

## **Cobalt-Catalyzed Esterification-Peroxidation of $\alpha$ -Diazoesters: Access to $\alpha$ -Acyloxy esters**

Rongxiang Chen,<sup>a</sup> Guoyang Ma,<sup>b</sup> Jinju Zhang,<sup>a</sup> Zhan-Yong Wang,<sup>a</sup> Shaohong Xu\*<sup>a</sup> and Kai-Kai Wang\*<sup>a</sup>

<sup>a</sup> School of Pharmacy, Xinxiang University, Xinxiang 453003, P.R. of China.

<sup>b</sup> School of Chemistry and Materials Engineering, Xinxiang University, Xinxiang 453003, P.R. China.

Email: xushaohong126@163.com; wangkaikai@163.com

Supporting Information

### **List of Contents**

<b>1. General information.....</b>	<b>S2</b>
<b>2. General procedures for reactions .....</b>	<b>S2</b>
<b>3. Compound characterizations .....</b>	<b>S3</b>
<b>4. Spectroscopic data for products.....</b>	<b>S12</b>

## 1. General information

All manipulations were carried out under air atmosphere. Column chromatography was generally performed on silica gel (300-400 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions. The  $^1\text{H}$  NMR (400 MHz),  $^{13}\text{C}$  NMR (100 MHz) and  $^{19}\text{F}$  NMR (376 MHz) data were recorded on a Bruker DPX-400 spectrometer with  $\text{CDCl}_3$  as solvent at room temperature unless specified otherwise. The chemical shifts ( $\delta$ ) are reported in ppm and coupling constants ( $J$ ) in Hz.  $^1\text{H}$  NMR spectra was recorded with tetramethylsilane ( $\delta = 0.00$  ppm) as internal reference;  $^{13}\text{C}$  NMR spectra was recorded with  $\text{CDCl}_3$  ( $\delta = 77.00$  ppm) as internal reference. HRMS were performed on Agilent ESI-quadrupole.

## 2. General procedures for reactions

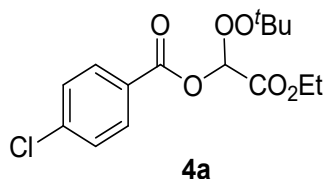
### 2.1 General procedures of synthesis of **4**

A solution of carboxylic acids **1** (0.4 mmol), diazo compound **2** (3.0 equiv, 1.2 mmol),  $\text{Co}(\text{acac})_2$  (0.08 mmol, 20 mol%), *tert*-butyl hydroperoxide (4.0 equiv, 1.6 mmol, 70% in water) and EtOAc (2 mL) was stirred in a 10 mL sealed tube at 80 °C for 12 h. After completion of the reaction, the reaction solution was then quenched with saturated  $\text{Na}_2\text{SO}_3$  solution and extracted with ethyl acetate (10 mL  $\times$  3). The combined organic layer was combined and dried with anhydrous  $\text{Na}_2\text{SO}_4$ . Removal of the organic solvent followed by flash column chromatographic purification afforded the desired products using petroleum and ethyl acetate.

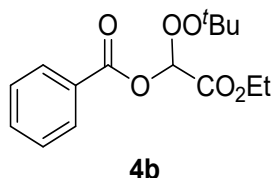
### 2.2 General procedures of synthesis of gram scale of **4a**

To an oven-dried 20 mL Schlenk tube equipped with a stir bar, were added 4-chlorobenzoic acid **1a** (5 mmol, 0.783g) and  $\text{Co}(\text{acac})_2$  (1.0 mmol, 356 mg). Then EtOAc (20 mL), ethyl 2-diazoacetate **2a** (15.0 mmol, 1.71g), and *tert*-butyl hydroperoxide (20.0 mmol, 2.74 mL) were added in sequence. The solution was then stirred at 80 °C for 18 h. After completion of the reaction, 30 mL of water was added and extracted by ethyl acetate (3  $\times$  10 mL). The combined organic layer was washed with brine (5 mL) and then dried over anhydrous  $\text{Na}_2\text{SO}_4$  and evaporated in vacuum. The desired **4a** was obtained in 62% yield (1.02 g) after purification by column chromatography on silica gel eluting with petroleum ether / ethyl acetate (15:1).

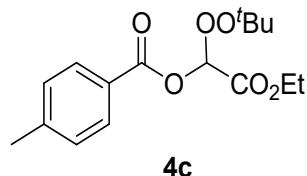
### 3. Compound characterizations



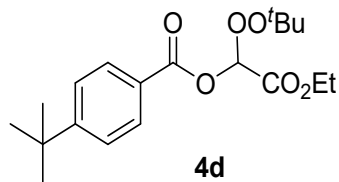
**1-(*tert*-butylperoxy)-2-ethoxy-2-oxoethyl 4-chlorobenzoate (4a).** Colorless liquid (75% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 (t,  $J = 9.6$  Hz, 2H), 7.45 (d,  $J = 7.8$  Hz, 2H), 6.61 (s, 1H), 4.32 (q,  $J = 7.1$  Hz, 2H), 1.34 (t,  $J = 6.9$  Hz, 3H), 1.28 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.4, 163.6, 140.2, 131.5, 128.9, 127.5, 95.0, 82.5, 62.4, 27.7, 26.3, 14.0; HRMS (ESI-TOF): Anal. Calcd. For  $\text{C}_{15}\text{H}_{19}^{35}\text{ClO}_6$ : 353.0768, Found: 353.0756 ( $\text{M}+\text{Na}^+$ );  $\text{C}_{15}\text{H}_{19}^{37}\text{ClO}_6$ : 355.0738, Found: 355.0724 ( $\text{M}+\text{Na}^+$ ).



**1-(*tert*-butylperoxy)-2-ethoxy-2-oxoethyl benzoate (4b).** Colorless liquid (77% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.15 (d,  $J = 7.7$  Hz, 2H), 7.60 (t,  $J = 7.4$  Hz, 1H), 7.47 (t,  $J = 7.6$  Hz, 2H), 6.64 (s, 1H), 4.32 (q,  $J = 7.1$  Hz, 2H), 1.33 (t,  $J = 7.0$  Hz, 3H), 1.29 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.2, 163.7, 133.6, 130.1, 129.0, 128.4, 94.9, 82.3, 62.3, 26.2, 14.0; HRMS (ESI-TOF): Anal. Calcd. For  $\text{C}_{15}\text{H}_{20}\text{O}_6$ : 319.1152, Found: 319.1147 ( $\text{M}+\text{Na}^+$ ).

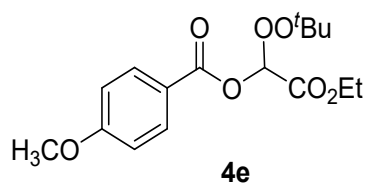


**1-(*tert*-butylperoxy)-2-ethoxy-2-oxoethyl 4-methylbenzoate (4c).** Colorless liquid (56% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 (d,  $J = 7.9$  Hz, 2H), 7.26 (d,  $J = 7.8$  Hz, 2H), 6.62 (s, 1H), 4.31 (q,  $J = 7.1$  Hz, 2H), 2.42 (s, 3H), 1.33 (t,  $J = 7.0$  Hz, 3H), 1.28 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.3, 163.8, 144.4, 130.1, 129.2, 126.3, 94.7, 82.3, 62.3, 26.2, 21.7, 14.0. HRMS (ESI-TOF): Anal. Calcd. For  $\text{C}_{16}\text{H}_{22}\text{O}_6$ : 333.1309, Found: 333.1301 ( $\text{M}+\text{Na}^+$ ).

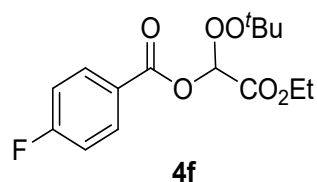


**1-(*tert*-butylperoxy)-2-ethoxy-2-oxoethyl 4-(*tert*-butyl)benzoate (4d).** Yellowish liquid (71% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 (d,  $J = 8.3$  Hz, 2H), 7.49 (d,  $J = 8.3$  Hz, 2H), 6.63 (s, 1H), 4.31 (q,  $J = 7.1$  Hz, 2H), 1.34 (s, 9H), 1.32 (d,  $J = 7.1$  Hz, 3H), 1.29 (s, 9H);  $^{13}\text{C}$  NMR (101

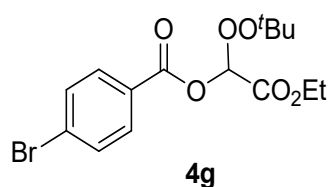
MHz, CDCl<sub>3</sub>)  $\delta$  165.2, 163.8, 157.3, 130.0, 126.2, 125.4, 94.7, 82.2, 62.2, 35.1, 31.0, 26.3, 14.0; HRMS (ESI-TOF): Anal. Calcd. For C<sub>19</sub>H<sub>28</sub>O<sub>6</sub>: 375.1778, Found: 375.1772 (M+Na<sup>+</sup>).



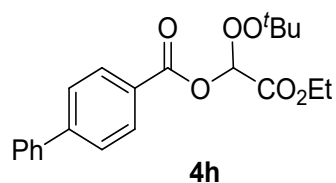
**1-(tert-butylperoxy)-2-ethoxy-2-oxoethyl 4-methoxybenzoate (4e).** Colorless liquid (63% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.10 (d, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 6.61 (s, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.28 (s, 9H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  164.9, 163.91, 163.88, 132.2, 121.3, 113.7, 94.6, 82.2, 62.2, 55.4, 26.2, 14.0; HRMS (ESI-TOF): Anal. Calcd. For C<sub>16</sub>H<sub>22</sub>O<sub>7</sub>: 349.1258, Found: 349.1252 (M+Na<sup>+</sup>).



**1-(tert-butylperoxy)-2-ethoxy-2-oxoethyl 4-fluorobenzoate (4f).** Colorless liquid (68% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.17 (dd, *J* = 8.4, 5.6 Hz, 2H), 7.15 (t, *J* = 8.5 Hz, 2H), 6.61 (s, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.29 (s, 9H); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -104.36; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  167.4, 164.9, 164.2, 163.6, 132.8, 132.7, 125.30, 125.27, 115.8, 115.6, 95.0, 82.4, 62.4, 26.2, 14.0; HRMS (ESI-TOF): Anal. Calcd. For C<sub>15</sub>H<sub>19</sub>FO<sub>6</sub>: 337.1058, Found: 337.1050 (M+Na<sup>+</sup>).

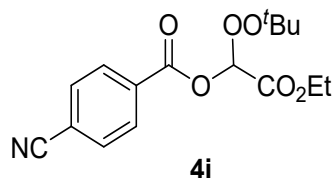


**1-(tert-butylperoxy)-2-ethoxy-2-oxoethyl 4-bromobenzoate (4g).** Colorless liquid (75% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.00 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 6.61 (s, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.28 (s, 9H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  164.5, 163.5, 131.8, 131.5, 128.8, 127.9, 95.0, 82.4, 62.4, 26.2, 14.0; HRMS (ESI-TOF): Anal. Calcd. For C<sub>15</sub>H<sub>19</sub><sup>79</sup>BrO<sub>6</sub>: 397.0263, Found: 397.0251 (M+ Na<sup>+</sup>); C<sub>15</sub>H<sub>19</sub><sup>81</sup>BrO<sub>6</sub>: 399.0242, Found: 399.0229 (M+ Na<sup>+</sup>).

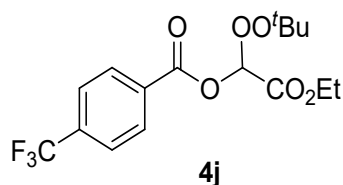


**1-(tert-butylperoxy)-2-ethoxy-2-oxoethyl [1,1'-biphenyl]-4-carboxylate (4h).** Colorless liquid

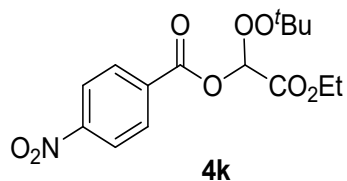
(47% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.21 (d,  $J = 8.1$  Hz, 2H), 7.69 (d,  $J = 8.1$  Hz, 2H), 7.63 (d,  $J = 7.7$  Hz, 2H), 7.47 (t,  $J = 7.5$  Hz, 2H), 7.40 (t,  $J = 7.2$  Hz, 1H), 6.66 (s, 1H), 4.33 (q,  $J = 7.1$  Hz, 2H), 1.34 (t,  $J = 7.2$  Hz, 3H), 1.30 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.1, 163.7, 146.4, 139.8, 130.6, 128.9, 128.2, 127.7, 127.3, 127.1, 94.9, 82.4, 62.3, 26.3, 14.0; HRMS (ESI-TOF): Anal. Calcd. For  $\text{C}_{21}\text{H}_{24}\text{O}_6$ : 395.1465, Found: 395.1458 ( $\text{M}+\text{Na}^+$ ).



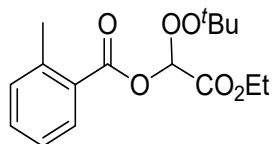
**1-(*tert*-butylperoxy)-2-ethoxy-2-oxoethyl 4-cyanobenzoate (4i).** Colorless liquid (32% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.24 (d,  $J = 8.0$  Hz, 2H), 7.79 (d,  $J = 8.0$  Hz, 2H), 6.62 (s, 1H), 4.33 (q,  $J = 7.1$  Hz, 2H), 1.34 (t,  $J = 7.1$  Hz, 3H), 1.29 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.7, 163.2, 132.9, 132.3, 130.6, 117.8, 117.1, 95.4, 82.6, 62.6, 26.3, 14.0; HRMS (ESI-TOF): Anal. Calcd. For  $\text{C}_{16}\text{H}_{19}\text{NO}_6$ : 344.1105, Found: 344.1098 ( $\text{M}+\text{Na}^+$ ).



**1-(*tert*-butylperoxy)-2-ethoxy-2-oxoethyl 4-(trifluoromethyl)benzoate (4j).** Colorless liquid (38% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.26 (d,  $J = 8.1$  Hz, 2H), 7.75 (d,  $J = 8.1$  Hz, 2H), 6.64 (s, 1H), 4.33 (q,  $J = 7.1$  Hz, 2H), 1.34 (t,  $J = 7.2$  Hz, 4H), 1.29 (s, 9H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.22;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.1, 163.4, 135.1 (q,  $J = 32.3$  Hz), 132.3, 130.5, 125.6 (q,  $J = 3.7$  Hz), 123.6 (q,  $J = 273.7$  Hz), 95.2, 82.6, 62.6, 26.3, 14.0; HRMS (ESI-TOF): Anal. Calcd. For  $\text{C}_{16}\text{H}_{19}\text{F}_3\text{O}_6$ : 387.1026, Found: 387.1019 ( $\text{M}+\text{Na}^+$ ).

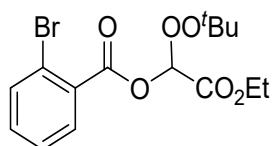


**1-(*tert*-butylperoxy)-2-ethoxy-2-oxoethyl 4-nitrobenzoate (4k).** Colorless liquid (38% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.32 (s, 4H), 6.64 (s, 1H), 4.34 (q,  $J = 7.1$  Hz, 2H), 1.35 (t,  $J = 6.9$  Hz, 3H), 1.30 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.4, 163.2, 150.9, 134.4, 131.2, 123.6, 95.4, 82.6, 62.6, 26.2, 14.0; HRMS (ESI-TOF): Anal. Calcd. For  $\text{C}_{15}\text{H}_{19}\text{NO}_8$ : 364.1003, Found: 364.0994 ( $\text{M}+\text{Na}^+$ ).



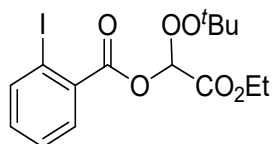
**4l**

**1-(*tert*-butylperoxy)-2-ethoxy-2-oxoethyl 2-methylbenzoate (4l).** Colorless liquid (90% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 (d,  $J = 7.7$  Hz, 1H), 7.43 (t,  $J = 7.5$  Hz, 1H), 7.27 (t,  $J = 7.7$  Hz, 2H), 6.61 (s, 1H), 4.32 (q,  $J = 7.1$  Hz, 2H), 2.64 (s, 3H), 1.33 (t,  $J = 7.1$  Hz, 3H), 1.28 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.0, 163.8, 141.0, 132.6, 131.7, 131.2, 128.3, 125.8, 94.7, 82.2, 62.2, 26.2, 21.6, 14.0; HRMS (ESI-TOF): Anal. Calcd. For  $\text{C}_{16}\text{H}_{22}\text{O}_6$ : 333.1309, Found: 333.1303 ( $\text{M}+\text{Na}^+$ ).



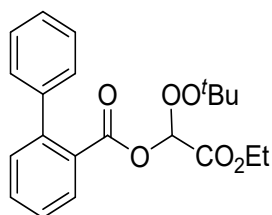
**4m**

**1-(*tert*-butylperoxy)-2-ethoxy-2-oxoethyl 2-bromobenzoate (4m).** Colorless liquid (84% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 – 7.98 (m, 1H), 7.69 (d,  $J = 7.3$  Hz, 1H), 7.43 – 7.33 (m, 2H), 6.62 (s, 1H), 4.33 (q,  $J = 7.1$  Hz, 2H), 1.34 (t,  $J = 7.1$  Hz, 3H), 1.29 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.2, 163.4, 134.5, 133.2, 132.0, 130.3, 127.2, 122.3, 95.1, 82.4, 62.4, 26.2, 13.9; HRMS (ESI-TOF): Anal. Calcd. For  $\text{C}_{15}\text{H}_{19}^{79}\text{BrO}_6$ : 397.0263, Found: 397.0252 ( $\text{M}+\text{Na}^+$ );  $\text{C}_{15}\text{H}_{19}^{81}\text{BrO}_6$ : 399.0242, Found: 399.0231 ( $\text{M}+\text{Na}^+$ ).



**4n**

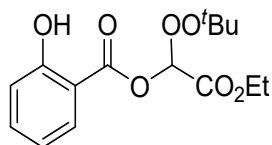
**1-(*tert*-butylperoxy)-2-ethoxy-2-oxoethyl 2-iodobenzoate (4n).** Colorless liquid (81% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 (t,  $J = 7.4$  Hz, 2H), 7.44 (t,  $J = 7.6$  Hz, 1H), 7.19 (t,  $J = 7.6$  Hz, 1H), 6.62 (s, 1H), 4.33 (q,  $J = 7.1$  Hz, 2H), 1.34 (t,  $J = 7.1$  Hz, 3H), 1.29 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.6, 163.4, 141.6, 133.3, 133.0, 131.8, 127.9, 95.2, 94.6, 82.4, 62.4, 26.2, 14.0; HRMS (ESI-TOF): Anal. Calcd. For  $\text{C}_{15}\text{H}_{19}\text{IO}_6$ : 445.0119, Found: 445.0112 ( $\text{M}+\text{Na}^+$ ).



**4o**

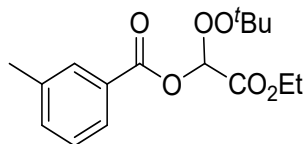
**1-(*tert*-butylperoxy)-2-ethoxy-2-oxoethyl [1,1'-biphenyl]-2-carboxylate (4o).** Colorless liquid (71% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 (d,  $J = 7.7$  Hz, 1H), 7.55 (t,  $J = 7.5$  Hz, 1H), 7.44

– 7.29 (m, 7H), 6.45 (s, 1H), 4.25 (q,  $J = 7.1$  Hz, 2H), 1.29 (t,  $J = 7.1$  Hz, 3H), 1.25 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.3, 163.5, 143.4, 140.7, 131.9, 131.0, 130.4, 129.1, 128.6, 127.9, 127.3, 127.1, 94.9, 82.2, 62.2, 26.2, 13.9; HRMS (ESI-TOF): Anal. Calcd. For  $\text{C}_{21}\text{H}_{24}\text{O}_6$ : 395.1465, Found: 395.1459 ( $\text{M}+\text{Na}^+$ ).



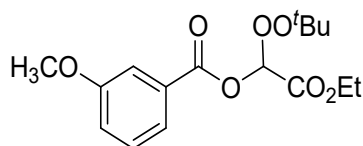
**4p**

**1-(tert-butylperoxy)-2-ethoxy-2-oxoethyl 2-hydroxybenzoate (4p).** Colorless liquid (26% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.33 (s, 1H), 8.01 (d,  $J = 8.0$  Hz, 1H), 7.50 (t,  $J = 7.8$  Hz, 1H), 7.00 (d,  $J = 8.4$  Hz, 1H), 6.93 (t,  $J = 7.6$  Hz, 1H), 6.62 (s, 1H), 4.33 (q,  $J = 7.1$  Hz, 2H), 1.35 (d,  $J = 7.8$  Hz, 3H), 1.29 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  168.7, 163.2, 162.0, 136.4, 130.6, 119.4, 117.7, 111.6, 94.9, 82.6, 26.3, 14.0; HRMS (ESI-TOF): Anal. Calcd. For  $\text{C}_{15}\text{H}_{20}\text{O}_7$ : 335.1101, Found: 335.1095 ( $\text{M}+\text{Na}^+$ ).



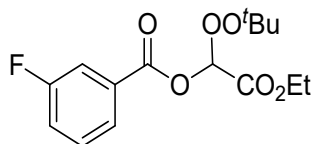
**4q**

**1-(tert-butylperoxy)-2-ethoxy-2-oxoethyl 3-methylbenzoate (4q).** Colorless liquid (76% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (d,  $J = 7.6$  Hz, 2H), 7.37 (dt,  $J = 15.3, 7.6$  Hz, 2H), 6.63 (s, 1H), 4.31 (q,  $J = 7.1$  Hz, 2H), 2.41 (s, 3H), 1.33 (t,  $J = 7.1$  Hz, 3H), 1.29 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.4, 163.7, 138.2, 134.4, 130.5, 128.9, 128.3, 127.2, 94.9, 82.3, 62.3, 26.2, 21.1, 14.0; HRMS (ESI-TOF): Anal. Calcd. For  $\text{C}_{16}\text{H}_{22}\text{O}_6$ : 333.1309, Found: 333.1303 ( $\text{M}+\text{Na}^+$ ).



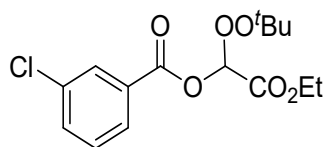
**4r**

**1-(tert-butylperoxy)-2-ethoxy-2-oxoethyl 3-methoxybenzoate (4r).** Colorless liquid (76% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75 (d,  $J = 7.7$  Hz, 1H), 7.64 (s, 1H), 7.37 (t,  $J = 7.9$  Hz, 1H), 7.14 (dd,  $J = 8.2, 1.6$  Hz, 1H), 6.62 (s, 1H), 4.32 (q,  $J = 7.1$  Hz, 2H), 3.85 (s, 3H), 1.33 (t,  $J = 7.1$  Hz, 3H), 1.29 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.1, 163.6, 159.6, 130.3, 129.5, 122.5, 120.2, 114.3, 95.0, 82.3, 62.3, 55.4, 26.2, 14.0; HRMS (ESI-TOF): Anal. Calcd. For  $\text{C}_{16}\text{H}_{22}\text{O}_7$ : 349.1258, Found: 349.1254 ( $\text{M}+\text{Na}^+$ ).



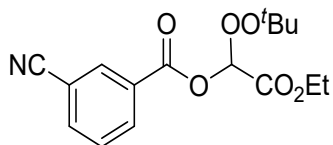
**4s**

**1-(tert-butylperoxy)-2-ethoxy-2-oxoethyl 3-fluorobenzoate (4s).** Colorless liquid (72% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (d,  $J = 7.7$  Hz, 1H), 7.82 (d,  $J = 9.2$  Hz, 1H), 7.46 (dd,  $J = 13.6$ , 7.9 Hz, 1H), 7.34 – 7.26 (m, 1H), 6.62 (s, 1H), 4.32 (q,  $J = 7.1$  Hz, 2H), 1.34 (t,  $J = 7.1$  Hz, 3H), 1.29 (s, 9H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -112.06;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.1 (d,  $J = 3.0$  Hz), 163.4, 162.5 (d,  $J = 248.5$  Hz), 131.2 (d,  $J = 7.1$  Hz), 130.1 (d,  $J = 8.1$  Hz), 125.8 (d,  $J = 3.0$  Hz), 120.7 (d,  $J = 21.2$  Hz), 116.9 (d,  $J = 23.2$  Hz), 95.1, 82.4, 62.4, 26.2, 14.0; HRMS (ESI-TOF): Anal. Calcd. For  $\text{C}_{15}\text{H}_{19}\text{FO}_6$ : 337.1058, Found: 337.105 ( $\text{M}+\text{Na}^+$ ).



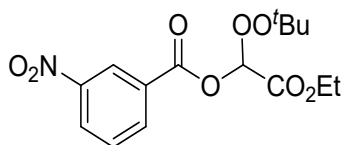
**4t**

**1-(tert-butylperoxy)-2-ethoxy-2-oxoethyl 3-chlorobenzoate (4t).** Colorless liquid (68% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 (s, 1H), 7.94 (d,  $J = 7.8$  Hz, 1H), 7.49 (d,  $J = 8.1$  Hz, 1H), 7.34 (t,  $J = 7.9$  Hz, 1H), 6.54 (s, 1H), 4.24 (q,  $J = 7.1$  Hz, 2H), 1.26 (t,  $J = 7.2$  Hz, 3H), 1.21 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.0, 163.4, 134.6, 133.6, 130.8, 130.0, 129.8, 128.2, 95.1, 82.5, 62.4, 26.2, 14.0; HRMS (ESI-TOF): Anal. Calcd. For  $\text{C}_{15}\text{H}_{19}^{35}\text{ClO}_6$ : 353.0768, Found: 353.0752 ( $\text{M}+\text{Na}^+$ );  $\text{C}_{15}\text{H}_{19}^{37}\text{ClO}_6$ : 355.0738, Found: 355.0728 ( $\text{M}+\text{Na}^+$ ).



**4u**

**1-(tert-butylperoxy)-2-ethoxy-2-oxoethyl 3-cyanobenzoate (4u).** Colorless liquid (57% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.43 (s, 1H), 8.36 (d,  $J = 7.9$  Hz, 1H), 7.90 (d,  $J = 7.8$  Hz, 1H), 7.64 (t,  $J = 7.8$  Hz, 1H), 6.63 (s, 1H), 4.33 (q,  $J = 7.1$  Hz, 2H), 1.35 (t,  $J = 7.1$  Hz, 3H), 1.30 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.3, 163.2, 136.5, 134.0, 133.6, 130.4, 129.5, 117.6, 113.1, 95.3, 82.6, 62.5, 26.2, 13.9; HRMS (ESI-TOF): Anal. Calcd. For  $\text{C}_{16}\text{H}_{19}\text{NO}_6$ : 344.1105, Found: 344.1102 ( $\text{M}+\text{Na}^+$ ).

