

## Supporting Information

### Synthesis of 3-(4-oxo-4*H*-chromen-3-yl)acrylates through the tandem reactions of 3-(2-buta-2,3-dienoylphenoxy)acrylates

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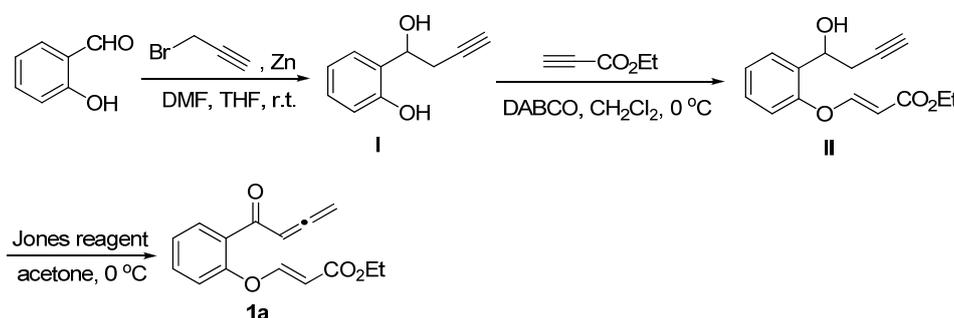
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# I. Experimental details and spectroscopic data

## 1. General experimental information

The  $^1\text{H}$ ,  $^{13}\text{C}$  NMR spectra were recorded at 400 MHz or 100 MHz, respectively. Chemical shifts were reported in ppm from tetramethylsilane (TMS) as internal standard in  $\text{CDCl}_3$  solutions. Multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); m (multiplet); dd (doublet of doublets), etc. and coupling constants were given in Hz. High resolution mass spectra (HRMS) were performed on a time-of-flight (microTOF) mass spectrometer. The conversion of starting materials were monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm) and components were visualized by observation under UV light (254 and 365 nm).

## 2. Synthetic procedure for the synthesis of ethyl 3-(2-buta-2,3-dienoylphenoxy)acrylate (1a)



### 2.1 Procedure for the synthesis of 2-(1-hydroxybut-3-ynyl)phenol (I)<sup>[1]</sup>

To a flask containing 2-hydroxybenzaldehyde (5 mmol), THF (10 mL), DMF (10 mL) and propargyl bromide (10 mmol) were added activated zinc dust (15 mmol) portion-wise with stirring. The mixture was then stirred at room temperature. Upon completion, it was diluted with saturated aqueous  $\text{NH}_4\text{Cl}$  (15 mL) and the excess zinc was filtered. The filtrate was concentrated and to the residue was added water. The aqueous phase was extracted with EtOAc (15 mL  $\times$  3). The combined organic phases were dried with anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated. The residue was purified by column chromatography on silica gel with petroleum ether-ethyl acetate (5:1) to give

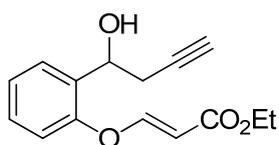
2-(1-hydroxybut-3-ynyl) phenol (**I**, 98%).

## 2.2 Procedure for the synthesis of (E)-ethyl 3-(2-(1-hydroxybut-3-ynyl)phenoxy)acrylate (**II**)

To a flask containing 2-(1-hydroxybut-3-ynyl)phenol (**I**, 4 mmol) and ethyl propiolate (4.4 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added DABCO (0.4 mmol). The resulting mixture was stirred at 0 °C for 3 h. Upon completion, the mixture was concentrated and the residue was purified by column chromatography on silica gel with petroleum ether-ethyl acetate (10:1) to give (E)-ethyl 3-(2-(1-hydroxybut-3-ynyl)phenoxy)acrylate (**II**, 83%).

## 2.3 Procedure for the synthesis of (E)-ethyl 3-(2-buta-2,3-dienoylphenoxy)acrylate (**1a**)

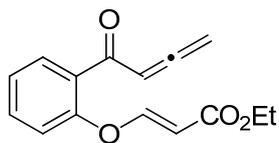
To a solution of (E)-ethyl 3-(2-(1-hydroxybut-3-ynyl)phenoxy)acrylate (**II**, 2 mmol) in acetone (20 mL) cooled to 0 °C was added Jones reagent (2.4 mmol) in a dropwise manner. Upon complete consumption of the starting material as monitored by TLC, the reaction mixture was quenched by addition of isopropanol. The mixture was filtered and the filtrate was concentrated under vacuum. The residue were purified by column chromatography on silica gel with petroleum ether-ethyl acetate (10:1) to give 1-(2-(allyloxy)phenyl)buta-2,3-dien-1-one (**1a**, 86%). **1b-1h**, **1r** were obtained in a similar manner.



## (E)-Ethyl 3-(2-(1-hydroxybut-3-yn-1-yl)phenoxy)acrylate (**II**)

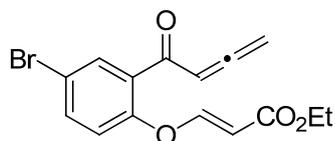
Eluent: petroleum ether-ethyl acetate (10:1); oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 1.22 (t, *J* = 7.6 Hz, 3H), 2.00 (t, *J* = 2.4 Hz, 1H), 2.50-2.56 (m, 1H), 2.60-2.66 (m, 1H), 3.27 (br s, 1H), 4.13 (q, *J* = 7.6 Hz, 2H), 5.08-5.11 (m, 1H), 5.49 (d, *J* = 12.4 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 12.0 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 14.3, 28.1, 60.2, 66.4, 71.0, 80.5, 102.4, 117.6, 125.4, 127.4, 129.1, 133.2, 152.3,

159.2, 167.2. MS:  $m/z$  261 (MH)<sup>+</sup>. HRMS (ESI) calcd for C<sub>15</sub>H<sub>17</sub>O<sub>4</sub>: 261.1127 [M+H], found: 261.1135.



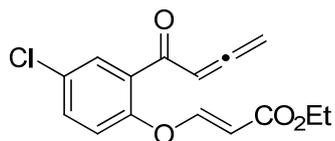
**(E)-Ethyl 3-(2-buta-2,3-dienoylphenoxy)acrylate (1a)**

Eluent: petroleum ether-ethyl acetate (10:1); oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 1.21 (t,  $J$  = 7.2 Hz, 3H), 4.12 (q,  $J$  = 6.8 Hz, 2H), 5.11 (d,  $J$  = 6.4 Hz, 2H), 5.47 (d,  $J$  = 12.4 Hz, 1H), 6.18 (t,  $J$  = 6.4 Hz, 1H), 7.04 (d,  $J$  = 7.6 Hz, 1H), 7.19 (t,  $J$  = 6.8 Hz, 1H), 7.44-7.48 (m, 2H), 7.67 (d,  $J$  = 12.0 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 14.3, 60.2, 79.7, 96.7, 103.0, 118.6, 125.1, 130.0, 130.6, 132.7, 153.0, 158.7, 166.8, 191.8, 218.0. HRMS (ESI) calcd for C<sub>15</sub>H<sub>15</sub>O<sub>4</sub>: 259.0970 [M+H], found: 259.0975.



**(E)-Ethyl 3-(4-bromo-2-buta-2,3-dienoylphenoxy)acrylate (1b)**

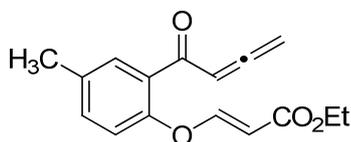
Eluent: petroleum ether-ethyl acetate (10:1); oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 1.26 (t,  $J$  = 7.2 Hz, 3H), 4.17 (q,  $J$  = 7.6 Hz, 2H), 5.19 (d,  $J$  = 6.4 Hz, 2H), 5.52 (d,  $J$  = 12.4 Hz, 1H), 6.20 (t,  $J$  = 6.4 Hz, 1H), 6.98 (d,  $J$  = 8.8 Hz, 1H), 7.56-7.61 (m, 2H), 7.65 (d,  $J$  = 12.4 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 14.3, 60.4, 80.1, 96.6, 103.7, 117.9, 120.3, 132.1, 132.7, 135.3, 152.0, 158.1, 166.6, 190.4, 218.3. HRMS (ESI) calcd for C<sub>15</sub>H<sub>14</sub>BrO<sub>4</sub>: 337.0075 [M+H], found: 337.0085.



**(E)-Ethyl 3-(2-buta-2,3-dienoyl-4-chlorophenoxy)acrylate (1c)**

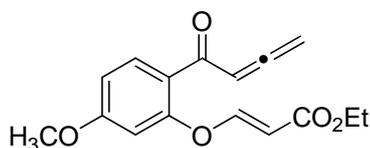
Eluent: petroleum ether-ethyl acetate (10:1); oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 1.19 (t,  $J$  = 7.2 Hz,

3H), 4.10 (q,  $J = 7.2$  Hz, 2H), 5.13 (d,  $J = 6.4$  Hz, 2H), 5.45 (d,  $J = 12.4$  Hz, 1H), 6.14 (t,  $J = 6.4$  Hz, 1H), 6.99 (d,  $J = 9.2$  Hz, 1H), 7.36-7.40 (m, 2H), 7.60 (d,  $J = 12.4$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 14.2, 60.3, 80.0, 96.5, 103.5, 120.0, 129.7, 130.4, 131.8, 132.3, 151.4, 158.2, 166.5, 190.4, 218.3. HRMS (ESI) calcd for  $\text{C}_{15}\text{H}_{14}\text{ClO}_4$ : 293.0580 [M+H], found: 293.0588.



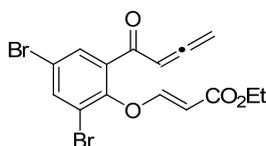
**(E)-Ethyl 3-(2-buta-2,3-dienoyl-4-methylphenoxy)acrylate (1d)**

Eluent: petroleum ether-ethyl acetate (10:1); oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.20 (t,  $J = 7.2$  Hz, 3H), 2.29 (s, 3H), 4.11 (q,  $J = 6.8$  Hz, 2H), 5.11 (d,  $J = 6.4$  Hz, 2H), 5.41 (d,  $J = 12.0$  Hz, 1H), 6.18 (t,  $J = 6.4$  Hz, 1H), 6.92 (d,  $J = 8.4$  Hz, 1H), 7.21-7.24 (m, 2H), 7.64 (d,  $J = 12.0$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 14.2, 20.6, 60.1, 79.6, 96.6, 102.5, 118.7, 130.3, 130.4, 133.3, 135.0, 151.0, 159.2, 166.8, 191.8, 217.8. HRMS (ESI) calcd for  $\text{C}_{16}\text{H}_{17}\text{O}_4$ : 273.1127 [M+H], found: 273.1122.



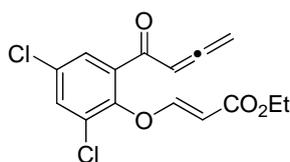
**(E)-Ethyl 3-(2-buta-2,3-dienoyl-5-methoxyphenoxy)acrylate (1e)**

Eluent: petroleum ether-ethyl acetate (10:1); oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.22 (t,  $J = 6.8$  Hz, 3H), 3.80 (s, 3H), 4.10-4.15 (m, 2H), 5.14 (d,  $J = 6.0$  Hz, 2H), 5.49 (d,  $J = 12.4$  Hz, 1H), 6.27-6.30 (m, 1H), 6.53 (s, 1H), 6.72 (d,  $J = 8.4$  Hz, 1H), 7.57 (d,  $J = 9.2$  Hz, 1H), 7.66 (d,  $J = 12.0$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 14.3, 55.8, 60.2, 79.4, 96.2, 103.2, 104.8, 110.4, 122.9, 132.3, 155.2, 158.5, 163.6, 166.8, 189.7, 217.1. HRMS (ESI) calcd for  $\text{C}_{16}\text{H}_{17}\text{O}_5$ : 289.1076 [M+H], found: 289.1088.



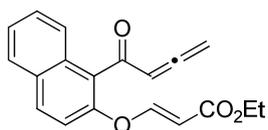
**(E)-Ethyl 3-(2,4-dibromo-6-buta-2,3-dienoylphenoxy)acrylate (1f)**

Eluent: petroleum ether-ethyl acetate (10:1); oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.24 (t,  $J = 6.8$  Hz, 3H), 4.14 (q,  $J = 7.2$  Hz, 2H), 5.14 (d,  $J = 11.6$  Hz, 1H), 5.24 (d,  $J = 6.0$  Hz, 2H), 6.15 (t,  $J = 6.4$  Hz, 1H), 7.52-7.55 (m, 2H), 7.85 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 14.2, 60.3, 80.6, 96.3, 101.9, 117.8, 119.4, 131.5, 135.0, 138.3, 148.0, 159.5, 166.4, 189.4, 218.8. HRMS (ESI) calcd for  $\text{C}_{15}\text{H}_{13}\text{Br}_2\text{O}_4$ : 414.9180 [M+H], found: 414.9189.



**(E)-Ethyl 3-(2-buta-2,3-dienoyl-4,6-dichlorophenoxy)acrylate (1g)**

Eluent: petroleum ether-ethyl acetate (10:1); oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.22 (t,  $J = 6.8$  Hz, 3H), 4.11 (q,  $J = 6.8$  Hz, 2H), 5.14 (d,  $J = 12.4$  Hz, 1H), 5.22 (d,  $J = 6.4$  Hz, 2H), 6.12-6.15 (m, 1H), 7.34 (s, 1H), 7.52-7.54 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 14.2, 60.3, 80.6, 96.3, 101.7, 127.9, 128.5, 131.8, 132.6, 134.7, 146.4, 159.6, 166.3, 189.5, 218.7. HRMS (ESI) calcd for  $\text{C}_{15}\text{H}_{13}\text{Cl}_2\text{O}_4$ : 327.0191 [M+H], found: 327.0198.

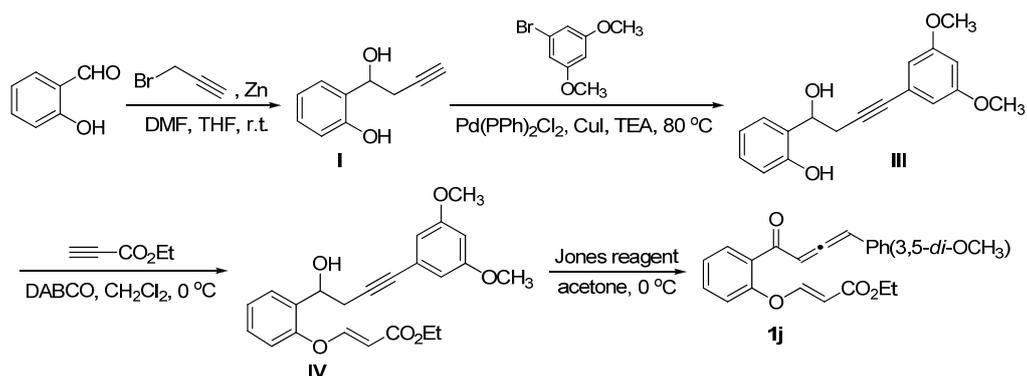


**(E)-Ethyl 3-(1-buta-2,3-dienoylnaphthalen-2-yloxy)acrylate (1h)**

Eluent: petroleum ether-ethyl acetate (10:1); oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.22 (t,  $J = 7.2$  Hz, 3H), 4.14 (q,  $J = 6.8$  Hz, 2H), 4.91 (d,  $J = 6.4$  Hz, 2H), 5.50 (d,  $J = 12.0$  Hz, 1H), 6.23 (t,  $J = 6.4$  Hz, 1H), 7.19 (d,  $J = 8.8$  Hz, 1H), 7.41-7.49 (m, 2H), 7.71-7.80 (m, 3H), 7.86 (d,  $J = 8.8$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 14.3, 60.2, 79.9, 98.7, 102.8, 117.6, 124.6, 126.0, 126.8, 127.9, 128.3, 130.8, 130.9, 131.8, 149.1, 159.2, 166.9, 194.7, 219.0. HRMS (ESI) calcd for  $\text{C}_{19}\text{H}_{17}\text{O}_4$ : 309.1127 [M+H], found: 309.1119.

**3. Synthetic procedure for the synthesis of ethyl 3-(2-(4-(3,5-dimethoxyphenyl)buta-**

## 2,3-dienoylphenoxyacrylate (**1j**)



### 3.1 Procedure for the synthesis of 2-(1-hydroxybut-3-ynyl)phenol (**I**)

To a flask containing 2-hydroxybenzaldehyde (5 mmol), THF (10 mL), DMF (10 mL) and propargyl bromide (10 mmol) were added activated zinc dust (15 mmol) portion-wise with stirring. The mixture was then stirred at room temperature. Upon completion, it was diluted with saturated aqueous NH<sub>4</sub>Cl (15 mL) and the excess zinc was filtered. The filtrate was concentrated and to the residue was added water. The aqueous phase was extracted with EtOAc (15 mL × 3). The combined organic phases were dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by column chromatography on silica gel with petroleum ether-ethyl acetate (5:1) to give 2-(1-hydroxybut-3-ynyl)phenol (**I**, 98%).

### 3.2 Procedure for the synthesis of 2-(4-(3,5-dimethoxyphenyl)-1-hydroxybut-3-ynyl)phenol (**III**)

To a flask containing 2-(1-hydroxybut-3-ynyl)phenol (**I**, 4 mmol) and 1-bromo-3,5-dimethoxybenzene (1.2 mmol) in Et<sub>3</sub>N (16 mL) were added Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.08 mmol) and CuI (0.04 mmol). After the mixture was stirred at 50 °C under N<sub>2</sub> atmosphere for 2 h, the reaction was quenched with aqueous NH<sub>4</sub>Cl and extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with water and brine and then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated under vacuum, and the crude product was purified by chromatography on silica gel by using petroleum ether-ethyl acetate (5:1) as the eluent to afford 2-(4-(3,5-dimethoxyphenyl)-1-hydroxybut-3-ynyl)phenol (**III**).

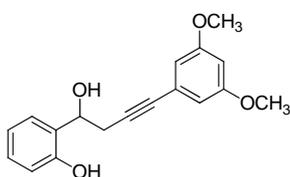
but-3-ynyl)phenol (**III**, 78%).

### 3.3 Procedure for the synthesis of ethyl 3-(2-(4-(3,5-dimethoxyphenyl)-1-hydroxybut-3-ynyl)phenoxy)acrylate (**IV**)

To a flask containing 2-(4-(3,5-dimethoxyphenyl)-1-hydroxybut-3-ynyl)phenol (**III**, 3 mmol), ethyl propiolate (3.3 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) was added DABCO (0.3 mmol). The resulting mixture was stirred at 0 °C for 3 h. Upon completion, the mixture was concentrated and the residue was purified by column chromatography on silica gel with petroleum ether-ethyl acetate (5:1) to give (E)- 3-(2-(4-(3,5-dimethoxyphenyl)-1-hydroxybut-3-ynyl)phenoxy)acrylate (**IV**, 85%).

### 3.4 Procedure for the synthesis of ethyl 3-(2-(4-(3,5-dimethoxyphenyl)buta-2,3-dienoyl)phenoxy)acrylate (**1j**)

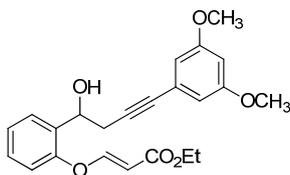
To a solution of (E)-ethyl 3-(2-(4-(3,5-dimethoxyphenyl)-1-hydroxybut-3-ynyl)phenoxy)acrylate (**IV**, 2 mmol) in acetone (20 mL) cooled to 0 °C was added Jones reagent (2.4 mmol) in a dropwise manner. Upon complete consumption of the starting material as monitored by TLC, the reaction mixture was quenched by addition of isopropanol. The mixture was filtered and the filtrate was concentrated under vacuum. The residue were purified by column chromatography on silica gel with petroleum ether-ethyl acetate (5:1) to give (E)-ethyl 3-(2-(4-(3,5-dimethoxyphenyl)buta-2,3-dienoyl)phenoxy)acrylate (**1j**, 78%). **1i** and **1k-1q** were obtained in a similar manner.



### 2-(4-(3,5-Dimethoxyphenyl)-1-hydroxybut-3-yn-1-yl)phenol (**III**)

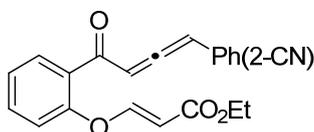
Eluent: petroleum ether-ethyl acetate (5:1); oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 2.86-3.00 (m, 2H), 3.73 (s, 6H), 5.07 (q, *J* = 7.2 Hz, 1H), 6.42 (t, *J* = 2.4 Hz, 1H), 6.57 (d, *J* = 2.8 Hz, 2H), 6.86 (t, *J* = 7.2 Hz, 2H), 7.09 (d, *J* = 7.2 Hz, 1H), 7.14-7.18 (m, 1H), 8.16 (br s, 1H). <sup>13</sup>C NMR (100 MHz,

CDCl<sub>3</sub>)  $\delta$ : 28.8, 55.4, 73.3, 83.2, 85.7, 101.5, 109.6, 117.0, 120.0, 124.6, 126.2, 127.5, 129.2, 155.0, 160.4. MS:  $m/z$  299 (MH)<sup>+</sup>. HRMS (ESI) calcd for C<sub>18</sub>H<sub>19</sub>O<sub>4</sub>: 299.1283 [M+H], found: 299.1285.



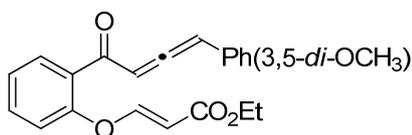
**(E)-Ethyl 3-(2-(4-(3,5-dimethoxyphenyl)-1-hydroxybut-3-yn-1-yl)phenoxy)acrylate (IV)**

Eluent: petroleum ether-ethyl acetate (5:1); oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 1.26 (t,  $J$  = 7.2 Hz, 3H), 2.75-2.81 (m, 1H), 2.88-2.93 (m, 1H), 3.75 (s, 6H), 4.17 (q,  $J$  = 7.2 Hz, 2H), 5.21 (dd,  $J_1$  = 7.2 Hz,  $J_2$  = 4.8 Hz, 1H), 5.54 (d,  $J$  = 12.0 Hz, 1H), 6.40-6.41 (m, 1H), 6.52-6.53 (m, 2H), 7.02 (d,  $J$  = 7.6 Hz, 1H), 7.24 (t,  $J$  = 7.2 Hz, 1H), 7.30-7.34 (m, 1H), 7.64 (d,  $J$  = 8.0 Hz, 1H), 7.77 (d,  $J$  = 12.0 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 14.3, 29.3, 55.4, 60.2, 66.9, 83.3, 85.3, 101.5, 102.6, 109.5, 117.7, 124.3, 125.4, 127.4, 129.2, 133.1, 152.4, 159.0, 160.4, 167.0. MS:  $m/z$  397 (MH)<sup>+</sup>. HRMS (ESI) calcd for C<sub>23</sub>H<sub>25</sub>O<sub>6</sub>: 397.1651 [M+H], found: 397.1655.



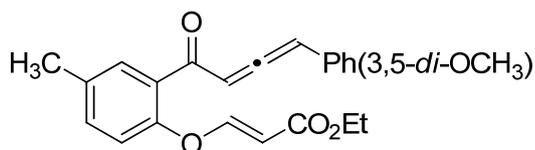
**(E)-Ethyl 3-(2-(4-(2-cyanophenyl)buta-2,3-dienoyl)phenoxy)acrylate (1i)**

Eluent: petroleum ether-ethyl acetate (10:1); oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 1.25 (t,  $J$  = 7.2 Hz, 3H), 4.16 (q,  $J$  = 7.2 Hz, 2H), 5.51 (d,  $J$  = 12.4 Hz, 1H), 6.75 (d,  $J$  = 6.4 Hz, 1H), 6.94 (d,  $J$  = 6.0 Hz, 1H), 7.07 (d,  $J$  = 7.2 Hz, 1H), 7.19-7.23 (m, 1H), 7.30-7.34 (m, 1H), 7.43-7.54 (m, 3H), 7.55-7.61 (m, 2H), 7.79 (d,  $J$  = 12.4 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 14.3, 60.4, 96.3, 100.8, 104.0, 111.0, 117.0, 120.2, 128.0, 128.6, 129.8, 130.6, 131.5, 132.9, 133.1, 133.3, 134.1, 151.6, 158.0, 166.4, 188.6, 217.5. MS:  $m/z$  360 (MH)<sup>+</sup>. HRMS (ESI) calcd for C<sub>22</sub>H<sub>18</sub>NO<sub>4</sub>: 360.1236 [M+H], found: 360.1237.



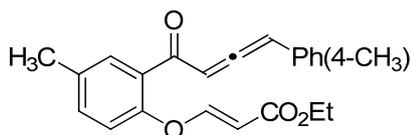
**(E)-Ethyl 3-(2-(4-(3,5-dimethoxyphenyl)buta-2,3-dienoyl)phenoxy)acrylate (1j)**

Eluent: petroleum ether-ethyl acetate (5:1); oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.27 (t,  $J = 7.2$  Hz, 3H), 3.75 (s, 6H), 4.18 (q,  $J = 7.2$  Hz, 2H), 5.53 (d,  $J = 12.4$  Hz, 1H), 6.36-6.37 (m, 3H), 6.48 (d,  $J = 6.0$  Hz, 1H), 6.59 (d,  $J = 6.8$  Hz, 1H), 7.06 (d,  $J = 8.0$  Hz, 1H), 7.17 (t,  $J = 7.2$  Hz, 1H), 7.42-7.46 (m, 1H), 7.50-7.52 (m, 1H), 7.69 (d,  $J = 12.0$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 14.3, 55.3, 60.2, 99.1, 100.4, 100.6, 103.2, 105.6, 109.5, 118.7, 125.0, 129.7, 130.8, 132.6, 132.7, 153.0, 158.7, 161.0, 166.8, 191.4, 217.2. MS:  $m/z$  395 ( $\text{MH}^+$ ). HRMS (ESI) calcd for  $\text{C}_{23}\text{H}_{23}\text{O}_6$ : 395.1494 [ $\text{M}+\text{H}$ ], found: 395.1489.



**(E)-Ethyl 3-(2-(4-(3,5-dimethoxyphenyl)buta-2,3-dienoyl)-4-methylphenoxy)acrylate (1l)**

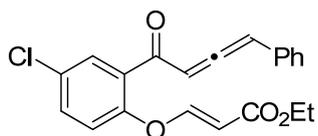
Eluent: petroleum ether-ethyl acetate (10:1); oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.27 (t,  $J = 7.6$  Hz, 3H), 2.23 (s, 3H), 3.77 (s, 6H), 4.17 (q,  $J = 7.6$  Hz, 2H), 5.47 (d,  $J = 12.4$  Hz, 1H), 6.37-6.40 (m, 3H), 6.48 (d,  $J = 6.0$  Hz, 1H), 6.57 (d,  $J = 6.0$  Hz, 1H), 6.94 (d,  $J = 8.4$  Hz, 1H), 7.21-7.31 (m, 2H), 7.68 (d,  $J = 12.4$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 14.2, 22.6, 55.4, 60.2, 99.0, 100.3, 100.5, 102.6, 105.5, 118.8, 130.2, 130.3, 132.7, 133.2, 134.8, 150.9, 159.3, 161.0, 166.9, 191.4, 217.2. MS:  $m/z$  409 ( $\text{MH}^+$ ). HRMS (ESI) calcd for  $\text{C}_{24}\text{H}_{25}\text{O}_6$ : 409.1651 [ $\text{M}+\text{H}$ ], found: 409.1655.



