

## Supporting Information

### Direct vinylation of natural alcohols and derivatives with calcium carbide

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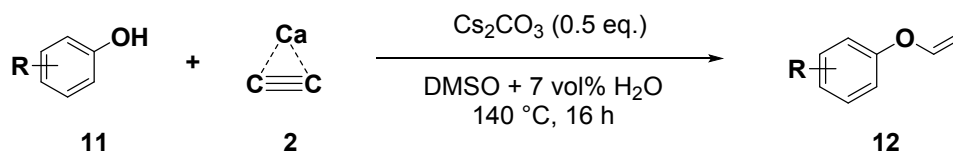
#### General Information

All solvents and chemicals used were obtained from commercial suppliers and used directly without any pre-treatment, unless otherwise indicated. All reactions were set up under argon atmosphere unless otherwise stated.

Analytical thin layer chromatography (TLC) was performed using Merck 60 F-254 silica gel plates with visualization by ultraviolet light (254 nm) and/or I<sub>2</sub> stain. <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra were recorded on Bruker AV-400 (400 MHz) spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) with the residual solvent peak of tetramethylsilane used as the internal standard at 0.00 ppm. <sup>1</sup>H NMR data are reported in the following order: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet), coupling constants (J, Hz), integration and assignment. High resolution mass spectra (HRMS) were recorded on a Bruker micrOTOF-QII spectrometer.

#### General Experimental Procedure

##### Preparation of Phenyl Vinyl Ethers



In a 8 mL pressure vial, Cs<sub>2</sub>CO<sub>3</sub> (0.5 mmol), alcohol (1 mmol) and CaC<sub>2</sub> (4 mmol) were added. The vial was then purged and refilled with argon thrice before DMSO + 7 vol%

H<sub>2</sub>O (5 mL) was added to the vial using a syringe. The reaction was stirred at 140 °C for 16 h, cooled to room temperature before it was diluted with H<sub>2</sub>O (10 mL) and extracted with diethyl ether (3 x 10 mL). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuum. The residue was further purified by column chromatography on silica gel to afford the corresponding vinyl ethers. The NMR spectra data of compounds **12a**<sup>1</sup>, **12d**<sup>2</sup>, **12f**<sup>3</sup>, **12g**<sup>3</sup>, **12h**<sup>3</sup> and **12k**<sup>2</sup>, are available in the literature and are referenced accordingly.

### **1,5-bis(vinyloxy)pentane (3b)**

This compound was prepared according to the optimized condition (Table S1, Entry 8) and purified by liquid-liquid extraction with ether as described above to give the product as an orange liquid (151 mg, 97%). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 6.47 (dd, *J* = 6.8, 14.4 Hz, 2H, CH), 4.17 (dd, *J* = 2.0, 14.4 Hz, 2H, =CH<sub>2</sub>), 3.98 (dd, *J* = 2.0, 6.9 Hz, 2H, =CH<sub>2</sub>), 3.69 (t, *J* = 6.5 Hz, 4H, CH<sub>2</sub>), 1.74 – 1.67 (m, 4H, CH<sub>2</sub>), 1.53 – 1.43 (m, 2H, CH<sub>2</sub>); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 152.0, 86.4, 67.9, 28.9, 22.8; HRMS (ESI+) calc. for C<sub>9</sub>H<sub>16</sub>O<sub>2</sub> [M+H]<sup>+</sup> 157.1223; found 157.1220

### **1,2,3-tris(vinyloxy)propane (6)**

This compound was prepared according to the optimized condition (Table S2, Entry 5) under general procedure and isolated by column chromatography (hexane) to give the product as a light yellow liquid (105 mg, 62%). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 6.48 (dd, *J* = 6.8, 14.4 Hz, 2H, CH), 6.39 (dd, *J* = 6.6, 14.1 Hz, 1H, CH), 4.40 (dd, *J* = 2.0, 14.1 Hz, 1H, =CH<sub>2</sub>), 4.29 – 4.25 (m, 1H, CH), 4.22 (dd, *J* = 2.4, 14.3 Hz, 2H, =CH<sub>2</sub>), 4.10 (dd, *J* = 2.0, 6.5 Hz, 1H, =CH<sub>2</sub>), 4.05 (dd, *J* = 2.4, 6.8 Hz, 2H, =CH<sub>2</sub>), 3.90 – 3.83 (m, 4H, CH<sub>2</sub>); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 151.4, 150.8, 89.5, 87.2, 75.8, 66.5; HRMS (ESI+) calc. for C<sub>9</sub>H<sub>14</sub>O<sub>3</sub> [M+H]<sup>+</sup> 171.1016; found 171.1015

### **1,2,3,4-tetrakis(vinyloxy)butane (8a)**

This compound was prepared according to the optimized condition (Scheme 3) under general procedure and isolated by column chromatography (ethyl acetate/hexane = 1/30) to give the product as a colourless liquid (90 mg, 40%). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ

6.48 (dd,  $J = 6.8, 14.3$  Hz, 2H, CH), 6.33 (dd,  $J = 6.5, 14.1$  Hz, 2H, CH), 4.40 (dd,  $J = 2.0, 14.0$  Hz, 2H, =CH<sub>2</sub>), 4.27 – 4.23 (m, 2H, CH), 4.22 (dd,  $J = 2.2, 14.2$  Hz, 2H, =CH<sub>2</sub>), 4.09 (dd,  $J = 2.1, 6.4$  Hz, 2H, =CH<sub>2</sub>), 4.05 (dd,  $J = 2.3, 6.8$  Hz, 2H, =CH<sub>2</sub>), 3.96 (dd,  $J = 2.8, 11.0$  Hz, 2H, CH<sub>2</sub>), 3.86 (dd,  $J = 4.5, 11.0$  Hz, 2H, CH<sub>2</sub>); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  151.6, 151.1, 90.0, 87.4, 76.5, 66.1; HRMS (ESI+) calc. for C<sub>12</sub>H<sub>18</sub>O<sub>4</sub> [M+Na]<sup>+</sup> 249.1097; found 249.1093

### **2,3-bis(vinyloxy)buta-1,3-diene (8b)**

This compound was prepared according to the optimized condition (Scheme 3) under general procedure and isolated by column chromatography (hexane) to give the product as a light yellow liquid (17 mg, 12%). Low isolated yield was attributed to the volatility of the product. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.48 (dd,  $J = 6.0, 13.7$  Hz, 2H, CH), 5.02 (d,  $J = 1.6$  Hz, 2H, =CH<sub>2</sub>), 4.81 (dd,  $J = 1.6, 13.8$  Hz, 2H, =CH<sub>2</sub>), 4.56 (d,  $J = 1.6$  Hz, 2H, =CH<sub>2</sub>), 4.45 (dd,  $J = 1.6, 6.0$  Hz, 2H, =CH<sub>2</sub>); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  153.4, 147.5, 96.0, 91.4; HRMS (ESI+) calc. for C<sub>8</sub>H<sub>10</sub>O<sub>2</sub> [M+H]<sup>+</sup> 139.0754; found 139.0753

### **1,2,3,4,5-pentakis(vinyloxy)pentane (10)**

This compound was prepared according to the optimized condition (Scheme 4) under general procedure and isolated by column chromatography (DCM/hexane = 1/5 to 1/3) to give the product as a colourless liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.47 (dd,  $J = 6.8, 14.3$  Hz, 2H, CH), 6.35 (dd,  $J = 6.6, 14.1$  Hz, 2H, overlapping CH), 6.31 (dd,  $J = 6.4, 14.0$  Hz, 1H, overlapping CH), 4.47 – 4.40 (m, 3H, overlapping =CH<sub>2</sub>), 4.28 – 4.19 (m, 5H, overlapping CH, =CH<sub>2</sub>), 4.11 (dd,  $J = 2.1, 6.5$  Hz, 2H, =CH<sub>2</sub>), 4.07 – 4.04 (m, 3H, overlapping CH, =CH<sub>2</sub>), 3.91 (dd,  $J = 4.7, 10.7$  Hz, 2H, CH<sub>2</sub>), 3.82 (dd,  $J = 5.0, 10.7$  Hz, 2H, CH<sub>2</sub>); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  152.6, 151.3, 151.1, 90.0, 89.7, 87.6, 78.4, 76.9, 65.9; HRMS (ESI+) calc. for C<sub>15</sub>H<sub>22</sub>O<sub>5</sub> [M+Na]<sup>+</sup> 305.1359; found 305.1360

### **(vinyloxy)benzene (12a)<sup>1</sup>**

This compound was prepared according to the general procedure and isolated by column chromatography (hexane) to give the product as a light yellow liquid (102 mg, 85%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.35 – 7.30 (m, 2H, ArH), 7.10 – 7.06 (m, 1H, ArH), 7.02 –

6.99 (m, 2H, ArH), 6.65 (dd,  $J = 6.1, 13.7$  Hz, 1H, CH), 4.77 (dd,  $J = 1.6, 13.7$  Hz, 1H, =CH<sub>2</sub>), 4.43 (dd,  $J = 1.7, 6.1$  Hz, 1H, =CH<sub>2</sub>); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 156.9, 148.3, 129.8, 123.3, 117.2, 95.2

#### **1,4-bis(vinyloxy)benzene (12b)**

This compound was prepared according to the general procedure and isolated by column chromatography (hexane) to give the product as a light yellow liquid (154 mg, 95%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.96 (s, 4H, ArH), 6.59 (dd,  $J = 6.1, 13.8$  Hz, 2H, CH), 4.70 (dd,  $J = 1.7, 13.8$  Hz, 2H, =CH<sub>2</sub>), 4.39 (dd,  $J = 1.7, 6.1$  Hz, 2H, =CH<sub>2</sub>); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.6, 149.0, 118.6, 94.7; HRMS (APCI+) calc. for C<sub>10</sub>H<sub>10</sub>O<sub>2</sub> [M+H]<sup>+</sup> 163.0754; found 163.0749

#### **1-(tert-butyl)-4-(vinyloxy)benzene (12d)<sup>2</sup>**

This compound was prepared according to the general procedure and isolated by column chromatography (hexane) to give the product as a light yellow liquid (162 mg, 92%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.35 – 7.32 (m, 2H, ArH), 6.96 – 6.92 (m, 2H, ArH), 6.64 (dd,  $J = 6.1, 13.7$  Hz, 1H, CH), 4.74 (dd,  $J = 1.6, 13.7$  Hz, 1H, =CH<sub>2</sub>), 4.39 (dd,  $J = 1.6, 6.1$  Hz, 1H, =CH<sub>2</sub>), 1.31 (s, 9H, CH<sub>3</sub>); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 154.7, 148.7, 146.1, 126.6, 116.7, 94.7, 34.4, 31.7

#### **1-ethynyl-3-(vinyloxy)benzene (12e)**

This compound was prepared according to the general procedure and isolated by column chromatography (hexane) to give the product as a light yellow liquid (58 mg, 40%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.29 – 7.20 (m, 2H, ArH), 7.13 – 7.12 (m, 1H, ArH), 7.02 – 6.99 (m, 1H, ArH), 6.61 (dd,  $J = 6.1, 13.7$  Hz, 1H, CH), 4.79 (dd,  $J = 1.8, 13.7$  Hz, 1H, =CH<sub>2</sub>), 4.48 (dd,  $J = 1.8, 6.1$  Hz, 1H, =CH<sub>2</sub>), 3.09 (s, 1H, CH); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 156.7, 147.8, 129.8, 127.1, 123.6, 120.6, 118.2, 96.1, 83.1, 77.8; HRMS (APCI+) calc. for C<sub>10</sub>H<sub>8</sub>O [M+H]<sup>+</sup> 145.0648; found 145.0653

#### **2-(vinyloxy)aniline (12f)<sup>3</sup>**

This compound was prepared according to the general procedure and isolated by column chromatography (ethyl acetate/hexane = 1/10) to give the product as an orange brown liquid (101 mg, 75%). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 6.95 – 6.89 (m, 2H, ArH), 6.77 – 6.69 (m, 2H, ArH), 6.61 (dd, *J* = 6.1, 13.8 Hz, 1H, CH), 4.68 (dd, *J* = 1.8, 13.8 Hz, 1H, =CH<sub>2</sub>), 4.39 (dd, *J* = 1.8, 6.1 Hz, 1H, =CH<sub>2</sub>), 3.80 (broad s, 2H, NH<sub>2</sub>); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 149.0, 143.8, 137.5, 124.4, 118.7, 117.6, 116.2, 94.0

### **3-(vinyloxy)aniline (12g)<sup>3</sup>**

This compound was prepared according to the general procedure and isolated by column chromatography (ethyl acetate/hexane = 1/5) to give the product as an orange liquid (88 mg, 65%). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.08 (t, 1H, ArH), 6.61 (dd, *J* = 6.1, 13.7 Hz, 1H, CH), 6.41 – 6.38 (m, 2H, ArH), 6.33 (t, 1H, ArH), 4.75 (dd, *J* = 1.6, 13.7 Hz, 1H, =CH<sub>2</sub>), 4.40 (dd, *J* = 1.6, 6.1 Hz, 1H, =CH<sub>2</sub>), 3.71 (broad s, 2H, NH<sub>2</sub>); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 158.1, 148.2, 148.0, 130.4, 110.2, 107.0, 104.0, 95.1

### **4-(vinyloxy)aniline (12h)<sup>3</sup>**

This compound was prepared according to the general procedure and isolated by column chromatography (ethyl acetate/hexane = 1/4) to give the product as a brown liquid (122 mg, 90%). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 6.84 – 6.82 (m, 2H, ArH), 6.65 – 6.62 (m, 2H, ArH), 6.56 (dd, *J* = 6.2, 13.8 Hz, 1H, CH), 4.60 (dd, *J* = 1.7, 13.8 Hz, 1H, =CH<sub>2</sub>), 4.29 (dd, *J* = 1.7, 6.2 Hz, 1H, =CH<sub>2</sub>), 3.54 (broad s, 2H, NH<sub>2</sub>); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 150.0, 149.4, 142.4, 118.9, 116.2, 93.1

### **1-methoxy-4-(vinyloxy)benzene (12i)**

This compound was prepared according to the general procedure and isolated by column chromatography (ethyl acetate/hexane = 1/30) to give the product as a light yellow liquid (123 mg, 82%). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 6.96 – 6.93 (m, 2H, ArH), 6.86 – 6.84 (m, 2H, ArH), 6.59 (dd, *J* = 6.1, 13.8 Hz, 1H, CH), 4.64 (dd, *J* = 1.7, 13.8 Hz, 1H, =CH<sub>2</sub>), 4.33 (dd, *J* = 1.7, 6.1 Hz, 1H, =CH<sub>2</sub>), 3.78 (s, 3H, CH<sub>3</sub>); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 155.8, 150.6, 149.6, 118.8, 114.8, 93.7, 55.8; HRMS (ESI) calc. for C<sub>9</sub>H<sub>10</sub>O<sub>2</sub> 150.0675; found 150.0674

### 5-methoxy-2-(vinyloxy)aniline (12j)

This compound was prepared according to the general procedure and isolated by column chromatography (ethyl acetate/hexane = 1/10) to give the product as an orange brown liquid (127 mg, 77%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.82 (d, *J* = 8.7 Hz, 1H, ArH), 6.55 (dd, *J* = 6.2, 13.8 Hz, 1H, CH), 6.32 (d, *J* = 2.9 Hz, 1H, ArH), 6.25 (dd, *J* = 2.9, 8.7 Hz, 1H, ArH), 4.56 (dd, *J* = 1.9, 13.8 Hz, 1H, =CH<sub>2</sub>), 4.29 (dd, *J* = 1.8, 6.2 Hz, 1H, =CH<sub>2</sub>), 3.80 (broad s, 2H, NH<sub>2</sub>), 3.74 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 156.9, 150.1, 138.8, 137.7, 119.4, 103.1, 102.2, 92.6, 55.6; HRMS (APCI+) calc. for C<sub>9</sub>H<sub>11</sub>NO<sub>2</sub> [M+H]<sup>+</sup> 166.0863; found 166.0863

