

## Supplementary Material

### A New Protocol for Total Synthesis of Natural Product Frutinone A and Its Derivatives

Kang Lei<sup>A,B</sup>, Dong-Wei Sun<sup>A,B</sup>, Yuan-Yuan Tao<sup>A,B</sup> and Xiao-Hua Xu\*

<sup>A</sup> State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Number 94, Weijin Road, Nankai District, Tianjin 300071, P. R. China

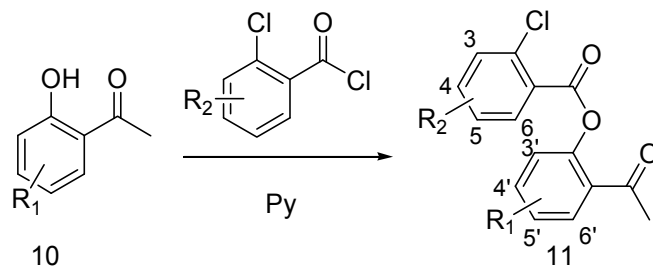
<sup>B</sup> Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300071, China

\* Address correspondence to this author at State Key Laboratory of Elemento-Organic Chemistry, Nankai University, No. 94, Weijin Road, Nankai District, Tianjin 300071, P. R. China (telephone +86 22 23501652; Fax: +86 22 23502737; E-mail: [xiaohuaxu@nankai.edu.cn](mailto:xiaohuaxu@nankai.edu.cn))

#### General information

Unless otherwise stated, all reactions were carried out under an argon atmosphere, and all commercially available reagents were used without further purification. <sup>1</sup>H NMR and <sup>13</sup>C NMR were obtained at 400 MHz using Bruker AV400 spectrometer in CDCl<sub>3</sub> or *d*<sub>6</sub>-DMSO solution with TMS as the internal standard. Chemical shift values (δ) are given in ppm. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiple), dd (doublet of doublet). Coupling constants were reported in Hertz (Hz). High-resolution mass Spectra were conducted using an Ionspec 7.0T spectrometer by ESI-FTICR technique. The melting points were determined on an X-4 binocular microscope melting point apparatus (Beijing Tech Instruments Co., Beijing, China) and were uncorrected.

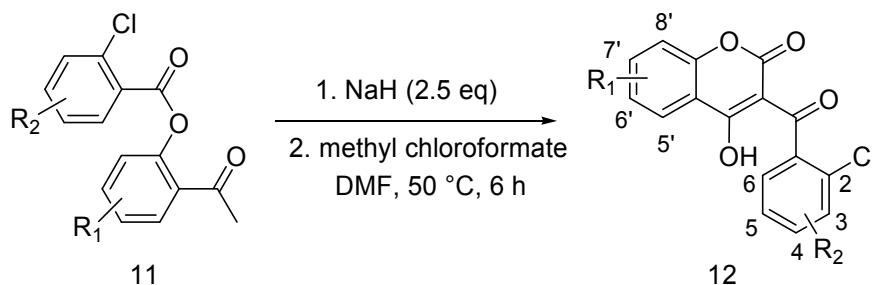
#### General Synthetic Procedure for compound 11-1 to 11-20



11-1 R <sub>1</sub> =H, R <sub>2</sub> =H	11-11 R <sub>1</sub> =H, R <sub>2</sub> =4-OMe
11-2 R <sub>1</sub> =H, R <sub>2</sub> =3-Cl	11-12 R <sub>1</sub> =4'-F, R <sub>2</sub> =H
11-3 R <sub>1</sub> =H, R <sub>2</sub> =4-Cl	11-13 R <sub>1</sub> =5'-F, R <sub>2</sub> =4-Cl
11-4 R <sub>1</sub> =H, R <sub>2</sub> =5-Cl	11-14 R <sub>1</sub> =5'-F, R <sub>2</sub> =H
11-5 R <sub>1</sub> =H, R <sub>2</sub> =6-F	11-15 R <sub>1</sub> =5'-Br, R <sub>2</sub> =4-Cl
11-6 R <sub>1</sub> =H, R <sub>2</sub> =4-F	11-16 R <sub>1</sub> =5'-Br, R <sub>2</sub> =H
11-7 R <sub>1</sub> =H, R <sub>2</sub> =5-F	11-17 R <sub>1</sub> =6'-OMe, R <sub>2</sub> =4-Cl
11-8 R <sub>1</sub> =H, R <sub>2</sub> =4-Br	11-18 R <sub>1</sub> =6'-OMe, R <sub>2</sub> =H
11-9 R <sub>1</sub> =H, R <sub>2</sub> =4-SO <sub>2</sub> Me	11-19 R <sub>1</sub> =5'-Me, R <sub>2</sub> =H
11-10 R <sub>1</sub> =H, R <sub>2</sub> =3-OMe	11-20 R <sub>1</sub> =4'-OMe, R <sub>2</sub> =H

A mixture of 2'-hydroxyacetophenone (10.0 mmol) and 2-chlorobenzoyl chloride (15.0 mmol) was stirred in dry pyridine (10 mL) at room temperature for 2 h. The reaction mixture was then poured into a mixture of crushed ice (15 mL) and concentrated HCl (5 mL), extracted twice with dichloromethane, washed three times with aqueous K<sub>2</sub>CO<sub>3</sub>, and then washed three times with water. The solvent was removed under reduced pressure. The residue was recrystallized from ethanol to give 2-acetylphenyl 2-chlorobenzoate **11-1** (2.52 g, 92%) as white solid. The rest of compounds were prepared by the similar procedure to **11-1**.

#### General Synthetic Procedure for compound 12-1 to 12-20

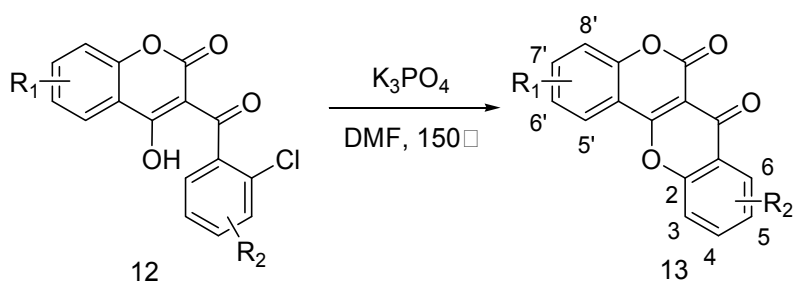


12-1 R <sub>1</sub> =H, R <sub>2</sub> =H	12-11 R <sub>1</sub> =H, R <sub>2</sub> =4-OMe
12-2 R <sub>1</sub> =H, R <sub>2</sub> =3-Cl	12-12 R <sub>1</sub> =7'-F, R <sub>2</sub> =H
12-3 R <sub>1</sub> =H, R <sub>2</sub> =4-Cl	12-13 R <sub>1</sub> =6'-F, R <sub>2</sub> =4-Cl
12-4 R <sub>1</sub> =H, R <sub>2</sub> =5-Cl	12-14 R <sub>1</sub> =6'-F, R <sub>2</sub> =H
12-5 R <sub>1</sub> =H, R <sub>2</sub> =6-F	12-15 R <sub>1</sub> =6'-Br, R <sub>2</sub> =4-Cl
12-6 R <sub>1</sub> =H, R <sub>2</sub> =4-F	12-16 R <sub>1</sub> =6'-Br, R <sub>2</sub> =H
12-7 R <sub>1</sub> =H, R <sub>2</sub> =5-F	12-17 R <sub>1</sub> =5'-OMe, R <sub>2</sub> =4-Cl
12-8 R <sub>1</sub> =H, R <sub>2</sub> =4-Br	12-18 R <sub>1</sub> =5'-OMe, R <sub>2</sub> =H
12-9 R <sub>1</sub> =H, R <sub>2</sub> =4-SO <sub>2</sub> Me	12-19 R <sub>1</sub> =6'-Me, R <sub>2</sub> =H
12-10 R <sub>1</sub> =H, R <sub>2</sub> =3-OMe	12-20 R <sub>1</sub> =7'-OMe, R <sub>2</sub> =H

To a solution of 2-acetylphenyl 2-chlorobenzoate **11-1** (5.0 mmol) in DMF (10 mL), NaH (12.5 mmol) were added and stirred for 2 h at 50 °C. Then, methyl chloroformate (5.5 mmol) was added to above solution and the mixture was stirred for 4 hours at 50 °C. After the reaction complete (TLC monitor), the above mixture was poured into a mixture of crushed ice (15 mL) and concentrated HCl (5 mL). White solid was precipitated. The formed precipitate was filtered,

washed with cold ethanol ( $3 \times 10$  mL) and then dried in vacuum to provide white solid **12-1** (0.92 g, 61 %). The rest of compounds were prepared by the similar procedure to **12-1**.

**General Synthetic Procedure for compound 13-1 to 13-20**

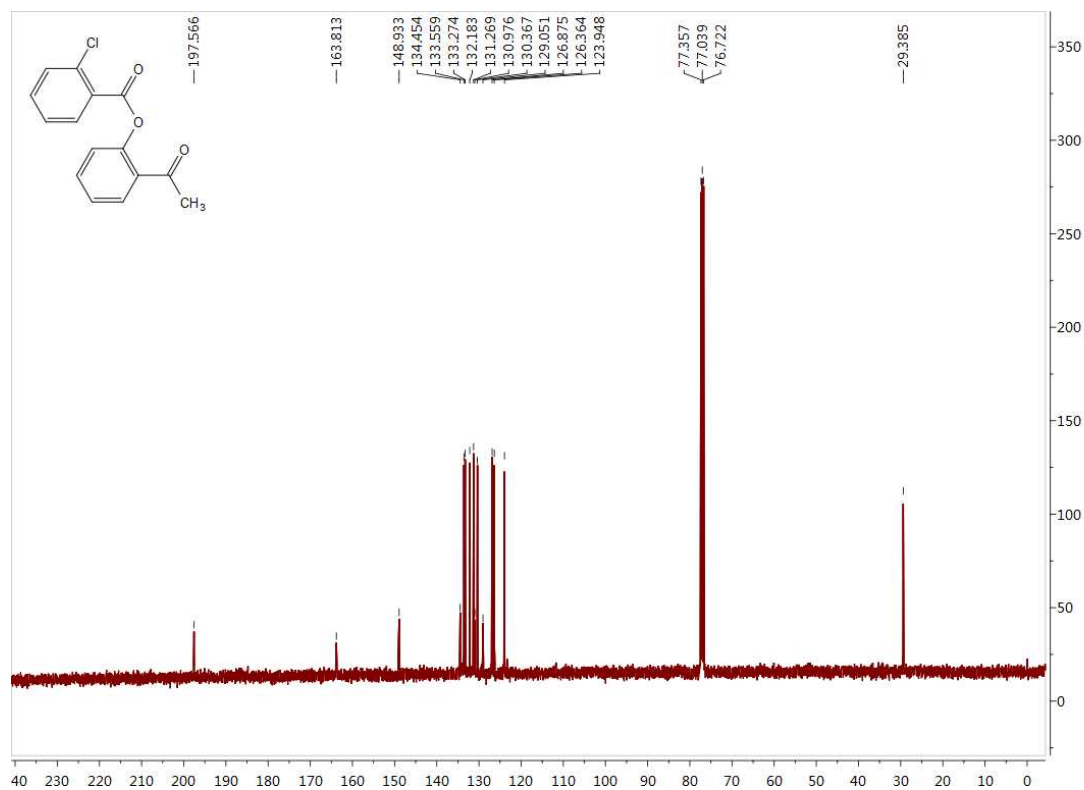
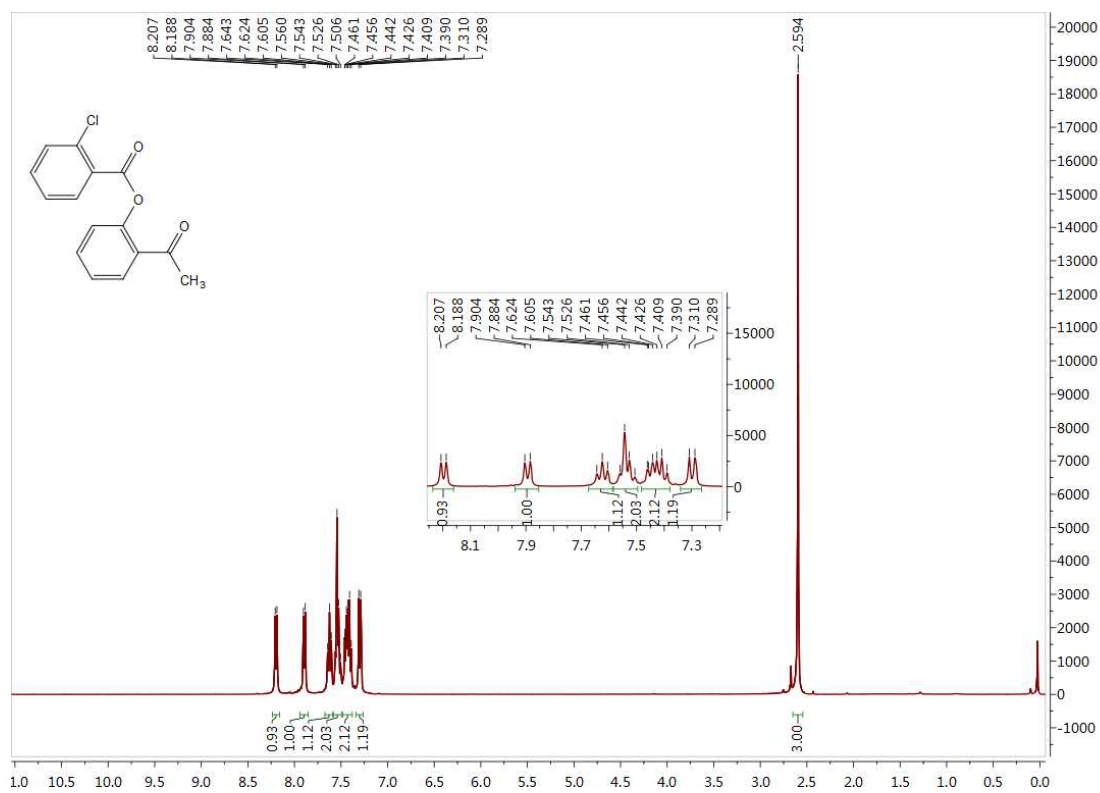


13-1 R <sub>1</sub> =H, R <sub>2</sub> =H	13-11 R <sub>1</sub> =H, R <sub>2</sub> =4-OMe
13-2 R <sub>1</sub> =H, R <sub>2</sub> =3-Cl	13-12 R <sub>1</sub> =7'-F, R <sub>2</sub> =H
13-3 R <sub>1</sub> =H, R <sub>2</sub> =4-Cl	13-13 R <sub>1</sub> =6'-F, R <sub>2</sub> =4-Cl
13-4 R <sub>1</sub> =H, R <sub>2</sub> =5-Cl	13-14 R <sub>1</sub> =6'-F, R <sub>2</sub> =H
13-5 R <sub>1</sub> =H, R <sub>2</sub> =6-Cl	13-15 R <sub>1</sub> =6'-Br, R <sub>2</sub> =4-Cl
13-6 R <sub>1</sub> =H, R <sub>2</sub> =4-F	13-16 R <sub>1</sub> =6'-Br, R <sub>2</sub> =H
13-7 R <sub>1</sub> =H, R <sub>2</sub> =5-F	13-17 R <sub>1</sub> =5'-OMe, R <sub>2</sub> =4-Cl
13-8 R <sub>1</sub> =H, R <sub>2</sub> =4-Br	13-18 R <sub>1</sub> =5'-OMe, R <sub>2</sub> =H
13-9 R <sub>1</sub> =H, R <sub>2</sub> =4-SO <sub>2</sub> Me	13-19 R <sub>1</sub> =6'-Me, R <sub>2</sub> =H
13-10 R <sub>1</sub> =H, R <sub>2</sub> =3-OMe	13-20 R <sub>1</sub> =7'-OMe, R <sub>2</sub> =H

To a solution of compound **12-1** (1.0 mmol) in DMF (10 mL), potassium phosphate (1.0 mmol) were added and heat to 150 °C for 2 h. After the reaction complete and cool down, the mixture was pour into 30 mL ice water and yellow solid was precipitate. The formed precipitate was filtered, washed with cold water ( $3 \times 10$  mL) and then dried in vacuum to give the natural product frutinone A **13-1** (247 mg, 94%). The rest of target compounds were prepared by the similar procedure to **13-1**.

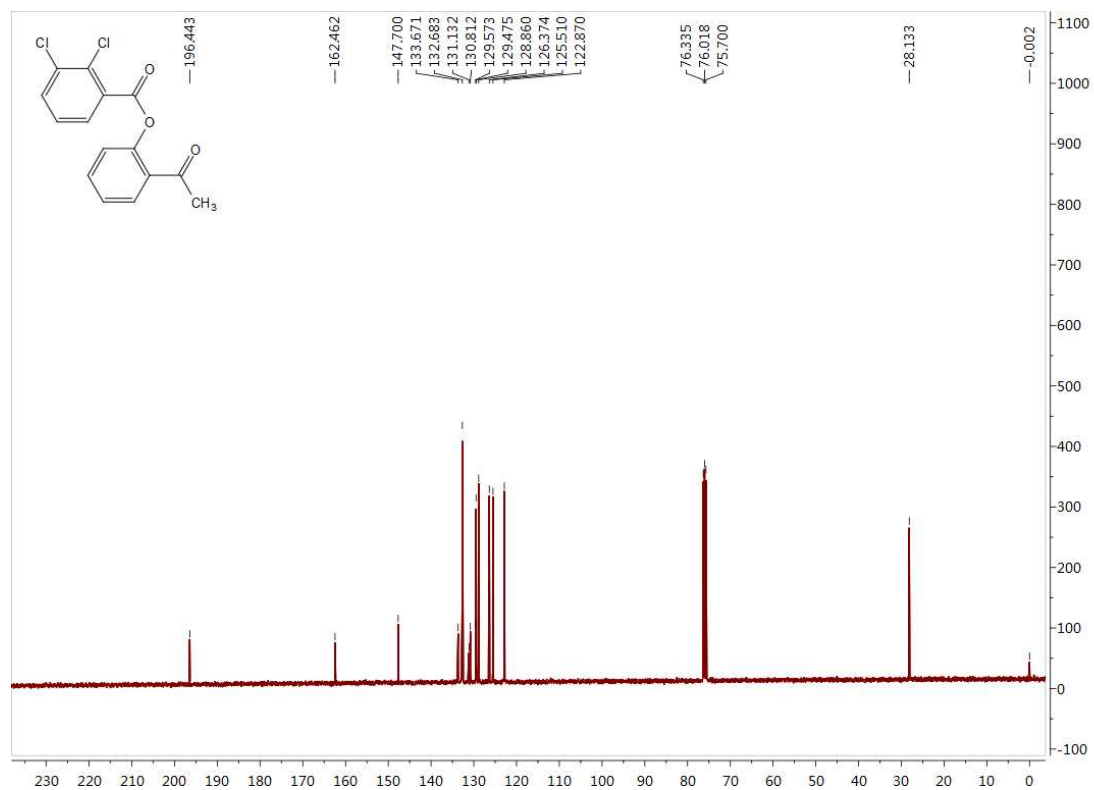
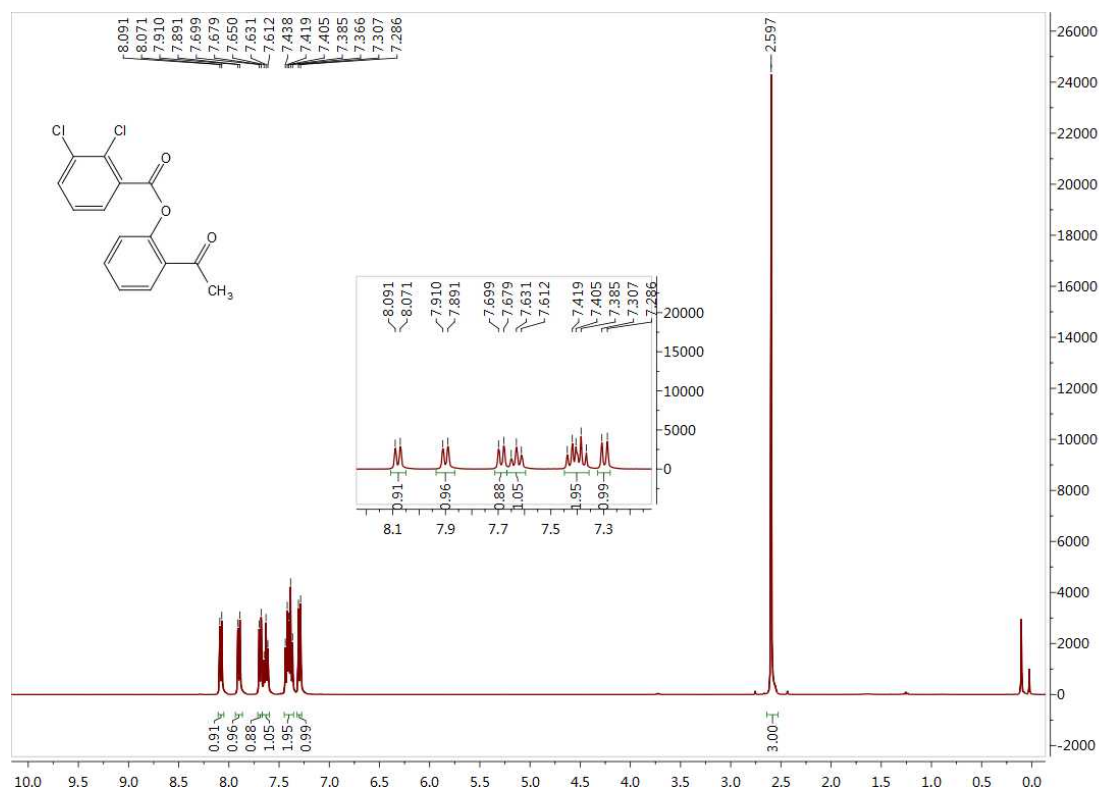
**Analytical Data for products 11-1 to 11-20:**

Data for **11-1**: white solid; yield 90 %; m.p. 53-55 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.20 (d, *J* = 7.6 Hz, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.59-7.49 (m, 2H), 7.47-7.37 (m, 2H), 7.30 (d, *J* = 8.2 Hz, 1H), 2.59 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 197.57, 163.81, 148.93, 134.45, 133.56, 133.27, 132.18, 131.12, 130.98, 130.37, 129.05, 126.87, 126.36, 123.95, 29.39; HRMS: calcd for C<sub>15</sub>H<sub>11</sub>ClO<sub>3</sub> [M+H]<sup>+</sup> 275.0397, found 275.0467.

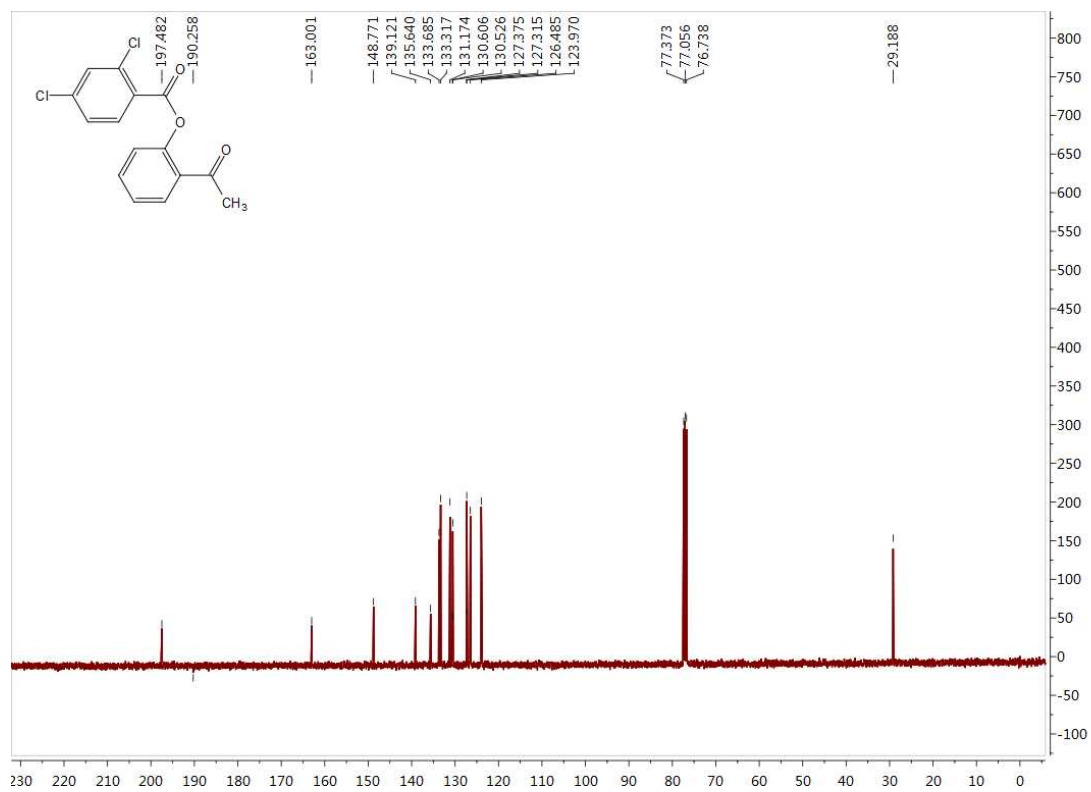
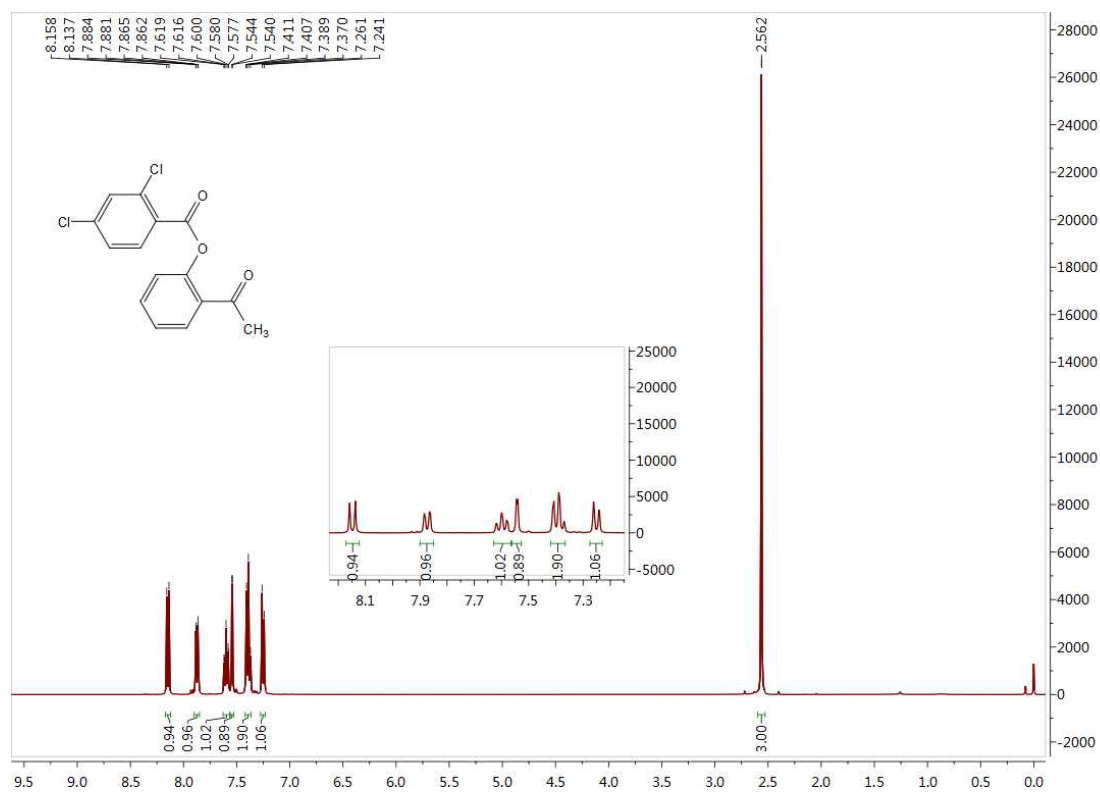


Data for **11-2**: white solid; yield 83 %; m.p. 95-96 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.08 (d,  $J$  = 7.6 Hz, 1H), 7.90 (d,  $J$  = 7.7 Hz, 1H), 7.69 (d,  $J$  = 8.0 Hz, 1H), 7.63 (t,  $J$  = 7.7 Hz, 1H), 7.46-7.35 (m, 2H), 7.30 (d,  $J$  = 8.4 Hz, 1H), 2.60 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 196.44, 162.46, 147.70, 133.67, 132.68, 132.67, 131.13, 130.81, 129.57, 129.48, 128.86, 126.37, 125.51, 122.87, 28.13; HRMS: calcd for  $\text{C}_{15}\text{H}_{10}\text{Cl}_2\text{O}_3$   $[\text{M}+\text{H}]^+$  309.0007, found 309.0084.

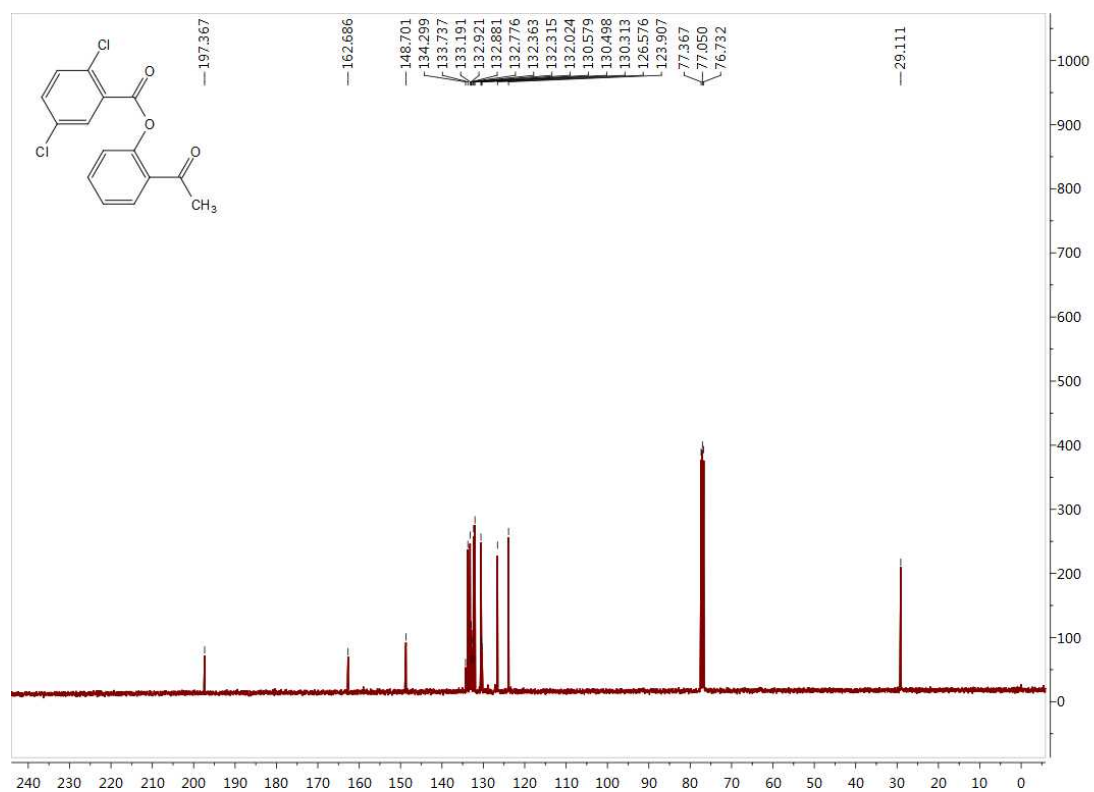
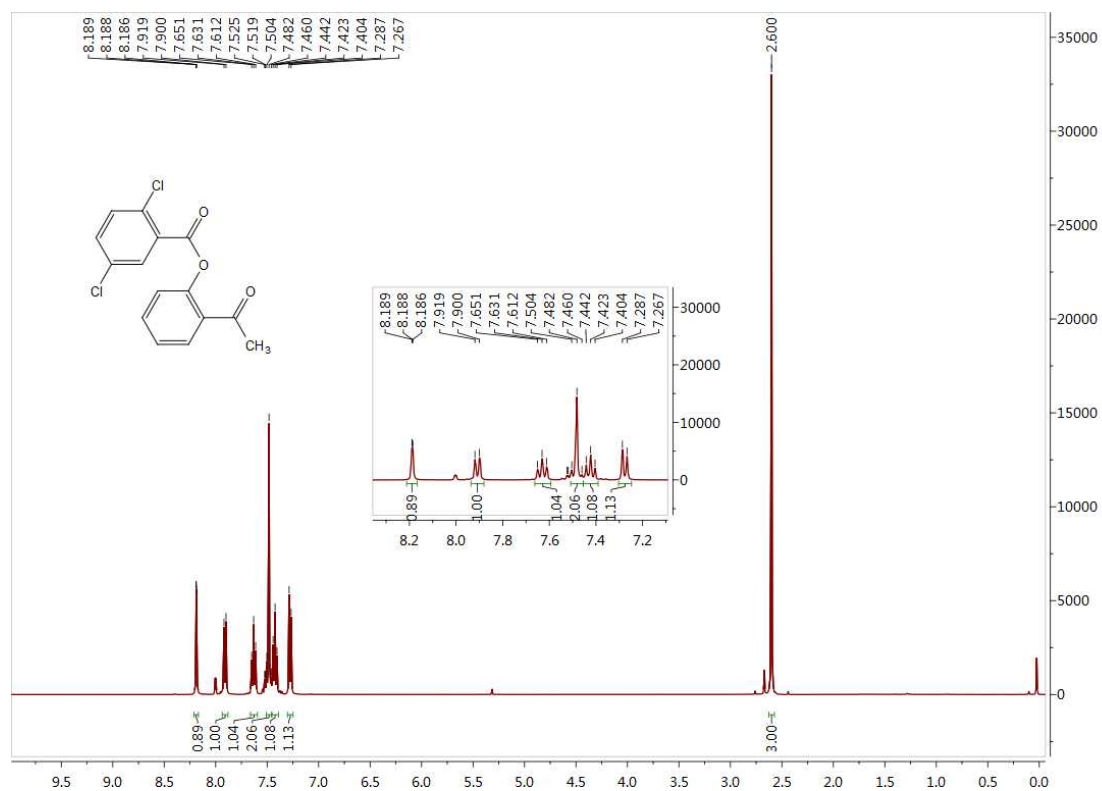




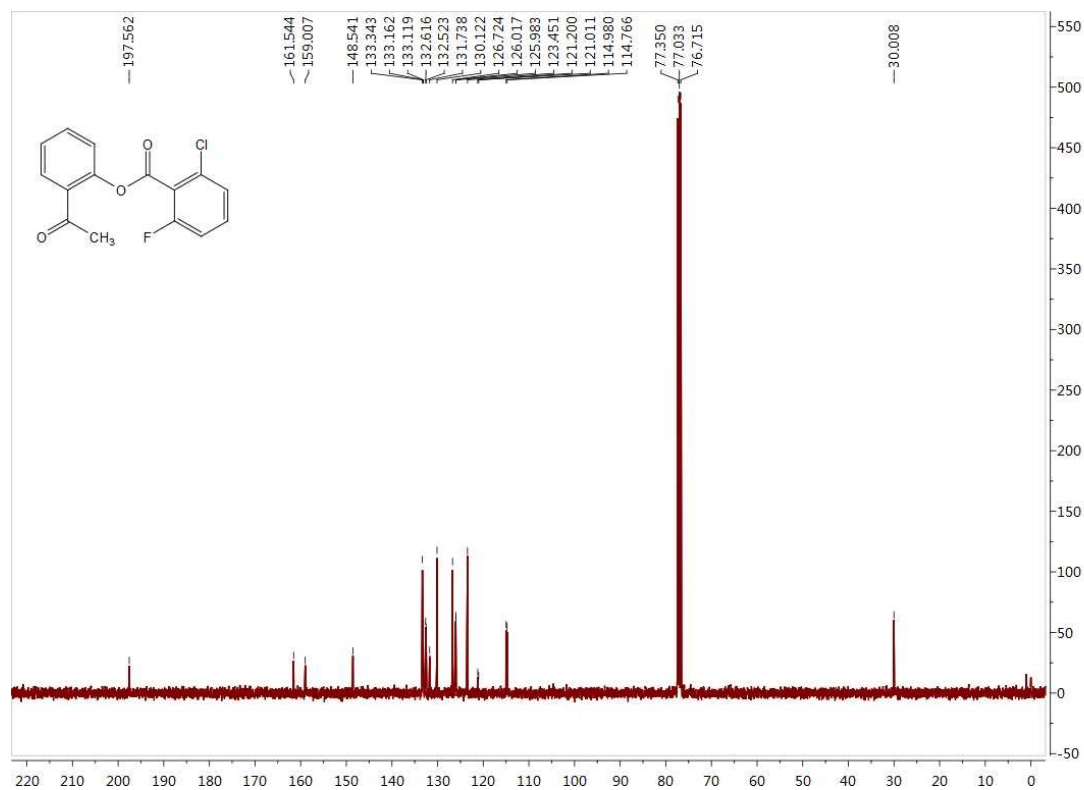
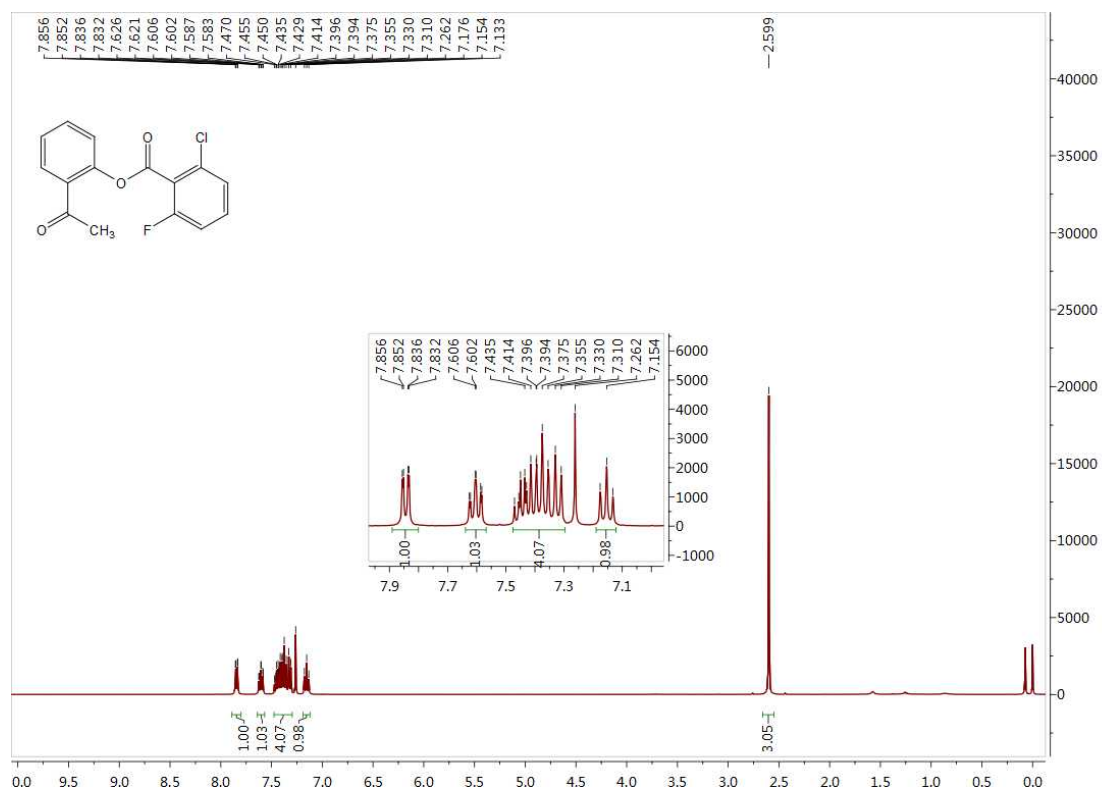
Data for **11-3**: white solid; yield 93 %; m.p. 63-65 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.15 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 7.7 Hz, 1H), 7.58 (t, *J* = 9.2 Hz, 1H), 7.54 (s, 1H), 7.39 (m, 2H), 7.25 (d, *J* = 7.8 Hz, 1H), 2.56 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 197.48, 163.00, 148.77, 139.12, 135.64, 133.68, 133.32, 131.17, 130.61, 130.53, 127.38, 127.31, 126.48, 123.97, 29.19; HRMS: calcd for C<sub>15</sub>H<sub>10</sub>Cl<sub>2</sub>O<sub>3</sub> [M+H]<sup>+</sup> 309.0007, found 309.0083.



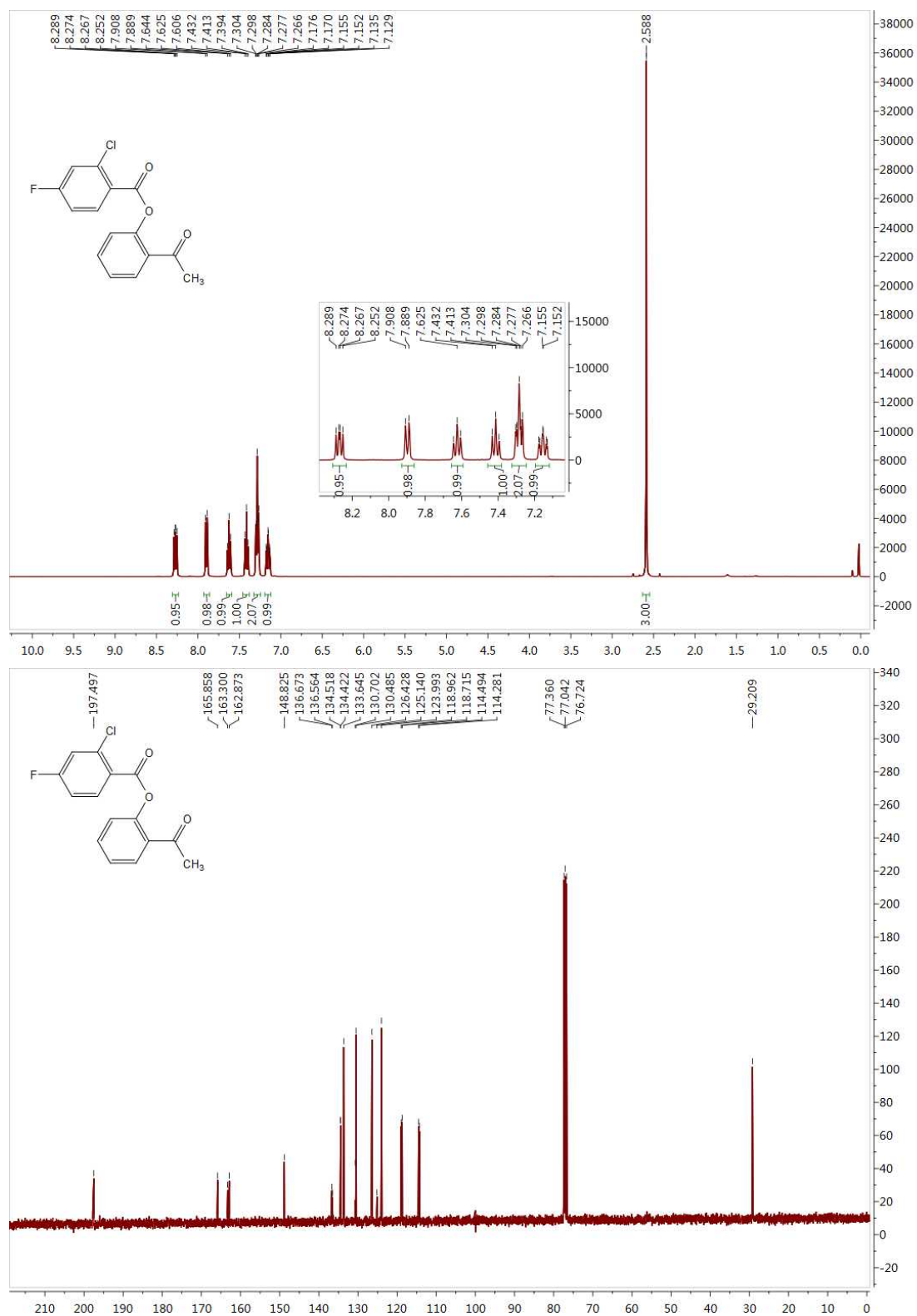
Data for **11-4**: white solid; yield 88 %; m.p. 104-106 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.19 (s, 1H), 7.91 (d,  $J = 7.8$  Hz, 1H), 7.63 (t,  $J = 7.8$  Hz, 1H), 7.53-7.45 (m, 2H), 7.42 (t,  $J = 7.6$  Hz, 1H), 7.28 (d,  $J = 7.8$  Hz, 1H), 2.60 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 197.37, 162.69, 148.70, 133.74, 133.19, 132.92, 132.78, 132.36, 132.02, 130.58, 130.50, 130.31, 126.58, 123.91, 29.11; HRMS: calcd for  $\text{C}_{15}\text{H}_{10}\text{Cl}_2\text{O}_3$   $[\text{M}+\text{H}]^+$  309.0007, found 309.0084.



