

Supplementary Material (ESI)

$\alpha$ -Functionalization of Non-activated Aliphatic Amines:  
Ruthenium-catalyzed Alkynylations and Alkylations  
- Supplementary Information -

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## Experimental Section

**General Remarks:** All reactions were carried out under an argon atmosphere. Chemicals were purchased from Aldrich, Fluka, Acros and Strem and unless otherwise noted were used without further purification. Amines were distilled under argon. All compounds were characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, MS, and HRMS.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AV 300 and AV 400 spectrometer. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts are reported relative to the centre of a solvent resonance ( $\text{CDCl}_3$ : 7.25 ( $^1\text{H}$ ), 77.0 ( $^{13}\text{C}$ )). EI mass spectra were recorded on a Nicolet Magna 550. GC was performed on a Hewlett-Packard HP 6890 chromatograph with HP-5 column.

### General procedure for the alkylation reaction

In an ACE-pressure tube under an argon atmosphere the Shvo catalyst (0.01 mmol) and silylacetylene (1 mmol) were dissolved in the corresponding amine (1 mL). The pressure tube was fitted with a Teflon cap and heated at 150 °C for 24 h. The reaction mixture was concentrated in vacuum, and the product was isolated by column chromatography with hexane/ethyl acetate (20:1). The compounds **10**, **13** were isolated by fractional vacuum distillation. GC yields were determined after the calibration, decane was the internal standard.

### *N,N*-Dibutyl-1-(trimethylsilyl)hex-1-yn-3-amine (**1**)

**Isolated yield:** 65%;  $^1\text{H}$  NMR (300.1 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.14 (s, 9 H;  $\text{Si}(\text{CH}_3)_3$ ), 0.89 (m, 9 H;  $3\times\text{CH}_3$ ), 1.20-1.57 (m, 12 H;  $6\times\text{CH}_2$ ), 2.25-2.50 (m, 4 H;  $\text{N}(\text{CH}_2)_2$ ), 3.40 (t,  $^3J(\text{H,H}) = 7.4$

Hz, 1 H; CH) ppm;  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  = 0.3 ( $\text{Si}(\text{CH}_3)_3$ ), 13.8 ( $\text{CH}_3$ ), 14.1 ( $2\times\text{CH}_3$ ), 19.8 ( $\text{CH}_2\text{CH}_3$ ), 20.7 ( $2\times\text{CH}_2\text{CH}_3$ ), 30.7 ( $2\times\text{CH}_2$ ), 36.2 ( $\text{CH}_2\text{CH}$ ), 51.0 ( $\text{N}(\text{CH}_2)_2$ ), 53.8 (CH), 88.0 ( $\text{C}\equiv$ ), 106.0 ( $\text{SiC}\equiv$ ) ppm; MS (EI, 70 eV),  $m/z$  (%): 281 (0.6) [ $\text{M}^+$ ], 280 (0.8) [ $\text{M}^+ - \text{H}$ ], 266 (11), 240 (24), 239 (90), 238 (100) [ $\text{M}^+ - \text{Pr}$ ], 182 (9), 109 (10), 97 (19), 86 (26), 73 (44) [ $\text{Me}_3\text{Si}^+$ ]; HRMS (EI, 70 eV): calcd for  $\text{C}_{17}\text{H}_{34}\text{NSi}$ : 280.2455, found 280.2457 [ $\text{M}^+ - \text{H}$ ].

#### ***N,N*-Diethyl-4-(trimethylsilyl)but-3-yn-2-amine (2)**

**Isolated yield:** 50%;  $^1\text{H}$  NMR (300.1 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.13 (s, 9 H;  $\text{Si}(\text{CH}_3)_3$ ), 1.05 (t,  $^3J$  (H,H) = 7.0 Hz,  $2\times\text{CH}_3$ ), 1.28 (d,  $^3J$  (H,H) = 7.2 Hz,  $\text{CHCH}_3$ ), 2.33-2.69 (m, 4 H;  $\text{N}(\text{CH}_2)_2$ ), 3.65 (q,  $^3J$  (H,H) = 7.2 Hz, 1 H; CH) ppm;  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  = 0.17 ( $\text{Si}(\text{CH}_3)_3$ ), 13.6 ( $2\times\text{CH}_3$ ), 19.9 ( $\text{CH}_3$ ), 44.5 ( $\text{N}(\text{CH}_2)_2$ ), 48.4 (CH), 87.8 ( $\text{C}\equiv$ ), 106.1 ( $\text{SiC}\equiv$ ) ppm; MS (EI, 70 eV),  $m/z$  (%): 197 (2) [ $\text{M}^+$ ], 196 (1) [ $\text{M}^+ - \text{H}$ ], 183 (15), 182 (100) [ $\text{M}^+ - \text{Me}$ ], 97 (13), 83 (8), 73 (4), 72 (5); HRMS (EI, 70 eV): calcd for  $\text{C}_{11}\text{H}_{23}\text{NSi}$ : 197.1594, found 197.1590 [ $\text{M}^+$ ].

#### ***N,N*-Diethyl-4-(triethylsilyl)but-3-yn-2-amine (3)**

**Isolated yield:** 50%;  $^1\text{H}$  NMR (300.1 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.53 (q,  $^3J$  (H,H) = 7.7 Hz, 6 H;  $\text{Si}(\text{CH}_2)_3$ ), 0.92 (t,  $^3J$  (H,H) = 7.7 Hz, 9 H;  $\text{Si}(\text{CH}_2\text{CH}_3)_3$ ), 1.28 (d,  $^3J$  (H,H) = 7.1 Hz,  $\text{CHCH}_3$ ), 2.32-2.64 (m, 4 H;  $\text{N}(\text{CH}_2)_2$ ), 3.63 (q,  $^3J$  (H,H) = 7.1 Hz, 1 H; CH) ppm;  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  = 4.6 ( $\text{Si}(\text{CH}_2)_3$ ), 7.4 ( $\text{Si}(\text{CH}_2\text{CH}_3)_3$ ), 13.6 ( $2\times\text{CH}_3$ ), 20.3 ( $\text{CH}_3$ ), 44.6 ( $\text{N}(\text{CH}_2)_2$ ), 48.5 (CH), 85.1 ( $\text{C}\equiv$ ), 106.2 ( $\text{SiC}\equiv$ ) ppm; MS (EI, 70 eV),  $m/z$  (%): 239 (3) [ $\text{M}^+$ ], 238 (1) [ $\text{M}^+ - \text{H}$ ], 225 (37), 224 (100) [ $\text{M}^+ - \text{Me}$ ], 111 (10), 100 (10), 83 (13), 72 (8); HRMS (EI, 70 eV): calcd for  $\text{C}_{14}\text{H}_{29}\text{NSi}$ : 239.2064, found 239.2061 [ $\text{M}^+$ ].

#### ***N,N*-Dibutyl-1-(triethylsilyl)hex-1-yn-3-amine (4)**

**Isolated yield:** 31%;  $^1\text{H}$  NMR (300.1 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.49 (q,  $^3J$  (H,H) = 8.0 Hz, 6 H;  $\text{Si}(\text{CH}_2)_3$ ), 0.85 (m, 9 H;  $3\times\text{CH}_3$ ), 0.89 (t,  $^3J$  (H,H) = 8.0 Hz, 9 H;  $\text{Si}(\text{CH}_2\text{CH}_3)_3$ ), 1.18-1.50 (m, 12 H;  $6\times\text{CH}_2$ ), 2.25-2.45 (m, 4 H;  $\text{N}(\text{CH}_2)_2$ ), 3.37 (t,  $^3J$  (H,H) = 7.4 Hz, 1 H; CH) ppm;  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  = 3.6 ( $\text{Si}(\text{CH}_2)_3$ ), 6.5 ( $\text{Si}(\text{CH}_2\text{CH}_3)_3$ ), 12.9 ( $\text{CH}_3$ ), 13.1 ( $2\times\text{CH}_3$ ), 18.9 ( $\text{CH}_2\text{CH}_3$ ), 19.7 ( $2\times\text{CH}_2\text{CH}_3$ ), 29.7 ( $2\times\text{CH}_2$ ), 35.4 ( $\text{CH}_2\text{CH}$ ), 50.2 ( $\text{N}(\text{CH}_2)_2$ ), 53.0 (CH), 84.0 ( $\text{C}\equiv$ ), 106.0 ( $\text{SiC}\equiv$ ) ppm; MS (EI, 70 eV),  $m/z$  (%): 323 (0.3) [ $\text{M}^+$ ], 280 (0.7) [ $\text{M}^+ - \text{H}$ ], 294 (8) [ $\text{M}^+ - \text{Et}$ ], 281 (100) [ $\text{M}^+ - \text{Pr} + \text{H}$ ], 280 (83) [ $\text{M}^+ - \text{Pr}$ ], 184

(12), 139 (22), 125 (12), 111 (28), 86 (26); **HRMS** (EI, 70 eV): calcd for  $C_{39}H_{40}NSi$ : 322.2922, found 322.2924 [ $M^+ - H$ ].