### 1-bromo-2-(vinyloxy)benzene (12k)<sup>2</sup>

This compound was prepared according to the general procedure and isolated by column chromatography (hexane) to give the product as a light yellow liquid (100 mg, 50%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.58 (dd, *J* = 1.6, 8.0 Hz, 1H, ArH), 7.30 – 7.26 (m, 1H, ArH), 7.05 – 6.96 (m, 2H, ArH), 6.59 (dd, *J* = 6.1, 13.7 Hz, 1H, CH), 4.76 (dd, *J* = 2.0, 13.8 Hz, 1H, =CH<sub>2</sub>), 4.50 (dd, *J* = 2.0, 6.1 Hz, 1H, =CH<sub>2</sub>); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 153.4, 148.2, 133.8, 128.7, 124.9, 118.5, 113.6, 96.0

### 1-bromo-3-(vinyloxy)benzene (12l)

This compound was prepared according to the general procedure and isolated by column chromatography (hexane) to give the product as a light yellow liquid (101 mg, 51%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.23 – 7.16 (m, 3H, ArH), 6.95 – 6.92 (m, 1H, ArH), 6.59 (dd, *J* = 6.0, 13.7 Hz, 1H, CH), 4.81 (dd, *J* = 1.8, 13.7 Hz, 1H, =CH<sub>2</sub>), 4.50 (dd, *J* = 1.8, 6.0 Hz, 1H, =CH<sub>2</sub>); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 157.6, 147.6, 130.9, 126.4, 123.0, 120.5, 115.9, 96.6; HRMS (APCI+) calc. for C<sub>8</sub>H<sub>7</sub>BrO [M+H]<sup>+</sup> 198.9753; found 198.9755

### 1-bromo-4-(vinyloxy)benzene (12m)

This compound was prepared according to the general procedure and isolated by column chromatography (hexane) to give the product as a light yellow liquid (86 mg, 43%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.43 – 7.41 (m, 2H, ArH), 6.90 – 6.87 (m, 2H, ArH), 6.58

(dd,  $J = 6.1, 13.7$  Hz, 1H, CH), 4.78 (dd,  $J = 1.8, 13.7$  Hz, 1H, =CH<sub>2</sub>), 4.47 (dd,  $J = 1.8, 6.0$  Hz, 1H, =CH<sub>2</sub>); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  156.0, 147.9, 132.7, 119.0, 115.8, 96.1; HRMS (APCI+) calc. for C<sub>8</sub>H<sub>7</sub>BrO [M+H]<sup>+</sup> 198.9753; found 198.9754

### 2-(vinyloxy)naphthalene (12p)

This compound was prepared according to the general procedure and isolated by column chromatography (hexane) to give the product as a light yellow liquid (92 mg, 54%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.79 – 7.72 (m, 3H, ArH), 7.47 – 7.43 (m, 1H, ArH), 7.40 – 7.36 (m, 1H, ArH), 7.32 – 7.31 (m, 1H, ArH), 7.23 – 7.20 (m, 1H, ArH), 6.76 (dd,  $J = 6.0, 13.7$  Hz, 1H, CH), 4.85 (dd,  $J = 1.7, 13.7$  Hz, 1H, =CH<sub>2</sub>), 4.51 (dd,  $J = 1.7, 6.1$  Hz, 1H, =CH<sub>2</sub>); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  154.8, 148.2, 134.3, 130.2, 130.0, 127.9, 127.2, 126.8, 124.8, 119.0, 111.7, 95.9; HRMS (APCI+) calc. for C<sub>12</sub>H<sub>10</sub>O [M+H]<sup>+</sup> 171.0804; found 171.0802

### 4-(vinyloxy)benzamide (12q)

This compound was prepared according to the general procedure and isolated by column chromatography (ethyl acetate/hexane = 1/1) to give the product as a light yellow solid (63 mg, 39%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.81 (d,  $J = 8.8$  Hz, 2H, ArH), 7.03 (d,  $J = 8.7$  Hz, 2H, ArH), 6.67 (dd,  $J = 6.0, 13.7$  Hz, 1H, CH), 6.27 (broad s, 2H, NH<sub>2</sub>), 4.89 (dd,  $J = 1.8, 13.6$  Hz, 1H, =CH<sub>2</sub>), 4.57 (dd,  $J = 1.8, 6.0$  Hz, 1H, =CH<sub>2</sub>); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  169.2, 159.8, 147.0, 129.5, 127.9, 116.6, 97.3; HRMS (APCI+) calc. for C<sub>9</sub>H<sub>9</sub>NO<sub>2</sub> [M+H]<sup>+</sup> 164.0706; found 164.0704

## References

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- [2] N. F. McKinley, D. F. O'Shea, *J. Org. Chem.*, **2004**, 69, 5087
- [3] E. Rattanangkool, T. Vilaivan, M. Sukwattanasinitt, S. Wacharasindhu, *Eur. J. Org. Chem.*, **2016**, 25, 4347

**Table S1.** Optimization of Reaction Conditions for Pentanediol<sup>a</sup>

Reaction scheme: 1,5-pentanediol + CaC<sub>2</sub> (with Ca bridging two C≡C groups)  $\xrightarrow[\text{DMSO + vol\% H}_2\text{O, 120 }^\circ\text{C, time}]{\text{Cs}_2\text{CO}_3}$  mono-allyl ether + di-allyl ether

Entry	CaC <sub>2</sub> (mmol)	Cs <sub>2</sub> CO <sub>3</sub> (mmol)	vol% H <sub>2</sub> O	Time (h)	Yield <sup>b</sup> (%) mono:di
1	-	0.3	4	3	NR
2	4	0.2	4	3	28 : 61
3	4	0.3	4	3	12 : 87
4	4	0.4	4	3	15 : 84
5	3	0.3	3	3	5 : 92
6	3	0.3	4	3	8 : 86
7	3	0.3	3	4	5 : 93
8	<b>3</b>	<b>0.3</b>	<b>3</b>	<b>8</b>	<b>0 : 99</b>
9 <sup>c</sup>	4	0.3	4	3	85
10 <sup>c,d</sup>	4	0.3	4	3	79

<sup>a</sup> Reaction conditions: Diol (1 mmol), DMSO + vol% H<sub>2</sub>O (5 mL), base (0.3 mmol), 120 °C, time. <sup>b</sup> NMR yield. <sup>c</sup> Ethylene glycol as the substrate. <sup>d</sup> Without argon atmosphere.



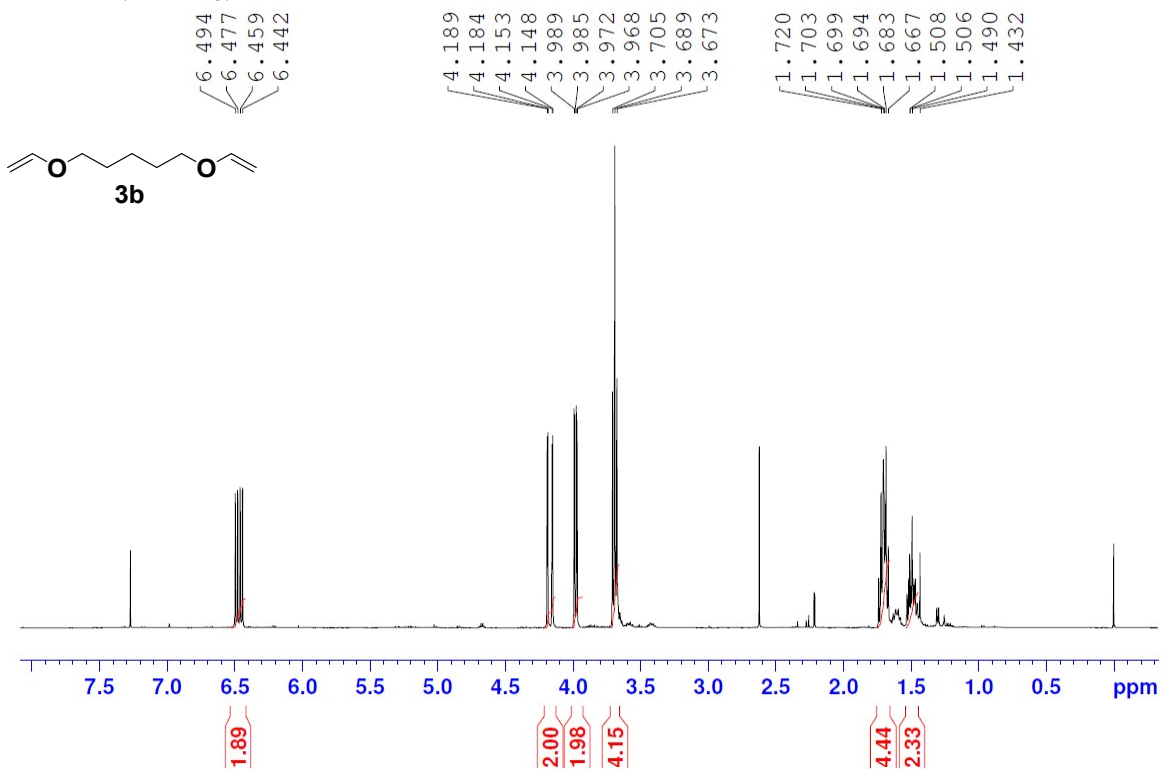
**Table S2.** Optimization of Reaction Condition for Glycerol<sup>a</sup>

Entry	CaC <sub>2</sub> (mmol)	vol% H <sub>2</sub> O	Temp (°C)	Time (h)	Yield <sup>b</sup> (%)
1	5	5	100	3	60
2	5	6	100	3	64
3	5	7	100	3	55
4	6	6	100	3	52
5	6	7	100	3	69
6	6	8	100	3	55
7	6	7	100	1	trace
8	6	7	100	5	30
9	6	7	120	0.5	38
10	6	7	120	1	46
11	6	7	120	2	trace
12	6	7	80	8	27
13	6	7	80	16	68
14	6	7	80	24	34

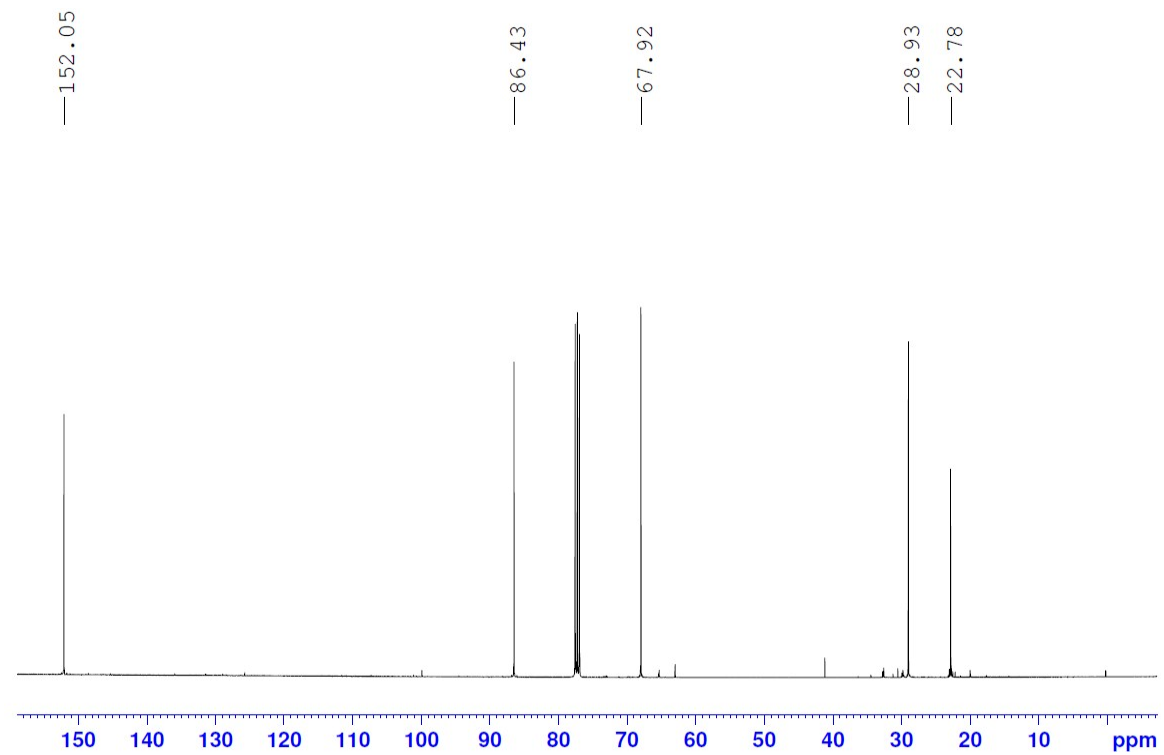
<sup>a</sup> Reaction conditions: Glycerol (1 mmol), DMSO + vol% H<sub>2</sub>O (5 mL), base (1.2 mmol), temp, time. <sup>b</sup> NMR yield.

# $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of Vinyl Ethers

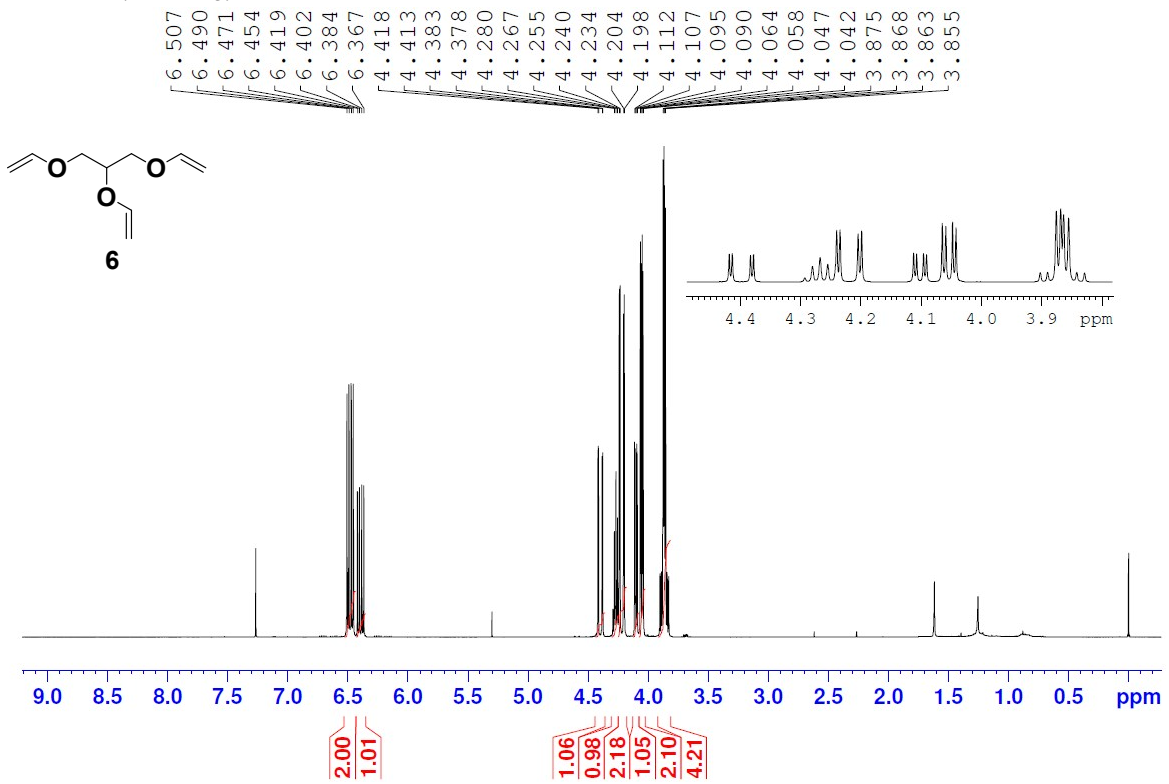
$^1\text{H}$  NMR,  $\text{CDCl}_3$ , 400 MHz



