# Iridium-catalyzed, β-selective C($sp^3$)–H silylation of aliphatic amines to form silapyrrolidines and 1,2-amino alcohols

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## Supporting Information

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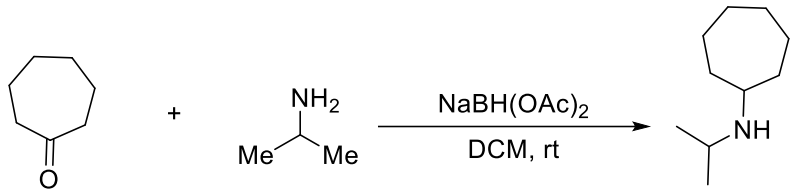
## *Methods and Materials*

All other solvents and reagents were used as received unless otherwise noted. Tetrahydrofuran (THF) was degassed by purging with nitrogen and then dried with a solvent purification system containing activated alumina. $[Ir(cod)Cl]_2$ and $[Ir(cod)OMe]_2$ were prepared according to a standard procedure.[1] The silylation reactions were assembled in an $N_2$-filled glovebox using oven-dried glassware and were stirred with Teflon-coated magnetic stirring bars.

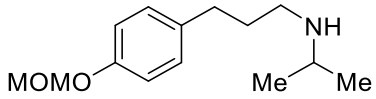
Reaction temperatures above 23 °C refer to temperatures of an aluminum heating block, which were controlled by an electronic temperature modulator. Silica gel chromatography was performed using a Teledyne Isco CombiFlash® $R_f$ system with Redi*Sep* $R_f$ Gold™ columns. $^1H$ and $^{13}C$ NMR spectra were recorded on Bruker AVB-400, AV-500, AV-600, and AV-700 spectrometers with $^{13}C$ operating frequencies of 100 MHz, 125 MHz, 150 MHz, and 175 MHz, respectively. $^{19}F$ NMR spectra were recorded on a Bruker AVQ-400 spectrometer with a $^{19}F$ operating frequency of 376 MHz. Chemical shifts ($\delta$) are reported in ppm relative to the residual solvent signal ($CDCl_3$: 7.26 ppm for $^1H$ NMR and 77.2 ppm for $^{13}C$ NMR; $C_6D_6$: 7.16 ppm for $^1H$ NMR and 128.1 ppm for $^{13}C$ NMR). High-resolution mass spectral data were obtained from the QB3/Chemistry Mass Spectrometry Facility at the University of California, Berkeley and the Lawrence-Berkeley National Laboratory Catalysis Center. Chiral GC analysis was conducted on an Agilent system.

## *Synthesis of secondary amines*



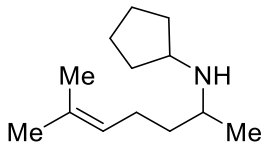

**N-isopropylcycloheptanamine (1c)**

**Procedure A**: To a solution of cycloheptanone (3.30 g, 30.0 mmol) and isopropylamine (1.77 g, 30.0 mmol) in dichloromethane (100 mL) was added sodium triacetoxyborohydride (7.50 g, 36.0 mmol) in portions at 0 °C. The mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched with saturated aqueous $NaHCO_3$ solution (60 mL) and extracted with dichloromethane (120 mL*3). The combined organic layers were washed with brine, dried over $Na_2SO_4$, filtered, and concentrated *in vacuo*. The residue was purified by Kugelrohr distillation to give the amine **1c** (62%, 2.87 g) as a colorless oil. **$^1$H NMR** (600 MHz, $CDCl_3$) $\delta$ 2.88 (hept, $J$ = 6.4 Hz, 1H), 2.75–2.65 (m, 1H), 1.89–1.76 (m, 2H), 1.68–1.58 (m, 2H), 1.58–1.45 (m, 4H), 1.45–1.37 (m, 2H), 1.36–1.22 (m, 4H), 1.03 (d, $J$ = 6.2 Hz, 6H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) $\delta$ 55.6, 45.1, 35.4, 31.5, 28.2, 24.5, 23.4, 22.6, 14.1; **HRMS** (ESI+) calcd for $C_{10}H_{22}N$ $[M+H]^+$ 156.1747, found 156.1737.




**N-isopropyl-3-(4-(methoxymethoxy)phenyl)propan-1-amine (1g)**

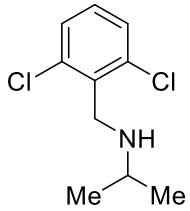
Following general procedure A, 3-(4-(methoxymethoxy)phenyl)propanal[2] (1.54 g, 7.94 mmol) and isopropylamine (1.72 mL, 20.0 mmol) were allowed to react. The crude product was purified by Kugelrohr distillation to give the amine **1g** (67%, 1.26 g) as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ 7.10 (d, $J$ = 8.6 Hz, 2H), 6.95 (d, $J$ = 8.6 Hz, 2H), 5.15 (s, 2H), 3.48 (s, 3H), 2.80 (hept, $J$ = 6.4 Hz, 1H), 2.67–2.56 (m, 4H), 1.80 (p, $J$ = 7.5 Hz, 2H), 1.06 (d, $J$ = 6.2 Hz, 6H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) $\delta$ 155.5, 135.7, 129.4, 116.3, 94.7, 56.0, 48.8, 47.2, 33.1, 32.3, 23.2; **HRMS** (ESI+) calcd for $C_{14}H_{24}NO_2$ $[M+H]^+$ 238.1802, found 238.1797.




**N-(6-methylhept-5-en-2-yl)cyclopentanamine (1j)**

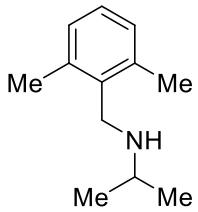
Following general procedure A, 6-methyl-5-hepten-2-one (2.23 mL, 15.0 mmol), cyclopentylamine (1.78 mL, 18.0 mmol), sodium triacetoxyborohydride (4.77 g, 22.5 mmol), and acetic acid (0.86 mL, 15 mmol) were allowed to react. The crude product was purified by Kugelrohr distillation to give the amine (2.66 g, 91%) as a colorless oil. **$^1$H NMR** (600 MHz, $CDCl_3$) $\delta$ 5.10–5.06 (m, 1H), 3.13 (p, $J$ = 7.1 Hz, 1H), 2.66 (h, $J$ = 6.3 Hz, 1H), 2.05–1.91 (m, 2H), 1.89–1.78 (m, 2H), 1.70–1.60 (m, 5H), 1.58 (s, 3H), 1.54–1.41 (m, 3H), 1.35–1.18 (m, 3H), 1.02 (d, $J$ = 6.2 Hz, 3H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) $\delta$ 131.5, 124.5, 57.0, 51.2, 37.4, 33.9, 33.3, 25.8, 24.8, 24.0, 23.9, 20.8, 17.8; **HRMS** (ESI+) calcd for $C_{13}H_{26}N$

$[M+H]^+$ 196.2060, found 196.2059.



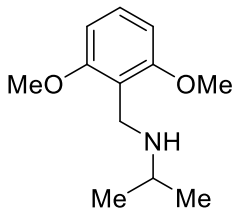

**N-(2,6-dichlorobenzyl)propan-2-amine (1n)**

Following general procedure A, 2,6-dichlorobenzaldehyde (3.50, 20.0 mmol), isopropylamine (1.41 g, 24.0 mmol), and sodium triacetoxyborohydride (5.09 g, 24.0 mmol) were allowed to react. The crude product was purified by Kugelrohr distillation to give the amine (3.24 g, 78%) as a colorless oil. **$^1$H NMR** (600 MHz, $CDCl_3$) $\delta$ 7.29 (d, $J$ = 8.0 Hz, 2H), 7.12 (t, $J$ = 8.0 Hz, 1H), 4.05 (s, 2H), 2.91–2.76 (m, 1H), 1.12 (dd, $J$ = 6.2, 0.8 Hz, 6H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) $\delta$ 136.3, 135.8, 128.7, 128.3, 48.1, 46.3, 23.0; **HRMS** (ESI+) calcd for $C_{10}H_{14}Cl_2N$ $[M+H]^+$ 218.0498, found 218.0489.




**N-(2,6-dimethylbenzyl)propan-2-amine (1o)**

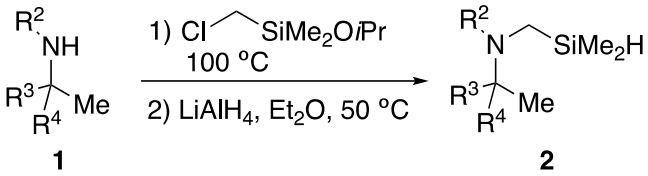
Following general procedure A, 2,6-dimethylbenzaldehyde (3.45, 25.0 mmol), isopropylamine (2.21 g, 37.5 mmol), and sodium triacetoxyborohydride (6.40 g, 30.0 mmol) were allowed to react. The crude product was purified by Kugelrohr distillation to give the amine (2.83 g, 64%) as a colorless oil. **$^1$H NMR** (600 MHz, $CDCl_3$) $\delta$ 7.04 (dd, $J$ = 8.8, 6.2 Hz, 1H), 7.00 (d, $J$ = 8.4 Hz, 2H), 3.74 (s, 2H), 2.91 (hept, $J$ = 6.2 Hz, 1H), 2.40 (s, 6H), 1.13 (d, $J$ = 6.3 Hz, 6H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) $\delta$ 137.1, 136.8, 128.2, 126.8, 49.5, 45.8, 23.0, 19.4; **HRMS** (ESI+) calcd for $C_{12}H_{20}N$ $[M+H]^+$ 178.1590, found 178.1586.




**N-(2,6-dimethoxybenzyl)propan-2-amine (1p)**

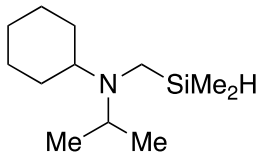
Following general procedure A, 2,6-dimethoxybenzaldehyde (3.32, 20.0 mmol), isopropylamine (1.80 g, 30.0 mmol), and sodium triacetoxyborohydride (5.10 g, 24.0 mmol) were allowed to react. The crude product was purified by Kugelrohr distillation to give the amine (2.46 g, 59%) as a colorless oil**. $^1$H NMR** (600 MHz, $CDCl_3$) $\delta$ 7.16 (t, $J$ = 8.4 Hz, 1H), 6.53 (d, $J$ = 8.4 Hz, 2H), 3.85 (s, 2H), 3.82 (s, 6H), 2.72 (hept, $J$ = 6.2 Hz, 1H), 1.06 (d, $J$ = 6.2 Hz, 6H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) $\delta$ 158.7, 127.9, 116.9, 103.6, 55.6, 47.3, 39.1, 22.9; **HRMS** (ESI+) calcd for $C_{12}H_{20}NO_2$ $[M+H]^+$ 210.1489, found 210.1486.

## *Synthesis of silylmethyl amines*



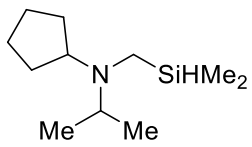

**1** **2**

**Procedure B**: In an $N_2$-filled glovebox, amine **1** (2 equiv) and (chloromethyl)-isopropoxyl-dimethylsilane (1 equiv) were added to a 20 mL screw-top vial. Alternatively, amine **1** (1 equiv), (chloromethyl)-isopropoxyl-dimethylsilane (1 equiv), and triethylamine (1 equiv) were added to the vial. The vial was capped with a Teflon-lined screw cap, and the resulting mixture was stirred at 100 °C overnight. After cooling to room temperature, the mixture was filtered, and the filter cake was washed with dry diethyl ether. Amine **1** that was used in excess as a base in this $S_N2$ reaction can be recovered from the filter cake as a hydrochloride salt if necessary. The filtrate was concentrated, and the resulting residue was brought back into the glove box and dissolved in diethyl ether ([silane] = 2 M). This solution was added dropwise to a slurry of $LiAlH_4$ (1 equiv) in diethyl ether (final concentration of silane = 1 M) in a 20 mL screw-top vial. If this reaction required more than 5 mL of solvent, the reaction was conducted in multiple vials to allow enough head space. The vial was capped with a Teflon-lined screw cap, and the resulting mixture was stirred at 50 °C overnight. The mixture was brought into the glovebox and slowly filtered through Celite to remove the majority of residual lithium aluminum hydride. The filtrate was concentrated, and the residue was purified by kugelrohr distillation with minimum exposure to moisture.




***N*-((dimethylsilyl)methyl)-*N*-isopropylcyclohexanamine (2a)**

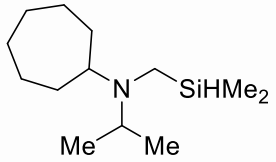
Following the general procedure B, *N*-cyclohexylisopropylamine **1a** (6.60 mL, 40.0 mmol) was allowed to react with (chloromethyl)-isopropoxyl-dimethylsilane (3.60 mL, 20.0 mmol). The crude reaction mixture was purified by kugelrohr distillation to give (silylmethyl)amine **2a** (1.91 g, 45%) as a colorless oil. **$^1$H NMR** (500 MHz, $C_6D_6$) $\delta$ 4.30–4.18 (m, 1H), 3.00 (hept, $J$ = 6.5 Hz, 1H), 2.51 (tt, $J$ = 10.8, 2.7 Hz, 1H), 2.09 (d, $J$ = 3.0 Hz, 2H), 1.77–1.64 (m, 4H), 1.60–1.52 (m, 1H), 1.28–1.12 (m, 4H), 1.07–0.92 (m, 7H), 0.14 (d, $J$ = 3.6 Hz, 6H); **$^{13}$C NMR** (150 MHz, $C_6D_6$) $\delta$ 59.7, 49.5, 34.0, 31.7, 27.0, 26.8, 20.8, -4.8; **HRMS** (ESI+) calcd for $C_{12}H_{28}N^+$ [M+H$^+$] 214.1986, found 214.1985.




**N-((dimethylsilyl)methyl)-N-isopropylcyclopentanamine (2b)**

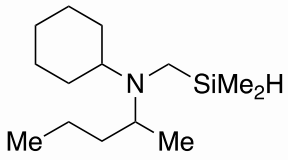
Following the general procedure B, N-cyclopentylisopropylamine **1b** (1.41 g, 11.1 mmol) was allowed to react with (chloromethyl)-isopropoxyl-dimethylsilane (0.92 g, 5.5 mmol). The crude reaction mixture was purified by kugelrohr distillation to give (silylmethyl)amine **2b** (0.74 g, 68%) as a colorless oil. **$^1$H**

**NMR** (700 MHz, $CDCl_3$) $\delta$ 3.95 (hept, $J$ = 3.6 Hz, 1H), 3.11–2.97 (m, 2H), 1.99 (dd, $J$ = 3.2, 1.8 Hz, 2H), 1.78–1.58 (m, 4H), 1.55–1.45 (m, 2H), 1.45–1.35 (m, 2H), 0.98 (dd, $J$ = 6.6, 2.0 Hz, 6H), 0.12 (dd, $J$ = 3.6, 2.0 Hz, 6H); **$^{13}$C NMR** (175 MHz, $CDCl_3$) $\delta$ 61.9, 51.6, 35.0, 30.4, 24.1, 18.9, -4.6; **HRMS** (EI+) calcd for $C_{11}H_{23}NSi$ [M] 199.1756, found 199.1759.



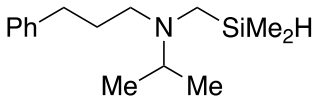

**N-((dimethylsilyl)methyl)-N-isopropylcycloheptanamine (2c)**

Following the general procedure B, *N*-cycloheptylisopropylamine **1c** (1.55 g, 10.0 mmol) was allowed to react with (chloromethyl)-isopropoxyl-dimethylsilane (0.83 g, 5.0 mmol). The crude reaction mixture was purified by kugelrohr distillation to give (silylmethyl)amine **2c** (0.58 g, 51%) as a colorless oil. **$^1$H NMR** (400 MHz, $C_6D_6$) $\delta$ 4.33 (hept, $J$ = 3.6 Hz, 1H), 3.15–2.94 (m, 1H), 2.85-2.75 (m, 1H), 2.14 (t, $J$ = 3.0 Hz, 2H), 1.93–1.80 (m, 2H), 1.77–1.38 (m, 10H), 1.06 (d, $J$ = 6.6 Hz, 6H), 0.22 (d, $J$ = 3.6 Hz, 6H); **$^{13}$C NMR** (175 MHz, $C_6D_6$) $\delta$ 60.4, 49.6, 33.7, 32.7, 28.1, 26.0, 20.5, -5.2; **HRMS** (EI+) calcd for $C_{11}H_{22}N$ [M-$SiHMe_2$] 168.1752, found 168.1754.



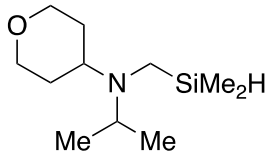

**N-((dimethylsilyl)methyl)-N-(pentan-2-yl)cyclohexanamine (2d)**

Following the general procedure B, amine **1d** (1.67 g, 9.88 mmol) was allowed to react with (chloromethyl)-isopropoxyl-dimethylsilane (1.79 mL, 9.88 mmol) and triethylamine (1.38 mL, 9.88 mmol). The crude reaction mixture was purified by kugelrohr distillation to give (silylmethyl)amine **2d** (464 mg, 20%) as a colorless oil. **$^1$H NMR** (400 MHz, $C_6D_6$) $\delta$ 4.30–4.20 (m, 1H), 2.78 (tq, $J$ = 7.8, 6.4 Hz, 1H), 2.53 (tt, $J$ = 11.1, 3.3 Hz, 1H), 2.17 (dd, $J$ = 14.9, 2.0 Hz, 1H), 2.05 (dd, $J$ = 14.8, 4.0 Hz, 1H), 1.87–1.62 (m, 4H), 1.61–0.87 (m, 16H), 0.16 (d, $J$ = 3.6 Hz, 3H), 0.10 (d, $J$ = 3.6 Hz, 3H); **$^{13}$C NMR** (150 MHz, $C_6D_6$) $\delta$ 60.0, 53.40, 38.7, 33.9, 33.4, 30.2, 27.2, 7.0, 26.8, 20.9, 17.7, 14.7, -4.6, -4.9; **HRMS** (EI+) calcd for $C_{14}H_{31}NSi$ [M] 241.2226, found 241.2229.



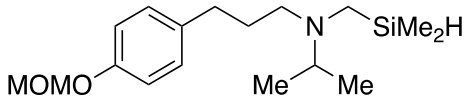

**N-((dimethylsilyl)methyl)-N-isopropyl-3-phenylpropan-1-amine (2e)**

Following the general procedure B, amine **1e**[3] (1.23 g, 6.94 mmol) was allowed to react with (chloromethyl)-isopropoxyl-dimethylsilane (1.26 mL, 6.94 mmol) and triethylamine (0.97 mL, 6.9 mmol). The crude reaction mixture was purified by kugelrohr distillation to give (silylmethyl)amine **2e** (479 mg, 28%) as a colorless oil. **$^1$H NMR** (500 MHz, $C_6D_6$) $\delta$ 4.23–4.15 (m, 1H), 3.98–3.90 (m, 2H), 3.18 (td, $J$ = 11.9, 2.0 Hz, 2H), 2.94 (hept, $J$ = 6.5 Hz, 1H), 2.57 (tt, $J$ = 11.6, 3.8 Hz, 1H), 1.97 (d, $J$ = 3.1 Hz, 2H), 1.60–1.49 (m, 2H), 1.37–1.30 (m, 2H), 0.91 (d, $J$ = 6.6 Hz, 6H), 0.09 (d, $J$ = 3.6 Hz, 6H); **$^{13}$C NMR** (150 MHz, $C_6D_6$) $\delta$ 143.1, 128.8, 128.6, 126.0, 51.8, 51.7, 38.9, 34.0, 30.9, 17.5, -4.8; **HRMS** (EI+) calcd for $C_{15}H_{27}NSi$ [M] 249.1913, found 249.1918.



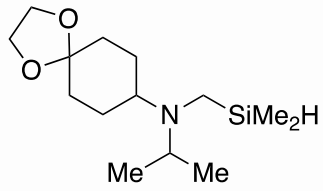

**N-((dimethylsilyl)methyl)-N-isopropyltetrahydro-2H-pyran-4-amine (2f)**

Following the general procedure B, amine **1f**[3] (1.26 g, 8.80 mmol) was allowed to react with (chloromethyl)-isopropoxyl-dimethylsilane (0.80 mL, 4.4 mmol). The crude reaction mixture was purified by kugelrohr distillation to give (silylmethyl)amine **2f** (573 mg, 60%) as a colorless oil. **$^1$H NMR** (500 MHz, $C_6D_6$) $\delta$ 4.23–4.15 (m, 1H), 3.98–3.90 (m, 2H), 3.18 (td, $J$ = 11.9, 2.0 Hz, 2H), 2.94 (hept, $J$ = 6.5 Hz, 1H), 2.57 (tt, $J$ = 11.6, 3.8 Hz, 1H), 1.97 (d, $J$ = 3.1 Hz, 2H), 1.60–1.49 (m, 2H), 1.37–1.30 (m, 2H), 0.91 (d, $J$ = 6.6 Hz, 6H), 0.09 (d, $J$ = 3.6 Hz, 6H); **$^{13}$C NMR** (150 MHz, $C_6D_6$) $\delta$ 68.1, 56.9, 49.7, 33.9, 32.1, 20.4, -4.9; **HRMS** (EI+) calcd for $C_{11}H_{25}NOSi$ [M] 215.1705, found 215.1710.



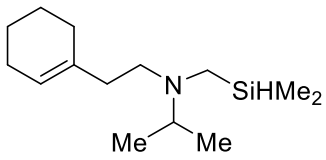

**1-(3-(4-(methoxymethoxy)phenyl)propyl)-3,3,5-trimethyl-1,3-azasilolidine (2g)**

Following the general procedure B, amine **1g** (1.11 g, 4.68 mmol) was allowed to react with (chloromethyl)-isopropoxyl-dimethylsilane (0.42 mL, 2.3 mmol). The crude reaction mixture was purified by kugelrohr distillation to give (silylmethyl)amine **2g** (93.0 mg, 13%) as a colorless oil. **$^1$H NMR** (500 MHz, $C_6D_6$) $\delta$ 7.13–7.04 (m, 4H), 4.89 (s, 2H), 4.26–4.13 (m, 1H), 3.15 (s, 3H), 2.91 (hept, $J$ = 6.6 Hz, 1H), 2.60–2.52 (m, 2H), 2.38–2.30 (m, 2H), 1.92 (d, $J$ = 3.1 Hz, 2H), 1.77–1.66 (m, 2H), 0.90 (d, $J$ = 6.6 Hz, 6H), 0.10 (d, $J$ = 3.6 Hz, 6H); **$^{13}$C NMR** (150 MHz, $C_6D6$) $\delta$ 156.2, 136.4, 129.7, 116.7, 94.7, 55.5, 51.8, 51.7, 39.0, 33.2, 31.1, 17.5, -4.8; **HRMS** (ESI+) calcd for $C_{17}H_{32}NO_2Si^+$ [M+H$^+$] 310.2197, found 310.2193.



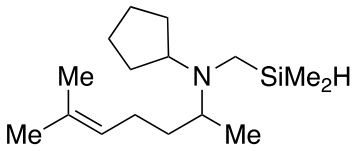

**N-((dimethylsilyl)methyl)-N-isopropyl-1,4-dioxaspiro[4.5]decan-8-amine (2h)**

Following the general procedure B, amine **1h**[4] (1.76 g, 8.83 mmol) was allowed to react with (chloromethyl)-isopropoxyl-dimethylsilane (0.80 mL, 4.4 mmol). The crude reaction mixture was purified by kugelrohr distillation to give (silylmethyl)amine **2h** (176 mg, 15%) as a colorless oil. **$^1$H NMR** (500 MHz, $C_6D_6$) $\delta$ 4.26–4.18 (m, 1H), 3.59–3.49 (m, 4H), 3.03 (hept, $J$ = 6.6 Hz, 1H), 2.60 (tt, $J$ = 11.5, 3.3 Hz, 1H), 2.08 (d, $J$ = 3.1 Hz, 2H), 1.88–1.78 (m, 4H), 1.70–1.60 (m, 4H), 0.94 (d, $J$ = 6.6 Hz, 6H), 0.09 (d, $J$ = 3.6 Hz, 6H); **$^{13}$C NMR** (150 MHz, $C_6D_6$) $\delta$ 108.8, 64.4, 64.3, 58.3, 49.8, 35.1, 34.2, 28.2, 20.6, -4.9; **HRMS** (ESI+) calcd for $C_{14}H_{30}NO_2Si^+$ [M+H$^+$] 272.2040, found 272.2038.



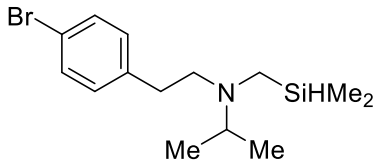
**N-(2-(cyclohex-1-en-1-yl)ethyl)-N-((dimethylsilyl)methyl)propan-2-amine (2i)**

Following the general procedure B, amine **1i** (1.41 g, 8.43 mmol) was allowed to react with (chloromethyl)-isopropoxyl-dimethylsilane (0.76 mL, 4.2 mmol). The crude reaction mixture was purified by kugelrohr distillation to give (silylmethyl)amine **2i** (0.69 g, 69%) as a colorless oil. **$^1$H NMR** (400 MHz, $C_6D_6$) $\delta$ 5.68–5.58 (m, 1H), 4.37–4.28 (m, 1H), 3.06–2.96 (m, 1H), 2.77–2.49 (m, 2H), 2.30–2.18 (m, 2H), 2.15–1.98 (m, 6H), 1.84–1.56 (m, 4H), 1.01 (d, *J* = 6.6 Hz, 6H), 0.20 (d, *J* = 3.6 Hz, 6H); **$^{13}$C NMR** (150 MHz, $C_6D_6$) $\delta$ 136.4, 121.6, 51.3, 51.2, 38.4, 37.6, 28.7, 25.3, 23.1, 22.6, 17.2, -5.3; **HRMS** (EI+) calcd for $C_{14}H_{28}NSi$ [M-H] 238.1991, found 238.1992.



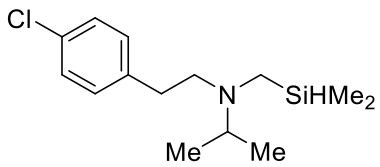

**N-((dimethylsilyl)methyl)-N-(6-methylhept-5-en-2-yl)cyclopentanamine (2j)**

Following the general procedure B, amine **1j** (1.95 g, 10.0 mmol) was allowed to react with (chloromethyl)-isopropoxyl-dimethylsilane (0.91 mL, 5.0 mmol). The crude reaction mixture was purified by kugelrohr distillation to give (silylmethyl)amine **2j** (666 mg, 50%) as a colorless oil. **$^1$H NMR** (600 MHz, $C_6D_6$) $\delta$ 5.29 (t, *J* = 7.2 Hz, 1H), 4.26–4.20 (m, 1H), 3.12–3.04 (m, 1H), 2.83 (h, *J* = 6.7 Hz, 1H), 2.28–2.18 (m, 1H), 2.13–2.04 (m, 1H), 2.03–1.95 (m, 2H), 1.74–1.34 (m, 15H), 1.27 (ddt, *J* = 13.4, 9.5, 6.2 Hz, 1H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.16 (d, *J* = 3.7 Hz, 3H), 0.10 (d, *J* = 3.7 Hz, 3H); **$^{13}$C NMR** (150 MHz, $C_6D_6$) $\delta$ 130.9, 125.8, 61.2, 56.0, 35.7, 35.1, 31.7, 28.7, 26.3, 25.9, 24.9, 24.1, 17.9, 15.8, -4.5, -4.7; **HRMS** (EI+) calcd for $C_{16}H_{33}NSi$ [M] 267.2382, found 267.2387.




**N-(4-bromophenethyl)-N-((dimethylsilyl)methyl)propan-2-amine (2k)**

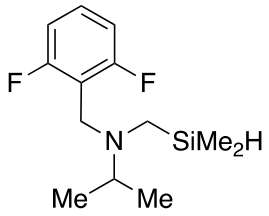
Following the general procedure B, amine **1k** (1.40 g, 5.80 mmol) was allowed to react with (chloromethyl)-isopropoxyl-dimethylsilane (0.49 g, 2.9 mmol). The crude reaction mixture was purified by kugelrohr distillation to give (silylmethyl)amine **2k** (0.49 g, 54%) as a colorless oil. **$^1$H NMR** (700 MHz, $C_6D_6$) $\delta$ 7.28 (d, *J* = 8.4 Hz, 2H), 6.75 (d, *J* = 8.4 Hz, 2H), 4.13 (hept, *J* = 3.6 Hz, 1H), 2.83 (hept, *J* = 6.6 Hz, 1H), 2.52–2.41 (m, 4H), 1.89 (d, *J* = 3.2 Hz, 2H), 0.83 (d, *J* = 6.6 Hz, 6H), 0.05 (d, *J* = 3.7 Hz, 6H); **$^{13}$C NMR** (175 MHz, $C_6D_6$) $\delta$ 139.9, 131.2, 130.7, 119.6, 53.9, 51.4, 38.6, 34.8, 17.2, -5.3; **HRMS** (EI+) calcd for $C_{13}H_{21}NSiBr$ [M-Me] 300.0606, found 300.0609.




**N-(4-chlorophenethyl)-N-((dimethylsilyl)methyl)propan-2-amine (2l)**

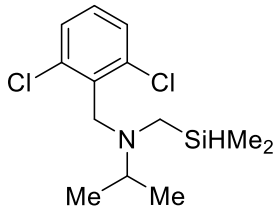
Following the general procedure B, amine **1l** (1.97 g, 10.0 mmol) was allowed to react with (chloromethyl)-isopropoxyl-dimethylsilane (0.83 g, 5.0 mmol). The crude reaction mixture was purified by kugelrohr distillation to give (silylmethyl)amine **2l** (0.75 g, 56%) as a colorless oil. **$^1$H NMR** (500

MHz, $CDCl_3$) $\delta$ 7.26 (d, $J$ = 8.4 Hz, 2H), 7.14 (d, $J$ = 8.4 Hz, 2H), 3.96 (hept, $J$ =3.6 Hz, 1H), 2.97 (p, $J$ = 6.6 Hz, 1H), 2.69 (dd, $J$ = 9.2, 6.0 Hz, 2H), 2.64–2.53 (m, 2H), 2.06 (d, $J$ = 3.2 Hz, 2H), 0.96 (d, $J$ = 6.6 Hz, 6H), 0.11 (d, $J$ = 3.6 Hz, 6H); **$^{13}$C NMR** (175 MHz, $CDCl_3$) $\delta$ 139.6, 131.4, 130.2, 128.2, 128.2, 54.2, 51.8, 38.9, 34.7, 17.5, -4.9; **HRMS** (EI+) calcd for $C_{13}H_{21}ClNSi$ [M-Me] 254.1132, found 254.1138.



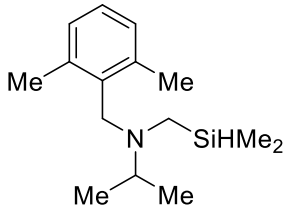

**N-(2,6-difluorobenzyl)-N-((dimethylsilyl)methyl)propan-2-amine (2m)**

Following the general procedure, amine **1m**[3] (2.35 g, 12.7 mmol) was allowed to react with (chloromethyl)-isopropoxyl-dimethylsilane (1.15 mL, 6.34 mmol). The crude reaction mixture was purified by kugelrohr distillation to give (silylmethyl)amine **2m** (1.00 g, 61%) as a colorless oil. **$^1$H NMR** (400 MHz, $C_6D_6$) $\delta$ 6.70–6.43 (m, 3H), 4.25–4.15 (m, 1H), 3.59 (s, 2H), 2.94 (hept, $J$ = 6.8 Hz, 1H), 2.00 (d, $J$ = 3.0 Hz, 2H), 0.95 (d, $J$ = 6.6 Hz, 6H), 0.06 (d, $J$ = 3.7 Hz, 6H); **$^{13}$C NMR** (150 MHz, $C_6D_6$) $\delta$ 162.85 (dd, $J$ = 248.5, 8.6 Hz), 128.86 (t, $J$ = 10.2 Hz), 116.7 (t, $J$ = 18.5 Hz), 111.2 (dd, $J$ = 21.3, 5.1 Hz), 51.7, 44.0, 38.2, 17.2, -5.1; **$^{19}$F NMR** (376 MHz, $C_6$D6) $\delta$ -113.1; **HRMS** (EI+) calcd for $C_{13}H_{21}F_2NSi$ [M] 257.1411, found 257.1414.




**N-(2,6-dichlorobenzyl)-N-((dimethylsilyl)methyl)propan-2-amine (2n)**

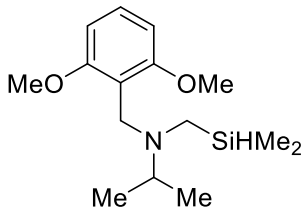
Following the general procedure B, amine **1n** (2.17 g, 10.0 mmol) was allowed to react with (chloromethyl)-isopropoxyl-dimethylsilane (0.83 g, 5.0 mmol). The crude reaction mixture was purified by kugelrohr distillation to give (silylmethyl)amine **2n** (0.88 g, 60%) as a colorless oil. **$^1$H NMR** (400 MHz, $C_6D_6$) $\delta$ 6.96 (d, $J$ = 8.0 Hz, 2H), 6.46 (t, $J$ = 8.0 Hz, 1H), 4.08 (hept, $J$ = 3.6, 1H), 3.77 (s, 2H), 2.97 (hept, $J$ = 6.8 Hz, 1H), 2.05 (d, $J$ = 3.2 Hz, 2H), 1.02 (d, $J$ = 6.6 Hz, 6H), 0.01 (d, $J$ = 3.6 Hz, 6H); **$^{13}$C NMR** (175 MHz, $C_6D_6$) $\delta$ 137.3, 135.8, 128.4, 128.2, 52.5, 51.2, 38.1, 17.1, -5.3; **HRMS** (EI+) calcd for $C_{13}H_{21}Cl_2NSi$ [M] 289.0820, found 289.0819.




**N-(2,6-dimethylbenzyl)-N-((dimethylsilyl)methyl)propan-2-amine (2o)**

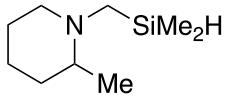
Following the general procedure B, amine **1o** (1.77 g, 10.0 mmol) was allowed to react with

(chloromethyl)-isopropoxyl-dimethylsilane (0.83 g, 5.0 mmol). The crude reaction mixture was purified by kugelrohr distillation to give (silylmethyl)amine **2o** (0.86 g, 68%) as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ 7.04 (t, $J$ = 8.4 Hz, 1H), 6.97 (d, $J$ = 8.4 Hz, 2H), 3.86 (hept, $J$ = 3.6 Hz, 1H), 3.58 (s, 2H), 2.92 (hept, $J$ = 6.6 Hz, 1H), 2.41 (s, 6H), 1.91 (d, $J$ = 3.0 Hz, 2H), 1.03 (d, $J$ = 6.6 Hz, 6H), -0.02 (d, $J$ = 3.6 Hz, 6H); **$^{13}$C NMR** (175 MHz, $CDCl_3$) $\delta$ 138.4, 136.2, 128.1, 126.4, 51.6, 48.8, 40.9, 20.6, 16.9, 0.2; **HRMS** (EI+) calcd for $C_{15}H_{27}NSi$ [M] 249.1913, found 249.1915.



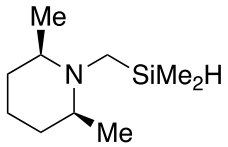

**N-(2,6-dimethoxybenzyl)-N-((dimethylsilyl)methyl)propan-2-amine (2p)**

Following the general procedure B, amine **1p** (2.09 g, 10.0 mmol) was allowed to react with (chloromethyl)-isopropoxyl-dimethylsilane (0.83 g, 5.0 mmol). The crude reaction mixture was purified by kugelrohr distillation to give (silylmethyl)amine **2p** (0.22 g, 16%) as a colorless oil. **$^1$H NMR** (700 MHz, $CDCl_3$) $\delta$ 7.20 (t, $J$ = 8.4 Hz, 1H), 6.56 (d, $J$ = 8.4 Hz, 2H), 3.98 (hept, $J$ = 3.6 Hz, 1H), 3.82 (s, 6H), 3.61 (s, 2H), 2.83 (hept, $J$ = 6.6 Hz, 1H), 1.99 (d, $J$ = 3.0 Hz, 2H), 0.98 (d, $J$ = 6.6 Hz, 6H), 0.08 (d, $J$ = 3.6 Hz, 6H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) $\delta$ 158.7, 127.9, 116.9, 103.6, 55.6, 47.3, 39.1, 22.9; **HRMS** (EI+) calcd for $C_{13}H_{21}NO_2$ [M-$SiMe_2$] 223.1572, found 223.1566.




**1-((dimethylsilyl)methyl)-2-methylpiperidine (2q)**

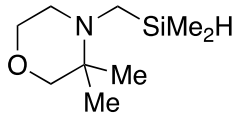
Following the general procedure B, amine **1q** (1.18 mL, 10.0 mmol) was allowed to react with (chloromethyl)-isopropoxyl-dimethylsilane (1.81 mL, 10.0 mmol) and triethylamine (1.39 mL, 10.0 mmol). The crude reaction mixture was purified by kugelrohr distillation to give (silylmethyl)amine **2q** (561 mg, 33%) as a colorless oil. **$^1$H NMR** (500 MHz, $C_6D_6$) $\delta$ 4.30–4.20 (m, 1H), 2.98–2.87 (m, 1H), 2.39 (dd, $J$ = 14.4, 4.1 Hz, 1H), 2.04–1.95 (m, 2H), 1.62–1.42 (m, 5H), 1.36–1.26 (m, 1H), 1.25–1.15 (m, 1H), 1.01 (d, $J$ = 6.2 Hz, 3H), 0.14 (d, $J$ = 3.6 Hz, 3H), 0.07 (d, $J$ = 3.6 Hz, 3H); **$^{13}$C NMR** (150 MHz, $C_6D_6$) $\delta$ 60.0, 56.1, 44.0, 35.1, 27.0, 24.5, 19.6, -4.5, -4.8; **HRMS** (EI+) calcd for $C_9H_{21}NSi$ [M] 171.1443, found 171.1443.




**(2S,6R)-1-((dimethylsilyl)methyl)-2,6-dimethylpiperidine (2r)**

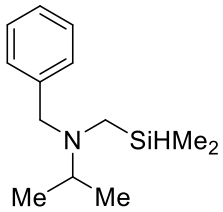
Following the general procedure B, amine **1r** (0.67 mL, 5.0 mmol) was allowed to react with (chloromethyl)-isopropoxyl-dimethylsilane (0.70 mL, 5.0 mmol) and triethylamine (0.70 mL, 5.0 mmol). The crude reaction mixture was purified by kugelrohr distillation to give (silylmethyl)amine **2r** (279 mg, 30%) as a colorless oil. **$^1$H NMR** (500 MHz, $C_6D_6$) $\delta$ 4.34–4.22 (m, 1H), 2.29–2.18 (m, 2H), 2.14 (d, $J$

= 3.4 Hz, 2H), 1.57–1.50 (m, 1H), 1.47–1.38 (m, 2H), 1.34–1.19 (m, 3H), 1.07 (d, *J* = 6.2 Hz, 6H), 0.11 (d, *J* = 3.7 Hz, 6H); **$^{13}$C NMR** (150 MHz, $C_6D_6$) *δ* 59.8, 40.5, 35.3, 24.7, 22.8, -3.8; **HRMS** (EI+) calcd for $C_{10}H_{23}NSi$ [M] 185.1600, found 185.1592.



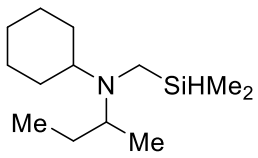

**4-((dimethylsilyl)methyl)-3,3-dimethylmorpholine (2s)**

Following the general procedure B, amine **1s** (1.00 g, 8.68 mmol) was allowed to react with (chloromethyl)-isopropoxyl-dimethylsilane (1.5 mL, 8.7 mmol) and triethylamine (1.21 mL, 8.68 mmol). The crude reaction mixture was purified by kugelrohr distillation to give (silylmethyl)amine **2s** (714 mg, 44%) as a colorless oil. **$^{1}$H NMR** (400 MHz, $C_6D_6$) *δ* 4.17–4.06 (m, 1H), 3.63–3.54 (m, 2H), 3.30 (s, 2H), 2.41–2.31 (m, 2H), 1.74 (d, *J* = 2.9 Hz, 2H), 0.83 (s, 6H), 0.05 (d, *J* = 3.7 Hz, 6H); **$^{13}$C NMR** (150 MHz, $C_6D_6$) *δ* 78.0, 68.4, 54.0, 50.0, 37.9, 18.4, -5.0; **HRMS** (EI+) calcd for $C_9H_{21}NOSi$ [M] 187.1392, found 187.1392.




**N-benzyl-N-((dimethylsilyl)methyl)propan-2-amine (2t)**

Following the general procedure B, amine **1t** (1.67 mL, 10.0 mmol) was allowed to react with (chloromethyl)-isopropoxyl-dimethylsilane (0.91 g, 5.0 mmol). The crude reaction mixture was purified by kugelrohr distillation to give (silylmethyl)amine **2t** (0.33 g, 30%) as a colorless oil. **$^{1}$H NMR** (700 MHz, $CDCl_3$) *δ* 7.40–7.36 (m, 2H), 7.35–7.29 (m, 2H), 7.27–7.22 (m, 1H), 4.00–3.92 (m, 1H), 3.56 (s, 2H), 2.93 (hept, *J* = 6.6 Hz, 1H), 2.01 (d, *J* = 3.0 Hz, 2H), 1.00 (d, *J* = 6.6 Hz, 6H), 0.11 (d, *J* = 3.6 Hz, 6H); **$^{13}$C NMR** (175 MHz, $CDCl_3$) *δ* 141.3, 128.5, 128.0, 126.4, 56.4, 50.6, 37.9, 17.1, -5.0; **HRMS** (EI+) calcd for $C_{13}H_{23}NSi$ [M] 221.1600, found 221.1605.

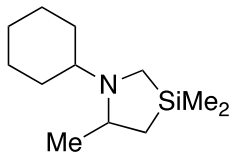



**N-(sec-butyl)-N-((dimethylsilyl)methyl)cyclohexanamine (2u)**

Following the general procedure B, amine **1u** (1.55 g, 10.0 mmol) was allowed to react with (chloromethyl)-isopropoxyl-dimethylsilane (0.83 g, 5.0 mmol). The crude reaction mixture was purified by kugelrohr distillation to give (silylmethyl)amine **2u** (0.37 g, 32%) as a colorless oil. **$^{1}$H NMR** (400 MHz, $C_6D_6$) *δ* 4.37–4.27 (m, 1H), 2.82–2.65 (m, 1H), 2.65–2.55 (m, 1H), 2.25 (dd, *J* = 14.8, 2.0 Hz, 1H), 2.11 (dd, *J* = 14.8, 4.0 Hz, 1H), 1.92–1.73 (m, 4H), 1.70–1.58 (m, 1H), 1.52–1.40 (m, 1H), 1.40–1.15 (m, 5H), 1.08–0.98 (m, 7H), 0.24 (d, *J* = 3.6 Hz, 3H), 0.18 (d, *J* = 3.6 Hz, 3H); **$^{13}$C NMR** (150 MHz, $C_6D6$) *δ* 59.5, 54.9, 33.5, 32.9, 29.7, 28.5, 26.7, 26.5, 26.3, 17.0, 11.8, -5.0, -5.3; **HRMS** (EI+) calcd for $C_{13}H_{29}NSi$ [M] 227.2069, found 227.2065.

## *C-H Silylation of Aliphatic Amines*

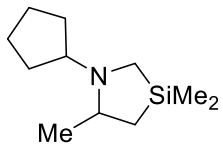
**Procedure C**: In an $N_2$-filled glovebox, (silylmethyl)amine **2** (1.0 equiv) was weighed into a 4 mL screw-top vial. The amine was then sequentially treated with norbornene (1.5 equiv) and a freshly prepared stock solution of $[Ir(cod)OMe]_2$ (2.0 mol %) and 2,4,7-trimethylphenanthroline **L5** (5.0 mol %) in THF ([silane] = 0.5 M). The vial was capped with a Teflon-lined screw cap and placed in a pre-heated aluminum heating block at 100 °C. After 17 hours, the reaction mixture was allowed to cool to room temperature, and the solvent was removed via rotary evaporation. The crude product was adsorbed into Celite and purified by column chromatograph on silica gel.




**1-cyclohexyl-3,3,5-trimethyl-1,3-azasilolidine (3a)**

Following the general procedure C, (silylmethyl)amine **2a** (54.4 mg, 0.255 mmol) was allowed to react with $[Ir(cod)OMe]_2$/2,4,7-trimethylphenanthroline in THF (0.5 mL) at 100 °C for 17 h. Concentration of the reaction mixture and purification by silica gel chromatography (hexanes with 1% $NEt_3$ : EtOAc 100:0→90:10) gave 39.4 mg (75%) of **3a** as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ 2.98–2.87 (m, 1H), 2.62 (tt, *J* = 10.7, 3.2 Hz, 1H), 2.01 (d, *J* = 12.8 Hz, 1H), 1.82 (d, *J* = 12.8 Hz, 1H), 1.80–1.58 (m, 5H), 1.41–1.07 (m, 5H), 1.05 (d, *J* = 6.2 Hz, 3H), 0.94 (dd, *J* = 14.2, 5.7 Hz, 1H), 0.57 (dd, *J* = 14.2, 8.5 Hz, 1H), 0.18 (s, 3H), 0.11 (s, 3H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 58.4, 55.1, 35.7, 33.3, 26.7, 26.5, 25.8, 23.6, 23.4, 19.6, -1.6, -2.0; **HRMS** (ESI+) calcd for $C_{12}H_{26}NSi^+$ $[M+H^+]$ 212.1829, found 212.1831.

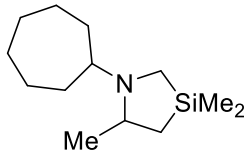
***Glovebox-free procedure*:** $[Ir(cod)OMe]_2$ (3.3 mg, 0.0050 mmol, 2.0 mol %), **L5** (2.8 mg, 0.013 mmol, 5.0 mol%), and a solution of **2a** (53.4 mg, 0.250 mmol) and norbornene (35.3 mg, 0.375 mmol, 1.5 equiv) in THF (0.5 mL) were quickly added in this order on the benchtop to a cooled, flame-dried Schlenk tube. The reaction vessel was degassed by reducing pressure briefly and backfilling with nitrogen (three cycles). The Schlenk tube was immersed in a preheated oil bath at 100 °C and stirred at this temperature for 17 h. After this time, the reaction was cooled to room temperature, and the yield was determined by $^1$H NMR spectroscopy with 1,3,5-trimethoxybenzene (8.2 mg, 0.049 mmol, 0.20 equiv) added as an internal standard added after the reaction (91%).




**1-cyclopentyl-3,3,5-trimethyl-1,3-azasilolidine (3b)**

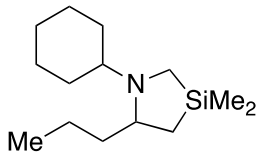
Following the general procedure C, (silylmethyl)amine **2b** (19.9 mg, 0.100 mmol) was allowed to react with $[Ir(cod)OMe]_2$/2,4,7-trimethylphenanthroline in THF (0.5 mL) at 100 °C for 10 h. Concentration of the reaction mixture and purification by silica gel chromatography (hexanes with 1% $NEt_3$ : EtOAc 100:0→90:10) gave 14.8 mg (75%) of **3b** as a colorless oil. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 3.22–2.99 (m, 2H), 2.00 (d, *J* = 13.0 Hz, 1H), 1.86 (d, *J* = 13.0 Hz, 1H), 1.88–1.80 (m, 1H), 1.76–1.60 (m, 3H), 1.59–1.41 (m, 4H), 1.07–0.99 (m, 1H), 0.99 (d, *J* = 6.6 Hz, 3H), 0.60 (dd, *J* = 14.2, 5.2 Hz, 1H), 0.21 (s,

3H), 0.17 (s, 3H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) $\delta$ 63.2, 57.1, 36.9, 31.9, 26.5, 24.5, 24.0, 22.5, 16.7, -1.3, -2.0; **HRMS** (ESI+) calcd for $C_{11}H_{24}NSi^+$ [M+H$^+$] 198.1673, found 198.1683.



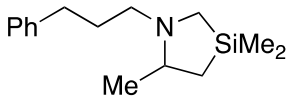

**1-cycloheptyl-3,3,5-trimethyl-1,3-azasilolidine (3c)**

Following the general procedure C, (silylmethyl)amine **2c** (22.7 mg, 0.100 mmol) was allowed to react with [Ir(cod)OMe]$_2$/2,4,7-trimethylphenanthroline in THF (0.5 mL) at 100 °C for 17 h. Concentration of the reaction mixture and purification by silica gel chromatography (hexanes with 1% $NEt_3$ : EtOAc 100:0→90:10) gave 18.4 mg (82%) of **3c** as a colorless oil. **$^1$H NMR** (600 MHz, $CDCl_3$) $\delta$ 2.98–2.85 (m, 1H), 2.66–2.55 (m, 1H), 2.15 (d, $J$ = 12.8 Hz, 1H), 1.81–1.27 (m, 13H), 1.12 (d, $J$ = 6.0 Hz, 3H), 0.91 (dd, $J$ = 14.0, 5.2 Hz, 1H), 0.54 (dd, $J$ = 14.0, 10.2 Hz, 1H), 0.17 (s, 3H), 0.10 (s, 3H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) $\delta$ 58.5, 55.7, 35.0, 34.9, 28.3, 28.0, 26.3, 25.7, 23.5, 23.1, 21.2, -2.2, -2.4; **HRMS** (ESI+) calcd for $C_{13}H_{28}NSi^+$ [M+H$^+$] 226.1986, found 226.1996.




**1-cyclohexyl-3,3-dimethyl-5-propyl-1,3-azasilolidine (3d)**

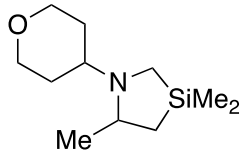
Following the general procedure C, (silylmethyl)amine **2d** (60.3 mg, 0.250 mmol) was allowed to react with [Ir(cod)OMe]$_2$/2,4,7-trimethylphenanthroline in THF (0.5 mL) at 100 °C for 17 h. Concentration of the reaction mixture and purification by silica gel chromatography (hexanes with 1% $NEt_3$ : EtOAc 100:0→95:5) gave 47.4 mg (79%) of **3d** as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ 2.98–2.87 (m, 1H), 2.62 (tt, $J$ = 10.7, 3.2 Hz, 1H), 2.01 (d, $J$ = 12.8 Hz, 1H), 1.82 (d, $J$ = 12.8 Hz, 1H), 1.80–1.58 (m, 5H), 1.41–1.07 (m, 5H), 1.05 (d, $J$ = 6.2 Hz, 3H), 0.94 (dd, $J$ = 14.2, 5.7 Hz, 1H), 0.57 (dd, $J$ = 14.2, 8.5 Hz, 1H), 0.18 (s, 3H), 0.11 (s, 3H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) $\delta$ 59.9, 57.9, 36.0, 35.3, 33.3, 26.8, 26.6, 25.8, 23.4, 20.1, 19.7, 14.7, -1.7, -2.0; **HRMS** (ESI+) calcd for $C_{14}H_{30}NSi^+$ [M+H$^+$] 240.2142, found 240.2152.




**3,3,5-trimethyl-1-(3-phenylpropyl)-1,3-azasilolidine (3e)**

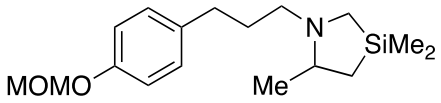
Following the general procedure C, (silylmethyl)amine **2e** (63.6 mg, 0.255 mmol) was allowed to react with [Ir(cod)OMe]$_2$/2,4,7-trimethylphenanthroline in THF (0.5 mL) at 100 °C for 17 h. Concentration of the reaction mixture and purification by silica gel chromatography (hexanes with 1% $NEt_3$ : EtOAc 100:0→95:5) gave 51.4 mg (81%) of **3e** as a colorless oil. **$^1$H NMR** (600 MHz, $CDCl_3$) $\delta$ 7.28 (t, $J$ = 7.6 Hz, 2H), 7.20 (d, $J$ = 7.3 Hz, 2H), 7.17 (t, $J$ = 7.3 Hz, 1H), 2.84 (ddd, $J$ = 11.7, 8.9, 6.6 Hz, 1H), 2.69–2.63 (m, 1H), 2.62–2.55 (m, 1H), 2.52–2.46 (m, 1H), 2.30 (d, $J$ = 12.9 Hz, 1H), 2.15 (ddd, $J$ = 11.7, 8.9, 6.0 Hz, 1H), 1.90–1.77 (m, 2H), 1.49 (d, $J$ = 12.9 Hz, 1H), 1.08 (d, $J$ = 6.1 Hz, 3H), 0.98 (dd, $J$ = 14.3, 5.9 Hz, 1H), 0.57 (dd, $J$ = 14.3, 8.9 Hz, 1H), 0.19 (s, 3H), 0.13 (s, 3H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) $\delta$

142.8, 128.56 128.4, 125.7, 60.2, 55.8, 42.9, 34.1, 29.6, 23.5, 20.6, -1.8, -2.0; **HRMS** (ESI+) calcd for $C_{15}H_{26}NSi^+$ [M+H$^+$] 248.1829, found 248.1835.



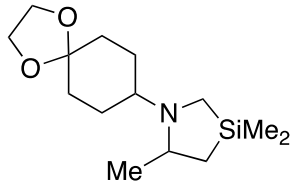

**3,3,5-trimethyl-1-(tetrahydro-2H-pyran-4-yl)-1,3-azasilolidine (3f)**

Following the general procedure C, (silylmethyl)amine **2f** (53.6 mg, 0.249 mmol) was allowed to react with [Ir(cod)OMe]$_2$/2,4,7-trimethylphenanthroline in THF (0.5 mL) at 100 °C for 17 h. Concentration of the reaction mixture and purification by silica gel chromatography (hexanes with 1% $NEt_3$ : EtOAc 100:0→90:10) gave 39.3 mg (74%) of **3f** as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ 4.04–3.97 (m, 2H), 3.42 (td, *J* = 11.2, 3.4 Hz, 1H), 3.36 (ddd, *J* = 14.5, 6.5, 4.3 Hz, 1H), 3.06–2.97 (m, 1H), 2.82 (tt, *J* = 10.1, 5.2 Hz, 1H), 1.95 (d, *J* = 12.7 Hz, 1H), 1.88 (d, *J* = 12.7 Hz, 1H), 1.77–1.66 (m, 2H), 1.64–1.55 (m, 2H), 1.04 (d, *J* = 6.2 Hz, 3H), 0.98 (dd, *J* = 14.2, 6.0 Hz, 1H), 0.58 (dd, *J* = 14.2, 7.5 Hz, 1H), 0.20 (s, 3H), 0.14 (s, 3H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) $\delta$ 68.1, 67.4, 56.3, 54.7, 35.6, 33.2, 25.4, 23.1, 18.8, -1.5, -2.0; **HRMS** (ESI+) calcd for $C_{11}H_{24}NOSi^+$ [M+H$^+$] 214.1622, found 214.1628.




**1-(3-(4-(methoxymethoxy)phenyl)propyl)-3,3,5-trimethyl-1,3-azasilolidine (3g)**

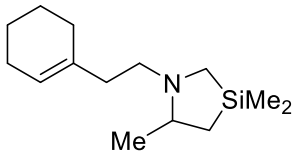
Following the general procedure C, (silylmethyl)amine **2g** (30.6 mg, 0.0989 mmol) was allowed to react with [Ir(cod)OMe]$_2$/2,4,7-trimethylphenanthroline in THF (0.2 mL) at 100 °C for 17 h. Concentration of the reaction mixture and purification by silica gel chromatography (hexanes with 1% $NEt_3$ : EtOAc 100:0→95:5) gave 25.5 mg (84%) of **3g** as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ 7.11 (d, *J* = 8.6 Hz, 2H), 6.95 (d, *J* = 8.6 Hz, 2H), 5.15 (s, 2H), 3.48 (s, 3H), 2.82 (ddd, *J* = 11.7, 8.9, 6.7 Hz, 1H), 2.65–2.41 (m, 3H), 2.29 (d, *J* = 13.0 Hz, 1H), 2.13 (ddd, *J* = 11.7, 8.8, 6.0 Hz, 1H), 1.89–1.72 (m, 2H), 1.48 (d, *J* = 12.9 Hz, 1H), 1.08 (d, *J* = 6.1 Hz, 3H), 0.97 (dd, *J* = 14.3, 5.8 Hz, 1H), 0.57 (dd, *J* = 14.3, 8.9 Hz, 1H), 0.18 (s, 3H), 0.12 (s, 3H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) $\delta$ 155.4, 136.2, 129.4, 116.3, 94.8, 60.2, 56.0, 55.8, 42.9, 33.3, 29.8, 23.5, 20.6, -1.8, -2.0; **HRMS** (EI+) calcd for $C_{17}H_{29}NO_2Si$ [M] 307.1968, found 307.1968.




**3,3,5-trimethyl-1-(1,4-dioxaspiro[4.5]decan-8-yl)-1,3-azasilolidine (3h)**

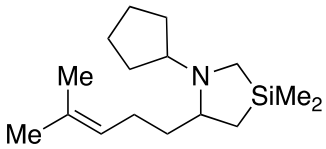
Following the general procedure C, (silylmethyl)amine **2h** (67.4 mg, 0.248 mmol) was allowed to react with [Ir(cod)OMe]$_2$/2,4,7-trimethylphenanthroline in THF (0.5 mL) at 100 °C for 17 h. Concentration of the reaction mixture and purification by silica gel chromatography (hexanes with 1% $NEt_3$ : EtOAc 100:0→90:10) gave 54.0 mg (80%) of **3h** as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ 3.93 (s, 4H), 2.88 (tq, *J* = 8.5, 6.0 Hz, 1H), 2.73 (tt, *J* = 10.2, 3.9 Hz, 1H), 2.03 (d, *J* = 12.7 Hz, 1H), 1.84–1.69 (m,

5H), 1.67–1.46 (m, 4H), 1.06 (d, $J$ = 6.1 Hz, 3H), 0.95 (dd, $J$ = 14.2, 5.7 Hz, 1H), 0.56 (dd, $J$ = 14.2, 8.5 Hz, 1H), 0.17 (s, 3H), 0.10 (s, 3H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) $\delta$ 109.0, 64.40, 64.35, 56.8, 55.5, 35.7, 34.2, 33.6, 29.8, 23.5, 20.3, 19.7, -1.7, -2.1; **HRMS** (ESI+) calcd for $C_{14}H_{28}NO_2Si^+$ [M+H$^+$] 270.1884, found 270.1887.



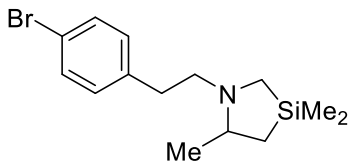

**1-(2-(cyclohex-1-en-1-yl)ethyl)-3,3,5-trimethyl-1,3-azasilolidine (3i)**

Following the general procedure C, (silylmethyl)amine **2i** (23.9 mg, 0.100 mmol) was allowed to react with [Ir(cod)OMe]$_2$/2,4,7-trimethylphenanthroline in THF (0.5 mL) at 100 °C for 10 h. Concentration of the reaction mixture and purification by silica gel chromatography (hexanes with 1% $NEt_3$ : EtOAc 100:0→90:10) gave 14.0 mg (59%) of **3i** as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ 5.88–5.02 (m, 1H), 2.90–2.08 (m, 1H), 2.55–2.45 (m, 1H), 2.31 (d, $J$ = 12.8 Hz, 1H), 2.25–2.00 (m, 3H), 2.01–1.87 (m, 4H), 1.67–1.48 (m, 5H), 1.10 (d, $J$ = 6.1 Hz, 3H), 0.96 (dd, $J$ = 14.2, 5.6 Hz, 1H), 0.57 (dd, $J$ = 14.2, 9.0 Hz, 1H), 0.18 (s, 3H), 0.12 (s, 3H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) $\delta$ 136.7, 121.6, 59.9, 55.2, 43.0, 35.9, 28.7, 25.3, 23.4, 23.1, 22.5, 20.6, -1.9, -2.1; **HRMS** (ESI+) calcd for $C_{14}H_{28}NSi^+$ [M+H$^+$] 238.1986, found 238.1989.




**1-cyclopentyl-3,3-dimethyl-5-(4-methylpent-3-en-1-yl)-1,3-azasilolidine (3j)**

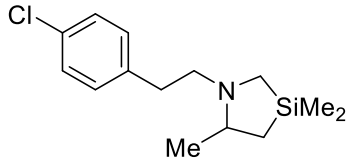
Following the general procedure C, (silylmethyl)amine **2j** (68.1 mg, 0.255 mmol) was allowed to react with [Ir(cod)OMe]$_2$/2,4,7-trimethylphenanthroline in THF (0.5 mL) at 100 °C for 17 h. Concentration of the reaction mixture and purification by silica gel chromatography (hexanes with 1% $NEt_3$) gave 42.1 mg (62%) of **3j** as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ 5.15–5.08 (m, 1H), 3.11 (p, $J$ = 8.1, 7.4 Hz, 1H), 2.92–2.83 (m, 1H), 2.07–1.92 (m, 2H), 1.91–1.77 (m, 3H), 1.75–1.36 (m, 14H), 1.04 (dtd, $J$ = 12.8, 10.0, 5.1 Hz, 1H), 0.92 (dd, $J$ = 14.3, 6.5 Hz, 1H), 0.66 (dd, $J$ = 14.3, 5.2 Hz, 1H), 0.18 (s, 3H), 0.15 (s, 3H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) $\delta$ 131.4, 124.7, 62.6, 62.0, 37.4, 32.0, 30.2, 26.4, 25.7, 25.6, 24.6, 24.1, 18.9, 17.7, -1.2, -1.8; **HRMS** (ESI+) calcd for $C_{16}H_{32}NSi^+$ [M+H$^+$] 266.2299, found 266.2298.




**1-(4-bromophenethyl)-3,3,5-trimethyl-1,3-azasilolidine (3k)**

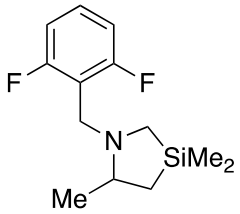
Following the general procedure C, (silylmethyl)amine **2k** (31.3 mg, 0.100 mmol) was allowed to react with [Ir(cod)OMe]$_2$/2,4,7-trimethylphenanthroline in THF (0.5 mL) at 100 °C for 17 h. Concentration of the reaction mixture and purification by silica gel chromatography (hexanes with 1% $NEt_3$ : EtOAc 100:0→90:10) gave 21.4 mg (68%) of **3k** as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ 7.39 (d, $J$ = 8.2 Hz, 2H), 7.08 (d, $J$ = 8.2 Hz, 2H), 2.98 (td, $J$ = 11.4, 5.4 Hz, 1H), 2.85–2.65 (m, 2H), 2.62–2.51 (m,

1H), 2.38 (d, *J* = 12.8 Hz, 1H), 2.46–2.29 (m, 1H), 1.63 (d, *J* = 12.8 Hz, 1H), 1.10 (d, *J* = 6.1 Hz, 3H), 1.07–0.92 (m, 1H), 0.59 (dd, *J* = 14.4, 8.8 Hz, 1H), 0.22 (s, 3H), 0.16 (s, 3H); **$^{13}$C NMR** (175 MHz, $CDCl_3$) $\delta$ 139.4, 130.7, 129.9, 118.9, 59.3, 57.4, 42.3, 33.0, 22.7, 19.8, -2.6, -2.8; **HRMS** (ESI+) calcd for $C_{14}H_{23}NSiBr^+$ [M+H$^+$] 312.0778, found 312.0771.



