

## SUPPORTING INFORMATION

### Site-specific introduction of gold-carbenoids by intermolecular oxidation of ynamides or ynol ethers.

Paul W. Davies\*, Alex Cremonesi and Nicolas Martin

*School of Chemistry, University of Birmingham*

*Edgbaston, Birmingham, B15 2TT, UK.*

*E-mail: [p.w.davies@bham.ac.uk](mailto:p.w.davies@bham.ac.uk)*

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## General Experimental

All reactions were carried out under Ar in flame-dried glassware unless otherwise mentioned. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF (Na), CH<sub>2</sub>Cl<sub>2</sub> (P<sub>4</sub>O<sub>10</sub>), Et<sub>3</sub>N (CaH<sub>2</sub>), toluene (Na). Anhydrous ClCH<sub>2</sub>CH<sub>2</sub>Cl was purchased from Aldrich or freshly distilled (CaH<sub>2</sub>). Asynt DrySin heating blocks on stirrer hotplates were employed for reactions with temperature controlled *via* external probe.

Flash chromatography: Fluorochem silica gel 60 (43-63  $\mu$ m). Thin layer chromatography (TLC): Macherey Nagel silica gel 60F<sub>254</sub> analytical plates (plastic support) which were developed using standard visualizing agents: UV fluorescence (254 and 366 nm), phosphomolybdic acid / $\Delta$ , and potassium permanganate / $\Delta$ . IR: Perkin–Elmer Spectrum 100 FTIR spectrometer, only selected absorbencies ( $\nu_{\text{max}}$ ) are reported in cm<sup>-1</sup>. MS and HRMS (EI): VG ProSpec or VG-ZabSpec at 70 eV. High resolution EI spectra were measured using perfluorokerosene (PFK) as an internal calibrant. MS and HRMS (ES): Micromass LCT using a methanol mobile phase. HRMS was obtained using a lock-mass to adjust the calibrated mass scale. MS data are reported as  $m/z$  (relative intensity). Commercially available compounds were purchased from Aldrich, Fluka, Acros, Strem or Alfa Aesar and used without further purification. Commercial pyridine *N*-oxide was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and dried over Na<sub>2</sub>SO<sub>4</sub>. The solution was filtered and solvent removed under reduced pressure to afford a white powder which was stored under Argon. NMR: Spectra were recorded on Bruker AC300 (<sup>1</sup>H = 300 MHz, <sup>13</sup>C = 75.5 MHz), Bruker AV300 (<sup>1</sup>H = 300 MHz, <sup>13</sup>C = 75.5 MHz), Bruker AV400 (<sup>1</sup>H = 400 MHz, <sup>13</sup>C = 101 MHz), and Bruker DRX500 (<sup>1</sup>H = 500 MHz, <sup>13</sup>C = 126 MHz) in the solvents indicated; Chemical shifts ( $\delta$ ) are given in ppm relative to TMS. The solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl<sub>3</sub>:  $\delta_{\text{C}} \equiv 77.0$  ppm; residual CHCl<sub>3</sub> in CDCl<sub>3</sub>:  $\delta_{\text{H}} \equiv 7.26$  ppm. Coupling constants ( $J$ ) are reported in Hz. Multiplicity is denoted in <sup>1</sup>H NMR by: s (singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet). 1D <sup>13</sup>C NMR spectra were recorded using the PENDANT pulse sequence from the Bruker standard pulse program library. 2D spectra were recorded using the following pulse sequences from the Bruker standard pulse program library: PENDANT, DEPT 45, DEPT 135; Gradient COSY 90; Gradient HSQC for <sup>1</sup> $J(\text{C},\text{H}) = 145$  Hz; Gradient HMBC for correlations via  <sup>$n$</sup>  $J(\text{C},\text{H})$ .

## Starting Materials

The following compounds were prepared following literature procedures:

### 4-Methyl-N-phenylbenzenesulfonamide (A)

(97% yield). Spectroscopic data were identical to those reported in literature.<sup>1</sup>

### N-Phenylmethanesulfonamide (B)

(92% yield). Spectroscopic data were identical to those reported in literature.<sup>2</sup>

### (3-(But-3-yn-1-yloxy)prop-1-yn-1-yl)trimethylsilane (C)

(92% yield). Spectroscopic data were identical to those reported in literature.<sup>3</sup>

### (But-3-yn-1-yloxy)(tert-butyl)dimethylsilane (D)

(59% yield). Spectroscopic data were identical to those reported in literature.<sup>4</sup>

### ((But-3-yn-1-yloxy)methyl)benzene (E)

(81% yield). Spectroscopic data were identical to those reported in literature.<sup>5</sup>

### S-Pent-4-yn-1-yl ethanethioate (F)

(60% yield).<sup>6</sup> Spectroscopic data were identical to those reported in literature.<sup>7</sup>

### 1-Cyclohexyl-3-ethoxyprop-2-yn-1-ol (G)

(81% yield). Spectroscopic data were identical to those reported in literature.<sup>8</sup>

## Formation of ynamides

All ynamides were prepared according to the method of Stahl using the following procedure.<sup>9</sup>

### General procedure 1 (GP1)

CuCl<sub>2</sub> (0.2 eq), amide (5 eq) and Na<sub>2</sub>CO<sub>3</sub> (2 eq) were added to a flame-dried 500 mL three-necked round-bottomed flask. The flask was purged with oxygen for 15 min and a solution of pyridine (2 eq) in dry toluene (0.1 M) was added. A balloon filled with oxygen was connected to the flask and the stirred mixture was heated at 70 °C. After 15 min, a solution of alkyne (1 eq) in dry toluene was added by syringe pump over 4 h. The mixture was allowed to stir at 70 °C for another 4h and was then cooled to rt. The reaction mixture was concentrated under reduced pressure and the residue was purified by flash chromatography.

<sup>1</sup> K. K. Park, J. J. Lee and J. Ryu, *Tetrahedron*, 2003, **59**, 7651.

<sup>2</sup> A. Kamal, M. Sandbhor and A. A. Shaik, *Bioorg. Med. Chem. Lett.*, 2004, **14**, 4581.

<sup>3</sup> J. B. Jones, J. M. Wright, G. Hynd, J. K. Wyatt, P. M. Warner, R. S. Huber, A. Li, M. W. Kilgore, R. P. Sticca and R. S. Pollenz, *J. Org. Chem.*, 2002, **67**, 5727.

<sup>4</sup> H. F. Sneddon, M. J. Gaunt and S. V. Ley, *Org. Lett.*, 2003, **5**, 1147.

<sup>5</sup> J. S. Yadav and P. Srihari, *Tetrahedron Asymm.*, 2004, **15**, 81.

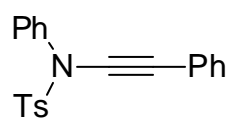
<sup>6</sup> P. W. Davies and S. J.-C. Albrecht, *Angew. Chem. In. Ed.*, 2009, **48**, 8372.

<sup>7</sup> L. Benati, G. Calestani, R. Leardini, M. Minozzi, D. Nanni, P. Spagnolo and S. Strazzari, *Org. Lett.*, 2008, **5**, 1313.

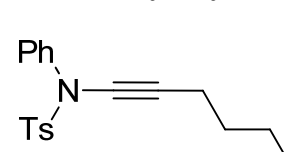
<sup>8</sup> D. A. Engel, S. S. Lopez and G. B. Dudley, *Tetrahedron*, 2006, **64**, 6988.

<sup>9</sup> T. Hamada, X. Ye and S. Stahl, *J. Am. Chem. Soc.*, 2008, **130**, 833.

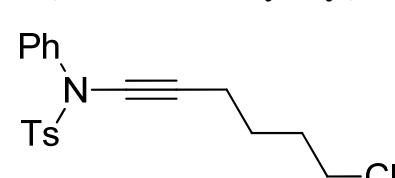
### ***N*-(3-Methoxyprop-1-yn-1-yl)-4-methyl-*N*-phenylbenzenesulfonamide (1a)<sup>10</sup>**

 Following GP1 using amide **A** (2.47 g) and phenylacetylene (0.11 mL, 2 mmol). After purification by flash chromatography [hexanes:EtOAc (20:1)] *ynamide* **1a** was isolated as a pale yellow solid (639 mg, 92%); <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.63 (d, *J* 8.3, 2H), 7.41-7.37 (m, 3H), 7.35-7.28 (m, 9H), 2.45 (s, 3H); <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>): δ = 145.0, 139.0, 133.0, 131.5 (2C), 129.5 (2C), 129.1 (2C), 128.3 (5C), 128.0, 126.3 (2C), 122.7, 83.0, 70.5, 21.7; IR (neat): ν = 3058, 2922, 2240, 1593, 1488, 1442, 1455, 1369, 1293, 1203, 1164, 1081, 1066, 1023, 9124, 893, 813, 783, 758, 690, 680; HR-MS (ES-TOF): *m/z*: calcd for C<sub>21</sub>H<sub>17</sub>NO<sub>2</sub>NaS: 370.0878, found 370.0872 [*M*+Na].

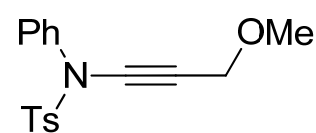
### ***N*-(Hex-1-yn-1-yl)-4-methyl-*N*-phenylbenzenesulfonamide (1b)**

 Following GP1 using amide **A** (2.47 g) and hex-1-yne (0.24 mL, 2 mmol). After purification by flash chromatography [hexanes:EtOAc (20:1)] *ynamide* **1b** was isolated as a colourless oil (320 mg, 98%); <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.49 (d, *J* 8.3, 2H), 7.29-7.17 (m, 7H), 2.38 (s, 3H), 2.24 (t, *J* 6.9, 2H), 1.50-1.26 (m, 4H), 0.85 (t, *J* 7.2, 3H); <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>): δ = 144.6, 139.4, 133.0, 129.3 (2C), 128.9 (2C), 128.3 (2C), 127.8, 126.1 (2C), 73.8, 70.4, 30.9, 21.9, 21.7, 18.2, 13.6; IR (neat): ν = 2957, 2930, 2871, 2254, 1594, 1488, 1455, 1369, 1269, 1173, 1156, 1089, 923, 892, 812, 755, 704, 690, 678; HR-MS (ES-TOF): *m/z*: calcd for C<sub>19</sub>H<sub>21</sub>NO<sub>2</sub>NaS: 350.1191, found 350.1185 [*M*+Na].

### ***N*-(6-Chlorohex-1-yn-1-yl)-4-methyl-*N*-phenylbenzenesulfonamide (1c)**

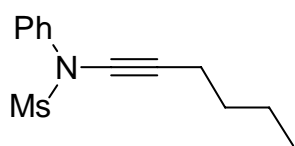
 Following GP1 using amide **A** (2.47 g) and 6-chlorohex-1-yne (0.25 mL, 2 mmol). After purification by flash chromatography [hexanes:EtOAc (15:1)] *ynamide* **1c** was isolated as a colourless oil (354 mg, 98%); <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.54 (d, *J* 8.4, 2H), 7.33-7.29 (m, 4H), 7.25-7.22 (m, 3H), 3.55 (t, *J* 6.5, 2H), 2.44 (s, 3H), 2.36 (t, *J* 6.8, 3H), 1.87 (m, 2H), 1.66 (m, 2H); <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>): δ = 144.7, 139.2, 133.0, 129.4 (2C), 129.0 (2C), 128.2 (2C), 128.0, 126.1 (2C), 74.5, 69.4, 44.5, 31.5, 26.0, 21.7, 17.8; IR (neat): ν = 2952, 2869, 2254, 2032, 1594, 1488, 1368, 1266, 1173, 1089, 1027, 923; HR-MS (ES-TOF): *m/z*: calcd for C<sub>19</sub>H<sub>20</sub>NO<sub>2</sub>NaSCl: 384.0801, found 384.0812 [*M*+Na].

### ***N*-(3-Methoxyprop-1-yn-1-yl)-4-methyl-*N*-phenylbenzenesulfonamide (1d)**

 Following GP1 using amide **A** (2.47 g) and 3-methoxyprop-1-yne (0.17 mL, 2 mmol). After purification by flash chromatography [hexanes:EtOAc (15:1)] *ynamide* **1d** was isolated as a colourless oil (540 mg, 86%); <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.54 (d, *J* 8.4, 2H), 7.30-7.19 (m, 7H), 4.22 (s, 2H), 3.30 (s, 3H), 2.40 (s, 3H); <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>): δ = 145.0, 138.7, 133.1, 129.8 (2C), 129.5 (2C), 128.3, 128.2 (2C), 126.3 (2C), 80.3, 66.9, 60.0, 57.2, 21.7; IR (neat): ν = 2925, 2860, 2824, 2244, 1595, 1489, 1454, 1370, 1292, 1172, 1160, 910, 894, 961, 812, 755, 685, 654; HR-MS (ES-TOF): *m/z*: calcd for C<sub>17</sub>H<sub>17</sub>NO<sub>3</sub>NaS: 338.0827, found 338.0815 [*M*+Na].

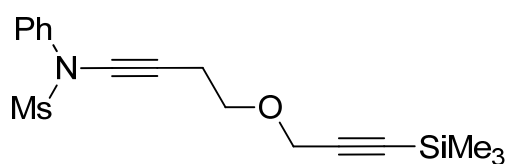
<sup>10</sup> M. F. Martinez-Esperon, D. Rodriguez, L. Castedo and C. Saa, *Tetrahedron*, 2006, **62**, 3843; D. Rodriguez, L. Castedo and C. Saa, *Synlett*, 2004, 783-786.

### ***N*-(Hex-1-yn-1-yl)-*N*-phenylmethanesulfonamide (**1e**)**



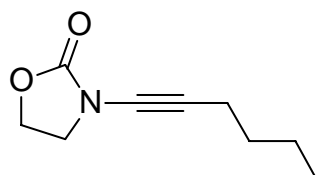
Following GP1 using amide **B** (1.71 g) and hex-1-yne (0.24 mL, 2 mmol). After purification by flash chromatography [hexanes:EtOAc (20:1)] *ynamide* **1e** was isolated as a colourless oil (576 mg, 98%);  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.51 (d,  $J$  7.9, 2H), 7.43-7.30 (m, 3H), 3.07 (s, 3H), 2.35 (t,  $J$  7.0, 2H), 1.60-1.49 (m, 2H), 1.48-1.37 (m, 2H), 0.92 (t,  $J$  7.2, 3H);  $^{13}\text{C-NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 139.1, 129.3 (2C), 128.0, 125.4 (2C), 73.1, 71.1, 36.1, 30.9, 22.0, 18.2, 13.6; IR (neat):  $\nu$  = 2957, 2929, 2858, 2256, 1593, 1490, 1456, 1362, 1322, 1270, 1168, 1155, 1075, 1027, 958, 924, 901, 825, 757, 737, 691; HR-MS (EI-TOF):  $m/z$ : calcd for  $\text{C}_{13}\text{H}_{17}\text{NO}_2\text{NaS}$ : 251.0980, found 251.0981 [ $M$ ].

### ***N*-Phenyl-*N*-(4-((3-(trimethylsilyl)prop-2-yn-1-yl)oxy)but-1-yn-1-yl)methanesulfonamide (**1f**)**



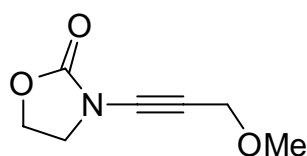
Following GP1 using amide **B** (1.71 g) and alkyne **C** (513 mg, 2 mmol). After purification by flash chromatography [hexanes:EtOAc (4:1)] *ynamide* **1f** was isolated as a colourless oil (617 mg, 59%);  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.54-7.49 (m, 2H), 7.45-7.30 (m, 3H), 4.18 (s, 2H), 3.66 (t,  $J$  7.0, 2H), 3.08 (s, 3H), 2.66 (t,  $J$  7.0, 2H), 0.18 (s, 9H);  $^{13}\text{C-NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 138.9, 129.3 (2C), 128.0, 125.4 (2C), 101.2, 91.6, 74.2, 68.2, 67.8, 58.9, 36.3, 19.8, -0.2 (3C); IR (neat):  $\nu$  = 3021, 2963, 2927, 2842, 2829, 2260, 2174, 1489, 1352, 1247, 1156, 1097, 990, 969, 840, 760, 697; HR-MS (ES-TOF):  $m/z$ : calcd for  $\text{C}_{17}\text{H}_{23}\text{NO}_3\text{NaSSi}$ : 372.1066, found 372.1076 [ $M+\text{Na}$ ].

### **3-(Hex-1-yn-1-yl)oxazolidin-2-one (**1g**)**



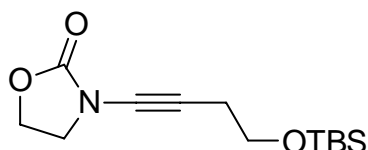
Following GP1 using oxazolidin-2-one (1.37 g) and hex-1-yne (0.35 mL, 3 mmol). After purification by flash chromatography [hexanes:EtOAc (7:3)] *ynamide* **1g** was isolated as a colourless oil (245 mg, 49%);  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 4.41 (t,  $J$  8.2, 2H), 3.87 (t,  $J$  8.2, 2H), 2.30 (t,  $J$  6.9, 2H), 1.58-1.34 (m, 4H), 0.91 (t,  $J$  7.2, 3H);  $^{13}\text{C-NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 156.6, 71.1, 70.0, 62.7, 47.0, 30.8, 21.9, 18.0, 13.5; IR (neat):  $\nu$  = 2959, 2931, 2873, 2273, 1759, 1479, 1413, 1298, 1201, 1113, 1032, 750, 729; HR-MS (EI-TOF):  $m/z$ : calcd for  $\text{C}_9\text{H}_{13}\text{NO}_2$ : 167.0946, found 167.0947 [ $M$ ].

### **3-(3-Methoxyprop-1-yn-1-yl)oxazolidin-2-one (**1h**)**



Following GP1 using oxazolidin-2-one (1.37 g) and 3-methoxyprop-1-yne (0.25 mL, 3 mmol). After purification by flash chromatography [hexanes:EtOAc (9:1)] *ynamide* **1h** was isolated as a light-yellow oil (409 mg, 88%);  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 4.44 (t,  $J$  7.9, 2H), 4.23 (s, 2H), 3.91 (t,  $J$  7.9, 2H), 3.36 (s, 3H);  $^{13}\text{C-NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 156.1, 76.3, 67.6, 63.0, 59.8, 57.4, 46.7; IR (neat):  $\nu$  = 2989, 2926, 2822, 2261, 1759, 1478, 1415, 1358, 1322, 1187, 1110, 1088, 1030, 931, 893, 748; HR-MS (EI-TOF):  $m/z$ : calcd for  $\text{C}_7\text{H}_9\text{NO}_3$ : 155.0582, found 155.0584 [ $M$ ].

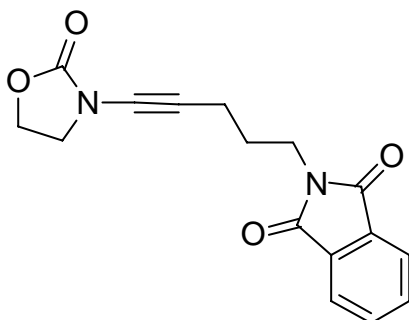
### 3-(4-((<sup>t</sup>Butyldimethylsilyl)oxy)but-1-yn-1-yl)oxazolidin-2-one (**1i**)



Following GP1 using oxazolidin-2-one (1.37 g) and alkyne **D** (552 mg, 3 mmol). After purification by flash chromatography [hexanes:EtOAc (3:1)] *ynamide* **1i** was isolated as a light-yellow oil (428 mg, 53%); <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ = 4.41 (t, *J* 8.0, 2H), 3.86 (t, *J* 8.0, 2H), 3.72 (t, *J* 7.1, 2H),

2.52 (t, *J* 7.1, 2H), 0.89 (s, 9H), 0.06 (s, 6H); <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>): δ = 156.4, 71.0, 68.2, 62.8, 61.9, 46.9, 25.9 (3C), 22.7, 18.3, -5.3 (2C); IR (neat): ν = 2954, 2928, 2856, 2268, 1765, 1413, 1252, 1202, 1101, 1035, 834, 775, 749; HR-MS (EI-TOF): *m/z*: calcd for C<sub>13</sub>H<sub>23</sub>NO<sub>3</sub>Si: 269.1447, found 269.1452 [*M*].

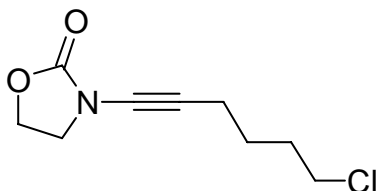
### 2-(5-(2-Oxooxazolidin-3-yl)pent-4-yn-1-yl)isoindoline-1,3-dione (**1j**)



Following GP1 using oxazolidin-2-one (1.37 g) and 2-(pent-4-yn-1-yl)isoindoline-1,3-dione (639 mg, 3 mmol). After purification by flash chromatography [hexanes:EtOAc (1:1)] *ynamide* **1j** was isolated as a white solid (661 mg, 74%); mp: 138-139 °C; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.88-7.81 (m, 2H), 7.75-7.68 (m, 2H), 4.38 (t, *J* 8.0, 2H), 3.86-3.76 (m, 4H), 2.39 (t, *J* 7.1, 2H), 1.94 (tt, *J* 7.1 and 7.1, 2H); <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>): δ = 168.2 (2C), 156.4, 133.9 (2C), 132.0 (2C), 123.2 (2C), 70.8, 69.6, 62.8, 46.8, 37.1, 27.4, 16.2; IR (neat): ν =

3492, 2988, 2935, 2929, 2265, 1771, 1704, 1466, 1422, 1402, 1375, 1341, 1210, 1402, 1088, 1030, 887, 742, 720; HR-MS (ES-TOF): *m/z*: calcd for C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>O<sub>4</sub>Na: 321.0851, found 321.0849 [*M*+Na]

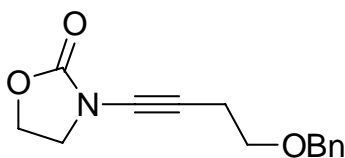
### 3-(6-Chlorohex-1-yn-1-yl)oxazolidin-2-one (**1k**)



Following GP1 using oxazolidin-2-one (1.37 g) and 6-chlorohex-1-yne (0.36 mL, 3 mmol). After purification by flash chromatography [hexanes:EtOAc (6:4)] *ynamide* **1k** was isolated as a light-yellow oil (410 mg, 68%); <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ = 4.41 (t, *J* 8.0, 2H), 3.86 (t, *J* 8.0, 2H), 3.56 (t, *J* 6.5, 2H), 2.35 (t, *J* 6.9, 2H), 1.95-1.82 (m, 2H), 1.73-

1.60 (m, 2H); <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>): δ = 156.5, 70.6, 70.2, 62.8, 46.9, 44.5, 31.5, 25.9, 17.7; IR (neat): ν = 2987, 2949, 2922, 2869, 2268, 1758, 1478, 1413, 1298, 1200, 1111, 1031, 746; HR-MS (EI-TOF): *m/z*: calcd for C<sub>9</sub>H<sub>12</sub>NO<sub>2</sub>Cl: 201.0557, found 201.0552 [*M*].

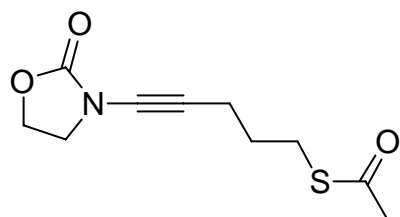
### 3-(4-(Benzyloxy)but-1-yn-1-yl)oxazolidin-2-one (**1l**)



Following GP1 using oxazolidin-2-one (1.37 g) and alkyne **E** (438 mg, 3 mmol). After purification by flash chromatography [hexanes:toluene (4:1)] *ynamide* **1l** was isolated as a light-yellow oil (580 mg, 79%); <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.37-7.27 (m, 5H), 4.55 (s, 2H), 4.41 (t, *J* 7.8, 2H), 3.86 (t,

*J* 7.8, 2H), 3.60 (t, *J* 7.0, 2H), 2.63 (t, *J* 7.0, 2H); <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>): δ = 156.5, 145.0, 129.6, 128.3 (2C), 127.6 (2C), 72.9, 70.9, 68.3, 67.9, 62.8, 46.8, 19.8; IR (neat): ν = 3031, 2914, 2864, 2272, 1760, 1718, 1478, 1413, 1270, 1200, 1109, 1030, 738, 698; HR-MS (ES-TOF): *m/z*: calcd for C<sub>14</sub>H<sub>15</sub>NO<sub>3</sub>Na: 268.0950, found 268.0956 [*M*+Na].

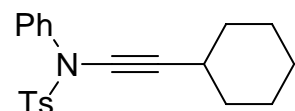
### ***S*-(5-(2-Oxooxazolidin-3-yl)pent-4-yn-1-yl) ethanethioate (1m)**



Following GP1 using oxazolidin-2-one (878 mg) and alkyne **F** (284 mg, 2 mmol). After purification by flash chromatography [hexanes:toluene (11:9)] *ynamide* **1m** was isolated as a colourless oil (290 mg, 64%); <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ = 4.42 (t, *J* 8.1, 2H), 3.88 (t, *J* 8.1, 2H), 2.97 (t, *J* 7.1, 2H), 2.40 (t, *J* 7.1, 2H), 2.33 (s, 3H), 1.80 (dt, *J* 7.1 and 7.1, 2H); <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>): δ = 195.5, 156.5, 70.9, 69.7, 62.8, 46.9,

30.6, 28.6, 28.0, 17.6; IR (neat): ν = 2987, 2928, 2854, 2258, 1734, 1449, 1312, 1247, 1193, 1170, 1135, 1079, 1040, 998, 886, 840; HR-MS (ES-TOF): *m/z*: calcd for C<sub>10</sub>H<sub>13</sub>NO<sub>3</sub>NaS: 250.0514, found 250.0511 [*M*+*Na*].

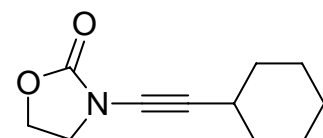
### ***N*-(Cyclohexylethynyl)-4-methyl-*N*-phenylbenzenesulfonamide (4a)**



Following GP1 using amide **4a** (2.47 g) and ethynylcyclohexane (0.26 mL, 2 mmol). After purification by flash chromatography [hexanes:EtOAc (20:1)] *ynamide* **4a** was isolated as a colourless oil (343 mg, 98%); <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.55 (d, *J* 8.3, 2H), 7.33-7.28 (m, 3H), 7.29-7.24 (m, 4H), 2.55-2.47 (m, 1H), 2.43 (s, 3H), 1.81-1.74 (m, 2H), 1.71-1.62 (m, 2H), 1.54-1.36 (m, 4H), 1.36-1.30 (m, 2H); <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>): δ = 144.6,

139.5, 132.9, 129.2 (2C), 128.9 (2C), 128.3 (2C), 127.8, 126.0 (2C), 74.3, 74.2, 32.7 (2C), 28.8, 25.9, 24.7 (2C), 21.7; IR (neat): ν = 2932, 2853, 2251, 1738, 1596, 1488, 1447, 1366, 1268, 1174, 1154, 1088, 1029, 921; HR-MS (ES-TOF): *m/z*: calcd for C<sub>21</sub>H<sub>23</sub>NO<sub>2</sub>NaS: 376.1347, found 376.1339 [*M*+*Na*].

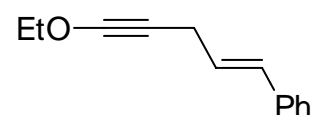
### **3-(Cyclohexylethynyl)oxazolidin-2-one (4b)**



Following GP1 using oxazolidin-2-one (878 mg) and ethynylcyclohexane (0.26 mL, 2 mmol). After purification by flash chromatography [hexanes:toluene (3:2)] *ynamide* **4b** was isolated as a colourless oil (208 mg, 54%); <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ = 4.40 (t, *J* 8.0, 2H), 3.86 (t, *J* 8.0, 2H), 2.47 (tt, *J* 9.3 and 3.6,

1H), 1.87-1.61 (m, 4H), 1.57-1.21 (m, 6H); <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>): δ = 156.5, 75.0, 70.2, 62.7, 47.1, 32.7 (2C), 28.8, 25.8, 24.9 (2C); IR (neat): ν = 2927, 2853, 2268, 1757, 1479, 1448, 1413, 1289, 1202, 1111, 1035, 973, 748; HR-MS (EI-TOF): *m/z*: calcd for C<sub>11</sub>H<sub>15</sub>NO<sub>2</sub>: 193.1103, found 193.1097 [*M*].

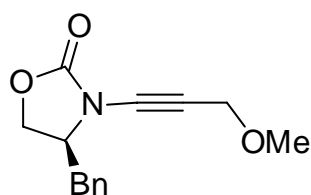
### **(*E*)-(5-ethoxypent-1-en-4-yn-1-yl)benzene (6)**



<sup>n</sup>Butyl lithium (2.5 M in hexane, 1.26 mL, 3.15 mmol) was added to a solution of ethoxyacetylene (40% in toluene, 0.72 mL, 3 mmol) in dry THF (1.9 mL) at -78 °C. After stirring for 30 min at -78 °C, cinnamyl bromide (650 mg, 3.3 mmol) and copper bromide (24 mg, 0.17 mmol) were added and the mixture was stirred

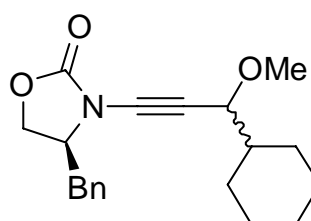
at 50 °C for 5 h. The reaction was quenched with EtOAc (5 mL) and the organic mixture was quickly washed with water (10 mL). The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography [hexanes:toluene (9:1)] to give *ynol ether* **6** as a colourless oil (492mg, 44%); <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.33-7.14 (m, 5H), 6.58 (dt, *J* 15.7 and 1.8, 1H), 6.15 (dt, *J* 15.7 and 5.5, 1H), 4.05 (q, *J* 7.1, 2H), 3.04 (dd, *J* 5.5 and 1.9), 1.35 (t, *J* 7.1, 3H); <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>): δ = 137.4, 130.3, 128.5 (2C), 127.1, 126.3, 126.2 (2C), 91.4, 74.1, 34.3, 20.9, 14.4; IR (neat): ν = 3038, 3060, 3028, 2982, 2899, 2270, 1495, 1448, 1221, 1011, 963, 868, 844, 750, 729, 691; HR-MS (EI-TOF): *m/z*: calcd for C<sub>13</sub>H<sub>14</sub>NO: 186.1045, found 186.1053 [*M*].

**(S)-4-Benzyl-3-(3-methoxyprop-1-yn-1-yl)oxazolidin-2-one (8a)**



Following GP1 using amide (S)-4-benzyloxazolidin-2-one (1.77 g) and 3-methoxyprop-1-yne (0.17 mL, 2 mmol). After purification by flash chromatography [hexanes:EtOAc (11:9 then 2:3)] *ynamide* **8a** was isolated as a light-yellow oil (289 mg, 59%) and unreacted (S)-4-benzyloxazolidin-2-one (1.45 g) was recovered; *ynamide* **8a** <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.38-7.28 (m, 3H), 7.24-7.18 (m, 2H), 4.38-4.22 (m, 4H), 4.16-4.10 (m, 1H), 3.41 (s, 3H), 3.24 (dd, *J* 13.8 and 3.8, 1H), 2.93 (dd, *J* 13.8 and 8.2, 1H); <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>): δ = 155.7, 134.1, 129.3 (2C), 129.0 (2C), 127.5, 75.3, 69.8, 67.4, 59.9, 58.1, 57.4, 37.9; IR (neat): ν = 2930, 2821, 2257, 1765, 1453, 1413, 1352, 1209, 1182, 1110, 1090, 1029, 895, 733, 701; HR-MS (ES-TOF): *m/z*: calcd for C<sub>14</sub>H<sub>15</sub>NO<sub>3</sub>Na: 268.0950, found 268.0949 [*M*+*Na*].

**(4S)-4-benzyl-3-(3-cyclohexyl-3-methoxyprop-1-yn-1-yl)oxazolidin-2-one (8b)**



<sup>n</sup>Butyl lithium (2.5 M in hexane, 1.6 mL, 4 mmol) was added to a solution of ethynyltrimethylsilane (0.56, 4 mmol) in dry THF (13.3 mL, 0.3 M) at -78 °C under argon. After stirring for 30 min at -78 °C, the reaction was allowed to warm to room temperature. The reaction was quenched with a saturated solution of ammonium chloride (15 mL) and the aqueous layer was extracted with EtOAc

(3 x 10 mL). The combined organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The residue was dissolved in dry THF (2 mL) under argon atmosphere and iodomethane (0.30 mL, 4.8 mmol) added. The solution was cooled down at 0 °C and then sodium hydride (57% suspension in oil, 202 mg, 4.8 mmol) was added. After stirring for 30 min at 0 °C, the mixture was stirred for further 3 h at room temperature. The reaction was quenched with a saturated solution of ammonium chloride (10 mL) and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography [hexanes:EtOAc (19:1)] to afford (3-cyclohexyl-3-methoxyprop-1-yn-1-yl)trimethylsilane as a colourless liquid (672 mg, 75% over two steps); <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ = 3.70 (d, *J* 6.1, 1H), 3.39 (s, 3H), 1.90-1.40 (m, 6H), 1.35-0.95 (m, 5H), 0.18 (s, 9H); <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>): δ = 103.8, 91.2, 76.7, 56.6, 42.4, 28.9, 28.3, 26.5, 26.0, 25.9, 0.0 (3C); IR (neat): ν = 2927, 2854, 2168, 1450, 1371, 1249, 1111, 1090, 842, 760, ; HR-MS (EI-TOF): *m/z*: calcd for C<sub>13</sub>H<sub>24</sub>NOSi: 224.1596, found 224.1596 [*M*+*Na*]. This alkyne (600 mg, 2.68 mmol) was dissolved in methanol (5 mL) and potassium carbonate (739 mg, 5.3 mmol) was added. The reaction mixture was stirred at RT for 2 h before being quenched with aqueous ammonium chloride and extracted with ethyl acetate. The combined organic phases were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. Evaporation under reduced pressure of the solvents afforded the desilylated product (443 mg) which was employed without further to prepare the ynamide: Following GP1 using amide (S)-4-benzyloxazolidin-2-one (1.77 g) and (1-methoxyprop-2-yn-1-yl)cyclohexane (304 mg, 2 mmol). After purification by flash chromatography [hexanes:EtOAc (3:2)] unreacted (S)-4-benzyloxazolidin-2-one (1.37 g) was recovered along with *ynamide* **8b** was isolated as a white solid (365 mg, 56%, *dr* ~1:1); mp: 73-74 °C; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): Both diastereomers δ = 7.39-7.27 (m, 6H), 7.71-7.24 (m, 4H), 4.37-4.21 (m, 4H), 4.17-4.09 (m, 2H), 3.95 (d, *J* 6.2, 1H), 3.94 (d, *J* 6.2, 1H), 3.43 (s, 3H), 3.42 (s, 3H), 3.23 (dd, *J* 13.7 and 2.7, 2H), 2.95 (dd, *J* 13.7 and 8.1, 2H), 1.92-1.62 (m, 12H), 1.34-1.06 (m, 10H); <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>): Both diastereomers δ = 155.6 (2C), 134.1, 134.1, 129.3 (4C), 129.0 (2C), 129.0 (2C), 127.5, 127.4, 76.4, 76.4, 75.4, 75.3, 71.3, 71.2, 67.3, 67.2, 58.2,



58.2, 56.6, 56.6, 42.6, 42.6, 37.8, 37.7, 29.1, 29.0, 28.5 (2C), 26.4 (2C), 25.9 (4C); IR (neat):  $\nu$  = 2982, 2924, 2853, 2820, 2253, 1769, 1451, 1410, 1179, 1102, 1083, 750, 737, 701; HR-MS (ES-TOF):  $m/z$ : calcd for  $C_{20}H_{25}NO_3Na$ : 350.1732, found 350.1720 [ $M+Na$ ].

## Catalysis optimisation study

An array of gold(I) and gold(III) species proved to be active for this process (Table S1, Entries 1-8), whilst platinum(II) salts, Brønsted acids and an electrophilic bromine source gave no reaction and/or degradation (Entries 9-13). The reaction proceeds well in a variety of solvents showing moderate (*E*)-selectivity (Entries 14-19). Use of acetonitrile, diethyl ether and acetone gave lower yields (<50%) Other nucleophilic oxidants were explored (diphenylsulfoxide, tempo, picolinic acid *N*-oxide, substituted pyridine and triethyl *N* oxides) with poor results.

**Table S1** Survey of reaction conditions

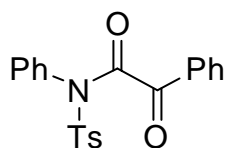
Reaction scheme: **1b** (N-(phenylthio)but-3-yn-2-amine) reacts with [Catalyst] (5 mol%), Solvent (0.2 M), and Py *N*-Oxide (1.1 eq.) to form **3b** (N-(phenylthio)-2-propen-1-one derivative).

Entry	[M]	solvent	time [h]	T [°C]	Yield [%] <sup>a</sup> ( <i>E</i> : <i>Z</i> Ratio)
1	Me <sub>2</sub> SAuCl	CH <sub>2</sub> Cl <sub>2</sub>	12	RT	61 (3.9:1)
2	PPh <sub>3</sub> AuCl/ AgOTs	ClCH <sub>2</sub> CH <sub>2</sub> Cl	12	70	80 (3.7:1)
3	PPh <sub>3</sub> AuNTf <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	12	RT	44 (1:1)
4	AuCl	CH <sub>2</sub> Cl <sub>2</sub>	12	RT	61 (3.8:1)
5	AuCl	ClCH <sub>2</sub> CH <sub>2</sub> Cl	0.25	80	76 (2.3:1)
6	NaAuCl <sub>4</sub> ·H <sub>2</sub> O	CH <sub>2</sub> Cl <sub>2</sub>	12	RT	54 (2.4:1)
7	Au- <b>I</b>	CH <sub>2</sub> Cl <sub>2</sub>	12	RT	48 (3.0:1)
8	Au- <b>I</b>	toluene	12	RT	52 (2.5:1)
9	PtBr <sub>2</sub>	toluene	12	70	- <sup>b</sup>
10	PtCl <sub>2</sub>	toluene	12	70	- <sup>b</sup>
11	p-TsOH	ClCH <sub>2</sub> CH <sub>2</sub> Cl	12	RT	- <sup>b</sup>
12	TfOH	ClCH <sub>2</sub> CH <sub>2</sub> Cl	12	RT	- <sup>c</sup>
13	NBS	ClCH <sub>2</sub> CH <sub>2</sub> Cl	12	RT	- <sup>b</sup>
14	AuCl <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	12	RT	42 (3.3:1)
15	AuBr <sub>3</sub>	ClCH <sub>2</sub> CH <sub>2</sub> Cl	0.33	70	82 (2.5:1)
16	AuBr <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	3	RT	84 (2.0:1)
17	AuBr <sub>3</sub>	THF	12	RT	86 (3.7:1) <sup>d</sup>
18	AuBr <sub>3</sub>	CH <sub>3</sub> NO <sub>2</sub>	24	RT	60 (3.8:1)
19	Au- <b>I</b>	ClCH <sub>2</sub> CH <sub>2</sub> Cl	2	50	66 (2.3:1)
20	Au- <b>I</b>	ClCH <sub>2</sub> CH <sub>2</sub> Cl	0.17	70	82 <sup>[b]</sup> (2.3:1)
21	Au- <b>I</b>	ClCH <sub>2</sub> CH <sub>2</sub> Cl	0.25	80	45 (2.5:1)

<sup>a</sup> Yields and ratios calculated by <sup>1</sup>H NMR spectroscopy against a known quantity of internal standard. <sup>b</sup> The starting material was partially recovered. <sup>c</sup> Degradation of starting material occurred. <sup>d</sup> 71% isolated yield after flash chromatography.

