Aryl Silane Oxidation – New Routes to Hydroxylated Aromatics

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Supporting Information

1. General Experimental Details

^{1}H nuclear magnetic resonance (NMR) spectra were recorded using an internal deuterium lock for the residual protons in $CDCl_3$ (δ_H 7.26 ppm) or C_6D_6 (δ_H 7.15 ppm) at ambient probe temperatures on the following instruments: Bruker AVII 500 (500 MHz), Bruker DPX400 (400 MHz), Bruker DPX250 (250 MHz) and Bruker DPX200 (200 MHz) spectrometers. Data are presented as follows: chemical shift (in ppm on a δ_H scale relative to $\delta_{TMS} = 0$), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, sex = sextet, sep = septet, m = multiplet, br = broad, obs = obscured, *app* = apparent), coupling constant (*J* / Hz) and assignment. Assignments were determined either on the basis of unambiguous chemical shift or coupling pattern, COSY experiments, or by analogy to fully interpreted spectra for related compounds. ^{13}C spectra were recorded by broadband proton spin decoupling, at ambient probe temperatures on the following instruments: Bruker AVII 500 (125 MHz), Bruker AV400 (100 MHz) and Bruker DPX250 (62.9 MHz) using an internal deuterium lock for $CDCl_3$ (δ_H 77.0 ppm). Chemical shifts are given in ppm on a δ scale relative to $\delta_{TMS} = 0$.

Infra-red spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer. The sample was prepared as a thin film between NaCl plates or KBr disc. Wavelengths of maximum absorbance (ν_{max}) are quoted in cm^{-1}.

Low resolution mass spectra were recorded on a Waters LCT Premier EX mass spectrometer, using electron spray (ES$^+$, ES$^-$) techniques. High resolution mass spectra were recorded by the Departmental Mass Spectrometry Service, University of Oxford, using electrospray ionisation (ESI$^+$) and field ionisation (FI) techniques. The parent ion $[M]^+$, $[M+H]^+$ or $[M+Na]^+$ is quoted.

Melting points were obtained using a Reichert-Koffler block and are uncorrected.

Analytical thin layer chromatography (TLC) was carried out on Merck Kieselgel 60 F_{254} plates with visualization by ultraviolet light (254 nm) and potassium permanganate dip. Flash column chromatography was carried out on Merck Kieselgel 60 (230 - 400 mesh) under positive pressure using distilled solvents; the procedure includes the subsequent evaporation of solvents *in vacuo*.

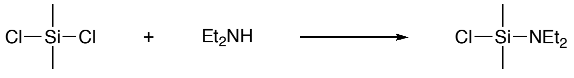
Reagents and solvents were purified by standard means.[1] Dichloromethane (DCM) and tetrahydrofuran (THF) were passed through an activated alumina column under an argon atmosphere; diethyl ether (Et_2O), methanol

(MeOH), ethanol (EtOH), toluene (PhMe) and benzene (PhH) were distilled from calcium hydride and stored under an argon atmosphere.

Triethylamine (Et_3N), pyridine (pyr) and *N,N,N,N*-tetramethylethylenediamine (TMEDA) were distilled from and stored over calcium hydride. All other chemicals were used as received, except where otherwise noted in the experimental text. All solutions of sodium bicarbonate ($NaHCO_3$), ammonium chloride (NH_4Cl), and sodium thiosulphate ($Na_2S_2O_3$) were aqueous and saturated. The term `brine' is used to describe a saturated aqueous solution of sodium chloride (NaCl).

All experiments were performed under anhydrous condition under an atmosphere of argon, except where stated, using oven-dried apparatus and employing standard techniques for handling air-sensitive materials. Unless stated otherwise, reaction were performed at room temperature (r.t.).

2. Preparation of Diethylaminochlorodimethylsilane 4[2]



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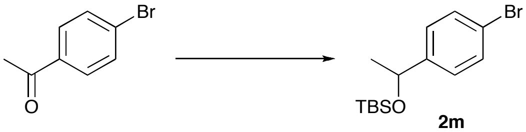
The title compound was prepared according to the procedure of Tamao.[2] To a stirred solution of dichlorodimethylsilane (30 mL, 249 mmol, 1.0 eq) and Et_3N (38.1 mL, 274 mmol, 1.1 eq) in THF (30 mL) at 0 °C was added distilled Et_2NH (25.7 mL, 249 mmol, 1.0 eq) in THF (30 mL) over a period of 2 h. Following addition of a further 40 mL of THF, the resulting reaction mixture was left to stir at r.t. overnight. Subsequent dilution with pentane (50 mL), filtration over celite, and concentration *in vacuo* yielded the crude product, which was purified by vacuum distillation to afford aminosilane **4** (18.9 g, 115 mmol, 46%) as a colourless liquid; **bp** 84 °C, 110 mbar (lit.[ref] bp 84 - 87 °C, 90 mmHg); **^{1}H NMR** (400 MHz, C_6D_6) δ_H 2.69 (4H, q, *J* = 7.0 Hz, $N(C\underline{H}_2CH_3)_2$), 0.89 (6H, t, *J* = 7.0 Hz, $N(CH_2C\underline{H}_3)_2$), 0.32 (6H, s, $SiMe_2$).

This data is in accordance with that reported by Beignet *et al.*[3]

3. Preparation of novel starting materials

(1-(4-Bromophenyl)ethoxy)(*tert*-butyl)dimethylsilane 2m



2m

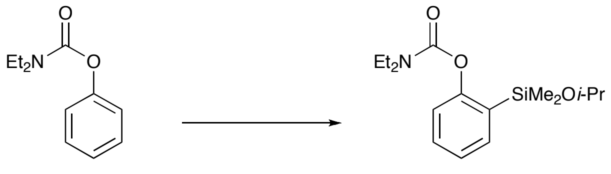
To a stirred solution of 4-bromoacetophenone (0.50 g, 2.51 mmol, 1.0 eq) in EtOH (25 mL) was added $NaBH_4$ (105 mg, 2.76 mmol, 1.1 eq) at r.t. After stirring for 3 h, the reaction mixture was concentrated *in vacuo*, diluted with DCM (10 mL) and washed with water (10 mL). The organic phase was dried ($MgSO_4$) and concentrated *in vacuo* to yield the crude alcohol as a yellow solid of sufficient purity to submit to the following step; **R_f** 0.45 (50% Et_2O / P.E. 40 - 60); **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.47 (2H, td, *J* = 1.9, 8.4 Hz, ArH), 7.25 (2H, td, *J* = 1.9, 8.4 Hz), 4.90 - 4.84 (1H, m, $ArC\underline{H}(OH)CH_3$), 1.80 (1H, d, *J* = 3.7 Hz, OH), 1.47 (3H, d, *J* = 6.5 Hz, $ArCH(OH)C\underline{H}_3$); This data is in agreement with that reported by Chen *et al.*[4] To a stirred solution of the crude alcohol and imidazole (0.43 g, 6.28 mmol, 2.5 eq) in DCM (6 mL) at 0 °C was added TBSCl (0.46 g, 3.01 mmol, 1.2 eq) following the dissolution of imidazole. The reaction was stirred at r.t. for 30 min, then quenched with NH_4Cl solution (6 mL). The phases were separated, the aqueous phase extracted with DCM (2 x 6 mL) and the combined organic phases dried ($MgSO_4$) and concentrated *in vacuo*. Purification by flash column chromatography (50% Et_2O / P.E. 40 - 60) afforded silylation product **2m** (670 mg, 2.12 mmol, 85% over two steps) as a colourless oil; **R_f** 0.70 (20% Et_2O / P.E. 40 - 60); **ν_{max}** (thin film) / cm^{-1} 2956, 2929, 2858, 1593, 1489, 1472, 1404, 1369, 1257, 1204, 1095, 1032, 1010, 958, 835, 777, 668; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.43 (2H, d, *J*

= 8.5 Hz, ArH), 7.20 (2H, d, *J* = 8.5 Hz), 4.82 (1H, q, *J* = 6.4 Hz, $\mathrm{ArC\underline{H}(OTBS)CH_3}$), 1.37 (3H, d, *J* = 6.4 Hz, $\mathrm{ArCH(OTBS)C\underline{H}_3}$), 0.89 (9H, s, $\mathrm{Si(CH_3)_2C(C\underline{H}_3)_3}$), 0.05 (3H, s, $\mathrm{Si(C\underline{H}_3)_2C(CH_3)_3}$), 0.03 (3H, s, $\mathrm{Si(C\underline{H}_3)_2C(CH_3)_3}$); **^{13}C NMR** (100 MHz, $\mathrm{CDCl_3}$) δ_C 146.0, 131.2, 127.0, 120.3, 70.3, 27.2, 25.8, 18.2, -4.83; **HRMS (FI)** calculated for $\mathrm{C_{14}H_{23}BrOSi}$ $[\mathrm{M}]^+$ 314.0702, found 314.0705.

4. Preparation of *iso*-propoxyarylsilanes

4.1. Silylation protocols using directed *ortho*-lithiation

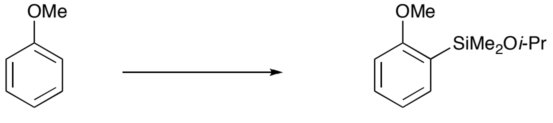
2-(*Iso*-propoxydimethylsilyl)phenyl diethylcarbamate 6a[5]



1a **6a**

To a stirred solution of phenyl diethylcarbamate **1a** (250 mg, 1.29 mmol, 1.0 eq) and TMEDA (0.25 mL, 1.68 mmol, 1.3 eq) in THF (5 mL) at -78 °C was added *s*-BuLi (1.21 mL of a 1.3M solution in cyclohexane/hexane, 1.68 mmol, 1.3 eq). The resulting mixture was stirred for 1 h before addition of $\mathrm{ClSiMe_2(NEt_2)}$ **4** (0.39 mL, 1.94 mmol, 1.5 eq), then stirring was continued at -78 °C for another 2 h. Upon warming to r.t., ^{i}PrOH (1 mL) and DMAP (crystal) were added before stirring overnight. The reaction mixture was concentrated *in vacuo*, and the resulting crude mixture was purified by flash column chromatography (30% $\mathrm{Et_2O}$ / P.E. 40 - 60) to afford silylation product **6a** (349 mg, 1.13 mmol, 88%) as a pale yellow oil; **R_f** 0.36 (40% $\mathrm{Et_2O}$ / P.E. 40 - 40); **ν_{max}** (thin film) / cm^{-1} 2972, 1721, 1595, 1469, 1416, 1381, 1317, 1259, 1226, 1194, 1156, 1080, 1026, 962, 882, 834, 786, 755, 719, 638; **^{1}H NMR** (400 MHz, $\mathrm{CDCl_3}$) δ_H 7.56 (1H, dd, *J* = 1.7, 7.3 Hz, ArH), 7.40 (1H, dt, *J* = 1.7, 7.9 Hz, ArH), 7.19 (1H, t, *J* = 7.3 Hz, ArH), 7.09 (1H, d, *J* = 7.9 Hz, ArH), 3.99 (1H, sep, *J* = 6.2 Hz, $\mathrm{OC\underline{H}(CH_3)_2}$), 3.50 (2H, q, *J* = 7.1 Hz, $\mathrm{NC\underline{H}_2CH_3}$), 3.40 (2H, q, *J* = 7.1 Hz, $\mathrm{NC\underline{H}_2CH_3}$), 1.26 (3H, t, *J* = 7.1 Hz, $\mathrm{NCH_2C\underline{H}_2}$), 1.19 (3H, t, *J* = 7.1 Hz, $\mathrm{NCH_2C\underline{H}_2}$), 1.14 (6H, d, *J* = 6.2 Hz, $\mathrm{OCH(C\underline{H}_3)_2}$), 0.37 (6H, s, $\mathrm{SiMe_2}$); **^{13}C NMR** (62.9 MHz, $\mathrm{CDCl_3}$) δ_C 156.2, 154.3, 135.2, 130.8, 129.9, 124.7, 122.3, 65.5, 42.0, 41.6, 25.6, 14.2, 13.3, -0.4; **HRMS (ESI$^+$)** calculated for $\mathrm{C_{16}H_{27}NNaO_3Si}$ $[\mathrm{M+Na}]^+$ 332.1652, found 332.1648.

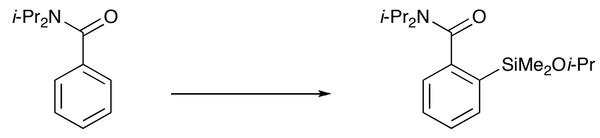
Iso-propoxy(2-methoxyphenyl)dimethylsilane 6b[6]



1b **6b**

To a solution of anisole **1b** (250 mg, 2.31 mmol, 1.0 eq) and TMEDA (0.45 mL, 3.00 mmol, 1.3 eq) in $\mathrm{Et_2O}$ (5 mL) at -78 °C was added *n*-BuLi (1.20 mL of a 2.5 M solution in hexanes, 3.00 mmol, 1.3 eq). The resulting mixture was stirred for 1 h before addition of $\mathrm{ClSiMe_2(NEt_2)}$ **4** (0.69 mL, 3.47 mmol, 1.5 eq), then stirring was continued at -78 °C for a further 2 h. Upon warming to r.t., ^{i}PrOH (1 mL) and DMAP (crystal) were added before stirring overnight. The reaction mixture was concentrated *in vacuo*, and the resulting crude mixture was purified by flash column chromatography (50% $\mathrm{Et_2O}$ / P.E. 40 - 60) to afford silylation product **6b** (478 mg, 2.13 mmol, 92%) as a colourless oil; **R_f** 0.66 (20% $\mathrm{Et_2O}$ / P.E. 40 - 60); **ν_{max}** (thin film) / cm^{-1} 2970, 1590, 1572, 1463, 1429, 1381, 1367, 1238, 1174, 1130, 1085, 1027, 881, 833, 784, 758; **^{1}H NMR** (400 MHz, $\mathrm{CDCl_3}$) δ_H 7.53 (1H, dd, *J* = 1.8, 7.6 Hz, ArH), 7.38 (1H, dd, *J* = 1.8, 8.0 Hz, ArH), 6.98 (1H, d, *J* = 7.2 Hz, ArH), 6.85 (1H, d, *J* = 8.0 Hz), 4.06 (1H, sep, *J* = 6.1 Hz, $\mathrm{OC\underline{H}(CH_3)_2}$), 3.82 (3H, s, ArOMe), 1.17 (6H, d, *J* = 6.1 Hz, $\mathrm{OCH(C\underline{H}_3)_2}$), 0.39 (6H, s, $\mathrm{SiMe_2}$); **^{13}C NMR** (62.9 MHz, $\mathrm{CDCl_3}$) δ_C 164.1, 135.5, 131.2, 126.2, 120.3, 109.4, 65.1, 54.8, 25.7, -0.50; **HRMS (ESI$^+$)** calculated for $\mathrm{C_{12}H_{20}O_2SiNa}$ $[\mathrm{M+Na}]^+$ 247.1125, found 247.1125.

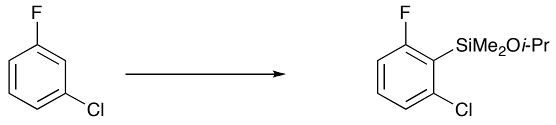
2-(isopropoxydimethylsilyl)-N,N-diisopropylbenzamide 6c[7]



1c **6c**

To a solution of *N,N*-di*iso*-propylbenzamide **1c** (250 mg, 1.19 mmol, 1.0 eq) and TMEDA (0.23 mL, 1.55 mmol, 1.3 eq) in THF (5 mL) at -78 °C was added *s*-BuLi (1.19 mL of a 1.3 M solution in hexanes, 1.55 mmol, 1.3 eq). The resulting mixture was stirred for 1 h before addition of $ClSiMe_2(NEt_2)$ **4** (0.35 mL, 1.79 mmol, 1.5 eq), then stirring was continued at -78 °C for a further 2 h. Upon warming to r.t., ^{i}PrOH (1 mL) and DMAP (crystal) were added before stirring overnight. The reaction mixture was concentrated *in vacuo*, and the resulting crude mixture was purified by flash column chromatography (50% Et_2O / P.E. 40 – 60) to afford silylation product **6c** (373 mg, 1.16 mmol, 98%) as a white solid; **mp** 67.6 – 72.7 °C; $\mathbf{R_f}$ 0.29 (50% Et_2O / P.E. 40 - 60); $\mathbf{v_{max}}$ (KBr disk) / cm^{-1} 2972, 1624, 1439, 1368, 1338, 1130, 1019, 876, 795, 756; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.88 – 7.84 (1H, m, ArH), 7.39 – 7.32 (2H, m, ArH), 7.19 – 7.15 (1H, m, ArH), 4.11 (1H, sep, *J* = 6.1 Hz, $OC\underline{H}(CH_3)_2$), 3.84 (1H, br s, $NC\underline{H}(CH_3)_2$), 3.50 (1H, br s, $NC\underline{H}(CH_3)_2$), 1.56 (6H, br s, $NCH(C\underline{H}_3)_2$), 1.20 (6H, d, *J* = 6.1 Hz, $OCH(C\underline{H}_3)_2$), 1.16 (6H, br s, $NCH(C\underline{H}_3)_2$), 0.42 (6H, s, $SiMe_2$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 172.3, 143.7, 136.9, 135.8, 128.6, 127.8, 124.9, 65.2, 50.9, 45.8, 25.8, 20.6, 0.42; **HRMS (FI)** calculated for $C_{18}H_{31}NO_2Si$ $[M]^+$ 321.2124, found 321.2117.

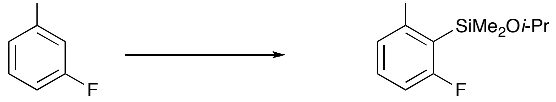
(2-chloro-6-fluorophenyl)(isopropoxy)dimethylsilane 6d[8]



1d **6d**

To a solution of 1-chloro-3-difluorobenzene **1d** (250 mg, 1.91 mmol, 1.0 eq) and TMEDA (0.34 mL, 2.30 mmol, 1.2 eq) in THF (5 mL) at -78 °C was added *n*-BuLi (0.92 mL of a 2.5 M solution in hexanes, 2.30 mmol, 1.2 eq). The resulting mixture was stirred for 3 h before addition of $ClSiMe_2(NEt_2)$ **4** (0.53 mL, 2.67 mmol, 1.4 eq), then stirring was continued at -78 °C for a further 2 h. Upon warming to r.t., ^{i}PrOH (2 mL) and DMAP (crystal) were added before stirring overnight. The reaction mixture was concentrated *in vacuo*, and the resulting crude mixture was purified by flash column chromatography (50% Et_2O / P.E. 40 - 60) to afford silylation product **6d** (467 mg, 1.89 mmol, 99%) as a colourless oil; $\mathbf{R_f}$ 0.69 (20% Et_2O / P.E. 40 - 60); $\mathbf{v_{max}}$ (thin film) / cm^{-1} 2973, 1590, 1562, 1432, 1261, 1229, 1124, 1107, 1032, 876, 823, 791; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.27 (1H, *app* q, *J* = 6.7 Hz, ArH), 7.16 (1H, d, *J* = 8.1 Hz, ArH), 6.91 (1H, *app* t, *J* = 8.1 Hz, ArH), 4.06 (1H, sep, *J* = 6.1 Hz, $OC\underline{H}(CH_3)_2$), 1.17 (6H, d, *J* = 6.1 Hz, $OCH(C\underline{H}_3)_2$), 0.54 (6H, d, *J* = 3.1 Hz, $SiMe_2$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 167.2 (d, $J^1_{C\text{-}F}$ = 246.2 Hz), 141.2 (d, $J^3_{C\text{-}F}$ 13.7 Hz), 132.0 (d, $J^3_{C\text{-}F}$ = 10.5 Hz), 125.9 (d, $J^4_{C\text{-}F}$ = 3.2 Hz), 124.7 (d, $J^2_{C\text{-}F}$ 27.3 Hz), 113.7 (d, $J^2_{C\text{-}F}$ 27.8 Hz), 66.2, 25.7, 1.96 (d, $J^4_{C\text{-}F}$ = 4.8 Hz); **HRMS (FI)** calculated for $C_{11}H_{16}F_2OSi$ $[M]^+$ 230.0939, found 230.0949.

(2,6-difluorophenyl)(isopropoxy)dimethylsilane 6e[8]



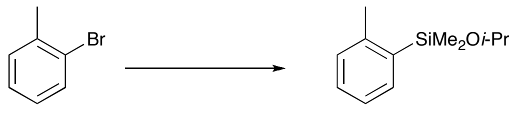
1e **6e**

To a solution of 1,3-difluorobenzene **1e** (250 mg, 2.19 mmol, 1.0 eq) and TMEDA (0.39 mL, 2.63 mmol, 1.2 eq) in THF (5 mL) at -78 °C was added *n*-BuLi (1.05 mL of a 2.5 M solution in hexanes, 2.63 mmol, 1.2 eq). The resulting mixture was stirred for 3 h before addition of $ClSiMe_2(NEt_2)$ **4** (0.61 mL, 3.07 mmol, 1.4 eq), then stirring was continued at -78 °C for a further 2 h. Upon warming to r.t., ^iPrOH (2 mL) and DMAP (crystal) were added before stirring overnight. The reaction mixture was concentrated *in vacuo*, and the resulting crude mixture was purified by flash column chromatography (50% Et_2O / P.E. 40 - 60) to afford silylation product **6e** (408 mg, 1.77 mmol, 81%) as a colourless oil; $\mathbf{R_f}$ 0.71 (20% Et_2O / P.E. 40 - 60); $\mathbf{v_{max}}$ (thin film) / cm^{-1} 2974, 1611, 1556, 1446, 1383, 1369, 1252, 1220, 1174, 1123, 1107, 1034, 977, 886, 824, 795; ^{1}**H NMR** (400 MHz, $CDCl_3$) δ_H 7.38 – 7.30 (2H, m, ArH), 6.83 (1H, t, J = 7.9 Hz, ArH), 4.06 (1H, sep, J = 6.1 Hz, $OC\underline{H}(CH_3)_2$), 1.15 (6H, d, J = 6.1 Hz, $OCH(C\underline{H}_3)_2$), 0.49 (6H, t, J = 1.9 Hz, $SiMe_2$); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ_C 167.0 (dd, $J^1_{C\text{-}F}$ = 245.4 Hz, $J^3_{C\text{-}F}$ = 15.3 Hz), 132.5 (t, $J^3_{C\text{-}F}$ = 10.5 Hz), 112.2 (t, $J^2_{C\text{-}F}$ = 33.5 Hz), 111.1 (d, $J^2_{C\text{-}F}$ = 30.4 Hz), 65.8, 25.4, 1.04 (t, $J^4_{C\text{-}F}$ = 3.1 Hz); **HRMS (FI)** calculated for $C_{11}H_{16}FClOSi$ $[M]^+$ 246.0643, found 246.0642.