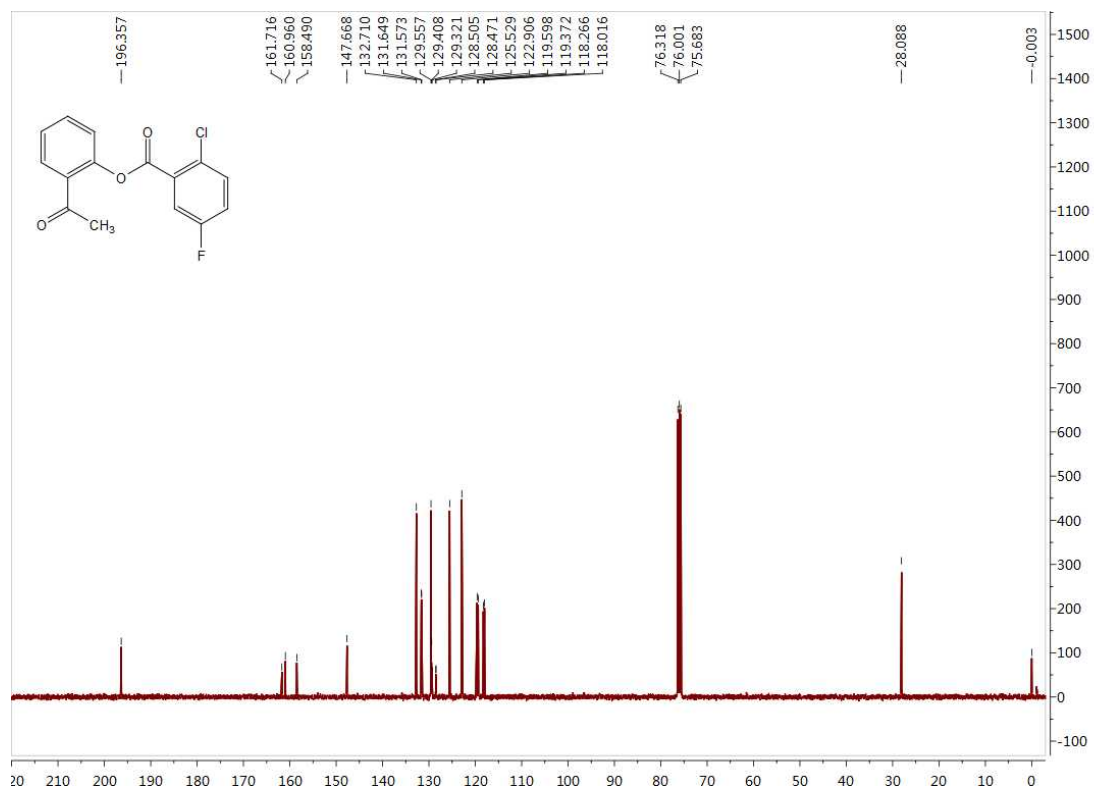
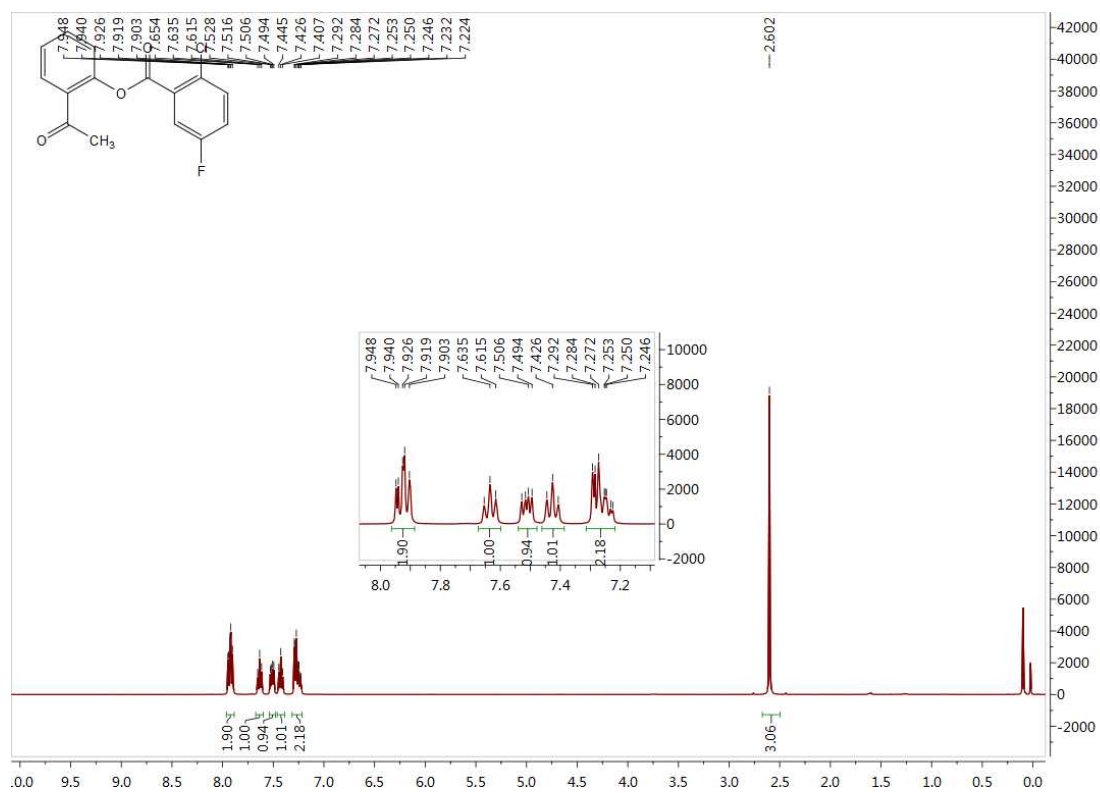
Data for **11-5**: white solid; yield 75 %; m.p. 70-71 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.84 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.60 (td, *J* = 8.0, 1.6 Hz, 1H), 7.50-7.29 (m, 4H), 7.15 (t, *J* = 8.7 Hz, 1H), 2.60 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 197.56, 161.54, 159.01, 148.54, 133.34, 133.14 (d), 132.57 (d), 131.74, 130.12, 126.72, 126.00 (d), 123.45, 121.11 (d), 114.87 (d), 30.01. HRMS: calcd for C<sub>15</sub>H<sub>10</sub>ClFO<sub>3</sub> [M+H]<sup>+</sup> 293.0303, found 293.0380.



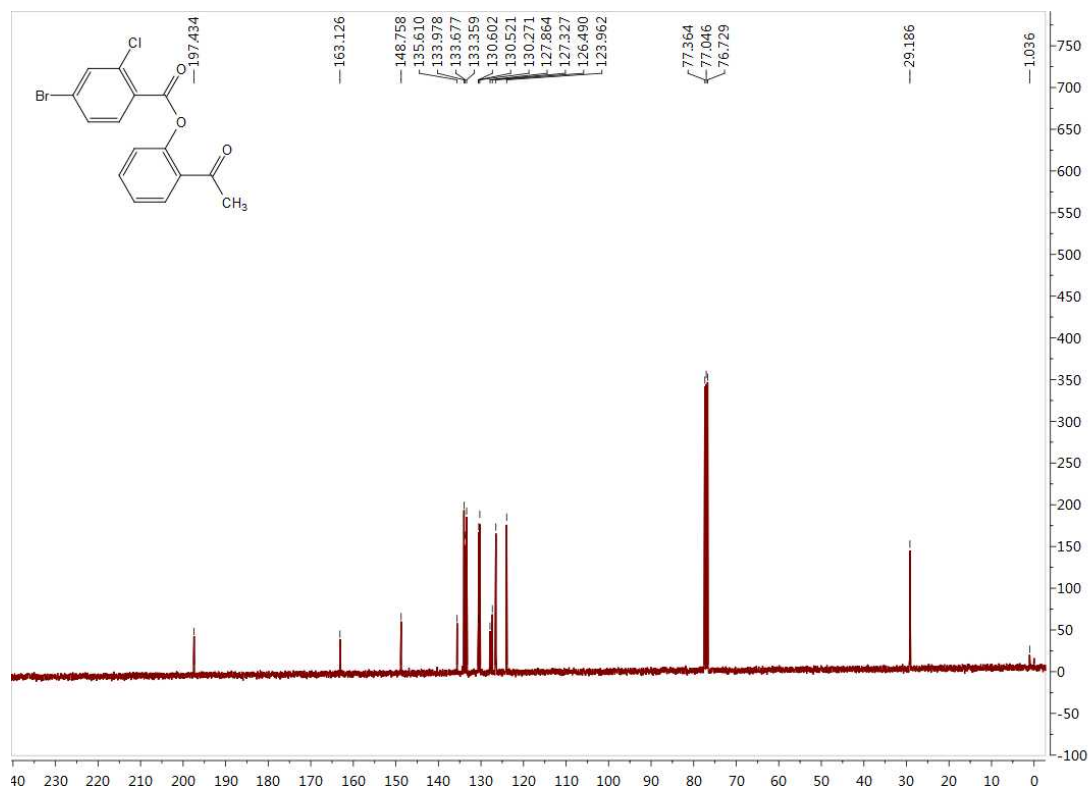
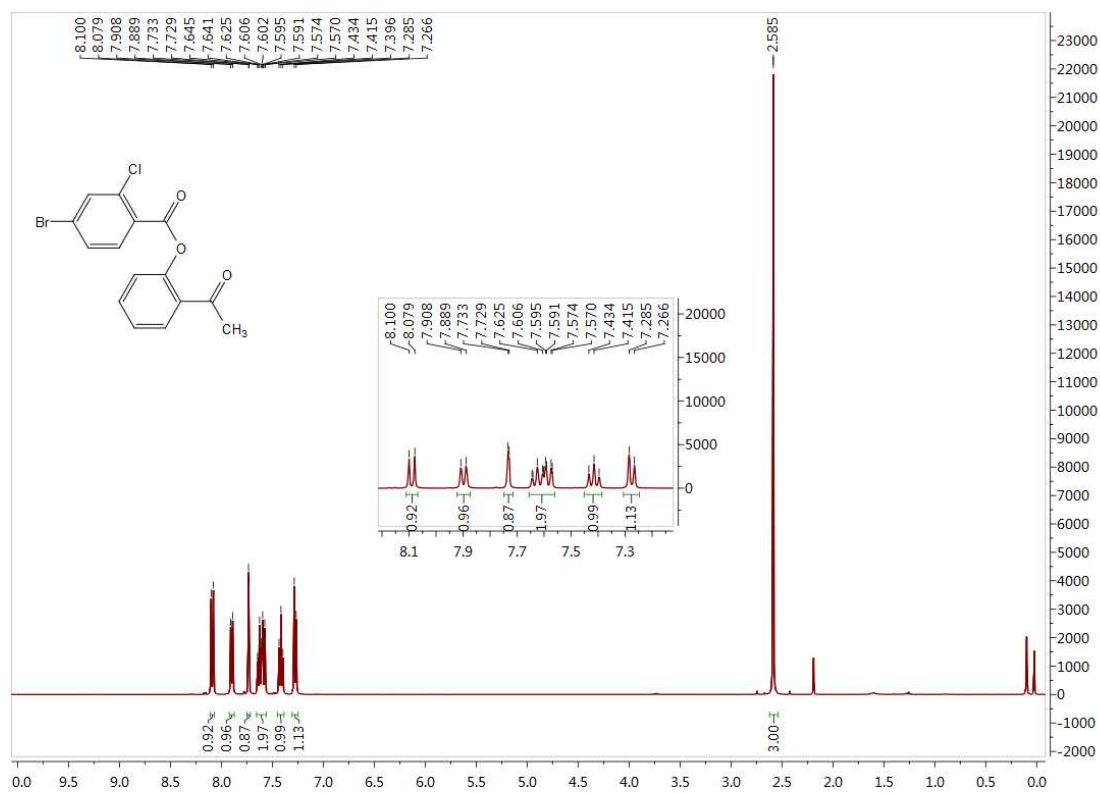
Data for **11-6**: white solid; yield 89 %; m.p. 78-79 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.27 (dd,  $J = 8.8$  Hz, 6.2 Hz, 1H), 7.90 (d,  $J = 7.8$  Hz, 1H), 7.63 (t,  $J = 7.7$  Hz, 1H), 7.41 (t,  $J = 7.6$  Hz, 1H), 7.32-7.24 (m, 2H), 7.15 (td,  $J = 8.8$  Hz, 2.4 Hz, 1H), 2.59 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 197.50, 165.86, 163.09 (d), 148.83, 136.62 (d), 134.47 (d), 133.65, 130.70, 130.48, 126.43, 125.14, 123.99, 118.84 (d), 114.39 (d), 29.21; HRMS: calcd for  $\text{C}_{15}\text{H}_{10}\text{ClFO}_3$   $[\text{M}+\text{H}]^+$  293.0303, found 293.0380.



Data for **11-7**: light yellow solid; yield 84 %; m.p. 103-105 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.96-7.89 (m, 2H), 7.63 (t, *J* = 7.7 Hz, 1H), 7.51 (dd, *J* = 8.8, 4.8 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.26 (m, 2H), 2.60 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 196.36, 161.72, 160.96, 158.49, 147.67, 132.71, 131.61 (d), 131.61 (d), 129.56, 128.49 (d), 125.53, 122.91, 119.49 (d), 118.14 (d), 28.09. HRMS: calcd for C<sub>15</sub>H<sub>10</sub>ClFO<sub>3</sub> [M+H]<sup>+</sup> 293.0303, found 293.0380.



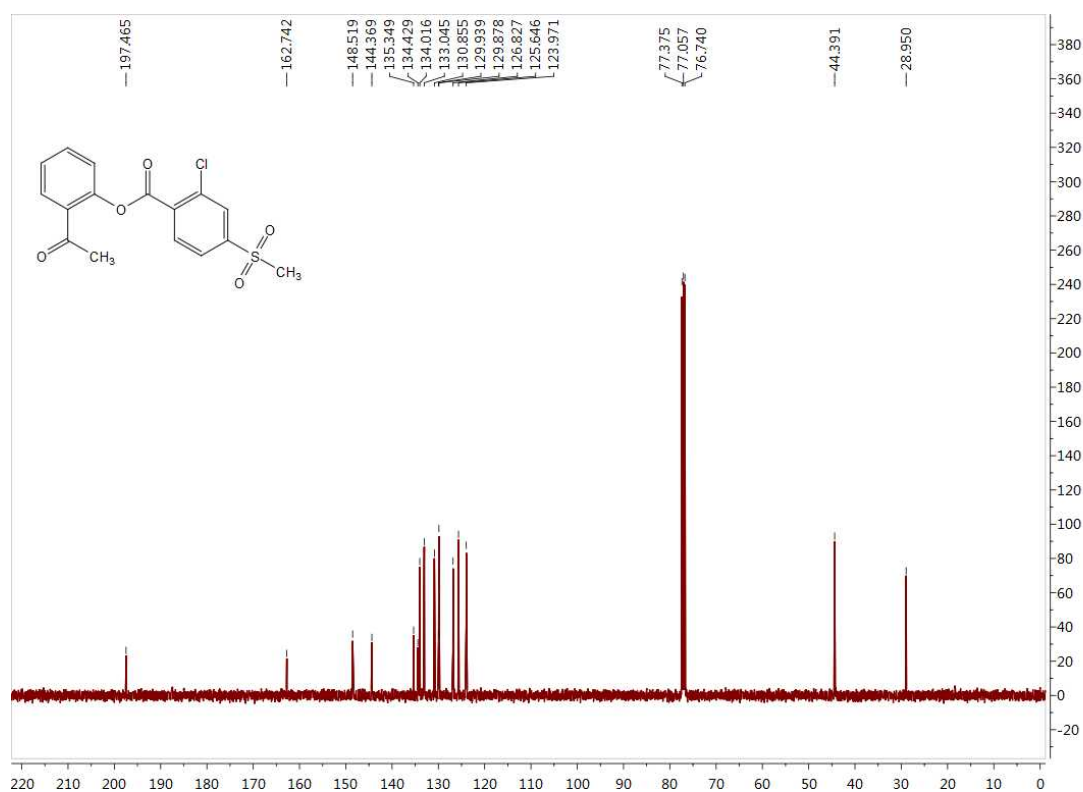
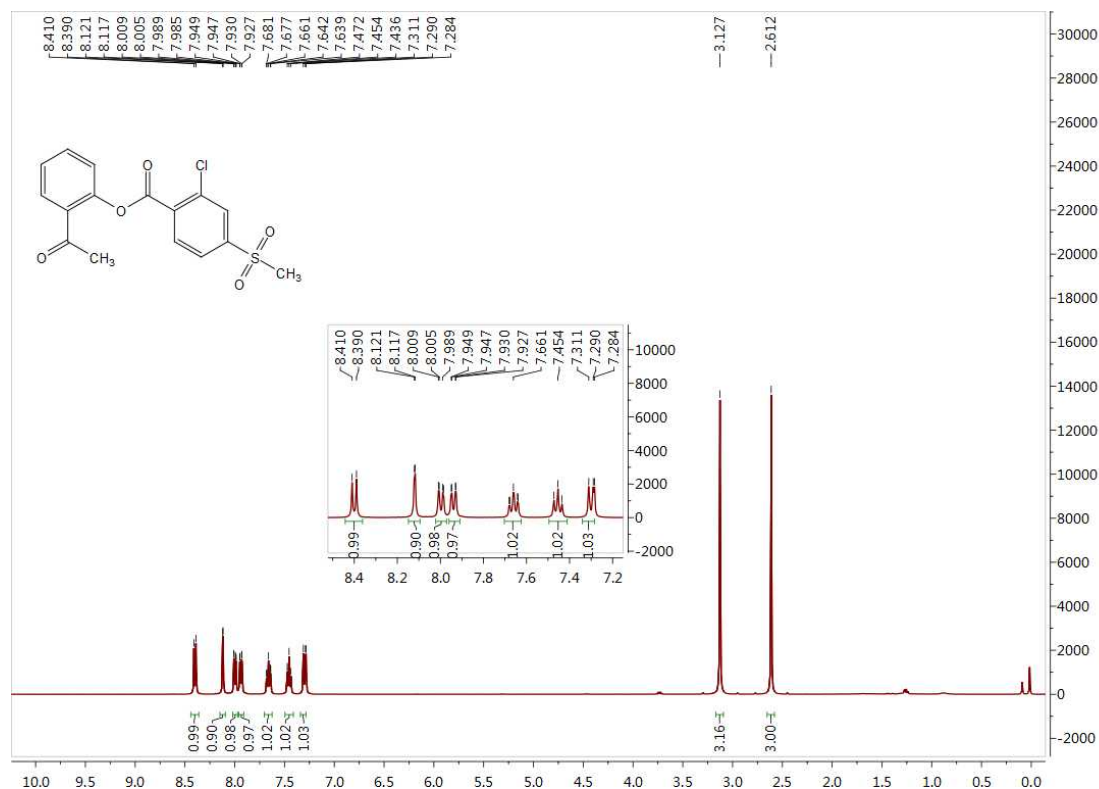
Data for **11-8**: white solid; yield 88 %; m.p. 75-76 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.09 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.73 (s, 1H), 7.67-7.56 (m, 2H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 7.7 Hz, 1H), 2.58 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 197.43, 163.13, 148.76, 135.61, 133.98, 133.68, 133.36, 130.60, 130.52, 130.27, 127.86, 127.33, 126.49, 123.96, 29.19; HRMS: calcd for C<sub>15</sub>H<sub>10</sub>BrClO<sub>3</sub> [M+H]<sup>+</sup> 352.9502, found 352.9580.



Data for **11-9**: light yellow solid; yield 91 %; m.p. 103-105 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.40 (d, *J* = 8.1 Hz, 1H), 8.12 (d, *J* = 1.3 Hz, 1H), 8.00 (dd, *J* = 8.1 Hz, 1.5 Hz, 1H), 7.94 (dd, *J* = 7.7 Hz, 1.1 Hz, 1H), 7.70-7.62 (m, 1H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.30 (d, *J* = 8.3 Hz, 1H), 3.13 (s, 3H), 2.61 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 197.47, 162.74, 148.52, 144.37, 135.35, 134.43, 134.02, 133.04, 130.86, 129.94, 129.88, 126.83, 125.65, 123.97, 44.39, 28.95; HRMS: calcd for

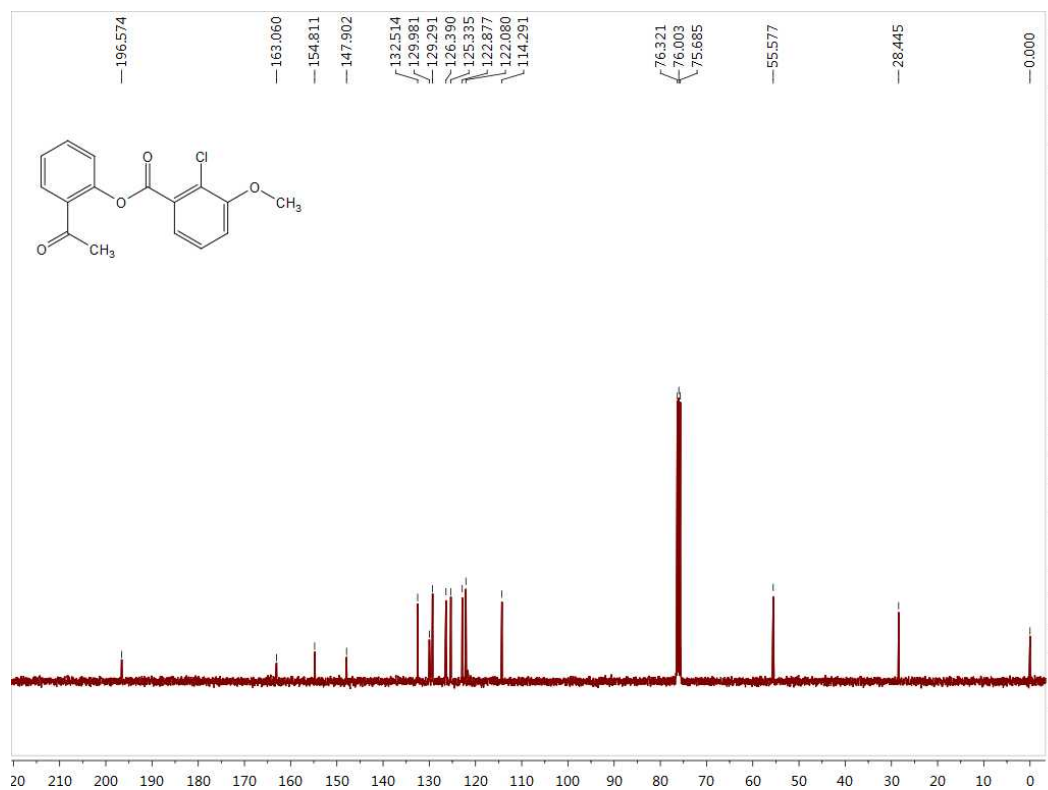
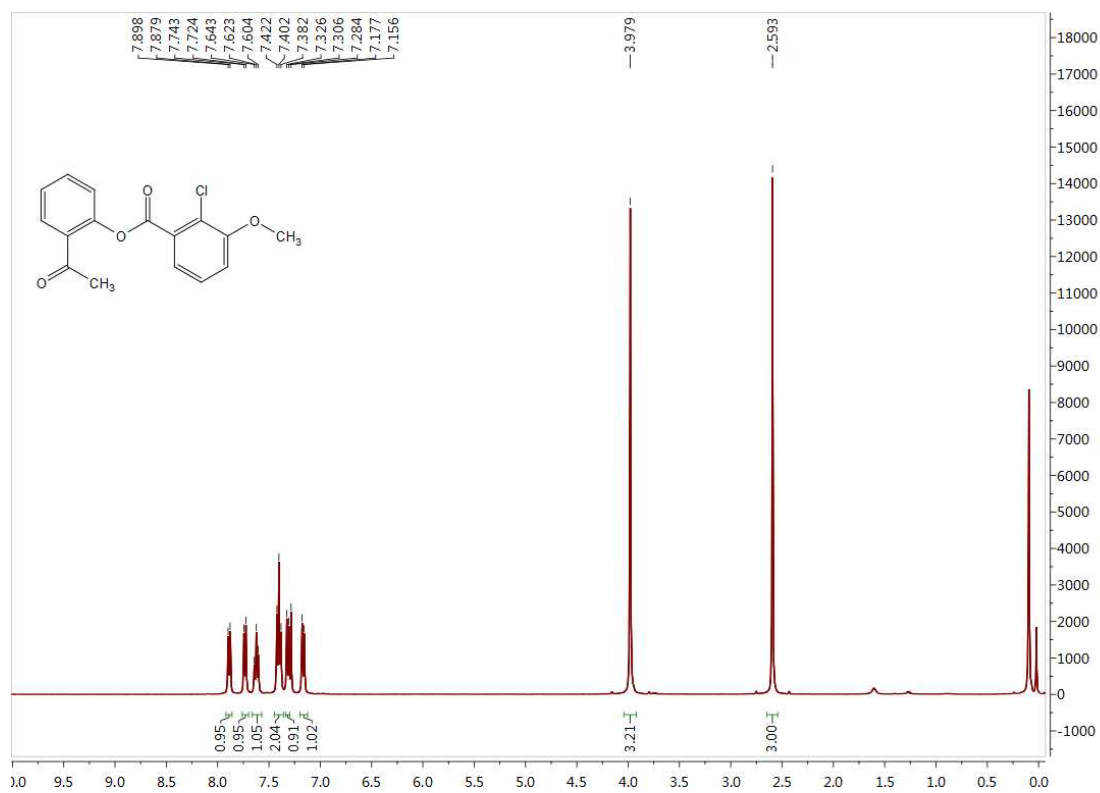


C<sub>16</sub>H<sub>13</sub>ClO<sub>5</sub>S [M+H]<sup>+</sup> 353.0172, found 353.0249.

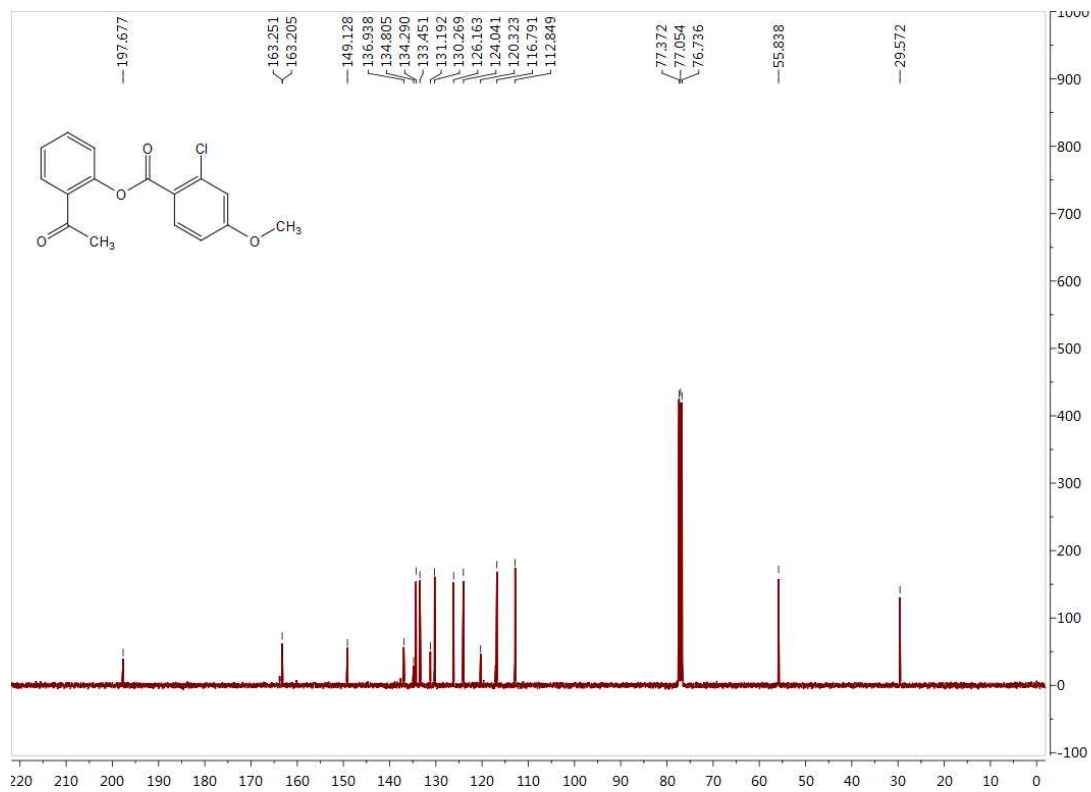
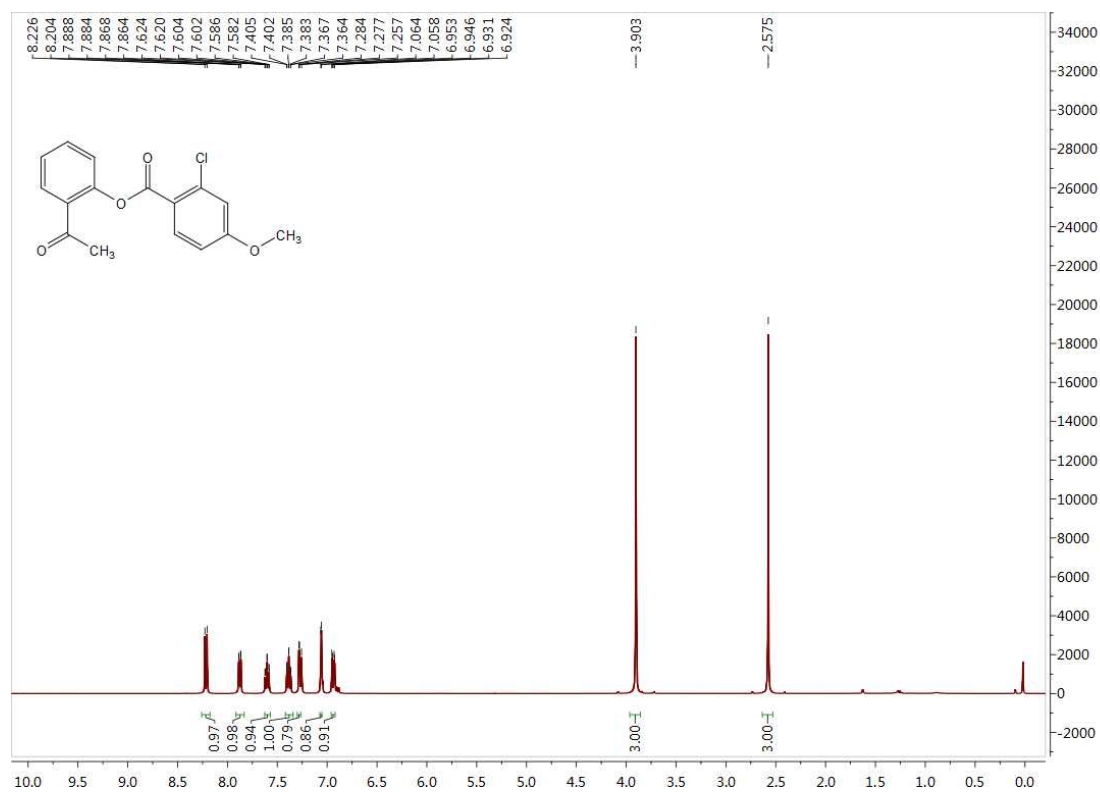


Data for **11-10**: white solid; yield 83 %; m.p. 106-108 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.89 (d, *J* = 7.7 Hz, 1H), 7.73 (d, *J* = 7.7 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.17 (d, *J* = 8.2 Hz, 1H), 3.98 (s, 3H), 2.59 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 196.57, 163.06, 154.81, 147.90, 132.51, 129.98, 129.29, 126.39, 125.33, 122.88, 122.08, 114.29, 55.58, 28.44; HRMS: calcd for C<sub>16</sub>H<sub>13</sub>ClO<sub>4</sub> [M+H]<sup>+</sup> 305.0502, found 305.0579.

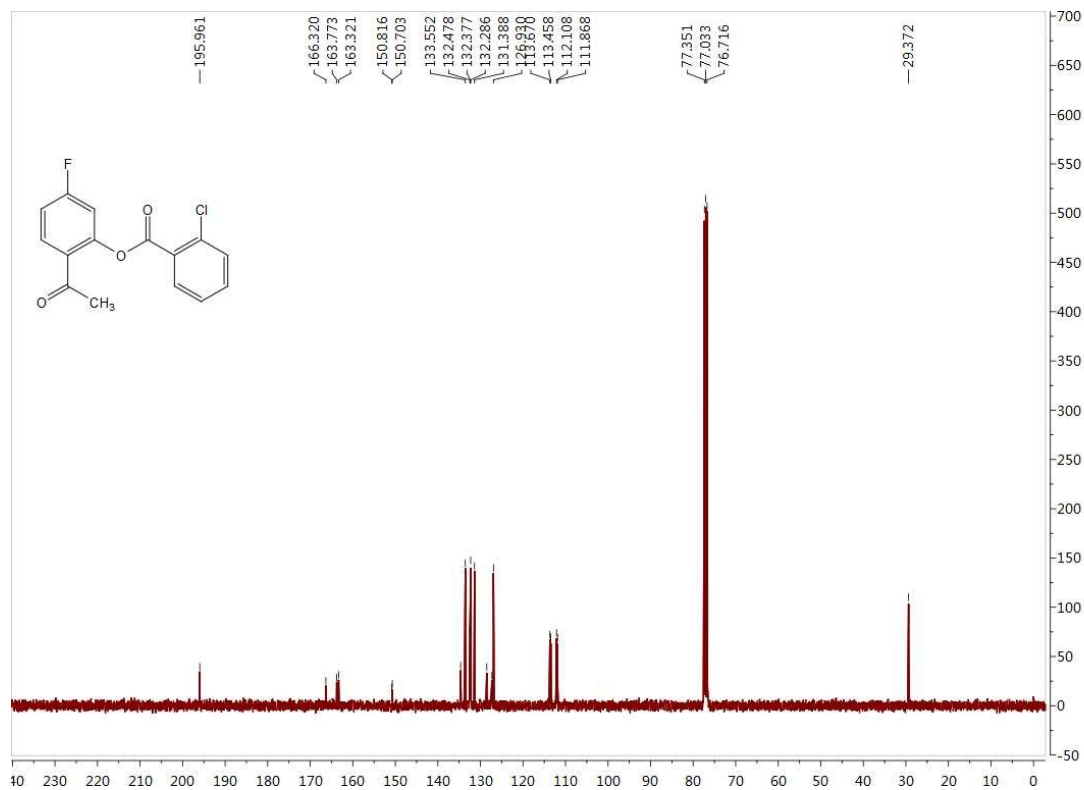
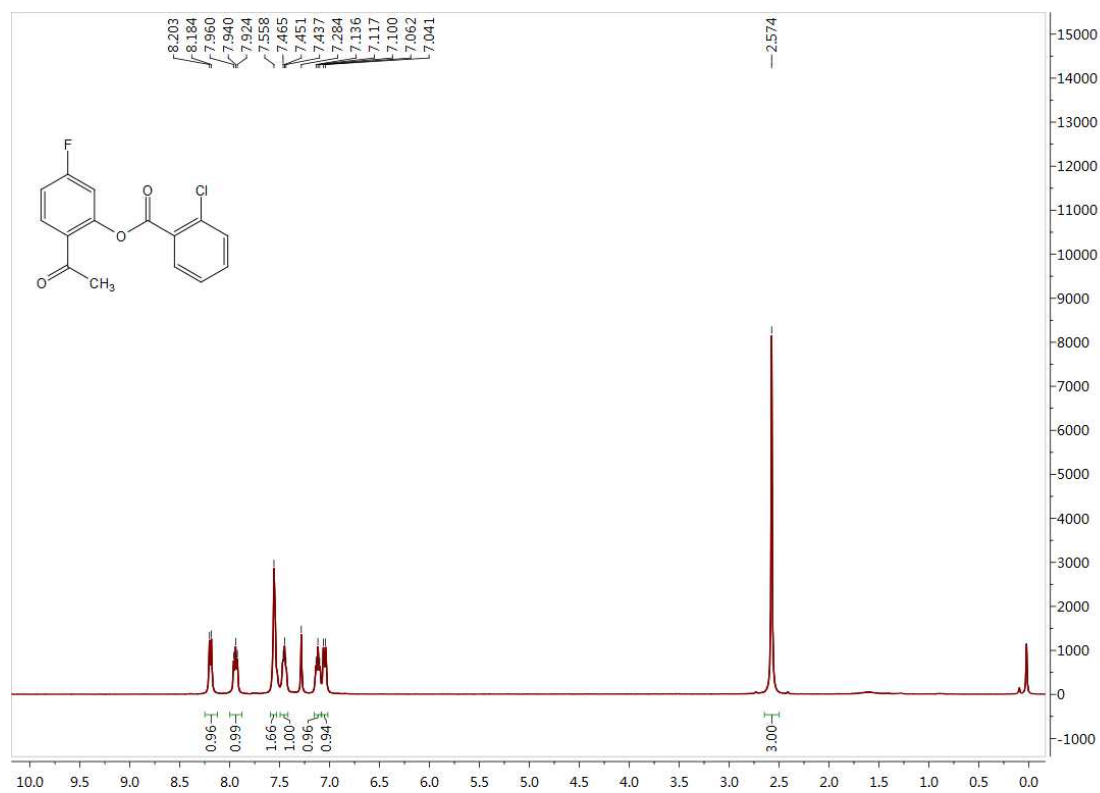




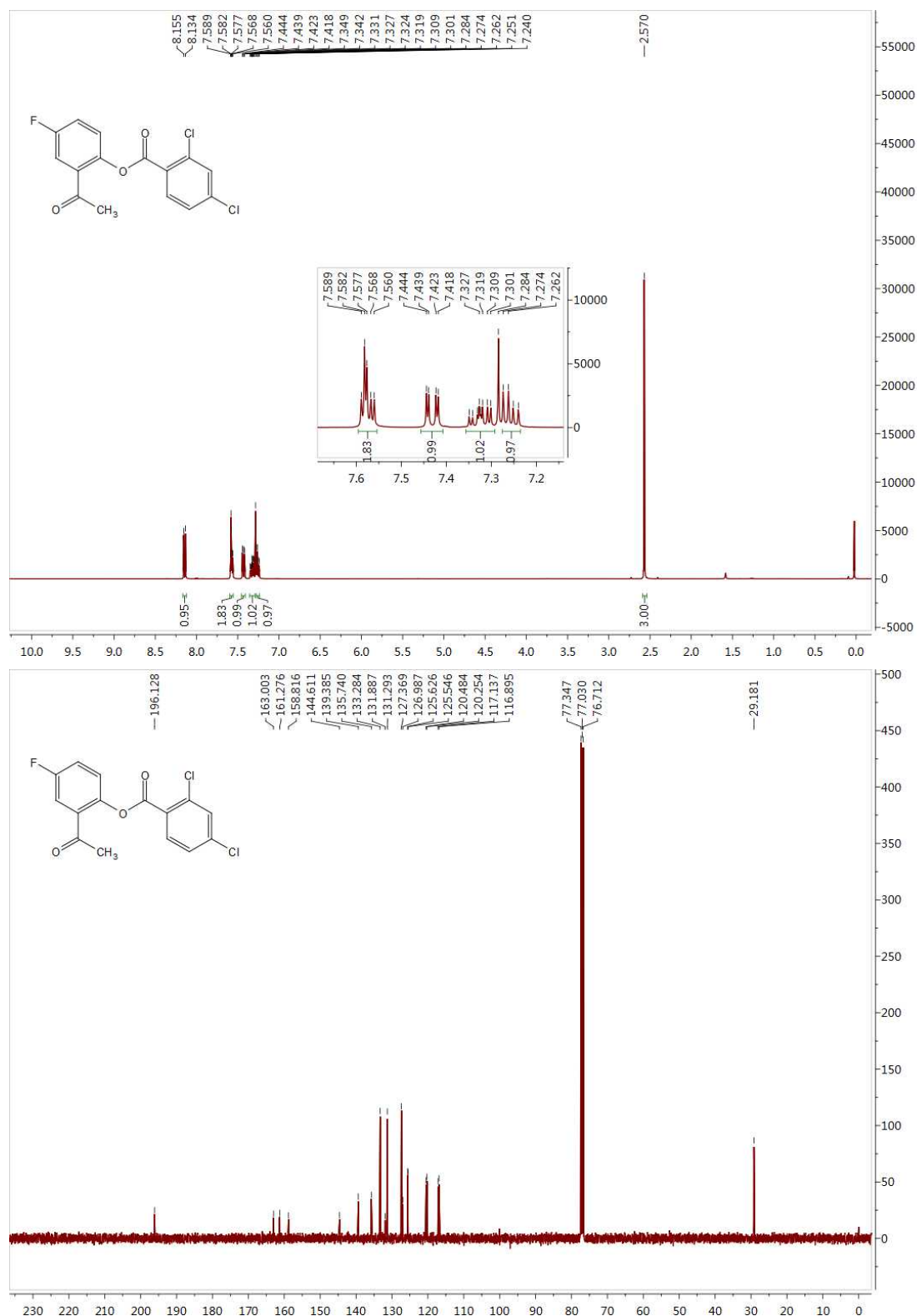
Data for **11-11**: white solid; yield 86 %; m.p. 110-111 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.22 (d, *J* = 8.8 Hz, 1H), 7.88 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.60 (td, *J* = 8.0, 1.6 Hz, 1H), 7.38 (td, *J* = 7.7, 0.9 Hz, 1H), 7.28 (d, *J* = 2.7 Hz, 1H), 7.06 (d, *J* = 2.5 Hz, 1H), 6.94 (dd, *J* = 8.8, 2.5 Hz, 1H), 3.90 (s, 1H), 2.57 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 197.68, 163.25, 163.21, 149.13, 136.94, 134.81, 134.29, 133.45, 131.19, 130.27, 126.16, 124.04, 120.32, 116.79, 112.85, 55.84, 29.57; HRMS: calcd for C<sub>16</sub>H<sub>13</sub>ClO<sub>4</sub> [M+H]<sup>+</sup> 305.0502, found 305.0579.



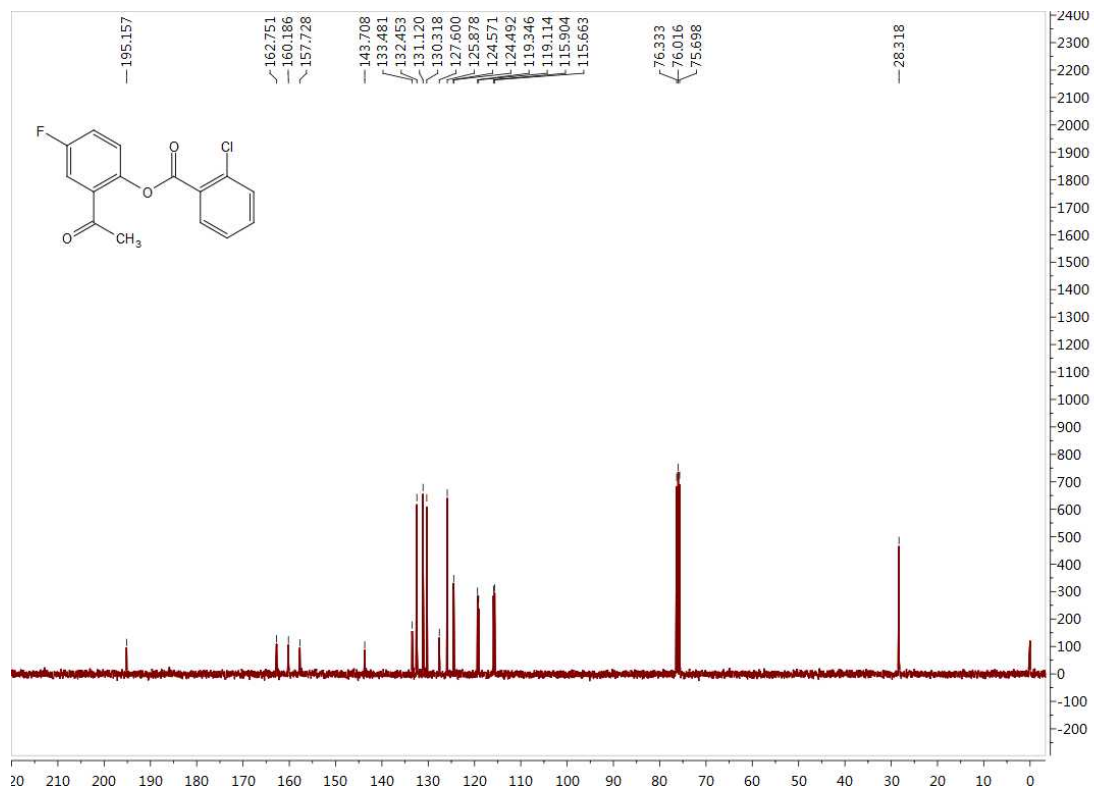
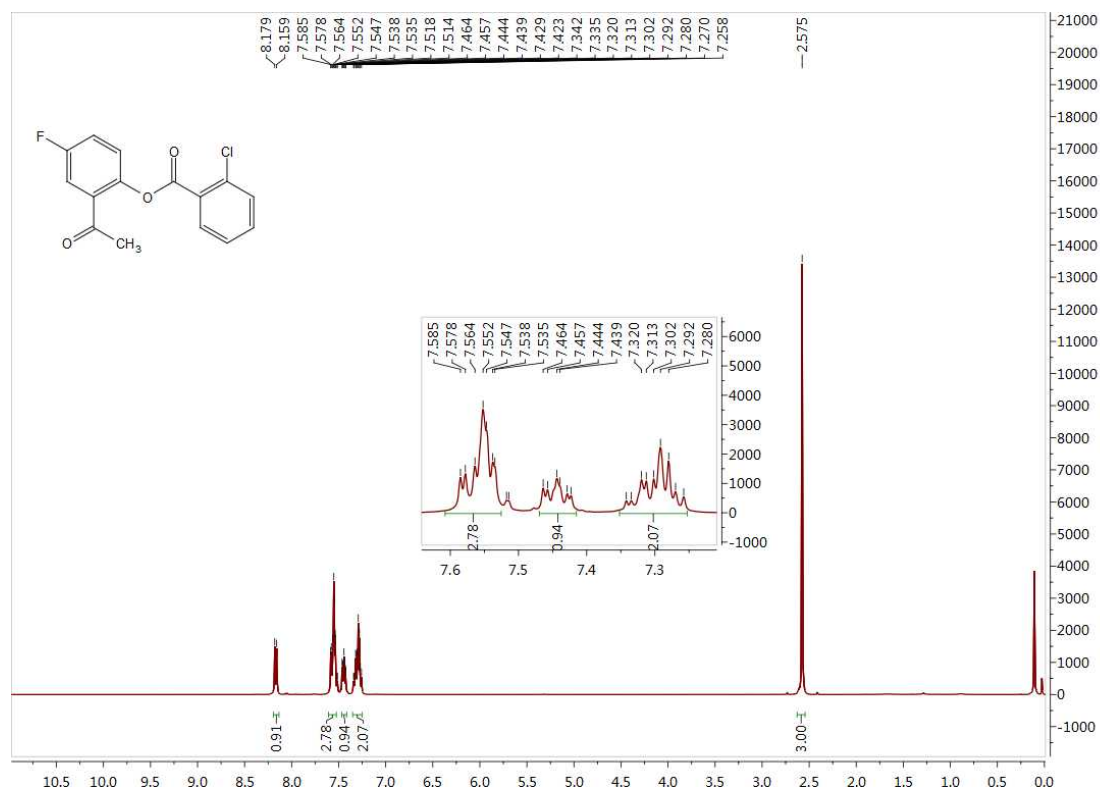
Data for **11-12**: white solid; yield 91 %; m.p. 71-72 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.19 (d,  $J$  = 7.6 Hz, 1H), 7.99-7.90 (m, 1H), 7.56 (s, 2H), 7.45 (t,  $J$  = 5.6 Hz, 1H), 7.12 (t,  $J$  = 7.2 Hz, 1H), 7.05 (d,  $J$  = 8.6 Hz, 1H), 2.57 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 195.96, 166.32, 163.55 (d), 150.76 (d), 134.65, 133.55, 132.43 (d), 132.29, 131.39, 128.51, 127.31, 126.93, 113.56 (d), 111.99 (d), 29.37; HRMS: calcd for  $\text{C}_{15}\text{H}_{10}\text{ClFO}_3$   $[\text{M}+\text{H}]^+$  293.0303, found 293.0381.