## Products of Catalysis

### 2-Oxo-*N*-2-diphenyl-*N*-tosylacetamide **2a**



The catalyst system was prepared by addition of  $\text{CH}_2\text{Cl}_2$  (1 mL) to  $\text{AuClPPh}_3$  (5 mg, 0.01 mmol) and  $\text{AgOTs}$  (4 mg, 0.01 mmol). After stirring for 10 min at RT, a white precipitate of  $\text{AgCl}$  was observed and ynamide **1a** (34.7 mg, 0.1 mmol) and pyridine-*N*-oxide (22 mg, 0.22 mmol) were added. The reaction mixture was stirred at rt until complete consumption of the starting material before being filtered through a pad of silica. The filtrate was then concentrated under reduced pressure and the residue purified by flash chromatography [hexanes:EtOAc (20:1)] to give *oxoacetamide 2a* (30 mg, 79%) as a colourless oil;  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.90-7.88 (m, 2H), 7.75 (d, *J* 8.4, 2H), 7.70-7.60 (m, 1H), 7.55-7.50 (m, 2H), 7.44-7.33 (m, 5H), 7.13 (d, *J* 6.9, 2H), 2.48 (s, 3H);  $^{13}\text{C-NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 187.6, 166.7, 145.9, 134.6, 134.1, 133.5, 132.7, 130.6 (2C), 130.2, 129.8 (2C), 129.6 (2C), 129.5 (2C), 129.1 (2C), 128.9 (2C), 21.8; IR (neat):  $\nu$  = 2921, 2988, 1685, 1672, 1595, 1487, 1449, 1374, 1325, 1306, 1229, 1191, 1173, 1148, 1086, 1073, 1034, 955, 912, 812, 758, 737, 710, 694, 662; HR-MS (ES-TOF): *m/z*: calcd for  $\text{C}_{21}\text{H}_{17}\text{NO}_4\text{NaS}$ : 402.0776, found 402.0765 [*M*+*Na*].

### Catalytic oxidative reactions: General procedure 2

#### System A (GP2A)

A solution of the corresponding ynamide (0.3 mmol, 1 eq) in  $\text{ClCH}_2\text{CH}_2\text{Cl}$  (1.5 mL) was added to a mixture of dichloro(2-pyridinecarboxylato)gold (5.9 mg, 0.015 mmol, 5 mol%) and pyridine-*N*-oxide (32 mg, 0.34 mmol, 1.1 eq). The reaction mixture was stirred at 70 °C until complete consumption of the starting material was observed before being filtered through a pad of silica. The filtrate was then concentrated under reduced pressure and purification of the residue was performed by flash chromatography.

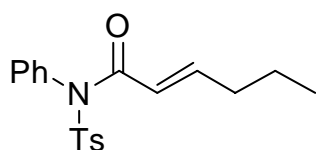
#### System B (GP2B)

A solution of the corresponding ynamide (0.3 mmol, 1 eq) in THF (1.5 mL) was added to a mixture of goldtribromide (6.6 mg, 0.015 mmol, 5 mol%) and pyridine-*N*-oxide (32 mg, 0.34 mmol, 1.1 eq). The reaction mixture was stirred at rt until complete consumption of the starting material was observed before being filtered through a pad of silica. The filtrate was then concentrated under reduced pressure and purification of the residue was performed by flash chromatography.

In many cases, co-elution of starting material and a product limits our ability to precisely determine the reaction time. In these cases reactions were left for an extended period of time (20 h) to ensure complete conversion which highlights the mildness of the reaction system.

### (*E*) and (*Z*)-*N*-Phenyl-*N*-tosylhex-2-enamides (**3b**)

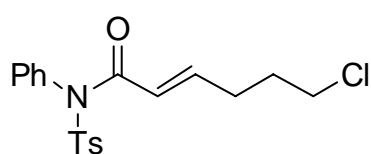
Following GP2A using ynamide **1b** (98 mg) for 10 min. After purification by flash chromatography [hexanes:EtOAc (15:1)] *enimide 3b* was afforded in combined yield of 70% [*E*:*Z* (2.3:1)]. Following GP2B using ynamide **1b** (98 mg) for 18 h. After purification by flash chromatography [hexanes:EtOAc (15:1)] *enimide 3b* was afforded in combined yield of 70% [*E*:*Z* (3.7:1)]; *enimide (E)-3b*, colourless oil:  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.93 (d, *J* 8.4, 2H), 7.53-7.45 (m, 3H), 7.34 (d, *J* 8.4, 2H), 7.29-7.23 (m, 2H), 6.95 (dt, *J*



15.1 and 7.1, 2H), 5.44 (dt, *J* 15.1 and 1.5, 1H), 2.45 (s, 3H), 1.97 (tdd, *J* 7.3, 7.1 and 1.5, 2H), 1.35-1.23 (m, 2H), 0.78 (t, *J* 7.4, 3H); <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>): δ = 165.3, 151.0, 144.7, 136.3, 136.1, 130.4 (2C), 129.8, 129.7 (2C), 129.3 (2C), 129.2 (2C), 121.3, 34.4, 21.7, 21.2, 13.5; IR (neat): ν = 2963, 2929, 2876, 1689, 1635, 1595, 1488, 1455, 1361, 1291, 1255, 1165, 1121, 1088, 975, 904, 814, 726, 695, 682; HR-MS (ES-TOF): *m/z*: calcd for C<sub>19</sub>H<sub>21</sub>NO<sub>2</sub>NaS: 366.1140, found 366.1131 [*M*+Na]; *enimide* (Z)-**3b**, colourless oil: <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.93 (d, *J* 8.4, 2H), 7.50-7.42 (m, 3H), 7.34 (d, *J* 8.4, 2H), 7.25-7.22 (m, 2H), 5.98 (dt, *J* 11.6 and 7.3, 1H), 5.41 (dt, *J* 11.6 and 1.8, 1H), 2.52 (tdd, *J* 7.5, 7.3 and 1.8, 2H), 2.46 (s, 3H), 1.44-1.31 (m, 2H), 0.87 (t, *J* 7.4, 3H); <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>): δ = 165.3, 151.4, 144.6, 136.5, 136.4, 130.3 (2C), 129.7, 129.6 (2C), 129.3 (2C), 129.2 (2C), 120.3, 31.1, 22.2, 21.7, 13.7; IR (neat): ν = 2964, 2931, 2877, 1688, 1623, 1597, 1488, 1455, 1420, 1357, 1241, 1174, 1149, 1120, 1087, 1074, 1002, 877, 819, 793, 733, 696, 685; HR-MS (ES-TOF): *m/z*: calcd for C<sub>19</sub>H<sub>21</sub>NO<sub>3</sub>NaS: 366.1140, found 366.1135 [*M*+Na].

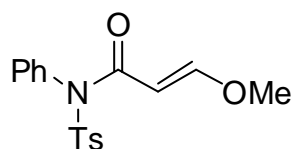
### (*E*) and (Z)-6-Chloro-*N*-Phenyl-*N*-tosylhex-2-enamides (**3c**)

Following GP2A using *ynamide* **1c** (109 mg) for 10 min. After purification by flash chromatography [hexanes:EtOAc (15:1)] *enimide* **3c** was afforded in combined yield of 73% [*E*:Z (1.9:1)]. Following GP2B using *ynamide* **1c** (109 mg) for 18 h. After purification by flash chromatography [hexanes:EtOAc (15:1)] *enimide* **3c** was afforded in combined yield of 70% [*E*:Z (3.5:1)]; *enimide* (*E*)-**3c**,



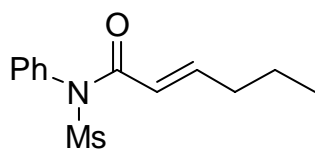
colourless oil: <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.92 (d, *J* 8.4, 2H), 7.55-7.46 (m, 3H), 7.34 (d, *J* 8.4, 2H), 7.29-7.23 (m, 2H), 6.90 (dt, *J* 15.0 and 7.2, 1H), 5.51 (dt, *J* 15.0 and 1.5, 1H), 3.39 (t, *J* 6.4, 2H), 2.45 (s, 3H), 2.17 (dtd, *J* 7.2, 7.1 and 1.5, 2H), 1.69 (m, 2H); <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>): δ = 164.9, 148.5, 144.8, 136.2, 135.9, 130.2 (2C), 129.9, 129.7 (2C), 129.3 (2C), 129.2 (2C), 122.4, 43.6, 30.4, 29.2, 21.7; IR (neat): ν = 2960, 2924, 2853, 1689, 1637, 1594, 1488, 1361, 1169, 1087, 907, 813, 725, 694, 681; HR-MS (ES-TOF): *m/z*: calcd for C<sub>19</sub>H<sub>20</sub>NO<sub>3</sub>NaS: 400.0750, found 400.0754 [*M*+Na]; *enimide* (Z)-**3b**, colourless oil: <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.92 (d, *J* 8.3, 2H), 7.49-7.45 (m, 3H), 7.35 (d, *J* 8.3, 2H), 7.26-7.23 (m, 2H), 5.95 (dt, *J* 11.5 and 7.5, 1H), 5.47 (dt, *J* 11.5 and 1.7, 1H), 3.47 (t, *J* 6.8, 2H), 2.68 (dtd, *J* 7.5, 7.4 and 1.7, 2H), 2.46 (s, 3H), 1.84 (tt, *J* 7.4 and 6.8, 2H); <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>): δ = 165.0, 148.7, 144.8, 136.3, 136.2, 130.3 (2C), 129.8, 129.7 (2C), 129.4 (2C), 129.2 (2C), 121.5, 44.2, 31.7, 26.6, 21.7; IR (neat): ν = 2924, 2855, 1688, 1627, 1595, 1489, 1454, 1415, 1359, 1242, 1159, 1088, 907, 881, 812, 726, 694, 684; HR-MS (ES-TOF): *m/z*: calcd for C<sub>19</sub>H<sub>20</sub>NO<sub>3</sub>NaS: 400.0750, found 400.0751 [*M*+Na].

### (*E*)-3-Methoxy-*N*-phenyl-*N*-tosylacrylamide (**3d**)



Following GP2A using *ynamide* **1d** (95 mg) for 12 h. After purification by flash chromatography [hexanes:EtOAc (20:1)] *enimide* (*E*)-**3d** was afforded in 70% yield. Following GP2B using *ynamide* **1d** (95 mg) for 18 h. After purification by flash chromatography [hexanes:EtOAc (20:1)] *enimide* (*E*)-**3d** was afforded in 65% yield; *enimide* (*E*)-**3d**, colourless oil: <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.93 (d, *J* 8.4, 2H), 7.56-7.46 (m, 4H), 7.34 (d, *J* 8.4, 2H), 7.30-7.27 (m, 2H), 4.82 (d, *J* 12.1, 1H), 3.46 (s, 3H), 2.45 (s, 3H); <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>): δ = 166.5, 164.6, 144.6, 136.7, 136.4, 130.4 (2C), 129.8, 129.6 (2C), 129.3 (2C), 129.1 (2C), 97.0, 58.1, 21.7; IR (neat): ν = 2976, 2936, 1682, 1605, 1488, 1453, 1438, 1354, 1331, 1256, 1169, 1113, 1084, 931, 906, 810, 723, 692, 683; HR-MS (ES-TOF): *m/z*: calcd for C<sub>17</sub>H<sub>17</sub>NO<sub>4</sub>NaS: 354.0776, found 354.0766 [*M*+Na].

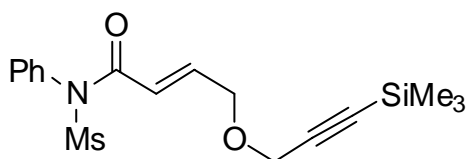
**(E) and (Z)-N-(Methylsulfonyl)-N-phenylhex-2-enamides (3e)**



Following GP2A using *ynamide 1e* (109 mg) for 10 min. After purification by flash chromatography [hexanes:EtOAc (15:1)] *enimide 3e* was afforded in combined yield of 75% [*E:Z* (3:1)]. Following GP2B using *ynamide 1e* (109 mg) for 18 h. After purification by flash chromatography [hexanes:EtOAc (15:1)]

*enimide 3e* was afforded in combined yield of 71% [*E:Z* (4:1)]; *enimide (E)-3e*, colourless oil: <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.52-7.47 (m, 3H), 7.32-7.26 (m, 2H), 7.10 (dt, *J* 15.2 and 7.1, 1H), 5.51 (dt, *J* 15.2 and 1.5, 1H), 3.48 (s, 3H), 2.05 (tdd, *J* 7.3, 7.1 and 1.5, 2H), 1.44-1.28 (m, 2H), 0.83 (t, *J* 7.4, 3H); <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>): δ = 166.4, 151.8, 135.3, 130.1 (2C), 130.0, 129.8 (2C), 121.0, 41.9, 34.4, 21.2, 13.5; IR (neat): ν = 2957, 2929; HR-MS (ES-TOF): *m/z*: calcd for C<sub>13</sub>H<sub>17</sub>NO<sub>2</sub>NaS: 290.0827, found 290.0830 [*M*]; *enimide (Z)-3e*, colourless oil: <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.50-7.45 (m, 3H), 7.30-7.26 (m, 2H), 6.12 (dt, *J* 11.5 and 7.4, 1H), 5.46 (dt, *J* 11.5 and 1.8, 1H), 3.48 (s, 3H), 2.66 (tdd, *J* 7.5, 7.4 and 1.8, 2H), 1.51-1.41 (m, 2H), 0.95 (t, *J* 7.4, 3H); <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>): δ = 166.5, 152.7, 135.6, 130.0 (2C), 129.9, 129.8 (2C), 119.8, 41.9, 31.3, 22.2, 13.8; IR (neat): ν = 2963, 2932, 2876, 1682, 1622, 1594, 1487, 1450, 1345, 1322, 1253, 1189, 1165, 1120, 840, 760, 736, 696; HR-MS (ES-TOF): *m/z*: calcd for C<sub>13</sub>H<sub>17</sub>NO<sub>2</sub>NaS: 290.0827, found 290.0823 [*M+Na*].

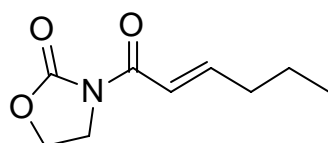
**(E) and (Z)-N-(Methylsulfonyl)-N-phenyl-4-((3-(trimethylsilyl)prop-2-yn-1-yl)oxy)but-2-enamide (3f)**



Following GP2A using *ynamide 1f* (105 mg) for 1 hour. After purification by flash chromatography [hexanes:EtOAc (4:1)] *enimide 3f* was afforded in combined yield of 66% [*E:Z* (2.8:1)].

Following GP2B using *ynamide 1f* (105 mg) for 20 h. After purification by flash chromatography [hexanes:EtOAc (4:1)] *enimide 3f* was afforded in combined yield of 68% [*E:Z* (3.2:1)]; *enimide (E)-3f*, light-yellow oil: <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.51-7.44 (m, 3H), 7.31-7.24 (m, 2H), 7.10 (dt, *J* 15.3 and 4.2, 1H), 5.77 (dt, *J* 15.3 and 2.1, 1H), 4.11 (dd, *J* 4.2 and 2.1, 2H), 4.02 (s, 2H), 3.47 (s, 3H), 0.14 (s, 9H); <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>): δ = 165.8, 145.9, 135.0, 130.0 (2C), 129.9, 129.9 (2C), 120.8, 100.4, 92.3, 67.9, 58.5, 41.9, -0.3 (3C); IR (neat): ν = 3041, 2960, 2901, 2850, 1687, 1643, 1351, 1249, 1153, 1119, 961, 840, 761, 694; HR-MS (ES-TOF): *m/z*: calcd for C<sub>17</sub>H<sub>23</sub>NO<sub>4</sub>NaSSi: 388.1015, found 388.1006 [*M+Na*]; *enimide (Z)-3f*, light-yellow oil: <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.51-7.45 (m, 3H), 7.31-7.26 (m, 2H), 6.32 (dt, *J* 11.7 and 4.6, 1H), 5.52 (dt, *J* 11.7 and 2.5, 1H), 4.70 (dd, *J* 4.6 and 2.5, 2H), 4.18 (s, 2H), 3.47 (s, 3H), 0.17 (s, 9H); <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>): δ = 166.1, 150.3, 135.3, 130.1, 130.0 (2C), 129.9 (2C), 119.0, 100.9, 91.9, 68.8, 59.0, 41.9, -0.2 (3C); IR (neat): ν = 3061, 2961, 2898, 2849, 1683, 1356, 1250, 1156, 1094, 964, 842, 733, 695; HR-MS (ES-TOF): *m/z*: calcd for C<sub>17</sub>H<sub>23</sub>NO<sub>4</sub>NaSSi: 388.1015, found 388.1027 [*M+Na*].

**(E) and (Z)-3-(hex-2-enoyl)oxazolidin-2-one (3g)**

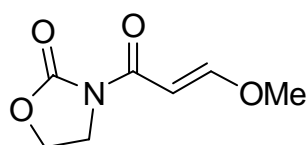


Following GP2A using *ynamide 1g* (35 mg) for 20 h. After purification by flash chromatography [hexanes:EtOAc (7:3)] *enimide 3g* was afforded in combined yield of 63% [*E:Z* (3.2:1)].

Following GP2B using *ynamide 1g* (35 mg) for 20 h. After purification by flash chromatography [hexanes:EtOAc (7:3)] *enimide 3g* was afforded in combined yield of 70% [*E:Z* (5.0:1)]; *enimide (E)-3g*, light-yellow oil: <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.22-7.09 (m, 2H), 4.41 (t, *J* 8.1, 2H), 4.06 (t,

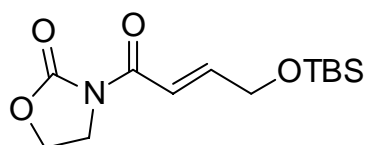
$J$  8.1, 2H), 2.25 (app td,  $J$  7.2 and 7.2, 2H), 1.51 (qt,  $J$  7.4 and 7.4, 2H), 0.93 (t,  $J$  7.4, 3H);  $^{13}\text{C}$ -NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 165.3, 153.5, 151.5, 120.1, 62.0, 42.7, 34.6, 21.3, 13.7; IR (neat):  $\nu$  = 2961, 2930, 2874, 1769, 1680, 1633, 1384, 1357, 1197, 1101, 1031, 968, 757, 704; HR-MS (EI-TOF):  $m/z$ : calcd for  $\text{C}_9\text{H}_{13}\text{NO}_3$ : 183.0895, found 183.0899 [ $M$ ]; *enimide* (*Z*)-**3g**, light-yellow oil:  $^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.00 (dt,  $J$  11.6 and 1.7, 1H), 6.37 (dt,  $J$  11.6 and 7.4, 1H), 4.41 (t,  $J$  8.4, 2H), 4.06 (t,  $J$  8.4, 2H), 2.61 (tdd,  $J$  7.4, 7.4 and 1.7, 2H), 1.49 (qt,  $J$  7.4 and 7.4, 2H), 0.95 (t,  $J$  7.4, 3H);  $^{13}\text{C}$ -NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 165.0, 153.3, 152.2, 118.7, 61.9, 42.5, 31.9, 22.2, 13.8; IR (neat):  $\nu$  = 2961, 2928, 2873, 1767, 1679, 1384, 1361, 1284, 1261, 1198, 1122, 1002, 1039, 1023, 952, 796, 758, 717; HR-MS (EI-TOF):  $m/z$ : calcd for  $\text{C}_9\text{H}_{13}\text{NO}_3$ : 183.0895, found 183.0892 [ $M$ ].

### (*E*) and (*Z*)-3-(3-methoxyacryloyl)oxazolidin-2-one (**3h**)



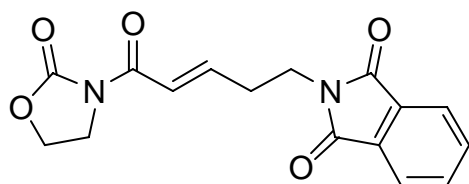
Following GP2A using *ynamide* **1h** (46 mg) for 12 h. After purification by flash chromatography [hexanes:EtOAc (7:3)] *enimide* (*E*)-**3h** was afforded in 89% yield; *enimide* (*E*)-**3h**, colourless oil:  $^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.81 (d,  $J$  12.3, 1H), 6.69 (d,  $J$  12.3, 1H), 4.38 (t,  $J$  8.7, 2H), 4.04 (t,  $J$  8.7, 2H), 3.75 (s, 3H);  $^{13}\text{C}$ -NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 165.8, 164.9, 153.7, 95.4, 61.8, 57.6, 42.6; IR (neat):  $\nu$  = 3124, 2985, 2924, 2850, 1761, 1672, 1594, 1386, 1358, 1197, 1169, 1036, 970, 928, 845, 821, 757, 704; HR-MS (EI-TOF):  $m/z$ : calcd for  $\text{C}_7\text{H}_9\text{NO}_4$ : 171.0532, found 171.0526 [ $M$ ].

### (*E*) and (*Z*)-3-(4-((*t*-Butyldimethylsilyl)oxy)but-2-enoyl)oxazolidin-2-one (**3i**)



Following GP2A using *ynamide* **1i** (81 mg) for 20 h. After purification by flash chromatography [hexanes:EtOAc (13:7)] *enimide* **3i** was afforded in combined yield of 75% [*E*:*Z* (6.7:1)]; *enimide* (*E*)-**3i**, light-yellow oil:  $^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.52 (dt,  $J$  15.2 and 2.2, 1H), 7.19 (dt,  $J$  15.2 and 3.4, 1H), 4.46-4.38 (m, 4H), 4.07 (t,  $J$  8.0, 2H), 0.94 (s, 9H), 0.10 (s, 6H);  $^{13}\text{C}$ -NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 165.1, 153.3, 149.5, 118.4, 62.9, 61.9, 42.6, 25.8 (3C), 18.2, -5.5 (2C); IR (neat):  $\nu$  2954, 2927, 2885, 2856, 1767, 1680, 1637, 1359, 1393, 1217, 1107, 1035, 948, 829, 776, 755, 709, 682; HR-MS (EI-TOF):  $m/z$ : calcd for  $\text{C}_{13}\text{H}_{23}\text{NO}_4\text{Si}$ : 285.1396, found 285.1398 [ $M$ ]; *enimide* (*Z*)-**3i**, light-yellow oil:  $^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.10 (dt,  $J$  11.8 and 2.5, 1H), 6.54 (dt,  $J$  11.8 and 4.5, 1H), 4.75 (dd,  $J$  4.5 and 2.5, 2H), 4.42 (t,  $J$  8.0, 2H), 4.05 (t,  $J$  8.0, 2H), 0.90 (s, 9H), 0.07 (s, 6H);  $^{13}\text{C}$ -NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = Carbamate CO not observed, 164.7, 155.1, 116.3, 62.7, 61.9, 42.4, 25.9 (3C), -5.3 (2C), *t*-butyl quaternary carbon not observed; IR (neat):  $\nu$  = 2955, 2927, 2888, 2856, 1767, 1681, 1637, 1393, 1330, 1217, 1107, 1035, 948, 829, 776, 756, 708, 682; HR-MS (EI-TOF):  $m/z$ : calcd for  $\text{C}_{13}\text{H}_{23}\text{NO}_4\text{Si}$ : 285.1396, found 285.1392 [ $M$ ].

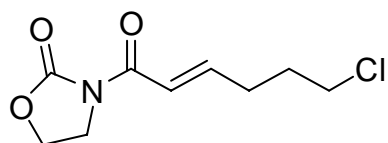
### (*E*) and (*Z*)-2-(5-Oxo-5-(2-oxooxazolidin-3-yl)pent-3-en-1-yl)isoindoline-1,3-dione (**3j**)



Following GP2A using *ynamide* **1j** (89 mg) for 20 h. After purification by flash chromatography [hexanes:EtOAc (11:9)] *enimide* **3j** was afforded in combined yield of 68% [*E*:*Z* (5.6:1)]. Following GP2B using *ynamide* **1j** (89 mg) for 20 h. After purification by flash chromatography [hexanes:EtOAc (7:3)] *enimide* **3j** was afforded in combined yield of 75% [*E*:*Z* (6.7:1)]; *enimide* (*E*)-**3j**, white solid: mp: 146-149 °C;  $^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.85-7.80 (m, 2H), 7.73-7.68 (m, 2H), 7.26 (dt,  $J$  15.4 and 1.5, 1H), 7.07 (dt,  $J$  15.4 and 7.0, 1H), 4.39 (t,  $J$  8.0, 2H), 4.03 (t,  $J$  8.0, 2H), 3.84 (t,  $J$  7.0, 2H), 2.66 (tdd,  $J$  7.0, 7.0 and

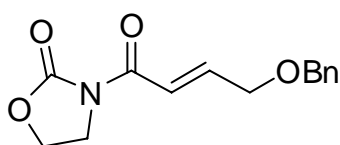
1.5);  $^{13}\text{C}$ -NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 168.0 (2C), 164.6, 153.3, 146.1, 133.9 (2C), 131.9 (2C), 123.3 (2C), 122.1, 62.0, 42.6, 36.3, 31.6; IR (neat):  $\nu$  = 3090, 2923, 2959, 2984, 2852, 1771, 1705, 1680, 1398, 1680, 1357, 1337, 1193, 1147, 957, 761, 721, 705; HR-MS (ES-TOF):  $m/z$ : calcd for  $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_4\text{Na}$ : 337.0800, found 337.0808 [ $M+\text{Na}$ ]; *enimide* (Z)-**3j**, white solid: mp: 136-138 °C;  $^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.86-7.82 (m, 2H), 7.73-7.69 (m, 2H), 7.06 (td,  $J$  11.6 and 1.7, 1H), 6.36 (td,  $J$  11.6 and 7.5, 1H), 4.37 (t,  $J$  8.0, 2H), 3.99 (t,  $J$  8.0, 2H), 3.87 (t,  $J$  7.5, 2H), 3.02 (tdd,  $J$  7.5, 7.5 and 1.7, 2H);  $^{13}\text{C}$ -NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 168.3 (2C), 164.6, 153.2, 146.0, 133.9 (2C), 132.1 (2C), 123.2 (2C), 121.4, 61.9, 42.4, 36.8, 29.1; IR (neat):  $\nu$  = 2991, 2926, 2856, 170, 1706, 1680, 1437, 1392, 1360, 1291, 1210, 1041, 1018, 720; HR-MS (ES-TOF):  $m/z$ : calcd for  $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_4\text{Na}$ : 337.0800, found 337.0806 [ $M+\text{Na}$ ].

### (E) and (Z)-3-(6-Chlorohex-2-enoyl)oxazolidin-2-one (3k)



Following GP2A using *ynamide* **1k** (60 mg) for 20 h. After purification by flash chromatography [hexanes:EtOAc (13:7)] *enimide* **3j** was afforded in combined yield of 63% [ $E:Z$  (2.9:1)]. Following GP2B using *ynamide* **1k** (60 mg) for 20 h. After purification by flash chromatography [hexanes:EtOAc (13:7)] *enimide* **3k** was afforded in combined yield of 65% [ $E:Z$  (4.0:1)]; *enimide* (E)-**3k**, light-yellow oil:  $^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.26 (dt,  $J$  15.2 and 1.4, 1H), 7.10 (dt,  $J$  15.2 and 6.6, 1H), 4.42 (t,  $J$  8.1, 2H), 4.05 (t,  $J$  8.1, 2H), 3.55 (t,  $J$  6.5, 2H), 2.44 (dtd,  $J$  6.6, 6.5 and 1.4, 2H), 1.96 (tt,  $J$  6.5 and 6.5, 2H);  $^{13}\text{C}$ -NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 164.9, 153.4, 149.0, 121.0, 62.0, 43.9, 42.6, 30.7, 29.7; IR (neat):  $\nu$  = 2960, 2920, 2850, 1767, 1677, 1627, 1423, 1384, 1361, 1284, 1216, 1195, 1111, 1038, 797, 757, 716; HR-MS (ES-TOF):  $m/z$ : calcd for  $\text{C}_9\text{H}_{12}\text{NO}_3\text{NaCl}$ : 240.0403, found 240.0400 [ $M+\text{Na}$ ]; *enimide* (Z)-**3k**, light-yellow oil:  $^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.06 (dt,  $J$  11.6 and 1.7, 1H), 6.33 (dt,  $J$  11.6 and 7.5, 1H), 4.43 (t,  $J$  8.1, 2H), 4.06 (t,  $J$  8.1, 2H), 3.57 (t,  $J$  6.7, 2H), 2.78 (dtd,  $J$  7.5, 7.1 and 1.7, 2H), 1.96 (tt,  $J$  7.1 and 6.7, 2H);  $^{13}\text{C}$ -NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 164.9, Carbamate CO not observed, 149.3, 120.0, 62.0, 44.3, 42.5, 31.8, 27.2; IR (neat):  $\nu$  = 2991, 2961, 2923, 2871, 1767, 1679, 1634, 1385, 1359, 1277, 1217, 1110, 1037, 977, 757, 705; HR-MS (ES-TOF):  $m/z$ : calcd for  $\text{C}_9\text{H}_{12}\text{NO}_3\text{NaCl}$ : 240.0403, found 240.0410 [ $M+\text{Na}$ ].

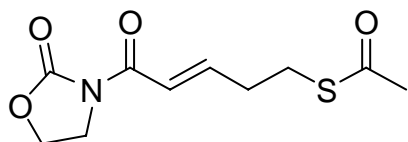
### (E) and (Z)-3-(4-(benzyloxy)but-2-enoyl)oxazolidin-2-one (3l)



Following GP2A using *ynamide* **1l** (74 mg) for 20 h. After purification by flash chromatography [hexanes:EtOAc (1:1)] *enimide* **3l** was afforded in combined yield of 73% [ $E:Z$  (2.8:1)]. Following GP2B using *ynamide* **1l** (74 mg) for 20 h. After purification by flash chromatography [hexanes:EtOAc (1:1)] *enimide* **3l** was afforded in combined yield of 68% [ $E:Z$  (3.1:1)]; *enimide* (E)-**3l**, light-yellow solid: mp: 81-83 °C;  $^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.51 (dt,  $J$  15.5 and 1.9, 1H), 7.40-7.23 (m, 5H), 7.15 (dt,  $J$  15.5 and 4.4, 1H), 4.57 (s, 2H), 4.40 (t,  $J$  7.5, 2H), 4.23 (dd,  $J$  4.4 and 1.9, 2H), 4.05 (t,  $J$  7.5, 2H);  $^{13}\text{C}$ -NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 164.8, 153.3, 146.1, 137.6, 129.6, 128.4 (2C), 127.7 (2C), 120.0, 72.7, 68.9, 62.0, 42.6; IR (neat):  $\nu$  = 3061, 3024, 2924, 2873, 2852, 1762, 1672, 1633, 1424, 1368, 1356, 1275, 1115, 1020, 958, 800, 759, 729, 693; HR-MS (ES-TOF):  $m/z$ : calcd for  $\text{C}_{14}\text{H}_{15}\text{NO}_4\text{Na}$ : 284.0899, found 284.0895 [ $M+\text{Na}$ ]; *enimide* (Z)-**3l**, waxy white solid: mp: 90-91 °C;  $^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.38-7.27 (m, 5H), 7.16 (dt,  $J$  11.8 and 2.5, 1H), 6.60 (dt,  $J$  11.8 and 4.6, 1H), 4.63 (dd,  $J$  4.6 and 2.5, 2H), 4.56 (s, 2H), 4.41 (t,  $J$  7.9, 2H), 4.03 (t,  $J$  7.9, 2H);  $^{13}\text{C}$ -NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 164.7, 153.2, 150.5, 137.9, 129.7, 128.5 (2C), 127.8 (2C), 117.9, 72.9, 69.4,

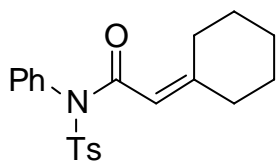
61.9, 42.4; IR (neat):  $\nu$  = 3061, 3024, 2921, 2874, 1762, 1672, 1634, 1424, 1387, 1356, 1276, 1213, 1117, 1102, 958, 799, 759, 728, 711, 693; HR-MS (ES-TOF):  $m/z$ : calcd for  $C_{14}H_{15}NO_4Na$ : 284.0899, found 284.0890 [ $M+Na$ ].

**(E) and (Z)-(5-Oxo-5-(2-oxooxazolidin-3-yl)pent-3-en-1-yl) ethanethioate (3m)**



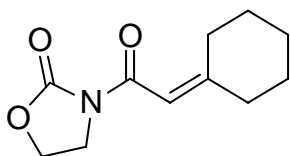
Following GP2A using ynamide **1m** (68 mg) for 20 h. After purification by flash chromatography [hexanes:EtOAc (3:2)] enamide **3m** was afforded in combined yield of 75% [ $E:Z$  (2.6:1)]. Following GP2B using ynamide **1m** (68 mg) for 20 h. After purification by flash chromatography [hexanes:EtOAc (3:2)] enamide **3m** was afforded in combined yield of 71% [ $E:Z$  (7.7:1)]; enamide (*E*)-**3m**, colourless oil:  $^1H$ -NMR (300 MHz,  $CDCl_3$ ):  $\delta$  = 7.25 (dt,  $J$  15.4 and 1.4, 1H), 7.05 (dt,  $J$  15.4 and 7.0, 1H), 4.41 (t,  $J$  7.9, 2H), 4.05 (t,  $J$  7.9, 2H), 2.99 (t,  $J$  7.0, 2H), 2.54 (tdd,  $J$  7.0, 7.0 and 1.4), 2.31 (s, 3H);  $^{13}C$ -NMR (101 MHz,  $CDCl_3$ ):  $\delta$  = 195.2, 164.7, 153.4, 147.7, 121.4, 62.0, 42.6, 32.3, 30.5, 27.3; IR (neat):  $\nu$  = 2982, 2925, 2859, 1768, 1679, 1634, 1385, 1356, 1218, 1133, 1108, 1037, 954, 757, 705; HR-MS (ES-TOF):  $m/z$ : calcd for  $C_{10}H_{13}NO_4NaS$ : 266.0463, found 266.0468 [ $M+Na$ ]; enamide (*Z*)-**3m**, colourless oil:  $^1H$ -NMR (300 MHz,  $CDCl_3$ ):  $\delta$  = 7.09 (dt,  $J$  11.6 and 1.7, 1H), 6.32 (dt,  $J$  11.6 and 7.1, 1H), 4.42 (t,  $J$  8.0, 2H), 4.05 (t,  $J$  8.0, 2H), 3.05-3.00 (m, 2H), 2.95-2.88 (m, 2H), 2.33 (s, 3H);  $^{13}C$ -NMR (101 MHz,  $CDCl_3$ ):  $\delta$  = 195.5, 164.7, carbamate CO not observed, 148.2, 120.3, 62.0, 42.5, 30.6, 29.6, 28.1; IR (neat):  $\nu$  = 2989, 2924, 2854, 1769, 1679, 1627, 1422, 1384, 1360, 1285, 1219, 1196, 1040, 1012, 955, 797, 757, 701; HR-MS (ES-TOF):  $m/z$ : calcd for  $C_{10}H_{13}NO_4NaS$ : 266.0463, found 266.0464 [ $M+Na$ ].

**2-Cyclohexylidene-N-phenyl-N-tosylacetamide (5a)**



Following GP2A using ynamide **4a** (109 mg) for 20 min. After purification by flash chromatography [hexanes:EtOAc (20:1)] enamide **5a** was afforded in 80% yield. Following GP2B using ynamide **4a** (109 mg) for 18 h. After purification by flash chromatography [hexanes:EtOAc (20:1)] enamide **5a** was afforded in yield of 78%; enamide **5a**, colourless oil:  $^1H$ -NMR (300 MHz,  $CDCl_3$ ):  $\delta$  = 7.92 (d,  $J$  8.4, 2H), 7.49-7.43 (m, 3H), 7.33 (d,  $J$  8.4, 2H), 7.28-7.22 (m, 2H), 5.21 (s, 1H), 2.75-2.60 (m, 2H), 2.44 (s, 3H), 1.97-1.83 (m, 2H), 1.64-1.41 (m, 6H);  $^{13}C$ -NMR (101 MHz,  $CDCl_3$ ):  $\delta$  = 165.7, 164.8, 144.4, 136.6, 136.5, 130.2 (2C), 129.5 (3C), 129.2 (2C), 129.0 (2C), 114.0, 38.2, 30.1, 28.5, 27.7, 26.0, 21.7; IR (neat):  $\nu$  = 2957, 2929; HR-MS (ES-TOF):  $m/z$ : calcd for  $C_{21}H_{23}NO_3NaS$ : 392.1296, found 392.1281 [ $M+Na$ ].

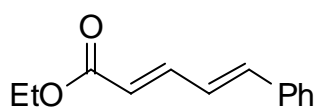
**3-(2-Cyclohexylideneacetyl)oxazolidin-2-one (5b)**



Following GP2A using ynamide **4b** (58 mg) for 20 h. After purification by flash chromatography [hexanes:EtOAc (7:3)] enamide **5b** was afforded in yield of 81%. Following GP2B using ynamide **4b** (58 mg) for 20 h. After purification by flash chromatography [hexanes:EtOAc (7:3)] enamide **5b** was afforded in yield of 81%; enamide **5b**, colourless oil:  $^1H$ -NMR (300 MHz,  $CDCl_3$ ):  $\delta$  = 6.78 (s, 1H), 4.37 (t,  $J$  7.7, 2H), 4.01 (t,  $J$  7.7, 2H), 2.77 (t,  $J$  5.2, 2H), 2.26 (t,  $J$  5.2, 2H), 1.71-1.54 (m, 6H);  $^{13}C$ -NMR (101 MHz,  $CDCl_3$ ):  $\delta$  = 165.8, 165.3, 153.3, 112.4, 61.7, 42.6, 38.3, 30.7, 28.6, 27.8, 26.1; IR (neat):  $\nu$  = 2926, 2852, 1756, 1666, 1621, 1390, 1621, 1390, 1368, 1281, 1258, 1222, 1188, 1111, 1045, 967, 854, 756, 708; HR-MS (EI-TOF):  $m/z$ : calcd for  $C_{11}H_{15}NO_3$ : 209.1052, found 209.1051 [ $M$ ].

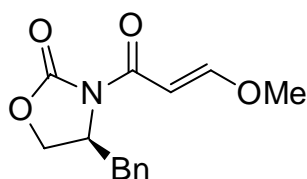


### (*E,E*) and (*Z,Z*)-ethyl 5-phenylpenta-2,4-dienoate (**7**)



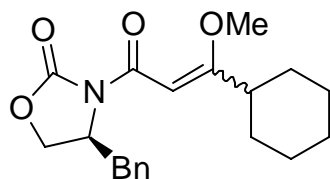
Following GP2A using *ynol ether* **6** (56 mg) for 20 min. After purification by flash chromatography [hexanes:EtOAc (24:1)] *ester* **7** was afforded in combined yield of 75% [*E,E:Z,E* (4.3:1)]. Following GP2B using *ynol ether* **6** (56 mg) for 1 h. After purification by flash chromatography [hexanes:EtOAc (24:1)] *ester* **7** was afforded in combined yield of 88% [*E,E:Z,E* (4.1:1)]; *ester* (*E,E*)-**7**, colourless oil:<sup>11</sup> <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.50-7.28 (m, 6H), 6.91-6.86 (m, 2H), 5.98 (d, *J* 15.3, 1H), 4.23 (q, *J* 7.2, 2H), 1.32 (t, *J* 7.2, 3H); <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>): δ = 167.0, 144.5, 140.3, 136.0, 129.0, 128.8 (2C), 127.1 (2C), 126.2, 121.3, 60.3, 14.3; IR (neat): ν = 3059, 3027, 2981, 2935, 2904, 1703, 1625, 1366, 1258, 1235, 1175, 1130, 1035, 996, 754, 713, 689; HR-MS (EI-TOF): *m/z*: calcd for C<sub>13</sub>H<sub>14</sub>O<sub>2</sub>: 202.0994, found 202.0986 [*M*]; *ester* (*Z,E*)-**7**, colourless oil: <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ = 8.15 (ddd, *J* 15.7, 11.4 and 0.9, 1H), 7.56-7.49 (m, 2H), 7.39-7.27 (m, 3H), 6.82 (d, *J* 15.7, 1H), 6.74 (ddd, *J* 11.4, 11.4 and 0.9, 1H), 5.72 (d, *J* 11.4, 1H), 4.23 (q, *J* 7.2, 2H), 1.33 (t, *J* 7.2, 3H); <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>): δ = 166.6, 144.7, 141.1, 136.4, 128.9, 128.7 (2C), 127.5 (2C), 125.0, 117.5, 60.0, 14.3; IR (neat): ν = 3063, 3027, 2981, 2932, 2871, 1709, 1622, 1601, 1450, 1419, 1175, 1233, 1030, 999, 960, 755, 698; HR-MS (EI-TOF): *m/z*: calcd for C<sub>13</sub>H<sub>14</sub>O<sub>2</sub>: 202.0994, found 202.0988 [*M*].