***N,N*-Dibutyl-1-(tert-butyldimethylsilyl)hex-1-yn-3-amine (5)**

**Isolated yield:** 22%;  **$^1H$  NMR** (300.1 MHz,  $CDCl_3$ ):  $\delta$  = 0.07 (s, 6 H;  $Si(CH_3)_2$ ), 0.79-0.92 (m, 18 H;  $6 \times CH_3$ ), 1.16-1.48 (m, 12 H;  $6 \times CH_2$ ), 2.20-2.46 (m, 4 H;  $N(CH_2)_2$ ), 3.41 (t,  $^3J$  (H,H) = 7.2 Hz, 1 H; CH) ppm;  **$^{13}C$  NMR** (100.6 MHz,  $CDCl_3$ , TMS):  $\delta$  = - 4.3 ( $Si(CH_3)_2$ ), 13.9 ( $CH_3$ ), 14.1 ( $2 \times CH_3$ ), 16.5 ( $CMe_3$ ), 19.9 ( $CH_2CH_3$ ), 20.7 ( $2 \times CH_2CH_3$ ), 26.13 ( $C(CH_3)$ ), 30.7 ( $2 \times CH_2$ ), 36.4 ( $CH_2CH$ ), 51.3 ( $N(CH_2)_2$ ), 53.9 (CH), 86.0 ( $C \equiv$ ), 106.5 ( $SiC \equiv$ ) ppm; **MS** (EI, 70 eV),  $m/z$  (%): 323 (0.6) [ $M^+$ ], 322 (1) [ $M^+ - H$ ], 282 (34), 281 (100) [ $M^+ - Pr + H$ ], 280 (78) [ $M^+ - Pr$ ], 184 (9), 139 (13), 128 (11), 109 (32), 97 (14), 86 (24), 83 (19), 73 (33); **HRMS** (EI, 70 eV): calcd for  $C_{20}H_{40}NSi$ : 322.2924, found 322.2922 [ $M^+ - H$ ].

***N,N*-Dibutyl-1-(dimethyl(phenyl)silyl)hex-1-yn-3-amine (6)**

**Isolated yield:** 24%;  **$^1H$  NMR** (300.1 MHz,  $CDCl_3$ ):  $\delta$  = 0.31 (s, 6 H;  $Si(CH_3)_2$ ), 0.81-0.87 (m, 9 H;  $3 \times CH_3$ ), 1.18-1.51 (m, 12 H;  $6 \times CH_2$ ), 2.28-2.42 (m, 4 H;  $N(CH_2)_2$ ), 3.34 (t,  $^3J$  (H,H) = 7.2 Hz, 1 H; CH), 7.35-7.58 (m, 5H, Ph) ppm;  **$^{13}C$  NMR** (100.6 MHz,  $CDCl_3$ , TMS):  $\delta$  = - 0.4 ( $Si(CH_3)_2$ ), 13.8 ( $CH_3$ ), 14.1 ( $2 \times CH_3$ ), 19.8 ( $CH_2CH_3$ ), 20.7 ( $2 \times CH_2CH_3$ ), 30.7 ( $2 \times CH_2$ ), 36.2 ( $CH_2CH$ ), 51.2 ( $N(CH_2)_2$ ), 54.0 (CH), 85.9 ( $C \equiv$ ), 108.1 ( $SiC \equiv$ ), Arom.:127.7 ( $2 \times CH$ ), 129.2 (CH), 133.7 ( $2 \times CH$ ), 137.7 (C) ppm; **MS** (EI, 70 eV),  $m/z$  (%): 343 (0.1) [ $M^+$ ], 342 (0.3) [ $M^+ - H$ ], 302 (29), 301 (100) [ $M^+ - Pr + H$ ], 300 (58) [ $M^+ - Pr$ ], 159 (60), 145 (28), 135 (22), 105 (12), 86 (25); **HRMS** (EI, 70 eV): calcd for  $C_{22}H_{36}NSi$ : 342.2611, found 342.2613 [ $M^+ - H$ ].

***N,N*-Dihexyl-1-(trimethylsilyl)oct-1-yn-3-amine (7)**

**Isolated yield:** 70%;  **$^1H$  NMR** (300.1 MHz,  $CDCl_3$ ):  $\delta$  = 0.17 (s, 9 H;  $Si(CH_3)_3$ ), 0.87 (m, 9 H;  $3 \times CH_3$ ), 1.25-1.57 (m, 24 H;  $12 \times CH_2$ ), 2.24-2.49 (m, 4 H;  $N(CH_2)_2$ ), 3.38 (t,  $^3J$  (H,H) = 7.3 Hz, 1 H; CH) ppm;  **$^{13}C$  NMR** (100.6 MHz,  $CDCl_3$ , TMS):  $\delta$  = 0.3 ( $Si(CH_3)_3$ ), 14.0 ( $CH_3$ ), 14.1 ( $2 \times CH_3$ ), 22.6 ( $CH_2CH_3$ ), 22.7 ( $2 \times CH_2CH_3$ ), 26.3 ( $CH_2$ ), 27.2 ( $2 \times CH_2$ ), 28.4 ( $2 \times CH_2$ ), 31.5 ( $CH_2$ ), 31.9 ( $2 \times CH_2$ ), 33.9 ( $CH_2CH$ ), 51.3 ( $N(CH_2)_2$ ), 54.1 (CH), 88.0 ( $C \equiv$ ), 106.1 ( $SiC \equiv$ ) ppm; **MS** (EI, 70 eV),  $m/z$  (%): 365 (0.5) [ $M^+$ ], 364 (1) [ $M^+ - H$ ], 350 (7) [ $M^+ - Me$ ], 296 (23), 295 (88), 294 (100) [ $M^+ - Pentyl$ ], 224 (7), 114 (9), 73 (28) [ $Me_3Si^+$ ]; **HRMS** (EI, 70 eV): calcd for  $C_{23}H_{46}NSi$ : 364.3394, found 364.3390 [ $M^+ - H$ ].

### ***N,N*-Dioctyl-1-(trimethylsilyl)dec-1-yn-3-amine (8)**

**Isolated yield:** 62%; **<sup>1</sup>H NMR** (300.1 MHz, CDCl<sub>3</sub>): δ = 0.14 (s, 9 H; Si(CH<sub>3</sub>)<sub>3</sub>), 0.73 (m, 9 H; 3xCH<sub>3</sub>), 1.12-1.41 (m, 36 H; 18xCH<sub>2</sub>), 2.14-2.28 (m, 4 H; N(CH<sub>2</sub>)<sub>2</sub>), 3.38 (t, <sup>3</sup>J (H,H) = 7.4 Hz, 1 H; CH) ppm; **<sup>13</sup>C NMR** (100.6 MHz, CDCl<sub>3</sub>, TMS): δ = 0.3 (Si(CH<sub>3</sub>)<sub>3</sub>), 13.8 (3xCH<sub>3</sub>), 22.4 (3xCH<sub>2</sub>CH<sub>3</sub>), 26.3 (CH<sub>2</sub>), 27.2 (2xCH<sub>2</sub>), 29.0 (2xCH<sub>2</sub>), 29.1 (2xCH<sub>2</sub>), 29.3 (2xCH<sub>2</sub>), 31.5 (CH<sub>2</sub>), 31.6 (2xCH<sub>2</sub>), 33.6 (CH<sub>2</sub>CH), 51.0 (N(CH<sub>2</sub>)<sub>2</sub>), 53.8 (CH), 87.7 (C≡), 105.8 (SiC≡) ppm; **MS** (EI, 70 eV), *m/z* (%): 449 (0.8) [M<sup>+</sup>], 448 (1.4) [M<sup>+</sup> – H], 434 (5), 352 (28), 351 (100), 350 (95) [M<sup>+</sup> – Heptyl], 73 (27) [Me<sub>3</sub>Si<sup>+</sup>]; **HRMS** (EI, 70 eV): calcd for C<sub>29</sub>H<sub>58</sub>NSi: 448.4333, found 448.4332 [M<sup>+</sup> – H].

