Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Silicon–Nitrogen Bond Formation via Dealkynative Coupling of Amines with Bis(trimethylsilyl)acetylene Mediated by KHMDS

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CONTENT

GENERAL INFORMATION

Air- and moisture sensitive reactions were carried out under argon atmosphere using standard Schlenk techniques or a glove box. Bis(trimethylsilyl)acetylene was purchased from Sigma Aldrich (Merck, CAS: 14630-40-1, 99%) and used as received. Solvents used for all experiments were purchased from Honeyweel or Sigma Aldrich (Merck), dried over calcium hydride (CaH_2) and purified by distillation. Toluene was additionally dried over sodium, and THF over sodium with benzophenone system. All reagents were commercially available and purchased from Sigma Aldrich (Merck), ABCR GmBH, Ambeed, or Apollo Scientific, dried over calcium hydride and purified by distillation. The progress of reactions (conversion of amines) was monitored by GC chromatography using Bruker Scion 460-GC and Agilent 5977B GC/MSD with Agilent 8860 GC System). The structures of products were determined by NMR spectroscopy and MS spectrometry. The ^{1}H NMR (400 or 600 MHz), ^{13}C NMR (101 or 151 MHz) and ^{29}Si NMR (79 or 119 MHz) spectra were recorded on Bruker Avance III HD NanoBay spectrometer, using benzene-d_6 (C_6D_6), chloroform-d_1 ($CDCl_3$), or acetonitrile-d_3 (CD_3CN) as the solvents. Deuterated solvents were purchased from Merck and Deutero GmbH and used as received.

GENERAL SYNTHETIC PROCEDURES

KHMDS-CATALYZED N–H SILYLATION OF SEVERAL PRIMARY AMINES

Compounds 3a-3n and 5a-5f

To a 25mL vial equipped with a magnetic stirring bar, potassium bis(trimethylsilyl)amide (0.030 mmol, 3.0 mol%) was added and stored under a high vacuum (10 min.). Subsequently, dry acetonitrile (1 mL), amine (**1a-1n or 4a-4f**, 1 mmol), and bis(trimethylsilyl)acetylene (1 mmol, 0.17 g) were added under argon atmosphere. The reaction mixture was stirred at **rt** (except **4e**/**5e**, where reaction was performed at 80°C) for a specified time (1-24 h). After this time, solvent and volatile residues were evaporated under reduced pressure. Next, the crude products were separated *via* bulb-to-bulb distillation under a high vacuum (0.47 mbar), to give corresponding products **3a-3n** and **5a-5f**. The pure products were identified by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopies and MS spectrometry.

Compound 3o

To a 25mL vial equipped with a magnetic stirring bar, potassium bis(trimethylsilyl)amide (0.03 mmol, 3 mol%) was added and stored under a high vacuum (10 min.). Subsequently, dry acetonitrile (1 mL), 4-aminophenol (1 mmol), and bis(trimethylsilyl)acetylene (1 mmol, 0.17 g) were added under argon atmosphere. The reaction mixture was stirred at rt for a specified time (2 h). After this time, solvent and volatile residues were evaporated under reduced pressure. Next, the crude product was separated *via* bulb-to-bulb distillation under a high vacuum (0.47 mbar), to give corresponding product **3o**. The pure product was identified by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopies and MS spectrometry.

Compound 3p

To a 25mL vial equipped with a magnetic stirring bar, potassium bis(trimethylsilyl)amide (0.03 mmol, 3 mol%) was added and stored under a high vacuum (10 min.). Subsequently, dry acetonitrile (1 mL), 3-ethynylaniline (1 mmol), and bis(trimethylsilyl)acetylene (2 mmol, 0.34 g) were added under argon atmosphere. The reaction mixture was stirred at rt for a specified time (2 h). After this time, solvent and volatile residues were evaporated under reduced pressure. Next, the crude product was separated *via* bulb-to-bulb distillation under a high vacuum (0.47 mbar), to give corresponding product **3p**. The pure product was identified by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopies and MS spectrometry.

KHMDS-CATALYZED SCALED UP N–H SILYLATION OF 3m.

To a 50mL vial equipped with a magnetic stirring bar, potassium bis(trimethylsilyl)amide (0.3 mmol, 3 mol%, 0.0597 g) was added and stored under a high vacuum (10 min.). Subsequently, dry acetonitrile (10 mL), 4-trifluoromethylaniline (10 mmol, 1.61 g), and bis(trimethylsilyl)acetylene (10 mmol, 1.7 g) were added under argon atmosphere. The reaction mixture was stirred at rt for a specified time (3 h). After this time, solvent and volatile residues were evaporated under reduced pressure. Next, the crude product was separated *via* bulb-to-bulb distillation under a high vacuum (0.47 mbar), to give a pure product **3m** (2.16 g, 92% yield).

KHMDS-CATALYZED N–H SILYLATION OF 3m IN THE PRESENCE OF TEMPO

To a 25mL vial equipped with a magnetic stirring bar, potassium bis(trimethylsilyl)amide (0.03 mmol, 3 mol%) was added and stored under a high vacuum (10 min.). Subsequently, dry acetonitrile (1 mL), 4-trifluoromethylaniline (1 mmol), and bis(trimethylsilyl)acetylene (2 mmol, 0.17 g) were added under argon atmosphere. The reaction mixture was stirred at rt for a specified time (3 h). After this time, solvent and volatile residues were evaporated under reduced pressure. Next, the crude product was separated *via* bulb-to-bulb distillation under a high vacuum (0.47 mbar), to give corresponding product **3m** (84%).

KHMDS-CATALYZED N–H SILYLATION OF 3m IN THE PRESENCE OF 18-CROWN-6

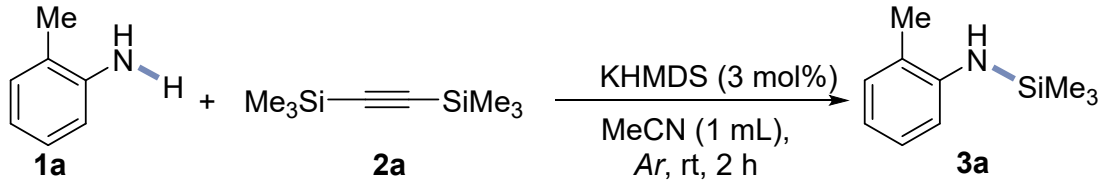
To a 25mL vial equipped with a magnetic stirring bar, potassium bis(trimethylsilyl)amide (0.03 mmol, 3 mol%), and 18-crown-6 (1 mmol) were added and stored under a high vacuum (10 min.). Subsequently, dry acetonitrile (1 mL), 4-trifluoromethylaniline (1 mmol), and bis(trimethylsilyl)acetylene (2 mmol, 0.17 g) were added under argon atmosphere. The reaction mixture was stirred at rt for a specified time (3 h). After this time, solvent and volatile residues were evaporated under reduced pressure. Next, the crude product was separated *via* bulb-to-bulb distillation under a high vacuum (0.47 mbar), to give corresponding product **3m** (82%).

KHMDS-CATALYZED N–H SILYLATION OF 3m IN THE PRESENCE OF QUADRA-PURE®

To a 25mL vial equipped with a magnetic stirring bar, potassium bis(trimethylsilyl)amide (0.03 mmol, 3 mol%) and 100 mg of Quadra-Pure® TU were added and stored under a high vacuum (10 min.). Subsequently, dry acetonitrile (1 mL), 4-trifluoromethylaniline (1 mmol), and bis(trimethylsilyl)acetylene (2 mmol, 0.17 g) were added under argon atmosphere. The reaction mixture was stirred at rt for a specified time (3 h). After this time, solvent and volatile residues were evaporated under reduced pressure. Next, the crude product was separated *via* bulb-to-bulb distillation under a high vacuum (0.47 mbar), to give corresponding product **3m** (85%).

OPTIMIZATION STUDIES

TABLE S1. OPTIMIZATION N–H silylation.[a]



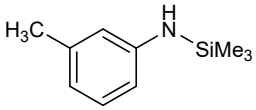
1a **2a** **3a**

Entry	Variation from standard conditions	Conversion of **1a** [%][b]
1	no change	99 (97)[c]
2	no catalyst	0[D]
3	under air atmosphere	97
4	trimethylsilylacetylene instead of BTMSA	95[E,F]
5	Trimethyl(phenylethynyl)silane instead of BTMSA	16[E]
6	0.5 eq. of BTMSA	85
7	1.5 mol% of KHMDS	95
8	3 mol% of KOH	85
9	5 mol% of KOH (rt/50°C)	90/95 (92)[c]
10	3 mol% of t-BuOK	94
11	3 mol% of KF	0
12	in tetrahydrofuran	75
13	in toluene	0
14	in dioxane	0

[a]Reaction conditions: **1a** (1 mmol), **2a** (1 mmol), under argon atmosphere. [b]Conversion determined *via* GC, with n-dodecane as internal standard. [c]Isolated yield in parenthesis. [d]In a brand-new set of equipment, to exclude the influence of any transition metal impurities. [e]After 2 h and 10 h, with 2 eq. of trimethylsilylacetylene. [f]2 eq. of trimethylsilylacetylene.

CHARACTERIZATION DATA FOR ALL PRODUCTS

1,1,1-Trimethyl-N-(m-tolyl)silanamine (3a)



1,1,1-Trimethyl-N-(m-tolyl)silanamine was obtained as pale-yellow oil in 97% yield.

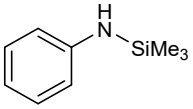
^{1}H NMR (400 MHz, C_6D_6) δ (ppm) = 7.08 (t, *J* = 7.7 Hz, 1H), 6.63 – 6.57 (m, 1H), 6.50 – 6.43 (m, 1H), 6.42 – 6.36 (m, 11H), 3.04 (s, 1H), 2.18 (s, 3H), 0.14 (s, 9H).

^{13}C NMR (101 MHz, C_6D_6) δ (ppm) = 147.7, 138.9, 119.0, 117.6, 113.7, 21.7, 0.1.

^{29}Si NMR (79 MHz, C_6D_6) δ (ppm) = 2.2.

EI-MS m/z (rel. int.): 179 (50%, $[M]^+$), 164 (100), 106 (30).

1,1,1-Trimethyl-N-phenylsilanamine (3b)



1,1,1-Trimethyl-N-phenylsilanamine was obtained as pale-yellow oil in 92% yield.

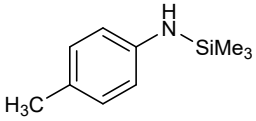
^{1}H NMR (400 MHz, C_6D_6) δ (ppm) = 7.19 – 7.12 (m, 2H), 6.82 – 6.73 (m, 1H), 6.62 – 6.55 (m, 2H), 0.12 (s, 9H).

^{13}C NMR (101 MHz, C_6D_6) δ (ppm) = 147.7, 129.6, 118.1, 116.6, -0.0.

^{29}Si NMR (79 MHz, C_6D_6) δ (ppm) = 2.3.

EI-MS m/z (rel. int.): 165 (35%, $[M]^+$), 150 (100), 134 (5).

1,1,1-Trimethyl-N-(p-tolyl)silanamine (3c)



1,1,1-Trimethyl-N-(p-tolyl)silanamine was obtained as pale-yellow oil in 95% yield.

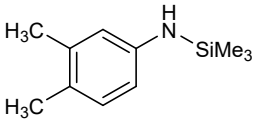
^{1}H NMR (400 MHz, C_6D_6) δ (ppm) = 7.08 – 6.90 (m, 2H), 6.54 (d, *J* = 8.4 Hz, 2H), 2.98 (s, 1H), 2.19 (s, 3H), 0.13 (s, 9H).

^{13}C NMR (101 MHz, C_6D_6) δ (ppm) = 145.2, 130.1, 126.7, 116.7, 20.6, 0.1.

^{29}Si NMR (79 MHz, C_6D_6) δ (ppm) = 2.0.

EI-MS m/z (rel. int.): 179 (45%, $[M]^+$), 164 (100), 106 (30).

N-(3,4-dimethylphenyl)-1,1,1-trimethylsilanamine (3d)



N-(3,4-dimethylphenyl)-1,1,1-trimethylsilanamine was obtained as pale-yellow oil in 97% yield.

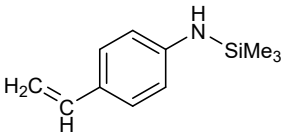
^{1}H NMR (600 MHz, C_6D_6) δ (ppm) = 6.94 (d, *J* = 8.0 Hz, 1H), 6.46 (dd, *J* = 8.0, 2.6 Hz, 1H), 6.42 (d, *J* = 2.6 Hz, 1H), 2.96 (s, 1H), 2.08 (s, 3H), 2.08 (s, 3H), 0.16 (s, 9H).

^{13}C NMR (151 MHz, C_6D_6) δ (ppm) = 145.6, 137.1, 130.7, 125.5, 118.6, 114.1, 20.1, 18.9, 0.2.

^{29}Si NMR (79 MHz, C_6D_6) δ (ppm) = 1.4.

EI-MS m/z (rel. int.): 193 (55%, $[M]^+$), 178 (100), 163 (20).

1,1,1-Trimethyl-N-(4-vinylphenyl)silanamine (3e)



1,1,1-Trimethyl-N-(4-vinylphenyl)silanamine was obtained as pale-yellow oil in 90% yield.

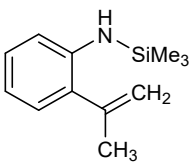
^{1}H NMR (400 MHz, C_6D_6) δ (ppm) = 7.20 (d, *J* = 8.5 Hz, 2H), 6.66 (dd, *J* = 17.5, 10.9 Hz, 1H), 6.48 (d, *J* = 8.6 Hz, 2H), 5.58 (dd, *J* = 17.6, 1.2 Hz, 1H), 5.04 (dd, *J* = 10.8, 1.2 Hz, 1H), 3.08 (s, 1H), 0.10 (s, 9H).

^{13}C NMR (101 MHz, C_6D_6) δ (ppm) = 147.9, 137.6, 128.3, 128.0, 116.8, 109.8, 0.2.

^{29}Si NMR (79 MHz, C_6D_6) δ (ppm) = 2.7.

EI-MS m/z (rel. int.): 191 (75%, $[M]^+$), 176 (100), 119 (20).

1,1,1-Trimethyl-N-(2-(prop-1-en-2-yl)phenyl)silanamine (3f)



1,1,1-Trimethyl-N-(2-(prop-1-en-2-yl)phenyl)silanamine was obtained as pale-yellow oil in 89% yield.

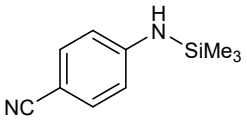
^{1}H NMR (600 MHz, C_6D_6) δ (ppm) = 7.11 – 7.03 (m, 2H), 6.91 – 6.85 (m, 1H), 6.79 – 6.71 (m, 1H), 5.16 (d, *J* = 1.4 Hz, 1H), 5.04 (d, *J* = 1.1 Hz, 1H), 4.07 (s, 3H), 1.90 (s, 9H).

^{13}C NMR (151 MHz, C_6D_6) δ (ppm) = 144.3, 143.6, 131.3, 128.3, 128.0, 127.9, 117.6, 115.3, 23.8, -0.3.

^{29}Si NMR (119 MHz, C_6D_6) δ (ppm) = 2.0.

EI-MS m/z (rel. int.): 205 (60%, $[M]^+$), 190 (30), 132 (100).

4-((Trimethylsilyl)amino)benzonitrile (3g)



4-((Trimethylsilyl)amino)benzonitrile was obtained as pale-yellow oil in 89% yield.

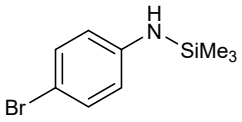
^{1}H NMR (600 MHz, C_6D_6) δ (ppm) = 7.06 (d, *J* = 8.6 Hz, 2H), 6.32 – 6.16 (m, 2H), 3.57 (s, 1H), 0.02 (s, 9H).

^{13}C NMR (151 MHz, C_6D_6) δ (ppm) = 151.7, 133.3, 120.0, 116.1, 99.9, -0.8.

^{29}Si NMR (119 MHz, C_6D_6) δ (ppm) = 4.1.

EI-MS m/z (rel. int.): 190 (25%, $[M]^+$), 175 (100), 159 (10).

N-(4-bromophenyl)-1,1,1-trimethylsilanamine (3h)



N-(4-bromophenyl)-1,1,1-trimethylsilanamine was obtained as pale-yellow oil in 99% yield.

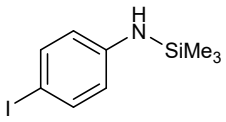
^{1}H NMR (400 MHz, C_6D_6) δ (ppm) = 7.15 (d, *J* = 9.0 Hz, 2H), 6.21 (dd, *J* = 8.9, 1.0 Hz, 2H), 2.95 (s, 1H), 0.04 (s, 9H).

^{13}C NMR (101 MHz, C_6D_6) δ (ppm) = 147.0, 132.5, 118.4, 110.0, 109.9, 0.0.

^{29}Si NMR (79 MHz, C_6D_6) δ (ppm) = 3.1.

EI-MS m/z (rel. int.): 243 (85%, $[M]^+$), 230 (90), 149 (100).

N-(4-iodophenyl)-1,1,1-trimethylsilanamine (3i)



N-(4-iodophenyl)-1,1,1-trimethylsilanamine was obtained as pale-yellow oil in 95% yield.

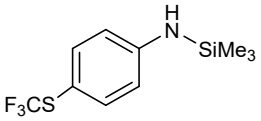
^{1}H NMR (600 MHz, C_6D_6) δ (ppm) = 7.32 (d, *J* = 8.7 Hz, 2H), 6.13 (d, *J* = 8.8 Hz, 2H), 2.95 (s, 1H), 0.04 (s, 9H).

^{13}C NMR (151 MHz, C_6D_6) δ (ppm) = 147.0, 137.9, 118.5, 78.5, -0.5.

^{29}Si NMR (119 MHz, C_6D_6) δ (ppm) = 2.7.

EI-MS m/z (rel. int.): 291 (100%, $[M]^+$), 276 (60), 149 (30).

1,1,1-Trimethyl-N-(4-((trifluoromethyl)thio)phenyl)silanamine (3j)



1,1,1-Trimethyl-N-(4-((trifluoromethyl)thio)phenyl)silanamine was obtained as pale-yellow oil in 88% yield.

^{1}H NMR (600 MHz, C_6D_6) δ (ppm) = 7.33 (d, *J* = 8.6 Hz, 2H), 6.36 – 6.16 (m, 2H), 3.10 (s, 1H), 0.01 (s, 9H).

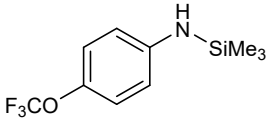
^{13}C NMR (151 MHz, C_6D_6) δ (ppm) = 150.7, 138.5, 130.75 (q, *J* = 308.1 Hz).117.2, 110.6, -0.4.

^{19}F NMR (565 MHz, C_6D_6) δ (ppm) = -44.3.

^{29}Si NMR (119 MHz, C_6D_6) δ (ppm) = 3.5.

EI-MS m/z (rel. int.): 265 (100%, $[M]^+$), 250 (50), 196 (45).

1,1,1-Trimethyl-N-(4-(trifluoromethoxy)phenyl)silanamine (3k)



1,1,1-Trimethyl-N-(4-(trifluoromethoxy)phenyl)silanamine was obtained as pale-yellow oil in 88% yield.

^{1}H NMR (600 MHz, C_6D_6) δ (ppm) = 6.88 (d, *J* = 8.2 Hz, 2H), 6.35 – 6.19 (m, 1H), 2.98 (s, 1H), 0.05 (s, 9H).

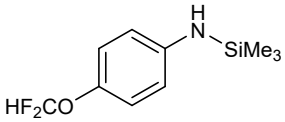
^{13}C NMR (151 MHz, C_6D_6) δ (ppm) = 146.8, 122.6, 121.9 (q, *J* = 182 Hz), 116.8, 115.3, -0.3.

^{19}F NMR (565 MHz, C_6D_6) δ (ppm) = -58.2.

^{29}Si NMR (119 MHz, C_6D_6) δ (ppm) = 2.8.

EI-MS m/z (rel. int.): 249 (40%, $[M]^+$), 234 (100), 218 (5).

N-(4-(difluoromethoxy)phenyl)-1,1,1-trimethylsilanamine (3l)



N-(4-(difluoromethoxy)phenyl)-1,1,1-trimethylsilanamine was obtained as pale-yellow oil in 88% yield.

^{1}H NMR (600 MHz, C_6D_6) δ (ppm) = 6.81 (d, *J* = 8.9 Hz, 2H), 6.39 – 6.25 (m, 2H), 6.12 – 5.75 (m, 1H), 2.96 (s, 1H), 0.08 (s, 9H).

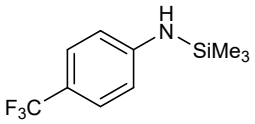
^{13}C NMR (151 MHz, C_6D_6) δ (ppm) = 144.39 (dd, *J* = 351.2, 3.1 Hz), 121.6, 117.3 (q, *J* = 176 Hz), 117.0, -0.2.

^{19}F NMR (565 MHz, C_6D_6) δ (ppm) = -79.52 (d, *J* = 75.1 Hz).

^{29}Si NMR (119 MHz, C_6D_6) δ (ppm) = 2.4.

EI-MS m/z (rel. int.): 231 (45%, $[M]^+$), 216 (100), 159 (15).

1,1,1-Trimethyl-N-(4-(trifluoromethyl)phenyl)silanamine (3m)



1,1,1-Trimethyl-N-(4-(trifluoromethyl)phenyl)silanamine was obtained as pale-yellow oil in 85% yield.

^{1}H NMR (600 MHz, C_6D_6) δ (ppm) = 7.29 (d, *J* = 8.5 Hz, 2H), 6.28 (d, *J* = 8.2 Hz, 2H), 3.10 (s, 1H), 0.03 (s, 9H).

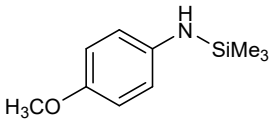
^{13}C NMR (151 MHz, C_6D_6) δ (ppm) = 151.1, 127,1, 126.1 (q, *J* = 186 Hz), 119.9 (q, *J* = 180 Hz), 116.2, -0.2.

^{19}F NMR (565 MHz, C_6D_6) δ (ppm) = -60.6.

^{29}Si NMR (119 MHz, C_6D_6) δ (ppm) = 3.4.

EI-MS m/z (rel. int.): 233 (35%, $[M]^+$), 218 (100), 149 (5).

N-(4-methoxyphenyl)-1,1,1-trimethylsilanamine (3n)



N-(4-methoxyphenyl)-1,1,1-trimethylsilanamine was obtained as pale-yellow oil in 95% yield.

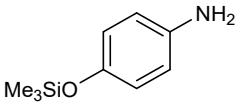
^{1}H NMR (600 MHz, C_6D_6) δ (ppm) = 6.80 – 6.71 (m, 2H), 6.52 (d, *J* = 8.8 Hz, 2H), 3.41 (s, 3H), 2.86 (s, 1H), 0.14 (s, 9H).

^{13}C NMR (151 MHz, C_6D_6) δ (ppm) = 153.0, 141.2, 117.6, 115.3, 55.3, 0.1.

^{29}Si NMR (119 MHz, C_6D_6) δ (ppm) = 1.4.

EI-MS m/z (rel. int.): 195 (80%, $[M]^+$), 180 (100), 108 (40).

4-((Trimethylsilyl)oxy)aniline (3o)



4-((Trimethylsilyl)oxy)aniline was obtained as pale-yellow oil in 95% yield.

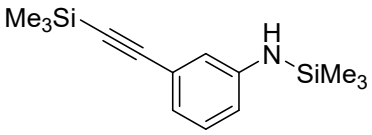
^{1}H NMR (400 MHz, C_6D_6) δ (ppm) = 6.99 – 6.51 (m, 2H), 6.39 – 6.14 (m, 2H), 2.80 (s, 2H), 0.19 (s, 9H).

^{13}C NMR (101 MHz, C_6D_6) δ (ppm) = 147.8, 141.6, 120.9, 116.3, 0.2.

^{29}Si NMR (79 MHz, C_6D_6) δ (ppm) = 18.0.

EI-MS m/z (rel. int.): 181 (90%, $[M]^+$), 166 (100), 149 (10).

1,1,1-Trimethyl-N-(3-((trimethylsilyl)ethynyl)phenyl)silanamine (3p)



1,1,1-Trimethyl-N-(3-((trimethylsilyl)ethynyl)phenyl)silanamine was obtained as pale-yellow oil in 88% yield.

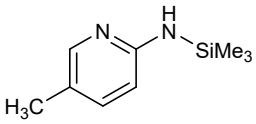
^{1}H NMR (400 MHz, C_6D_6) δ (ppm) = 7.06 (t, *J* = 7.9 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, 1H), 6.75 (s, 1H), 6.67 – 6.58 (m, 1H), 3.42 (s, 1H), 0.28 (s, 9H), 0.26 (s, 9H).

^{13}C NMR (101 MHz, C_6D_6) δ (ppm) = 147.4, 129.2, 123.9, 121.6, 119.4, 116.8, 105.9, 93.2, 0.2.

^{29}Si NMR (79 MHz, C_6D_6) δ (ppm) = 3.5, -18.0.

EI-MS m/z (rel. int.): 261 (55%, $[M]^+$), 246 (100), 174 (50).

5-Methyl-N-(trimethylsilyl)pyridin-2-amine (5a)



5-Methyl-N-(trimethylsilyl)pyridin-2-amine was obtained as pale-yellow oil in 98% yield.

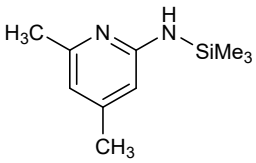
^{1}H NMR (600 MHz, C_6D_6) δ (ppm) = 7.98 (d, *J* = 2.5 Hz, 1H), 6.89 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.03 (d, *J* = 8.1 Hz, 1H), 3.74 (s, 1H), 1.88 (s, 3H), 0.31 (s, 9H).

^{13}C NMR (151 MHz, C_6D_6) δ (ppm) = 158.2, 148.2, 137.9, 121.4, 109.5, 17.2, 0.1.

^{29}Si NMR (119 MHz, C_6D_6) δ (ppm) = 1.9.

EI-MS m/z (rel. int.): 180 (20%, $[M]^+$), 165 (100), 135 (5).

4,6-Dimethyl-N-(trimethylsilyl)pyridin-2-amine (5b)



4,6-Dimethyl-N-(trimethylsilyl)pyridin-2-amine was obtained as pale-yellow oil in 97% yield.

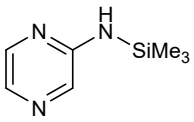
^{1}H NMR (600 MHz, C_6D_6) δ (ppm) = 6.12 (s, 1H), 5.74 (s, 1H), 3.72 (s, 1H), 2.30 (s, 3H), 1.91 (s, 3H), 0.33 (s, 9H).

^{13}C NMR (151 MHz, C_6D_6) δ (ppm) = 160.0, 156.6, 148.1, 113.8, 107.3, 24.2, 20.8, 0.4.

^{29}Si NMR (119 MHz, C_6D_6) δ (ppm) = 1.7.

EI-MS m/z (rel. int.): 194 (15%, $[M]^+$), 179 (100), 149 (5).

N-(trimethylsilyl)pyrazin-2-amine (5c)



N-(trimethylsilyl)pyrazin-2-amine was obtained as pale-yellow oil in 91% yield.

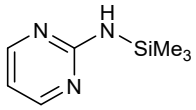
^{1}H NMR (600 MHz, C_6D_6) δ (ppm) = 7.84 – 7.59 (m, 3H), 4.00 (s, 1H), 0.24 (s, 9H).

^{13}C NMR (151 MHz, C_6D_6) δ (ppm) = 157.1, 142.2, 134.9, 134.0, -0.1.

^{29}Si NMR (119 MHz, C_6D_6) δ (ppm) = 4.5.

EI-MS m/z (rel. int.): 167 (35%, $[M]^+$), 152 (100), 125 (15).

N-(trimethylsilyl)pyrimidin-2-amine (5d)



N-(trimethylsilyl)pyrimidin-2-amine was obtained as pale-yellow oil in 91% yield.

^{1}H NMR (400 MHz, C_6D_6) δ (ppm) = 8.02 (d, *J* = 4.8 Hz, 2H), 6.00 (t, *J* = 4.8 Hz, 1H), 5.81 (s, 1H), 0.27 (s, 9H).

^{13}C NMR (101 MHz, C_6D_6) δ (ppm) = 165.4, 158.0, 111.1, -0.3.

^{29}Si NMR (79 MHz, C_6D_6) δ (ppm) = 3.9.

EI-MS m/z (rel. int.): 167 (35%, $[M]^+$), 152 (100), 125 (15).

N-(trimethylsilyl)quinolin-8-amine (5e)

N-(trimethylsilyl)quinolin-8-amine was obtained as pale-yellow oil in 99% yield.

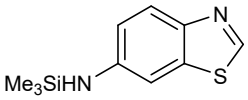
^{1}H NMR (600 MHz, C_6D_6) δ (ppm) = 8.65 (d, *J* = 1.7 Hz, 1H), 7.71 – 7.63 (m, 1H), 7.40 – 7.30 (m, 1H), 7.11 – 7.01 (m, 2H), 6.92 – 6.84 (m, 1H), 6.68 (s, 1H), 0.31 (s, 9H).

^{13}C NMR (151 MHz, C_6D_6) δ (ppm) = 146.8, 145.7, 139.9, 135.8, 129.2, 128.1, 121.2, 115.0, 109.4, -0.5.

^{29}Si NMR (119 MHz, C_6D_6) δ (ppm) = 2.7.

EI-MS m/z (rel. int.): 216 (15%, $[M]^+$), 201 (100), 171 (40).

N-(trimethylsilyl)benzo[d]thiazol-6-amine (5f)



N-(trimethylsilyl)benzo[d]thiazol-6-amine was obtained as pale-yellow oil in 98% yield.

^{1}H NMR (400 MHz, C_6D_6) δ (ppm) = 8.19 (s, 1H), 8.01 (d, *J* = 8.7 Hz, 1H), 6.90 (d, *J* = 2.4 Hz, 1H), 6.57 (dd, *J* = 8.7, 2.4 Hz, 1H), 3.18 (s, 1H), 0.07 (s, 9H).