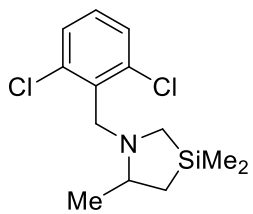

**1-(4-chlorophenethyl)-3,3,5-trimethyl-1,3-azasilolidine (3l)**

Following the general procedure C, (silylmethyl)amine **2l** (26.9 mg, 0.100 mmol) was allowed to react with [Ir(cod)OMe]$_2$/2,4,7-trimethylphenanthroline in THF (0.5 mL) at 100 °C for 17 h. Concentration of the reaction mixture and purification by silica gel chromatography (hexanes with 1% $NEt_3$ : EtOAc 100:0→90:10) gave 19.7 mg (73%) of **3l** as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ 7.27 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 3.13–2.94 (m, 1H), 2.90–2.72 (m, 2H), 2.59 (dt, *J* = 9.2, 6.0 Hz, 1H), 2.41 (d, *J* = 12.4 Hz, 1H), 2.46–2.28 (m, 1H), 1.67 (d, *J* = 12.8 Hz, 1H), 1.13 (d, *J* = 6.0 Hz, 3H), 1.03 (dd, *J* = 14.2, 5.8 Hz, 1H), 0.62 (dd, *J* = 14.2, 9.0 Hz, 1H), 0.25 (s, 3H), 0.19 (s, 3H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) $\delta$ 139.5, 131.6, 130.1, 128.4, 60.0, 58.1, 43.0, 33.6, 23.3, 20.4, -1.9, -2.1; **HRMS** (ESI+) calcd for $C_{14}H_{23}NSiCl^+$ [M+H$^+$] 268.1283, found 268.1292.



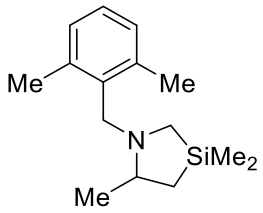

**1-(2,6-difluorobenzyl)-3,3,5-trimethyl-1,3-azasilolidine (3m)**

Following the general procedure C, (silylmethyl)amine **2m** (64.9 mg, 0.252 mmol) was allowed to react with [Ir(cod)OMe]$_2$/2,4,7-trimethylphenanthroline in THF (0.5 mL) at 100 °C for 17 h. Concentration of the reaction mixture and purification by silica gel chromatography (hexanes with 1% $NEt_3$) gave 50.6 mg (79%) of **3m** as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ 7.20 (tt, *J* = 8.3, 6.4 Hz, 1H), 6.90–6.81 (m, 2H), 4.02 (d, *J* = 12.4 Hz, 1H), 3.49 (d, *J* = 12.4 Hz, 1H), 2.63–2.53 (m, 1H), 2.18 (d, *J* = 13.0 Hz, 1H), 1.55 (d, *J* = 13.0 Hz, 1H), 1.28 (d, *J* = 5.9 Hz, 3H), 0.98 (dd, *J* = 14.4, 6.0 Hz, 1H), 0.58 (dd, *J* = 14.4, 9.1 Hz, 1H), 0.12 (s, 3H), 0.07 (s, 3H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) $\delta$ 162.4 (dd, *J* = 248.0, 8.8 Hz), 128.6 (t, *J* = 10.4 Hz), 115.1 (t, *J* = 19.8 Hz), 111.1 (dd, *J* = 21.6, 5.1 Hz), 59.8, 46.6, 43.0, 23.6, 21.6, -1.9, -2.1; **$^{19}$F NMR** (376 MHz, $CDCl_3$) $\delta$ -112.5; **HRMS** (ESI+) calcd for $C_{13}H_{20}F_2NSi^+$ [M+H$^+$] 256.1328, found 256.1334.



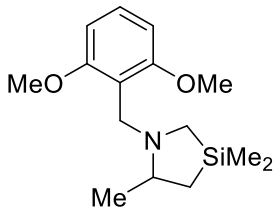
**1-(2,6-dichlorobenzyl)-3,3,5-trimethyl-1,3-azasilolidine (3n)**

Following the general procedure C, (silylmethyl)amine **2k** (28.9 mg, 0.100 mmol) was allowed to react with [Ir(cod)OMe]$_2$/2,4,7-trimethylphenanthroline in THF (0.5 mL) at 100 °C for 17 h. Concentration of the reaction mixture and purification by silica gel chromatography (hexanes with 1% $NEt_3$ : EtOAc 100:0→90:10) gave 20.2 mg (70%) of **3k** as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ 7.27 (d, $J$ = 8.0 Hz, 2H), 7.10 (t, $J$ = 8.0 Hz, 1H), 4.08 (d, $J$ = 12.0 Hz, 1H), 3.65 (d, $J$ = 12.0 Hz, 1H), 2.90–2.78 (m, 1H), 1.98 (d, $J$ = 12.6 Hz, 1H), 1.70 (d, $J$ = 12.6 Hz, 1H), 1.21 (d, $J$ = 6.2 Hz, 3H), 0.98 (dd, $J$ = 14.2, 6.6 Hz, 1H), 0.54 (dd, $J$ = 14.2, 7.0 Hz, 1H), 0.09 (s, 3H), 0.07 (s, 3H); **$^{13}$C NMR** (175 MHz, $CDCl_3$) $\delta$ 136.2, 135.5, 127.6, 127.5, 59.7, 53.7, 40.7, 22.3, 19.1, -2.4, -2.9; **HRMS** (ESI+) calcd for $C_{13}H_{20}NSiCl_2^+$ [M+H$^+$] 288.0737, found 288.0730.



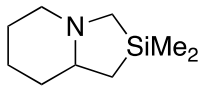

**1-(2,6-dimethylbenzyl)-3,3,5-trimethyl-1,3-azasilolidine (3o)**

Following the general procedure C, (silylmethyl)amine **2o** (24.9 mg, 0.100 mmol) was allowed to react with [Ir(cod)OMe]$_2$/2,4,7-trimethylphenanthroline in THF (0.5 mL) at 100 °C for 17 h. Concentration of the reaction mixture and purification by silica gel chromatography (hexanes with 1% $NEt_3$ : EtOAc 100:0→90:10) gave 18.0 mg (73%) of **3o** as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ 7.04 (t, $J$ = 7.6 Hz, 1H), 6.98 (d, $J$ = 7.6 Hz, 2H), 3.93 (d, $J$ = 12.0 Hz, 1H), 3.29 (d, $J$ = 12.0 Hz, 1H), 2.63 (dt, $J$ = 7.8, 6.0 Hz, 1H), 2.40 (s, 6H), 1.93 (d, $J$ = 12.4 Hz, 1H), 1.41 (d, $J$ = 12.4 Hz, 1H), 1.22 (d, $J$ = 6.2 Hz, 3H), 1.00 (dd, $J$ = 14.4, 6.4 Hz, 1H), 0.53 (dd, $J$ = 14.4, 7.6 Hz, 1H), 0.06 (s, 3H), 0.05 (s, 3H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) $\delta$ 137.9, 136.8, 127.9, 126.2, 60.6, 53.6, 41.5, 23.3, 20.4, 20.2, -1.9, -2.5; **HRMS** (ESI+) calcd for $C_{15}H_{26}NSi^+$ [M+H$^+$] 248.1829, found 248.1833.



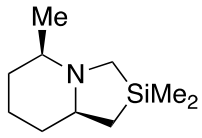

**1-(2,6-dimethoxybenzyl)-3,3,5-trimethyl-1,3-azasilolidine (3p)**

Following the general procedure C, (silylmethyl)amine **2p** (28.1 mg, 0.100 mmol) was allowed to react with [Ir(cod)OMe]$_2$/2,4,7-trimethylphenanthroline in THF (0.5 mL) at 100 °C for 17 h. Concentration of the reaction mixture and purification by silica gel chromatography (hexanes with 1% $NEt_3$ : EtOAc 100:0→90:10) gave 22.9 mg (82%) of **3p** as a colorless oil. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.18 (t, $J$ = 8.2 Hz, 1H), 6.55 (d, $J$ = 8.2 Hz, 2H), 3.99 (d, $J$ = 12.0 Hz, 1H), 3.80 (s, 6H), 3.52 (d, $J$ = 12.0 Hz, 1H), 2.62 (dt, $J$ = 8.8, 6.2 Hz, 1H), 2.19 (d, $J$ = 13.6 Hz, 1H), 1.63 (d, $J$ = 13.6 Hz, 1H), 1.29 (d, $J$ = 6.0 Hz, 3H), 0.94 (dd, $J$ = 14.2, 6.0 Hz, 1H), 0.56 (dd, $J$ = 14.2, 9.0 Hz, 1H), 0.11 (s, 3H), 0.05 (s, 3H); **$^{13}$C NMR** (175 MHz, $CDCl_3$) $\delta$ 159.6, 128.0, 106.8, 104.2, 59.9, 55.9, 46.6, 42.6, 23.4, 21.7, -1.9, -1.9; **HRMS** (ESI+) calcd for $C_{15}H_{26}NO_2Si^+$ [M+H$^+$] 280.1727, found 280.1721.



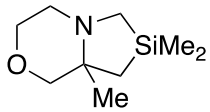
**2,2-dimethyloctahydro-[1,3]azasilolo[1,5-a]pyridine (3q)**

Following the general procedure, (silylmethyl)amine **2q** (42.1 mg, 0.246 mmol) was allowed to react with [Ir(cod)OMe]$_2$/2,4,7-trimethylphenanthroline in THF (0.5 mL) at 100 °C for 17 h. Concentration of the reaction mixture and purification by silica gel chromatography (hexanes with 1% $NEt_3$ : EtOAc 100:0→95:5) gave 15.5 mg (37%) of **3q** as a colorless oil. **$^1$H NMR** (600 MHz, $CDCl_3$) $\delta$ 3.13–3.02 (m, 1H), 2.43 (d, $J$ = 13.0 Hz, 1H), 2.00–1.91 (m, 1H), 1.86–1.75 (m, 2H), 1.74–1.66 (m, 1H), 1.63–1.54 (m, 2H), 1.39 (d, $J$ = 13.1 Hz, 1H), 1.26–1.15 (m, 2H), 0.90 (dd, $J$ = 14.1, 4.9 Hz, 1H), 0.51 (dd, $J$ = 14.2, 11.4 Hz, 1H), 0.21 (s, 3H), 0.11 (s, 3H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) $\delta$ 65.0, 59.3, 48.1, 36.2, 26.4, 25.2, 22.4, -2.05, -2.07; **HRMS** (ESI+) calcd for $C_9H_{20}NSi^+$ [M+H$^+$] 170.1360, found 170.1368.



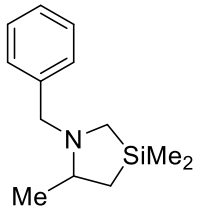
**2,2,5-trimethyloctahydro-[1,3]azasilolo[1,5-a]pyridine (3r)**

Following the general procedure C, (silylmethyl)amine **2r** (46.9 mg, 0.253 mmol) was allowed to react with [Ir(cod)OMe]$_2$/2,4,7-trimethylphenanthroline in THF (0.5 mL) at 100 °C for 17 h. Concentration of the reaction mixture and purification by silica gel chromatography (hexanes with 1% $NEt_3$ : EtOAc 100:0→95:5) gave 22.2 mg (48%) of **3r** as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ 2.64 (d, $J$ = 13.0 Hz, 1H), 1.99–1.88 (m, 2H), 1.86–1.75 (m, 1H), 1.70–1.61 (m, 1H), 1.60–1.51 (m, 1H), 1.37–1.18 (m, 4H), 1.11 (d, $J$ = 6.3 Hz, 3H), 0.89 (dd, $J$ = 14.2, 4.8 Hz, 1H), 0.59 (dd, $J$ = 14.2, 11.8 Hz, 1H), 0.20 (s, 3H), 0.10 (s, 3H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) $\delta$ 65.5, 62.9, 44.5, 36.4, 34.8, 25.0, 22.4, 21.8, -2.0, -2.1; **HRMS** (ESI+) calcd for $C_{10}H_{22}NSi^+$ [M+H$^+$] 184.1516, found 184.1519.



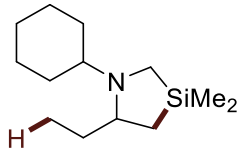
**2,2,8a-trimethylhexahydro-1H-[1,3]azasilolo[5,1-c][1,4]oxazine (3s)**

Following the general procedure C, (silylmethyl)amine **2s** (46.1 mg, 0.246 mmol) was allowed to react with [Ir(cod)OMe]$_2$/2,4,7-trimethylphenanthroline in THF (0.5 mL) at 100 °C for 17 h. Concentration of the reaction mixture and purification by silica gel chromatography (hexanes with 1% $NEt_3$ : EtOAc 100:0→90:10) gave 26.3 mg (58%) of **3s** as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ 3.86–3.74 (m, 1H), 3.67–3.53 (m, 2H), 3.20 (d, $J$ = 10.6 Hz, 1H), 2.72 (td, $J$ = 11.7, 3.6 Hz, 1H), 2.54 (d, $J$ = 11.9 Hz, 1H), 2.20 (d, $J$ = 12.9 Hz, 1H), 1.81 (d, $J$ = 12.8 Hz, 1H), 0.96 (s, 3H), 0.59 (d, $J$ = 13.6 Hz, 1H), 0.52 (d, $J$ = 13.9 Hz, 1H), 0.23 (s, 3H), 0.21 (s, 3H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) $\delta$ 79.6, 67.5, 59.9, 51.0, 42.2, 24.8, 13.6, -1.2, -1.6; **HRMS** (ESI+) calcd for $C_9H_{20}NOSi^+$ [M+H$^+$] 186.1309, found 186.1313.




**1-benzyl-3,3,5-trimethyl-1,3-azasilolidine (3t)**

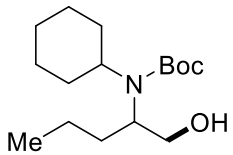
Following the general procedure C, (silylmethyl)amine **2t** (44.0 mg, 0.199 mmol) was allowed to react with [Ir(cod)OMe]$_2$/2,4,7-trimethylphenanthroline in THF (1.0 mL) at 100 °C for 20 h. Concentration of the reaction mixture and purification by silica gel chromatography (hexanes with 1% $NEt_3$ : EtOAc 100:0→90:10) gave 37.1 mg (84%) of **3t** and **3tt** as an inseparable mixture (10:1). For the major product **3t**: **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.38–7.28 (m, 4H), 7.26–7.19 (m, 1H), 4.05 (d, $J$ = 12.8 Hz, 1H), 3.22 (d, $J$ = 12.8 Hz, 1H), 2.70–2.53 (m, 1H), 2.09 (d, $J$ = 13.0 Hz, 1H), 1.44 (d, $J$ = 13.0 Hz, 1H), 1.22 (d, $J$ = 6.0 Hz, 3H), 1.03 (dd, $J$ = 14.2, 6.0 Hz, 1H), 0.61 (dd, $J$ = 14.2, 8.6 Hz, 1H), 0.15 (s, 3H), 0.10 (s, 3H); **$^{13}$C NMR** (175 MHz, $CDCl_3$) $\delta$ 140.2, 129.1, 128.0, 126.5, 60.6, 59.8, 43.2, 23.3, 20.9, -1.9, -2.2; **HRMS** (ESI+) calcd for $C_{13}H_{22}NSi^+$ [M+H$^+$] 220.1516, found 220.1512.




**1-cyclohexyl-5-ethyl-3,3-dimethyl-1,3-azasilolidine (3u)**

Following the general procedure C, (silylmethyl)amine **2u** (22.7 mg, 0.100 mmol) was allowed to react with [Ir(cod)OMe]$_2$/2,4,7-trimethylphenanthroline in THF (0.5 mL) at 100 °C for 12 h. Concentration of the reaction mixture and purification by silica gel chromatography (hexanes with 1% $NEt_3$ : EtOAc 100:0→90:10) gave 18.5 mg (82%) of **3u** as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ 2.78–2.59 (m, 2H), 2.06 (d, $J$ = 12.8 Hz, 1H), 1.80 (d, $J$ = 12.8 Hz, 1H), 1.81–1.70 (m, 3H), 1.69–1.58 (m, 2H), 1.44–1.33 (m, 1H), 1.32–1.23 (m, 2H), 1.23–1.17 (m, 2H), 1.15–1.01 (m, 2H), 0.93 (dd, $J$ = 14.2, 5.8 Hz, 1H), 0.87 (t, $J$ = 7.4 Hz, 3H), 0.52 (dd, $J$ = 14.2, 8.8 Hz, 1H), 0.17 (s, 3H), 0.11 (s, 3H); **$^{13}$C NMR** (175 MHz, $CDCl_3$) $\delta$ 61.5, 57.8, 35.9, 33.1, 26.6, 26.5, 25.7, 25.4, 23.1, 18.9, 10.9, -1.9, -2.1; **HRMS** (ESI+) calcd for $C_{13}H_{28}NSi^+$ [M+H$^+$] 226.1986, found 226.1995.

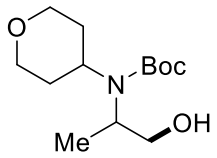
## *Oxidation of the silylation products*




**tert-butyl cyclohexyl(1-hydroxypentan-2-yl)carbamate (5d)**

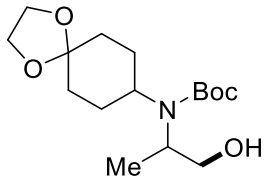
**Procedure D**: In an $N_2$-filled glovebox, a solution of *t*-BuOOH (0.20 mL, 5-6 M in dodecane) was added to a suspension of cesium hydroxide monohydrate (0.17 g, 1.0 mmol) in THF (1.0 mL). The resulting mixture was stirred for 5 min, followed by addition of a solution of silapyrrolidine **3d** (24.0 mg, 0.0996

mmol, 0.10 M in THF) and TBAF (1.0 mL, 1.0 M in THF). The reaction was stirred at room temperature overnight and quenched with aqueous $Na_2S_2O_3$ (1.0 M, 3.0 mL). The reaction mixture was diluted with water (5.0 mL) and aqueous NaOH (1.0 mL, 2.0 M) and extracted with DCM (20 mL*3). The combined organic layers were washed with brine, dried over $Na_2SO_4$, filtered, and concentrated. The residue was used in the next step without further purification. The yield of **4** was determined by $^1$H NMR spectroscopy with $CH_2Br_2$ as the internal standard. The residue was dissolved in DCM (5 mL), followed by addition of $Boc_2O$ (44mg, 0.20 mmol), TEA (30 mg, 0.30 mmol), and DMAP (5-10 mg). The resulting reaction mixture was stirred at room temperature overnight and diluted with DCM (10 mL). The mixture was exacted with DCM (20 mL*3), and the combined organic layers were washed with water (5 mL) and brine (5 mL), dried over $Na_2SO_4$, filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane : EA, 90:10 to 70:30) to give compound **5d** (19.2 mg) as a colorless oil in 68% yield over two steps. **$^1$H NMR** (700 MHz, $CDCl_3$) $\delta$ 4.02 (dd, $J$ = 10.8, 5.4 Hz, 1H), 3.99 (dd, $J$ = 10.8, 5.4 Hz, 1H), 2.93–2.86 (m, 1H), 2.55–2.55 (m, 1H), 1.94–1.83 (m, 2H), 1.76–1.70 (m, 2H), 1.69–1.59 (m, 1H), 1.51 (s, 9H), 1.50–1.35 (m, 5H), 1.30–1.23 (m, 1H), 1.06–1.00 (m, 1H), 0.95 (t, $J$ = 7.0 Hz, 3H); **$^{13}$C NMR** (175 MHz, $CDCl_3$) $\delta$ 153.7, 81.9, 69.4, 54.2, 52.9, 34.8, 34.3, 34.1, 27.8, 26.1, 25.2, 19.2, 14.2; **HRMS** (ESI+) calcd for $C_{16}H_{32}NO_3^+$ [M+H$^+$] 286.2377, found 286.2371.



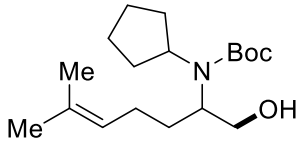

**tert-butyl (1-hydroxypropan-2-yl)(tetrahydro-2H-pyran-4-yl)carbamate (5f)**

Following the general procedure D, silapyrrolidine **3f** (38.0 mg, 0.178 mmol) was used in the oxidation process. The crude product was purified by column chromatography on silica gel (hexane : EA, 90:10 to 50:50) to give **5f** (34.0 mg) as a colorless oil in 77% yield over two steps. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ 4.17–3.75 (m, 4H), 3.50–3.35 (m, 2H), 3.20–3.10 (m, 1H), 2.84–2.76 (m, 1H), 1.88–1.80 (m, 2H), 1.52 (s, 9H), 1.45–1.33 (m, 2H), 1.12 (d, $J$ = 6.4 Hz, 3H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) $\delta$ 153.6, 82.2, 70.9, 67.0, 66.9, 50.9, 47.9, 34.5, 34.0, 27.8, 18.1; **HRMS** (ESI+) calcd for $C_{13}H_{26}NO_4^+$ [M+H$^+$] 260.1856, found 260.1862.



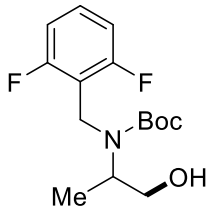

**tert-butyl (1-hydroxypropan-2-yl)(1,4-dioxaspiro[4.5]decan-8-yl)carbamate (5h)**

Following the general procedure D, silapyrrolidine **3h** (36.0 mg, 0.134 mmol) was used in the oxidation process. The crude product was purified by column chromatography on silica gel (hexane : EA, 90:10 to 30:70) to give **5h** (24.0 mg) as a colorless oil in 51% yield over two steps. **$^1$H NMR** (600 MHz, $CDCl_3$) $\delta$ 3.93 (d, $J$ = 6.0 Hz, 2H), 3.93 (s, 4H), 3.10–3.04 (m, 1H), 2.68–2.60 (m, 1H), 1.92–1.83 (m, 2H), 1.80–1.70 (m, 2H), 1.57 (dd, $J$ = 13.2, 4.0 Hz, 1H), 1.53 (dd, $J$ = 13.4, 4.0 Hz, 1H), 1.48 (s, 9H), 1.43–1.31 (m, 2H), 1.07 (d, $J$ = 6.6 Hz, 3H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) $\delta$ 153.6, 108.6, 82.0, 71.0, 64.3, 64.2, 52.0, 48.5, 33.2, 33.0, 31.0, 30.3, 27.8, 18.0; **HRMS** (ESI+) calcd for $C_{16}H_{30}NO_5^+$ [M+H$^+$] 316.2118, found 316.2114.



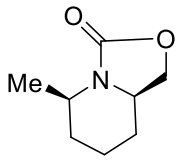

**tert-butyl cyclopentyl(1-hydroxy-6-methylhept-5-en-2-yl)carbamate (5j)**

Following the general procedure D, silapyrrolidine **3j** (34.0 mg, 0.128 mmol) was used in the oxidation process. The crude product was purified by column chromatography on silica gel (hexane : EA, 90:10 to 50:50) to give **5j** (25.1 mg) as a colorless oil in 63% yield over two steps. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ 5.22–5.01 (m, 1H), 4.20–3.97 (m, 2H), 3.24–3.17 (m, 1H), 2.88–2.78 (m, 1H), 2.14–2.06 (m, 2H), 1.95–1.79 (m, 2H), 1.71 (s, 3H), 1.78–1.65 (m, 2H), 1.63 (s, 3H), 1.60–1.36 (m, 6H), 1.51 (s, 9H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) $\delta$ 153.7, 131.9, 124.1, 81.9, 69.0, 57.2, 54.6, 33.8, 33.5, 32.2, 27.8, 25.7, 24.5, 23.8, 23.8, 17.8; **HRMS** (ESI+) calcd for $C_{18}H_{34}NO_3^+$ [M+H$^+$] 312.2533, found 312.2540.




**tert-butyl (2,6-difluorobenzyl)(1-hydroxypropan-2-yl)carbamate (5m)**

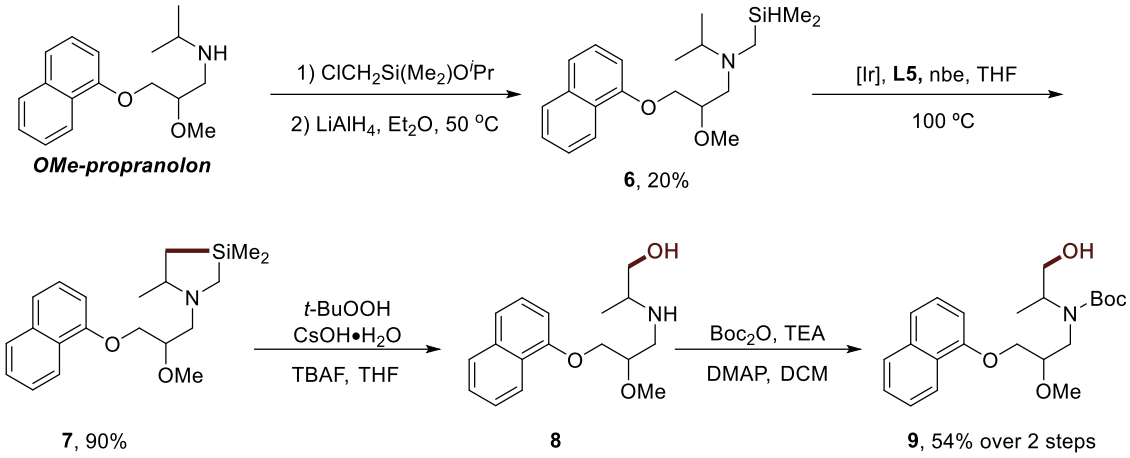
Following the general procedure D, silapyrrolidine **3m** (40.0 mg, 0.157 mmol) was used in the oxidation process. The crude product was purified by column chromatography on silica gel (hexane : EA, 90:10 to 50:50) to give **5m** (26.3mg) as a colorless oil in 59% yield over two steps. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ 7.25–7.18 (m, 1H), 6.87 (d, $J$ = 7.6 Hz, 1H), 4.02 (dd, $J$ = 10.8, 4.8 Hz, 1H), 3.98–3.86 (m, 3H), 1.71 (brs, 1H), 1.47 (s, 9H), 1.11 (d, $J$ = 6.4 Hz, 3H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) $\delta$ 161.7 (dd, $J$ = 247.6, 8.8 Hz), 153.5, 128.9 (t, $J$ = 10.4 Hz), 115.8 (t, $J$ = 20.2 Hz), 111.3 (m), 82.1, 70.4, 50.8, 38.1 (t, $J$ = 3.1 Hz), 27.8, 17.1; **HRMS** (ESI+) calcd for $C_{15}H_{22}NF_2O_3^+$ [M+H$^+$] 302.1562, found 302.1568.




**5-methylhexahydro-3H-oxazolo[3,4-a]pyridin-3-one (5r)**

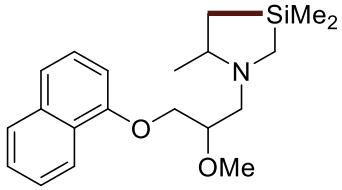
Following the general procedure D, silapyrrolidine **3r** (19.0 mg, 0.104 mmol) was used in the oxidation process. The crude product was purified by column chromatography on silica gel (hexane : EA, 90:10 to 70:30) to give **5r** (10.1 mg) as a colorless oil in 65% yield over two steps. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ 4.42–4.25 (m, 1H), 4.05–3.75 (m, 1H), 3.62–3.50 (m, 1H), 3.26–3.17 (m, 1H), 1.99–1.78 (m, H), 1.77–1.69 (m, 1H), 1.63 (dd, $J$ = 6.5, 1.4 Hz, 4H), 1.50–1.42 (m, 1H), 1.40–1.29 (m, 2H); **$^{13}$C NMR** (175 MHz, $CDCl_3$) $\delta$ 157.0, 67.4, 57.3, 52.0, 34.2, 29.7, 23.3, 18.9; **HRMS** (ESI+) calcd for $C_8H_{14}NO_2^+$ [M+H$^+$] 156.1019, found 156.1015.

## *Modification of Propranolon through C-H silylation and oxidation*




**N-((dimethylsilyl)methyl)-N-isopropyl-2-methoxy-3-(naphthalen-1-yloxy)propan-1-amine (6)**

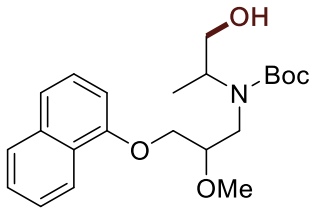
Following the general procedure B, OMe-propranolon[5] (2.2 g, 8.2 mmol) was allowed to react with (chloromethyl)-isopropoxyl-dimethylsilane (0.68 g, 4.1 mmol). The crude reaction mixture was purified by kugelrohr distillation to give (silylmethyl)amine **6** (0.26 g, 20%) as a colorless oil. **$^1$H NMR** (500 MHz, $C_6D_6$) $\delta$ 8.63 (d, $J$ = 8.4 Hz, 1H), 7.66 (d, $J$ = 8.2 Hz, 1H), 7.39–7.32 (m, 2H), 7.29 (ddd, $J$ = 8.2, 6.8, 1.4 Hz, 1H), 7.25 (t, $J$ = 8.0 Hz, 1H), 6.75 (d, $J$ = 7.6 Hz, 1H), 4.26 (dd, $J$ = 9.8, 3.6 Hz, 1H), 4.22–4.09 (m, 2H), 3.70–3.60 (m, 1H), 3.39 (s, 3H), 2.92 (hept, $J$ = 6.4 Hz, 1H), 2.74 (dd, $J$ = 13.4, 7.2 Hz, 1H), 2.58 (dd, $J$ = 13.4, 5.4 Hz, 1H), 2.11–1.97 (m, 2H), 0.87 (d, $J$ = 6.6 Hz, 3H), 0.85 (d, $J$ = 6.6 Hz, 3H), 0.06 (d, $J$ = 3.6 Hz, 3H), 0.05 (d, $J$ = 3.6 Hz, 3H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) $\delta$ 155.1, 135.0, 127.6, 126.4, 126.2, 126.0, 125.2, 122.4, 120.4, 104.7, 79.3, 69.0, 57.9, 53.1, 52.4, 40.5, 18.2, 15.9, -5.2, -5.3; **HRMS** (EI+) calcd for $C_{20}H_{31}NO_2Si$ [M] 345.2124, found 345.2127.




**1-(2-methoxy-3-(naphthalen-1-yloxy)propyl)-3,3,5-trimethyl-1,3-azasilolidine (7)**

Following the general procedure C, (silylmethyl)amine **6** (34.5 mg, 0.100 mmol) was allowed to react with $[Ir(cod)OMe]_2$ (1.3 mg) and 2,4,7-trimethylphenanthroline (1.0 mg) in THF (0.5 mL) at 100 °C for 12 h. Concentration of the reaction mixture, and the crude product was pyrified by column chromatography on silica gel (hexanes with 1% $NEt_3$ : EtOAc 100:0→80:20) to give **7** (30.5 mg, 90%, d.r. = 1:1) as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ 8.34 (t, $J$ = 7.6 Hz, 2H), 7.83 (d, $J$ = 7.6 Hz, 2H), 7.63–7.43 (m, 6H), 7.41 (t, $J$ = 8.0 Hz, 2H), 6.89 (t, $J$ = 6.8 Hz, 2H), 4.43 (dd, $J$ = 10.2, 2.8 Hz, 1H), 4.32 (dd, $J$ = 10.0, 4.0 Hz, 1H), 4.23 (dd, $J$ = 10.0, 5.6 Hz, 1H), 4.19 (dd, $J$ = 10.2, 6.2 Hz, 1H), 3.98–3.85 (m, 2H), 3.63 (s, 6H), 3.11 (dd, $J$ = 12.2, 8.2 Hz, 1H), 3.08 (dd, $J$ = 12.8, 6.6 Hz, 1H),2.76 (h, $J$ = 6.4 Hz, 1H), 2.67–2.52 (m, 2H), 2.49–2.42 (m, 1H), 2.46 (d, $J$ = 12.8 Hz, 1H), 2.36 (d, $J$ = 12.8 Hz, 1H), 1.80 (d, $J$ = 12.8 Hz, 1H), 1.65 (d, $J$ = 12.8 Hz, 1H), 1.14 (d, $J$ = 5.6 Hz, 3H), 1.13 (d, $J$ = 5.6 Hz, 3H), 1.08–0.98 (m, 2H), 0.64 (dd, $J$ = 14.2, 7.2 Hz, 1H), 0.55 (dd, $J$ = 14.2, 8.8 Hz, 1H), 0.24 (s, 3H), 0.21 (s,

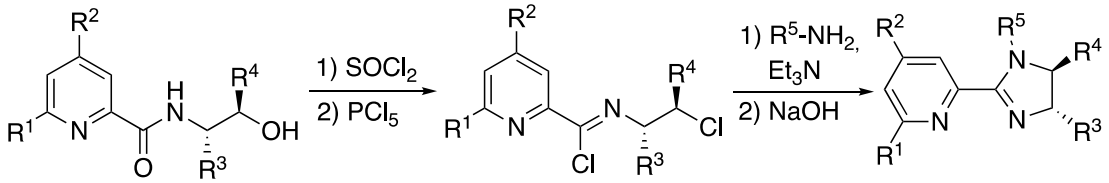
3H), 0.18 (s, 6H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) $\delta$ 154.8, 154.7, 134.5 (2C), 127.5, 127.4, 126.4, 126.3, 125.9 (2C), 125.8, 125.7, 125.2, 125.1, 122.2, 122.1, 120.3, 120.2, 104.8, 104.7, 78.6 (2C), 69.8, 69.6, 61.0, 60.4, 58.4, 58.3, 57.9, 57.1, 44.6, 43.4, 23.2, 23.0, 21.3, 19.7, -1.7, -1.8, -2.1, -2.3; **HRMS** (ESI+) calcd for $C_{20}H_{30}NO_2Si^+$ [M+H$^+$] 344.2040, found 344.2044.




**tert-butyl (1-hydroxypropan-2-yl)(2-methoxy-3-(naphthalen-1-yloxy)propyl)carbamate (9)**

Following the general procedure D, silapyrrolidine **7** (20.0 mg, 0.0583 mmol) was allowed to react in the oxidation process. The crude product was purified by column chromatography on silica gel (hexane : EA, 90:10 to 50:50) to give **9** (12.2 mg, 54% over two steps, d.r. = 1:1) as a colorless oil. **$^1$H NMR** (600 MHz, $CDCl_3$) $\delta$ 8.25 (d, $J$ = 7.6, 2H), 7.80 (d, $J$ = 8.2, 1.4 Hz, 2H), 7.53–7.43 (m, 4H), 7.43 (d, $J$ = 8.2 Hz, 2H), 7.37 (t, $J$ = 8.0 Hz, 2H), 6.83 (d, $J$ = 7.6 Hz, 2H), 4.25–4.25 (m, 4H), 4.08–3.95 (m, 4H), 3.90–3.81 (m, 2H), 3.58 (s, 6H), 3.03 (dd, $J$ = 12.2, 4.4 Hz, 1H), 306–2.96 (m, 3H), 2.94 (dd, $J$ = 12.2, 7.2 Hz, 1H), 2.88 (dd, $J$ = 12.0, 7.2 Hz, 1H), 1.48 (s, 9H), 1.47 (s, 9H), 1.13 (d, $J$ = 3.2 Hz, 3H), 1.12 (d, $J$ = 3.2 Hz, 3H); **$^{13}$C NMR** (175 MHz, $CDCl_3$) $\delta$ 154.5, 153.6, 134.5 (2C), 127.5 (2C), 126.4 (2C), 125.8 (2C), 125.6 (2C), 125.2 (2C), 122.0 (2C), 120.5 (2C), 104.7 (2C), 82.1, 82.0, 79.4, 79.2, 70.6 (2C), 68.72, 68.70, 58.3 (2C), 52.1, 52.0, 48.4, 48.2, 27.8 (2C), 17.5, 17.4; **HRMS** (ESI+) calcd for $C_{22}H_{32}NO_5^+$ [M+H$^+$] 390.2275, found 390.2272.

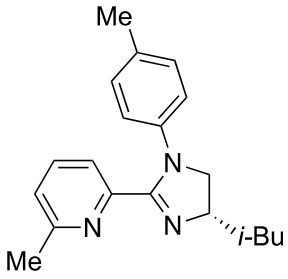
## *Synthesis of 2-pyridyl imidazoline ligands*




**Sn** **Ln**

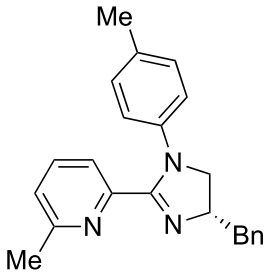
**General procedure E**: The procedure we employed was slightly modified from the conditions developed by Casey.[4] To a solution of *N*-(pyridinoyl)-amino alcohol (1 equiv) in chloroform (1 M solution), thionyl chloride (1.1 equiv) was added dropwise at room temperature, and the resulting mixture was stirred at reflux for 2 h. After completion of the reaction, phosphorus pentachloride (1 equiv) was added at room temperature, and the resulting suspension was refluxed until the reaction was complete, as determined by $^1$H NMR spectroscopy (If the reaction was not complete in 2 h, an additional amount of $PCl_5$ was added to the reaction mixture.). Upon completion of this step, the solvent was evaporated, and $POCl_3$ was removed under high vacuum. The resulting residue was dissolved in chloroform again. The solution was cooled to 0 °C, and a solution of *p*-toluidine (1.2 equiv) and triethylamine (3 equiv) in chloroform was added dropwise. The solution was stirred at 0 °C for 30 min and then refluxed for 12 h. After removal of the volatile materials, aqueous NaOH (20%, 10 mL) was added to the residue. The mixture was

extracted with dichloromethane, and the combined organic layers were washed with brine, dried over $Na_2SO_4$, filtered, and concentrated. The residue was purified by column chromatography on silica gel. (Synthesis of **L9** and **L14** was previously reported.[4])



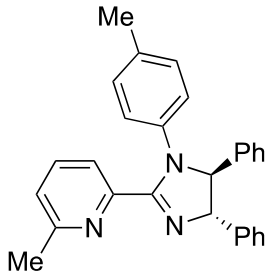

**(*S*)-2-(4-isobutyl-1-(p-tolyl)-4,5-dihydro-1H-imidazol-2-yl)-6-methylpyridine (L10)**

Following the general procedure E, amide **S10** (473 mg, 2.00 mmol) was converted into **L10**. The crude product was purified by column chromatography on silica gel (first run with DCM : MeOH 100:0→80:20, then second run with hexanes : EtOAc 50:50→0:100) to give **L10** (151 mg, 25%) as a tan solid. **$^1$H NMR** (500 MHz, $CDCl_3$) 7.51 (t, *J* = 7.7 Hz, 1H), 7.31 (d, *J* = 7.7 Hz, 1H), 7.10 (d, *J* = 7.8 Hz, 1H), 6.93 (d, *J* = 8.1 Hz, 2H), 6.63 (d, *J* = 8.4 Hz, 2H), 4.33 (dtd, *J* = 9.8, 8.4, 5.8 Hz, 1H), 4.09 (dd, *J* = 10.2, 9.0 Hz, 1H), 3.64 (t, *J* = 9.0 Hz, 1H), 2.47 (s, 3H), 2.24 (s, 3H), 1.90–1.79 (m, 2H), 1.50–1.41 (m, 1H), 0.98 (d, *J* = 6.4 Hz, 3H), 0.96 (d, *J* = 6.3 Hz, 3H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) *δ* 160.7, 158.5, 150.3, 140.8, 136.6, 132.7, 129.2, 123.9, 122.1, 121.3, 63.5, 59.9, 46.4, 25.5, 24.6, 23.2, 22.8, 20.9; **HRMS** (ESI+) calcd for $C_{20}H_{26}N_3^+$ [M+H$^+$] 308.2121, found 308.2121; $[\alpha]_D^{25}$ = –127 (c 0.858, $CHCl_3$).



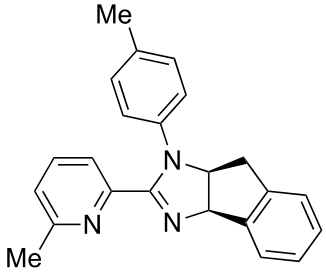

**(*S*)-2-(4-benzyl-1-(p-tolyl)-4,5-dihydro-1H-imidazol-2-yl)-6-methylpyridine (L11)**

Following the general procedure E, amide **S11** (624 mg, 2.31 mmol) was converted into **L11**. The crude product was purified by column chromatography on silica gel (first run with DCM : MeOH 100:0→80:20, then second run with hexanes : EtOAc 50:50→0:100) to give **L11** (125 mg, 18%) as a viscous oil. **$^1$H NMR** (500 MHz, $CDCl_3$) *δ* 7.52 (t, *J* = 7.7 Hz, 1H), 7.33–7.26 (m, 5H), 7.24–7.19 (m, 1H), 7.11 (d, *J* = 7.7 Hz, 1H), 6.89 (d, *J* = 8.2 Hz, 2H), 6.55 (d, *J* = 8.4 Hz, 2H), 4.60 (tdd, *J* = 9.8, 8.0, 4.5 Hz, 1H), 3.94 (t, *J* = 9.8 Hz, 1H), 3.75 (dd, *J* = 9.5, 8.0 Hz, 1H), 3.36 (dd, *J* = 13.7, 4.5 Hz, 1H), 2.84 (dd, *J* = 13.7, 9.4 Hz, 1H), 2.47 (s, 3H), 2.22 (s, 3H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) *δ* 161.3, 158.5, 149.9, 140.4, 138.6, 136.6, 133.1, 129.5, 129.2, 128.5, 126.4, 124.1, 122.4, 121.3, 66.0, 58.5, 42.4, 24.6, 20.9; **HRMS** (ESI+) calcd for $C_{23}H_{24}N_3^+$ [M+H$^+$] 342.1965, found 342.1969; $[\alpha]_D^{25}$ = –11 (c 0.18, $CHCl_3$).



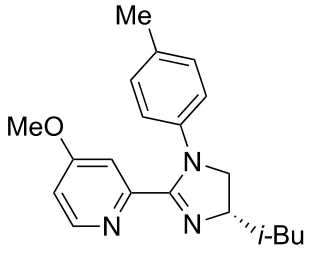

**2-((4*S*,5*S*)-4,5-diphenyl-1-(p-tolyl)-4,5-dihydro-1H-imidazol-2-yl)-6-methylpyridine (L12)**

Following the general procedure E, amide **S12** (447 mg, 1.34 mmol) was converted into **L12**. The crude product was purified by column chromatography on silica gel (first run with DCM : MeOH 100:0→80:20, then second run with hexanes : EtOAc 50:50→0:100) to give **L12 (**37.2 mg, 7%) as a viscous oil. **$^{1}$H NMR** (600 MHz, $CDCl_3$) $\delta$ 7.55 (d, $J$ = 4.6 Hz, 2H), 7.43–7.27 (m, 10H), 7.14–7.11 (m, 1H), 6.84 (d, $J$ = 8.0 Hz, 2H), 6.65 (d, $J$ = 8.0 Hz, 2H), 5.17 (d, $J$ = 7.8 Hz, 1H), 4.88 (d, $J$ = 7.8 Hz, 1H), 2.47 (s, 3H), 2.18 (s, 3H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) $\delta$ 162.5, 158.5, 149.7, 143.3, 142.6, 140.2, 136.4, 134.2, 129.2, 129.0, 128.7, 127.8, 127.4, 127.2, 127.0, 124.2, 124.1, 121.7, 78.8, 78.4, 24.6, 20.9; **HRMS** (ESI+) calcd for $C_{28}H_{26}N_3^+$ [M+H$^+$] 404.2121, found 404.2115; $[\alpha]_D^{25}$ = +110 (c 0.33, $CHCl_3$).



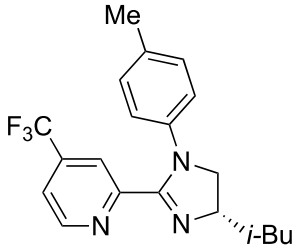

**(3a*R*,8a*S*)-2-(6-methylpyridin-2-yl)-1-(p-tolyl)-1,3a,8,8a-tetrahydroindeno[1,2-d]imidazole (L13)**

Following the general procedure E, amide **S13** (509 mg, 1.90 mmol) was converted into **L13**. The crude product was purified by column chromatography on silica gel (first run with DCM : MeOH 100:0→80:20, then second run with hexanes : EtOAc 50:50→0:100) to give **L13** (120 mg, 19%) as a tan soild. **$^{1}$H NMR** (600 MHz, $CDCl_3$) $\delta$ 7.66 (d, $J$ = 6.9 Hz, 1H), 7.44 (t, $J$ = 7.7 Hz, 1H), 7.30–7.21 (m, 4H), 7.04 (d, $J$ = 7.7 Hz, 1H), 6.99 (d, $J$ = 7.9 Hz, 2H), 6.77 (d, $J$ = 7.8 Hz, 2H), 5.83 (d, $J$ = 9.2 Hz, 1H), 5.05–4.95 (m, 1H), 3.42 (dd, $J$ = 17.1, 7.1 Hz, 1H), 3.35 (d, $J$ = 16.9 Hz, 1H), 2.41 (s, 3H), 2.27 (s, 3H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) $\delta$ 161.2, 158.4, 149.7, 143.0, 140.5, 139.5, 136.4, 134.2, 129.5, 128.2, 127.4, 126.1, 125.1, 124.3, 124.0, 121.6, 75.8, 68.5, 40.1, 24.5, 21.0; **HRMS** (ESI+) calcd for $C_{23}H_{22}N_3^+$ [M+H$^+$] 340.1808, found 340.1808; $[\alpha]_D^{25}$ = +360 (c 0.46, $CHCl_3$).



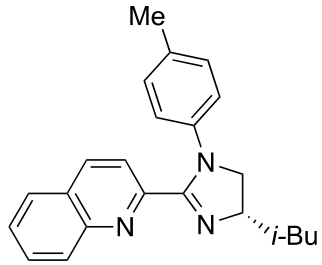

**(*S*)-2-(4-isobutyl-1-(p-tolyl)-4,5-dihydro-1H-imidazol-2-yl)-4-methoxypyridine (L15)**

Following the general procedure E, amide **S15** (73.7 mg, 0.290 mmol) was converted into **L15**. The crude product was purified by column chromatography on silica gel (DCM : MeOH 100:0→80:20) to give **L15** (26.4 mg, 28%) as a colorless oil. **$^1$H NMR** (600 MHz, $CDCl_3$) $\delta$ 8.29 (d, $J$ = 5.6 Hz, 1H), 7.21 (d, $J$ = 2.4 Hz, 1H), 6.93 (d, $J$ = 7.9 Hz, 2H), 6.76 (dd, $J$ = 5.8, 2.5 Hz, 1H), 6.63 (d, $J$ = 7.9 Hz, 2H), 4.35–4.26 (m, 1H), 4.13 (t, $J$ = 9.6 Hz, 1H), 3.83 (s, 3H), 3.62 (t, $J$ = 8.9 Hz, 1H), 2.23 (s, 3H), 1.92–1.75 (m, 2H), 1.48–1.40 (m, 1H), 0.98 (d, $J$ = 6.5 Hz, 3H), 0.96 (d, $J$ = 6.6 Hz, 3H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) $\delta$ 166.1, 160.6, 152.5, 150.5, 140.7, 132.7, 129.3, 121.9, 111.1, 109.9, 63.3, 59.9, 55.4, 46.3, 25.4, 23.1, 22.8, 20.9; **HRMS** (ESI+) calcd for $C_{20}H_{26}N_3O^+$ [M+H$^+$] 324.2070, found 324.2074; $[\alpha]_D^{25}$ = –74 (c 0.26, $CHCl_3$).




**(*S*)-2-(4-isobutyl-1-(p-tolyl)-4,5-dihydro-1H-imidazol-2-yl)-4-(trifluoromethyl)pyridine (L16)**

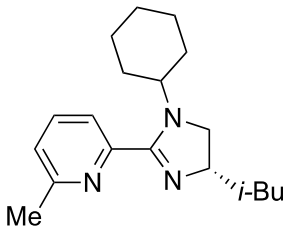
Following the general procedure E, amide **S16** (678 mg, 2.34 mmol) was converted into **L16**. The crude product was purified by column chromatography on silica gel (DCM : MeOH 100:0→80:20) to give **L16** (191 mg, 23%) as a colorless oil. **$^1$H NMR** (600 MHz, $CDCl_3$) $\delta$ 8.65 (d, $J$ = 5.0 Hz, 1H), 7.98 (s, 1H), 7.46 (d, $J$ = 5.0 Hz, 1H), 6.96 (d, $J$ = 7.9 Hz, 2H), 6.64 (d, $J$ = 7.9 Hz, 2H), 4.35 (p, $J$ = 8.5 Hz, 2H), 4.17 (t, $J$ = 9.6 Hz, 1H), 3.63 (t, $J$ = 8.9 Hz, 1H), 2.25 (s, 3H), 1.94–1.74 (m, 2H), 1.49–1.43 (m, 1H), 1.00 (d, $J$ = 6.6 Hz, 3H), 0.98 (d, $J$ = 6.6 Hz, 3H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) $\delta$ 159.7, 152.3, 150.2, 140.6, 139.0 (q, $J$ = 34.4 Hz), 133.5, 129.5, 122.7 (q, $J$ = 273 Hz), 122.5, 120.1 (q, $J$ = 3.6 Hz), 120.1 (q, $J$ = 3.6 Hz), 119.8 (q, $J$ = 3.6 Hz), 63.7, 60.4, 46.3, 25.4, 23.1, 22.8, 20.9; **HRMS** (ESI+) calcd for $C_{20}H_{23}F_3N_3^+$ [M+H$^+$] 362.1839, found 362.1837; $[\alpha]_D^{25}$ = –80 (c 0.32, $CHCl_3$).




**(*S*)-2-(4-isobutyl-1-(p-tolyl)-4,5-dihydro-1H-imidazol-2-yl)quinolone (L17)**

Following the general procedure E, amide **S17** (757 mg, 2.34 mmol) was converted into **L17**. The crude product was purified by column chromatography on silica gel (first run with DCM : MeOH 100:0→80:20, then second run with hexanes : EtOAc 100:00→50:50) to give **L17 (**279 mg, 29%) as a yellow viscous oil. **$^1$H NMR** (600 MHz, $CDCl_3$) $\delta$ 8.11 (d, $J$ = 8.4 Hz, 1H), 8.02 (d, $J$ = 8.5 Hz, 1H), 7.78 (d, $J$ = 8.1 Hz, 1H), 7.70–7.63 (m, 2H), 7.54 (t, $J$ = 7.5 Hz, 1H), 6.90 (d, $J$ = 7.9 Hz, 2H), 6.68 (d, $J$ = 7.9 Hz, 2H), 4.46–4.36 (m, 1H), 4.17 (t, $J$ = 9.6 Hz, 1H), 3.70 (t, $J$ = 9.0 Hz, 1H), 2.21 (s, 3H), 1.95–1.85 (m, 2H), 1.55–1.46 (m, 1H), 1.01 (d, $J$ = 6.1 Hz, 3H), 0.99 (d, $J$ = 6.1 Hz, 3H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) $\delta$ 160.8, 150.9, 147.7, 140.9, 136.5, 133.0, 130.3, 129.7, 129.4, 128.2, 127.6, 127.4, 122.3, 121.4,

63.8, 60.2, 46.4, 25.5, 23.2, 22.8, 20.9; **HRMS** (ESI+) calcd for $C_{23}H_{26}N_3^+$ [M+H$^+$] 344.2121, found 344.2125; $[\alpha]_D^{25}$ = –130. (c 1.13, $CHCl_3$).

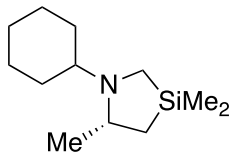



**(*S*)-2-(1-cyclohexyl-4-isobutyl-4,5-dihydro-1H-imidazol-2-yl)-6-methylpyridine (L18)**

Following the general procedure E, amide **S18** (823 mg, 6.00 mmol) was converted into **L18**. The crude product was purified by column chromatography on silica gel (DCM : MeOH 100:0→90:10) to give **L18** (290 mg, 20%) as a colorless oil. **$^1$H NMR** (500 MHz, $C_6D_6$) $\delta$ 8.03 (d, *J* = 7.8 Hz, 1H), 7.02 (t, *J* = 7.7 Hz, 1H), 6.55 (d, *J* = 7.7 Hz, 1H), 4.57 (tt, *J* = 11.7, 3.7 Hz, 1H), 4.21 (dddd, *J* = 10.3, 9.1, 7.7, 6.4 Hz, 1H), 3.44 (dd, *J* = 10.3, 8.7 Hz, 1H), 2.98 (t, *J* = 9.0 Hz, 1H), 2.33 (s, 3H), 2.17–2.06 (m, 1H), 1.92–1.81 (m, 2H), 1.81–1.74 (m, 1H), 1.69–1.58 (m, 2H), 1.53–1.45 (m, 1H), 1.41 (dt, *J* = 13.6, 7.0 Hz, 1H), 1.30 (pd, *J* = 11.7, 11.3, 3.3 Hz, 2H), 1.25–1.13 (m, 2H), 1.06 (d, *J* = 6.6 Hz, 3H), 1.01 (d, *J* = 6.7 Hz, 3H), 0.95 (qt, *J* = 12.8, 3.9 Hz, 1H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) $\delta$ 163.6, 157.7, 151.1, 136.8, 123.7, 121.3, 62.6, 54.6, 51.0, 46.6, 31.5, 30.5, 26.0, 25.8, 25.8, 25.4, 24.6, 23.2, 22.8; **HRMS** (ESI+) calcd for $C_{19}H_{30}N_3^+$ [M+H$^+$] 300.2434, found 300.2433; $[\alpha]_D^{25}$ = –73 (c 0.55, $CHCl_3$).

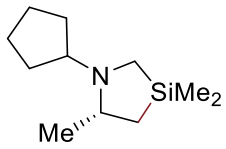
## *Enantioselective Silylation of Aliphatic Amines*

General procedure F: In an $N_2$-filled glovebox, (silylmethyl)amine **2** (1.0 equiv) was weighed into a 4 mL screw-top vial. The amine was then sequentially treated with norbornene (2 equiv) and a cold stock solution of $[Ir(cod)Cl]_2$ (2.0 mol %) and **L18** (5.0 mol %) in THF ([silane] = 0.5 M). The vial was capped with a Teflon-lined screw cap and stirred at 4 °C. After 72 hours, the solvent was removed via rotary evaporation, and the crude product was adsorbed into Celite and purified by column chromatography on silica gel.



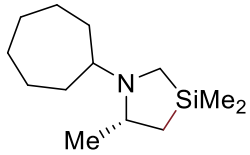

**(*S*)-1-cyclohexyl-3,3,5-trimethyl-1,3-azasilolidine (*S*-3a)**

Following the general procedure F, (silylmethyl)amine **2a** (52.9 mg, 0.248 mmol) was allowed to react with the combination of $[Ir(cod)Cl]_2$ and **L18** in THF (0.5 mL) at 4 °C for 72 h. The crude product was purified by column chromatography on silica gel (hexanes with 1% $NEt_3$ : EtOAc 100:0→90:10) to give 42.0 mg (80%) of **(*S*)-3a** as a colorless oil. **Chiral GC analysis**: 91.5 : 8.5 er, Cyclodex-B column (30 m x 0.25 mm ID x 0.25 um film), 120 °C, FID detector, $t_R$ = 14.5 min (minor), $t_R$ = 14.9 min (major); $[\alpha]_D^{25}$ = +48 (c 0.68, $CHCl_3$). $^1$H and $^{13}$C NMR data were consistent with the values reported above.



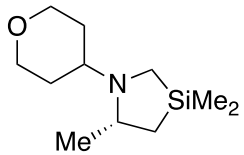

**(*S*)-1-cyclopentyl-3,3,5-trimethyl-1,3-azasilolidine (*S*-3b)**

Following the general procedure F, (silylmethyl)amine **2b** (19.9 mg, 0.100 mmol) was allowed to react with the combination of $[Ir(cod)Cl]_2$ and **L18** in THF (0.5 mL) at 4 °C for 72 h. The crude product was purified by column chromatography on silica gel (hexanes with 1% $NEt_3$ : EtOAc 100:0→90:10) to give 12.6 mg (64%) of **(*S*)-3b** as a colorless oil. **Chiral GC analysis**: 89 : 11 er, Cyclodex-B column (30 m x 0.25 mm ID x 0.25 um film), 90 °C, FID detector, $t_R$ = 90.8 min (minor), $t_R$ = 91.4 min (major); $[\alpha]_D^{25}$ = +13 (c 0.05, $CHCl_3$); $^1H$ and $^{13}C$ NMR data were consistent with the values reported above.



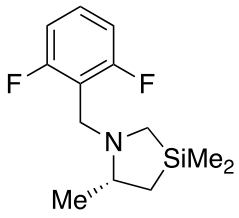

**(*S*)-1-cycloheptyl-3,3,5-trimethyl-1,3-azasilolidine (*S*-3c)**

Following the general procedure F, (silylmethyl)amine **2c** (22.7 mg, 0.100 mmol) was allowed to react with $[Ir(cod)Cl]_2$/**L18** in THF (0.5 mL) at 4 °C for 72 h. The crude product was purified by column chromatography on silica gel (hexanes with 1% $NEt_3$ : EtOAc 100:0→90:10) to give 15.5 mg (80%) of **(*S*)-3c** as a colorless oil. **Chiral GC analysis**: 89.5 : 10.5 er, Cyclodex-B column (30 m x 0.25 mm ID x 0.25 um film), 100 °C, FID detector, $t_R$ = 70.8 min (minor), $t_R$ = 71.6 min (major); $[\alpha]_D^{25}$ = +14 (c 0.05, $CHCl_3$); $^1H$ and $^{13}C$ NMR data were consistent with the values reported above.




**(*S*)-3,3,5-trimethyl-1-(tetrahydro-2H-pyran-4-yl)-1,3-azasilolidine (*S*-3f)**

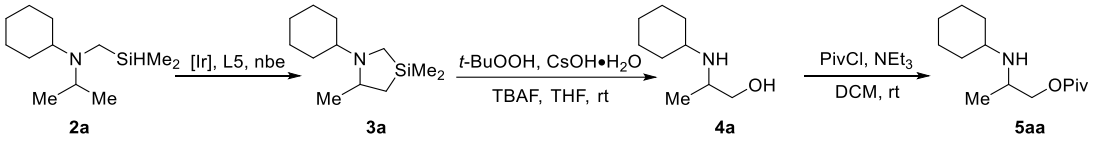
Following the general procedure F, (silylmethyl)amine **2f** (53.4 mg, 0.248 mmol) was allowed to react with the combination of $[Ir(cod)Cl]_2$ an d**L18** in THF (0.5 mL) at 4 °C for 72 h. The crude product was purified by column chromatography on silica gel (hexanes with 1% $NEt_3$ : EtOAc 100:0→90:10) to give 43.0 mg (81%) of **(*S*)-3f** as a colorless oil. **Chiral GC analysis**: 90.5 : 9.5 er, Cyclodex-B column (30 m x 0.25 mm ID x 0.25 um film), 120 °C, FID detector, $t_R$ = 25.5 min (minor), $t_R$ = 25.8 min (major); $[\alpha]_D^{25}$ = +51 (c 0.72, $CHCl_3$). $^1H$ and $^{13}C$ NMR data were consistent with the values reported above.




**(*S*)-1-(2,6-difluorobenzyl)-3,3,5-trimethyl-1,3-azasilolidine (*S*-3m)**

Following the general procedure F, (silylmethyl)amine **2m** (64.6 mg, 0.253 mmol) was allowed to react with the combination of $[Ir(cod)Cl]_2$ and **L18** in THF (0.5 mL) at 4 °C for 72 h. The crude product was purified by column chromatography on silica gel (hexanes with 1% $NEt_3$ : EtOAc 100:0→90:10) to give 39.4 mg (73%) of **(*S*)-3m** as a colorless oil. Enantiomeric ratio of 87.5 : 12.5 er was determined by $^1H$ NMR spectroscopy with (*S*)-*O*-acetylmandelic acid in $C_6D_6$. $[\alpha]_D^{25}$ = +38 (c 0.65, $CHCl_3$); $^1H$ and $^{13}C$ NMR data were consistent with the values reported above.

## *Assignment of absolute configuration*




**2a** **3a** **4a** **5aa**

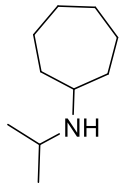
In an $N_2$-filled glovebox, (silylmethyl)amine **2a** (53.1 mg, 0.249 mml) was weighed into a 4 mL screw-top vial. The amine was then sequentially treated with norbornene (35.3 mg, 0.375 mmol) and a freshly prepared stock solution of $[Ir(cod)OMe]_2$ (2.0 mol %) and 2,4,7-trimethylphenanthroline **L5** (5.0 mol %) in THF (0.5 mL). The vial was capped with a Teflon-lined screw cap and placed in a pre-heated aluminum heating block at 100 °C. After 17 hours, the reaction mixture was allowed to cool to room temperature, and the volatile materials were removed via rotary evaporation. The crude reaction mixture was dissolved in THF (2.5 mL) and sequentially treated with $CsOH{\cdot}H_2O$ (505 mg, 3.37 mmol), *t*-BuOOH (0.70 mL, 5.0–6.0 M in decane), and TBAF (2.5 mL, 1M in THF). The vial was sealed with a Teflon-lined screw cap, and the resulting mixture was stirred overnight at room temperature. The reaction was carefully quenched with an aqueous solution of $Na_2SO_3$, and the aqueous layer was extracted with DCM. The combined organic layers were washed with brine, dried over $Na_2SO_4$, filtered through Celite, and concentrated via rotary evaporation. The crude mixture was dissolved in DCM (3.75 mL) and was treated with triethylamine (0.88 mL) and pivaloyl chloride (0.31 mL, 2.5 mmol). The vial was sealed with a Teflon-lined screw cap, and the resulting mixture was stirred overnight at room temperature. The reaction mixture was quenched with water, and the aqueous layer was extracted with DCM. The combined organic layers were washed with brine, dried with $Na_2SO_4$, filtered, and concentrated via rotary evaporation. The residue was purified by column chromatography on silica gel (DCM : MeOH 100:0→90:10) to give 29.6 mg (49%) of **5aa** as a yellow oil. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ 4.003.89 (m, 2H), 3.06 (h, $J$ = 6.2 Hz, 1H), 2.51 (tt, $J$ = 10.5, 3.8 Hz, 1H), 1.92–1.80 (m, 2H), 1.76–1.66 (m, 2H), 1.64–1.55 (m, 1H), 1.31–1.10 (m, 12H), 1.09–0.96 (m, 5H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) $\delta$ 178.5, 68.6, 53.9, 48.6, 39.0, 34.6, 34.2, 27.4, 26.3, 25.3, 25.3, 18.7; $^1H$ and $^{13}C$ NMR data were consistent with the previously reported values.[6]

Following the same procedure, the asymmetric silylation of **2a**, followed by oxidation and protection, yielded protected amino alcohol (*S*)-**5aa** for which the optical rotation $[\alpha]_D^{25}$ was +7.8 (c 0.35, $CHCl_3$). An authentic sample of (*S*)- **5aa** was prepared according to a literature protocol[6] and determined to have an $[\alpha]_D^{25}$ value of +6.6 (c 0.48, $CHCl_3$). Therefore, compounds **5aa** and **3a** were assigned to have the (*S*) absolute configuration.

## *References*


1. Uson, R.; Oro, L. A.; Cabeza, J. A.; Bryndza, H. E.; Stepro, M. P., Dinuclear Methoxy, Cyclooctadiene, and Barrelene Complexes of Rhodium(I) and Iridium(I). In *Inorg. Synth.* , Kirschner, S., Ed. John Wiley & Sons, Inc.: Hoboken, NJ, USA, , 2007; Vol. 231, pp 126-130.
2. Gebauer, K.; Fürstner, A., *Angew. Chem. Int. Ed.* **2014,** *53*, 6393-6396.
3. Diaba, F.; Montiel, J. A.; Serban, G.; Bonjoch, J., *Org. Lett.* **2015,** *17*, 3860-3863.
4. Boland, N. A.; Casey, M.; Hynes, S. J.; Matthews, J. W.; Smyth, M. P., *J. Org. Chem.* **2002,** *67*, 3919-3922.
5. Upthagrove, A. L.; Nelson, W. L., *Drug Metabolism and Disposition* **2001,** *29*, 1377-1388.
6. Willcox, D.; Chappell, B. G. N.; Hogg, K. F.; Calleja, J.; Smalley, A. P.; Gaunt, M. J., *Science* **2016,** *354*, 851-857.

