

## 4-(Propargylthio)sydnone imines: synthesis and reactivity in the azide–alkyne cycloaddition

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### Experimental Section

General Remarks: NMR spectra were recorded on the Bruker Avance™400 spectrometer with an operating frequency of 400.13 MHz for <sup>1</sup>H, 100.62 MHz for <sup>13</sup>C and 161.96 MHz for <sup>31</sup>P, on the Bruker AvanceIIIHD-500 NMR (500.13 MHz for <sup>1</sup>H, 125.78 MHz for <sup>13</sup>C). Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as an internal standard (deuteriochloroform:  $\delta$  7.28 ppm for <sup>1</sup>H and 77.0 ppm for <sup>13</sup>C, dimethyl sulfoxide:  $\delta$  2.50 ppm for <sup>1</sup>H and 39.5 ppm for <sup>13</sup>C). Data are reported as follows: chemical shifts ( $\delta$ ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (*J*, Hz). Orthophosphoric acid was used as an internal standard in the <sup>31</sup>P spectra. Elemental analyses (excepting Fe) were performed using the Carlo-Erba CE-1106 elemental analyzer; the contents of Fe were determined by the X-ray fluorescence (XRF) method using the VRA-30 XRF-spectrometer. Melting points were determined with an Electrothermal 1002 MEL-TEMP® capillary melting point apparatus and are uncorrected. All reactions with organometallic compounds were carried out in an atmosphere of dry argon in absolute solvents (THF was distilled over sodium-benzophenone ketyl). The reactions were monitored by the thin-layer chromatography on Pre-coated sheets ALUGRAM Xtra SIL G/UV<sub>254</sub> (MACHEREY-NAGEL, Germany) plates, and spots were visualized by UV light at 254 nm and in camera with iodine. The column chromatography on SiO<sub>2</sub> 30–70 mesh was used for the routine purification of reaction products. All commercially available ABCR and Aldrich reagents were used without preliminary purification. The starting unsubstituted sydnone imines **1** were prepared as described in articles<sup>S1,S2</sup>.

#### Synthesis of 2-azidoethyl (*S*)-5-(1,2-dithiolan-3-yl)pentanoate [(*S*)-lipoic acid 2-azidoethyl ester]

A solution of 2-azidoethanol (3 mmol) and lipoic acid (3 mmol) in dichloromethane (40 mL) was cooled to 0°C, and *N,N'*-dicyclohexylcarbodiimide (3 mmol) and DMAP (2.1 mmol) were added under stirring. After 30 min, the reaction mixture was allowed to warm to room temperature and stirred for an additional 18 h. Upon completion, the organic layer was washed with water (3 × 20 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The crude product was obtained as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  4.28 (t, *J* = 5.3 Hz, 2H), 3.66 – 3.55 (m, 1H), 3.50 (t, *J* = 5.3 Hz, 2H), 3.25 – 3.10 (m, 2H), 2.55 – 2.44 (m, 1H), 2.40 (t, *J* = 7.4 Hz, 2H), 1.96 – 1.89 (m, 1H), 1.78 – 1.67 (m, 4H), 1.56 – 1.44 (m, 2H).

### General procedure for the synthesis of 4-(propargylthio)sydnone imines (**3**)

To a solution of unsubstituted sydnone imine **1** (2 mmol) in dry THF (60 mL), under an argon atmosphere, a *n*-BuLi solution in hexane (2.7 M, 2 mmol) and elemental sulfur solution in toluene (0.0078 M, 2 mmol) were sequentially added at 10 min intervals at  $-80^{\circ}\text{C}$ . The reaction mixture was heated on a bath to  $-20^{\circ}\text{C}$ . Propargyl bromide (2.4 mmol) was added, and the reaction mixture was stirred for 20 min at room temperature. The solvent was evaporated at reduced pressure; the residue was purified by column chromatography ( $\text{SiO}_2$ , 2x15 cm, ethyl acetate/dichloromethane from 1:10 to 1:1). The products **3** were recrystallized from a toluene/petroleum ether in a ratio of 1:3 v/v.

#### *N*<sup>6</sup>-(*tert*-Butoxycarbonyl)-3-isopropyl-4-(propargylthio)sydnone imine (**3a**).

Yield 83%, beige crystals, m.p. 148–149 $^{\circ}\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.32 (hept,  $J = 6.8$  Hz, 1H,  $\text{CH}(\text{CH}_3)_2$ ), 3.58 (d,  $J = 2.5$  Hz, 2H,  $\text{SCH}_2$ ), 2.26 (t<sub>br</sub>,  $J = 2.5$  Hz, 1H,  $\text{C}\equiv\text{CH}$ ), 1.66 (d,  $J = 6.8$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ), 1.53 (s, 9H,  $\text{C}(\text{CH}_3)_3$ ).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.0, 158.9, 103.6, 79.4, 79.2, 72.9, 56.7, 28.2, 22.6, 21.9. Anal. Calc. for  $\text{C}_{13}\text{H}_{19}\text{N}_3\text{O}_3\text{S}$ : C, 52.51; H, 6.44; N, 14.13; S, 10.78%. Found: C, 52.39; H, 6.51; N, 14.03; S, 10.82%.

#### *N*<sup>6</sup>-Benzoyl-3-isopropyl-4-(propargylthio)sydnone imine (**3b**).

Yield 77%, light brown crystals, m.p. 99–101 $^{\circ}\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.33 – 8.24 (m, 2H, *o*- $\text{C}_6\text{H}_5$ ), 7.53 – 7.40 (m, 3H, *m,p*- $\text{C}_6\text{H}_5$ ), 5.35 (hept,  $J = 6.7$  Hz, 1H,  $\text{CH}(\text{CH}_3)_2$ ), 3.79 (d,  $J = 2.5$  Hz, 2H,  $\text{SCH}_2$ ), 2.28 (t,  $J = 2.5$  Hz, 1H,  $\text{C}\equiv\text{CH}$ ), 1.71 (d,  $J = 6.8$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.9, 167.9, 137.1, 131.6, 129.7, 128.0, 105.7, 79.1, 73.0, 57.0, 22.05, 21.96. Anal. Calc. for  $\text{C}_{15}\text{H}_{15}\text{N}_3\text{O}_2\text{S}$ : C, 59.78; H, 5.02; N, 13.94; S, 10.64%. Found: C, 59.82; H, 5.13; N, 14.05; S, 10.75%.

#### 3-Isopropyl-4-(propargylthio)-*N*<sup>6</sup>-tosylsydnone imine (**3c**).

Yield 67%, light brown crystals, m.p. 166–167 $^{\circ}\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (d,  $J = 8.0$  Hz, 2H) and 7.29 (d,  $J = 8.0$  Hz, 2H,  $\text{C}_6\text{H}_4\text{CH}_3$ ), 5.28 (hept,  $J = 6.8$  Hz, 1H,  $\text{CH}(\text{CH}_3)_2$ ), 3.61 (d,  $J = 2.6$  Hz, 2H,  $\text{SCH}_2$ ), 2.41 (s, 3H,  $\text{C}_6\text{H}_4\text{CH}_3$ ), 2.26 (t,  $J = 2.6$  Hz, 1H,  $\text{C}\equiv\text{CH}$ ), 1.66 (d,  $J = 6.7$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.6, 142.7, 139.4, 129.2, 127.2, 104.8, 78.6, 73.4, 57.6, 22.4, 21.9, 21.6. Anal. Calc. for  $\text{C}_{15}\text{H}_{17}\text{N}_3\text{O}_3\text{S}_2$ : C, 51.26; H, 4.88; N, 11.96; S, 18.24%. Found: C, 51.13; H, 5.02; N, 12.07; S, 18.29%.

#### 3-(Adamantan-1-yl)-*N*<sup>6</sup>-(*tert*-butoxycarbonyl)-4-(propargylthio)sydnone imine (**3d**).

Yield 74%, light brown crystals, m.p. 154–155 $^{\circ}\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.83 (d,  $J = 2.6$  Hz, 2H,  $\text{SCH}_2$ ), 2.57 – 2.46 (m, 6H) and 2.35 – 2.29 (m, 3H, 1-Ad), 2.21 (t,  $J = 2.6$  Hz, 1H,  $\text{C}\equiv\text{CH}$ ), 1.83 – 1.76 (m, 6H, 1-Ad), 1.52 (s, 9H,  $\text{C}(\text{CH}_3)_3$ ).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.8, 158.9, 103.5, 79.0, 78.5, 73.1, 71.1, 40.7, 35.4, 29.6, 28.2, 21.2. Anal. Calc. for  $\text{C}_{20}\text{H}_{27}\text{N}_3\text{O}_3\text{S}$ : C, 61.67; H, 6.99; N, 10.79; S, 8.23%. Found: C, 61.73; H, 7.13; N, 10.91; S, 8.27%.

#### *N*<sup>6</sup>-(*tert*-Butoxycarbonyl)-3-(1-piperidinyl)-4-(propargylthio)sydnone imine (**3e**).

Yield 60%, brown crystals, m.p. 133–134 $^{\circ}\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.68 (d,  $J = 2.7$  Hz, 2H,  $\text{SCH}_2$ ), 3.48 – 3.37 (m, 4H,  $\text{CH}_2\text{NCH}_2$ ), 2.22 (t,  $J = 2.6$  Hz, 1H,  $\text{C}\equiv\text{CH}$ ), 1.93 – 1.84 (m, 4H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 1.67 – 1.59 (m, 2H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 1.53 (s, 9H,  $\text{C}(\text{CH}_3)_3$ ).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.8, 158.7, 103.0, 79.3, 78.6, 72.8, 56.8, 28.2, 25.3, 22.9, 21.7. Anal. Calc. for  $\text{C}_{15}\text{H}_{22}\text{N}_4\text{O}_3\text{S}$ : C, 53.24; H, 6.55; N, 16.56; S, 9.47%. Found: C, 53.41; H, 6.39; N, 16.61; S, 9.49%.

#### *N*<sup>6</sup>-(*tert*-Butoxycarbonyl)-3-(4-methoxyphenyl)-4-(propargylthio)sydnone imine (**3f**).

Yield 59%, brown crystals, m.p. 126–128 $^{\circ}\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 (d,  $J = 9.1$  Hz, 2H) and 7.08 (d,  $J = 9.1$  Hz, 2H,  $\text{CH}_3\text{OC}_6\text{H}_4$ ), 3.91 (s, 3H,  $\text{CH}_3\text{OC}_6\text{H}_4$ ), 3.60 (d,  $J = 2.6$  Hz, 2H,  $\text{SCH}_2$ ), 2.16 (t,  $J = 2.6$  Hz, 1H,  $\text{C}\equiv\text{CH}$ ), 1.55 (s, 9H,  $\text{C}(\text{CH}_3)_3$ ).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.7, 162.6, 158.8, 127.1, 125.4, 114.8, 106.9, 79.5, 78.6, 73.2, 55.9, 28.2, 21.9. Anal. Calc. for  $\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_4\text{S}$ : C, 56.50; H, 5.30; N, 11.63; S, 8.87%. Found: C, 56.59; H, 5.53; N, 11.57; S, 8.91%.

#### *N*<sup>6</sup>-Ferrocenylcarbonyl-3-isopropyl-4-(propargylthio)sydnone imine (**3g**).

Yield 55%, dark orange crystals, m.p. 148–149 $^{\circ}\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.32 (hept,  $J = 6.7$  Hz, 1H,  $\text{CH}(\text{CH}_3)_2$ ), 4.94 (s, 2H), 4.39 (s, 2H) and 4.21 (s, 5H, Fc), 3.87 (d,  $J = 2.6$  Hz, 2H,  $\text{SCH}_2$ ), 2.30 – 2.26 (m, 1H,  $\text{C}\equiv\text{CH}$ ), 1.72 (d,  $J = 6.7$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  178.1, 165.8, 104.4, 79.5, 79.2, 72.9, 70.9, 70.6, 69.7, 56.7, 21.9, 21.5. Anal. Calc. for  $\text{C}_{19}\text{H}_{19}\text{FeN}_3\text{O}_2\text{S}$ : C, 55.76; H, 4.68; Fe, 13.64; N, 10.27; S, 7.83%. Found: C, 55.93; H, 4.84; Fe, 13.60; N, 10.40; S, 7.81%.

*N*<sup>6</sup>-(*tert*-Butoxycarbonyl)-3-dimethylamino-4-(propargylthio)sydnone imine (**3h**).

Yield 65%, brown crystals, m.p. 121–123 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.77 – 3.62 (m, 2H, SCH<sub>2</sub>), 3.26 – 3.09 (m, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 2.32 – 2.18 (m, 1H, C≡CH), 1.53 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.7, 158.5, 102.9, 79.5, 78.6, 73.0, 46.9, 28.2, 21.6. Anal. Calc. for C<sub>12</sub>H<sub>18</sub>N<sub>4</sub>O<sub>3</sub>S: C, 48.31; H, 6.08; N, 18.78; S, 10.75%. Found: C, 48.36; H, 6.26; N, 18.71; S, 10.82%.

*N*<sup>6</sup>-Diphenylphosphoryl-3-isopropyl-4-(propargylthio)sydnone imine (**3i**).

As a solvate of half a toluene molecule. Yield 41%, brown crystals, m.p. 135–137 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.99 – 7.91 (m, 4H, 2 *o*-C<sub>6</sub>H<sub>5</sub>), 7.46 – 7.38 (m, 6H, 2 *m,p*-C<sub>6</sub>H<sub>5</sub>), 7.28 – 7.23 (m, 2H) and 7.23 – 7.13 (m, 3H, 1/2 Tol), 5.23 (hept, *J* = 6.8 Hz, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.67 (d, *J* = 2.5 Hz, 2H, SCH<sub>2</sub>), 2.37 (s, 3H, 1/2 Tol), 2.25 (t, *J* = 2.6 Hz, 1H, C≡CH), 1.62 (d, *J* = 6.7 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.7 (d, *J* = 2.3 Hz), 137.9 (Tol), 136.4 (d, *J* = 130.8 Hz), 131.4 (d, *J* = 9.8 Hz), 130.8 (d, *J* = 2.9 Hz), 129.0 (Tol), 128.2 (Tol), 128.1 (d, *J* = 12.7 Hz), 125.3 (Tol), 103.2 (d, *J* = 13.4 Hz), 79.2, 73.0, 56.9, 22.5, 21.8, 21.5 (Tol). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>) δ 16.0. Anal. Calc. for C<sub>20</sub>H<sub>20</sub>N<sub>3</sub>O<sub>2</sub>PS + 1/2C<sub>7</sub>H<sub>8</sub>: C, 63.64; H, 5.45; N, 9.47; P, 6.98; S, 7.23%. Found: C, 63.59; H, 5.61; N, 9.41; P, 7.06; S, 7.20%.

*N*<sup>6</sup>-(*tert*-Butoxycarbonyl)-3-(morpholin-4-yl)-4-(propargylthio)sydnone imine (**3j**).

Yield 61%, brown crystals, m.p. 126–127 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.01 – 3.93 (m, 4H, CH<sub>2</sub>OCH<sub>2</sub>), 3.71 (d, *J* = 2.6 Hz, 2H, SCH<sub>2</sub>), 3.58 – 3.50 (m, 4H, CH<sub>2</sub>NCH<sub>2</sub>), 2.24 (t, *J* = 2.6 Hz, 1H, C≡CH), 1.53 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.5, 158.5, 102.9, 79.6, 78.7, 73.0, 66.0, 55.6, 28.2, 21.7. Anal. Calc. for C<sub>14</sub>H<sub>20</sub>N<sub>4</sub>O<sub>4</sub>S: C, 49.40; H, 5.92; N, 16.46; S, 9.42%. Found: C, 49.48; H, 6.08; N, 16.52; S, 9.36%.

*N*<sup>6</sup>-Ethoxycarbonyl-3-(morpholin-4-yl)-4-(propargylthio)sydnone imine (**3k**).

Yield 70%, brown crystals, m.p. 107–109 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.17 (q, *J* = 7.1 Hz, 2H, CH<sub>2</sub>CH<sub>3</sub>), 4.00 – 3.83 (m, 4H, CH<sub>2</sub>OCH<sub>2</sub>), 3.71 (d, *J* = 2.6 Hz, 2H, SCH<sub>2</sub>), 3.58 – 3.41 (m, 4H, CH<sub>2</sub>NCH<sub>2</sub>), 2.23 (t, *J* = 2.6 Hz, 1H, C≡CH), 1.29 (t, *J* = 7.1 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.0, 159.1, 103.4, 78.6, 73.1, 66.0, 61.4, 55.6, 21.5, 14.5. Anal. Calc. for C<sub>12</sub>H<sub>16</sub>N<sub>4</sub>O<sub>4</sub>S: C, 46.15; H, 5.16; N, 17.94; S, 10.26%. Found: C, 46.24; H, 5.01; N, 18.09; S, 10.34%.

*N*<sup>6</sup>-(*tert*-Butoxycarbonyl)-3-phenyl-4-(propargylthio)sydnone imine (**3l**).

Yield 55%, brown crystals, m.p. 125–126 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.75 – 7.60 (m, 5H, C<sub>6</sub>H<sub>5</sub>), 3.62 (d, *J* = 2.7 Hz, 2H, SCH<sub>2</sub>), 2.17 (t, *J* = 2.6 Hz, 1H, C≡CH), 1.57 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.6, 158.7, 132.9, 132.6, 129.7, 125.7, 107.1, 79.7, 78.6, 73.3, 28.2, 21.9. Anal. Calc. for C<sub>16</sub>H<sub>17</sub>N<sub>3</sub>O<sub>3</sub>S: C, 57.99; H, 5.17; N, 12.68; S, 9.67%. Found: C, 57.83; H, 5.01; N, 12.81; S, 9.84%.

3-Cyclohexyl-4-(propargylthio)-*N*<sup>6</sup>-(*tert*-butoxycarbonyl)sydnone imine (**3m**).

Yield 77%, brown crystals, m.p. 137–138 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.02 – 4.89 (m, 1H, *cyclo*-(CH<sub>2</sub>)<sub>5</sub>CH), 3.56 (d, *J* = 2.6 Hz, 2H, SCH<sub>2</sub>), 2.26 (t, *J* = 2.6 Hz, 1H, C≡CH), 2.19 – 2.10 (m, 2H), 2.02 – 1.89 (m, 4H) and 1.82 – 1.74 (m, 1H, *cyclo*-(CH<sub>2</sub>)<sub>5</sub>CH), 1.52 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.49 – 1.40 (m, 2H) and 1.39 – 1.28 (m, 1H, *cyclo*-(CH<sub>2</sub>)<sub>5</sub>CH). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.1, 158.9, 103.8, 79.4, 79.2, 72.8, 63.0, 32.4, 28.2, 25.0, 24.6, 22.8. Anal. Calc. for C<sub>16</sub>H<sub>23</sub>N<sub>3</sub>O<sub>3</sub>S: C, 56.95; H, 6.87; N, 12.45; S, 9.50%. Found: C, 57.06; H, 6.69; N, 12.54; S, 9.38%.

**General procedure for the synthesis of 4-(((1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl)thio)sydnone imines (**4**)**

A solution of compound **3** (1 mmol), TEA (0.2 mmol), and CuI (0.1 mmol) in 3 mL of acetonitrile was degassed by stirred under an argon flow for 5 minutes. The benzyl azide (1 mmol) was then added, and the reaction mixture was stirred for an additional 5–10 minutes. After completion (TLC-control), the solvent was removed under reduced pressure. The residue was dissolved in chloroform and passed through a short column of SiO<sub>2</sub> (2×3 cm), eluting with a mixture of ethyl acetate and chloroform. The product was recrystallized from toluene/petroleum ether.

4-(((1-Benzyl-1*H*-1,2,3-triazol-4-yl)methyl)thio)-*N*<sup>6</sup>-(*tert*-butoxycarbonyl)-3-isopropylsydnone imine (**4a**).

A solvate with half of methyl *tert*-butyl ether molecule. Yield 77%, gray yellow crystals, m.p. 67–68 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.46 – 7.33 (m, 4H, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> + C<sub>2</sub>H<sub>5</sub>N<sub>3</sub>), 7.27 – 7.19 (m, 2H, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 5.44 (s, 2H, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 4.99 – 4.83 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 4.16 (s, 2H, SCH<sub>2</sub>), 3.21 (s, 3H, 1/2MTBE), 1.54 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.34 (d, *J* = 6.5 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.19 (s, 9H, 1/2MTBE). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.3, 158.9, 143.2,

134.3, 129.2, 128.9, 128.1, 122.9, 104.3, 79.3, 77.3, 72.8 (MTBE), 56.6, 54.3, 49.5 (MTBE), 28.2, 27.0 (MTBE), 21.3. Anal. Calc. for  $C_{20}H_{26}N_6O_3S + 1/2C_5H_{12}O$ : C, 56.94; H, 6.80; N, 17.71; S, 6.76%. Found: C, 57.08; H, 6.91; N, 17.62; S, 6.78%.

*N*<sup>6</sup>-Benzoyl-4-(((1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl)thio)-3-isopropylsydnone imine (**4b**).

Yield 74%, light brown crystals, m.p. 65–66 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.31 (d, *J* = 7.6 Hz, 2H), 7.57–7.42 (m, 3H, + C<sub>2</sub>HN<sub>3</sub>), 7.42–7.31 (m, 4H), 7.25–7.15 (m, 2H), 5.38 (s, 2H), 4.97 (hept, *J* = 6.8 Hz, 1H), 4.35 (s, 2H), 1.38 (d, *J* = 6.8 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 172.8, 168.3, 143.0, 137.2, 134.3, 131.6, 129.6, 129.2, 128.9, 128.1, 128.0, 123.0, 106.5, 56.8, 54.3, 27.5, 21.3. Anal. Calc. for C<sub>22</sub>H<sub>22</sub>N<sub>6</sub>O<sub>2</sub>S: C, 60.81; H, 5.10; N, 19.34; S, 7.38%. Found: C, 60.76; H, 4.98; N, 19.21; S, 7.29%.

4-(((1-Benzyl-1*H*-1,2,3-triazol-4-yl)methyl)thio)-3-isopropyl-*N*<sup>6</sup>-tosylsydnone imine (**4c**).

Yield 68%, beige crystals, m.p. 142–143 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.98 (d, *J* = 8.1 Hz, 2H), 7.48 (s, 1H, C<sub>2</sub>HN<sub>3</sub>), 7.42–7.34 (m, 3H), 7.32–7.21 (m, 4H), 5.41 (s, 2H), 4.90 (hept, *J* = 6.2 Hz, 1H), 4.23 (s, 2H), 2.40 (s, 3H), 1.31 (d, *J* = 6.7 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 164.81, 142.73, 142.38, 139.52, 134.48, 129.30, 129.20, 128.83, 128.18, 127.21, 123.48, 105.72, 57.47, 54.27, 27.59, 21.55, 21.24. Anal. Calc. for C<sub>22</sub>H<sub>24</sub>N<sub>6</sub>O<sub>3</sub>S<sub>2</sub>: C, 54.53; H, 4.99; N, 17.34; S, 13.23%. Found: C, 54.62; H, 5.12; N, 17.26; S, 13.27%.

3-(Adamantan-1-yl)-4-(((1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl)thio)-*N*<sup>6</sup>-(*tert*-butoxycarbonyl)sydnone imine (**4d**).

Yield 82%, beige crystals, m.p. 148–149 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.38 (d, *J* = 18.0 Hz, 4H, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> + C<sub>2</sub>HN<sub>3</sub>), 7.27 (d, *J* = 4.8 Hz, 2H, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 5.42 (s, 2H, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 4.36 (s, 2H, SCH<sub>2</sub>), 2.15 (s, 3H), 2.06 (s, 6H) and 1.65 (q<sub>br</sub>, *J* = 13.1 Hz, 6H, 1-Ad), 1.54 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.9, 159.0, 142.8, 134.7, 129.2, 128.8, 128.2, 122.8, 104.3, 79.1, 70.8, 54.2, 39.9, 35.2, 29.4, 28.3, 27.2. Anal. Calc. for C<sub>27</sub>H<sub>34</sub>N<sub>6</sub>O<sub>3</sub>S: C, 62.05; H, 6.56; N, 16.08; S, 6.13%. Found: C, 61.92; H, 6.73; N, 16.13; S, 6.06%.

4-(((1-Benzyl-1*H*-1,2,3-triazol-4-yl)methyl)thio)-*N*<sup>6</sup>-*tert*-butoxycarbonyl-3-(piperidin-1-yl)sydnone imine (**4e**).

A solvate with half of a toluene molecule. Yield 74%, gray crystals, m.p. 81–82 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.54 (s, 1H, C<sub>2</sub>HN<sub>3</sub>), 7.43–7.35 (m, 3H, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 7.33–7.11 (m, 2H, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> + 5H, 1/2Tol), 5.46 (s, 2H, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 4.23 (s, 2H, SCH<sub>2</sub>), 3.22–3.06 (m, 4H, CH<sub>2</sub>NCH<sub>2</sub>), 2.37 (s, 3H, 1/2Tol), 1.83–1.70 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.54 (s, 11H, C(CH<sub>3</sub>)<sub>3</sub> + CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.1, 158.6, 143.5, 137.9 (Tol), 134.5, 129.2, 129.0 (Tol), 128.8, 128.23 (Tol), 128.17, 125.3 (Tol), 122.8, 103.5, 79.3, 56.2, 54.3, 28.3, 27.9, 25.2, 22.9, 21.5 (Tol). Anal. Calc. for C<sub>22</sub>H<sub>29</sub>N<sub>7</sub>O<sub>3</sub>S + 1/2C<sub>7</sub>H<sub>8</sub>: C, 59.17; H, 6.43; N, 18.94; S, 6.19%. Found: C, 59.07; H, 6.55; N, 19.03; S, 6.25%.

4-(((1-Benzyl-1*H*-1,2,3-triazol-4-yl)methyl)thio)-*N*<sup>6</sup>-(*tert*-butoxycarbonyl)-3-(4-methoxyphenyl)sydnone imine (**4f**).