### (*E*) and (*Z*)-(S)-4-benzyl-3-(3-methoxyacryloyl)oxazolidin-2-one (**9a**)



Following GP2A using *ynamide* **8a** (74 mg) for 20 h. After purification by flash chromatography [hexanes:EtOAc (1:1)] **9a** was afforded in combined yield of 81% [*E:Z* (1.5:1)]. Following GP2B using *ynamide* **8a** (74 mg) for 20 h. After purification by flash chromatography [hexanes:EtOAc (1:1)] **9a** was afforded in combined yield of 91% [*E:Z* (1.9:1)]; *enimide* (*E*)-**9a**, white solid: mp: 117-119 °C; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.41-7.24 (m, 5H), 6.69 (d, *J* 7.1, 1H), 6.43 (d, *J* 7.1, 1H), 4.79-4.70 (m, 1H), 4.24-4.14 (m, 2H), 4.02 (s, 3H), 3.42 (dd, *J* 13.2 and 3.0, 1H), 2.79 (dd, *J* 13.2 and 9.8, 1H); <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>): δ = 162.8, 162.6, 153.4, 135.6, 129.4 (2C), 128.8 (2C), 127.1, 95.1, 65.8, 63.1, 55.2, 38.0; IR (neat): ν = 3118, 3066, 3034, 2997, 2939, 2867, 1767, 1669, 1606, 1387, 1347, 1309, 1206, 1171, 1107, 1076, 1019, 978, 798, 753, 702; HR-MS (EI-TOF): *m/z*: calcd for C<sub>14</sub>H<sub>15</sub>NO<sub>4</sub>: 261.1001, found 261.1008 [*M*]; (*Z*)-**9a**, colourless oil: <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.91 (d, *J* 12.4, 1H), 7.40-7.21 (m, 5H), 6.77 (d, *J* 12.4, 1H), 4.81-4.71 (m, 1H), 4.26-4.14 (m, 2H), 3.81 (s, 3H), 3.34 (dd, *J* 13.4 and 3.3, 1H), 2.82 (dd, *J* 13.4 and 9.5, 1H); <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>): δ = 165.6, 165.2, 153.6, 135.5, 129.4 (2C), 128.9 (2C), 127.2, 95.8, 65.9, 57.7, 55.2, 38.0; IR (neat): ν = 3125, 3063, 3029, 2981, 2940, 1769, 1677, 1599, 1388, 1355, 1202, 1171, 1054, 823, 811, 730, 699; HR-MS (EI-TOF): *m/z*: calcd for C<sub>14</sub>H<sub>15</sub>NO<sub>4</sub>: 261.1001, found 261.0998 [*M*].

### (*E*) and (*Z*)-(S)-4-benzyl-3-(3-cyclohexyl-3-methoxyacryloyl)oxazolidin-2-one (**9b**)



Following GP2A using *ynamide* **8b** (98 mg) for 20 h. After purification by flash chromatography [hexanes:EtOAc (4:1)] **9b** was afforded in combined yield of 79% [*E:Z* (10.9:1)]. Following GP2B using *ynamide* **8b** (98 mg) for 20 h. After purification by flash chromatography [hexanes:EtOAc (4:1)] **9b** was

<sup>11</sup> S. Xu, L. Zhou, S. Zeng, R. Ma, Z. Wang and Z. He, *Org. Lett.*, 2009, **11**, 3498.

afforded in combined yield of 88% [*E*:*Z* (1:6.1)]; (*Z*)-**9a**, colourless oil:  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.32-7.16 (m, 5H), 6.29 (s, 1H), 4.71-4.61 (m, 1H), 4.14-4.00 (m, 2H), 3.89 (s, 3H), 3.32 (dd, *J* 13.3 and 3.2, 1H), 2.70 (dd, *J* 13.3 and 9.8, 1H), 2.30-2.16 (m, 1H), 1.96-1.60 (m, 5H), 1.42-1.09 (m, 5H);  $^{13}\text{C-NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 179.7, 163.2, 153.6, 135.7, 129.4 (2C), 128.8 (2C), 127.1, 93.2, 65.6, 58.8, 55.2, 43.1, 38.1, 31.2, 31.2, 26.1 (2C), 25.8; IR (neat):  $\nu$  = 2930, 2855, 1768, 1668, 1600, 1451, 1385, 1347, 1246, 1194, 1077, 1006, 826, 735, 732, 700; HR-MS (ES-TOF): *m/z*: calcd for  $\text{C}_{20}\text{H}_{25}\text{NO}_4\text{Na}$ : 366.1681, found 366.1688 [*M*+*Na*]; (*E*)-**11a**, colourless oil:  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.32-7.17 (m, 5H), 6.43 (s, 1H), 4.77-4.66 (m, 1H), 4.14-4.02 (m, 2H), 3.74-3.58 (m, 1H), 3.67 (s, 3H), 3.31 (dd, *J* 13.4 and 3.4, 1H), 2.74 (dd, *J* 13.4 and 9.6, 1H), 1.81-1.59 (m, 5H), 1.53-1.06 (m, 5H);  $^{13}\text{C-NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 182.8, 164.8, 153.8, 135.7, 129.5 (2C), 128.8 (2C), 127.1, 89.2, 65.5, 55.9, 55.2, 40.6, 38.2, 29.8, 29.5, 26.1, 26.0, 25.9; IR (neat):  $\nu$  = 2926, 2853, 1764, 1673, 1588, 1384, 1347, 1286, 1196, 1170, 1069, 1037, 822, 810, 728, 699; HR-MS (ES-TOF): *m/z*: calcd for  $\text{C}_{20}\text{H}_{25}\text{NO}_4\text{Na}$ : 366.1681, found 366.1672 [*M*+*Na*].

### Comments on structure analysis:

NOE experiments were performed to assign *E/Z* configurations in cases where ambiguous *J* values are observed between the vinylic protons or when the product contains a quaternary vinylic carbon.

In the case of *enimide* (*E*)-**3h**, a NOE contact is evident between the vinylic proton at 7.81 ppm and the methyl protons at 3.75 ppm. No NOE contacts were observed between the vinylic protons or between the vinylic protons at 6.69 and the methyl protons at 3.75 ppm.

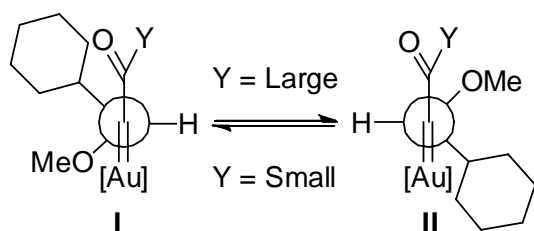
In the case of *enimide* (*E*)-**9b**, a NOE contact is evident between the vinylic proton at 6.43 ppm and the methyl protons at 3.67 ppm. No NOE contacts were observed between the vinylic proton and the proton at 1.82-3.67 ppm, or between the vinylic proton and the methylene protons at 1.81-1.59 ppm or 1.53-1.06 ppm.

### Control Reactions on the isomerization of **9b**

*Test n°1*: A solution of (*Z*)-**9b** (35 mg, 0.1 mmol, 1 eq) in  $\text{ClCH}_2\text{CH}_2\text{Cl}$  (0.5 mL) was added to a mixture of dichloro(2-pyridinecarboxylato)gold (2 mg, 0.005 mmol, 5 mol%) and pyridine-*N*-oxide (11 mg, 0.12 mmol, 1.2 eq). The reaction mixture was stirred at 70 °C for 20 h before being filtered through a pad of silica. The filtrate was then concentrated under reduced pressure. Analysis of the crude mixture showed **9b** (*E*:*Z* 21.9:1).

*Test n°2*: A mixture of dichloro(2-pyridinecarboxylato)gold (1 mg, 2.5  $\mu\text{mol}$ , 5 mol%) and pyridine-*N*-oxide (6 mg, 0.06 mmol, 1.2 eq) were added to a solution of **9b** (*E*:*Z* 1:5.4) (18 mg, 0.05 mmol, 1 eq) in  $\text{ClCH}_2\text{CH}_2\text{Cl}$  (0.3 mL). The reaction mixture was stirred at room temperature for 8 h before being filtered through a pad of silica. The filtrate was then concentrated under reduced pressure. Analysis of the crude mixture showed **9b** (*E*:*Z* 2.5:1).

*Test n°3*: Pyridine-*N*-oxide (6 mg, 0.06 mmol, 1.2 eq) was added to a solution of **9b** (*E*:*Z* 1:5.4) (18 mg, 0.05 mmol, 1 eq) in  $\text{ClCH}_2\text{CH}_2\text{Cl}$  (0.3 mL). The reaction mixture was stirred at 70 °C for 8 h before being filtered through a pad of silica. The filtrate was then concentrated under reduced pressure. Analysis of the crude mixture showed **9b** (*E*:*Z* 9.5:1).



These control reactions show that (*Z*)-**9b** is readily converted into the thermodynamic product (*E*)-**9b**. While we should not set-aside stereoelectronic rationalisation, in particular the role of solvent on preferred conformation, the

discrepancy in the results observed between **8a** and **3h** under the same reaction conditions (System A, i.e. for **3h** only the (*E*)-isomer is observed whereas for **8a** significant amounts of (*Z*)-isomer are observed), show that the benzyl appendage on the oxazolidinone unit in **8a** plays a leading role in determining the nature of the kinetic product. We can initially rationalise the impact of the benzyl appendage for the formation of (*Z*)-**9b** as the major isomer on purely steric grounds if we consider the reactive conformations for 1,2-insertion (**I** and **II**).<sup>12</sup> Under System B, which is seen to favour the potential isolation of kinetic products [as a result of slower isomerisation to the thermodynamic products than observed with System A]: if Y is large (e.g. 4-benzyloxazolidin-2-one of **8b**) conformer **II** is preferred to minimise unfavourable steric interactions between Y and the  $\beta$ -substituents, thus affording (*Z*)-**9b** as the kinetic product. Further studies to identify the control factors for *E/Z* selectivity will be pursued in due course.

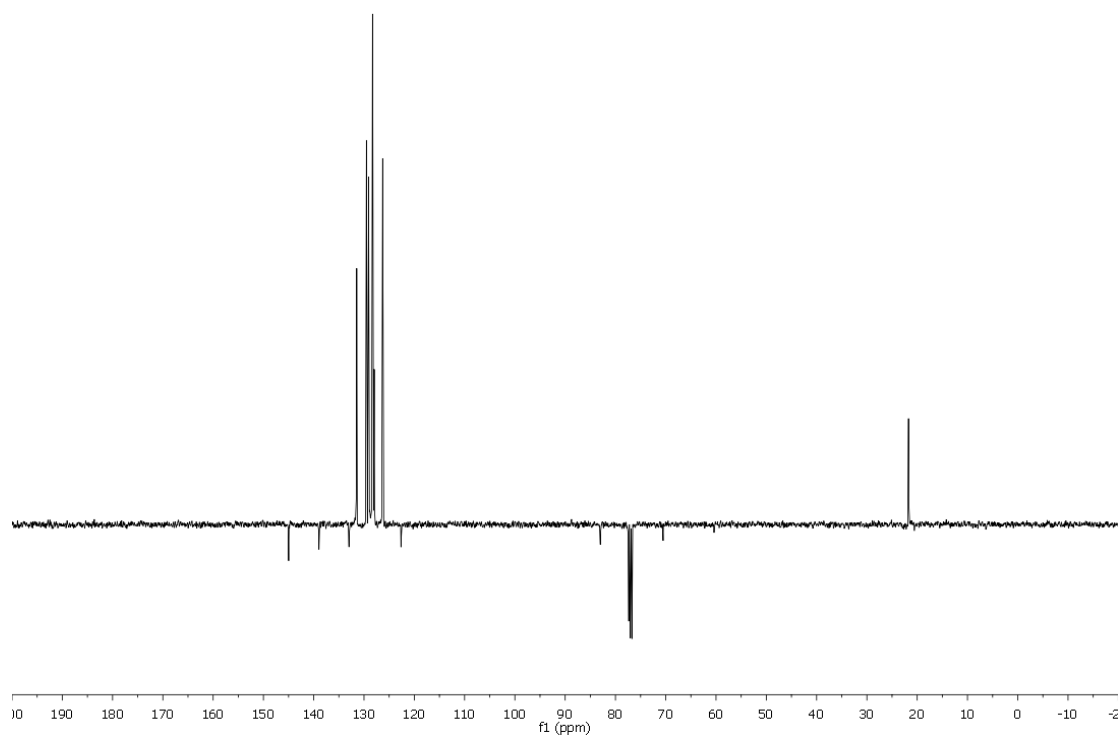
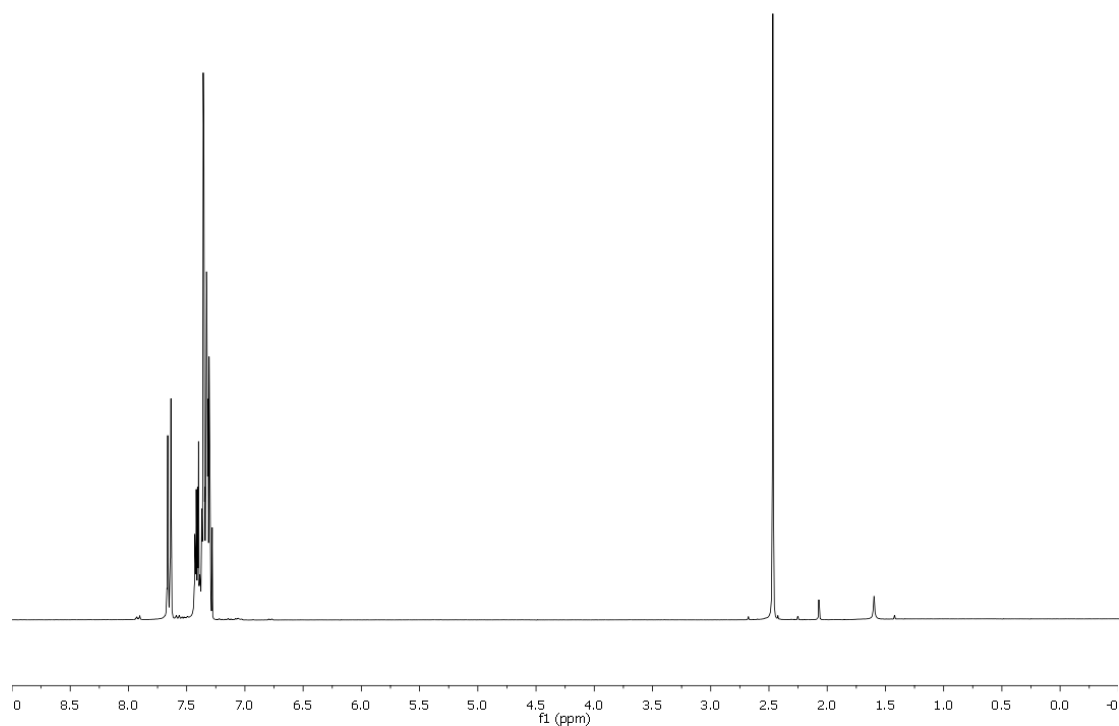
We thank the University of Birmingham for financial support and Johnson Matthey plc for a generous loan of metal salts. This research was part supported through Birmingham Science City: Innovative Uses for Advanced Materials in the Modern World (West Midlands Centre for Advanced Materials Project 2), with support from Advantage West Midlands (AWM) and part funded by the European Regional Development Fund (ERDF).

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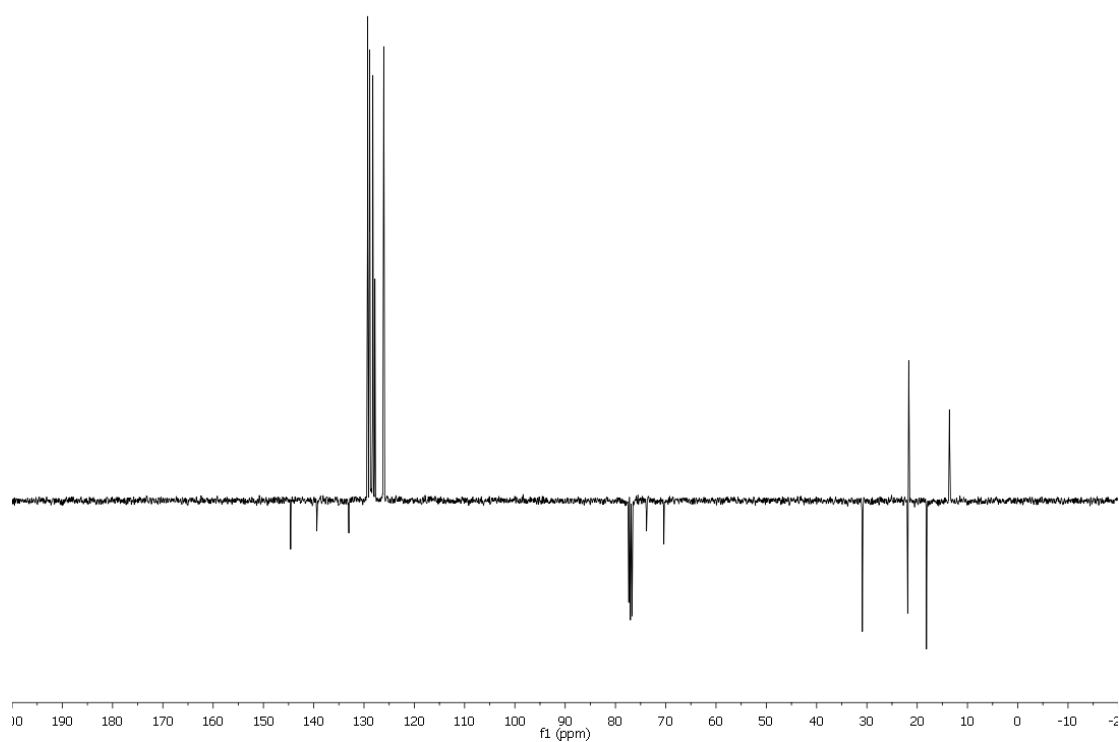
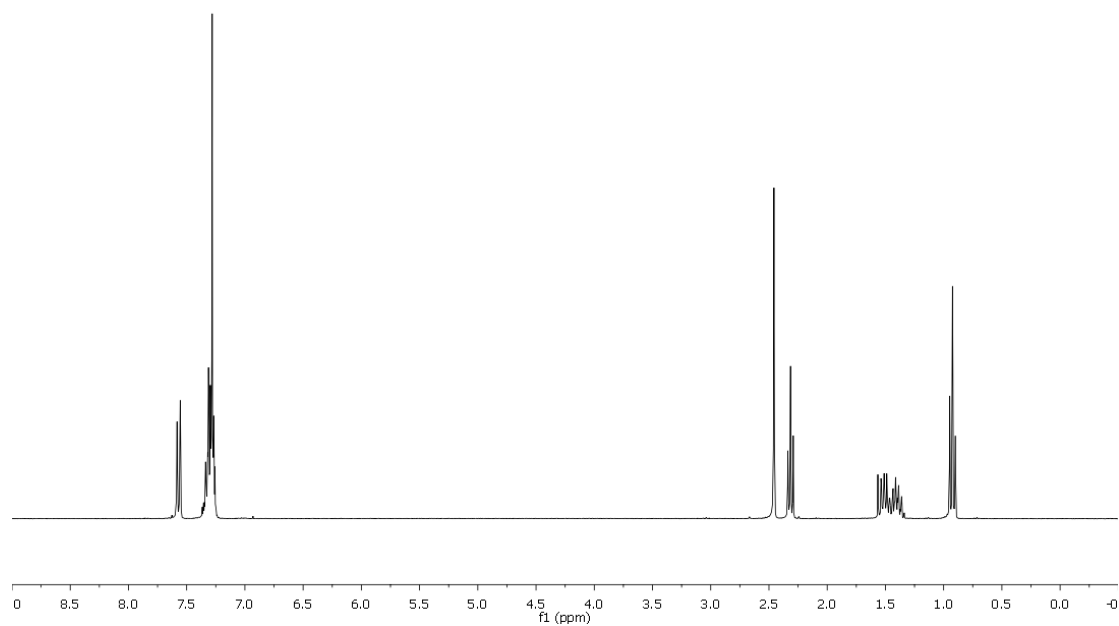
<sup>12</sup> This applies to either a concerted migration process or a proton-elimination/protodeauration pathway, as double-bond character is installed.

## $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of Reaction Substrates

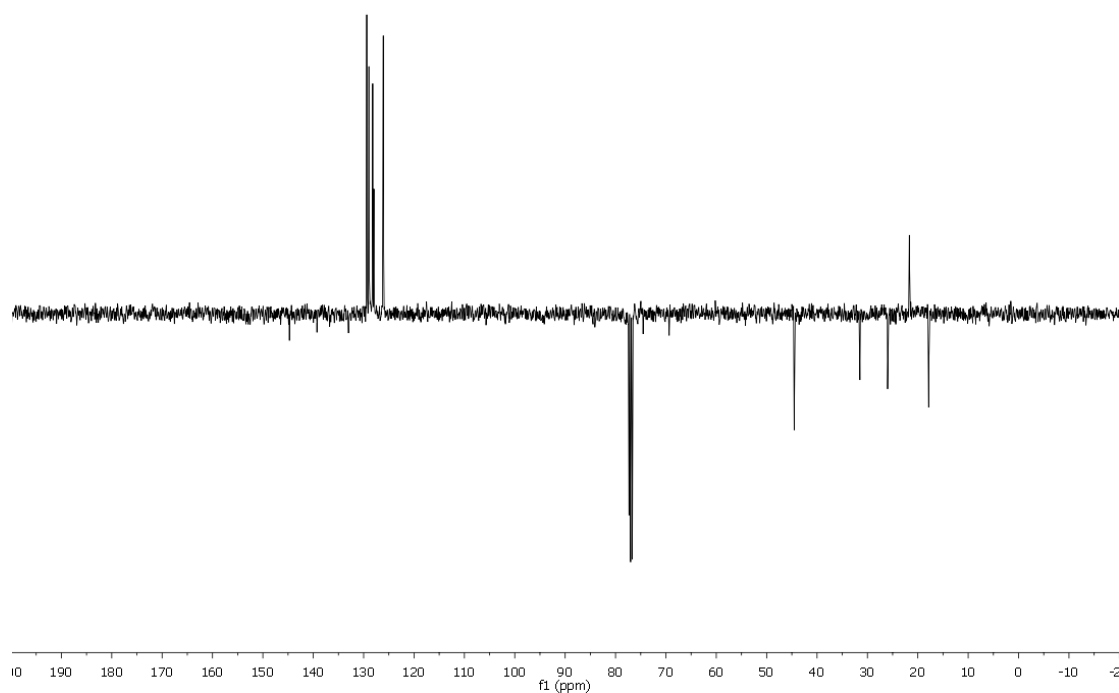
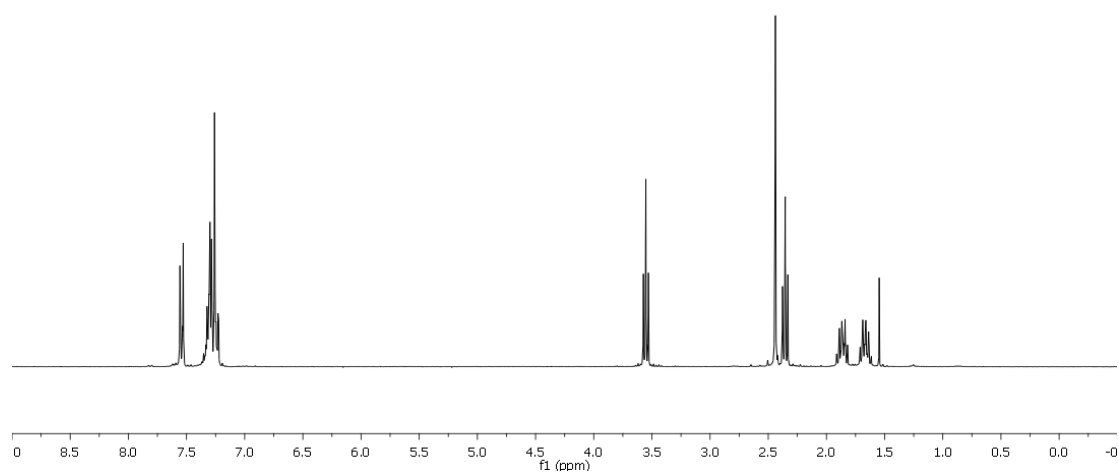
### Compound 1a



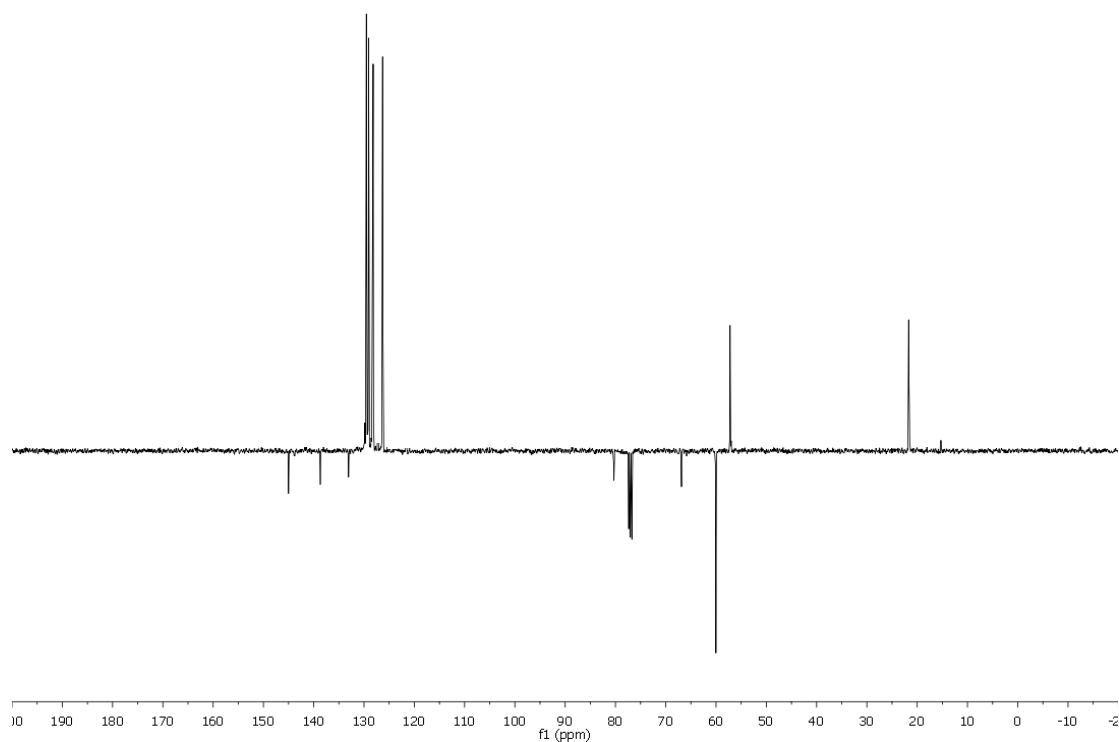
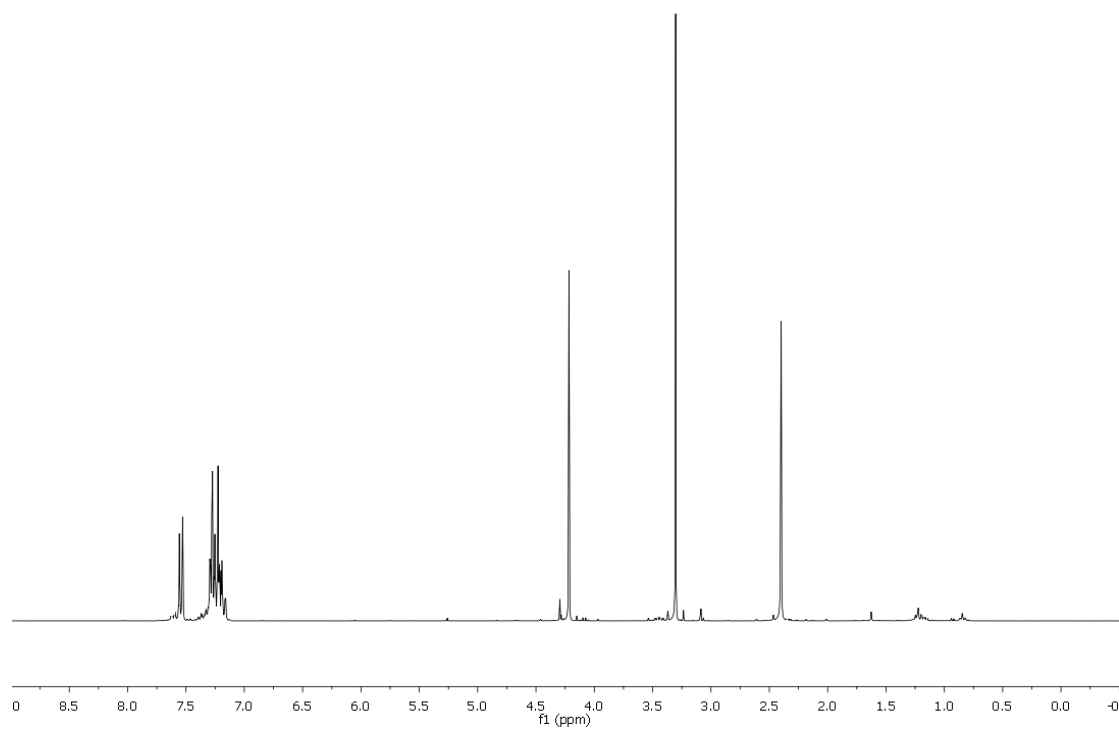
**Compound 1b**



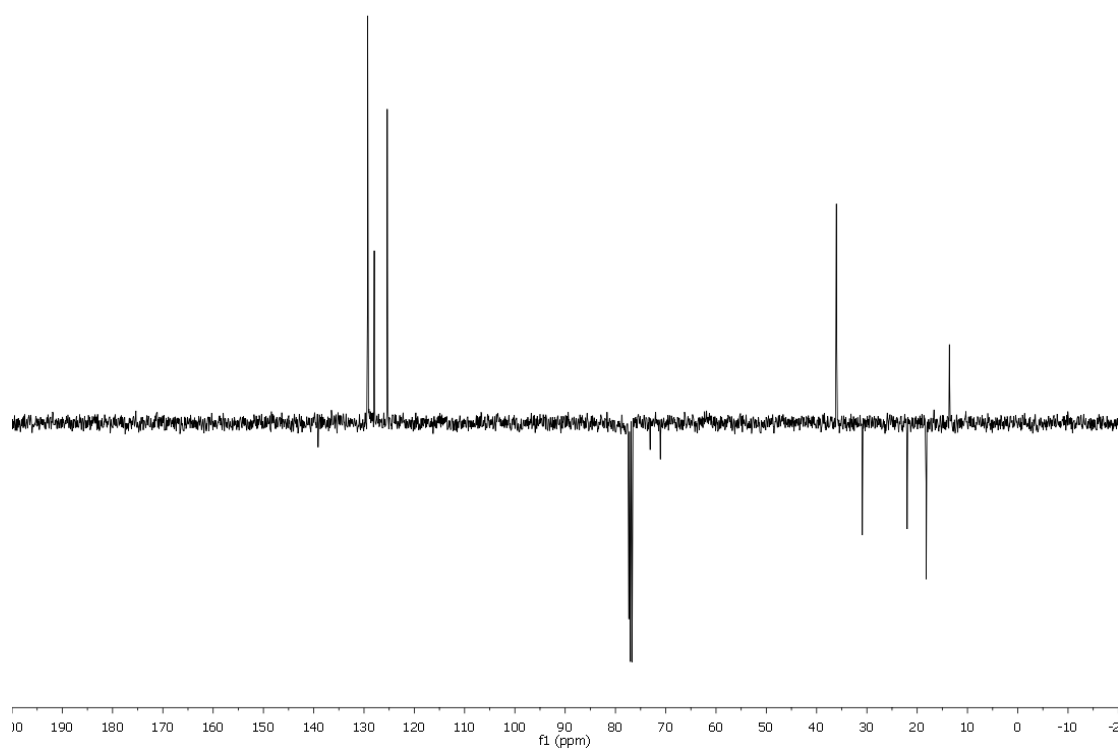
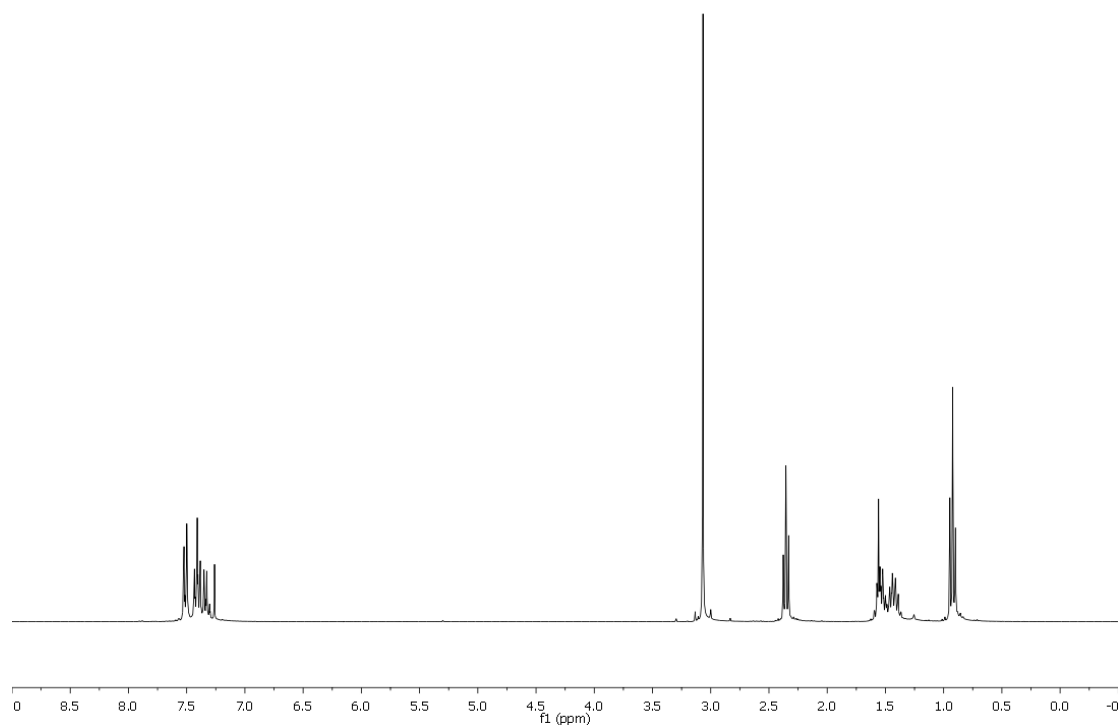
**Compound 1c**



**Compound 1d**

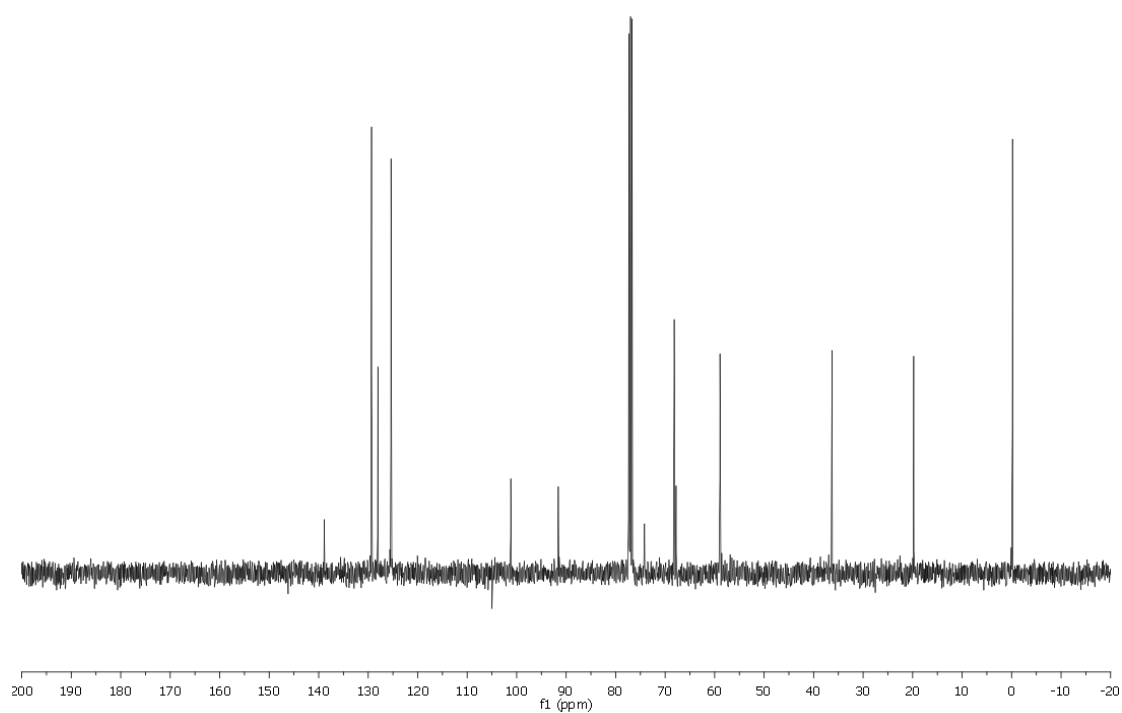
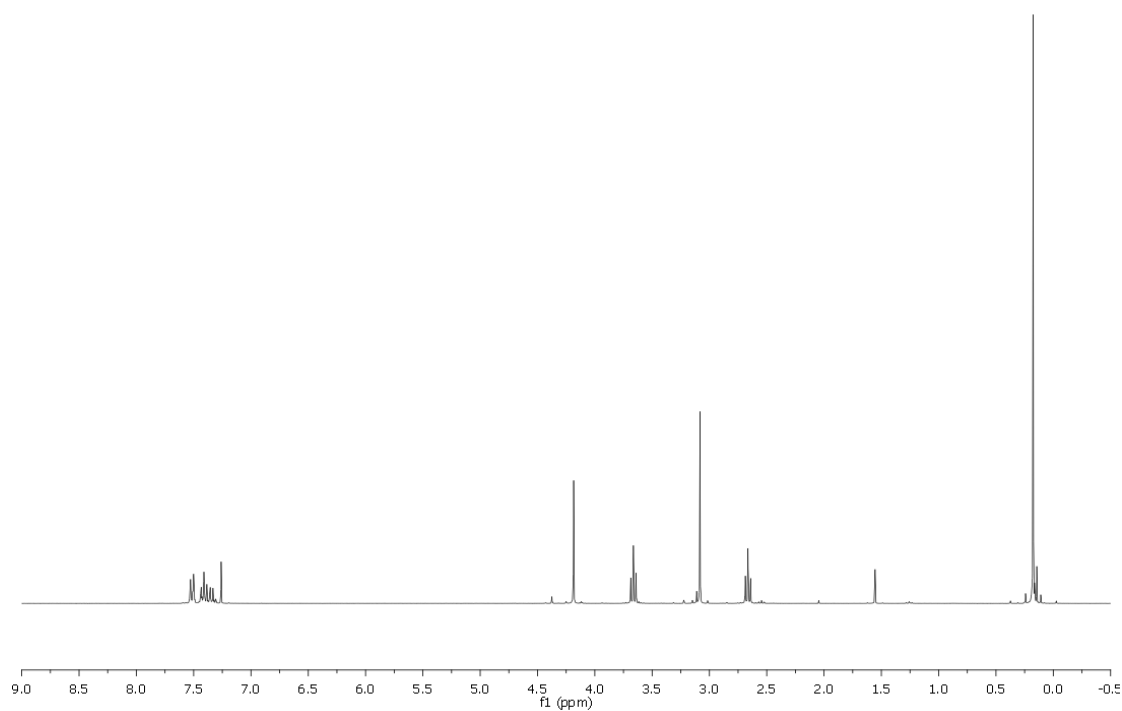