### **1-Methyl-2-((trimethylsilyl)ethynyl)pyrrolidine (9)**

**Isolated yield:** 30%; **<sup>1</sup>H NMR** (300.1 MHz, CDCl<sub>3</sub>): δ = 0.14 (s, 9 H; Si(CH<sub>3</sub>)<sub>3</sub>), 1.71 (m, 2 H; 4-CH<sub>2</sub>), 1.87 (m, 2 H; 3-CH<sub>2</sub>), 2.30 (m, 2 H; 5-CH<sub>2</sub>), 2.38 (s, 3 H; NCH<sub>3</sub>), 3.04 (t, <sup>3</sup>J (H,H) = 7.3 Hz, 1 H; CH) ppm; **<sup>13</sup>C NMR** (100.6 MHz, CDCl<sub>3</sub>, TMS): δ = 0.4 (Si(CH<sub>3</sub>)<sub>3</sub>), 22.3 (4-CH<sub>2</sub>), 32.2 (3-CH<sub>2</sub>), 39.7 (NCH<sub>3</sub>), 54.8 (5-CH<sub>2</sub>), 57.1 (CH), 88.1 (C≡), 105.6 (SiC≡) ppm; **MS** (EI, 70 eV), *m/z* (%): 181 (45) [M<sup>+</sup>], 180 (98) [M<sup>+</sup> – H], 166 (56) [M<sup>+</sup> – Me], 153 (31), 152 (14), 138 (74), 108 (100) [M<sup>+</sup> – SiMe<sub>3</sub>], 97 (12), 94 (30), 84 (26), 73 (24) [Me<sub>3</sub>Si<sup>+</sup>]; **HRMS** (EI, 70 eV): calcd for C<sub>10</sub>H<sub>18</sub>NSi: 180.1203, found 180.1204 [M<sup>+</sup> – H].

### **1-Methyl-2-(2-(trimethylsilyl)ethyl)pyrrolidine (10)**

**Isolated yield:** 25%; **<sup>1</sup>H NMR** (300.1 MHz, CDCl<sub>3</sub>): δ = 0.02 (s, 9 H; Si(CH<sub>3</sub>)<sub>3</sub>), 0.23-0.32 (m, 2H; SiCH<sub>2</sub>), 1.28 (m, 2 H; CH<sub>2</sub>), 1.42-1.70 (m, 4 H; 3,4-CH<sub>2</sub>), 2.28-2.37 (m, 2 H; 5-CH<sub>2</sub>), 2.38 (s, 3 H; NCH<sub>3</sub>), 2.53 (m, 1 H; CH) ppm; **<sup>13</sup>C NMR** (100.6 MHz, CDCl<sub>3</sub>, TMS): δ = 0.2 (Si(CH<sub>3</sub>)<sub>3</sub>), 21.6 (SiCH<sub>2</sub>), 24.1 (4-CH<sub>2</sub>), 25.4 (CH<sub>2</sub>), 30.2 (3-CH<sub>2</sub>), 40.5 (NCH<sub>3</sub>), 57.2 (5-CH<sub>2</sub>), 70.2 (CH) ppm; **MS** (EI, 70 eV), *m/z* (%): 185 (1) [M<sup>+</sup>], 184 (1) [M<sup>+</sup> – H], 170 (15) [M<sup>+</sup> – Me], 85 (16), 84 (100) [Het], 73 (12) [Me<sub>3</sub>Si<sup>+</sup>]; **HRMS** (EI, 70 eV): calcd for C<sub>10</sub>H<sub>22</sub>NSi: 184.1516, found 184.1514 [M<sup>+</sup> – H].

### **1-Ethyl-2-((trimethylsilyl)ethynyl)piperidine (11)**

**Isolated yield:** 30%; **<sup>1</sup>H NMR** (300.1 MHz, CDCl<sub>3</sub>): δ = 0.15 (s, 9 H; Si(CH<sub>3</sub>)<sub>3</sub>), 1.05 (t, <sup>3</sup>J (H,H) = 7.2 Hz, 3 H; CH<sub>3</sub>) 1.29-1.62 (m, 6 H; 3xCH<sub>2</sub>), 2.24-2.43 (m, 4 H; N(CH<sub>2</sub>)<sub>2</sub>), 3.60 (t, <sup>3</sup>J (H,H) = 5.2 Hz, 1 H; CH) ppm; **<sup>13</sup>C NMR** (100.6 MHz, CDCl<sub>3</sub>, TMS): δ = 0.22 (Si(CH<sub>3</sub>)<sub>3</sub>), 11.8 (CH<sub>3</sub>), 20.4 (4-CH<sub>2</sub>), 25.4 (5-CH<sub>2</sub>), 31.0 (3-CH<sub>2</sub>), 48.4 (CH<sub>2</sub>CH<sub>3</sub>), 49.5 (6-CH<sub>2</sub>), 51.5 (CH), 90.2 (C≡), 103.3 (SiC≡) ppm; **MS** (EI, 70 eV), *m/z* (%): 209 (17) [M<sup>+</sup>], 208 (17) [M<sup>+</sup> –

H], 195 (18), 194 (100) [ $M^+ - Me$ ], 180 (45), 151 (12), 136 (26), 112 (10), 108 (13), 83 (13), 73 (28) [ $Me_3Si^+$ ]; **HRMS** (EI, 70 eV): calcd for  $C_{12}H_{22}NSi$ : 208.1516, found 208.1511 [ $M^+ - H$ ].

### 1-Methyl-2-((trimethylsilyl)ethynyl)piperidine (12)

**Isolated yield:** 57%;  **$^1H$  NMR** (300.1 MHz,  $CDCl_3$ ):  $\delta$  = 0.14 (s, 9 H;  $Si(CH_3)_3$ ), 1.46-1.77 (m, 6 H;  $3xCH_2$ ), 2.28 (s, 3 H;  $NCH_3$ ), 2.28-2.90 (m, 2 H;  $NCH_2$ ), 3.27 (t,  $^3J$  (H,H) = 5.2 Hz, 1 H;  $CH$ ) ppm;  **$^{13}C$  NMR** (100.6 MHz,  $CDCl_3$ , TMS):  $\delta$  = 2.0 ( $Si(CH_3)_3$ ), 20.7 (4- $CH_2$ ), 25.6 (5- $CH_2$ ), 31.6 (3- $CH_2$ ), 44.2 ( $NCH_3$ ), 54.7 (6- $CH_2$ ), 65.6 ( $CH$ ), 83.2 ( $C\equiv$ ), 97.5 ( $SiC\equiv$ ) ppm; **MS** (EI, 70 eV),  $m/z$  (%): 195 (44) [ $M^+$ ], 194 (66) [ $M^+ - H$ ], 181 (17), 180 (100) [ $M^+ - Me$ ], 167 (22), 166 (88), 153 (23), 152 (29), 138 (53), 124 (28), 122 (90), 109 (22), 108 (18), 98 (21), 97 (20), 94 (30), 83 (24), 73 (30) [ $Me_3Si^+$ ]; **HRMS** (EI, 70 eV): calcd for  $C_{11}H_{20}NSi$ : 194.1359, found 194.1355 [ $M^+ - H$ ].