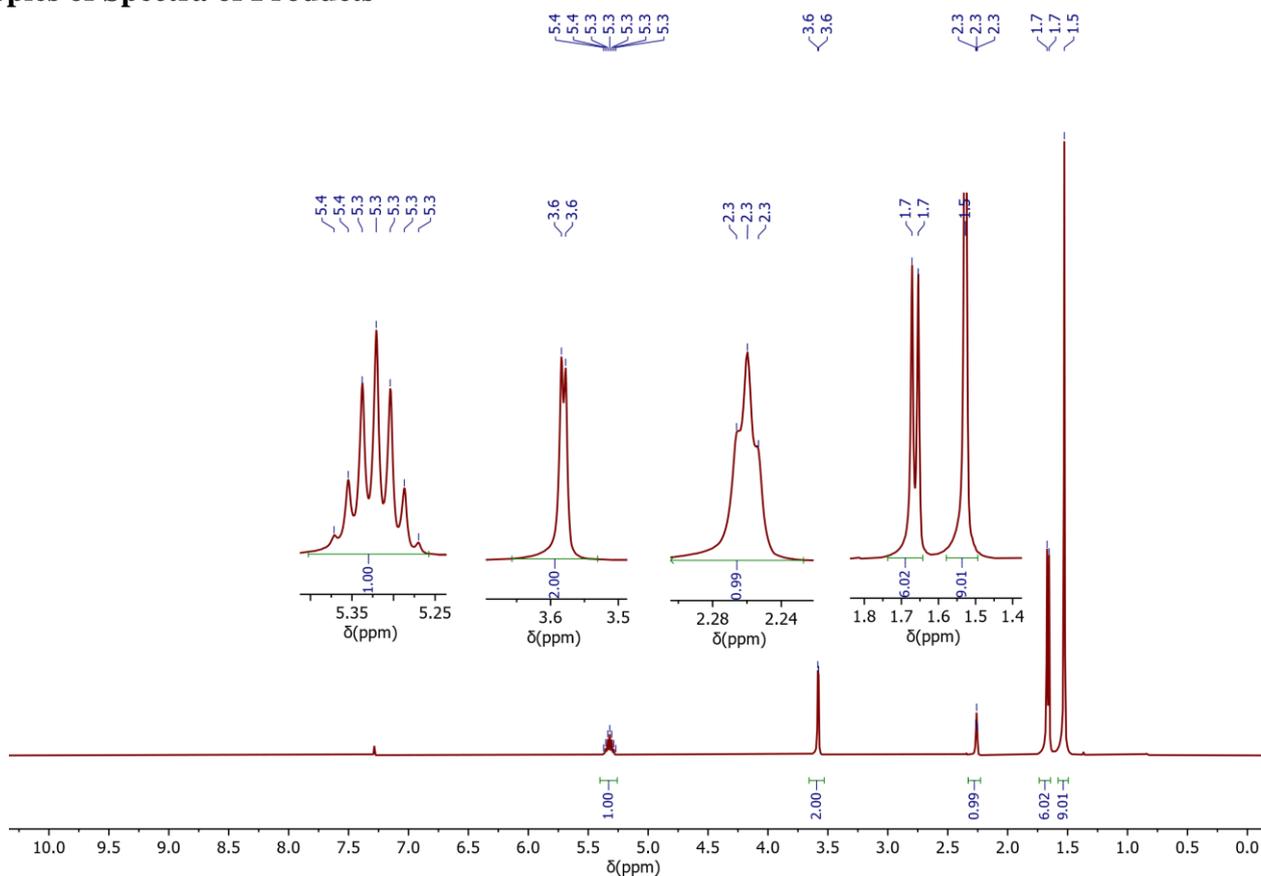
As a solvate of a dichloromethane molecule. Yield 79%, white crystal, m.p. 71–72 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.43 (s, 1H, C<sub>2</sub>HN<sub>3</sub>), 7.40–7.32 (m, 3H, CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub> + CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 7.26–7.18 (m, 4H, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 7.02–6.92 (m, 2H, CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>), 5.45 (s, 2H, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 5.31 (s, 2H, DCM), 4.12 (s, 2H, SCH<sub>2</sub>), 3.89 (s, 3H), 1.57 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.9, 162.4, 158.8, 143.1, 134.5, 129.2, 128.9, 128.1, 126.6, 125.2, 122.9, 114.7, 107.6, 79.5, 55.8, 54.2, 53.5 (DCM), 28.3, 28.1. Anal. Calc. for C<sub>24</sub>H<sub>26</sub>N<sub>6</sub>O<sub>4</sub>S + CH<sub>2</sub>Cl<sub>2</sub>: C, 51.82; H, 4.87; Cl, 12.23; N, 14.50; S, 5.53%. Found: C, 51.95; H, 4.93; Cl, 12.11; N, 14.62; S, 5.69%.

### Synthesis of 4-(((*S*)-(4-(((1-(2-(((5-(1,2-dithiolan-3-yl)pentanoyl)oxy)ethyl)-1*H*-1,2,3-triazol-4-yl)methyl)thio)-*N*<sup>6</sup>-ethoxycarbonyl-3-(morpholin-4-yl)sydnone imine (**5**))

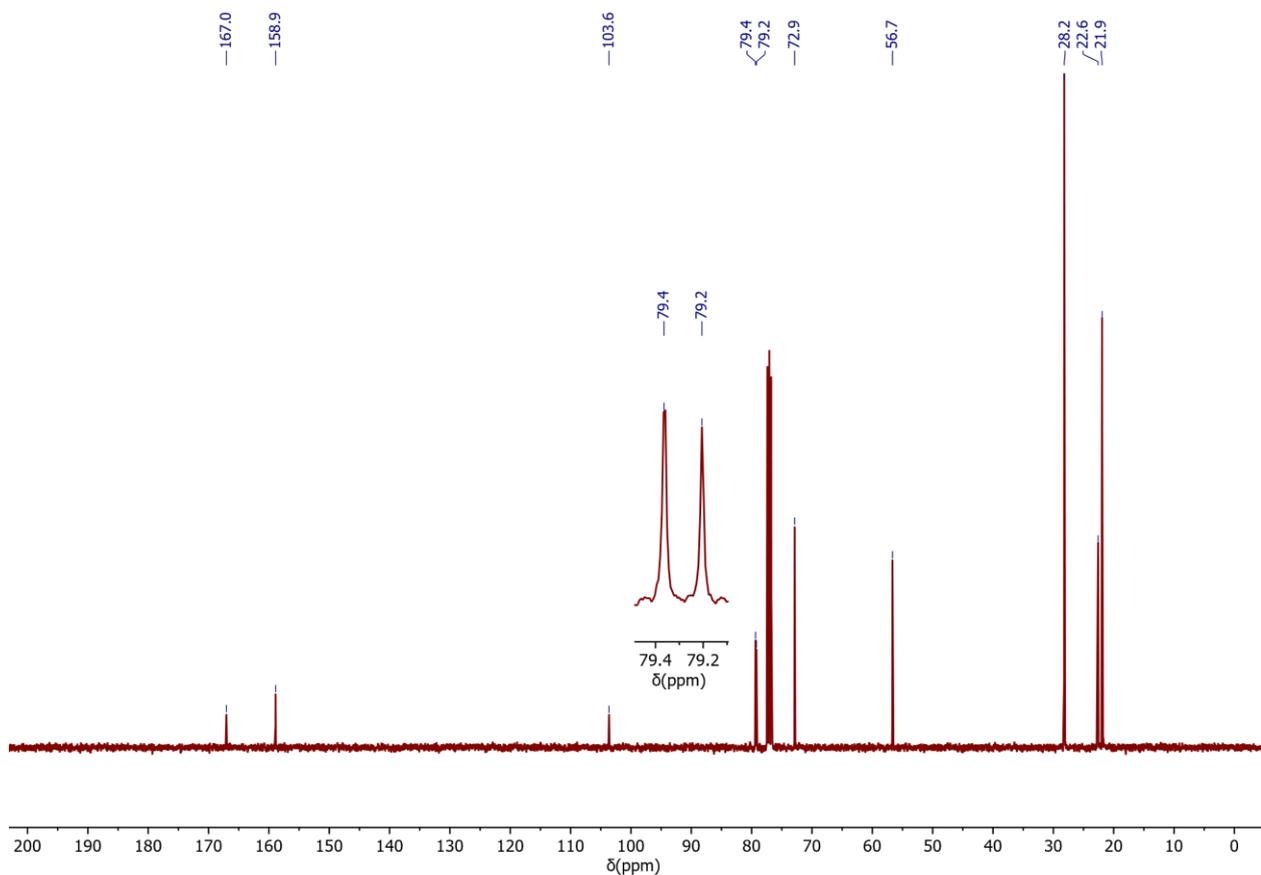
A solution of compound **3k** (1 mmol), TEA (0.2 mmol), and CuI (0.1 mmol) in 3 mL of acetonitrile was degassed by stirred under an argon flow for 5 minutes. The 2-azidoethyl ester of (*S*)-lipoic acid (1 mmol) was then added, and the reaction mixture was stirred for an additional 10 minutes. After completion (TLC-control). The solvent was evaporated at reduced pressure; the residue was purified by column chromatography (SiO<sub>2</sub>, 2x15 cm, ethyl acetate/dichloromethane from 1:10 to 1:1).

Yield 66%, yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.65 (s, 1H, C<sub>2</sub>HN<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>O), 4.56 (t, *J* = 5.1 Hz, 2H, C<sub>2</sub>HN<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>O), 4.43 (t, *J* = 5.1 Hz, 2H, C<sub>2</sub>HN<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>O), 4.28 (s, 2H, SCH<sub>2</sub>), 4.19 (q, *J* = 7.1 Hz, 2H, CH<sub>2</sub>CH<sub>3</sub>), 3.98–3.84 (m, 4H, CH<sub>2</sub>OCH<sub>2</sub>), 3.60–3.52 (m, 1H, Lip), 3.46–3.32 (m, 4H, CH<sub>2</sub>NCH<sub>2</sub>), 3.24–3.05 (m, 2H), 2.52–2.41 (m, 1H), 2.33 (t, *J* = 7.4 Hz, 2H), 1.94–1.85 (m, 1H), 1.73–1.59 (m, 4H), 1.50–1.40 (m, 2H, Lip), 1.32 (t, *J* = 7.1 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 172.9, 167.5, 159.2, 143.0, 123.6, 103.9, 66.0, 62.1, 61.4, 56.3, 55.1, 49.3, 40.2, 38.5, 34.5, 33.6, 29.7, 28.6, 27.7, 24.4. Anal. Calc. for C<sub>22</sub>H<sub>33</sub>N<sub>7</sub>O<sub>6</sub>S<sub>3</sub>: C, 44.96; H, 5.66; N, 16.68; S, 16.36%. Found: C, 45.07; H, 5.74; N, 16.62; S, 16.45%.

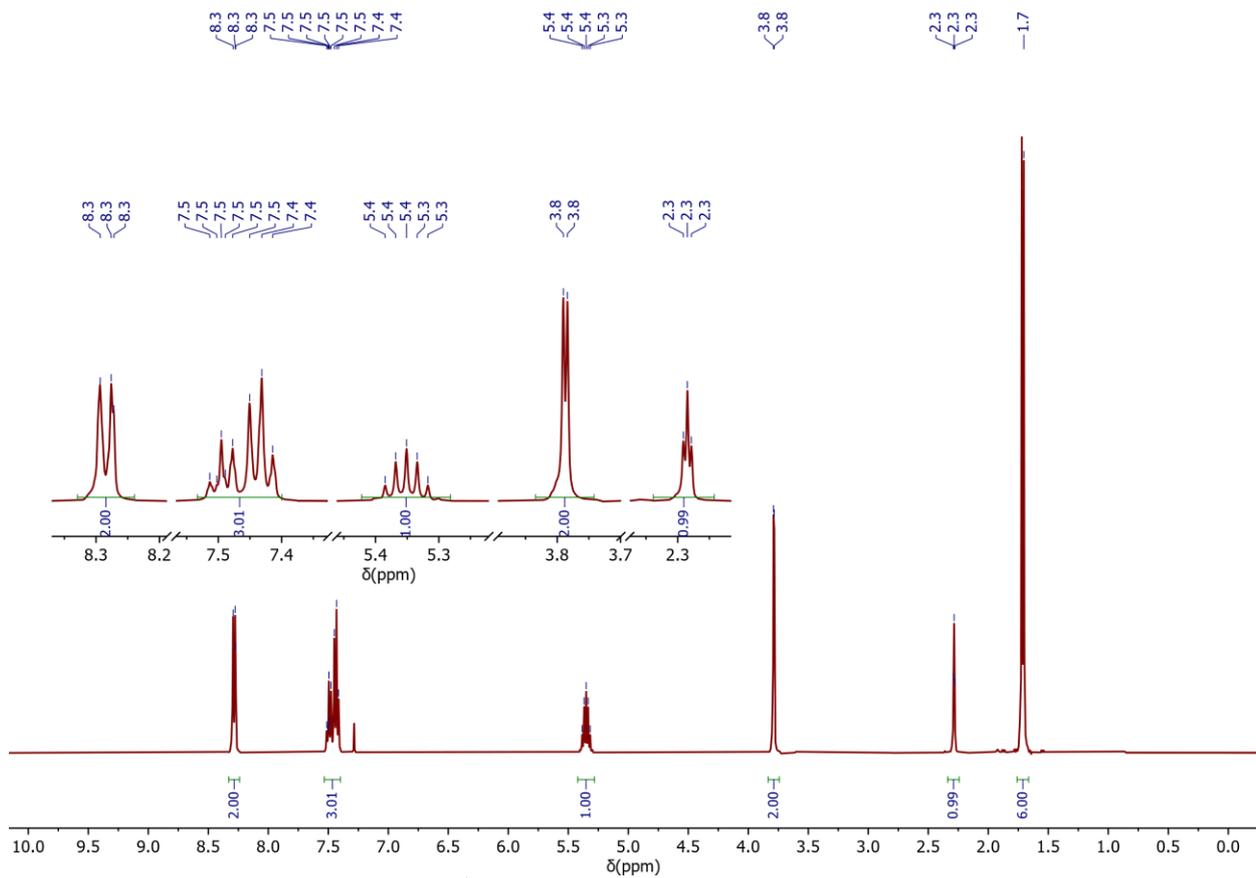
## Copies of Spectra of Products



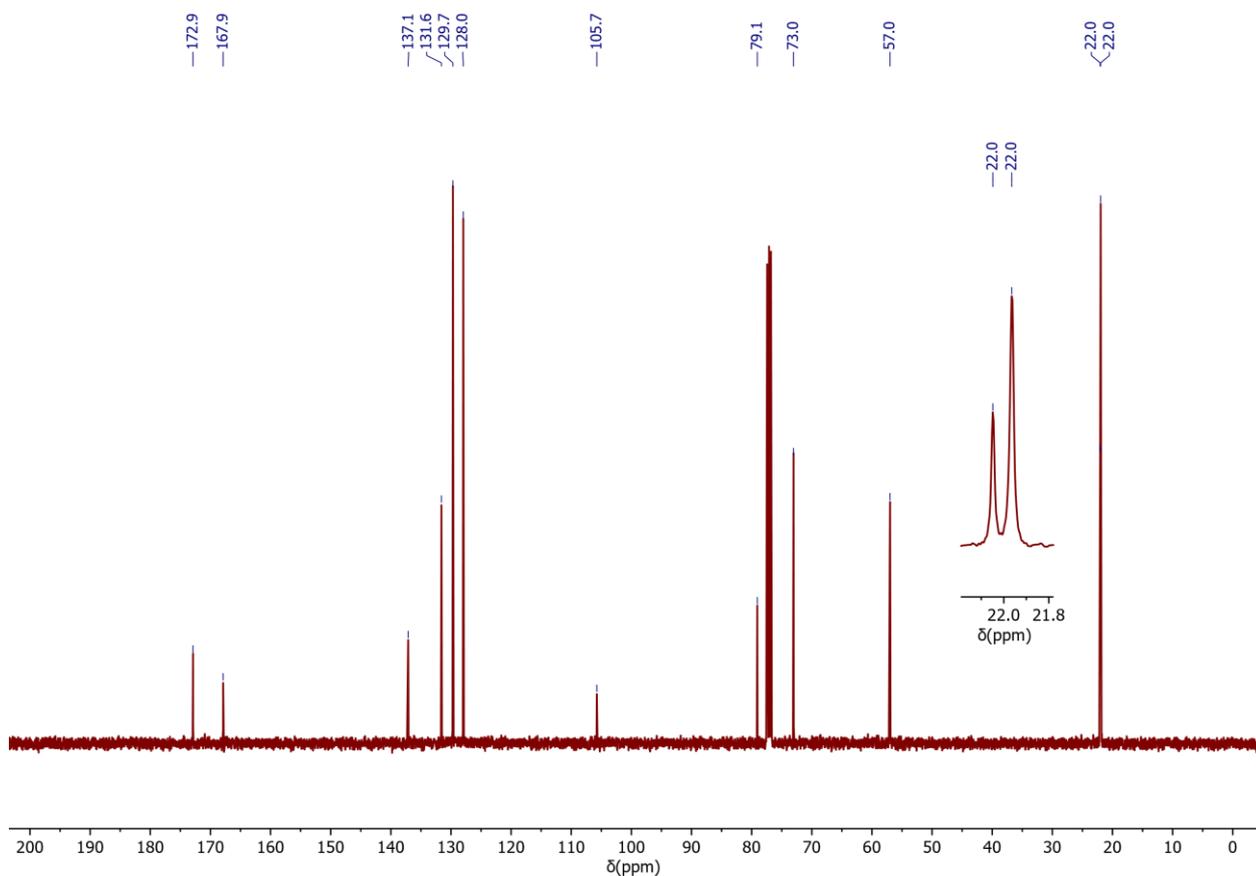
**Figure S1.**  $^1\text{H}$  NMR-spectra of **3a**,  $\text{CDCl}_3$ , 400 MHz



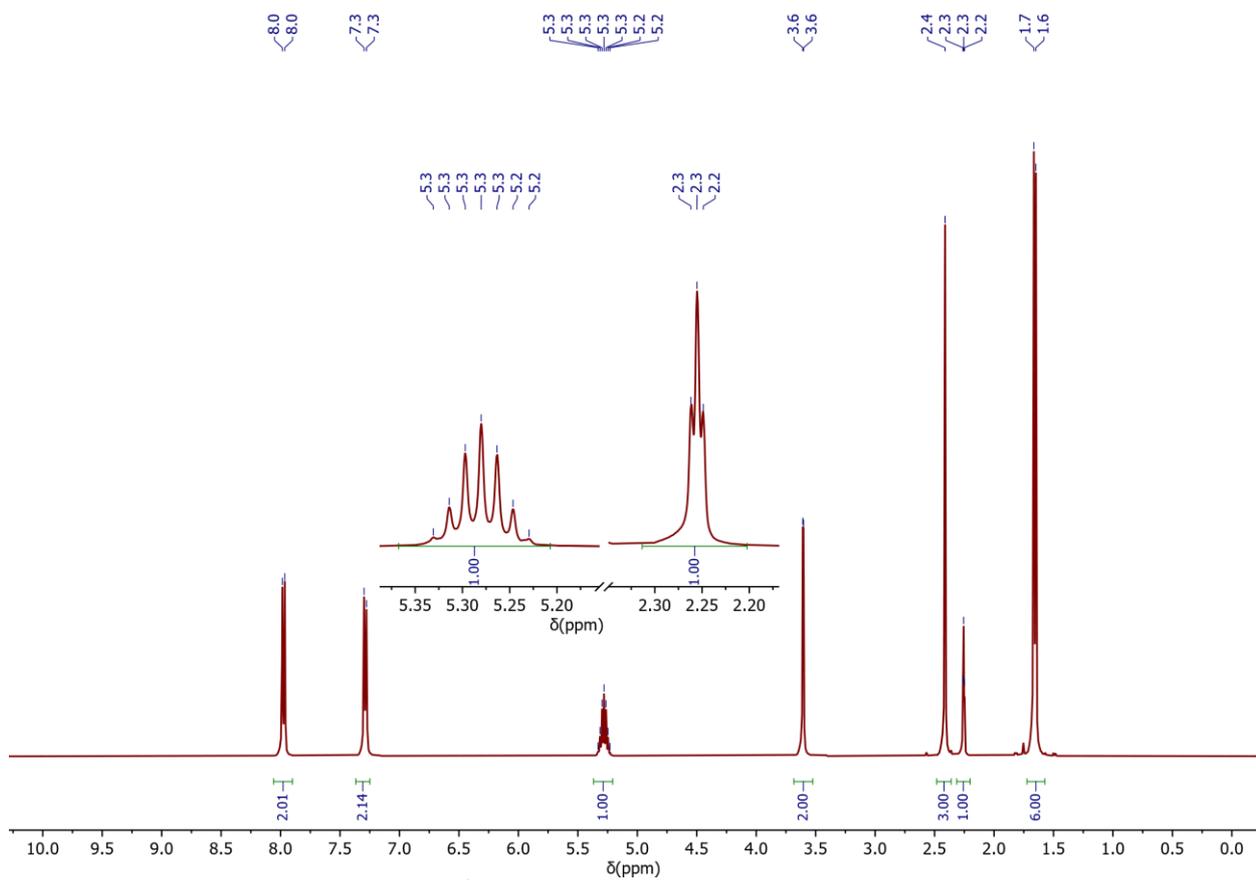
**Figure S2.**  $^{13}\text{C}$  NMR-spectra of **3a**,  $\text{CDCl}_3$ , 101 MHz



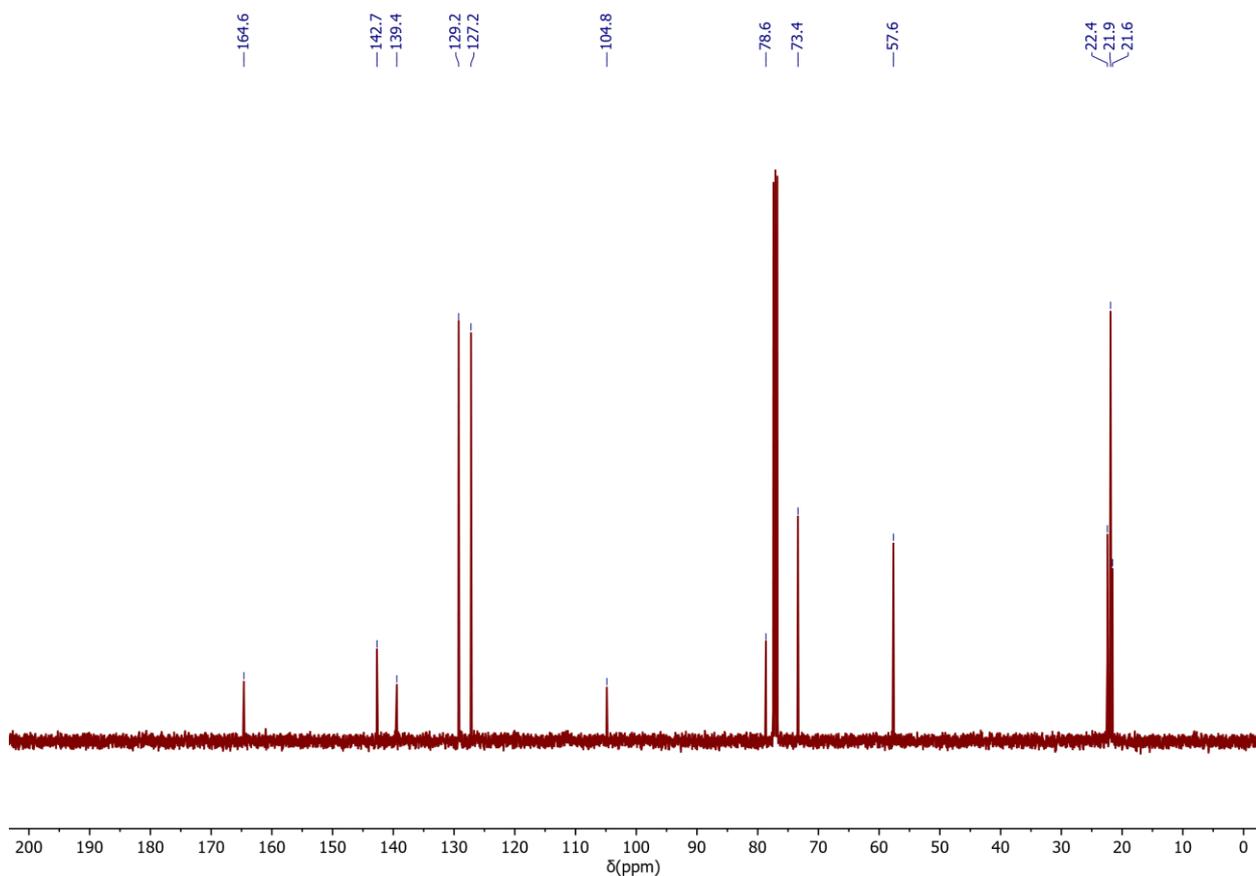
**Figure S3.**  $^1\text{H}$  NMR-spectra of **3b**,  $\text{CDCl}_3$ , 400 MHz