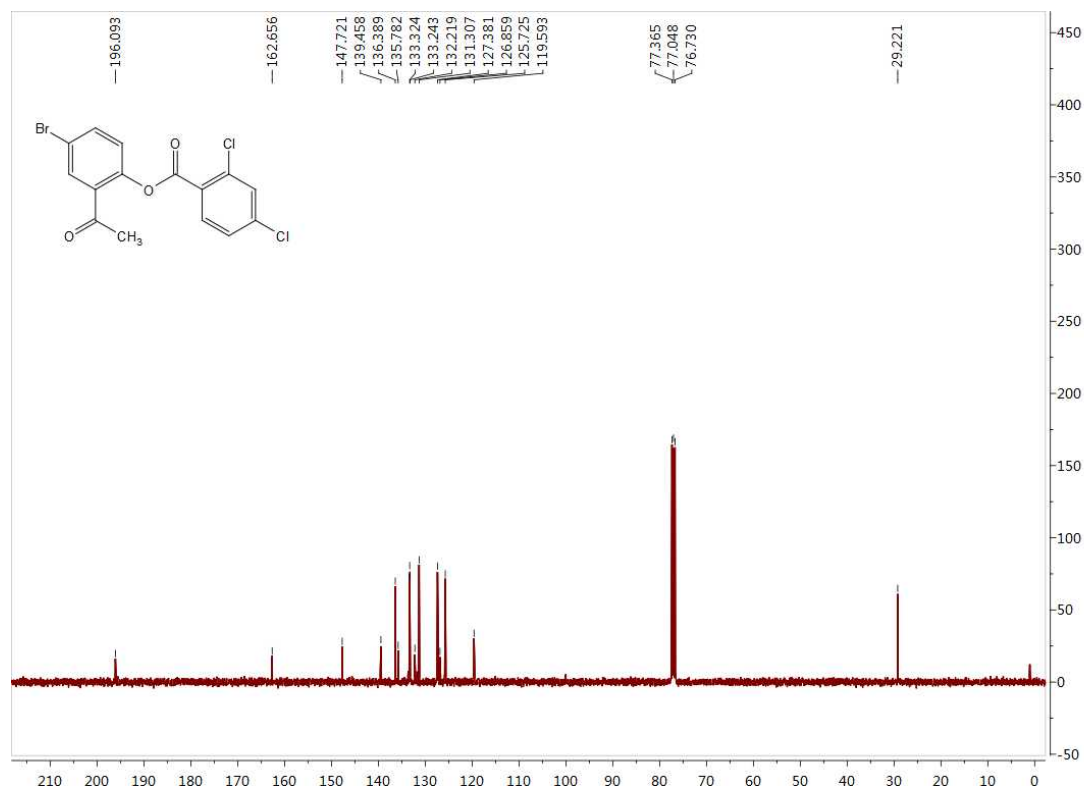
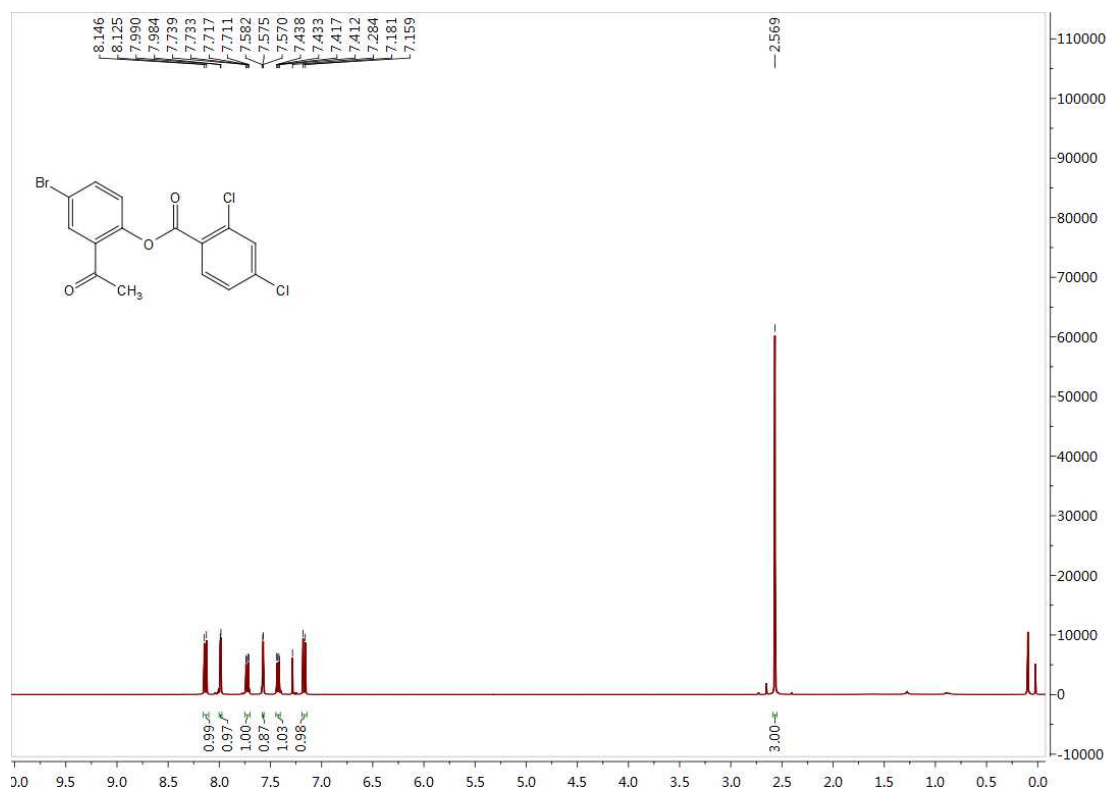
Data for **11-13**: white solid; yield 89 %; m.p. 114-115 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.14 (d, *J* = 8.5 Hz, 1H), 7.60-7.55 (m, 2H), 7.43 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H), 7.33 (m, 1H), 7.26 (dd, *J* = 8.9 Hz, 4.7 Hz, 1H), 2.57 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 196.13, 163.00, 161.28, 158.82, 144.61, 139.39, 135.74, 133.28, 131.89, 131.29, 127.37, 126.99, 125.59 (d), 120.37 (d), 117.02 (d), 29.18; HRMS: calcd for C<sub>15</sub>H<sub>9</sub>Cl<sub>2</sub>FO<sub>3</sub> [M+H]<sup>+</sup> 326.9913, found 326.9991.



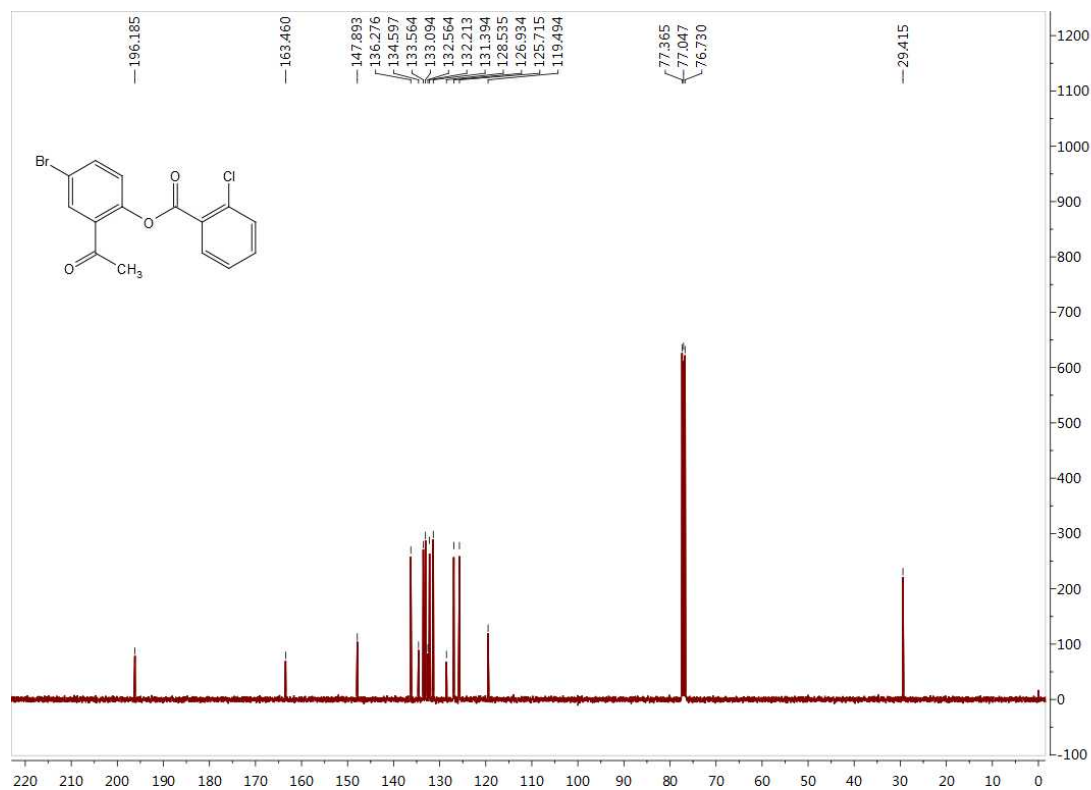
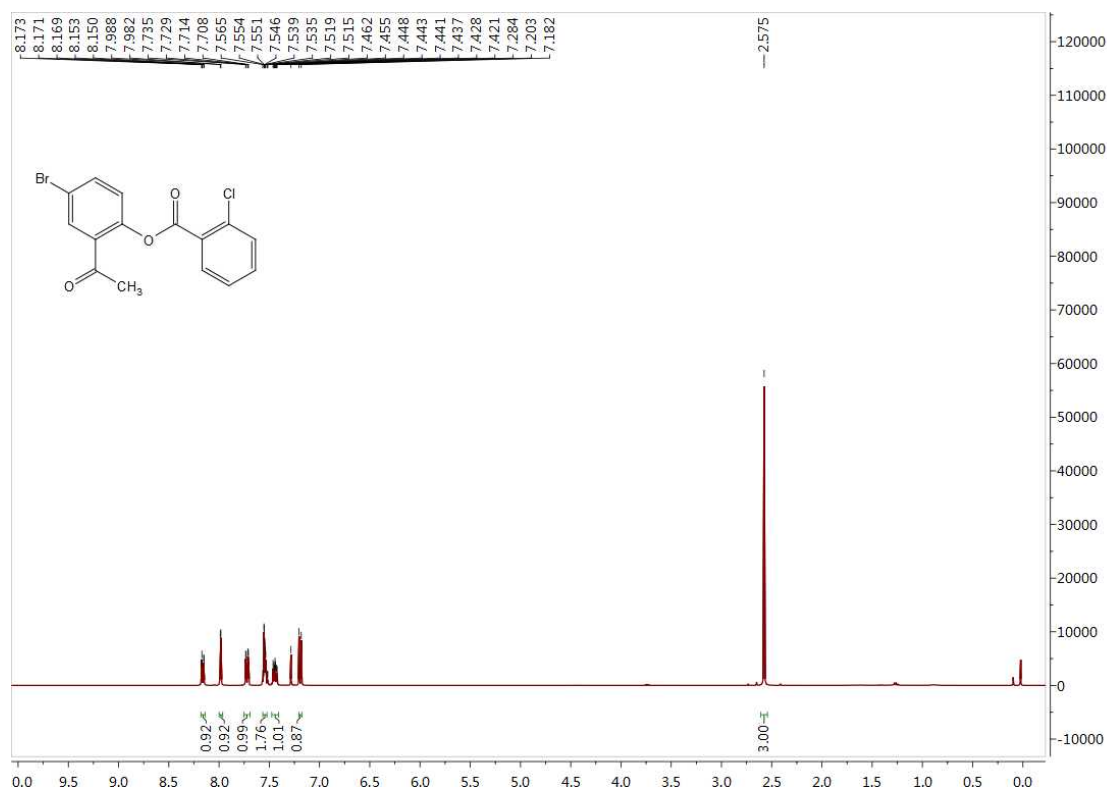
Data for **11-14**: white solid; yield 86 %; m.p. 68-70 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.17 (d, *J* = 8.1 Hz, 1H), 7.59-7.48 (m, 3H), 7.47-7.39 (m, 1H), 7.35-7.19 (m, 2H), 2.57 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 195.16, 162.75, 160.19, 157.73, 143.71, 133.48, 132.45, 131.12, 130.32, 127.60, 125.88, 124.53 (d), 119.23 (d), 115.78 (d), 28.32; HRMS: calcd for C<sub>15</sub>H<sub>10</sub>ClFO<sub>3</sub> [M+H]<sup>+</sup> 293.0303, found 293.0381.



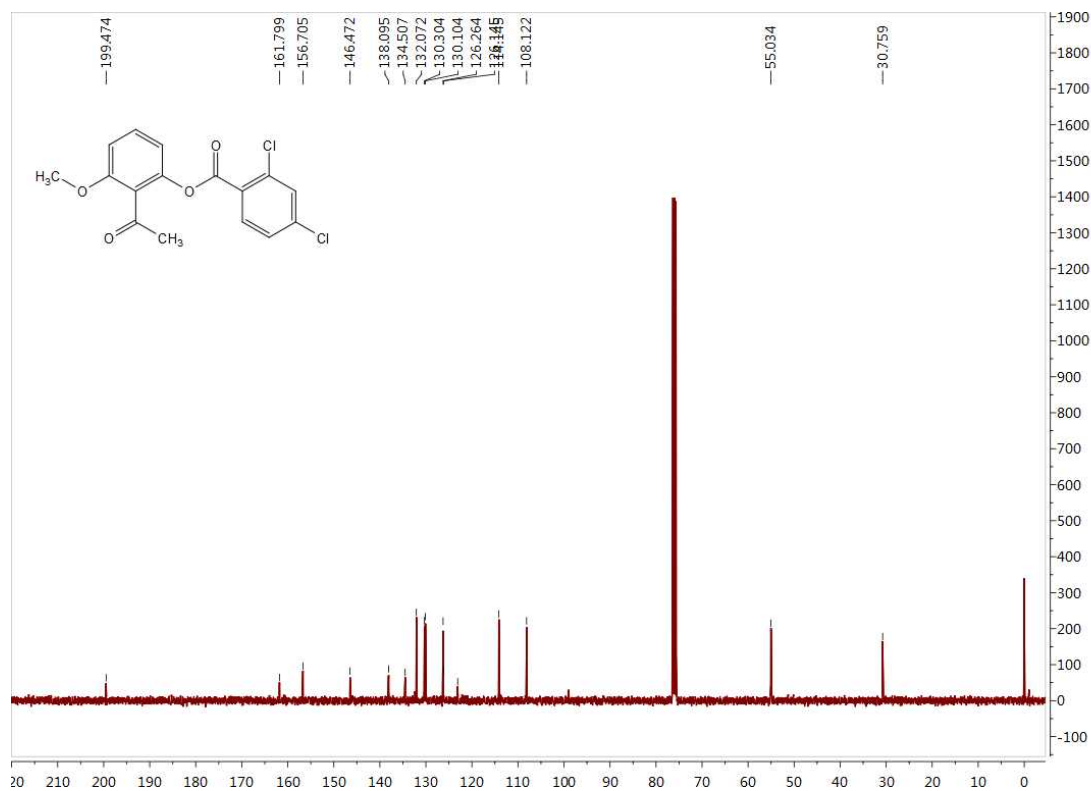
Data for **11-15**: white solid; yield 90 %; m.p. 99-101 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.14 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 2.4 Hz, 1H), 7.72 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.57 (d, *J* = 2.0 Hz, 1H), 7.43 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.17 (d, *J* = 8.6 Hz, 1H), 2.57 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 196.09, 162.66, 147.72, 139.46, 136.39, 135.78, 133.32, 133.24, 132.22, 131.31, 127.38, 126.86, 125.73, 119.59, 119.59, 29.22; HRMS: calcd for C<sub>15</sub>H<sub>9</sub>BrCl<sub>2</sub>O<sub>3</sub> [M+H]<sup>+</sup> 386.9112, found 386.9189.



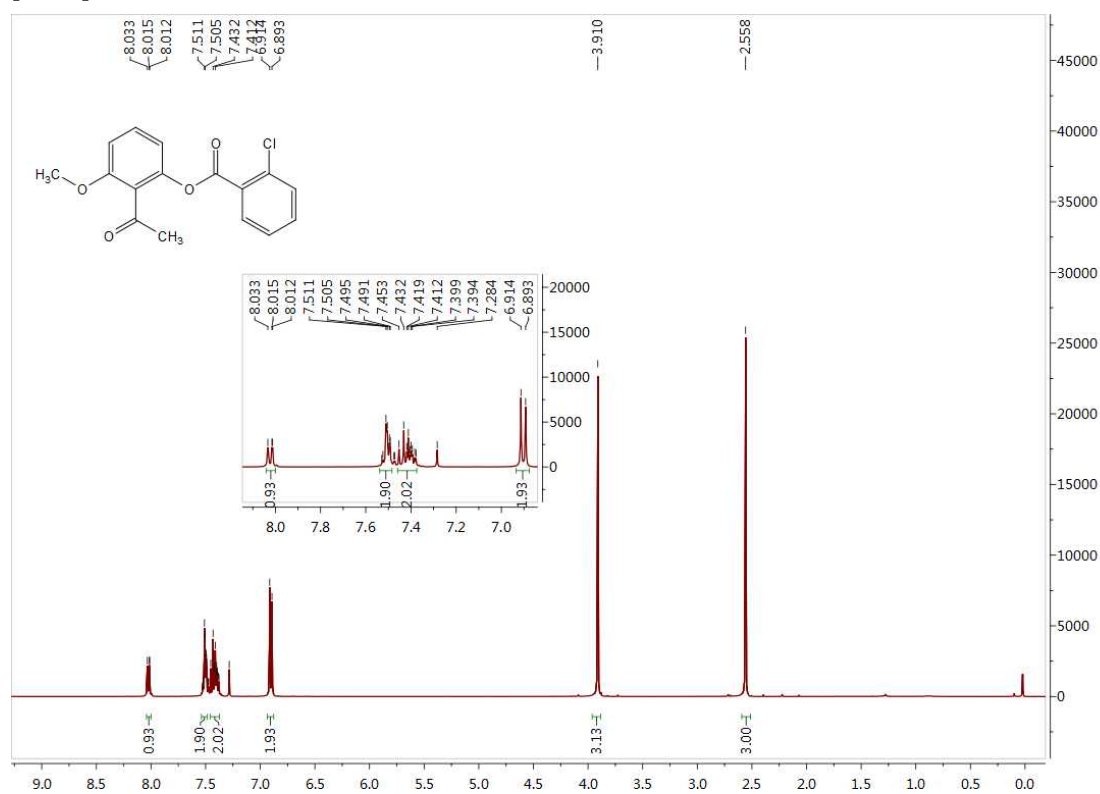
Data for **11-16**: light yellow solid; yield 87 %; m.p. 79-80 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.18-8.13 (m, 1H), 7.98 (d, *J* = 2.4 Hz, 1H), 7.72 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.56-7.53 (m, 2H), 7.44 (m, 1H), 7.19 (d, *J* = 8.6 Hz, 1H), 2.57 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 196.19, 163.46, 147.89, 136.28, 134.60, 133.56, 133.09, 132.56, 132.21, 131.39, 128.53, 126.93, 125.72, 119.49, 29.41; HRMS: calcd for C<sub>15</sub>H<sub>10</sub>BrClO<sub>3</sub> [M+H]<sup>+</sup> 352.9502, found 352.9580.



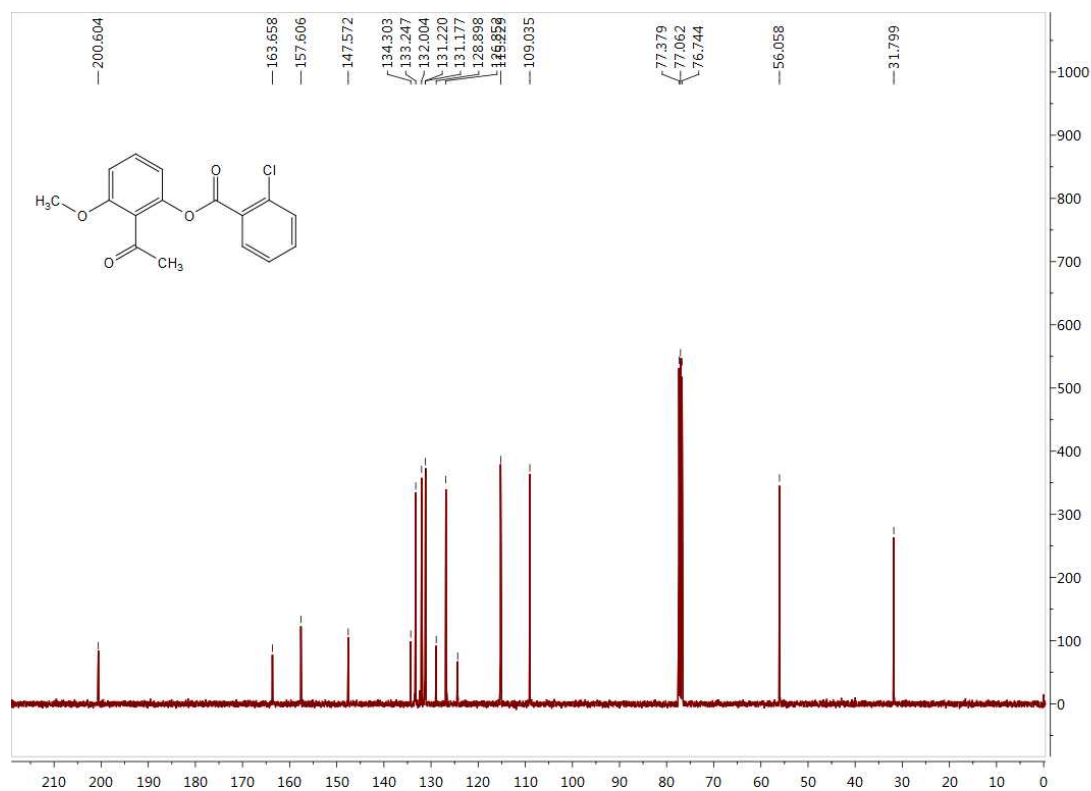
Data for **11-17**: white solid; yield 83 %; m.p. 84-85 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.98 (d, *J* = 8.4 Hz, 1H), 7.52 (d, *J* = 2.0 Hz, 1H), 7.45-7.31 (m, 1H), 6.94-6.79 (m, 2H), 3.90 (s, 3H), 2.53 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 199.47, 161.80, 156.70, 146.47, 138.09, 134.51, 132.07, 130.30, 130.10, 126.20 (d), 123.10, 114.15, 108.12, 55.03, 30.76; HRMS: calcd for C<sub>16</sub>H<sub>12</sub>Cl<sub>2</sub>O<sub>4</sub> [M+H]<sup>+</sup> 339.0113, found 339.0113.



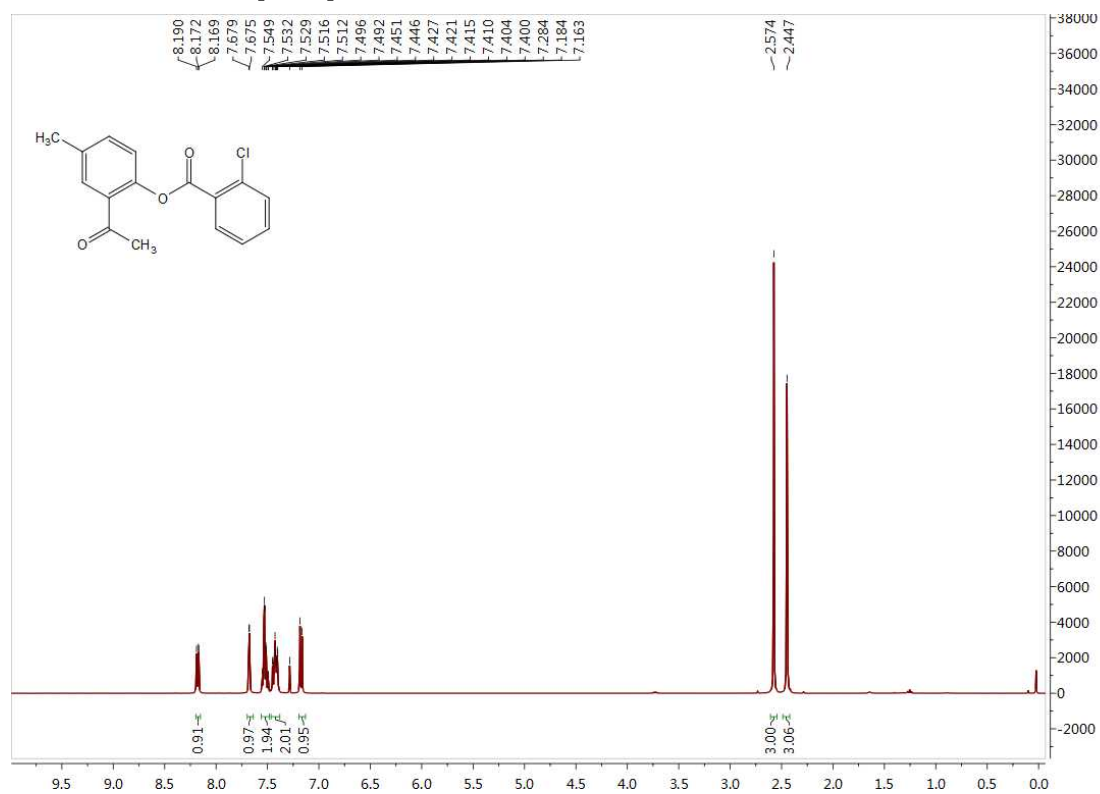
Data for **11-18**: white solid; yield 91 %; m.p. 64-65 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.28-7.82 (m, 1H), 7.53-7.47 (m, 2H), 7.46-7.37 (m, 2H), 6.90 (d,  $J = 8.3$  Hz, 2H), 3.91 (s, 3H), 2.56 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 200.60, 163.66, 157.61, 147.57, 134.30, 133.25, 132.00, 131.22, 131.18, 128.90, 126.85, 124.35, 115.23, 109.04, 56.06, 31.80; HRMS: calcd for  $\text{C}_{16}\text{H}_{13}\text{ClO}_4$   $[\text{M}+\text{H}]^+$  305.0502, found 305.0579.

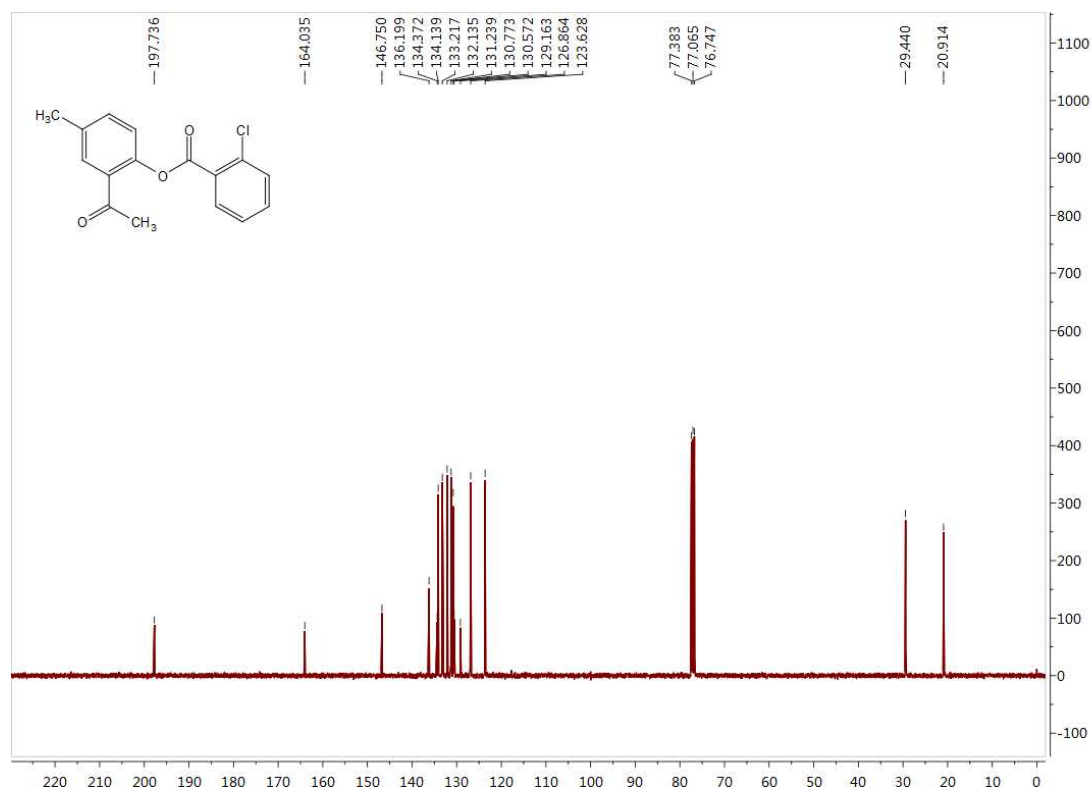




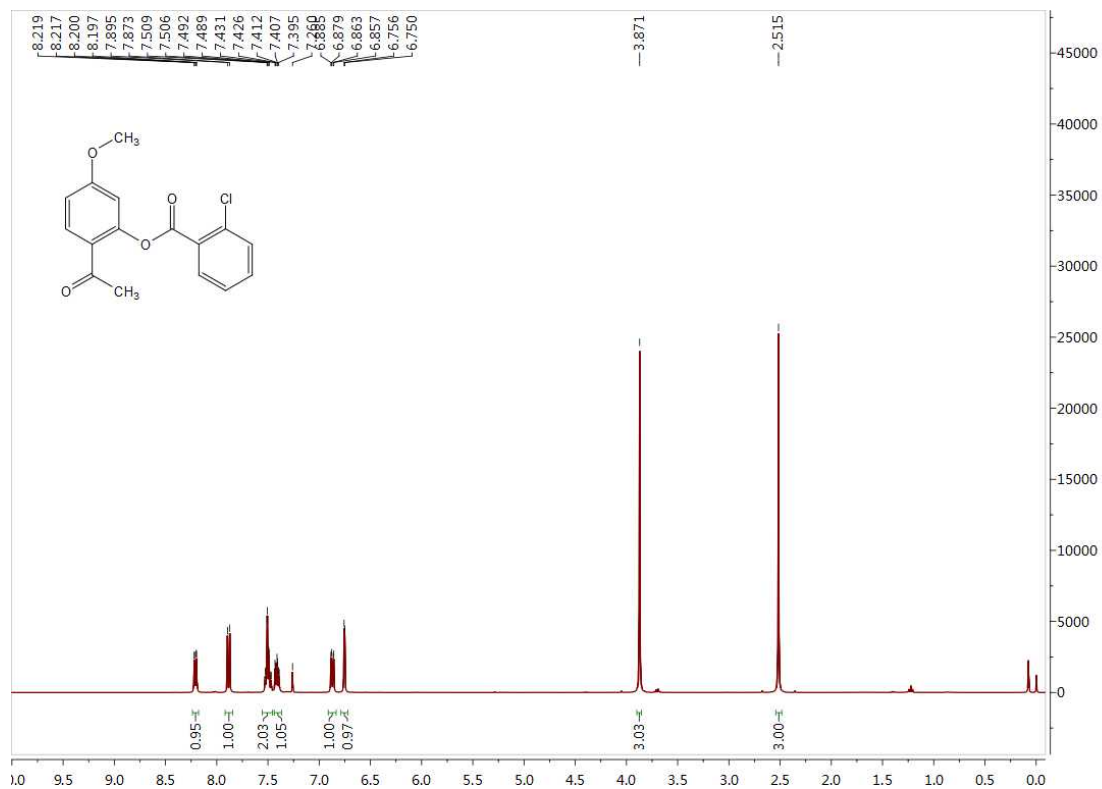


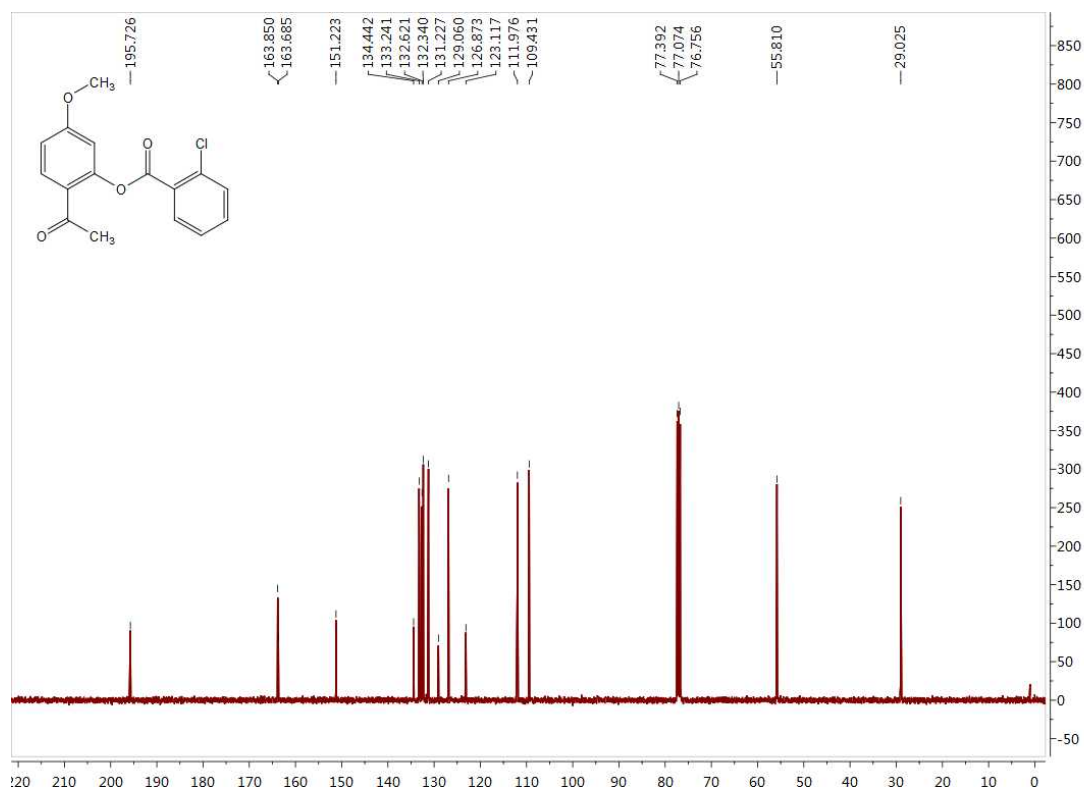
Data for **11-19**: light yellow solid; yield 93 %; m.p. 80-81 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.23-8.11 (m, 1H), 7.68 (d, *J* = 1.5 Hz, 1H), 7.52 (m, 2H), 7.42 (m, 2H), 7.17 (d, *J* = 8.2 Hz, 1H), 2.57 (s, 3H), 2.45 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 197.74, 164.03, 146.75, 136.20, 134.37, 134.14, 133.22, 132.13, 131.24, 130.77, 130.57, 129.16, 126.86, 123.63, 29.44, 20.91; HRMS: calcd for C<sub>16</sub>H<sub>13</sub>ClO<sub>3</sub> [M+H]<sup>+</sup> 289.0553, found 289.0624.





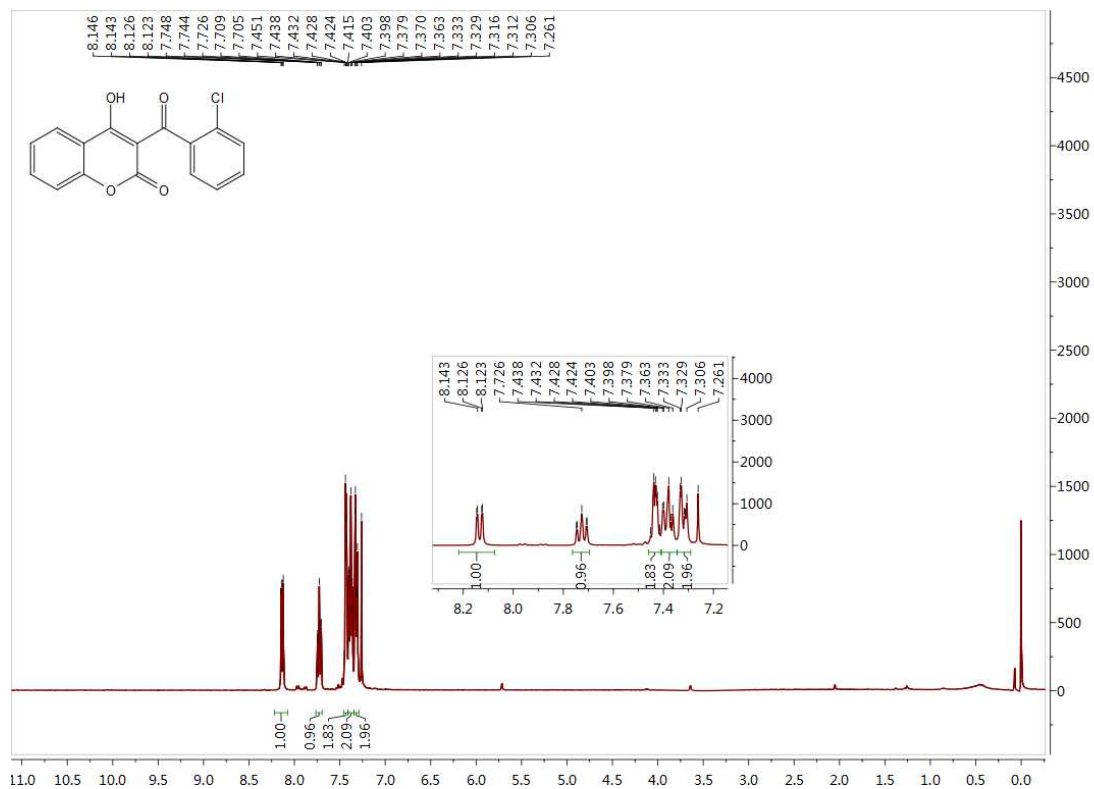
Data for **11-20**: white solid; yield 88.4%; m.p. 74-76 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.21 (dd,  $J = 7.8$  Hz, 1.0 Hz, 1H), 7.88 (d,  $J = 8.8$  Hz, 1H), 7.49 (m, 1H), 7.43-7.35 (m, 2H), 6.87 (dd,  $J = 8.8$  Hz, 2.5 Hz, 1H), 6.75 (d,  $J = 2.5$  Hz, 1H), 3.87 (s, 3H), 2.52 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.73, 163.85, 163.68, 151.22, 134.44, 133.24, 132.62, 132.34, 131.23, 129.06, 126.87, 123.12, 111.98, 109.43, 55.81, 29.03; HRMS: calcd for  $\text{C}_{16}\text{H}_{13}\text{ClO}_4$   $[\text{M}+\text{H}]^+$  305.0502, found 305.0581.

