Supplemental material for:

Iridium-catalyzed Arene *ortho*-Silylation by Formal Hydroxyl-directed C-H Activation

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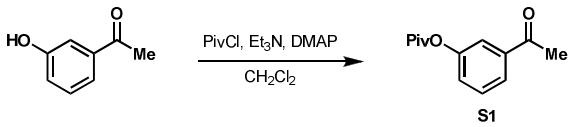
Materials and Methods

Silylation reactions were set up in an N_2-filled glovebox using oven-dried glassware and were stirred with Teflon-coated magnetic stirring bars. $[Ir(cod)OMe]_2$ was obtained as a gift from Johnson Matthey and was used as received. 1,10-Phenanthroline (phen) was purchased from Strem and was used as received. Diethylsilane (Et_2SiH_2) was purchased from Alfa Aesar and was used as received. Norbornene (nbe) was purchased from Aldrich and was used as received. Tetrahydrofuran (THF) was degassed by purging with nitrogen and then dried with a solvent purification system containing activated alumina. All other solvents and reagents were used as received, with the exception of 3-methylbenzaldehyde, 2-ethylbenzaldehyde and 2-acetylthiophene, which were purified by bulb-to-bulb vacuum transfer. Reaction temperatures above 23 °C refer to temperatures of an aluminum heating block, which were either controlled by an electronic temperature modulator, or manually controlled and monitored using a standard alcohol thermometer. Silica gel chromatography was performed using a Teledyne Isco CombiFlash® R_f system with Redi*Sep* R_f Gold™ columns. Kugelrohr distillation was performed using a Büchi Glass Oven B-580. ^1H and ^{13}C NMR spectra were recorded on Varian U-500, VXR-500 and U-400 spectrometers with ^{13}C operating frequencies of 125 MHz, 125 MHz and 100 MHz, respectively. Chemical shifts (δ) are reported in ppm relative to the residual solvent signal (δ = 7.26 for ^1H NMR and δ = 77.0 for ^{13}C NMR). ^{19}F NMR spectra were recorded on a Varian U-500 spectrometer with a ^{19}F operating frequency of 470 MHz. Data for ^1H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constants, number of hydrogens). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). 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. High-resolution mass spectral data were obtained from the University of Illinois SCS Mass Spectrometry Laboratory.

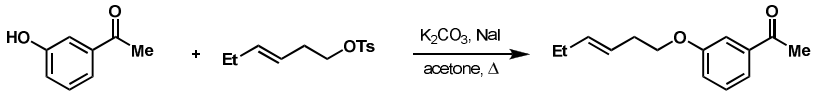
Experimental Procedures

Synthesis of Substrates



S1

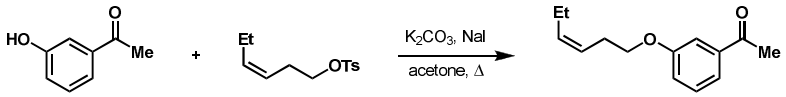
Pivalate S1[1]: To a solution of 3'-hydroxyacetophenone (403 mg, 2.96 mmol), pivaloyl chloride (0.44 mL, 3.6 mmol) and DMAP (18.3 mg, 0.150 mmol) in CH_2Cl_2 (6.0 mL) at rt was added Et_3N (0.50 mL, 3.6 mmol). Rapid evolution of heat and formation of a precipitate were observed. The resulting suspension was stirred at rt for 21 h and then diluted with CH_2Cl_2 (30 mL). The organic layer was washed (30 mL water, then 30 mL 1 N HCl, then 30 mL sat. aq. Na_2CO_3), dried ($MgSO_4$) and concentrated to give 721 mg of a dark orange/brown oil. The crude product was adsorbed onto SiO_2 and purified by silica gel chromatography (12 g SiO_2 column, 100:0→80:20 hexanes/EtOAc) to give 552 mg (2.51 mmol, 85%) of **S1**[1] as a light yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.63 (t, *J* = 2.0 Hz, 1H), 7.47 (t, *J* = 7.9 Hz, 1H), 7.26 (ddd, *J* = 8.1, 2.3, 0.9 Hz, 1H), 2.60 (s, 3H), 1.36 (s, 9H) (lit. ^{1}H NMR data not reported); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 197.0, 176.8, 151.3, 138.4, 129.5, 126.4, 125.6, 121.2, 39.1, 27.1, 26.7 (lit. ^{13}C NMR data not reported).



S2 **S3**

(*E*)-Alkene S3: A solution of 3'-hydroxyacetophenone (404 mg, 2.97 mmol), (*E*)-tosylate **S2**[2] (918 mg, 3.61 mmol) and NaI (51.8 mg, 0.346 mmol) in acetone (7.5 mL) in a 20 mL vial was treated with K_2CO_3 (994 mg, 7.19 mmol). The vial was sealed with a Teflon-lined screw-cap, and the resulting suspension was stirred at 65 °C for 66 h. After cooling to rt, the reaction mixture was poured onto water (30 mL) and extracted with Et_2O (2 x 30 mL). The combined organic layers were washed (2 x 20 mL 1 N NaOH, then 20 mL aq. $NaHSO_3$), dried ($MgSO_4$) and concentrated to give 670 mg of a dark orange oil. The crude product was adsorbed onto Celite (ca. 1.5 g) and purified by silica gel

chromatography (40 g SiO_2 column, 100:0→95:5 hexanes/EtOAc) to give 453 mg (2.07 mmol, 70%) of **S3** as a pale golden oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51 (ddd, *J* = 7.6, 1.5, 0.9 Hz, 1H), 7.49-7.45 (m, 1H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.09 (ddd, *J* = 8.2, 2.6, 0.9 Hz, 1H), 5.66-5.58 (m, 1H), 5.52-5.43 (m, 1H), 4.00 (t, *J* = 6.9 Hz, 2H), 2.58 (s, 3H), 2.48 (qd, *J* = 6.8, 1.0 Hz, 2H), 2.08-1.99 (m, 2H), 0.98 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 197.9, 159.1, 138.3, 135.0, 129.4, 124.1, 120.9, 120.0, 113.1, 68.0, 32.4, 26.7, 25.6, 13.7; **HRMS** (EI+) calcd for $[C_{14}H_{18}O_2]^+$: *m/z* 218.1307, found 218.1295.



S4 S5

(*Z*)-Alkene S5: A solution of 3'-hydroxyacetophenone (409 mg, 3.00 mmol), (*Z*)-tosylate **S4**[3] (obtained by the same general procedure described for the preparation of (*E*)-tosylate **S2**[2]) (920 mg, 3.62 mmol) and NaI (48.0 mg, 0.320 mmol) in acetone (7.5 mL) in a 20 mL vial was treated with K_2CO_3 (996 mg, 7.21 mmol). The vial was sealed with a Teflon-lined screw-cap and the resulting suspension was stirred at 65 °C for 65 h. After cooling to rt, the reaction mixture was poured onto water (30 mL) and extracted with Et_2O (2 x 30 mL). The combined organic layers were washed (2 x 20 mL 1 N NaOH, then 20 mL aq. Na_2SO_3), dried ($MgSO_4$) and concentrated to give 605 mg of an orange oil. The crude product was adsorbed onto Celite (ca. 1.5 g) and purified by silica gel chromatography (40 g SiO_2 column, 100:0→95:5 hexanes/EtOAc) to give 410 mg (1.87 mmol, 63%) of **S5** as a pale golden oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 7.6, 0.7 Hz, 1H), 7.48-7.44 (m, 1H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.08 (dd, *J* = 8.2, 2.6 Hz, 1H), 5.57-5.49 (m, 1H), 5.46-5.38 (m, 1H), 3.99 (t, *J* = 6.9 Hz, 2H), 2.57 (s, 3H), 2.54 (q, *J* = 7.0 Hz, 2H), 2.09 (pent, *J* = 7.5 Hz, 2H), 0.98 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 197.9, 159.1, 138.3, 134.4, 129.4, 123.8, 120.9, 119.9, 113.0, 67.6, 27.2, 26.6, 20.6, 14.2; **HRMS** (EI+) calcd for $[C_{14}H_{18}O_2]^+$: *m/z* 218.1307, found 218.1302.

General Procedures

General procedure for intramolecular arene silylation – 1.0 mmol scale: In an N_2-filled glovebox, ca. 1.0 mmol of the ketone, aldehyde or alcohol substrate was weighed into a 1 dram screw-top vial. A stir bar was added, and the substrate was dissolved in THF (0.50 mL). The resulting solution was treated first with a freshly prepared stock solution of $[Ir(cod)OMe]_2$ (0.5 μmol, 0.05 mol %) in THF (0.50 mL) and then neat Et_2SiH_2 (1.20 mmol). The vial was capped with a Teflon-lined screw-cap, and the resulting solution was stirred in the glovebox at rt until complete conversion to the corresponding diethyl(hydrido)silyl ether was observed, as determined by GC-MS analysis (generally 5-12 h). The volatile materials were then removed by placing the reaction mixture directly under high-vacuum for 1 h (the stir bar was temporarily removed during this operation to prevent bumping). The stir bar was replaced, and the concentrated diethyl(hydrido)silyl ether was then sequentially treated with freshly prepared stock solutions of norbornene (1.20 mmol) in THF (1.0 mL), $[Ir(cod)OMe]_2$ (4.5 μmol, 0.45 mol %) in THF (0.50 mL) and 1,10-phenanthroline (12.5 μmol, 1.25 mol %) in THF (0.50 mL). The Teflon-lined screw-cap was replaced, and the resulting solution was stirred in the glovebox for 1 h (to ensure complete formation of the active Ir species). The vial was then removed from the glovebox, placed in a pre-heated aluminum heating block at the specified temperature and stirred for the indicated period of time. After the cyclization was complete (as determined by GC-MS analysis), the reaction mixture was allowed to cool to rt and the solvent was removed via rotary evaporation. The crude product was purified either by silica gel chromatography or by Kugelrohr distillation, as indicated for each product (*vide infra*).

General procedure for intramolecular arene silylation – 5.0 mmol scale: In an N_2-filled glovebox, ca. 5.0 mmol of substrate was weighed into a 20 mL screw-top vial. A stir bar was added, followed by THF (2.5 mL). The resulting solution was treated first with a freshly prepared solution of $[Ir(cod)OMe]_2$ (2.5 μmol, 0.05 mol %) in THF (2.5 mL) and then neat Et_2SiH_2 (ca. 5.5 mmol). The vial was capped with a Teflon-lined screw-cap and the resulting solution was stirred in the glovebox at rt until GC-MS

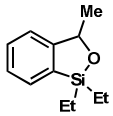
analysis indicated full conversion to the corresponding diethyl(hydrido)silyl ether. The volatile materials were removed by placing the reaction mixture directly under high-vacuum for 1.5 h (the stir bar was temporarily removed during this operation to prevent bumping). The stir bar was replaced, and the concentrated diethyl(hydrido)silyl ether was then sequentially treated with freshly prepared solutions of norbornene (ca. 6.0 mmol) in THF (6.0 mL), $[Ir(cod)OMe]_2$ (10 μmol, 0.20 mol %) in THF (2.0 mL) and 1,10-phenanthroline (31 μmol, 0.63 mol %) in THF (2.0 mL). The Teflon-lined screw-cap was replaced, and the resulting solution was stirred in the glovebox for 1 h. The vial was then removed from the glovebox, placed in a pre-heated aluminum heating block at the specified temperature and stirred until the cyclization was complete (as determined by GC-MS analysis). The reaction mixture was then allowed to cool to rt and the solvent was removed via rotary evaporation. The crude product was adsorbed onto Celite (ca. 2.0 g) and purified by silica gel chromatography (40 g SiO_2 column) to provide the benzoxasilole product.

General procedure for Tamao-Fleming oxidation of benzoxasilole products: A solution of benzoxasilole (0.50 mmol) in 1:1 THF/MeOH (2.0 mL) was treated sequentially with $KHCO_3$ (1.0 mmol) and H_2O_2 (30% solution in H_2O, 4.0 mmol). The resulting mixture was stirred at rt until complete consumption of the benzoxasilole was observed, as judged by TLC analysis (typically 14-18 h). The reaction was carefully quenched by slow addition of the reaction mixture (via pipette) to a solution of aq. $NaHSO_3$ (15 mL), and the resulting mixture was extracted with EtOAc (3 x 15 mL). The combined organic layers were washed (15 mL water, then 15 mL sat. $NaHCO_3$), dried ($MgSO_4$) and concentrated. Without further purification, the crude phenol was dissolved in CH_2Cl_2 (1.5 mL) and Et_3N (0.75 mL), and the resulting solution was treated with Ac_2O (3 equiv). After being stirred at rt overnight, the reaction mixture was concentrated. The resulting residue was adsorbed onto SiO_2 and purified by silica gel chromatography to provide the diacetate product.

General procedure for Hiyama coupling of benzoxasilole products: In an N_2-filled glovebox, a 1 dram screw-top vial was charged with benzoxasilole (0.25 mmol), aryl

iodide (0.30 mmol) and a stir bar. A freshly prepared solution of $Pd(OAc)_2$ (2.3 mg, 10 μmol, 4 mol %) and 1,2-bis(dicyclohexylphosphino)ethane (4.7 mg, 11 μmol, 4.5 mol %) in dioxane (1.25 mL) was then added. The vial was capped with a screw cap containing a PTFE-lined septum and removed from the glovebox. After being stirred at rt for 5-10 min, the light yellow/golden solution was treated with 2 M aq. NaOH (0.63 mL, 1.25 mmol), and the resulting biphasic mixture was further stirred at rt for 30 min. The vial was then placed in a pre-heated aluminum heating block at 65 °C and stirred for 14 h. The reaction mixture was allowed to cool to rt and then diluted with EtOAc, filtered through SiO_2 and concentrated. The residue was adsorbed onto SiO_2 and purified by silica gel chromatography to provide the biaryl alcohol product.

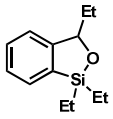
Spectral data for benzoxasilole products:



7a

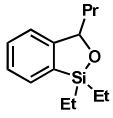
Benzoxasilole 7a: Following the general procedure, acetophenone (123 mg, 1.02 mmol) was converted to the corresponding diethyl(hydrido)silyl ether using $[Ir(cod)OMe]_2$ (0.05 mol %) at rt. **GC/MS**: *m/z* 208.1 (0.5%, $[M]^+$), 193.1 (23.9%, $[M\text{-}Me]^+$), 179.1 (13.6%, $[M\text{-}Et]^+$), 103.0 (100.0%, $[OSi(H)Et_2]^+$). The subsequent cyclization was conducted with $[Ir(cod)OMe]_2$/phen (1.0 mol %) at 80 °C for 12 h. Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel chromatography (4 g SiO_2 column, 100:0→90:10 hexanes/EtOAc) gave 154 mg (73%) of **7a** as a colorless oil. Following the general procedure for silylation on 5.0 mmol scale, 600 mg (4.99 mmol) of acetophenone was converted to the corresponding diethyl(hydrido)silyl ether and allowed to cyclize at 100 °C over 14 h. Purification by silica gel chromatography (100:0→95:5 hexanes/EtOAc) gave 824 mg (80%) of **7a** as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.2 Hz, 1H), 7.41 (td, *J* = 7.6, 1.2 Hz, 1H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 7.7 Hz, 1H), 5.36 (q, *J* = 6.5 Hz, 1H), 1.52 (d, *J* = 6.5 Hz, 3H), 0.98 (t, *J* = 7.7 Hz, 3H), 0.95 (t, *J* = 7.8 Hz, 3H), 0.92-0.76 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 154.9, 132.9, 131.4, 129.6, 126.7, 122.1, 78.1, 25.1,

7.1, 7.0, 6.7, 6.4; **GC/MS**: *m/z* 206.1 (2.2%, $[M]^+$), 191.1 (26.2%, $[M\text{-}Me]^+$), 177.1 (100.0%, $[M\text{-}Et]^+$); **HRMS** (EI+) calcd for $[C_{12}H_{18}OSi]^+$: *m/z* 206.1127, found 206.1139.



7b

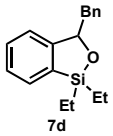
Benzoxasilole 7b: Following the general procedure, propiophenone (135 mg, 1.01 mmol) was converted to the corresponding diethyl(hydrido)silyl ether using $[Ir(cod)OMe]_2$ (0.05 mol %) at rt. **GC/MS**: *m/z* 193.1 (100.0%, $[M\text{-}Et]^+$). The subsequent cyclization was conducted with $[Ir(cod)OMe]_2$/phen (1.0 mol %) at 80 °C for 11 h. Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel chromatography (4 g SiO_2 column, 100:0→90:10 hexanes/EtOAc) gave 140 mg (63%) of **7b** as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.2 Hz, 1H), 7.40 (td, *J* = 7.6, 1.1 Hz, 1H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.23 (d, *J* = 7.7 Hz, 1H), 5.21 (dd, *J* = 7.6, 3.5 Hz, 1H), 2.00 (dqd, *J* = 14.7, 7.4, 3.6 Hz, 1H), 1.64 (dq, *J* = 14.7, 7.4 Hz, 1H), 1.05-0.97 (m, 6H), 0.94 (t, *J* = 7.6 Hz, 3H), 0.91-0.79 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 153.6, 133.7, 131.4, 129.5, 126.7, 122.1, 82.9, 31.7, 9.5, 7.2, 7.0, 6.7, 6.4; **GC/MS**: *m/z* 220.1 (0.5%, $[M]^+$), 219.1 (1.3%, $[M\text{-}H]^+$), 191.1 (100.0%, $[M\text{-}Et]^+$); **HRMS** (EI+) calcd for $[C_{13}H_{19}OSi]^+$ $(M\text{-}H)^+$: *m/z* 219.1205, found 219.1211.



7c

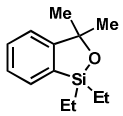
Benzoxasilole 7c: Following the general procedure, butyrophenone (145 mg, 0.978 mmol) was converted to the corresponding diethyl(hydrido)silyl ether using $[Ir(cod)OMe]_2$ (0.05 mol %) at rt. **GC/MS**: *m/z* 236.1 (0.1%, $[M]^+$), 235.1 (0.1%, $[M\text{-}H]^+$), 207.1 (3.0%, $[M\text{-}Et]^+$), 193.1 (100.0%, $[M\text{-}Pr]^+$). The subsequent cyclization was conducted with $[Ir(cod)OMe]_2$/phen (1.0 mol %) at 80 °C for 18 h. Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel chromatography (12 g SiO_2 column, 100:0→95:5 hexanes/EtOAc) gave 150 mg (65%) of **7c** as a colorless oil. Following the general procedure for silylation on 5.0 mmol scale, 735 mg (4.96 mmol) of butyrophenone was converted to the corresponding

diethyl(hydrido)silyl ether and allowed to cyclize at 100 °C over 17 h. Purification by silica gel chromatography (100:0→95:5 hexanes/EtOAc) gave 912 mg (78%) of **7c** as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.2 Hz, 1H), 7.40 (td, *J* = 7.6, 1.2 Hz, 1H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.23 (dd, *J* = 7.7, 0.7 Hz, 1H), 5.25 (dd, *J* = 7.8, 3.3 Hz, 1H), 1.95-1.85 (m, 1H), 1.65-1.44 (m, 3H), 1.04-0.91 (m, 9H), 0.91-0.77 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 154.0, 133.5, 131.4, 129.4, 126.6, 122.1, 81.7, 41.4, 18.6, 14.2, 7.2, 7.0, 6.7, 6.4; **GC/MS**: *m/z* 234.2 (0.5%, $[M]^+$), 233.1 (1.3%, $[M-H]^+$), 205.1 (20.9%, $[M-Et]^+$), 191.1 (100.0%, $[M-Pr]^+$); **HRMS** (EI+) calcd for $[C_{14}H_{21}OSi]^+$ $(M-H)^+$: *m/z* 233.1362, found 233.1367.



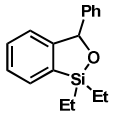
7d

Benzoxasilole 7d: Following the general procedure, 1,2-diphenylethanol[4] (193 mg, 0.973 mmol) was converted to the corresponding diethyl(hydrido)silyl ether using $[Ir(cod)OMe]_2$ (0.05 mol %) at rt. **GC/MS**: *m/z* 283.3 (0.2%, $[M-H]^+$), 255.1 (4.8%, $[M-Et]^+$), 193.1 (100.0%, $[M-Bn]^+$). The subsequent cyclization was conducted with $[Ir(cod)OMe]_2$/phen (1.0 mol %) at 80 °C for 12 h. Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel chromatography (12 g SiO_2 column, 100:0→95:5 hexanes/EtOAc) gave 241 mg (88%) of **7d** as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.1 Hz, 1H), 7.43 (td, *J* = 7.5, 0.9 Hz, 1H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.32-7.27 (m, 2H), 7.27-7.21 (m, 4H), 5.52 (dd, *J* = 7.3, 4.5 Hz, 1H), 3.20 (dd, *J* = 13.9, 4.5 Hz, 1H), 3.00 (dd, *J* = 13.9, 7.4 Hz, 1H), 1.00 (t, *J* = 8.0 Hz, 3H), 0.92 (t, *J* = 7.6 Hz, 3H), 0.89-0.77 (m, 2H), 0.75-0.63 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.0, 138.3, 133.8, 131.5, 129.8, 129.3, 128.0, 126.9, 126.2, 122.5, 82.4, 45.6, 7.1, 6.9, 6.7, 6.4; **GC/MS**: *m/z* 281.2 (0.6%, $[M-H]^+$), 253.1 (3.8%, $[M-Et]^+$), 191.1 (100.0%, $[M-Bn]^+$); **HRMS** (EI+) calcd for $[C_{18}H_{20}OSi]^+$ $(M-H_2)^+$: *m/z* 280.1283, found 280.1272.



7e

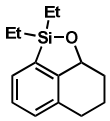
Benzoxasilole 7e: Following the general procedure, 2-phenyl-2-propanol (139 mg, 1.02 mmol) was converted to the corresponding diethyl(hydrido)silyl ether using $[Ir(cod)OMe]_2$ (0.05 mol %) at rt. **GC/MS**: *m/z* 222.1 (0.3%, $[M]^+$), 207.1 (37.2%, $[M\text{-}Me]^+$), 193.1 (9.6%, $[M\text{-}Et]^+$), 103.1 (100.0%, $[OSi(H)Et_2]^+$). The subsequent cyclization was conducted with $[Ir(cod)OMe]_2$/phen (1.0 mol %) at 80 °C for 13 h. Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel chromatography (4 g SiO_2 column, 100:0→90:10 hexanes/EtOAc) gave 156 mg (70%) of **7e** as a colorless oil. In a separate experiment, the cyclization was conducted at 60 °C for 44 h (under otherwise identical conditions) and provided **7e** in 68% isolated yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.1 Hz, 1H), 7.41 (td, *J* = 7.6, 1.3 Hz, 1H), 7.29 (td, *J* = 7.3, 0.8 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 1H), 1.56 (s, 6H), 0.97 (t, *J* = 7.8 Hz, 6H), 0.90-0.77 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 158.5, 132.3, 131.3, 129.7, 126.6, 122.1, 83.3, 32.0, 7.2, 6.7; **GC/MS**: *m/z* 220.2 (0.1%, $[M]^+$), 205.1 (100.0%, $[M\text{-}Me]^+$), 191.1 (33.2%, $[M\text{-}Et]^+$); **HRMS** (EI+) calcd for $[C_{13}H_{20}OSi]^+$: *m/z* 220.1283, found 220.1279.



7f

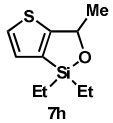
Benzoxasilole 7f: Following the general procedure, benzophenone (181 mg, 0.993 mmol) was converted to the corresponding diethyl(hydrido)silyl ether using $[Ir(cod)OMe]_2$ (0.05 mol %) at rt. **GC/MS**: *m/z* 241.1 (15.9%, $[M\text{-}Et]^+$), 167.1 (100.0%, $[M\text{-}OSi(H)Et_2]^+$). The subsequent cyclization was conducted with $[Ir(cod)OMe]_2$/phen (1.0 mol %) at 80 °C for 12 h. Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel chromatography (12 g SiO_2 column, 100:0→90:10 hexanes/EtOAc) gave 224 mg (84%) of **7f** as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 5.7, 2.4 Hz, 1H), 7.40-7.28 (m, 7H), 7.06 (dd, *J* = 5.7, 2.4 Hz, 1H), 6.20 (s, 1H), 1.12 (t, *J* = 7.7 Hz, 3H), 1.04 (t, *J* = 7.6 Hz, 3H), 1.06-0.87 (m, 4H); **^{13}C NMR**

(125 MHz, $CDCl_3$) δ 153.0, 143.7, 133.4, 131.2, 129.7, 128.4, 127.8, 127.3, 126.9, 123.7, 84.2, 7.2, 6.9, 6.8, 6.5; **GC/MS**: *m/z* 268.1 (45.6%, $[M]^+$), 239.1 (100.0%, $[M\text{-}Et]^+$); **HRMS** (EI+) calcd for $[C_{17}H_{20}OSi]^+$: *m/z* 268.1283, found 268.1276.



7g

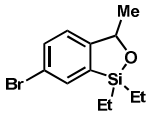
Benzoxasilole 7g: Following the general procedure, α-tetralone (150 mg, 1.03 mmol) was converted to the corresponding diethyl(hydrido)silyl ether using $[Ir(cod)OMe]_2$ (0.05 mol %) at rt. **GC/MS**: *m/z* 205.1 (10.6%, $[M\text{-}Et]^+$), 129.1 (100.0%). The subsequent cyclization was conducted with $[Ir(cod)OMe]_2$/phen (1.0 mol %) at 80 °C for 11 h. Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel chromatography (4 g SiO_2 column, 100:0→90:10 hexanes/EtOAc) gave 170 mg (71%) of **7g** as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 7.1, 0.6 Hz, 1H), 7.24 (t, *J* = 7.3 Hz, 1H), 7.14 (dd, *J* = 7.5, 0.9 Hz, 1H), 4.96 (dd, *J* = 11.4, 5.0 Hz, 1H), 2.85 (ddd, *J* = 17.1, 7.6, 3.0 Hz, 1H), 2.73 (ddd, *J* = 16.9, 8.9, 7.9 Hz, 1H), 2.35 (ddd, *J* = 11.7, 9.0, 4.2 Hz, 1H), 2.06-1.98 (m, 1H), 1.94-1.83 (m, 1H), 1.47 (ddd, *J* = 24.0, 11.7, 4.6 Hz, 1H), 1.03 (t, *J* = 7.8 Hz, 3H), 0.93-0.85 (m, 5H), 0.84-0.77 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 150.7, 133.7, 132.8, 128.81, 128.78, 127.3, 78.5, 31.2, 26.5, 20.4, 6.7, 6.6, 6.5, 6.4; **GC/MS**: *m/z* 232.1 (23.9%, $[M]^+$), 203.1 (100.0%, $[M\text{-}Et]^+$); **HRMS** (EI+) calcd for $[C_{14}H_{20}OSi]^+$: *m/z* 232.1283, found 232.1286.



7h

Benzoxasilole 7h: Following the general procedure, 2-acetylthiophene (128 mg, 1.01 mmol) was converted to the corresponding diethyl(hydrido)silyl ether using $[Ir(cod)OMe]_2$ (0.05 mol %) at rt. **GC/MS**: *m/z* 214.1 (11.5%, $[M]^+$), 199.0 (14.3%, $[M\text{-}Me]^+$), 185.0 (36.2%, $[M\text{-}Et]^+$), 111.0 (100.0%, $[M\text{-}OSi(H)Et_2]^+$). The subsequent cyclization was conducted with $[Ir(cod)OMe]_2$/phen (1.0 mol %) at 50 °C for 42 h. Concentration of the reaction mixture and purification of the resulting residue by

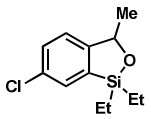
Kugelrohr distillation (30 mTorr, 60 °C) gave 131 mg (61%) of **7h** as a colorless oil. (Note: the purified material obtained by Kugelrohr distillation was accompanied by ca. 5% unidentified by-products; however, further purification by chromatography was precluded by the instability of **7h** on SiO_2). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 4.7, 0.6 Hz, 1H), 6.96 (d, *J* = 4.7 Hz, 1H), 5.39 (q, *J* = 6.4 Hz, 1H), 1.54 (d, *J* = 6.4 Hz, 3H), 0.98-0.92 (m, 6H), 0.86-0.74 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.0, 136.2, 128.8, 126.6, 75.0, 26.2, 7.4, 6.6, 6.4; **GC/MS**: *m/z* 212.1 (41.3%, $[M]^+$), 197.0 (17.7%, $[M\text{-}Me]^+$), 183.0 (100.0%, $[M\text{-}Et]^+$); **HRMS** (EI+) calcd for $[C_{10}H_{16}OSSi]^+$: *m/z* 212.0691, found 212.0701.



7i

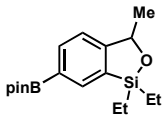
Benzoxasilole 7i: Following the general procedure, 4'-bromoacetophenone (194 mg, 0.975 mmol) was converted to the corresponding diethyl(hydrido)silyl ether using $[Ir(cod)OMe]_2$ (0.05 mol %) at rt. **GC/MS**: *m/z* 286.1 (0.2%, $[M]^+$), 285.0 (0.4%, $[M\text{-}H]^+$), 271.0 (31.4%, $[M\text{-}Me]^+$), 257.0 (6.1%, $[M\text{-}Et]^+$), 183.0 (28.5%, $[M\text{-}OSi(H)Et_2]^+$), 103.0 (100.0%, $[OSi(H)Et_2]^+$). The subsequent cyclization was conducted with $[Ir(cod)OMe]_2$/phen (1.0 mol %) at 80 °C for 18 h. Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel chromatography (12 g SiO_2 column, 100:0→90:10 hexanes/EtOAc) gave 207 mg (75%) of **7i** as a bright yellow oil. Following the general procedure for silylation on 5.0 mmol scale, 984 mg (4.94 mmol) of 4'-bromoacetophenone was converted to the corresponding diethyl(hydrido)silyl ether and allowed to cyclize at 100 °C over 17 h. Purification by silica gel chromatography (100:0→90:10 hexanes/EtOAc) gave 1.14 g (81%) of **7i** as a golden oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 1.9 Hz, 1H), 7.50 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.08 (d, *J* = 8.2 Hz, 1H), 5.28 (q, *J* = 6.5 Hz, 1H), 1.48 (d, *J* = 6.5 Hz, 3H), 0.95 (t, *J* = 7.6 Hz, 3H), 0.92 (t, *J* = 7.0 Hz, 3H), 0.89-0.73 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 153.7, 136.2, 133.8, 132.3, 123.9, 121.4, 77.7, 25.0, 7.0, 6.9, 6.6, 6.3; **GC/MS**: *m/z* 284.0 (7.5%, $[M]^+$), 269.0 (45.4%, $[M\text{-}Me]^+$), 257.0 (100.0%, $[M(^{81}Br)\text{-}Et]^+$), 255.0

(98.3%, [M(^{79}Br)-Et]$^+$); **HRMS** (EI+) calcd for [$C_{12}H_{17}BrOSi$]$^+$: *m/z* 284.0232, found 284.0224.



7j

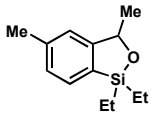
Benzoxasilole 7j: Following the general procedure, 4'-chloroacetophenone (154 mg, 1.00 mmol) was converted to the corresponding diethyl(hydrido)silyl ether using [Ir(cod)OMe]$_2$ (0.05 mol %) at rt. **GC/MS**: *m/z* 241.1 (1.2%, [M-H]$^+$), 227.1 (64.7%, [M-Me]$^+$), 213.0 (12.7%, [M-Et]$^+$), 139.0 (56.9%, [M-OSi(H)Et$_2$]$^+$), 103.1 (100.0%, [OSi(H)Et$_2$]$^+$). The subsequent cyclization was conducted with [Ir(cod)OMe]$_2$/phen (1.0 mol %) at 80 °C for 17 h. Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel chromatography (12 g SiO_2 column, 100:0→90:10 hexanes/EtOAc) gave 185 mg (77%) of **7j** as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 2.0 Hz, 1H), 7.35 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.13 (d, *J* = 8.2 Hz, 1H), 5.30 (q, *J* = 6.5 Hz, 1H), 1.48 (d, *J* = 6.5 Hz, 3H), 0.95 (t, *J* = 7.6 Hz, 3H), 0.92 (t, *J* = 7.0 Hz, 3H), 0.90-0.73 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 153.2, 135.6, 133.0, 130.9, 129.7, 123.5, 77.7, 25.0, 7.0, 6.9, 6.6, 6.3; **GC/MS**: *m/z* 240.0 (6.9%, [M]$^+$), 225.0 (49.0%, [M-Me]$^+$), 211.1 (100.0%, [M-Et]$^+$); **HRMS** (EI+) calcd for [$C_{12}H_{17}ClOSi$]$^+$: *m/z* 240.0737, found 240.0731.



7k

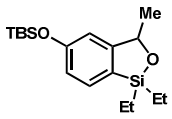
Benzoxasilole 7k: Following the general procedure, 4'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acetophenone[5] (246 mg, 1.00 mmol) was converted to the corresponding diethyl(hydrido)silyl ether using [Ir(cod)OMe]$_2$ (0.05 mol %) at rt. **GC/MS**: *m/z* 334.3 (1.7%, [M]$^+$), 319.2 (24.6%, [M-Me]$^+$), 305.2 (9.4%, [M-Et]$^+$), 226.3 (100.0%). The subsequent cyclization was conducted with [Ir(cod)OMe]$_2$/phen (1.0 mol %) at 80 °C for 15 h. Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel chromatography (12 g SiO_2 column,

100:0→90:10 hexanes/EtOAc) gave 279 mg (84%) of **7k** as a viscous colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.86 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.22 (d, *J* = 7.7 Hz, 1H), 5.34 (q, *J* = 6.5 Hz, 1H), 1.50 (d, *J* = 6.5 Hz, 3H), 1.36 (s, 12H), 0.98-0.72 (m, 10H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 158.2, 138.2, 136.1, 132.1, 121.4, 83.7, 78.1, 24.93, 24.85, 24.8, 7.11, 7.08, 6.7, 6.5; **GC/MS**: *m/z* 332.2 (1.9%, $[M]^+$), 317.2 (18.9%), 303.2 (100.0%, $[M\text{-}Et]^+$); **HRMS** (EI+) calcd for $[C_{18}H_{29}BO_3Si]^+$: *m/z* 332.1979, found 332.1983.



7l

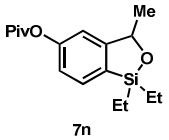
Benzoxasilole 7l: Following the general procedure, 3'-methylacetophenone (133 mg, 0.992 mmol) was converted to the corresponding diethyl(hydrido)silyl ether using $[Ir(cod)OMe]_2$ (0.05 mol %) at rt. **GC/MS**: *m/z* 222.1 (1.3%, $[M]^+$), 207.1 (13.5%, $[M\text{-}Me]^+$), 193.1 (10.0%, $[M\text{-}Et]^+$), 119.1 (45.6%, $[M\text{-}OSi(H)Et_2]^+$), 103.1 (100.0%, $[OSi(H)Et_2]^+$). The subsequent cyclization was conducted with $[Ir(cod)OMe]_2$/phen (1.0 mol %) at 80 °C for 48 h. Concentration of the reaction mixture and purification of the resulting residue by Kugelrohr distillation (30 mTorr, 60 °C) gave 157 mg (72%) of **7l** as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.4 Hz, 1H), 7.13 (d, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 0.6 Hz, 1H), 5.30 (q, *J* = 6.5 Hz, 1H), 2.39 (s, 3H), 1.50 (d, *J* = 6.5 Hz, 3H), 0.96 (t, *J* = 7.8 Hz, 3H), 0.93 (t, *J* = 7.8 Hz, 3H), 0.89-0.73 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.4, 139.6, 131.2, 129.4, 127.9, 122.8, 25.1, 21.6, 7.2, 7.1, 6.7, 6.4; **GC/MS**: *m/z* 220.1 (4.5%, $[M]^+$), 205.1 (16.4%, $[M\text{-}Me]^+$), 191.1 (100.0%, $[M\text{-}Et]^+$); **HRMS** (EI+) calcd for $[C_{13}H_{20}OSi]^+$: *m/z* 220.1283, found 220.1279.



7m

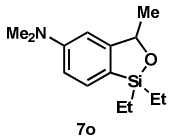
Benzoxasilole 7m: Following the general procedure, 3'-*tert*-butyldimethylsilyloxy-acetophenone[6] (245 mg, 0.978 mmol) was converted to the corresponding diethyl(hydrido)silyl ether using $[Ir(cod)OMe]_2$ (0.05 mol %) at rt. **GC/MS**: *m/z* 338.2 (66.1%, $[M]^+$), 323.2 (9.0%, $[M\text{-}Me]^+$), 309.2 (36.7%, $[M\text{-}Et]^+$), 281.1 (87.9%, [M-(*t*-

Bu)]$^+$), 177.1 (100.0%). The subsequent cyclization was conducted with [Ir(cod)OMe]$_2$/phen (1.0 mol %) at 80 °C for 12 h. Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel chromatography (12 g SiO_2 column, 100:0→90:10 hexanes/EtOAc) gave 282 mg (86%) of **7m** as a pale yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.9 Hz, 1H), 6.78 (dd, *J* = 7.9, 2.1 Hz, 1H), 6.66 (d, *J* = 2.0 Hz, 1H), 5.26 (q, *J* = 6.5 Hz, 1H), 1.48 (d, *J* = 6.5 Hz, 3H), 1.00 (s, 9H), 0.95 (t, *J* = 7.8 Hz, 3H), 0.93 (t, *J* = 7.7 Hz, 3H), 0.88-0.72 (m, 4H), 0.22 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 157.3, 157.2, 132.3, 124.4, 119.2, 113.6, 77.7, 25.6, 25.1, 18.2, 7.3, 7.2, 6.7, 6.5, -4.37, -4.40; **GC/MS**: *m/z* 336.2 (9.3%, [M]$^+$), 321.2 (2.8%, [M-Me]$^+$), 307.2 (100.0%, [M-Et]$^+$), 279.1 (18.8%, [M-(*t*-Bu)]$^+$); **HRMS** (EI+) calcd for $[C_{18}H_{32}O_2Si_2]^+$: *m/z* 336.1941, found 336.1930.



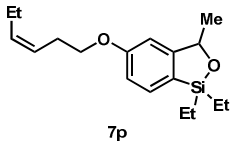
7n

Benzoxasilole 7n: Following the general procedure, pivalate **S1** (220 mg, 1.00 mmol) was converted to the corresponding diethyl(hydrido)silyl ether using [Ir(cod)OMe]$_2$ (0.05 mol %) at rt. **GC/MS**: *m/z* 308.1 (9.0%, [M]$^+$), 293.1 (2.7%, [M-Me]$^+$), 57.1 (100.0%, $[C_4H_9]^+$). The subsequent cyclization was conducted with [Ir(cod)OMe]$_2$/phen (1.0 mol %) at 100 °C for 12 h. Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel chromatography (12 g SiO_2 column, 100:0→85:15 hexanes/EtOAc) gave 254 mg (83%) of **7n** as a pale yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.8 Hz, 1H), 7.00 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.91 (d, *J* = 1.9 Hz, 1H), 5.31 (q, *J* = 6.5 Hz, 1H), 1.50 (d, *J* = 6.5 Hz, 3H), 1.36 (s, 9H), 0.95 (t, *J* = 7.8 Hz, 3H), 0.93 (t, *J* = 7.8 Hz, 3H), 0.90-0.73 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 176.9, 156.8, 152.6, 132.3, 129.9, 120.3, 115.2, 77.7, 39.0, 27.0, 24.9, 7.1, 7.0, 6.6, 6.3; **GC/MS**: *m/z* 306.2 (5.1%, [M]$^+$), 291.1 (7.3%, [M-Me]$^+$), 277.1 (100.0%, [M-Et]$^+$); **HRMS** (EI+) calcd for $[C_{17}H_{26}O_3Si]^+$: *m/z* 306.1651, found 306.1641.



7o

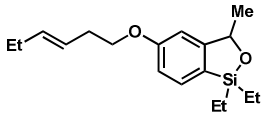
Benzoxasilole 7o: Following the general procedure, 3'-dimethylaminoacetophenone (161 mg, 0.986 mmol) was converted to the corresponding diethyl(hydrido)silyl ether using $[Ir(cod)OMe]_2$ (0.05 mol %) at rt. **GC/MS**: *m/z* 251.2 (56.6%, $[M]^+$), 236.1 (2.8%, $[M\text{-}Me]^+$), 222.1 (18.4%, $[M\text{-}Et]^+$), 149.1 (100.0%, $[M\text{-}OSiEt_2]^+$). The subsequent cyclization was conducted with $[Ir(cod)OMe]_2$/phen (1.0 mol %) at 80 °C for 39 h. Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel chromatography (4 g SiO_2 column, 100:0→90:10 hexanes/EtOAc) gave 203 mg (82%) of **7o** as a pale golden oil. Following the general procedure for silylation on 5.0 mmol scale, 814 mg (4.99 mmol) of 3'-dimethylaminoacetophenone was converted to the corresponding diethyl(hydrido)silyl ether and allowed to cyclize at 100 °C over 25 h. Purification by silica gel chromatography (100:0→90:10 hexanes/EtOAc) gave 987 mg (79%) of **7o** as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.1 Hz, 1H), 6.73 (dd, *J* = 8.1, 2.2 Hz, 1H), 6.52 (d, *J* = 2.2 Hz, 1H), 5.30 (q, *J* = 6.5 Hz, 1H), 3.01 (s, 6H), 1.54 (d, *J* = 6.5 Hz, 3H), 0.98 (t, *J* = 7.8 Hz, 3H), 0.96 (t, *J* = 7.9 Hz, 3H), 0.89-0.74 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.8, 151.7, 132.1, 118.1, 111.8, 105.2, 78.0, 40.3, 25.3, 7.4, 7.3, 6.8, 6.5; **GC/MS**: *m/z* 249.1 (36.0%, $[M]^+$), 234.1 (1.2%, $[M\text{-}Me]^+$), 220.1 (100.0%, $[M\text{-}Et]^+$); **HRMS** (EI+) calcd for $[C_{14}H_{23}NOSi]^+$: *m/z* 249.1549, found 249.1540.



7p

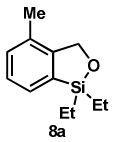
Benzoxasilole 7p: Following the general procedure, alkene **S5** (216 mg, 0.990 mmol) was converted to the corresponding diethyl(hydrido)silyl ether using $[Ir(cod)OMe]_2$ (0.05 mol %) at rt. **GC/MS**: *m/z* 306.2 (8.5%, $[M]^+$), 291.2 (5.5%, $[M\text{-}Me]^+$), 277.2 (10.3%, $[M\text{-}Et]^+$), 223.1 (100.0%, $[M\text{-}C_6H_{11}]^+$). The subsequent cyclization was conducted with $[Ir(cod)OMe]_2$/phen (1.0 mol %) at 80 °C for 16 h. Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel

chromatography (12 g SiO_2 column, 100:0→95:5 hexanes/EtOAc) gave 242 mg (80%) of **7p** as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.0 Hz, 1H), 6.87 (dd, *J* = 8.0, 2.1 Hz, 1H), 6.73 (d, *J* = 2.1 Hz, 1H), 5.59-5.51 (m, 1H), 5.48-5.41 (m, 1H), 5.29 (q, *J* = 6.5 Hz, 1H), 3.99 (t, *J* = 6.9 Hz, 2H), 2.56 (q, *J* = 6.8 Hz, 2H), 2.15-2.07 (m, 2H), 1.51 (d, *J* = 6.5 Hz, 3H), 1.00 (t, *J* = 7.5 Hz, 3H), 0.96 (t, *J* = 7.8 Hz, 3H), 0.94 (t, *J* = 7.8 Hz, 3H), 0.89-0.73 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.6, 157.2, 134.4, 132.4, 123.9, 123.6, 114.0, 107.8, 77.8, 67.3, 27.3, 25.2, 20.7, 14.2, 7.3, 7.2, 6.7, 6.4; **GC/MS**: *m/z* 304.2 (9.3%, $[M]^+$), 289.2 (2.3%, $[M\text{-}Me]^+$), 275.1 (100.0%, $[M\text{-}Et]^+$); **HRMS** (EI+) calcd for $[C_{18}H_{28}O_2Si]^+$: *m/z* 304.1859, found 304.1840.



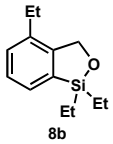
7q

Benzoxasilole 7q: Following the general procedure, alkene **S3** (222 mg, 1.02 mmol) was converted to the corresponding diethyl(hydrido)silyl ether using $[Ir(cod)OMe]_2$ (0.05 mol %) at rt. **GC/MS**: *m/z* 306.2 (11.3%, $[M]^+$), 291.3 (5.6%, $[M\text{-}Me]^+$), 277.2 (14.9%, $[M\text{-}Et]^+$), 223.2 (100.0%, $[M\text{-}C_6H_{11}]^+$). The subsequent cyclization was conducted with $[Ir(cod)OMe]_2$/phen (1.0 mol %) at 80 °C for 22 h. Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel chromatography (12 g SiO_2 column, 100:0→95:5 hexanes/EtOAc) gave 262 mg (85%) of **7q** as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.0 Hz, 1H), 6.88 (dd, *J* = 8.0, 1.9 Hz, 1H), 6.73 (d, *J* = 1.6 Hz, 1H), 5.63 (dd, *J* = 14.0, 7.6 Hz, 1H), 5.54-5.46 (m, 2H), 5.29 (q, *J* = 6.4 Hz, 1H), 4.00 (t, *J* = 6.9 Hz, 2H), 2.50 (q, *J* = 6.8 Hz, 2H), 2.10-2.00 (m, 2H), 1.51 (d, *J* = 6.5 Hz, 3H), 1.00 (t, *J* = 7.5 Hz, 3H), 0.96 (t, *J* = 7.8 Hz, 3H), 0.94 (t, *J* = 7.8 Hz, 3H), 0.89-0.72 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 160.7, 157.2, 134.9, 132.4, 124.3, 123.6, 114.1, 107.9, 77.8, 67.7, 32.5, 25.6, 25.1, 13.7, 7.3, 7.2, 6.7, 6.4; **GC/MS**: *m/z* 304.2 (9.4%, $[M]^+$), 289.2 (2.3%, $[M\text{-}Me]^+$), 275.2 (100.0%, $[M\text{-}Et]^+$); **HRMS** (EI+) calcd for $[C_{18}H_{28}O_2Si]^+$: *m/z* 304.1859, found 304.1866.