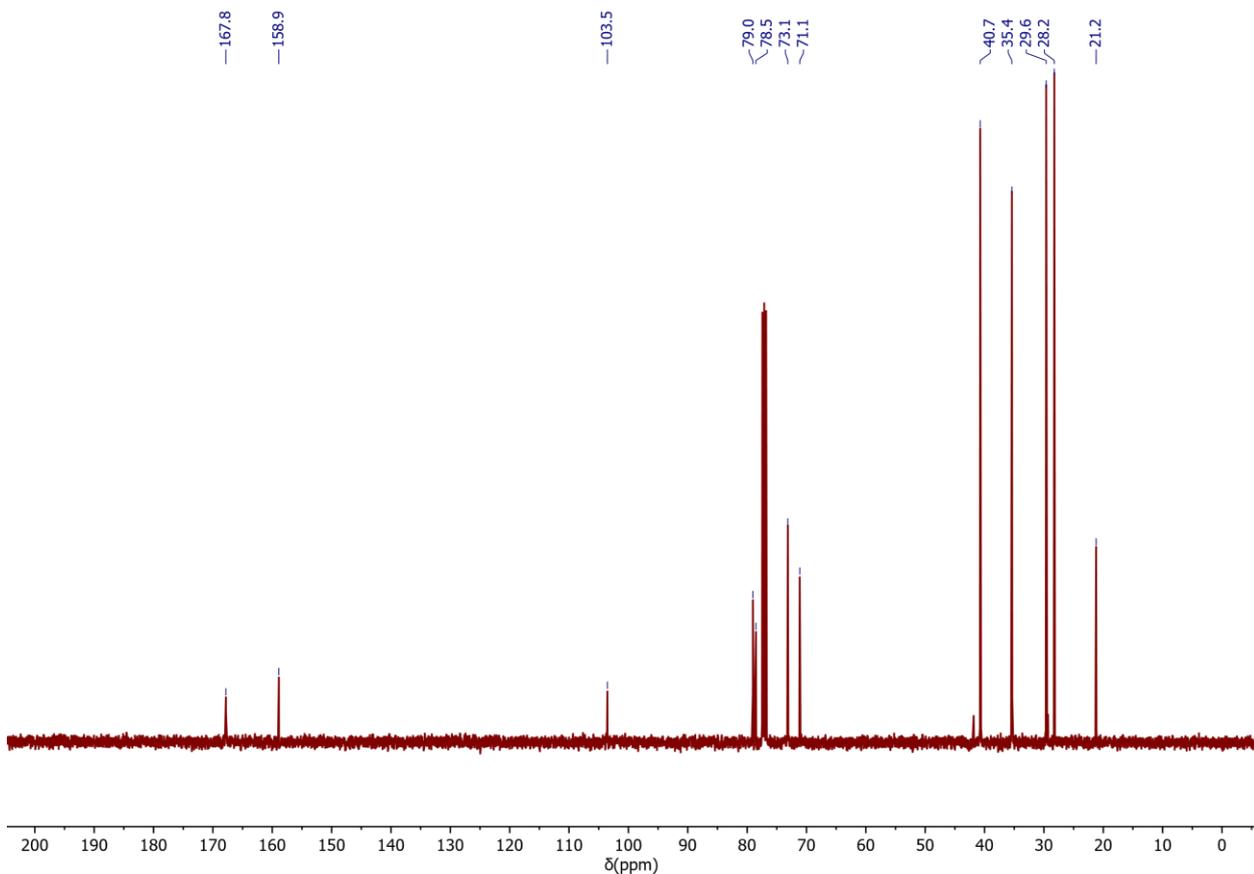
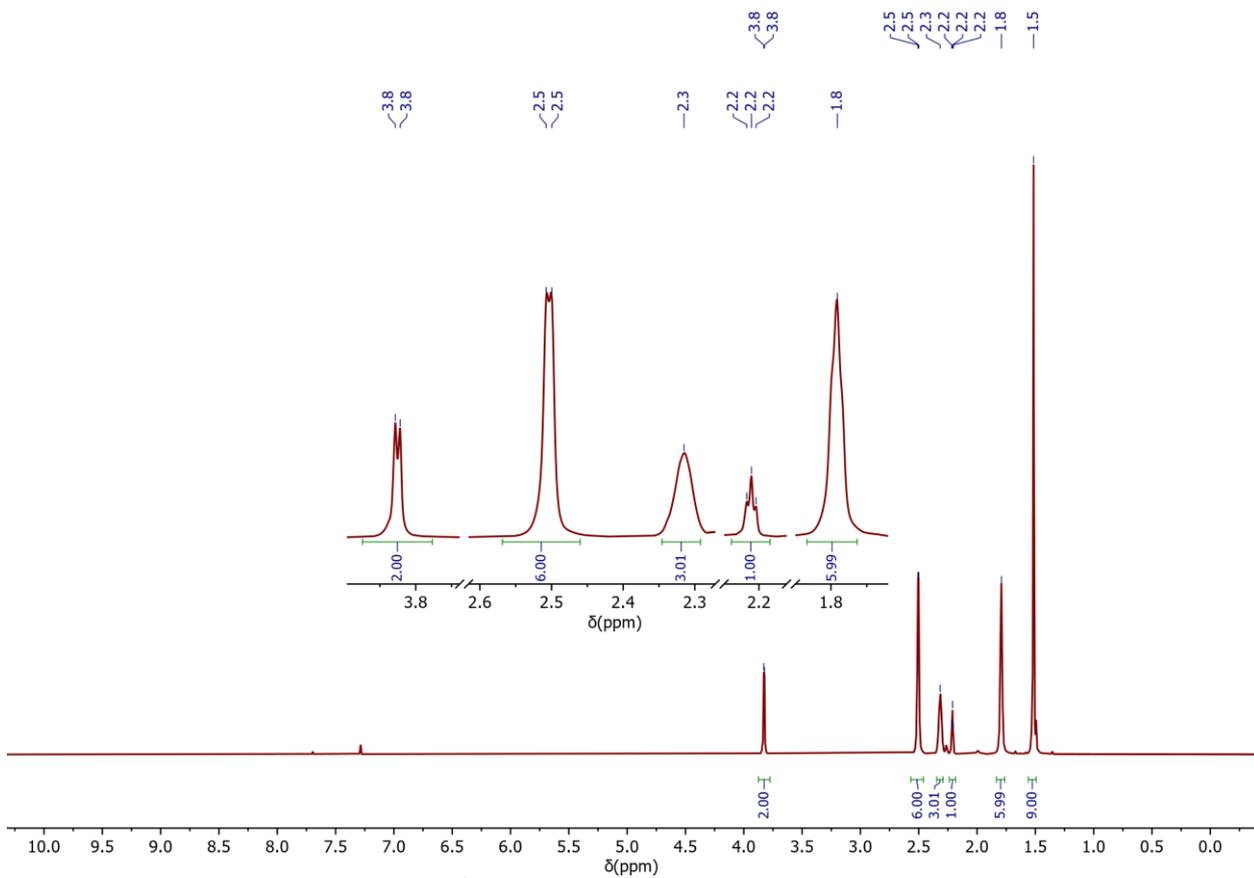
**Figure S4.**  $^{13}\text{C}$  NMR-spectra of **3b**,  $\text{CDCl}_3$ , 101 MHz