**(E)-Ethyl 3-(4-methyl-2-(4-(p-tolyl)buta-2,3-dienoyl)phenoxy)acrylate (1m)**

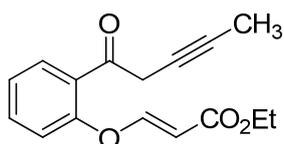
Eluent: petroleum ether-ethyl acetate (10:1); oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.28 (t,  $J = 7.2$  Hz,

3H), 2.13 (s, 3H), 2.33 (s, 3H), 4.19 (q,  $J = 7.2$  Hz, 2H), 5.45 (d,  $J = 12.8$  Hz, 1H), 6.55 (dd,  $J_1 = 13.2$  Hz,  $J_2 = 6.0$  Hz, 1H), 6.93 (d,  $J = 8.0$  Hz, 1H), 7.71-7.26 (m, 6H), 7.30 (s, 1H), 7.68 (d,  $J = 12.0$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 14.3, 20.4, 21.2, 60.1, 98.6, 100.5, 102.4, 118.8, 127.4, 127.7, 129.6, 130.2, 130.5, 133.2, 134.8, 138.2, 150.8, 159.4, 166.9, 191.6, 217.2. MS:  $m/z$  363 ( $\text{MH}$ ) $^+$ . HRMS (ESI) calcd for  $\text{C}_{23}\text{H}_{23}\text{O}_4$ : 363.1596 [ $\text{M}+\text{H}$ ], found: 363.1593.



**(E)-Ethyl 3-(4-chloro-2-(4-phenylbuta-2,3-dienoyl)phenoxy)acrylate (1q)**

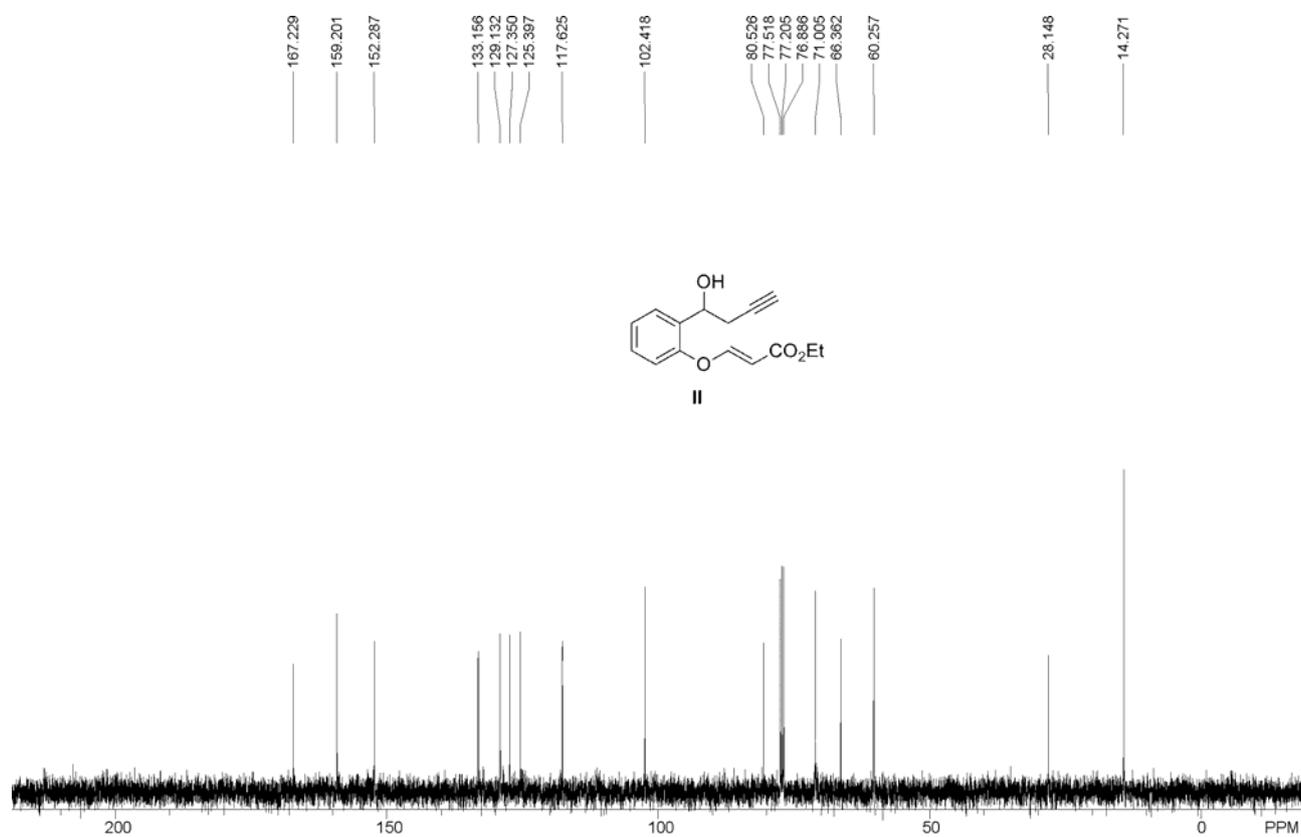
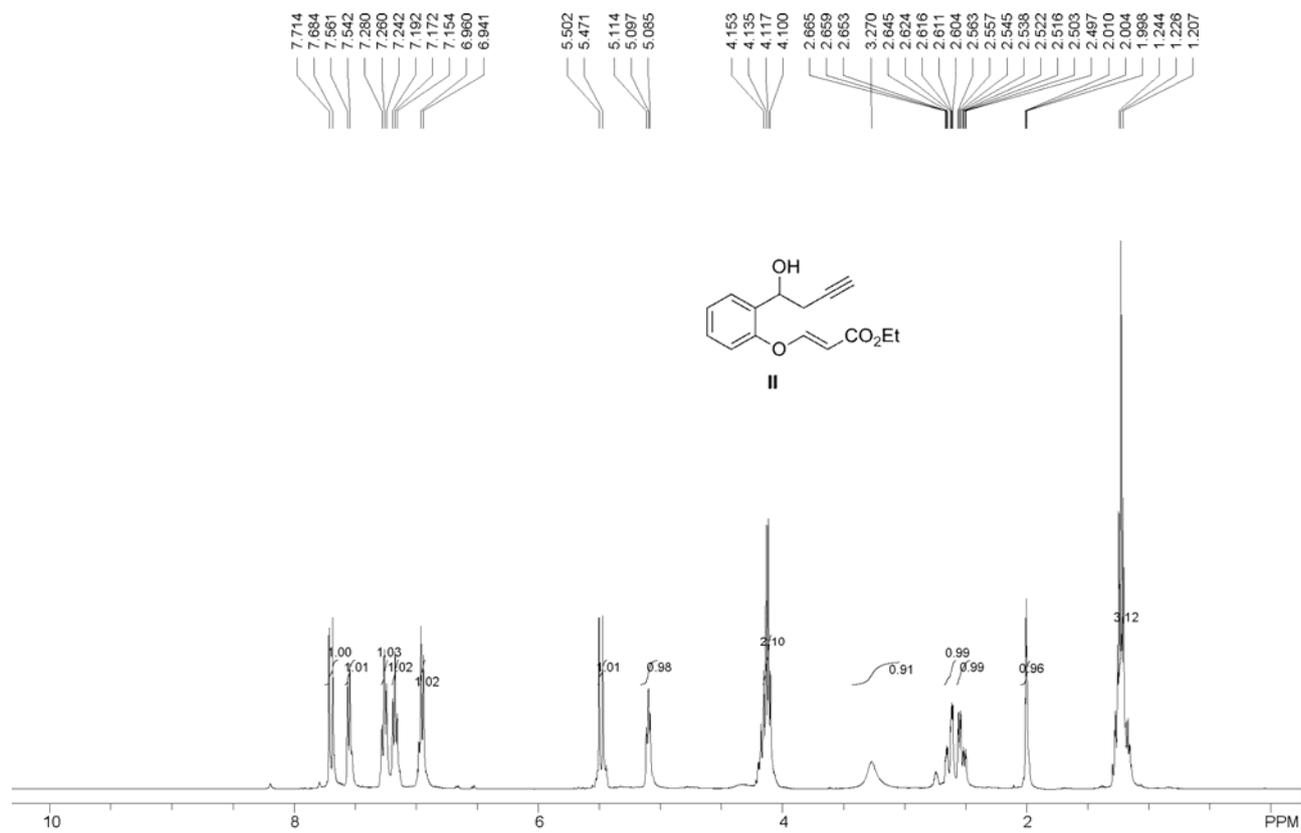
Eluent: petroleum ether-ethyl acetate (10:1); oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.28 (t,  $J = 7.6$  Hz, 3H), 4.19 (q,  $J = 7.6$  Hz, 2H), 5.53 (d,  $J = 12.4$  Hz, 1H), 6.58 (dd,  $J_1 = 10.4$  Hz,  $J_2 = 6.0$  Hz, 1H), 6.99 (d,  $J = 8.4$  Hz, 1H), 7.22-7.31 (m, 7H), 7.47 (d,  $J = 2.4$  Hz, 1H), 7.63 (d,  $J = 12.4$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 14.3, 60.4, 99.3, 100.4, 103.7, 120.1, 127.6, 128.4, 129.0, 129.6, 130.3, 130.4, 132.0, 132.4, 151.4, 158.3, 166.6, 190.1, 217.6 MS:  $m/z$  369 ( $\text{MH}$ ) $^+$ . HRMS (ESI) calcd for  $\text{C}_{21}\text{H}_{18}\text{ClO}_4$ : 369.0893 [ $\text{M}+\text{H}$ ], found: 369.0892.

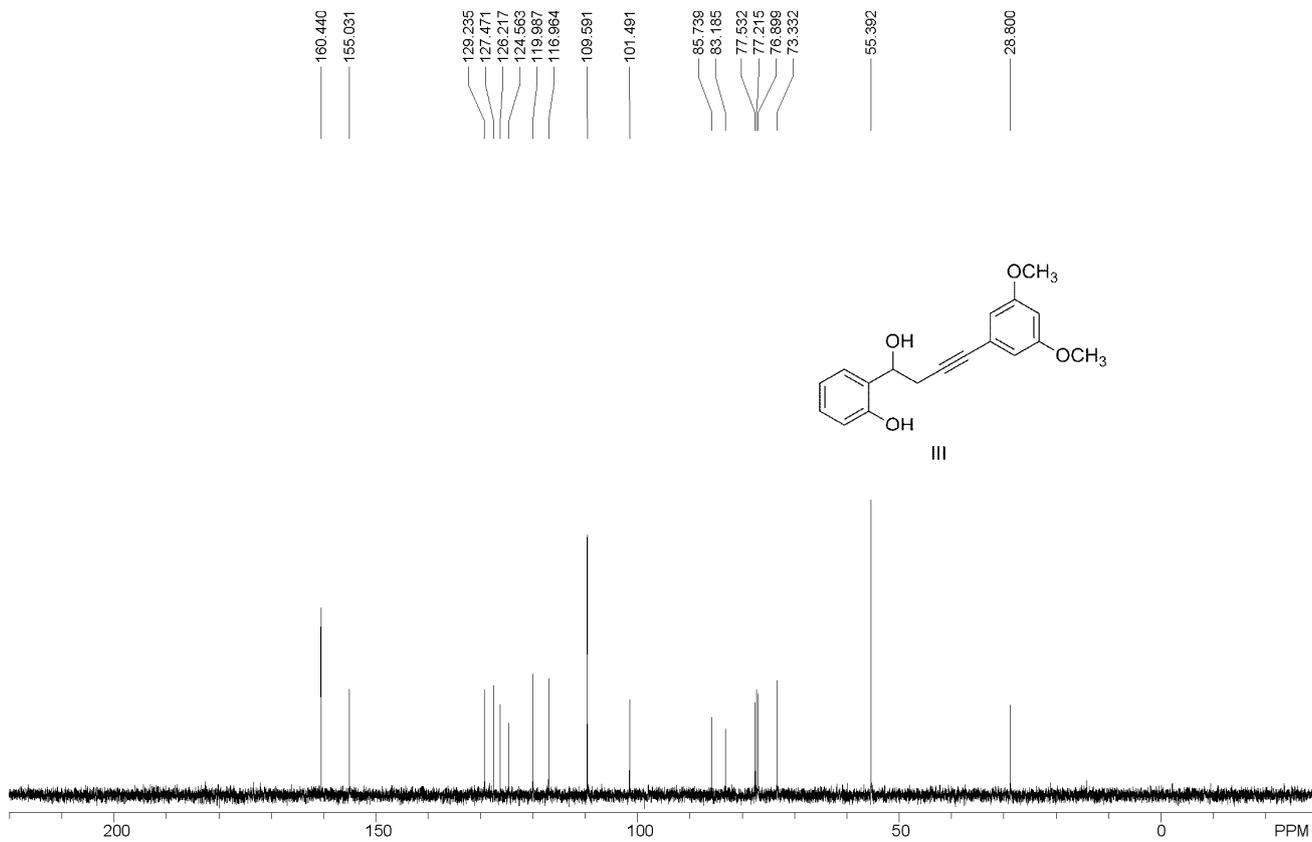
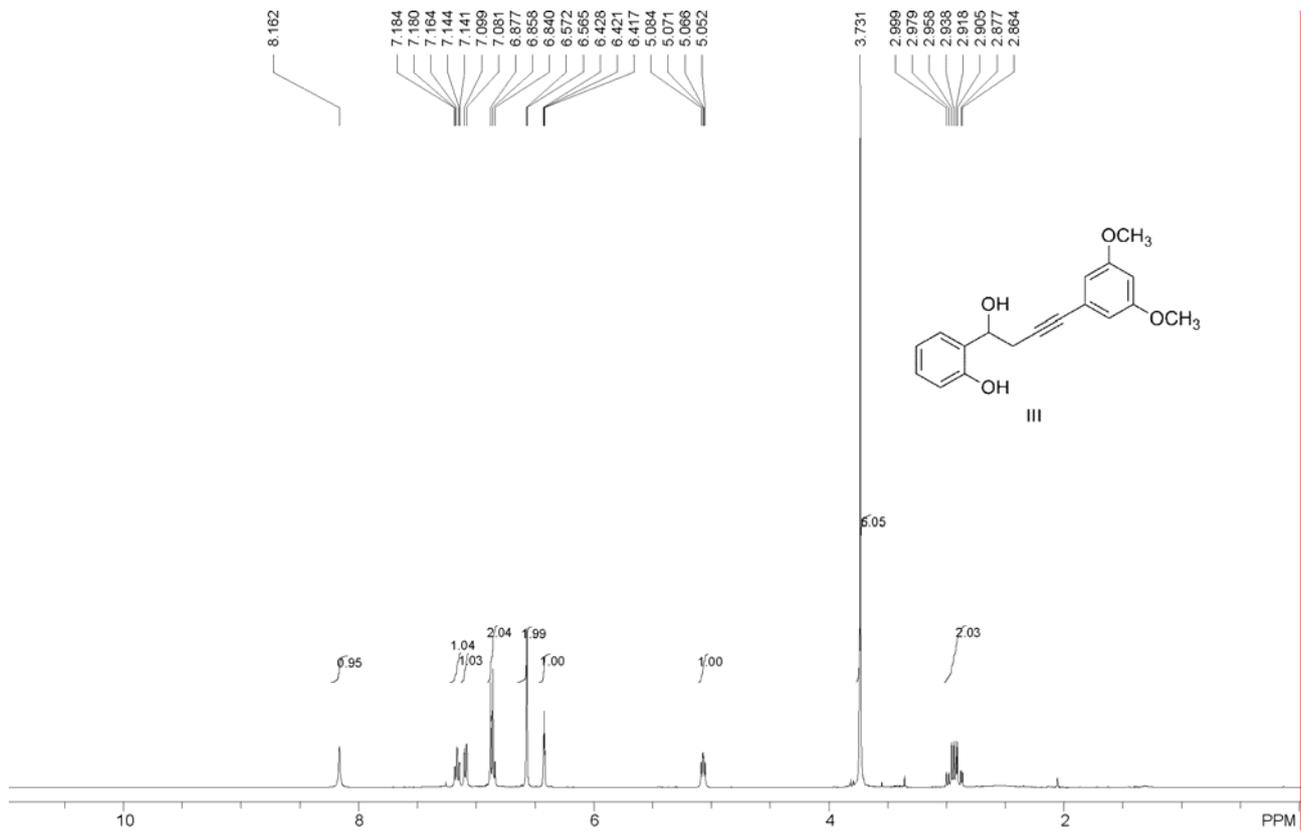


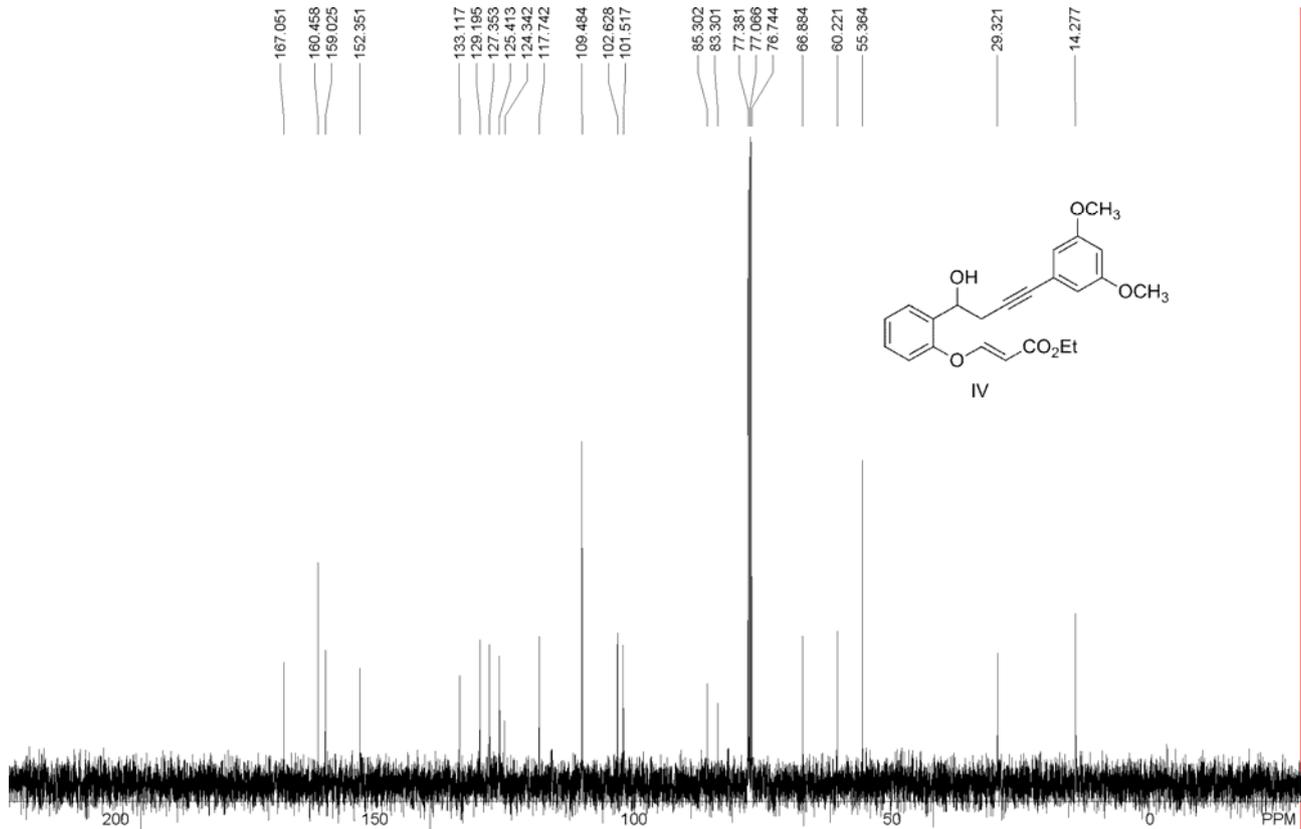
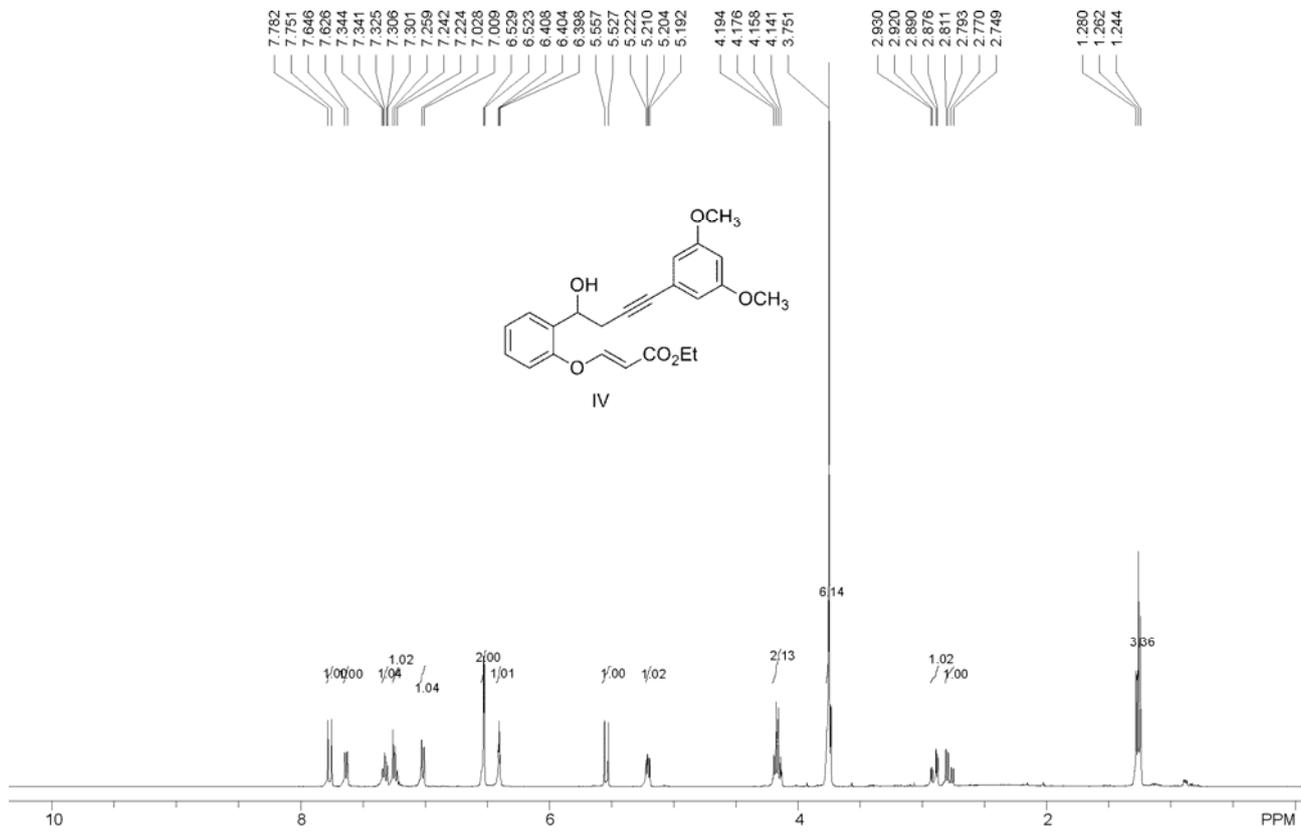
**(E)-Ethyl 3-(2-pent-3-ynoylphenoxy)acrylate (1r)**

Eluent: petroleum ether-ethyl acetate (10:1); oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.20 (t,  $J = 7.2$  Hz, 3H), 1.71 (t,  $J = 2.4$  Hz, 3H), 3.69 (t,  $J = 2.4$  Hz, 2H), 4.11 (q,  $J = 7.2$  Hz, 2H), 5.58 (d,  $J = 12.4$  Hz, 1H), 7.03 (d,  $J = 8.4$  Hz, 1H), 7.20 (t,  $J = 8.0$  Hz, 1H), 7.46-7.50 (m, 1H), 7.67 (d,  $J = 12.0$  Hz, 1H), 7.73 (q,  $J = 7.6$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 3.56, 14.2, 35.1, 60.3, 71.3, 80.7, 103.8, 118.5, 125.3, 128.3, 131.0, 134.2, 154.4, 158.0, 166.6, 194.4. MS:  $m/z$  273 ( $\text{MH}$ ) $^+$ . HRMS (ESI) calcd for  $\text{C}_{16}\text{H}_{17}\text{O}_4$ : 273.1127 [ $\text{M}+\text{H}$ ], found: 273.1122.

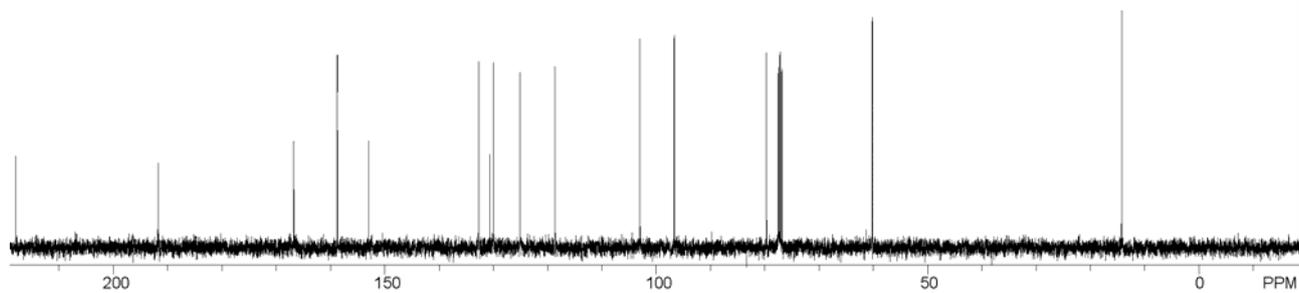
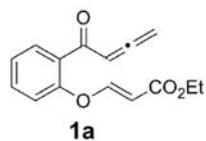
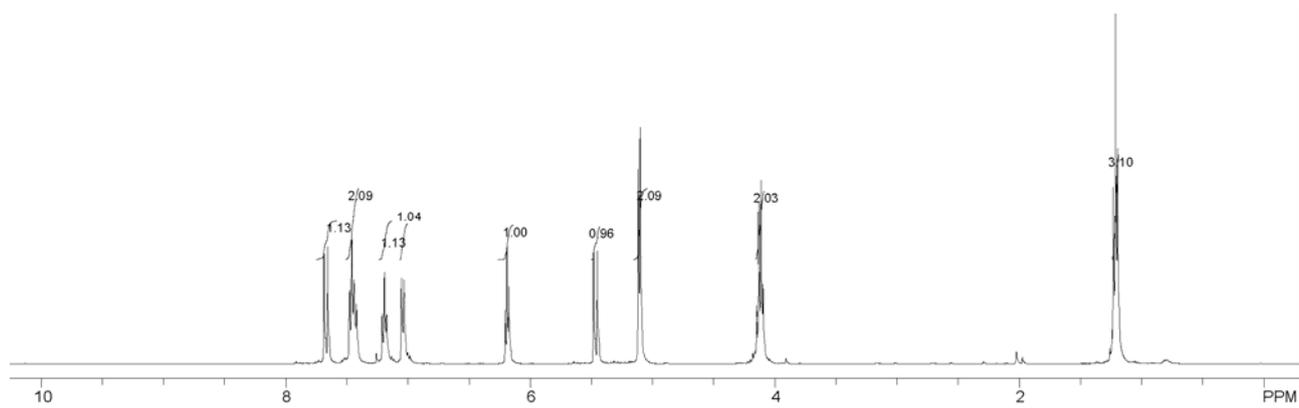
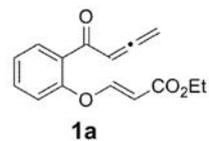
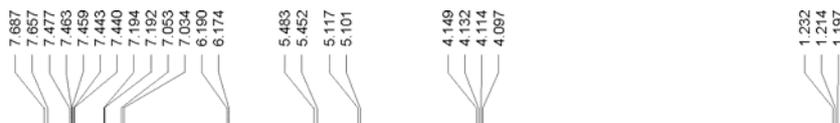
## II. Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of compounds II, III, IV