8a

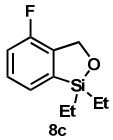
Benzoxasilole 8a: Following the general procedure, 2-methybenzaldehyde (118 mg, 0.982 mmol) was converted to the corresponding diethyl(hydrido)silyl ether using $[Ir(cod)OMe]_2$ (0.05 mol %) at rt. **GC/MS**: *m/z* 208.1 (3.1%, $[M]^+$), 179.1 (23.6%, $[M\text{-}Et]^+$), 105.1 (100.0%, $[M\text{-}OSi(H)Et_2]^+$). The subsequent cyclization was conducted with $[Ir(cod)OMe]_2$/phen (1.0 mol %) at 100 °C for 33 h. Concentration of the reaction mixture and purification of the resulting residue by Kugelrohr distillation (45 mTorr, 85 °C) gave 154 mg (76%) of **8a** as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.1 Hz, 1H), 7.25 (t, *J* = 7.3 Hz, 1H), 7.20 (d, *J* = 7.4 Hz, 1H), 5.12 (s, 2H), 2.23 (s, 3H), 0.98 (t, *J* = 7.7 Hz, 6H), 0.93-0.79 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 148.8, 132.7, 131.4, 130.6, 128.8, 126.9, 71.4, 18.1, 7. 0, 6.4; **GC/MS**: *m/z* 206.1 (7.3%, $[M]^+$), 177.1 (100.0%, $[M\text{-}Et]^+$); **HRMS** (EI+) calcd for $[C_{12}H_{18}OSi]^+$: *m/z* 206.1127, found 206.1119.



8b

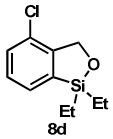
Benzoxasilole 8b: Following the general procedure, 2-ethybenzaldehyde (136 mg, 1.01 mmol) was converted to the corresponding diethyl(hydrido)silyl ether using $[Ir(cod)OMe]_2$ (0.05 mol %) at rt. **GC/MS**: *m/z* 222.0 (0.5%, $[M]^+$), 221.1 (1.0%, $[M\text{-}H]^+$), 193.1 (25.2%, $[M\text{-}Et]^+$), 119.1 (100.0%, $[M\text{-}OSi(H)Et_2]^+$). The subsequent cyclization was conducted with $[Ir(cod)OMe]_2$/phen (1.0 mol %) at 120 °C for 44 h. Concentration of the reaction mixture and purification of the resulting residue by Kugelrohr distillation (35 mTorr, 90 °C) gave 147 mg (66%) of **8b** as a colorless oil. In a separate experiment, the cyclization was conducted at 100 °C for 7 d (under otherwise identical conditions) and similarly provided **8b** in 66% isolated yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.0 Hz, 1H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.25 (d, *J* = 7.8 Hz, 1H), 5.18 (s, 2H), 2.56 (q, *J* = 7.6 Hz, 2H), 1.26 (t, *J* = 7.6 Hz, 3H), 0.98 (t, *J* = 7.8 Hz, 6H), 0.93-0.80 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 148.1, 137.5, 132.9, 128.9,

128.6, 127.1, 71.1, 25.0, 13.8, 7.0, 6.4; **GC/MS**: *m/z* 220.1 (5.8%, $[M]^+$), 191.1 (100.0%, $[M\text{-}Et]^+$); **HRMS** (EI+) calcd for $[C_{13}H_{20}OSi]^+$: *m/z* 220.1283, found 220.1291.



8c

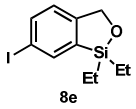
Benzoxasilole 8c: Following the general procedure, 2-fluorobenzaldehyde (128 mg, 1.03 mmol) was converted to the corresponding diethyl(hydrido)silyl ether using $[Ir(cod)OMe]_2$ (0.05 mol %) at rt. **GC/MS**: *m/z* 211.1 (0.5%, $[M\text{-}H]^+$), 183.1 (33.6%, $[M\text{-}Et]^+$), 91.1 (100.0%). The subsequent cyclization was conducted with $[Ir(cod)OMe]_2$/phen (1.0 mol %) at 100 °C for 22 h. Concentration of the reaction mixture and purification of the resulting residue by Kugelrohr distillation (50 mTorr, 50 °C) gave 130 mg (60%) of **8c** as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36-7.27 (m, 2H), 7.04 (ddd, *J* = 9.5, 7.5, 1.4 Hz, 1H), 5.21 (s, 2H), 0.95 (t, *J* = 7.6 Hz, 6H), 0.92-0.78 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 157.8 (d, *J* = 250 Hz), 137.2, 136.5 (d, *J* = 14 Hz), 129.1 (d, *J* = 5.6 Hz), 126.9 (d, *J* = 3.7 Hz), 115.9 (d, *J* = 20 Hz), 68.6, 6.8, 6.30; **^{19}F NMR** (470 MHz, $CDCl_3$) δ -119.86; **GC/MS**: *m/z* 210.1 (6.6%, $[M]^+$), 181.1 (100.0%, $[M\text{-}Et]^+$); **HRMS** (EI+) calcd for $[C_{11}H_{15}FOSi]^+$: *m/z* 210.0876, found 210.0885.



8d

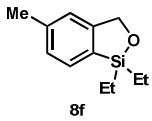
Benzoxasilole 8d: Following the general procedure, 2-chlorobenzaldehyde (143 mg, 1.02 mmol) was converted to the corresponding diethyl(hydrido)silyl ether using $[Ir(cod)OMe]_2$ (0.05 mol %) at rt. **GC/MS**: *m/z* 228.1 (0.4%, $[M]^+$), 199.0 (100.0%, $[M\text{-}Et]^+$). The subsequent cyclization was conducted with $[Ir(cod)OMe]_2$/phen (1.0 mol %) at 100 °C for 42 h. Concentration of the reaction mixture and purification of the resulting residue by Kugelrohr distillation (25 mTorr, 80 °C) gave 159 mg (69%) of **8d** as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.0 Hz, 1H), 7.35 (dd, *J* = 7.8, 0.7 Hz, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 5.15 (s, 2H), 0.95 (t, *J* = 7.6 Hz, 6H), 0.92-0.78 (m,

4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 147.6, 136.1, 129.8, 129.6, 129.1, 128.6, 71.4, 7.0, 6.3; **GC/MS**: *m/z* 226.1 (6.6%, $[M]^+$), 197.0 (100.0%, $[M\text{-}Et]^+$); **HRMS** (EI+) calcd for $[C_{11}H_{15}ClOSi]^+$: *m/z* 226.0581, found 226.0584.



8e

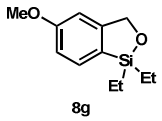
Benzoxasilole 8e: Following the general procedure, 4-iodobenzyl alcohol (235 mg, 1.00 mmol) was converted to the corresponding diethyl(hydrido)silyl ether using $[Ir(cod)OMe]_2$ (0.05 mol %) at rt. **GC/MS**: *m/z* 320.0 (6.0%, $[M]^+$), 291.0 (25.0%, $[M\text{-}Et]^+$), 216.9 (100.0%, $[M\text{-}OSi(H)Et_2]^+$). The subsequent cyclization was conducted with $[Ir(cod)OMe]_2$/phen (1.0 mol %) at 100 °C for 31 h. Concentration of the reaction mixture and purification of the resulting residue by Kugelrohr distillation (40 mTorr, 110 °C) gave 275 mg (86%) of **8e** as pale yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.68 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.00 (d, *J* = 8.1 Hz, 1H), 5.08 (s, 2H), 0.94 (t, *J* = 7.6 Hz, 6H), 0.90-0.76 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 149.7, 140.1, 138.1, 136.9, 123.7, 93.3, 71.8, 6.8, 6.3; **GC/MS**: *m/z* 318.0 (16.1%, $[M]^+$), 289.0 (100.0%, $[M\text{-}Et]^+$); **HRMS** (EI+) calcd for $[C_{11}H_{15}IOSi]^+$: *m/z* 317.9937, found 317.9928.



8f

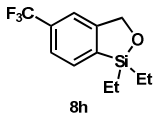
Benzoxasilole 8f: Following the general procedure, 3-methylbenzaldehyde (118 mg, 0.982 mmol) was converted to the corresponding diethyl(hydrido)silyl ether using $[Ir(cod)OMe]_2$ (0.05 mol %) at rt. **GC/MS**: *m/z* 208.1 (0.9%, $[M]^+$), 179.1 (25.3%, $[M\text{-}Et]^+$), 105.1 (100.0%, $[M\text{-}OSi(H)Et_2]^+$). The subsequent cyclization was conducted with $[Ir(cod)OMe]_2$/phen (1.0 mol %) at 100 °C for 19 h. Concentration of the reaction mixture and purification of the resulting residue by Kugelrohr distillation (45 mTorr, 60 °C) gave 117 mg (58%) of **8f** as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.4 Hz, 1H), 7.14 (d, *J* = 7.4 Hz, 1H), 7.08 (s, 1H), 5.13 (s, 2H), 2.40 (s, 3H), 0.97 (t, *J* = 7.8 Hz, 6H), 0.91-0.78 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 150.9, 139.6, 131.4,

129.5, 127.8, 122.2, 72.0, 21.6, 7.0, 6.4; **GC/MS**: *m/z* 206.1 (6.2%, $[M]^+$), 177.1 (100.0%, $[M\text{-}Et]^+$); **HRMS** (EI+) calcd for $[C_{12}H_{18}OSi]^+$: *m/z* 206.1127, found 206.1115.



8g

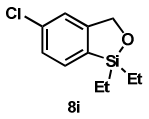
Benzoxasilole 8g: Following the general procedure, 3-methoxybenzaldehyde (134 mg, 0.984 mmol) was converted to the corresponding diethyl(hydrido)silyl ether using $[Ir(cod)OMe]_2$ (0.05 mol %) at rt. **GC/MS**: *m/z* 224.1 (11.4%, $[M]^+$), 209.1 (2.4%, $[M\text{-}Me]^+$), 195.1 (17.6%, $[M\text{-}Et]^+$), 121.1 (100.0%, $[M\text{-}OSi(H)Et_2]^+$). The subsequent cyclization was conducted with $[Ir(cod)OMe]_2$/phen (1.0 mol %) at 100 °C for 13 h. Concentration of the reaction mixture and purification of the resulting residue by Kugelrohr distillation (35 mTorr, 100 °C) gave 192 mg (88%) of **8g** as a light yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.0 Hz, 1H), 6.88 (dd, *J* = 8.0, 2.2 Hz, 1H), 6.76 (d, *J* = 1.7 Hz, 1H), 5.12 (s, 2H), 3.82 (s, 3H), 0.96 (t, *J* = 7.8 Hz, 6H), 0.89-0.75 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.2, 152.7, 132.6, 123.8, 113.9, 106.2, 71.9, 55.1, 7.1, 6.4; **GC/MS**: *m/z* 222.1 (10.5%, $[M]^+$), 193.1 (100.0%, $[M\text{-}Et]^+$); **HRMS** (EI+) calcd for $[C_{12}H_{18}O_2Si]^+$: *m/z* 222.1076, found 222.1072.



8h

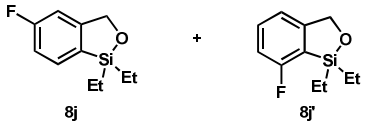
Benzoxasilole 8h: Following the general procedure, 3-(trifluoromethyl)benzaldehyde (172 mg, 0.988 mmol) was converted to the corresponding diethyl(hydrido)silyl ether using $[Ir(cod)OMe]_2$ (0.05 mol %) at rt. **GC/MS**: *m/z* 262.1 (1.5%, $[M]^+$), 261.1 (7.0%, $[M\text{-}H]^+$), 233.1 (5.2%, $[M\text{-}Et]^+$), 159.0 (100.0%, $[M\text{-}OSi(H)Et_2]^+$). The subsequent cyclization was conducted with $[Ir(cod)OMe]_2$/phen (1.0 mol %) at 100 °C for 48 h. Concentration of the reaction mixture and purification of the resulting residue by Kugelrohr distillation (40 mTorr, 60 °C) gave 142 mg (55%) of **8h** as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.49 (s, 1H), 5.19 (s, 2H), 0.95 (t, *J* = 7.5 Hz, 6H), 0.92-0.80 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 151.1, 138.0, 132.0, 131.8 (q, *J* = 32 Hz), 124.2 (q, *J* = 272 Hz), 123.5 (q, *J* =

3.6 Hz), 118.3 (q, *J* = 3.9 Hz), 71.9, 6.8, 6.3; **^{19}F NMR** (470 MHz, $CDCl_3$) δ -63.09; **GC/MS**: *m/z* 260.1 (2.8%, $[M]^+$), 231.0 (100.0%, $[M\text{-}Et]^+$); **HRMS** (EI+) calcd for $[C_{12}H_{15}F_3OSi]^+$: *m/z* 260.0844, found 260.0831.



8i

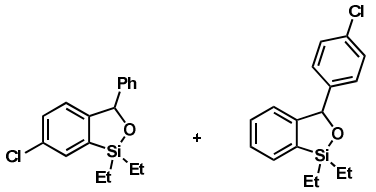
Benzoxasilole 8i: Following the general procedure, 3-chlorobenzaldehyde (143 mg, 1.02 mmol) was converted to the corresponding diethyl(hydrido)silyl ether using $[Ir(cod)OMe]_2$ (0.05 mol %) at rt. **GC/MS**: *m/z* 228.0 (0.4%, $[M]^+$), 199.0 (19.5%, $[M\text{-}Et]^+$), 125.0 (100.0%, $[M\text{-}OSi(H)Et_2]^+$). The subsequent cyclization was conducted with $[Ir(cod)OMe]_2$/phen (1.0 mol %) at 100 °C for 42 h. Concentration of the reaction mixture and purification of the resulting residue by Kugelrohr distillation (35 mTorr, 85 °C) gave 179 mg (78%) of **8i** as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 0.8 Hz, 1H), 5.11 (s, 2H), 0.94 (t, *J* = 7.7 Hz, 6H), 0.90-0.76 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 152.5, 136.0, 132.6, 131.3, 127.1, 121.9, 71.6, 6.9, 6.3; **GC/MS**: *m/z* 226.1 (6.5%, $[M]^+$), 197.0 (100.0%, $[M\text{-}Et]^+$); **HRMS** (EI+) calcd for $[C_{11}H_{15}ClOSi]^+$: *m/z* 226.0581, found 226.0575.



8j 8j'

Benzoxasiloles 8j and 8j': Following the general procedure, 3-fluorobenzaldehyde (127 mg, 1.02 mmol) was converted to the corresponding diethyl(hydrido)silyl ether using $[Ir(cod)OMe]_2$ (0.05 mol %) at rt. **GC/MS**: *m/z* 211.1 (1.2%, $[M\text{-}H]^+$), 183.1 (16.6%, $[M\text{-}Et]^+$), 109.0 (100.0%, $[M\text{-}OSi(H)Et_2]^+$). The subsequent cyclization was conducted with $[Ir(cod)OMe]_2$/phen (1.0 mol %) at 100 °C for 13 h. Concentration of the reaction mixture and purification of the resulting residue by Kugelrohr distillation (60 mTorr, 60 °C) gave 157 mg (73%) of a 1.0:0.79 mixture of **8j** and **8j'** as a colorless oil In a separate experiment, the cyclization was conducted at 80 °C for 5 d (under otherwise identical conditions) and gave a 1.0:0.75 mixture of **8j** and **8j'** in a combined 60% yield. (Note: the assignment of **8j** as the major isomer is tentative). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.52

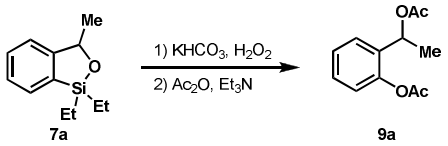
(dd, *J* = 7.9, 6.0 Hz, 1H, *major*), 7.38 (td, *J* = 7.8, 5.8 Hz, 1H, *minor*), 7.04-6.98 (m, 1H), 6.96-6.88 (m, 1H), 5.14 (s, 2H, *minor*), 5.12 (s, 2H, *major*), 1.03-0.76 (m, 10H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.4 (d, *J* = 244 Hz), 164.4 (d, *J* = 248 Hz), 153.5 (d, *J* = 11 Hz), 153.3 (d, *J* = 7.3 Hz), 133.1 (d, *J* = 8.5 Hz), 132.3 (d, *J* = 7.1 Hz), 128.2 (d, *J* = 2.7 Hz), 119.6 (d, *J* = 38 Hz), 117.5 (d, *J* = 3.2 Hz), 114.4 (d, *J* = 21 Hz), 112.7 (d, *J* = 25 Hz), 108.6 (d, *J* = 21 Hz), 71.9, 71.7 (d, *J* = 3.0 Hz), 6.93, 6.91, 6.32, 6.25; **^{19}F NMR** (470 MHz, $CDCl_3$) δ -100.48 (*minor*), -112.28 (*major*); **GC/MS**: *m/z* 210.1 (6.2%, $[M]^+$), 181.0 (100.0%, $[M\text{-}Et]^+$); **HRMS** (EI+) calcd for $[C_{11}H_{15}FOSi]^+$: *m/z* 210.0876, found 210.0872.



Benzoxasiloles 13a and 13b: Following the general procedure, 4-chlorobenzophenone (215 mg, 0.992 mmol) was converted to the corresponding diethyl(hydrido)silyl ether using $[Ir(cod)OMe]_2$ (0.05 mol %) at rt. **GC/MS**: *m/z* 304.0 (0.4%, $[M]^+$), 303.1 (0.9%, $[M\text{-}H]^+$), 275.1 (16.9%, $[M\text{-}Et]^+$), 201.0 (100.0%, $[M\text{-}OSi(H)Et_2]^+$). The subsequent cyclization was conducted with $[Ir(cod)OMe]_2$/phen (1.0 mol %) at 80 °C for 13 h. Concentration of the reaction mixture, adsorption of the resulting residue onto Celite, and purification by silica gel chromatography (12 g SiO_2 column, 100:0→90:10 hexanes/EtOAc) gave 259 mg (86%) of a 71:29 mixture (as determined by GC analysis) of **13a** and **13b** as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 5.7, 2.4 Hz, 1H, *minor*), 7.57 (d, *J* = 2.0 Hz, 1H, *major*), 7.39-7.22 (m, 6H), 7.03-6.99 (m, 1H, *minor*), 6.96 (d, *J* = 8.3 Hz, 1H, *major*), 6.15 (s, 1H, *minor*), 6.14 (s, 1H, *major*), 1.12-1.05 (m, 3H), 1.04-0.83 (m, 7H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 152.4, 151.3, 143.2, 142.3, 136.2, 133.5, 133.4, 133.3, 131.3, 130.7, 129.9, 129.8, 128.7, 128.6, 128.5, 128.0, 127.2, 127.1, 125.2, 123.6, 83.9, 83.4, 7.2, 7.1, 6.9, 6.84, 6.80, 6.7, 6.44, 6.40; **GC/MS** (*major, 1st eluting*): *m/z* 302.1 (59.1%, $[M]^+$), 273.1 (100.0%, $[M\text{-}Et]^+$), 245.0 (47.3%);

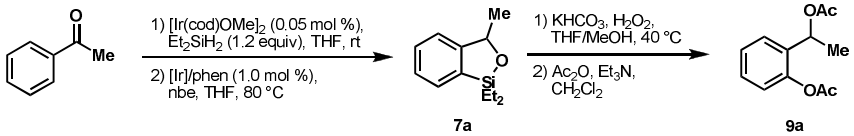
(*minor, 2nd eluting*): *m/z* 302.1 (20.3%, $[M]^+$), 273.0 (100.0%, $[M\text{-}Et]^+$), 245.0 (40.6%); **HRMS** (EI+) calcd for $[C_{17}H_{19}ClOSi]^+$: *m/z* 302.0894, found 302.0900.

Spectral data for products of Tamao-Fleming oxidation:



7a 9a

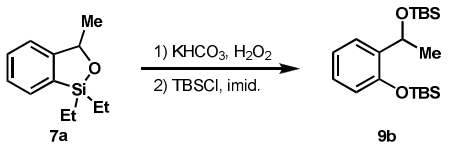
Tamao-Fleming oxidation/acylation of 7a: Following the general procedure, benzoxasilole **7a** (105 mg, 0.509 mmol) was oxidized with $KHCO_3/H_2O_2$ at rt. The crude phenol was acylated with Ac_2O/Et_3N according to the general procedure, and the resulting diactate was purified by silica gel chromatography (4 g SiO_2 column, 100:0→80:20 hexanes/EtOAc) to give 69.3 mg (0.312 mmol, 61% over 2 steps) of **9a**[7] as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.32 (td, *J* = 7.8, 1.5 Hz, 1H), 7.25 (t, *J* = 7.2 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.03 (q, *J* = 6.6 Hz, 1H), 2.33 (s, 3H), 2.03 (s, 3H), 1.52 (d, *J* = 6.6 Hz, 3H) (lit. ^{1}H NMR data not reported); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.0, 169.3, 147.8, 133.1, 128.8, 127.2, 126.2, 122.8, 67.0, 21.1, 20.9, 20.6 (lit. ^{13}C NMR data not reported); **HRMS** (EI+) calcd for $[C_{12}H_{14}O_4]^+$: *m/z* 222.0892, found 222.0887.



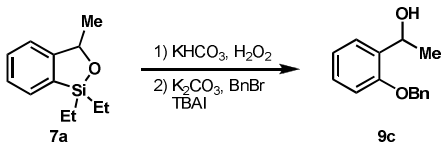
7a 9a

One-pot silylation/Tamao-Fleming oxidation of acetophenone: Following the general procedure for intramolecular arene silylation on 1.0 mmol scale (except using a 20 mL screw-top vial), acetophenone (122 mg, 1.02 mmol) was converted to benzoxasilole **7a**. After the cyclization was complete, the crude reaction mixture was sequentially treated with MeOH (2.0 mL), $KHCO_3$ (203 mg, 2.03 mmol) and H_2O_2 (30% solution in H_2O, 0.91 mL, 8.03 mmol). The vial was re-sealed with a Teflon-lined screw cap, and the resulting mixture was stirred at 40 °C until complete consumption of the benzoxasilole was observed (as determined by GC-MS analysis). The reaction was carefully quenched

with aq. $NaHSO_3$ (30 mL), and the resulting mixture was extracted with EtOAc (30 mL, then 2 x 15 mL). The combined organic layers were washed (30 mL 1 N HCl, then 30 mL sat. $NaHCO_3$), dried ($MgSO_4$), filtered through Celite, and concentrated. The crude phenol was acylated with Ac_2O/Et_3N according to the general procedure, and the resulting diactate was purified by silica gel chromatography (12 g SiO_2 column, 100:0→80:20 hexanes/EtOAc) to give 128 mg (0.575 mmol, 57% overall yield) of **9a** as a pale yellow oil, which gave spectral data identical to that obtained previously.

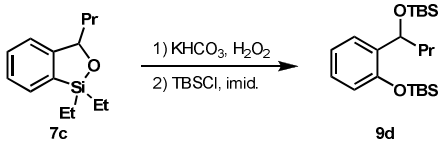


Tamao-Fleming oxidation/silylation of 7a: Following the general procedure, benzoxasilole **7a** (100 mg, 0.485 mmol) was oxidized with $KHCO_3/H_2O_2$ at rt. The crude phenol was dissolved in DMF (2.0 mL) and sequentially treated with imidazole (103 mg, 1.51 mmol) and TBSCl (188 mg, 1.25 mmol). The resulting solution was stirred at rt for 19 h, at which point TLC analysis indicated full conversion of the phenol. The reaction mixture was poured onto water (30 mL) and extracted with Et_2O (30 mL, then 2 x 15 mL). The combined organic layers were washed (30 mL water, then 30 mL sat. NH_4Cl, then 30 mL brine), dried ($MgSO_4$) and concentrated. The resulting residue was adsorbed onto SiO_2 and purified by silica gel chromatography (12 g SiO_2 column, 100:0→90:10 hexanes/EtOAc) to give 123 mg (0.335 mmol, 69% over 2 steps) of **9b**[8] as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.10 (td, *J* = 7.8, 1.8 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.75 (dd, *J* = 8.0, 0.9 Hz, 1H), 5.23 (q, *J* = 6.2 Hz, 1H), 1.38 (d, *J* = 6.2 Hz, 3H), 1.04 (s, 9H), 0.92 (s, 9H), 0.29 (s, 3H), 0.25 (s, 3H), 0.06 (s, 3H), 0.00 (s, 3H) (^{1}H NMR data were consistent with previously reported values[8]); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.1, 137.6, 127.1, 126.4, 121.1, 117.5, 65.5, 25.9, 25.7, 18.3, 18.2, -3.9, -4.3, -4.9, -5.0 (lit. ^{13}C NMR data not reported).



7a 9c

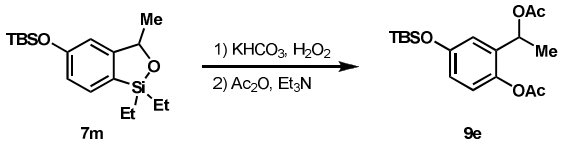
Tamao-Fleming oxidation/benzylation of 7a: Following the general procedure, benzoxasilole **7a** (103 mg, 0.499 mmol) was oxidized with $KHCO_3/H_2O_2$ at rt. The crude phenol was dissolved in acetone (1.0 mL) in a 20 mL vial and sequentially treated with tetrabutylammonium iodide (18.9 mg, 0.051 mmol) and K_2CO_3 (111 mg, 0.803 mmol), followed by a solution of BnBr (113 mg, 0.661 mmol) in acetone (1.0 mL). The vial was sealed with a Teflon-lined screw-cap, and the resulting suspension was stirred at 65 °C for 63 h. After cooling to rt, the reaction mixture was poured onto water (30 mL) and extracted with Et_2O (30 mL, then 2 x 15 mL). The combined organic layers were washed (30 mL aq. $NaHSO_3$, then 30 mL brine), dried ($MgSO_4$) and concentrated. The resulting residue was adsorbed onto SiO_2 and purified by silica gel chromatography (12 g SiO_2 column, 100:0→75:25 hexanes/EtOAc) to give 67.3 mg (0.295 mmol, 59% over 2 steps) of **9c**[9] as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48-7.40 (m, 5H), 7.40-7.34 (m, 1H), 7.26 (td, *J* = 8.1, 1.7 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 5.20 (q, *J* = 6.5 Hz, 1H), 5.13 (s, 2H), 2.76 (br s, 1H), 1.55 (d, *J* = 6.5 Hz, 3H) (The previously reported ^{1}H NMR data[9] were missing one aromatic proton in the range 7.48-7.34, but were otherwise consistent with the data reported herein.); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.5, 136.7, 133.8, 128.6, 128.2, 128.0, 127.2, 126.1, 121.0, 111.6, 69.9, 66.3, 23.0 (lit. ^{13}C NMR data not reported).



7c 9d

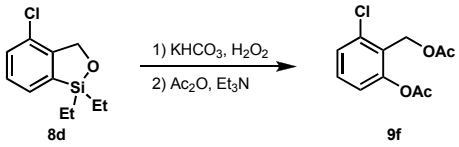
Tamao-Fleming oxidation/silylation of 7c: Following the general procedure (but increasing the temperature to 40 °C), benzoxasilole **7c** (115 mg, 0.491 mmol) was oxidized with $KHCO_3/H_2O_2$ at 40 °C. The crude phenol was dissolved in DMF (2.0 mL) and sequentially treated with imidazole (103 mg, 1.51 mmol) and TBSCl (188 mg, 1.25 mmol). The resulting solution was stirred at rt for 17 h. The reaction mixture was poured onto water (30 mL) and extracted with Et_2O (30 mL, then 2 x 15 mL). The combined

organic layers were washed (30 mL water, then 30 mL sat. NH_4Cl, then 30 mL brine), dried ($MgSO_4$) and concentrated. The resulting residue was adsorbed onto SiO_2 and purified by silica gel chromatography (12 g SiO_2 column, 100:0→95:5 hexanes/EtOAc) to give 117 mg (0.296 mmol, 60% over 2 steps) of **9d** as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.09 (td, *J* = 7.8, 1.8 Hz, 1H), 6.95 (td, *J* = 7.6, 0.8 Hz, 1H), 6.75 (dd, *J* = 8.1, 1.0 Hz, 1H), 5.11 (t, *J* = 6.0 Hz, 1H), 1.63-1.55 (m, 2H), 1.55-1.45 (m, 1H), 1.43-1.31 (m, 1H), 1.05 (s, 9H), 0.93-0.89 (m, 12H), 0.29 (s, 3H), 0.26 (s, 3H), 0.04 (s, 3H), -0.11 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.2, 136.6, 127.3, 127.0, 120.8, 117.4, 68.8, 41.8, 25.9, 25.8, 19.2, 18.3, 18.2, 14.3, -3.9, -4.2, -4.7, -5.0; **HRMS** (EI+) calcd for $[C_{19}H_{35}O_2Si_2]^+$ $(M-C_3H_7)^+$: *m/z* 351.2176, found 351.2183.



7m 9e

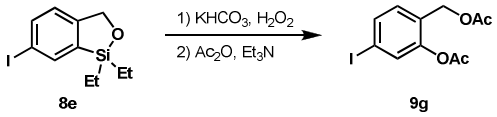
Tamao-Fleming oxidation/acylation of 7m: Following the general procedure, benzoxasilole **7m** (167 mg, 0.496 mmol) was oxidized with $KHCO_3/H_2O_2$ at rt. The crude phenol was acylated with Ac_2O/Et_3N according to the general procedure, and the resulting diactate was purified by silica gel chromatography (4 g SiO_2 column, 100:0→80:20 hexanes/EtOAc) to give 126 mg (0.359 mmol, 72% over 2 steps) of **9e** as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.90 (d, *J* = 11.8 Hz, 1H), 6.89 (s, 1H), 6.75 (dd, *J* = 8.7, 2.9 Hz, 1H), 5.93 (q, *J* = 6.6 Hz, 1H), 2.30 (s, 3H), 2.03 (s, 3H), 1.47 (d, *J* = 6.6 Hz, 3H), 0.98 (s, 9H), 0.20 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 169.9, 169.6, 153.4, 141.6, 134.1, 123.4, 119.9, 118.2, 66.9, 25.6, 21.1, 20.9, 20.7, 18.1, -4.5; **HRMS** (EI+) calcd for $[C_{18}H_{28}O_5Si]^+$: *m/z* 352.1706, found 352.1715.



8d 9f

Tamao-Fleming oxidation/acylation of 8d: Following the general procedure, benzoxasilole **8d** (114 mg, 0.503 mmol) was oxidized with $KHCO_3/H_2O_2$ at rt. The crude

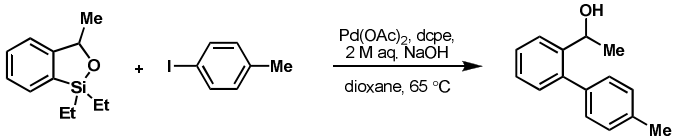
phenol was acylated with Ac_2O/Et_3N according to the general procedure, and the resulting diactate was purified by silica gel chromatography (4 g SiO_2 column, 100:0→80:20 hexanes/EtOAc) to give 87.5 mg (0.361 mmol, 72% over 2 steps) of **9f** as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33-7.28 (m, 2H), 7.05-7.00 (m, 1H), 5.22 (s, 2H), 2.32 (s, 3H), 2.04 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.5, 169.0, 150.6, 136.3, 130.2, 127.3, 126.4, 121.5, 58.0, 20.7, 20.6; **HRMS** (EI+) calcd for $[C_{11}H_{11}ClO_4]^+$: *m/z* 242.0346, found 242.0328.



8e 9g

Tamao-Fleming oxidation/acylation of 8e: Following the general procedure, benzoxasilole **8e** (157 mg, 0.493 mmol) was oxidized with $KHCO_3/H_2O_2$ at rt. The crude phenol was acylated with Ac_2O/Et_3N according to the general procedure, and the resulting diactate was purified by silica gel chromatography (4 g SiO_2 column, 100:0→80:20 hexanes/EtOAc) to give 129 mg (0.386 mmol, 78% over 2 steps) of **9g** as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.46 (d, *J* = 1.6 Hz, 1H), 7.16 (d, *J* = 8.1 Hz, 1H), 5.00 (s, 2H), 2.31 (s, 3H), 2.06 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.4, 168.8, 149.2, 135.3, 131.7, 131.6, 128.0, 93.5, 60.8, 20.74, 20.68; **HRMS** (EI+) calcd for $[C_{11}H_{11}IO_4]^+$: *m/z* 333.9702, found 333.9711.

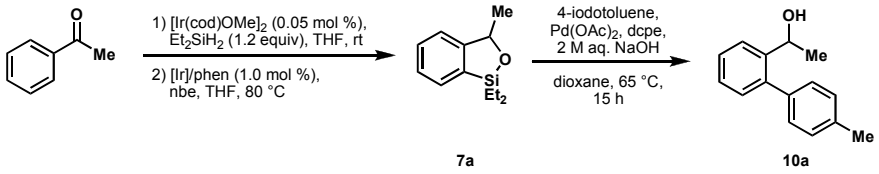
Spectral data for products of Hiyama coupling:



7a 10a

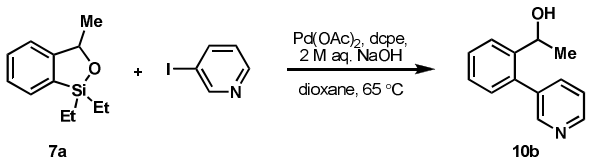
Hiyama coupling of 7a with 4-iodotoluene: Following the general procedure, benzoxasilole **7a** (54.0 mg, 0.262 mmol) was coupled with 4-iodotoluene (65.6 mg, 0.301 mmol) with $Pd(OAc)_2$/dcpe at 65 °C. The crude product was purified by silica gel chromatography (12 g SiO_2 column, 100:0→85:15 hexanes/EtOAc) to give 49.3 mg (0.232 mmol, 89%) of **10a**[10] as a white solid. The coupling of **7a** with 4-bromotoluene

(1.2 equiv) was conducted at 65 °C for 16 h (under otherwise identical conditions), and provided **10a** in 60% isolated yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 7.8, 0.7 Hz, 1H), 7.43 (td, *J* = 7.7, 1.3 Hz, 1H), 7.33 (td, *J* = 7.4, 1.3 Hz, 1H), 7.28-7.20 (m, 5H), 5.02 (q, *J* = 6.4 Hz, 1H), 2.45 (s, 3H), 1.92 (br s, 1H), 1.43 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.1, 140.2, 137.9, 136.7, 130.0, 129.1, 128.8, 127.8, 127.0, 125.3, 66.4, 24.8, 21.1. (^{1}H and ^{13}C NMR data were consistent with previously reported values.[10])

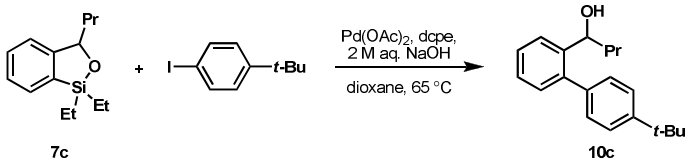


7a **10a**

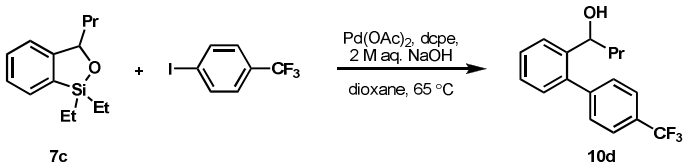
One-pot silylation/Hiyama coupling of acetophenone: Following the general procedure for intramolecular arene silylation on 1.0 mmol scale (except using a 20 mL screw-top vial), acetophenone (122 mg, 1.02 mmol) was converted to benzoxasilole **7a**. After the cyclization was complete, the vial was taken into an N_2-filled glovebox and the crude reaction mixture was concentrated under high-vacuum for 1.5 h (the stir bar was temporarily removed during this operation to prevent bumping). 4-Iodotoluene (264 mg, 1.21 mmol) was added to the concentrated benzoxasilole, and the stir bar was replaced. A freshly prepared solution of $Pd(OAc)_2$ (8.9 mg, 40 μmol) and 1,2-bis(dicyclohexylphosphino)ethane (18.3 mg, 43 μmol) in dioxane (5.0 mL) was then added, and the vial was capped with a septum and removed from the glovebox. After being stirred at rt for 10 min, the dark green solution was treated with 2 M aq. NaOH (2.5 mL, 5.00 mmol). The septum was quickly replaced with a Teflon-lined screw cap under a stream of N_2, and the resulting mixture was further stirred at rt for 30 min. The vial was then placed in a pre-heated aluminum heating block at 65 °C and stirred for 15 h. The reaction mixture was allowed to cool to rt and then diluted with EtOAc, filtered through SiO_2 and concentrated. The residue was adsorbed onto SiO_2 and purified by silica gel chromatography (12 g SiO_2 column, 100:0→85:15 hexanes/EtOAc) to give 136 mg (0.639 mmol, 63% overall yield) of **10a** as a pale yellow solid, which gave spectral data identical to that obtained previously.



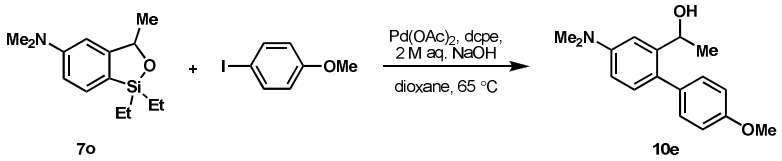
Hiyama coupling of 7a with 3-iodopyridine: Following the general procedure, benzoxasilole **7a** (53.4 mg, 0.259 mmol) was coupled with 3-iodopyridine (67.9 mg, 0.331 mmol) with $Pd(OAc)_2$/dcpe at 65 °C. After 14 h, the reaction mixture was allowed to cool to rt and then diluted with EtOAc + 1% Et_3N, filtered through SiO_2 and concentrated. The crude product was purified by silica gel chromatography (12 g SiO_2 column, 100:0→0:100 hexanes/EtOAc) to give 35.9 mg (0.180 mmol, 70%) of **10b** as a faint yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.51 (dd, *J* = 4.9, 1.5 Hz, 1H), 8.45 (d, *J* = 1.7 Hz, 1H), 7.73 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.65 (dt, *J* = 7.8, 1.9 Hz, 1H), 7.46 (td, *J* = 7.7, 1.1 Hz, 1H), 7.36-7.30 (m, 2H), 7.14 (dd, *J* = 7.6, 1.2 Hz, 1H), 4.88 (q, *J* = 6.4 Hz, 1H), 1.40 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.3, 147.9, 143.6, 137.0, 136.8, 136.1, 129.9, 128.8, 127.3, 125.8, 123.1, 66.0, 25.0; **HRMS** (EI+) calcd for $[C_{13}H_{13}NO]^+$: *m/z* 199.0997, found 199.0998.



Hiyama coupling of 7c with 4-*tert*-butyliodobenzene: Following the general procedure, benzoxasilole **7c** (56.2 mg, 0.240 mmol) was coupled with 4-*tert*-butyliodobenzene (77.4 mg, 0.298 mmol) with $Pd(OAc)_2$/dcpe at 65 °C. The crude product was purified by silica gel chromatography (12 g SiO_2 column, 100:0→85:15 hexanes/EtOAc) to give 50.2 mg (0.178 mmol, 74%) of **10c** as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 7.8, 0.8 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 2H), 7.40 (td, *J* = 7.8, 1.3 Hz, 1H), 7.31 (td, *J* = 7.5, 1.3 Hz, 1H), 7.27-7.22 (m, 3H), 4.84 (dd, *J* = 8.1, 5.1 Hz, 1H), 1.83 (br s, 1H), 1.80-1.71 (m, 1H), 1.69-1.60 (m, 1H), 1.42-1.29 (m, 1H), 1.40 (s, 9H), 1.29-1.17 (m, 1H), 0.80 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 149.9, 142.4, 140.8, 138.0, 130.0, 129.0, 127.6, 127.0, 125.7, 124.9, 70.0, 40.9, 34.5, 31.4, 19.1, 13.7; **HRMS** (EI+) calcd for $[C_{20}H_{26}O]^+$: *m/z* 282.1984, found 282.1993.

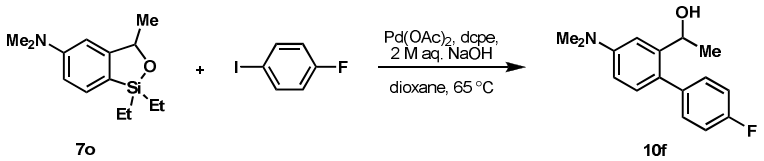


Hiyama coupling of 7c with 4-iodobenzotrifluoride: Following the general procedure, benzoxasilole **7c** (59.6 mg, 0.254 mmol) was coupled with 4-iodobenzotrifluoride (83.9 mg, 0.308 mmol) with $Pd(OAc)_2$/dcpe at 65 °C. The crude product was purified by silica gel chromatography (12 g SiO_2 column, 100:0→85:15 hexanes/EtOAc) to give 55.3 mg (0.188 mmol, 74%) of **10d** as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.64 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.47-7.42 (m, 1H), 7.44 (d, *J* = 8.3 Hz, 2H), 7.34 (td, *J* = 7.5, 1.3 Hz, 1H), 7.20 (dd, *J* = 7.6, 1.3 Hz, 1H), 4.72 (dd, *J* = 7.9, 5.3 Hz, 1H), 1.89 (br s, 1H), 1.78-1.67 (m, 1H), 1.65-1.56 (m, 1H), 1.36-1.25 (m, 1H), 1.23-1.12 (m, 1H), 0.79 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.8, 142.1, 139.4, 129.8, 129.73 (q, *J* = 33 Hz), 129.68, 128.5, 127.3, 126.0, 125.1 (q, *J* = 3.6 Hz), 124.3 (q, *J* = 271 Hz), 70.0, 41.0, 19.0, 13.7; **^{19}F NMR** (470 MHz, $CDCl_3$) δ -62.84; **HRMS** (EI+) calcd for $[C_{17}H_{17}F_3O]^+$: *m/z* 294.1231, found 294.1245.



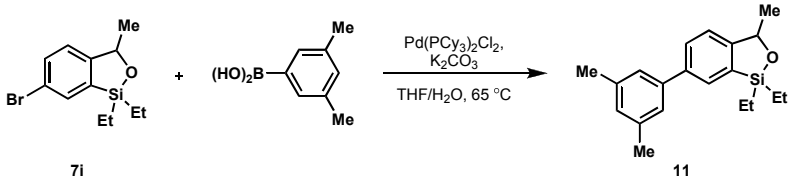
Hiyama coupling of 7o with 4-iodoanisole: Following the general procedure, benzoxasilole **7o** (63.4 mg, 0.254 mmol) was coupled with 4-iodoanisole (71.5 mg, 0.306 mmol) with $Pd(OAc)_2$/dcpe at 65 °C. The crude product was purified by silica gel chromatography (12 g SiO_2 column, 100:0→60:40 hexanes/EtOAc) to give 62.3 mg (0.230 mmol, 90%) of **10e** as a colorless oil that began crystallizing to a white solid on standing at rt. The coupling of **7o** with 4-chloroanisole (1.2 equiv) was conducted at 65 °C for 16 h (under otherwise identical conditions), and provided **10e** in 74% isolated yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.7 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 1H), 7.05 (d, *J* = 2.7 Hz, 1H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.72 (dd, *J* = 8.5, 2.8 Hz, 1H), 5.02 (q, *J* = 6.4 Hz, 1H), 3.85 (s, 3H), 3.01 (s, 6H), 1.98 (br s, 1H), 1.43 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 158.3, 150.2, 144.0, 133.6, 130.9, 130.6, 128.5, 113.5, 111.7,

108.9, 66.8, 55.2, 40.6, 24.8; **HRMS** (EI+) calcd for $[C_{17}H_{21}NO_2]^+$: *m/z* 271.1572, found 271.1570.



7o 10f

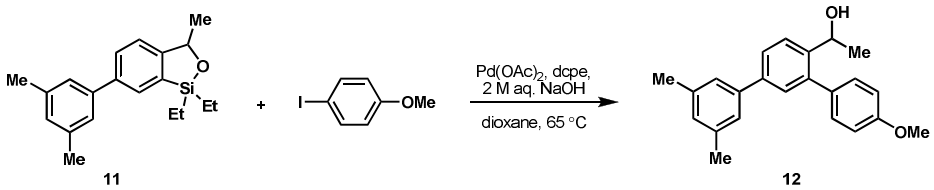
Hiyama coupling of 7o with 4-fluoroiodobenzene: Following the general procedure, benzoxasilole **7o** (63.2 mg, 0.253 mmol) was coupled with 4-fluoroiodobenzene (69.4 mg, 0.313 mmol) with $Pd(OAc)_2$/dcpe at 65 °C. The crude product was purified by silica gel chromatography (12 g SiO_2 column, 100:0→60:40 hexanes/EtOAc) to give 59.0 mg (0.228 mmol, 90%) of **10f** as a pale golden oil. The coupling of **7o** with 1-bromo-4-fluorobenzene (1.2 equiv) was conducted at 65 °C for 16 h (under otherwise identical conditions), and provided **10f** in 76% isolated yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.11-7.05 (m, 3H), 7.04 (d, *J* = 2.7 Hz, 1H), 6.71 (dd, *J* = 8.5, 2.8 Hz, 1H), 4.96 (q, *J* = 6.4 Hz, 1H), 3.02 (s, 6H), 1.99 (br s, 1H), 1.41 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.7, 160.8, 150.4, 143.9, 137.2, 131.1, 131.0, 130.8, 127.7, 114.9, 114.8, 111.6, 108.8, 66.7, 40.6, 24.9; **^{19}F NMR** (470 MHz, $CDCl_3$) δ -116.95; **HRMS** (EI+) calcd for $[C_{16}H_{18}FNO]^+$: *m/z* 259.1372, found 259.1380.



