SUPPLEMENTARY MATERIAL

The Design, Synthesis and Validation of Recoverable and Readily Reusable Siloxane Transfer Agents for Pd-Catalyzed Cross-Coupling Reactions

Dionicio Martinez-Solorio, Adam T. Hoye, Minh H. Nguyen and Amos B. Smith, III*

Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104

smithab@sas.upenn.edu

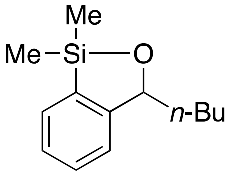
Experimental procedures and spectral data for all new compounds, including copies of ^{1}H and ^{13}C NMR spectra.

General. All moisture-sensitive reactions were performed using syringe-septum cap techniques under an inert atmosphere of N_2. All glassware was flame dried or dried in an oven (140 °C) for at least 4 h prior to use. Reactions were magnetically stirred unless otherwise stated. Tetrahydrofuran (THF), dichloromethane (CH_2Cl_2) and diethyl ether (Et_2O) were dried by passage through alumina in a Pure Solve™ PS-400 solvent purification system. Unless otherwise stated, solvents and reagents were used as received. Analytical thin layer chromatography was performed on pre-coated silica gel 60 F-254 plates (particle size 40-55 micron, 230-400 mesh) and visualized by a uv lamp or by staining with PMA (2 g phosphomolybdic acid dissolved in 20 mL absolute ethanol), $KMnO_4$ (1.5 g of $KMnO_4$, 10 g of K_2CO_3 and 2.5 mL of 5% aq. NaOH in 150 mL H_2O), or CAM (4.8 g of $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ and 0.2 g of $Ce(SO_4)_2$ in 100 mL of a 3.5 N H_2SO_4 solution) stain. Column chromatography was performed using silica gel (40-63 micron particle size, 230-300 mesh) and compressed air pressure with commercial grade solvents. Yields refer to chromatographically and spectroscopically pure compounds, unless otherwise stated. NMR spectra were recorded at 500 MHz/125 MHz (^{1}H NMR/^{13}C NMR) on a 500 MHz spectrometer at 300 K. Chemical shifts are reported in parts per million with the residual solvent peak as an internal standard. ^{1}H NMR spectra are tabulated as follows: chemical shift, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, qn=quintet, dd=doublet of doublets, ddd= doublet of doublet of doublets, dddd= doublet of doublet of doublet of doublets, dt= doublet of triplets, m=multiplet, b=broad), coupling constant and integration. ^{13}C NMR spectra are tabulated by observed peak. Melting points were determined using a capillar melting point apparatus and are uncorrected. Infrared spectra were measured on a FT/IR 480 plus spectrometer. High-resolution mass spectra (HRMS) were obtained at the University of Pennsylvania on a Waters GCT Premier spectrometer. Single crystal X-ray structures were determined at the University of Pennsylvania. X-ray intensity data were collected on a Rigaku Mercury CCD or Bruker APEXII CCD area detector employing graphite-monochromated Mo-Ka radiation (l = 0.71073 Å) at a temperature of 143(1) K.

Experimental Procedures.

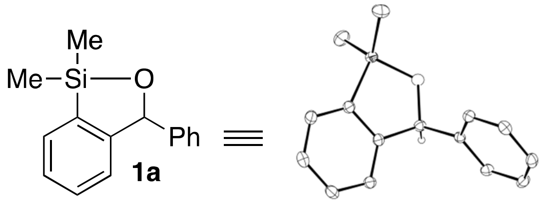
Compounds **1e**,[1] **1f**,[1,2] **16b**[3], Et_2SiHCl[4] and the corresponding vinyl iodides of **13a**,[3] **13b**,[5] and **13c**[6] were prepared according to previously reported procedures.

Preparation of water-washed silica gel for column chromatography (where specified): Silica gel was suspended in H_2O and the slurry mixture was then packed into a prepared column. The obtained H_2O-washed silica gel packed column was then rinsed with 2 column volumes of acetone, 1 column volume of EtOAc and 2 column volumes of hexanes, successively. The obtained column is then ready for use. Note: Water-washed silica gel proved optimal in minimizing the "streakeage" of siloxanes **1**, **1a**, **1b**, **1c**, and **1d** leading to improved purification.



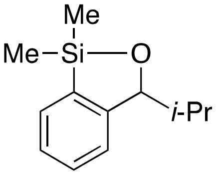
3-Butyl-1,1-dimethyl-1,3-dihydrobenzo[*c*][1,2]oxasilole (1). To a cooled solution of benzaldehyde **10** (21.0 g, 198 mmol, 1.00 equiv) in hexanes (733 mL, pre-dried over $MgSO_4$) and Et_2O (587 mL) at 0 °C was added *n*-BuLi (224 mL, 1.94 M in hexanes, 435 mmol, 2.20 equiv) dropwise. The reaction mixture was allowed to warm to room temperature and was stirred for 30 minutes. The flask was then fitted with a reflux condenser and the reaction mixture was heated to reflux (75 °C) for 16 h. A dark solution resulted and the reaction mixture was allowed to cool to room temperature. The reflux condenser was removed and the reaction mixture was cooled to −78 °C and Me_2SiHCl (48.4 mL, 435 mmol, 2.20 equiv) was then added dropwise. The reaction mixture was allowed to slowly warm to room temperature and stirred for 8 h. The resulting pale yellow slurry was then quenched with H_2O (300 mL) and the aqueous phase extracted with Et_2O (3 × 100 mL). The combined organic layers were washed with brine, dried ($MgSO_4$), filtered and concentrated under reduced pressure.

The resulting crude orange oil was taken up in THF (200 mL) at room temperature and 4 Å molecular sieves (3.00 g) and KO*t*-Bu (1.10 g, 9.90 mmol, 0.05 equiv) were added as a single portion and vigorous evolution of H_2 was observed. The reaction mixture was allowed to stir at room temperature for 5 h, quenched with H_2O (50 mL) and the aqueous phase extracted with Et_2O (3 × 100 mL). The combined organic layers were washed with brine, dried ($MgSO_4$), filtered and concentrated under reduced pressure. Flash chromatography on water-washed silica (100 % hexanes then 1% EtOAc in hexanes) followed by Kugelrohr distillation (85-95 °C, 0.05 mmHg) provided **1** (22.7 g, 103 mmol, 52% yield) as a colorless oil. Analytical data matches that which has been previously reported:[7] **R_f** 0.35 (1% EtOAc in hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ7.56 (d, *J* = 7.0 Hz, 1H), 7.41 (td, *J* = 7.5, 1.0 Hz, 1H), 7.29 (t, *J* = 7.0 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 5.26 (dd, J = 7.5, 3.5 Hz, 1H), 1.93 (m, 1H), 1.62 (m, 1H), 1.50-1.20 (m, 4H), 0.90 (t, J = 7.5 Hz, 3H), 0.41 (s, 3H), 0.38 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 153.5, 135.8, 131.0, 129.7, 127.0, 122.4, 81.9, 38.9, 27.5, 23.0. 14.2, 1.5, 0.8; **IR** (neat) 3059 (s), 2958 (m), 2927 (m), 2858 (m), 1594 (s), 1443 (s), 1250 (s), 1080 (s), 919 (m), 865 (s), 830 (s), 789 (s), 744 (s) cm^{-1}; **HRMS** (ES+) *m/z* calcd for $C_{13}H_{21}OSi$ $[M+H]^+$ 221.1362, found 221.1367.



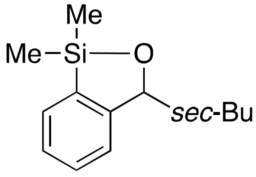
1,1-Dimethyl-3-phenyl-1,3-dihydrobenzo[*c*][1,2]oxasilole (1a): Phenylmagnesium bromide (10.4 mL, 3.00 M in Et_2O, 31.3 mmol, 1.20 equiv) was added dropwise to a vigorously stirred solution of 2-bromobenzaldehyde (4.82 g, 26.1 mmol, 1.00 equiv) in Et_2O (75 mL) at 0 °C. The reaction mixture was stirred at room temperature for 12 h, quenched with sat. aq. NH_4Cl (25 mL) and the aqueous phase extracted with Et_2O (2 x 25 mL). The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated under reduced pressure. Flash chromatography on silica (1% Et_2O in hexanes then 10% Et_2O in hexanes) provided the desired (2-bromophenyl)(phenyl)methanol (**S1**) (6.44 g, 24.5 mmol, 94% yield) as a white solid. Analytical data matches that which has been previously reported:[8] **R_f** 0.3 (10% EtOAc in hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.61-7.52 (m, 2 H), 7.41 (d, J = 6.9 Hz, 2 H), 7.37-7.31 (m, 3 H), 7.28 (t, J = 7.1 Hz, 1 H), 7.15 (dt, J = 1.6, 7.6 Hz, 1 H), 6.21 (d, J = 3.8 Hz, 1 H), 2.34 (d, J = 4.0 Hz, 1 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 142.6, 142.3, 133.0, 129.3, 128.6, 127.9, 127.8, 127.2, 126.7, 122.9, 74.9.

The resulting (2-bromophenyl)(phenyl)methanol (**S1**) (4.29 g, 16.3 mmol, 1.00 equiv) was dissolved in THF (50 mL) and *n*-BuLi (14.7 mL, 2.45 M in hexanes, 35.9 mmol, 2.20 equiv) was added dropwise at –78 °C. The reaction mixture was stirred for 1 h, followed by the addition of Me_2SiHCl (3.90 mL, 35.9 mmol, 2.20 equiv) at –78 °C. The resulting reaction mixture was allowed to warm to room temperature and stirred for 12 h. The reaction mixture was quenched by addition of *t*-BuOH (20 mL) and stirred for 5 h, followed by the addition of H_2O (20 ml) and stirred for another 2 h. The aqueous phase was then extracted with Et_2O (2 x 25 mL) and the combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated under reduced pressure. Flash chromatography on water-washed silica gel (100% hexanes then 1% Et_2O/Hexanes) provided the desired siloxane **1a** (1.82 g, 26.8 mmol, 46% yield) as a white crystalline solid: **m.p.** 45.5 - 46.5 °C; **R_f**0.3 (5% Et_2O in hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.63-7.59 (m, 1 H), 7.36-7.26 (m, 7 H), 7.05-7.01 (m, 1 H), 6.17 (s, 1 H), 0.53 (s, 3 H), 0.45 (s, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 152.6, 143.9, 135.3, 130.8, 129.9, 128.7, 127.9, 127.3, 127.3, 123.9, 84.2, 1.4, 0.7; **IR** (CH_2Cl_2) 3057 (m), 2964 (m), 2874 (m), 1447 (m), 1265 (s), 1181 (m), 1136 (m), 1042 (s), 1016 (s), 862 (s), 822 (s), 793 (s), 740 (s), 702 (s), 656 (m) cm^{-1}; **HRMS** (CI$^+$) *m/z* calculated for $C_{15}H_{17}SiO$ [M+H]$^+$ 241.1049, found 241.1034.

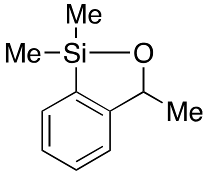


3-Isopropyl-1,1-dimethyl-1,3-dihydrobenzo[*c*][1,2]oxasilole (1b): Phenylmagnesium bromide (11.7 mL, 3.00 M in Et_2O, 35.1 mmol, 1.20 equiv) was added dropwise to a vigorously stirred solution of isobutyraldehyde (2.11 g, 29.3 mmol, 1.00 equiv) in Et_2O (50 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 12 h, then quenched with sat. aq. NH_4Cl (25 mL). The aqueous phase extracted with Et_2O (2 x 25 mL) and the combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Flash chromatography on silica, (10% Et_2O in hexanes) provided the desired 2-methyl-1-phenylpropan-1-ol (**S2**) (4.09 g, 27.2 mmol, 93% yield) as a colorless oil. Analytical data matches that which has been previously reported:[9] $\mathbf{R}_f$ 0.15 (10% Et_2O in hexanes); ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.36-7.26 (m, 5 H), 4.37 (dd, *J* = 3.3, 6.8 Hz, 1 H), 2.02-1.91 (m, 1 H), 1.82 (d, *J* = 3.4 Hz, 1 H), 1.01 (d, *J* = 6.7 Hz, 3 H), 0.81 (d, *J* = 6.7 Hz, 3 H); ^{13}**C NMR** (125 MHz, $CDCl_3$) δ 143.8, 128.3, 127.6, 126.7, 80.2, 35.4, 19.2, 18.4.

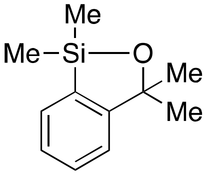
The resulting 2-methyl-1-phenylpropan-1-ol (**S2**) (2.76 g, 18.4 mmol, 1.00 equiv) was dissolved in hexanes (125 ml, pre-dried over $MgSO_4$) and Et_2O (100 ml) at 0 °C and *n*-BuLi (22.9 ml, 1.77 M in hexanes, 40.5 mmol, 2.20 equiv) was added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred for 30 minutes. The flask was then fitted with a reflux condenser and the system was heated to reflux (75 °C) for 16 h. A dark solution resulted and the reaction mixture was allowed to cool to room temperature. The reflux condenser was removed and the reaction mixture was cooled to −78 °C. Me_2SiHCl (4.40 ml, 40.5 mmol, 2.20 equiv) was added dropwise. The reaction mixture was allowed to slowly warm to room temperature and stirred for 12 h. The slurry was quenched by addition of *t*-BuOH (20 mL) and stirred for 5 h, followed by the addition of H_2O (20 ml) and stirred for another 2 h. The aqueous phase was extracted with Et_2O (2 x 25 mL) and the combined organic layers were washed with brine, dried ($MgSO_4$), filtered and concentrated under reduced pressure. Flash chromatography on water-washed silica gel (100% hexanes then 1% Et_2O/Hexanes) followed by Kugelrohr distillation (75-80 °C, 0.025 mmHg) provided **1b** (1.48 g, 7.17 mmol, 39% yield) as a colorless oil: $\mathbf{R}_f$0.5 (5% Et_2O in hexanes); ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.1 Hz, 1 H), 7.39 (dt, *J* = 1.0, 7.5 Hz, 1 H), 7.29 (t, *J* = 7.2 Hz, 1 H), 7.20 (d, *J* = 7.7 Hz, 1 H), 5.17 (d, *J* = 2.2 Hz, 1 H), 2.12 (dspt, *J* = 2.5, 6.8 Hz, 1 H), 1.17 (d, *J* = 6.9 Hz, 3 H), 0.60 (d, *J* = 6.7 Hz, 3 H), 0.41 (s, 3 H), 0.36 (s, 3 H); ^{13}**C NMR** (125 MHz, $CDCl_3$) δ 152.5, 136.4, 130.8, 129.7, 127.0, 122.4, 86.5, 34.6, 20.4, 15.0, 1.0, 0.8; **IR** (neat) 3060 (m), 2963 (s), 2873 (m), 1594 (m), 1469 (m), 1442 (m), 1383 (m), 1365 (m), 1251 (s), 1198 (m), 1137 (m), 1120 (m), 1102 (m), 1067 (s), 1014 (s), 953 (s), 874 (s), 830 (s), 788 (s), 744 (s), 704 (m), 651 (m) cm^{-1}; **HRMS** (CI$^+$) *m/z* calculated for $C_{11}H_{15}SiO$ [M-Me]$^+$ 191.0892, found 191.0893.



3-(*sec*-Butyl)-1,1-dimethyl-1,3-dihydrobenzo[*c*][1,2]oxasilole (1c): To a cooled solution of benzaldehyde **10** (3.25 g, 30.6 mmol, 1.00 equiv) in hexanes (125 ml, pre-dried over $MgSO_4$) and Et_2O (100 mL) at 0 °C was added *sec*-BuLi (26.2 mL, 1.4 M in cyclohexane, 36.7 mmol, 1.20 equiv) dropwise. The reaction mixture was allowed to warm to room temperature and was stirred for 5 h, at which time *n*-BuLi (20.7 mL, 1.77 M in hexanes, 36.7 mmol, 1.20 equiv) was added dropwise. The flask was then fitted with a reflux condenser and the system was heated to reflux (75 °C) for 16 h. A dark solution resulted and the reaction mixture was allowed to cool to room temperature. The reflux condenser was removed and the reaction mixture was cooled to −78 °C and Me_2SiHCl (7.97 ml, 67.3 mmol, 2.20 equiv) was added dropwise. The reaction mixture was allowed to slowly warm to room temperature and stirred for 12 h. The slurry was quenched by addition of *t*-BuOH (20 mL) and stirred for 5 h, followed by the addition of H_2O (20 ml) and stirred for another 2 h. The aqueous phase was extracted with Et_2O (2 x 25 mL) and the combined organic layers were washed with brine, dried ($MgSO_4$), filtered and concentrated under reduced pressure. Flash chromatography on water-washed silica gel (100% hexanes then 1% Et_2O/Hexanes) followed by Kugelrohr distillation (140-160 °C, 0.01 mmHg) provided **1c**, isolated as a 5:3 ratio of diastereomers by ^1H NMR spectroscopy (2.02 g, 9.17 mmol, 30% yield) as a colorless oil: $\mathbf{R_f}$ 0.55 (5% Et_2O in hexanes); *Major diastereoisomer*: ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.1 Hz, 1 H), 7.39 (t, *J* = 7.5 Hz, 1 H), 7.29 (t, *J* = 7.1 Hz, 1 H), 7.21 (d, *J* = 7.7 Hz, 1 H), 5.20 (d, *J* = 2.2 Hz, 1 H), 1.88-1.79 (m, 1 H), 1.13 (d, *J* = 6.9 Hz, 3 H), 1.08-1.01 (m, 2 H), 0.79 (t, *J* = 7.4 Hz, 3 H), 0.40 (s, 3 H), 0.36 (s, 3 H); ^{13}**C NMR** (125 MHz, $CDCl_3$) δ 152.3, 136.6, 130.9, 129.6, 126.9, 122.4, 86.7, 41.8, 22.5, 16.9, 12.5, 1.0, 0.8. *Minor diastereoisomer*: ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.1 Hz, 1 H), 7.39 (t, *J* = 7.5 Hz, 1 H), 7.29 (t, *J* = 7.1 Hz, 1 H), 7.19 (d, *J* = 7.7 Hz, 1 H), 5.20 (d, *J* = 1.2 Hz, 1 H), 1.88-1.79 (m, 1 H), 1.74-1.65 (m, 1 H), 1.53-1.43 (m, 1 H), 1.04 (t, *J* = 7.7 Hz, 3 H), 0.55 (d, *J* = 6.7 Hz, 3 H), 0.40 (s, 3 H), 0.36 (s, 3 H); ^{13}**C NMR** (125 MHz, $CDCl_3$) δ 152.7, 136.4, 130.8, 129.7, 126.9, 122.2, 84.62, 41.5, 31.9, 27.5, 12.5, 1.0, 0.7; **IR** (neat) 3060 (m), 2962 (s), 2875 (s), 1594 (m), 1443 (s), 1375 (m), 1323 (m), 1250 (s), 1197 (m), 1137 (m), 1107 (s), 1068 (s), 1040 (s), 1014 (s), 960 (s), 875 (s), 826 (s), 789 (s), 746 (s), 705 (m), 653 (m) cm^{-1}; **HRMS** (CI$^+$) *m/z* calculated for $C_{13}H_{19}SiO$ [M-H]$^+$ 221.1362, found 221.1368.