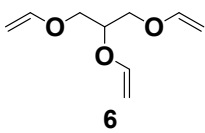
$^{13}\text{C}$  NMR,  $\text{CDCl}_3$ , 101 MHz

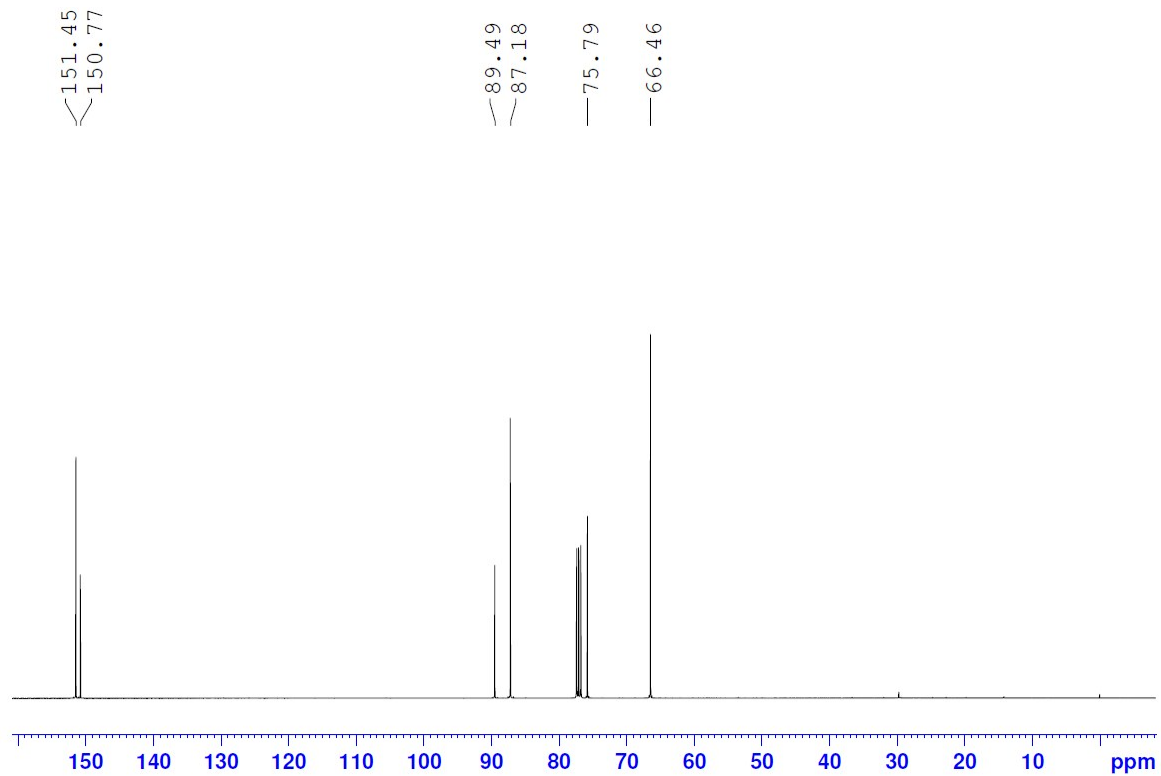


$^1\text{H}$  NMR,  $\text{CDCl}_3$ , 400 MHz

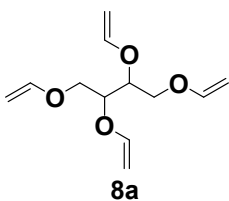
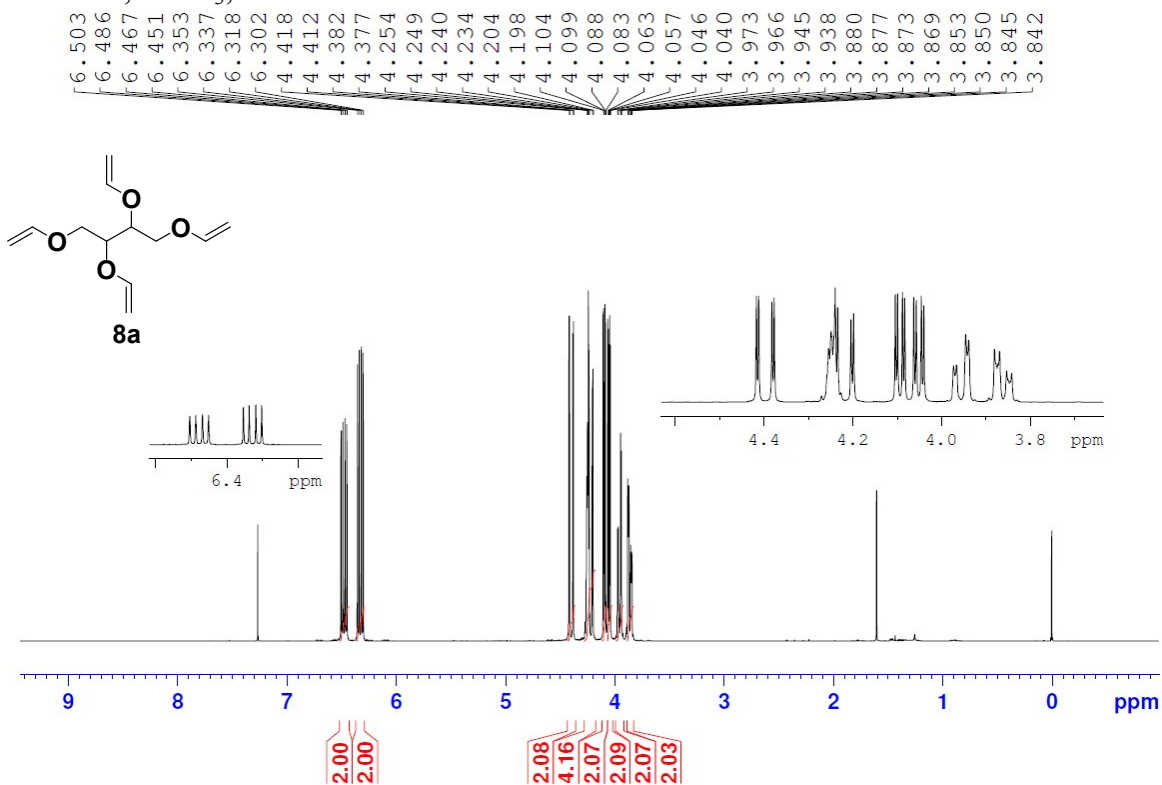


$^{13}\text{C}$  NMR,  $\text{CDCl}_3$ , 101 MHz

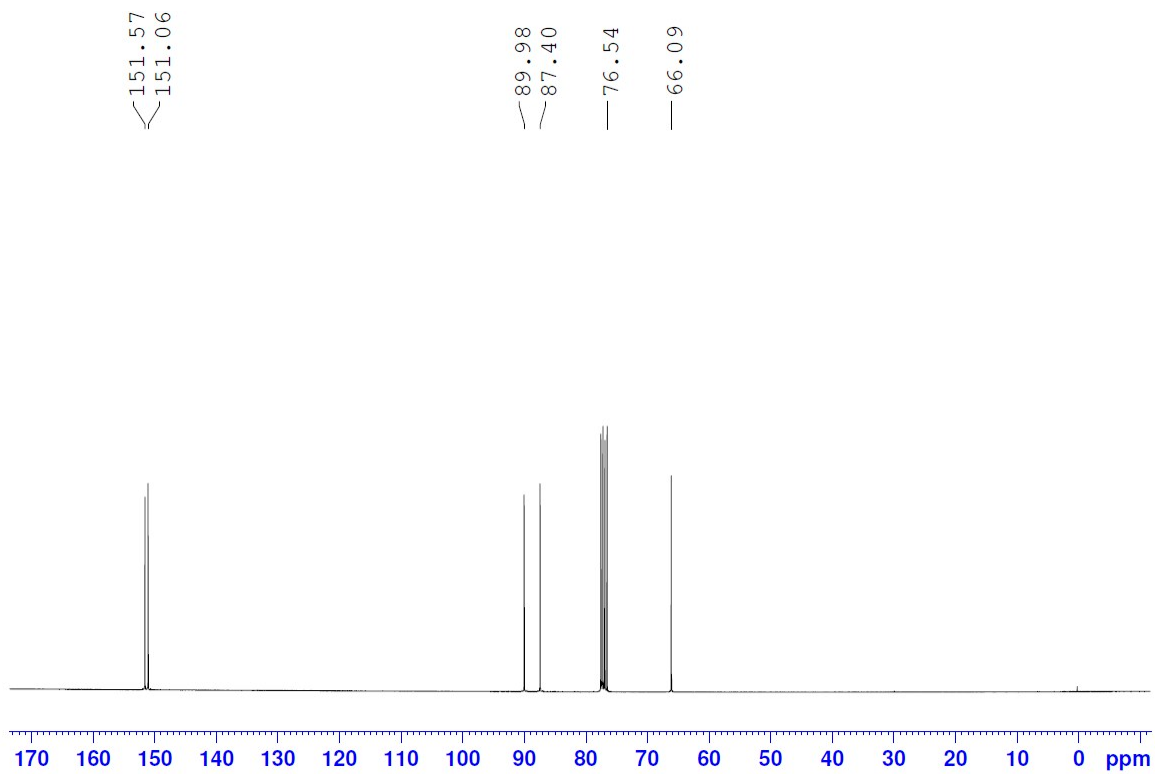




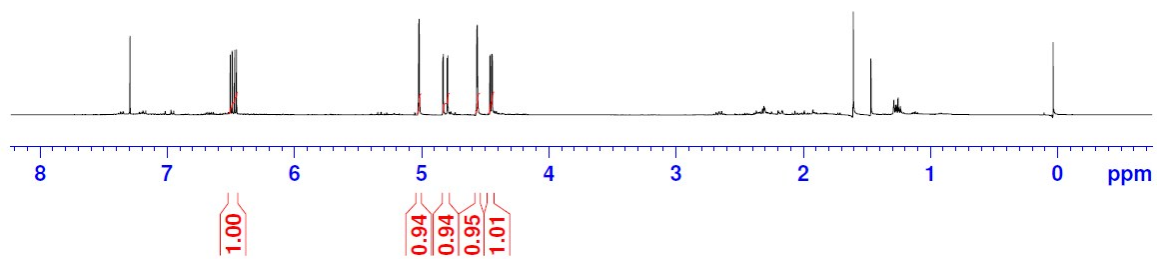
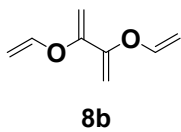
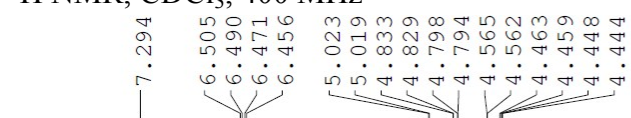
$^1\text{H}$  NMR,  $\text{CDCl}_3$ , 400 MHz



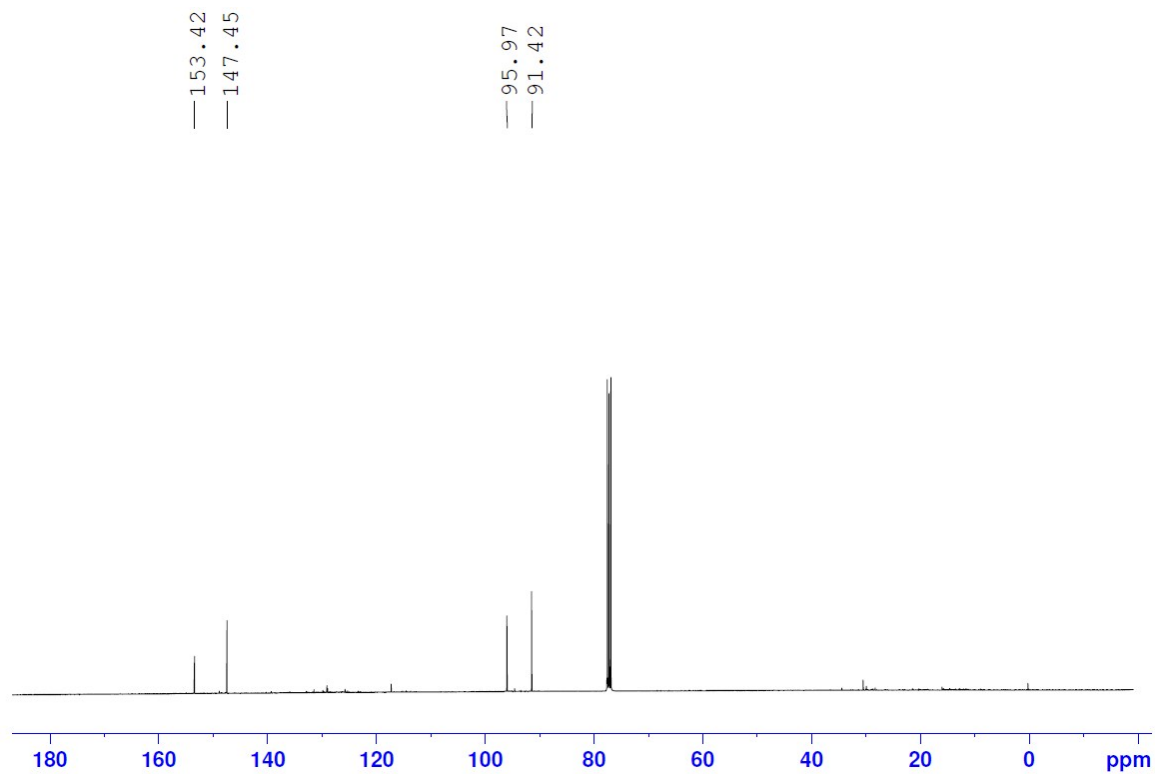
$^{13}\text{C}$  NMR,  $\text{CDCl}_3$ , 101 MHz



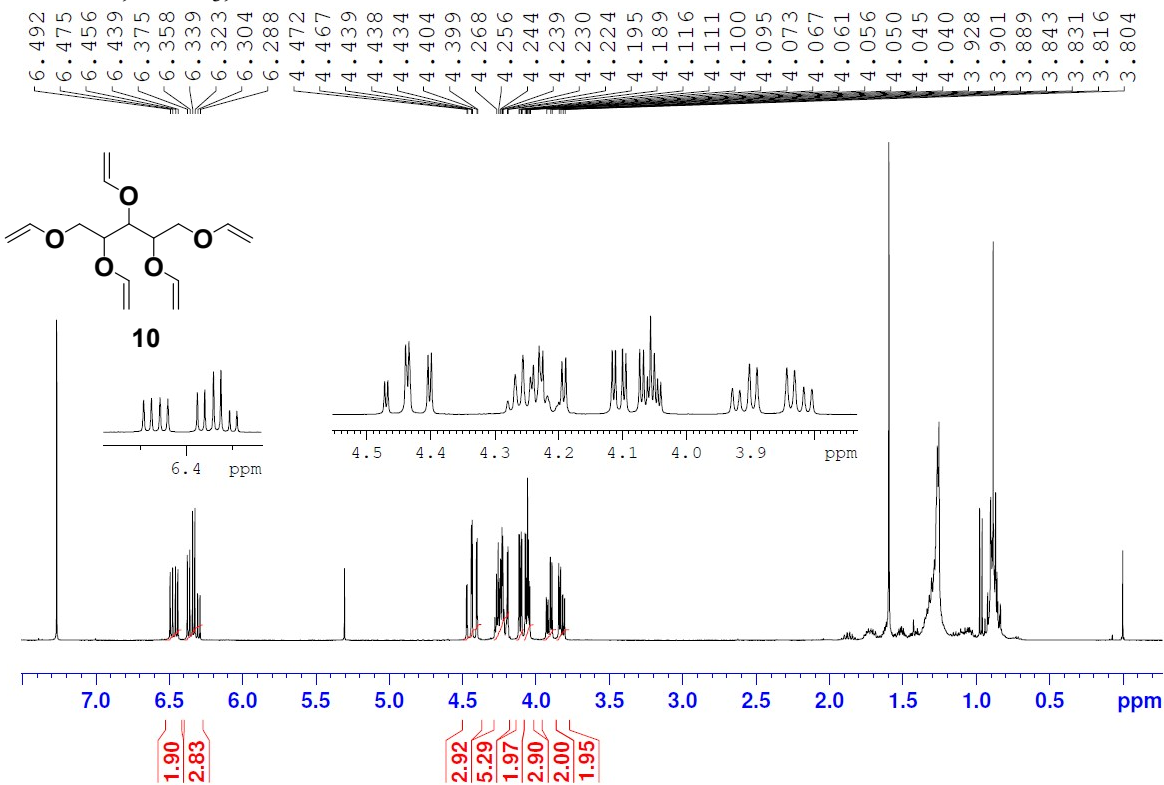
$^1\text{H}$  NMR,  $\text{CDCl}_3$ , 400 MHz