### 1-Methyl-2-(2-(trimethylsilyl)ethyl)piperidine (13)

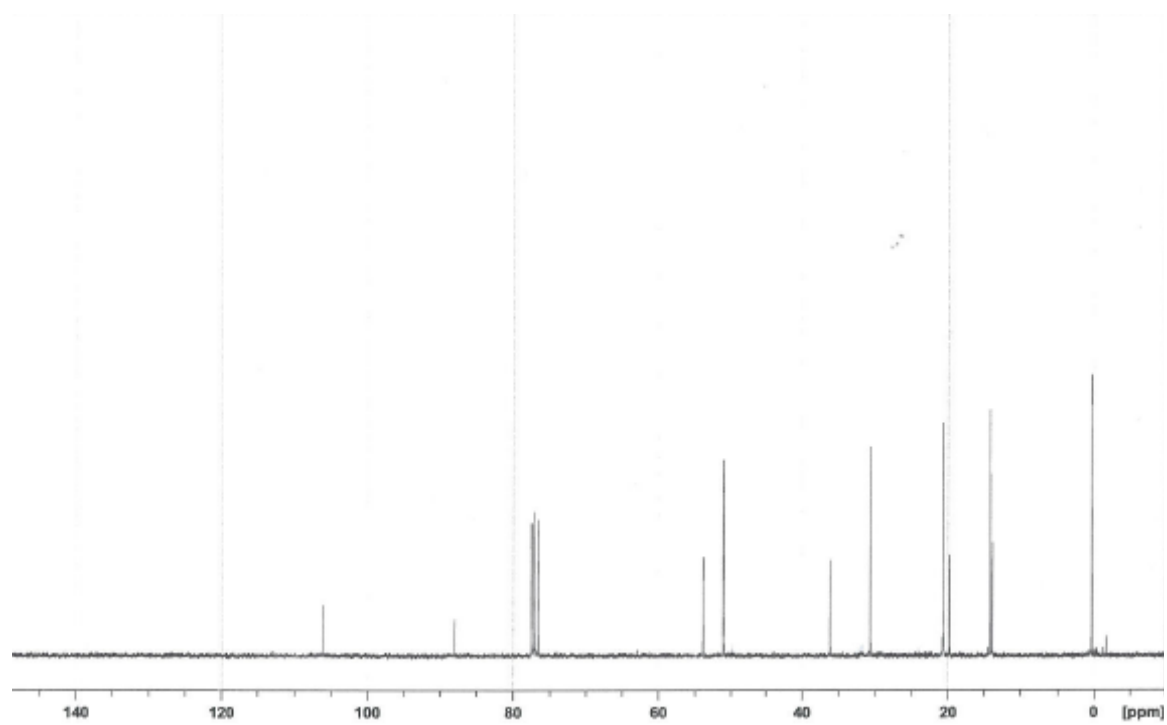
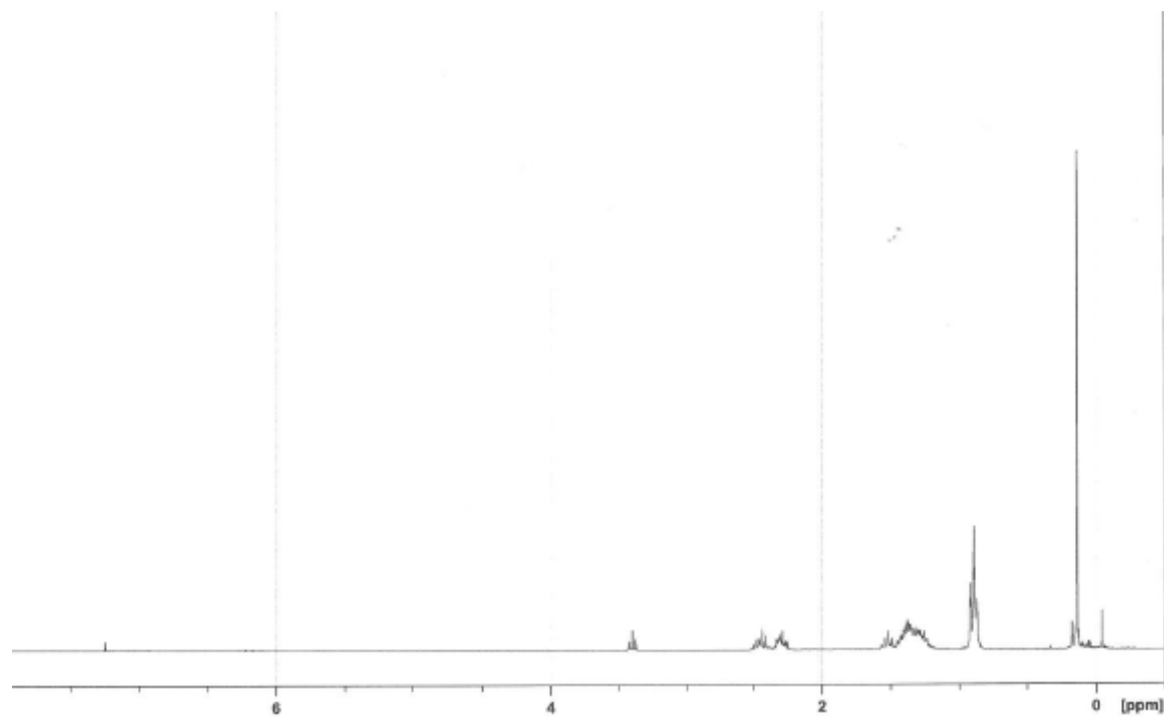
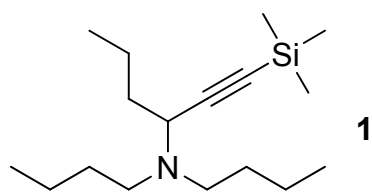
**Isolated yield:** 18%;  **$^1H$  NMR** (300.1 MHz,  $CDCl_3$ ):  $\delta$  = 0.02 (s, 9 H;  $Si(CH_3)_3$ ), 0.33-0.60 (m, 2H;  $SiCH_2$ ), 1.30-1.41 (m, 2 H;  $CH_2$ ), 1.42-1.65 (m, 6 H;  $3xCH_2$ ), 2.25 (s, 3 H;  $NCH_3$ ), 2.45-2.57 (m, 2 H;  $NCH_2$ ), 2.58 (m, 1 H;  $CH$ ) ppm;  **$^{13}C$  NMR** (100.6 MHz,  $CDCl_3$ , TMS):  $\delta$  = 1.1 ( $Si(CH_3)_3$ ), 12.6 ( $SiCH_2$ ), 22.6 (4- $CH_2$ ), 27.8 (5- $CH_2$ ), 28.6 ( $CH_2$ ), 33.5 (3- $CH_2$ ), 44.7 ( $NCH_3$ ), 59.2 (6- $CH_2$ ), 657.5 ( $CH$ ) ppm; **MS** (EI, 70 eV),  $m/z$  (%): 199 (0.2) [ $M^+$ ], 198 (0.5) [ $M^+ - H$ ], 185 (2), 180 (9) [ $M^+ - Me$ ], 99 (10), 98 (100) [ $Het$ ], 73 (8) [ $Me_3Si^+$ ]; **HRMS** (EI, 70 eV): calcd for  $C_{11}H_{24}NSi$ : 198.1672, found 198.1669 [ $M^+ - H$ ].

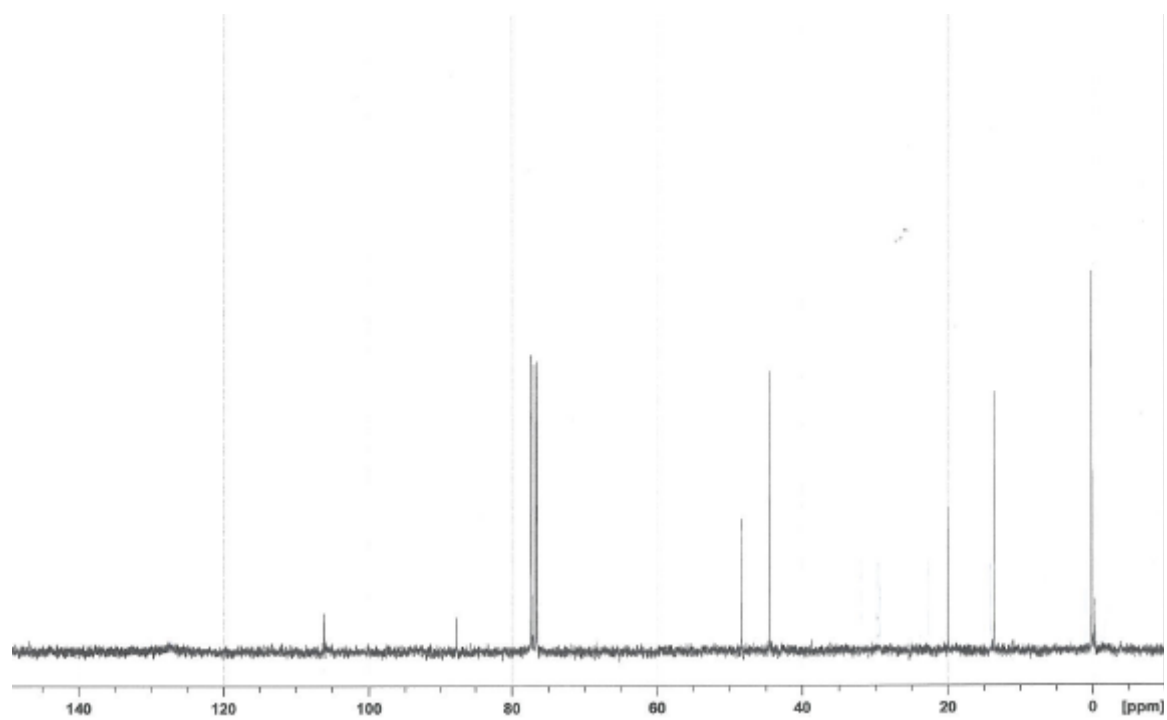
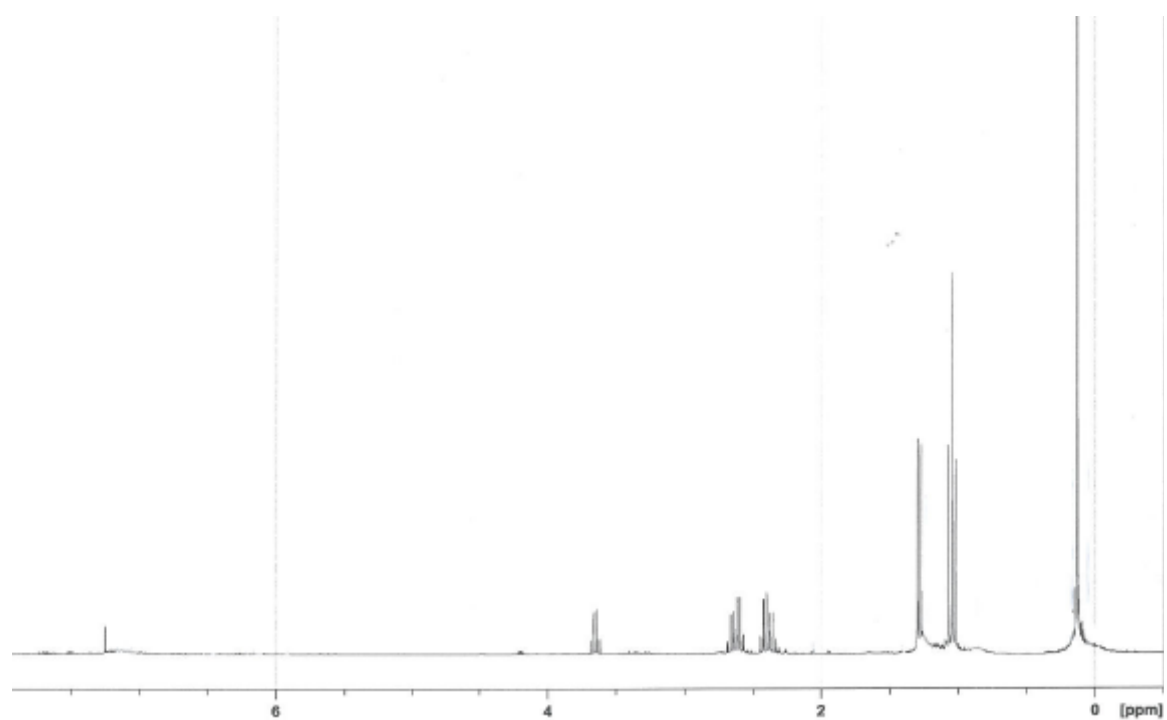
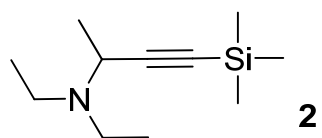
### 1,4-Dimethyl-2-((trimethylsilyl)ethynyl)piperazine (14)