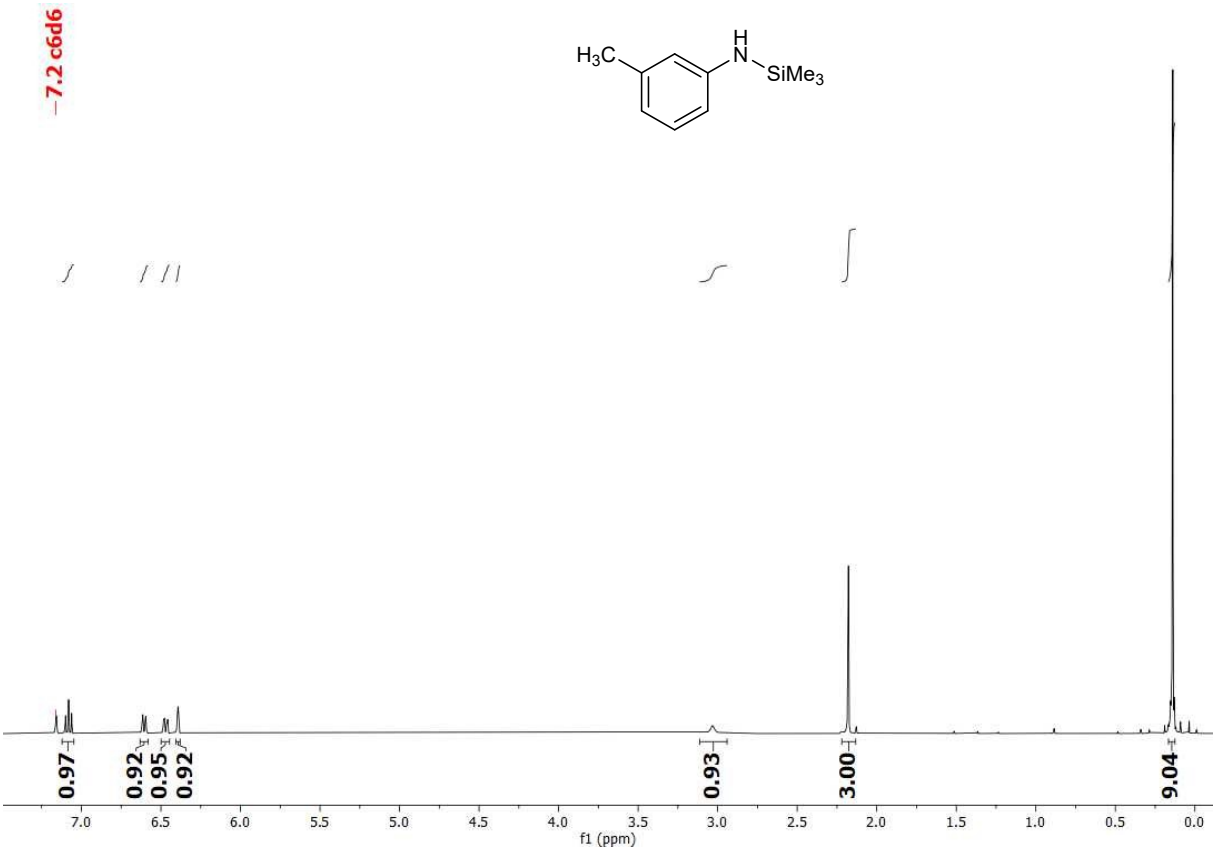
^{13}C NMR (101 MHz, C_6D_6) δ (ppm) = 149.0, 147.3, 146.2, 136.4, 124.5, 117.4, 106.8, -0.1.

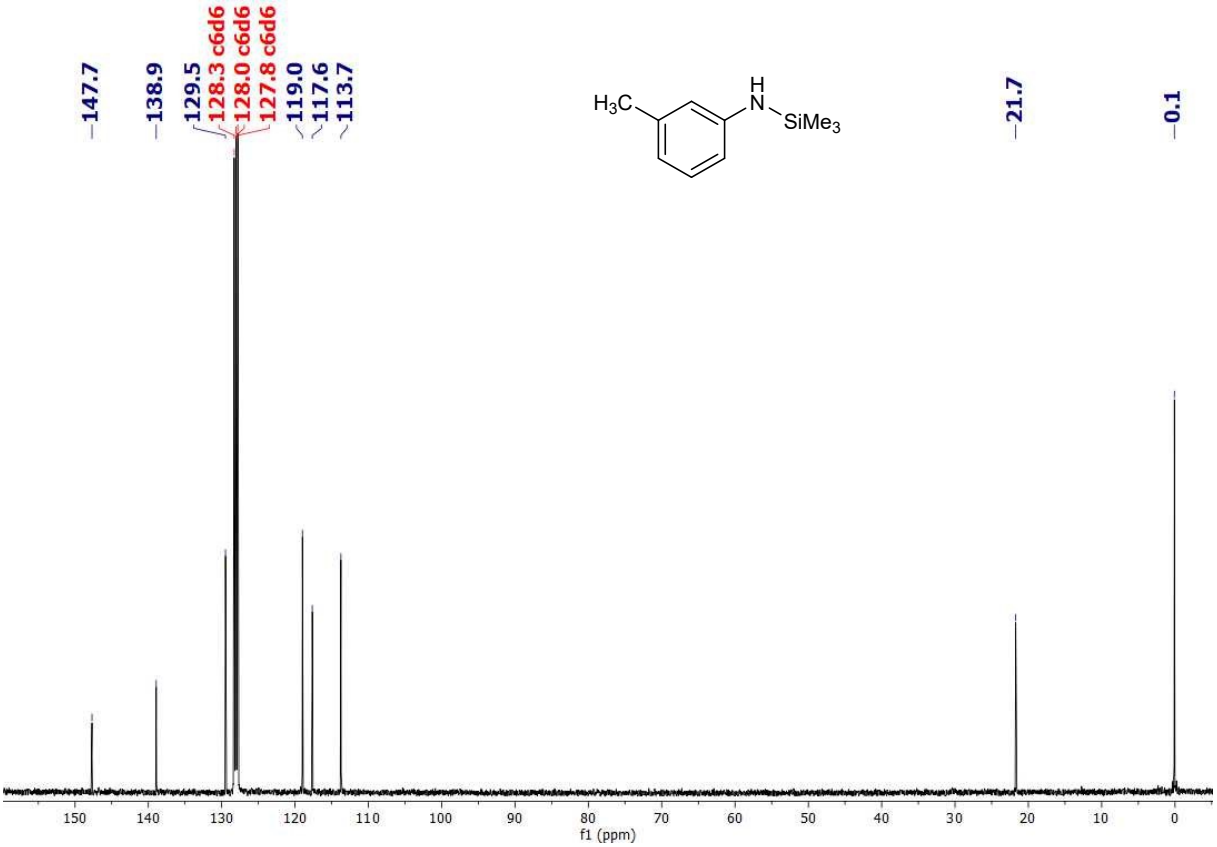
^{29}Si NMR (79 MHz, C_6D_6) δ (ppm) = 3.2.

EI-MS m/z (rel. int.): 222 (50%, $[M]^+$), 207 (100), 150 (30).

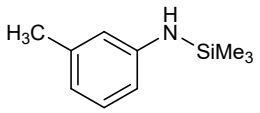
SPECTRA FOR ALL PRODUCTS

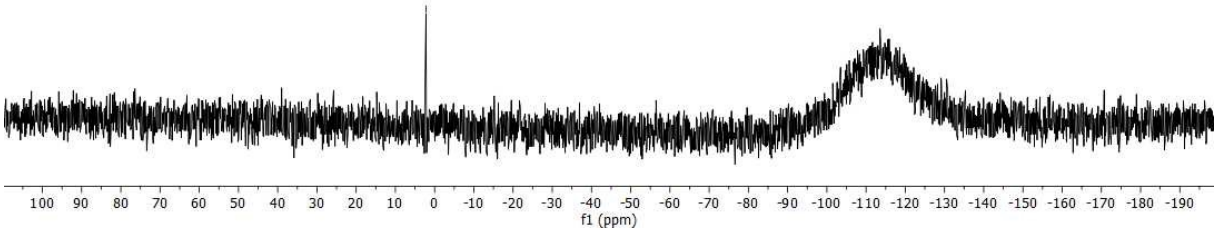
1,1,1-Trimethyl-N-(m-tolyl)silanamine (3a)



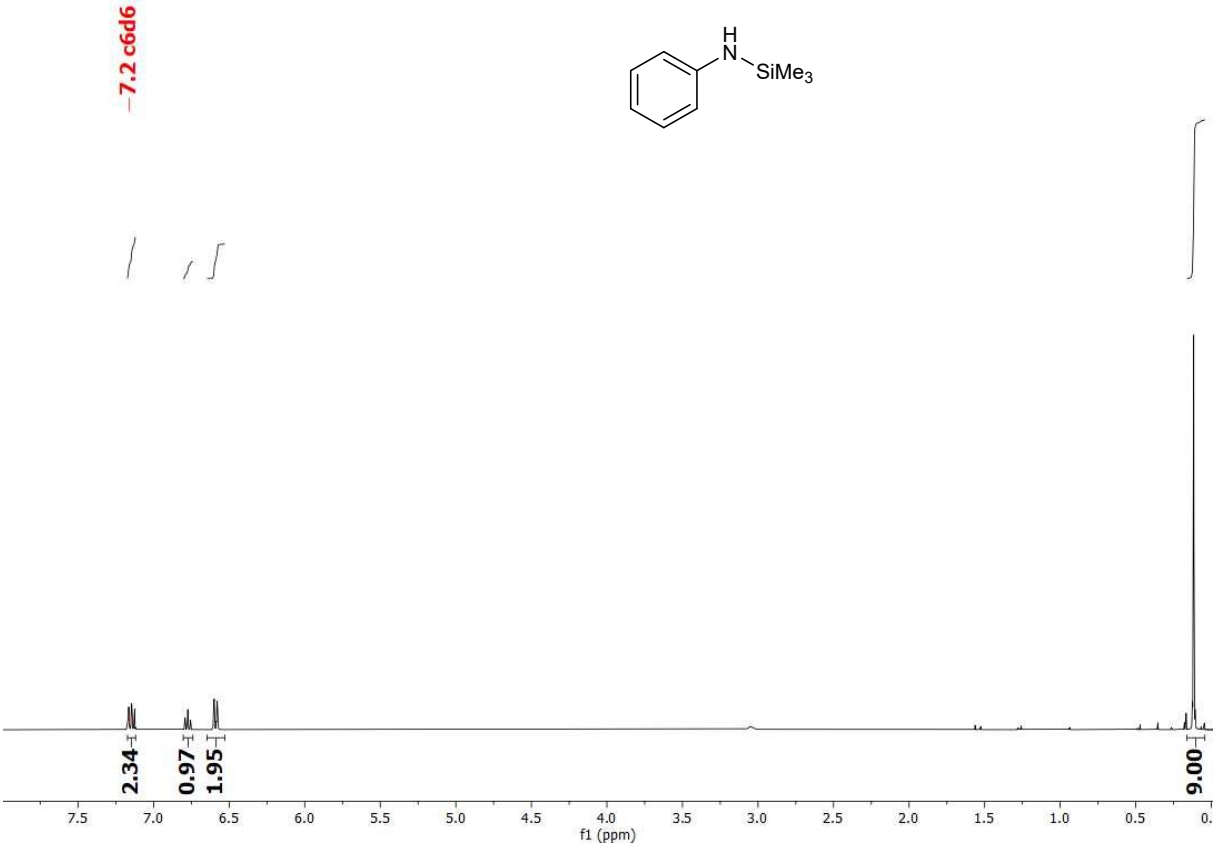


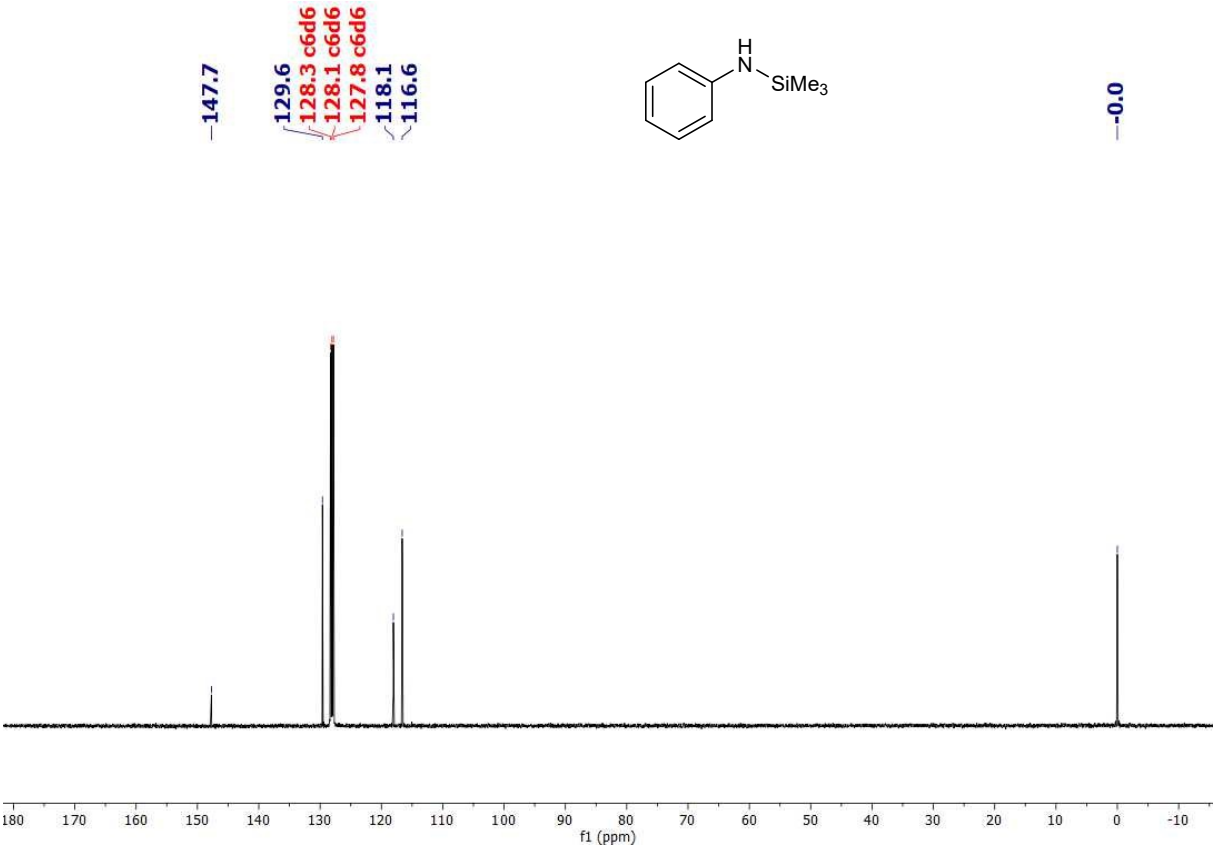
2.2

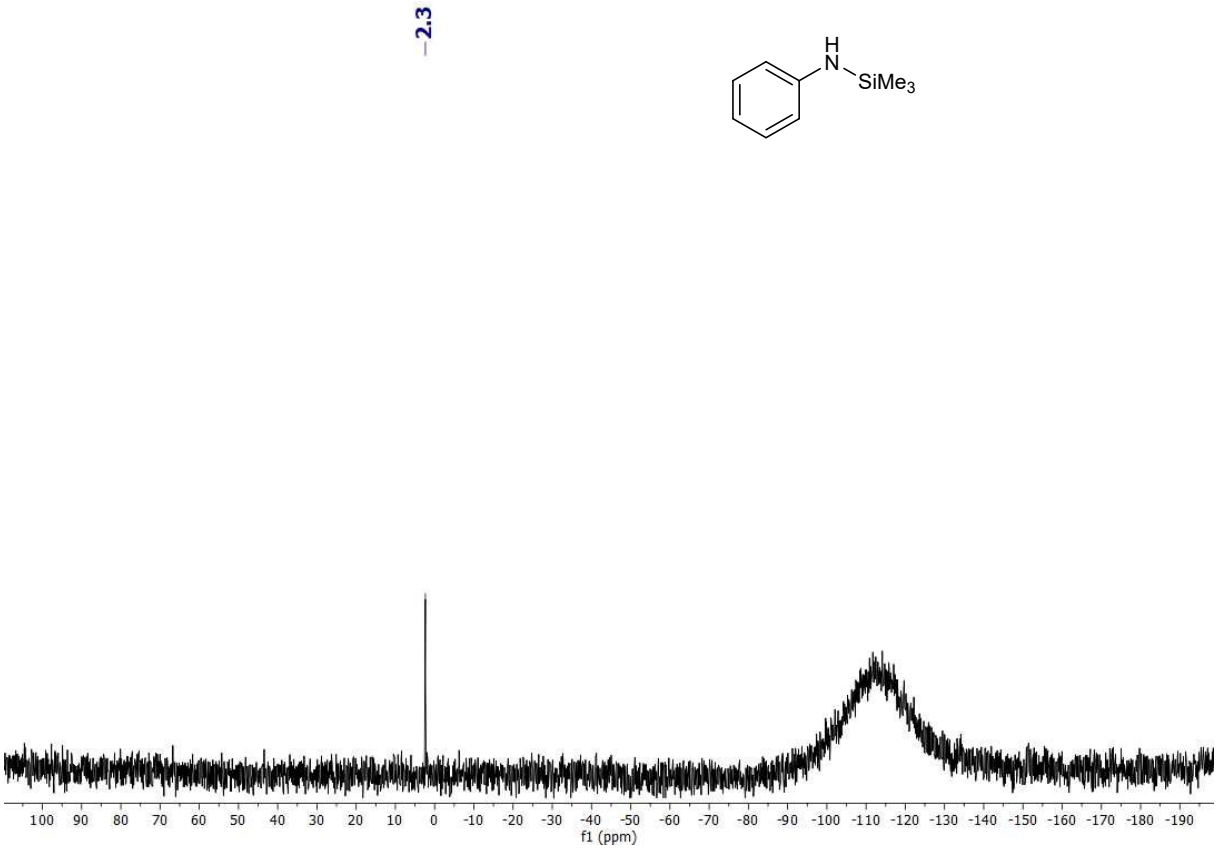

H3C
H
N
SiMe3


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

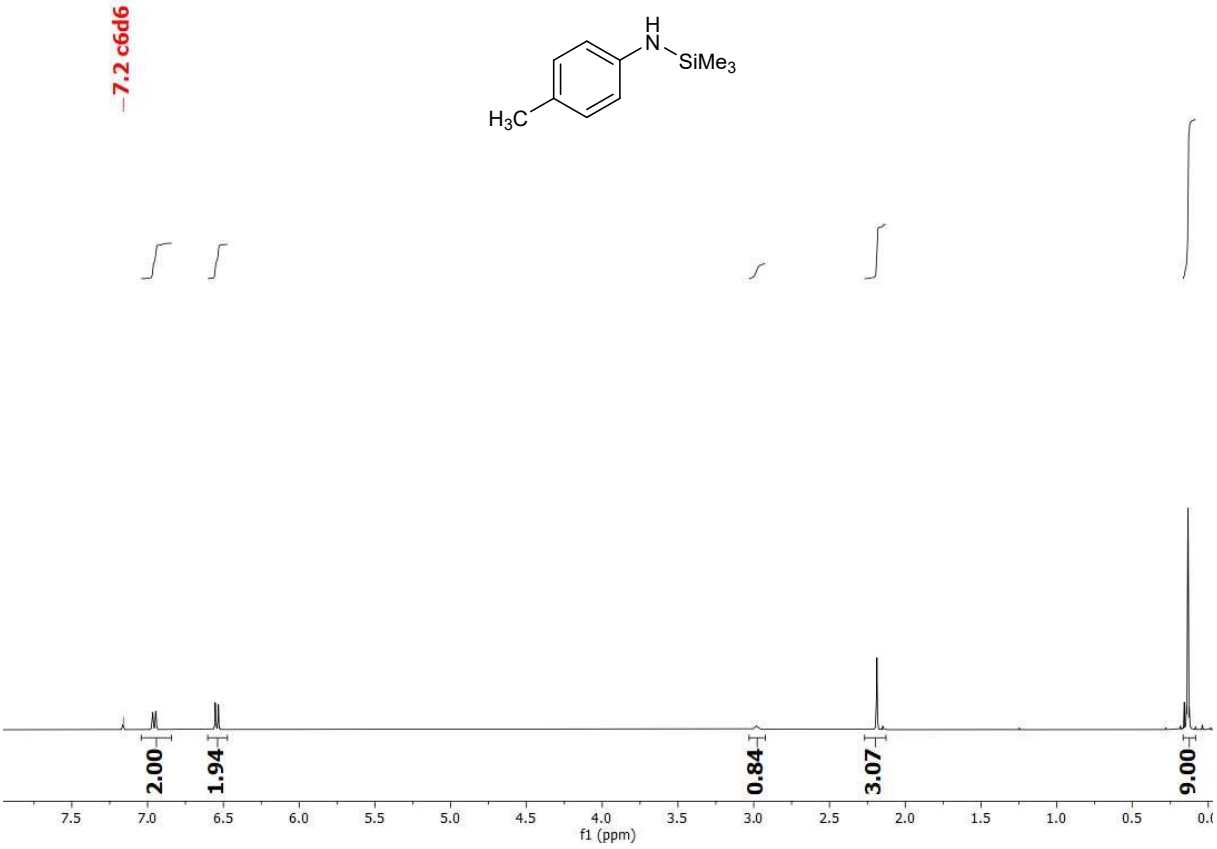
1,1,1-Trimethyl-N-phenylsilanamine (3b)

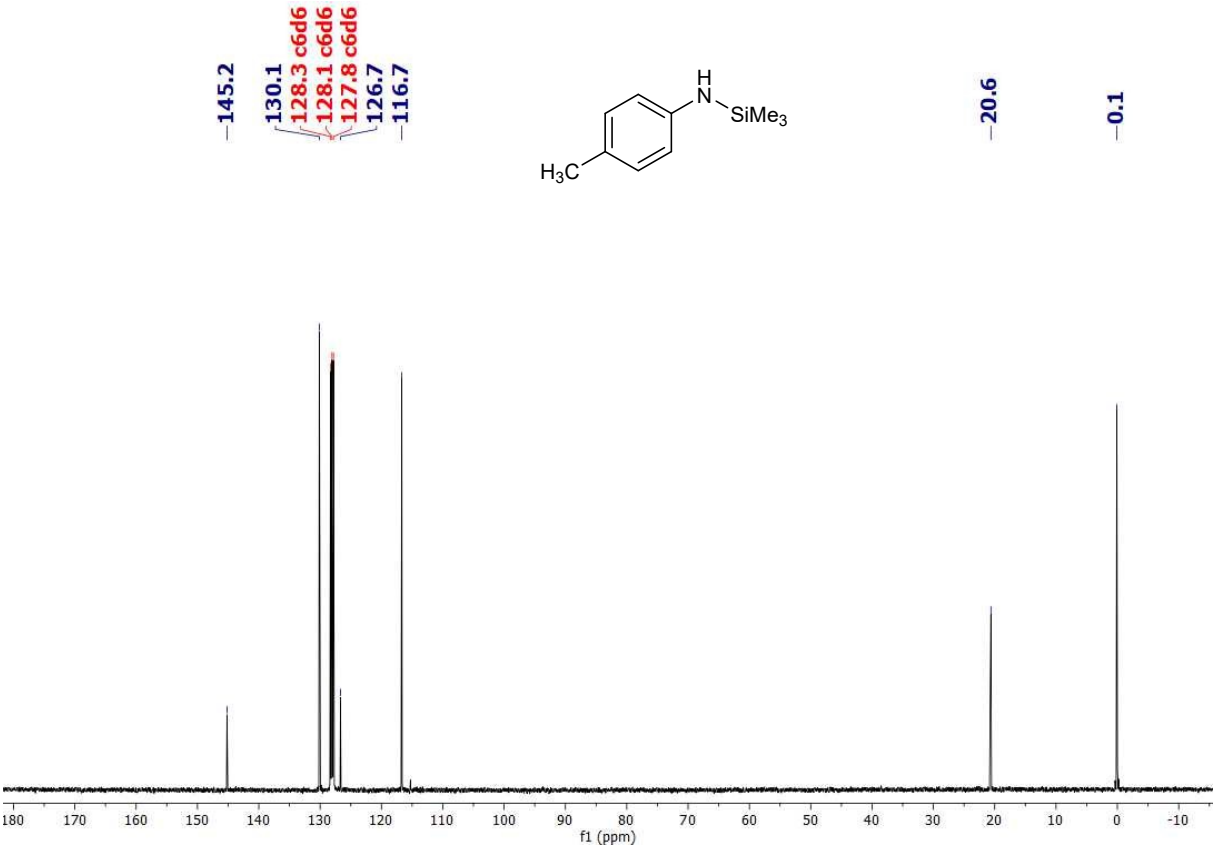


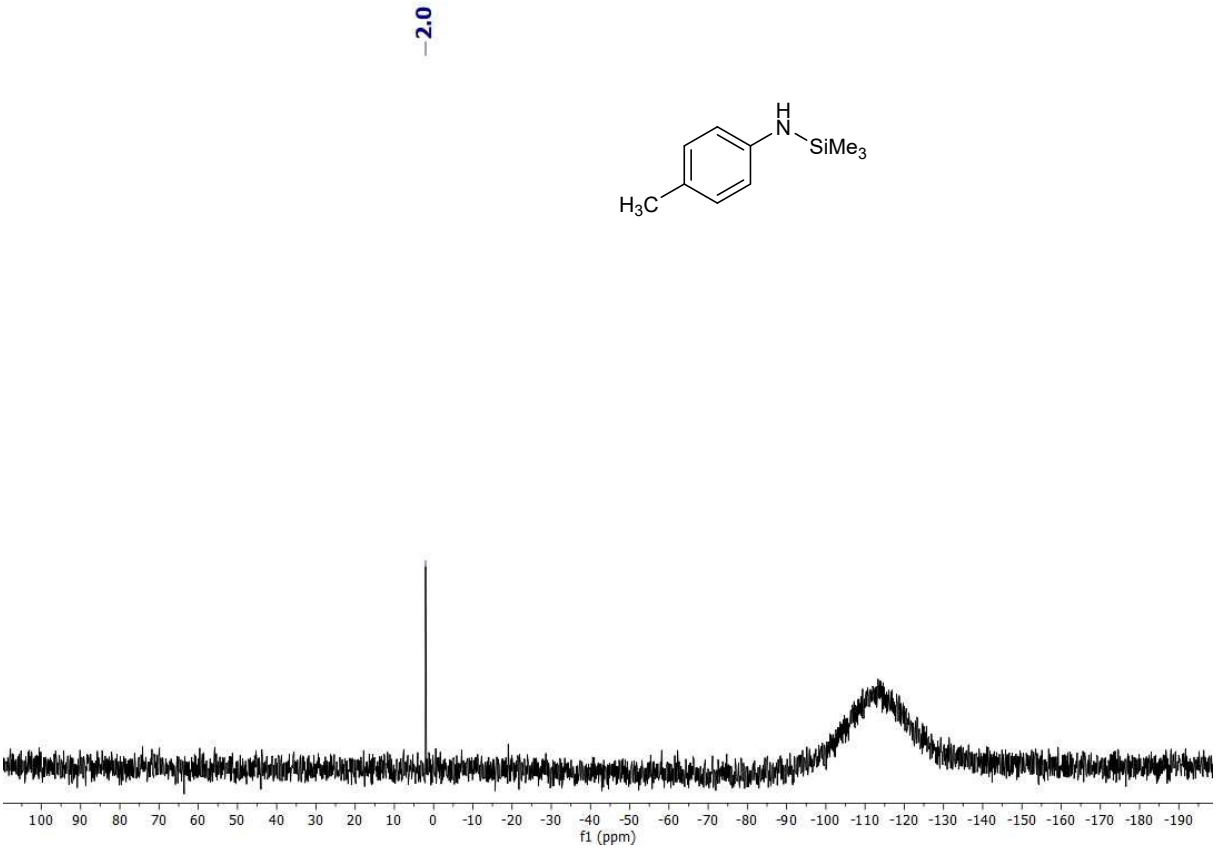



-2.3
H
N
SiMe3
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

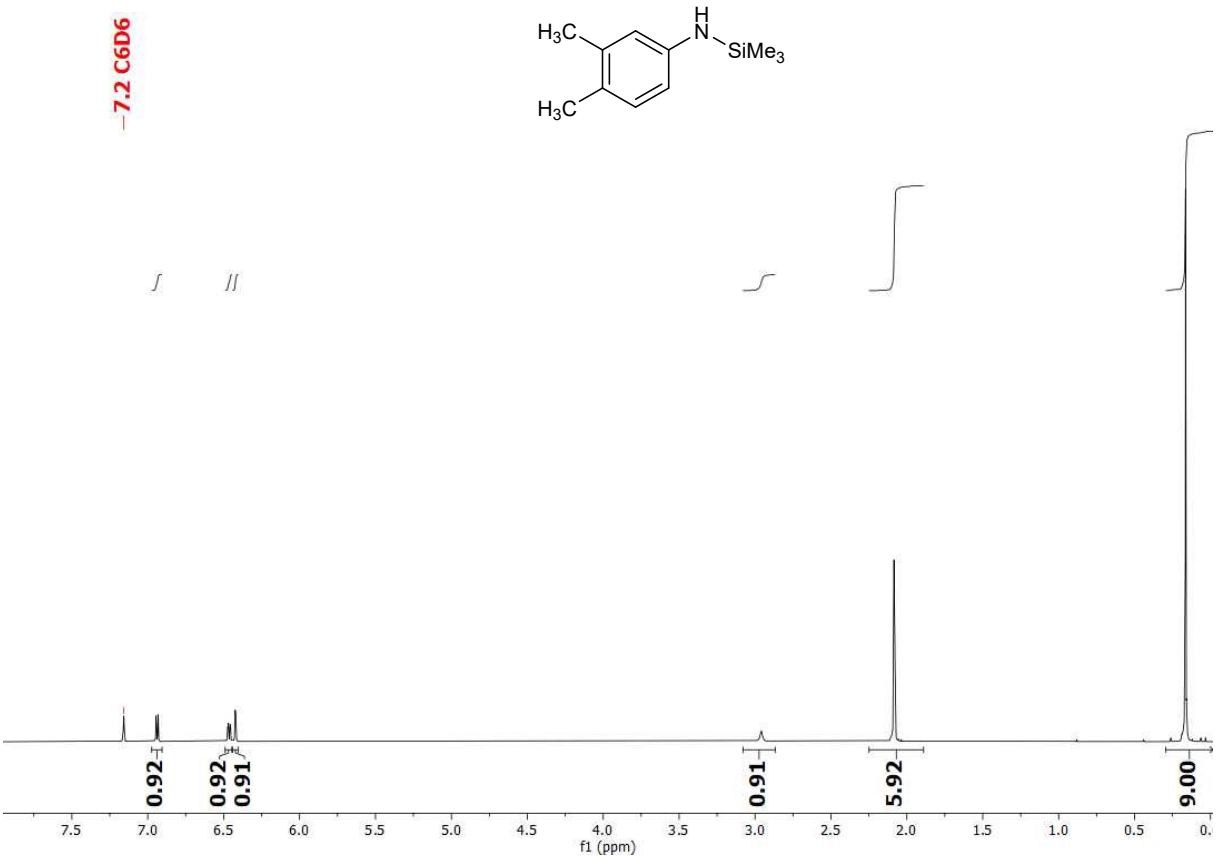
1,1,1-Trimethyl-N-(p-tolyl)silanamine (3c)