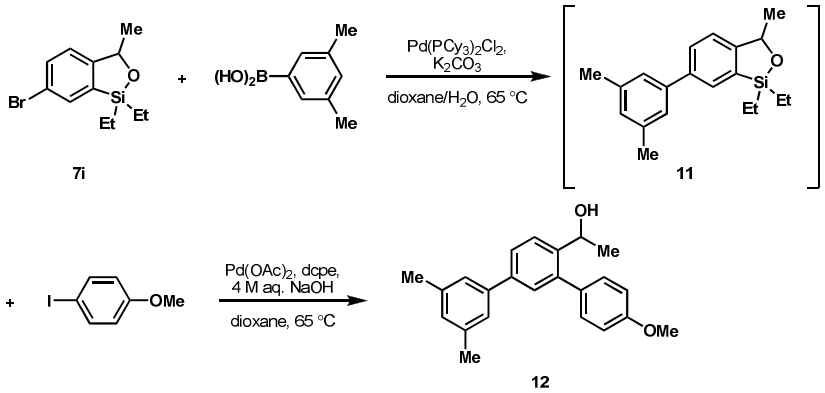
7i 11

Suzuki coupling of 7i with 3,5-dimethylphenylboronic acid: In an N_2-filled glovebox, a 1 dram screw-top vial was sequentially charged with $Pd(PCy_3)_2Cl_2$ (3.6 mg, 4.9 μmol), 3,5-dimethylphenylboronic acid (44.0 mg, 0.293 mmol), K_2CO_3 (93.8 mg, 0.679 mmol), benzoxasilole **7i** (70.5 mg, 0.247 mmol), THF (0.62 mL) and a stir bar. The vial was capped with a screw cap containing a PTFE-lined septum and removed from the glovebox. Distilled water (0.62 mL) was then added via syringe, and the resulting mixture was stirred at rt for 20 min to give a faint yellow biphasic mixture. The vial was then placed in a pre-heated aluminum heating block at 65 °C and stirred for 12 h. The

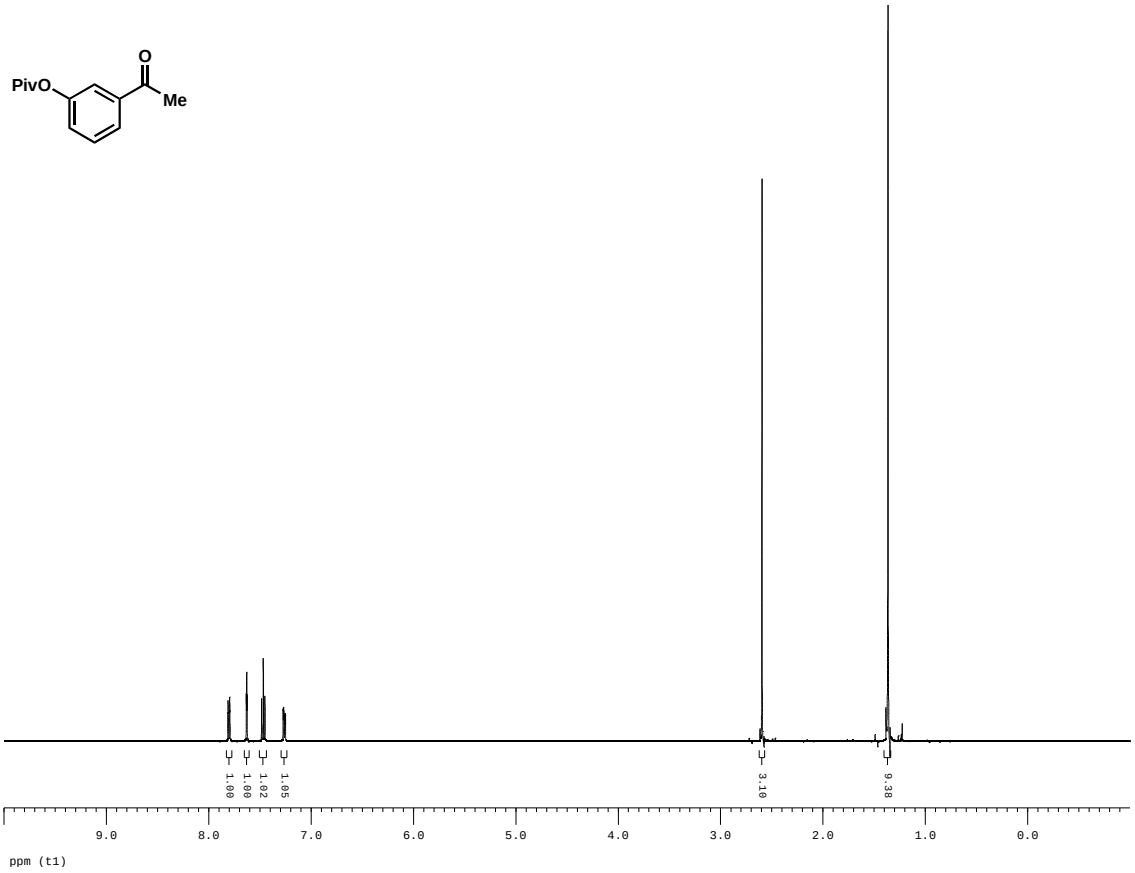
reaction mixture was allowed to cool to rt and then diluted with EtOAc, filtered through SiO_2 and concentrated. The residue was adsorbed onto Celite and purified by silica gel chromatography (12 g SiO_2 column, 100:0→95:5 hexanes/EtOAc) to give 68.1 mg (0.219 mmol, 89%) of **11** as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 1.5 Hz, 1H), 7.65 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.27 (s, 2H), 7.04 (s, 1H), 5.42 (q, *J* = 6.5 Hz, 1H), 2.43 (s, 6H), 1.59 (d, *J* = 6.5 Hz, 3H), 1.04 (t, *J* = 7.7 Hz, 3H), 1.02 (t, *J* = 7.6 Hz, 3H), 0.99-0.83 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 153.9, 141.2, 140.1, 138.2, 133.6, 129.9, 128.9, 128.8, 125.2, 122.3, 77.9, 25.1, 21.4, 7.2, 7.1, 6.7, 6.5; **GC/MS**: *m/z* 310.2 (42.4%, $[M]^+$), 295.2 (66.9%, $[M\text{-}Me]^+$), 281.2 (100.0%, $[M\text{-}Et]^+$).



Hiyama coupling of 11 with 4-iodoanisole: Following the general procedure for Hiyama coupling, benzoxasilole **11** (68.1 mg, 0.219 mmol) was coupled with 4-iodoanisole (61.6 mg, 0.263 mmol) with $Pd(OAc)_2$/dcpe at 65 °C. The crude product was purified by silica gel chromatography (12 g SiO_2 column, 95:5→85:15 hexanes/EtOAc) to give 57.3 mg (0.172 mmol, 79%) of **12** as a white foam. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 1H), 7.64 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.45 (d, *J* = 1.9 Hz, 1H), 7.31 (d, *J* = 8.6 Hz, 2H), 7.26 (s, 2H), 7.02 (s, 1H), 6.99 (d, *J* = 8.7 Hz, 2H), 5.05 (q, *J* = 6.4 Hz, 1H), 3.88 (s, 3H), 2.40 (s, 6H), 1.93 (br s, 1H), 1.47 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.8, 142.0, 140.5, 140.3, 140.1, 138.2, 133.2, 130.3, 128.95, 128.85, 126.4, 125.8, 125.0, 113.6, 66.3, 55.3, 24.8, 21.3; **HRMS** (EI+) calcd for $[C_{23}H_{24}O_2]^+$: *m/z* 332.1776, found 332.1767.



One-pot sequential Suzuki and Hiyama couplings of 7i: In an N_2-filled glovebox, a 1 dram screw-top vial was sequentially charged with $Pd(PCy_3)_2Cl_2$ (3.6 mg, 4.9 μmol), 3,5-dimethylphenylboronic acid (45.0 mg, 0.300 mmol), K_2CO_3 (85.8 mg, 0.621 mmol), benzoxasilole **7i** (72.6 mg, 0.255 mmol), dioxane (0.62 mL) and a stir bar. The vial was capped with a screw cap containing a PTFE-lined septum and removed from the glovebox. Distilled water (0.62 mL) was then added via syringe, and the resulting mixture was stirred at rt for 20 min to give a faint yellow biphasic mixture. The vial was then placed in a pre-heated aluminum heating block at 65 °C and stirred for 12 h. The reaction mixture was allowed to cool to rt, and a solution of 4-iodoanisole (70.9 mg, 0.303 mmol), $Pd(OAc)_2$ (2.0 mg, 8.9 μmol) and 1,2-bis(dicyclohexylphosphino)ethane (4.7 mg, 11 μmol) in dioxane (0.62 mL) was added via syringe. After being stirred at rt for 10 min, the light tan/yellow suspension was treated with 4 M aq. NaOH (0.31 mL, 1.25 mmol), and the resulting biphasic mixture was further stirred at rt for 35 min. The vial was then placed in a pre-heated aluminum heating block at 65 °C and stirred for 14 h. The reaction mixture was allowed to cool to rt and then diluted with EtOAc, filtered through SiO_2 and concentrated. The residue was adsorbed onto SiO_2 and purified by silica gel chromatography (12 g SiO_2 column, 95:5→85:15 hexanes/EtOAc) to give 54.8 mg (0.165 mmol, 65%) of **12** as a white foam, which gave spectral data identical to that obtained previously.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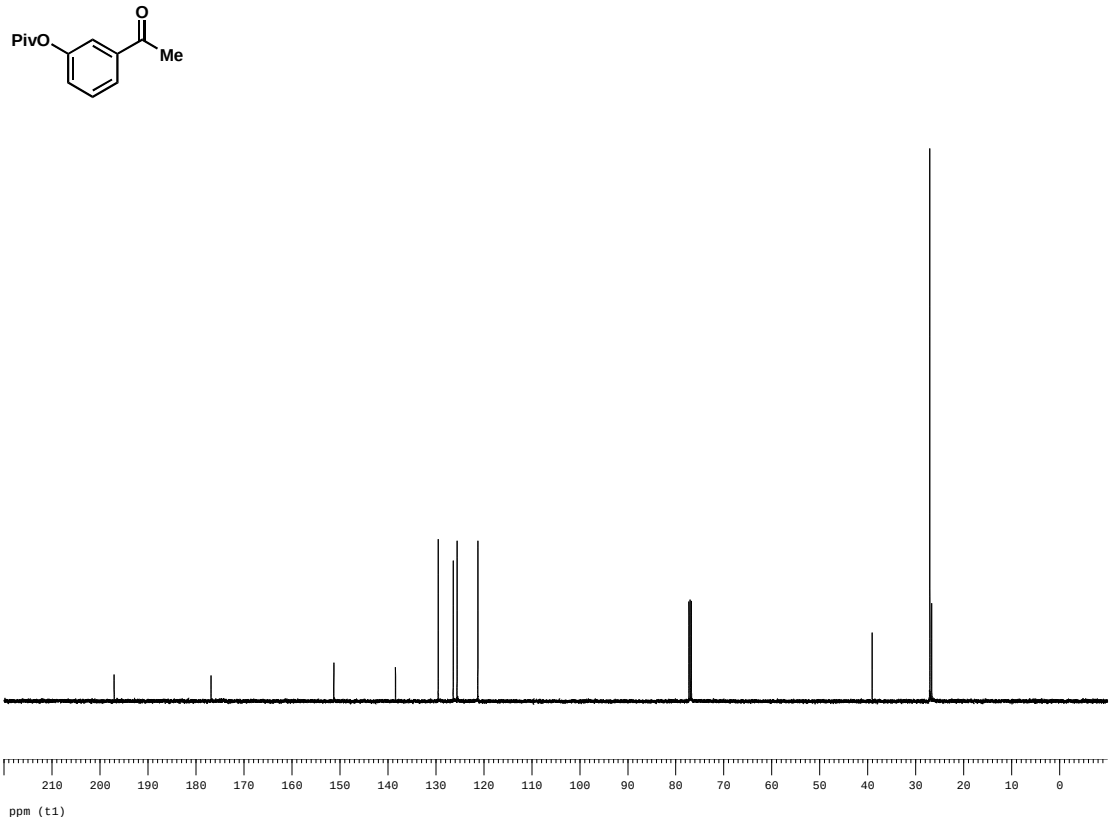
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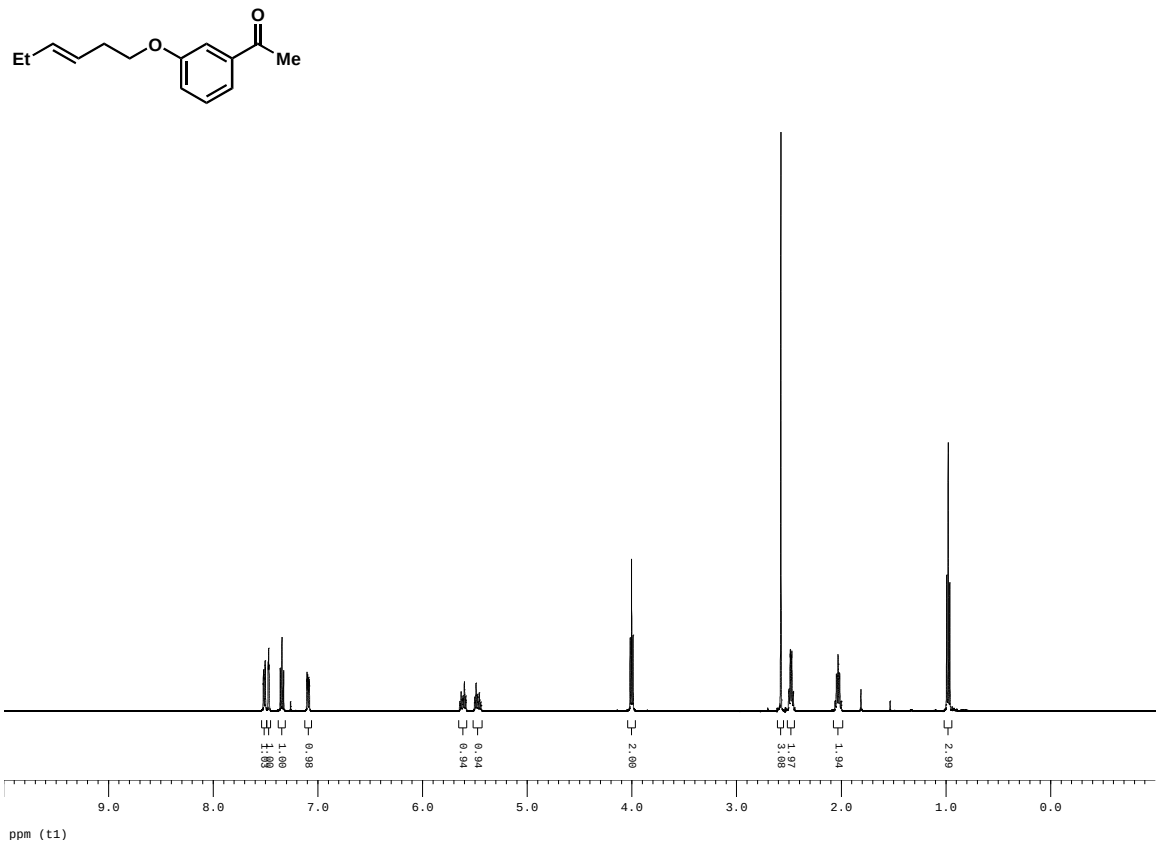
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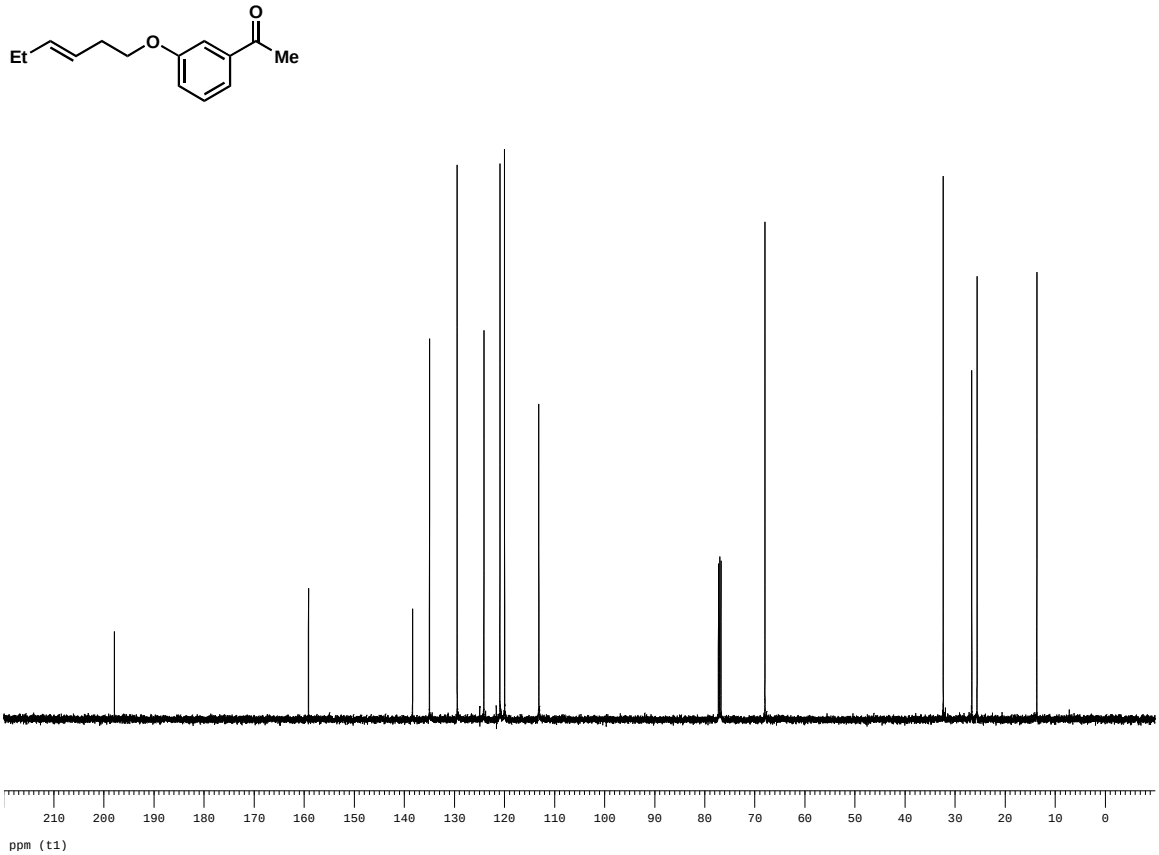
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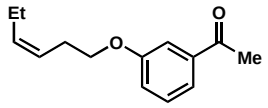
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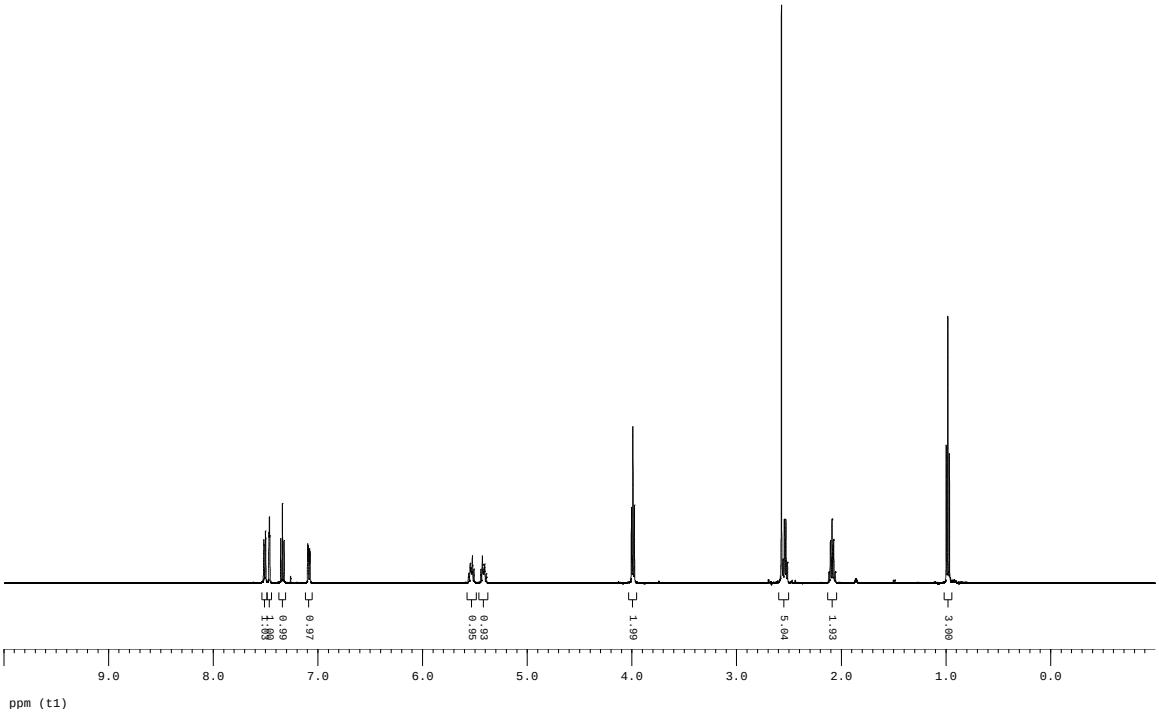
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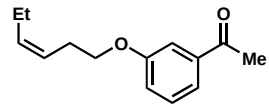
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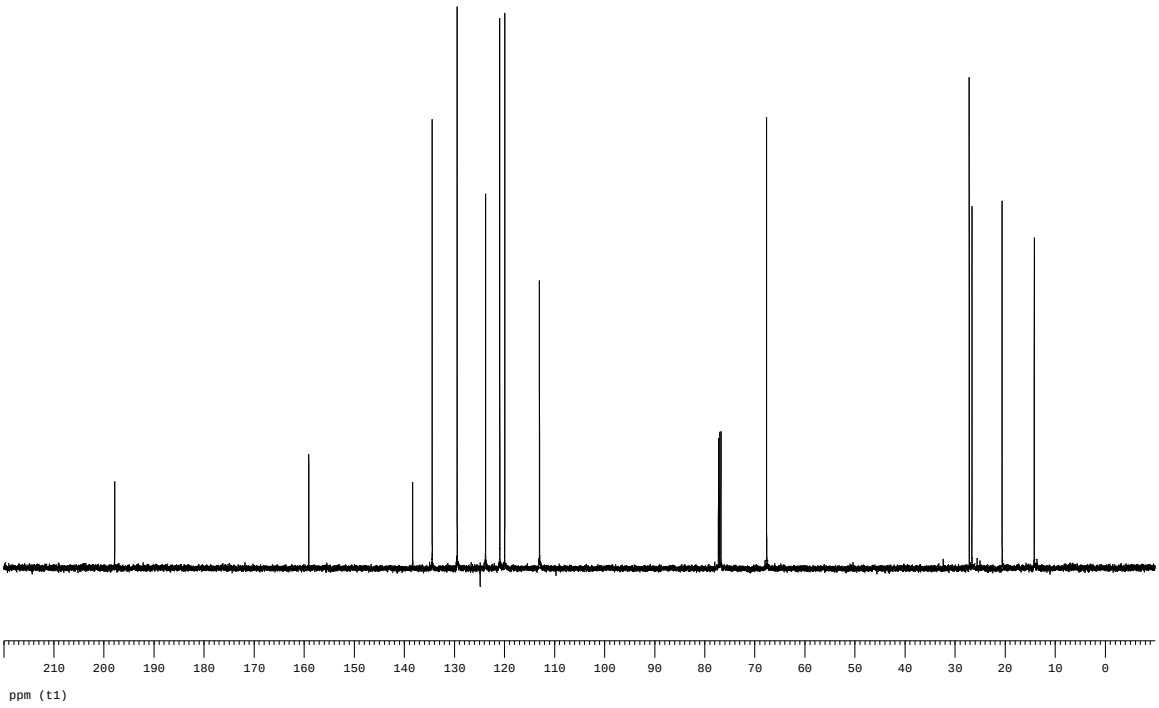
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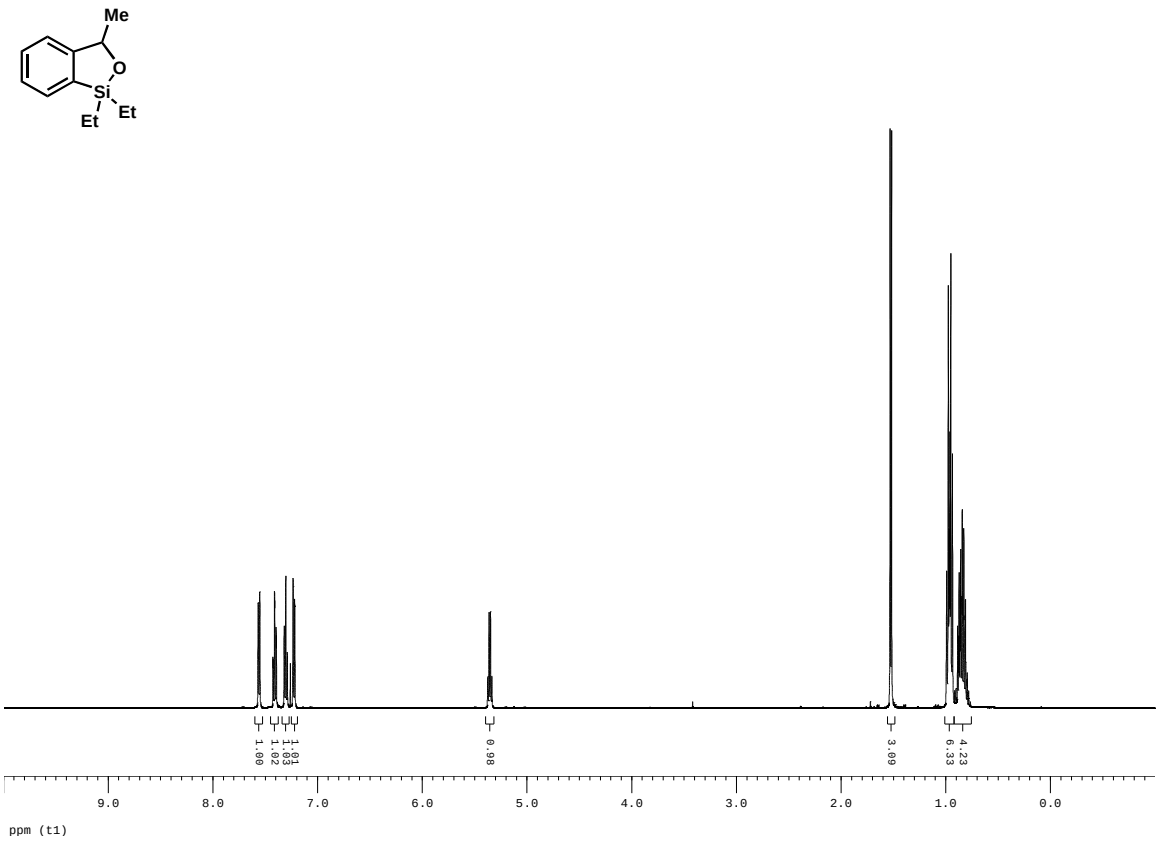
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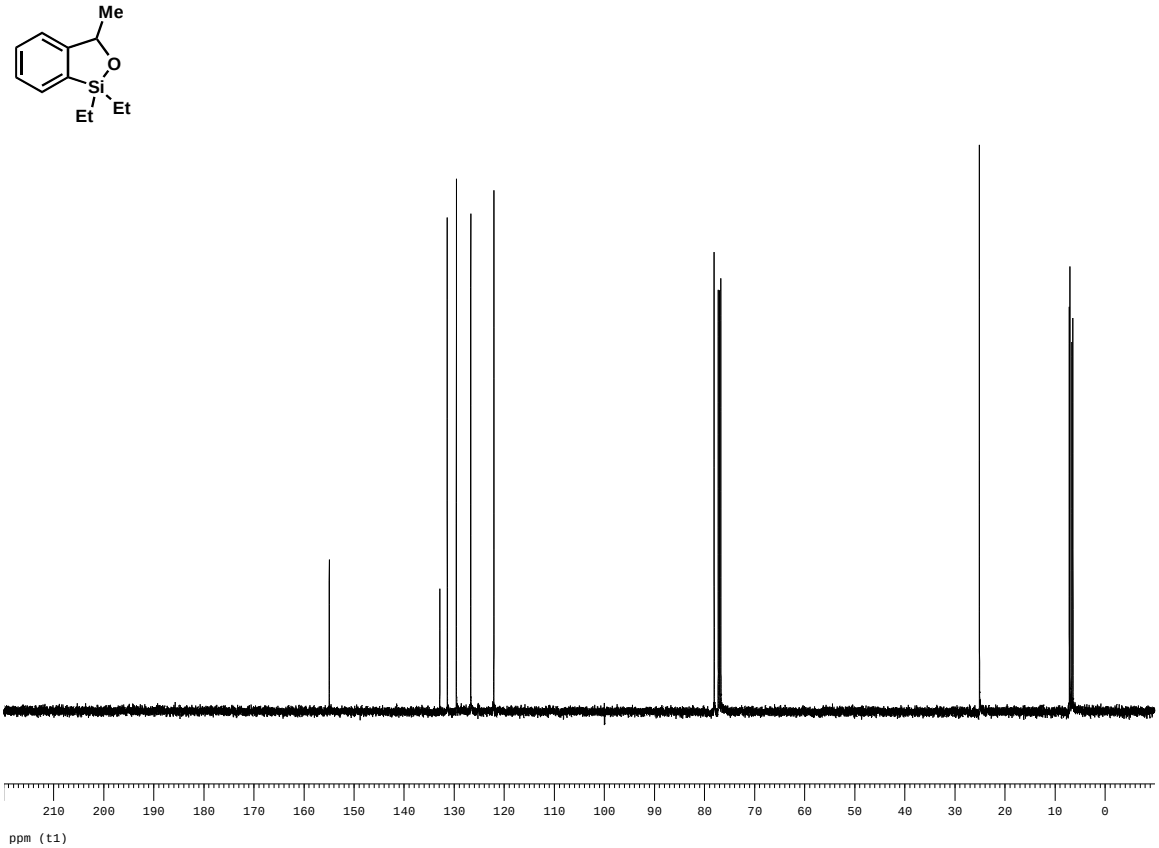
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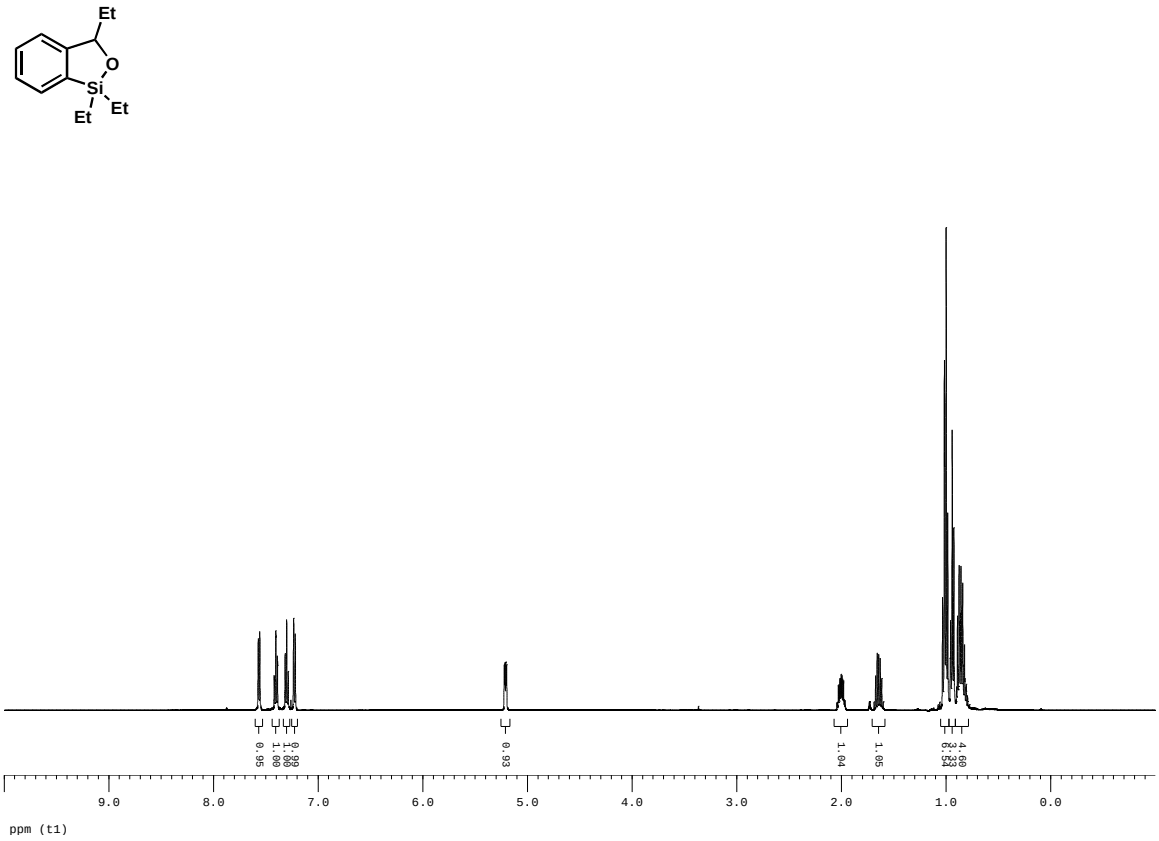
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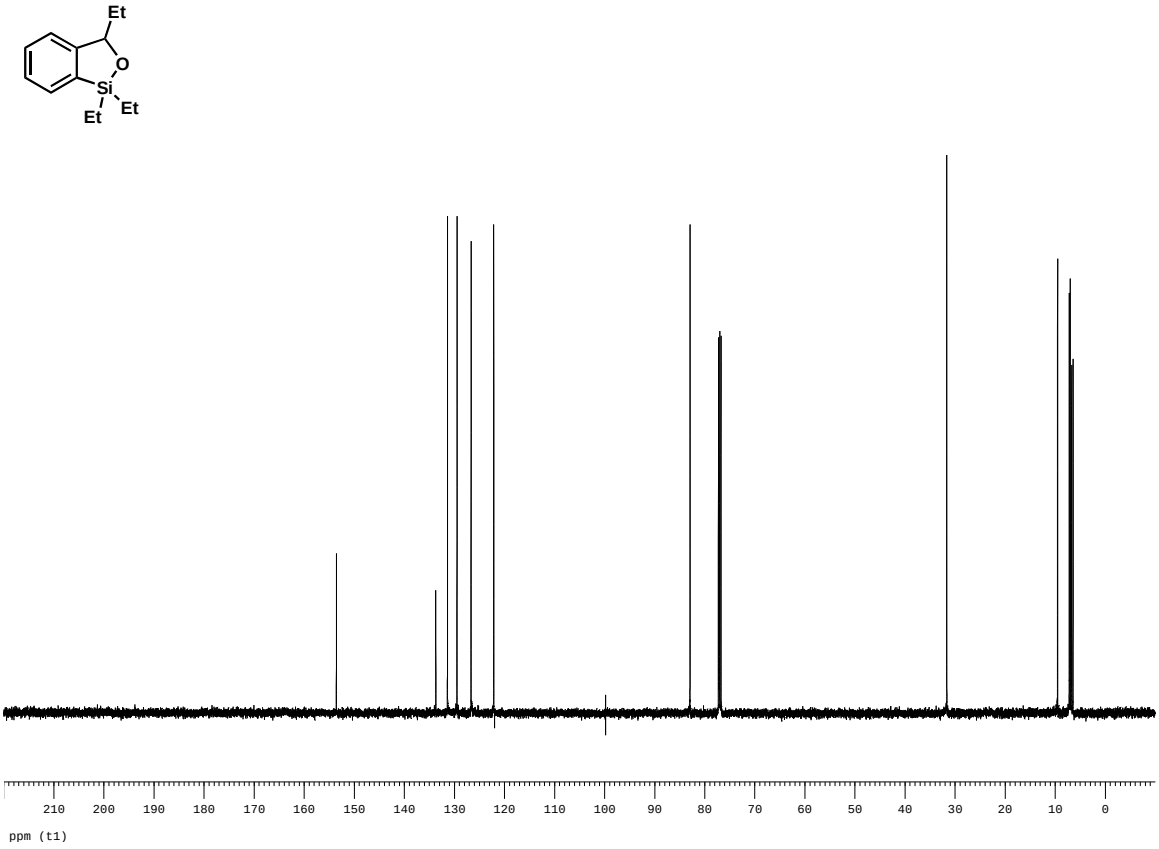
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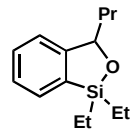
ppm (t1)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Si
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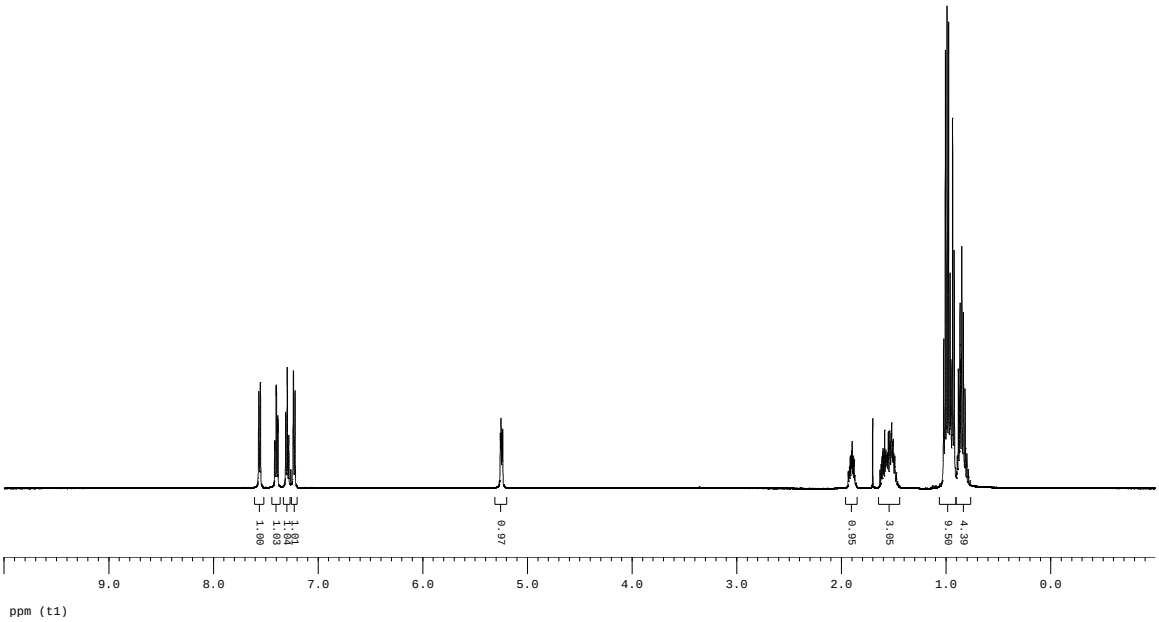
Et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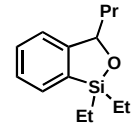
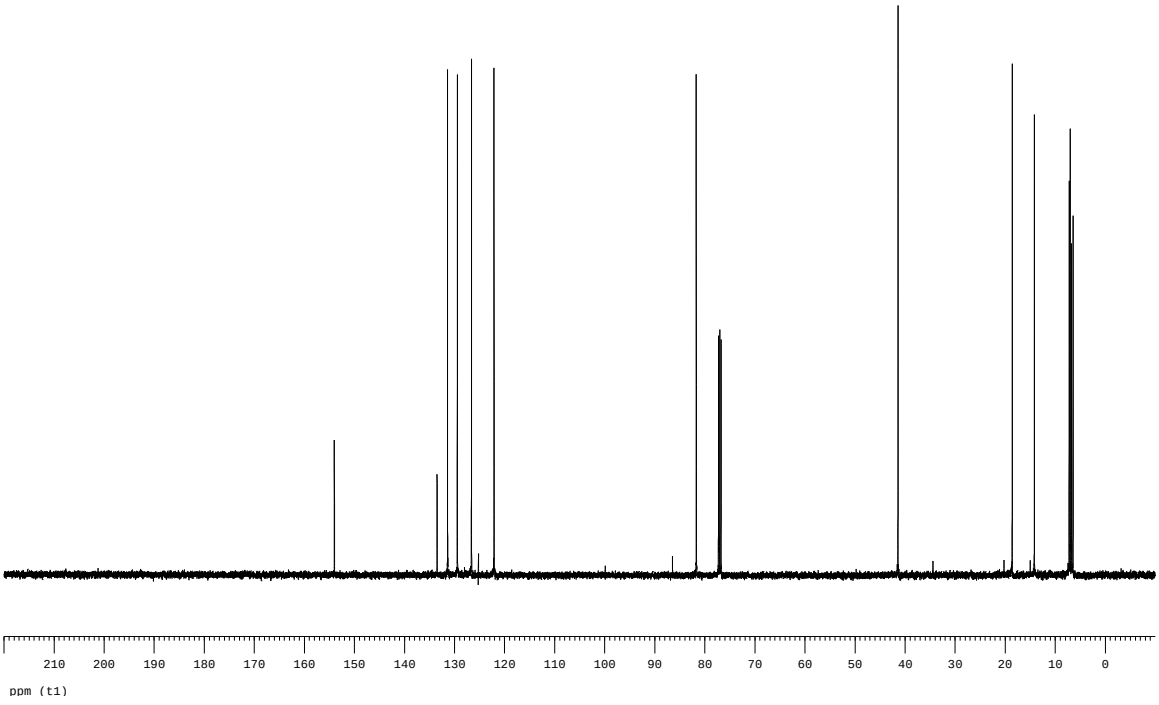
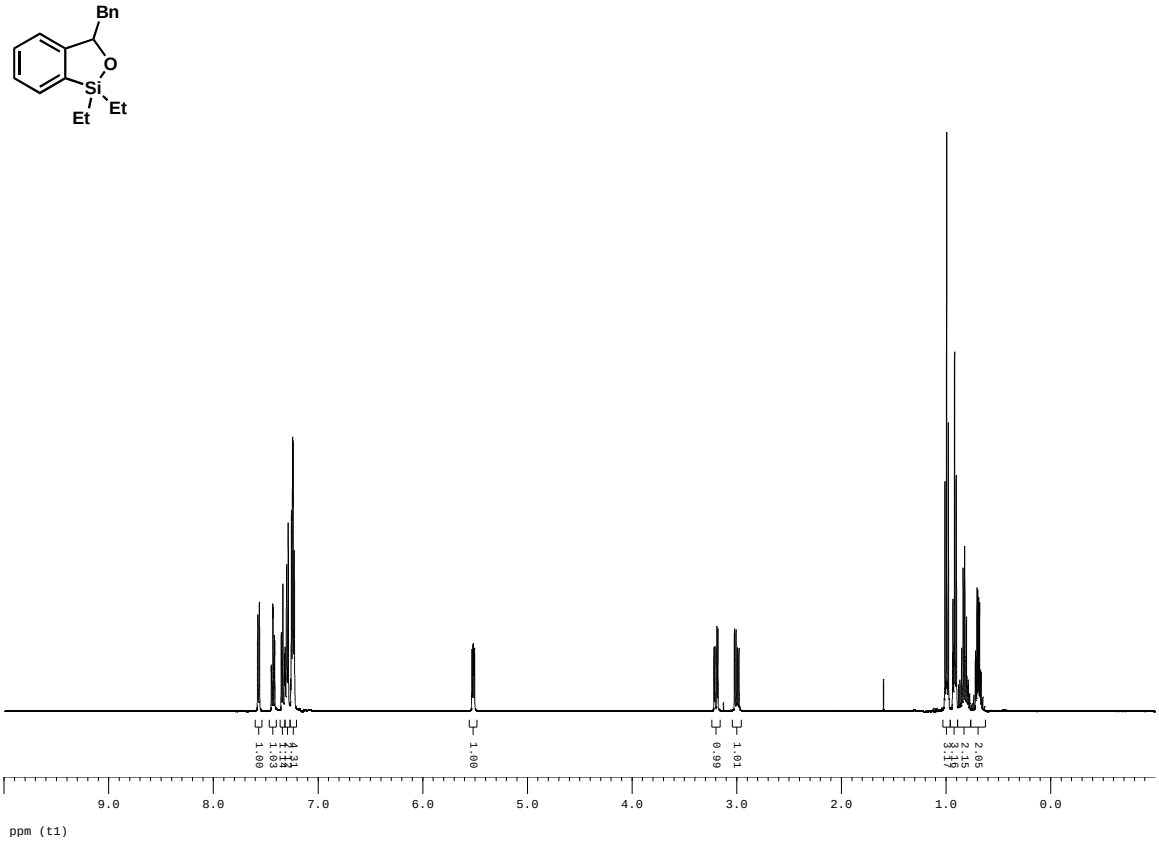
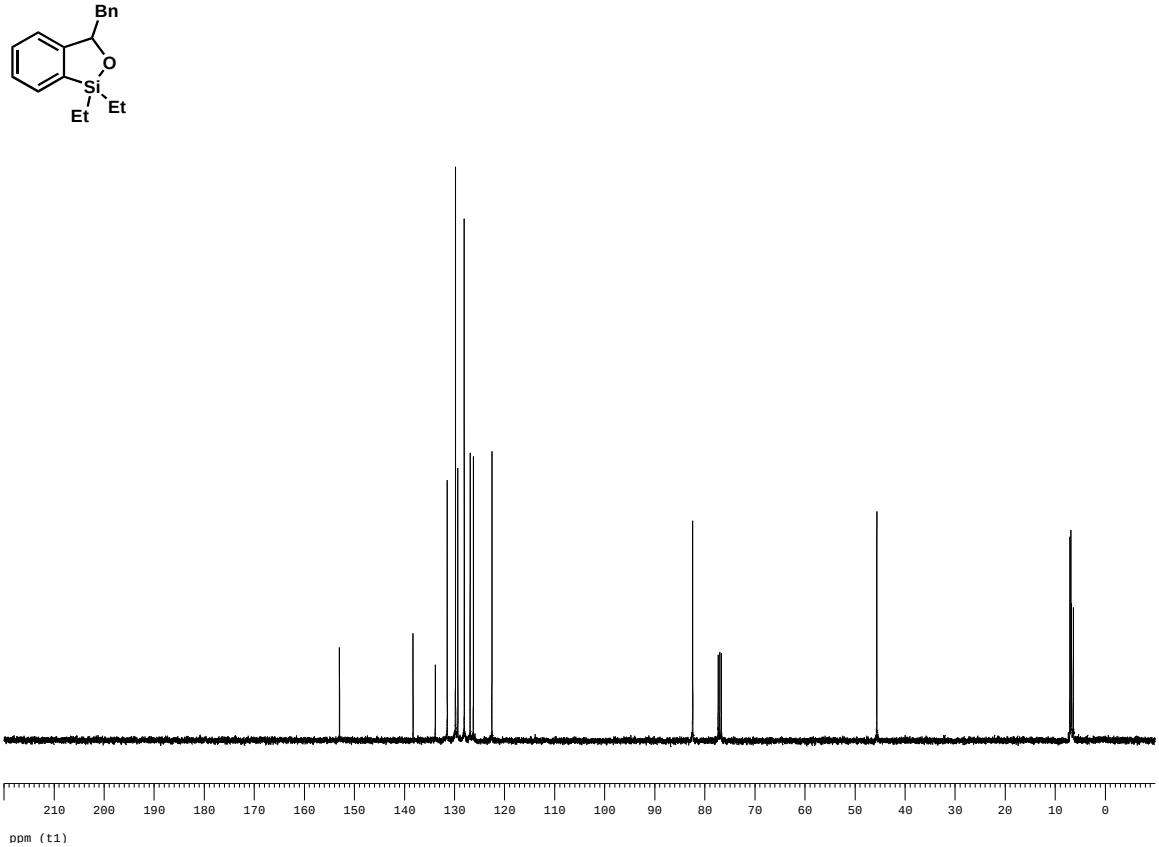
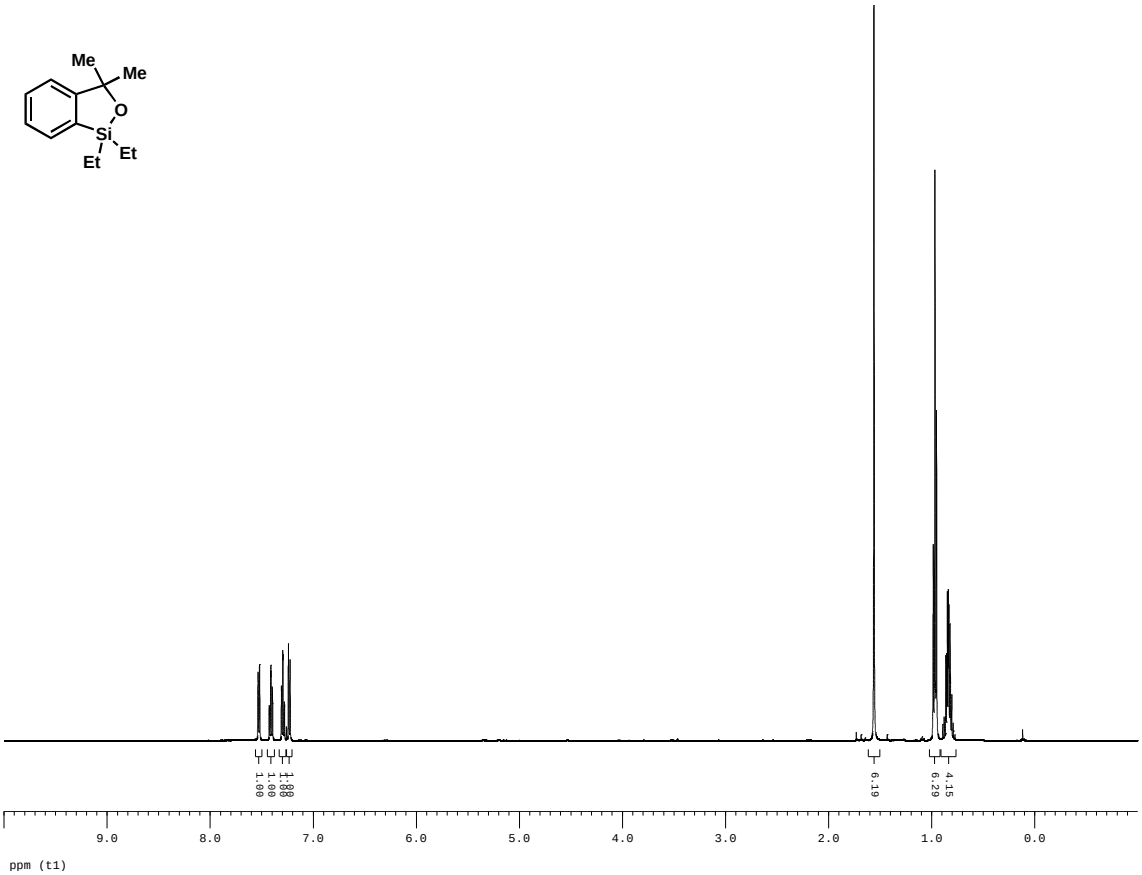
0.0
ppm (t1)