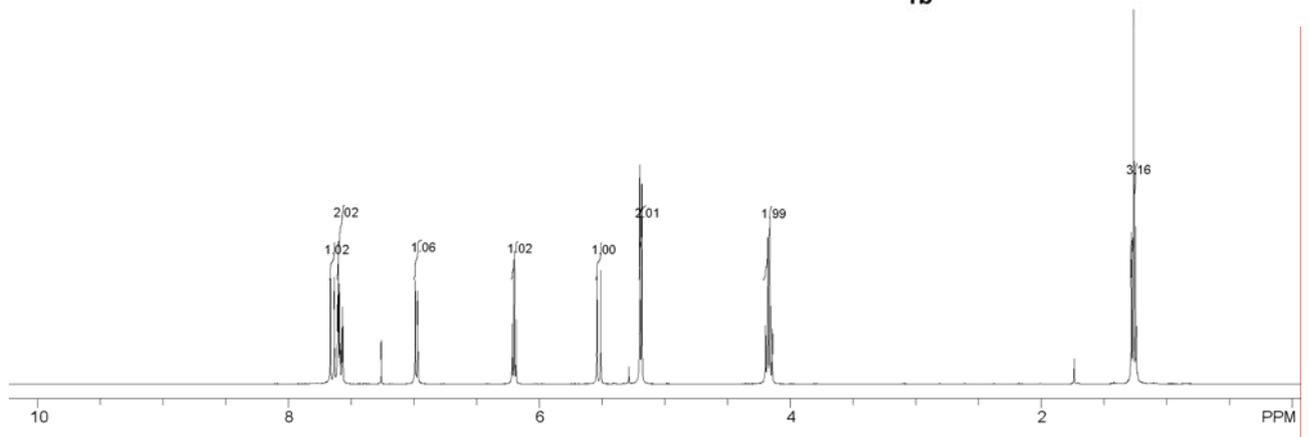
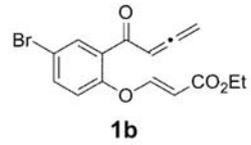




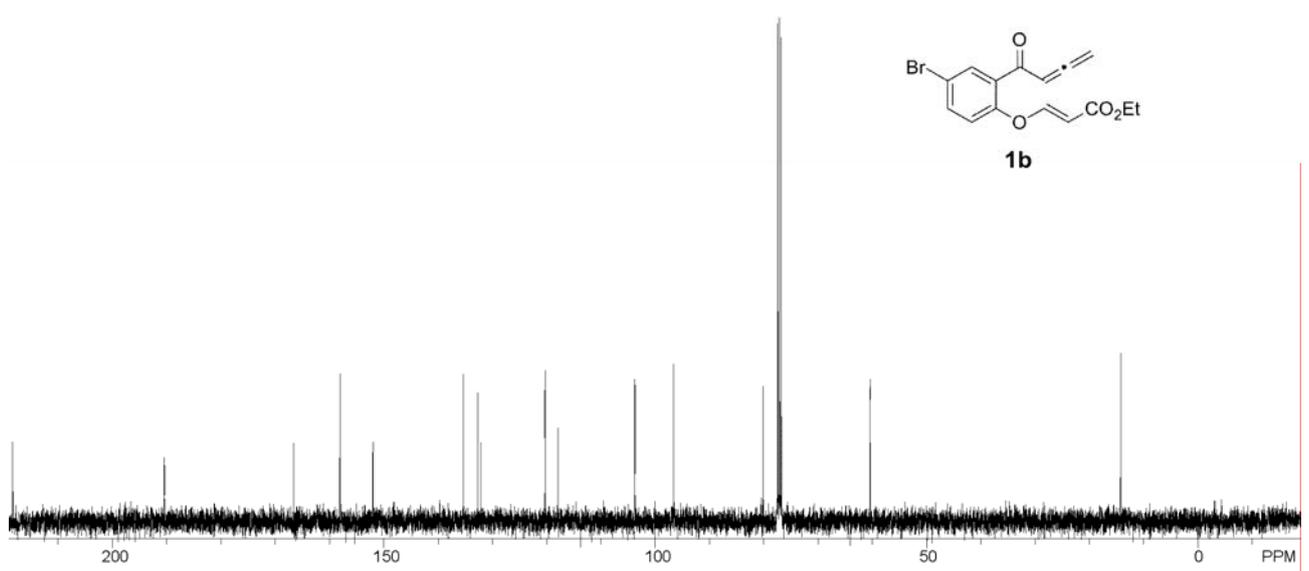
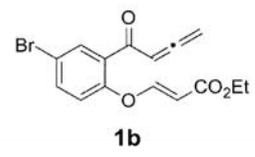
### III. Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of compounds 1a-1j, 1l-1m, 1q-1r

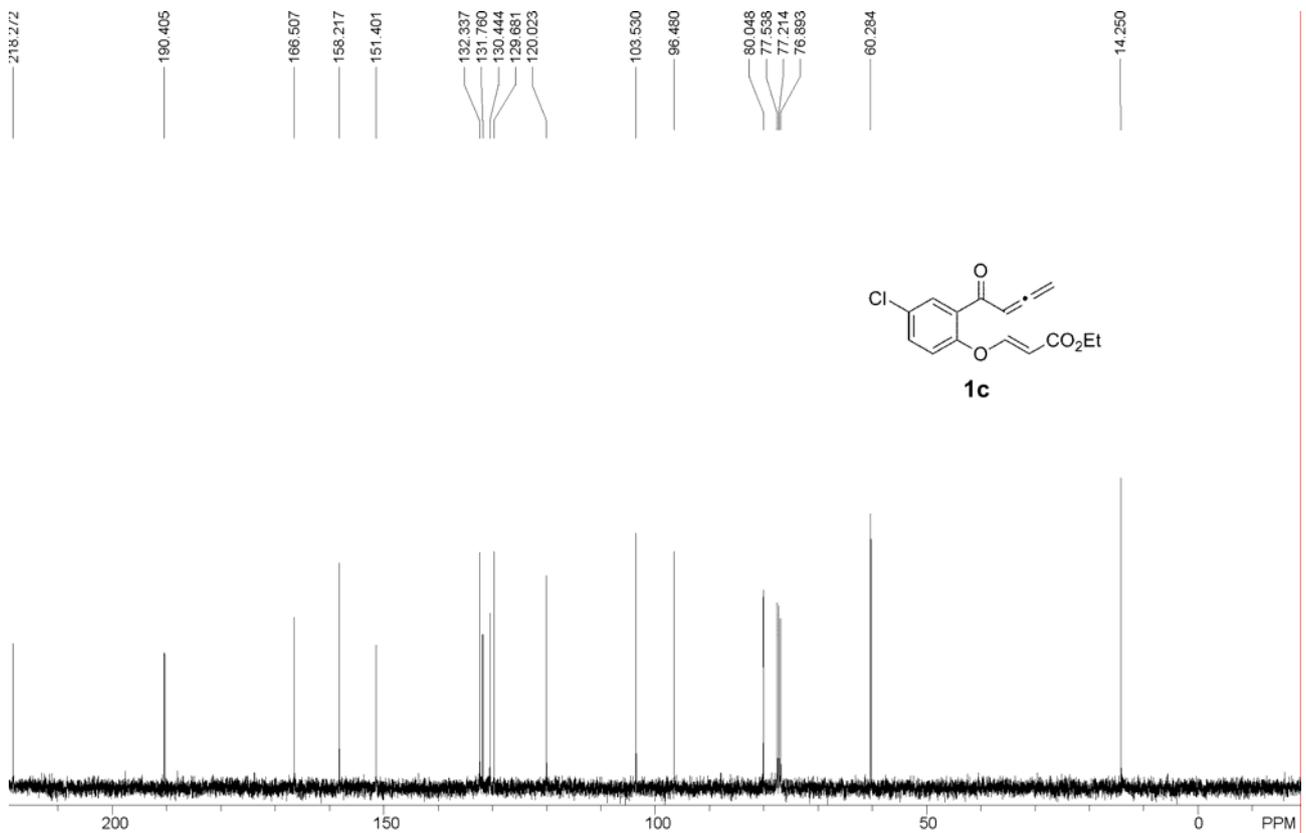
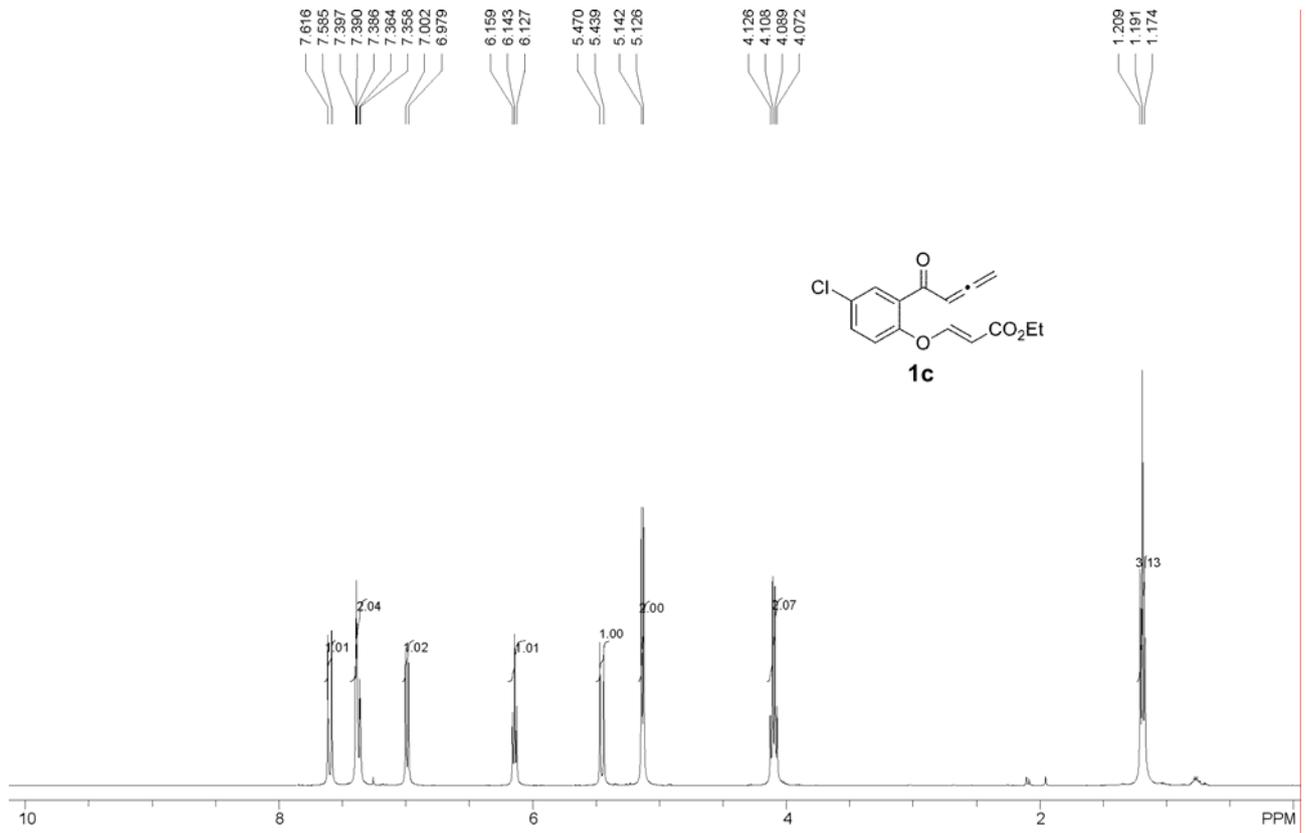


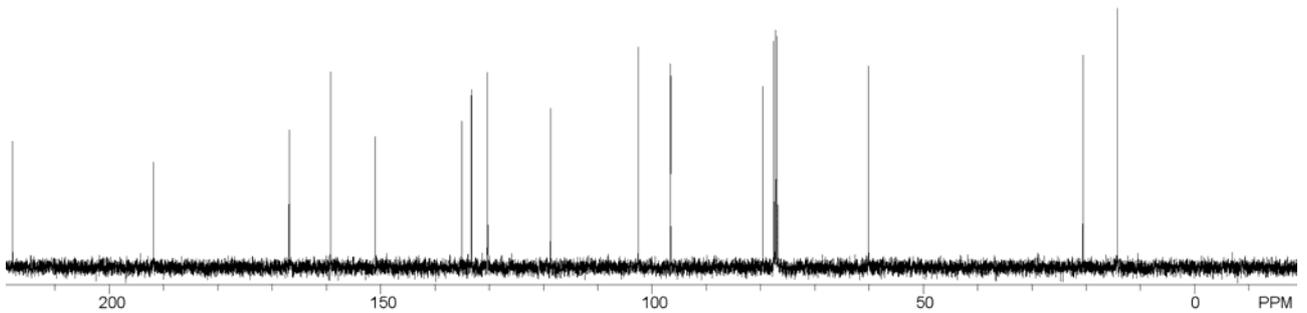
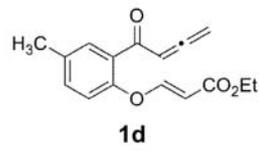
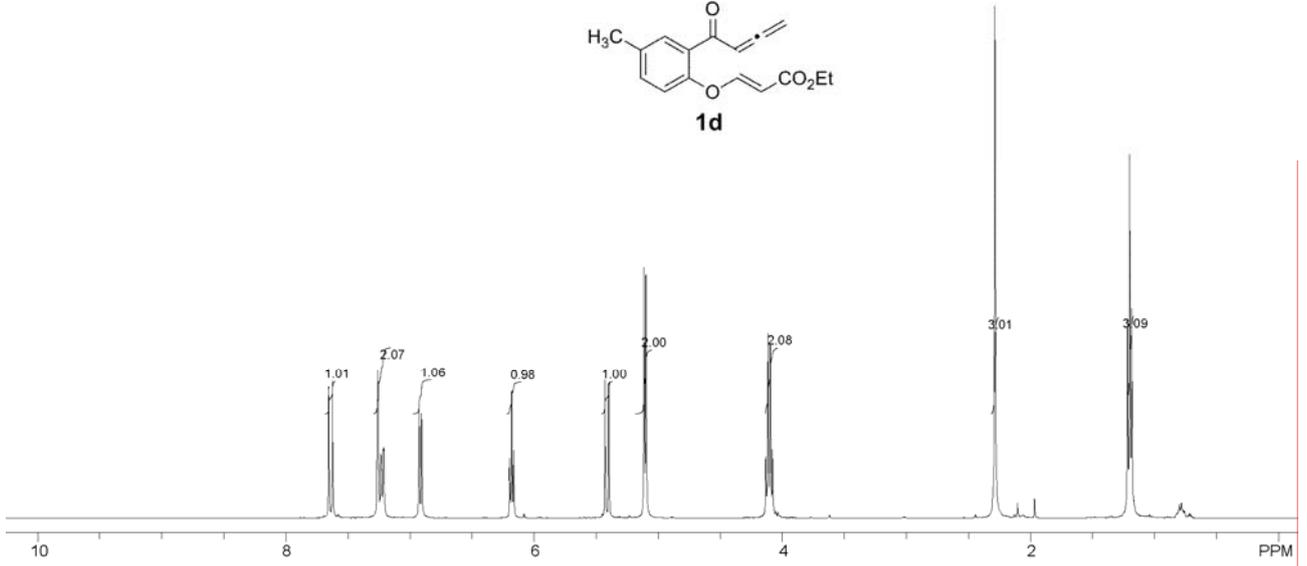
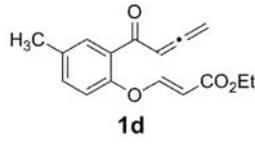
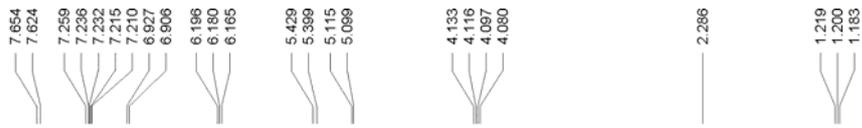
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7.607  
7.601  
7.592  
7.570  
7.564  
7.259  
6.988  
6.966  
6.216  
6.200  
6.184  
5.539  
5.508  
5.198  
5.182  
4.198  
4.177  
4.161  
4.142  
1.278  
1.261  
1.242

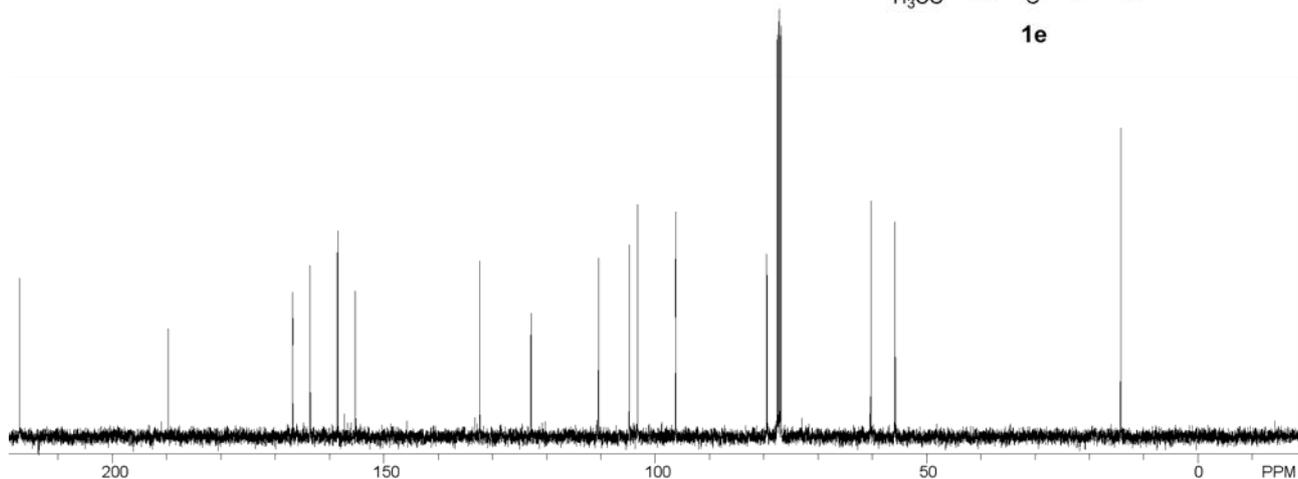
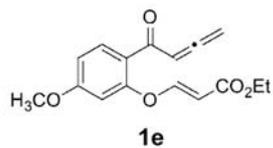
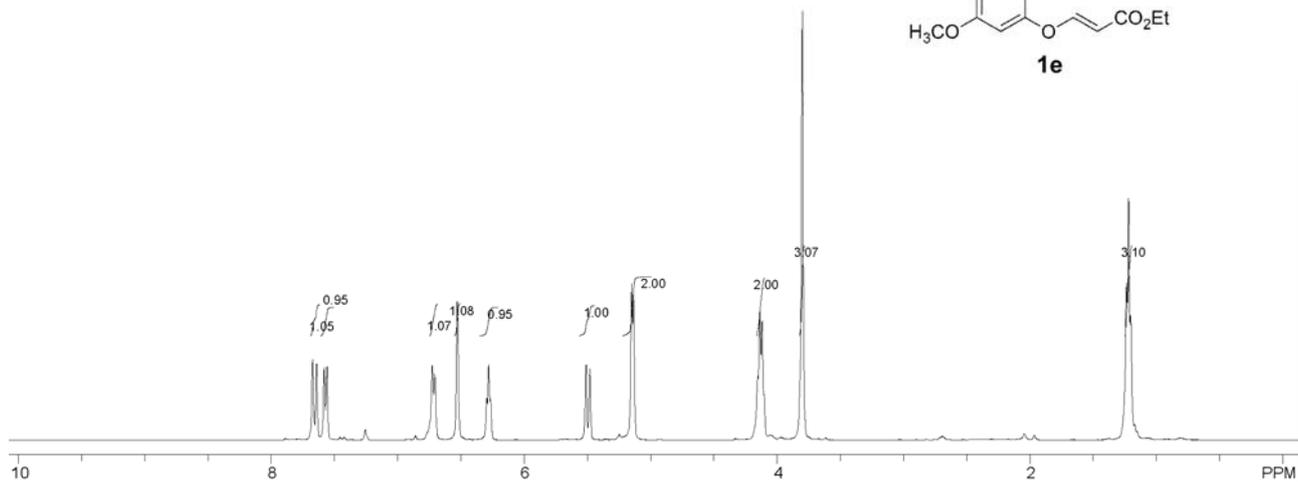
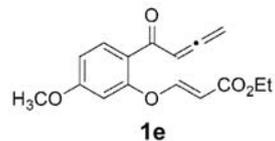
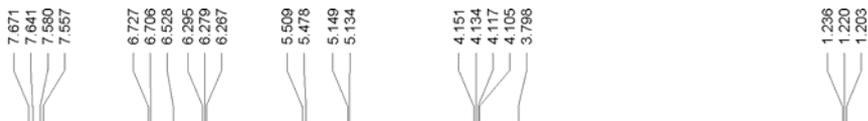


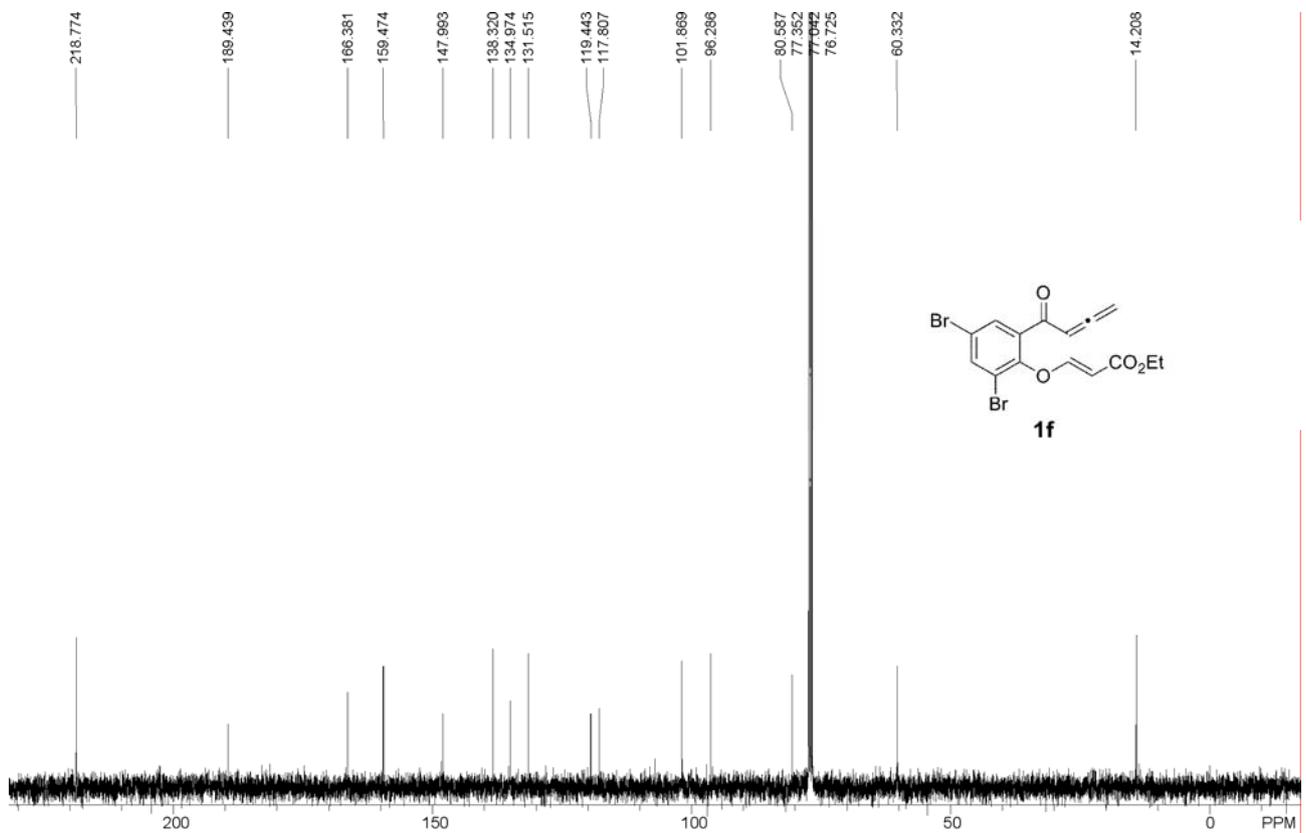
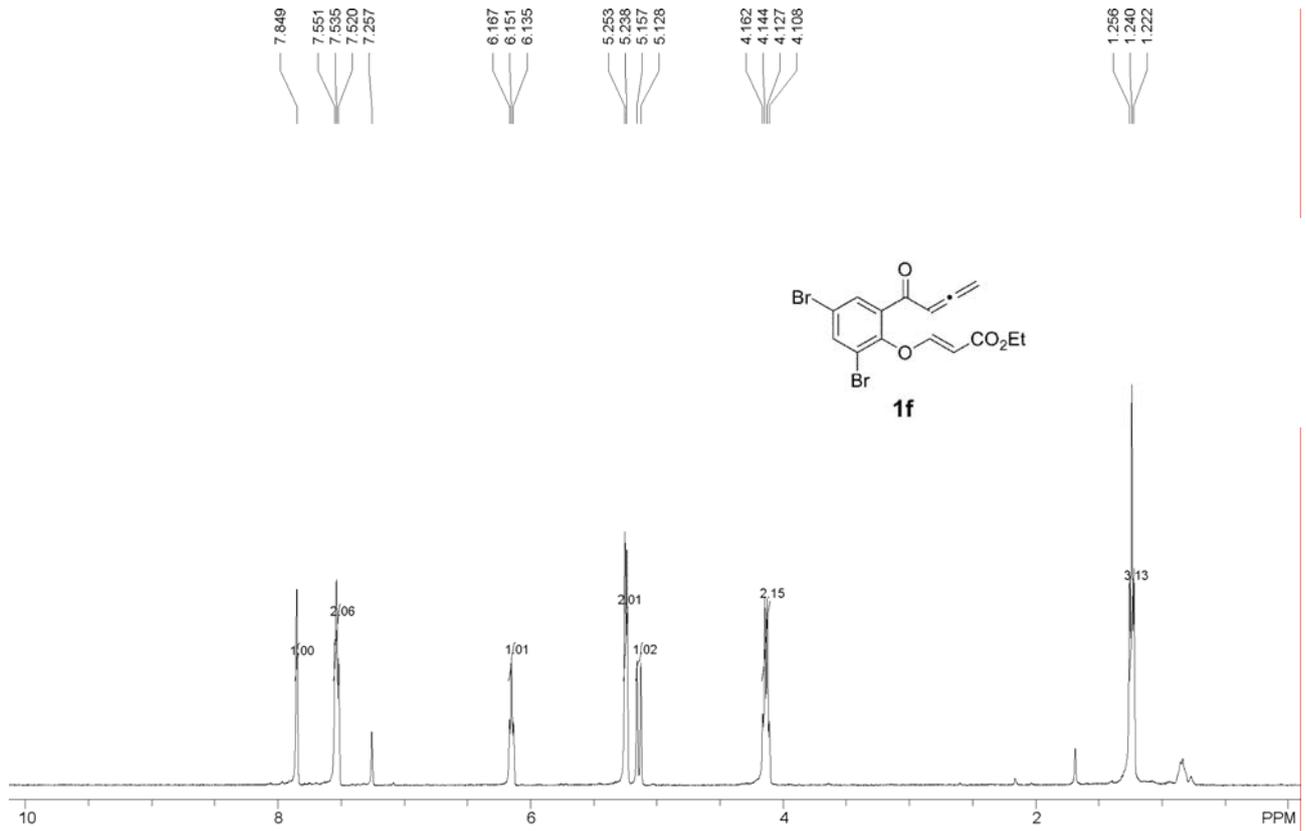
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190.428  
166.613  
158.088  
151.985  
135.333  
132.672  
132.144  
120.292  
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103.724  
96.578  
80.096  
77.404  
77.088  
76.763  
60.382  
14.293