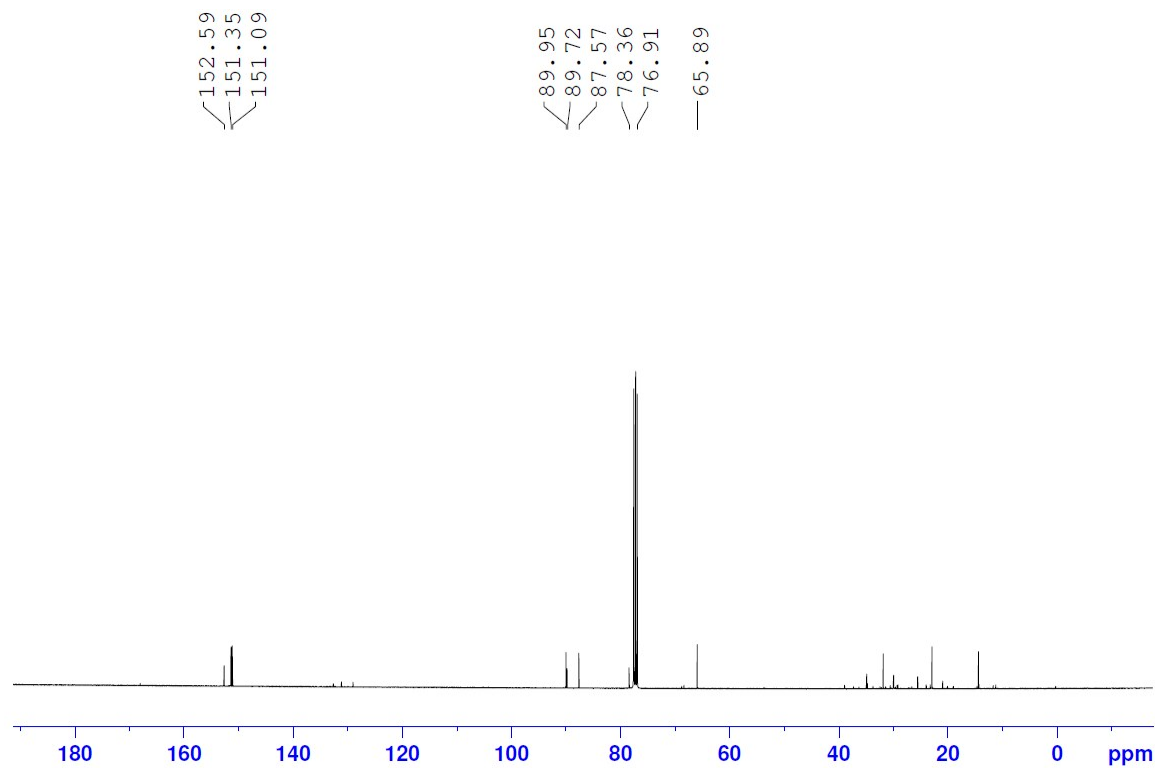
$^{13}\text{C}$  NMR,  $\text{CDCl}_3$ , 101 MHz



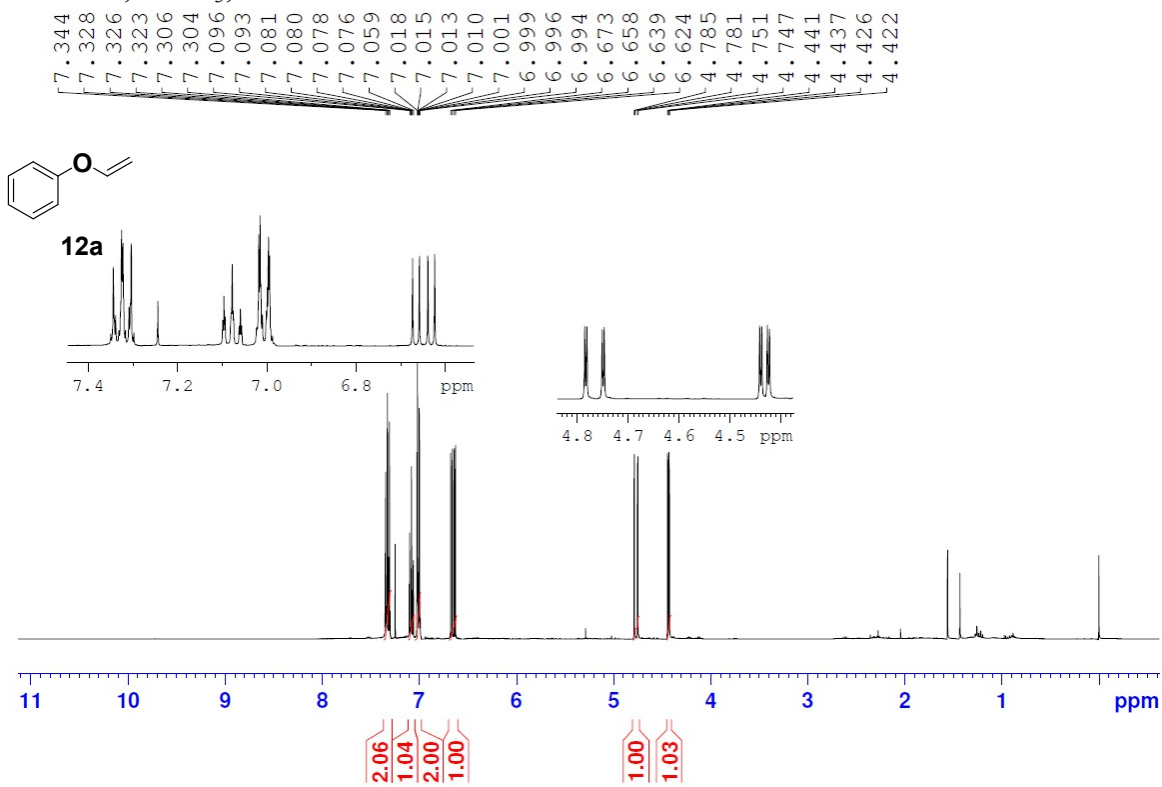
$^1\text{H}$  NMR,  $\text{CDCl}_3$ , 400 MHz



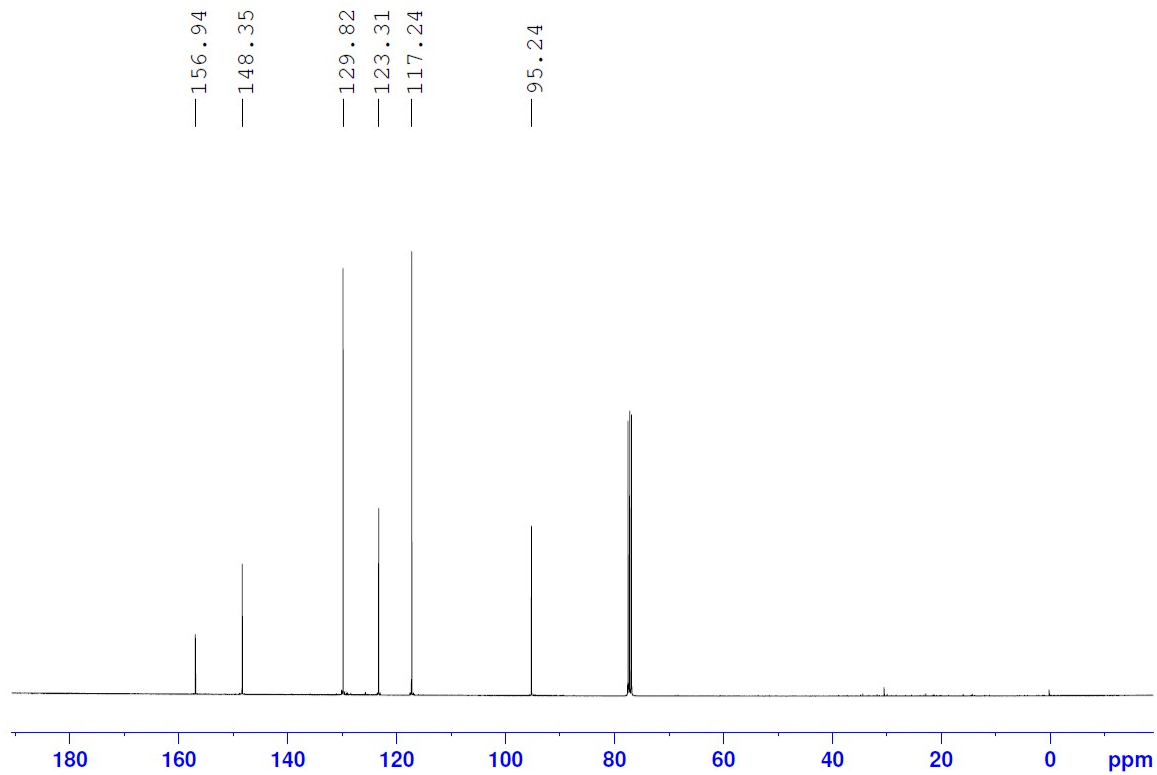
$^{13}\text{C}$  NMR,  $\text{CDCl}_3$ , 101 MHz



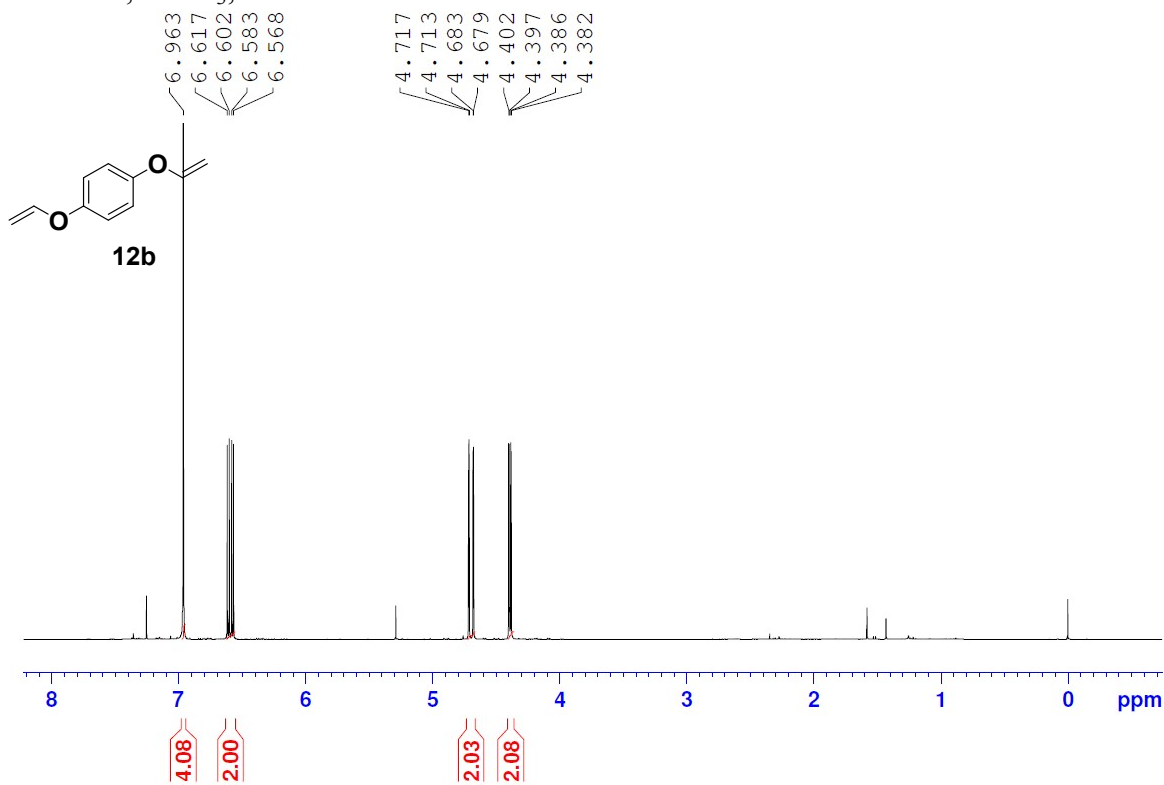
$^1\text{H}$  NMR,  $\text{CDCl}_3$ , 400 MHz