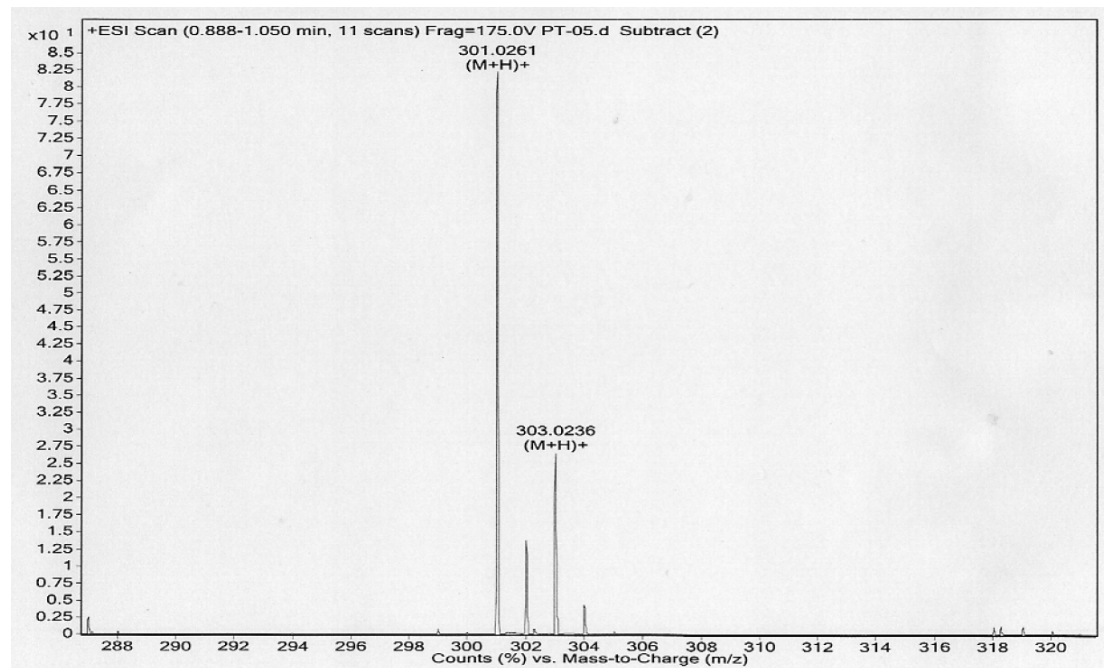
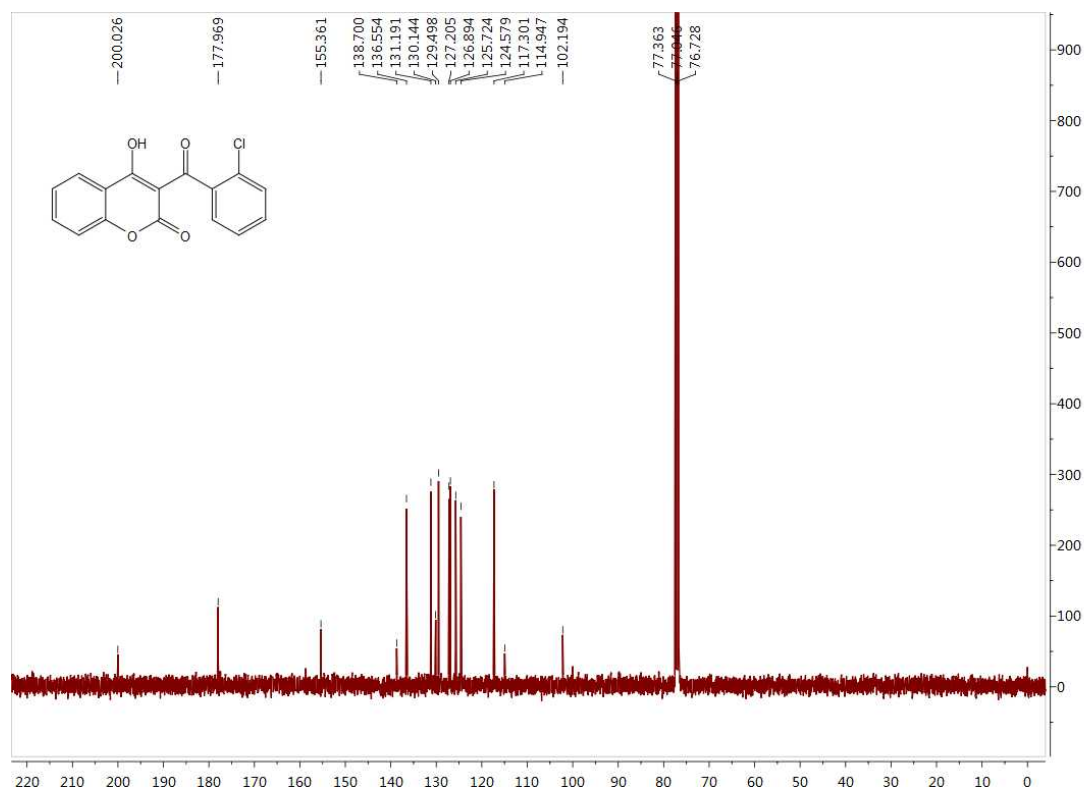




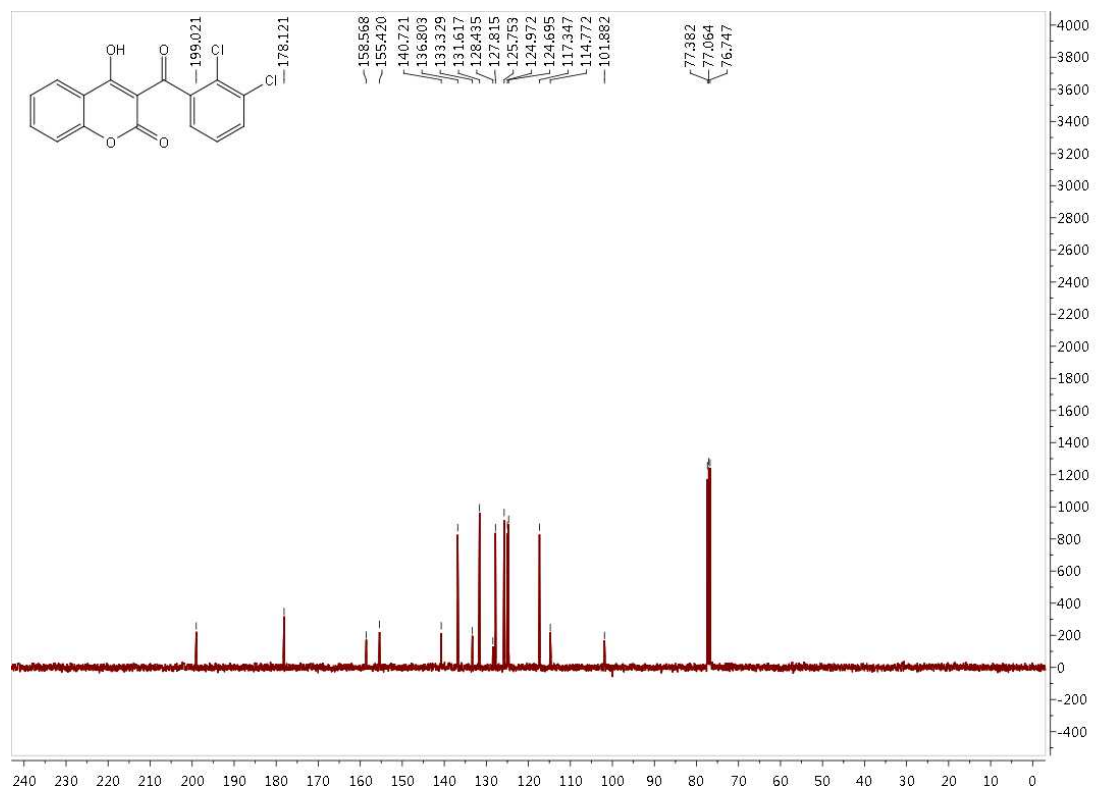
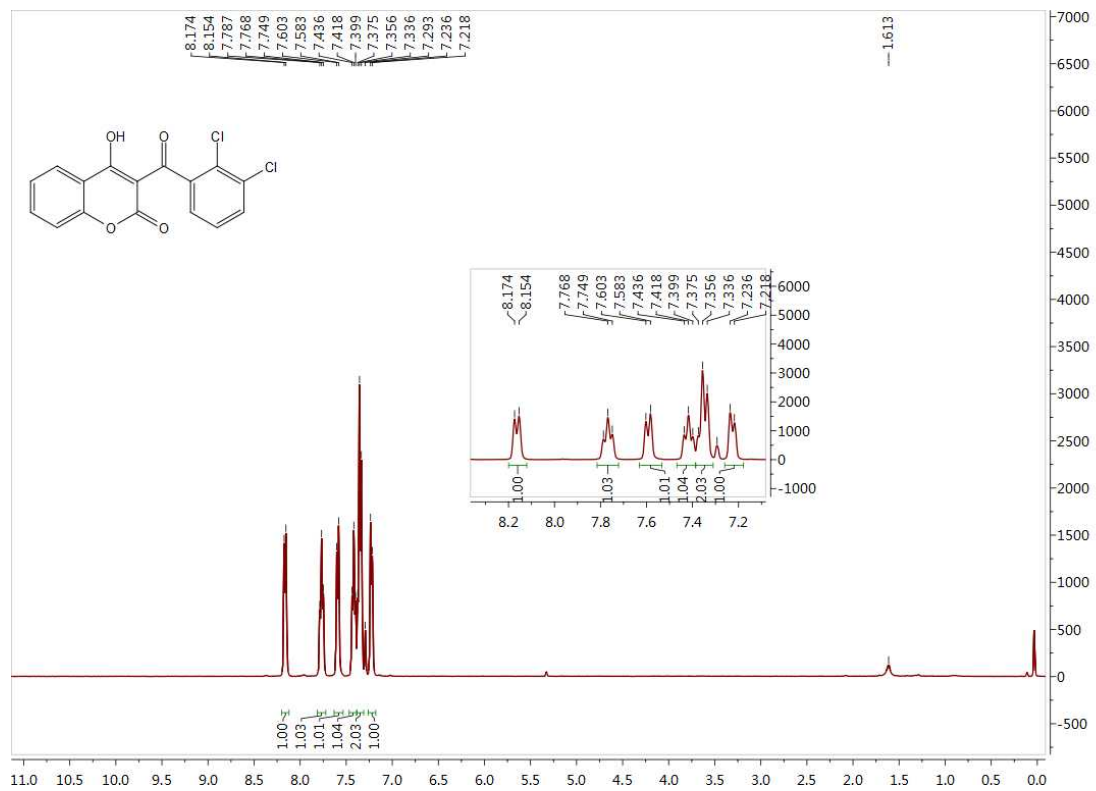
**Analytical Data for products 12-1 to 12-20:**

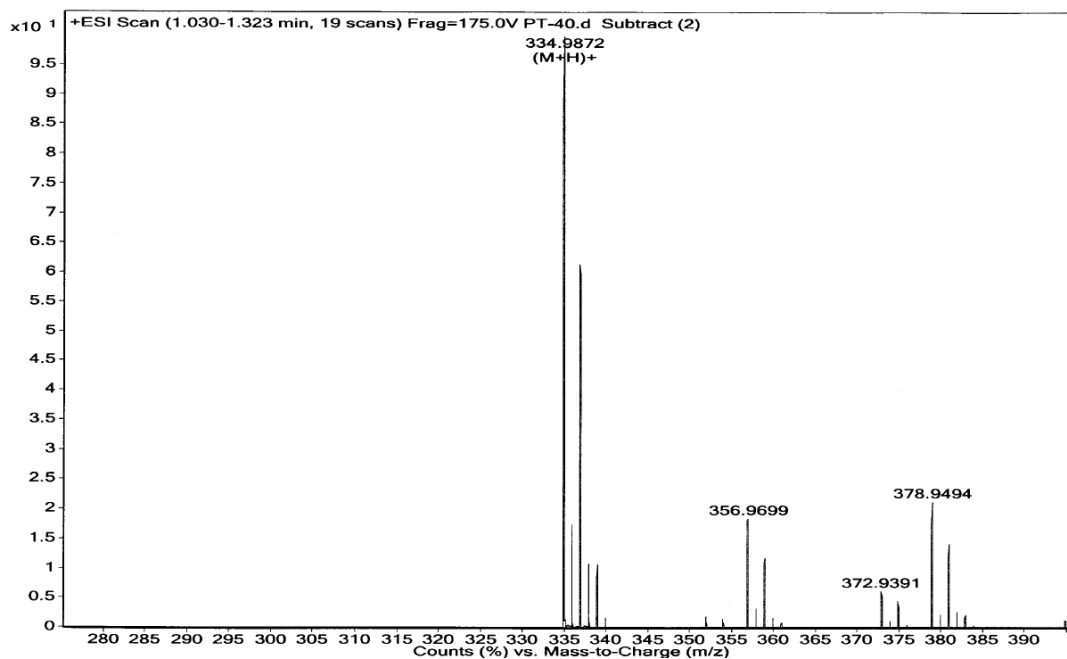
Data for **12-1**<sup>[1]</sup>: white solid; yield 61%; m.p. 126-127 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.13 (dd,  $J = 8.0$  Hz, 1.4 Hz, 1H), 7.72 (m, 1H), 7.45-7.41 (m, 2H), 7.40-7.36 (m, 2H), 7.33-7.30 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 200.02, 177.97, 155.36, 138.70, 136.55, 131.19, 130.14, 129.50, 127.20, 126.89, 125.72, 124.58, 117.30, 114.94, 102.19; HRMS: calcd for  $\text{C}_{16}\text{H}_9\text{ClO}_4$   $[\text{M}+\text{H}]^+$  301.0189, found 301.0261.



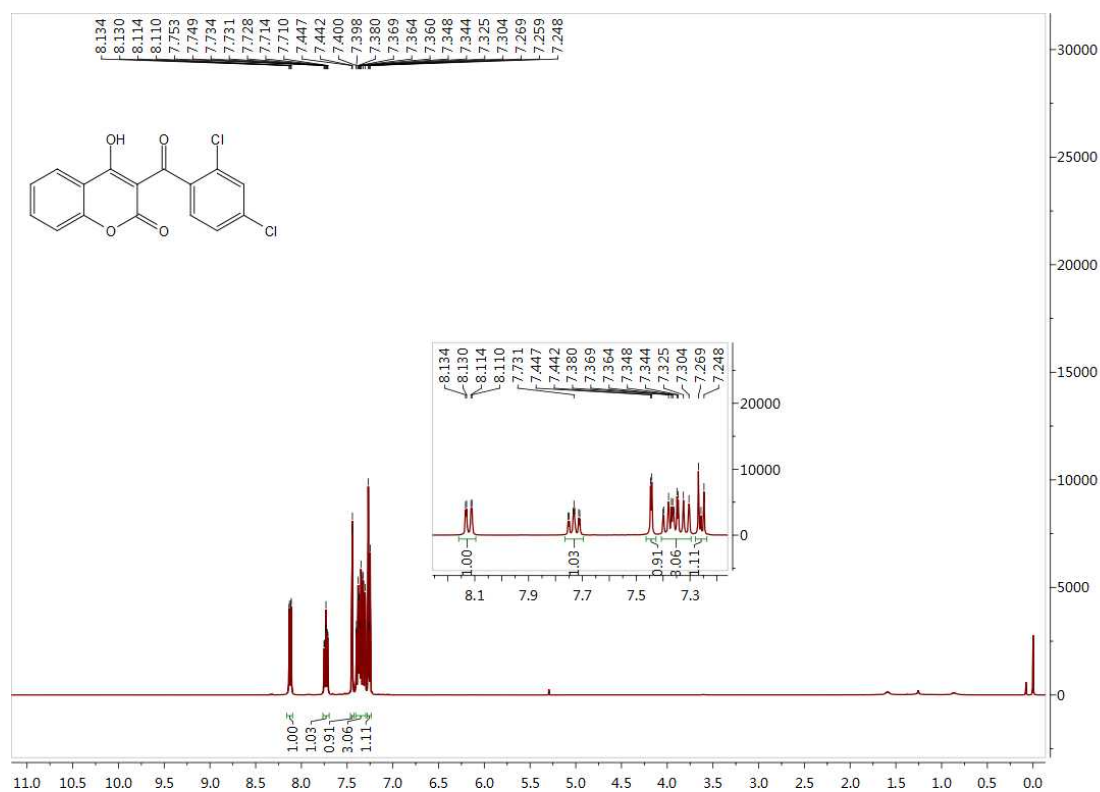


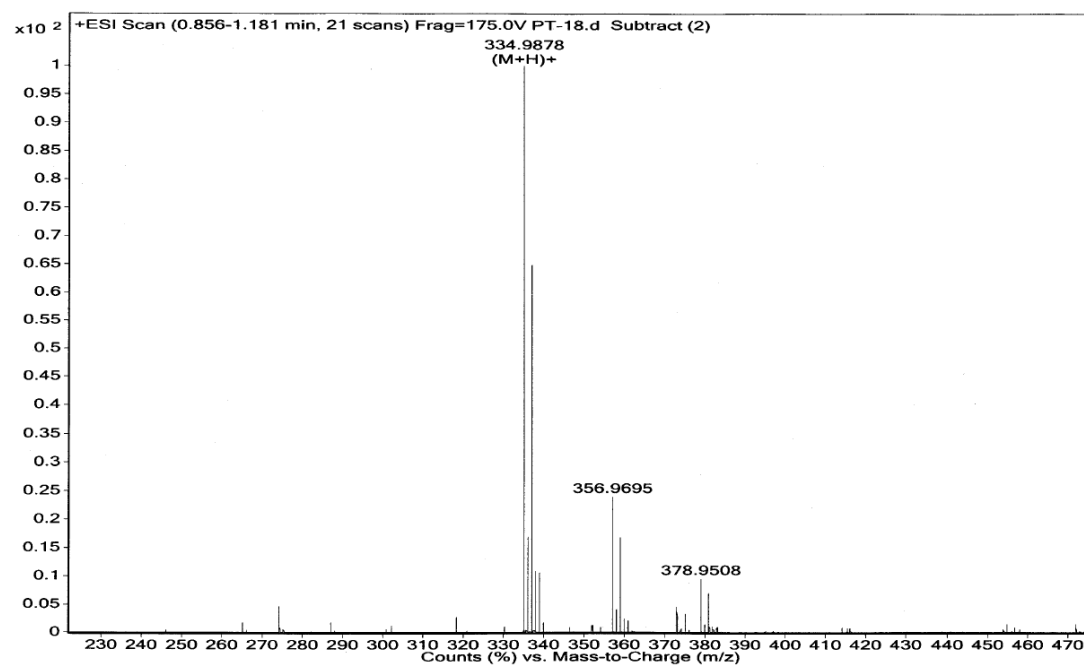
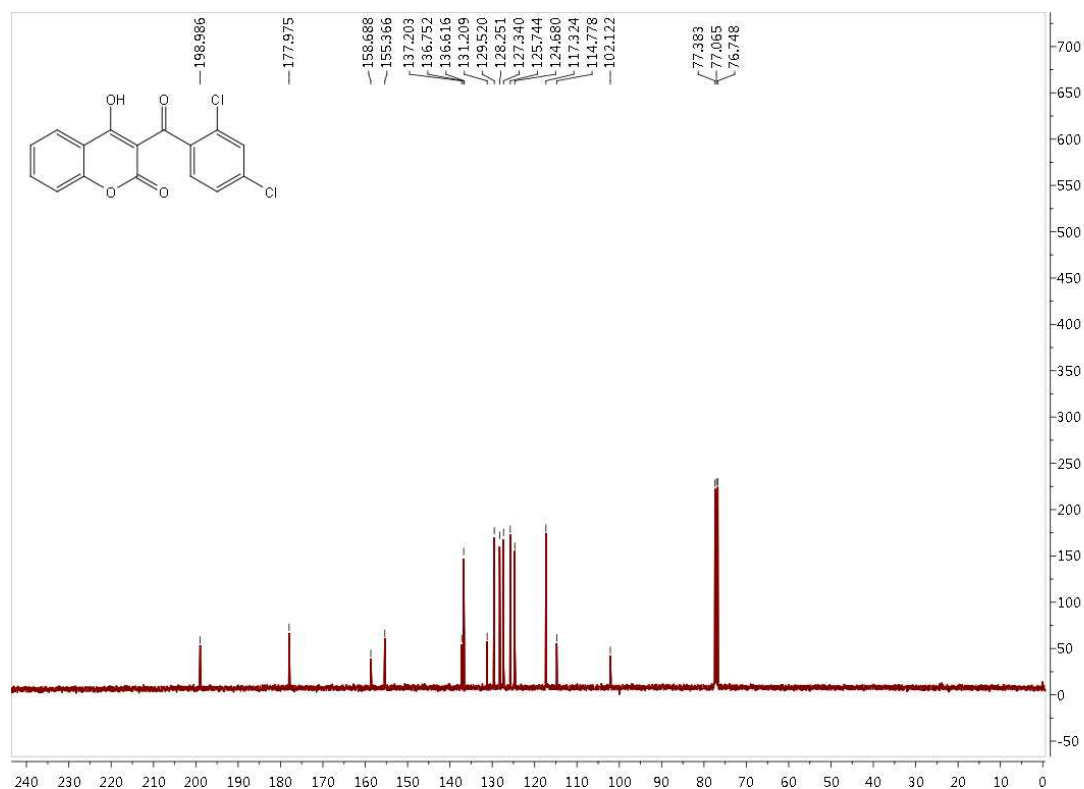
Data for **12-2**: light yellow solid; yield 68.0%; m.p. 154-156 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.16 (d,  $J = 7.8$  Hz, 1H), 7.77 (t,  $J = 7.7$  Hz, 1H), 7.59 (d,  $J = 8.0$  Hz, 1H), 7.42 (t,  $J = 7.5$  Hz, 1H), 7.36 (t,  $J = 7.8$  Hz, 2H), 7.23 (d,  $J = 7.4$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 199.02, 178.12, 158.57, 155.42, 140.72, 136.80, 133.33, 131.62, 128.43, 127.81, 125.75, 124.97, 124.69, 117.35, 114.77, 101.88; HRMS: calcd for  $\text{C}_{16}\text{H}_8\text{Cl}_2\text{O}_4$   $[\text{M}+\text{H}]^+$  334.9800, found 334.9872.



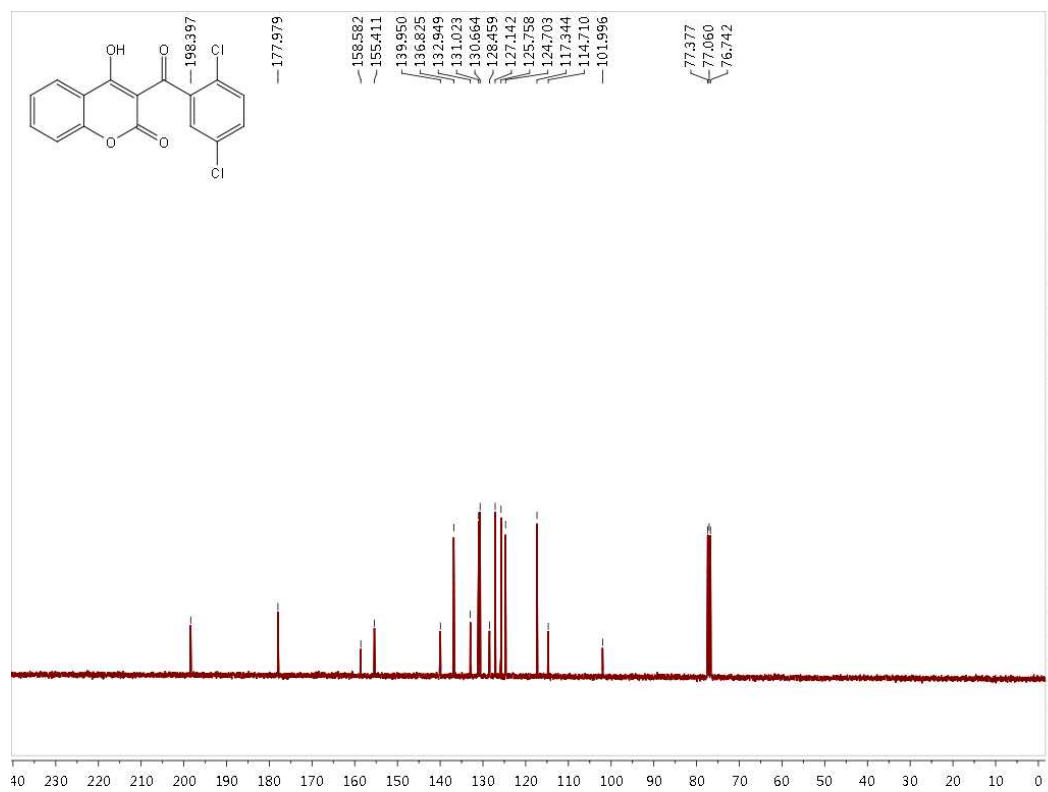
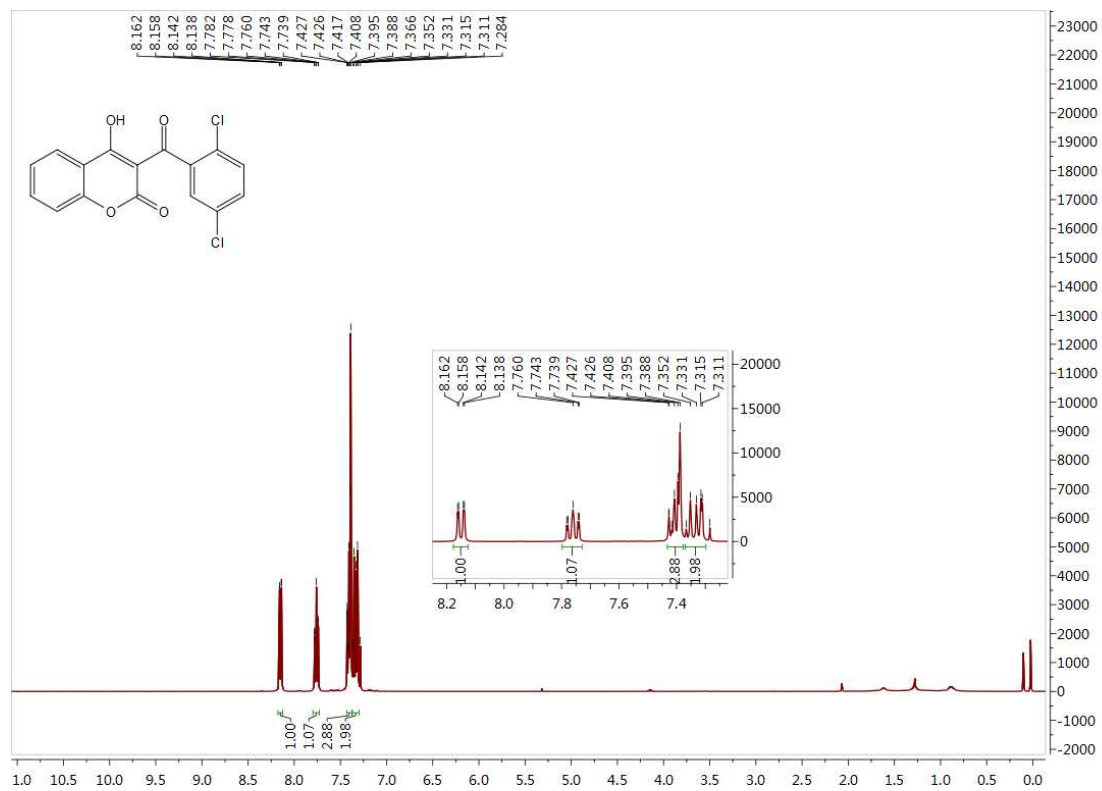


Data for **12-3**<sup>[1]</sup>: pale yellow solid; yield 70%; m.p. 186-187 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.12 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.77-7.69 (m, 1H), 7.44 (d, *J* = 1.9 Hz, 1H), 7.41-7.29 (m, 3H), 7.28-7.23 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 198.99, 177.97, 158.69, 155.37, 137.20, 136.75, 136.62, 131.21, 129.52, 128.25, 127.34, 125.74, 124.68, 117.32, 114.78, 102.12; HRMS: calcd for C<sub>16</sub>H<sub>8</sub>Cl<sub>2</sub>O<sub>4</sub> [M+H]<sup>+</sup> 334.9800, found 334.9878.

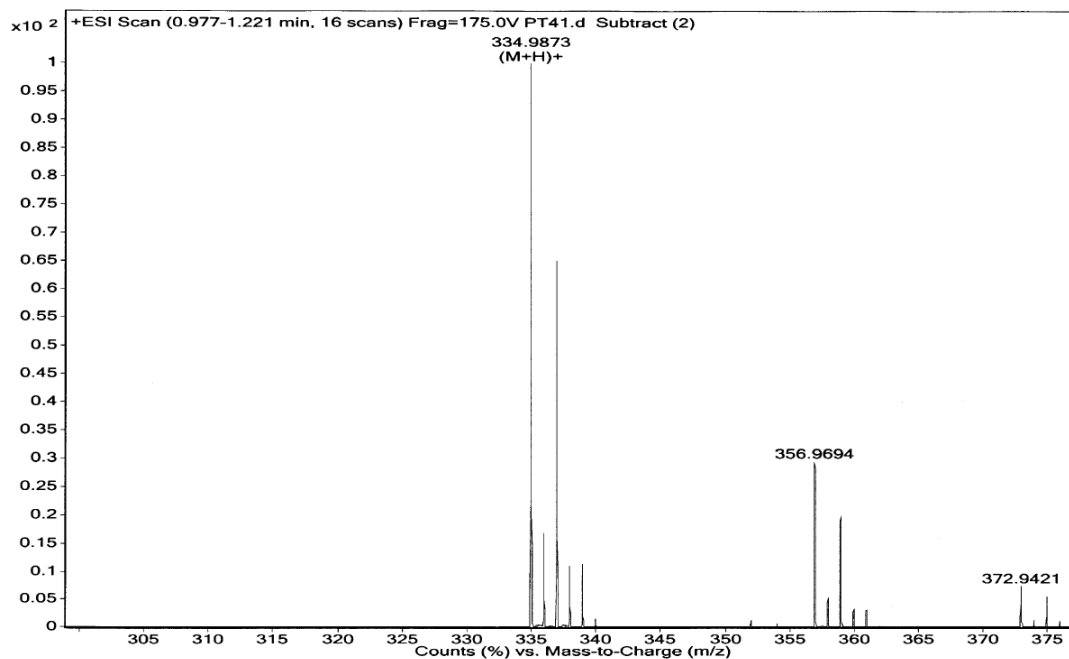




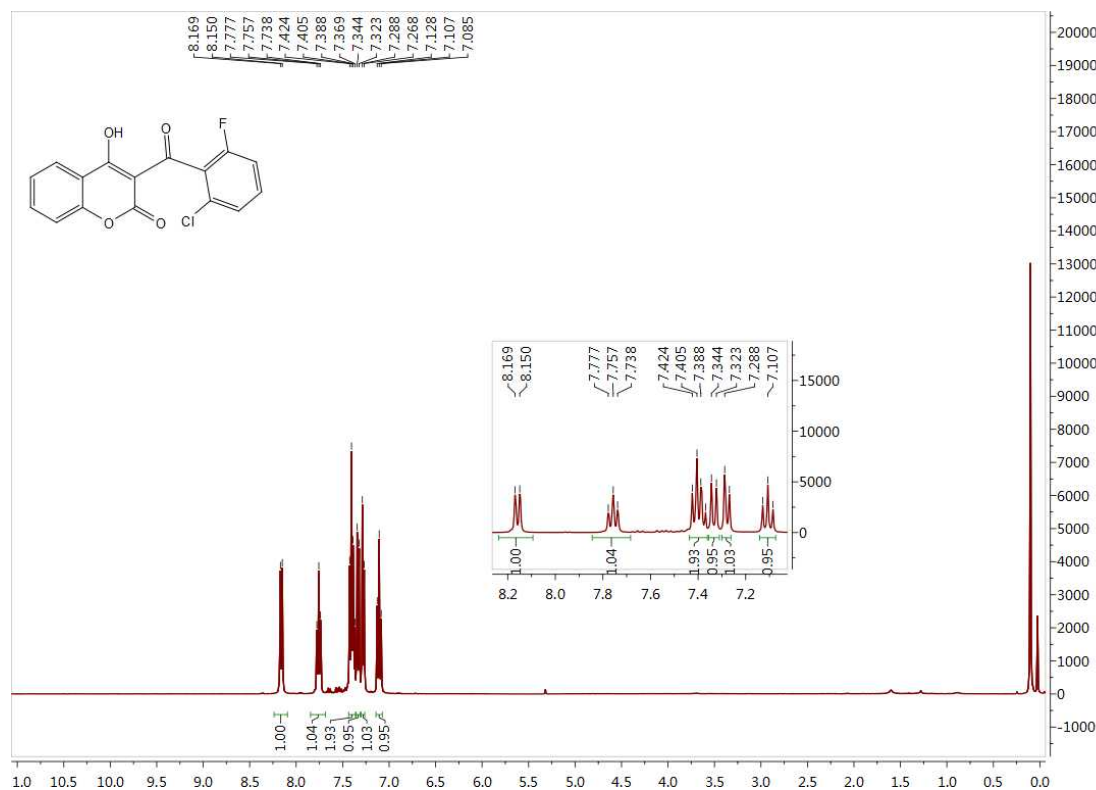
Data for **12-4**: pale yellow solid; yield 64%; m.p. 246-249 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.15 (dd, *J* = 8.0 Hz, 1.5 Hz, 1H), 7.80-7.73 (m, 1H), 7.45-7.37 (m, 3H), 7.37-7.30 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 198.40, 177.98, 158.58, 155.41, 139.95, 136.83, 132.95, 131.02, 130.66, 128.46, 127.14, 125.76, 124.70, 117.34, 114.71, 102.00; HRMS: calcd for C<sub>16</sub>H<sub>8</sub>Cl<sub>2</sub>O<sub>4</sub> [M+H]<sup>+</sup> 334.9800, found 334.9873.

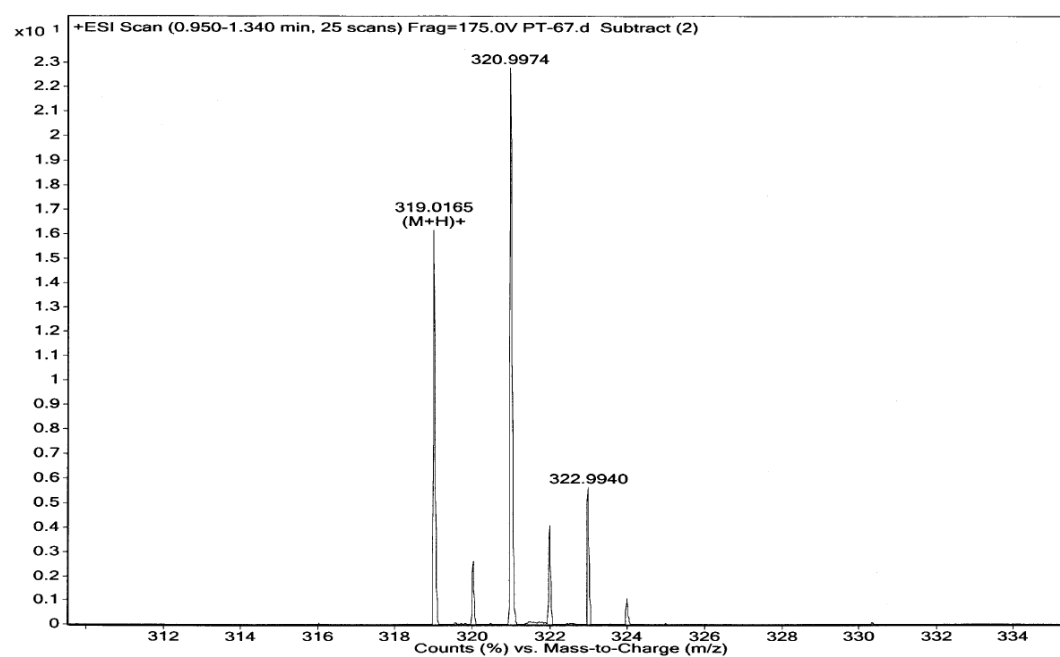
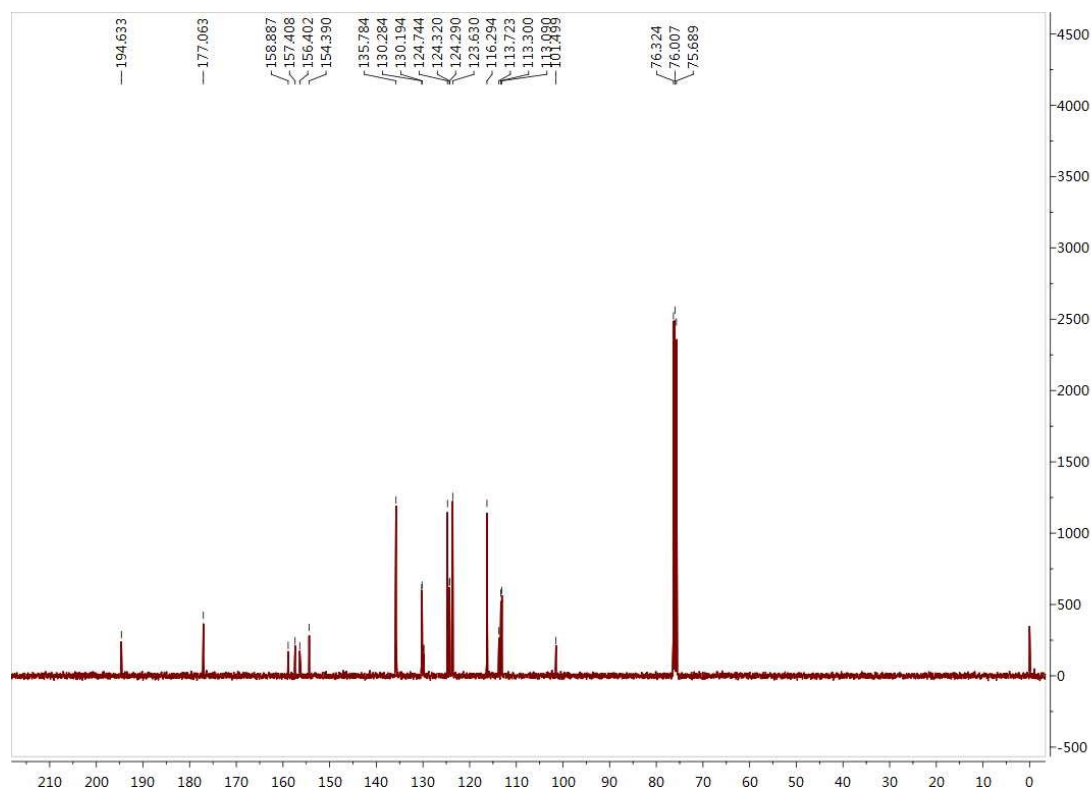




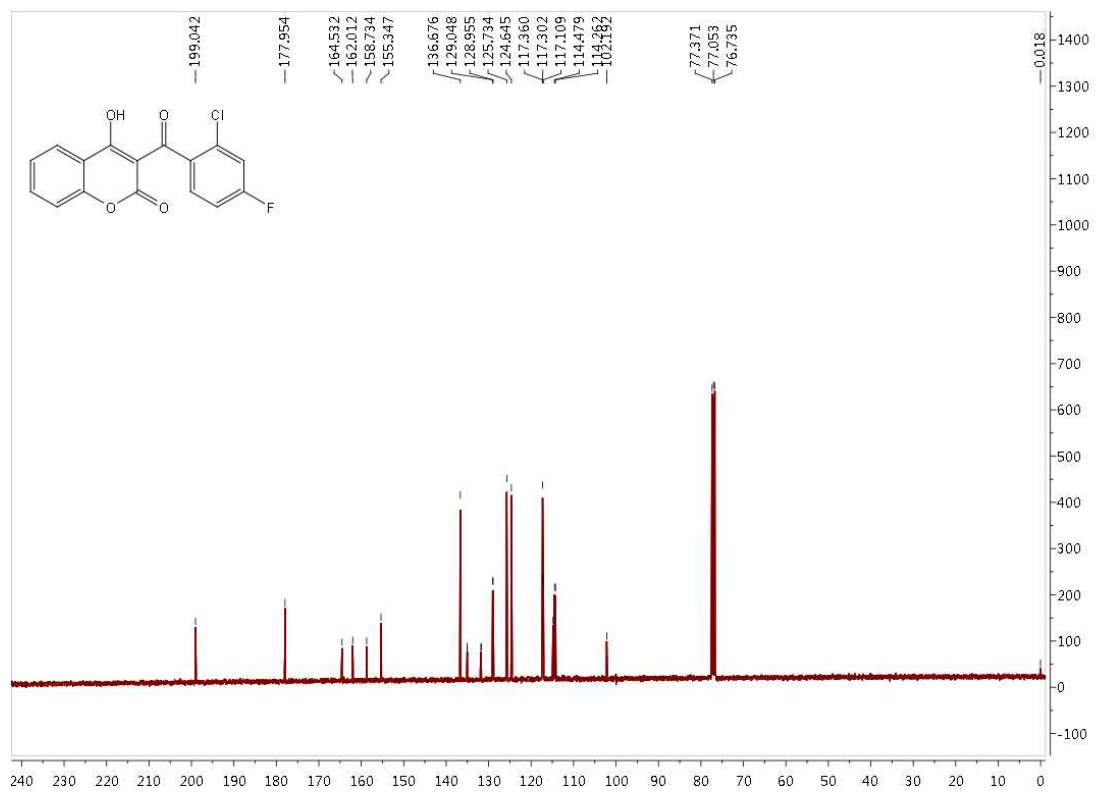
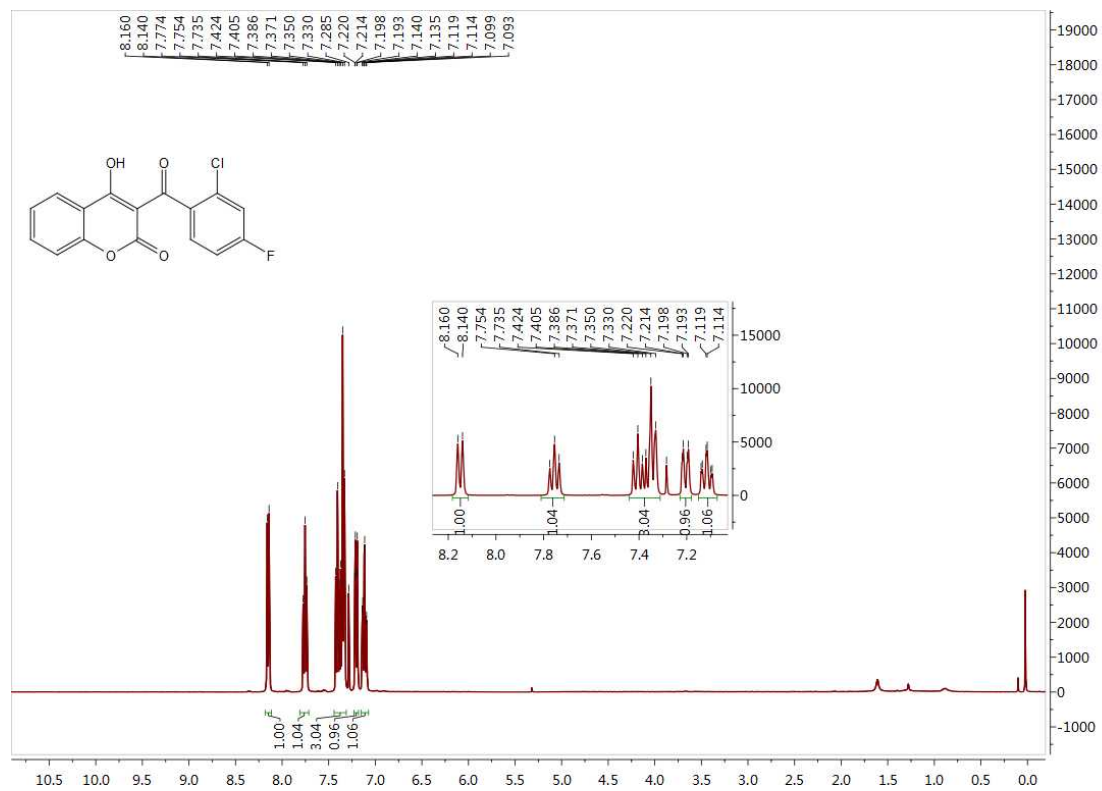


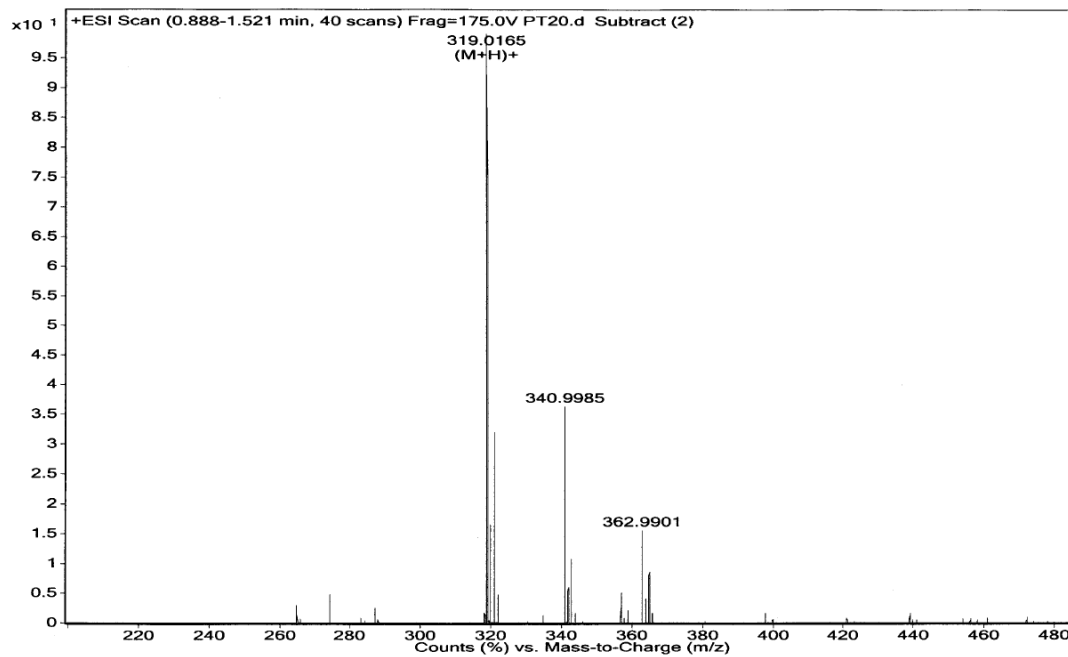
Data for **12-5**: pale yellow solid; yield 38%; m.p. 143-144 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.16 (d,  $J = 7.9$  Hz, 1H), 7.76 (t,  $J = 7.8$  Hz, 1H), 7.40 (dd,  $J = 14.4$  Hz, 7.9 Hz, 2H), 7.33 (d,  $J = 8.4$  Hz, 1H), 7.28 (d,  $J = 7.9$  Hz, 1H), 7.11 (t,  $J = 8.6$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 194.63, 177.06, 158.89, 157.41, 156.40, 154.39, 135.78, 130.24 (d), 129.83 (d), 124.74, 124.30 (d), 123.63, 116.29, 113.72, 113.20 (d), 101.50; HRMS: calcd for  $\text{C}_{16}\text{H}_8\text{ClFO}_4$   $[\text{M}+\text{H}]^+$  319.0095, found 319.0165.



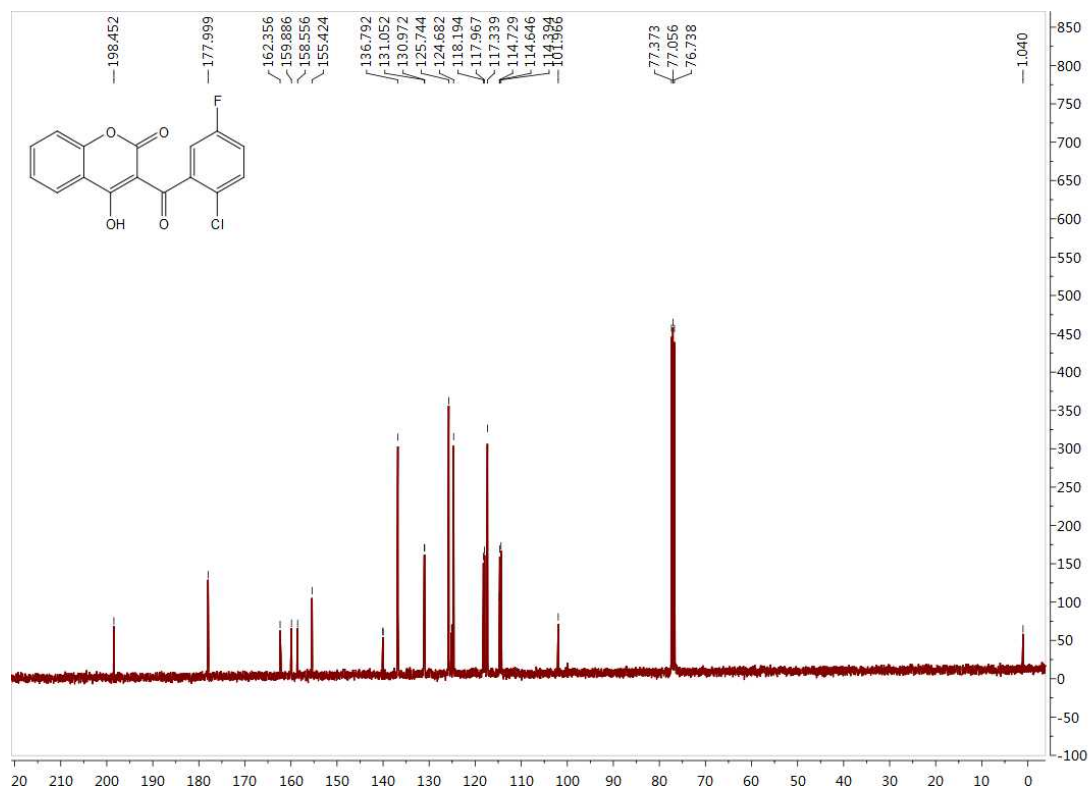
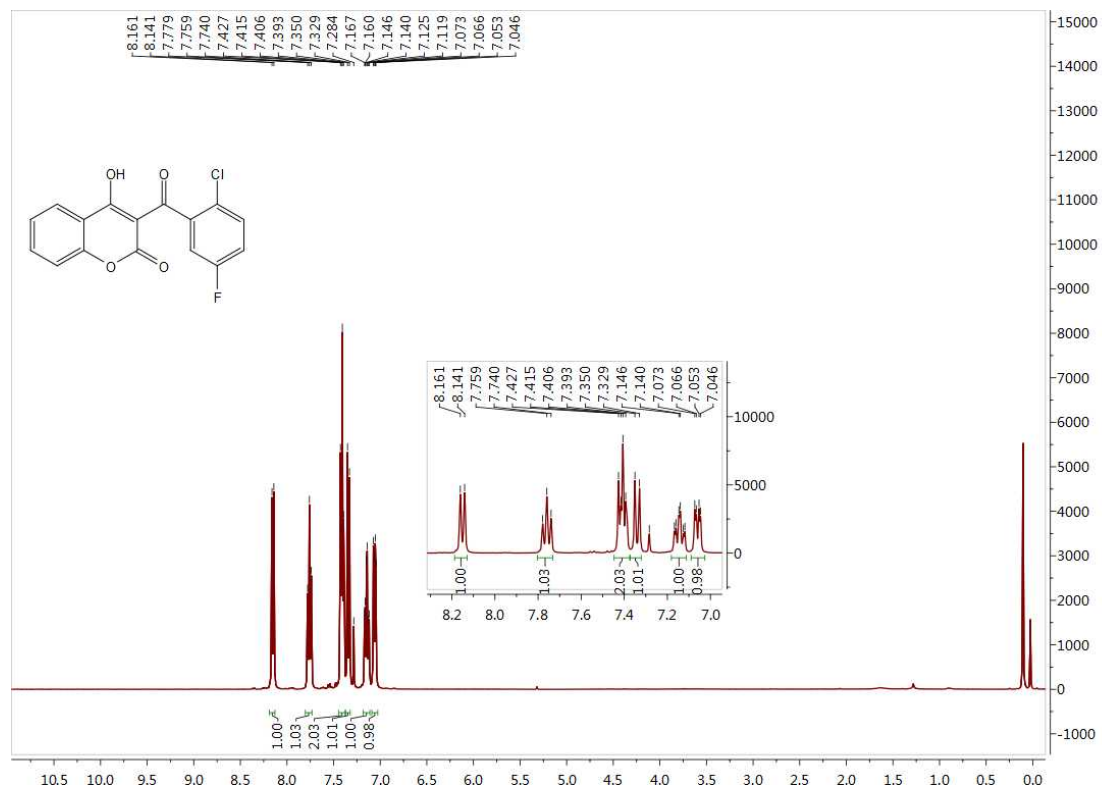


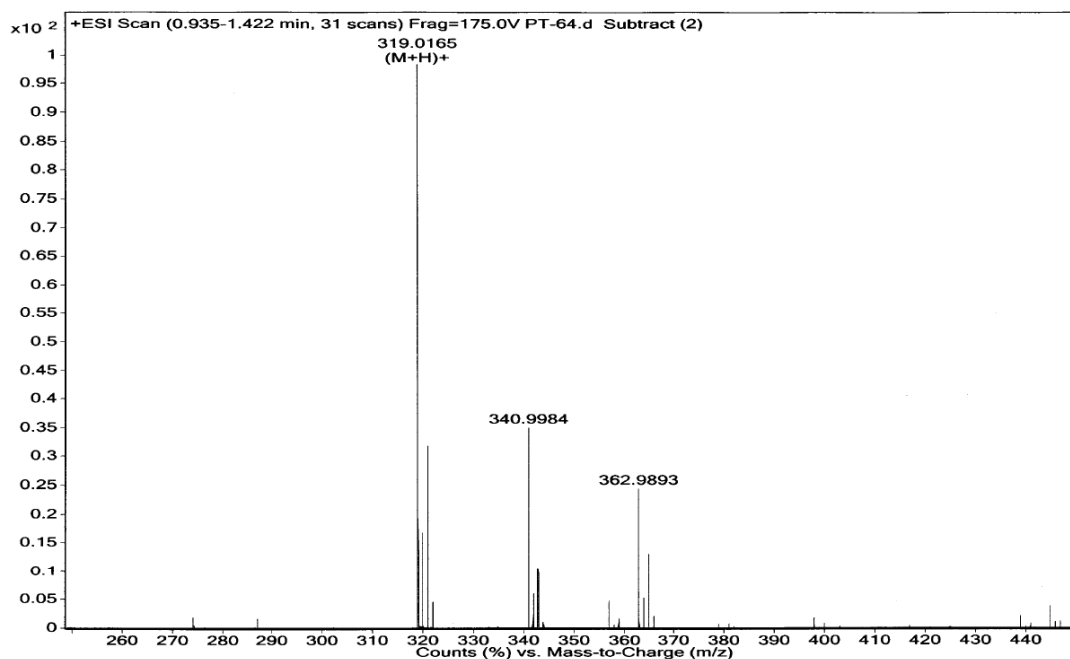
Data for **12-6**: pale yellow solid; yield 71%; m.p. 174-176 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.15 (d,  $J = 8.0$  Hz, 1H), 7.75 (t,  $J = 7.8$  Hz, 1H), 7.42-7.33 (m, 3H), 7.21 (dd,  $J = 8.5$  Hz, 2.0 Hz, 1H), 7.14-7.09 (td,  $J = 8.3$  Hz, 2.1 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 199.04, 177.95, 164.53, 162.01, 158.73, 155.35, 136.68, 135.03 (d), 131.79 (d), 129.00 (d), 125.73, 124.64, 117.26 (d), 114.83, 114.37 (d), 102.19; HRMS: calcd for  $\text{C}_{16}\text{H}_8\text{ClFO}_4$   $[\text{M}+\text{H}]^+$  319.0095, found **319.0165**.