1,1,3-Trimethyl-1,3-dihydrobenzo[*c*][1,2]oxasilole (1d): To a cooled solution of benzaldehyde **10** (2.63 g, 24.8 mmol, 1.00 equiv) in hexanes (125 ml, pre-dried over $MgSO_4$) and Et_2O (100 ml) at 0 °C was added MeLi (1.36 M in Et_2O, 29.7 mmol, 1.20 equiv) dropwise. The resulting solution was allowed to warm to room temperature and stirred for 5 h, at which time *n*-BuLi (12.1 mL, 2.45 M in hexanes, 29.7 mmol, 1.20 equiv) was added dropwise. The flask was then fitted with a reflux condenser and the system was heated to reflux (75 °C) for 16 h. A dark solution resulted and the reaction mixture was allowed to cool to room temperature. The reflux condenser was removed and the reaction mixture was cooled to −78 °C and Me_2SiHCl (5.20 ml, 54.6 mmol, 2.20 equiv) was added dropwise. The reaction mixture was allowed to slowly warm to room temperature and stirred for 12 h. The reaction mixture was quenched by addition of *t*-BuOH (20 mL) and stirred for 5 h, followed by the addition of H_2O (20 ml) and stirred for another 2 h. The aqueous phase was extracted with Et_2O (2 x 25 mL) and the combined organic layers were washed with brine, dried ($MgSO_4$), filtered and concentrated under reduced pressure. Flash chromatography on water-washed silica gel (100% hexanes then 1% Et_2O/Hexanes) followed by Kugelrohr distillation (55 °C, 0.01 mmHg) provided **1d** (1.55 g, 8.69 mmol, 35 % yield) as a colorless oil: $\mathbf{R}_{\boldsymbol{f}}$ 0.45 (5% Et_2O in hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.1 Hz, 1 H), 7.40 (dt, *J* = 0.8, 7.5 Hz, 1 H), 7.30 (t, *J* = 7.3 Hz, 1 H), 7.22 (d, *J* = 7.7 Hz, 1 H), 5.34 (q, *J* = 6.5 Hz, 1 H), 1.51 (d, *J* = 6.5 Hz, 3 H), 0.41 (s, 3 H), 0.37 (s, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 154.5, 135.2, 131.0, 129.8, 127.0, 122.3, 78.0, 25.4, 1.7, 0.6; **IR** (neat) 3060 (m), 2968 (s), 2924 (m), 2867 (m), 1595 (m), 1444 (s), 1368 (m), 1318 (s), 1251 (s), 1199 (m), 1137 (m), 1086 (s), 1028 (s), 929 (s), 855 (s), 828 (s), 793 (s), 759 (s), 742 (s), 696 (m), 653 (m) cm^{-1}; **HRMS** (CI^+) *m/z* calculated for $C_9H_{11}SiO$ $[M-Me]^+$ 163.0579, found 163.0578.



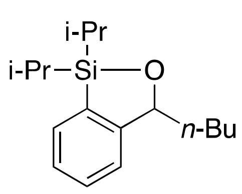
1,1,3,3-Tetramethyl-1,3-dihydrobenzo[*c*][1,2]oxasilole (1f):[1] Following a previously reported procedure,[1] methyl 2-bromobenzoate (9.70 g, 45.0 mmol, 1.00 equiv) was dissolved in Et_2O (100 ml) and cooled to 0 °C. Methylmagnesium bromide (99 mL, 1.0 M in Bu_2O, 99.0 mmol, 2.20 equiv) was then added via cannula into the reaction mixture. The resulting solution was heated to reflux (40 °C) for 2 h then cooled to room temperature before being quenched with sat. aq. NH_4Cl (75 mL). The aqueous phase extracted with Et_2O (2 x 50 mL). The combined organic layers were washed with brine, dried ($MgSO_4$), filtered and concentrated under reduced pressure to afford 2-(2-

bromophenyl)propan-2-ol (**S3**) (8.30 g, ca. 38.8 mmol, 1.00 equiv), which was used without further purification.

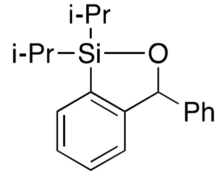
To the crude alcohol was added conc. HCl (3 drops) and 3,4-dihydro-2H-pyran (**S3**) (4.07 g, 48.5 mmol, 1.20 equiv) and stirred neat at room temperature for 24 h. The mixture was diluted with Et_2O (50 mL), and washed with a sat. aq. $NaHCO_3$ (25 mL). The aqueous layer was extracted with Et_2O (2 x 50 mL) and the combined organic layers were washed with brine, dried ($MgSO_4$), filtered and concentrated under reduced pressure to afford 2-((2-(2-bromophenyl)propan-2-yl)oxy)tetrahydro-2*H*-pyran (**S4**) (8.30 g, ca. 38.8 mmol, 1.00 equiv) which was used without further purification.

The crude THP-protected product (**S4**) was dissolved in THF (50 mL) and *n*-BuLi (23.3 mL, 2.00 M in hexanes, 46.6 mmol, 1.20 equiv) was added dropwise at –78 °C. The reaction mixture was stirred for 1 h, followed by the addition of Me_2SiHCl (6.30 mL, 58.2 mmol, 1.50 equiv) at –78 °C. The resulting reaction mixture was allowed to warm to room temperature and stirred for 12 h. The reaction mixture was quenched by addition of H_2O (50 ml). The aqueous phase was then extracted with Et_2O (2 x 30 mL) and the combined organic layers were washed with brine, dried ($MgSO_4$), filtered and concentrated under reduced pressure to afford dimethyl(2-(2-((tetrahydro-2*H*-pyran-2-yl)oxy)propan-2-yl)phenyl)silane (**S5**) (8.30 g, ca. 38.8 mmol, 1.00 equiv) which was used without further purification.

To this crude material (**S5**) was added MeOH (50 mL) and *p*-toluenesulfonic acid monohydrate (370 mg, 1.94 mmol, 0.05 equiv), and the mixture was stirred at room temperature for 12 h before concentration under reduced pressure. The residue was diluted with Et_2O (25 mL), and washed with a sat. aq. $NaHCO_3$ (25 mL). The aqueous layer was extracted with Et_2O (2 x 25 mL), and the combined organic layers were washed with brine, dried ($MgSO_4$), filtered and concentrated under reduced pressure. Kugelrohr distillation (60 °C, 0.01 mmHg) provided **1f** (3.27 g, 17.0 mmol, 38% yield from methyl 2-bromobenzoate) as a colorless oil. Analytical data matches that which has been previously reported:[2] **R*f*** 0.3 (1% Et_2O in hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.52 (dt, *J* = 7.1, 0.9 Hz, 1 H), 7.41 (td, *J* = 7.5, 1.3 Hz, 1 H), 7.30 (dt, *J* = 7.2, 0.9 Hz, 1 H), 7.22 (d, *J* = 7.7 Hz, 1 H), 1.55 (s, 6 H), 0.39 (s, 6 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 157.6, 134.4, 130.6, 129.7, 126.6, 122.1, 83.5, 32.1, 1.37.



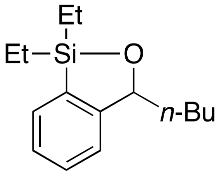
3-Butyl-1,1-diisopropyl-1,3-dihydrobenzo[*c*][1,2]oxasilole (2c): To a cooled solution of benzaldehyde **10** (3.08 g, 29.0 mmol, 1.00 equiv) in hexanes (125 ml, pre-dried over $MgSO_4$) and Et_2O (100 ml) at 0 °C was added *n*-BuLi (27.8 mL, 2.3 M in hexanes, 63.9 mmol, 2.20 equiv) dropwise. The reaction mixture was allowed to warm to room temperature and was stirred for 30 minutes. The flask was then fitted with a reflux condenser and the system was heated to reflux (75 °C) for 16 h. A dark solution resulted and was allowed to cool to room temperature, the reflux condenser was removed and the reaction mixture was cooled to −78 °C and *i*-Pr$_2$SiHCl (10.9 ml, 63.8 mmol, 2.20 equiv) was added dropwise. The reaction mixture was allowed to slowly warm to room temperature and stirred for 12 h. The reaction mixture was quenched by addition of 3M HCl in MeOH (40 mL) at 0 °C and stirred for 12 h at room temperature. Water (100 mL) was added and stirred for another 2 h and the aqueous phase extracted with Et$_2$O (2 x 50 mL). The combined organic layers were washed with brine, dried (MgSO$_4$), filtered and concentrated under reduced pressure. Flash chromatography on silica (1% Et$_2$O/Hexanes) provided **2c** (5.94 g, 21.5 mmol, 74% yield) as a colorless oil: **R*f*** 0.70 (5% Et$_2$O in hexanes); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.53 (d, *J* = 7.1 Hz, 1 H), 7.38 (t, *J* = 7.5 Hz, 1 H), 7.27 (t, *J* = 7.1 Hz, 1 H), 7.20 (d, *J* = 7.7 Hz, 1 H), 5.18-5.14 (m, 1 H), 1.94-1.86 (m, 1 H), 1.60-1.48 (m, 3 H), 1.45-1.30 (m, 2 H), 1.25-1.16 (m, 2 H), 1.06 (d, *J* = 6.7 Hz, 3 H), 1.05 (d, *J* = 7.1 Hz, 3 H), 1.00 (d, *J* = 7.5 Hz, 3 H), 0.93 (d, *J* = 7.3 Hz, 3 H), 0.92 (t, *J* = 7.3 Hz, 3 H); **^{13}C NMR** (125 MHz, CDCl$_3$) δ 154.7, 132.4, 132.2, 129.5, 126.7, 122.2, 82.3, 39.1, 28.1, 23.0, 17.6, 17.5, 17.2, 17.1, 14.2, 13.4, 12.9; **IR** (neat) 3059 (m), 3000 (m), 2941 (s), 2864 (s), 1595 (m), 1464 (s), 1443 (m), 1381 (m), 1261 (m), 1111 (m), 1080 (s), 1054 (m), 1012 (m), 988 (m), 973 (m), 917 (s), 880 (s), 846 (m), 831 (m), 816 (m), 749 (s), 716 (s), 668 (s), 648 (m), 612 (m) cm^{-1}; **HRMS** (CI$^+$) *m/z* calculated for C$_{14}$H$_{21}$SiO [M-C$_3$H$_7$]$^+$ 233.1726, found 233.1726.



1,1-Diisopropyl-3-phenyl-1,3-dihydrobenzo[*c*][1,2]oxasilole (2d): To the previously prepared (2-bromophenyl)(phenyl)methanol (**S1**) (5.18 g, 19.7 mmol, 1.00 equiv) dissolved in THF (50 mL) was added *n*-BuLi (19.0 mL, 2.28 M in hexanes, 43.3 mmol 2.20 equiv) dropwise at –78 °C. The reaction mixture was stirred for 1 h, followed by the addition of *i*-Pr$_2$SiHCl (7.39 mL, 43.3 mmol, 2.20 equiv) at –78 °C. The resulting reaction mixture was allowed to warm to room temperature and stirred for 12 h. The slurry was quenched by addition of 3M HCl in MeOH (40 mL) at 0 °C and stirred for 4 h at room temperature. Water (100 mL) was added and stirred for another 2 h and the aqueous phase extracted with Et$_2$O (2 x 50 mL). The combined organic layers were washed with brine, dried (MgSO$_4$), filtered and concentrated under reduced pressure. Flash chromatography on silica (1% Et$_2$O/Hexanes) provided **2d** (4.12 g, 13.9 mmol, 71% yield) as a colorless oil: **R*f*** 0.45 (5% Et$_2$O in hexanes); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.63-7.59 (m, 1 H), 7.37-7.27 (m, 7 H), 6.99 (d, *J* = 6.9 Hz, 1 H), 6.12 (s, 1 H), 1.39-1.24 (m, 2 H), 1.16 (d, *J* = 7.5 Hz, 3 H), 1.13 (d, *J* = 7.5 Hz, 3 H), 1.06 (d, *J* = 5.7 Hz, 3 H), 1.04 (d, *J* = 5.7 Hz, 3 H); **^{13}C NMR**

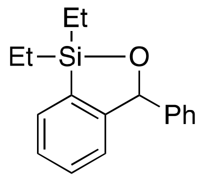
(125 MHz, $CDCl_3$) δ 153.4, 143.8, 132.7, 131.9, 129.8, 128.6, 128.0, 127.8, 127.0, 123.9, 84.6, 17.7, 17.2, 13.6, 13.3; **IR** (neat) 3061 (m), 3031 (m), 3000 (m), 2942 (s), 2891 (m), 2864 (s), 1592 (m), 1494 (m), 1463 (s), 1442 (s), 1383 (m), 1263 (m), 1182 (m), 1133 (m), 1077 (m), 1065 (s), 1038 (s), 1014 (s), 988 (s), 919 (m), 881 (m), 815 (s), 747 (s), 732 (s), 713 (s), 698 (s), 669 (s), 633 (m) cm^{-1}; **HRMS** (CI^+) *m/z* calculated for $C_{16}H_{17}SiO$ $[M-C_3H_7]^+$ 253.1049, found 253.1056.

Preparation of Et_2SiHCl from commercially available Et_2SiH_2:[4] Anhydrous $CuCl_2$ (96.5 g, 714 mmol, 2.10 equiv) was dried under vacuum at 200 °C in a 2000 two-necked RBF for 12 hours with stirring. Upon cooling to room temperature, CuI (3.24 g, 17.0 mmol, 0.05 equiv), Et_2O (680 mL ~ 0.5 M) and Et_2SiH_2 (30.0 g, 340 mmol, 1.00 equiv) were successively added and the resulting slurry was stirred at room temperature for 43 hours. After 4 hours, it was noted that reaction went from and orange brown to light grey in color with black precipitate. After 43 hours, the reaction mixture was filtered under N_2 atmosphere and the flask rinsed with Et_2O (2 x 50 mL). The Et_2O was distilled (35 °C) and the reaction mixture transferred to a 100 mL flame-dried RBF via syringe, carefully leaving behind any remaining Cu salts. Kugelrohr distillation (95-100 °C) of this crude reaction mixture under N_2 provided Et_2SiHCl (32.2 g, 263 mmol, 77% yield) whose analytical data matches that which has been previously reported.[4]

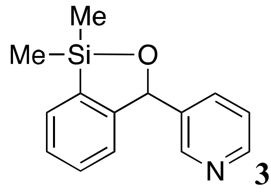


3-Butyl-1,1-diethyl-1,3-dihydrobenzo[*c*][1,2]oxasilole (2a): To a cooled solution of benzaldehyde **10** (10.0 g, 94.2 mmol, 1.00 equiv) in hexanes (500 mL, pre-dried over $MgSO_4$) and Et_2O (400 mL) at 0 °C was added *n*-BuLi (86.4 mL, 2.40 M in hexanes, 2.20 equiv) dropwise. The reaction mixture was allowed to warm to room temperature and was stirred for 30 minutes. The flask was then fitted with a reflux condenser and the system was heated to reflux (75 °C) for 16 h. A dark solution resulted and the reaction mixture was allowed to cool to room temperature. The reflux condenser was removed and the reaction mixture was cooled to −78 °C and Et_2SiHCl (28.9 mL, 207 mmol, 2.20 equiv) was added dropwise. The reaction mixture was allowed to slowly warm to room temperature and stirred for 8 h. The resulting pale yellow slurry was then quenched with H_2O (300 mL) with vigorous evolution of H_2 gas observed. The reaction mixture was allowed to stir for 5 h and the aqueous layer extracted with Et_2O (3 × 100 mL). The combined organic layers were washed with brine, dried ($MgSO_4$), filtered and concentrated under reduced pressure. Flash chromatography on silica (100 % hexanes to 1% EtOAc in hexanes) provided **2a** (6.2 g, 25.0 mmol, 53% yield) as a colorless oil: **R_f** 0.45 (1% EtOAc in hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54 (d, J = 7.1 Hz, 1H), 7.39 (td, J = 7.5, 1.0 Hz, 1H), 7.28 (t, J = 7.2 Hz, 1H), 7.22 (d, J = 7.5 Hz, 1H), 5.22 (dd, J = 8.0, 3.3 Hz, 1H), 1.92 (m, 1H), 1.59 (m, 1H), 1.52-1.30 (m, 4H), 0.99 (t, J = 7.7 Hz, 3H), 0.94-

0.88 (m, 6H), 0.88-0.78 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 154.2, 133.7, 131.6, 129.6, 126.8, 122.3, 82.12, 39.1, 27.8, 22.9, 14.2, 7.38, 7.16, 6.88, 6.60; **IR** (neat) 3058 (m), 2956 (s), 2932 (m), 2874 (m), 1459 (s), 1080 (s), 1013 (m), 916 (s), 741 (s) cm^{-1}; **HRMS** (CI^{+}) *m/z* calculated for $C_{15}H_{24}OSi$ $[M]^{+}$ 248.1596, found 248.1593.

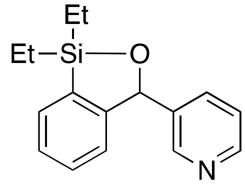


1,1-Diethyl-3-phenyl-1,3-dihydrobenzo[*c*][1,2]oxasilole (2b): To the previously prepared (2-bromophenyl)(phenyl)methanol (**S1**) (4.16 g, 15.8 mmol, 1.00 equiv) dissolved in THF (120 mL) was added *n*-BuLi (14.6 mL, 2.39 M in hexanes, 34.8 mmol, 2.20 equiv) dropwise at –78 °C. The reaction mixture was stirred for 1 h, followed by the addition of Et_2SiHCl (4.84 mL, 34.8 mmol, 2.20 equiv) at –78 °C. The resulting pale yellow slurry was then quenched with H_2O (300 mL) with vigorous evolution of H_2 gas observed. The reaction mixture was allowed to stir for 5 h and the aqueous phase was extracted with Et_2O (2 x 50 mL), the combined organic layers were washed with brine, dried ($MgSO_4$), filtered and concentrated under reduced pressure. Flash chromatography on silica (100% hexanes to 5% Et_2O in hexanes) provided **2b** (1.74 g, 6.48 mmol, 41% yield) as a colorless oil: **R_f** 0.45 (5% Et_2O in hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.63-7.60 (m, 1 H), 7.36-7.27 (m, 7 H), 7.02 (d, *J* = 7.1 Hz, 1 H), 6.16 (s, 1 H), 1.08 (t, *J* = 7.9 Hz, 3 H), 1.02-0.95 (m, 5 H), 0.95-0.82 (m, 2 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 153.2, 143.9, 133.6, 131.4, 129.9, 128.6, 128.0, 127.5, 127.1, 123.9, 84.4, 7.4, 7.1, 7.0, 6.7; **IR** (neat) 3059 (m), 2999 (m), 2956 (s), 2878 (s), 1595 (m), 1486 (m), 1451 (s), 1412 (m), 1343 (w), 1265 (m), 1236 (m), 1182 (m), 1133 (m), 1012 (bs), 964 (m), 926 (m), 871 (m), 817 (s), 739 (bs), 661 (m), 629 (m) cm^{-1}; **HRMS** (CI^{+}) *m/z* calculated for $C_{17}H_{21}SiO$ $[M+H]^{+}$ 269.1362, found 269.1366.

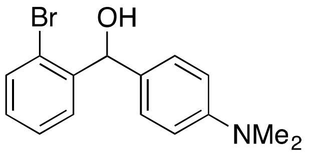


3-(1,1-Dimethyl-1,3-dihydrobenzo[*c*][1,2]oxasilol-3-yl)pyridine (3a): To a cooled solution of Et_2O (420 mL) containing *n*-BuLi (48.7 mL, 2.00 M in hexanes, 1.30 equiv) at −78 °C was added 3-bromopyridine (20.0 g, 127 mmol, 1.20 equiv) dropwise. The resulting yellow slurry was allowed to stir at −78 °C for 30 min. 2-Bromobenzaldehyde (19.5 g, 106 mmol, 1.00 equiv) was added dropwise and the reaction mixture was allowed to stir for 5 h at −78 °C. The reaction was then warmed to 0 °C and quenched with 3M aq. HCl (100 mL). The organic layer was washed with another portion of 3M aq. HCl (50 mL). The acidic aqueous layers were collected and neutralized to pH 8-9 with 1M aq. NaOH (350 mL), producing a white turbid mixture that was extracted with Et_2O (3 × 150 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure. Flash chromatography on silica (0.5% to 1% to 5% MeOH in CH_2Cl_2) provided of (2-bromophenyl)(pyridin-3-yl)methanol (**S6**) (23.6 g, 89.4 mmol, 85% yield) as an off-white crystalline solid: Analytical data matches that which has been previously reported:[10] **R**$_f$ 0.35 (5% MeOH in CH_2Cl_2); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 1.8 Hz, 1H), 8.41 (dd, *J* = 4.7, 1.1 Hz, 1H), 7.69 (td, *J* = 7.6, 1.6 Hz, 1H), 7.62 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.53 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1 H), 7.23 (dd, *J* = 7.8, 4.8 Hz, 1H), 7.16 (td, *J* = 7.5, 1.5 Hz, 1H), 6.21 (s, 1 H), 3.93 (s, 1 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 148.9, 148.7, 142.1, 138.2, 134.9, 133.1, 129.6, 128.5, 128.1, 123.6, 122.7, 72.7.