## *NMR Spectra*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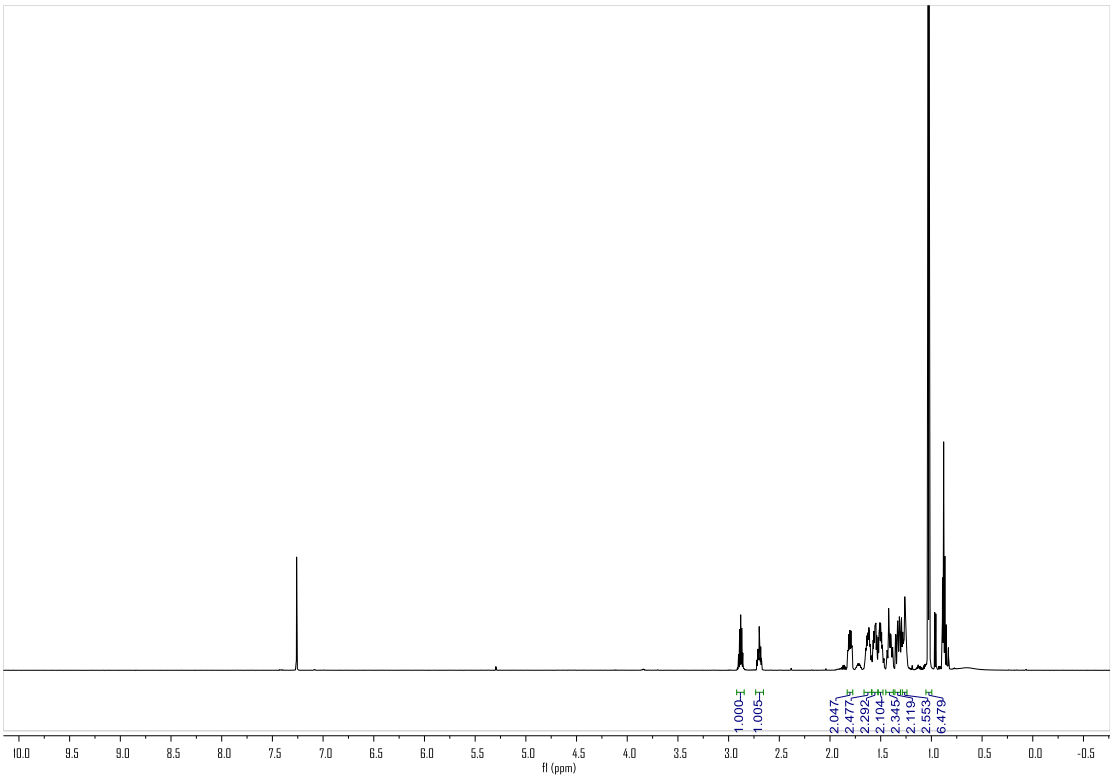
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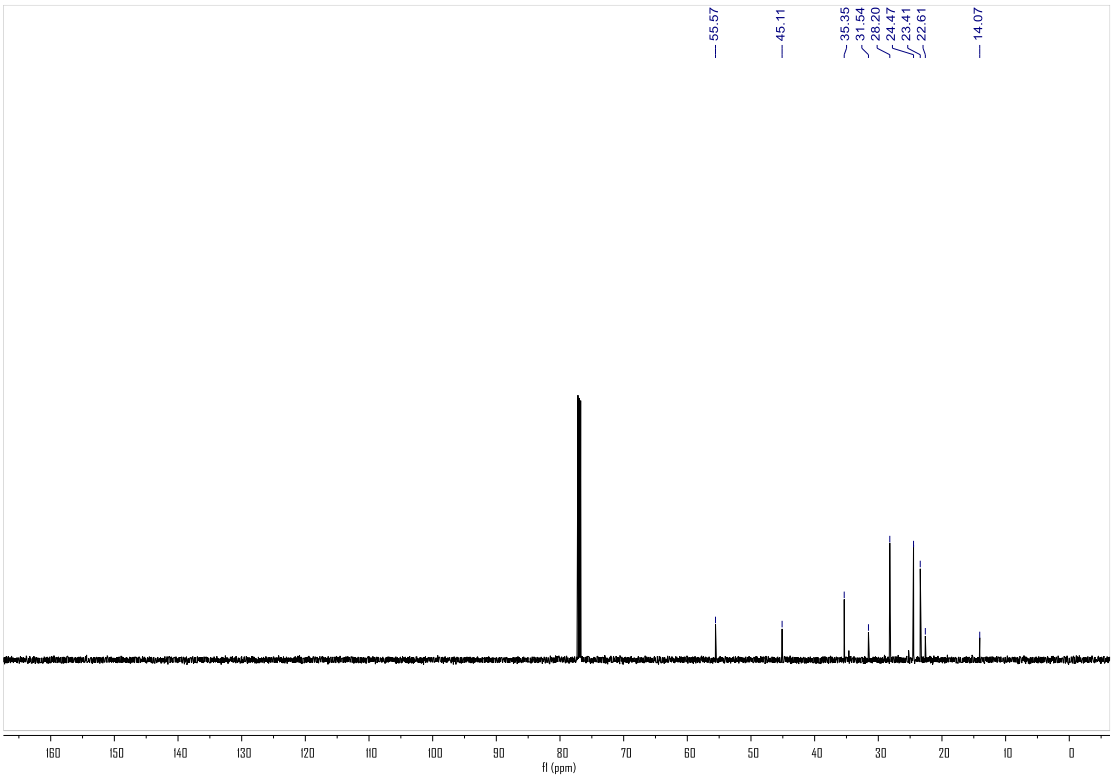
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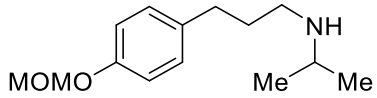
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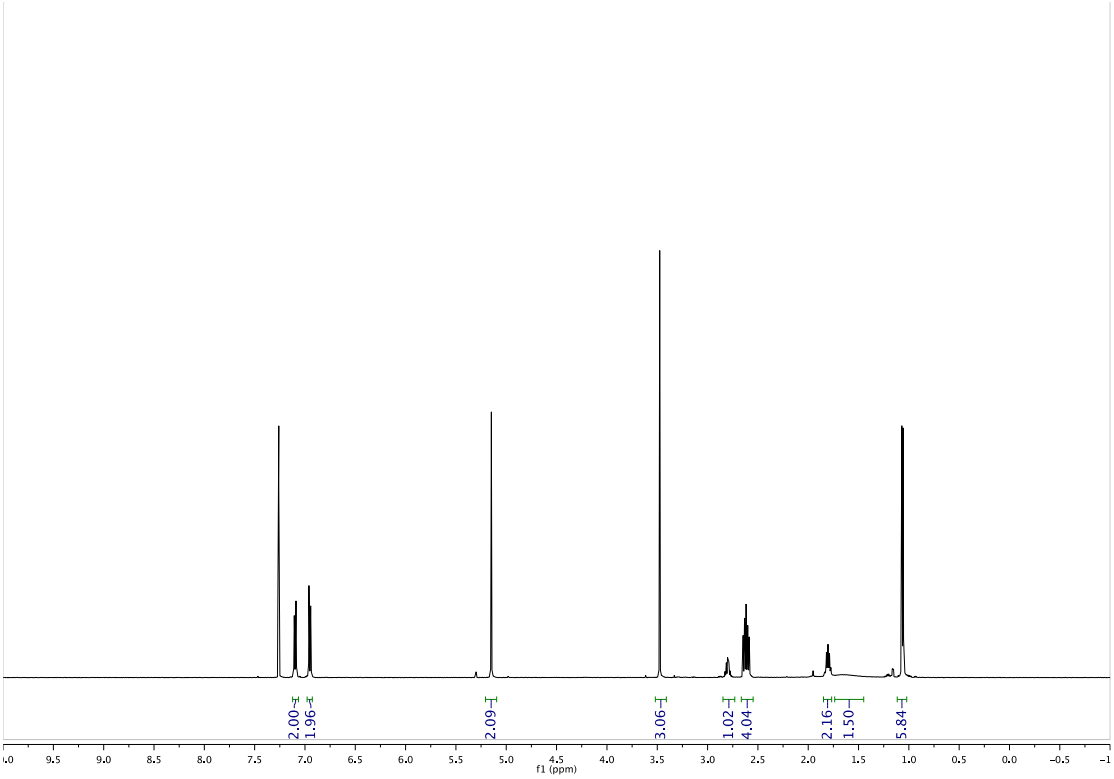
Me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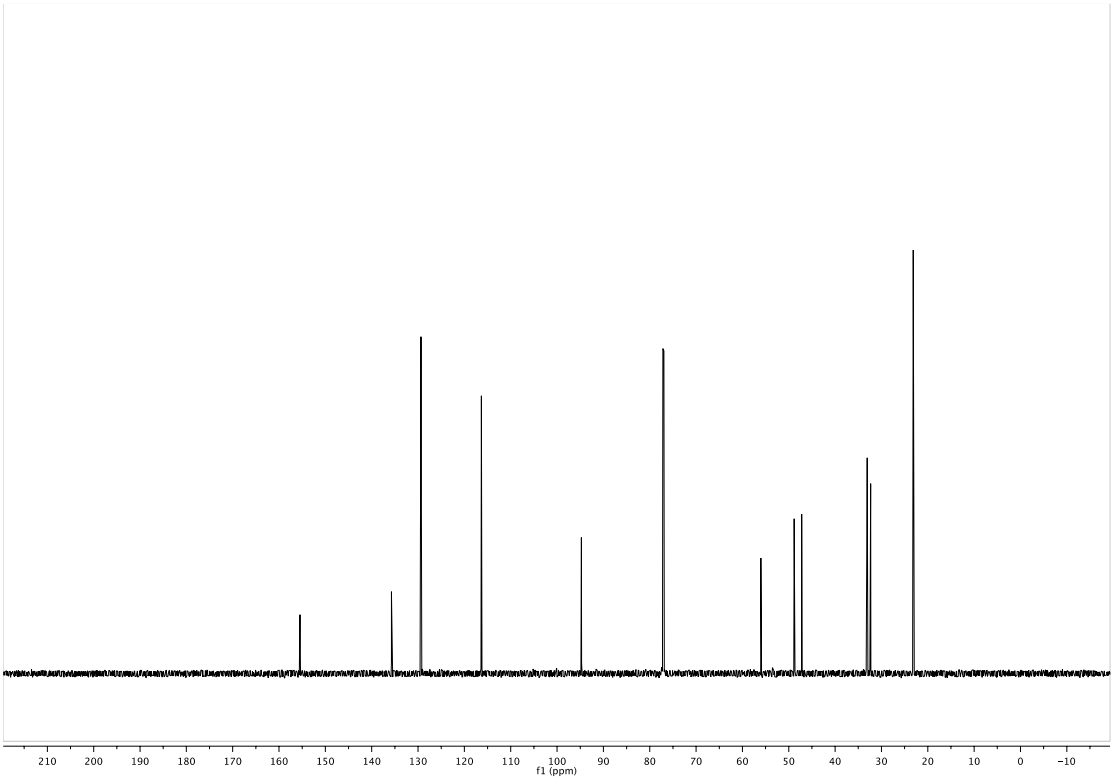
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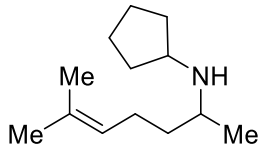
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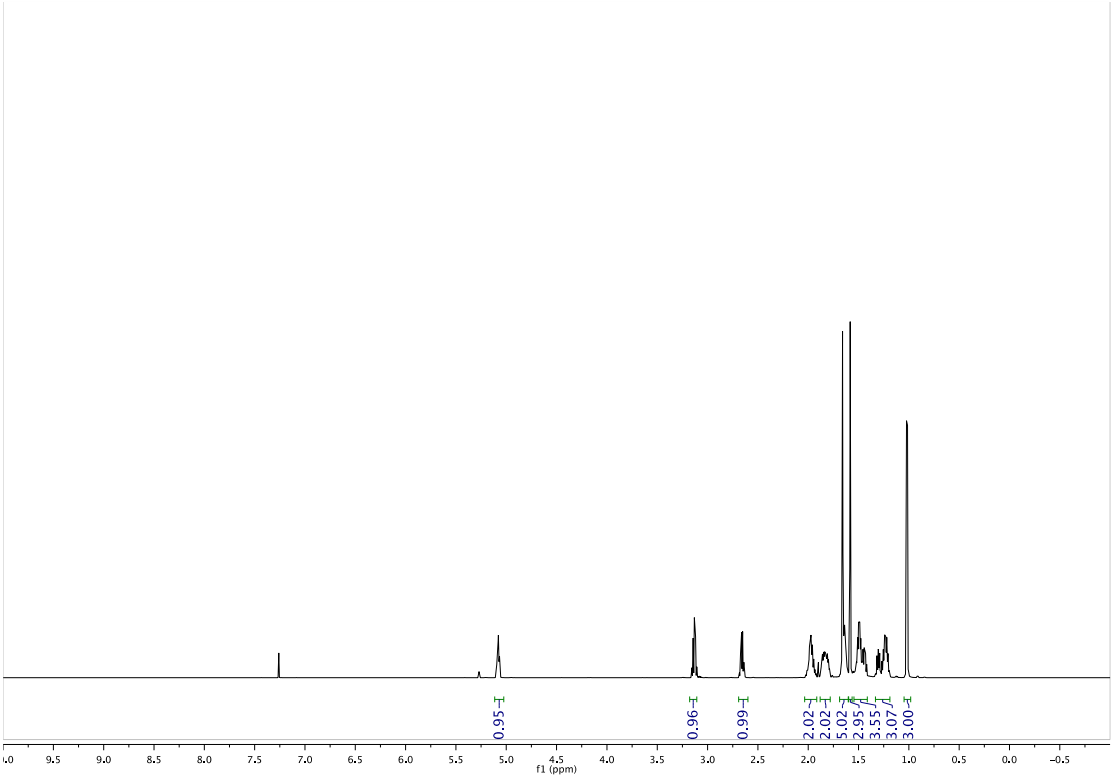
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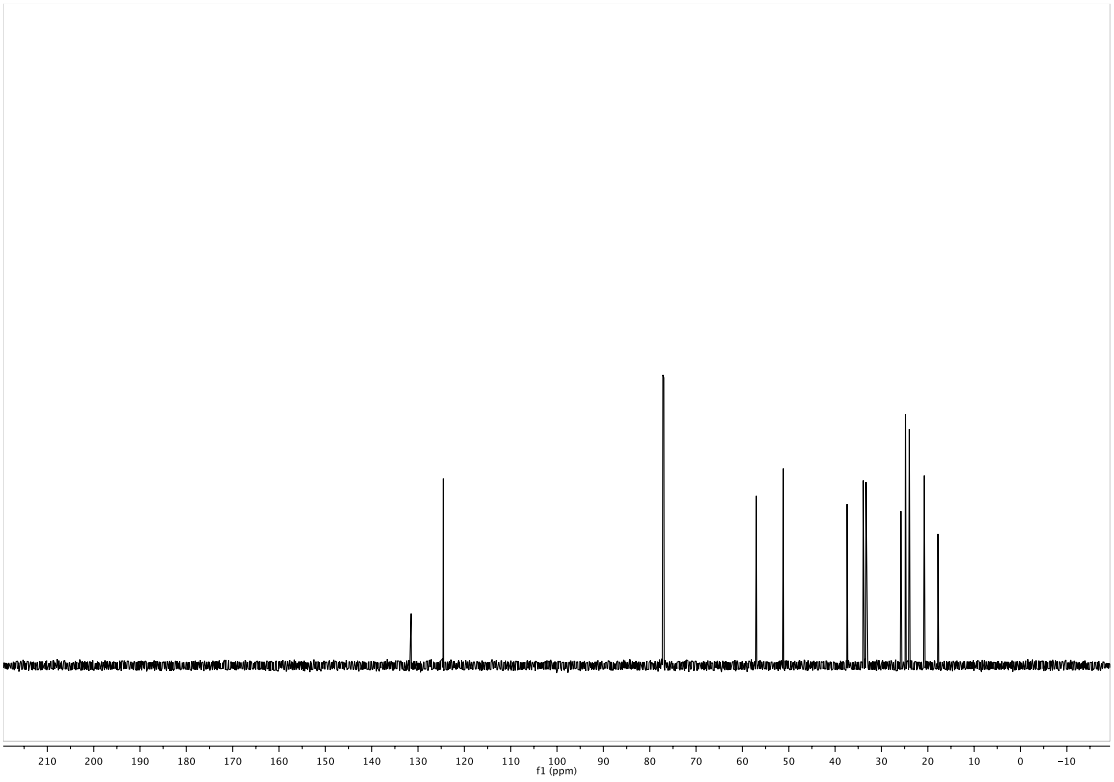
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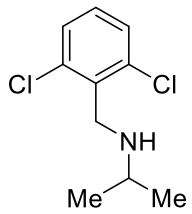
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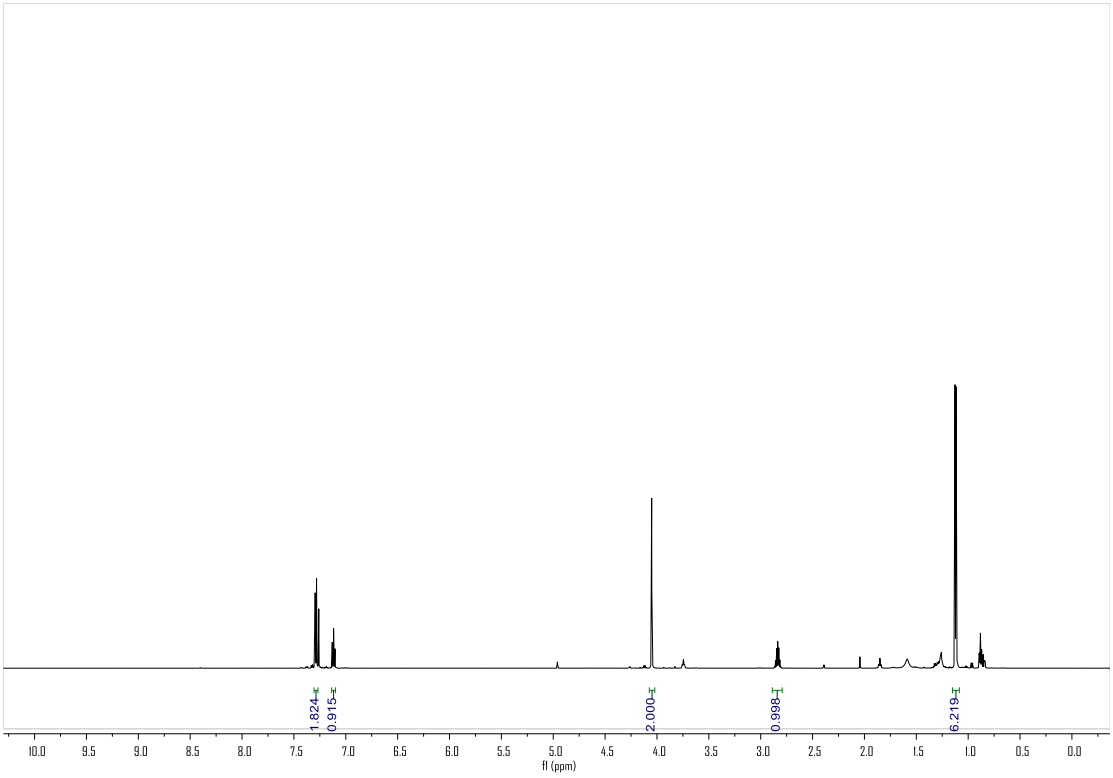
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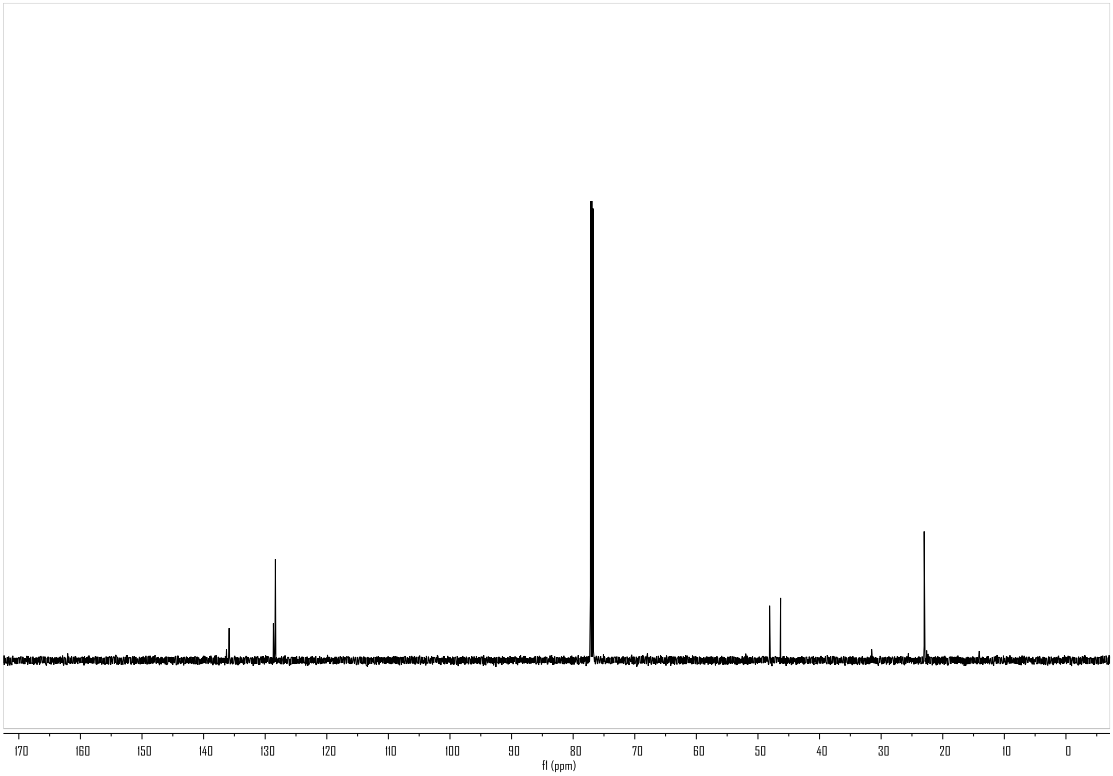
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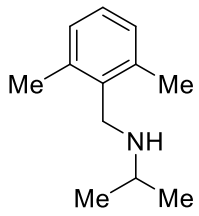
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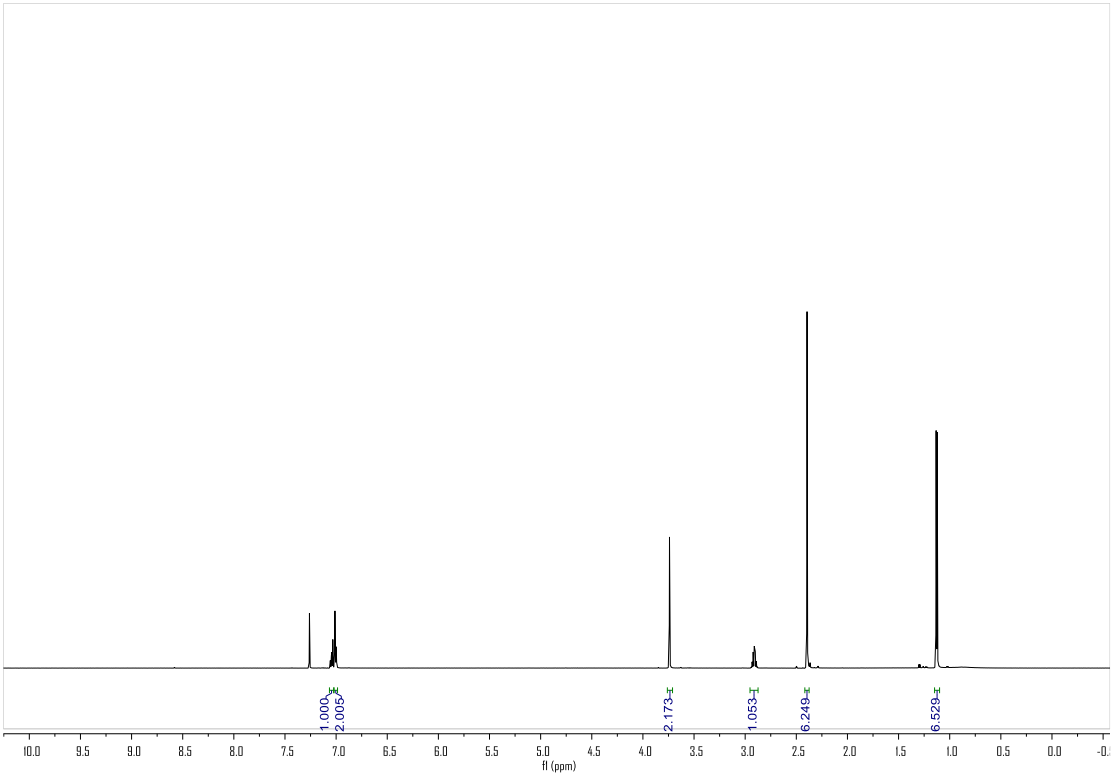
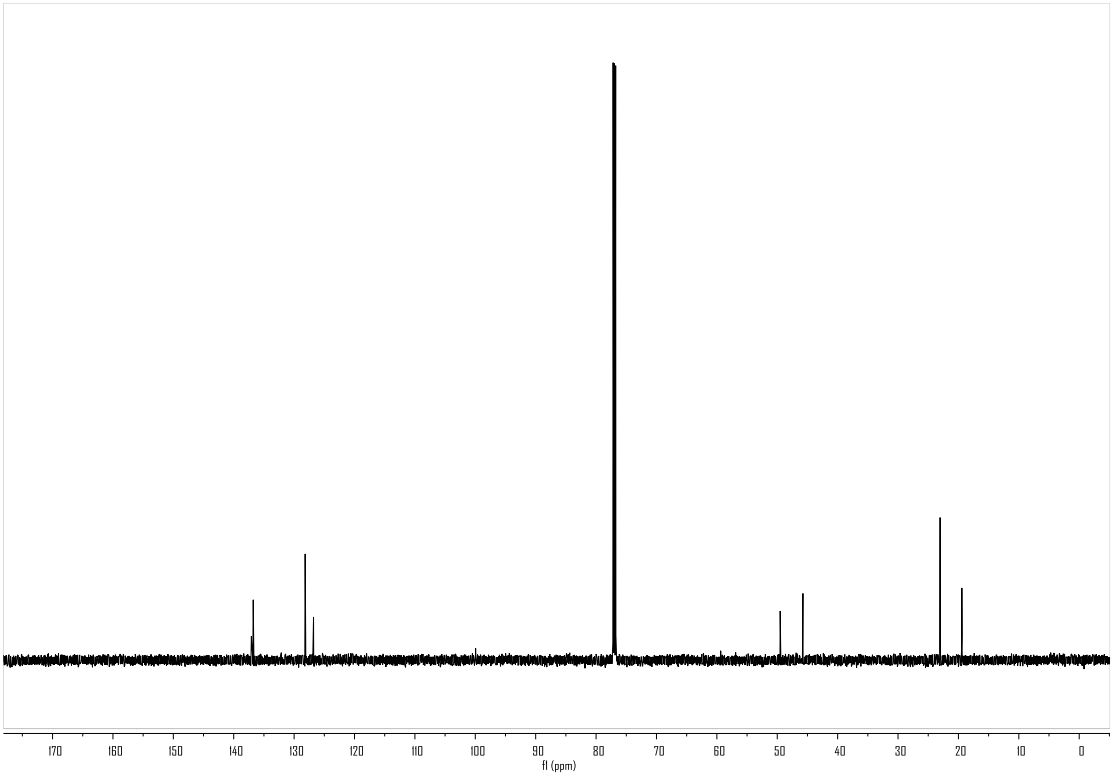
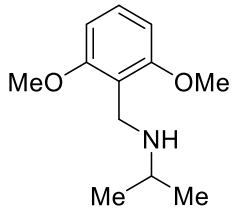
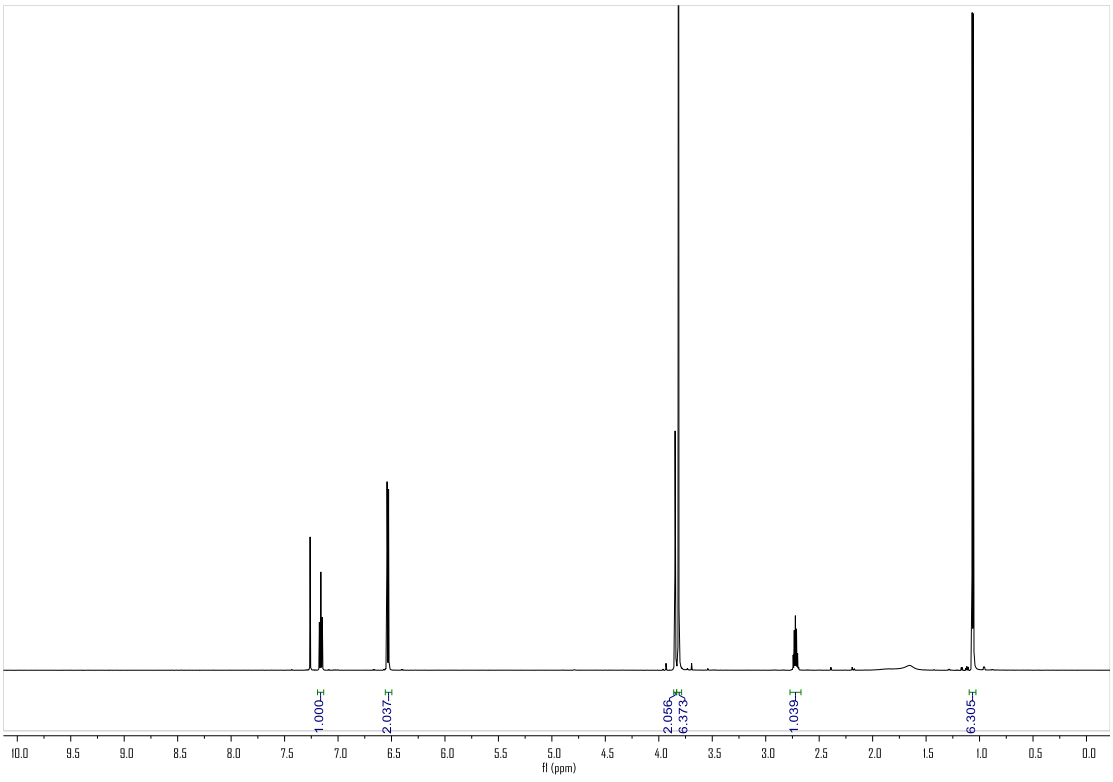
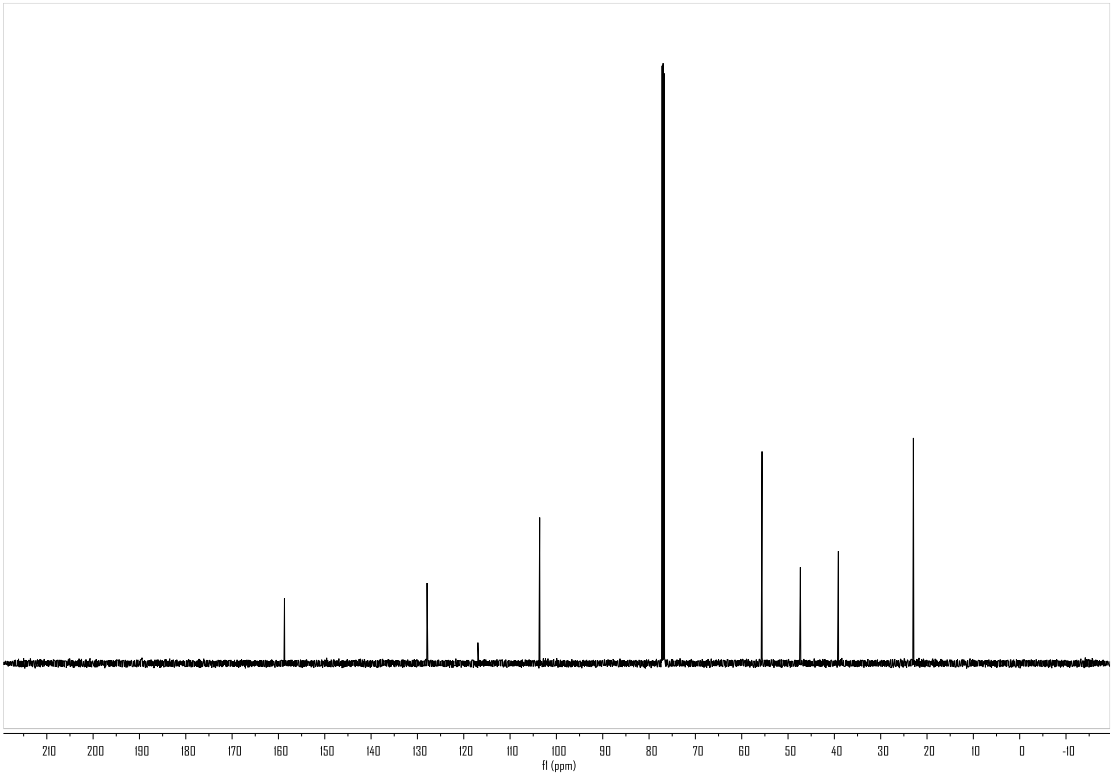
Me
Me

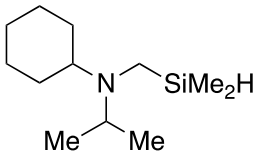

1.000
2.005
2.173
1.053
6.249
6.529
f1 (ppm)

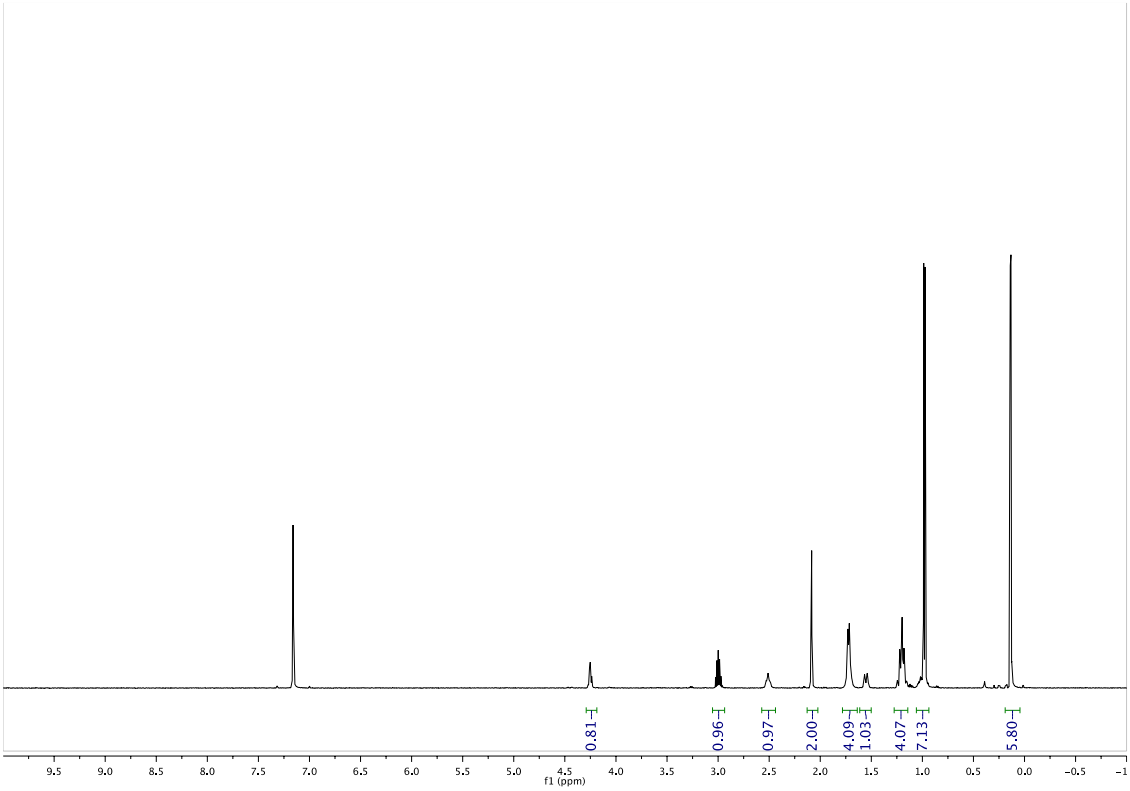

f1 (ppm)

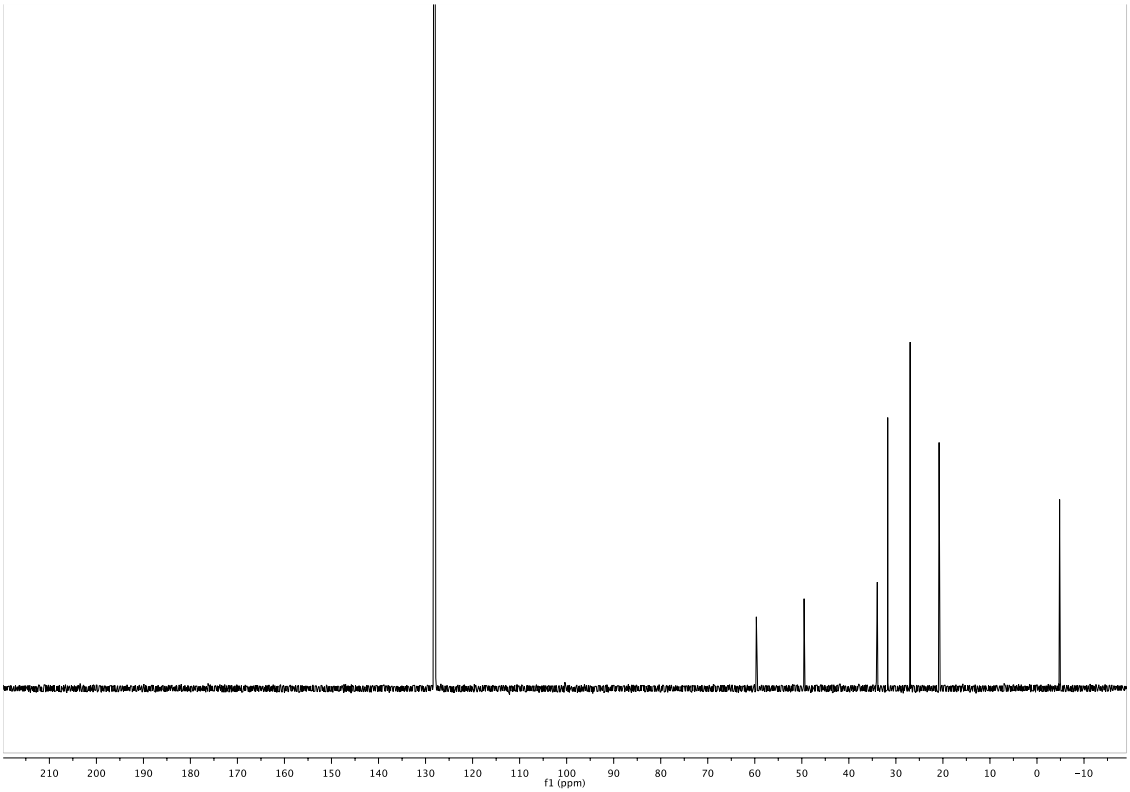

MeO
OMe
NH
Me
Me

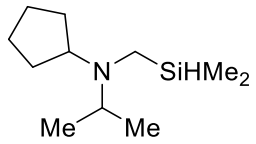

1.000
2.037
2.056
6.373
1.039
6.305
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

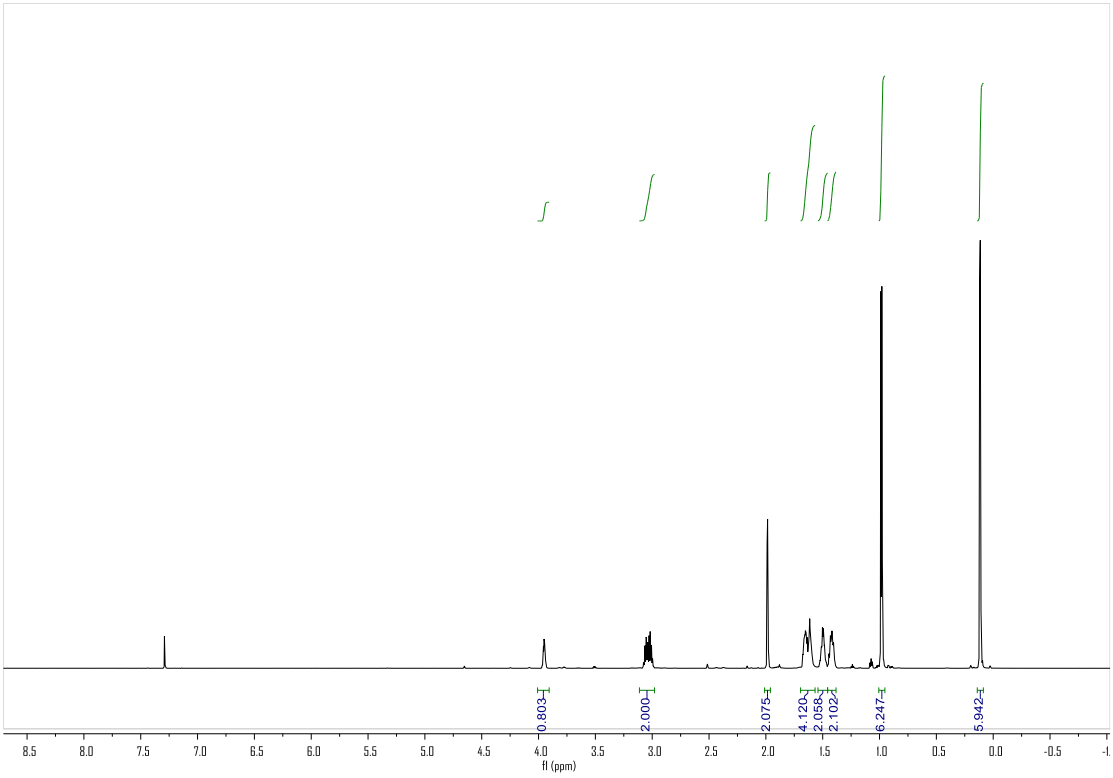

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

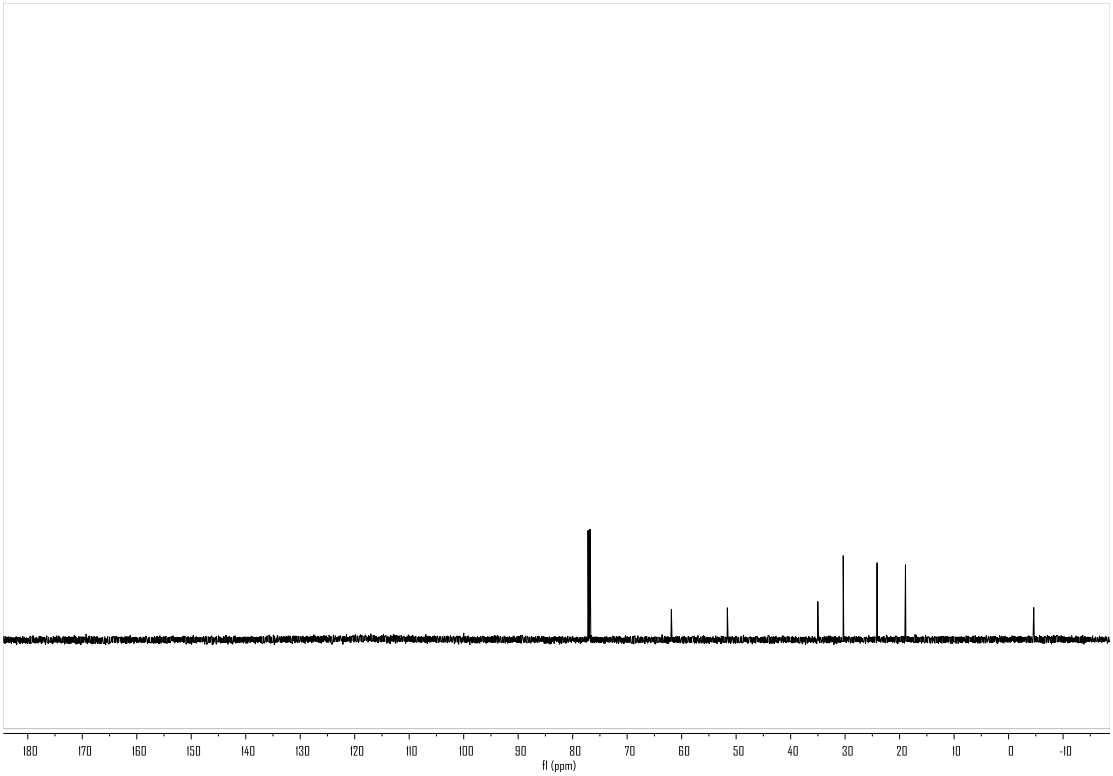

N
SiMe2H
Me
Me

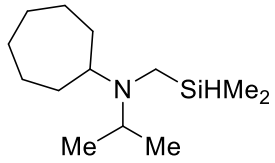

0.81
0.96
0.97
2.00
4.09
1.03
4.07
7.13
5.80
f1 (ppm)

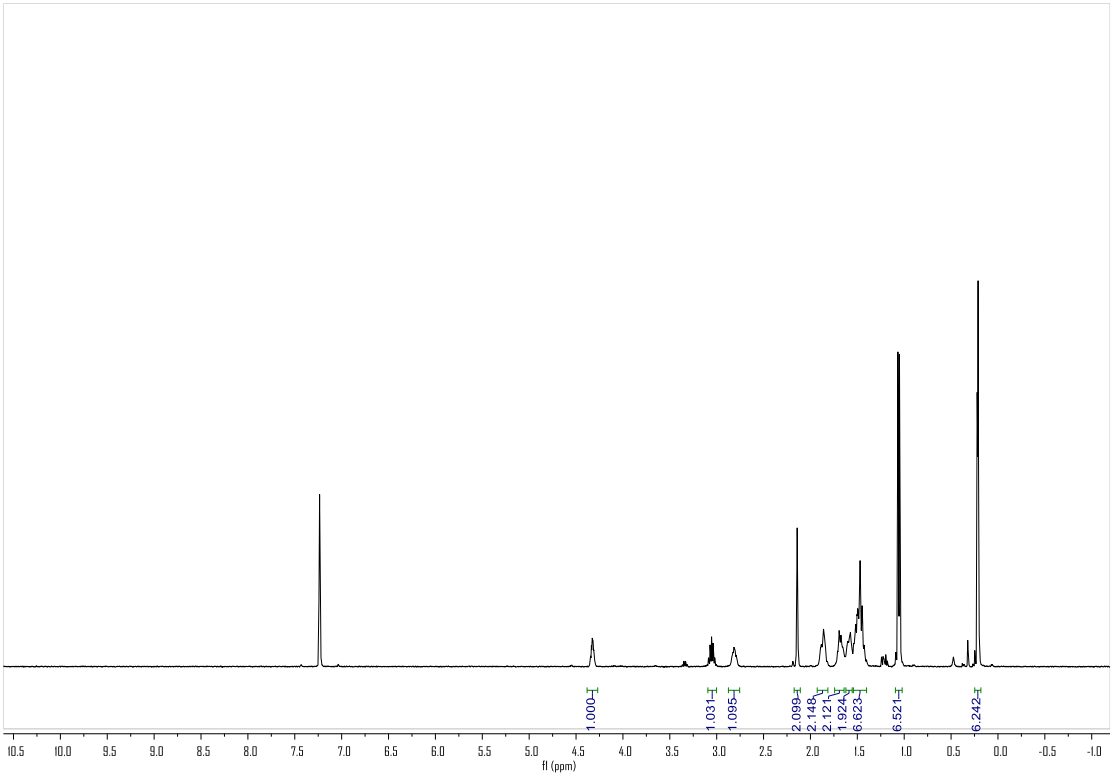

f1 (ppm)

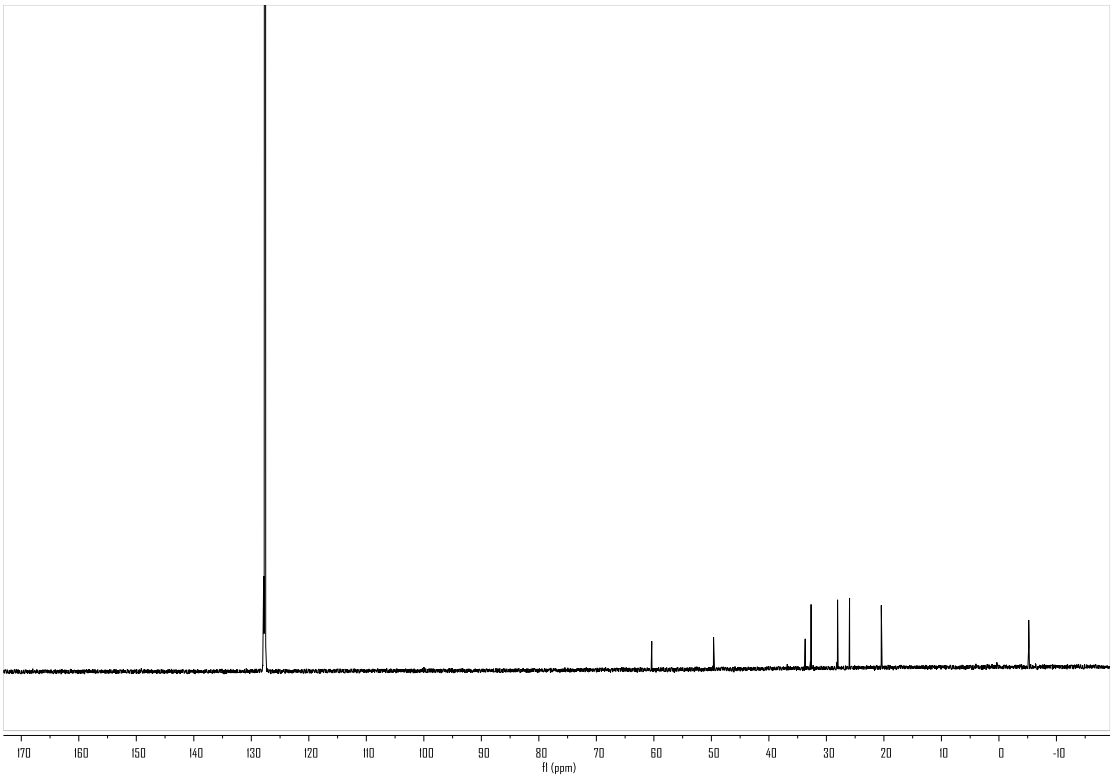

N
SiHMe2
Me
Me

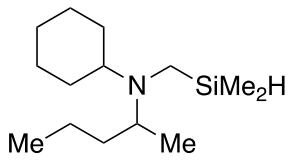

0.803
2.000
2.075
4.120
2.058
2.102
6.247
5.942
f1 (ppm)

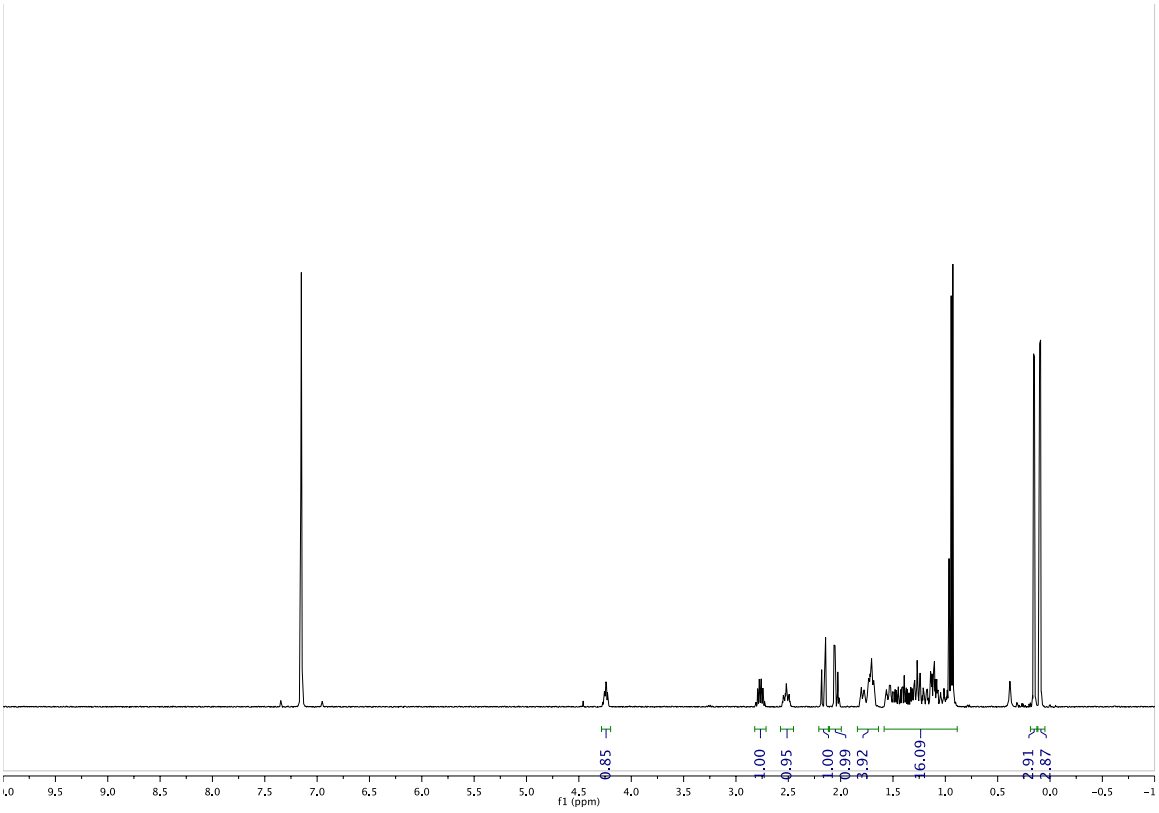

f1 (ppm)

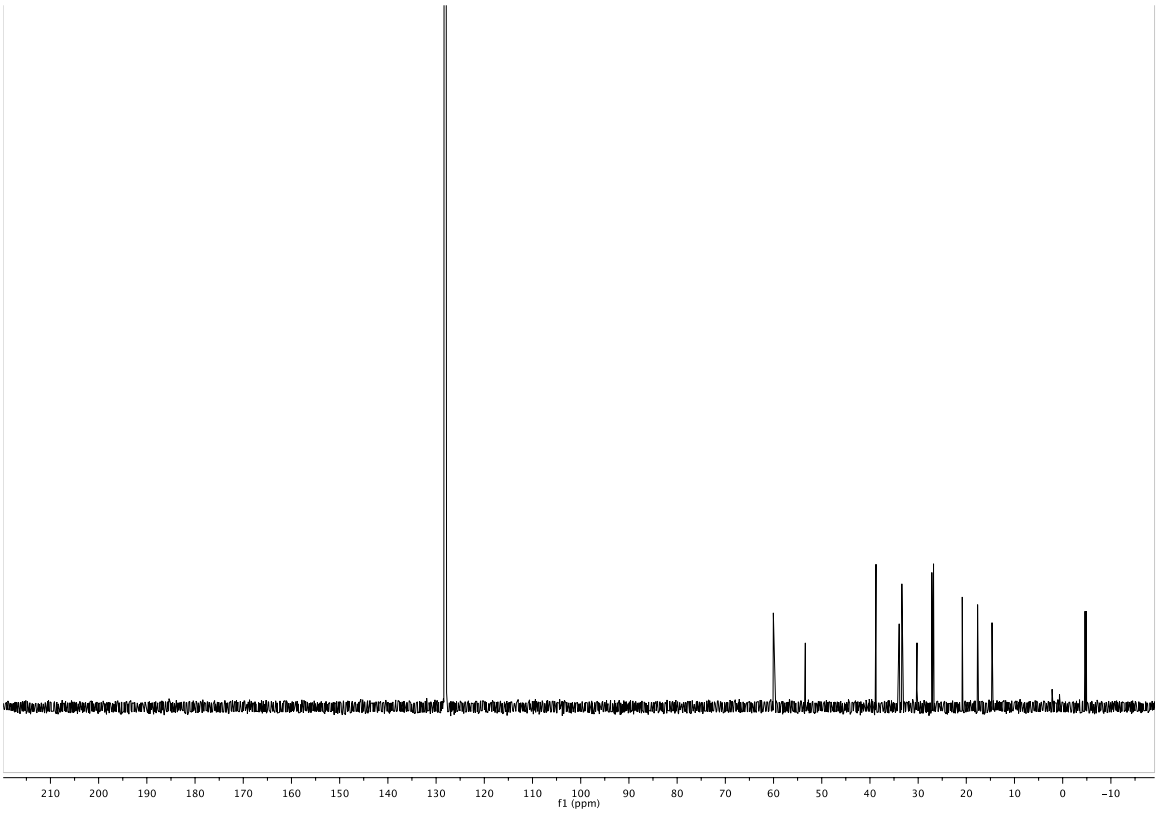

N
SiHMe2
Me
Me

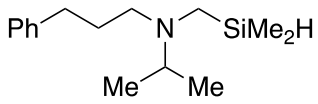

1.000
1.031
1.095
2.099
2.148
2.121
1.924
6.623
6.521
6.242
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

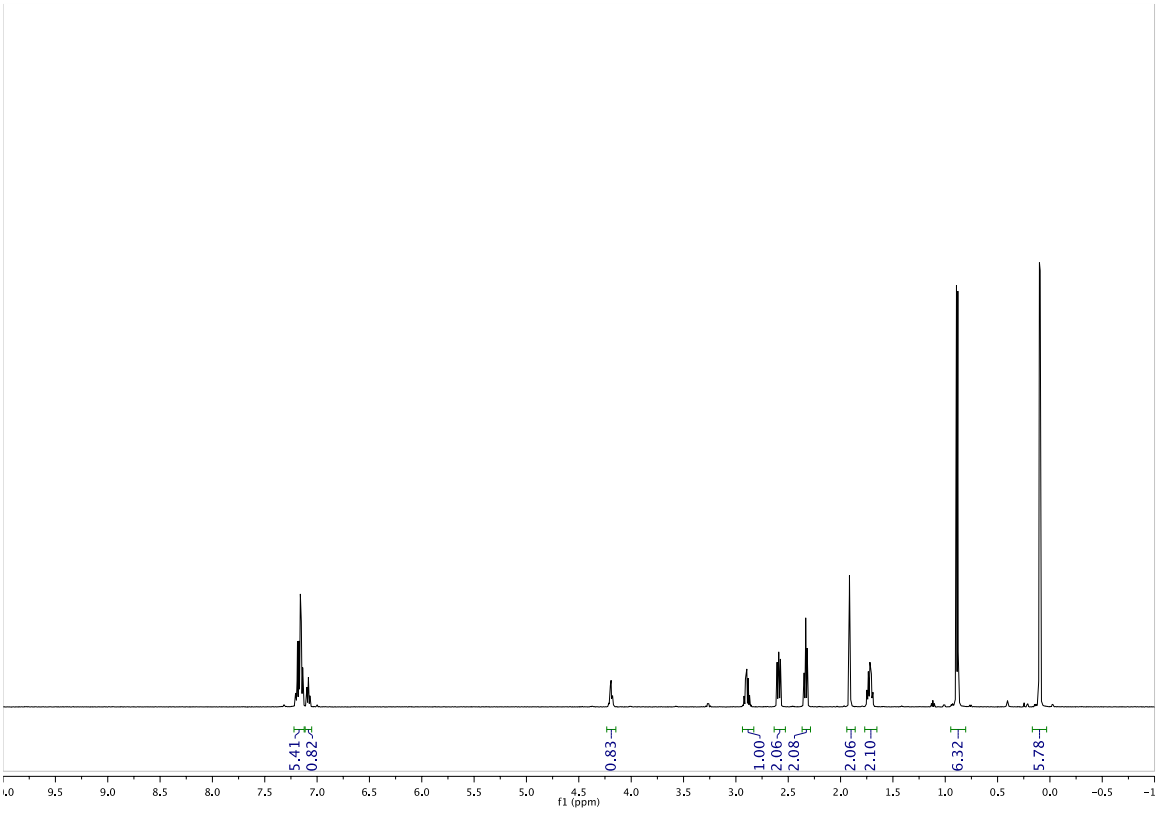

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

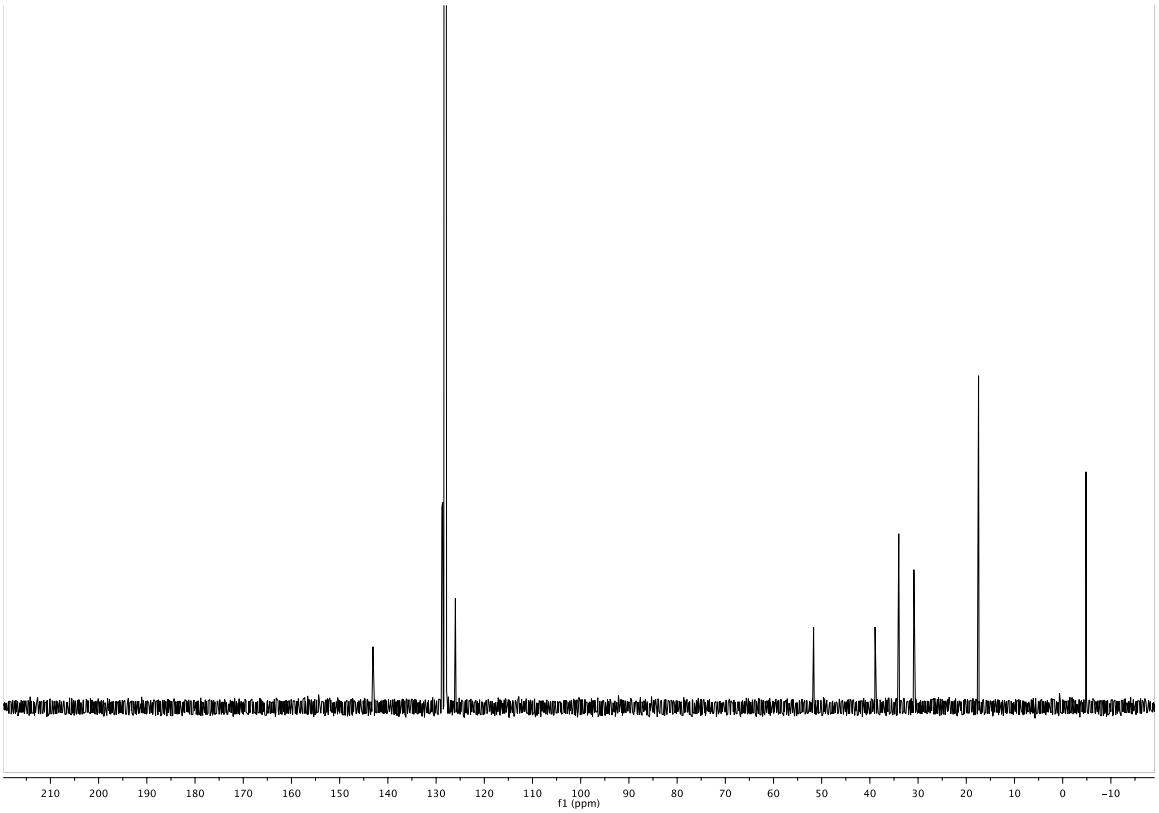

N
SiMe2H
Me
Me

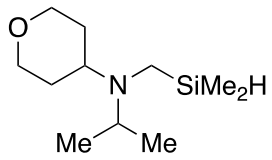

0.85
1.00
0.95
1.00
0.99
3.92
16.09
2.91
2.87
f1 (ppm)