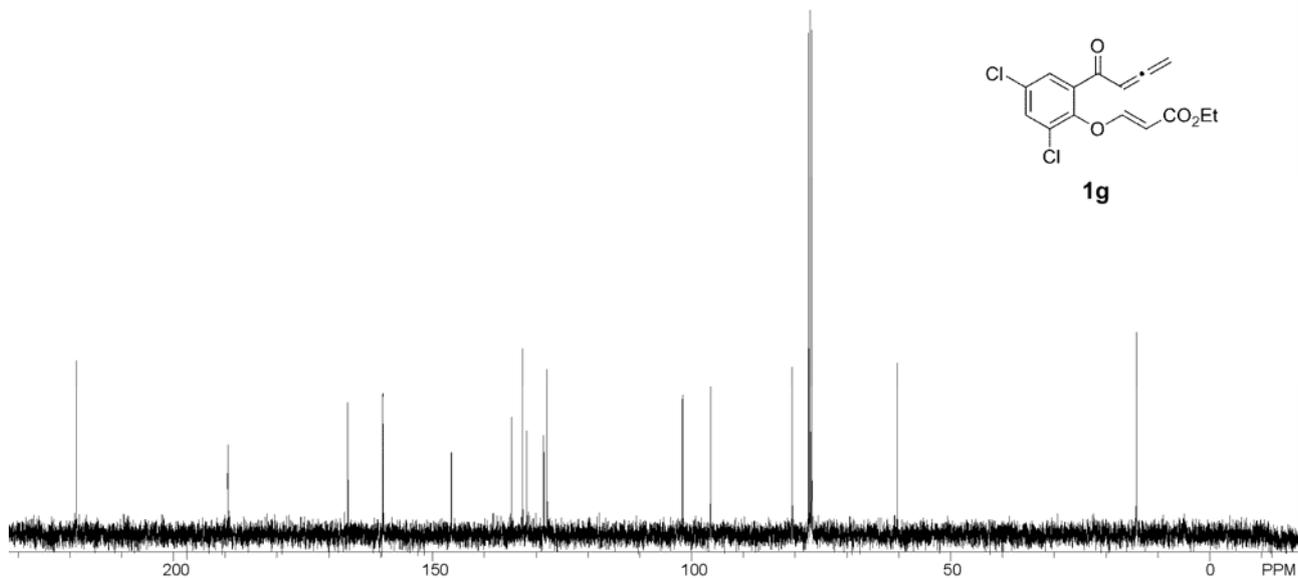
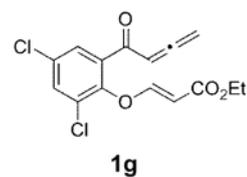
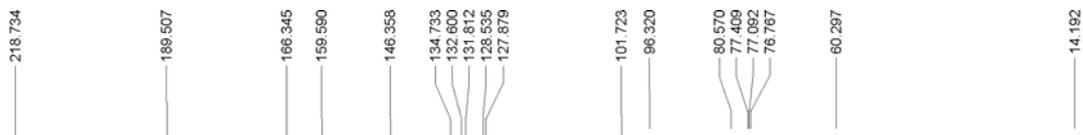
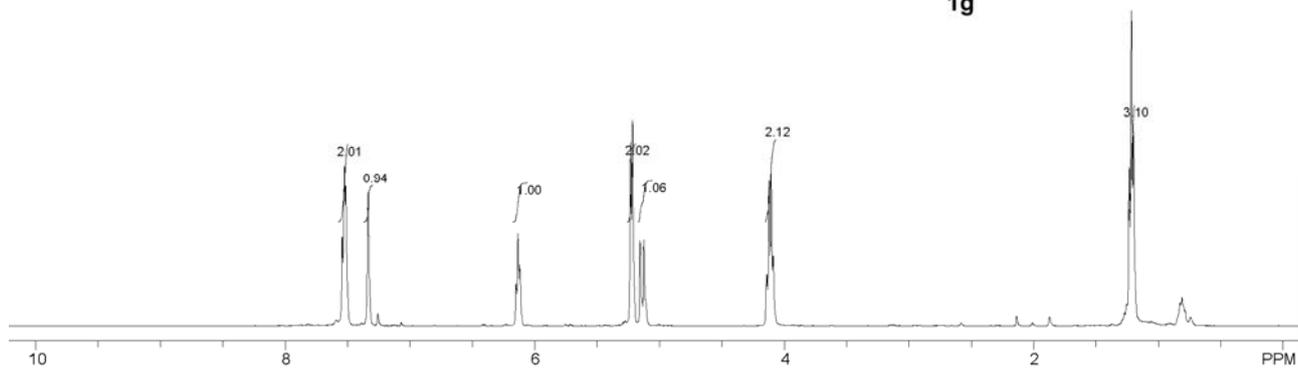
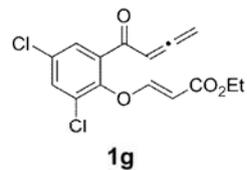
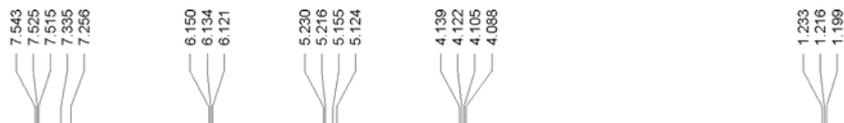


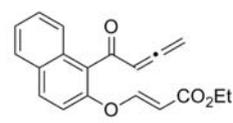
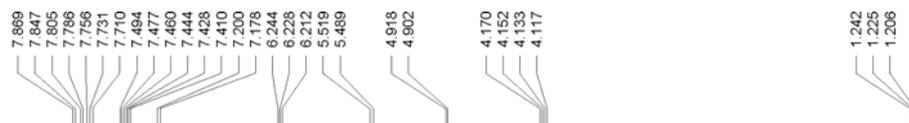




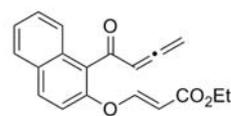
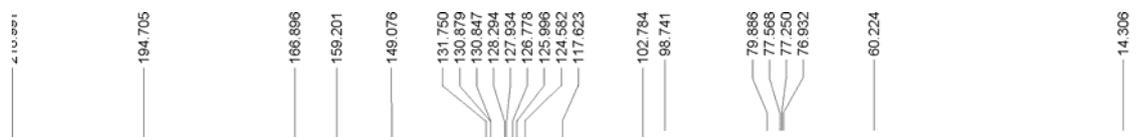
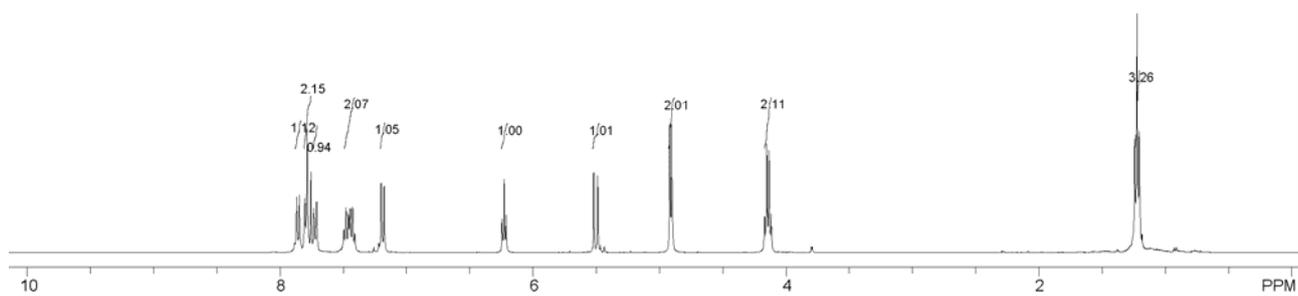




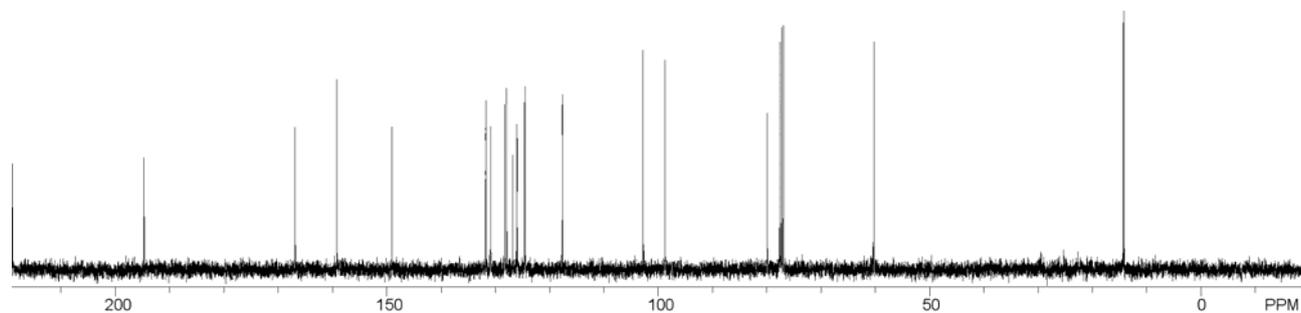


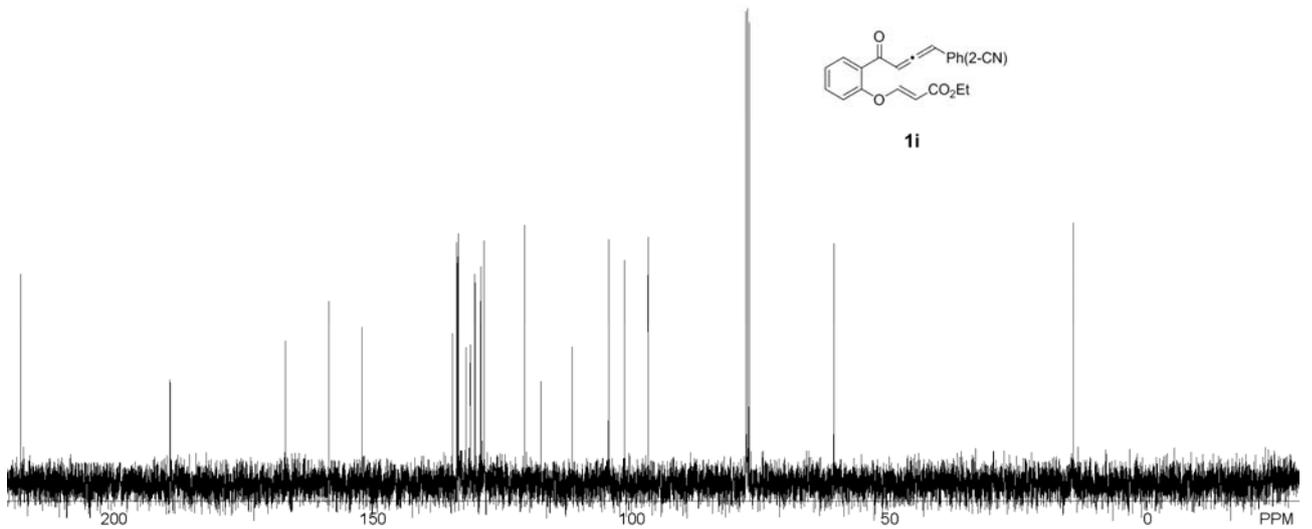
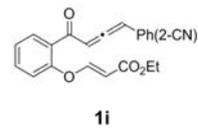
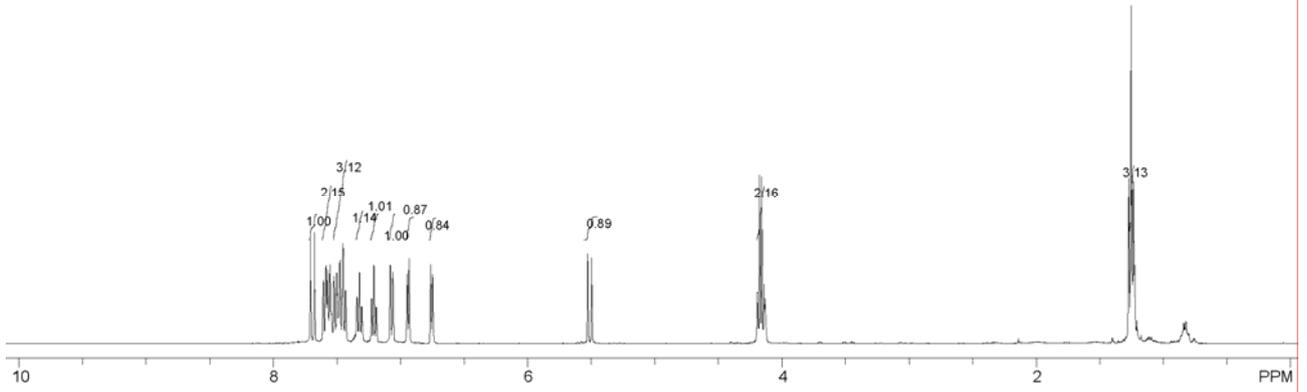
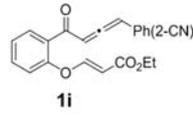
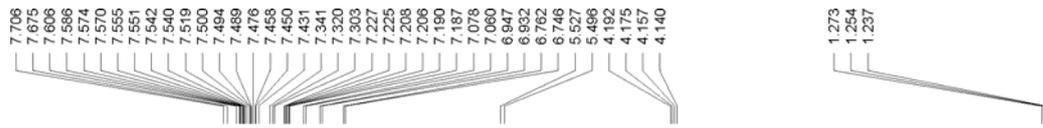


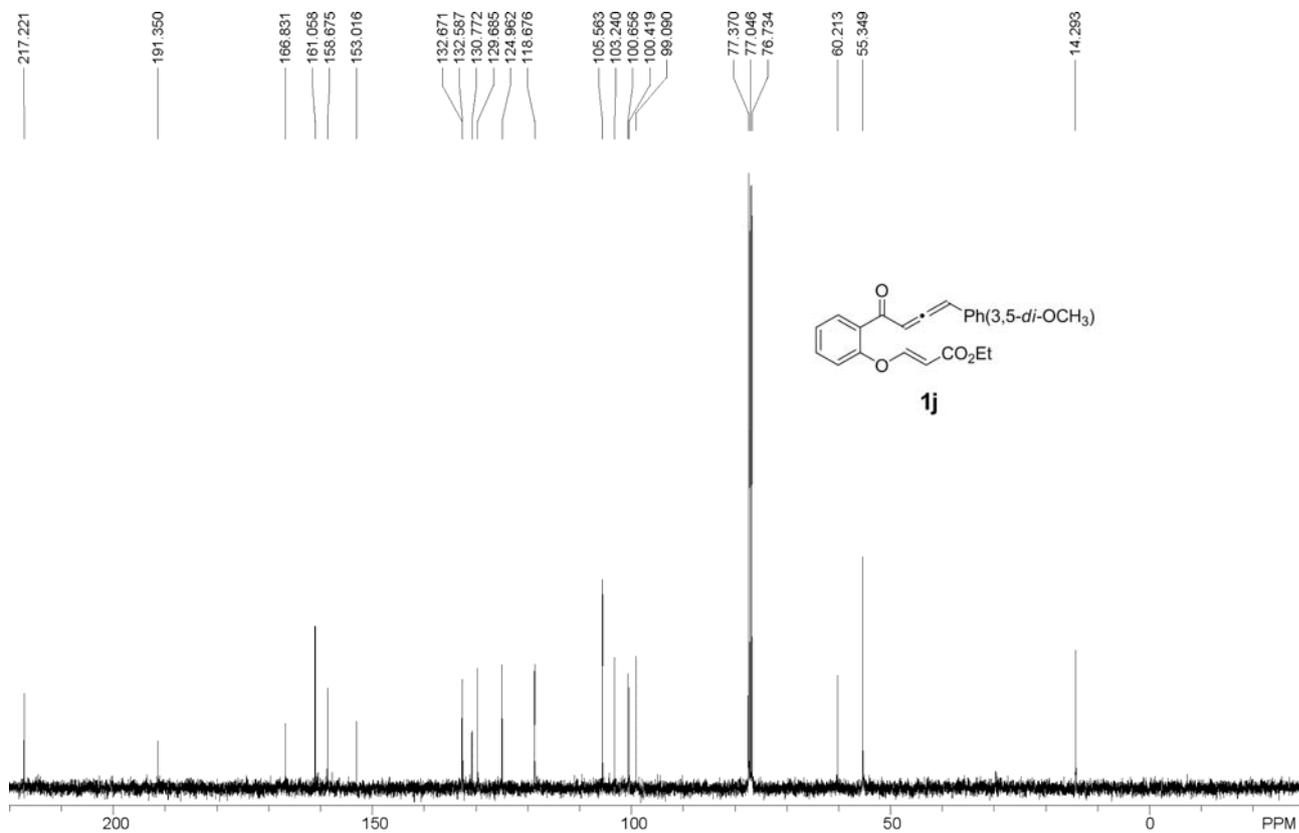
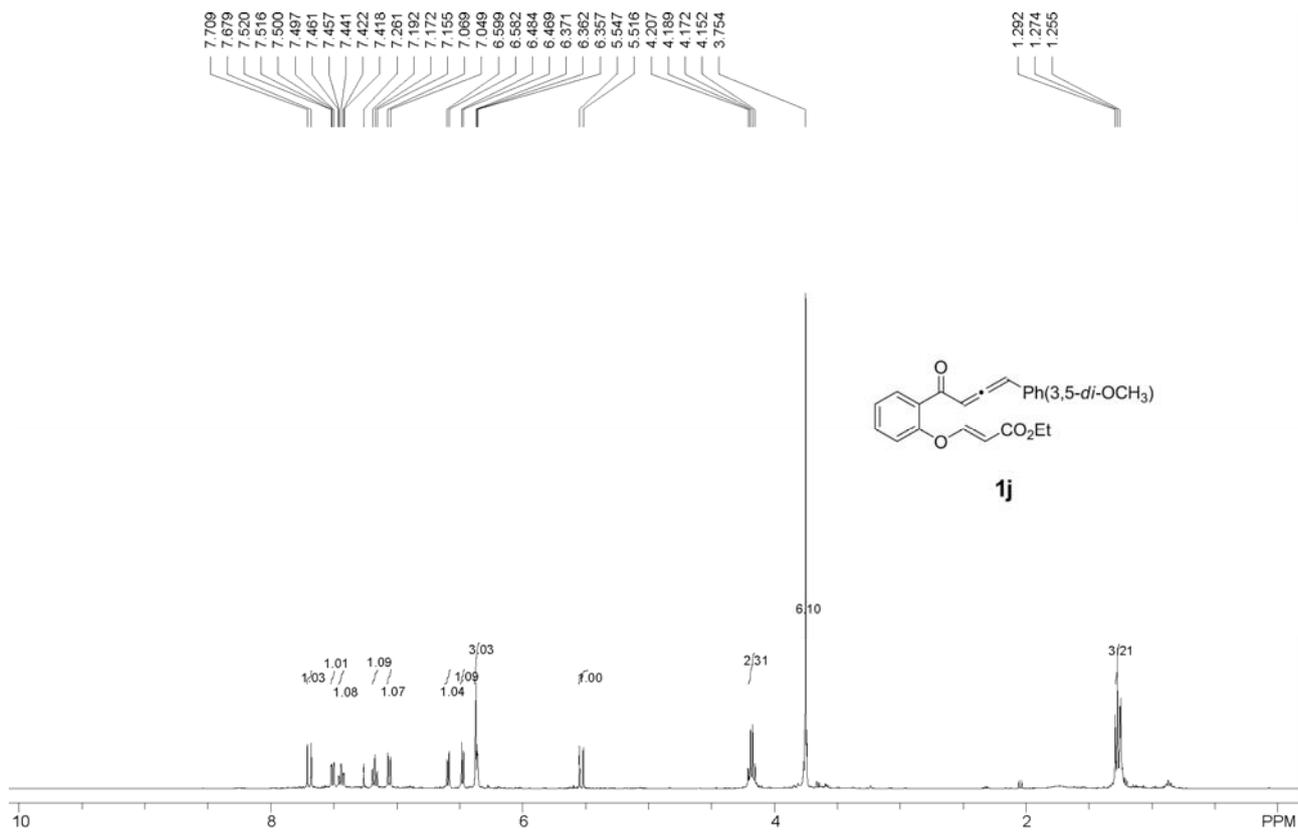
**1h**

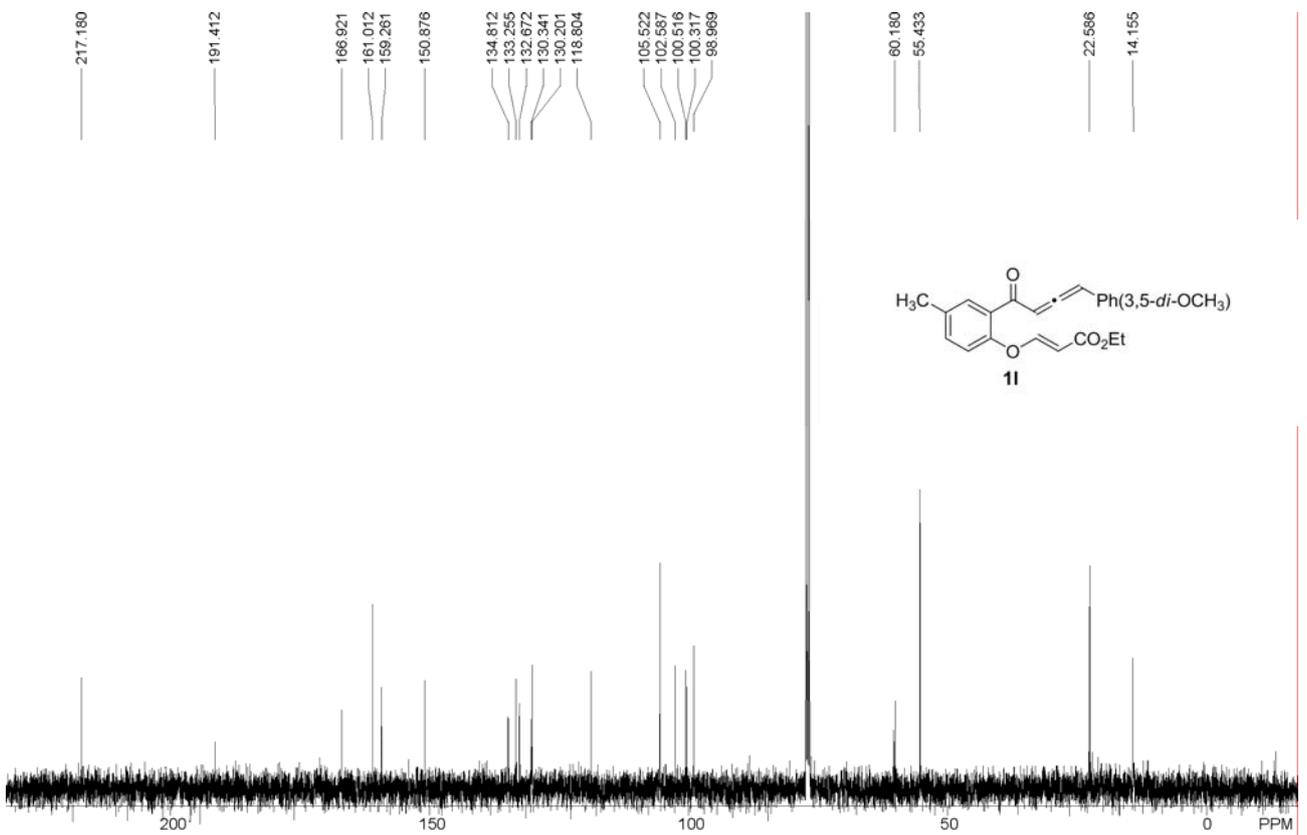
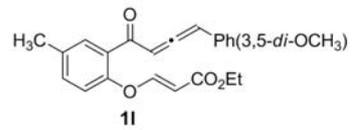
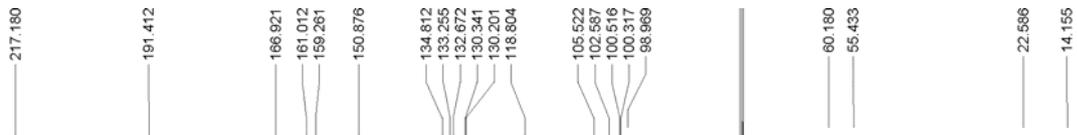
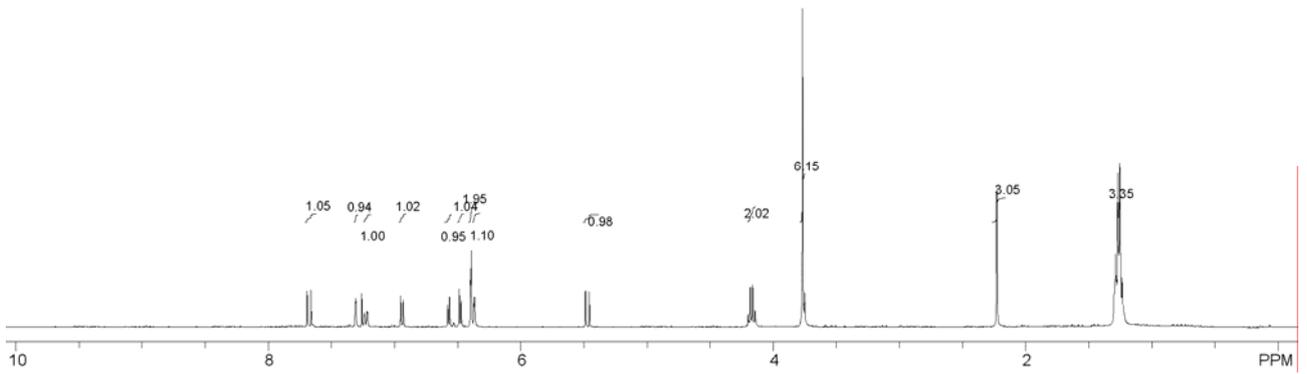
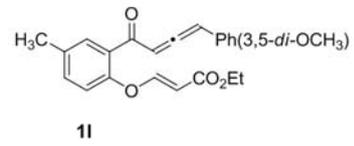
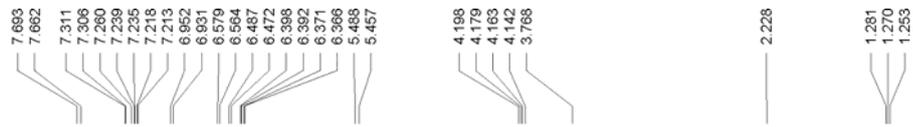