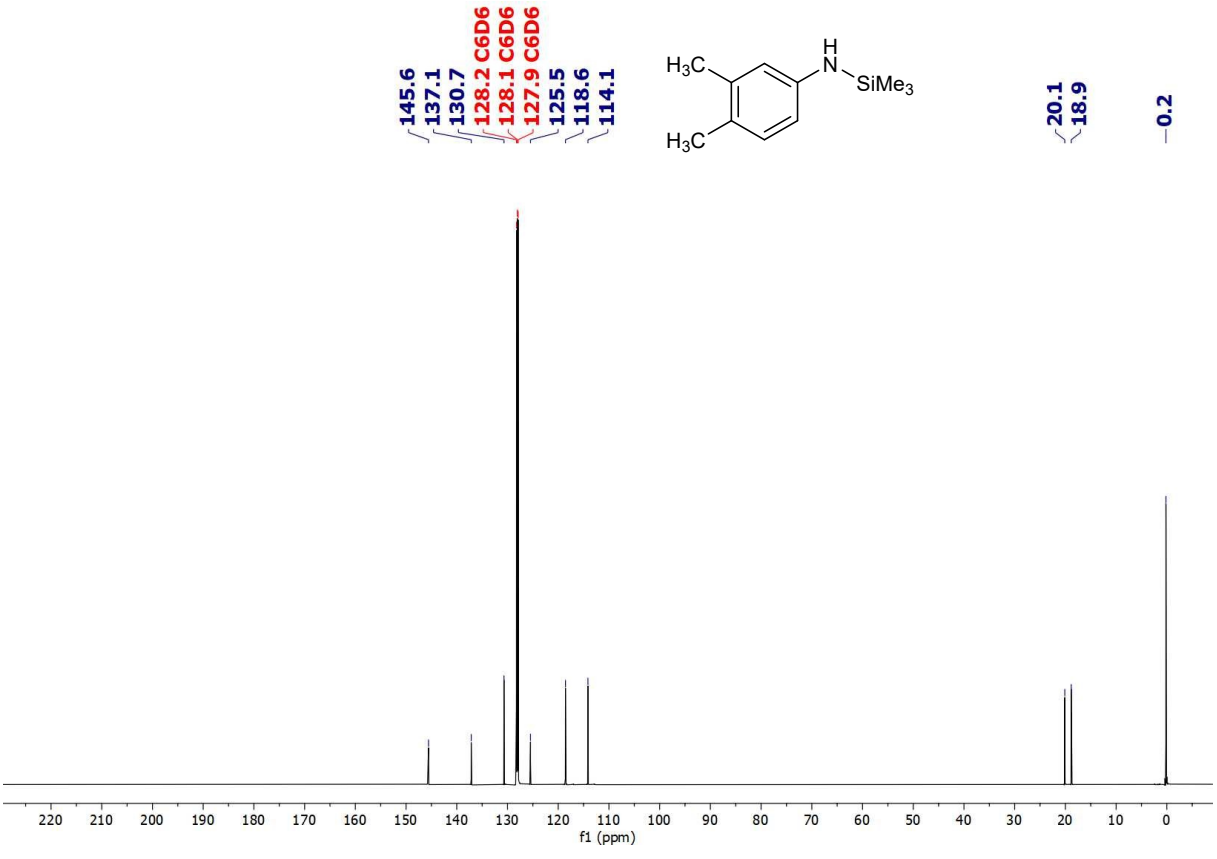


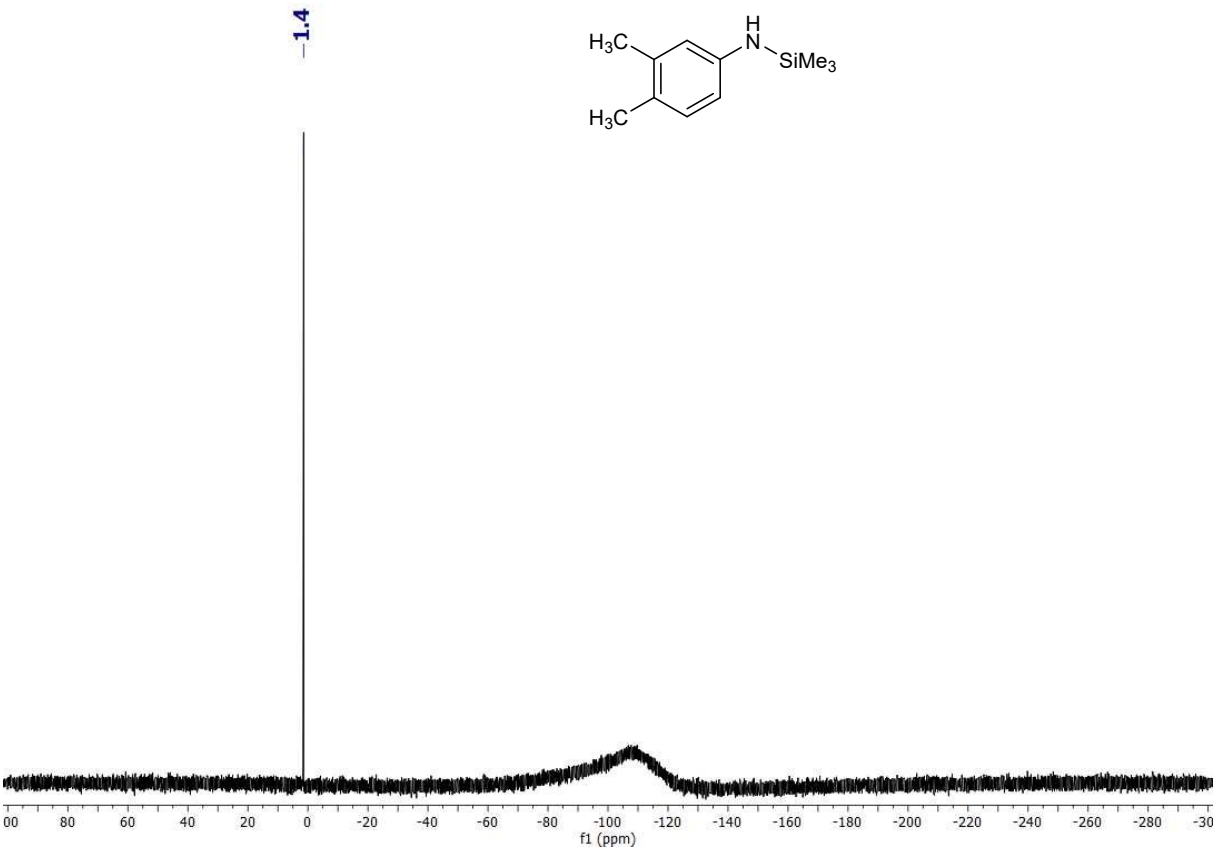



2.0
H
N
SiMe3
H3C
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

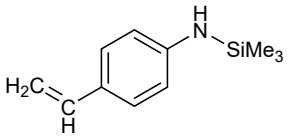
N-(3,4-dimethylphenyl)-1,1,1-trimethylsilanamine (3d)

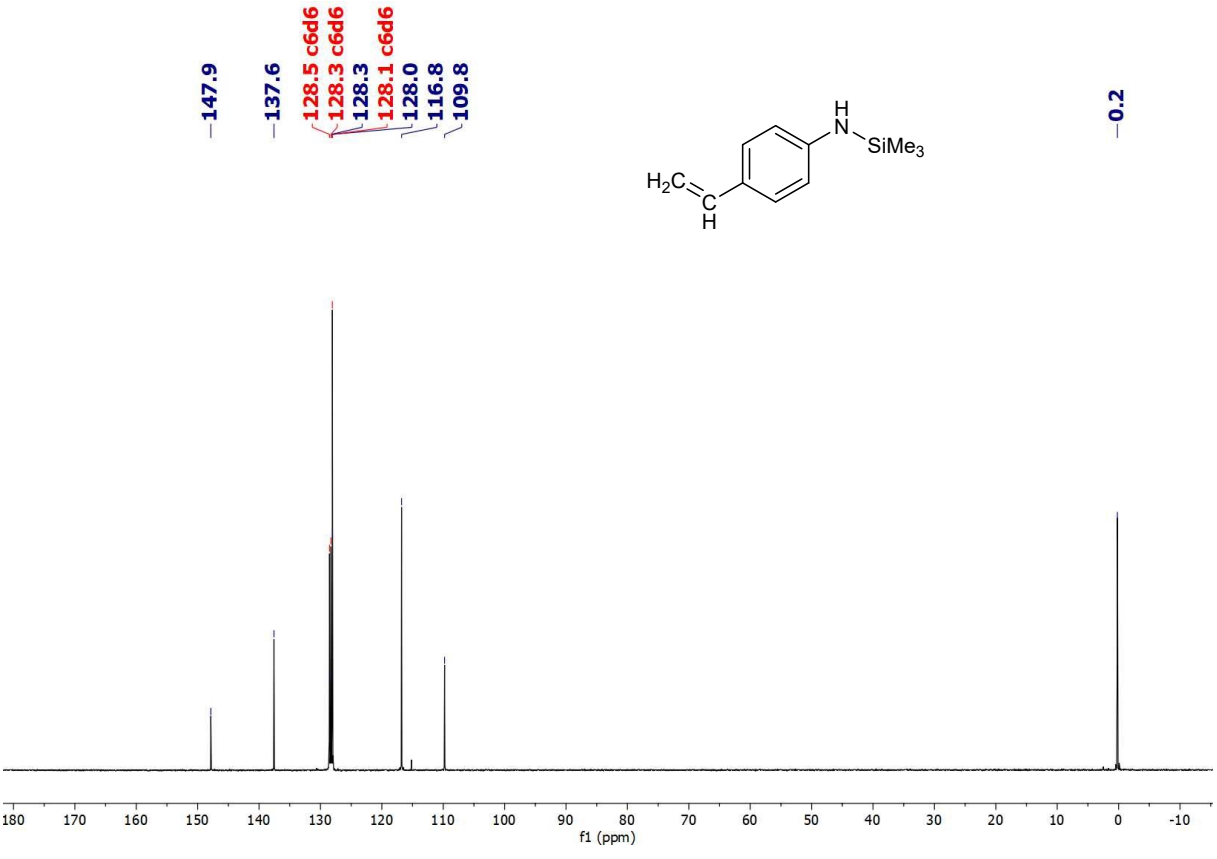


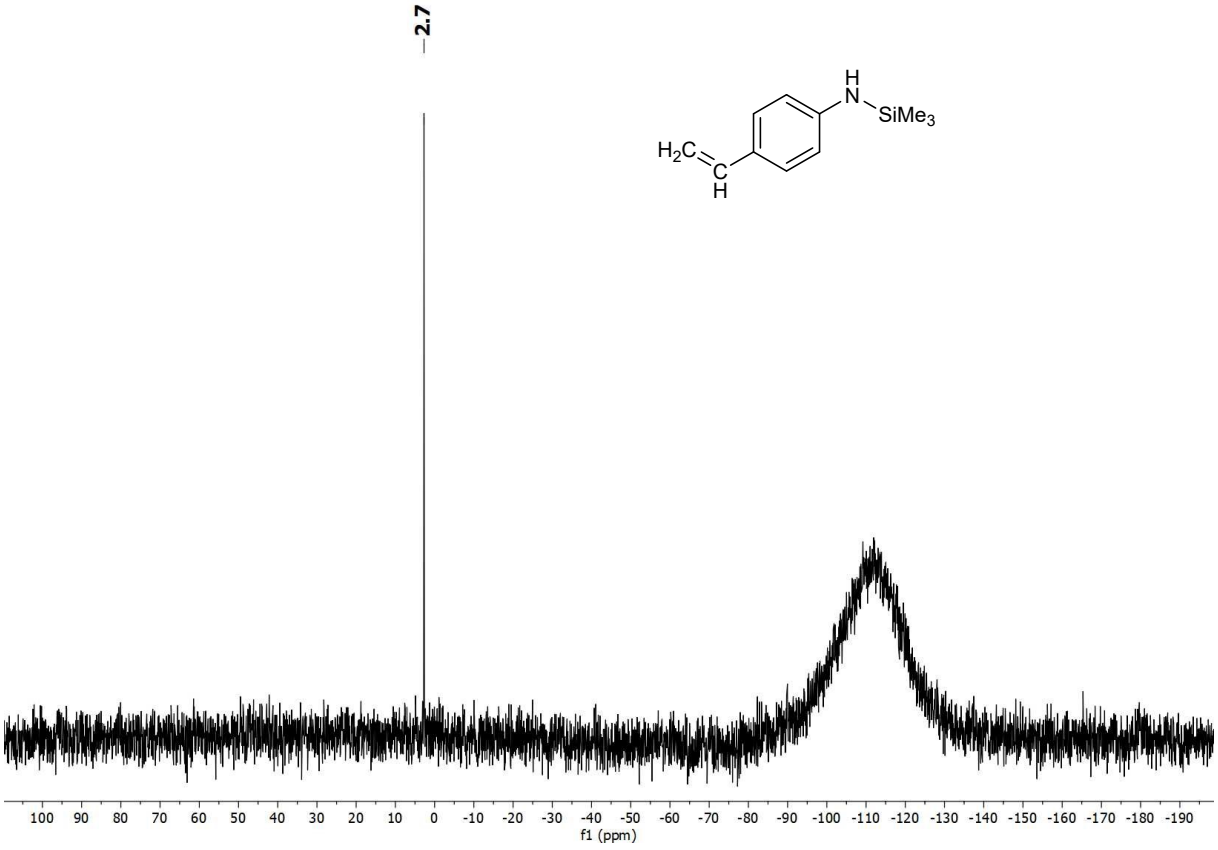



-1.4
H3C
H3C
H
N
SiMe3
00
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
-30
f1 (ppm)

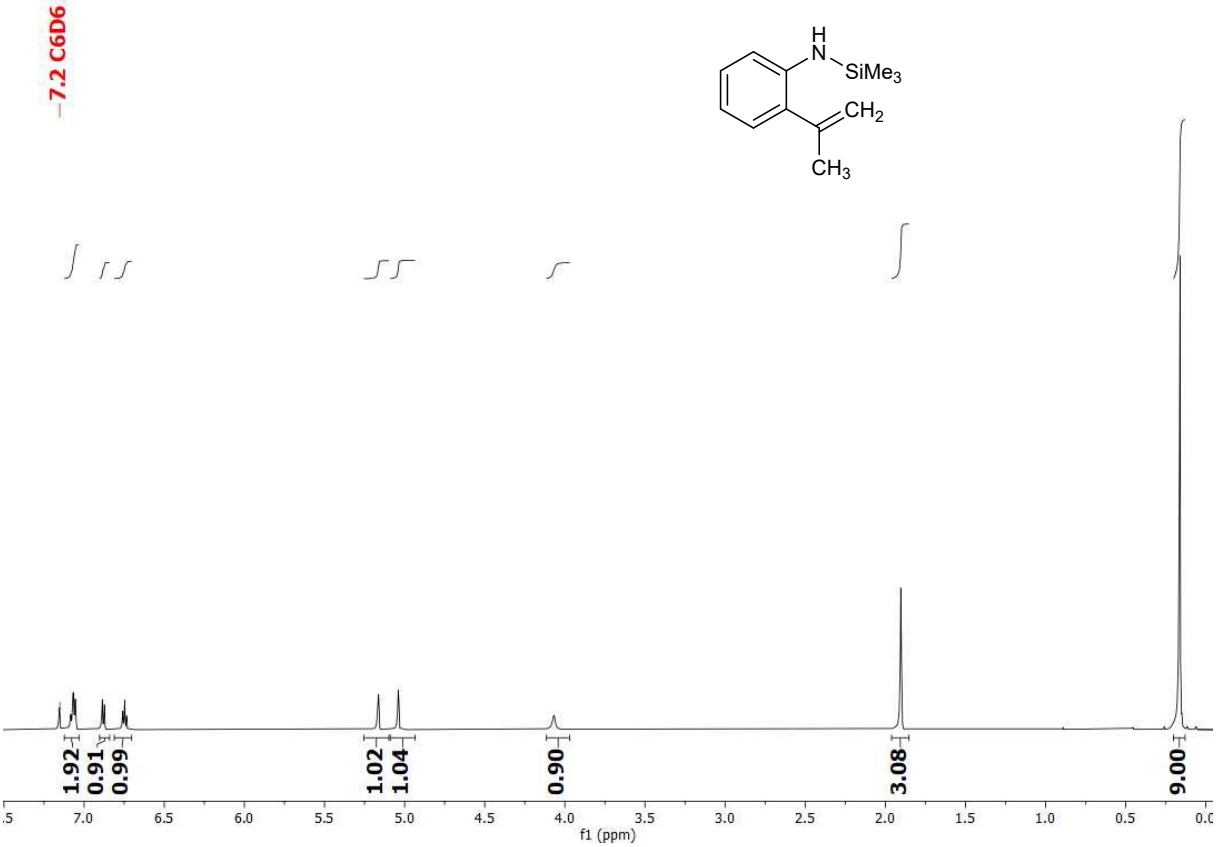
1,1,1-Trimethyl-N-(4-vinylphenyl)silanamine (3e)

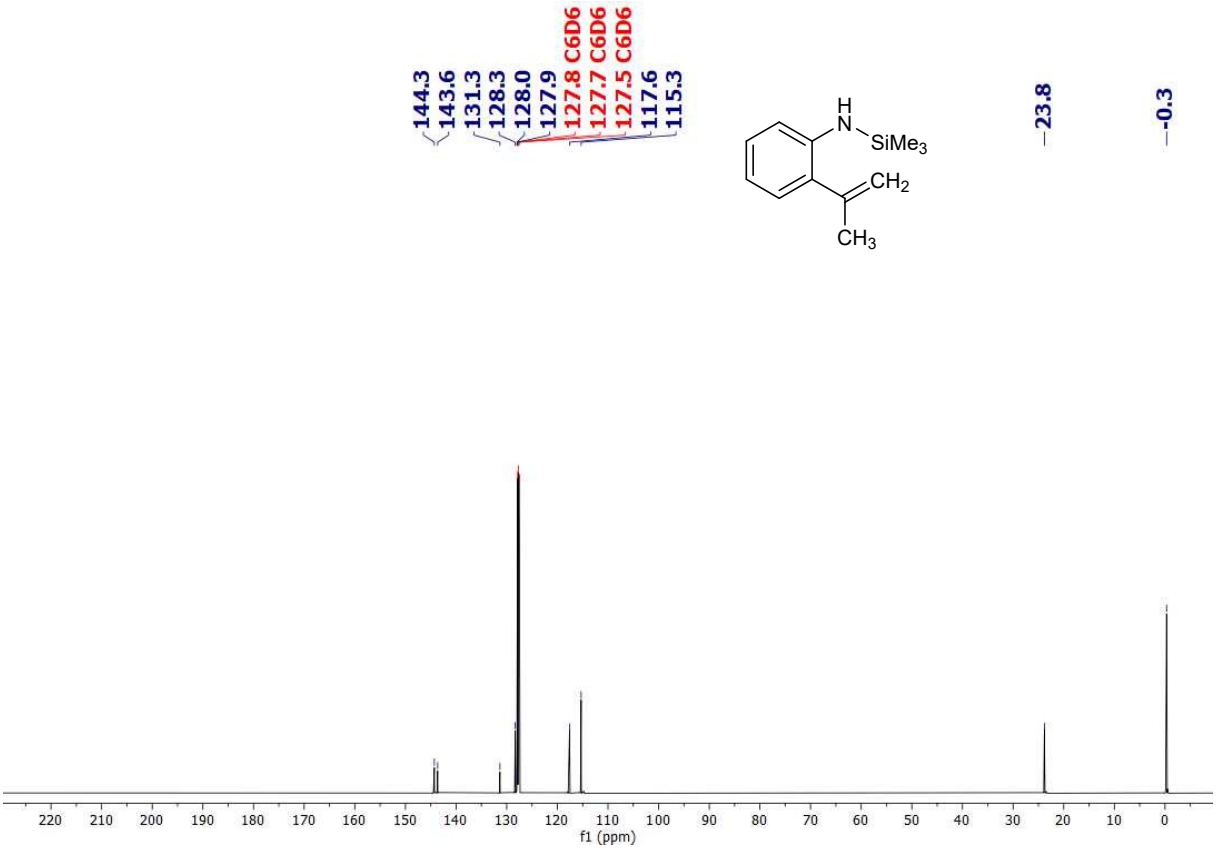


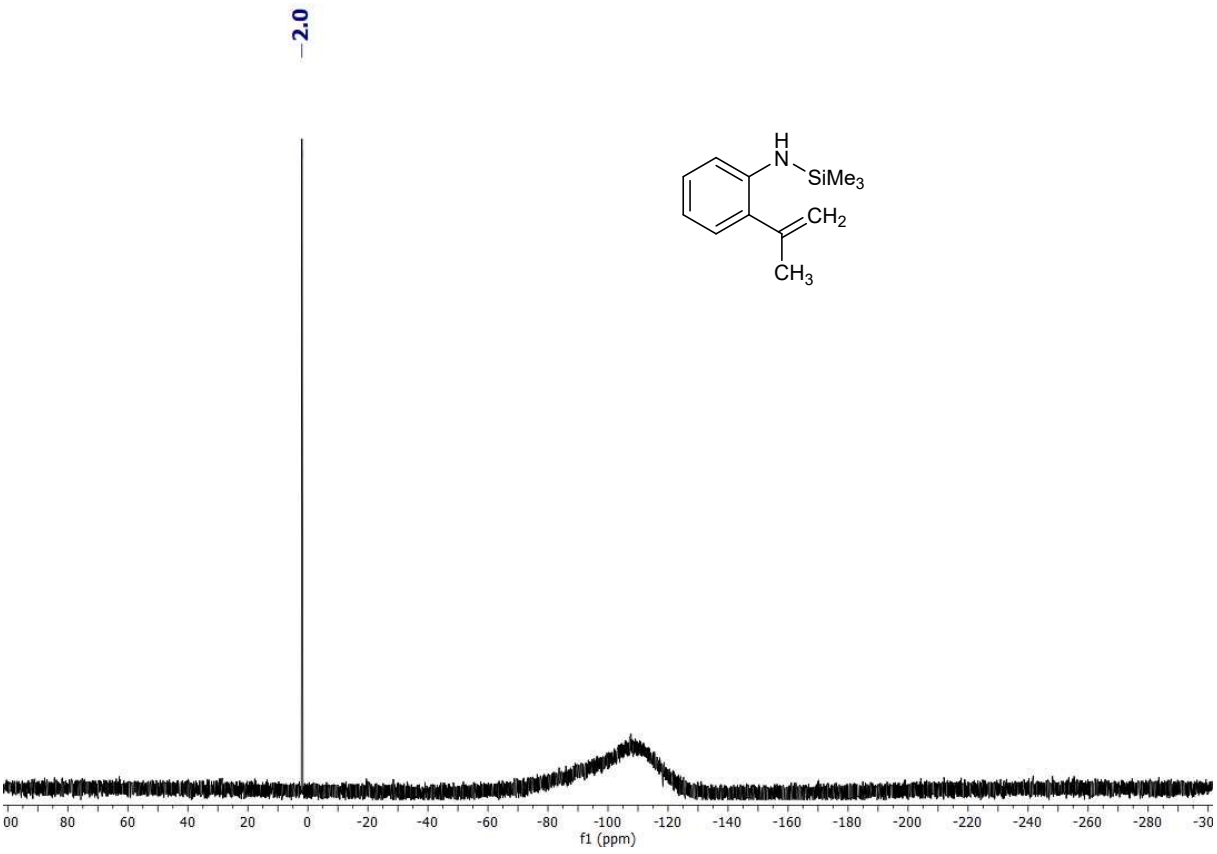



2.7
H
N
SiMe3
H2C
C
H
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

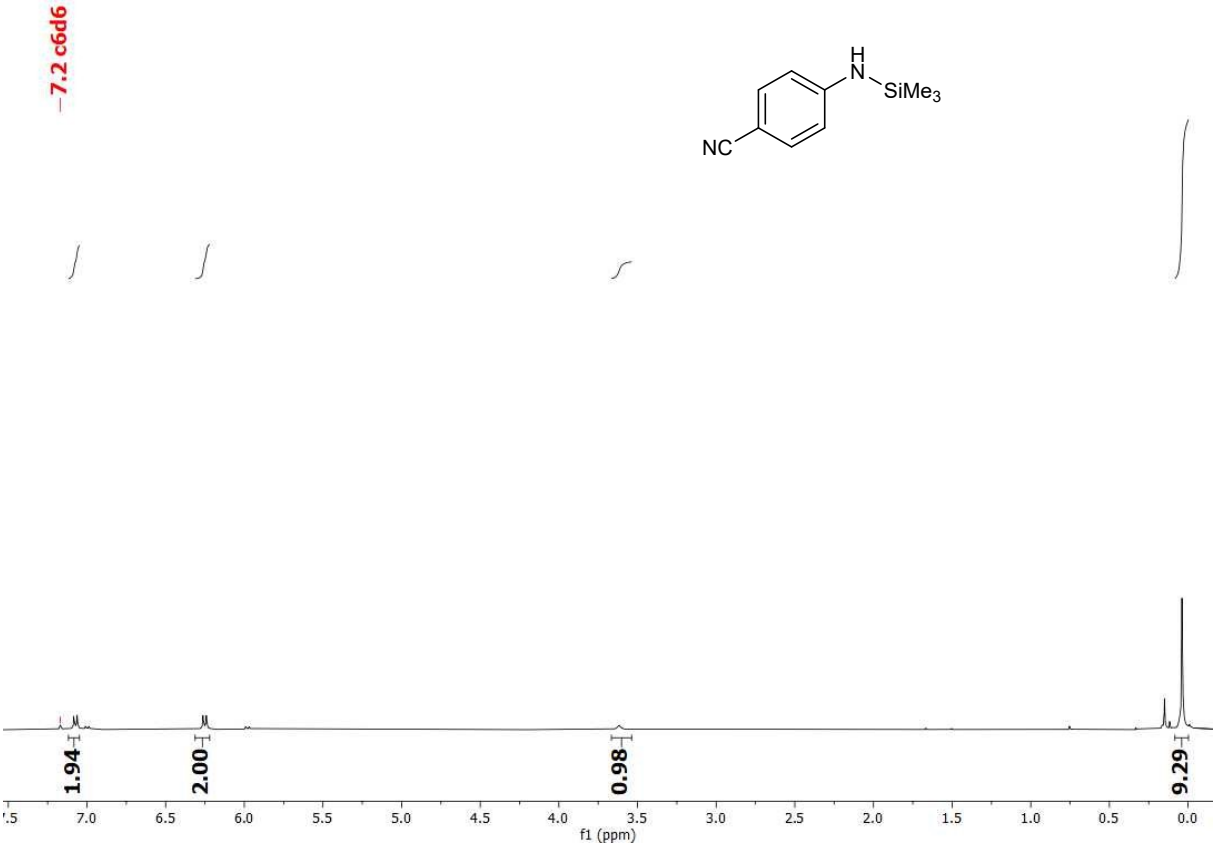
1,1,1-Trimethyl-N-(2-(prop-1-en-2-yl)phenyl)silanamine (3f)

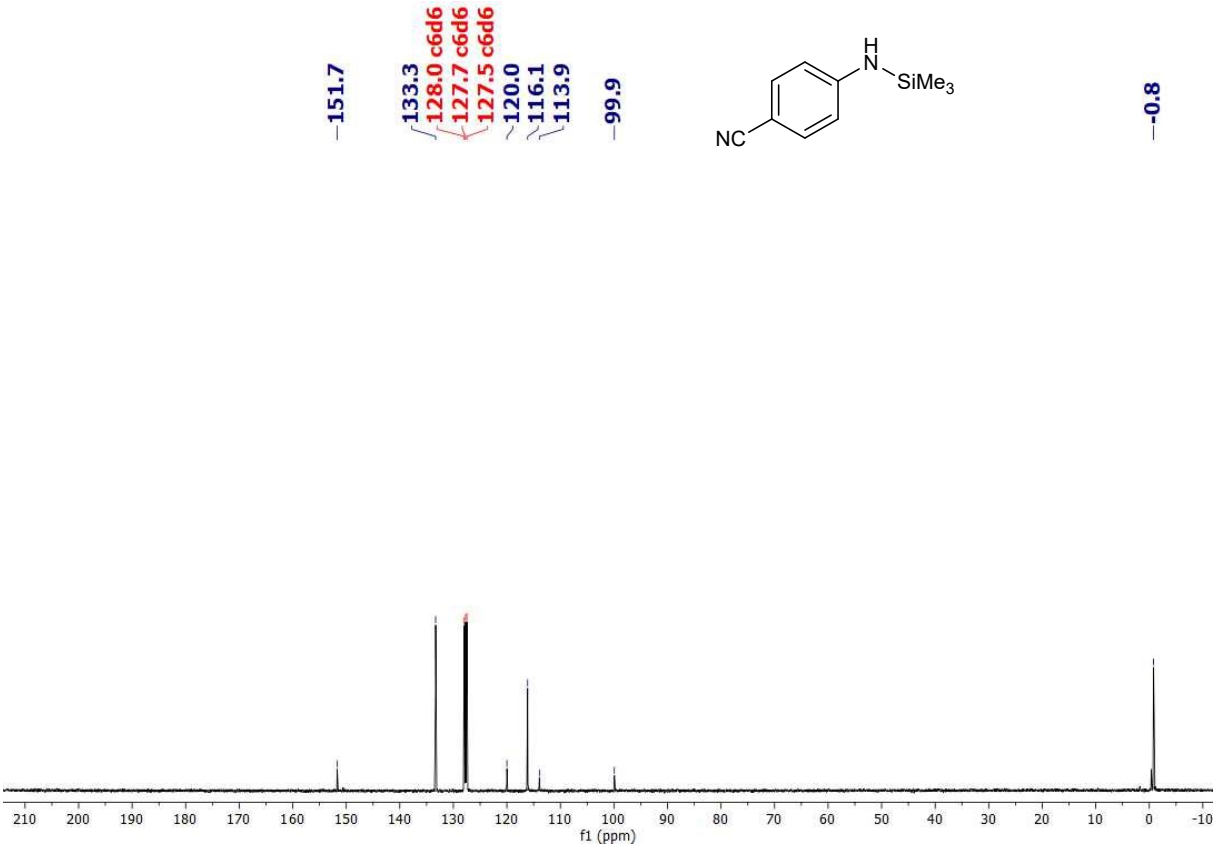


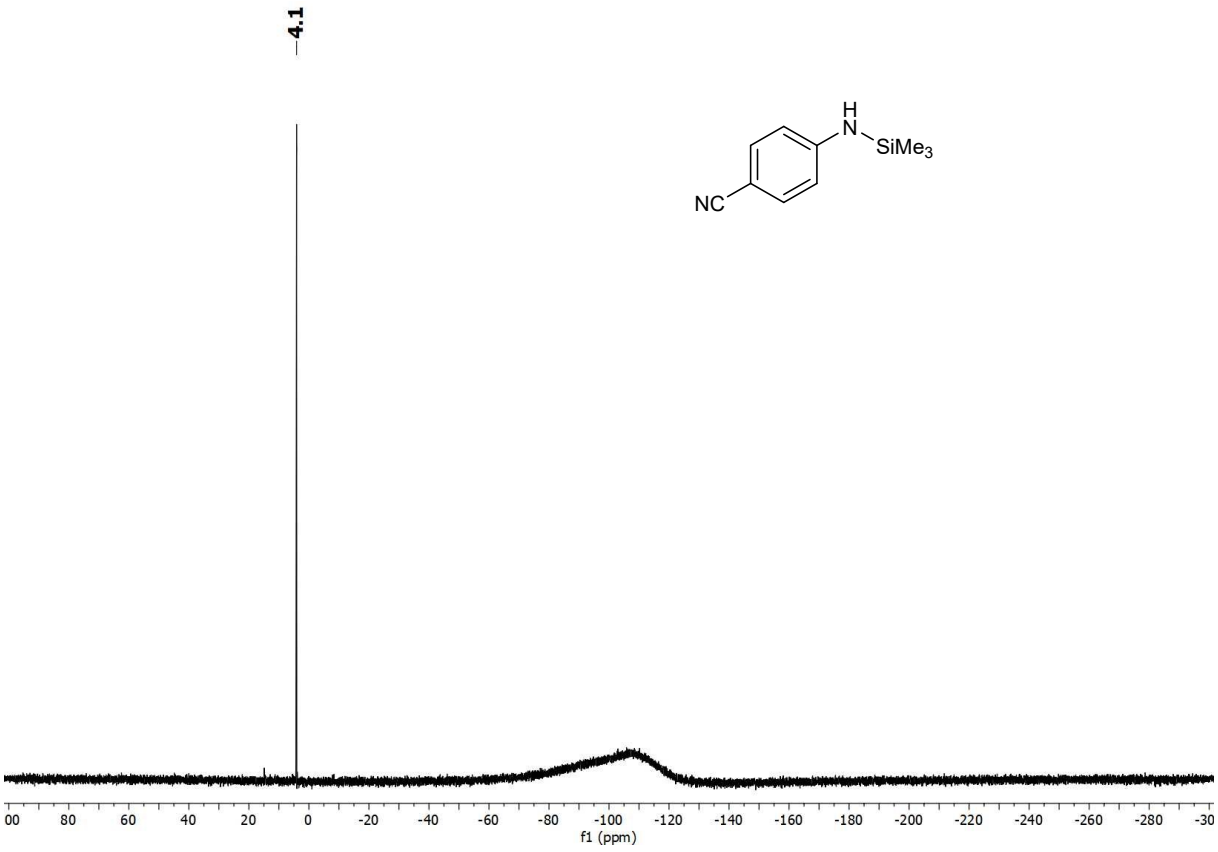



2.0
H
N
SiMe3
CH2
CH3
00
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
-30
f1 (ppm)

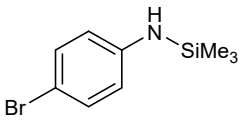
4-((Trimethylsilyl)amino)benzonitrile (3g)