4.2. General silylation protocol using bromine-lithium exchange

To a stirred solution of the aryl bromide (250m mg, 1.0 eq) in THF or Et_2O (5 mL) at -78 °C was added *n*- or *t*-BuLi (1.2 - 2.0 eq). $ClSiMe_2(NEt_2)$ **4** (1.4 eq) was subsequently added, and stirring continued for a further 2 h at -78 °C. Upon warming to r.t., ^iPrOH (1 mL) and DMAP (crystal) were added before stirring overnight. The reaction mixture was concentrated *in vacuo*, and the resulting crude mixture was purified by flash column chromatography (Et_2O / P.E. 40 - 60) to afford the silylation product (75 - 99%) as a colourless or pale yellow oil.

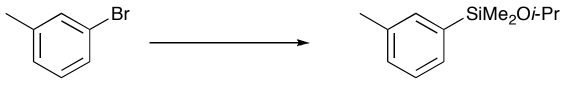
Iso-propoxydimethyl(*o*-tolyl)silane 6f



2a **6f**

Following the general bromine-lithium exchange protocol with 2-bromotoluene **2a** (250 mg, 1.46 mmol, 1.0 eq) and *n*-BuLi (0.70 mL of a 2.5 M solution in hexanes, 1.75 mmol, 1.2 eq) in THF, the resulting crude mixture was purified by flash column chromatography (50% Et_2O / P.E. 40 - 60) to afford silylation product **6f** (302 mg, 1.45 mmol, 99%) as a colourless oil; $\mathbf{R_f}$ 0.68 (20% Et_2O / P.E. 40 - 60); $\mathbf{v_{max}}$ (thin film) / cm^{-1} 2971, 1450, 1381, 1368, 1252, 1130, 1025, 881, 832, 782, 747; ^{1}**H NMR** (400 MHz, $CDCl_3$) δ_H 7.53 (1H, dd, J = 1.7, 7.7 Hz, ArH), 7.29 (1H, dt, J = 1.4, 7.7 Hz, ArH), 7.19 - 7.16 (2H, m, ArH), 3.99 (1H, sep, J = 5.9 Hz, $OC\underline{H}(CH_3)_2$), 2.53 (3H, s, ArMe), 1.51 (6H, d, J = 5.9 Hz, $OCH(C\underline{H}_3)_2$), 0.43 (6H, s, $SiMe_2$); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ_C 143.8, 136.7, 134.6, 129.8, 129.7, 124.7, 65.3, 25.6, 22.6, -0.14; **HRMS (FI)** calculated for $C_{12}H_{20}OSi$ $[M]^+$ 208.1283, found 208.1281.

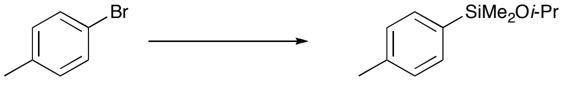
Iso-propoxydimethyl(*m*-tolyl)silane 6g



2b **6g**

Following the general bromo-lithium exchange protocol with 3-bromotoluene **2b** (250 mg, 1.46 mmol, 1.0 eq) and *n*-BuLi (0.70 mL of a 2.5 M solution in hexanes, 1.75 mmol, 1.2 eq) in THF, the resulting crude mixture was purified by flash column chromatography (50% Et_2O / P.E. 40 - 60) to afford silylation product **6g** (301 mg, 1.45 mmol, 99%) as a colourless oil; $\mathbf{R_f}$ 0.61 (20% Et_2O / P.E. 40 - 60); $\mathbf{v_{max}}$ (thin film) / cm^{-1} 2971, 1381, 1368, 1252, 1120, 1029, 883, 867, 810, 772; ^{1}**H NMR** (500 MHz, $CDCl_3$) δ_H 7.41 - 7.40 (2H, m, ArH), 7.28 (1H, t, J = 7.7 Hz, ArH), 7.22 (1H, d, J = 7.7 Hz, ArH), 4.00 (1H, sep, J = 5.9 Hz, $OC\underline{H}(CH_3)_2$), 2.38 (3H, s, ArMe), 1.15 (6H, d, J = 5.9 Hz, $OCH(C\underline{H}_3)_2$), 0.38 (6H, s, $SiMe_2$); ^{13}**C NMR** (125 MHz, $CDCl_3$) δ_C 138.3, 136.9, 134.1, 130.5, 130.4, 127.7, 65.2, 25.7, 21.5, -1.13; **HRMS (FI)** calculated for $C_{12}H_{20}OSi$ $[M]^+$ 208.1283, found 208.1285.

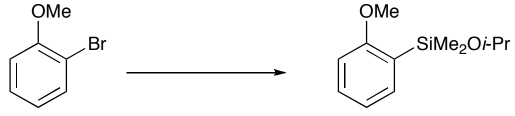
Iso-propoxydimethyl(*p*-tolyl)silane 6h



2c **6h**

Following the general bromo-lithium exchange protocol with 4-bromotoluene **2c** (250 mg, 1.46 mmol, 1.0 eq) and *n*-BuLi (0.70 mL of a 2.5 M solution in hexanes, 1.75 mmol, 1.2 eq) in THF, the resulting crude mixture was purified by flash column chromatography (50% Et_2O / P.E. 40 - 60) to afford silylation product **6h** (302 mg, 1.45 mmol, 99%) as a colourless oil; **R_f** 0.62 (20% Et_2O / P.E. 40 - 60); **ν_{max}** (thin film) / cm^{-1} 2971, 1381, 1368, 1251, 1111, 1030, 882, 832, 782; **^1H NMR** (500 MHz, $CDCl_3$) δ_H 7.50 (2H, d, *J* = 7.6 Hz, ArH), 7.21 (2H, d, *J* = 7.6 Hz, ArH), 4.00 (1H, sep, *J* = 6.0 Hz, $OC\underline{H}(CH_3)_2$), 2.37 (3H, s, ArMe), 1.14 (6H, d, *J* = 5.9 Hz, $OCH(C\underline{H}_3)_2$), 0.38 (6H, s, $SiMe_2$); **^{13}C NMR** (125 MHz, $CDCl_3$) δ_C 139.3, 136.3, 133.7, 128.5, 65.2, 25.5, 21.6, -1.11; **HRMS (FI)** calculated for $C_{12}H_{20}OSi$ $[M]^+$ 208.1283, found 208.1289.

Iso-propoxy(2-methoxyphenyl)dimethylsilane 6b

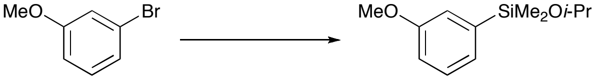


2d **6b**

Following the general bromo-lithium exchange protocol with 2-bromoanisole **2d** (250 mg, 1.34 mmol, 1.0 eq) and *n*-BuLi (0.64 mL of a 2.5 M solution in hexanes, 1.61 mmol, 1.2 eq) in THF, the resulting crude mixture was purified by flash column chromatography (50% Et_2O / P.E. 40 - 60) to afford silylation product **6b** (283 mg, 1.26 mmol, 94%) as a colourless oil; **R_f** 0.66 (20% Et_2O / P.E. 40 - 60); **^1H NMR** (400 MHz, $CDCl_3$) δ_H 7.53 (1H, dd, *J* = 1.8, 7.4 Hz, ArH), 7.38 (1H, dd, *J* = 1.8, 8.0 Hz, ArH), 6.98 (1H, d, *J* = 7.4 Hz, ArH), 6.85 (1H, d, *J* = 8.0 Hz), 4.06 (1H, sep, *J* = 6.1 Hz, $OC\underline{H}(CH_3)_2$), 3.82 (3H, s, ArOMe), 1.17 (6H, d, *J* = 6.1 Hz, $OCH(C\underline{H}_3)_2$), 0.39 (6H, s, $SiMe_2$).

This data is in accordance with that reported above for *iso*-propoxy(2-methoxyphenyl)dimethylsilane 6b.

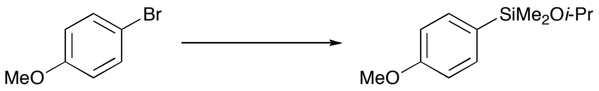
Iso-propoxy(3-methoxyphenyl)dimethylsilane 6i



2e **6i**

Following the general bromo-lithium exchange protocol with 3-bromoanisole **2e** (250 mg, 1.34 mmol, 1.0 eq) and *t*-BuLi (2 mL of a 1.6 M solution in pentane, 2.68 mmol, 2.0 eq) in THF, the resulting crude mixture was purified by flash column chromatography (50% Et_2O / P.E. 40 - 60) to afford silylation product **6i** (297 mg, 1.32 mmol, 99%) as a colourless oil; **R_f** 0.60 (30% Et_2O / P.E. 40 - 60); **ν_{max}** (thin film) / cm^{-1} 2970, 1571, 1482, 1464, 1408, 1283, 1249, 1230, 1173, 1122, 1027, 860, 809, 778, 697; **^1H NMR** (400 MHz, $CDCl_3$) δ_H 7.33 (1H, t, *J* = 7.7 Hz, ArH), 7.19 - 7.14 (2H, m, ArH), 6.94 (1H, dd, *J* = 2.8, 8.2 Hz, ArH), 4.00 (1H, sep, *J* = 6.0 Hz, $OC\underline{H}(CH_3)_2$), 3.84 (3H, s, ArOMe), 1.15 (6H, d, *J* = 6.0 Hz, $OCH(C\underline{H}_3)_2$), 0.38 (6H, s, $SiMe_2$); **^{13}C NMR** (125 MHz, $CDCl_3$) δ_C 158.9, 140.2, 129.0, 125.8, 118.9, 114.7, 65.3, 55.1, 25.7, -1.14; **HRMS (FI)** calculated for $C_{12}H_{20}O_2Si$ $[M]^+$ 224.1233, found 224.1234.

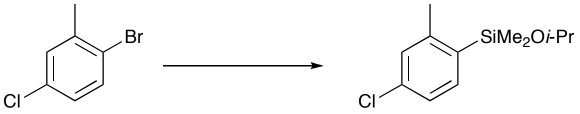
Iso-propoxy(4-methoxyphenyl)dimethylsilane 6j



2f **6j**

Following the general bromo-lithium exchange protocol with 4-bromoanisole **2f** (250 mg, 1.34 mmol, 1.0 eq) and *t*-BuLi (2 mL of a 1.6 M solution in pentane, 2.68 mmol, 2.0 eq) in THF, the resulting crude mixture was purified by flash column chromatography (50% Et$_2$O / P.E. 40 - 60) to afford silylation product **6j** (292 mg, 1.30 mmol, 97%) as a colourless oil; **R$_f$** 0.56 (20% Et$_2$O / P.E. 40 - 60); **ν$_{max}$** (thin film) / cm^{-1} 2971, 1596, 1504, 1464, 1381, 1368, 1311, 1279, 1249 ,1182, 1116, 1029, 881, 832, 783; **^{1}H NMR** (400 MHz, CDCl$_3$) δ_H 7.53 (2H, d, *J* = 8.6 Hz, ArH), 6.93 (2H, d, *J* = 8.6 Hz, ArH), 3.97 (1H, sep, *J* = 6.1 Hz, OC$\underline{H}$(CH$_3$)$_2$), 3.83 (3H, s, ArOMe), 1.13 (6H, d, *J* = 6.1 Hz, OCH(C$\underline{H}_3$)$_2$), 0.37 (6H, s, SiMe$_2$); **^{13}C NMR** (100 MHz, CDCl$_3$) δ_C 160.7, 135.1, 129.5, 113.5, 65.1, 55.0, 25.7, -1.07; **HRMS (FI)** calculated for $C_{12}H_{20}O_2Si$ [M]$^+$ 224.1233, found 224.1230.

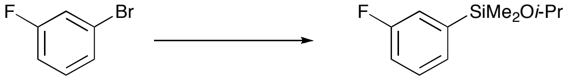
(4-Chloro-2-methylphenyl)(*iso*-propoxy)dimethylsilane 6k



2g **6k**

Following the general bromo-lithium exchange protocol with 1-bromo-4-chloro-2-methylbenzene **2g** (250 mg, 1.22 mmol, 1.0 eq) and *n*-BuLi (0.58 mL of a 2.5 M solution in hexanes, 1.46 mmol, 1.2 eq) in THF, the resulting crude mixture was purified by flash column chromatography (50% Et$_2$O / P.E. 40 - 60) to afford silylation product **6k** (267 mg, 1.10 mmol, 90%) as a colourless oil; **R$_f$** 0.63 (20% Et$_2$O / P.E. 40 - 60); **ν$_{max}$** (thin film) / cm^{-1} 2972, 1581, 1551, 1470, 1381, 1255, 1172, 1124, 1026, 873, 811, 781; **^{1}H NMR** (500 MHz, CDCl$_3$) δ_H 7.45 (1H, d, *J* = 7.9 Hz, ArH), 7.17 - 7.15 (2H, m, ArH), 3.99 (1H, sep, *J* = 6.0 Hz, OC$\underline{H}$(CH$_3$)$_2$), 2.50 (3H, s, ArMe), 1.15 (6H, d, *J* = 6.0 Hz, OCH(C$\underline{H}_3$)$_2$), 0.42 (6H, s, SiMe$_2$); **^{13}C NMR** (500 MHz, CDCl$_3$) δ_C 145.7, 135.9, 135.7, 135.3, 129.8, 125.1, 65.4, 25.5, 22.5, -0.21; **HRMS (FI)** calculated for $C_{12}H_{19}OSiCl$ [M]$^+$ 242.0894, found 242.0888.

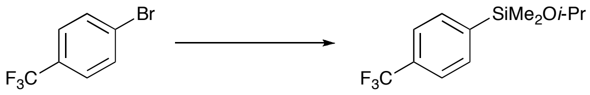
(3-Fluorophenyl)(*iso*-propoxy)dimethylsilane 6l



2h **6l**

Following the general bromo-lithium exchange protocol with 1-bromo-3-fluorobenzene **2h** (250 mg, 1.43 mmol, 1.0 eq) and *n*-BuLi (0.68 mL of a 2.5 M solution in hexanes, 1.72 mmol, 1.2 eq) in THF, the resulting crude mixture was purified by flash column chromatography (50% Et$_2$O / P.E. 40 - 60) to afford silylation product **6l** (253 mg, 1.19 mmol, 83%) as a pale yellow oil; **R$_f$** 0.63 (20% Et$_2$O / P.E. 40 - 60); **ν$_{max}$** (thin film) / cm^{-1} 2973, 1575, 1478, 1406, 1259, 1218, 1173, 1124, 1106, 1030, 886, 812, 781, 690; **^{1}H NMR** (500 MHz, CDCl$_3$) δ_H 7.37 - 7.35 (2H, m, ArH), 7.27 (1H, dd, *J* = 2.7, 8.9 Hz, ArH), 7.09 - 7.05 (1H, m, ArH), 4.00 (1H, sep, *J* = 6.2 Hz, OC$\underline{H}$(CH$_3$)$_2$), 1.16 (6H, d, *J* = 6.2 Hz, OCH(C$\underline{H}_3$)$_2$), 0.39 (6H, s, SiMe$_2$); **^{13}C NMR** (125 MHz, CDCl$_3$) δ_C 162.6 (d, $J^1_{C\text{-}F}$ = 248 Hz), 141.7 (d, $J^3_{C\text{-}F}$ = 3.8 Hz), 129.5 (d, $J^3_{C\text{-}F}$ = 7.1 Hz), 128.9 (d, $J^4_{C\text{-}F}$ = 2.9 Hz), 119.7 (d, $J^2_{C\text{-}F}$ = 18.9 Hz), 116.2 (d, $J^2_{C\text{-}F}$ = 20.9 Hz), 65.5, 25.5, -1.22; **HRMS (FI)** calculated for $C_{11}H_{17}OFSi$ [M]$^+$ 212.1033, found 212.1023.

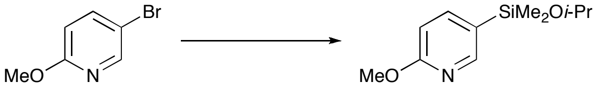
Iso-propoxydimethyl(4-(trifluoromethyl)phenyl)silane 6m



2i **6m**

Following the general bromo-lithium exchange protocol with 1-bromo-4-(trifluoromethyl)benzene **2i** (250 mg, 1.11 mmol, 1.0 eq) and *n*-BuLi (0.53 mL of a 2.5 M solution in hexanes, 1.33 mmol, 1.2 eq) in THF, the resulting crude mixture was purified by flash column chromatography (50% Et_2O / P.E. 40 - 60) to afford silylation product **6m** (276 mg, 1.03 mmol, 95%) as a colourless oil; $\mathbf{R_f}$ 0.66 (20% Et_2O / P.E. 40 - 60); $\mathbf{v_{max}}$ (thin film) / cm^{-1} 2974, 1391, 1327, 1256, 1167, 1129, 1061, 1033, 884, 830, 786, 699; ^{1}**H NMR** (400 MHz, $CDCl_3$) δ_H 7.70 (2H, d, *J* = 7.8 Hz, ArH), 7.61 (2H, d, *J* = 7.8 Hz, ArH), 4.00 (1H, sep, *J* = 6.1 Hz, $OC\underline{H}(CH_3)_2$), 1.15 (6H, d, *J* = 6.1 Hz, $OCH(C\underline{H}_3)_2$), 0.40 (6H, s, $SiMe_2$); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ_C 143.5, 133.7, 131.3 (q, $J^2_{C\text{-}F}$ = 32.6 Hz), 124.3 (q, $J^3_{C\text{-}F}$ = 3.6 Hz), 124.2 (q, $J^1_{C\text{-}F}$ = 271.7 Hz), 65.6, 25.6, -1.26; **HRMS (FI)** calculated for $C_{12}H_{17}OF_3Si$ $[M]^+$ 262.1001, found 262.0991.

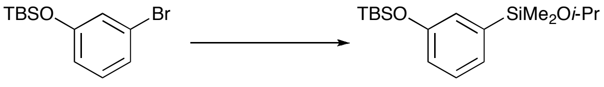
5-(*Iso*-propoxydimethylsilyl)-2-methoxypyridine 6n



2j **6n**

Following the general bromo-lithium exchange protocol with 5-bromo-2-methoxypyridine **2j** (250 mg, 1.33 mmol, 1.0 eq) and *n*-BuLi (0.64 mL of a 2.5 M solution in hexanes, 1.60 mmol, 1.2 eq) in Et_2O, the resulting crude mixture was purified by flash column chromatography (50% Et_2O / P.E. 40 - 60) to afford silylation product **6n** (297 mg, 1.32 mmol, 99%) as a pale yellow oil; $\mathbf{R_f}$ 0.48 (20% Et_2O / P.E. 40 - 60); $\mathbf{v_{max}}$ (thin film) / cm^{-1} 2972, 1587, 1557, 1488, 1355, 1286, 1253, 1174, 1118, 1027, 883, 839, 786; ^{1}**H NMR** (400 MHz, $CDCl_3$) δ_H 8.29 (1H, s, ArH), 7.69 (1H, td, *J* = 2.1, 8.2 Hz, ArH), 6.72 - 6.70 (1H, m, ArH), 3.95 (1H, sep, *J* = 6.0 Hz, $OC\underline{H}(CH_3)_2$), 3.91 (3H, s, ArOMe), 1.09 (6H, d, *J* = 6.0 Hz, $OCH(C\underline{H}_3)_2$), 0.33 (6H, s, $SiMe_2$); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ_C 165.1, 152.1, 143.5, 124.8, 110.7, 65.4, 53.2, 25.7, -1.04; **HRMS (ESI$^+$)** calculated for $C_{11}H_{20}NO_2Si$ $[M+H]^+$ 226.1258, found 226.1255.

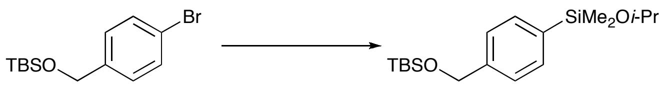
tert-Butyl(3-(*iso*-propoxydimethylsilyl)phenoxy)dimethylsilane 6o



2k **6o**

Following the general bromo-lithium exchange protocol with (3-bromophenoxy)(*tert*-butyl)dimethylsilane **2k** (170 mg, 0.59 mmol, 1.0 eq) and *t*-BuLi (0.74 mL of a 1.6 M solution in pentane, 1.18 mmol, 2.0 eq) in THF, the resulting crude mixture was purified by flash column chromatography (20% Et_2O / P.E. 40 - 60) to afford silylation product **6o** (145 mg, 0.45 mmol, 63%, inseperable mixture with *tert*-butyldimethyl(phenoxy)silane) as a colourless oil; $\mathbf{R_f}$ 0.70 (20% Et_2O / P.E. 40 - 60); $\mathbf{v_{max}}$ (thin film) / cm^{-1} 2960, 2931, 2860, 1587, 1570, 1479, 1398, 1264, 1114, 1029, 951, 881, 835, 782; ^{1}**H NMR** (400 MHz, $CDCl_3$) δ_H 7.24 (1H, d, *J* = 7.8 Hz, ArH), 7.16 (1H, d, *J* = 7.4 Hz, ArH), 7.06 (1H, d, *J* = 2.5 Hz, ArH), 6.87 - 6.83 (1H, m, ArH), 3.98 (1H, sep, *J* = 6.2 Hz, $OC\underline{H}(CH_3)_2$), 1.13 (6H, d, *J* = 6.2 Hz, $OCH(C\underline{H}_3)_2$), 0.99 (9H, s, $Si(CH_3)_2C(C\underline{H}_3)_3$), 0.36 (6H, s, $SiMe_2$), 0.20 (6H, s, $Si(C\underline{H}_3)_2C(CH_3)_3$); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ_C 155.1, 140.1, 129.0, 126.3, 124.9, 121.3, 65.3, 25.72, 25.67, 18.4, -1.19, -4.38; **HRMS (ESI$^+$)** calculated for $C_{17}H_{32}NaO_2Si_2$ $[M+Na]^+$ 347.1833, found 347.1831.

