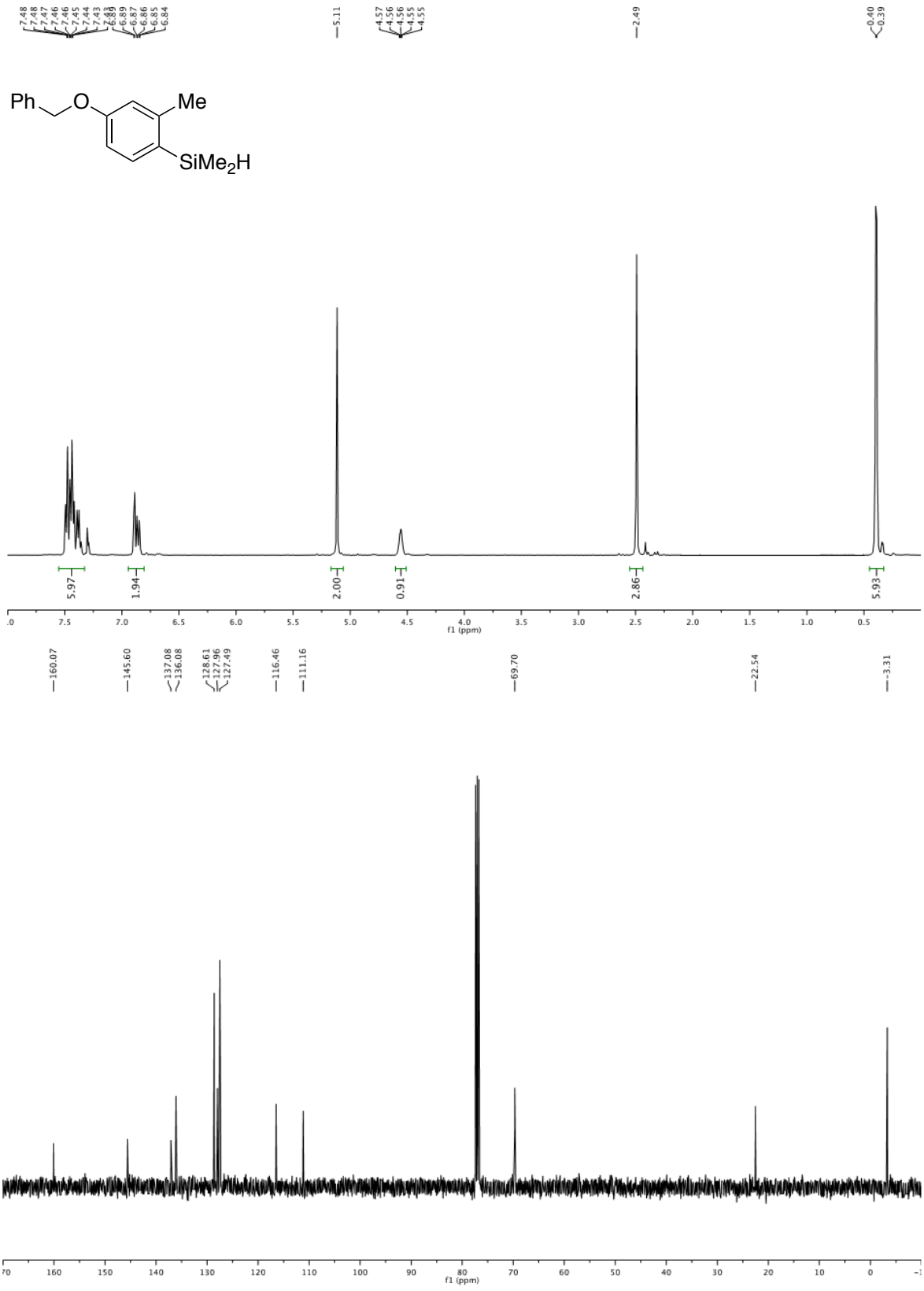
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4.56
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f1 (ppm)
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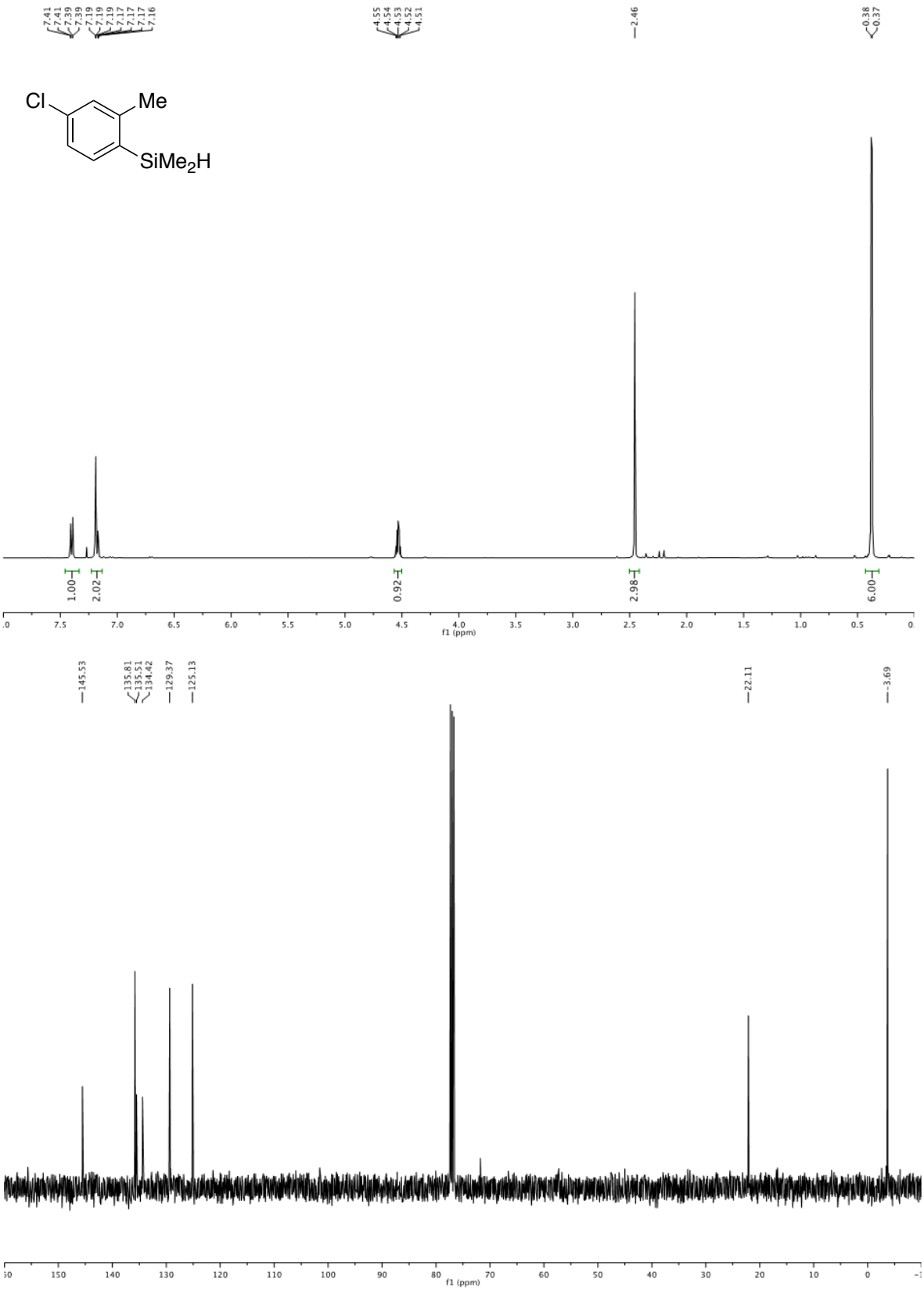