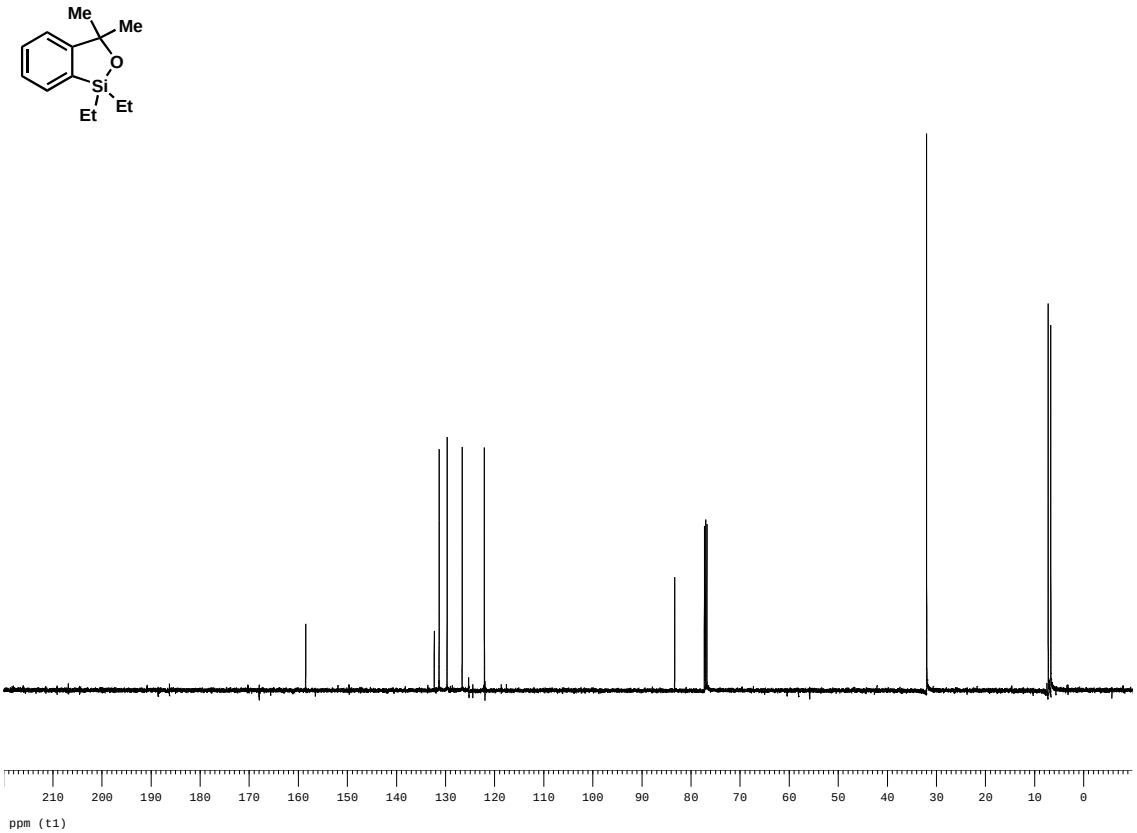

Pr
O
Si
Et
Et

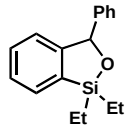

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

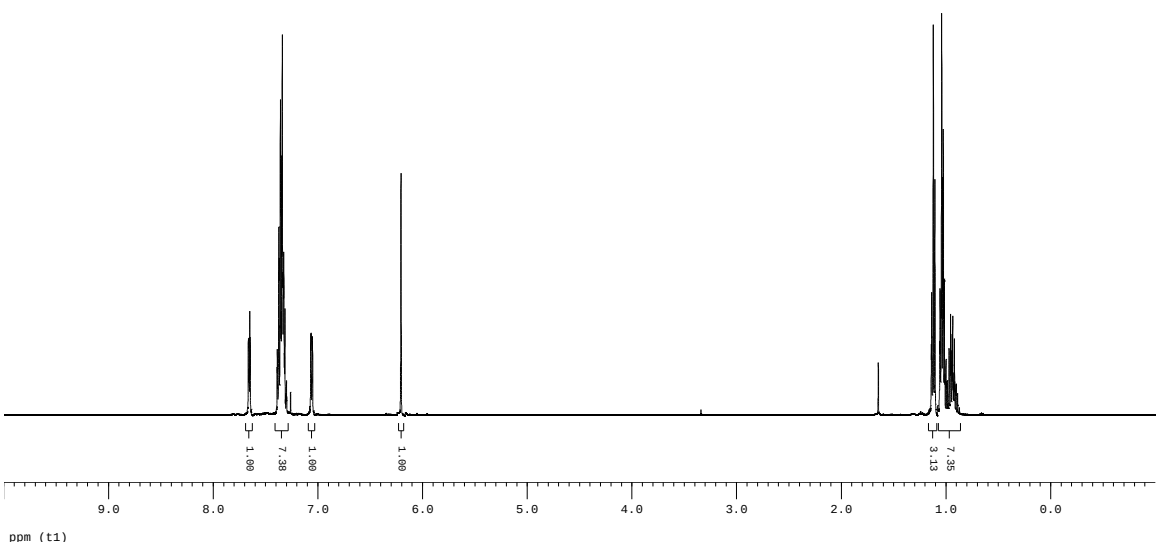

Bn
O
Si
Et
Et
1.00
1.00
0.99
1.01
2.05
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

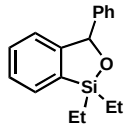

Bn
O
Si
Et
Et
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

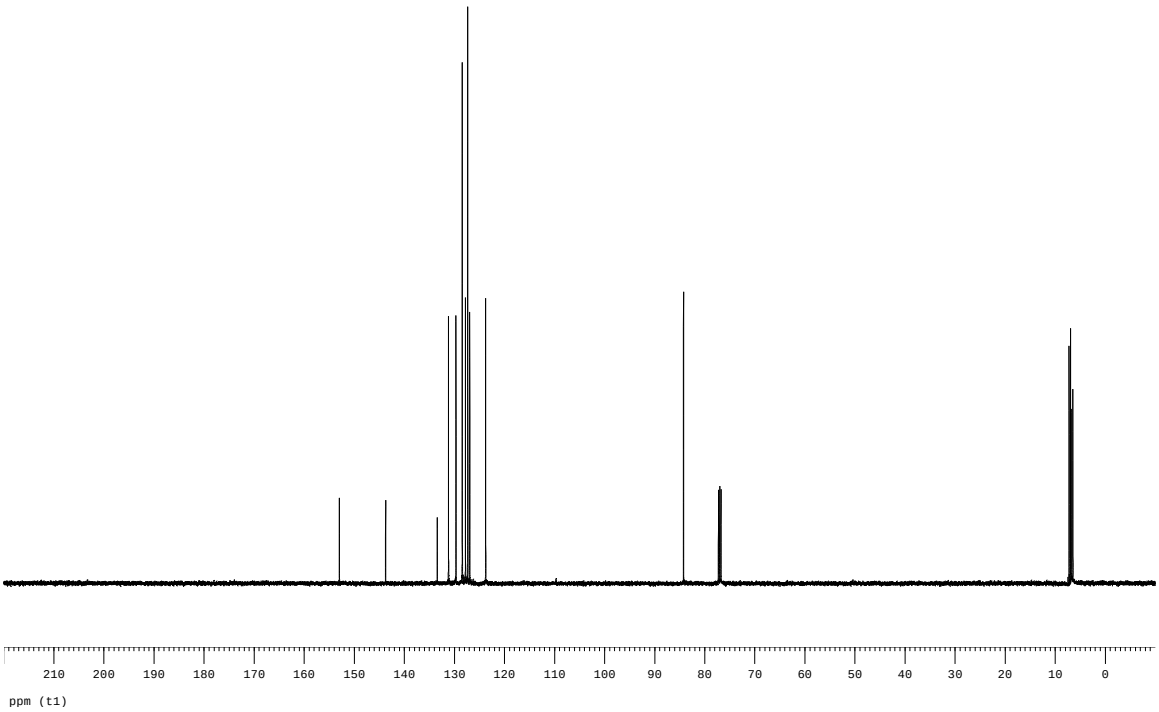

Me
Me
O
Si
Et
Et
1.00
1.00
1.00
1.00
1.00
6.19
6.29
4.15
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

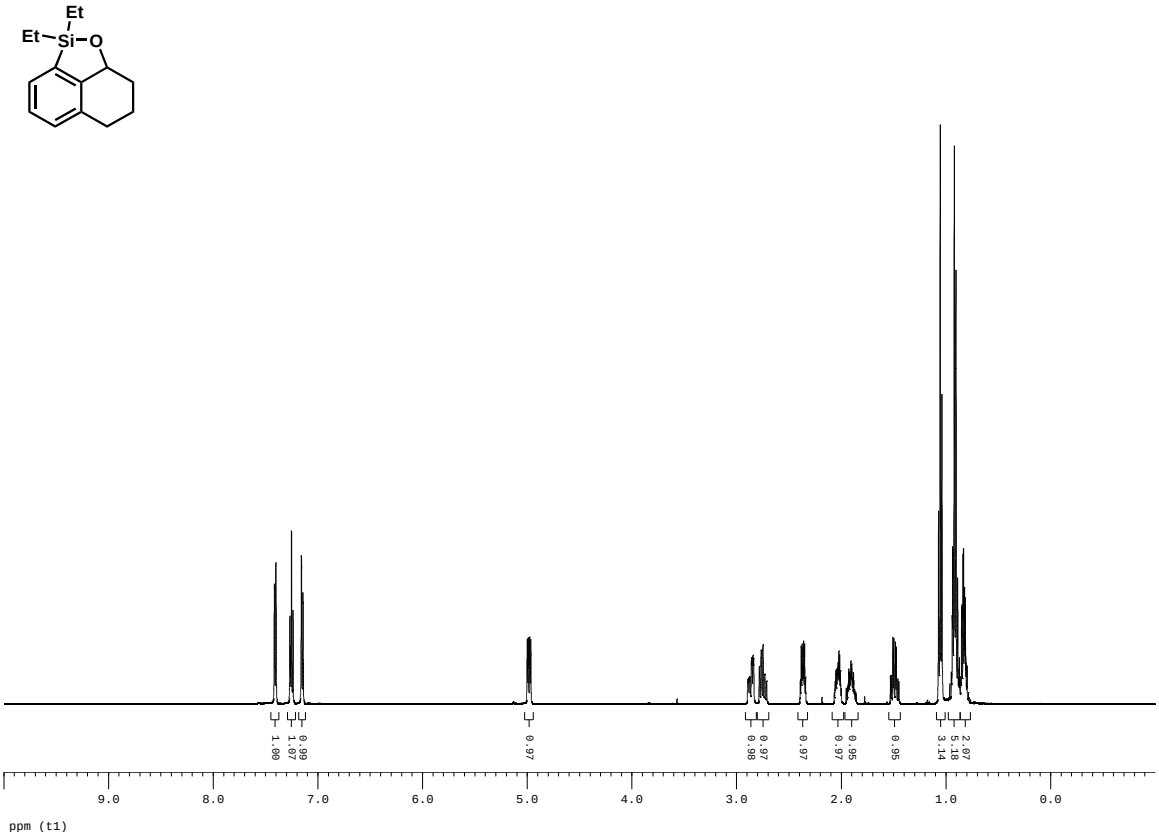

Me
Me
O
Si
Et
Et
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

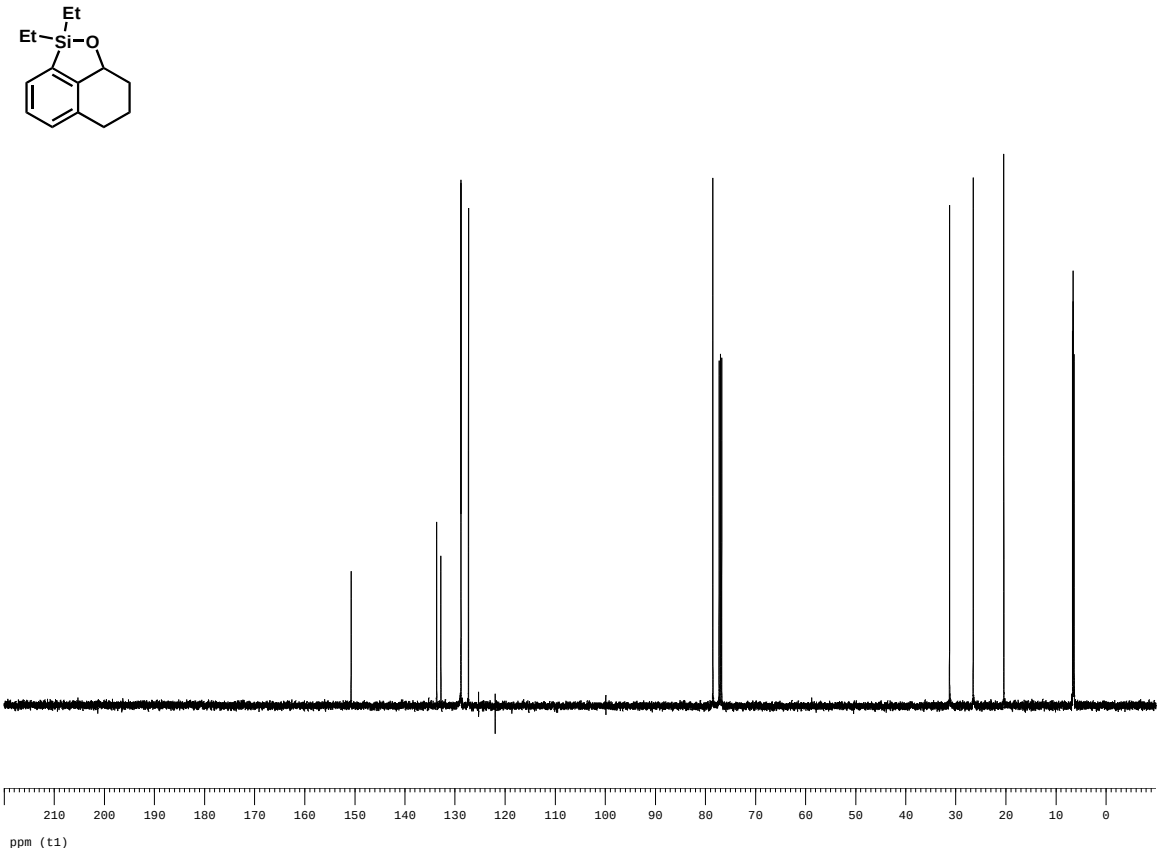

Ph
O
Si
Et
Et

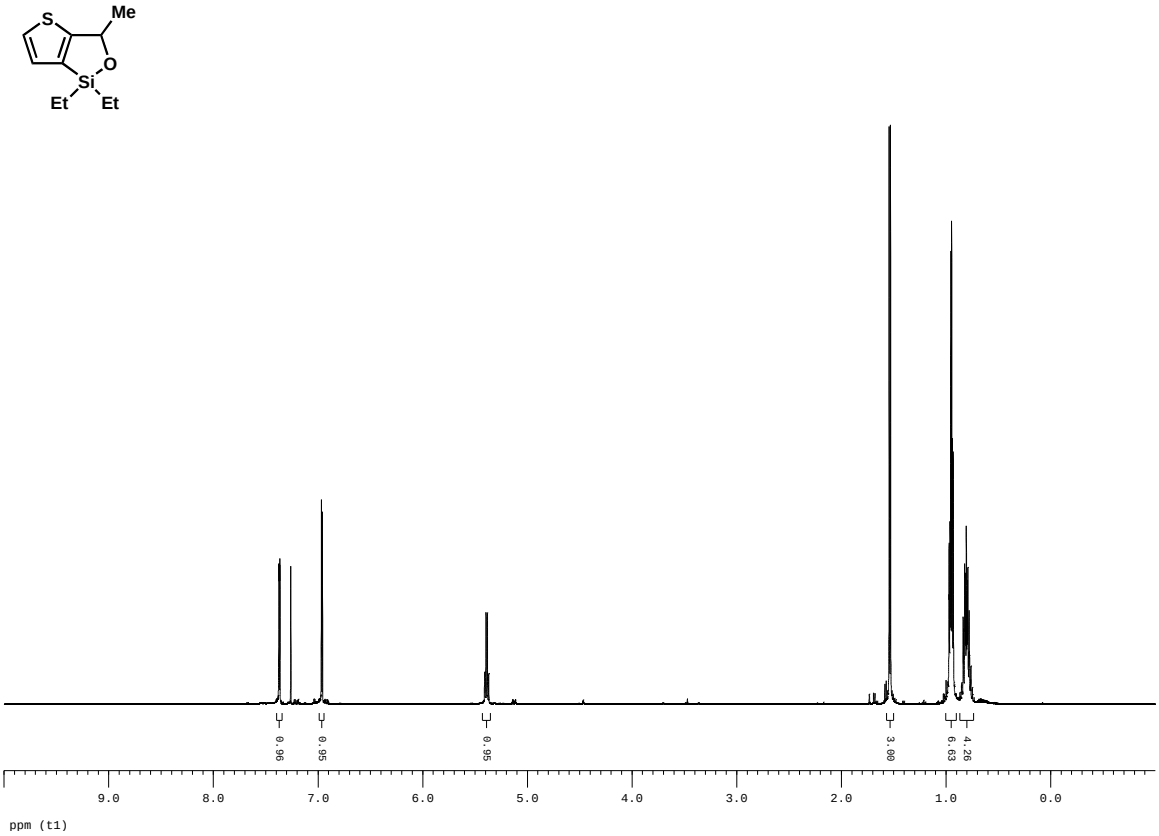

1.00
7.38
1.00
1.00
3.13
7.35
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

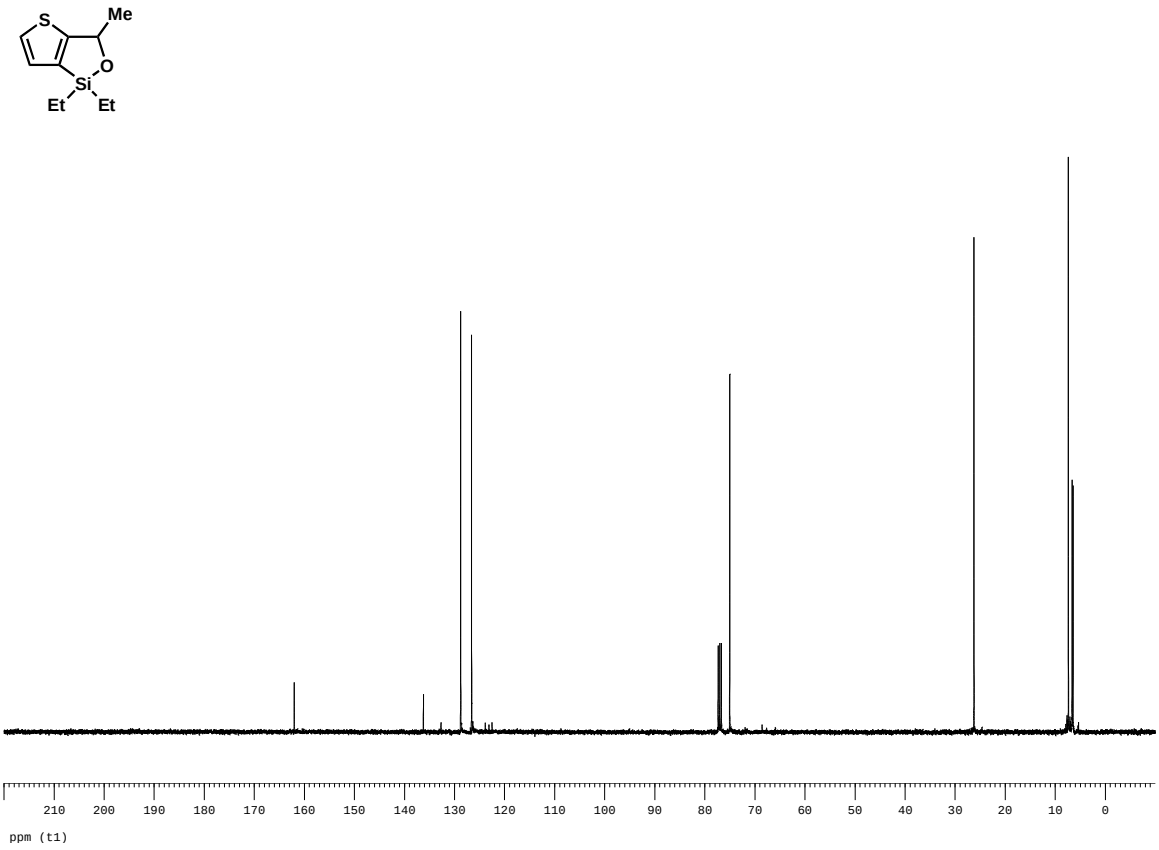

Ph
O
Si
Et
Et

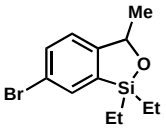

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

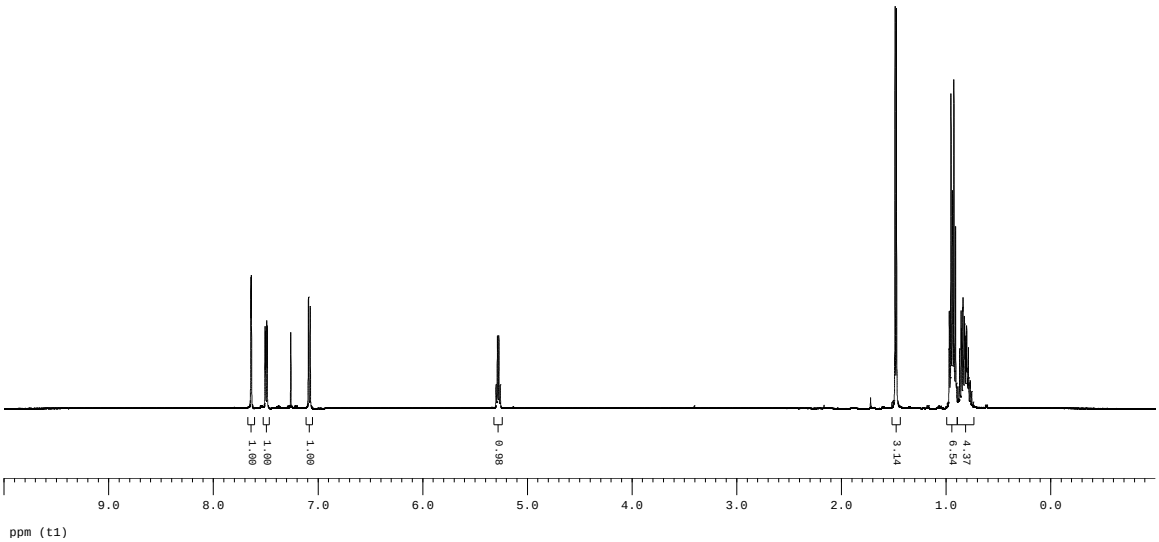

Et
Et
Si
O
1.00
1.07
0.99
0.97
0.98
0.97
0.97
0.97
0.95
0.95
3.14
5.37
2.07
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

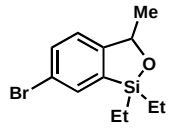

Et
Et
Si
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

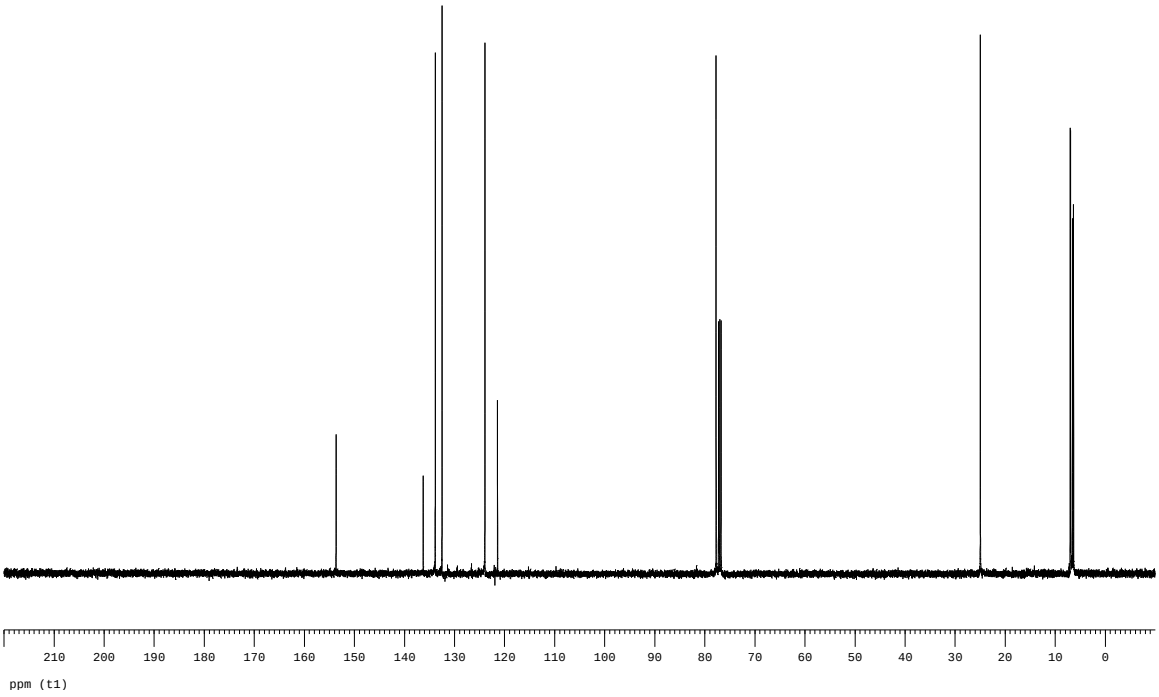

S
Me
O
Si
Et
Et
0.96
0.95
0.95
3.00
6.63
4.26
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

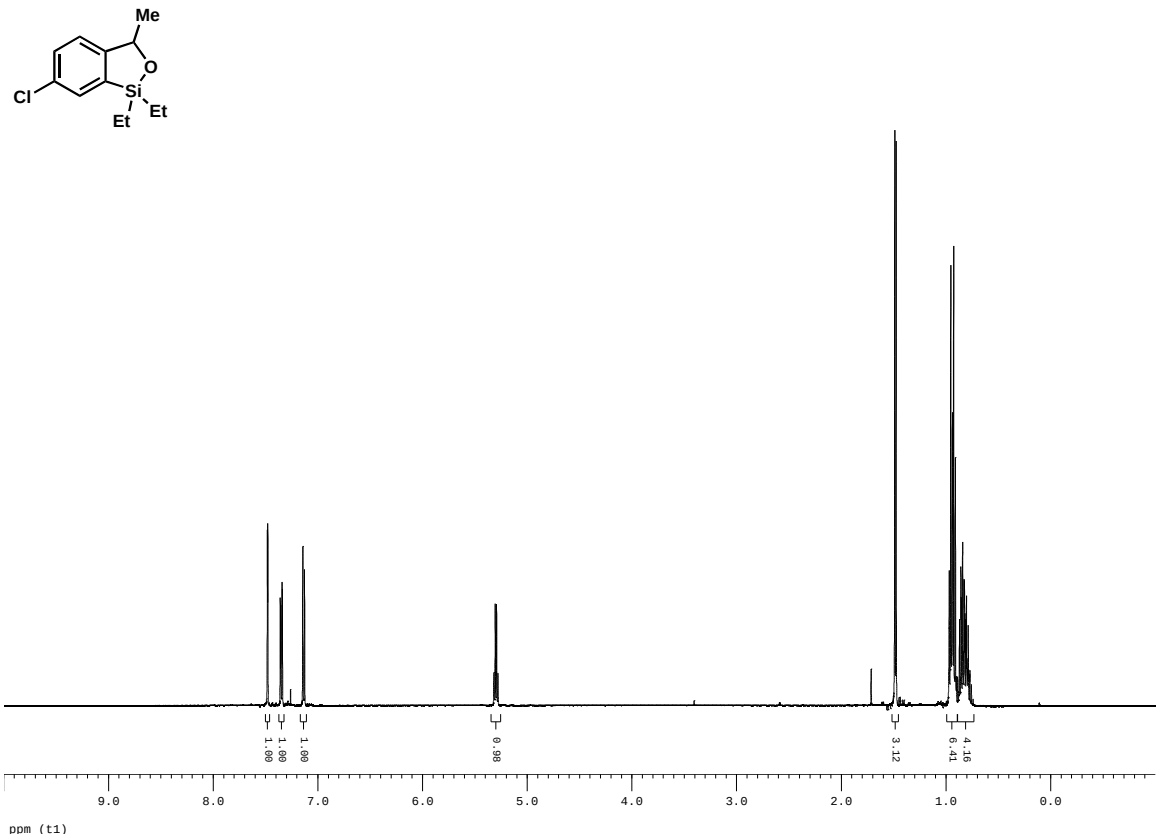

S
Me
O
Si
Et
Et
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

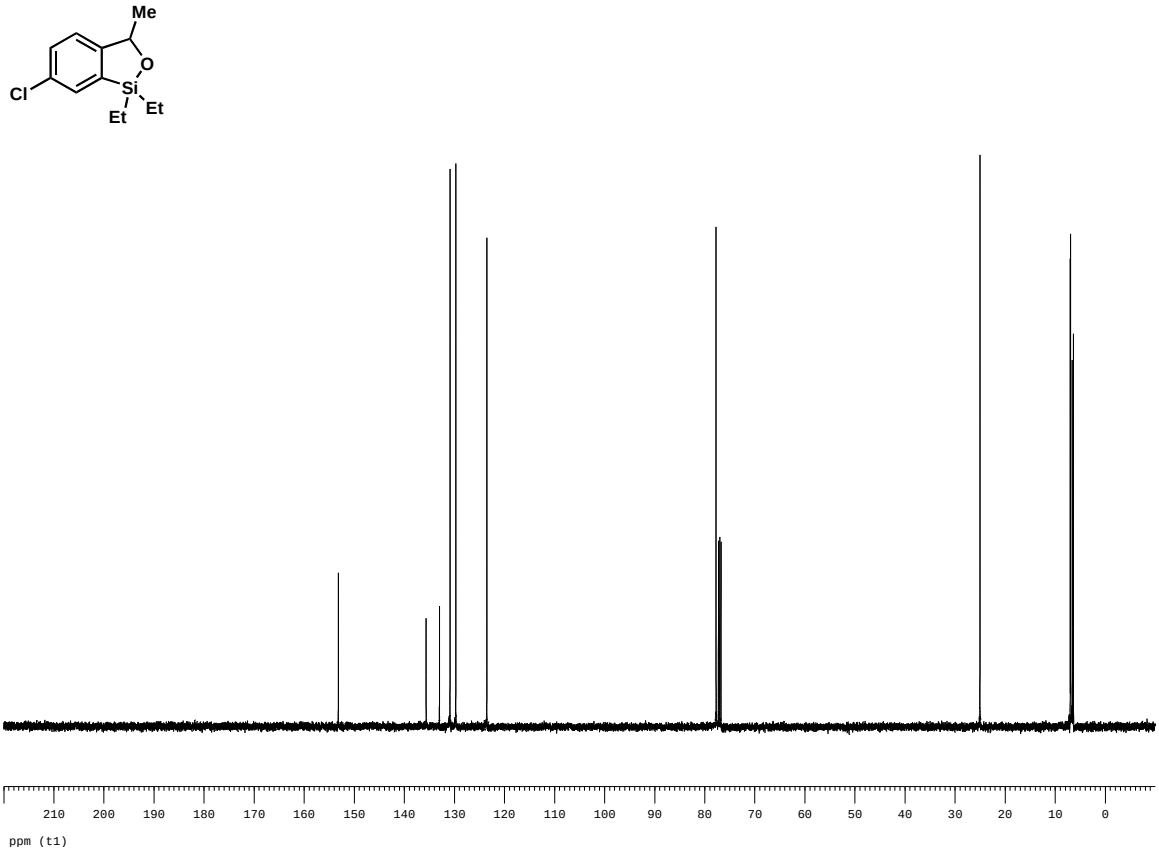

Me
O
Br
Si
Et
Et

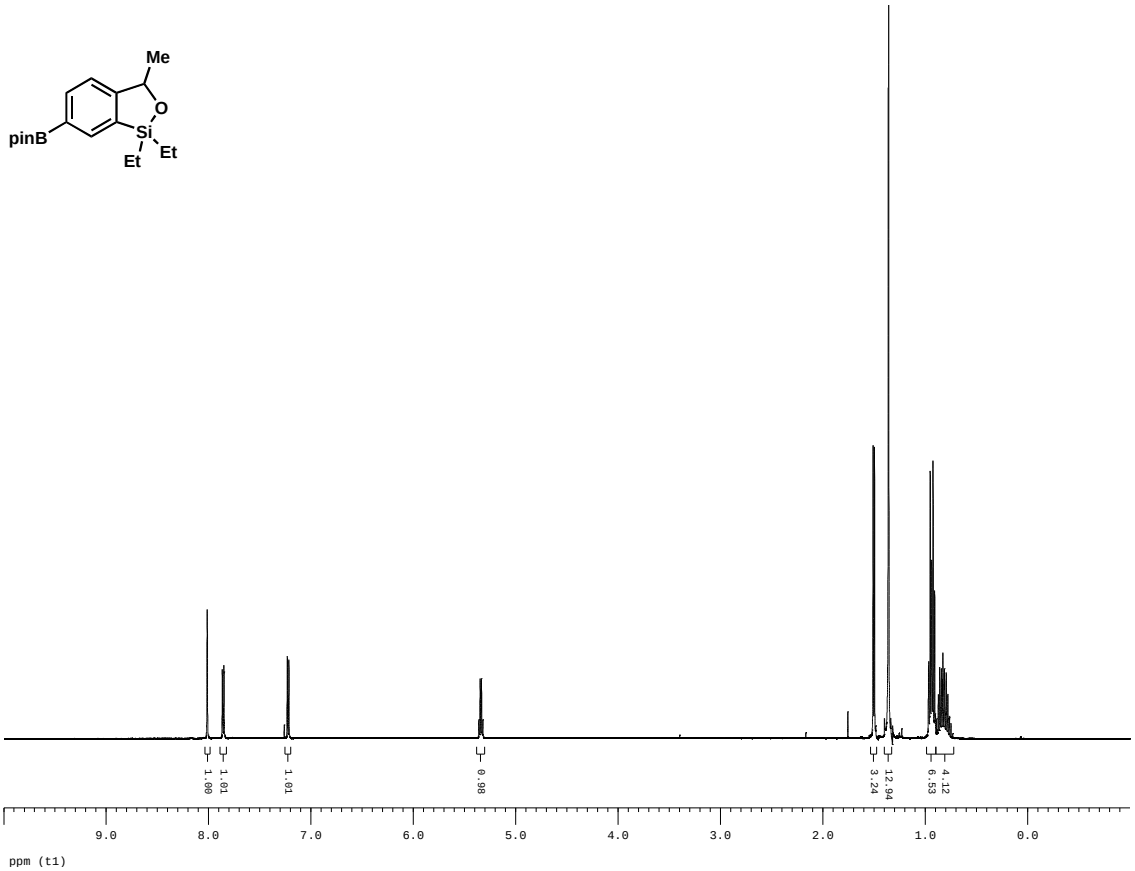

1.00
1.00
1.00
0.98
3.14
6.54
4.37
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

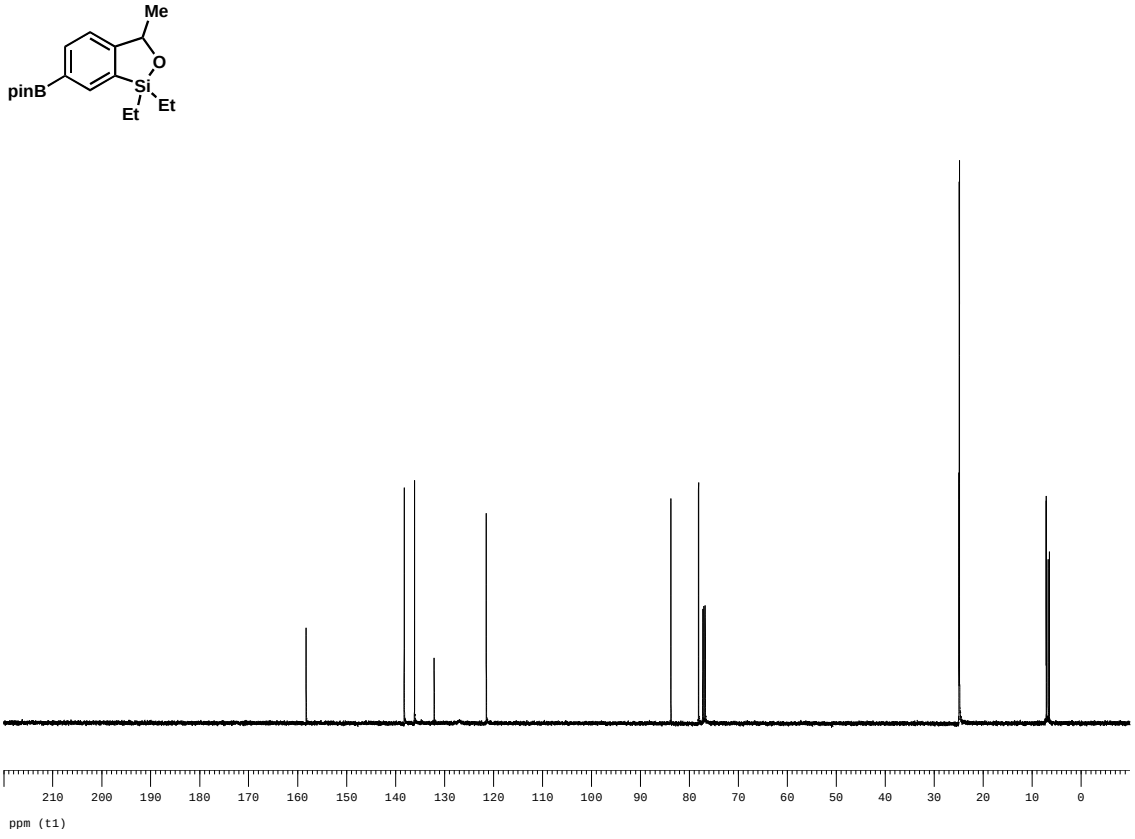

Me
O
Br
Si
Et
Et

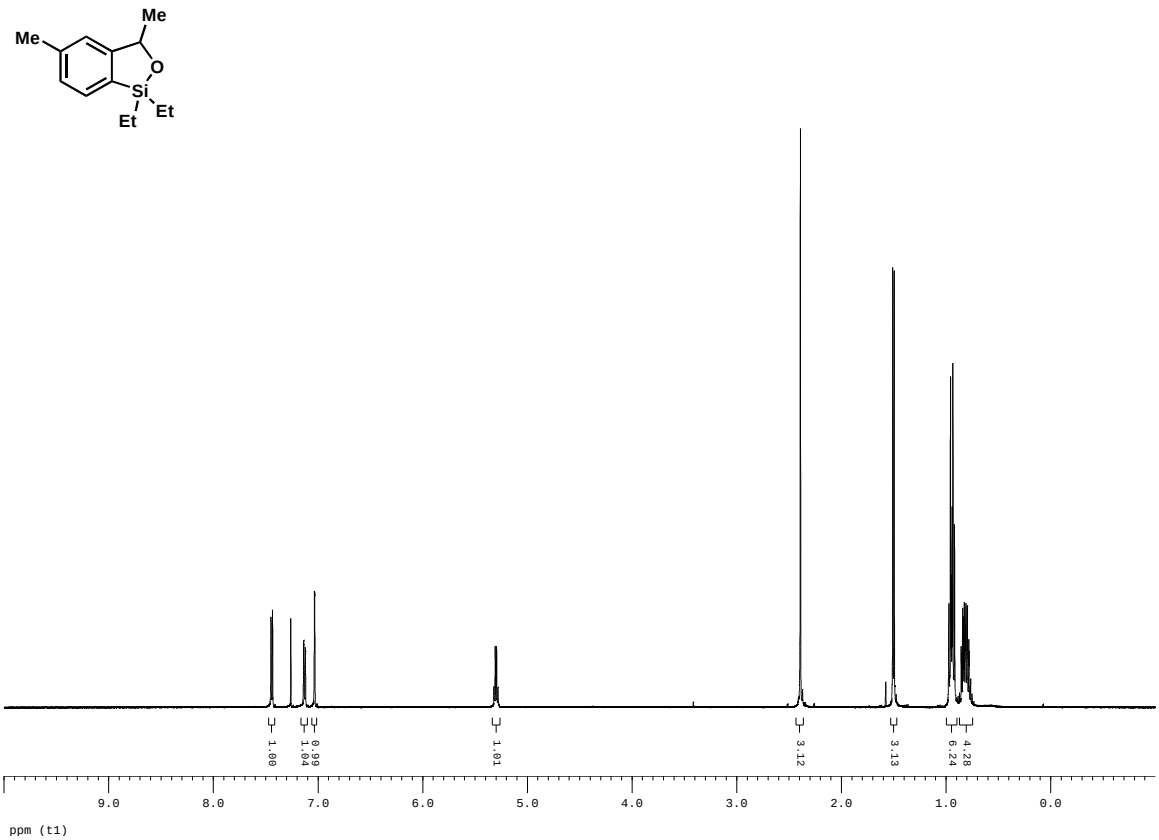

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

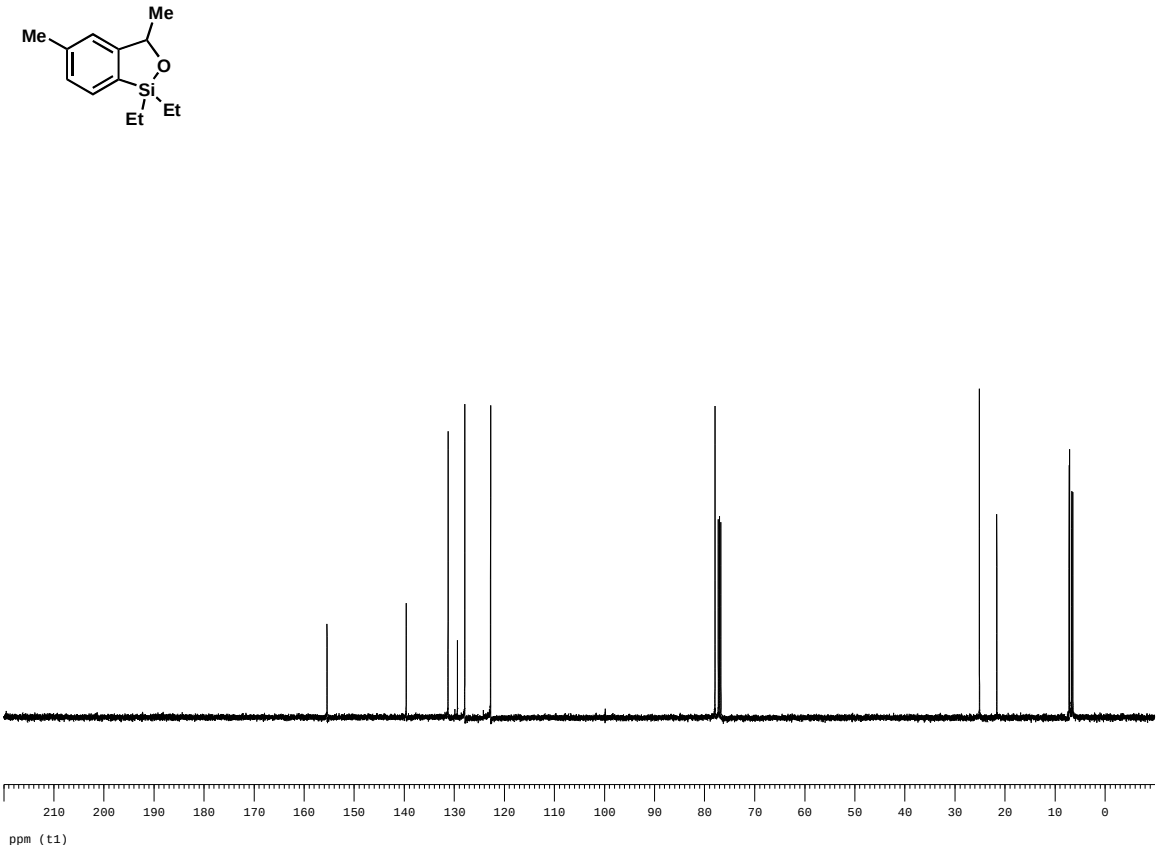

Me
O
Si
Et
Et
Cl
1.00
1.00
1.00
0.98
3.12
6.41
4.16
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