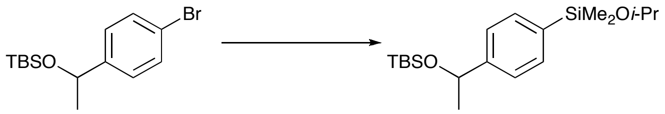
tert-butyl(4-(*iso*-propoxydimethylsilyl)benzyloxy)dimethylsilane 6p



2l **6p**

Following the general bromo-lithium exchange protocol with (4-bromobenzyloxy)(tert-butyl)dimethylsilane **2l** (250 mg, 0.83 mmol, 1.0 eq) and *n*-BuLi (0.40 mL of a 2.5 M solution in hexanes, 1.00 mmol, 1.2 eq) in THF, the resulting crude mixture was purified by flash column chromatography (50% Et_2O / P.E. 40 - 60) to afford silylation product **6p** (278 mg, 0.82 mmol, 99%) as a colourless oil; $\mathbf{R_f}$ 0.64 (20% Et_2O / P.E. 40 - 60); $\boldsymbol{\nu}_{\mathbf{max}}$ (thin film) / cm^{-1} 2958, 2858, 1463, 1369, 1254, 1173, 1088, 1030, 882, 836, 778, 666; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.57 (2H, d, *J* = 8.0 Hz, ArH), 7.34 (2H, d, *J* = 8.0 Hz, ArH), 4.76 (2H, s, $ArC\underline{H}_2OTBS$), 3.98 (1H, sep, *J* = 6.0 Hz, $OC\underline{H}(CH_3)_2$), 1.14 (6H, d, *J* = 6.0 Hz, $OCH(C\underline{H}_3)_2$), 0.96 (9H, s, $Si(CH_3)_2C(C\underline{H}_3)_3$), 0.38 (6H, s, $SiMe_2$), 0.16 (6H, s, $Si(C\underline{H}_3)_2C(CH_3)_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 142.8, 136.8, 135.5, 125.4, 65.2, 64.9, 26.0, 25.7, 18.5, -1.04, -5.24; **HRMS (ES$^+$)** calculated for $C_{18}H_{34}NaO_2Si_2$ $[M+Na]^+$ 361.1990, found 361.1983.

tert-Butyl(1-(4-(*iso*-propoxydimethylsilyl)phenyl)ethoxy)dimethylsilane 6q



2m **6q**

Following the general bromo-lithium exchange protocol with (1-(4-bromophenyl)ethoxy)(*tert*-butyl)-dimethylsilane **2m** (250 mg, 0.79 mmol, 1.0 eq) and *t*-BuLi (1.04 mL of a 1.6 M solution in pentane, 1.66 mmol, 2.1 eq) in Et_2O, the resulting crude mixture was purified by flash column chromatography (50% Et_2O / P.E. 40 - 60) to afford silylation product **6q** (277 mg, 0.79 mmol, 99%) as a colourless oil; $\mathbf{R_f}$ 0.66 (20% Et_2O / P.E. 40 - 60); $\boldsymbol{\nu}_{\mathbf{max}}$ (thin film) / cm^{-1} 2958, 2930, 2859, 1472, 1383, 1368, 1253, 1095, 1031, 959, 882, 835, 778, 665; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.54 (2H, d, *J* = 8.0 Hz, ArH), 7.34 (2H, d, *J* = 8.0 Hz, ArH), 4.87 (1H, q, *J* = 6.3 Hz, $ArC\underline{H}(OTBS)CH_3$), 3.99 (1H, sep, *J* = 6.1 Hz, $OC\underline{H}(CH_3)_2$), 1.14 (3H, d, *J* = 6.3 Hz, $ArCH(OTBS)C\underline{H}_3$), 1.13 (6H, d, *J* = 6.1 Hz, $OCH(C\underline{H}_3)_2$), 0.91 (9H, s, $Si(CH_3)_2C(C\underline{H}_3)_3$), 0.38 (6H, s, $SiMe_2$), 0.06 (3H, s, $Si(C\underline{H}_3)_2C(CH_3)_3$), -0.02 (3H, s, $Si(C\underline{H}_3)_2C(CH_3)_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 148.2, 136.5, 133.4, 124.6, 70.8, 65.2, 27.2, 25.9, 25.7, 18.3, -1.08, -4.77; **HRMS (ES$^+$)** calculated for $C_{19}H_{36}NaO_2Si_2$ $[M+Na]^+$ 375.2146, found 375.2145.

5. Aryl Silane Oxidations

General Protocol A for the oxidation of the *iso*-propoxyarylsilane substrates

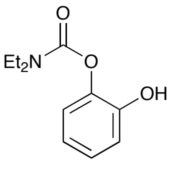
To a stirred solution of the aryl silane (50 - 243 mg, 1.0 eq) in MeOH/THF (1:1, 1 mL) was added $KHCO_3$ (2.0 eq), TBAF (0.1, 1.0 or 2.0 eq of a 1.0M solution in THF) or KF (2.0 eq) and H_2O_2 (6.0 eq of a 35% w/w aqueous solution). The reaction mixture was stirred at r.t. or 60 °C for 16 h, before quenching with NH_4Cl or 1N HCl solution. The phases were separated, the aqueous phase extracted with Et_2O (2 x 2 mL) and the combined organic extracts dried ($MgSO_4$) and concentrated *in vacuo*. Purification by flash column chromatography afforded the phenol (31 - 99%).

General Protocol B for the one-pot oxidation of the diethylaminoarylsilane intermediates

The appropriate lithiation protocol was followed to afford the aryl amino silane intermediate, omitting the introduction of ^{i}-PrOH and DMAP to the reaction vessel. The reaction mixture was concentrated *in vacuo*, and MeOH/THF was added (1:1, 3 mL) followed by $KHCO_3$ (2.0 eq), TBAF (0.1, 1.0 or 2.0 eq of a 1.0M solution in

THF) or KF (2.0 eq) and H_2O_2 (6.0 eq of a 35% w/w aqueous solution). The reaction mixture was stirred at r.t. or 60 °C for 16 h, before quenching with NH_4Cl or 1N HCl solution. The phases were separated, the aqueous phase extracted with Et_2O (2 x 2 mL) and the combined organic extracts dried ($MgSO_4$) and concentrated *in vacuo*. Purification by flash column chromatography afforded the phenol (43 - 99%).

2-Hydroxyphenyl diethylcarbamate 7a



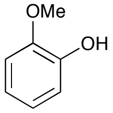
7a

Following the *iso*-propoxy silane oxidation protocol (100 mg, 0.32 mmol, 1.0 eq of **6a**) with 0.1 eq of TBAF at r.t. and quenching with 1N HCl solution, purification by flash column chromatography (70% Et_2O / P.E. 40 - 60) afforded phenol **7a** (66.3 mg, 0.32 mmol, 99%) as an orange solid; **mp** 56.1 °C; $\mathbf{R_f}$ 0.14 (50% Et_2O / P.E. 40 - 60); **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.27 (1H, br s, OH), 7.11 (1H, dt, *J* = 1.7, 8.1 Hz, ArH), 7.04 (1H, dd, *J* = 1.6, 8.3 Hz, ArH), 7.02 (1H, dd, *J* = 1.6, 8.1 Hz, ArH), 6.89 (1H, dt, *J* = 1.7, 8.3 Hz, ArH), 3.48 (2H, q, *J* = 7.1 Hz, $NC\underline{H}_2CH_3$), 3.42 (2H, q, *J* = 7.1 Hz, $NC\underline{H}_2CH_3$), 1.29 (3H, t, *J* = 7.1 Hz, $NCH_2C\underline{H}_3$), 1.22 (3H, t, *J* = 7.1 Hz, $NCH_2C\underline{H}_3$).

Following the one-pot oxidation protocol (250 mg, 1.29 mmol, 1.0 eq of phenyl diethylcarbamate **1a**) with 0.1 eq of TBAF at r.t. and quenching with 1N HCl solution, purification by flash column chromatography (70% Et_2O / P.E. 40 - 60) afforded phenol **7a** (228 mg, 1.09 mmol, 85%) as an orange oil; $\mathbf{R_f}$ and **^{1}H NMR** data in agreement with that recorded above for 2-hydroxyphenyl diethylcarbamate **7a**.

This data is in agreement with that reported by Julia *et al.*[9]

2-Methoxyphenol 7b



7b

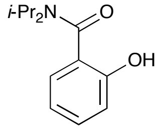
Following the *iso*-propoxy silane oxidation protocol (58.4 mg, 0.26 mmol, 1.0 eq of **6b**) with 0.1 eq of TBAF at r.t. and quenching with 1N HCl solution, purification by flash column chromatography (50% Et_2O / P.E. 40 - 60) afforded phenol **7b** (9.9 mg, 0.08 mmol, 31%) as an orange oil; $\mathbf{R_f}$ 0.38 (50% Et_2O / P.E. 40 - 60); **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 6.95 - 6.85 (4H, m, ArH), 5.63 (1H, s, OH), 3.89 (3H, s, ArOMe).

Following the one-pot oxidation protocol (250 mg, 2.31 mmol, 1.0 eq of anisole **1b**) with 0.1 eq of TBAF at r.t. and quenching with 1N HCl solution, purification by flash column chromatography (50% Et_2O / P.E. 40 – 60) afforded phenol 7b (284 mg, 2.29 mmol, 99%) as an orange oil; $\mathbf{R_f}$ and **^{1}H NMR** data in agreement with that recorded above for 2-methoxyphenol **7b**.

Following the one-pot oxidation protocol (250 mg, 1.34 mmol, 1.0 eq of 2-bromoanisole **2d**) with 0.1 eq of TBAF at r.t. and quenching with 1N HCl solution, purification by flash column chromatography (50% Et_2O / P.E. 40 - 60) afforded phenol **7b** (149 mg, 1.20 mmol, 90%) as an orange oil; $\mathbf{R_f}$ and **^{1}H NMR** data in agreement with that recorded above for 2-methoxyphenol **7b**.

This data is in agreement with that reported by Anderson *et al.*[10]

2-hydroxy-*N,N*-di*iso*-propylbenzamide 7c



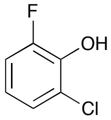
7c

Following the *iso*-propoxy silane oxidation protocol (47.3 mg, 0.15 mmol, 1.0 eq of **6c**) with 0.1 eq of TBAF at r.t. and quenching with 1N HCl solution, purification by flash column chromatography (50% Et_2O / P.E. 40 – 60) afforded phenol **7c** (32.8 mg, 0.15 mmol, 99%) as a white solid; **mp** 151.0 – 158.4 °C; **R_f** 0.16 (50% Et_2O / P.E. 40 - 60); **^{1}H NMR** (200 MHz, $CDCl_3$) δ_H 7.34 – 7.26 (1H, m, ArH), 7.21 – 7.16 (1H, m, ArH), 7.03 – 6.98 (1H, m, ArH), 6.89 – 6.81 (1H, m, ArH), 3.96 (2H, br s, $NC\underline{H}(CH_3)_2$), 1.42 (6H, br s, $NCH(C\underline{H}_3)_2$), 1.39 (6H, br s, $NCH(C\underline{H}_3)_2$).

Following the one-pot oxidation protocol (250 mg, 1.19 mmol, 1.0 eq of *N,N*-di*iso*-propylbenzamide **1c**) with 0.1 eq of TBAF at r.t. and quenching with 1N HCl solution, purification by flash column chromatography (50% Et_2O / P.E. 40 - 60) afforded phenol **7c** (203 mg, 0.92 mmol, 77%) as an white solid; **R_f** and **^{1}H NMR** data in agreement with that recorded above for 2-hydroxy-*N,N*-di*iso*-propylbenzamide **7c**.

This data is in agreement with that reported by Naka *et al.*[11]

2-chloro-6-fluorophenol 7d



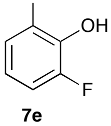
7d

Following the *iso*-propoxy silane oxidation protocol (98 mg, 0.40 mmol, 1.0 eq of **6d**) with 0.1 eq of TBAF at r.t. and quenching with 1N HCl solution, purification by flash column chromatography (50% Et_2O / P.E. 40 – 60) afforded phenol **7d** (54.5 mg, 0.37 mmol, 94%) as a thick yellow oil; **R_f** 0.51 (50% Et_2O / P.E. 40 - 60); **^{1}H NMR** (200 MHz, $CDCl_3$) δ_H 7.16 – 6.97 (2H, m, ArH), 6.87 – 6.76 (1H, m, ArH), 5.89 (1H, br s, OH).

Following the one-pot oxidation protocol (250 mg, 1.91 mmol, 1.0 eq of **1d**) with 0.1 eq of TBAF at r.t. and quenching with 1N HCl solution, purification by flash column chromatography (50% Et_2O / P.E. 40 – 60) afforded phenol **7d** (277 mg, 1.89 mmol, 94%) as a thick yellow oil; **R_f** and **^{1}H NMR** data in agreement with that recorded above for 2-chloro-6-fluorophenol **7d**.

This data is in agreement with that of a commercially available sample (Aldrich)

2,6-difluorophenol 7e



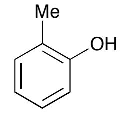
7e

Following the *iso*-propoxy silane oxidation protocol (98 mg, 0.43 mmol, 1.0 eq of **6e**) with 0.1 eq of TBAF and mesitylene (29.6 µL, 0.21 mmol, 0.5 eq) at r.t. and quenching with 1N HCl solution, phenol **7e** (0.26 mmol, 61% by NMR measured against an internal standard) was obtained; **R_f** 0.52 (50% Et_2O / P.E. 40 - 60); **^{1}H NMR** (200 MHz, $CDCl_3$) δ_H 6.90 – 6.70 (3H, m, ArH).

Following the one-pot oxidation protocol (250 mg, 2.19 mmol, 1.0 eq of 1e) with 0.1 eq of TBAF and mesitylene (152 µL, 1.10 mmol, 0.5 eq) at r.t. and quenching with 1N HCl solution, phenol **7e** (1.95 mmol, 89% by NMR measured against an internal standard) was obtained; **R$_f$** and **^{1}H NMR** data in agreement with that recorded above for 2,6-difluorophenol **7e**.

This data is in agreement with that of a commercially available sample (Aldrich)

_o_-Cresol 7f



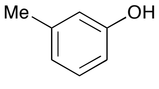
7f

Following the *iso*-propoxy silane oxidation protocol (63 mg, 0.30 mmol, 1.0 eq of **6f**) with 0.1 eq of TBAF at r.t. and quenching with 1N HCl solution, purification by flash column chromatography (50% Et_2O / P.E. 40 - 60) afforded phenol **7f** (29.7 mg, 0.27 mmol, 90%) as an orange oil; **R$_f$** 0.42 (50% Et_2O / P.E. 40 - 60); **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.13 (1H, d, *J* = 7.4 Hz, ArH), 7.09 (1H, t, *J* = 7.8 Hz, ArH), 6.85 (1H, t, *J* = 7.4 Hz, ArH), 6.77 (1H, d, *J* = 7.8 Hz, ArH), 4.85 (1H, br s, OH), 2.26 (3H, s, ArMe).

Following the one-pot oxidation protocol (250 mg, 1.46 mmol, 1.0 eq of 2-bromotoluene **2a**) with 0.1 eq of TBAF at r.t. and quenching with 1N HCl solution, purification by flash column chromatography (50% Et_2O / P.E. 40 - 60) afforded phenol **7f** (137 mg, 1.27 mmol, 87%) as an orange oil; **R$_f$** and **^{1}H NMR** data in agreement with that recorded above for *o*-cresol **7f**.

This data is in agreement with that reported by Sunderhaus *et al.*[12]

_m_-Cresol 7g



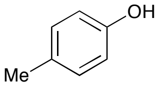
7g

Following the *iso*-propoxy silane oxidation protocol (100 mg, 0.48 mmol, 1.0 eq of **6g**) with 0.1 eq of TBAF at r.t. and quenching with 1N HCl solution, purification by flash column chromatography (50% Et_2O / P.E. 40 - 60) afforded phenol 7g (37.4 mg, 0.35 mmol, 72%) as a pale pink oil; **R$_f$** 0.42 (50% Et_2O / P.E. 40 - 60); **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.12 (1H, t, *J* = 7.8 Hz, ArH), 6.75 (1H, d, *J* = 7.8 Hz, ArH), 6.67 - 6.62 (2H, m, ArH), 5.45 (1H, br s, OH), 2.31 (3H, s, ArMe).

Following the one-pot oxidation protocol (250 mg, 1.46 mmol, 1.0 eq of 3-bromotoluene **2b**) with 0.1 eq of TBAF at r.t. and quenching with 1N HCl solution, purification by flash column chromatography (50% Et_2O / P.E. 40 - 60) afforded phenol **7g** (139 mg, 1.29 mmol, 88%) as a pale pink oil; **R$_f$** and **^{1}H NMR** data in agreement with that recorded above for *m*-cresol **7g**.

This data is in agreement with that reported by Mirza-Aghayan *et al.*[13]

_p_-Cresol 7h



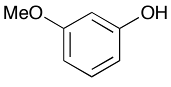
7h

Following the *iso*-propoxy silane oxidation protocol (62 mg, 0.48 mmol, 1.0 eq of **6h**) with 0.1 eq of TBAF at r.t. and quenching with 1N HCl solution, purification by flash column chromatography (50% Et_2O / P.E. 40 - 60) afforded phenol **7h** (26.2 mg, 0.24 mmol, 81%) as an orange oil; **R$_f$** 0.41 (50% Et$_2$O / P.E. 40 - 60); **^{1}H NMR** (400 MHz, CDCl$_3$) δ_H 7.04 (2H, d, *J* = 8.3 Hz, ArH), 6.73 (2H, d, *J*= 8.3, ArH), 4.82 (1H, br s, OH), 2.28 (3H, s, ArMe).

Following the one-pot oxidation protocol (250 mg, 1.46 mmol, 1.0 eq of 4-bromotoluene **2c**) with 0.1 eq of TBAF at r.t. and quenching with 1N HCl solution, purification by flash column chromatography (50% Et$_2$O / P.E. 40 - 60) afforded phenol **7h** (156.5 mg, 1.45 mmol, 99%) as an orange oil; **R$_f$** and **^{1}H NMR** data in agreement with that recorded above for *p*-cresol **7h**.

This data is in agreement with that reported by Mirza-Aghayan *et al.*[13]

3-Methoxyphenol 7i



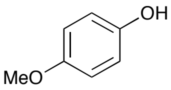
7i

Following the *iso*-propoxy silane oxidation protocol (150 mg, 0.69 mmol, 1.0 eq of **6i**) with 0.1 eq of TBAF at r.t. and quenching with 1N HCl solution, purification by flash column chromatography (50% Et$_2$O / P.E. 40 - 60) afforded phenol **7i** (66.8 mg, 0.54 mmol, 81%) as an orange oil; **R$_f$** 0.37 (50% Et$_2$O / P.E. 40 - 60); **^{1}H NMR** (400 MHz, CDCl$_3$) δ_H 7.13 (1H, td, *J* = 1.4, 8.3 Hz, ArH), 6.51 - 6.48 (1H, m, ArH), 6.44 - 6.41 (2H, m, ArH), 5.02 (1H, br s, OH), 3.79 (3H, s, ArOMe).

Following the one-pot oxidation protocol (250 mg, 1.34 mmol, 1.0 eq of 3-bromoanisole **2e**) with 1.0 eq of TBAF at r.t. and quenching with 1N HCl solution, purification by flash column chromatography (50% Et$_2$O / P.E. 40 - 60) afforded phenol **7i** (165 mg, 1.33 mmol, 99%) as an orange oil; **R$_f$** and **^{1}H NMR** data in agreement with that recorded above for 3-methoxyphenol **7i**.

This data is in agreement with that reported by Sunderhaus *et al*.[12]

4-Methoxyphenol 7j



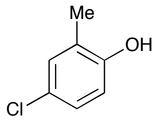
7j

Following the *iso*-propoxy silane oxidation protocol (66 mg, 0.29 mmol, 1.0 eq of **6j**) with 0.1 eq of TBAF at r.t. and quenching with 1N HCl solution, purification by flash column chromatography (50% Et$_2$O / P.E. 40 - 60) afforded phenol **7j** (32.7 mg, 0.26 mmol, 90%) as an light orange solid; **mp** 52.5 °C (lit.[ref] mp 52 - 53 °C); **R$_f$** 0.32 (50% Et$_2$O / P.E. 40 - 60); **^{1}H NMR** (400 MHz, CDCl$_3$) δ_H 6.77 (4H, *app* s, ArH), 4.61 (1H, br s, OH), 3.76 (3H, s, ArOMe).

Following the one-pot oxidation protocol (250 mg, 1.34 mmol, 1.0 eq of 4-bromoanisole **2f**) with 1.0 eq of TBAF at r.t. and quenching with 1N HCl solution, purification by flash column chromatography (50% Et$_2$O / P.E. 40 - 60) afforded phenol **7j** (137 mg, 1.10 mmol, 82%) as a light orange solid; **mp**, **R$_f$** and **^{1}H NMR** data in agreement with that recorded above for 4-methoxyphenol **7j**.