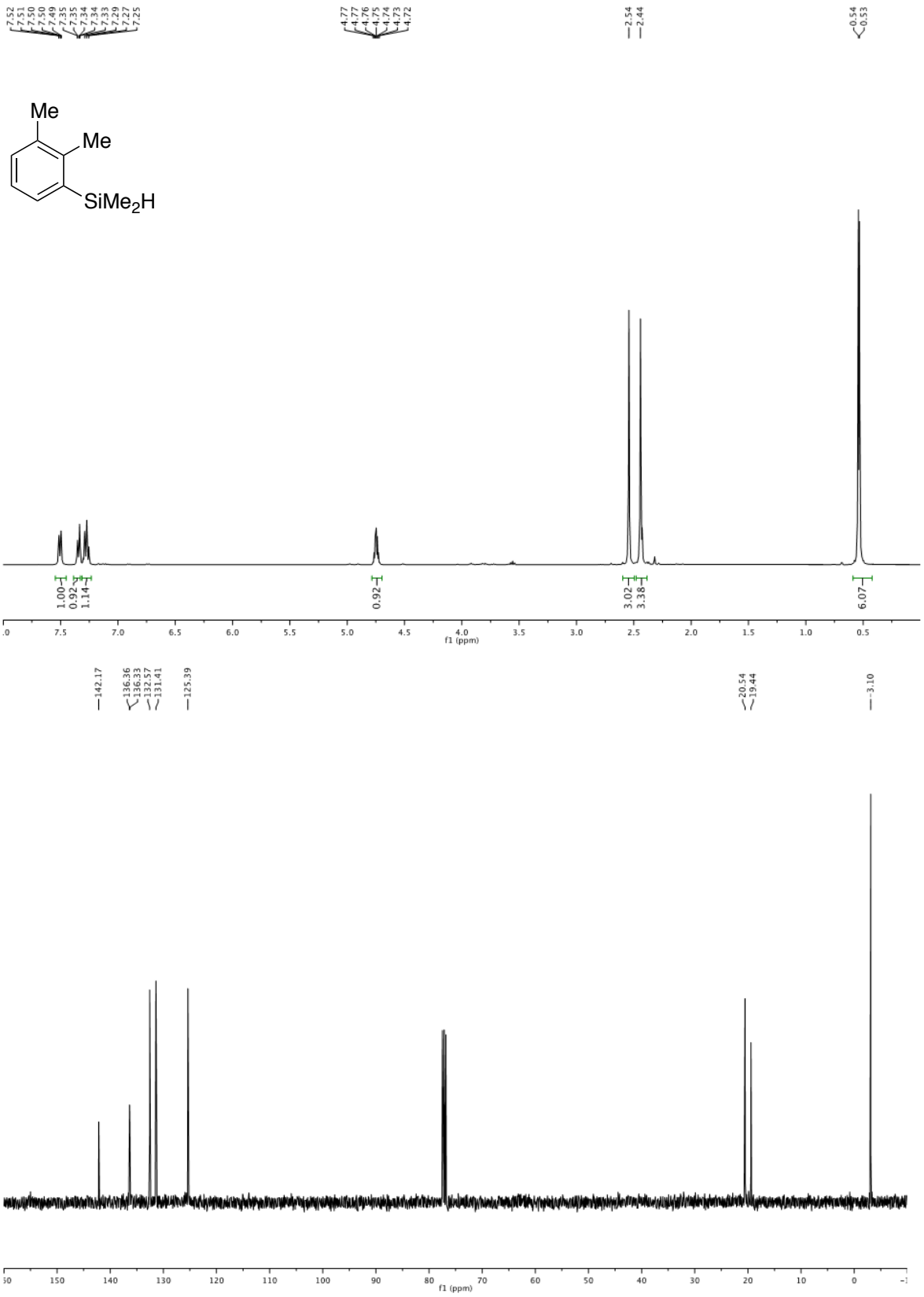
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6.07
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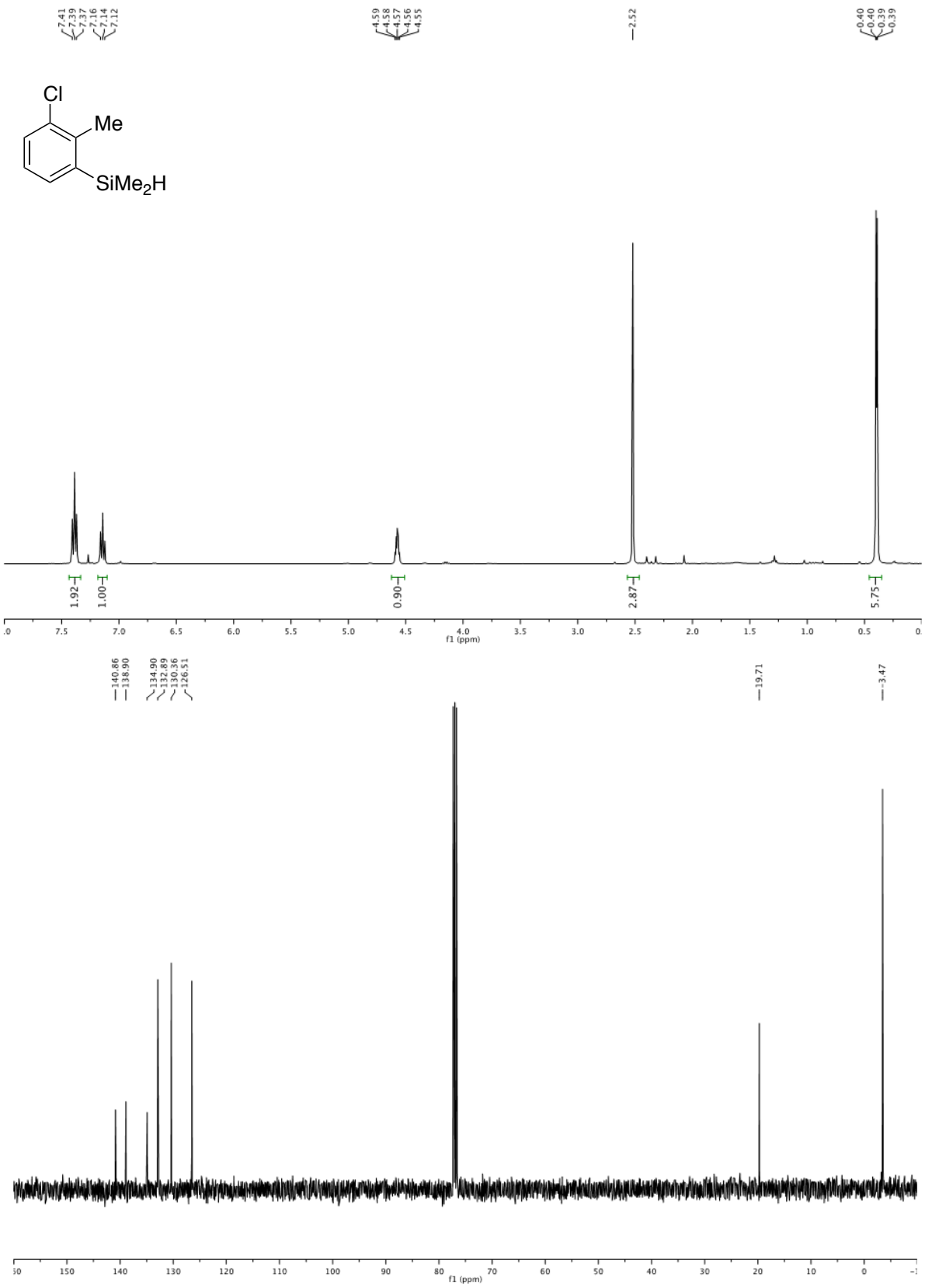
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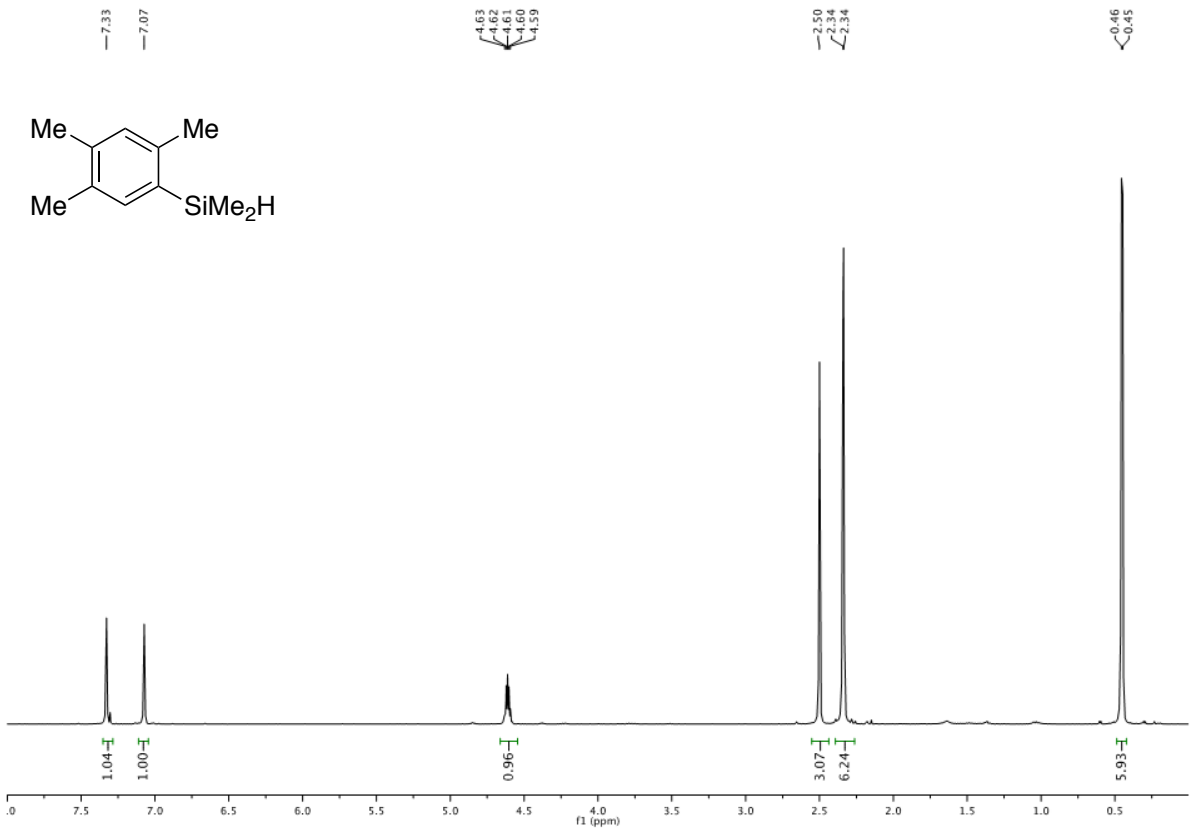
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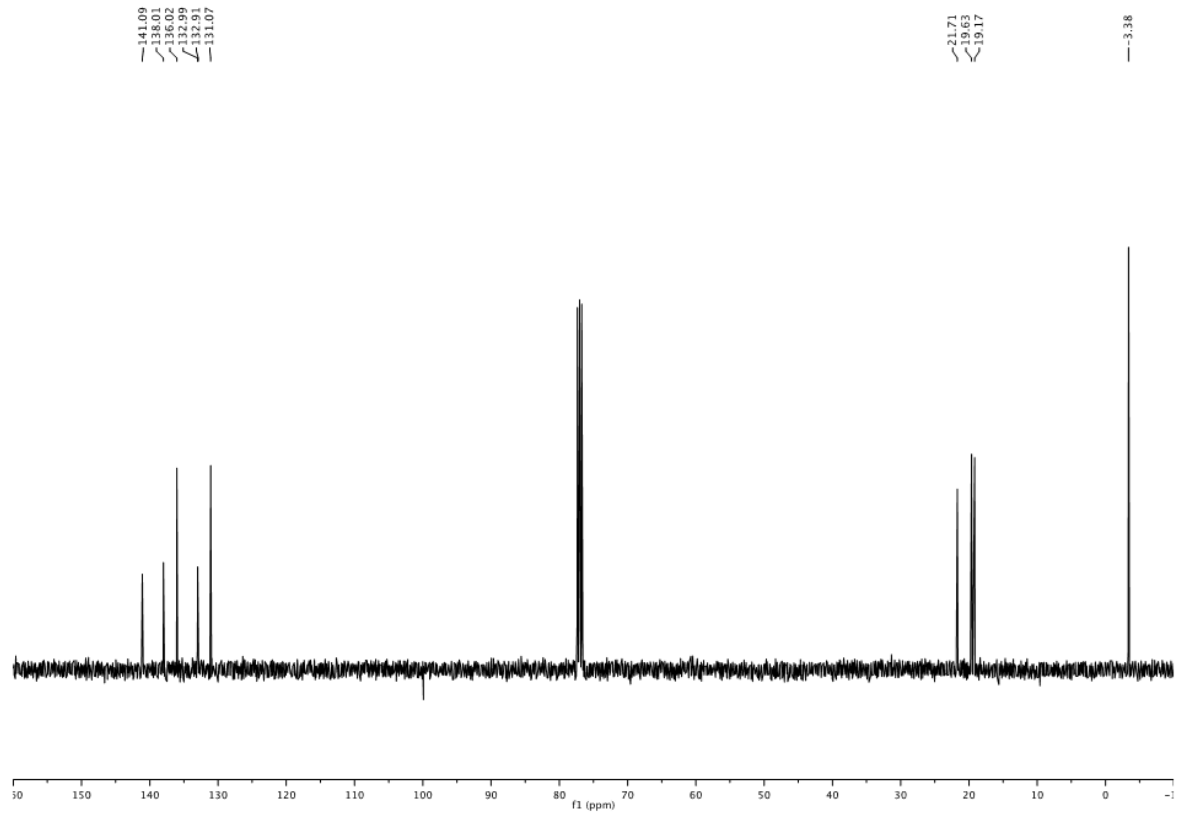
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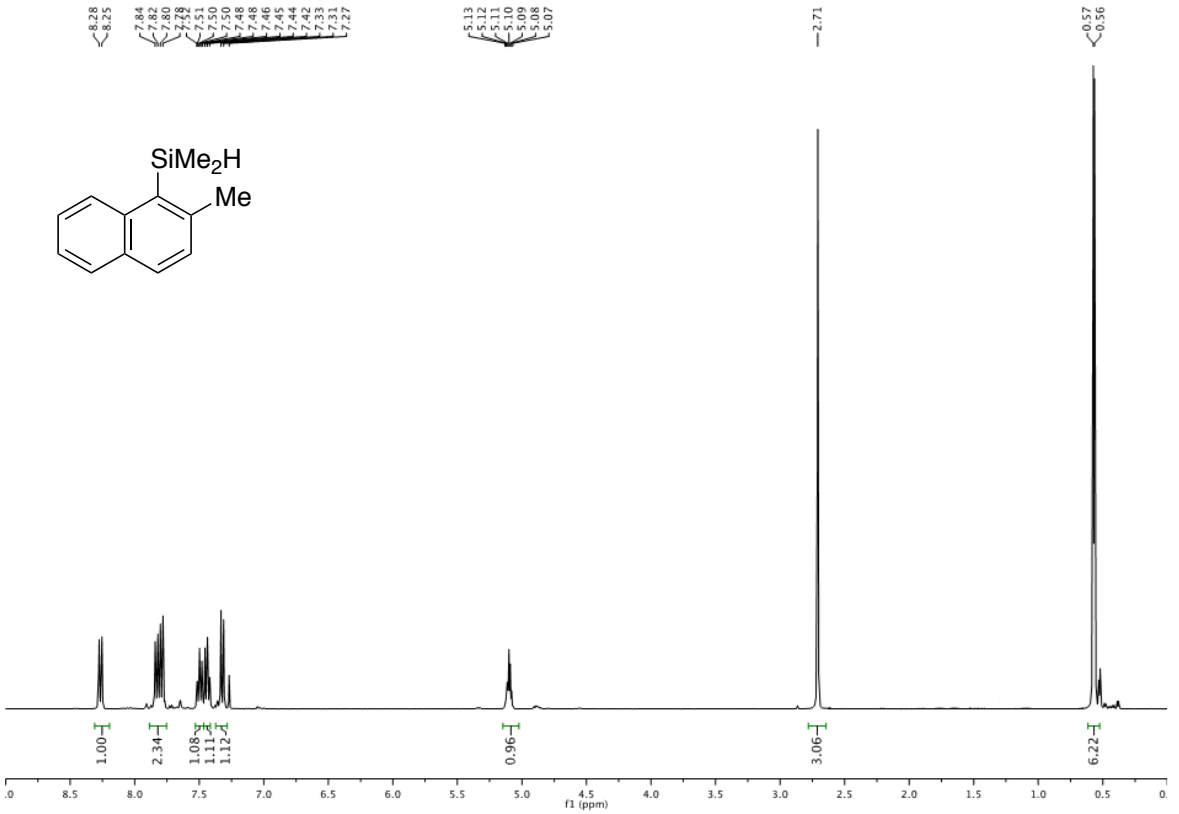
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7.31
7.27
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5.12
5.11
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5.09
5.08
5.07
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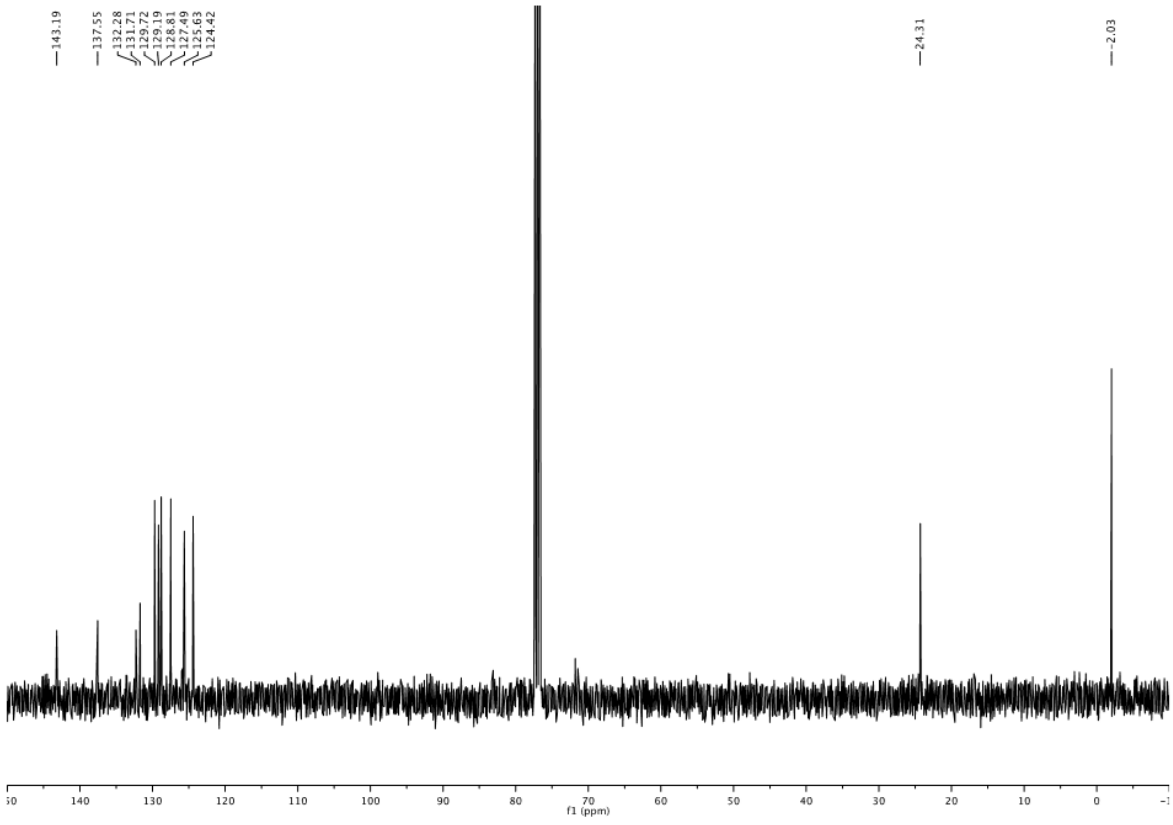
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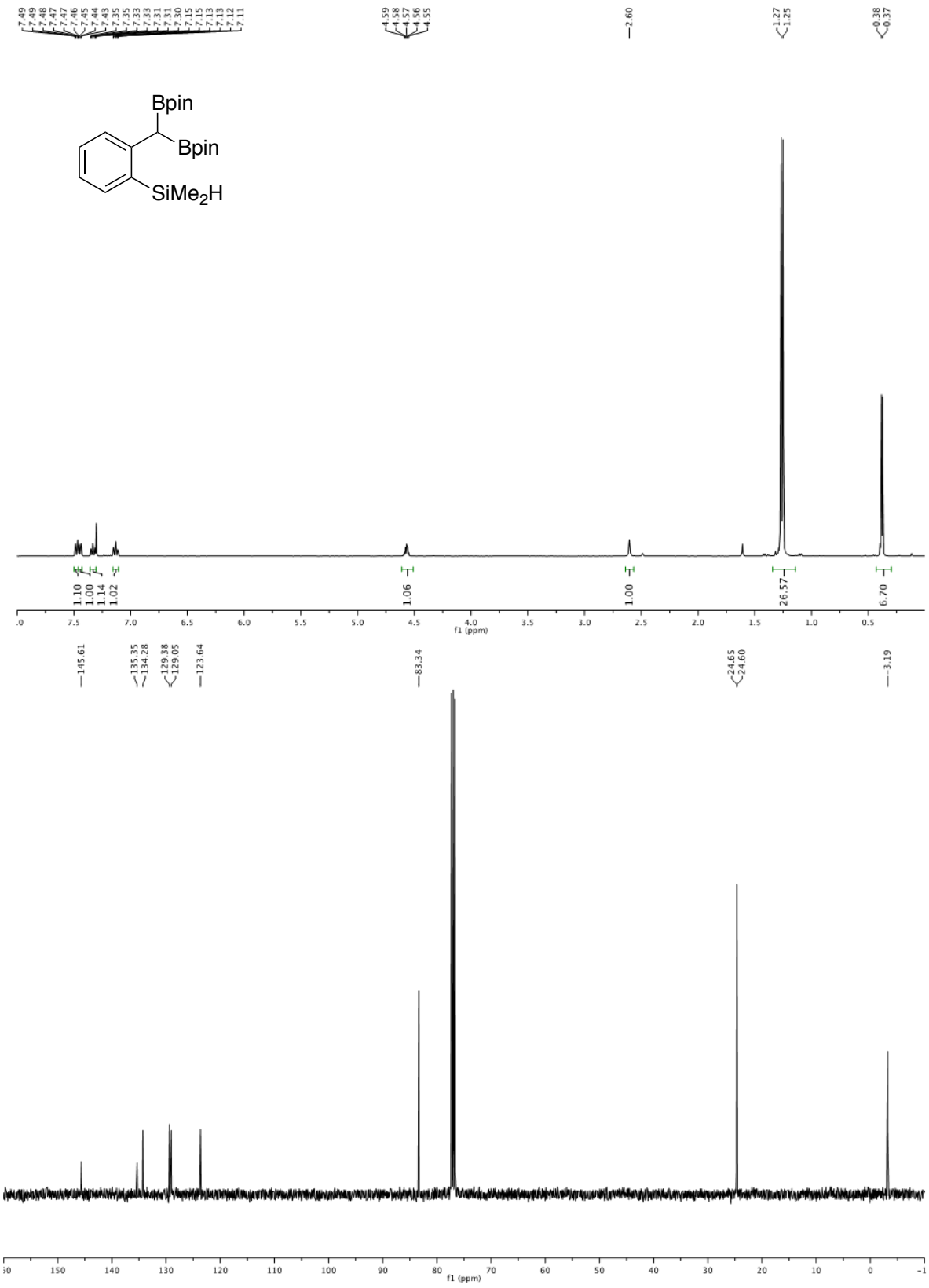
f1 (ppm)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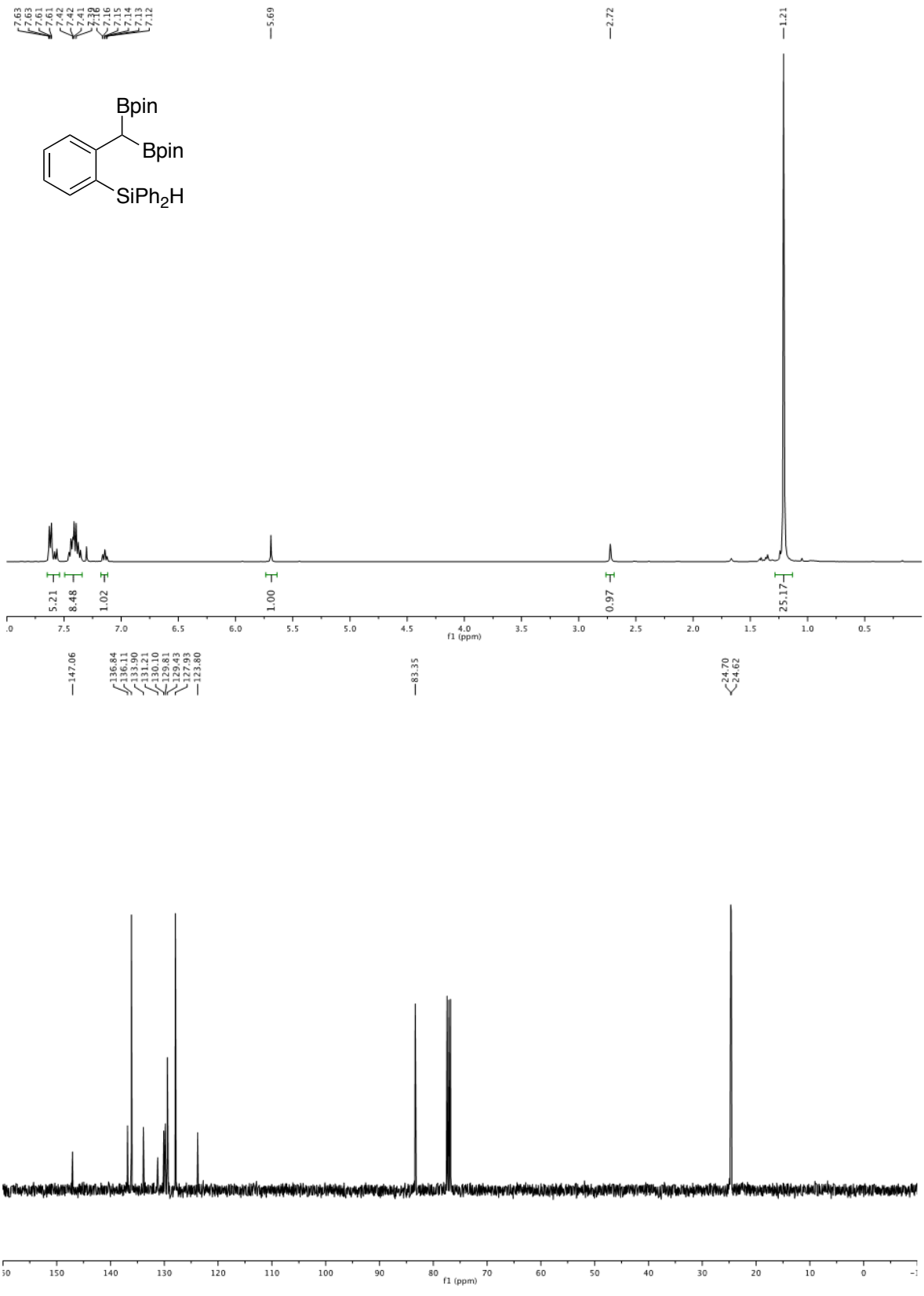
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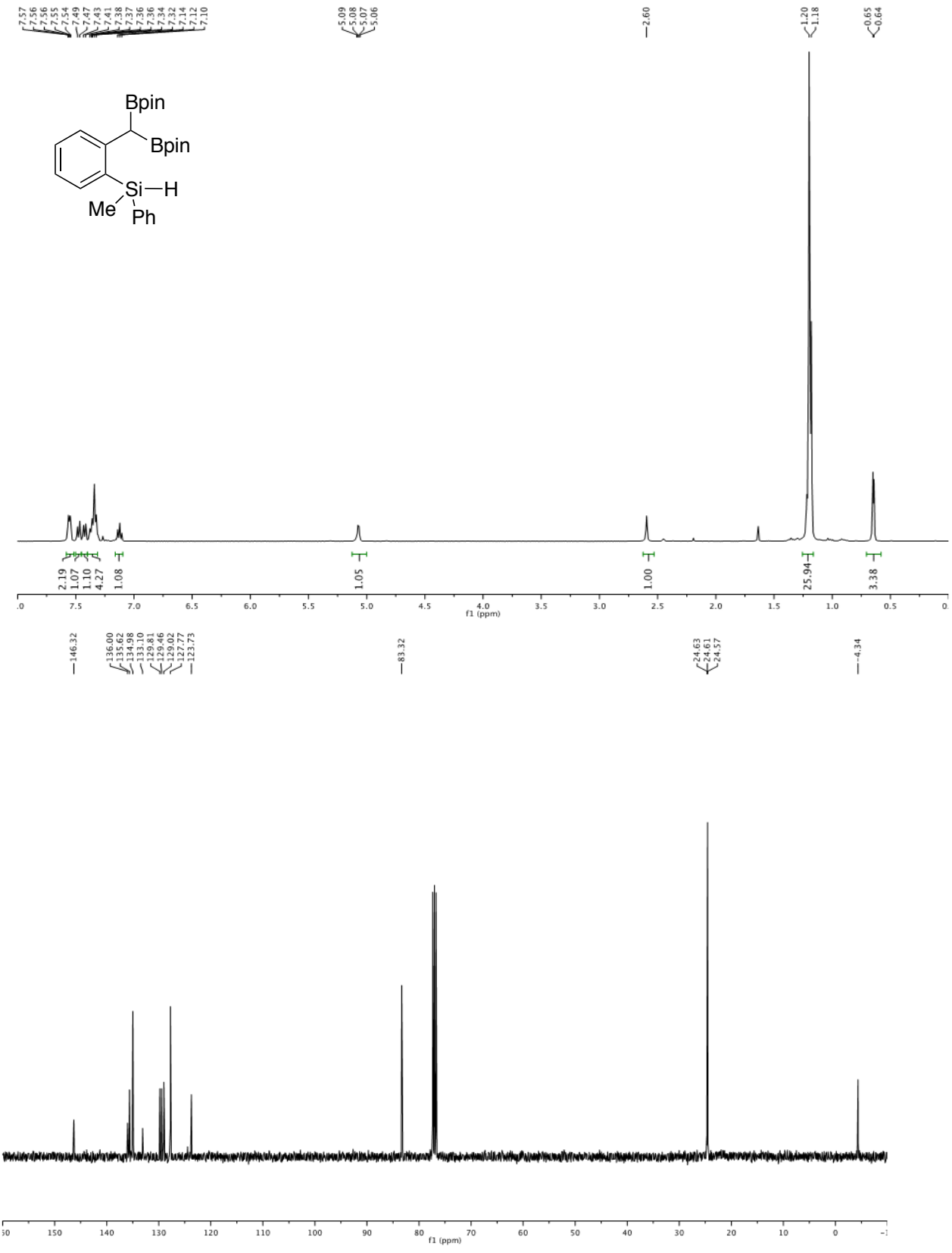
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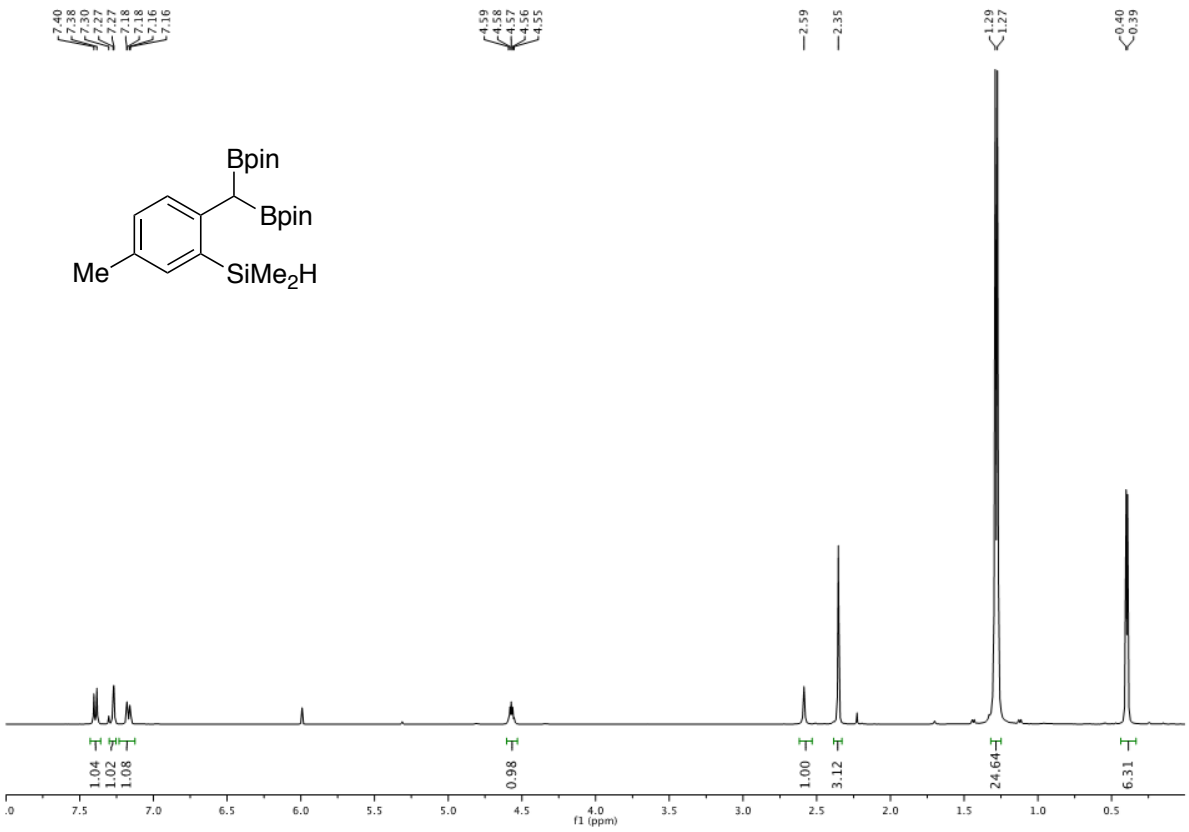
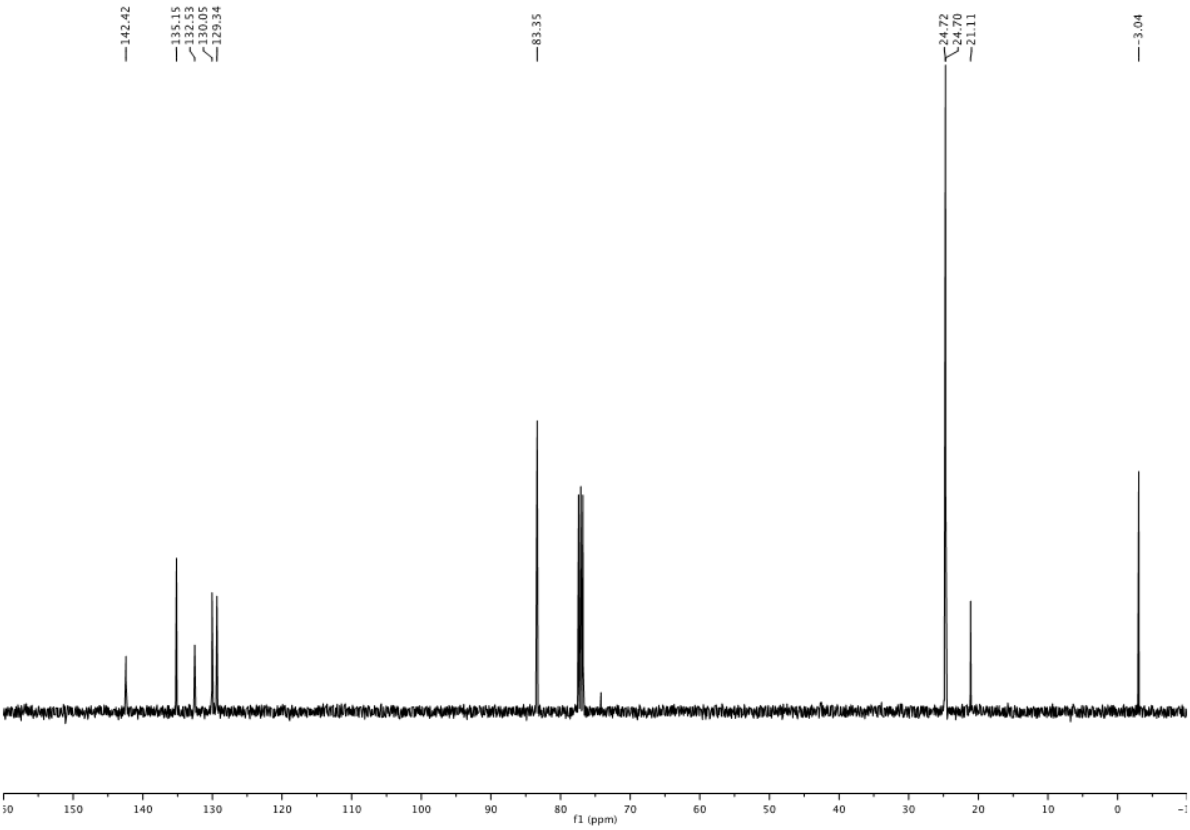
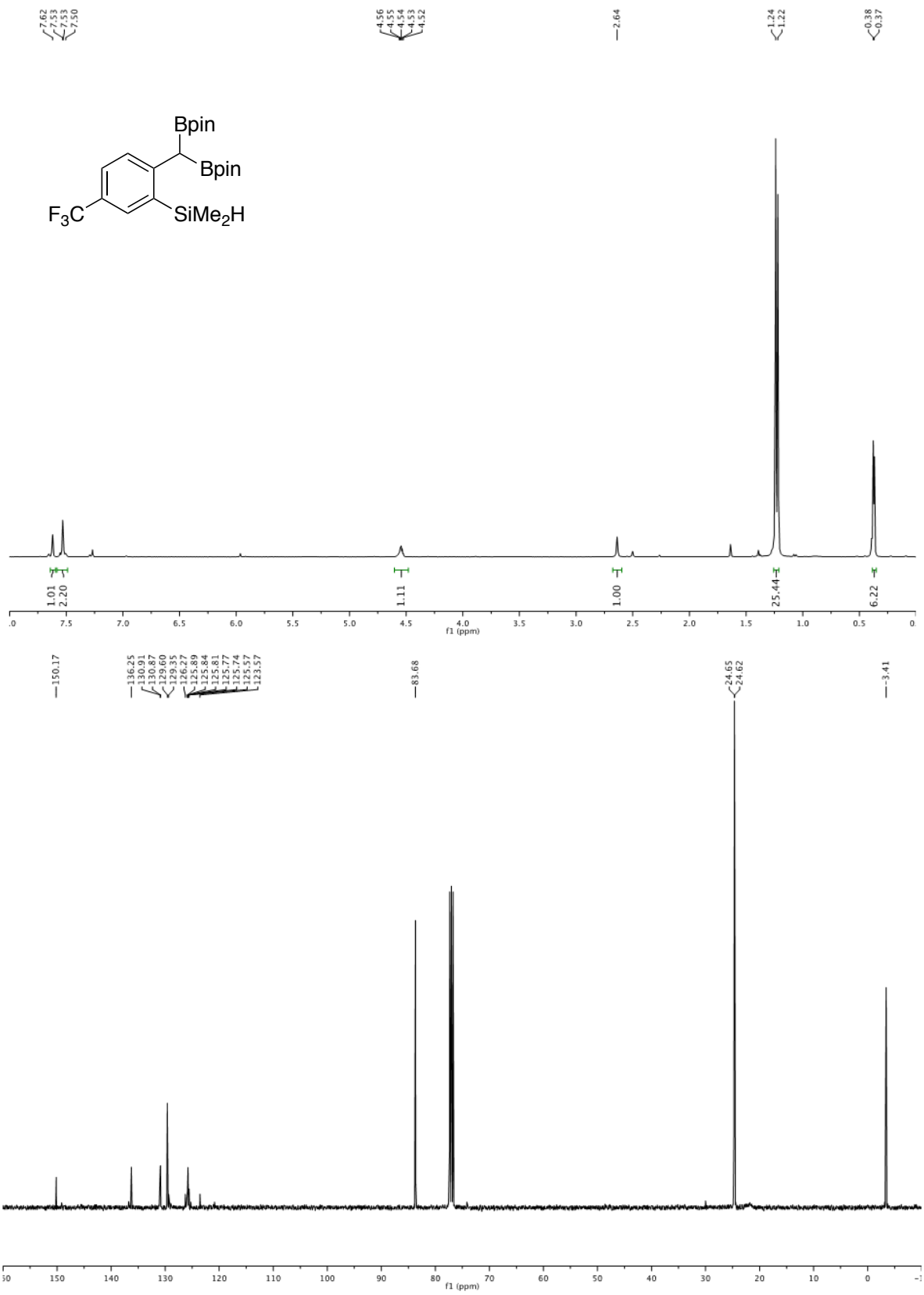
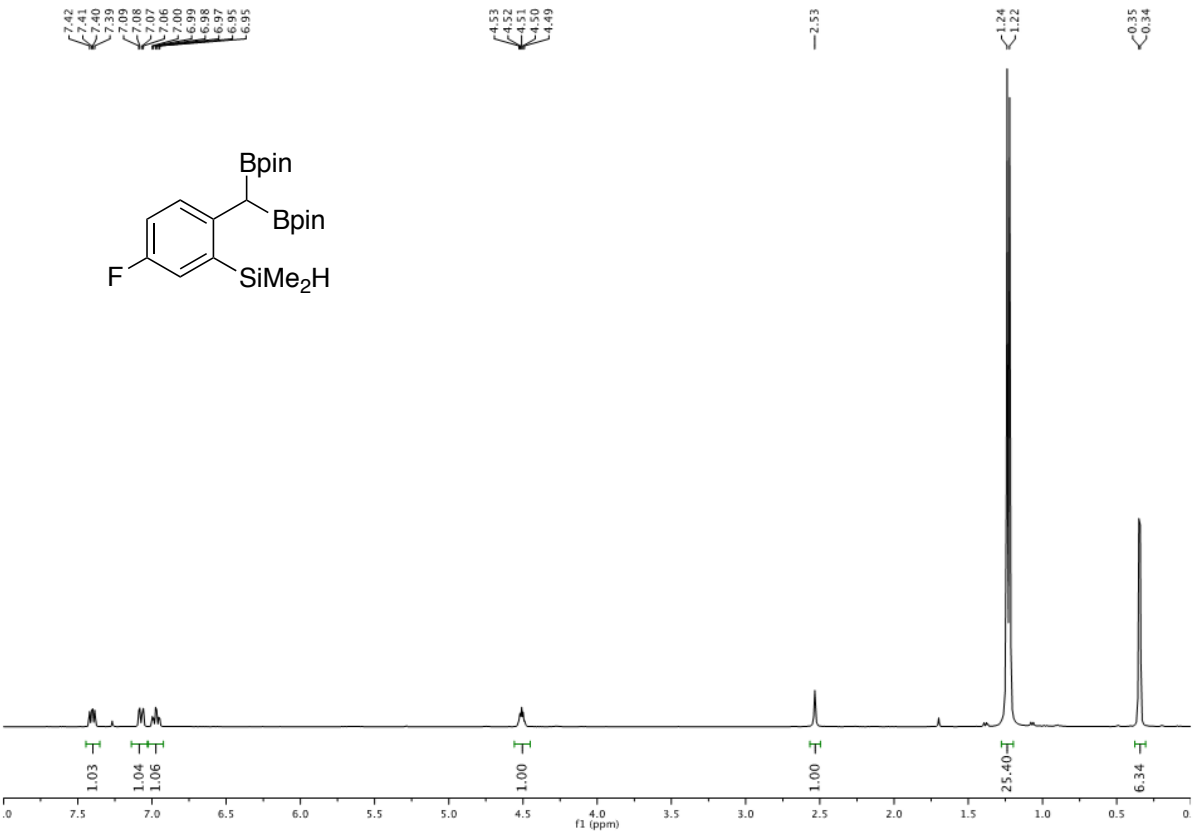
f1 (ppm)