$^{13}\text{C}$  NMR,  $\text{CDCl}_3$ , 101 MHz

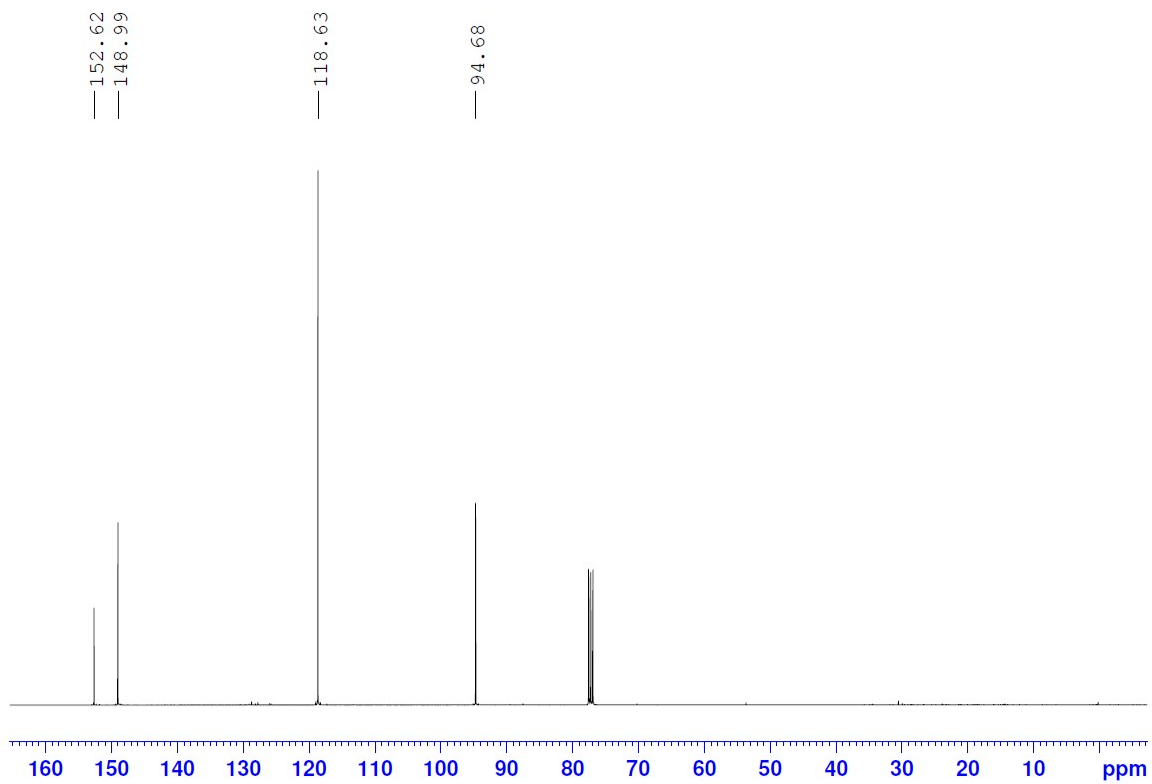


$^1\text{H}$  NMR,  $\text{CDCl}_3$ , 400 MHz

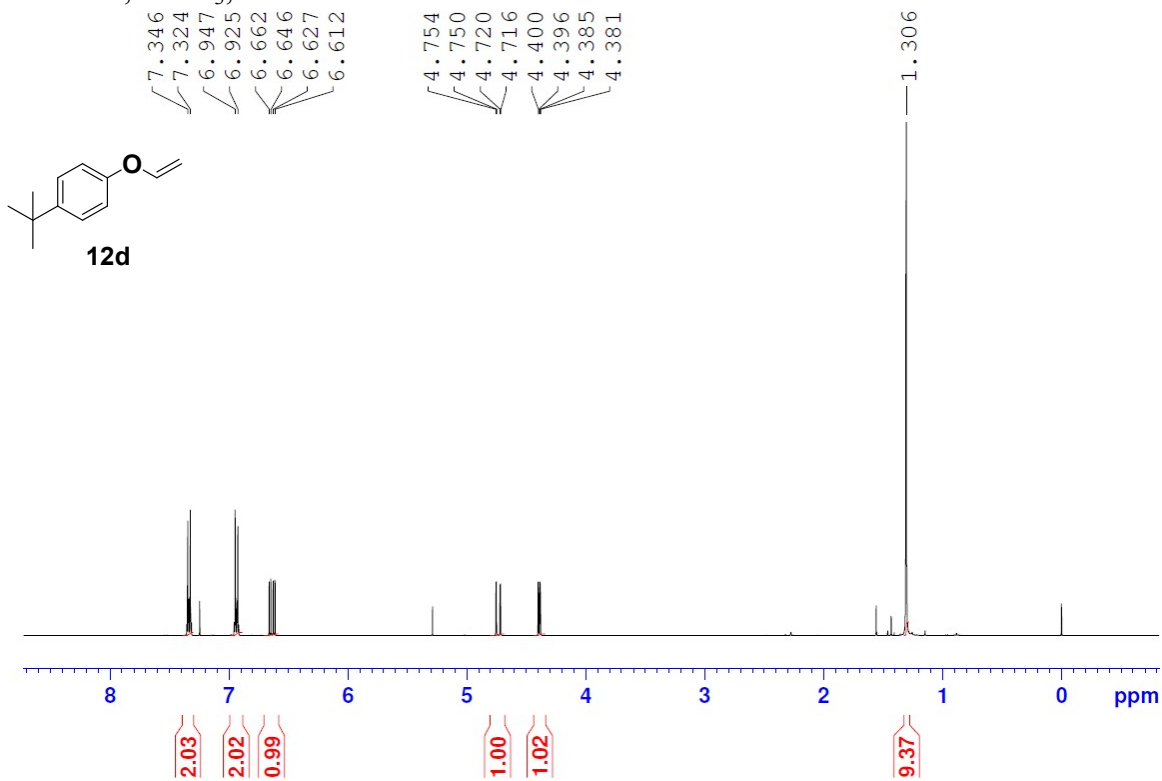


$^{13}\text{C}$  NMR,  $\text{CDCl}_3$ , 101 MHz

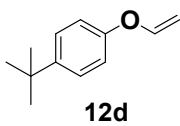


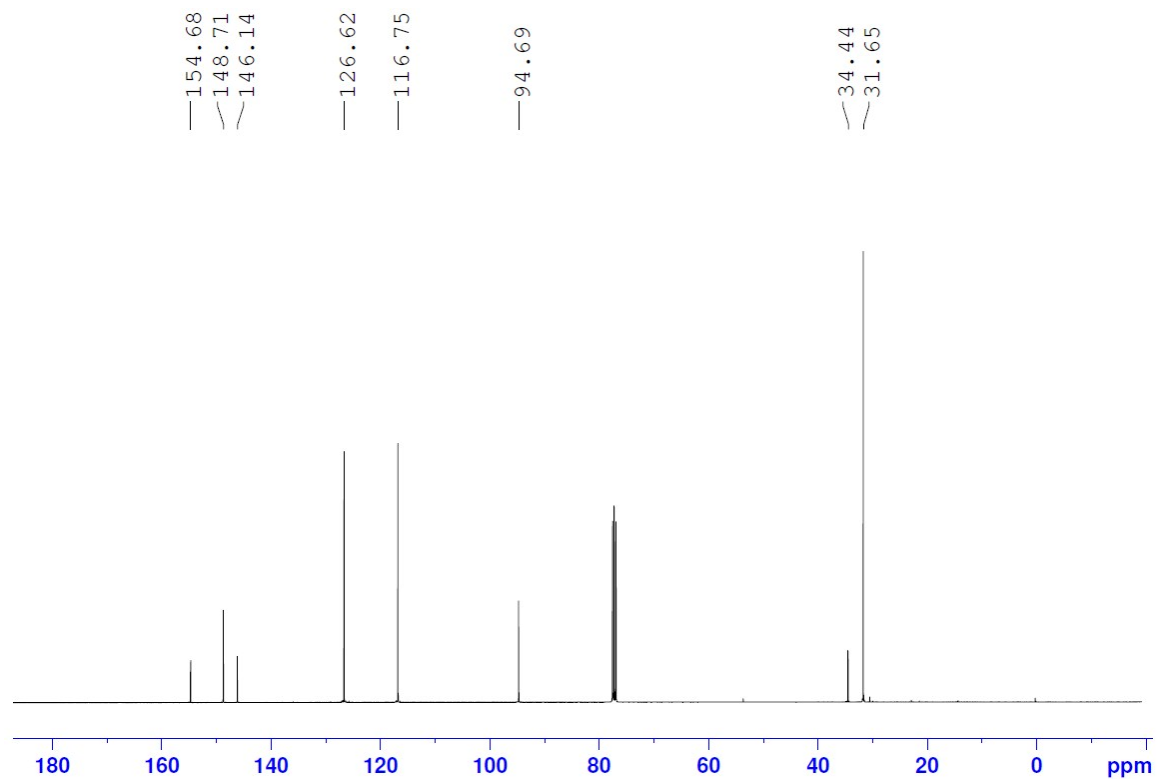


$^1\text{H}$  NMR,  $\text{CDCl}_3$ , 400 MHz

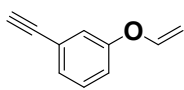
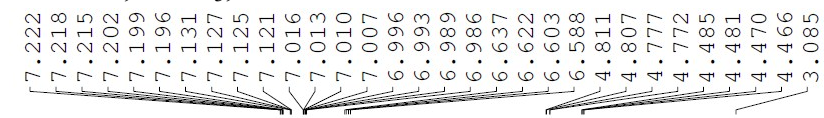


$^{13}\text{C}$  NMR,  $\text{CDCl}_3$ , 101 MHz

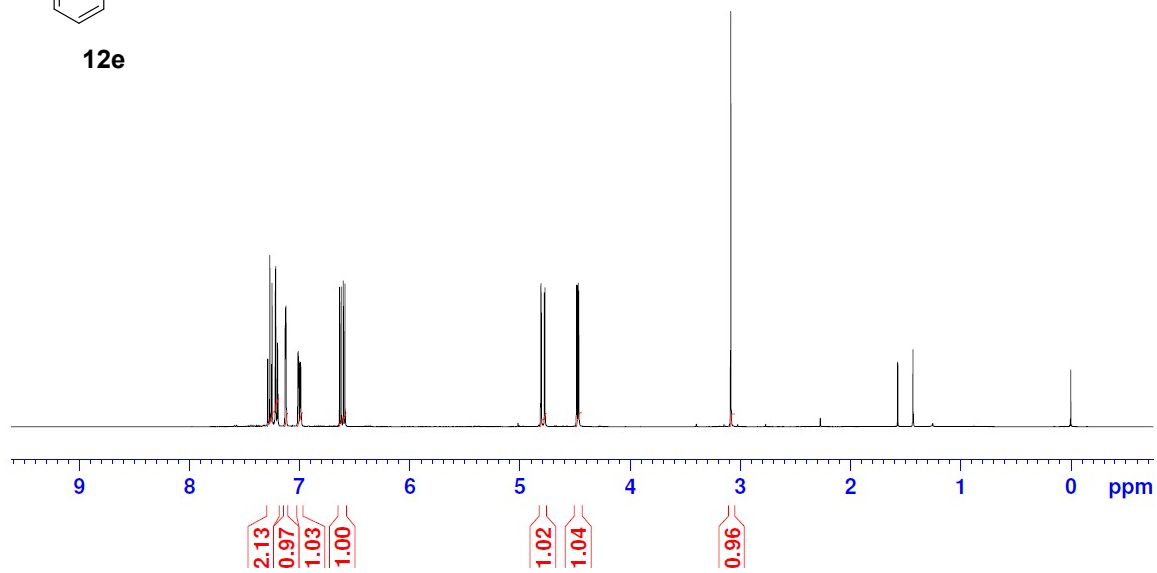




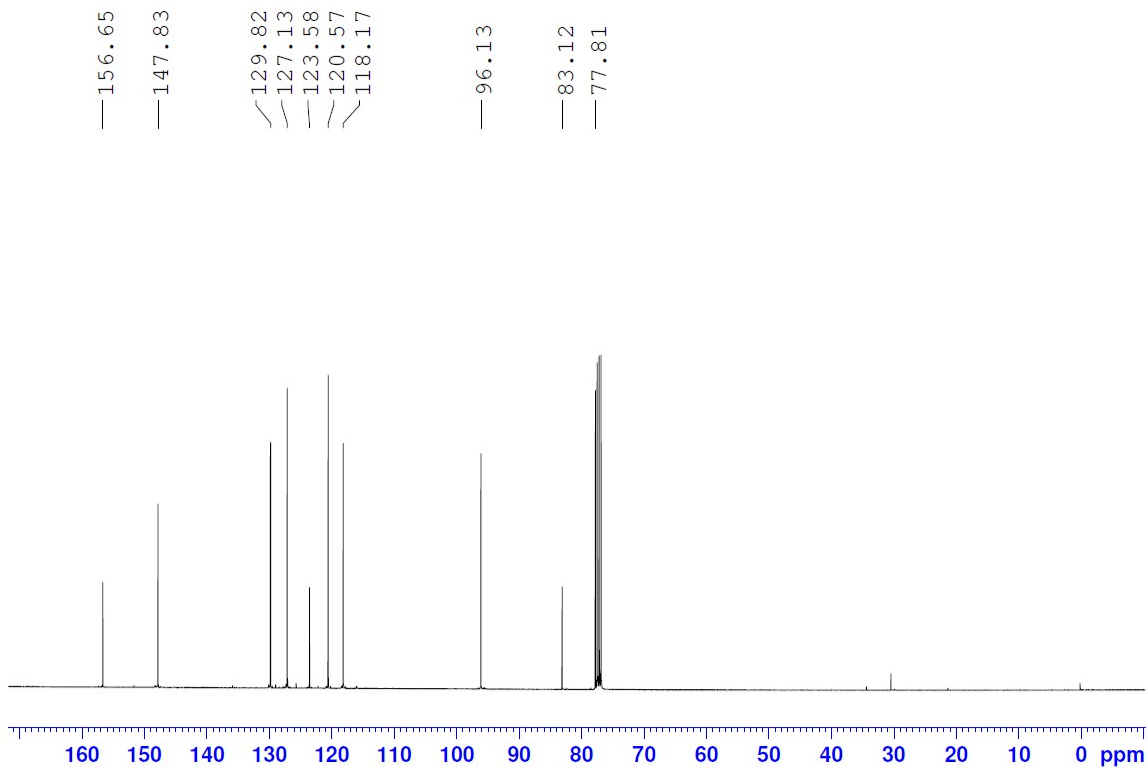
$^1\text{H}$  NMR,  $\text{CDCl}_3$ , 400 MHz



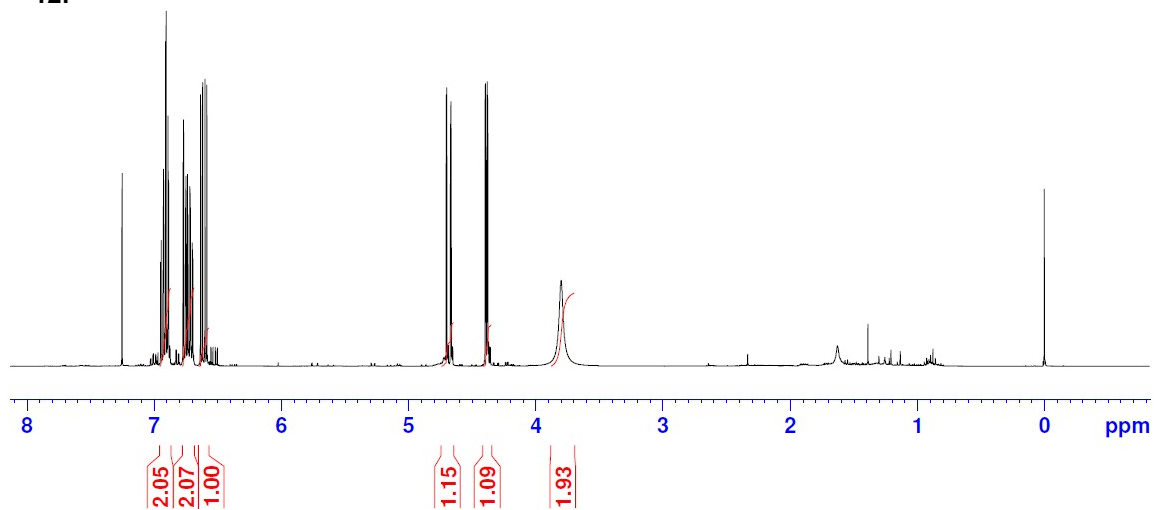
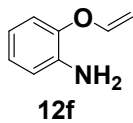
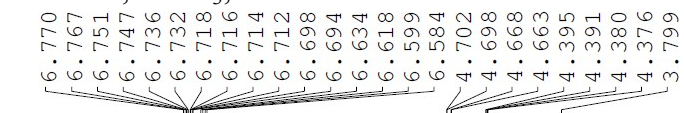
12e



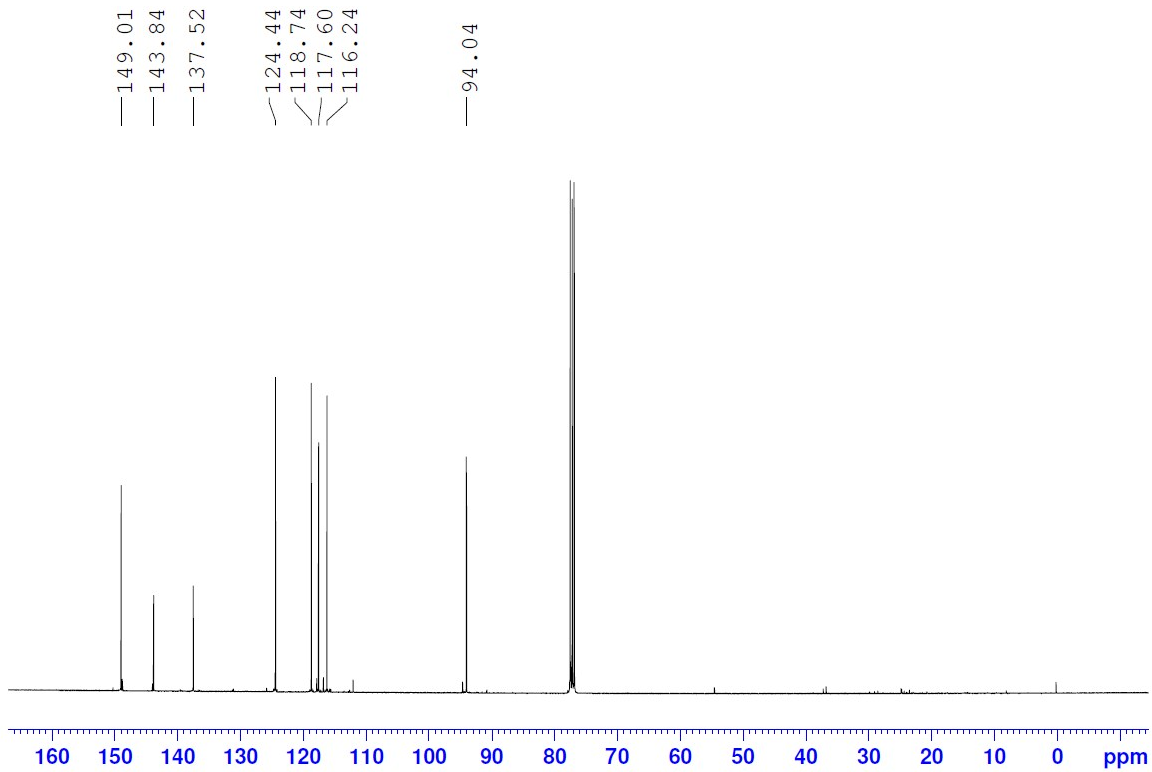
$^{13}\text{C}$  NMR,  $\text{CDCl}_3$ , 101 MHz