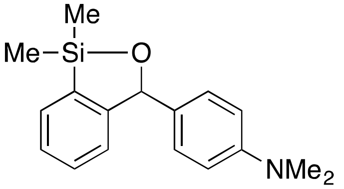
To a cooled solution of (2-bromophenyl)(pyridin-3-yl)methanol (**S6**) (7.00 g, 26.5 mmol, 1.00 equiv) in a mixture (1:1) of THF (100 mL) and Et_2O (100 mL) at −78 °C was added *n*-BuLi (29.2 mL, 2.00 M in hexanes, 2.20 equiv) dropwise. The resulting dark yellow slurry was allowed to stir at −78 °C for 30 min and Me_2SiHCl (6.50 mL, 58.3 mmol, 2.20 equiv) was added dropwise. The reaction mixture was allowed to slowly warm to room temperature and stirred for 12 h. The resulting orange slurry was then quenched with H_2O (100 mL) with vigorous evolution of H_2 gas observed. The reaction mixture was allowed to stir for 5 h and extracted with Et_2O (3 × 50 mL). The combined organic layers were collected and washed with 1M aq. HCl (3 ×50 mL). The acidic aqueous layers were collected and neutralized to pH 8-9 with 1M aq. NaOH (150 mL) producing a white turbid mixture that was extracted with Et_2O (3 × 100 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure. Flash chromatography on silica (0.5% to 1% to 5% MeOH in CH_2Cl_2) followed by Kugelrohr distillation (135 - 150 °C, 0.01 mmHg) provided **3a** (3.14 g, 13.0 mmol, 49% yield) as an off-white amorphous solid: **R**$_f$ 0.2 (5% MeOH in CH_2Cl_2); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.61 (d, *J* = 1.7 Hz, 1H), 8.53 (dd, *J* = 4.7, 1.5 Hz, 1H), 7.63 (m, 1 H), 7.53 (dt, *J* = 7.8, 1.8 Hz, 1H), 7.33 (m, 2 H), 7.25 (m, 1 H), 7.00 (m, 1 H), 6.20 (s, 1 H), 0.53 (s, 3 H), 0.46 (s, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 151.4, 149.3, 148.8, 139.3, 135.2, 134.7, 131.0, 130.1, 127.6, 123.6, 123.5, 81.7, 1.23, 0.56; **IR** (neat) 3057 (m), 2959 (s), 1662 (m), 1579 (m), 1475 (s), 1427 (s), 1252 (s), 1181 (s), 1136 (s), 1051 (m), 860 (m), 822 (s), 791 (s), 750 (s), 713 (s) cm^{-1}; **HRMS** (ES$^+$) *m/z* calculated for $C_{14}H_{16}NOSi$ $[M+H]^+$ 242.1001, found 242.0993.



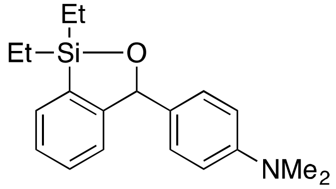
3-(1,1-Diethyl-1,3-dihydrobenzo[*c*][1,2]oxasilol-3-yl)pyridine (3b): To a cooled solution of (2-bromophenyl)(pyridin-3-yl)methanol (**S6**) (7.00 g, 26.5 mmol, 1.00 equiv) in a mixture (1 : 1) of dry THF (100 mL) and dry Et_2O (100 mL) at −78 °C was added *n*-BuLi (26.5 mL, 2.20 M in hexanes, 2.20 equiv) dropwise. The resulting dark yellow slurry was allowed to stir at −78 °C for 30 min and Et_2SiHCl (8.15 mL, 58.3 mmol, 2.20 equiv) was added dropwise. The reaction mixture was allowed to slowly warm to room temperature and stirred for 12 h. The resulting red-brown solution was then quenched with H_2O (100 mL) with vigorous evolution of H_2 gas observed. The reaction mixture was allowed to stir for 5 h and extracted with Et_2O (3 × 50 mL). The combined organic layers were collected and washed with 1M aq. HCl (3 ×50 mL). The acidic aqueous layers were collected and neutralized to pH 8-9 with 1M aq. NaOH (150 mL) producing a white turbid mixture that was extracted with Et_2O (3 × 100 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure. Flash chromatography on silica (0.5% to 1% to 3% MeOH in CH_2Cl_2) provided **3b** (3.6 g, 13.4 mmol, 51% yield) as pale yellow oil: **R**$_f$ 0.45 (5% MeOH in CH_2Cl_2); **^{1}H NMR** (500 MHz, $CDCl_3$) δ **^{1}H NMR** (500MHz, $CDCl_3$) δ 8.62 (d, *J* = 1.0 Hz, 1H), 8.53 (dd, *J* = 4.6, 1.2 Hz, 1H), 7.62 (m, 1 H), 7.53 (dt, *J* = 7.7, 1.6 Hz, 1H), 7.33 (m, 2 H), 7.23 (m, 1 H), 6.99 (d, *J* = 6.6 Hz, 1H), 6.19 (s, 1 H), 1.05 (m, 3 H), 1.0-0.88 (m, 7 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 152.0, 149.4, 149.2, 139.3, 134.8, 133.6, 131.5, 130.1, 127.5, 123.7, 123.6, 81.9, 7.25, 7.00, 6.87, 6.51; **IR** (neat) 3057 (m), 2957 (m), 2876 (s), 2942 (s), 1580 (s), 1425 (m), 1235 (s), 1183 (s), 1134 (s), 1050 (m), 1017 (m), 817 (m), 744 (s) cm^{-1}; **HRMS** (ES^{+}) *m/z* calculated for $C_{16}H_{20}NOSi$ $[M+H]^+$ 270.1314, found 270.1314.



(2-Bromophenyl)(4-(dimethylamino)phenyl)methanol (S9): In a two-necked 500 mL round-bottom flask, Mg turnings (10.5 g, 432 mmol, 10.0 equiv) were flame-dried under vacuum. Upon cooling to room temperature, THF (72 mL), 4-bromo-*N*,*N*-dimethylaniline (12.9 g, 64.9 mmol, 1.50 equiv) as a solution in THF (72 mL) and a crystal of I_2 were added. The flask fitted with a reflux condenser and the solution vigorously stirred. Once the resulting exotherm had subsided, the reaction mixture was heated to reflux (70 °C) for 1 h. This Grignard reagent was then allowed to cool to room temperature and added to a cooled solution of 2-bromobenzaldehyde (8.00 g, 43.2 mmol, 1.00 equiv) in THF (87 mL) at 0°C via cannula over 10 min. The reaction was then allowed to reach room temperature and stirred for 12 h and quenched with sat. aq. NH_4Cl (100 mL). The aqueous phase was then extracted with EtOAc (3 x 50 mL). The combined organic layers were washed with brine, dried (Na_2SO_4) and concentrated under reduced pressure. Flash chromatography on silica (3% to 10% EtOAc in hexanes) provided of the desired (2-bromophenyl)(4-(dimethylamino)phenyl)methanol (**S9**) (12.6 g, 41.2 mmol, 95% yield) as a blue crystalline solid: **R**$_f$ 0.2 (10% EtOAc in hexanes); **^{1}H NMR** (500MHz, $CDCl_3$) δ 7.71 (dd, *J* = 7.7, 1.5 Hz, 1 H), 7.53 (dd, *J* = 7.9, 1.0 Hz, 1 H), 7.37 (td, *J* = 7.6, 1.0 Hz, 1 H), 7.24 (m, 2 H), 7.14 (td, *J* = 7.7, 1.5 Hz, 1 H), 6.69 (m, 2 H), 6.07 (s, 1 H), 2.94 (s, 6 H), 2.58 (bs, 1 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 150.3, 143.2, 132.9, 130.3, 128.8, 128.6, 128.4, 128.3, 127.7, 122.8, 112.8, 112.6, 112.3, 74.8, 40.7; **IR** (neat) 3387 (bs), 2887 (m), 2802 (s), 1613 (s), 1521 (s), 1352 (s), 1162 (s), 1017 (m), 810 (s), 758 (s), 741 (s) cm^{-1}; **HRMS** (ES$^+$) *m/z* calculated for $C_{15}H_{17}NOBr$ [M+H]$^+$ 306.0494, found 306.0497.



4-(1,1-Dimethyl-1,3-dihydrobenzo[*c*][1,2]oxasilol-3-yl)-*N*,*N*-dimethylaniline (3c): (2-Bromophenyl)(4-(dimethylamino)phenyl)methanol (**S9**) (2.33 g, 7.61 mmol, 1.00 equiv) was dissolved in THF (25 mL) and *n*-BuLi (7.6 mL, 2.20 M in hexanes, 16.7 mmol, 2.20 equiv) was added dropwise at –78 °C. The reaction mixture was stirred for 45 min, followed by the addition of Me_2SiHCl (2.00 mL, 16.7 mmol, 2.20 equiv) at –78 °C. The resulting reaction mixture was allowed to warm to room temperature and stirred for 12 h. The slurry was quenched with H_2O (50 mL) with vigorous evolution of H_2 gas observed. The reaction mixture was allowed to stir for 5 h and extracted with EtOAc (3 × 25 mL). The combined organic layers were collected and washed with 3M aq. HCl (3 × 25 mL). The acidic aqueous layers were collected and neutralized to pH 8-9 with 1M aq. NaOH producing a white turbid mixture that was extracted with Et_2O (3 × 75 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure. Flash chromatography on silica (5% Et_2O in hexanes) provided **3c** (795 mg, 2.81 mmol, 37% yield) as an yellow crystalline solid: **R*f*** 0.1 (25% EtOAc in hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 6.0, 1.8 Hz, 1 H), 7.33 (m, 2 H), 7.14 (m, 2 H), 7.06 (m, 1 H), 6.72 (m, 2 H), 6.14 (s, 1 H), 2.95 (s, 6 H), 0.52 (s, 3 H), 0.46 (s, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 153.3, 150.5, 135.5, 132.1, 130.6, 129.8, 128.5, 128.3, 127.1, 124.1, 112.7, 84.2, 40.8, 1.57, 0.66; **IR** (neat) 3419 (bs), 2921 (m), 1615 (s), 1523 (s), 1443 (s), 1348 (s), 1251 (s), 1163 (s), 1134 (s), 861 (s), 822 (s), 789 (s), 743 (s) cm^{-1}; **HRMS** (CI$^+$) *m/z* calculated for $C_{17}H_{22}NOSi$ [M+H]$^+$ 284.1471, found 284.1459.

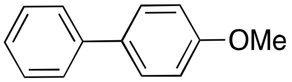


4-(1,1-Diethyl-1,3-dihydrobenzo[*c*][1,2]oxasilol-3-yl)-*N*,*N*-dimethylaniline (3d): (2-Bromophenyl)(4-(dimethylamino)phenyl)methanol (**S9**) (7.00 g, 22.9 mmol, 1.00 equiv) dissolved in THF (230 mL), *n*-BuLi (22.9 mL, 2.20 M in hexanes, 50.4 mmol, 2.20 equiv) was added dropwise at –78 °C. The reaction mixture was stirred for 45 min, followed by the addition of Et_2SiHCl (7.00 mL, 50.4 mmol, 2.20 equiv) at –78 °C. The resulting reaction mixture was allowed to warm to room temperature and stirred for 12 h. The slurry was quenched with H_2O (100 mL) with vigorous evolution of H_2 gas observed. The reaction mixture was allowed to stir for 5 h and extracted with EtOAc (3 × 50 mL). The combined organic layers were collected and washed with 3M aq. HCl (3 × 50 mL). The acidic aqueous layers were collected and neutralized to pH 8-9 with 1M aq. NaOH (300 mL) producing a white turbid mixture that was extracted with Et_2O (3 × 100 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure. Flash chromatography on silica (5% EtOAc in hexanes) provided **3d** (3.6 g, 11.6 mmol, 51% yield) as an yellow oil: **R*f*** 0.3 (15% EtOAc in hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 6.0, 1.5 Hz, 1 H), 7.37-7.30 (m, 2 H), 7.17-7.15 (m, 2 H), 7.06 (m, 1 H), 6.74- 6.70 (m, 2 H), 6.15 (s, 1 H), 2.95 (s, 6 H), 1.08 (m, 3 H), 1.04-0.88 (m, 7 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 153.8, 150.4, 133.8, 132.0, 131.2, 129.7, 128.7, 126.8, 124.1, 112.5, 84.3, 40.7, 7.43, 7.11, 6.99, 6.65; **IR** (neat) 2955 (m), 2875 (m), 2800 (s), 1614 (s), 1523 (s), 1444 (m), 1348 (s), 1230 (s), 1162 (s), 1132 (s), 997 (m), 949 (s), 823 (m), 723 (m) cm^{-1}; **HRMS** (ES^+) *m/z* calculated for $C_{19}H_{26}NOSi$ $[M+H]^+$ 312.1784, found 312.1783.

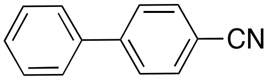
General Procedure A: To a cooled solution of siloxane (0.81 mmol, 1.8 equiv) in Et_2O (1.2 mL) for siloxanes **3a-d** or THF (1.2 mL) for siloxanes **1**, **1a-f**, **2a-d**, at room temperature was added a solution of PhLi in Bu_2O (0.68 mmol, 1.5 equiv) and allowed to stir for 2 h. After 1.5 h had elapsed following PhLi addition, in a separate flask were combined $PdCl_2$ (2.50 mg, 0.014 mmol, 0.03 equiv), CuI (8.60 mg, 0.045 mmol, 0.1 equiv) and dpca (6.7 mg, 0.018 mmol, 0.04 equiv) in THF (1 mL) at room temperature and stirred for 30 min. The aryl halide (0.45 mmol, 1.0 equiv) was added to the orange slurry, followed by addition of the siloxane/PhLi reaction mixture by cannula (flask rinsed with 0.5 mL of THF). After 2 h at room temperature, the reaction mixture was diluted with Et_2O (2 mL) and quenched according to the siloxane used in the reaction; **1**, **1a-f**, **2a-d** quenched with sat. aq. NH_4Cl (5 mL); **3a-b** quenched with 1M aq. HCl (5 mL); **3c-d** quenched with 3M aq. HCl (5 mL).

For siloxanes **1**, **1a-f**, **2a-d** the aqueous layer was extracted with Et_2O (3 × 5 mL) and the combined organic layers were dried ($MgSO_4$), filtered, and concentrated under reduced pressure. Flash chromatography provided the cross-coupled product and the recovered siloxane (where possible as with siloxanes **2a-d**).

For siloxanes **3a-d**, the organic layer was washed with either 1M or 3M aq. HCl (3 × 5 mL) (according to siloxane, see above), and the acidic aqueous layers were collected. The organic layer was then washed with sat. aq. $NaHCO_3$ (5 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure. Flash chromatography provided the cross-coupled product. The acidic aqueous layer was then basified to pH 8-9 with 1M aq. NaOH, producing a white turbid mixture that was then extracted with Et_2O (3 × 50 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated under reduced pressure to provide the recovered siloxane.



4-Methoxy-1,1'-bipheny (S10): Following General Procedure A, the product was purified by chromatography on SiO_2 (1% EtOAc in hexanes) to afford **S10** (80.0 mg, 0.43 mmol, 96% with siloxane **2a**, 163 mg, 81% recovery; 81.0 mg, 0.44 mmol, 98% with siloxane **2b**, 185 mg, 85% recovery; 81.0 mg, 0.44 mmol, 98% with siloxane **3b**, 210 mg, 96% recovery; 81.0 mg, 0.44 mmol, 98% with siloxane **3d**, 242 mg, 96% recovery) as a colorless solid. Analytical data matches that which has been previously reported for **S10**:[11] **R_f** 0.5 (1% EtOAc in hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57-7.53 (m, 4 H), 7.42 (t, *J* = 7.6 Hz, 2 H), 7.31 (t, *J* = 7.4 Hz, 1 H), 6.99 (d, *J* = 8.7 Hz, 2 H), 3.86 (s, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 159.3, 141.0, 133.9, 128.9, 128.3, 126.9, 126.8, 114.3, 55.5.

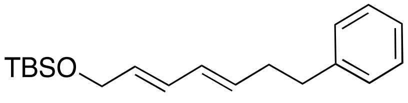


[1,1'-Biphenyl]-4-carbonitrile (S11): Following General Procedure A, the product was purified by chromatography on SiO_2 (1% EtOAc in hexanes) to afford **S11** (74.0 mg, 0.41 mmol, 92% with siloxane **2a**, 175 mg, 87% recovery; 73.0 mg, 0.40 mmol, 91% with siloxane **2b**, 193 mg, 89% recovery; 77.0 mg, 0.43 mmol, 96% with siloxane **3b**, 214 mg, 98% recovery; 75.0 mg, 0.42 mmol, 94% with siloxane **3d**, 242 mg, 96% recovery) as a colorless solid. Analytical data matches that which has been previously reported for **S11**:[12] **R_f** 0.3 (1% EtOAc in hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) 7.73 (d, *J* = 8.3 Hz, 2 H), 7.69 (d, *J* = 8.4 Hz, 2 H), 7.59 (d, *J* = 7.4 Hz, 2 H), 7.49 (t, *J* = 7.2 Hz, 2 H), 7.43 (t, *J* = 7.3 Hz, 1 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 145.8, 139.3, 132.8, 129.3, 128.8, 127.9, 127.4, 119.1, 111.1.

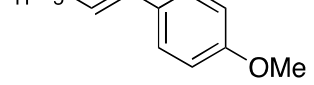
General Procedure B: To a solution of alkenyl iodide or aryl iodide (0.68 mmol, 1.50 equiv) in Et_2O (1 mL) for siloxanes **3a-d** or THF (1 mL) for siloxanes **1**, **1a-f**, **2a-d**, at –78 °C was added *t*-BuLi in pentane (1.35 mmol, 3.00 equiv), and a white or yellow (depending on alkenyl iodide or aryl idodide) slurry developed. The reaction mixture was allowed to stir for 40 min at –78 °C and 20 min at room temperature, at which time a solution of siloxane (0.81 mmol, 1.80 equiv) in THF or Et_2O, according to siloxane as noted above (0.5 mL + 0.2 mL rinse), was added and allowed to stir at room temperature for 2 h. After 1.5 h had elapsed following siloxane addition, in a separate flask were combined $PdCl_2$ (2.50 mg, 0.014 mmol, 0.03 equiv), CuI (8.60 mg, 0.045 mmol, 0.1 equiv) and dpca (6.7 mg, 0.018 mmol, 0.04 equiv) in THF (1 mL) at room temperature and stirred for 30 min. The alkenyl halide or aryl iodide (0.45 mmol, 1.00 equiv) was added as a solution in THF (0.3 mL) to the orange slurry, immediately followed by addition of the siloxane reaction mixture by cannula (flask rinsed with 0.5 mL of THF). After 2-12 h at room temperature, the reaction mixture was diluted with Et_2O (2 mL) and quenched according to the siloxane used in the reaction; **1**, **1a-f**, **2a-d** quenched with sat. aq. NH_4Cl (5 mL); **3a-b** quenched with 1M aq. HCl (5 mL); **3c-d** quenched with 3M aq. HCl (5 mL).

For siloxanes **1**, **1a-f**, **2a-d**, the aqueous layer was extracted with Et_2O (3 × 5 mL) and the combined organic layers were dried ($MgSO_4$), filtered, and concentrated under reduced pressure. Flash chromatography provided the cross-coupled product and the recovered siloxane (where possible as with siloxanes **2a-d**).

For siloxanes **3a-d**, the organic layer was washed with either 1M or 3M aq. HCl (3 × 5 mL) (according to siloxane, see above), and the acidic aqueous layers were collected. The organic layer was then washed with sat. aq. $NaHCO_3$ (5 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure. Flash chromatography provided the cross-coupled product. The acidic aqueous layer was then basified to pH 8-9 with 1M aq. NaOH, producing a white turbid mixture which was then extracted with Et_2O (3 × 50 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated under reduced pressure to provide the recovered siloxane.