**Figure S5.**  $^1\text{H}$  NMR-spectra of **3c**,  $\text{CDCl}_3$ , 400 MHz



**Figure S6.**  $^{13}\text{C}$  NMR-spectra of **3c**,  $\text{CDCl}_3$ , 101 MHz



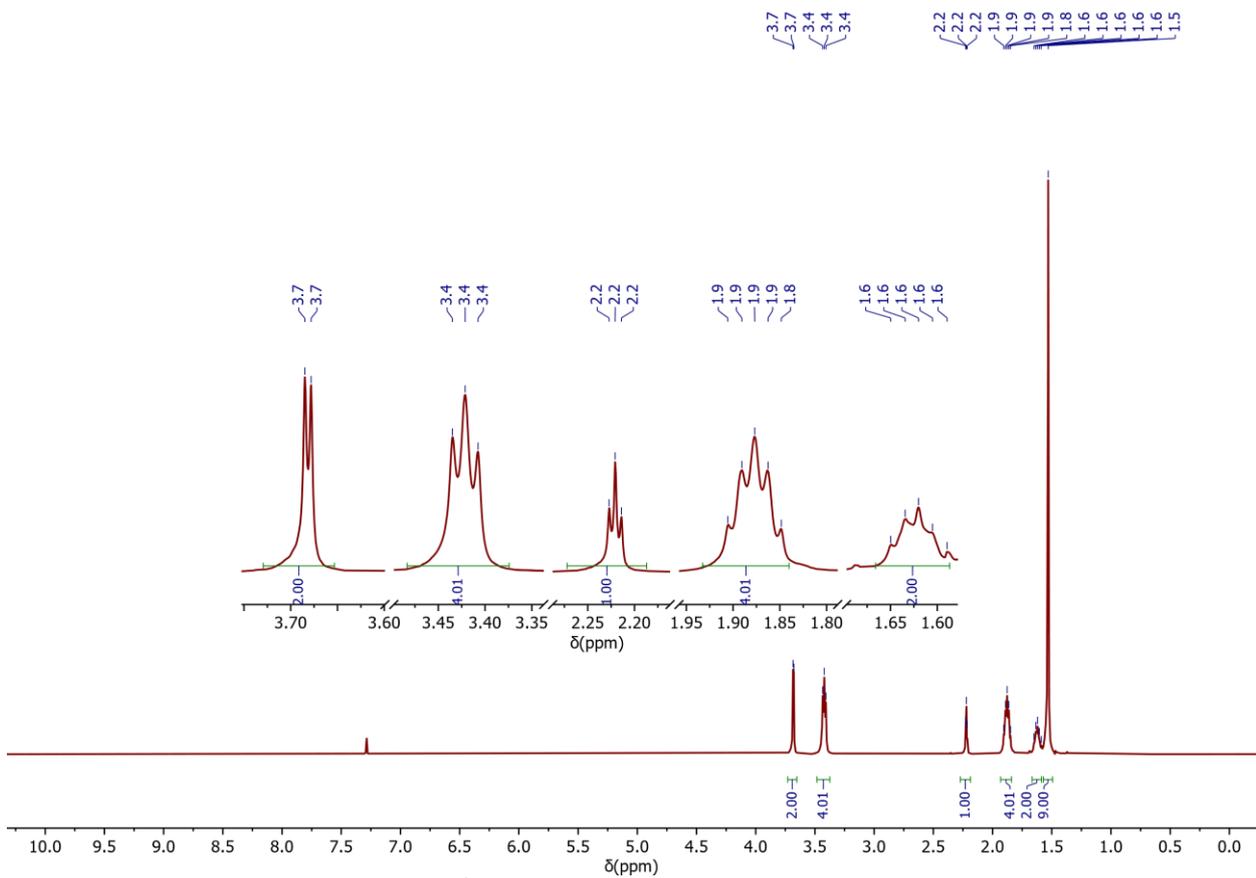


Figure S9.  $^1\text{H}$  NMR-spectra of **3e**,  $\text{CDCl}_3$ , 400 MHz

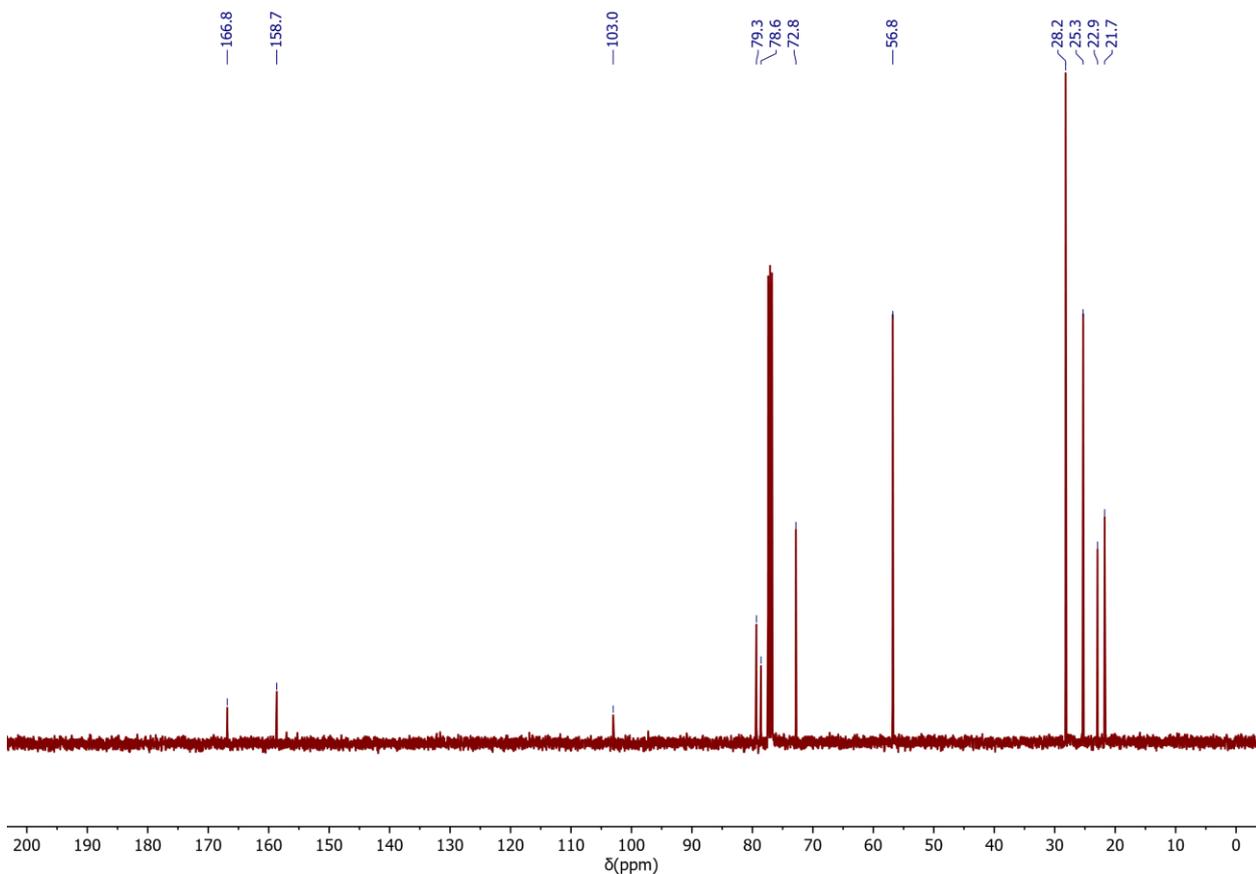


Figure S10.  $^{13}\text{C}$  NMR-spectra of **3e**,  $\text{CDCl}_3$ , 101 MHz

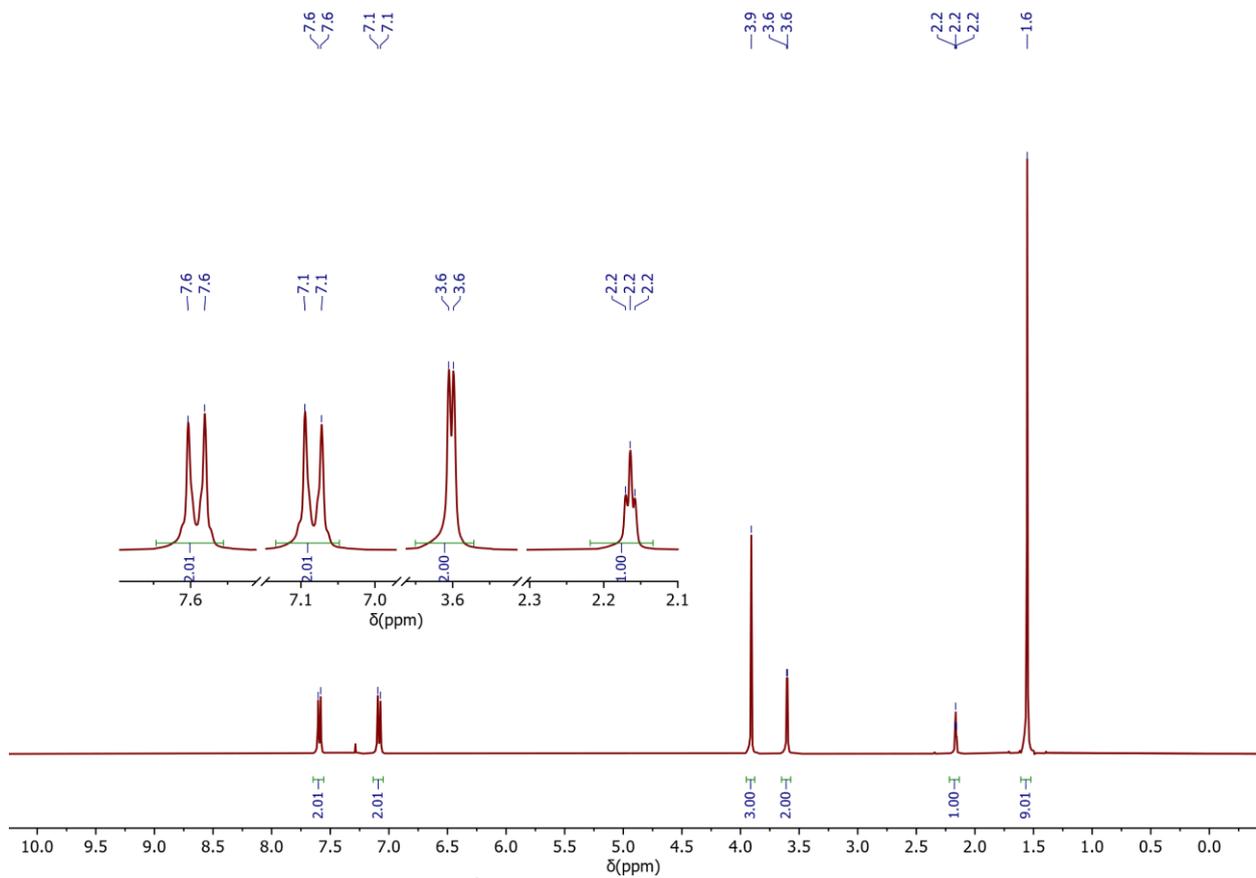


Figure S11.  $^1\text{H}$  NMR-spectra of **3f**,  $\text{CDCl}_3$ , 400 MHz

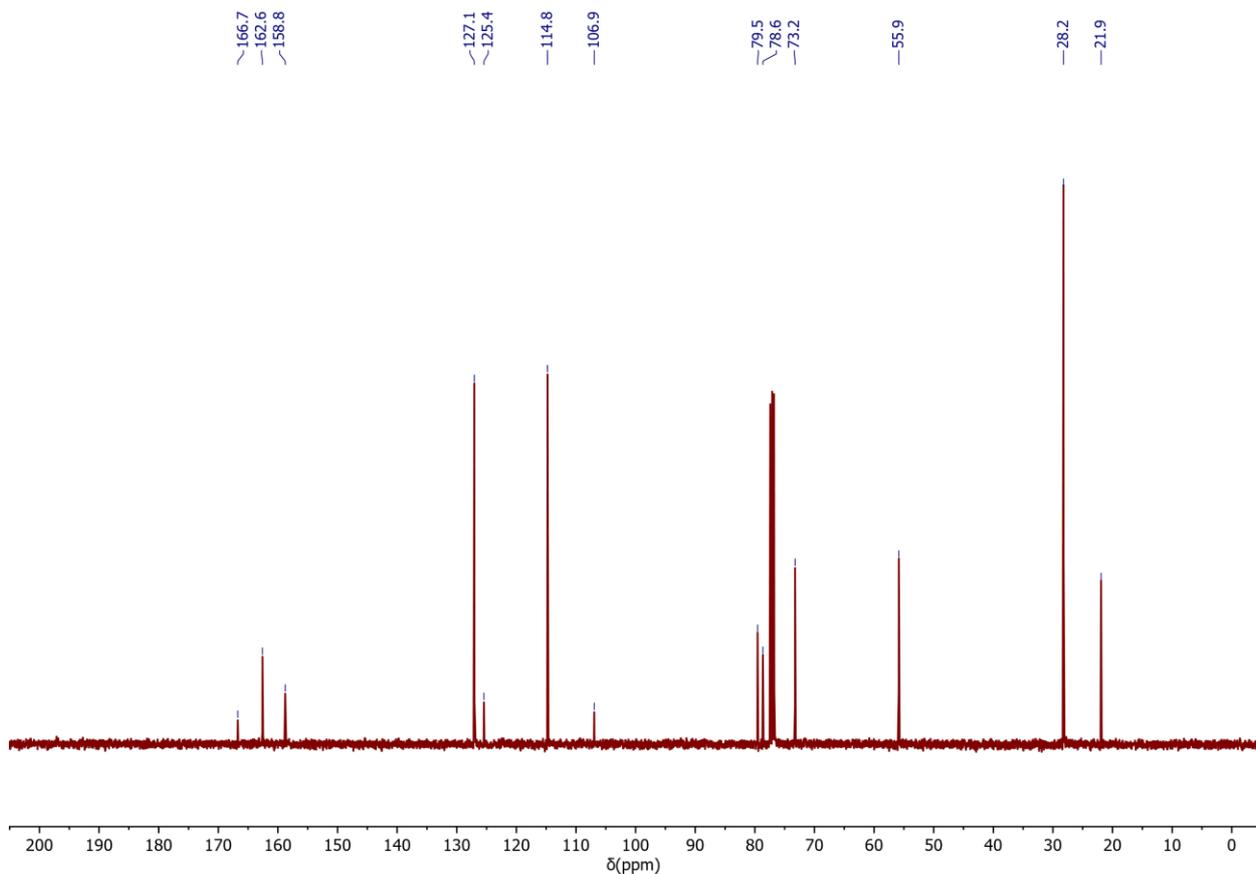


Figure S12.  $^{13}\text{C}$  NMR-spectra of **3f**,  $\text{CDCl}_3$ , 101 MHz

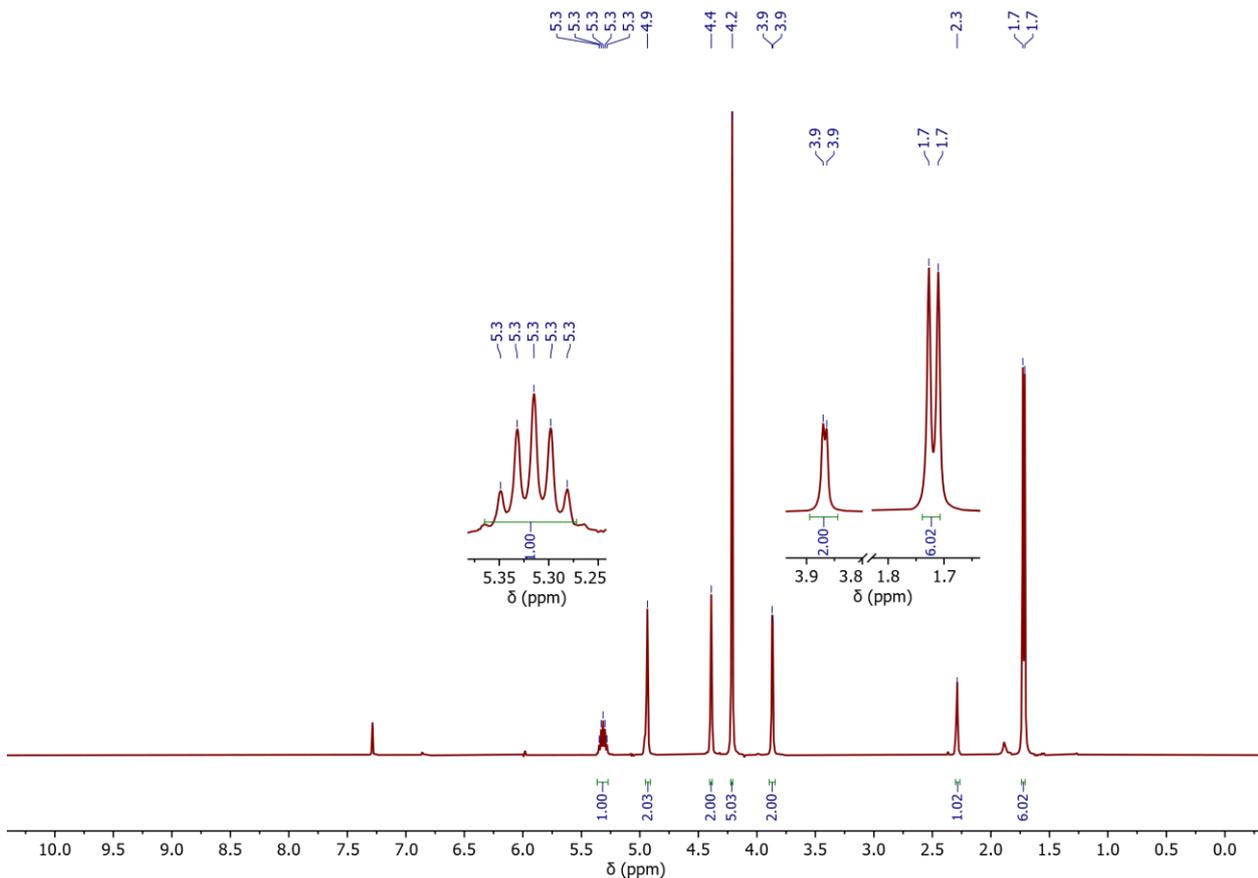


Figure S13.  $^1\text{H}$  NMR-spectra of **3g**,  $\text{CDCl}_3$ , 400 MHz

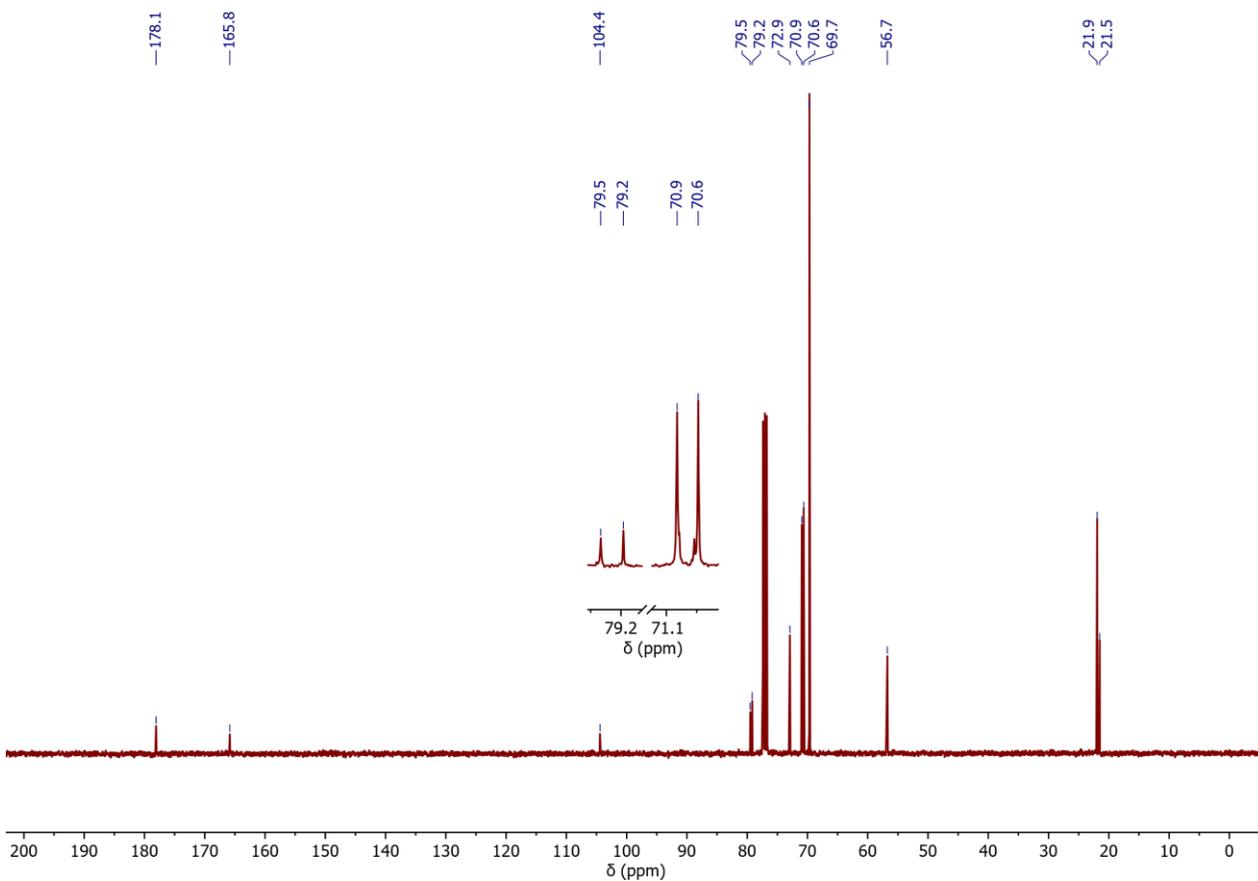
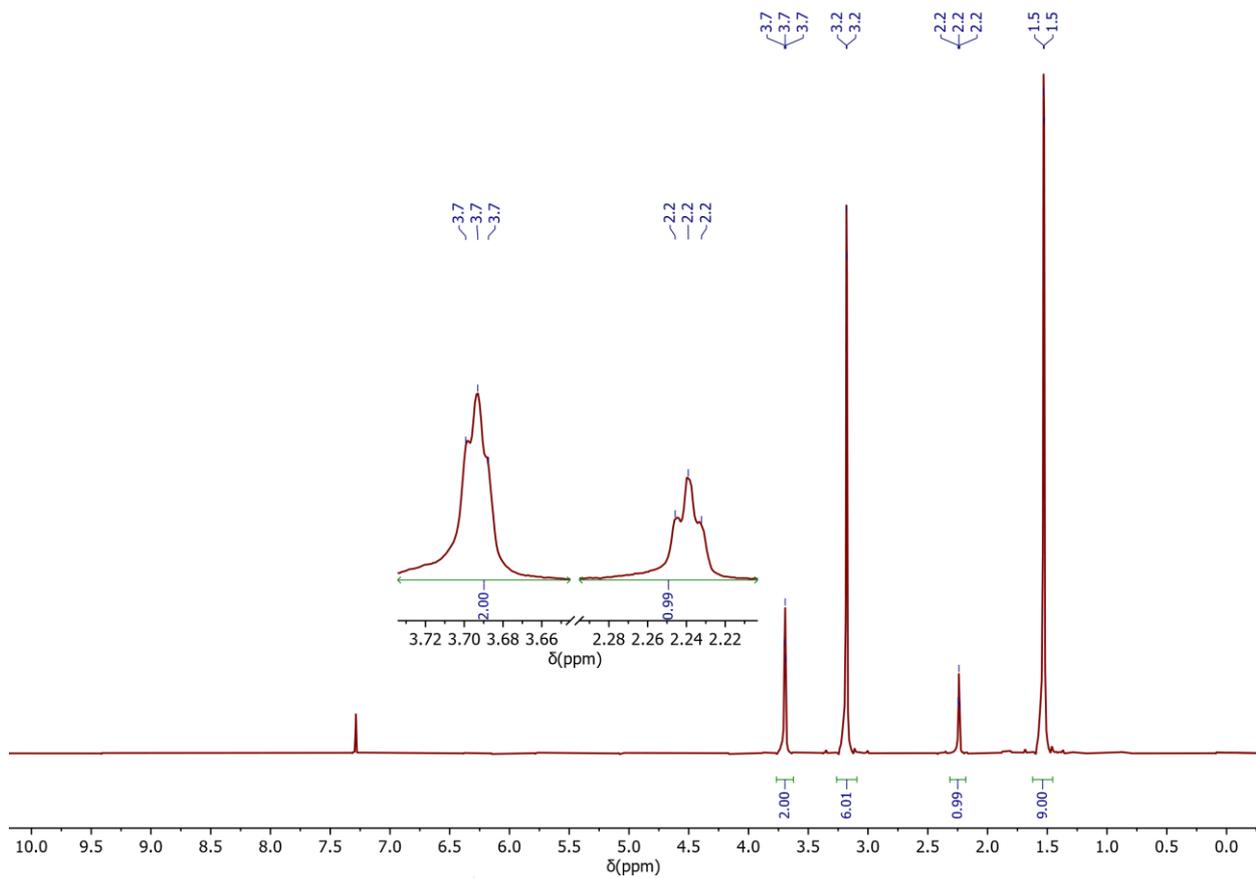
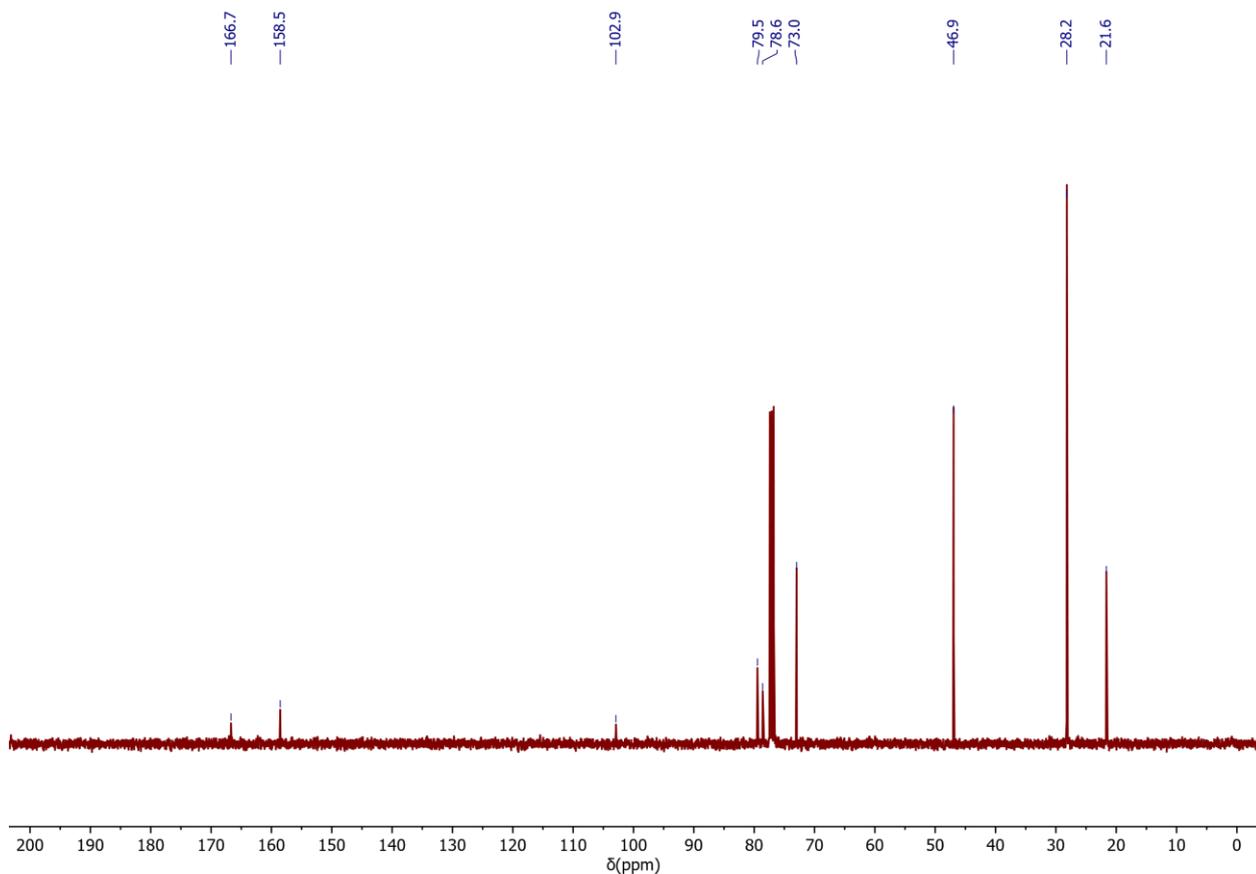


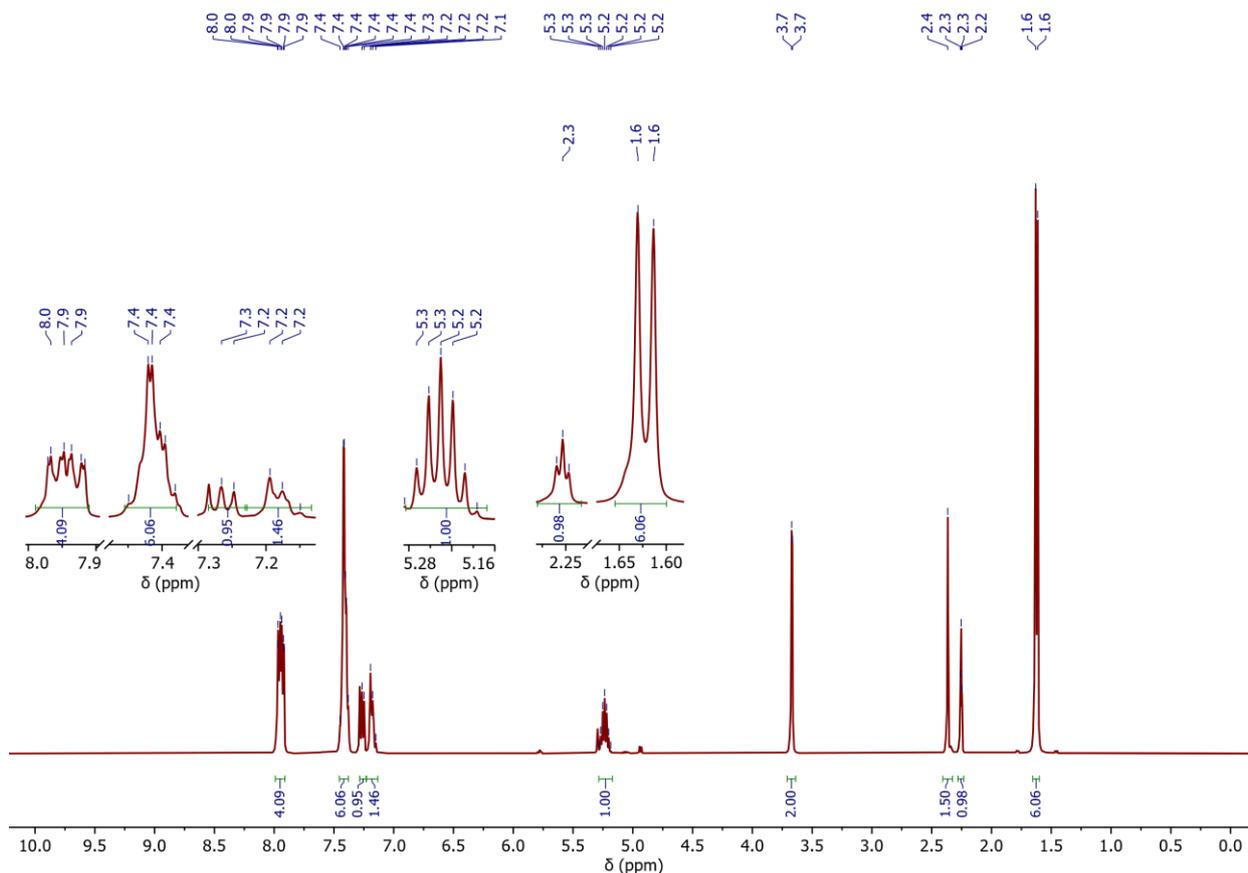
Figure S14.  $^{13}\text{C}$  NMR-spectra of **3g**,  $\text{CDCl}_3$ , 101 MHz



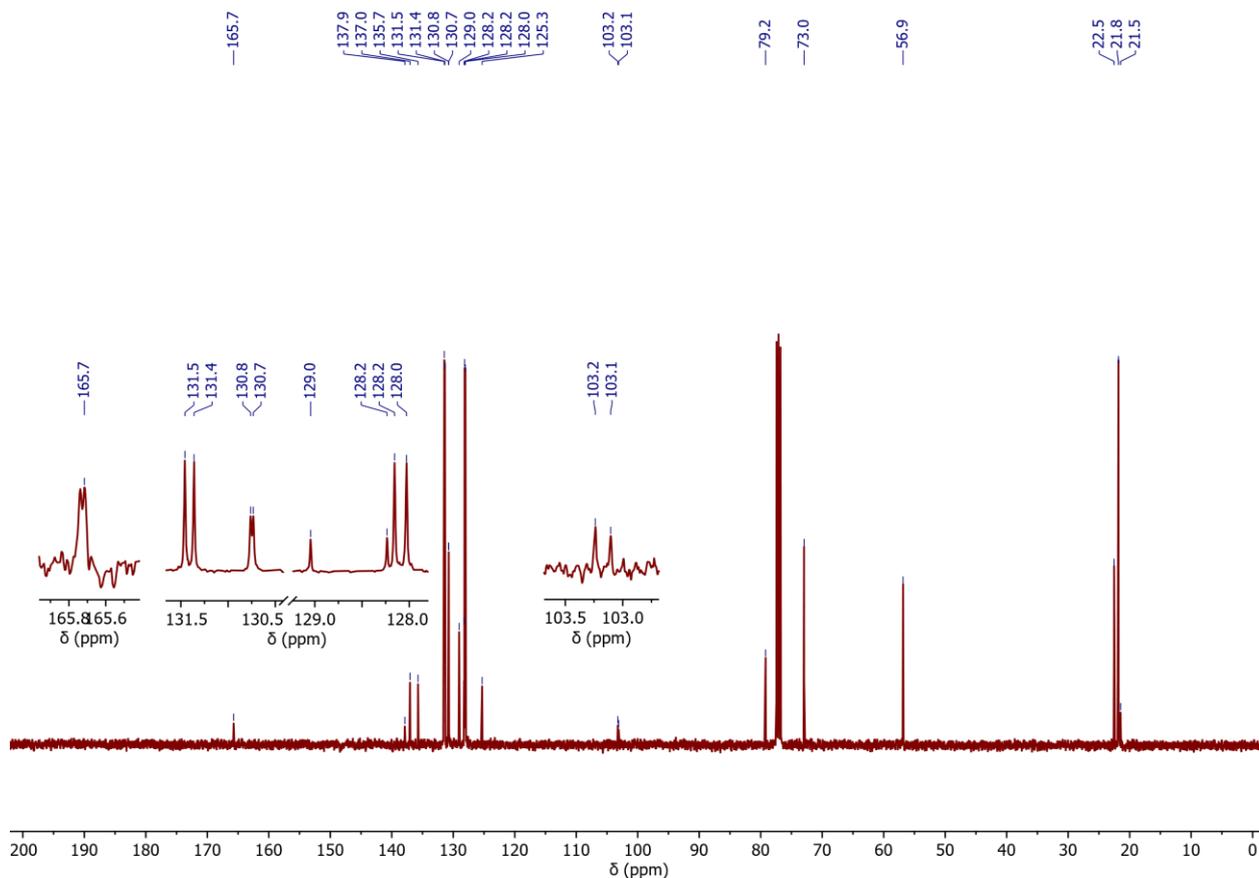
**Figure S15.**  $^1\text{H}$  NMR-spectra of **3h**,  $\text{CDCl}_3$ , 400 MHz



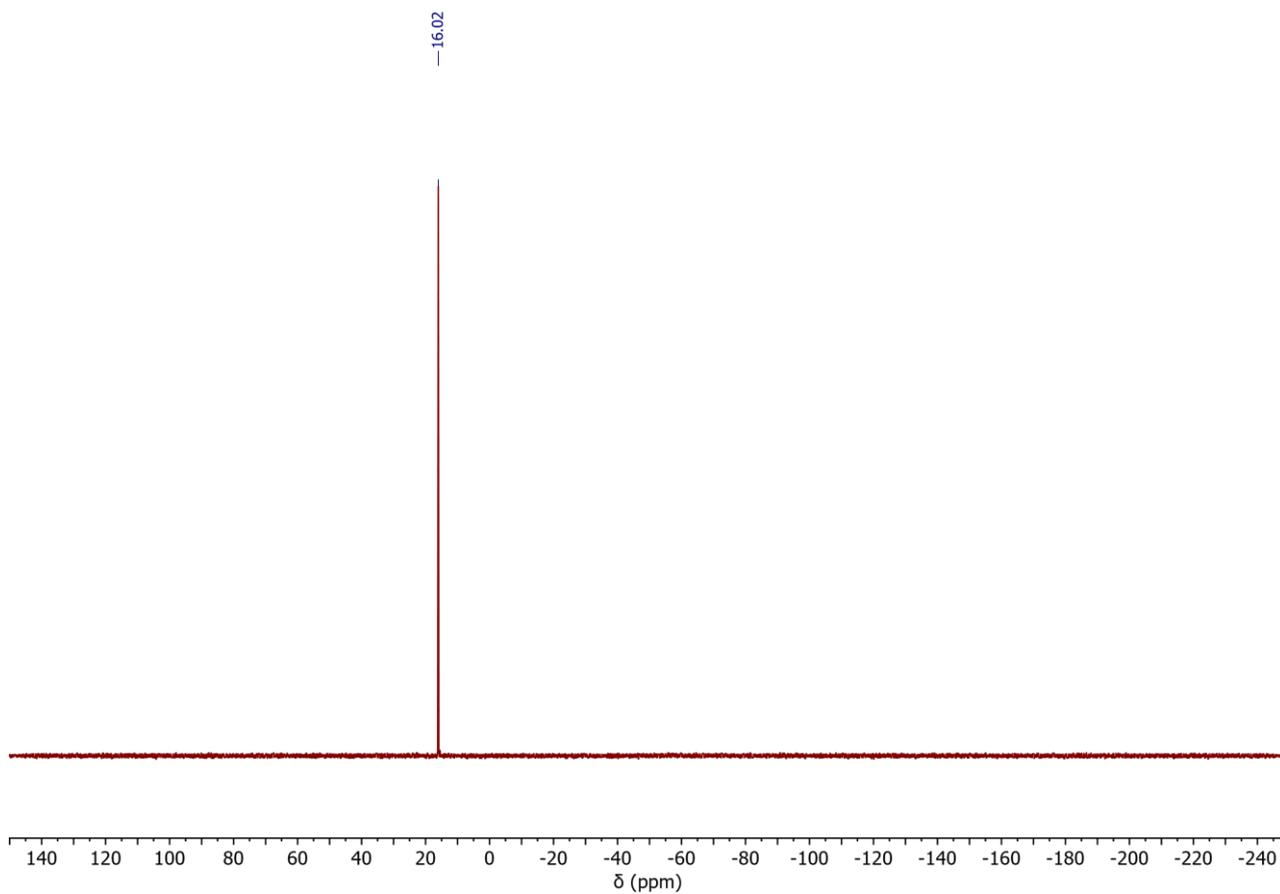
**Figure S16.**  $^{13}\text{C}$  NMR-spectra of **3h**,  $\text{CDCl}_3$ , 101 MHz



**Figure S17.**  $^1\text{H}$  NMR-spectra of **3i** as a solvate of half a toluene molecule,  $\text{CDCl}_3$ , 400 MHz



**Figure S18.**  $^{13}\text{C}$  NMR-spectra of **3i** as a solvate of half a toluene molecule,  $\text{CDCl}_3$ , 101 MHz



**Figure S19.**  $^{31}\text{P}$  NMR-spectra of **3i** as a solvate of half a toluene molecule,  $\text{CDCl}_3$ , 121 MHz