This data is in agreement with that reported by Anderson *et al.*[10]

4-Chloro-2-methylphenol 7k



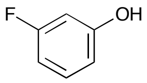
7k

Following the *iso*-propoxy silane oxidation protocol (69 mg, 0.29 mmol, 1.0 eq of **6k**) with 0.1 eq of TBAF at r.t. and quenching with 1N HCl solution, purification by flash column chromatography (50% Et_2O / P.E. 40 - 60) afforded phenol **7k** (22.0 mg, 0.16 mmol, 55%) as an orange oil; **R$_f$** 0.42 (50% Et_2O / P.E. 40 - 60); **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.10 (1H, d, *J* = 2.5 Hz, ArH), 7.03 (1H, dd, *J* = 2.5, 8.5 Hz, ArH), 6.69 (1H, d, *J* = 8.5 Hz, ArH), 4.73 (1H, br s, OH), 2.22 (3H, s, ArMe).

Following the one-pot oxidation protocol (250 mg, 1.22 mmol, 1.0 eq of 1-bromo-4-chloro-2-methylbenzene **2g**) with 0.1 eq of TBAF at r.t. and quenching with 1N HCl solution, purification by flash column chromatography (50% Et_2O / P.E. 40 - 60) afforded phenol **7k** (136 mg, 0.95 mmol, 78%) as an orange oil; **R$_f$** and **^{1}H NMR** data in agreement with that recorded above for 4-chloro-2-methylphenol **7k**.

This data is in agreement with that reported by Wang *et al.*[14]

3-Fluorophenol 7l



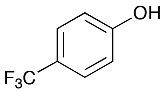
7l

Following the *iso*-propoxy silane oxidation protocol (69 mg, 0.33 mmol, 1.0 eq of **6l**) with 0.1 eq of TBAF at r.t. and quenching with 1N HCl solution, purification by flash column chromatography (50% Et_2O / P.E. 40 - 60) afforded phenol **7l** (18.9 mg, 0.17 mmol, 52%) as a light orange oil; **R$_f$** 0.38 (50% Et_2O / P.E. 40 - 60); **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.21 - 7.15 (1H, m, ArH), 6.67 - 6.55 (3H, m, ArH), 5.08 (1H, br s, OH).

Following the one-pot oxidation protocol (250 mg, 1.43 mmol, 1.0 eq of 1-bromo-3-fluorobenzene **2h**) with 0.1 eq of TBAF at r.t. and quenching with 1N HCl solution, purification by flash column chromatography (50% Et_2O / P.E. 40 - 60) afforded phenol **7l** (69.7 mg, 0.62 mmol, 43%) as an orange oil; **R$_f$** and **^{1}H NMR** data in agreement with that recorded above for 3-fluorophenol **7l**.

This data is in agreement with that of commercially available 3-fluorophenol **7l** (Aldrich).

4-(trifluoromethyl)phenol 7m



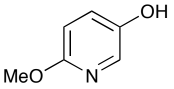
7m

Following the *iso*-propoxy silane oxidation protocol (100 mg, 0.38 mmol, 1.0 eq of **6m**) with 0.1 eq of TBAF at r.t. and quenching with 1N HCl solution, purification by flash column chromatography (50% Et_2O / P.E. 40 - 60) afforded phenol **7m** (53.7 mg, 0.33 mmol, 87%) as a yellow oil; **R$_f$** 0.49 (50% Et_2O / P.E. 40 - 60); **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.51 (2H, d, *J* = 8.6 Hz, ArH), 6.90 (2H, d, *J* = 8.6 Hz, ArH), 5.37 (1H, br s, OH).

Following the one-pot oxidation protocol (250 mg, 1.11 mmol, 1.0 eq of 1-bromo-4-(trifluoromethyl)benzene **2i**) with 0.1 eq of TBAF at r.t. and quenching with 1N HCl solution, purification by flash column chromatography (50% Et_2O / P.E. 40 - 60) afforded phenol **7m** (108 mg, 0.66 mmol, 59%) as a yellow oil; **R$_f$** and **^{1}H NMR** data in agreement with that recorded above for 4-(trifluoromethyl)phenol **7m**.

This data is in agreement with that reported by Tordeux *et al.*[15]

6-Methoxypyridin-3-ol 7n



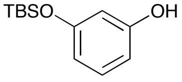
7n

Following the *iso*-propoxy silane oxidation protocol (50 mg, 0.22 mmol, 1.0 eq of **6n**) with 2.0 eq of KF at 60 °C and quenching with 1N HCl solution, purification by flash column chromatography (50% Et_2O / P.E. 40 - 60) afforded pyridinol **7n** (18.8 mg, 0.15 mmol, 68%) as an brown solid; **mp** 81.1 °C (lit. mp 80 – 82 °C); $\mathbf{R_f}$ 0.16 (50% Et_2O / P.E. 40 - 60); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ_H 7.76 (1H, d, *J* = 2.8 Hz, ArH), 7.39 (1H, br s, OH), 7.24 (1H, dd, *J* = 2.8, 8.9 Hz, ArH), 6.68 (1H, d, *J* = 8.9 Hz, ArH), 3.87 (3H, s, ArOMe).

Following the one-pot oxidation protocol (250 mg, 1.33 mmol, 1.0 eq of 5-bromo-2-methoxypyridine **2j**) with 2.0 eq of KF at 60 °C and quenching with 1N HCl solution, purification by flash column chromatography (50% Et_2O / P.E. 40 - 60) afforded pyridinol **7n** (124.8 mg, 1.00 mmol, 75%) as a brown solid; $\mathbf{R_f}$ and ^{1}**H NMR** data in agreement with that recorded above for 6-methoxypyridin-3-ol **7n**.

This data is in agreement with that reported by Bierer *et al.*[16]

3-(*tert*-Butyldimethylsilyloxy)phenol 7o

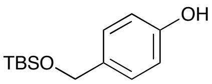


7o

Following the one-pot oxidation protocol (250 mg, 0.87 mmol, 1.0 eq of aryl bromide **2k**) with 0.1 eq of TBAF at r.t. and quenching with NH_4Cl solution, purification by flash column chromatography (20% Et_2O / P.E. 40 - 60) afforded phenol **7o** (147 mg, 0.66 mmol, 76%) as a light orange oil; $\mathbf{R_f}$ 0.50 (50% Et_2O / P.E. 40 - 60); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ_H 7.07 (1H, t, *J* = 8.1 Hz, ArH), 6.44 - 6.41 (2H, m, ArH), 6.35 (1H, t, *J* = 2.2 Hz, ArH), 4.75 (1H, br s, OH), 0.97 (9H, s, $Si(CH_3)_2C(C\underline{H}_3)_3$), 0.19 (6H, s, $Si(C\underline{H}_3)_2C(CH_3)_3$).

This data is in agreement with that reported by Holladay *et al.*.[17]

4-((tert-butyldimethylsilyloxy)methyl)phenol 7p



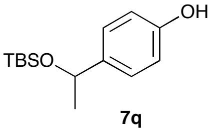
7p

Following the *iso*-propoxy silane oxidation protocol (103 mg, 0.30 mmol, 1.0 eq of **6p**) with 0.1 eq of TBAF at r.t. and quenching with NH_4Cl solution, purification by flash column chromatography (20% Et_2O / P.E. 40 – 60) afforded phenol **7p** (71.7 mg, 0.30 mmol, 99%) as a pale yellow oil; $\mathbf{R_f}$ 0.38 (50% Et_2O / P.E. 40 - 60); ^{1}**H NMR** (200 MHz, $CDCl_3$) δ_H 7.20 (2H, d, *J* = 8.6 Hz, ArH), 6.80 (2H, d, *J* = 8.6 Hz, ArH), 4.72 (1H, br s, OH), 4.67 (2H, s, $ArCH_2OTBS$), 0.93 (9H, s, $Si(CH_3)_2C(C\underline{H}_3)_3$), 0.09 (6H, s, $Si(C\underline{H}_3)_2C(CH_3)_3$).

Following the one-pot oxidation protocol (250 mg, 0.83 mmol, 1.0 eq of aryl bromide **2l**) with 0.1 eq of TBAF at r.t. and quenching with NH_4Cl solution, purification by flash column chromatography (20% Et_2O / P.E. 40 – 60) afforded phenol **7p** (196 mg, 0.82 mmol, 99%) as a pale yellow oil; $\mathbf{R_f}$ and ^{1}**H NMR** data in agreement with that reported above for 4-((tert-butyldimethylsilyloxy)methyl)phenol **7p**.

This data is in agreement with that reported by Oyama *et al.*[18]

4-(1-(*tert*-Butyldimethylsilyloxy)ethyl)phenol 7 q



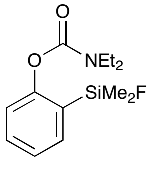
7q

Following the *iso*-propoxy silane oxidation protocol (103 mg, 0.30 mmol, 1.0 eq of **6q**) with 0.1 eq of TBAF at r.t. and quenching with NH_4Cl solution, purification by flash column chromatography (20% Et_2O / P.E. 40 - 60) afforded phenol **7q** (71.7 mg, 0.30 mmol, 99%) as an orange oil; **R$_f$** 0.45 (50% Et_2O / P.E. 40 - 60); **ν$_{max}$** (thin film) / cm^{-1} 3347 (br), 2957, 2858, 1615, 1514, 1472, 1369, 1254, 1170, 1092, 1031, 960, 834, 777; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.19 (2H, d, *J* = 8.4 Hz, ArH), 6.77 (2H, *J* = 8.4 Hz, ArH), 4.81 (1H, q, *J* = 6.5 Hz, ArC$\underline{H}$(OTBS)CH_3), 4.69 (1H, br m, OH), 1.37 (3H, *J* = 6.5 Hz, ArCH(OTBS)C$\underline{H}_3$), 0.88 (9H, s, Si$(CH_3)_2$C(C$\underline{H}_3$)$_3$), 0.03 (3H, s, Si(C$\underline{H}_3$)$_2$C$(CH_3)_3$), -0.05 (3H, s, Si(C$\underline{H}_3$)$_2$C$(CH_3)_3$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 154.7, 138.8, 126.6, 115.1, 70.7, 27.3, 26.0, 18.3, -4.73, -4.82; **HRMS (FI)** calculated for $C_{14}H_{24}O_2Si$ $[M]^+$ 252.1546, found 252.1546.

Following the one-pot oxidation protocol (250 mg, 0.79 mmol, 1.0 eq of aryl bromide **2m**) with 0.1 eq of TBAF at r.t. and quenching with NH_4Cl solution, purification by flash column chromatography (20% Et_2O / P.E. 40 - 60) afforded phenol **7q** (197 mg, 0.78 mmol, 99%) as an orange oil; **R$_f$** and **^{1}H NMR** data in agreement with that reported above for 4-(1-(*tert*-butyldimethylsilyloxy)ethyl)phenol **7q**.

6. Fluorosilane Synthesis

2-(fluorodimethylsilyl)phenyl diethylcarbamate 8



8

To a stirred solution of 2-(*Iso*-propoxydimethylsilyl)phenyl diethylcarbamate **6a** (103mg, 0.33 mmol, 1.0 eq) in MeOH/THF (1 : 1, 2 mL) was added TBAF (0.66 mL of a 1 M solution in THF, 0.66 mmol, 2.0 eq) and $KHCO_3$ (0.67 mg, 0.66 mmol, 2.0 eq). The reaction mixture was stirred at r.t. for 16 h before quenching with 1N HCl solution. The phases were separated, and the aqueous phase was extracted with Et_2O (2 x 2 mL). The combined organic phases were dried ($MgSO_4$) and concentrated *in vacuo*, then purification by flash column chromatography (50% Et_2O / P.E. 40 – 60) afforded fluorosilane **8** (87.8 mg, 0.33 mmol, 99%) as a pale yellow oil; **R$_f$** 0.41 (50% Et_2O / P.E. 40 – 60); **ν$_{max}$** (thin film) / cm^{-1} 2975, 1724, 1596, 1470, 1417, 1381, 1274, 1196, 1154, 1082, 961, 875, 841, 798, 755; **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.56 (d, *J* = 7.5 Hz, ArH), 7.46 (t, *J* = 8.1 Hz, ArH), 7.24 (t, *J* = 7.5 Hz, ArH), 7.13 (d, *J* = 8.1 Hz, ArH), 3.48 (q, *J* = 7.0 Hz, NC$\underline{H}_2$$CH_3$), 3.40 (q, *J* = 7.0 Hz, NC$\underline{H}_2$$CH_3$), 1.26 (t, *J* = 7.0 Hz, NCH_2C$\underline{H}_3$), 1.21 (t, *J* = 7.0 Hz, NCH_2C$\underline{H}_3$), 0.49 (d, J^3_{H-F} = 7.6 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C 155.9, 154.1, 134.4, 131.6, 129.2, 125.0, 122.3, 42.1, 41.7, 14.2, 13.3, -0.50 (d, J^2_{C-F} = 15.3 Hz); **^{19}F NMR** (377 MHz, $CDCl_3$) δ_F -162.7 (sep, J^3_{H-F} = 7.6 Hz); **HRMS (FI)** calculated for $C_{13}H_{20}$FNO2Si $[M]^+$ 269.1247, found 269.1243.

7. References

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Aryl Silane Oxidation – New Routes to Hydroxylated Aromatics

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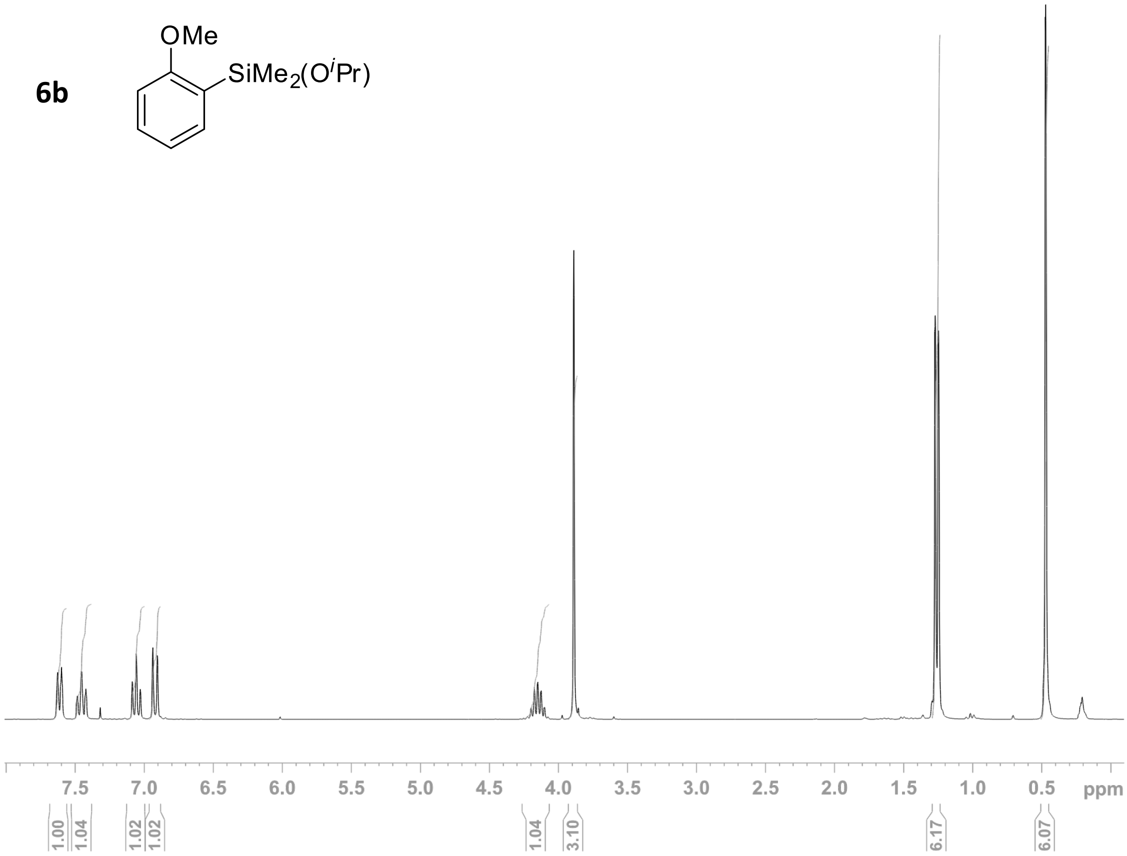
E-mail: edward.anderson@chem.ox.ac.uk