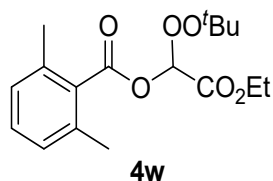


**4v**

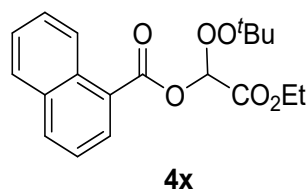
**1-(tert-butylperoxy)-2-ethoxy-2-oxoethyl 3-nitrobenzoate (4v).** Colorless liquid (37% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.96 (s, 1H), 8.47 (d,  $J = 7.9$  Hz, 2H), 7.71 (t,  $J = 8.0$  Hz, 1H), 6.65 (s,



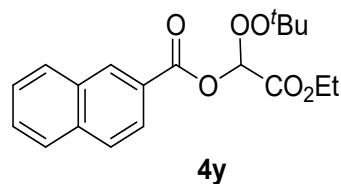
1H), 4.34 (q,  $J = 7.1$  Hz, 2H), 1.36 (t,  $J = 6.9$  Hz, 3H), 1.31 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.2, 163.2, 148.4, 135.6, 130.9, 129.8, 128.0, 95.5, 82.7, 62.6, 26.2, 14.0; HRMS (ESI-TOF): Anal. Calcd. For  $\text{C}_{15}\text{H}_{19}\text{NO}_8$ : 364.1003, Found: 364.0998 ( $\text{M}+\text{Na}^+$ ).



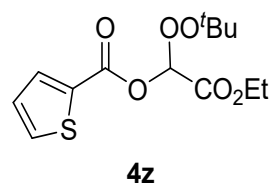
**1-(tert-butylperoxy)-2-ethoxy-2-oxoethyl 2,6-dimethylbenzoate (4w).** Colorless liquid (86% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.11 (t,  $J = 7.6$  Hz, 1H), 6.95 (d,  $J = 7.6$  Hz, 2H), 6.57 (s, 1H), 4.23 (q,  $J = 7.1$  Hz, 2H), 2.33 (s, 6H), 1.25 (t,  $J = 7.2$  Hz, 3H), 1.20 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  168.6, 163.5, 135.6, 132.4, 129.7, 127.6, 94.7, 82.3, 62.3, 26.2, 19.7, 13.9; HRMS (ESI-TOF): Anal. Calcd. For  $\text{C}_{17}\text{H}_{24}\text{O}_6$ : 347.1465, Found: 347.1461 ( $\text{M}+\text{Na}^+$ ).



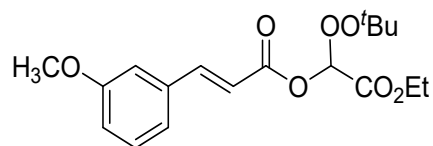
**1-(tert-butylperoxy)-2-ethoxy-2-oxoethyl 1-naphthoate (4x).** Yellowish liquid (64% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.00 (d,  $J = 8.7$  Hz, 1H), 8.40 (d,  $J = 7.3$  Hz, 1H), 8.04 (d,  $J = 8.2$  Hz, 1H), 7.88 (d,  $J = 8.1$  Hz, 1H), 7.62 (t,  $J = 7.7$  Hz, 1H), 7.52 (dd,  $J = 14.0, 6.9$  Hz, 2H), 6.74 (s, 1H), 4.35 (q,  $J = 7.1$  Hz, 2H), 1.35 (t,  $J = 7.1$  Hz, 3H), 1.30 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.0, 163.9, 134.1, 133.8, 131.4, 131.2, 128.5, 128.0, 126.3, 125.7, 125.6, 124.5, 94.9, 82.3, 62.4, 26.3, 14.0; HRMS (ESI-TOF): Anal. Calcd. For  $\text{C}_{19}\text{H}_{22}\text{O}_6$ : 369.1309, Found: 369.1305 ( $\text{M}+\text{Na}^+$ ).



**1-(tert-butylperoxy)-2-ethoxy-2-oxoethyl 2-naphthoate (4y).** Colorless liquid (63% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.74 (s, 1H), 8.14 (d,  $J = 8.6$  Hz, 1H), 7.97 (d,  $J = 8.0$  Hz, 1H), 7.89 (t,  $J = 8.4$  Hz, 2H), 7.57 (dt,  $J = 14.9, 7.1$  Hz, 2H), 6.72 (s, 1H), 4.34 (q,  $J = 7.1$  Hz, 2H), 1.34 (t,  $J = 7.2$  Hz, 3H), 1.31 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.4, 163.8, 135.8, 132.4, 131.9, 129.5, 128.6, 128.2, 127.7, 126.7, 126.2, 125.3, 95.0, 82.4, 62.4, 26.3, 14.0; HRMS (ESI-TOF): Anal. Calcd. For  $\text{C}_{19}\text{H}_{22}\text{O}_6$ : 369.1309, Found: 369.1305 ( $\text{M}+\text{Na}^+$ ).

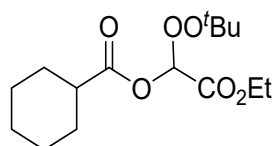


**1-(*tert*-butylperoxy)-2-ethoxy-2-oxoethyl thiophene-2-carboxylate (4z).** Yellowish liquid (57% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (d,  $J = 3.7$  Hz, 1H), 7.64 (d,  $J = 5.0$  Hz, 1H), 7.14 (t,  $J = 4.2$  Hz, 1H), 6.59 (s, 1H), 4.31 (q,  $J = 7.1$  Hz, 2H), 1.33 (t,  $J = 7.1$  Hz, 3H), 1.29 (s, 9H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.5, 160.7, 134.6, 133.6, 132.3, 127.9, 94.7, 82.4, 62.3, 26.2, 13.9; HRMS (ESI-TOF): Anal. Calcd. For  $\text{C}_{13}\text{H}_{18}\text{O}_6\text{S}$ : 325.0716, Found: 325.0711 ( $\text{M}+\text{Na}^+$ ).



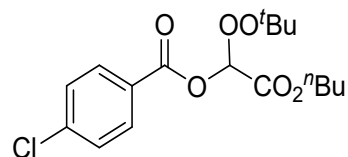
**4aa**

**(*E*)-1-(*tert*-butylperoxy)-2-ethoxy-2-oxoethyl 3-(3-methoxyphenyl)acrylate (4aa).** Colorless liquid (43% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78 (d,  $J = 16.0$  Hz, 1H), 7.31 (t,  $J = 7.9$  Hz, 1H), 7.14 (d,  $J = 7.5$  Hz, 1H), 7.07 (s, 1H), 6.96 (d,  $J = 8.2$  Hz, 1H), 6.55 (d,  $J = 15.1$  Hz, 2H), 4.32 (q,  $J = 7.1$  Hz, 2H), 3.83 (s, 3H), 1.34 (t,  $J = 7.1$  Hz, 3H), 1.29 (s, 9H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.3, 163.8, 159.9, 146.7, 135.4, 129.9, 121.0, 117.0, 116.7, 112.9, 94.4, 82.3, 62.3, 55.2, 26.2, 14.0; HRMS (ESI-TOF): Anal. Calcd. For  $\text{C}_{18}\text{H}_{24}\text{O}_7$ : 375.1414, Found: 375.1407 ( $\text{M}+\text{Na}^+$ ).



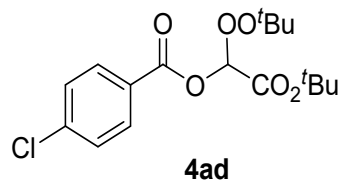
**4ab**

**1-(*tert*-butylperoxy)-2-ethoxy-2-oxoethyl cyclohexanecarboxylate (4ab).** Colorless liquid (53% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.30 (s, 1H), 4.20 (q,  $J = 7.1$  Hz, 2H), 2.40 (tt,  $J = 11.0, 3.2$  Hz, 1H), 1.91 (t,  $J = 13.7$  Hz, 2H), 1.70 (d,  $J = 11.7$  Hz, 2H), 1.58 (d,  $J = 8.0$  Hz, 1H), 1.44 (dd,  $J = 23.8, 11.9$  Hz, 2H), 1.24 (dd,  $J = 13.3, 6.0$  Hz, 6H), 1.20 (s, 9H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.7, 163.8, 94.3, 82.2, 62.2, 42.8, 28.8, 28.5, 26.2, 25.6, 25.22, 25.16, 13.9; HRMS (ESI-TOF): Anal. Calcd. For  $\text{C}_{15}\text{H}_{26}\text{O}_6$ : 325.1622, Found: 325.1625 ( $\text{M}+\text{Na}^+$ ).



**4ac**

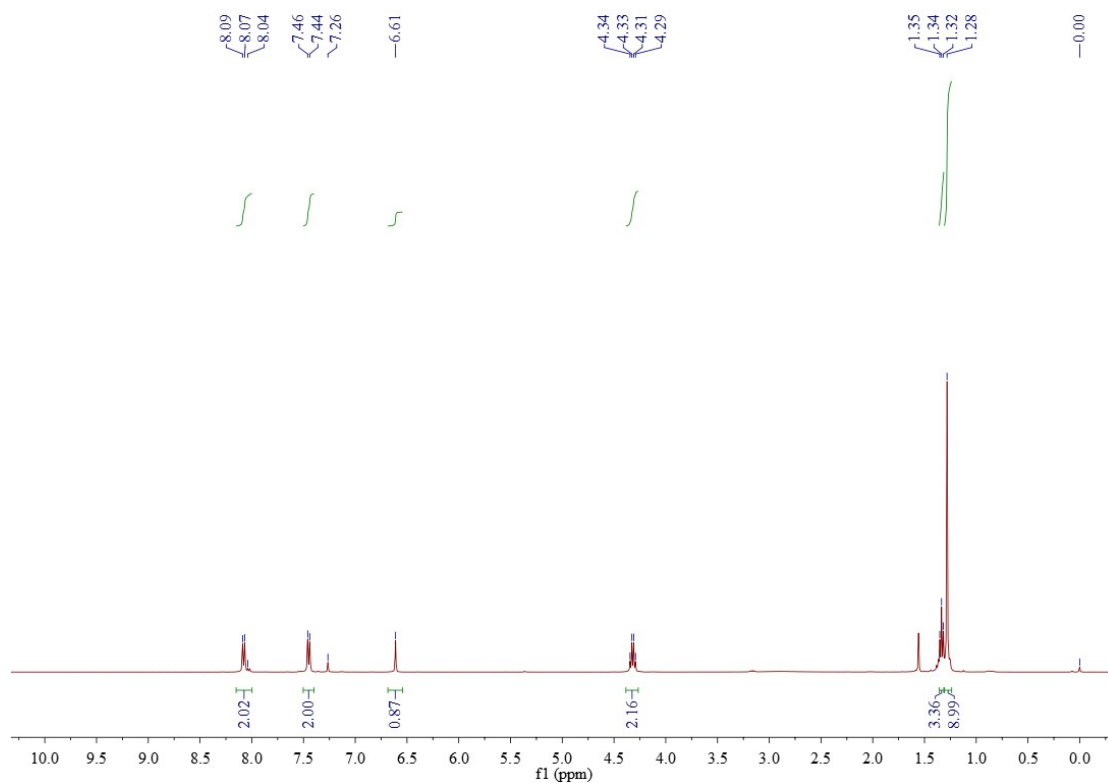
**2-butoxy-1-(*tert*-butylperoxy)-2-oxoethyl 4-chlorobenzoate (4ac).** Colorless liquid (90% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 (d,  $J = 8.0$  Hz, 2H), 7.45 (d,  $J = 8.0$  Hz, 2H), 6.62 (s, 1H), 4.27 (t,  $J = 6.3$  Hz, 2H), 1.72 – 1.63 (m, 2H), 1.41 (dd,  $J = 14.7, 7.4$  Hz, 2H), 1.28 (s, 9H), 0.93 (t,  $J = 7.3$  Hz, 3H), -0.95 – -0.96 (m, 1H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.3, 163.5, 140.1, 131.2, 128.8, 127.5, 95.0, 82.3, 66.1, 30.3, 26.2, 18.8, 13.5; HRMS (ESI-TOF): Anal. Calcd. For  $\text{C}_{17}\text{H}_{23}\text{ClO}_6$ : 381.1075, Found: 381.1069 ( $\text{M}+\text{Na}^+$ ).



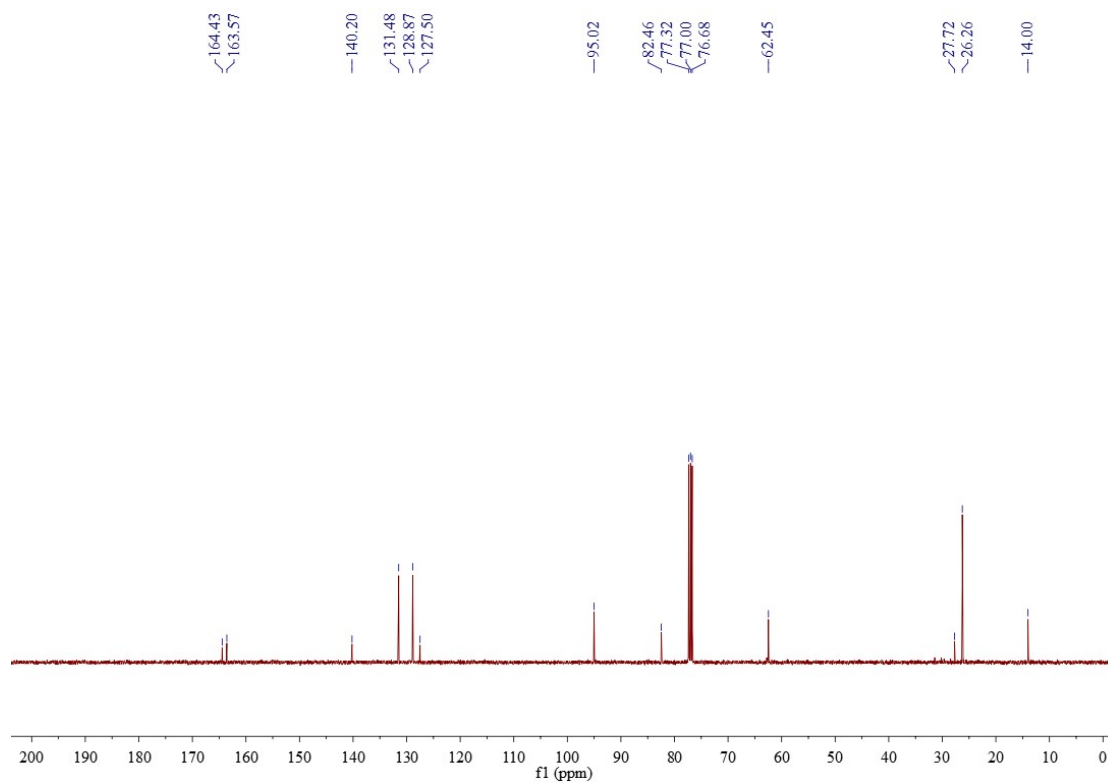
**2-(*tert*-butoxy)-1-(*tert*-butylperoxy)-2-oxoethyl 4-chlorobenzoate (4ad).** Colorless liquid (73% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 (d,  $J = 8.1$  Hz, 2H), 7.44 (d,  $J = 8.1$  Hz, 2H), 6.50 (s, 1H), 1.52 (s, 9H), 1.29 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.4, 162.3, 140.0, 131.4, 128.8, 127.7, 95.6, 83.6, 82.2, 27.8, 26.2; HRMS (ESI-TOF): Anal. Calcd. For  $\text{C}_{17}\text{H}_{23}\text{ClO}_6$ : 381.1075, Found: 381.1069 ( $\text{M}+\text{Na}^+$ ).

## 4. Spectroscopic data for products

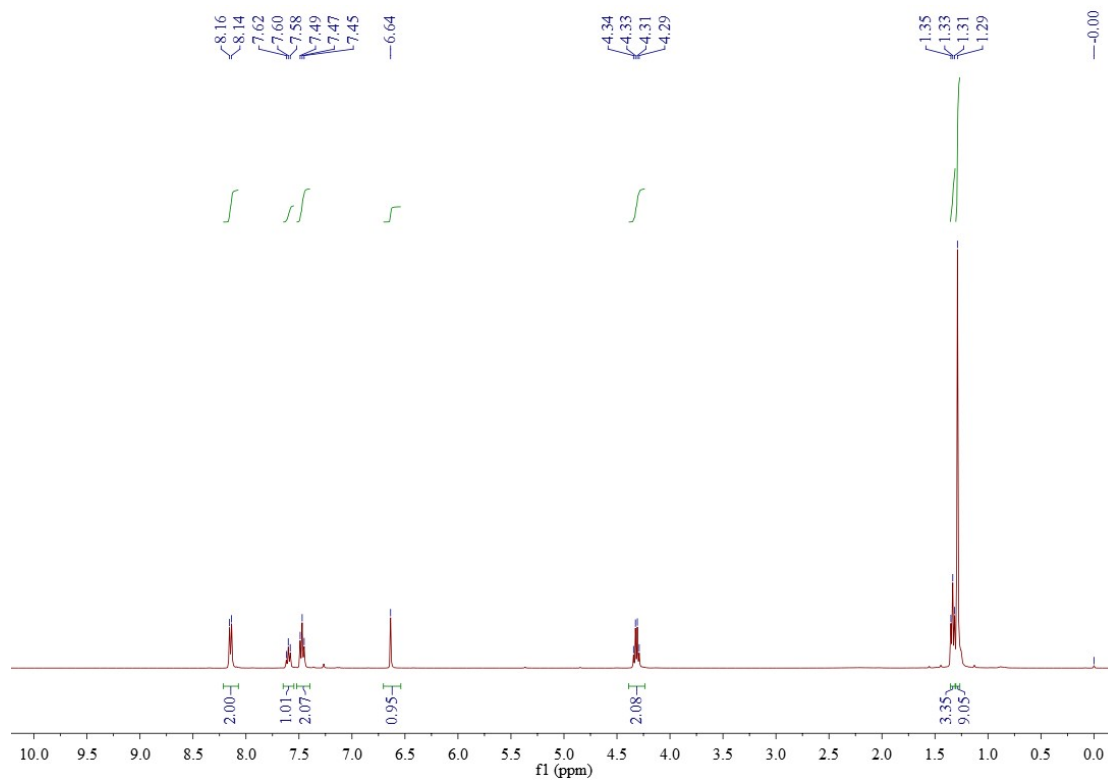
$^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ) spectra of **4a**



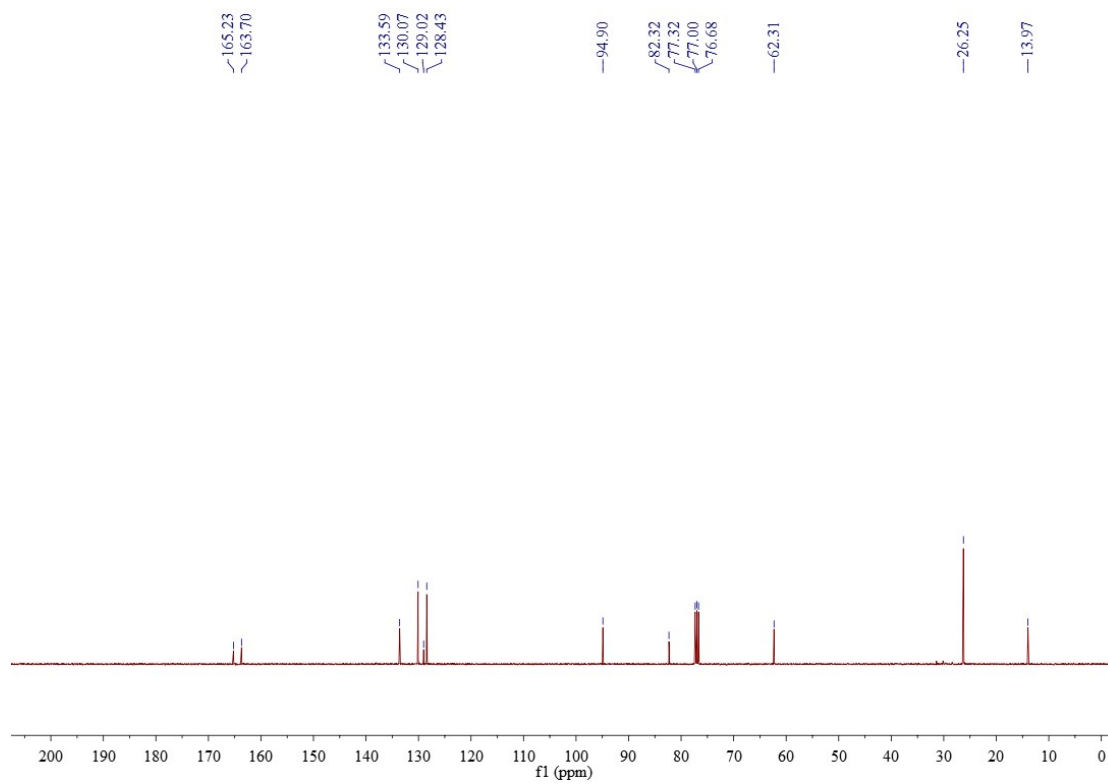
$^{13}\text{C}$  NMR (101MHz,  $\text{CDCl}_3$ ) spectra of **4a**



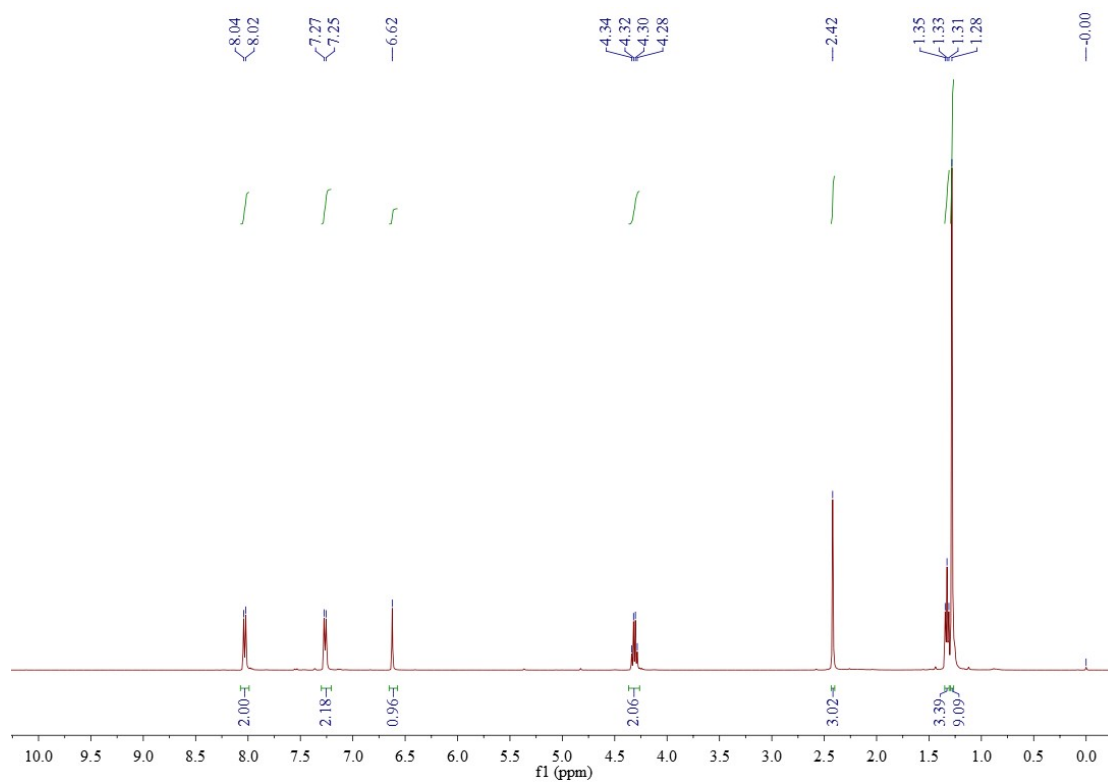
<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) spectra of **4b**



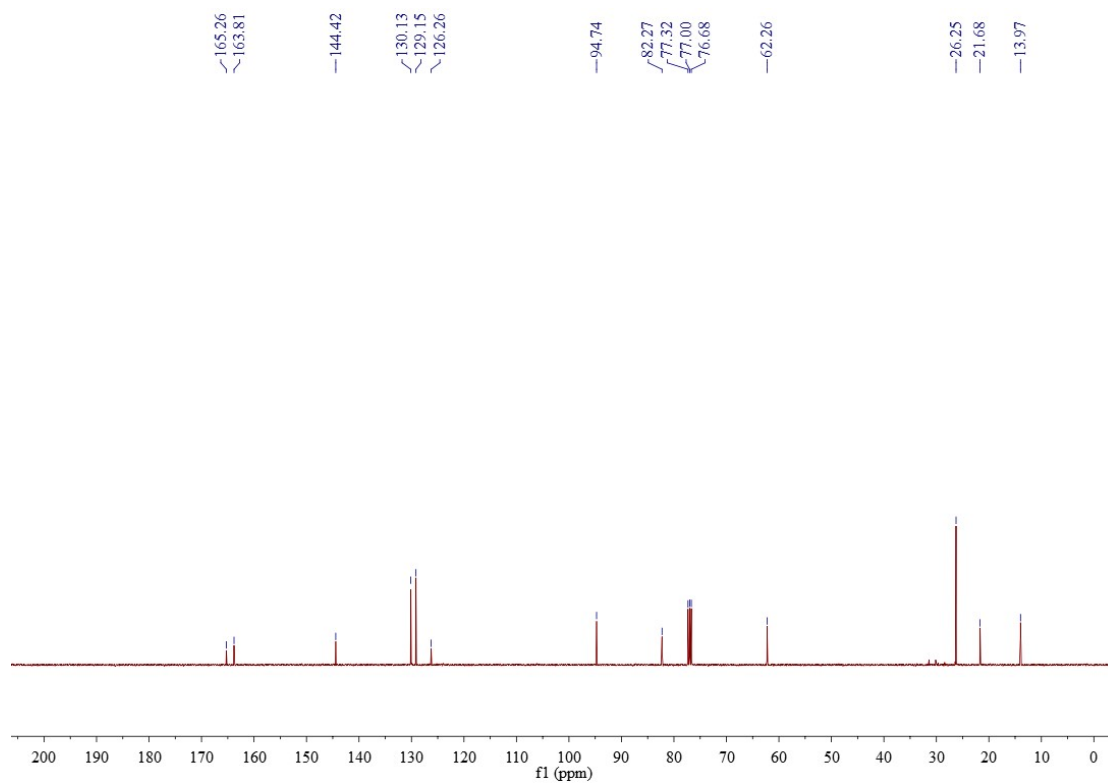
<sup>13</sup>C NMR (101MHz, CDCl<sub>3</sub>) spectra of **4b**



