

## Supporting Information

### Simple and high yield access to octafunctional azido, amine and urea group bearing cubic sphaerosilicates

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**Materials.** Tetraethoxysilane was provided by Wacker Silicones. Chlorodimethylsilane, and Karstedt catalyst (in xylene, Pt 2.1-2.4%) were purchased from ABCR. Tetramethylammonium hydroxide pentahydrate, 10-undecen-1-ol, triphenylphosphine, tetrabromomethane, NaN<sub>3</sub>, Pd/C on carbon (10 wt%), propyl isocyanate, 18-crown-6, toluene (abs.), ACN (abs.), DMF (abs.) and ethanol (abs.) were purchased from Sigma–Aldrich. 1,4- dibromobutane, 1,5- dibromopentane, 1,6-dibromohexane and potassium *tert*-butoxide were purchased from Alfa Aesar. Alumina 90 active neutral was purchased from Merck Millipore. All chemicals were used as received. All synthetic procedures were carried out under inert gas atmosphere applying Schlenk techniques.

**Characterization.** Fourier transform infrared (FTIR) spectroscopy measurements were performed applying a Bruker Vertex 70 spectrometer under ambient air (40 scans at a resolution of 4 cm<sup>-1</sup>) in attenuated total reflectance (ATR) mode. Solution NMR spectra were recorded with a Bruker Avance 300 spectrometer at 25 °C (<sup>1</sup>H at 300.13 MHz, <sup>13</sup>C at 75.48 MHz, <sup>29</sup>Si at 59.63 MHz) with 400 MHz using CDCl<sub>3</sub>, or MeOD-*d*4 and the residual protons as reference. Elemental analysis was performed with a Leco 900 CHN analyzer. High-resolution mass spectrometry (HRMS) was performed with a solarix 7 Tesla FTICR mass spectrometer (Bruker Daltonics, Bremen, Germany). All samples were ionized by electrospray ionization (ESI). In MS/MS mode, precursor ions were isolated first in the quadrupole and externally accumulated in the hexapole for 0.1 s. For collision- induced dissociation (CID), a collision voltage of 2–10 V was applied. Thermogravimetric analysis (TGA) was performed on a Netzsch Iris TG 209C in an alumina crucible heating from room temperature to 700 °C under nitrogen followed by heating to 800 °C under a mixture of nitrogen and oxygen (1:1) with a rate of 20 K/min or completely under mixture of nitrogen and oxygen (1:1) with the same rate. Differential scanning calorimetry (DSC) measurements were performed with a Netzsch DSC 204 F1 Phoenix calorimeter and with a TA instruments Q100 with samples in aluminum crucibles with pierced lids and heated under nitrogen at a rate of 10 K/min.

## Synthesis

**$\omega$ -Alkenylbromides** (C4-C6, C11; **1a-d**). 4-Bromo-1-butene, 5-Bromo-1-Pentene, 6-Bromo-1-hexene were synthesized according to literature<sup>[i]</sup>, using an elimination reaction with potassium *tert*-butoxide in diethyl ether. The reaction was catalyzed via 18-crown-6 ether. Synthesis of 11-bromo undecene (**1d**)<sup>[ii]</sup> was described elsewhere.

Octakis(hydridodimethylsiloxy)octasilsesquioxane (**2**) was synthesized according to a literature procedure.<sup>[iii]</sup>

### Octakis(bromoalkyldimethylsiloxy)octasilsesquioxane (3a-d).

Octakis(hydridodimethylsiloxy)octasilsesquioxane (**2**) (3.00 g, 2.95 mmol) and  $\omega$ -bromo alkene (**1a-d**) (23.6 mmol) were dissolved in anhydrous toluene (30 mL). Karstedt-catalyst (2 % in xylene, 350  $\mu$ L) was added and the mixture was heated to 80 °C for 1-2 h. The mixture was filtered through Al<sub>2</sub>O<sub>3</sub> (active neutral) and the solvent was removed under reduced pressure. The product was obtained as colorless oil and used without further purification for the following reactions.

**3a** (C4): Colorless Oil. **Yield:** 6.12 g (100 %, 2.95 mmol). **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>)  $\delta$  3.41 (t, *J* = 6.8 Hz, 16H, CH<sub>2</sub>Br), 1.97 – 1.80 (m, 16H, CH<sub>2</sub>CH<sub>2</sub>Br), 1.56 – 1.45 (m, 16H, CH<sub>2</sub>CH<sub>2</sub>Si), 0.67 – 0.54 (m, 16H, CH<sub>2</sub>Si), 0.16 (s, 48H, Si(CH<sub>3</sub>)<sub>2</sub>). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>)  $\delta$  36.14 (CH<sub>2</sub>Br), 33.44 (CH<sub>2</sub>CH<sub>2</sub>Br), 21.72 (CH<sub>2</sub>Si), 16.81 (CH<sub>2</sub>CH<sub>2</sub>Si), -0.16 (Si(CH<sub>3</sub>)<sub>2</sub>). **<sup>29</sup>Si NMR** (60 MHz, CDCl<sub>3</sub>)  $\delta$  12.68 (OSi(CH<sub>3</sub>)<sub>2</sub>R), -108.96 (SiO<sub>4</sub>). **IR**  $\nu$  = 2960 ( $\nu$  C-H), 2935 ( $\nu$  C-H), 1254 ( $\nu$  Si-C), 1072 ( $\nu$  Si-O), 840 ( $\delta$  C-H), 694 ( $\nu$  C-Br), 548 ( $\delta$  Si-O cage deformation) cm<sup>-1</sup>. **CHN**<sub>theo</sub> (C<sub>48</sub>H<sub>112</sub>Br<sub>8</sub>O<sub>20</sub>Si<sub>16</sub>): C: 27.48; H: 5.38; N – **CHN**<sub>exp</sub>. C: 27.36; H: 5.37; N -.

**3b** (C5): Colorless Oil. **Yield:** 6.52 g (100 %, 2.95 mmol). **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>)  $\delta$  3.40 (t, *J* = 6.9 Hz, 16H, CH<sub>2</sub>Br), 1.86 (m, 16H, CH<sub>2</sub>CH<sub>2</sub>Br), 1.54 – 1.31 (m, 32H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 0.66 – 0.56 (m, 16H, CH<sub>2</sub>Si), 0.13 (s, 48H, Si(CH<sub>3</sub>)<sub>2</sub>). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>)  $\delta$  33.93 (CH<sub>2</sub>Br), 32.72 (CH<sub>2</sub>CH<sub>2</sub>Br), 31.91 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br), 22.36 (CH<sub>2</sub>Si), 17.65 (CH<sub>2</sub>CH<sub>2</sub>Si), -0.14 (Si(CH<sub>3</sub>)<sub>2</sub>). **<sup>29</sup>Si NMR** (60 MHz, CDCl<sub>3</sub>)  $\delta$  12.66 (OSi(CH<sub>3</sub>)<sub>2</sub>R), -108.93 (SiO<sub>4</sub>). **IR**  $\nu$  = 2958 ( $\nu$  C-H), 2926 ( $\nu$  C-H), 1253 ( $\nu$  Si-C), 1070 ( $\nu$  Si-O), 835 ( $\delta$  C-H), 694 ( $\nu$  C-Br), 546 ( $\delta$  Si-O cage deformation) cm<sup>-1</sup>. **CHN**<sub>theo</sub> (C<sub>56</sub>H<sub>128</sub>Br<sub>8</sub>O<sub>20</sub>Si<sub>16</sub>): C: 30.43; H: 5.84; N – **CHN**<sub>exp</sub>. C: 30.43; H: 5.84; N -.

**3c** (C6): Colorless Oil. **Yield:** 6.85 g (100 %, 2.95 mmol). **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>)  $\delta$  3.40 (t, *J* = 6.9 Hz, 2H, CH<sub>2</sub>Br), 1.85 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>Br), 1.52 – 1.27 (m, 48H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 0.65 – 0.54 (m, 16H, CH<sub>2</sub>Si), 0.13 (s, 48H, Si(CH<sub>3</sub>)<sub>2</sub>). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>)  $\delta$  34.08 (CH<sub>2</sub>Br), 32.93 (CH<sub>2</sub>CH<sub>2</sub>Br), 32.58 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br), 28.03 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 22.94 (CH<sub>2</sub>Si), 17.73 (CH<sub>2</sub>CH<sub>2</sub>Si), -0.14 (Si(CH<sub>3</sub>)<sub>2</sub>). **<sup>29</sup>Si NMR** (60 MHz, CDCl<sub>3</sub>)  $\delta$  12.68 (OSi(CH<sub>3</sub>)<sub>2</sub>R), -108.91 (SiO<sub>4</sub>). **IR**  $\nu$  = 2958 ( $\nu$  C-H), 2924 ( $\nu$  C-H), 1252 ( $\nu$  Si-C), 1071 ( $\nu$  Si-O), 839 ( $\delta$  C-H), 694 ( $\nu$  C-Br), 548 ( $\delta$  Si-O cage deformation) cm<sup>-1</sup>. **CHN**<sub>theo</sub> (C<sub>64</sub>H<sub>144</sub>Br<sub>8</sub>O<sub>20</sub>Si<sub>16</sub>): C: 33.10; H: 6.25; N – **CHN**<sub>exp</sub>. C: 33.54; H: 6.34; N -.

**3d** (C11): Colorless Oil. **Yield:** 8.51 g (100 %, 2.95 mmol). **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>)  $\delta$  3.40 (t, *J* = 6.9 Hz, 16H, CH<sub>2</sub>Br), 1.91 – 1.80 (m, 16H, CH<sub>2</sub>CH<sub>2</sub>Br), 1.48 – 1.18 (m, 128H, CH<sub>2</sub> alkyl), 0.88 (t, *J* = 6.7 Hz, 1H, CH<sub>2</sub>Si small amount  $\alpha$  product), 0.67 – 0.51 (m, 15H, CH<sub>2</sub>Si), 0.13 (s, 48H, Si(CH<sub>3</sub>)<sub>2</sub>). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>)  $\delta$  34.13 (CH<sub>2</sub>Br), 33.64 (CH<sub>2</sub>CH<sub>2</sub>Br), 33.03 (C<sub>alkyl</sub>), 29.82 (C<sub>alkyl</sub>), 29.81 (C<sub>alkyl</sub>), 29.66 (C<sub>alkyl</sub>), 29.58 (C<sub>alkyl</sub>), 28.99 (C<sub>alkyl</sub>), 28.37 (C<sub>alkyl</sub>), 23.14 (CH<sub>2</sub>Si), 17.87 (CH<sub>2</sub>CH<sub>2</sub>Si), -0.17 ((CH<sub>3</sub>)<sub>2</sub>Si). **<sup>29</sup>Si NMR** (60 MHz, CDCl<sub>3</sub>)  $\delta$  12.58 (OSi(CH<sub>3</sub>)<sub>2</sub>R), -108.88 (SiO<sub>4</sub>). **IR**  $\nu$  = 2921 ( $\nu$  C-H), 2856 ( $\nu$  C-H), 1252 ( $\nu$  Si-C), 1074 ( $\nu$  Si-O), 838 ( $\delta$  C-H), 548 ( $\delta$  Si-O cage deformation) cm<sup>-1</sup>. **CHN**<sub>theo</sub> (C<sub>104</sub>H<sub>244</sub>Br<sub>8</sub>O<sub>20</sub>Si<sub>16</sub>): C: 43.51; H: 7.89; N – **CHN**<sub>exp</sub>. C: 43.23; H: 7.75; N -.

**Octakis(azidoalkyldimethylsiloxy)octasilsesquioxane (4a-d):** Sodium azide (4.60 g, 70.8 mmol, 4 eq per C-Br group) was suspended in a mixture of anhydrous ACN:DMF (10:1 v/v; 40 mL) and the appropriate octakis(bromoalkyldimethylsiloxy)octasilsesquioxane (2.95 mmol) was added. The reaction mixture was heated to 80 °C for 4-5 h. After cooling to room temperature, the mixture was extracted with *n*-hexane (3 x 20 mL). Afterwards, the hexane layer was extracted with water to remove the residual DMF. The organic layer was dried over MgSO<sub>4</sub> and the solvent was removed in vacuo. The product was obtained as colorless oil.

**4a:** Colorless Oil. **Isolated Yield:** 4.58 g (87 %, 2.57 mmol). **Conversion:** 100 %. **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 3.27 (t, *J* = 6.9 Hz, 16H, CH<sub>2</sub>N<sub>3</sub>), 1.69 – 1.57 (m, 16H, CH<sub>2</sub>CH<sub>2</sub>N<sub>3</sub>), 1.51 – 1.37 (m, 16H, CH<sub>2</sub>CH<sub>2</sub>Si), 0.68 – 0.56 (m, 16H, CH<sub>2</sub>Si), 0.15 (s, 48H, Si(CH<sub>3</sub>)<sub>2</sub>). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 51.19 (CH<sub>2</sub>N<sub>3</sub>), 32.36 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 20.33 (CH<sub>2</sub>Si), 17.30 (CH<sub>2</sub>CH<sub>2</sub>Si), -0.23 ((CH<sub>3</sub>)<sub>2</sub>Si). **<sup>29</sup>Si NMR** (60 MHz, CDCl<sub>3</sub>) δ 12.66 (OSi(CH<sub>3</sub>)<sub>2</sub>R), -108.95 (SiO<sub>4</sub>). **IR** ν = 2956 (ν C-H), 2928 (ν C-H), 2092 (ν N<sub>3</sub>), 1254 (ν Si-C), 1072 (ν Si-O), 827 (δ C-H), 552 (δ Si-O cage deformation) cm<sup>-1</sup>. **CHN**<sub>theo</sub> (C<sub>48</sub>H<sub>112</sub>N<sub>24</sub>O<sub>20</sub>Si<sub>16</sub>): C: 32.12; H: 6.29; N: 18.73 **CHN**<sub>exp</sub>: C: 31.78, H: 6.10; N: 18.22.

**4b:** Colorless Oil. **Isolated Yield:** 5.23 g (93 %, 2.74 mmol). **Conversion:** 100 %. **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 3.25 (t, *J* = 6.9 Hz, 16H, CH<sub>2</sub>N<sub>3</sub>), 1.69 – 1.49 (m, 16H, CH<sub>2</sub>CH<sub>2</sub>N<sub>3</sub>), 1.47 – 1.26 (m, 32H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 0.69 – 0.49 (m, 16H, CH<sub>2</sub>Si), 0.13 (s, 48H, Si(CH<sub>3</sub>)<sub>2</sub>). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 51.57 (CH<sub>2</sub>N<sub>3</sub>), 30.49 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 28.72 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 22.72 (CH<sub>2</sub>Si), 17.70 (CH<sub>2</sub>CH<sub>2</sub>Si), -0.20 ((CH<sub>3</sub>)<sub>2</sub>Si). **<sup>29</sup>Si NMR** (60 MHz, CDCl<sub>3</sub>) δ 12.67 (OSi(CH<sub>3</sub>)<sub>2</sub>R), -108.90 (SiO<sub>4</sub>). **IR** ν = 2956 (ν C-H), 2928 (ν C-H), 2091 (ν N<sub>3</sub>), 1252 (ν Si-C), 1070 (ν Si-O), 837 (δ C-H), 550 (δ Si-O cage deformation) cm<sup>-1</sup>. **CHN**<sub>theo</sub> (C<sub>56</sub>H<sub>128</sub>N<sub>24</sub>O<sub>20</sub>Si<sub>16</sub>): C: 35.27; H: 6.77; N: 17.63 **CHN**<sub>exp</sub>: C: 35.26; H: 6.69; N: 16.89.

**4c:** Colorless Oil. **Isolated Yield:** 5.41 g (91 %, 2.68 mmol). **Conversion:** 100 %. **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 3.25 (t, *J* = 6.9 Hz, 16H, CH<sub>2</sub>N<sub>3</sub>), 1.66 – 1.52 (m, 16H, CH<sub>2</sub>CH<sub>2</sub>N<sub>3</sub>), 1.44 – 1.28 (m, 48H), 0.68 – 0.53 (m, 16H, CH<sub>2</sub>Si), 0.13 (s, 48H, Si(CH<sub>3</sub>)<sub>2</sub>). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 51.63 (CH<sub>2</sub>N<sub>3</sub>), 32.98 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 28.96 (CH<sub>2</sub>CH<sub>2</sub>N<sub>3</sub>), 26.57 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N<sub>3</sub>), 22.97 (CH<sub>2</sub>Si), 17.72 (CH<sub>2</sub>CH<sub>2</sub>Si), -0.19 ((CH<sub>3</sub>)<sub>2</sub>Si). **<sup>29</sup>Si NMR** (60 MHz, CDCl<sub>3</sub>) δ 12.67 (OSi(CH<sub>3</sub>)<sub>2</sub>R), -108.90 (SiO<sub>4</sub>). **IR** ν = 2958 (ν C-H), 2926 (ν C-H), 2092 (ν N<sub>3</sub>), 1252 (ν Si-C), 1062 (ν Si-O), 839 (δ C-H), 548 (δ Si-O cage deformation) cm<sup>-1</sup>. **CHN**<sub>theo</sub> (C<sub>64</sub>H<sub>144</sub>N<sub>24</sub>O<sub>20</sub>Si<sub>16</sub>): C: 38.07; H: 7.19; N: 16.65 **CHN**<sub>exp</sub>: C: 37.95; H: 7.13; N: 16.25.

**4d:** Colorless Oil. **Isolated Yield:** 6.79 g (89 %, 2.63 mmol). **Conversion:** 100 %. **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 3.26 (t, *J* = 6.9 Hz, 16H, CH<sub>2</sub>N<sub>3</sub>), 1.66 – 1.54 (m, 16H, CH<sub>2</sub>CH<sub>2</sub>N<sub>3</sub>), 1.46 – 1.22 (m, 128H, CH<sub>2</sub> alkyl), 0.91 – 0.85 (m, 1H, CH<sub>2</sub>Si small amount α product), 0.66 – 0.52 (m, 15H, CH<sub>2</sub>Si), 0.09 (s, 48H, Si(CH<sub>3</sub>)<sub>2</sub>). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 51.64 (CH<sub>2</sub>N<sub>3</sub>), 33.64 (CH<sub>2</sub>CH<sub>2</sub>N<sub>3</sub>), 29.80, 29.70, 29.58, 29.37, 29.01, 26.91, 23.14 (CH<sub>2</sub>Si), 17.86 (CH<sub>2</sub>CH<sub>2</sub>Si), -0.18 ((CH<sub>3</sub>)<sub>2</sub>Si). **<sup>29</sup>Si NMR** (60 MHz, CDCl<sub>3</sub>) δ 12.58 (OSi(CH<sub>3</sub>)<sub>2</sub>R), -108.88 (SiO<sub>4</sub>). **IR** ν = 2921 (ν C-H), 2856 (ν C-H), 2091 (ν N<sub>3</sub>), 1252 (ν Si-C), 1074 (ν Si-O), 838 (δ C-H), 548 (δ Si-O cage deformation) cm<sup>-1</sup>. **CHN**<sub>theo</sub> (C<sub>104</sub>H<sub>244</sub>N<sub>8</sub>O<sub>20</sub>Si<sub>16</sub>): C 48.41; H: 8.75; N 13.03 **CHN**<sub>exp</sub>: C: 48.54; H: 8.10; N 12.15.

#### **Octakis(aminoalkyldimethylsiloxy)octasilsesquioxane (5a-d).**

Octakis(azidoalkyldimethylsiloxy)octasilsesquioxane (Yield from **4a-d**) and palladium catalyst on activated carbon (10 wt%, ca. 200 mg) was suspended in anhydrous ethanol (200 mL). Hydrogen was bubbled slowly through the suspension for 1-2 h at 20-25 °C. The quantitative conversion was determined by <sup>1</sup>H NMR spectroscopy. Therefore, the catalyst was removed by filtering through a glas

filter under inert atmosphere and the solvent was evaporated at room temperature in vacuo.  $^{29}\text{Si}$  was not possible to acquire due to long measurement time in which the cube structure decomposes.

**5a:** Not isolated. **Conversion:** 100 %, 2.57 mmol.  $^1\text{H NMR}$  (300 MHz, MeOD)  $\delta$  2.64 (t, 16H,  $\text{CH}_2\text{NH}_2$ ), 1.55 – 1.37 (m, 32H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$ ), 0.68 – 0.59 (m, 16H,  $\text{CH}_2\text{Si}$ ), 0.11 (s, 42H (should be 48,  $(\text{CH}_3)_2\text{Si}$ )).  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  42.20 ( $\text{CH}_2\text{NH}_2$ ), 37.37 ( $\text{CH}_2\text{CH}_2\text{NH}_2$ ), 21.58 ( $\text{CH}_2\text{Si}$ ), 16.59 ( $\text{CH}_2\text{CH}_2\text{Si}$ ), -2.69 ( $(\text{CH}_3)_2\text{Si}$ ). **IR**  $\nu$  = 3300 ( $\nu$  N-H), 2958 ( $\nu$  C-H), 2924 ( $\nu$  C-H), 1579 ( $\delta$  N-H), 1251 ( $\nu$  Si-C), 1045 ( $\nu$  Si-O), 836 ( $\delta$  C-H), 545 ( $\delta$  Si-O cage deformation)  $\text{cm}^{-1}$ . **ESI-MS:** +MS:  $[\text{M}+\text{H}^+]$ : 1586.59,  $[\text{M}+2\text{H}^+]$ : 793.33 m/z.

**5b:** Not isolated. **Conversion:** 100 %, 2.74 mmol.  $^1\text{H NMR}$  (300 MHz, MeOD)  $\delta$  2.63 (t,  $J$  = 6.9 Hz, 16H,  $\text{CH}_2\text{NH}_2$ ), 1.55 – 1.37 (m, 48H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$ ), 0.72 – 0.61 (m, 16H,  $\text{CH}_2\text{Si}$ ), 0.17 (s, 48H,  $(\text{CH}_3)_2\text{Si}$ ).  $^{13}\text{C NMR}$  (75 MHz, MeOD)  $\delta$  42.50 ( $\text{CH}_2\text{NH}_2$ ), 33.53 ( $\text{CH}_2\text{CH}_2\text{NH}_2$ ), 31.74 ( $\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ ), 24.10 ( $\text{CH}_2\text{Si}$ ), 16.70 ( $\text{CH}_2\text{CH}_2\text{Si}$ ), -2.69 ( $(\text{CH}_3)_2\text{Si}$ ). **IR**  $\nu$  = 3300 ( $\nu$  N-H), 2958 ( $\nu$  C-H), 2924 ( $\nu$  C-H), 1579 ( $\delta$  N-H), 1251 ( $\nu$  Si-C), 1045 ( $\nu$  Si-O), 836 ( $\delta$  C-H), 545 ( $\delta$  Si-O cage deformation)  $\text{cm}^{-1}$ . **ESI-MS:** +MS:  $[\text{M}+\text{H}^+]$ : 1699.70  $[\text{M}+2\text{H}^+]$ : 849.89 m/z.

**5c:** Not isolated. **Conversion:** 100 %, 2.68 mmol.  $^1\text{H NMR}$  (300 MHz, MeOD)  $\delta$  2.70 – 2.57 (m, 16H,  $\text{CH}_2\text{NH}_2$ ), 1.45 (dd,  $J$  = 21.1, 14.2 Hz, 64H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$ ), 0.66 (s, 16H,  $\text{CH}_2\text{Si}$ ), 0.16 (d,  $J$  = 3.3 Hz, 48H,  $(\text{CH}_3)_2\text{Si}$ ).  $^{13}\text{C NMR}$  (75 MHz, MeOD)  $\delta$  42.60 ( $\text{CH}_2\text{NH}_2$ ), 34.35 ( $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ ), 33.78 ( $\text{CH}_2\text{CH}_2\text{NH}_2$ ), 27.72 ( $\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ ), 24.16 ( $\text{CH}_2\text{Si}$ ), 16.68 ( $\text{CH}_2\text{CH}_2\text{Si}$ ), -2.69 ( $(\text{CH}_3)_2\text{Si}$ ). **IR**  $\nu$  = 3300 ( $\nu$  N-H), 2958 ( $\nu$  C-H), 2924 ( $\nu$  C-H), 1579 ( $\delta$  N-H), 1251 ( $\nu$  Si-C), 1045 ( $\nu$  Si-O), 836 ( $\delta$  C-H), 545 ( $\delta$  Si-O cage deformation)  $\text{cm}^{-1}$ . **ESI-MS:** +MS:  $[\text{M}+\text{H}^+]$ : 1811.90,  $[\text{M}+2\text{H}^+]$ : 906.42 m/z.

**5d:** Slightly yellow solid. **Conversion:** 100 %, 2.63 mmol. **Isolated Yield:** 4.49 g (1.89 mmol, 72 %).  $^1\text{H NMR}$  (300 MHz, MeOD)  $\delta$  2.92 (d,  $J$  = 7.1 Hz, 16H,  $\text{CH}_2\text{NH}_2$ ), 1.74 – 1.58 (m, 16H,  $\text{CH}_2\text{CH}_2\text{NH}_2$ ), 1.48 – 1.24 (m, 128H, ,  $\text{CH}_2$  alkyl), 0.69 – 0.62 (m, 16H,  $\text{CH}_2\text{Si}$ ), 0.16 (s, 48H,  $(\text{Si}(\text{CH}_3)_2)$ ).  $^{13}\text{C NMR}$  (75 MHz, MeOD)  $\delta$  40.82 ( $\text{CH}_2\text{NH}_2$ ), 34.70 ( $\text{CH}_2\text{CH}_2\text{N}$ ), 30.92 ( $\text{C}_{\text{alkyl}}$ ), 30.89 ( $\text{C}_{\text{alkyl}}$ ), 30.72 ( $\text{C}_{\text{alkyl}}$ ), 30.68 ( $\text{C}_{\text{alkyl}}$ ), 30.41 ( $\text{C}_{\text{alkyl}}$ ), 28.66 ( $\text{C}_{\text{alkyl}}$ ), 27.62 ( $\text{C}_{\text{alkyl}}$ ), 24.26 ( $\text{CH}_2\text{Si}$ ), 18.75 ( $\text{CH}_2\text{CH}_2\text{Si}$ ), 0.09 ( $(\text{Si}(\text{CH}_3)_2)$ ).  $^{29}\text{Si NMR}$  (60 MHz, MeOD)  $\delta$  13.00 ( $\text{OSi}(\text{CH}_3)_2\text{R}$ ), -108.63 ( $\text{SiO}_4$ ). **CHN**<sub>theo</sub> ( $\text{C}_{104}\text{H}_{240}\text{N}_8\text{O}_{20}\text{Si}_{16}$ ): C, 52.65; H, 10.20; N, 4.72 **CHN**<sub>exp</sub>. C, 47.44; H, 9.25; N, 4.78. **IR**  $\nu$  = 3300 ( $\nu$  N-H), 2921 ( $\nu$  C-H), 2856 ( $\nu$  C-H), 1579 ( $\delta$  N-H), 1252 ( $\delta$  C-H), 1074 ( $\nu$  Si-O), 838 ( $\delta$  C-H), 548 ( $\delta$  Si-O cage deformation)  $\text{cm}^{-1}$ . **TG residual mass:**  $\text{N}_2$ : 29.93 %,  $\text{O}_2$ : 33.22 % (theoretical residual mass: 32.43%). **ESI-MS:**  $[\text{M}+2\text{H}^+]$ : 1186.73,  $[\text{M}+3\text{H}^+]$ : 791.49 m/z.