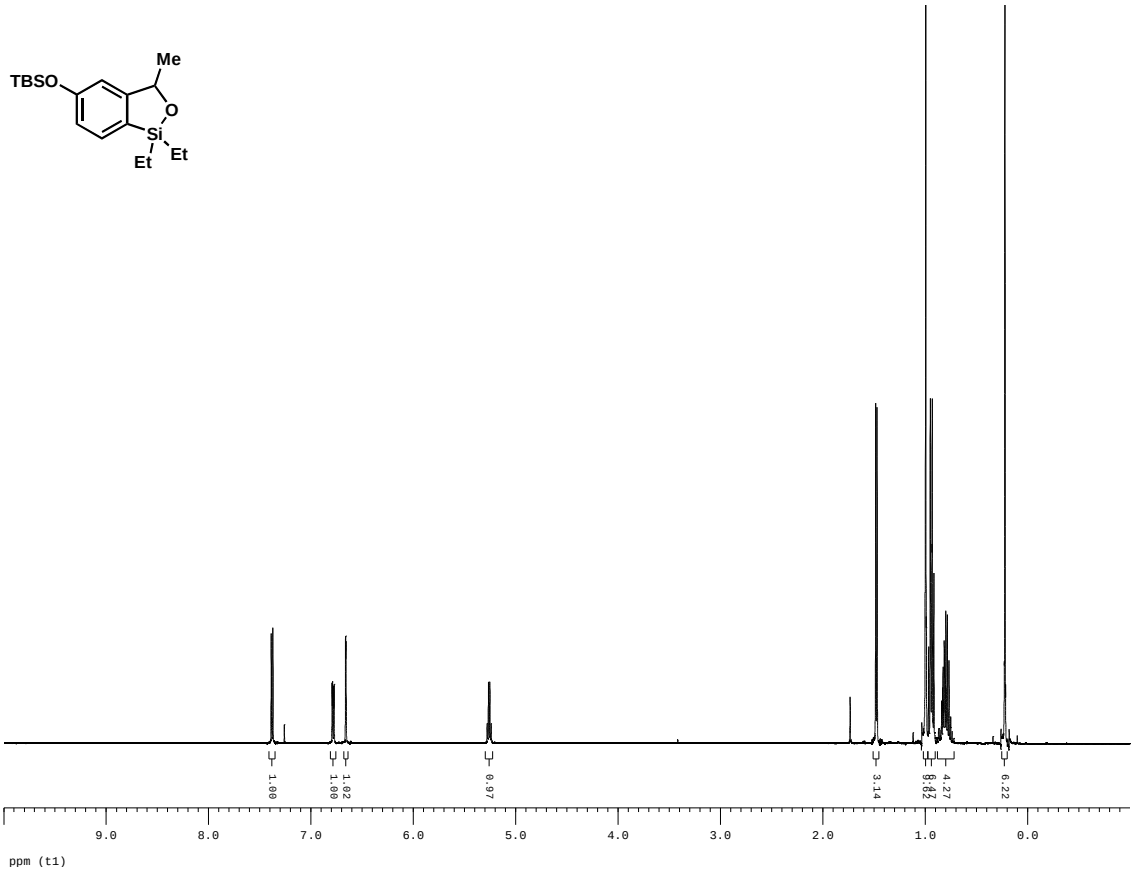

Me
O
Si
Et
Et
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

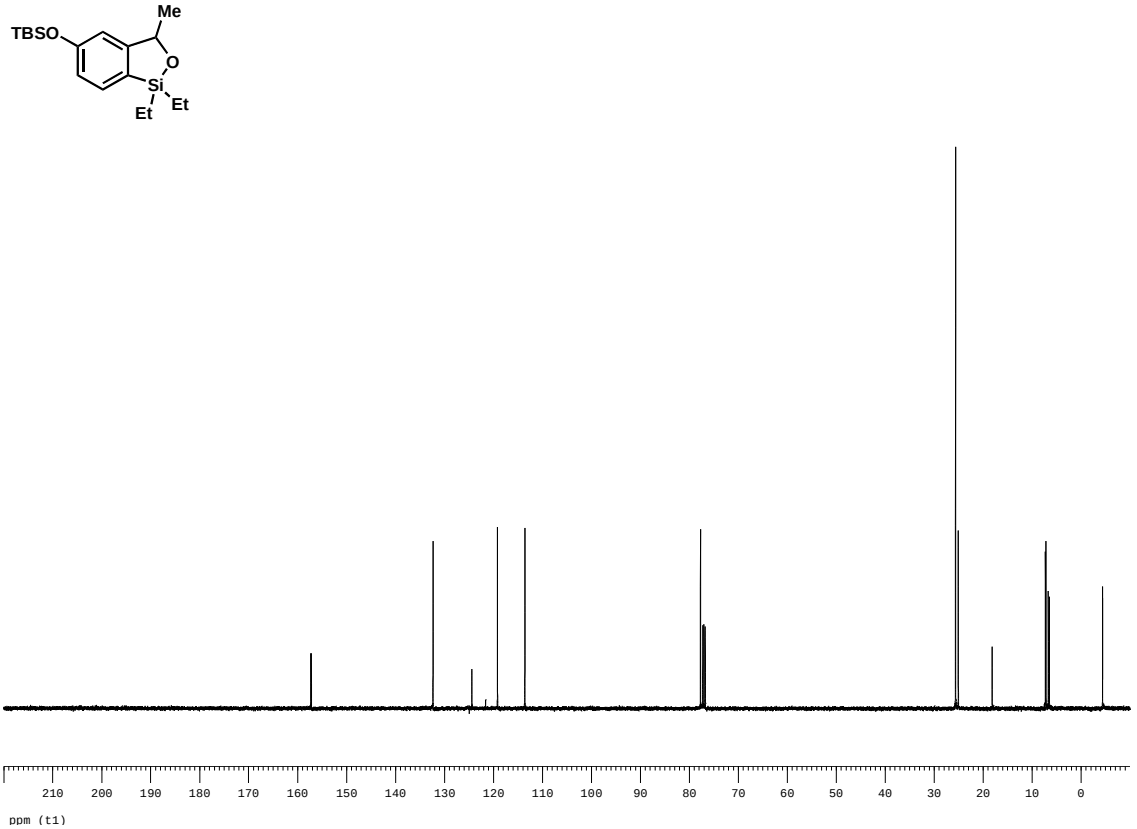

Me
O
Si
pinB
Et
Et
1.00
1.01
1.01
0.98
3.24
12.94
6.53
4.12
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

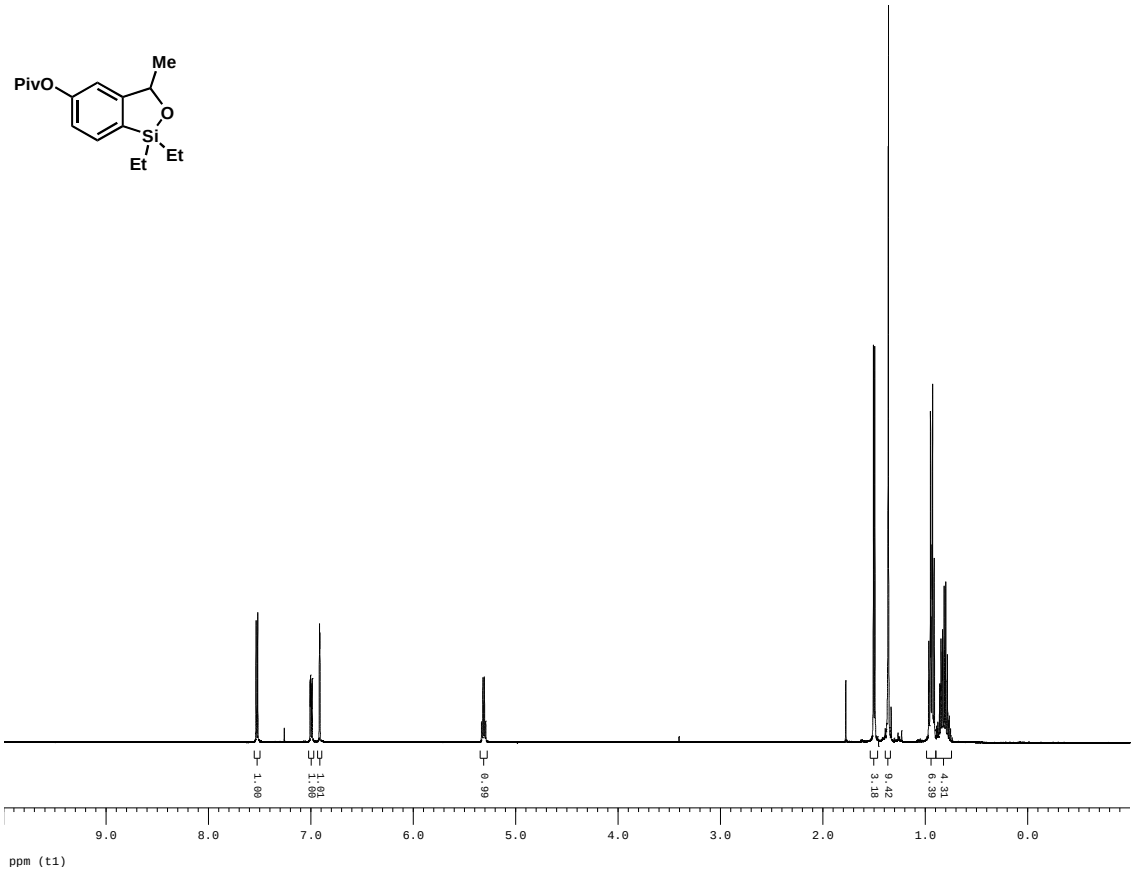

Me
O
Si
pinB
Et
Et
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

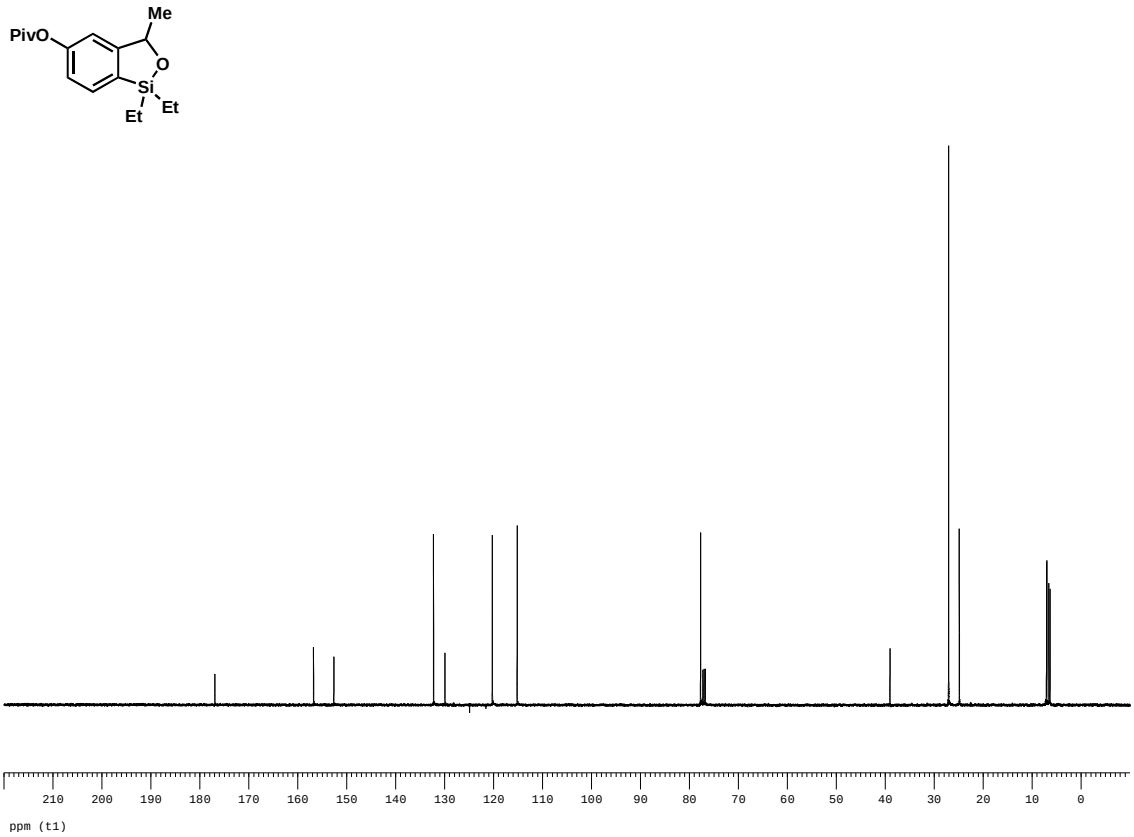

Me
Me
O
Si
Et
Et
1.00
1.04
0.99
1.01
3.12
3.13
6.24
4.28
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

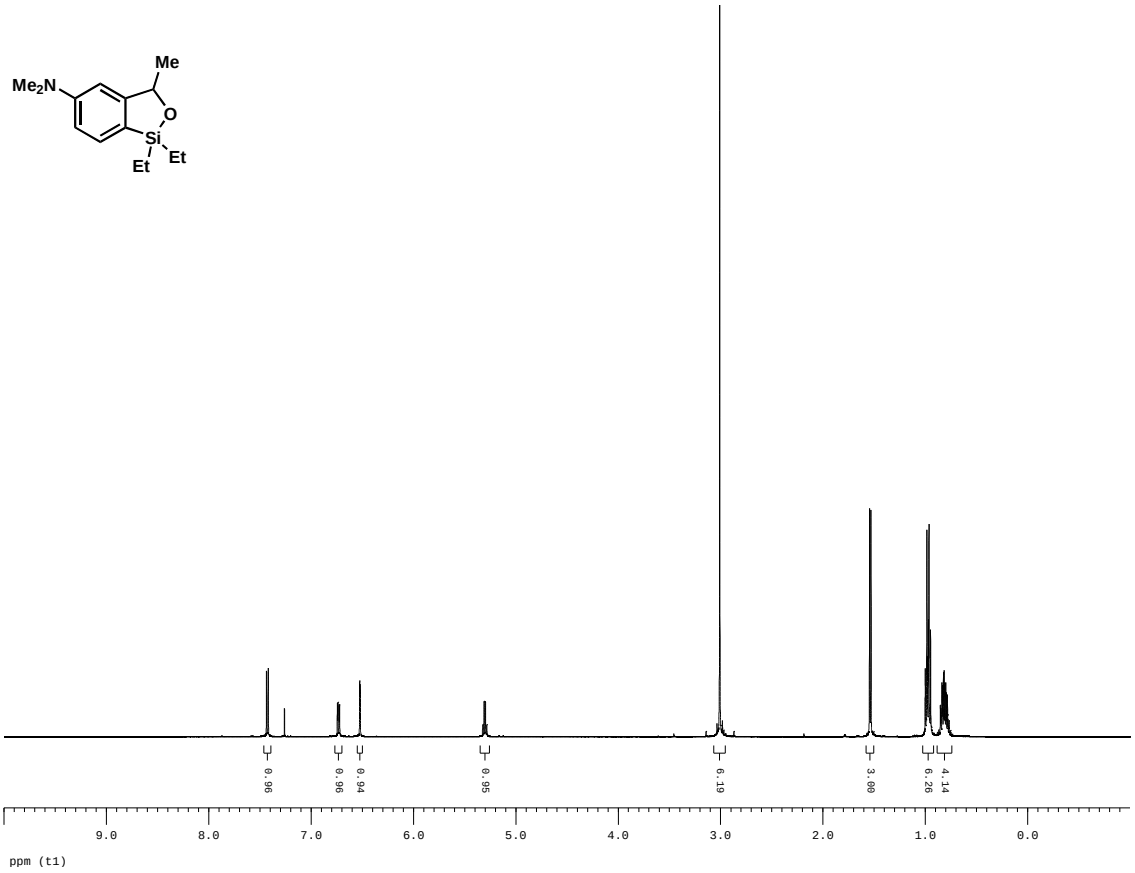

Me
Me
O
Si
Et
Et
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

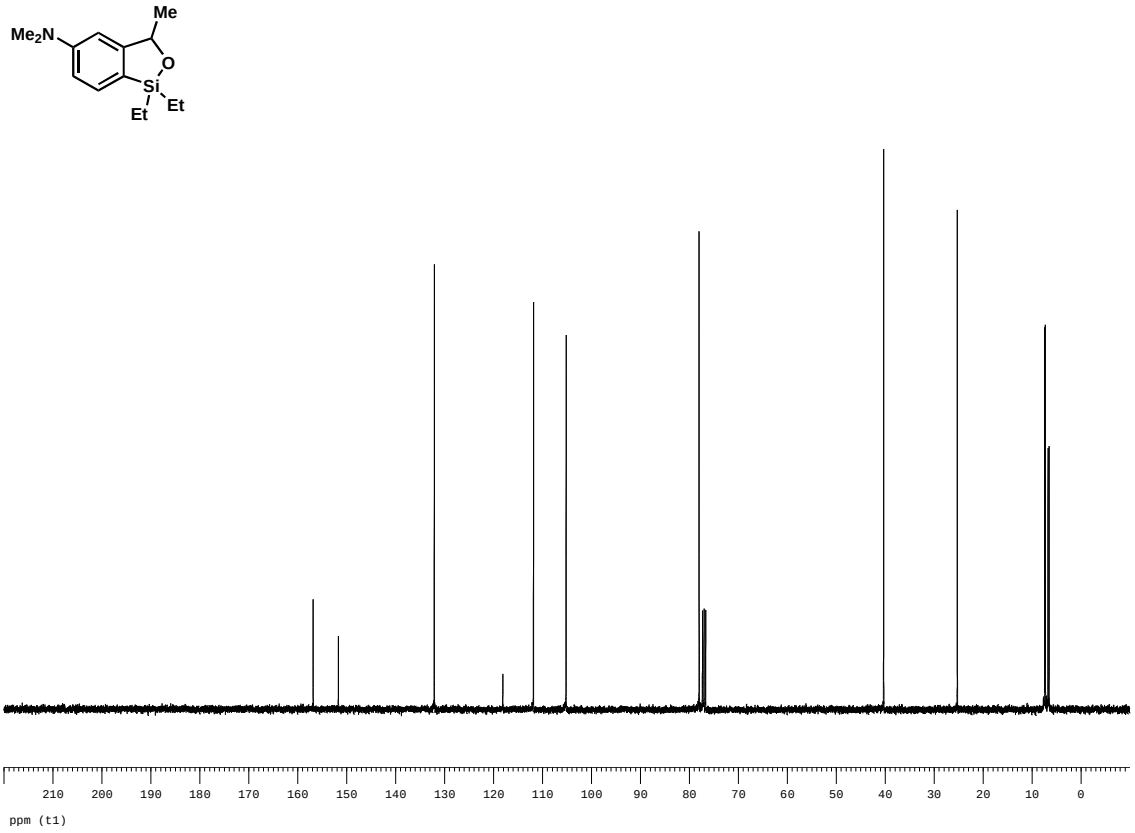

TBSO
Me
O
Si
Et
Et
1.00
1.00
1.02
0.97
3.14
6.02
4.27
6.22
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

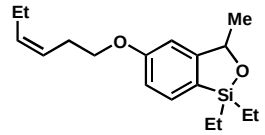

TBSO
Me
O
Si
Et
Et
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

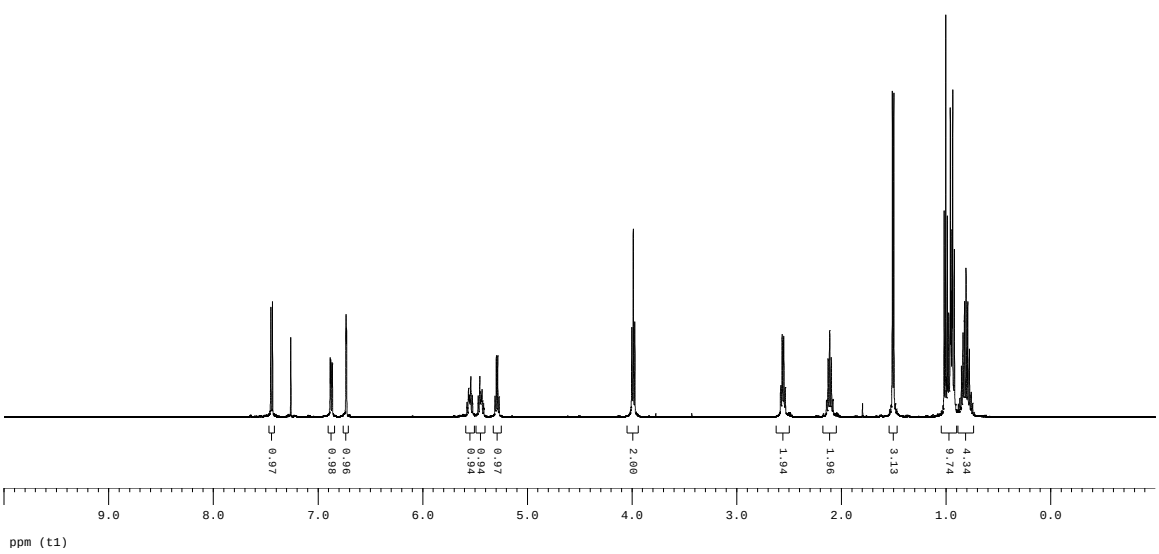

PivO
Me
O
Si
Et
Et
1.00
1.00
1.01
0.99
3.18
9.42
6.39
4.31
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

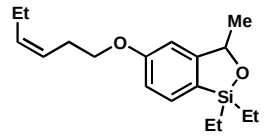

PivO
Me
O
Si
Et
Et
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

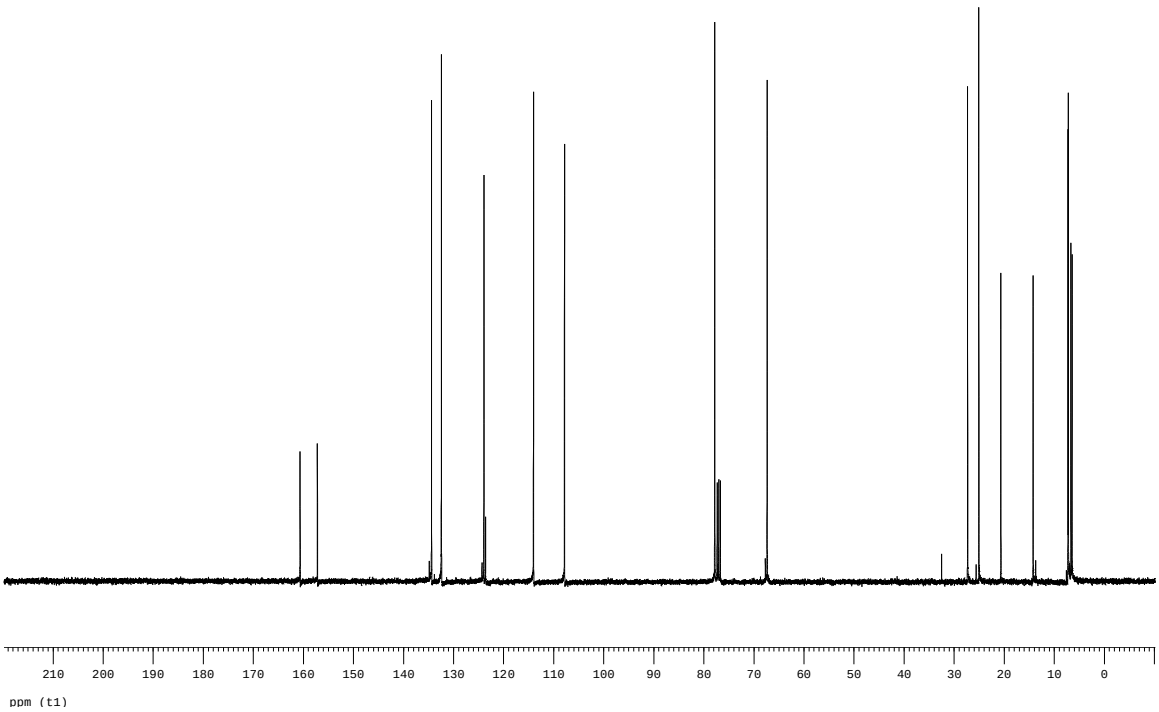

Me
Me2N
O
Si
Et
Et
0.96
0.96
0.94
0.95
6.19
3.00
6.26
4.14
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

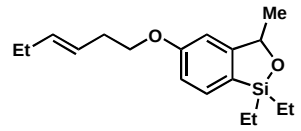

Me
Me2N
O
Si
Et
Et
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

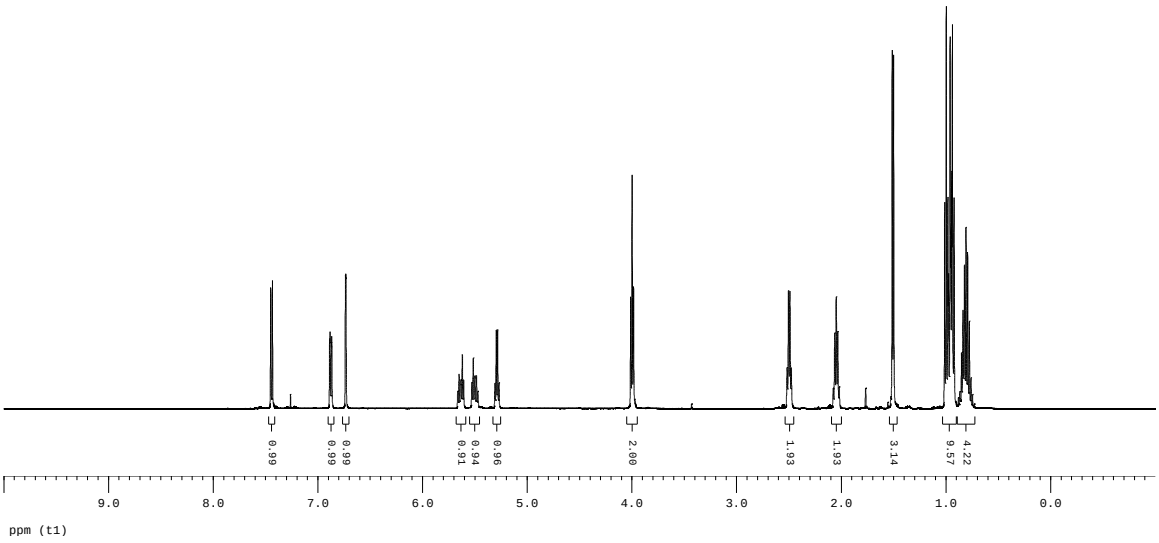

Et
Me
O
O
Si
Et
Et

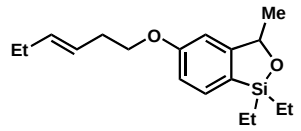

0.97
0.98
0.96
0.94
0.94
0.97
2.00
1.94
1.96
3.13
9.74
4.34
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

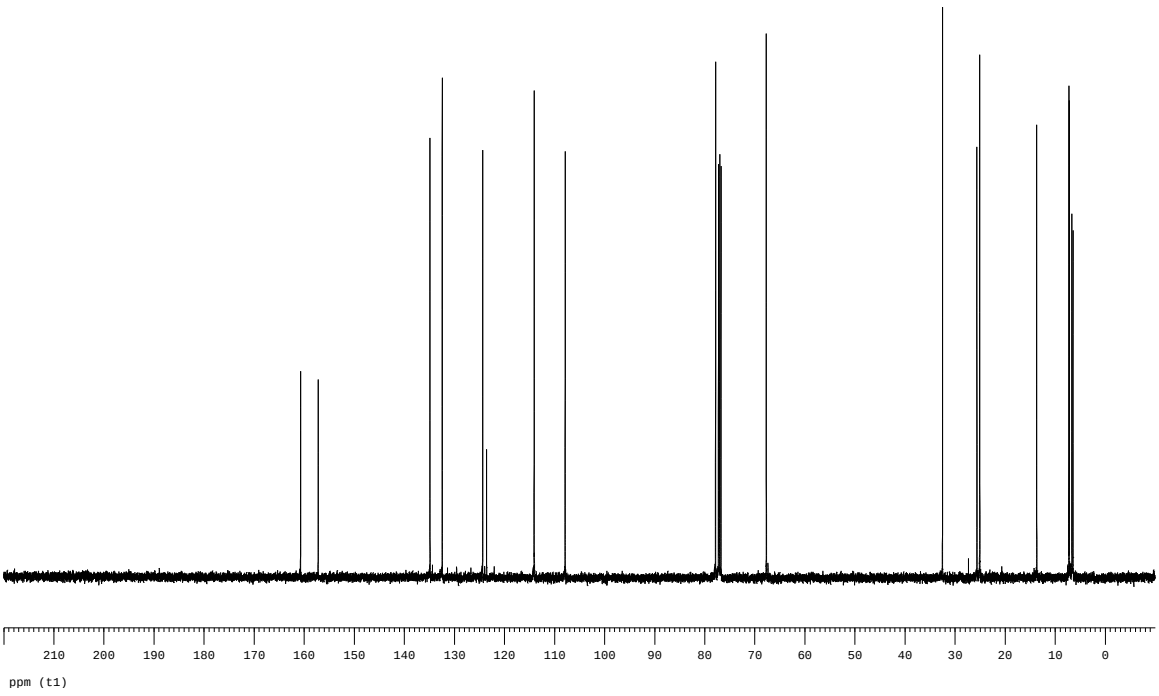

Et
Me
O
O
Si
Et
Et

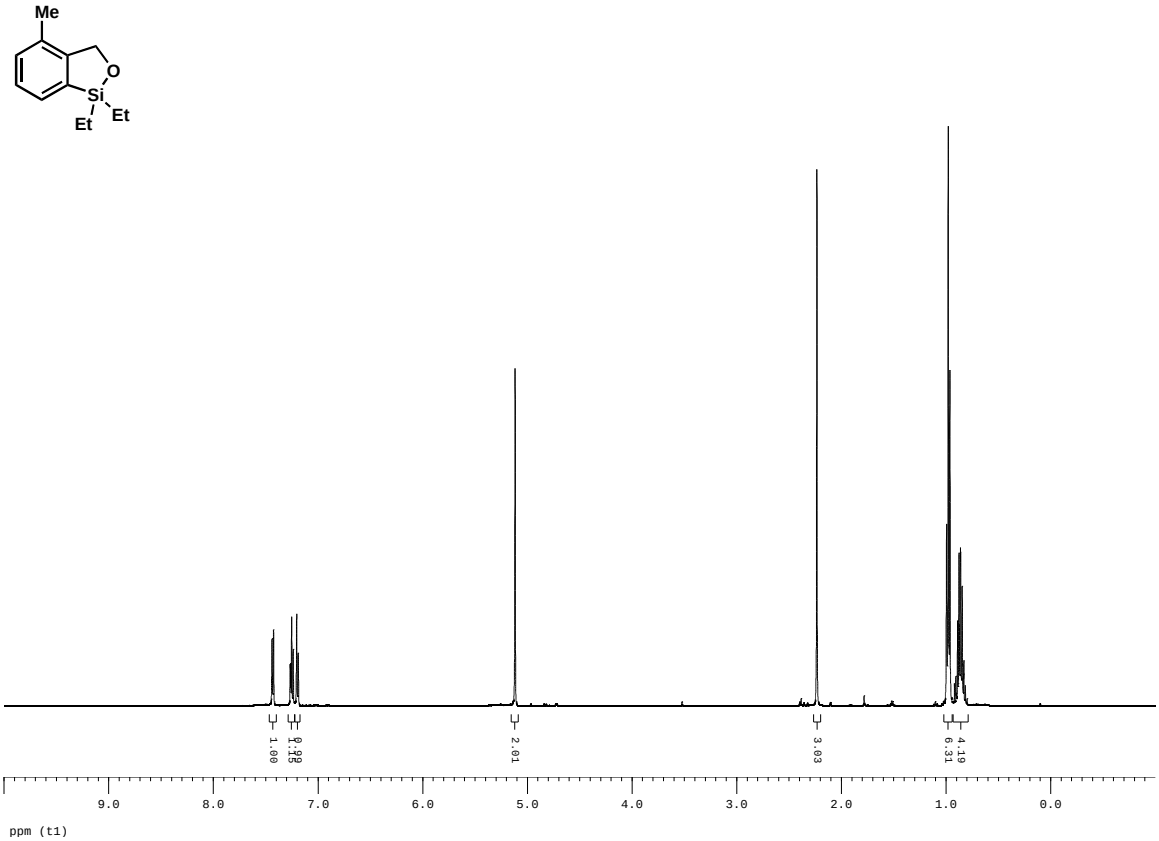

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

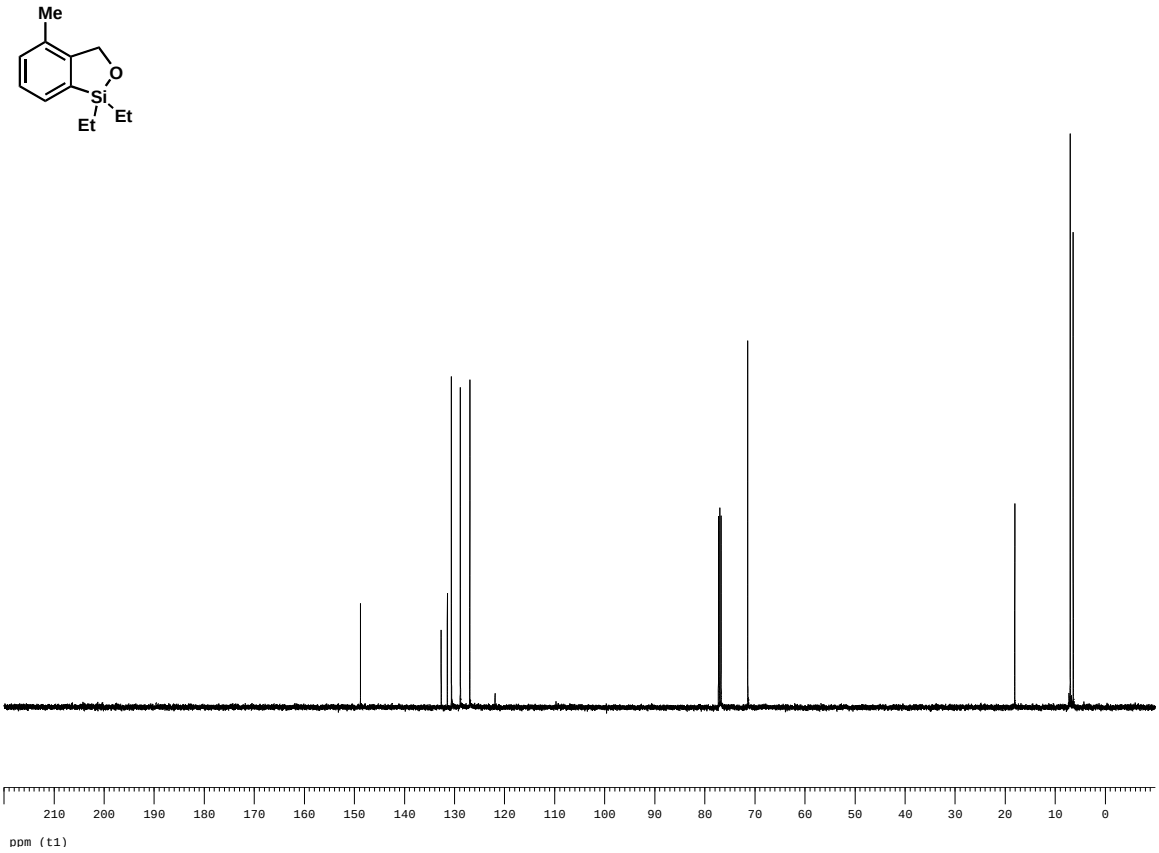

Me
Et
O
O
Si
Et
Et

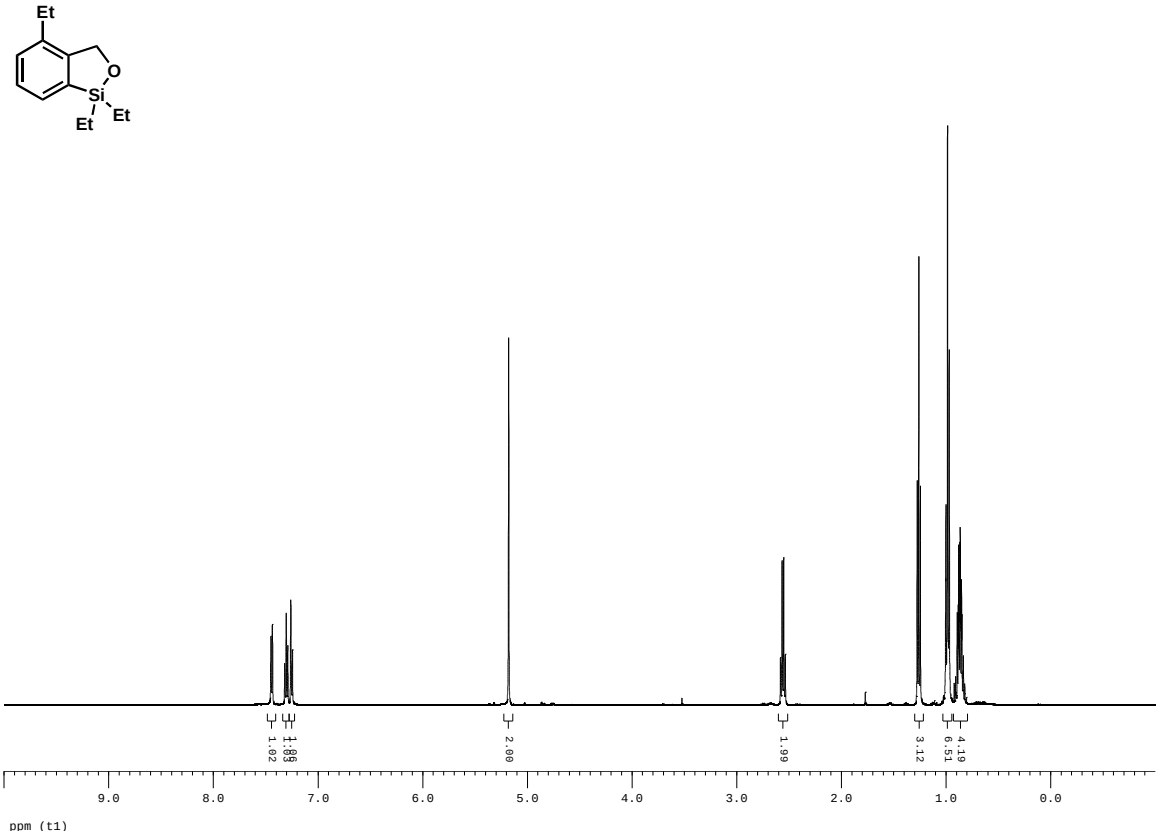

0.99
0.99
0.99
0.91
0.94
0.96
2.00
1.93
1.93
3.14
9.57
4.22
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

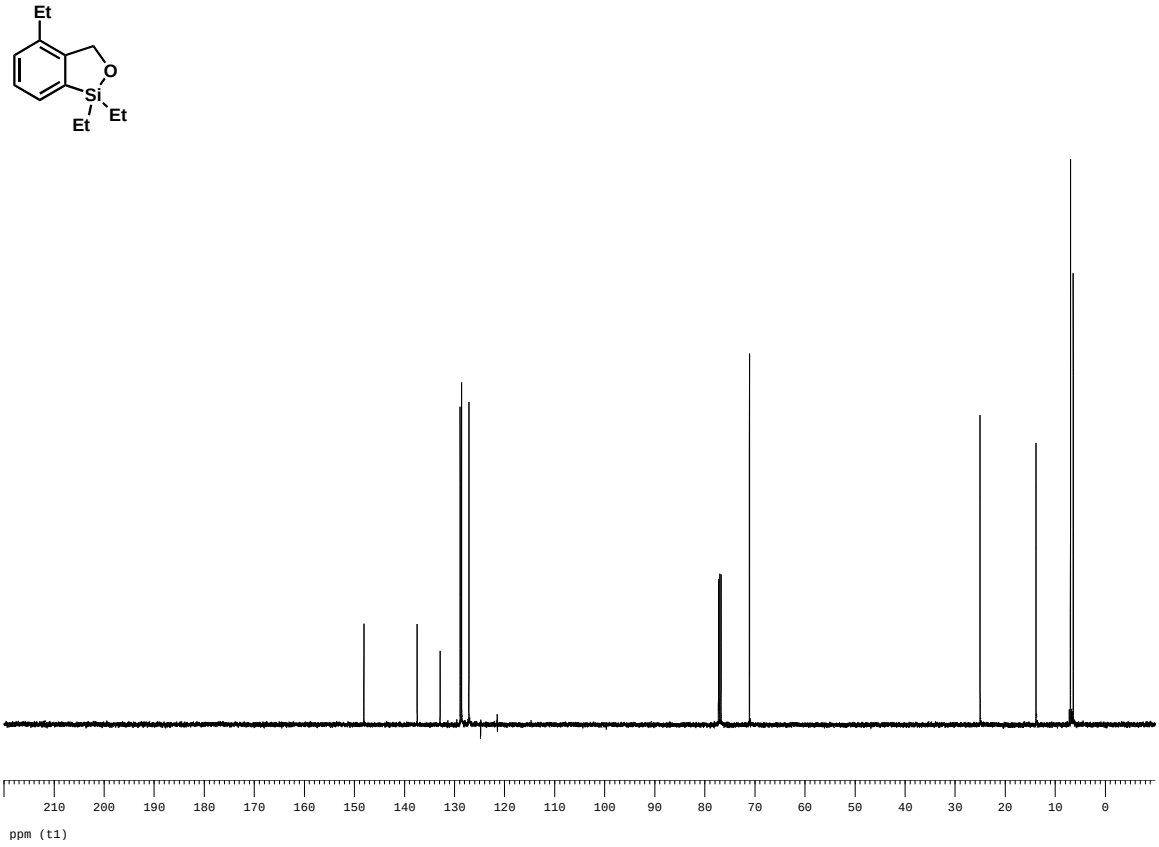

Me
Et
O
O
Si
Et
Et

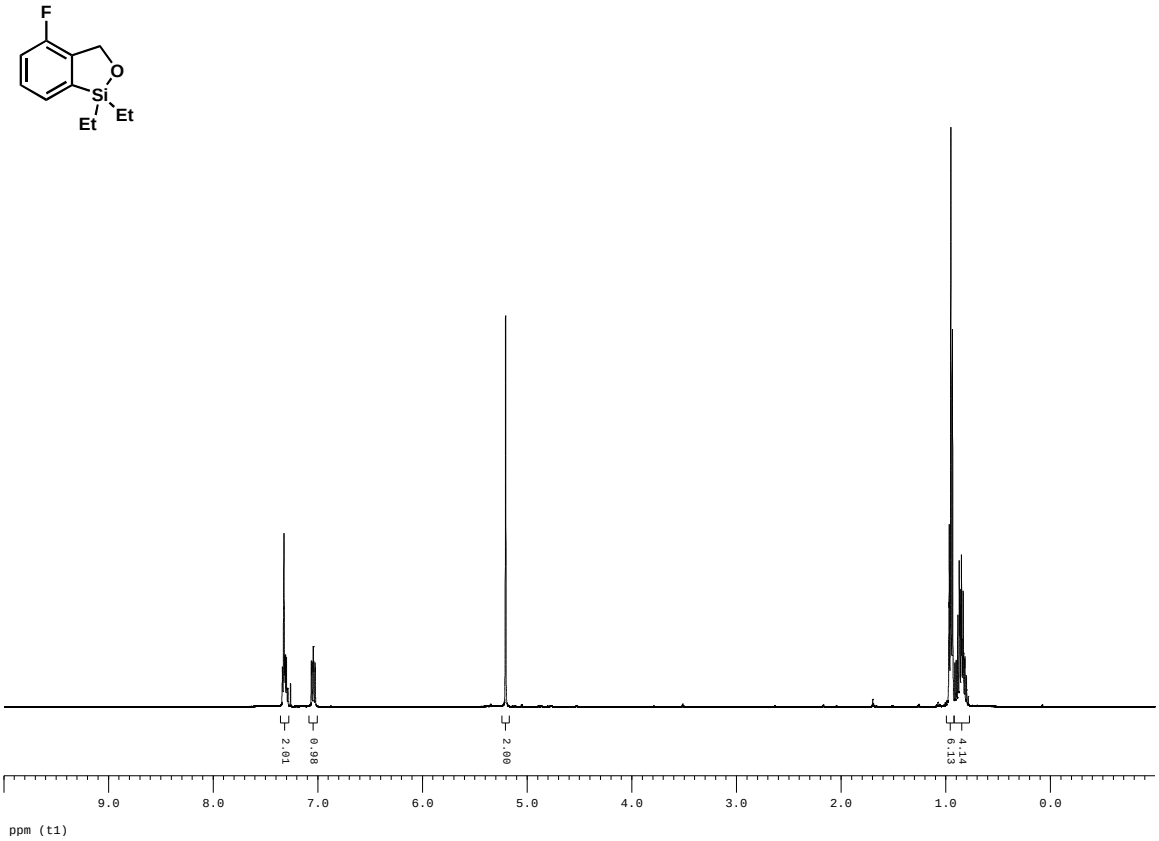

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

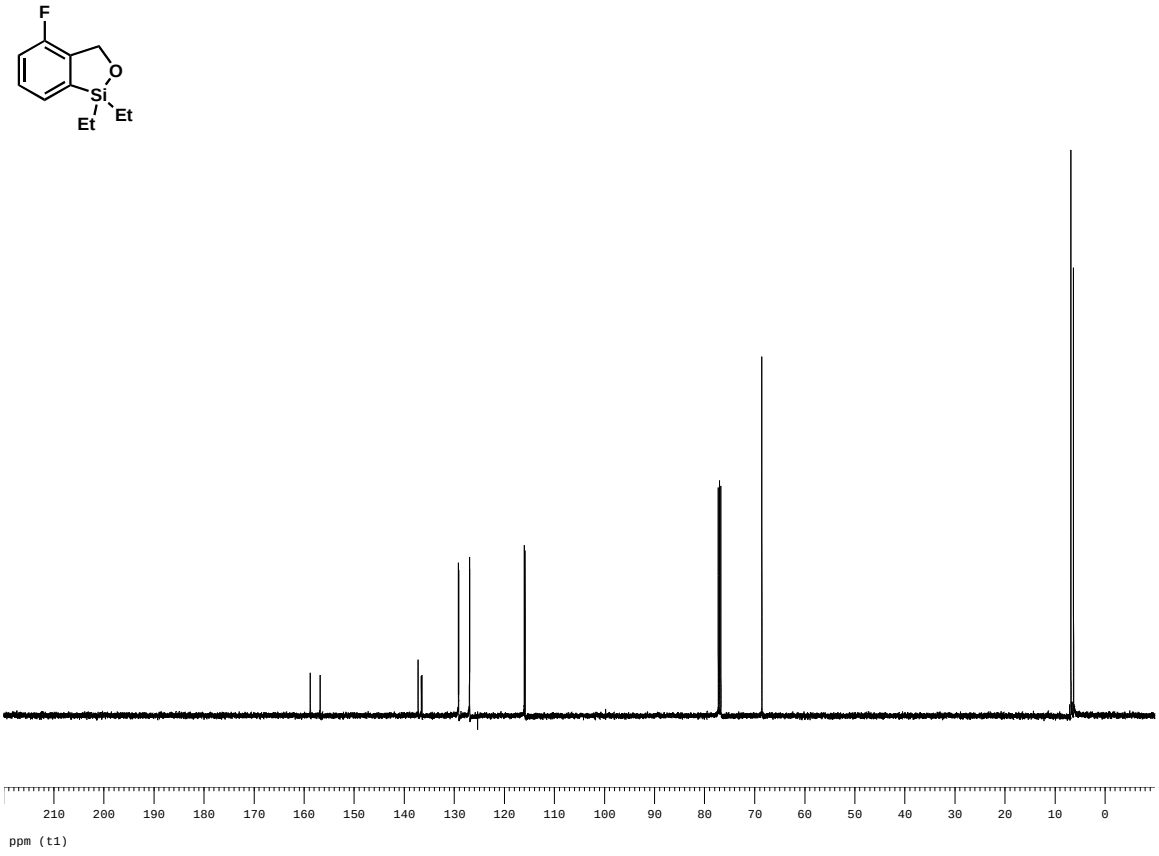

Me
O
Si
Et
Et
1.00
1.15
0.99
2.01
3.03
6.31
4.19
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