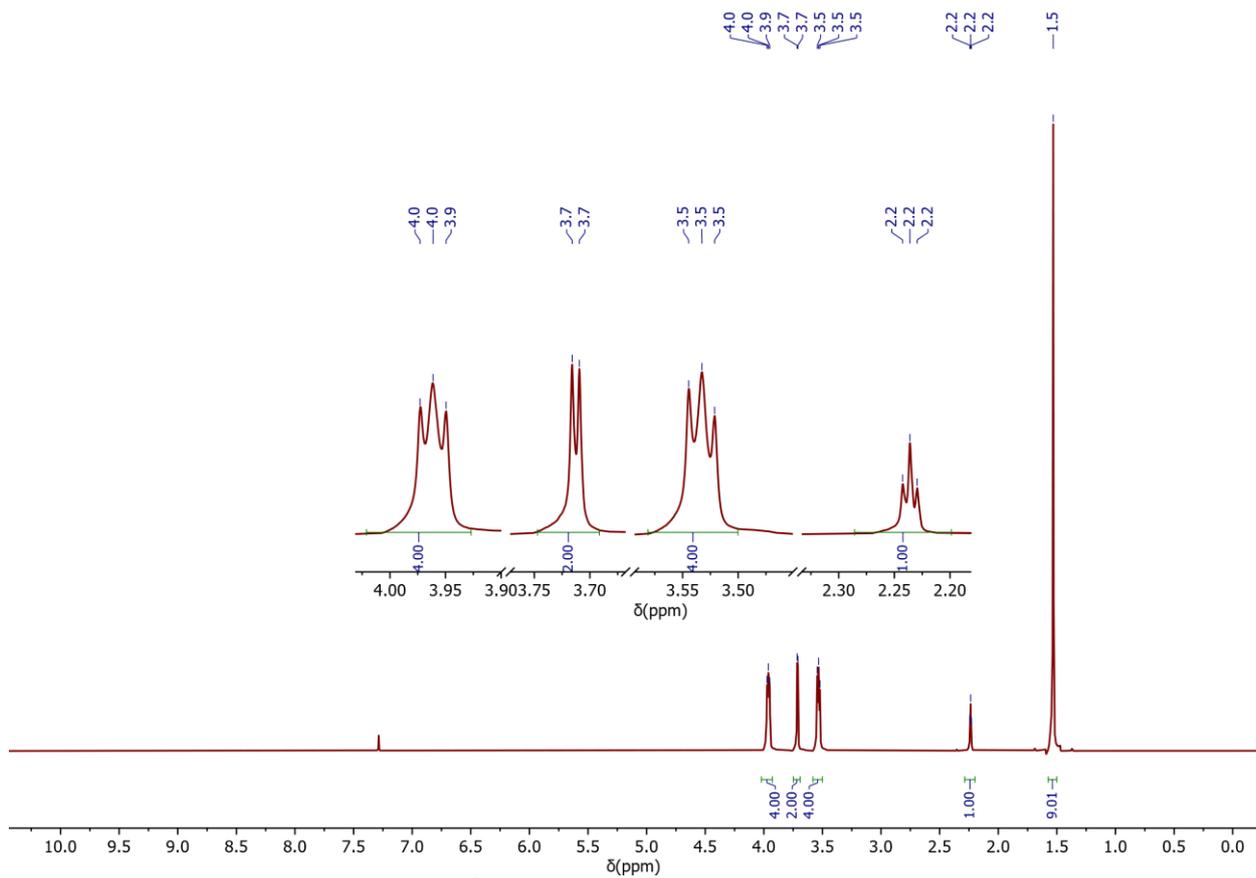


Figure S20.  $^1\text{H}$  NMR-spectra of **3j**,  $\text{CDCl}_3$ , 400 MHz

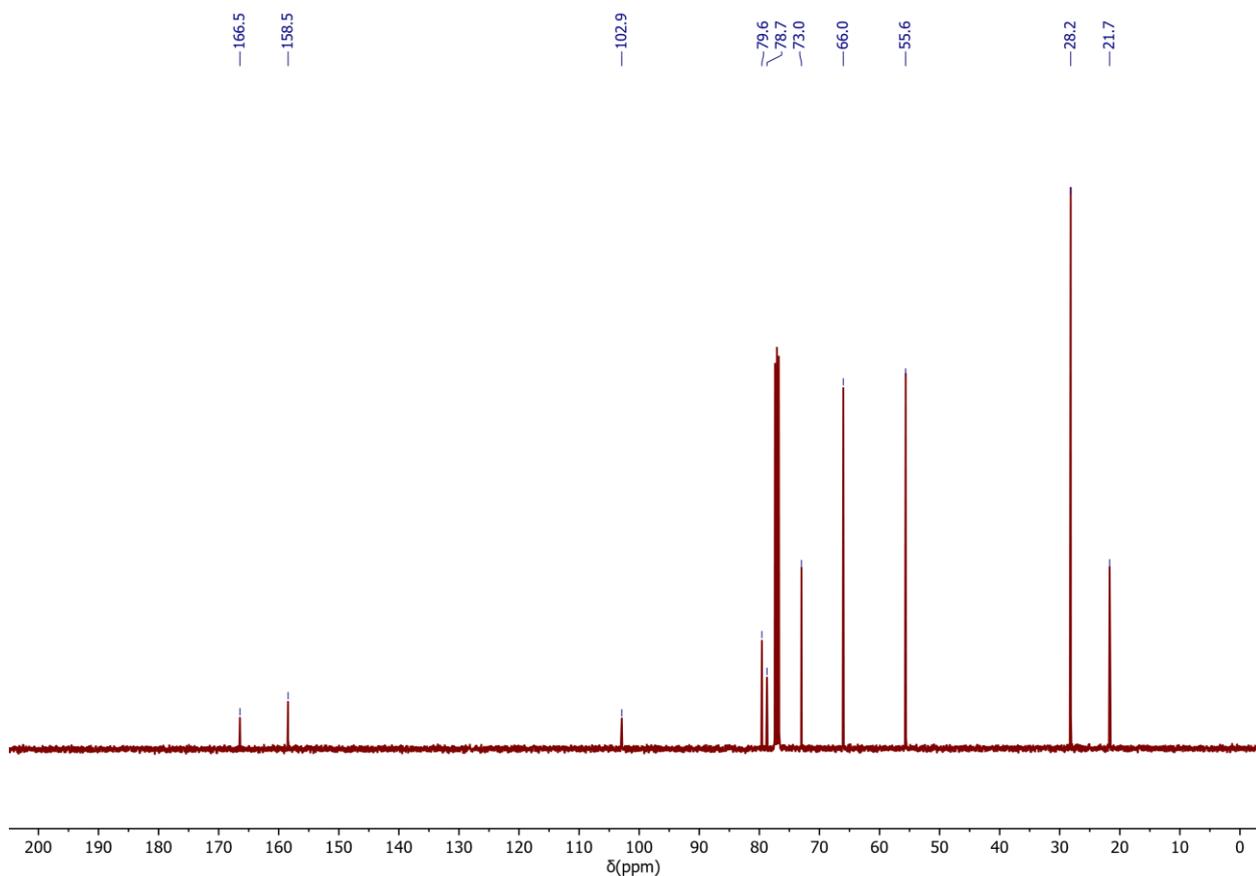


Figure S21.  $^{13}\text{C}$  NMR-spectra of **3j**,  $\text{CDCl}_3$ , 101 MHz

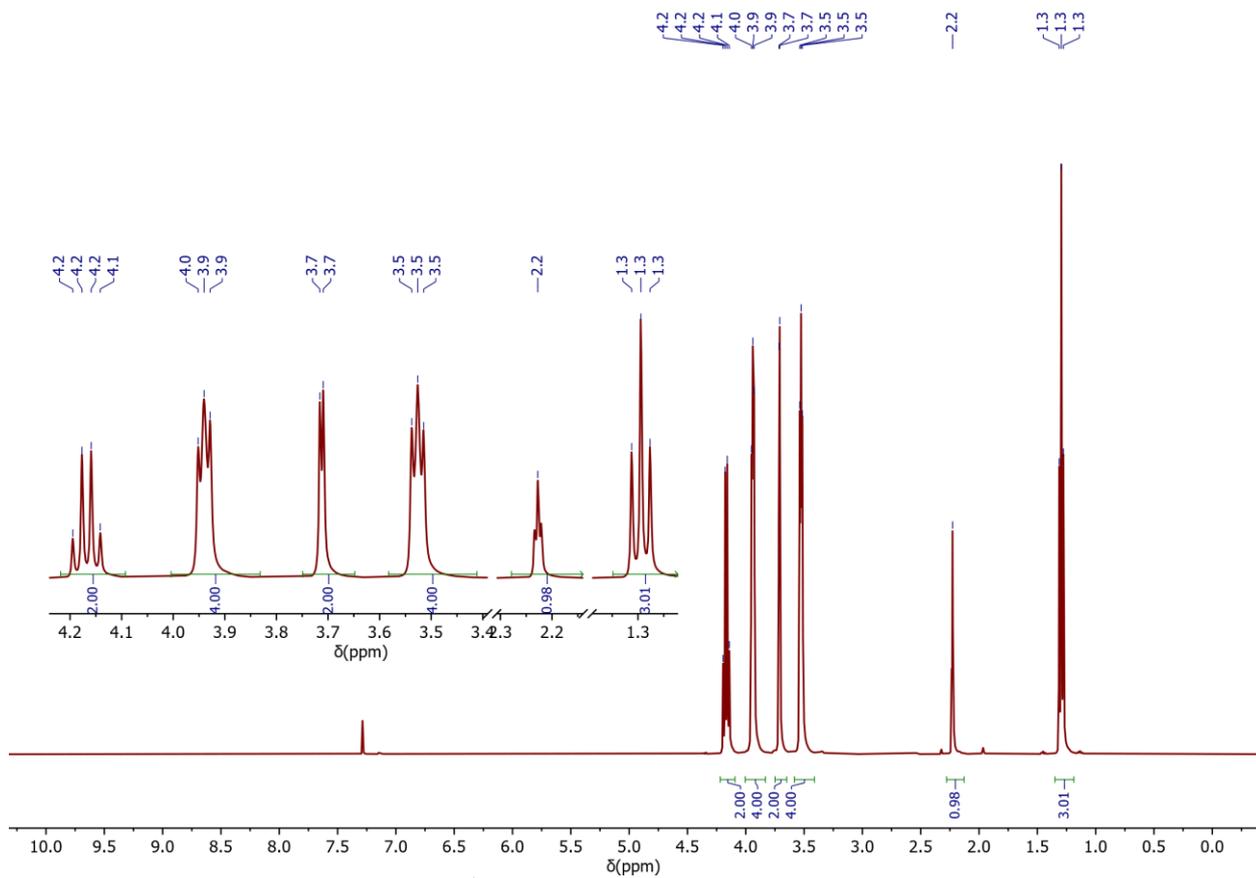


Figure S22.  $^1\text{H}$  NMR-spectra of **3k**,  $\text{CDCl}_3$ , 400 MHz

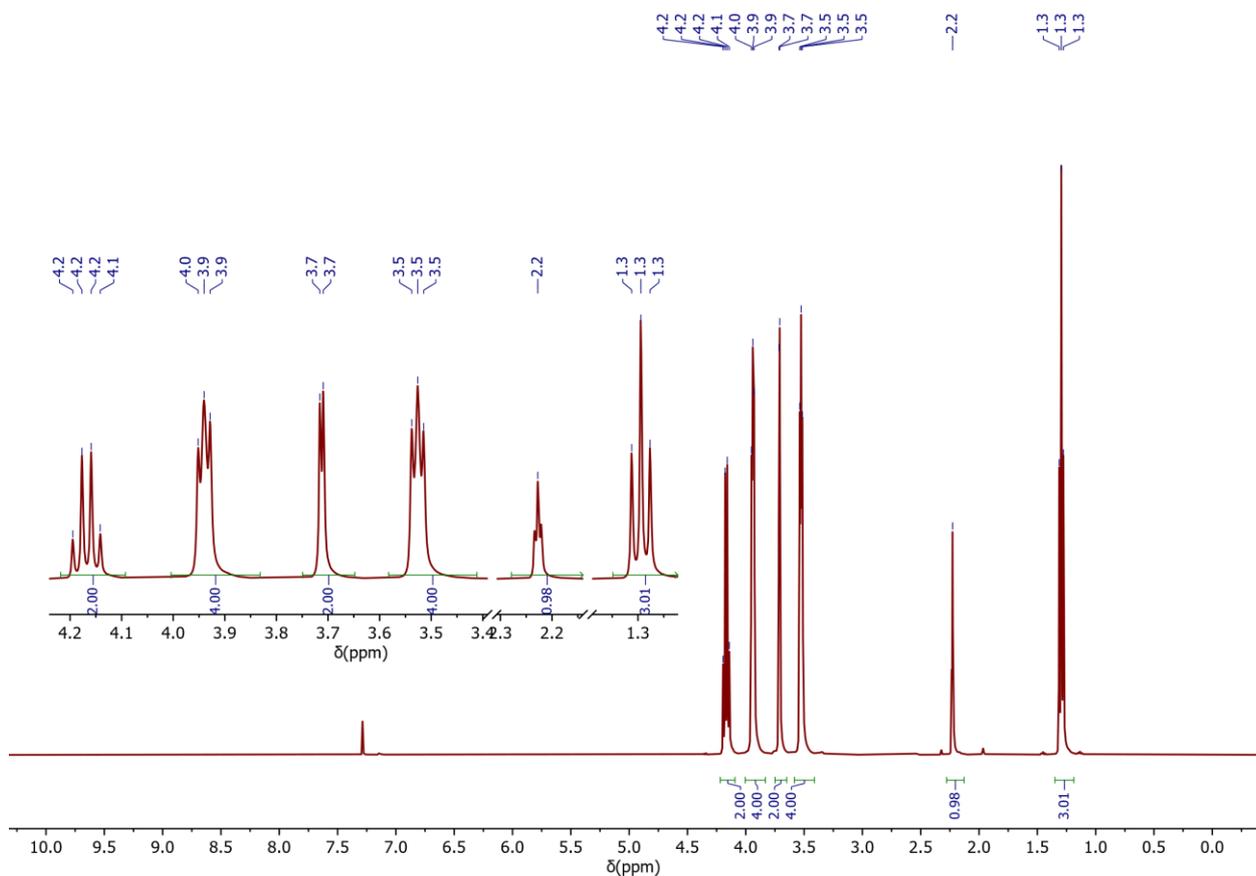


Figure S23.  $^{13}\text{C}$  NMR-spectra of **3k**,  $\text{CDCl}_3$ , 101 MHz

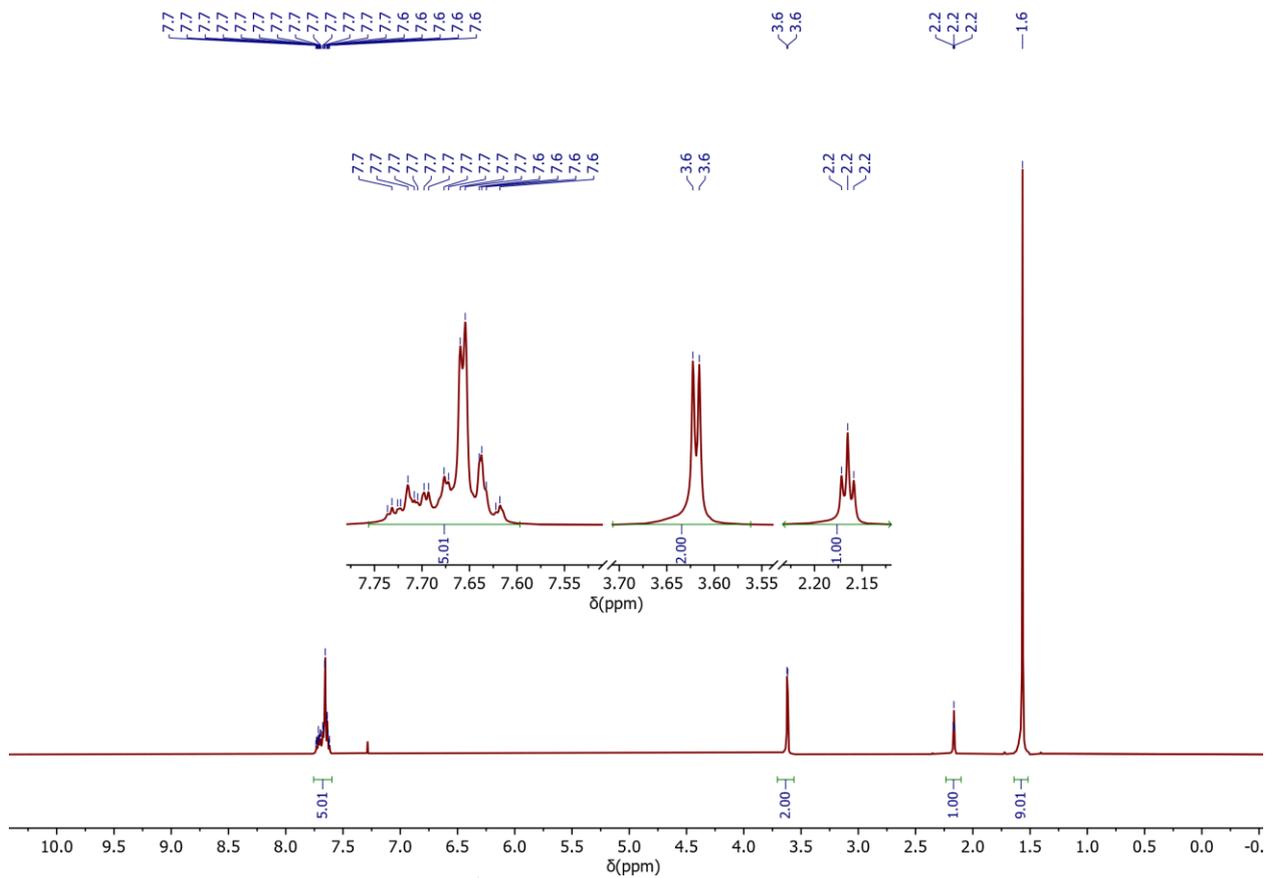


Figure S24.  $^1\text{H}$  NMR-spectra of **31**,  $\text{CDCl}_3$ , 400 MHz

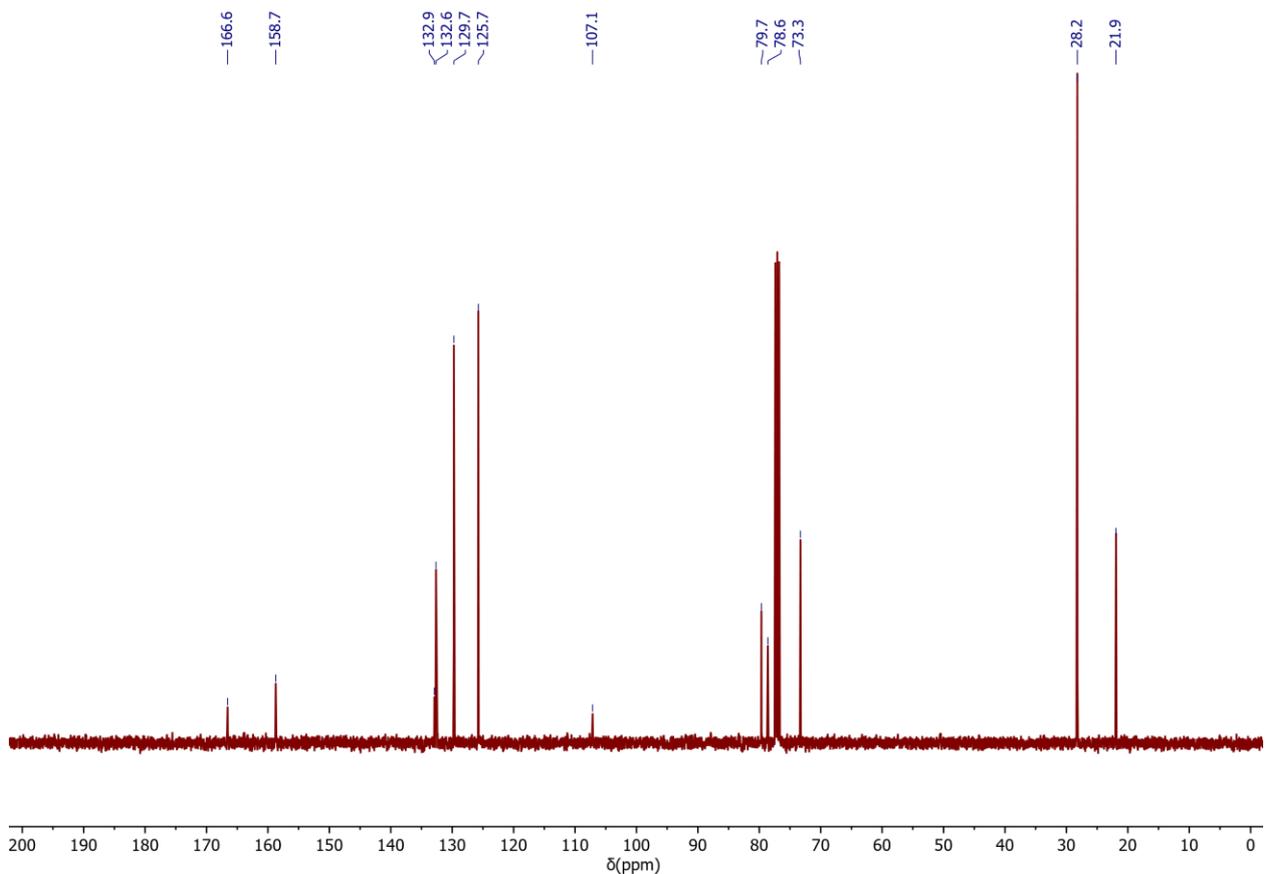


Figure S25.  $^{13}\text{C}$  NMR-spectra of **31**,  $\text{CDCl}_3$ , 101 MHz

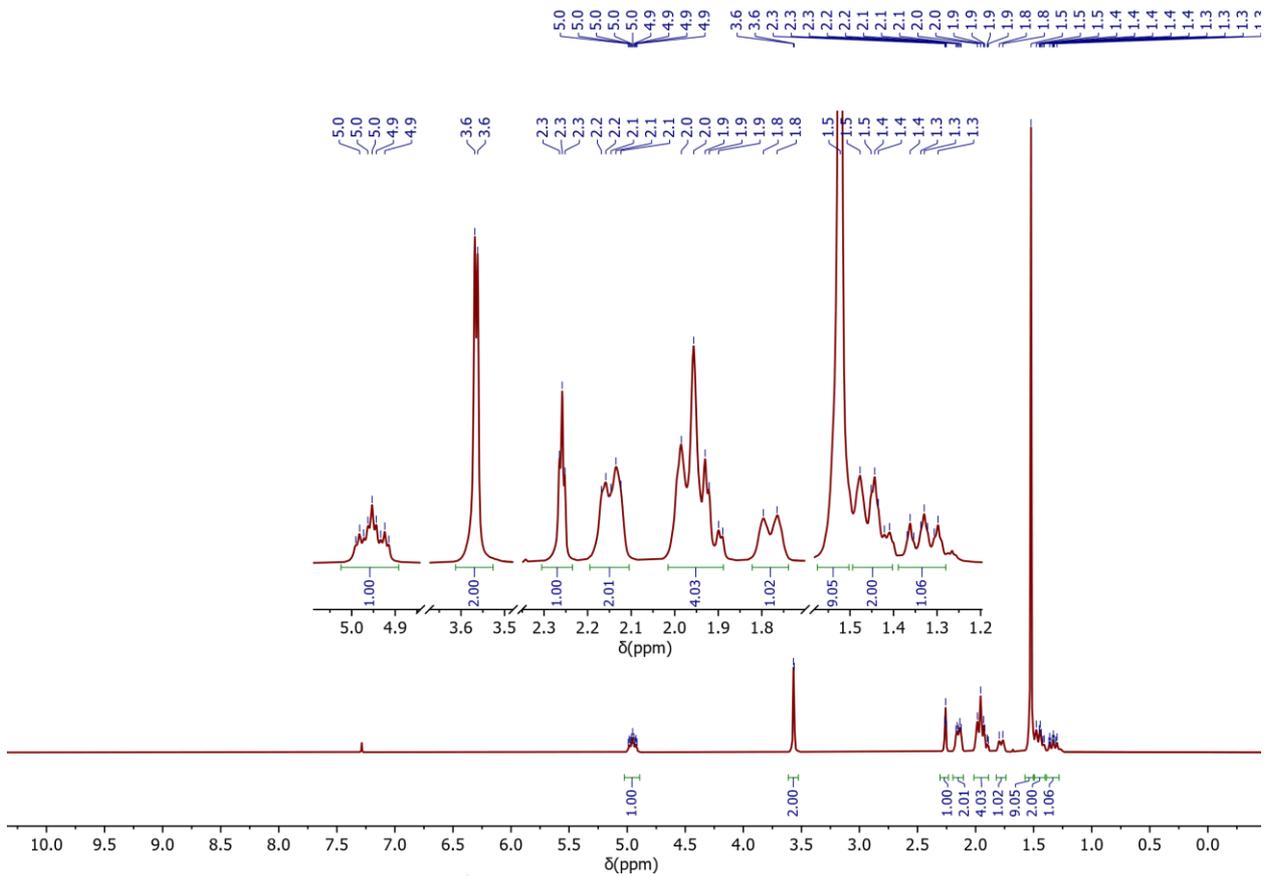


Figure S26.  $^1\text{H}$  NMR-spectra of **3m**,  $\text{CDCl}_3$ , 400 MHz

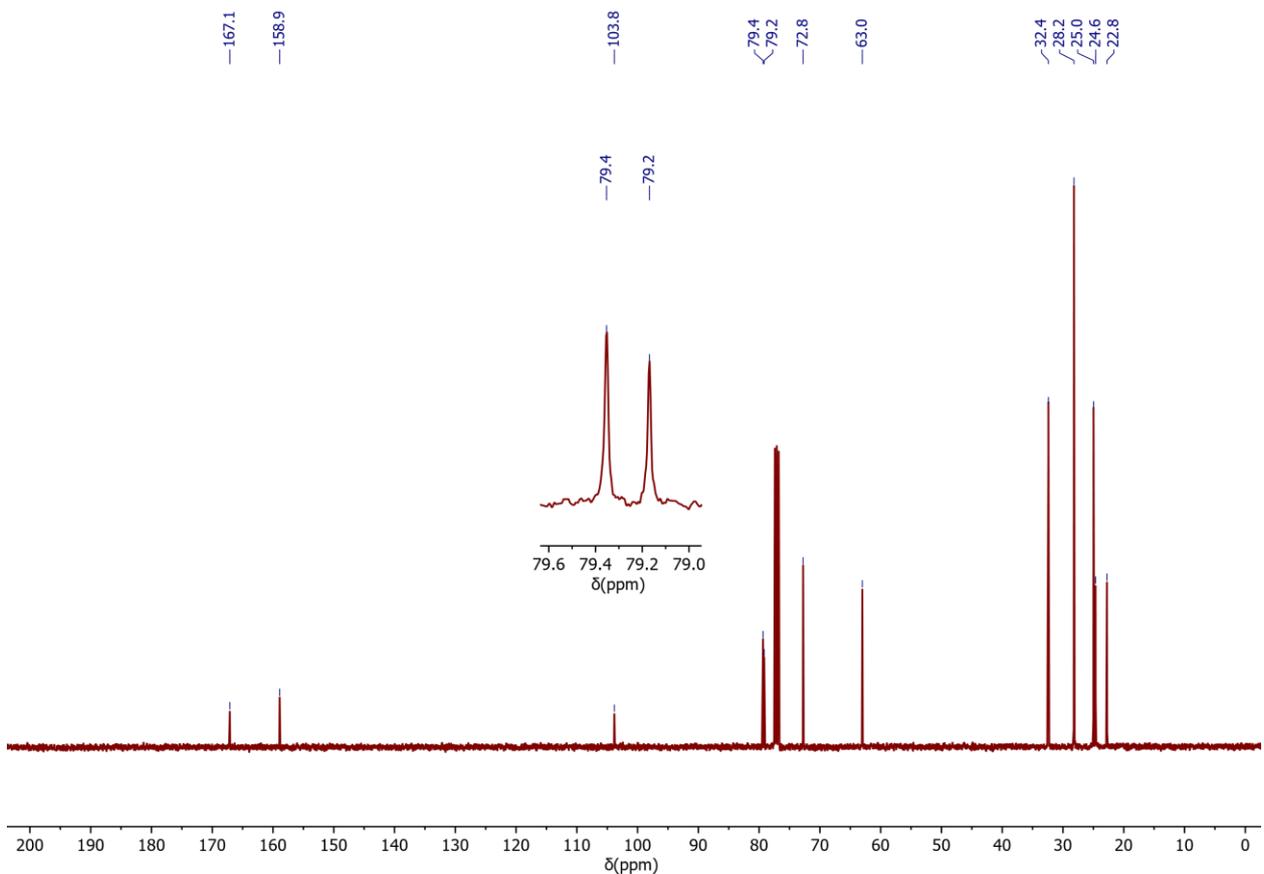
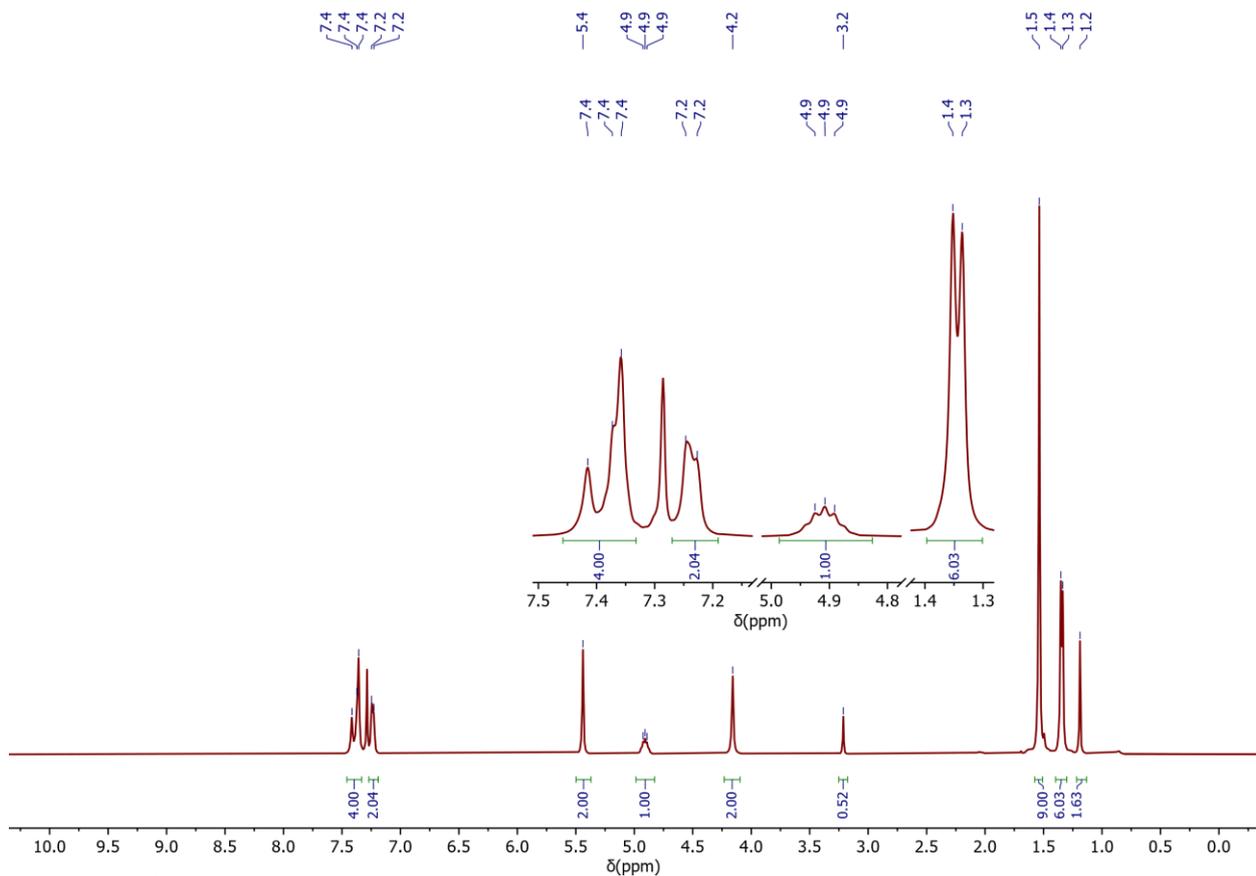
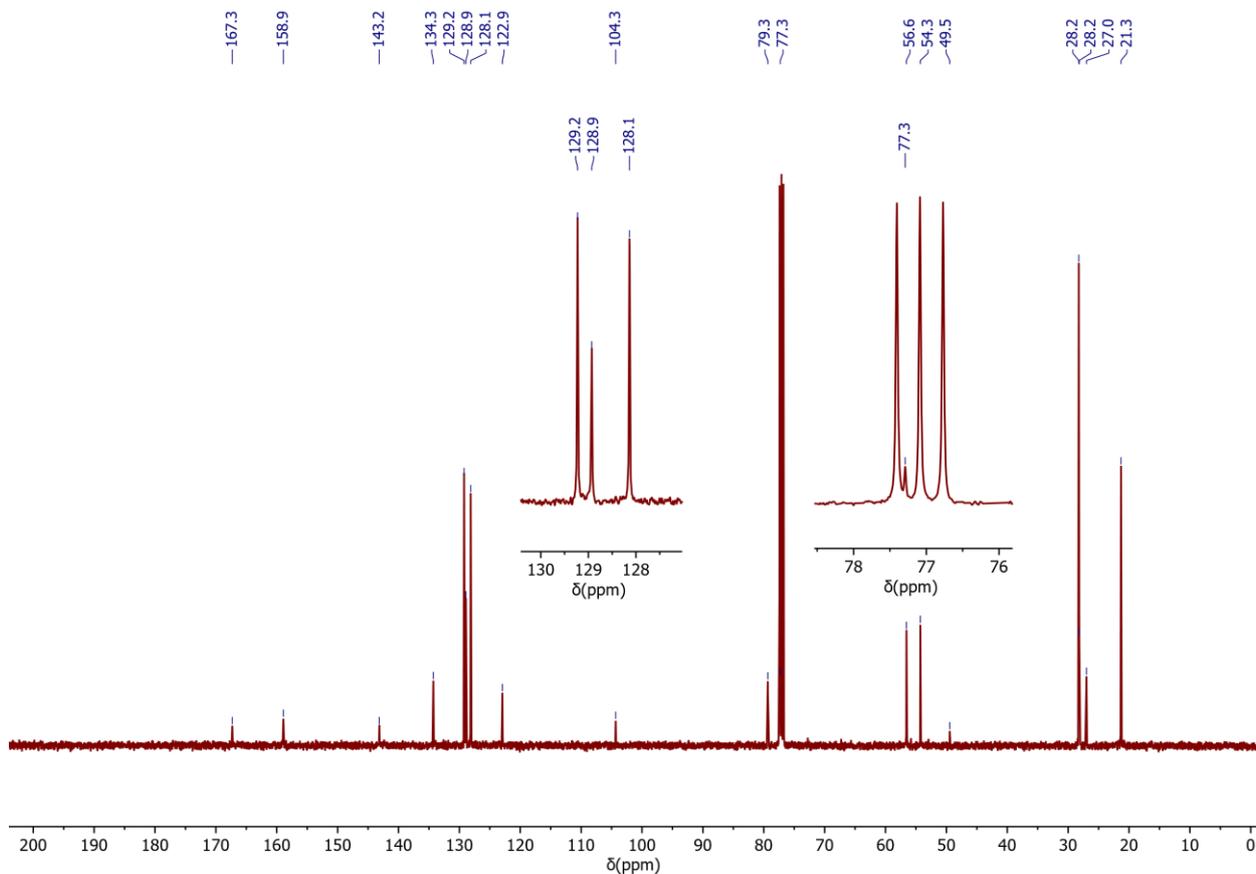