**Compound 1e**

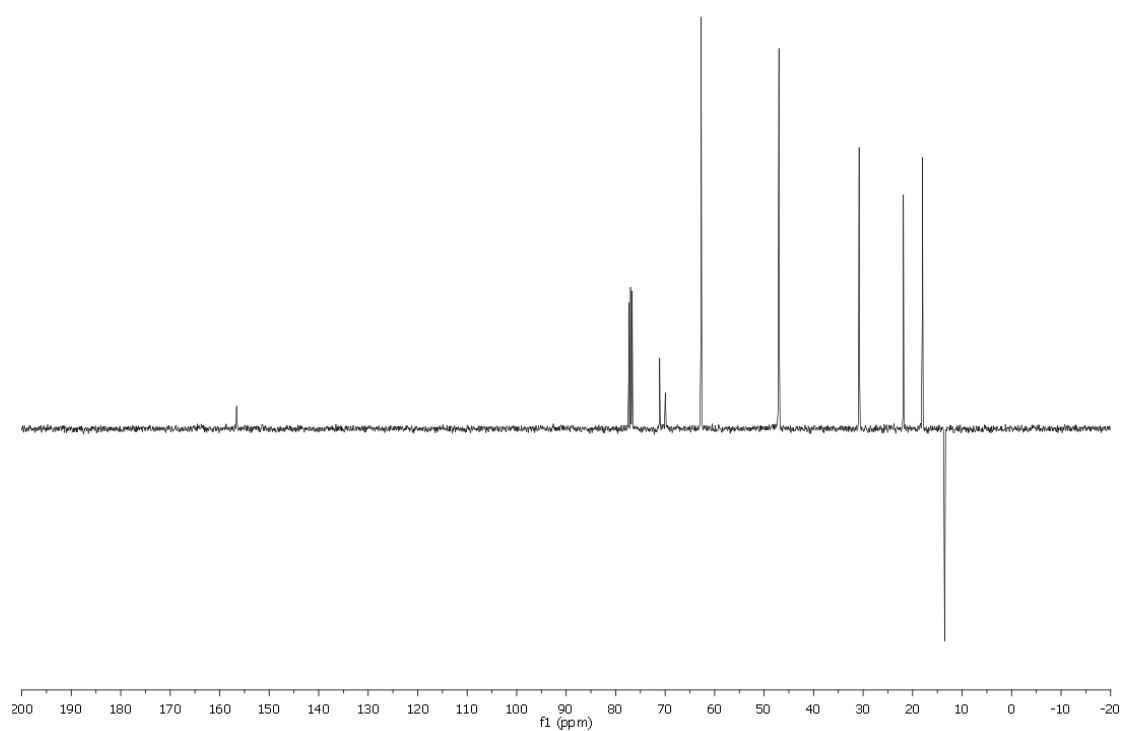
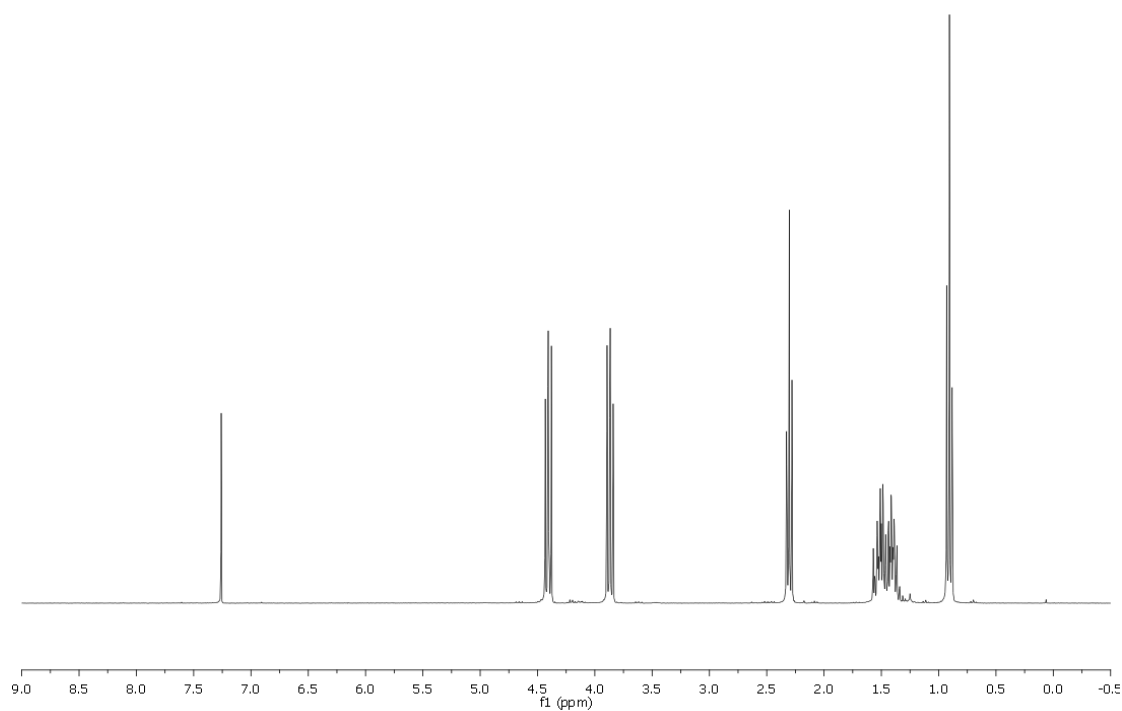




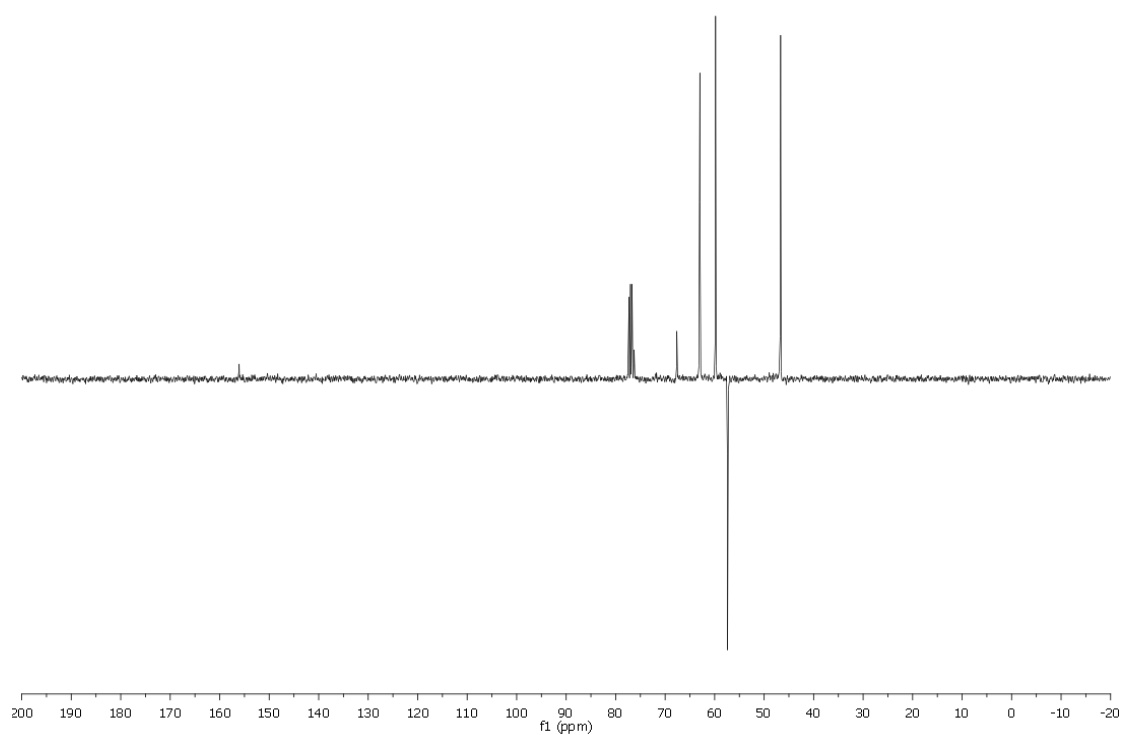
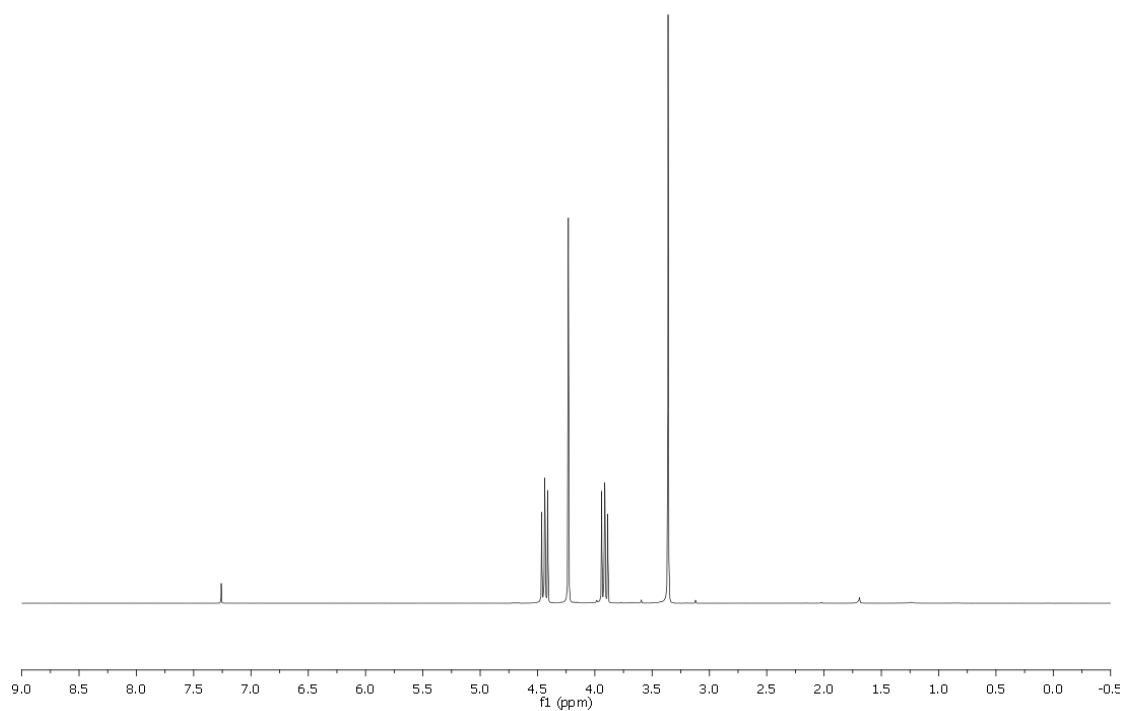
**Compound 1f**



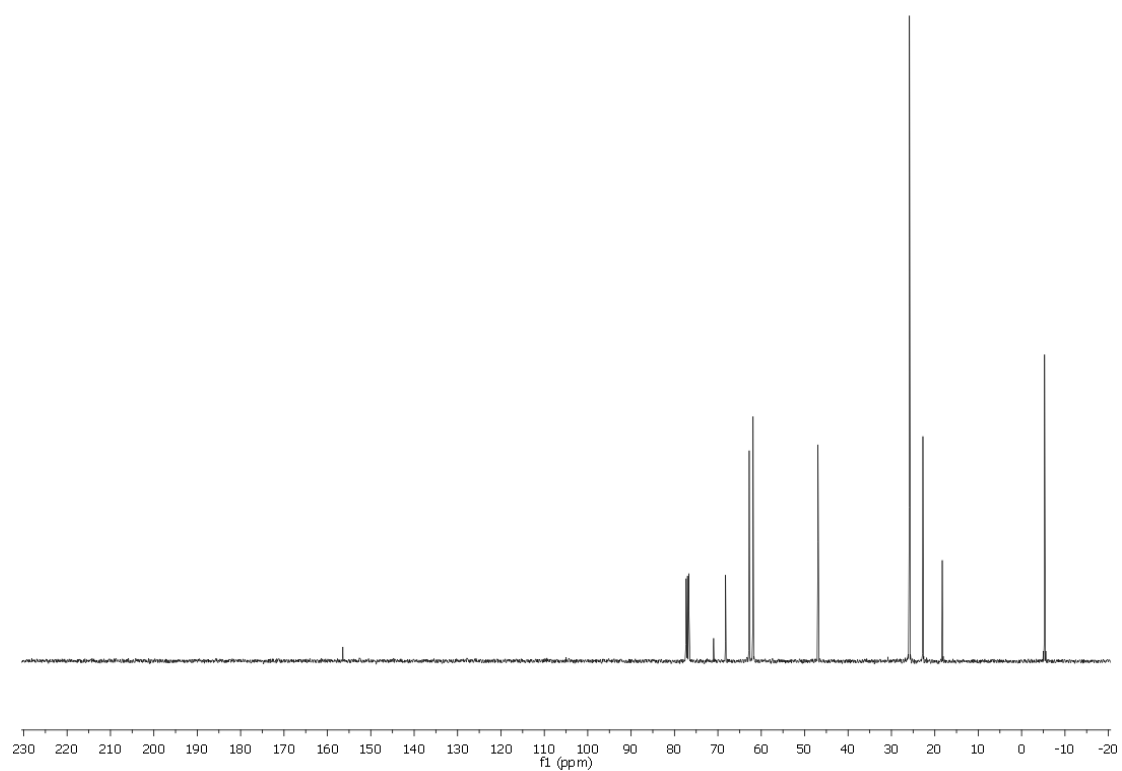
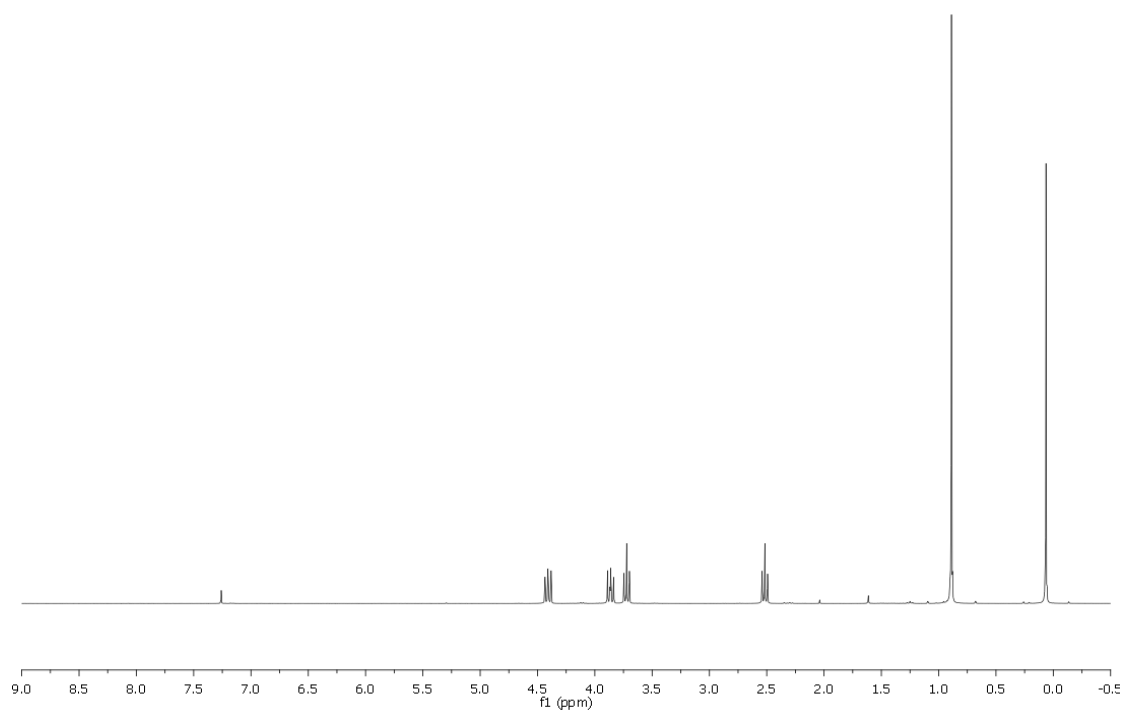
**Compound 1g**



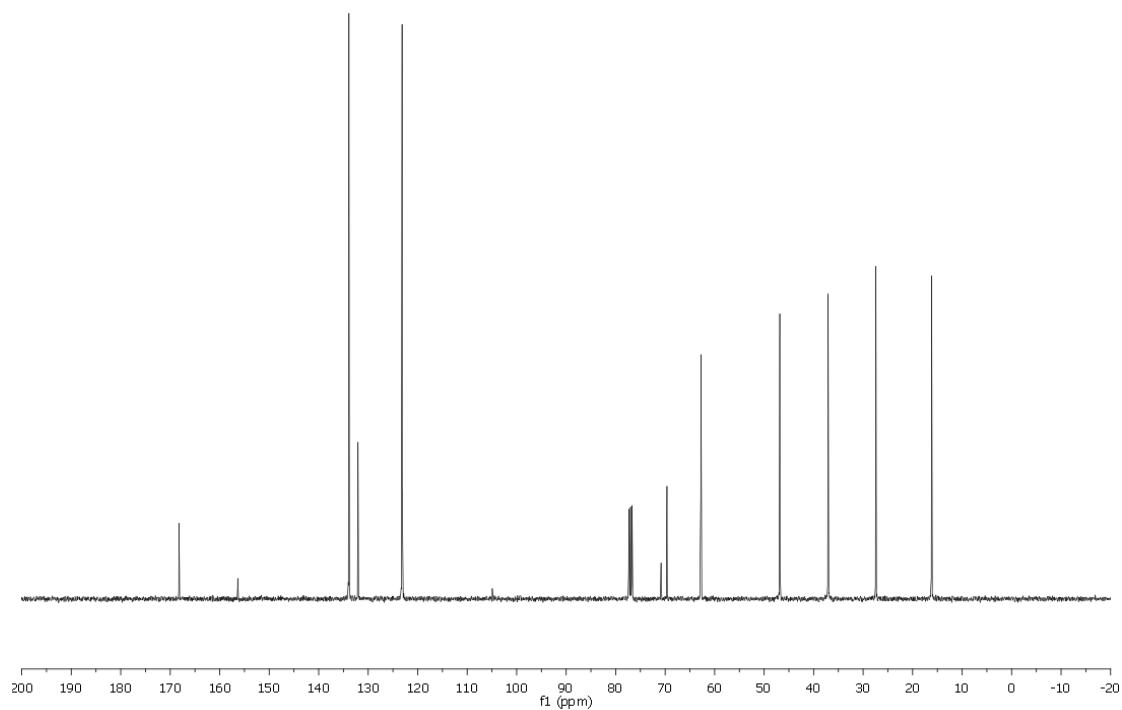
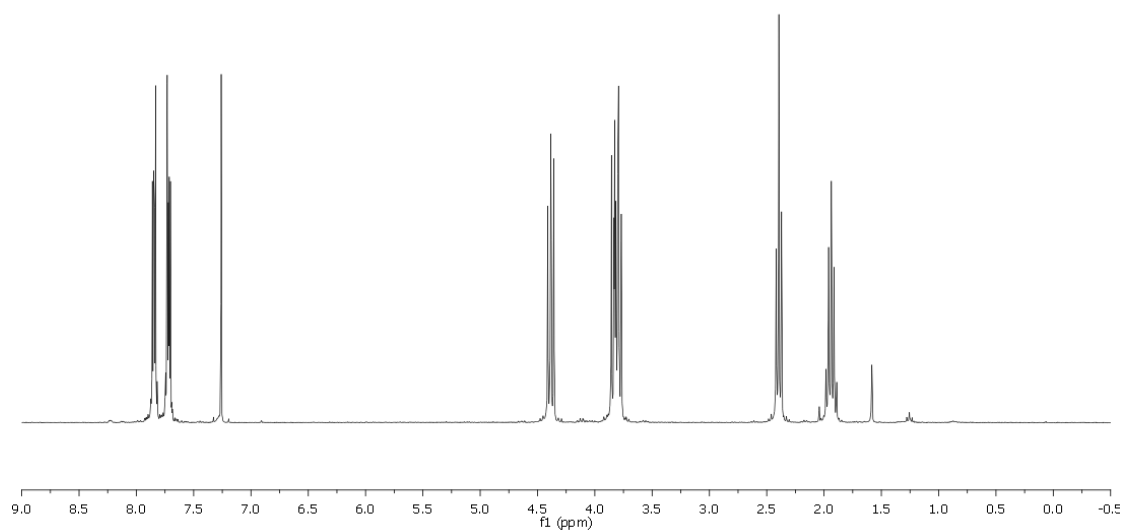
**Compound 1h**



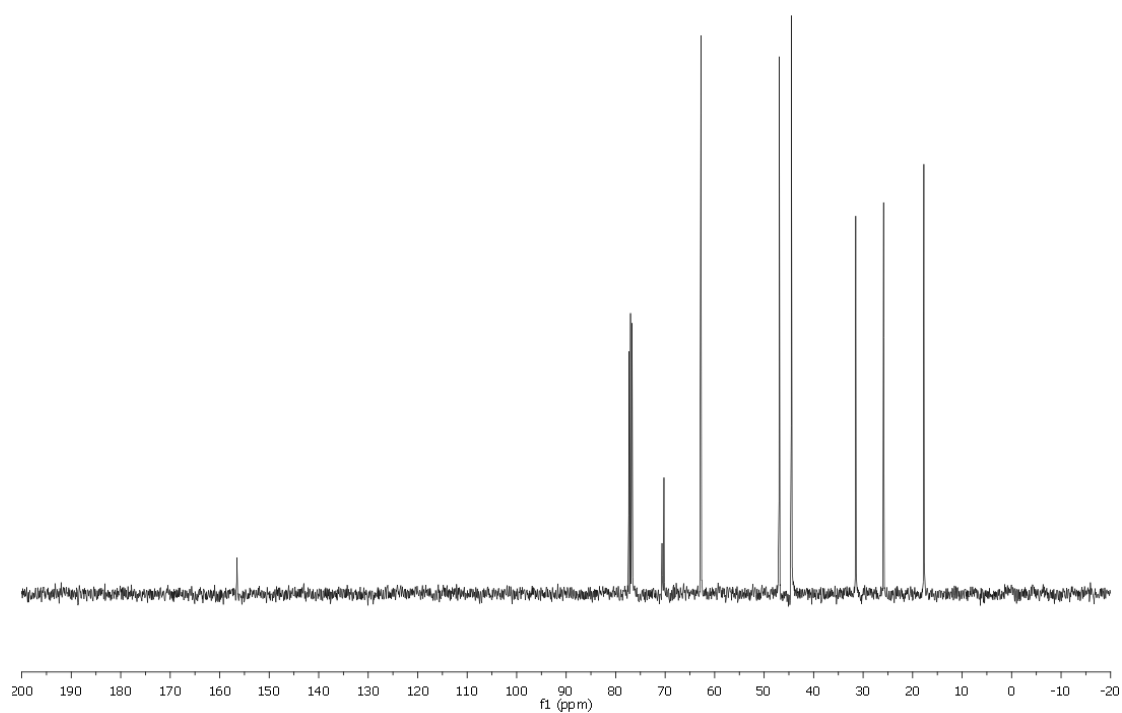
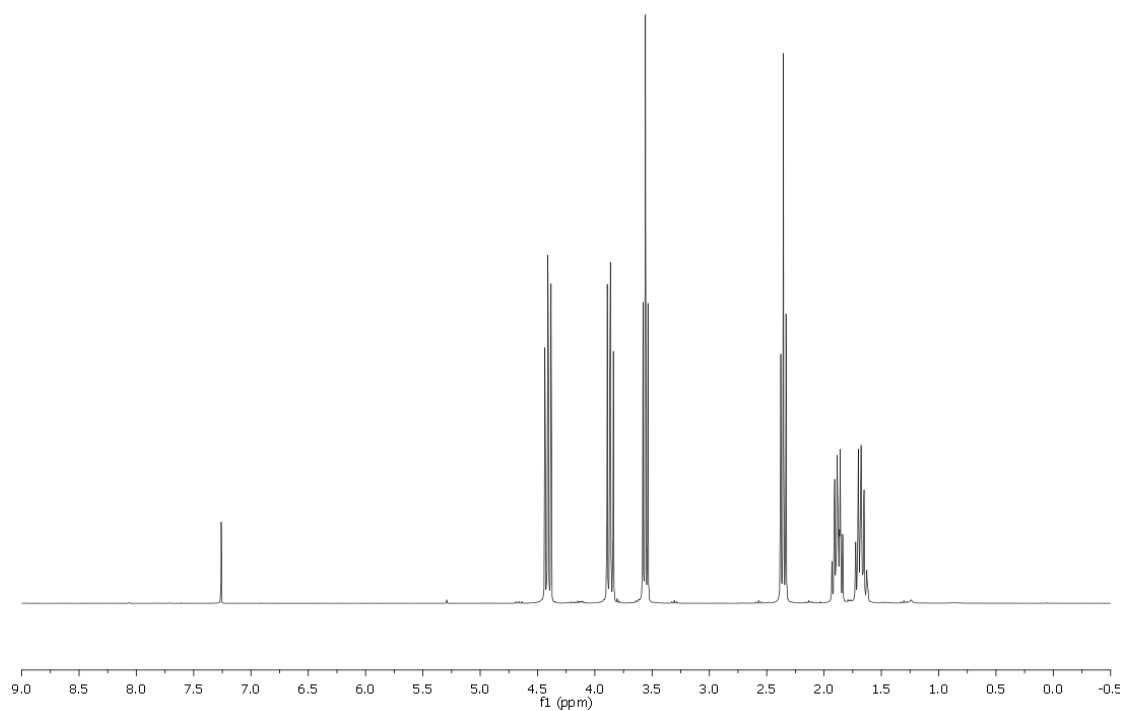
**Compound 1i**



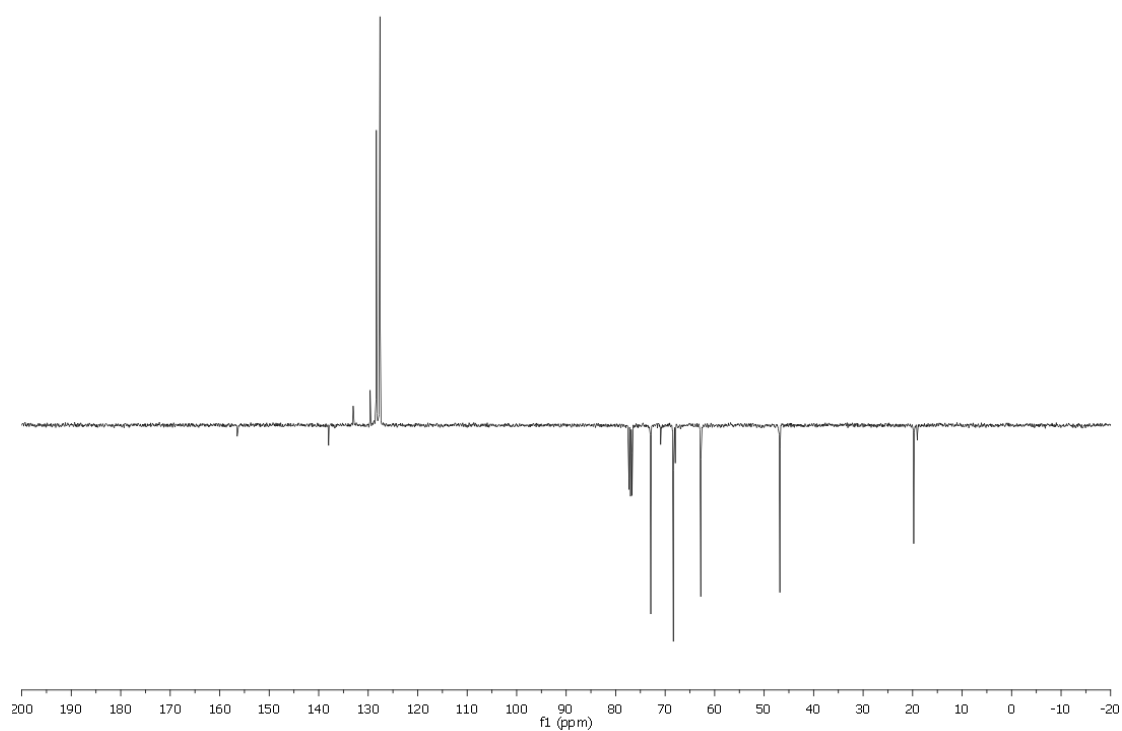
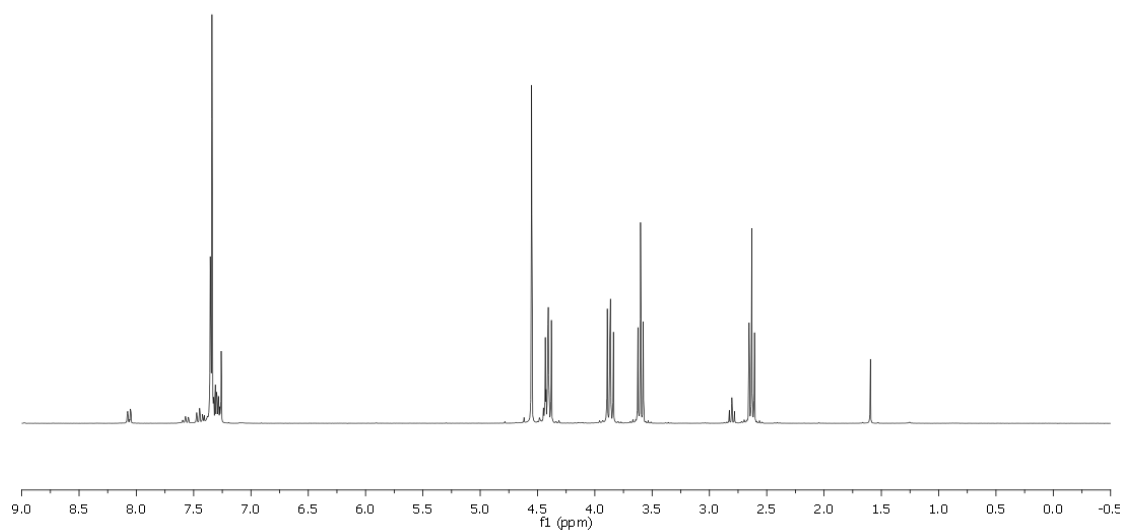
**Compound 1j**



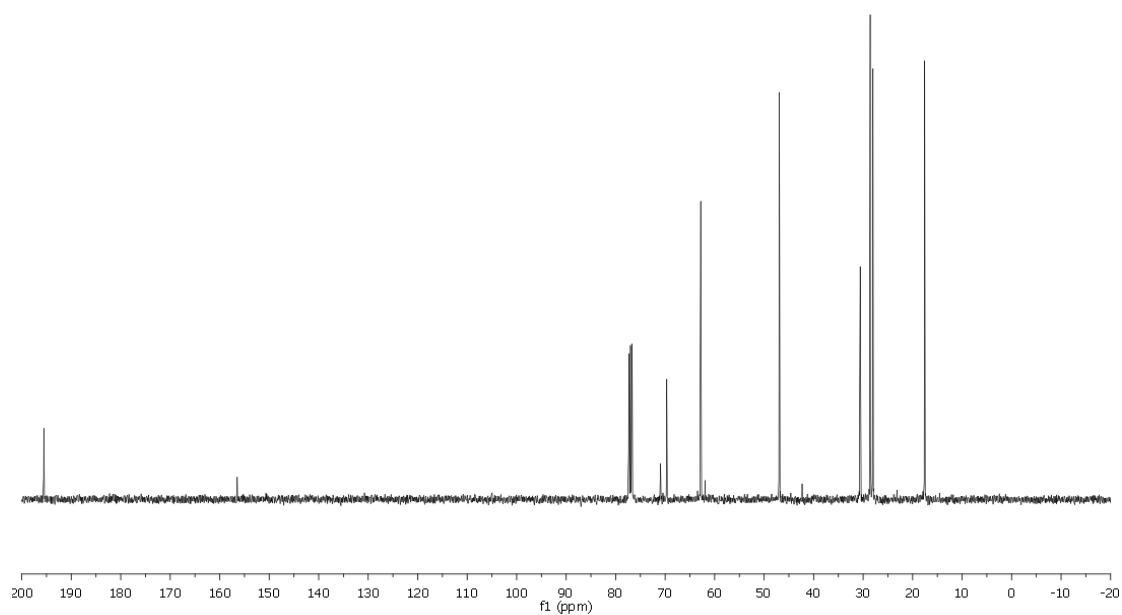
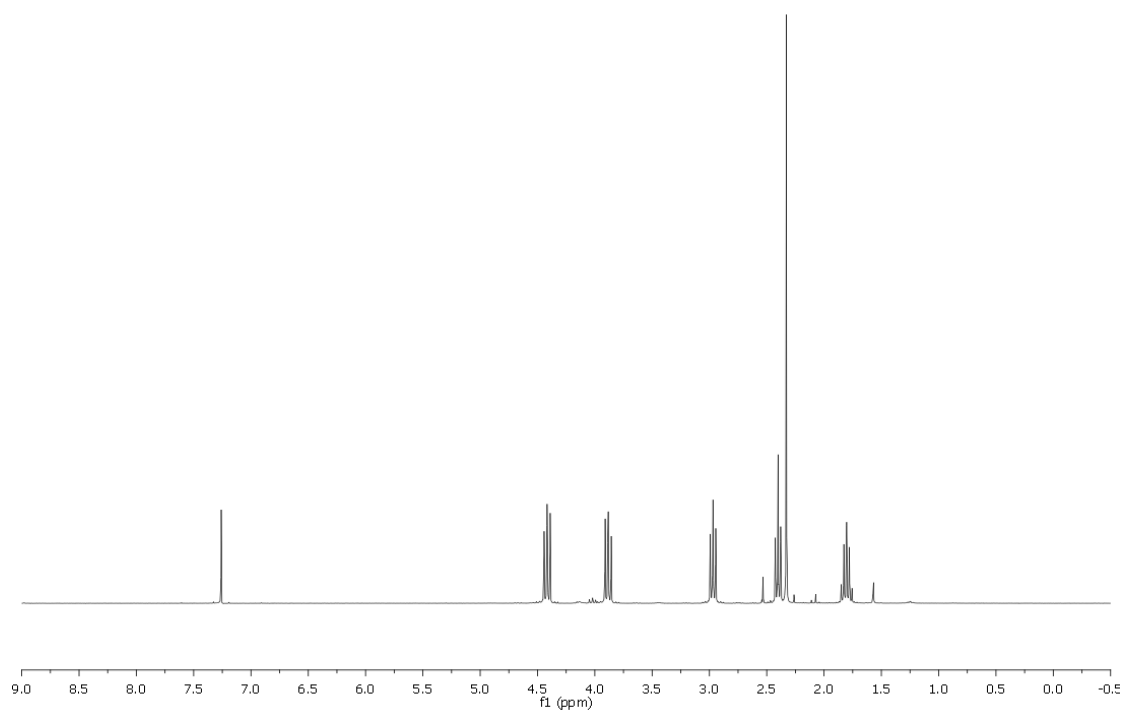
**Compound 1k**



**Compound 1l**

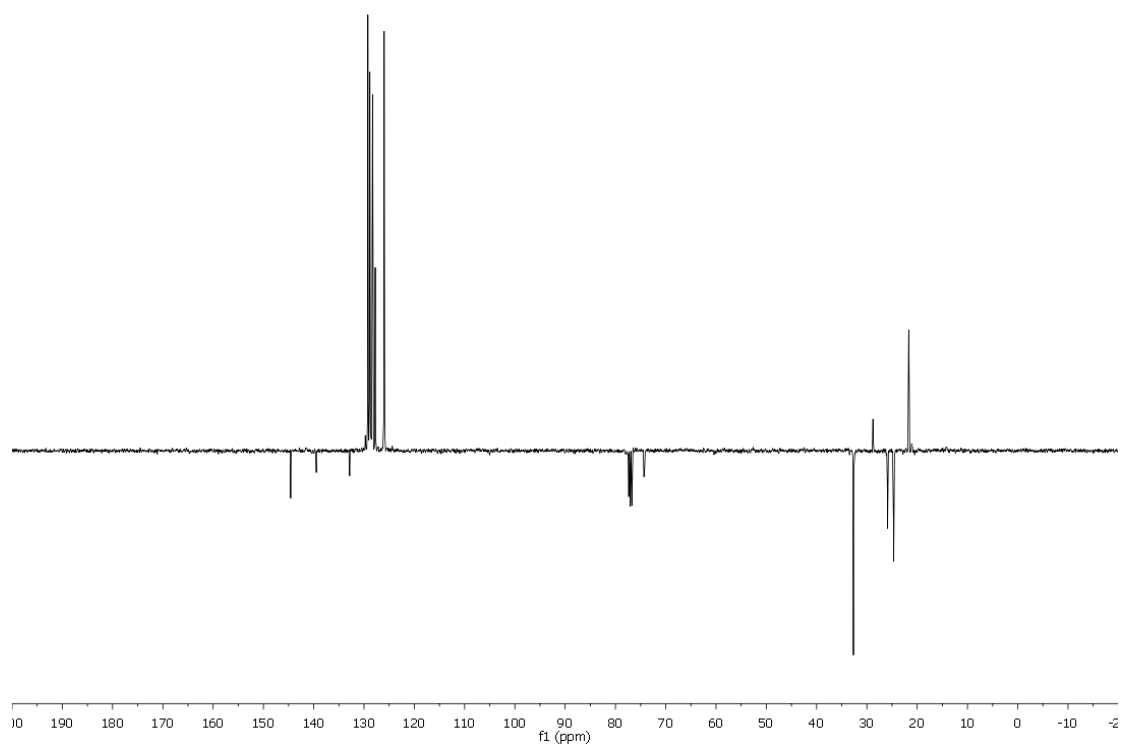
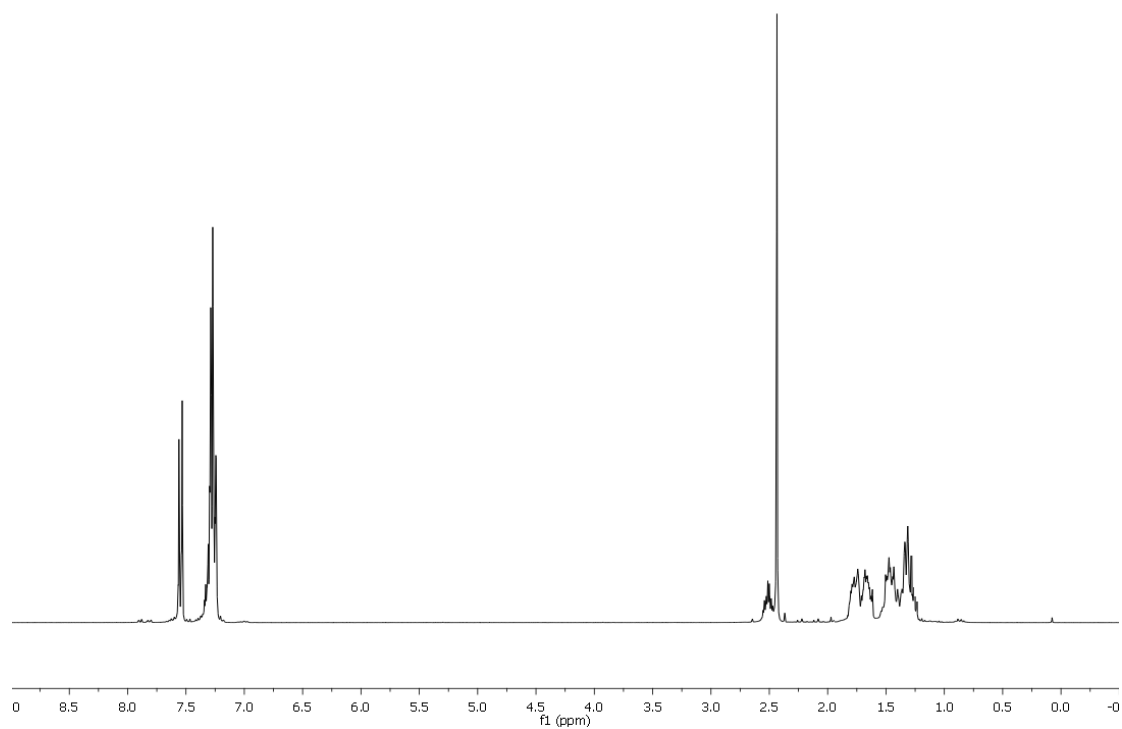