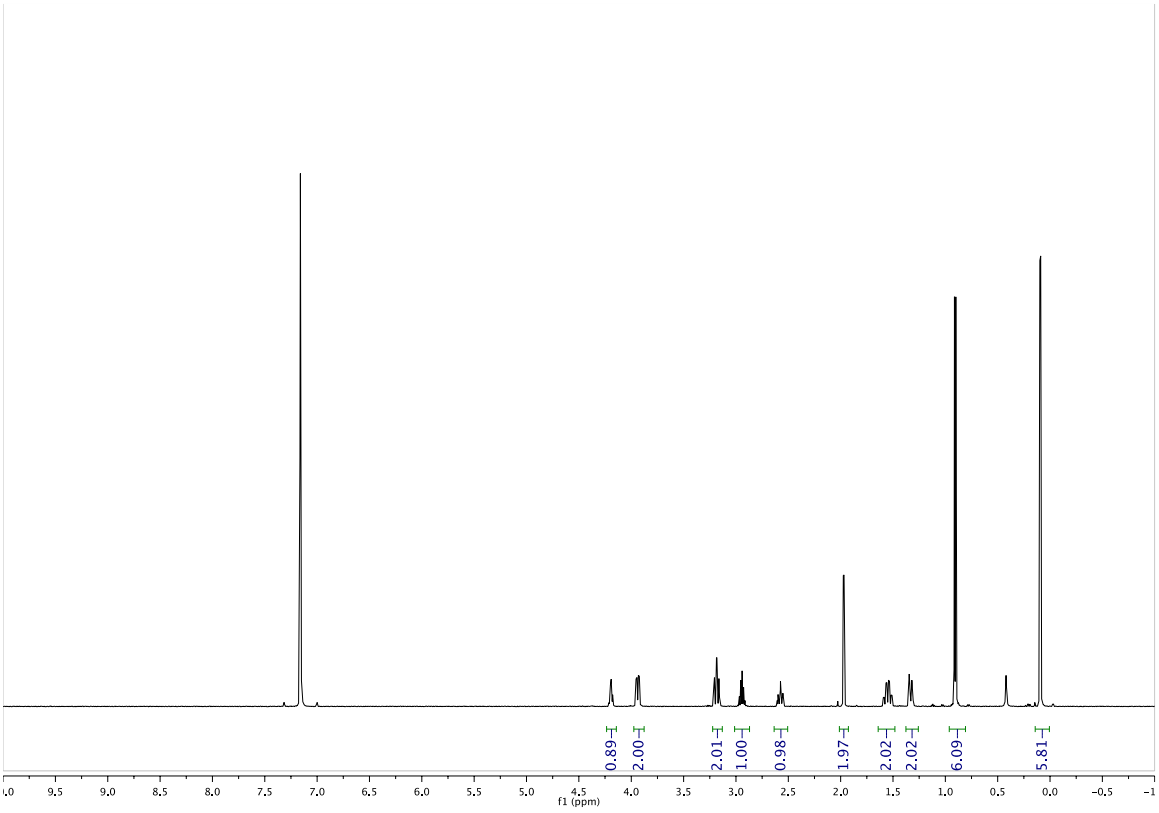

f1 (ppm)

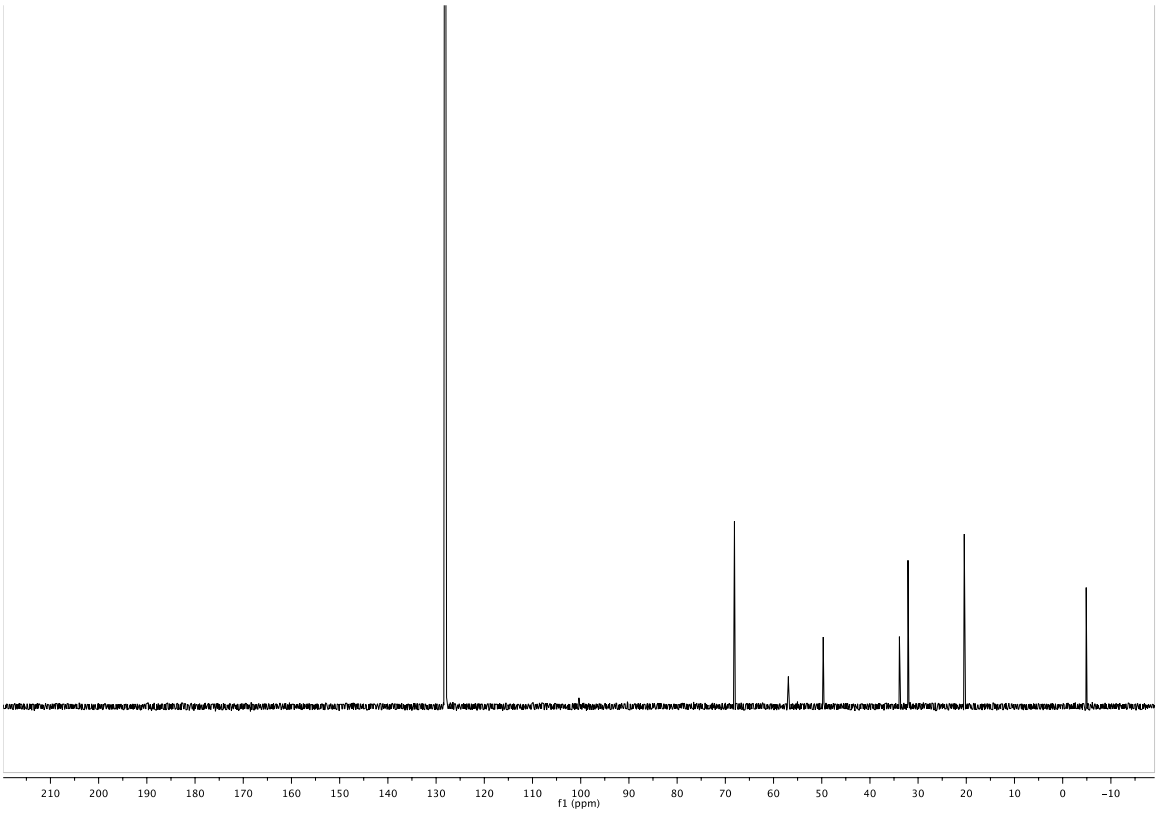

Ph
N
SiMe2H
Me
Me

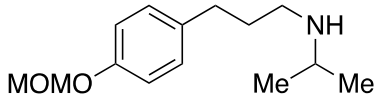

5.41
0.82
0.83
1.00
2.06
2.08
2.06
2.10
6.32
5.78
f1 (ppm)

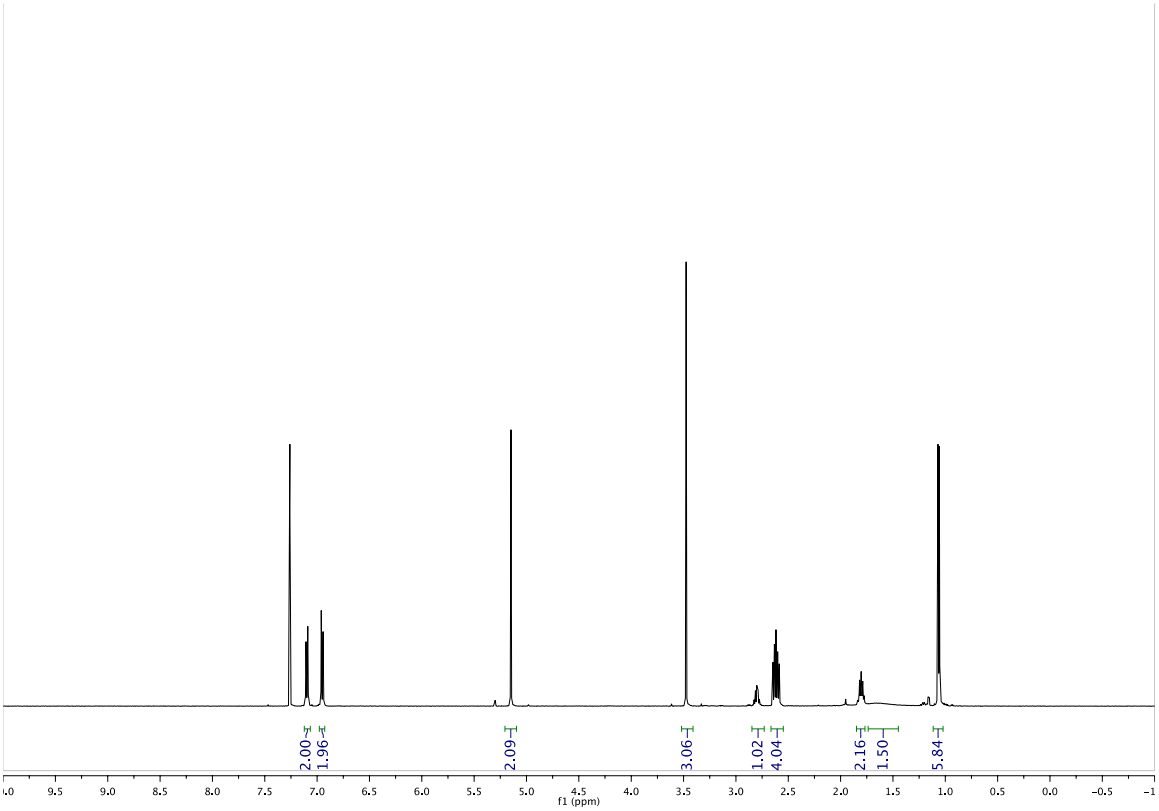

f1 (ppm)

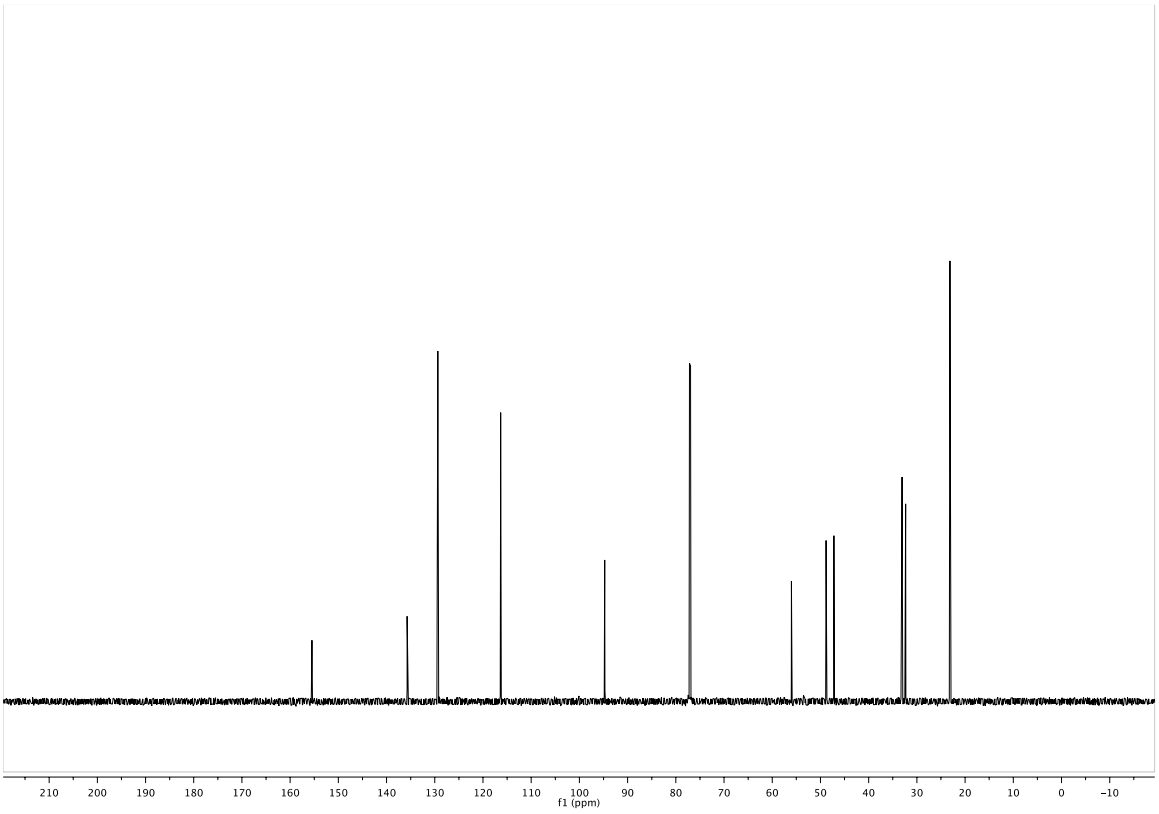

O
N
SiMe2H
Me
Me

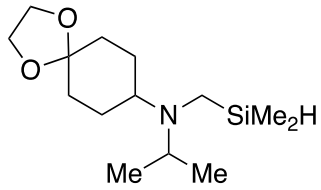

0.89
2.00
2.01
1.00
0.98
1.97
2.02
2.02
6.09
5.81
f1 (ppm)

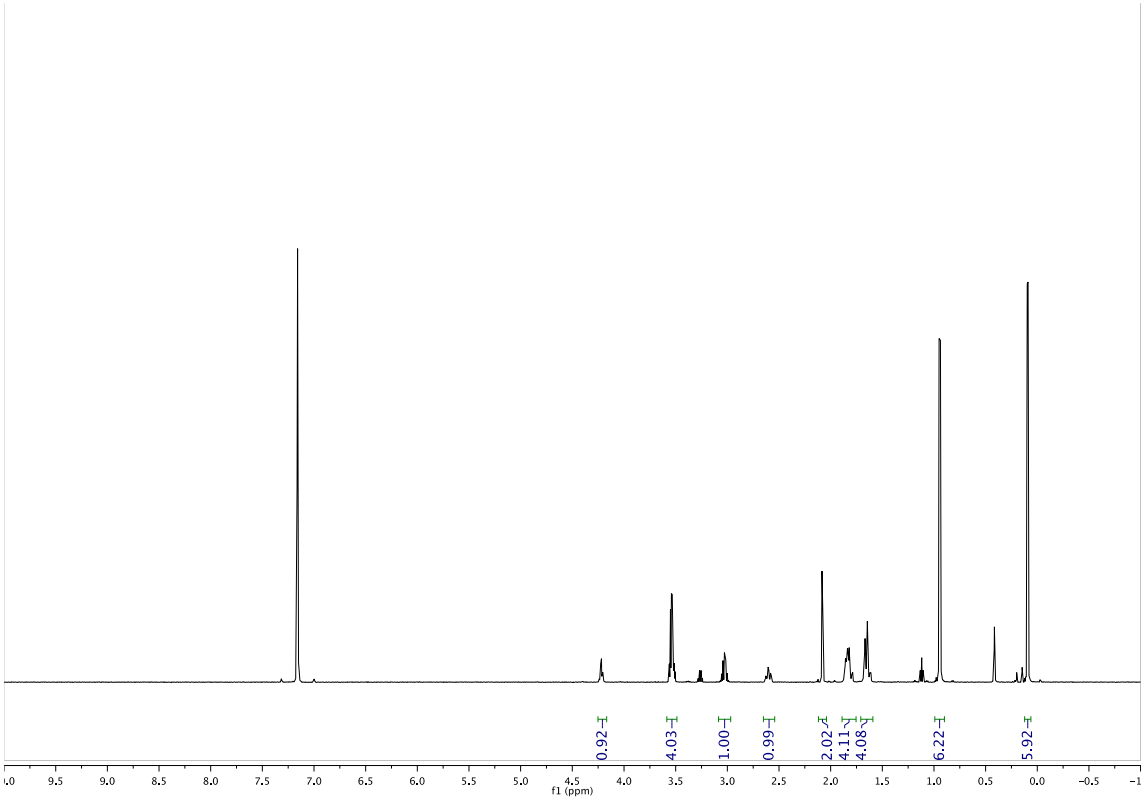

f1 (ppm)

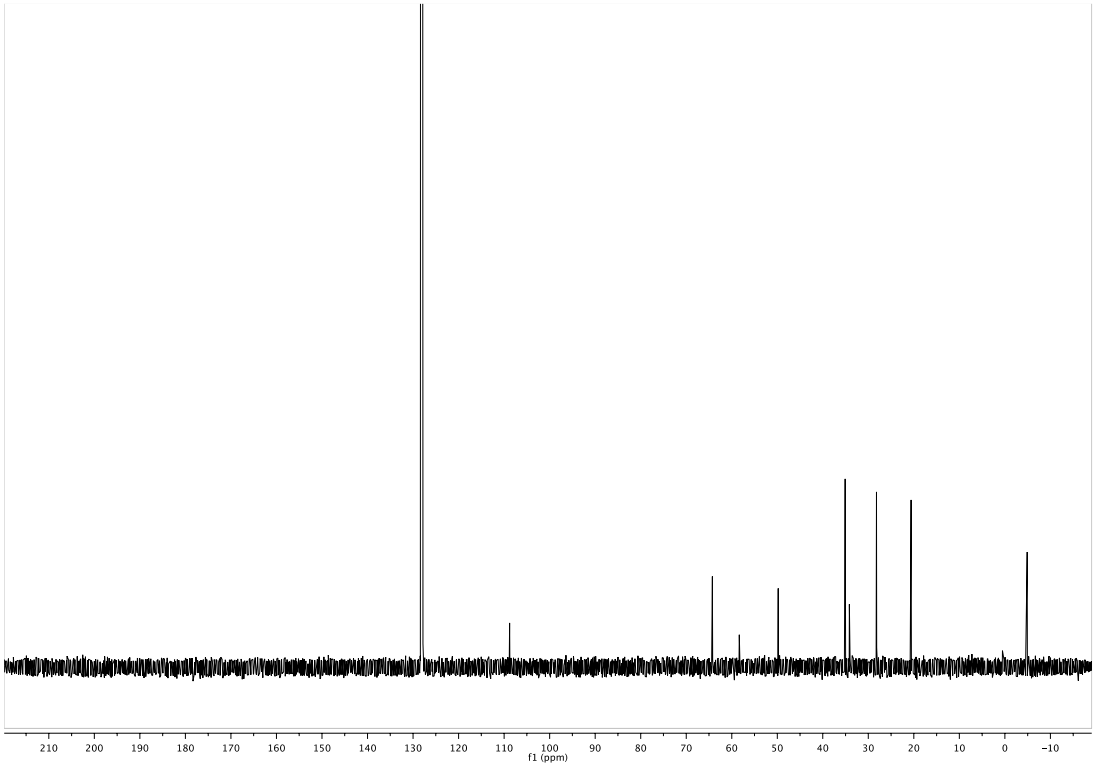

NH
MOMO
Me
Me

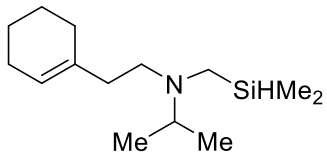

2.00
1.96
2.09
3.06
1.02
4.04
2.16
1.50
5.84
f1 (ppm)

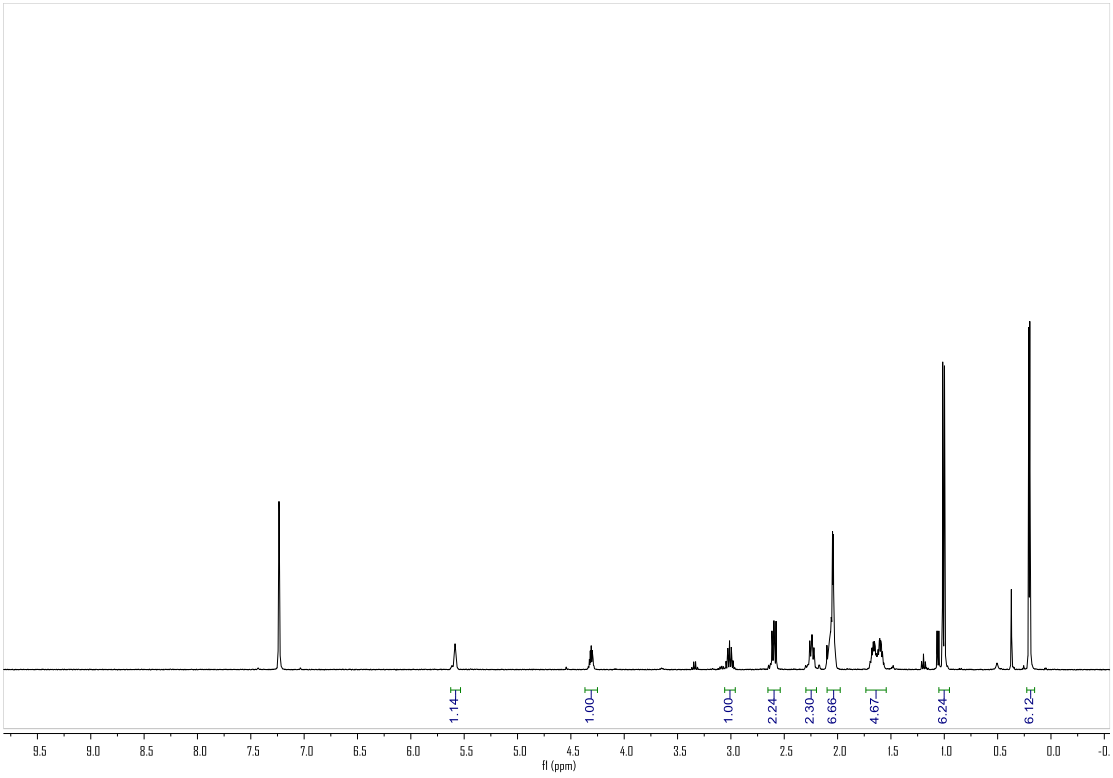

f1 (ppm)

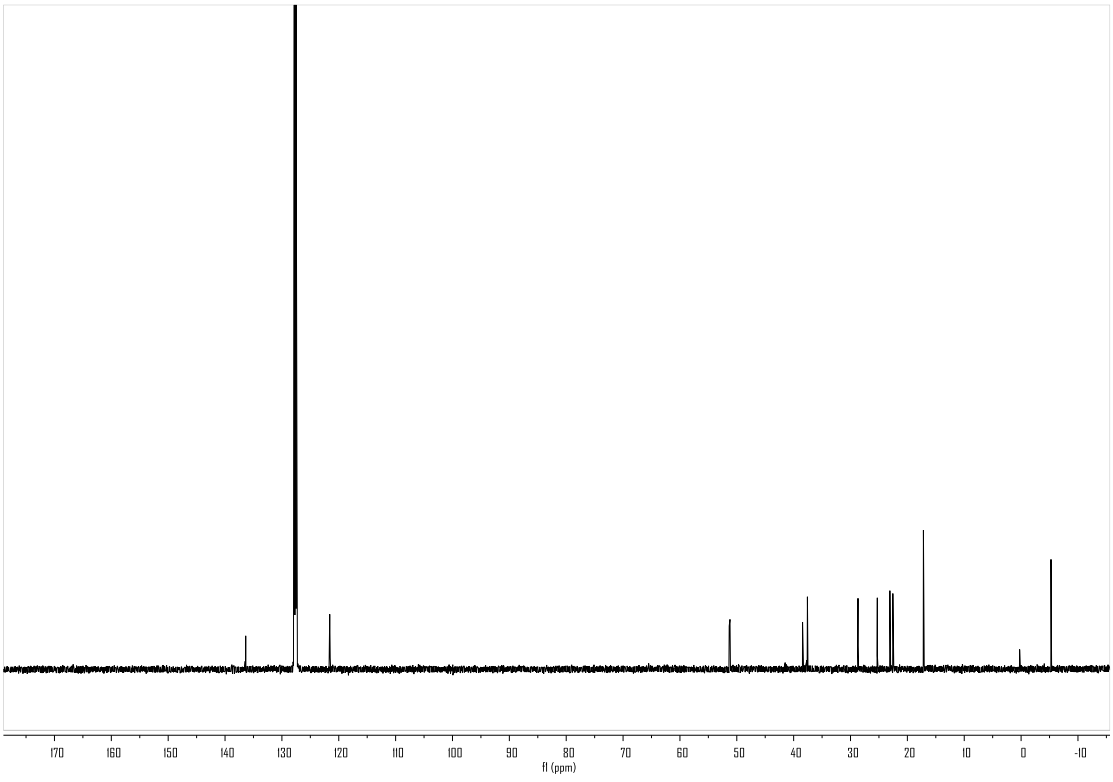

O
O
N
SiMe2H
Me
Me

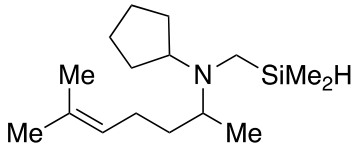

0.92
4.03
1.00
0.99
2.02
4.11
4.08
6.22
5.92
f1 (ppm)

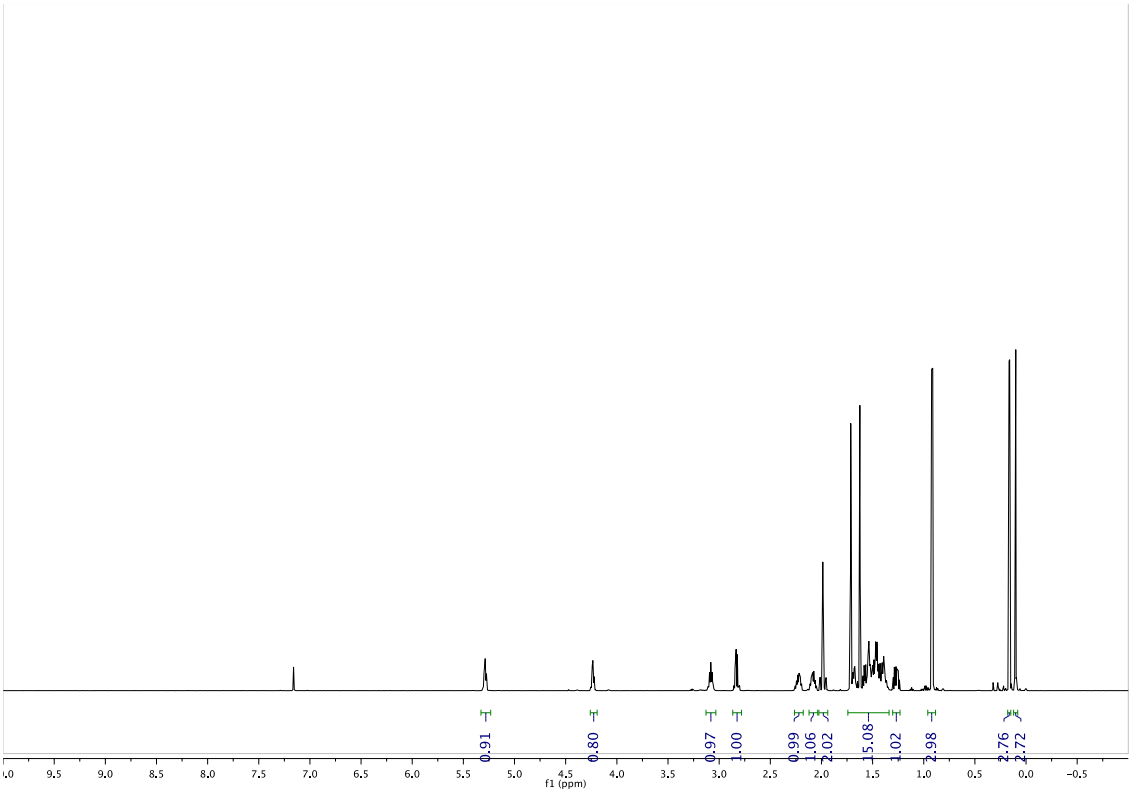

f1 (ppm)

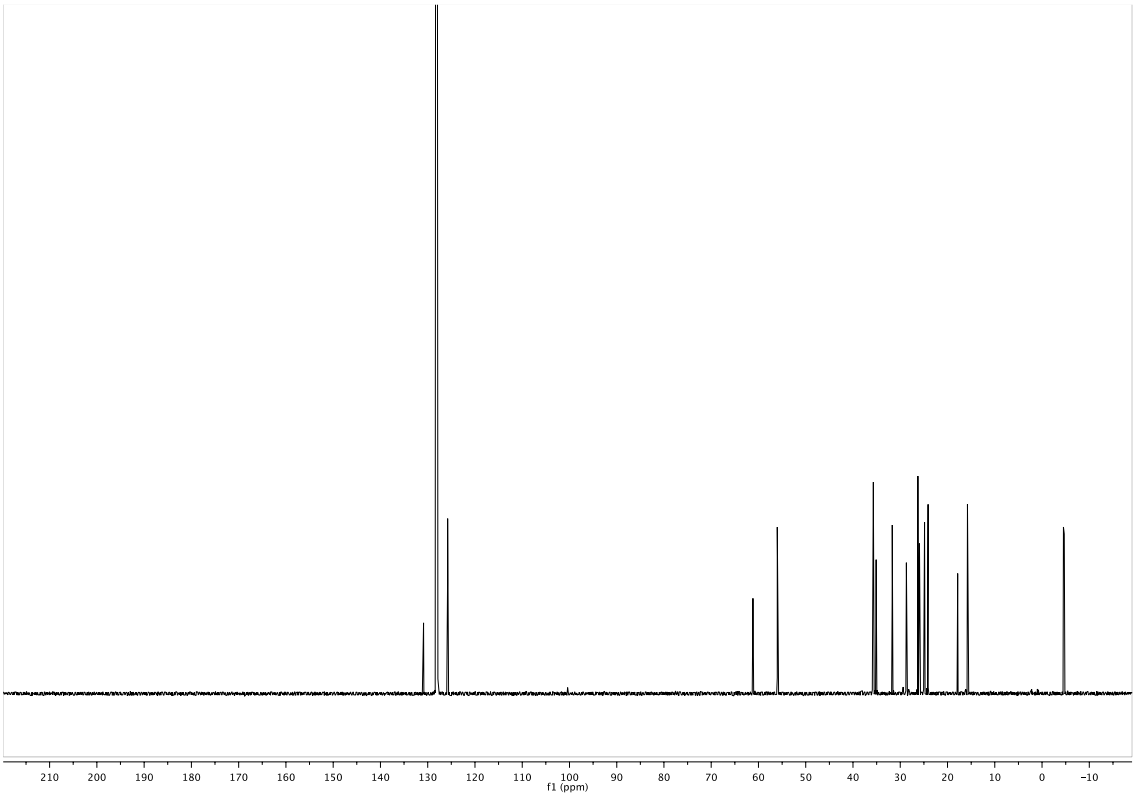

N
SiHMe2
Me
Me

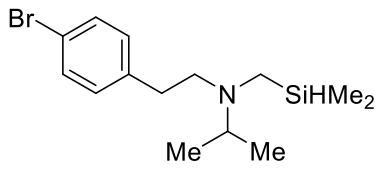

1.14
1.00
1.00
2.24
2.30
6.66
4.67
6.24
6.12
f1 (ppm)

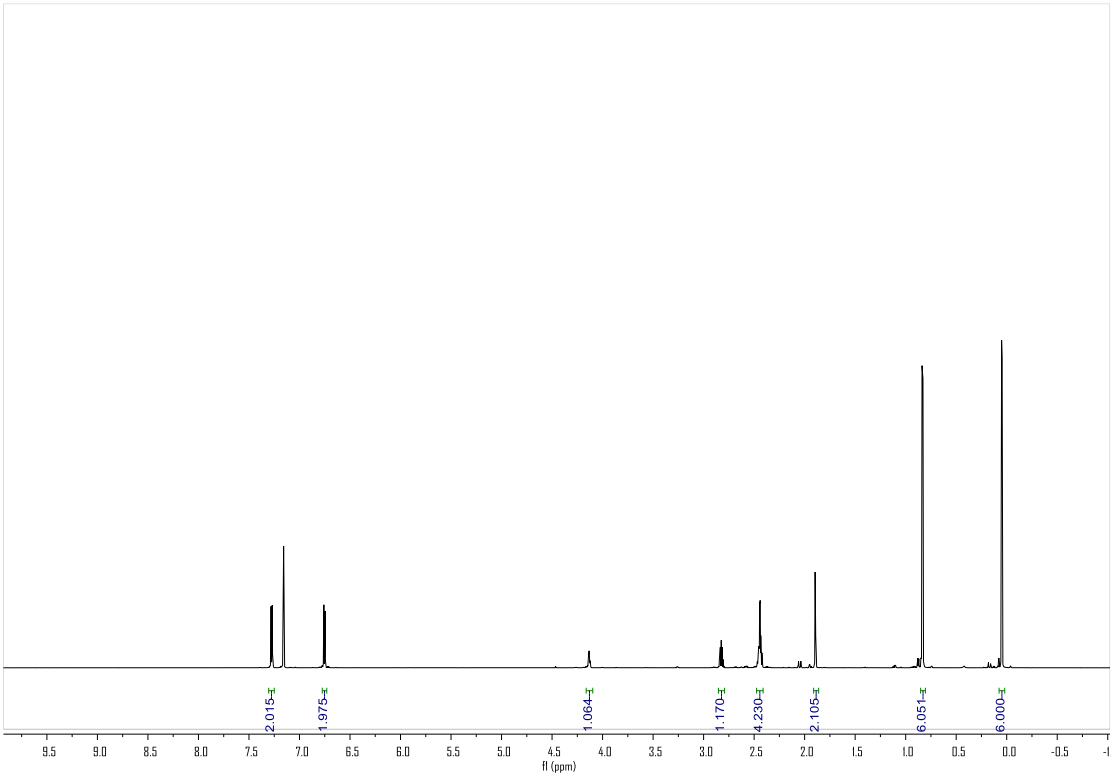

f1 (ppm)

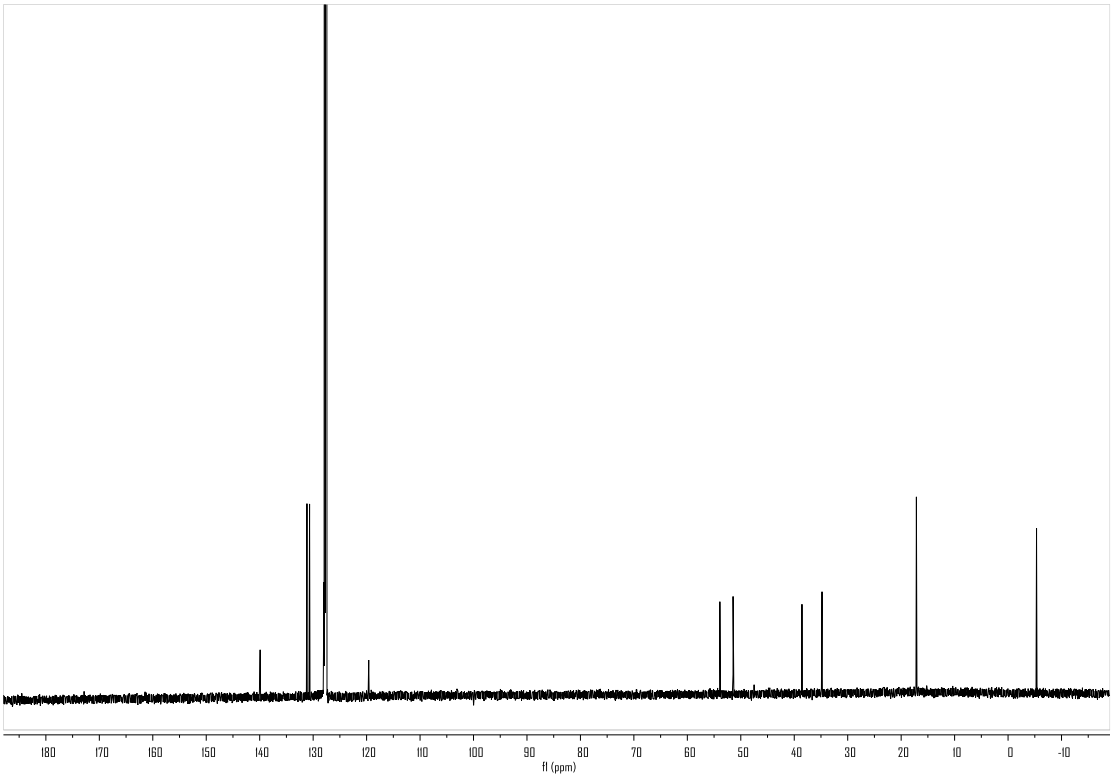

Me
N
SiMe2H
Me
Me

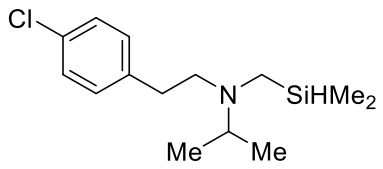

0.91
0.80
0.97
1.00
0.99
1.06
2.02
15.08
1.02
2.98
2.76
2.72
f1 (ppm)

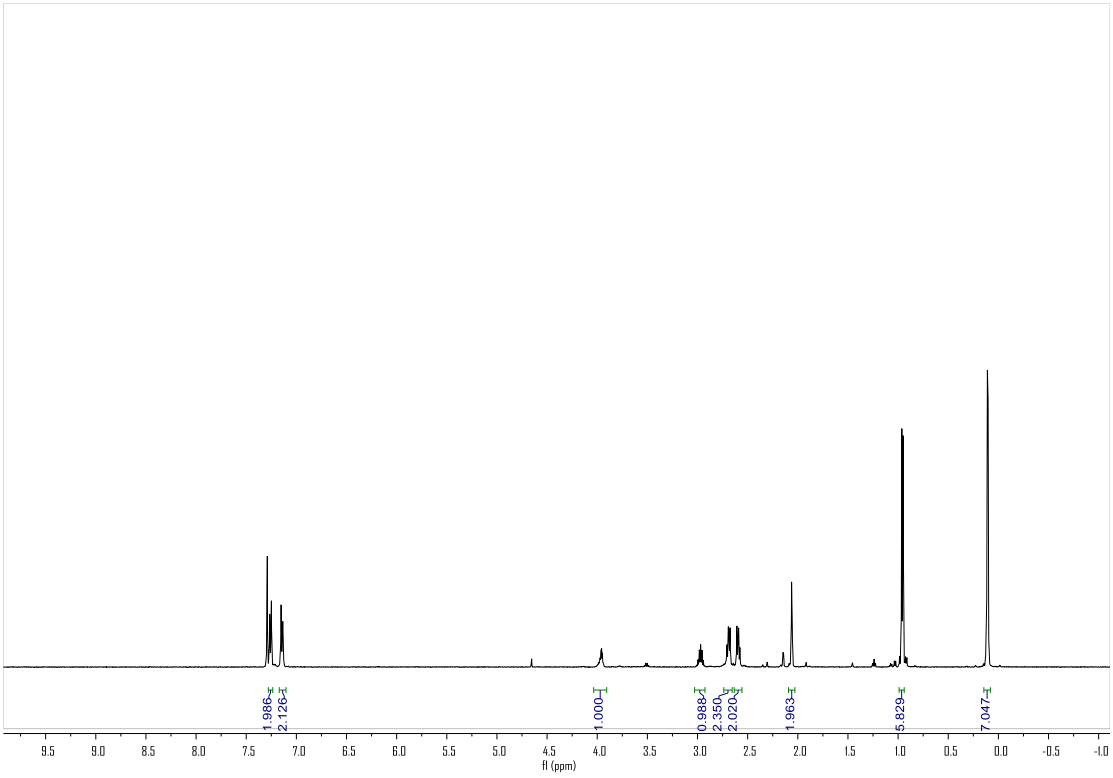

f1 (ppm)

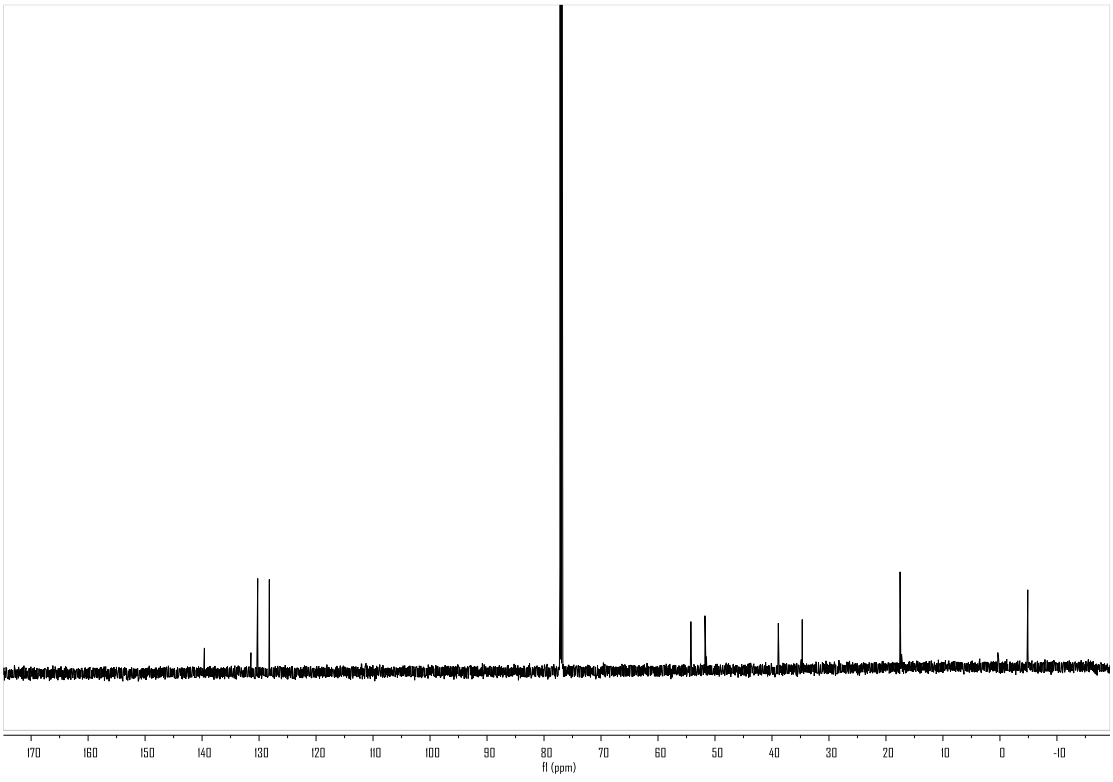

Br
N
SiHMe2
Me
Me

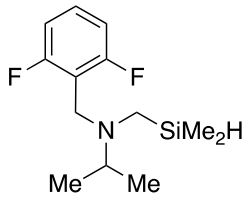

2.015
1.975
1.064
1.170
4.230
2.105
6.051
6.000
f1 (ppm)

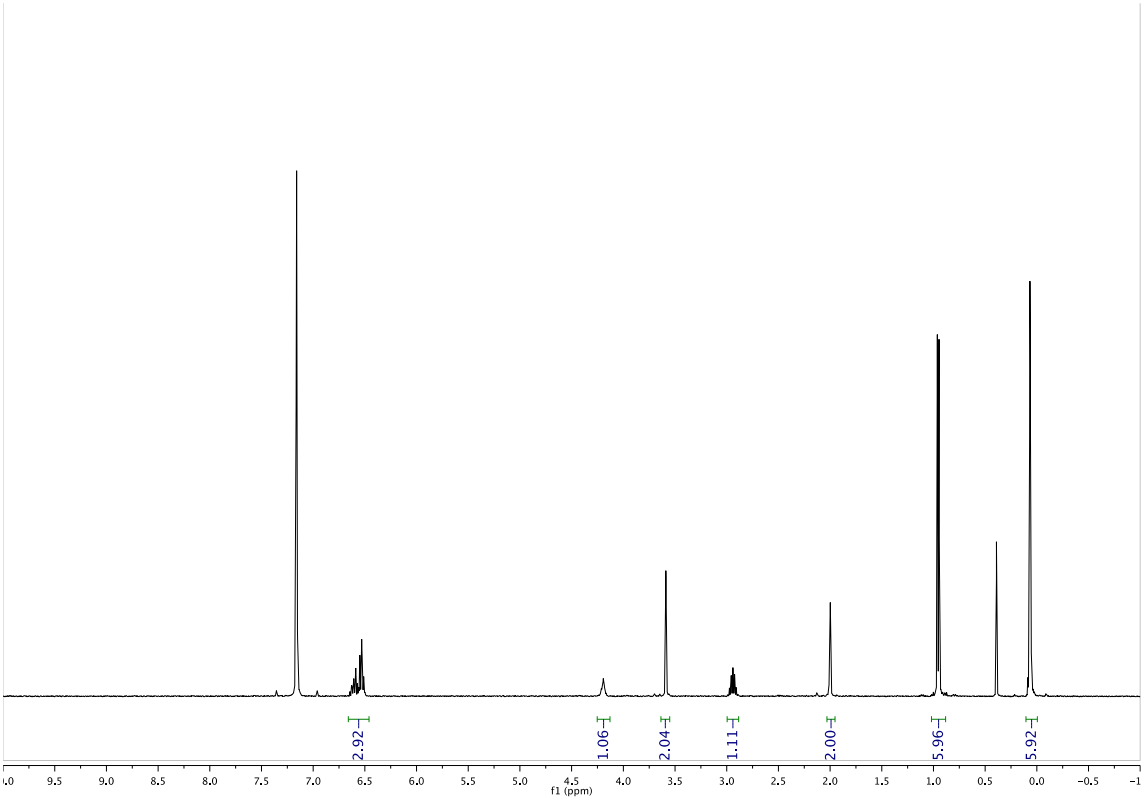

f1 (ppm)

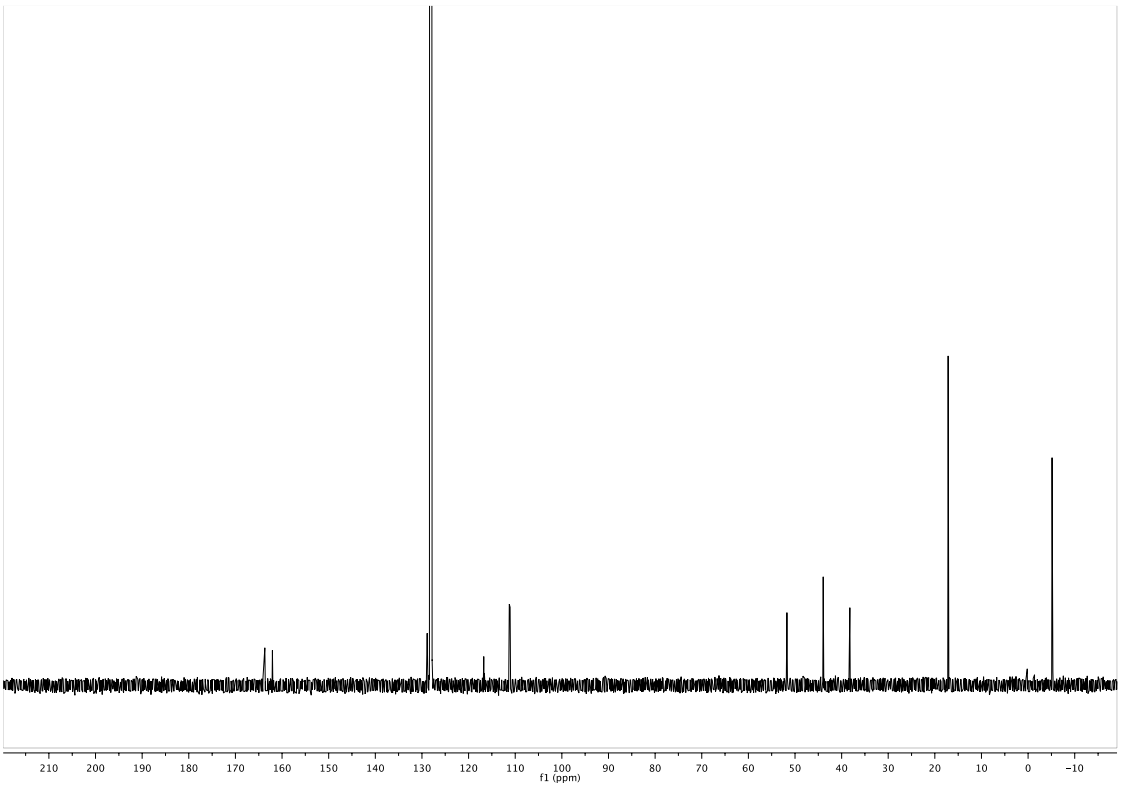

Cl
N
SiHMe2
Me
Me

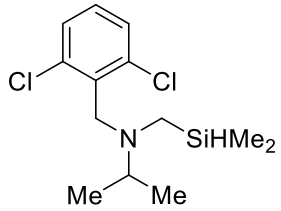

1.986
2.126
1.000
0.988
2.350
2.020
1.963
5.829
7.047
f1 (ppm)

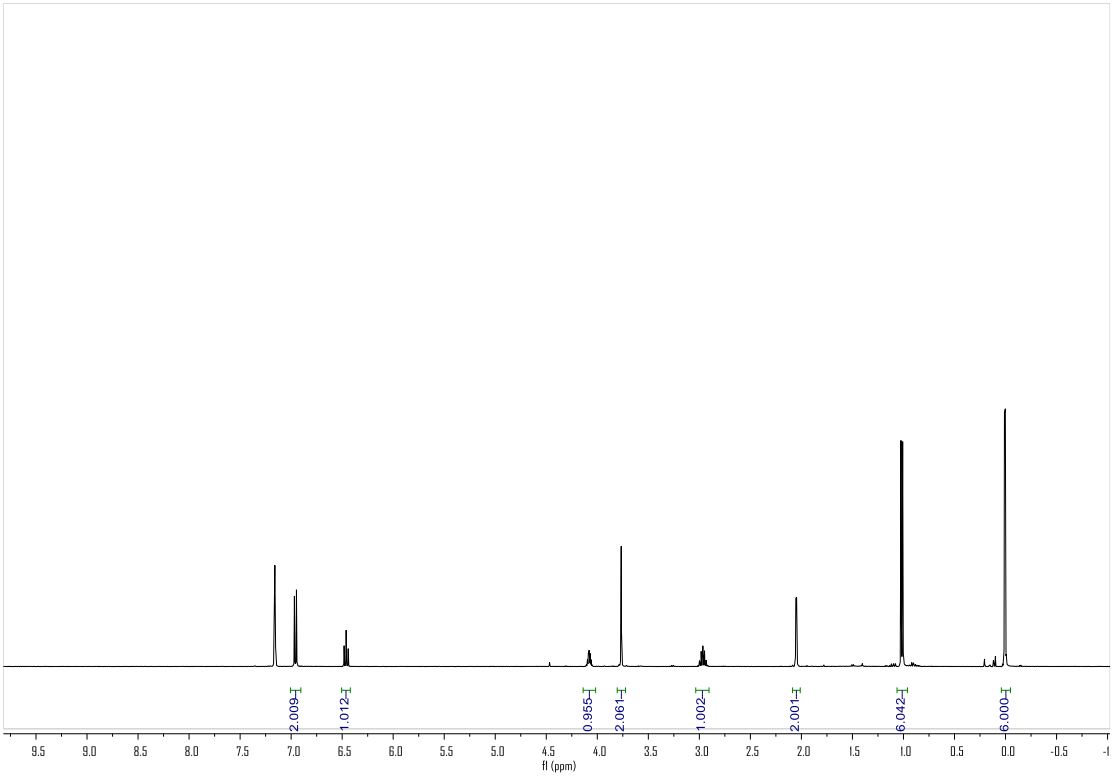

f1 (ppm)

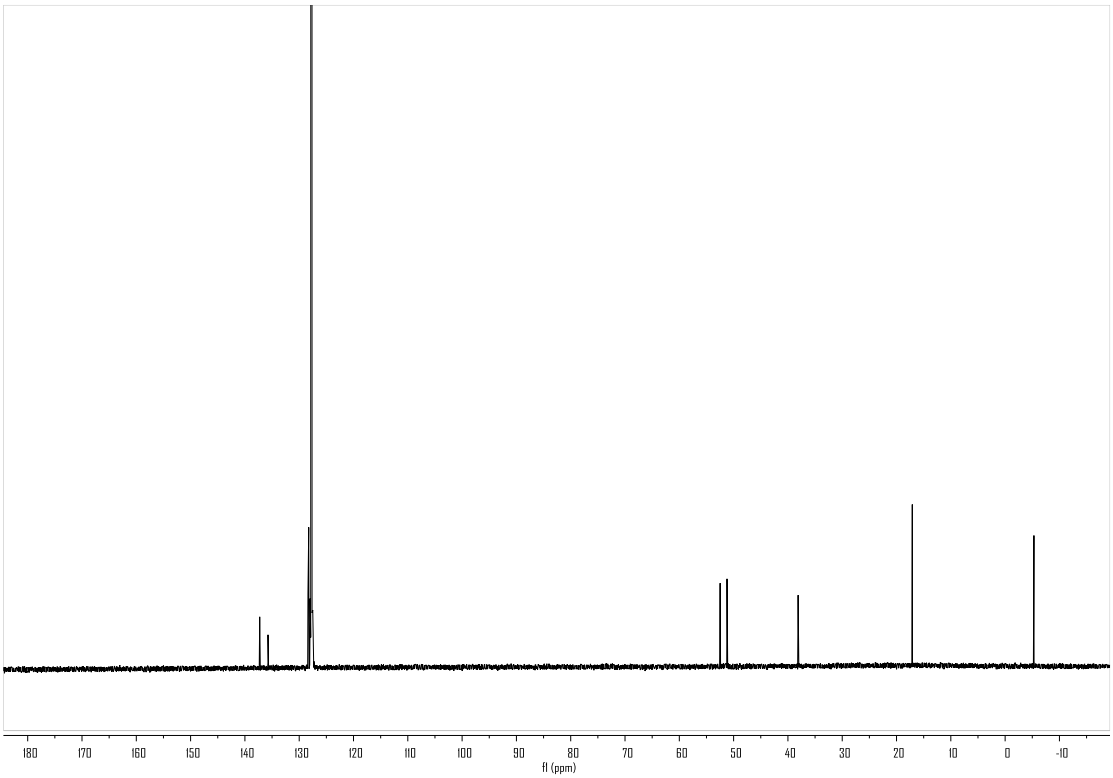

F
F
N
SiMe2H
Me
Me

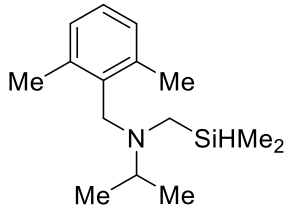

2.92
1.06
2.04
1.11
2.00
5.96
5.92
f1 (ppm)

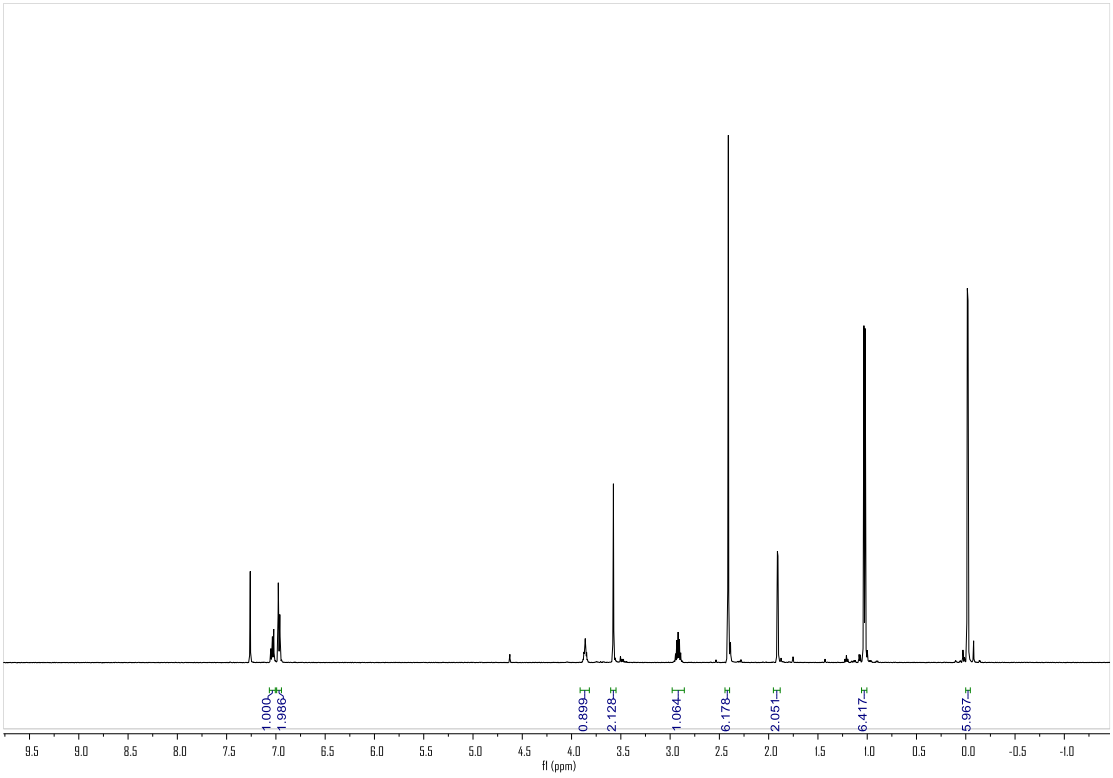

f1 (ppm)

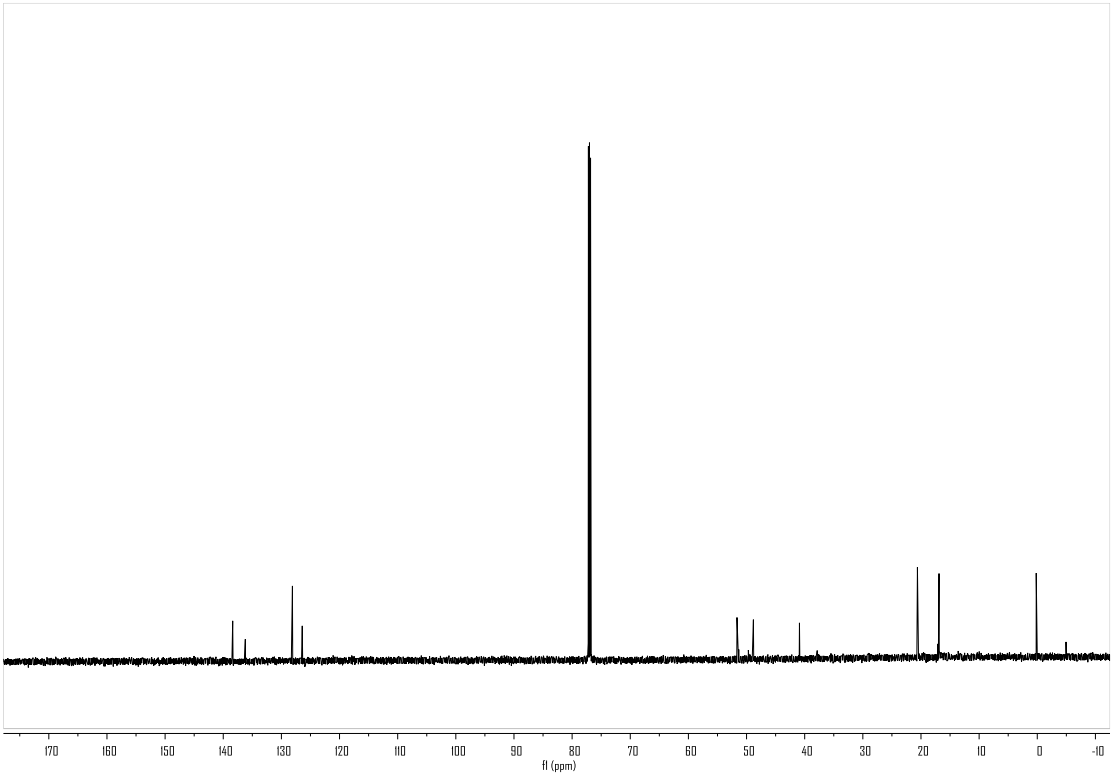

Cl
Cl
N
SiHMe2
Me
Me

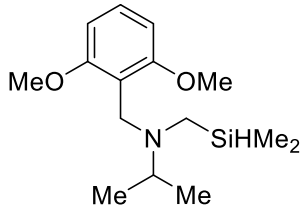

2.009
1.012
0.955
2.061
1.002
2.001
6.042
6.000
f1 (ppm)

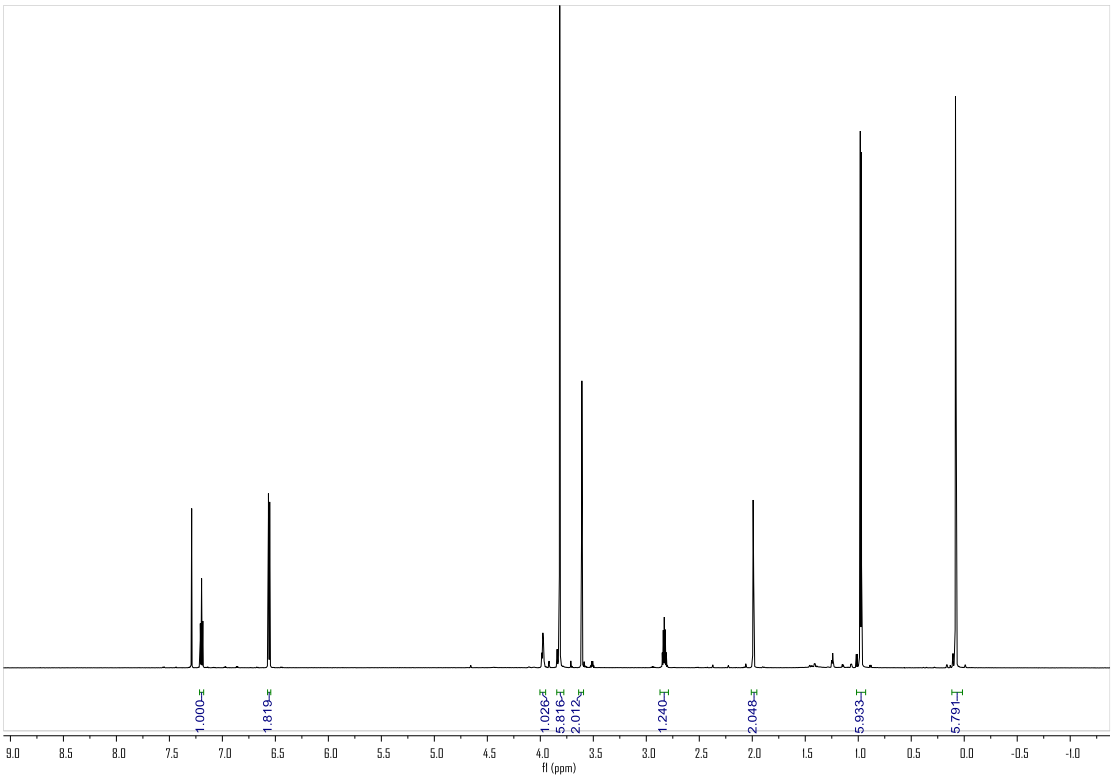

f1 (ppm)

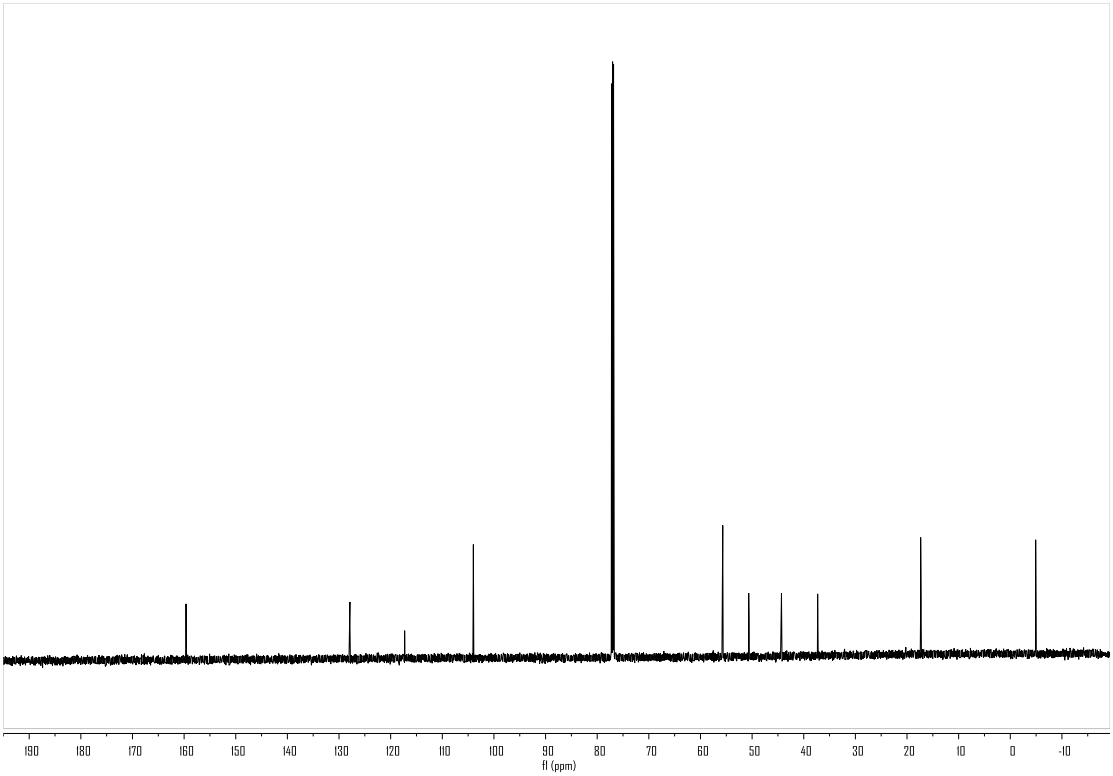

Me
Me
N
SiHMe2
Me
Me

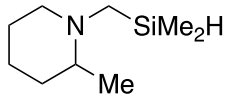

1.000
1.986
0.899
2.128
1.064
6.178
2.051
6.417
5.967
f1 (ppm)