Figure S27.  $^{13}\text{C}$  NMR-spectra of **3m**,  $\text{CDCl}_3$ , 101 MHz



**Figure S28.**  $^1\text{H}$  NMR-spectra of **4a** as a solvate of half a methyl tert-butyl ether molecule,  $\text{CDCl}_3$ , 400 MHz



**Figure S29.**  $^{13}\text{C}$  NMR-spectra of **4a** as a solvate of half a methyl tert-butyl ether molecule,  $\text{CDCl}_3$ , 101 MHz

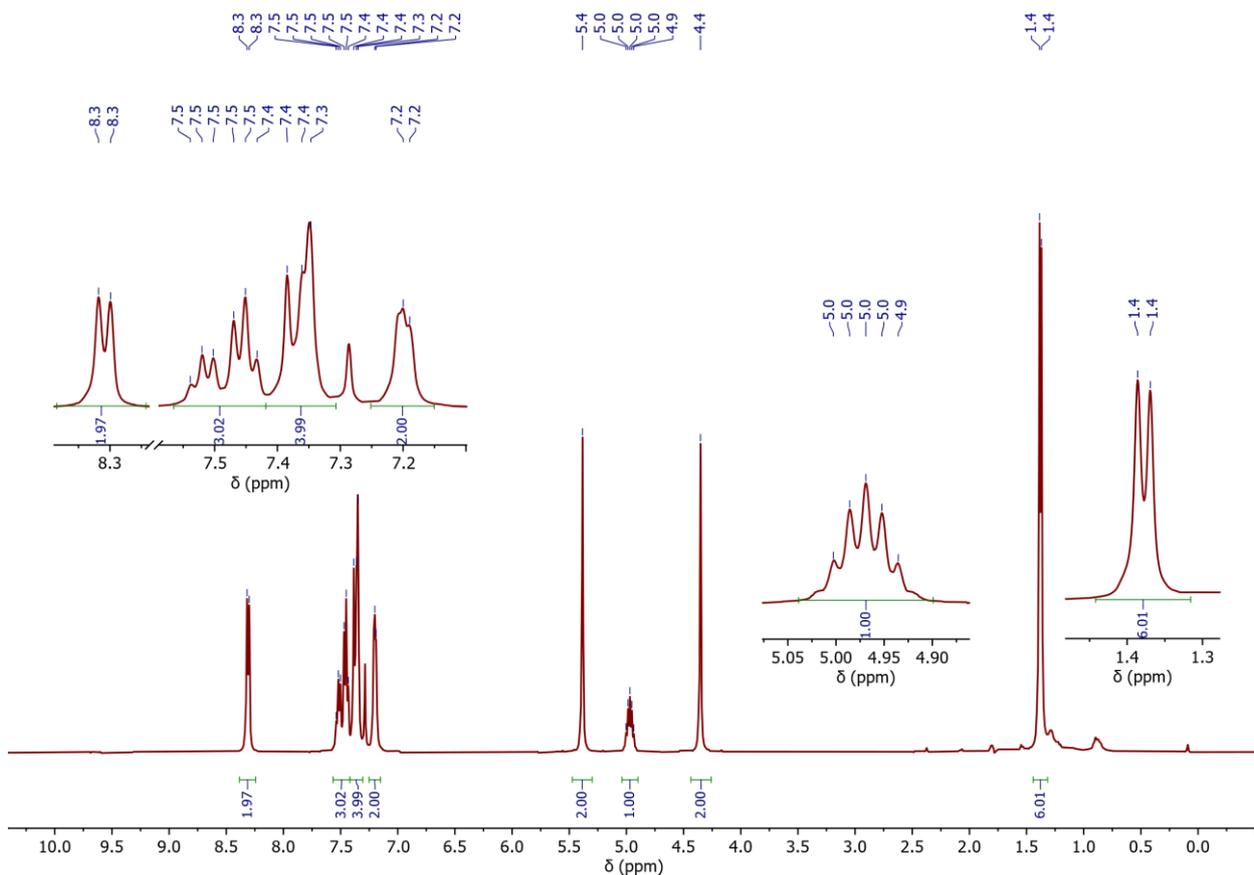


Figure S30.  $^1\text{H}$  NMR-spectra of **4b**,  $\text{CDCl}_3$ , 400 MHz

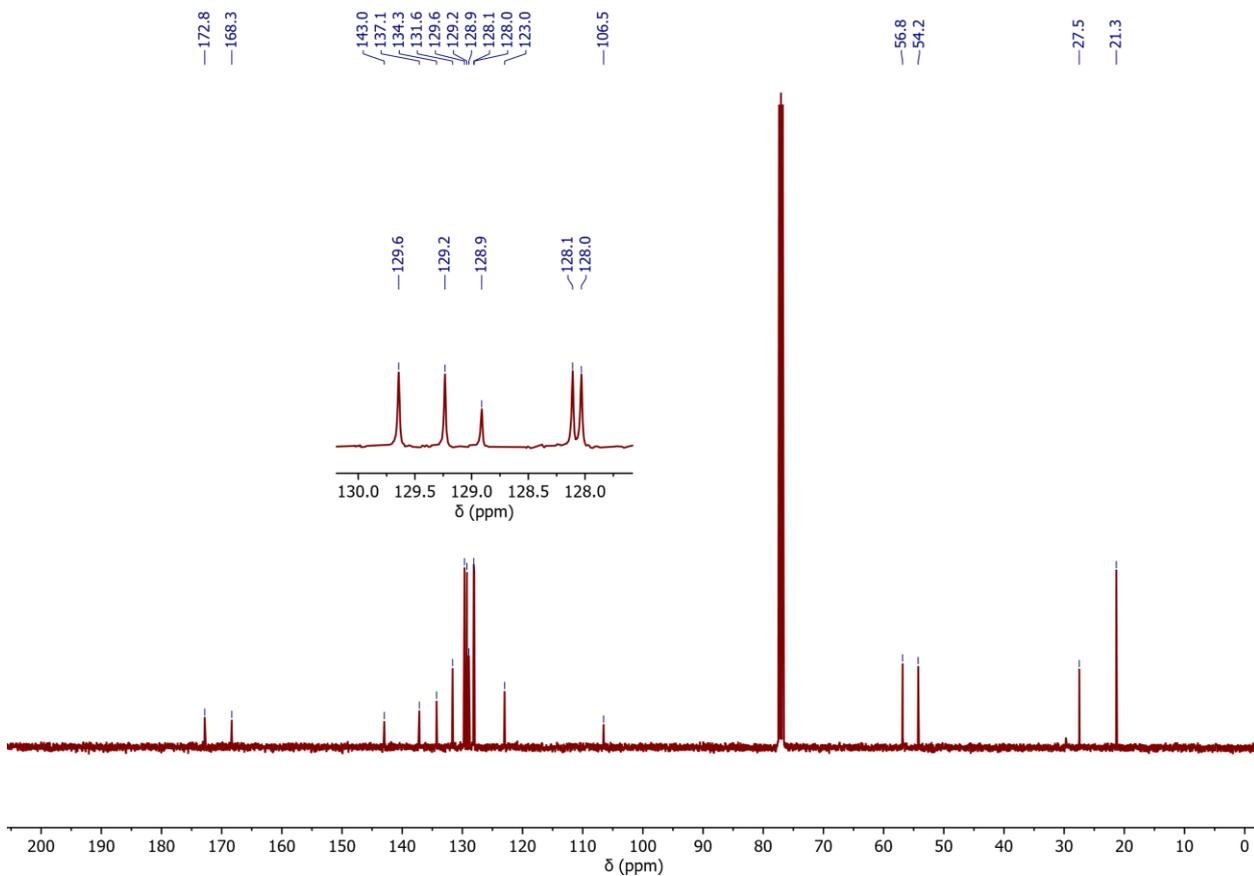


Figure S31.  $^{13}\text{C}$  NMR-spectra of **4b**,  $\text{CDCl}_3$ , 101 MHz

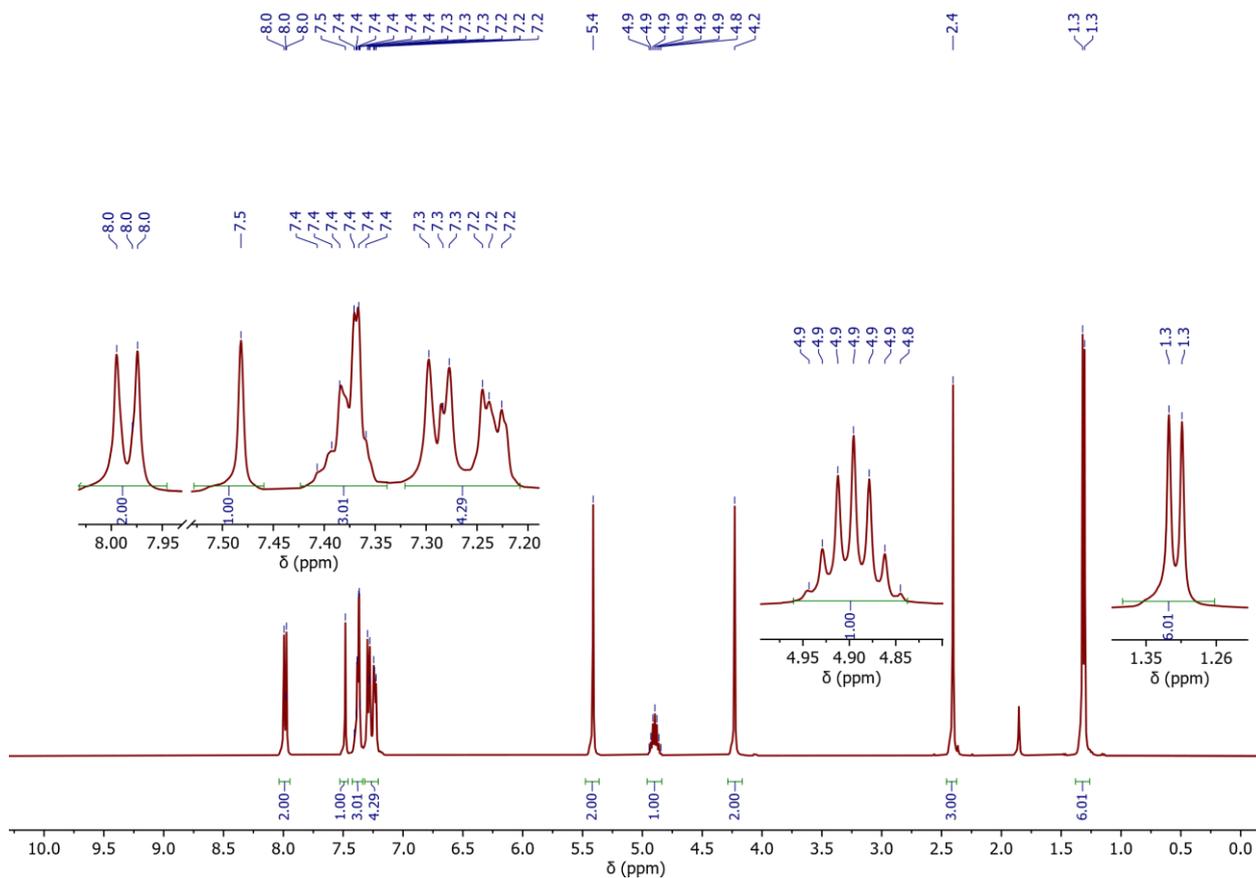


Figure S32.  $^1\text{H}$  NMR-spectra of **4c**,  $\text{CDCl}_3$ , 400 MHz

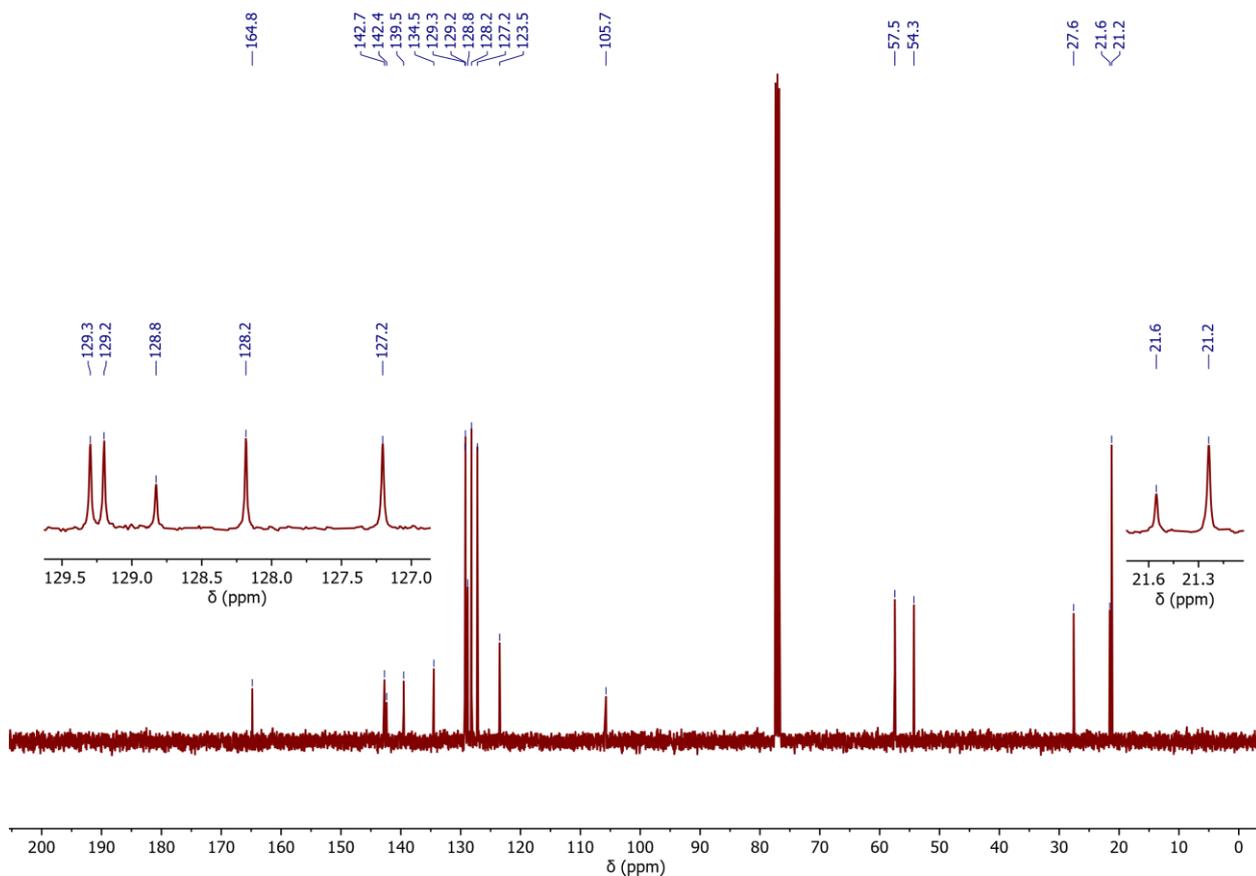


Figure S33.  $^{13}\text{C}$  NMR-spectra of **4c**,  $\text{CDCl}_3$ , 101 MHz

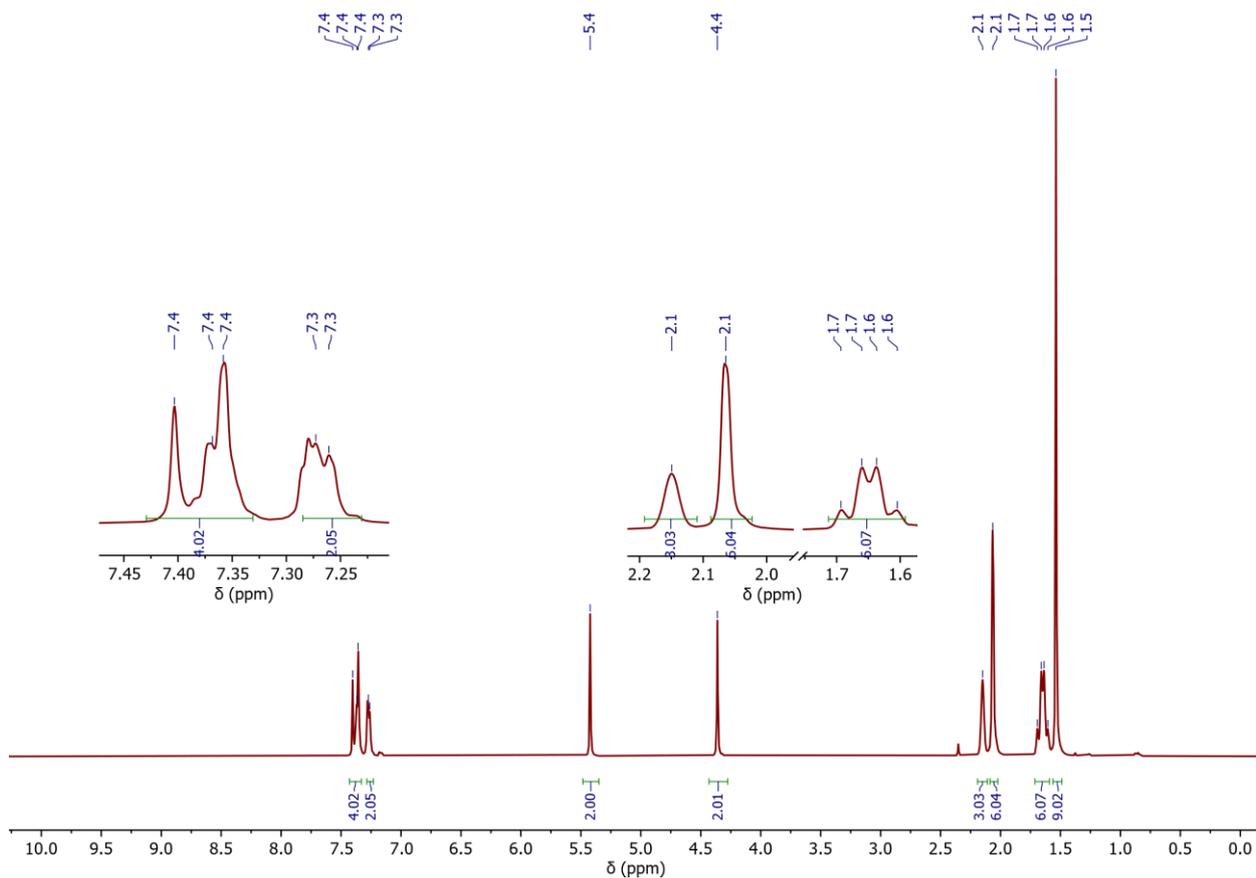


Figure S34.  $^1\text{H}$  NMR-spectra of **4d**,  $\text{CDCl}_3$ , 400 MHz

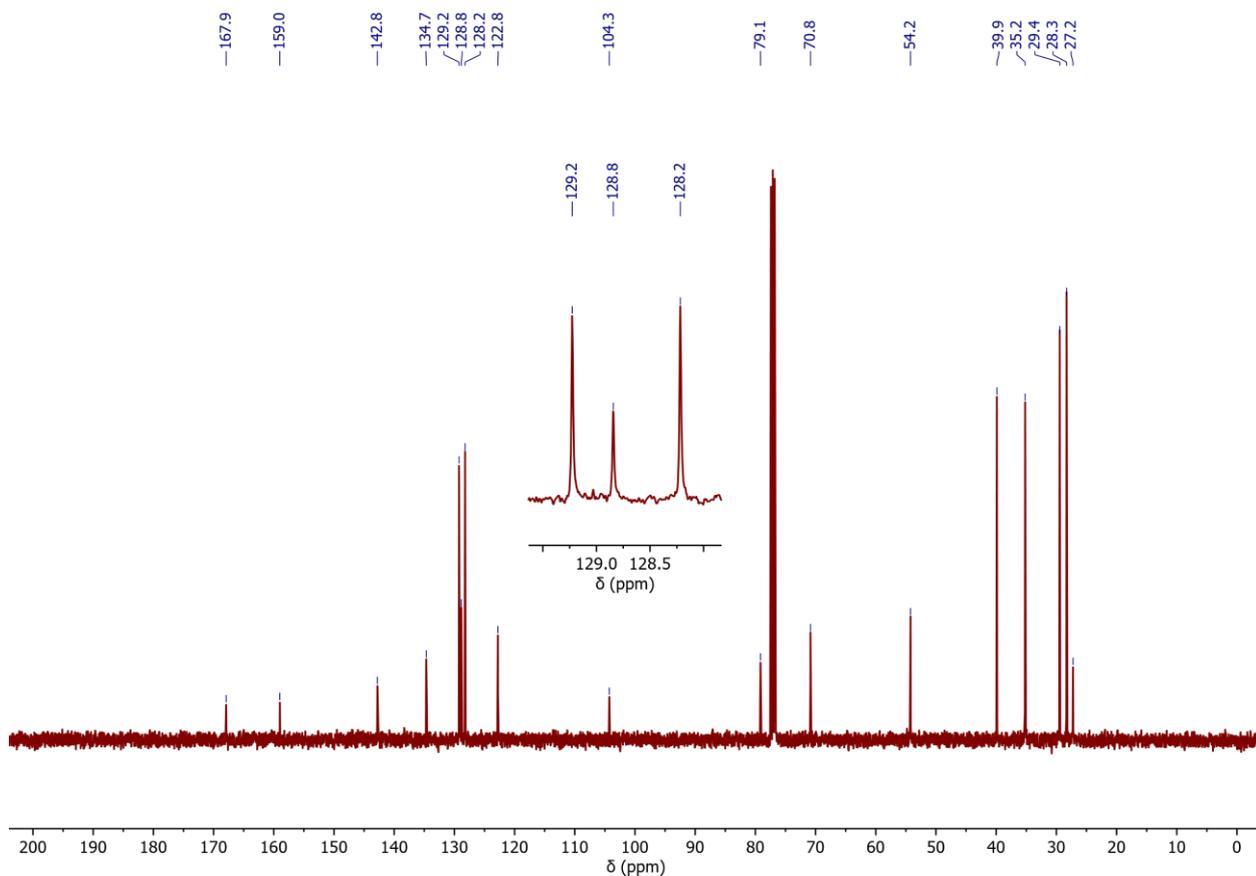
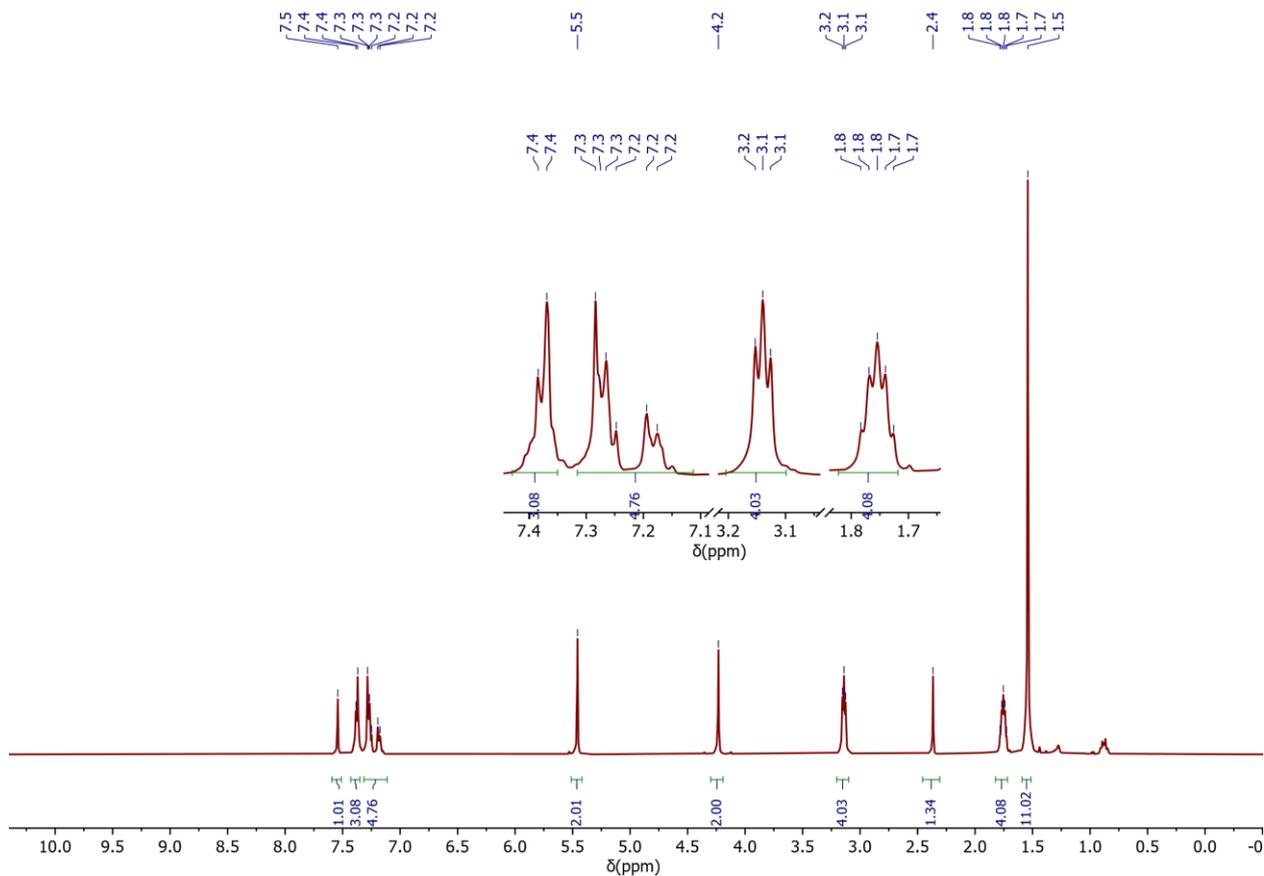
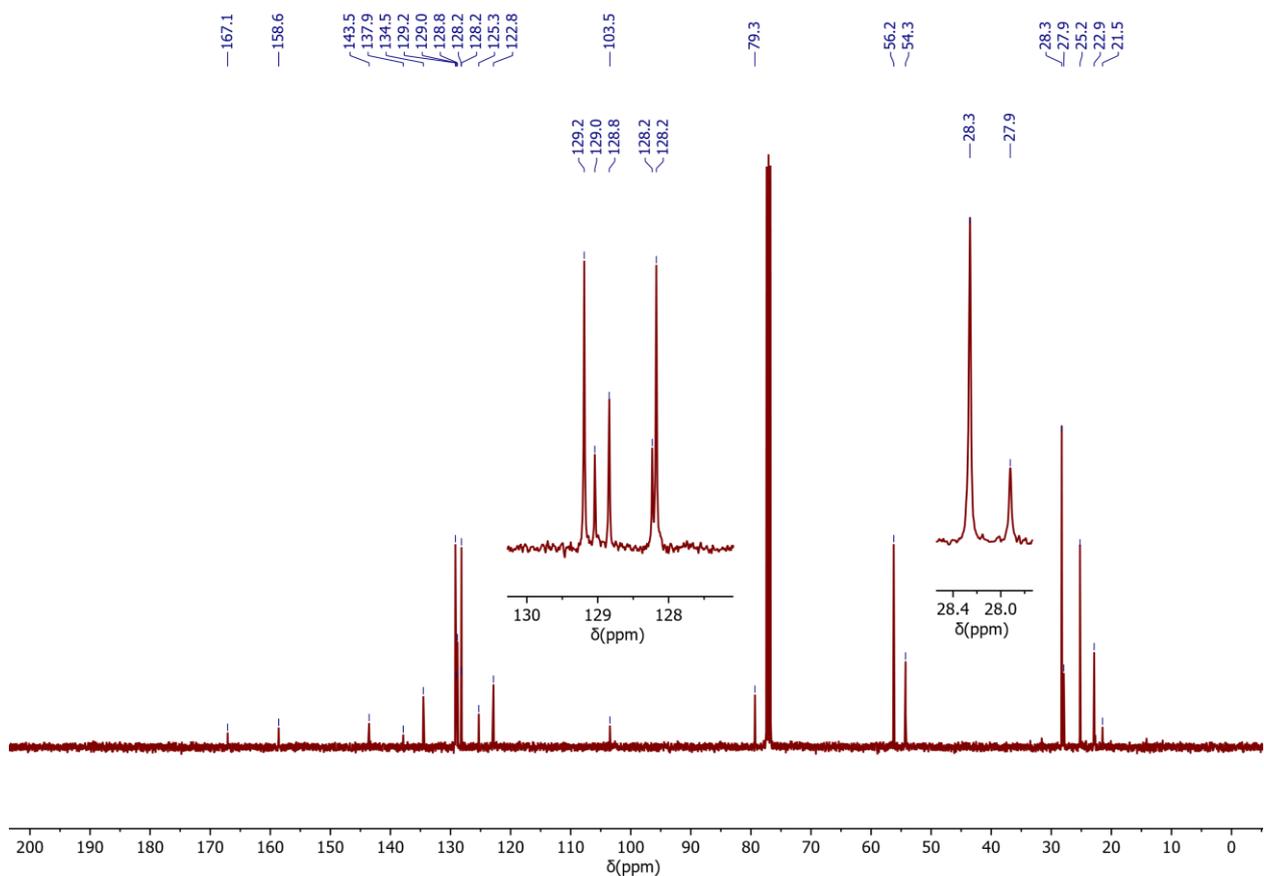


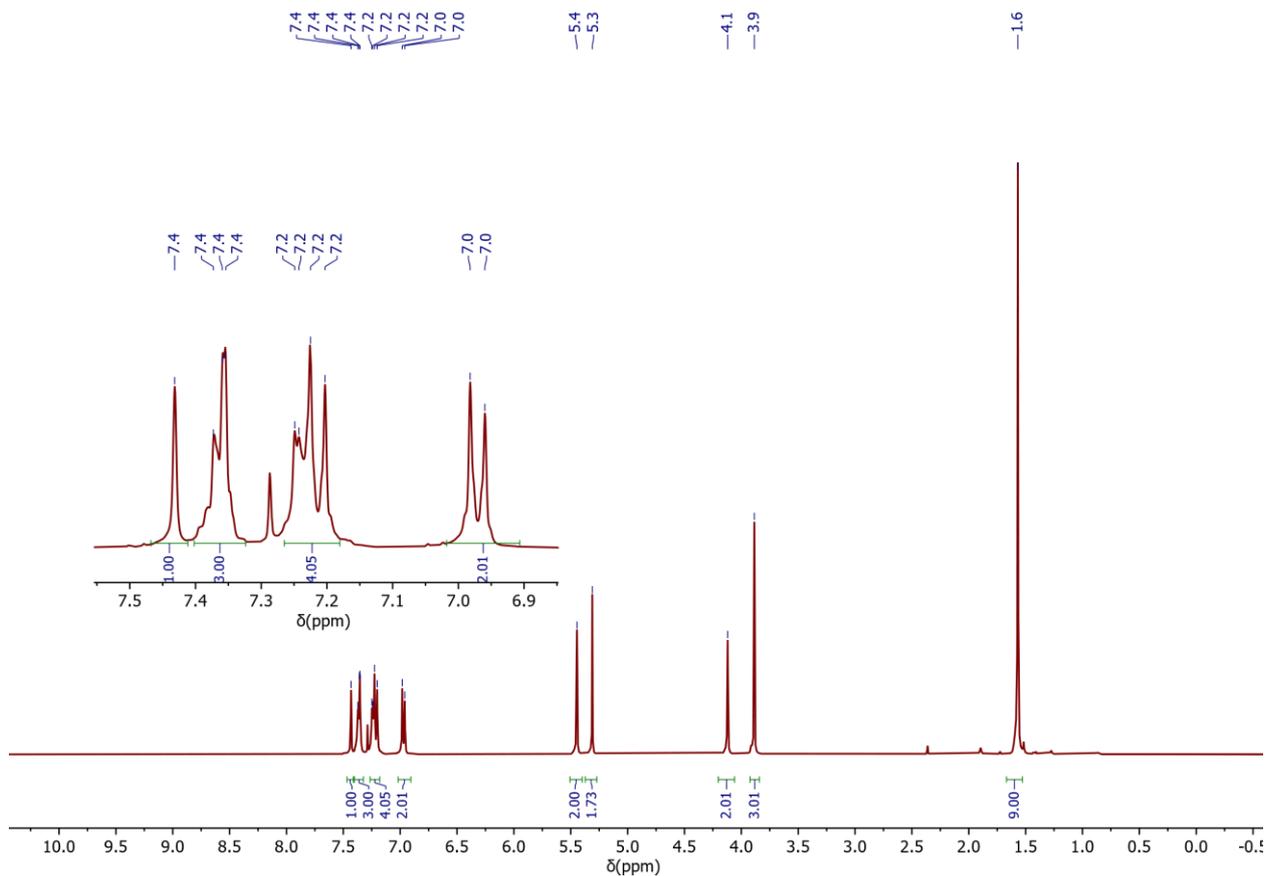
Figure S35.  $^{13}\text{C}$  NMR-spectra of **4d**,  $\text{CDCl}_3$ , 101 MHz



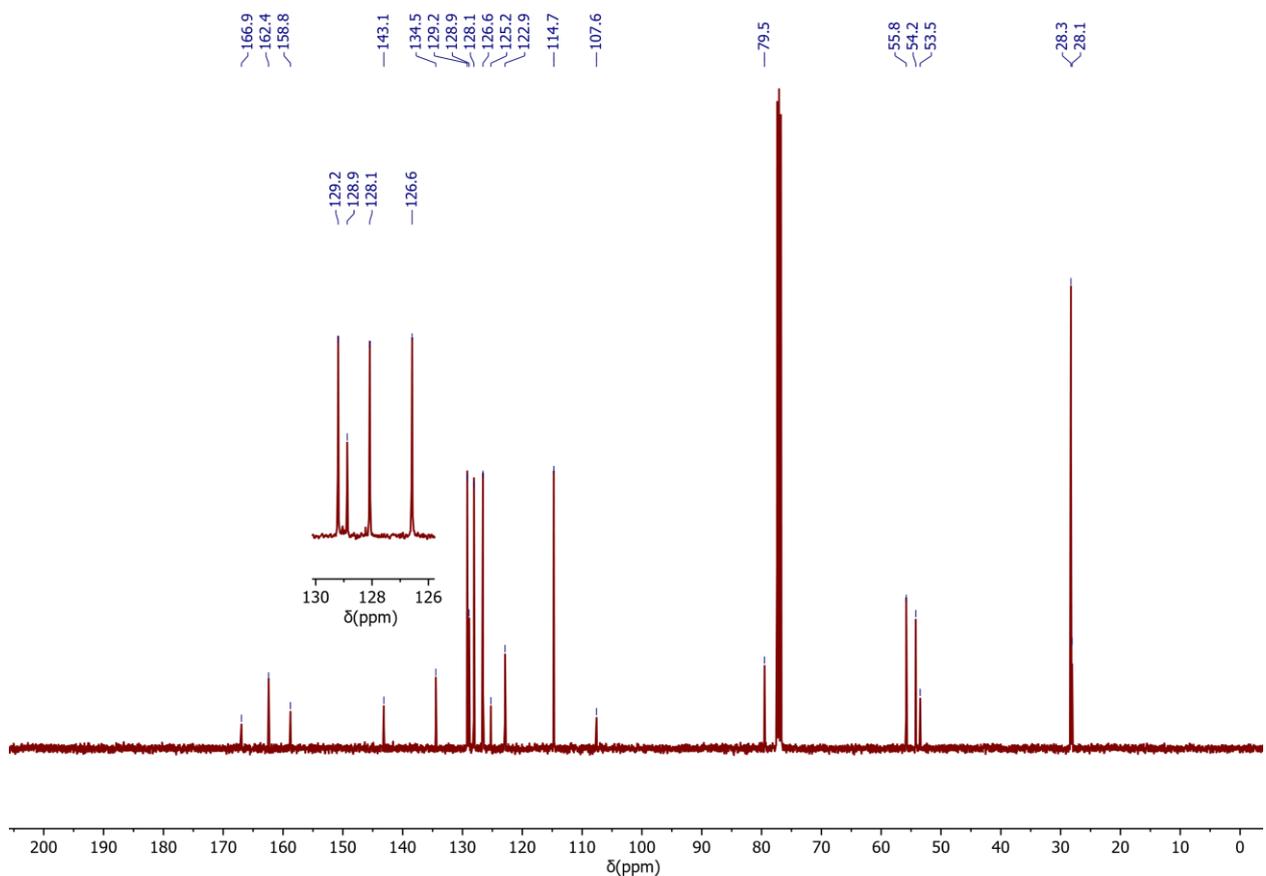
**Figure S36.**  $^1\text{H}$  NMR-spectra of **4e** as a solvate of half a toluene molecule,  $\text{CDCl}_3$ , 400 MHz



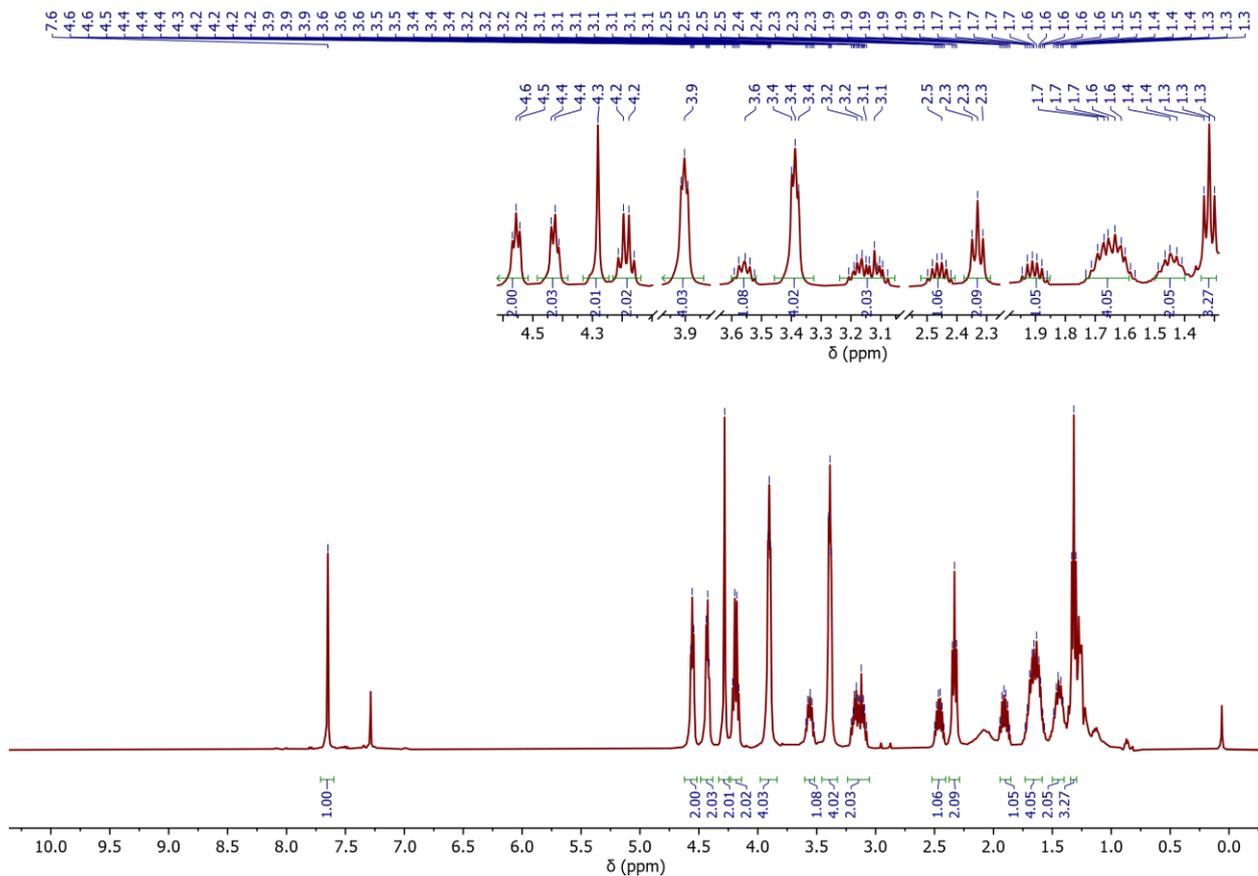
**Figure S37.**  $^{13}\text{C}$  NMR-spectra of **4e** as a solvate of half a toluene molecule,  $\text{CDCl}_3$ , 101 MHz



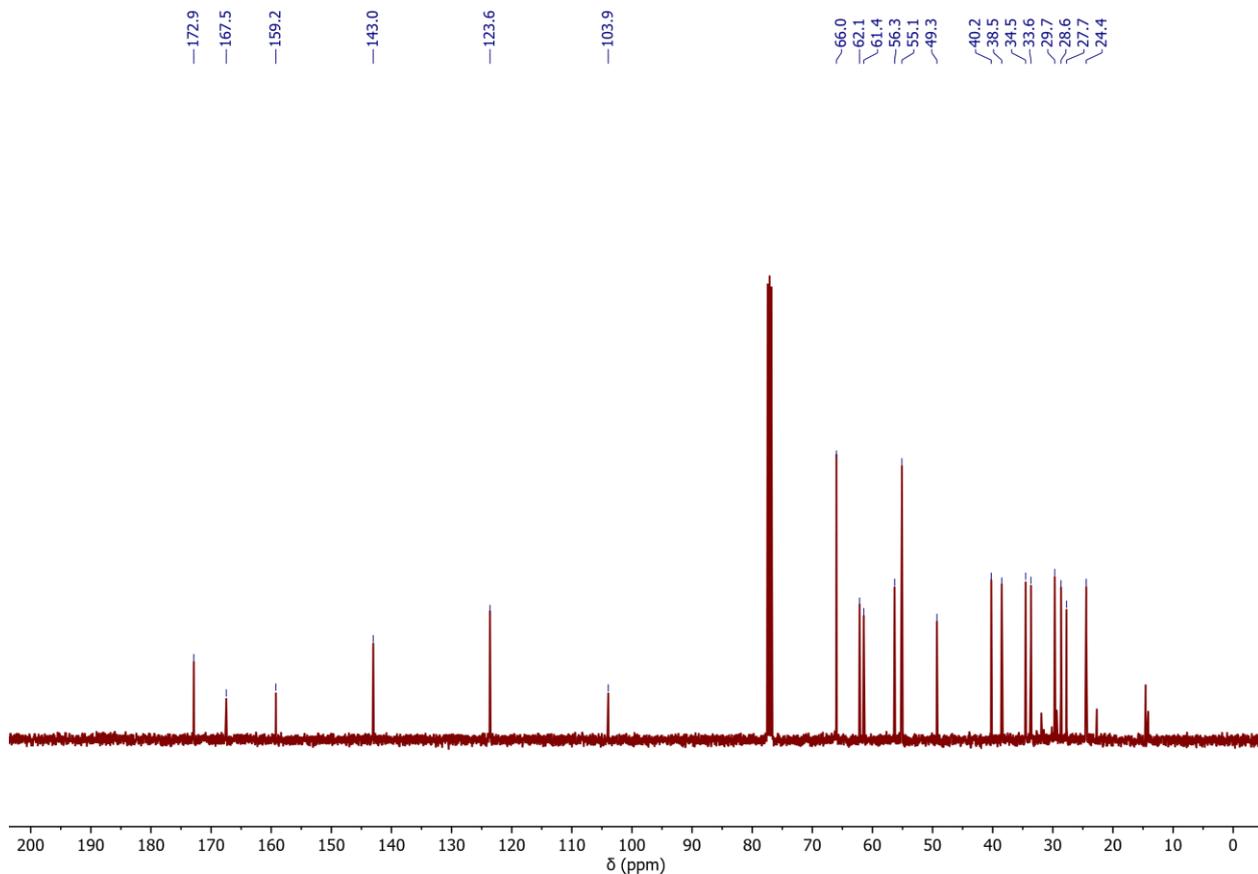