**Compound 1m**

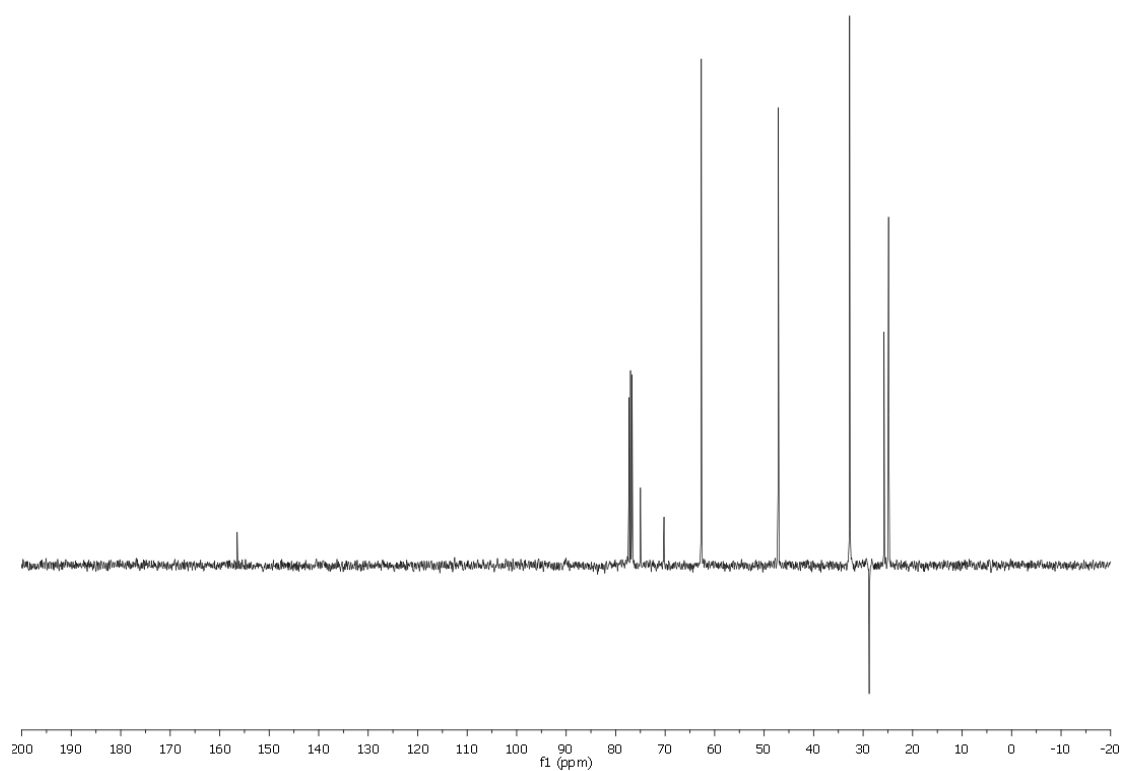
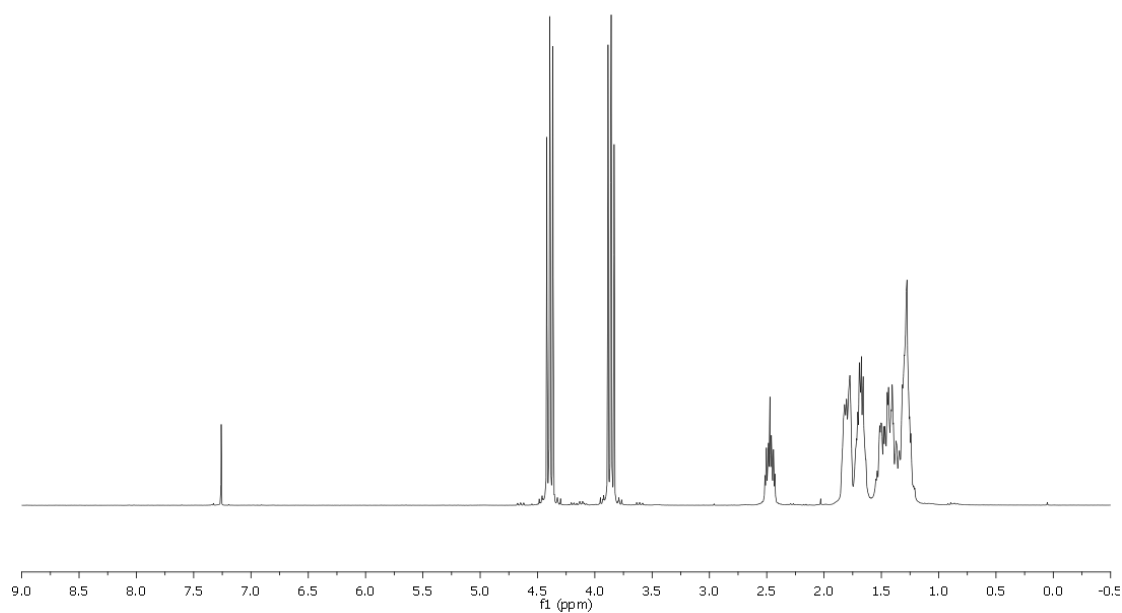




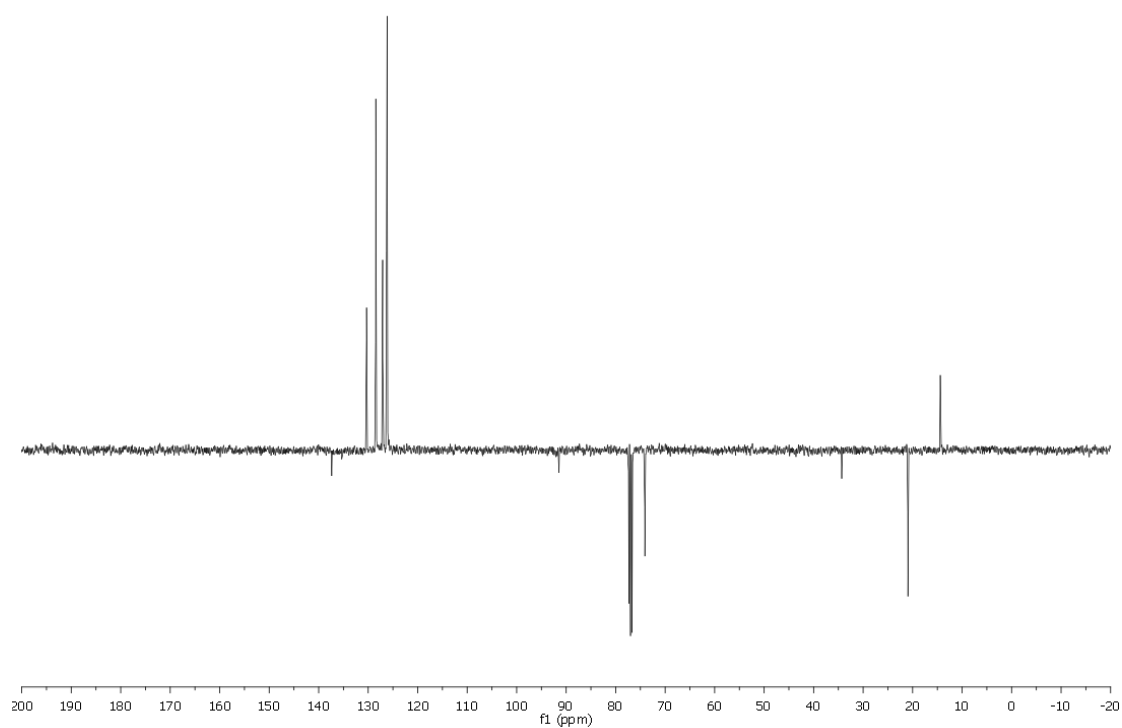
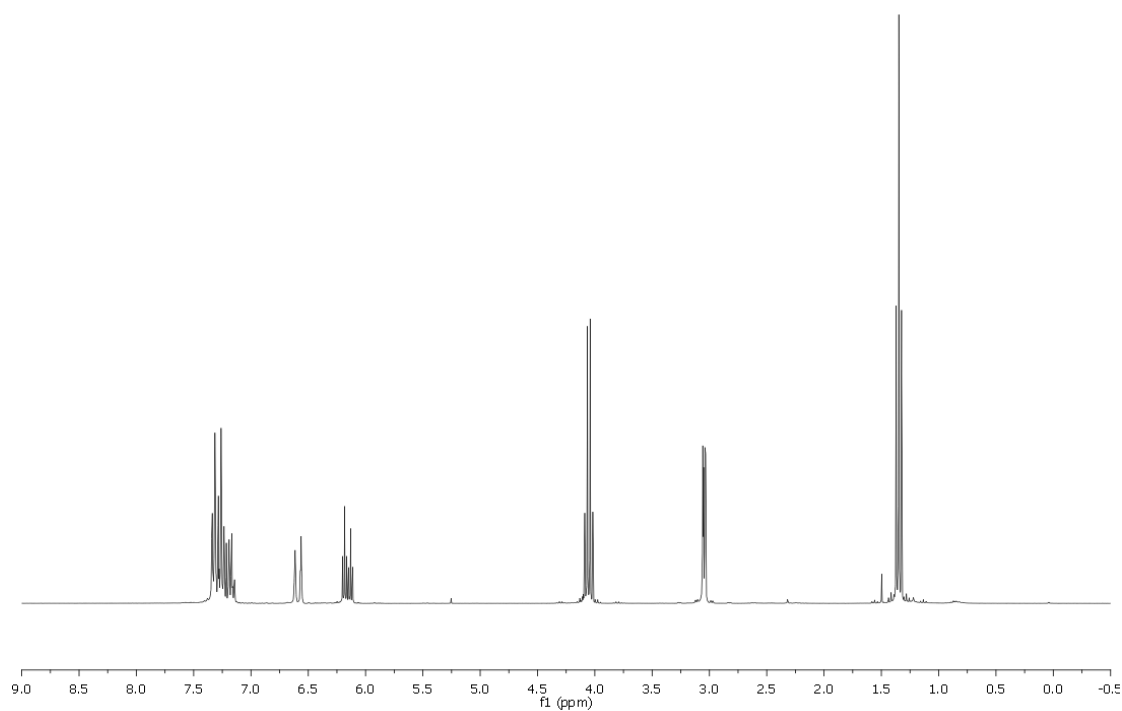
**Compound 4a**



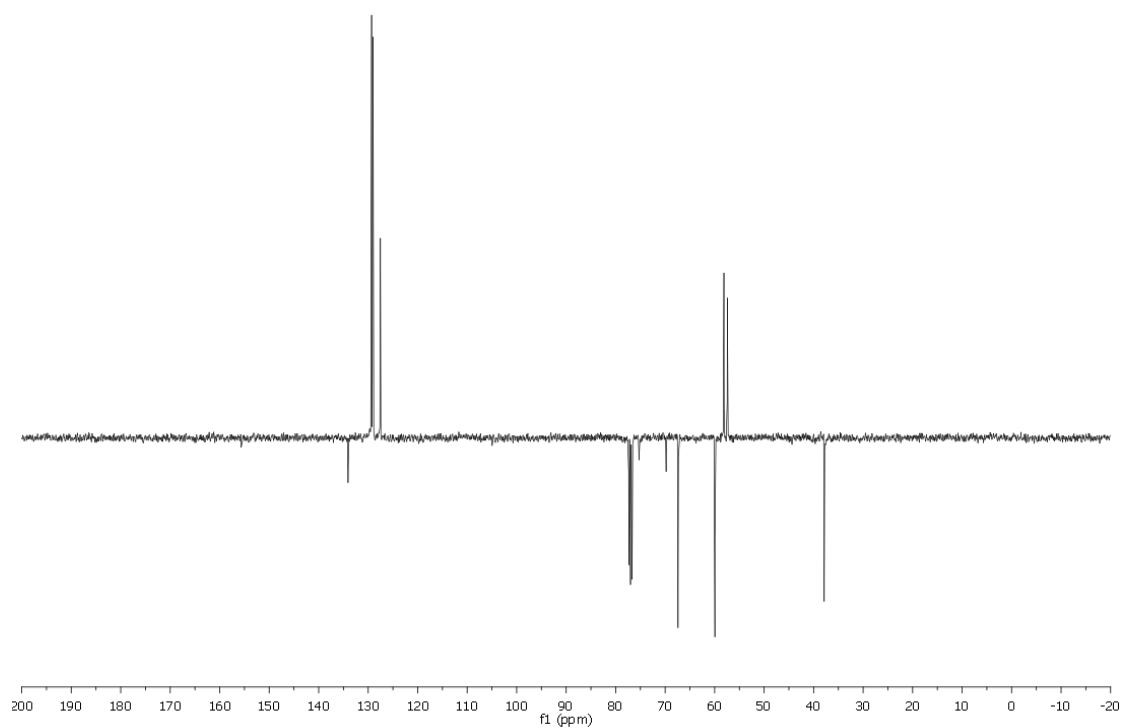
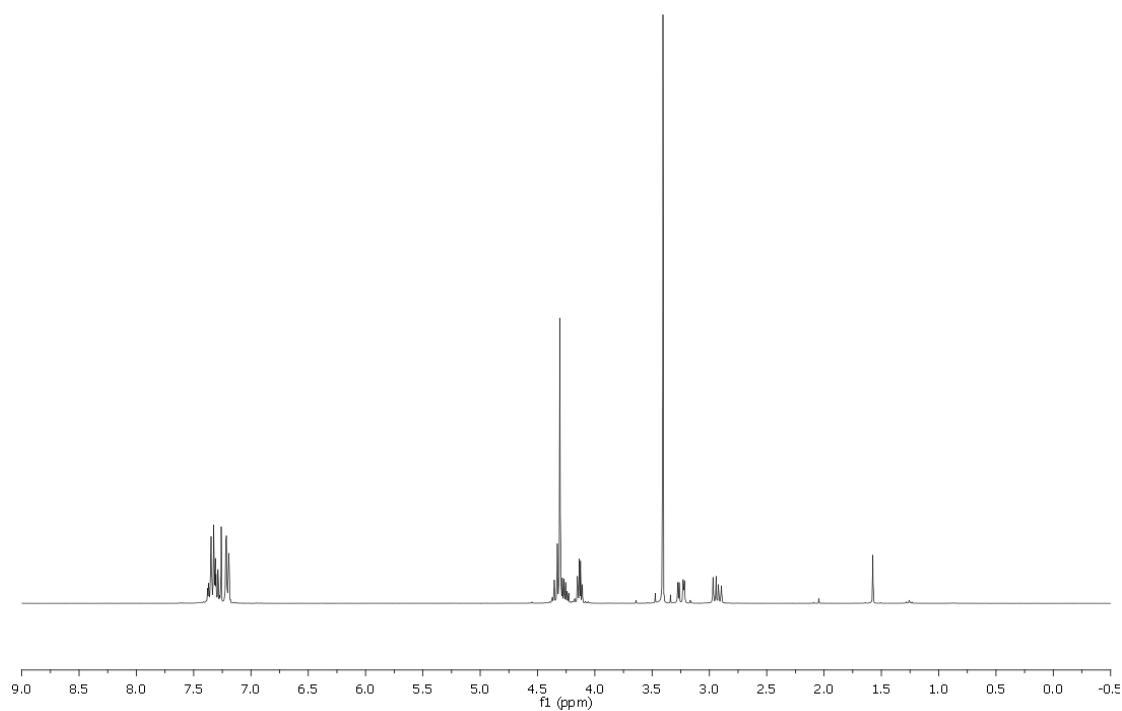
**Compound 4b**



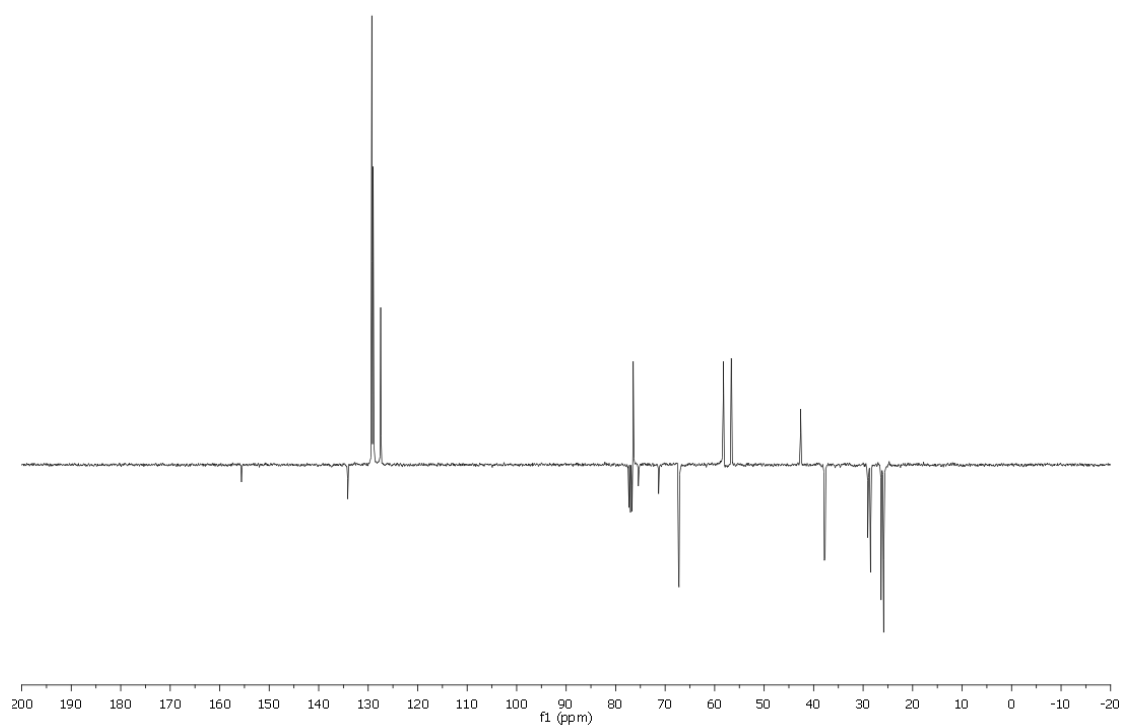
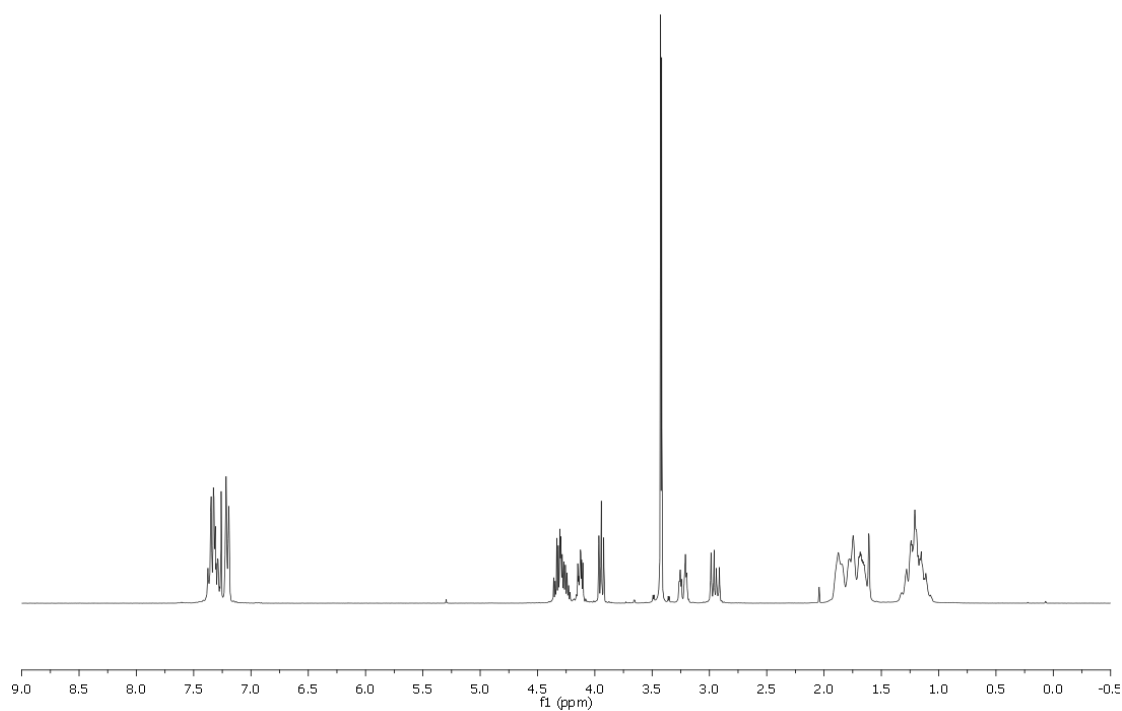
**Compound 6**



**Compound 8a**

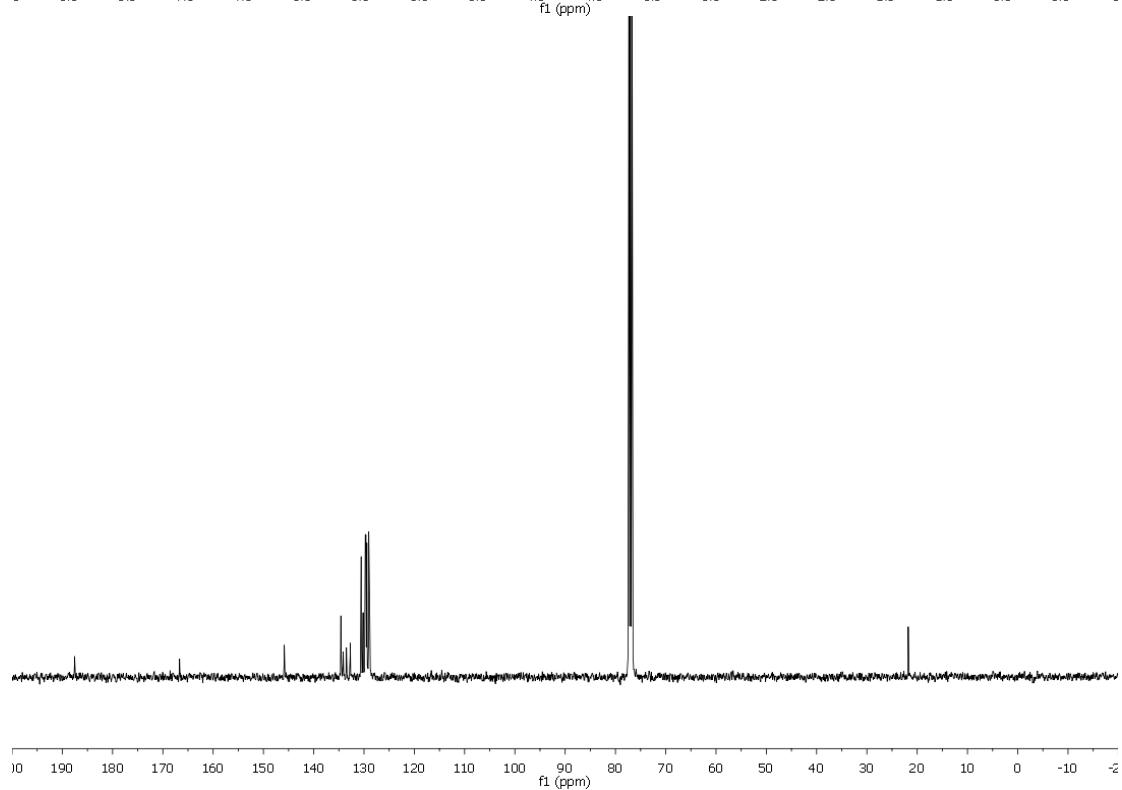
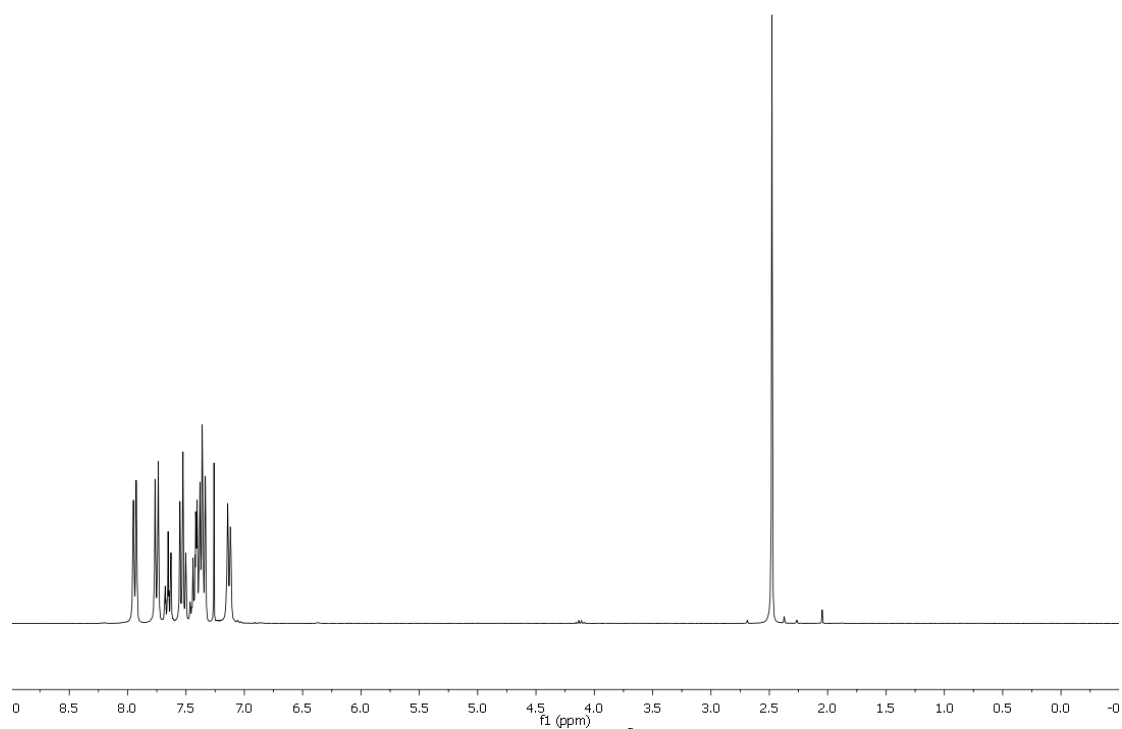


**Compound 8b**

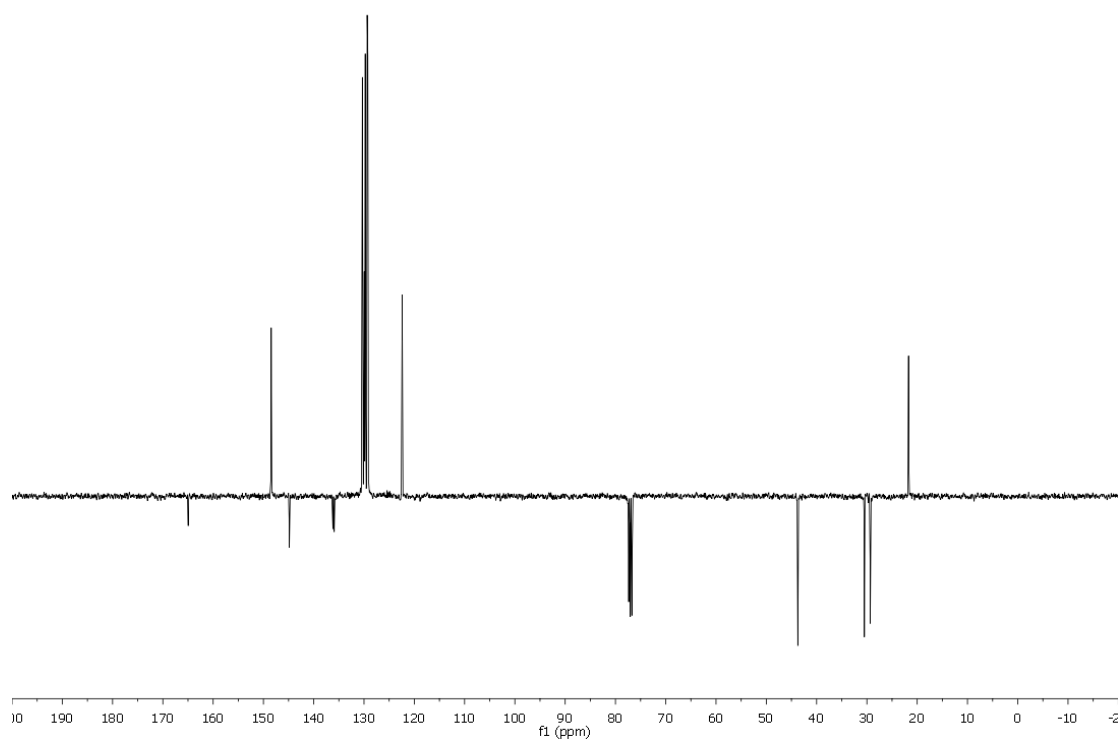
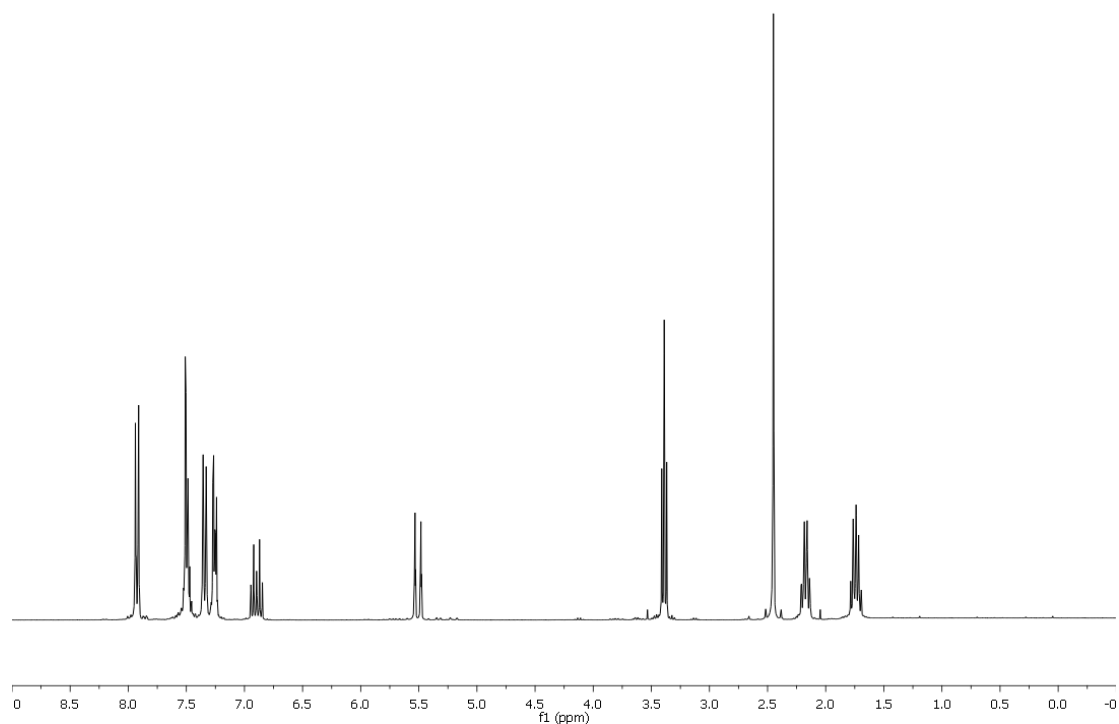


## $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of Oxidation Products

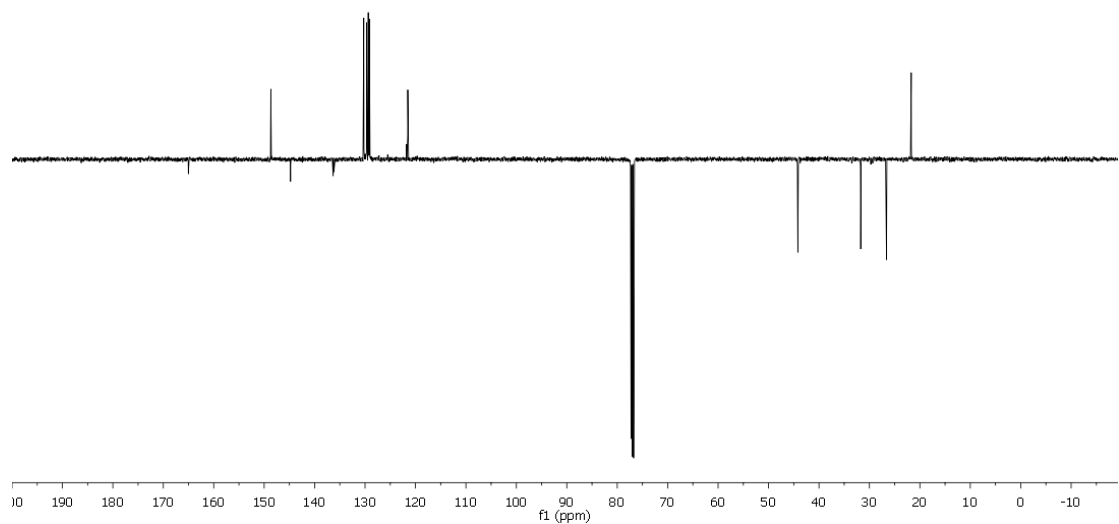
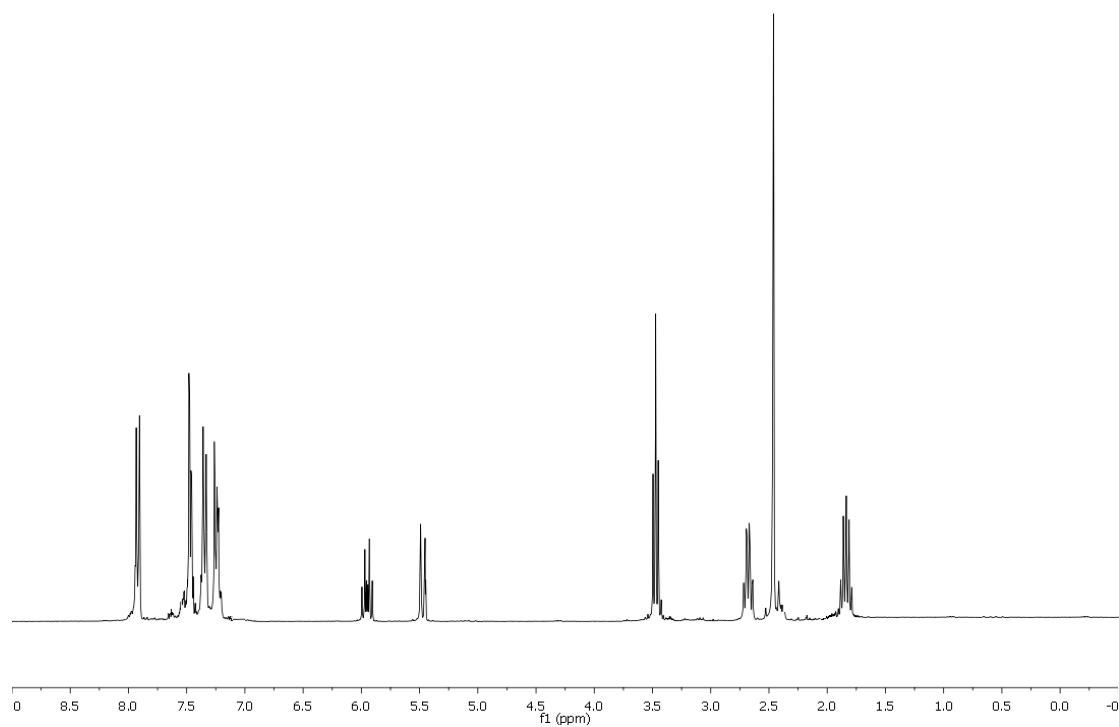
### Compound 2a