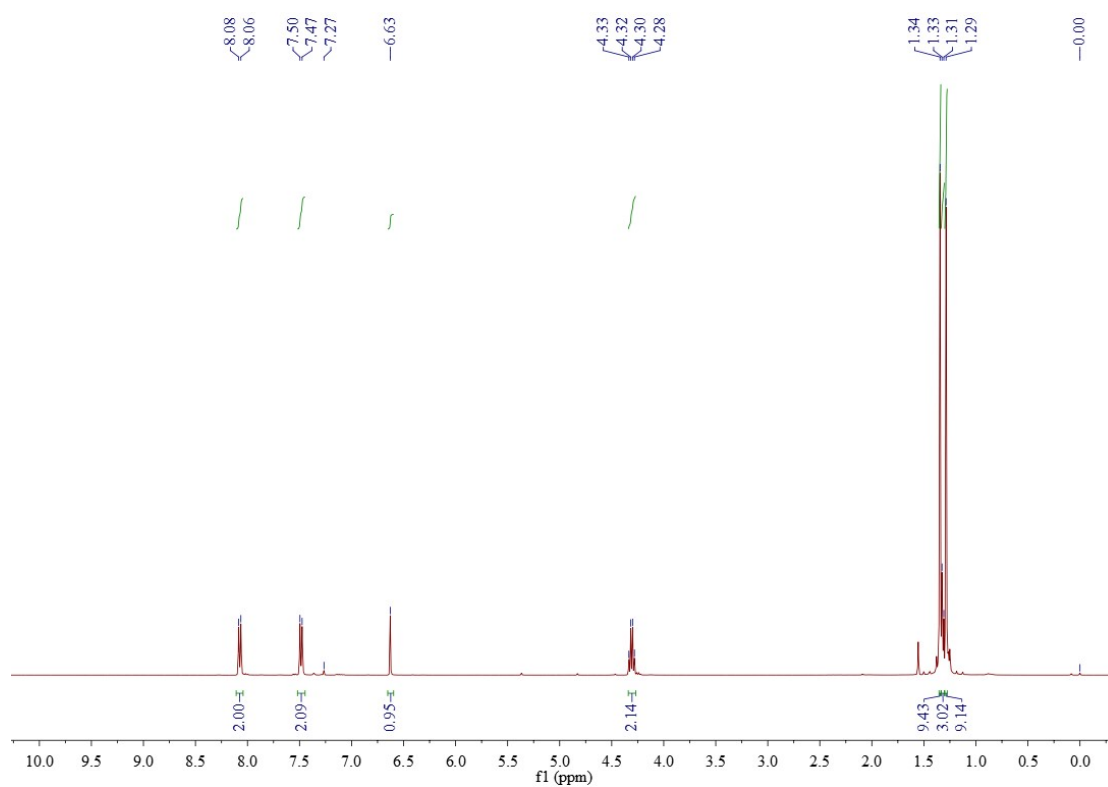
$^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ) spectra of **4c**



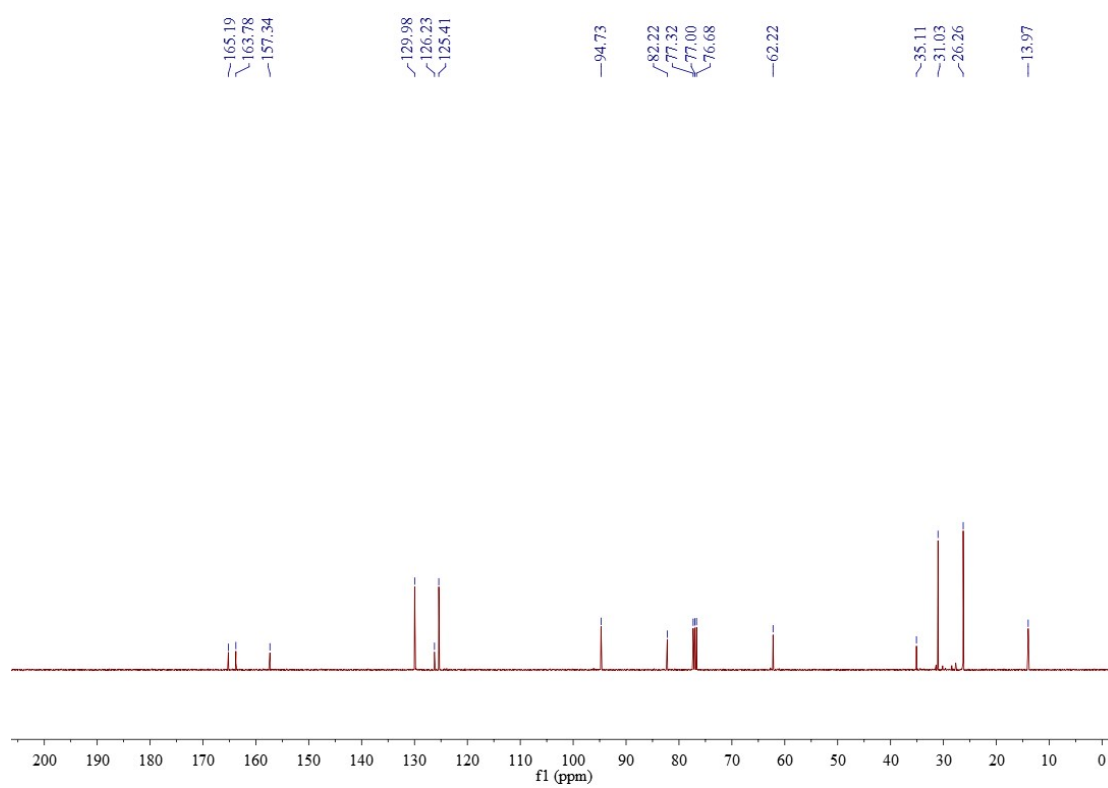
$^{13}\text{C}$  NMR (101MHz,  $\text{CDCl}_3$ ) spectra of **4c**



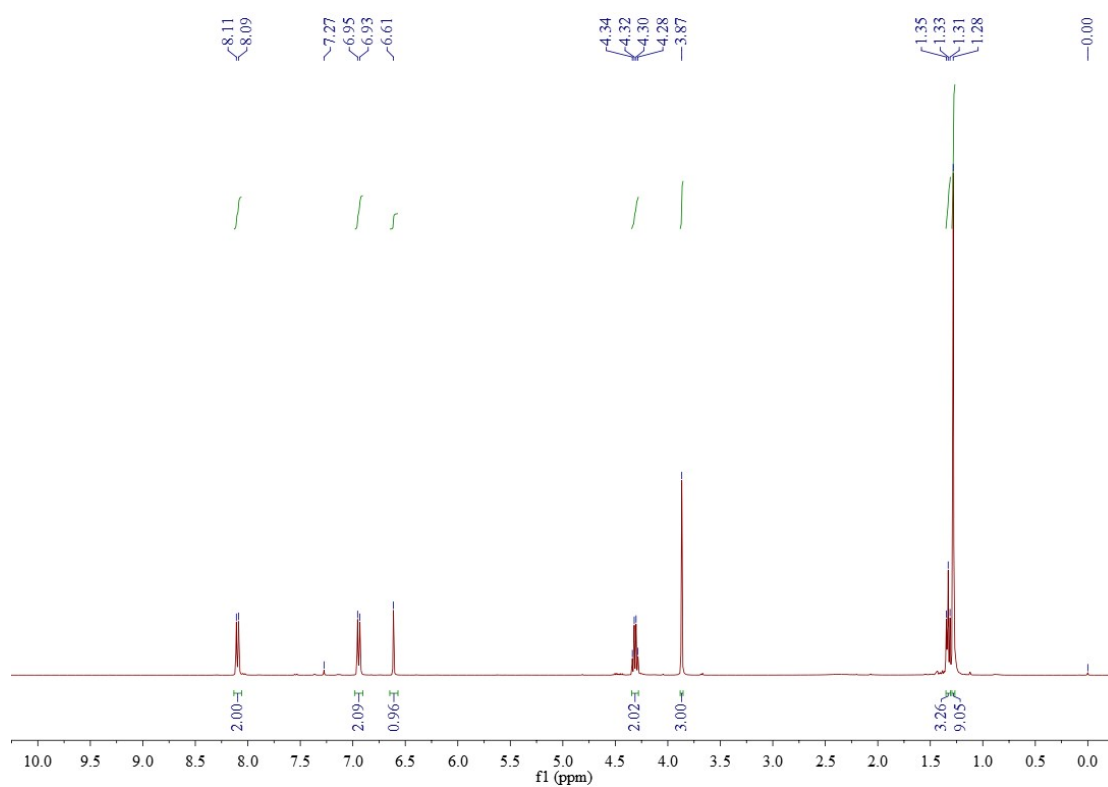
<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) spectra of **4d**



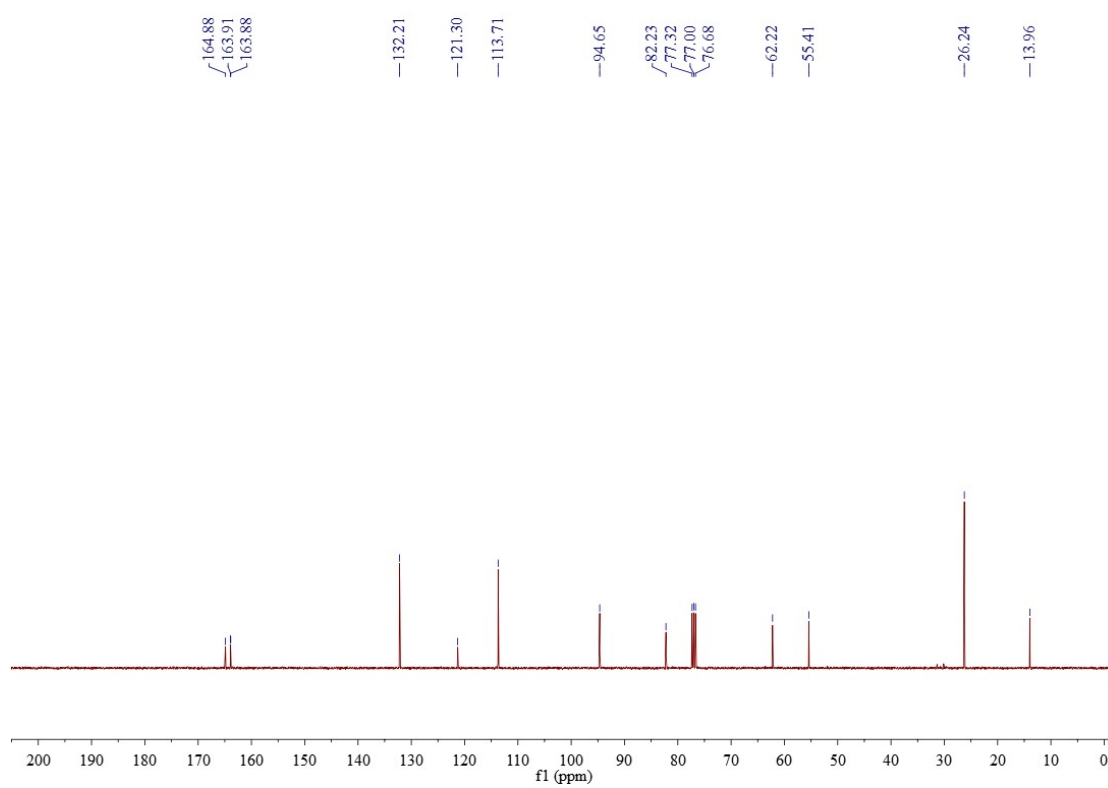
<sup>13</sup>C NMR (101MHz, CDCl<sub>3</sub>) spectra of **4d**



<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) spectra of **4e**

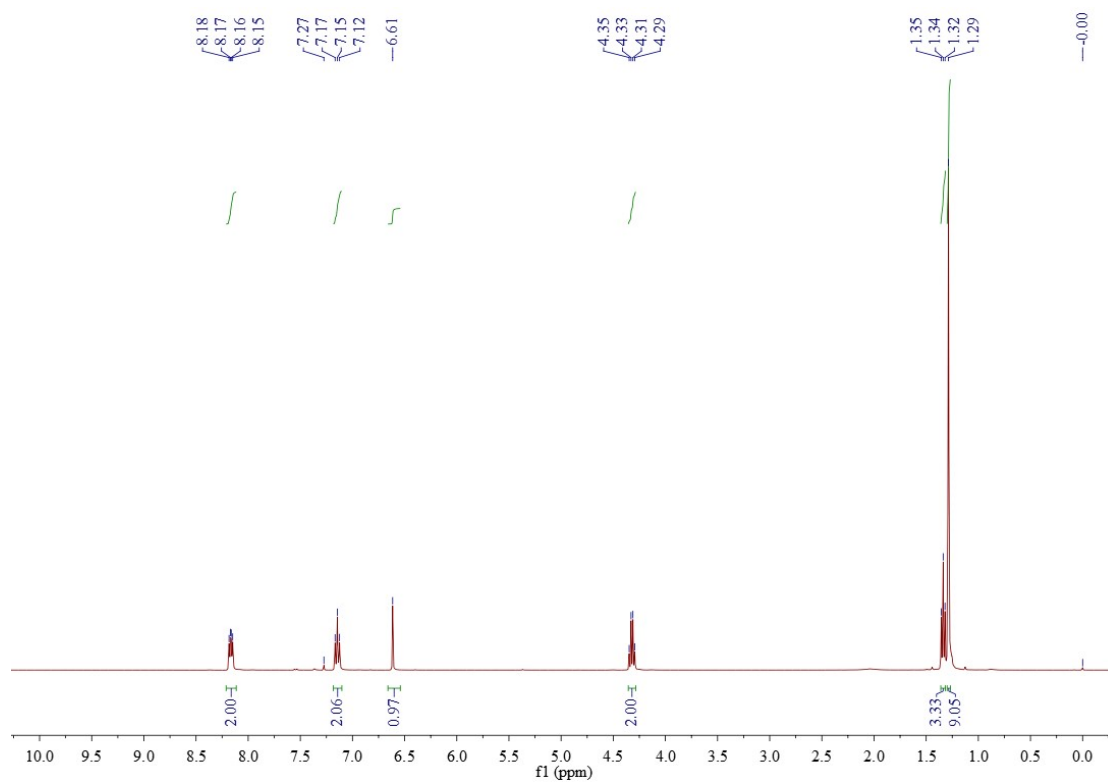


<sup>13</sup>C NMR (101MHz, CDCl<sub>3</sub>) spectra of **4e**

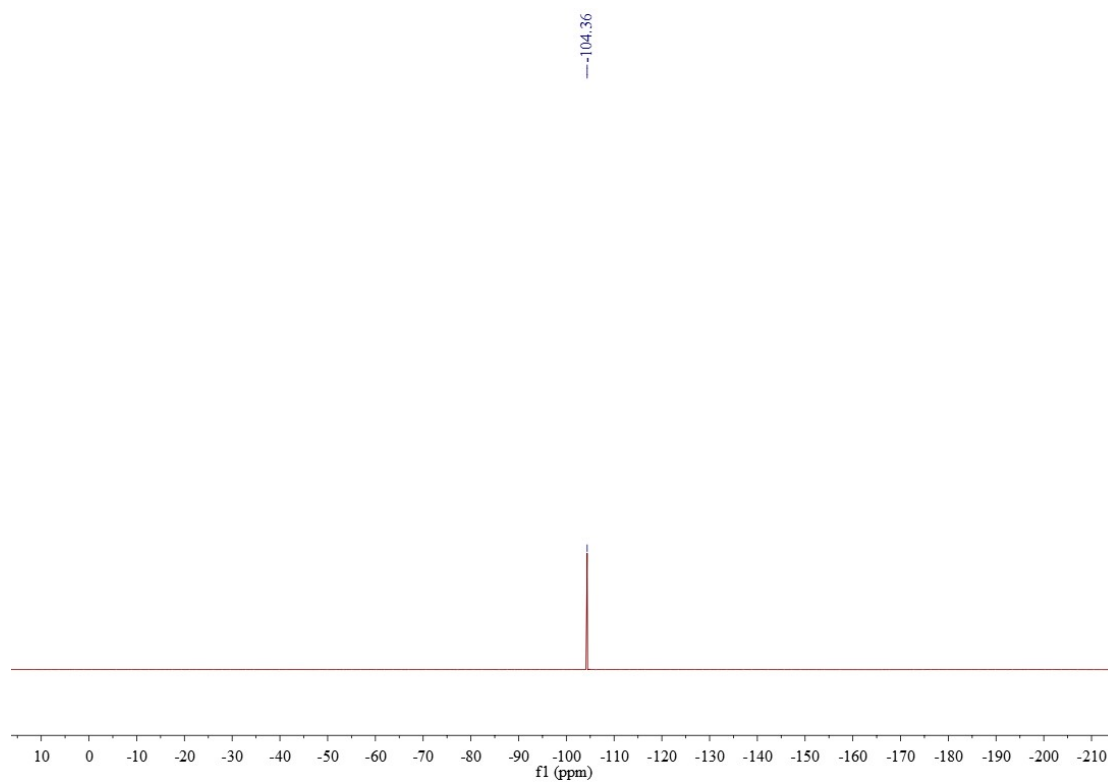




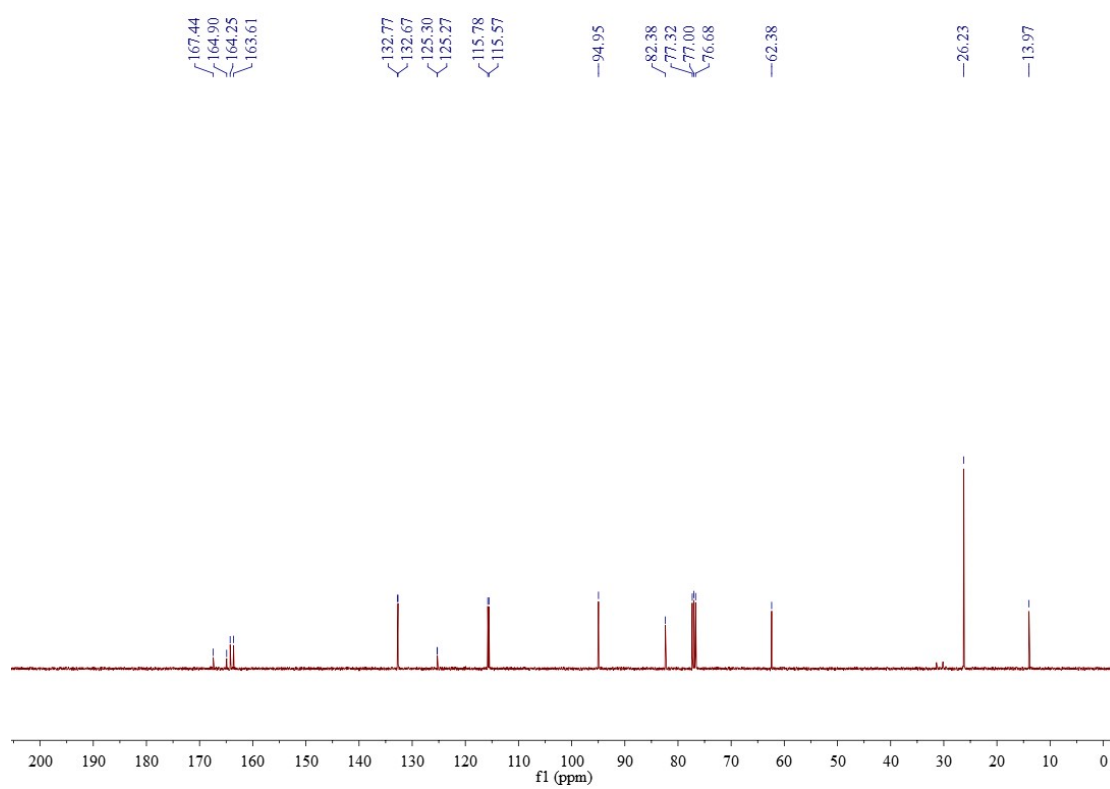
$^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ) spectra of **4f**



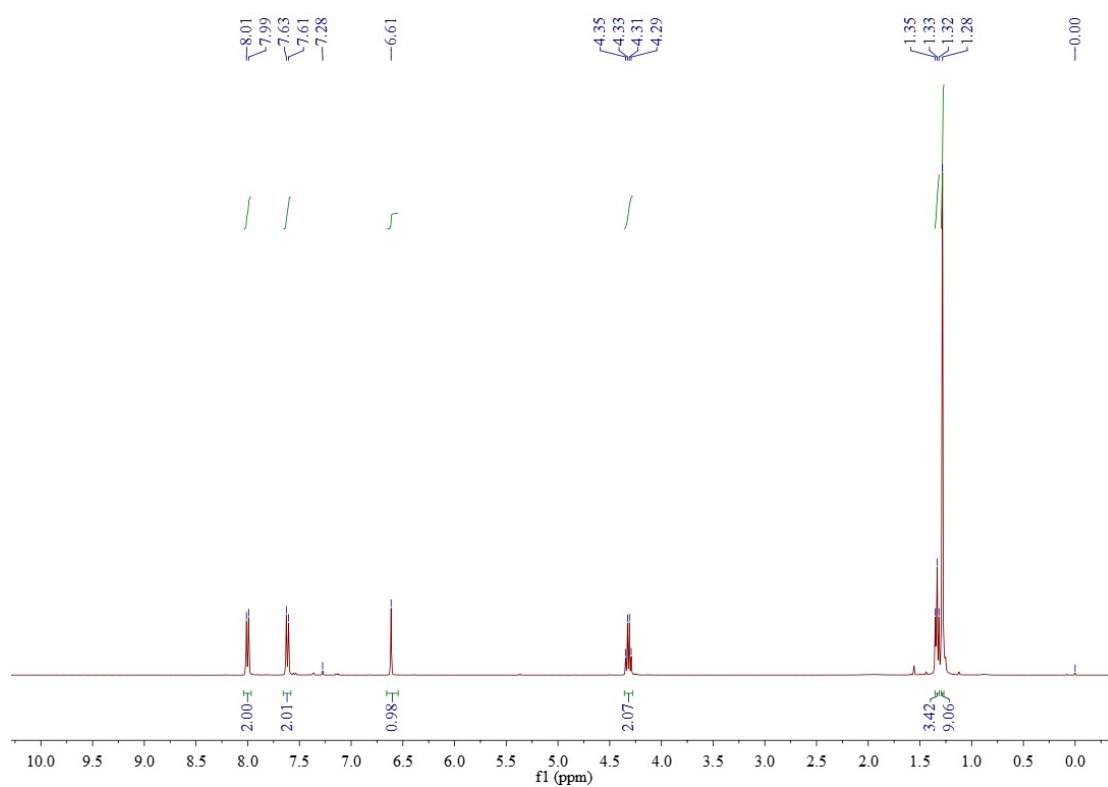
$^{19}\text{F}$  NMR (376MHz,  $\text{CDCl}_3$ ) spectra of **3f**



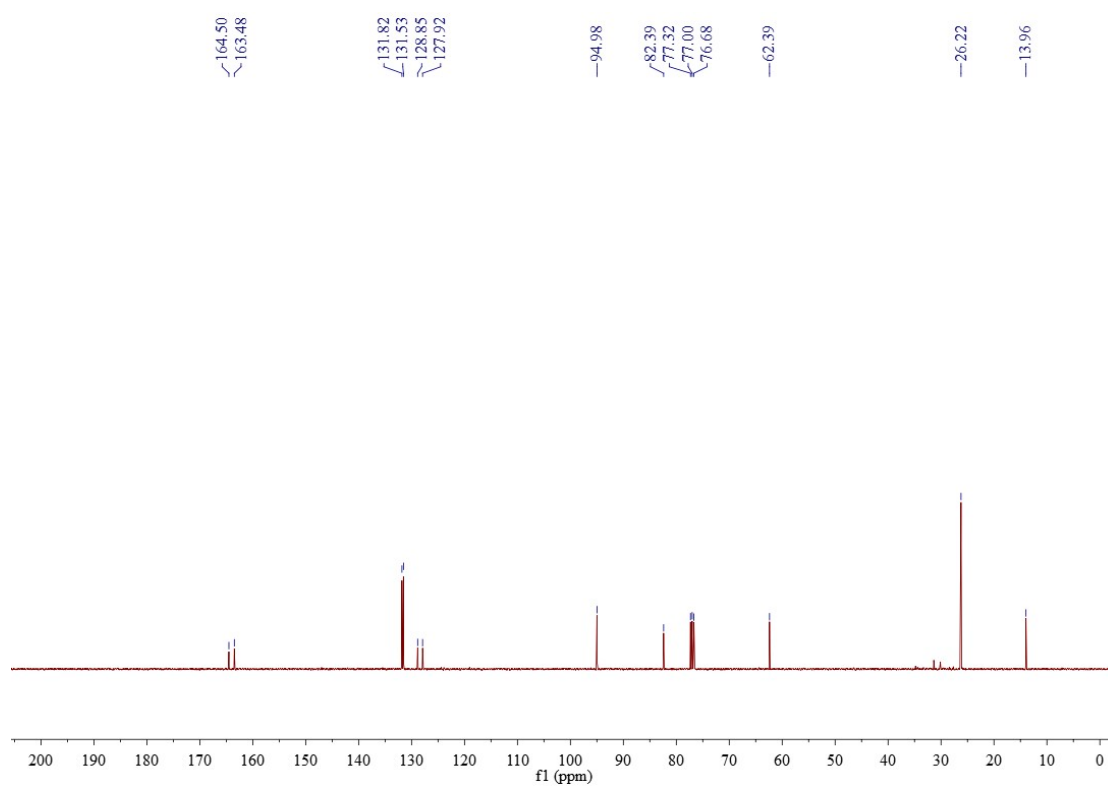
<sup>13</sup>C NMR (101MHz, CDCl<sub>3</sub>) spectra of **4f**