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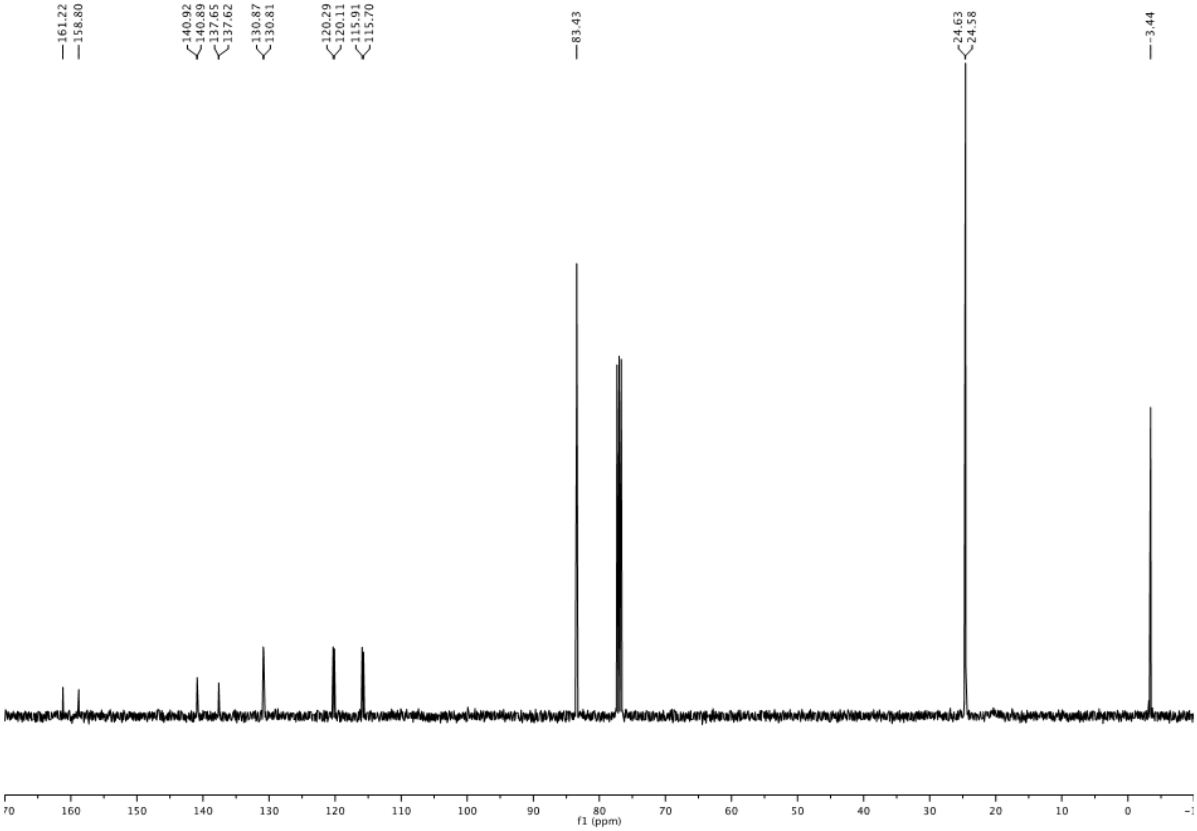
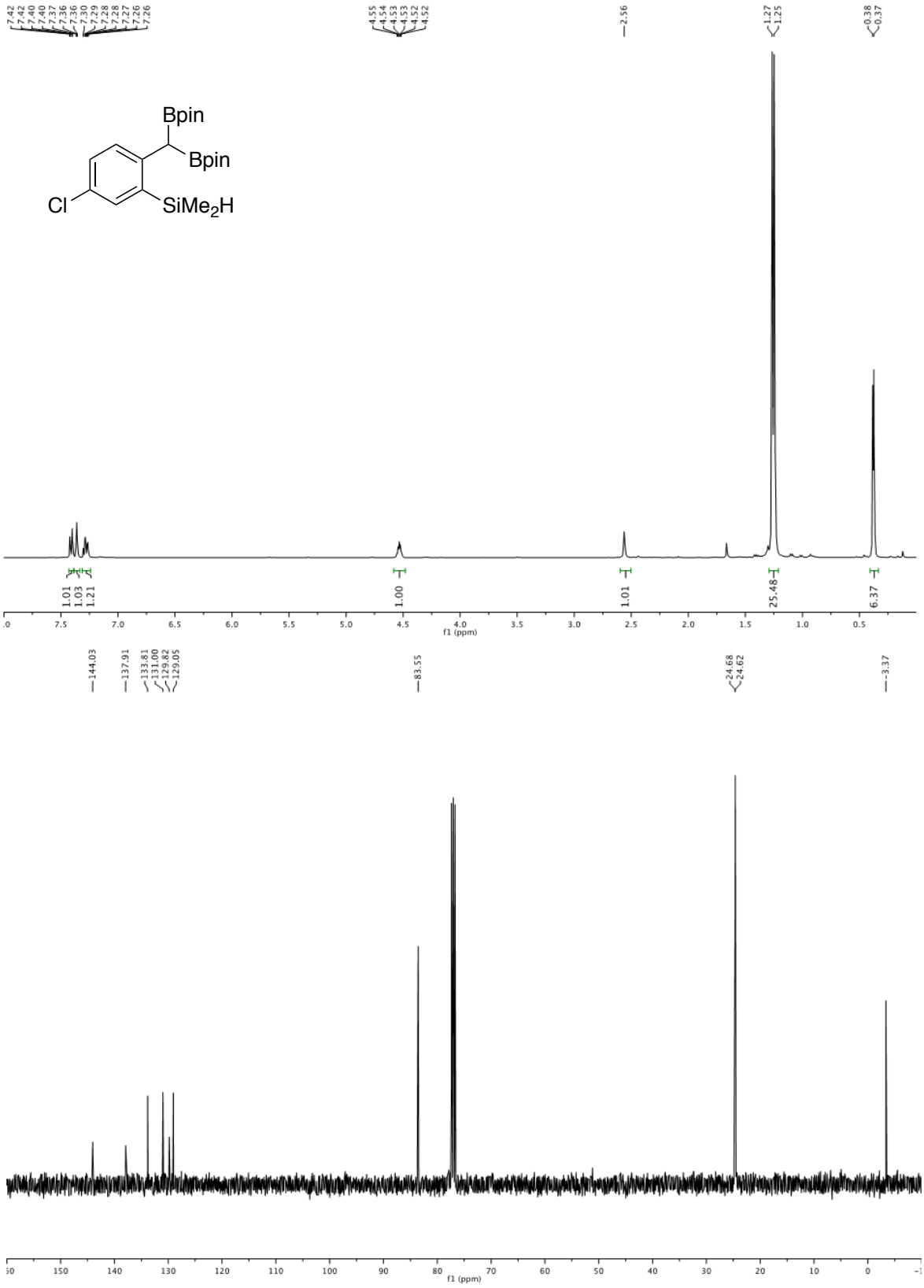
Bpin
F
SiMe2H
f1 (ppm)


f1 (ppm)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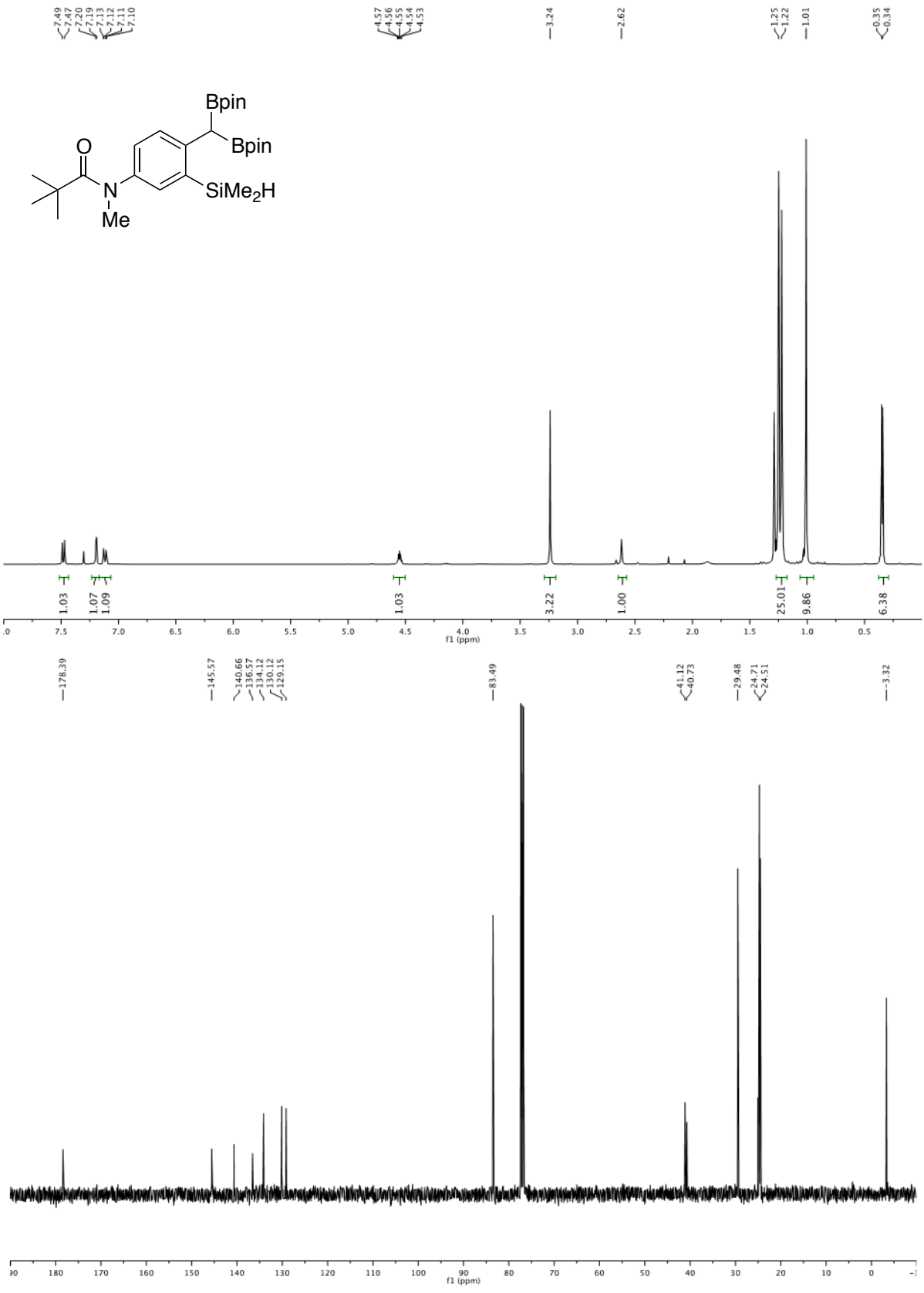
Bpin
Cl
SiMe2H
f1 (ppm)
f1 (ppm)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Bpin
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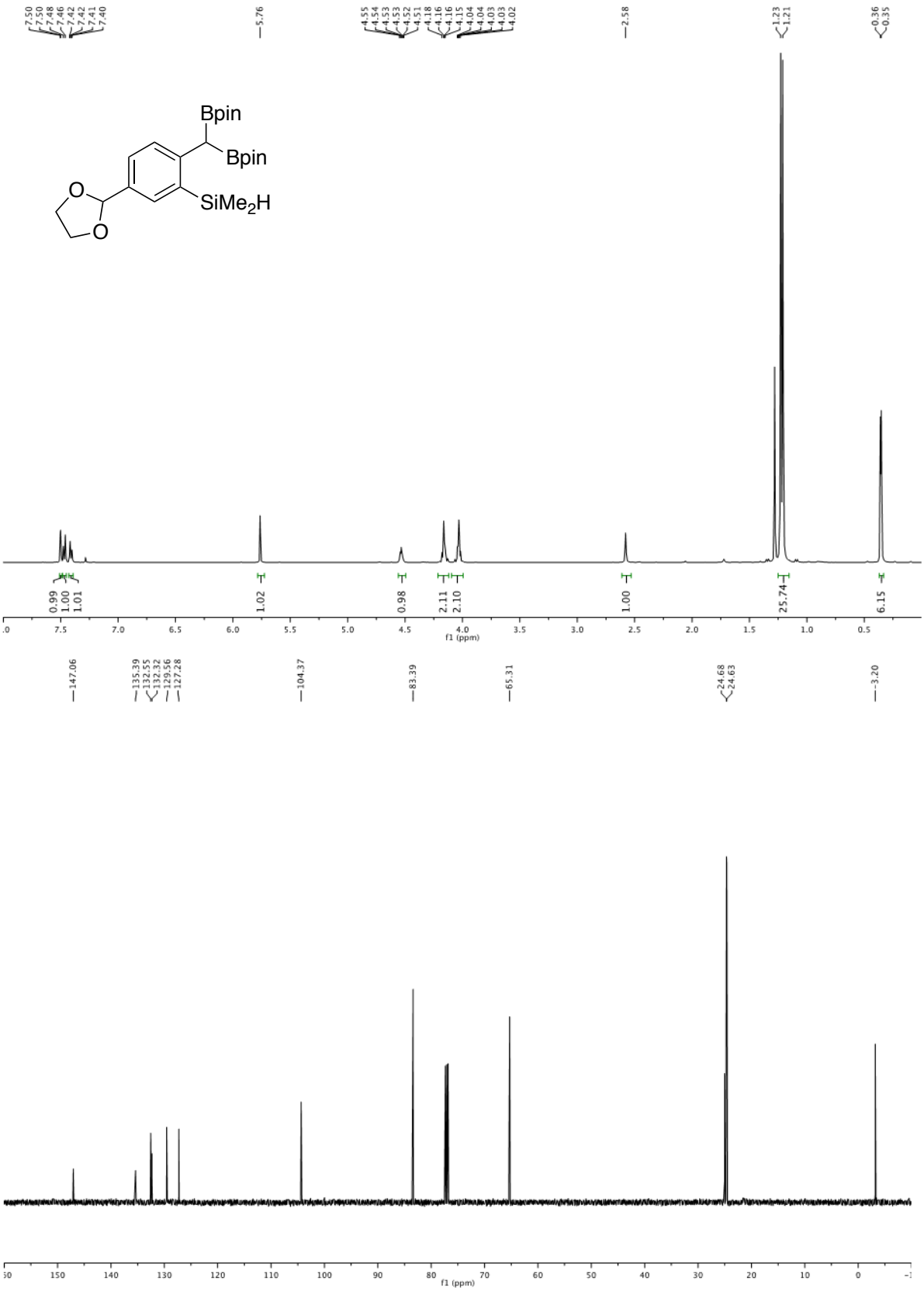
N
Me
SiMe2H
f1 (ppm)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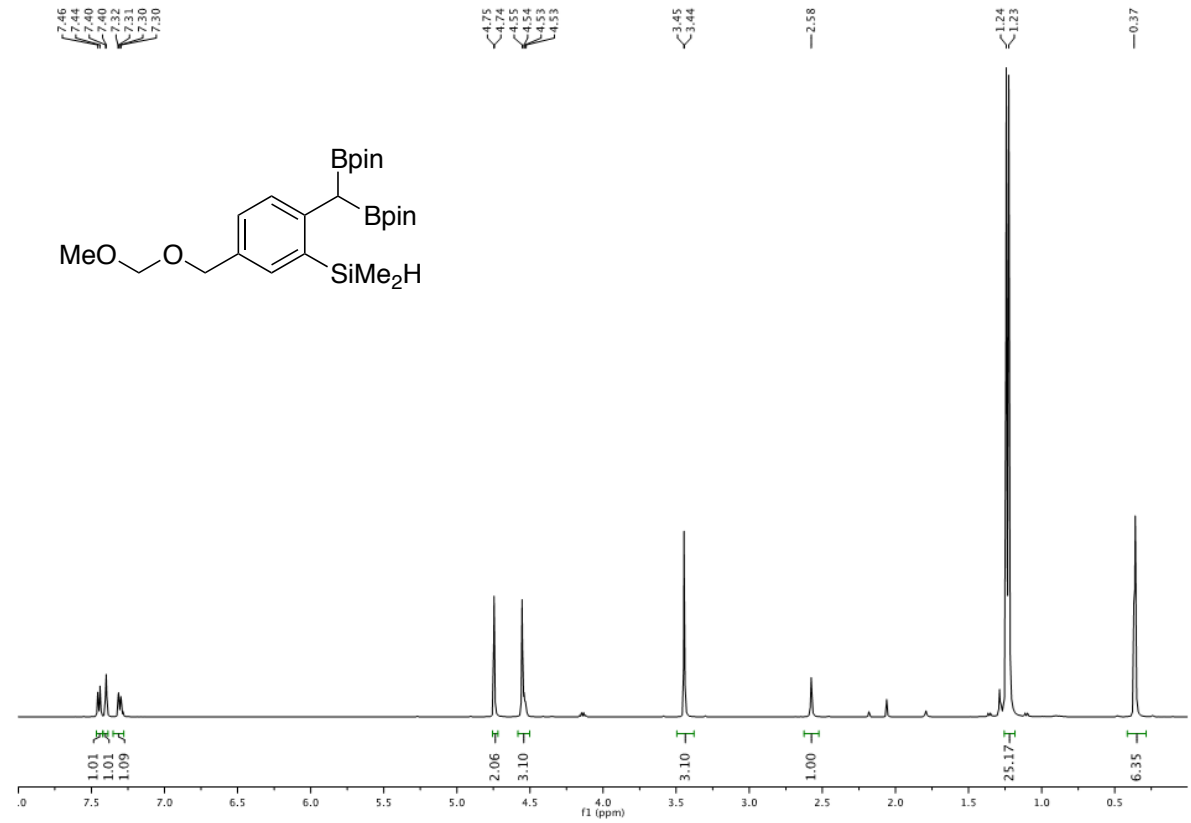
Bpin
SiMe2H
O
O
f1 (ppm)
f1 (ppm)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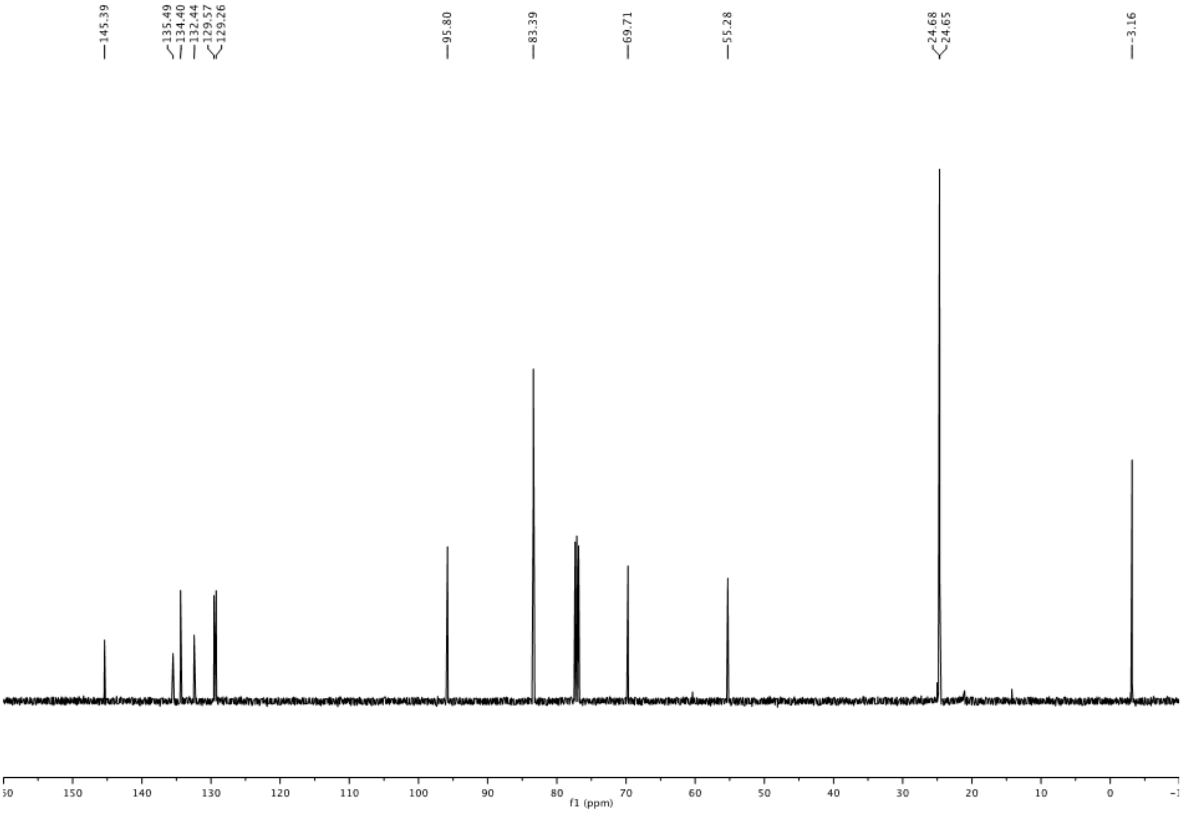
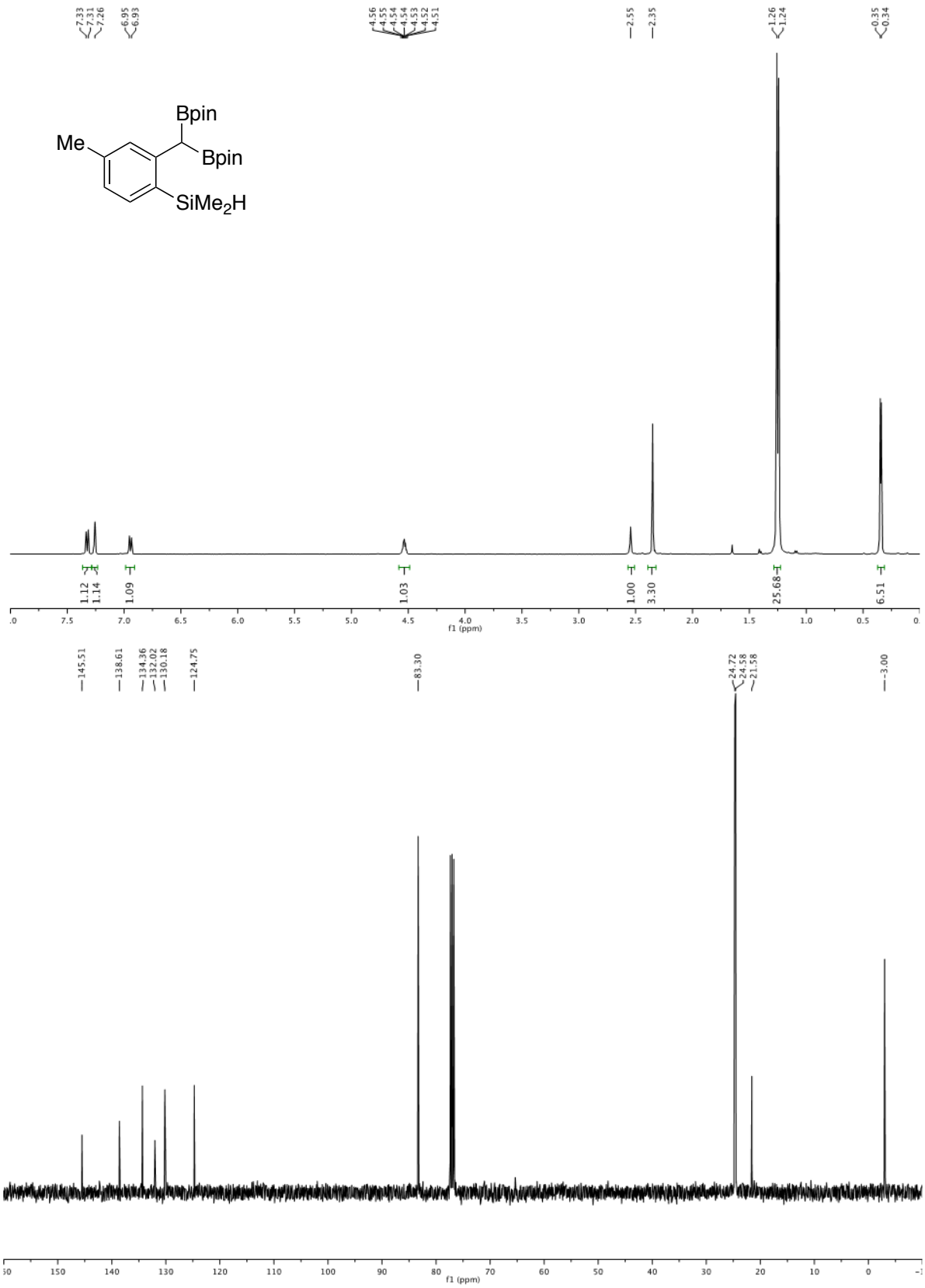
Bpin
MeO
O
SiMe2H
f1 (ppm)