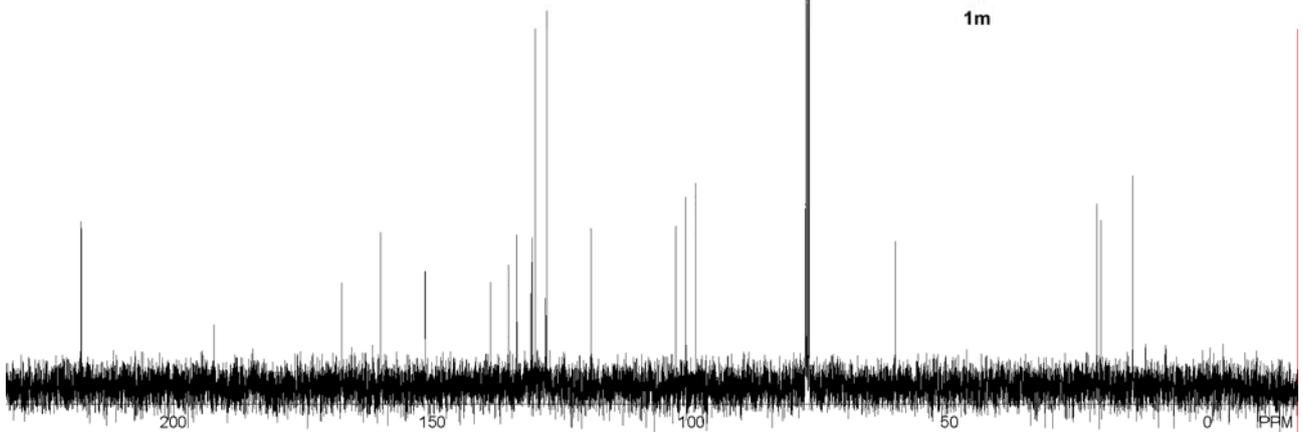
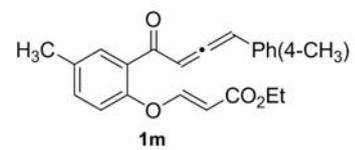
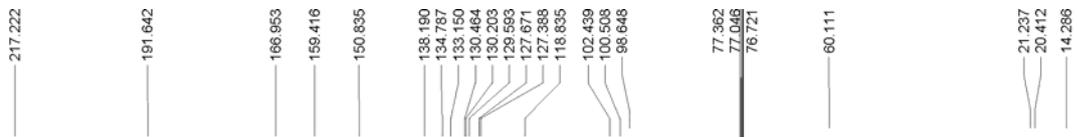
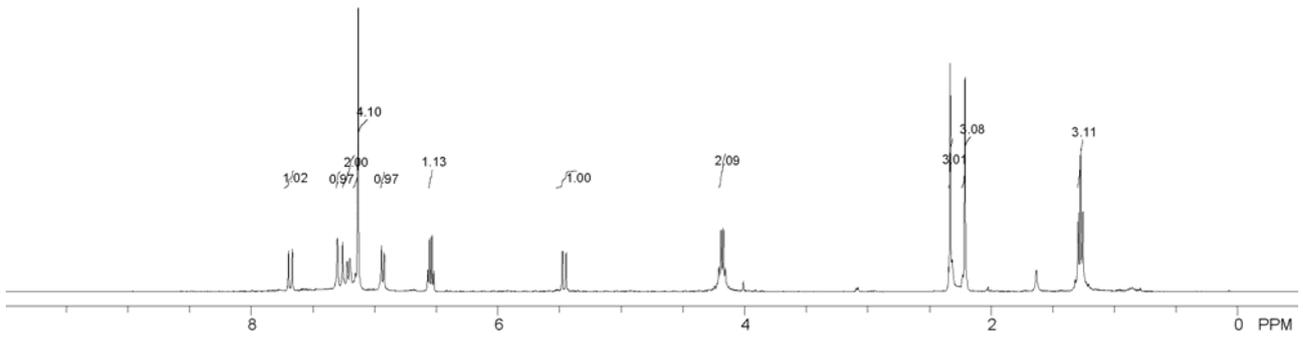
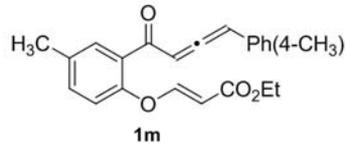
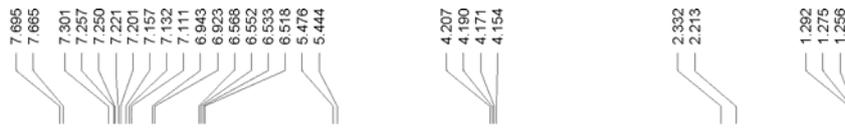
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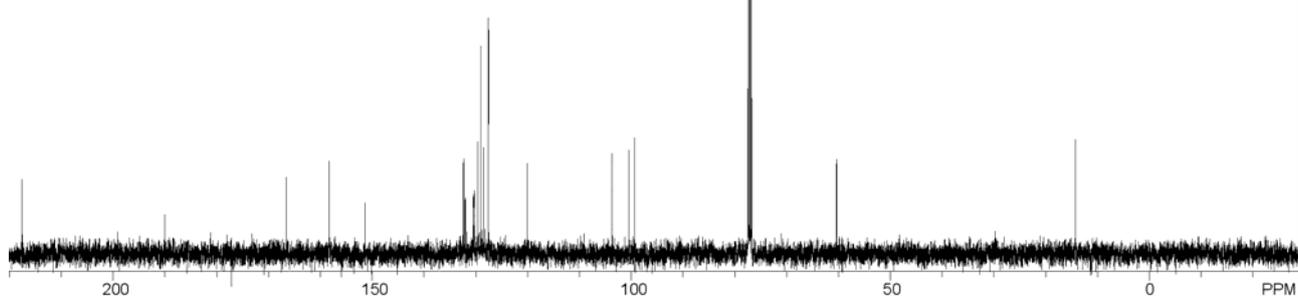
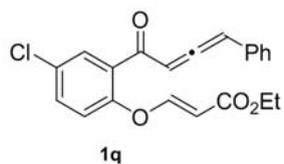
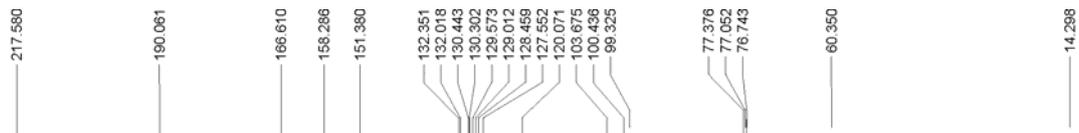
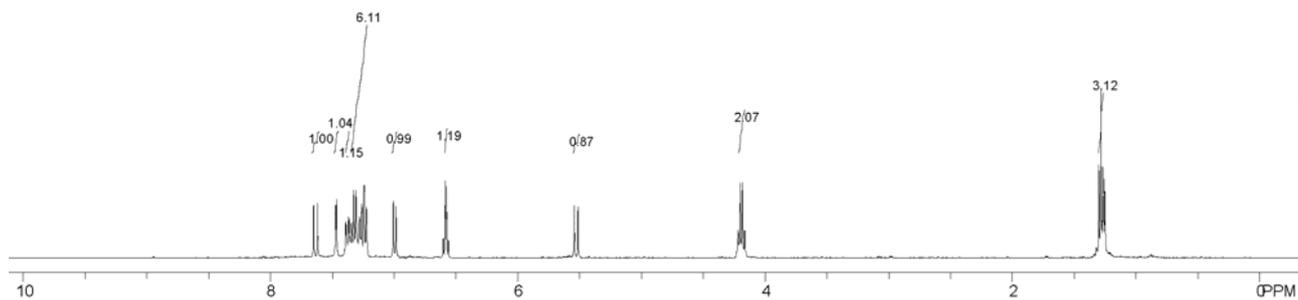
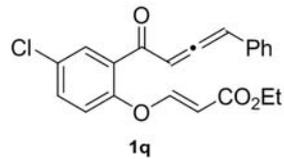
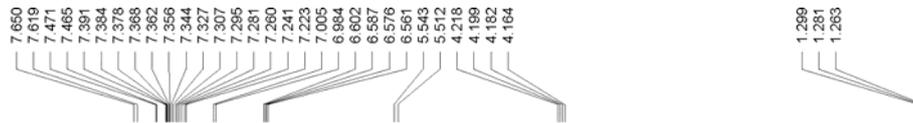


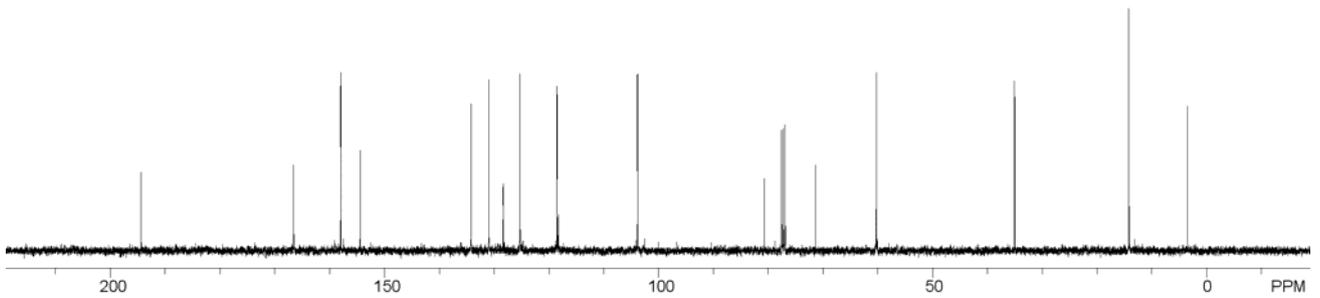
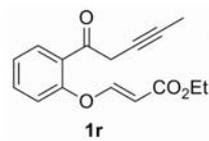
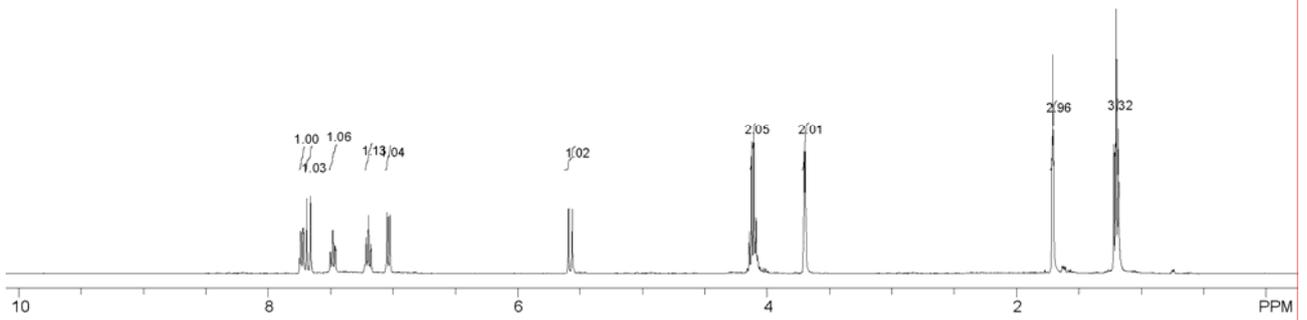
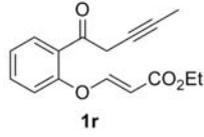
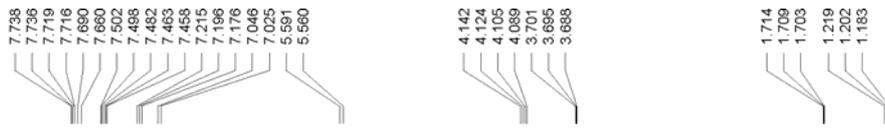




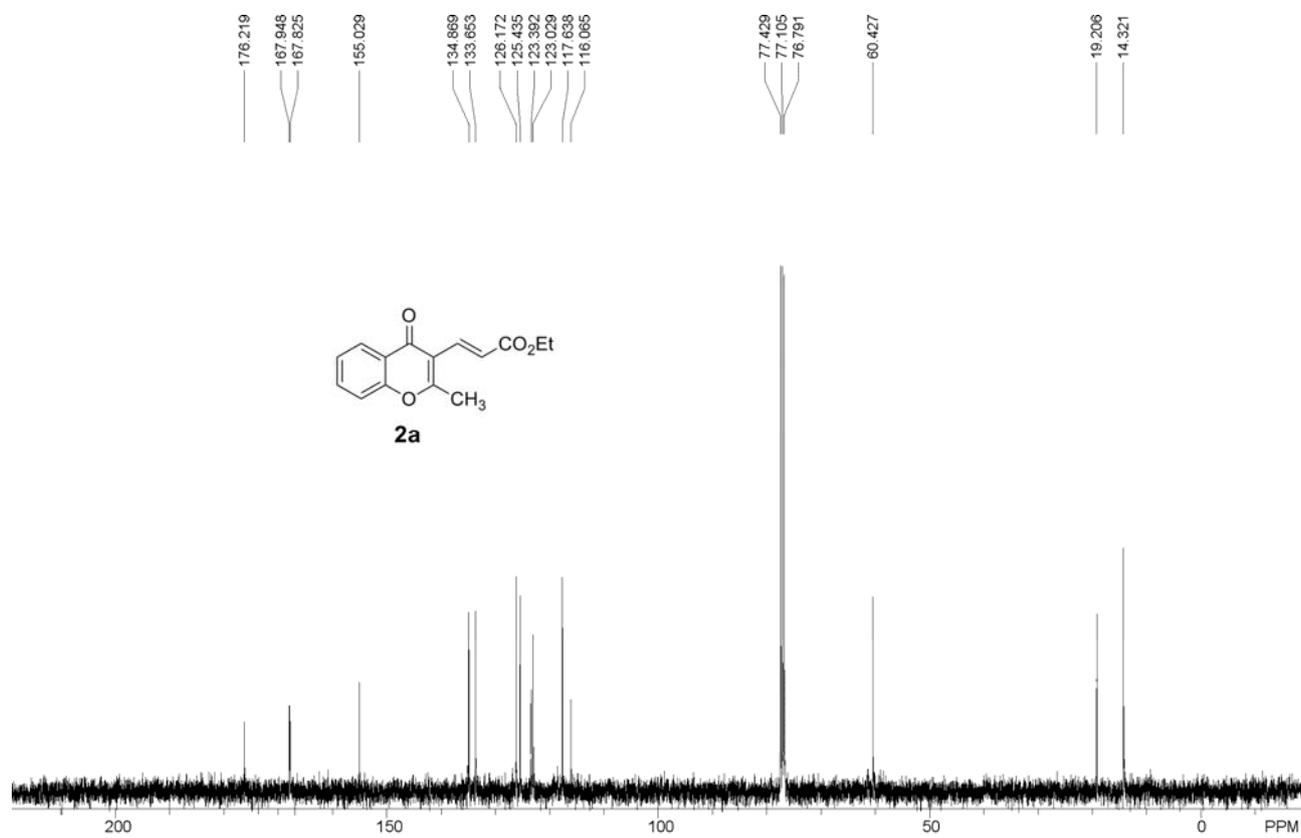
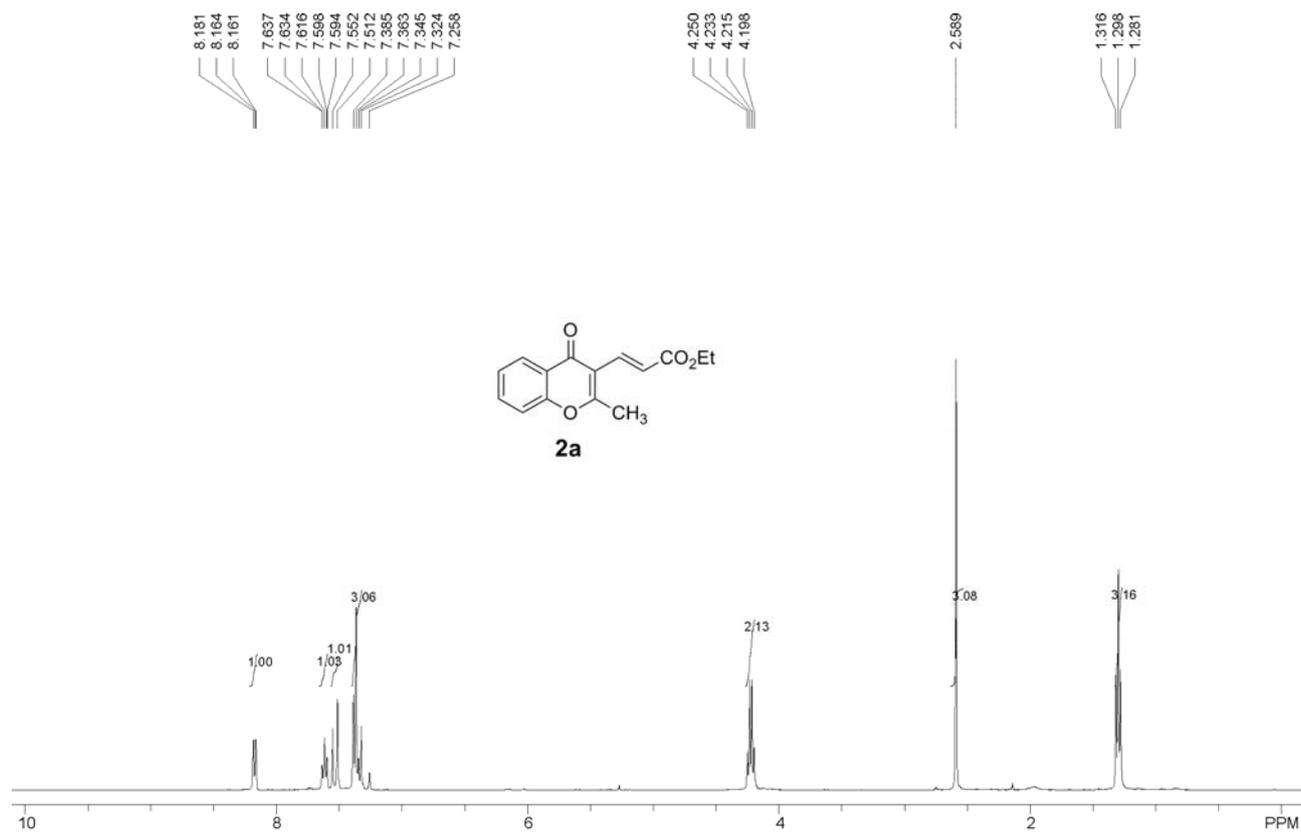


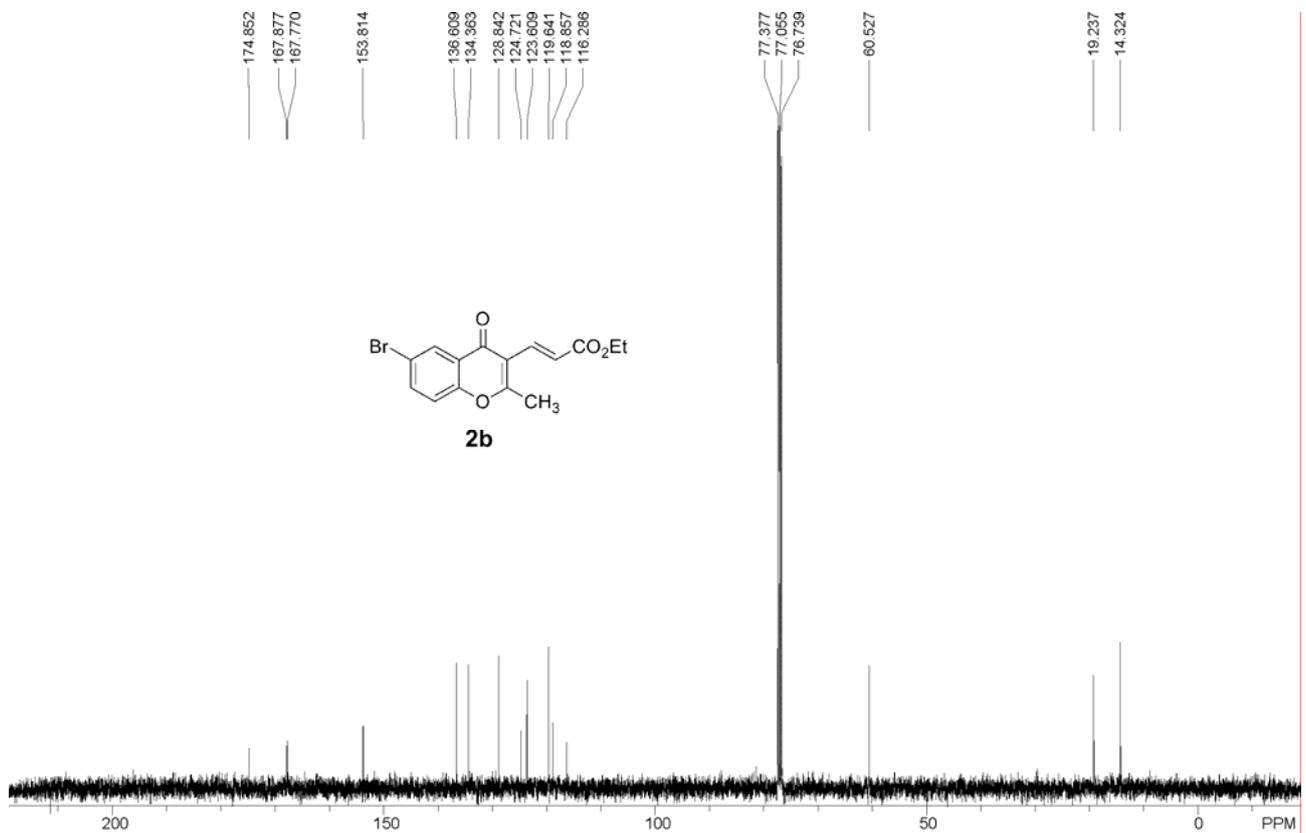
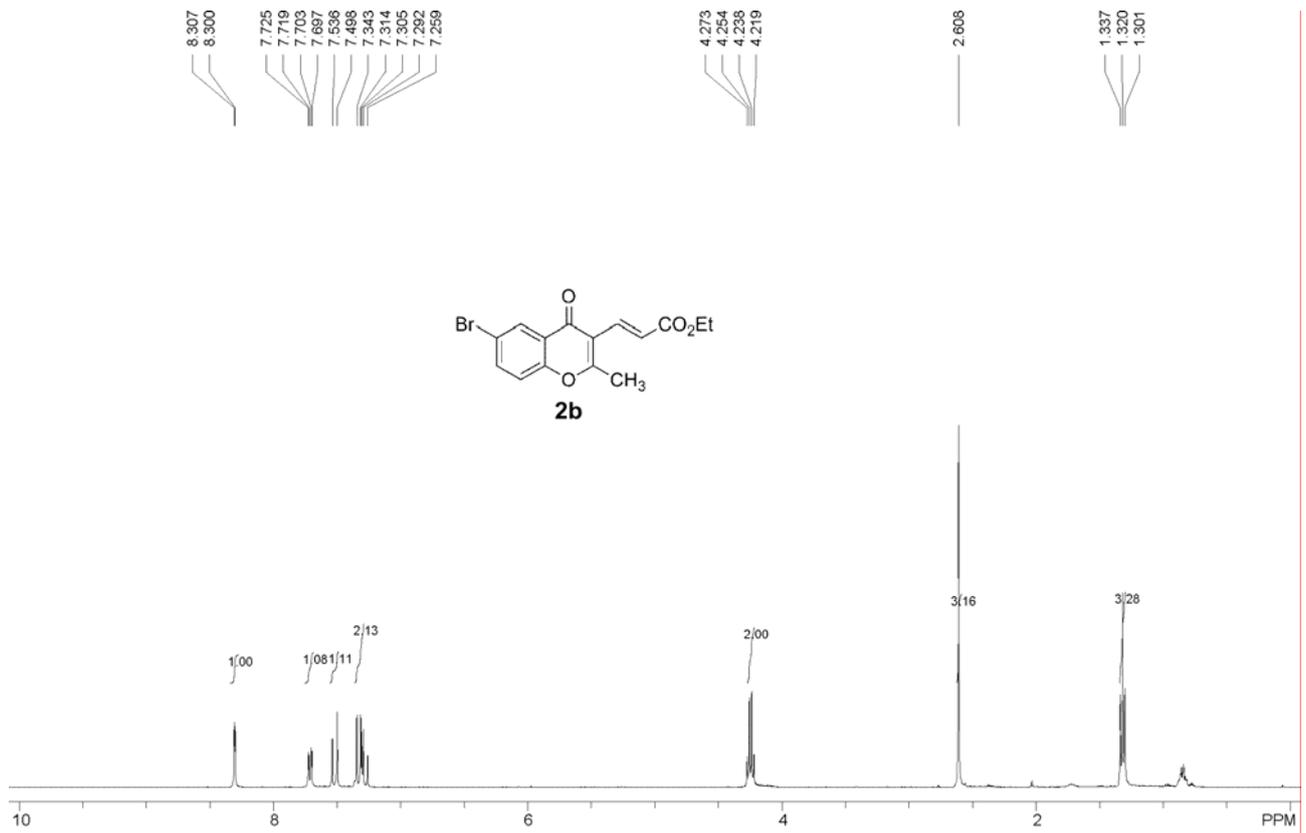


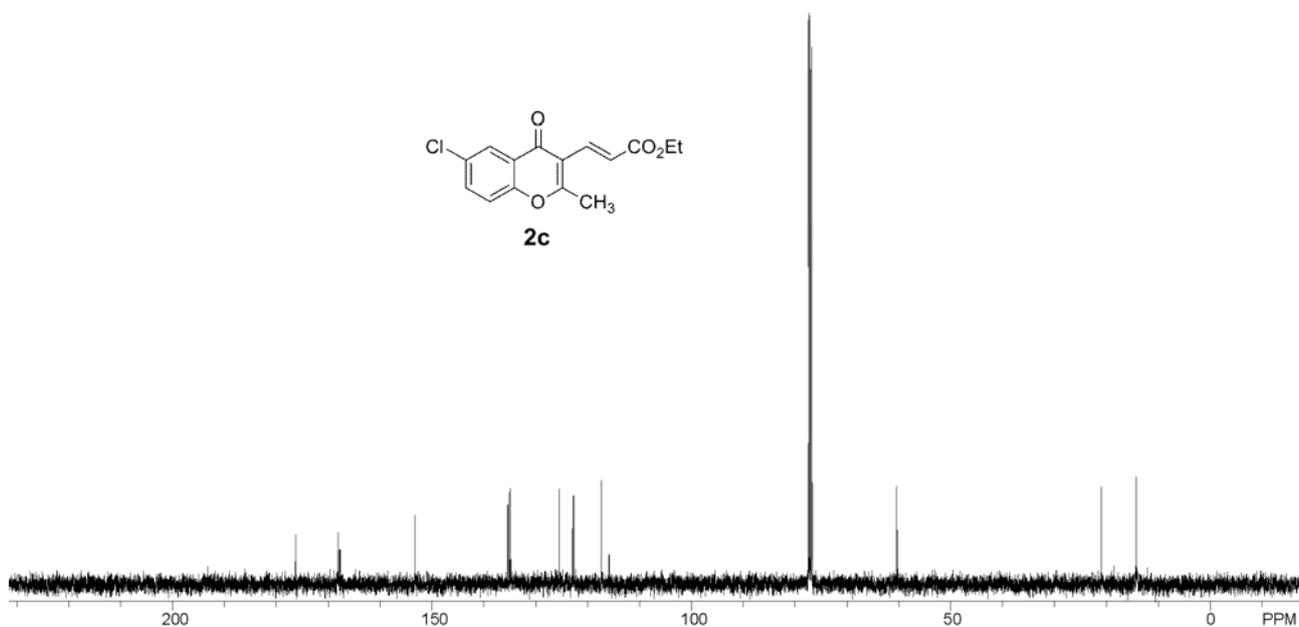
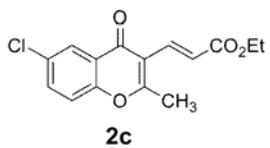
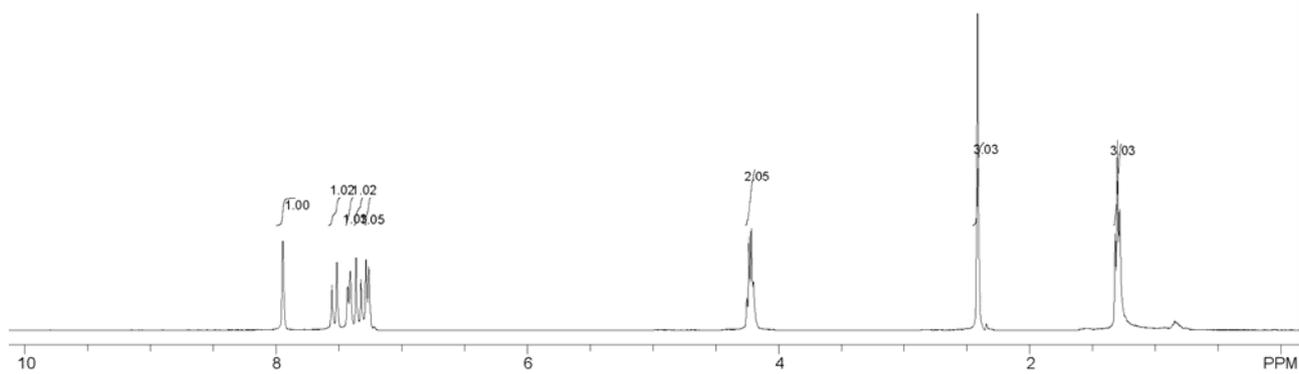
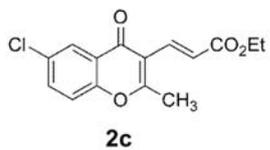
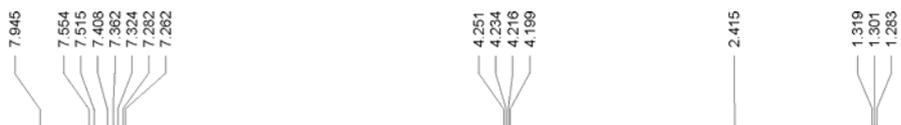