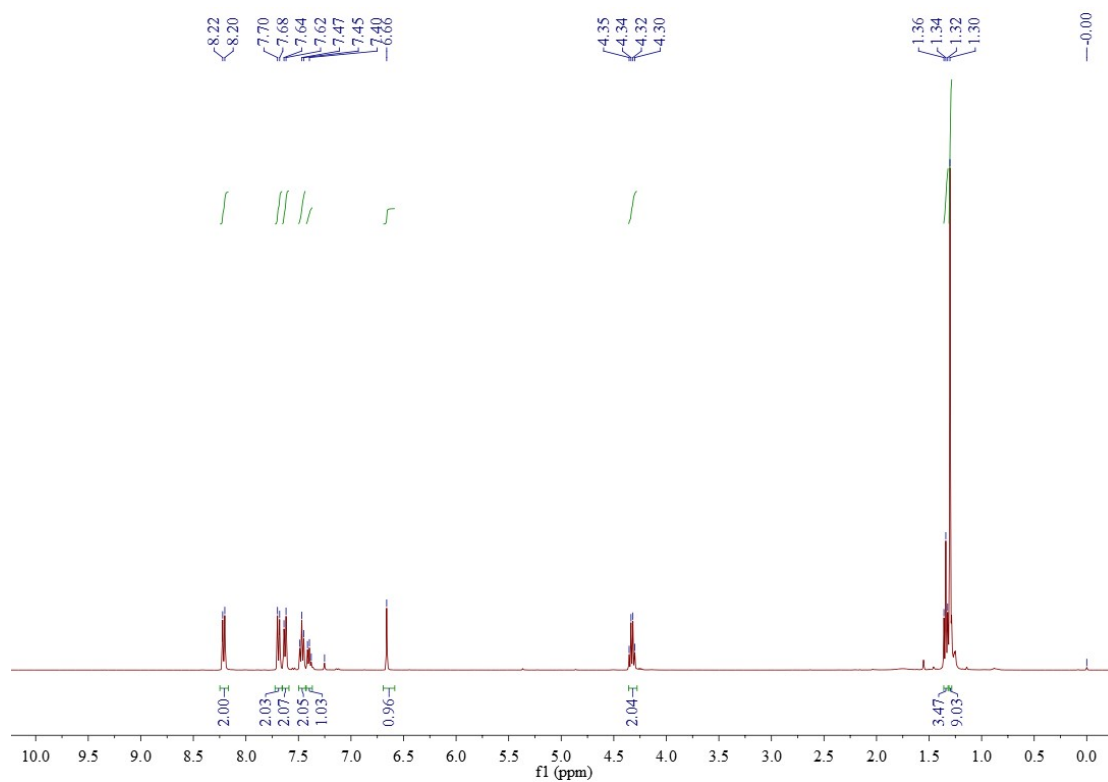
<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) spectra of **4g**



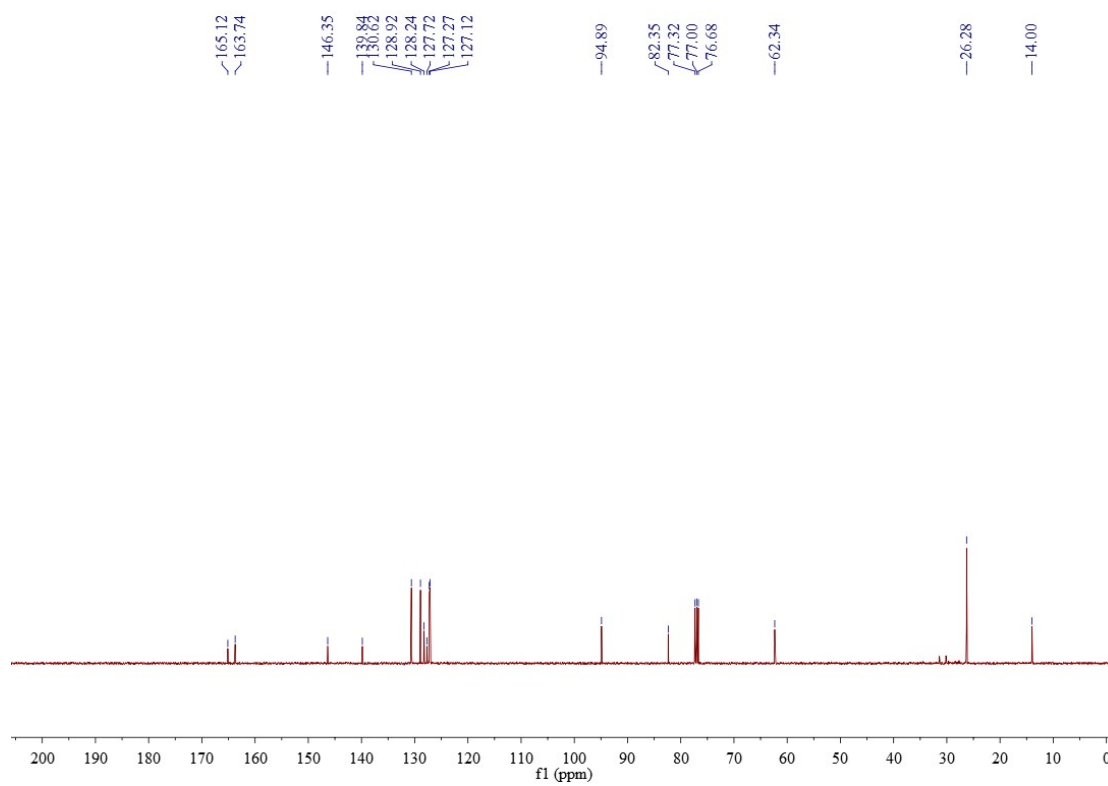
<sup>13</sup>C NMR (101MHz, CDCl<sub>3</sub>) spectra of **4g**



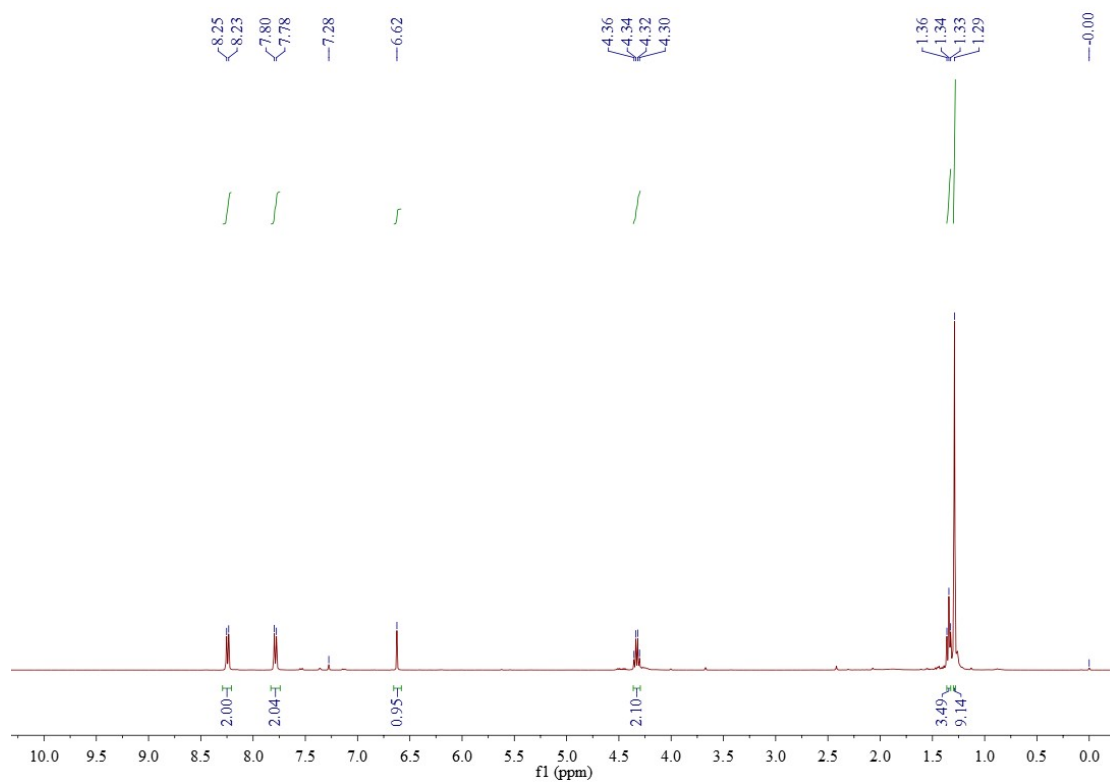
<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) spectra of **4h**



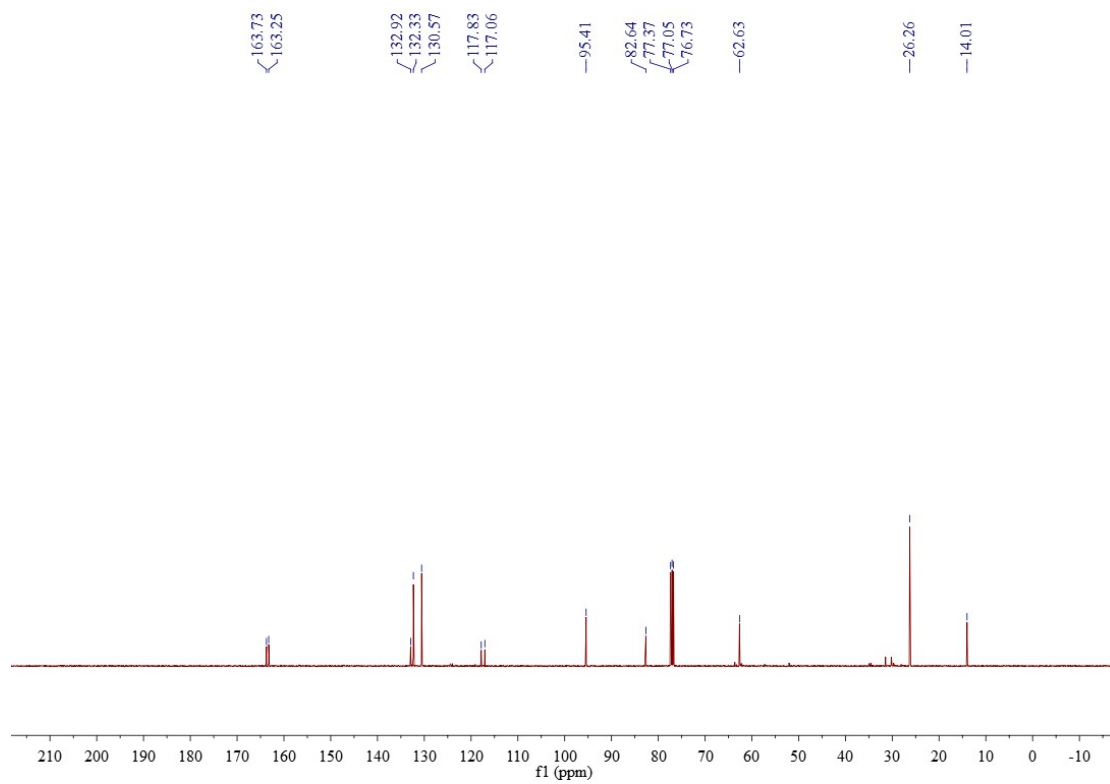
<sup>13</sup>C NMR (101MHz, CDCl<sub>3</sub>) spectra of **4h**



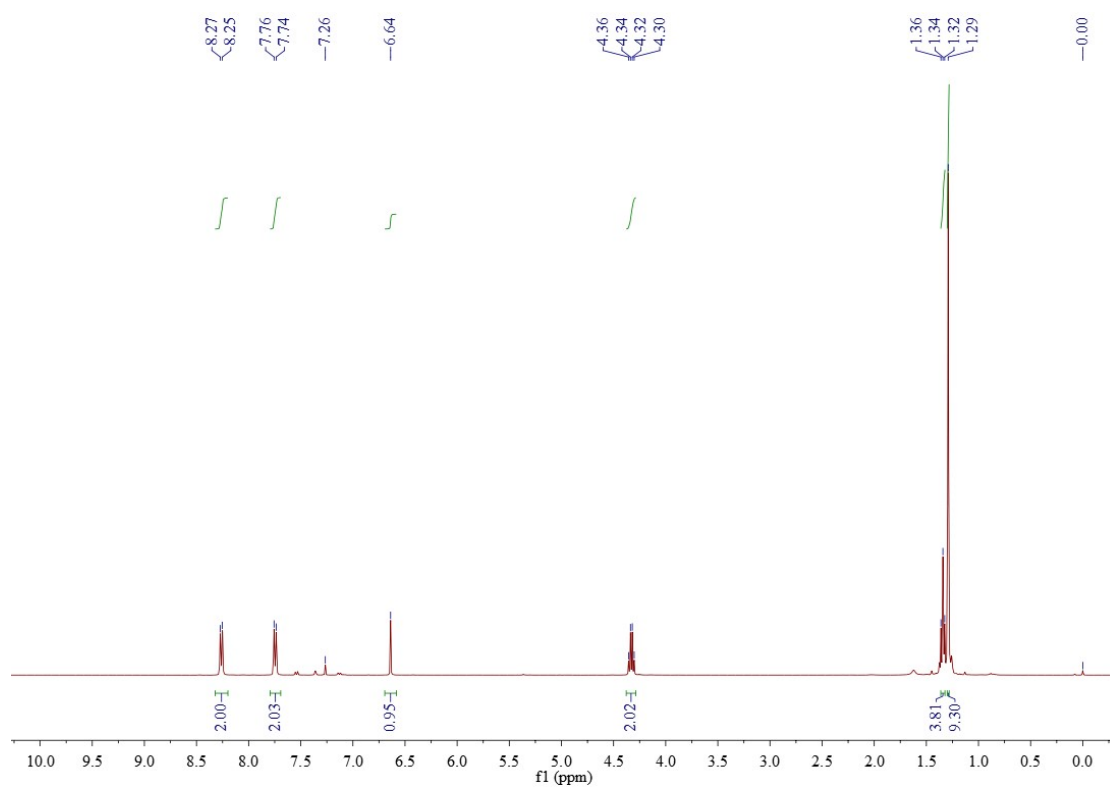
$^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ) spectra of **4i**



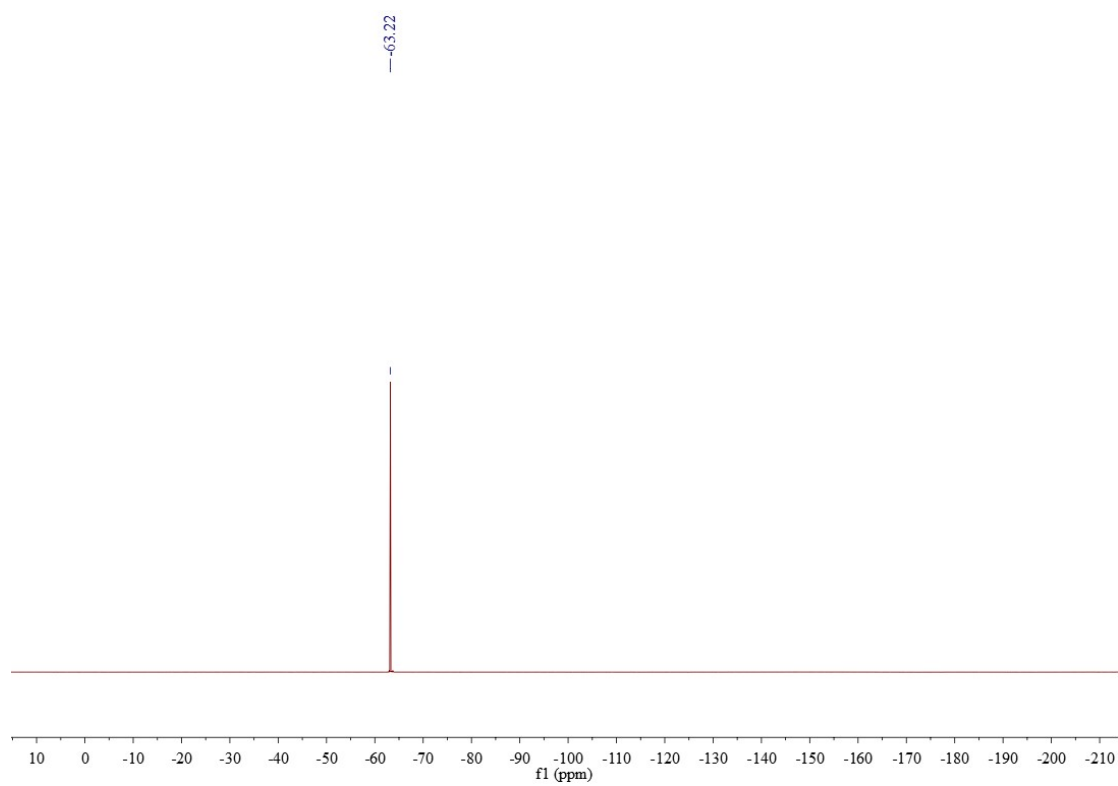
$^{13}\text{C}$  NMR (101MHz,  $\text{CDCl}_3$ ) spectra of **4i**



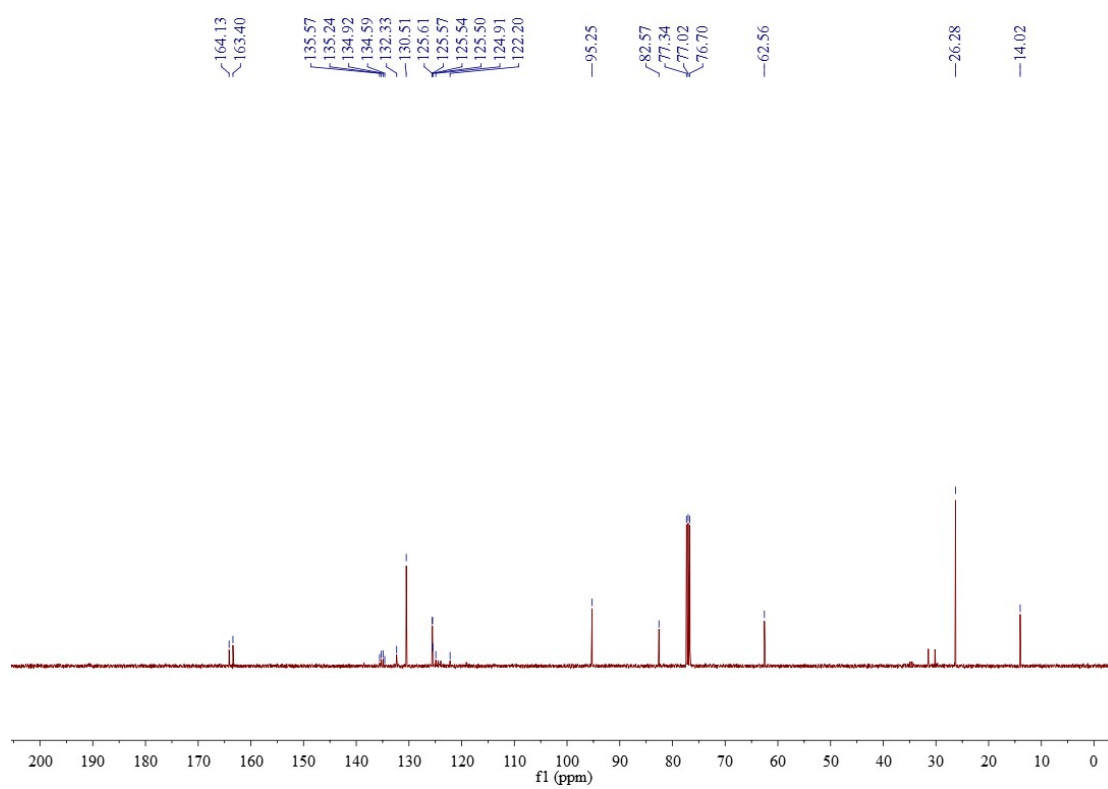
<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) spectra of **4j**



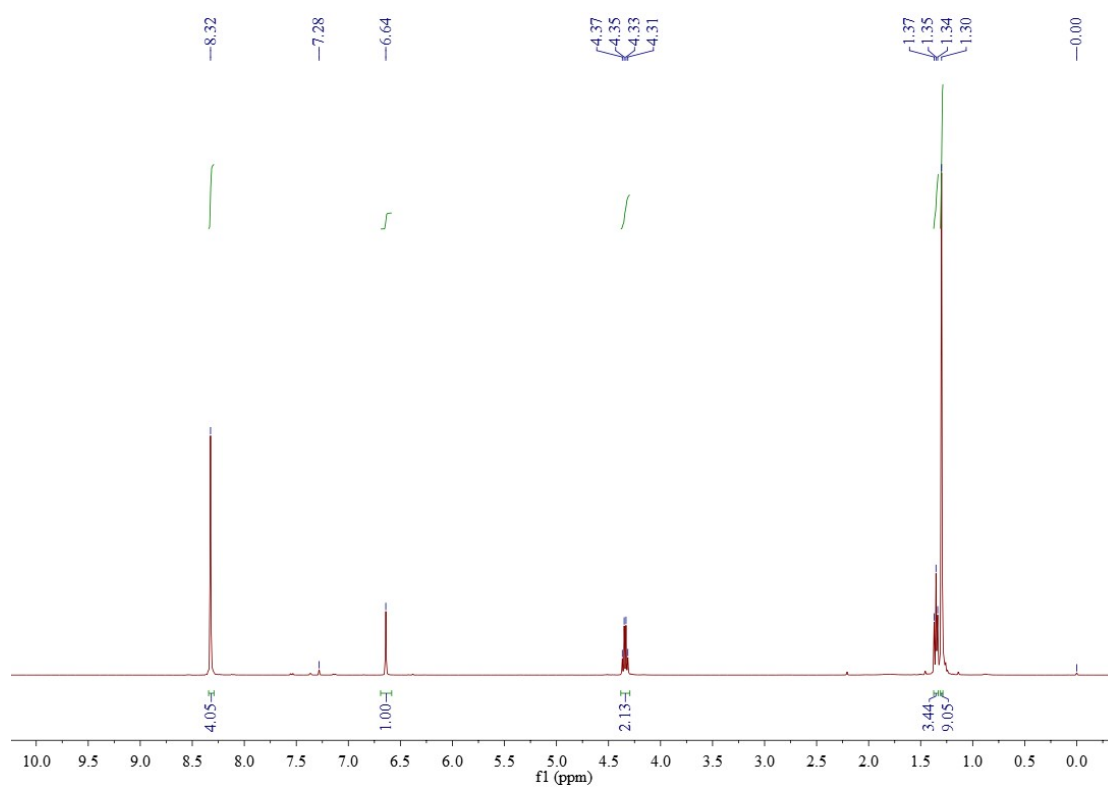
<sup>19</sup>F NMR (376MHz, CDCl<sub>3</sub>) spectra of **4j**



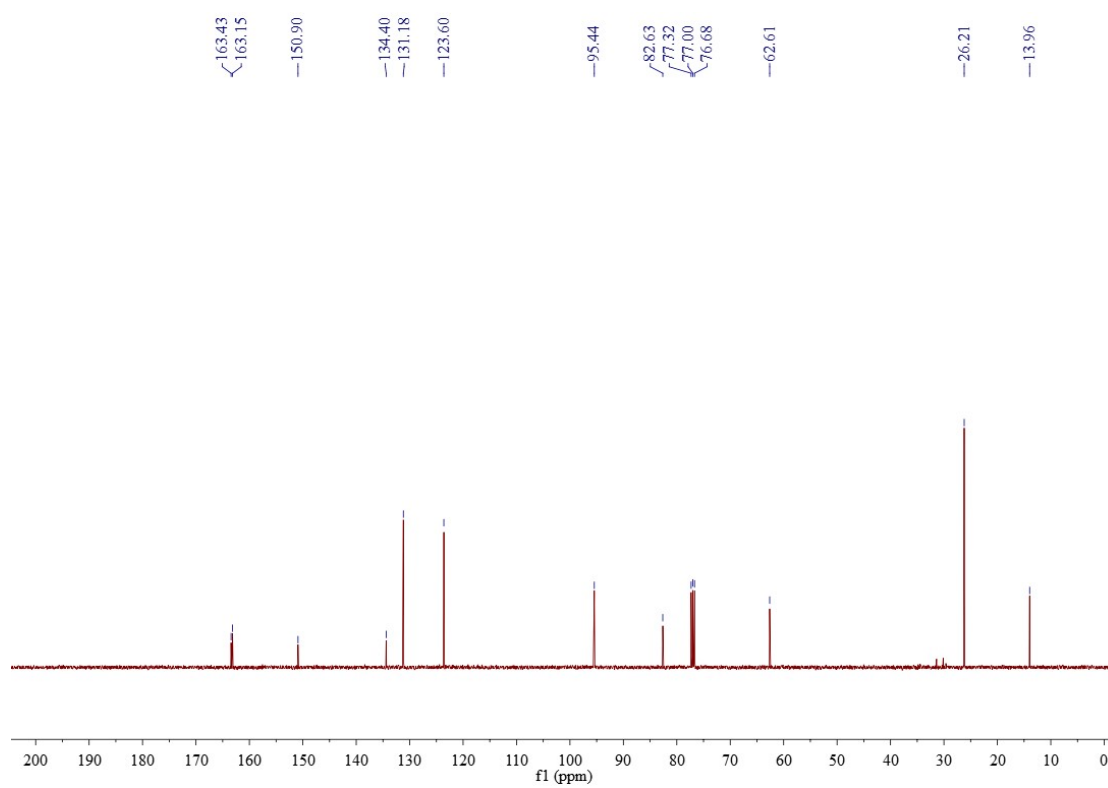
<sup>13</sup>C NMR (101MHz, CDCl<sub>3</sub>) spectra of **4j**