f1 (ppm)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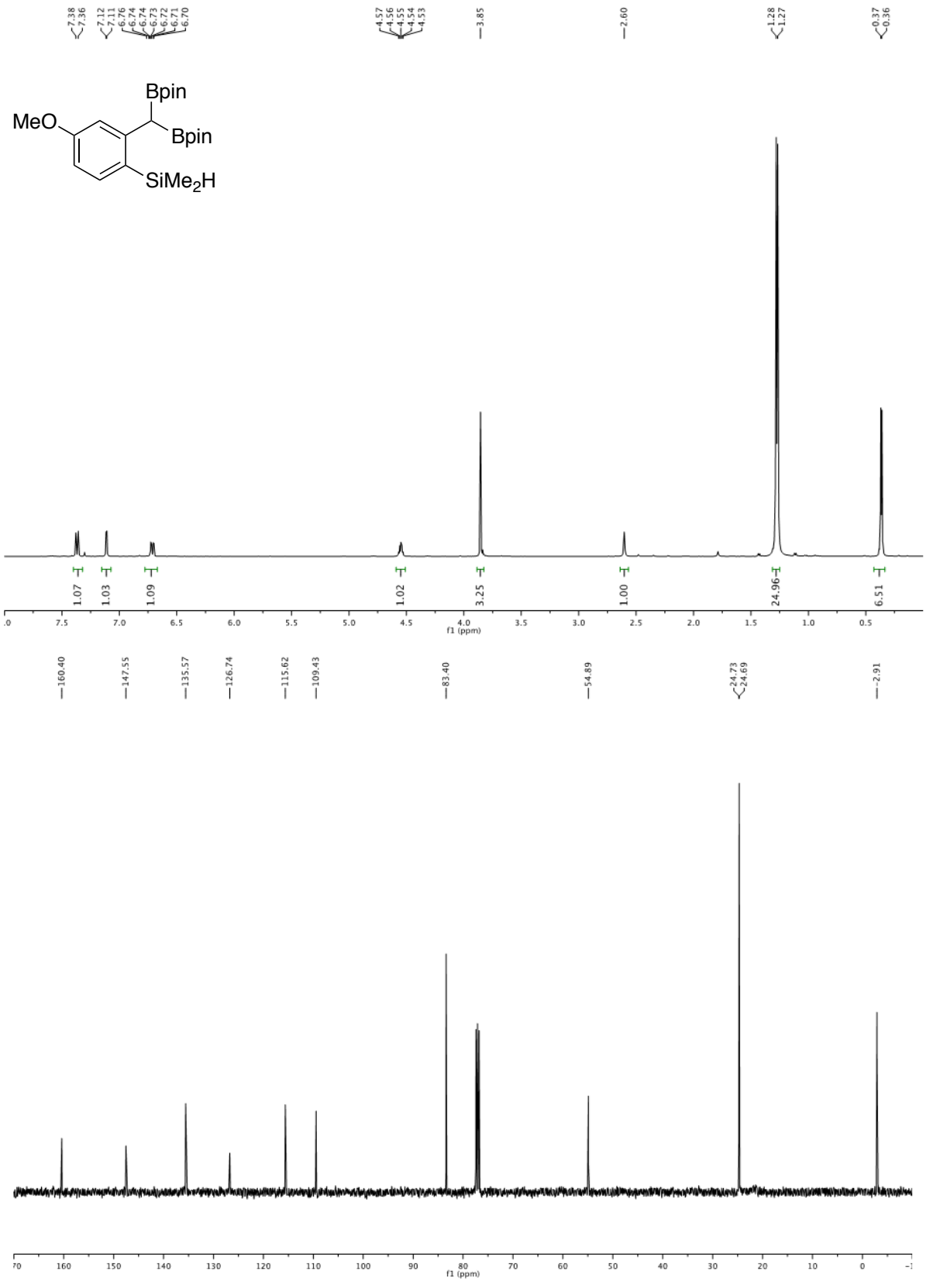
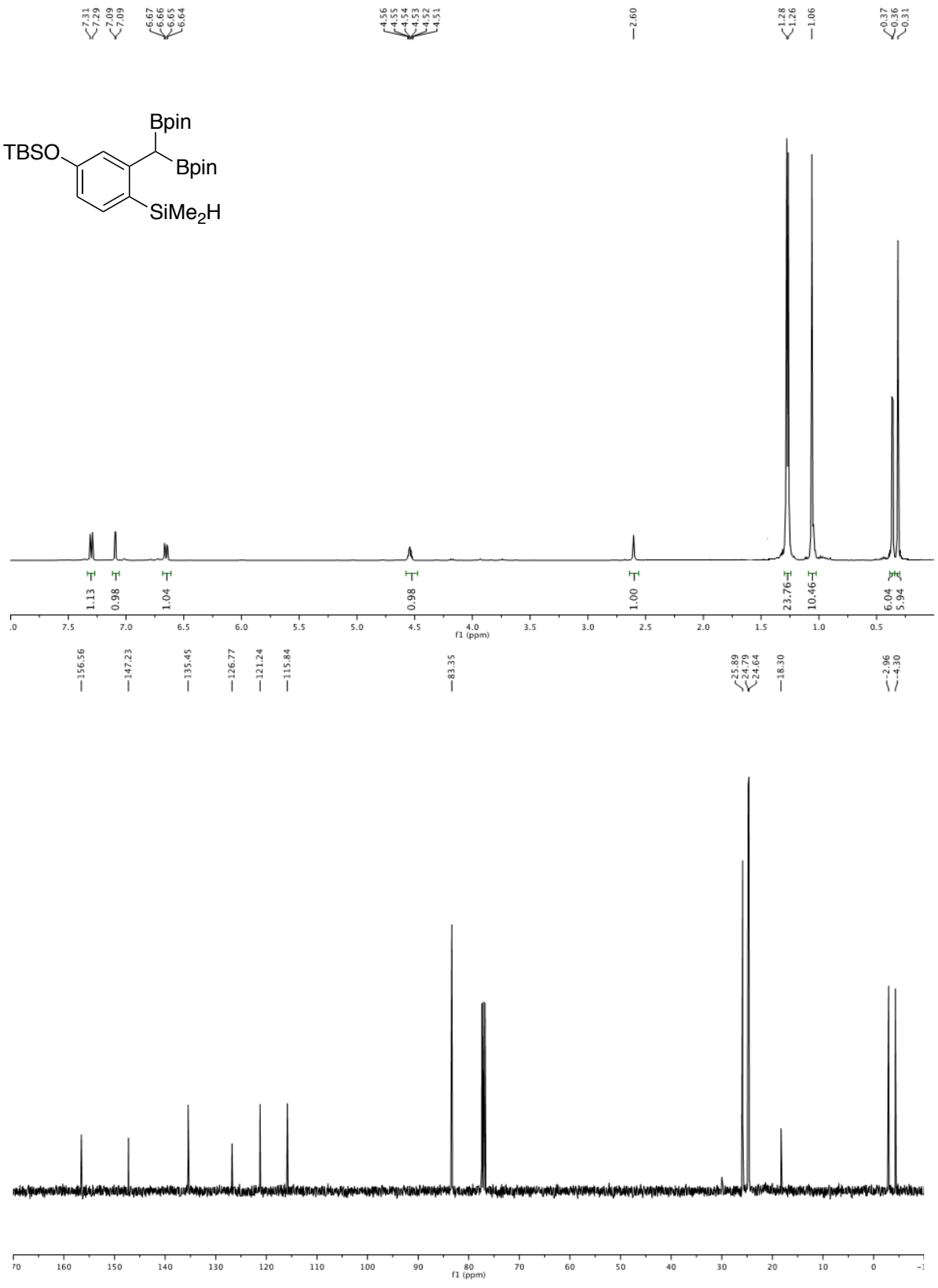
Me
Bpin
SiMe2H
f1 (ppm)
f1 (ppm)


Bpin
MeO
Bpin
SiMe2H
f1 (ppm)
f1 (ppm)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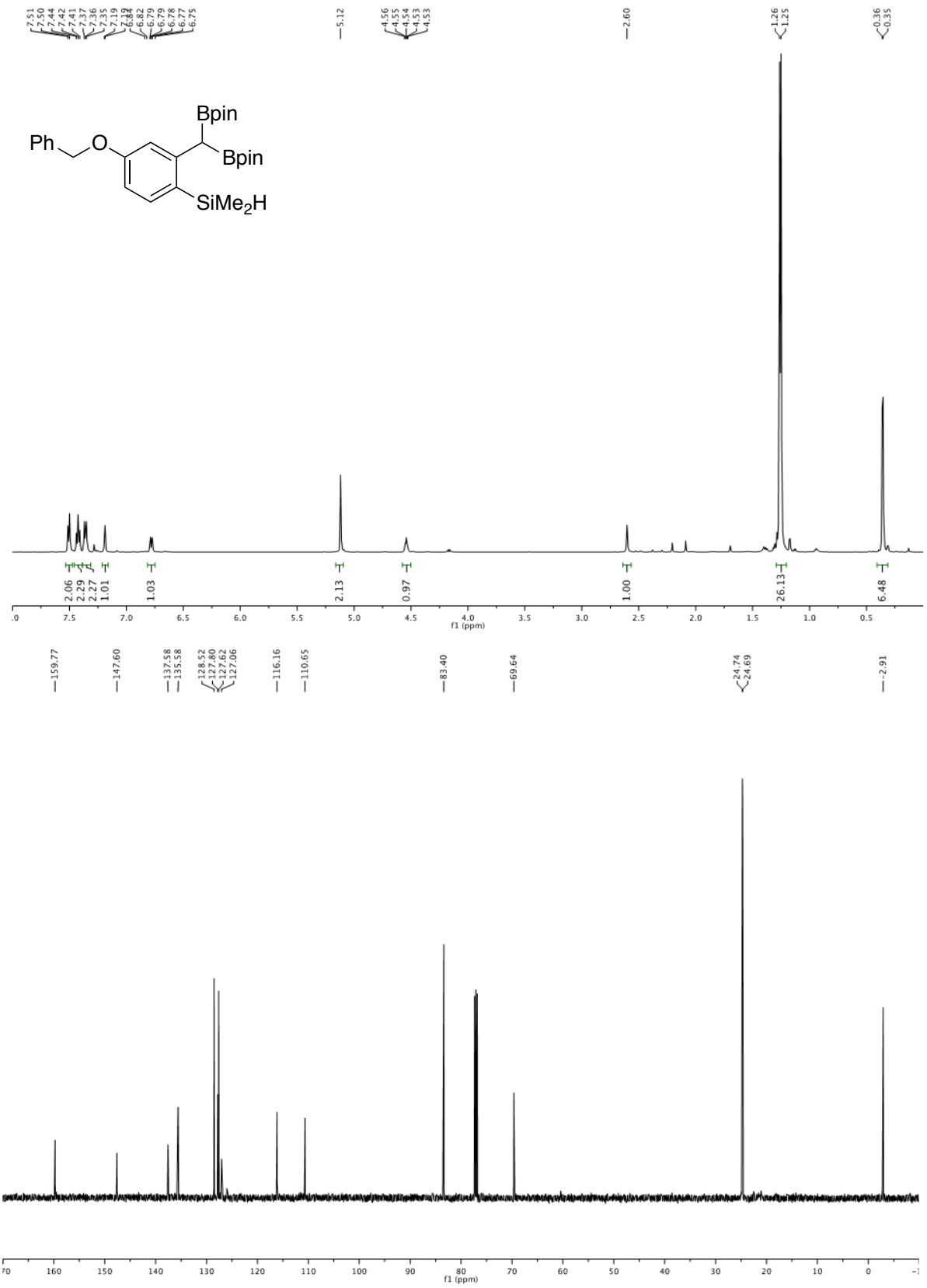
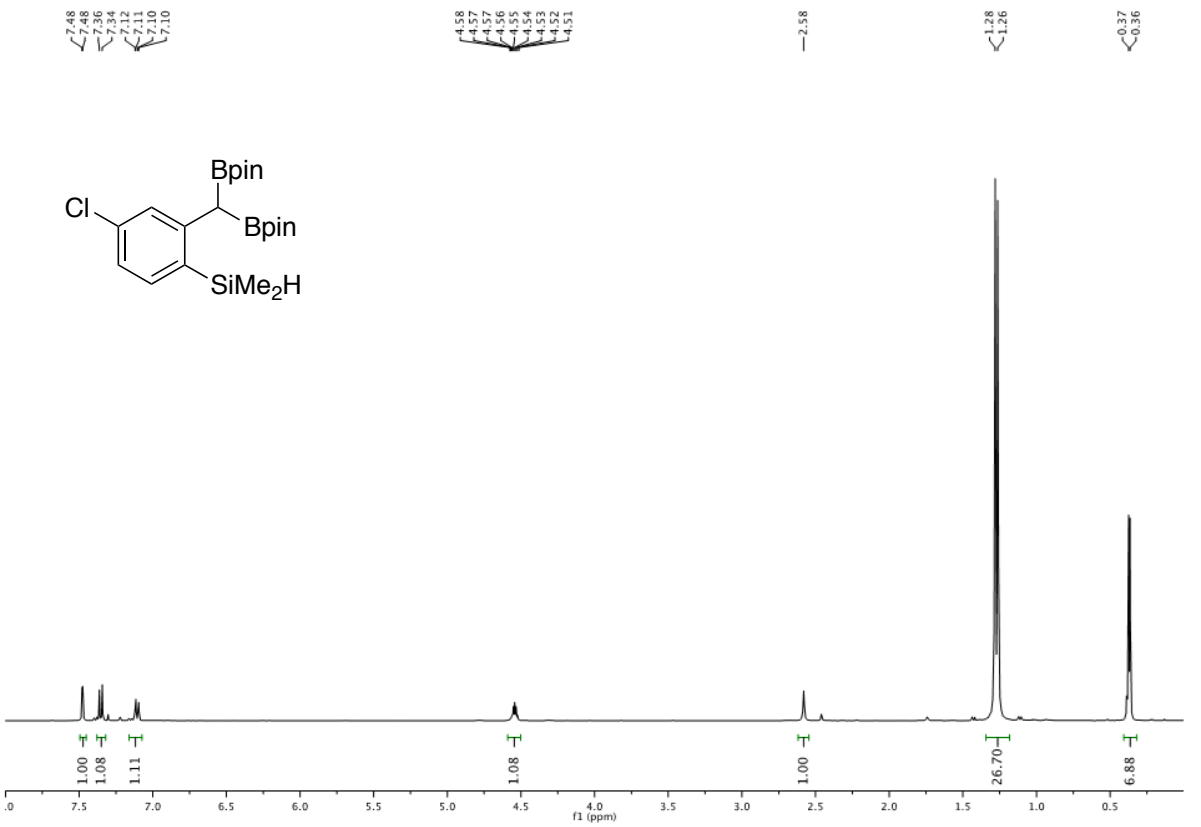
7.29
7.09
7.09
6.67
6.66
6.65
6.64
4.56
4.55
4.54
4.53
4.52
4.51
2.60
1.28
1.26
1.06
0.37
0.36
0.31
Bpin
TBSO
Bpin
SiMe2H
1.13
0.98
1.04
0.98
1.00
23.76
10.46
6.04
5.94
f1 (ppm)
156.56
147.23
135.45
126.77
121.24
115.84
83.35
25.89
24.79
24.64
18.30
2.96
-4.30
f1 (ppm)