### Octakis(X-(3-propylurea)alkyl-1-dimethylsiloxy)octasilsesquioxane (X = 4, 5, 6, 11).

The amine cube solutions in ethanol were filtered off from reaction solution under inert atmosphere. Propyl isocyanate (1 eq) was added at room temperature to the reaction mixture. Afterwards, the solvent was removed in vacuo and in case of residual free propyl isocyanate, the product was extracted with chloroform.

**6a:** Colorless Solid. **Yield:** 5.53 g (95 %, 2.44 mmol).  $^1\text{H NMR}$  (300 MHz, MeOD)  $\delta$  3.20 – 3.01 (m, 32H,  $\text{CH}_2\text{NHCONHCH}_2$ ), 1.49 (td,  $J$  = 14.6, 7.3 Hz, 48H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{NHCONHCH}_2\text{CH}_2$ ), 0.91 (t,  $J$  = 7.4 Hz, 24H,  $\text{CH}_3$ ), 0.75 – 0.61 (m, 16H,  $\text{CH}_2\text{Si}$ ), 0.18 (s, 48H,  $(\text{Si}(\text{CH}_3)_2)$ ).  $^{13}\text{C NMR}$  (75 MHz, MeOD)  $\delta$  161.33 (CO), 42.83 (CONHCH<sub>2</sub>), 40.74 (CONHCH<sub>2</sub>—Si), 35.01 ( $\text{C}_{\text{alkyl}}$ ), 24.57 ( $\text{CH}_2\text{Si}$ ), 21.46 ( $\text{C}_{\text{alkyl}}$ ), 18.39 ( $\text{CH}_2\text{CH}_2\text{Si}$ ), 11.69 ( $\text{CH}_3$ ), 0.01 ( $(\text{Si}(\text{CH}_3)_2)$ ).  $^{29}\text{Si NMR}$  (60 MHz, MeOD)  $\delta$  13.31 ( $\text{OSi}(\text{CH}_3)_2\text{R}$ ), -108.57 ( $\text{SiO}_4$ ). **IR**  $\nu$  = 3332 ( $\nu$  N-H), 2960 ( $\nu$  C-H), 2928 ( $\nu$  C-H), 1632 (amide I  $\nu$  C=O), 1568 (amide II,  $\delta$  N-H, C=O,  $\nu$  C-N), 1252 ( $\delta$  C-H), 1070 ( $\nu$  Si-O), 842 ( $\delta$  C-H), 554 ( $\delta$  Si-O cage deformation)  $\text{cm}^{-1}$ . **ESI-MS:**  $[\text{M}+\text{H}^++\text{Na}^+]$ : 1156.50 m/z.

**6b:** Colorless Solid. **Yield:** 6.19 g (95 %, 2.60 mmol). **<sup>1</sup>H NMR** (300 MHz, MeOD)  $\delta$  3.09 (dt,  $J = 13.9, 6.9$  Hz, 32H,  $\text{CH}_2\text{NHCONHCH}_2$ ), 1.57 – 1.33 (m, 64H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NHCONHCH}_2\text{CH}_2\text{CH}_3$ ), 0.91 (t,  $J = 7.4$  Hz, 24H,  $\text{CH}_3$ ), 0.73 – 0.59 (m, 16H,  $\text{CH}_2\text{Si}$ ), 0.17 (s, 48H,  $\text{Si}(\text{CH}_3)_2$ ). **<sup>13</sup>C NMR** (75 MHz, MeOD)  $\delta$  161.33 (CO), 42.84 ( $\text{CONHCH}_2$ ), 41.07 ( $\text{CONHCH}_2\text{—Si}$ ), 31.81 ( $\text{C}_{\text{alkyl}}$ ), 31.21 ( $\text{C}_{\text{alkyl}}$ ), 24.56 ( $\text{C}_{\text{alkyl}}$ ), 23.99 ( $\text{C}_{\text{alkyl}}$ ), 23.56 ( $\text{CH}_2\text{Si}$ ), 18.70 ( $\text{CH}_2\text{CH}_2\text{Si}$ ), 11.68 ( $\text{CH}_3$ ), 0.04 ( $\text{Si}(\text{CH}_3)_2$ ). **<sup>29</sup>Si NMR** (60 MHz, MeOD)  $\delta$  13.24 ( $\text{OSi}(\text{CH}_3)_2\text{R}$ ), -108.55 ( $\text{SiO}_4$ ). **IR**  $\nu = 3333$  ( $\nu$  N-H), 2960 ( $\nu$  C-H), 2926 ( $\nu$  C-H), 1628 (amide I  $\nu$  C=O), 1570 (amide II,  $\delta$  N-H, C=O,  $\nu$  C-N), 1252 ( $\nu$  Si-C), 1070 ( $\nu$  Si-O), 839 ( $\delta$  C-H), 548 ( $\delta$  Si-O cage deformation)  $\text{cm}^{-1}$ . **ESI-MS:**  $[\text{M}+\text{H}^++\text{Na}^+]$ : 1212.56  $m/z$ .

**6c:** Colorless Solid. **Yield:** 6.41 g (96 %, 2.57 mmol). **<sup>1</sup>H NMR** (300 MHz, MeOD)  $\delta$  3.16 – 2.99 (m, 32H,  $\text{CH}_2\text{NHCONHCH}_2$ ), 1.57 – 1.27 (m, 80H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NHCONHCH}_2\text{CH}_2$ ), 0.91 (t,  $J = 7.4$  Hz, 24H,  $\text{CH}_3$ ), 0.72 – 0.55 (m,  $J = 14.7$  Hz, 16H,  $\text{CH}_2\text{Si}$ ), 0.16 (s, 48H,  $\text{Si}(\text{CH}_3)_2$ ). **<sup>13</sup>C NMR** (75 MHz, MeOD)  $\delta$  161.34 (CO), 42.84 ( $\text{CONHCH}_2$ ), 41.15 ( $\text{CONHCH}_2\text{—Si}$ ), 34.51 ( $\text{C}_{\text{alkyl}}$ ), 31.51 ( $\text{C}_{\text{alkyl}}$ ), 27.78 ( $\text{C}_{\text{alkyl}}$ ), 24.56 ( $\text{C}_{\text{alkyl}}$ ), 24.16 ( $\text{CH}_2\text{Si}$ ), 18.84 ( $\text{CH}_2\text{CH}_2\text{Si}$ ), 11.68 ( $\text{CH}_3$ ), 0.07 ( $\text{Si}(\text{CH}_3)_2$ ). **<sup>29</sup>Si NMR** (60 MHz, MeOD)  $\delta$  13.23 ( $\text{OSi}(\text{CH}_3)_2\text{R}$ ), -108.56 ( $\text{SiO}_4$ ). **IR**  $\nu = 3329$  ( $\nu$  N-H), 2960 ( $\nu$  C-H), 2924 ( $\nu$  C-H), 2858 ( $\nu$  C-H), 1628 (amide I  $\nu$  C=O), 1572 (amide II,  $\delta$  N-H, C=O,  $\nu$  C-N), 1252 ( $\delta$  Si-C), 1062 ( $\nu$  Si-O), 839 ( $\delta$  C-H), 548 ( $\delta$  Si-O cage deformation)  $\text{cm}^{-1}$ . **ESI-MS:**  $[\text{M}+2\text{Na}^+]$ : 1268.63  $m/z$ .

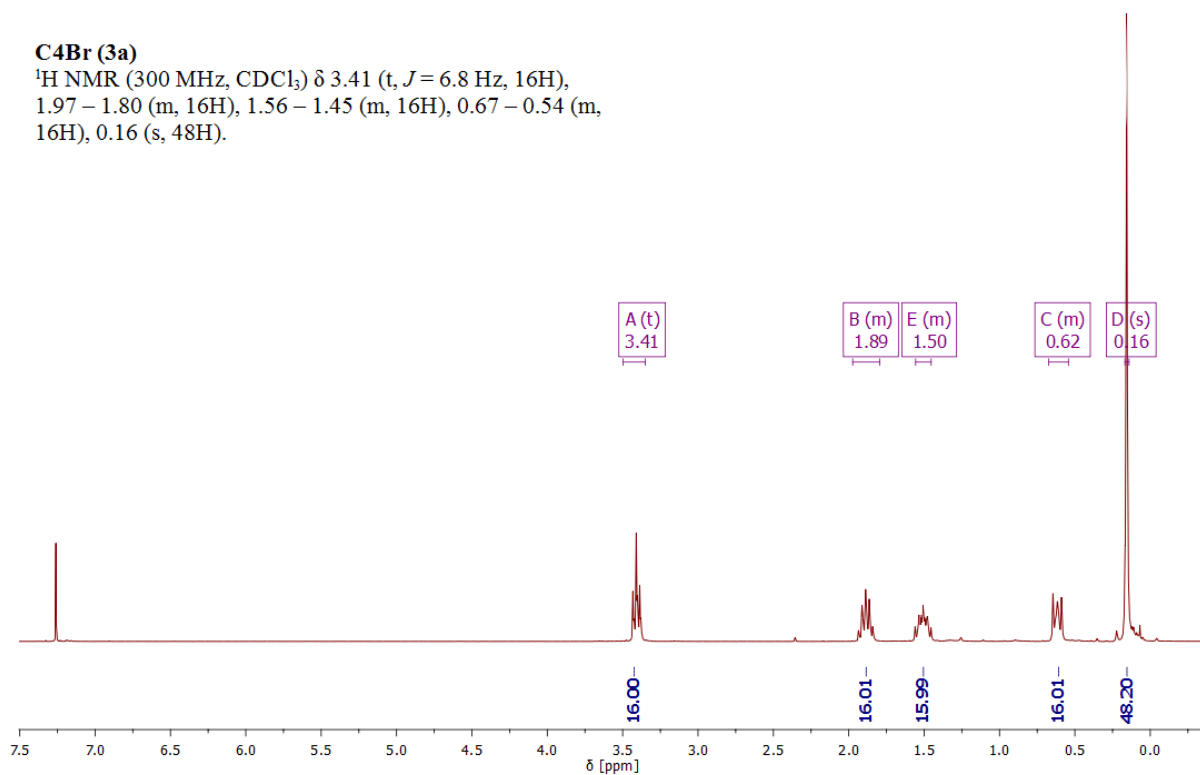
**6d:** Colorless Solid. **Yield:** 7.63 g (2.50 mmol, 95 %). **<sup>1</sup>H NMR** (300 MHz, MeOD)  $\delta$  3.16 – 3.03 (m,  $J = 9.7, 7.0$  Hz, 32H,  $\text{CH}_2\text{NHCONHCH}_2$ ), 1.56 – 1.23 (m, 160H,  $\text{CH}_{2\text{alkyl}}$ ), 0.91 (t,  $J = 7.4$  Hz, 24H,  $\text{CH}_3$ ), 0.70 – 0.61 (m, 16H,  $\text{CH}_2\text{Si}$ ), 0.14 (s, 48H,  $\text{Si}(\text{CH}_3)_2$ ). **<sup>13</sup>C NMR** (75 MHz, MeOD)  $\delta$  161.36 (CO), 42.84 ( $\text{CONHCH}_2$ ), 41.10 ( $\text{CONHCH}_2\text{—Si}$ ), 34.69 ( $\text{C}_{\text{alkyl}}$ ), 31.49 ( $\text{C}_{\text{alkyl}}$ ), 30.94 ( $\text{C}_{\text{alkyl}}$ ), 30.69 ( $\text{C}_{\text{alkyl}}$ ), 28.10 ( $\text{C}_{\text{alkyl}}$ ), 24.55 ( $\text{C}_{\text{alkyl}}$ ), 24.27 ( $\text{CH}_2\text{Si}$ ), 18.77 ( $\text{CH}_2\text{CH}_2\text{Si}$ ), 11.67 ( $\text{CH}_3$ ), 0.15 ( $\text{Si}(\text{CH}_3)_2$ ). **<sup>29</sup>Si NMR** (60 MHz, MeOD)  $\delta$  12.98 ( $\text{OSi}(\text{CH}_3)_2\text{R}$ ), -108.63 ( $\text{SiO}_4$ ). **IR**  $\nu = 3325$  ( $\nu$  N-H), 2960 ( $\nu$  C-H), 2922 ( $\nu$  C-H), 1624 (amide I,  $\nu$  C=O), 1579 (amide II,  $\delta$  N-H, C=O,  $\nu$  C-N), 1252 ( $\nu$  Si-C), 1072 ( $\nu$  Si-O), 840 ( $\delta$  C-H), 550 ( $\delta$  Si-O cage deformation)  $\text{cm}^{-1}$ . **TG residual mass:**  $\text{N}_2$ : 28.19 %, (theoretical residual mass: 29.39 %). **ESI-MS:**  $[\text{M}+2\text{Na}^+]$ : 1549.40,  $[\text{M}+\text{Na}^++\text{K}^+]$ : 1557.39,  $[\text{M}+2\text{K}^+]$ : 1564.89  $m/z$ .

## NMR

### C4Br (3a)

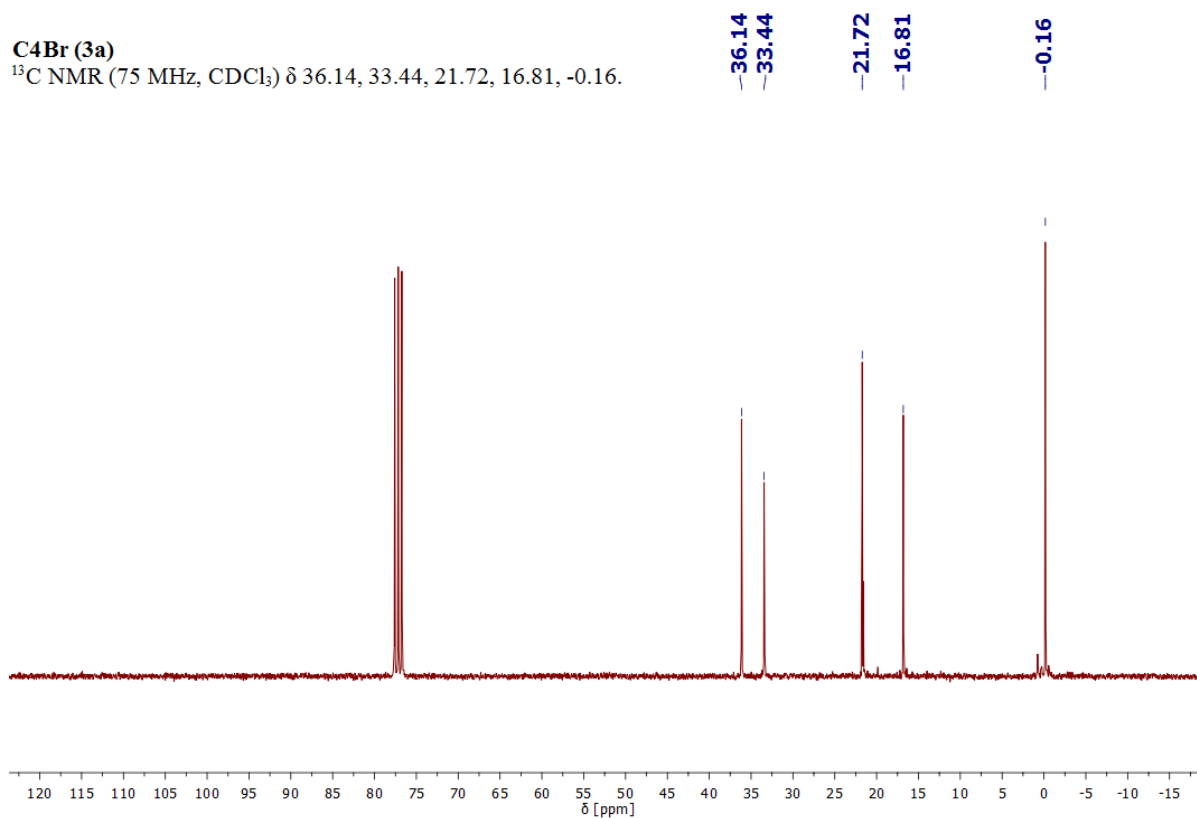
#### C4Br (3a)

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.41 (t,  $J = 6.8$  Hz, 16H),  
1.97 – 1.80 (m, 16H), 1.56 – 1.45 (m, 16H), 0.67 – 0.54 (m,  
16H), 0.16 (s, 48H).



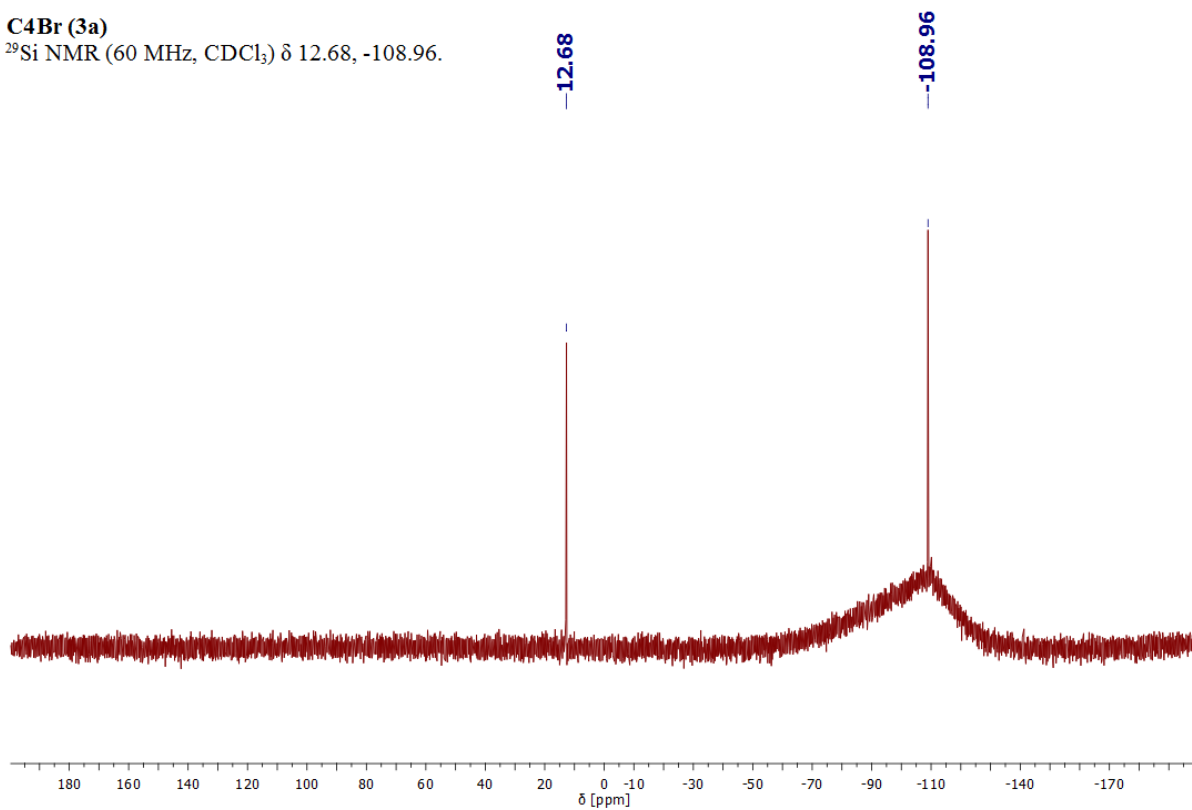
#### C4Br (3a)

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  36.14, 33.44, 21.72, 16.81, -0.16.



**C4Br (3a)**

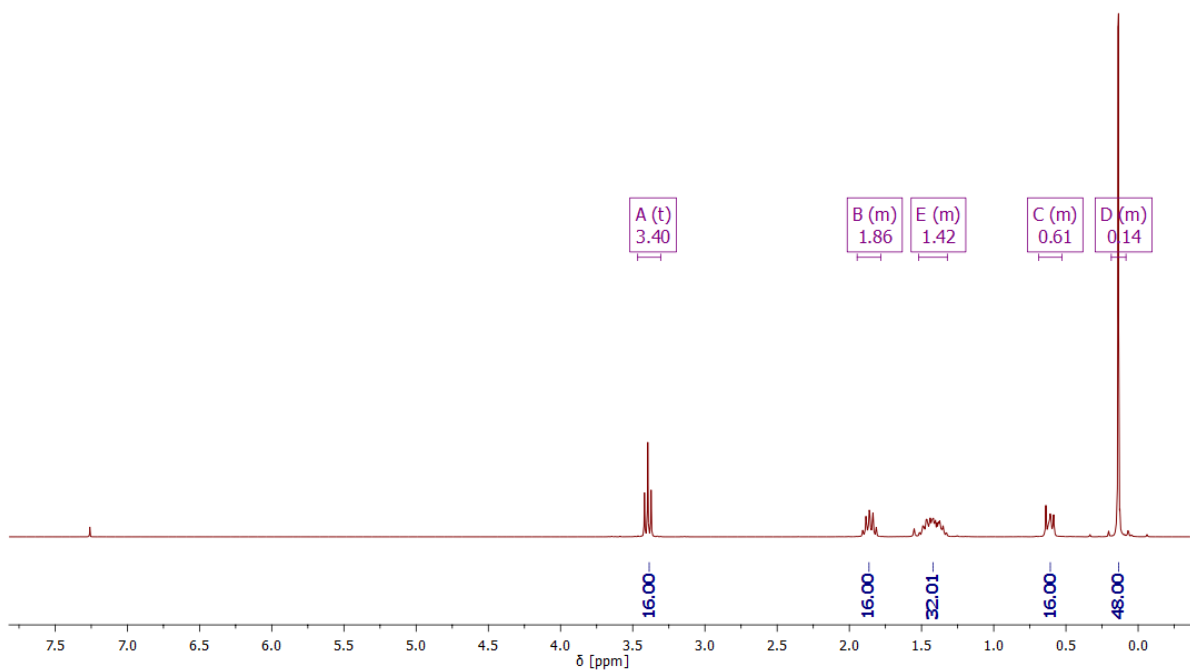
$^{29}\text{Si}$  NMR (60 MHz,  $\text{CDCl}_3$ )  $\delta$  12.68, -108.96.



**C5Br (3b)**

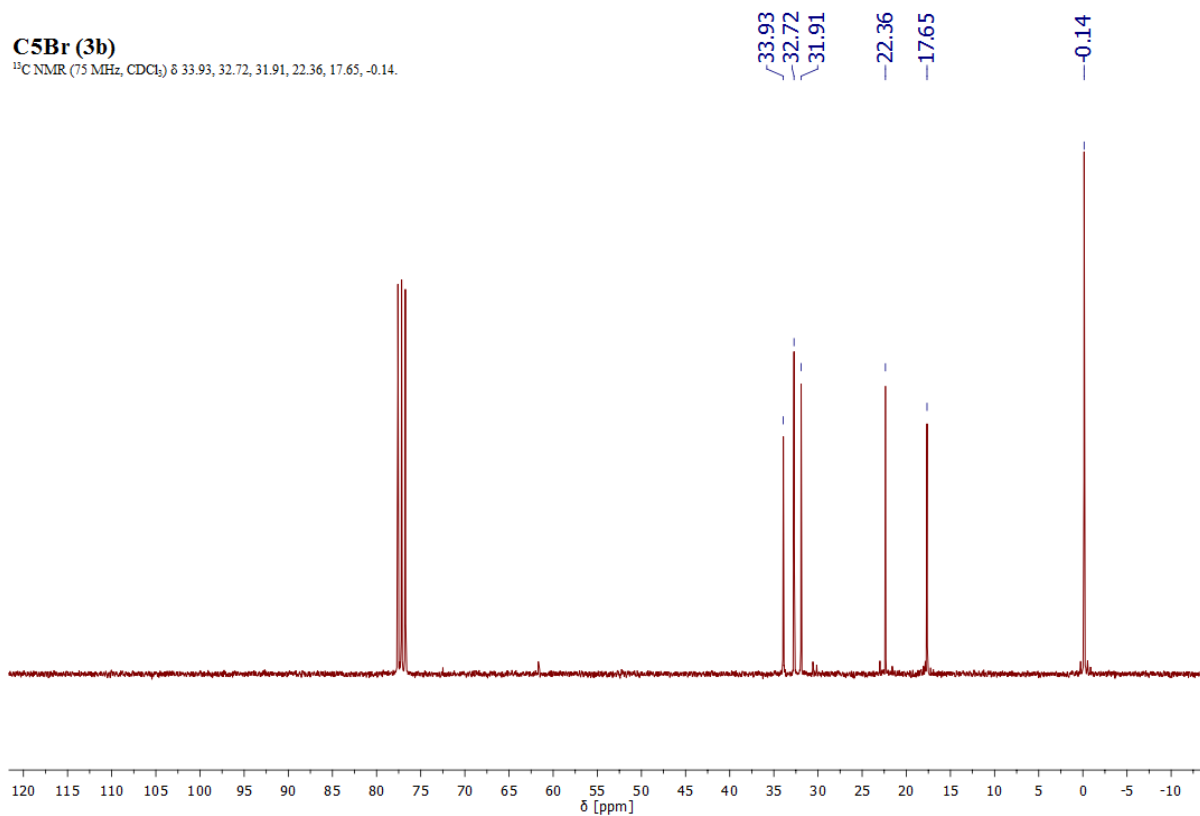
**C5Br (3b)**

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.40 (t,  $J = 6.9$  Hz, 1H), 1.95 – 1.78 (m, 16H), 1.52 – 1.32 (m, 2H), 0.69 – 0.53 (m, 1H), 0.19 – 0.08 (m, 3H).