**Isolated yield:** 20%;  **$^1H$  NMR** (300.1 MHz,  $CDCl_3$ ):  $\delta$  = 0.11 (s, 9 H;  $Si(CH_3)_3$ ), 2.23 (s, 3H;  $NCH_3$ ), 2.37 (s, 3H;  $NCH_3$ ), 2.49-2.83 (m, 6 H;  $3xCH_2$ ), 3.34 (m, 1 H;  $CH$ ) ppm;  **$^{13}C$  NMR** (100.6 MHz,  $CDCl_3$ , TMS):  $\delta$  = 2.1 ( $Si(CH_3)_3$ ), 43.5 (1- $NCH_3$ ), 45.7 (4- $NCH_3$ ), 54.8 (6- $CH_2$ ), 55.0 (5- $CH_2$ ), 59.5 (3- $CH_2$ ), 64.1 ( $CH$ ), 89.2 ( $C\equiv$ ), 103.7 ( $SiC\equiv$ ) ppm; **MS** (EI, 70 eV),  $m/z$  (%): 210 (100) [ $M^+$ ], 195 (38) [ $M^+ - Me$ ], 166 (11), 152 (13), 138 (17), 137 (29), 124 (13), 109 (19), 108 (12), 97 (11), 94 (10), 83 (12), 73 (13), [ $Me_3Si^+$ ]; **HRMS** (EI, 70 eV): calcd for  $C_{11}H_{22}N_2Si$ : 210.1547, found 210.1540 [ $M^+$ ].

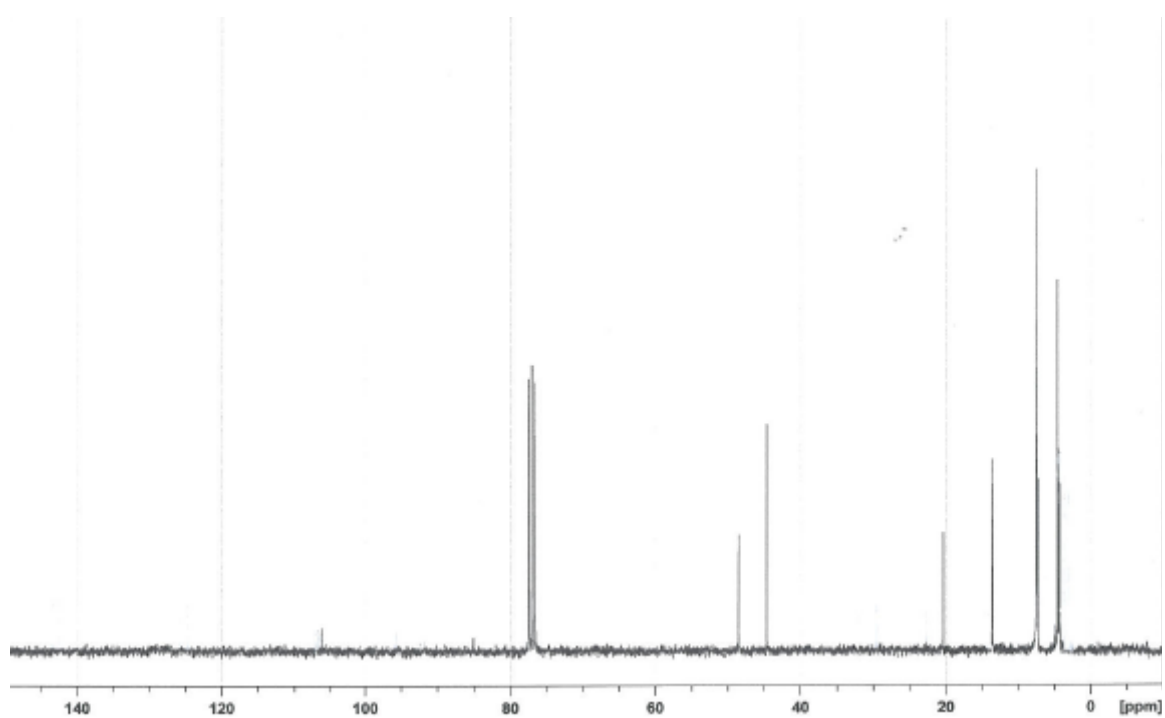
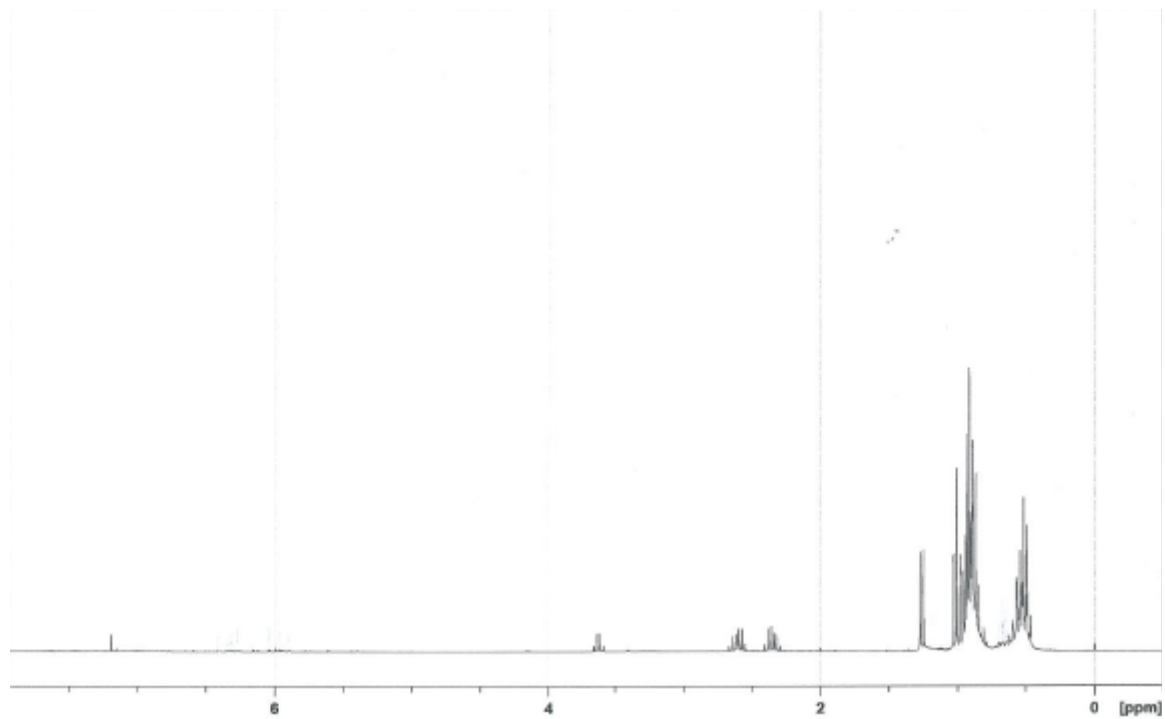
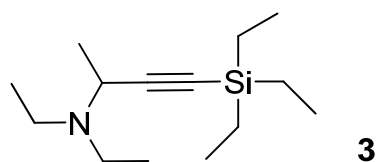
**1,4-Dimethyl-2-(2-(trimethylsilyl)ethyl)piperazine (15)**