Bpin
Ph
O
Bpin
SiMe2H
f1 (ppm)
f1 (ppm)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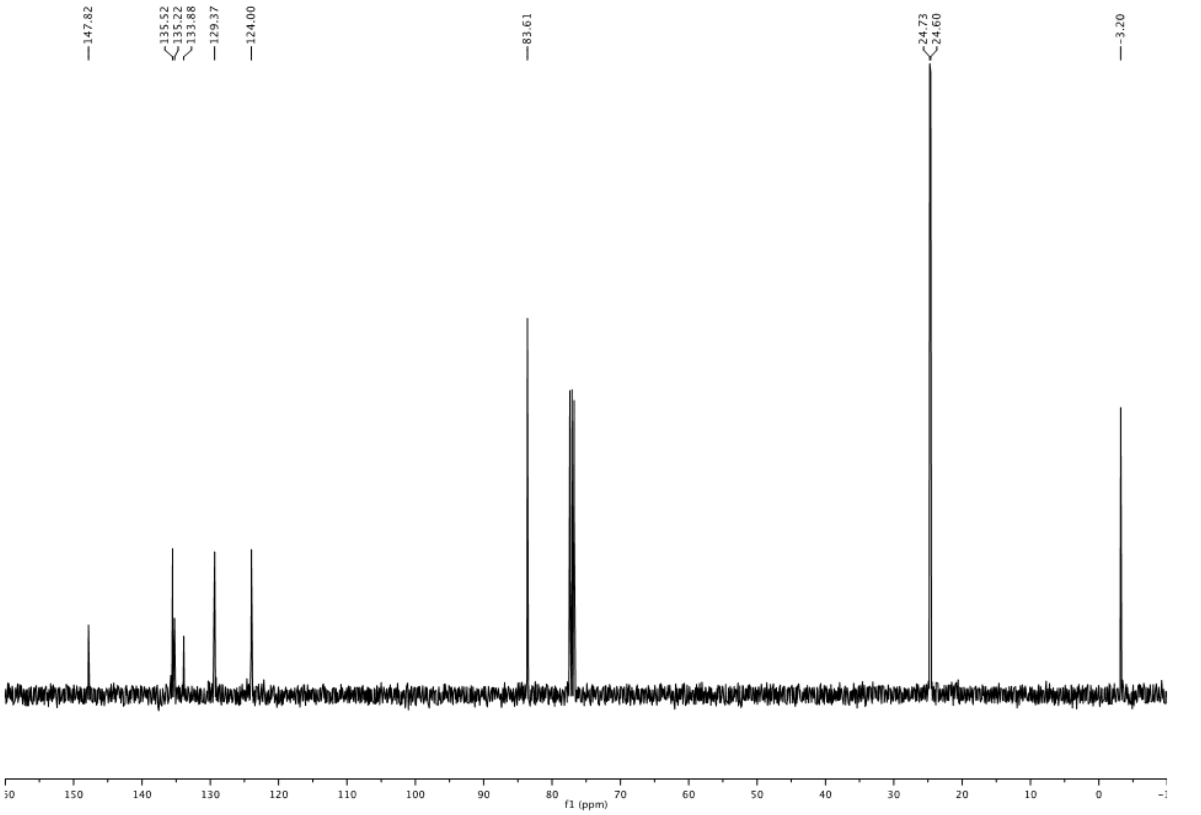
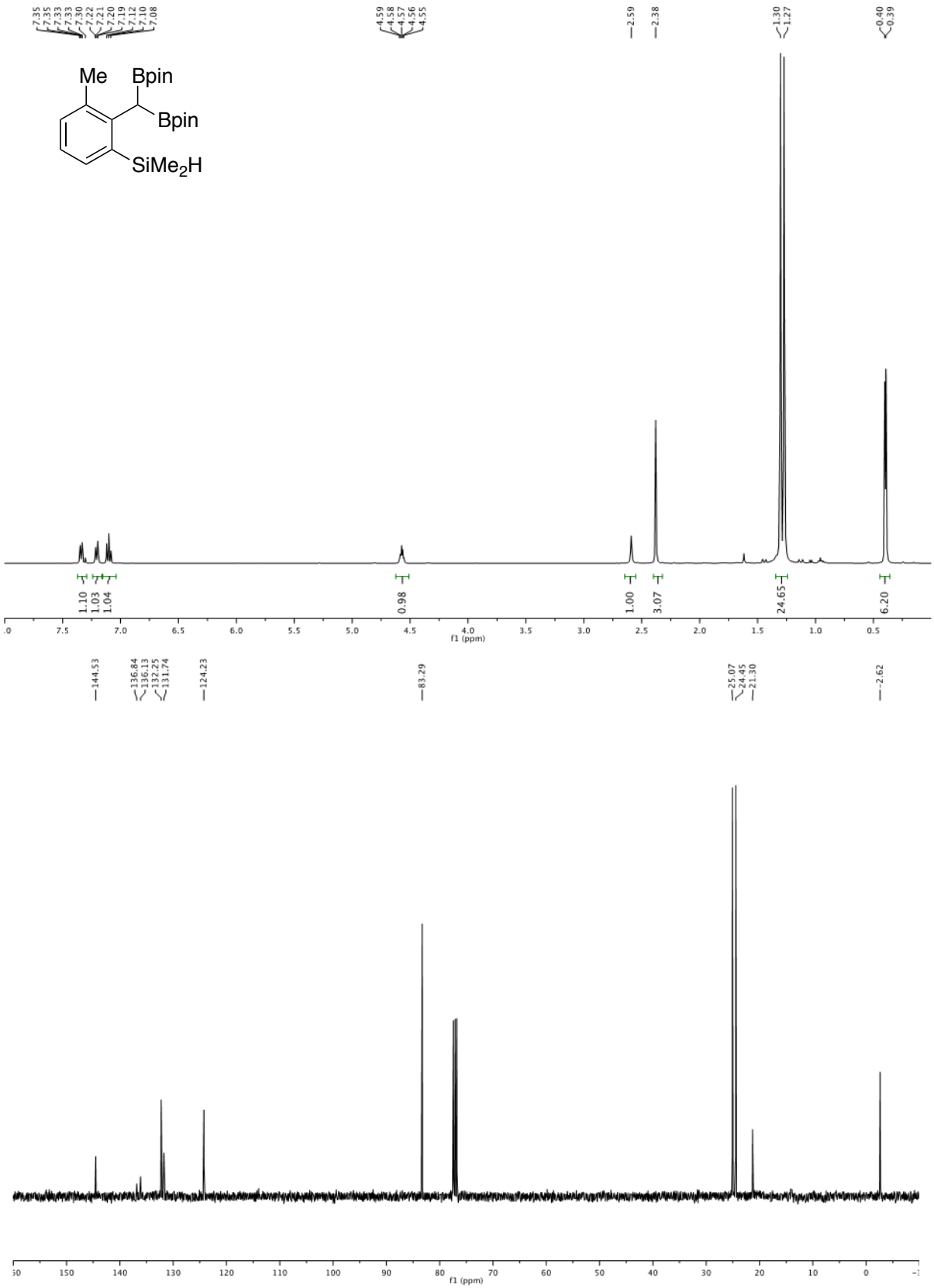
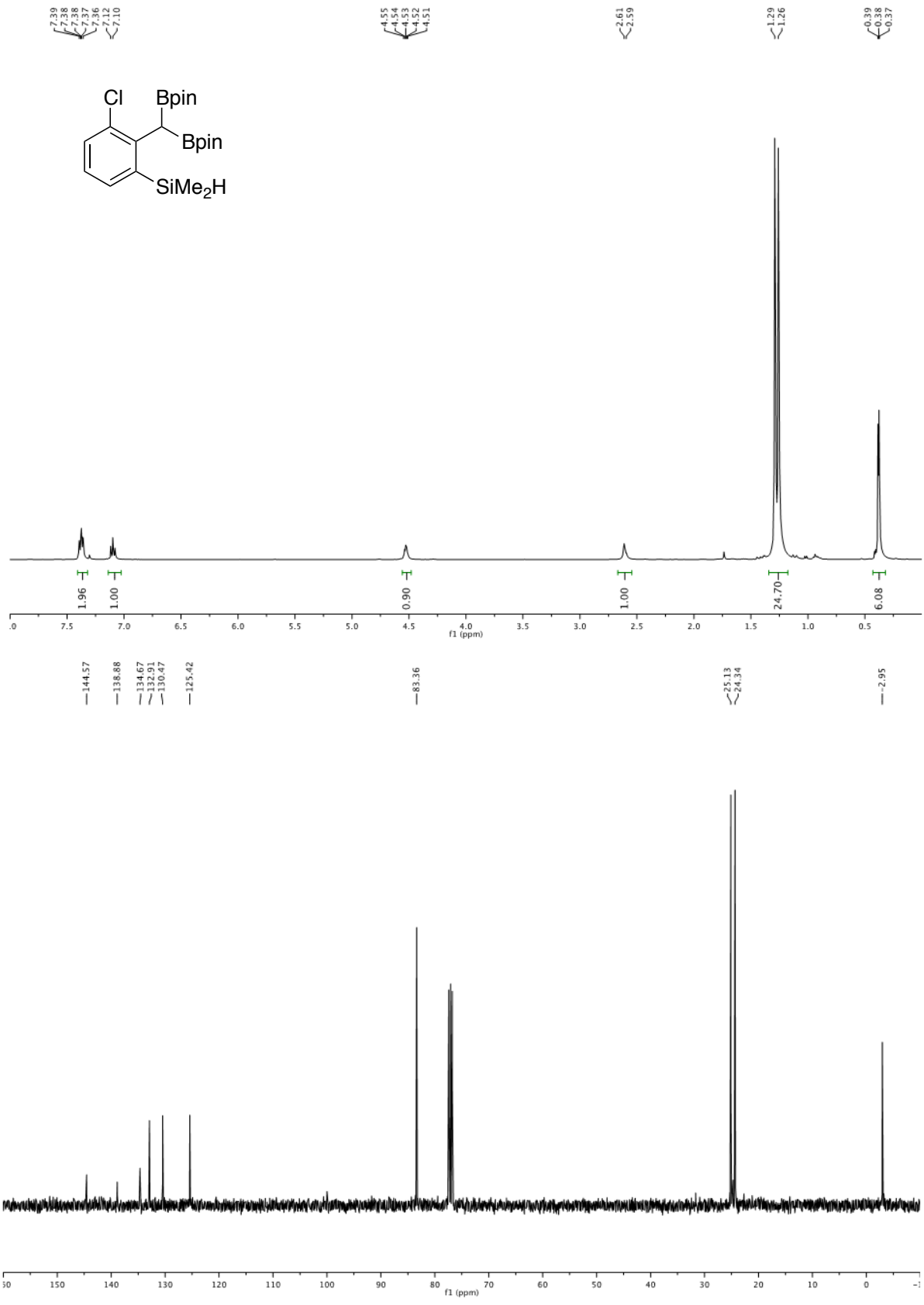
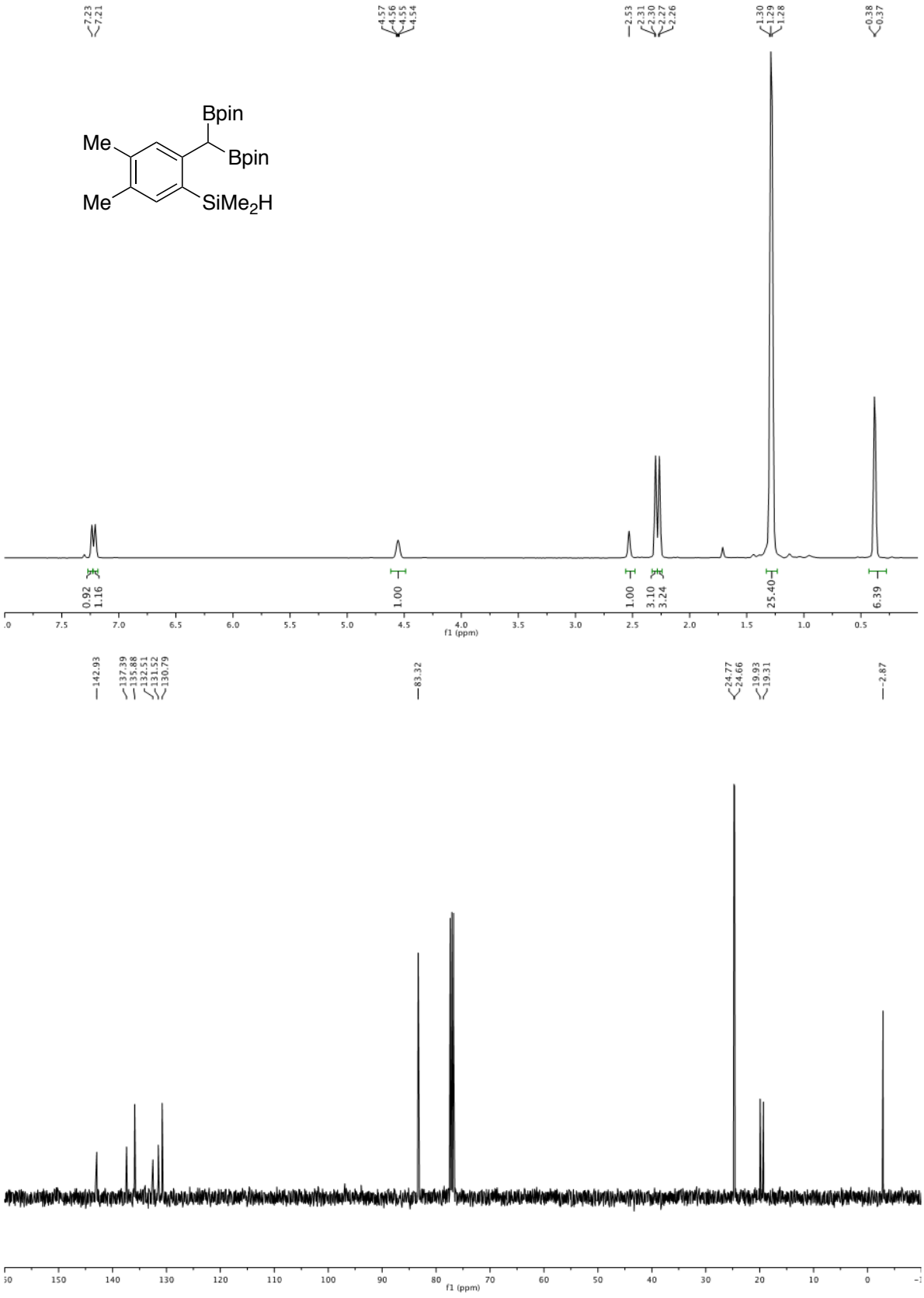
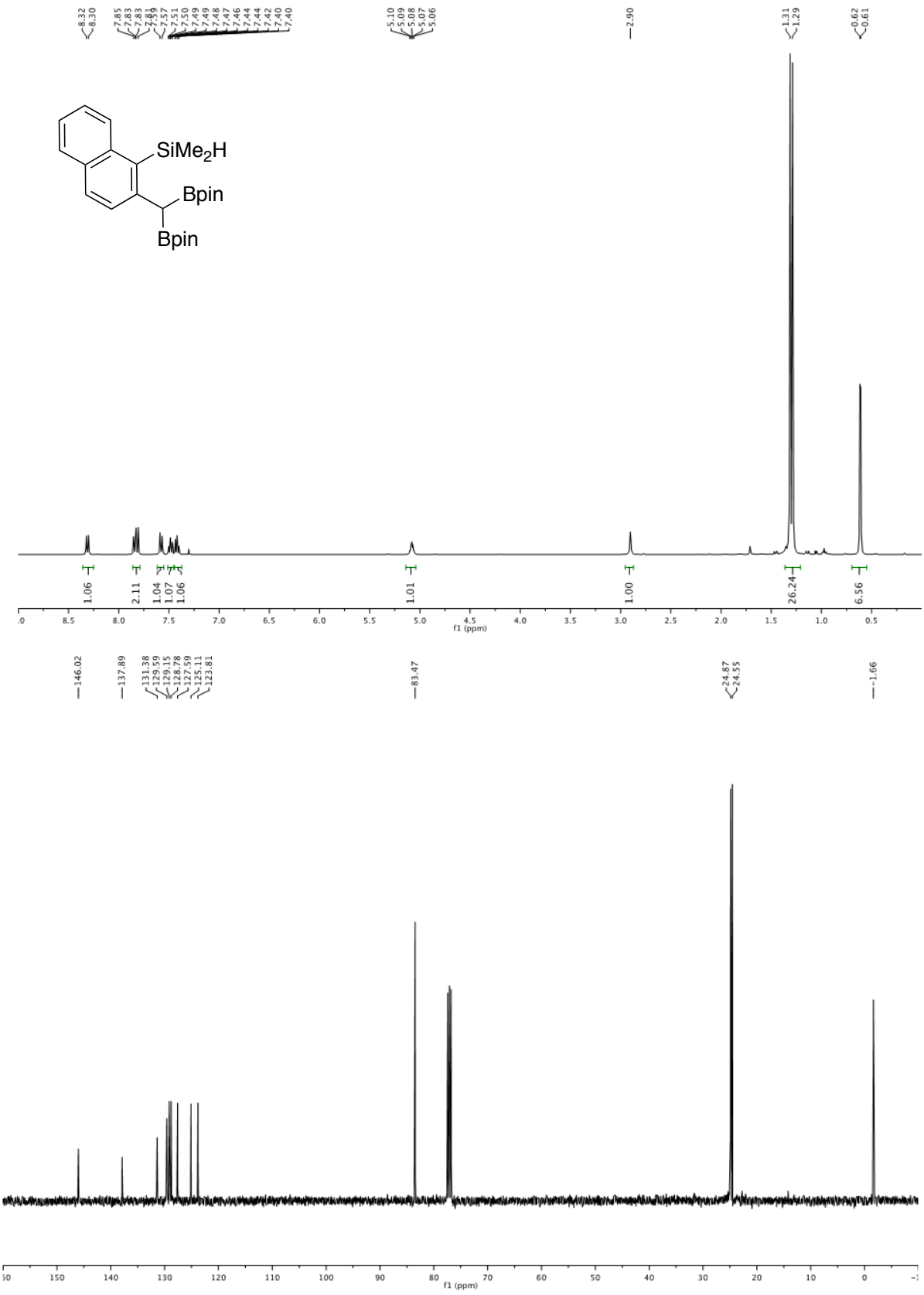
7.48
7.36
7.36
7.34
7.12
7.11
7.10
7.10
4.58
4.57
4.57
4.56
4.55
4.54
4.53
4.52
4.51
2.58
1.28
1.26
0.37
0.36
Bpin
Cl
Bpin
SiMe2H
1.00
1.08
1.11
1.08
1.00
26.70
6.88
f1 (ppm)

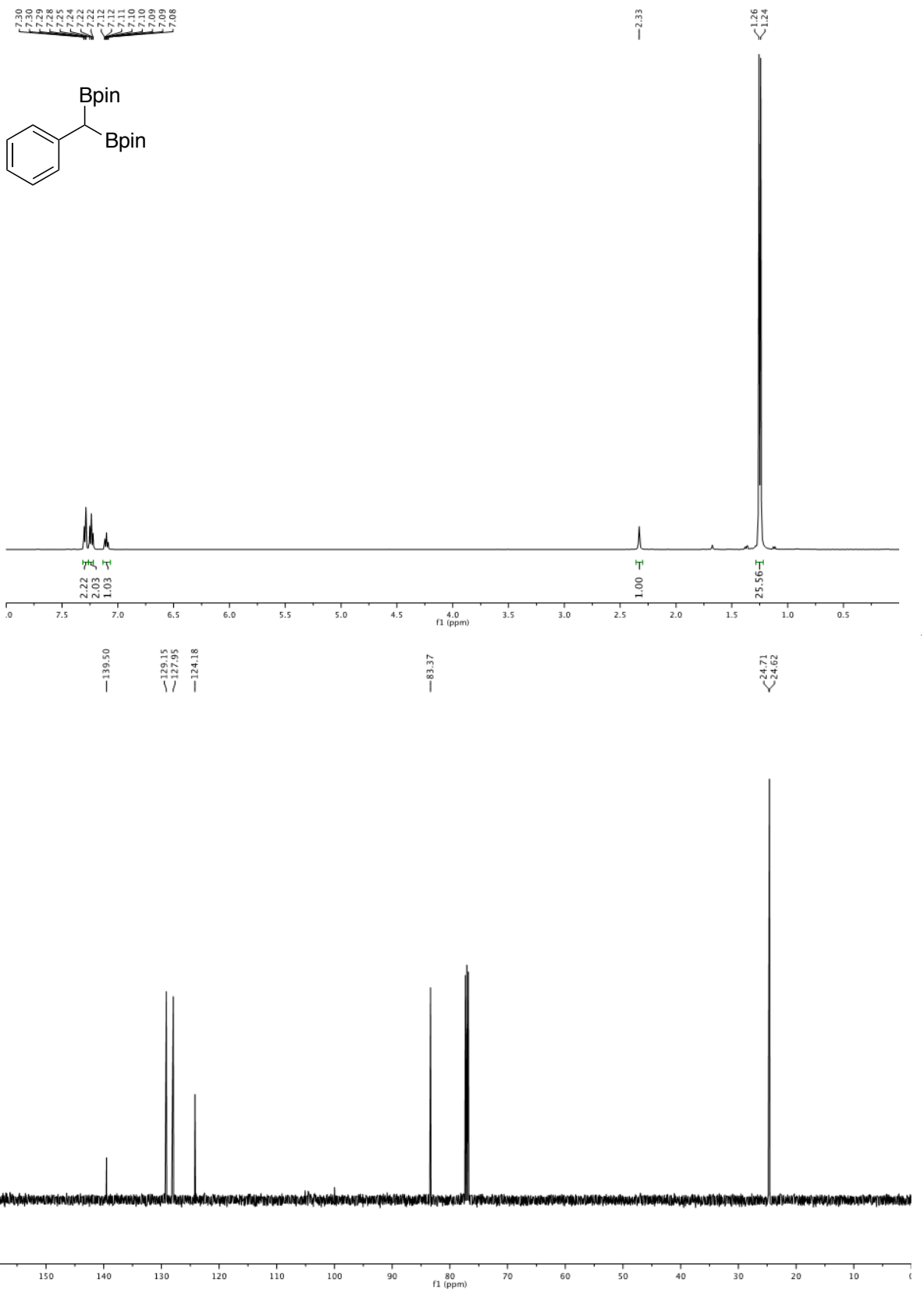

147.82
135.52
135.22
133.88
129.37
124.00
83.61
24.73
24.60
3.20
f1 (ppm)

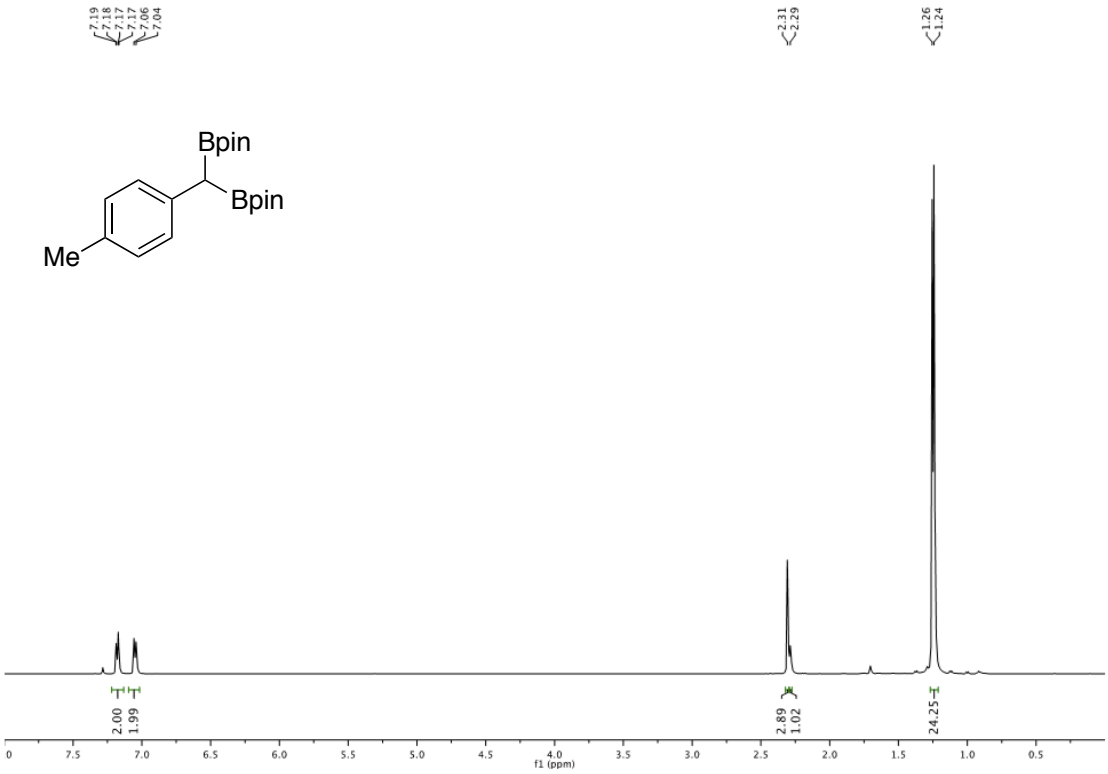

Me
Bpin
Bpin
SiMe2H
f1 (ppm)
f1 (ppm)

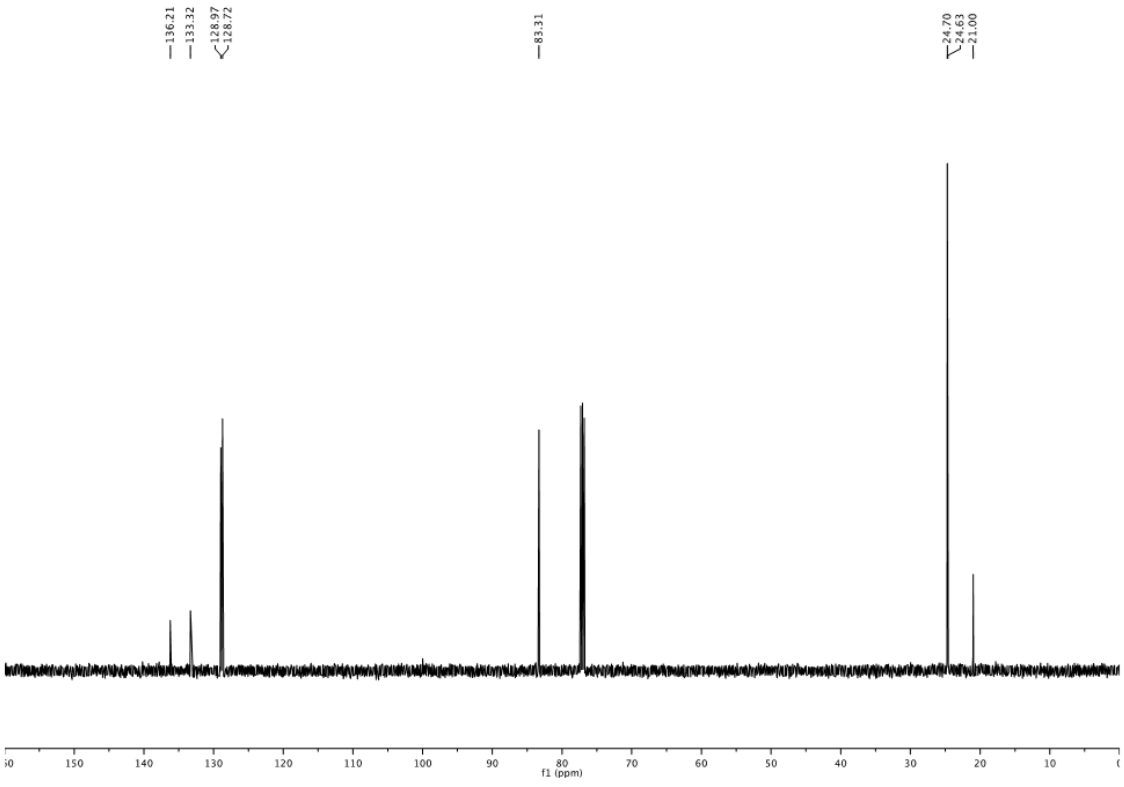


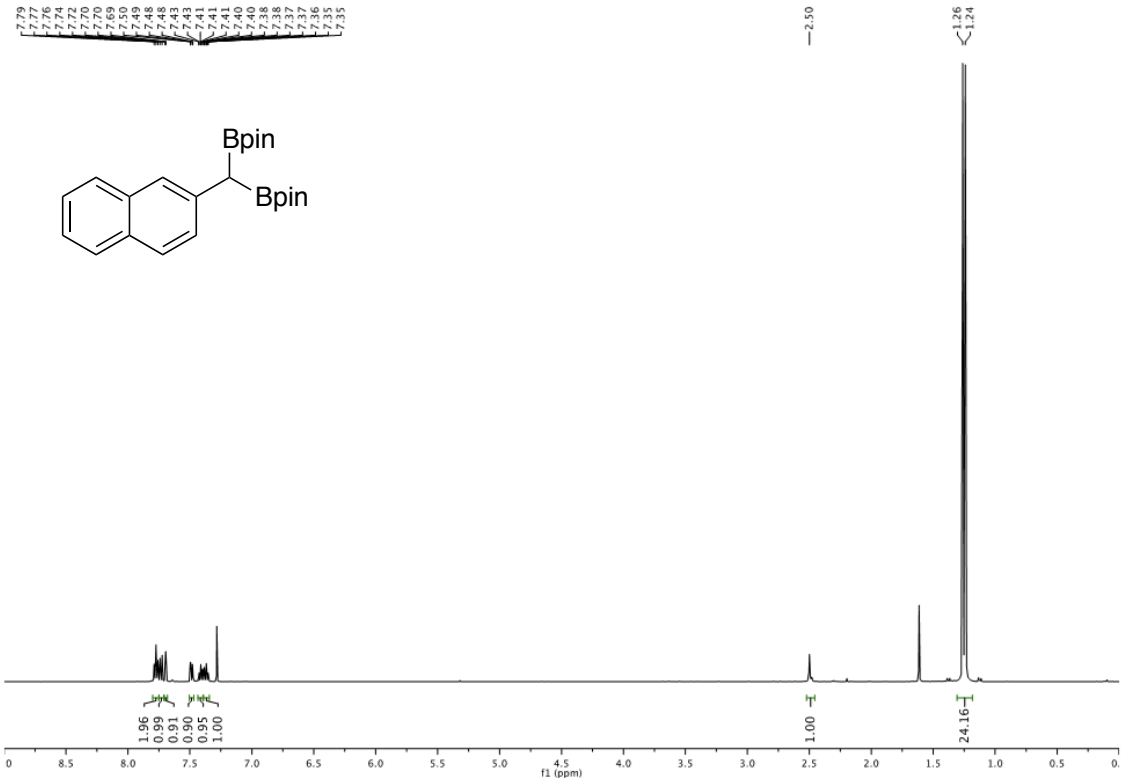

Bpin
Me
Bpin
Me
SiMe2H
f1 (ppm)
f1 (ppm)

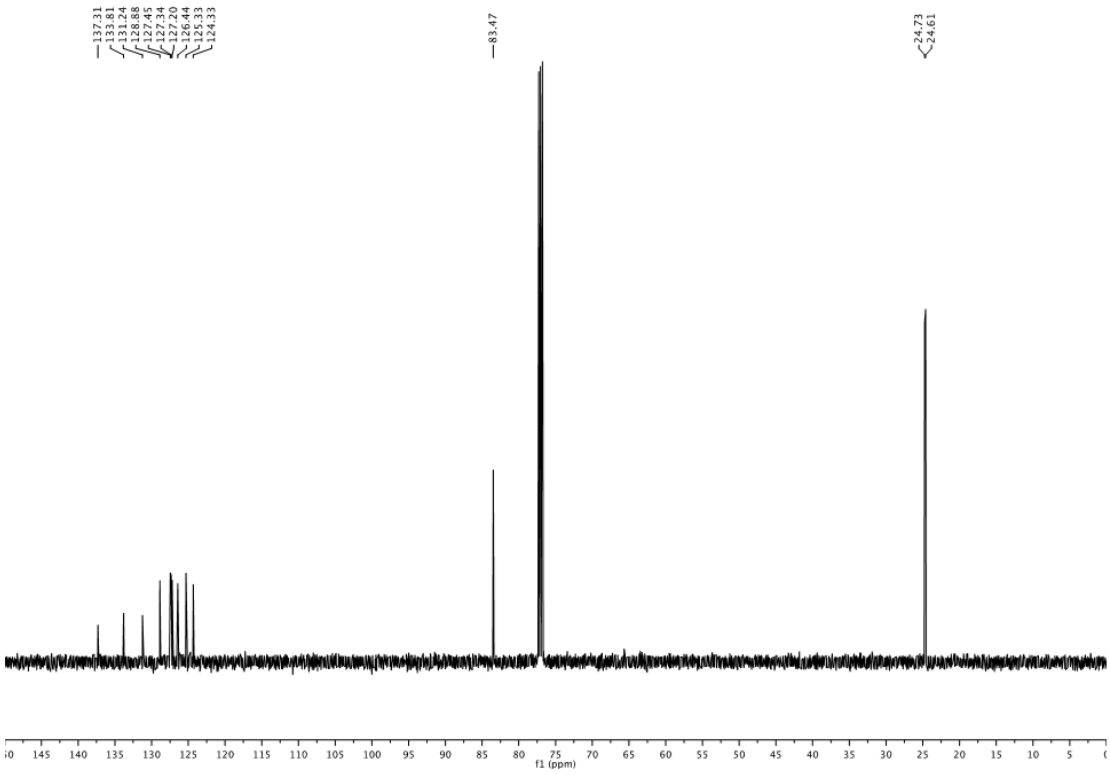

SiMe2H
Bpin
Bpin
f1 (ppm)
f1 (ppm)