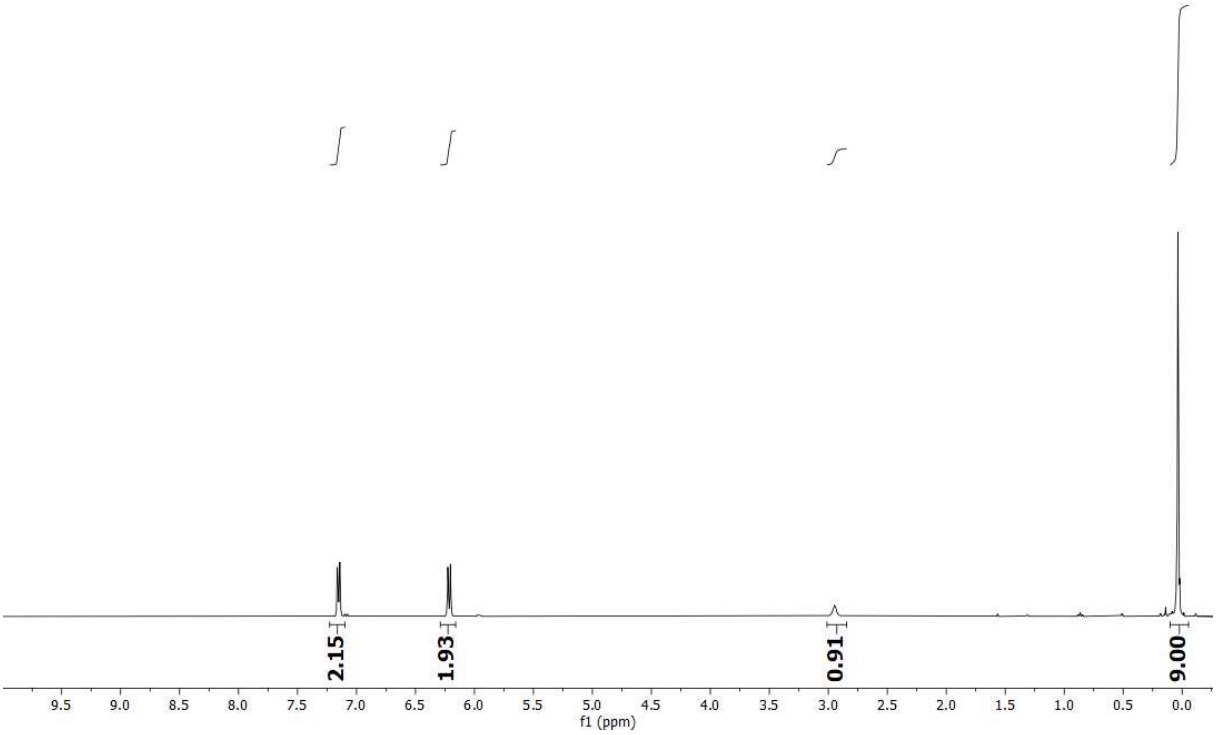


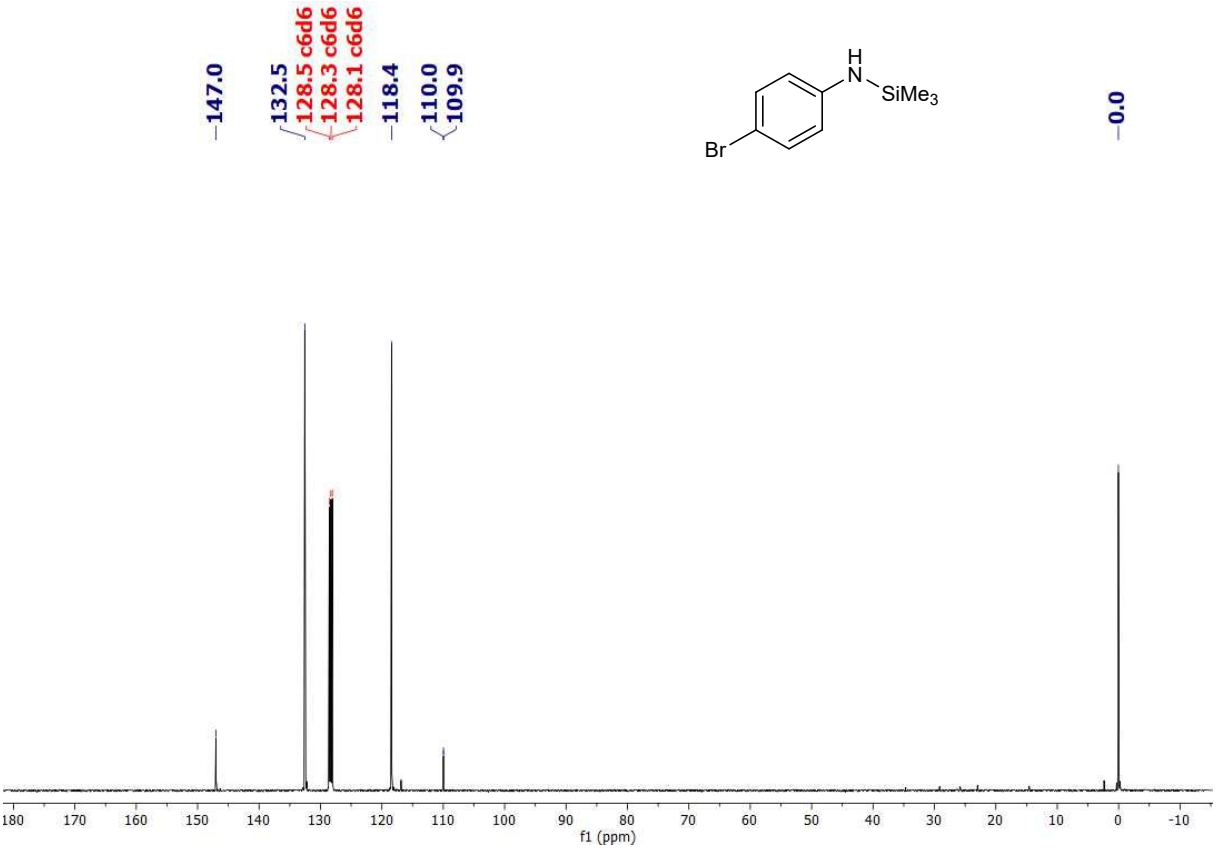


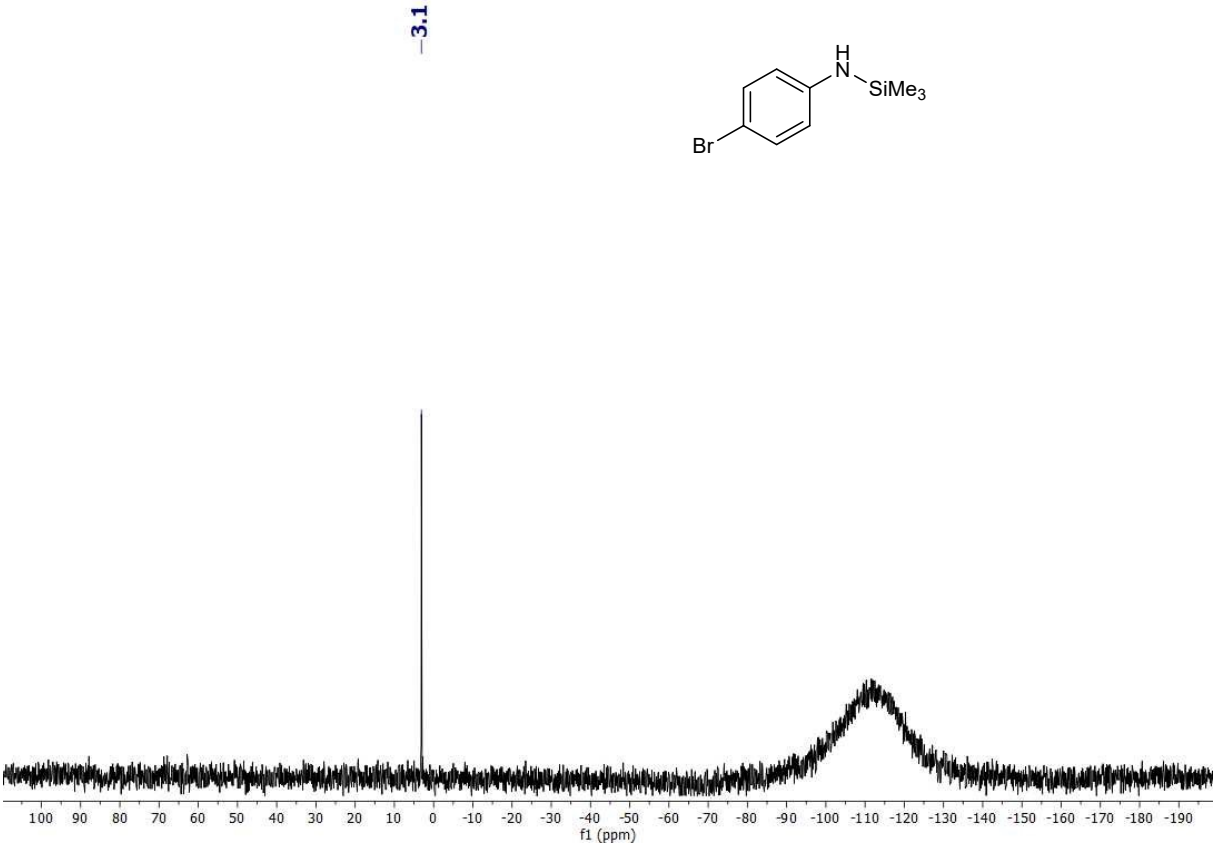

4.1
H
N
SiMe3
NC
00
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
-30
f1 (ppm)

N-(4-bromophenyl)-1,1,1-trimethylsilanamine (3h)

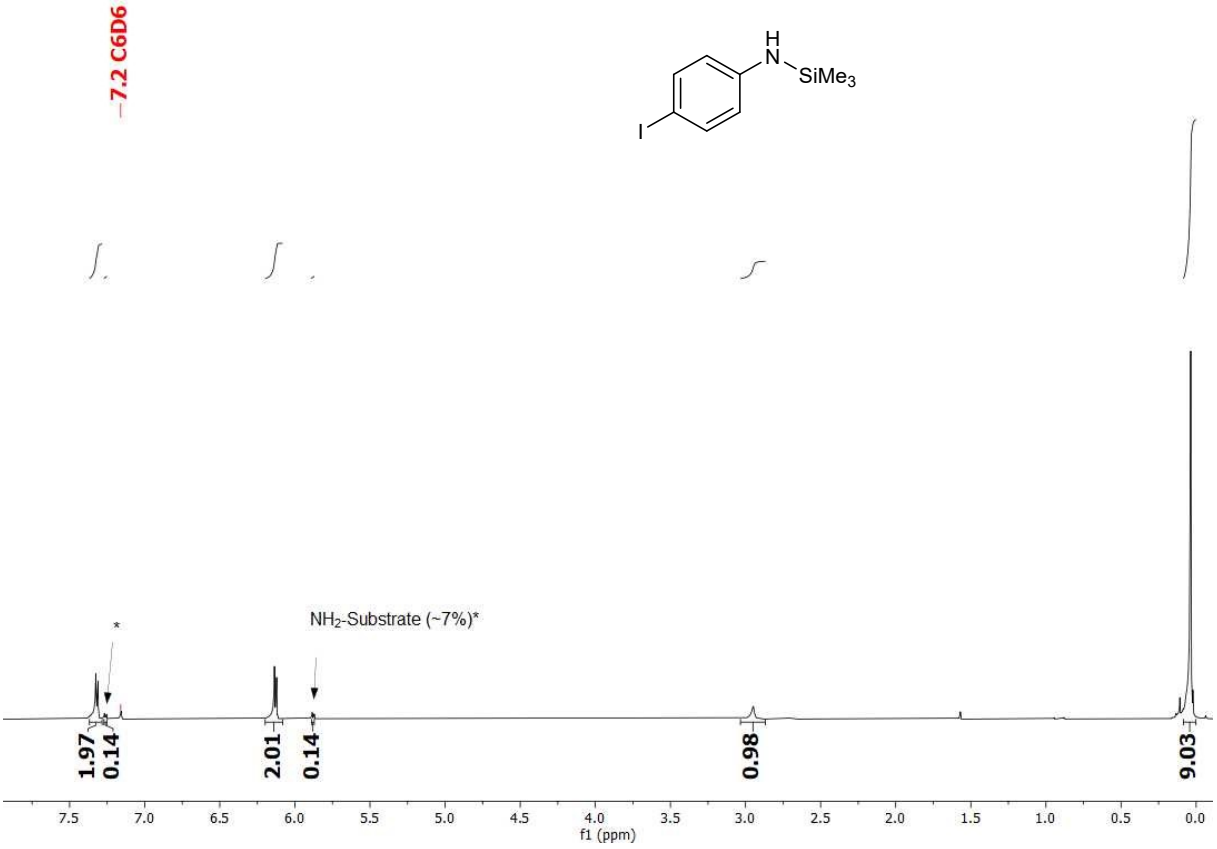


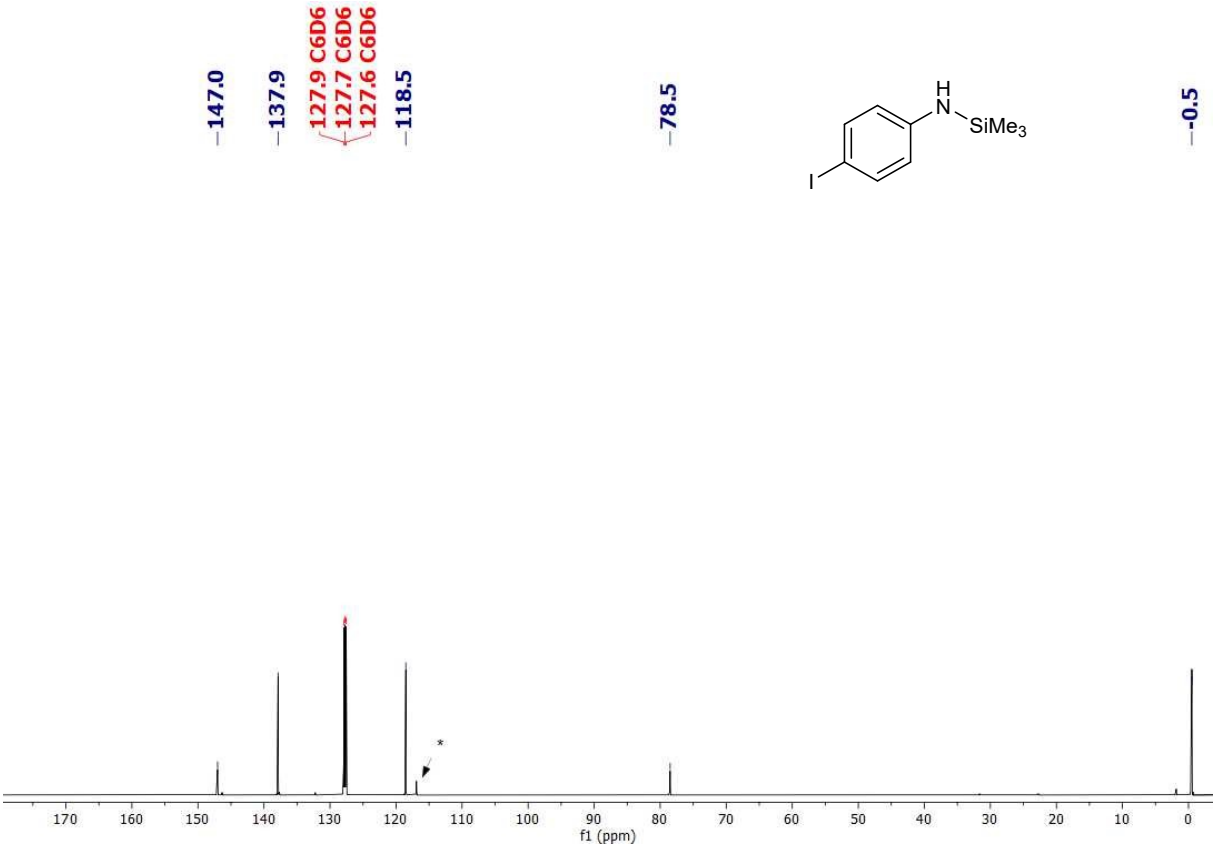




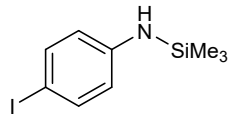

-3.1
H
N
SiMe3
Br
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

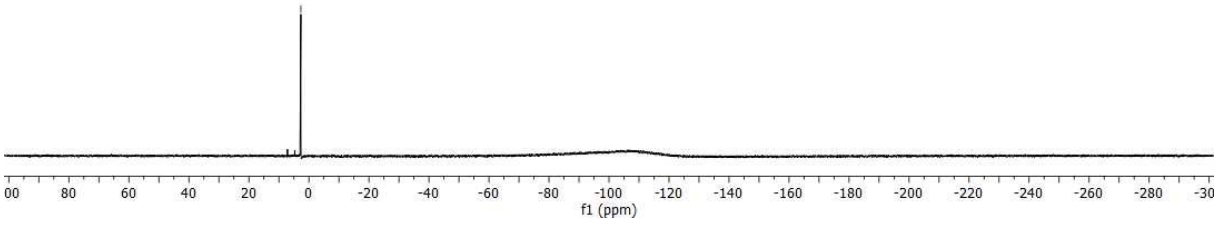
N-(4-iodophenyl)-1,1,1-trimethylsilanamine (3i)



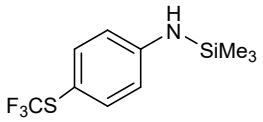


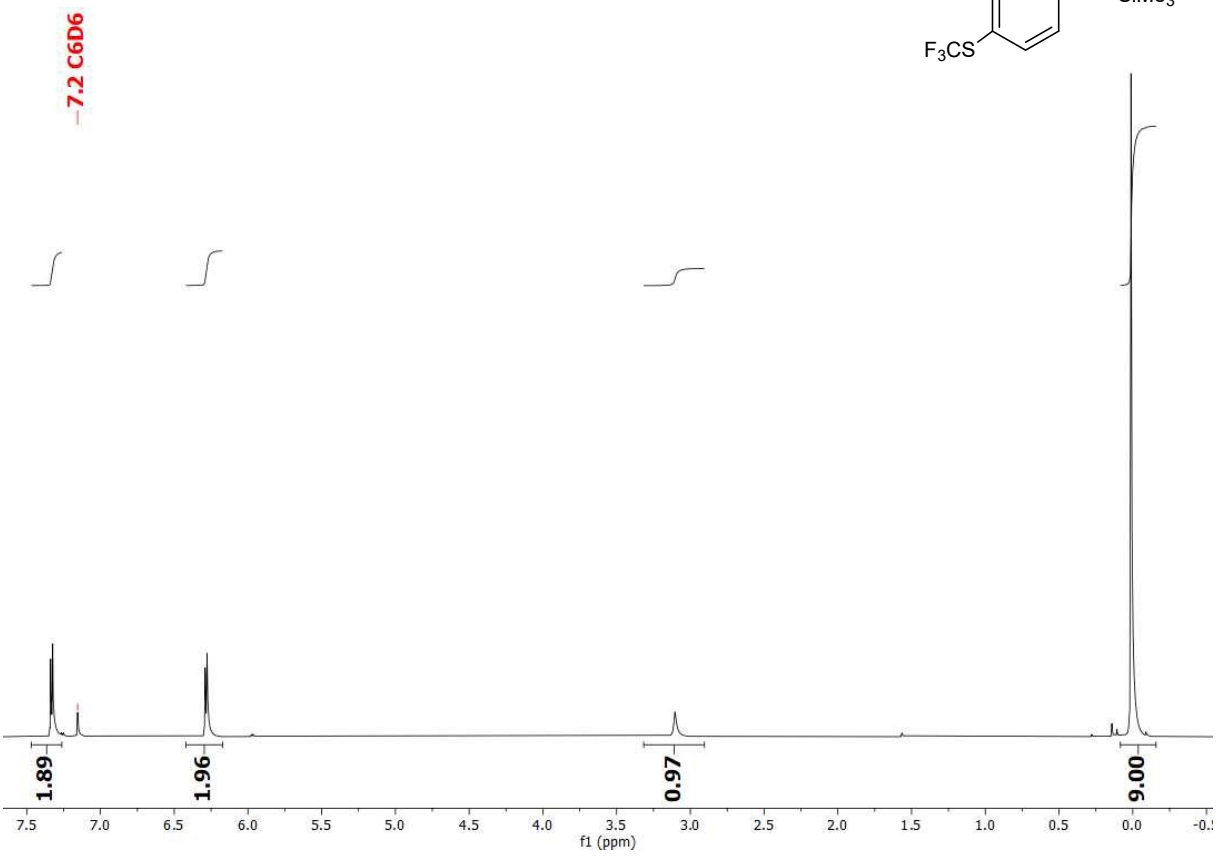
2.7

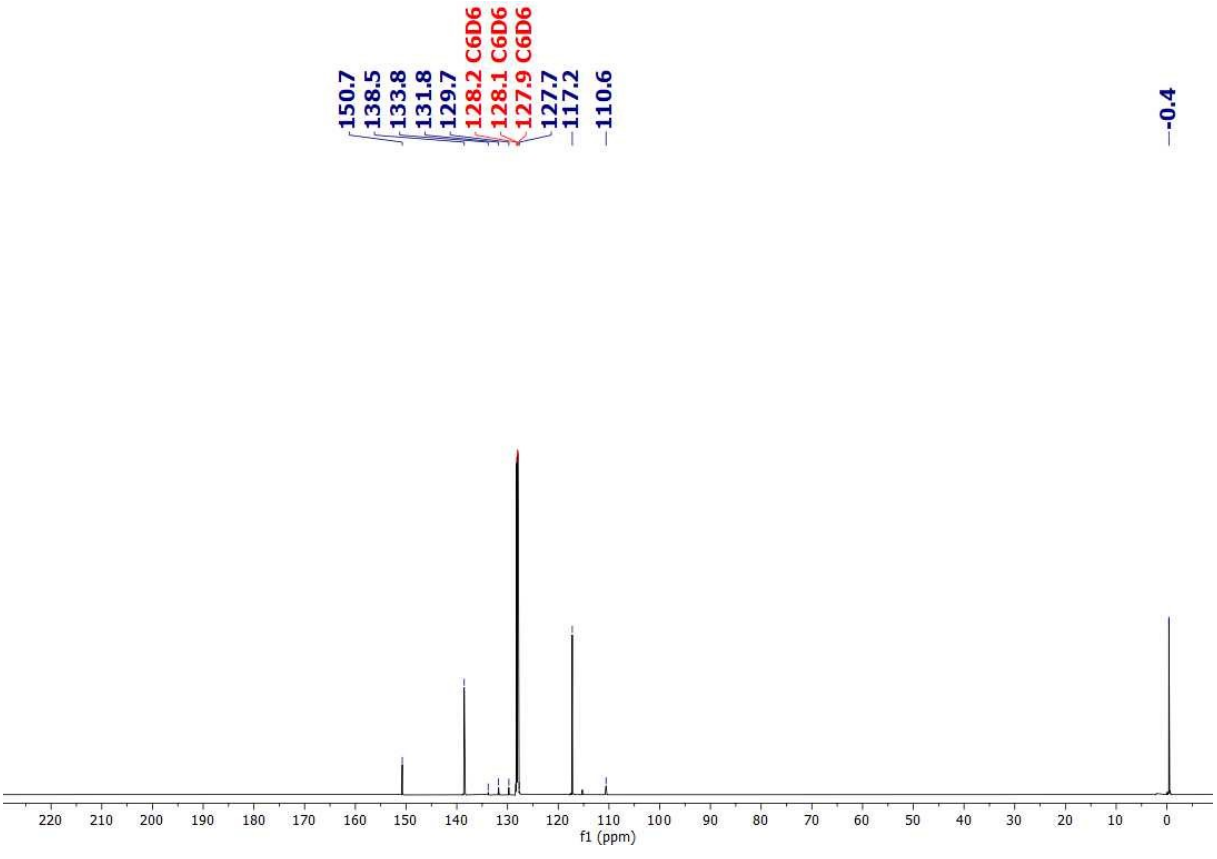

H
N
SiMe3
I

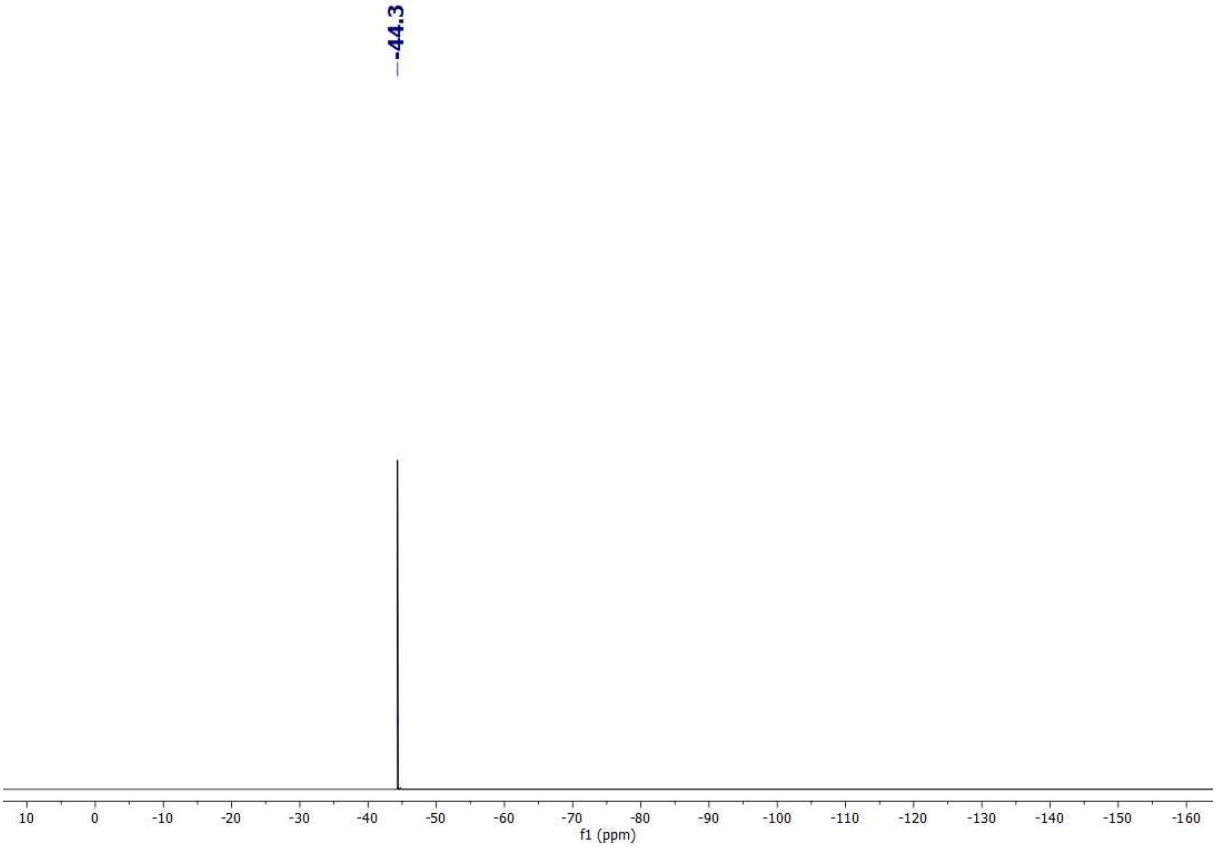

00
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
-30
f1 (ppm)