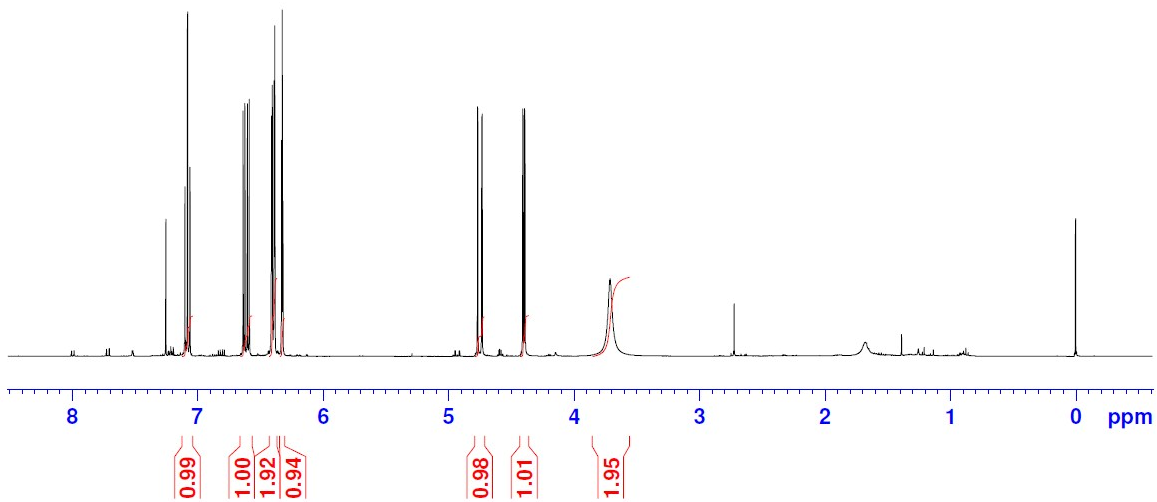
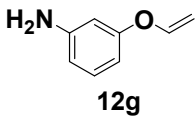
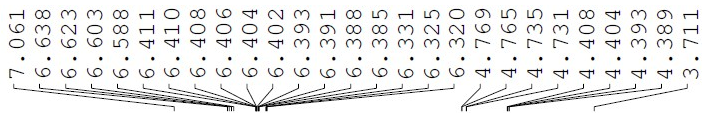
$^1\text{H}$  NMR,  $\text{CDCl}_3$ , 400 MHz



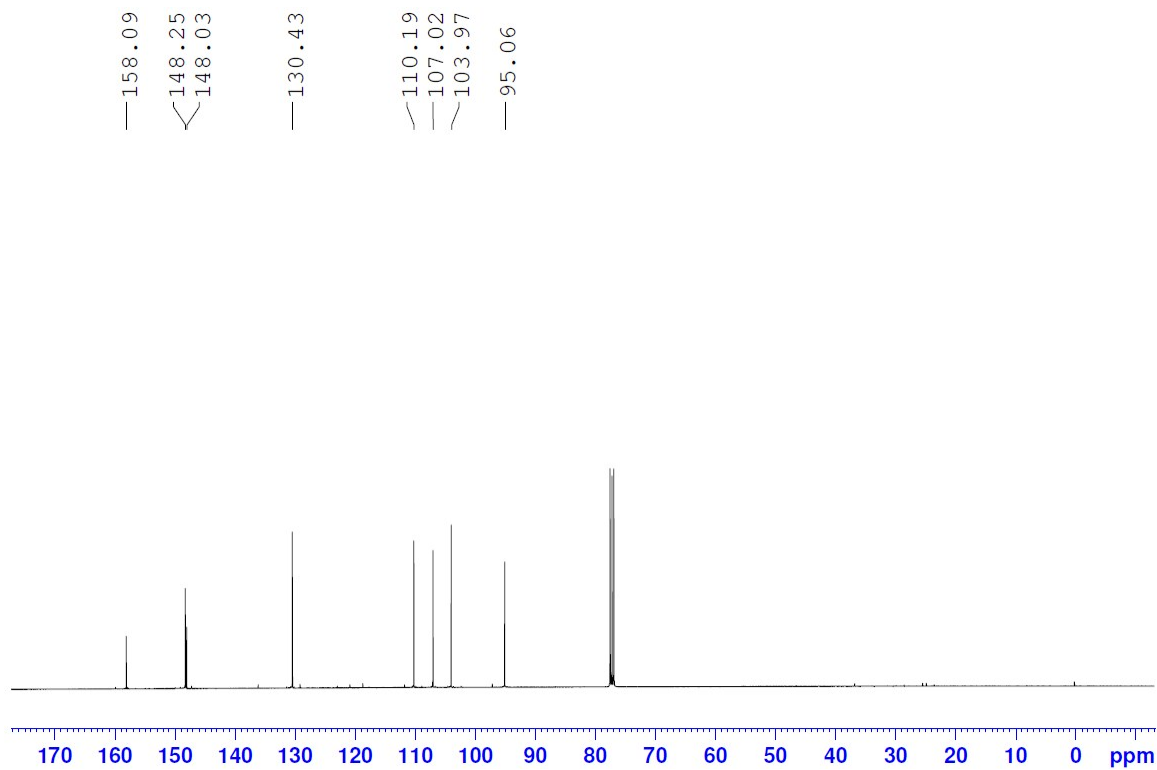
$^{13}\text{C}$  NMR,  $\text{CDCl}_3$ , 101 MHz



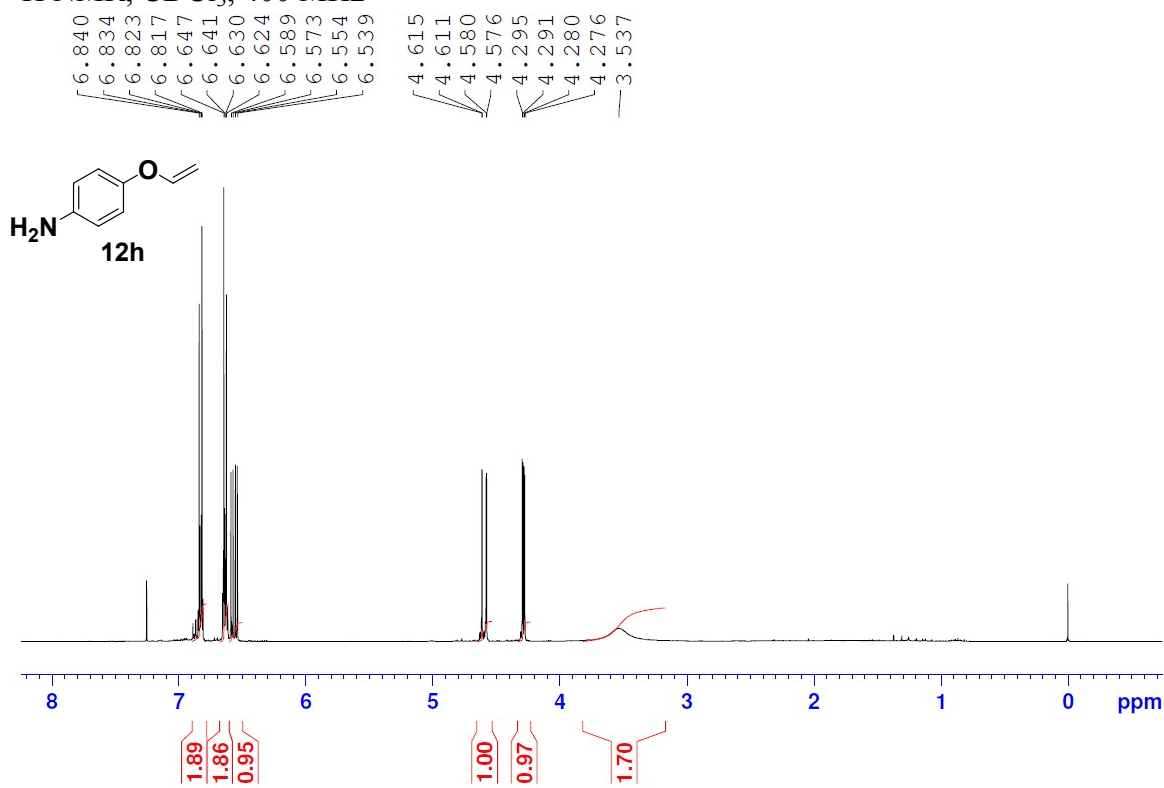
$^1\text{H}$  NMR,  $\text{CDCl}_3$ , 400 MHz



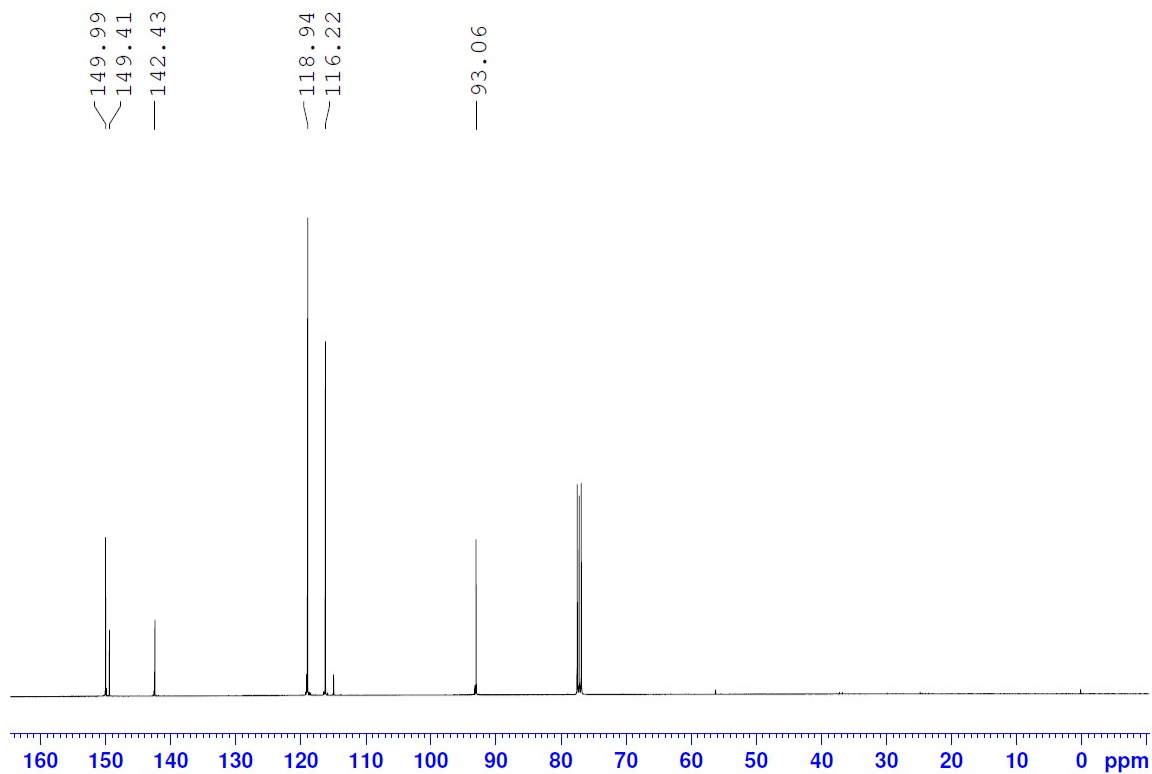
$^{13}\text{C}$  NMR,  $\text{CDCl}_3$ , 101 MHz



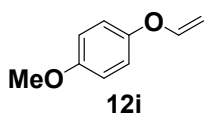
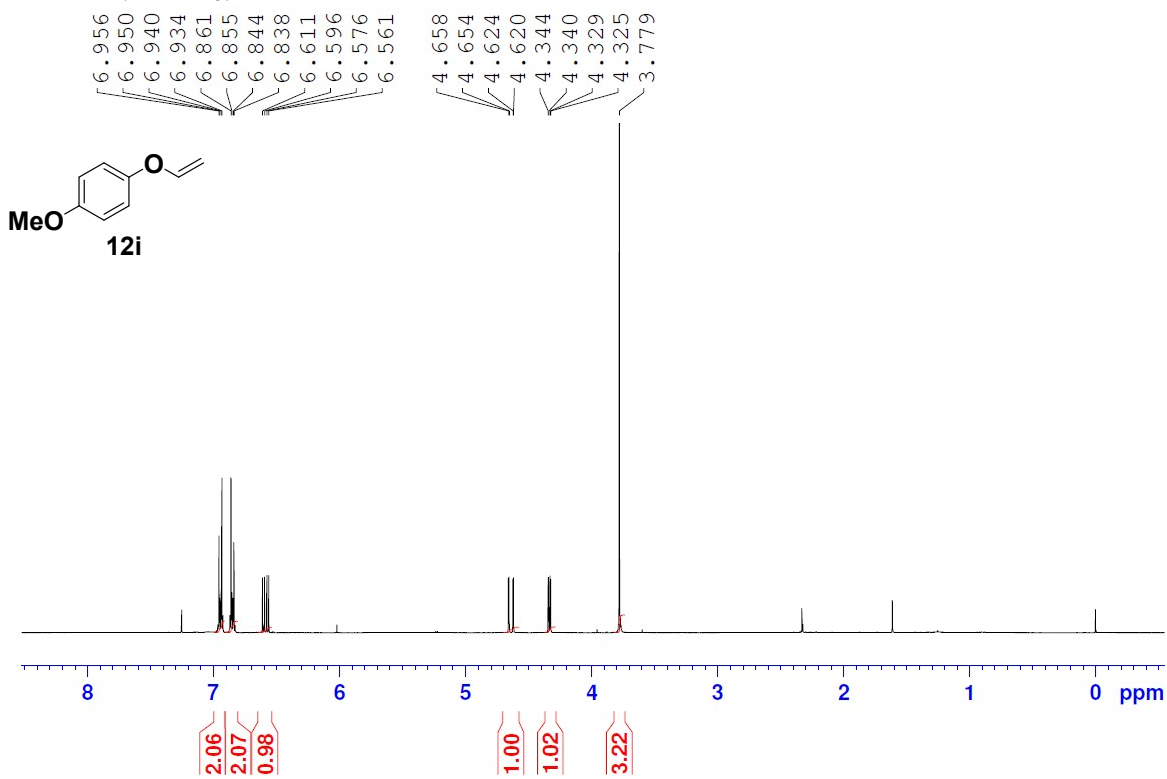
$^1\text{H}$  NMR,  $\text{CDCl}_3$ , 400 MHz