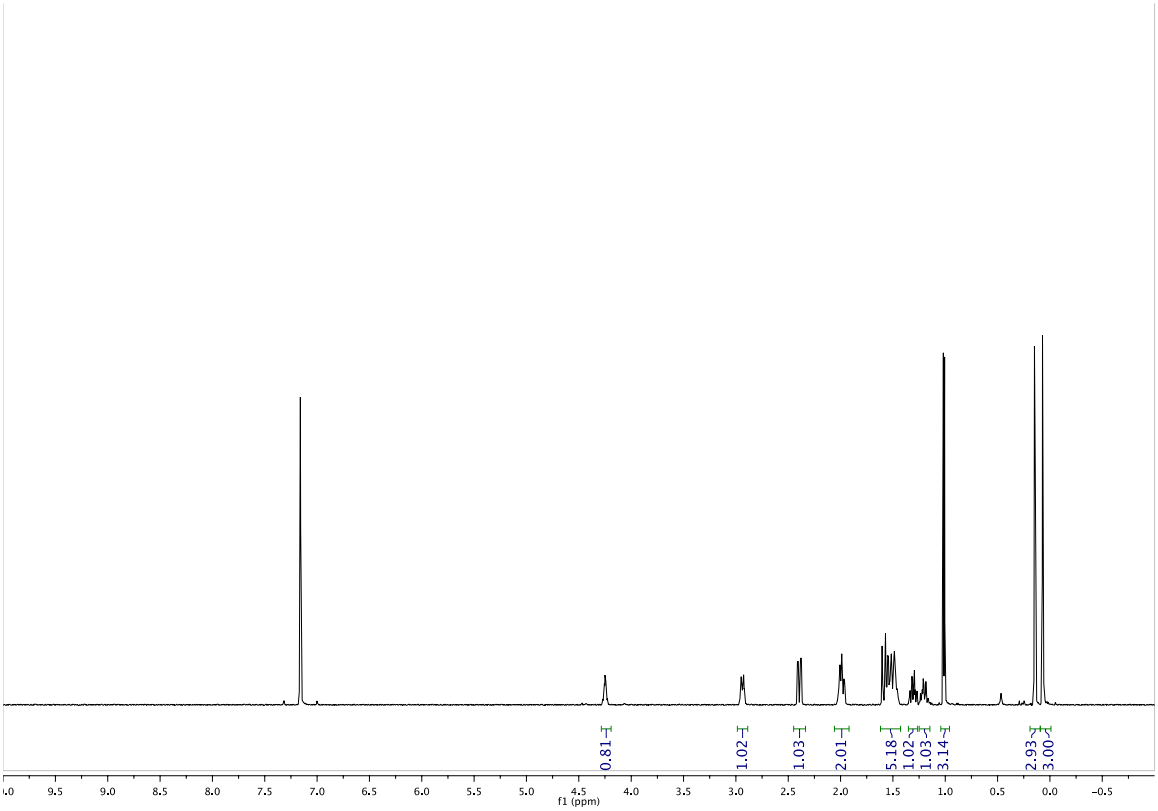

f1 (ppm)

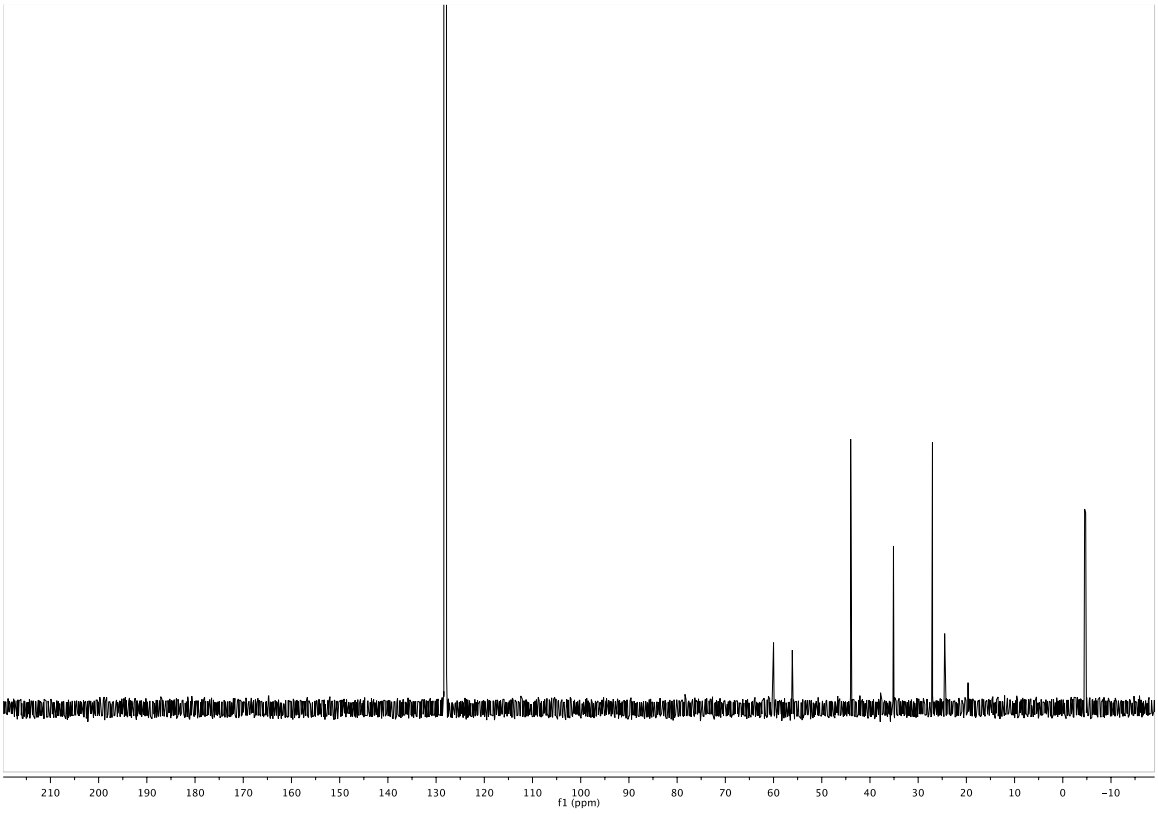

MeO
OMe
N
SiHMe2
Me
Me

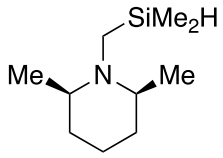

1.000
1.819
1.026
5.816
2.012
1.240
2.048
5.933
5.791
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

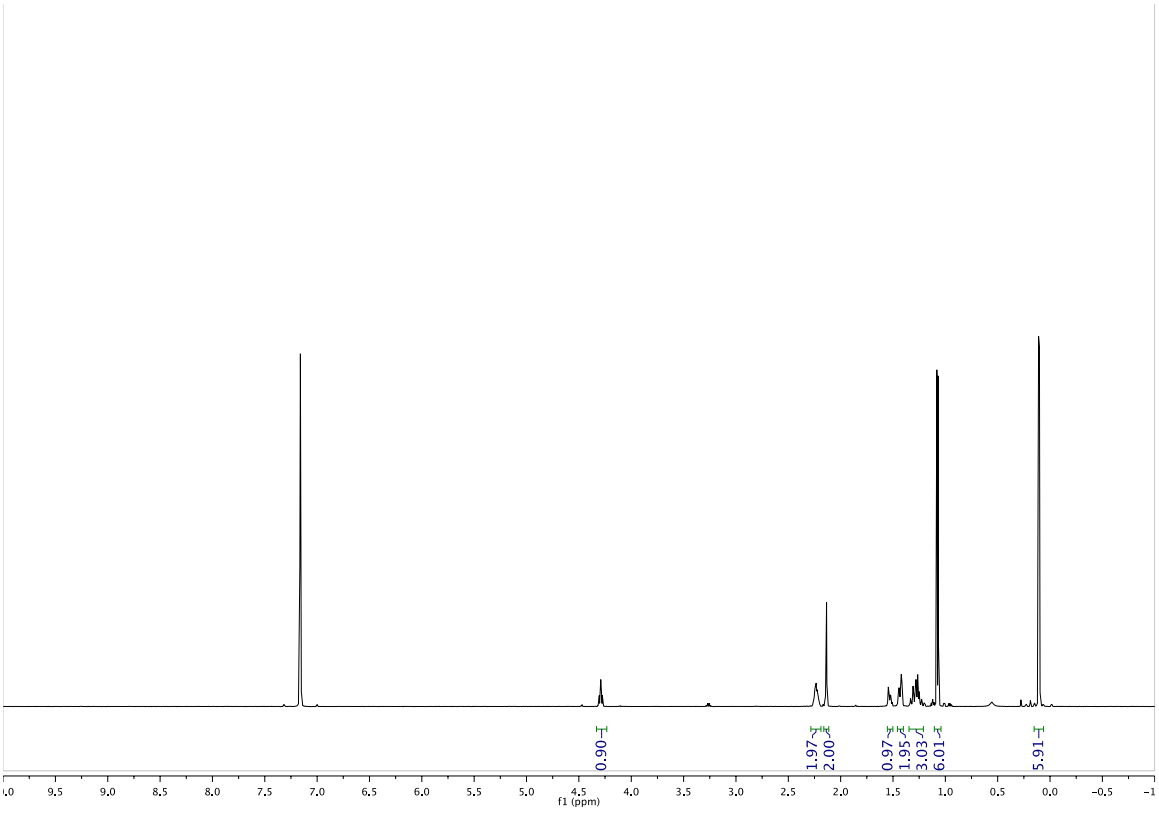

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

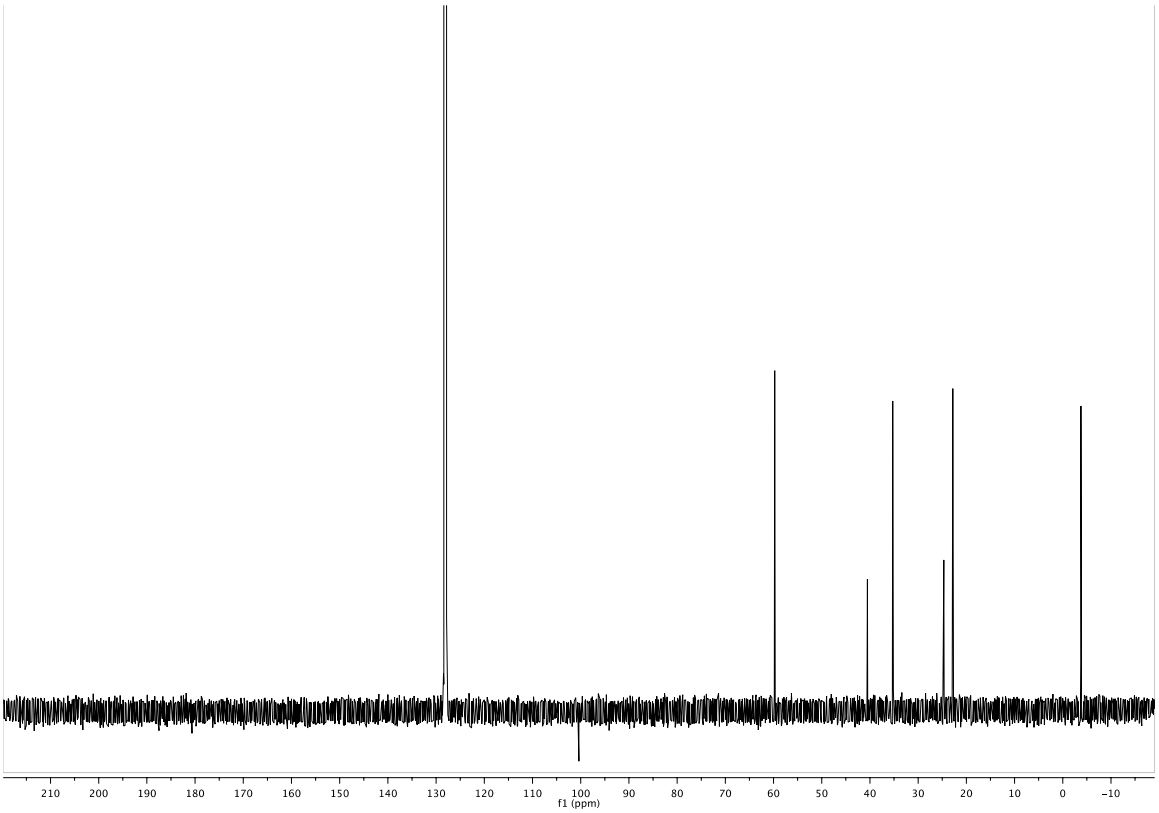

N
SiMe2H
Me

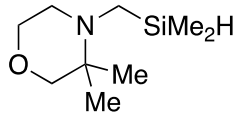

0.81
1.02
1.03
2.01
5.18
1.02
1.03
3.14
2.93
3.00
f1 (ppm)

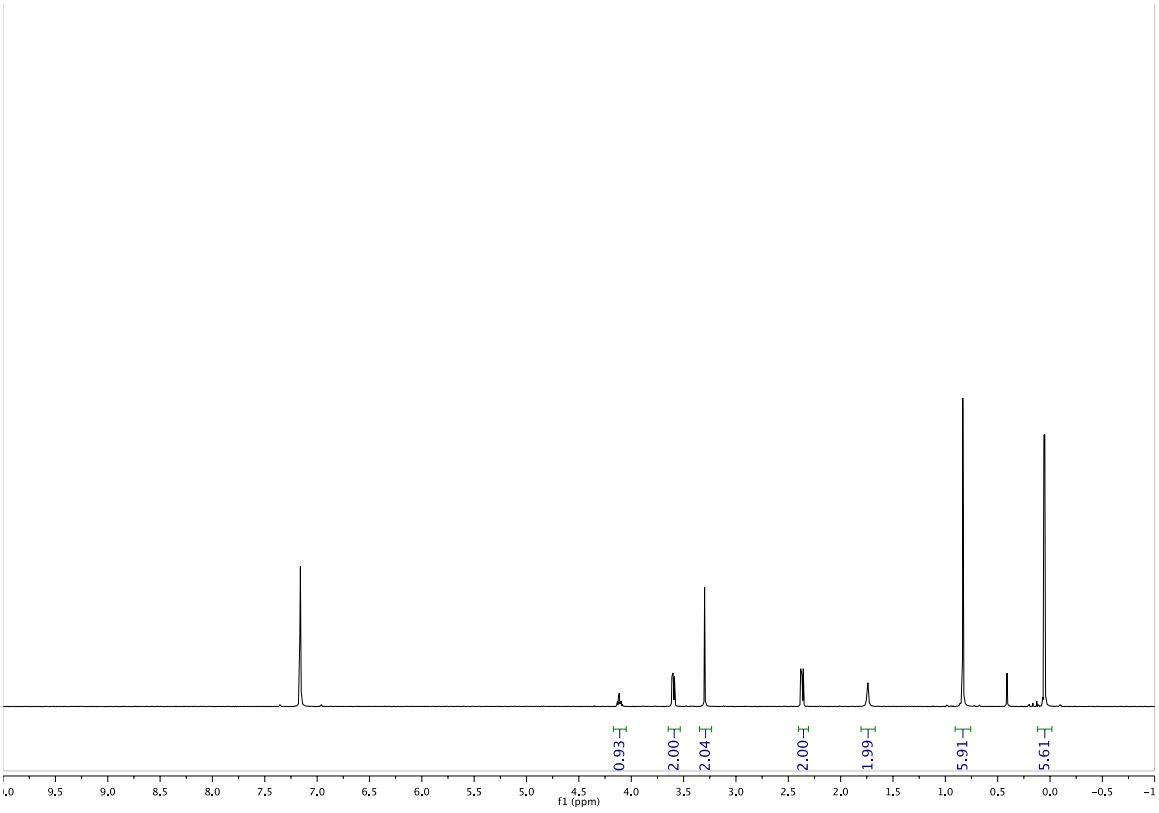

f1 (ppm)

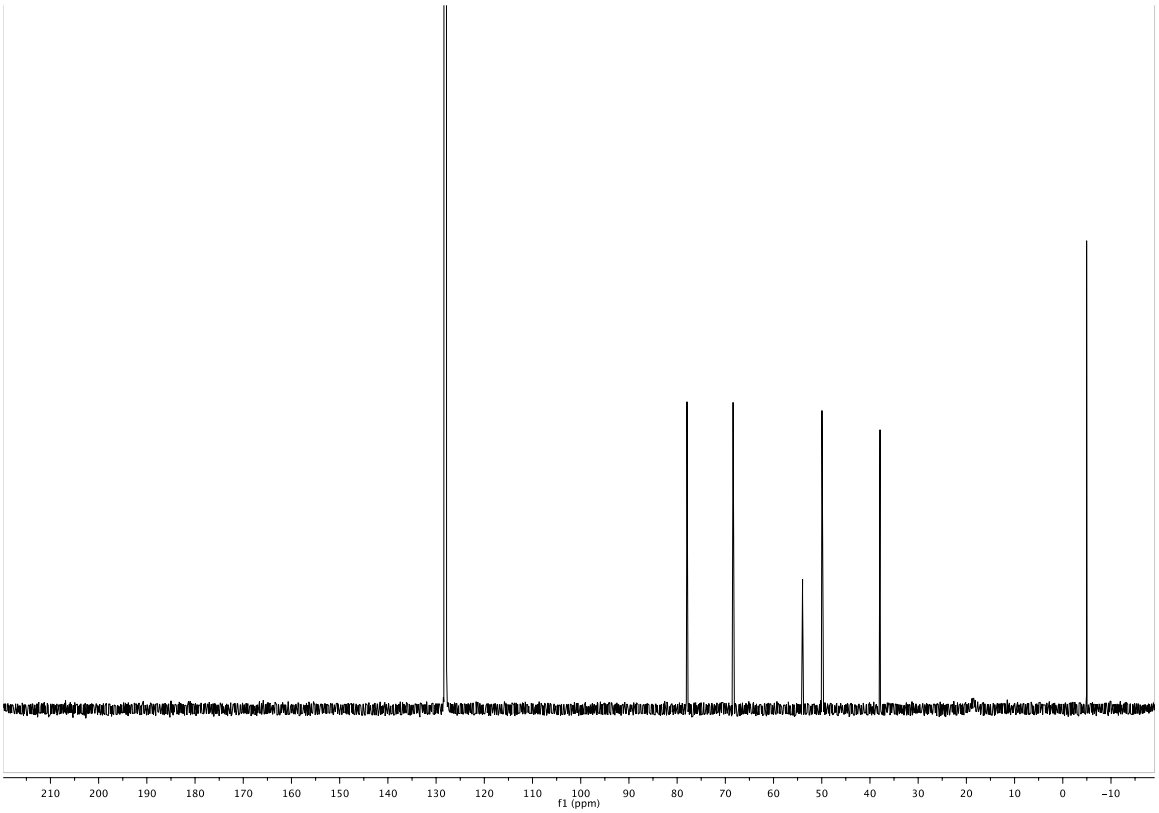

SiMe2H
Me
N
Me

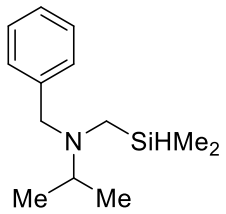

0.90
1.97
2.00
0.97
1.95
3.03
6.01
5.91
f1 (ppm)

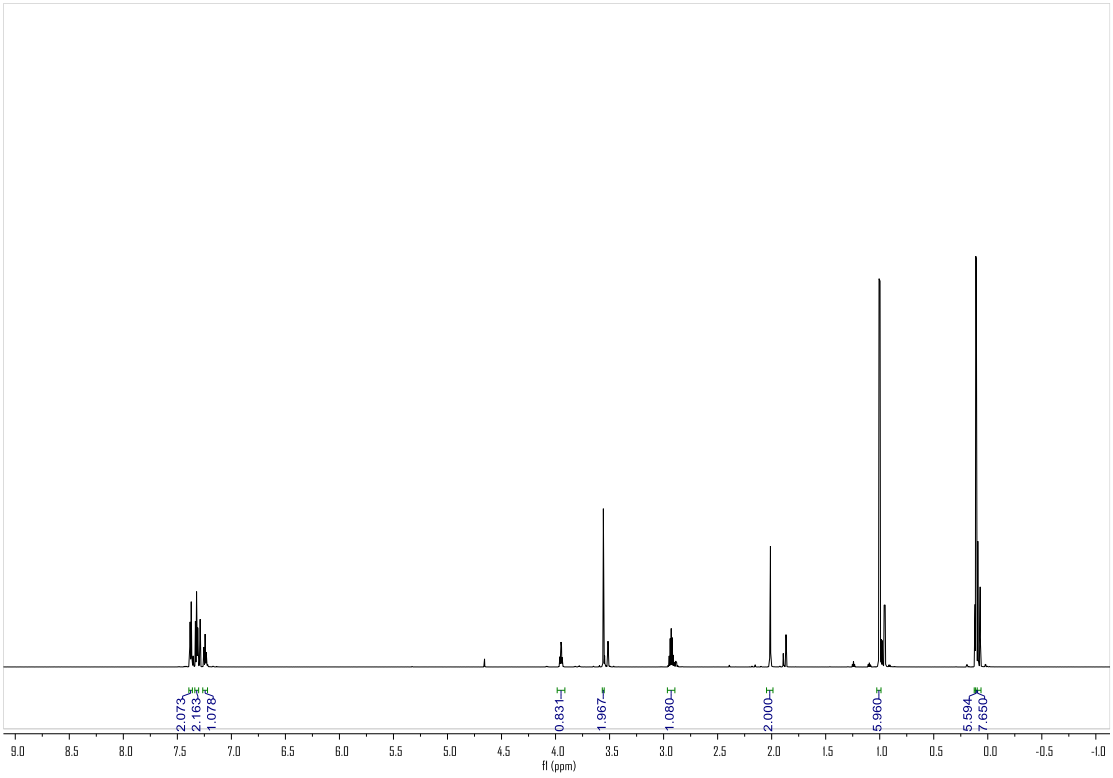

f1 (ppm)

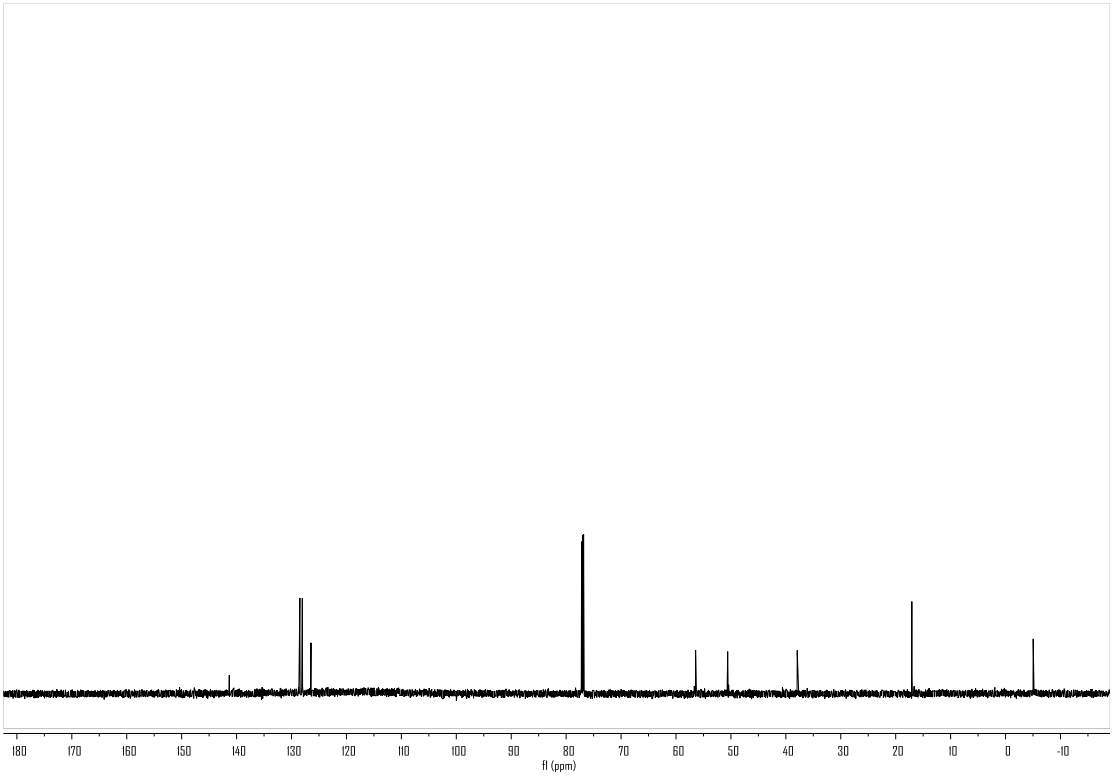

N
SiMe2H
O
Me
Me

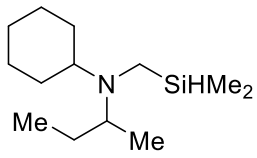

0.93
2.00
2.04
2.00
1.99
5.91
5.61
f1 (ppm)

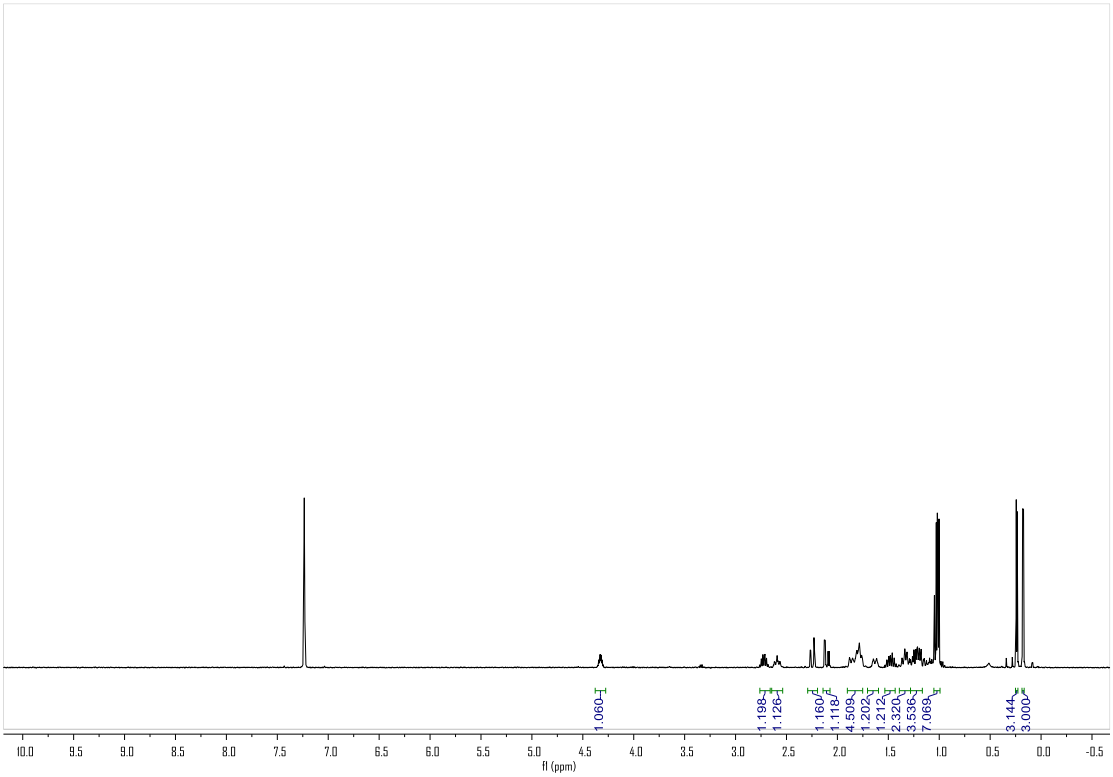

f1 (ppm)

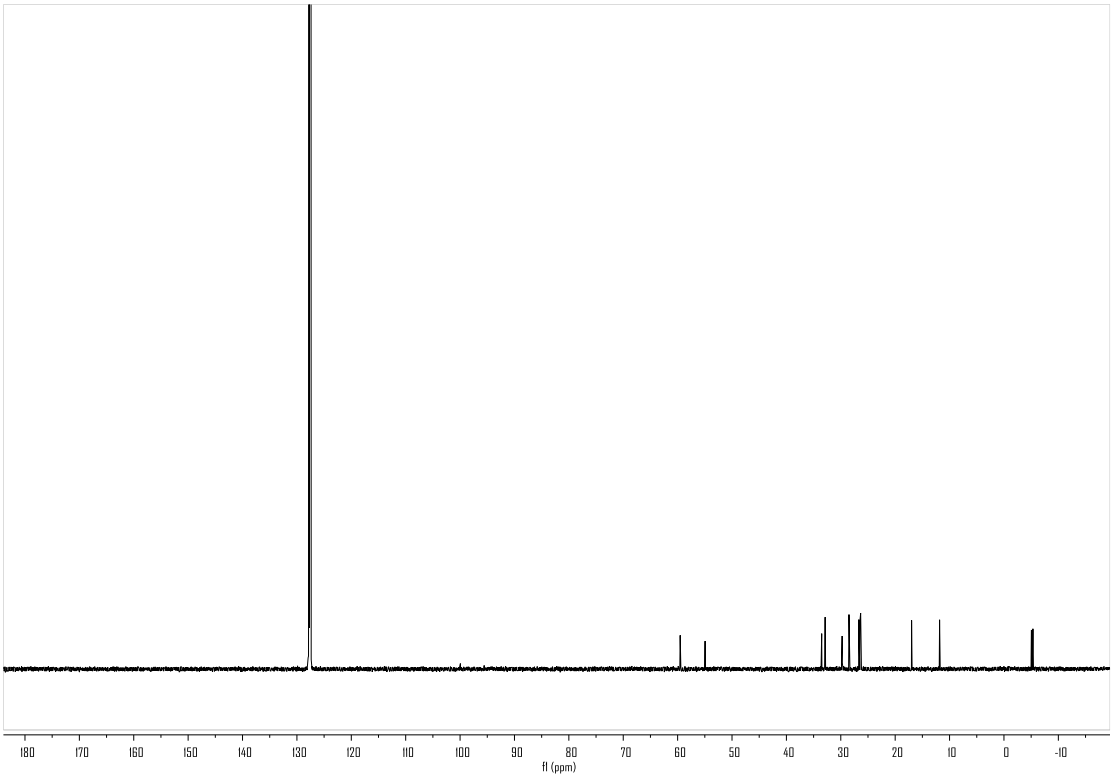

N
SiHMe2
Me
Me

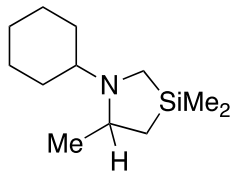

2.073
2.163
1.078
0.831
1.967
1.080
2.000
5.960
5.594
7.650
f1 (ppm)

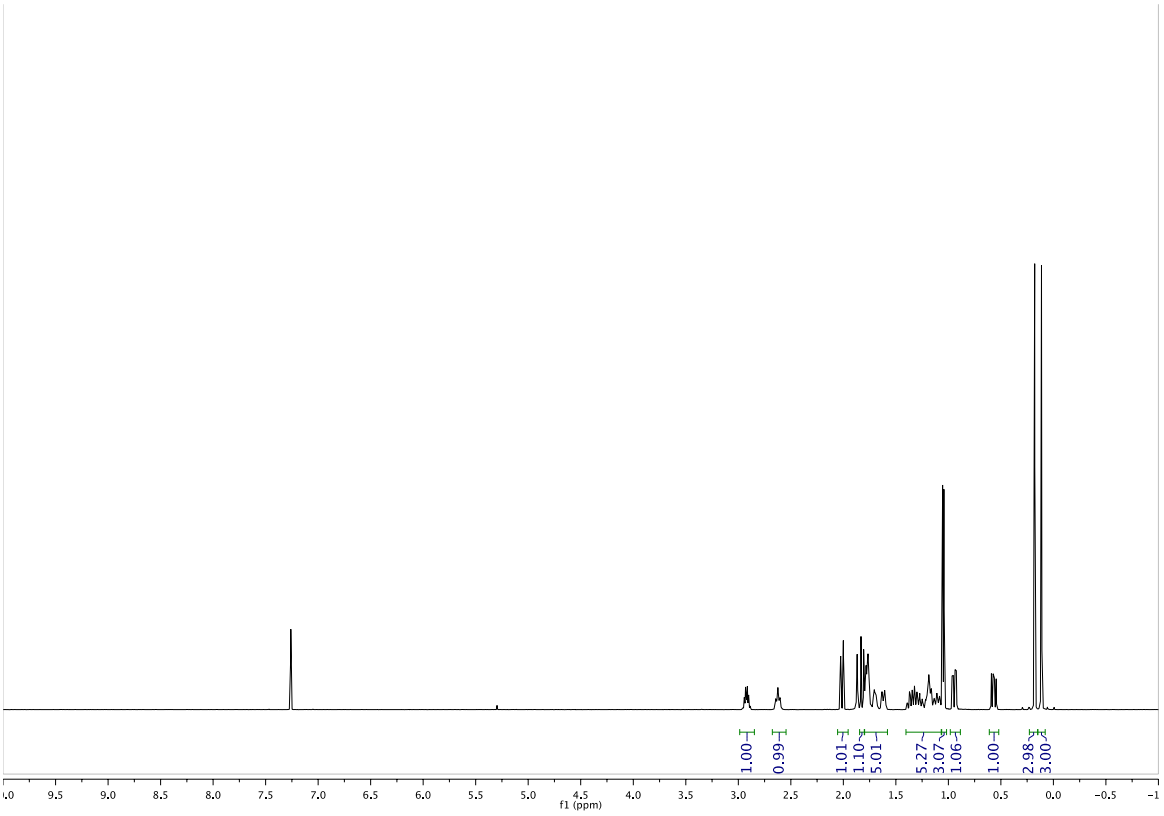

f1 (ppm)

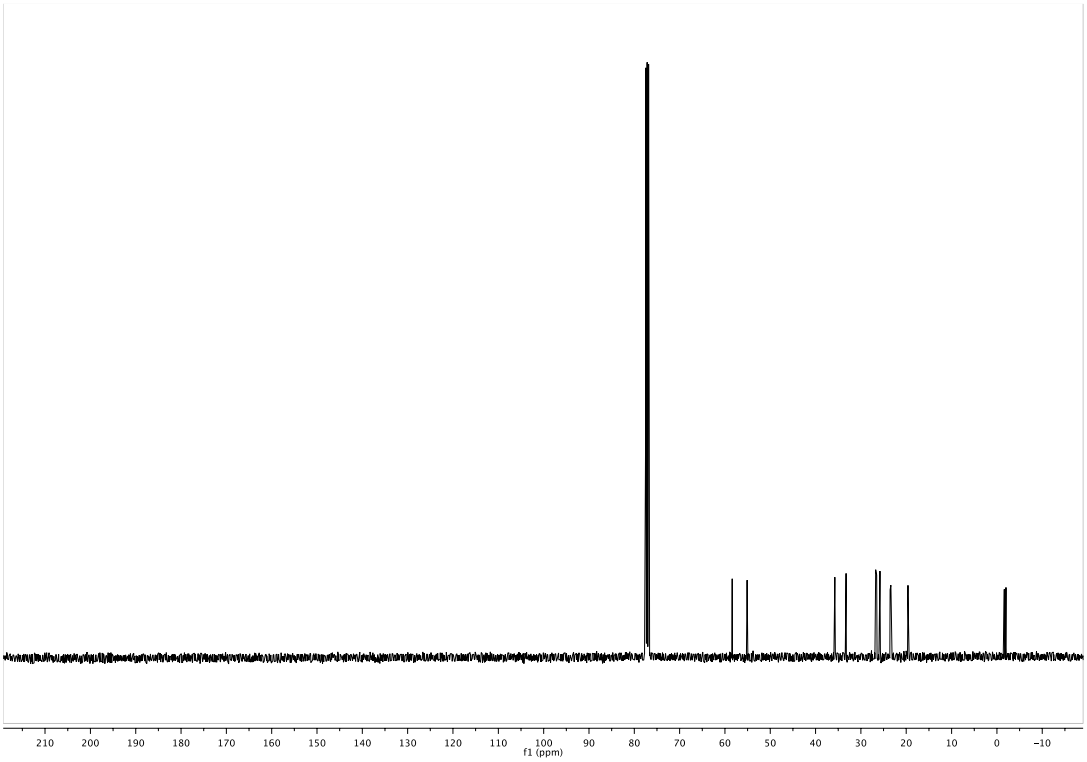

N
SiHMe2
Me
Me

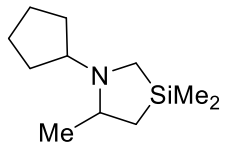

1.060
1.198
1.126
1.160
1.118
4.509
1.202
1.212
2.320
3.536
7.069
3.144
3.000
f1 (ppm)

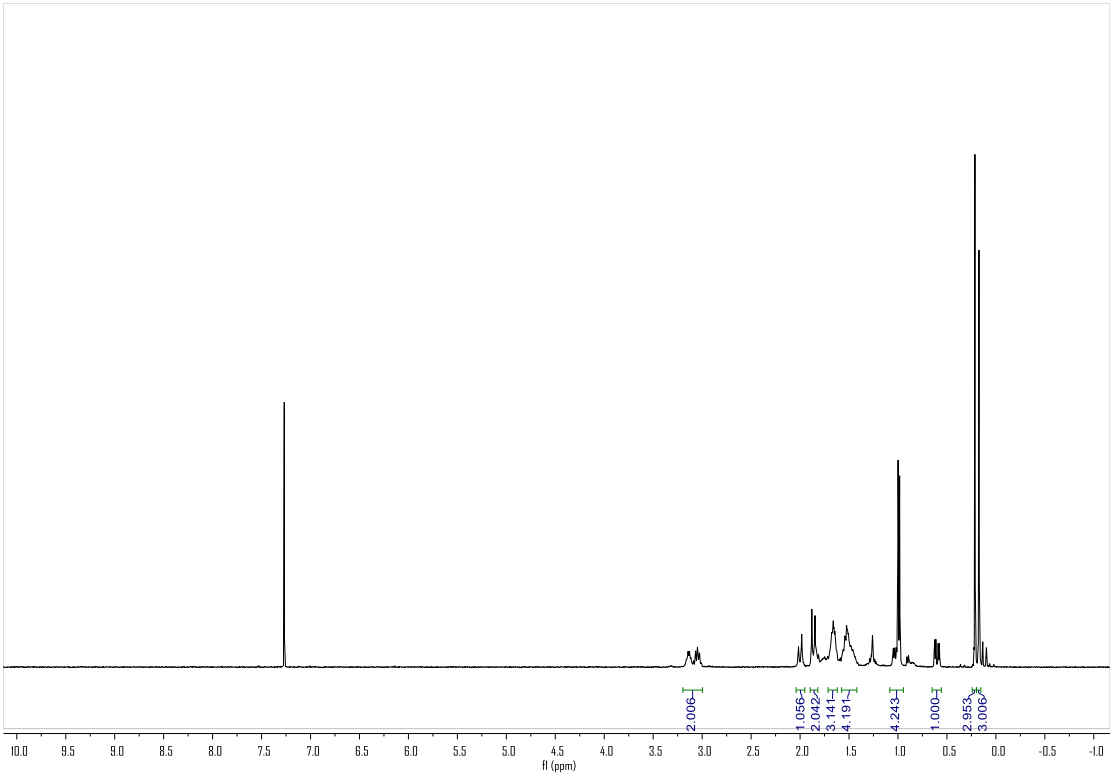

f1 (ppm)

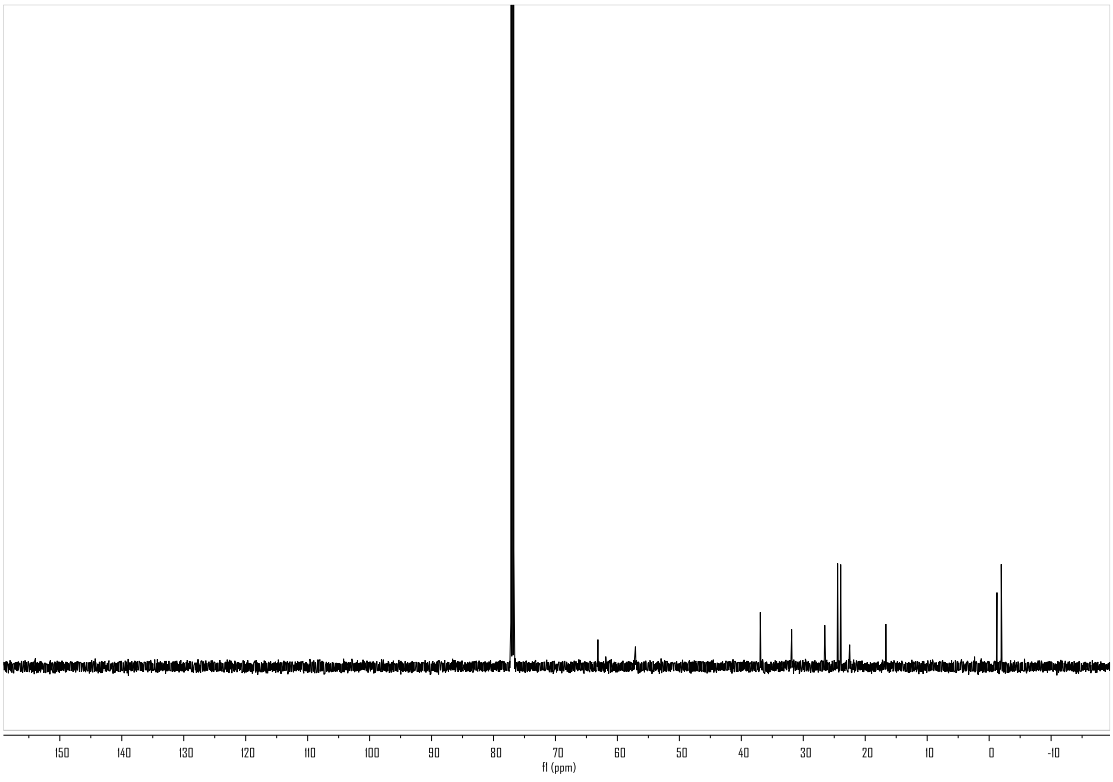

N
SiMe2
Me
H

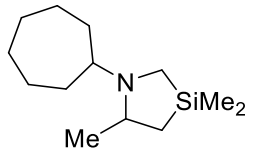

1.00
0.99
1.01
1.10
5.01
5.27
3.07
1.06
1.00
2.98
3.00
f1 (ppm)

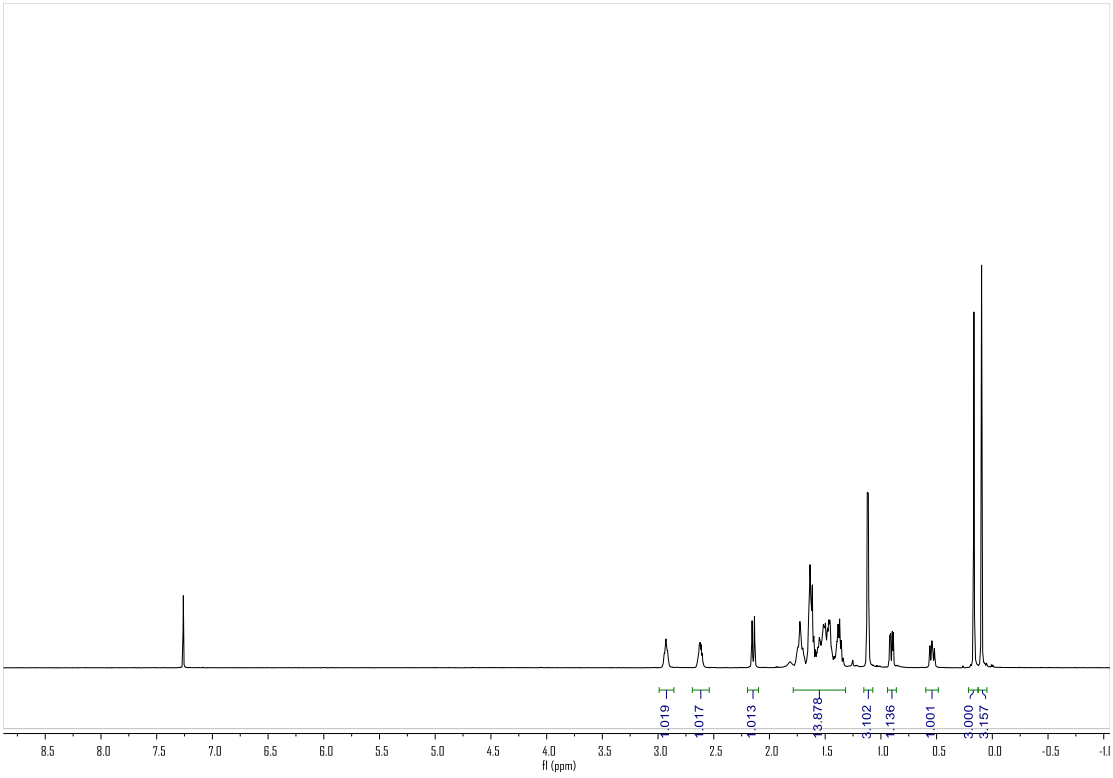

f1 (ppm)

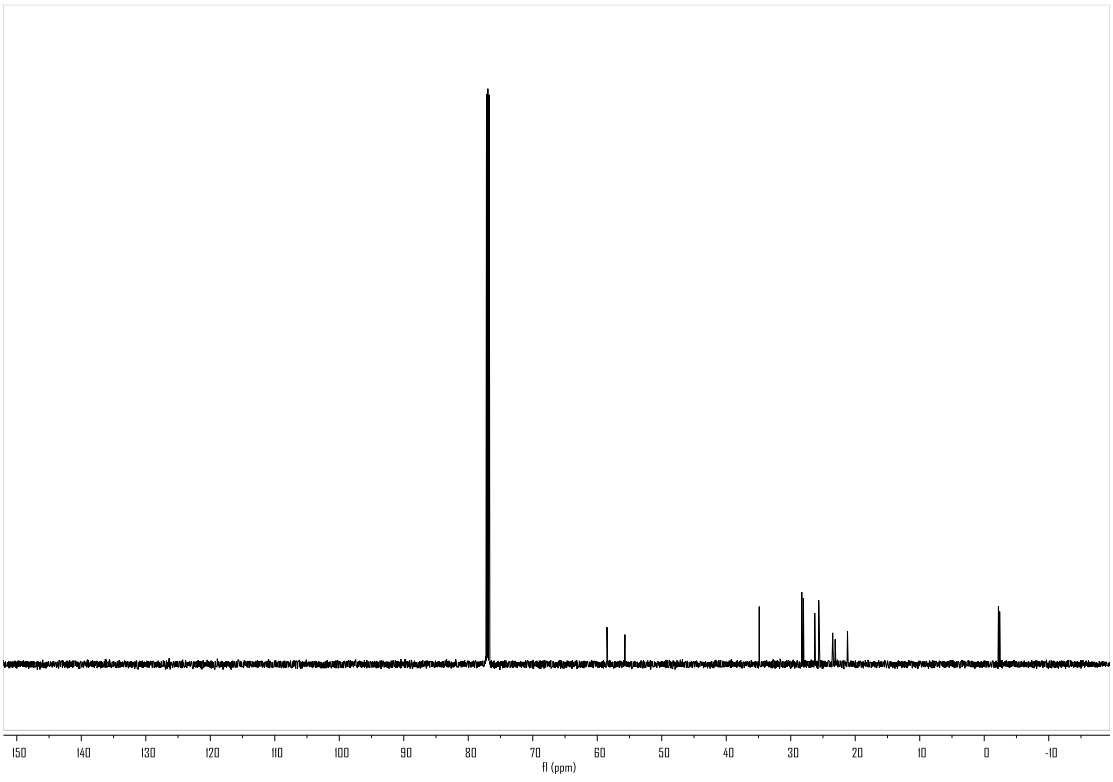

N
SiMe2
Me

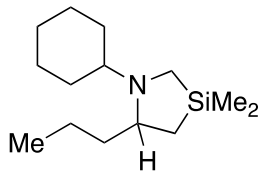

2.006
1.056
2.042
3.141
4.191
4.243
1.000
2.953
3.006
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

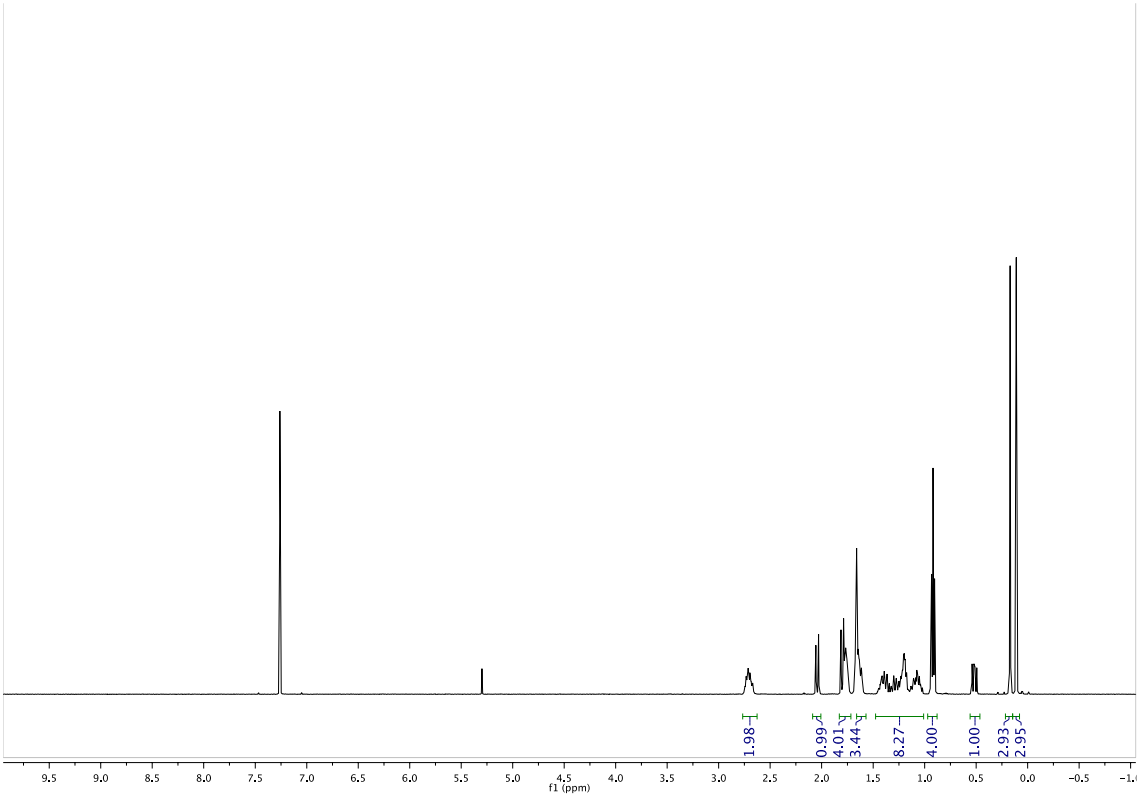

150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

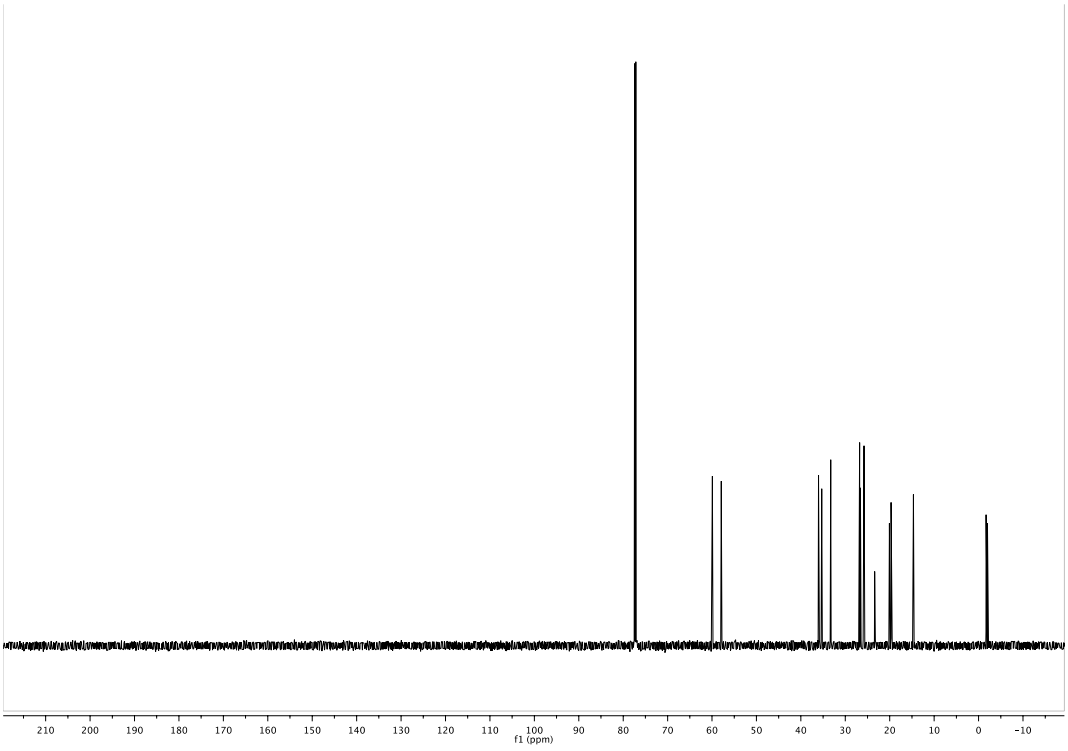

N
SiMe2
Me

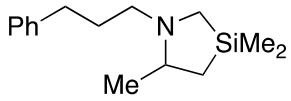

1.019
1.017
1.013
13.878
3.102
1.136
1.001
3.000
3.157
f1 (ppm)

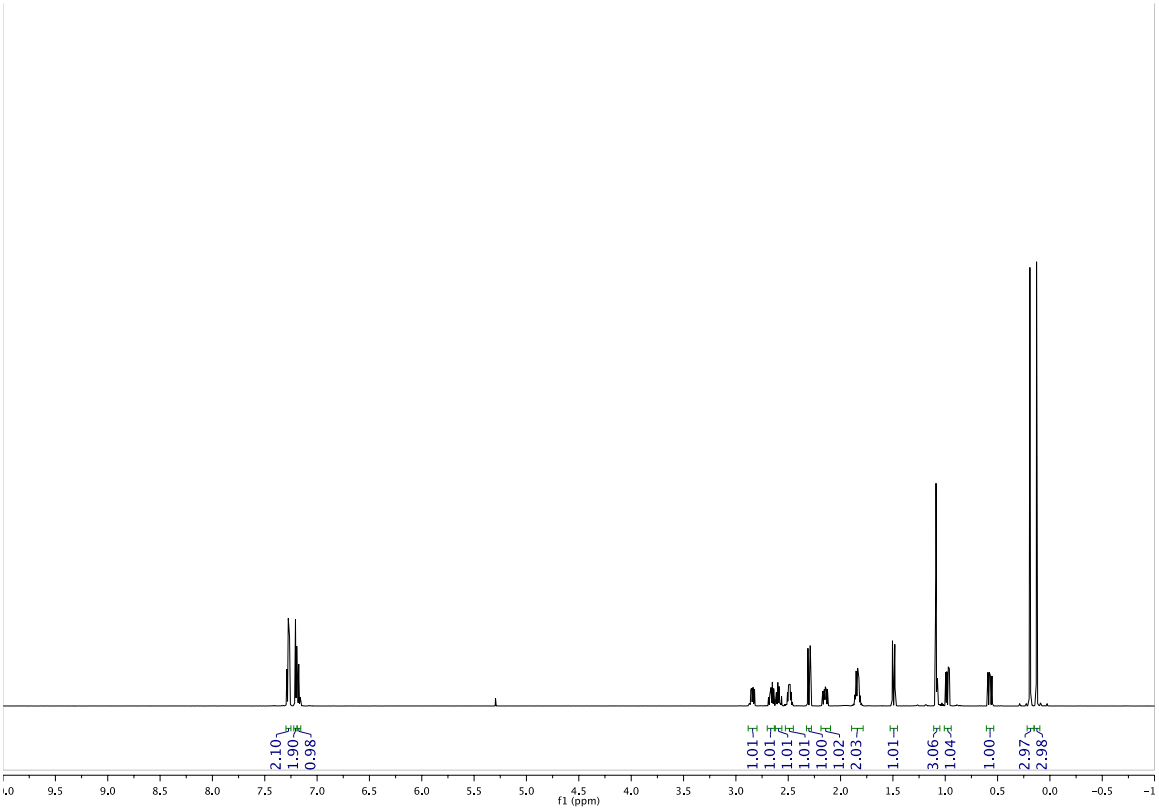

f1 (ppm)

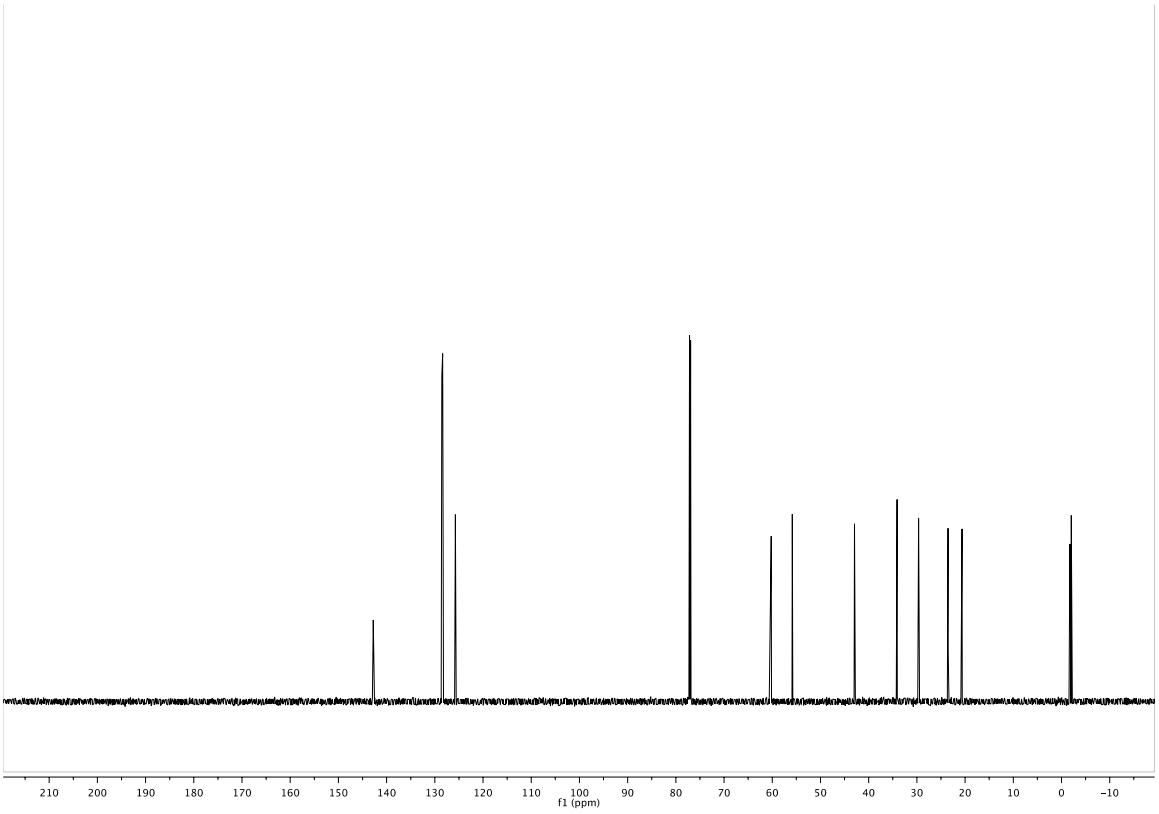

N
SiMe2
Me
H

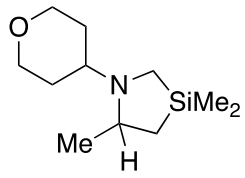

1.98
0.99
4.01
3.44
8.27
4.00
1.00
2.93
2.95
f1 (ppm)

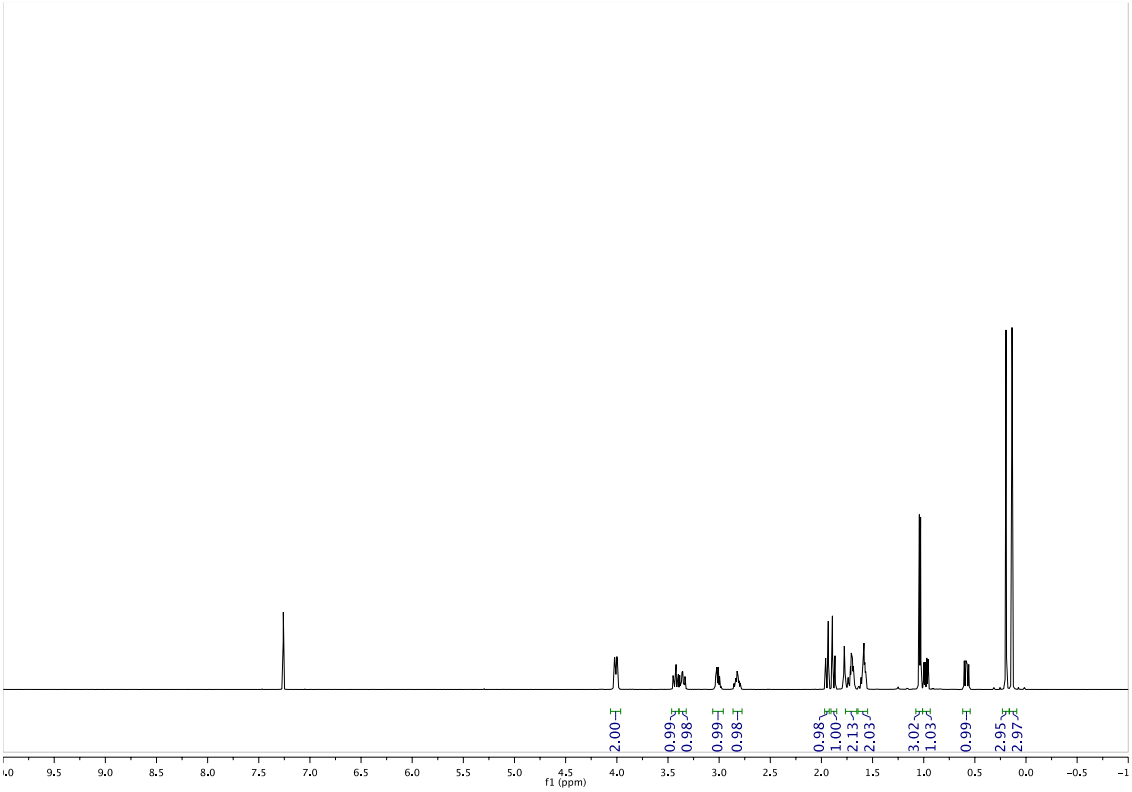

f1 (ppm)