6. Selected 1H NMR and 13C NMR spectra

6b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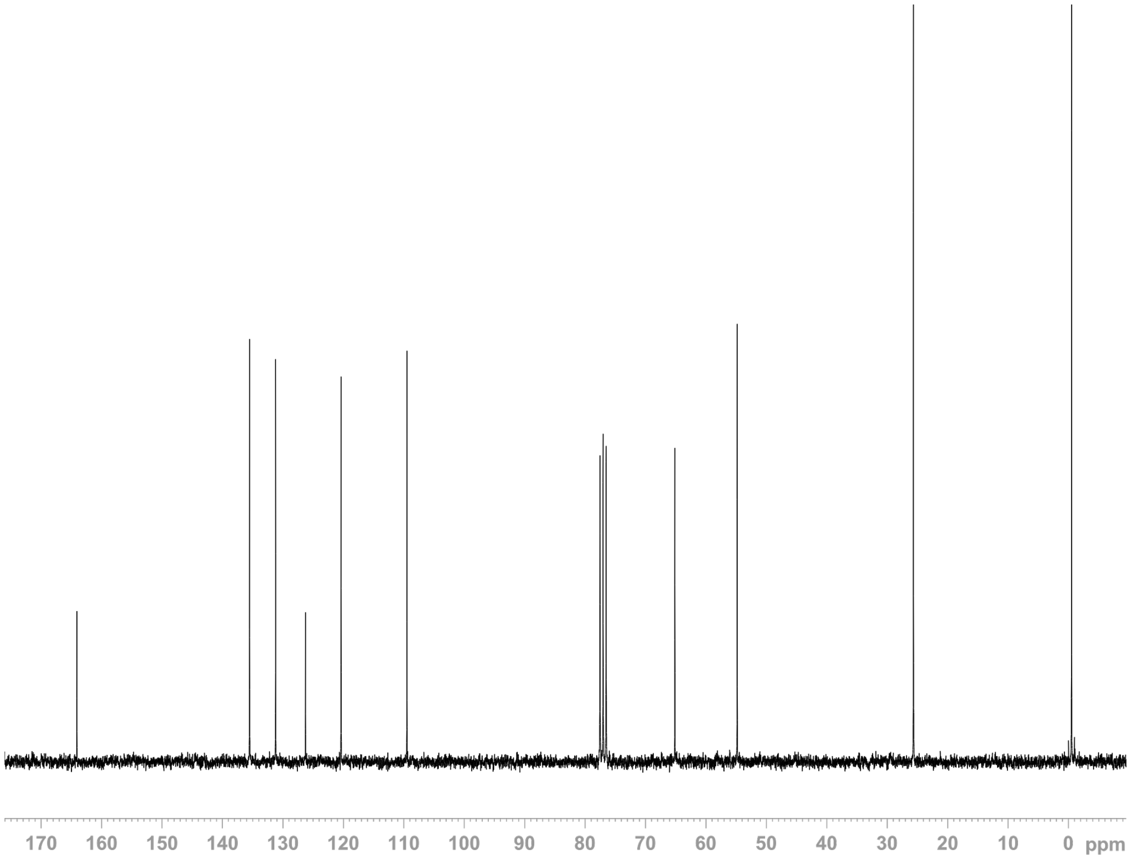
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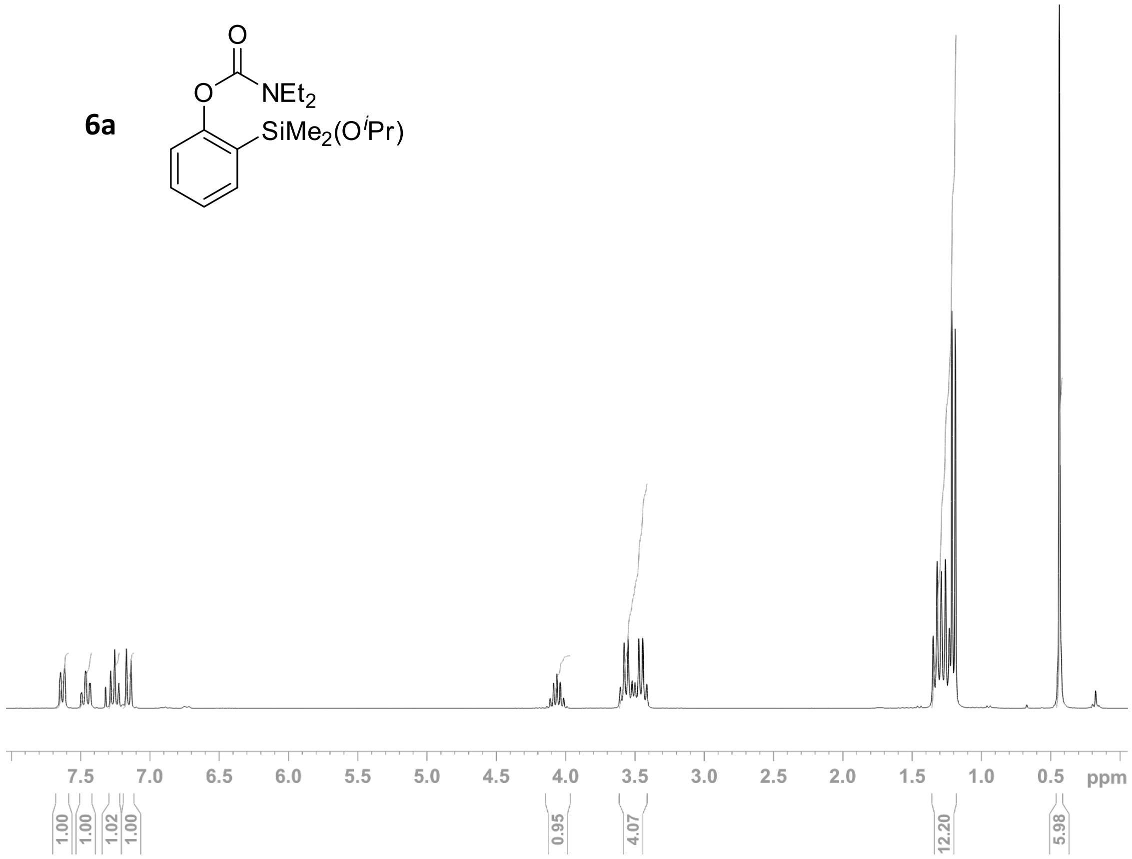
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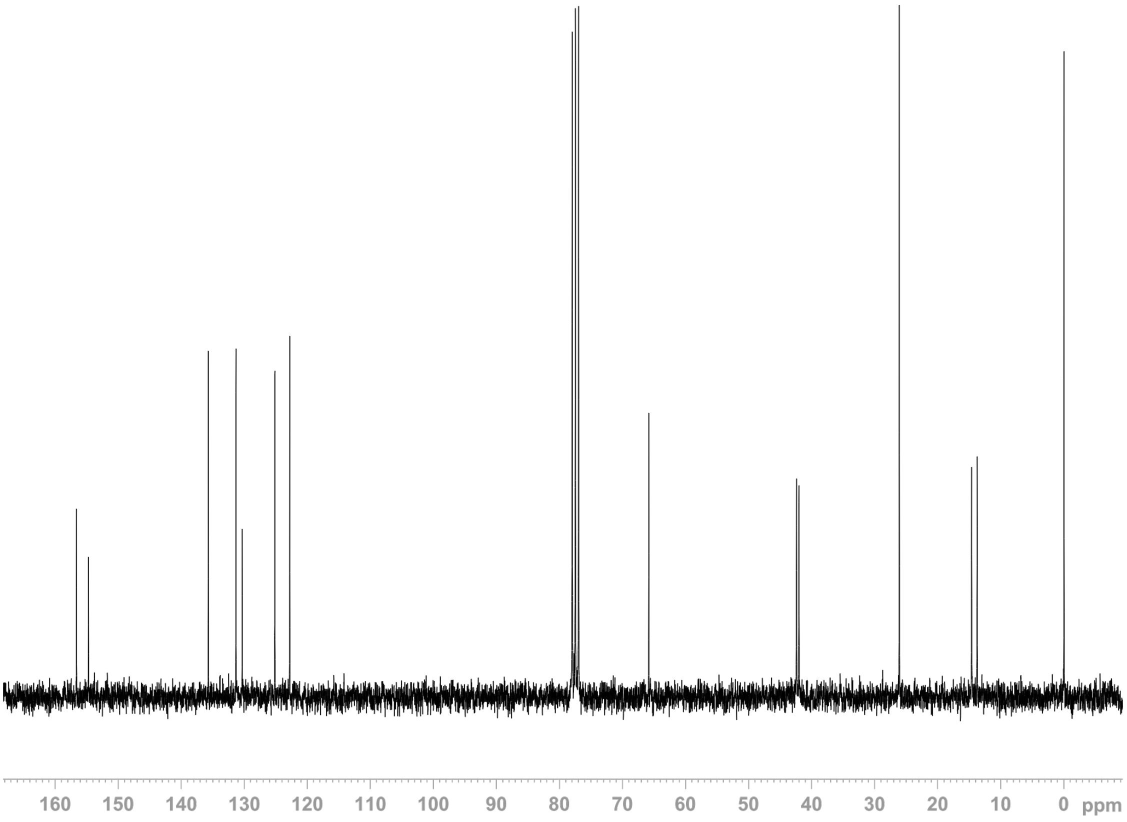
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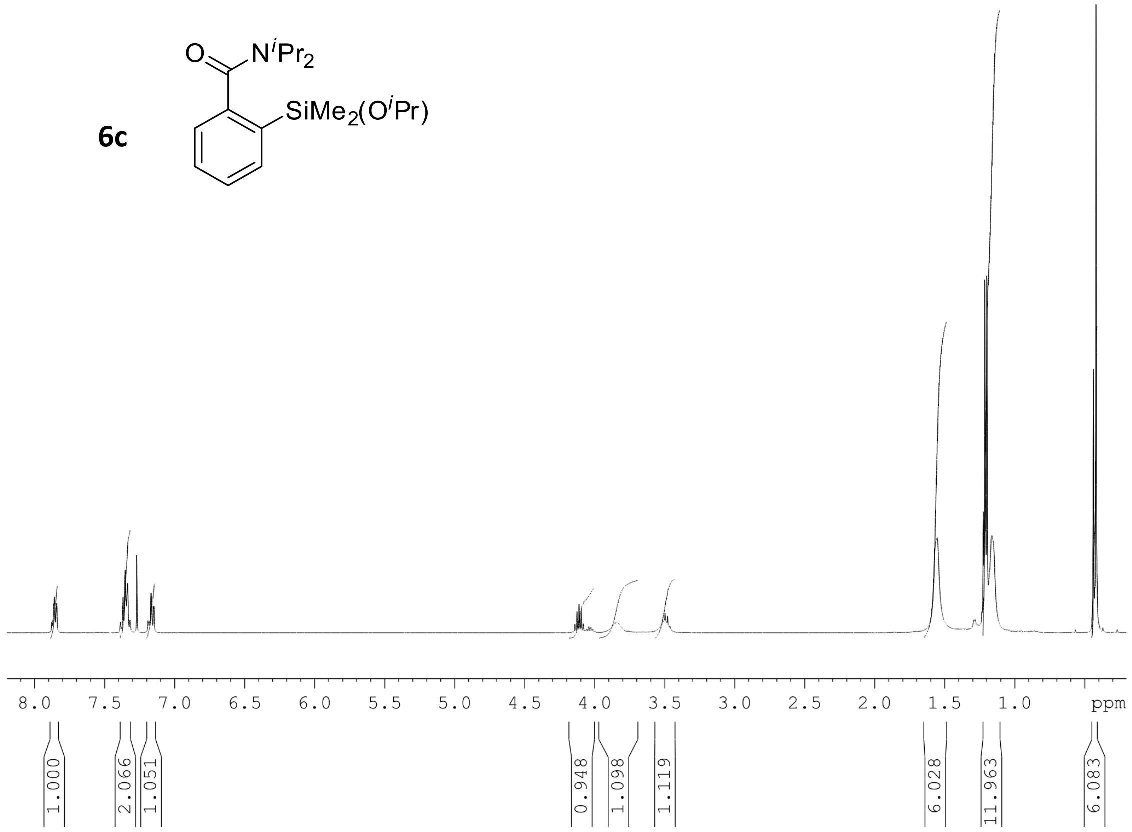
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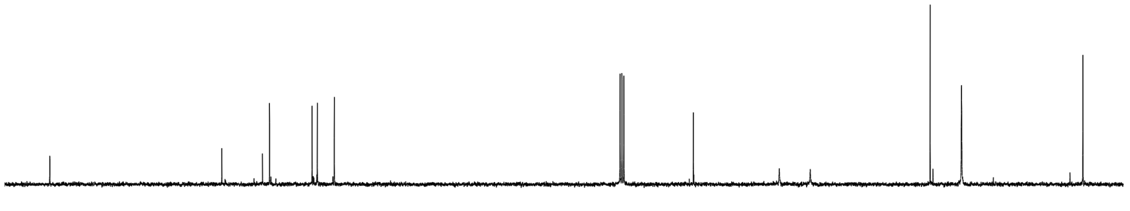
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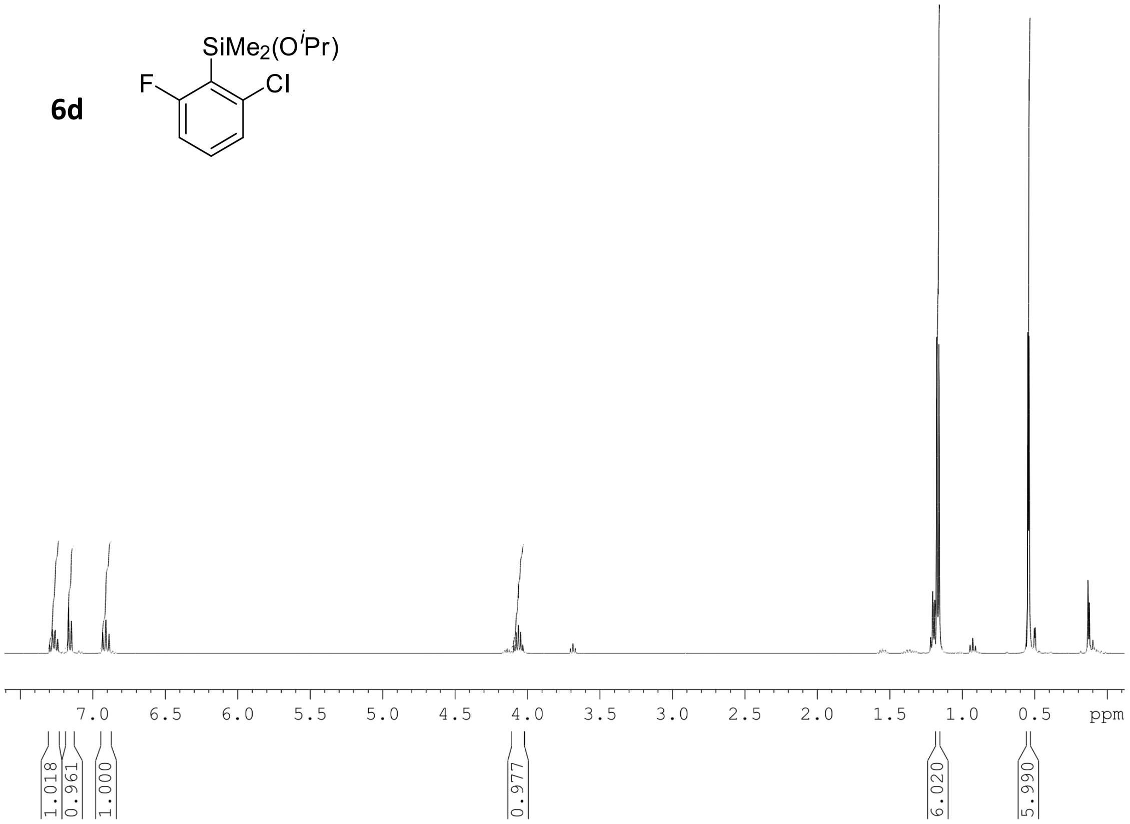
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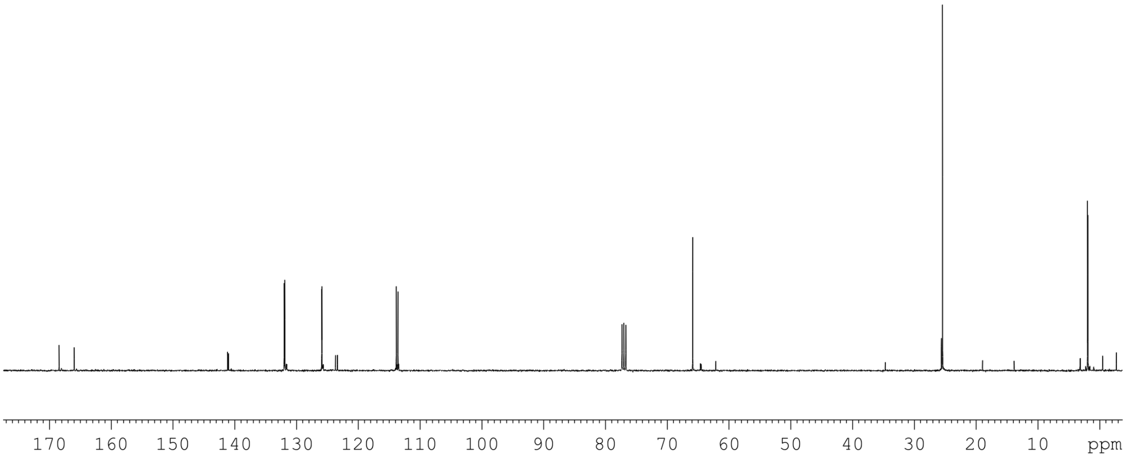
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ppm