<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) spectra of **4k**

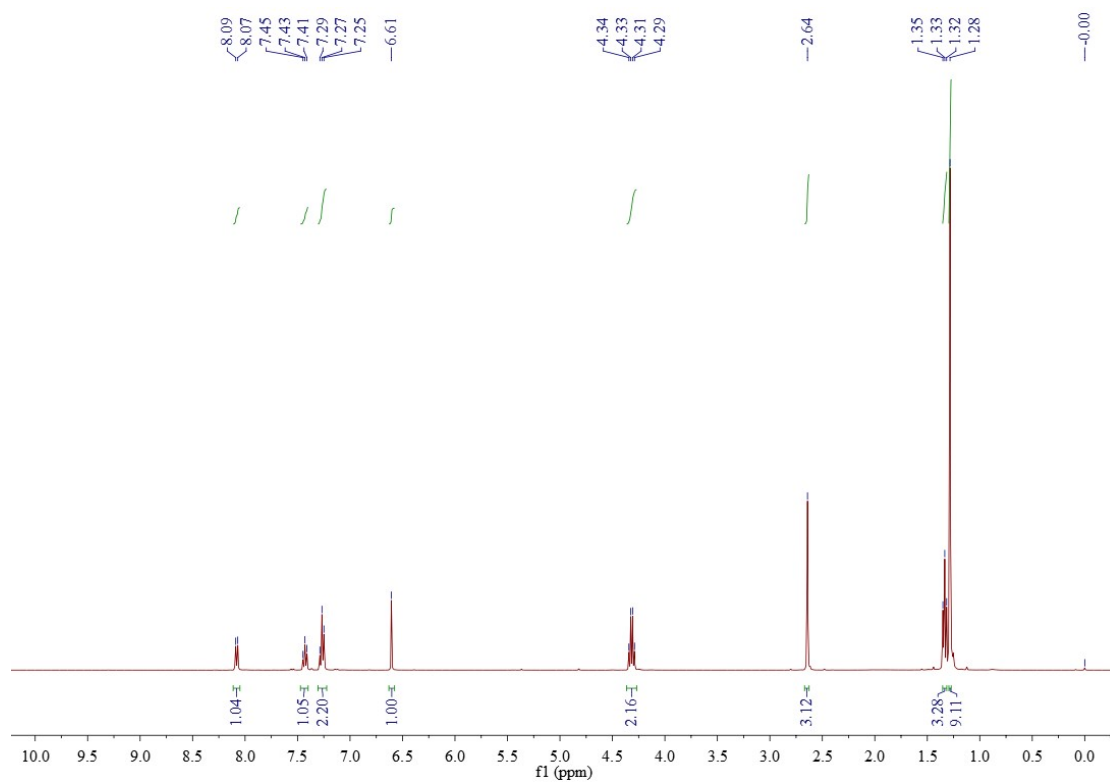


<sup>13</sup>C NMR (101MHz, CDCl<sub>3</sub>) spectra of **4k**

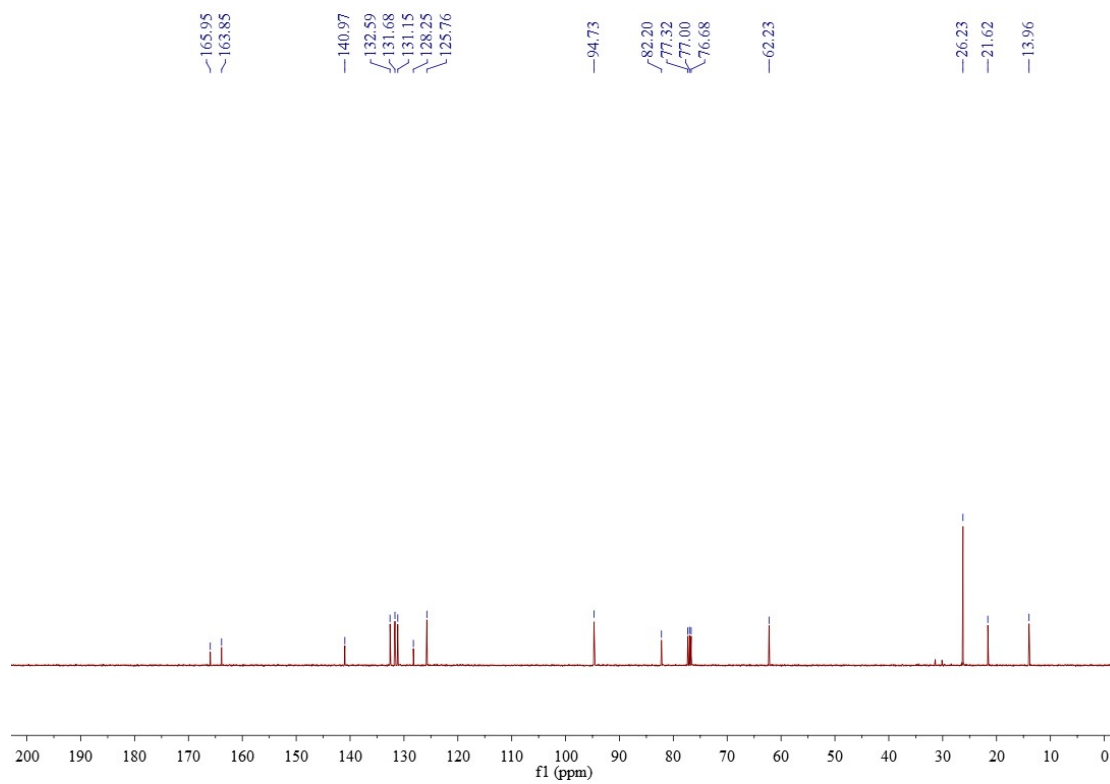




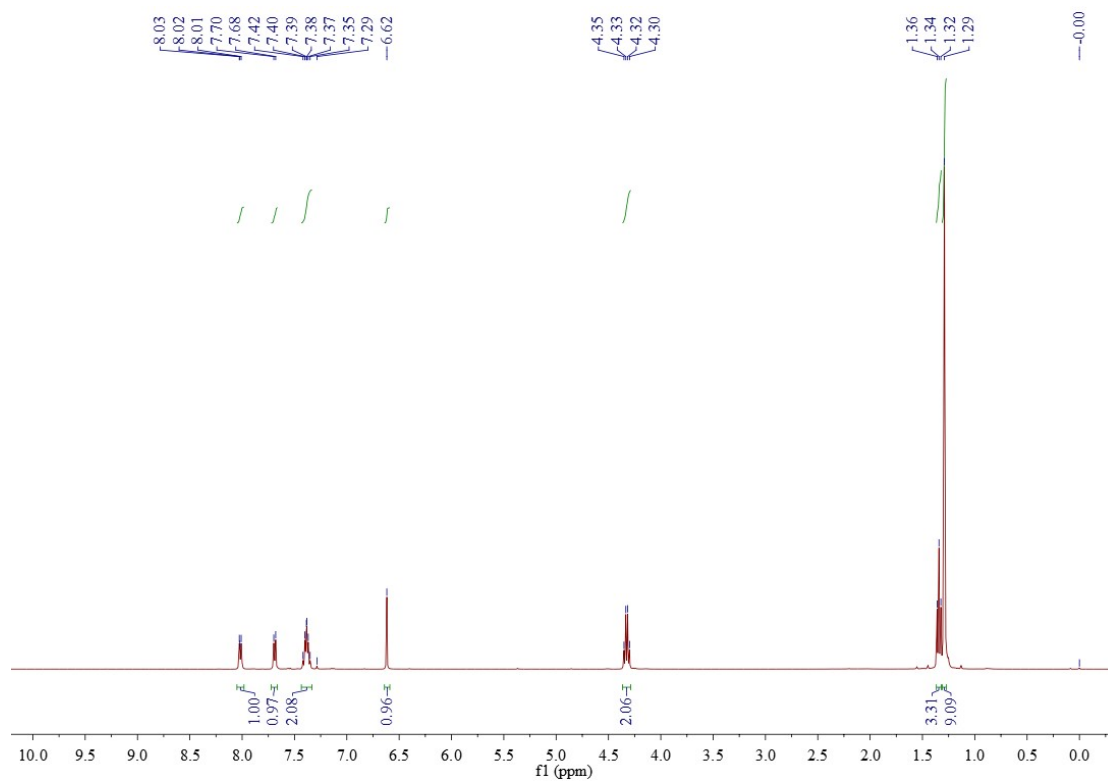
<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) spectra of **41**



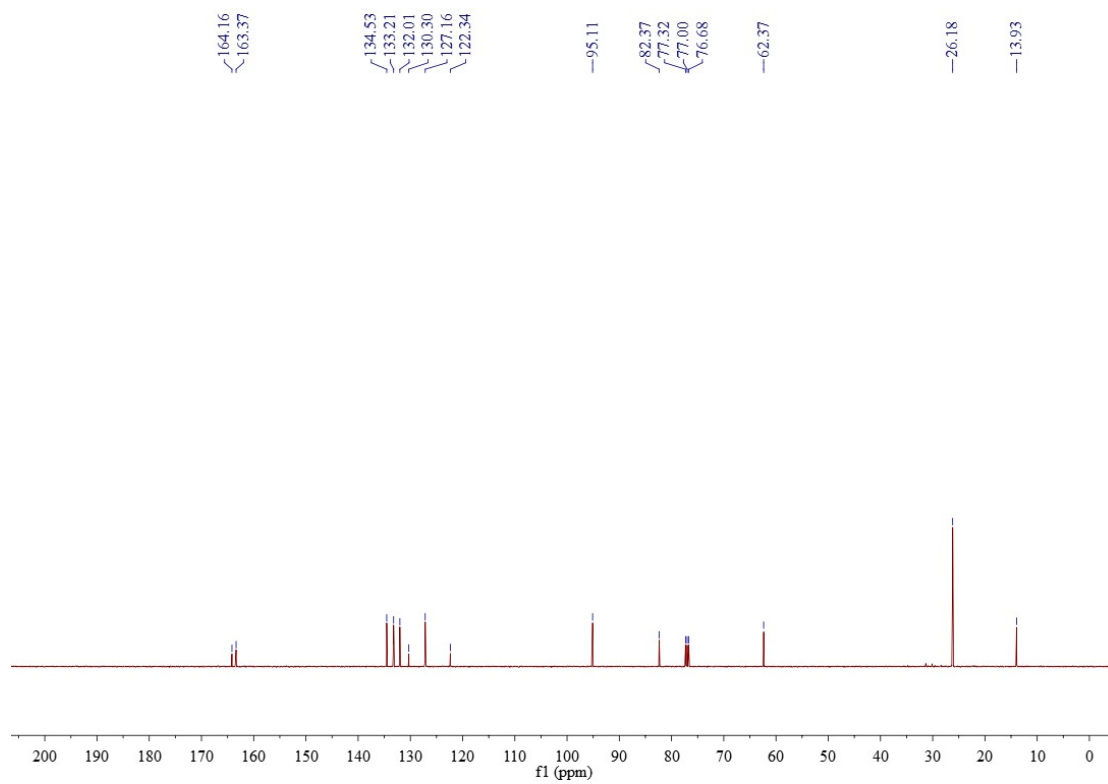
<sup>13</sup>C NMR (101MHz, CDCl<sub>3</sub>) spectra of **41**



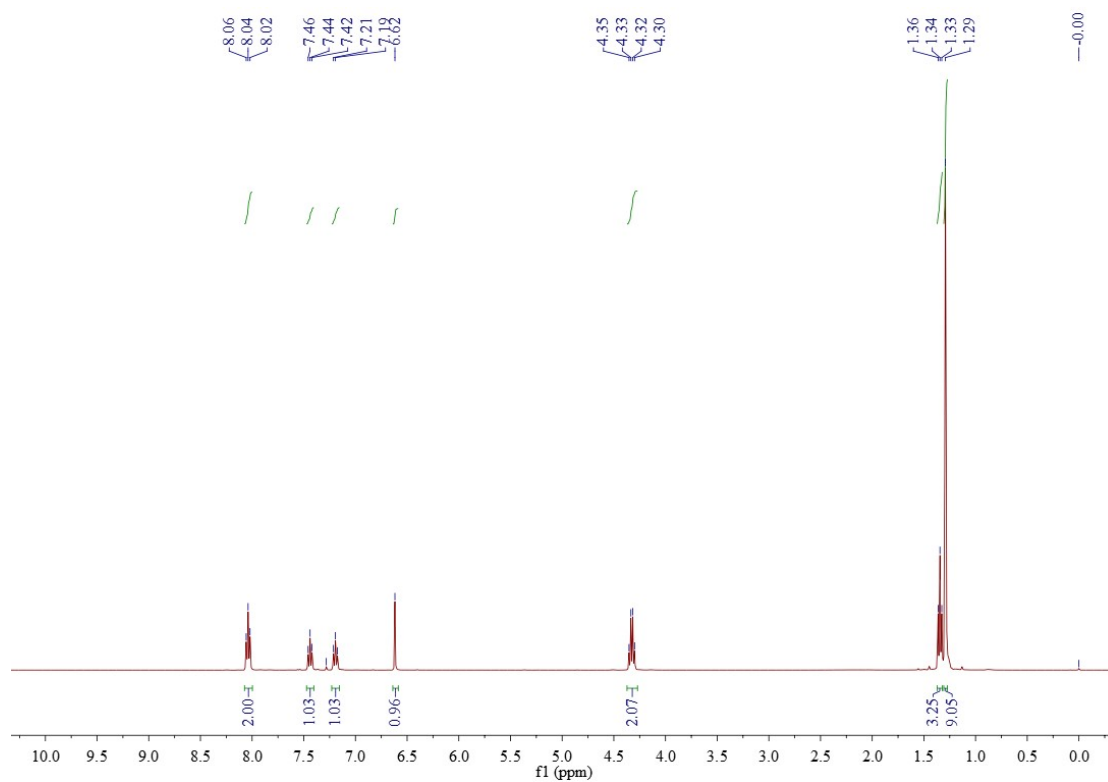
$^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ) spectra of **4m**



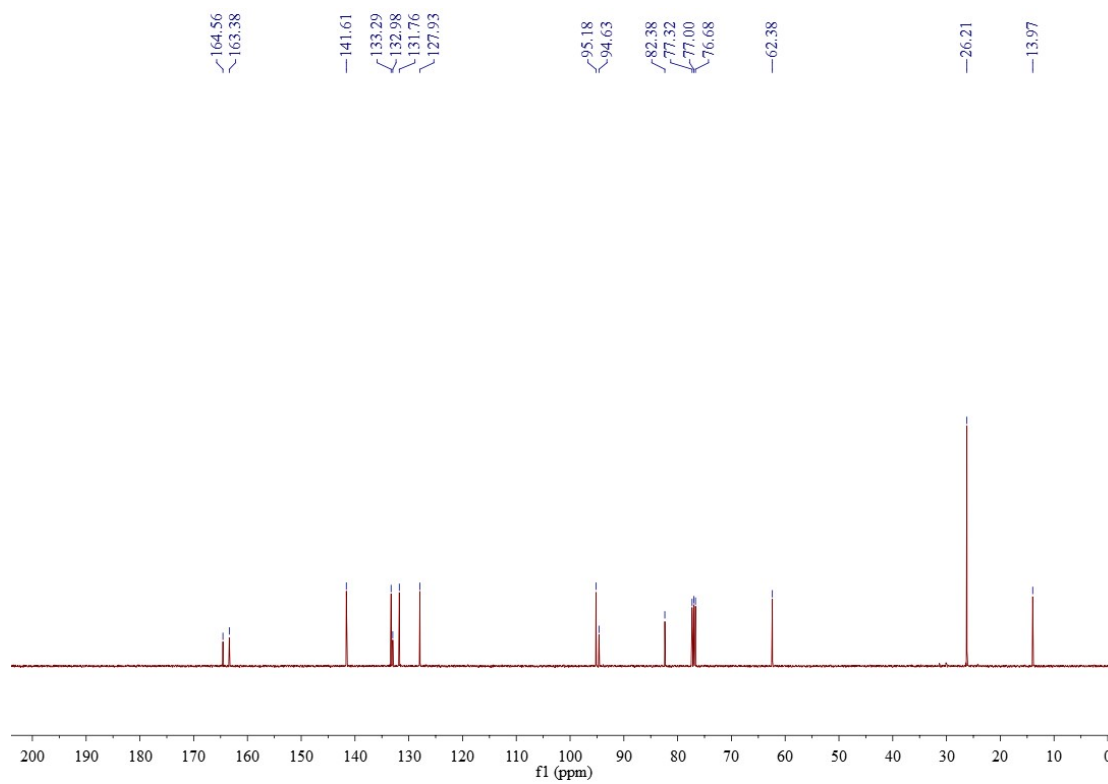
$^{13}\text{C}$  NMR (101MHz,  $\text{CDCl}_3$ ) spectra of **4m**



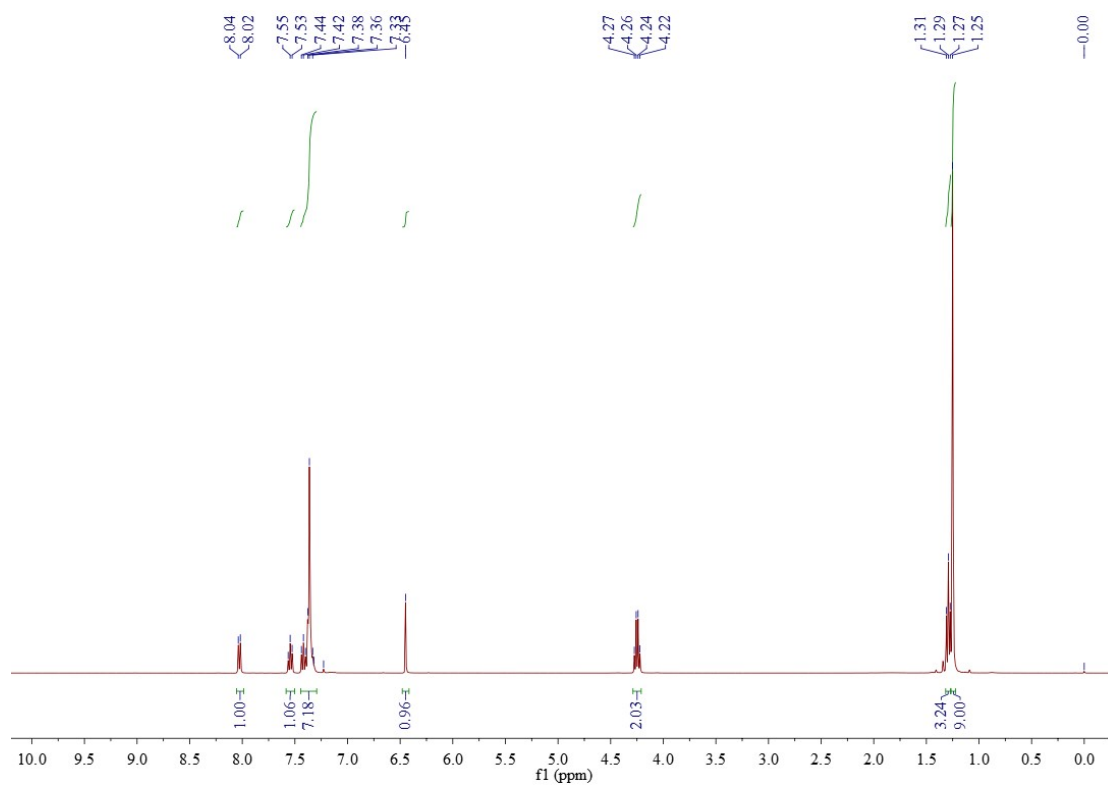
<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) spectra of **4n**



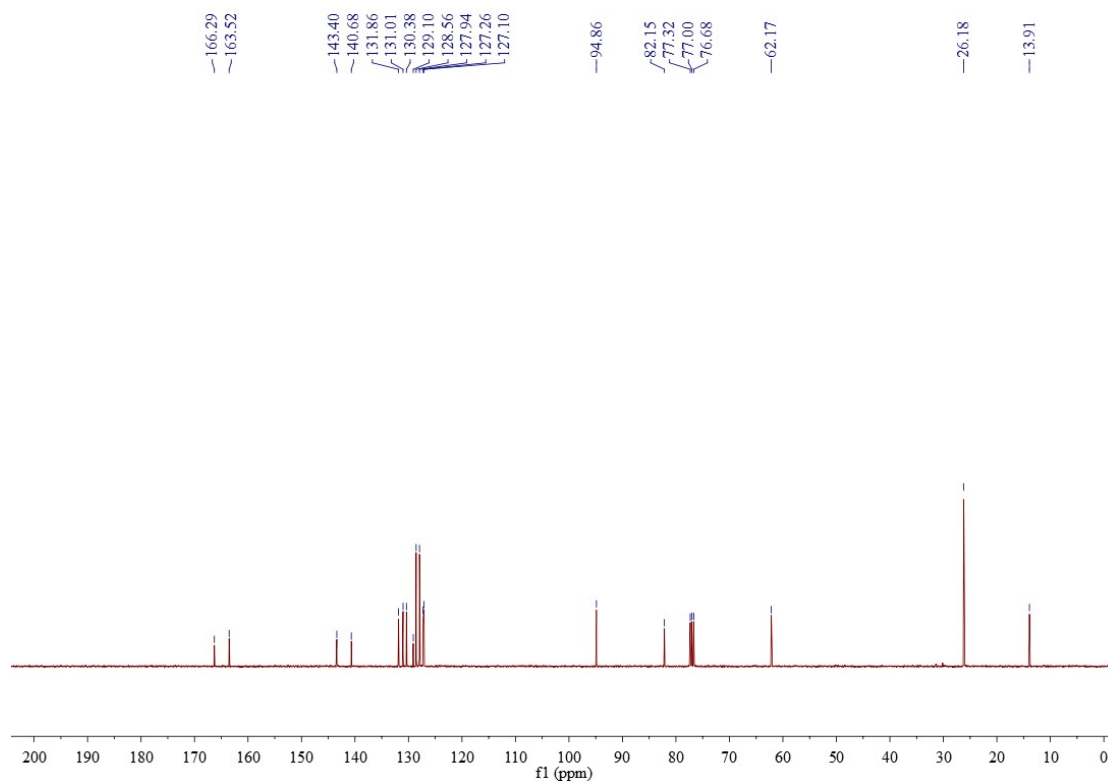
<sup>13</sup>C NMR (101MHz, CDCl<sub>3</sub>) spectra of **4n**



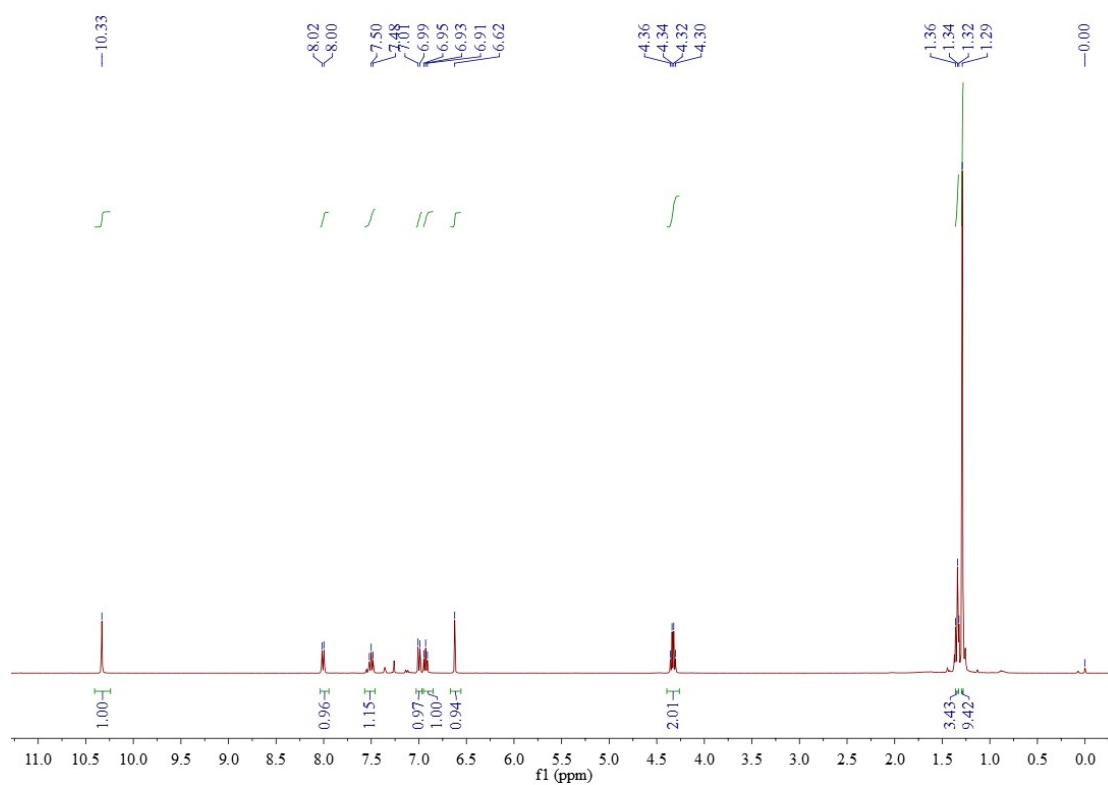
$^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ) spectra of **4o**



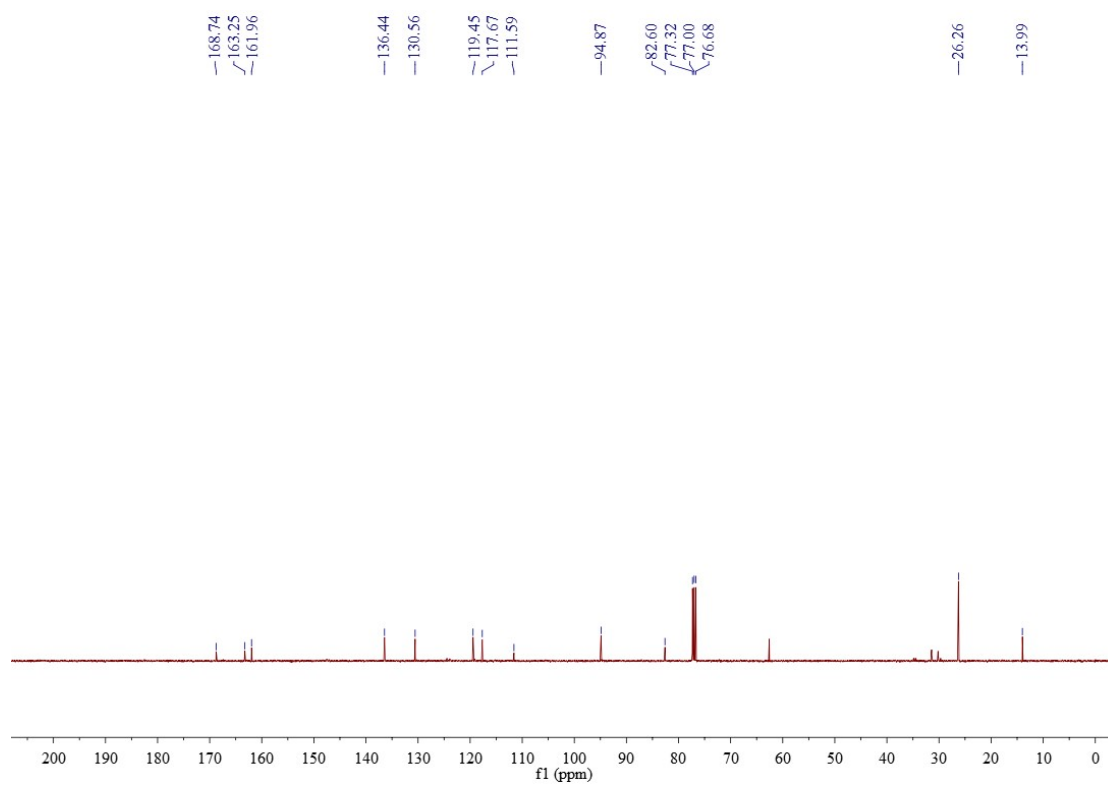
$^{13}\text{C}$  NMR (101MHz,  $\text{CDCl}_3$ ) spectra of **4o**