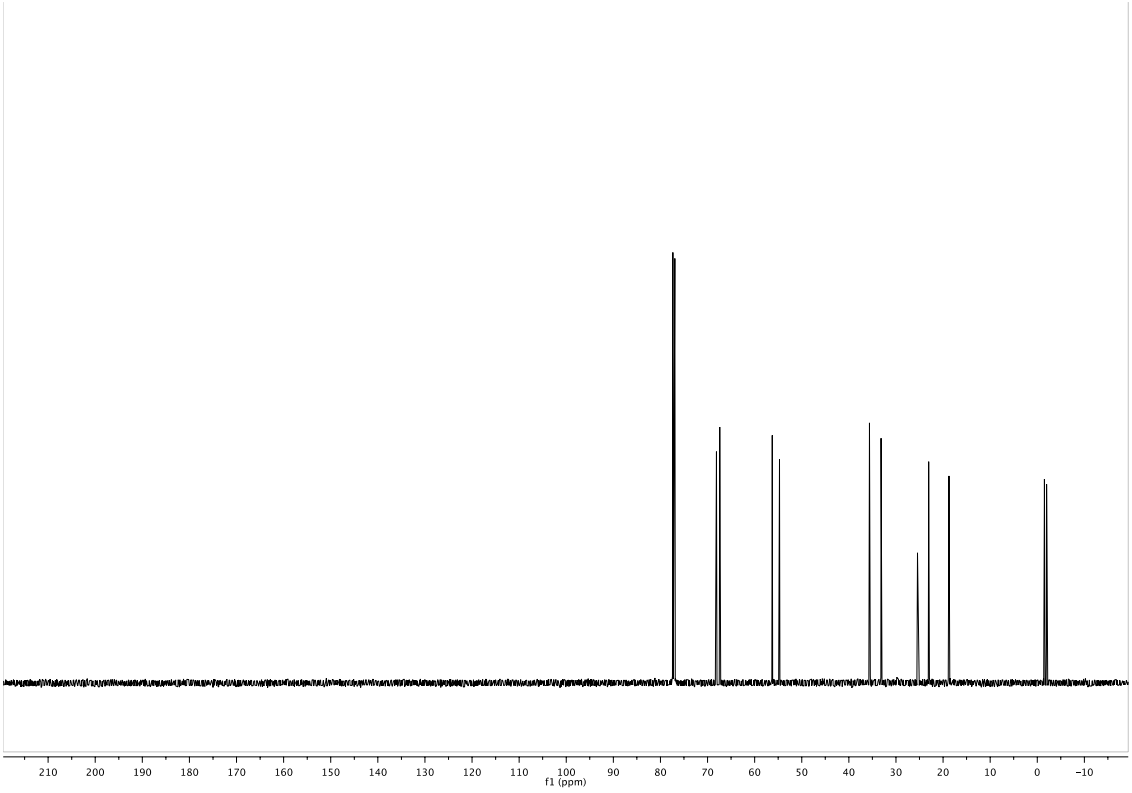

Ph
N
SiMe2
Me

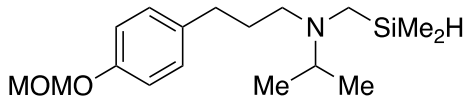

2.10
1.90
0.98
1.01
1.01
1.01
1.01
1.00
1.02
2.03
1.01
3.06
1.04
1.00
2.97
2.98
f1 (ppm)

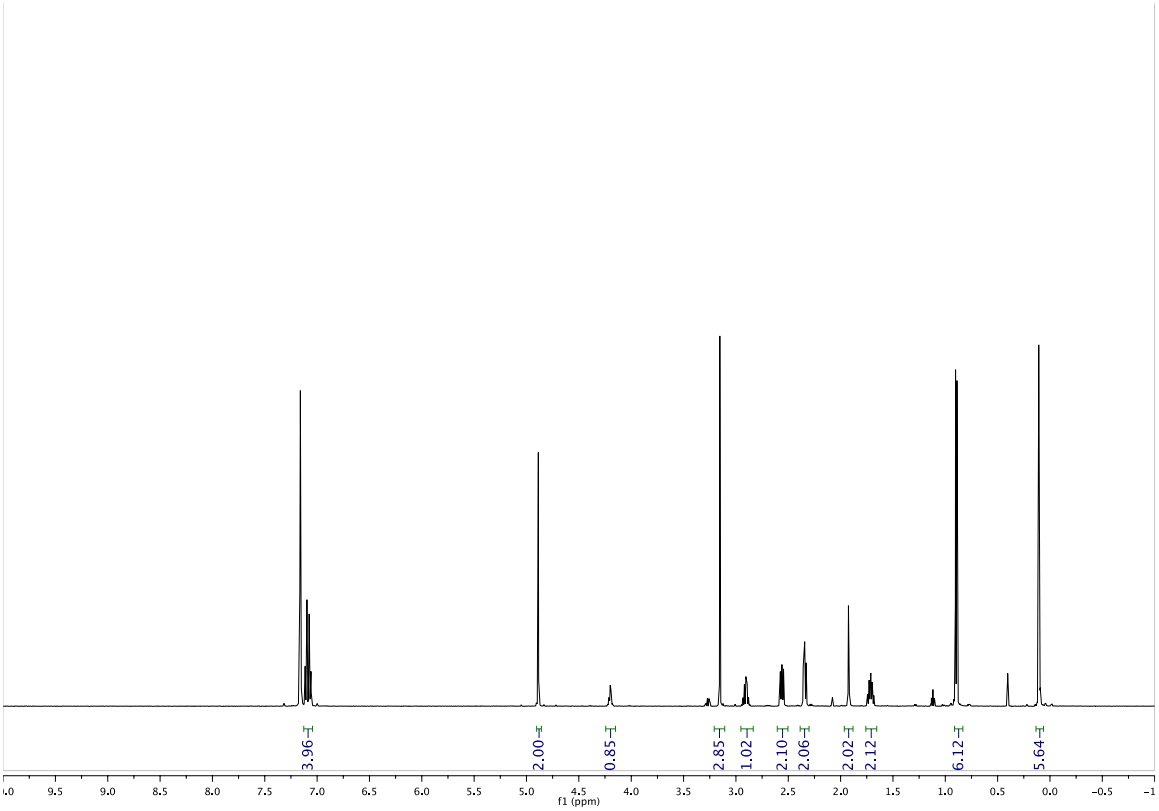

f1 (ppm)

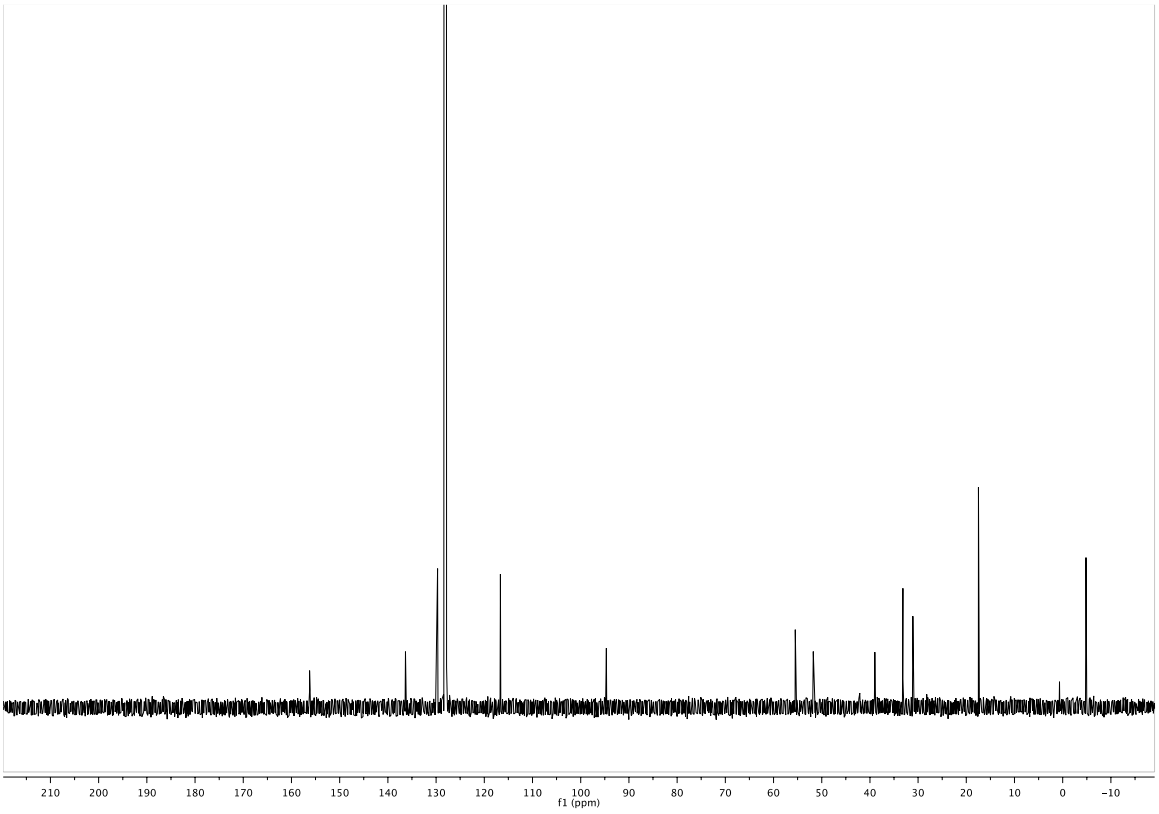

O
N
SiMe2
Me
H

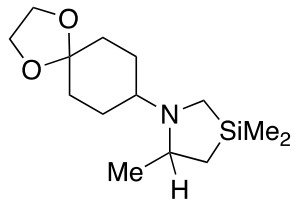

2.00
0.99
0.98
0.99
0.98
0.98
1.00
2.13
2.03
3.02
1.03
0.99
2.95
2.97
f1 (ppm)

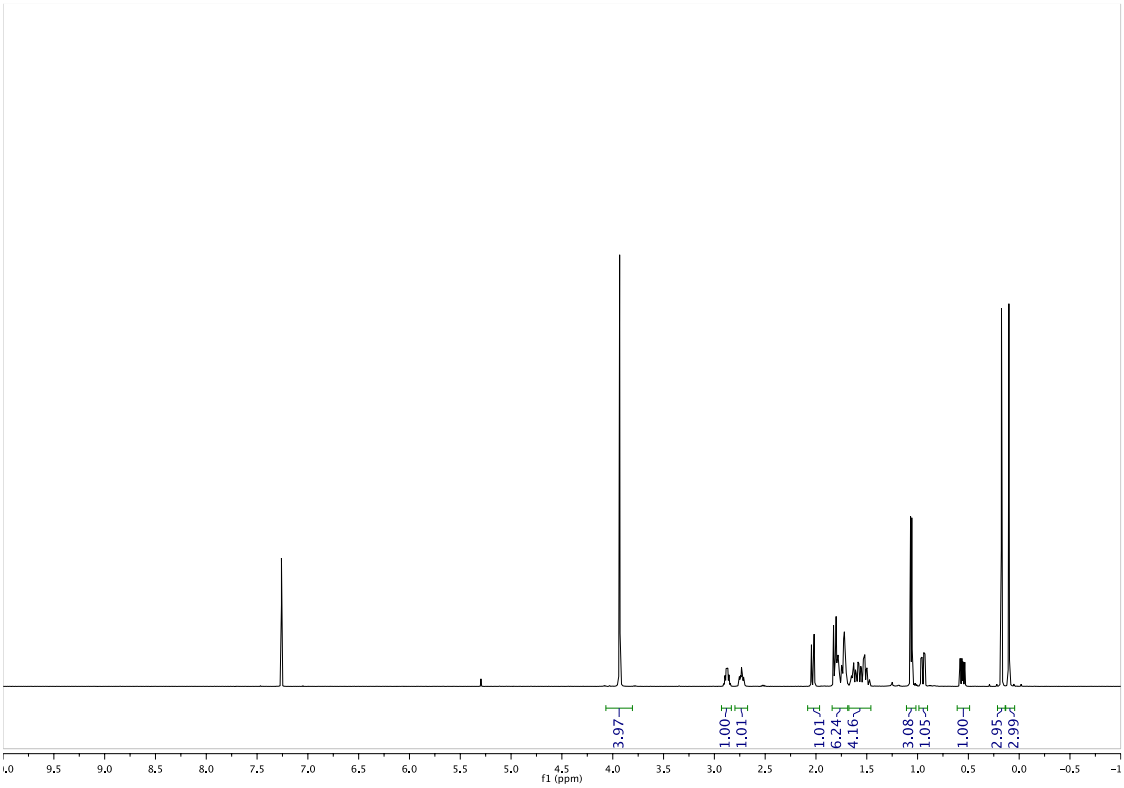

f1 (ppm)

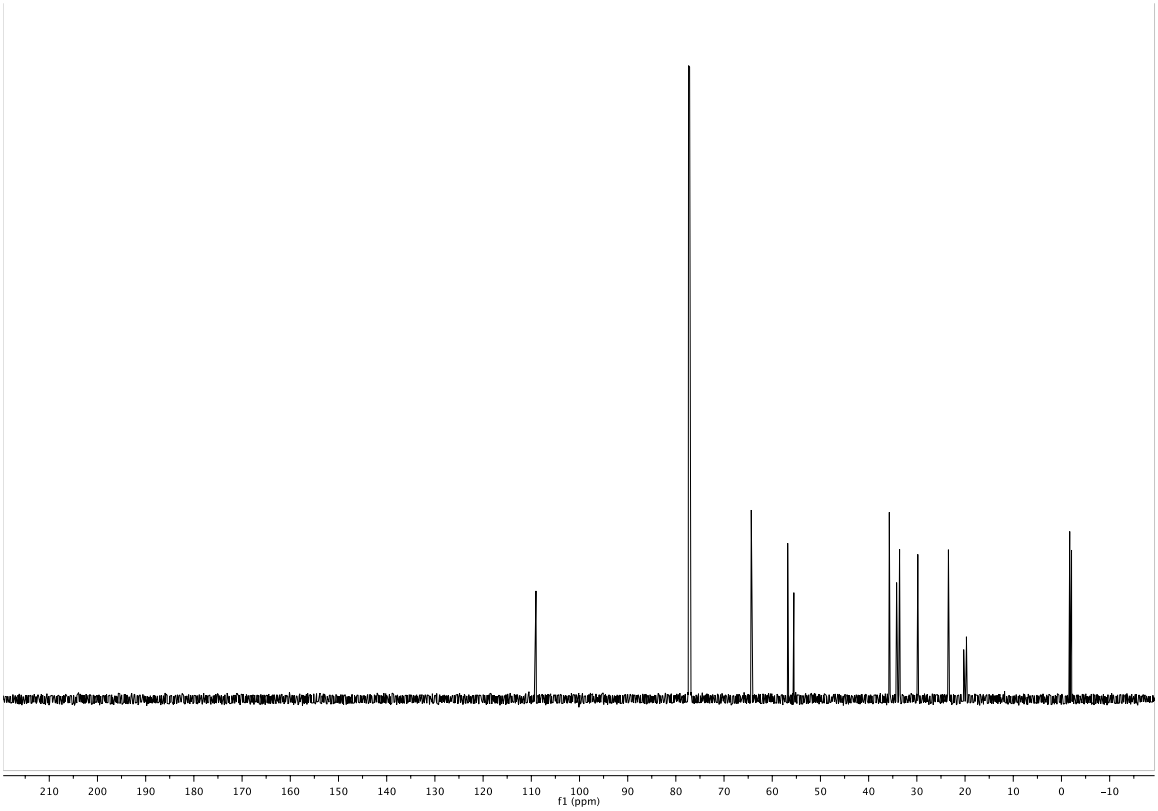

MOMO
N
SiMe2H
Me
Me

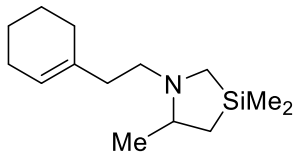

3.96
2.00
0.85
2.85
1.02
2.10
2.06
2.02
2.12
6.12
5.64
f1 (ppm)

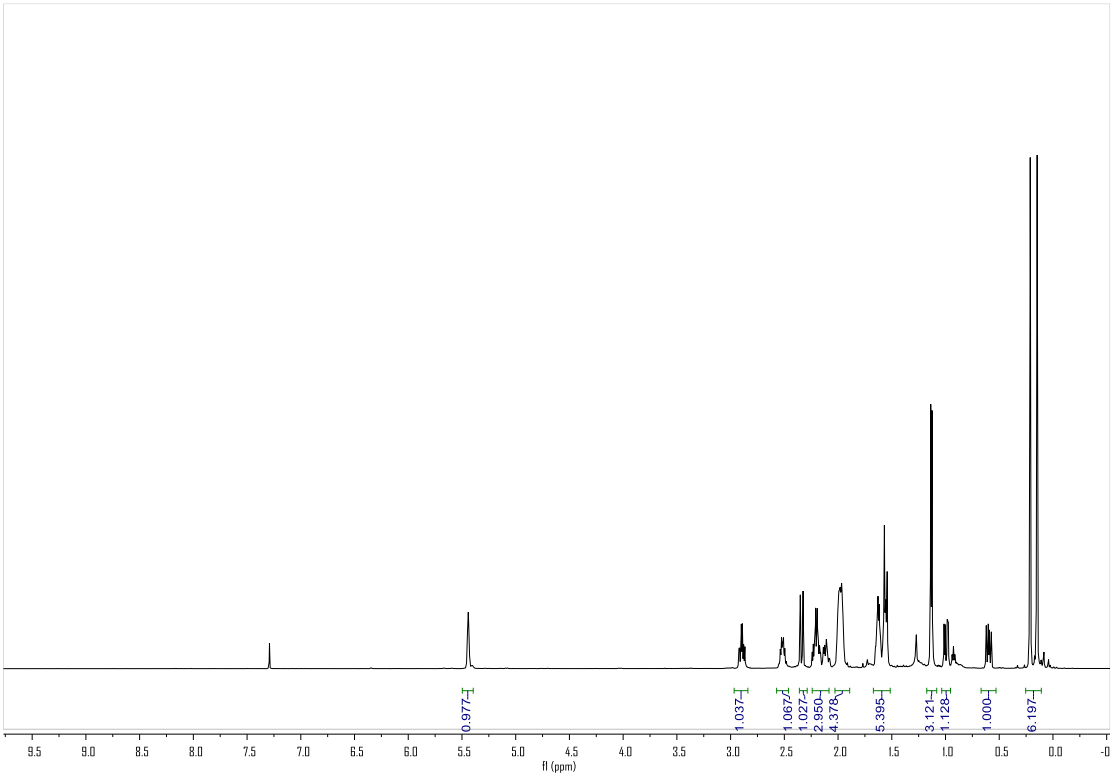

f1 (ppm)

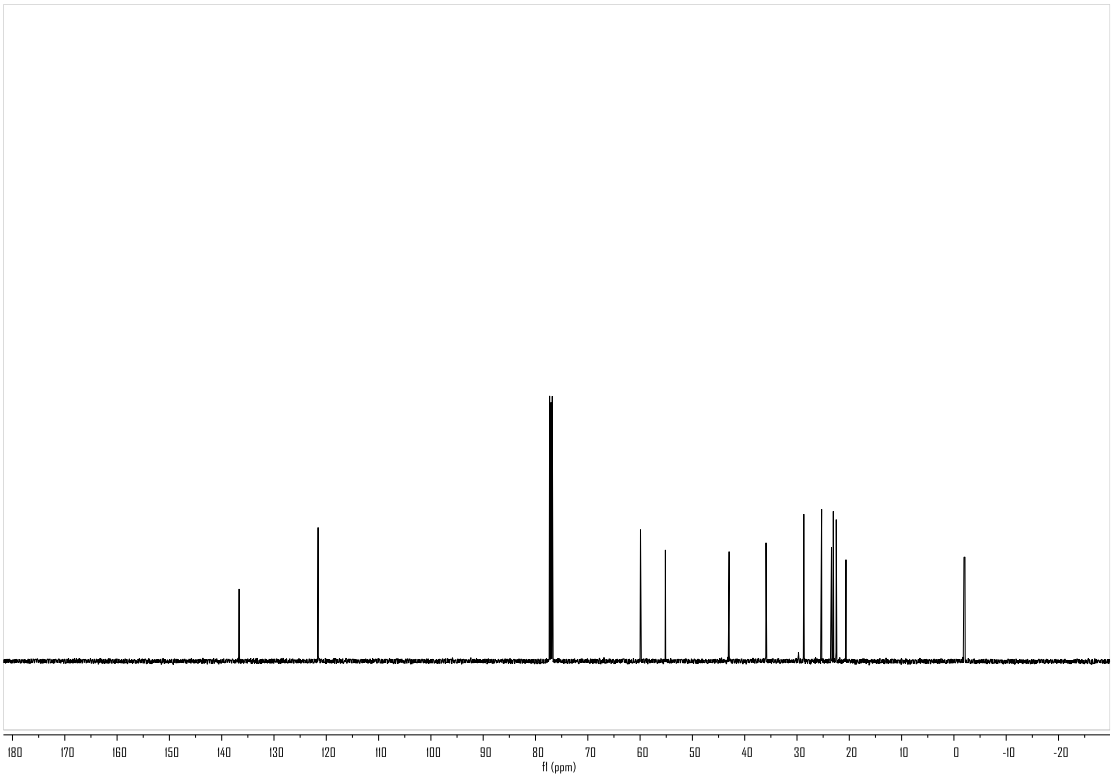

O
O
N
SiMe2
Me
H

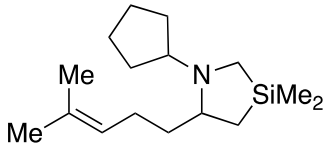

3.97
1.00
1.01
1.01
6.24
4.16
3.08
1.05
1.00
2.95
2.99
f1 (ppm)

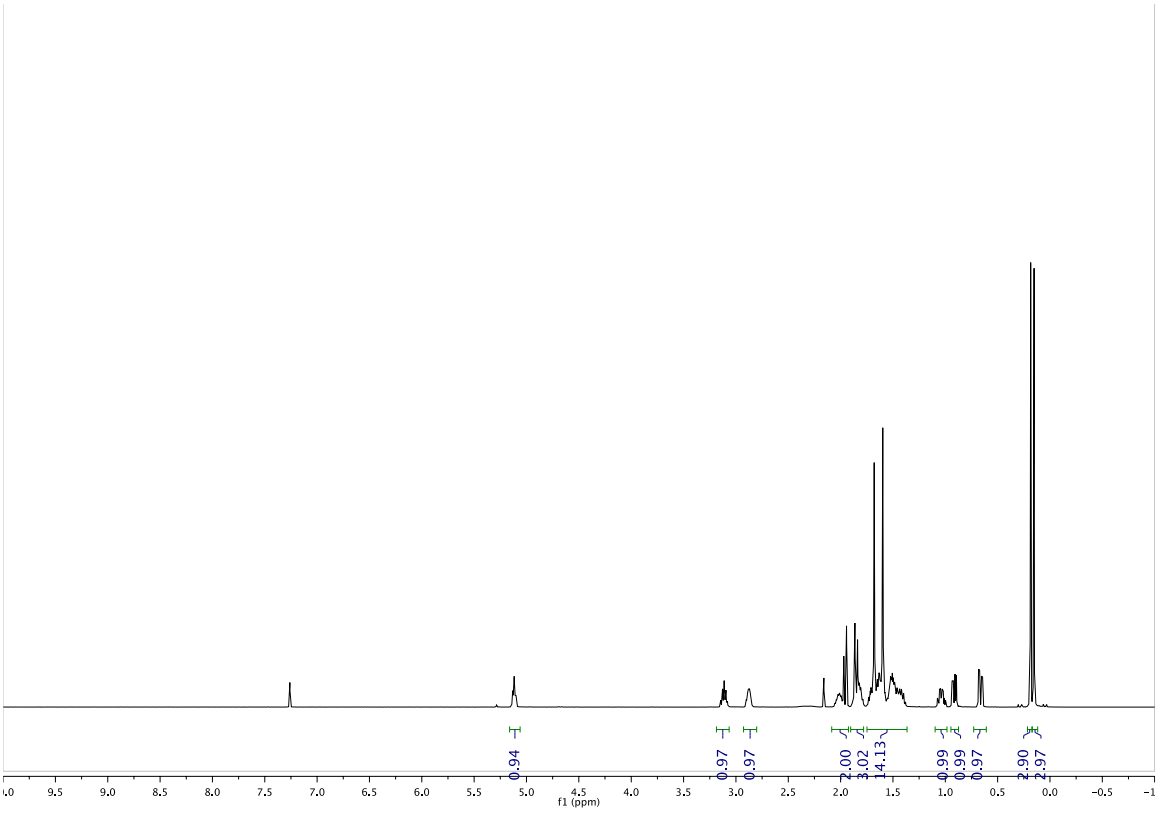

f1 (ppm)

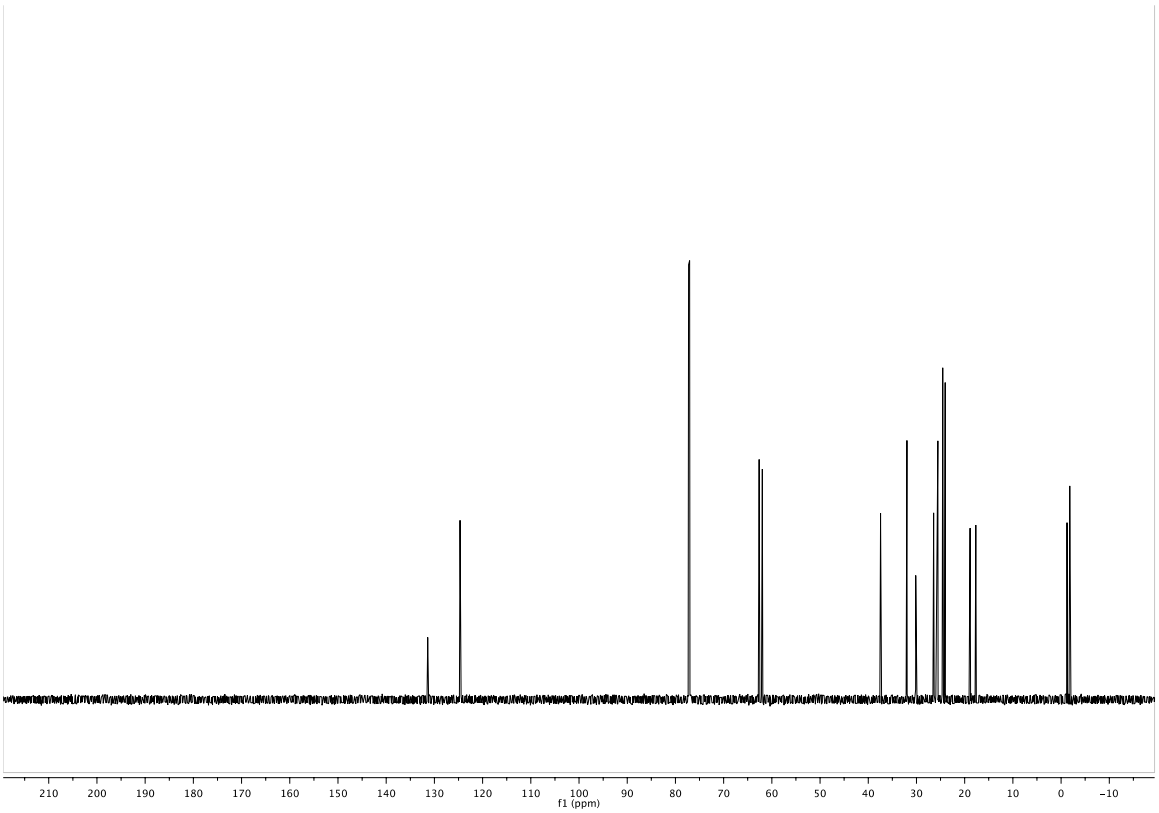

N
SiMe2
Me

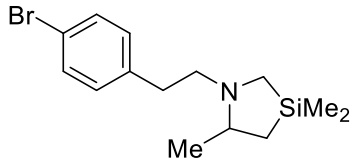

0.977
1.037
1.067
1.027
2.950
4.378
5.395
3.121
1.128
1.000
6.197
f1 (ppm)

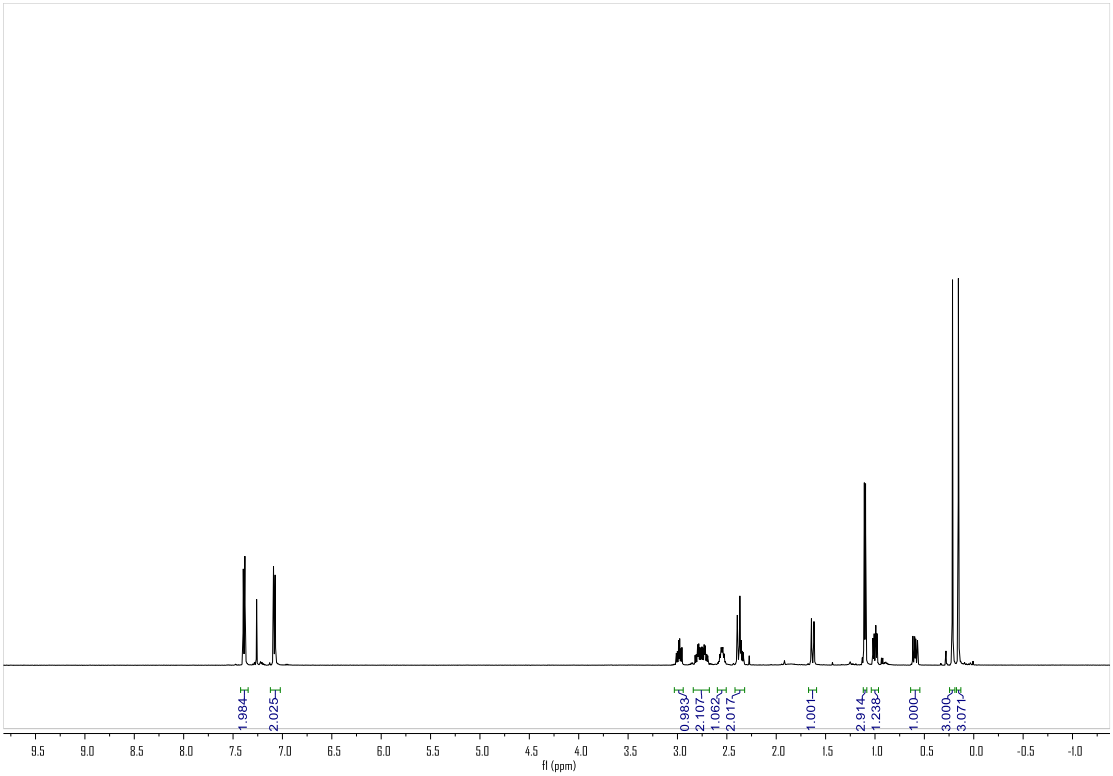

f1 (ppm)

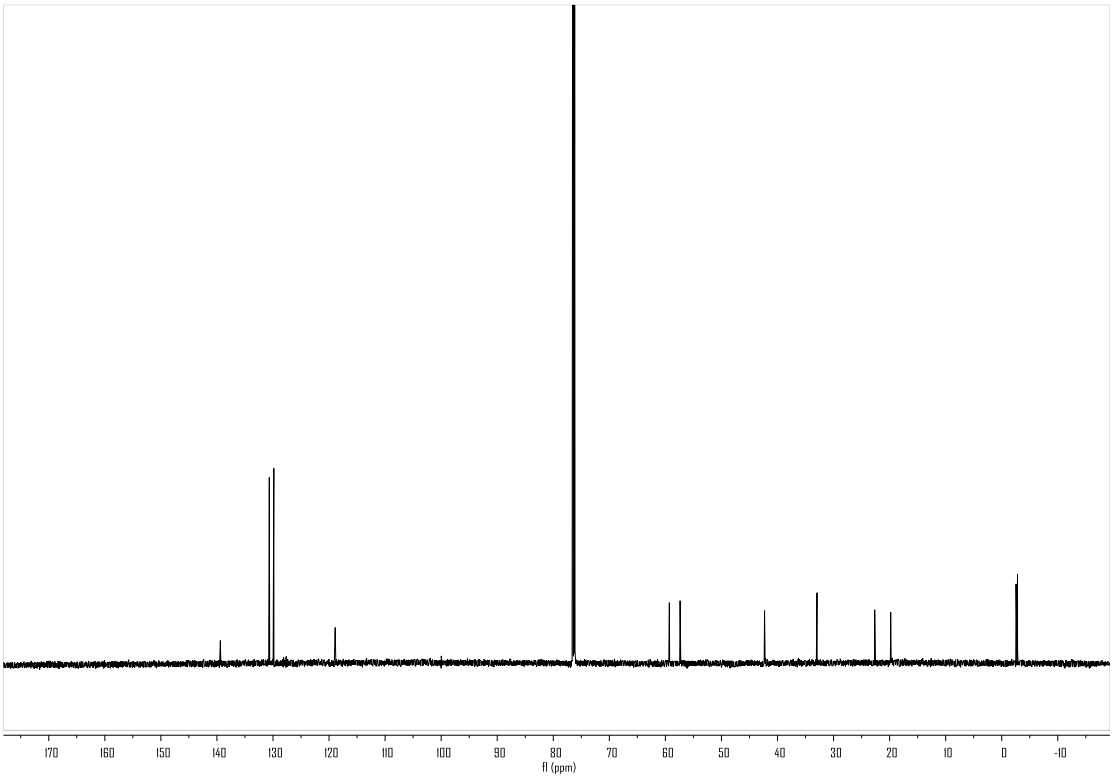

Me
N
SiMe2
Me

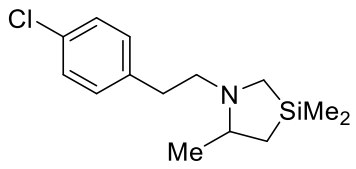

0.94
0.97
0.97
2.00
3.02
14.13
0.99
0.99
0.97
2.90
2.97
f1 (ppm)

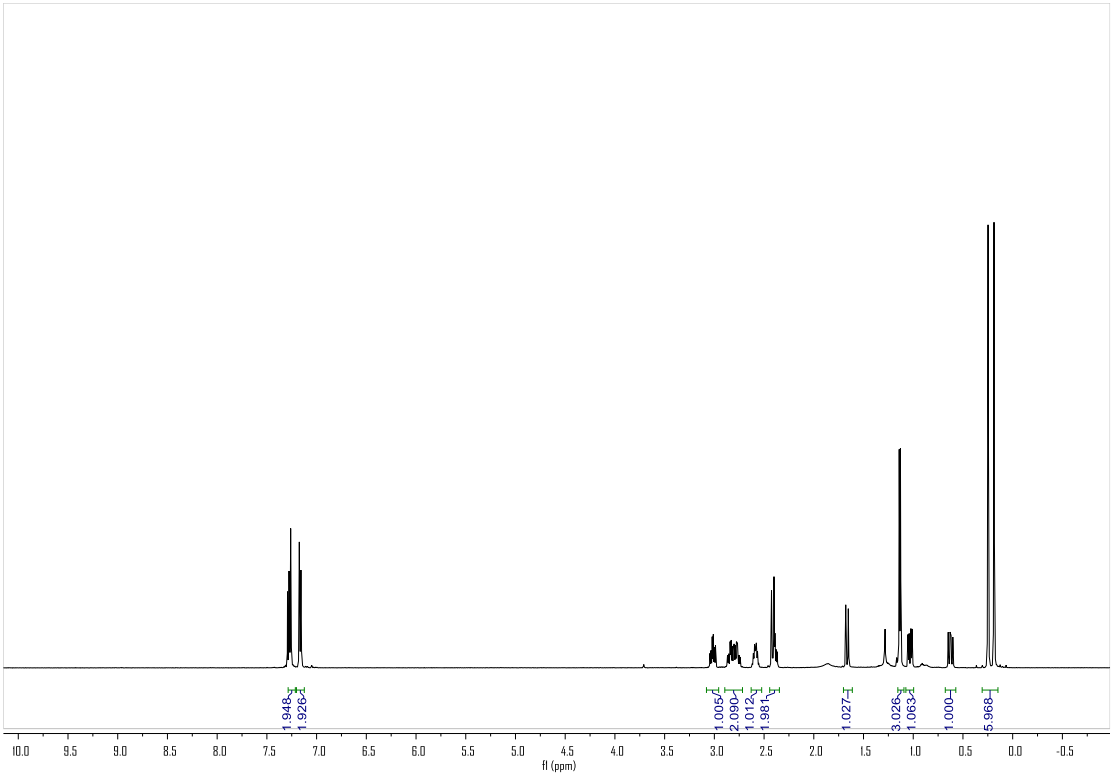

f1 (ppm)

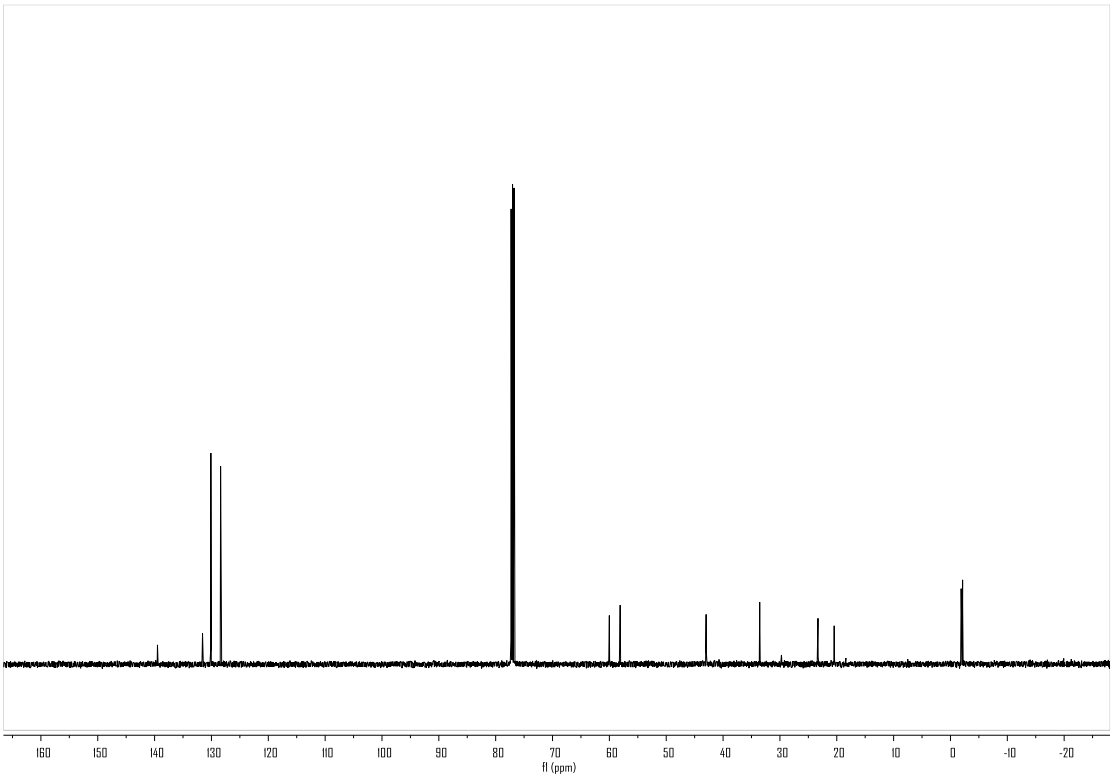

Br
N
SiMe2
Me

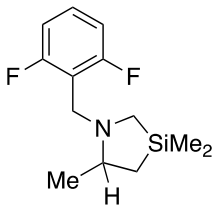

1.984
2.025
0.983
2.107
1.062
2.017
1.001
2.914
1.238
1.000
3.000
3.071
f1 (ppm)

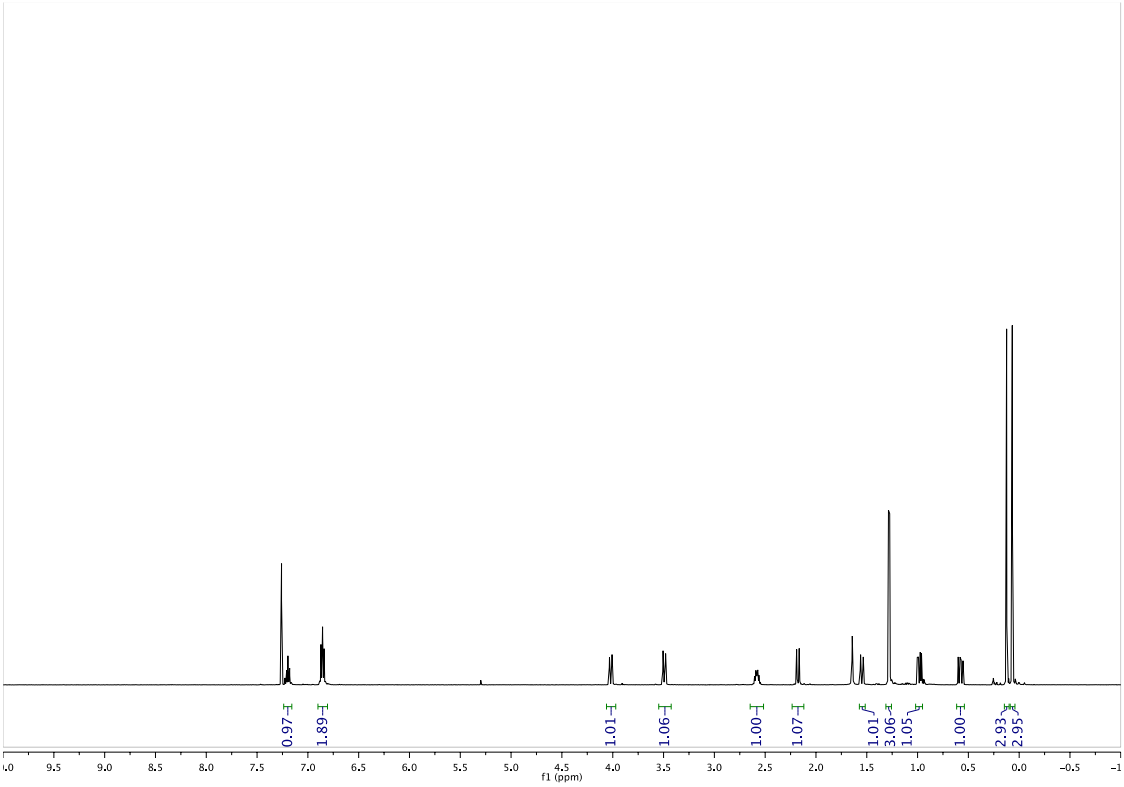

f1 (ppm)

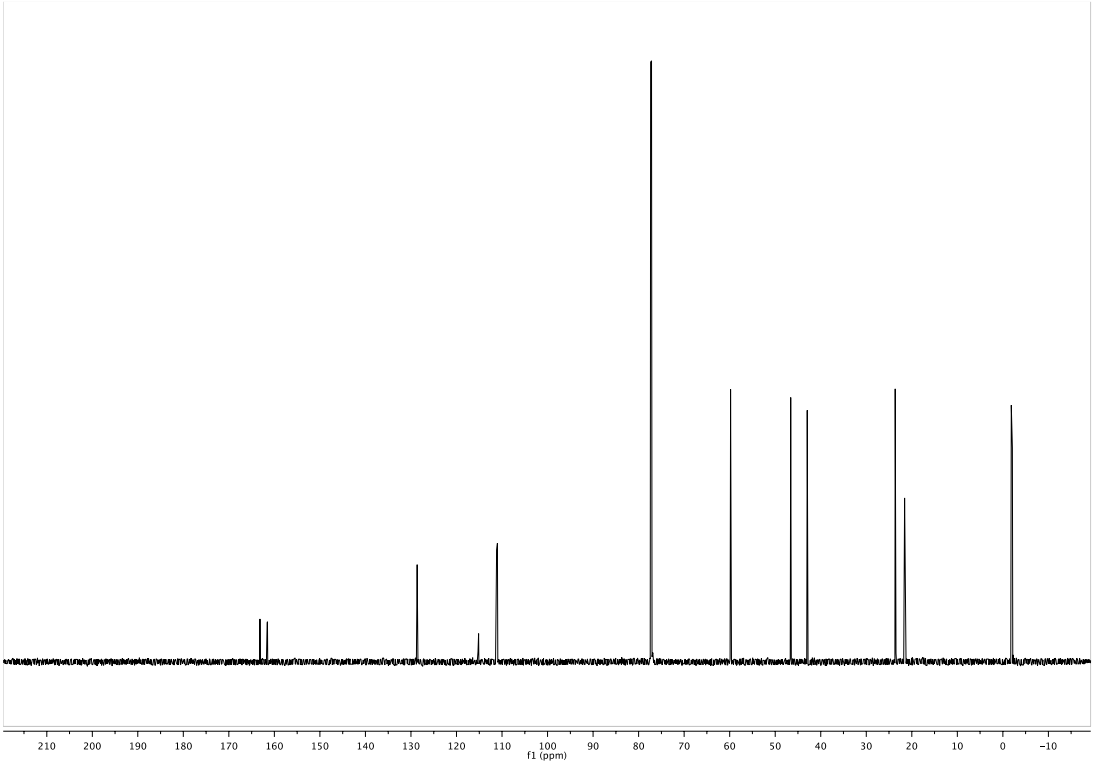

Cl
N
SiMe2
Me

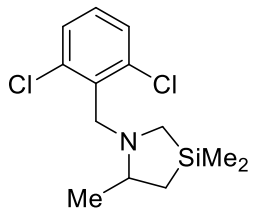

1.948
1.926
1.005
2.090
1.012
1.981
1.027
3.026
1.063
1.000
5.968
f1 (ppm)

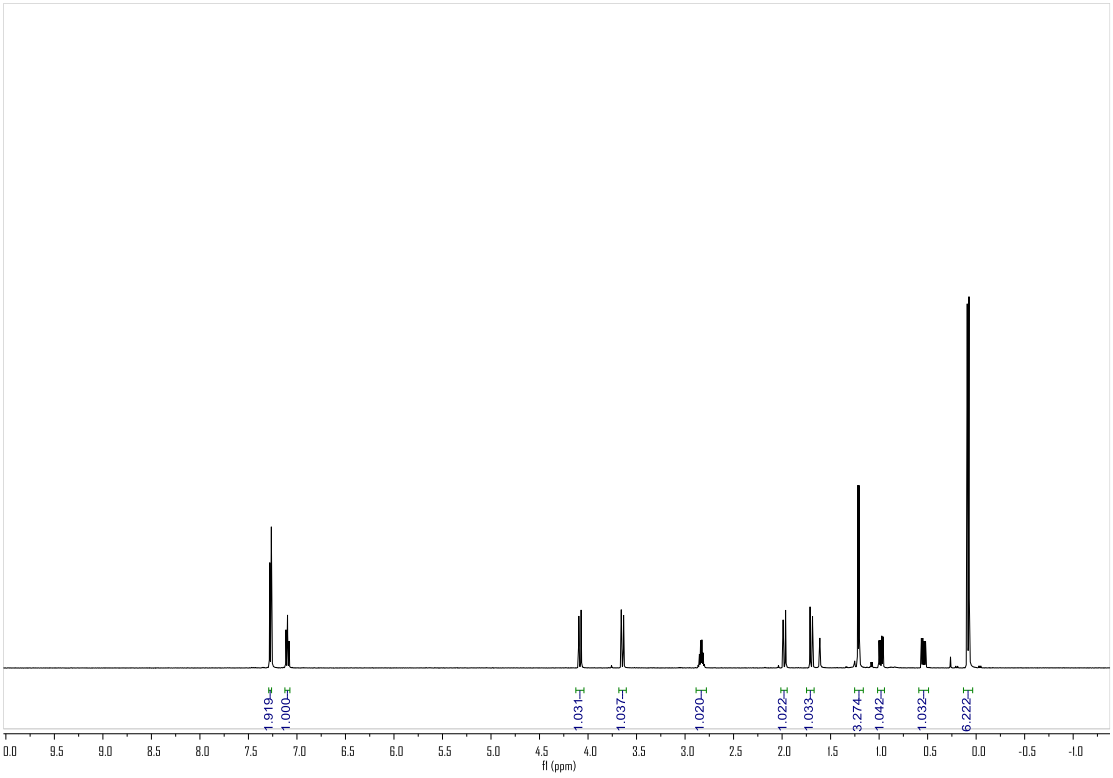

f1 (ppm)

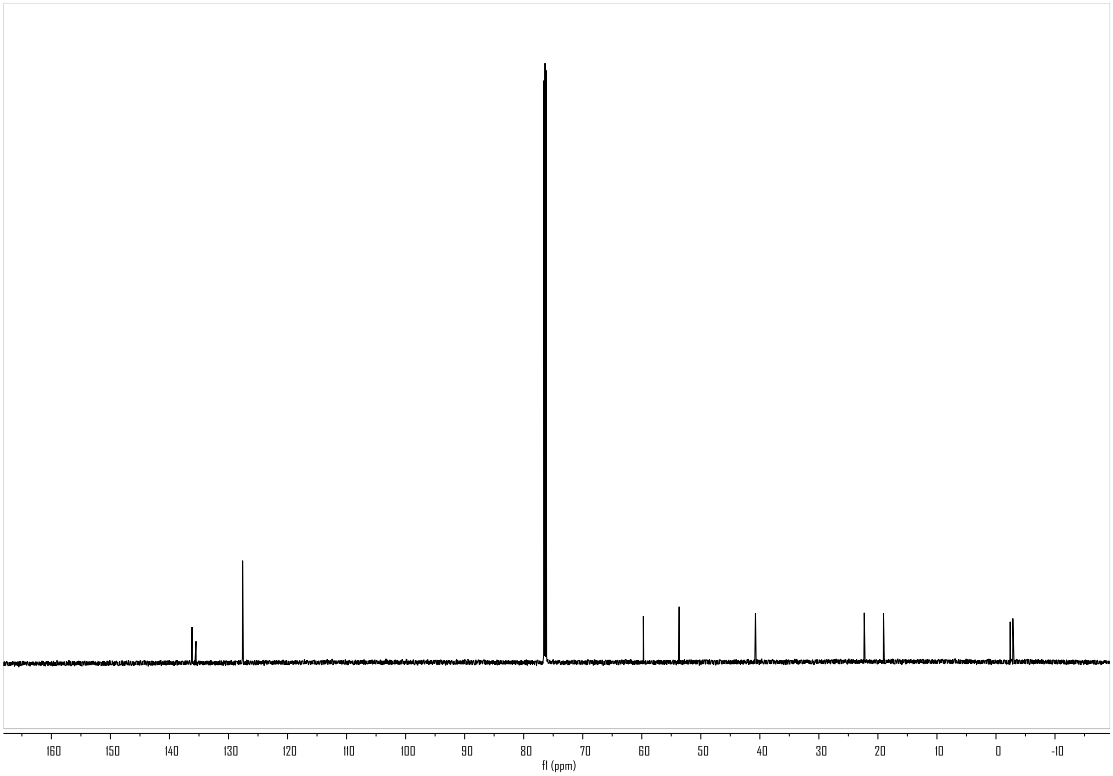

F
F
N
SiMe2
Me
H

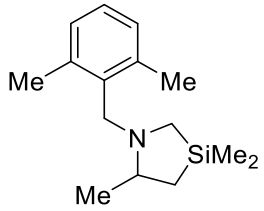

0.97
1.89
1.01
1.06
1.00
1.07
1.01
3.06
1.05
1.00
2.93
2.95
f1 (ppm)

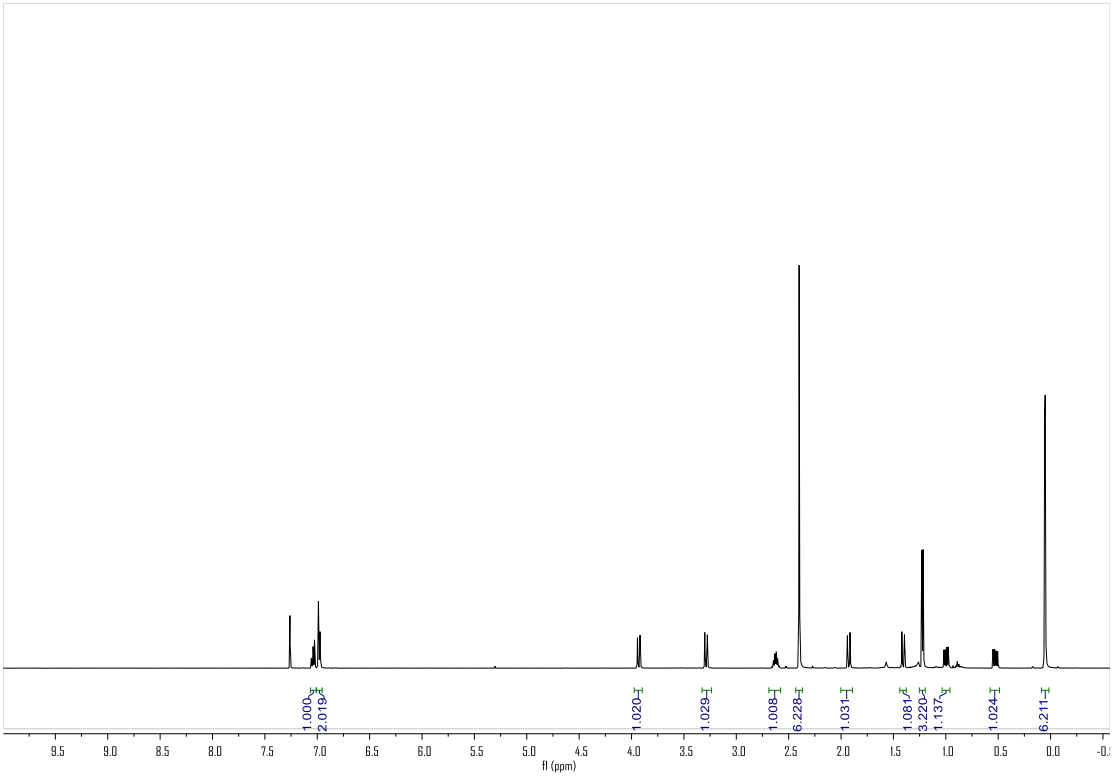

f1 (ppm)

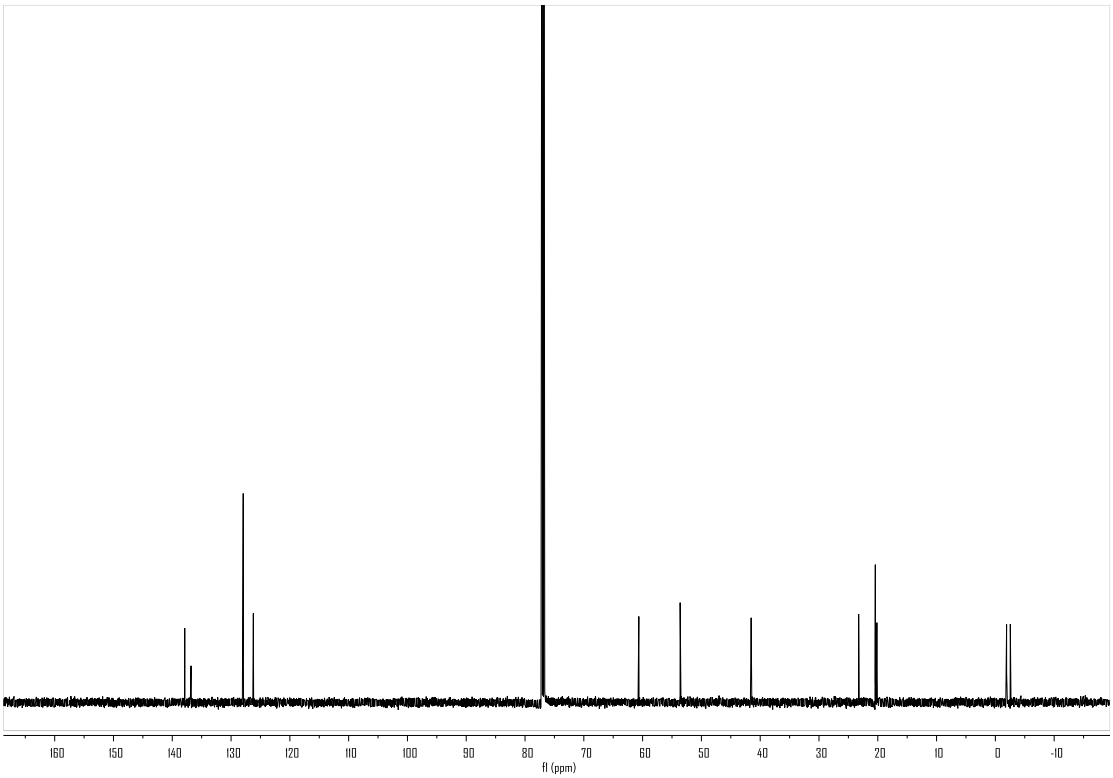

Cl
Cl
N
SiMe2
Me

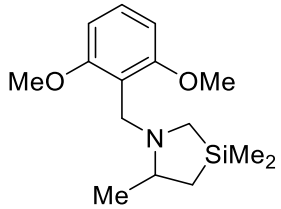

1.919
1.000
1.031
1.037
1.020
1.022
1.033
3.274
1.042
1.032
6.222
f1 (ppm)

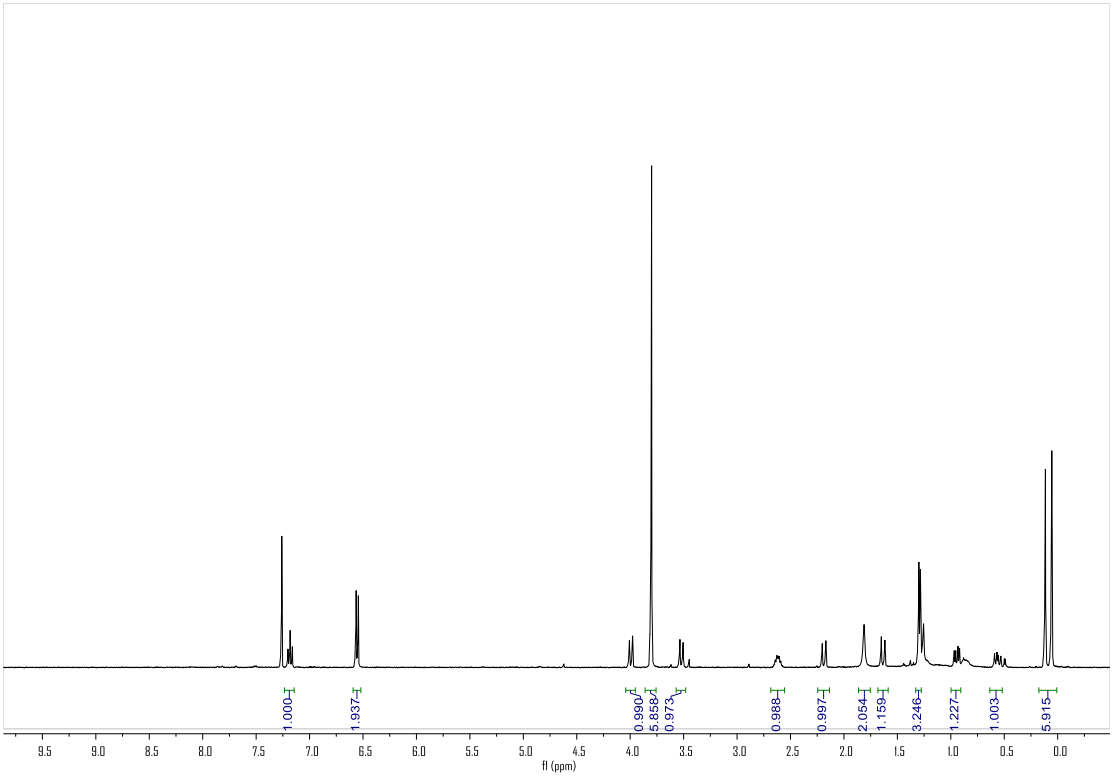

f1 (ppm)

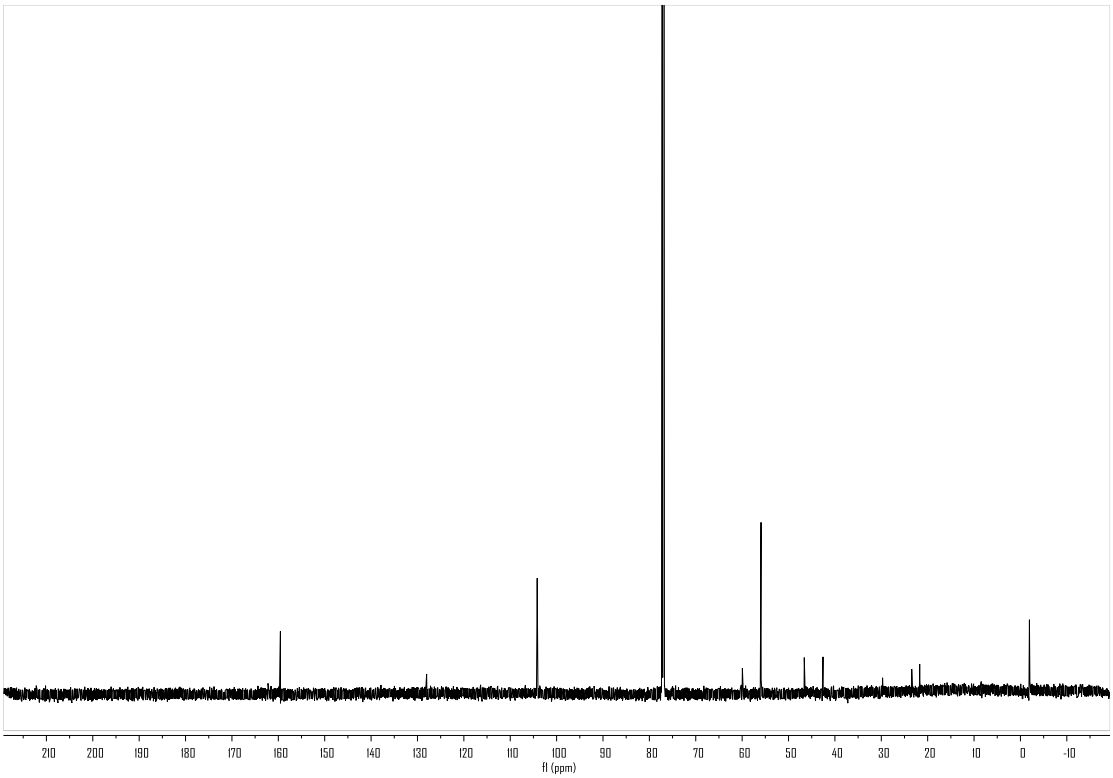

Me
Me
N
SiMe2
Me

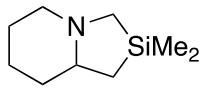

1.000
2.019
1.020
1.029
1.008
6.228
1.031
1.081
3.220
1.137
1.024
6.211
f1 (ppm)