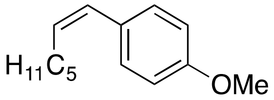


tert**-Butyldimethyl(((2*E*,4*E*)-7-phenylhepta-2,4-dien-1-yl)oxy)silane (S13):** Following General Procedure B, the product was purified by chromatography on SiO_2 (1% EtOAc in hexanes) to afford **S13** in >20:1 E/Z ratio as a colorless oil (125 mg, 0.41 mmol, 92% with siloxane **2a**, 171 mg, 85% recovery; 124 mg, 0.41 mmol, 91% with siloxane **2b**, 191 mg, 88% recovery; 131 mg, 0.43 mmol, 96% with siloxane **3b**, 214 mg, 98% recovery; 135 mg, 0.44 mmol, 99% with siloxane **3d**, 239 mg, 95% recovery): **R_f** 0.3 (1% EtOAc in hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31-7.25 (m, 2 H), 7.21-7.17 (m, 3 H), 6.19 (dd, J = 10.6, 15.0 Hz, 1 H), 6.08 (dd, J = 10.6, 15.0 Hz, 1 H), 5.75-5.62 (m, 2H), 4.21 (d, J = 5.5 Hz, 2 H), 2.72 (t, J = 7.5 Hz, 2 H), 2.41 (q, J = 7.5 Hz, 2 H), 0.93 (s, 9 H), 0.83 (s, 6 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 141.9, 133.4, 130.8, 130.4, 130.3, 128.6, 128.5, 126.0, 63.8, 35.9, 34.6, 26.1, 18.6, -5.01. **IR** (neat) 3026 (m), 2954 (m), 2930 (s), 2856 (s) 1468 (m), 1254 (s), 1109 (m), 1066 (bs), 988 (s), 837 (s), 776 (s) cm^{-1}; **HRMS** (CI$^+$) *m/z* calculated for $C_{15}H_{21}OSi$ $[M-C_4H_9]^+$ 245.1362, found 245.1368.



(*E*)-1-(Hept-1-en-1-yl)-4-methoxybenzene (S14): Following General Procedure B, the product was purified by chromatography on SiO_2 (1% EtOAc in hexanes) to afford **S14** in >20:1 E/Z ratio as a colorless oil (89.0 mg, 0.44 mmol, 97% with siloxane **2a**, 169 mg, 84% recovery; 88.0 mg, 0.43 mmol, 96% with siloxane **2b**, 195 mg, 90% recovery; 87.0 mg, 0.43 mmol, 95% with siloxane **3b**, 212 mg, 97% recovery; 87.0 mg, 0.42 mmol, 94% with siloxane **3d**, 237 mg, 94% recovery) as a colorless solid. Analytical data matches that which has been previously reported for **S14**:[14] **R_f** 0.3 (1% EtOAc in hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28 (dd, J = 2.0, 6.5 Hz, 2 H), 6.84 (dd, J = 2.1, 6.6 Hz, 2 H), 6.32 (d, J = 15.7 Hz, 1 H), 6.09 (dt, J = 7.2, 15.8 Hz, 1 H), 3.80 (s, 3 H), 2.18 (qd, J = 1.3, 7.3 Hz, 2 H), 1.46 (qn, J = 7.2 Hz, 2 H), 1.40-1.37 (m, 4 H), 0.90

(t, *J* = 7.1 Hz, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 158.6, 131.2, 129.6, 129.5, 127.1, 114.2, 55.7, 33.5, 31.4, 29.5, 22.7, 14.1.



(*Z*)-1-(Hept-1-en-1-yl)-4-methoxybenzene (S15): Following General Procedure A, the product was purified by chromatography on SiO_2 (1% EtOAc in hexanes) to afford **S15** in >20:1 Z/E ratio as a colorless oil (80.0 mg, 0.39 mmol, 87% with siloxane **2a**, 173 mg, 86% recovery; 82.0 mg, 0.40 mmol, 89 % with siloxane **2b**, 189 mg, 87% recovery; 88.0 mg, 0.43 mmol, 96% with siloxane **3b**, 212 mg, 97% recovery, 87.0 mg, 0.42 mmol, 94% with siloxane **3d**, 242 mg, 96% recovery). Analytical data matches that which has been previously reported for **S15**:[14] **R_f** 0.3 (1% EtOAc in hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.6 Hz, 2 H), 6.87 (d, *J* = 8.8 Hz, 2 H), 6.33 (d, *J* = 11.7 Hz, 1 H), 5.55 (dt, *J* = 7.3, 11.6 Hz, 1 H), 3.82 (s, 3 H), 2.29 (qd, *J* = 1.3, 7.3 Hz, 2 H), 1.45 (qn, *J* = 7.6 Hz, 2 H), 1.36-1.28 (m, 4 H), 0.90 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 158.6, 131.7, 130.5, 130.1, 128.4, 113.5, 55.1, 31.4, 29.7, 28.9, 22.6, 14.2.

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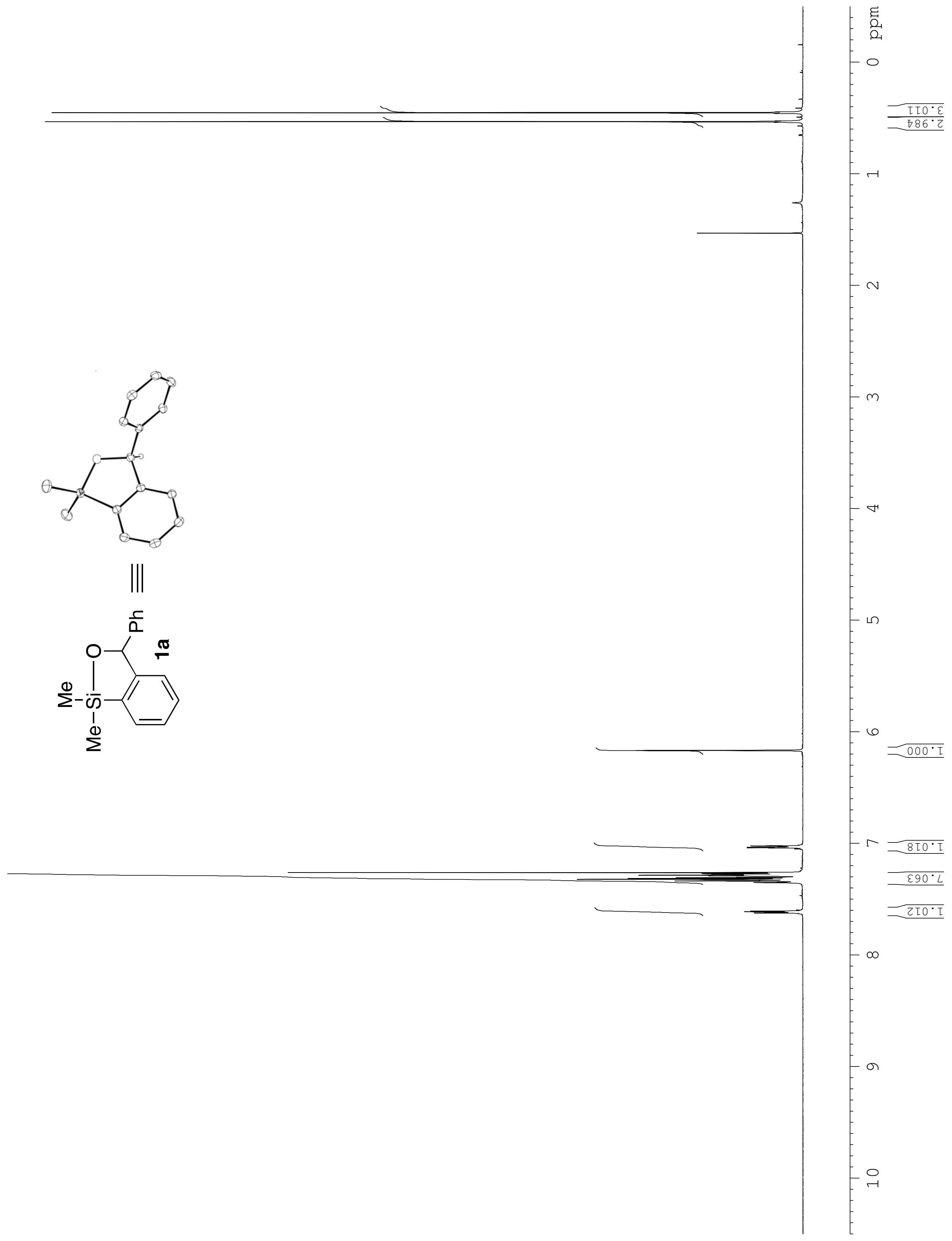
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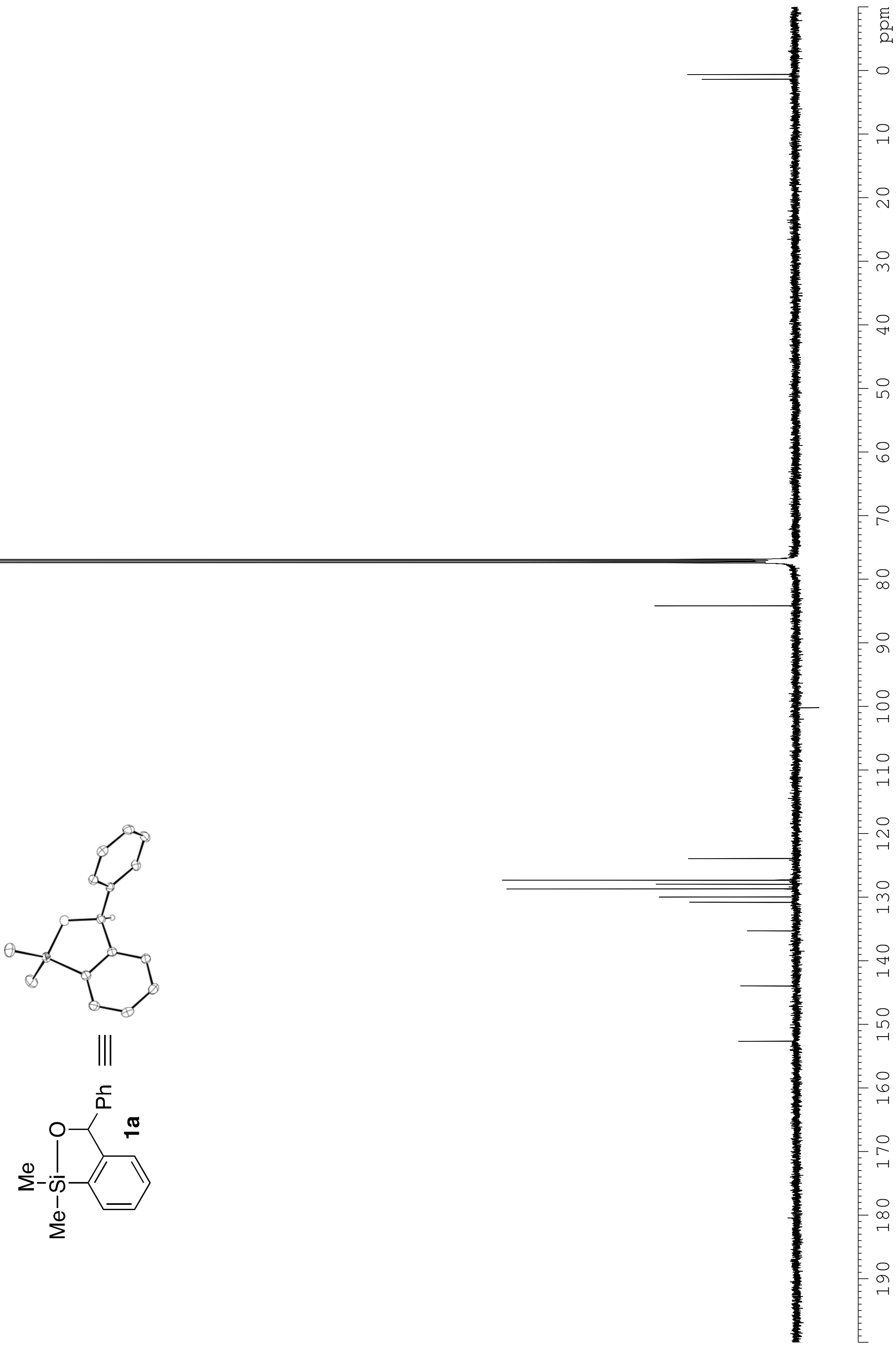
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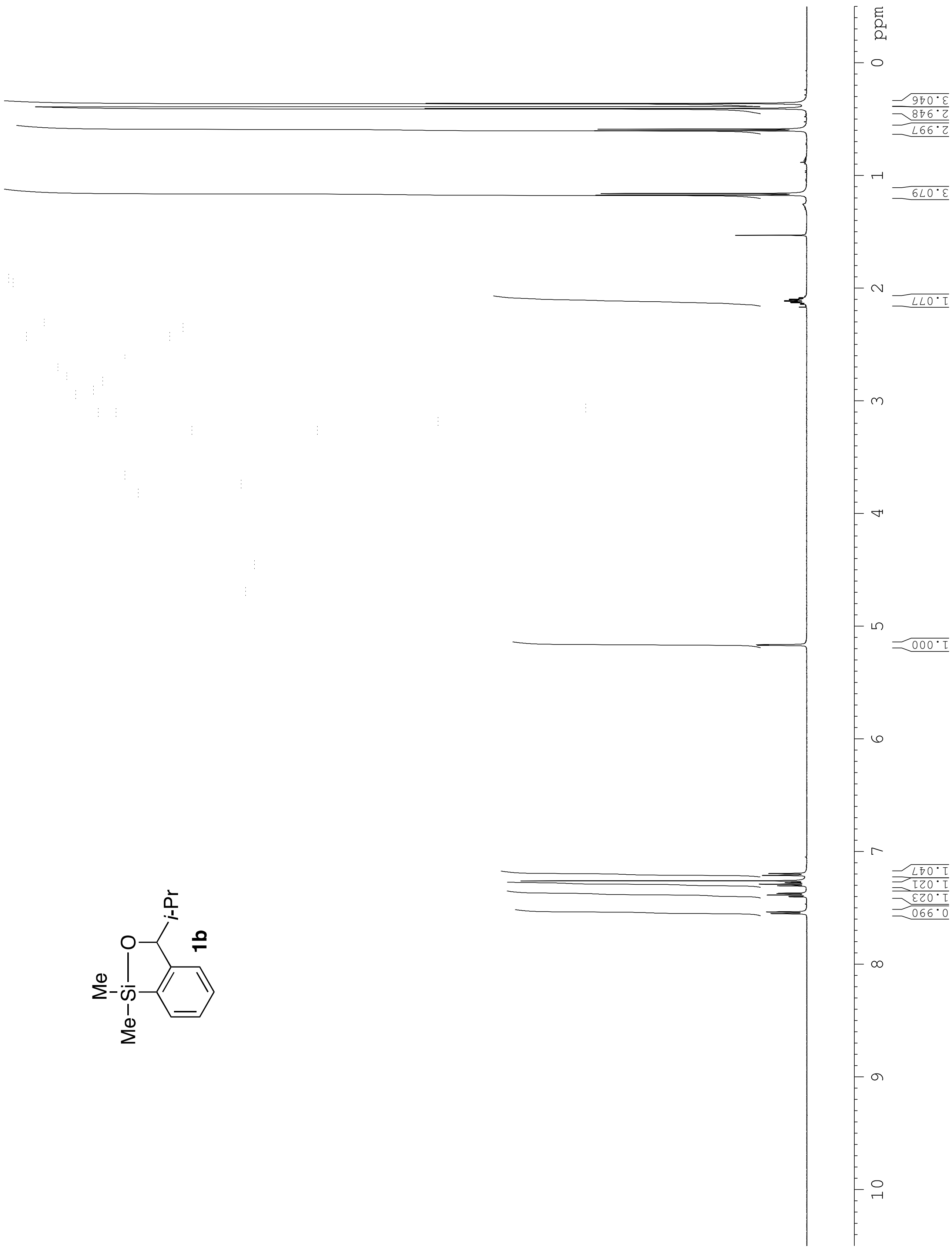
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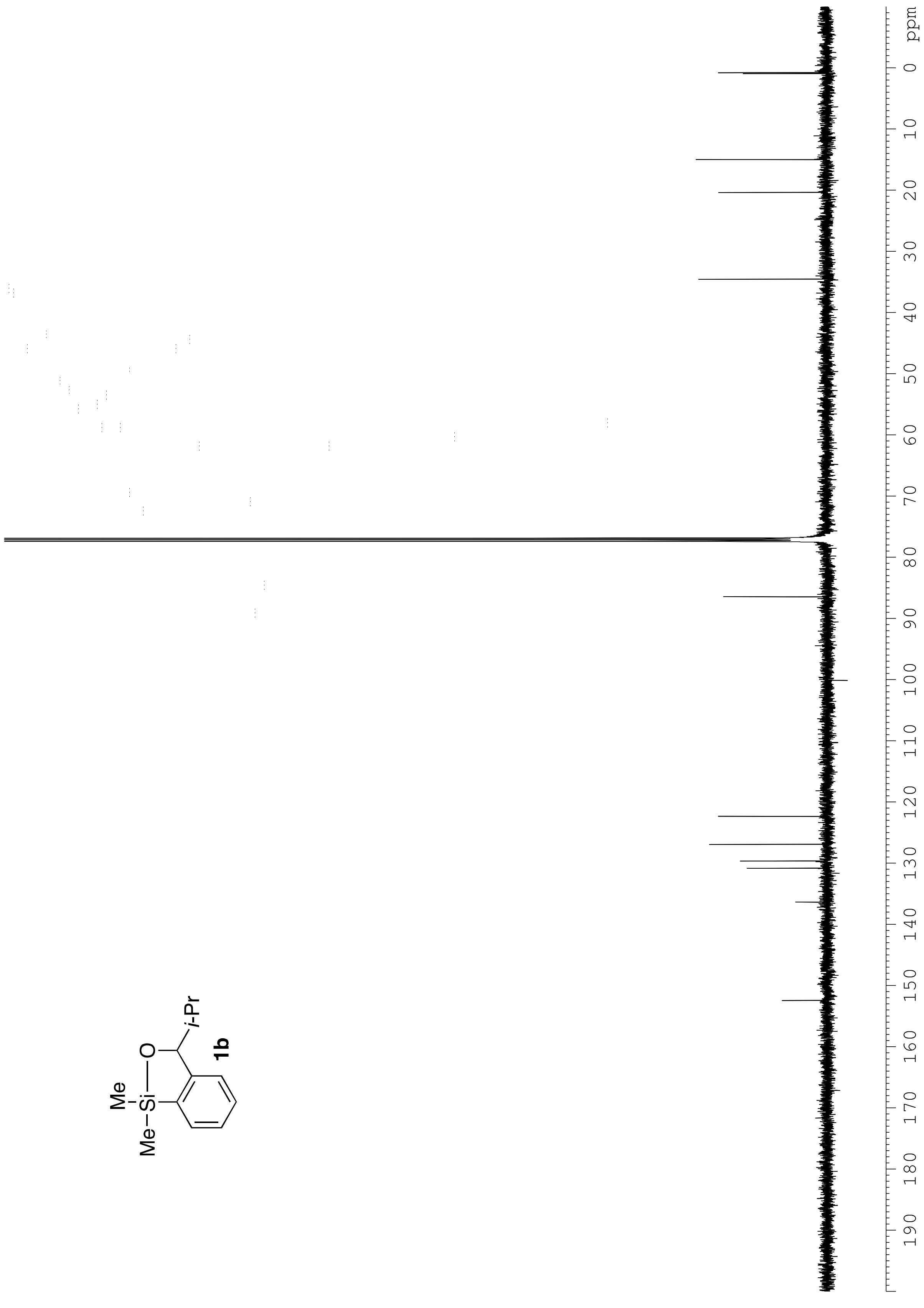