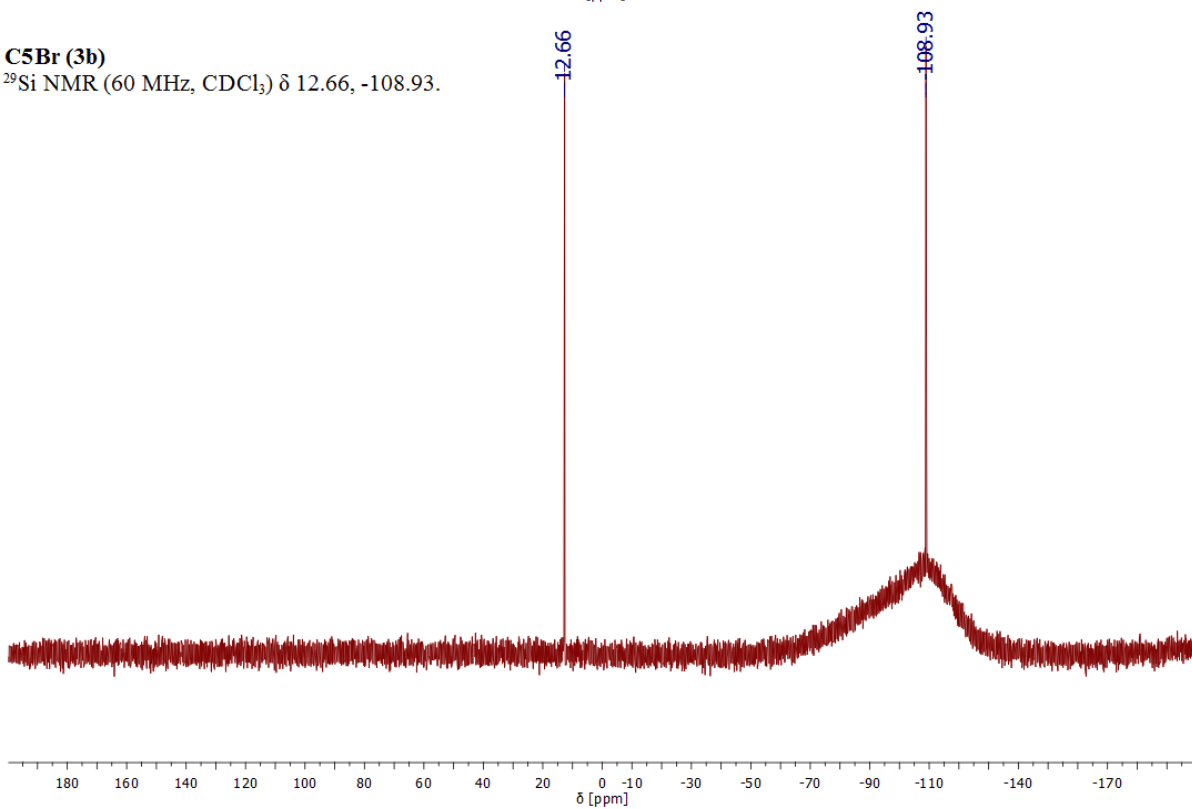
**C5Br (3b)**

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  33.93, 32.72, 31.91, 22.36, 17.65, -0.14.



**C5Br (3b)**

$^{29}\text{Si}$  NMR (60 MHz,  $\text{CDCl}_3$ )  $\delta$  12.66, -108.93.

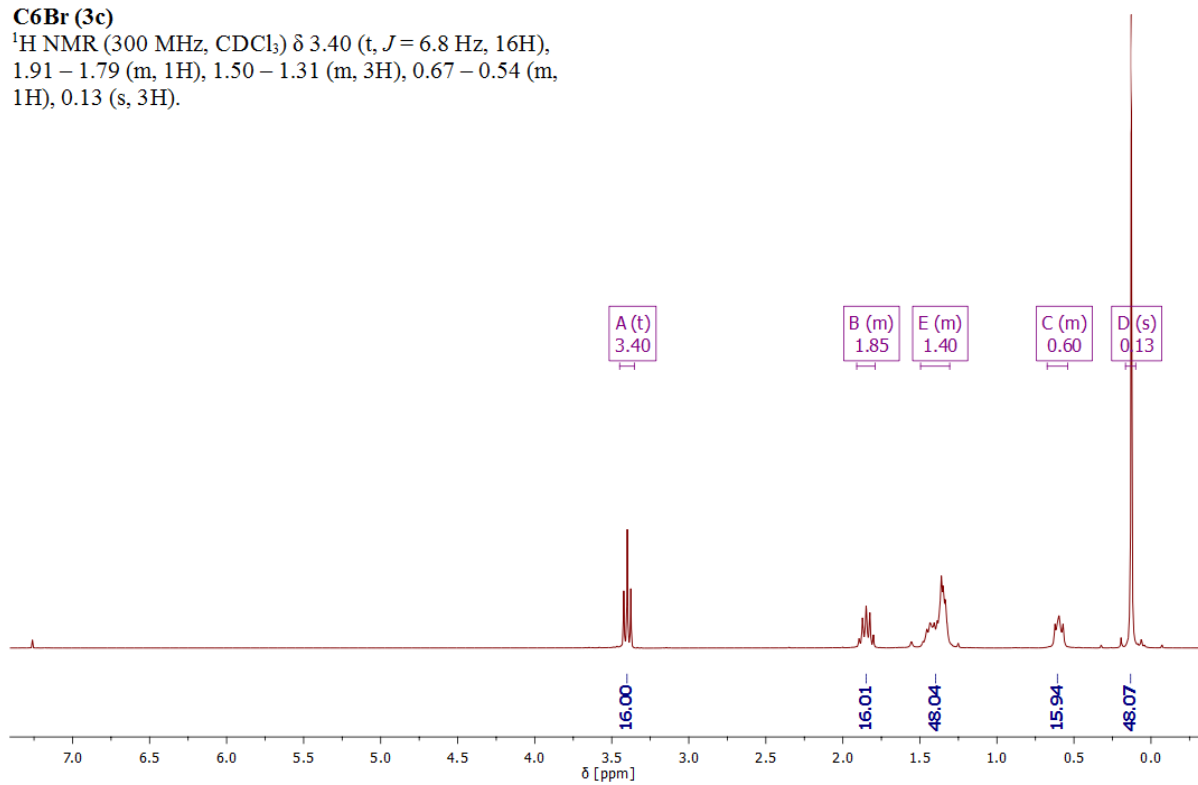




### C6Br (3c)

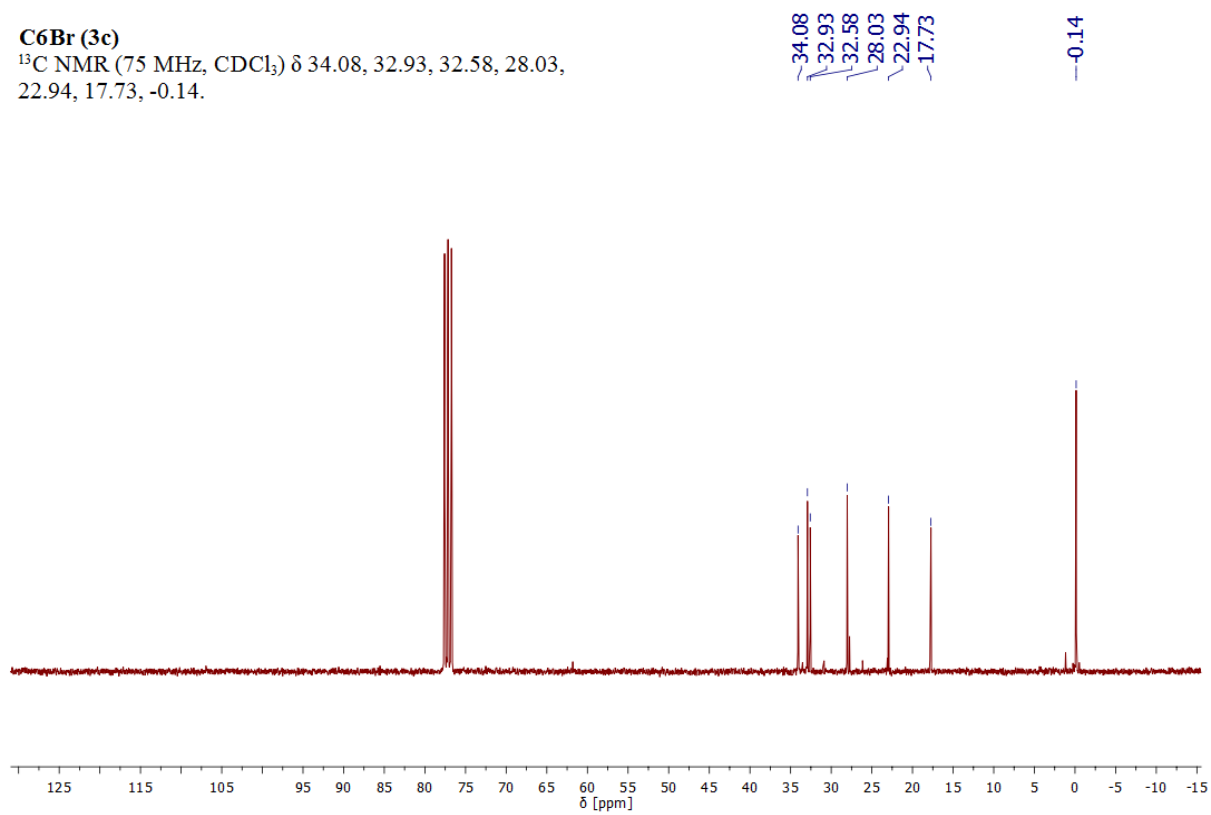
#### **C6Br (3c)**

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.40 (t,  $J = 6.8$  Hz, 16H), 1.91 – 1.79 (m, 1H), 1.50 – 1.31 (m, 3H), 0.67 – 0.54 (m, 1H), 0.13 (s, 3H).

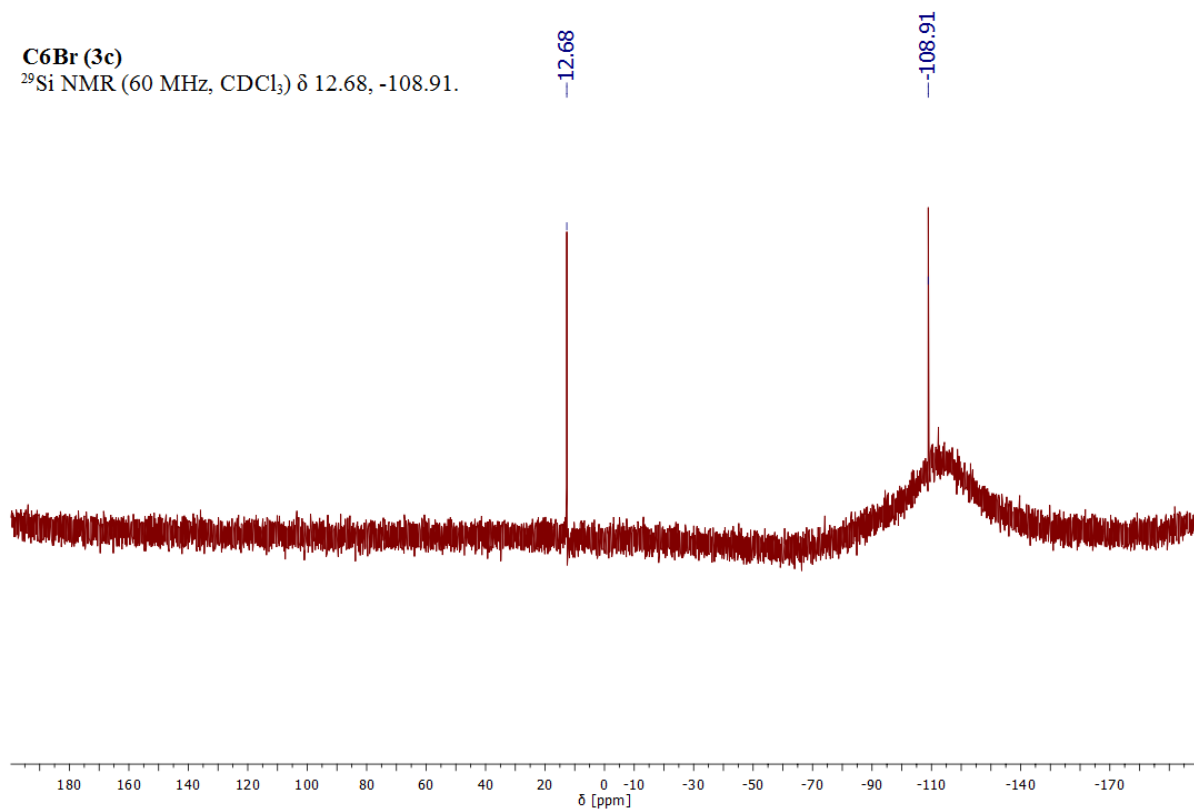


#### **C6Br (3c)**

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  34.08, 32.93, 32.58, 28.03, 22.94, 17.73, -0.14.

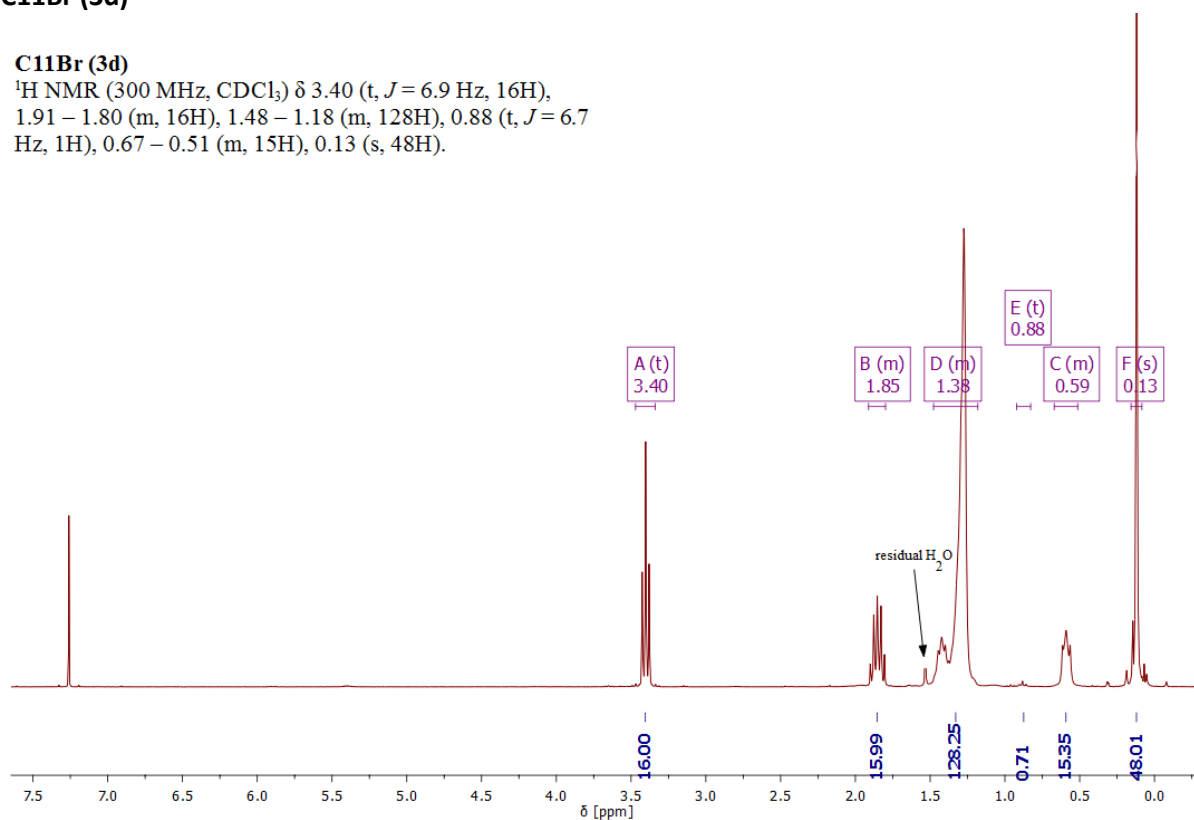


**C6Br (3c)**  
 $^{29}\text{Si}$  NMR (60 MHz,  $\text{CDCl}_3$ )  $\delta$  12.68, -108.91.



**C11Br (3d)**

**C11Br (3d)**  
 $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.40 (t,  $J = 6.9$  Hz, 16H),  
1.91 – 1.80 (m, 16H), 1.48 – 1.18 (m, 128H), 0.88 (t,  $J = 6.7$   
Hz, 1H), 0.67 – 0.51 (m, 15H), 0.13 (s, 48H).

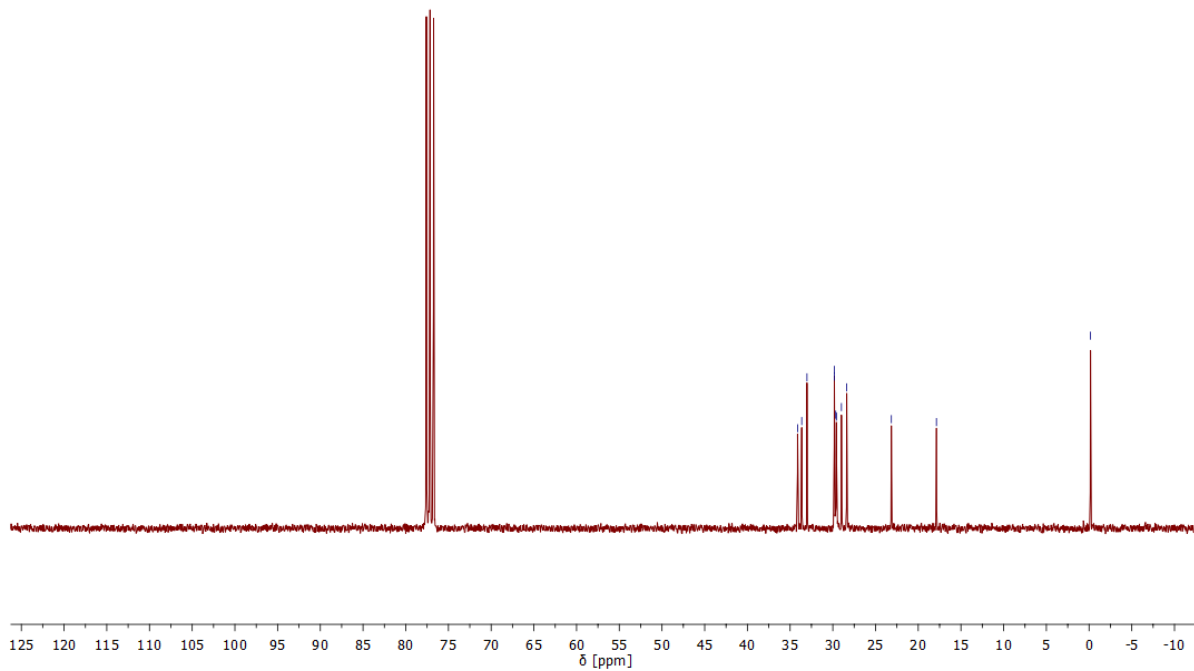


**C11Br (3d)**

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  34.13, 33.64, 33.03, 29.82, 29.81, 29.66, 29.58, 28.99, 28.37, 23.14, 17.87, -0.17.

34.13  
33.64  
33.03  
29.82  
29.81  
29.66  
29.58  
28.99  
28.37  
23.14  
17.87

-0.17

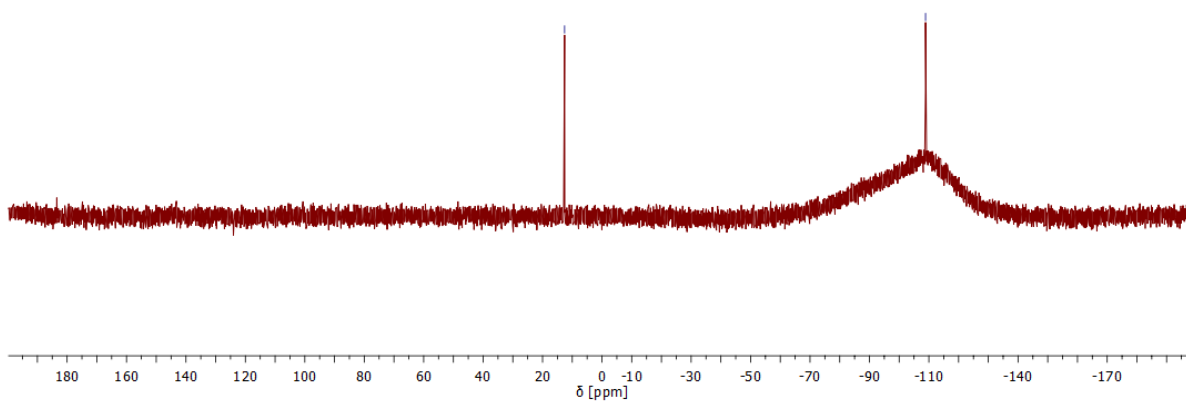


**C11Br (3d)**

$^{29}\text{Si}$  NMR (60 MHz,  $\text{CDCl}_3$ )  $\delta$  12.58, -108.88.

12.58

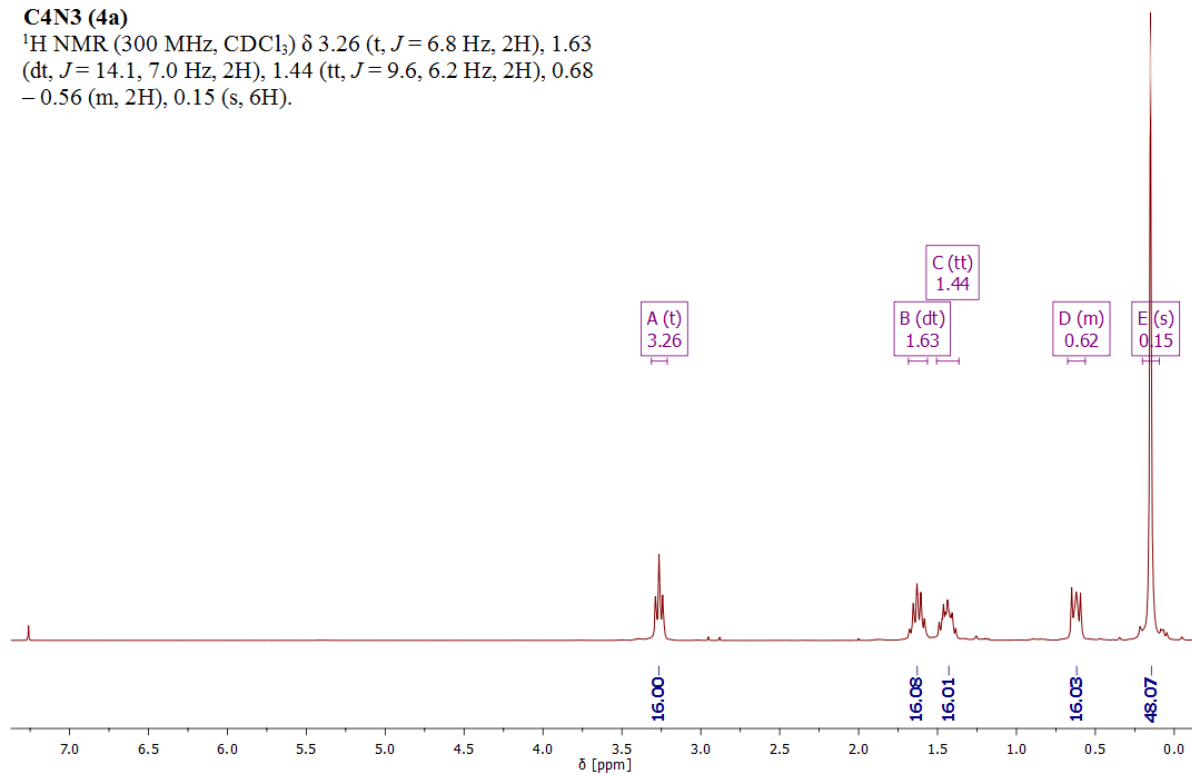
-108.88



**C4N3 (4a)**

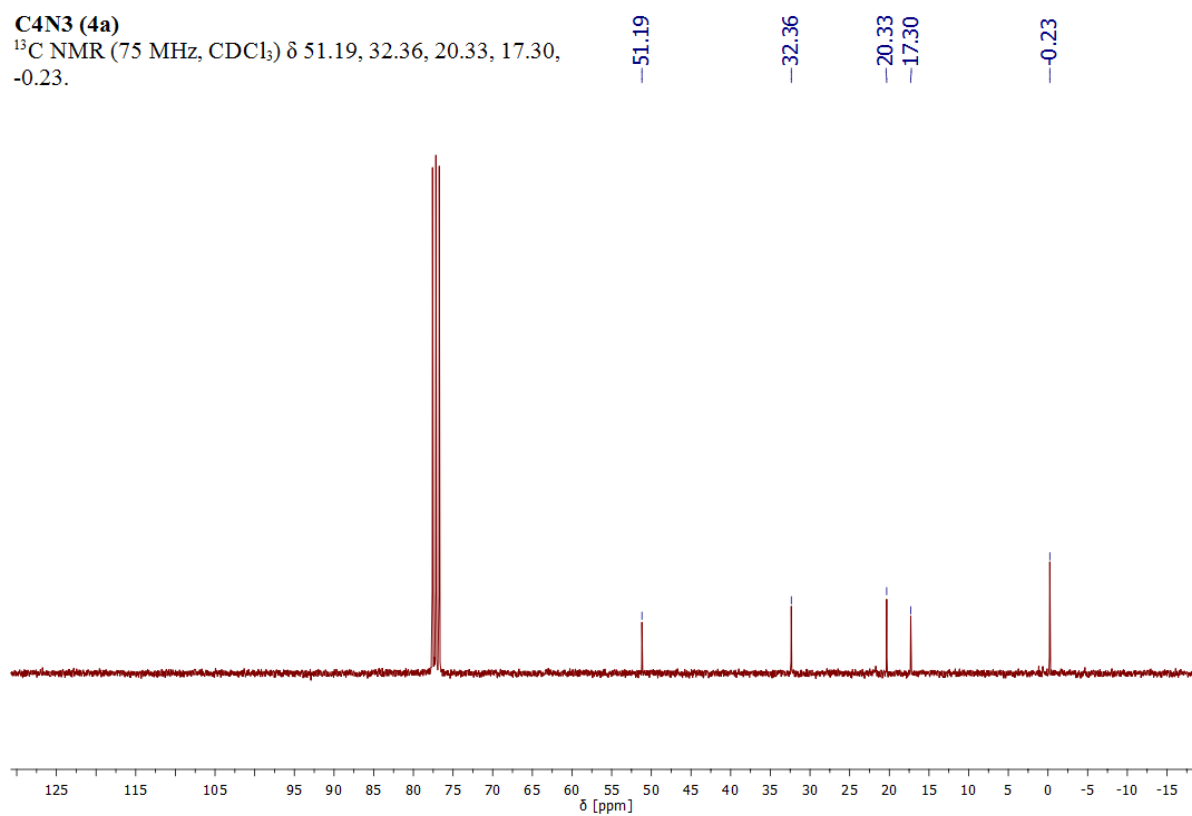
**C4N3 (4a)**

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.26 (t,  $J = 6.8$  Hz, 2H), 1.63 (dt,  $J = 14.1, 7.0$  Hz, 2H), 1.44 (tt,  $J = 9.6, 6.2$  Hz, 2H), 0.68 – 0.56 (m, 2H), 0.15 (s, 6H).