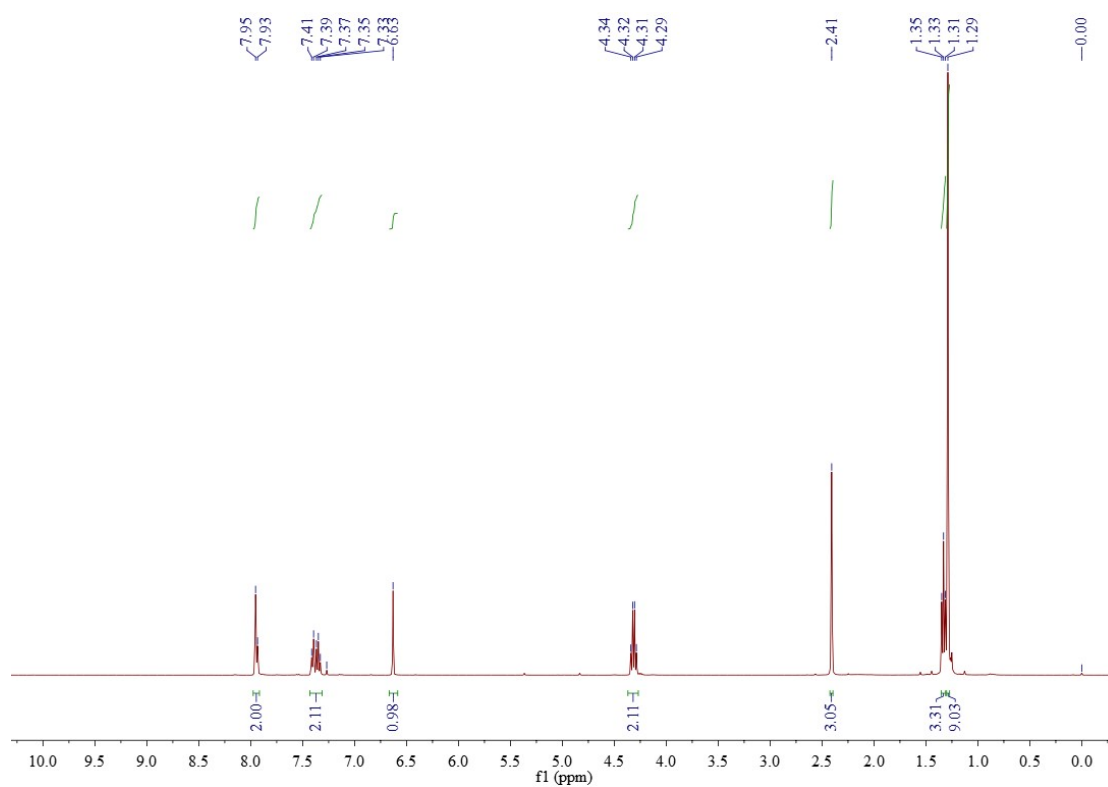
<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) spectra of **4p**



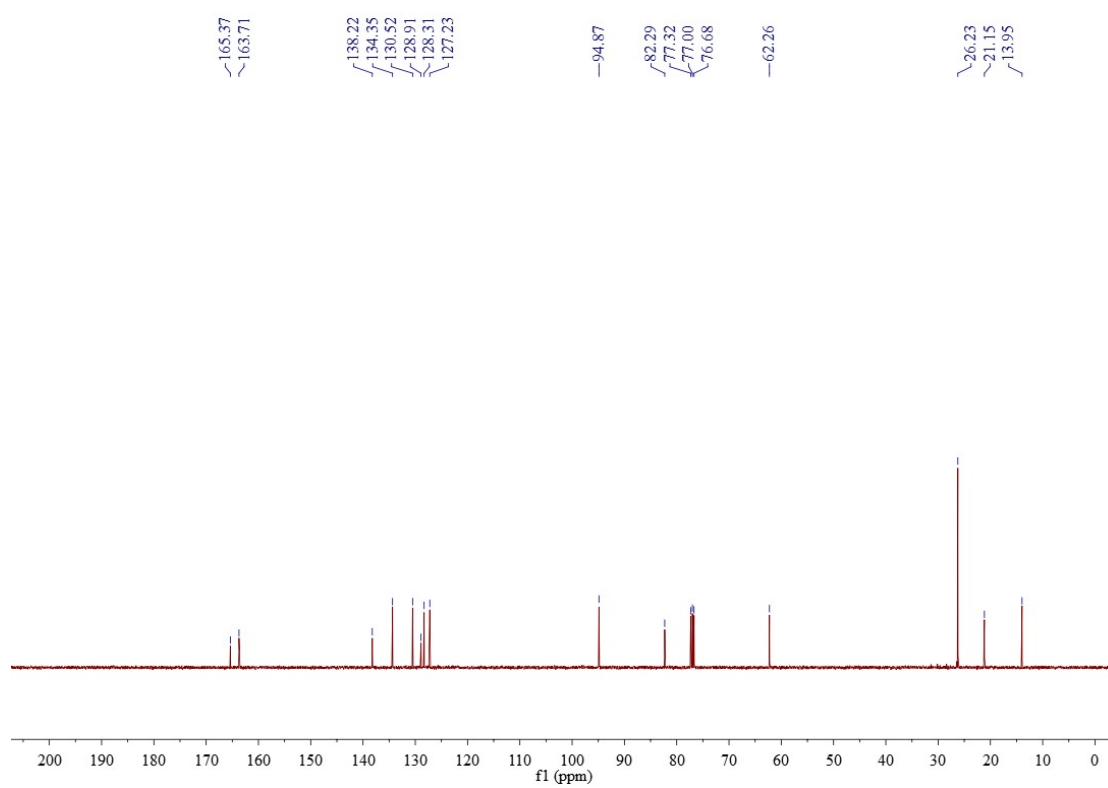
<sup>13</sup>C NMR (101MHz, CDCl<sub>3</sub>) spectra of **4p**



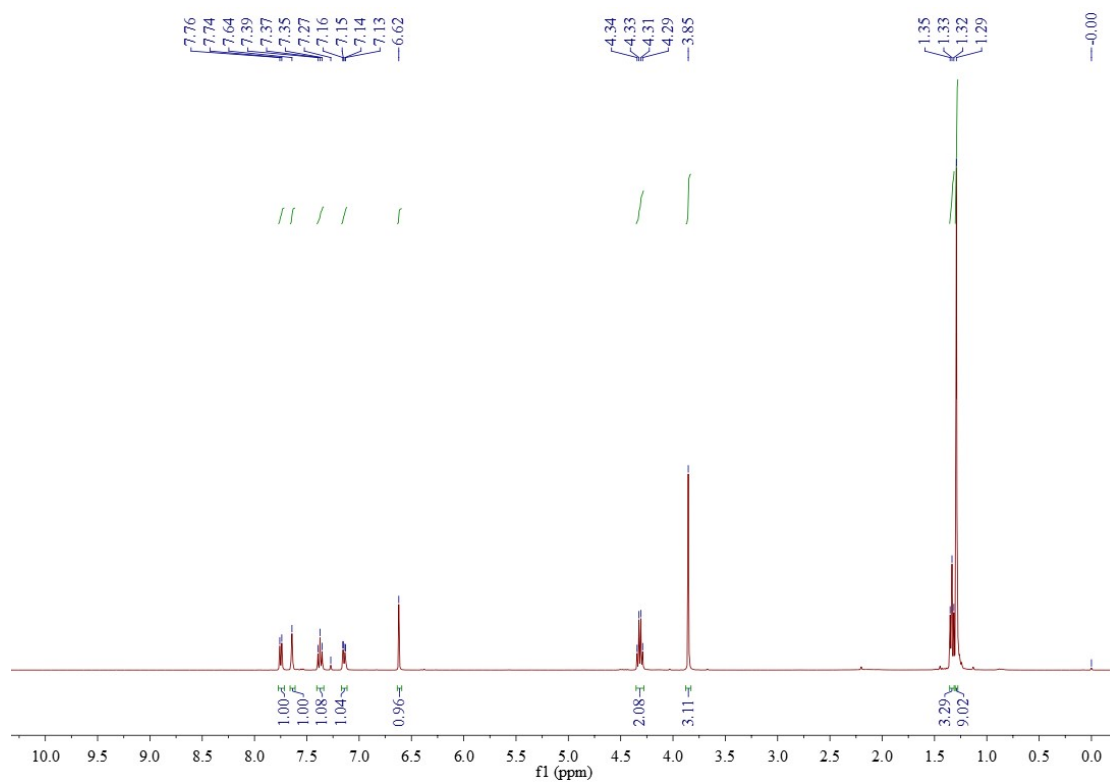
<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) spectra of **4q**



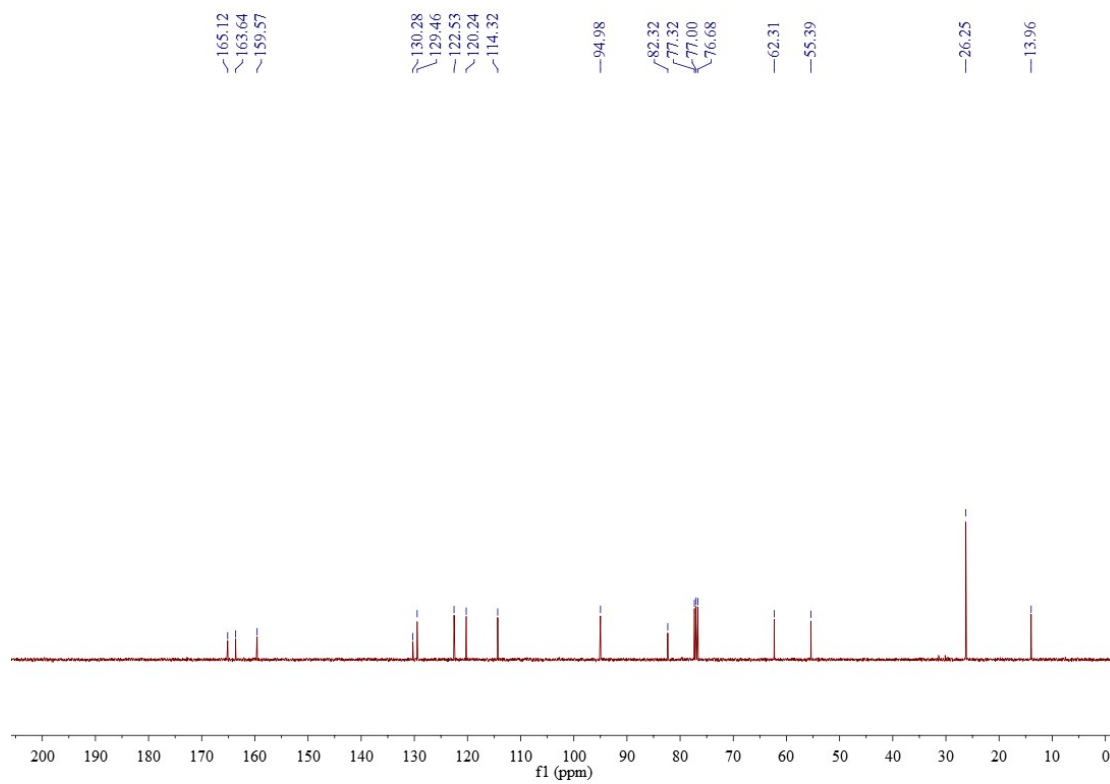
<sup>13</sup>C NMR (101MHz, CDCl<sub>3</sub>) spectra of **4q**



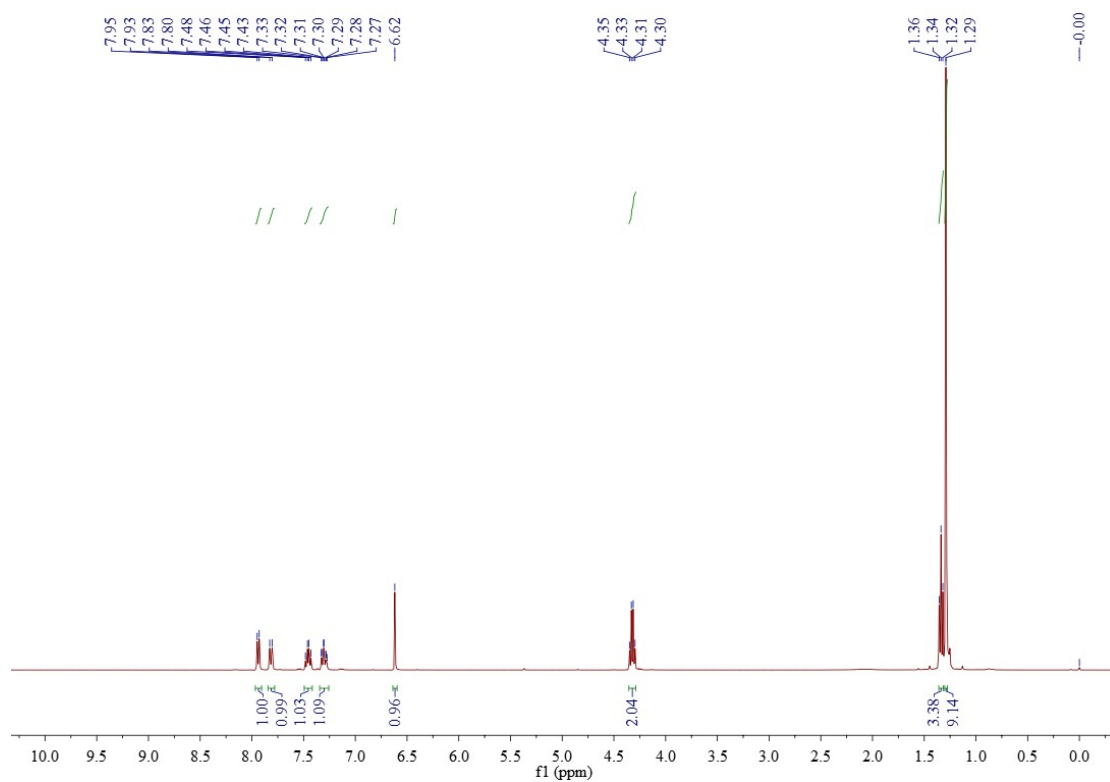
<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) spectra of **4r**



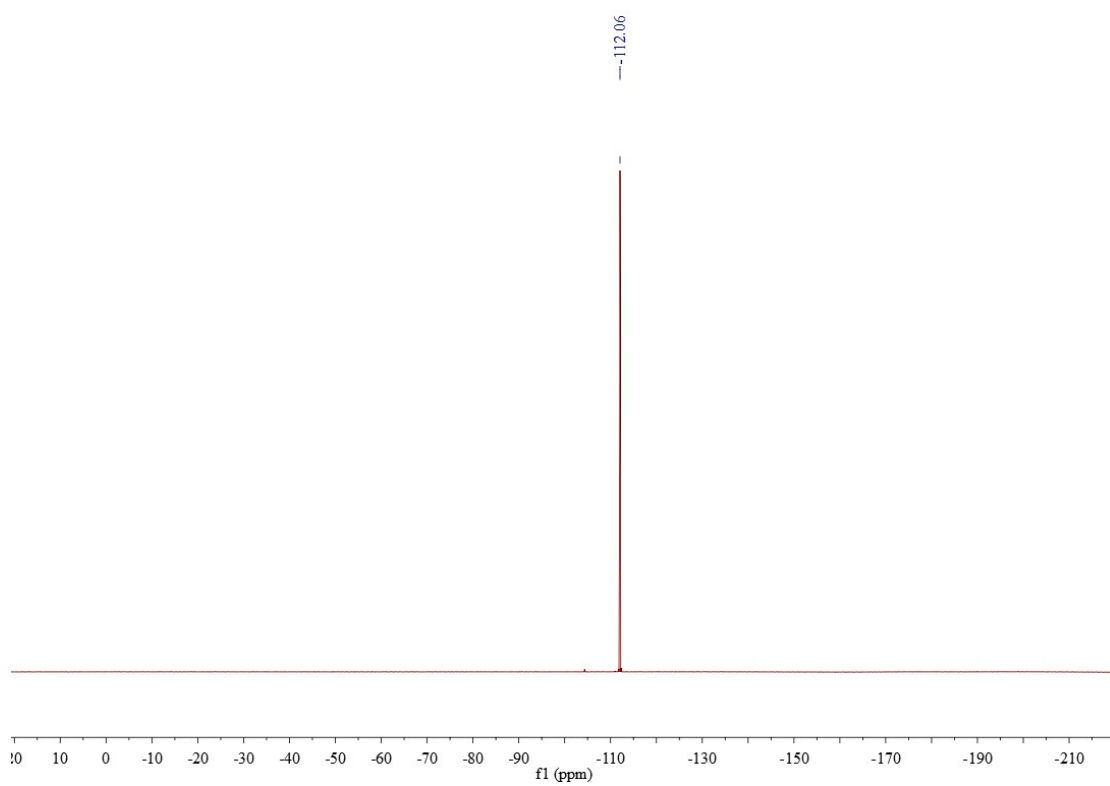
<sup>13</sup>C NMR (101MHz, CDCl<sub>3</sub>) spectra of **4r**



$^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ) spectra of **4s**

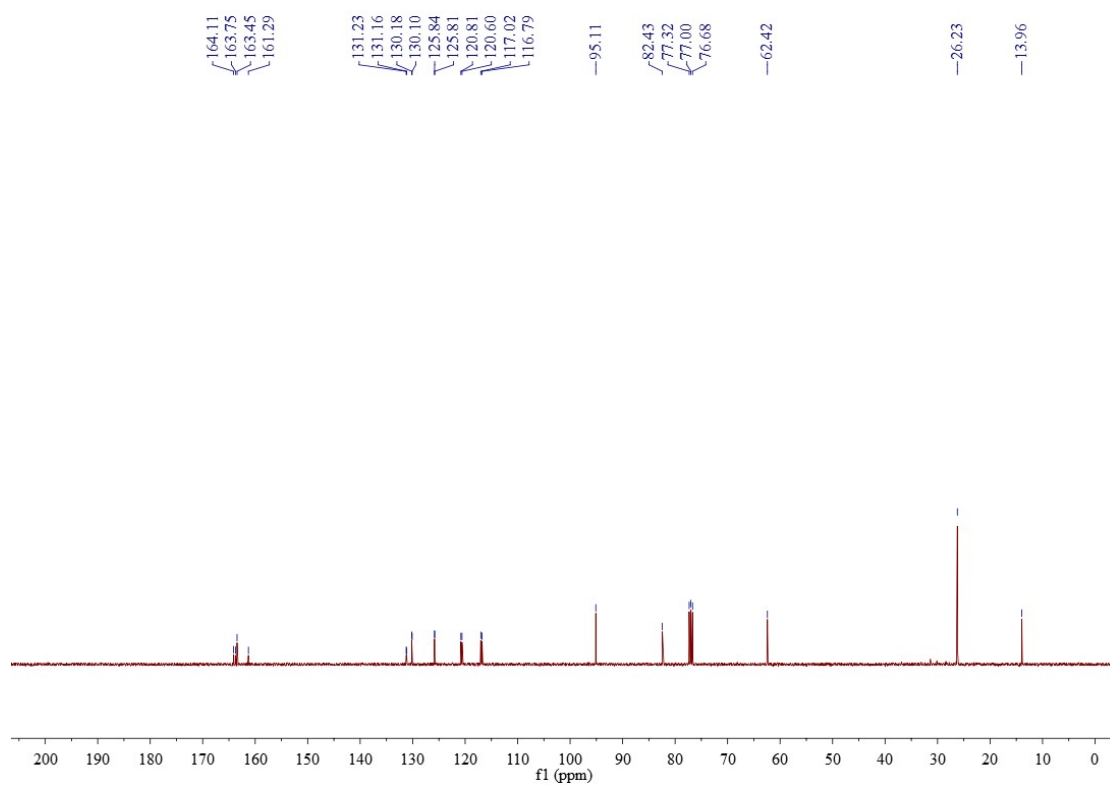


$^{19}\text{F}$  NMR (376MHz,  $\text{CDCl}_3$ ) spectra of **4s**

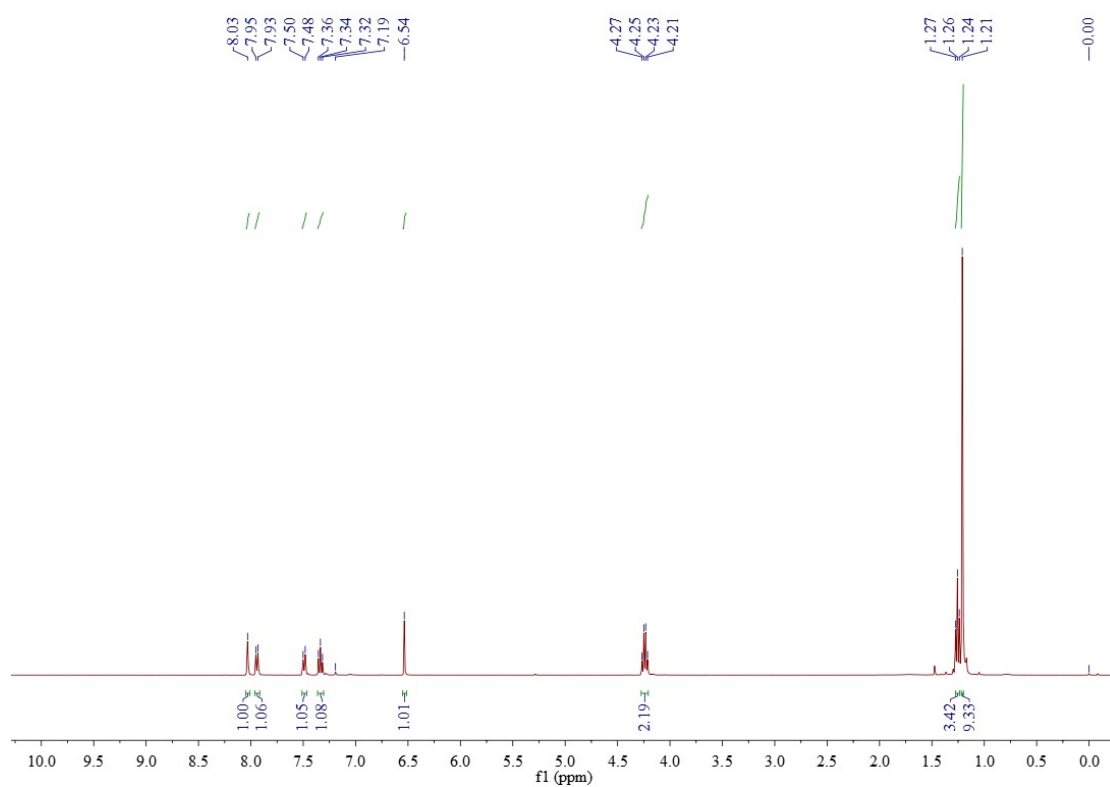




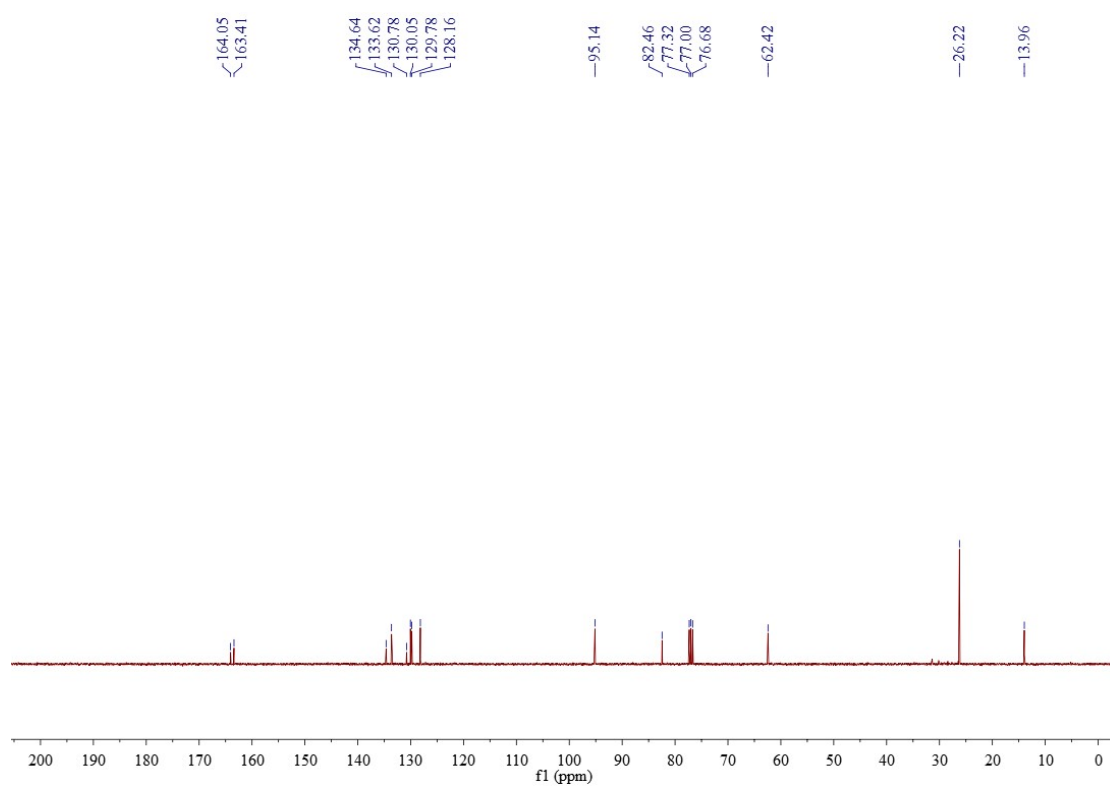
<sup>13</sup>C NMR (101MHz, CDCl<sub>3</sub>) spectra of **4s**