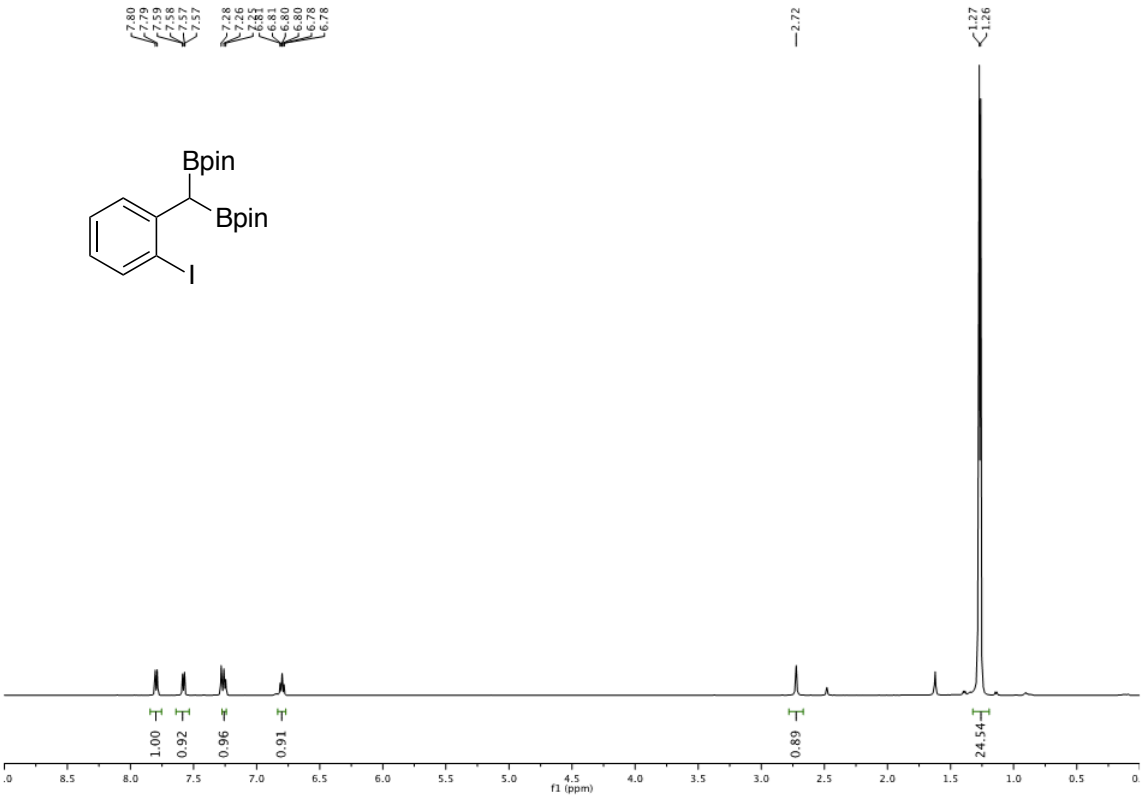

Bpin
Bpin
f1 (ppm)
f1 (ppm)

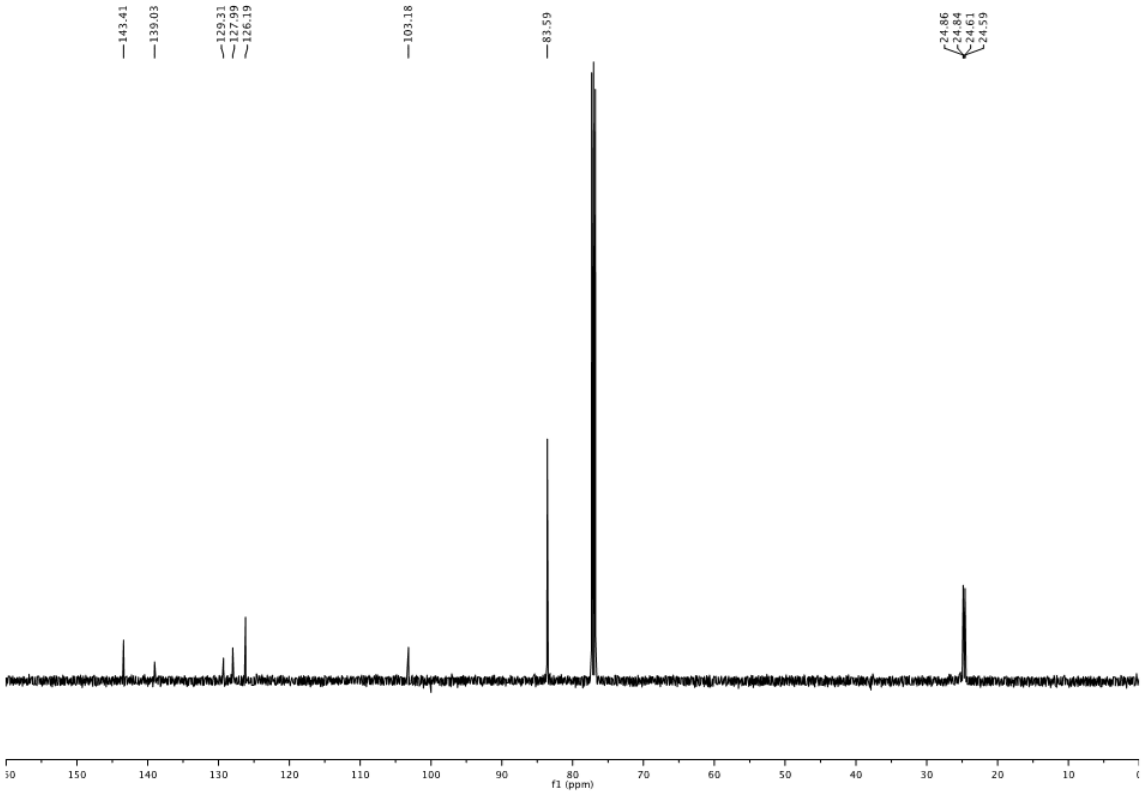

7.19
7.18
7.17
7.17
7.17
7.06
7.04
2.31
2.29
1.26
1.24
Bpin
Bpin
Me
2.00
1.99
2.89
1.02
24.25
f1 (ppm)

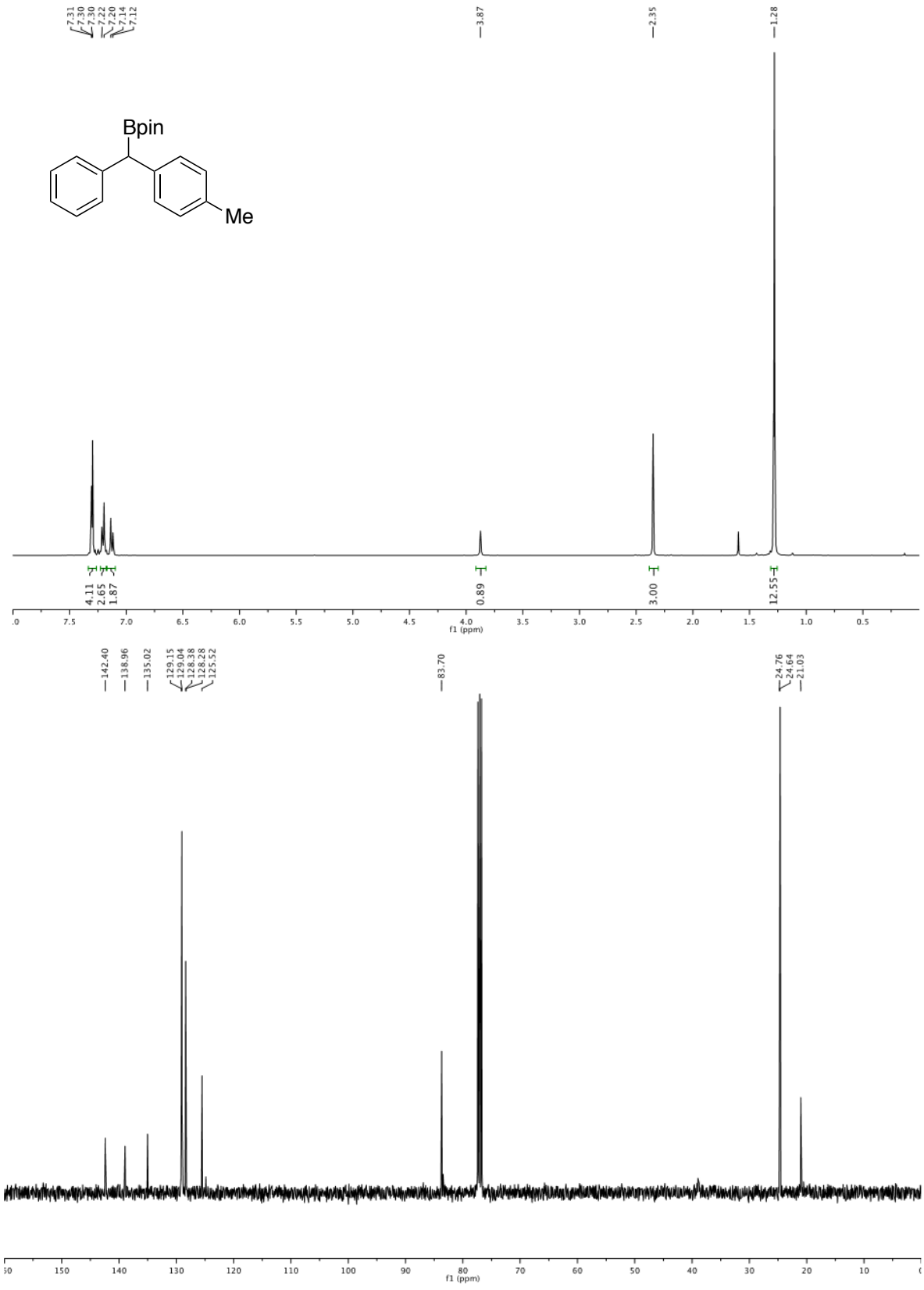

136.21
133.32
128.97
128.72
83.31
24.70
24.63
21.00
f1 (ppm)

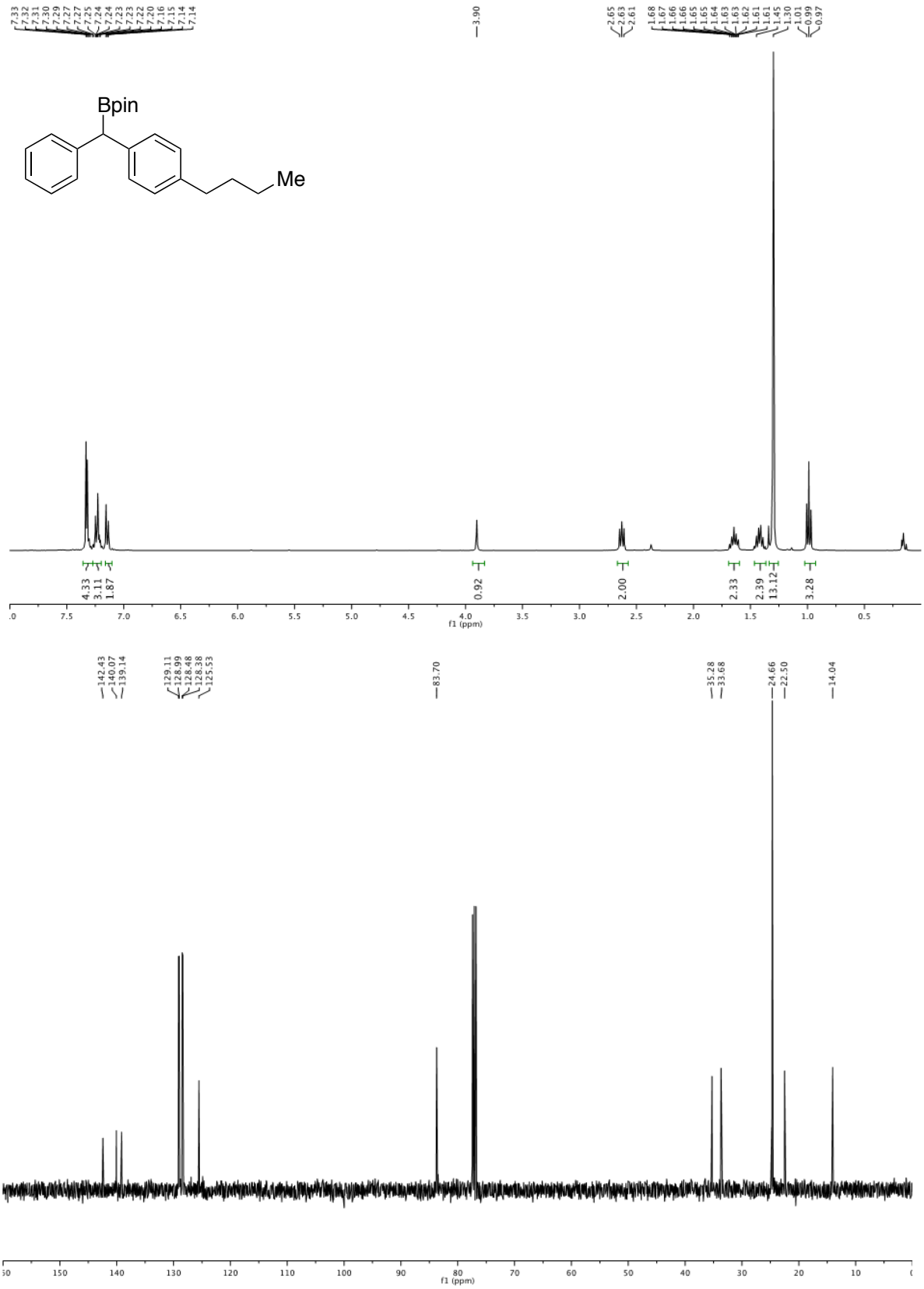

Bpin
Bpin
f1 (ppm)

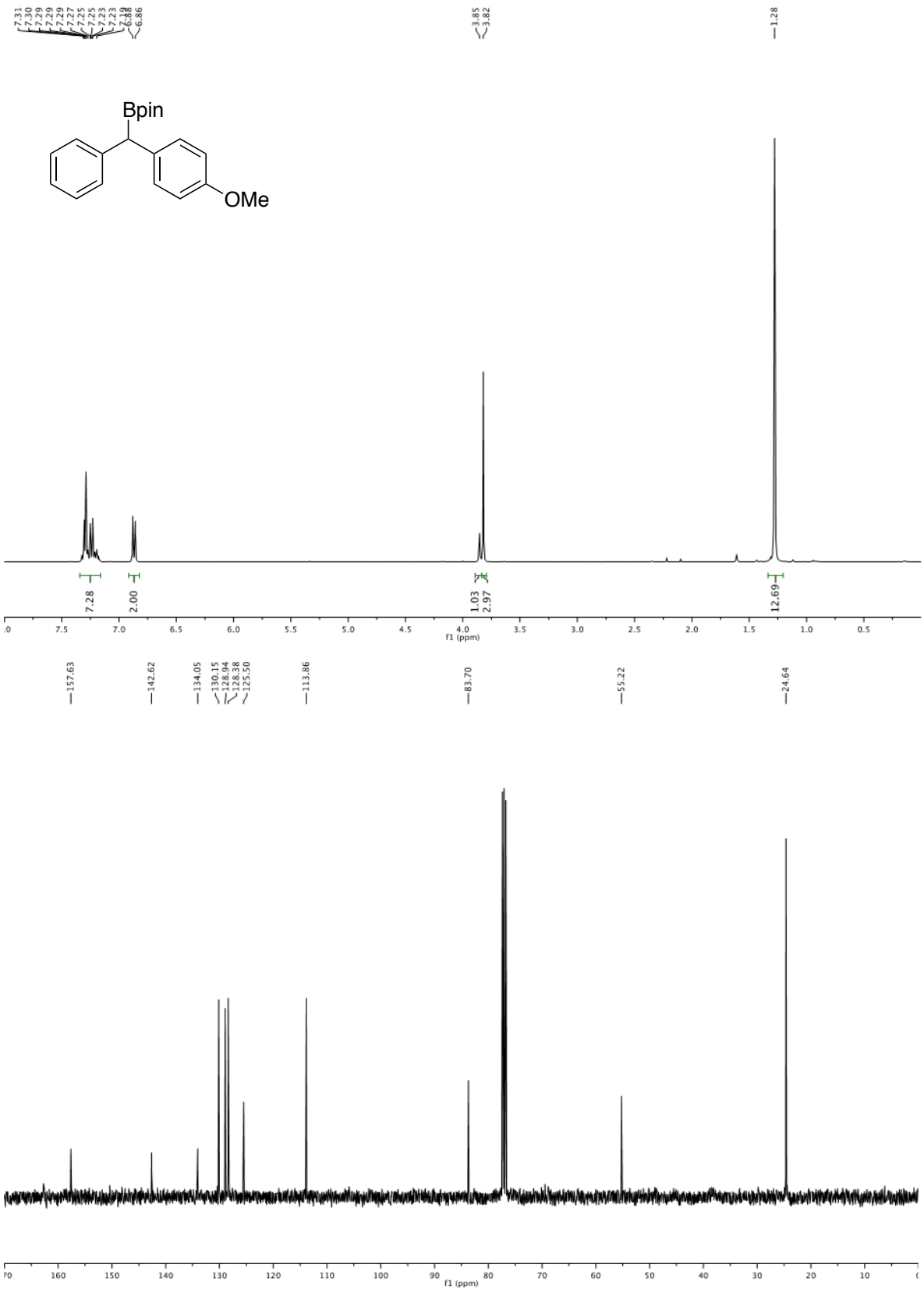

f1 (ppm)






Bpin
Me
7.31
7.30
7.30
7.22
7.20
7.14
7.12
3.87
2.35
1.28
4.11
2.65
1.87
0.89
3.00
12.55
f1 (ppm)
142.40
138.96
135.02
129.15
129.04
128.38
128.28
125.52
83.70
24.76
24.64
21.03
f1 (ppm)


Bpin
Me
f1 (ppm)
f1 (ppm)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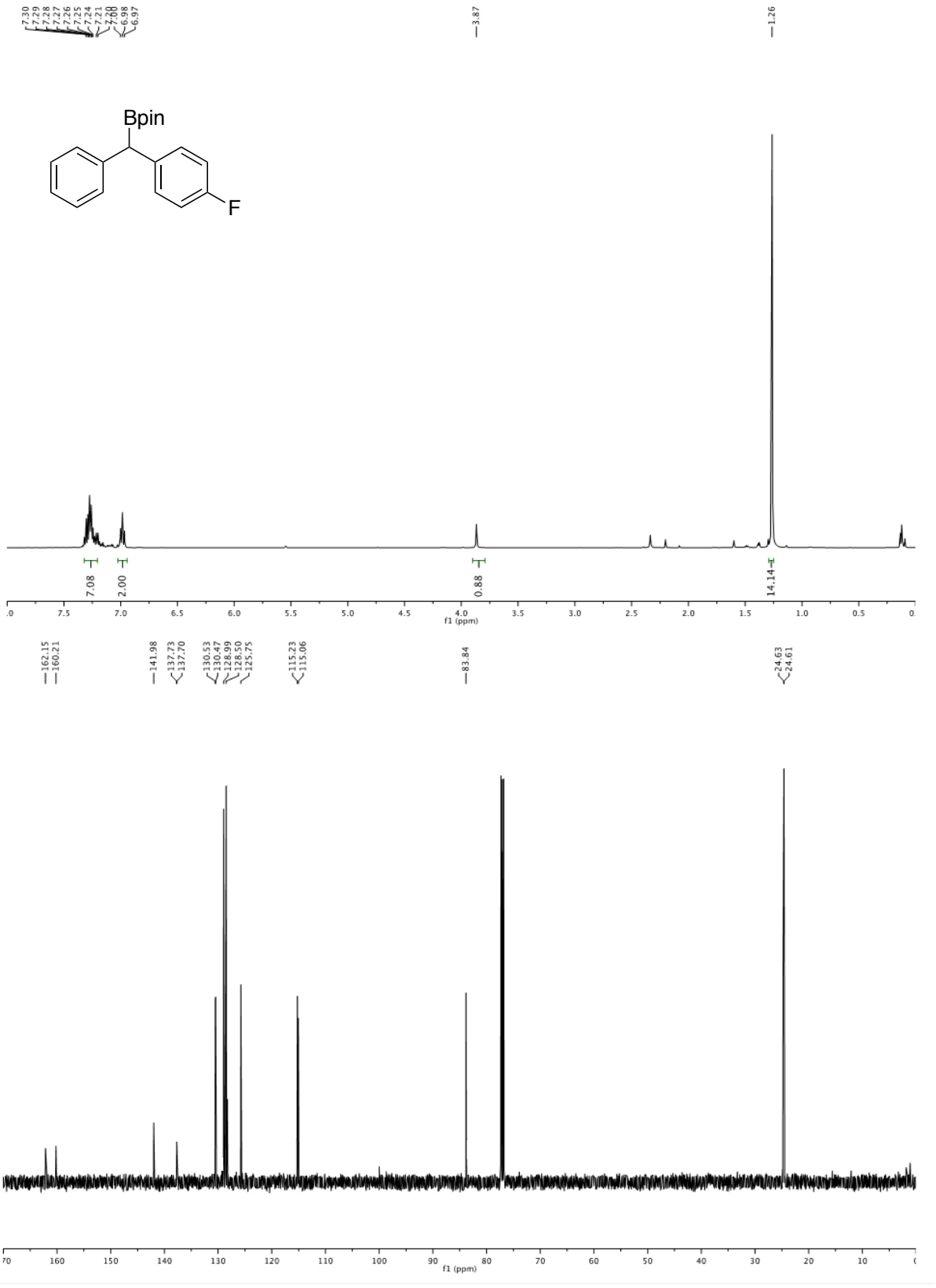
7.29
7.29
7.29
7.27
7.25
7.25
7.23
7.23
6.88
6.86
3.85
3.82
1.28
Bpin
OMe
7.28
2.00
1.03
2.97
12.69
f1 (ppm)
157.63
142.62
134.05
130.15
128.94
128.38
125.50
113.86
83.70
55.22
24.64
f1 (ppm)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7.29
7.28
7.27
7.26
7.25
7.24
7.21
7.08
6.98
6.97
3.87
1.26
Bpin
F
7.08
2.00
0.88
14.14
f1 (ppm)
162.15
160.21
141.98
137.73
137.70
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130.47
128.99
128.50
125.75
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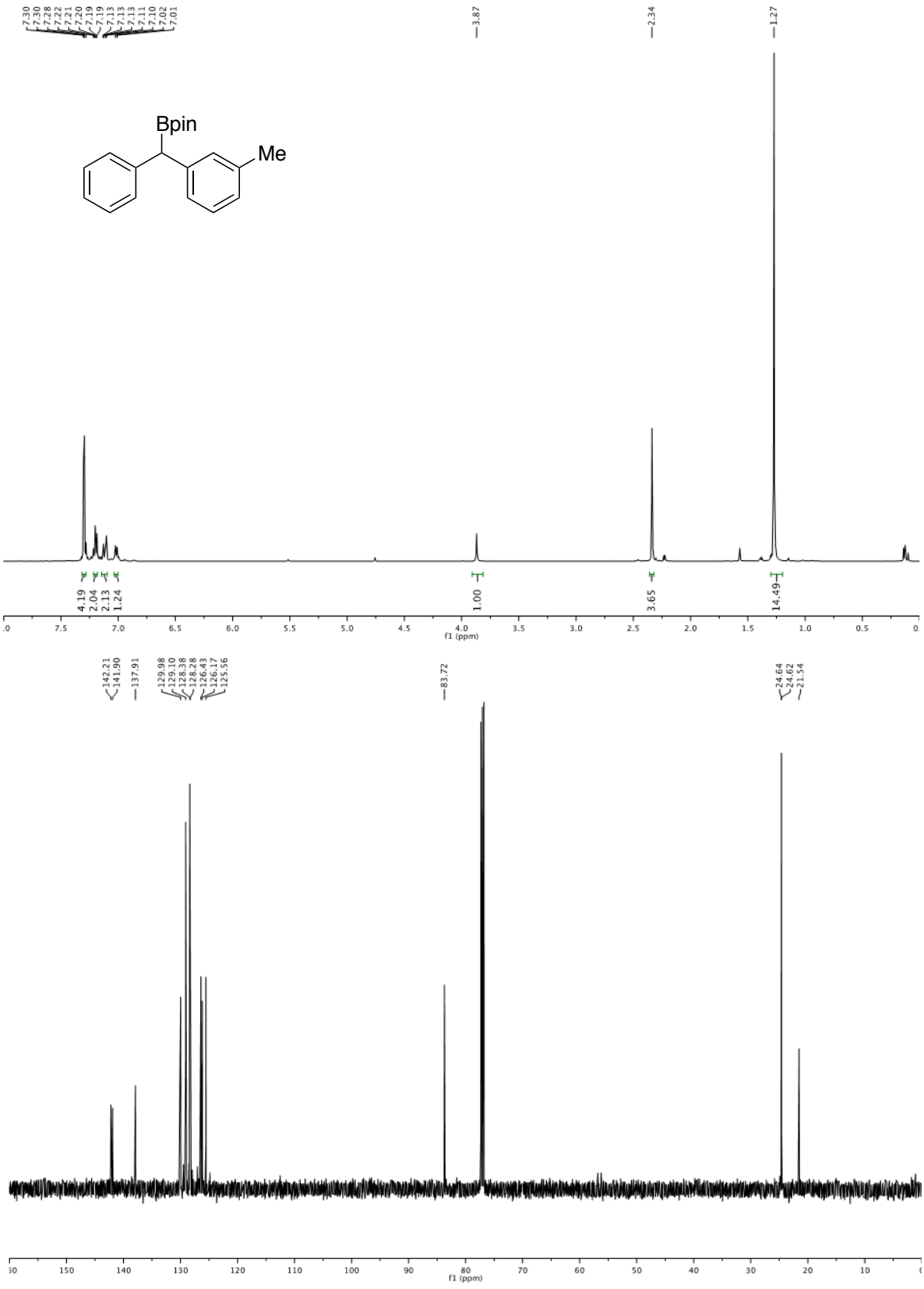
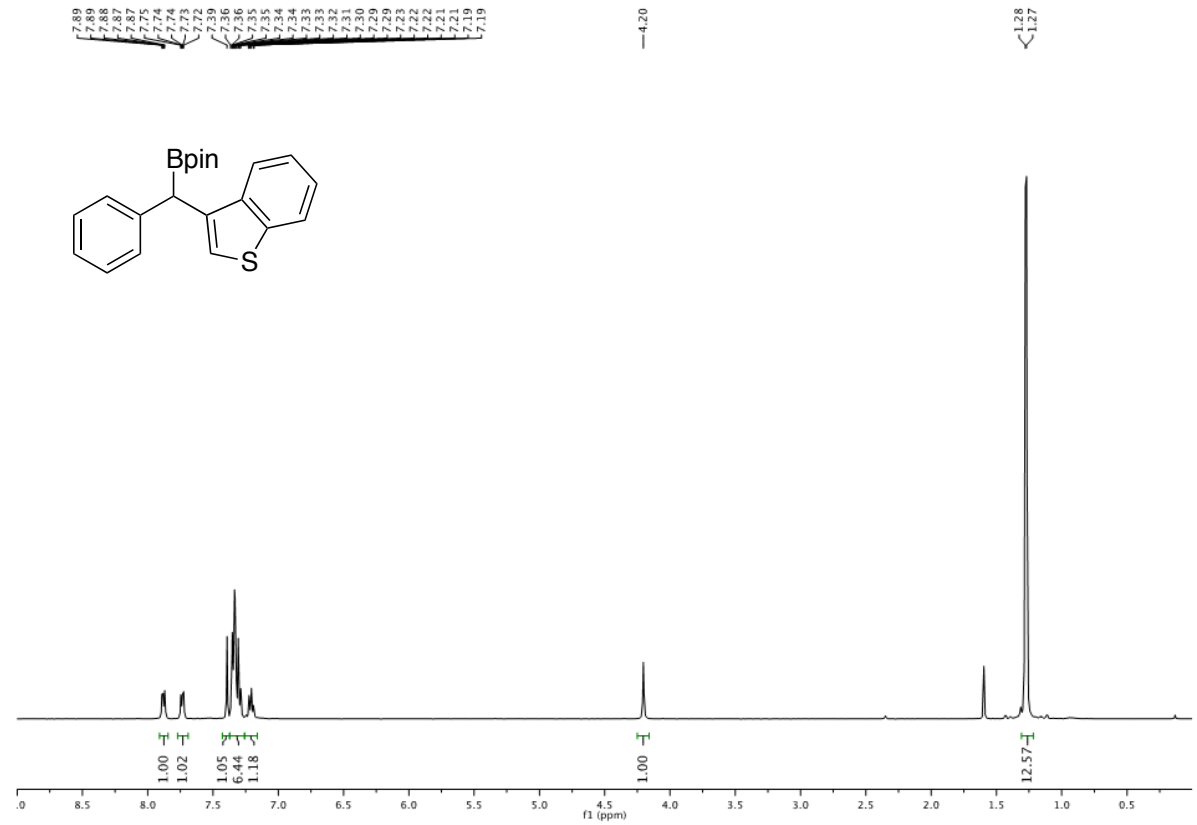
115.06
83.84
24.63
24.61
f1 (ppm)