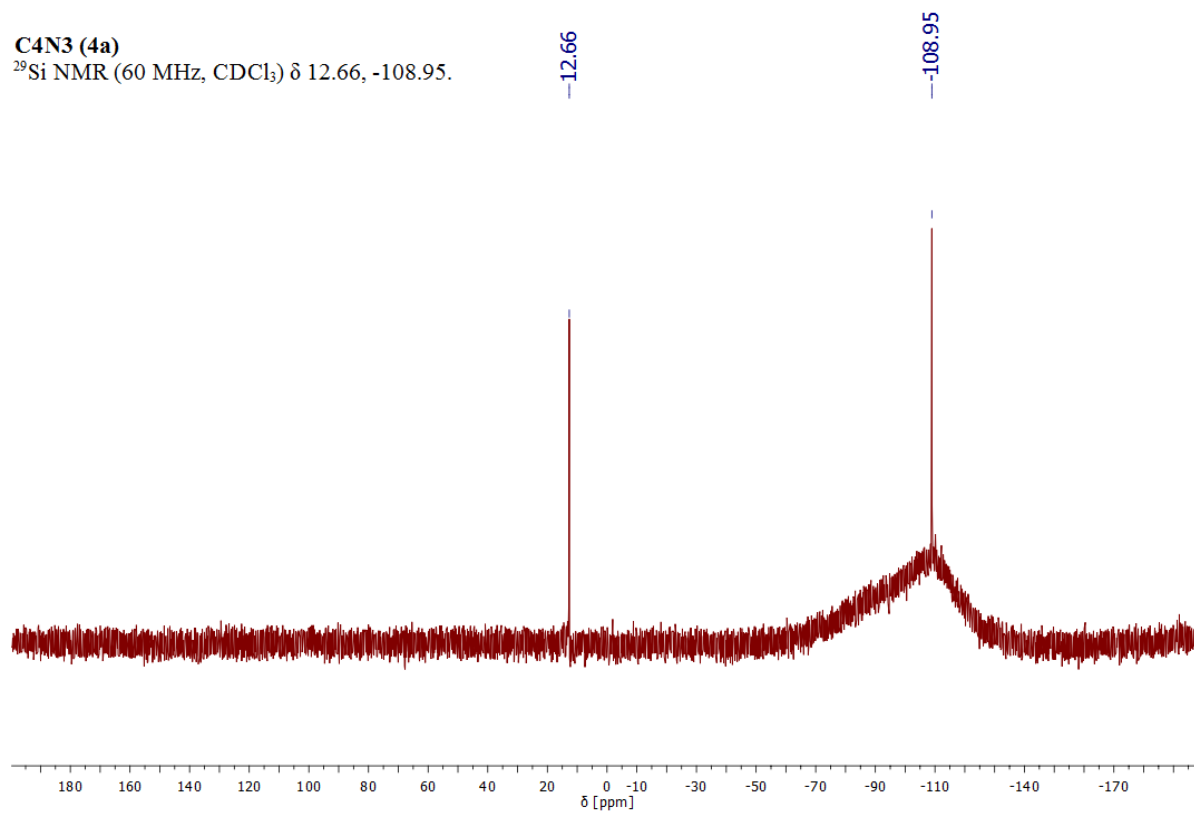


**C4N3 (4a)**

$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  51.19, 32.36, 20.33, 17.30, -0.23.



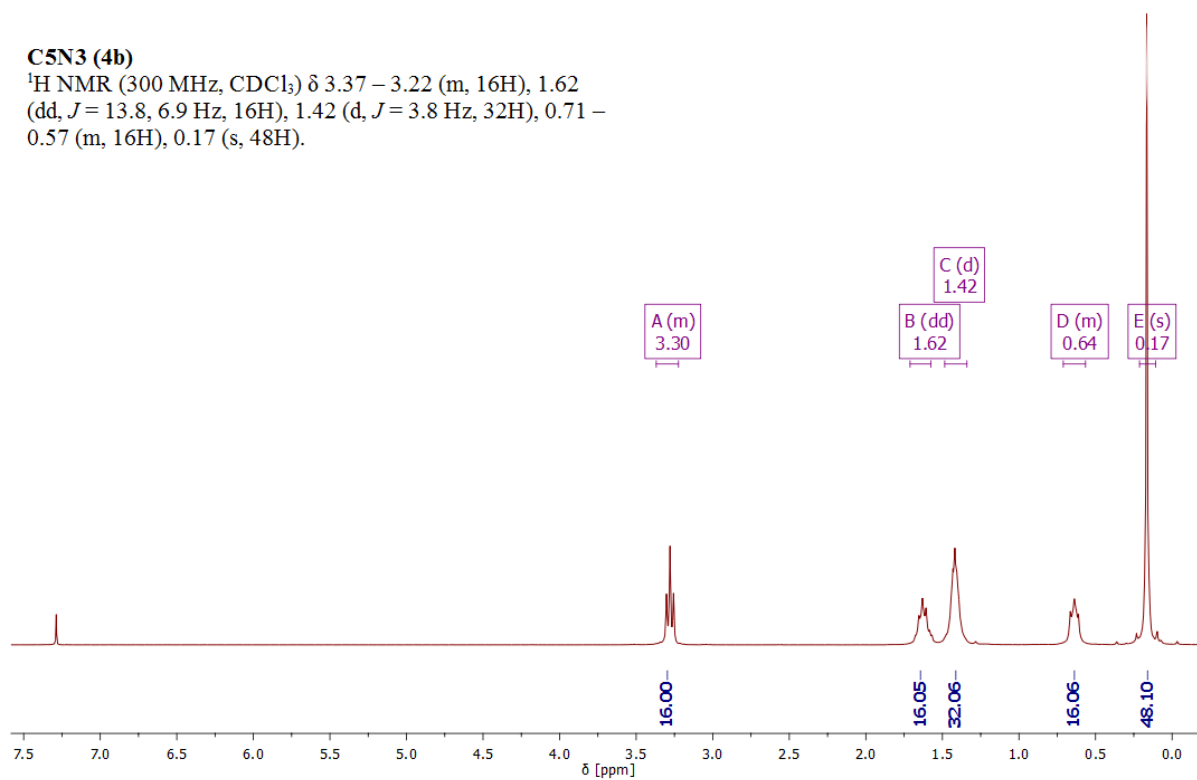
**C4N3 (4a)**  
 $^{29}\text{Si}$  NMR (60 MHz,  $\text{CDCl}_3$ )  $\delta$  12.66, -108.95.



**C5N3 (4b)**

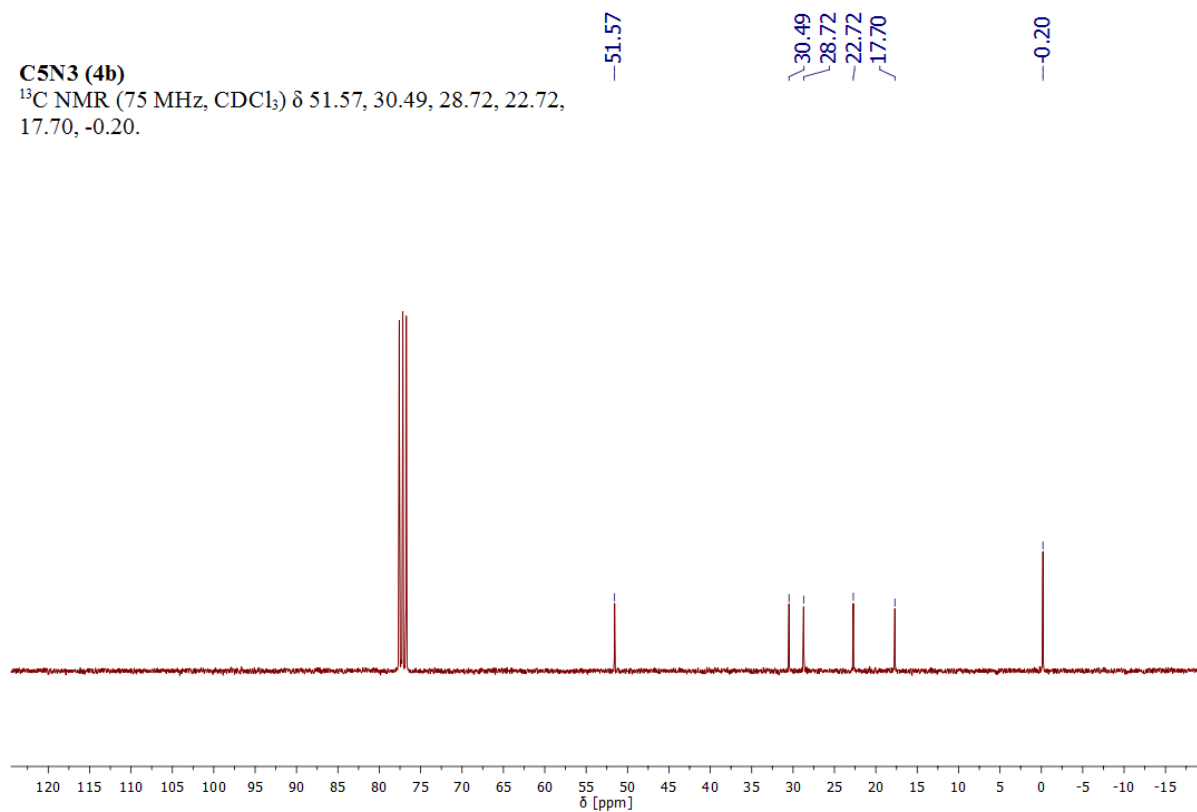
**C5N3 (4b)**

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.37 – 3.22 (m, 16H), 1.62 (dd,  $J = 13.8, 6.9$  Hz, 16H), 1.42 (d,  $J = 3.8$  Hz, 32H), 0.71 – 0.57 (m, 16H), 0.17 (s, 48H).

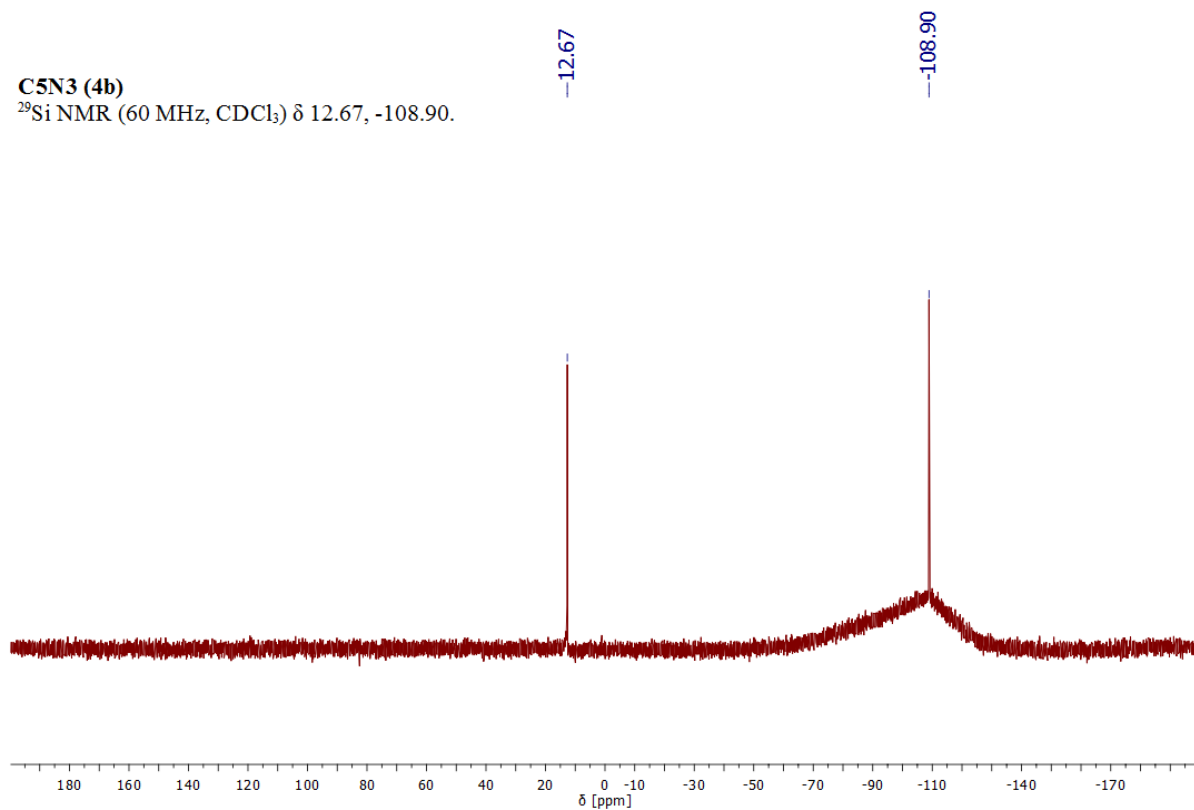


**C5N3 (4b)**

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  51.57, 30.49, 28.72, 22.72, 17.70, -0.20.

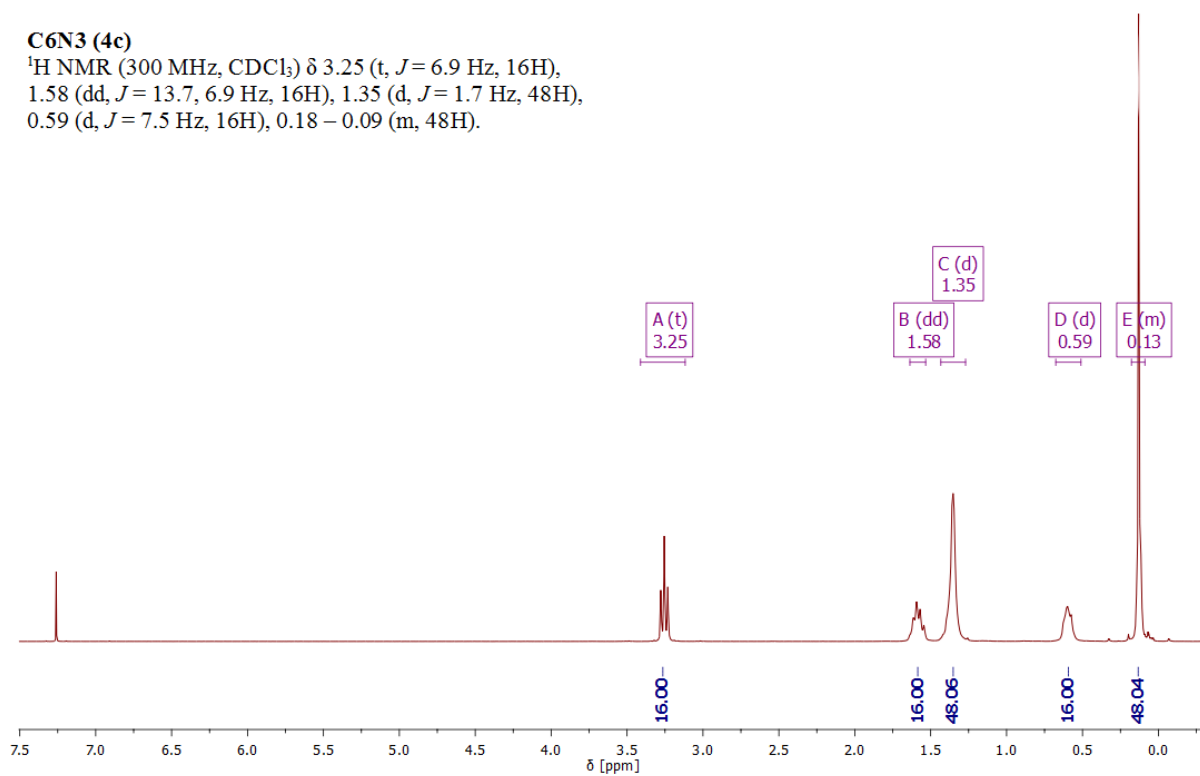


**C5N3 (4b)**  
 $^{29}\text{Si}$  NMR (60 MHz,  $\text{CDCl}_3$ )  $\delta$  12.67, -108.90.



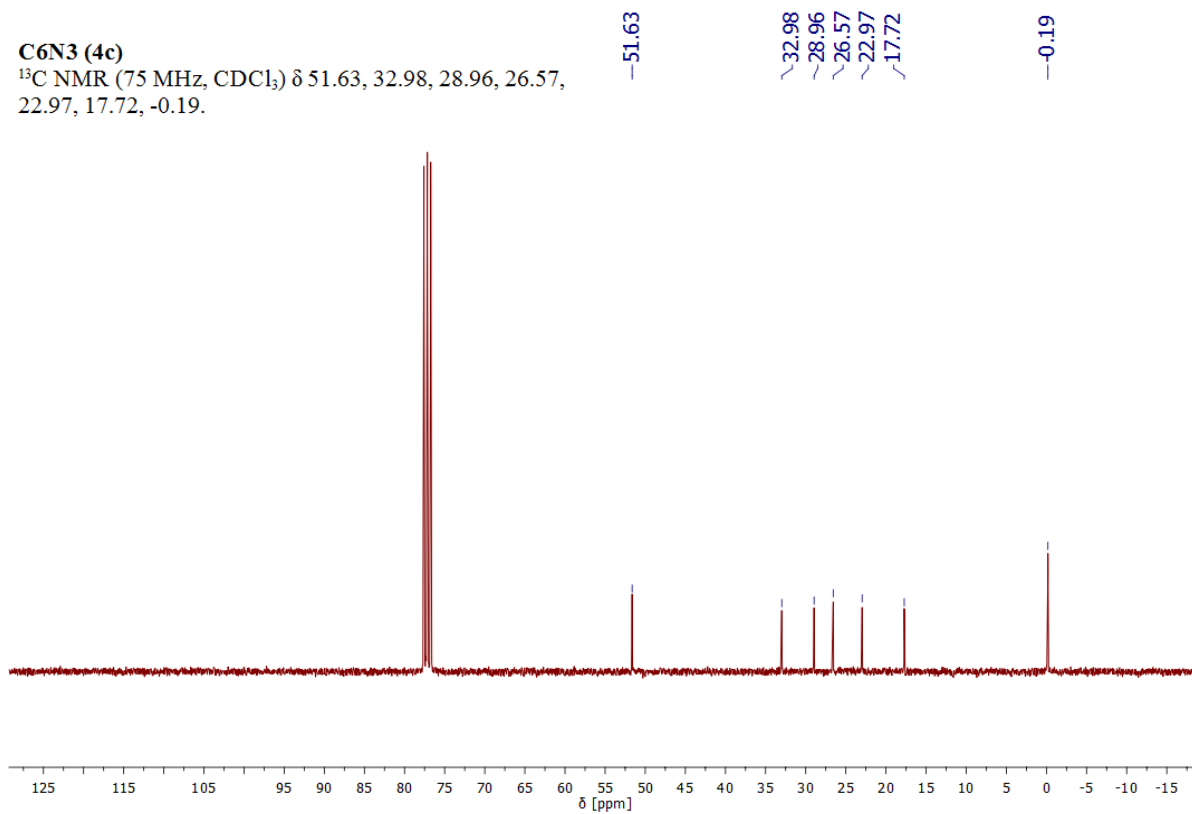
**C6N3 (4c)**

**C6N3 (4c)**  
 $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.25 (t,  $J = 6.9$  Hz, 16H),  
1.58 (dd,  $J = 13.7, 6.9$  Hz, 16H), 1.35 (d,  $J = 1.7$  Hz, 48H),  
0.59 (d,  $J = 7.5$  Hz, 16H), 0.18 – 0.09 (m, 48H).



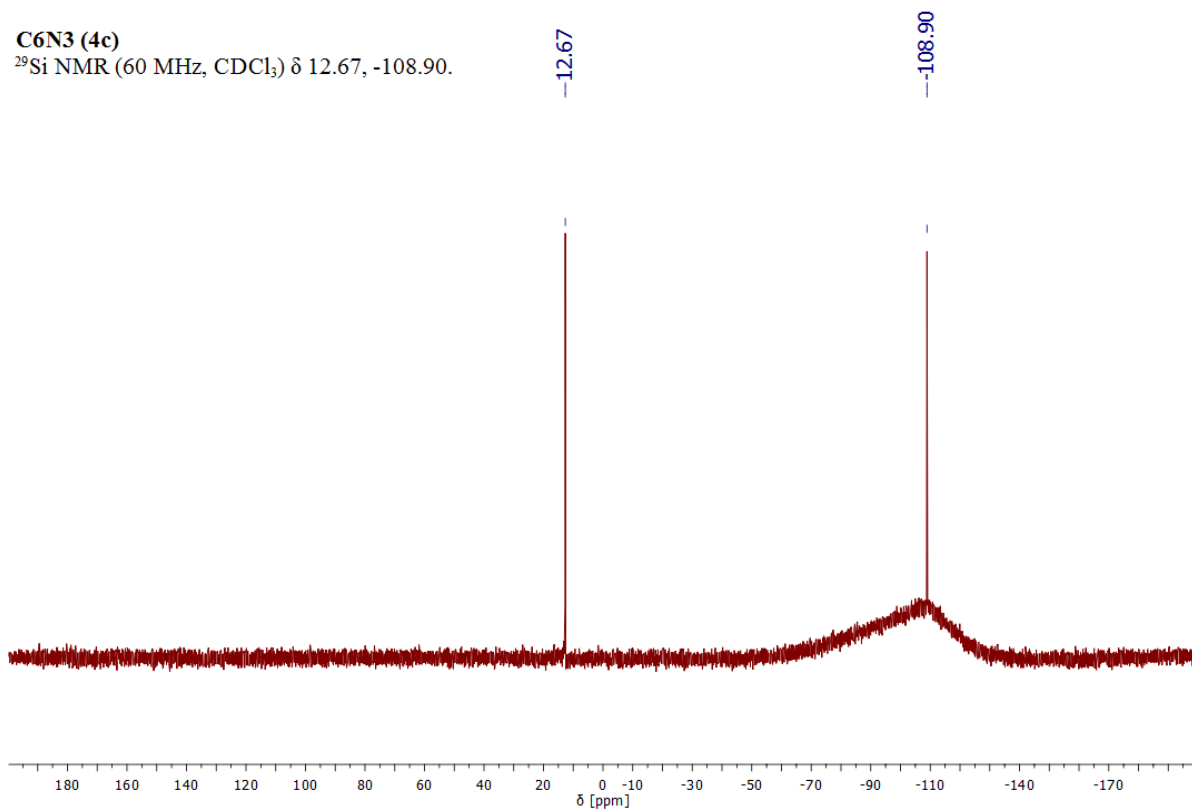
**C6N3 (4c)**

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  51.63, 32.98, 28.96, 26.57, 22.97, 17.72, -0.19.



**C6N3 (4c)**

$^{29}\text{Si}$  NMR (60 MHz,  $\text{CDCl}_3$ )  $\delta$  12.67, -108.90.

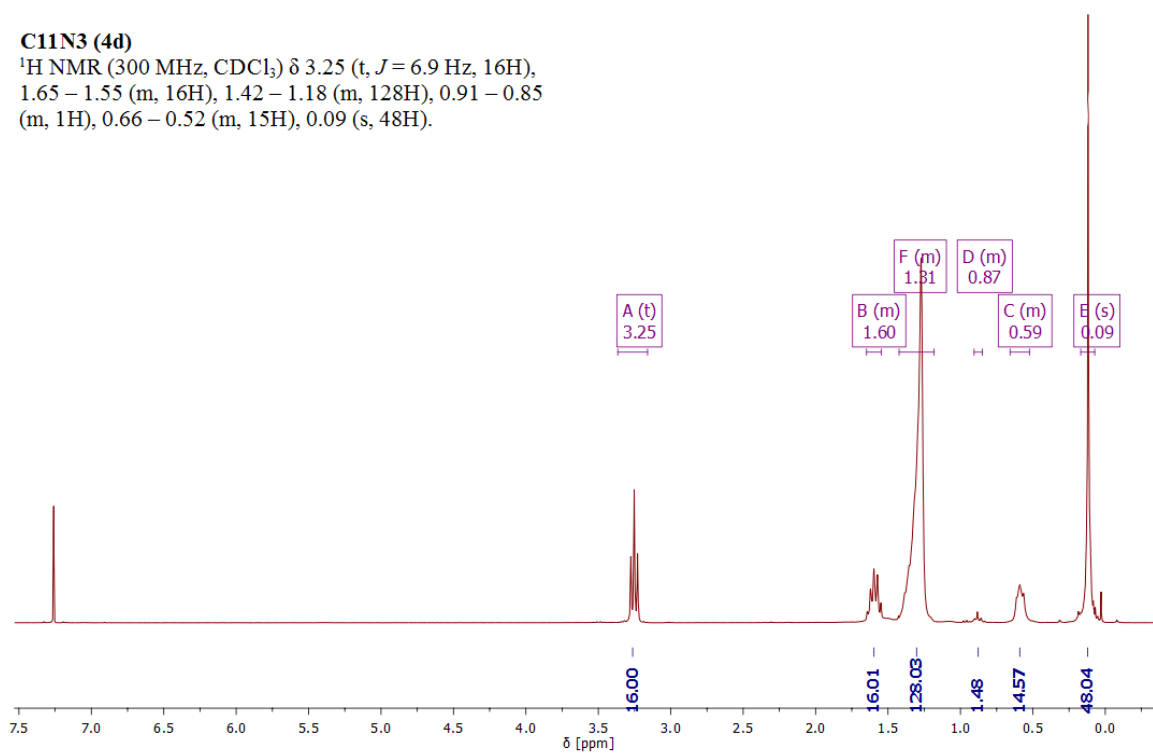




## C11N3 (4d)

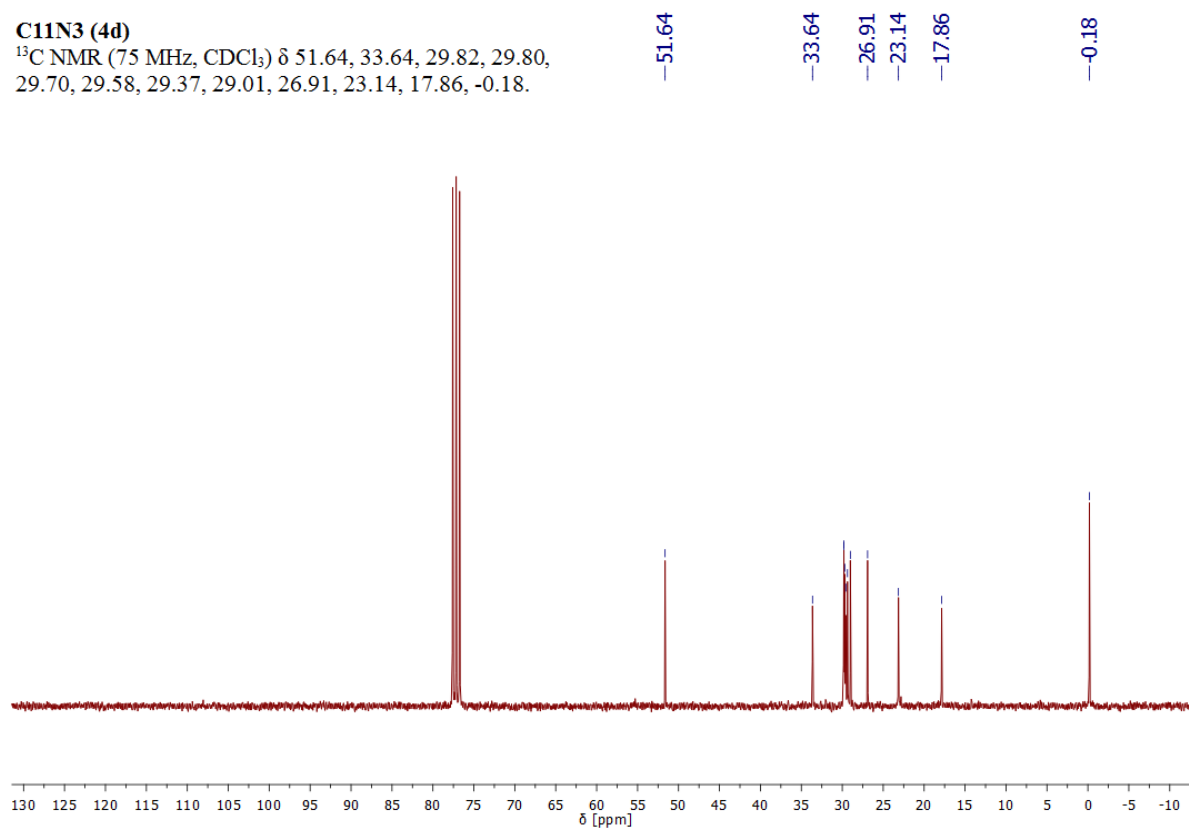
### C11N3 (4d)

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.25 (t,  $J = 6.9$  Hz, 16H), 1.65 – 1.55 (m, 16H), 1.42 – 1.18 (m, 128H), 0.91 – 0.85 (m, 1H), 0.66 – 0.52 (m, 15H), 0.09 (s, 48H).