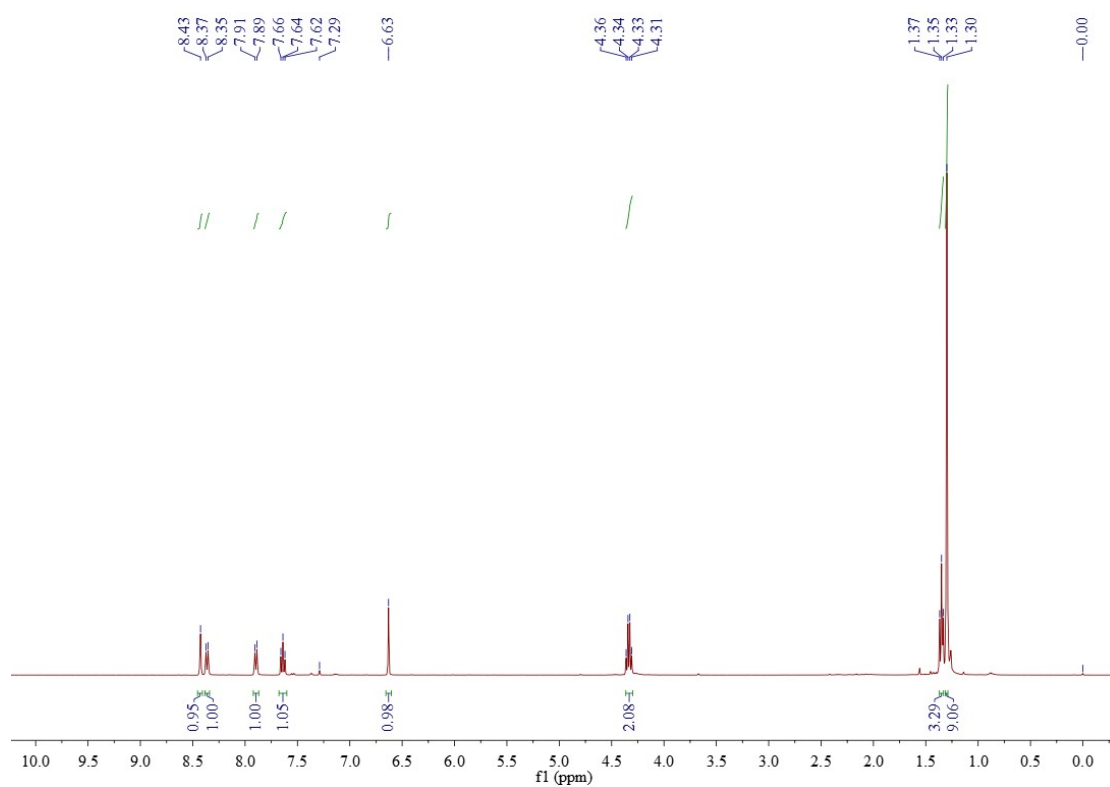
<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) spectra of **4t**



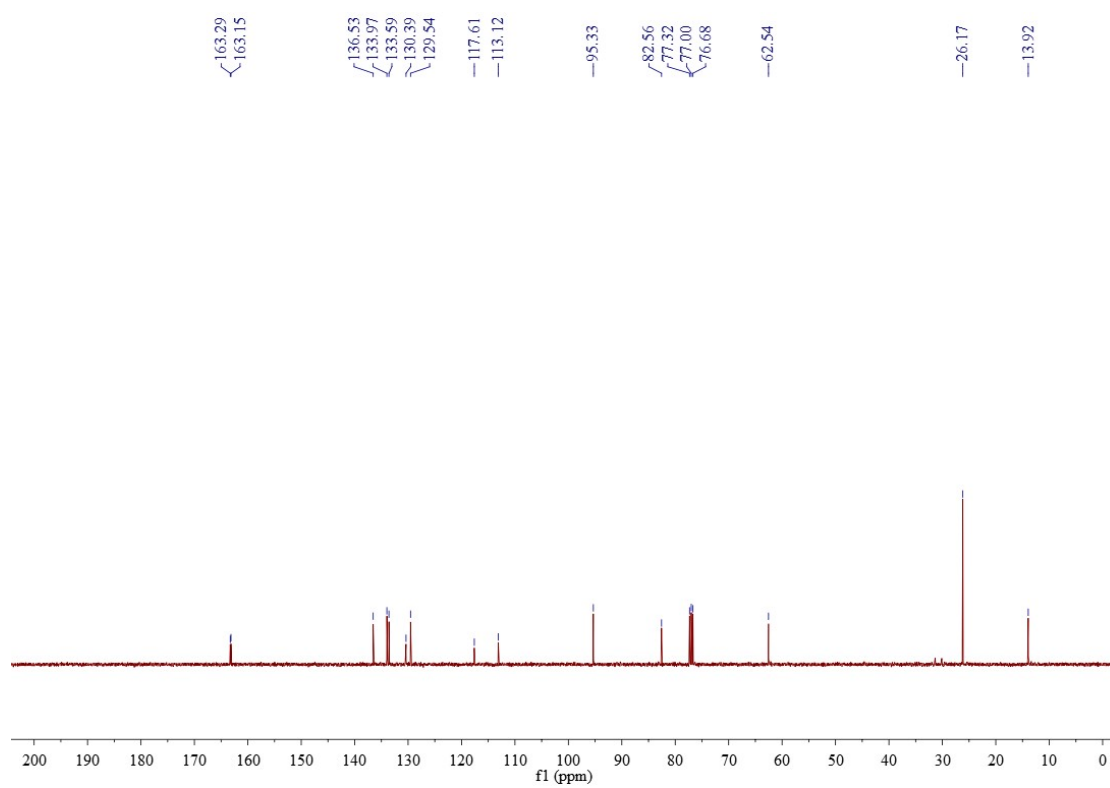
<sup>13</sup>C NMR (101MHz, CDCl<sub>3</sub>) spectra of **4t**



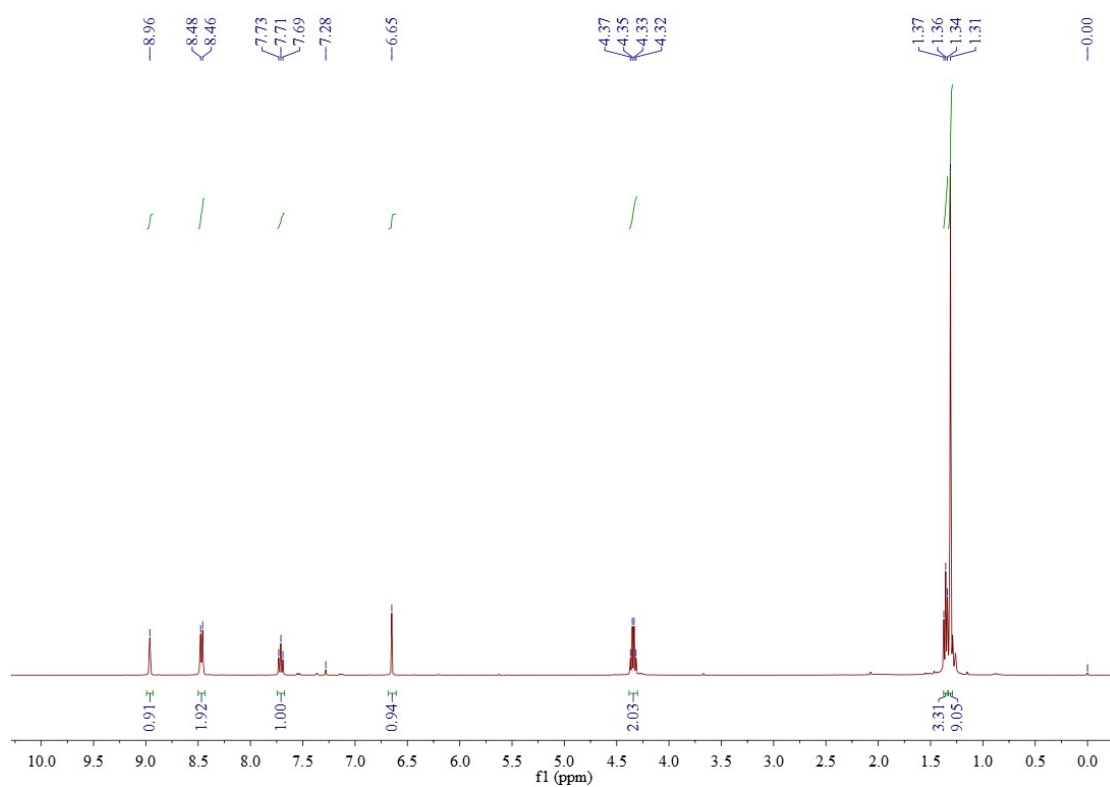
<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) spectra of **4u**



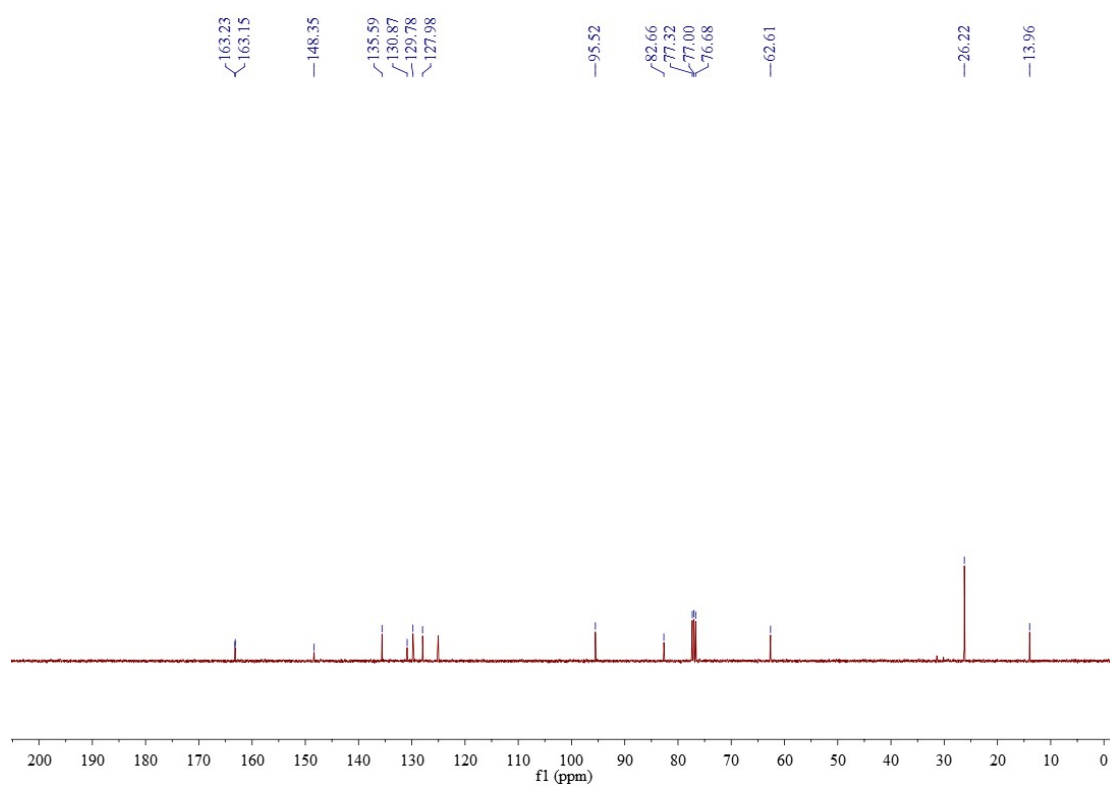
<sup>13</sup>C NMR (101MHz, CDCl<sub>3</sub>) spectra of **4u**



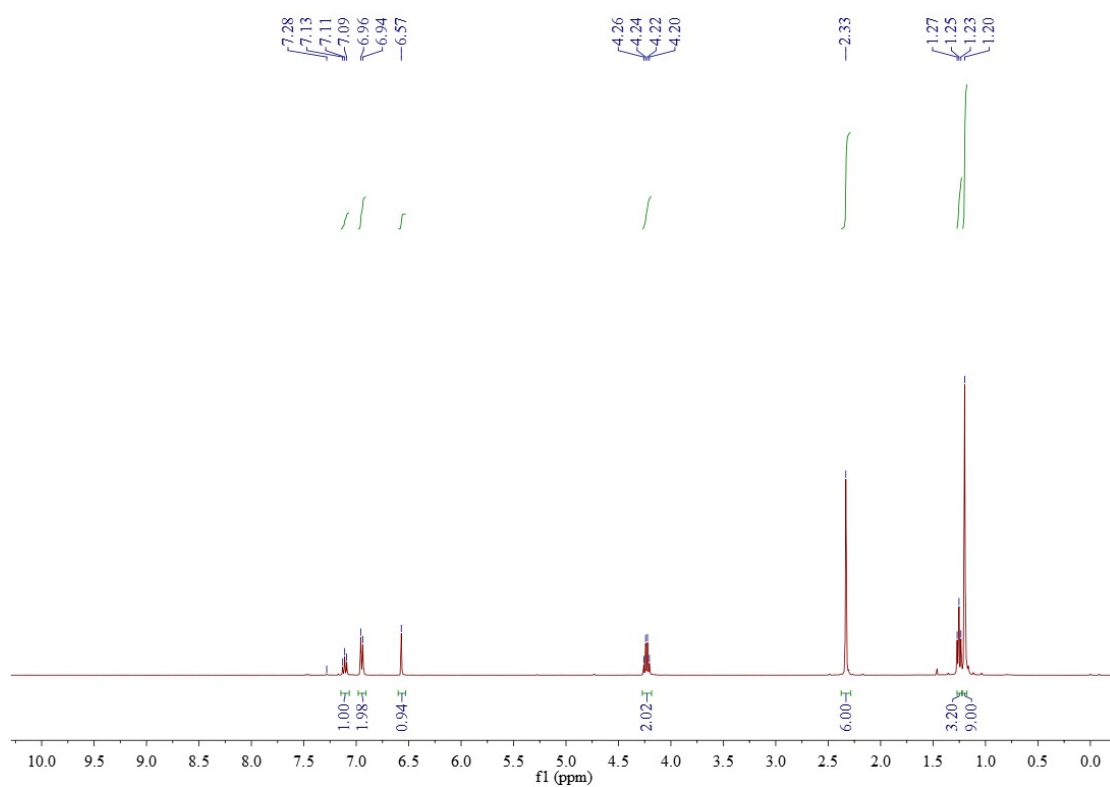
<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) spectra of **4v**



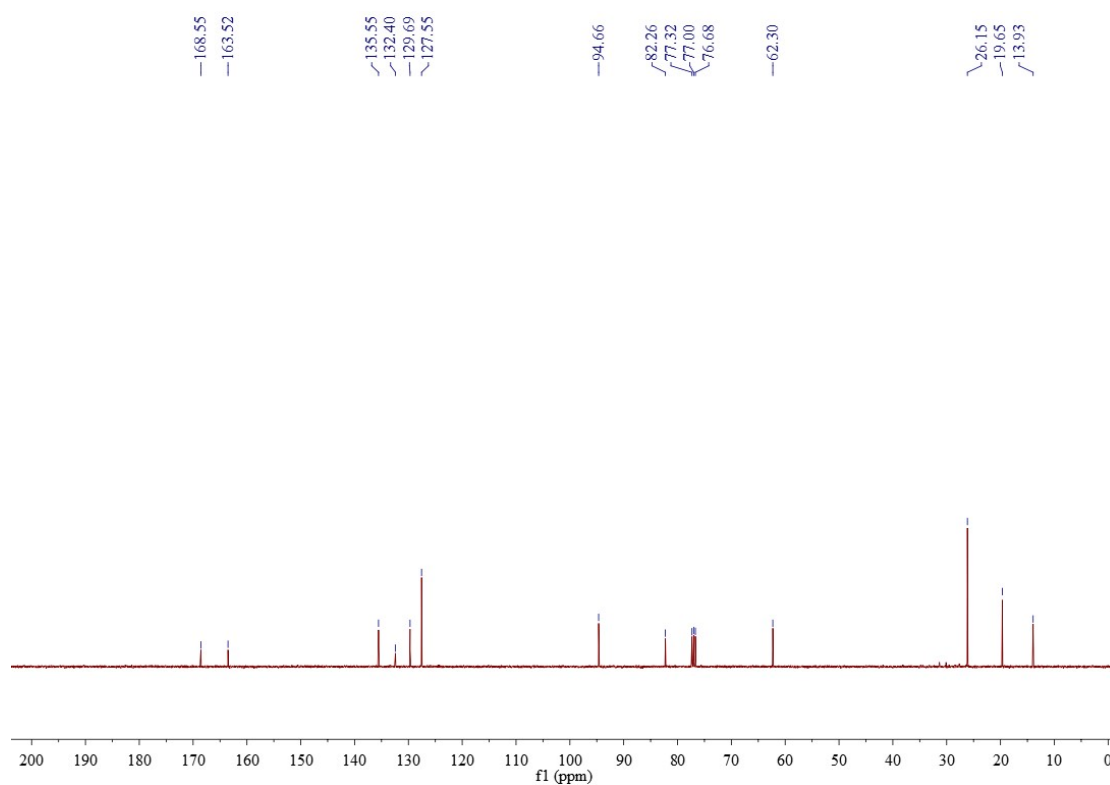
<sup>13</sup>C NMR (101MHz, CDCl<sub>3</sub>) spectra of **4v**



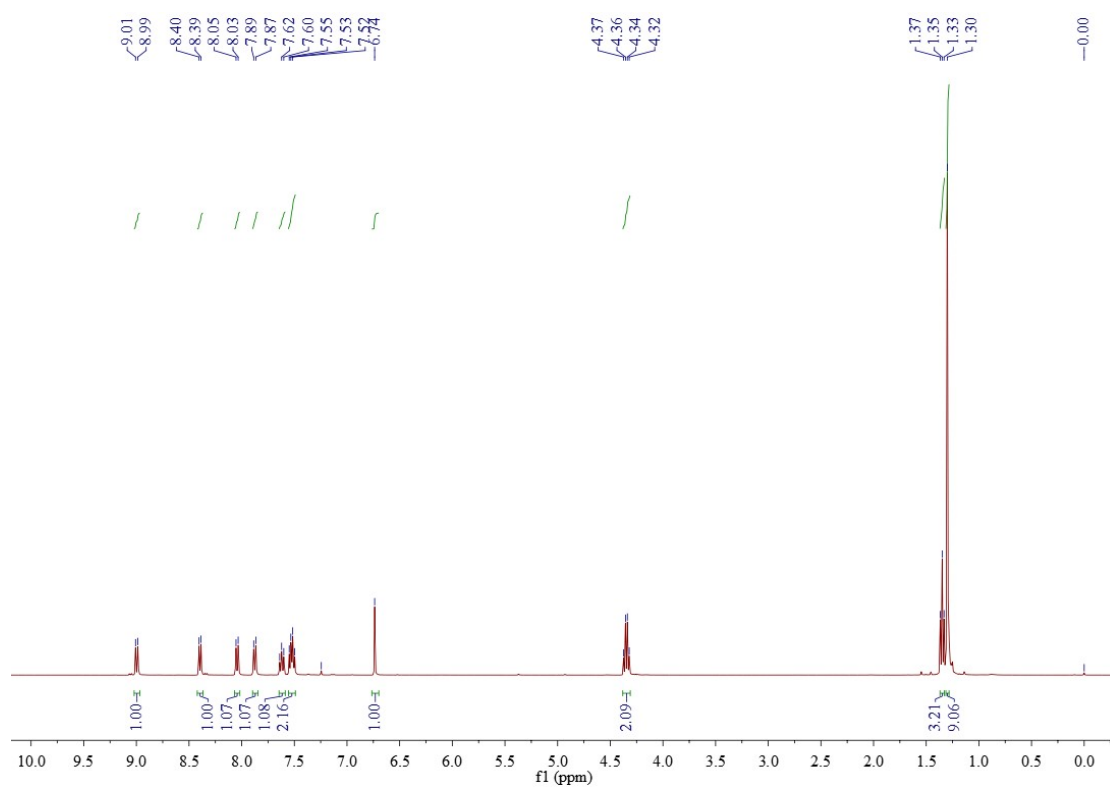
<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) spectra of **4w**



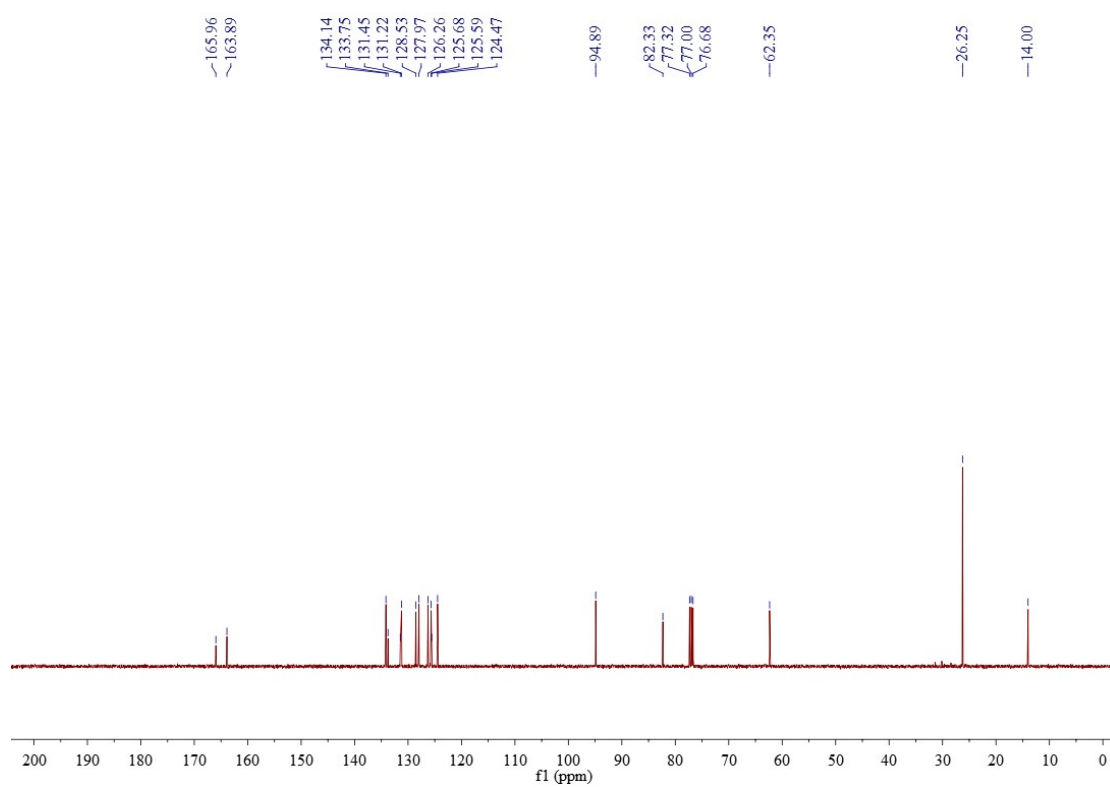
<sup>13</sup>C NMR (101MHz, CDCl<sub>3</sub>) spectra of **4w**



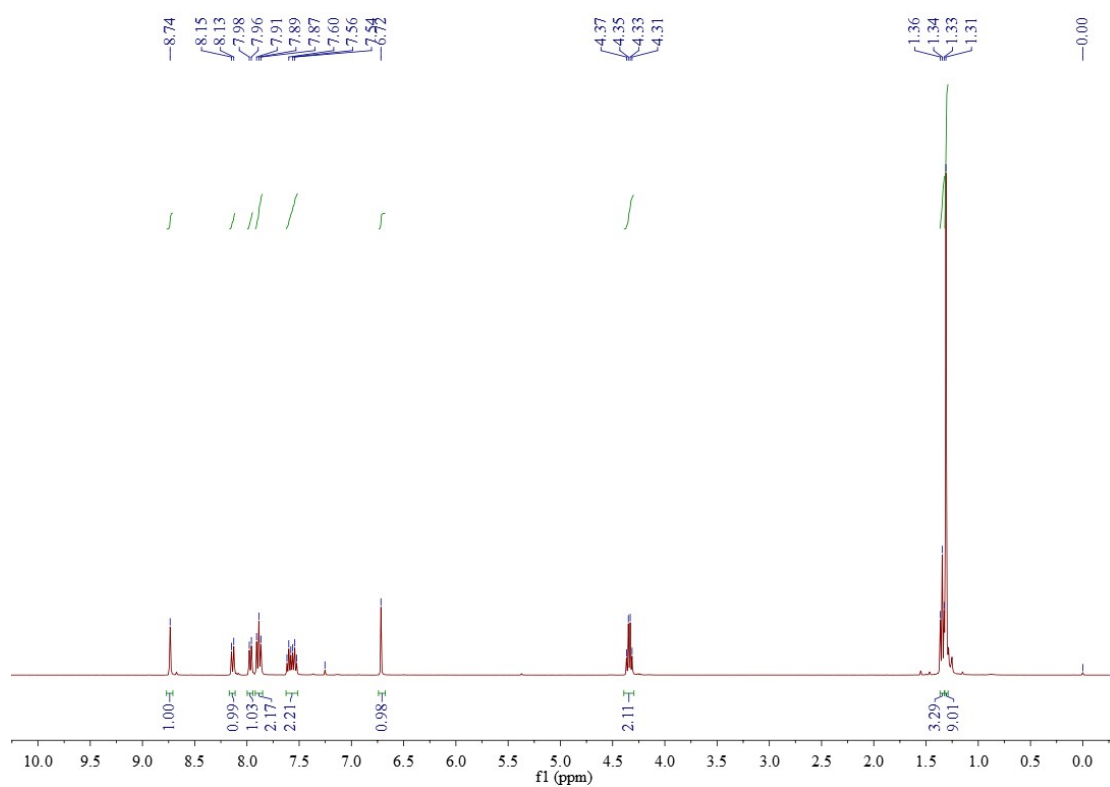
<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) spectra of **4x**



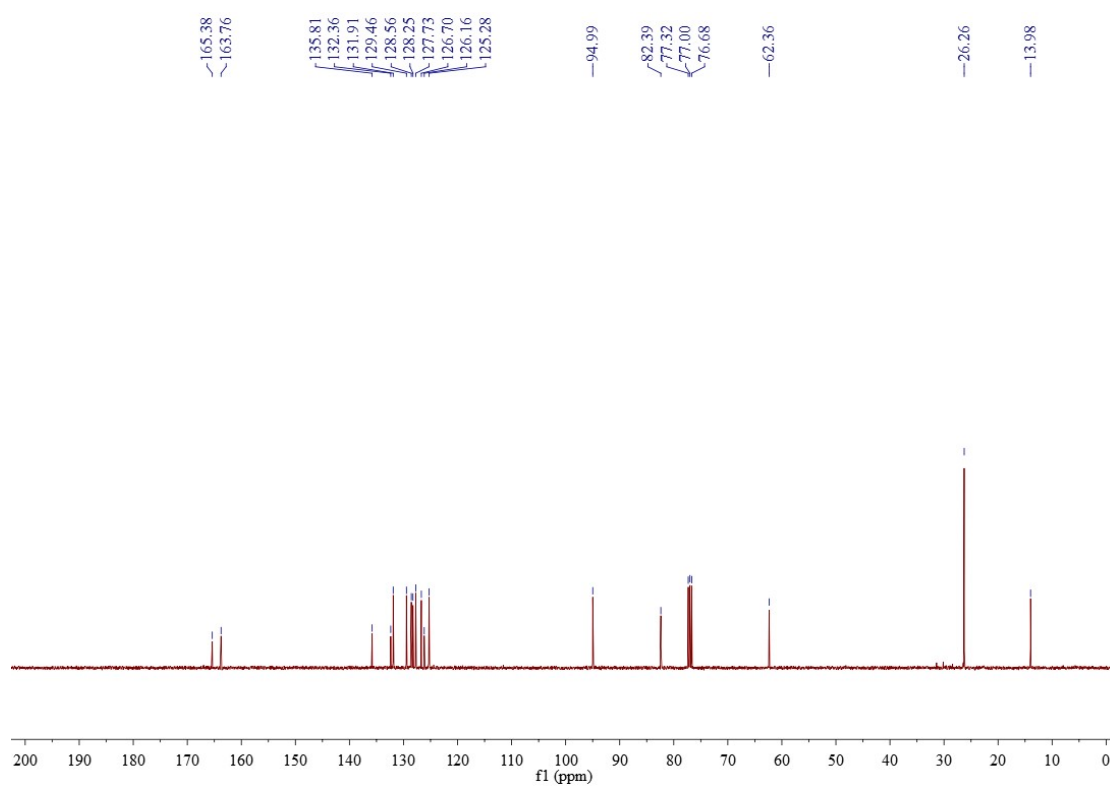
<sup>13</sup>C NMR (101MHz, CDCl<sub>3</sub>) spectra of **4x**