**Compound 3c (E)**

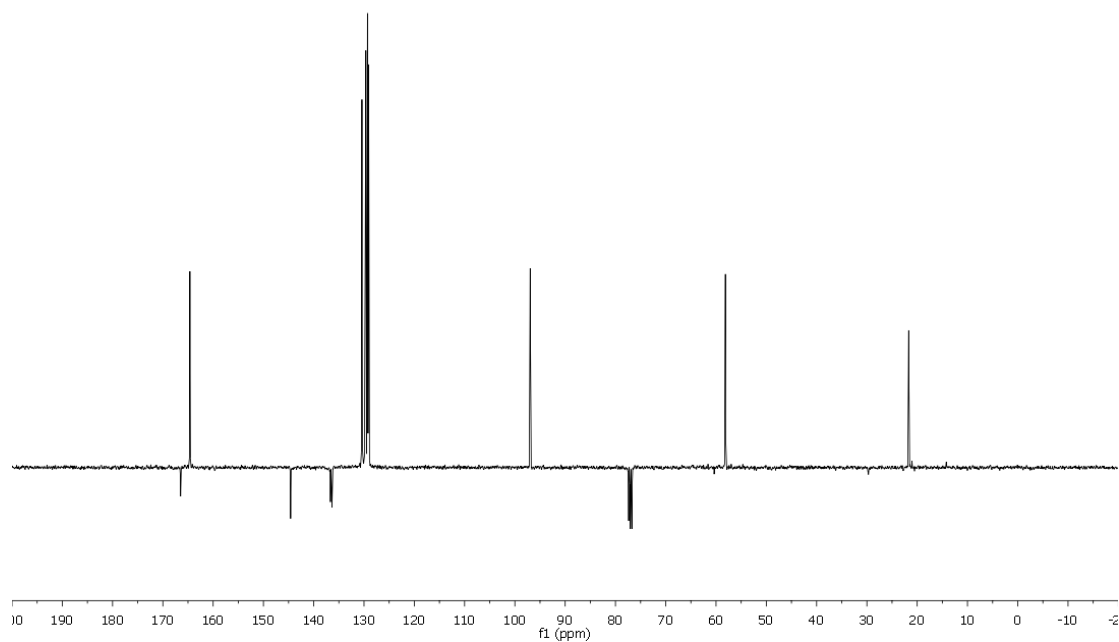
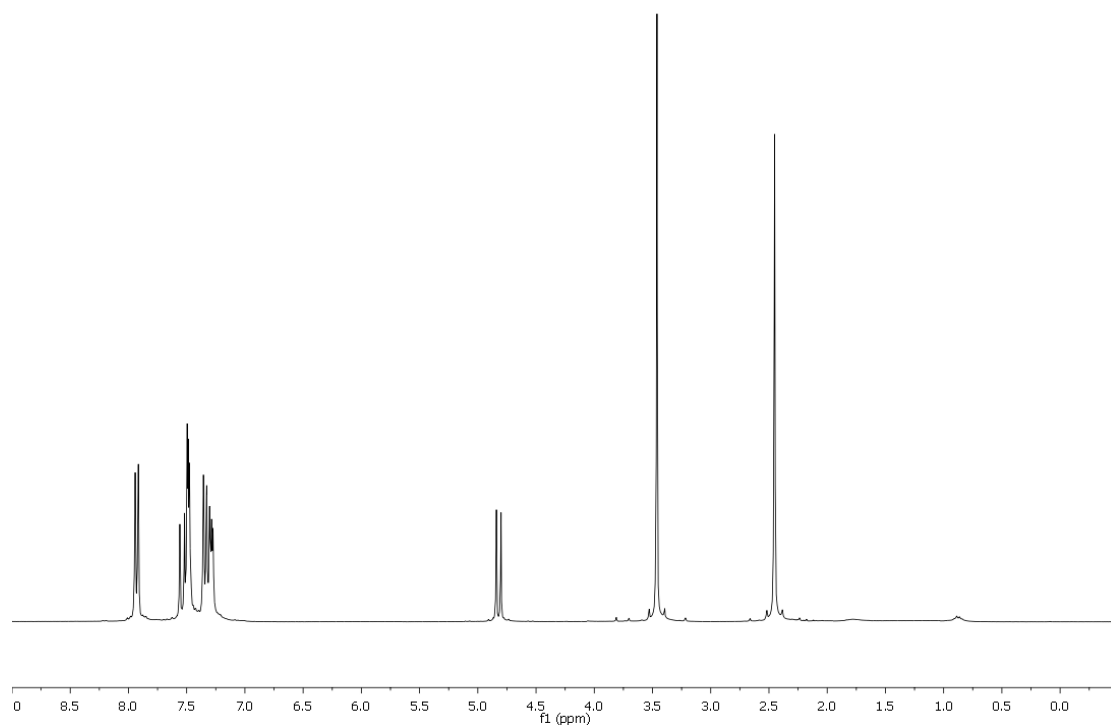


**Compound 3c (Z)**

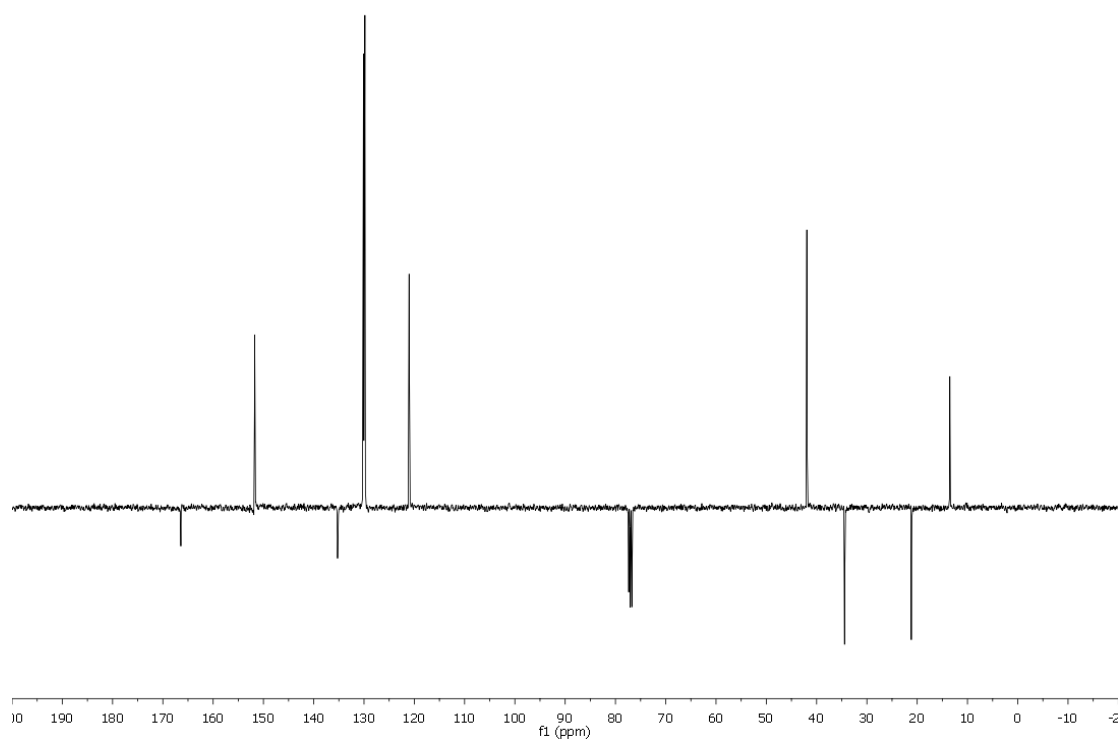
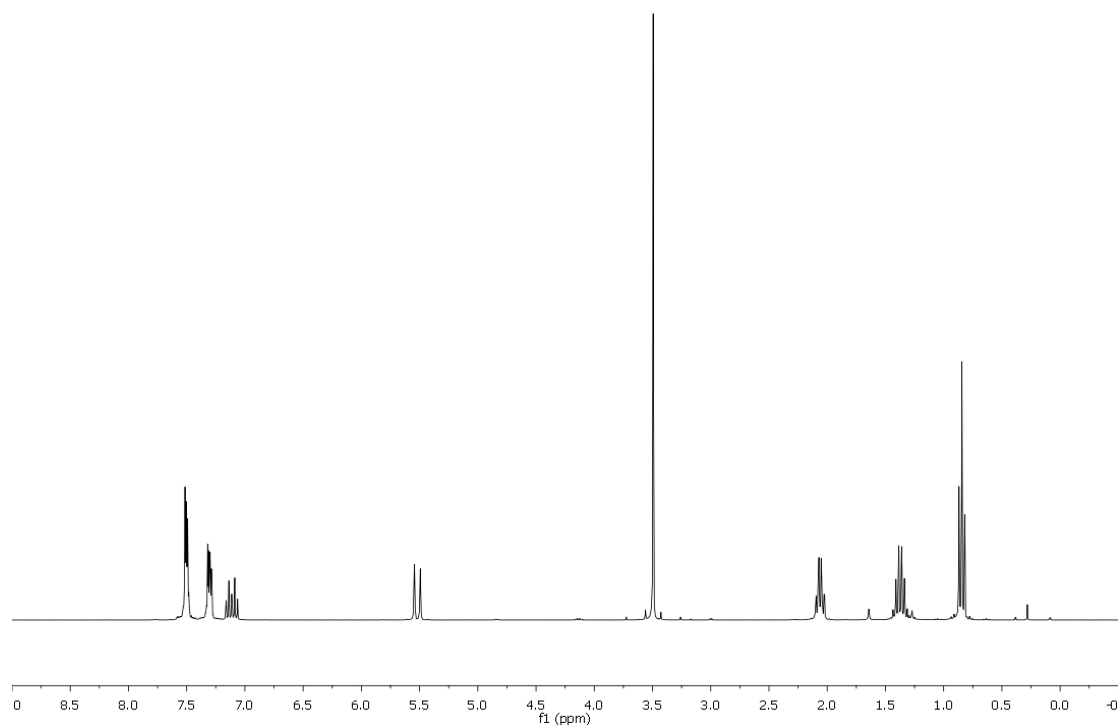




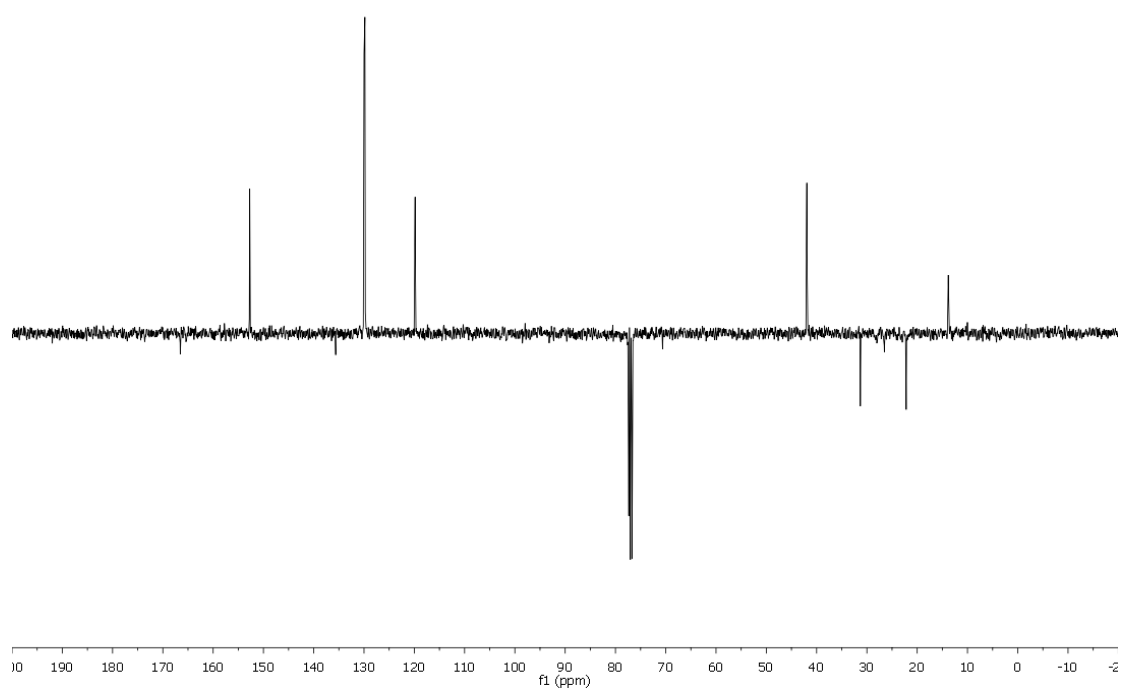
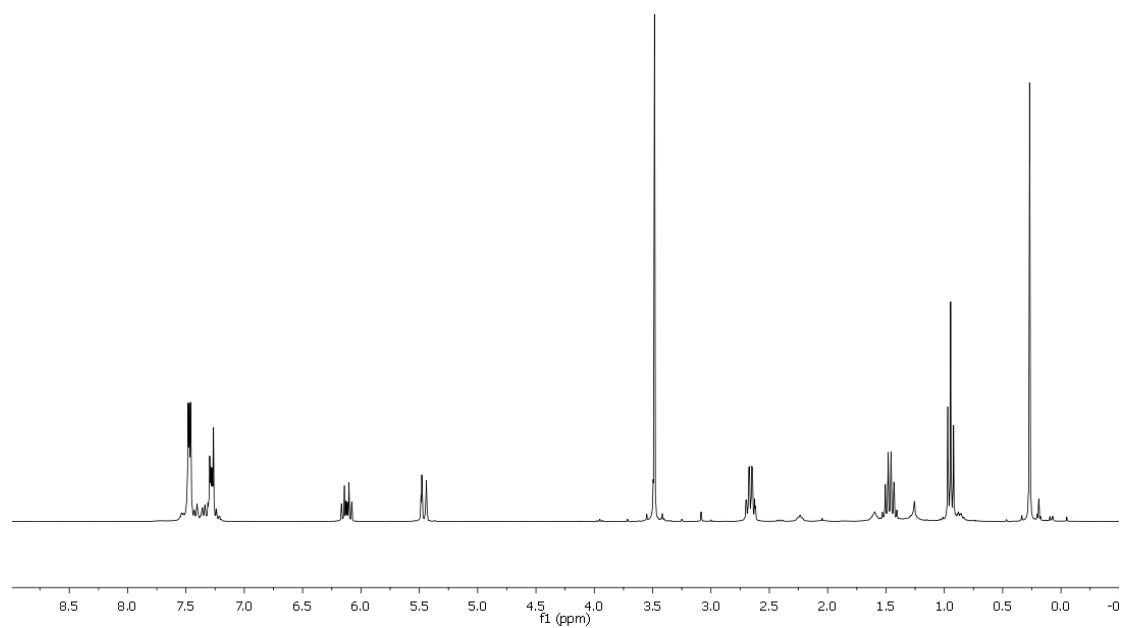
**Compound 3d**



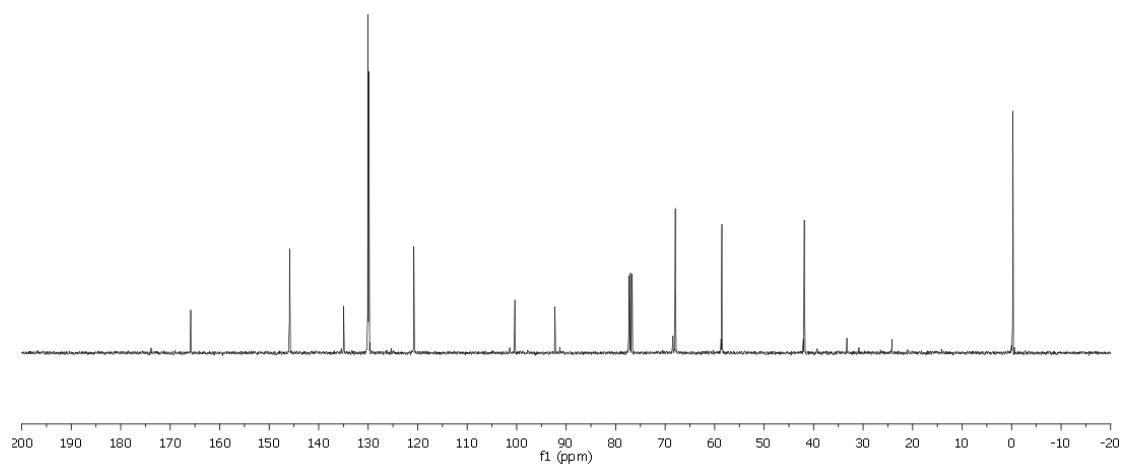
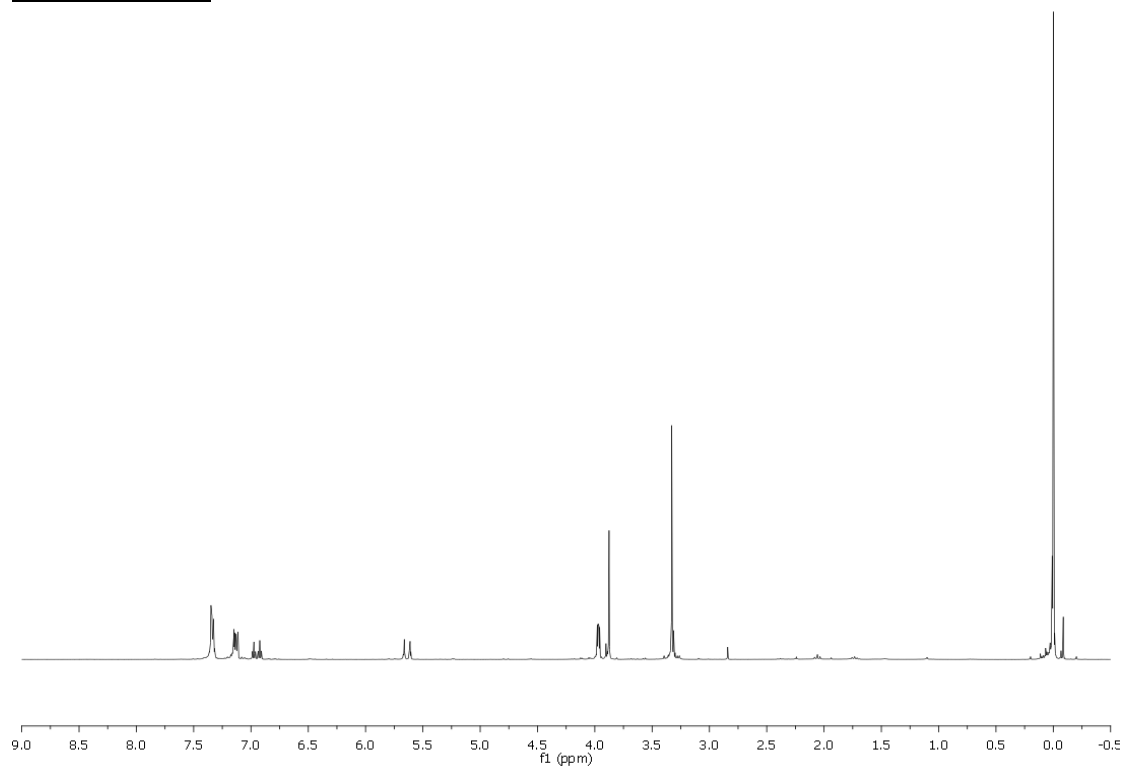
**Compound 3e (E)**



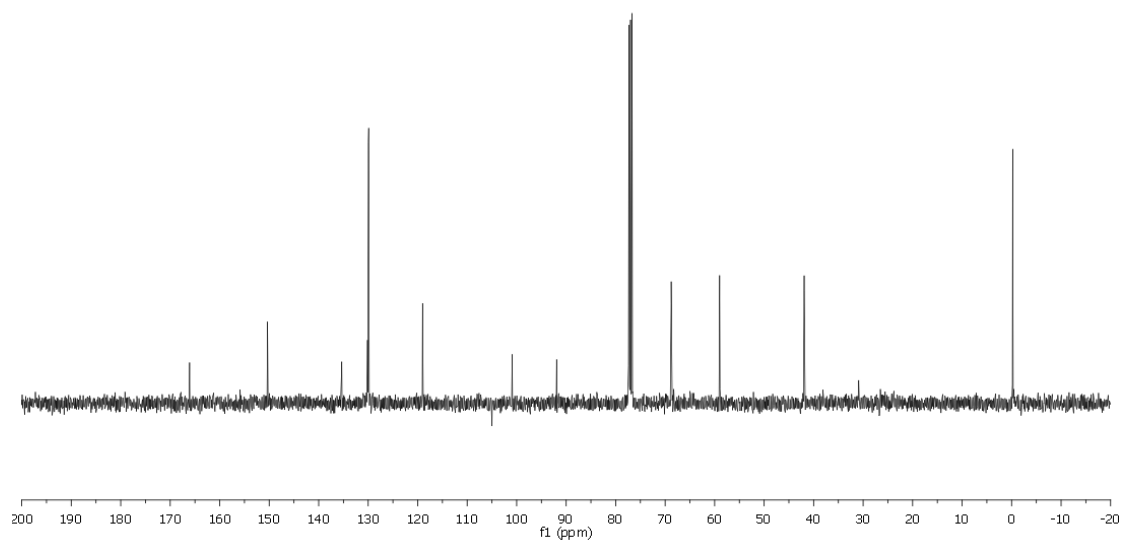
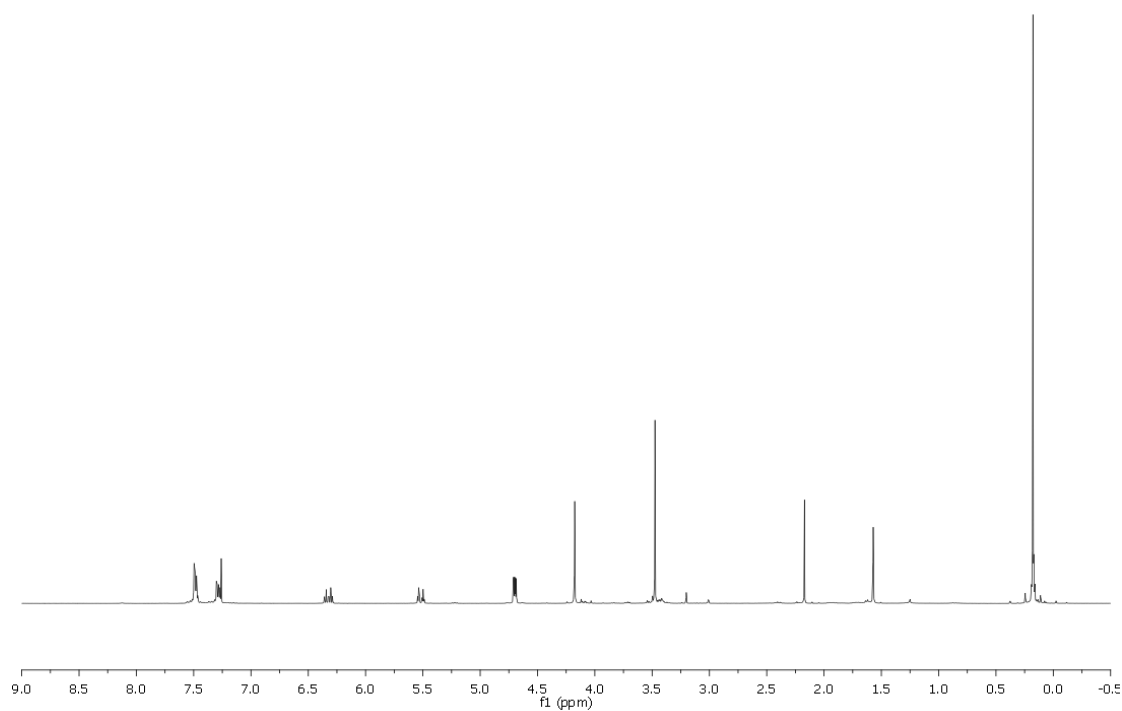
**Compound 3e (Z)**



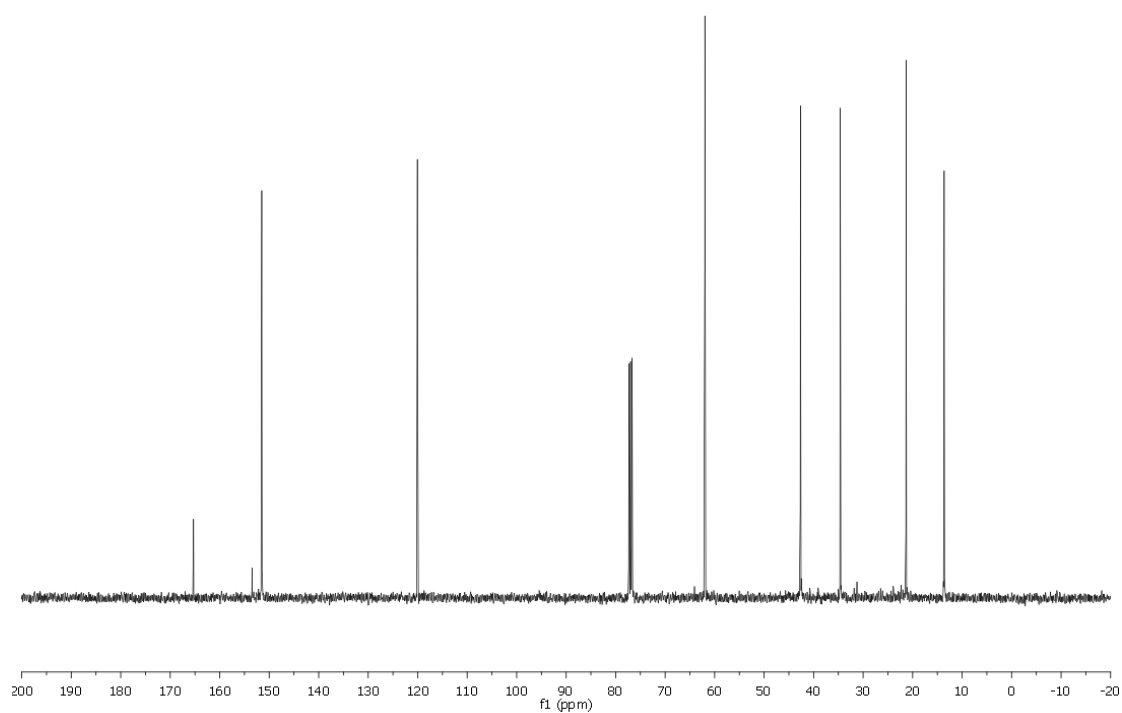
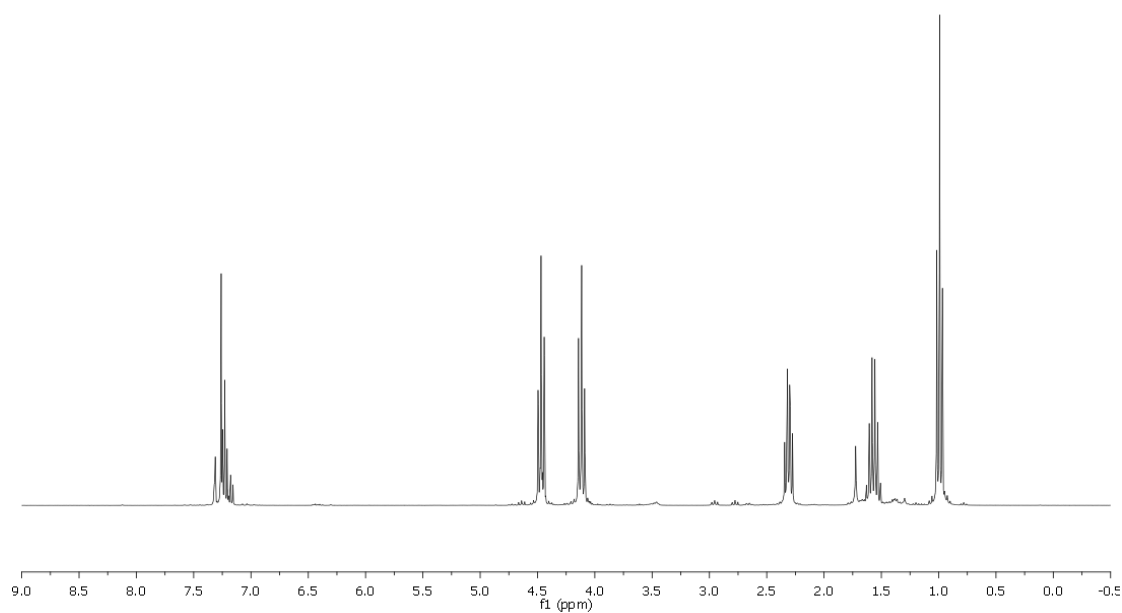
**Compound 3f (E)**



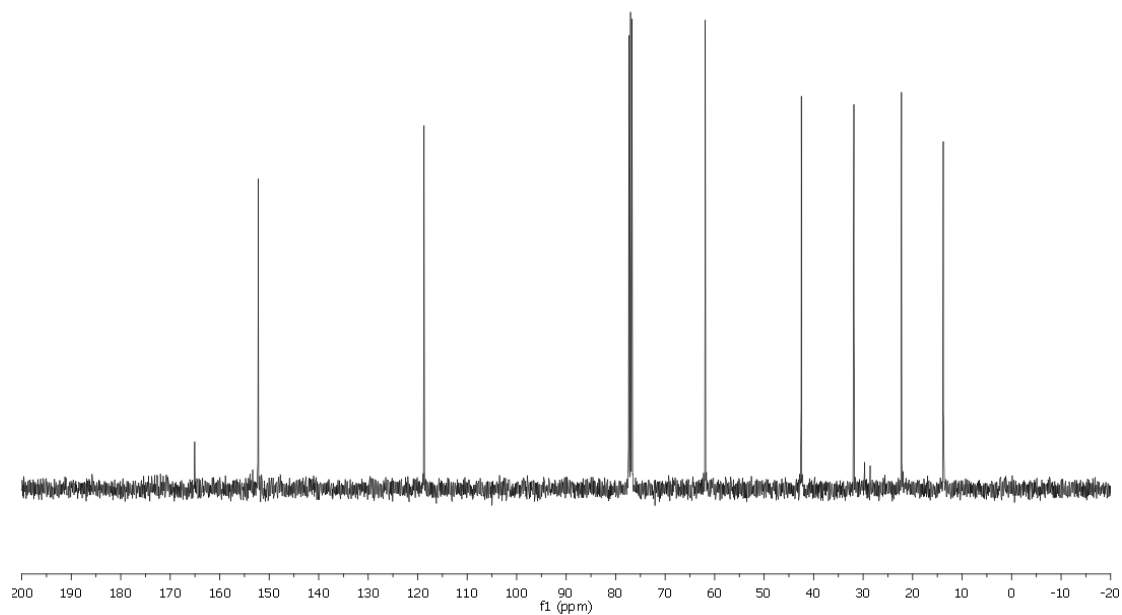
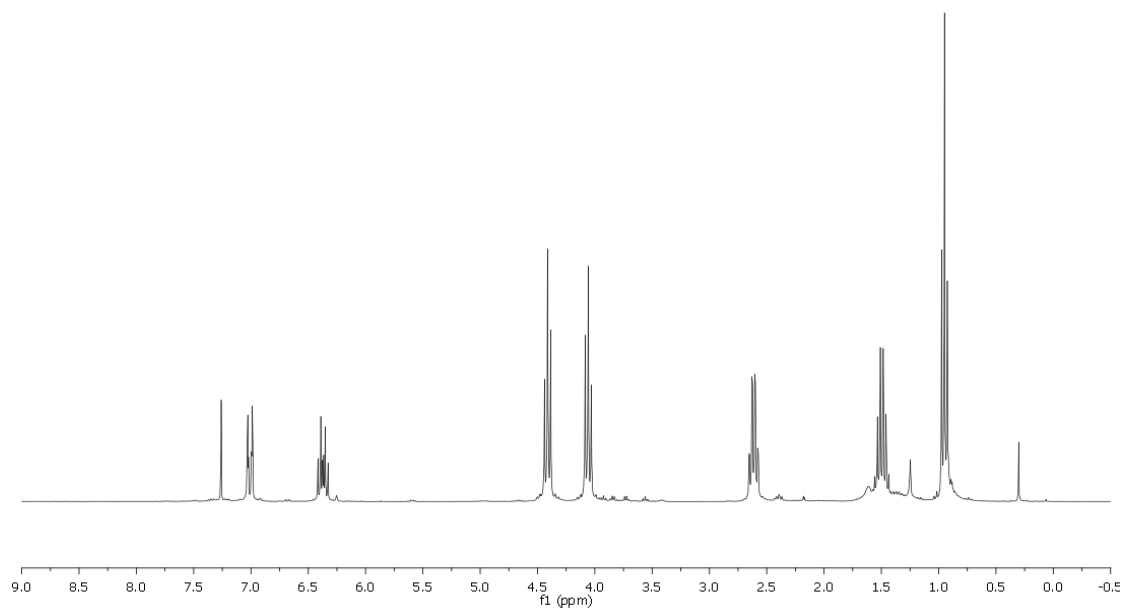
**Compound 3f (Z)**



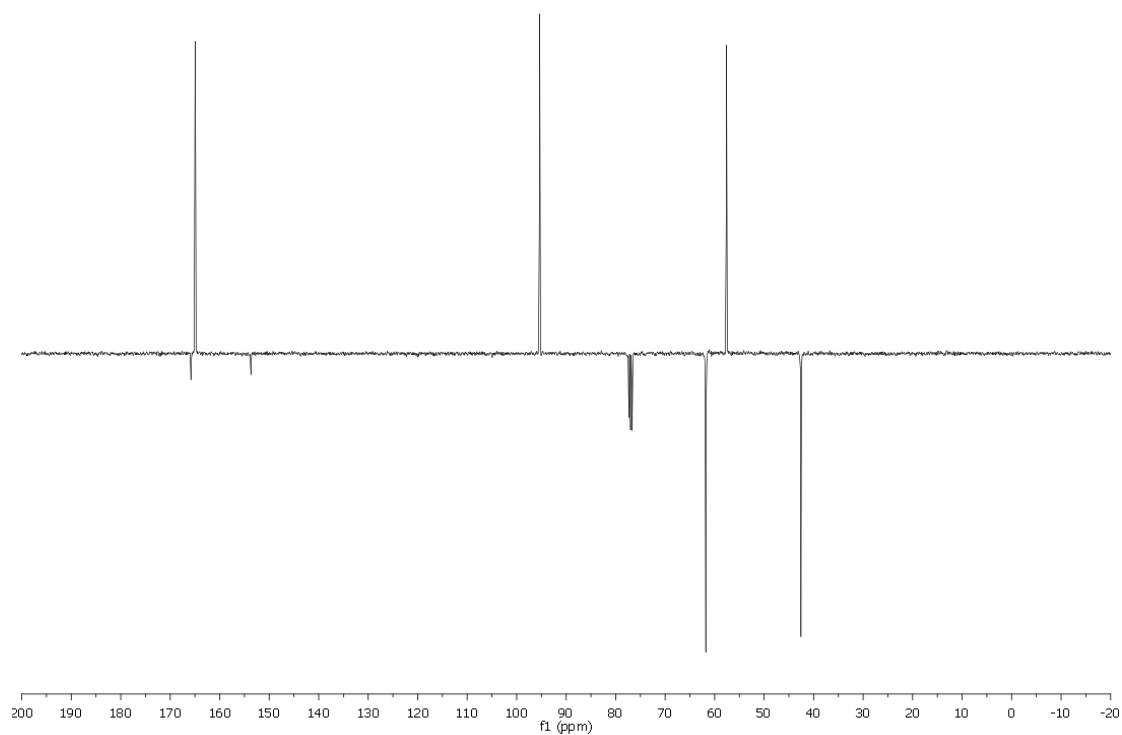
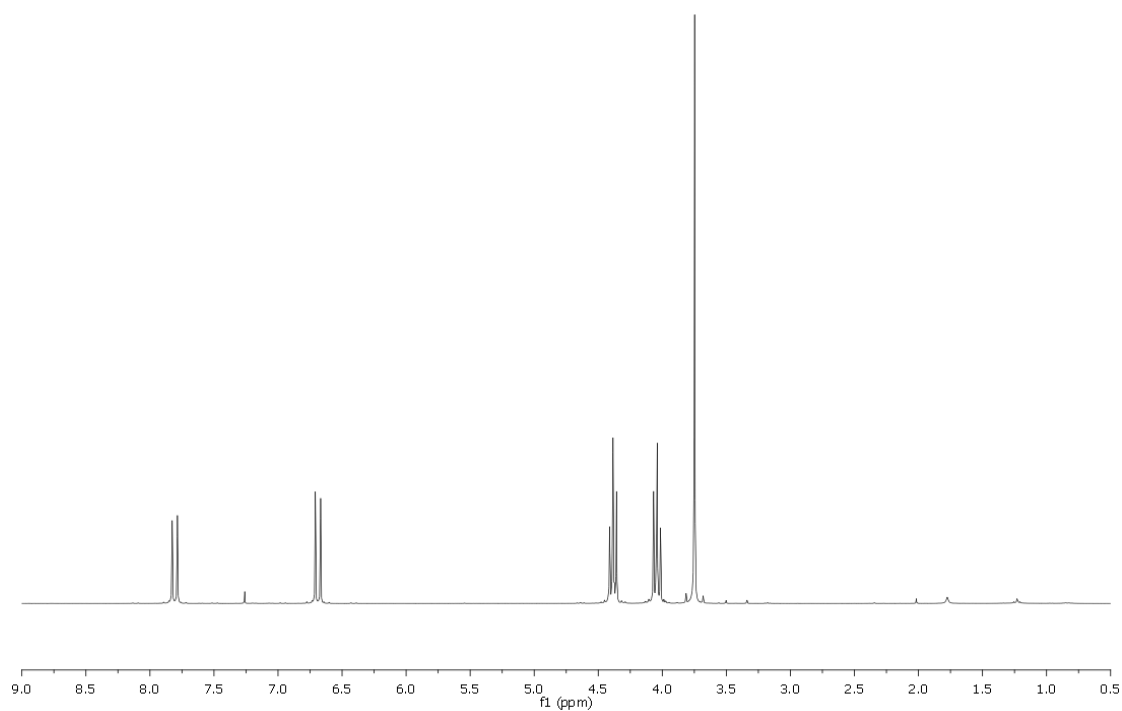
**Compound 3g (E)**



**Compound 3g (Z)**

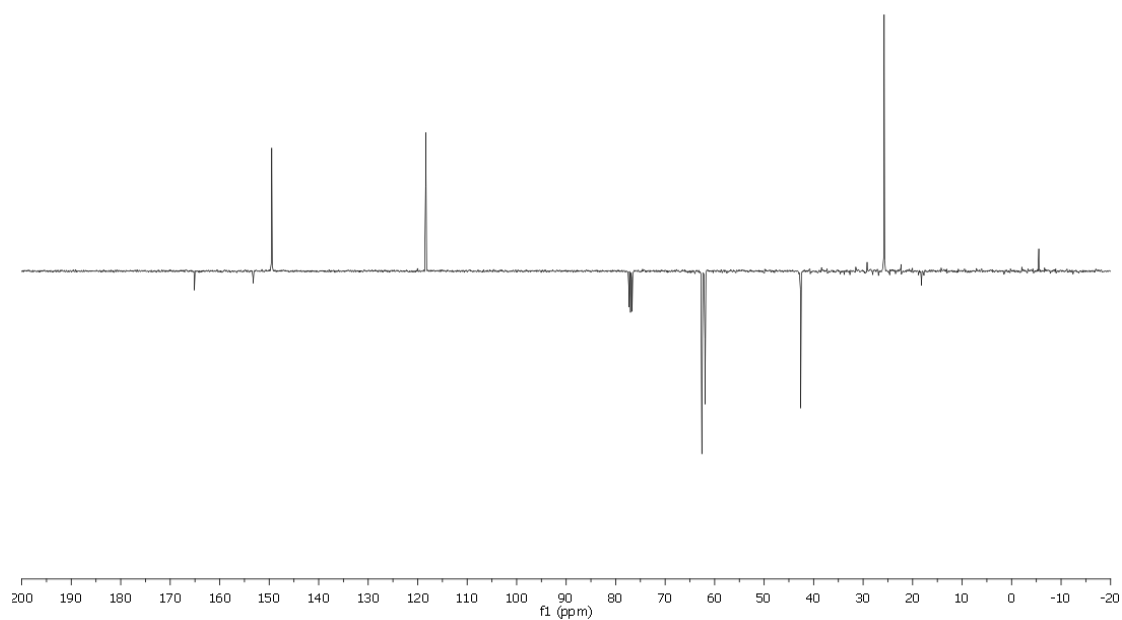
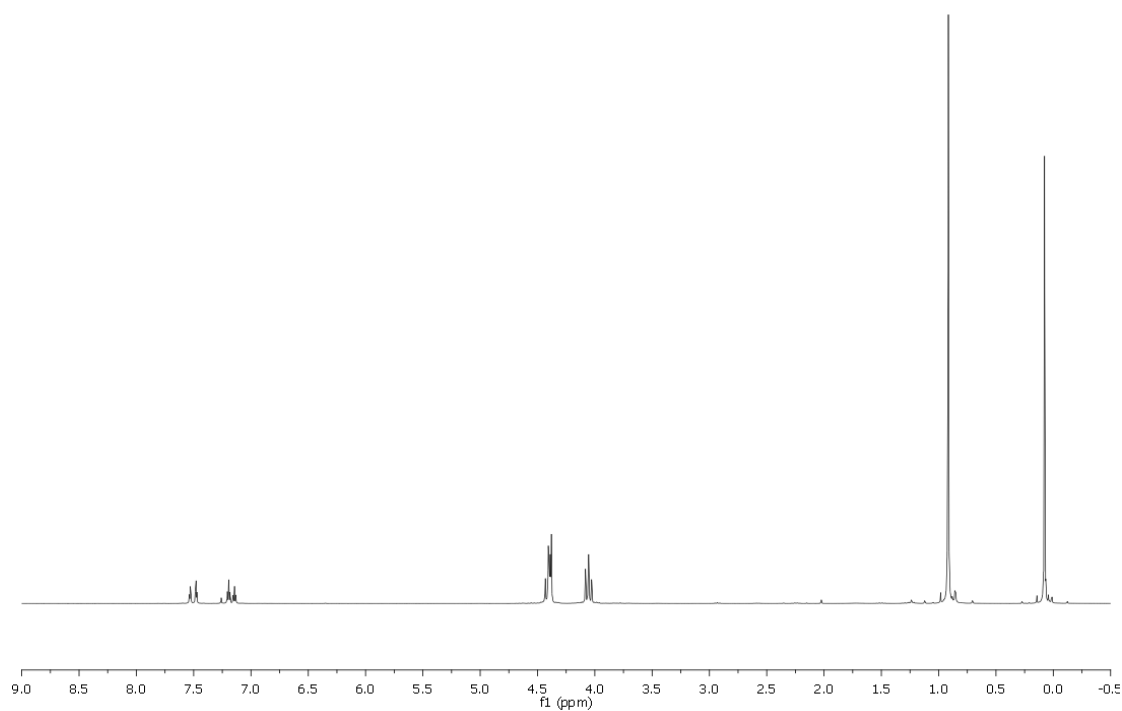