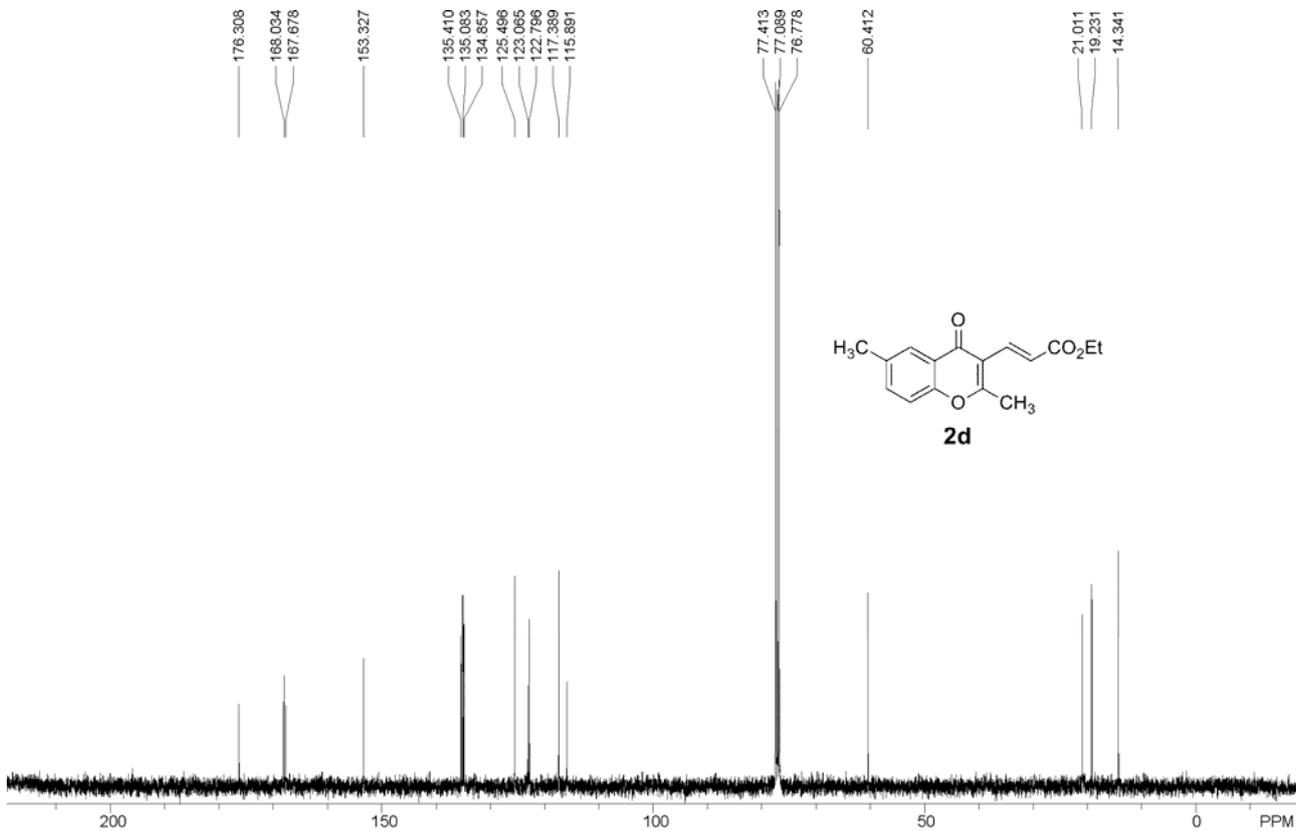
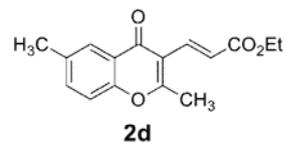
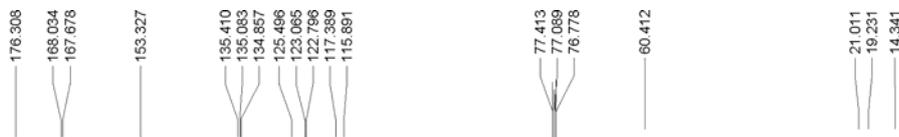
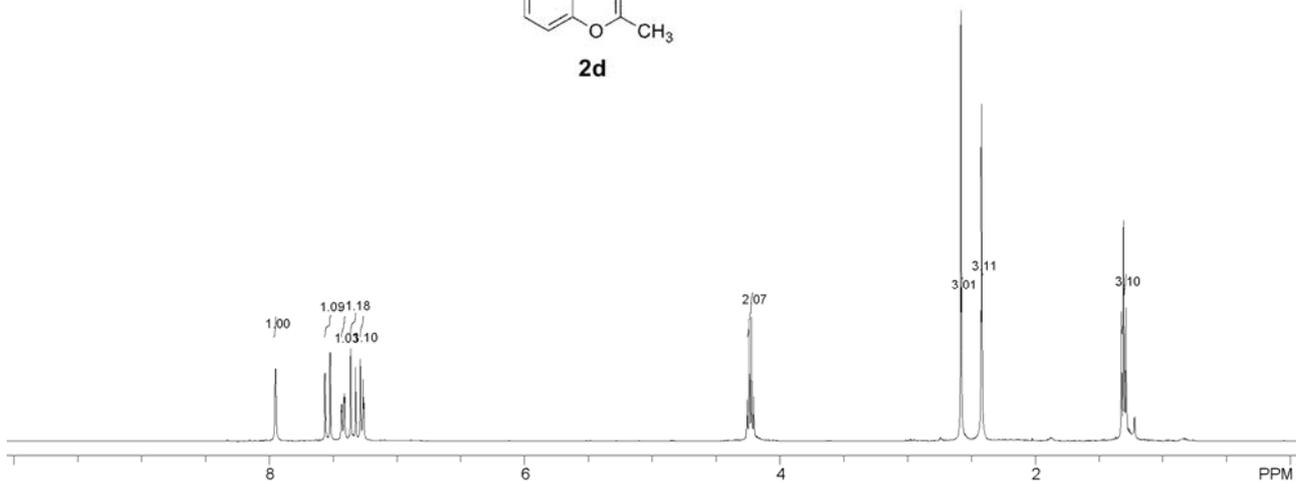
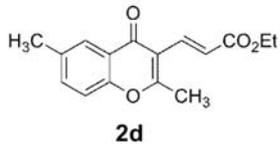
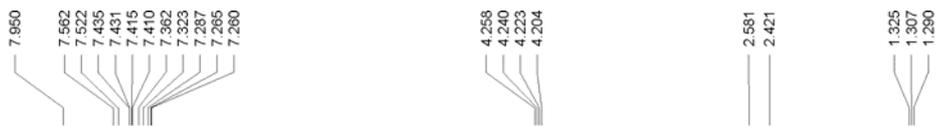


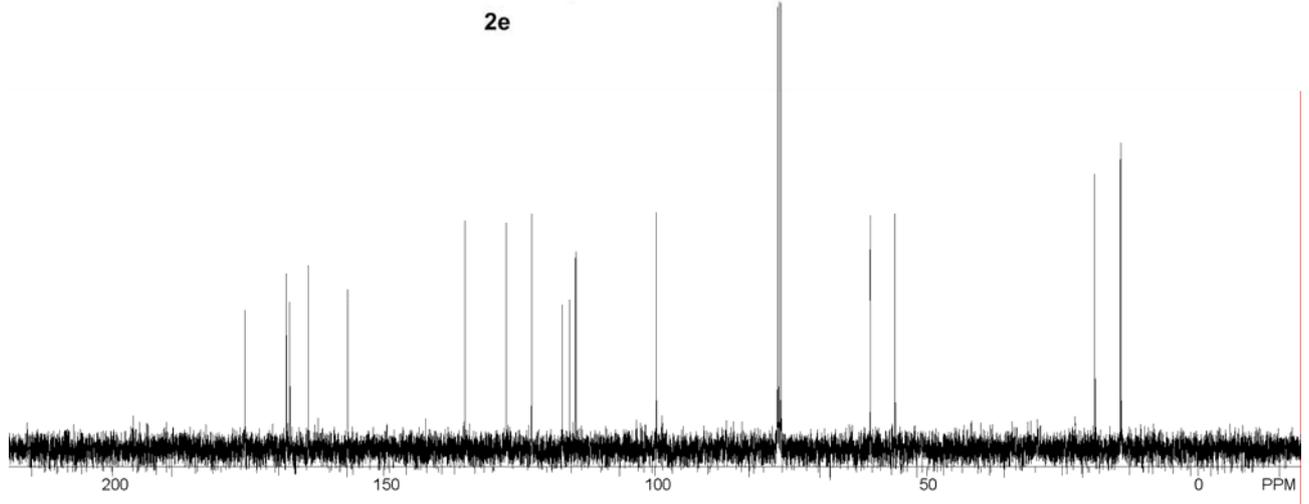
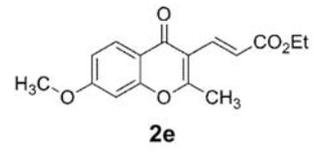
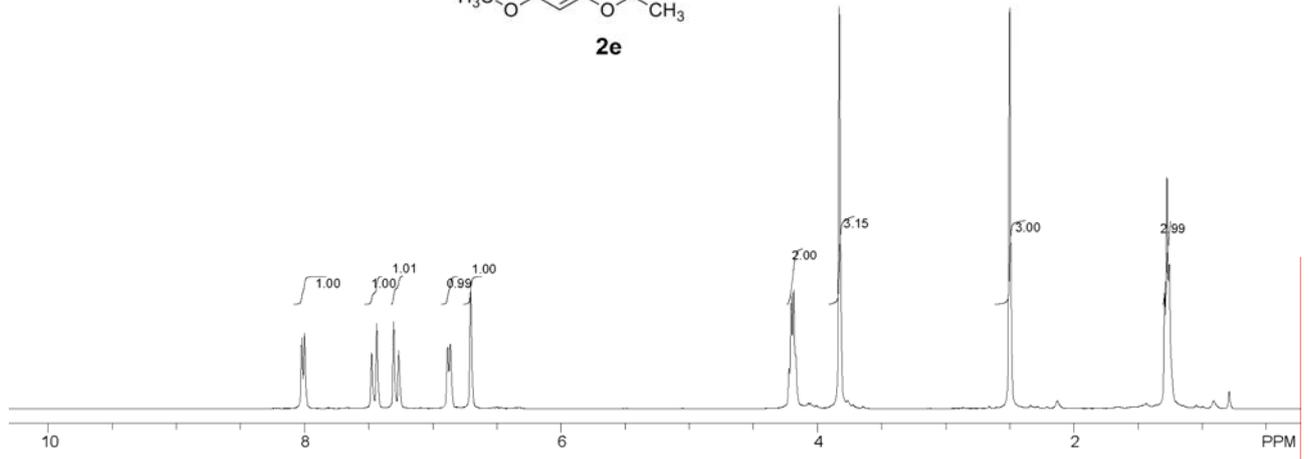
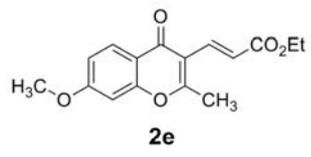
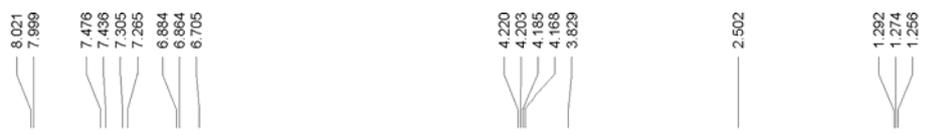
#### IV. Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of compounds 2a-2r

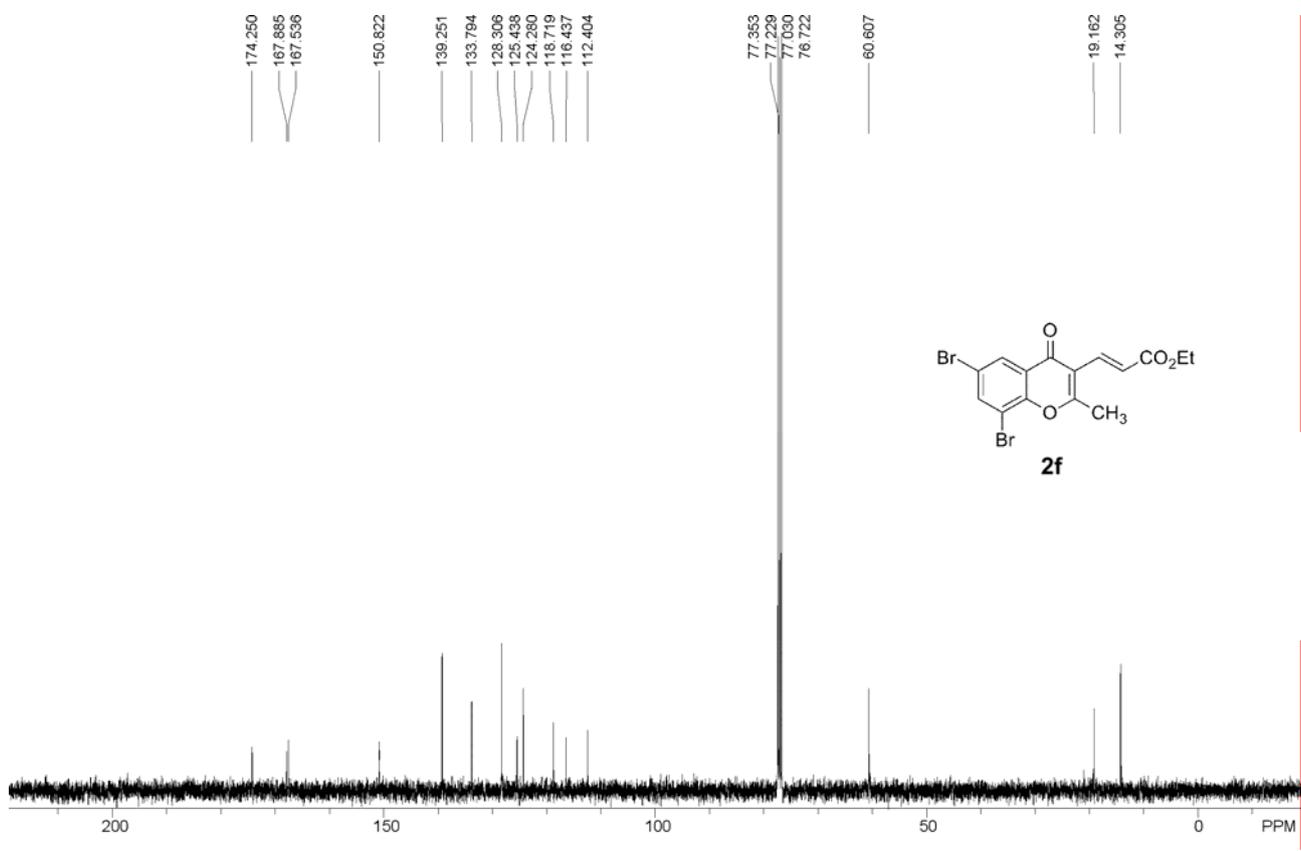
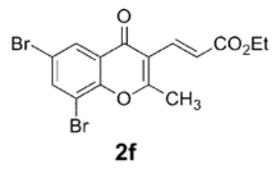
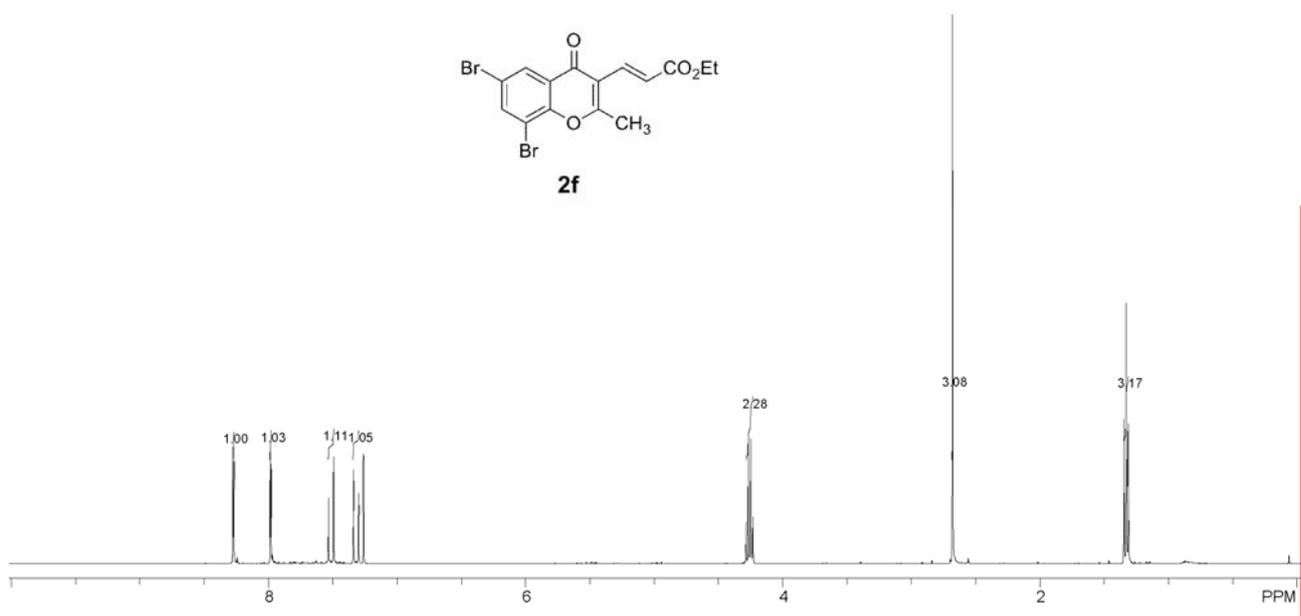
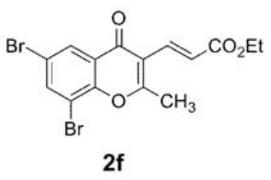
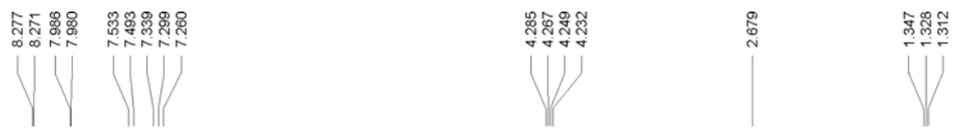










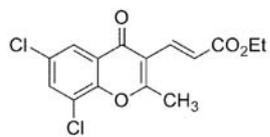


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7.685  
7.679  
7.535  
7.495  
7.339  
7.300  
7.258

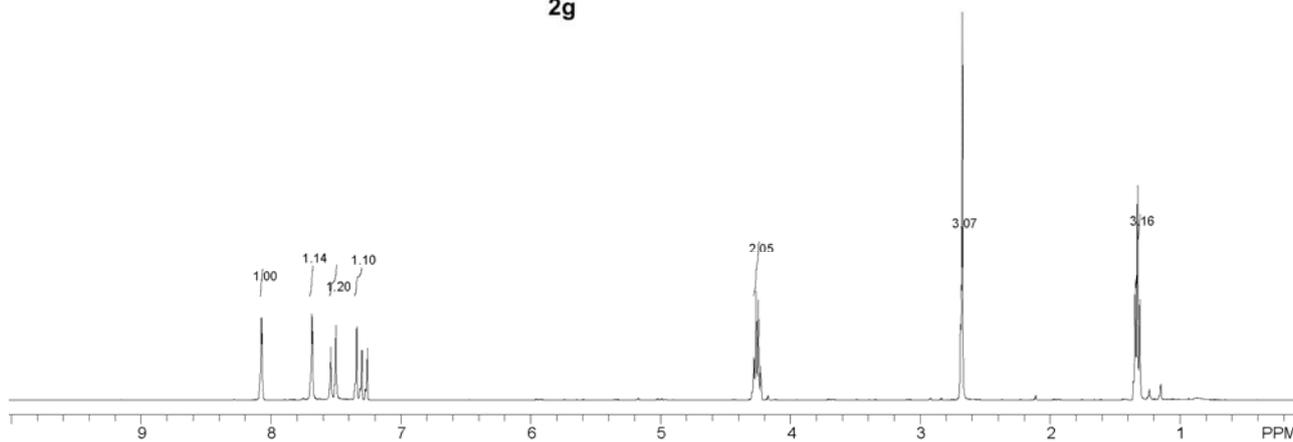
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4.284  
4.245  
4.229

2.675

1.343  
1.326  
1.308



**2g**



174.407  
167.762  
167.535

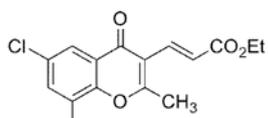
149.460

133.805  
133.688  
131.085  
125.173  
124.375  
124.293  
123.873  
116.447

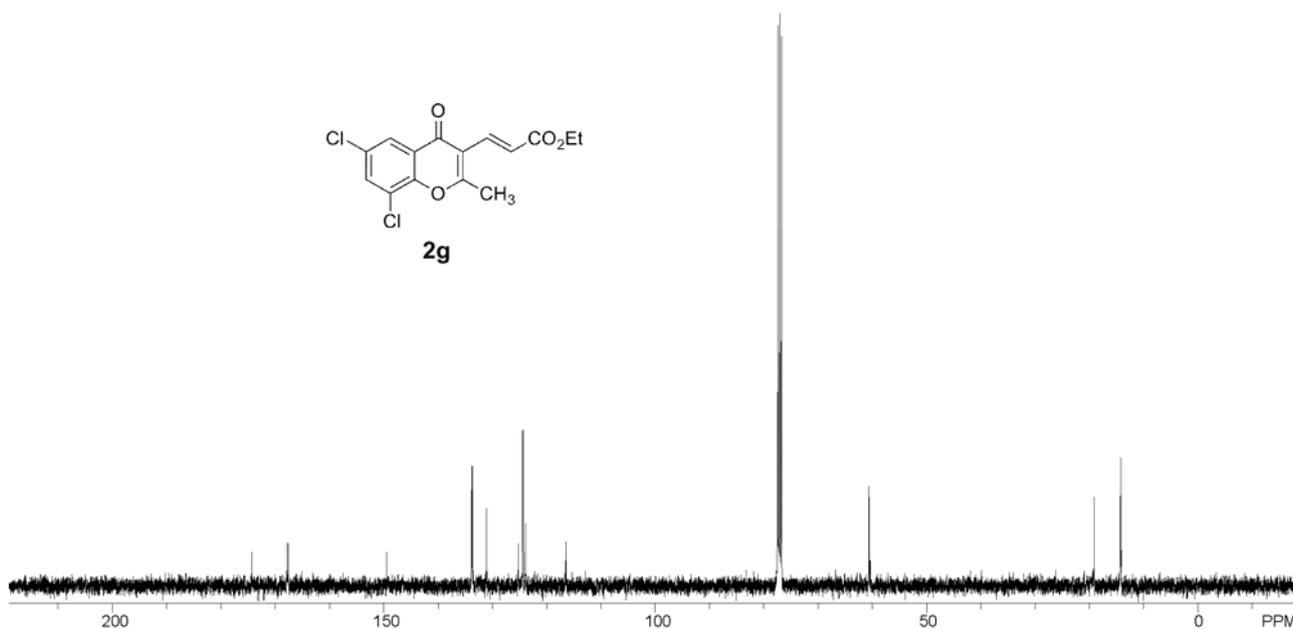
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77.034  
76.710

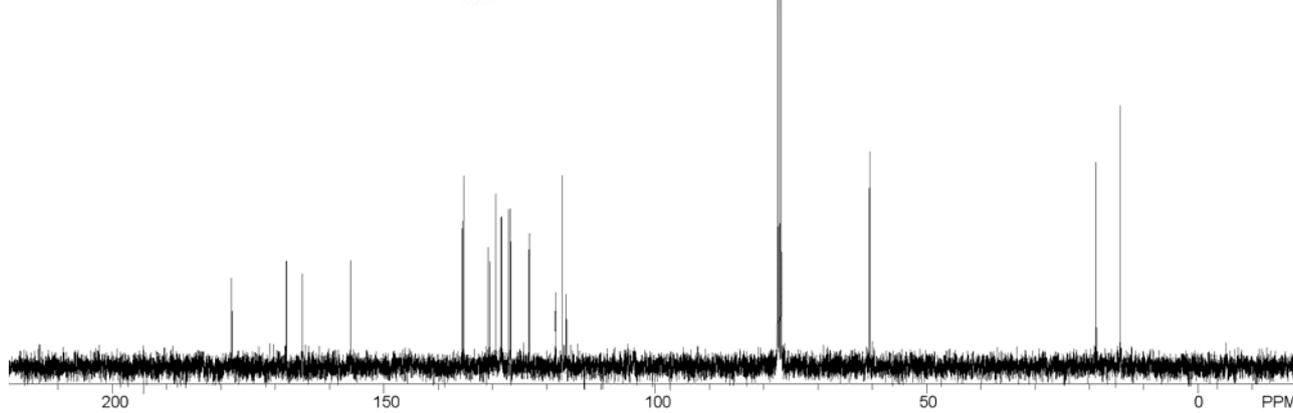
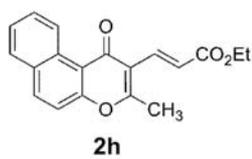
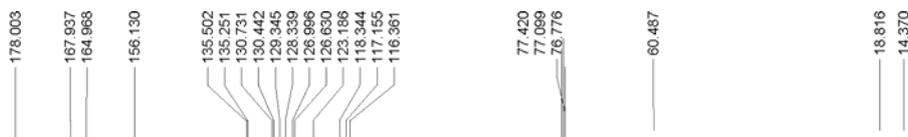
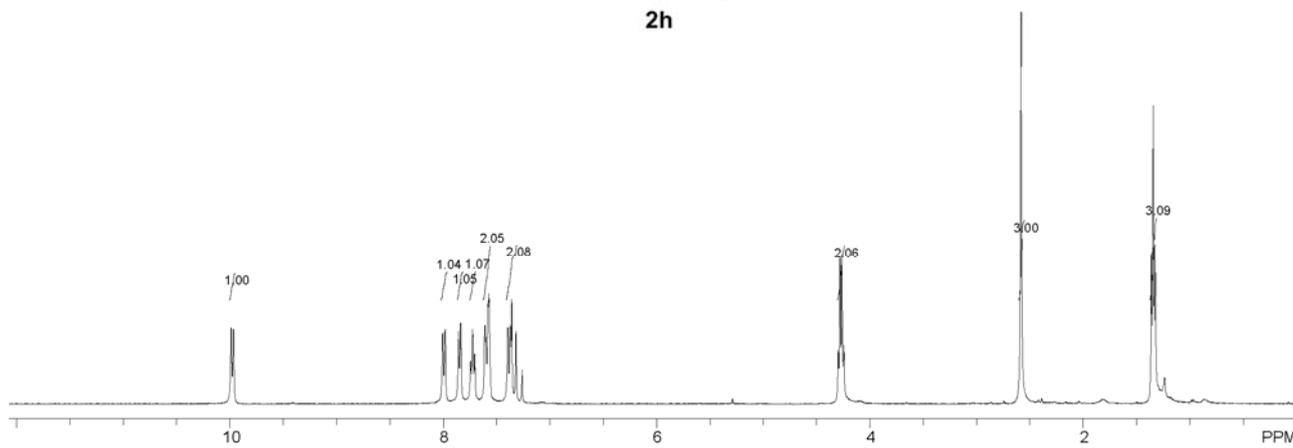
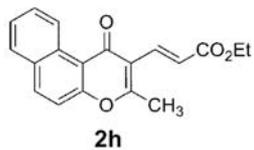
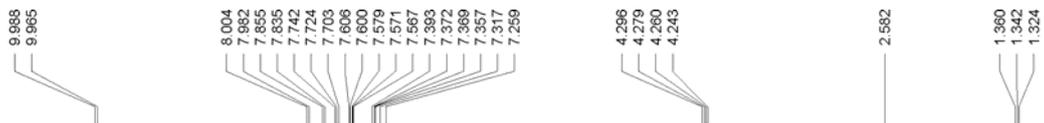
60.606