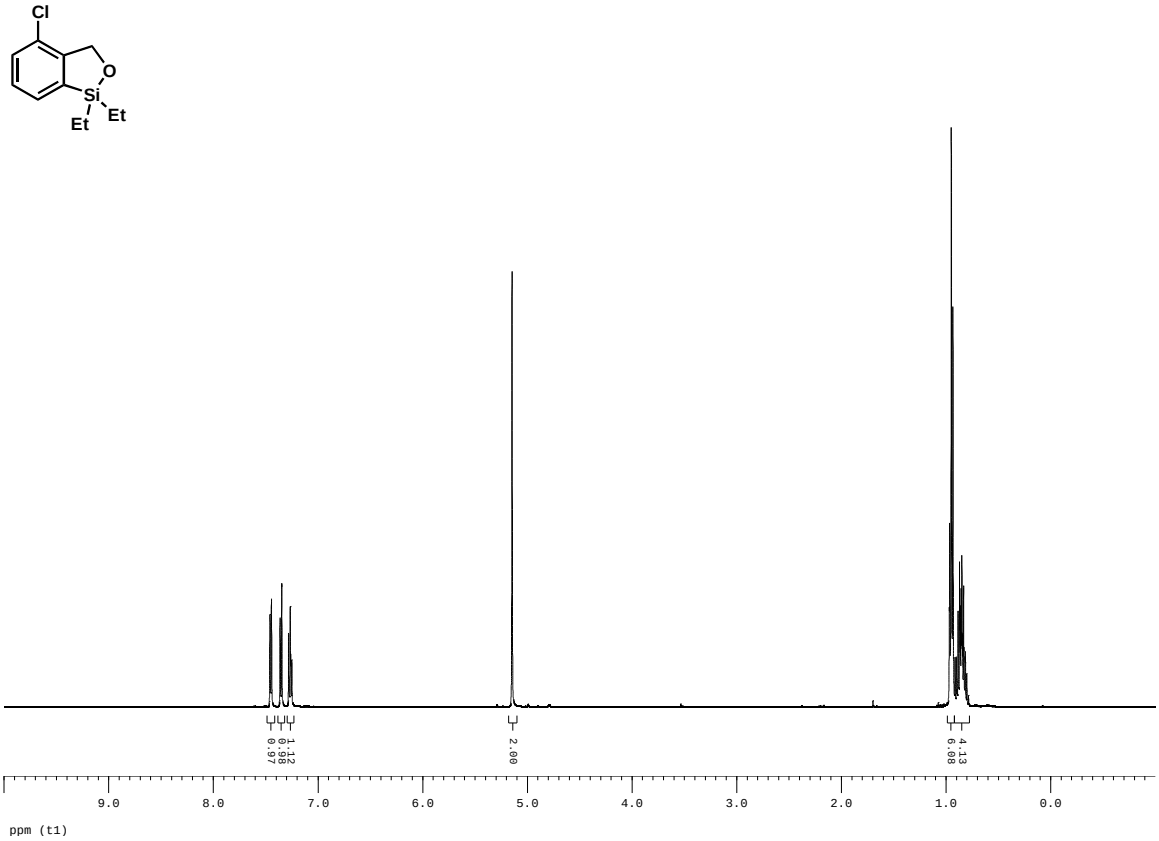

Me
O
Si
Et
Et
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

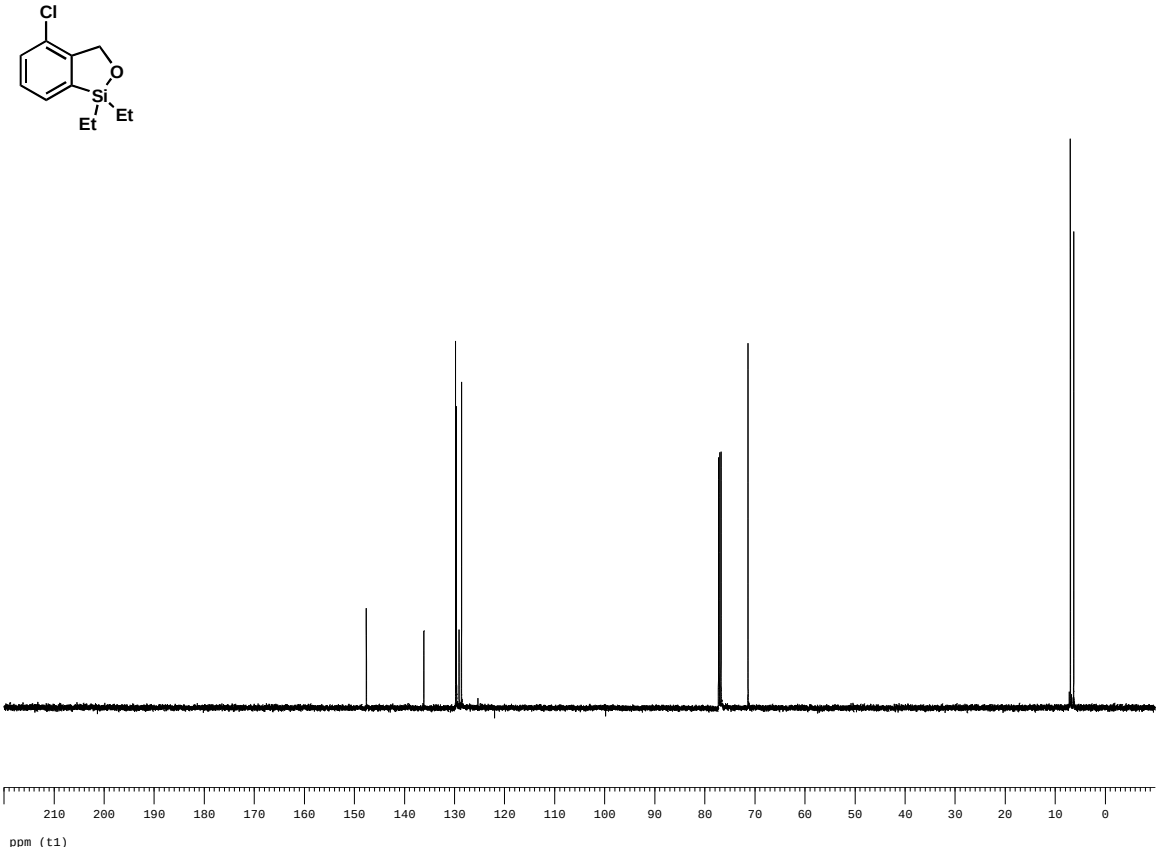

Et
O
Si
Et
Et
1.02
1.00
1.05
2.00
1.99
3.12
6.51
4.19
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

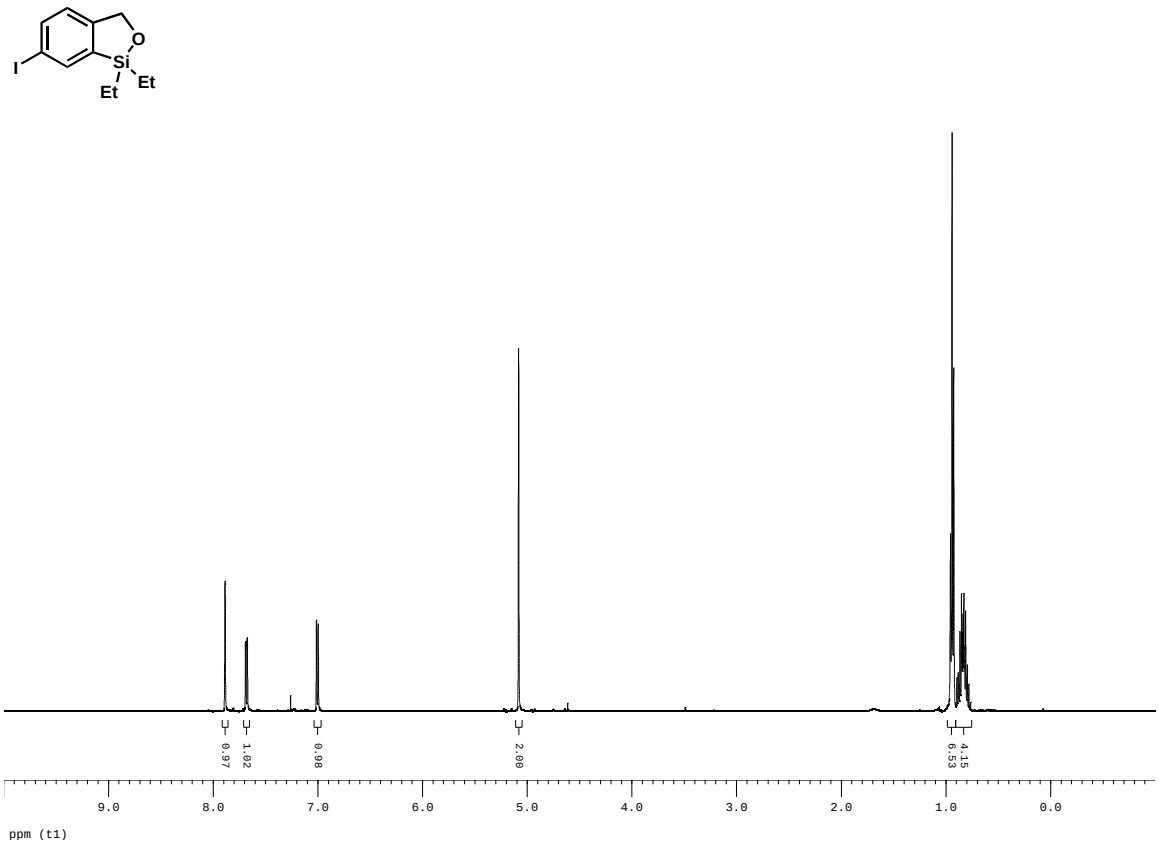

Et
O
Si
Et
Et
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

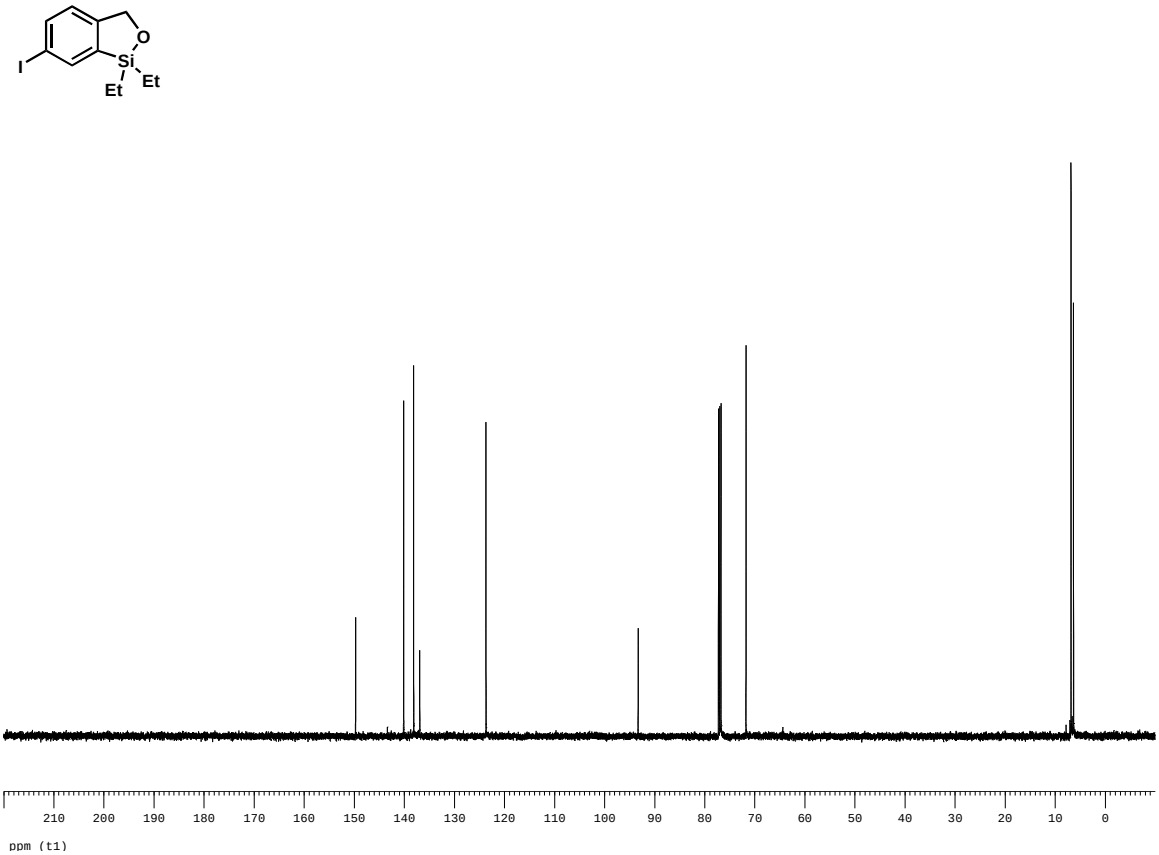

F
O
Si
Et
Et
2.01
0.98
2.00
6.13
4.14
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

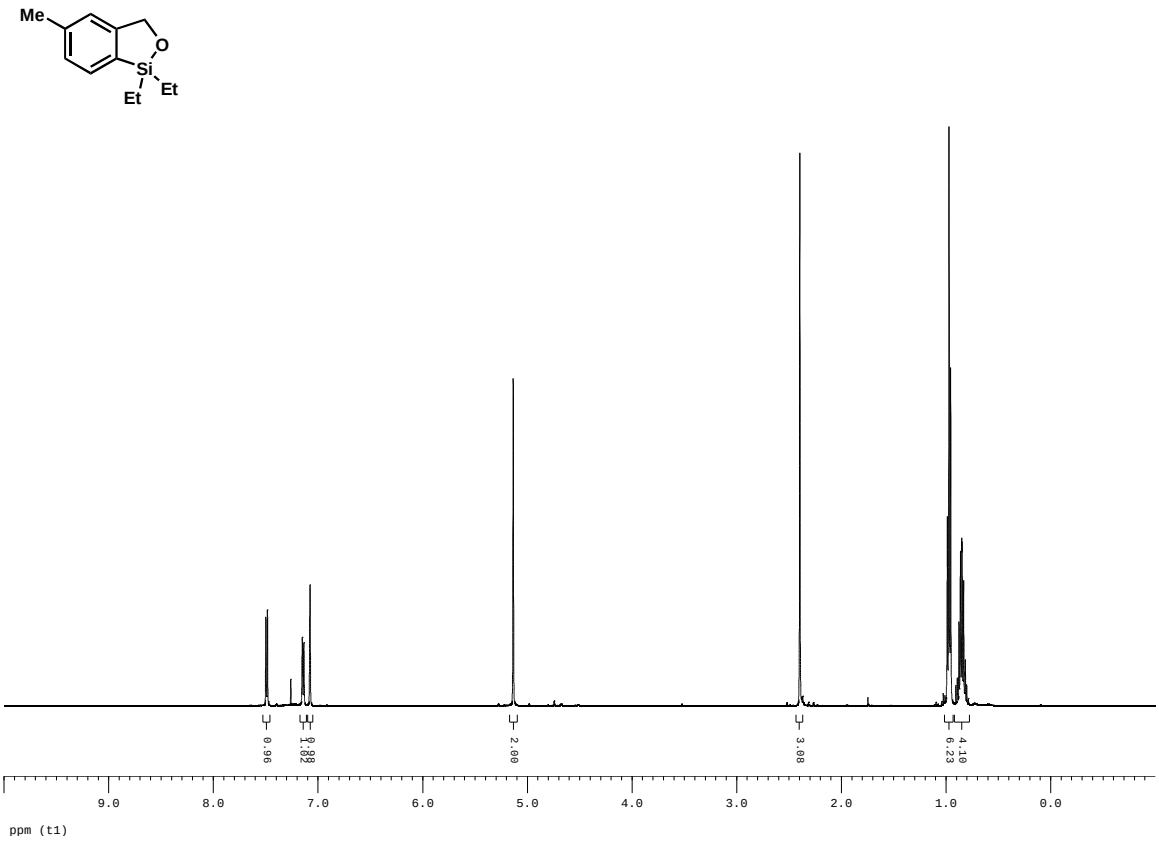

F
O
Si
Et
Et
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

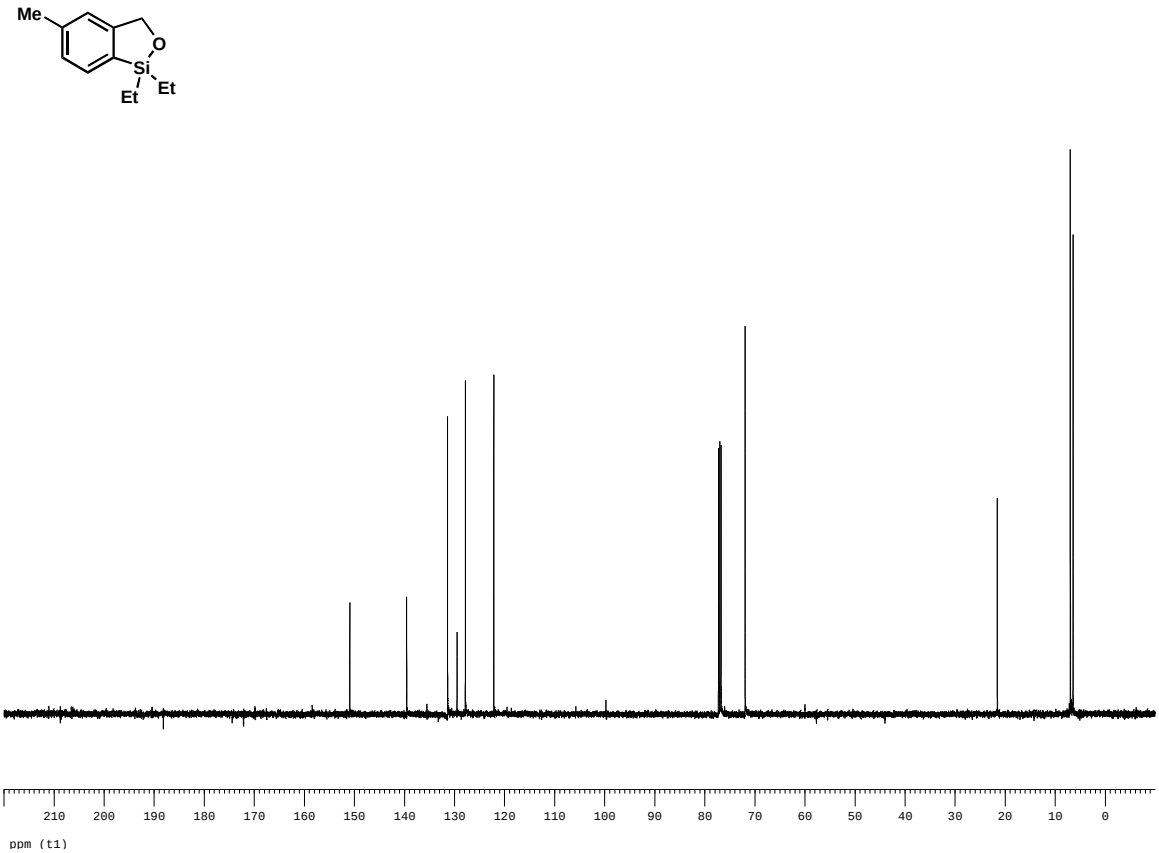

Cl
O
Si
Et
Et
0.97
1.12
1.08
2.00
4.13
6.08
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

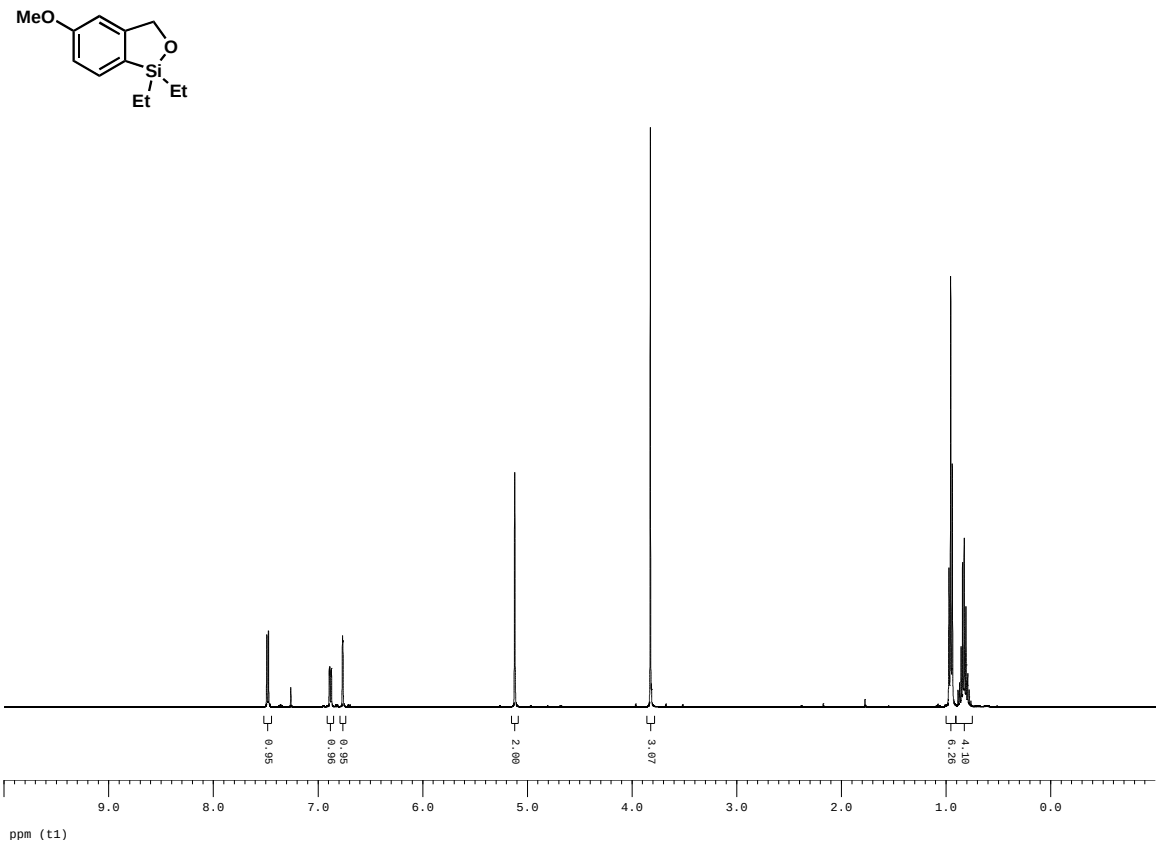

Cl
O
Si
Et
Et
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

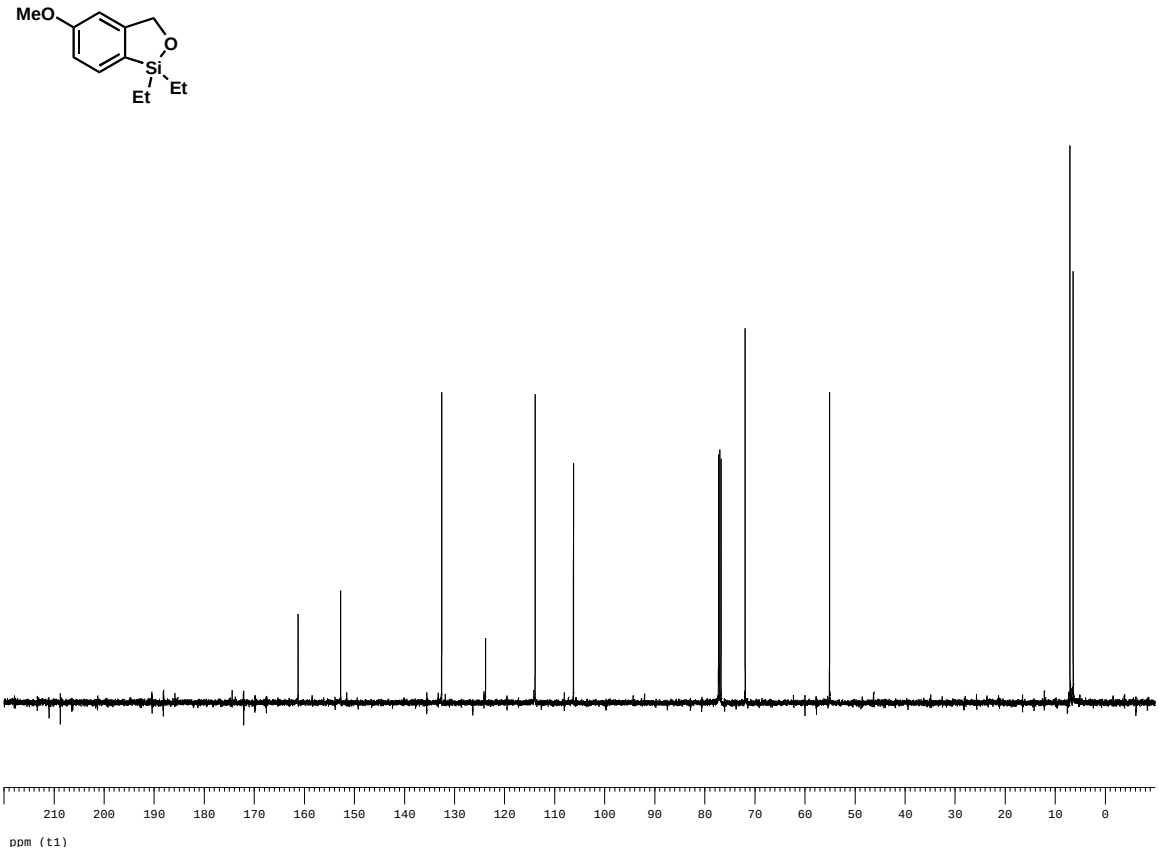

I
O
Si
Et
Et
0.97
1.02
0.98
2.00
6.53
4.15
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

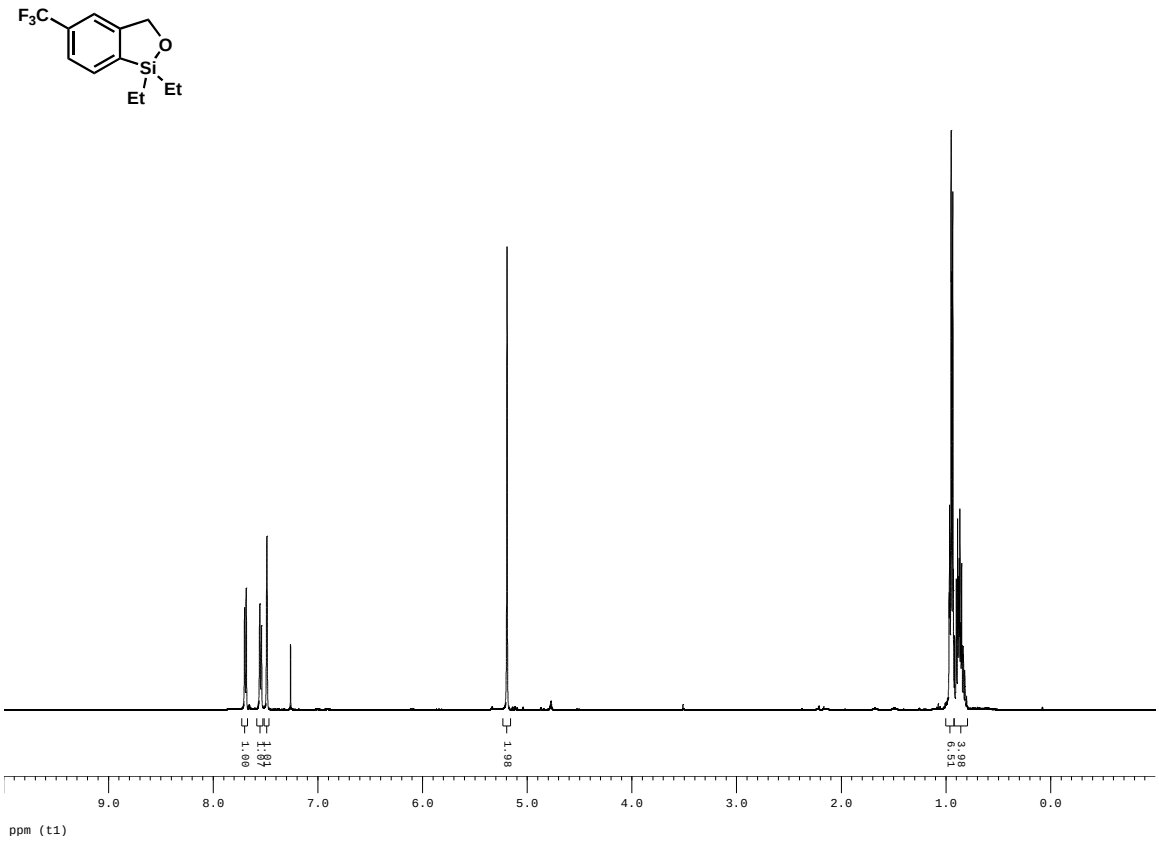

I
O
Si
Et
Et
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

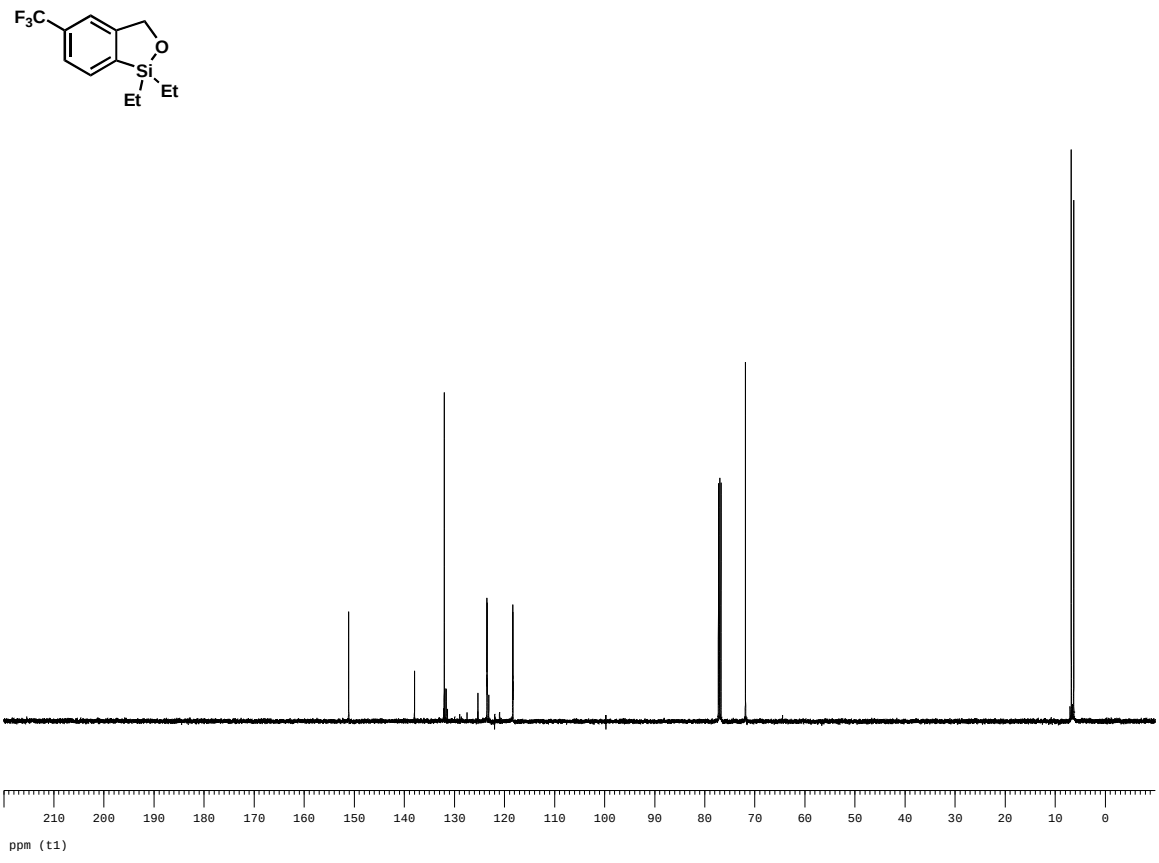

Me
O
Si
Et
Et
0.96
0.88
1.82
2.00
3.08
6.23
4.10
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

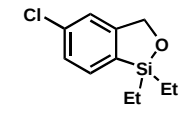

Me
O
Si
Et
Et
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

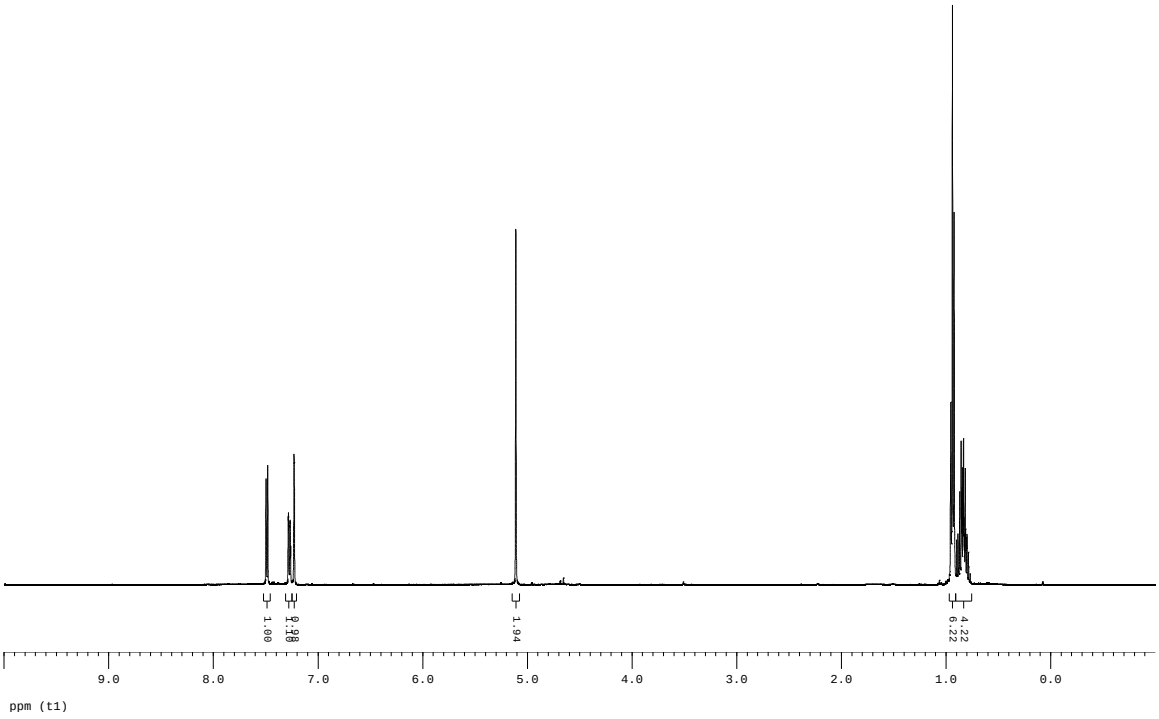

MeO
O
Si
Et
Et
0.95
0.96
0.95
2.00
3.07
6.26
4.19
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

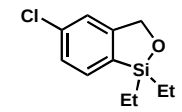

MeO
O
Si
Et
Et
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

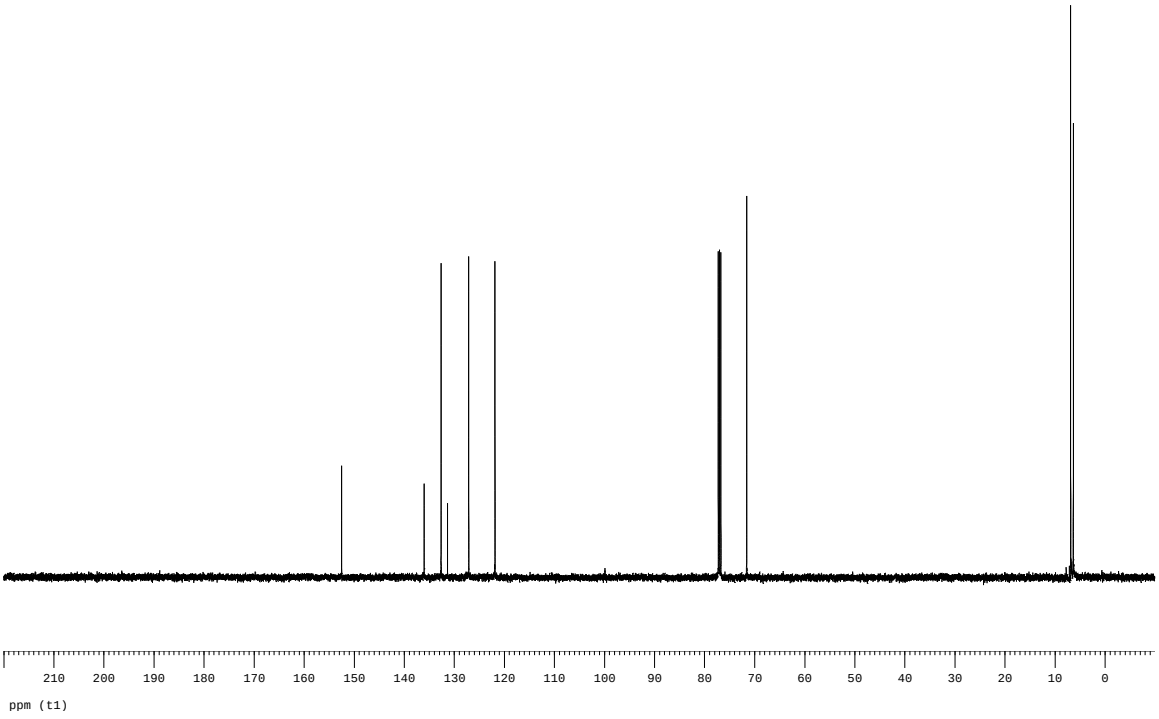

F3C
O
Si
Et
Et
1.00
1.07
1.07
1.98
6.51
3.98
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

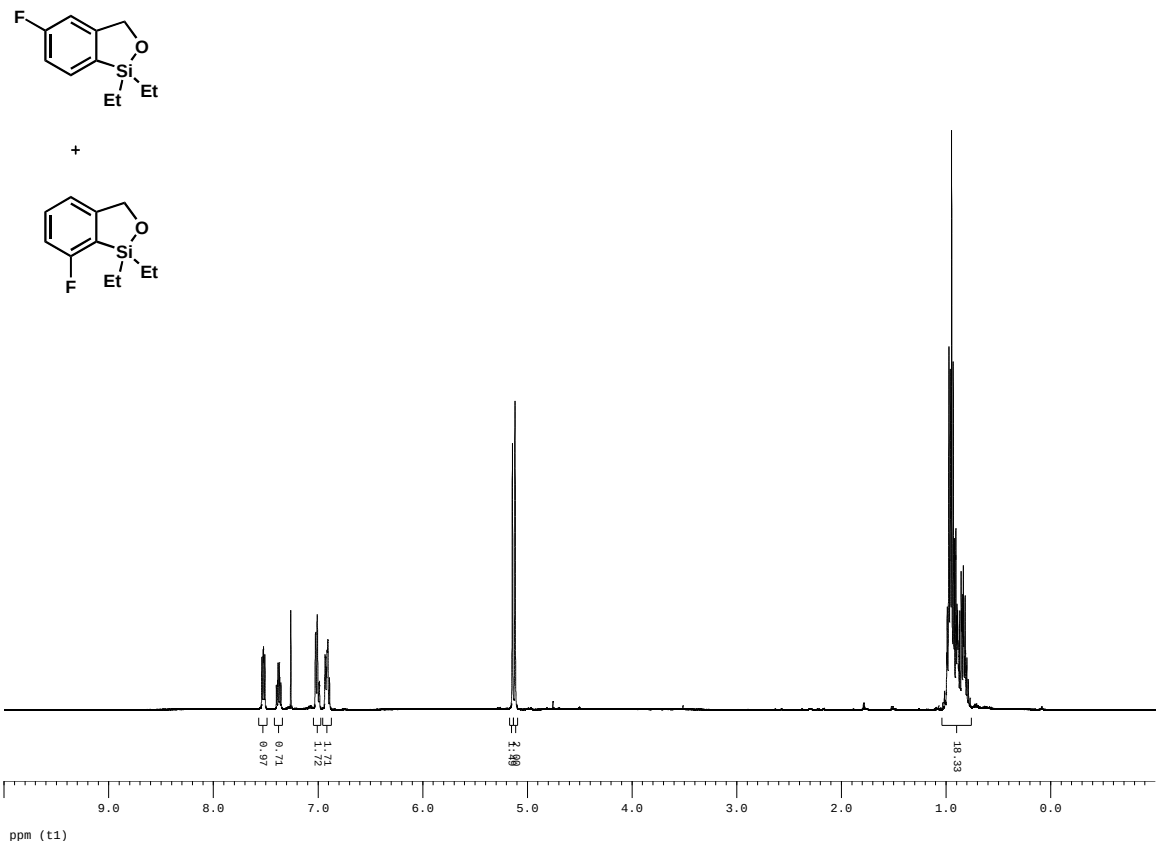

F3C
O
Si
Et
Et
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

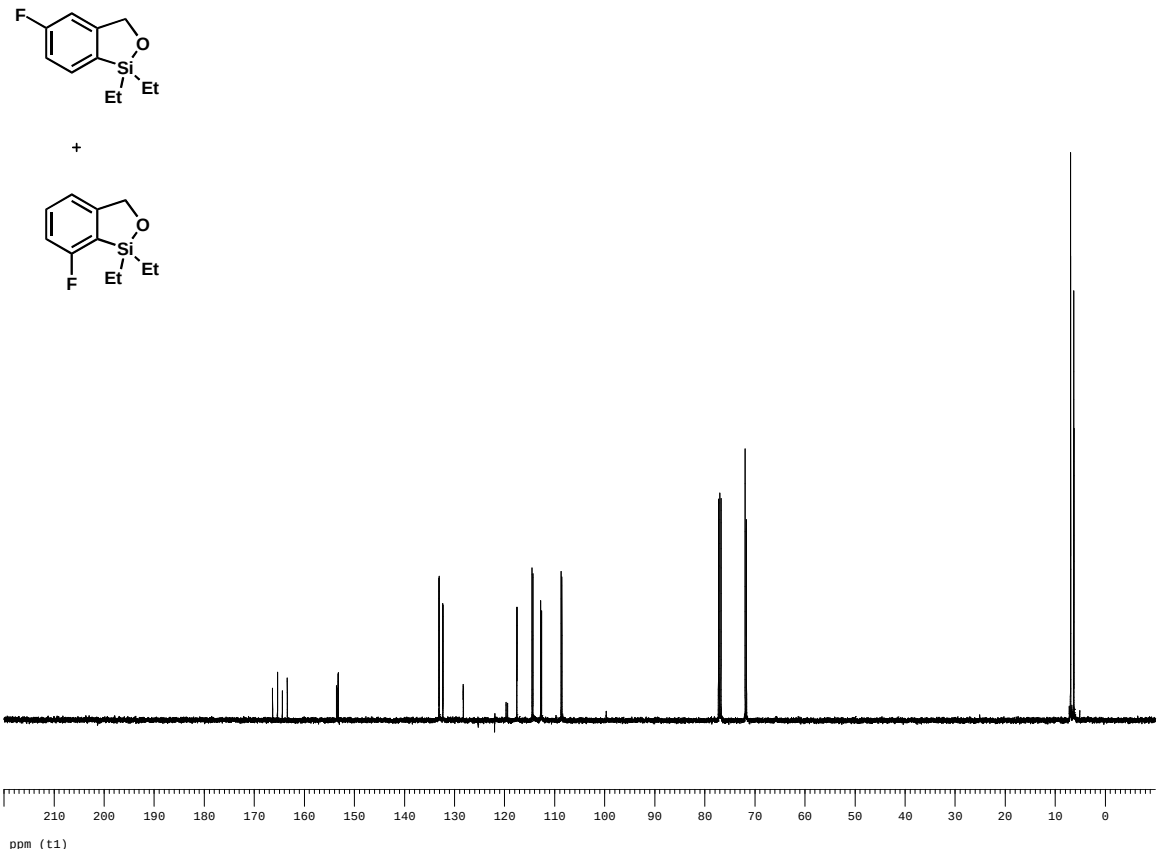

Cl
O
Si
Et
Et

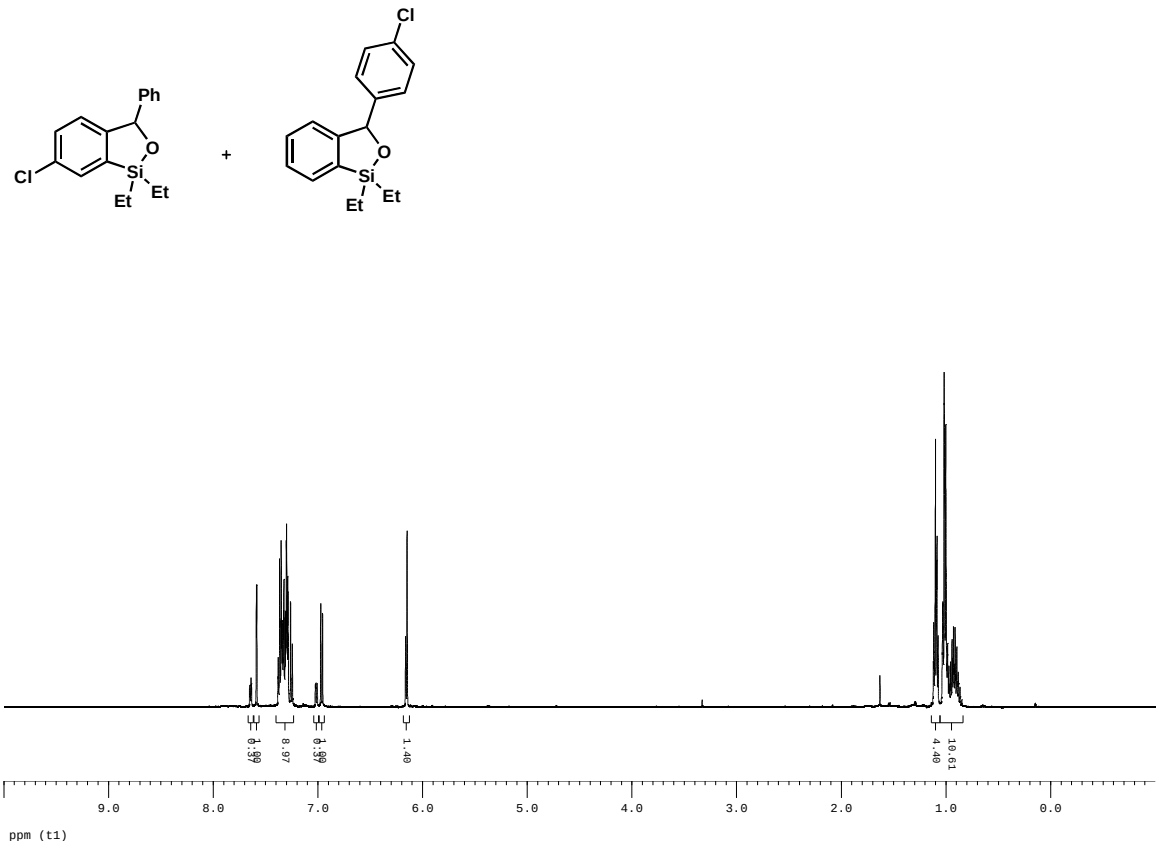

1.00
0.98
1.18
1.94
6.22
4.22
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