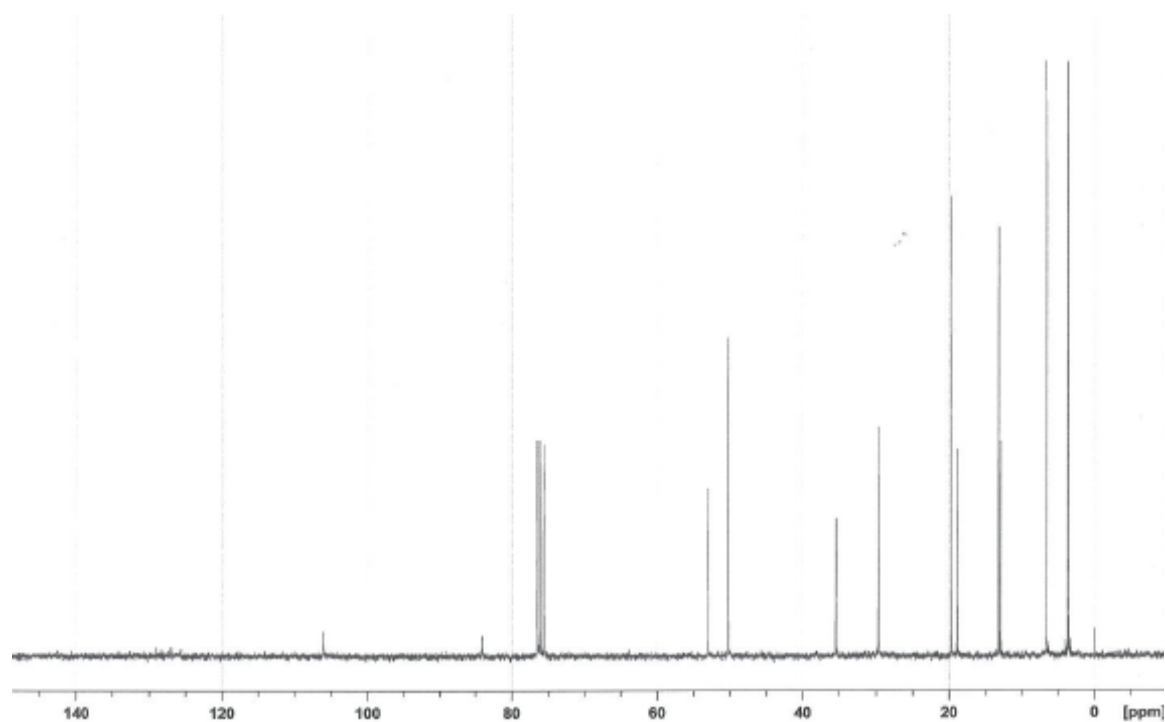
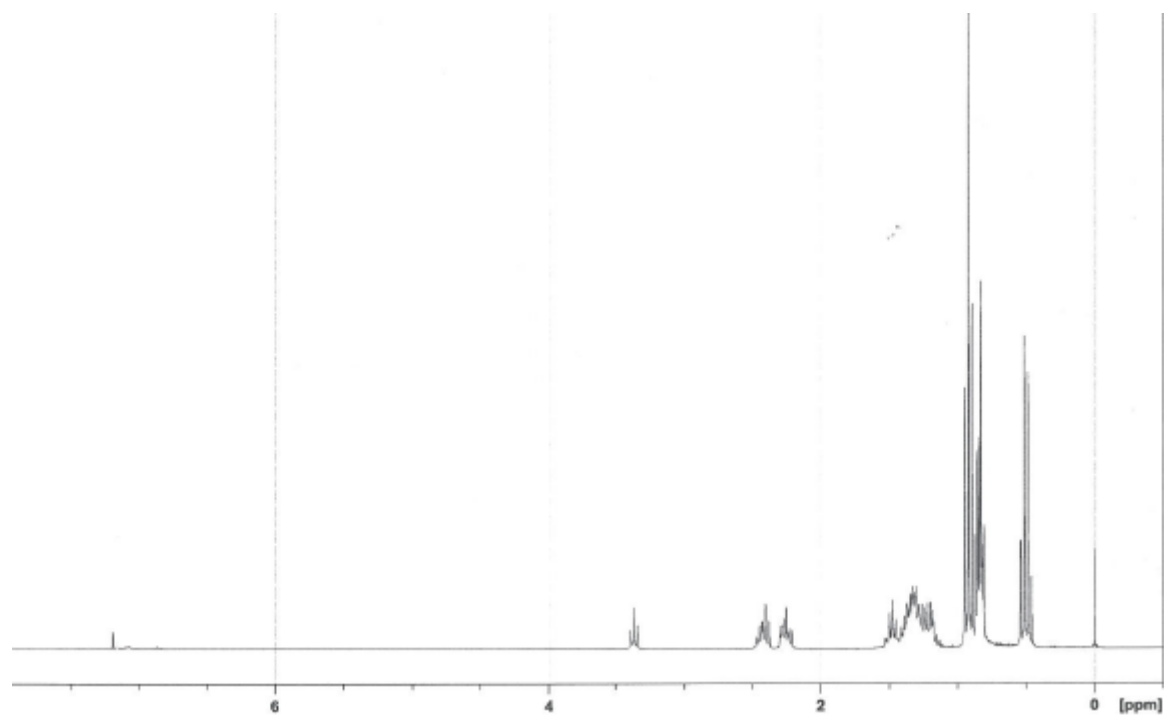
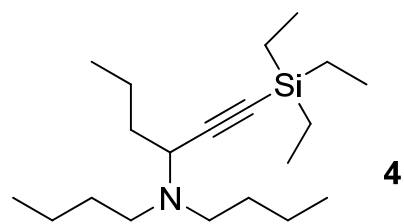
**Isolated yield:** 32%; **<sup>1</sup>H NMR** (300.1 MHz, CDCl<sub>3</sub>): δ = 0.02 (s, 9 H; Si(CH<sub>3</sub>)<sub>3</sub>), 0.36-0.61 (m, 2H; SiCH<sub>2</sub>), 1.31-1.64 (m, 2 H; CH<sub>2</sub>), 2.00-2.21 (m, 2 H; 3-CH<sub>2</sub>), 2.28 (s, 6H; 2xCH<sub>3</sub>), 2.31-2.53 (m, 4 H; 5-CH<sub>2</sub>, 6-CH<sub>2</sub>), 2.72 (m, 1 H; CH) ppm; **<sup>13</sup>C NMR** (100.6 MHz, CDCl<sub>3</sub>, TMS): δ = 1.3 (Si(CH<sub>3</sub>)<sub>3</sub>), 13.3 (SiCH<sub>2</sub>), 26.8 (CH<sub>2</sub>), 44.2 (1-NCH<sub>3</sub>), 48.1 (4-NCH<sub>3</sub>), 57.1 (6-CH<sub>2</sub>), 57.9 (5-CH<sub>2</sub>), 61.5 (3-CH<sub>2</sub>), 66.1 (CH) ppm; **MS** (EI, 70 eV), *m/z* (%): 214 (3) [M<sup>+</sup>], 199 (12) [M<sup>+</sup> – Me], 156 (12), 113 (100) [Het], 98 (10), 73 (13) [Me<sub>3</sub>Si<sup>+</sup>]; **HRMS** (EI, 70 eV): calcd for C<sub>11</sub>H<sub>26</sub>N<sub>2</sub>Si: 213.1781, found 213.1779 [M<sup>+</sup> – H].