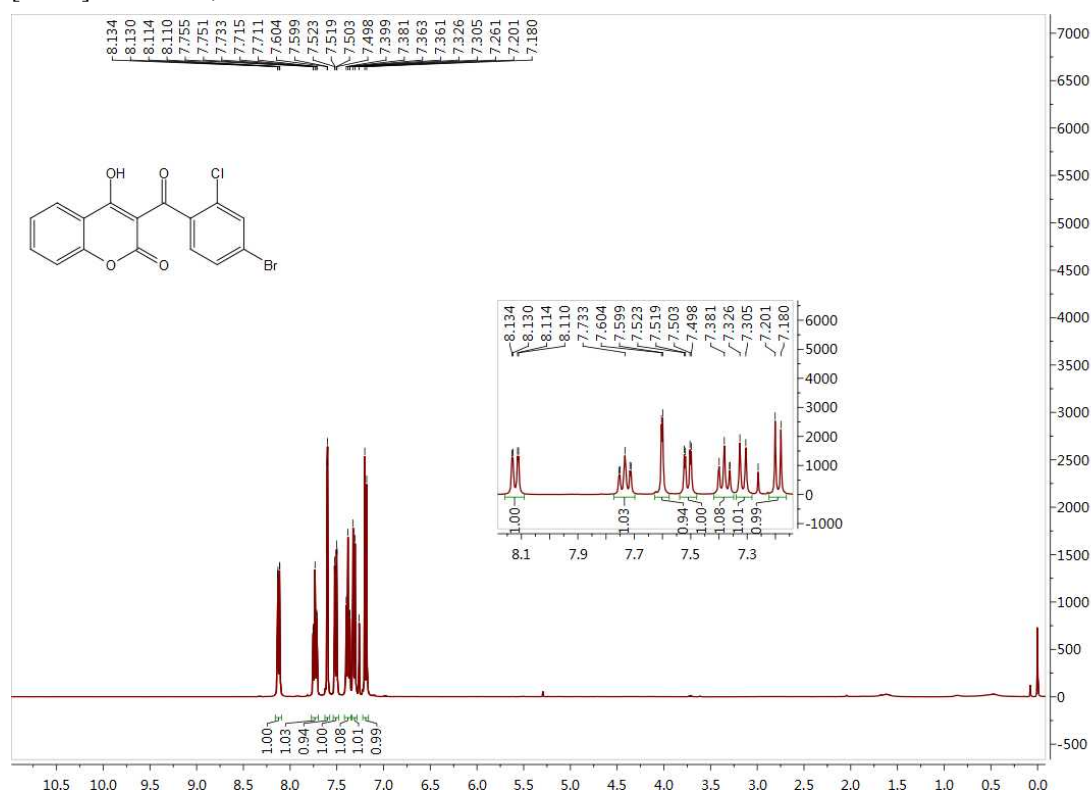


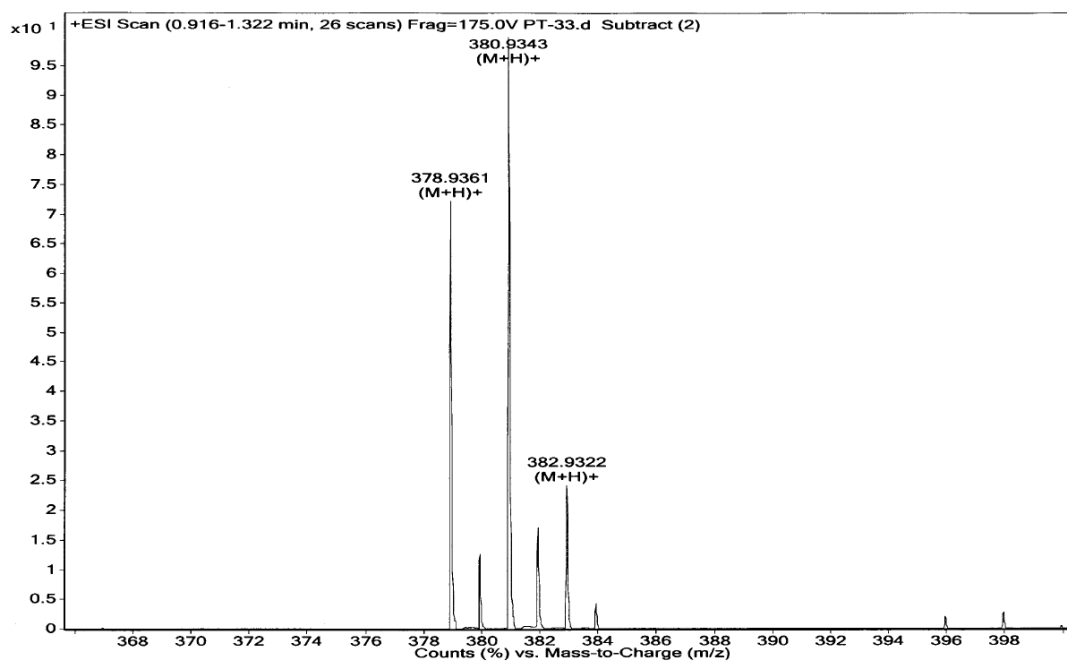
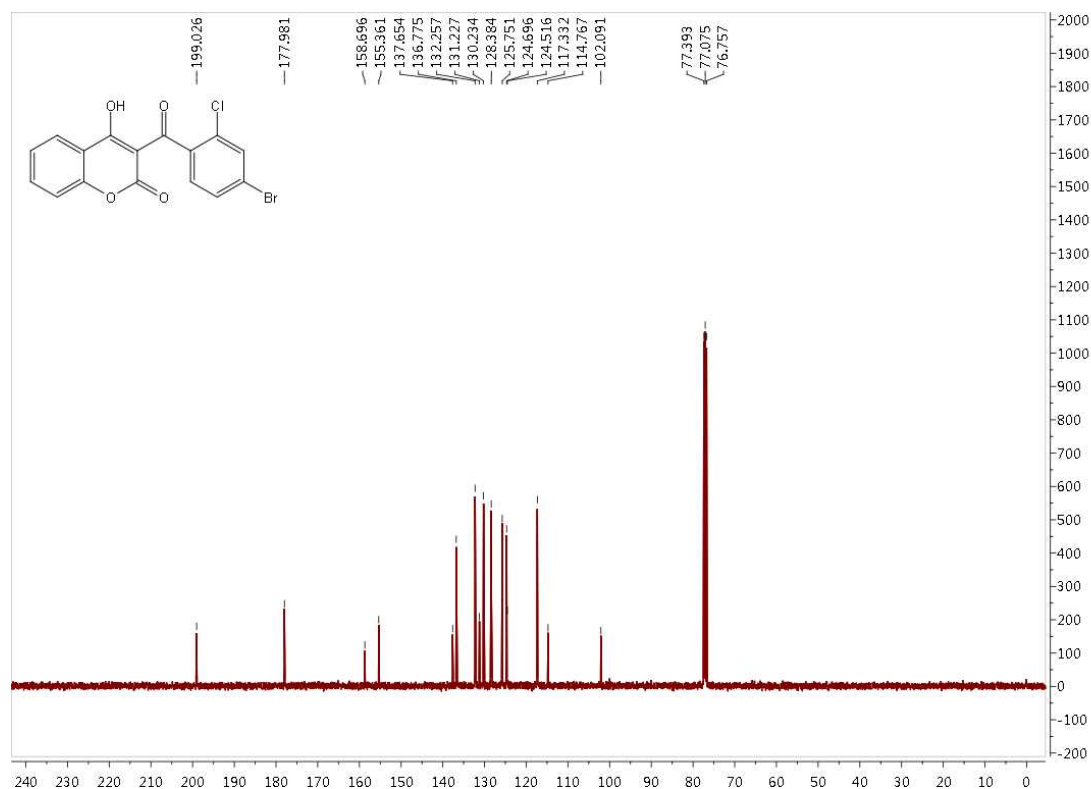
Data for **12-7**: pale yellow solid; yield 69%; m.p. 176-178 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.15 (d,  $J = 8.0$  Hz, 1H), 7.76 (t,  $J = 7.8$  Hz, 1H), 7.41 (m, 2H), 7.34 (d,  $J = 8.4$  Hz, 1H), 7.14 (td,  $J = 8.4$  Hz, 2.7 Hz, 1H), 7.06 (dd,  $J = 7.9$  Hz, 2.7 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 198.45, 178.00, 162.36, 159.89, 158.56, 155.42, 140.02 (d), 136.79, 131.01 (d), 125.74, 125.11 (d), 124.68, 118.08 (d), 117.34, 114.52 (d), 101.97; HRMS: calcd for  $\text{C}_{16}\text{H}_8\text{ClFO}_4$   $[\text{M}+\text{H}]^+$  319.0095, found 319.0165.



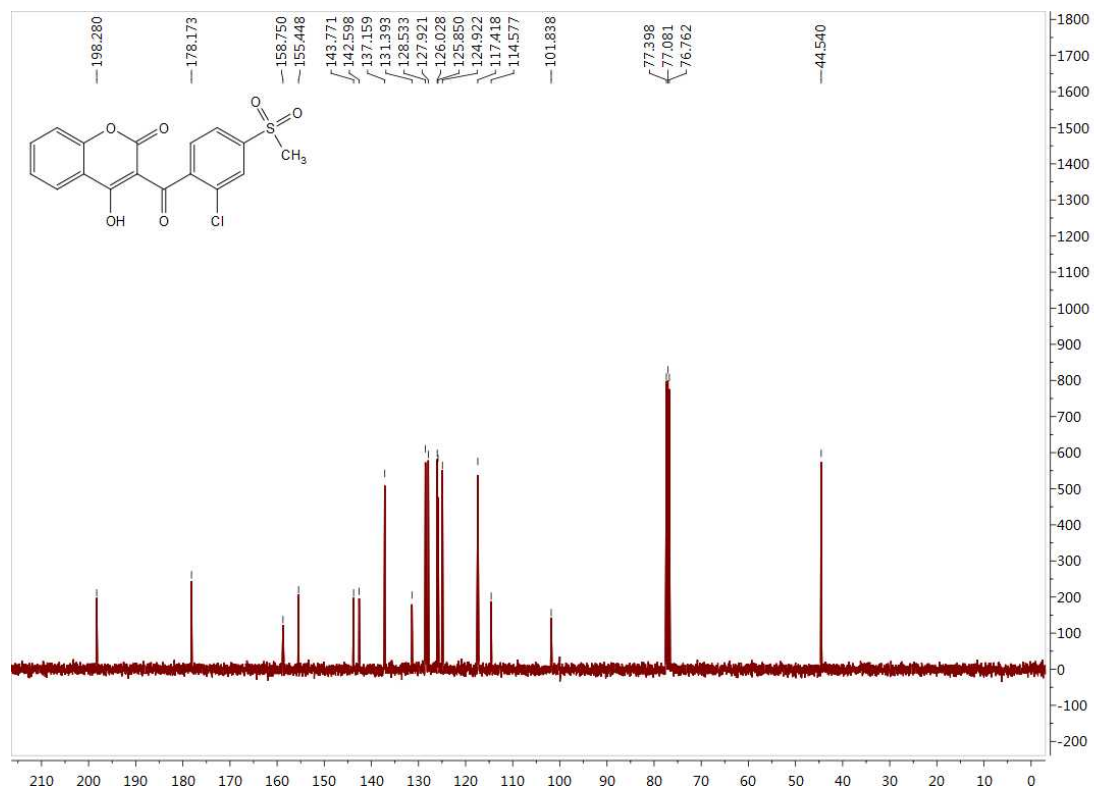
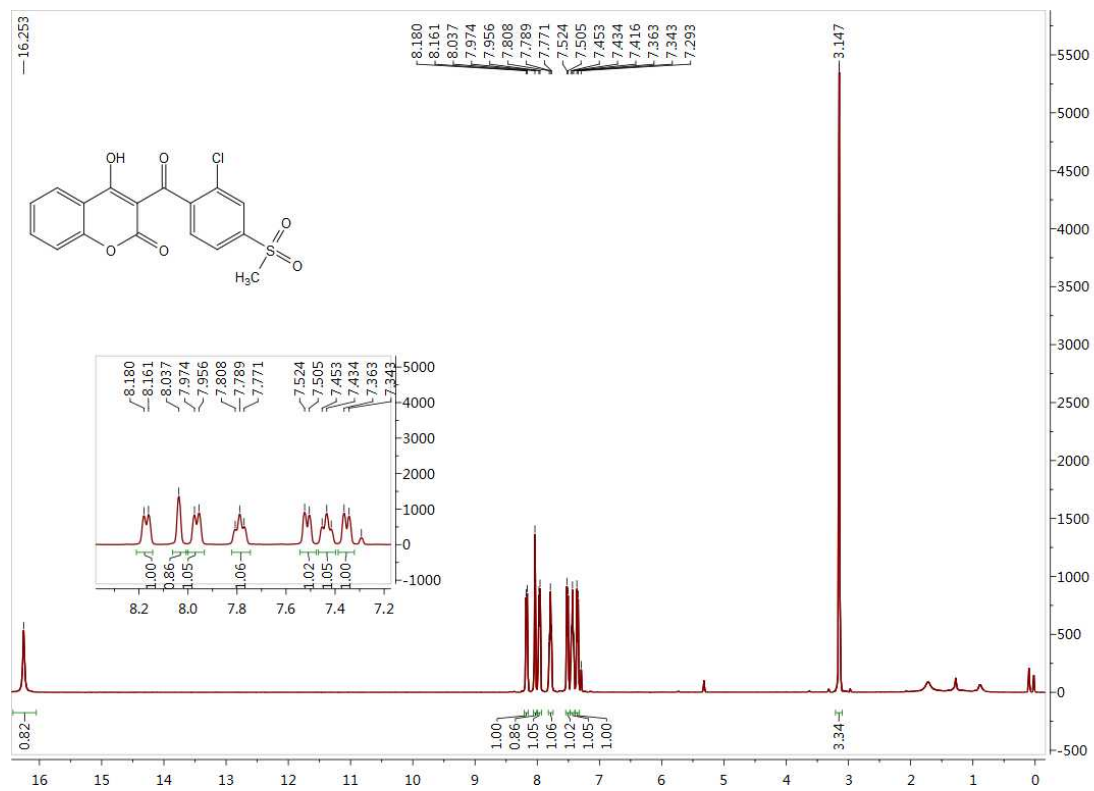


Data for **12-8**: pale yellow solid; yield 66%; m.p. 183-185 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.12 (dd,  $J = 8.0$  Hz, 1.4 Hz, 1H), 7.77-7.69 (m, 1H), 7.60 (d,  $J = 1.7$  Hz, 1H), 7.51 (dd,  $J = 8.2$  Hz, 1.7 Hz, 1H), 7.38 (dd,  $J = 11.3$  Hz, 4.0 Hz, 1H), 7.32 (d,  $J = 8.4$  Hz, 1H), 7.19 (d,  $J = 8.2$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 199.03, 177.98, 158.70, 155.36, 137.65, 136.78, 132.26, 131.23, 130.23, 128.38, 125.75, 124.70, 124.52, 117.33, 114.77, 102.09; HRMS: calcd for  $\text{C}_{16}\text{H}_8\text{BrClO}_4$   $[\text{M}+\text{H}]^+$  378.9294, found 378.9361.

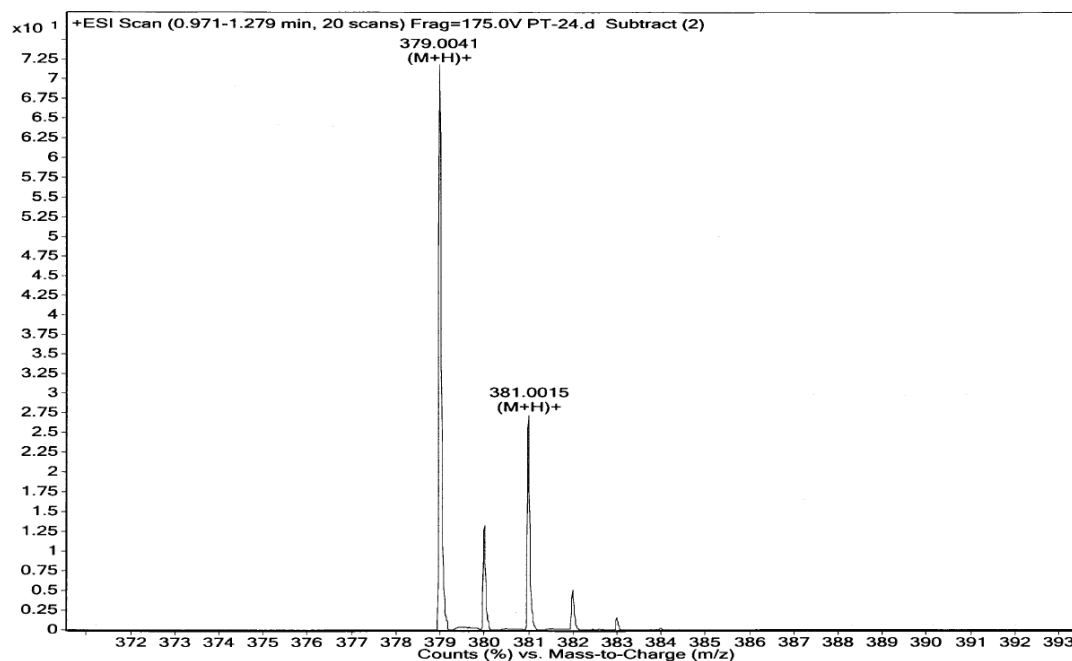




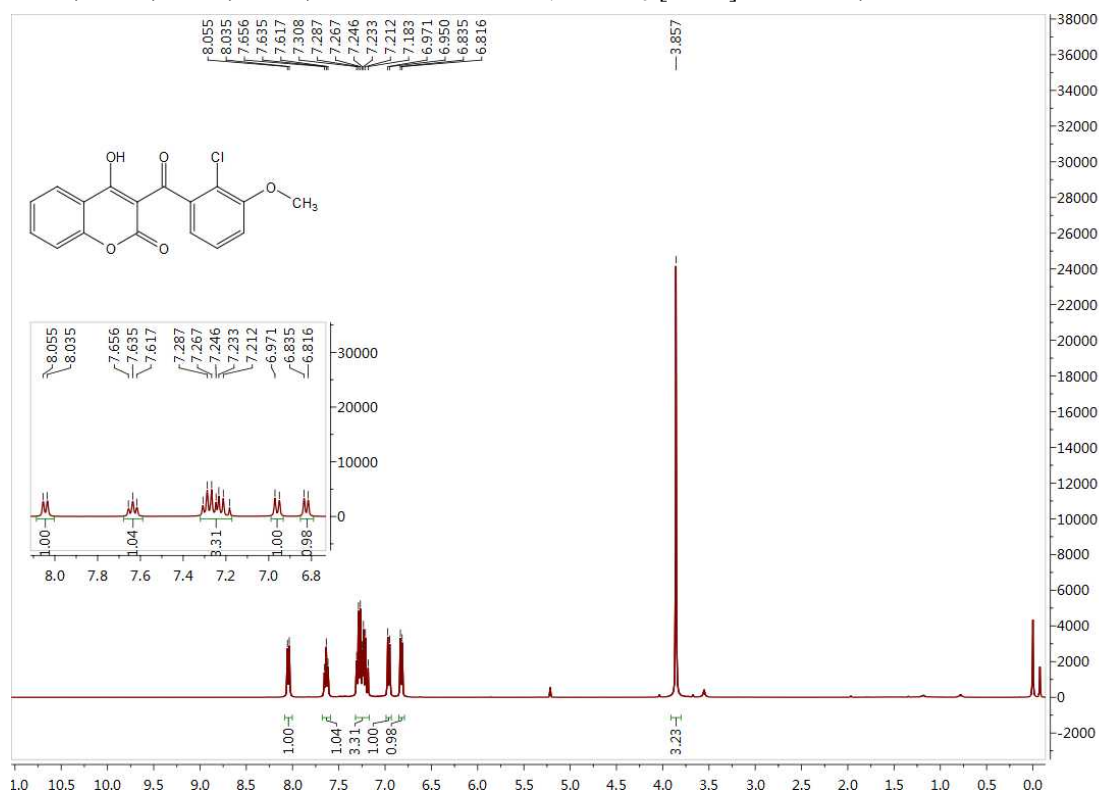
Data for **12-9**: pale yellow solid; yield 72%; m.p. 223-225 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 16.25 (s, 1H), 8.17 (d,  $J = 7.4$  Hz, 1H), 8.04 (s, 1H), 7.96 (d,  $J = 7.2$  Hz, 1H), 7.79 (t,  $J = 7.3$  Hz, 1H), 7.51 (d,  $J = 7.7$  Hz, 1H), 7.43 (t,  $J = 7.5$  Hz, 1H), 7.35 (d,  $J = 8.2$  Hz, 1H), 3.15 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 198.28, 178.17, 158.75, 155.45, 143.77, 142.60, 137.16, 131.39, 128.53, 127.92, 126.03, 125.85, 124.92, 117.42, 114.58, 101.84, 44.54; HRMS: calcd for  $\text{C}_{17}\text{H}_{11}\text{ClO}_6\text{S}$   $[\text{M}+\text{H}]^+$  378.9965, found 379.0041.

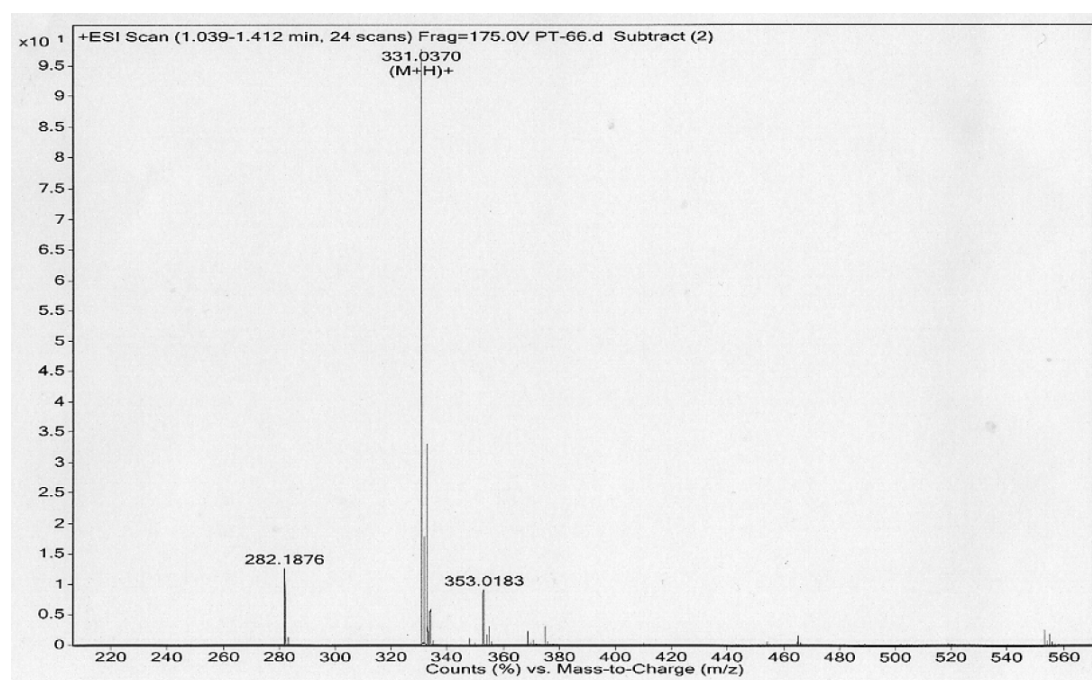
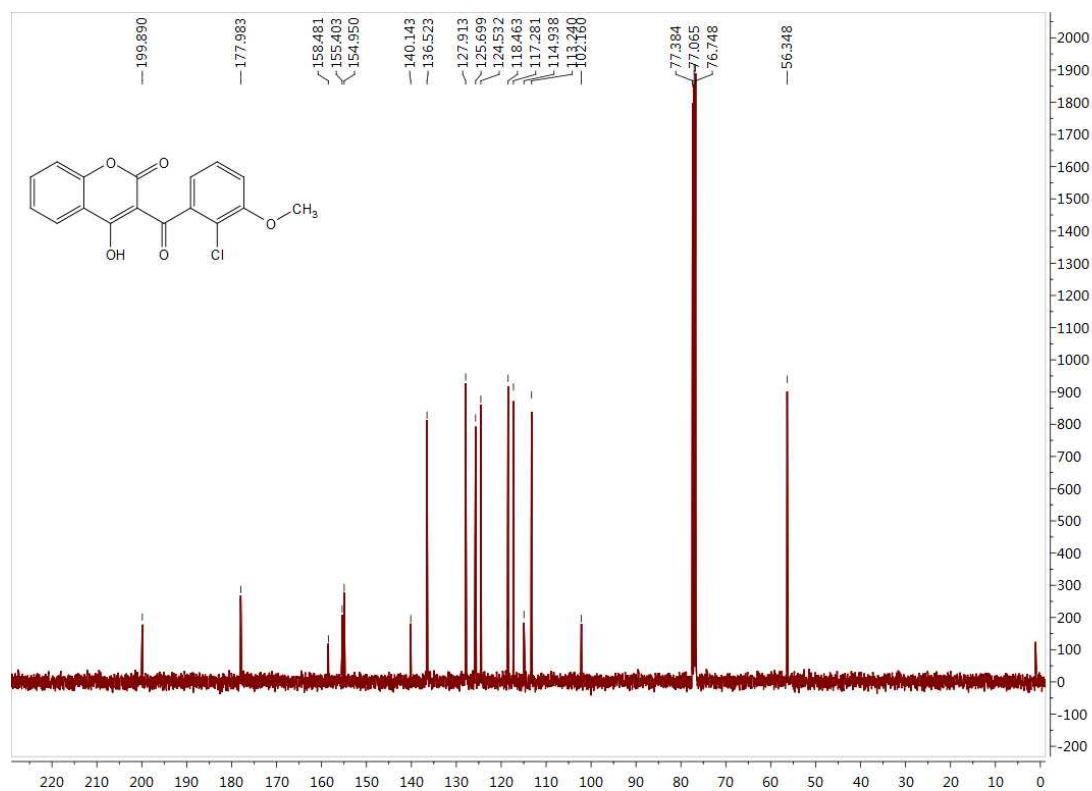




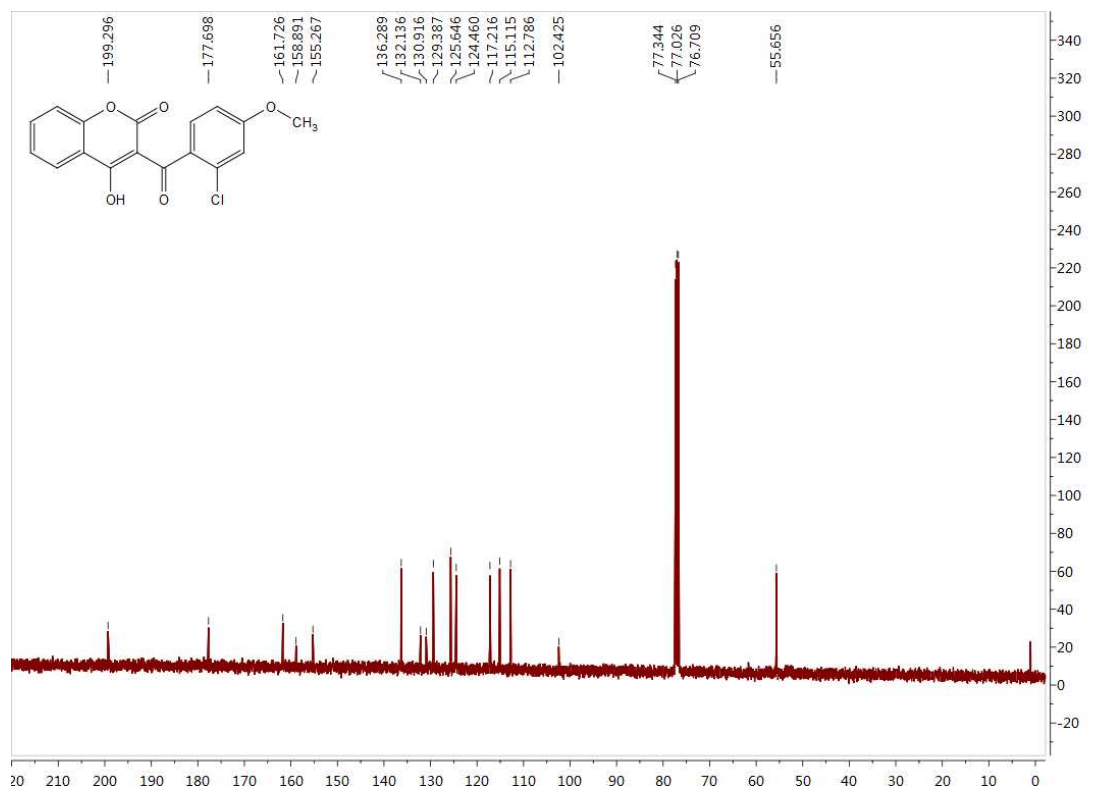
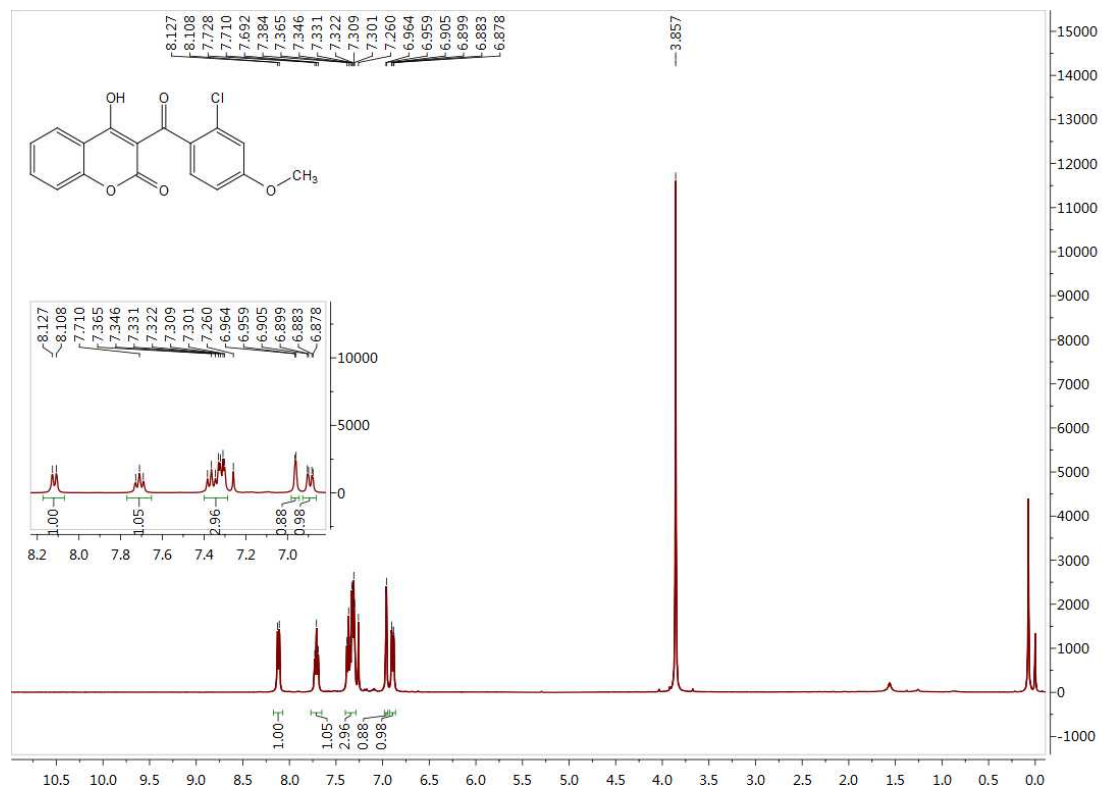


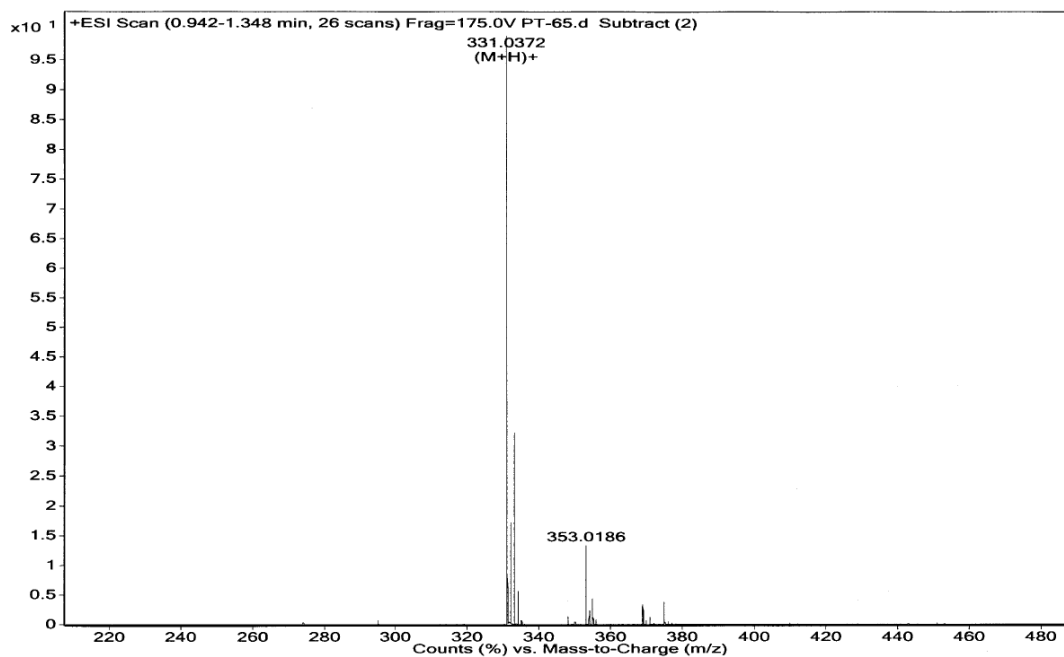
Data for **12-10**: pale yellow solid; yield 47%; m.p. 152-155 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.05 (d, *J* = 7.8 Hz, 1H), 7.64 (t, *J* = 7.8 Hz, 1H), 7.34-7.17 (m, 3H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 3.86 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 199.89, 177.98, 158.48, 155.40, 154.95, 140.14, 136.52, 127.91, 125.70, 124.53, 118.52, 118.46, 117.28, 114.94, 113.24, 102.16, 77.38, 77.07, 76.75, 56.35; HRMS: calcd for C<sub>17</sub>H<sub>11</sub>ClO<sub>5</sub> [M+H]<sup>+</sup> 331.0295, found 331.0370.



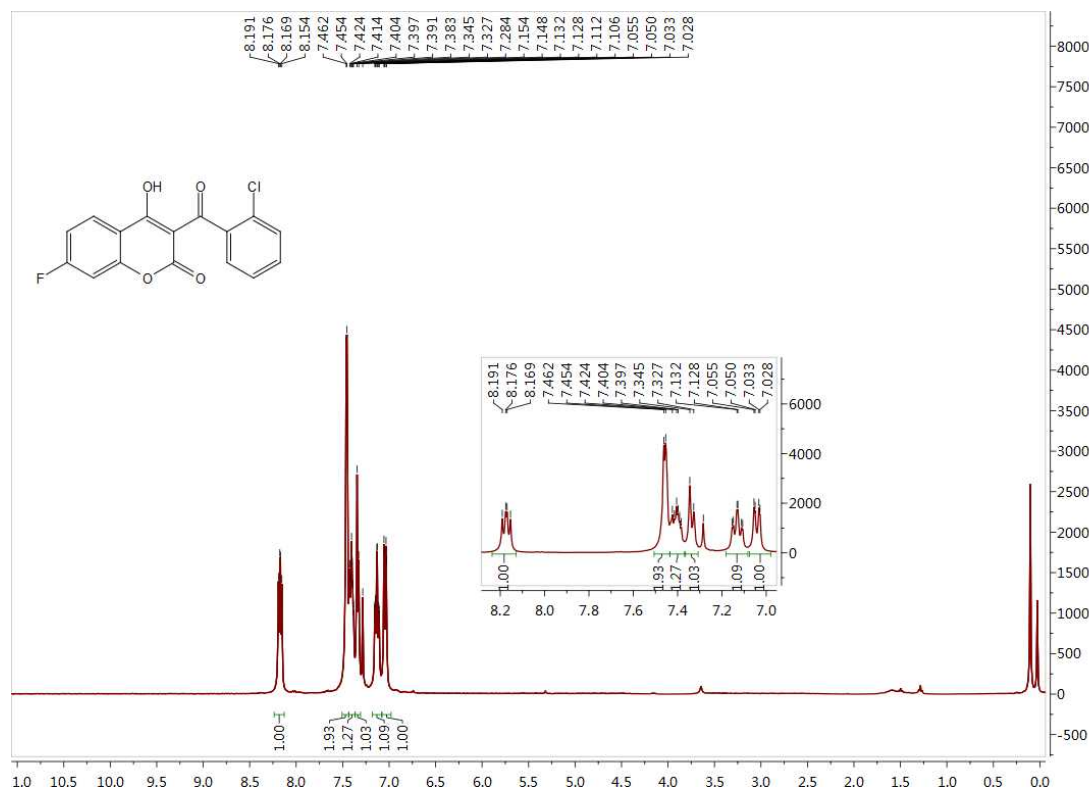


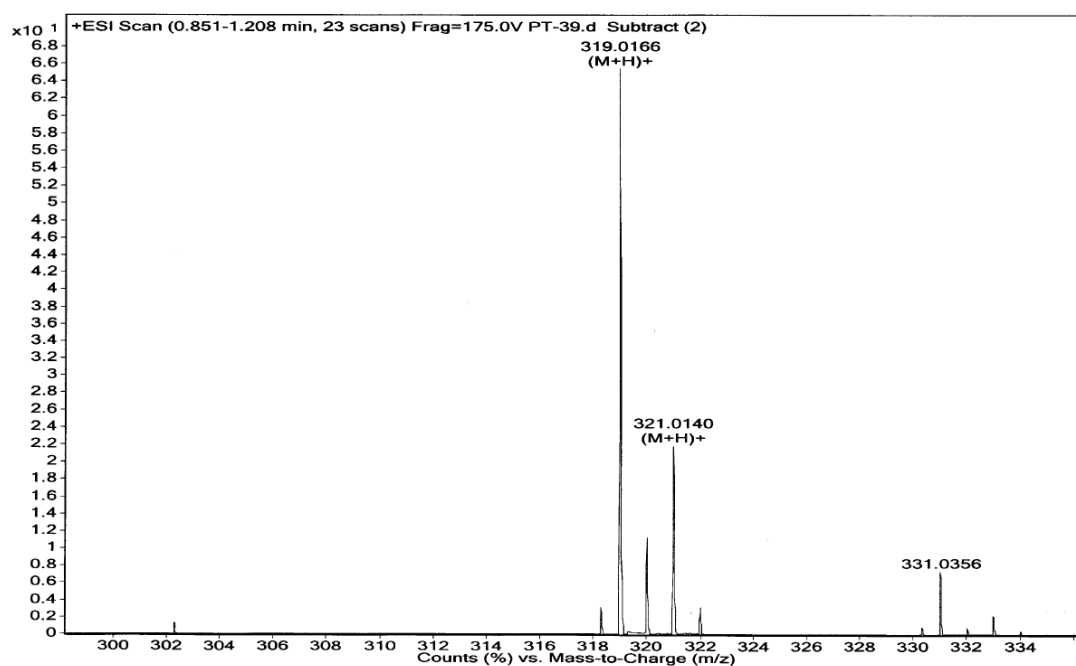
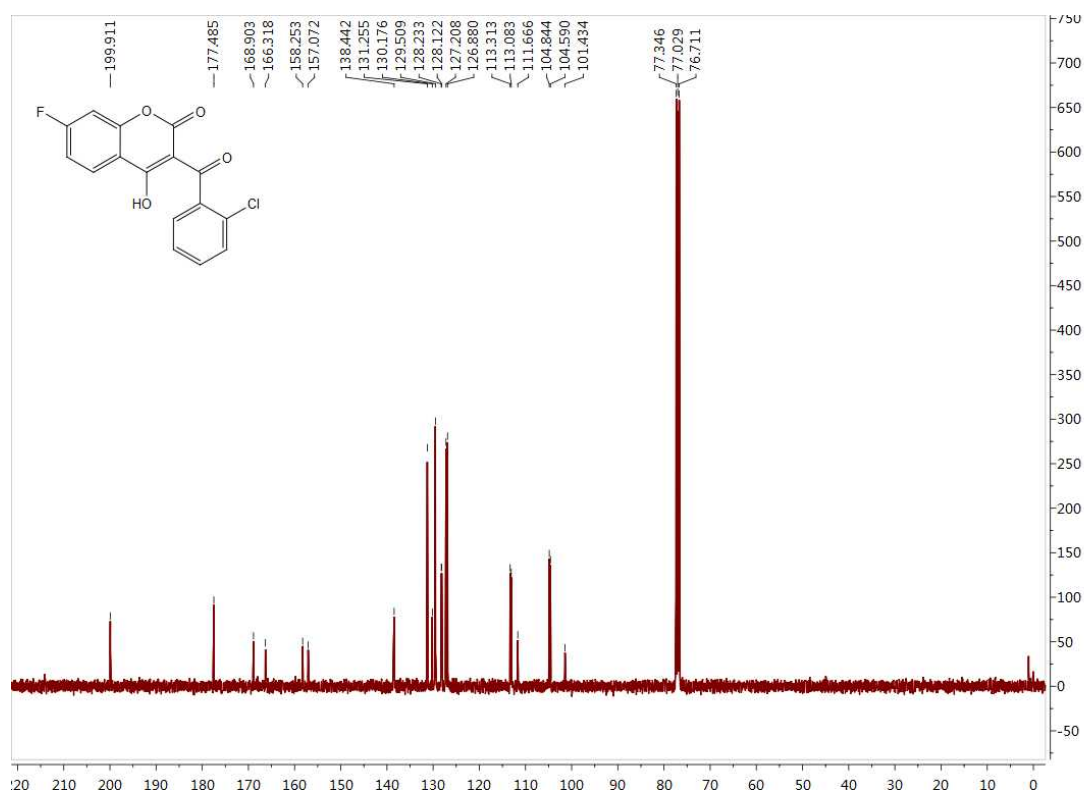
Data for **12-11**: light yellow solid; yield 56%; m.p. 195-197 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.04 (d,  $J = 7.4$  Hz, 1H), 7.64 (t,  $J = 7.3$  Hz, 1H), 7.35-7.22 (m, 3H), 6.89 (d,  $J = 2.1$  Hz, 1H), 6.82 (dd,  $J = 8.5, 2.1$  Hz, 1H), 3.78 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 199.30, 177.70, 161.73, 158.89, 155.27, 136.29, 132.14, 130.92, 129.39, 125.65, 124.46, 117.22, 115.12, 112.79, 102.43, 55.66; HRMS: calcd for  $\text{C}_{17}\text{H}_{11}\text{ClO}_5$   $[\text{M}+\text{H}]^+$  331.0295, found 331.0372.