**Compound 3h**

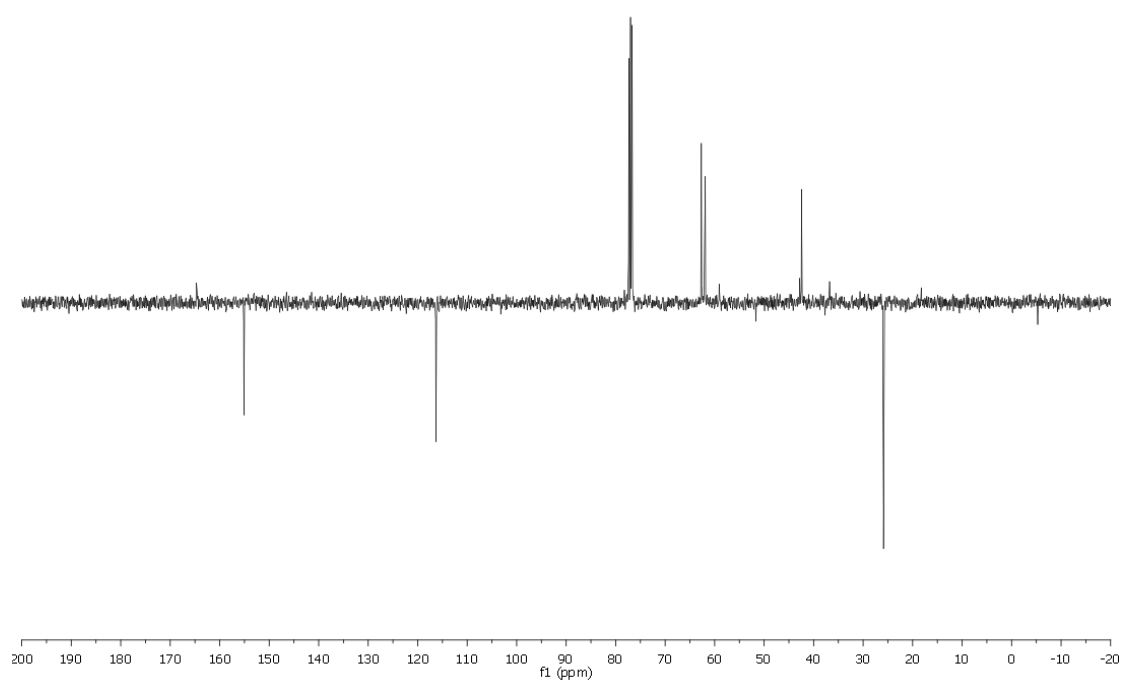
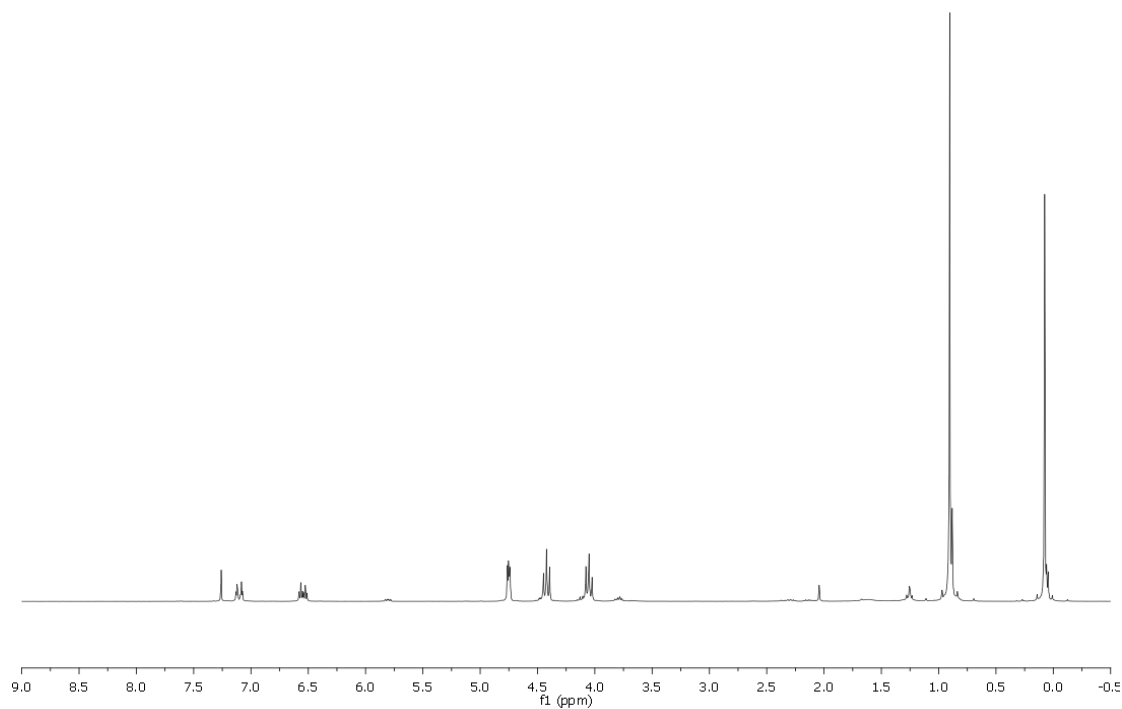




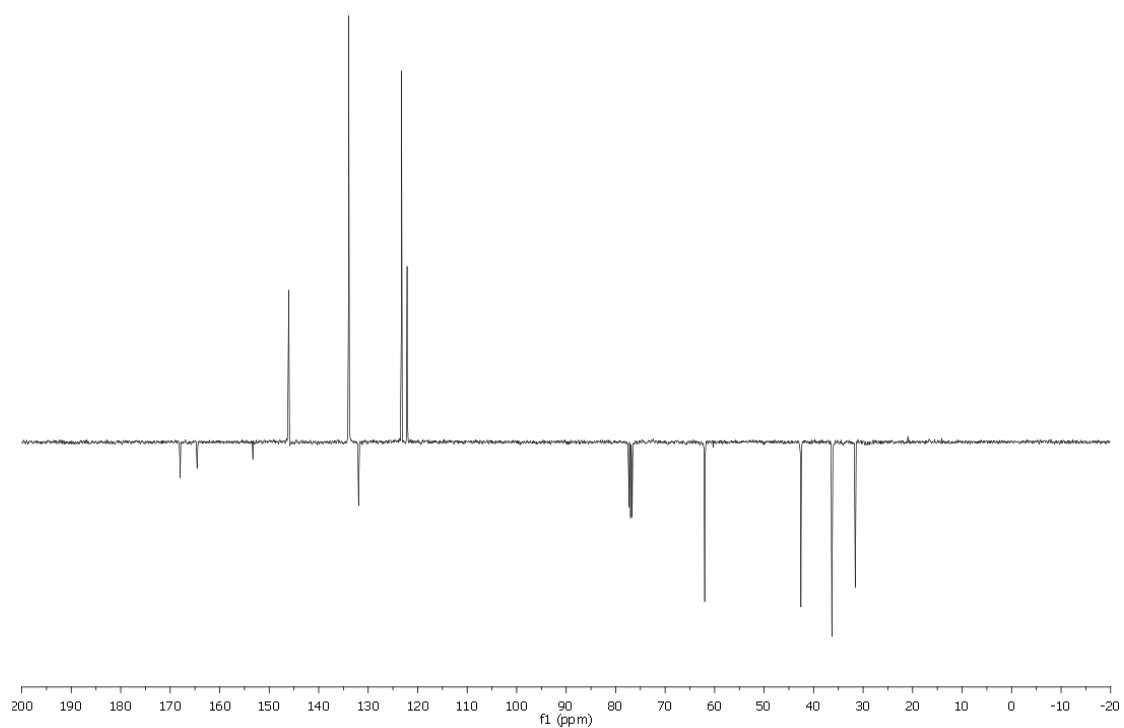
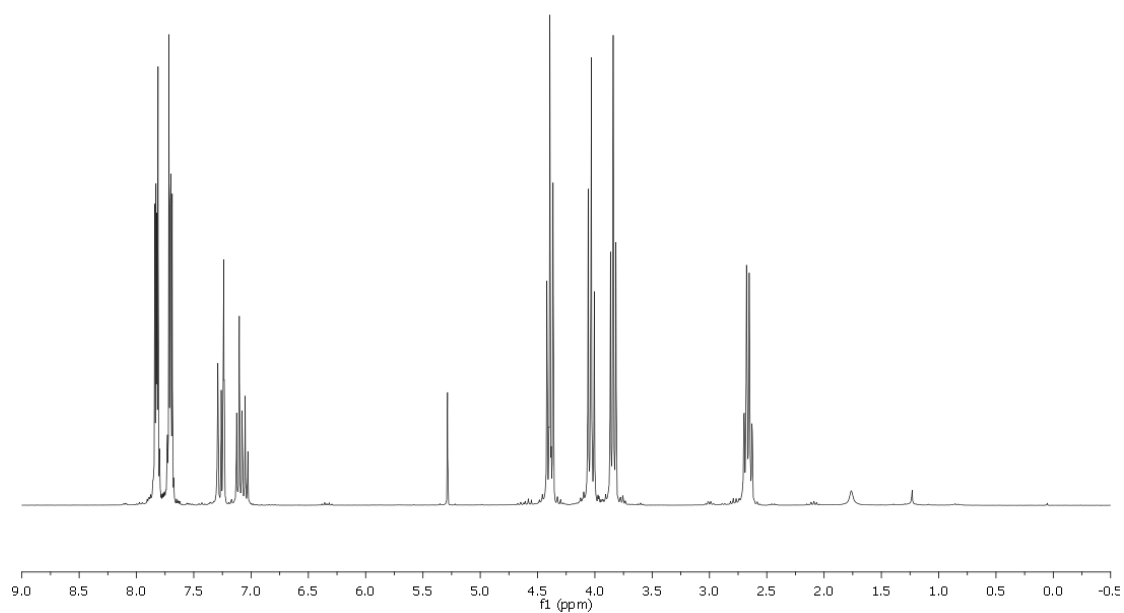
**Compound 3i (E)**



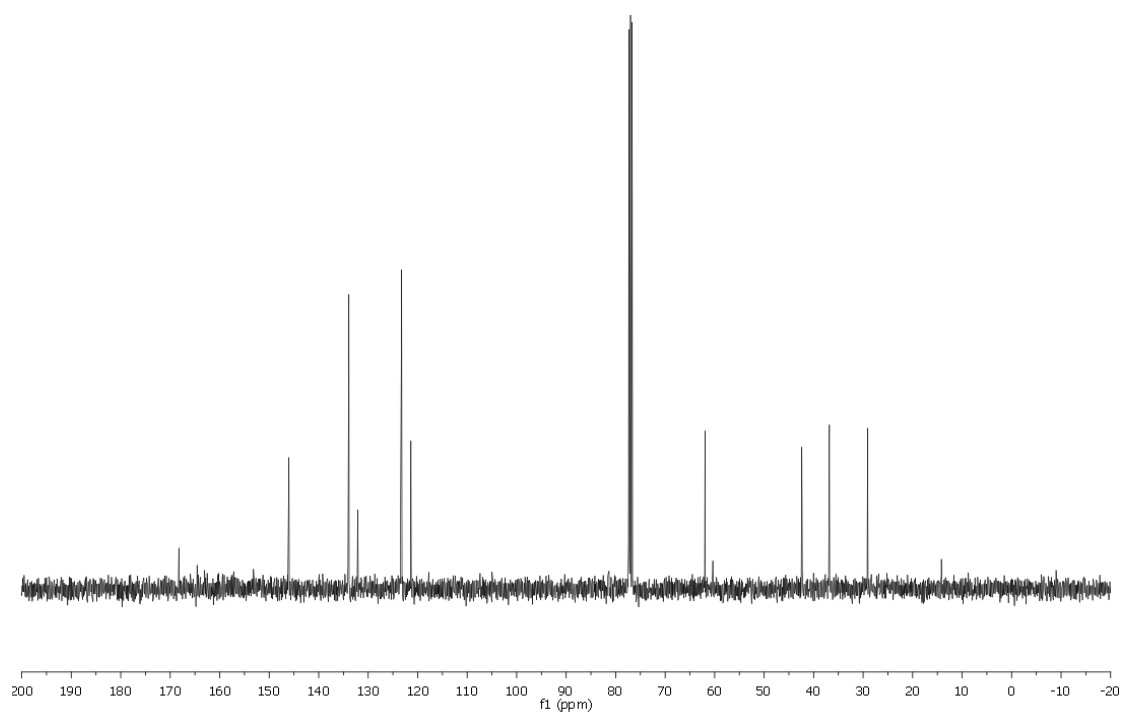
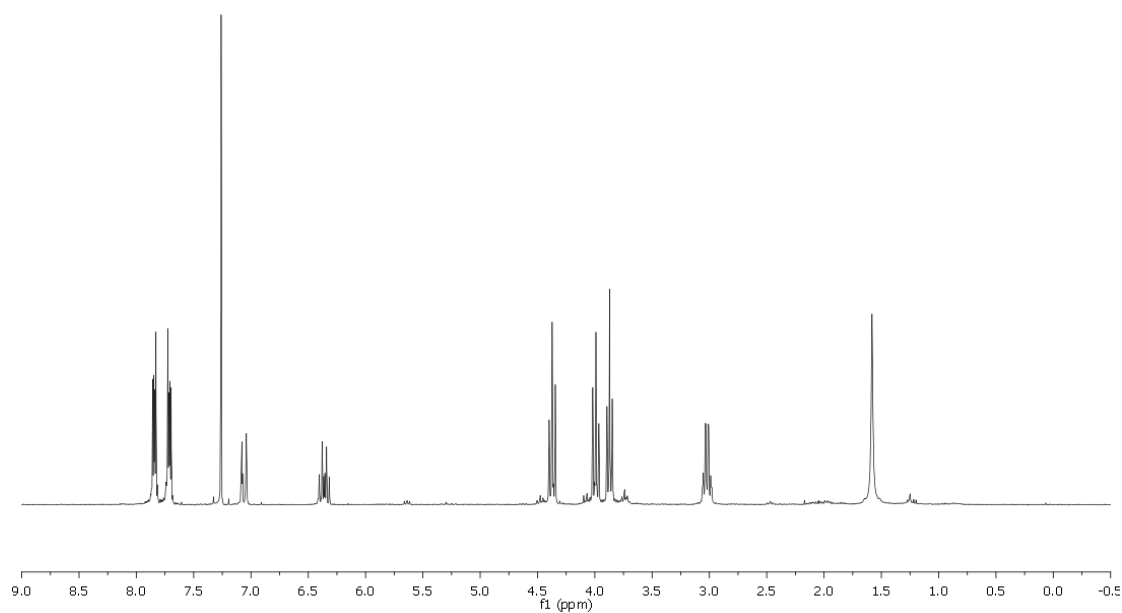
**Compound 3i (Z)**



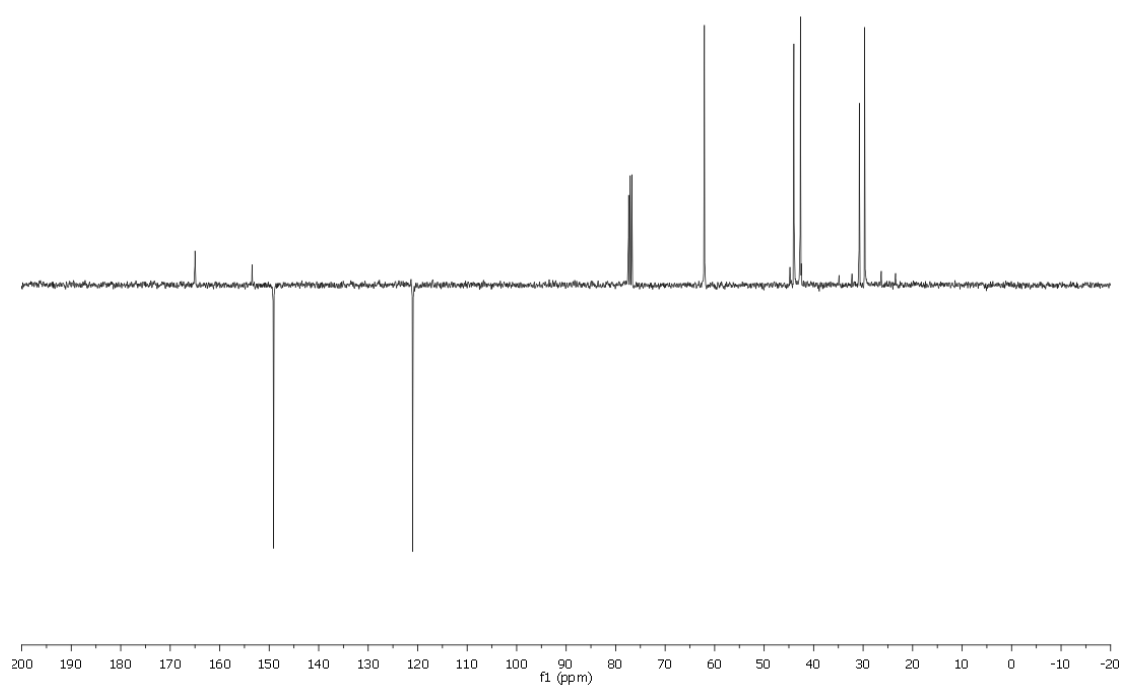
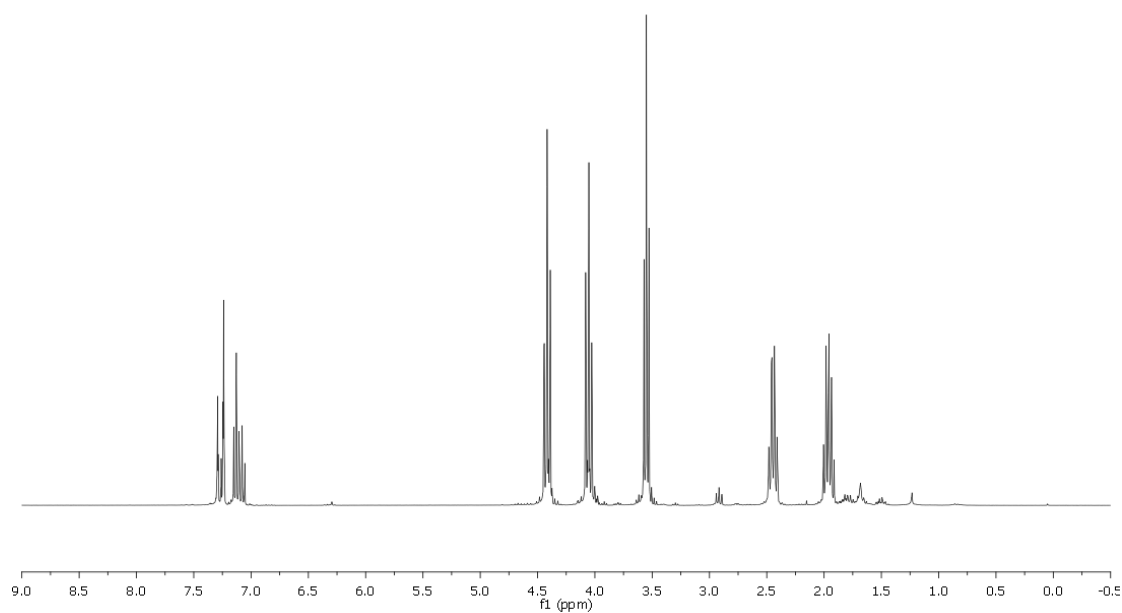
**Compound 3j (E)**



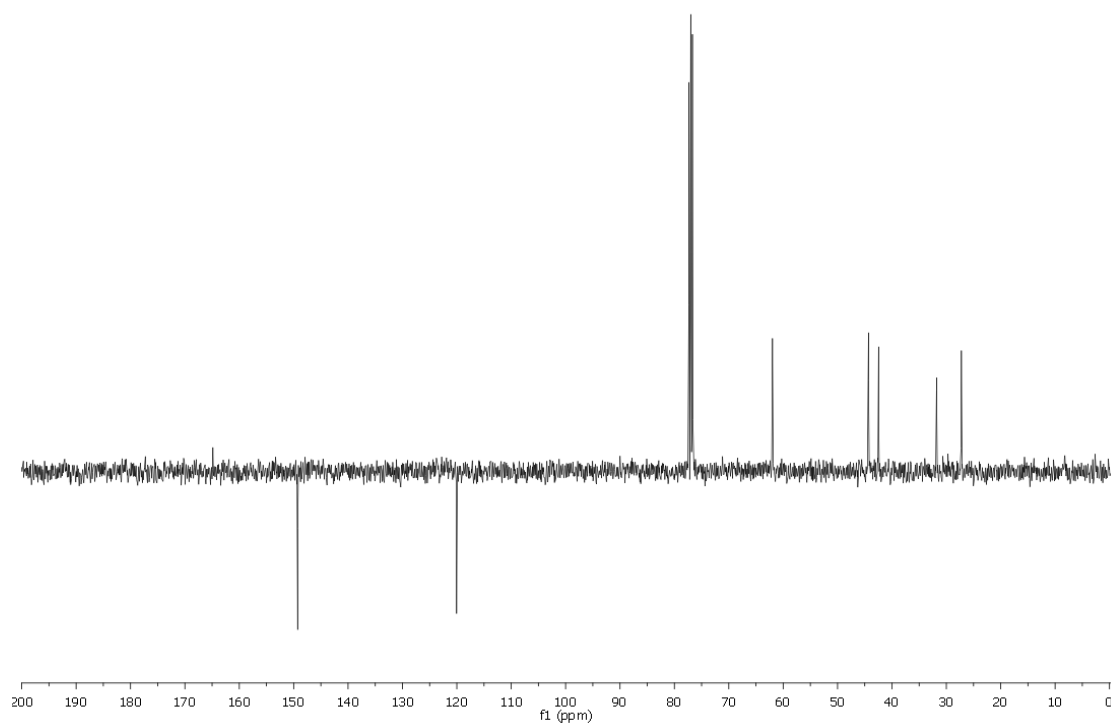
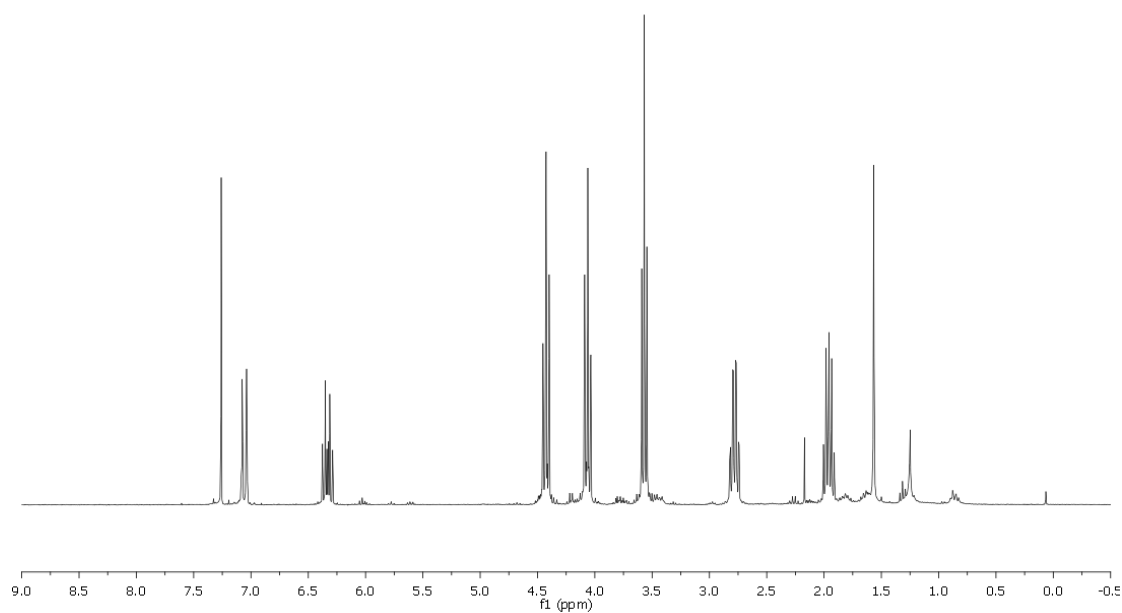
**Compound 3j (Z)**



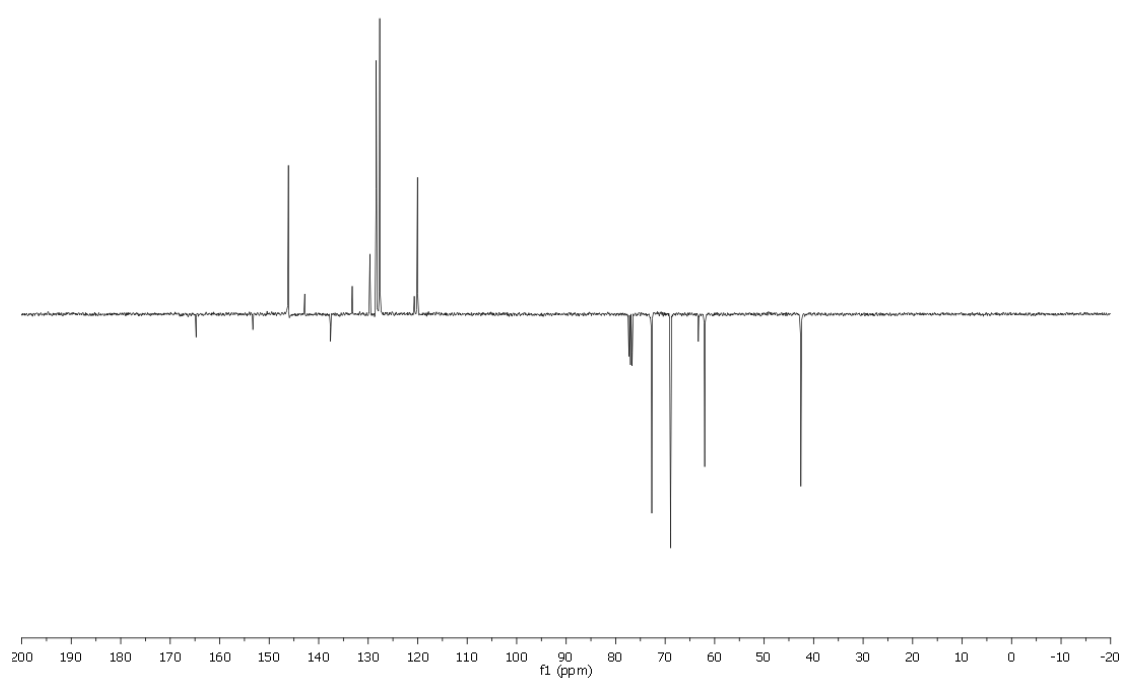
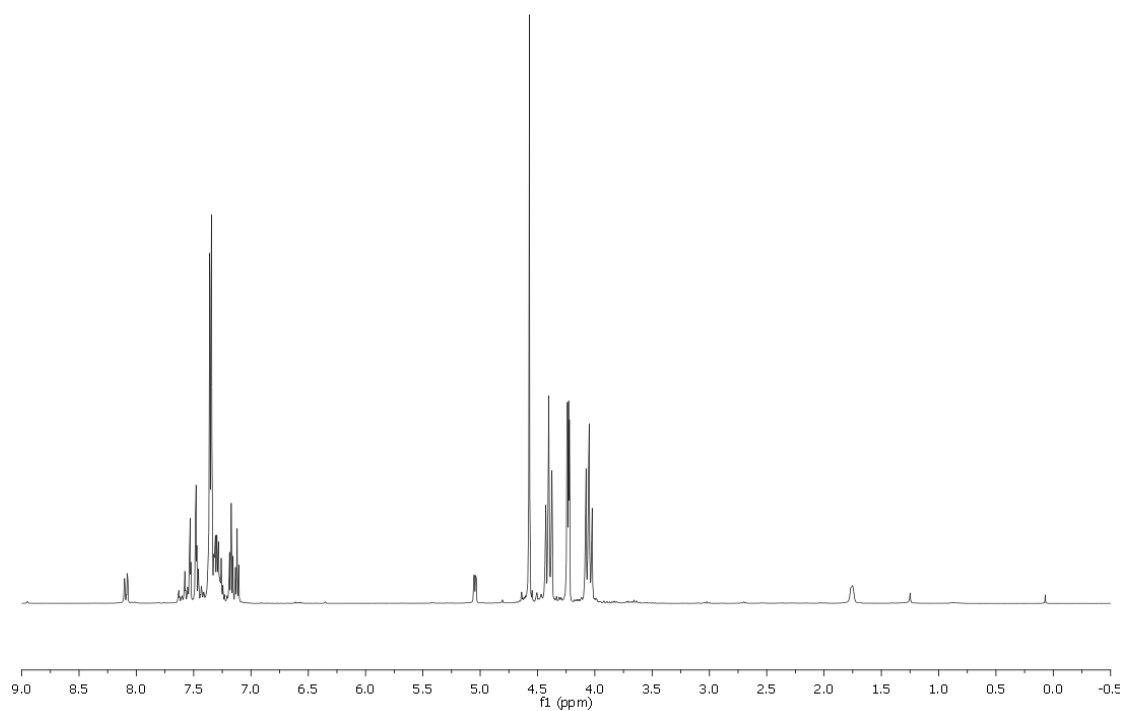
**Compound 3k (E)**



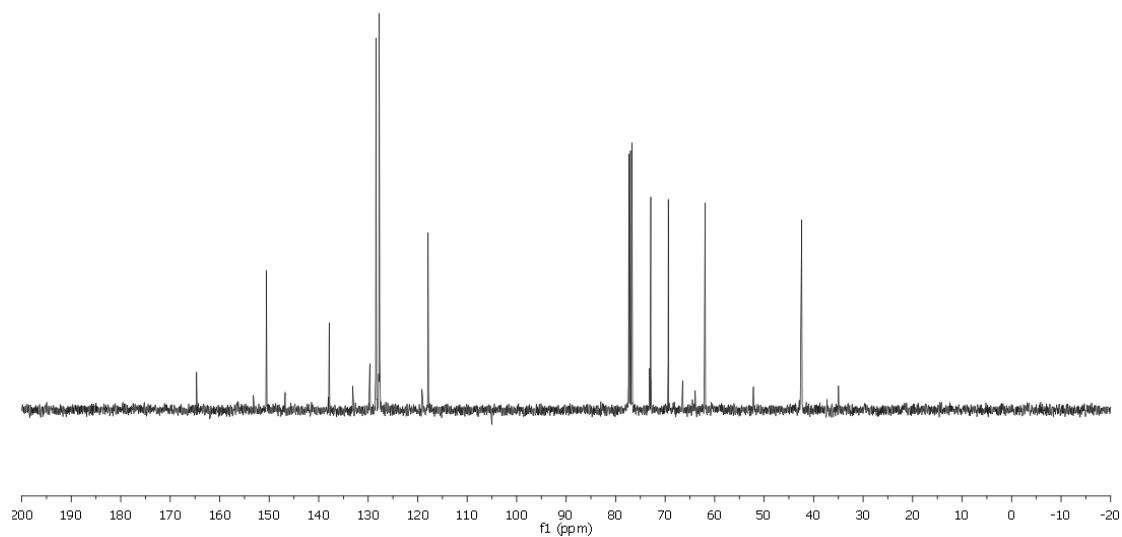
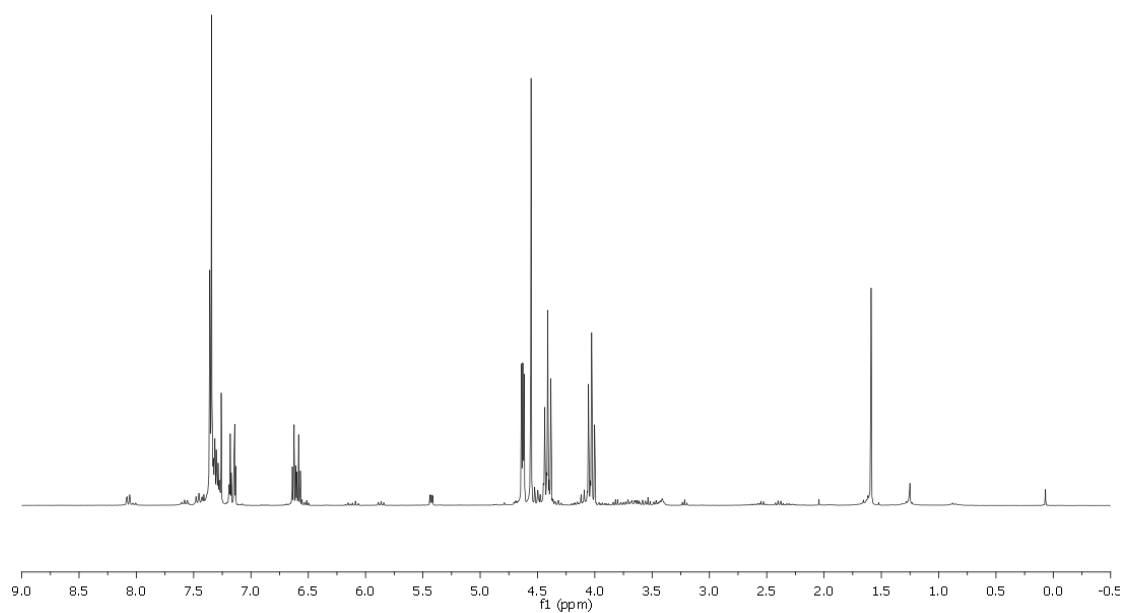
**Compound 3k (Z)**



**Compound 3l (E)**

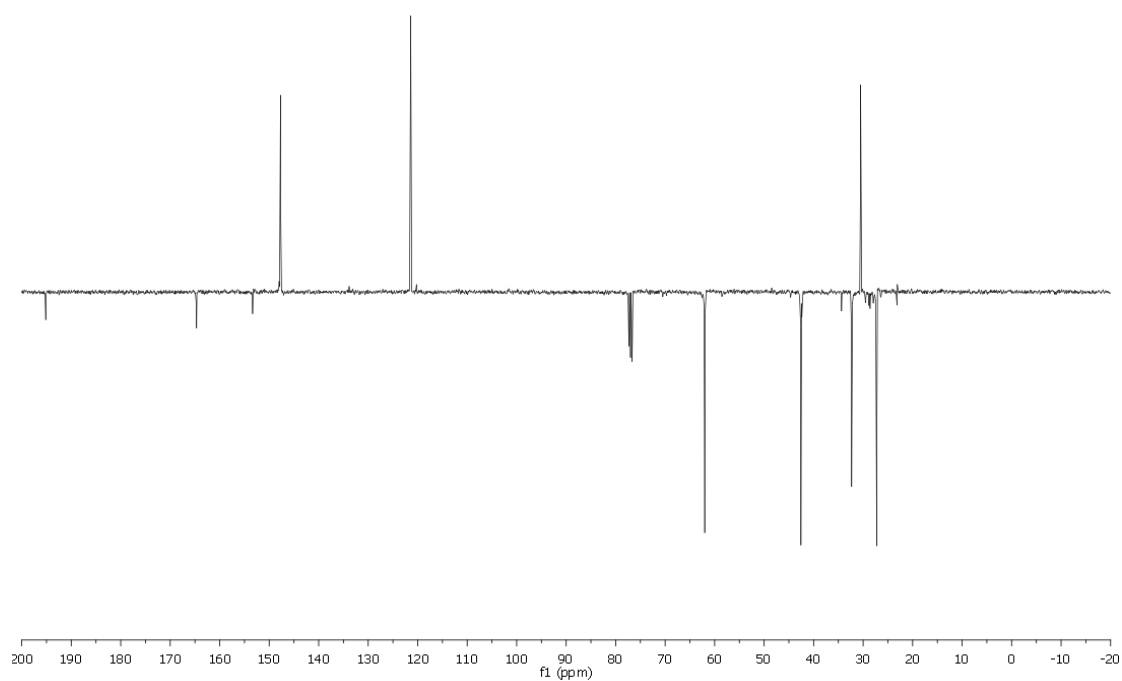
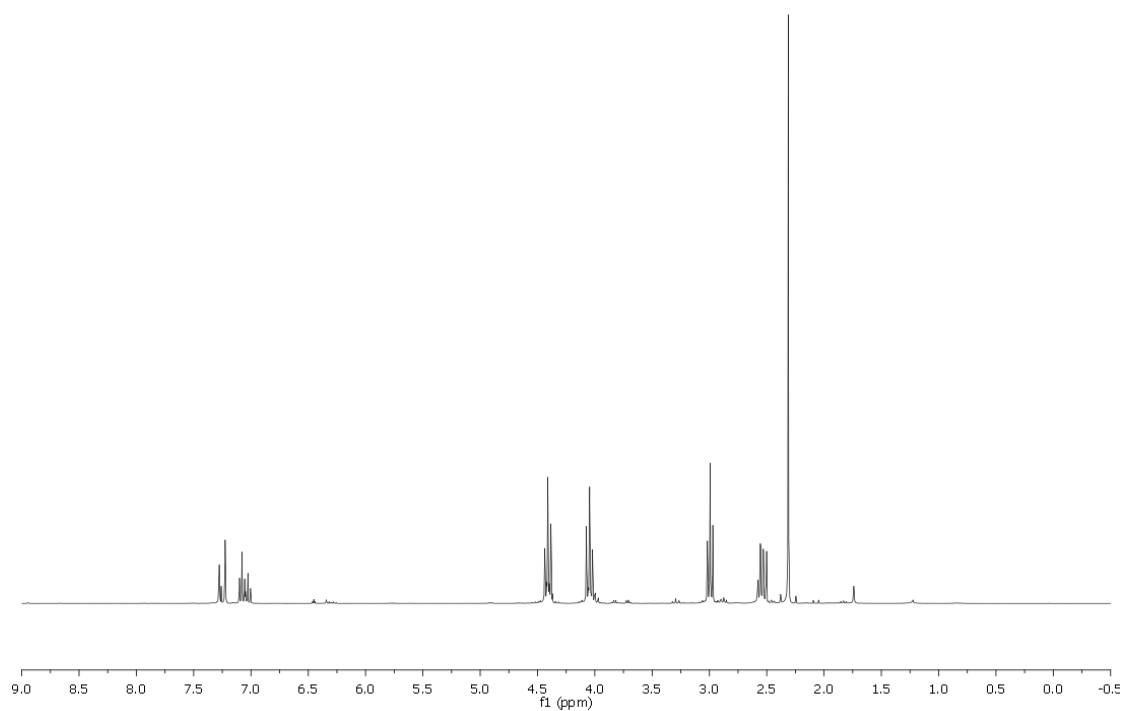