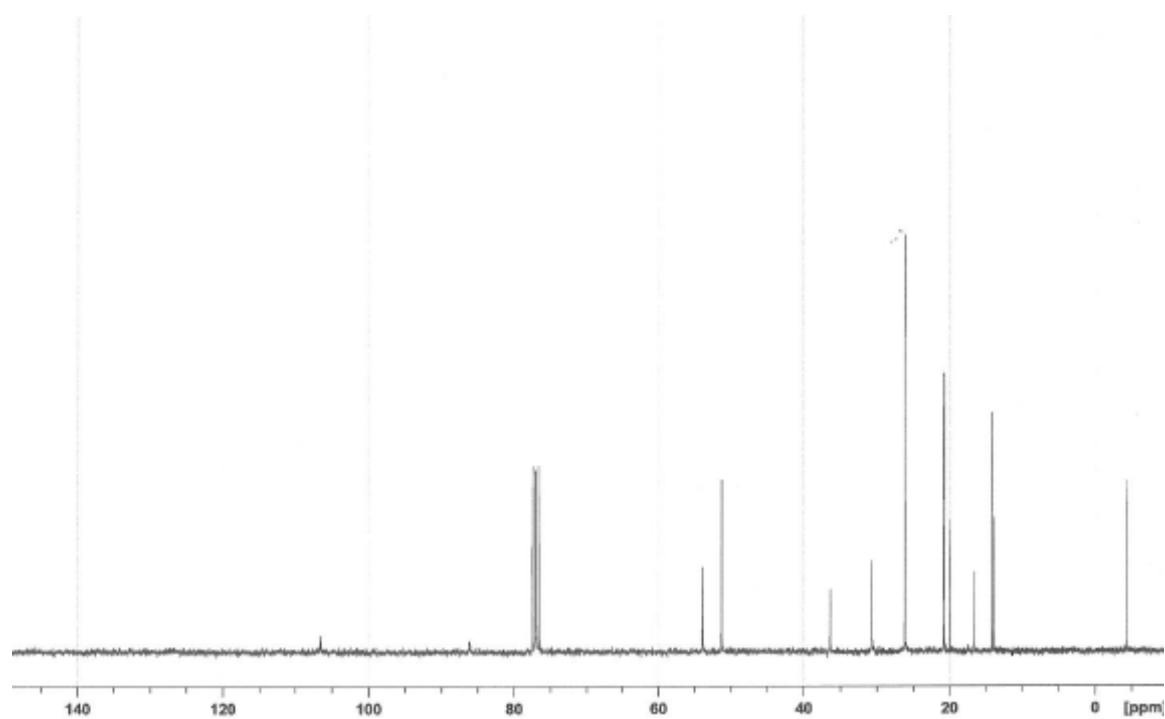
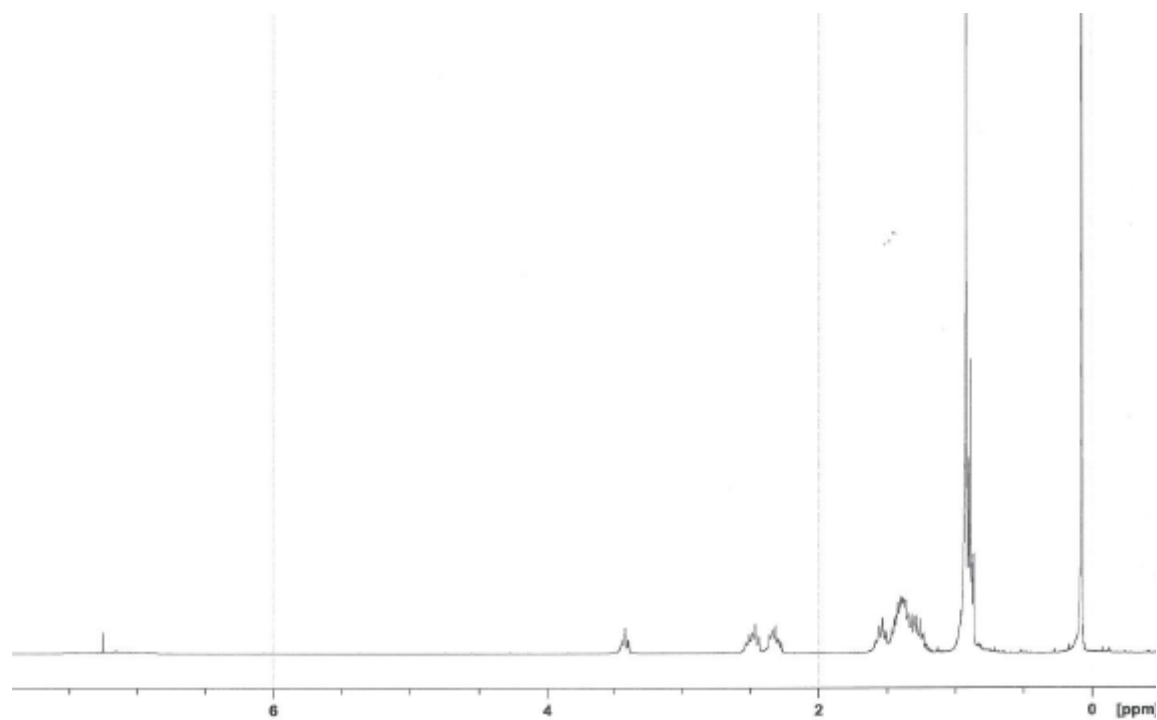
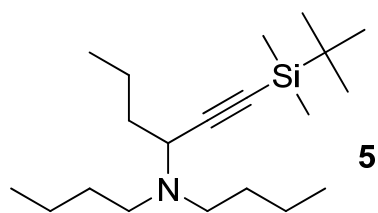


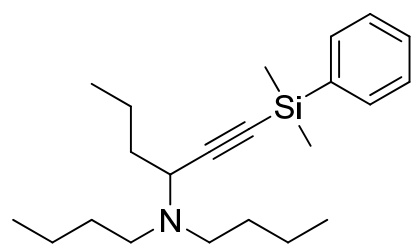




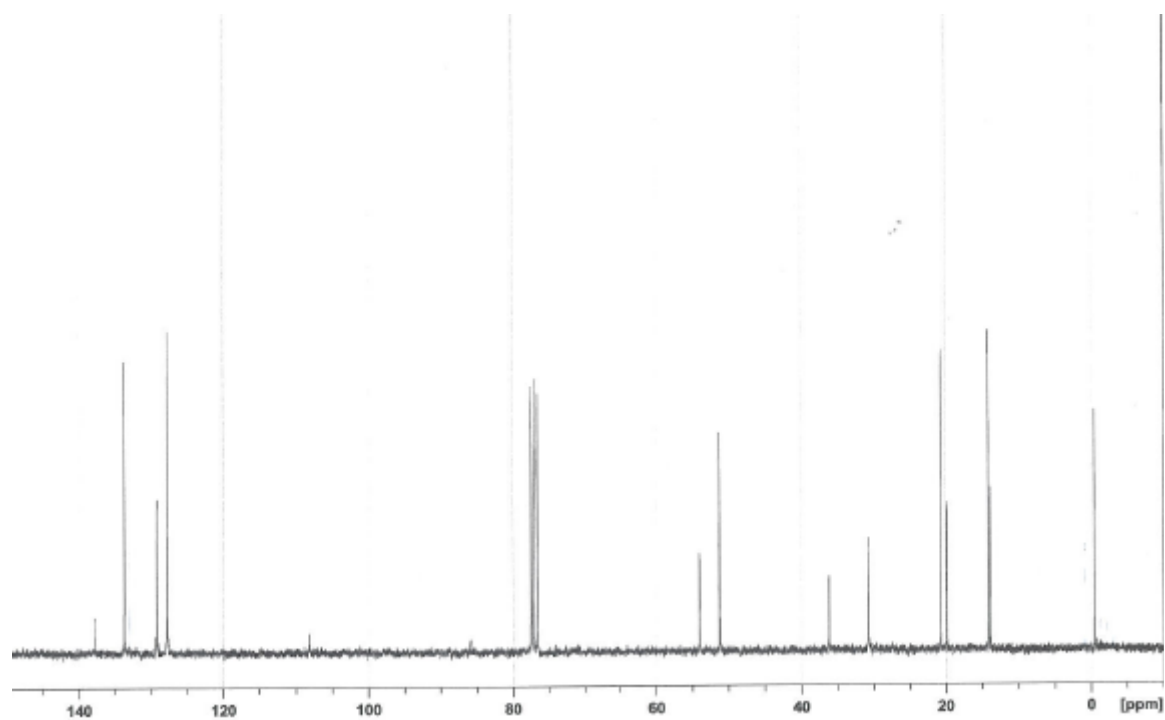
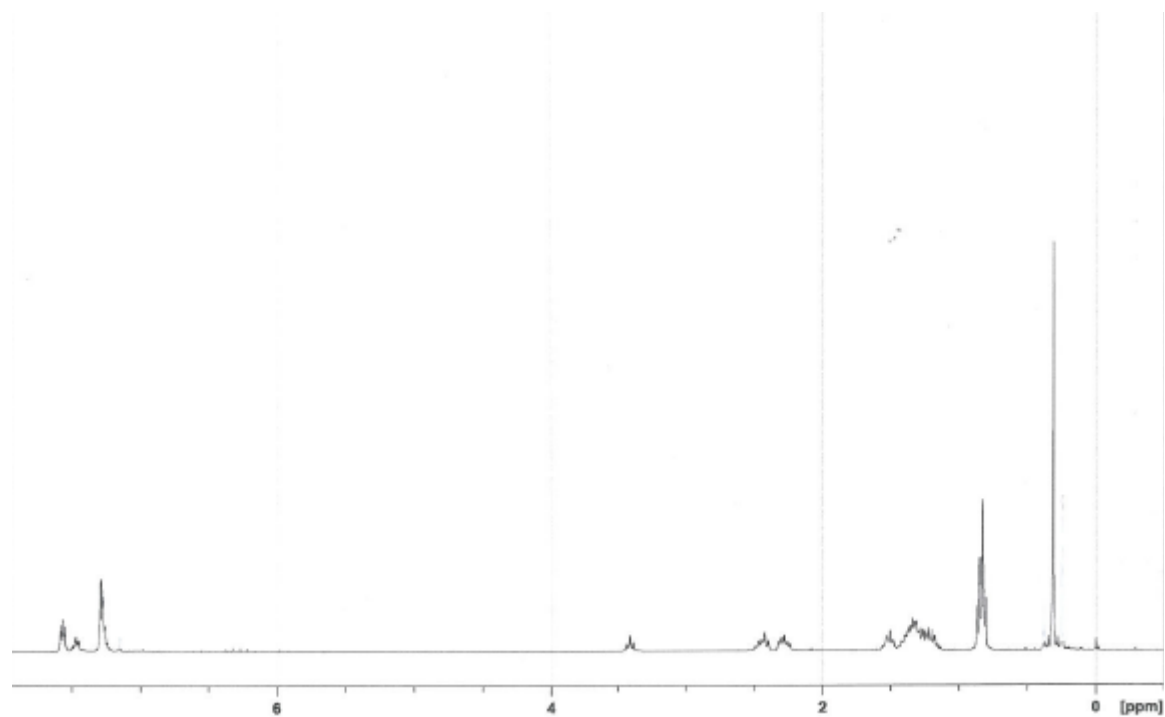