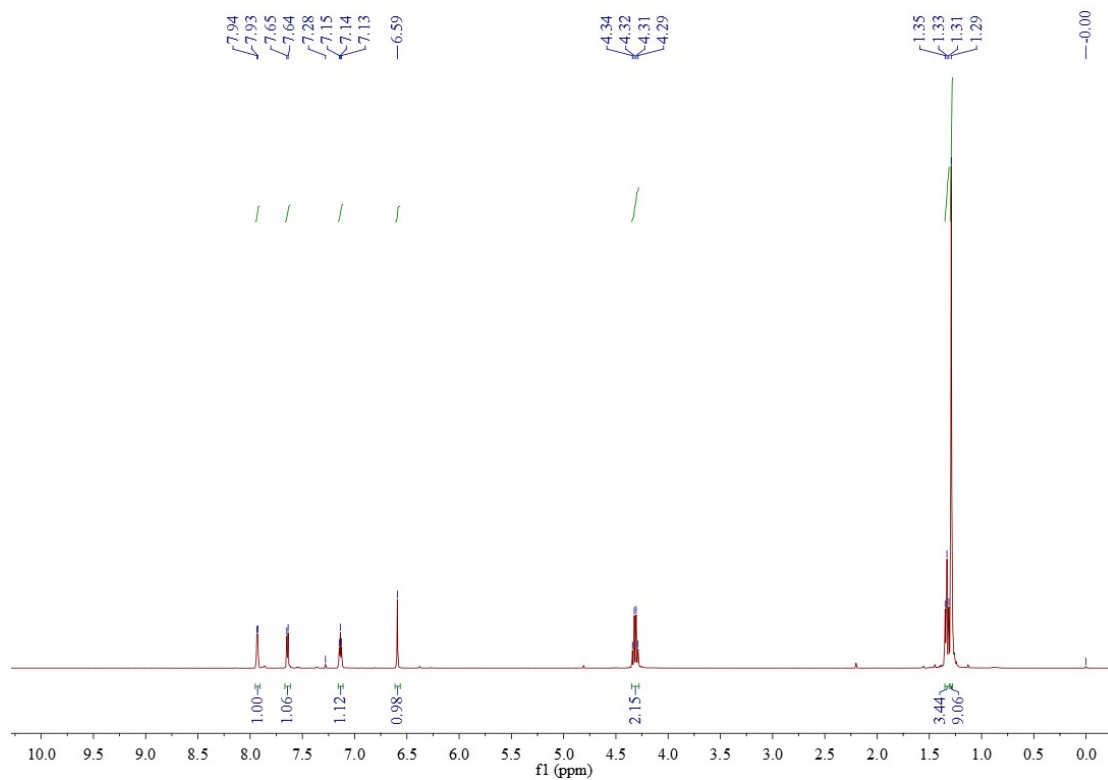
<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) spectra of **4y**



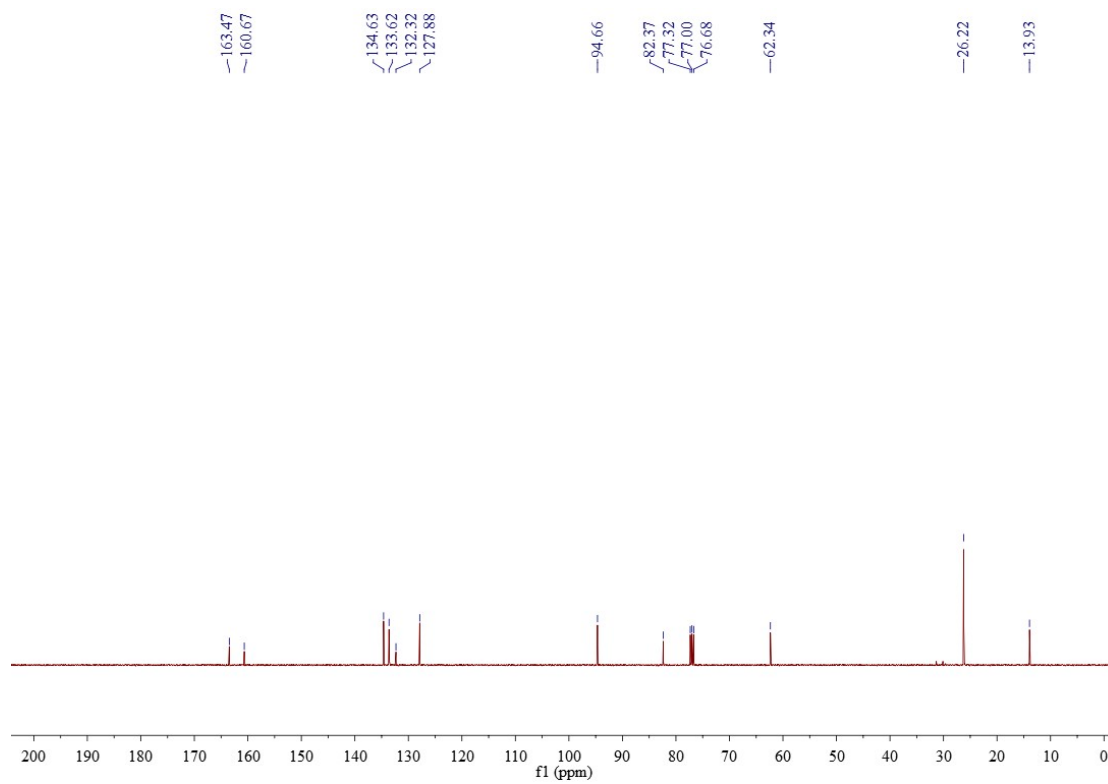
<sup>13</sup>C NMR (101MHz, CDCl<sub>3</sub>) spectra of **4y**



<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) spectra of **4z**

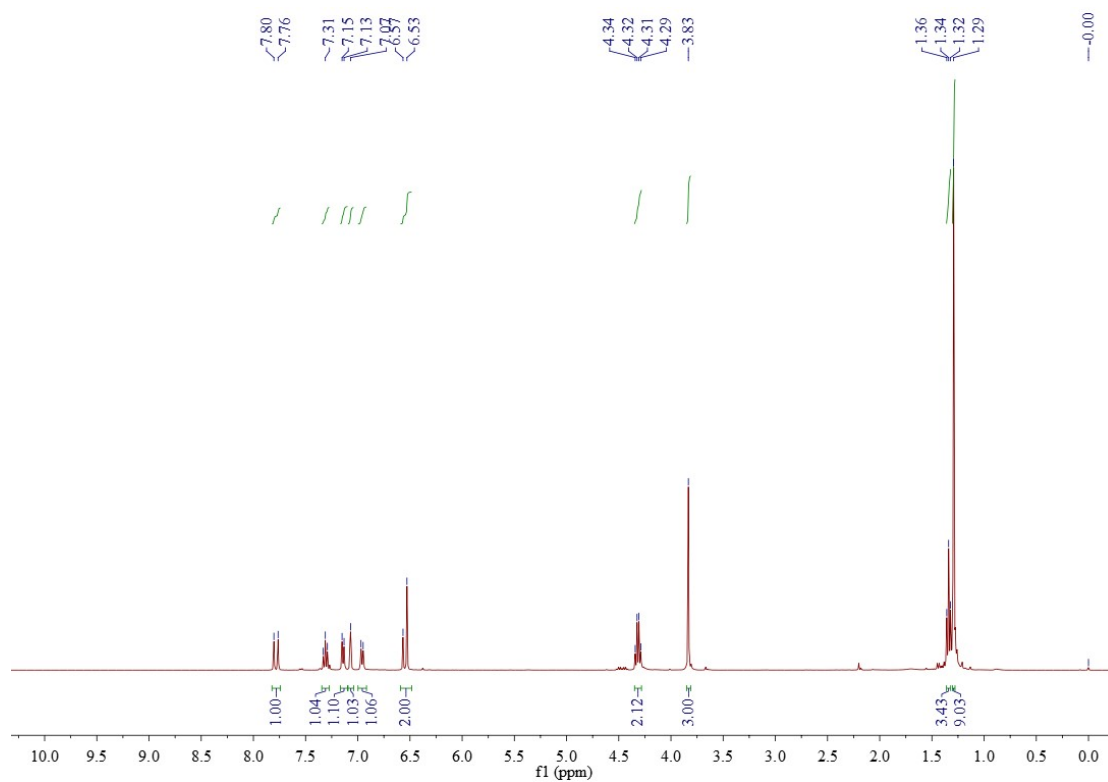


<sup>13</sup>C NMR (101MHz, CDCl<sub>3</sub>) spectra of **4z**

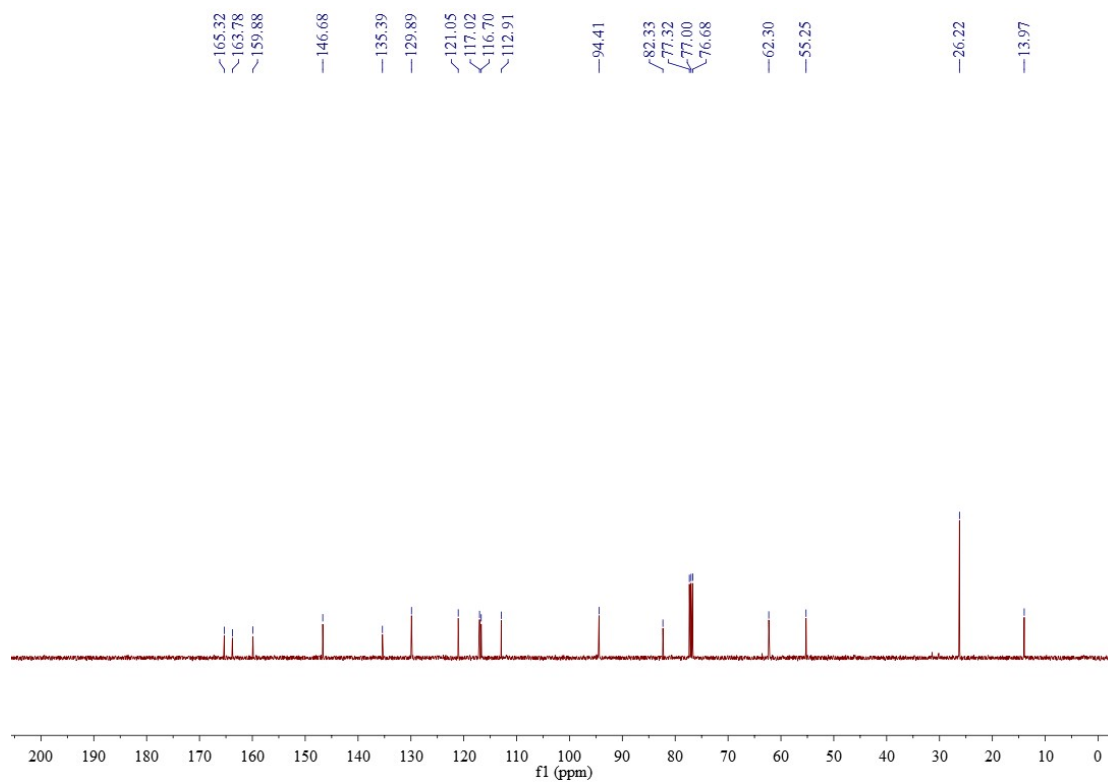




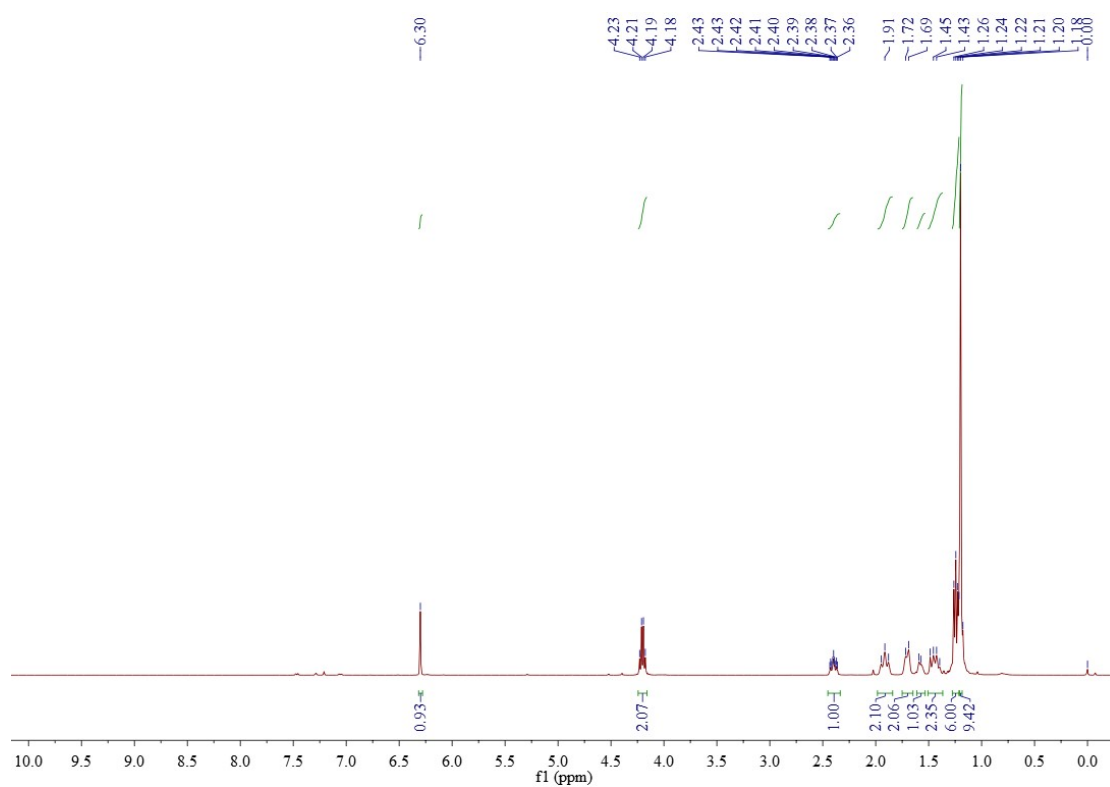
<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) spectra of **4aa**



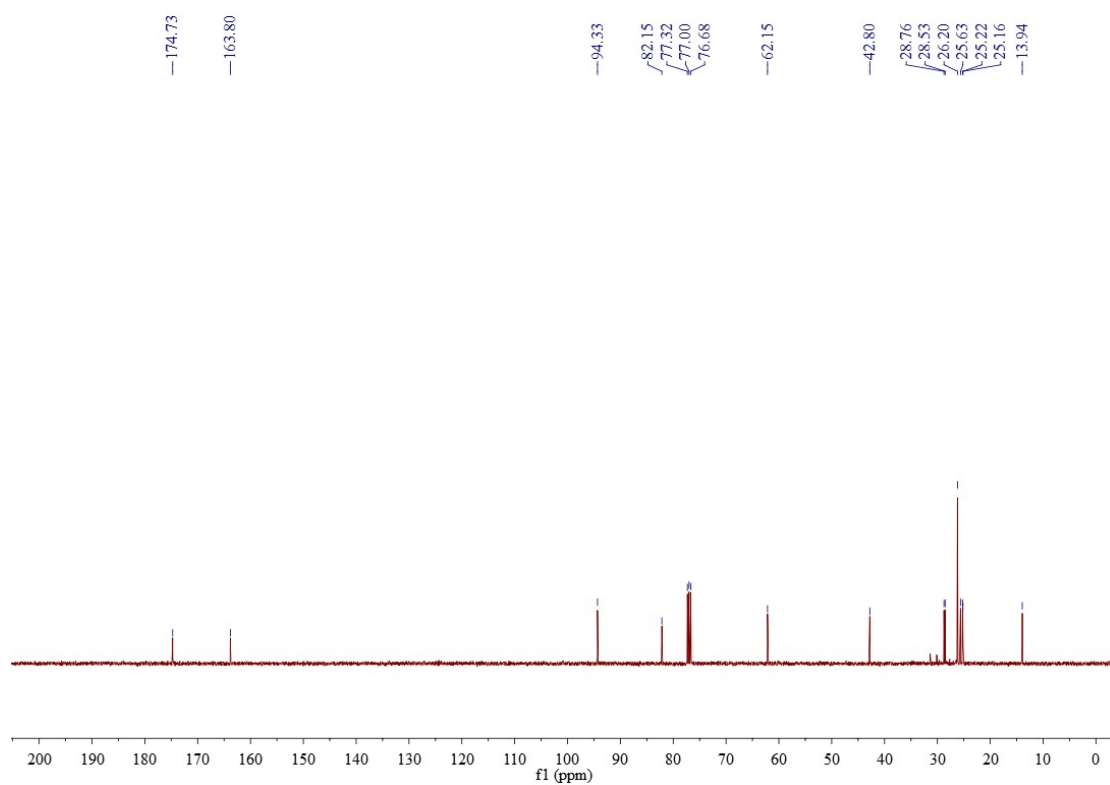
<sup>13</sup>C NMR (101MHz, CDCl<sub>3</sub>) spectra of **4aa**



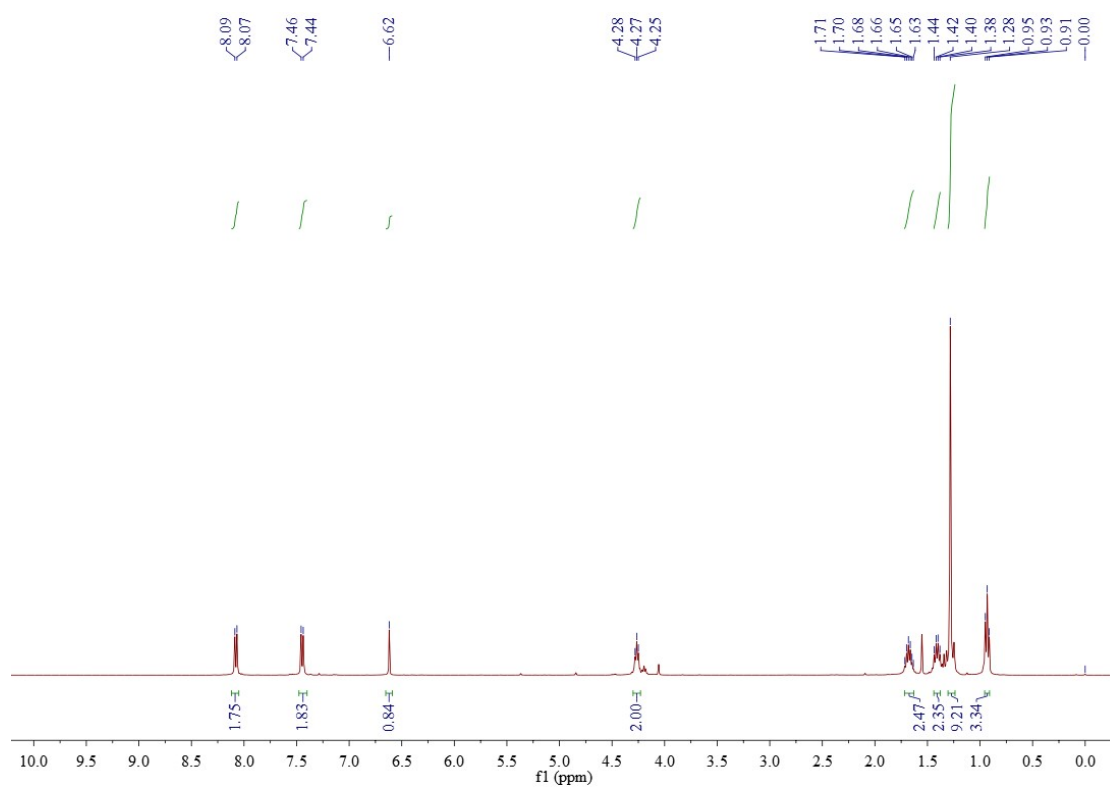
<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) spectra of **4ab**



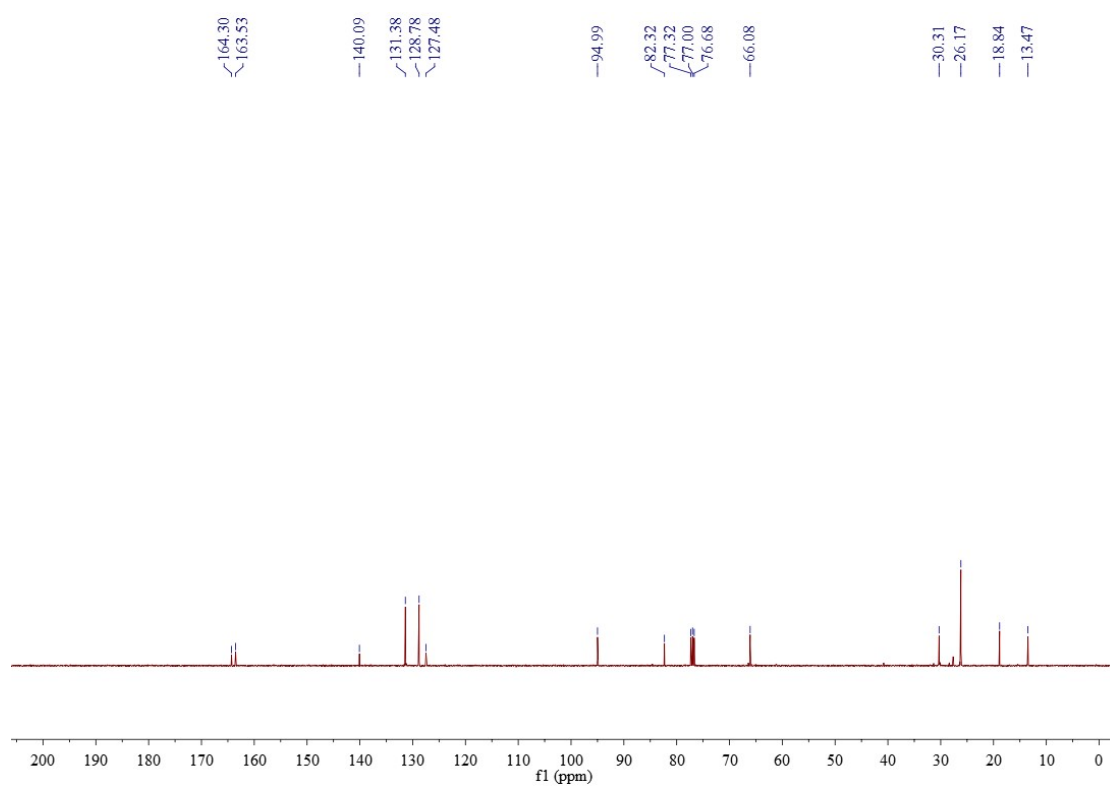
<sup>13</sup>C NMR (101MHz, CDCl<sub>3</sub>) spectra of **4ab**



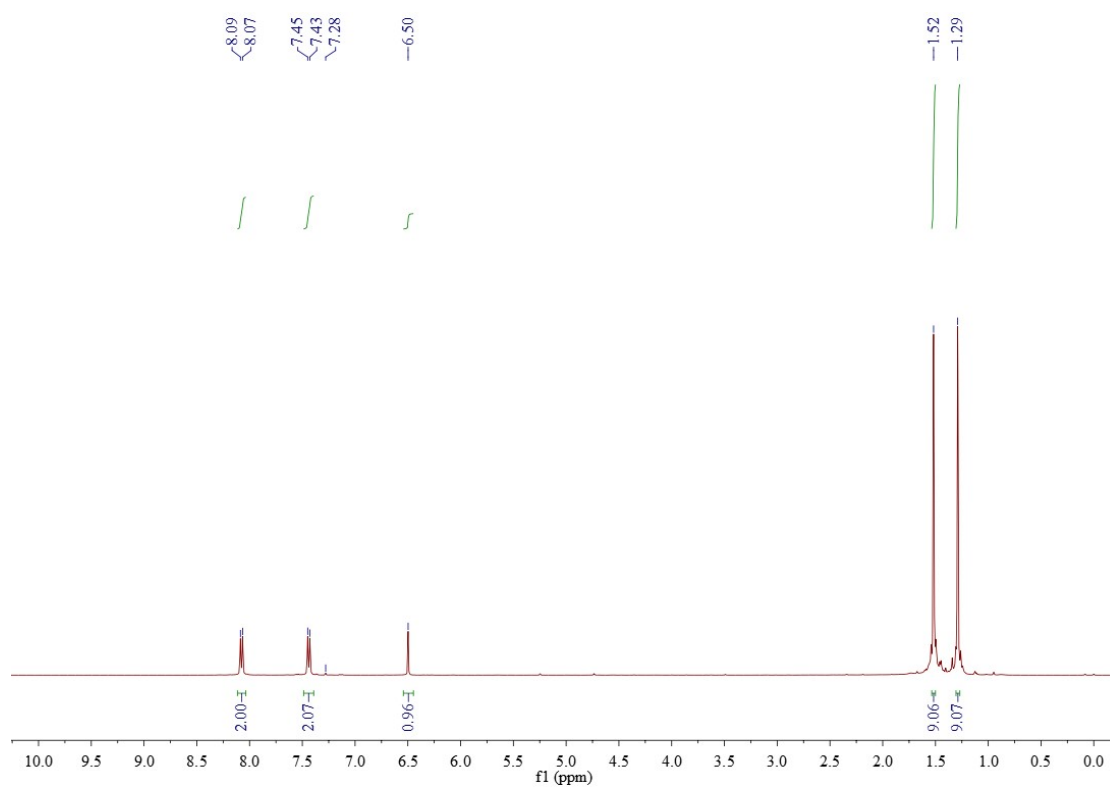
<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) spectra of **4ac**



<sup>13</sup>C NMR (101MHz, CDCl<sub>3</sub>) spectra of **4ac**



<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) spectra of **4ad**



<sup>13</sup>C NMR (101MHz, CDCl<sub>3</sub>) spectra of **4ad**