**Compound 3l (Z)**

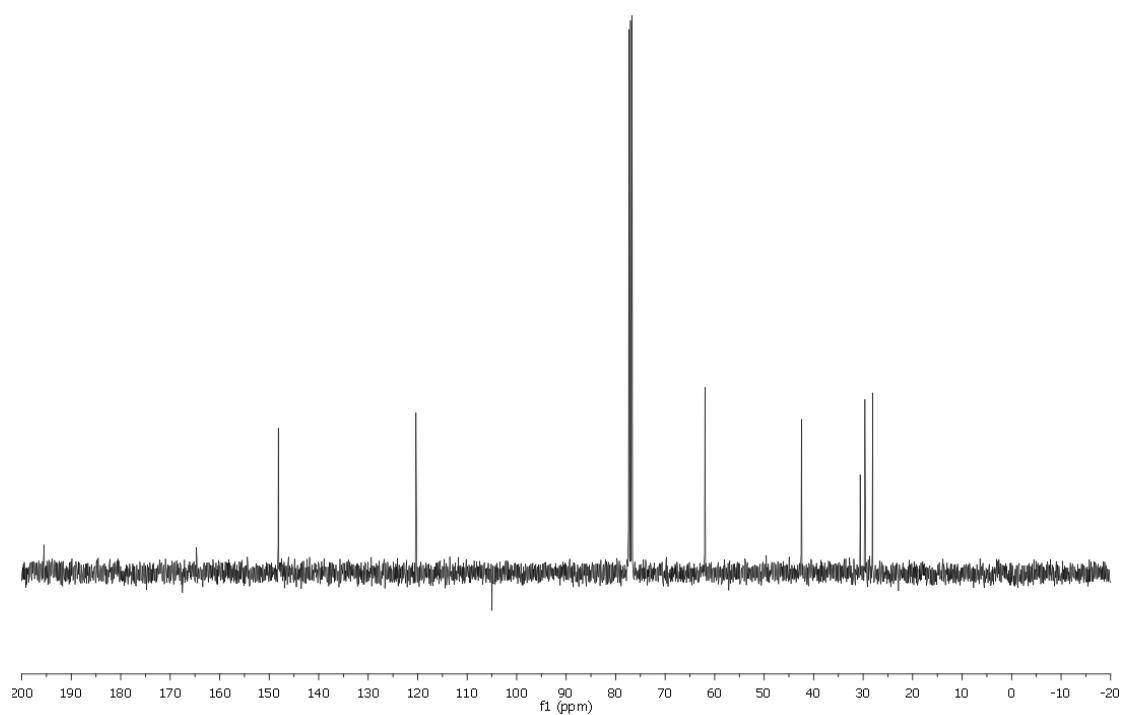
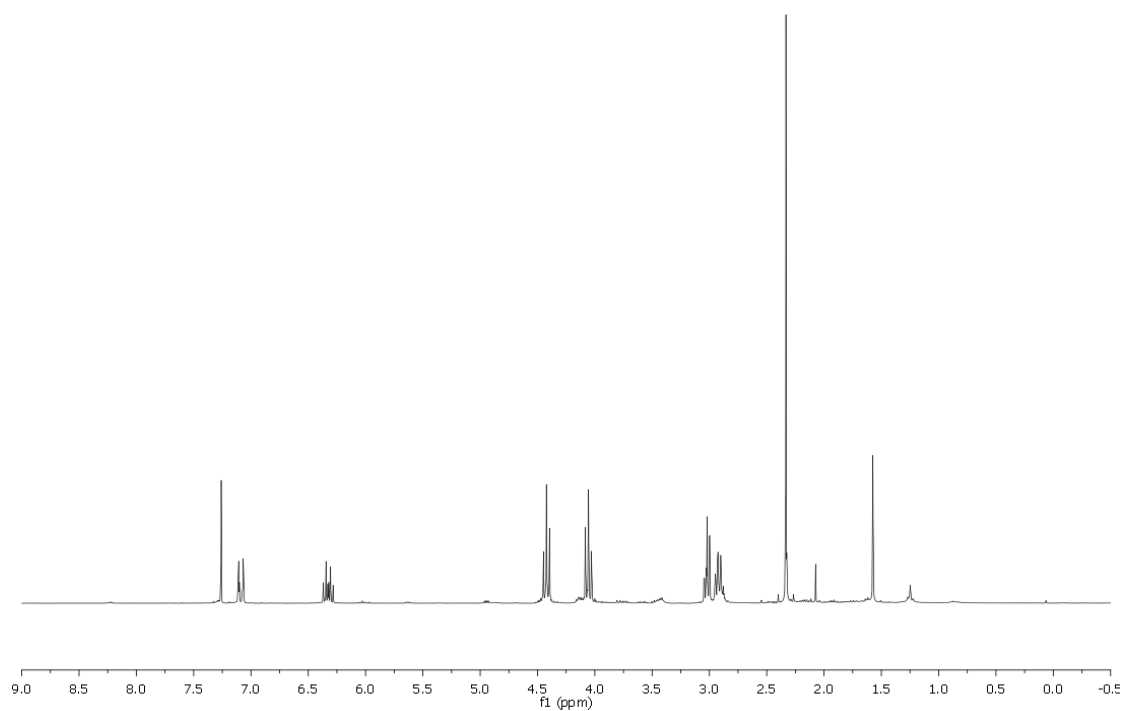




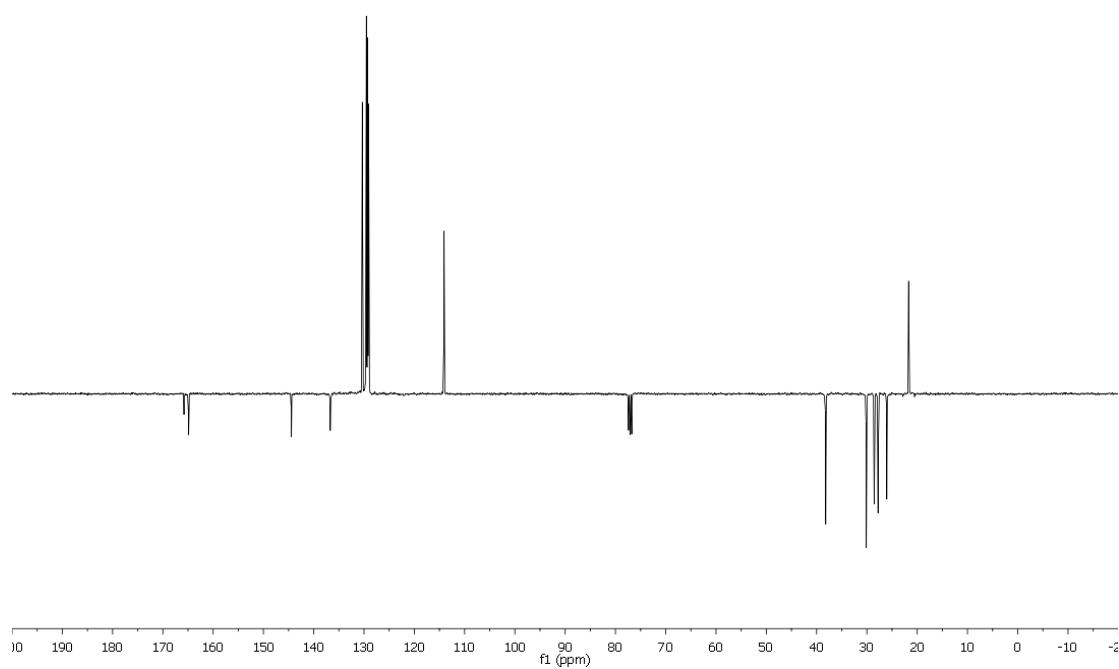
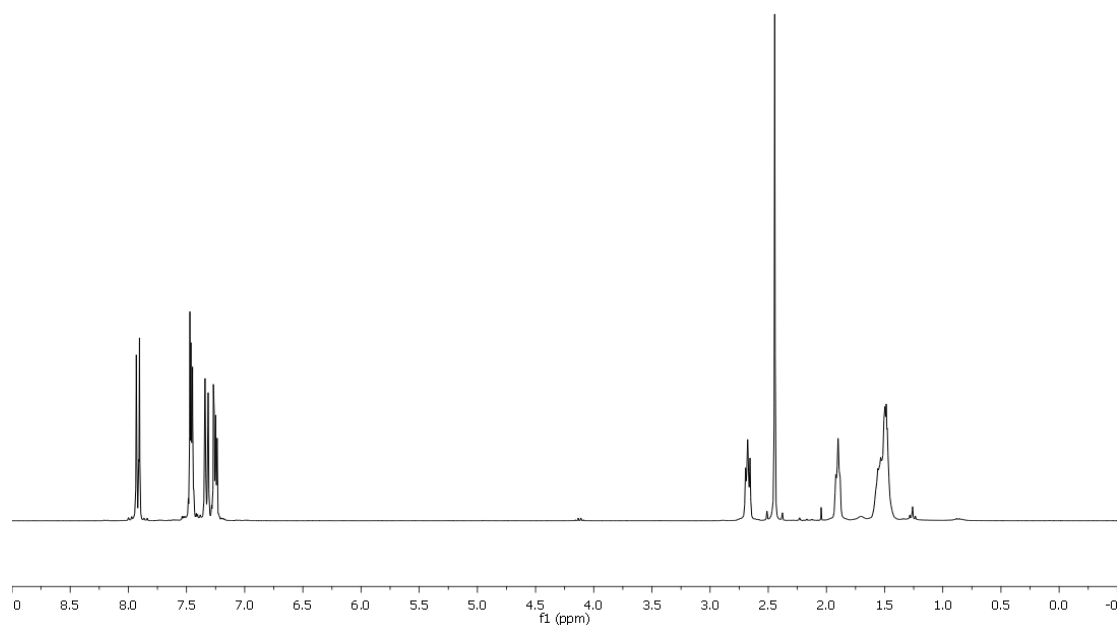
**Compound 3m (E)**



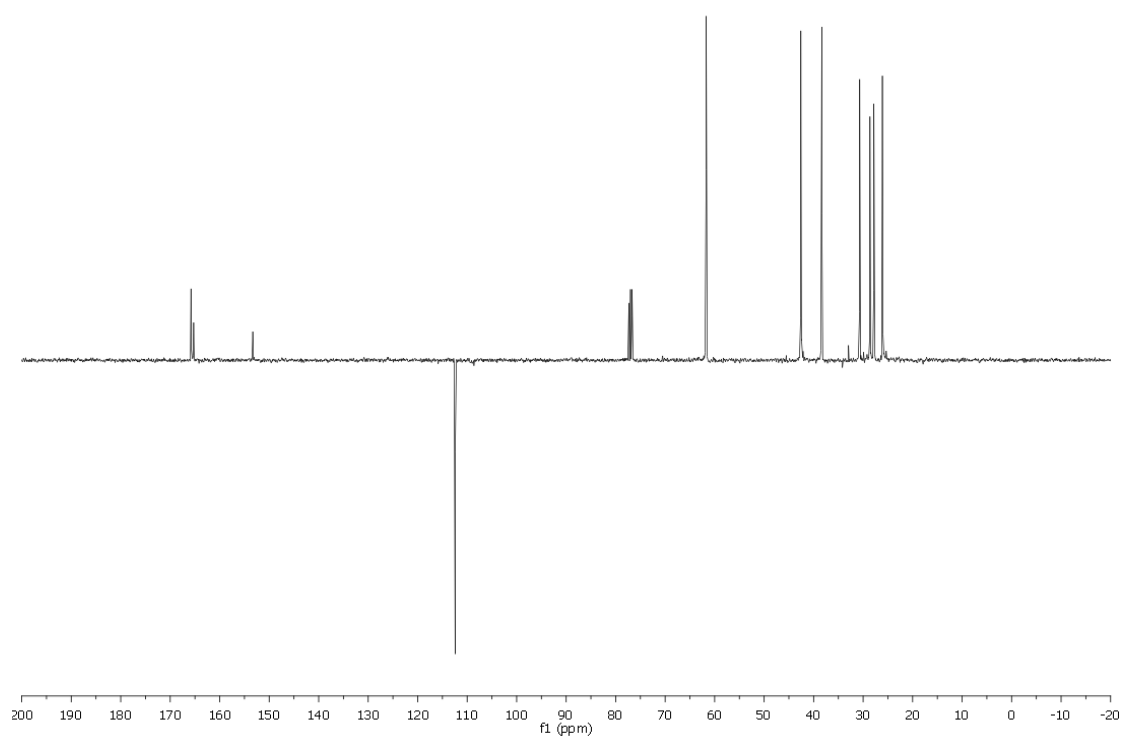
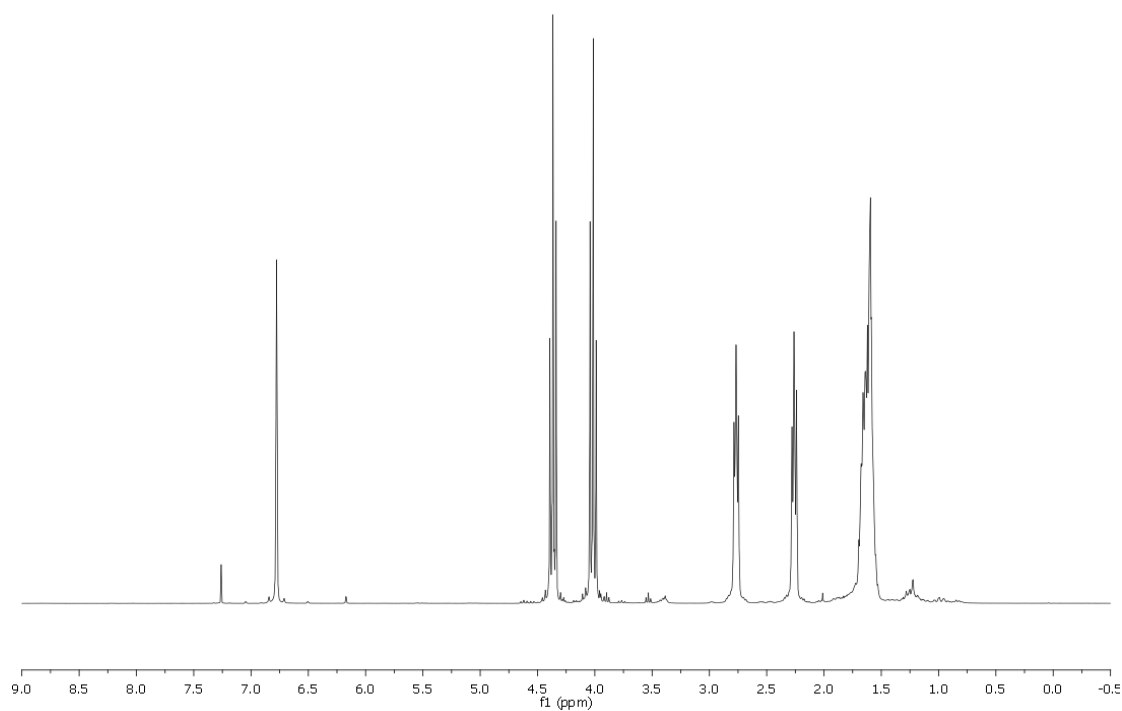
**Compound 3m (Z)**



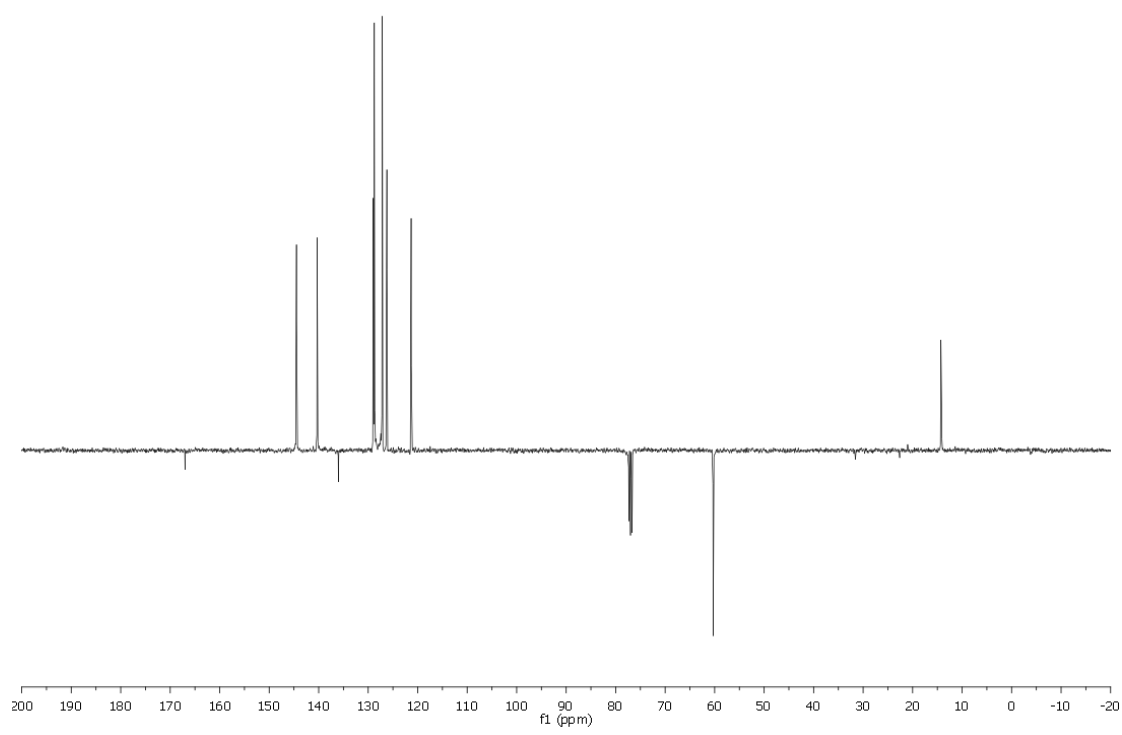
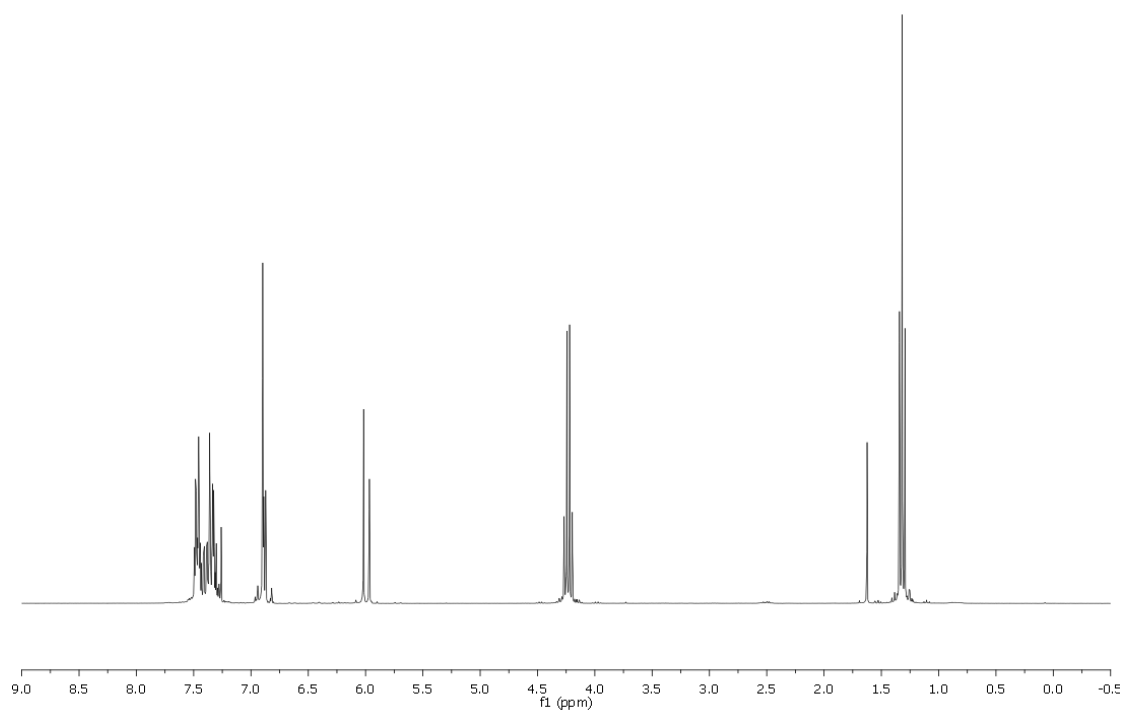
**Compound 5a**



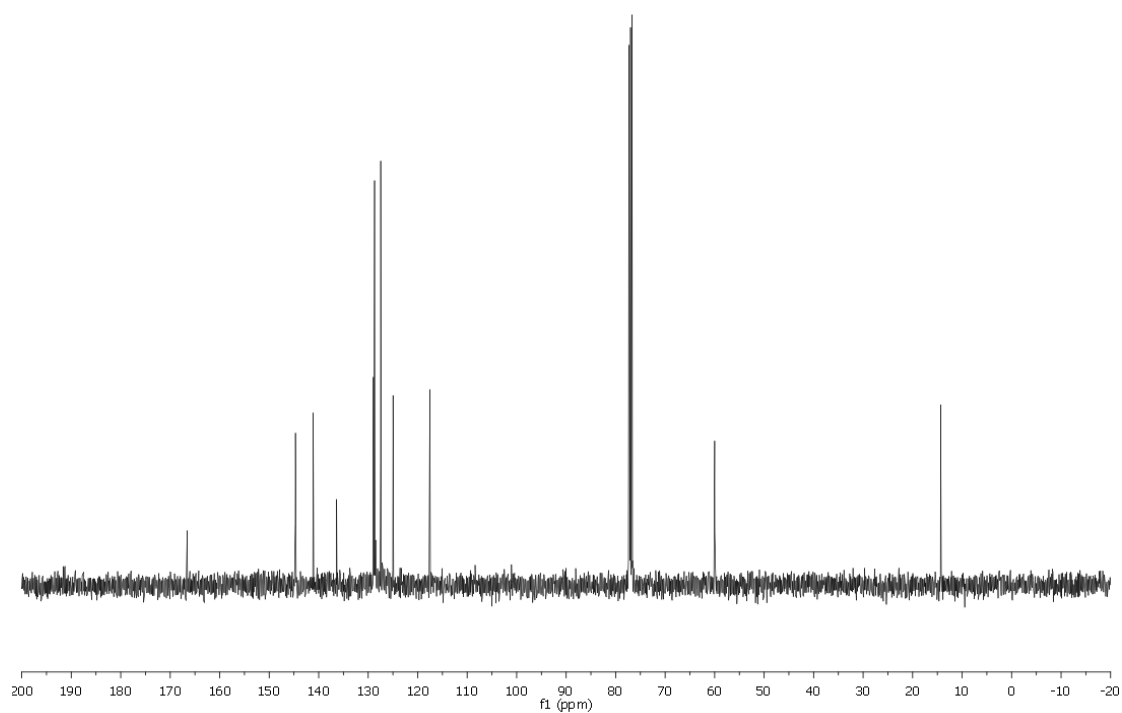
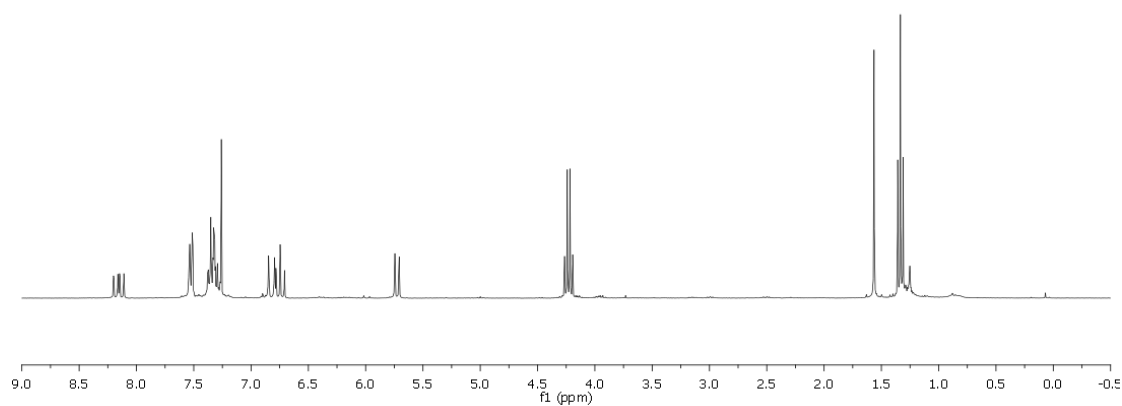
**Compound 5b**



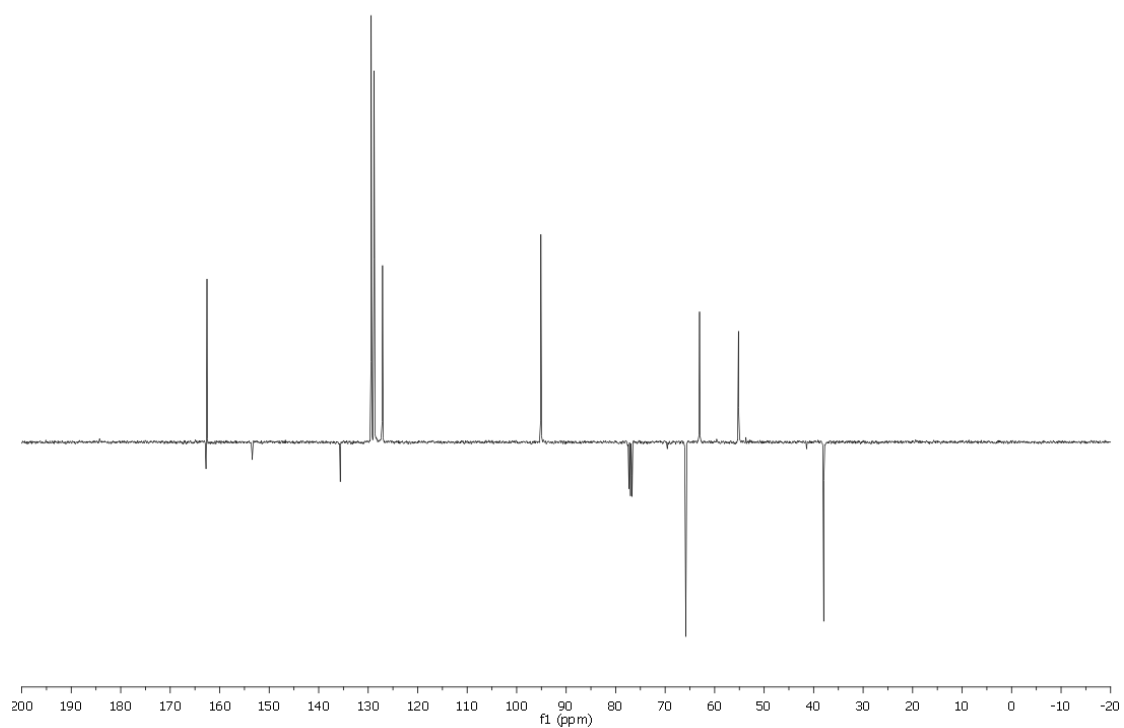
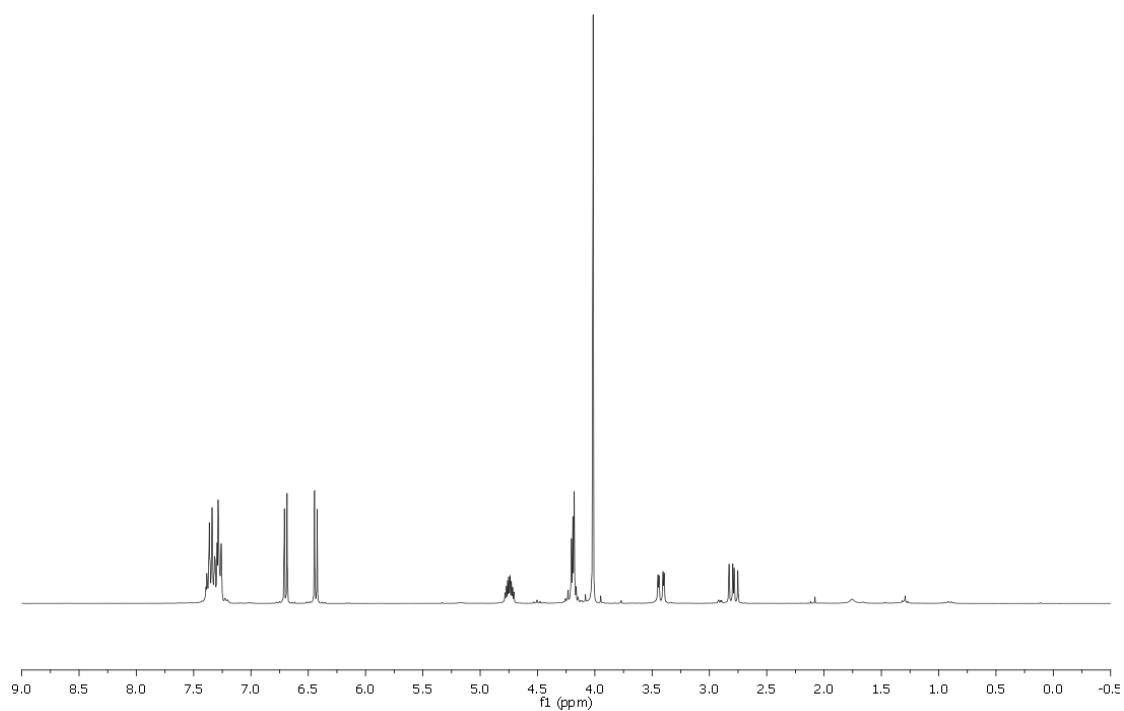
**Compound 7 (E,E)**



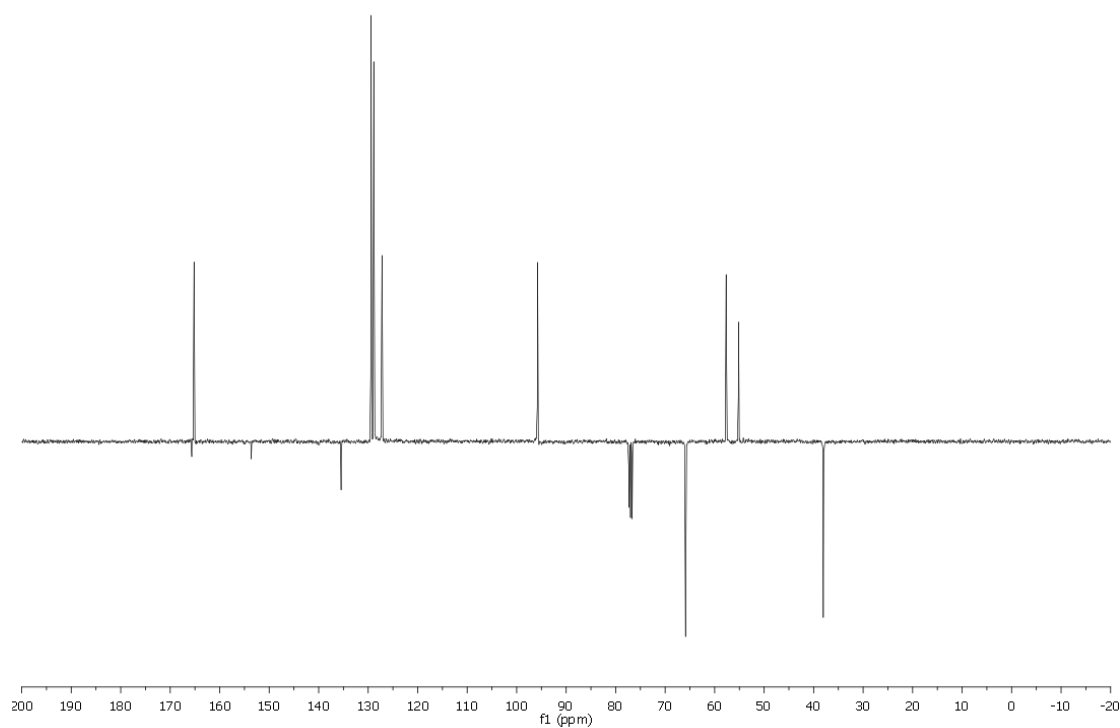
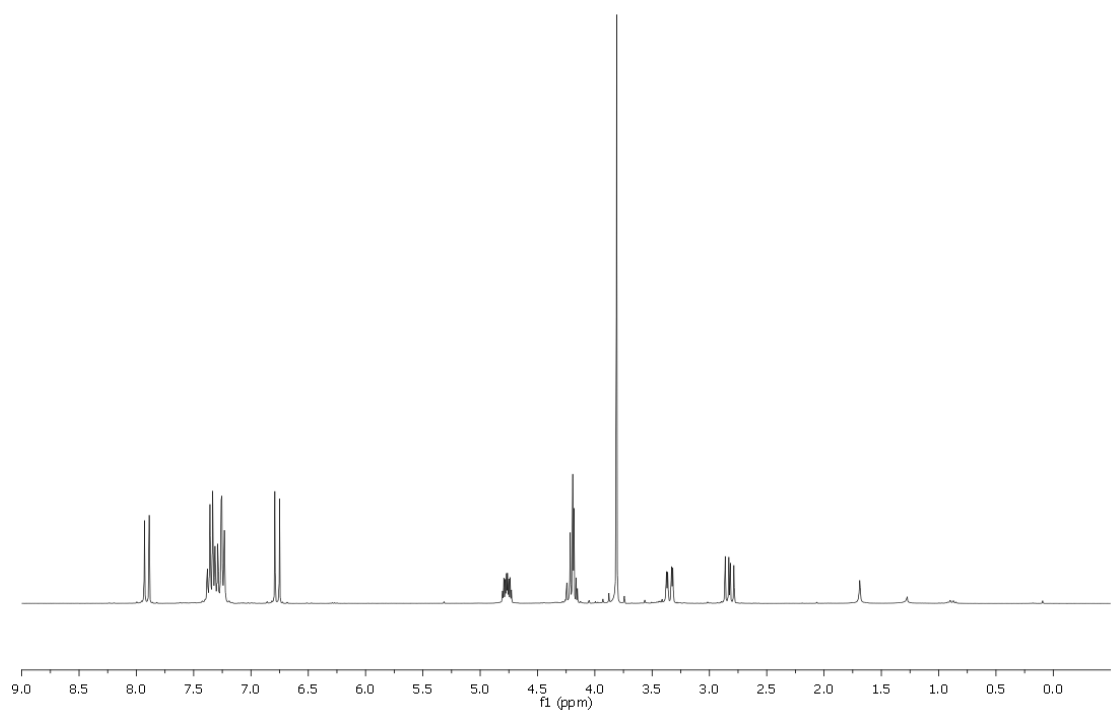
**Compound 7 (Z,E)**



**Compound 9a (E)**

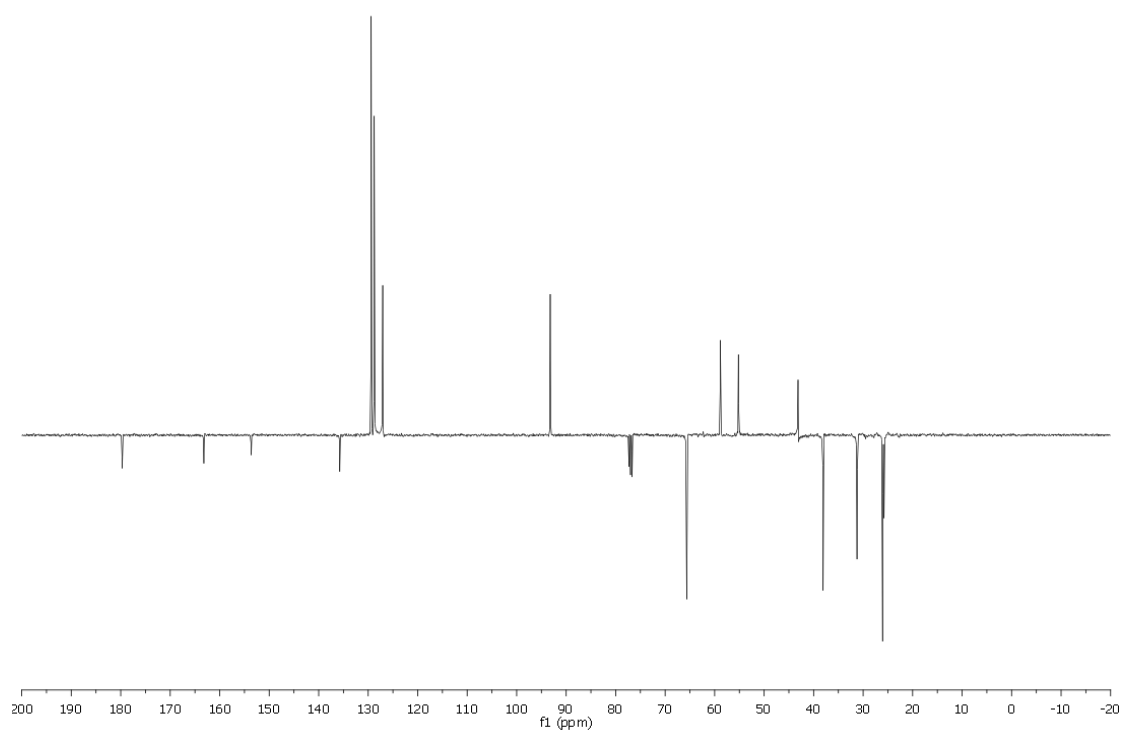
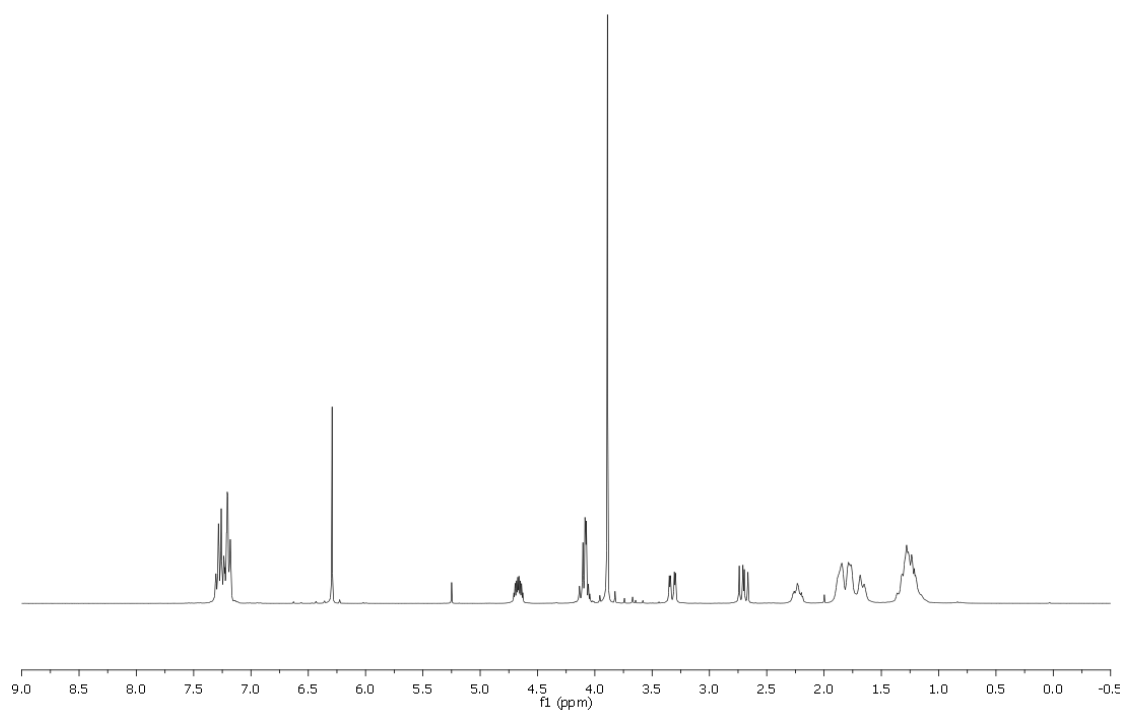


**Compound 9a (Z)**





**Compound 9b (Z)**



**Compound 9b (E)**