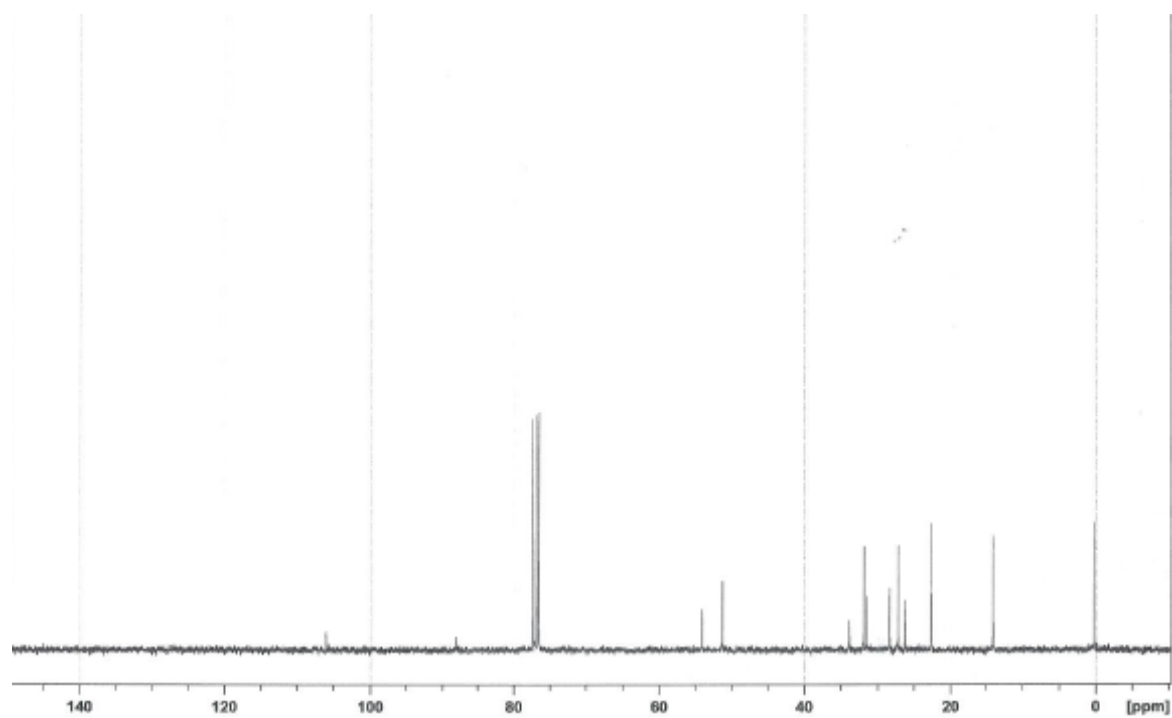
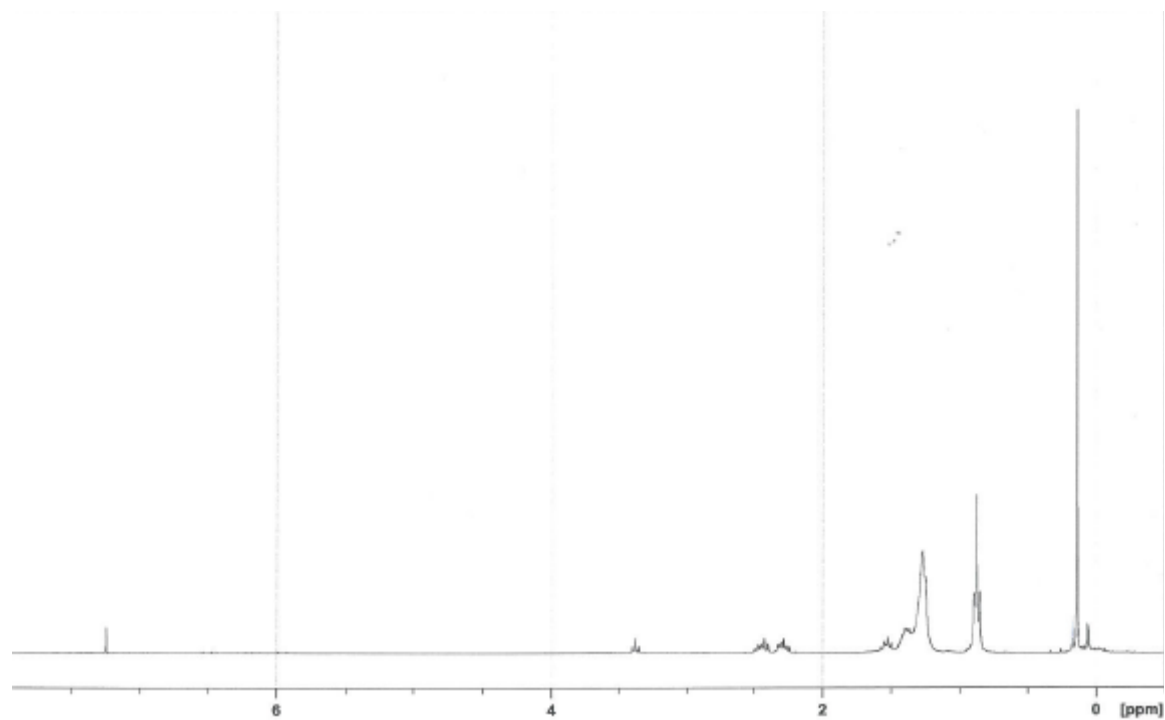
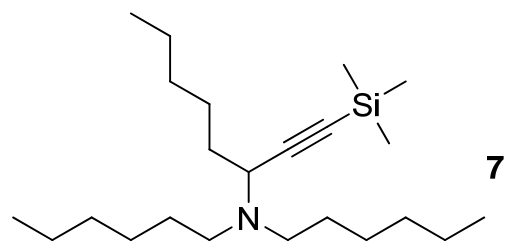


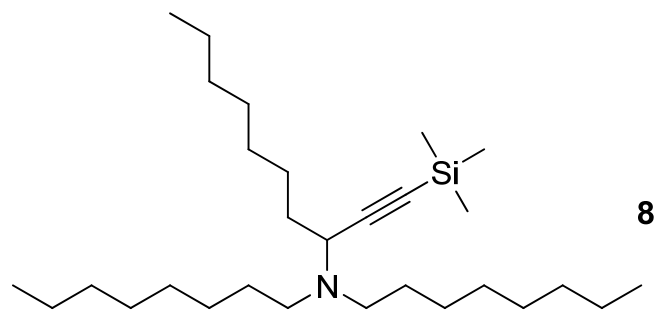


**6**









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