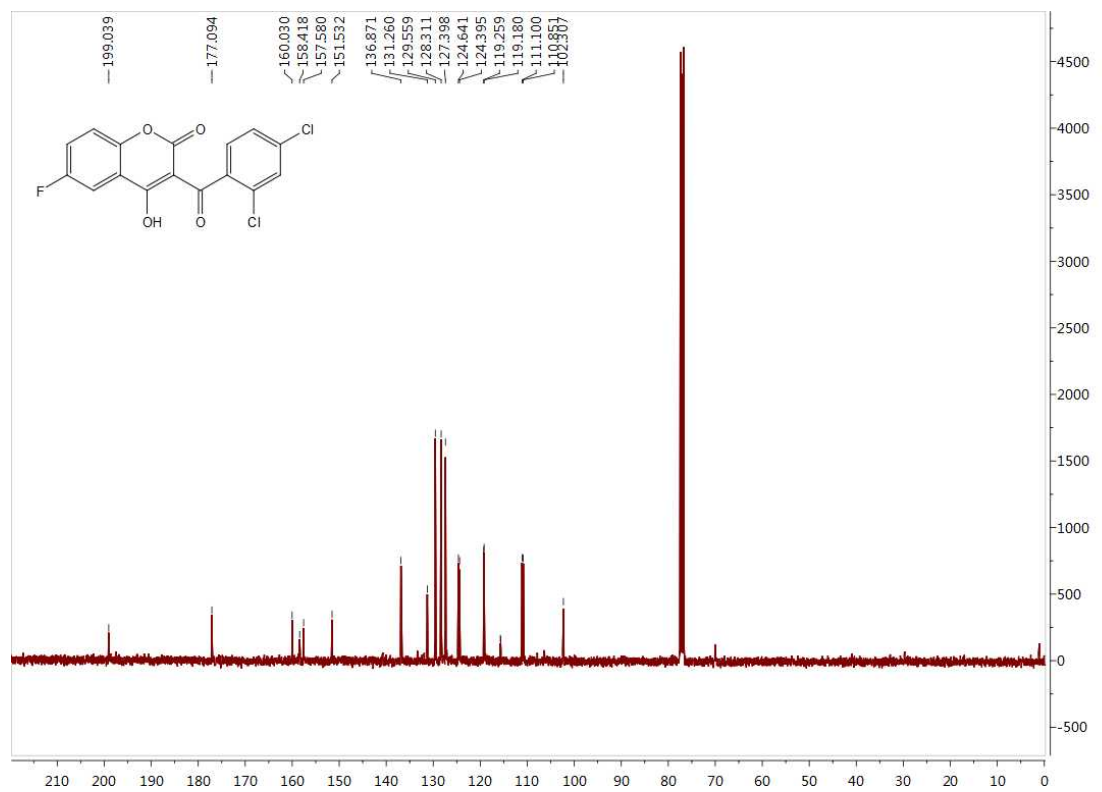
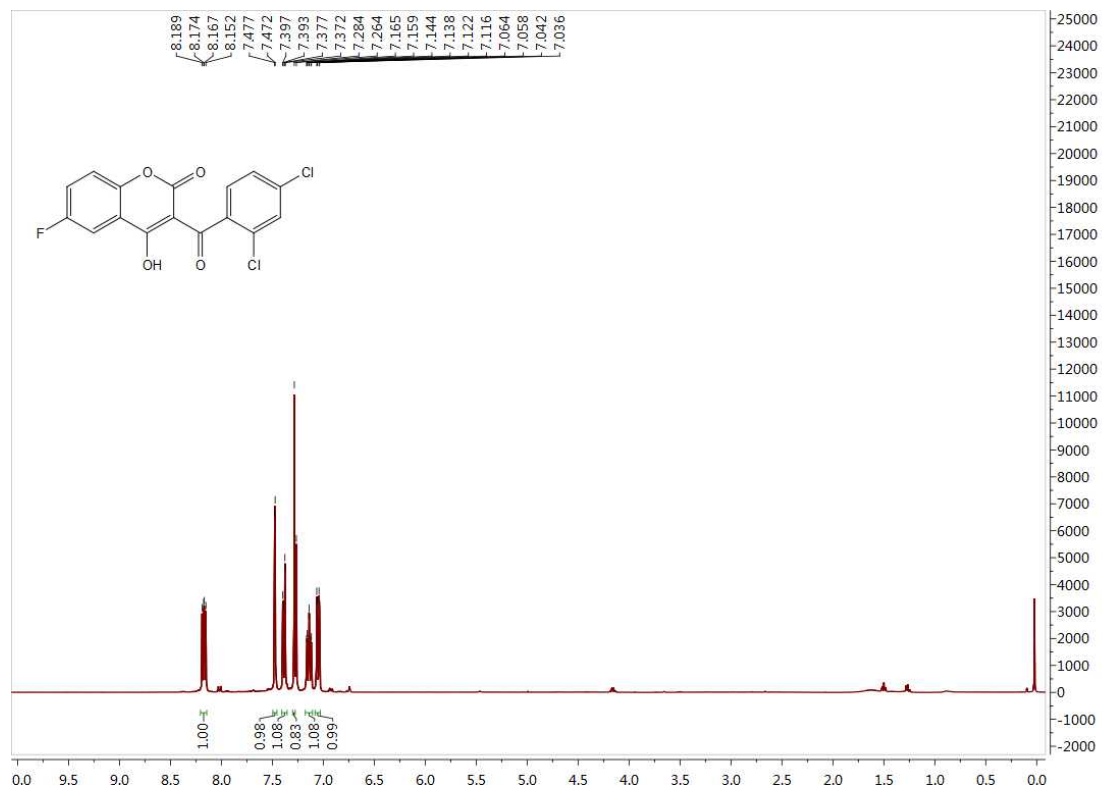


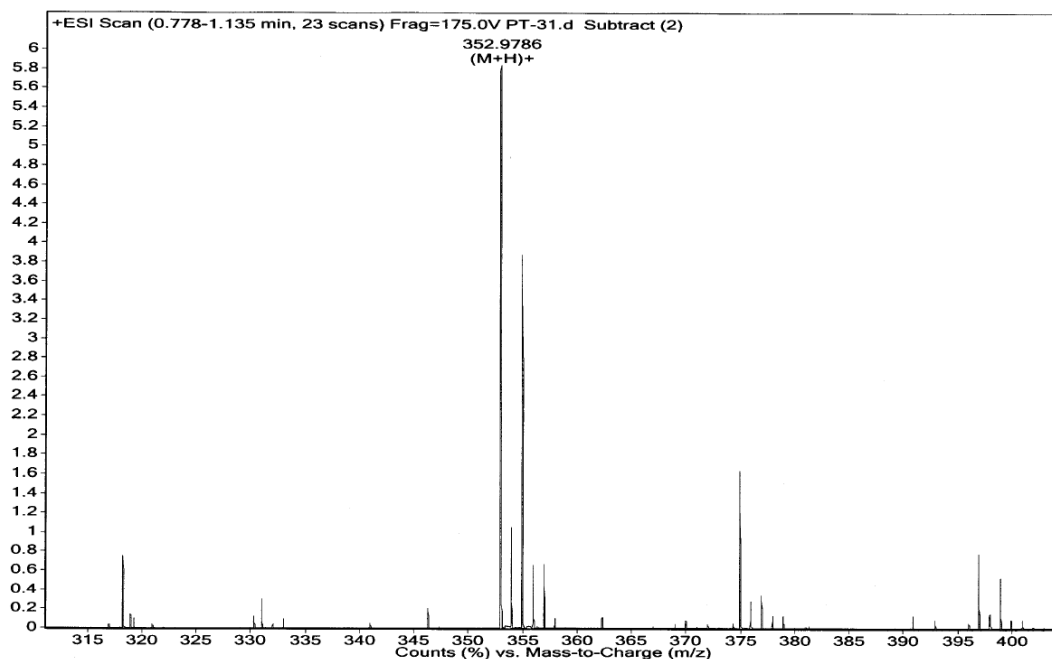
Data for **12-12**: light yellow solid; yield 62%; m.p. 148-150 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.17 (dd, *J* = 8.7 Hz, 6.1 Hz, 1H), 7.46 (d, *J* = 3.2 Hz, 2H), 7.44-7.37 (m, 1H), 7.34 (d, *J* = 7.1 Hz, 1H), 7.13 (td, *J* = 8.6 Hz, 2.1 Hz, 1H), 7.04 (dd, *J* = 8.9 Hz, 2.0 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 199.91, 177.48, 168.90, 166.32, 158.25, 157.00 (d), 138.44, 131.25, 130.18, 129.51, 128.18 (d), 127.04 (d), 113.20 (d), 111.67, 104.72 (d), 101.43; HRMS: calcd for C<sub>16</sub>H<sub>8</sub>ClFO<sub>4</sub> [M+H]<sup>+</sup> 319.0095, found 319.0166.



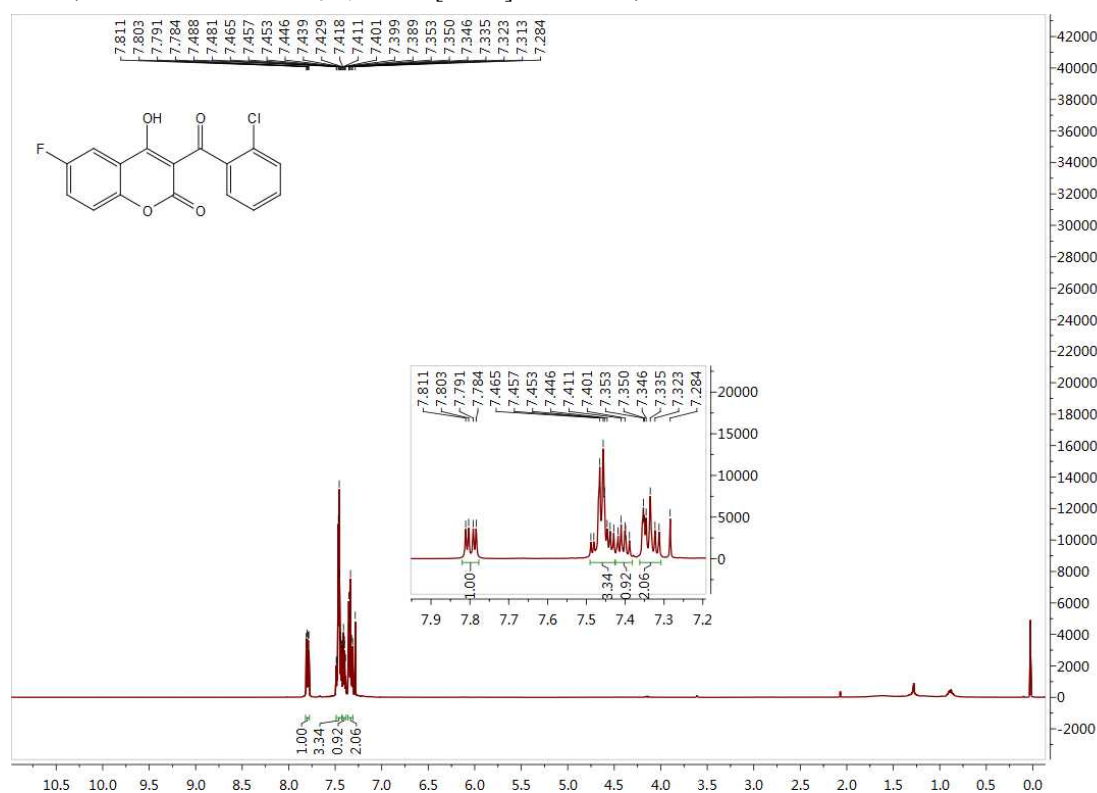


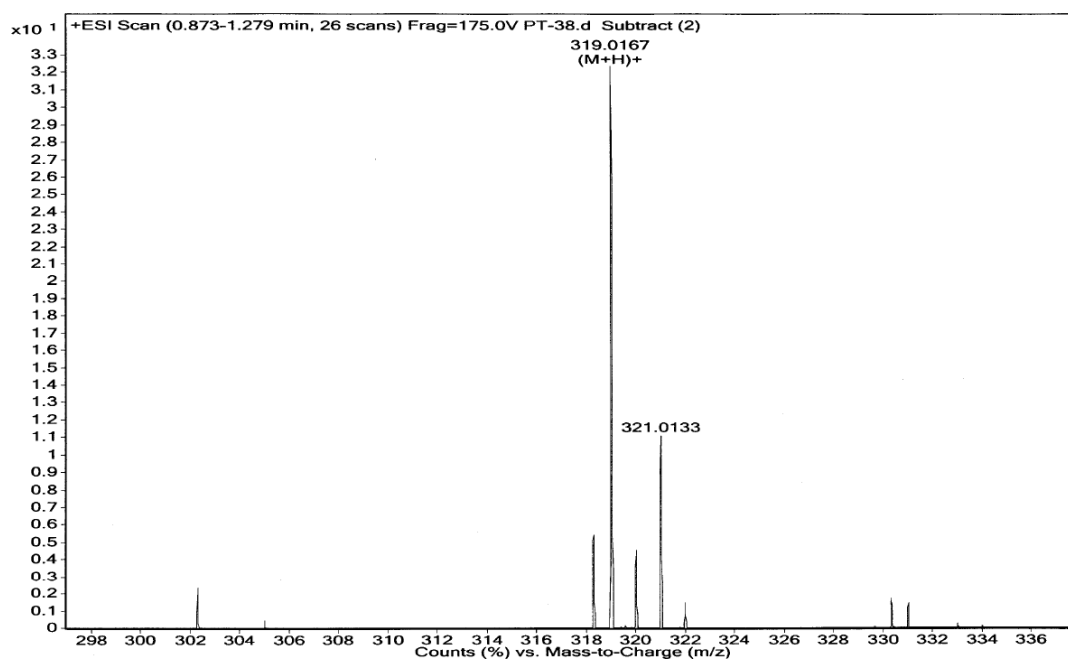
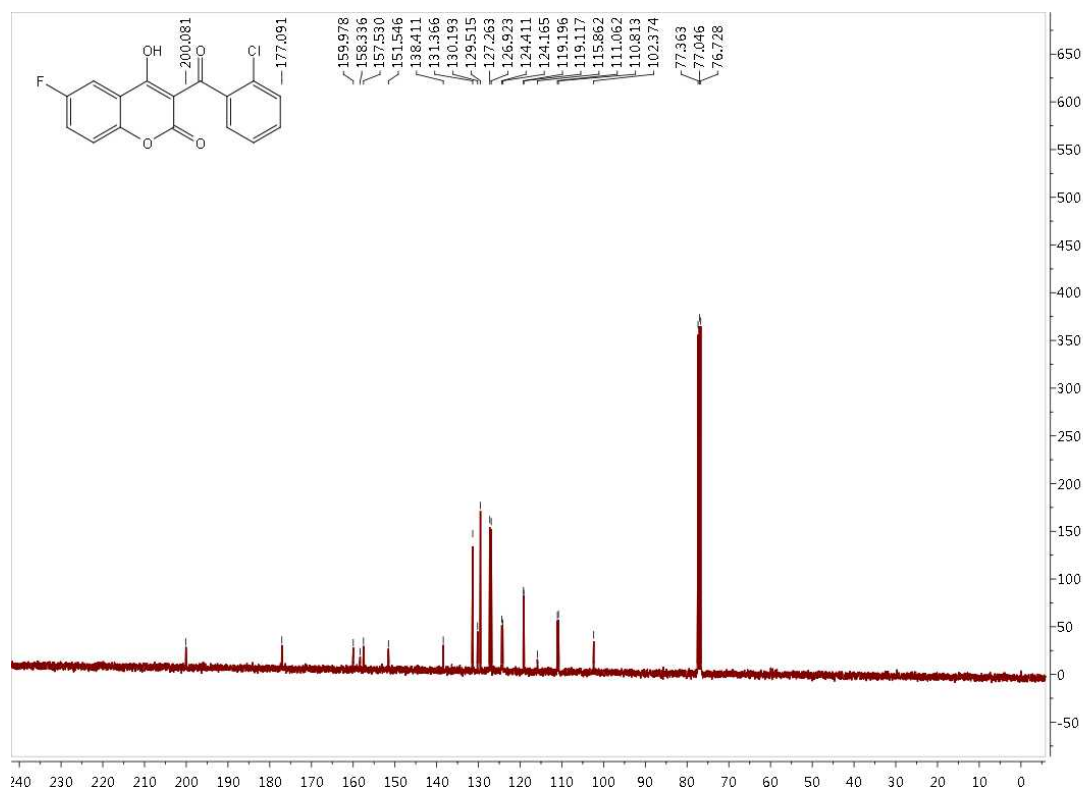
Data for **12-13**: light yellow solid; yield 66%; m.p. 137-139 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.17 (dd,  $J = 8.9$  Hz, 6.0 Hz, 1H), 7.47 (d,  $J = 1.8$  Hz, 1H), 7.38 (dd,  $J = 8.2$  Hz, 1.9 Hz, 1H), 7.28 (s, 1H), 7.14 (td,  $J = 8.5$  Hz, 2.3 Hz, 1H), 7.05 (dd,  $J = 8.9$  Hz, 2.3 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 199.04, 177.09, 160.03, 158.42, 157.58, 151.53, 136.87, 131.26, 129.56, 128.31, 127.40, 124.52 (d), 119.22 (d), 115.69 (d), 110.98 (d), 102.31; HRMS: calcd for  $\text{C}_{16}\text{H}_7\text{Cl}_2\text{FO}_4$   $[\text{M}+\text{H}]^+$  352.9705, found 352.9786.





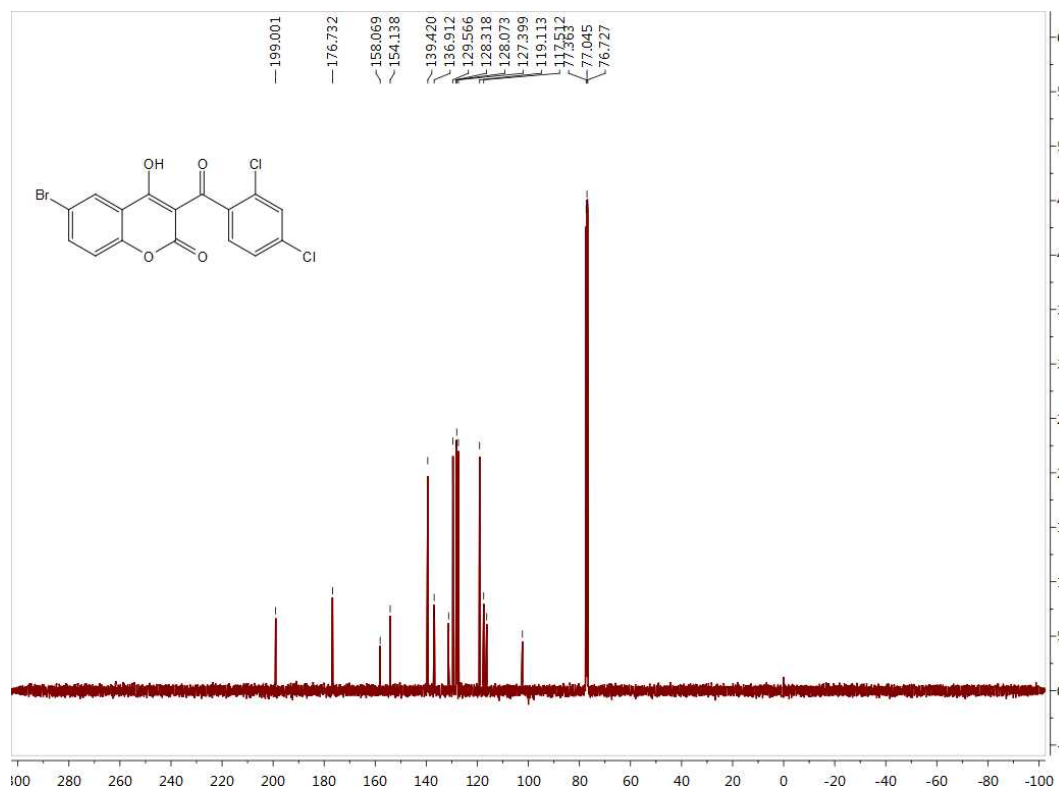
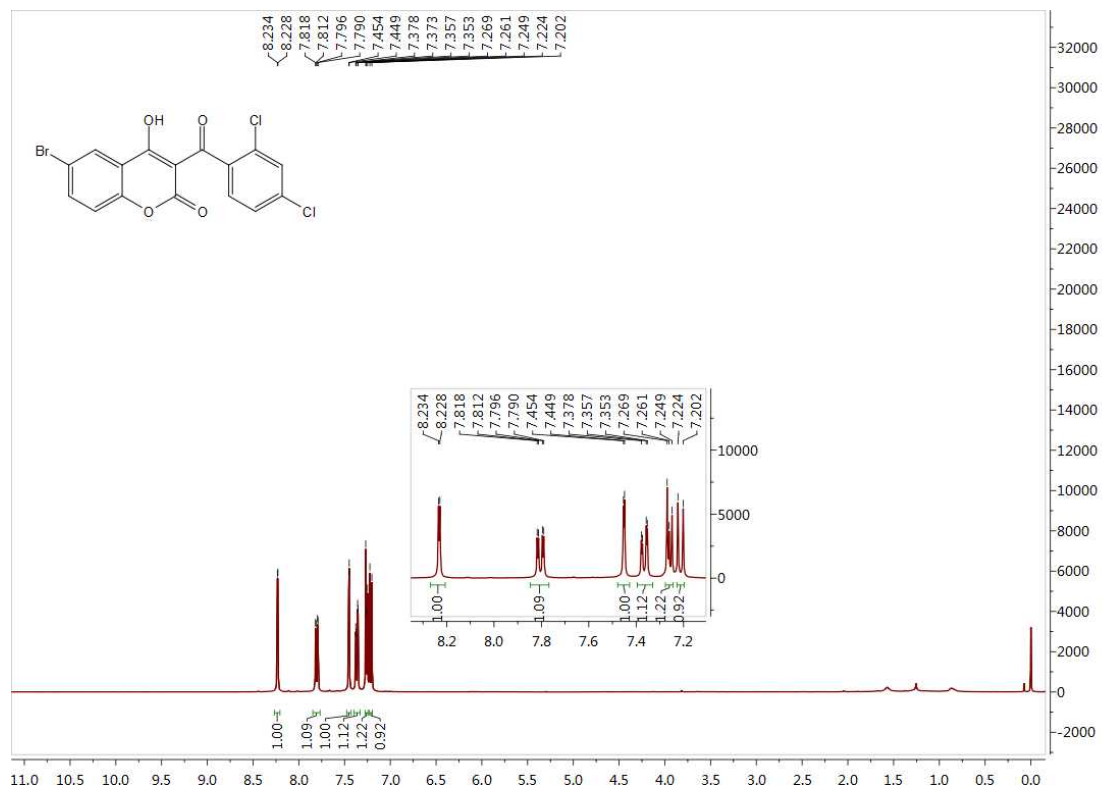
Data for **12-14**: pale yellow solid; yield 70%; m.p. 140-142 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.80 (dd,  $J = 7.8$  Hz, 3.0 Hz, 1H), 7.49-7.43 (m, 3H), 7.42-7.38 (m, 1H), 7.36-7.31 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 200.08, 177.09, 159.98, 158.34, 157.53, 151.55, 138.41, 131.37, 130.19, 129.52, 127.09 (d), 124.28 (d), 119.16 (d), 115.86, 111.06, 110.81, 102.37, 77.36, 77.05, 76.73; HRMS: calcd for  $\text{C}_{16}\text{H}_7\text{ClFO}_4$   $[\text{M}+\text{H}]^+$  319.0095, found 319.0167.

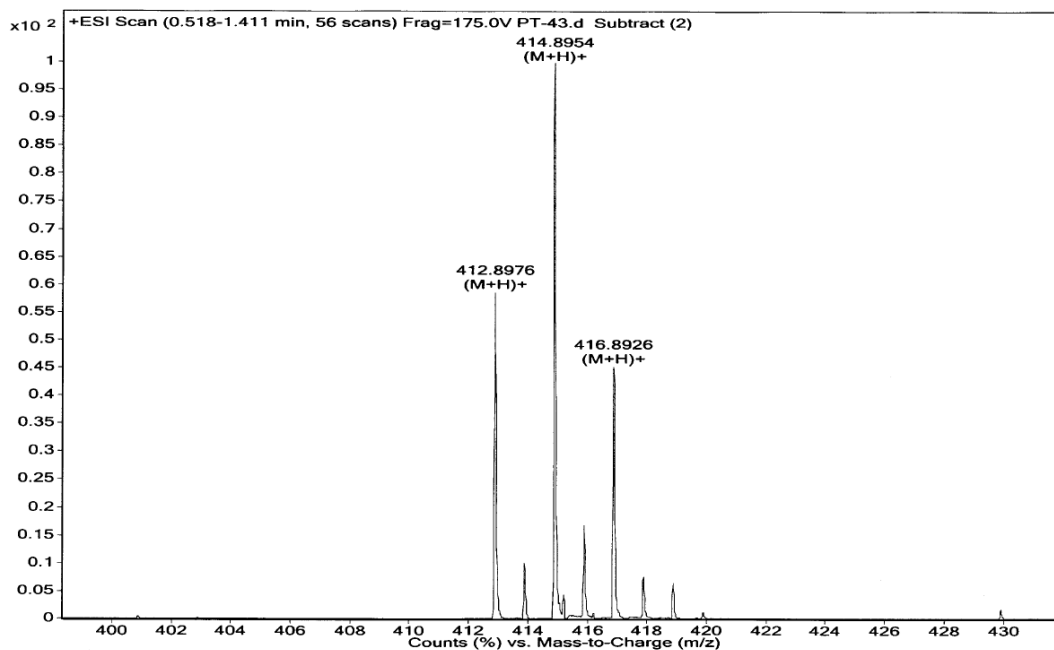




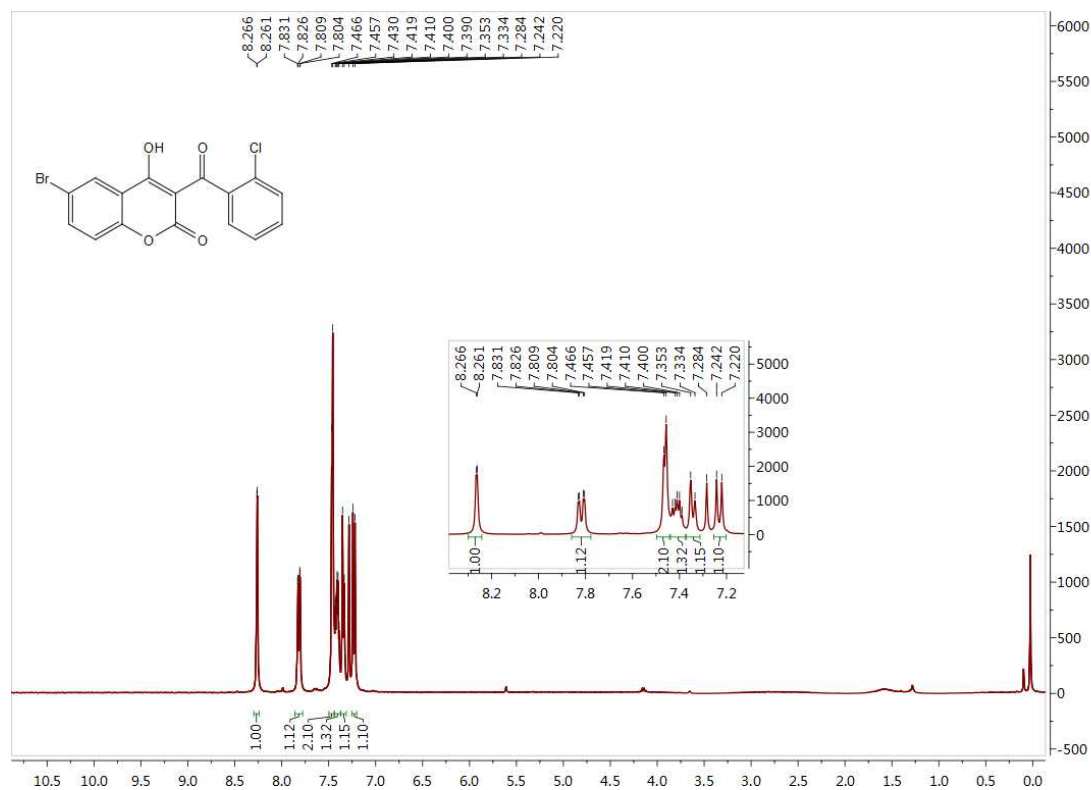
Data for **12-15**: pale yellow solid; yield 68%; m.p. 221-223 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.23 (d,  $J = 2.4$  Hz, 1H), 7.80 (dd,  $J = 8.8$  Hz, 2.4 Hz, 1H), 7.45 (d,  $J = 1.8$  Hz, 1H), 7.37 (dd,  $J = 8.2$  Hz, 1.8 Hz, 1H), 7.24 (dd, m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 199.00, 176.73, 158.07, 154.14, 139.42, 136.91, 136.82, 131.26, 129.57, 128.32, 128.07, 127.40, 119.11, 117.51, 116.31, 102.34; HRMS: calcd for  $\text{C}_{16}\text{H}_7\text{BrCl}_2\text{O}_4$  [ $\text{M}+\text{H}$ ] $^+$  411.8905, found 412.8976.

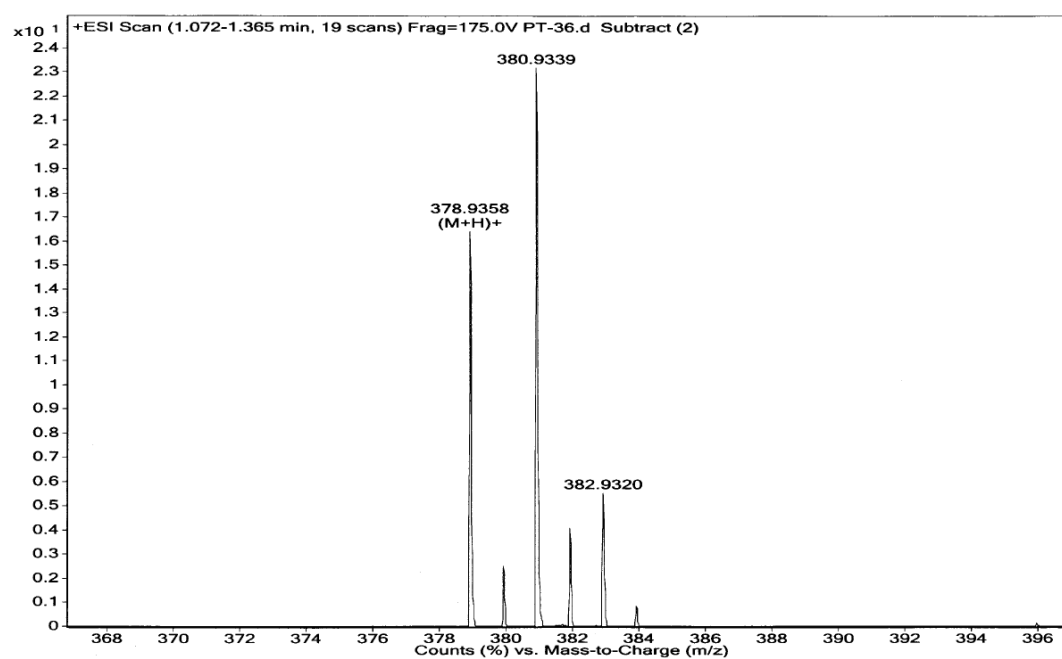
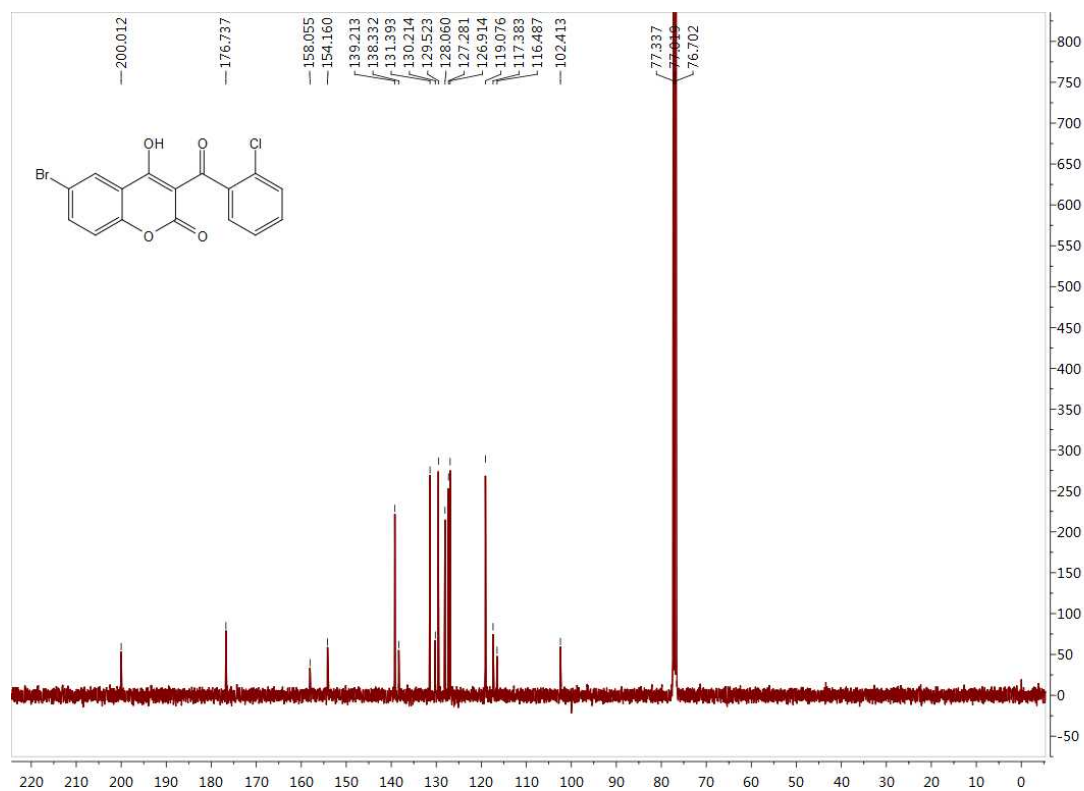




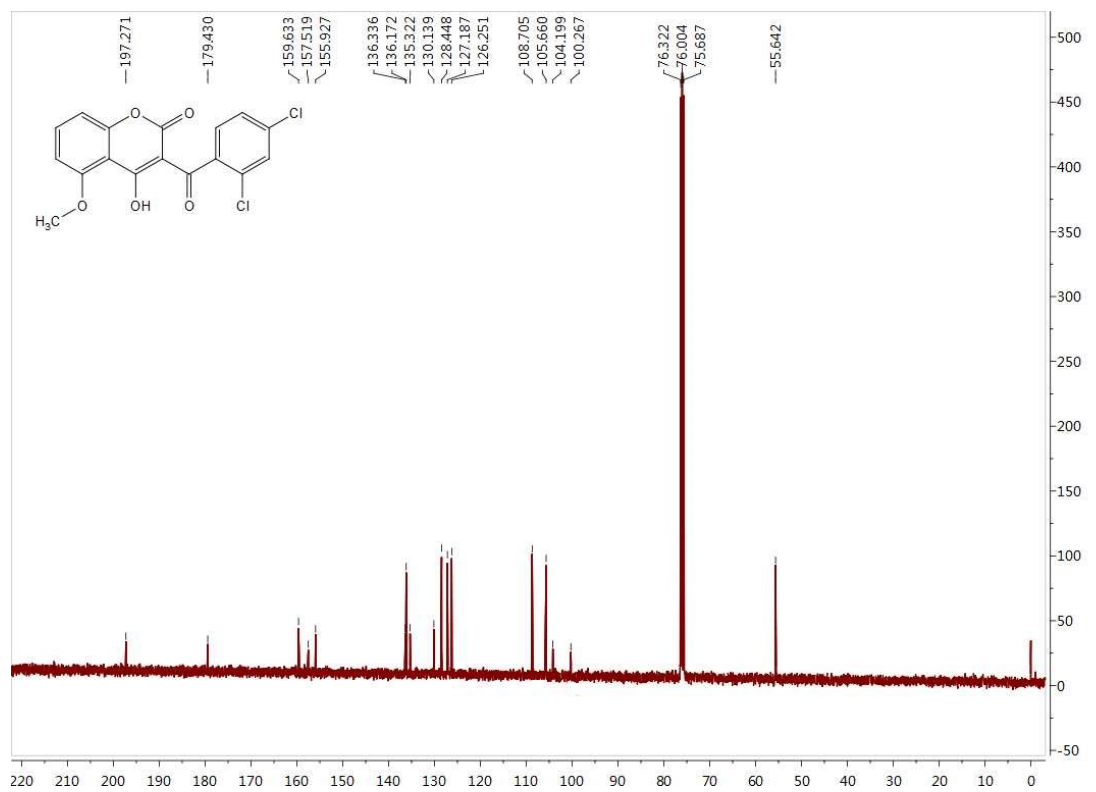
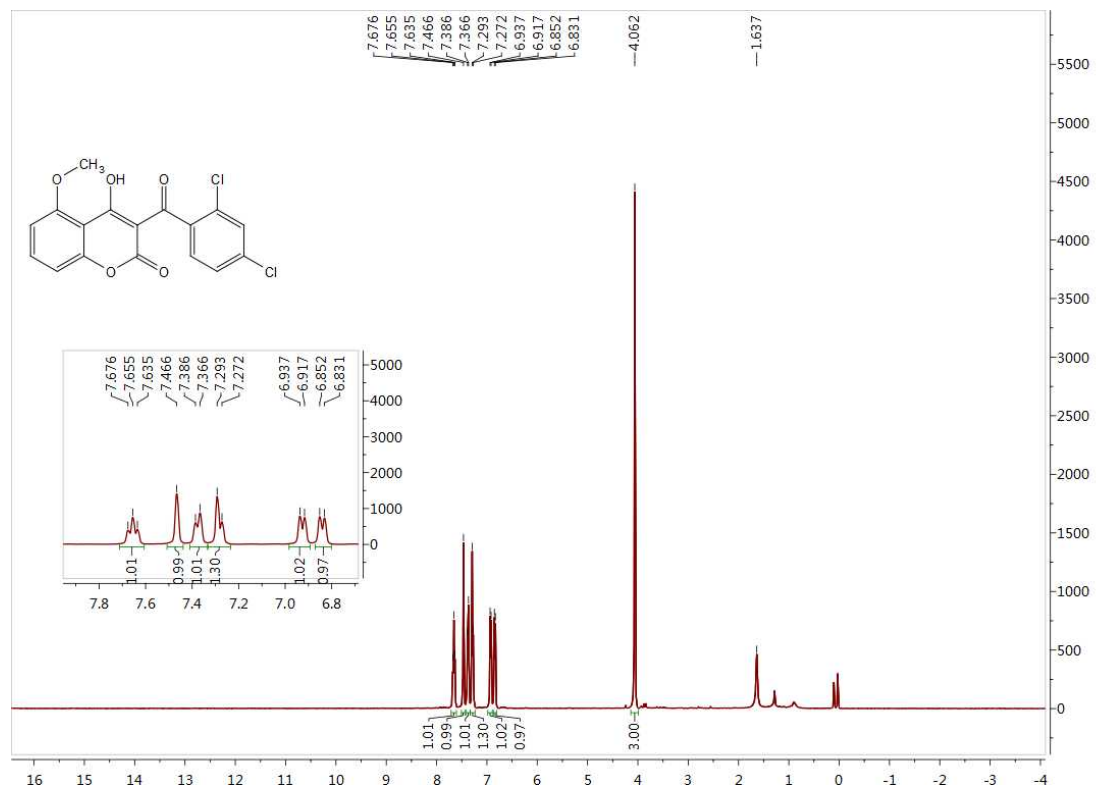


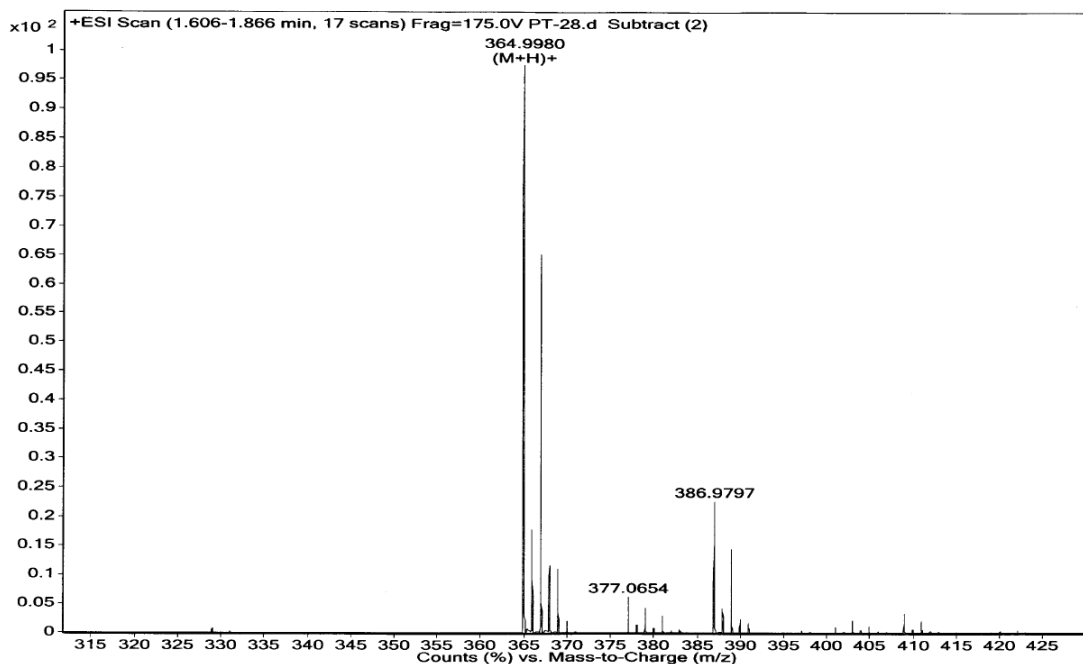
Data for **12-16**: pale yellow solid; yield 64%; m.p. 159-160 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.26 (d, *J* = 1.9 Hz, 1H), 7.82 (dd, *J* = 8.8 Hz, 2.0 Hz, 1H), 7.46 (d, *J* = 3.7 Hz, 2H), 7.44-7.37 (m, 1H), 7.34 (d, *J* = 7.4 Hz, 1H), 7.23 (d, *J* = 8.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 200.01, 176.74, 158.05, 154.16, 139.21, 138.33, 131.39, 130.21, 129.52, 128.06, 127.28, 126.91, 119.08, 117.38, 116.49, 102.41; HRMS: calcd for C<sub>16</sub>H<sub>8</sub>BrClO<sub>4</sub> [M+H]<sup>+</sup> 378.9294, found 378.9358.