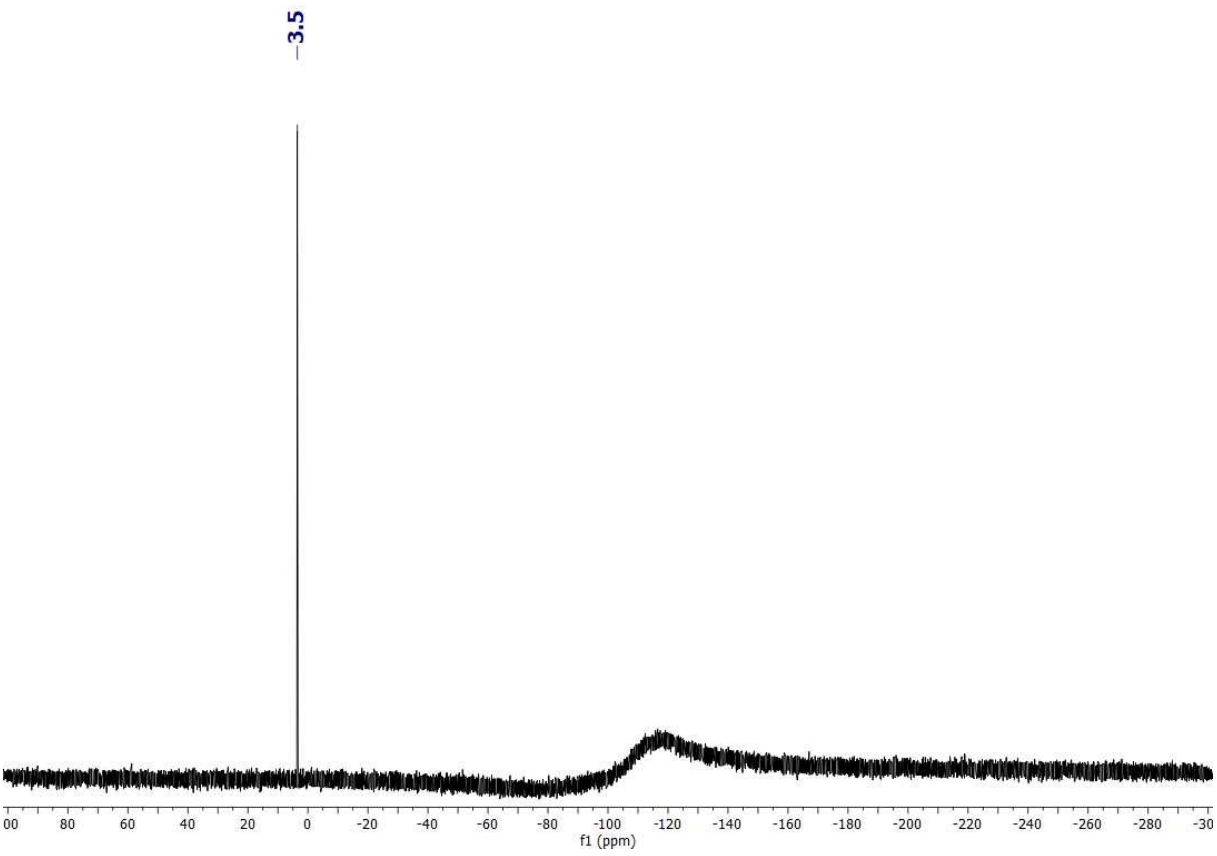
1,1,1-Trimethyl-N-(4-((trifluoromethyl)thio)phenyl)silanamine (3j)



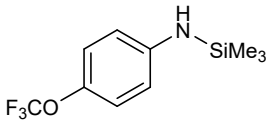


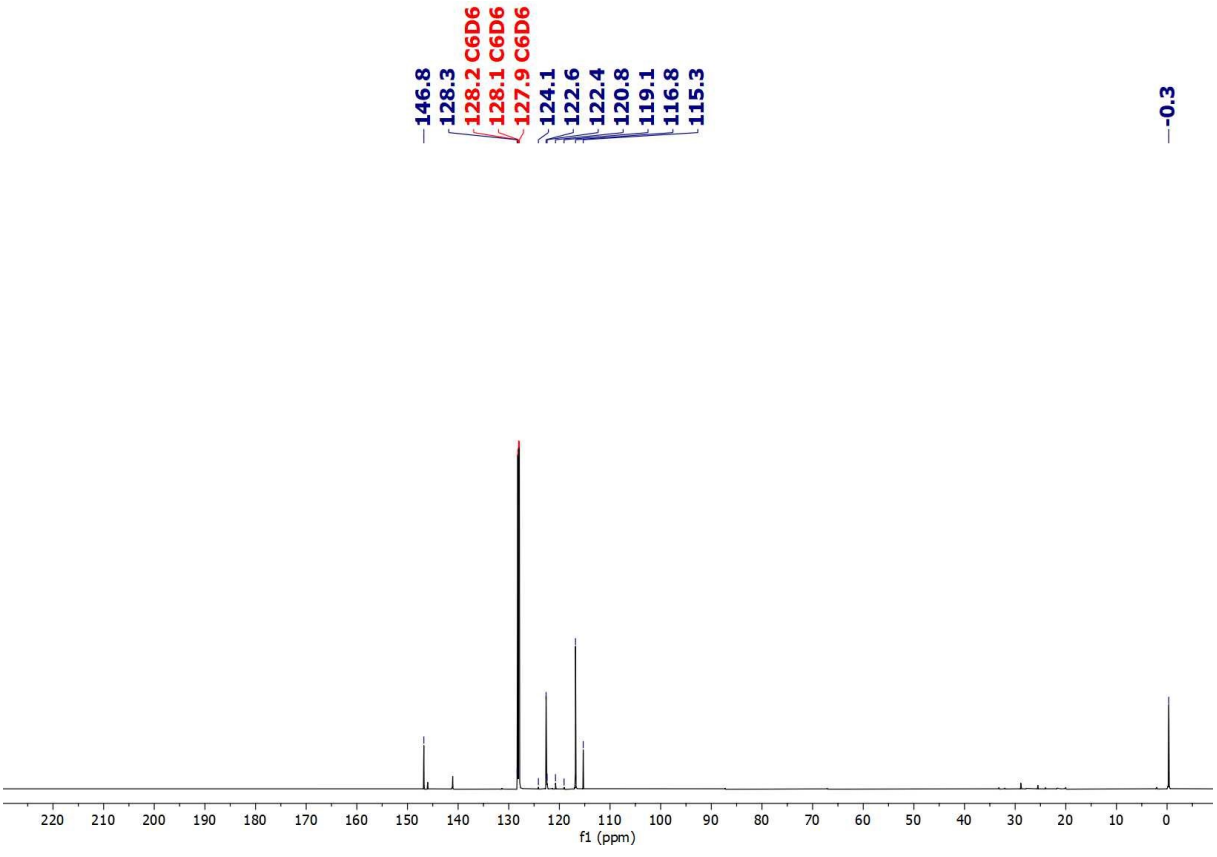


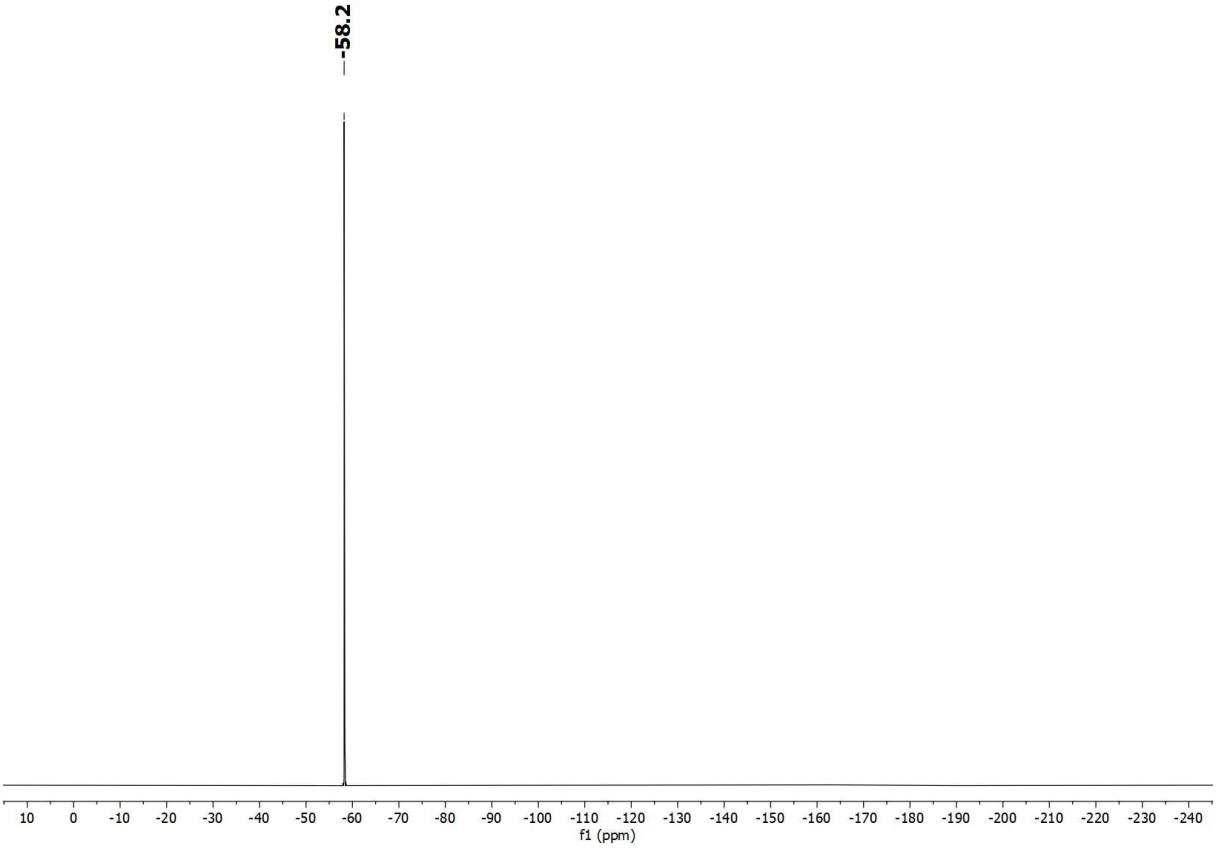

-44.3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

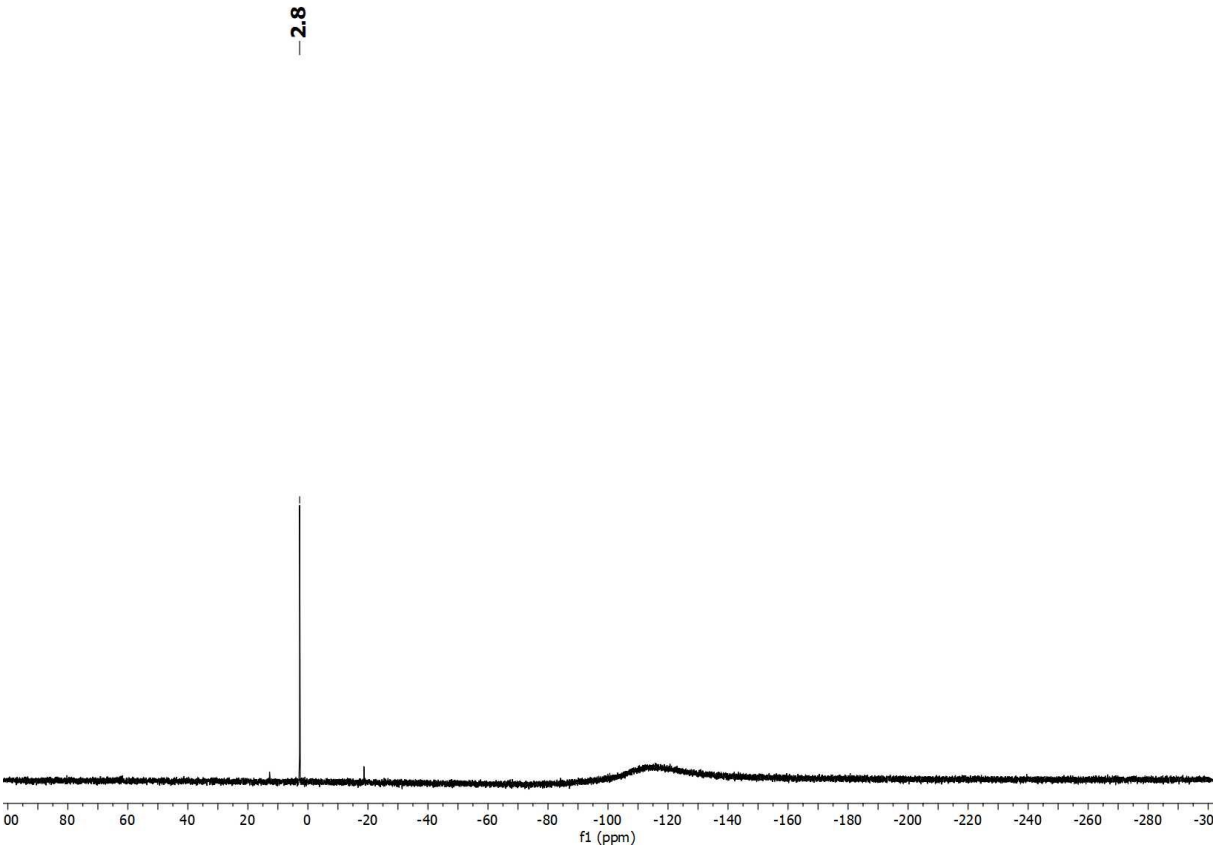

-3.5
00 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -30
f1 (ppm)

1,1,1-Trimethyl-N-(4-(trifluoromethoxy)phenyl)silanamine (3k)

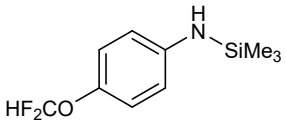


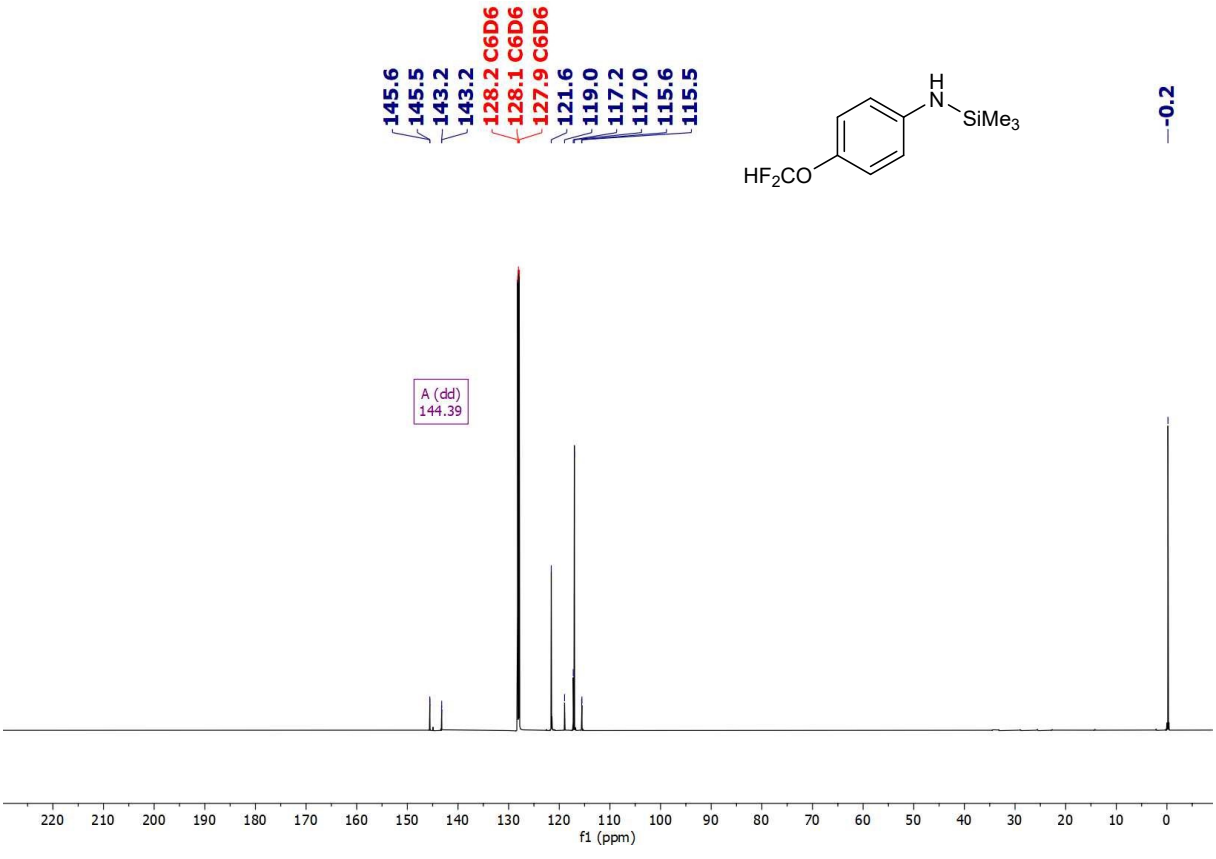


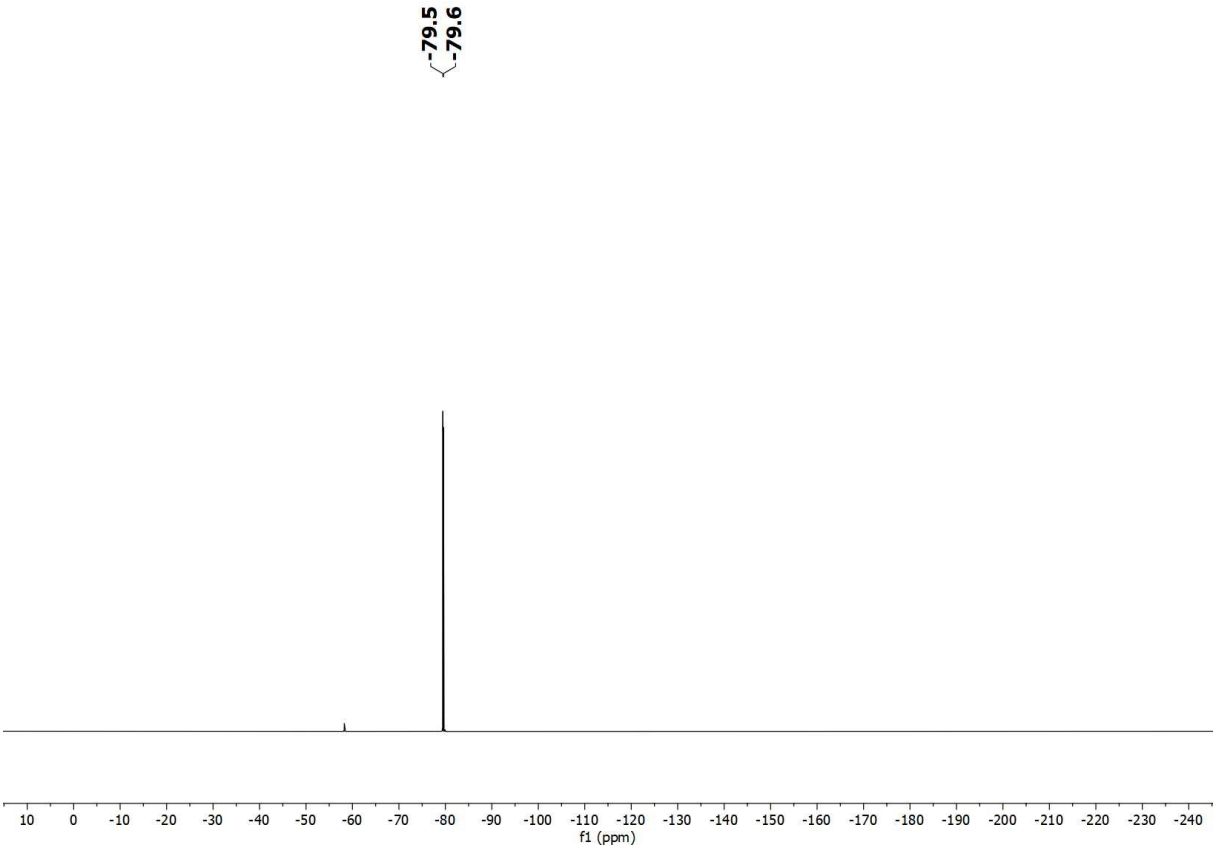

-58.2
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

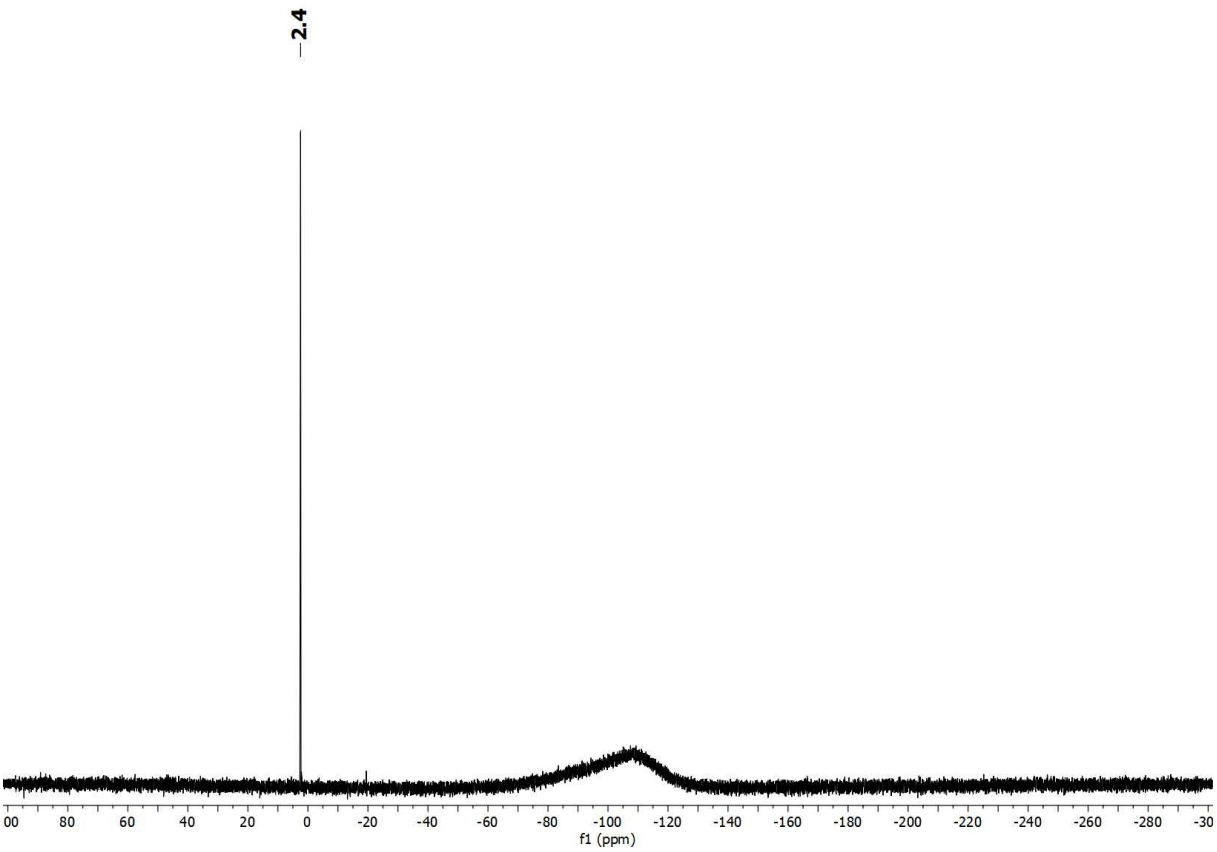

2.8
00 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -30
f1 (ppm)

N-(4-(difluoromethoxy)phenyl)-1,1,1-trimethylsilanamine (3l)