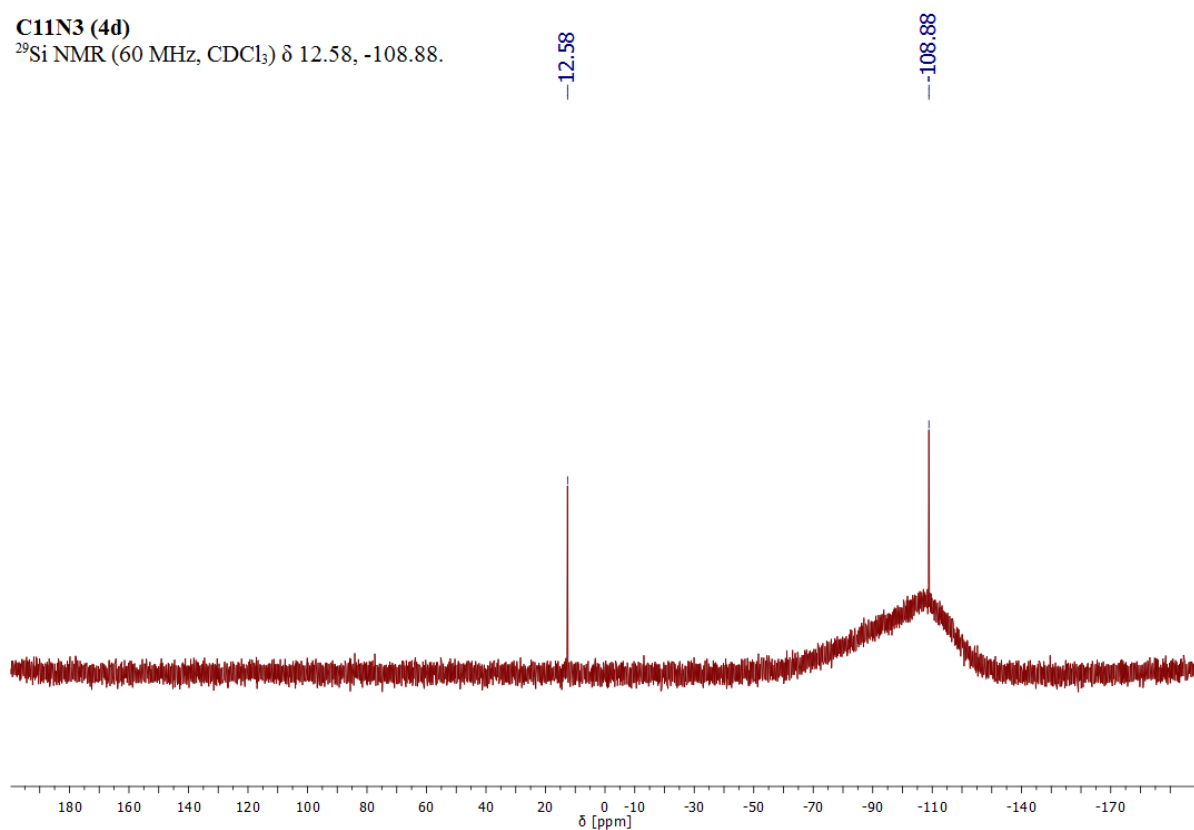


### C11N3 (4d)

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  51.64, 33.64, 29.82, 29.80, 29.70, 29.58, 29.37, 29.01, 26.91, 23.14, 17.86, -0.18.



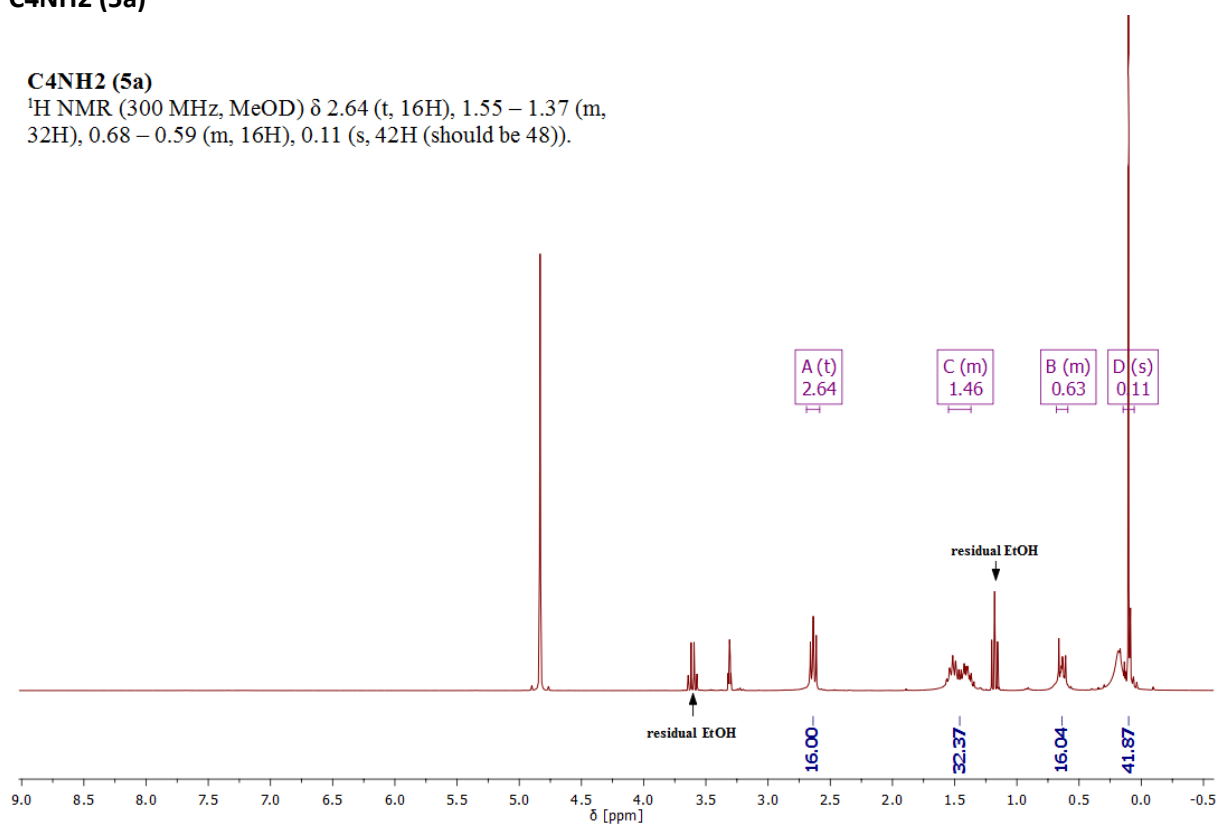
**C11N3 (4d)**  
 $^{29}\text{Si}$  NMR (60 MHz,  $\text{CDCl}_3$ )  $\delta$  12.58, -108.88.



**C4NH2 (5a)**

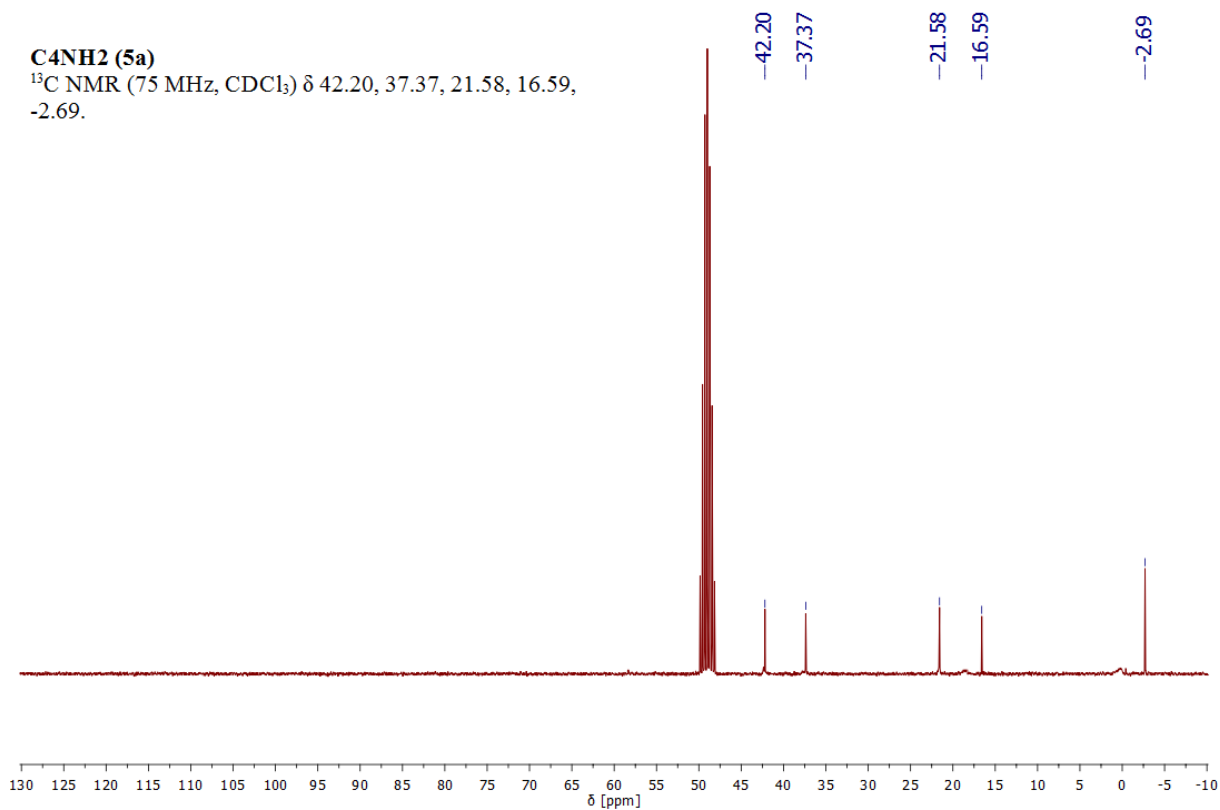
**C4NH2 (5a)**

$^1\text{H}$  NMR (300 MHz, MeOD)  $\delta$  2.64 (t, 16H), 1.55 – 1.37 (m, 32H), 0.68 – 0.59 (m, 16H), 0.11 (s, 42H (should be 48)).



**C4NH2 (5a)**

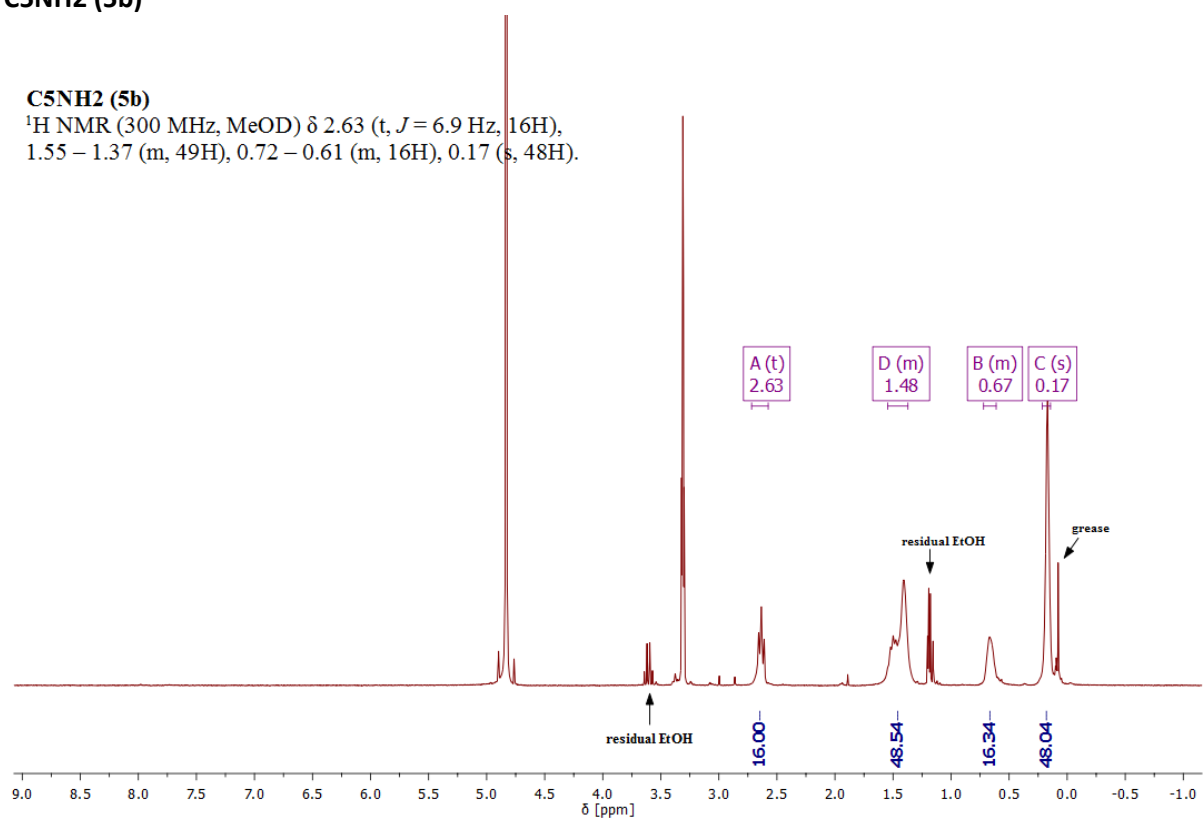
$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  42.20, 37.37, 21.58, 16.59, -2.69.



**C5NH2 (5b)**

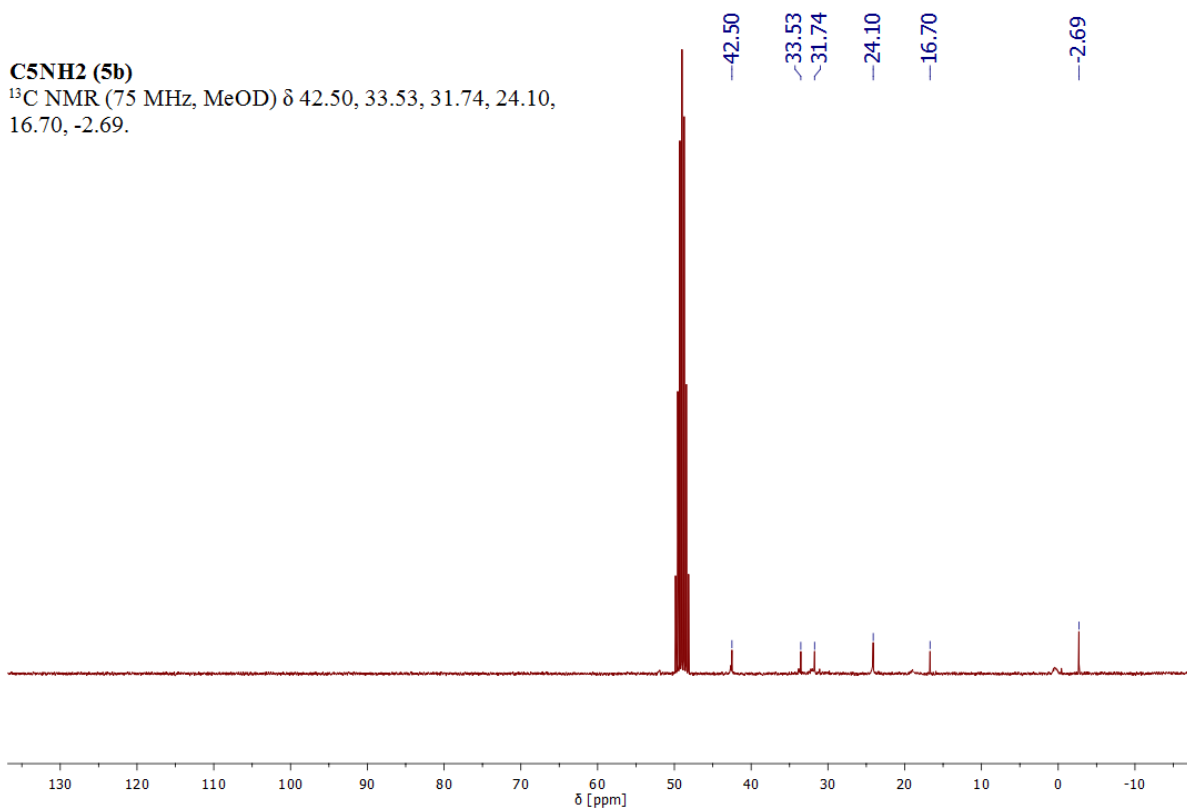
**C5NH2 (5b)**

$^1\text{H}$  NMR (300 MHz, MeOD)  $\delta$  2.63 (t,  $J = 6.9$  Hz, 16H), 1.55 – 1.37 (m, 49H), 0.72 – 0.61 (m, 16H), 0.17 (s, 48H).



**C5NH2 (5b)**

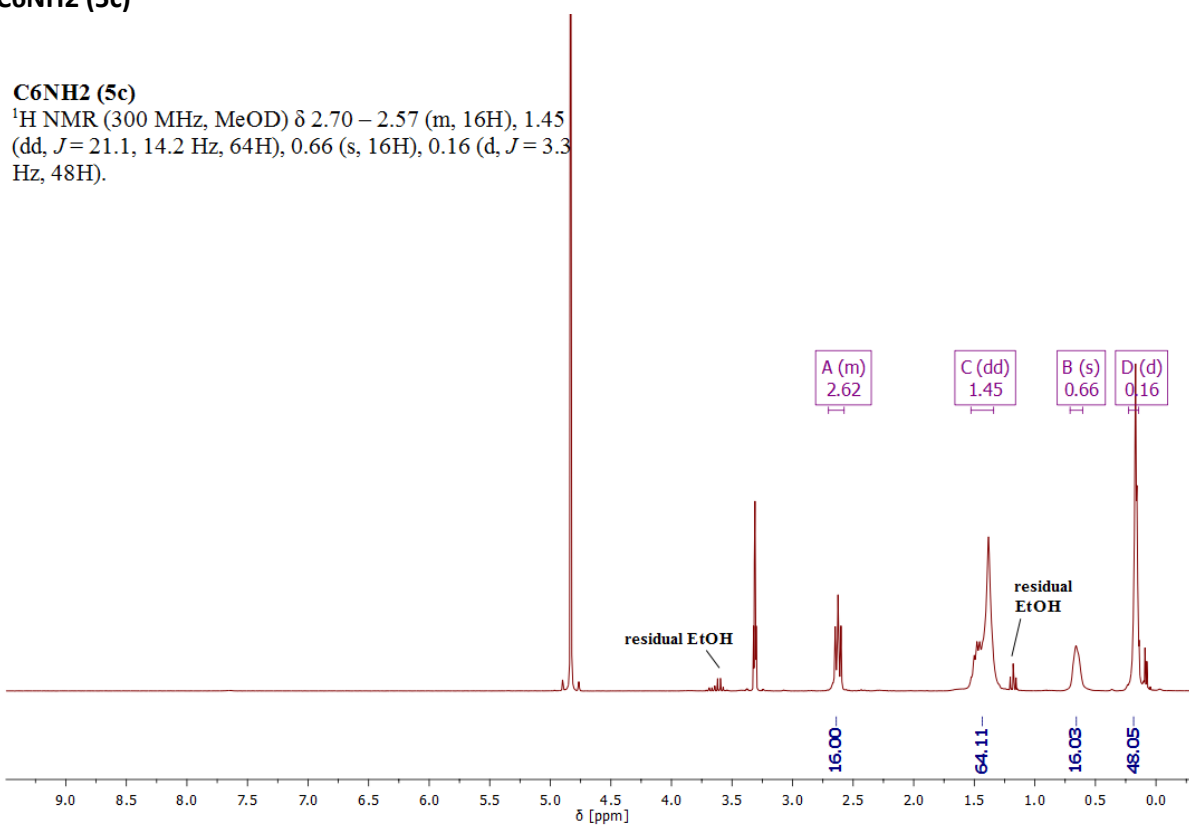
$^{13}\text{C}$  NMR (75 MHz, MeOD)  $\delta$  42.50, 33.53, 31.74, 24.10, 16.70, -2.69.



**C6NH2 (5c)**

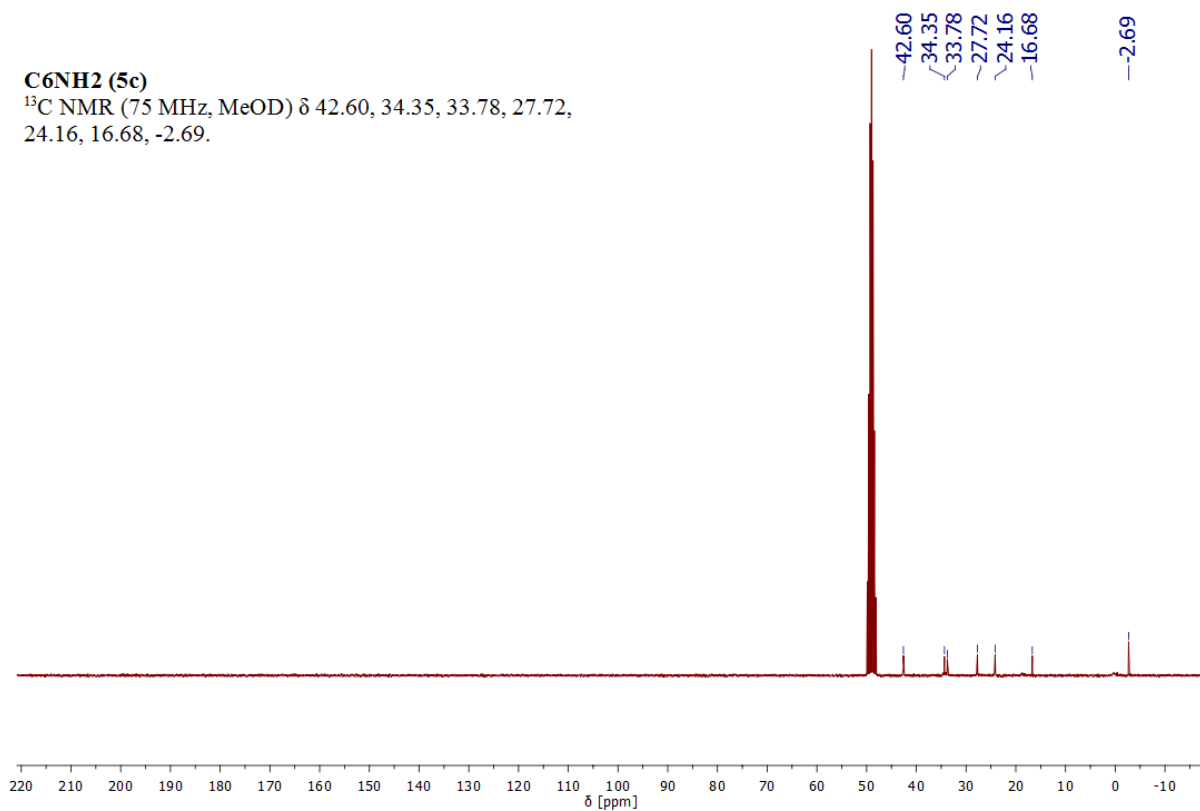
**C6NH2 (5c)**

$^1\text{H}$  NMR (300 MHz, MeOD)  $\delta$  2.70 – 2.57 (m, 16H), 1.45 (dd,  $J = 21.1, 14.2$  Hz, 64H), 0.66 (s, 16H), 0.16 (d,  $J = 3.3$  Hz, 48H).



**C6NH2 (5c)**

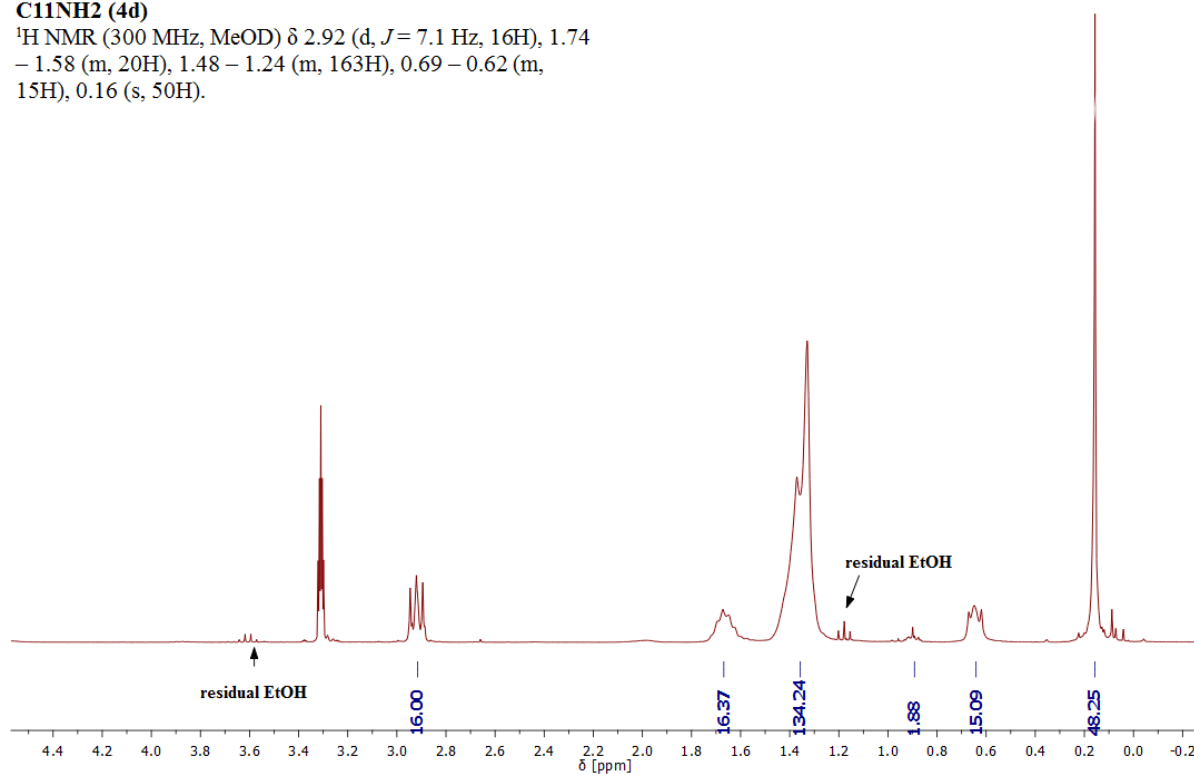
$^{13}\text{C}$  NMR (75 MHz, MeOD)  $\delta$  42.60, 34.35, 33.78, 27.72, 24.16, 16.68, -2.69.