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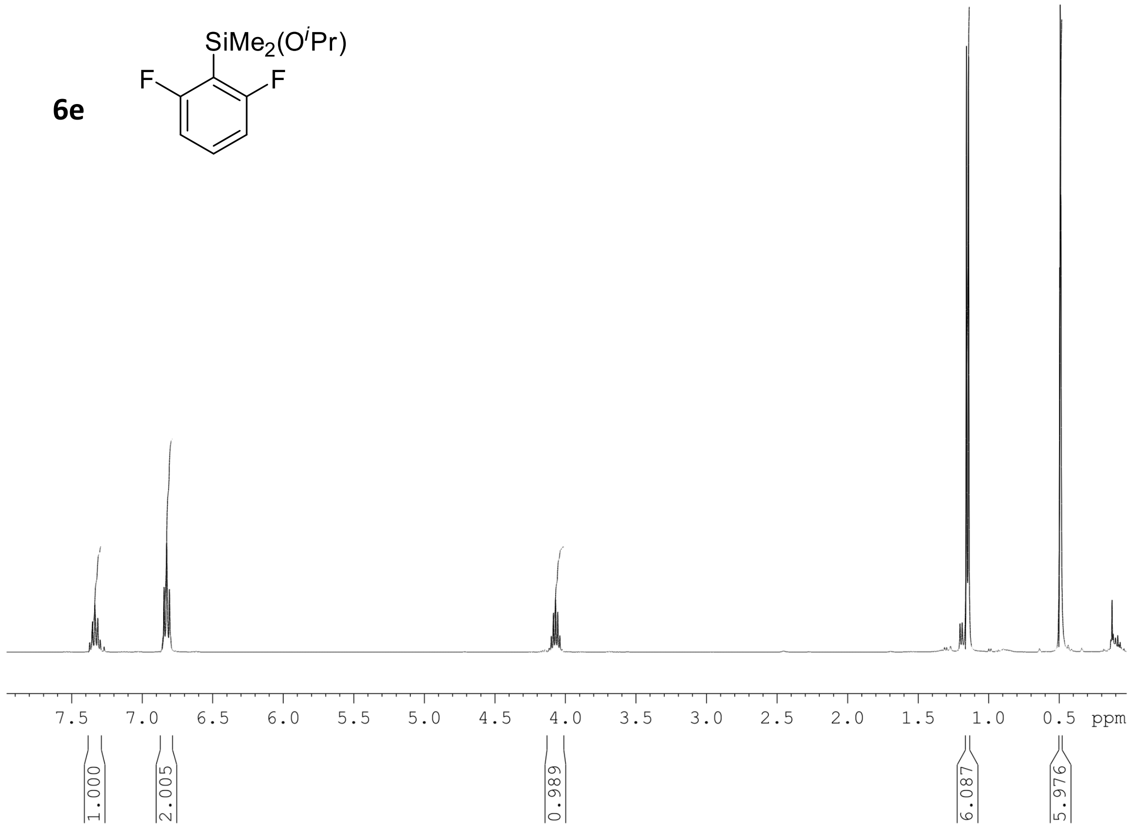
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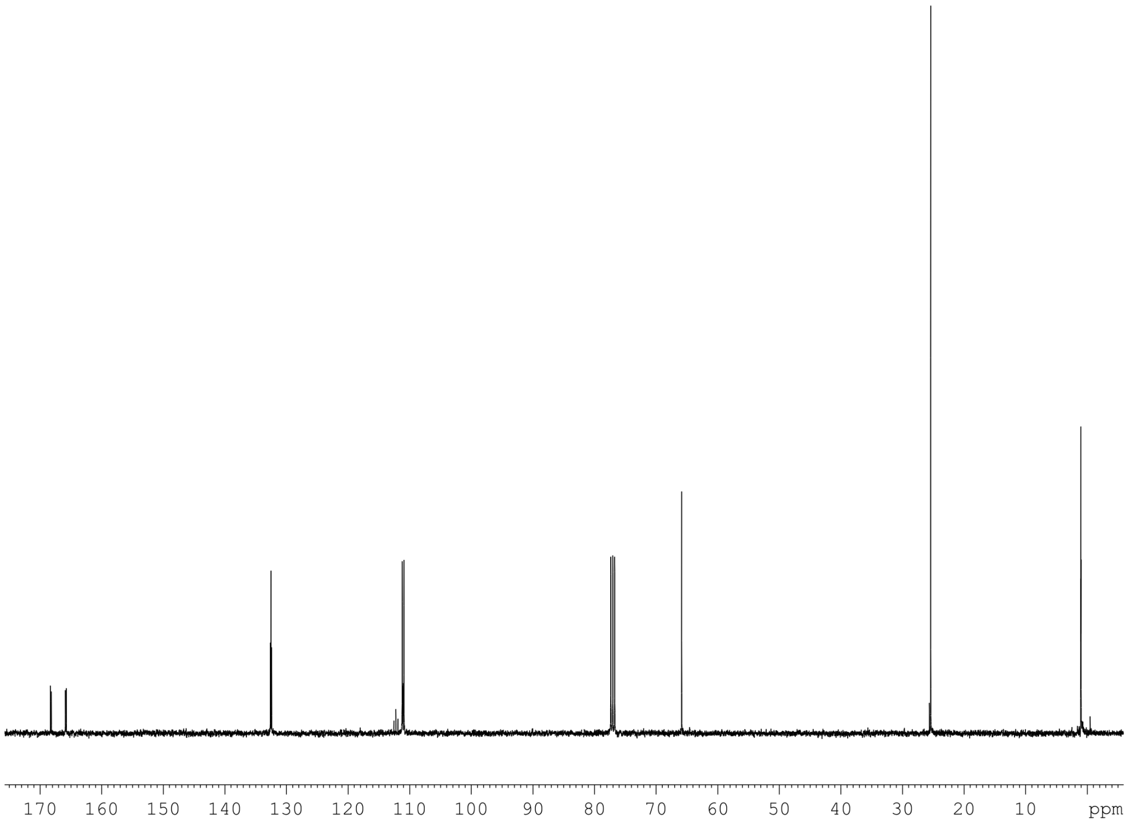
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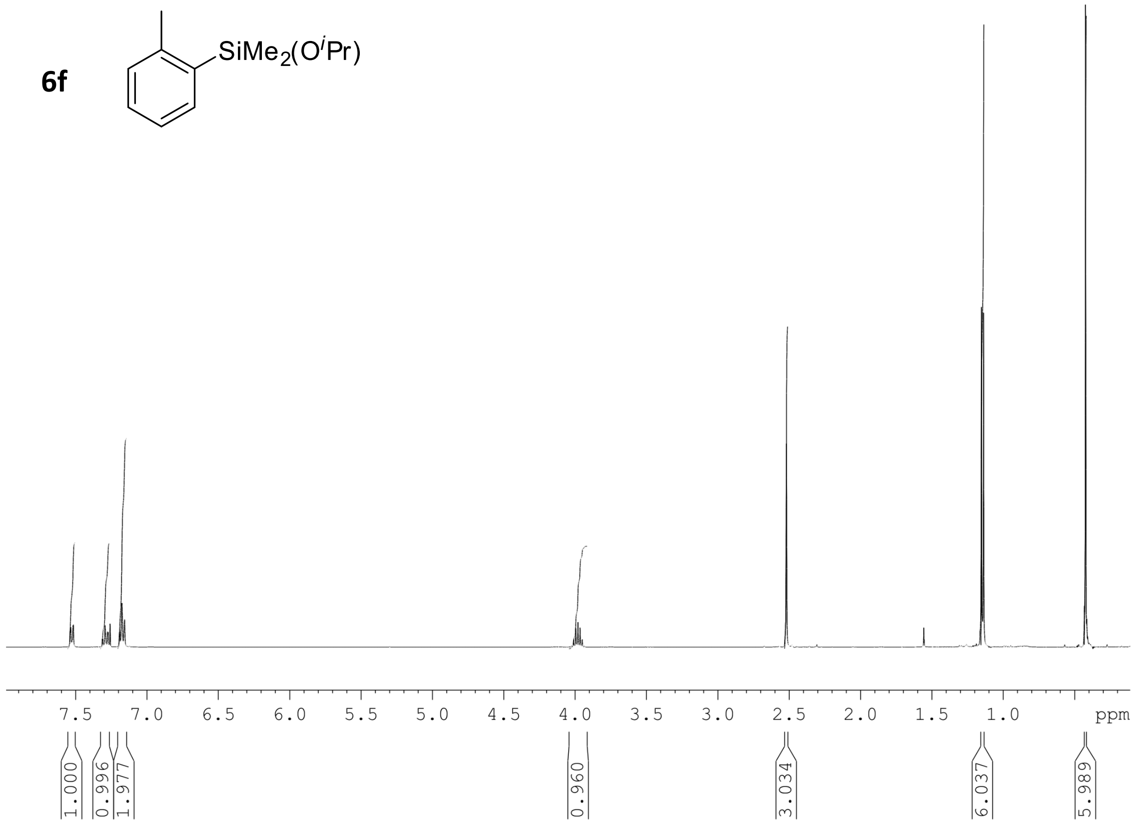
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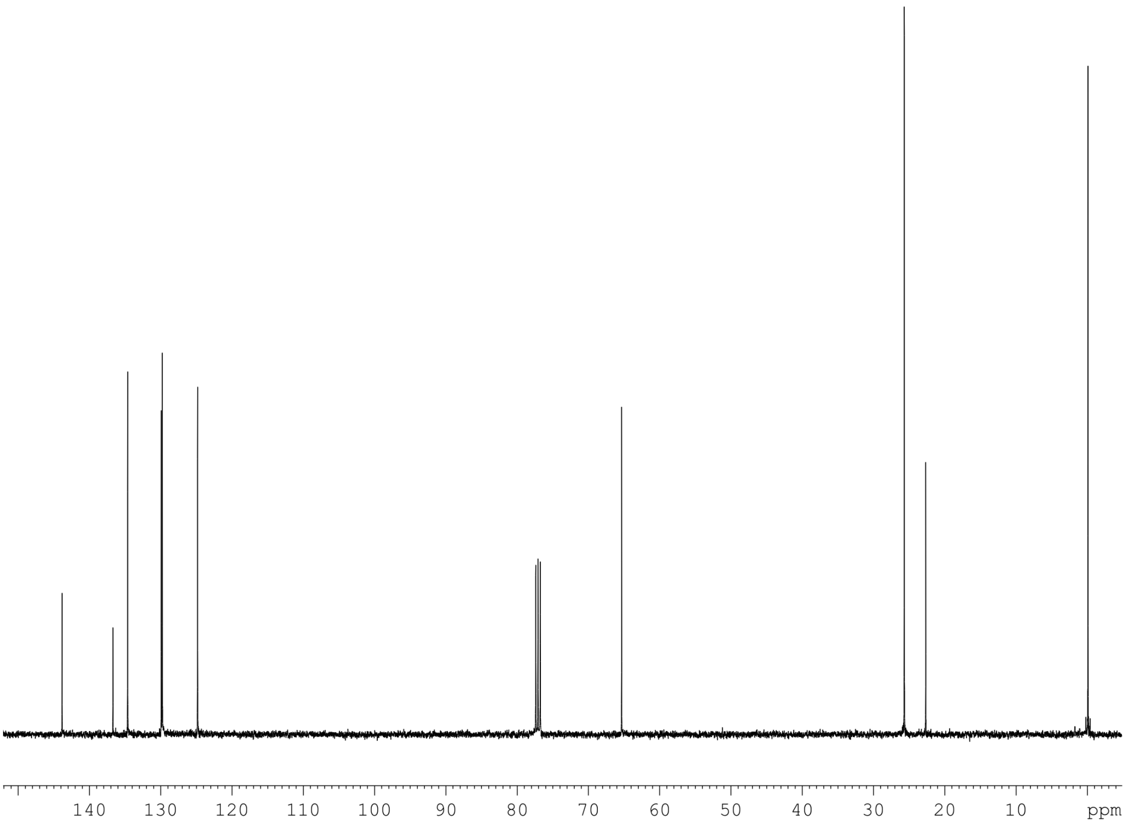
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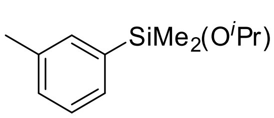
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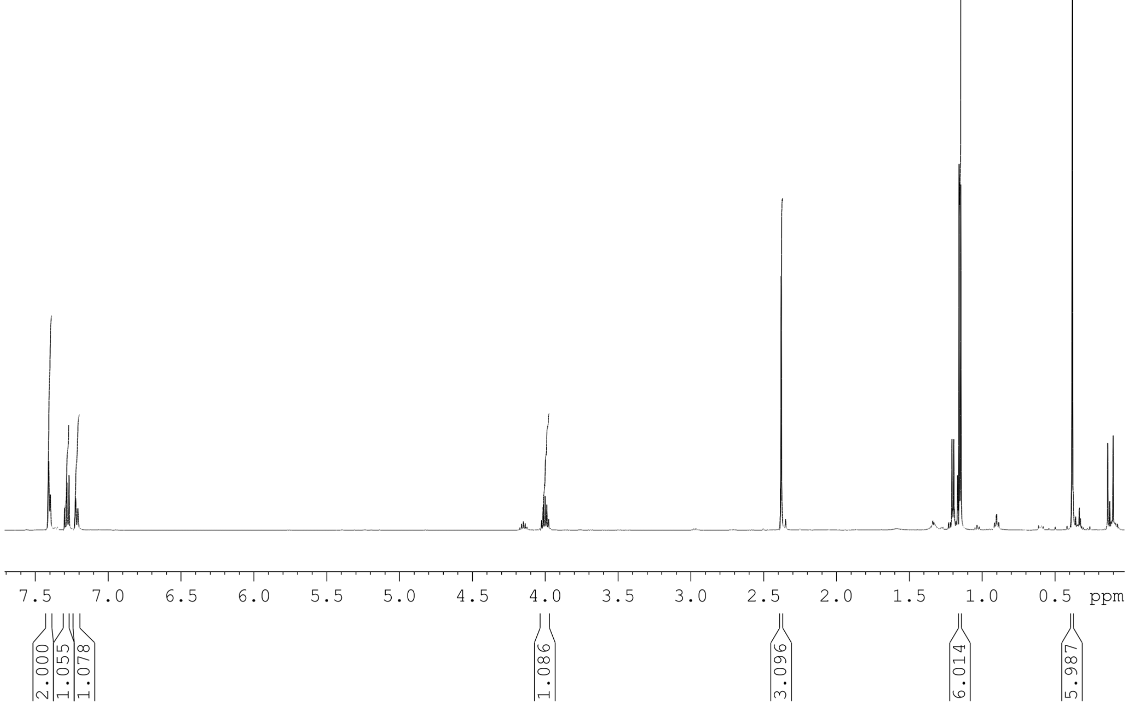
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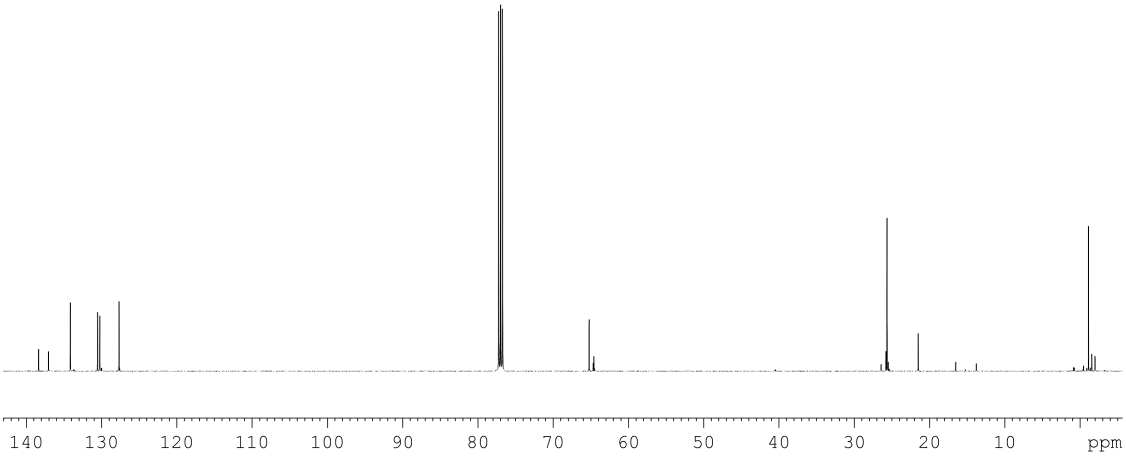
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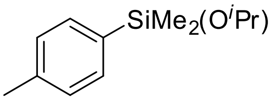
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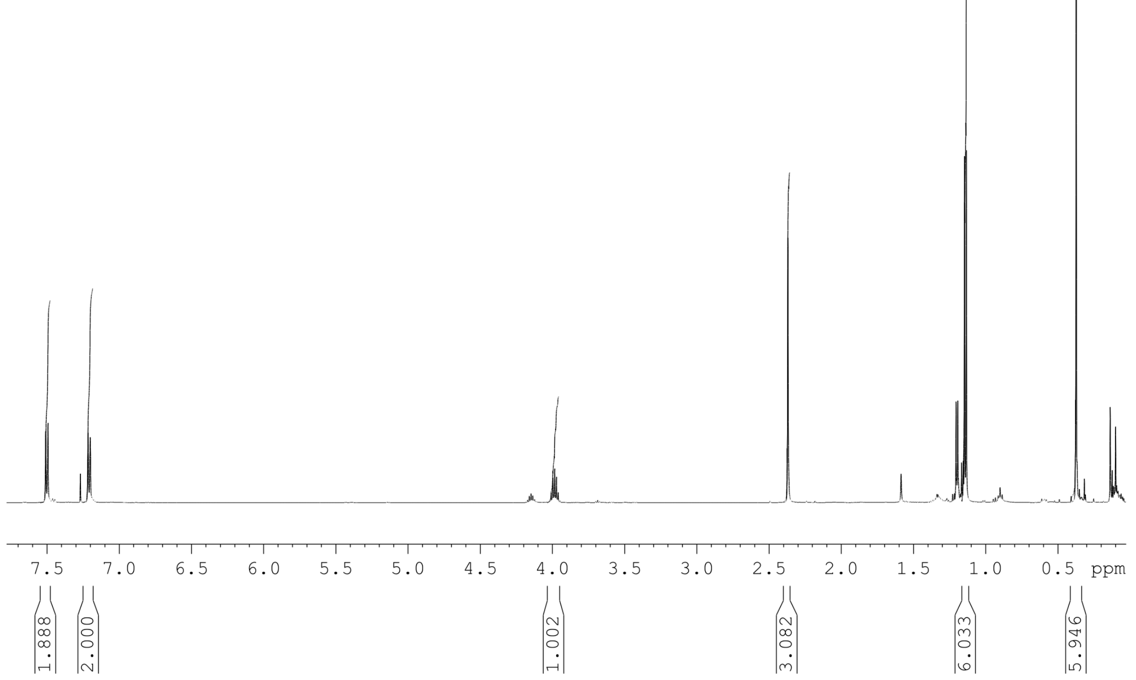
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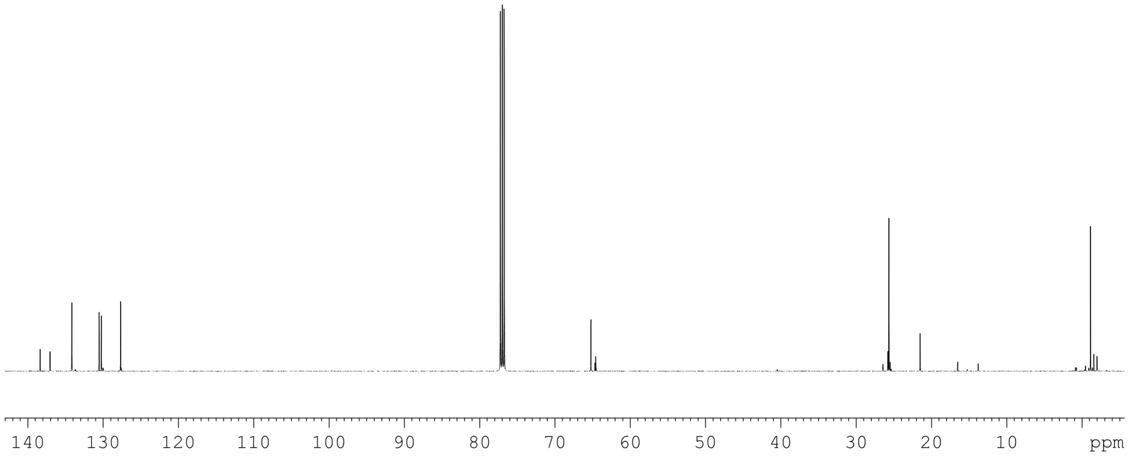
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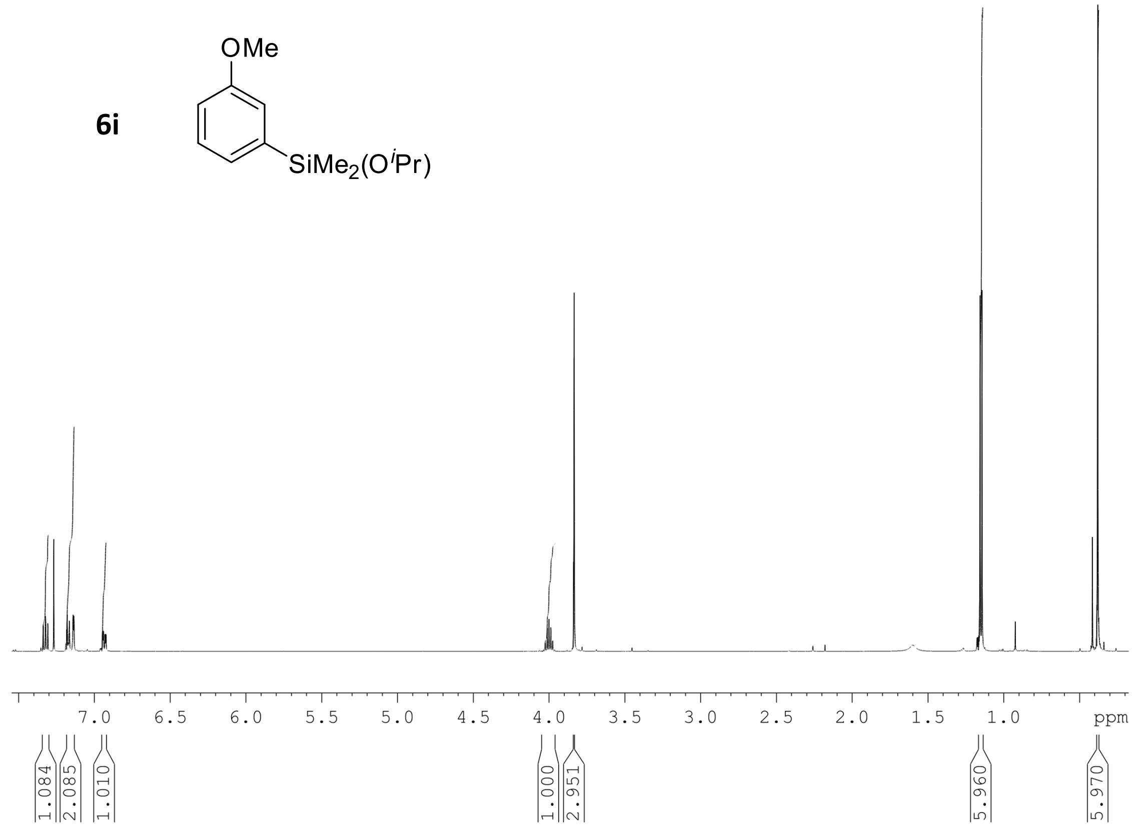
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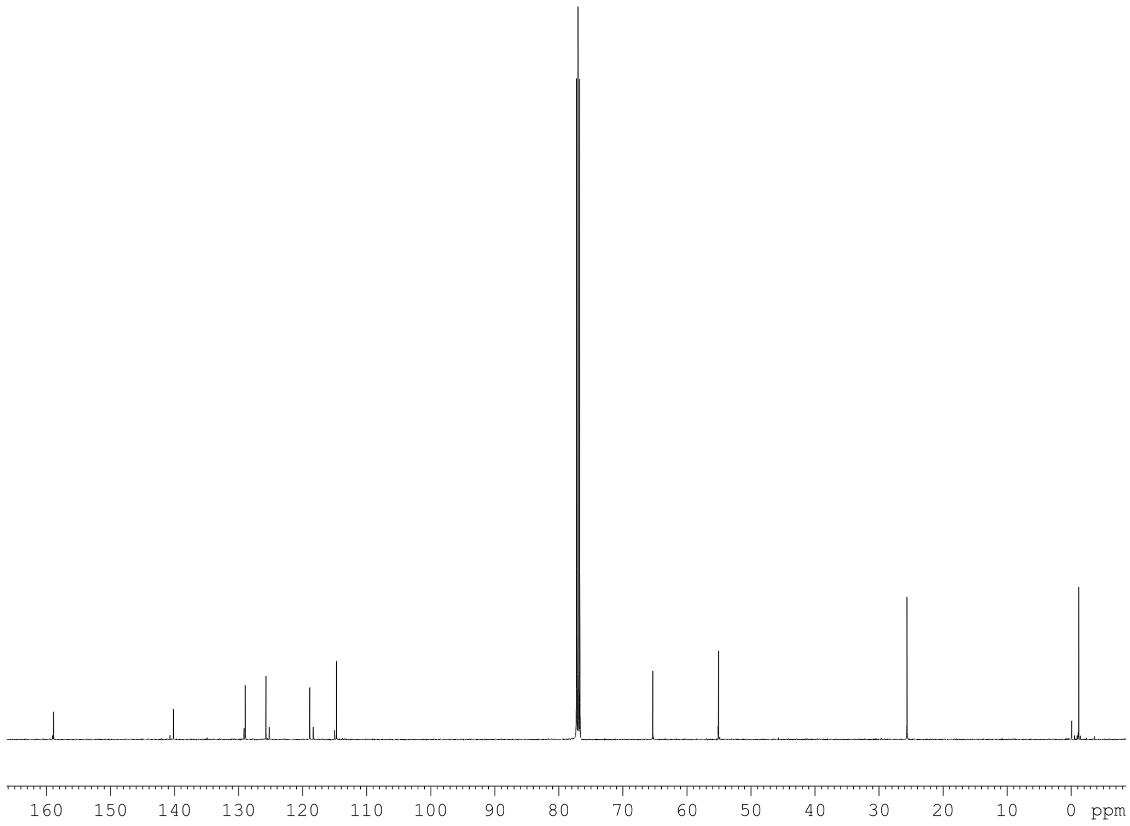
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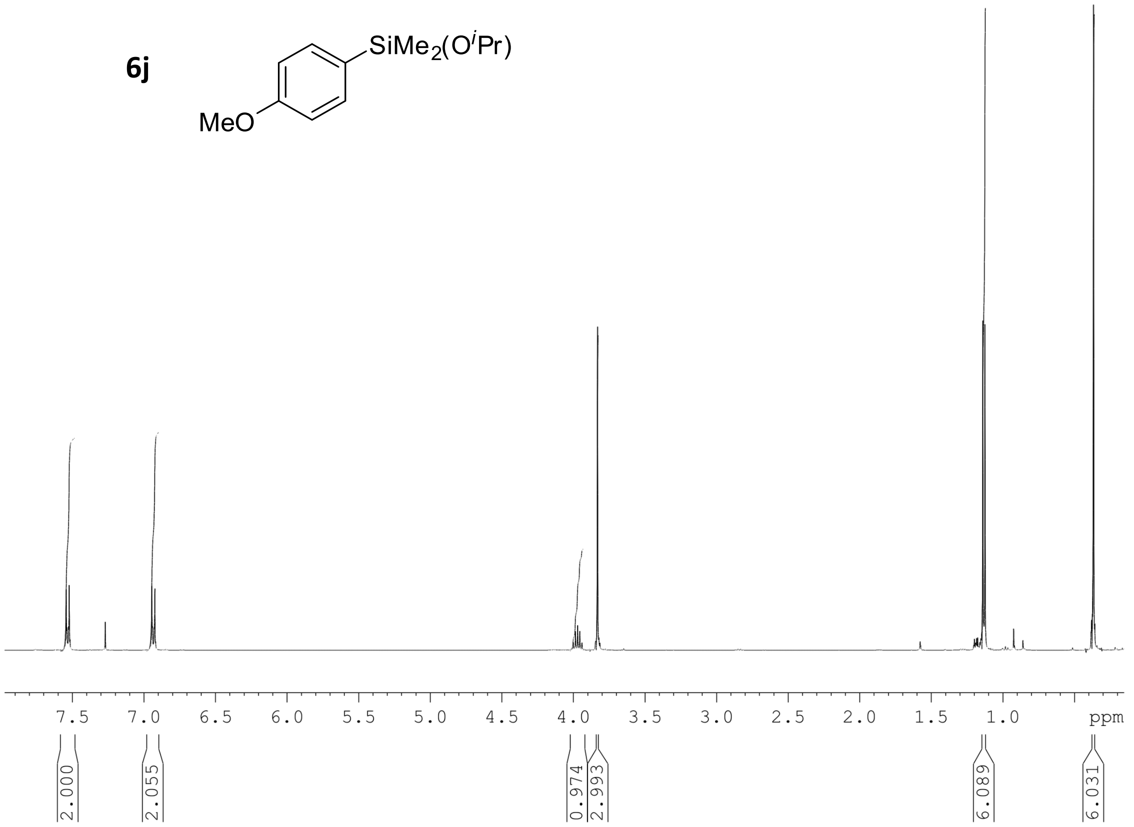
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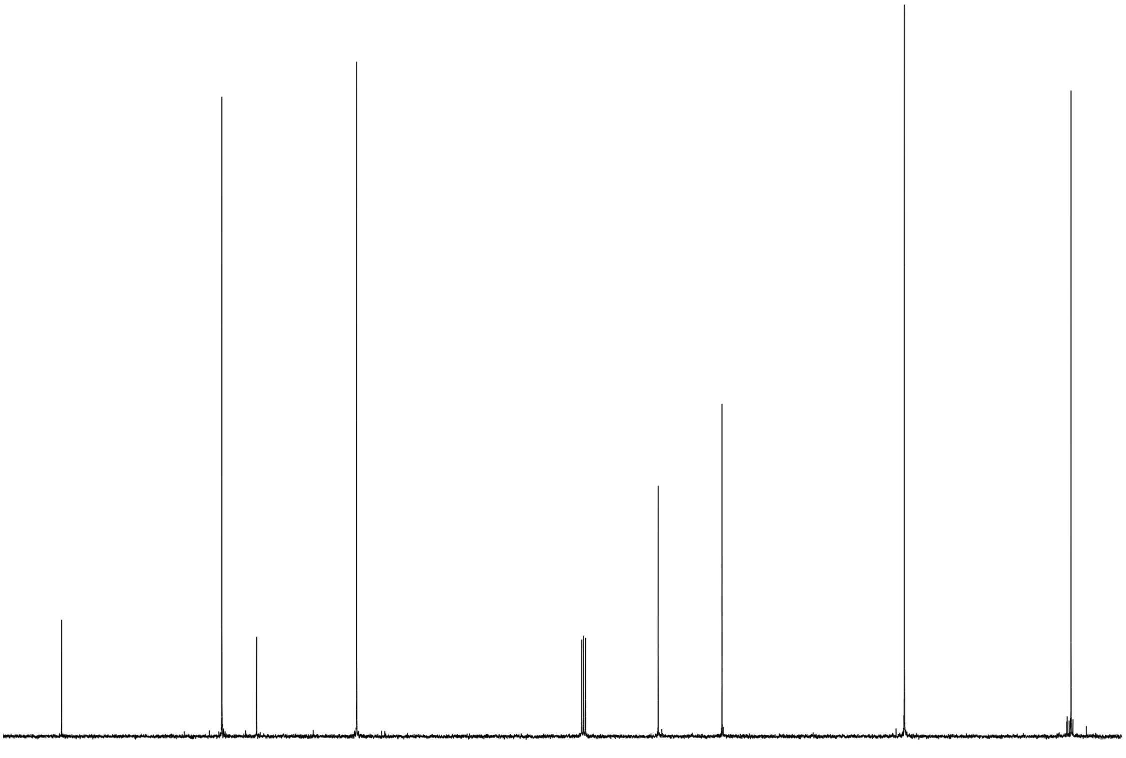
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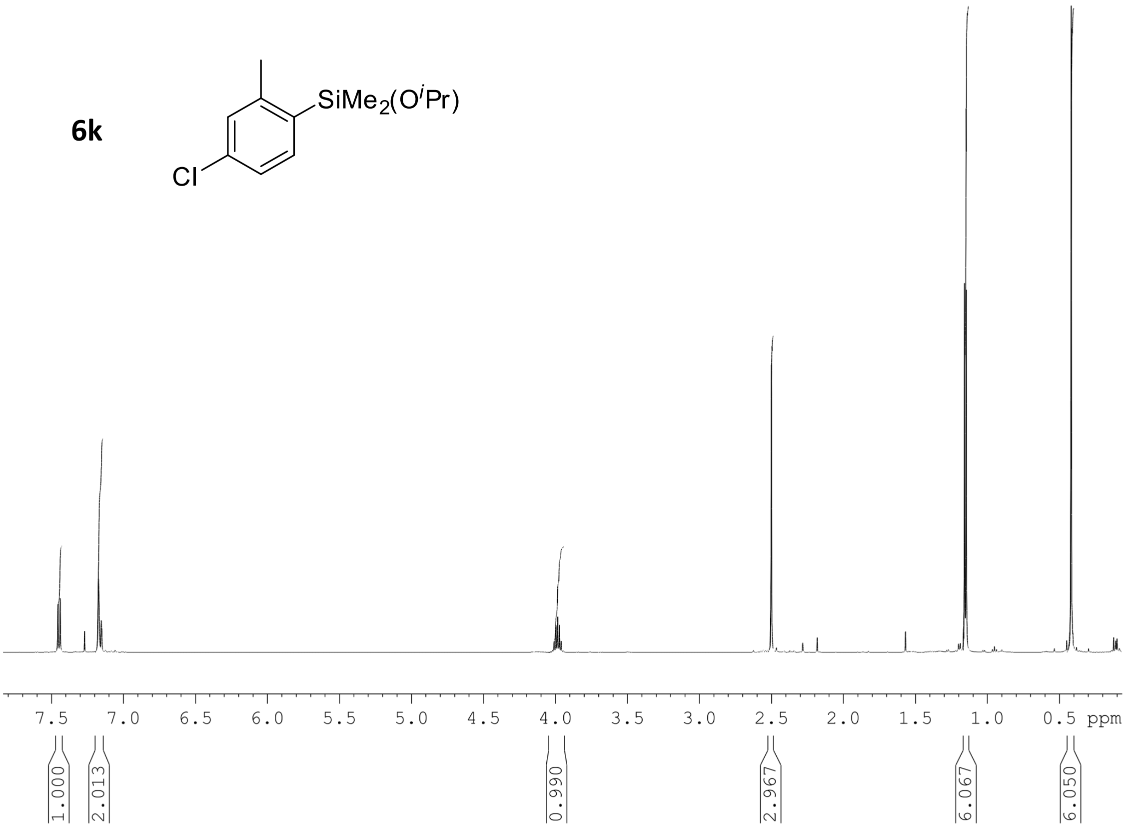