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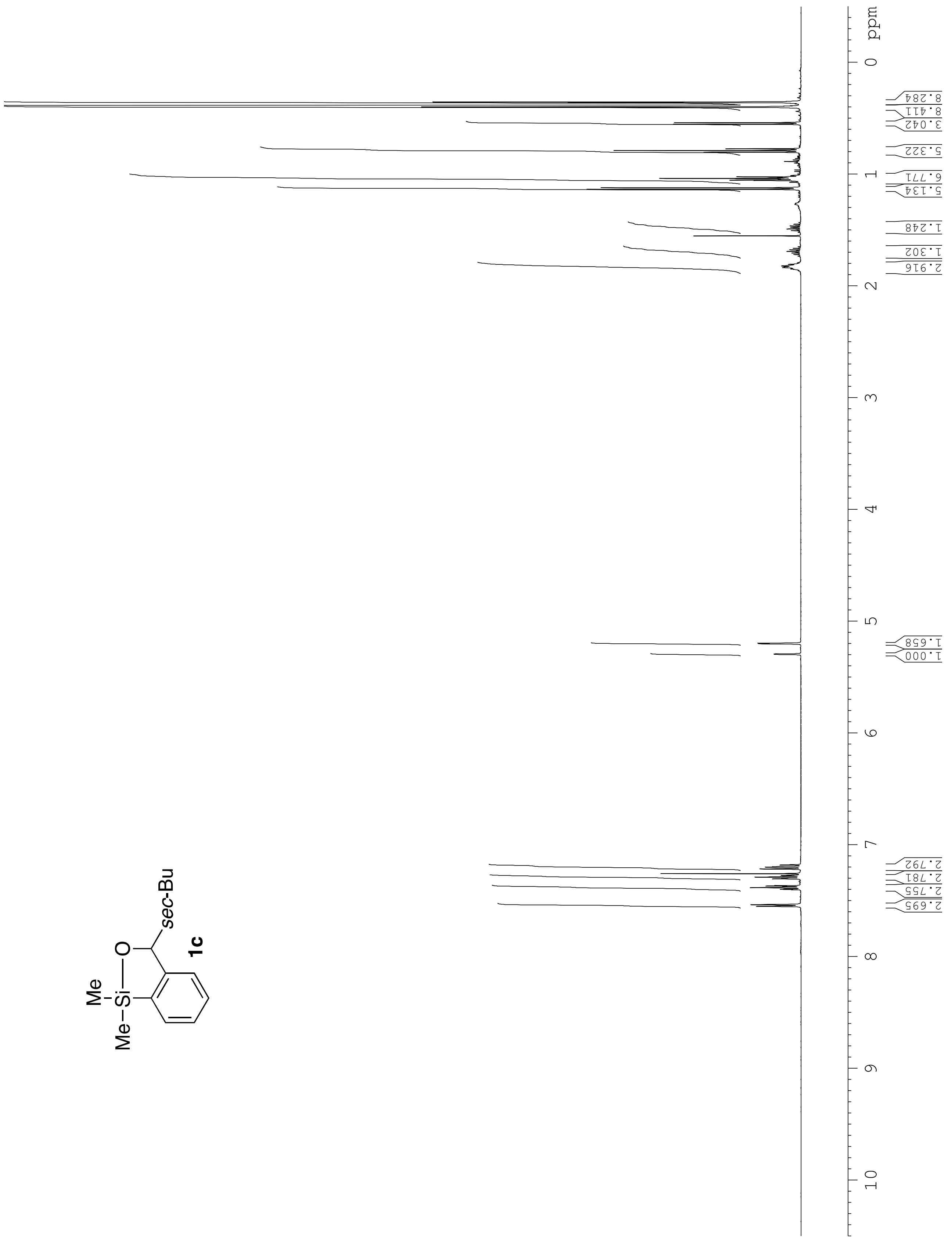

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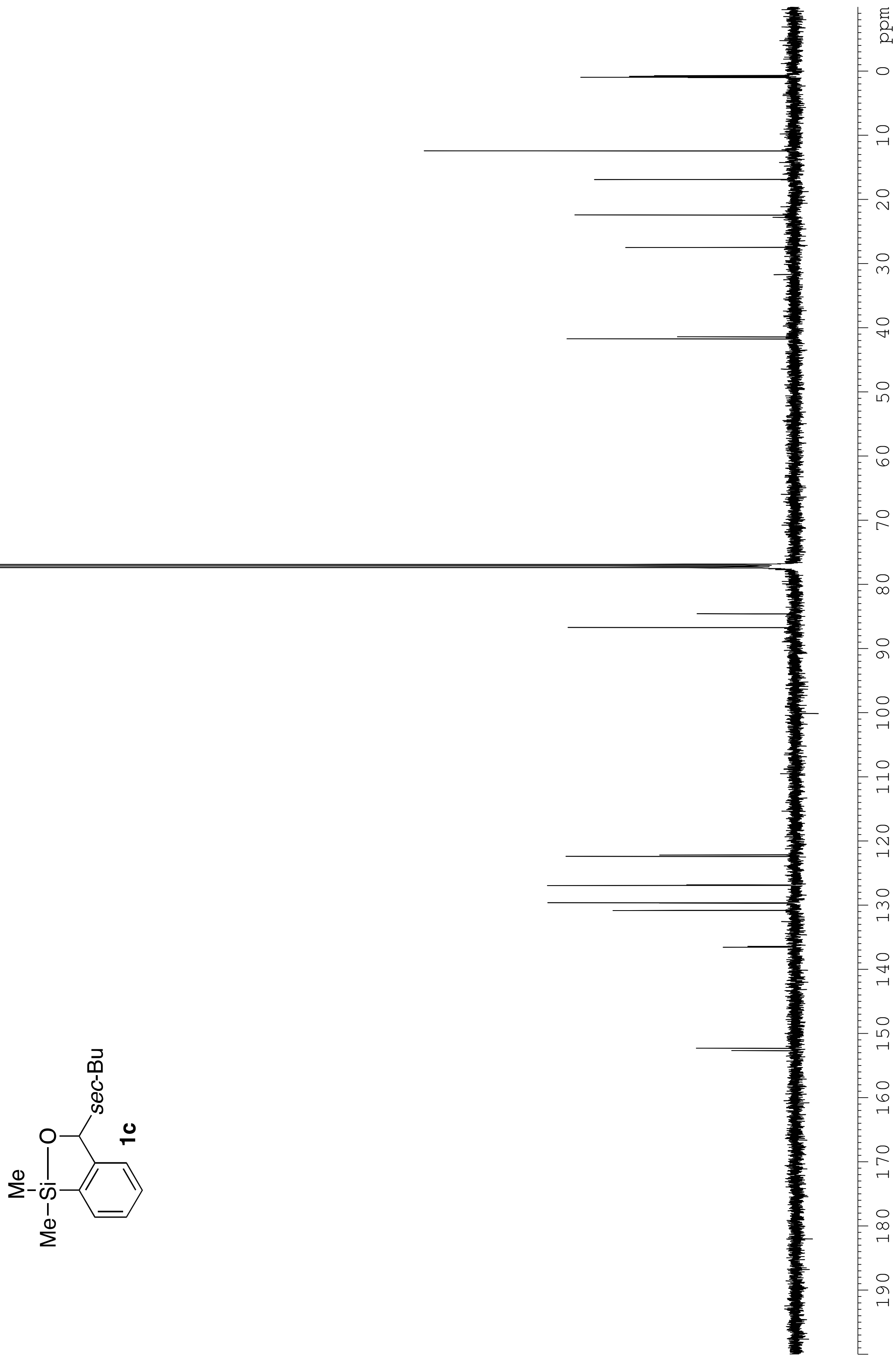
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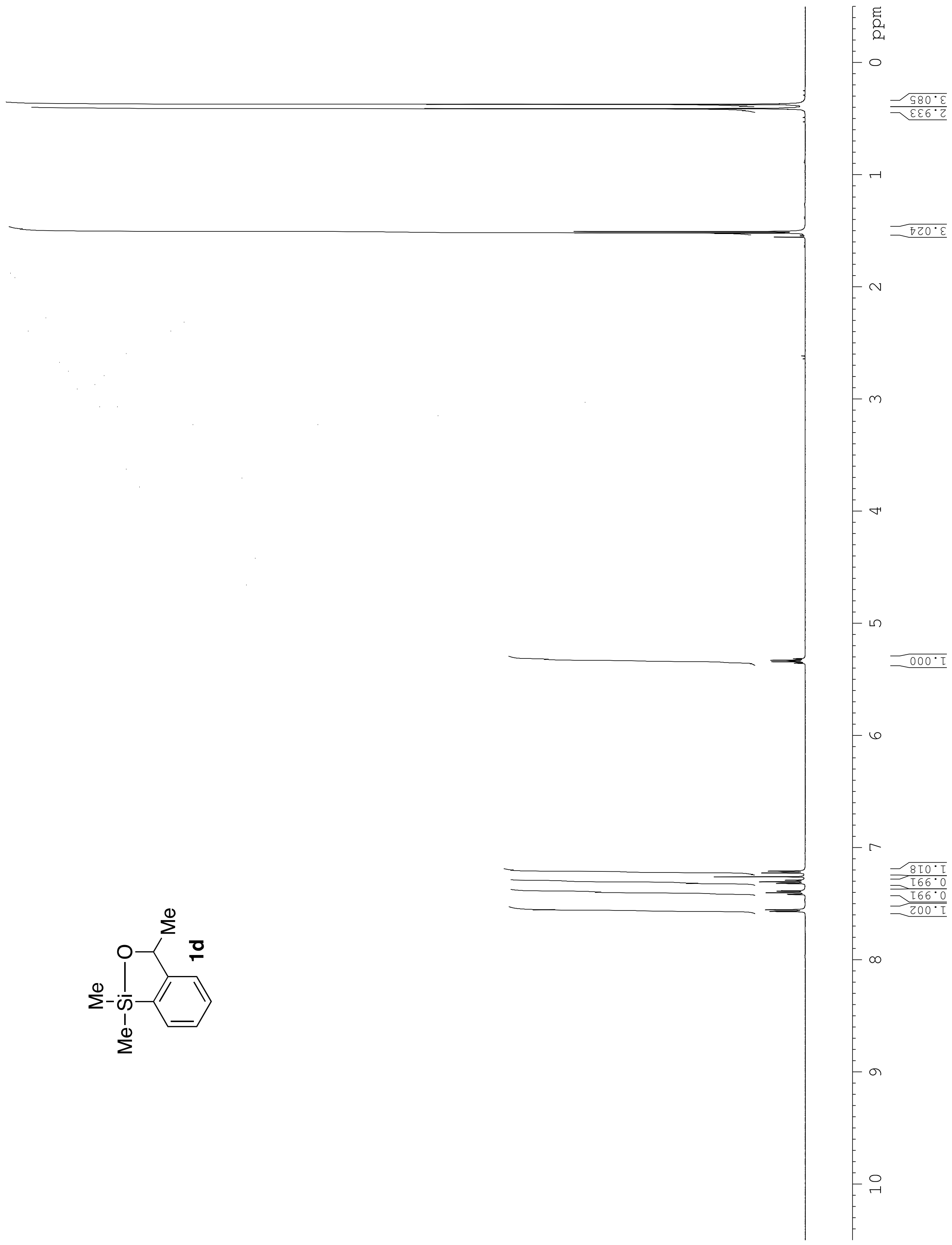
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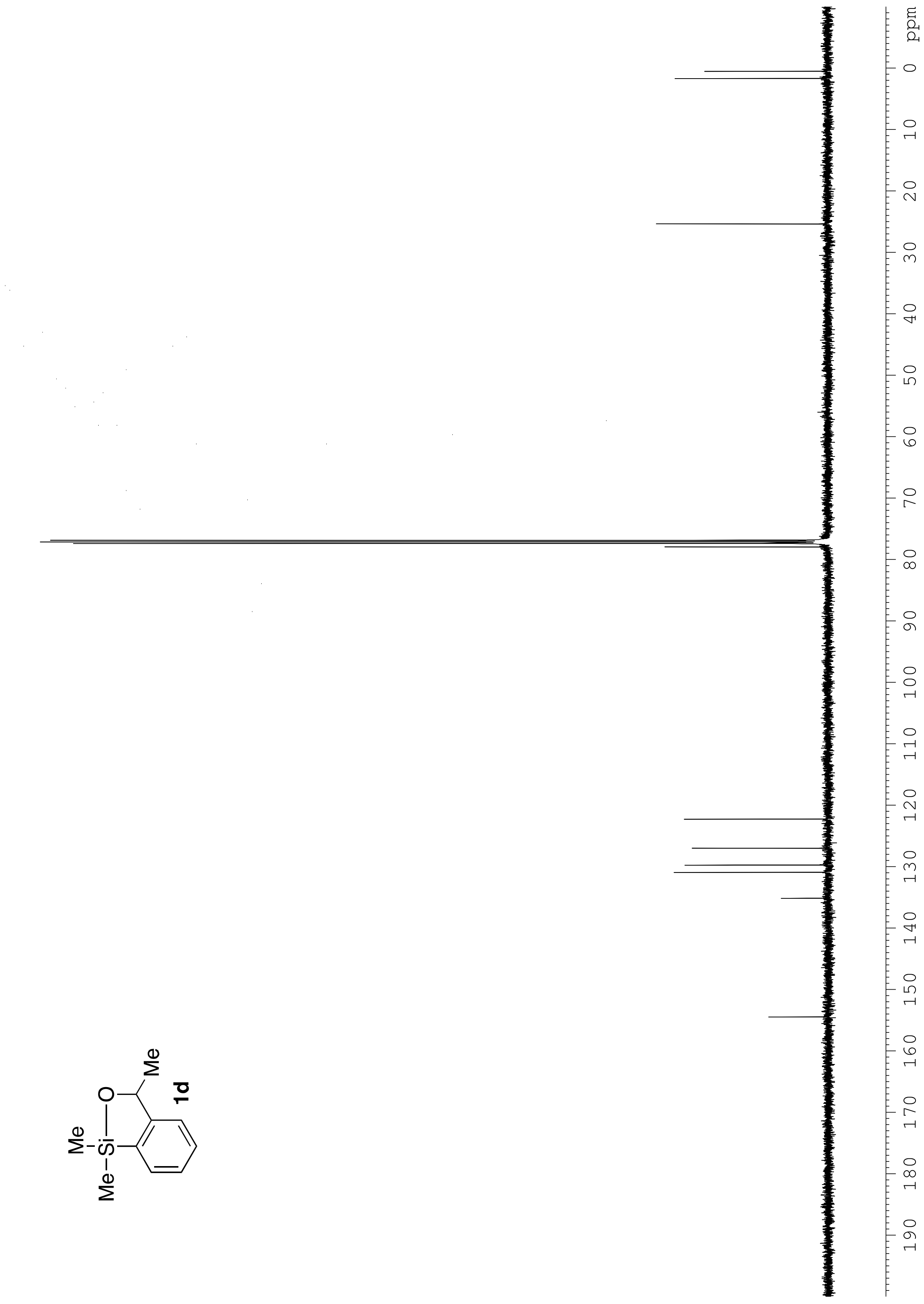

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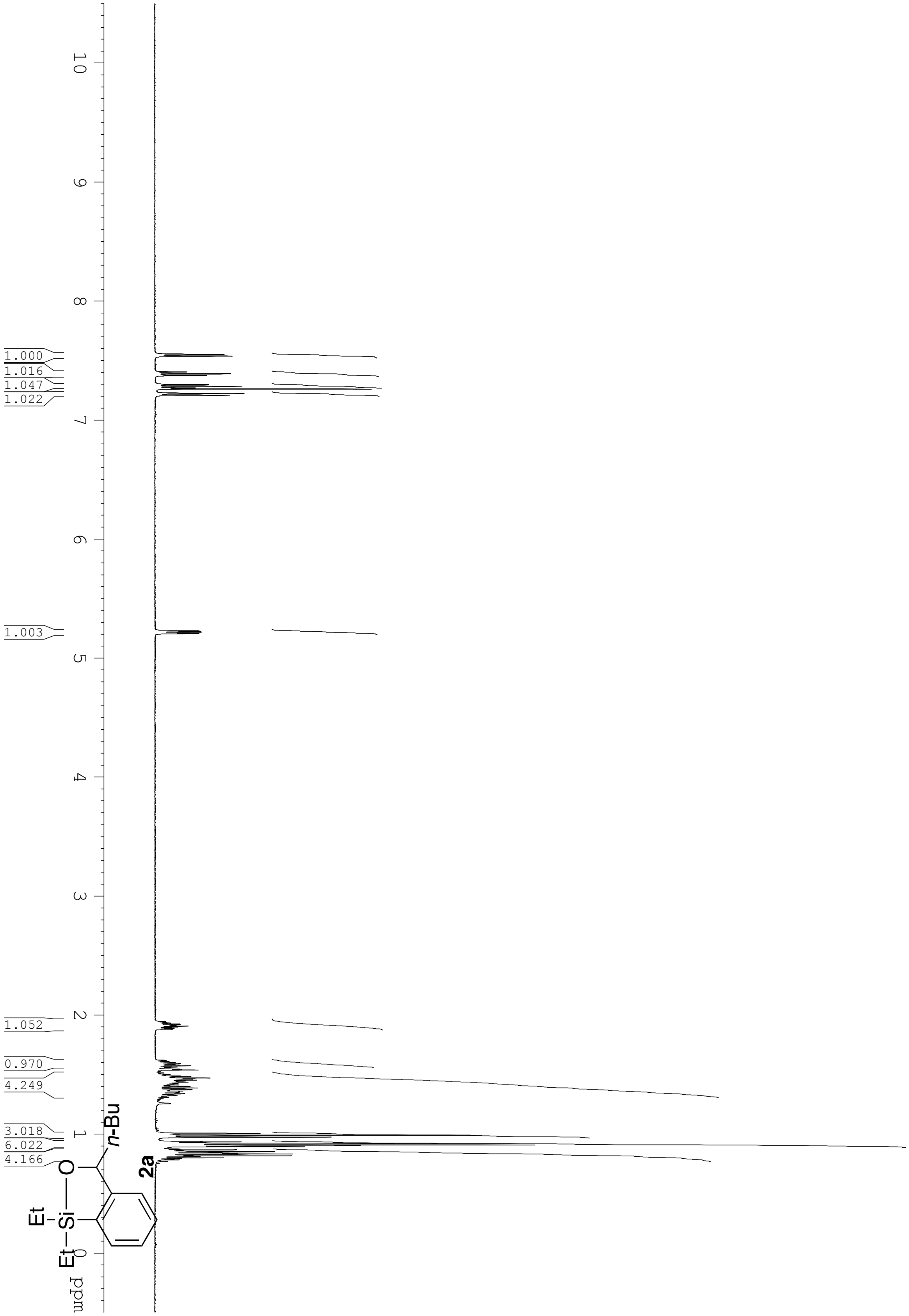
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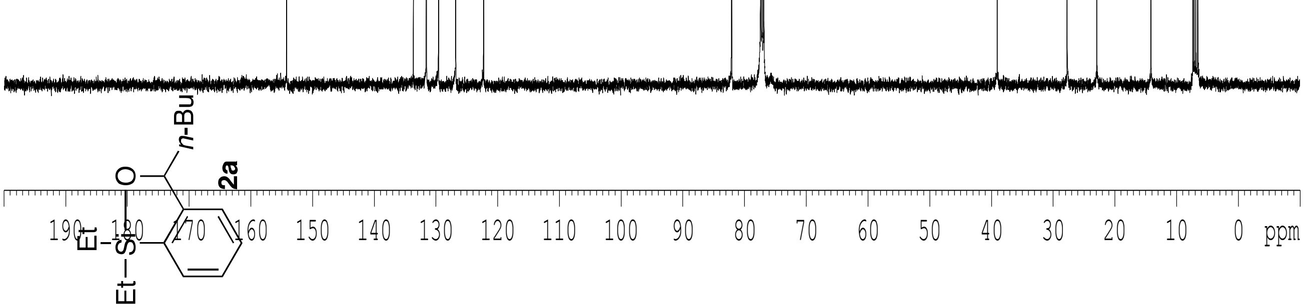
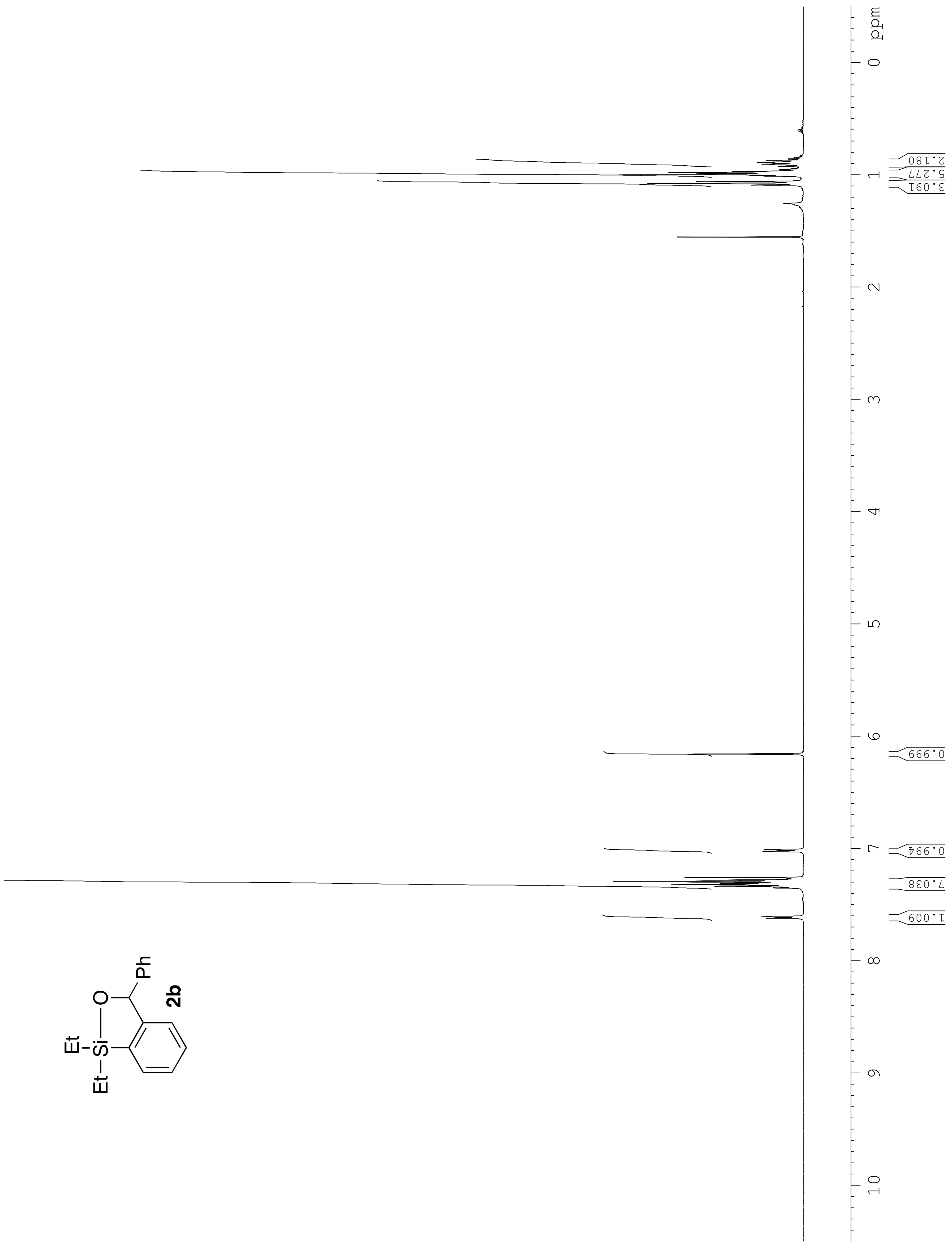
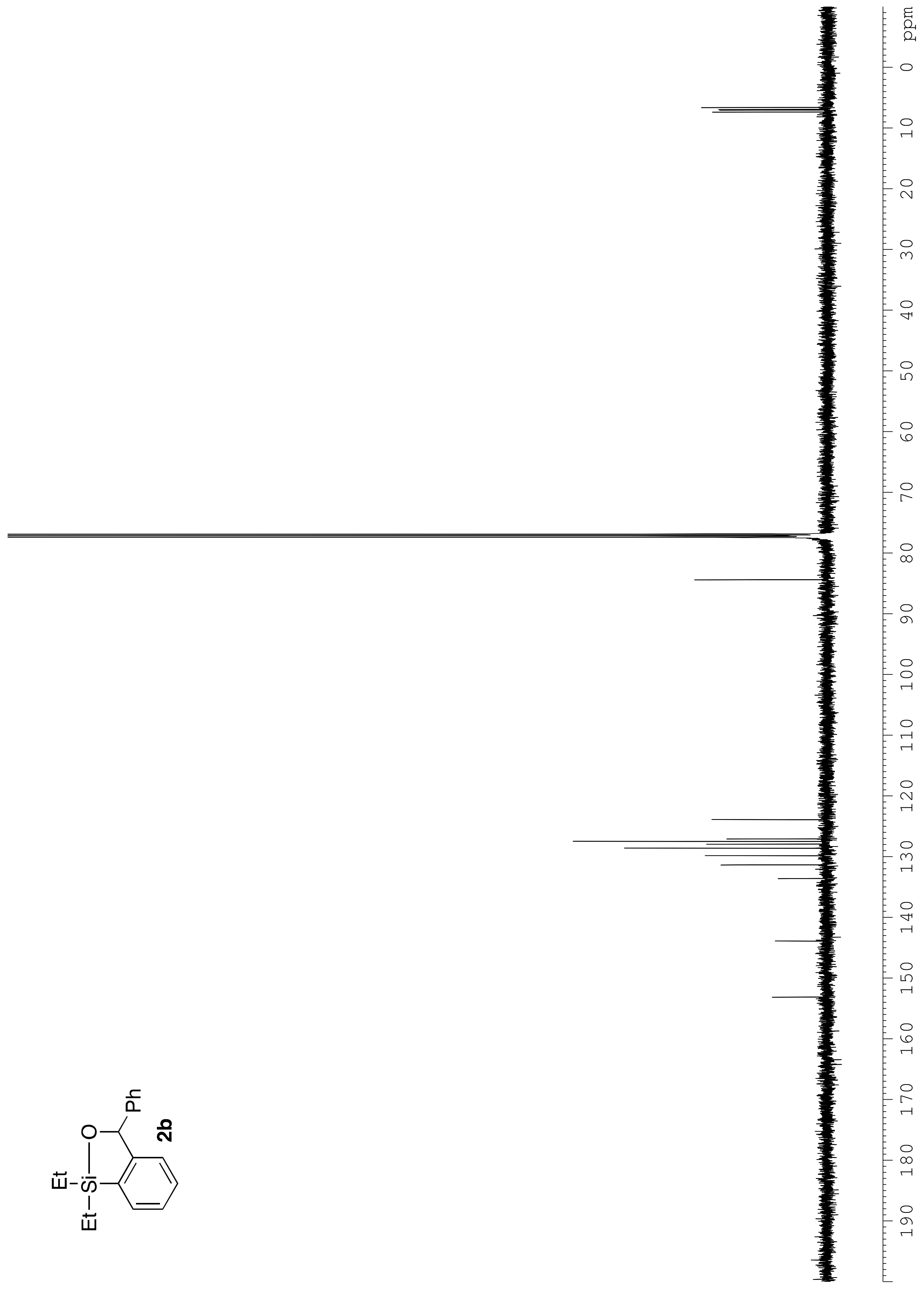
2a