**C11NH2 (5d)**

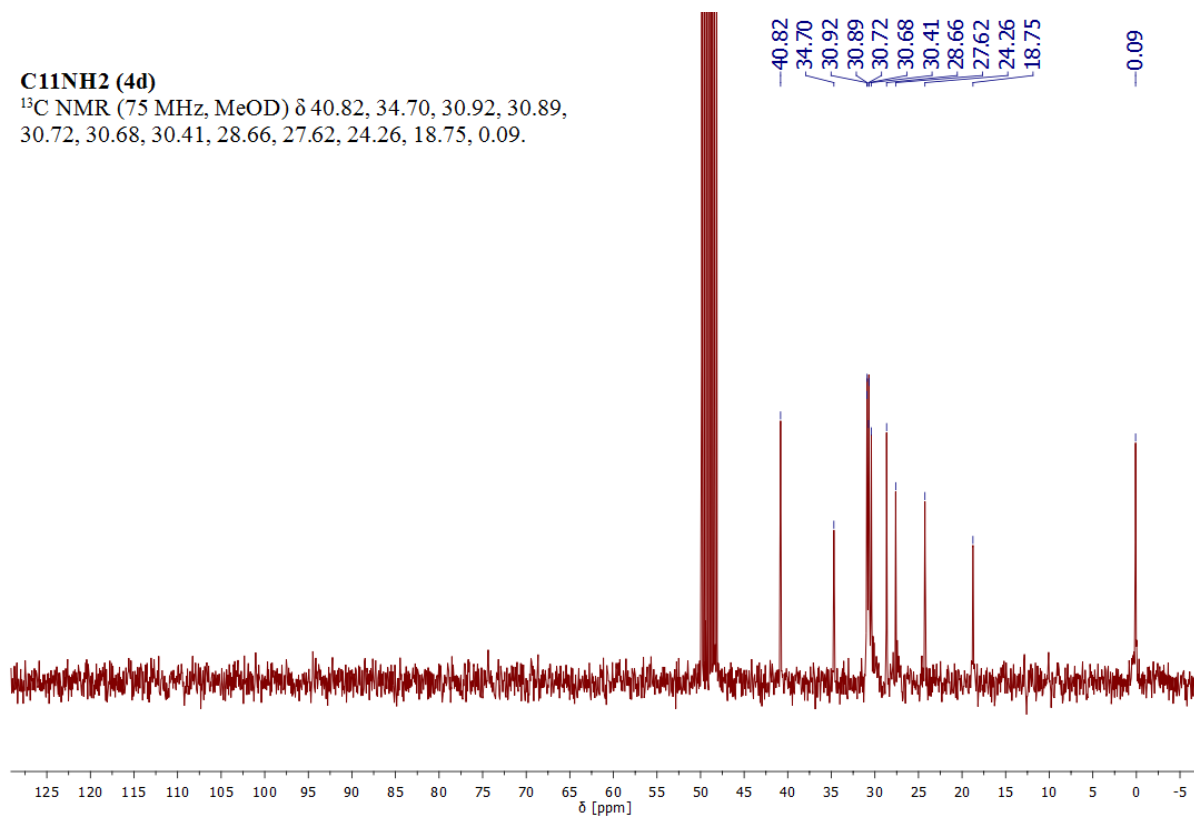
**C11NH2 (4d)**

$^1\text{H}$  NMR (300 MHz, MeOD)  $\delta$  2.92 (d,  $J = 7.1$  Hz, 16H), 1.74 – 1.58 (m, 20H), 1.48 – 1.24 (m, 163H), 0.69 – 0.62 (m, 15H), 0.16 (s, 50H).



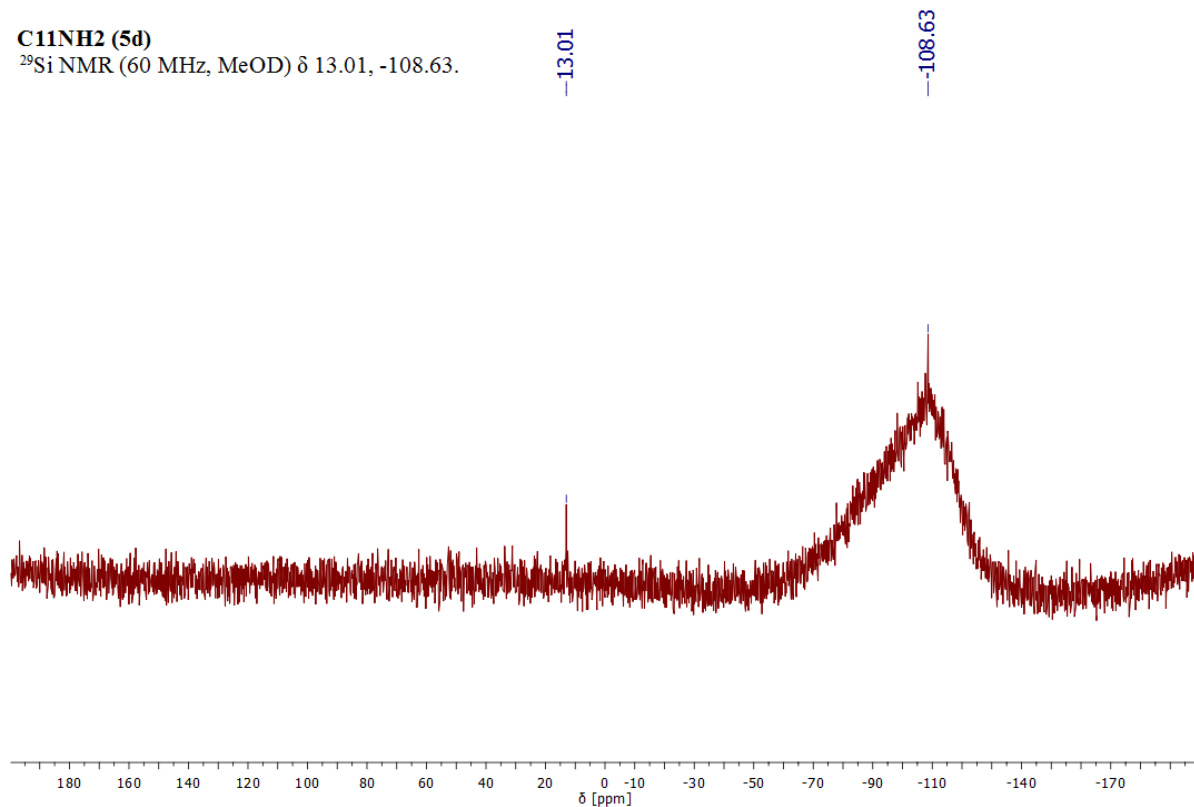
**C11NH2 (4d)**

$^{13}\text{C}$  NMR (75 MHz, MeOD)  $\delta$  40.82, 34.70, 30.92, 30.89, 30.72, 30.68, 30.41, 28.66, 27.62, 24.26, 18.75, 0.09.



**C11NH2 (5d)**

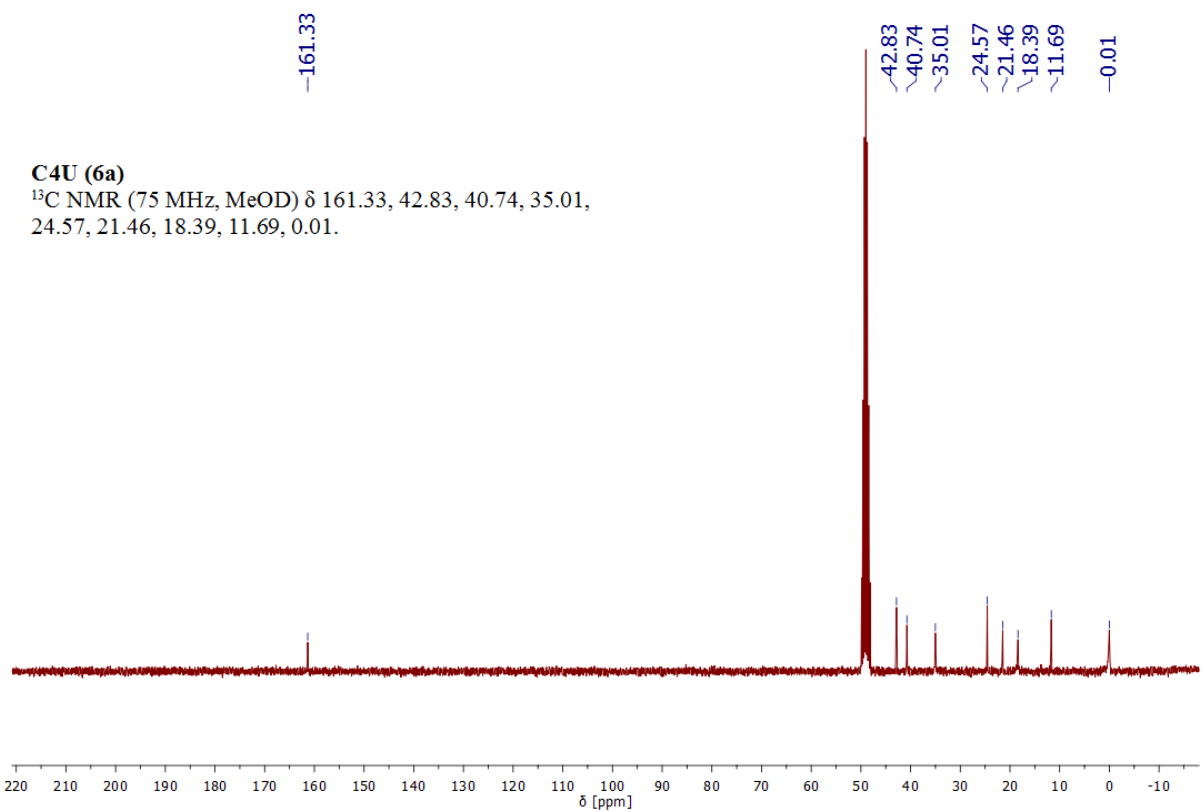
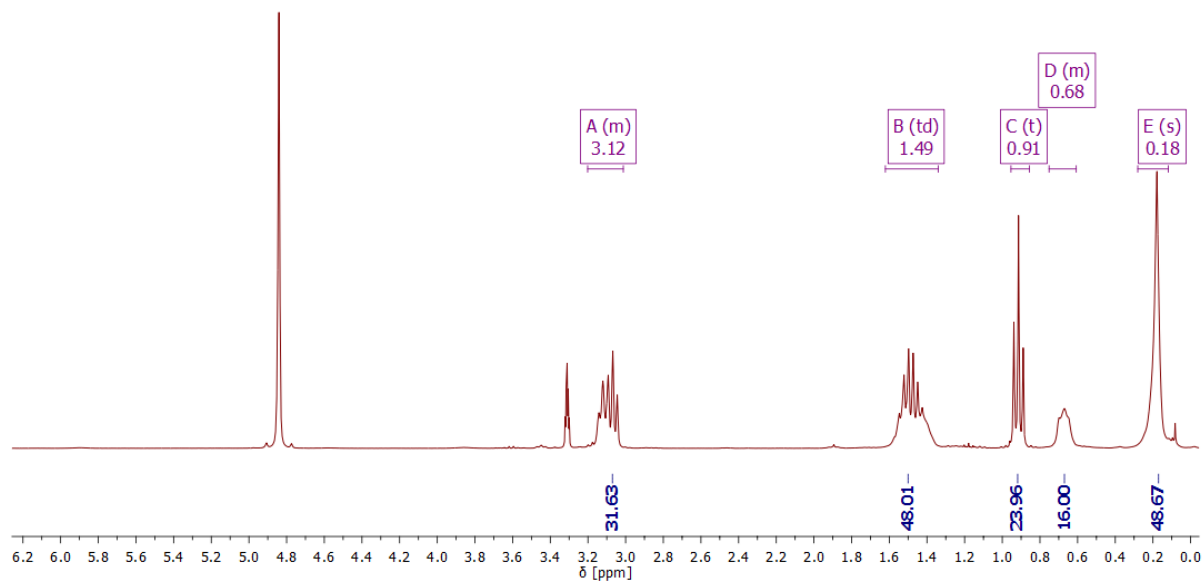
$^{29}\text{Si}$  NMR (60 MHz, MeOD)  $\delta$  13.01, -108.63.



## C4Urea (6a)

### C4U (6a)

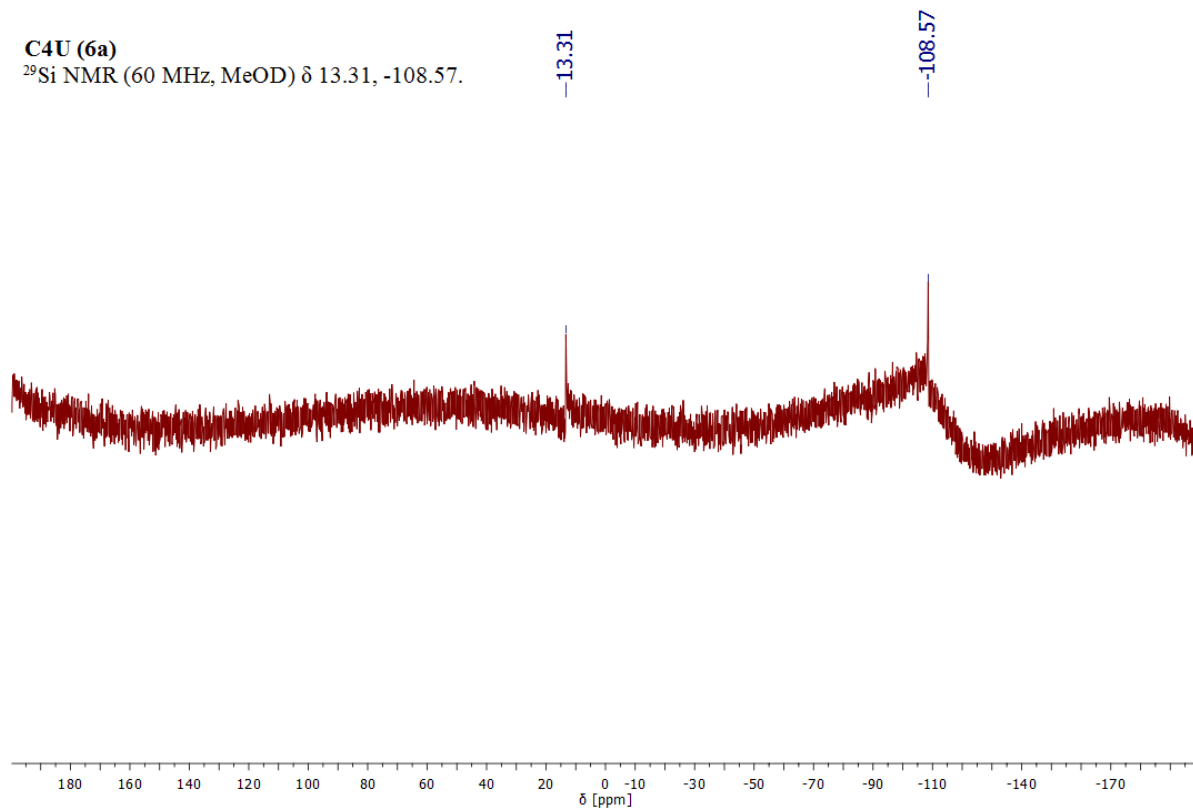
$^1\text{H}$  NMR (300 MHz, MeOD)  $\delta$  3.20 – 3.01 (m, 32H), 1.49 (td,  $J = 14.6, 7.3$  Hz, 48H), 0.91 (t,  $J = 7.4$  Hz, 24H), 0.75 – 0.61 (m, 16H), 0.18 (s, 48H).



### C4U (6a)

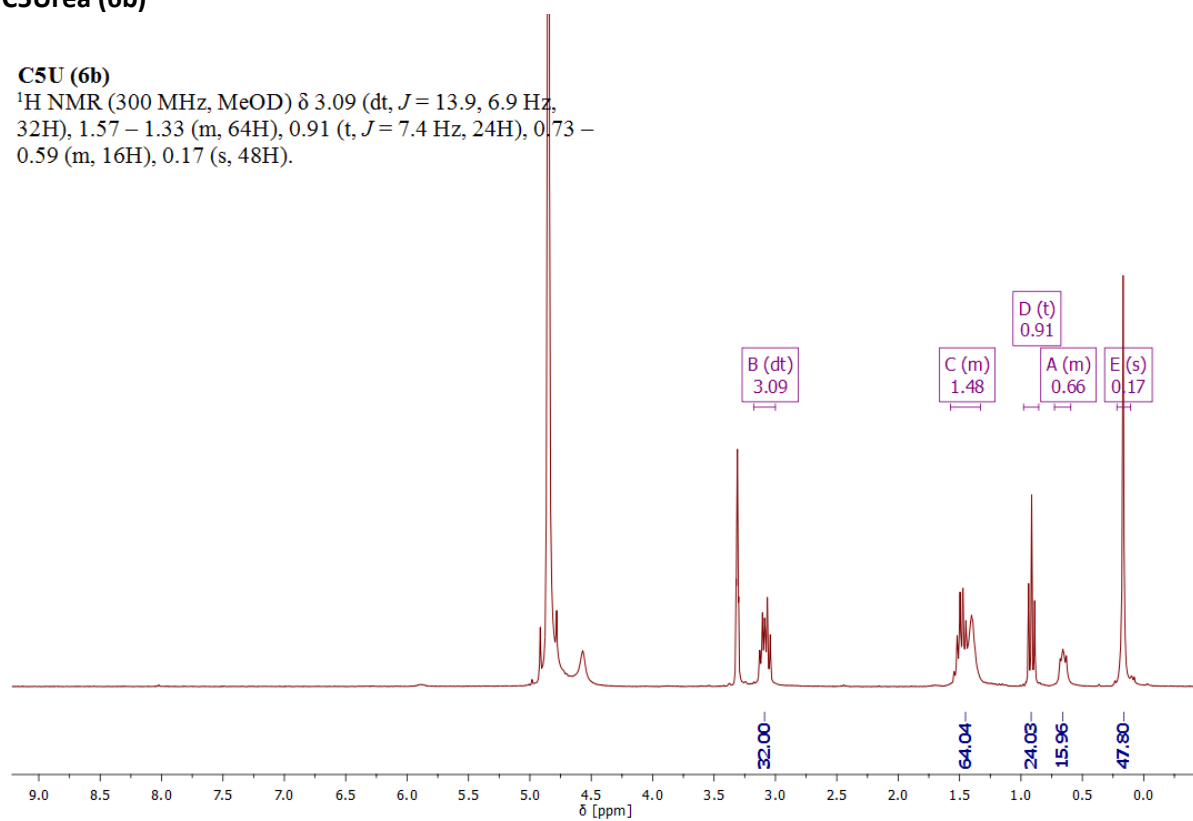
$^{13}\text{C}$  NMR (75 MHz, MeOD)  $\delta$  161.33, 42.83, 40.74, 35.01, 24.57, 21.46, 18.39, 11.69, 0.01.

**C4U (6a)**  
<sup>29</sup>Si NMR (60 MHz, MeOD) δ 13.31, -108.57.

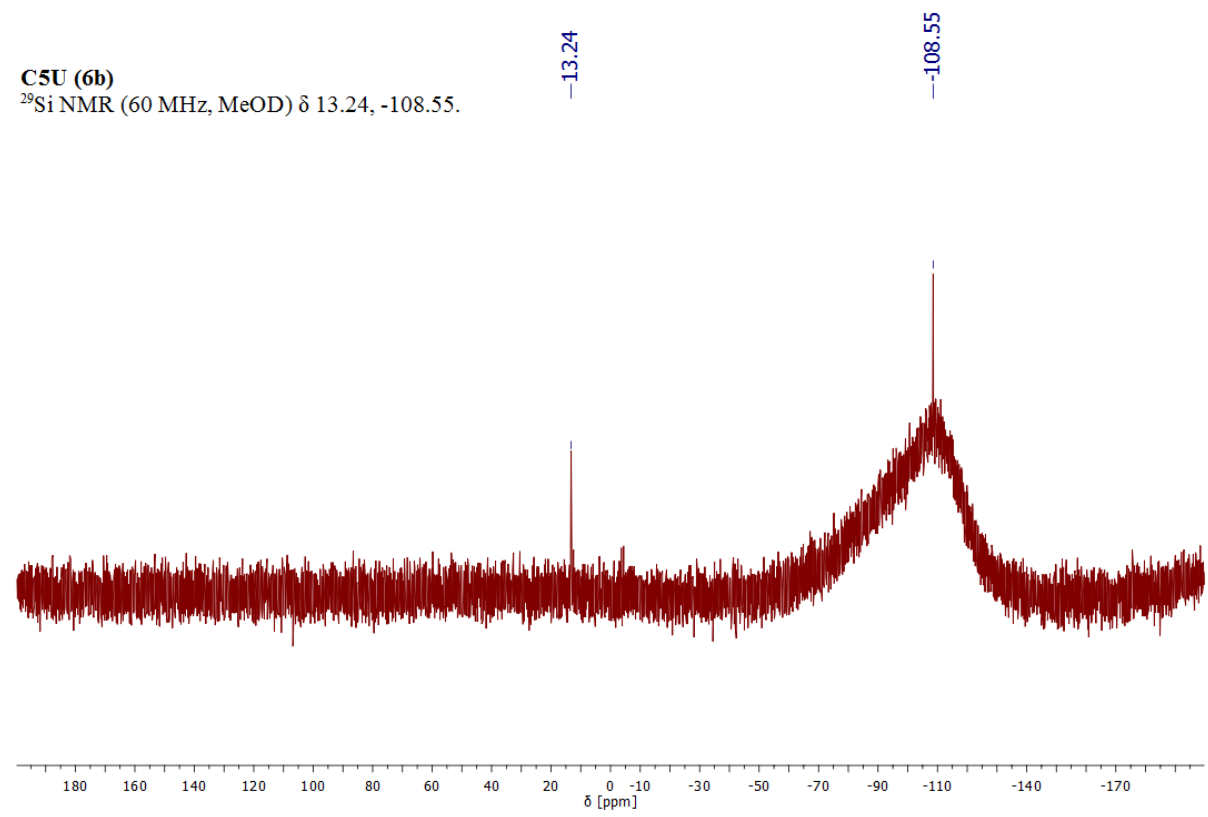
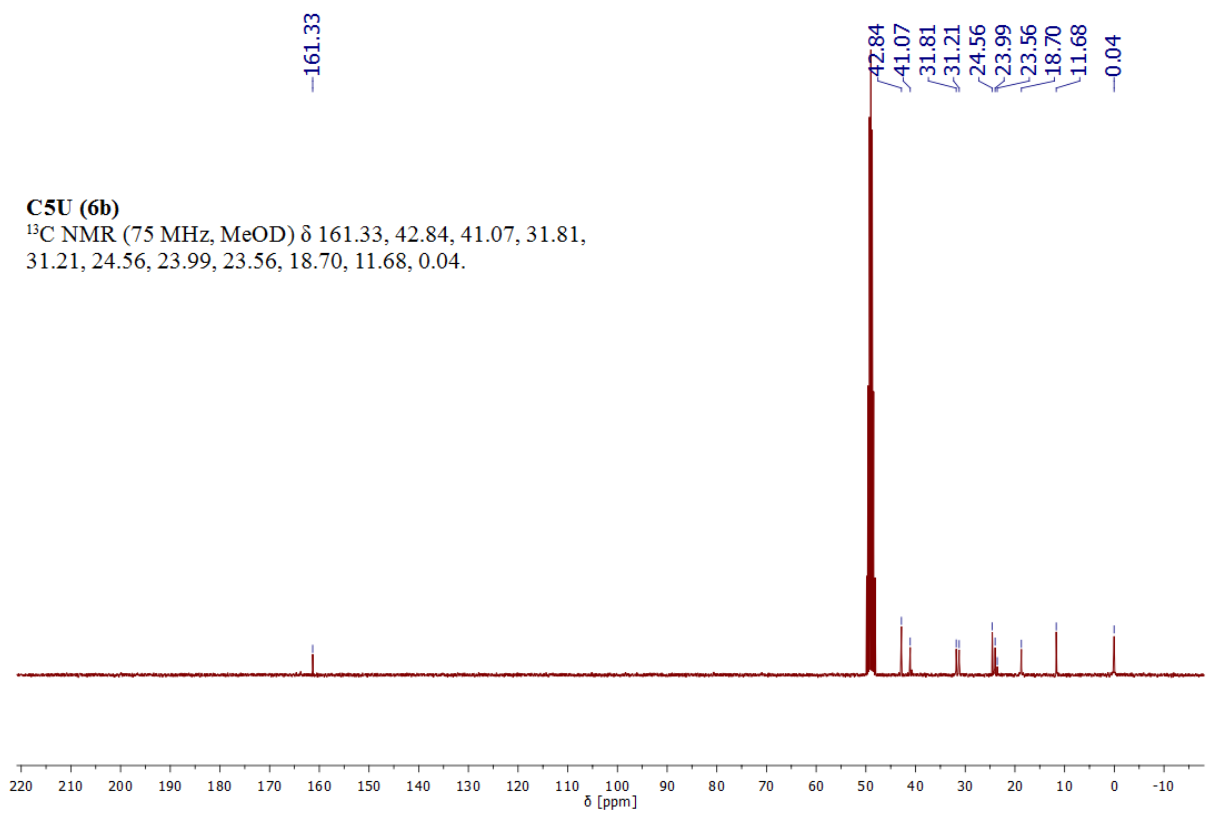


**C5Urea (6b)**

**C5U (6b)**  
<sup>1</sup>H NMR (300 MHz, MeOD) δ 3.09 (dt, *J* = 13.9, 6.9 Hz, 32H), 1.57 – 1.33 (m, 64H), 0.91 (t, *J* = 7.4 Hz, 24H), 0.73 – 0.59 (m, 16H), 0.17 (s, 48H).