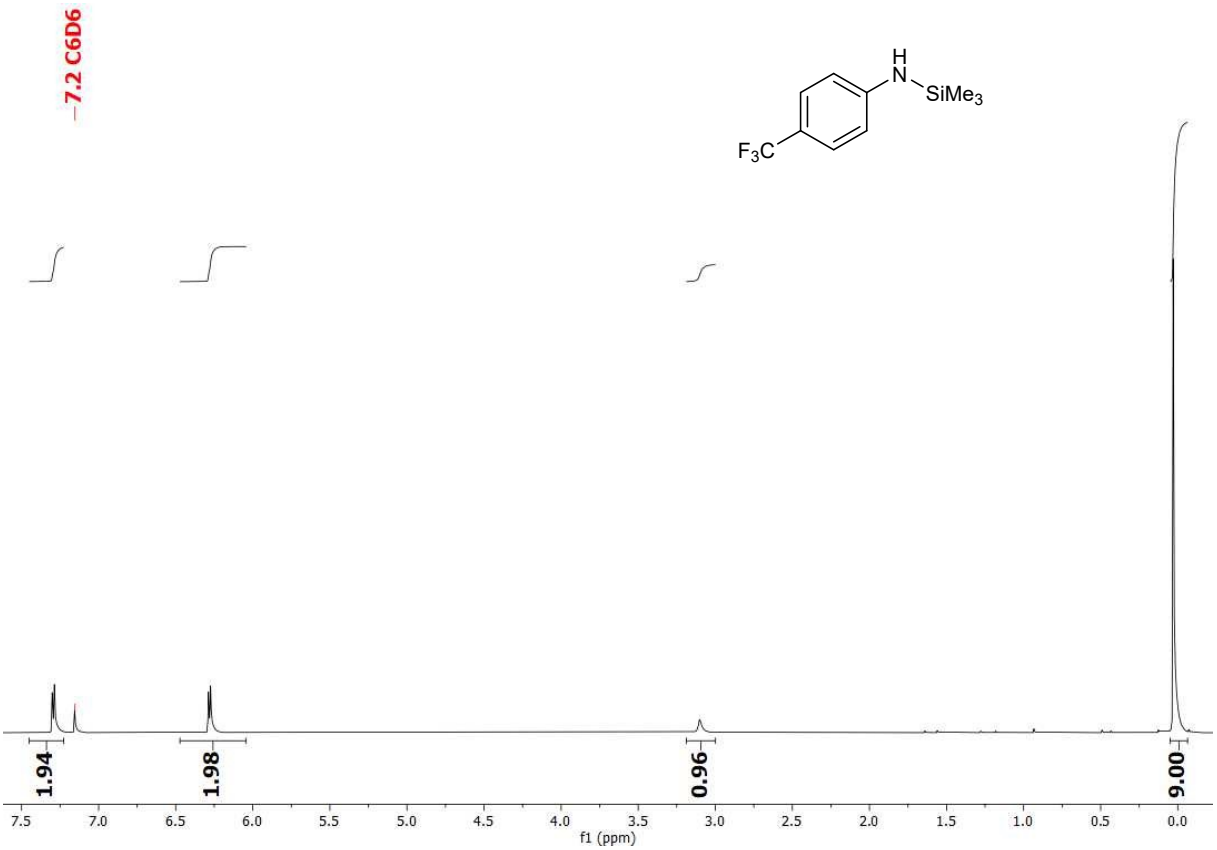


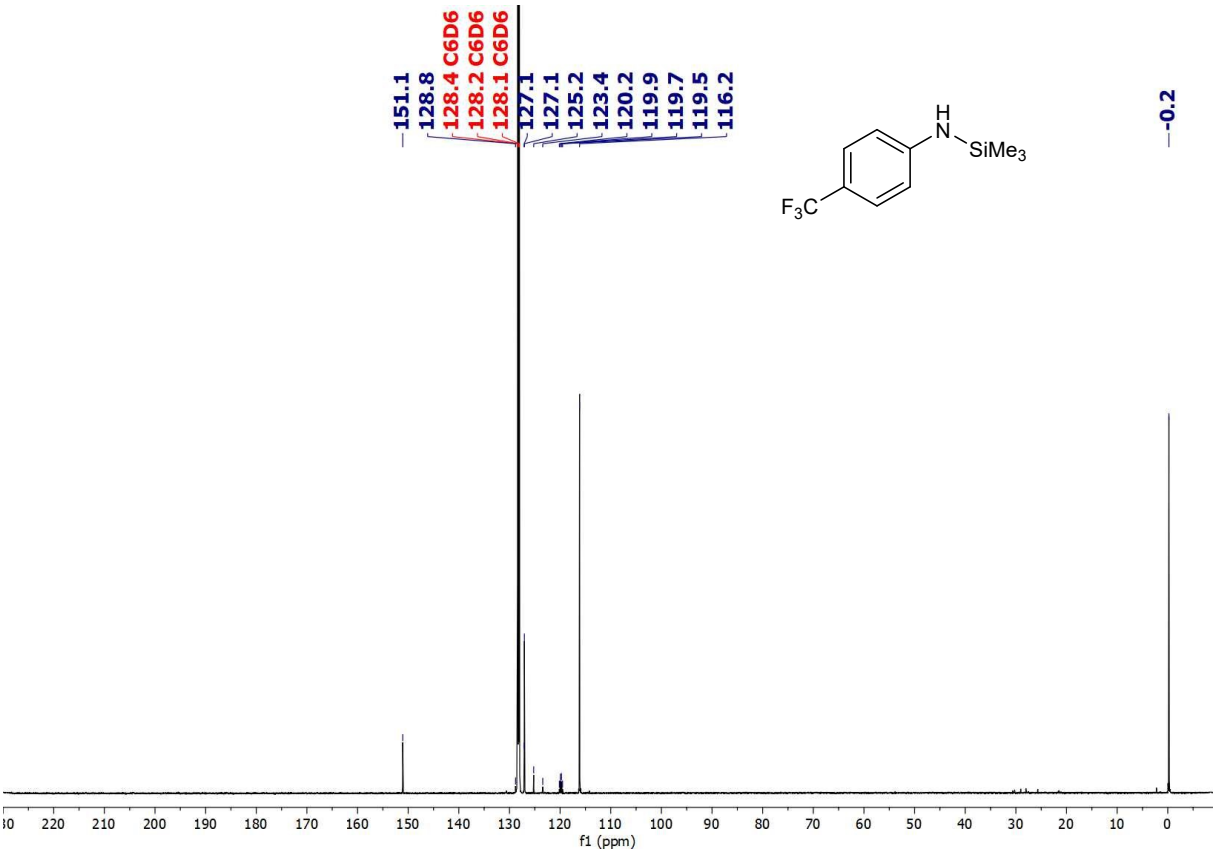


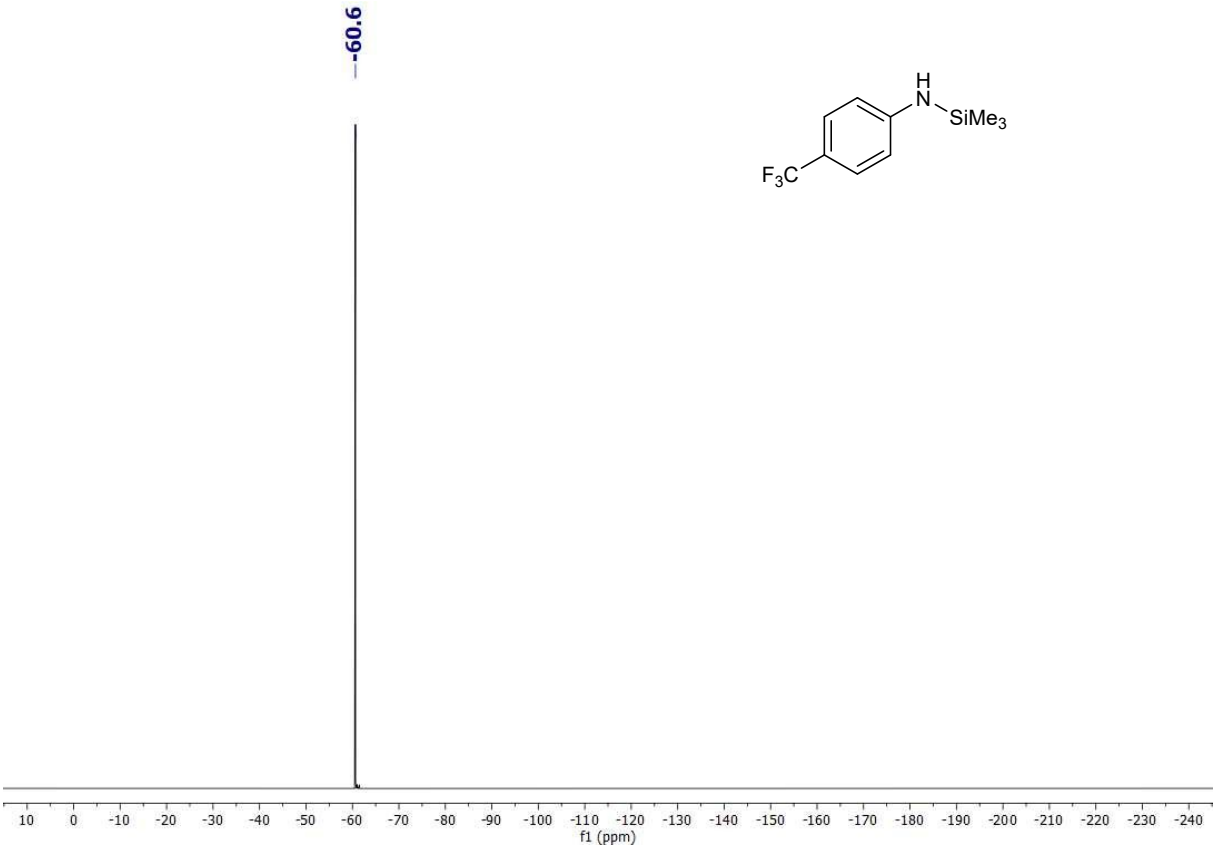

-79.5
-79.6
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

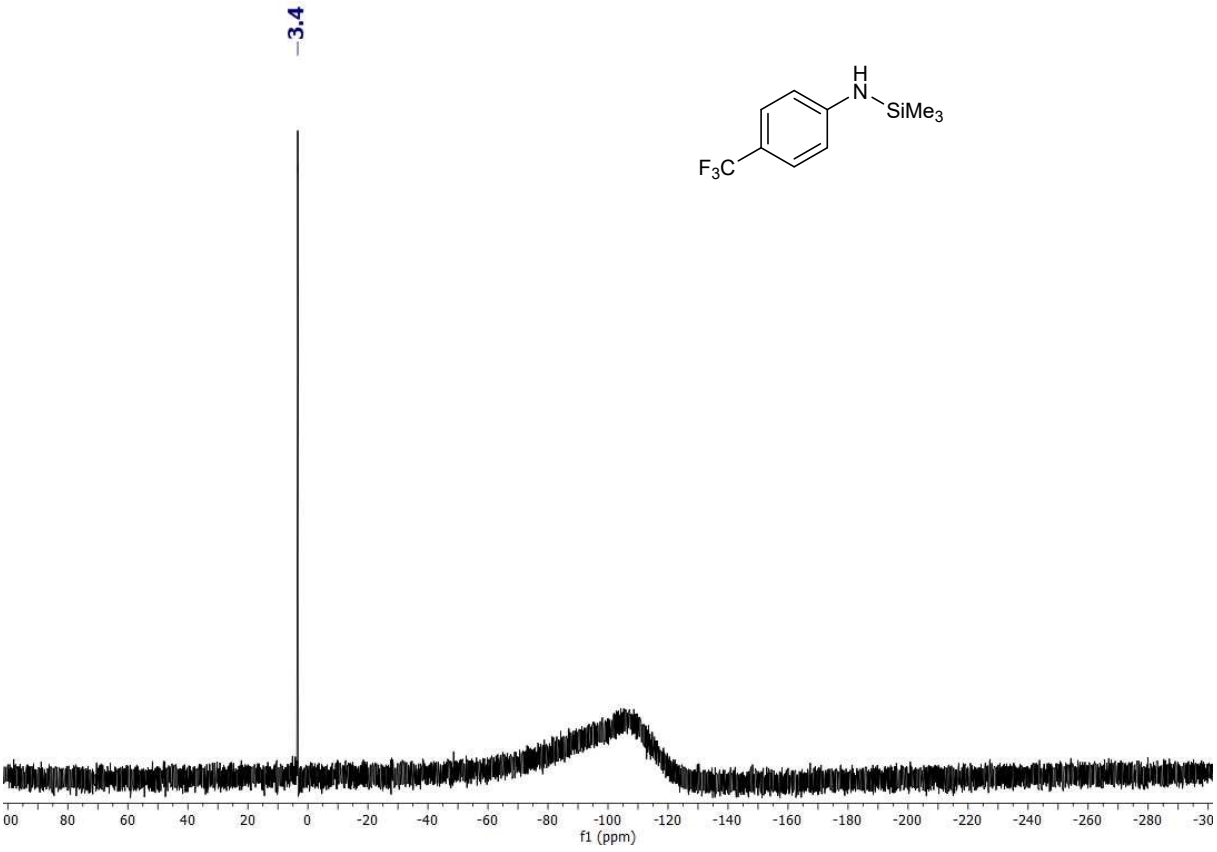

2.4
00 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -30
f1 (ppm)

1,1,1-Trimethyl-N-(4-(trifluoromethyl)phenyl)silanamine (3m)

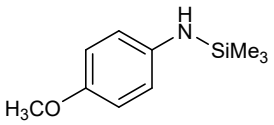


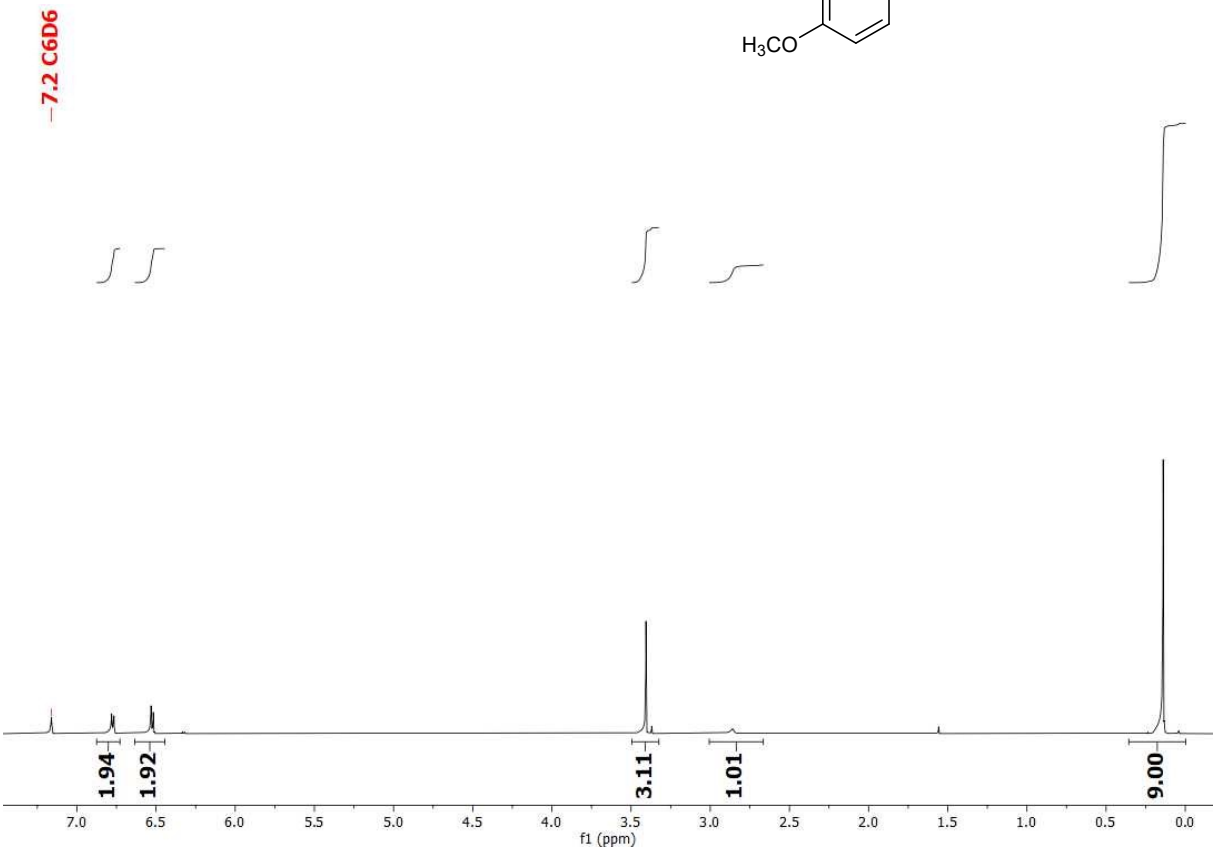


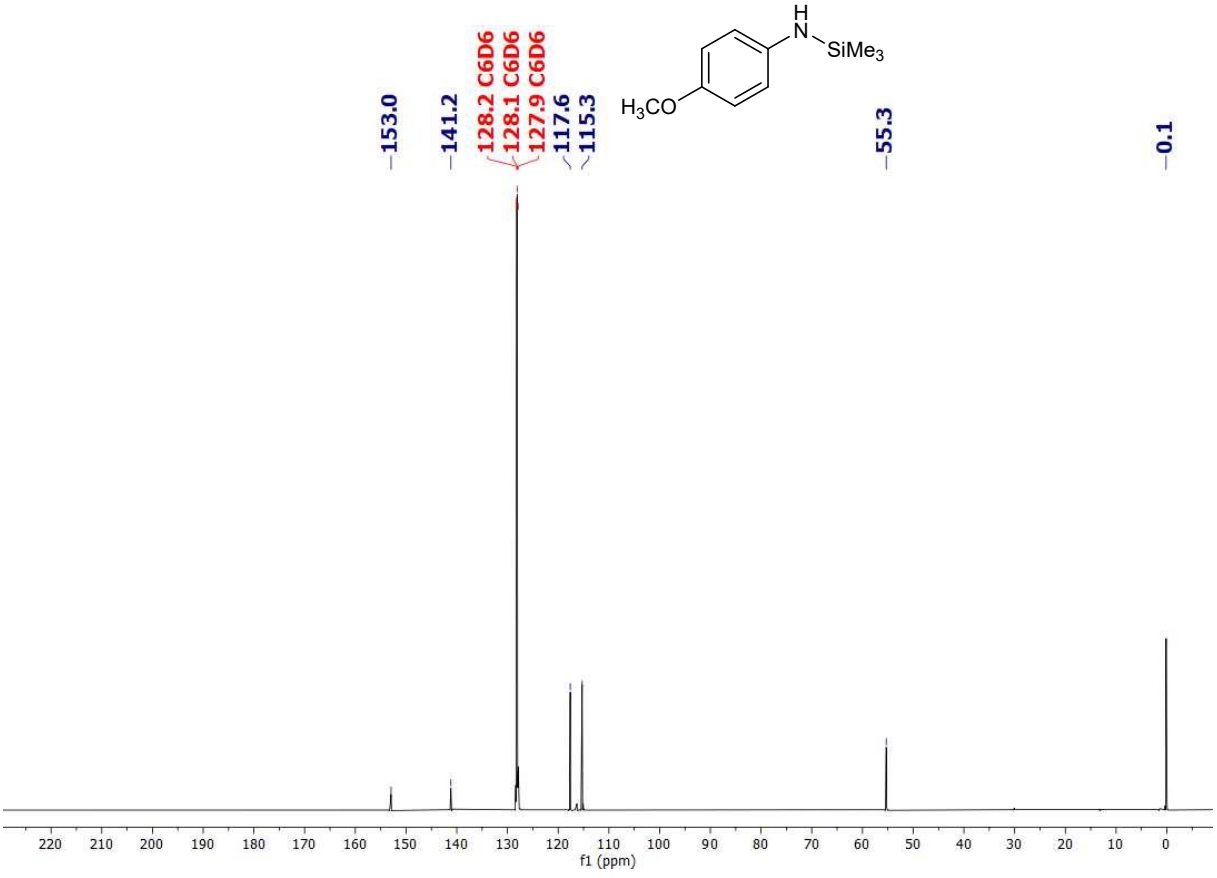

-60.6
H
N
SiMe3
F3C
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

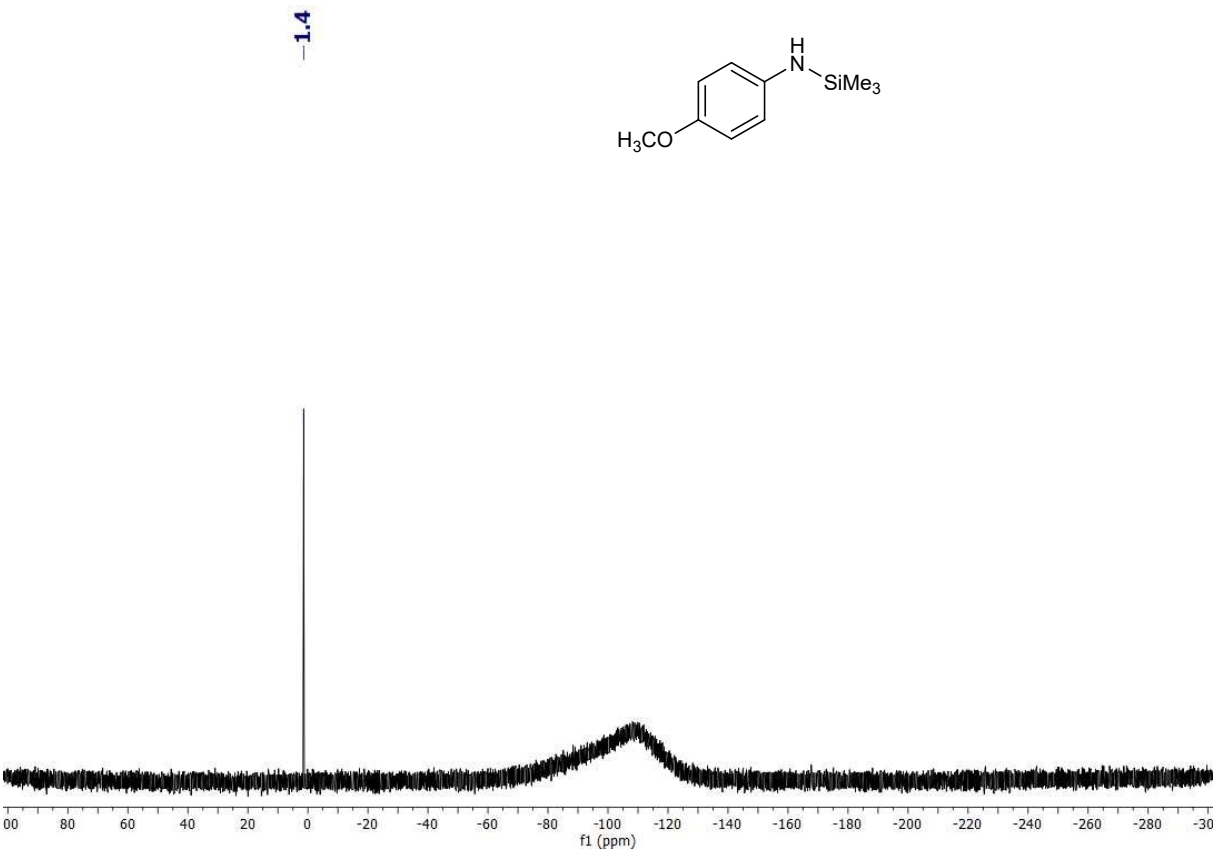

-3.4
H
N
SiMe3
F3C
00 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -30
f1 (ppm)

N-(4-methoxyphenyl)-1,1,1-trimethylsilanamine (3n)

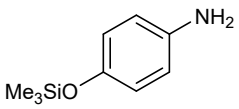


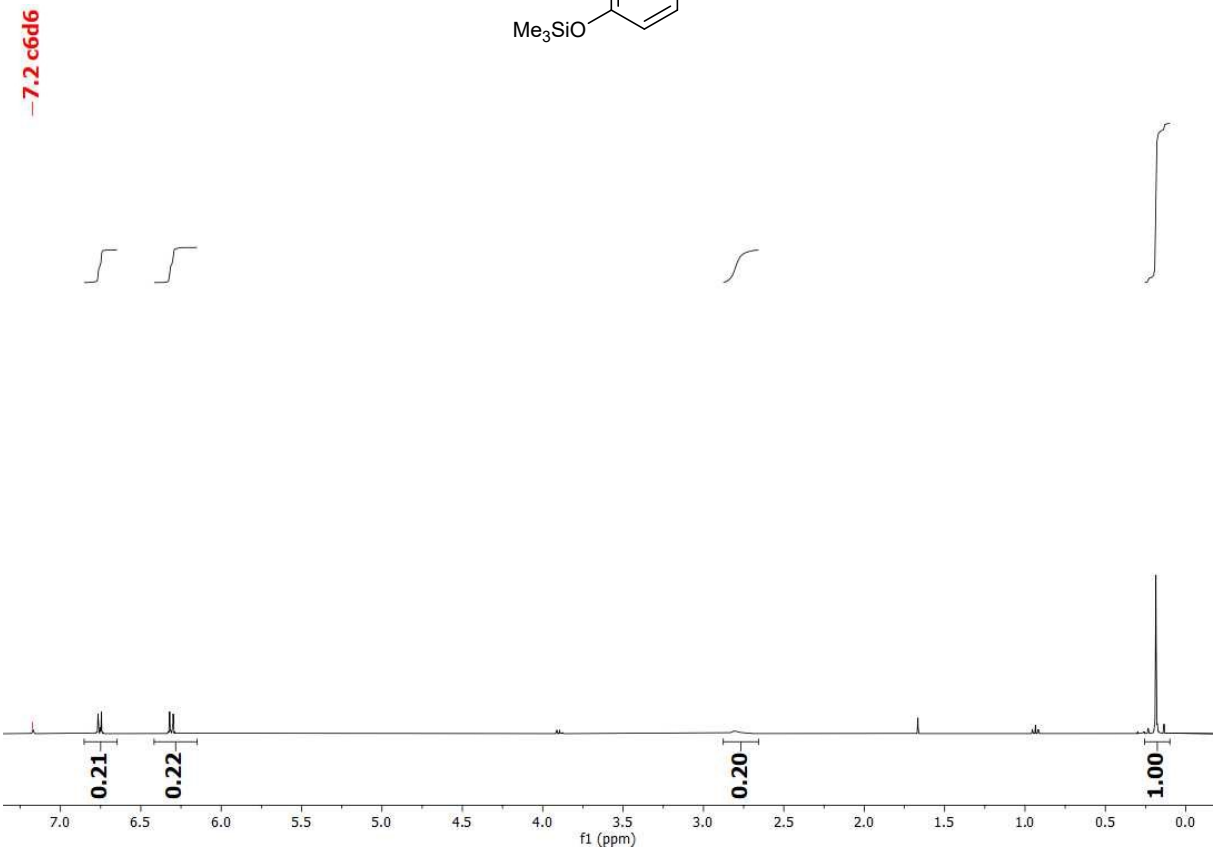


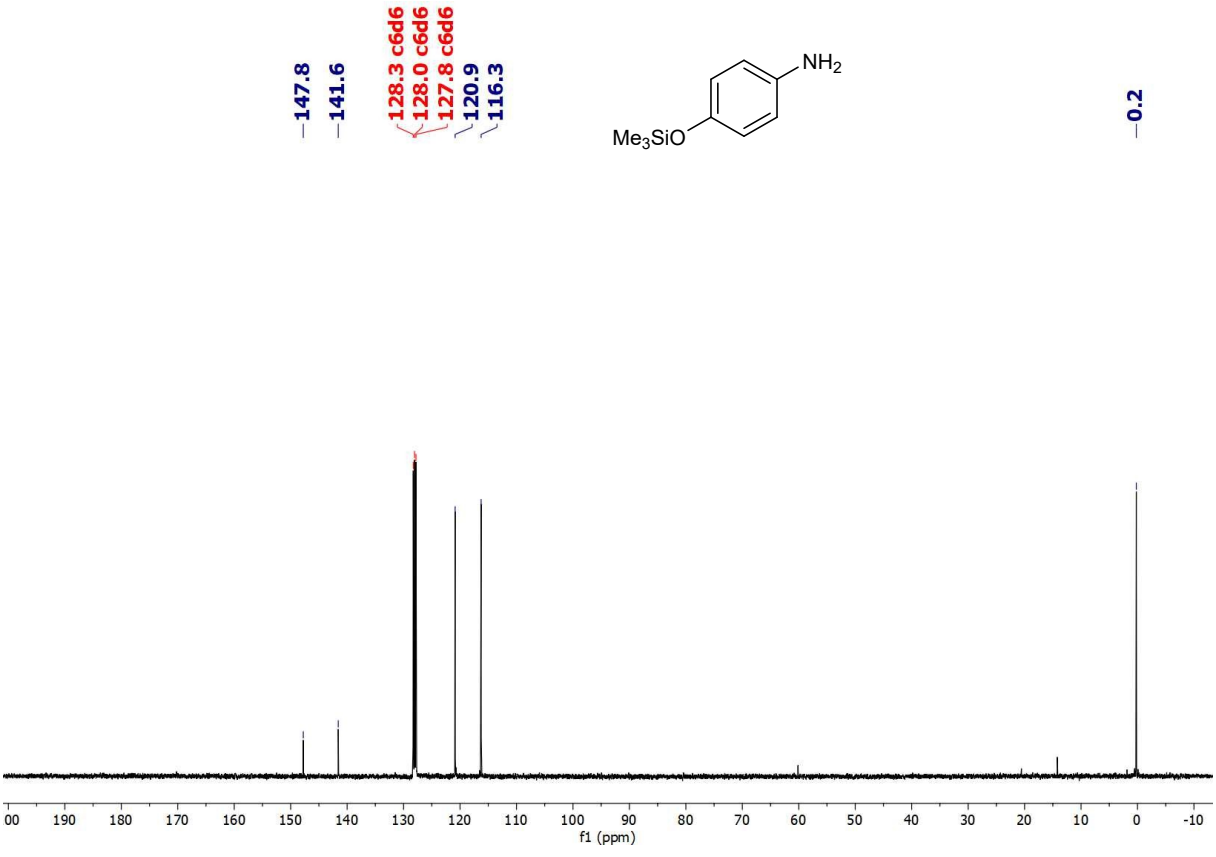


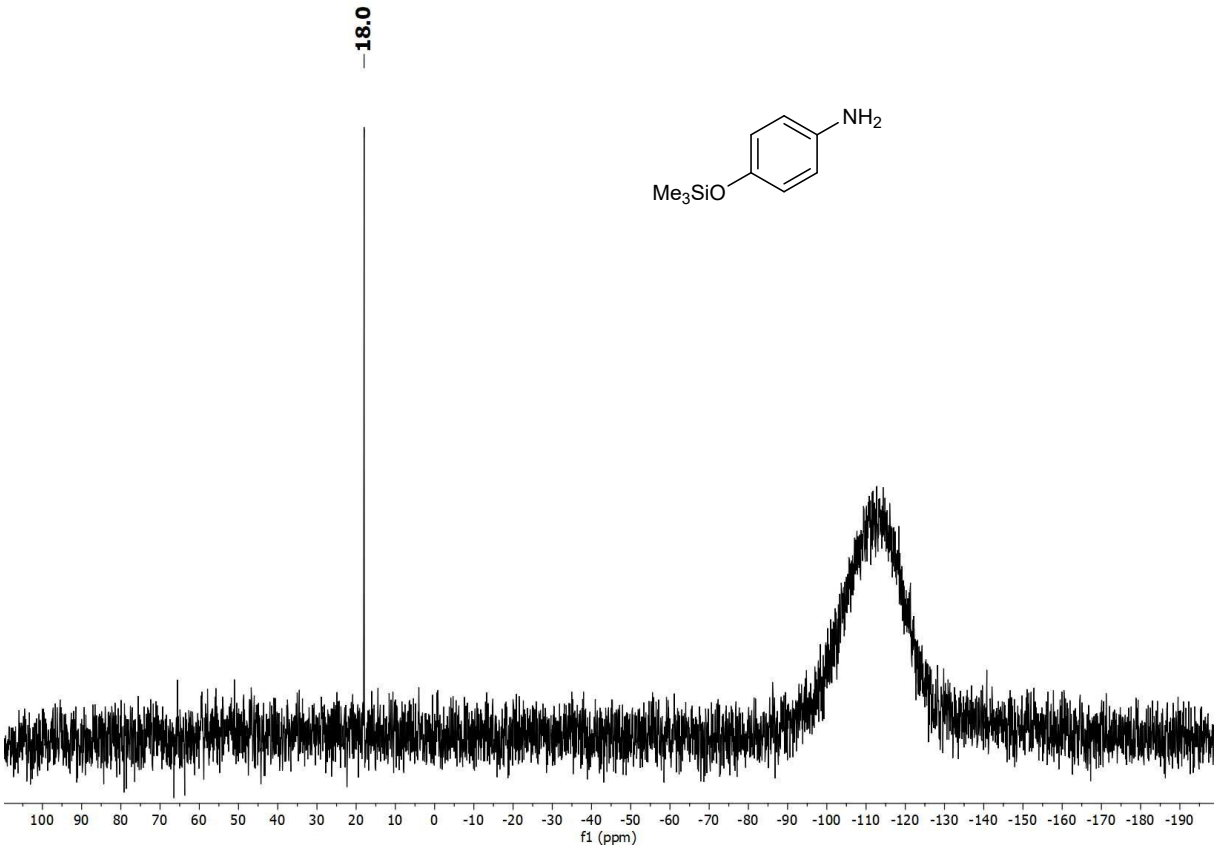

-1.4
H
N
SiMe3
H3CO
00
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
-30
f1 (ppm)

4-((Trimethylsilyl)oxy)aniline (3o)