6k

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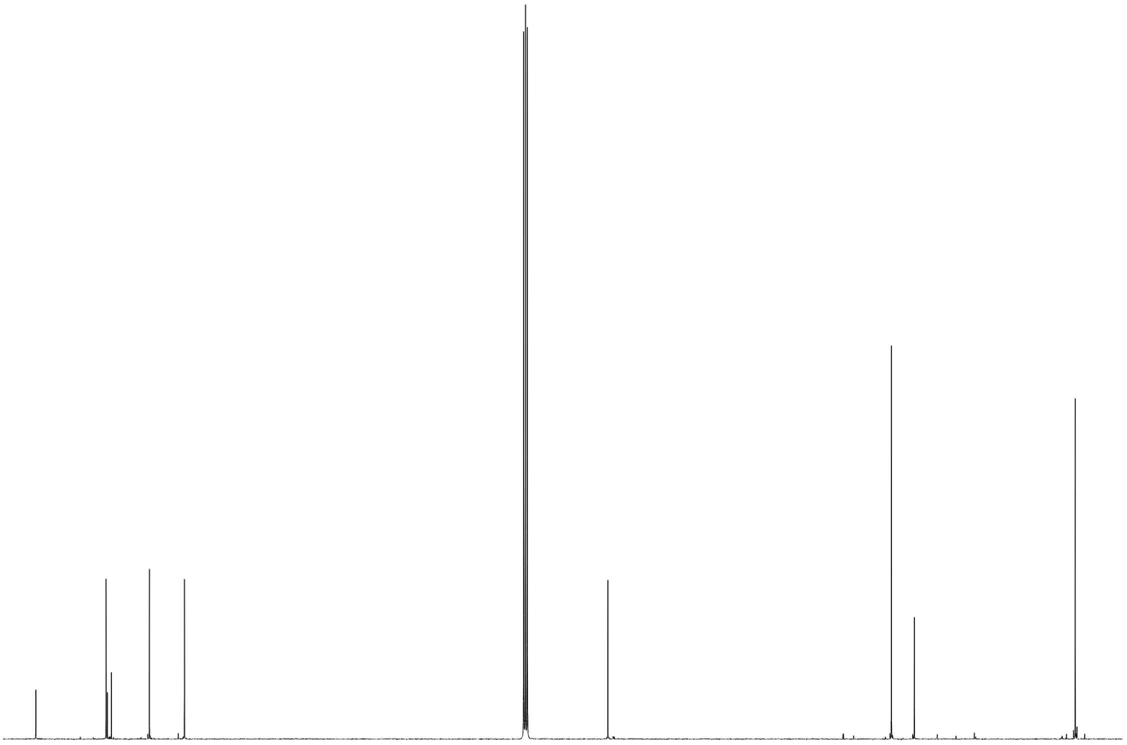

140
130
120
110
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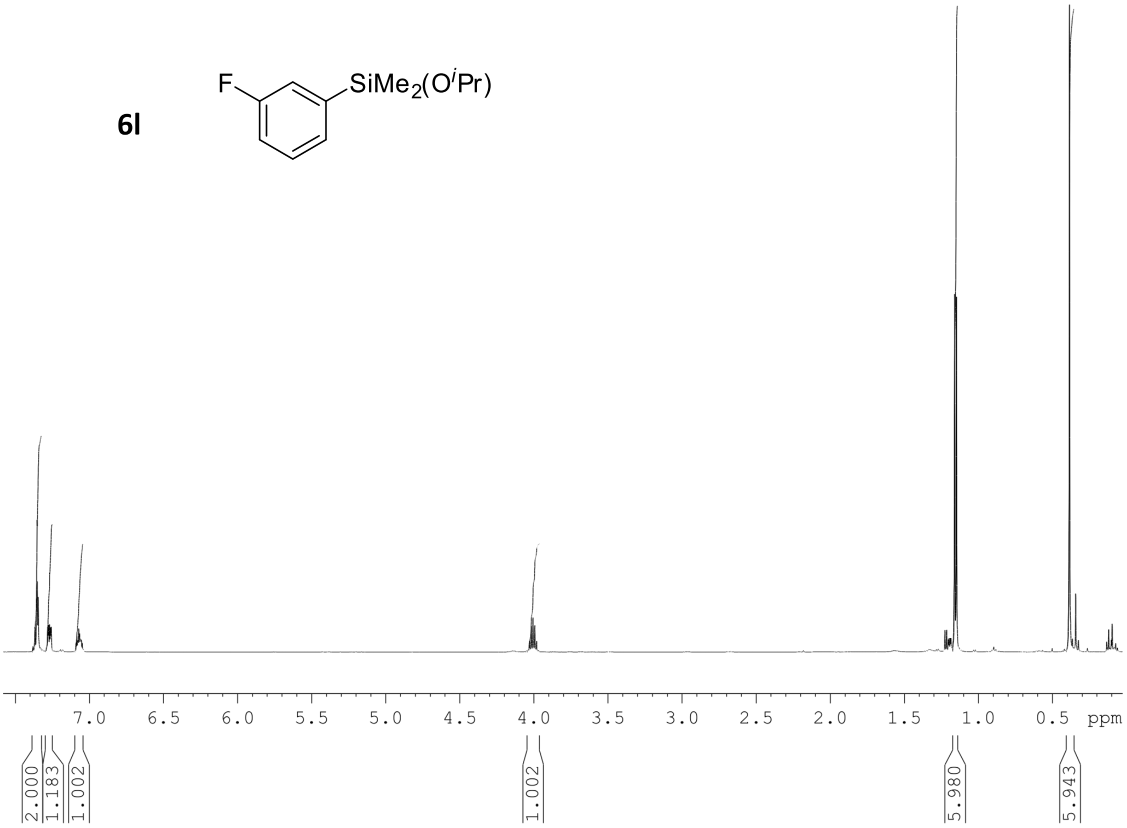
90
80
70
60
50
40
30
20
10
ppm

6l

F
SiMe$_2$(O^{i}Pr)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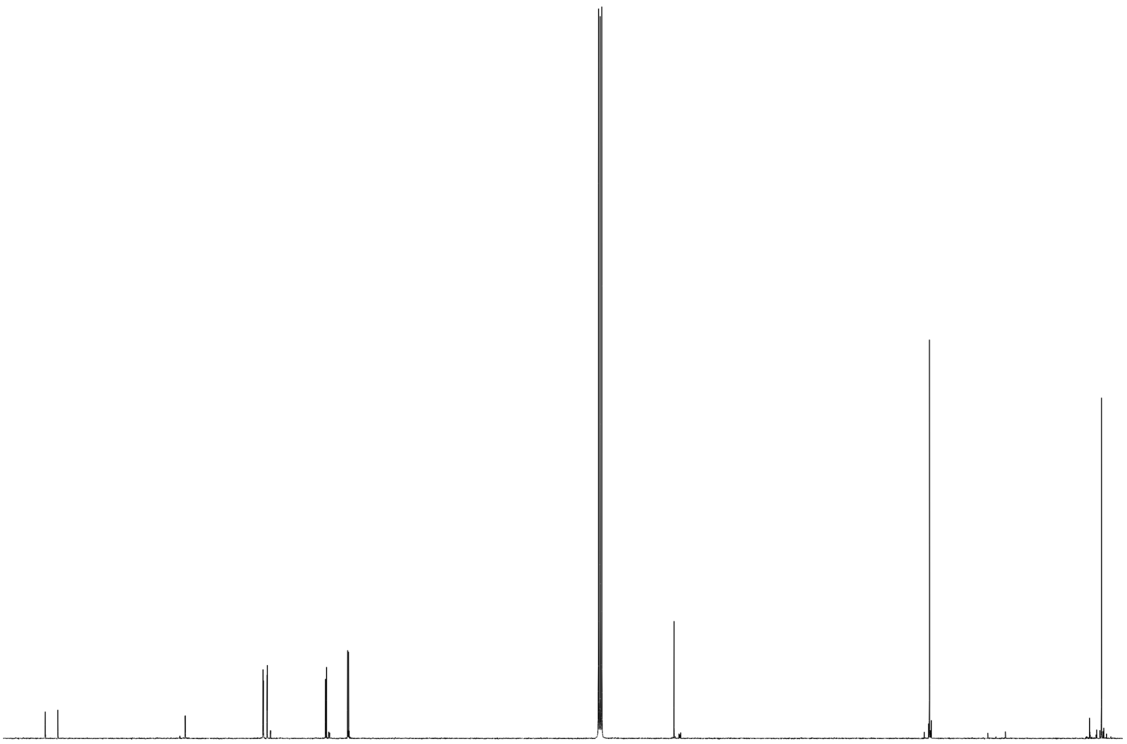
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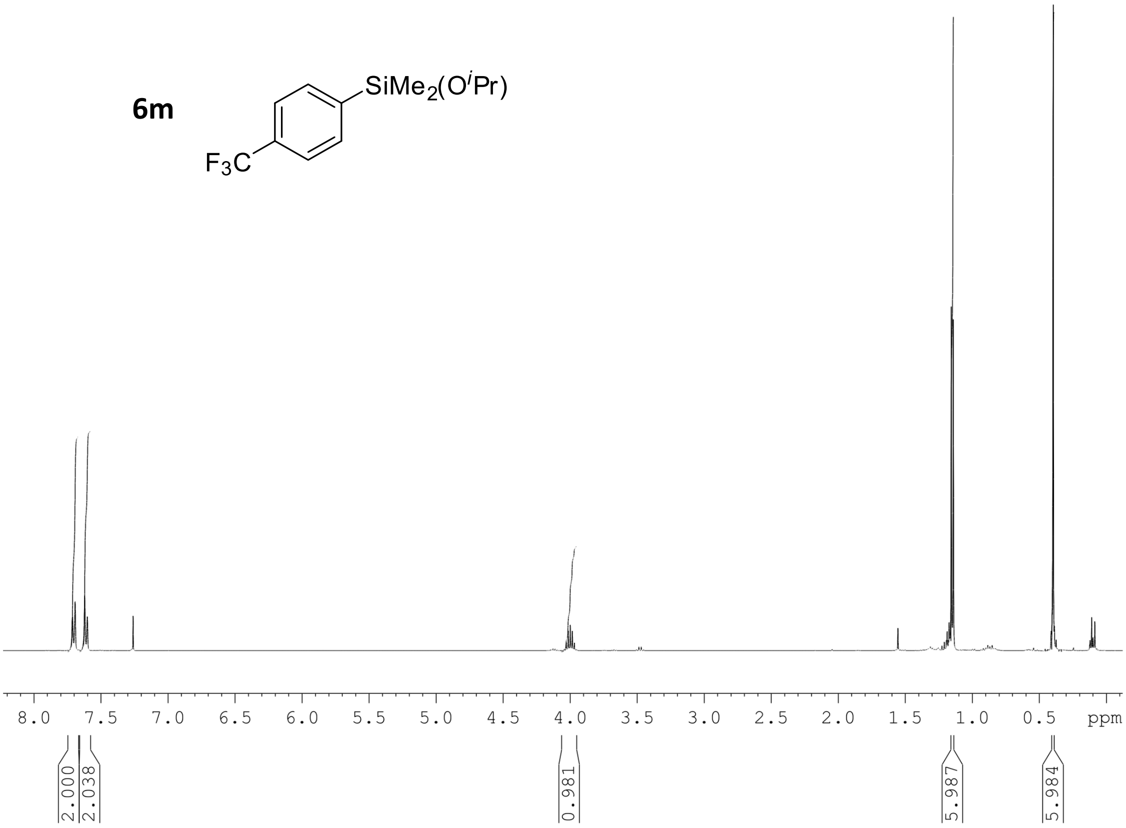
6m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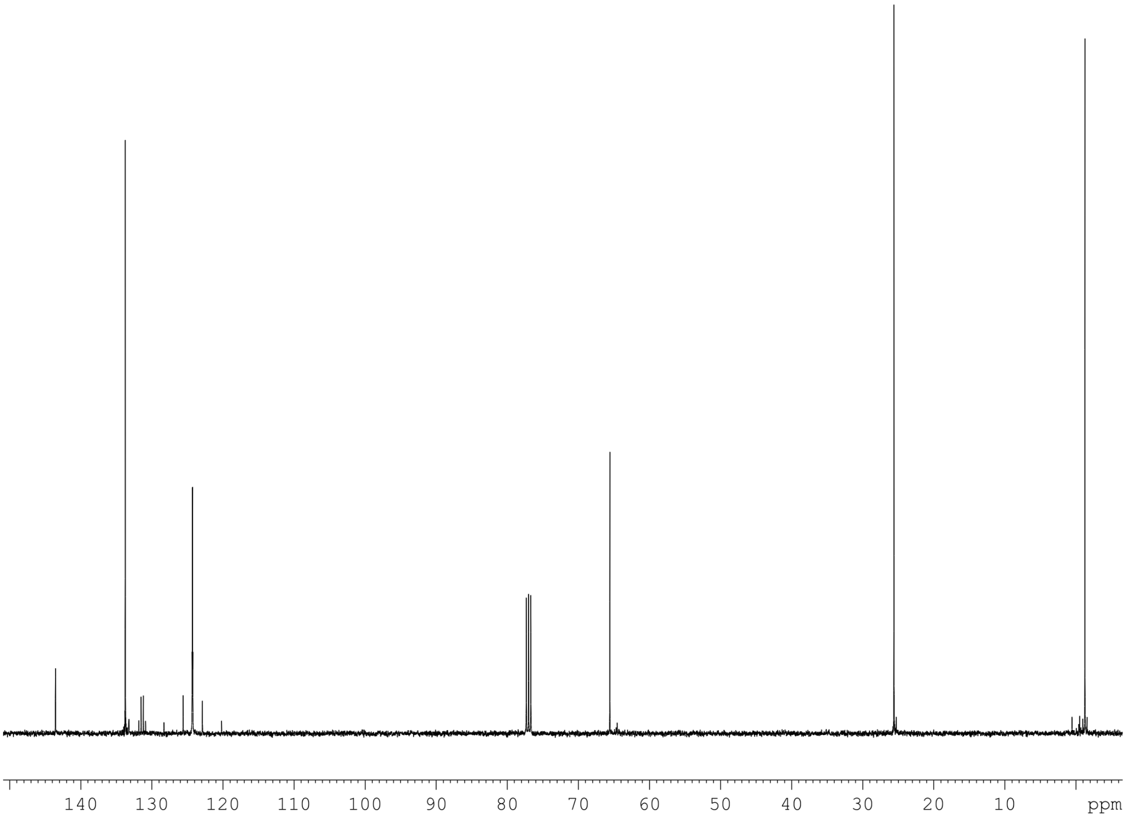
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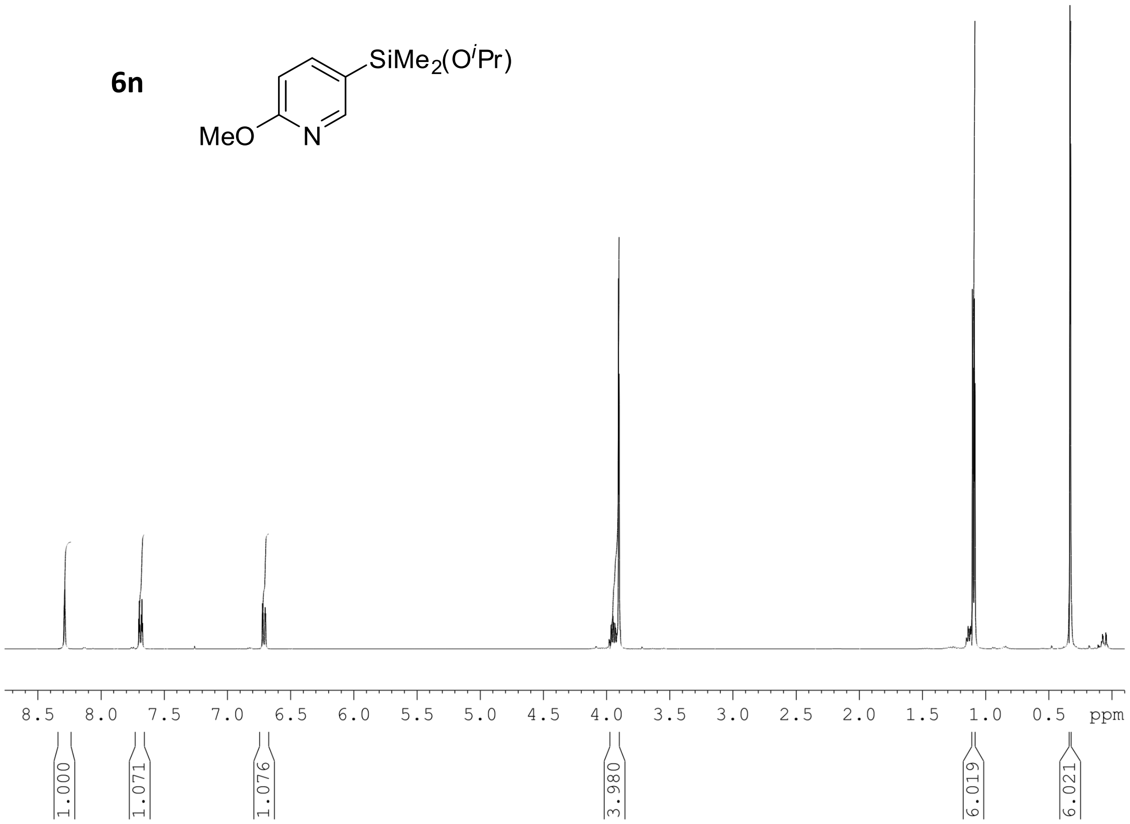
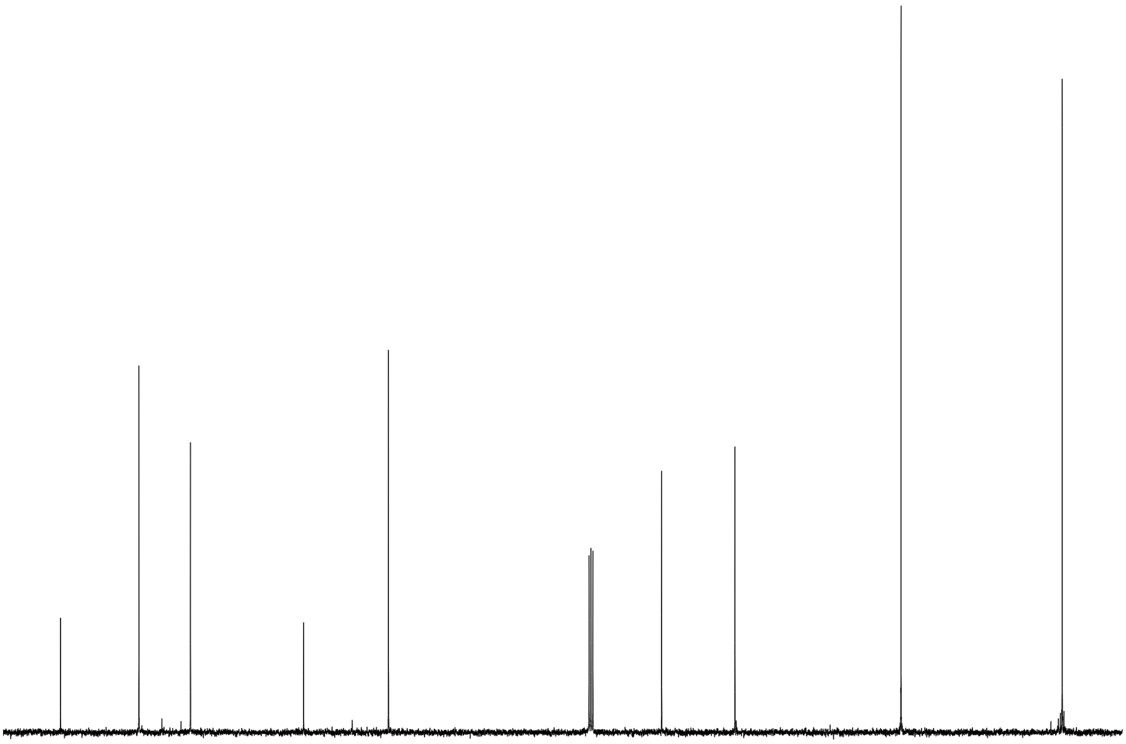
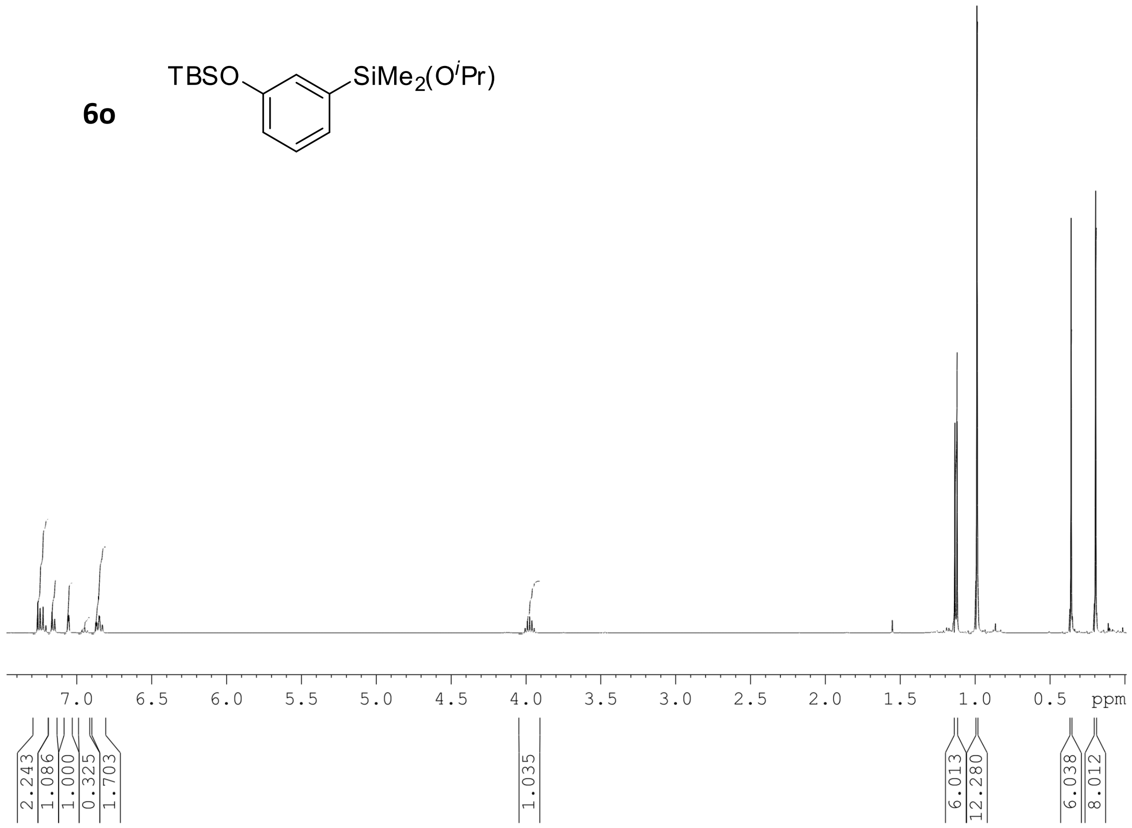
90
80
70
60
50
40
30
20
10
ppm