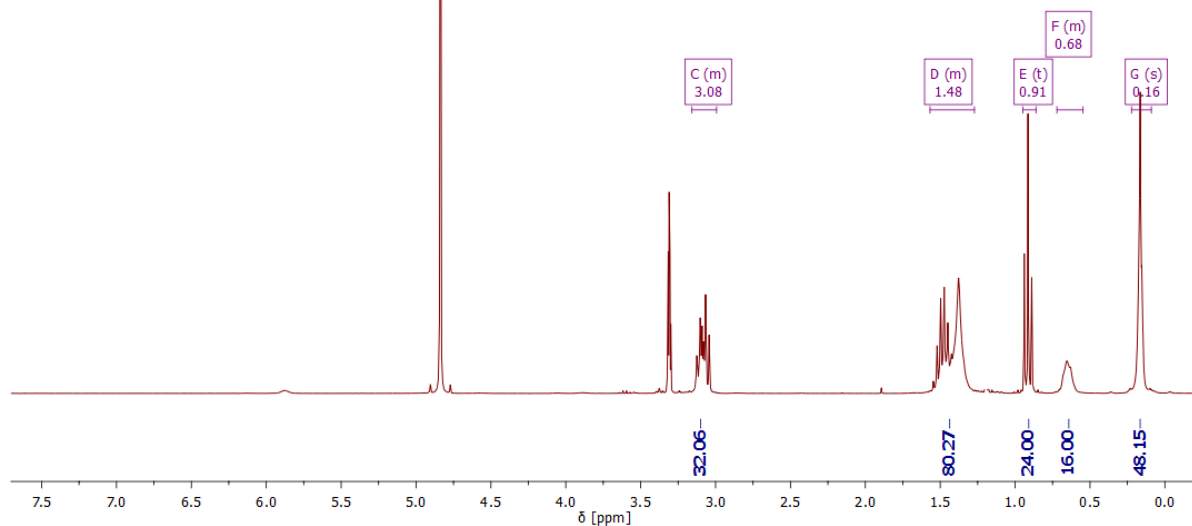




## C6Urea (6c)

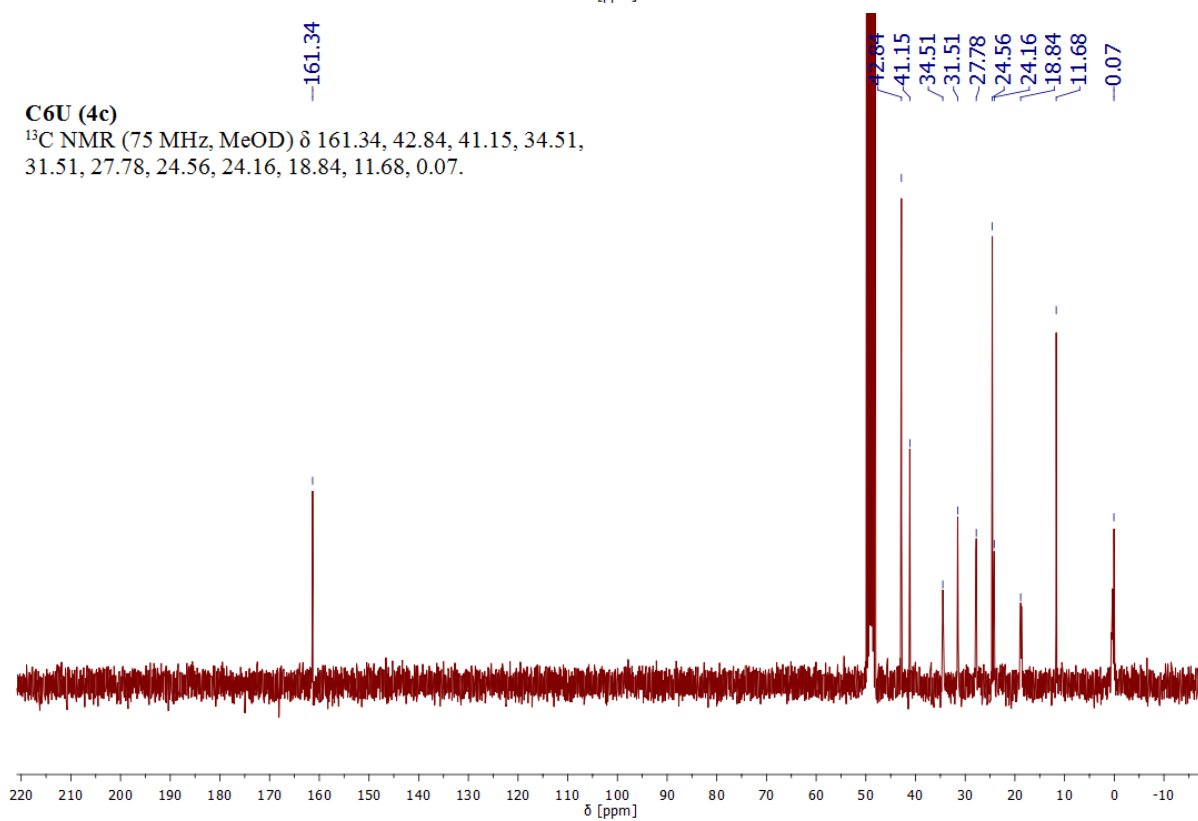
### C6U (6c)

$^1\text{H}$  NMR (300 MHz, MeOD)  $\delta$  3.16 – 2.99 (m, 32H), 1.57 – 1.27 (m, 80H), 0.91 (t,  $J = 7.4$  Hz, 24H), 0.72 – 0.55 (m,  $J = 14.7$  Hz, 16H), 0.16 (s, 48H).



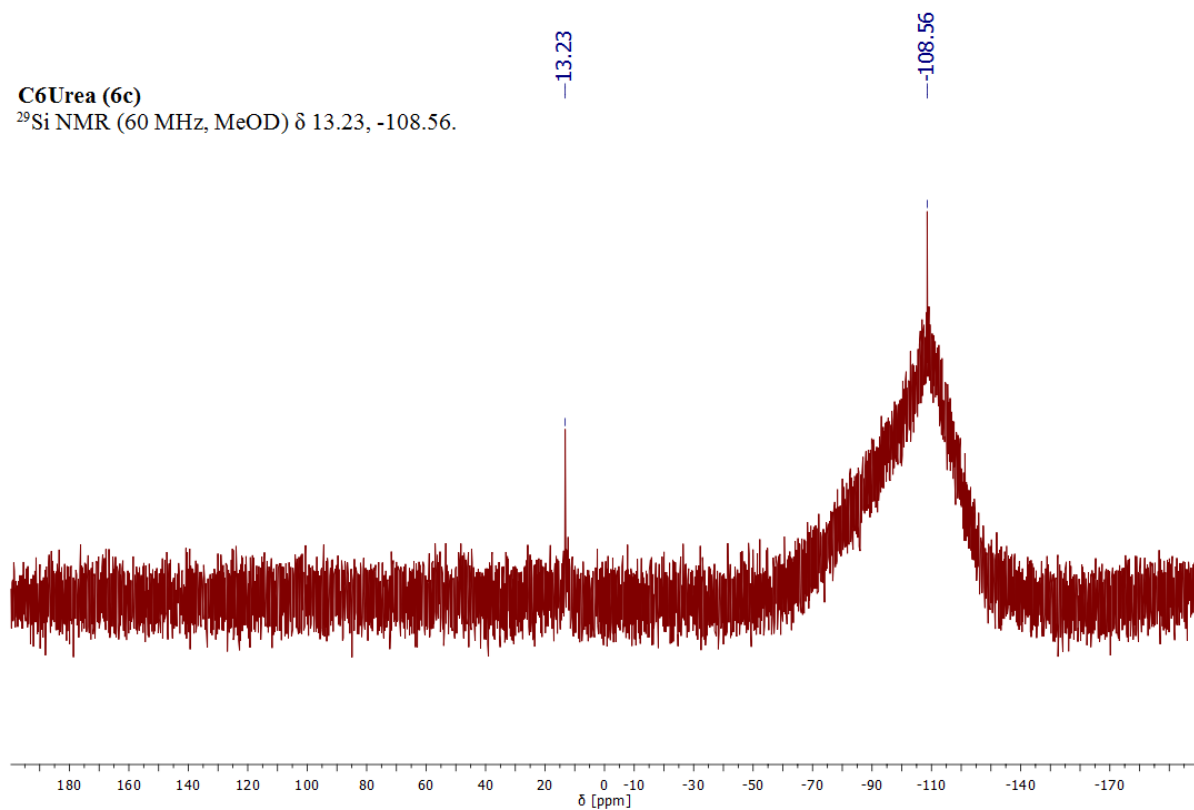
### C6U (4c)

$^{13}\text{C}$  NMR (75 MHz, MeOD)  $\delta$  161.34, 42.84, 41.15, 34.51, 31.51, 27.78, 24.56, 24.16, 18.84, 11.68, 0.07.



**C6Urea (6c)**

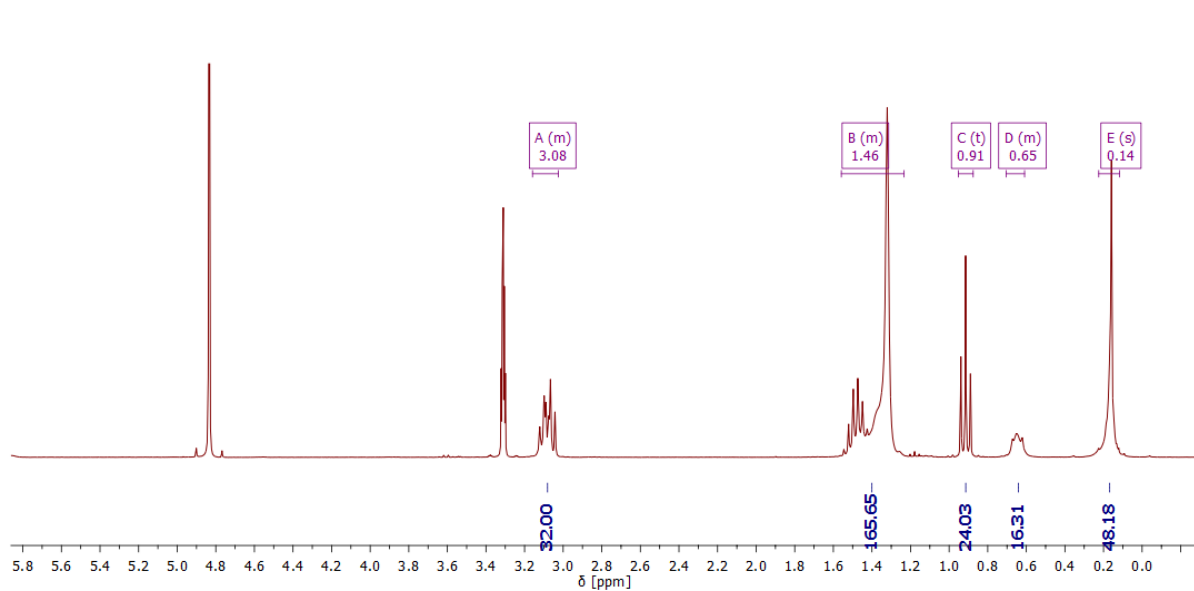
$^{29}\text{Si}$  NMR (60 MHz, MeOD)  $\delta$  13.23, -108.56.

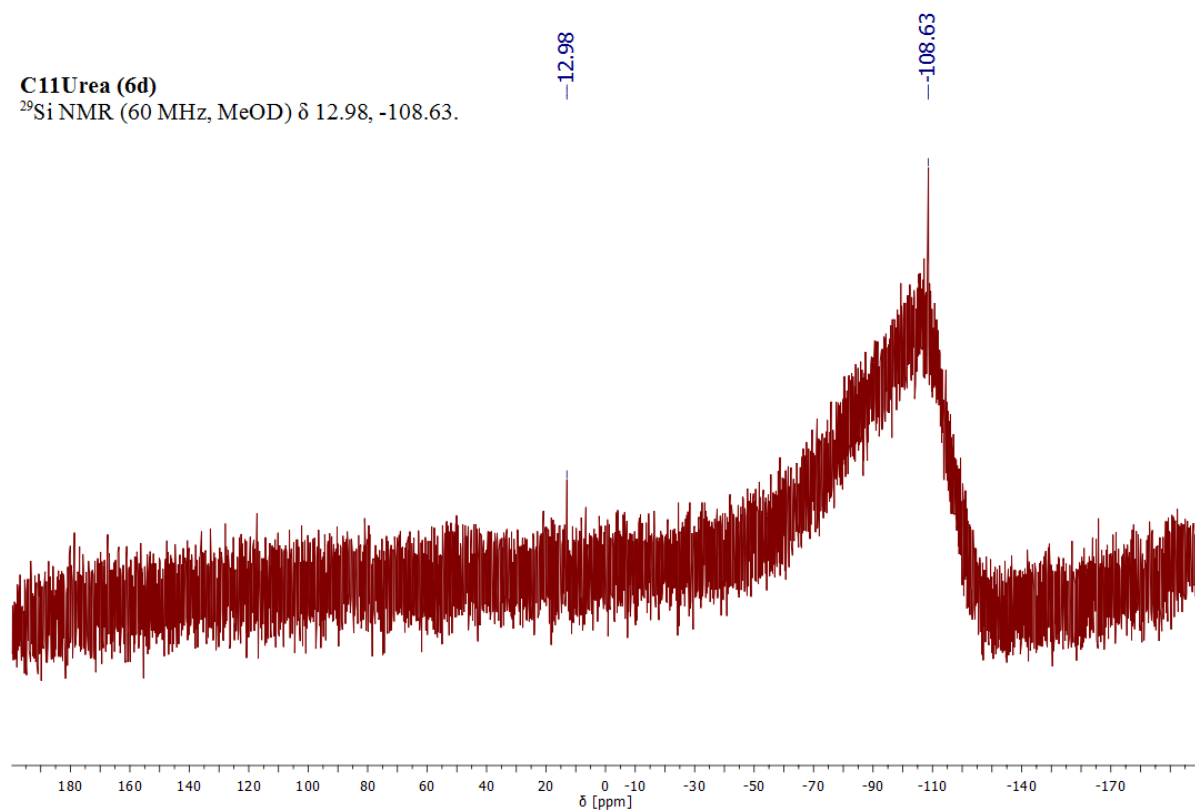
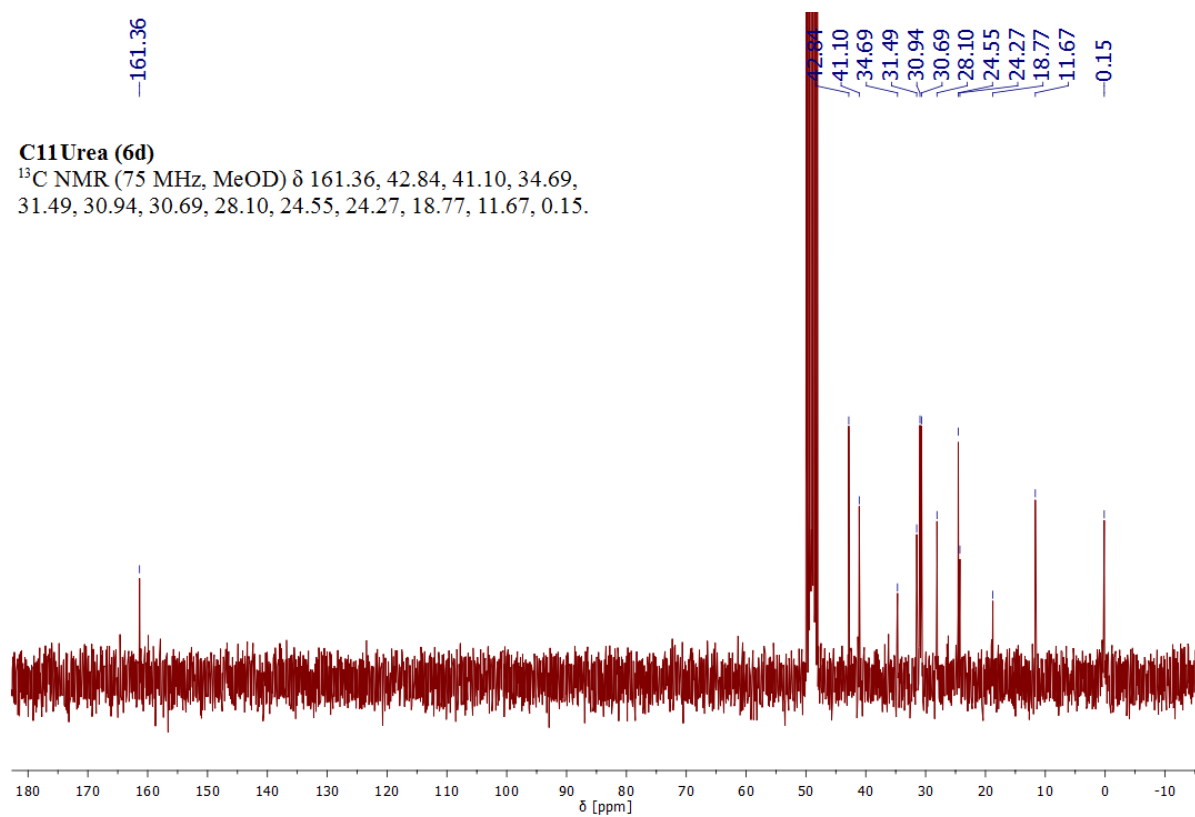


**C11Urea (6d)**

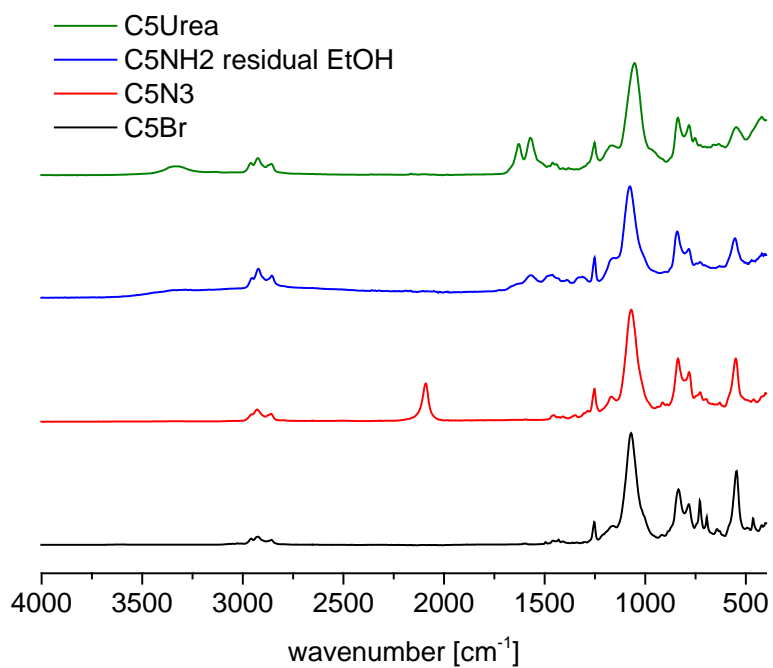
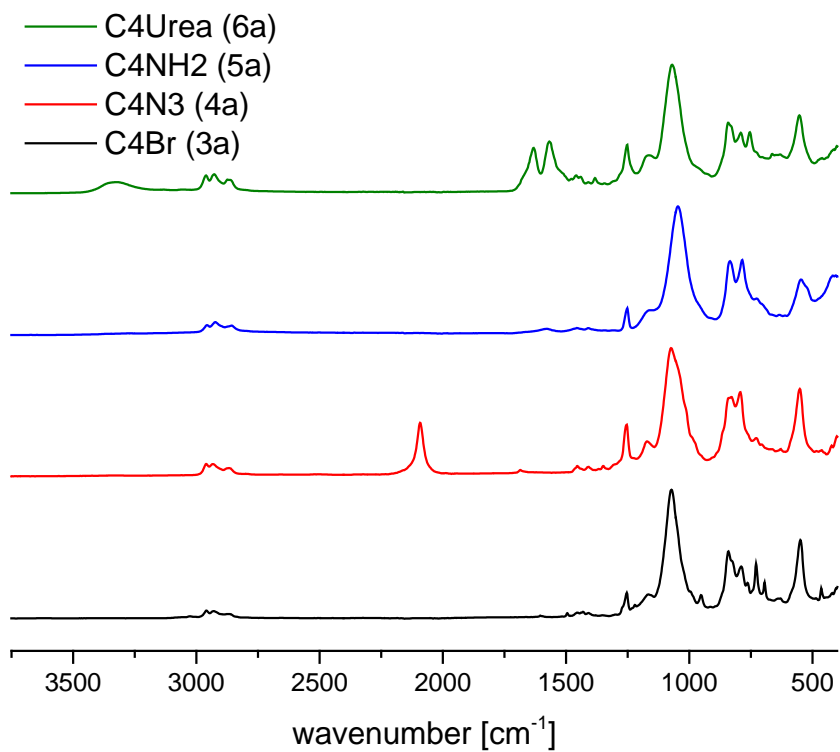
**C11Urea (6d)**

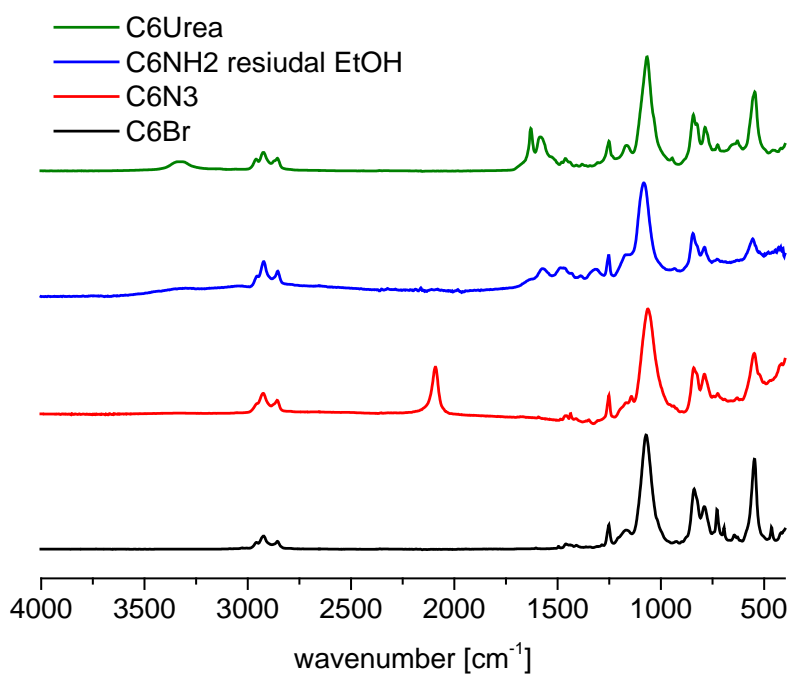
$^1\text{H}$  NMR (300 MHz, MeOD)  $\delta$  3.16 – 3.03 (m,  $J=9.7, 7.0$  Hz, 32H), 1.56 – 1.23 (m, 160H), 0.91 (t,  $J=7.4$  Hz, 24H), 0.70 – 0.61 (m, 16H), 0.14 (s, 48H).