**Figure S38.**  $^1\text{H}$  NMR-spectra of **4f** as a solvate of a dichloromethane molecule,  $\text{CDCl}_3$ , 400 MHz



**Figure S39.**  $^{13}\text{C}$  NMR-spectra of **4f** as a solvate of a dichloromethane molecule,  $\text{CDCl}_3$ , 101 MHz



**Figure S40.**  $^1\text{H}$  NMR-spectra of **5**,  $\text{CDCl}_3$ , 400 MHz



**Figure S41.**  $^{13}\text{C}$  NMR-spectra of **5**,  $\text{CDCl}_3$ , 101 MHz

## X-Ray study data

Single crystals of  $C_{40}H_{44}N_6O_6P_2S_2$  **3i**. A suitable crystal was selected and characterized on a Bruker SMART APEX CCD area detector diffractometer. The crystal was kept at 296.15 K during data collection. Using Olex2<sup>S3</sup>, the structure was solved with the SHELXT<sup>S4</sup> structure solution program using Intrinsic Phasing and refined with the XL<sup>S5</sup> refinement package using Least Squares minimization.

Crystal structure determination of **3i**.

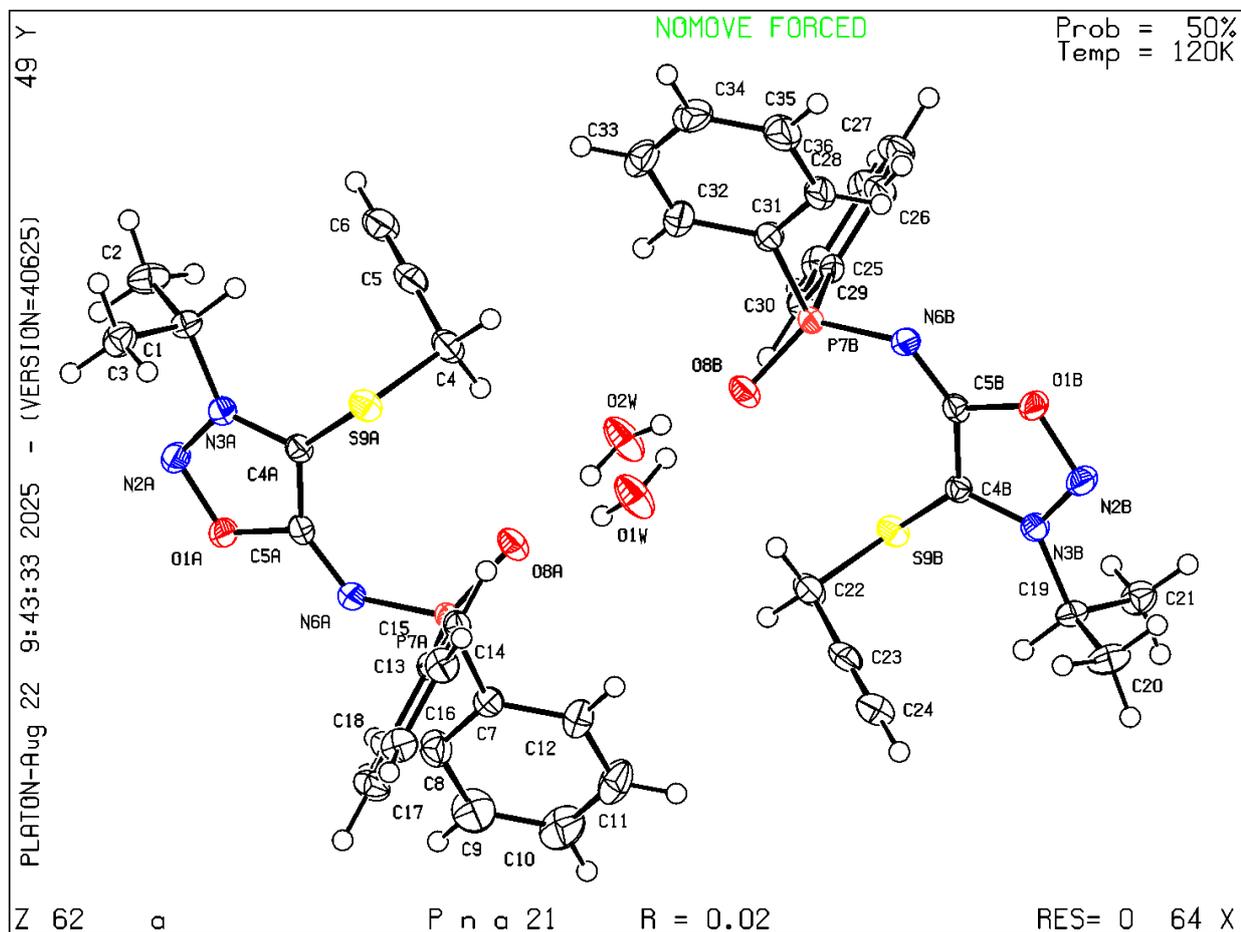


Figure S42 Crystal structure determination of **3i**.

Crystal Data for  $C_{40}H_{44}N_6O_6P_2S_2$  ( $M=830.87$  g/mol): orthorhombic, space group  $Pna2_1$  (no. 33),  $a = 18.3645(9)$  Å,  $b = 8.5628(4)$  Å,  $c = 26.5061(12)$  Å,  $V = 4168.1(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 296.15$  K,  $\mu(\text{MoK}\alpha) = 0.258$  mm<sup>-1</sup>,  $D_{\text{calc}} = 1.324$  g/cm<sup>3</sup>, 60082 reflections measured ( $3.074^\circ \leq 2\theta \leq 54.902^\circ$ ), 9422 unique ( $R_{\text{int}} = 0.0221$ ,  $R_{\text{sigma}} = 0.0156$ ) which were used in all calculations. The final  $R_1$  was 0.0236 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.0670 (all data).

Table S1. Crystal data and structure refinement for **3i**.