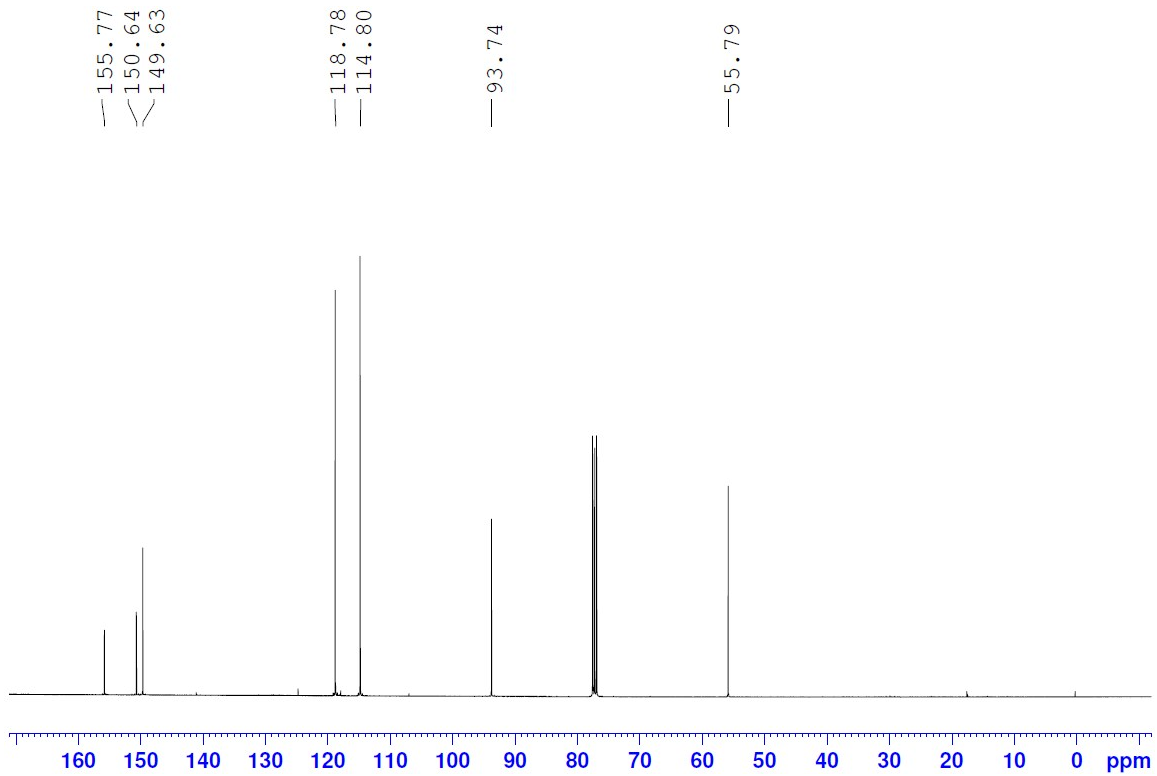
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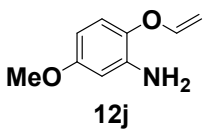
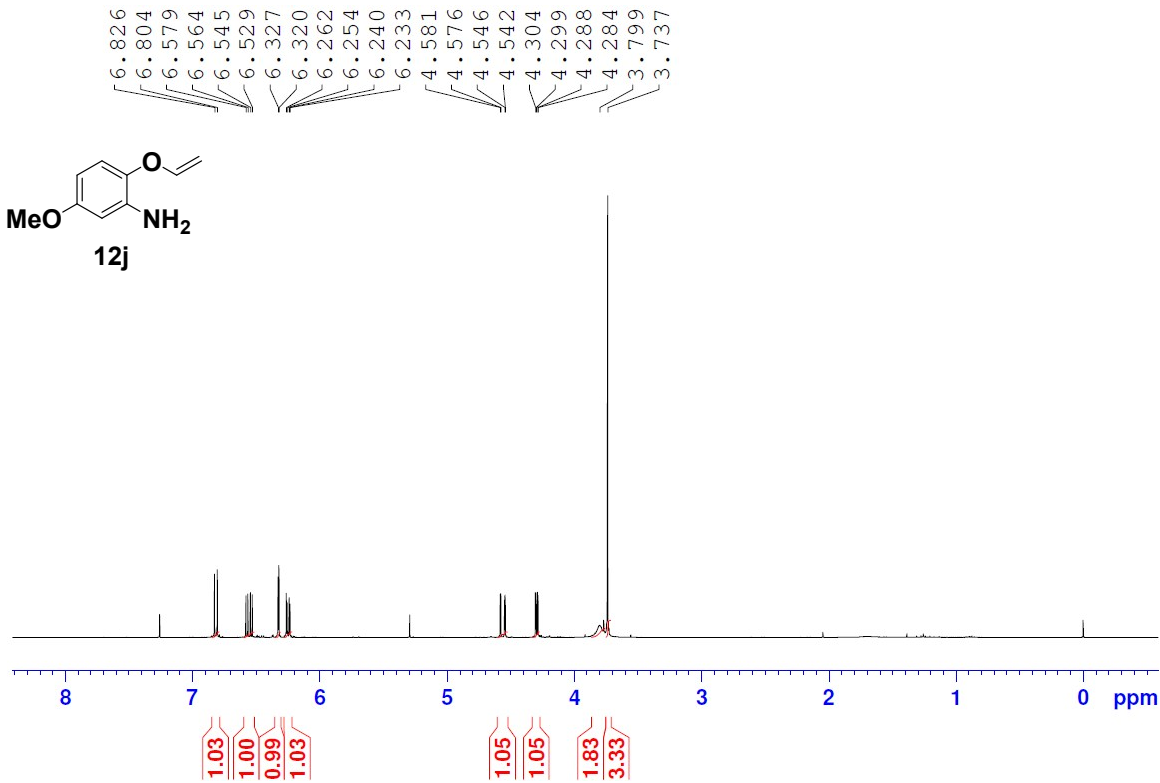
$^1\text{H}$  NMR,  $\text{CDCl}_3$ , 400 MHz



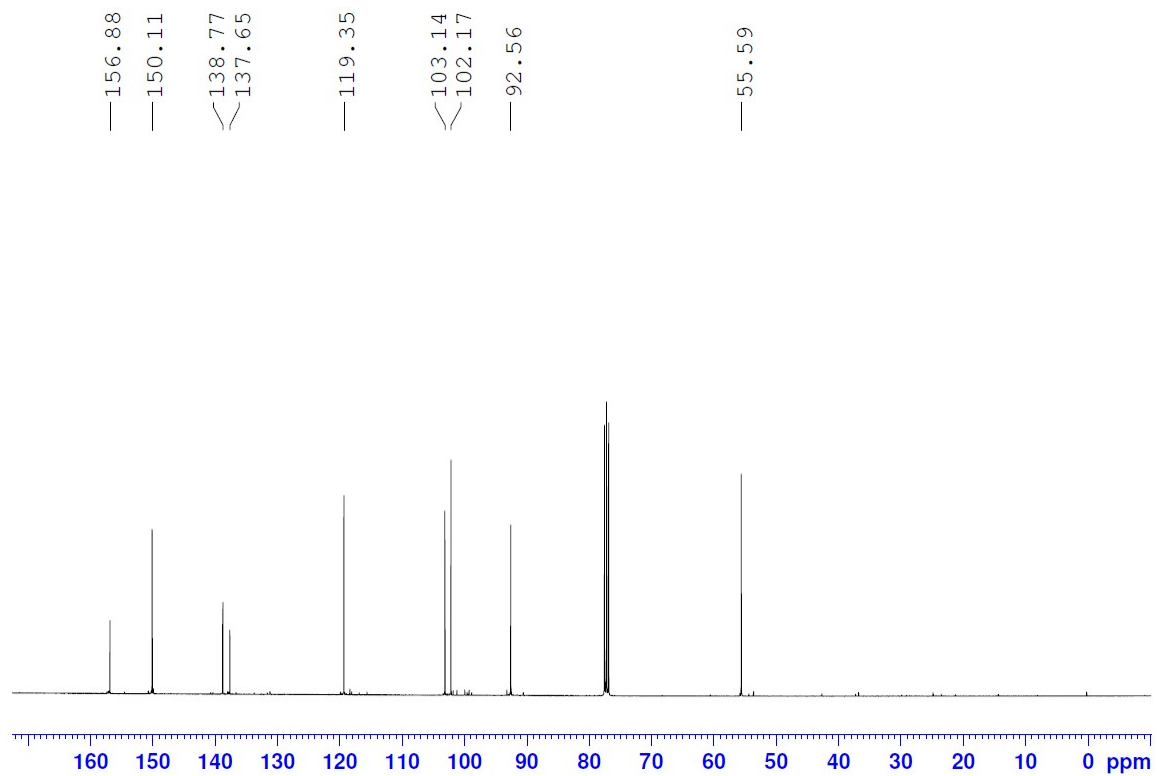
$^{13}\text{C}$  NMR,  $\text{CDCl}_3$ , 101 MHz



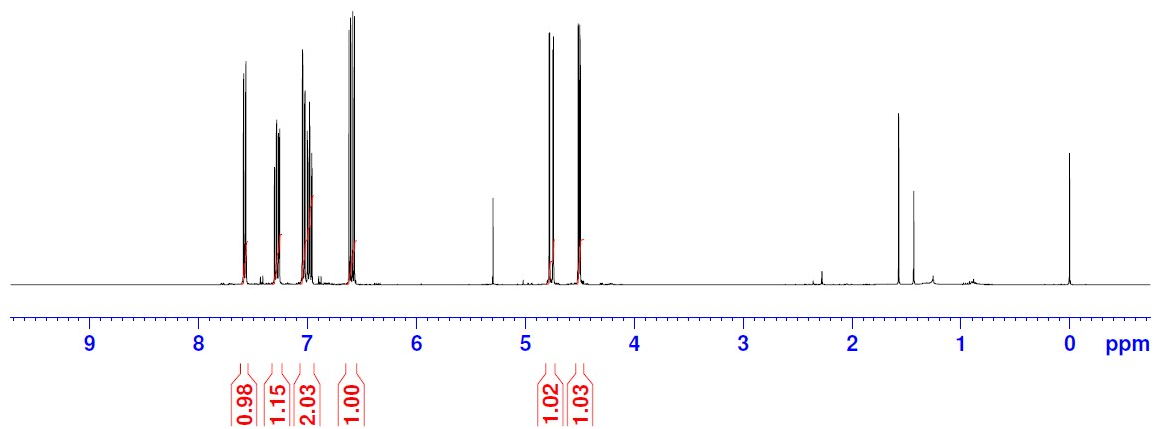
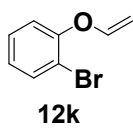
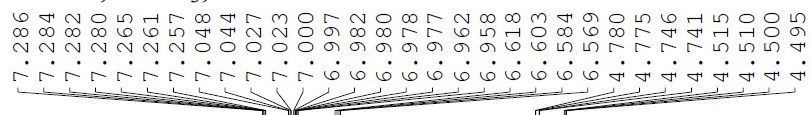
$^1\text{H}$  NMR,  $\text{CDCl}_3$ , 400 MHz



$^{13}\text{C}$  NMR,  $\text{CDCl}_3$ , 101 MHz

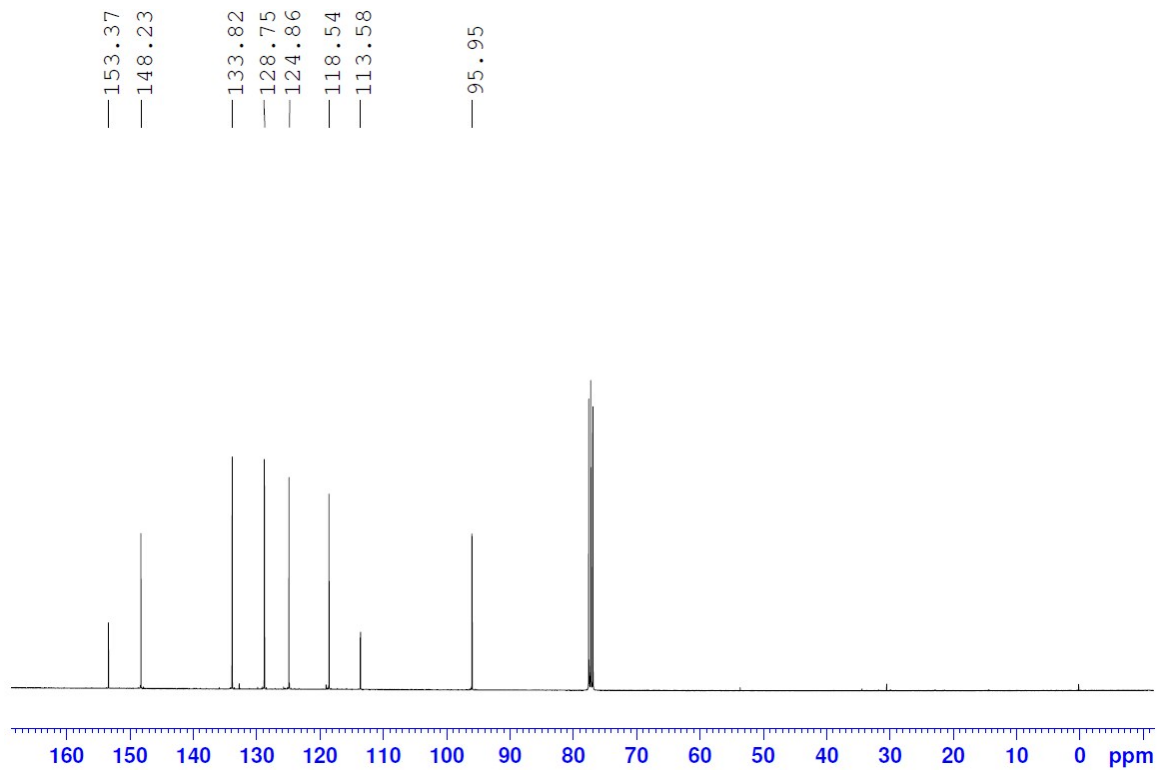


$^1\text{H}$  NMR,  $\text{CDCl}_3$ , 400 MHz

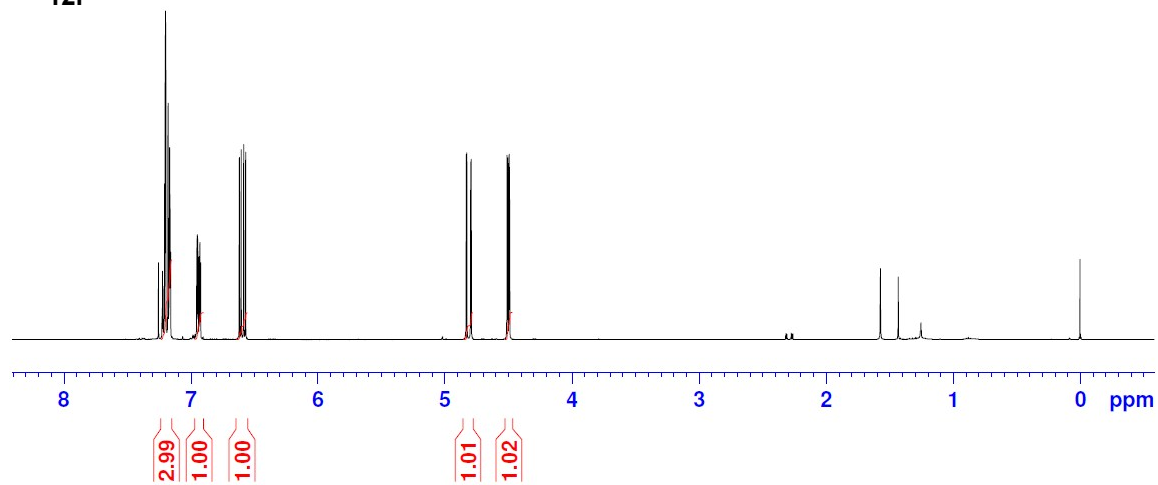
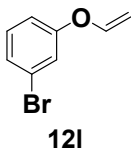
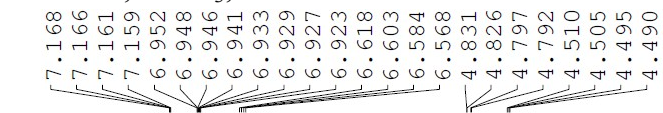