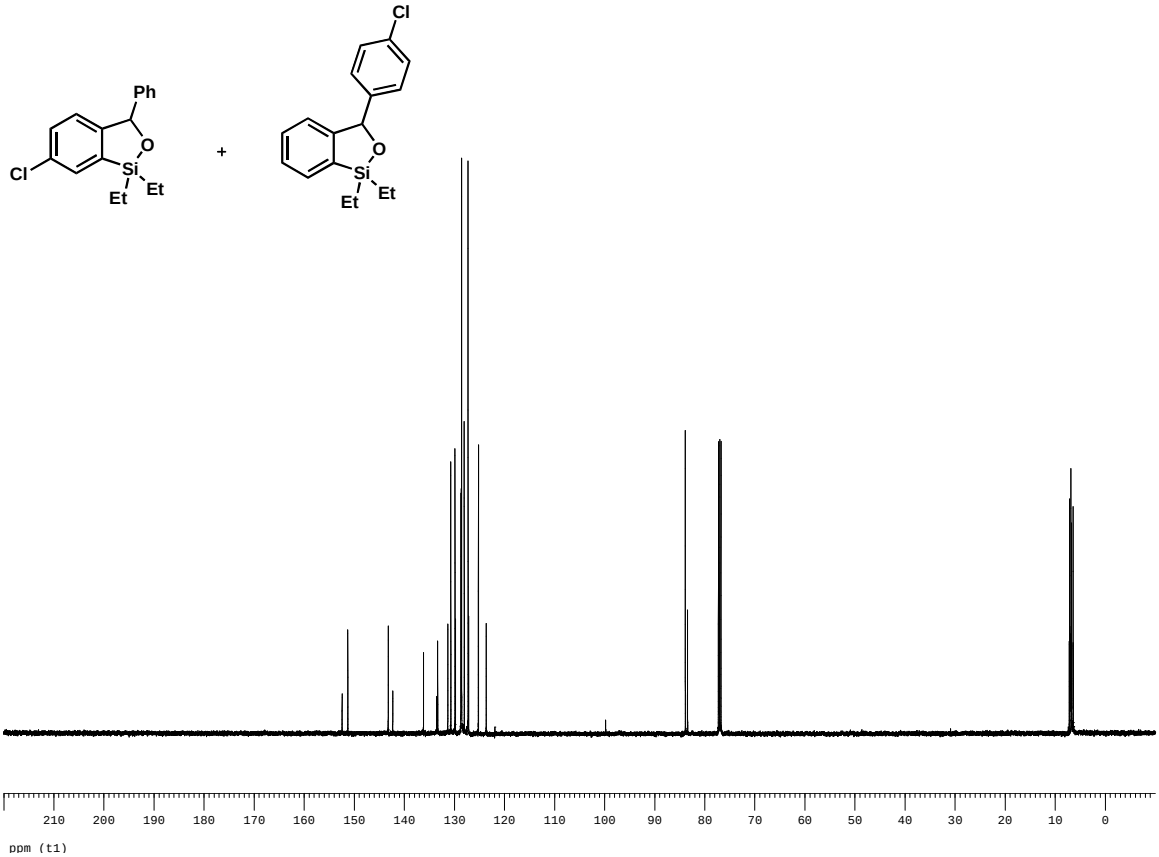

Cl
O
Si
Et
Et

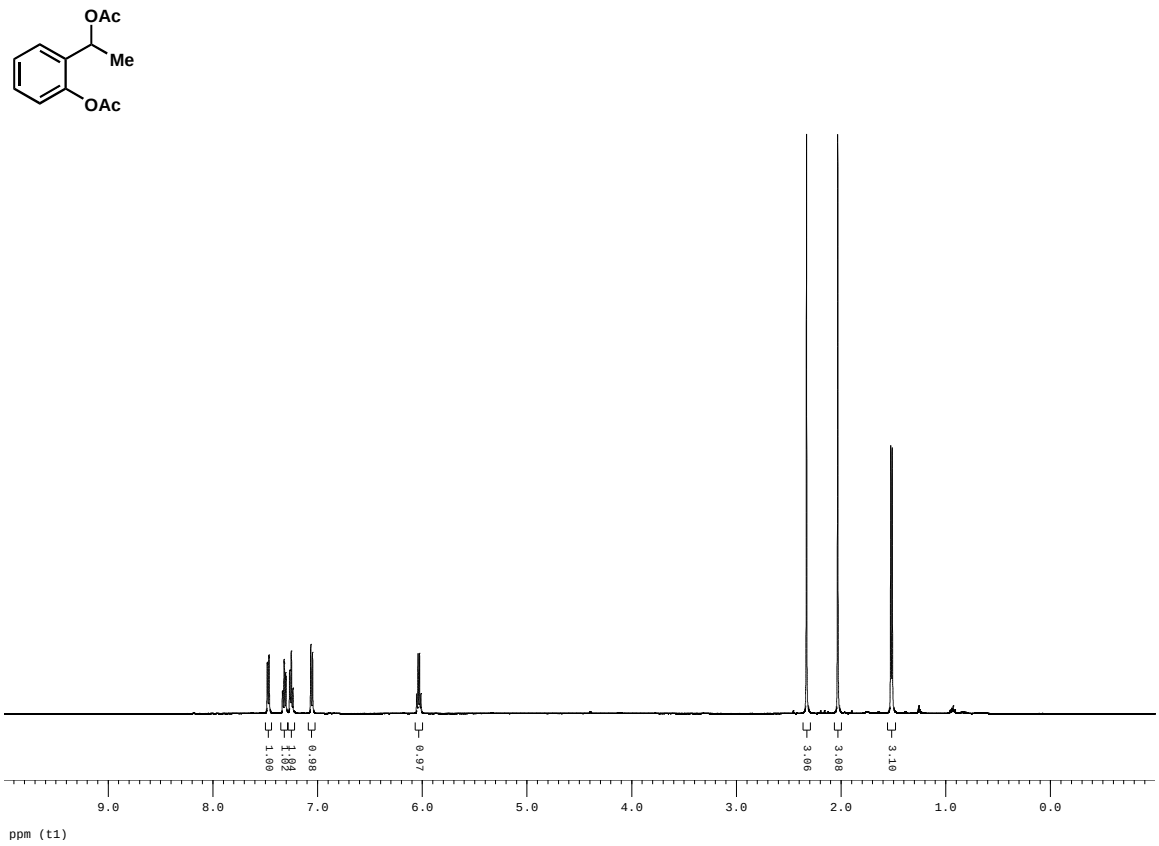

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

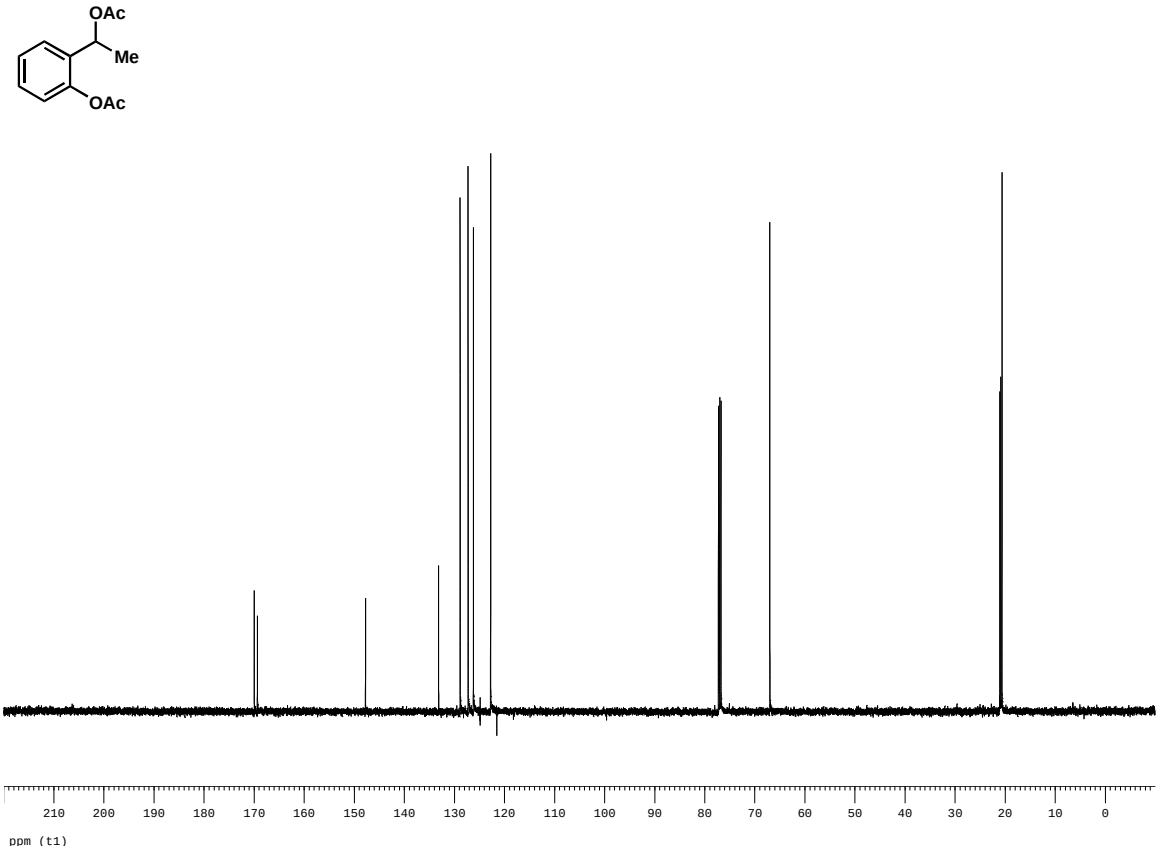

F
O
Si
Et
Et
+
O
Si
Et
Et
F
0.97
0.71
1.72
1.71
18.33
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

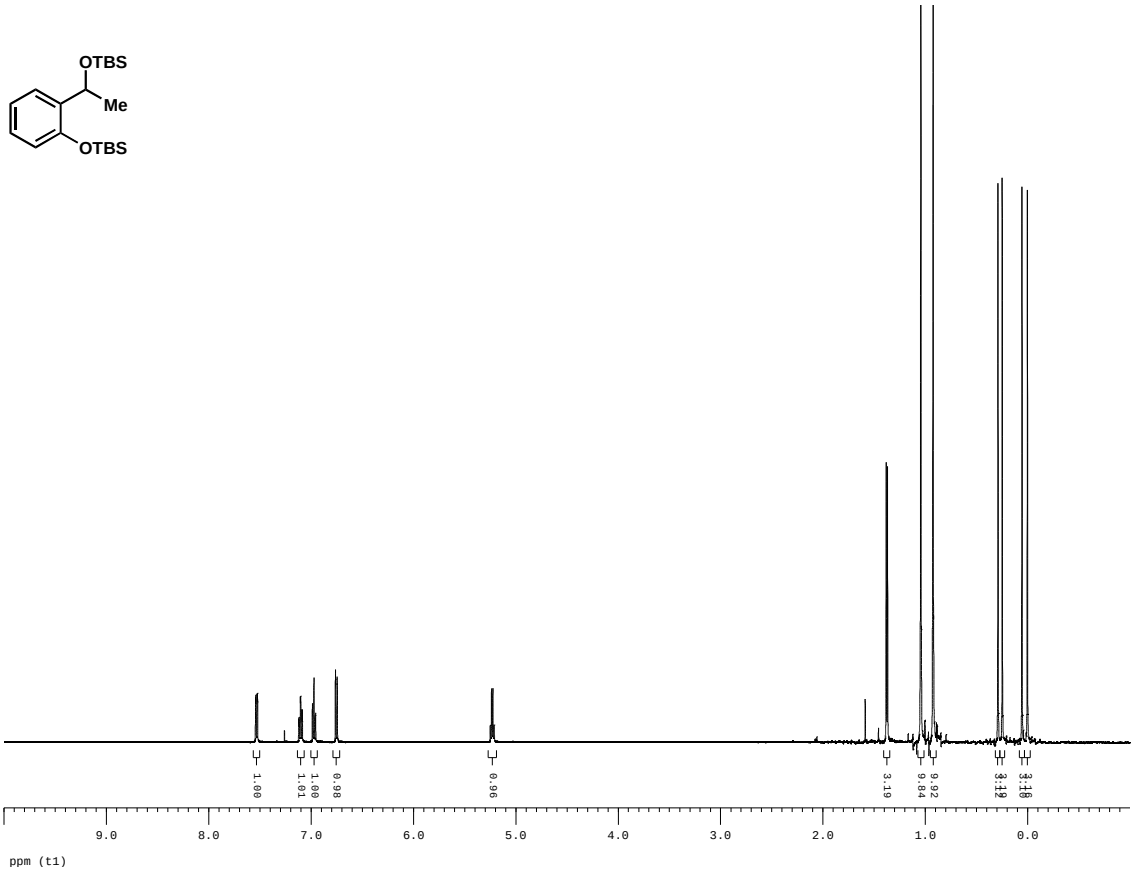

F
O
Si
Et
Et
+
O
Si
Et
Et
F
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

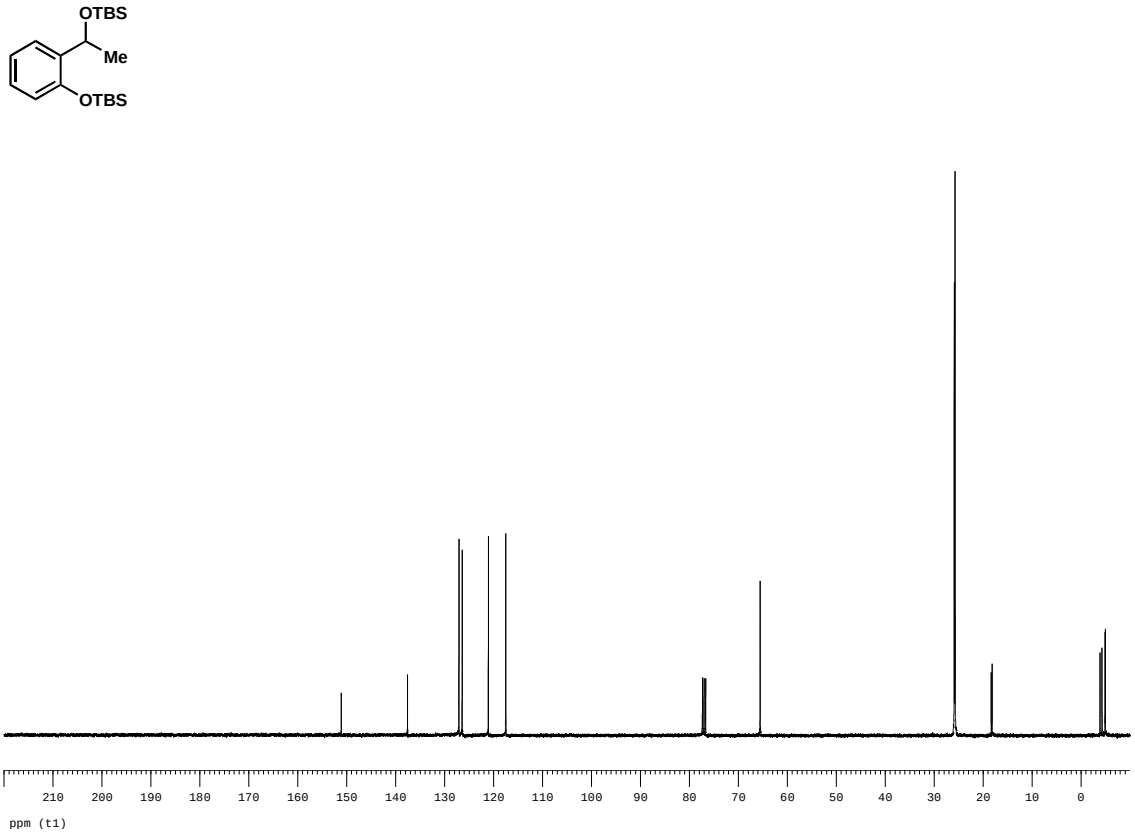

Ph
O
Si
Et
Et
Cl
+
Cl
O
Si
Et
Et
0.97
8.97
1.40
4.40
10.61
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

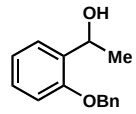

Ph
O
Si
Et
Et
Cl
+
Cl
O
Si
Et
Et
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

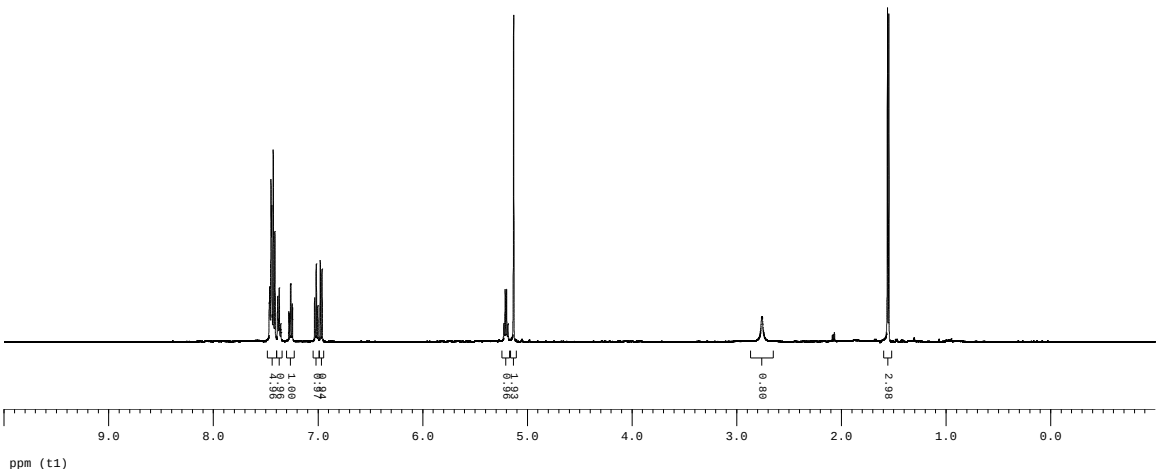

OAc
Me
OAc
1.00
1.04
1.04
0.98
0.97
3.06
3.08
3.10
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

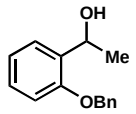

OAc
Me
OAc
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

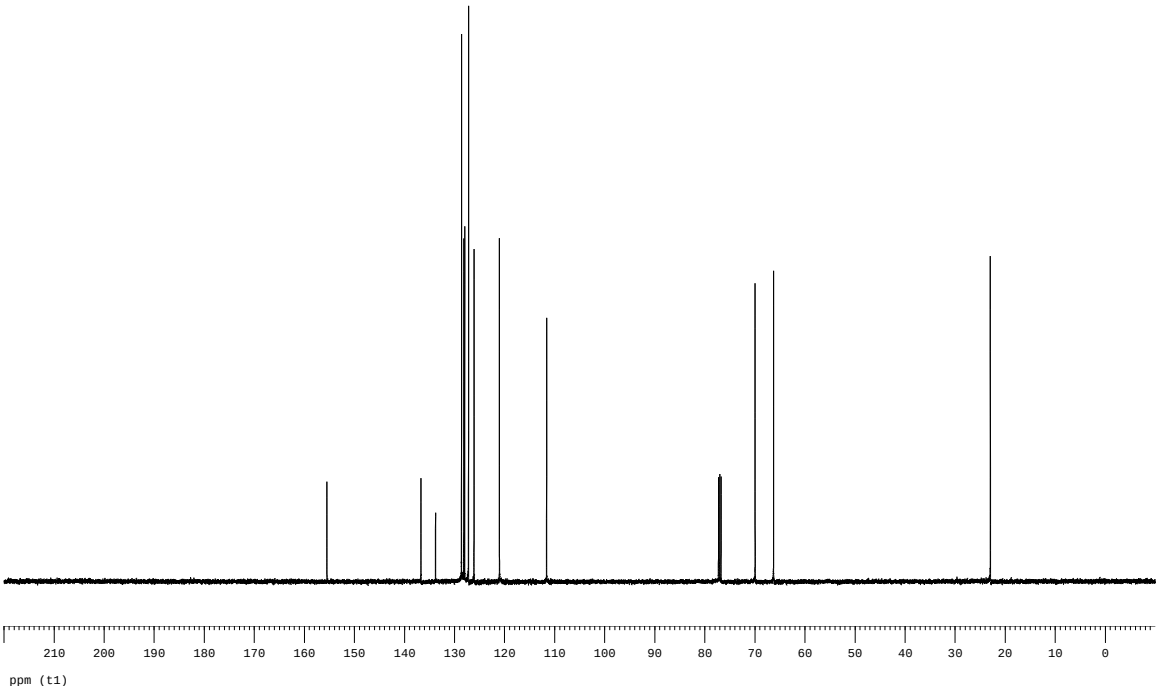

OTBS
Me
OTBS
1.00
1.01
1.00
0.98
0.96
3.19
9.84
9.92
3.12
3.12
3.16
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

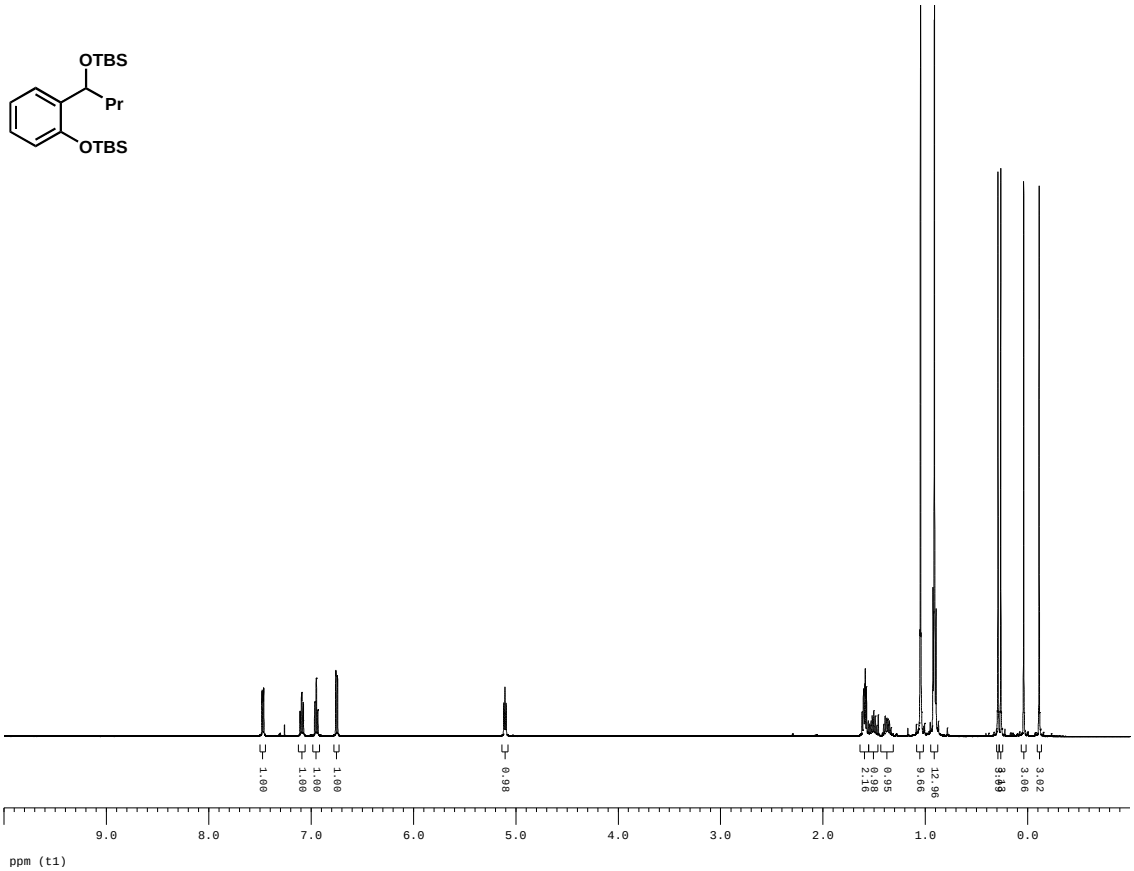

OTBS
Me
OTBS
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

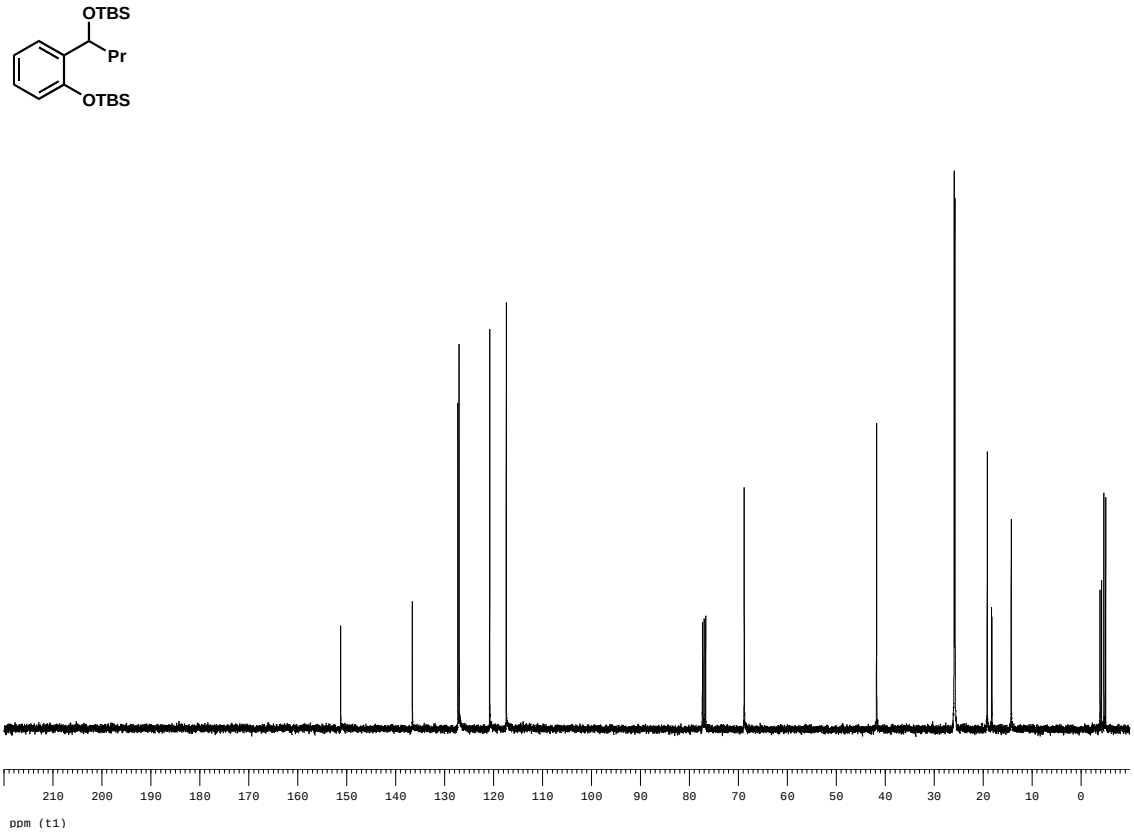

OH
Me
OBn

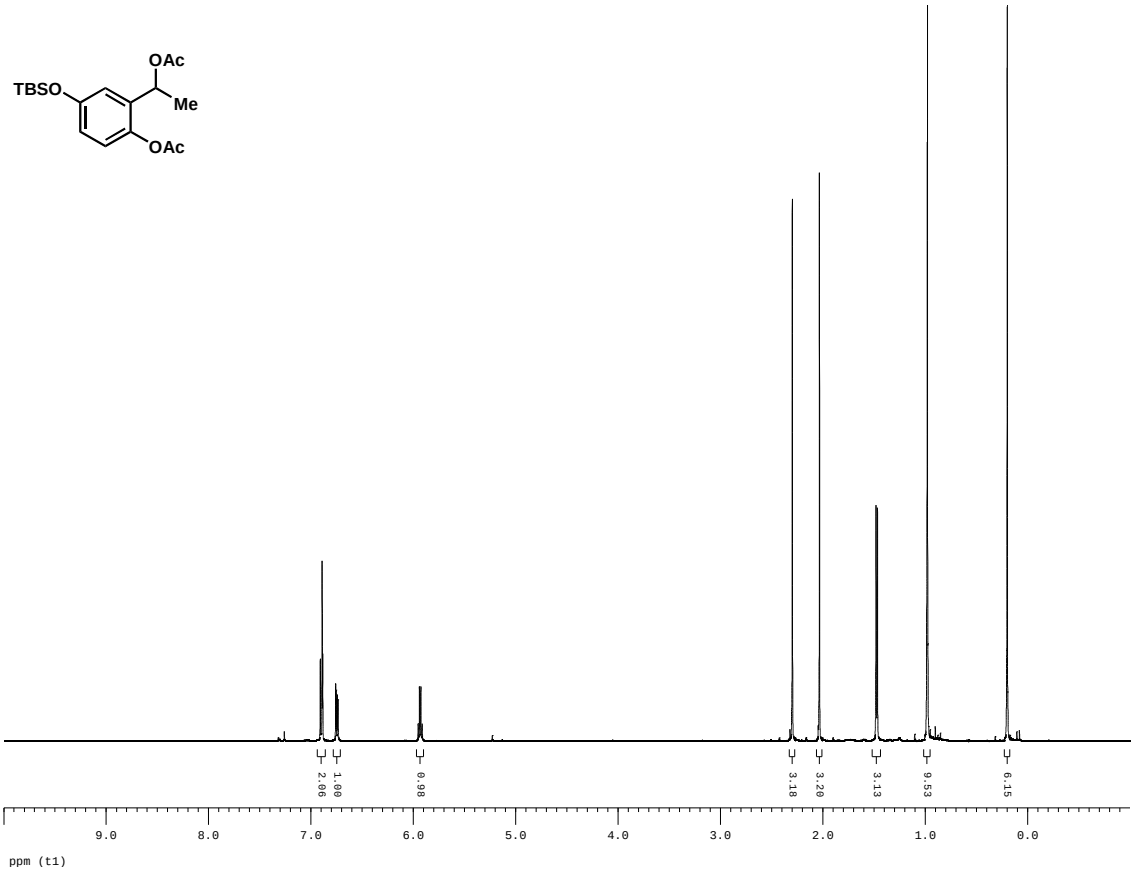

4.09
4.06
1.00
0.97
1.03
0.80
2.98
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

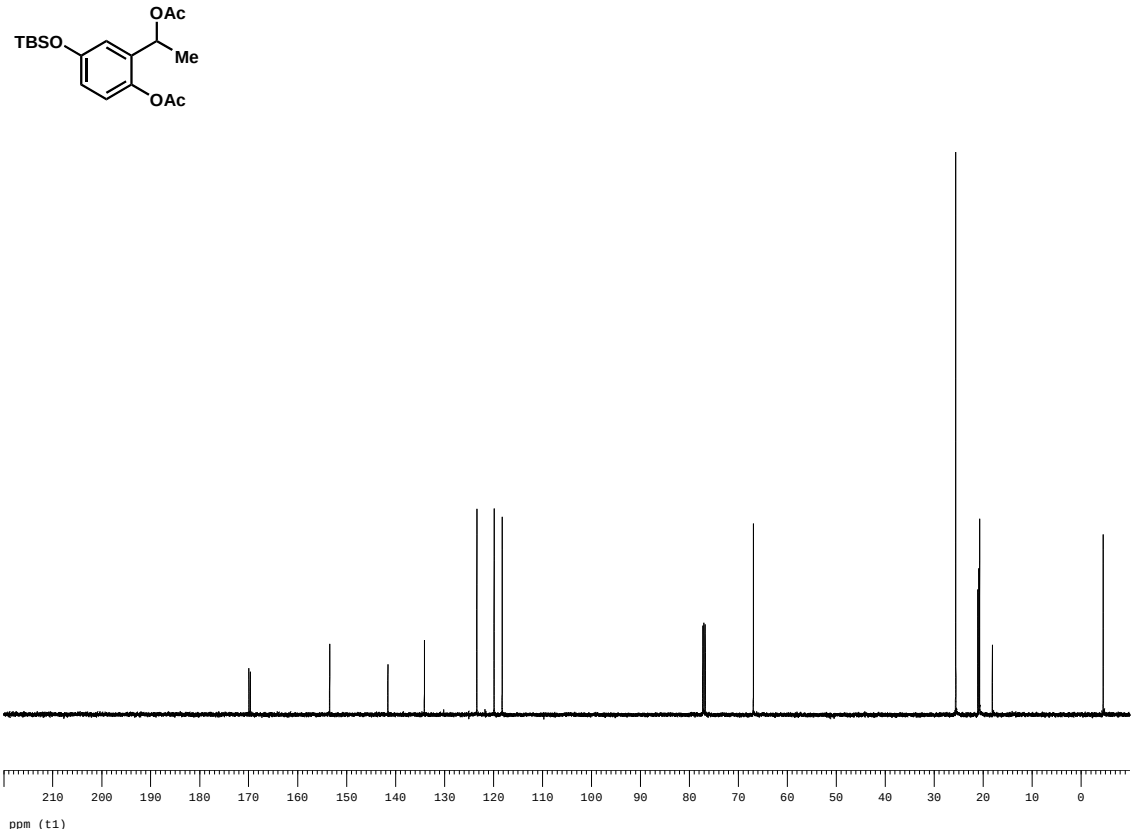

OH
Me
OBn

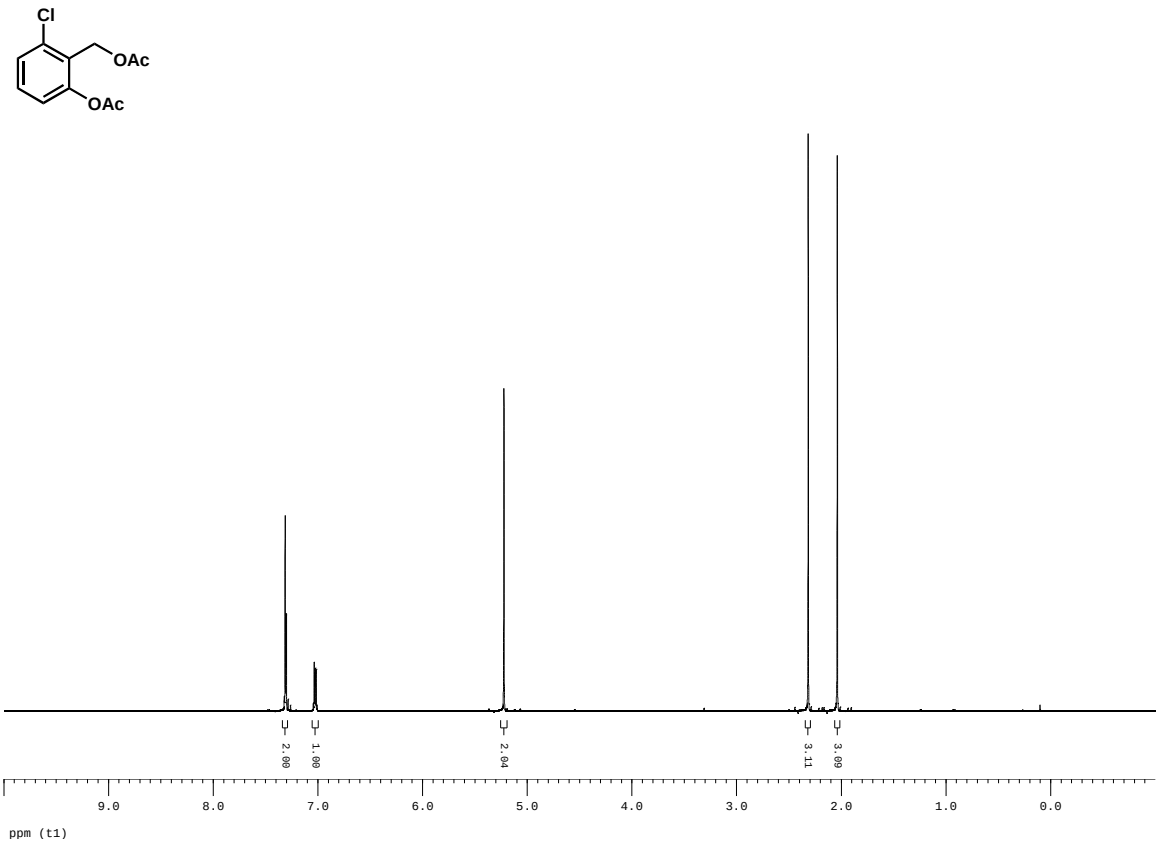

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

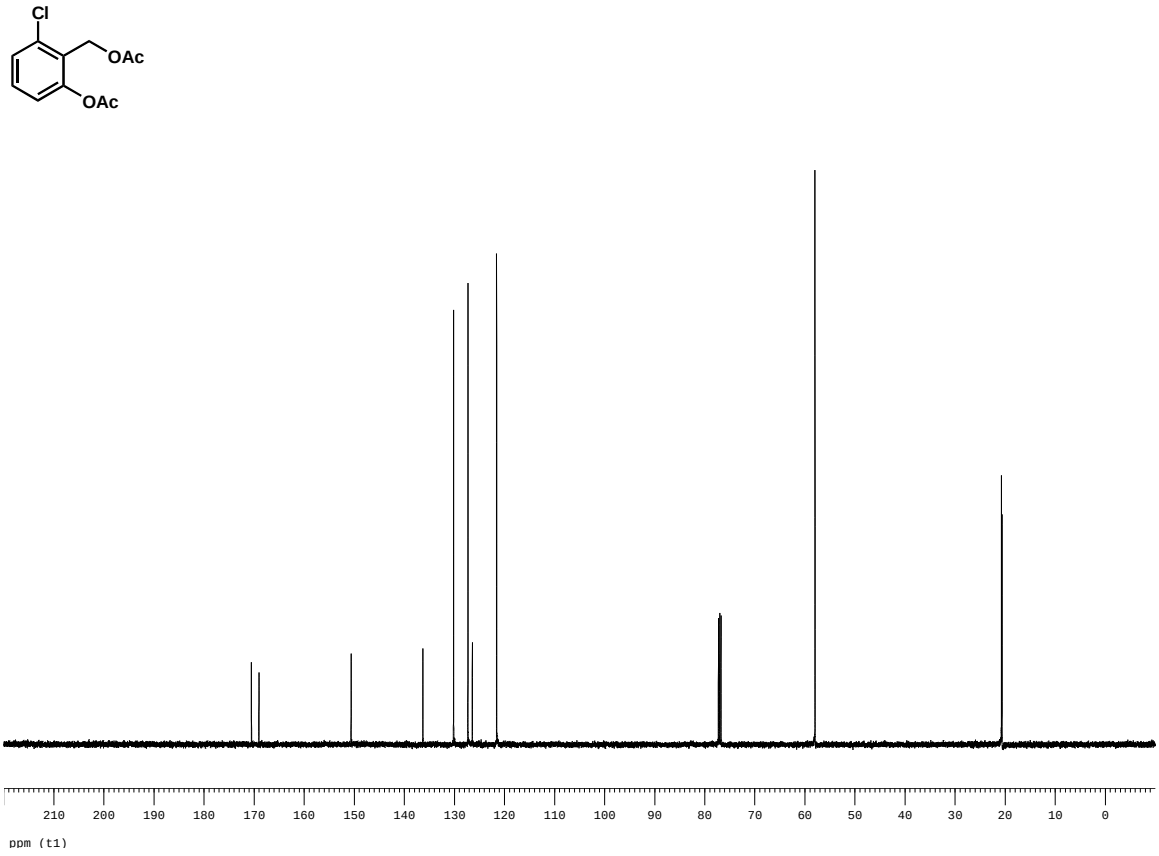

OTBS
Pr
OTBS
1.00
1.00
1.00
1.00
0.98
2.16
0.98
0.95
9.66
12.96
3.06
3.02
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

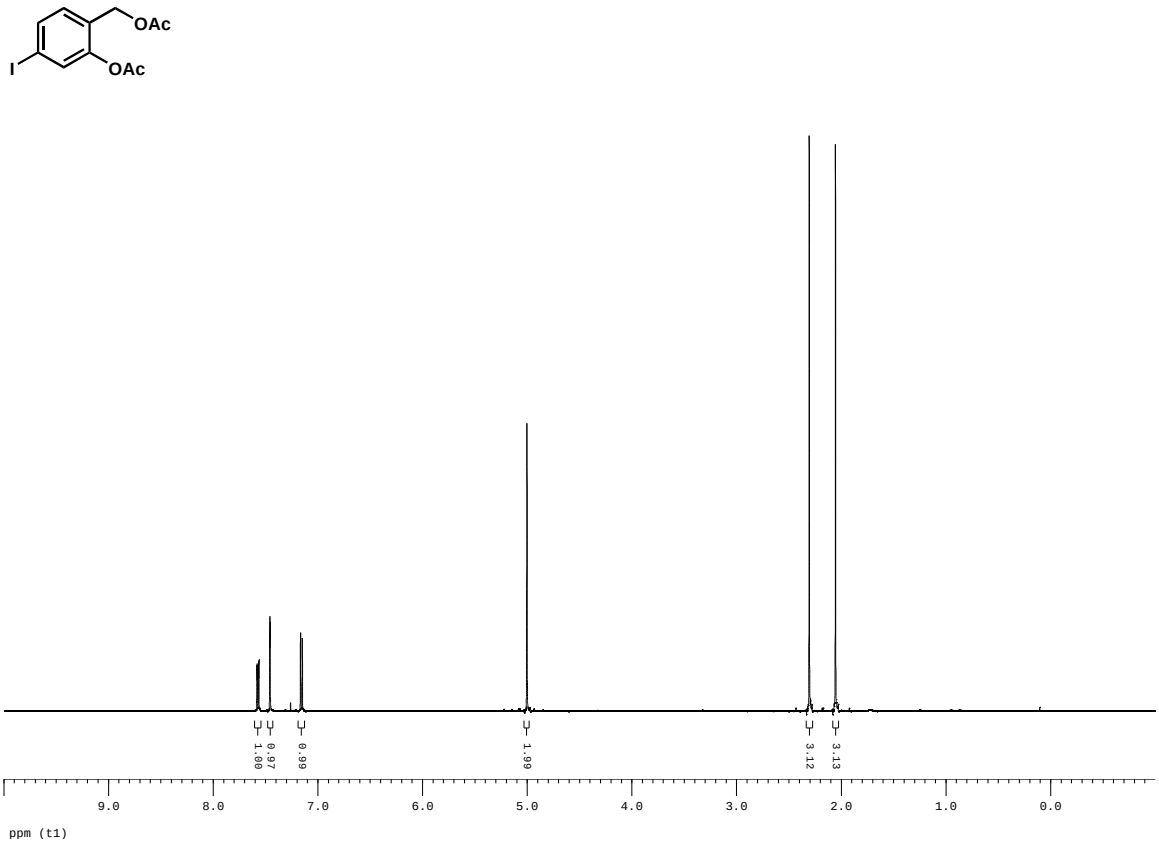

OTBS
Pr
OTBS
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

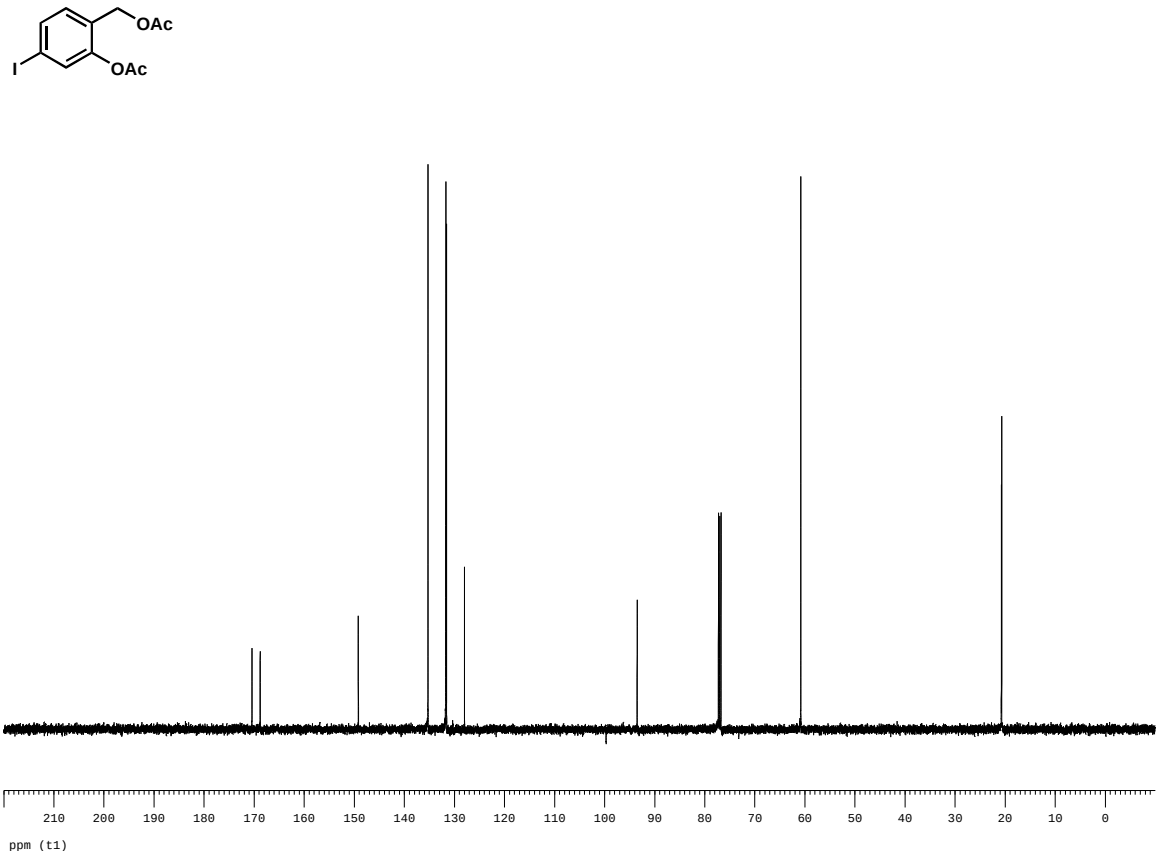

OAc
TBSO
Me
OAc
2.06
1.00
0.98
3.18
3.20
3.13
9.53
6.15
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