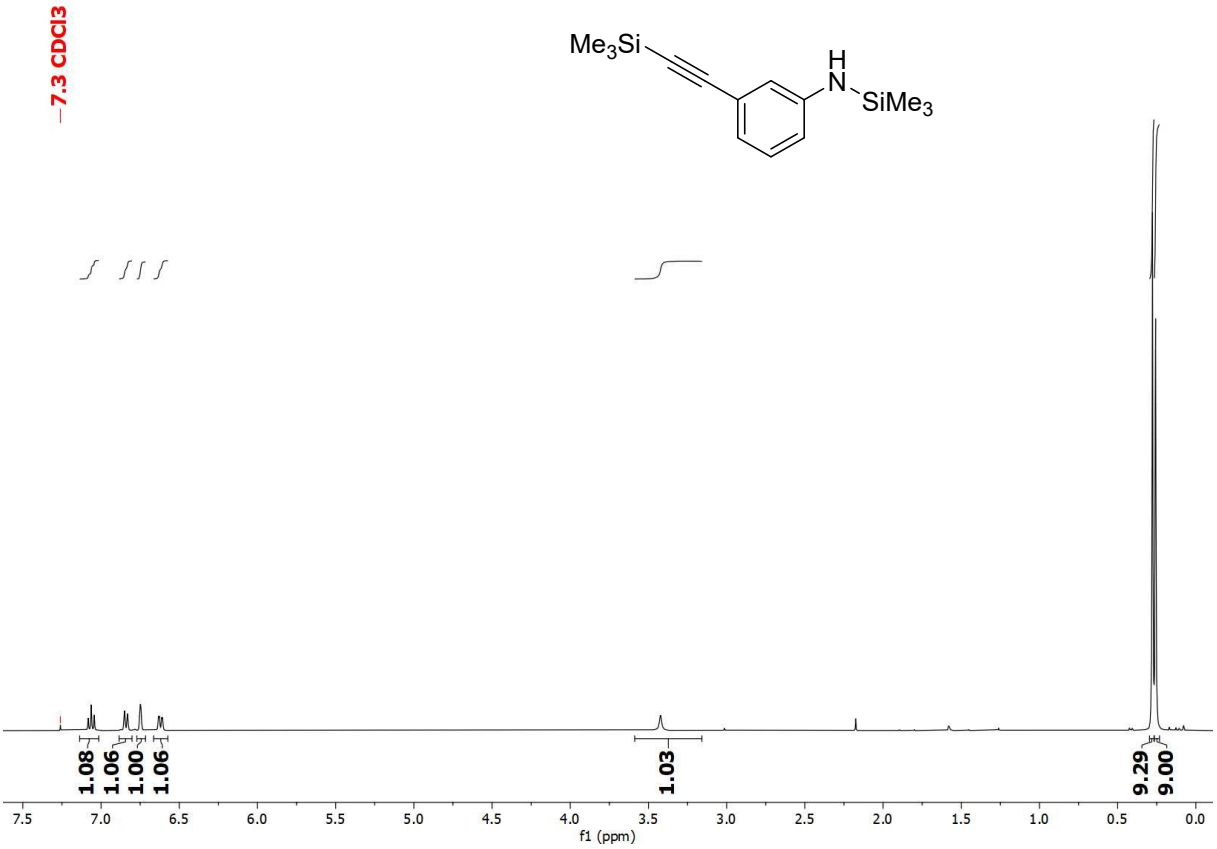


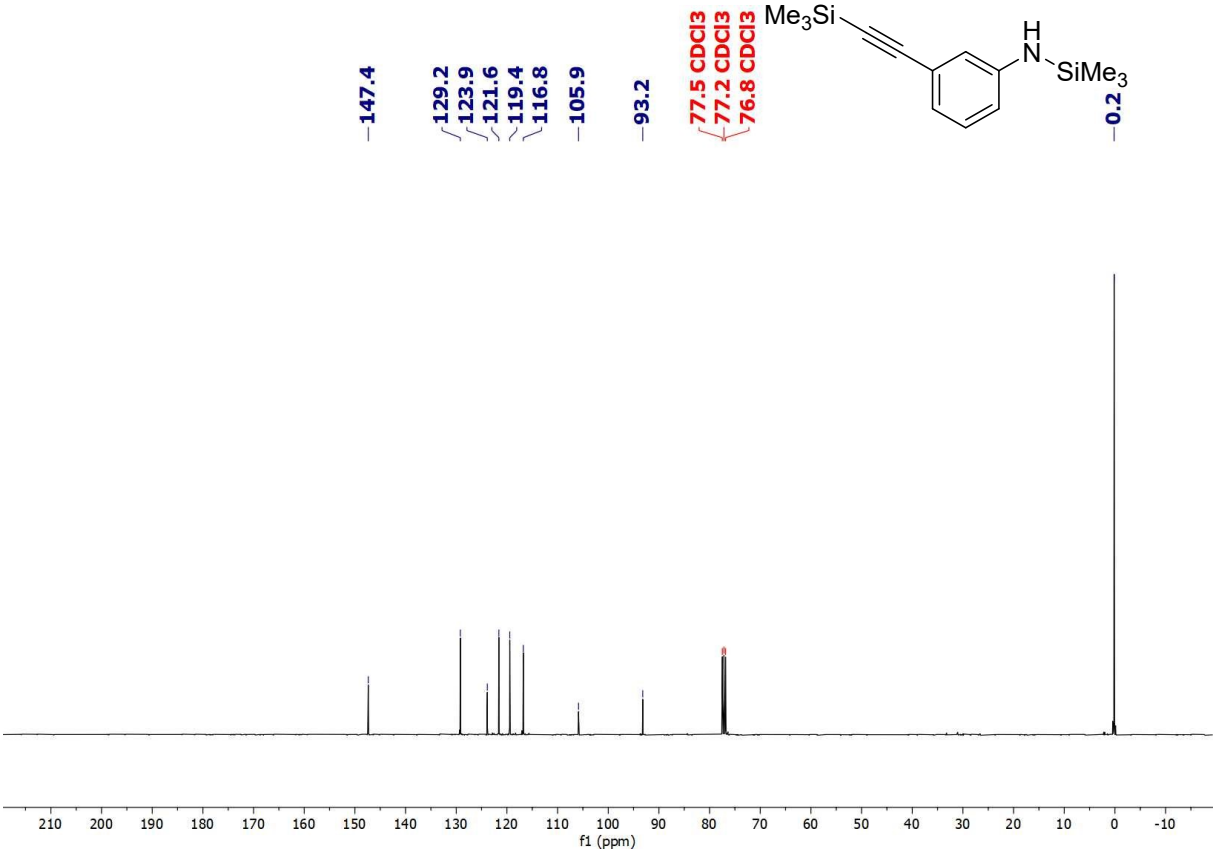


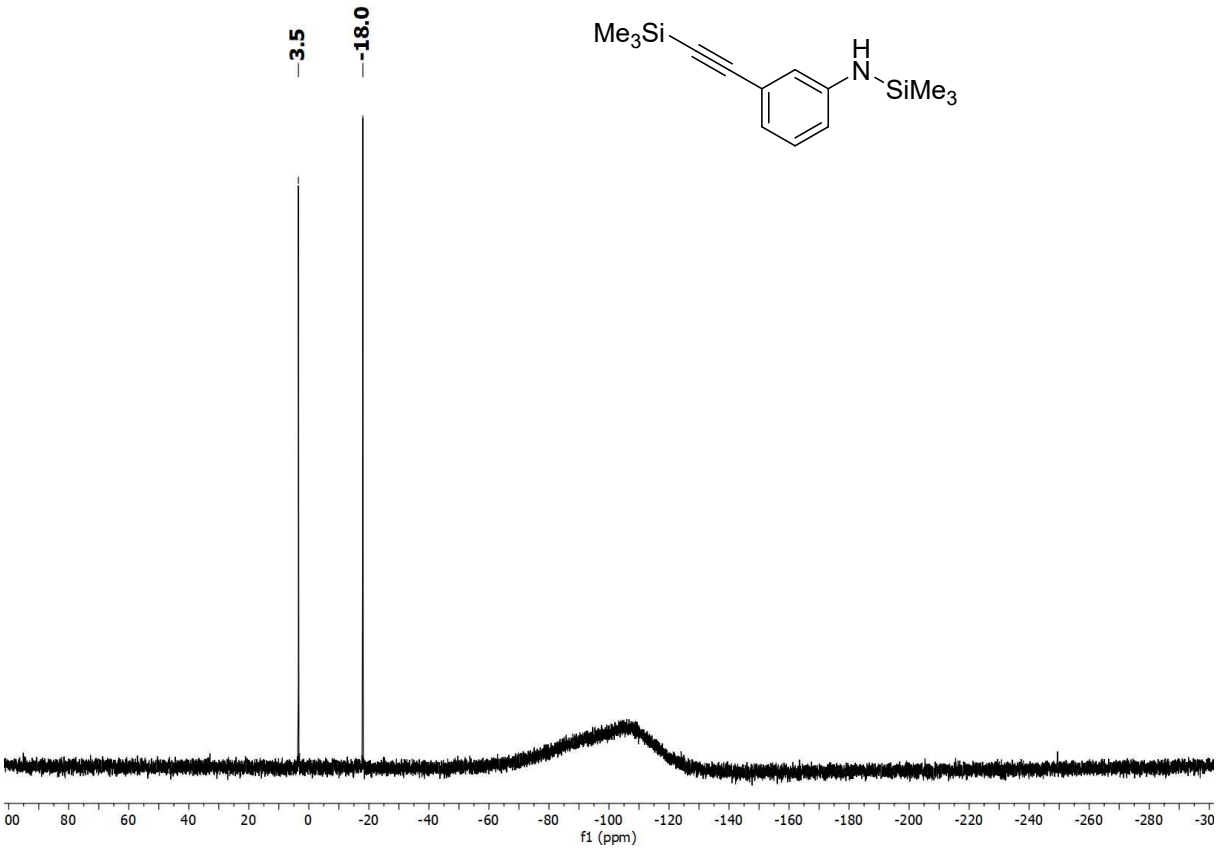



-18.0
NH2
Me3SiO
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

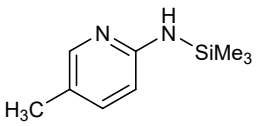
1,1,1-Trimethyl-N-(3-((trimethylsilyl)ethynyl)phenyl)silanamine (3p)

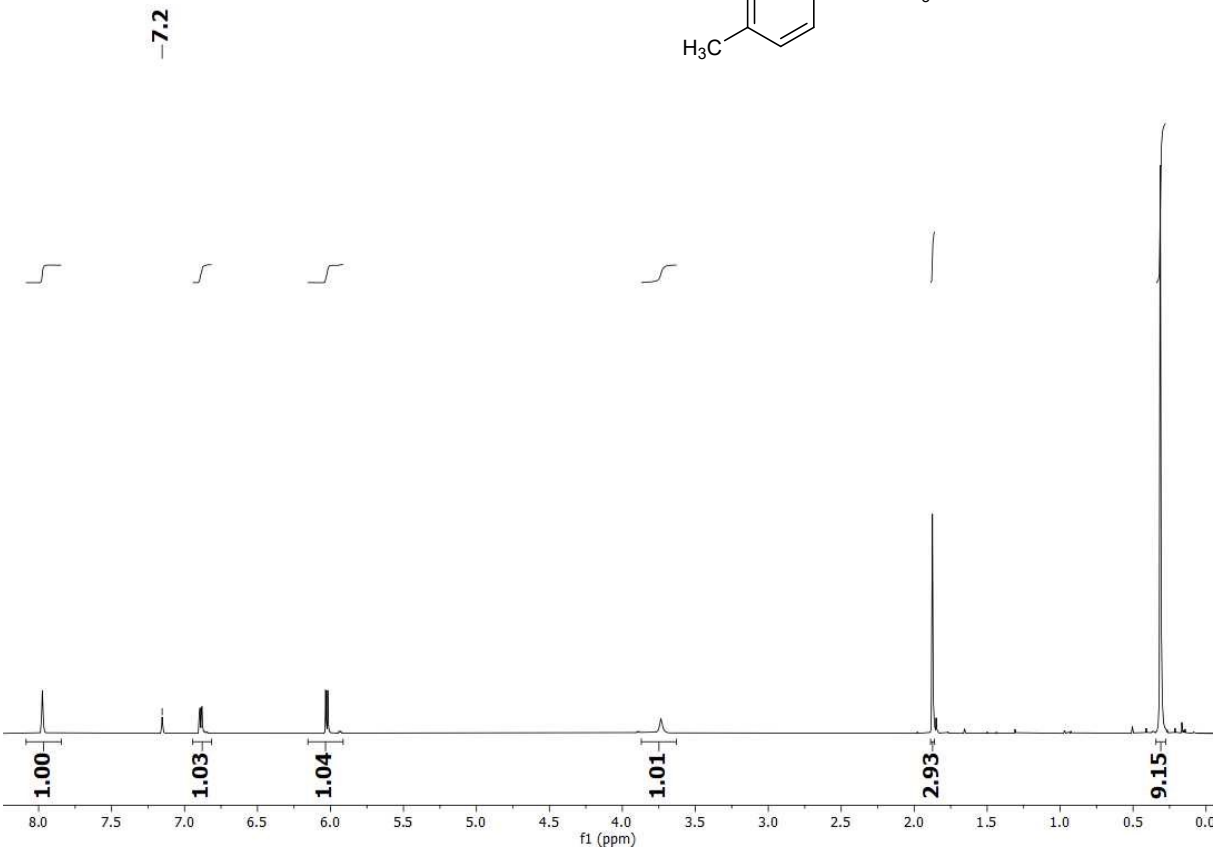


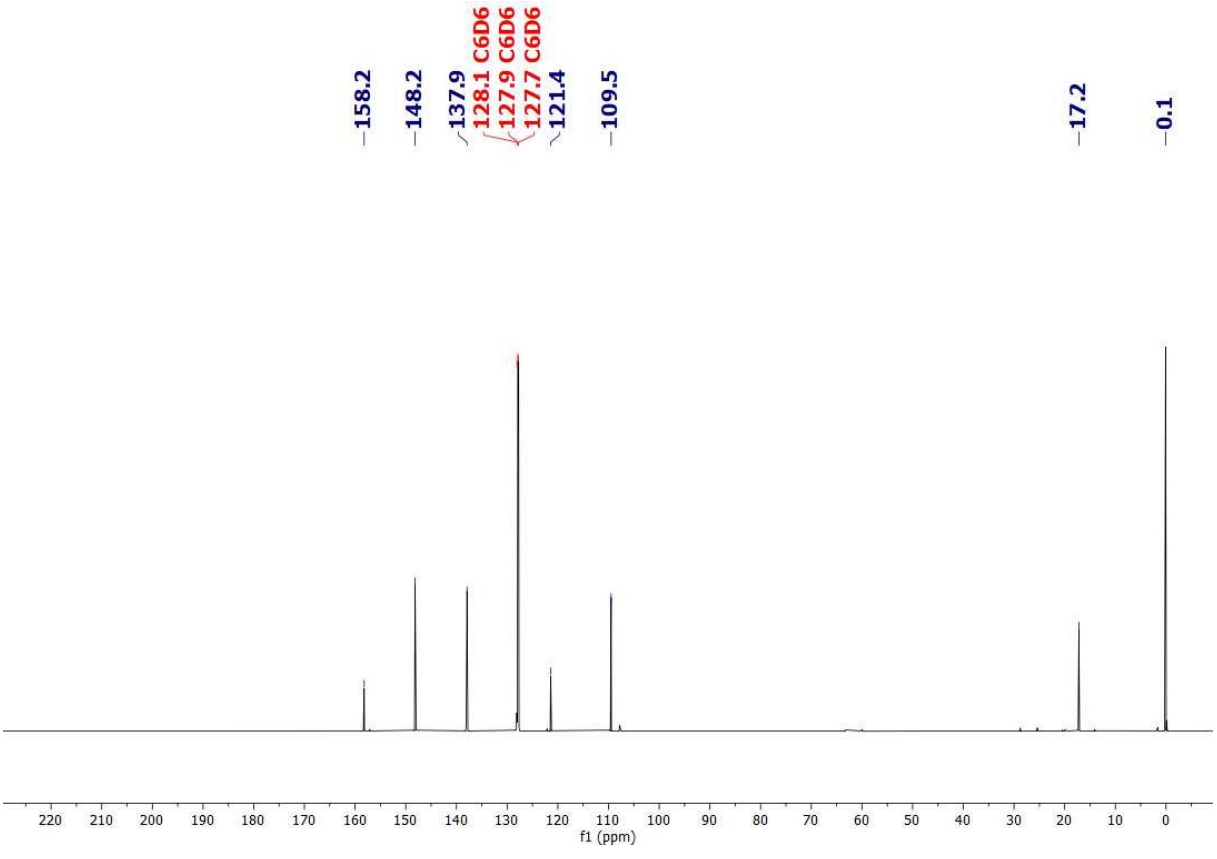


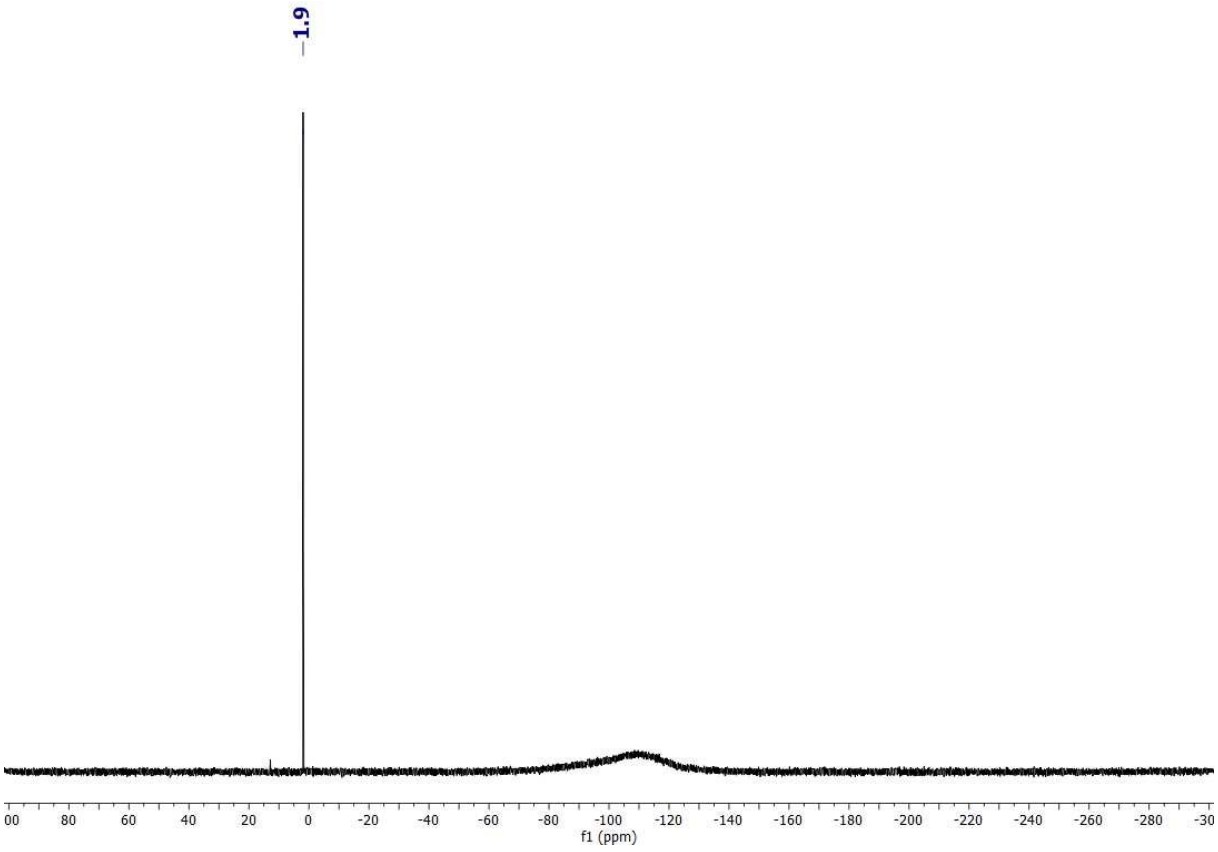

-3.5
-18.0
Me3Si
H
N
SiMe3
00
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
-30
f1 (ppm)

5-Methyl-N-(trimethylsilyl)pyridin-2-amine (5a)

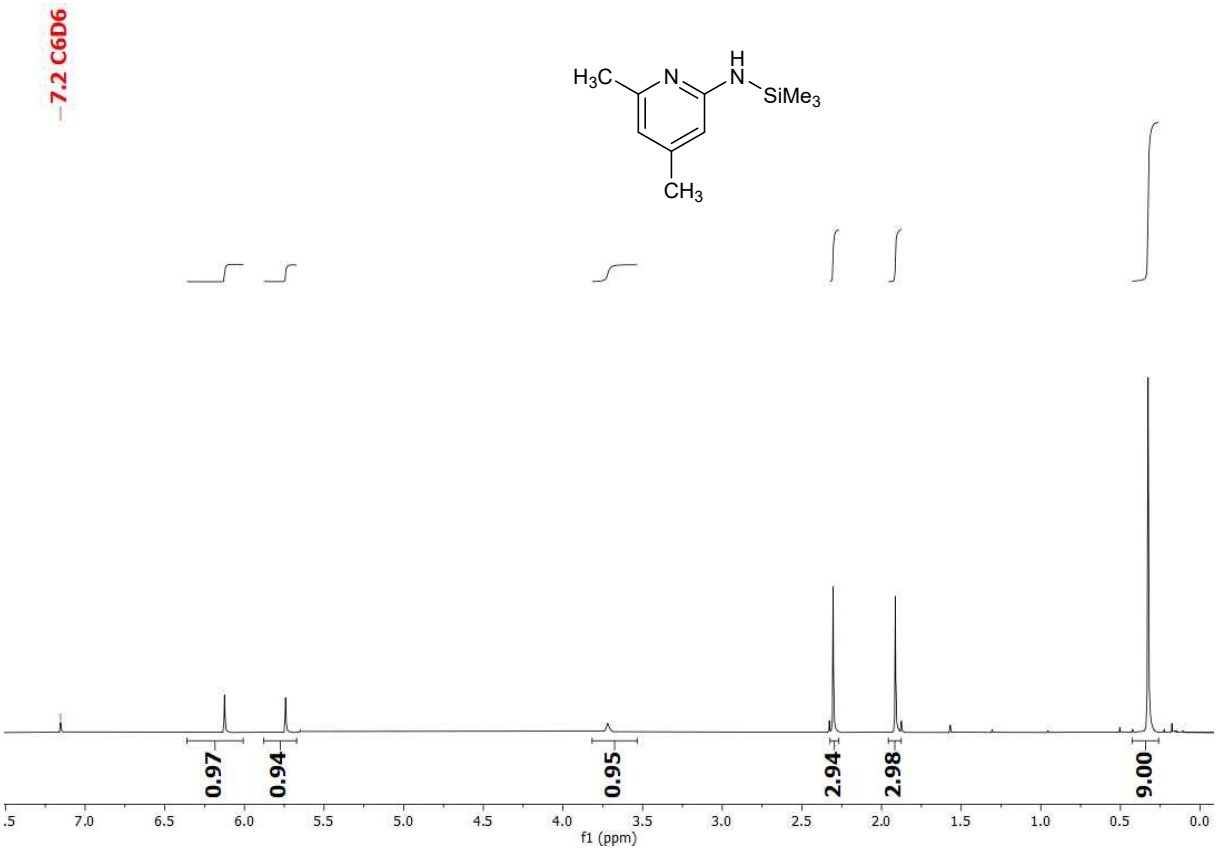


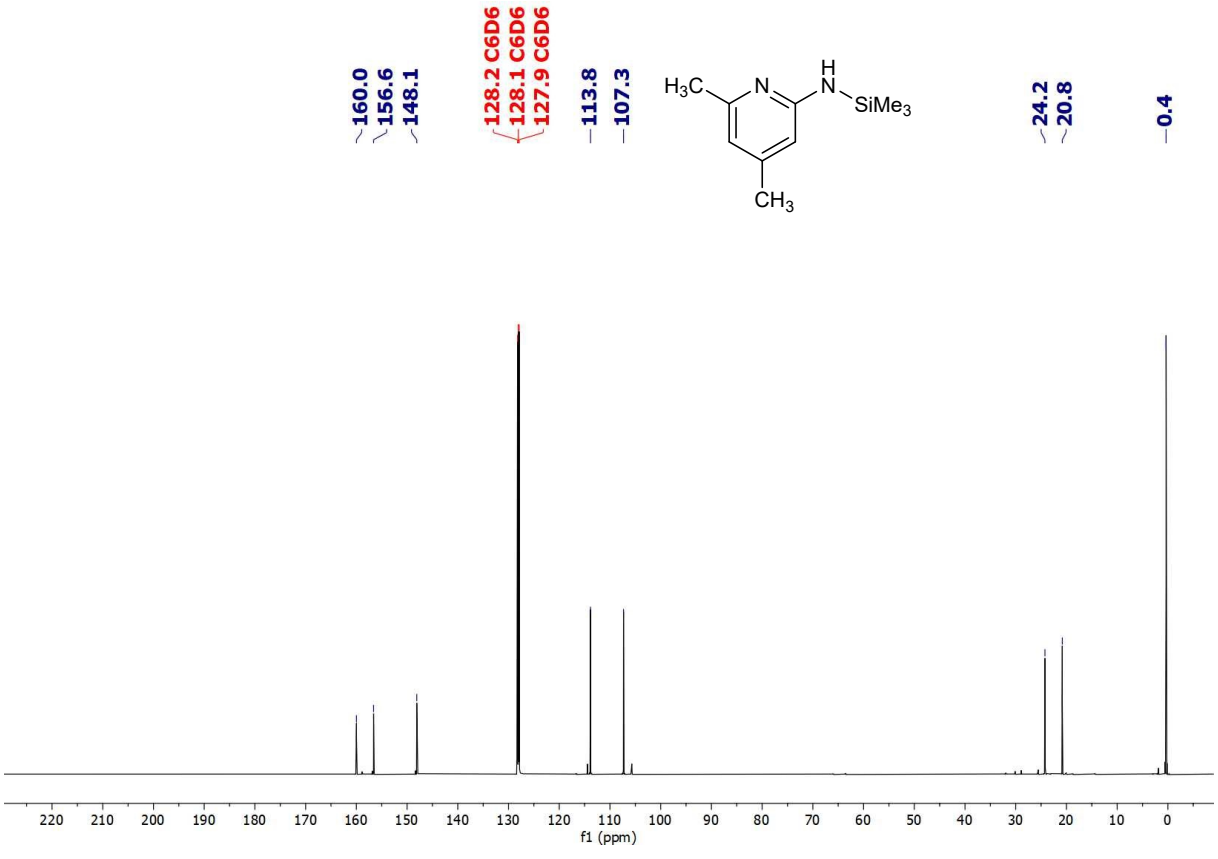




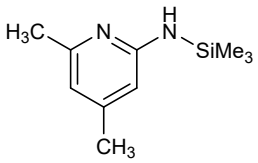

1.9
00 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -30
f1 (ppm)

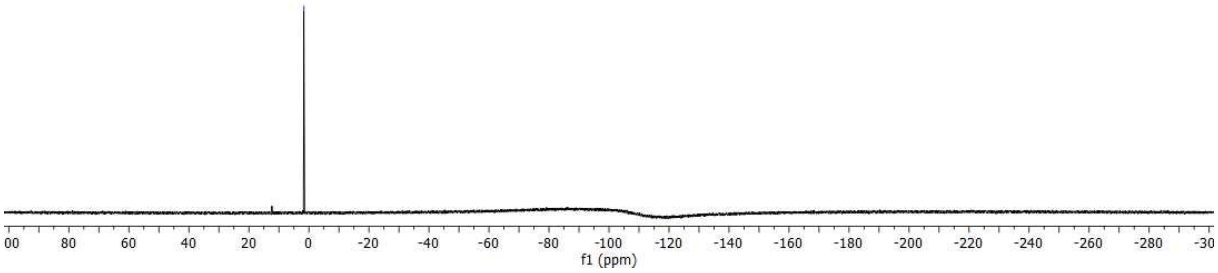
4,6-Dimethyl-N-(trimethylsilyl)pyridin-2-amine (5b)



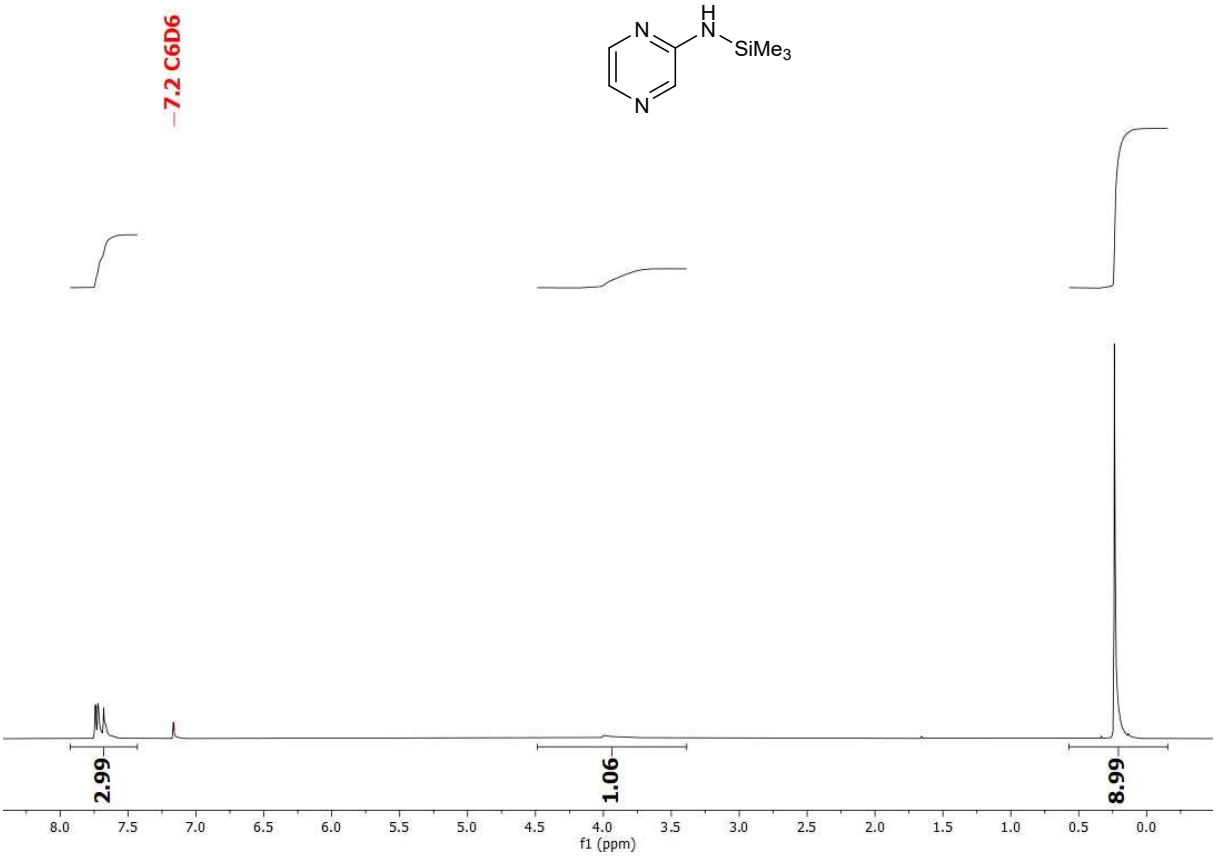


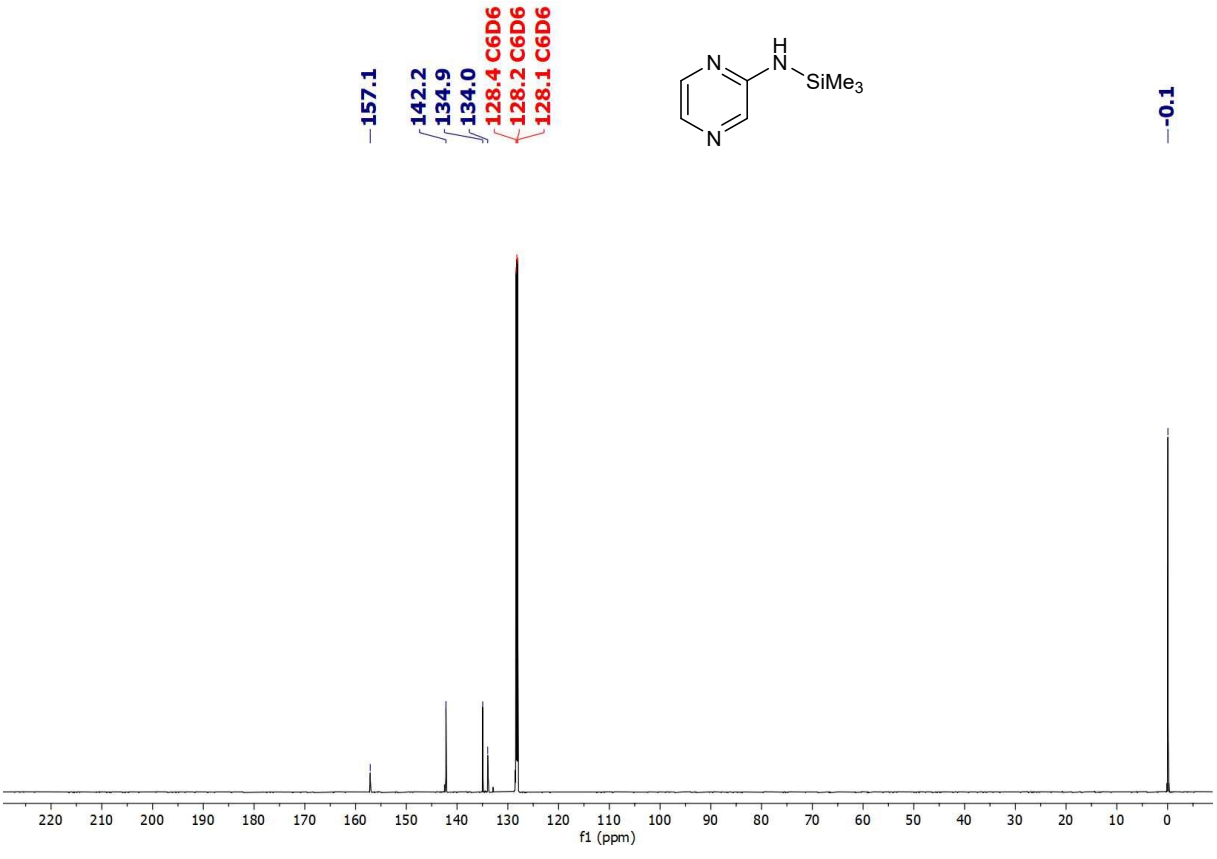
-1.7

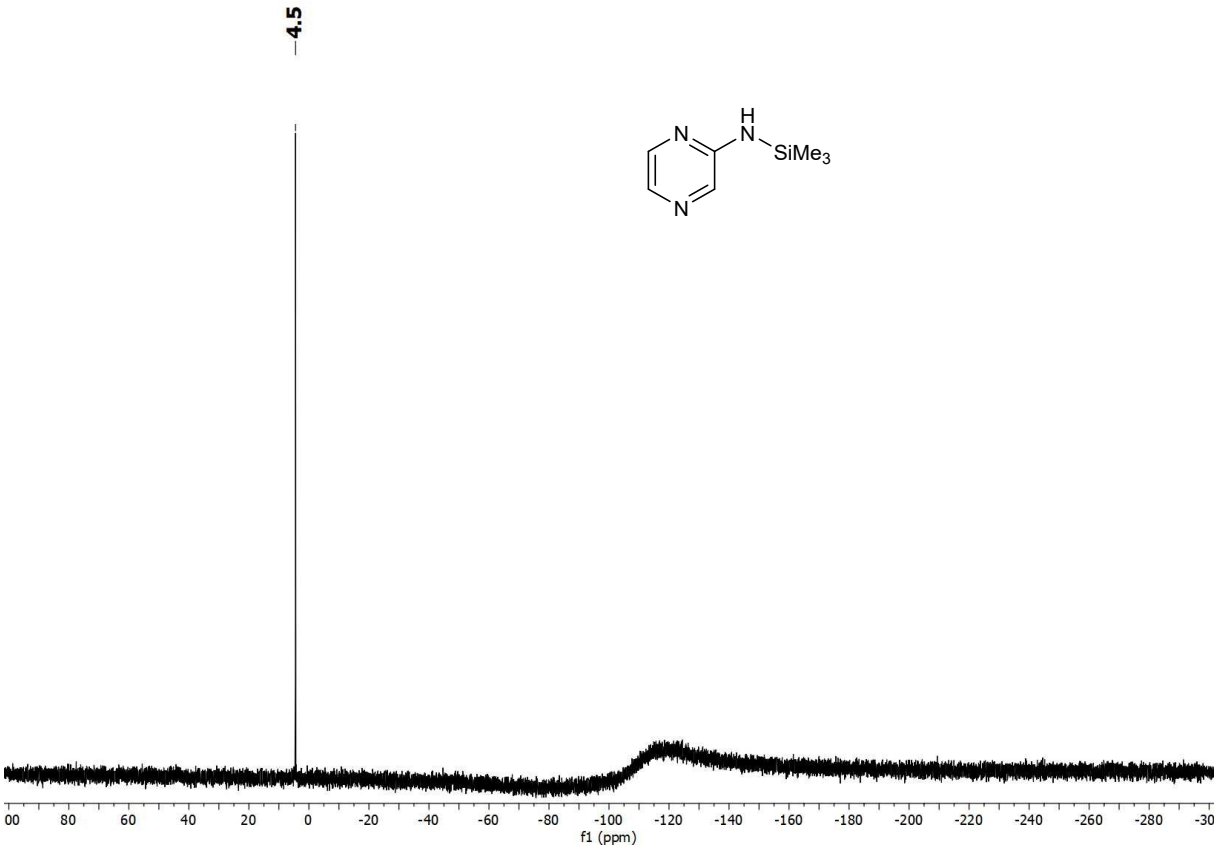

H3C
N
H
N
SiMe3
CH3


00
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
-30
f1 (ppm)