$^{13}\text{C}$  NMR,  $\text{CDCl}_3$ , 101 MHz

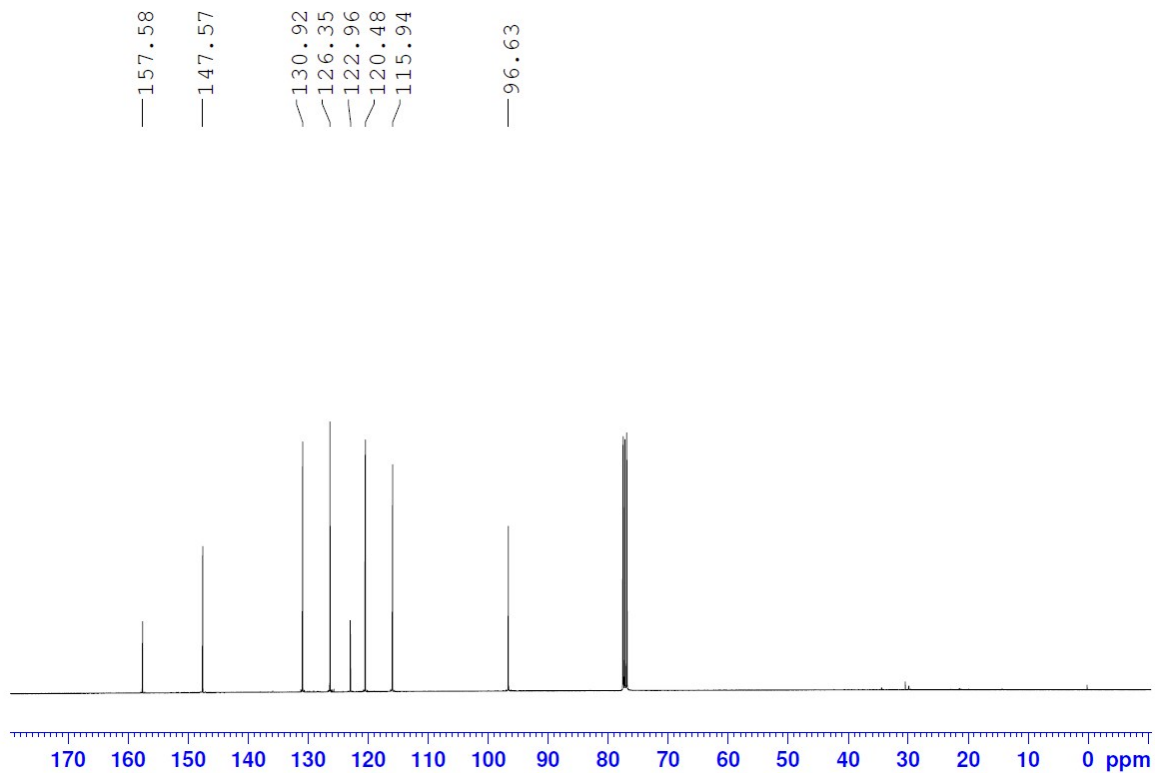




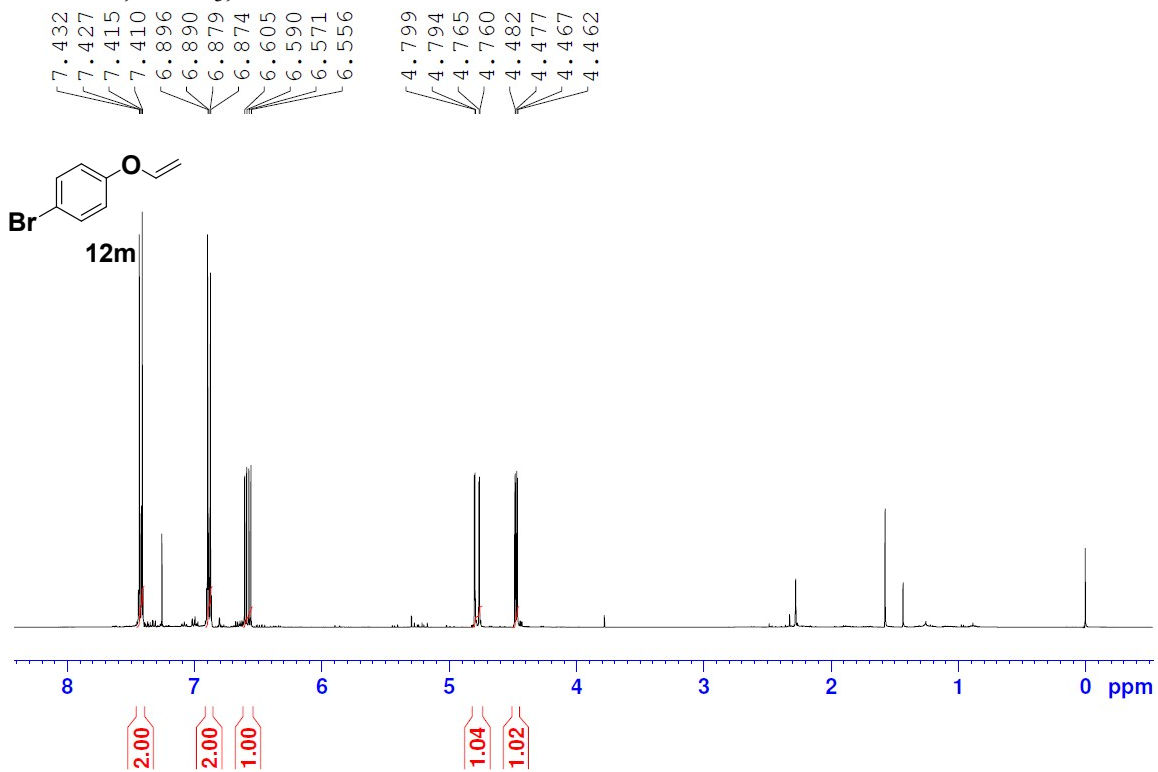
$^1\text{H}$  NMR,  $\text{CDCl}_3$ , 400 MHz



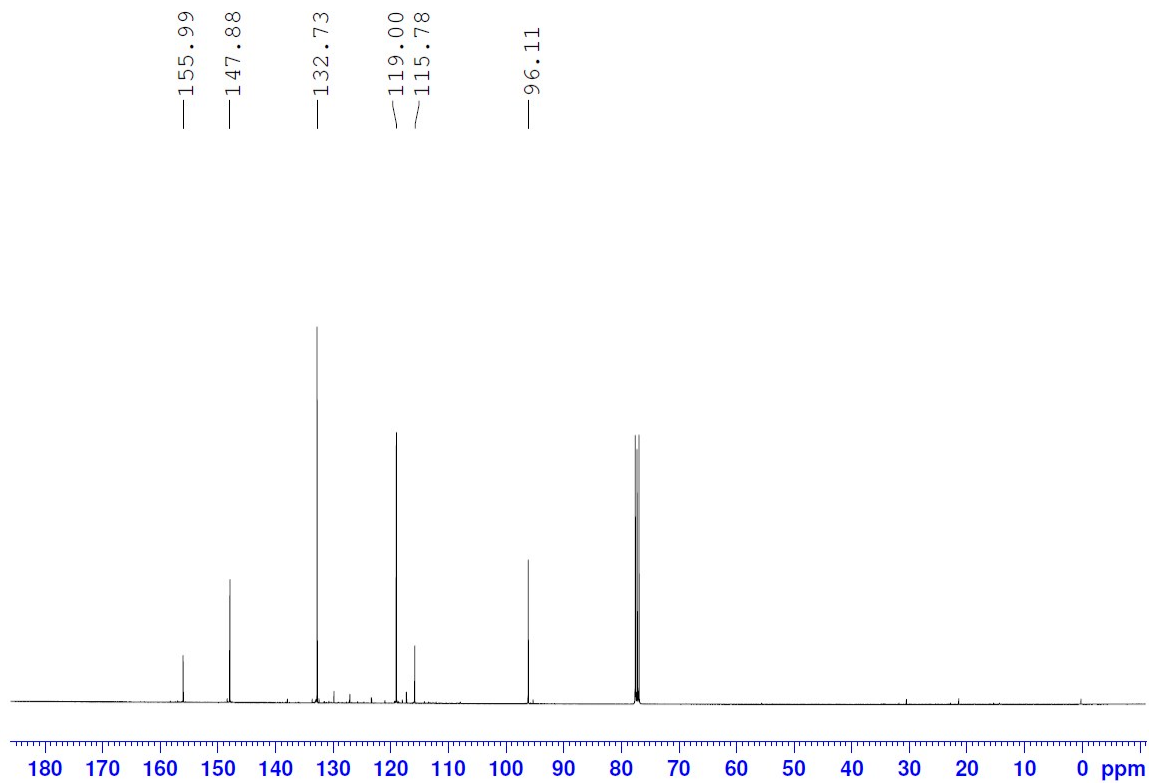
$^{13}\text{C}$  NMR,  $\text{CDCl}_3$ , 101 MHz



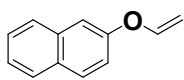
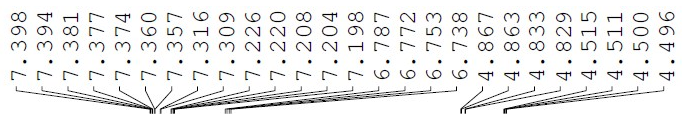
$^1\text{H}$  NMR,  $\text{CDCl}_3$ , 400 MHz



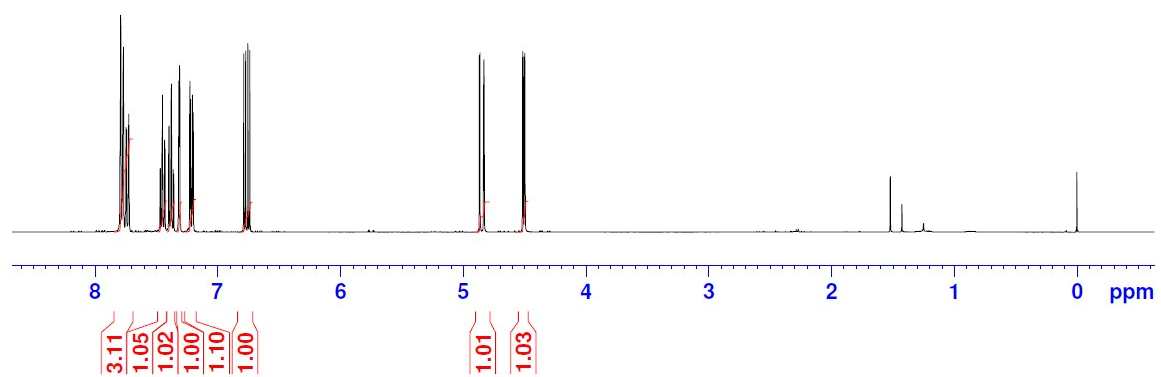
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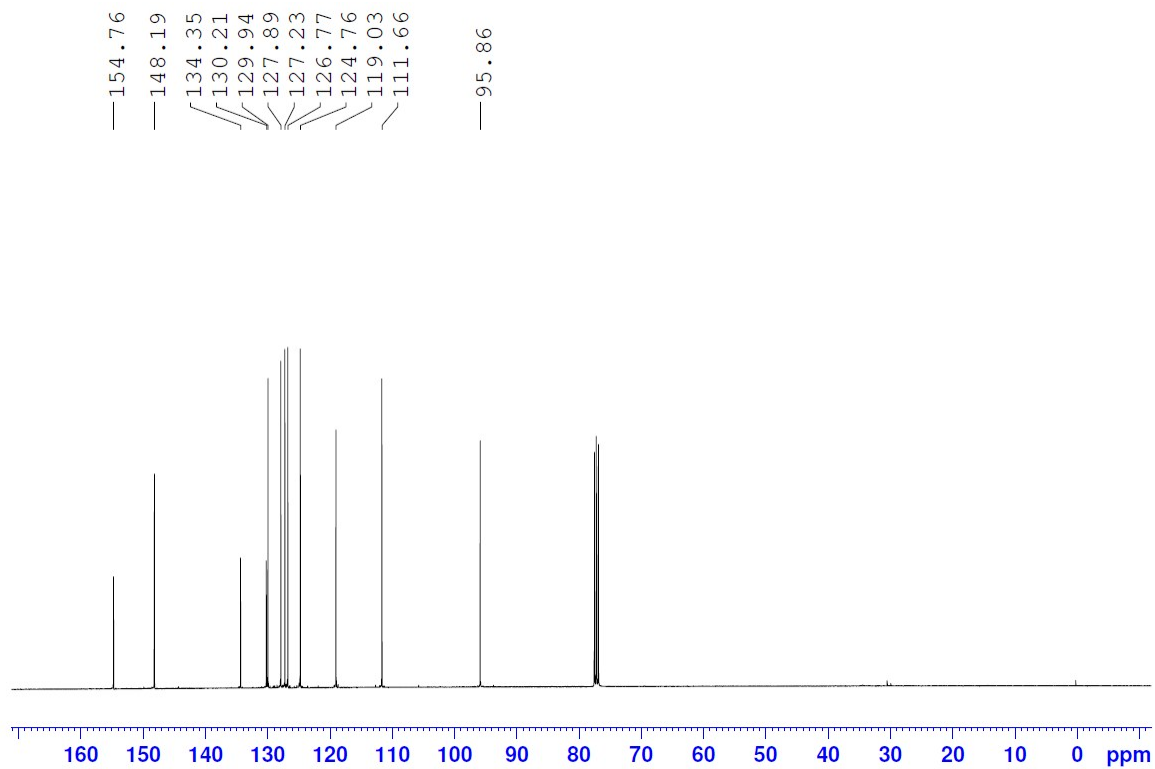
$^1\text{H}$  NMR,  $\text{CDCl}_3$ , 400 MHz



**12p**



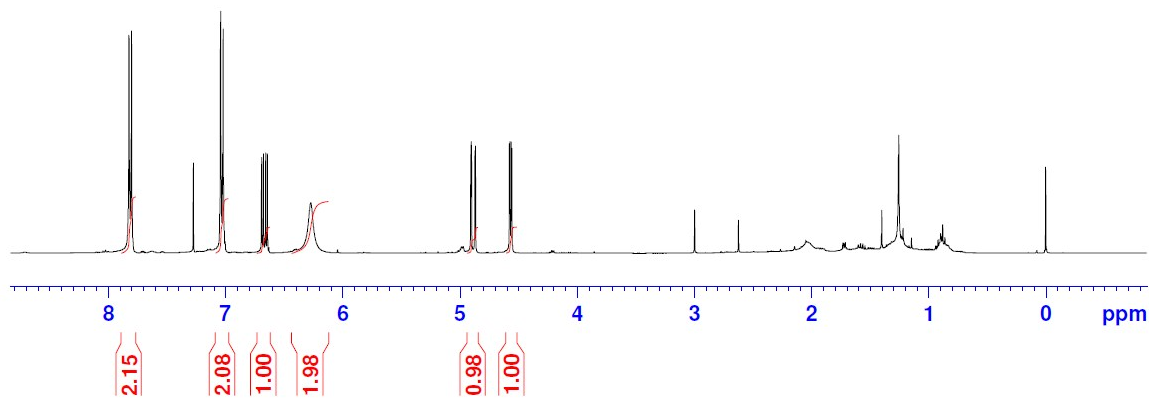
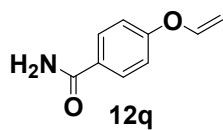
$^{13}\text{C}$  NMR,  $\text{CDCl}_3$ , 101 MHz



<sup>1</sup>H NMR, CDCl<sub>3</sub>, 400 MHz

Chemical shifts (ppm):

- 7.823
- 7.802
- 7.041
- 7.019
- 6.691
- 6.676
- 6.657
- 6.642
- 6.272
- 4.905
- 4.901
- 4.871
- 4.867
- 4.576
- 4.571
- 4.561
- 4.556



<sup>13</sup>C NMR, CDCl<sub>3</sub>, 101 MHz