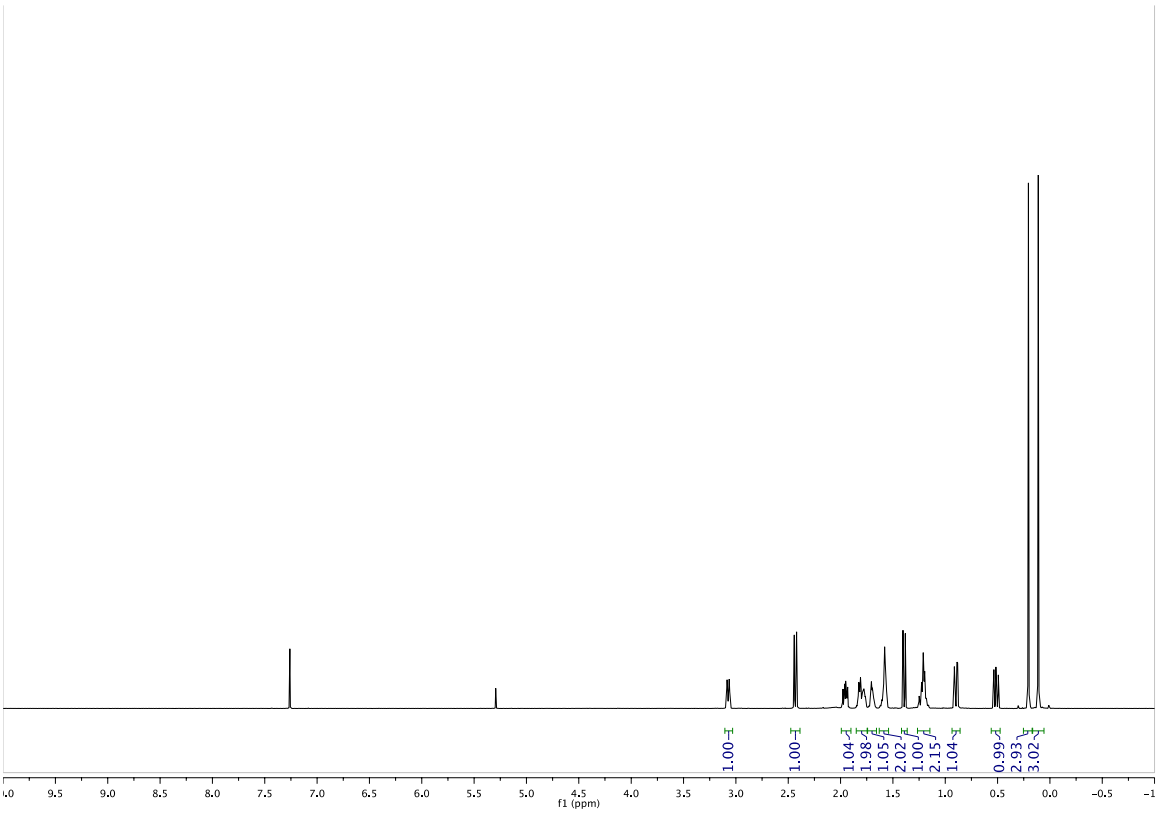

f1 (ppm)

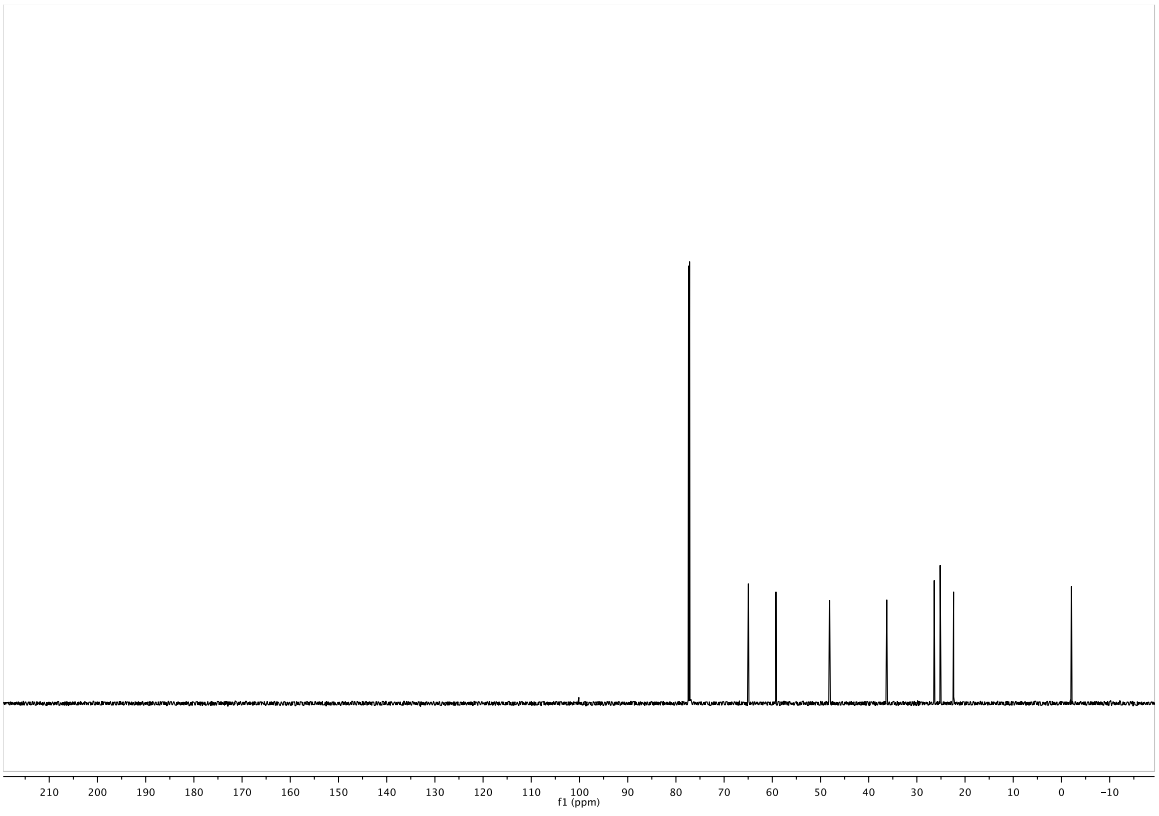

MeO
OMe
N
SiMe2
Me

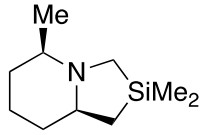

1.000
1.937
0.990
5.858
0.973
0.988
0.997
2.054
1.159
3.246
1.227
1.003
5.915
f1 (ppm)

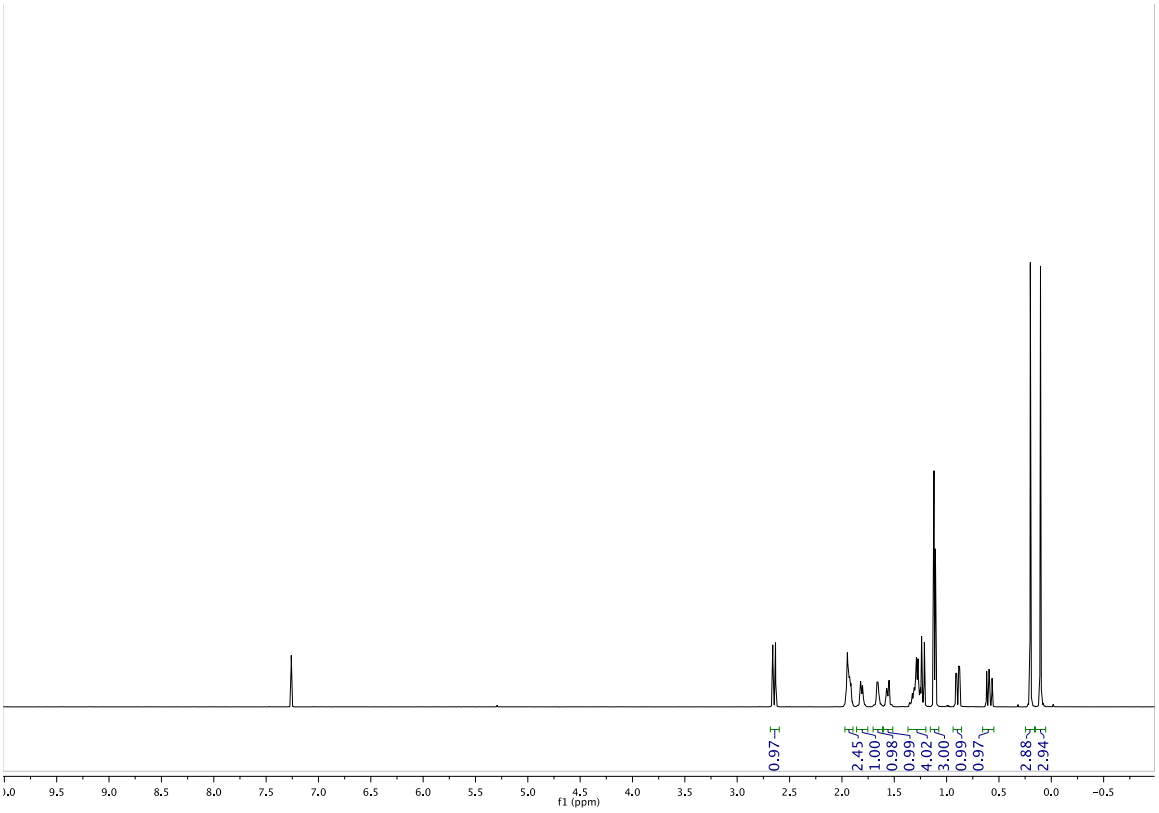

f1 (ppm)

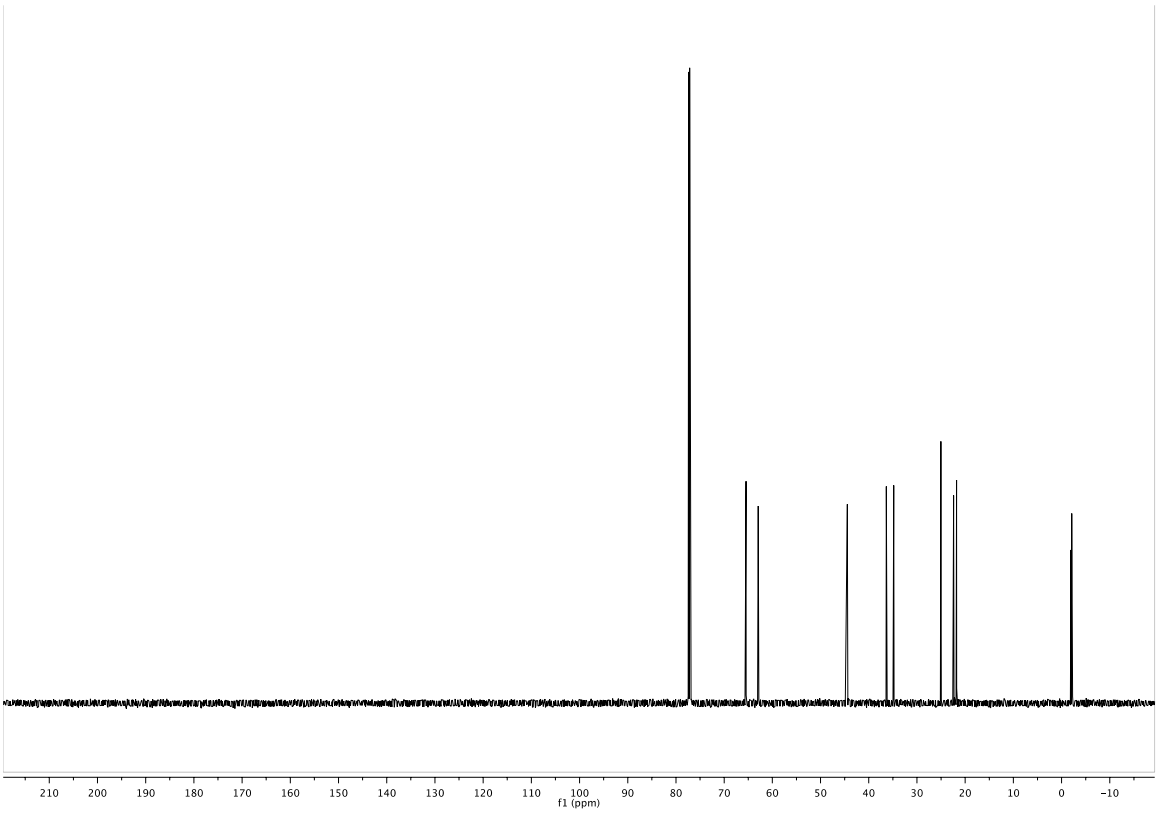

N
SiMe2

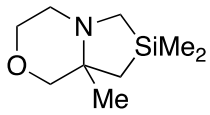

1.00
1.00
1.04
1.98
1.05
2.02
1.00
2.15
1.04
0.99
2.93
3.02
f1 (ppm)

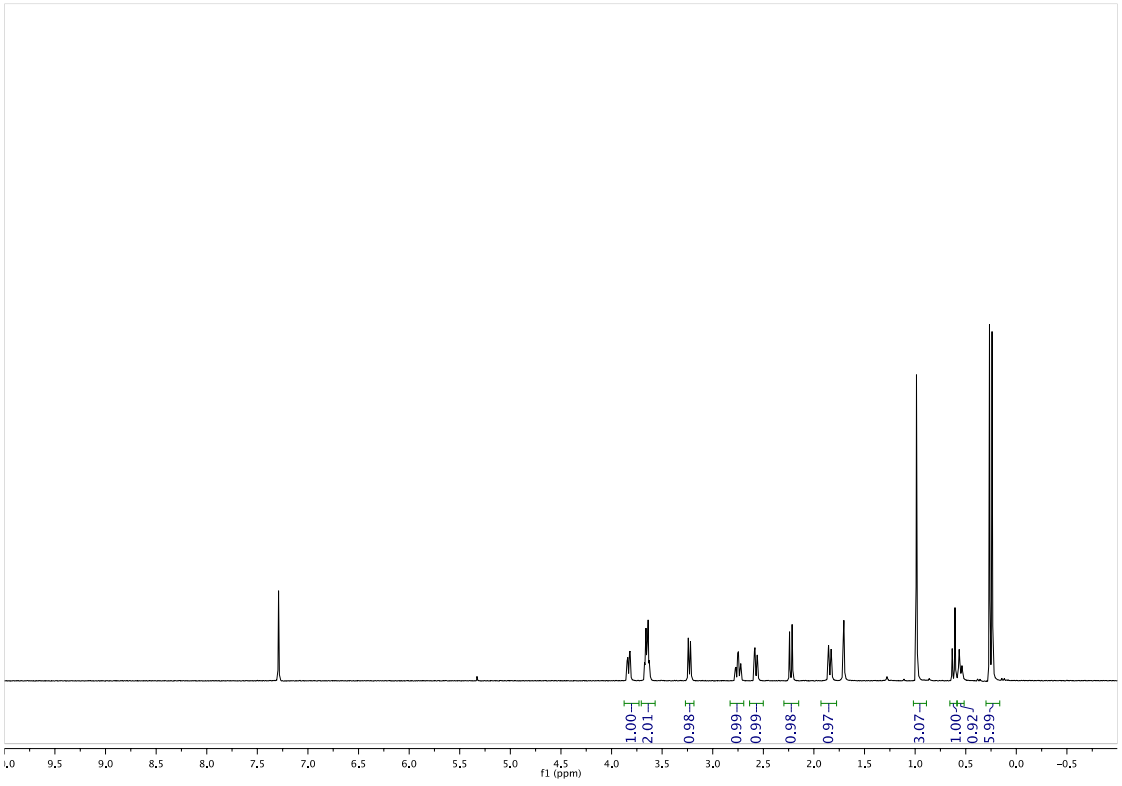

f1 (ppm)

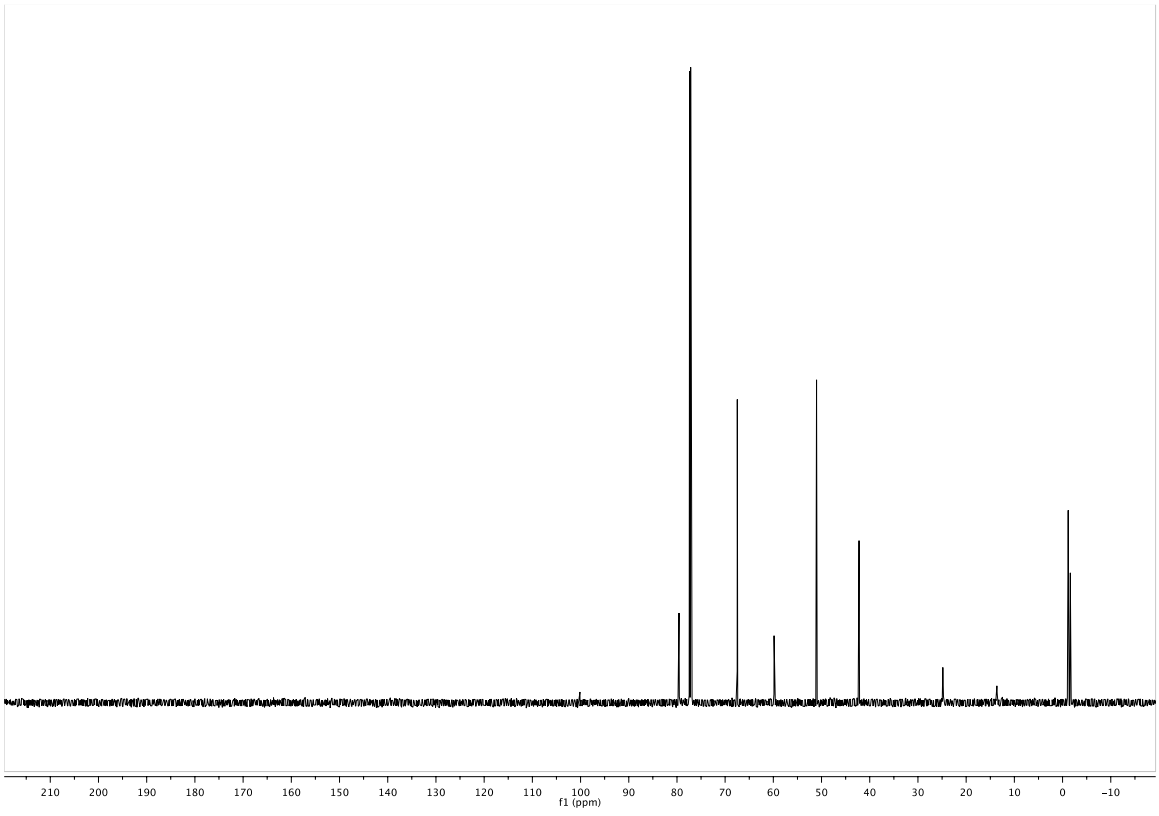

Me
N
SiMe2

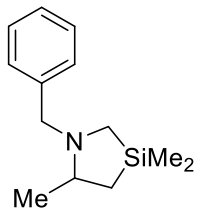

0.97
2.45
1.00
0.98
0.99
4.02
3.00
0.99
0.97
2.88
2.94
f1 (ppm)

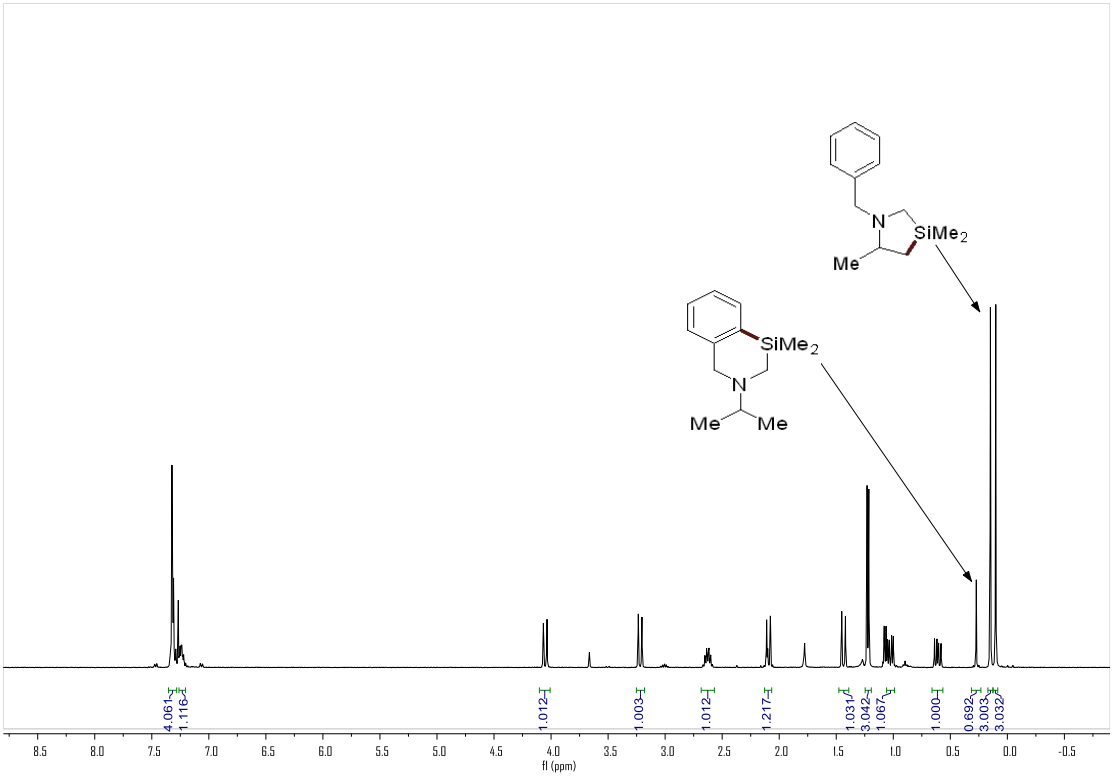

f1 (ppm)

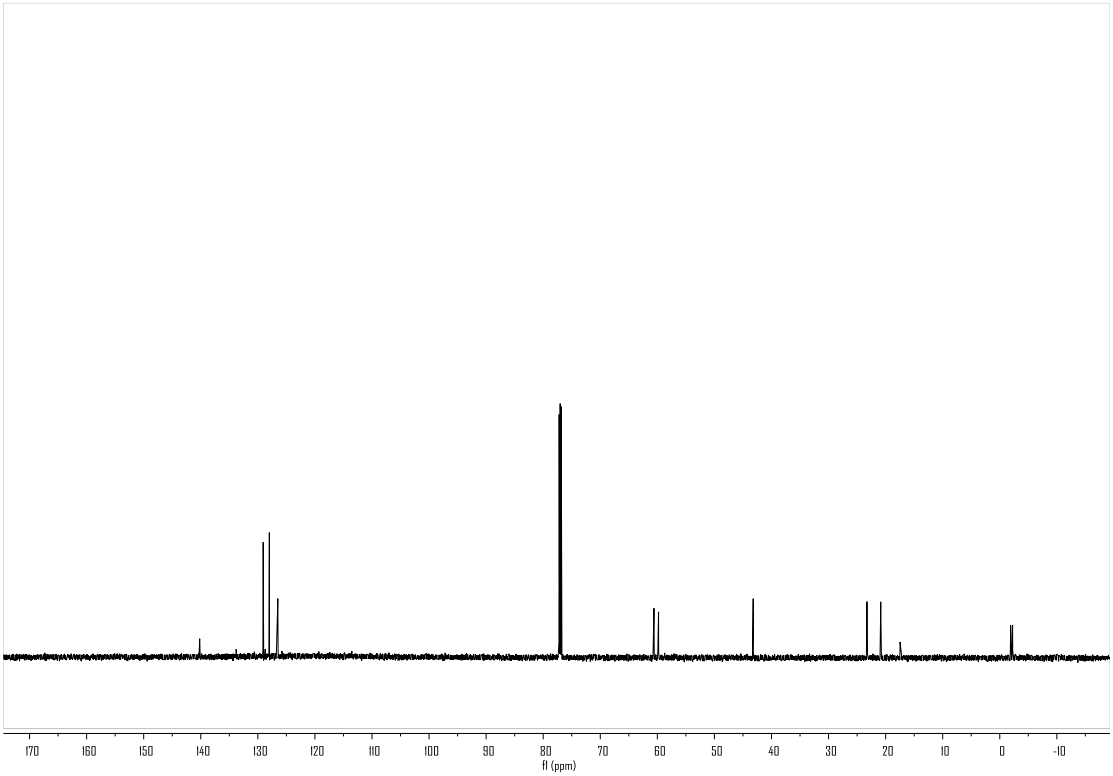

N
SiMe2
O
Me

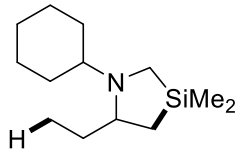

1.00
2.01
0.98
0.99
0.99
0.98
0.97
3.07
1.00
0.92
5.99
f1 (ppm)

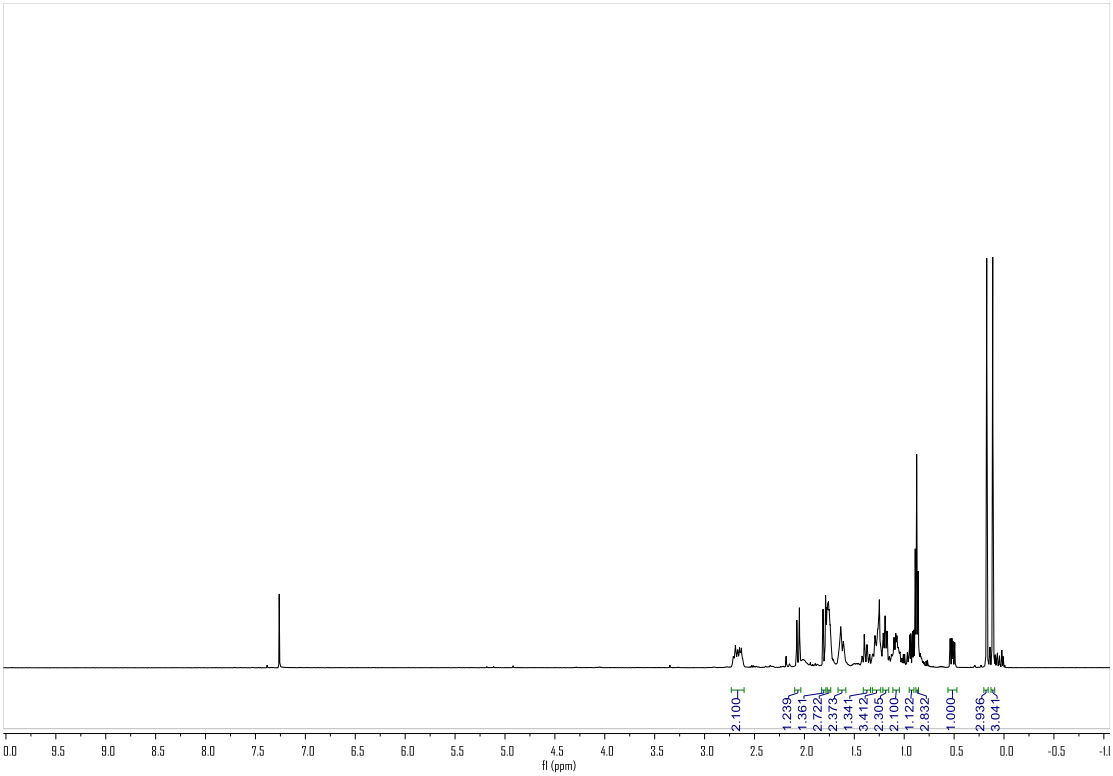

f1 (ppm)

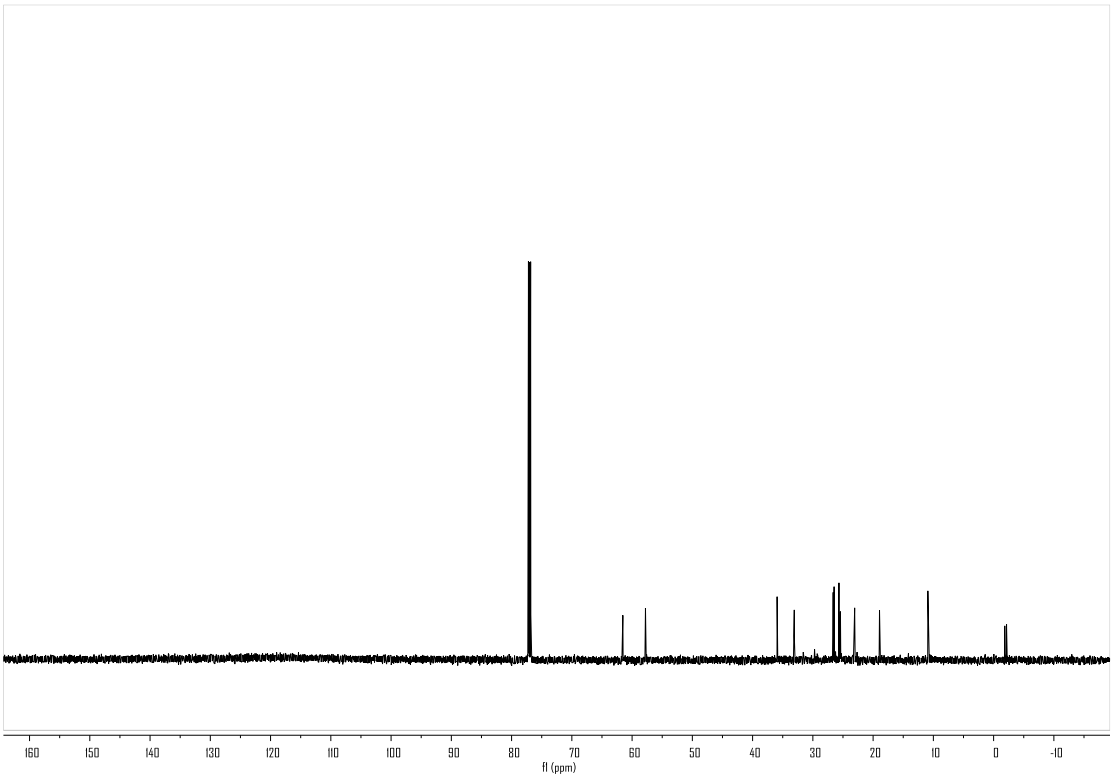

N
SiMe2
Me

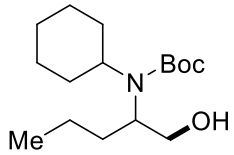

SiMe2
N
Me
Me
SiMe2
N
Me
4.061
1.116
1.012
1.003
1.012
1.217
1.031
3.042
1.067
1.000
0.692
3.003
3.032
f1 (ppm)

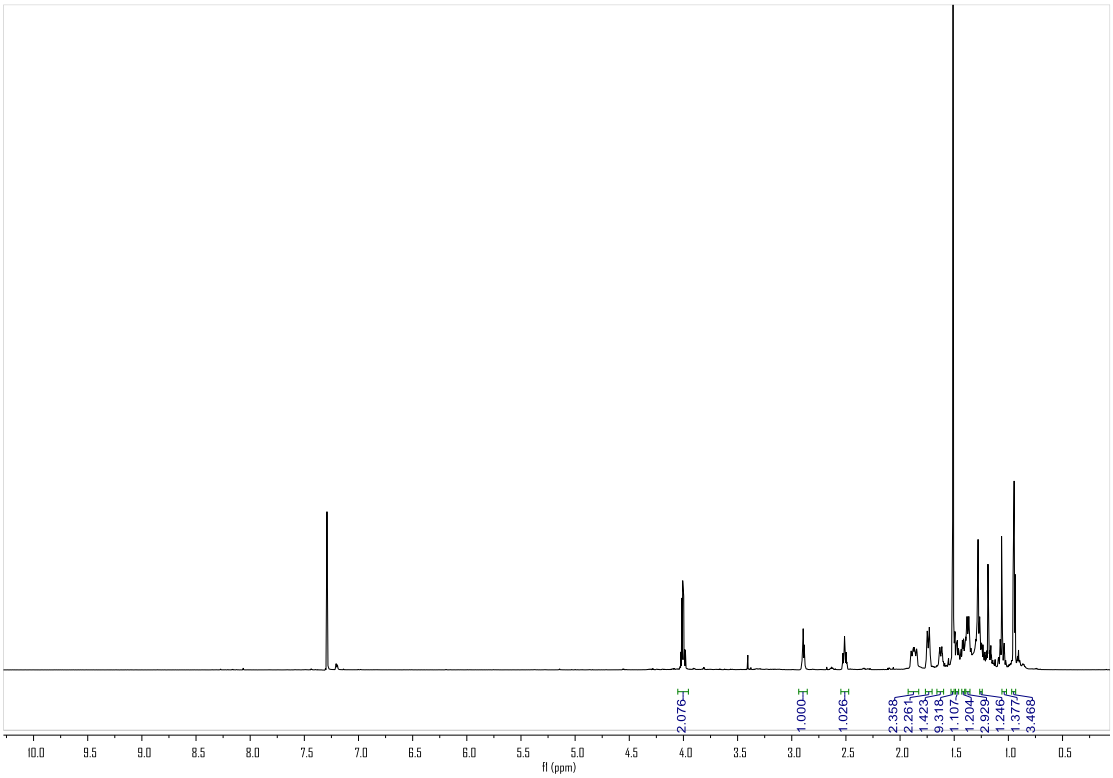

f1 (ppm)

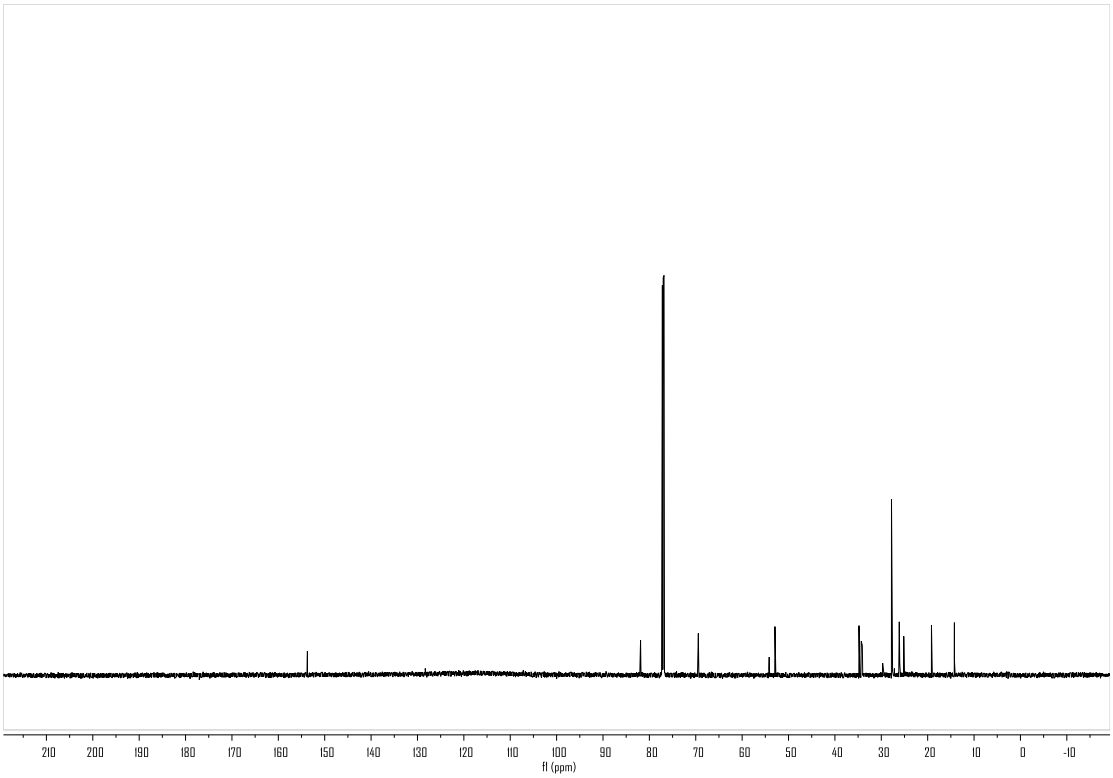

N
SiMe2
H

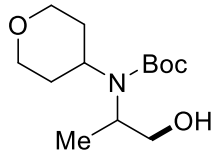

2.100
1.239
1.361
2.722
2.373
1.341
3.412
2.305
2.100
1.122
2.832
1.000
2.936
3.041
f1 (ppm)

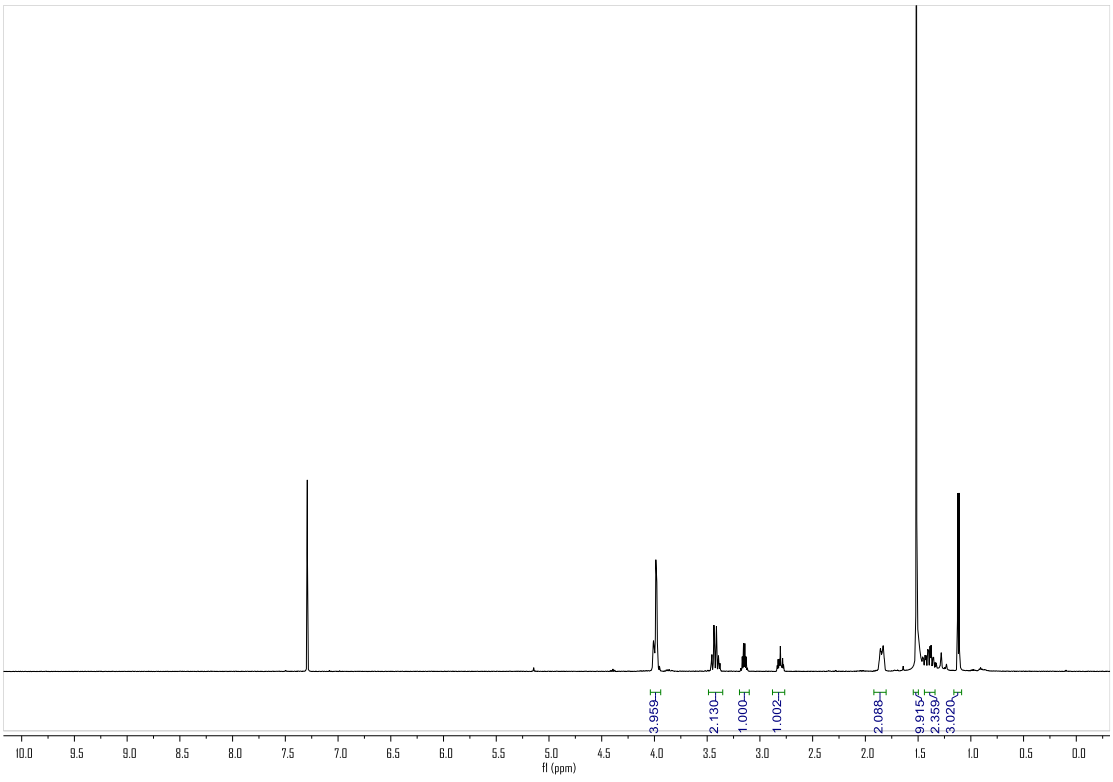

f1 (ppm)

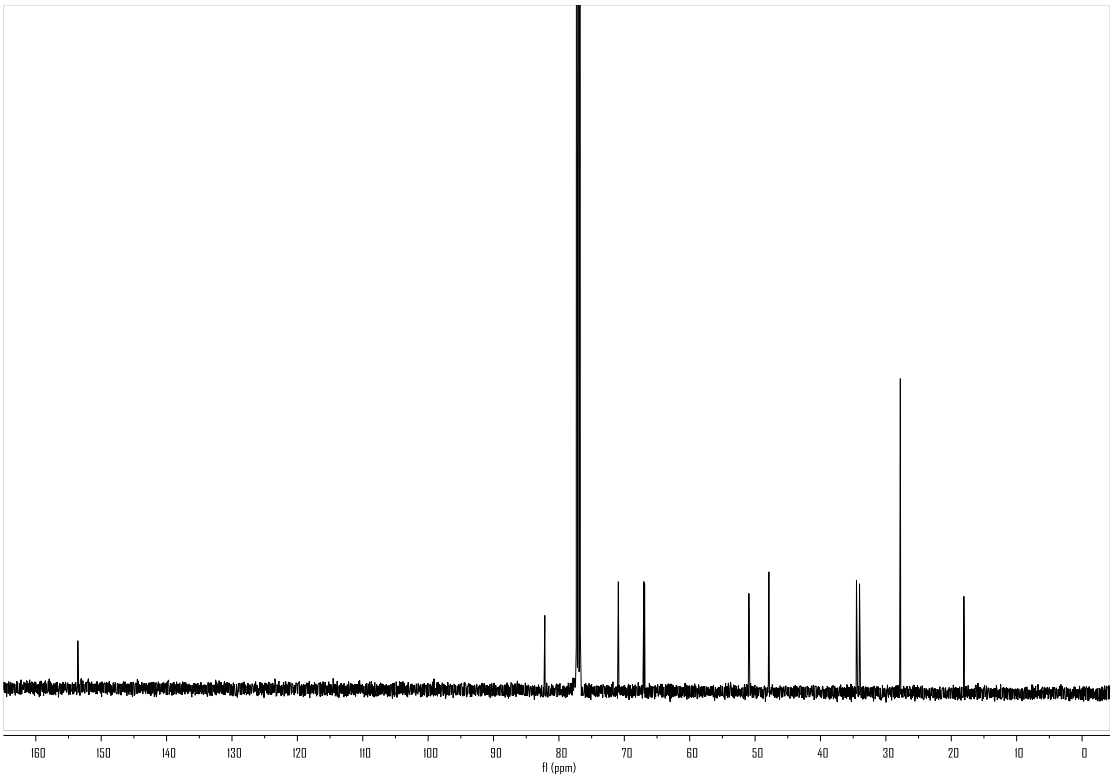

Boc
N
OH
Me

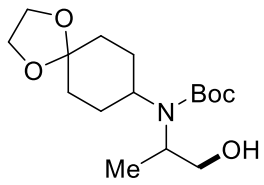

2.076
1.000
1.026
2.358
2.261
1.423
9.318
1.107
1.204
2.929
1.246
1.377
3.468
f1 (ppm)

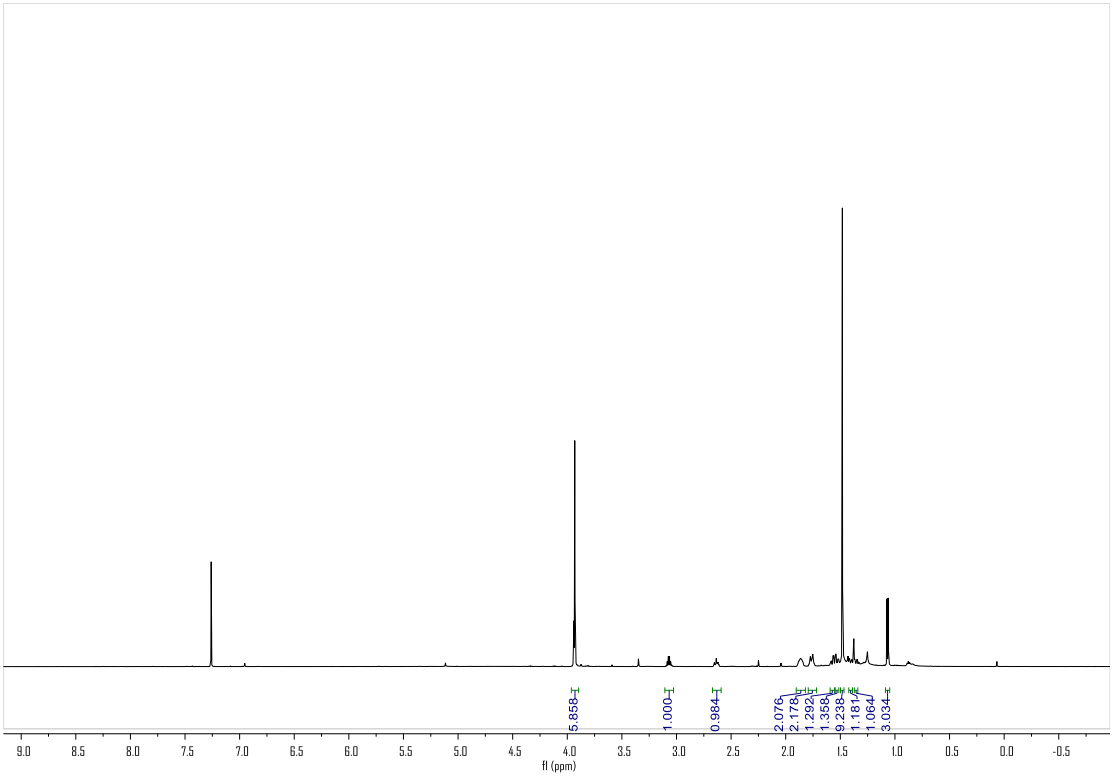

f1 (ppm)

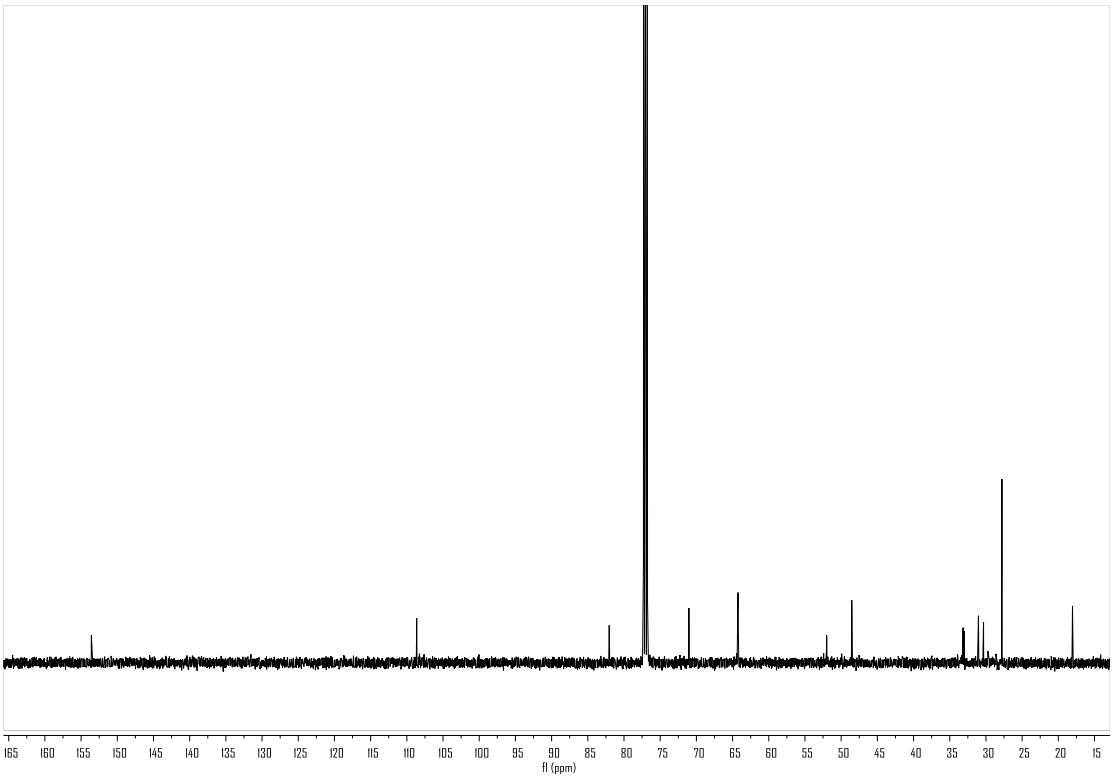

O
N
Boc
Me
OH

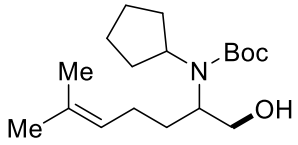

3.959
2.130
1.000
1.002
2.088
9.915
2.359
3.020
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

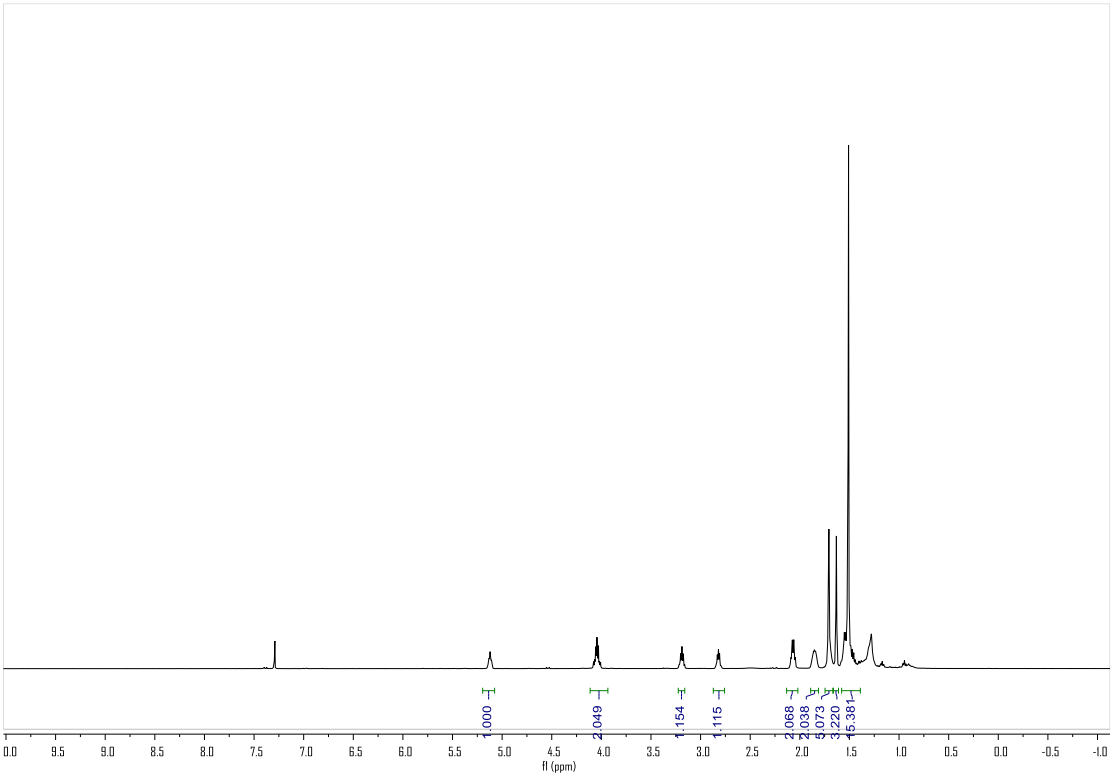

160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

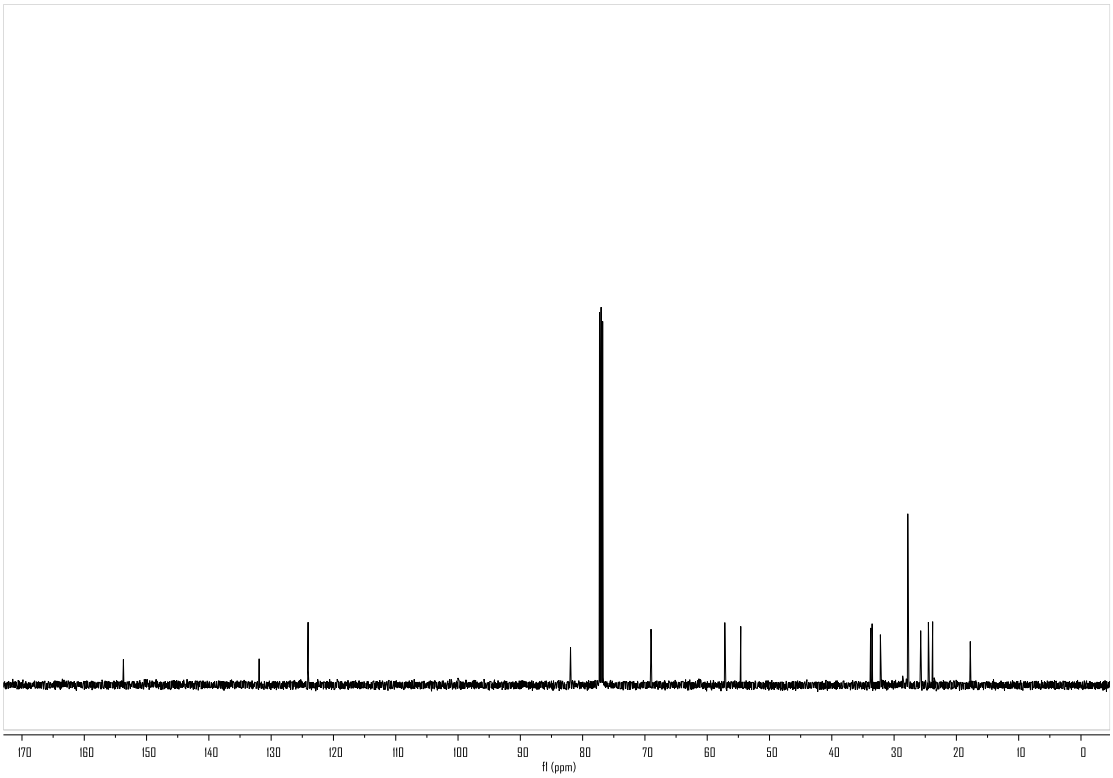

O
O
N
Boc
Me
OH

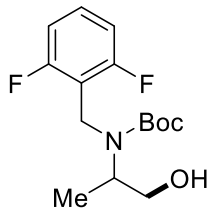

5.858
1.000
0.984
2.076
2.178
1.292
1.358
9.238
1.181
1.064
3.034
f1 (ppm)

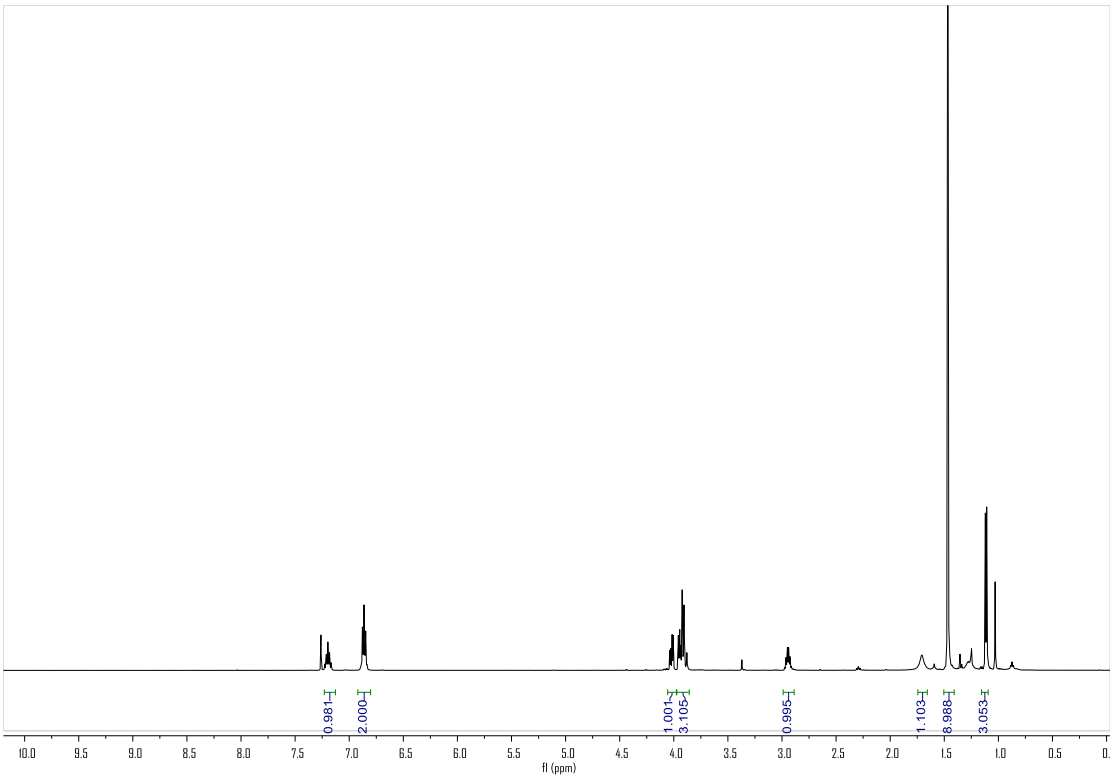

f1 (ppm)

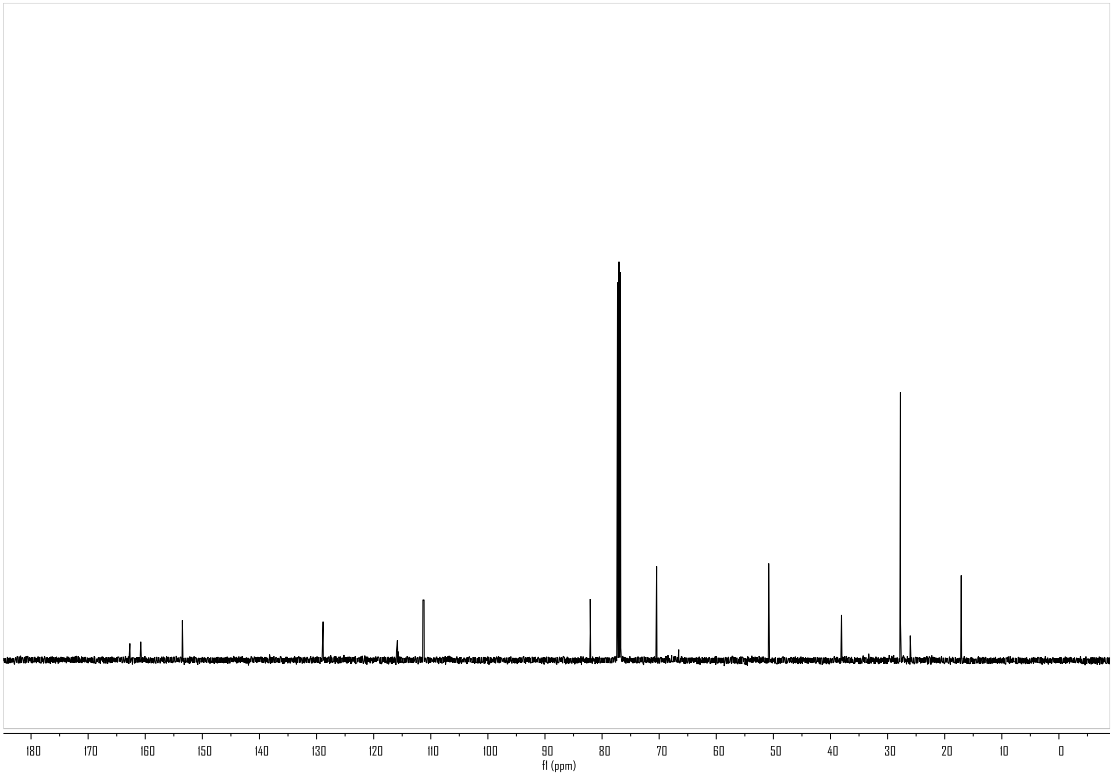

Me
N
Boc
Me
OH

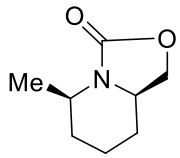

1.000
2.049
1.154
1.115
2.068
2.038
5.073
3.220
15.381
f1 (ppm)

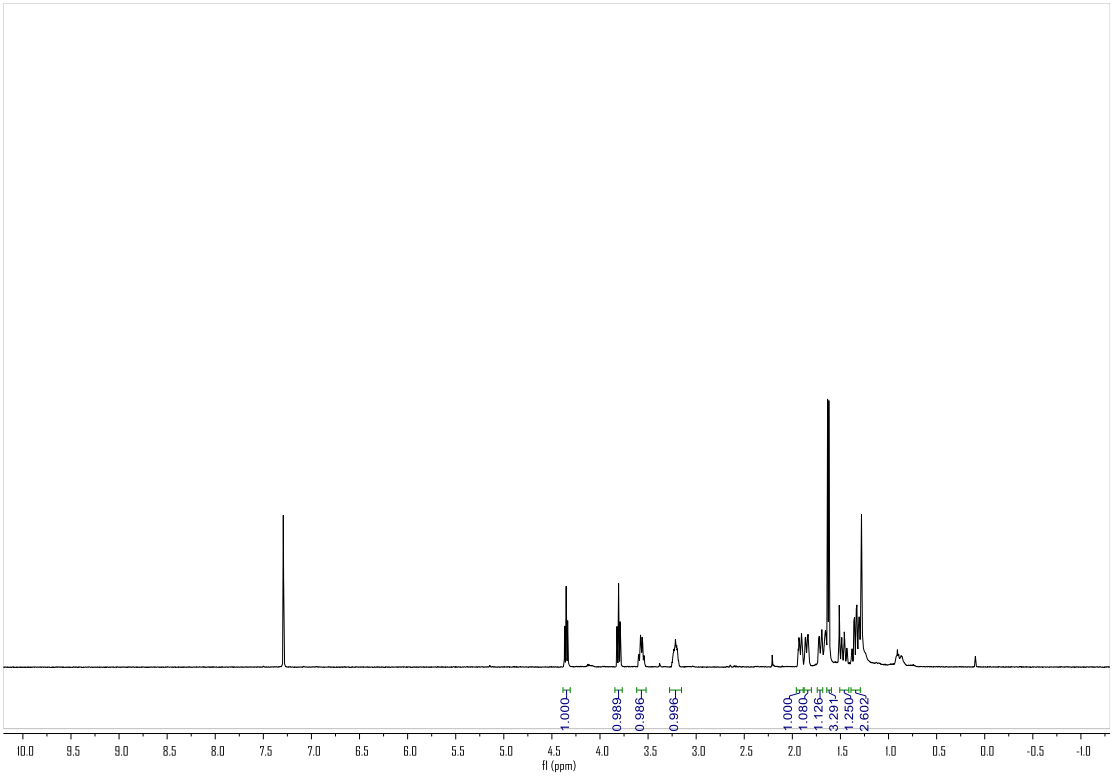

f1 (ppm)

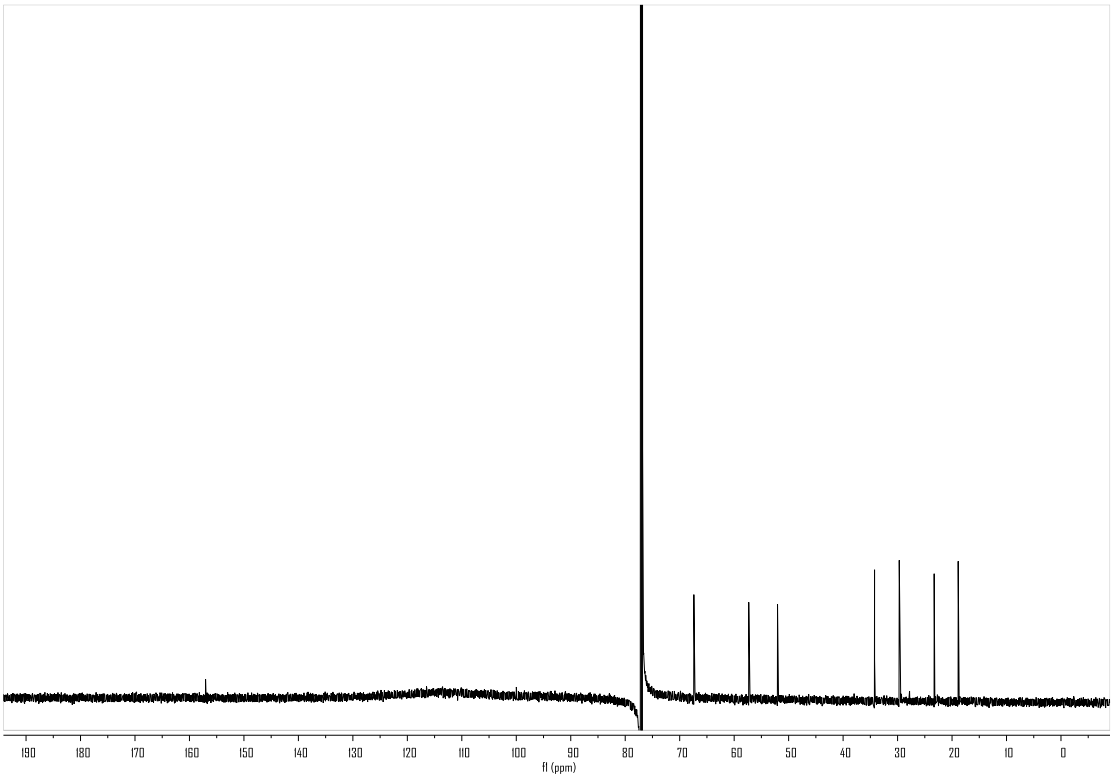

F
F
N
Boc
Me
OH

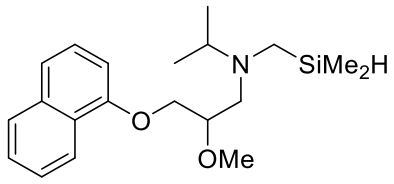

0.981
2.000
1.001
3.105
0.995
1.103
8.988
3.053
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