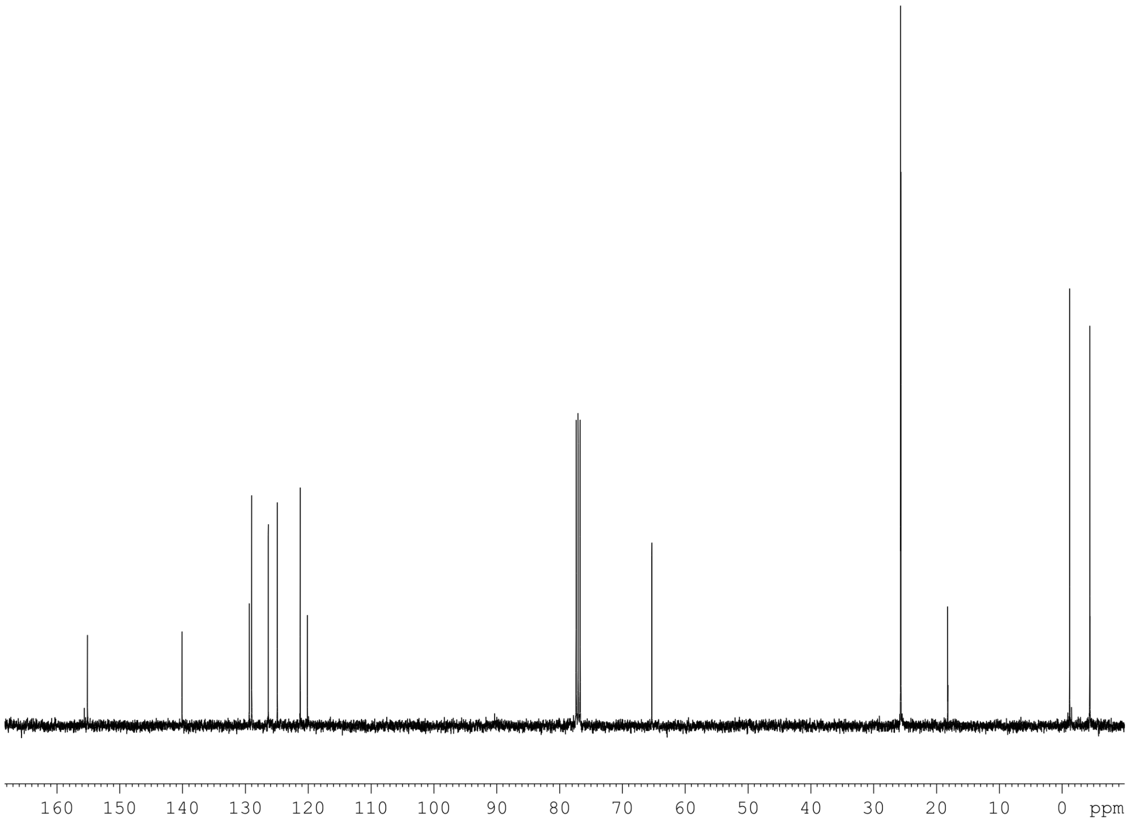
6n


SiMe2(OiPr)
MeO
N
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.000
1.071
1.076
3.980
6.019
6.021

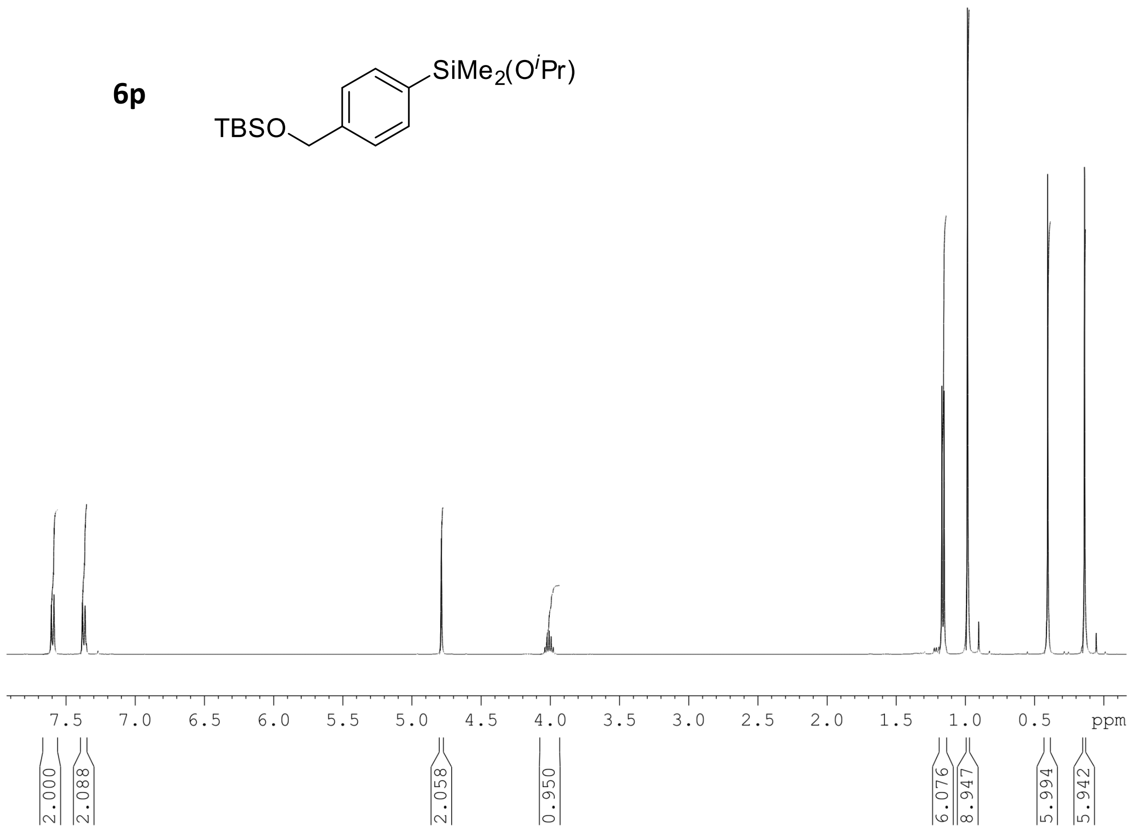

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

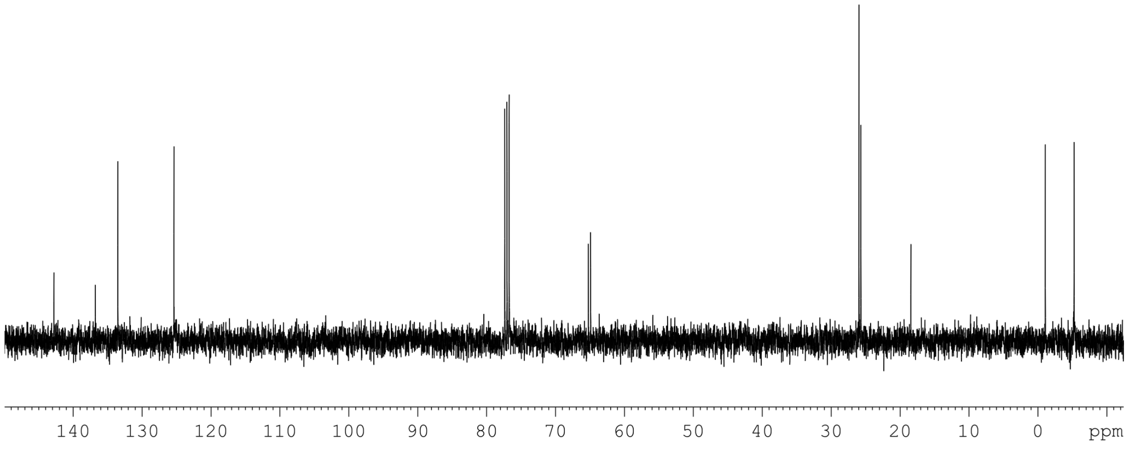
6o


TBSO
SiMe$_2$(O^{i}Pr)
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.243
1.086
1.000
0.325
1.703
1.035
6.013
12.280
6.038
8.012

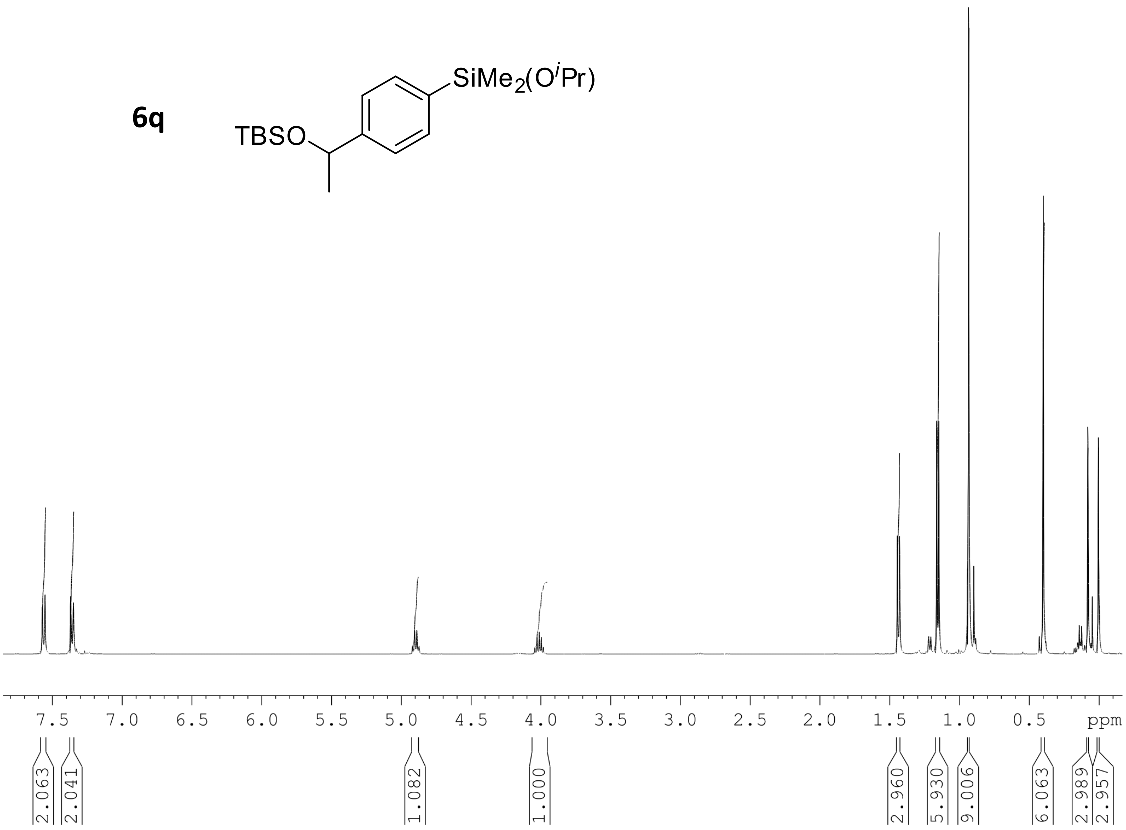

160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

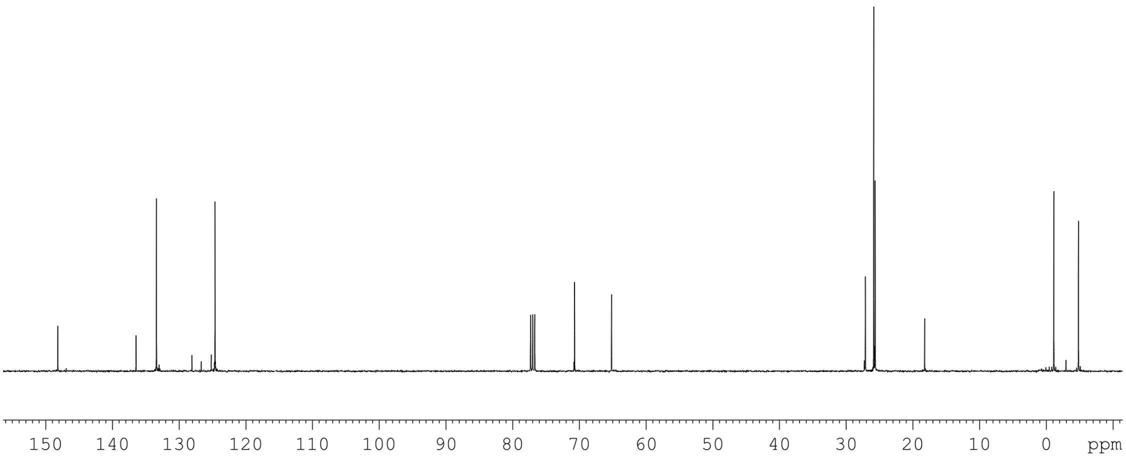
6p


TBSO
SiMe$_2$(O^{i}Pr)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.000
2.088
2.058
0.950
6.076
8.947
5.994
5.942

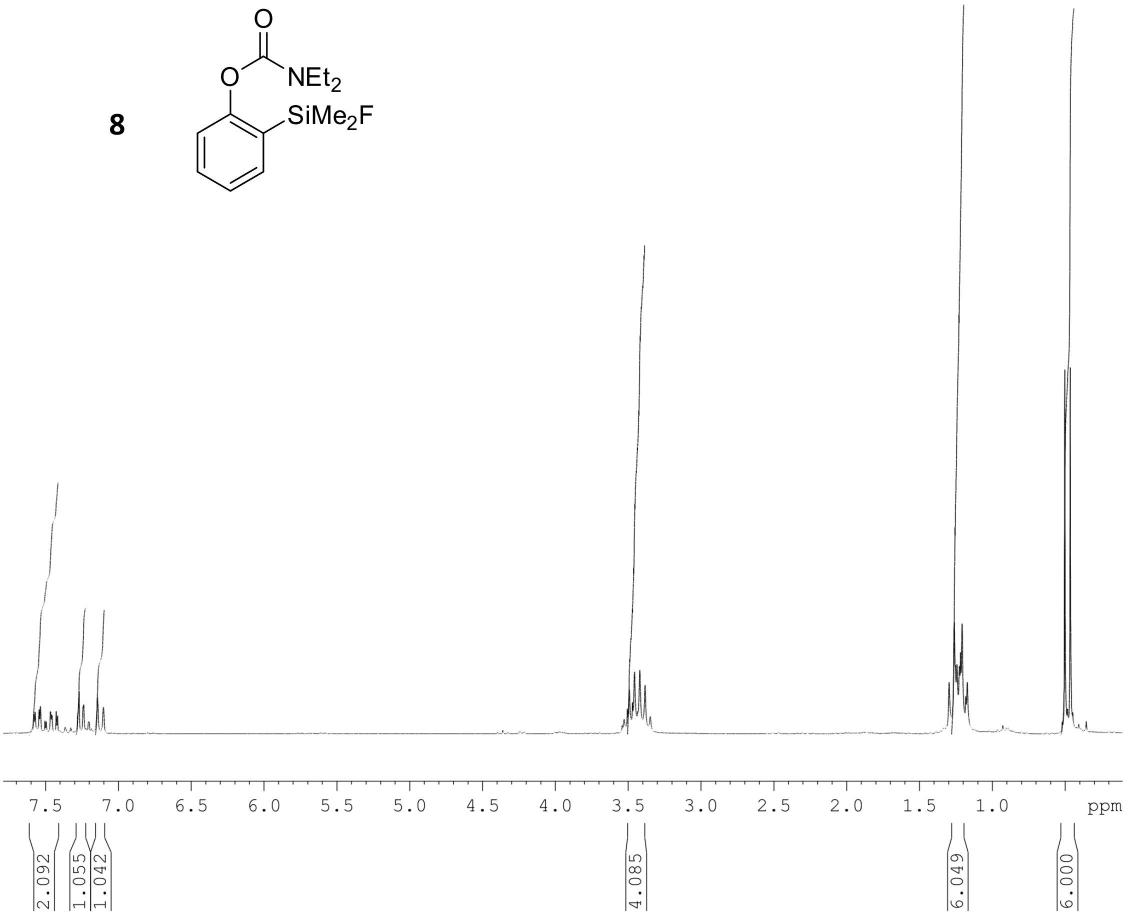

140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

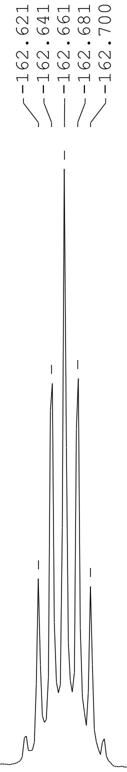
6q


SiMe$_2$(O^{i}Pr)
TBSO
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.063
2.041
1.082
1.000
2.960
5.930
9.006
6.063
2.989
2.957


150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

8


O
O
NEt$_2$
SiMe$_2$F
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.092
1.055
1.042
4.085
6.049
6.000


-162.621
-162.641
-162.661
-162.681
-162.700
-162.0
-162.2
-162.4
-162.6
-162.8
-163.0
-163.2
ppm