Identification code	3e
Empirical formula	$C_{40}H_{44}N_6O_6P_2S_2$
Formula weight	830.87
Temperature/K	296.15
Crystal system	orthorhombic
Space group	$Pna2_1$
$a/\text{Å}$	18.3645(9)
$b/\text{Å}$	8.5628(4)
$c/\text{Å}$	26.5061(12)
$\alpha/^\circ$	90

$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/ $\text{\AA}^3$	4168.1(3)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.324
$\mu/\text{mm}^{-1}$	0.258
F(000)	1744.0
Crystal size/ $\text{mm}^3$	? $\times$ ? $\times$ ?
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ )
2 $\Theta$ range for data collection/ $^\circ$	3.074 to 54.902
Index ranges	$-23 \leq h \leq 23, -11 \leq k \leq 11, -34 \leq l \leq 34$
Reflections collected	60082
Independent reflections	9422 [ $R_{\text{int}} = 0.0221, R_{\text{sigma}} = 0.0156$ ]
Data/restraints/parameters	9422/1/519
Goodness-of-fit on $F^2$	1.059
Final R indexes [ $I > 2\sigma(I)$ ]	$R_1 = 0.0236, wR_2 = 0.0666$
Final R indexes [all data]	$R_1 = 0.0246, wR_2 = 0.0670$
Largest diff. peak/hole / $e \text{\AA}^{-3}$	0.28/-0.21
Flack parameter	0.076(8)

**Table S2.** Fractional Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for 3e.  $U_{\text{eq}}$  is defined as 1/3 of the trace of the orthogonalised  $U_{ij}$  tensor.

Atom	x	y	z	U(eq)
S9A	5588.0(3)	478.4(6)	4424.7(2)	23.44(11)
P7A	6230.8(3)	3955.8(6)	3691.8(2)	17.7(1)
O1A	4751.4(8)	1355.2(18)	3092.5(5)	23.5(3)
O8A	6090.7(8)	4216.4(19)	4240.8(6)	24.9(3)
N2A	4341.5(10)	106(2)	3251.6(7)	24.3(4)
N3A	4570.6(9)	-180.1(19)	3704.4(6)	19.7(3)
N6A	5622.8(10)	3041(2)	3357.4(7)	21.7(4)
C1	4231.9(11)	-1528(2)	3978.5(8)	21.5(4)
C2	3412.0(12)	-1493(3)	3899.1(10)	30.7(5)
C3	4587.9(13)	-3016(2)	3792.8(9)	28.0(5)
C4	5112.1(12)	1773(3)	4866.7(8)	28.9(5)
C4A	5114.9(10)	778(2)	3870.3(7)	19.2(4)
C5	4342.0(13)	1415(3)	4921.2(8)	27.3(4)
C5A	5235.6(11)	1828(2)	3468.1(7)	19.2(4)
C6	3704.9(14)	1152(3)	4955.9(9)	31.5(5)
C7	6302.7(11)	5806(2)	3367.8(8)	20.8(4)
C8	6027.0(14)	6068(3)	2885.3(9)	29.7(5)
C9	6075.4(17)	7551(3)	2671.7(11)	43.4(6)
C10	6410.8(18)	8754(3)	2930.1(13)	44.0(7)
C11	6689.0(13)	8507(3)	3409.5(12)	37.4(6)
C12	6631.6(11)	7033(3)	3628.0(9)	27.1(5)
C13	7088.5(11)	2968(2)	3594.0(7)	18.2(4)
C14	7449.8(11)	2237(2)	3991.4(8)	20.9(4)
C15	8111.9(12)	1485(2)	3904.8(9)	25.7(4)
C16	8408.8(12)	1460(2)	3422.6(9)	26.5(4)
C17	8051.4(13)	2185(3)	3027.3(9)	27.4(5)
C18	7393.5(12)	2937(2)	3111.0(8)	22.7(4)
S9B	6644.4(3)	9538.4(6)	5582.7(2)	22.32(11)

**Table S2.** Fractional Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for **3e**.  $U_{\text{eq}}$  is defined as 1/3 of the trace of the orthogonalised  $U_{ij}$  tensor.

Atom	x	y	z	U(eq)
P7B	6002.1(3)	6055.6(6)	6317.6(2)	18.31(11)
O1B	7493.4(8)	8636.4(17)	6907.7(6)	24.2(3)
O8B	6117.8(8)	5811.0(18)	5763.1(6)	24.8(3)
N2B	7904.3(10)	9896(2)	6749.1(7)	25.3(4)
N3B	7672.0(9)	10180.6(19)	6298.0(6)	19.3(3)
N6B	6622.7(9)	6959(2)	6644.4(7)	21.9(4)
C4B	7122.9(10)	9229(2)	6133.7(7)	17.8(4)
C5B	7008.8(11)	8167(2)	6534.5(8)	18.8(4)
C19	8010.9(11)	11535(2)	6025.8(8)	21.3(4)
C20	8828.3(12)	11487(3)	6100.9(10)	31.2(5)
C21	7655.5(12)	13021(3)	6214.6(9)	29.0(5)
C22	7109.7(12)	8227(3)	5139.9(8)	28.1(5)
C23	7884.5(13)	8559(3)	5086.1(8)	26.4(4)
C24	8518.4(13)	8802(3)	5054.7(9)	30.7(5)
C25	5152.5(10)	7050(2)	6436.1(7)	19.0(4)
C26	4883.2(12)	7151(3)	6930.1(8)	24.2(4)
C27	4230.3(13)	7902(3)	7025.0(9)	28.7(5)
C28	3843.0(13)	8570(3)	6633.2(9)	28.5(5)
C29	4101.3(12)	8481(3)	6141.2(9)	26.7(4)
C30	4756.2(12)	7718(2)	6042.2(8)	23.3(4)
C31	5945.4(11)	4190(2)	6633.2(8)	21.9(4)
C32	5605.2(11)	2963(3)	6373.4(10)	27.1(5)
C33	5577.8(13)	1479(3)	6583.9(11)	34.3(6)
C34	5886.1(16)	1197(3)	7048.0(11)	37.3(6)
C35	6225.9(16)	2400(3)	7309.1(10)	39.9(6)
C36	6252.3(15)	3893(3)	7100.8(10)	31.1(5)
O1W	6996.3(10)	4060(2)	5098.1(7)	37.7(4)
O2W	5219.9(10)	5965(2)	4910.8(7)	38.5(4)

**Table S3.** Anisotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for **3i**. The Anisotropic displacement factor exponent takes the form:  $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$ .

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
S9A	21.3(2)	29.9(3)	19.2(2)	1.3(2)	-2.96(18)	2.90(19)
P7A	17.6(2)	19.3(2)	16.2(2)	-3.25(19)	1.23(18)	0.42(17)
O1A	26.7(7)	25.7(7)	18.2(7)	1.4(6)	-3.4(6)	-7.5(6)
O8A	24.7(7)	31.1(8)	18.8(7)	-6.2(6)	2.9(6)	3.5(6)
N2A	28.2(9)	23.5(9)	21.3(9)	1.6(7)	-3.6(7)	-7.5(7)
N3A	20.8(8)	19.6(8)	18.8(8)	-0.3(7)	-0.1(6)	-0.4(6)
N6A	23.0(9)	24.6(9)	17.6(8)	-0.7(7)	0.8(7)	-4.8(7)
C1	21.8(10)	19.5(10)	23.3(10)	2.9(8)	1.6(8)	-1.8(7)
C2	19.9(10)	37.1(12)	35.1(12)	9.3(10)	3.3(9)	0.4(9)
C3	28.7(11)	21.0(10)	34.1(12)	-1.1(9)	1.5(9)	0.2(8)
C4	28.6(11)	38.7(13)	19.6(10)	-5.8(9)	1.2(8)	-1.1(9)
C4A	18.3(9)	22.0(9)	17.4(9)	-2.2(7)	0.5(7)	0.7(7)
C5	33.9(12)	31.2(11)	16.7(9)	-0.3(8)	3.1(8)	2.2(9)
C5A	19.1(9)	21.5(9)	16.9(9)	-3.9(7)	-1.0(7)	1.0(7)
C6	32.0(12)	39.2(13)	23.4(11)	-2.1(9)	4.7(9)	0.7(10)
C7	18.6(9)	19.0(9)	24.7(10)	-2.4(8)	3.1(8)	3.3(7)
C8	39.4(13)	23.3(11)	26.5(12)	-2.0(9)	-2.1(9)	0.8(9)

**Table S3.** Anisotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for **3i**. The Anisotropic displacement factor exponent takes the form:  $-2\pi^2[h^2a^*2U_{11}+2hka^*b^*U_{12}+\dots]$ .

Atom	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>23</sub>	U <sub>13</sub>	U <sub>12</sub>
C9	60.6(17)	30.6(13)	38.9(15)	8.8(11)	-5.3(12)	7.5(12)
C10	52.3(17)	20.8(12)	59.0(19)	8.1(12)	1.9(14)	5.0(11)
C11	32.1(13)	21.0(11)	58.9(17)	-9.3(11)	0.4(12)	-0.4(9)
C12	20.7(10)	22.8(10)	37.7(12)	-6.4(9)	-2.7(9)	1.1(8)
C13	19.5(9)	15.7(8)	19.5(9)	-3.8(7)	1.9(7)	-0.8(7)
C14	24.9(10)	18.9(9)	18.8(9)	-2.7(7)	1.0(8)	0.4(7)
C15	28.8(11)	21.0(10)	27.2(11)	1.6(8)	-2.1(8)	5.5(8)
C16	24.4(10)	20.4(9)	34.7(12)	0.8(9)	4.9(9)	6.7(8)
C17	31.2(12)	27.6(11)	23.6(10)	-0.8(8)	9.6(9)	6.8(9)
C18	26.1(10)	24.0(10)	18.1(9)	-0.1(8)	2.7(8)	3.4(8)
S9B	20.7(2)	28.5(3)	17.7(2)	1.5(2)	-3.02(18)	3.30(19)
P7B	18.4(2)	19.8(2)	16.7(2)	-3.50(19)	2.33(18)	-1.42(17)
O1B	27.2(7)	26.3(7)	19.1(7)	3.8(6)	-5.4(6)	-10.0(6)
O8B	24.5(7)	31.9(8)	17.9(7)	-5.9(6)	3.0(6)	2.6(6)
N2B	28.2(9)	26.5(9)	21.3(8)	5.3(7)	-4.7(7)	-9.7(7)
N3B	19.6(8)	19.9(8)	18.5(8)	0.8(7)	-1.2(6)	-1.1(6)
N6B	22.5(9)	24.1(9)	18.9(8)	1.1(7)	-0.4(6)	-5.4(7)
C4B	16.6(9)	19.6(9)	17.1(9)	-1.0(7)	0.6(7)	0.1(7)
C5B	17.9(9)	22.3(10)	16.0(9)	-2.2(8)	-1.1(7)	0.6(7)
C19	21.6(10)	20.9(10)	21.5(9)	4.8(8)	1.8(8)	-2.4(7)
C20	20.4(10)	34.5(12)	38.8(13)	11.4(10)	3.5(9)	-1.8(9)
C21	28.5(11)	22.8(10)	35.6(12)	1.5(9)	3.5(9)	0.9(8)
C22	29.3(11)	36.5(12)	18.5(10)	-5.0(9)	2.4(8)	-0.5(9)
C23	34.5(12)	30.4(11)	14.4(9)	1.1(8)	2.6(8)	2.7(9)
C24	31.0(12)	38.3(12)	22.6(11)	0.5(9)	4.6(9)	2.4(10)
C25	20.3(9)	17.0(9)	19.8(9)	-4.7(7)	1.8(7)	-2.8(7)
C26	26.8(11)	25.1(10)	20.6(10)	-1.4(8)	3.0(8)	2.1(8)
C27	32.5(12)	27.5(11)	26.1(11)	-0.9(9)	9.8(9)	4.7(9)
C28	27.8(11)	24.5(10)	33.3(12)	-3.1(9)	6.1(9)	5.6(8)
C29	29.5(11)	21.8(10)	28.7(11)	-0.7(8)	-2.8(9)	2.9(8)
C30	28.9(11)	21.4(10)	19.7(9)	-4.5(8)	1.0(8)	-0.5(8)
C31	20.3(9)	18.9(9)	26.5(11)	-4.2(8)	6.1(8)	0.0(8)
C32	18.1(9)	26.2(11)	37.1(12)	-9.2(9)	3.3(8)	-0.6(8)
C33	28.3(12)	22.1(11)	52.3(16)	-10.2(11)	12.1(10)	-4.7(8)
C34	48.2(14)	19.1(11)	44.4(15)	0.5(10)	17.8(12)	-2.3(10)
C35	63.9(18)	28.1(13)	27.7(12)	2.2(10)	6.5(11)	-3.3(12)
C36	47.8(15)	22.0(11)	23.5(11)	-1.9(9)	3.9(10)	-4.9(9)
O1W	31.1(9)	56.1(11)	25.9(8)	-11.9(8)	-0.9(7)	16.1(8)
O2W	32.4(9)	57.3(12)	25.9(8)	-12.3(8)	-0.8(7)	18.3(8)

**Table S4.** Bond Lengths for **3i**.

Atom	Atom	Length/ $\text{\AA}$	Atom	Atom	Length/ $\text{\AA}$
S9A	C4	1.835(2)	S9B	C4B	1.725(2)
S9A	C4A	1.726(2)	S9B	C22	1.836(2)
P7A	O8A	1.4945(16)	P7B	O8B	1.4995(16)
P7A	N6A	1.6265(18)	P7B	N6B	1.6270(18)
P7A	C7	1.807(2)	P7B	C25	1.805(2)
P7A	C13	1.806(2)	P7B	C31	1.806(2)

**Table S4.** Bond Lengths for **3i**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1A	N2A	1.374(2)	O1B	N2B	1.382(2)
O1A	C5A	1.395(2)	O1B	C5B	1.390(2)
N2A	N3A	1.295(2)	N2B	N3B	1.293(2)
N3A	C1	1.499(3)	N3B	C4B	1.368(2)
N3A	C4A	1.366(3)	N3B	C19	1.501(3)
N6A	C5A	1.292(3)	N6B	C5B	1.288(3)
C1	C2	1.521(3)	C4B	C5B	1.414(3)
C1	C3	1.515(3)	C19	C20	1.515(3)
C4	C5	1.454(3)	C19	C21	1.515(3)
C4A	C5A	1.412(3)	C22	C23	1.458(3)
C5	C6	1.195(3)	C23	C24	1.185(3)
C7	C8	1.393(3)	C25	C26	1.402(3)
C7	C12	1.394(3)	C25	C30	1.396(3)
C8	C9	1.394(4)	C26	C27	1.384(3)
C9	C10	1.382(4)	C27	C28	1.383(3)
C10	C11	1.386(4)	C28	C29	1.390(3)
C11	C12	1.393(4)	C29	C30	1.393(3)
C13	C14	1.393(3)	C31	C32	1.403(3)
C13	C18	1.398(3)	C31	C36	1.385(3)
C14	C15	1.395(3)	C32	C33	1.389(3)
C15	C16	1.390(3)	C33	C34	1.376(4)
C16	C17	1.384(3)	C34	C35	1.389(4)
C17	C18	1.387(3)	C35	C36	1.393(4)

**Table S5.** Bond Angles for **3i**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C4A	S9A	C4	102.36(10)	C4B	S9B	C22	102.15(10)
O8A	P7A	N6A	118.96(9)	O8B	P7B	N6B	119.27(9)
O8A	P7A	C7	110.14(10)	O8B	P7B	C25	111.04(9)
O8A	P7A	C13	111.09(9)	O8B	P7B	C31	109.79(10)
N6A	P7A	C7	102.33(10)	N6B	P7B	C25	106.77(9)
N6A	P7A	C13	107.15(9)	N6B	P7B	C31	102.36(10)
C13	P7A	C7	106.17(9)	C25	P7B	C31	106.66(9)
N2A	O1A	C5A	110.87(15)	N2B	O1B	C5B	111.04(15)
N3A	N2A	O1A	104.70(15)	N3B	N2B	O1B	104.39(15)
N2A	N3A	C1	117.40(17)	N2B	N3B	C4B	115.17(17)
N2A	N3A	C4A	114.98(17)	N2B	N3B	C19	116.97(17)
C4A	N3A	C1	127.59(17)	C4B	N3B	C19	127.81(17)
C5A	N6A	P7A	129.88(16)	C5B	N6B	P7B	130.33(16)
N3A	C1	C2	109.19(17)	N3B	C4B	S9B	123.63(15)
N3A	C1	C3	108.13(16)	N3B	C4B	C5B	104.67(17)
C3	C1	C2	113.52(19)	C5B	C4B	S9B	131.25(15)
C5	C4	S9A	113.52(16)	O1B	C5B	C4B	104.70(16)
N3A	C4A	S9A	123.58(15)	N6B	C5B	O1B	115.09(18)
N3A	C4A	C5A	104.73(17)	N6B	C5B	C4B	140.20(19)
C5A	C4A	S9A	131.17(15)	N3B	C19	C20	109.06(17)
C6	C5	C4	178.1(3)	N3B	C19	C21	108.15(16)
O1A	C5A	C4A	104.70(16)	C20	C19	C21	113.98(19)
N6A	C5A	O1A	114.98(18)	C23	C22	S9B	113.43(16)

**Table S5.** Bond Angles for **3i**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N6A	C5A	C4A	140.29(19)	C24	C23	C22	178.0(2)
C8	C7	P7A	123.39(17)	C26	C25	P7B	119.78(16)
C8	C7	C12	119.4(2)	C30	C25	P7B	120.92(15)
C12	C7	P7A	117.20(17)	C30	C25	C26	119.30(19)
C7	C8	C9	119.7(2)	C27	C26	C25	120.3(2)
C10	C9	C8	120.4(3)	C28	C27	C26	120.1(2)
C9	C10	C11	120.4(2)	C27	C28	C29	120.4(2)
C10	C11	C12	119.4(2)	C28	C29	C30	119.8(2)
C11	C12	C7	120.7(2)	C29	C30	C25	120.09(19)
C14	C13	P7A	121.13(15)	C32	C31	P7B	117.44(18)
C14	C13	C18	119.54(18)	C36	C31	P7B	123.62(17)
C18	C13	P7A	119.33(15)	C36	C31	C32	118.8(2)
C13	C14	C15	119.88(19)	C33	C32	C31	120.3(2)
C16	C15	C14	120.0(2)	C34	C33	C32	120.3(2)
C17	C16	C15	120.24(19)	C33	C34	C35	120.0(2)
C16	C17	C18	120.0(2)	C34	C35	C36	119.9(3)
C17	C18	C13	120.3(2)	C31	C36	C35	120.6(2)

**Table S6.** Torsion Angles for **3i**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S9A	C4A	C5A	O1A	170.48(16)	S9B	C4B	C5B	O1B	-170.39(15)
S9A	C4A	C5A	N6A	-11.8(4)	S9B	C4B	C5B	N6B	11.1(4)
P7A	N6A	C5A	O1A	179.01(15)	P7B	N6B	C5B	O1B	179.83(15)
P7A	N6A	C5A	C4A	1.4(4)	P7B	N6B	C5B	C4B	-1.8(4)
P7A	C7	C8	C9	177.0(2)	P7B	C25	C26	C27	-179.60(17)
P7A	C7	C12	C11	-178.18(17)	P7B	C25	C30	C29	179.98(16)
P7A	C13	C14	C15	-179.94(16)	P7B	C31	C32	C33	176.59(16)
P7A	C13	C18	C17	-179.97(18)	P7B	C31	C36	C35	-176.1(2)
O1A	N2A	N3A	C1	-178.70(15)	O1B	N2B	N3B	C4B	0.9(2)
O1A	N2A	N3A	C4A	-0.4(2)	O1B	N2B	N3B	C19	178.73(16)
O8A	P7A	N6A	C5A	-41.1(2)	O8B	P7B	N6B	C5B	40.7(2)
O8A	P7A	C7	C8	-141.98(18)	O8B	P7B	C25	C26	169.05(16)
O8A	P7A	C7	C12	35.82(19)	O8B	P7B	C25	C30	-10.73(19)
O8A	P7A	C13	C14	14.58(19)	O8B	P7B	C31	C32	-35.67(18)
O8A	P7A	C13	C18	-165.49(16)	O8B	P7B	C31	C36	140.7(2)
N2A	O1A	C5A	N6A	-177.28(17)	N2B	O1B	C5B	N6B	177.48(17)
N2A	O1A	C5A	C4A	1.1(2)	N2B	O1B	C5B	C4B	-1.5(2)
N2A	N3A	C1	C2	-43.8(2)	N2B	N3B	C4B	S9B	171.17(15)
N2A	N3A	C1	C3	80.1(2)	N2B	N3B	C4B	C5B	-1.9(2)
N2A	N3A	C4A	S9A	-171.47(15)	N2B	N3B	C19	C20	44.4(3)
N2A	N3A	C4A	C5A	1.1(2)	N2B	N3B	C19	C21	-80.1(2)
N3A	C4A	C5A	O1A	-1.3(2)	N3B	C4B	C5B	O1B	1.9(2)
N3A	C4A	C5A	N6A	176.5(3)	N3B	C4B	C5B	N6B	-176.6(3)
N6A	P7A	C7	C8	-14.5(2)	N6B	P7B	C25	C26	-59.42(19)
N6A	P7A	C7	C12	163.27(16)	N6B	P7B	C25	C30	120.80(17)
N6A	P7A	C13	C14	-116.88(17)	N6B	P7B	C31	C32	-163.32(15)
N6A	P7A	C13	C18	63.04(18)	N6B	P7B	C31	C36	13.0(2)
C1	N3A	C4A	S9A	6.7(3)	C4B	S9B	C22	C23	-58.53(18)
C1	N3A	C4A	C5A	179.20(18)	C4B	N3B	C19	C20	-138.1(2)

**Table S6.** Torsion Angles for **3i**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C4	S9A	C4A	N3A	-97.17(18)	C4B	N3B	C19	C21	97.4(2)
C4	S9A	C4A	C5A	92.4(2)	C5B	O1B	N2B	N3B	0.4(2)
C4A	S9A	C4	C5	59.18(19)	C19	N3B	C4B	S9B	-6.3(3)
C4A	N3A	C1	C2	138.1(2)	C19	N3B	C4B	C5B	-179.36(18)
C4A	N3A	C1	C3	-98.0(2)	C22	S9B	C4B	N3B	97.64(18)
C5A	O1A	N2A	N3A	-0.5(2)	C22	S9B	C4B	C5B	-91.3(2)
C7	P7A	N6A	C5A	-162.67(19)	C25	P7B	N6B	C5B	-86.0(2)
C7	P7A	C13	C14	134.32(17)	C25	P7B	C31	C32	84.73(17)
C7	P7A	C13	C18	-45.76(18)	C25	P7B	C31	C36	-98.9(2)
C7	C8	C9	C10	1.6(4)	C25	C26	C27	C28	-0.6(4)
C8	C7	C12	C11	-0.3(3)	C26	C25	C30	C29	0.2(3)
C8	C9	C10	C11	-1.4(5)	C26	C27	C28	C29	0.6(4)
C9	C10	C11	C12	0.4(4)	C27	C28	C29	C30	-0.2(3)
C10	C11	C12	C7	0.5(4)	C28	C29	C30	C25	-0.2(3)
C12	C7	C8	C9	-0.8(3)	C30	C25	C26	C27	0.2(3)
C13	P7A	N6A	C5A	85.9(2)	C31	P7B	N6B	C5B	162.1(2)
C13	P7A	C7	C8	97.67(19)	C31	P7B	C25	C26	49.46(19)
C13	P7A	C7	C12	-84.54(17)	C31	P7B	C25	C30	-130.32(17)
C13	C14	C15	C16	-0.2(3)	C31	C32	C33	C34	-0.2(3)
C14	C13	C18	C17	0.0(3)	C32	C31	C36	C35	0.2(4)
C14	C15	C16	C17	0.2(3)	C32	C33	C34	C35	0.1(4)
C15	C16	C17	C18	-0.1(4)	C33	C34	C35	C36	0.2(4)
C16	C17	C18	C13	0.0(3)	C34	C35	C36	C31	-0.3(4)
C18	C13	C14	C15	0.1(3)	C36	C31	C32	C33	0.1(3)

**Table S7.** Hydrogen Atom Coordinates ( $\text{\AA}\times 10^4$ ) and Isotropic Displacement Parameters ( $\text{\AA}^2\times 10^3$ ) for **3i**.

Atom	x	y	z	U(eq)
H1	4332.29	-1414.59	4339.78	26
H2A	3224.04	-498.36	4004.28	46
H2B	3188.99	-2306.07	4094.71	46
H2C	3305.26	-1651.27	3548.3	46
H3A	4478.03	-3161.45	3441.81	42
H3B	4405.51	-3887.57	3982.41	42
H3C	5105.68	-2942.77	3836.4	42
H4A	5343.73	1697.86	5194.69	35
H4B	5162.42	2842.52	4751.07	35
H6	3186(17)	930(30)	4980(12)	39(7)
H8	5811.66	5255.17	2706.58	36
H9	5880.59	7732.79	2353.21	52
H10	6450.05	9734.06	2781.43	53
H11	6912.15	9319.4	3583.85	45
H12	6814.36	6865.13	3950.72	32
H14	7249.9	2250.81	4313.7	25
H15	8354.65	999.52	4169.87	31
H16	8849.34	954.69	3365.49	32
H17	8252.33	2168.16	2705.26	33
H18	7154.23	3422.86	2844.53	27
H19	7907.78	11429.03	5664.67	26
H20A	8938.28	11605.21	6452.89	47

**Table S7.** Hydrogen Atom Coordinates ( $\text{\AA}\times 10^4$ ) and Isotropic Displacement Parameters ( $\text{\AA}^2\times 10^3$ ) for **3i**.

Atom	x	y	z	U(eq)
H20B	9050.56	12321.28	5914.16	47
H20C	9014.06	10504.68	5983.16	47
H21A	7137.69	12950.03	6170.54	43
H21B	7838.5	13896.1	6026.9	43
H21C	7765.05	13159.07	6565.9	43
H22A	7050.51	7159.04	5254.88	34
H22B	6879.08	8312.94	4811.81	34
H24	9015.67	8992.1	5029.98	37
H26	5144.49	6711.83	7194.98	29
H27	4051.81	7958.38	7352.89	34
H28	3406.71	9082.23	6699.25	34
H29	3837.86	8928.84	5878.83	32
H30	4929.4	7654.57	5713.13	28
H32	5397.12	3143.7	6058.95	33
H33	5349.95	671.4	6410.24	41
H34	5867.1	201.13	7187.09	45
H35	6435.39	2209.71	7622.51	48
H36	6478.07	4696.71	7277.32	37
H1WA	6749.85	4206.12	4830.73	57
H1WB	6738.71	4459.32	5331.05	57
H2WA	5484.73	5927.5	5173.56	58
H2WB	5476.95	5540.76	4682.11	58

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