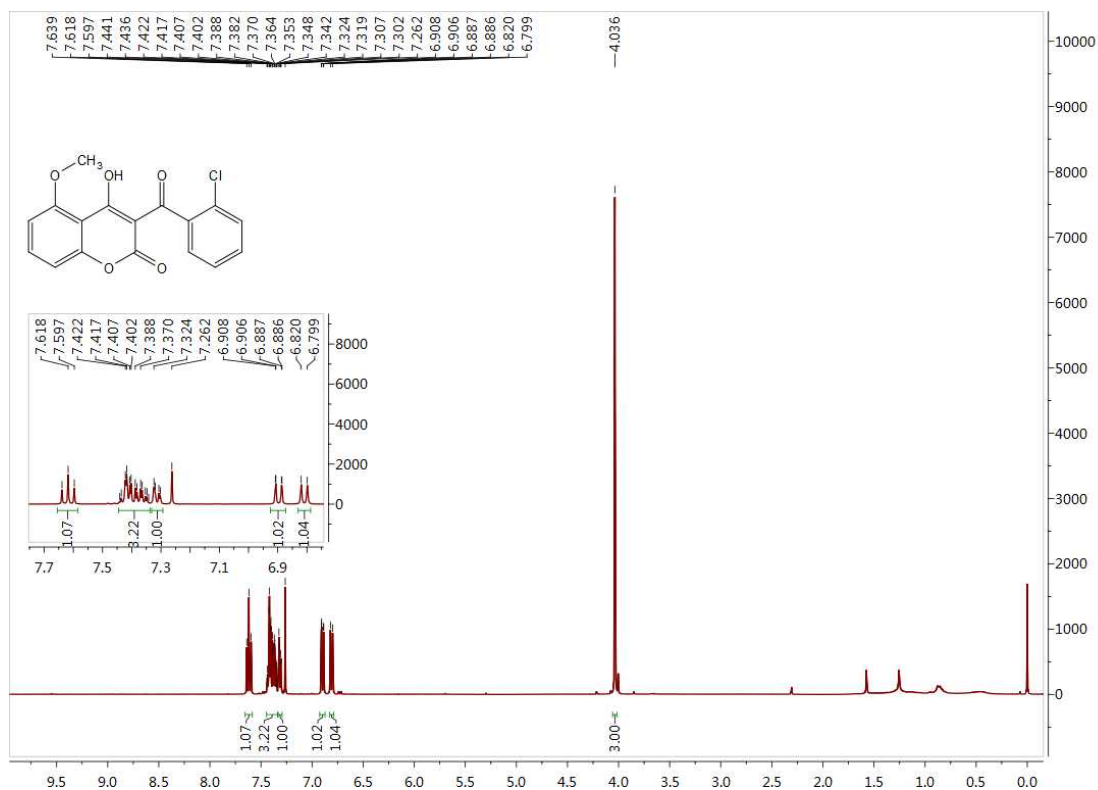


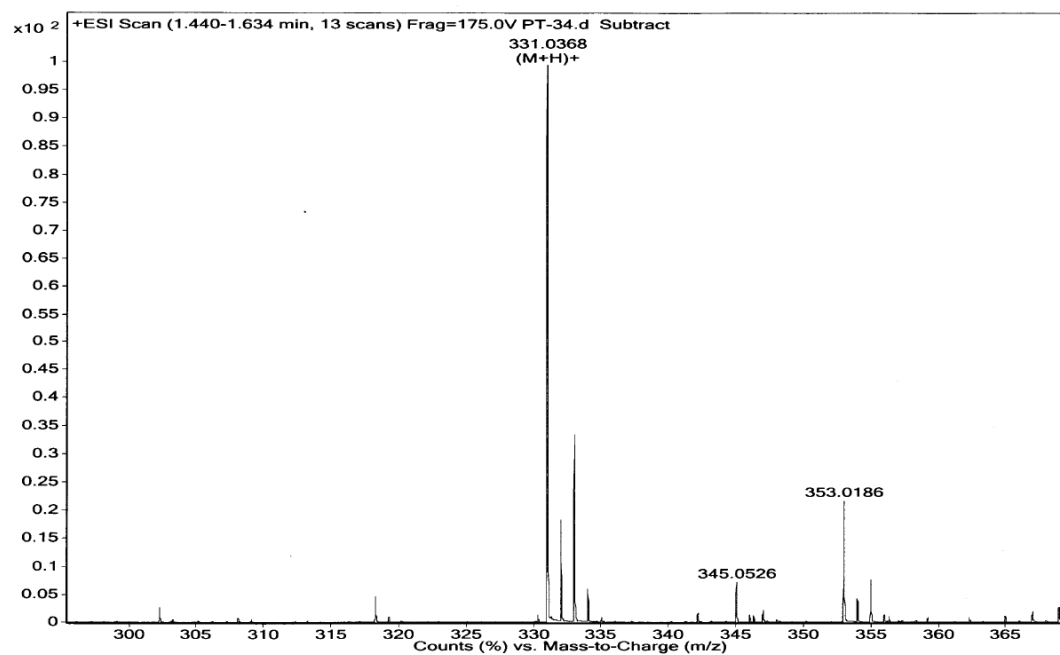
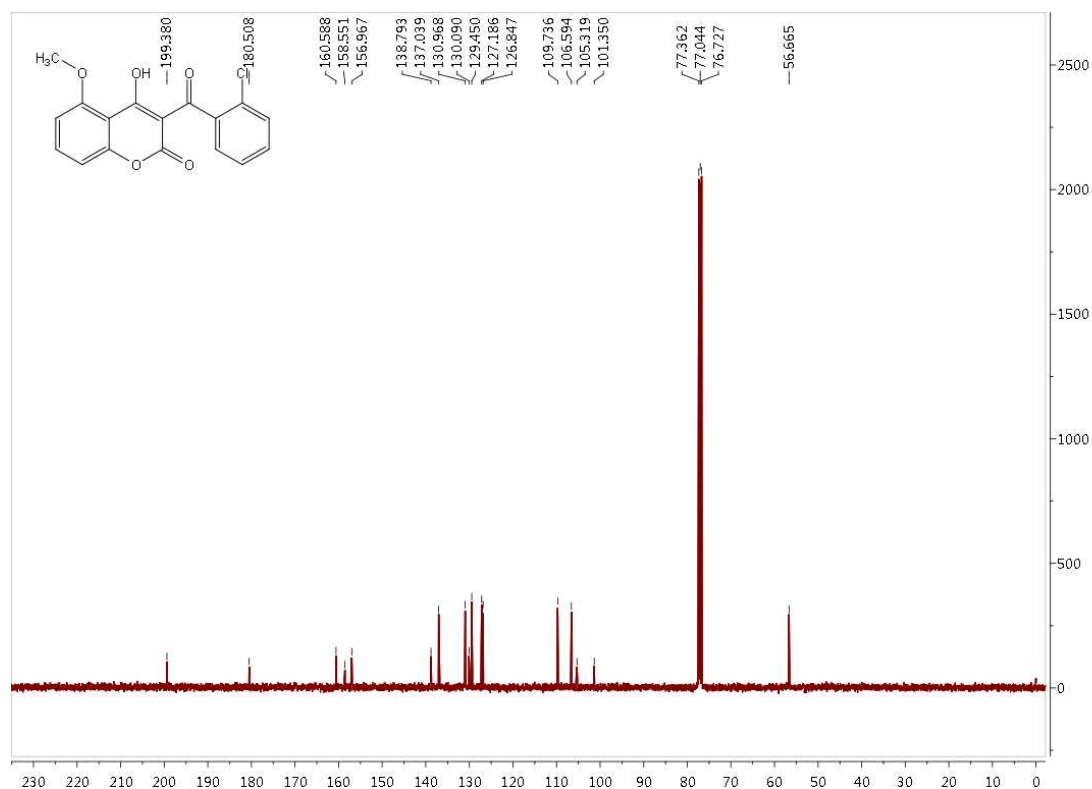
Data for **12-17** <sup>[1]</sup>: pale yellow solid; yield 59%; m.p. 176-179 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.65 (t, *J* = 8.4 Hz, 1H), 7.46 (d, *J* = 1.6 Hz, 1H), 7.37 (dd, *J* = 8.2 Hz, 1.6 Hz, 1H), 7.28 (s, 1H), 6.92 (d, *J* = 8.3 Hz, 1H), 6.83 (d, *J* = 8.5 Hz, 1H), 4.05 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 197.27, 179.43, 159.63, 157.52, 155.93, 136.34, 136.17, 135.32, 130.14, 128.45, 127.19, 126.25, 108.71, 105.66, 104.20, 100.27, 55.64; HRMS: calcd for C<sub>17</sub>H<sub>10</sub>Cl<sub>2</sub>O<sub>5</sub> [M+H]<sup>+</sup> 364.9905, found 364.9980.



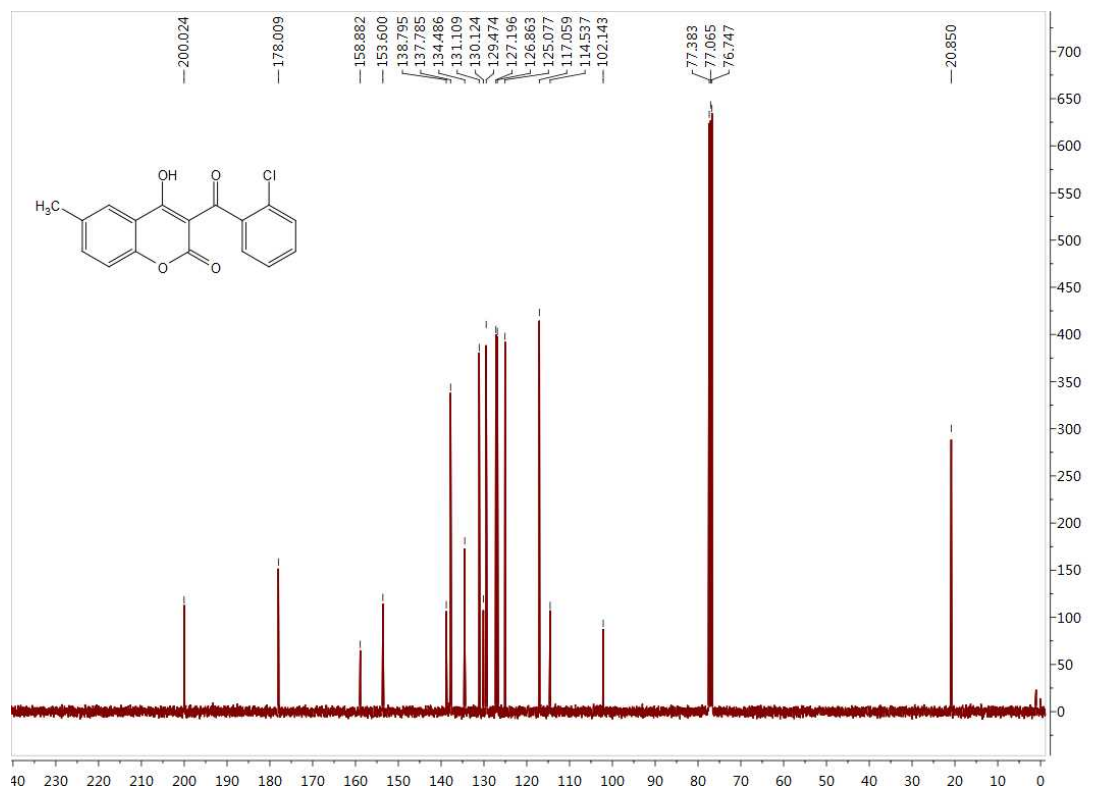
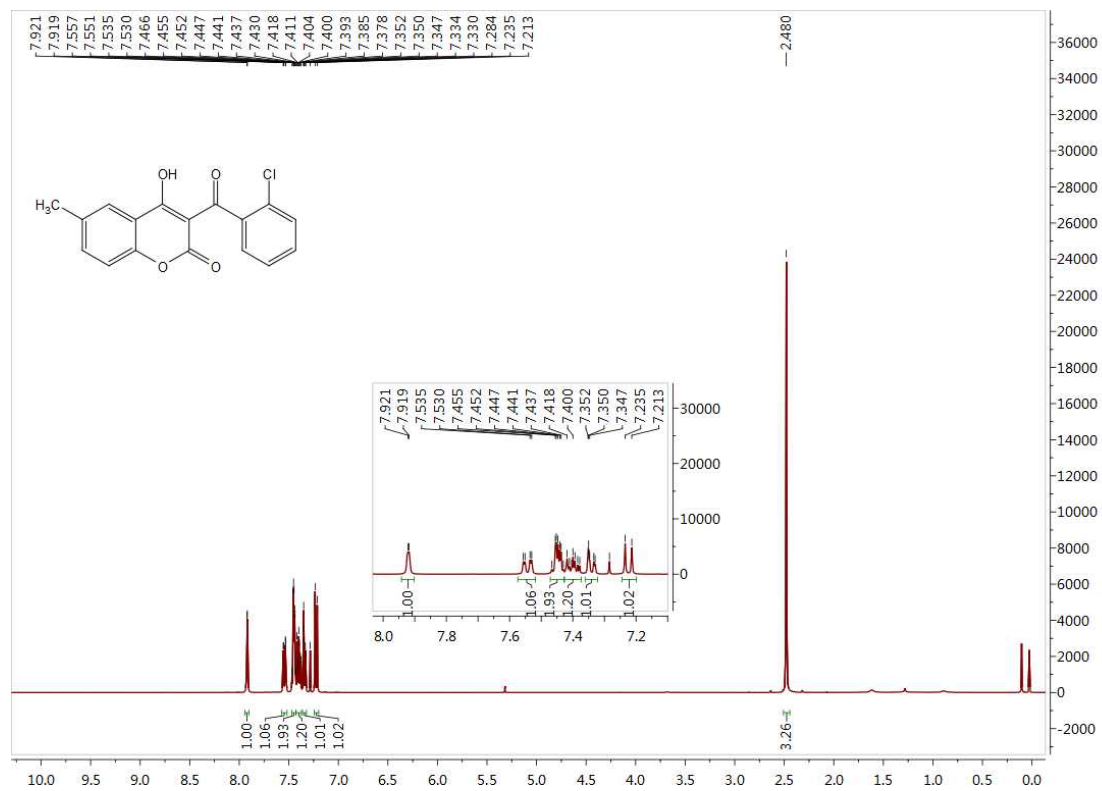


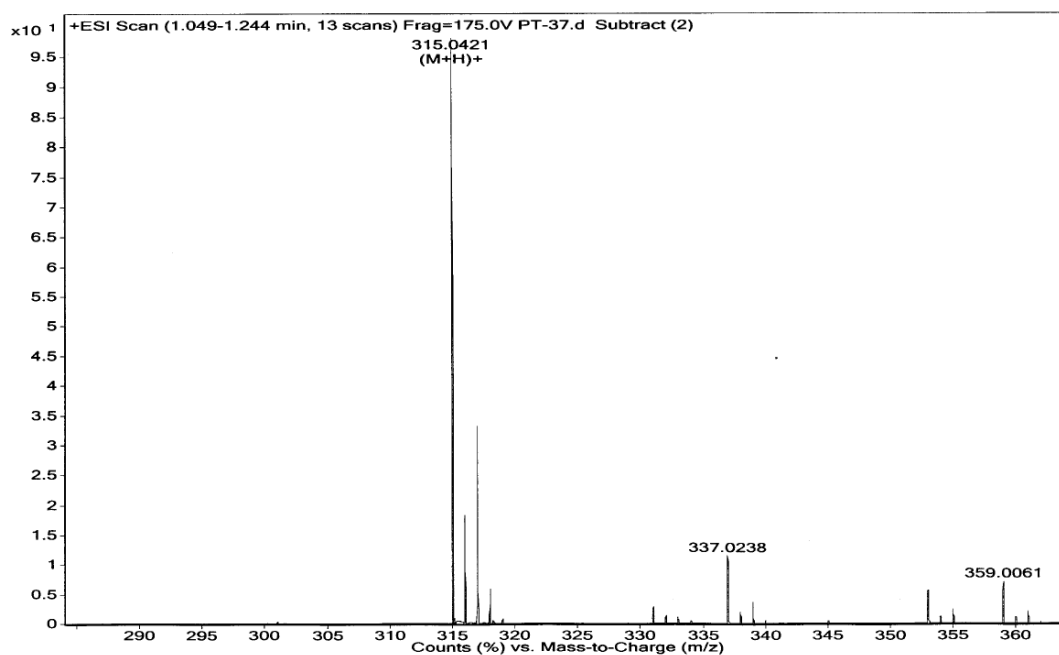
Data for **12-18**: pale yellow solid; yield 50%; m.p. 208-211 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.62 (t,  $J = 8.4$  Hz, 1H), 7.45-7.34 (m, 3H), 7.31 (dd,  $J = 6.8$  Hz, 1.8 Hz, 1H), 6.90 (dd,  $J = 8.4$  Hz, 0.7 Hz, 1H), 6.81 (d,  $J = 8.4$  Hz, 1H), 4.04 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 199.38, 180.51, 160.59, 158.55, 156.97, 138.79, 137.04, 130.97, 130.09, 129.45, 127.19, 126.85, 109.74, 106.59, 105.32, 101.35, 56.67; HRMS: calcd for  $\text{C}_{17}\text{H}_{10}\text{ClO}_5$   $[\text{M}+\text{H}]^+$  331.0295, found 331.0368.



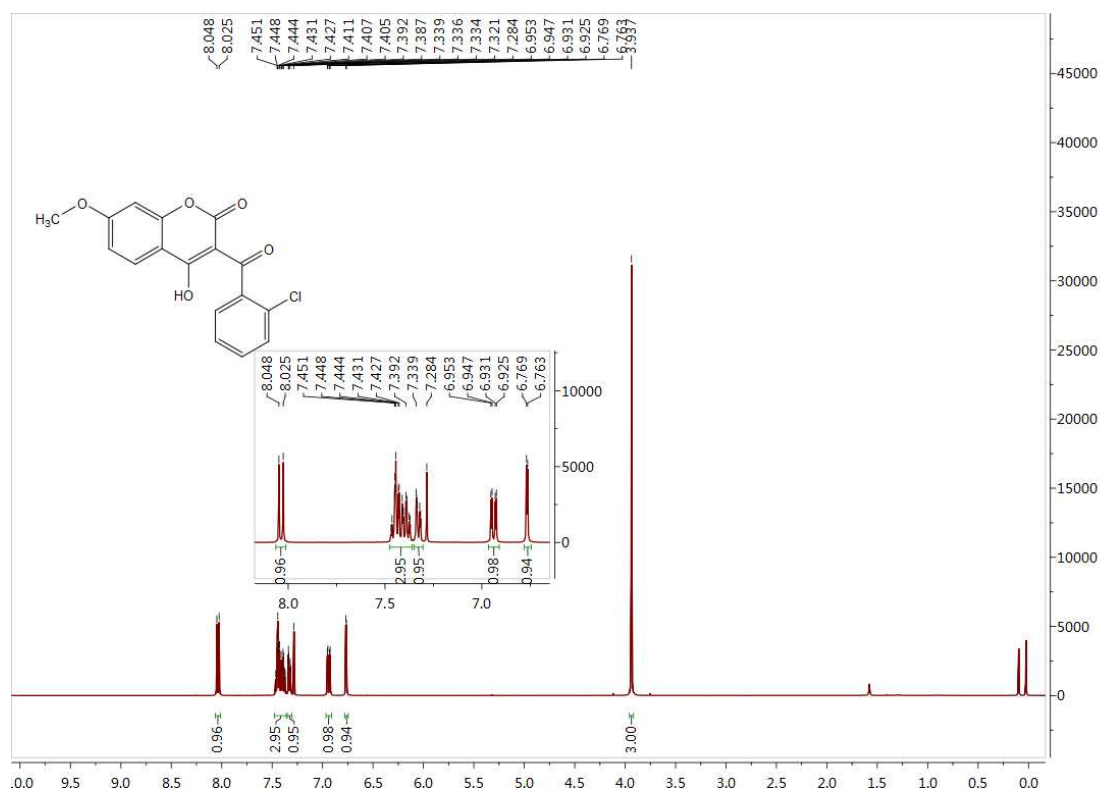


Data for **12-19**: light yellow solid; yield 55%; m.p. 177-179 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.92 (d,  $J = 1.1$  Hz, 1H), 7.54 (dd,  $J = 8.5$  Hz, 2.1 Hz, 1H), 7.47-7.43 (m, 2H), 7.42-7.37 (m, 1H), 7.36-7.32 (m, 1H), 7.22 (d,  $J = 8.5$  Hz, 1H), 2.48 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 200.01, 178.01, 158.86, 153.62, 138.81, 137.75, 134.47, 130.14, 129.47, 127.19, 126.84, 125.08, 117.06, 114.57, 102.16, 20.83; HRMS: calcd for  $\text{C}_{17}\text{H}_{11}\text{ClO}_4$   $[\text{M}+\text{H}]^+$  315.0346, found 315.0421.

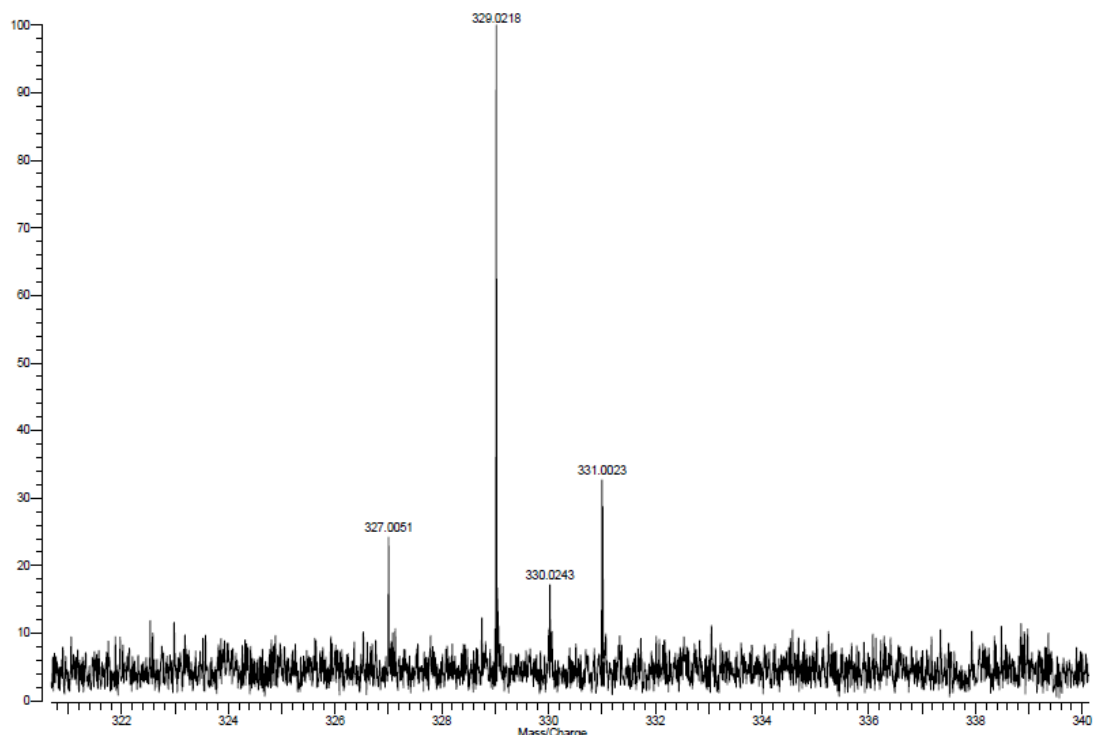
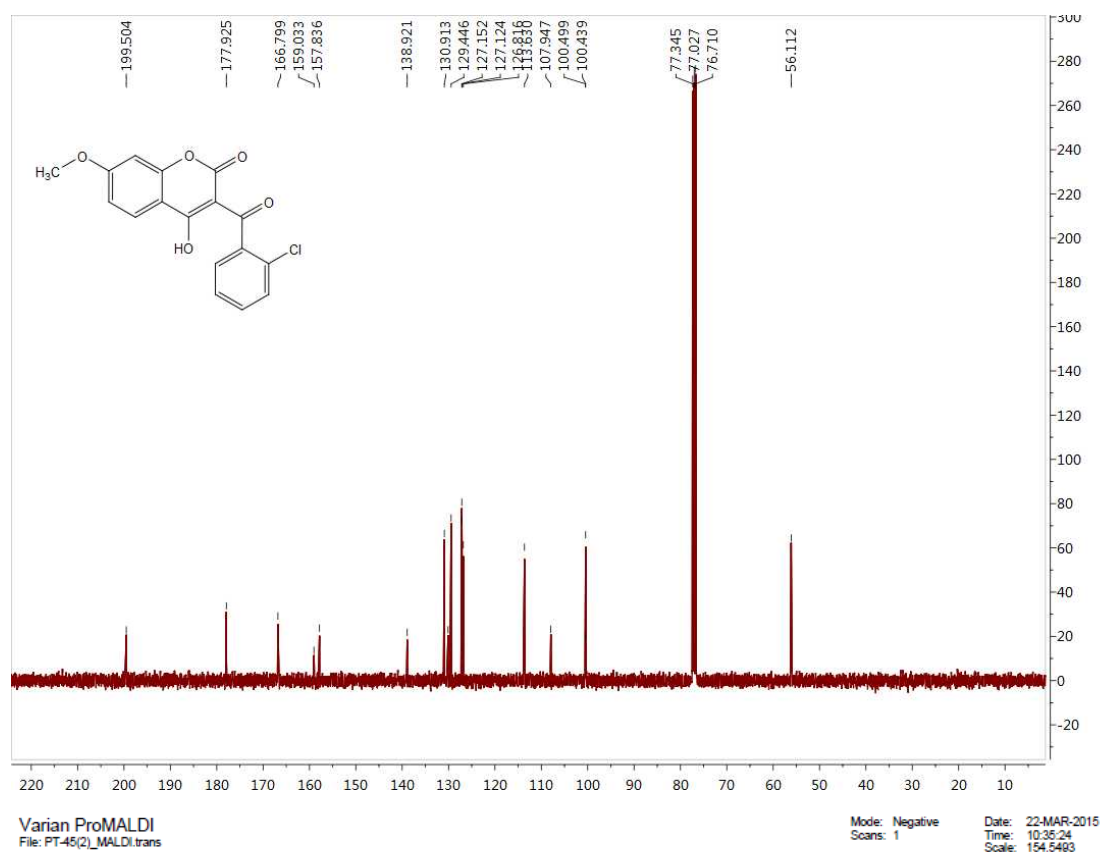




Data for **12-20**: white solid; yield 52%; m.p. 204-206 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.04 (d, *J* = 8.9 Hz, 1H), 7.48-7.36 (m, 3H), 7.35-7.31 (m, 1H), 6.94 (dd, *J* = 8.9 Hz, 2.4 Hz, 1H), 6.77 (d, *J* = 2.3 Hz, 1H), 3.94 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 199.50, 177.92, 166.80, 159.03, 157.84, 138.92, 130.91, 130.10, 129.45, 127.15, 127.12, 126.82, 113.63, 107.95, 100.50, 100.44, 56.11; HRMS: calcd for C<sub>17</sub>H<sub>11</sub>ClO<sub>5</sub> [M-H]<sup>-</sup> 329.0295, found 329.0218.





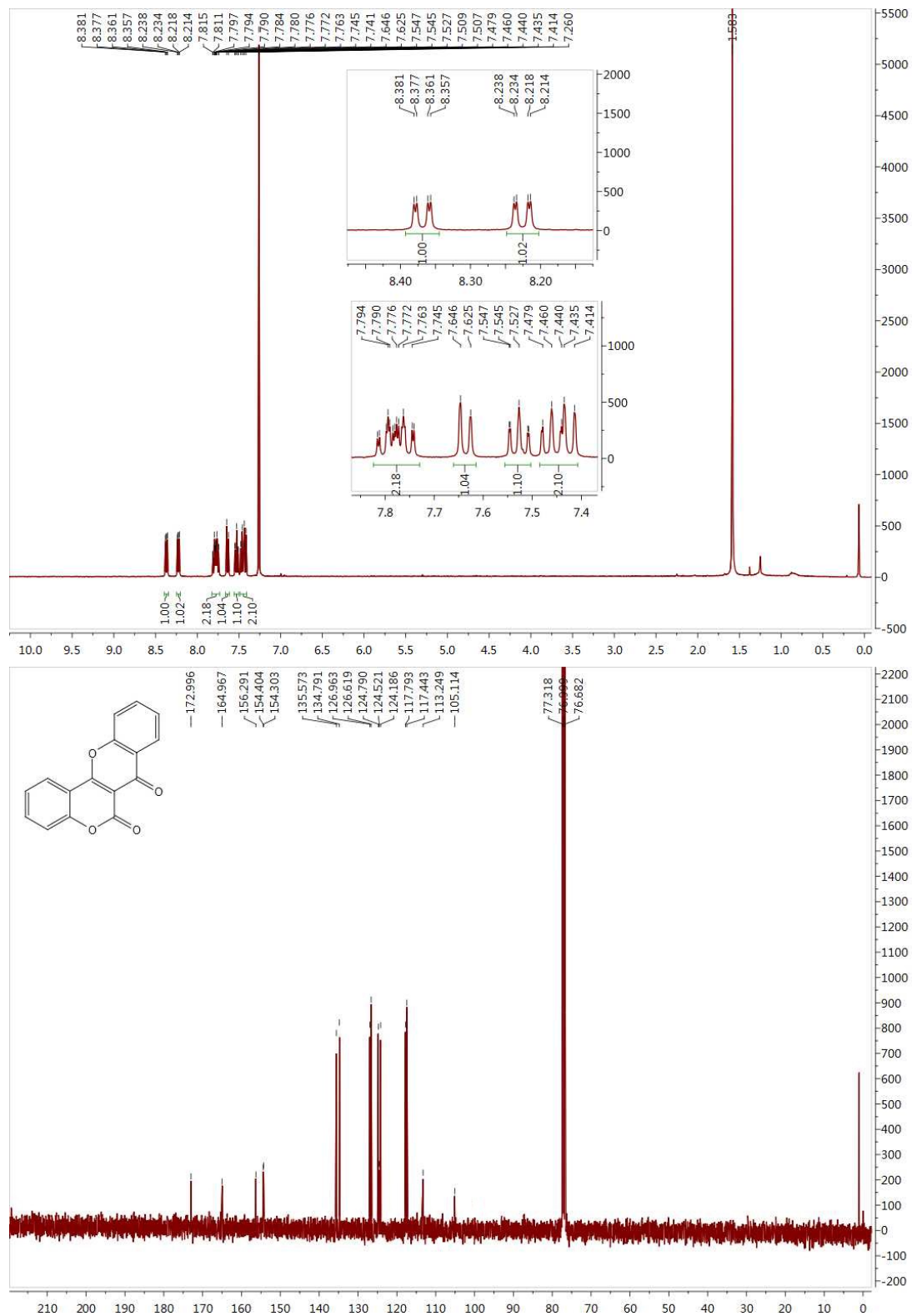


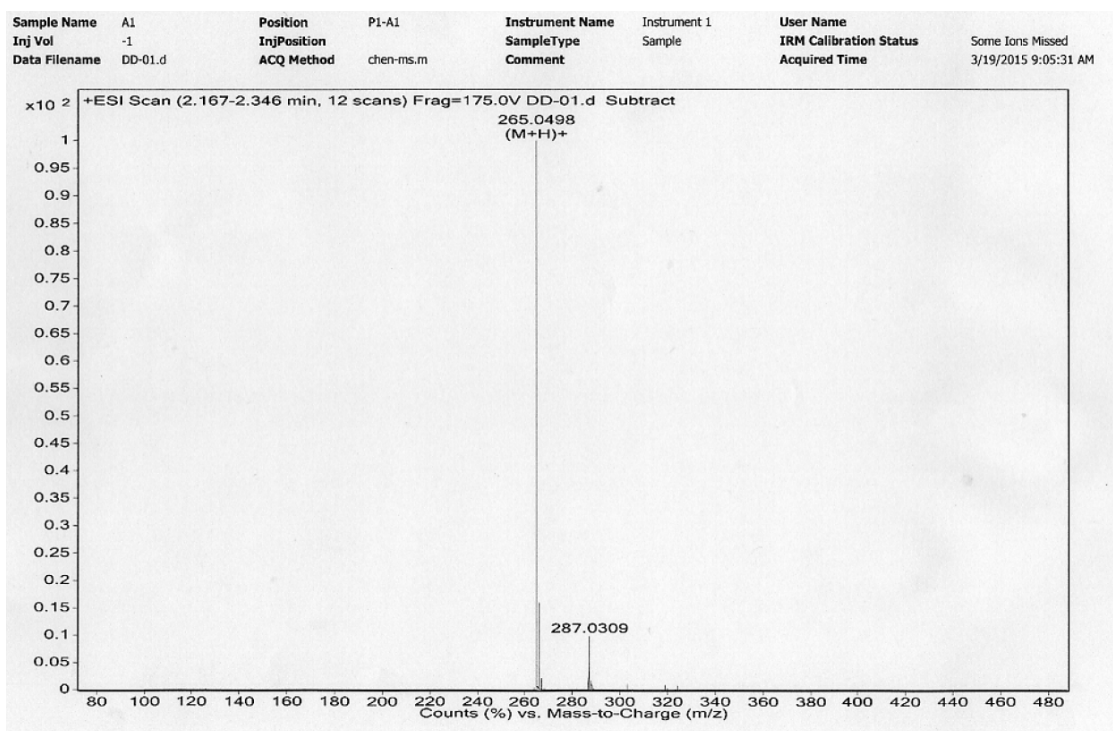
### Analytical Data for products 13-1 to 13-20:

Data for **13-1** <sup>[2]</sup>: white solid; yield 94%; m.p. 240-242 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.37

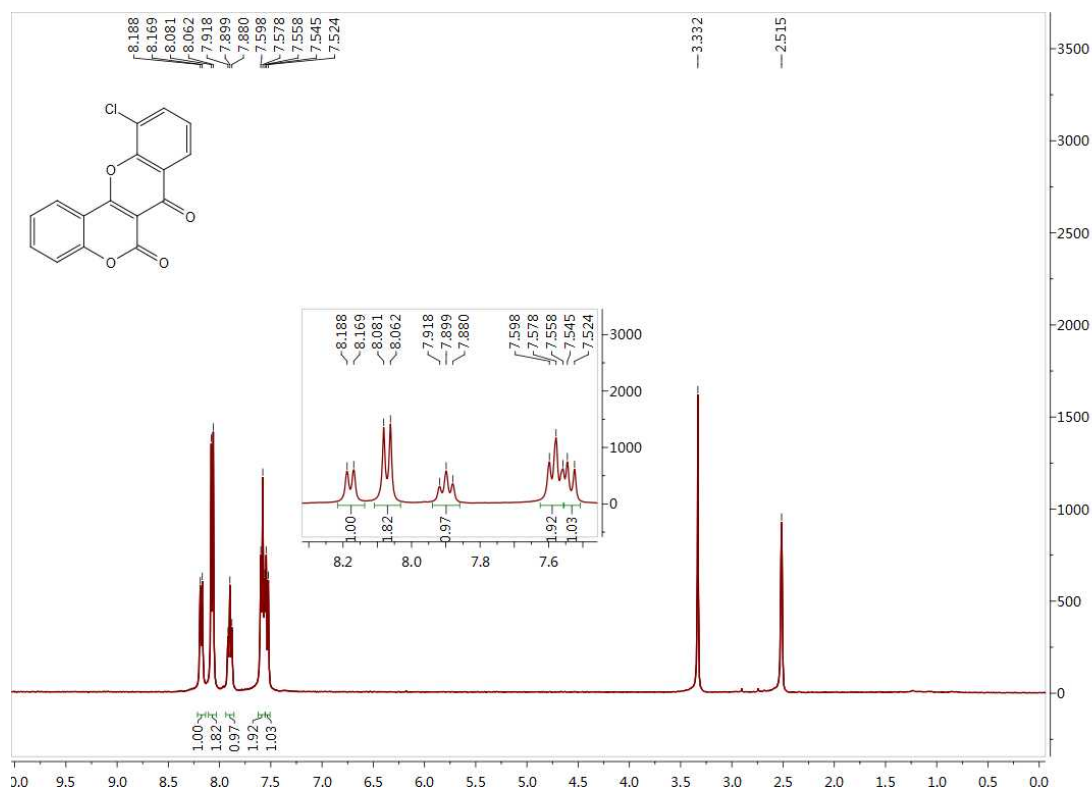
(dd, *J* = 7.9 Hz, 1.6 Hz, 1H), 8.23 (dd, *J* = 8.0 Hz, 1.5 Hz, 1H), 7.83-7.71 (m, 2H), 7.64 (d, *J* = 8.3

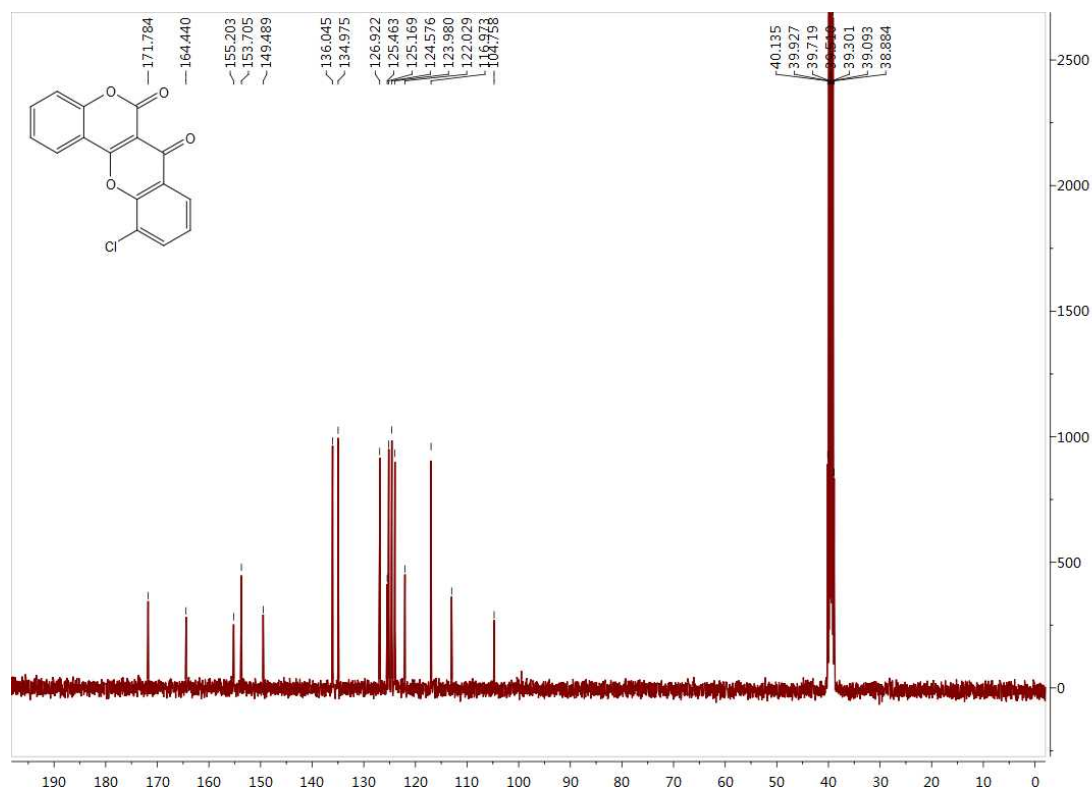
Hz, 1H), 7.56-7.50 (m, 1H), 7.49-7.40 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 173.00, 164.97, 156.29, 154.40, 154.30, 135.57, 134.79, 126.96, 126.62, 124.79, 124.52, 124.19, 117.79, 117.44, 113.25, 105.11; HRMS: calcd for  $\text{C}_{16}\text{H}_8\text{O}_4$   $[\text{M}+\text{H}]^+$  265.0423, found 265.0498.



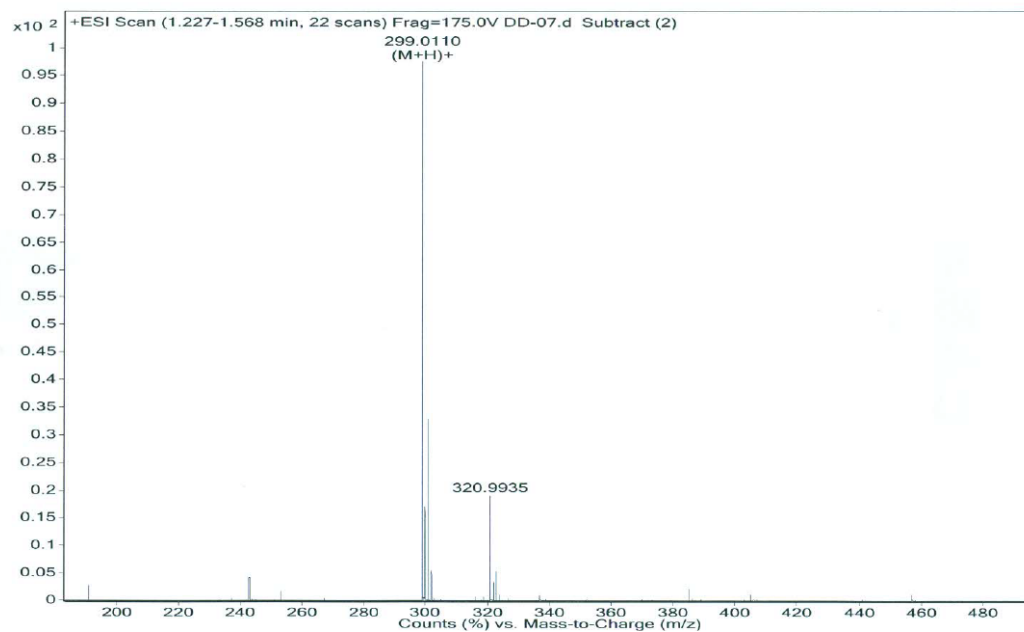


Data for **13-2**: white solid; yield 90%; m.p. 294-296 °C; <sup>1</sup>H NMR (400 MHz, DMSO) δ: 8.18 (d, *J* = 7.7 Hz, 1H), 8.07 (d, *J* = 7.9 Hz, 2H), 7.90 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.9 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 1H); <sup>13</sup>C NMR (100 MHz, DMSO) δ: 171.78, 164.44, 155.20, 153.71, 149.49, 136.04, 134.97, 126.92, 125.46, 125.17, 124.58, 123.98, 122.03, 116.97, 112.98, 104.76; HRMS: calcd for C<sub>16</sub>H<sub>7</sub>ClO<sub>4</sub> [M+H]<sup>+</sup> 299.0033, found 299.0110.

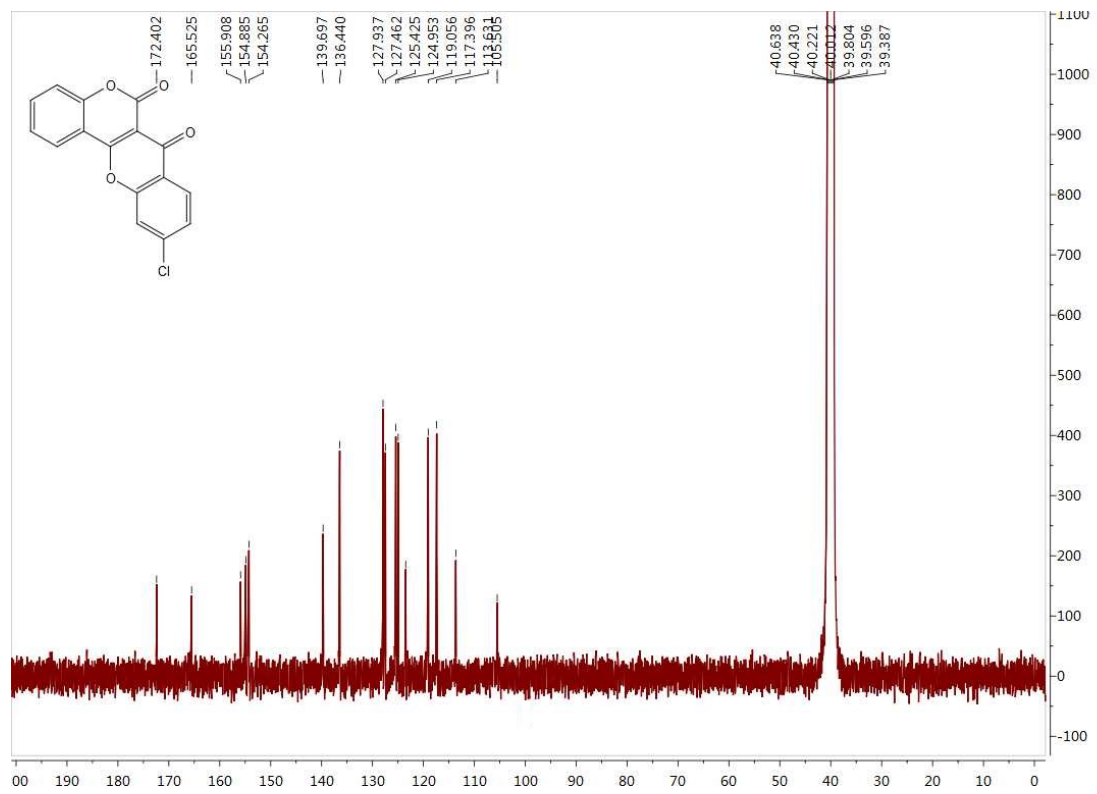
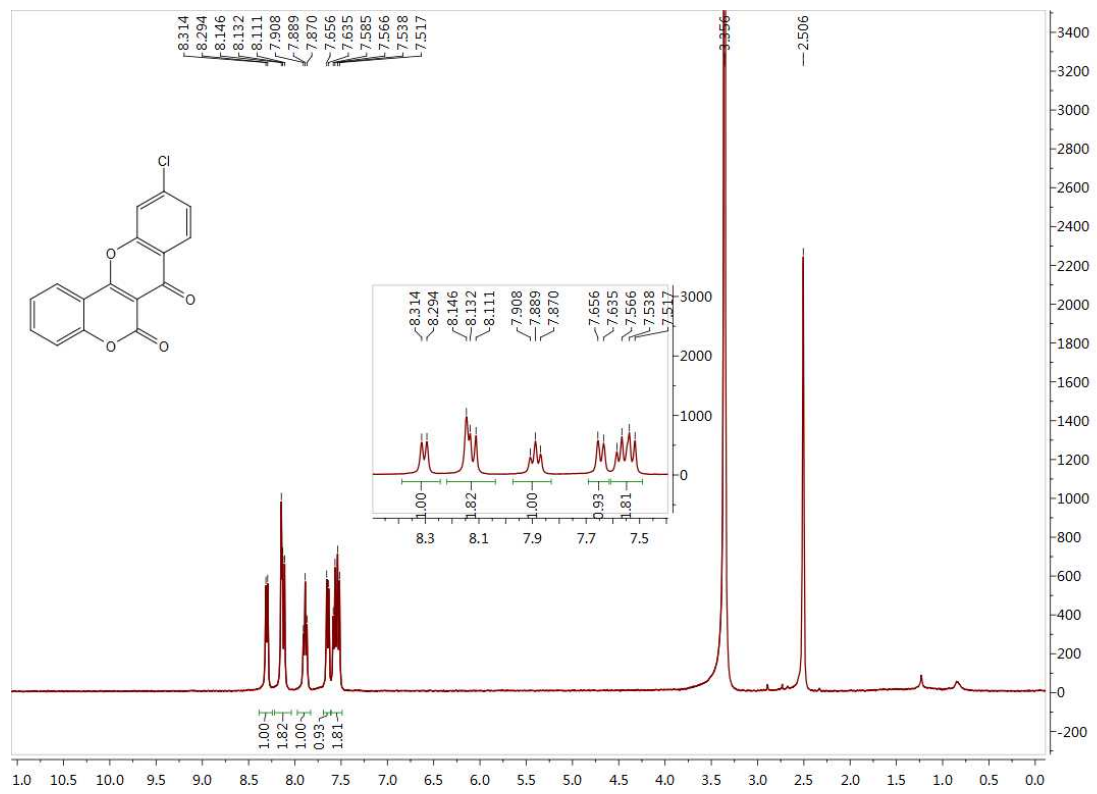


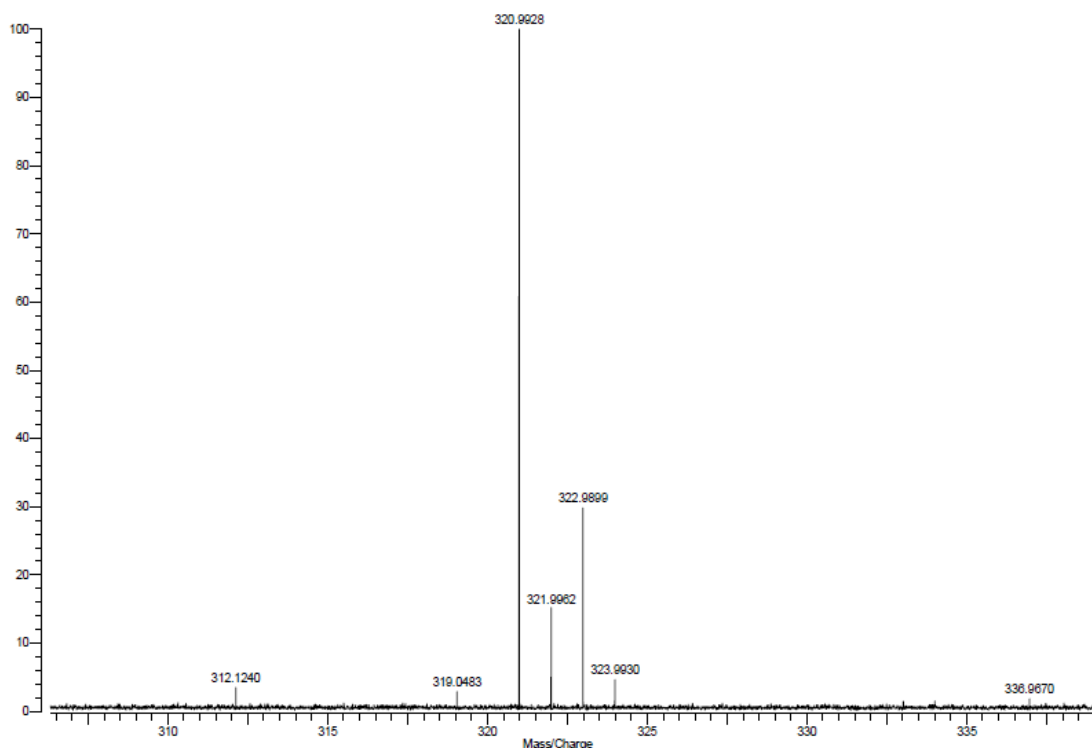


Sample Name	A3	Position	P1-A3	Instrument Name	Instrument 1	User Name	
Inj Vol	-1	InjPosition		SampleType	Sample	IRM Calibration Status	Some Ions Missed
Data Filename	DD-07.d	ACQ Method	chem-ms.m	Comment		Acquired Time	1/23/2015 8:53:58 AM

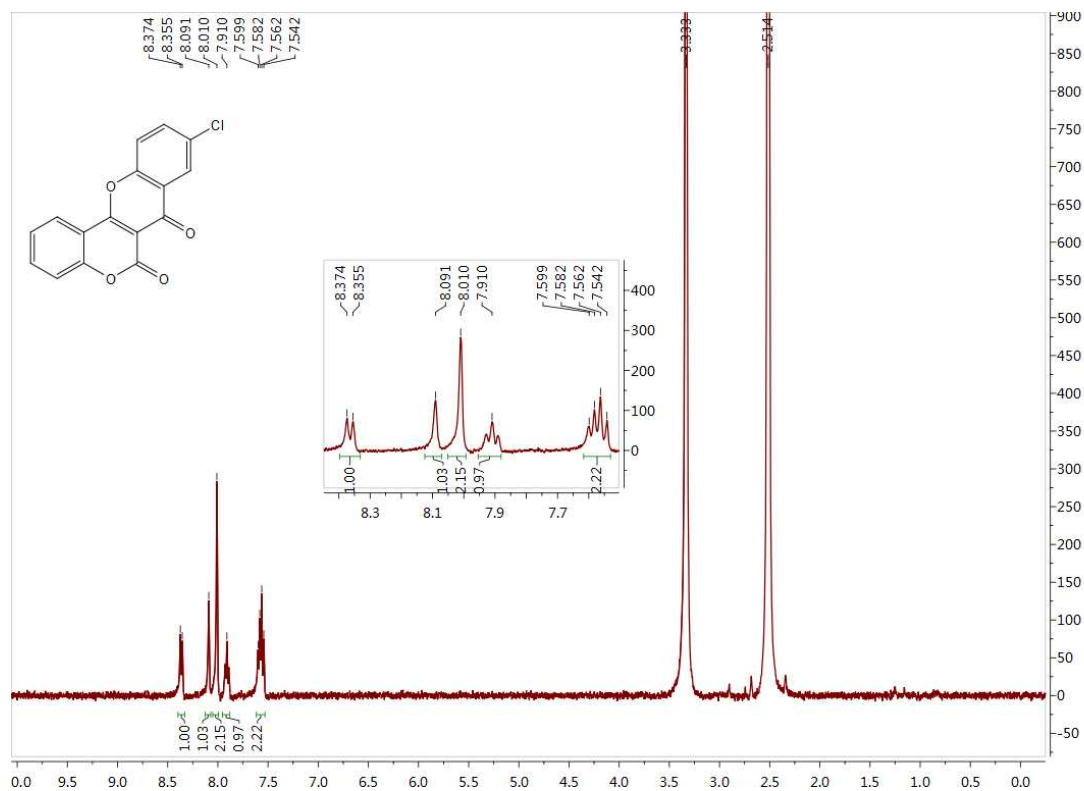


Data for **13-3**: white solid; yield 96%; m.p. > 300 °C;  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$ : 8.30 (d,  $J$  = 7.8 Hz, 1H), 8.18-8.07 (m, 2H), 7.89 (t,  $J$  = 7.7 Hz, 1H), 7.65 (d,  $J$  = 8.5 Hz, 1H), 7.55 (dd,  $J$  = 19.2 Hz, 8.0 Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz, DMSO)  $\delta$ : 172.40, 165.52, 155.91, 154.88, 154.26, 139.70, 136.44, 127.94, 127.46, 125.42, 124.95, 123.48, 119.06, 117.40, 113.63, 105.50; HRMS: calcd for  $\text{C}_{16}\text{H}_7\text{ClO}_4$   $[\text{M}+\text{Na}]^+$  321.0033, found 320.9928.