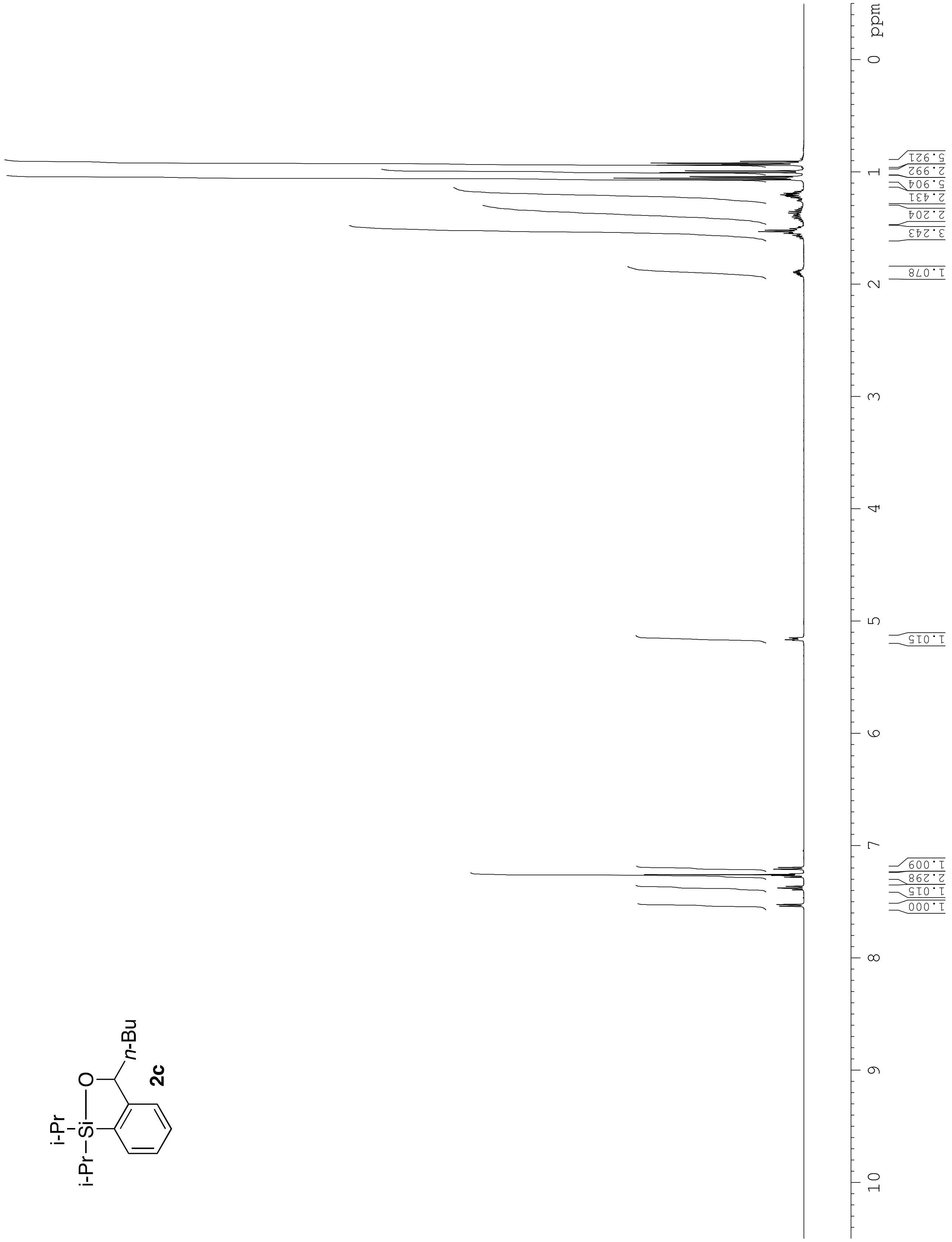

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
Et
Et
Si
O
n-Bu

2a

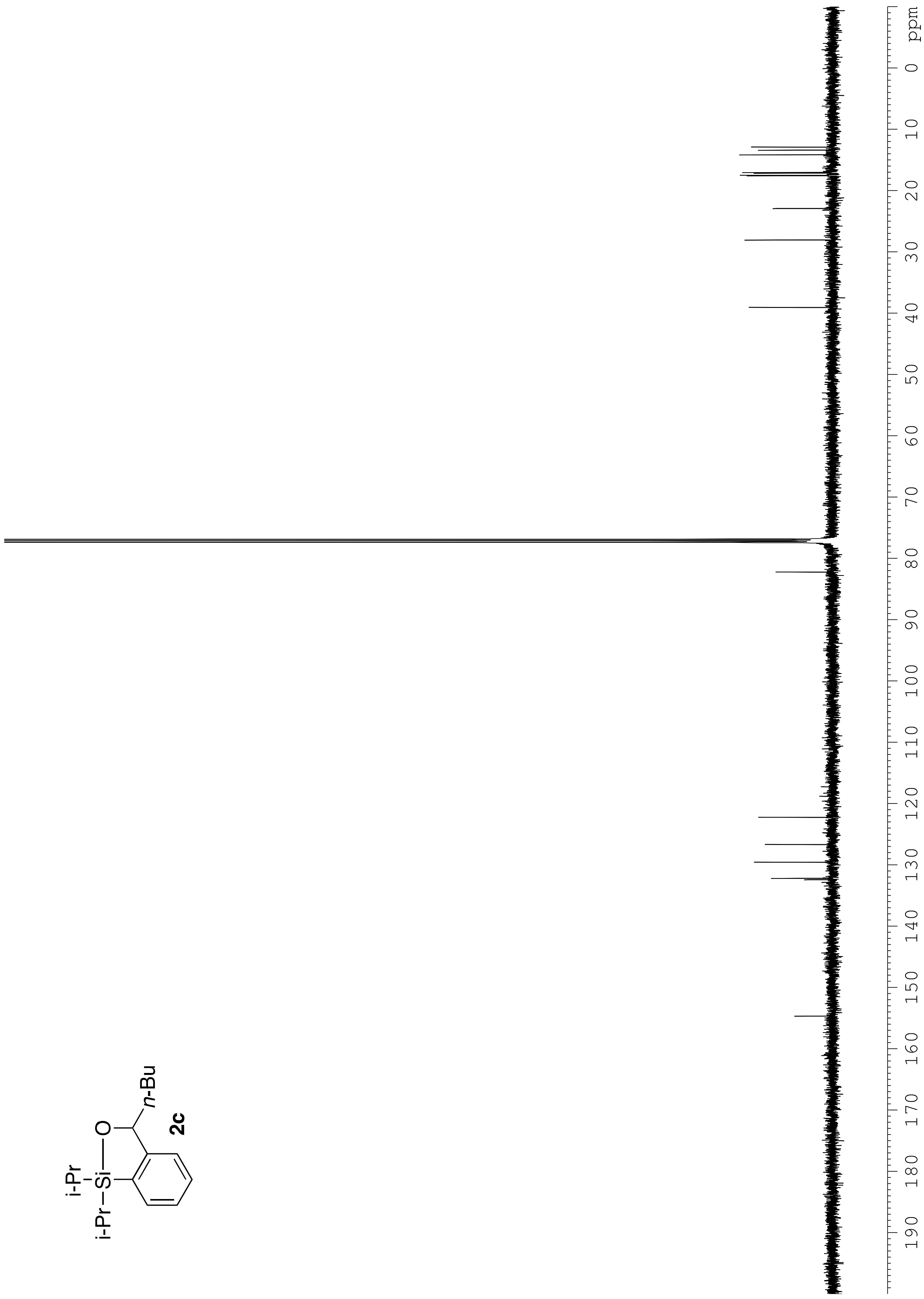

Et
Et
Si
O
Ph
ppm
0
1
2
3
4
5
6
7
8
9
10
2.180
5.277
3.091
0.999
0.994
7.038
1.009

2b

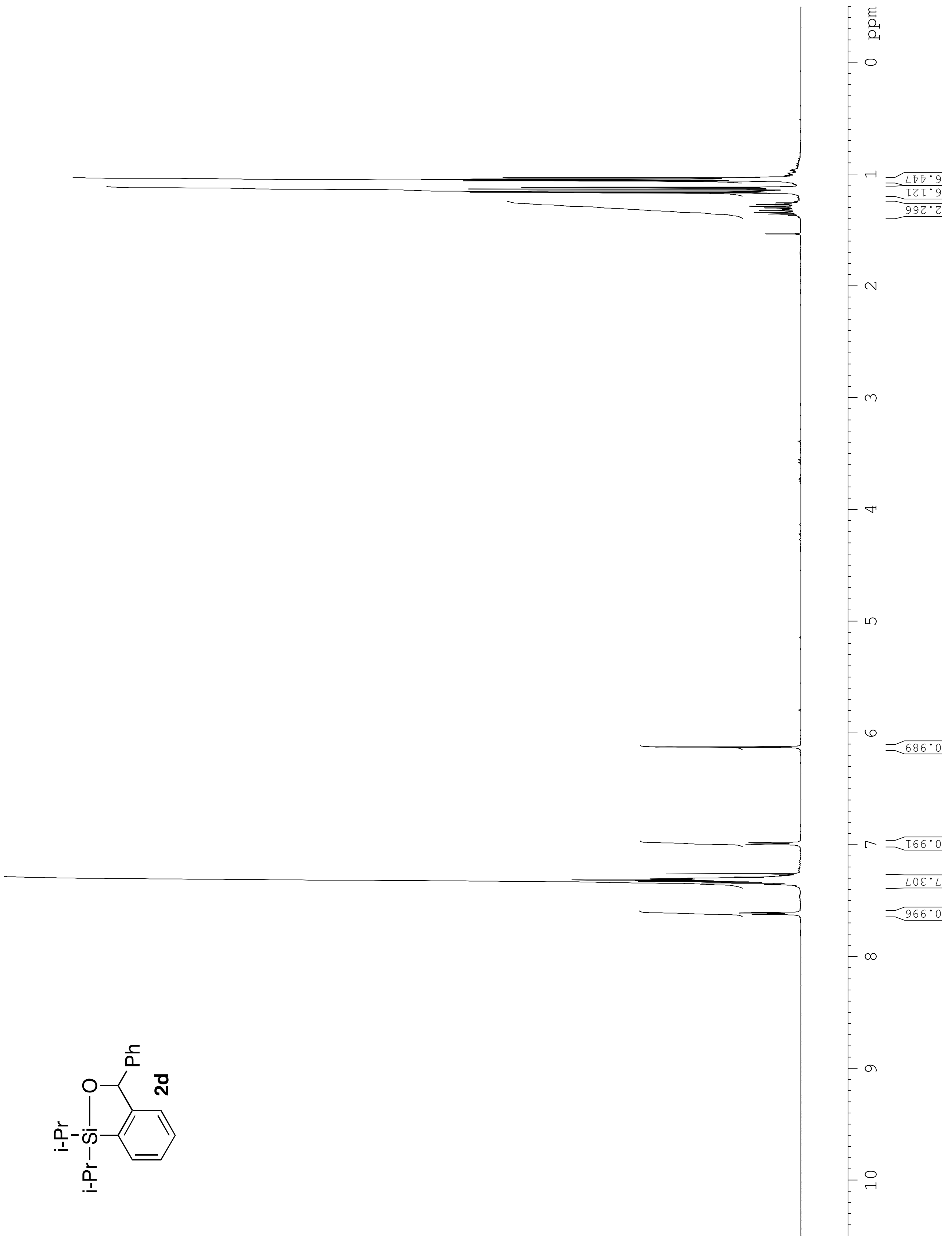

Et
Et
Si
O
Ph
2b
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190

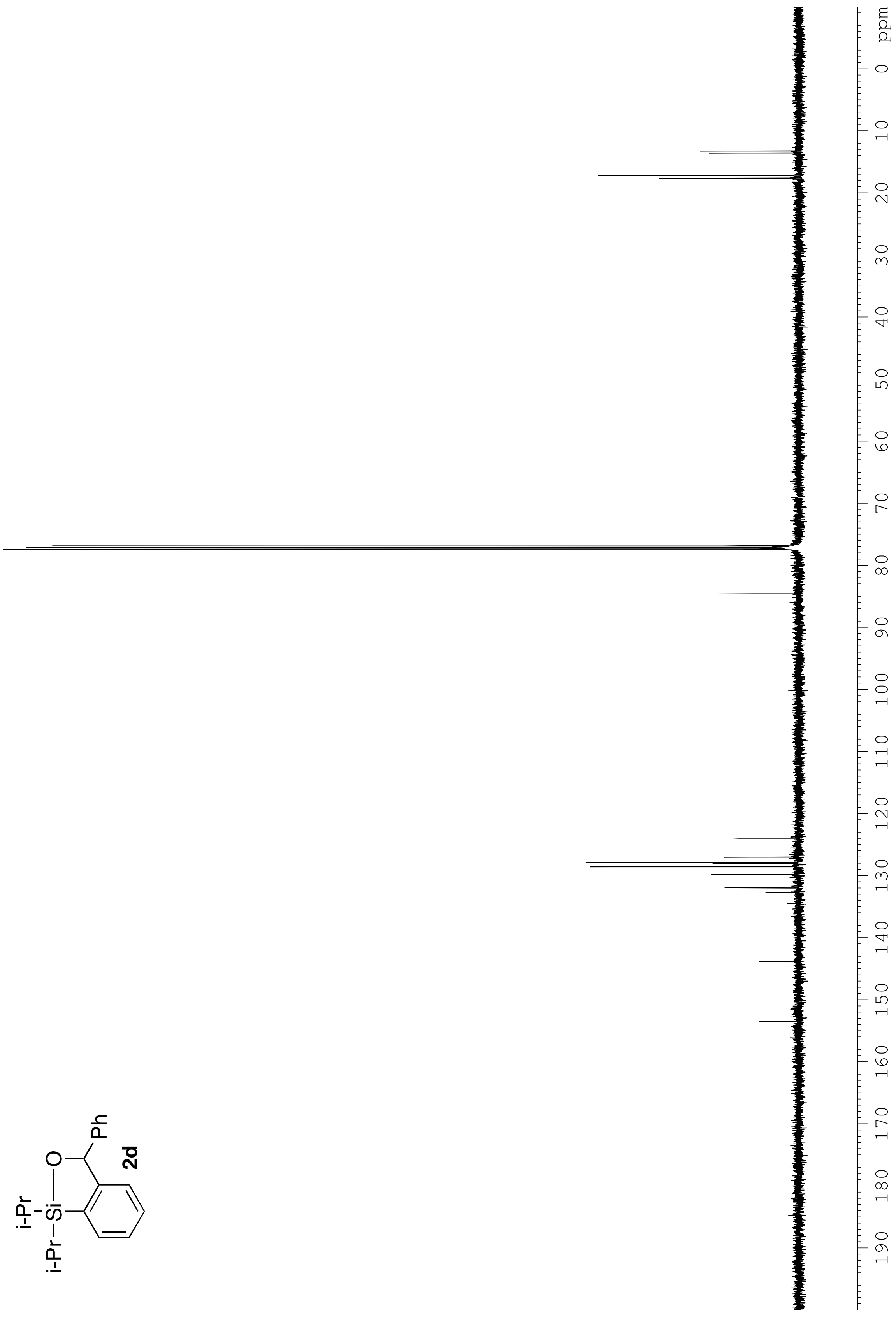


i-Pr
i-Pr
Si
O
n-Bu
2c
ppm
0
1
2
3
4
5
6
7
8
9
10
5.921
2.992
5.904
2.431
2.204
3.243
1.078
1.015
1.009
2.298
1.015
1.000


ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
i-Pr
i-Pr
Si
O
n-Bu

2c


i-Pr
i-Pr
Si
O
Ph
2d
ppm
0
1
2
3
4
5
6
7
8
9
10
6.447
6.121
2.266
0.989
0.991
7.307
0.996


2d
i-Pr
i-Pr
Si
O
Ph
ppm
0
10
20
30
40
50
60
70
80
90
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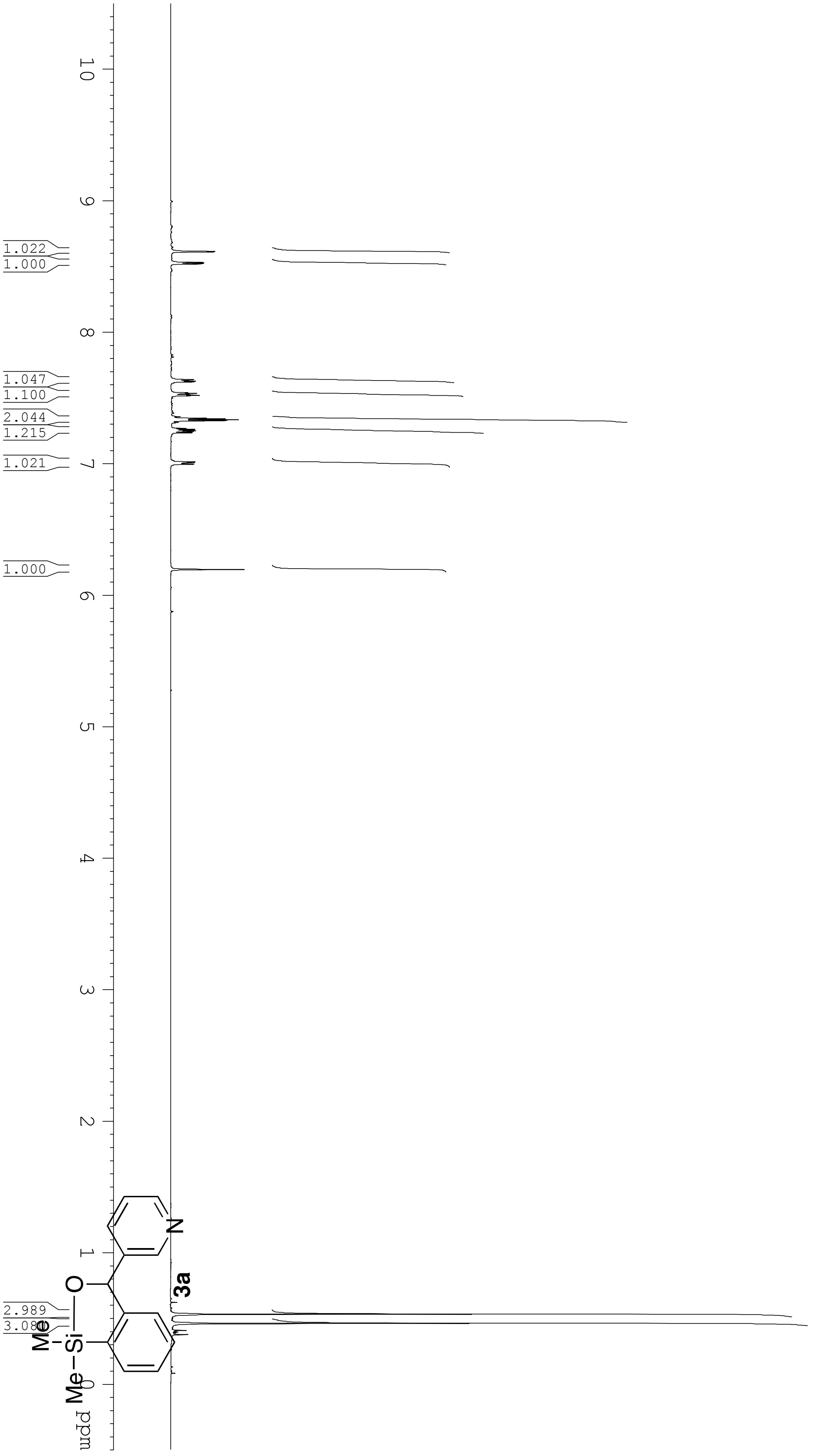
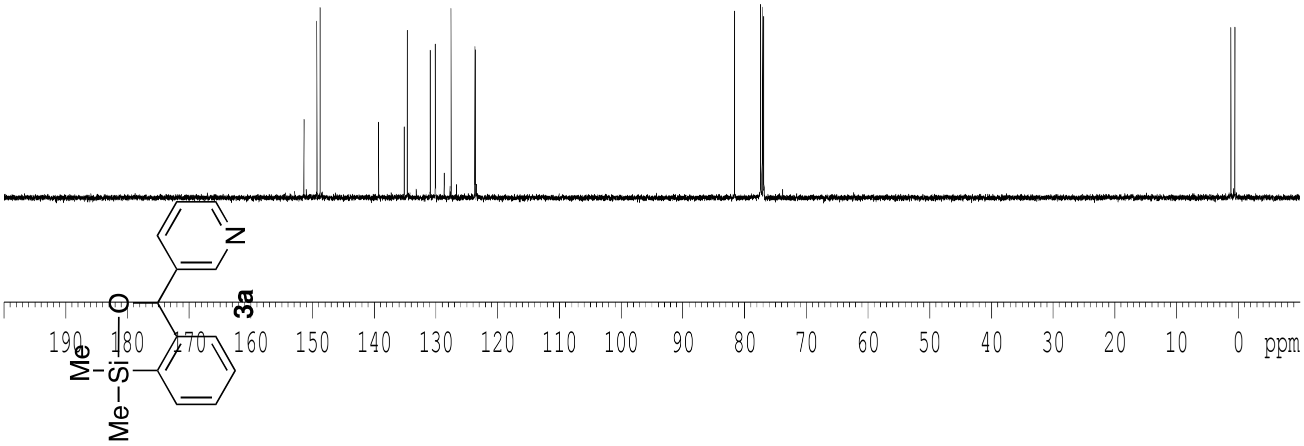
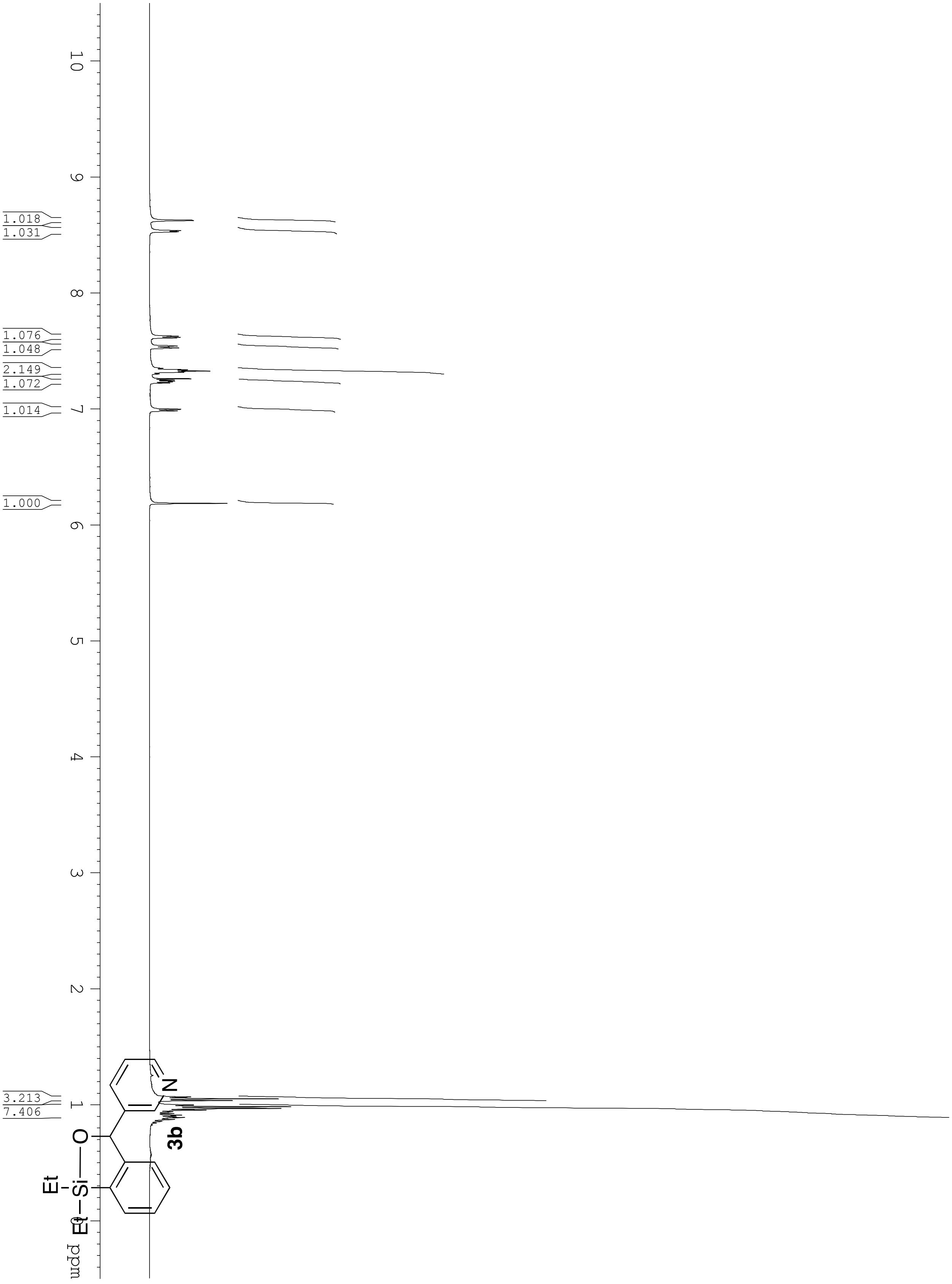
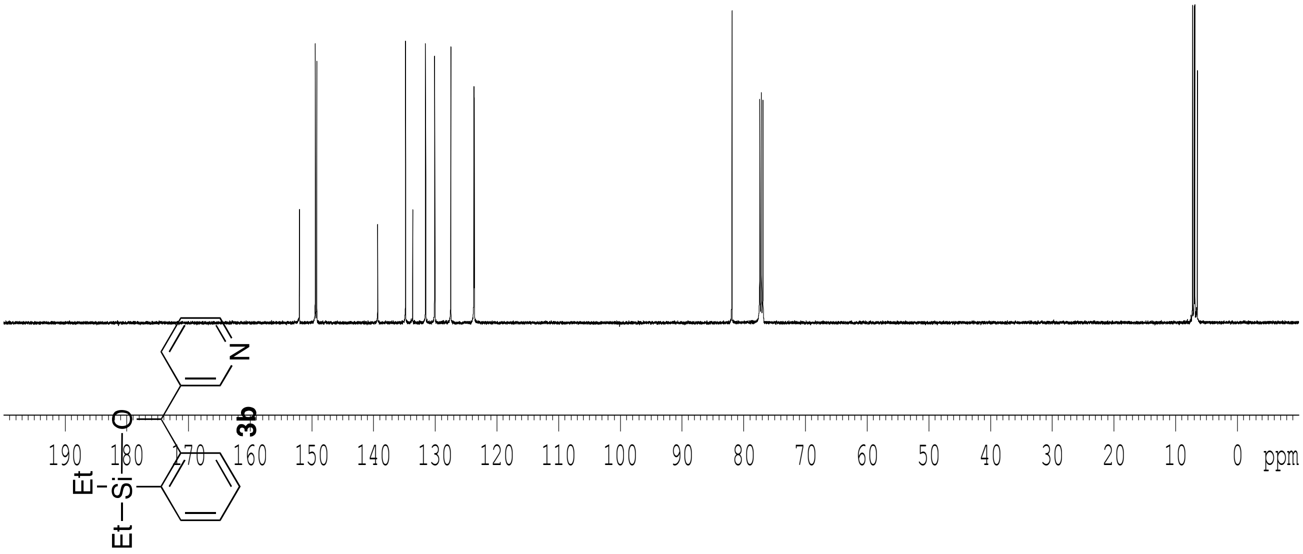
120
130
140
150
160
170
180
190


10
9
8
7
6
5
4
3
2
1
0
ppm
1.022
1.000
1.047
1.100
2.044
1.215
1.021
1.000
2.989
3.08
N
O
Me
Si
Me
3a

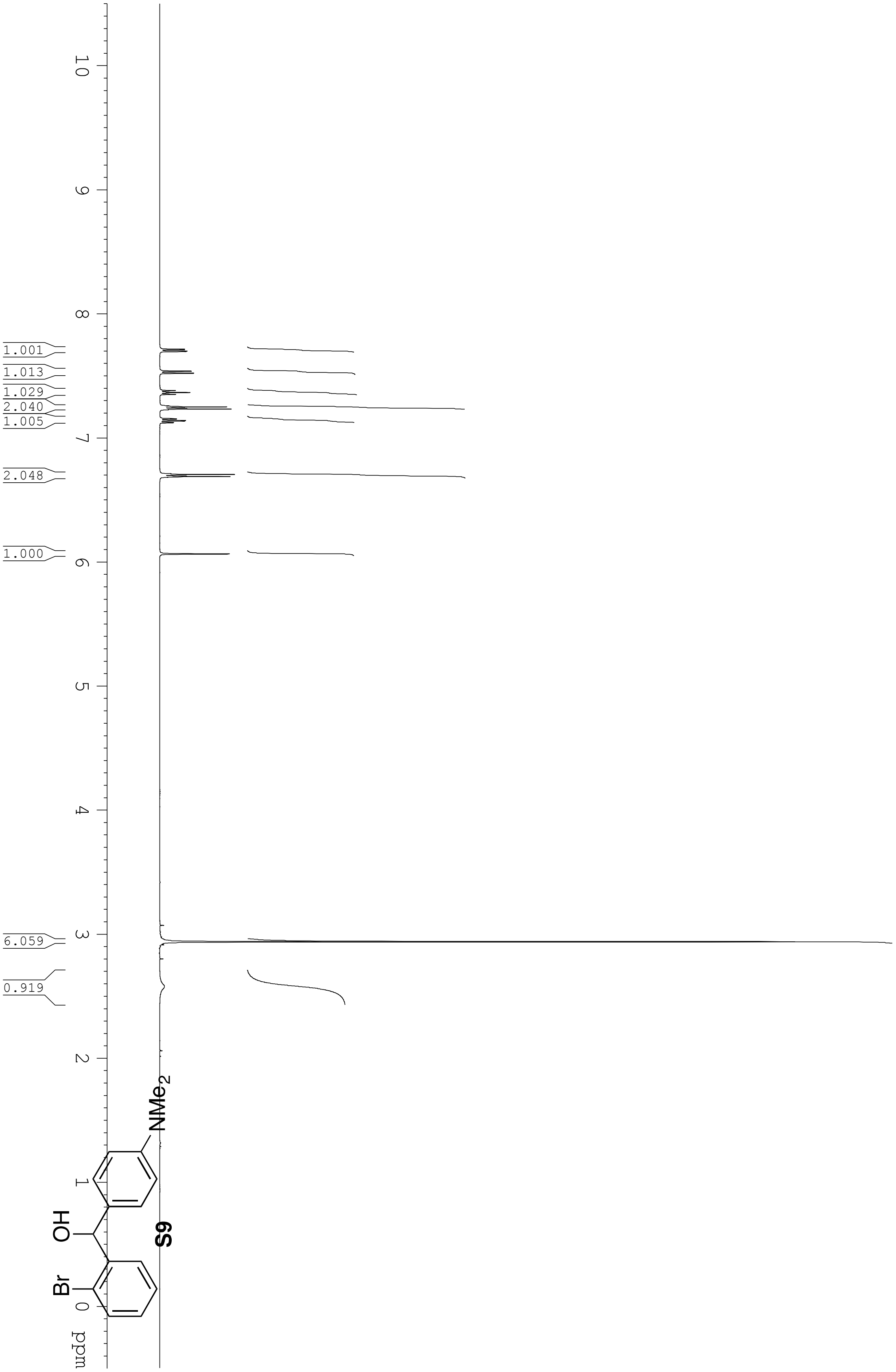

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
Me
Me
Si
O
N
3a


10
9
8
7
6
5
4
3
2
1
ppm
1.018
1.031
1.076
1.048
2.149
1.072
1.014
1.000
3.213
7.406
Et
Et
Si
O
N

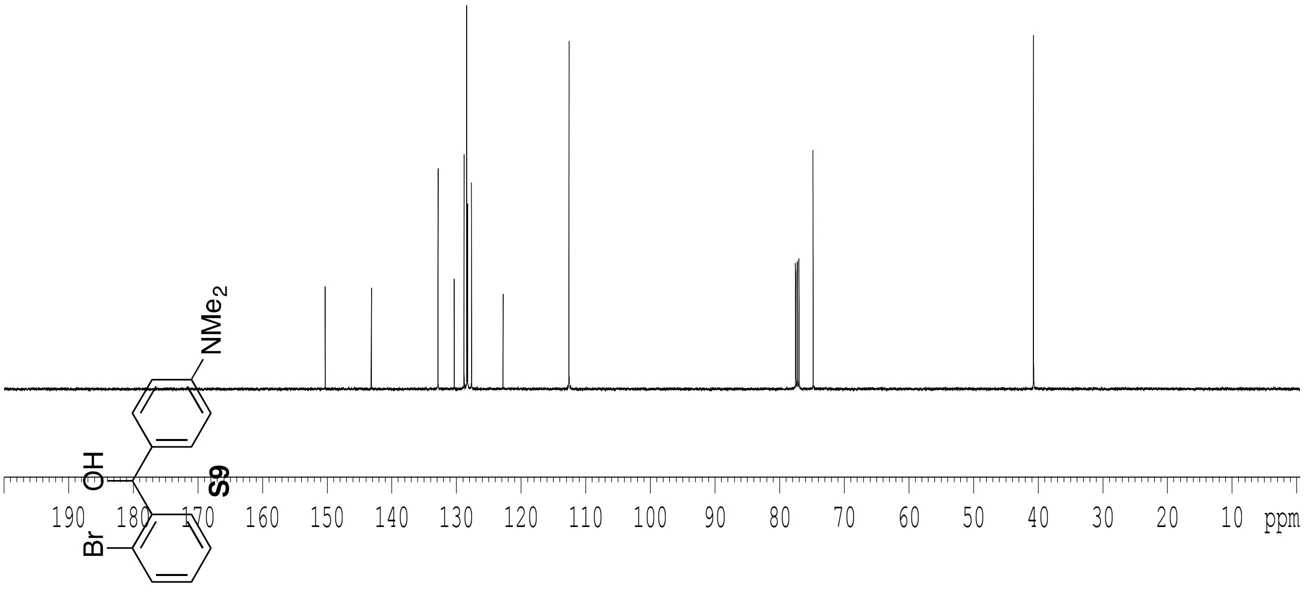
3b


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

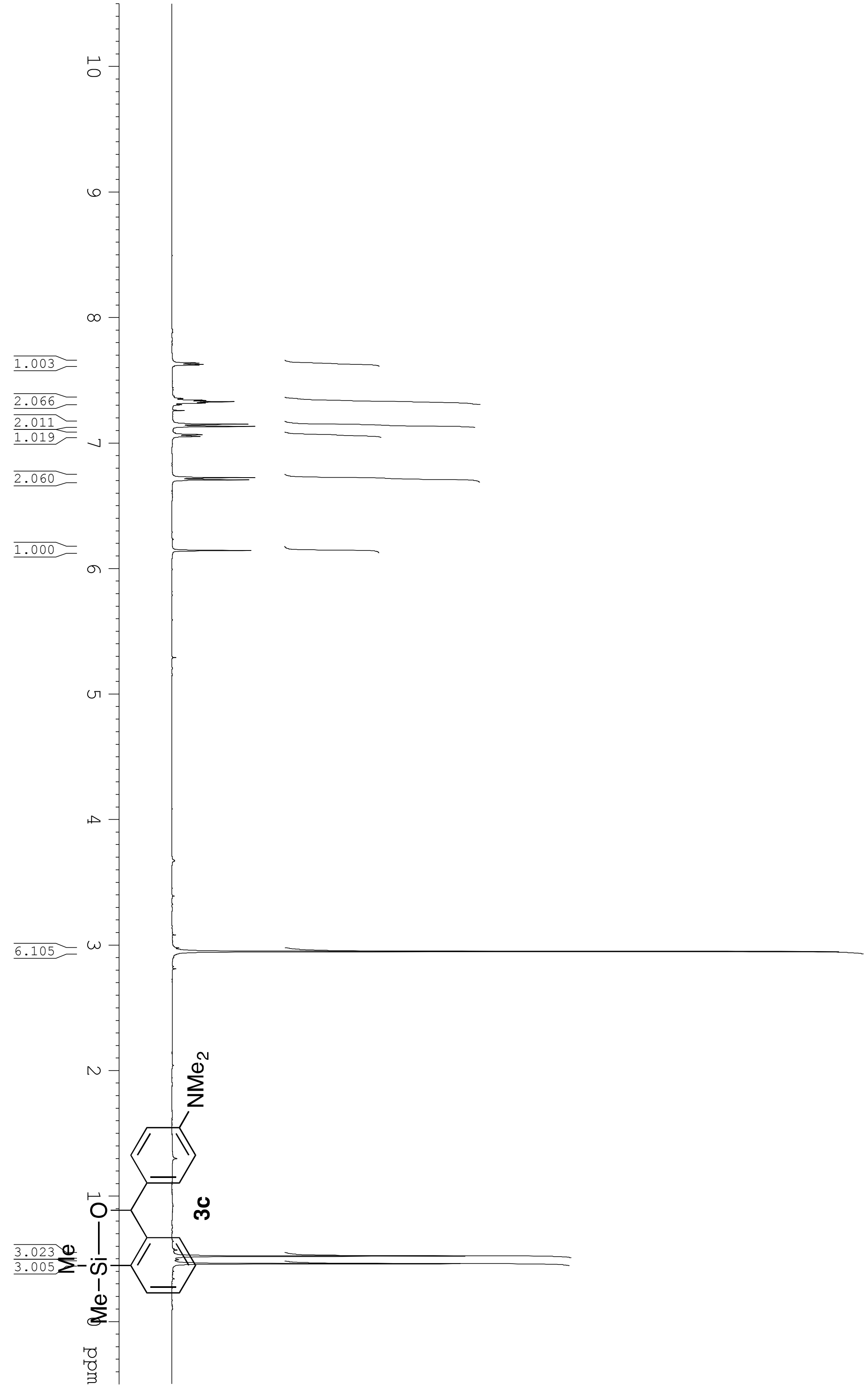
3b


ppm
0
1
2
3
4
5
6
7
8
9
10
1.001
1.013
1.029
2.040
1.005
2.048
1.000
6.059
0.919
Br
OH
NMe$_2$