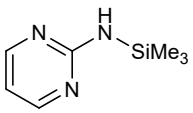
N-(trimethylsilyl)pyrazin-2-amine (5c)

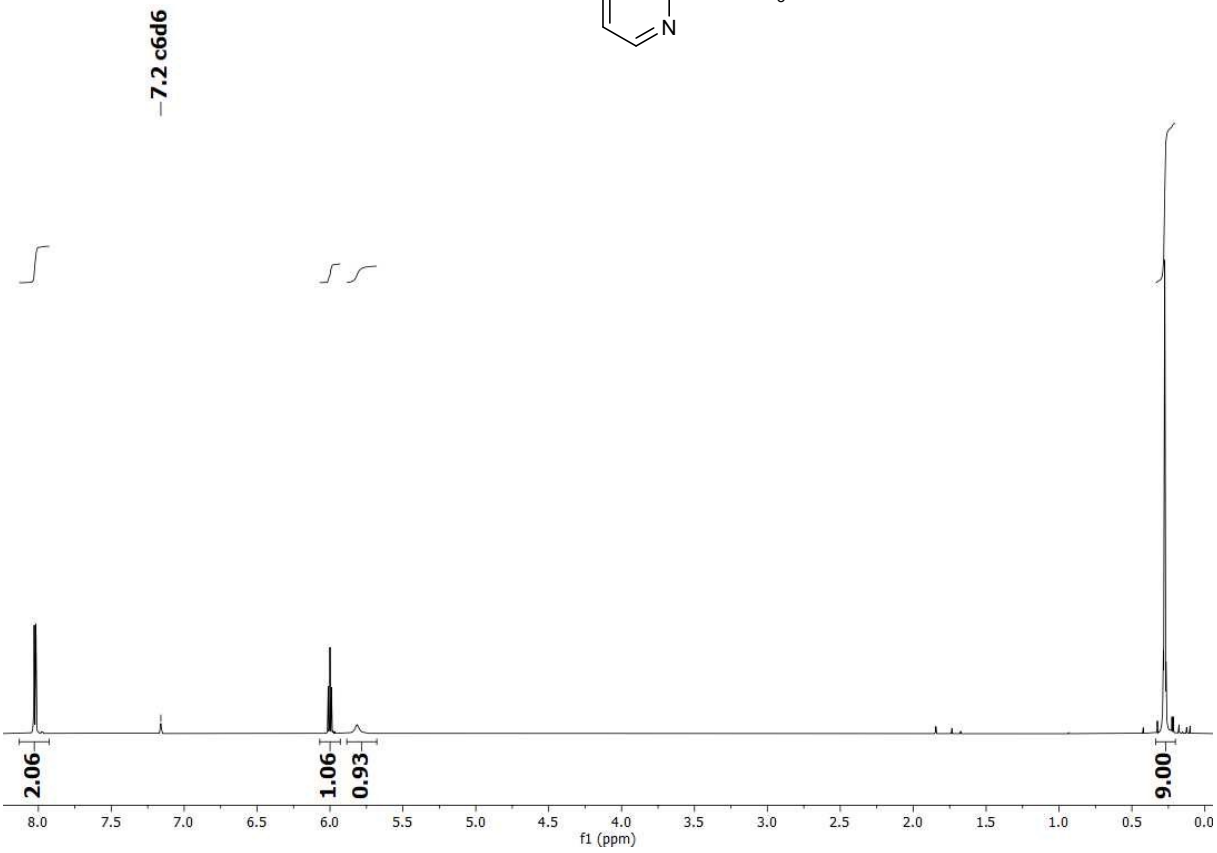


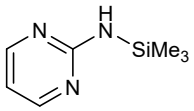



4.5
N
H
N
SiMe3
N
00
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
-30
f1 (ppm)

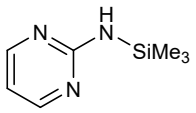
N-(trimethylsilyl)pyrimidin-2-amine (5d)

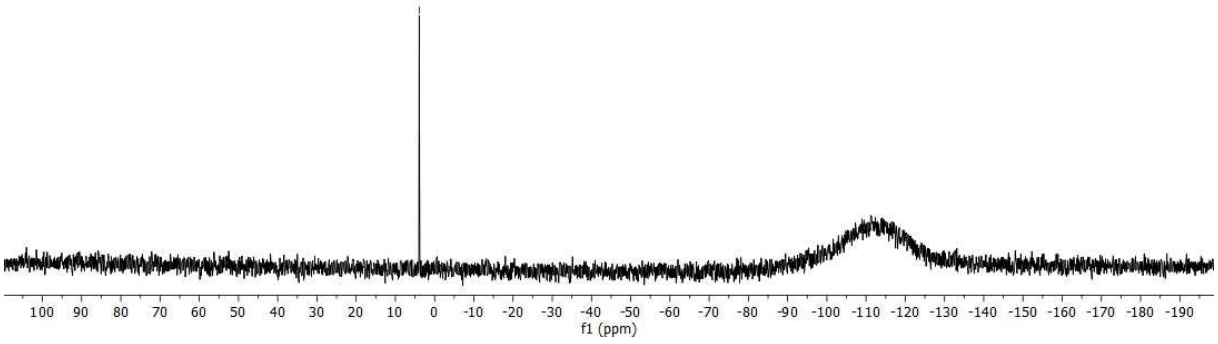




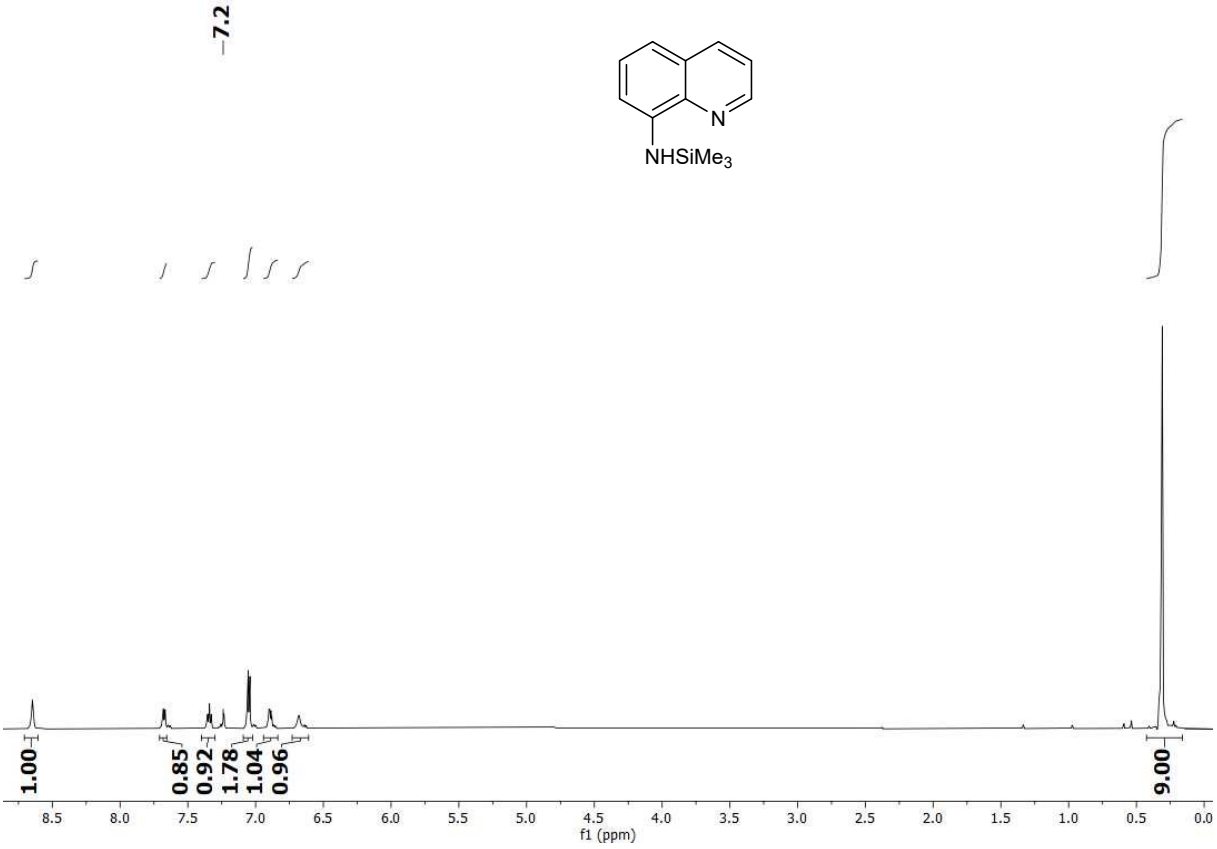


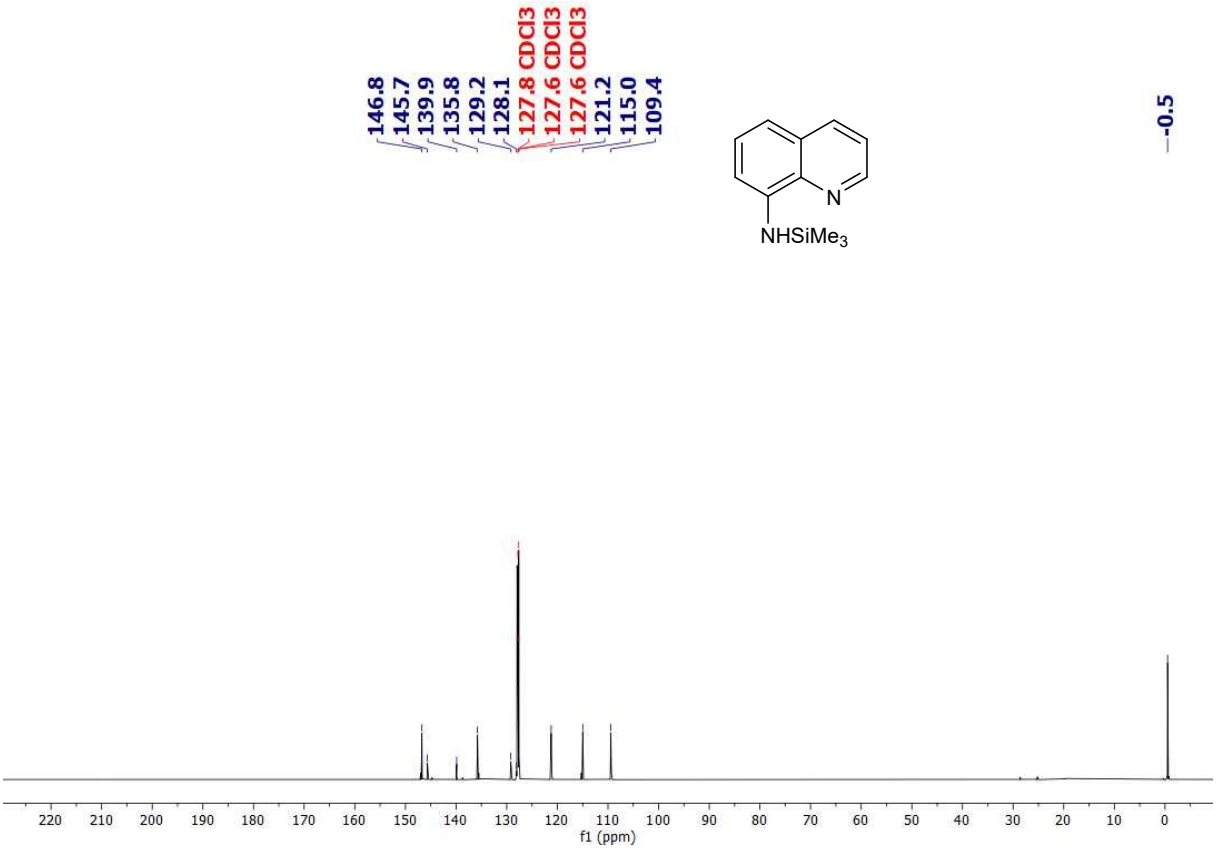
3.9

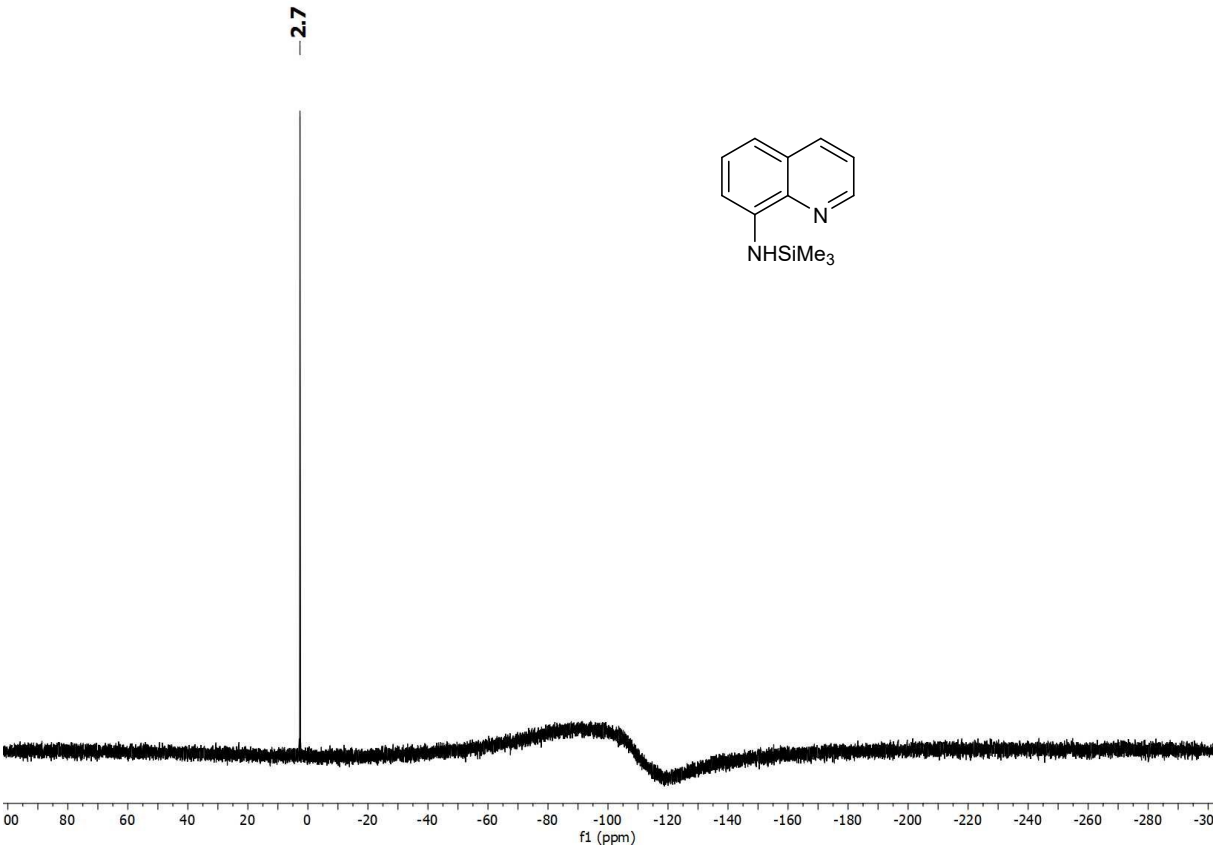

H
N
N
N
SiMe3


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

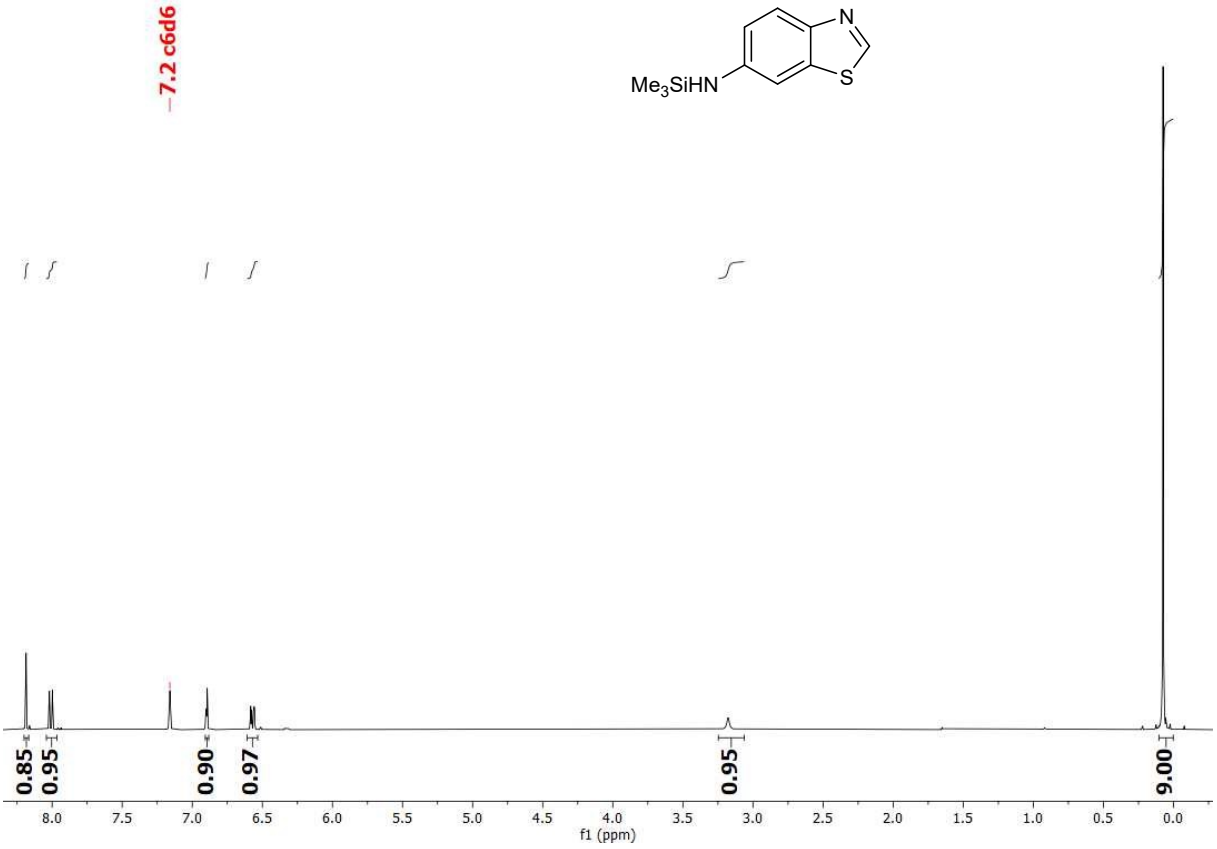
N-(trimethylsilyl)quinolin-8-amine (5e)

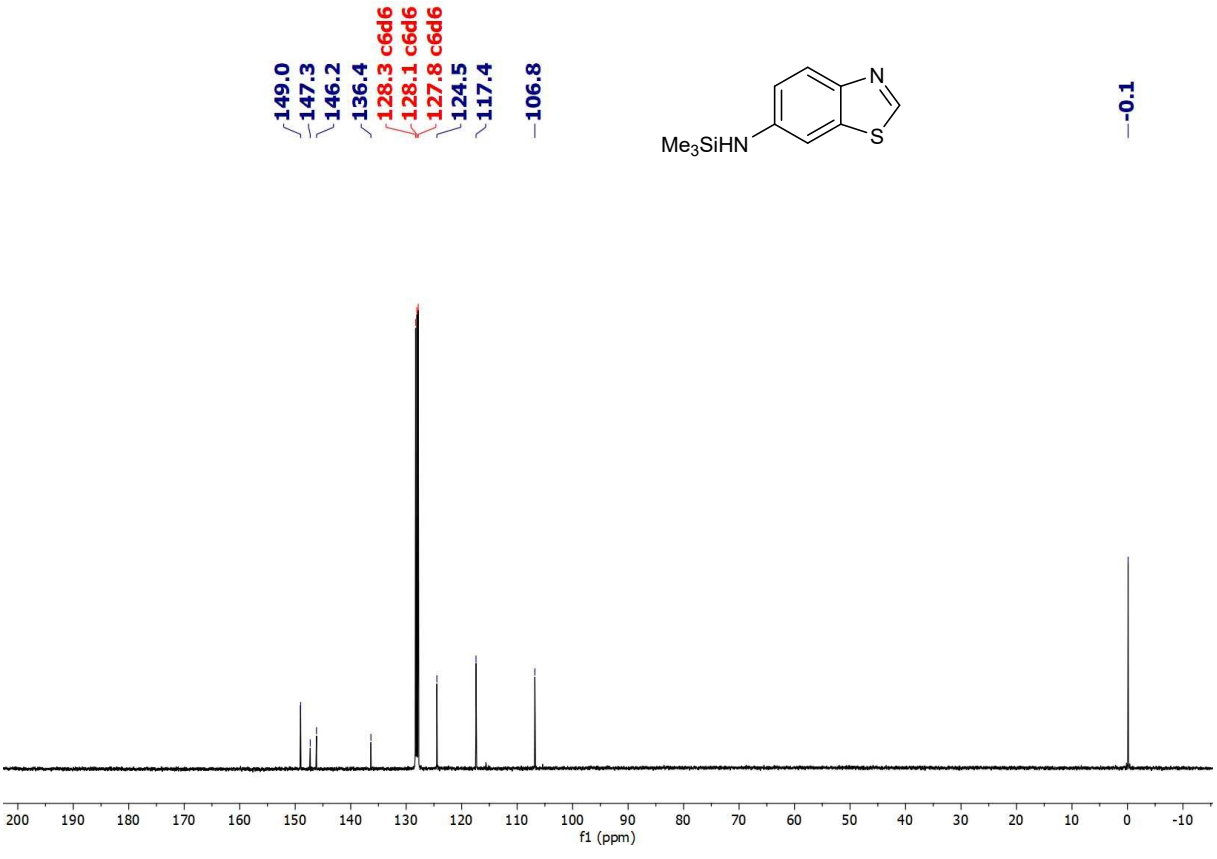




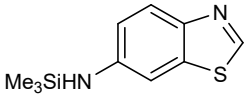

2.7
N
NHSiMe3
00 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -30
f1 (ppm)

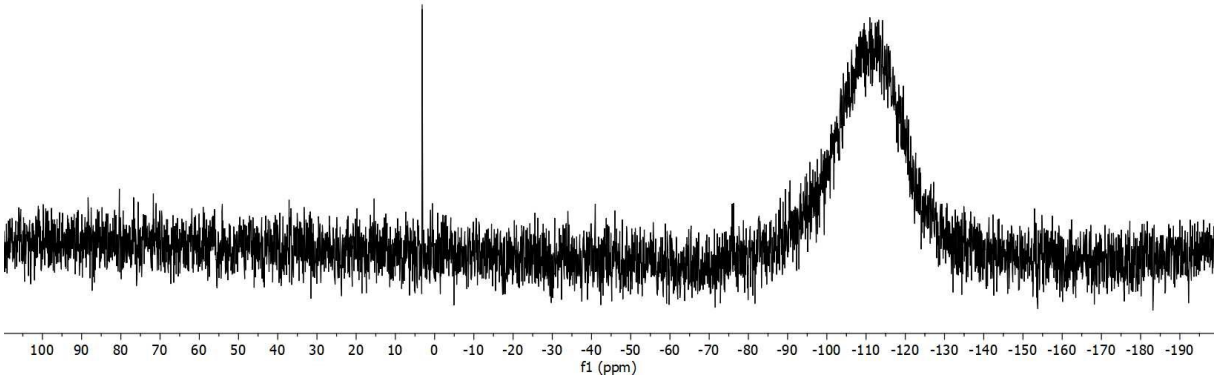
N-(trimethylsilyl)benzo[d]thiazol-6-amine (5f)





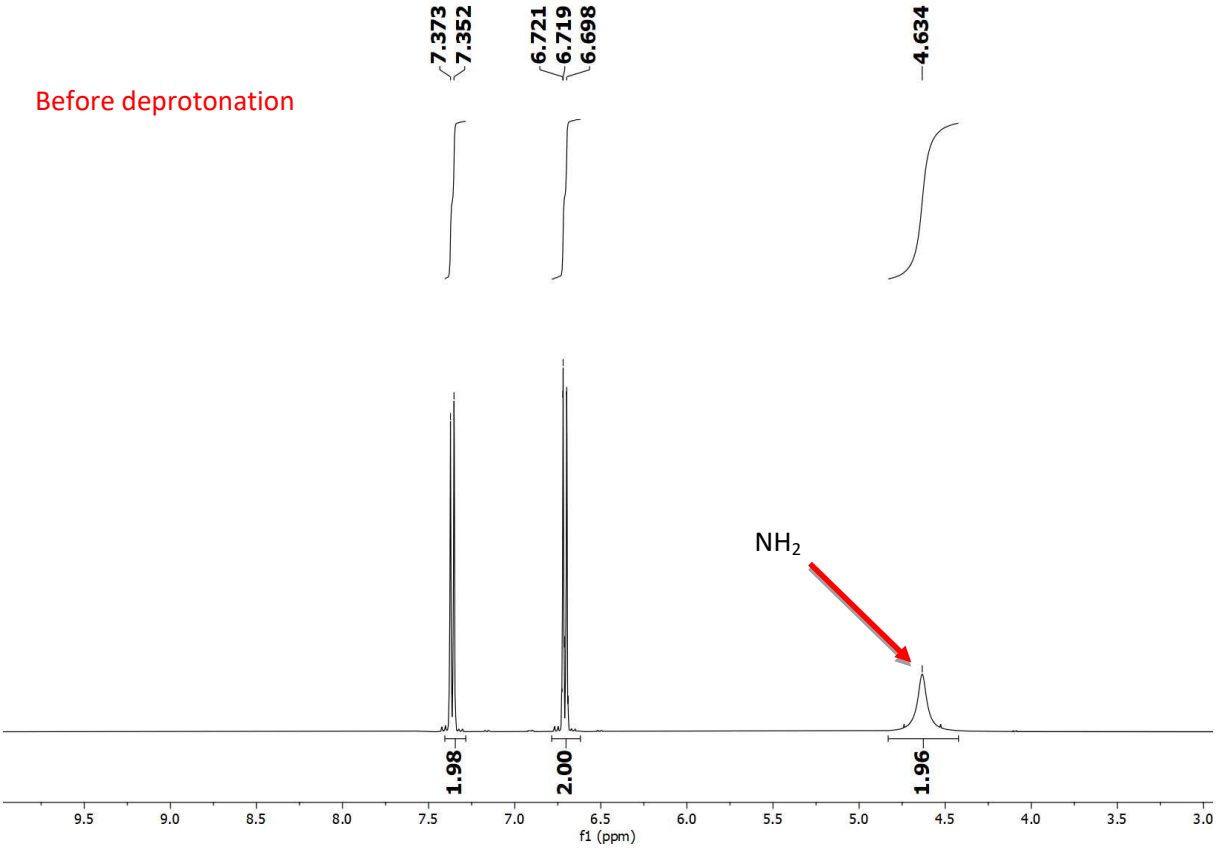
3.2


N
S
Me3SiHN


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

CONFIRMATION FOR A DEPROTONATION OF 4-CF_3-ANILINE BY KHMDS

Before deprotonation



After deprotonation