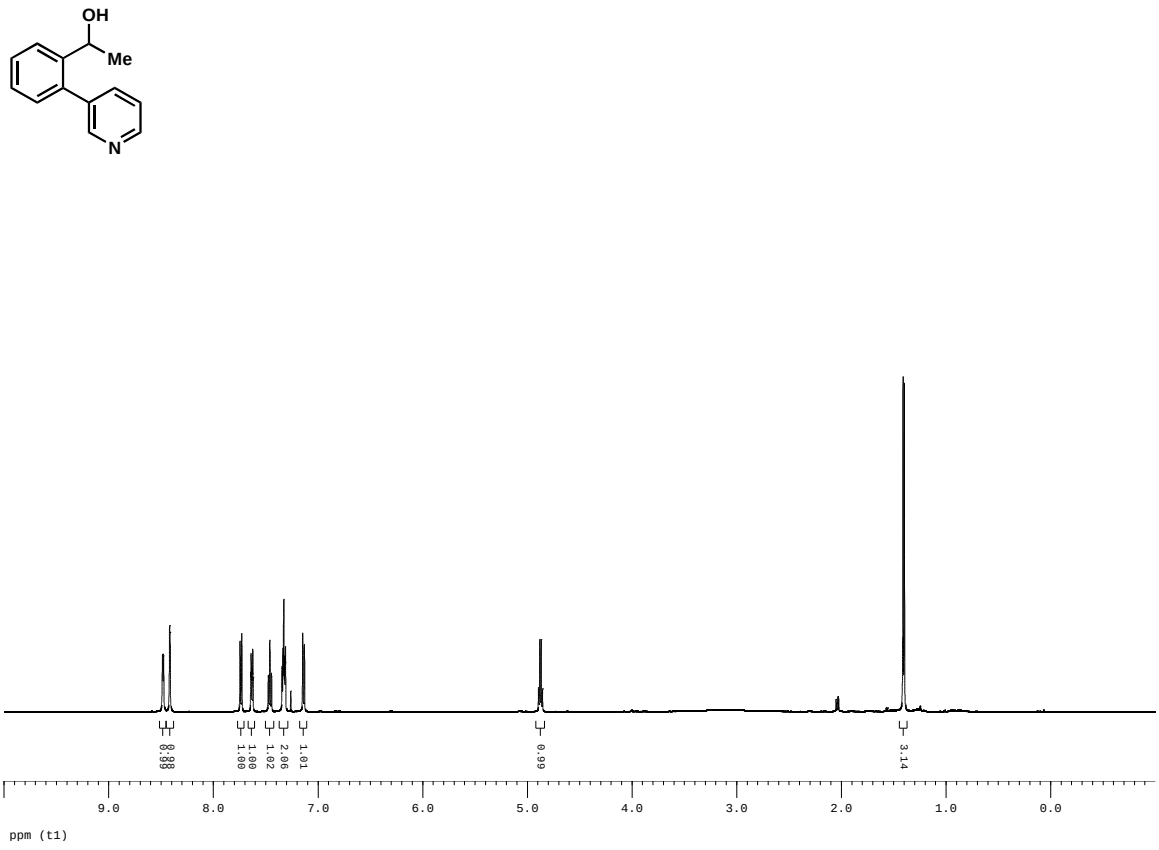

OAc
TBSO
Me
OAc
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

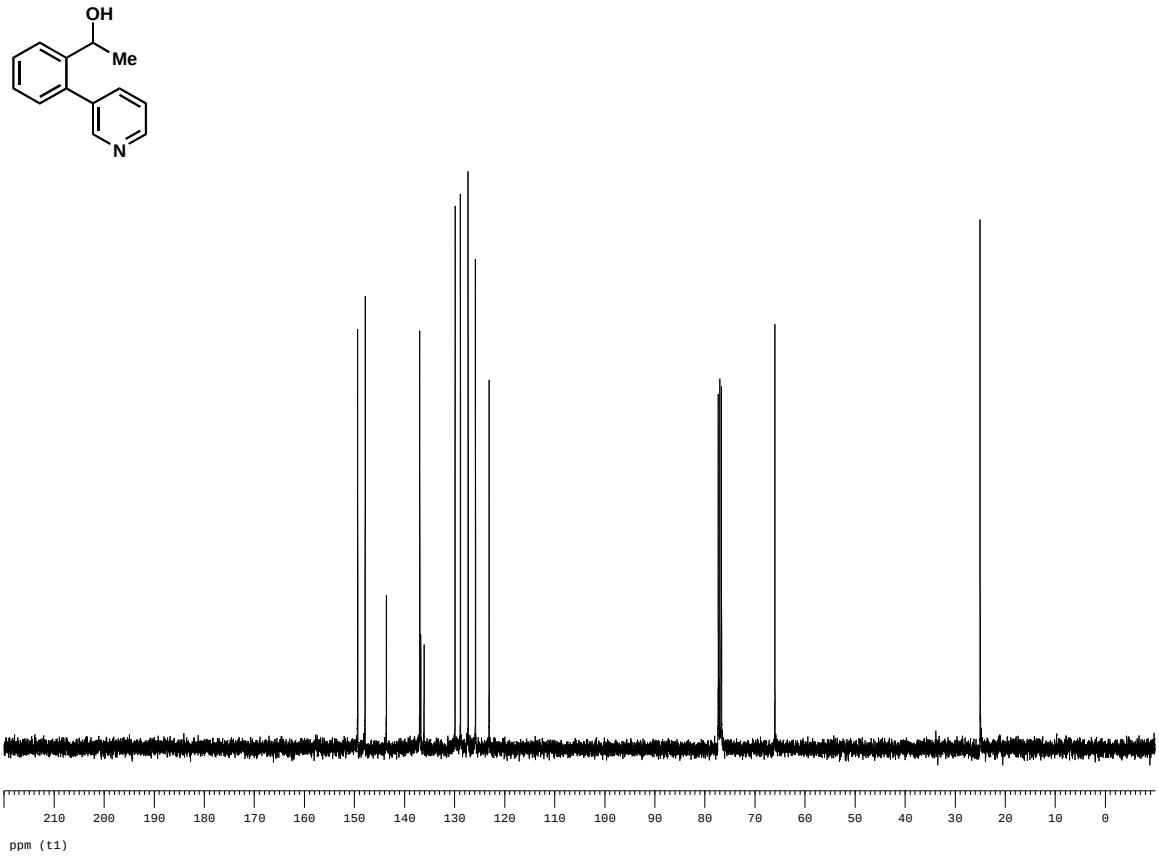

Cl
OAc
OAc
2.00
1.00
2.04
3.11
3.09
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

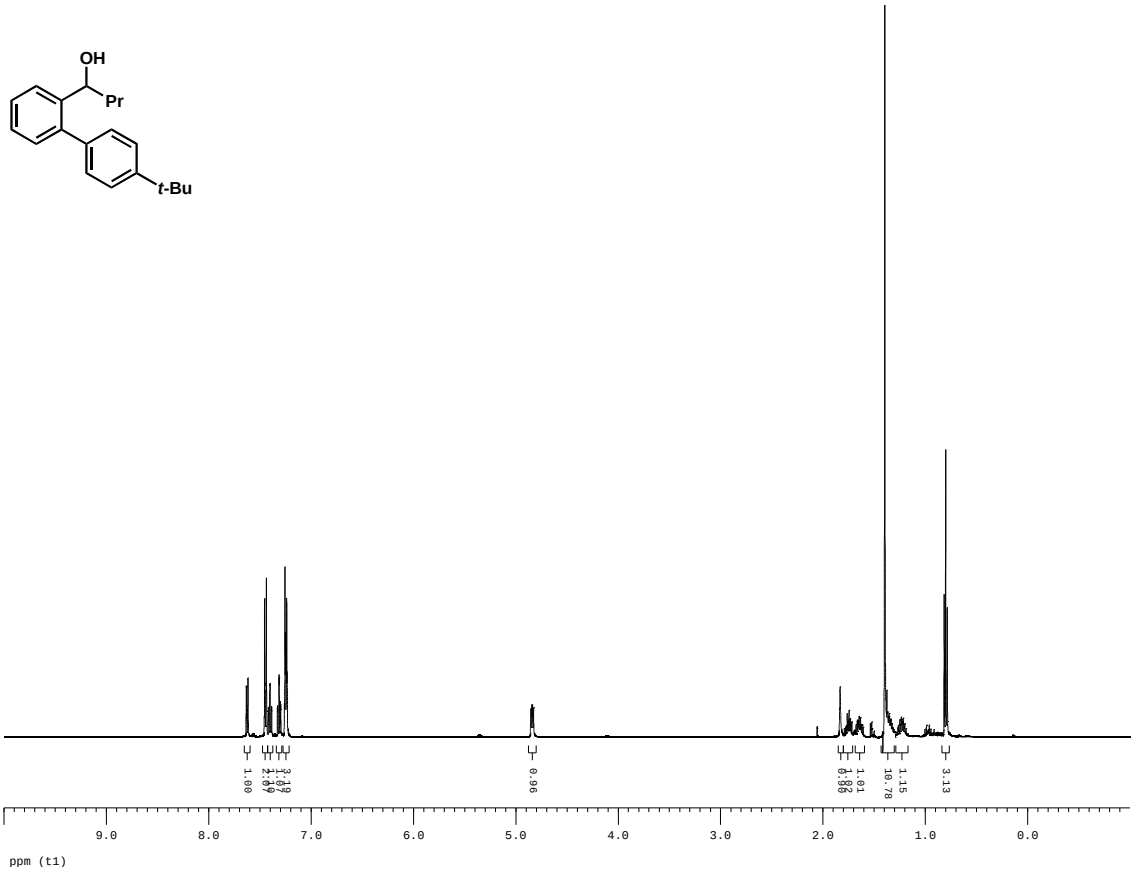

Cl
OAc
OAc
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

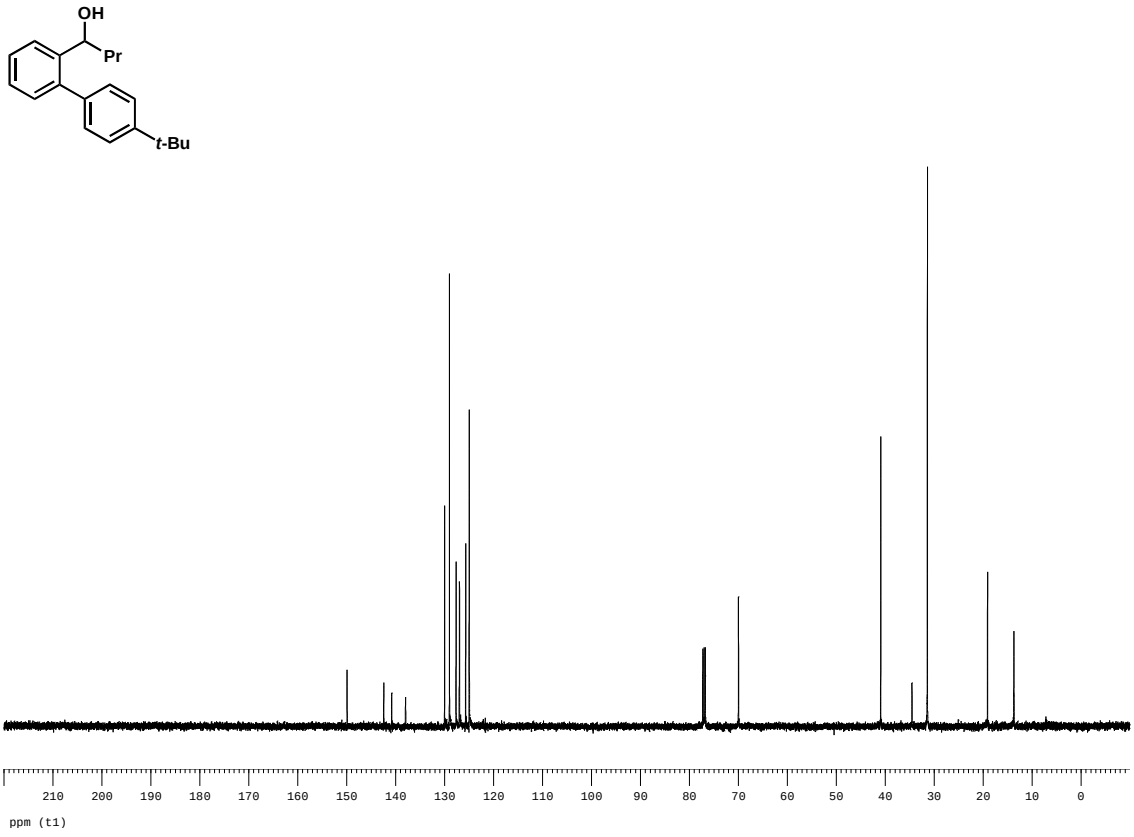

OAc
I
OAc
1.00
0.97
0.99
1.99
3.12
3.13
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

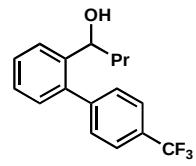

OAc
I
OAc
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

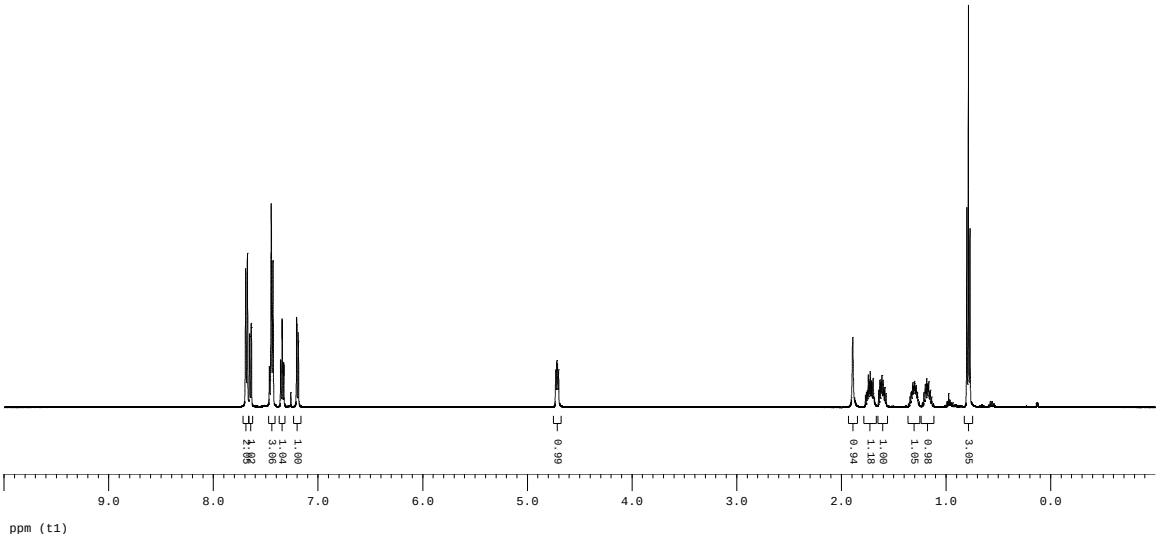

OH
Me
N
0.98
0.99
1.00
1.00
1.02
2.06
1.01
0.99
3.14
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

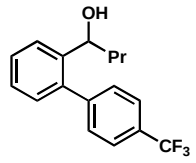

OH
Me
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

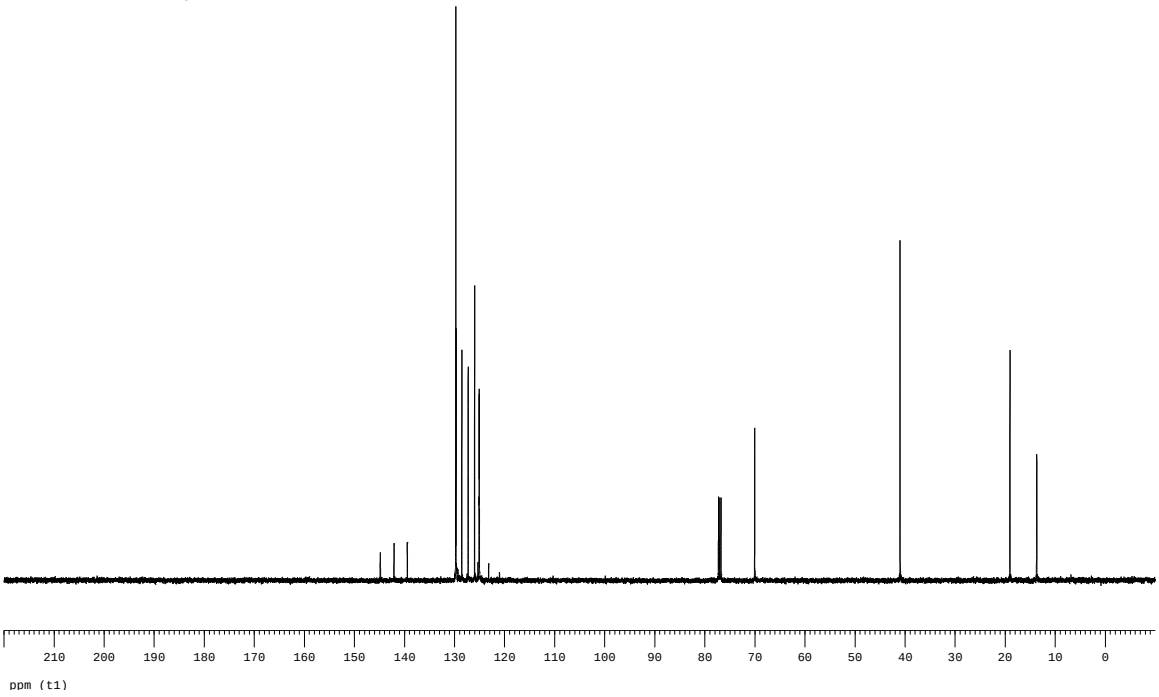

OH
Pr
t-Bu
1.00
2.07
3.13
0.96
0.90
1.01
10.78
1.15
3.13
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

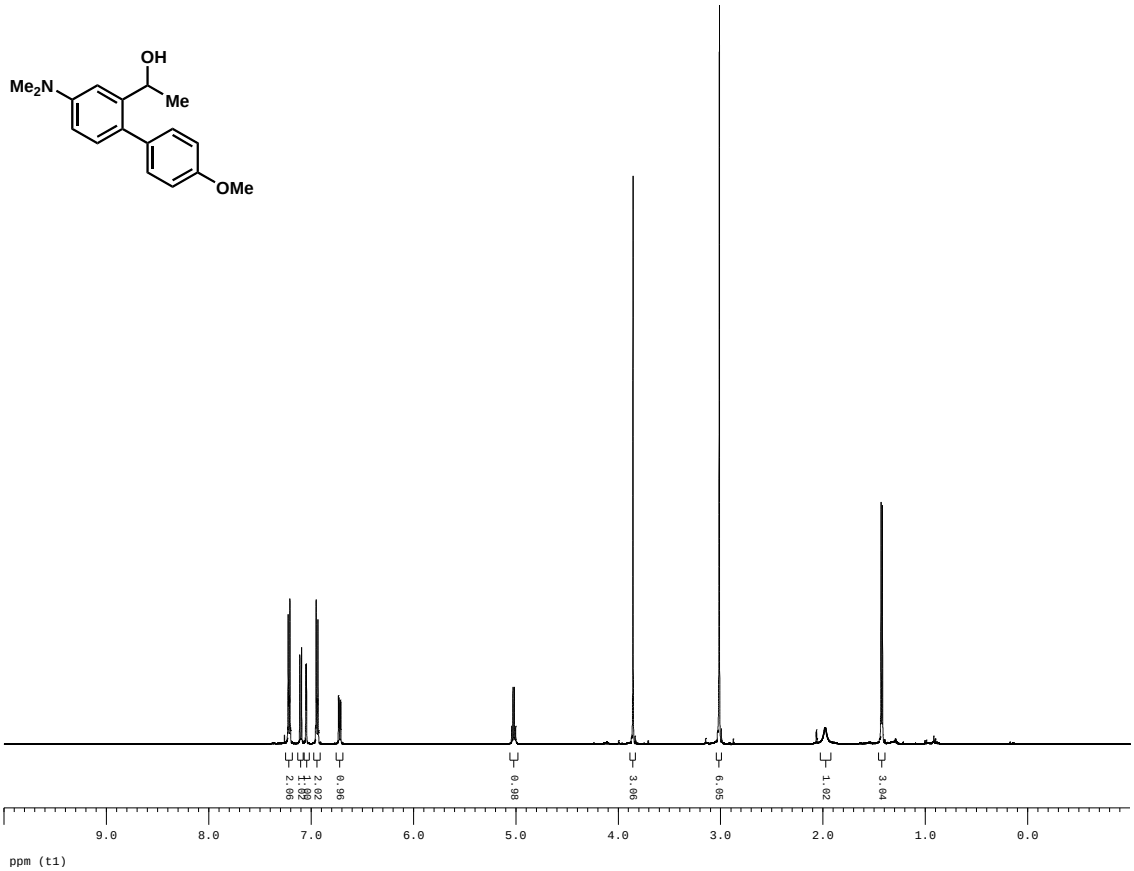

OH
Pr
t-Bu
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

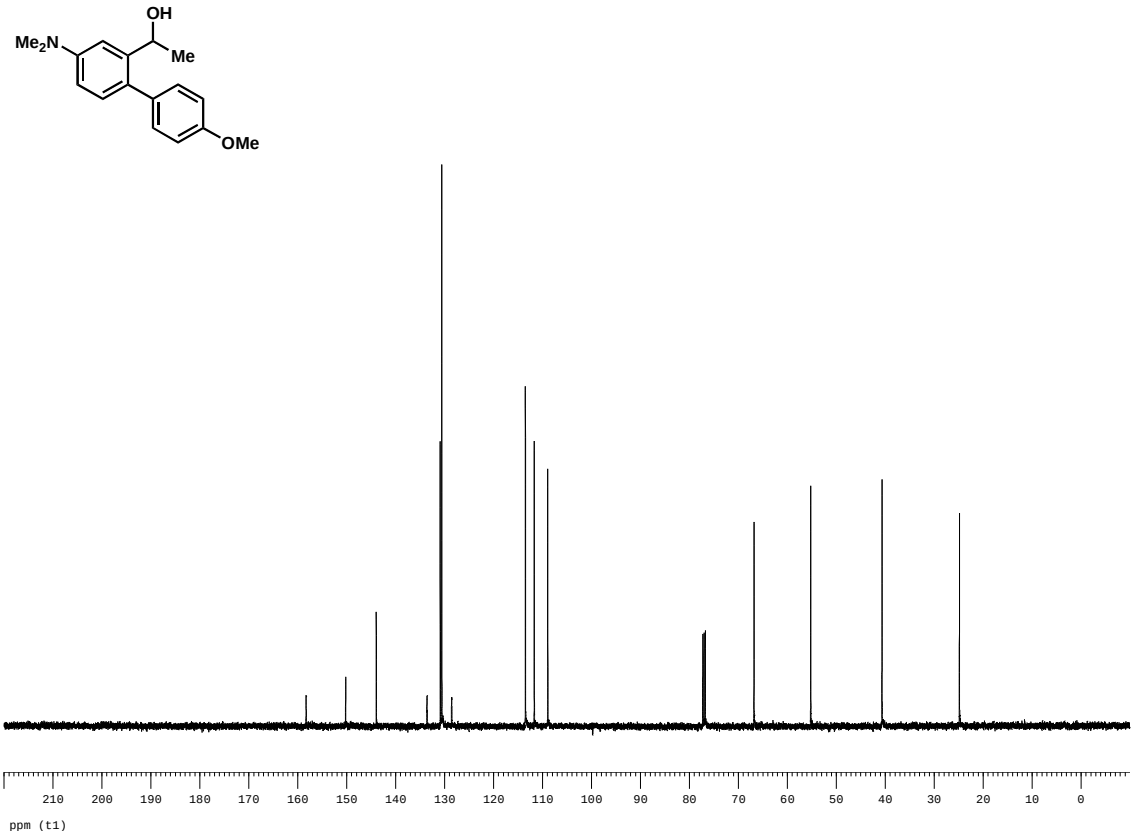

OH
Pr
CF3

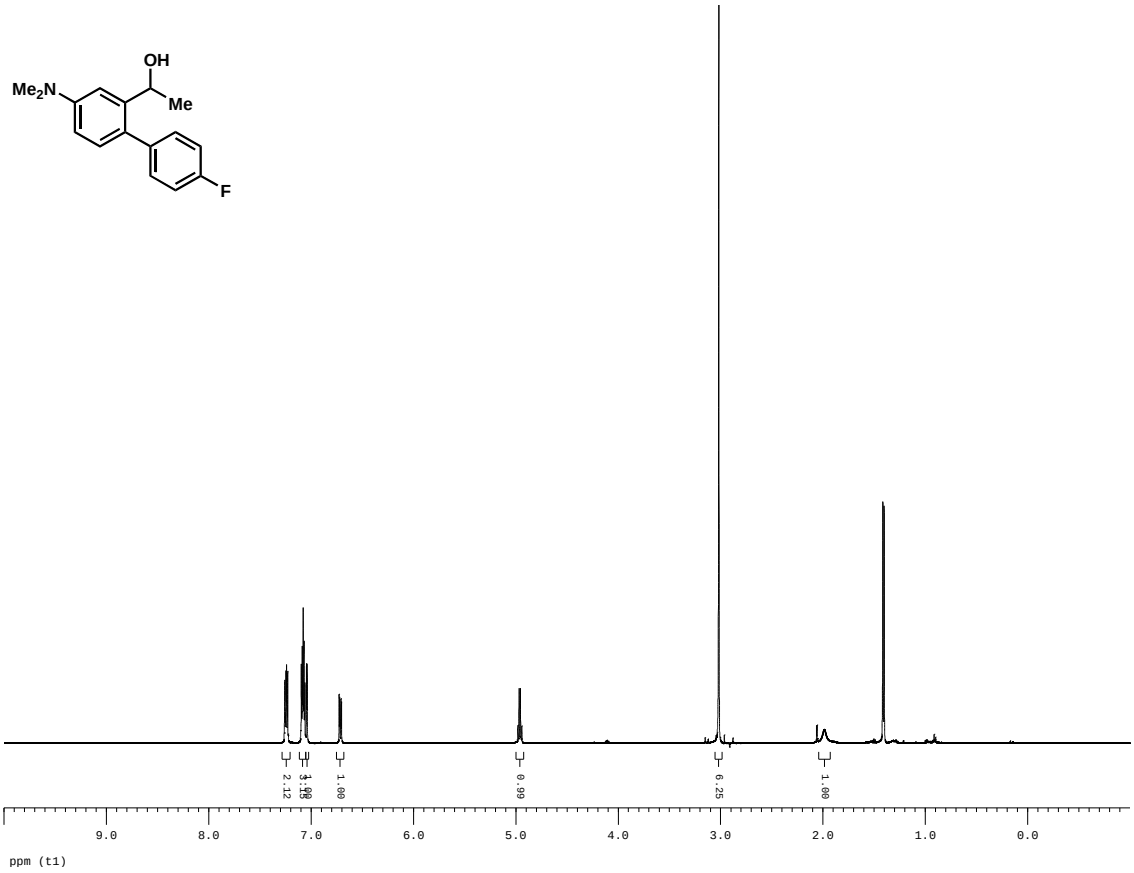

2.00
3.06
1.04
1.00
0.99
0.94
1.18
1.00
1.05
0.98
3.05
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

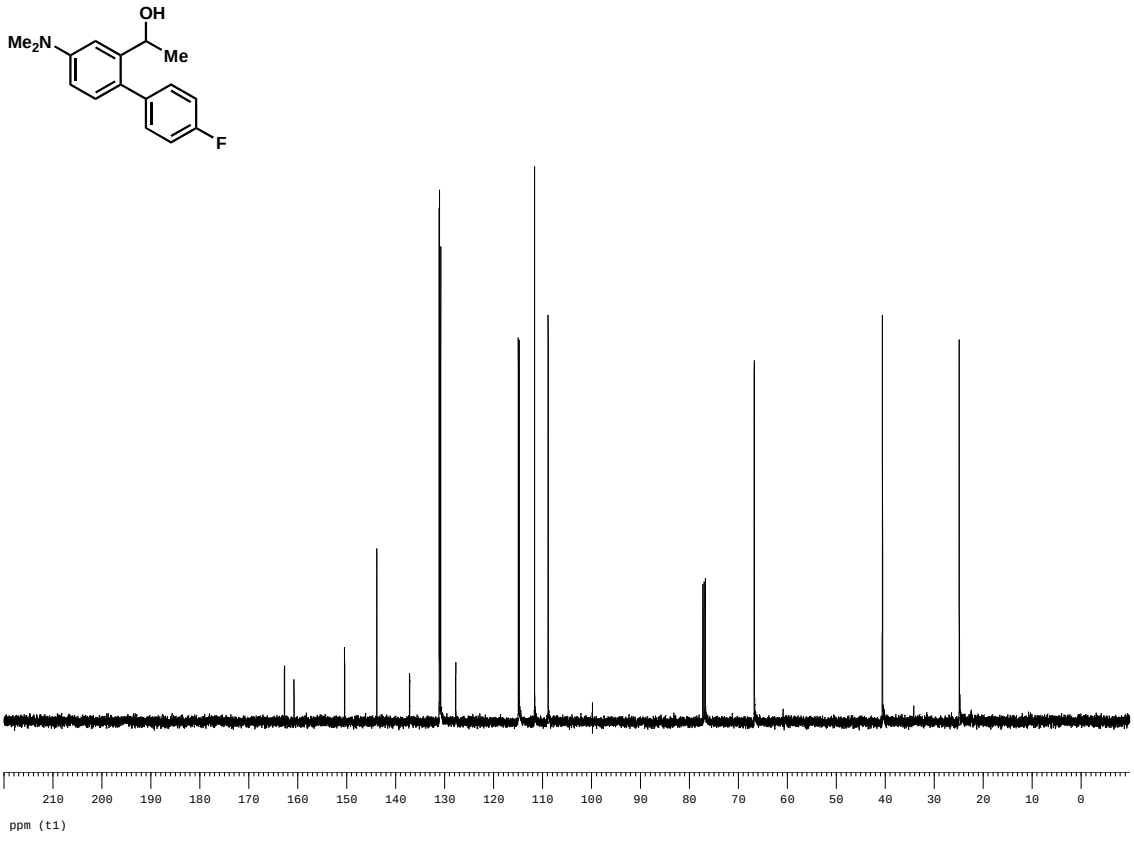

OH
Pr
CF3

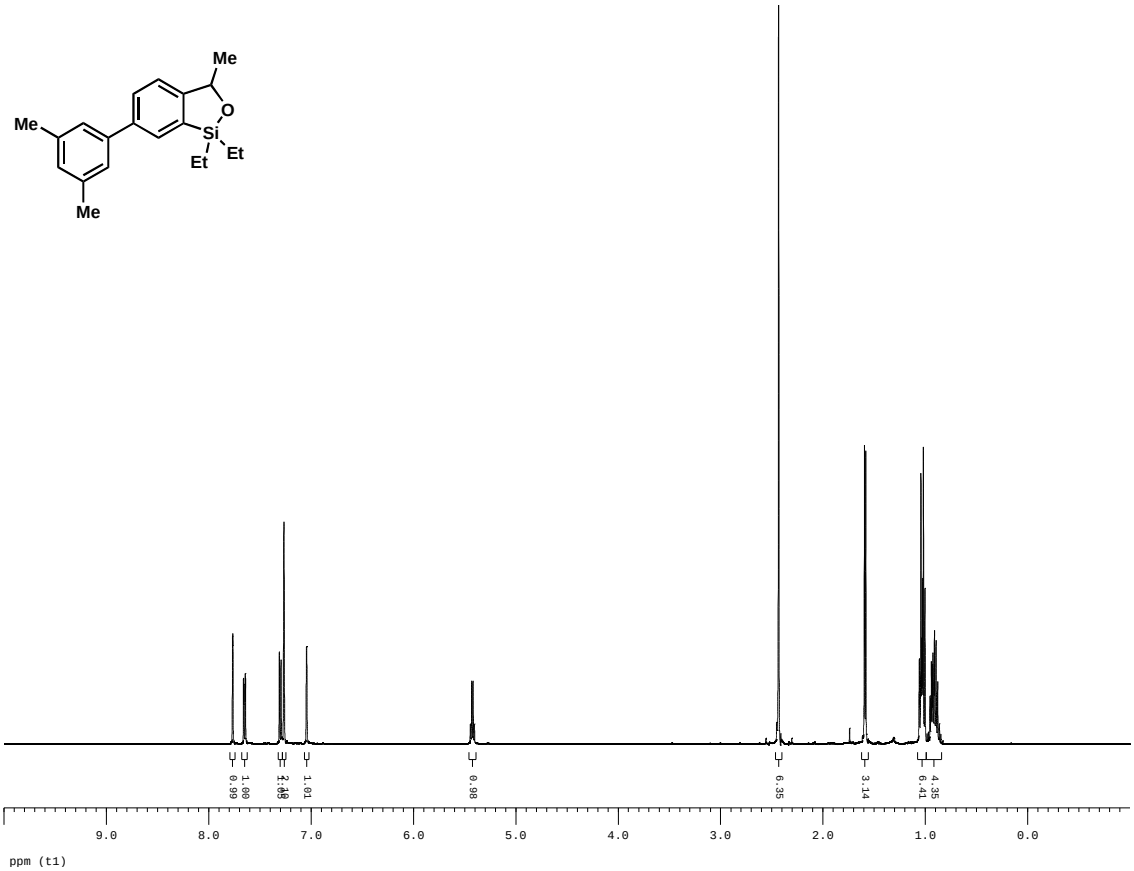

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

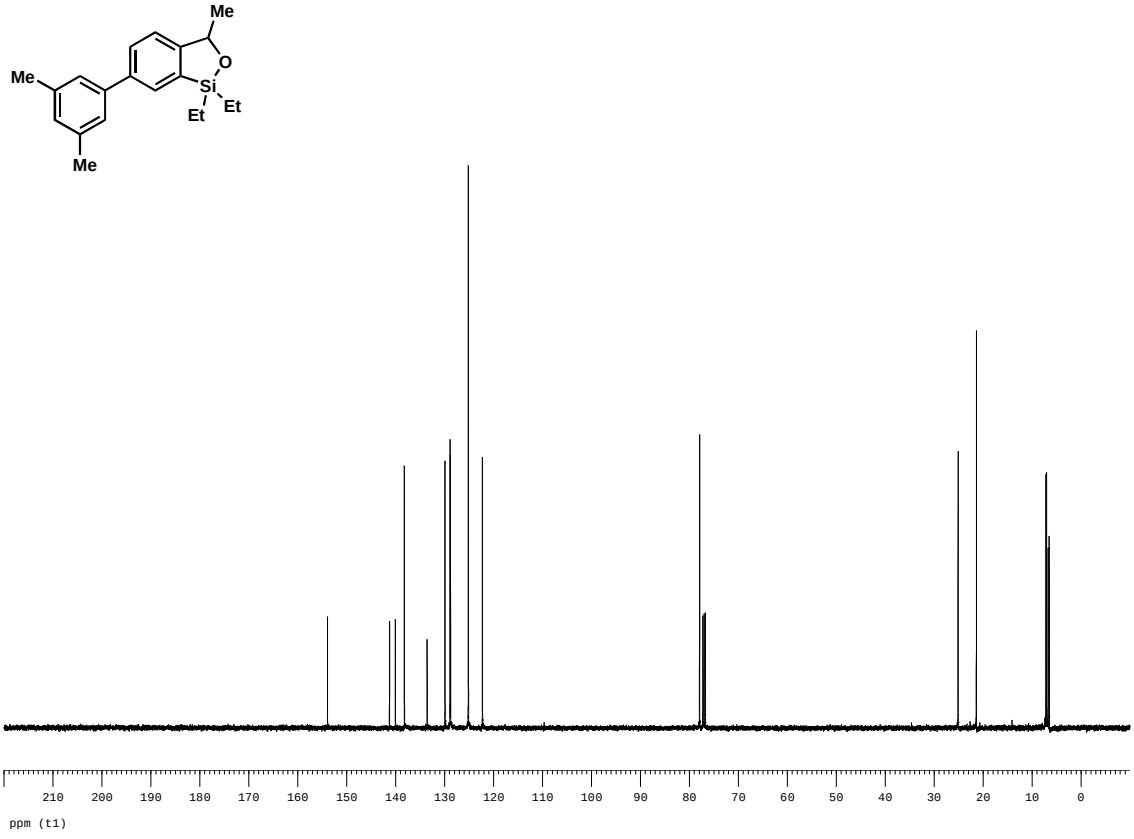

OH
Me2N
Me
OMe
2.06
1.00
1.02
2.02
0.96
0.98
3.06
6.05
1.92
3.04
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

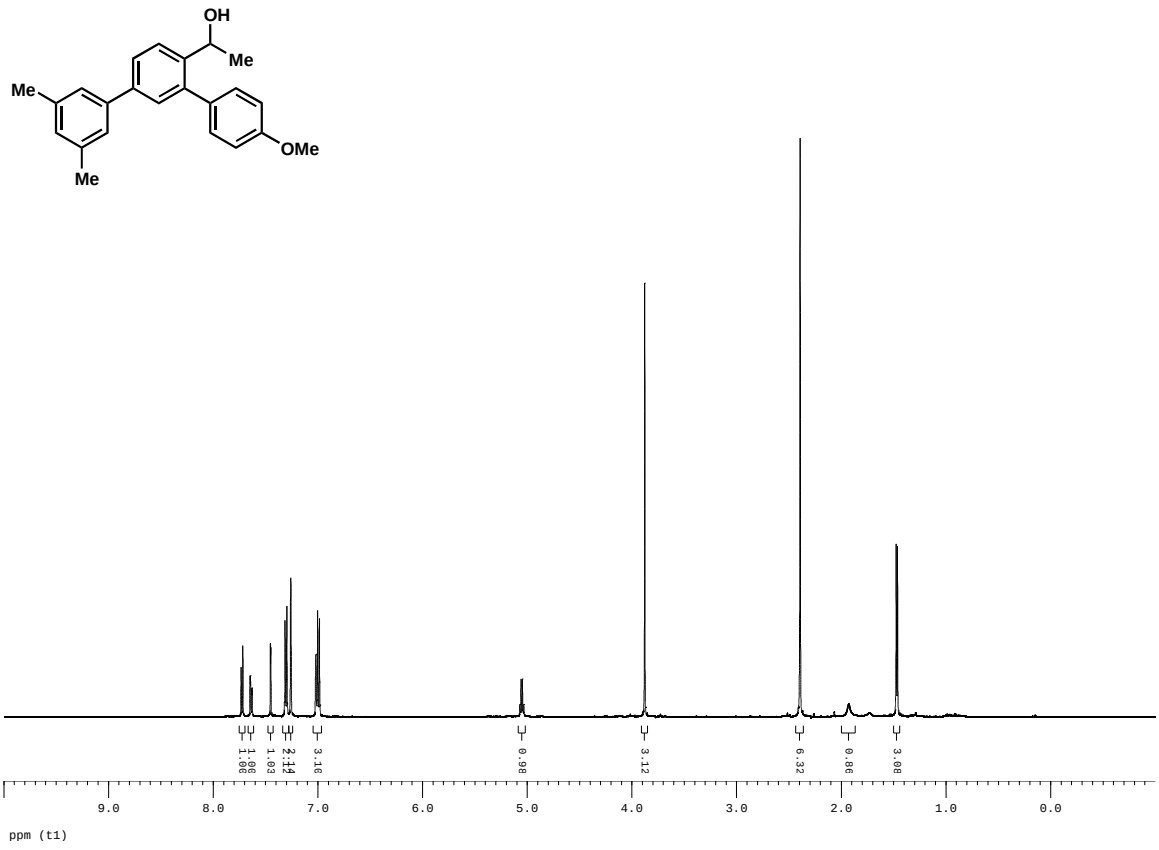

OH
Me2N
Me
OMe
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

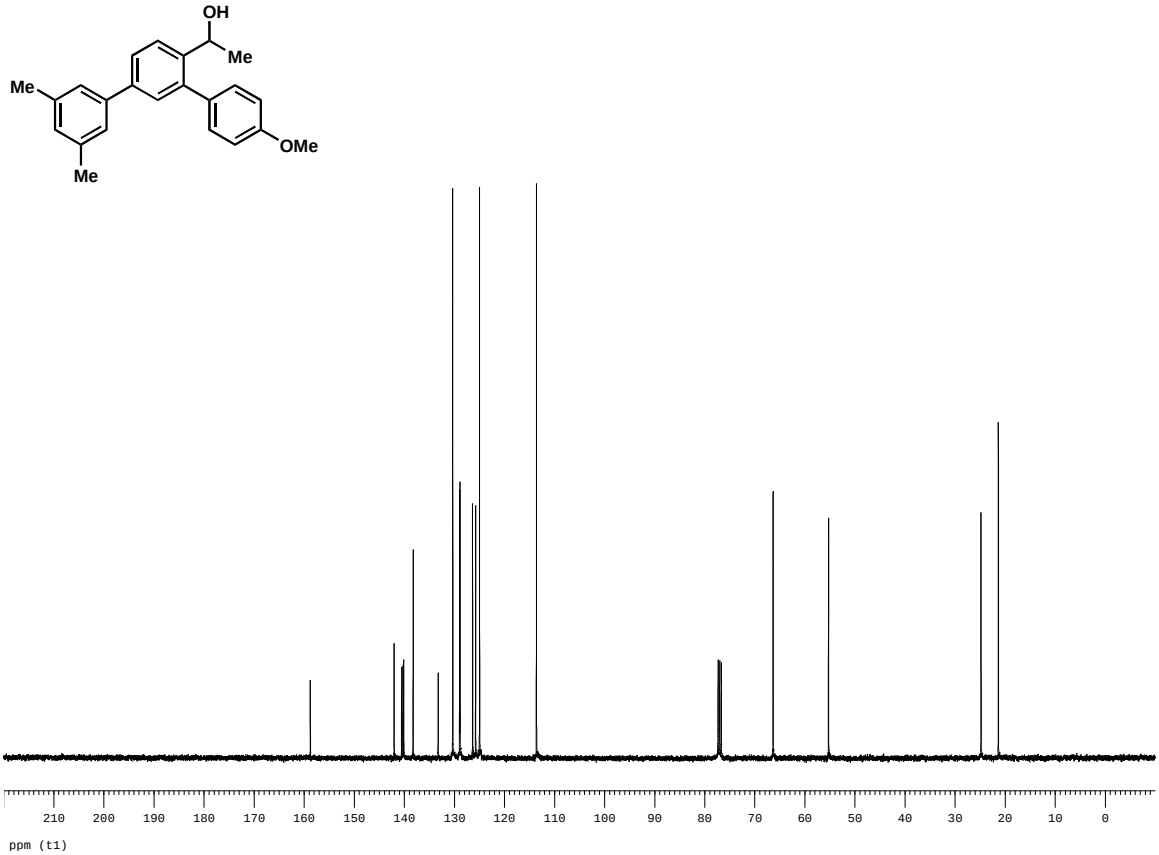

OH
Me2N
Me
F
2.12
1.00
0.99
6.25
1.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


OH
Me2N
Me
F
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)


Me
Me
O
Si
Et
Et
Me
0.99
1.00
2.00
1.01
0.98
6.35
3.14
6.41
4.35
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


Me
Me
O
Si
Et
Et
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)


OH
Me
Me
OMe
Me
1.00
1.06
1.03
2.14
3.10
0.98
3.12
6.32
0.86
3.08
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


OH
Me
Me
OMe
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

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