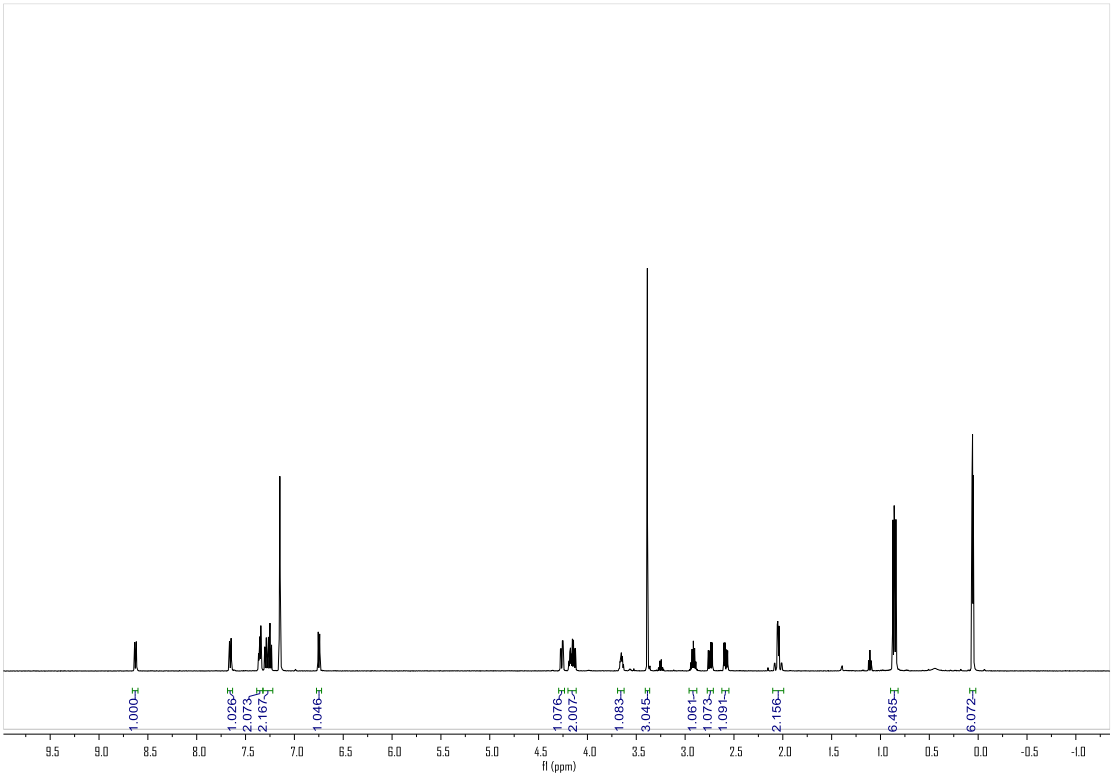

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

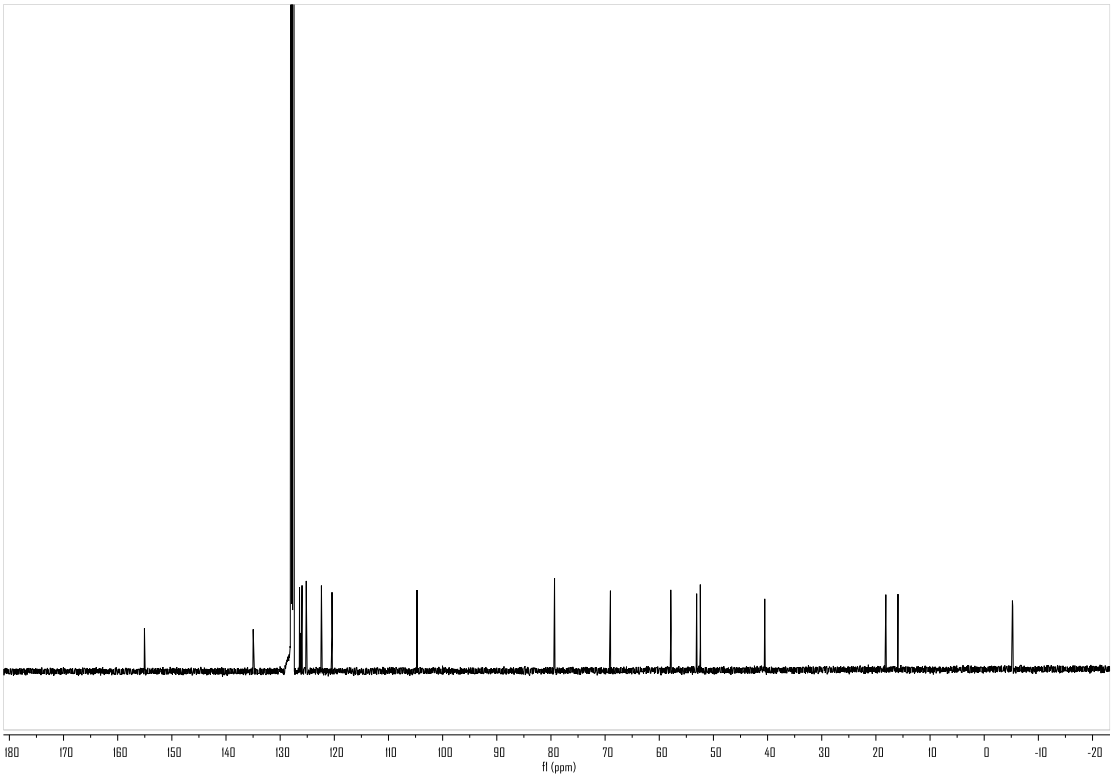

O
O
Me
N

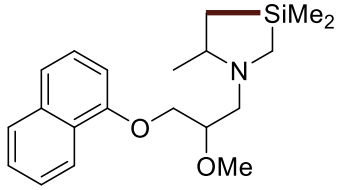

1.000
0.989
0.986
0.996
1.000
1.080
1.126
3.291
1.250
2.602
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

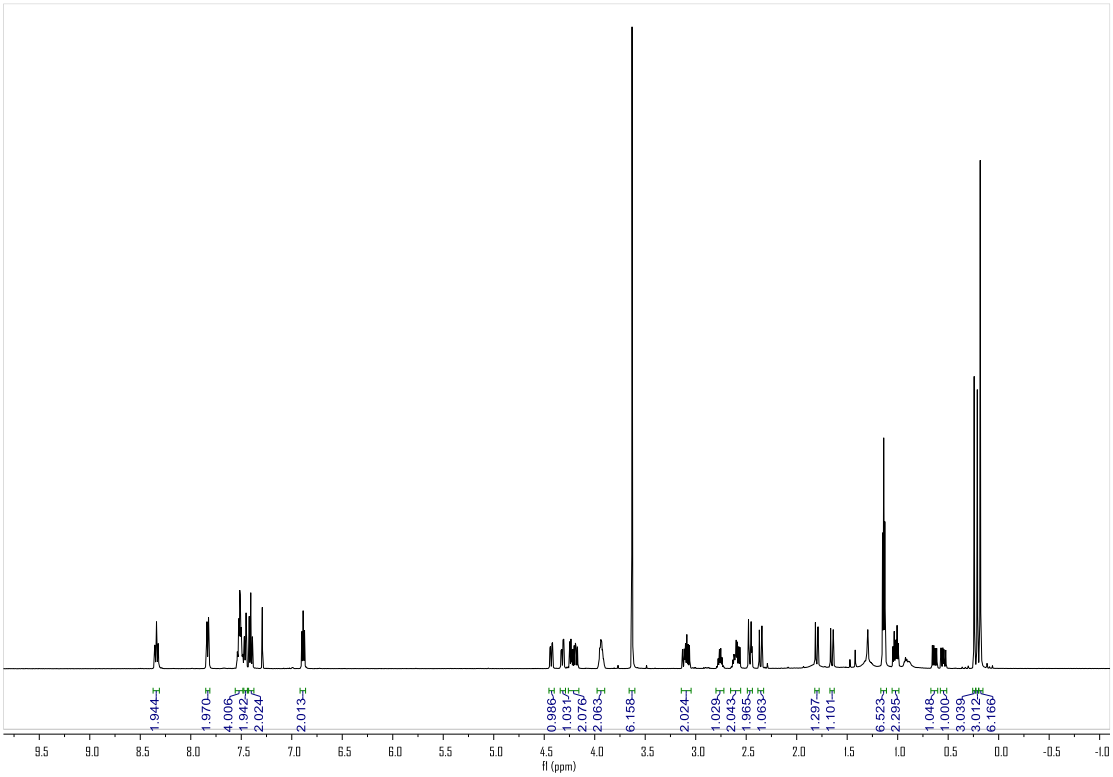

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

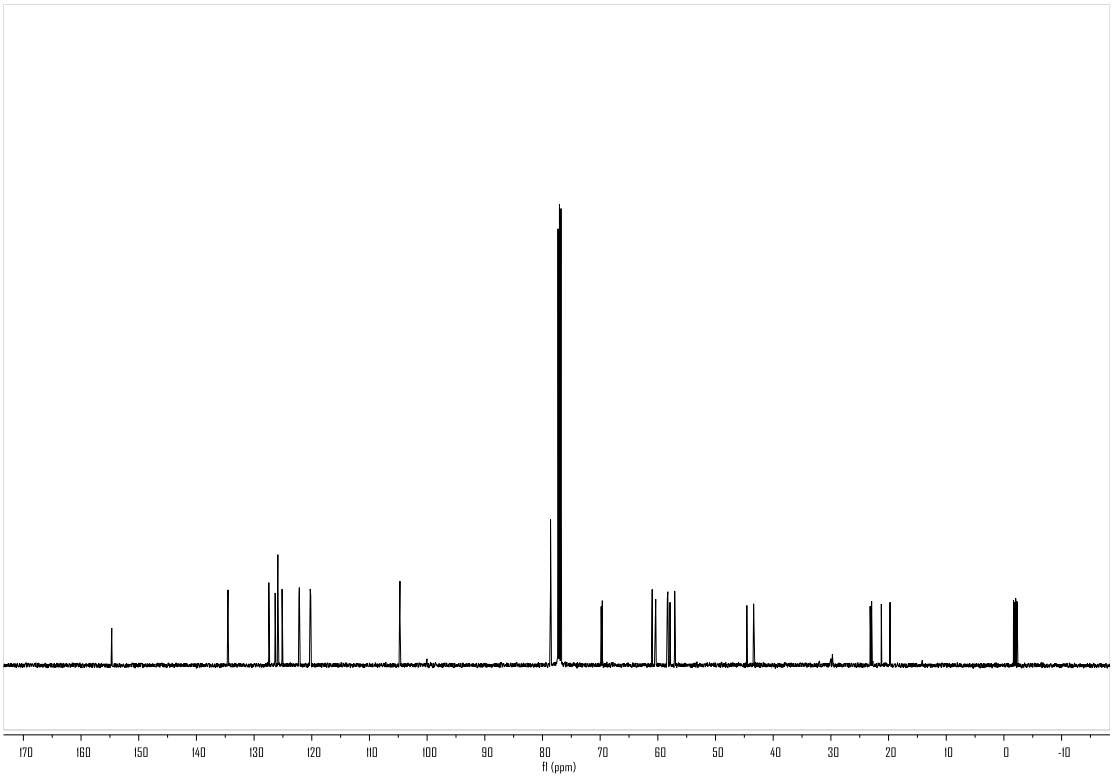

N
SiMe2H
O
OMe

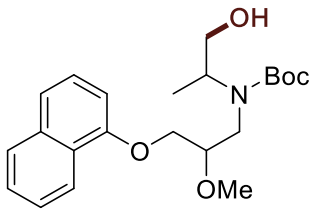

1.000
1.026
2.073
2.167
1.046
1.076
2.007
1.083
3.045
1.061
1.073
1.091
2.156
6.465
6.072
f1 (ppm)

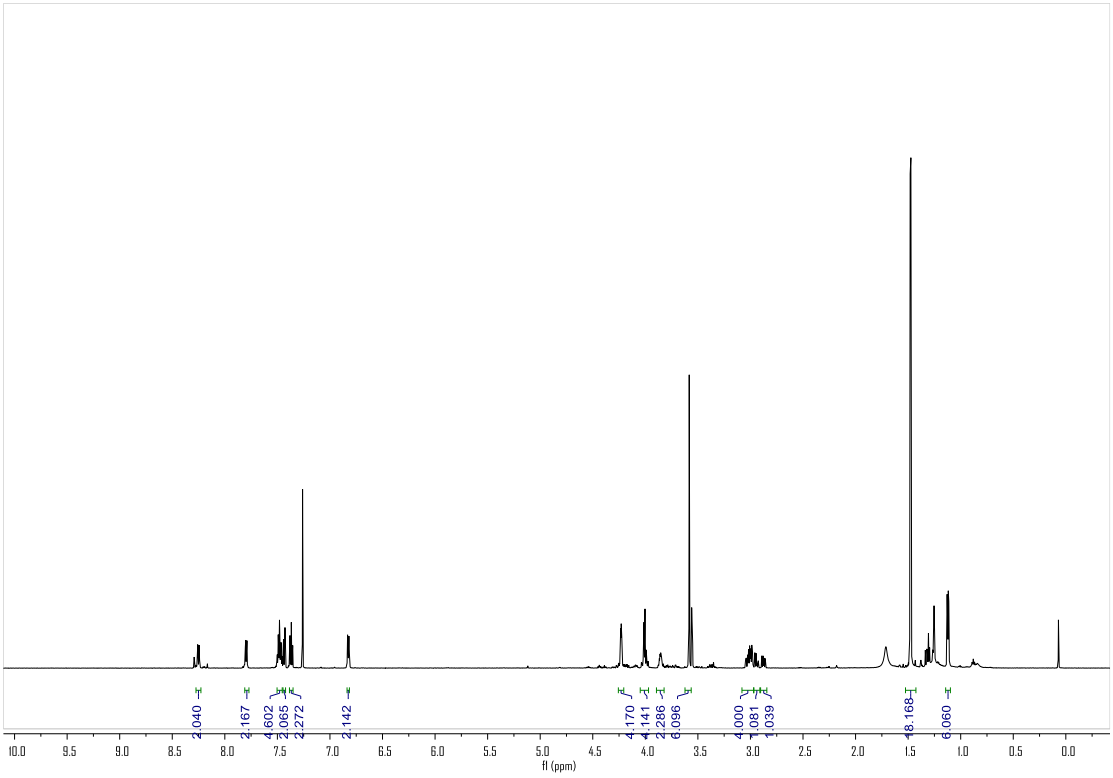

f1 (ppm)

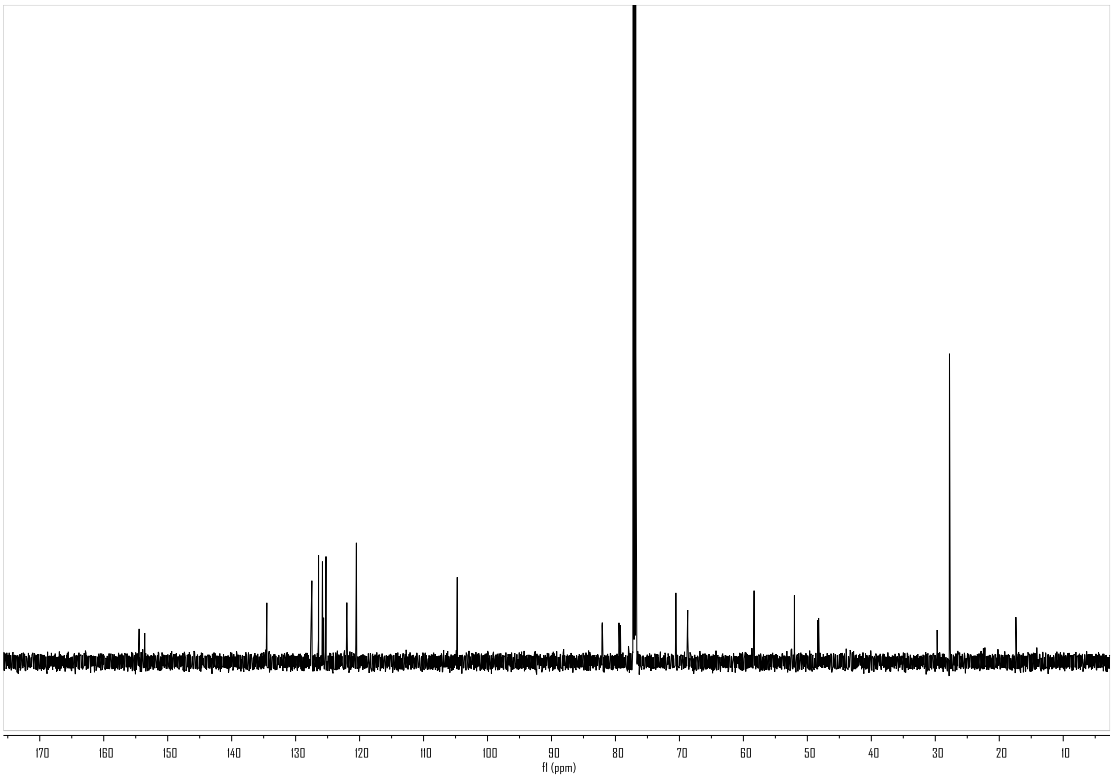

SiMe2
N
O
OMe

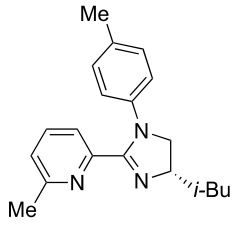

1.944
1.970
4.006
1.942
2.024
2.013
0.986
1.031
2.076
2.063
6.158
2.024
1.029
2.043
1.965
1.063
1.297
1.101
6.523
2.295
1.048
1.000
3.039
3.012
6.166
f1 (ppm)

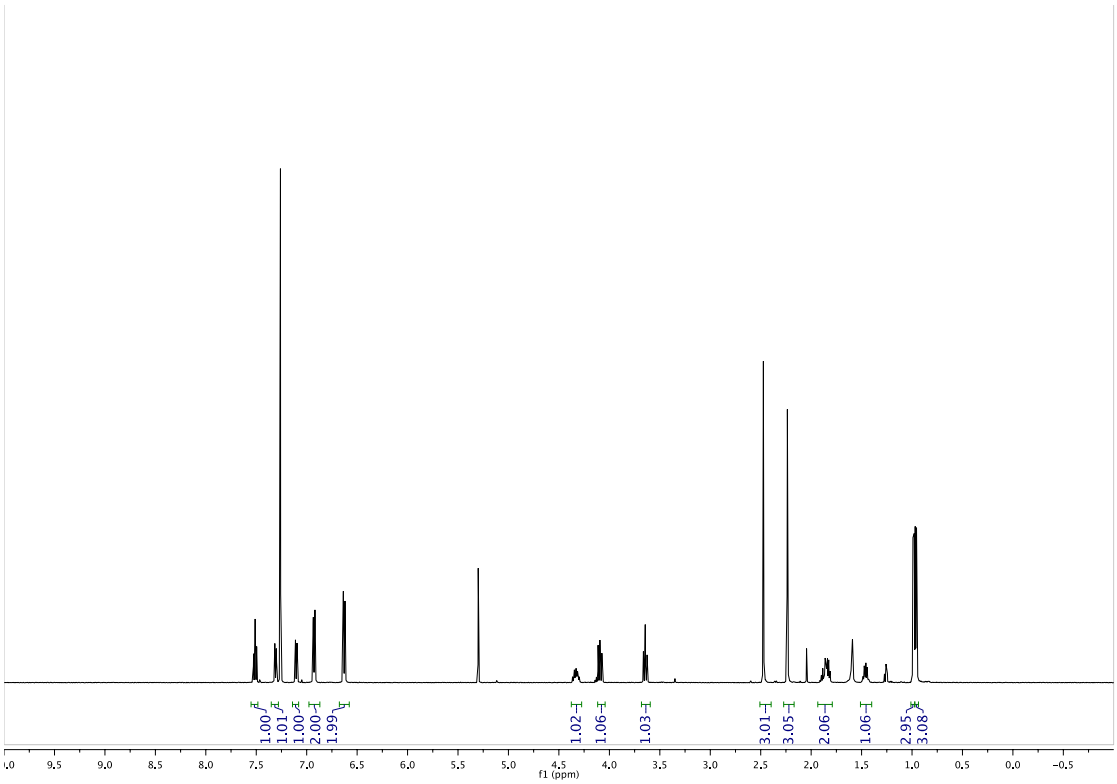

f1 (ppm)

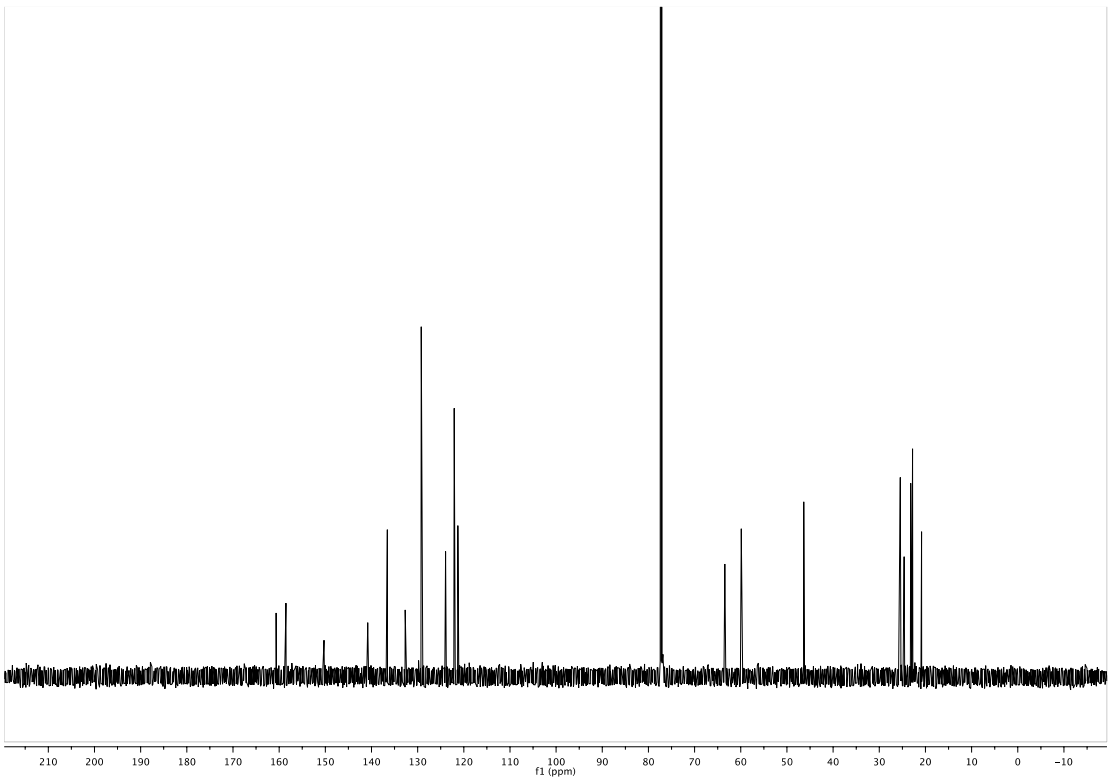

OH
Boc
N
O
OMe

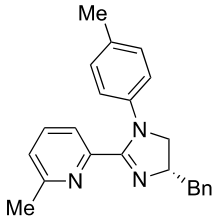

2.040
2.167
4.602
2.065
2.272
2.142
4.170
4.141
2.286
6.096
4.000
3.081
1.039
48.168
6.060
f1 (ppm)

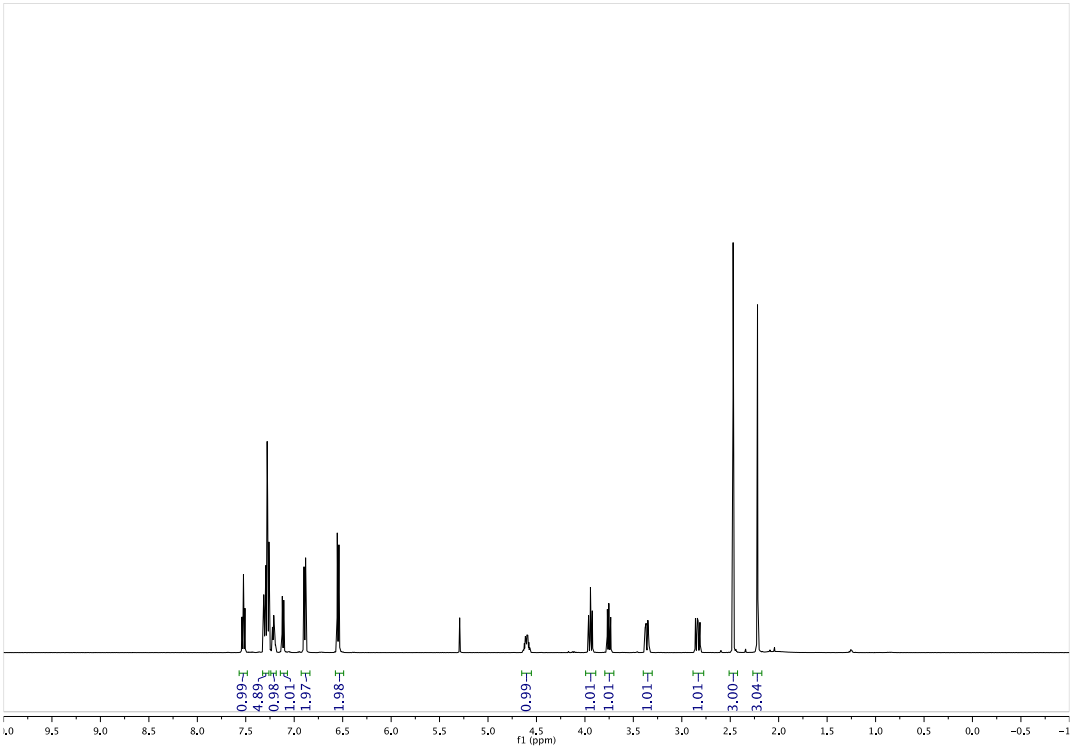

f1 (ppm)

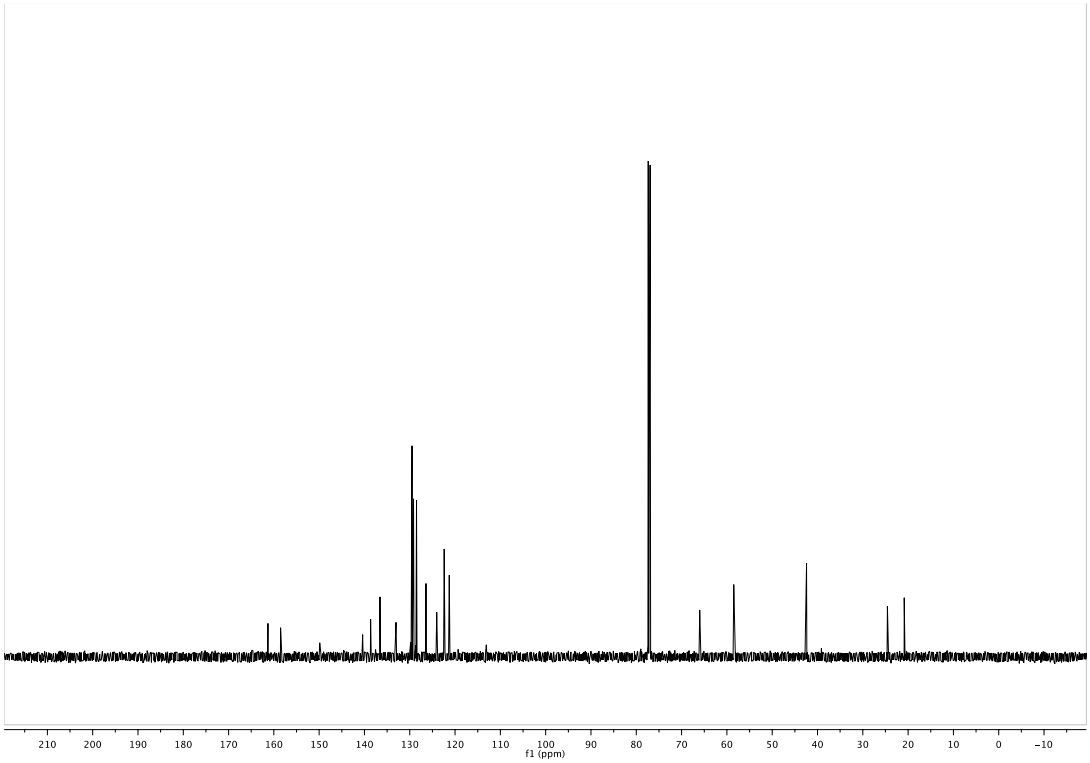

Me
N
N
N
i-Bu
Me

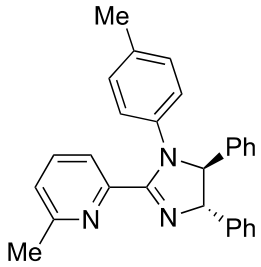

1.00
1.01
1.00
2.00
1.99
1.02
1.06
1.03
3.01
3.05
2.06
1.06
2.95
3.08
f1 (ppm)

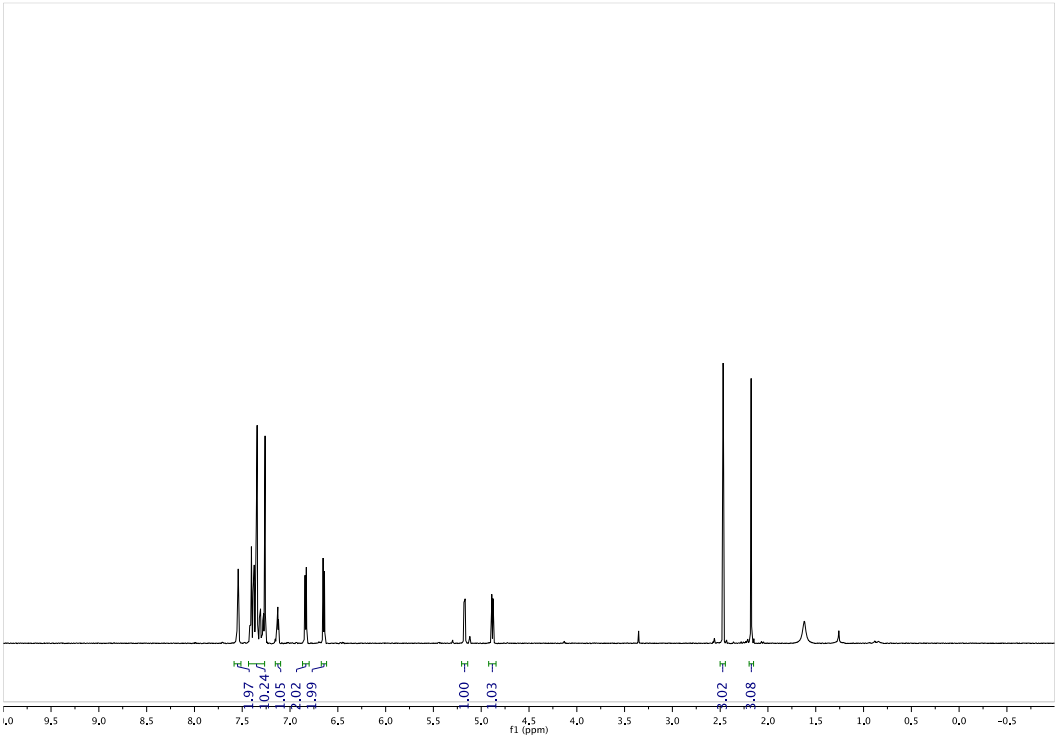

f1 (ppm)

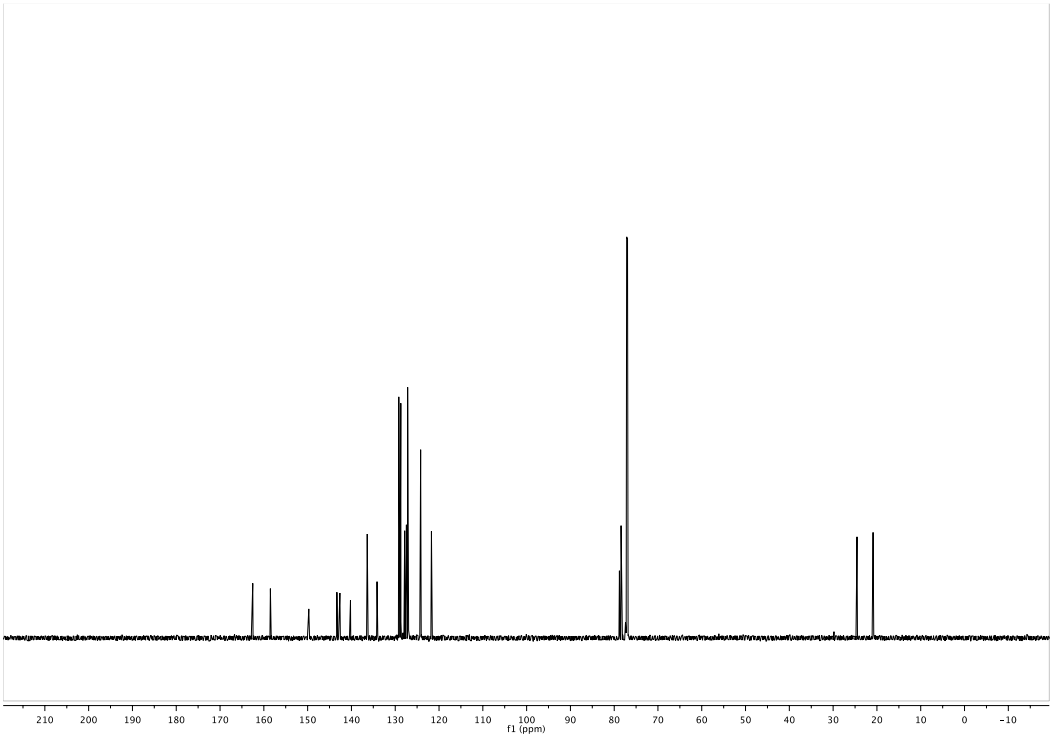

Me
N
N
N
Bn
Me

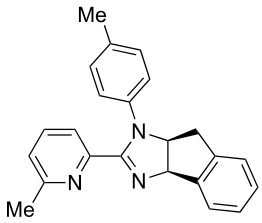

0.99
4.89
0.98
1.01
1.97
1.98
0.99
1.01
1.01
1.01
1.01
3.00
3.04
f1 (ppm)

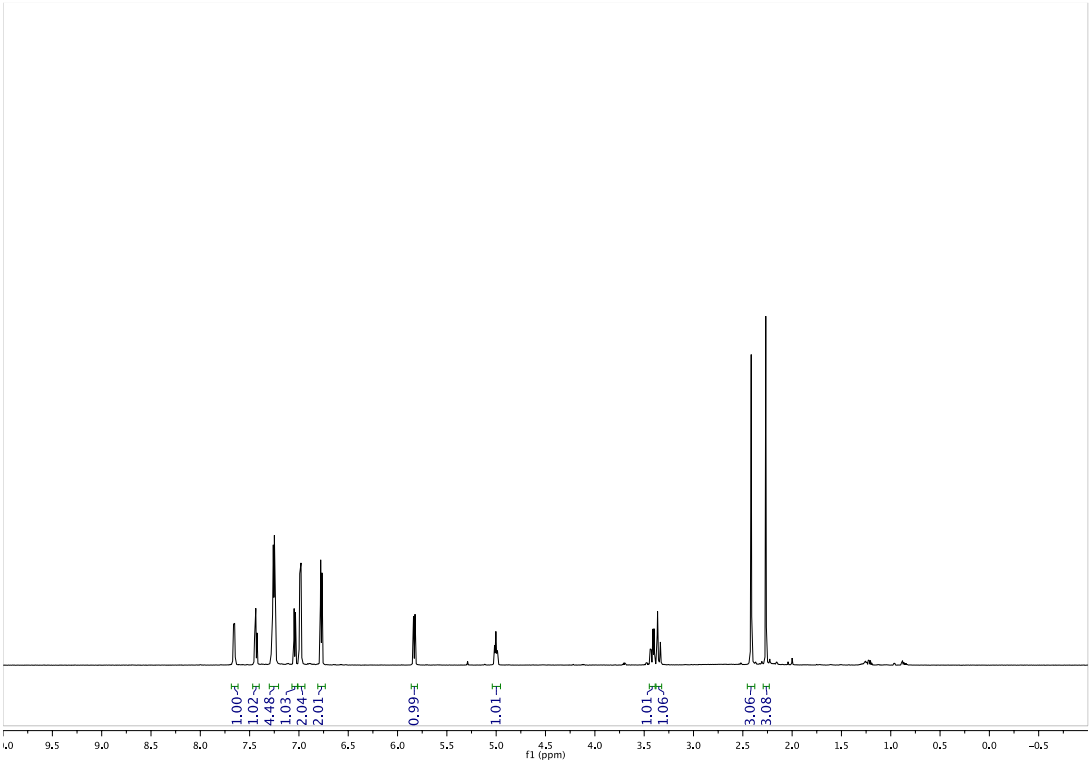

f1 (ppm)

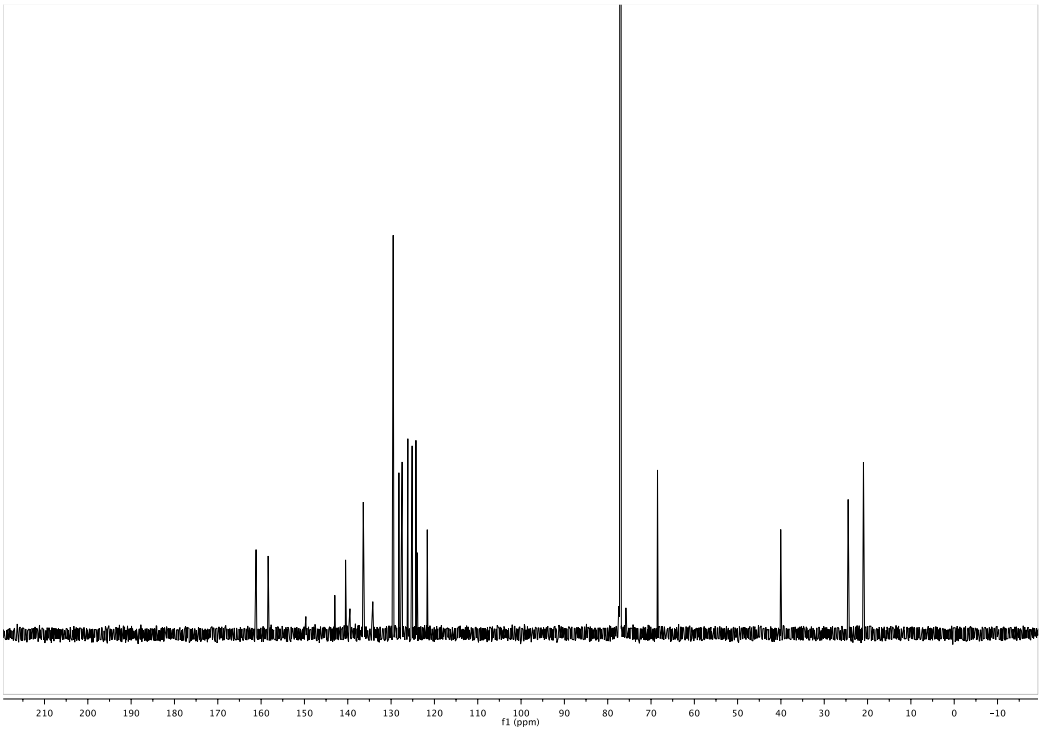

Me
N
Ph
N
N
Ph
Me

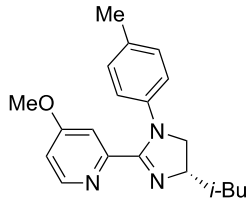

1.97
10.24
1.05
2.02
1.99
1.00
1.03
3.02
3.08
f1 (ppm)

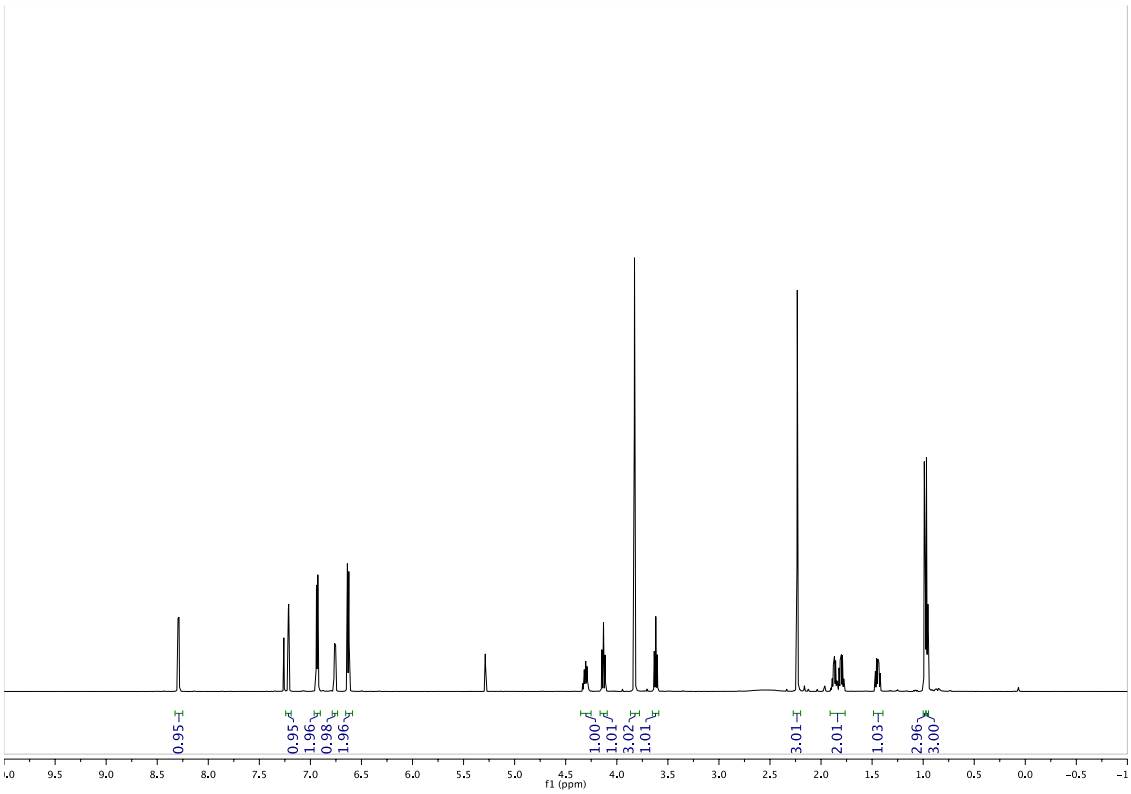

f1 (ppm)

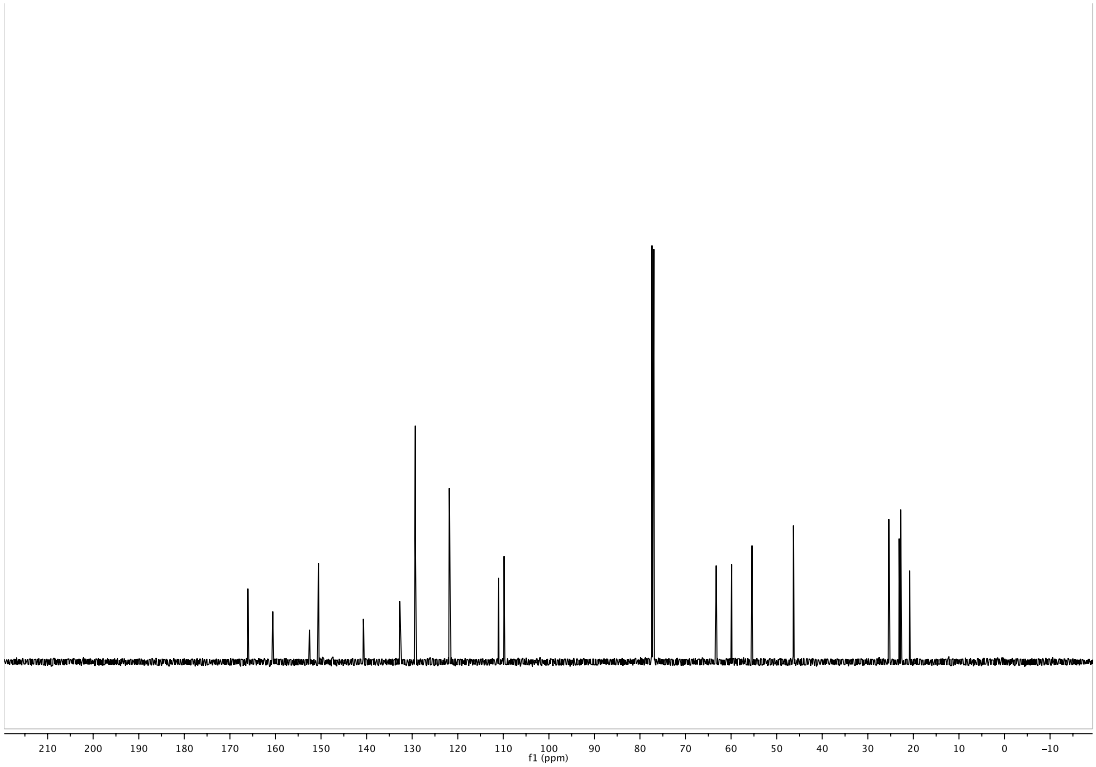

Me
N
N
N
Me

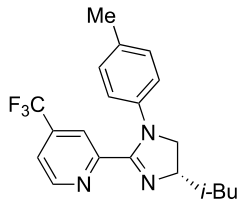

1.00
1.02
4.48
1.03
2.04
2.01
0.99
1.01
1.01
1.06
3.06
3.08
f1 (ppm)

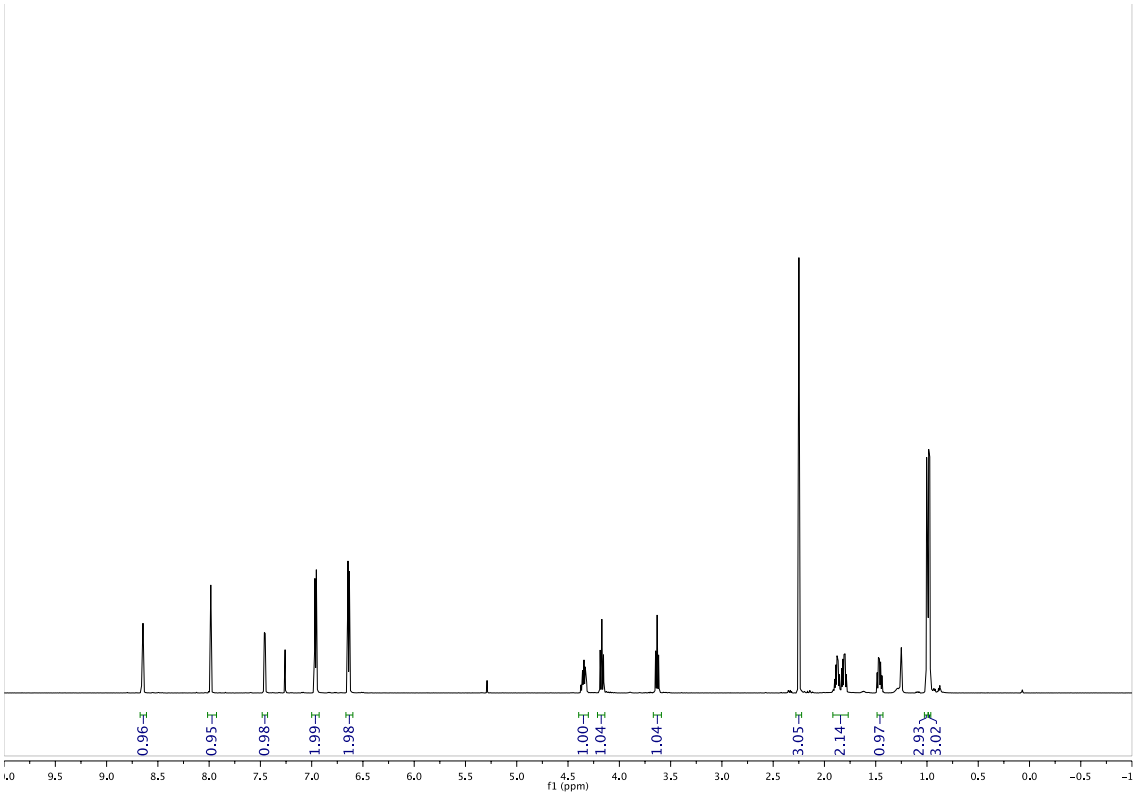

f1 (ppm)

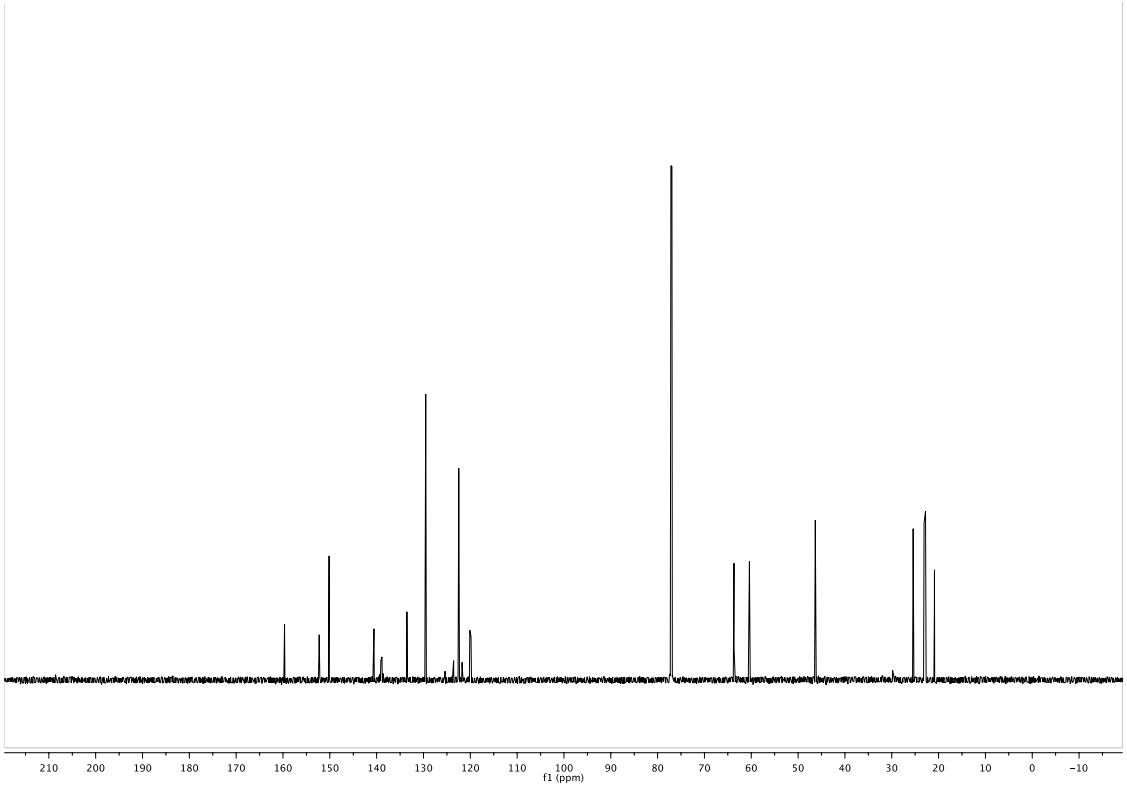

Me
MeO
N
N
N
i-Bu

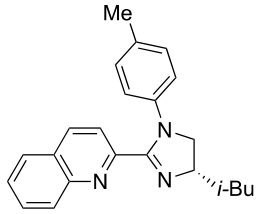

0.95
0.95
1.96
0.98
1.96
1.00
1.01
3.02
1.01
3.01
2.01
1.03
2.96
3.00
f1 (ppm)

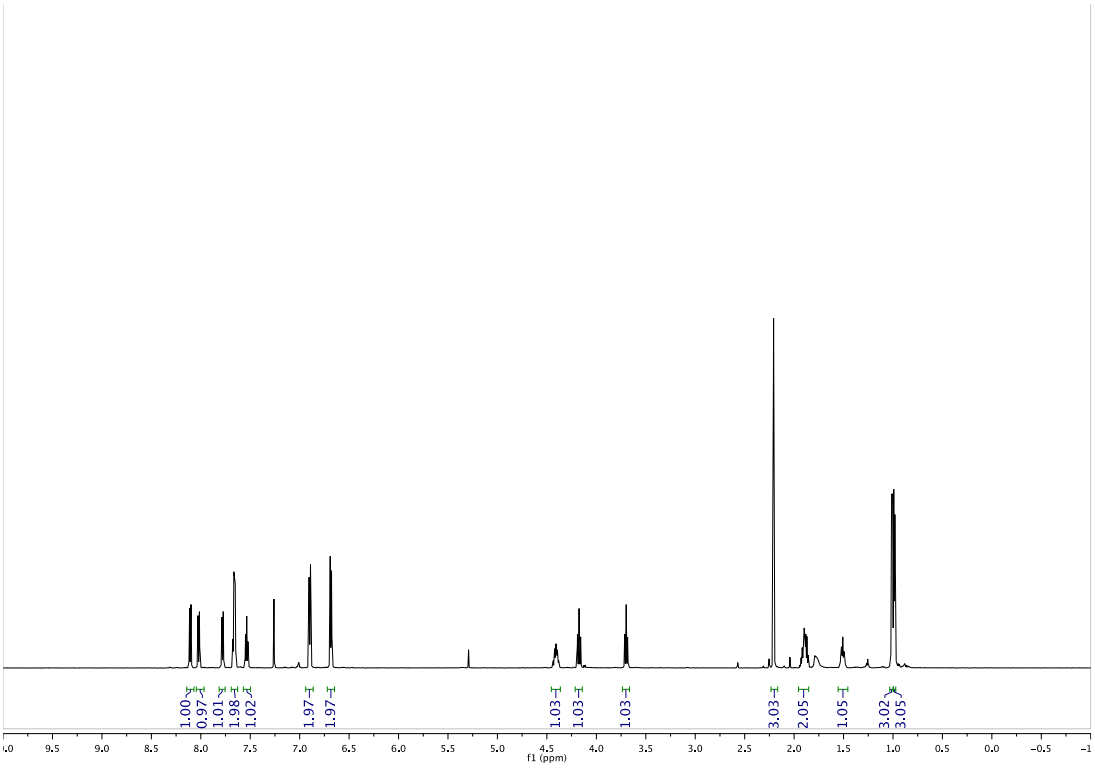

f1 (ppm)

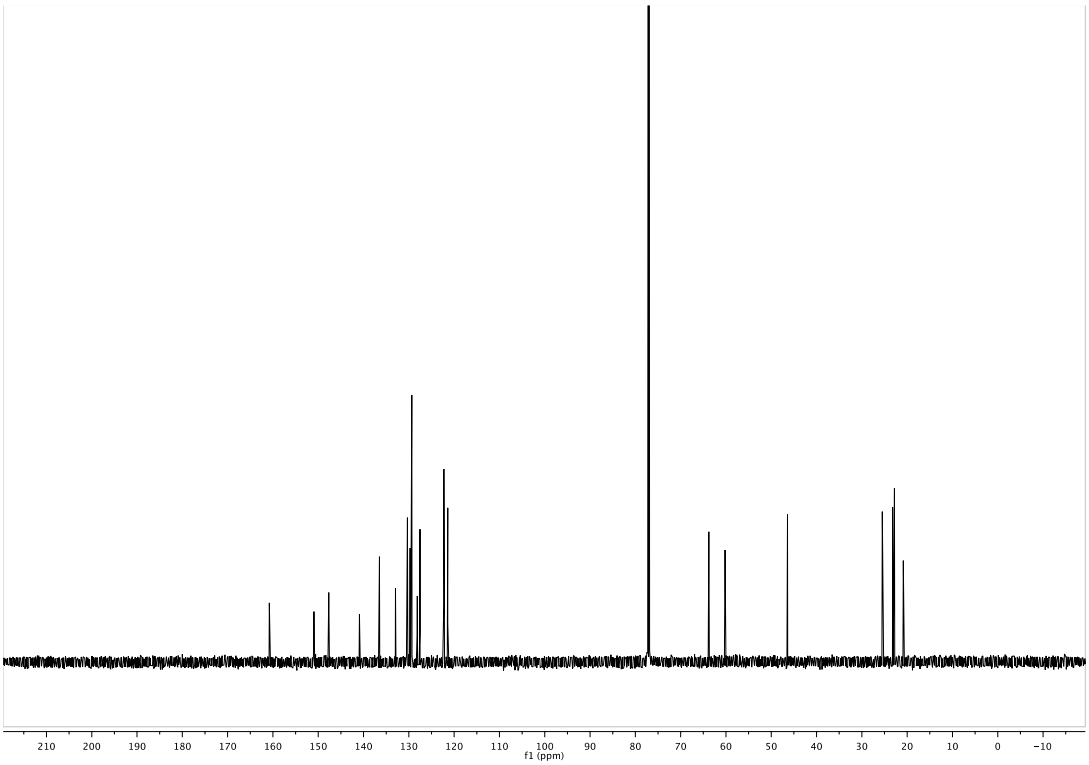

Me
F3C
N
N
N
i-Bu

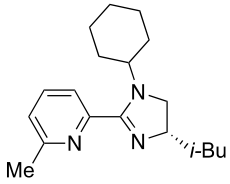

0.96
0.95
0.98
1.99
1.98
1.00
1.04
1.04
3.05
2.14
0.97
2.93
3.02
f1 (ppm)

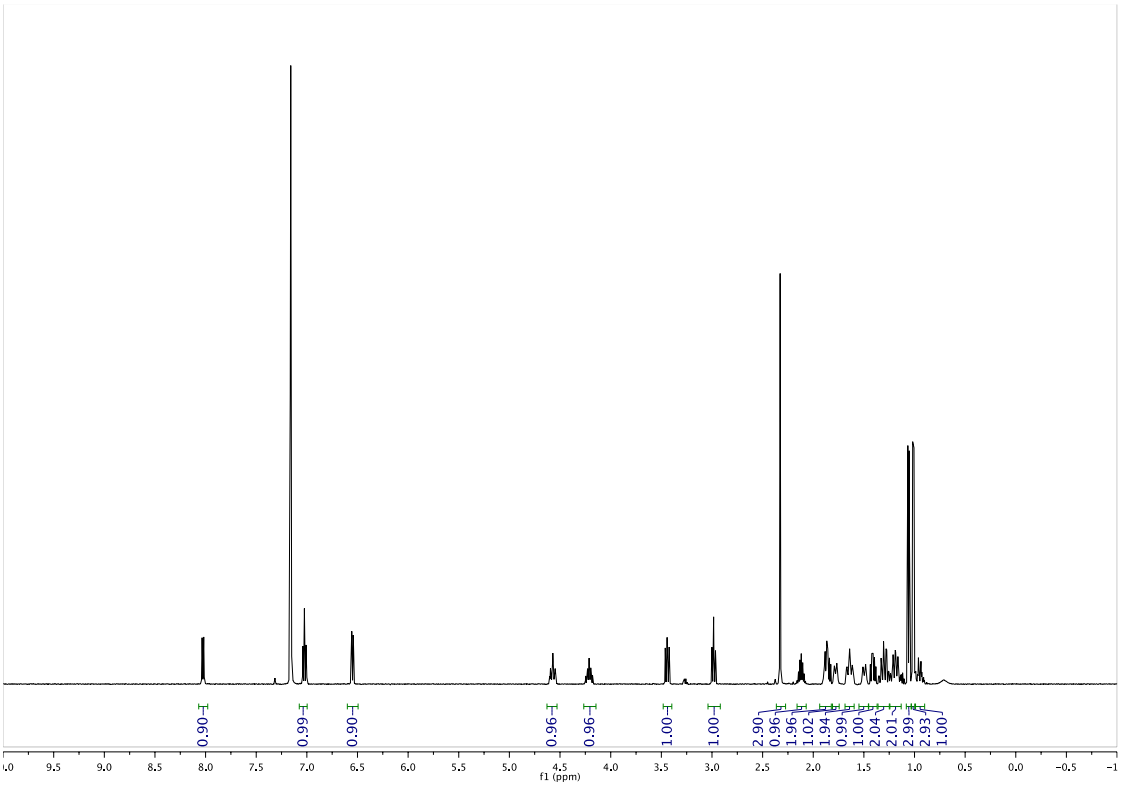

f1 (ppm)

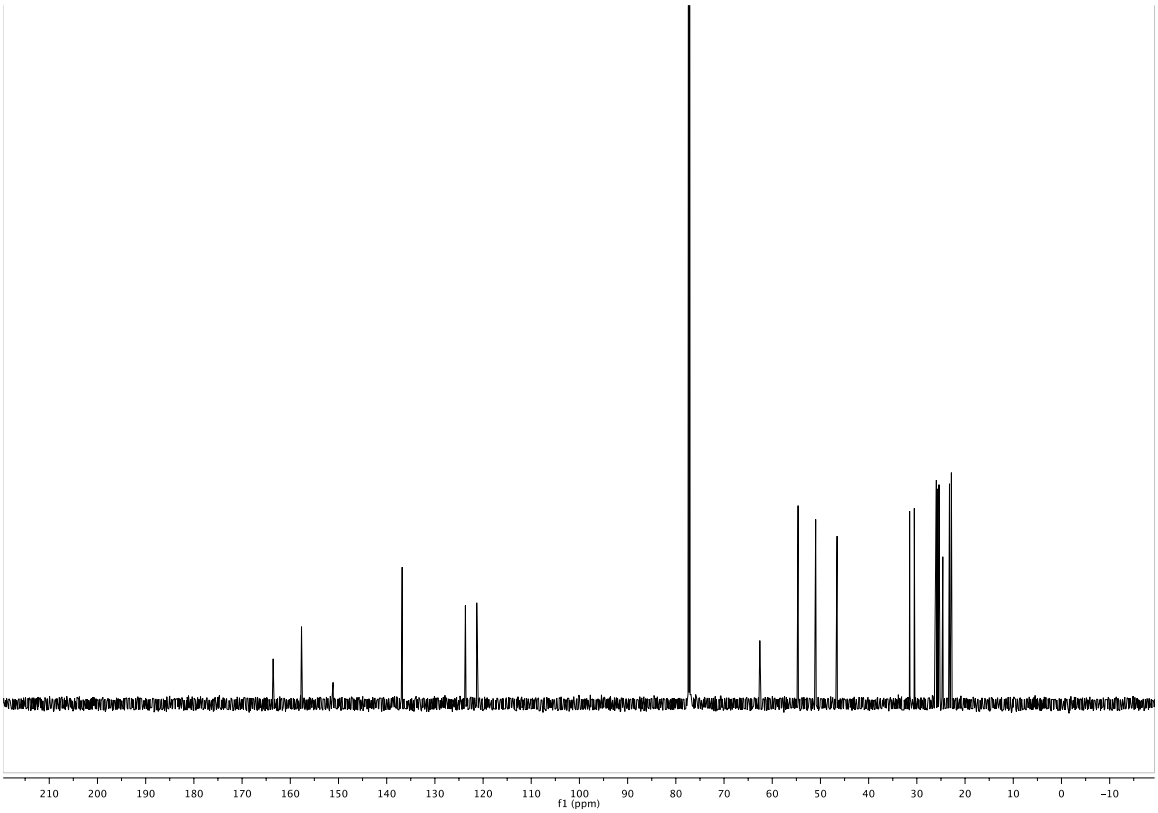

Me
N
N
N
i-Bu


1.00
0.97
1.01
1.98
1.02
1.97
1.97
1.03
1.03
1.03
3.03
2.05
1.05
3.02
3.05
f1 (ppm)


f1 (ppm)


N
N
N
Me
i-Bu


0.90
0.99
0.90
0.96
0.96
1.00
1.00
2.90
0.96
1.96
1.02
1.94
0.99
1.00
2.04
2.01
2.99
2.93
1.00
f1 (ppm)


f1 (ppm)