Bpin
Me
f1 (ppm)
f1 (ppm)


Bpin
S
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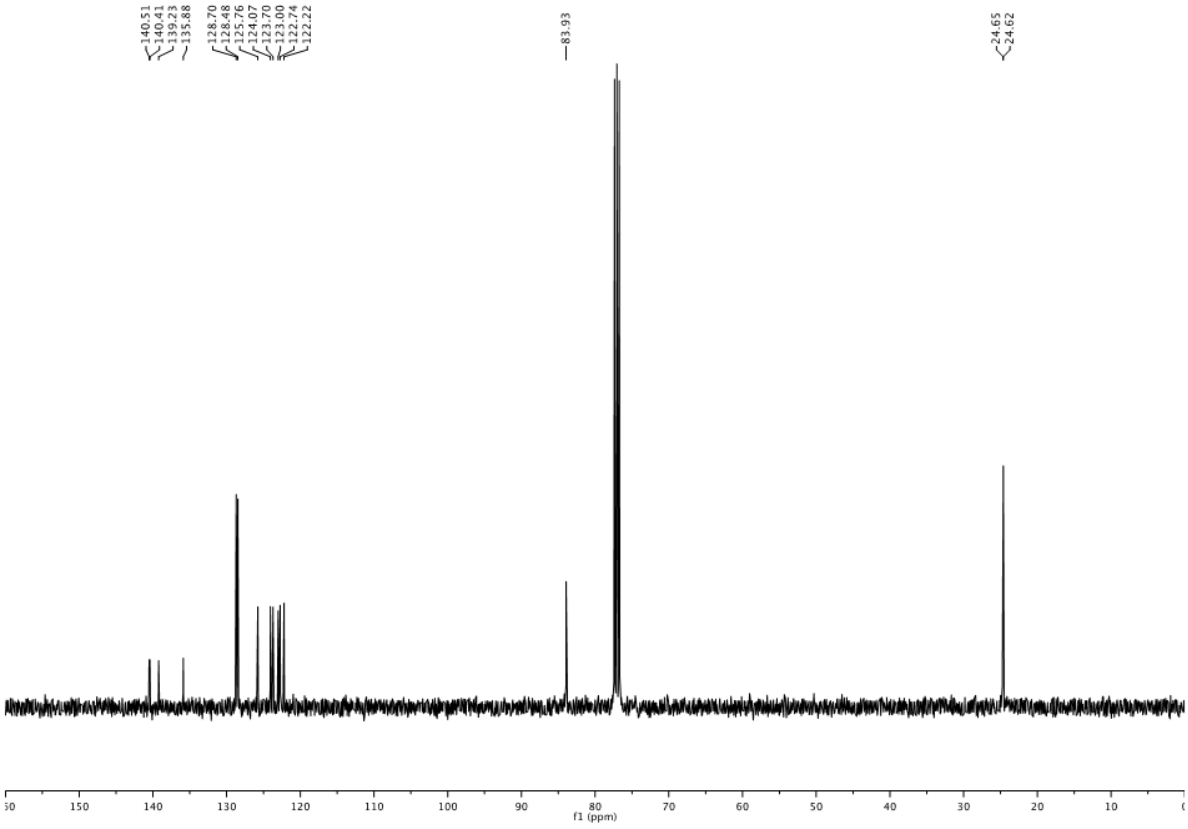
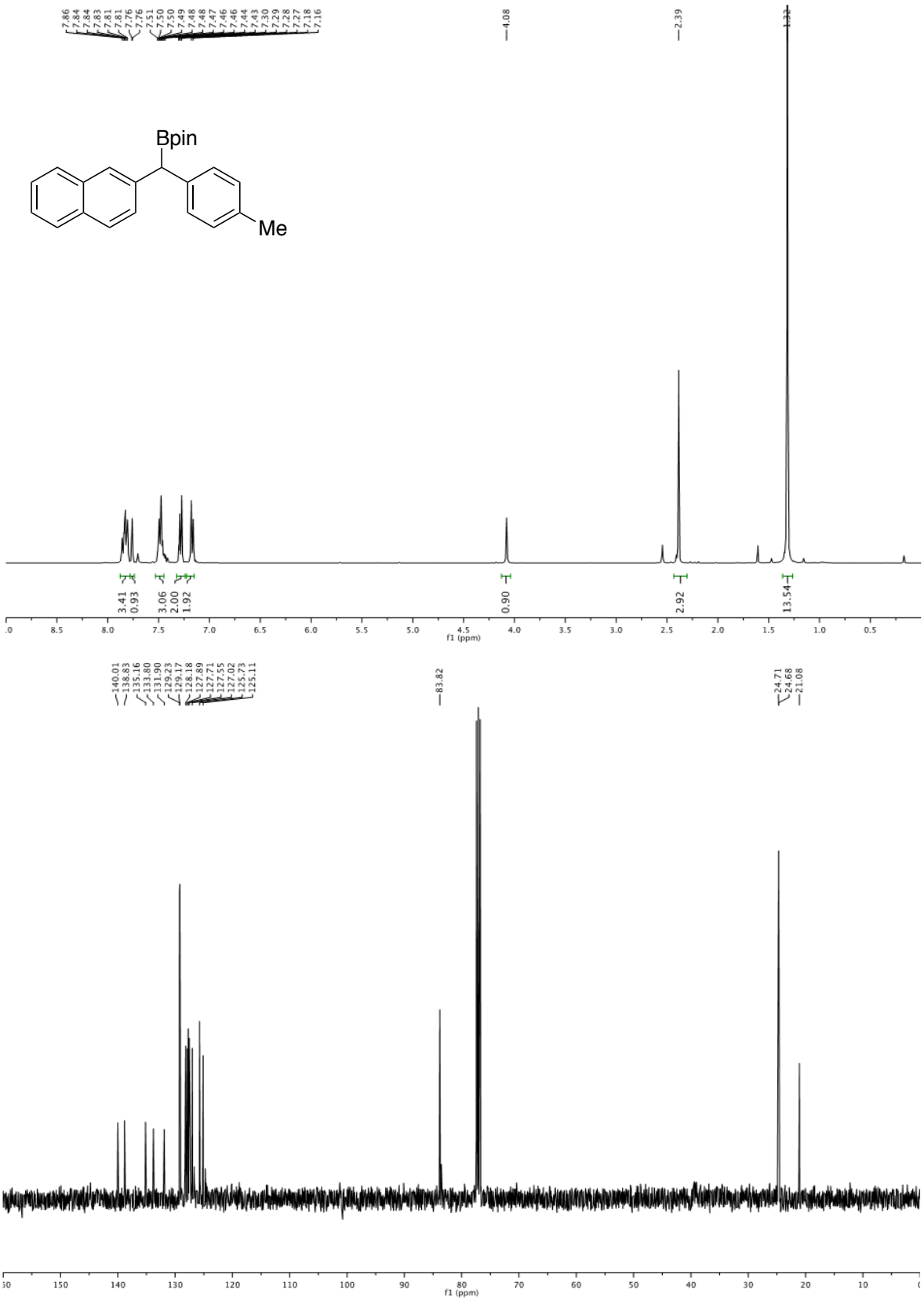
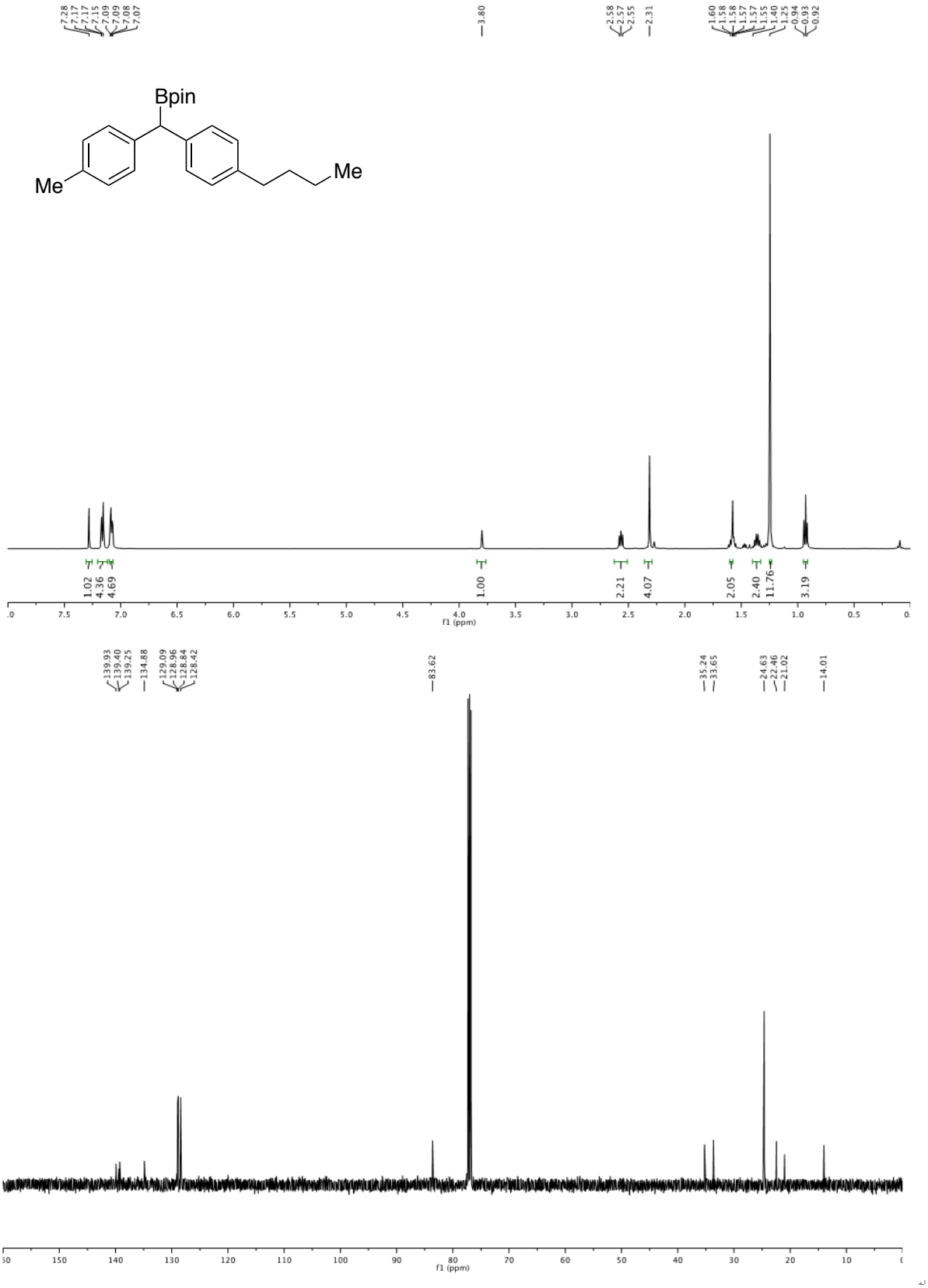
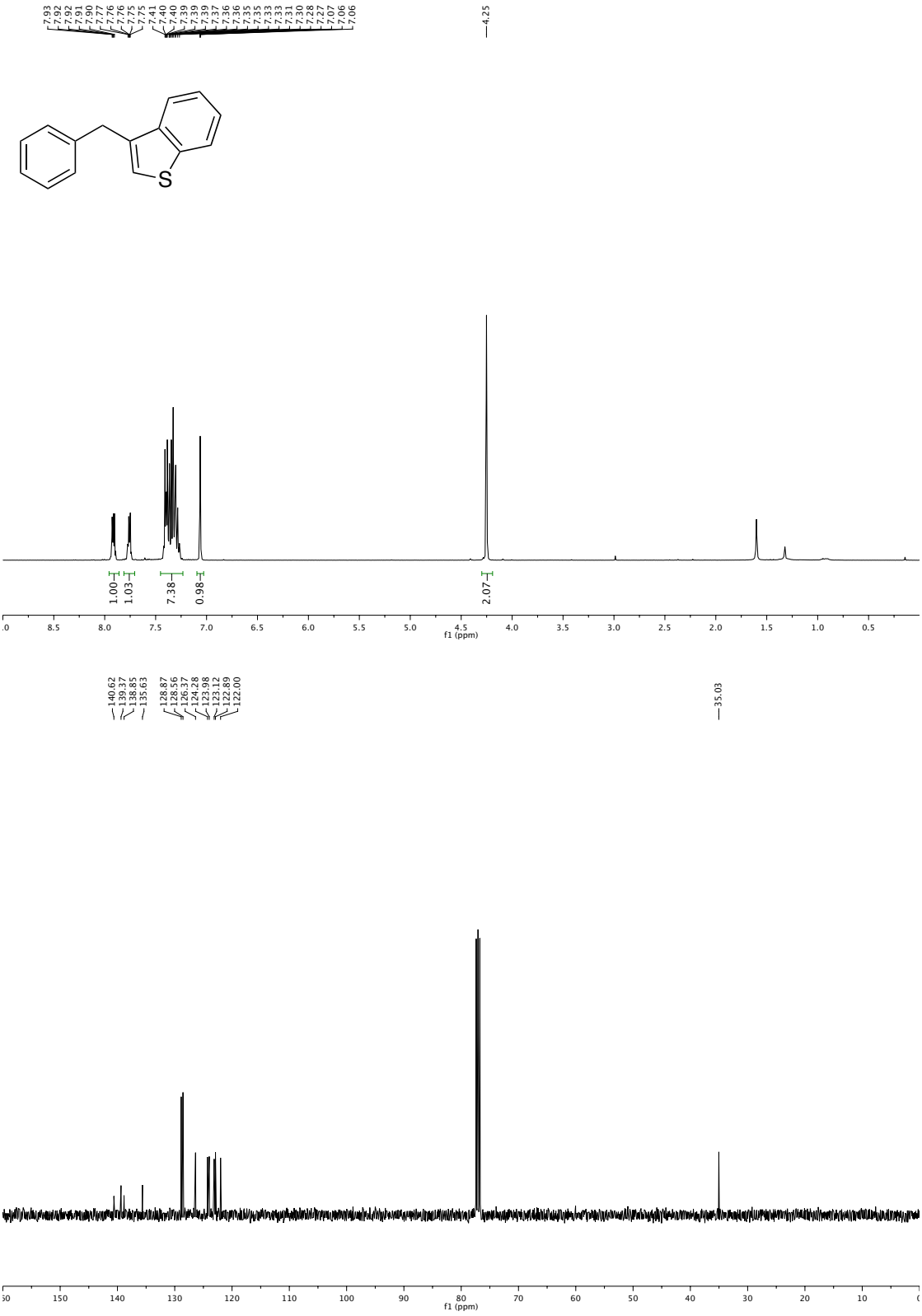
1.02
1.05
6.44
1.18
1.00
12.57
f1 (ppm)


f1 (ppm)


Bpin
Me
f1 (ppm)
f1 (ppm)