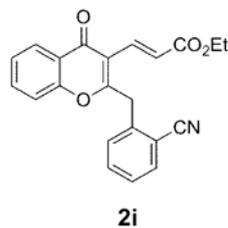
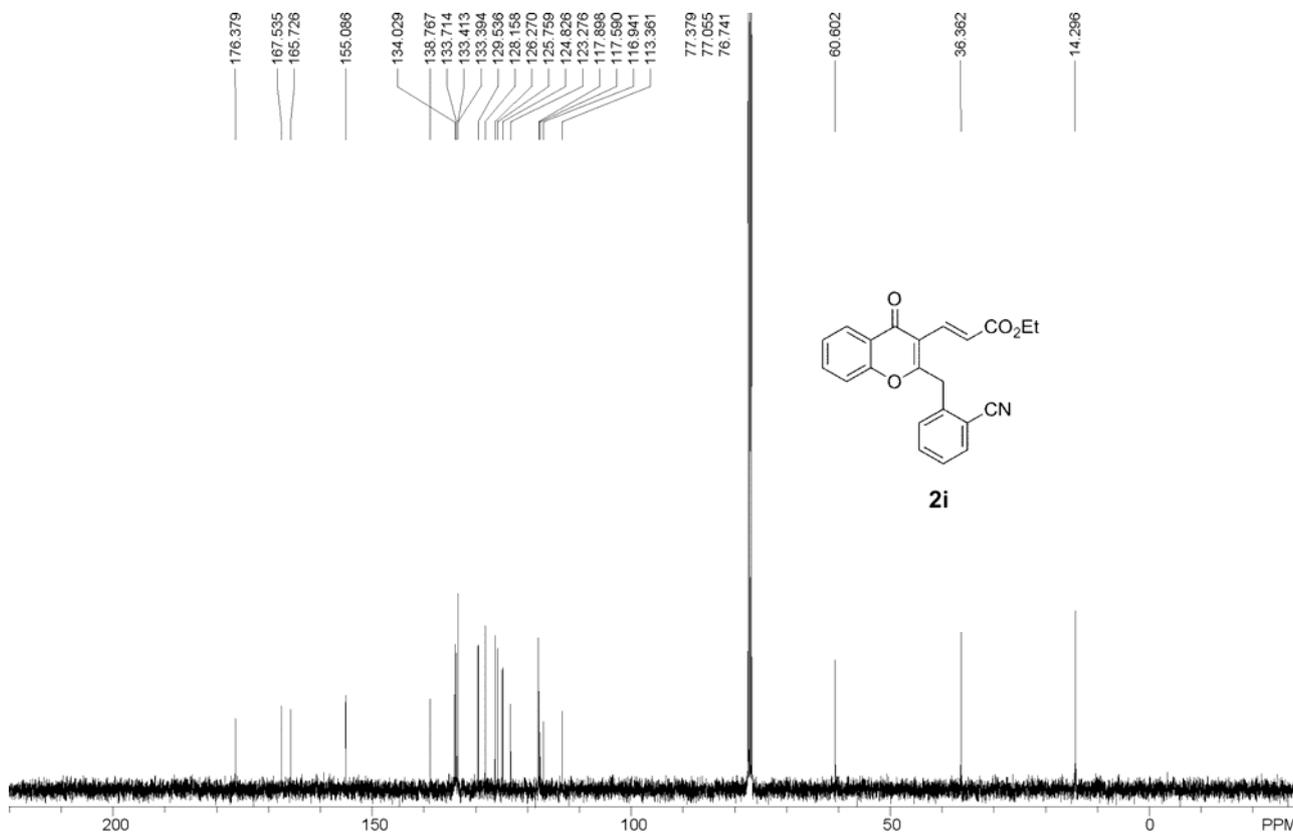
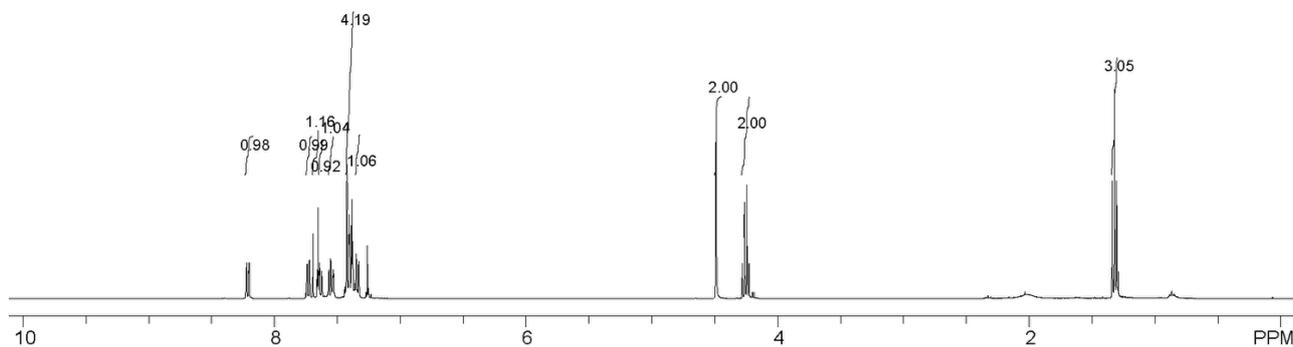
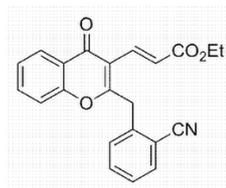
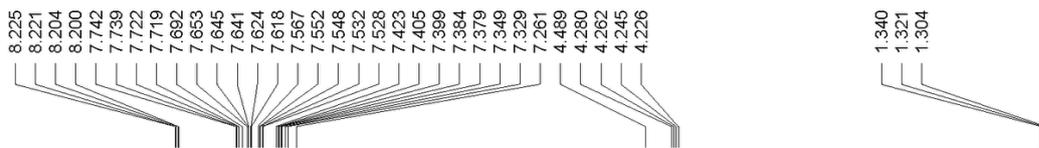
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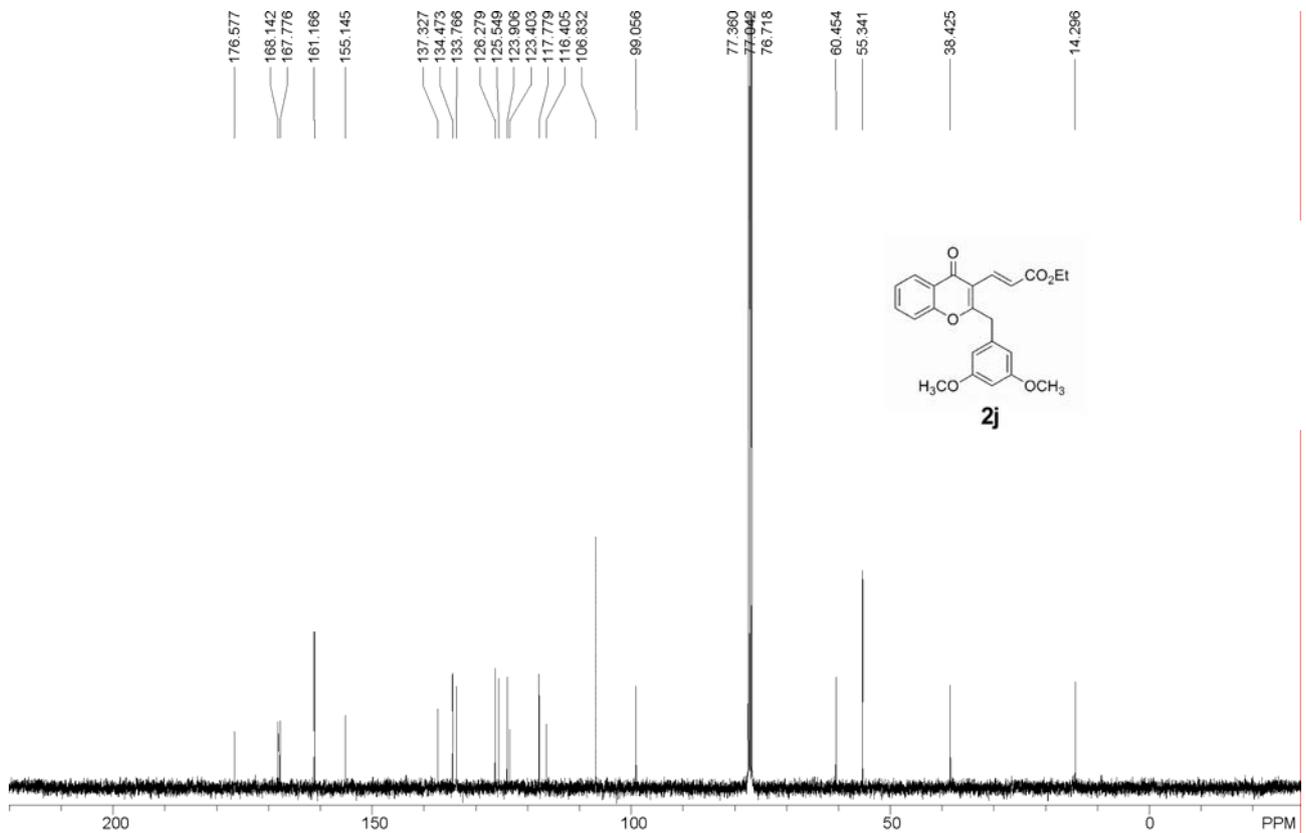
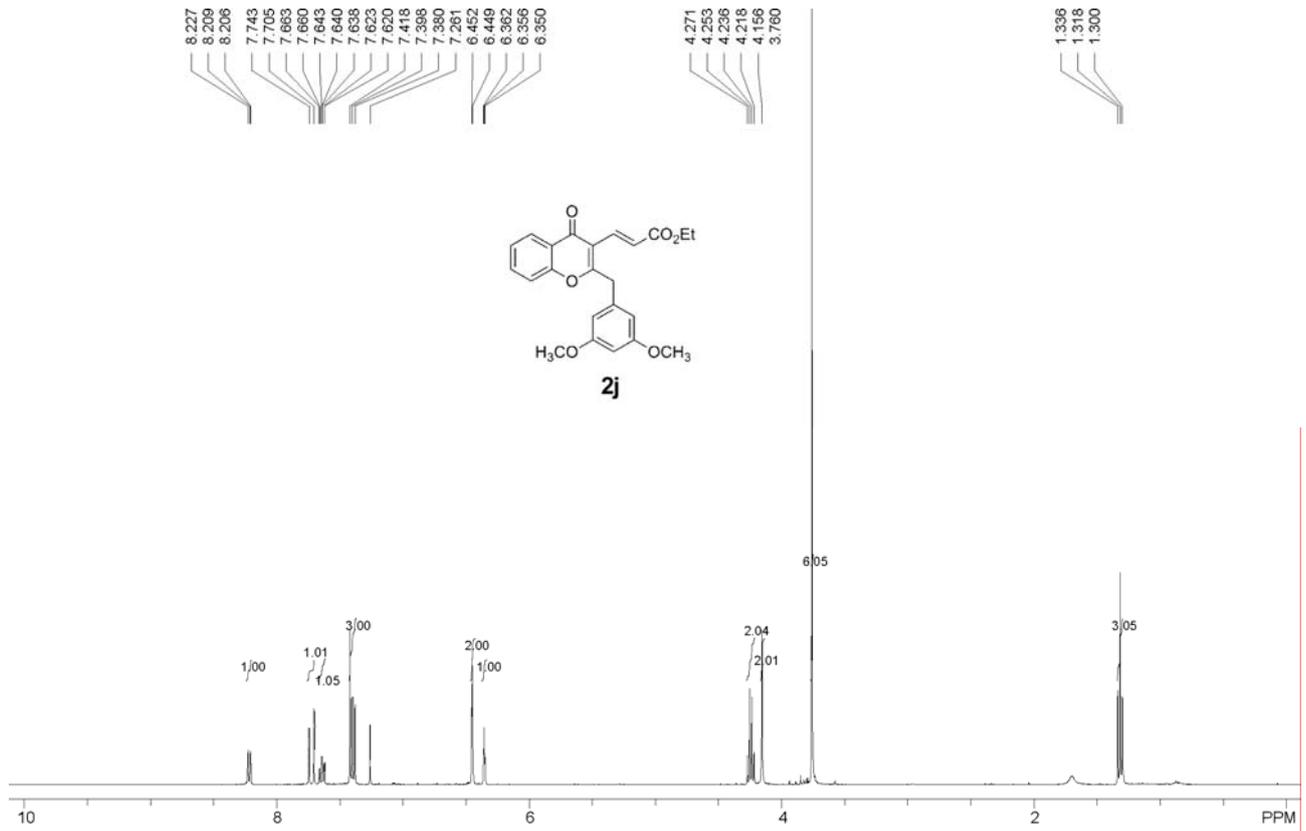


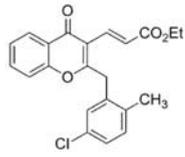
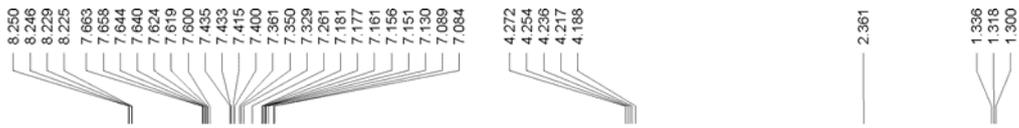
**2g**



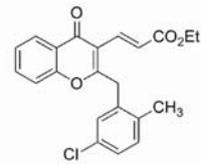
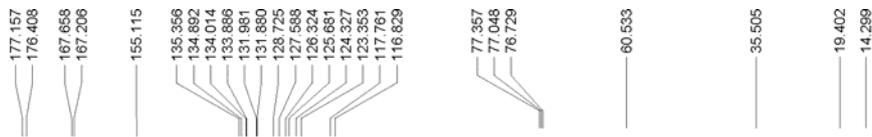
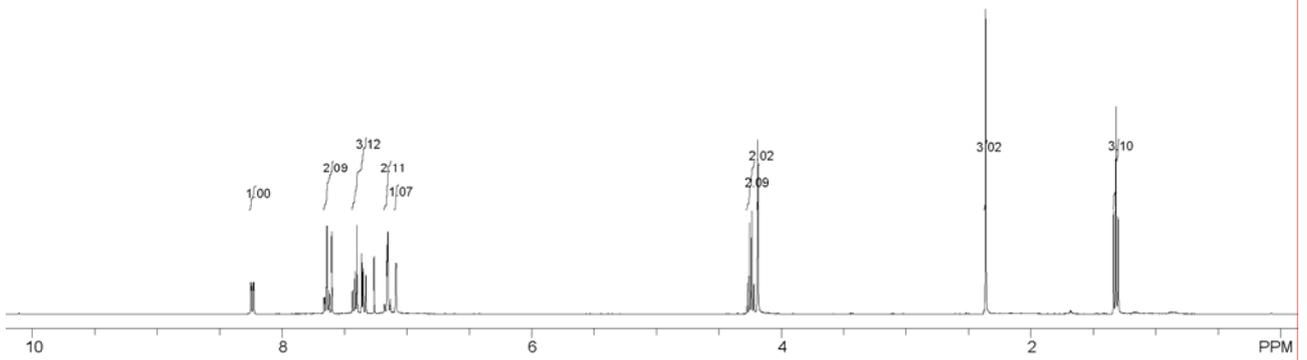




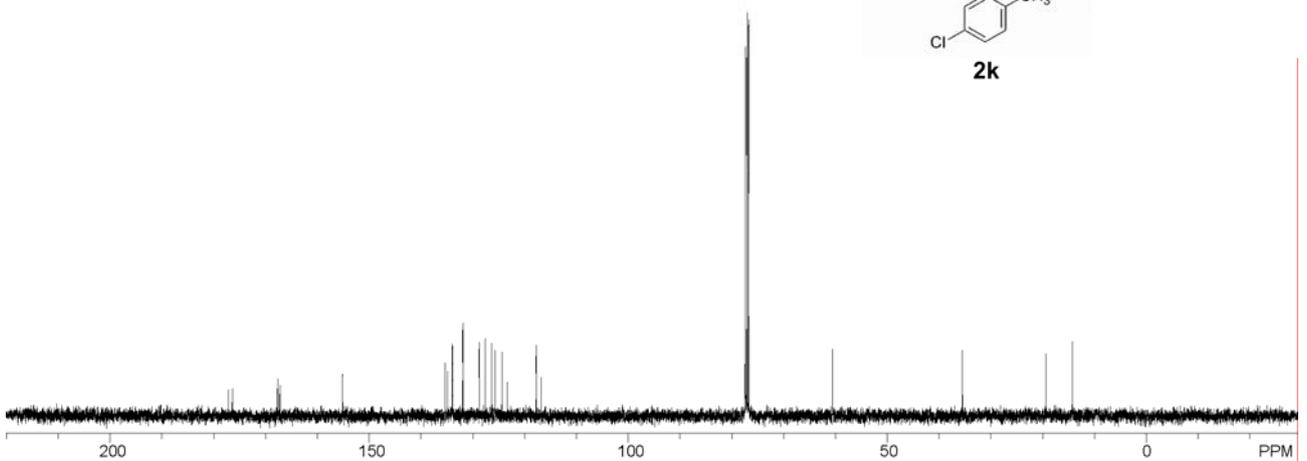


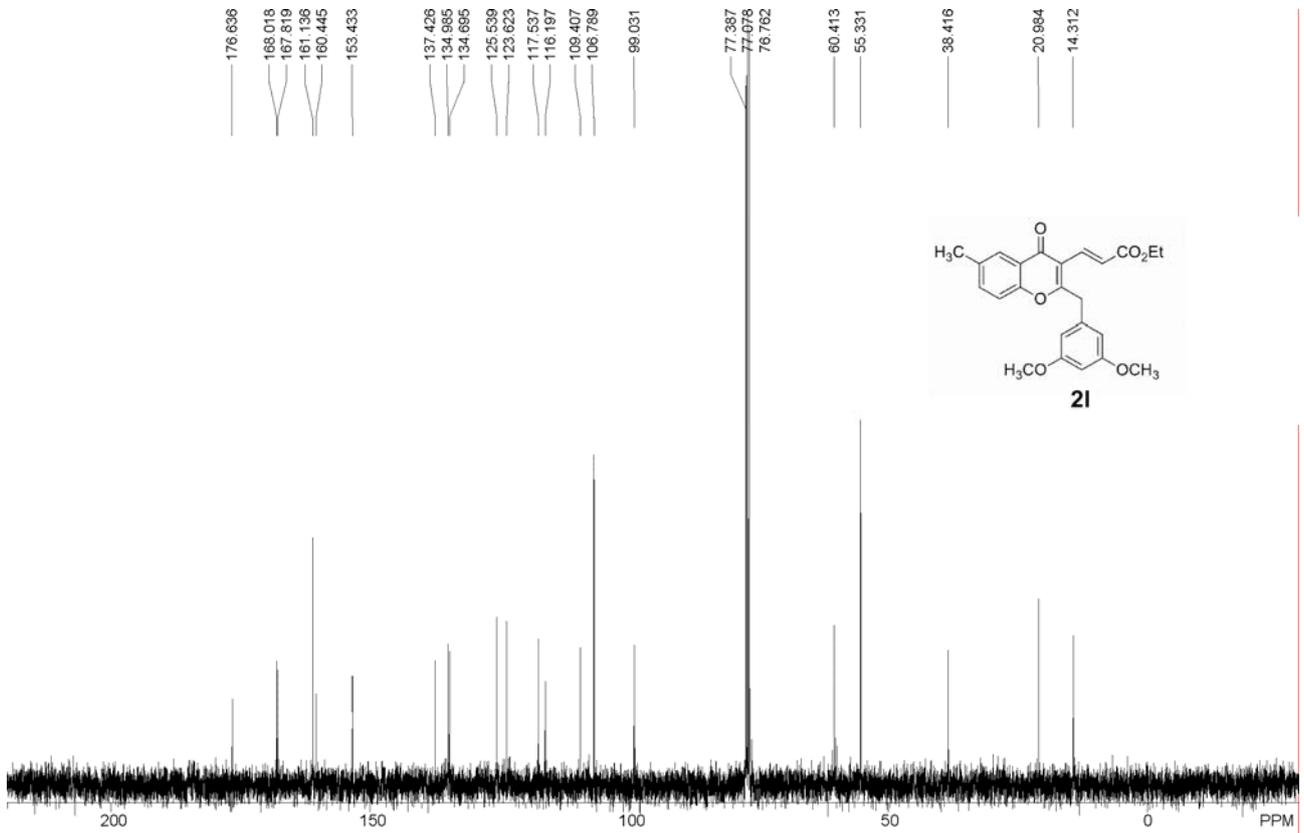
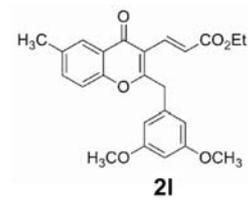
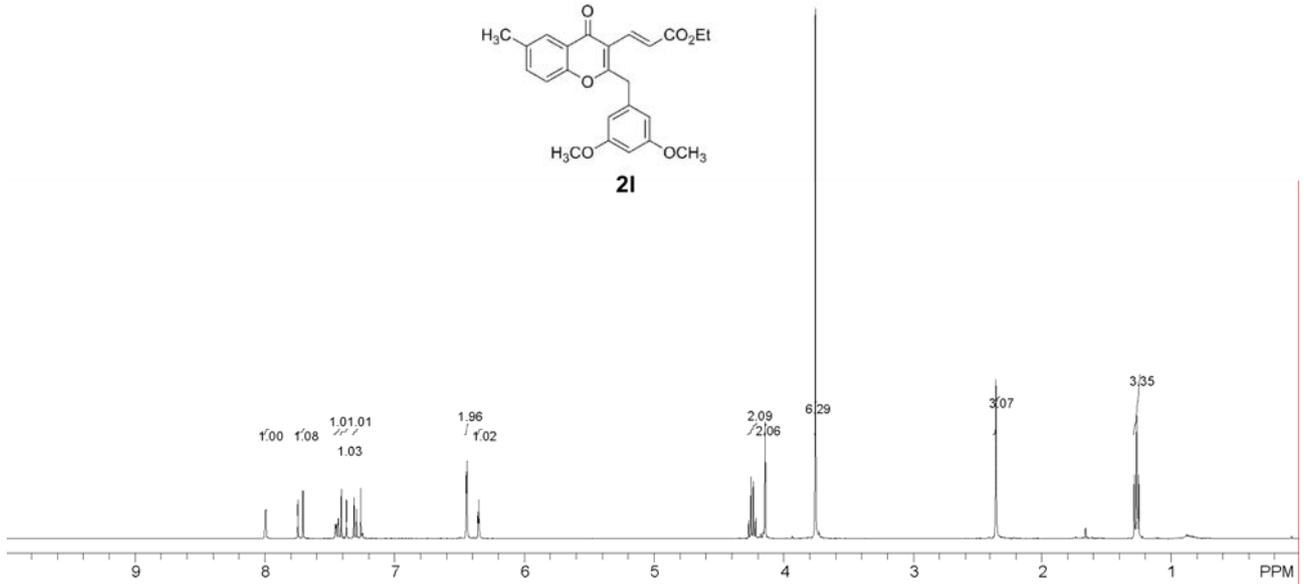
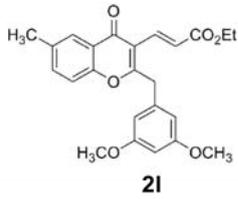
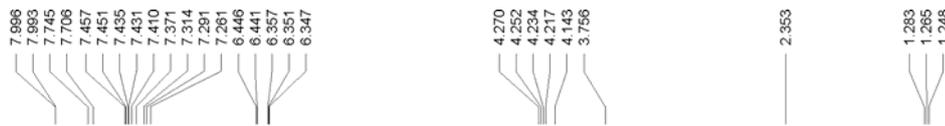


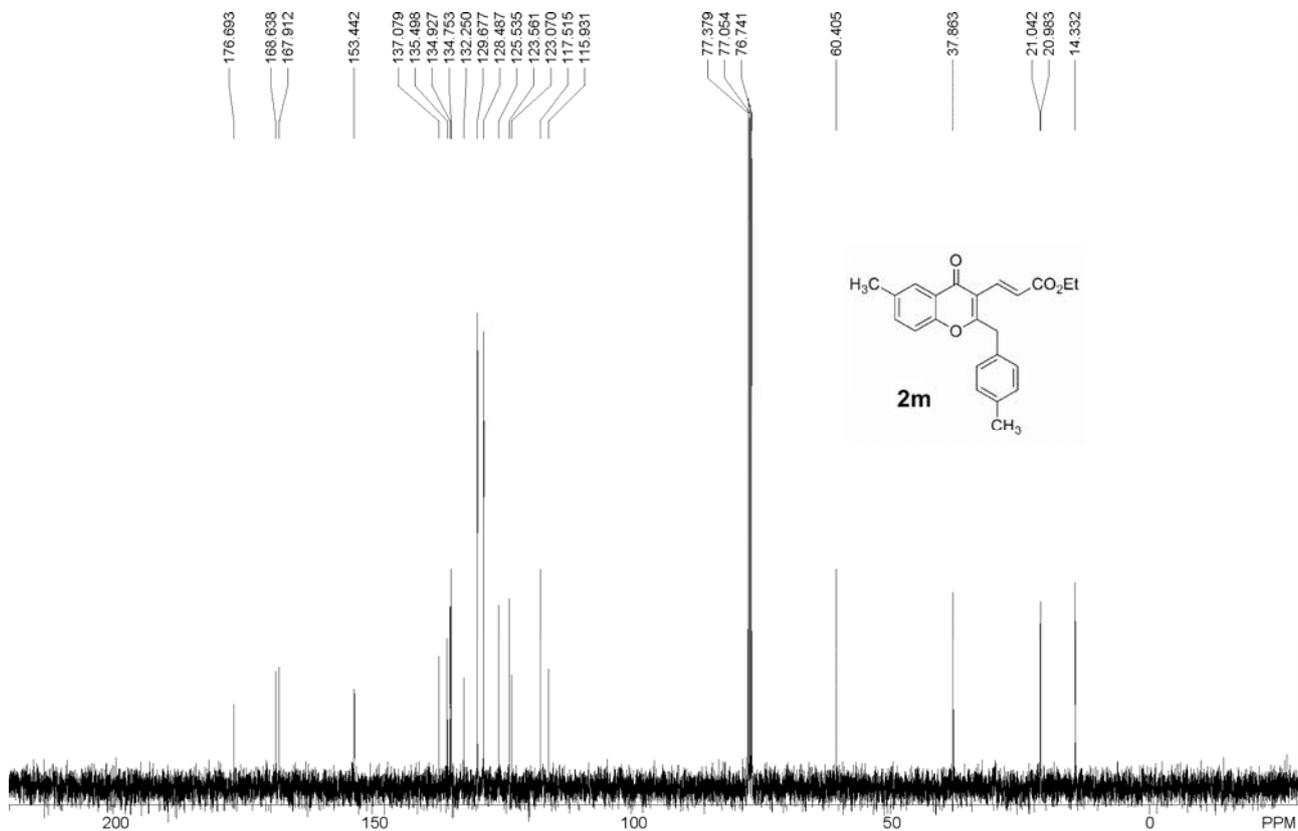
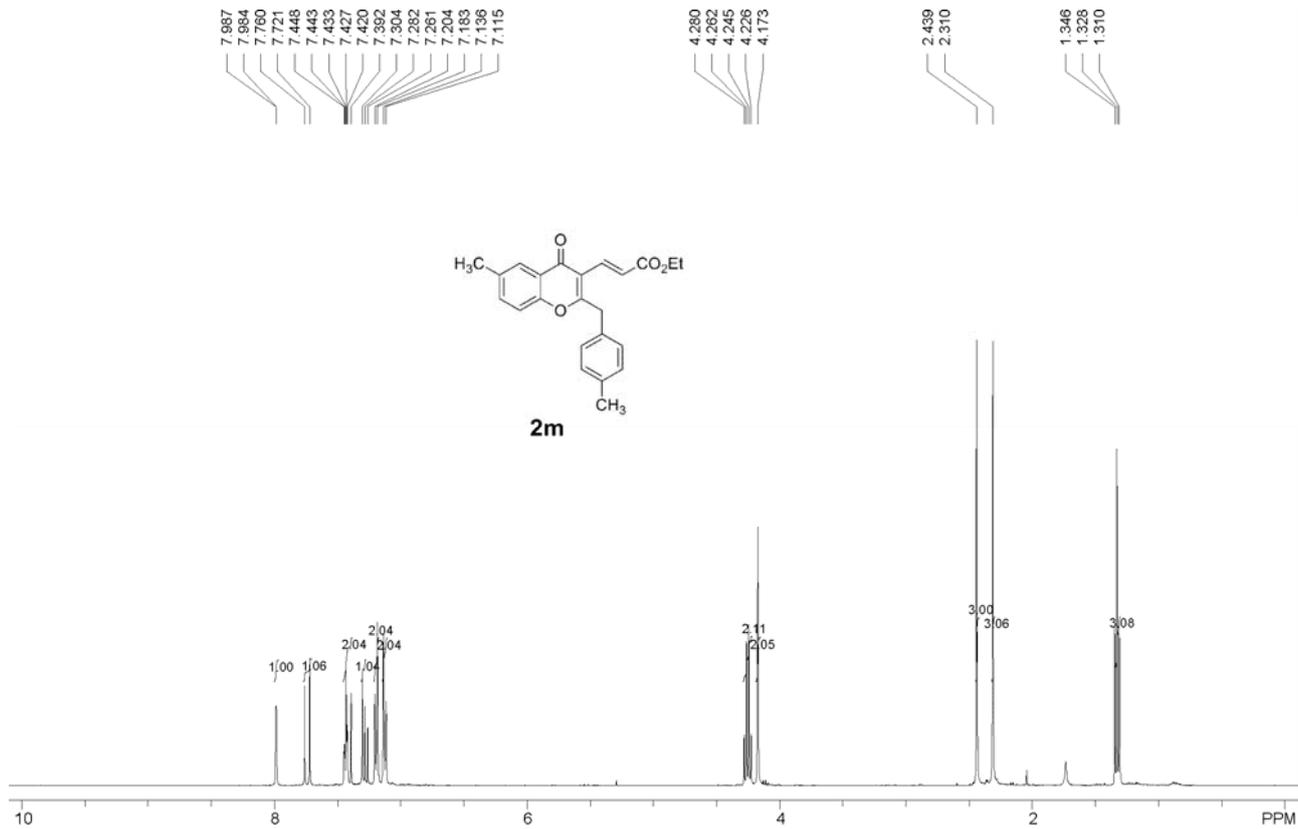
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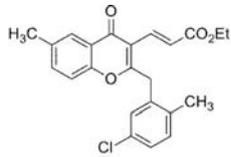
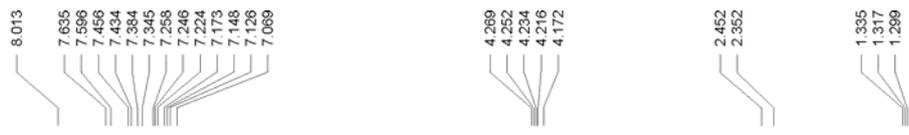