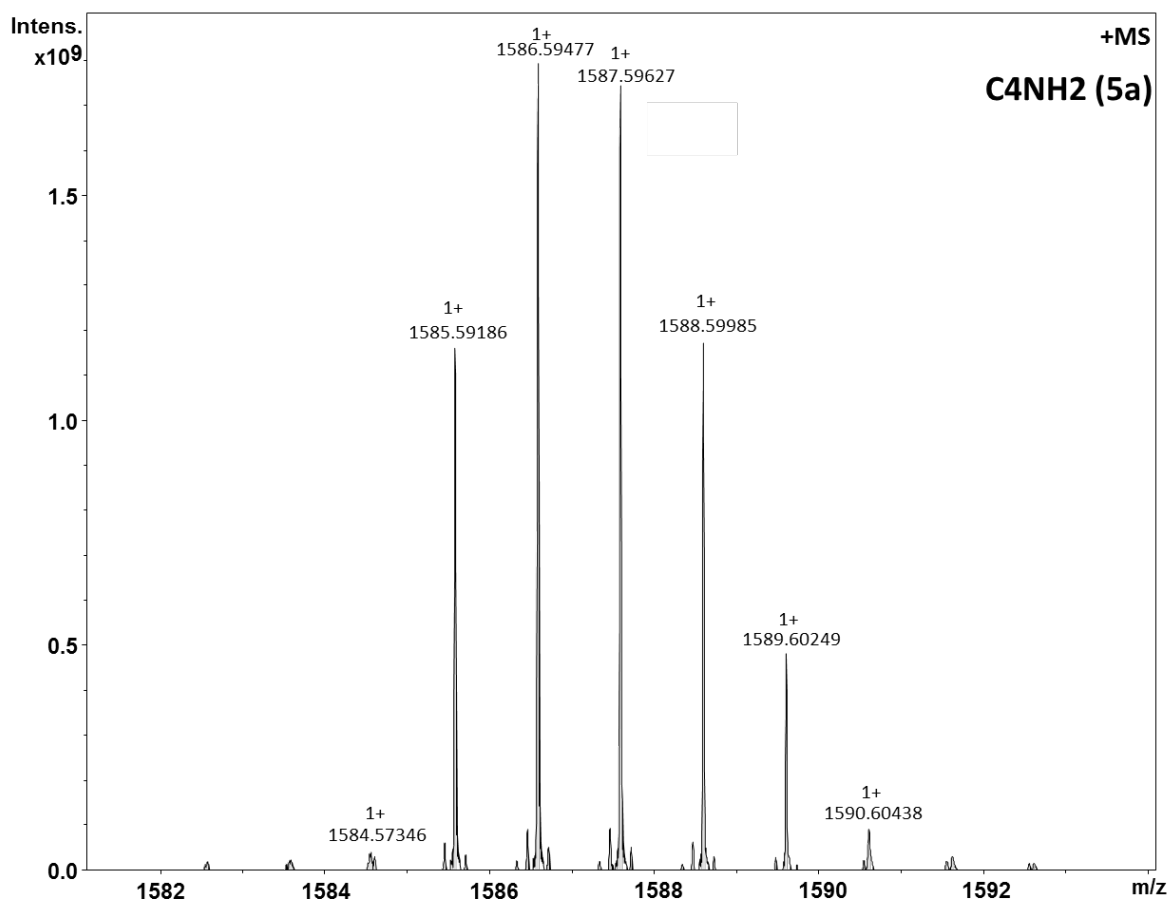
# IR spectroscopy



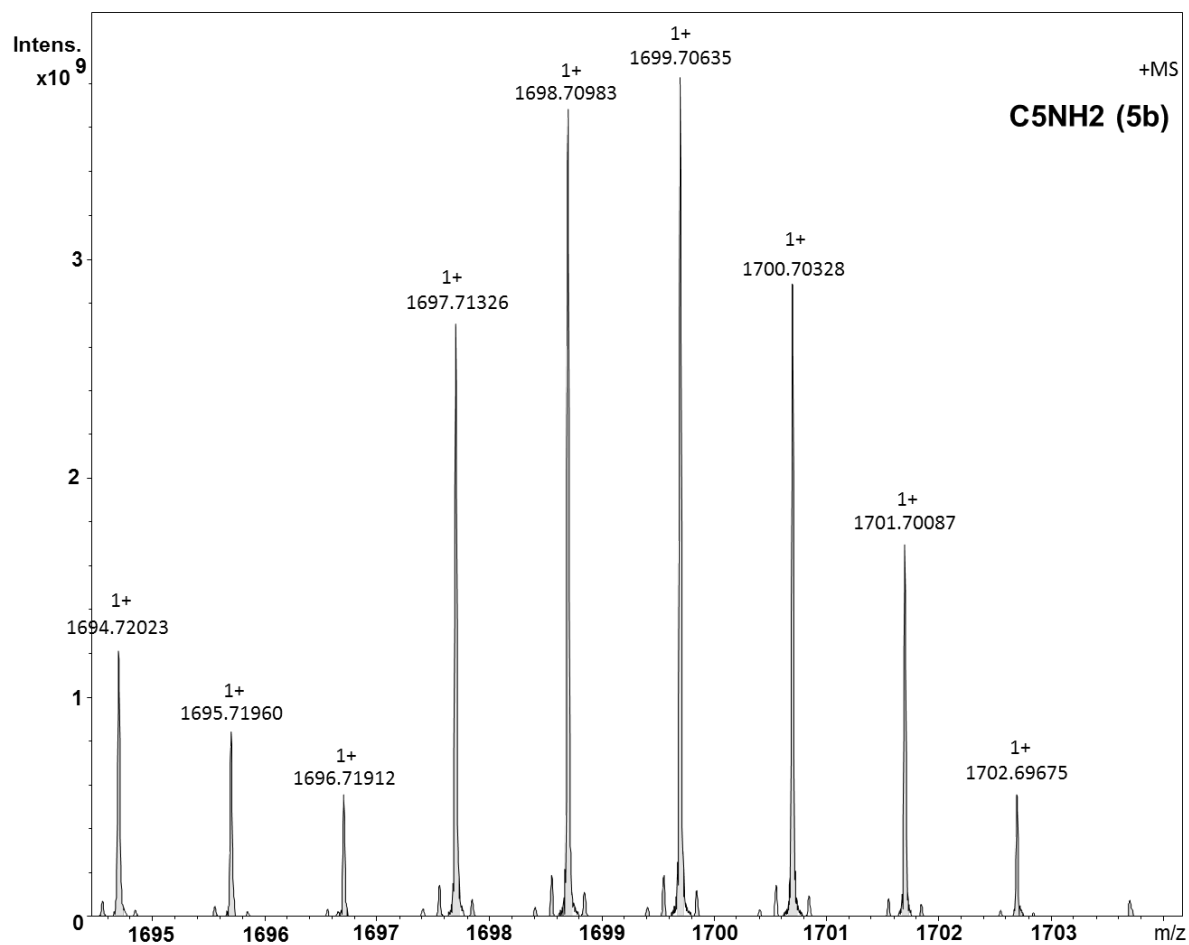


ESI- MS spectra

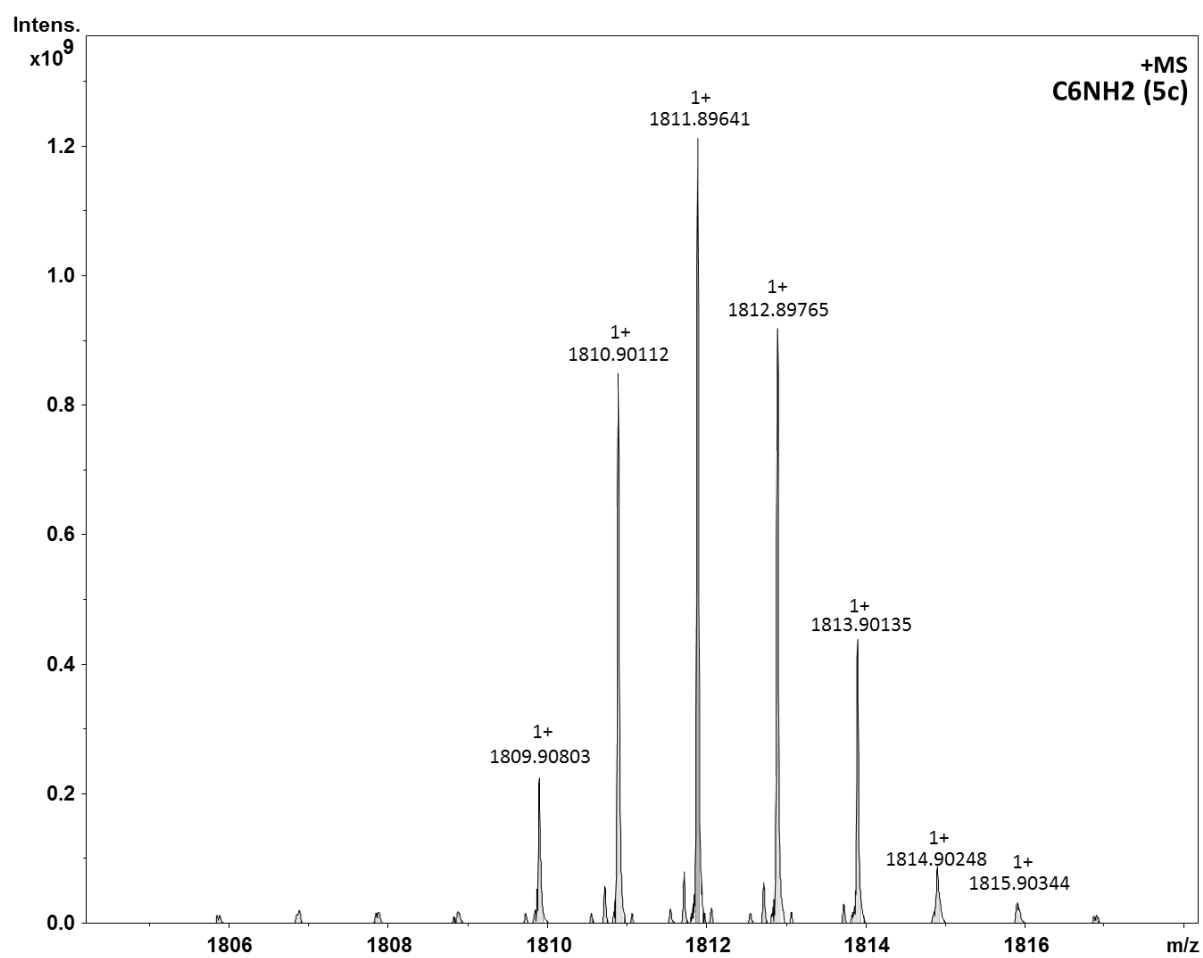
C4NH2 (5a)



**C5NH2 (5b)**

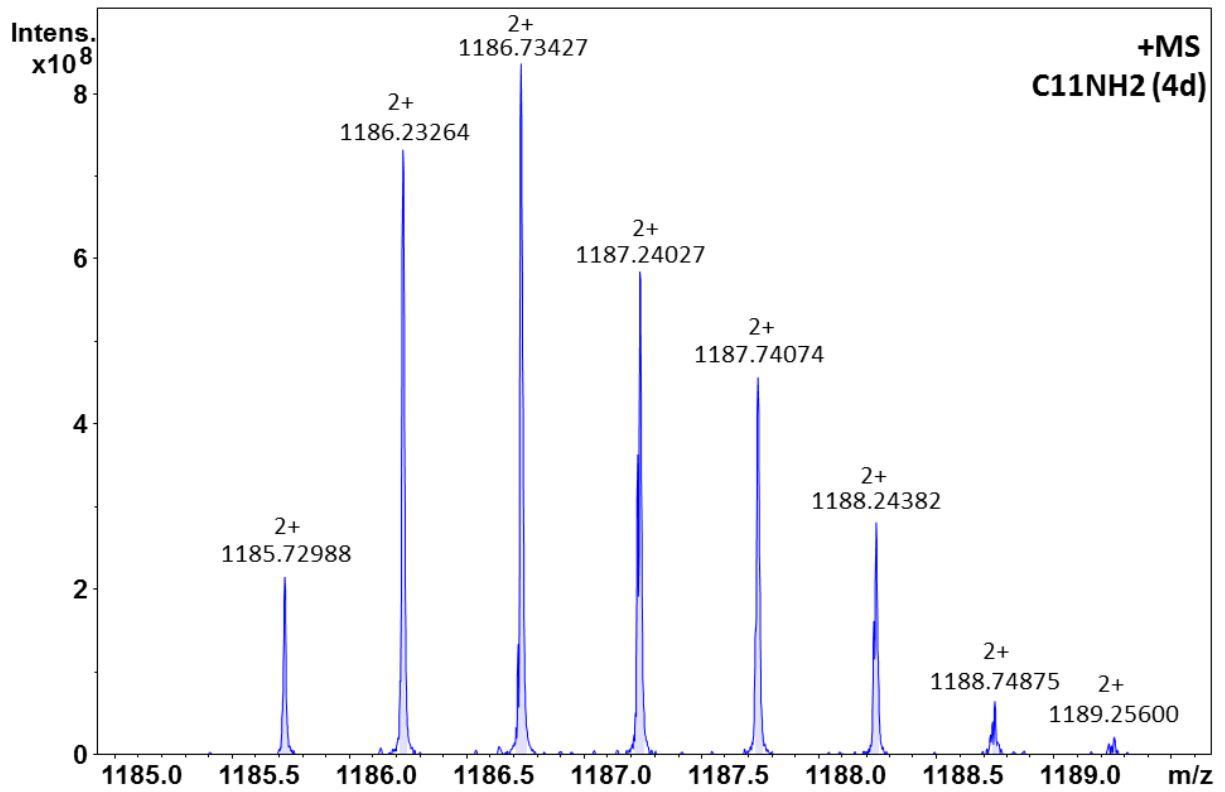


### C6NH2 (5c)

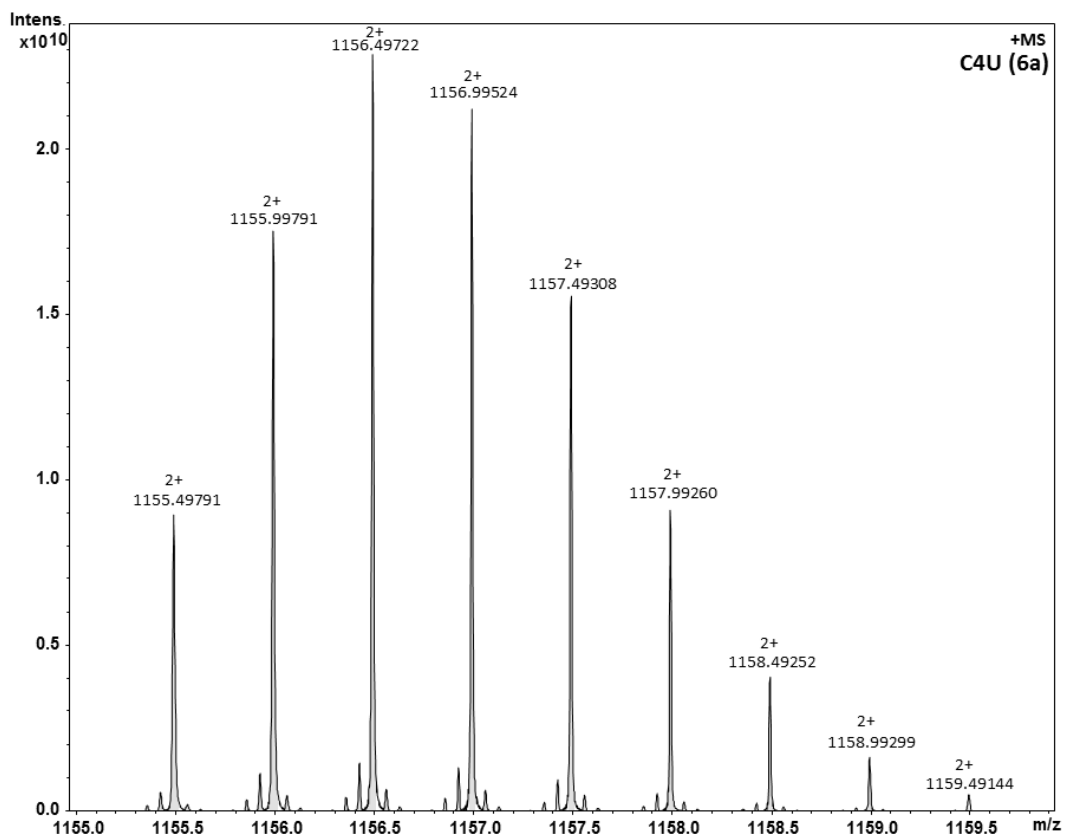


### C11 Amin

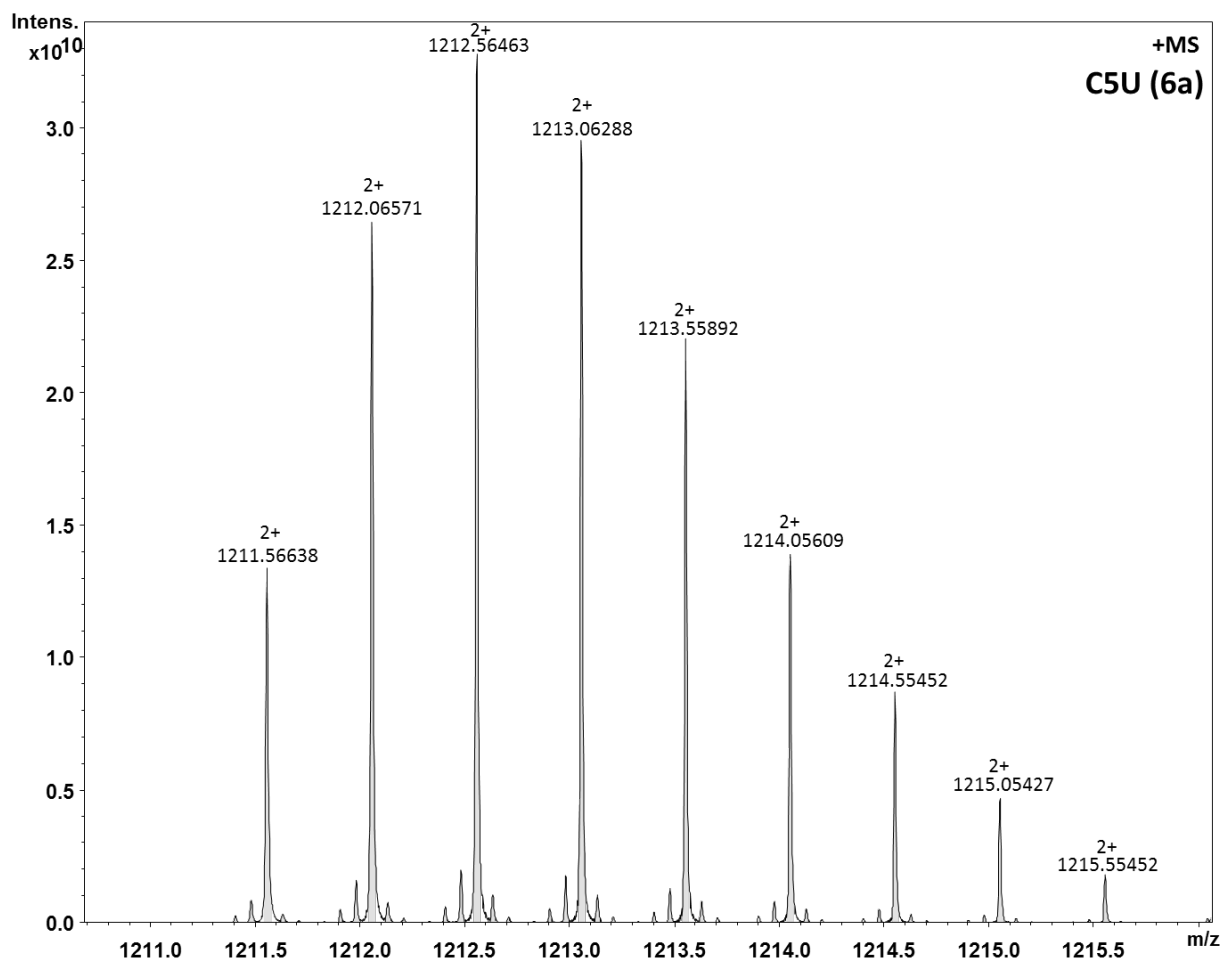




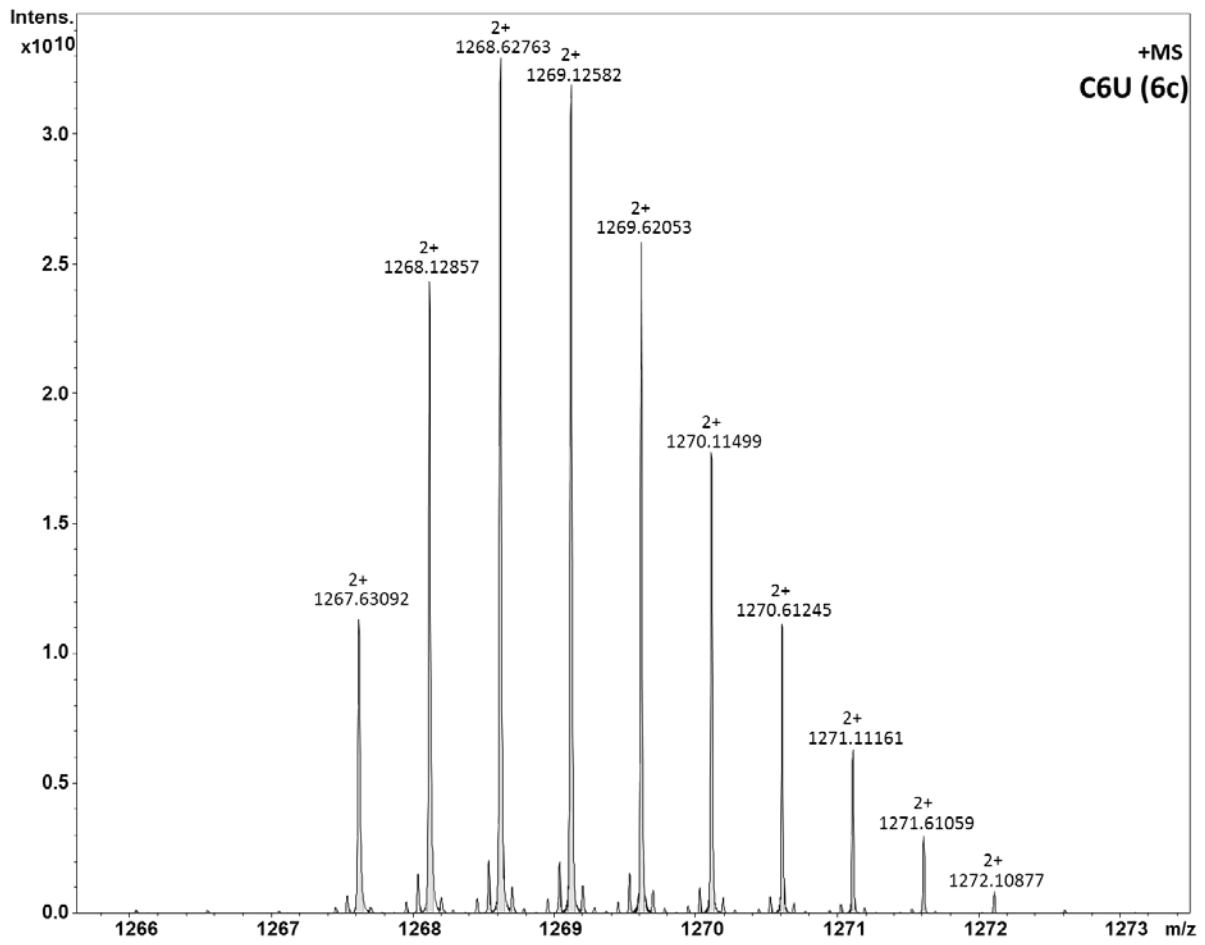
**C4 Urea (6a)**



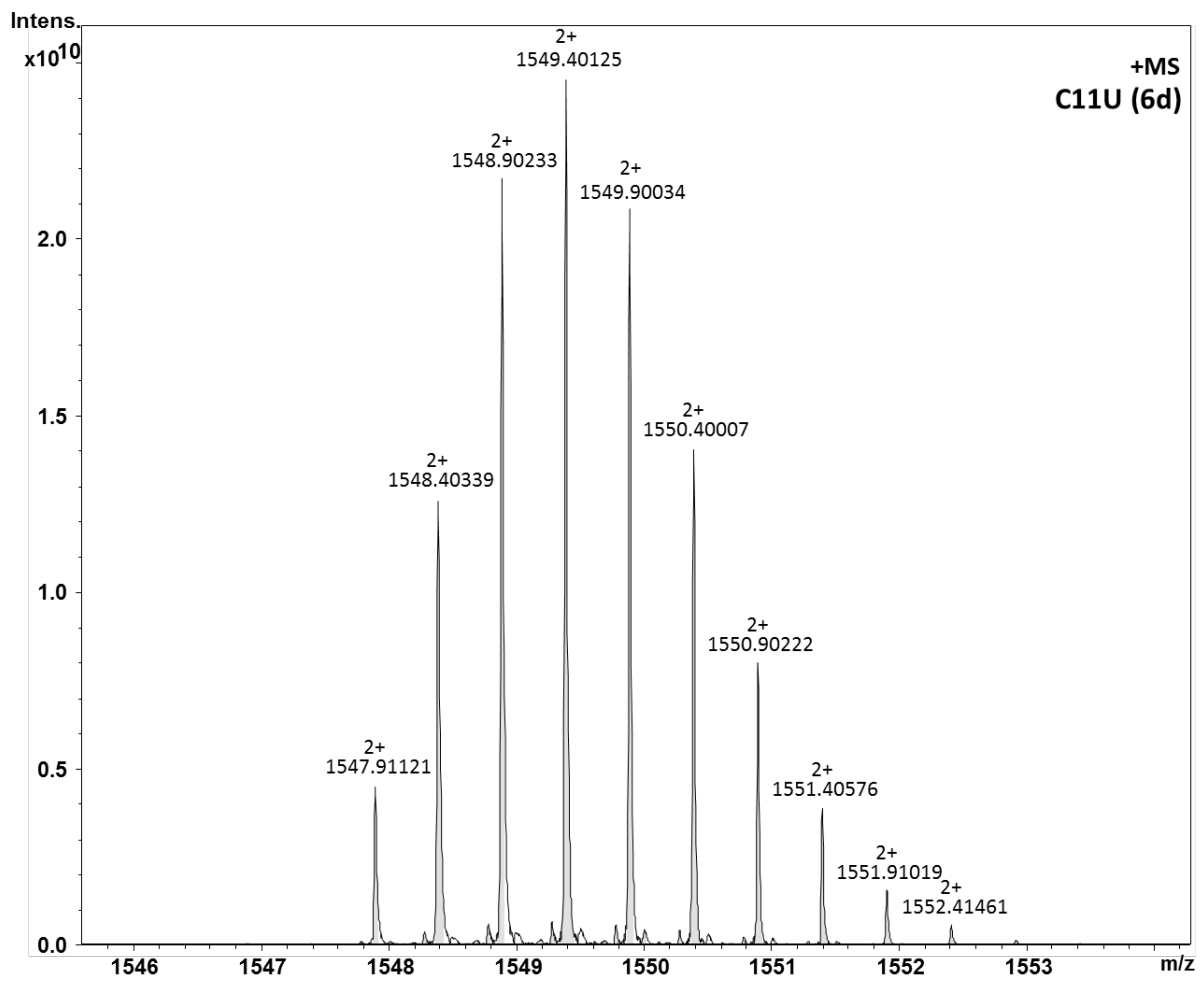
### C5 Urea (6b)



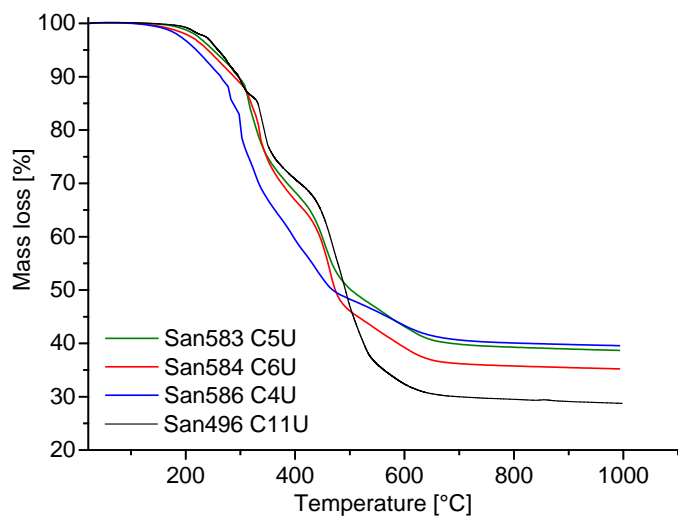
### C6 Urea (6c)



C11 Urea (6d)



**TG curves**



	T <sub>5%</sub> [°C]	Onset [°C]	m <sub>residual mass</sub> [%]
<b>C4</b>	217	167	39.58
<b>C5</b>	247	181	38.69
<b>C6</b>	237	198	35.22
<b>C11</b>	259	204	28.76

**Remark:** Measurements were conducted under N<sub>2</sub>, therefore the residual mass corresponds not to value of inorganic part. Measurements were conducted to determine thermal stability.

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<sup>i</sup> Lübbe C., Dumrath A., Neumann H., Beller M., Kadyrov R., *ChemCatChem* **2014**, *6*, 105-108.

<sup>ii</sup> Kobayashi Y., Nakano M., Kumar G.B., Kishihara K., *J. Org. Chem.* **1998**, *63*, 7505-7515.

<sup>iii</sup> a) Dutkiewicz M., Maciejewski H., Marciniec B., Karasiewicz J., *Organomet.* **2011**, *30*, 2149-2153; b) Hasegawa I., Motojima S., *J. Organomet. Chem.* **1992**, *441*, 373-380.