Bpin
Me
Me
f1 (ppm)
f1 (ppm)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7.92
7.91
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7.77
7.76
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7.75
7.41
7.40
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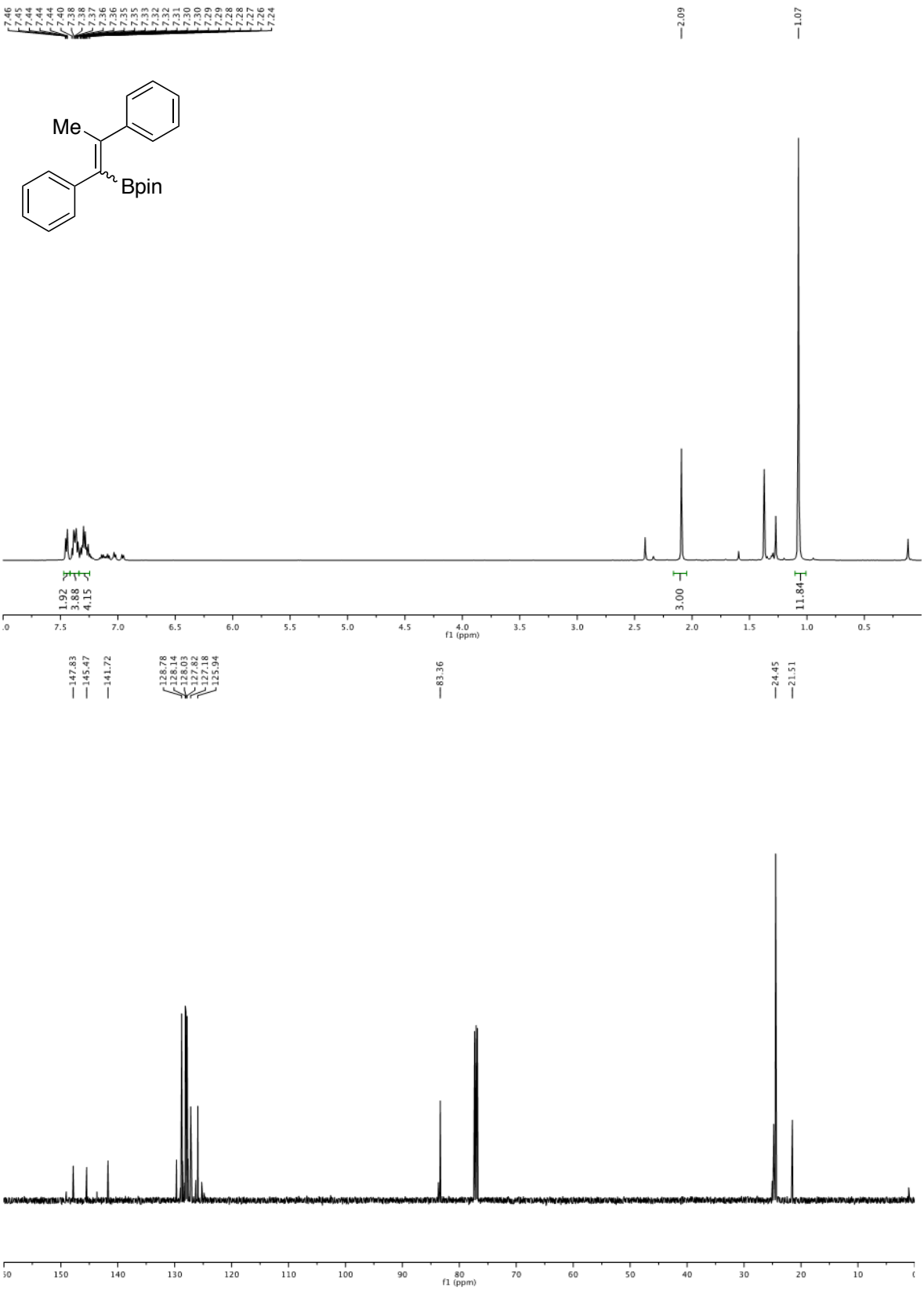
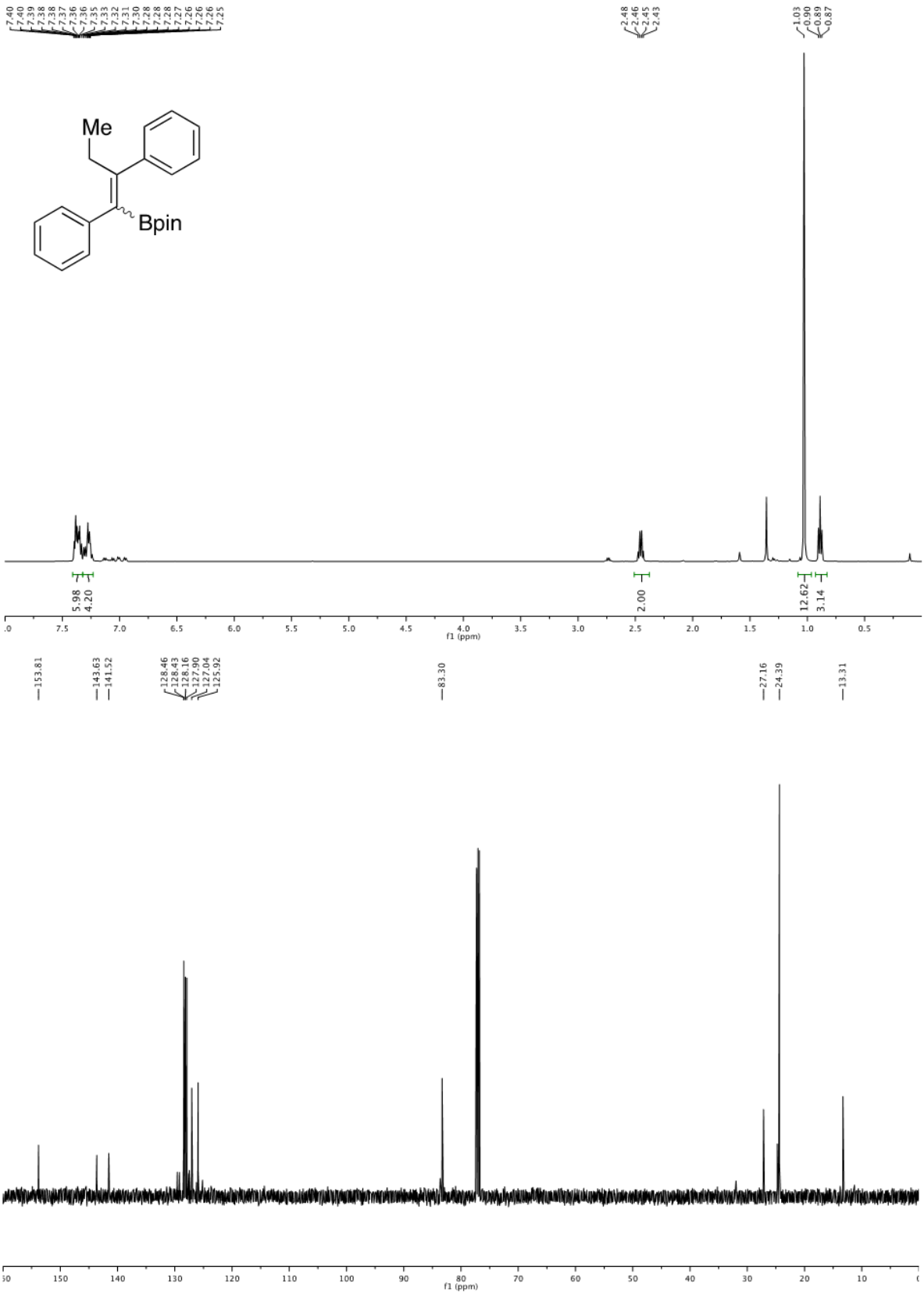
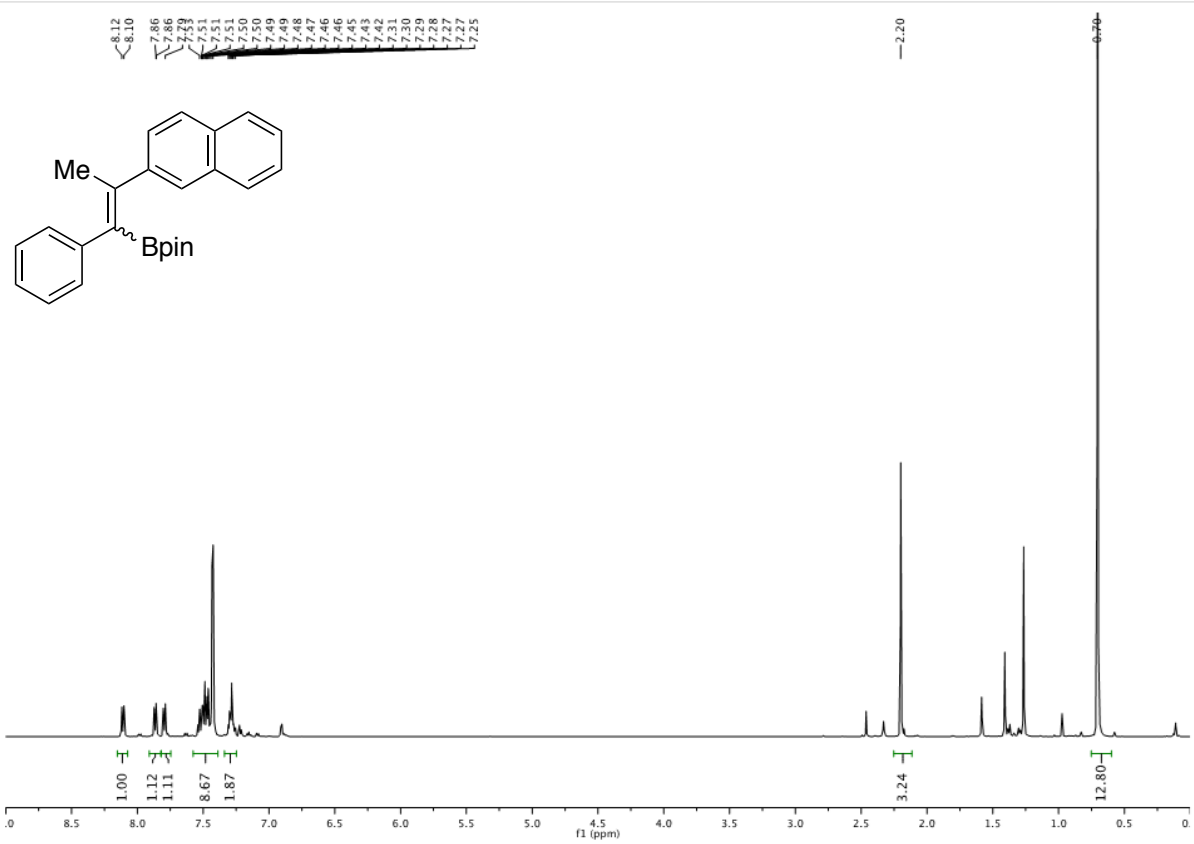
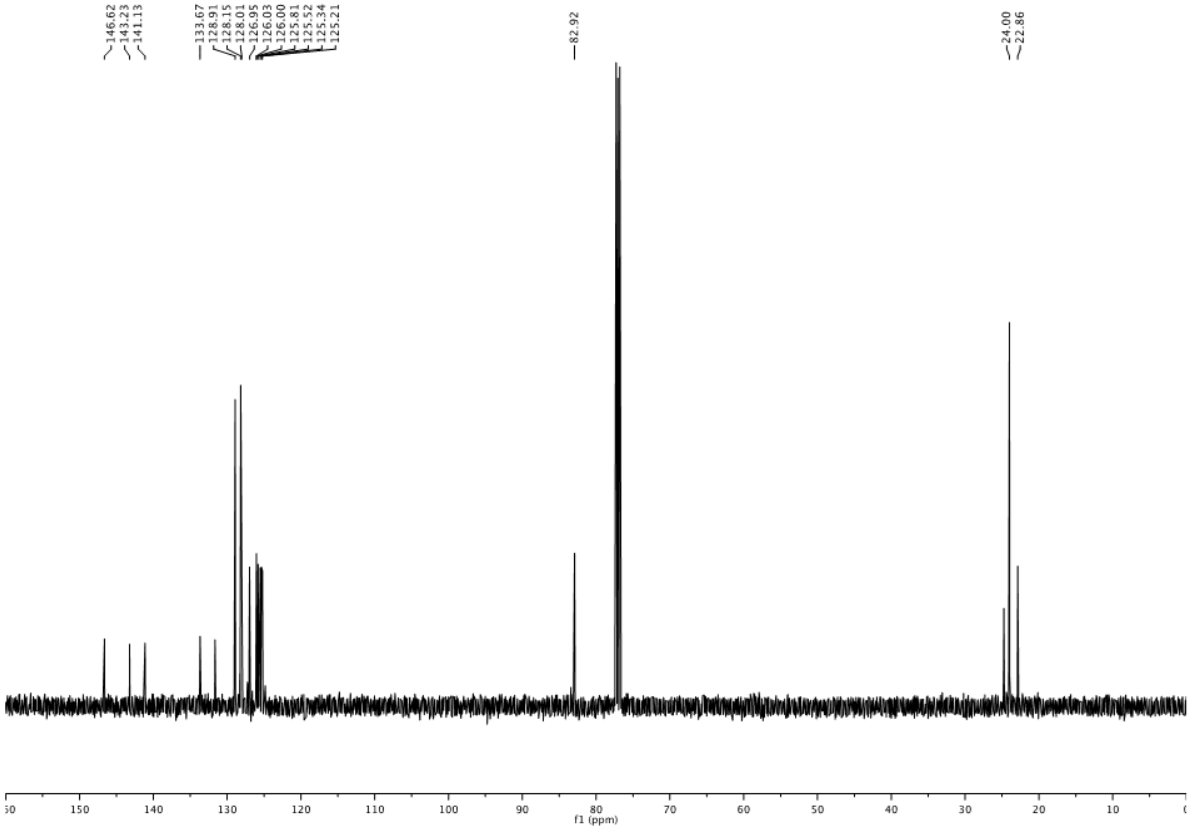
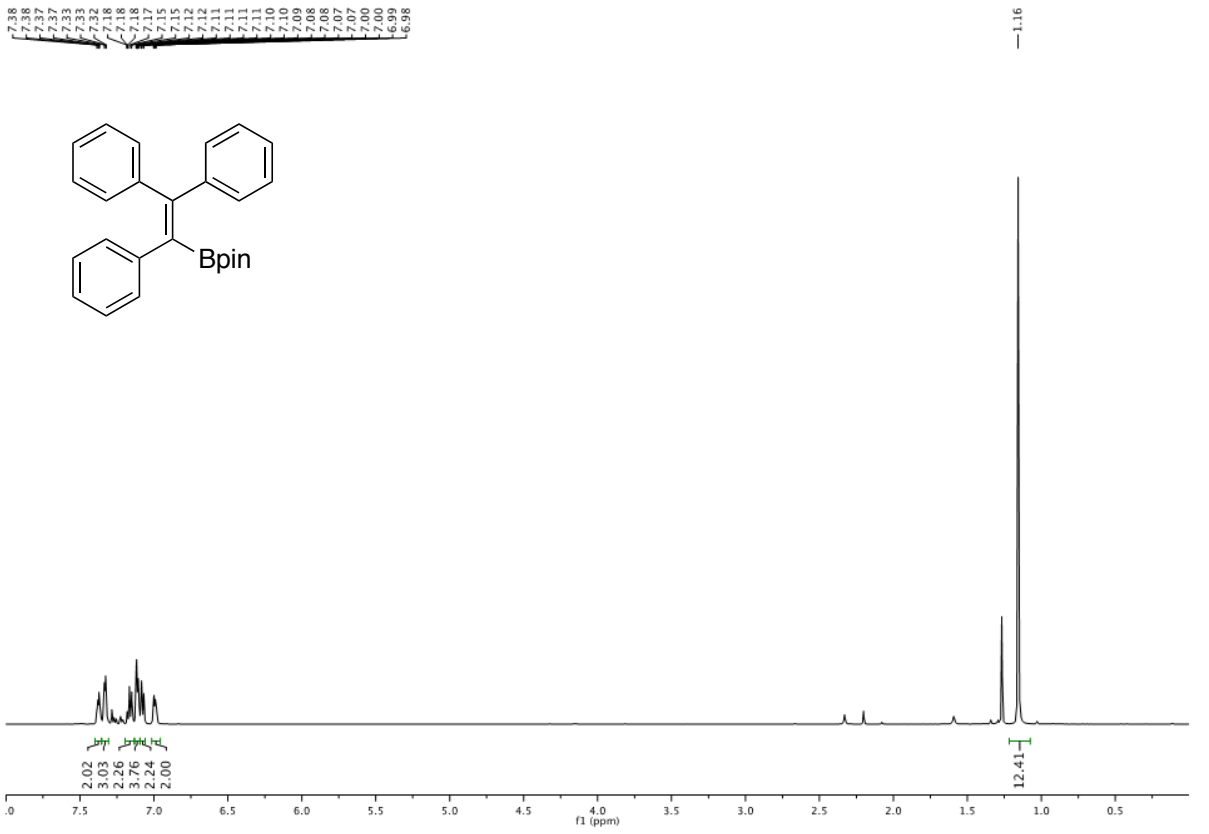
7.39
7.39
7.37
7.36
7.35
7.35
7.33
7.33
7.31
7.30
7.28
7.27
7.07
7.06
7.06
4.25
S
1.00
1.03
7.38
0.98
2.07
f1 (ppm)
140.62
139.37
138.85
135.63
128.87
128.56
126.37
124.28
123.98
123.12
122.89
122.00
35.03
f1 (ppm)

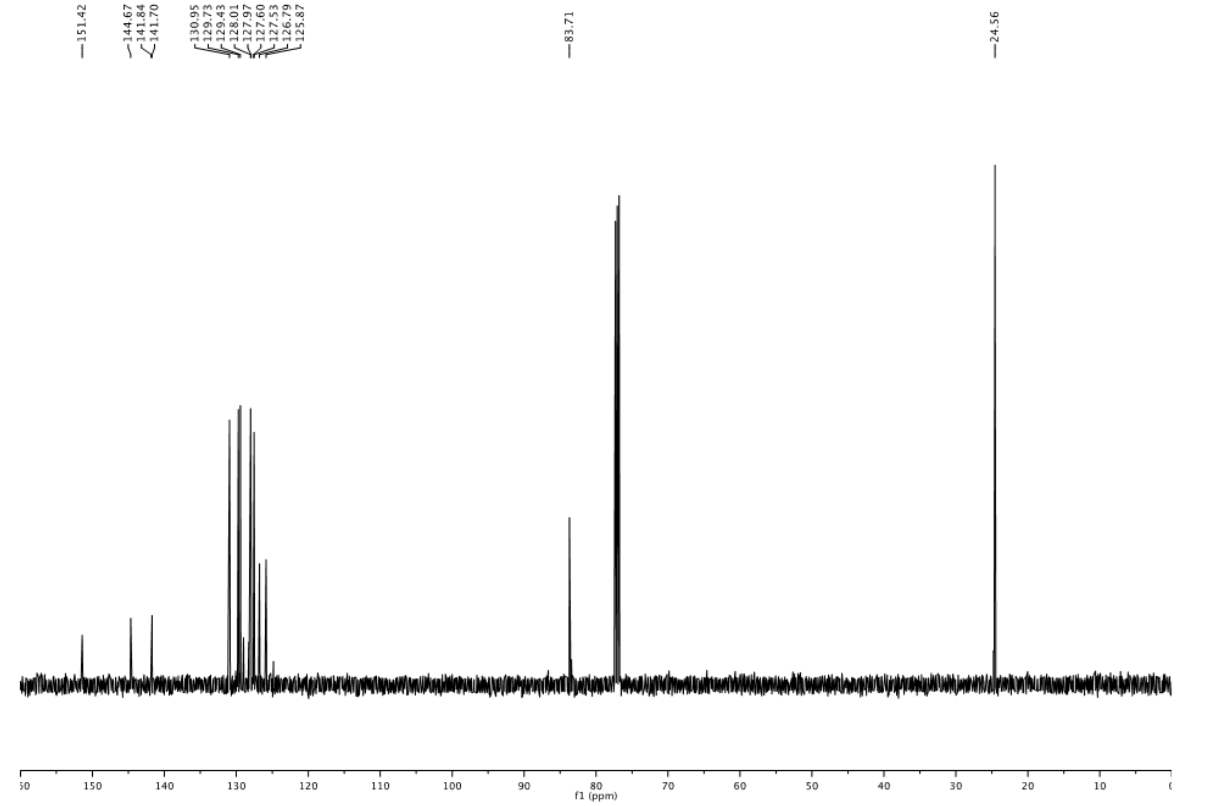

Me
Bpin
f1 (ppm)
f1 (ppm)

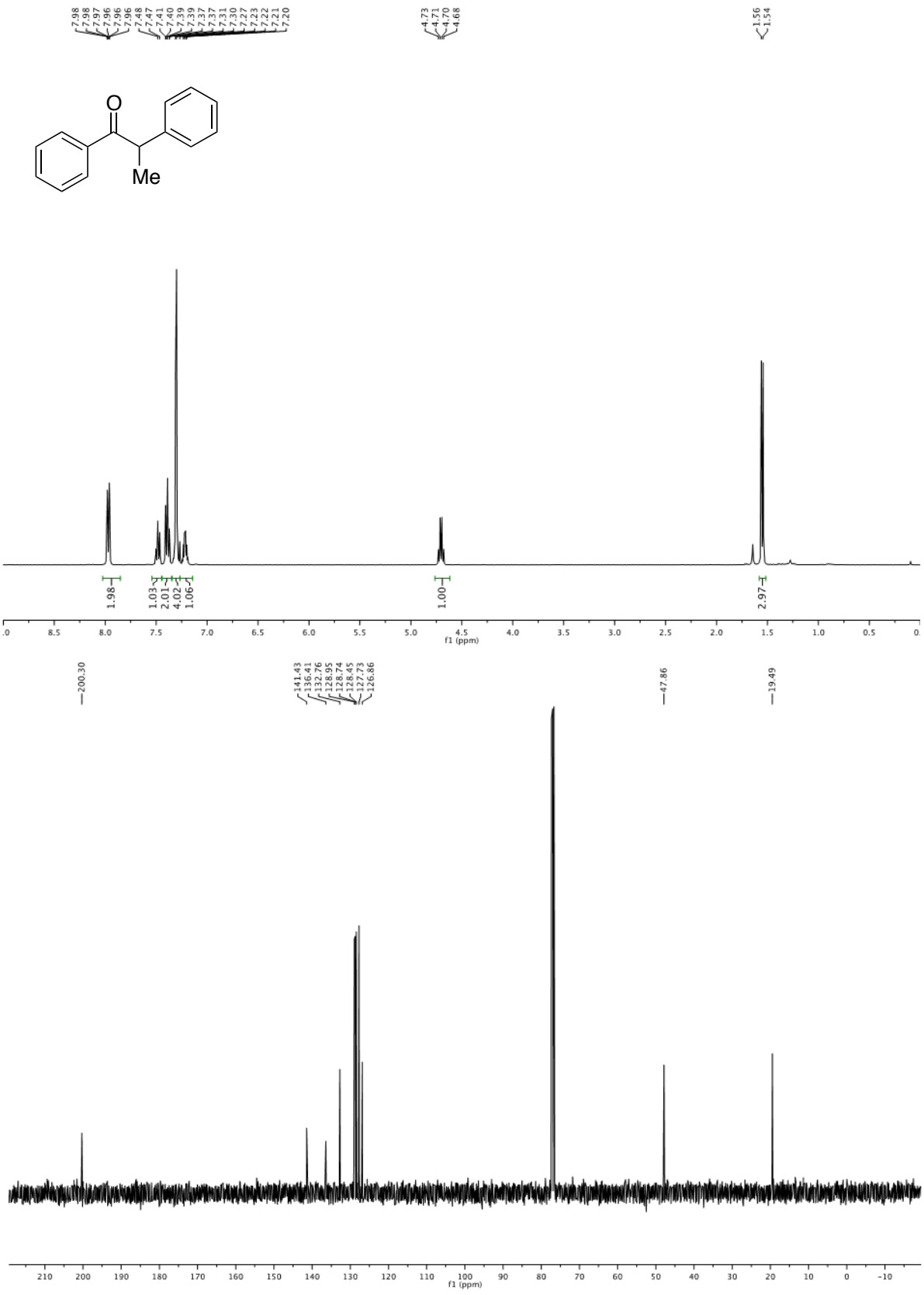

Me
Bpin
f1 (ppm)

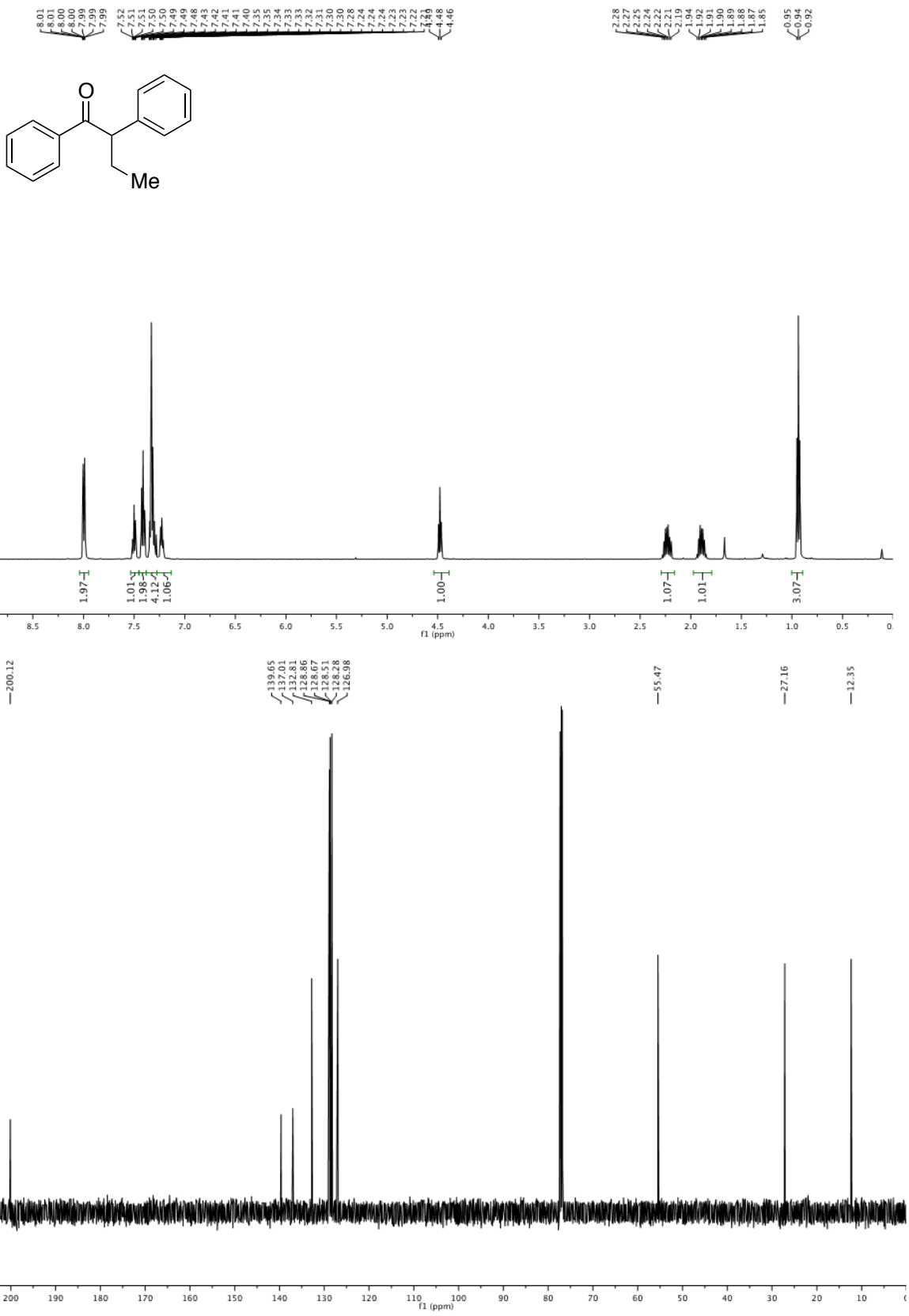

Me
Bpin
f1 (ppm)

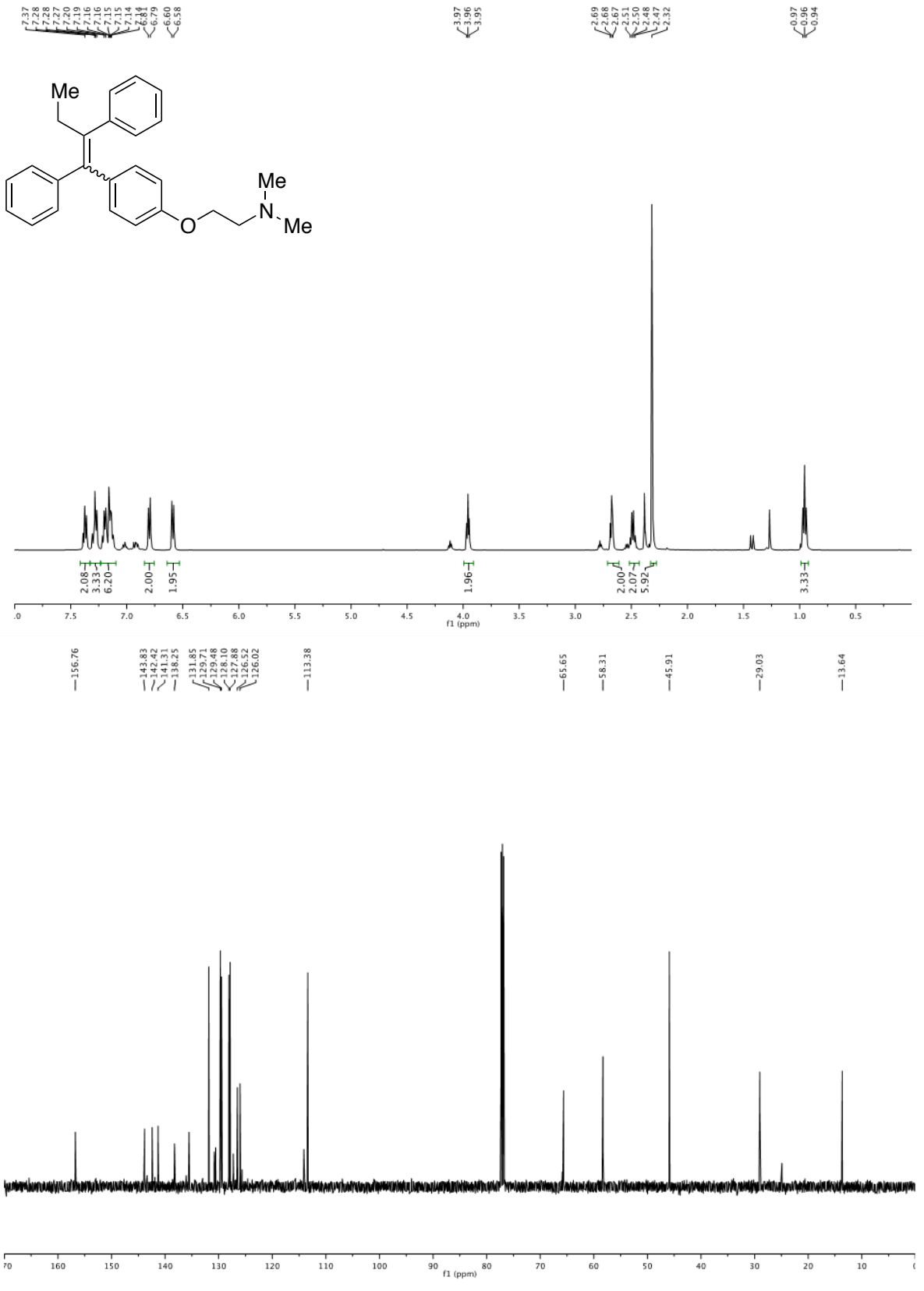

f1 (ppm)


Bpin
f1 (ppm)


f1 (ppm)




O
Me
f1 (ppm)
f1 (ppm)


Me
Me
N
Me
O
f1 (ppm)
f1 (ppm)