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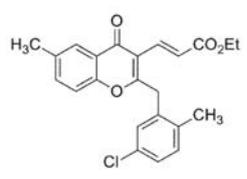
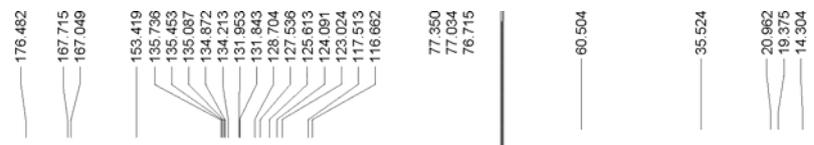
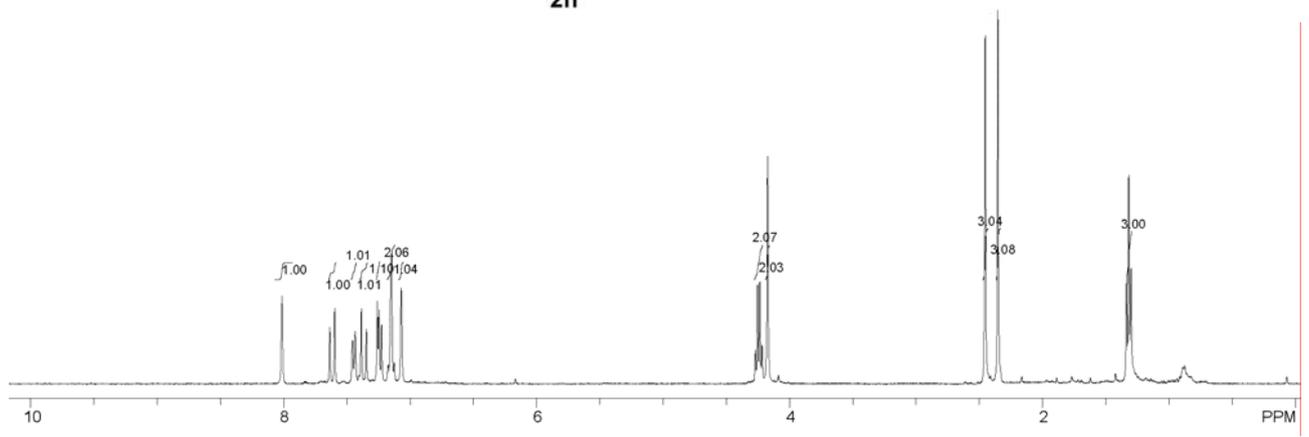




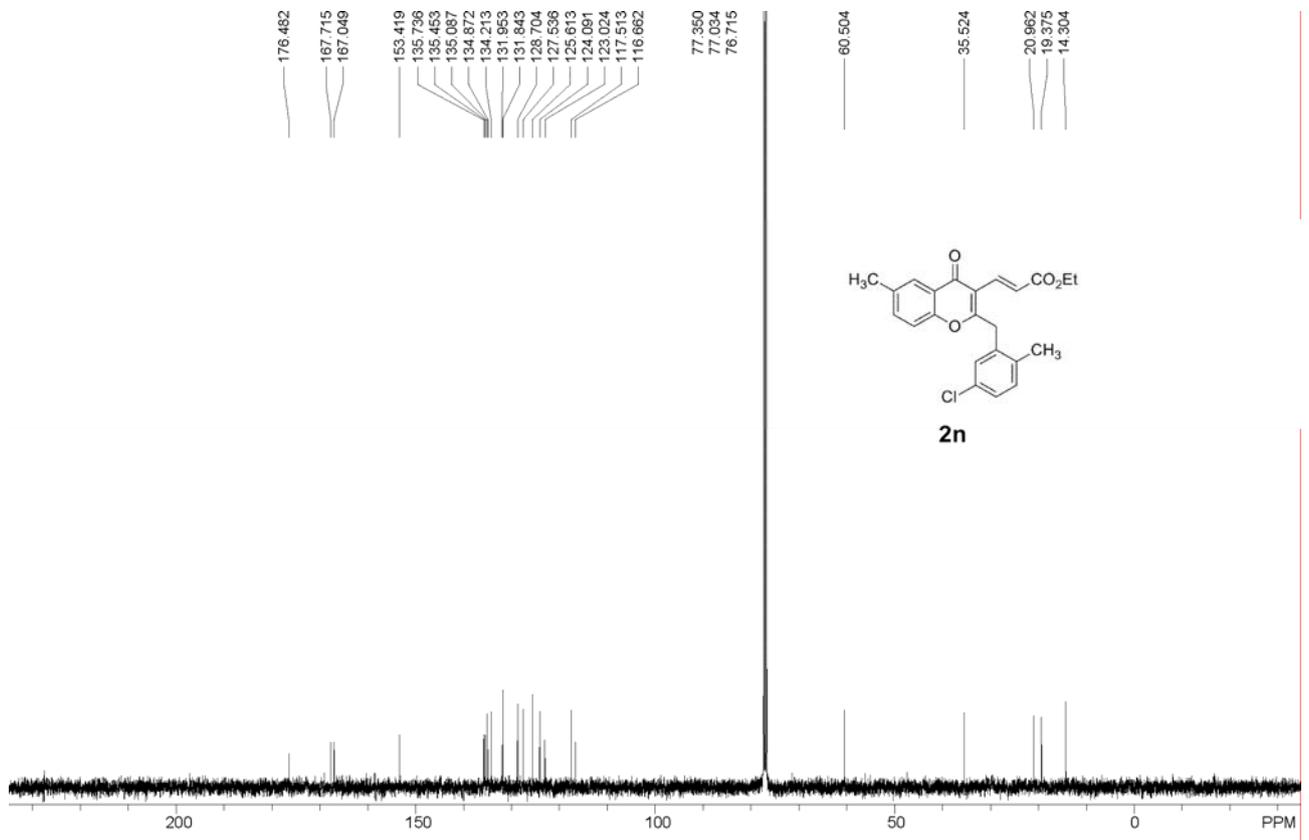


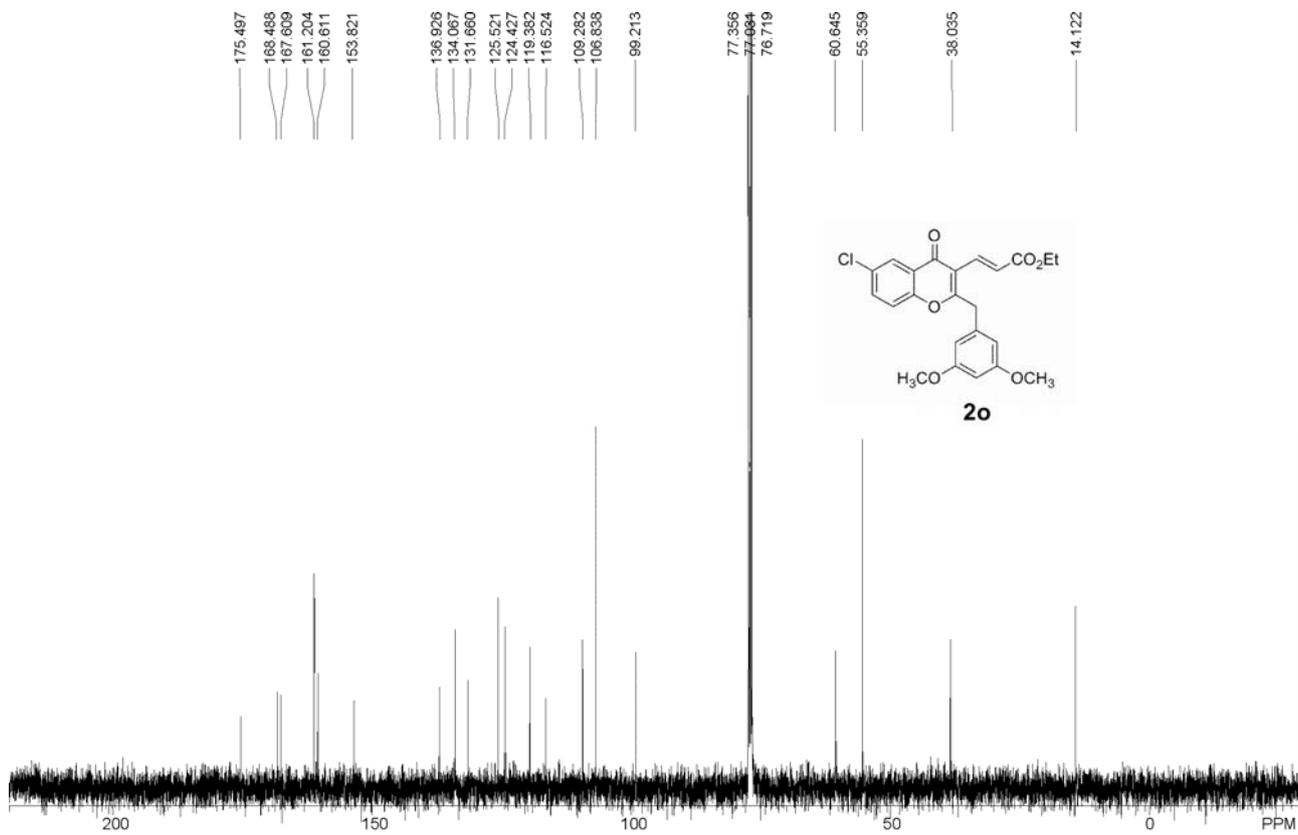
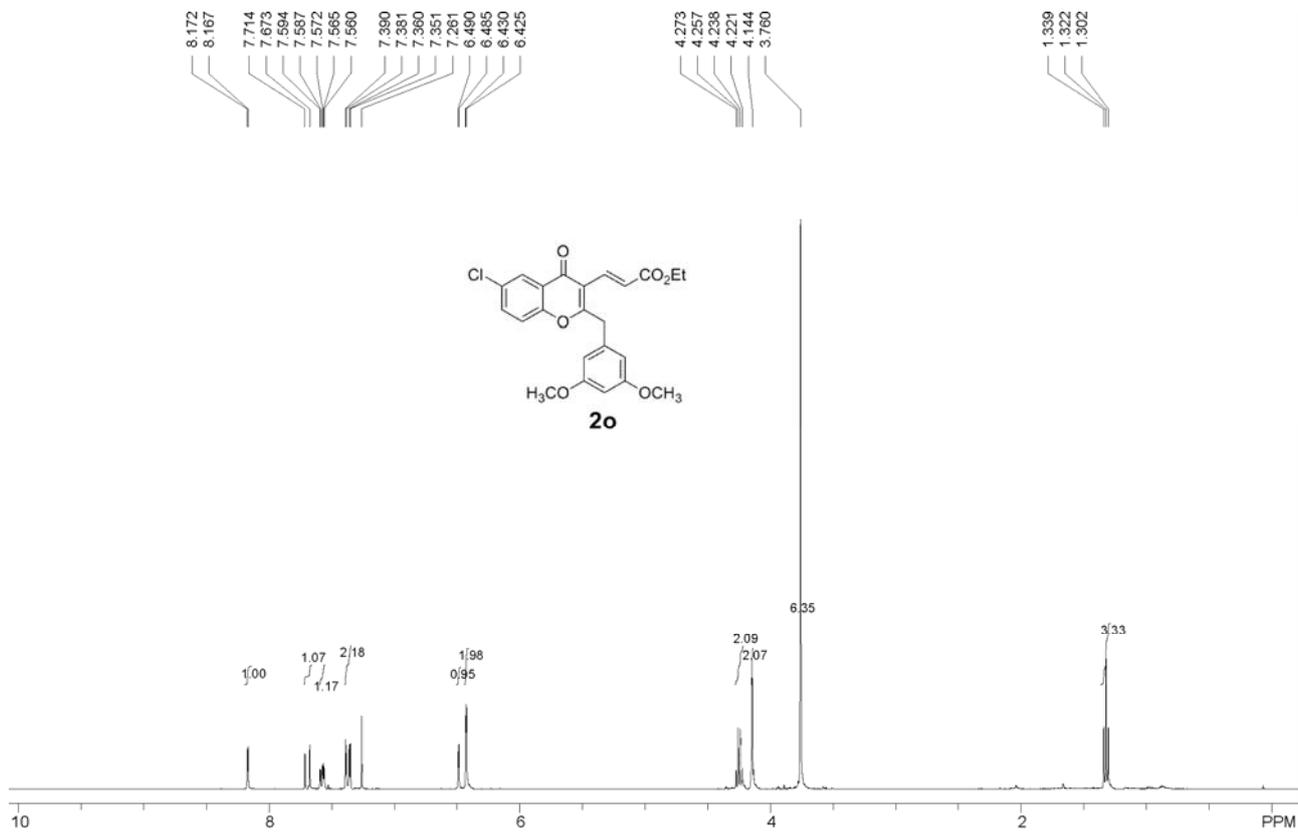


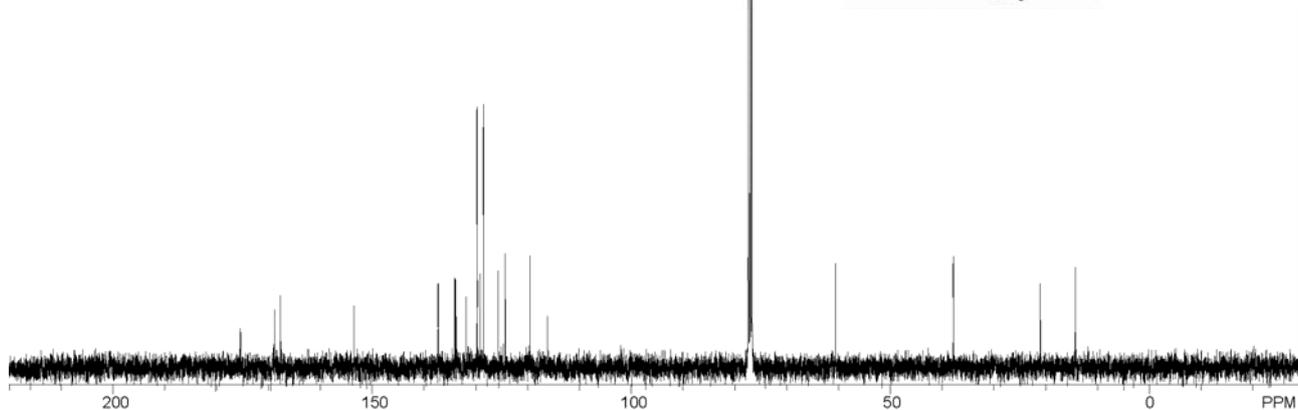
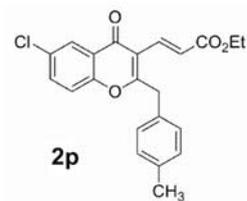
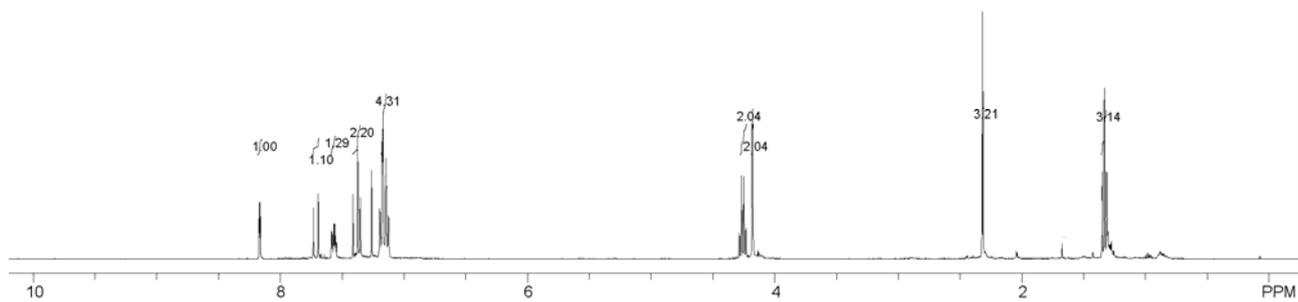
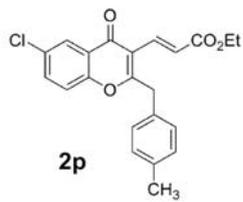
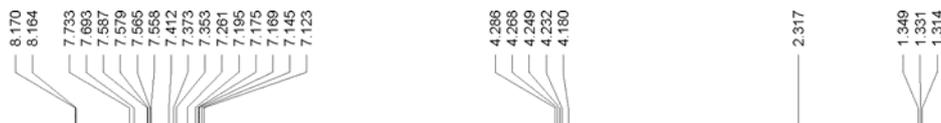
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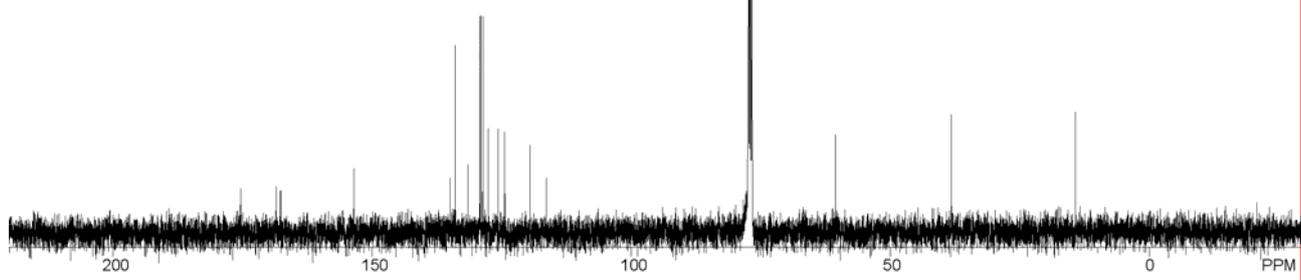
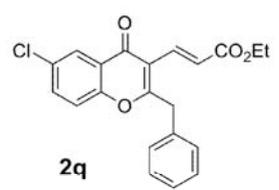
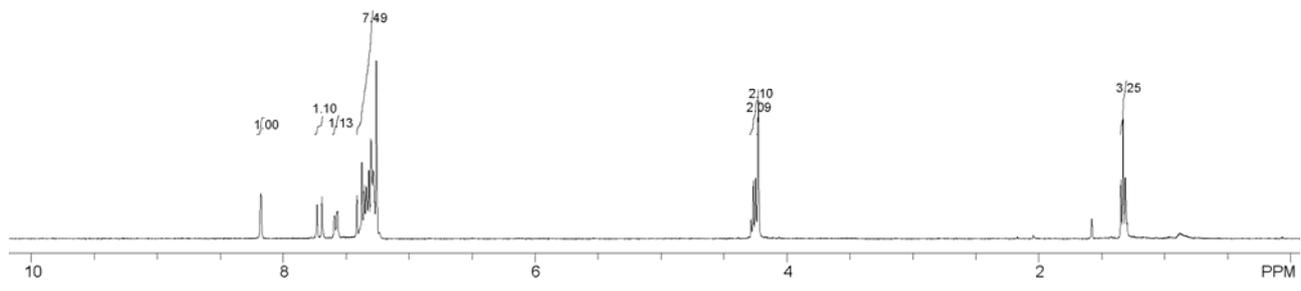
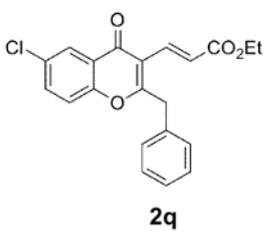
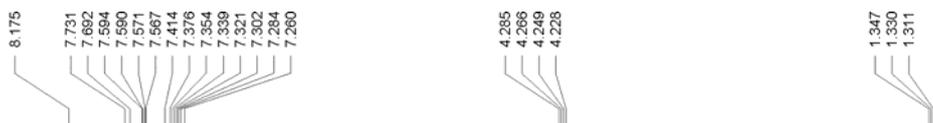


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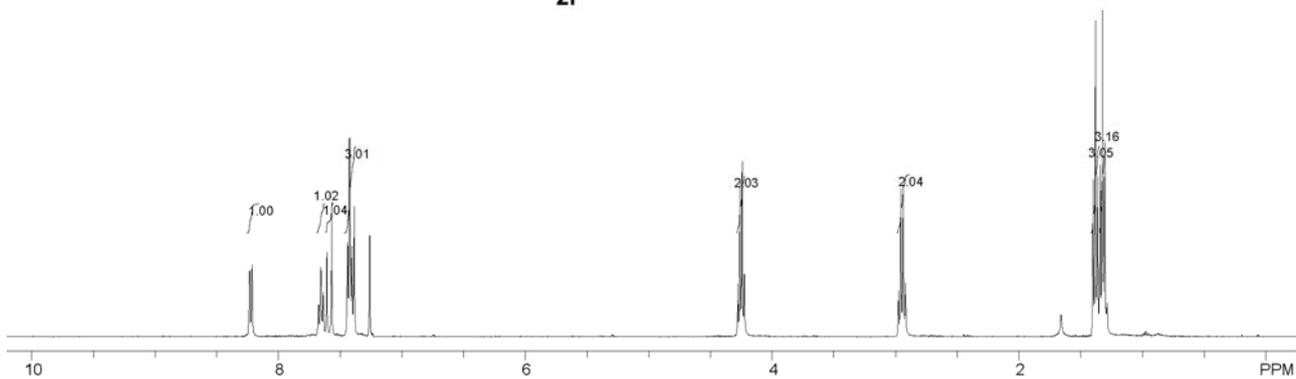
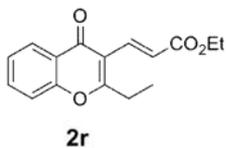


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155.164

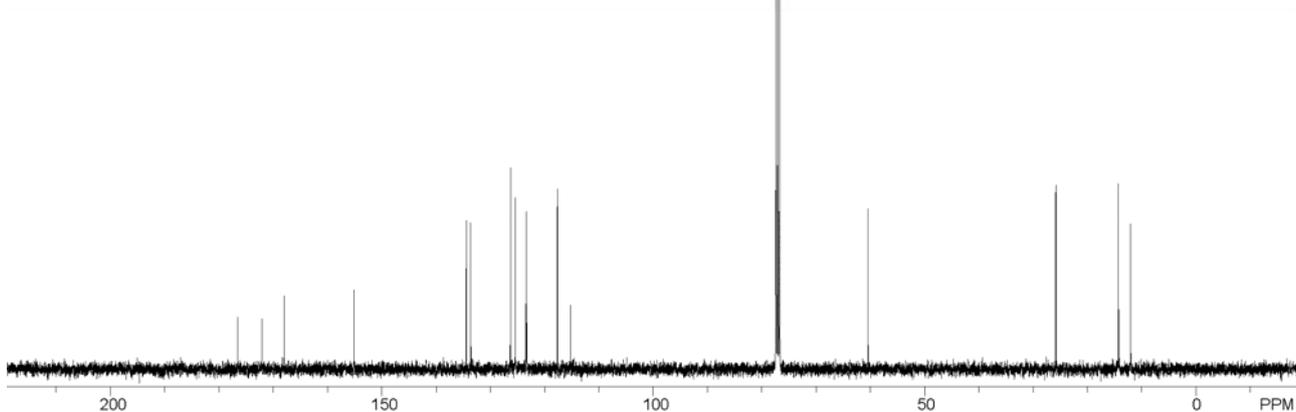
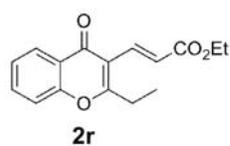
134.432  
133.605  
128.288  
126.400  
123.429  
123.325  
117.627  
115.230

77.343  
77.094  
76.714

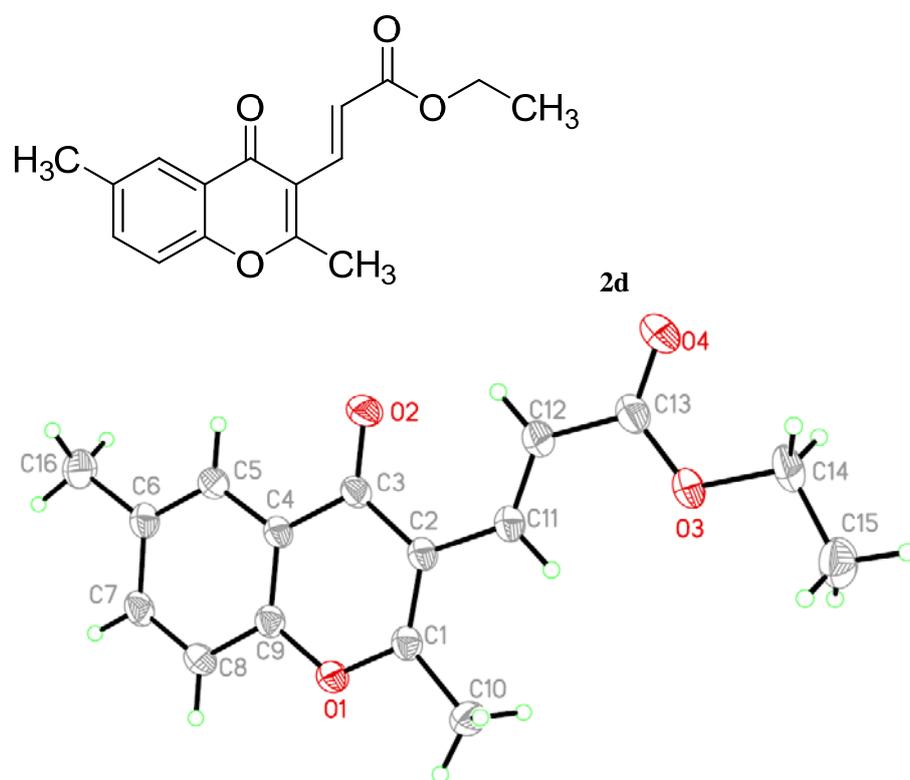
60.406

25.853

14.211  
12.006



## V. X-ray crystal structure of 2d



## VI. Reference

- [1] X. S. Fan, Y. Y. Wang, Y. Y. Qu, H. Y. Xu, Y. He, X. Y. Zhang, J. J. Wang, *J. Org. Chem.*, 2011, **76**, 982.