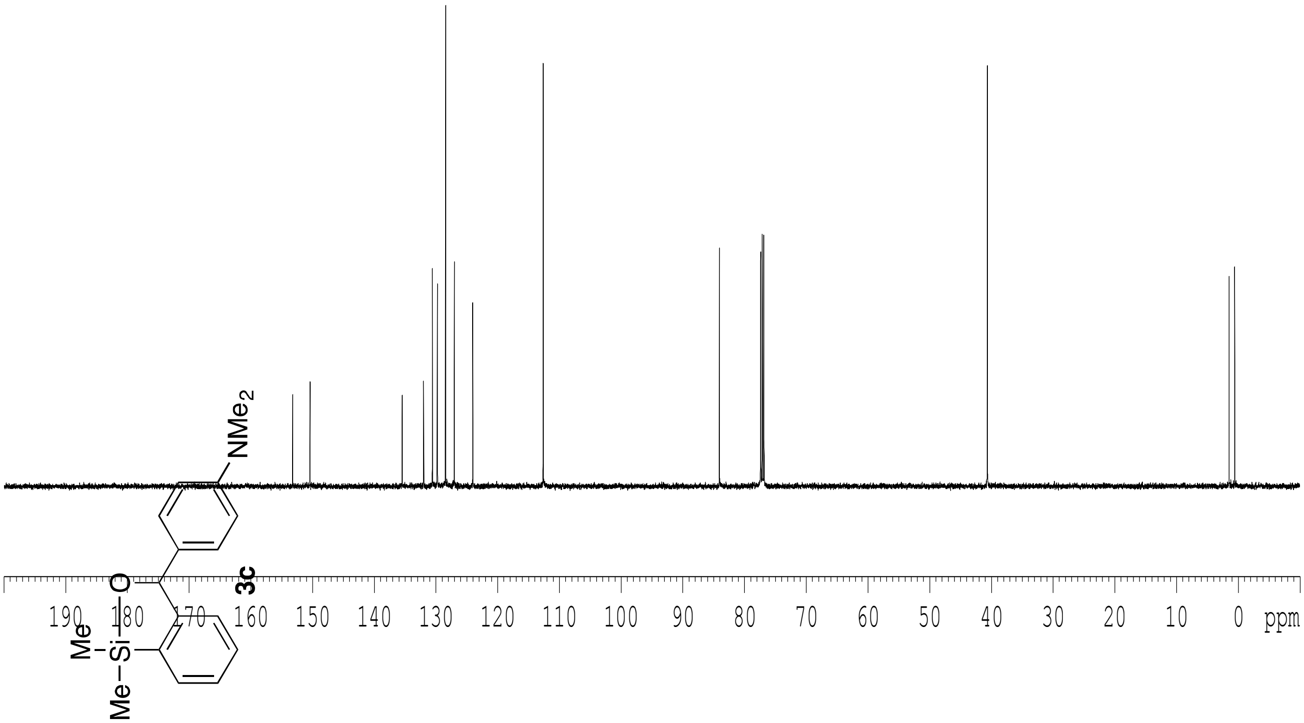
S9


NMe$_2$
OH
Br
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

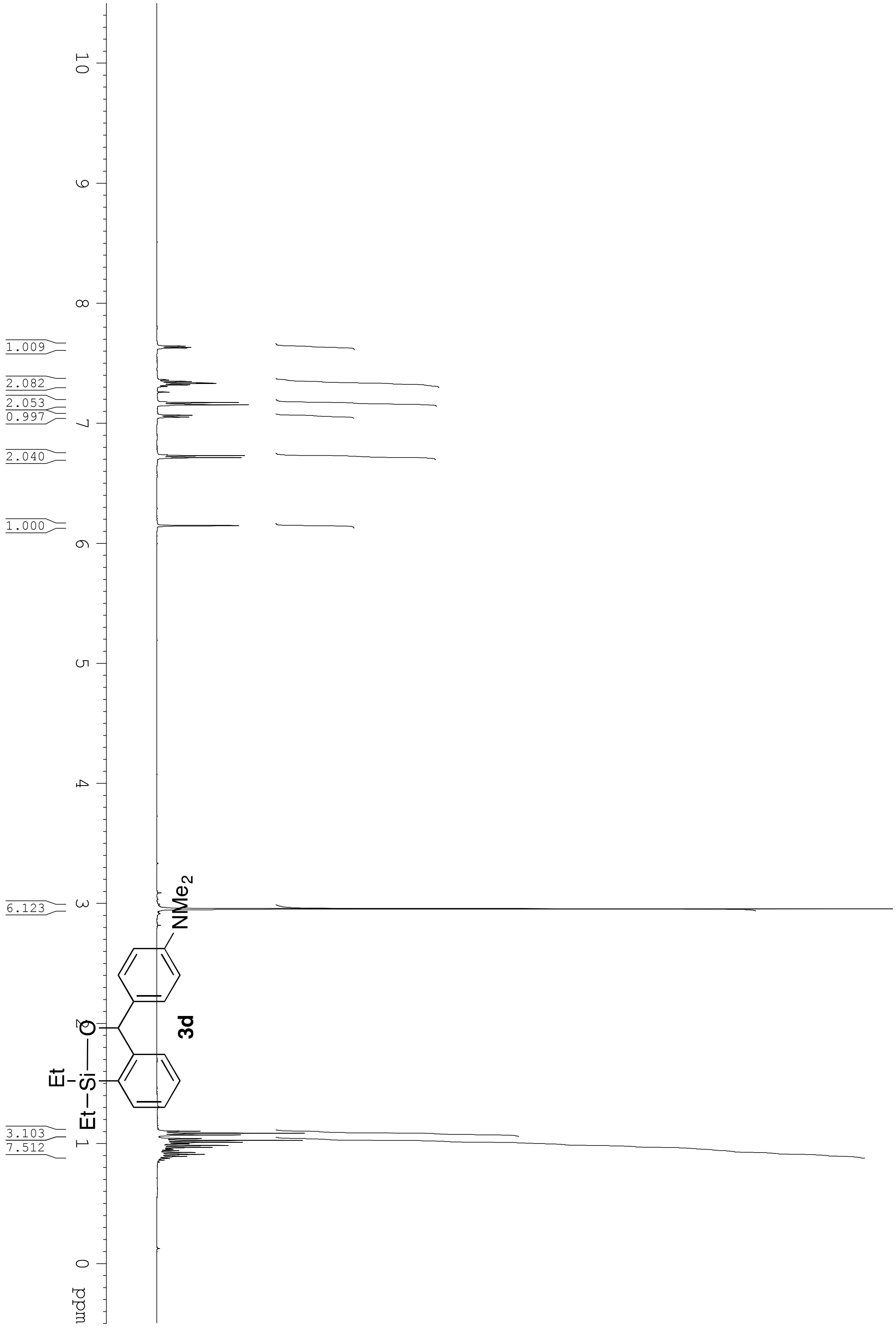
S9


10
9
8
7
6
5
4
3
2
1
0
ppm
1.003
2.066
2.011
1.019
2.060
1.000
6.105
3.023
3.005
NMe$_2$
Me
Me–Si–O

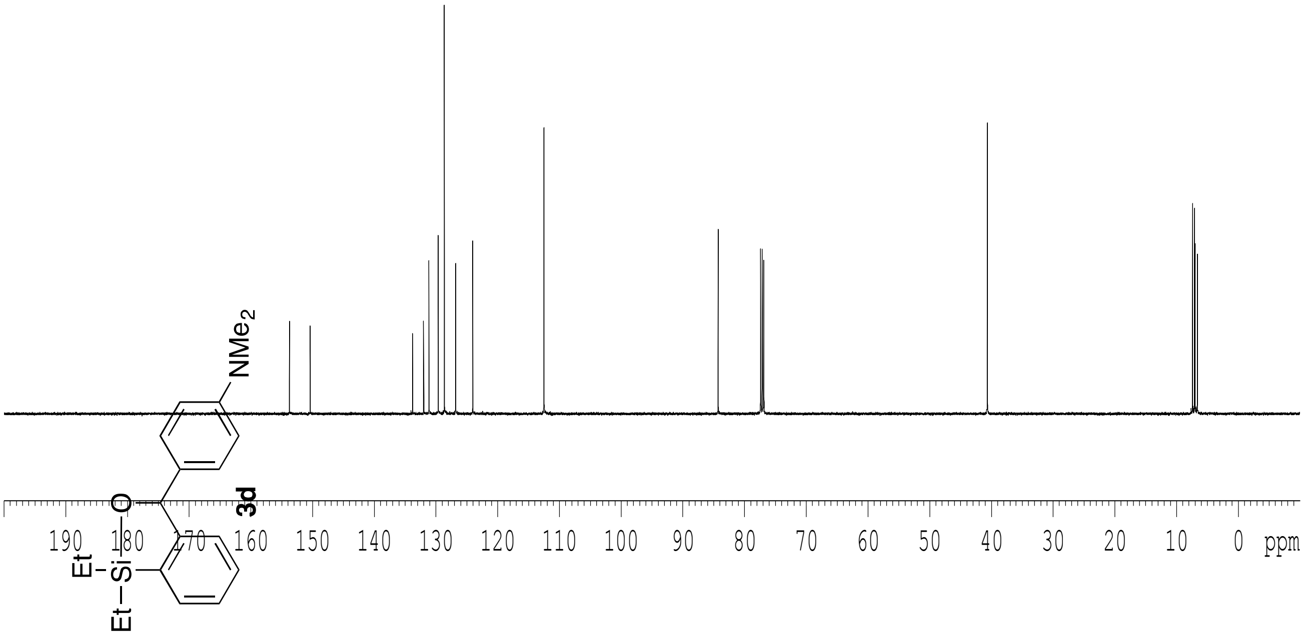
3c


NMe2
Me
Me–Si–O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

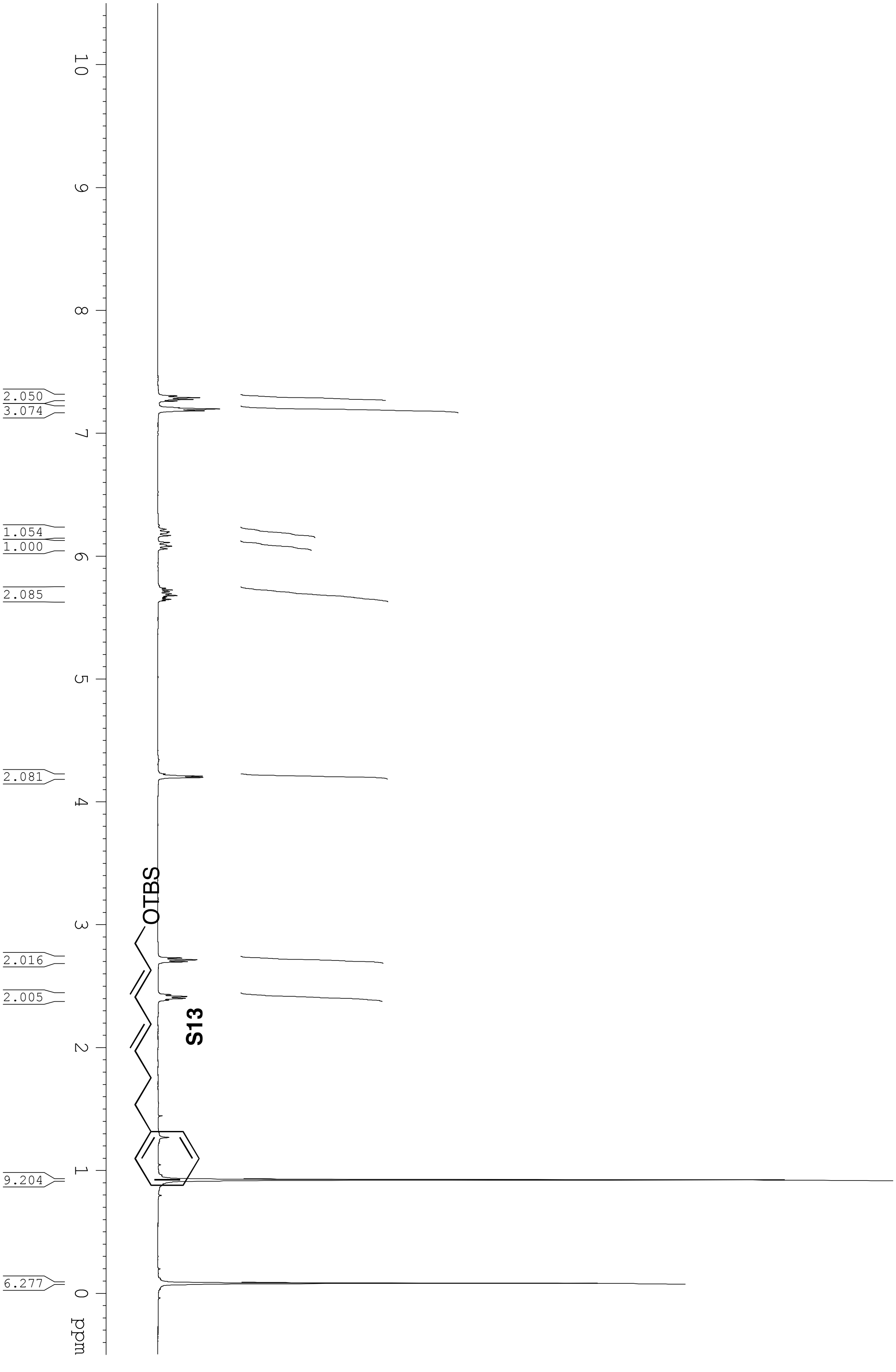
3c


10
9
8
7
6
5
4
3
2
1
0
ppm
1.009
2.082
2.053
0.997
2.040
1.000
6.123
3.103
7.512
NMe2
Et
Et–Si
O

3d

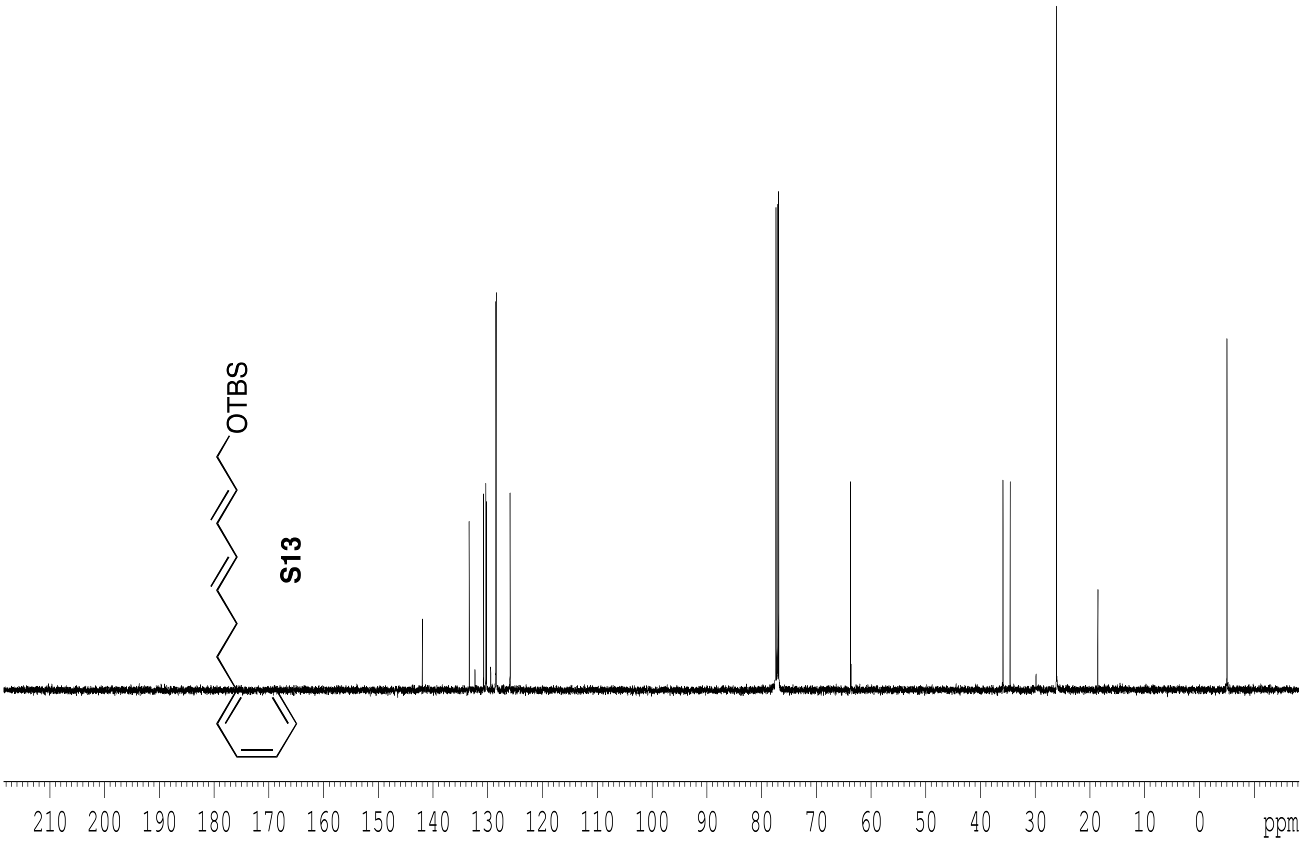

NMe2
Et
Et
Si
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

3d



2.050
3.074
1.054
1.000
2.085
2.081
2.016
2.005
9.204
6.277
10
9
8
7
6
5
4
3
2
1
0
ppm
OTBS

S13


S13

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