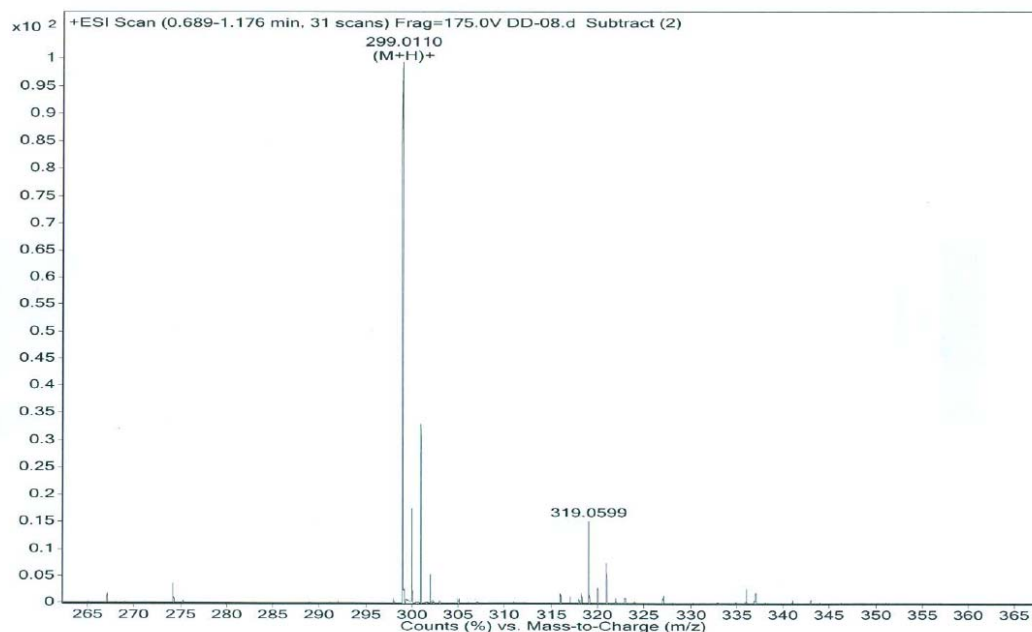




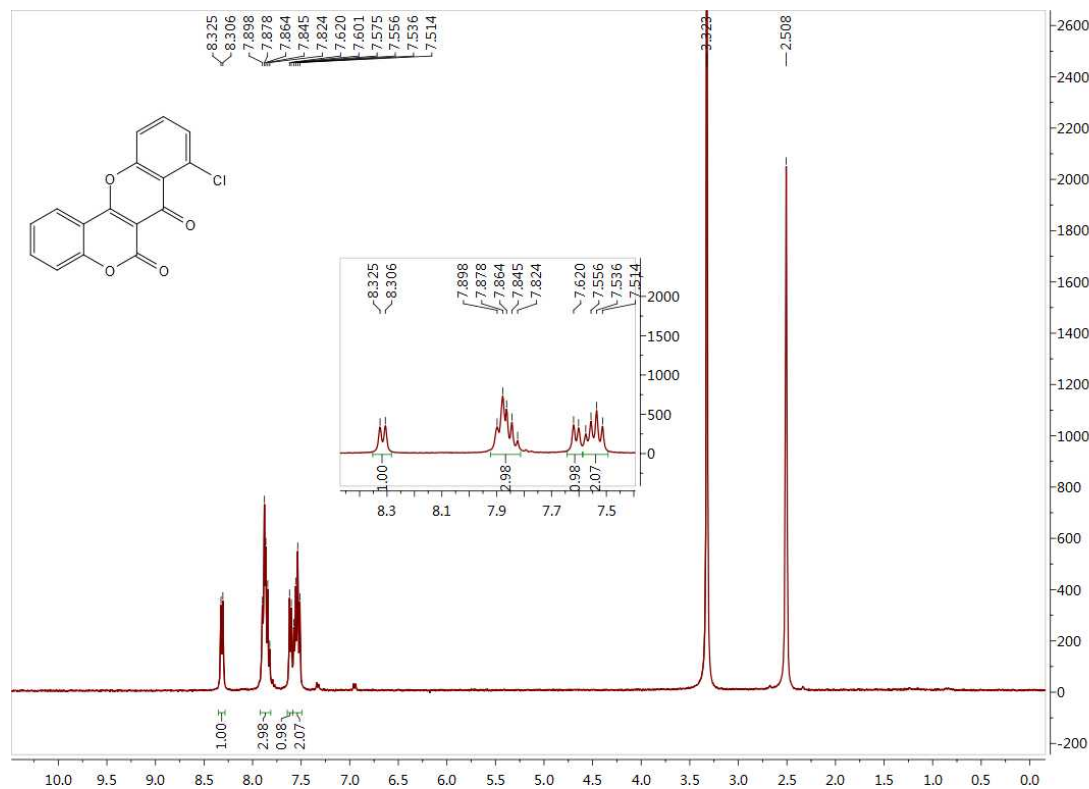
Data for **13-4**: white solid; yield 91%; m.p. > 300 °C;  $^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$ : 8.36 (d,  $J = 7.6$  Hz, 1H), 8.09 (s, 1H), 8.01 (s, 2H), 7.91 (t,  $J = 7.8$  Hz, 1H), 7.57 (m, 2H); HRMS: calcd for  $\text{C}_{16}\text{H}_7\text{ClO}_4$   $[\text{M}+\text{Na}]^+$  321.0033, found 320.9928.



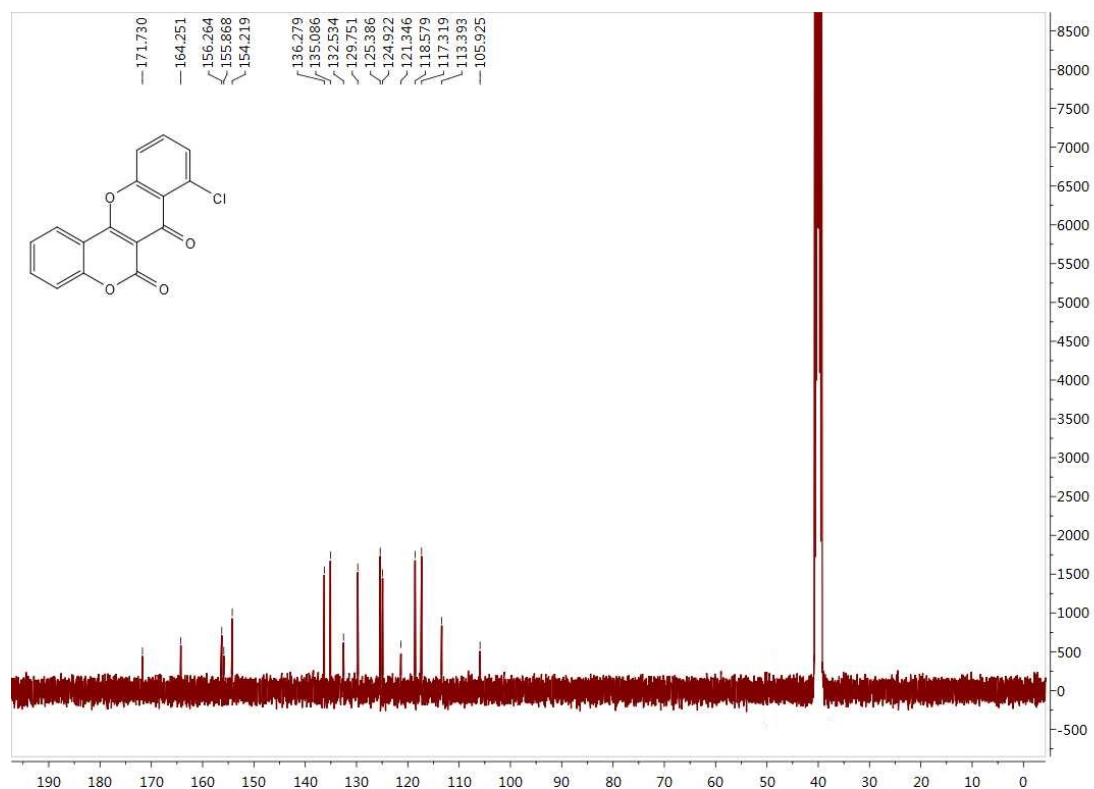
Sample Name	Position	Instrument Name	User Name
A4	P1-A4	Instrument 1	
Inj Vol	InjPosition	SampleType	IRM Calibration Status
-1		Sample	Some Ions Missed
Data Filename	ACQ Method	Comment	Acquired Time
DD-08.d	chen-ms.m		1/23/2015 8:58:43 AM



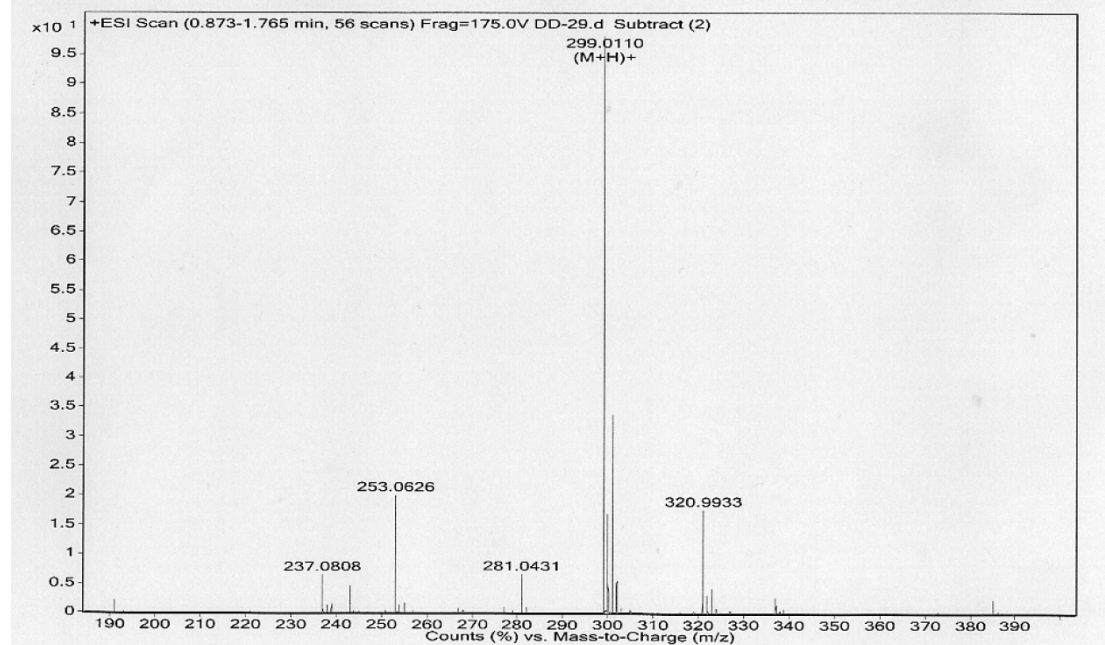
Data for **13-5**: white solid; yield 97%; m.p. > 300 °C;  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$ : 8.32 (d,  $J = 7.7$  Hz, 1H), 8.01-7.77 (m, 3H), 7.61 (d,  $J = 7.3$  Hz, 1H), 7.55 (dd,  $J = 16.4$  Hz, 8.2 Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz, DMSO)  $\delta$ : 171.73, 164.25, 156.26, 155.87, 154.22, 136.28, 135.09, 132.53, 129.75, 125.39, 124.92, 121.35, 118.58, 117.32, 113.39, 105.92; HRMS: calcd for  $\text{C}_{16}\text{H}_7\text{ClO}_4$   $[\text{M}+\text{Na}]^+$  299.0033, found 299.0110.





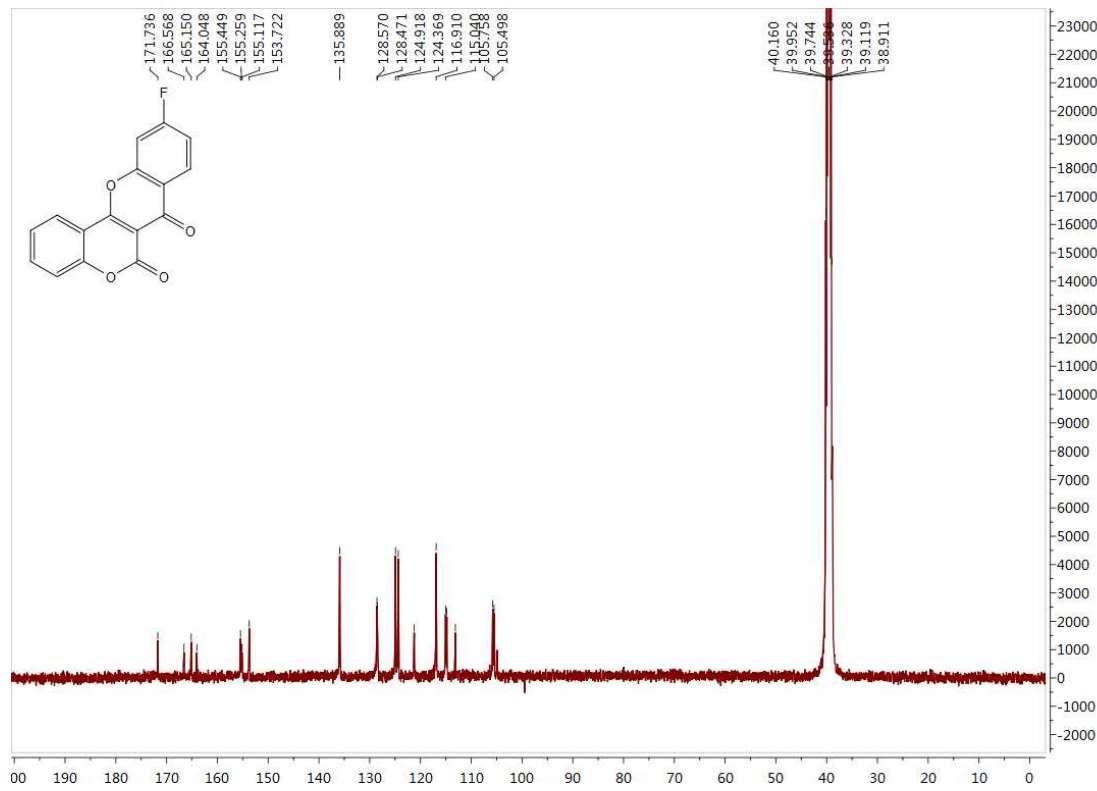
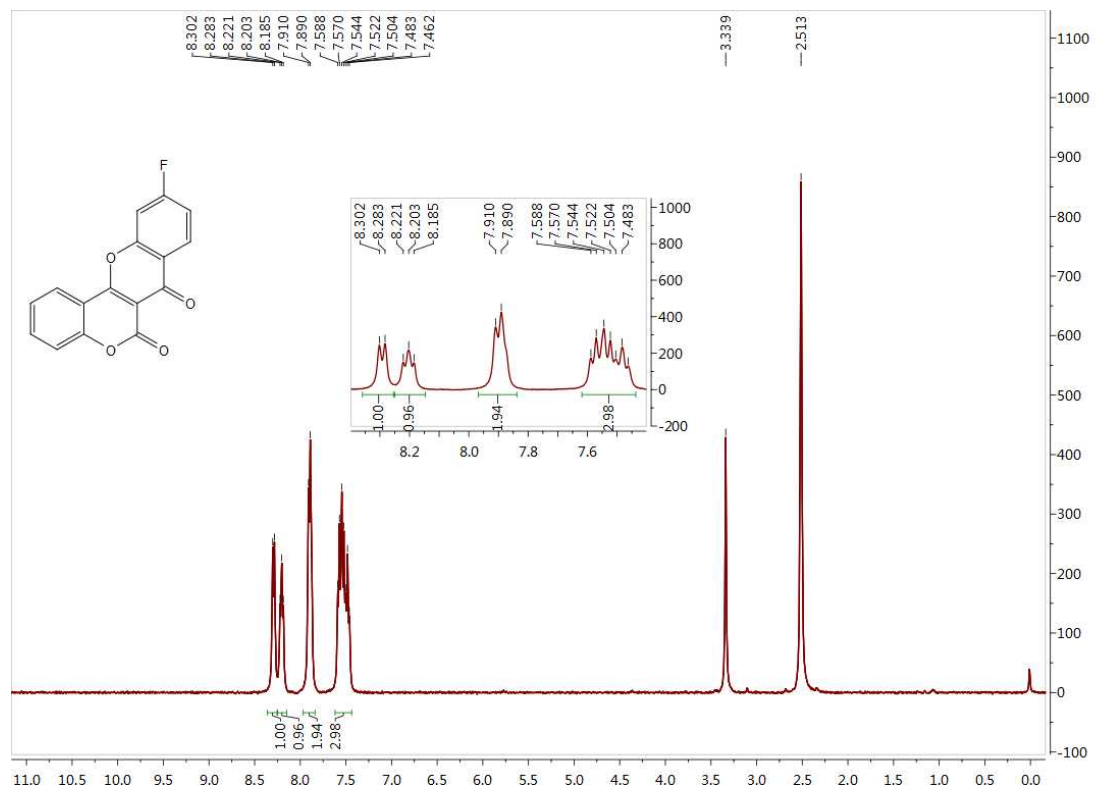


Sample Name	A2	Position	P1-A2	Instrument Name	Instrument 1	User Name	
Inj Vol	-1	InjPosition		SampleType	Sample	IRM Calibration Status	Some Ions Missed
Data Filename	DD-29.d	ACQ Method	chen-rs.m	Comment		Acquired Time	3/19/2015 9:10:18 AM

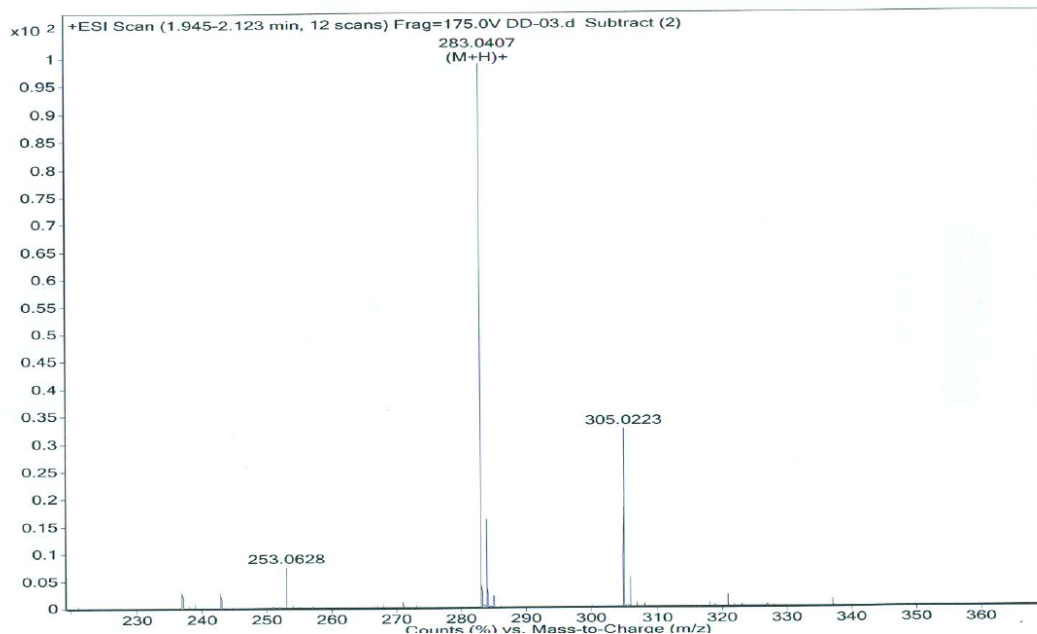


Data for **13-6**: white solid; yield 94%; m.p. > 300 °C;  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$ : 8.29 (d,  $J = 7.6$  Hz, 1H), 8.20 (t,  $J = 7.2$  Hz, 1H), 7.90 (d,  $J = 7.7$  Hz, 2H), 7.62-7.40 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz, DMSO)  $\delta$ : 171.74, 166.57, 165.15, 164.05, 155.45, 155.19 (d), 153.72, 135.89, 128.52 (d), 124.64 (d), 121.24, 116.91, 114.93 (d), 113.13, 105.63 (d); HRMS: calcd for  $\text{C}_{16}\text{H}_7\text{FO}_4$   $[\text{M}+\text{H}]^+$  283.0328, found 283.0407.

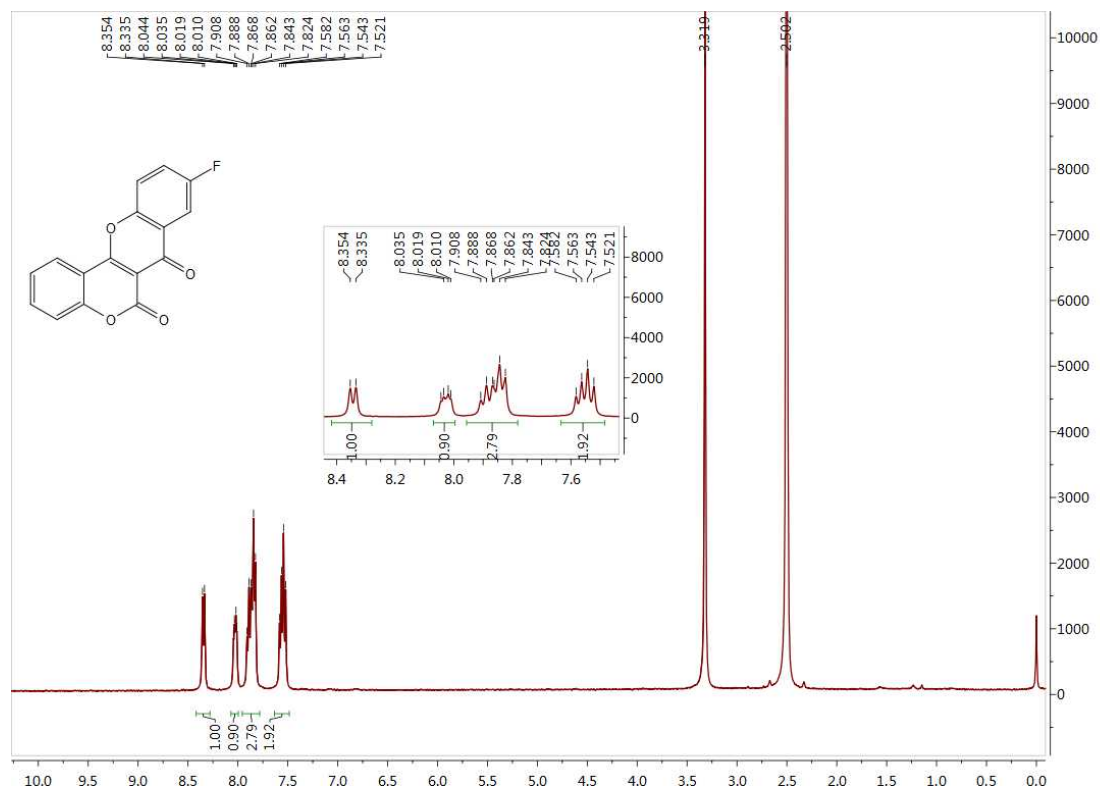




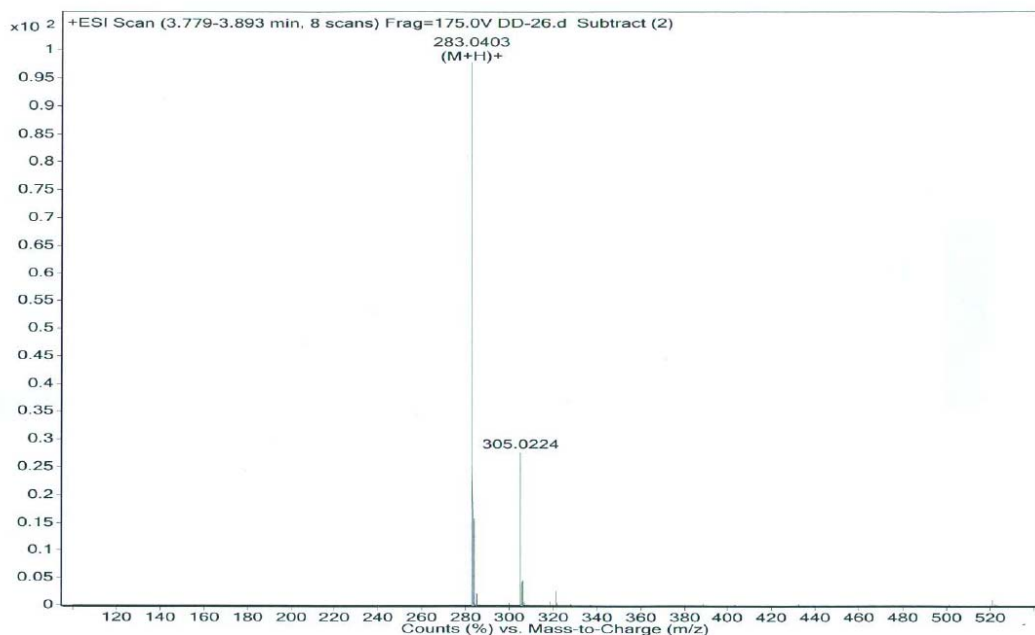
Sample Name	lc/ms	Position	P1-A3	Instrument Name	Instrument 1	User Name	
Inj Vol	2	InjPosition		SampleType	Sample	IRM Calibration Status	Some Ions Missed
Data Filename	DD-03.d	ACQ Method	chen-ms.m	Comment		Acquired Time	12/26/2014 8:05:43 AM



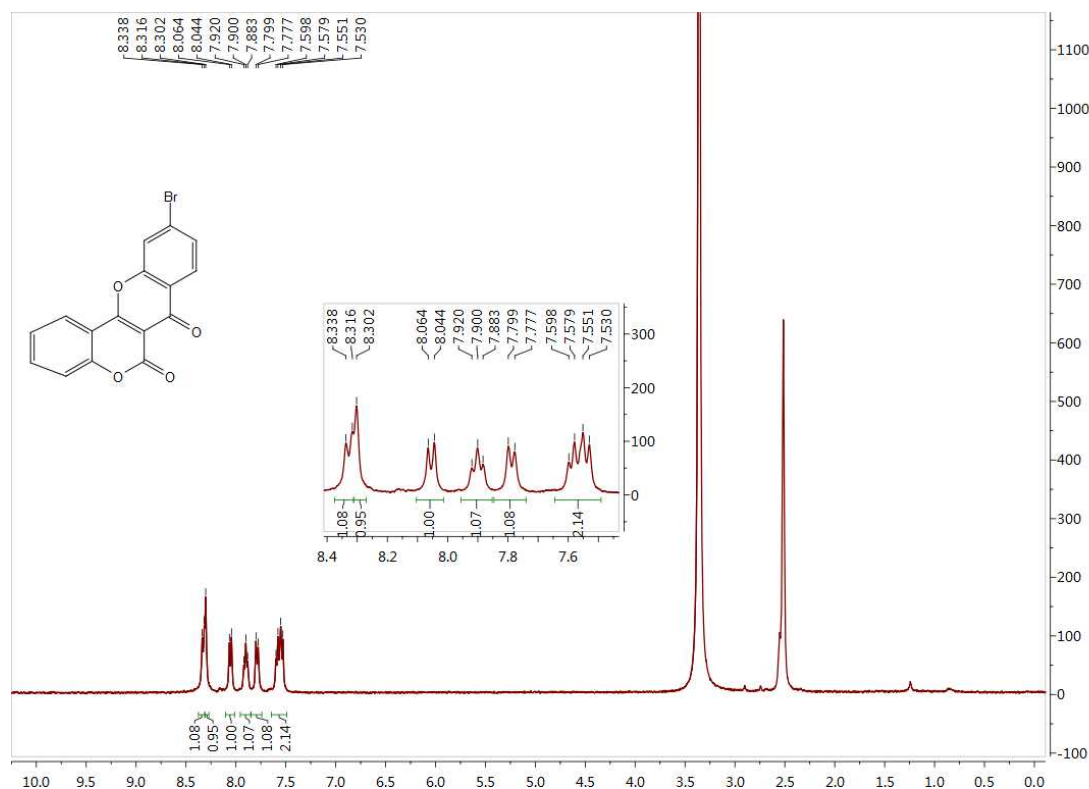
Data for **13-7**: white solid; yield 91%; m.p. > 300 °C; <sup>1</sup>H NMR (400 MHz, DMSO) δ: 8.34 (d, *J* = 7.8 Hz, 1H), 8.03 (d, *J* = 6.3 Hz, 1H), 7.94-7.78 (m, 3H), 7.55 (m, 2H); HRMS: calcd for C<sub>16</sub>H<sub>7</sub>FO<sub>4</sub> [M+H]<sup>+</sup> 283.0328, found 283.0403.

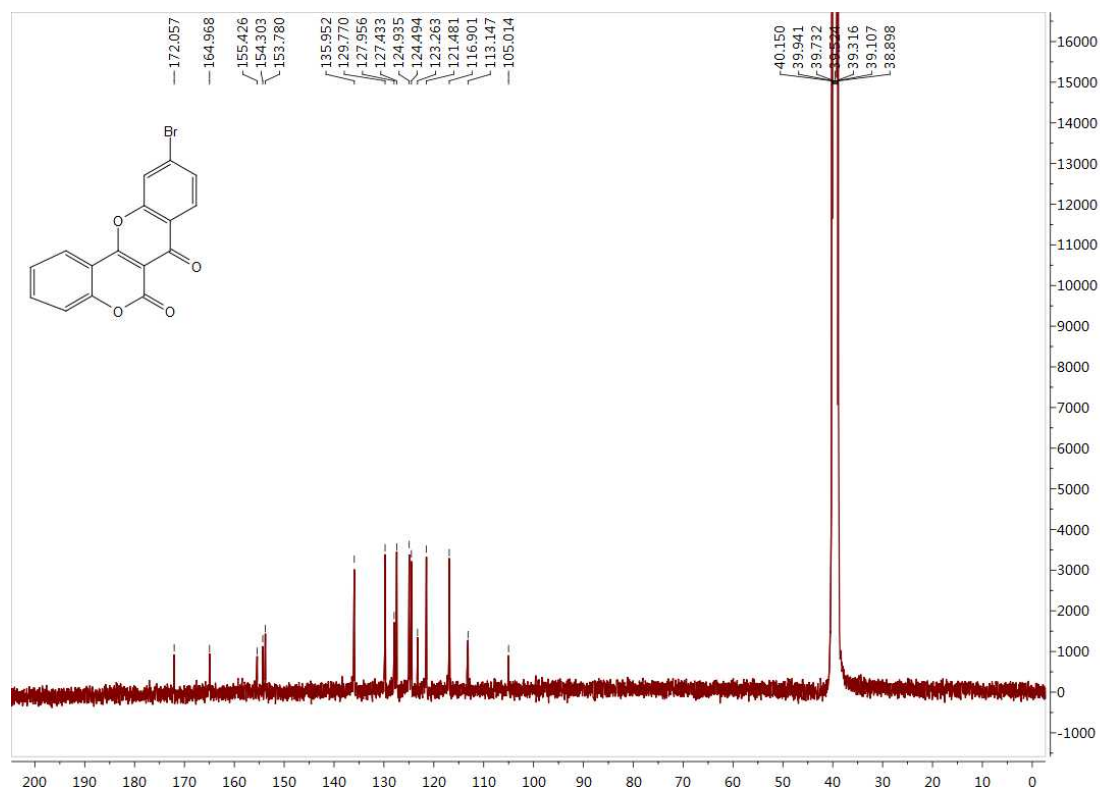


Sample Name	lc/ms	Position	P1-A5	Instrument Name	Instrument 1	User Name	
Inj Vol	2	InjPosition		SampleType	Sample	IRM Calibration Status	Some Ions Missed
Data Filename	DD-26.d	ACQ Method	chen-ms.m	Comment		Acquired Time	12/26/2014 8:15:16 AM



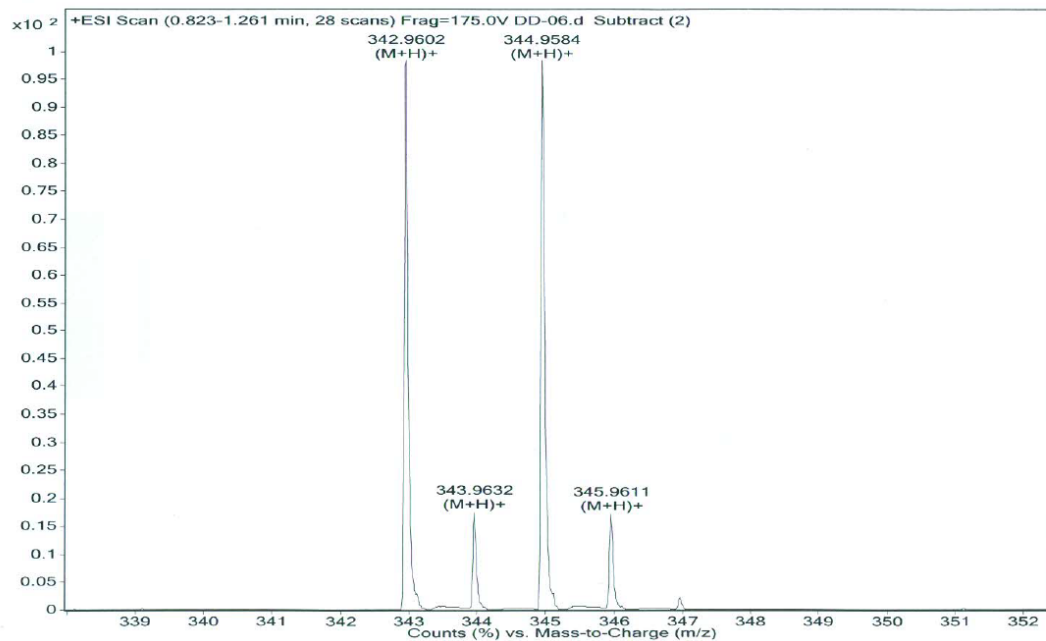
Data for **13-8**: white solid; yield 94%; m.p. > 300 °C;  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$ : 8.33 (d,  $J = 8.5$  Hz, 1H), 8.30 (s, 1H), 8.05 (d,  $J = 8.1$  Hz, 1H), 7.90 (t,  $J = 7.4$  Hz, 1H), 7.79 (d,  $J = 8.6$  Hz, 1H), 7.56 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz, DMSO)  $\delta$ : 172.06, 164.97, 155.43, 154.30, 153.78, 135.95, 129.77, 127.96, 127.43, 124.93, 124.49, 123.26, 121.48, 116.90, 113.15, 105.01; HRMS: calcd for  $\text{C}_{16}\text{H}_7\text{BrO}_4$   $[\text{M}+\text{H}]^+$  342.9528, found 342.9602.



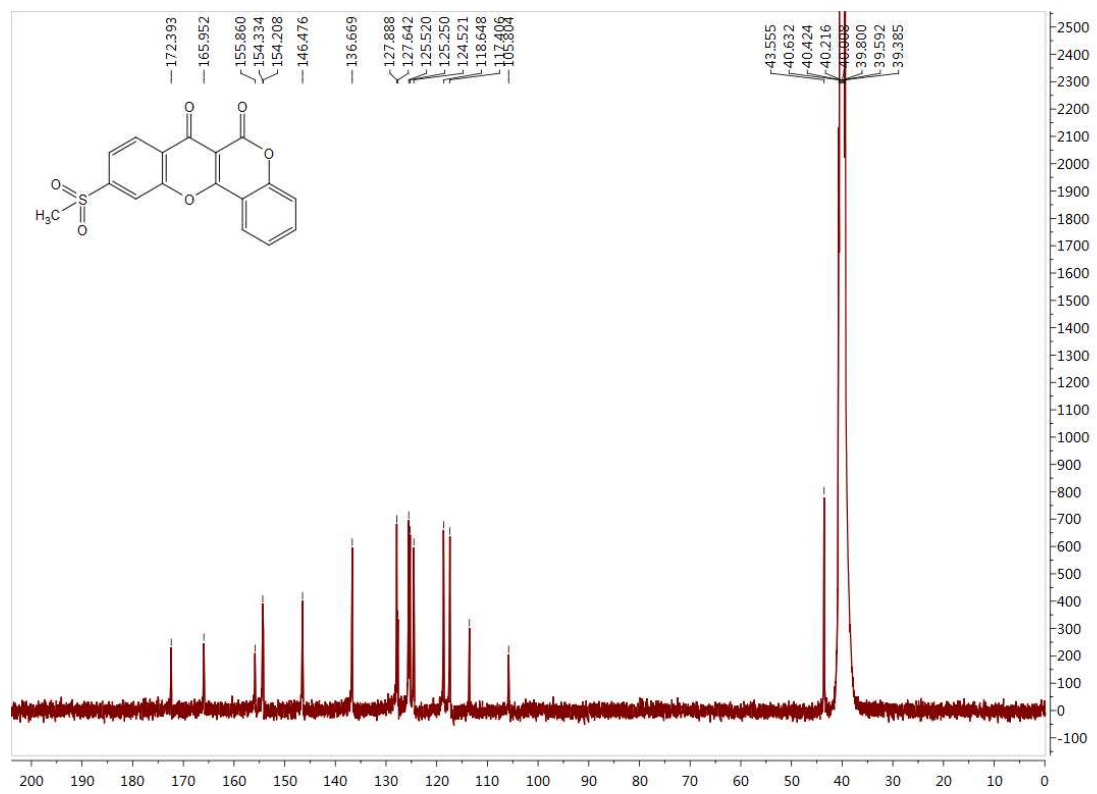
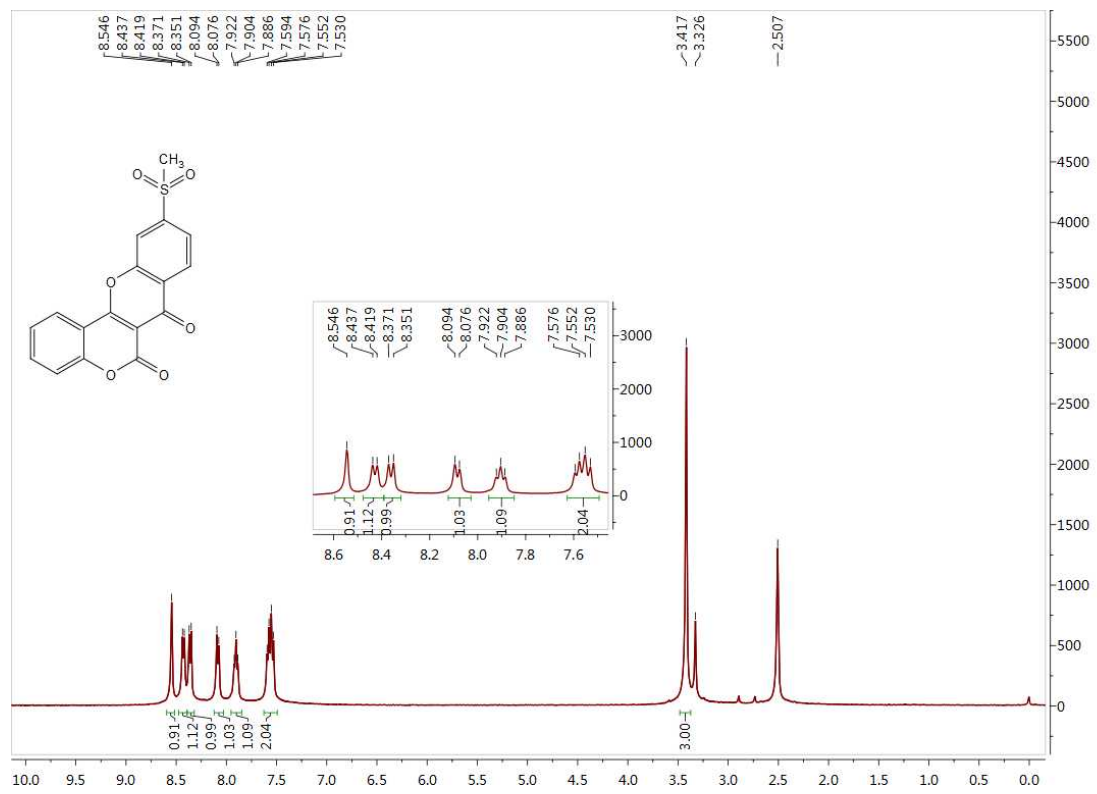


Sample Name	A2	Position	P1-A2	Instrument Name	Instrument 1	User Name
Inj Vol	-1	InjPosition		SampleType	Sample	IRM Calibration Status
Data Filename	DD-06.d	ACQ Method	chen-rs.m	Comment		Acquired Time

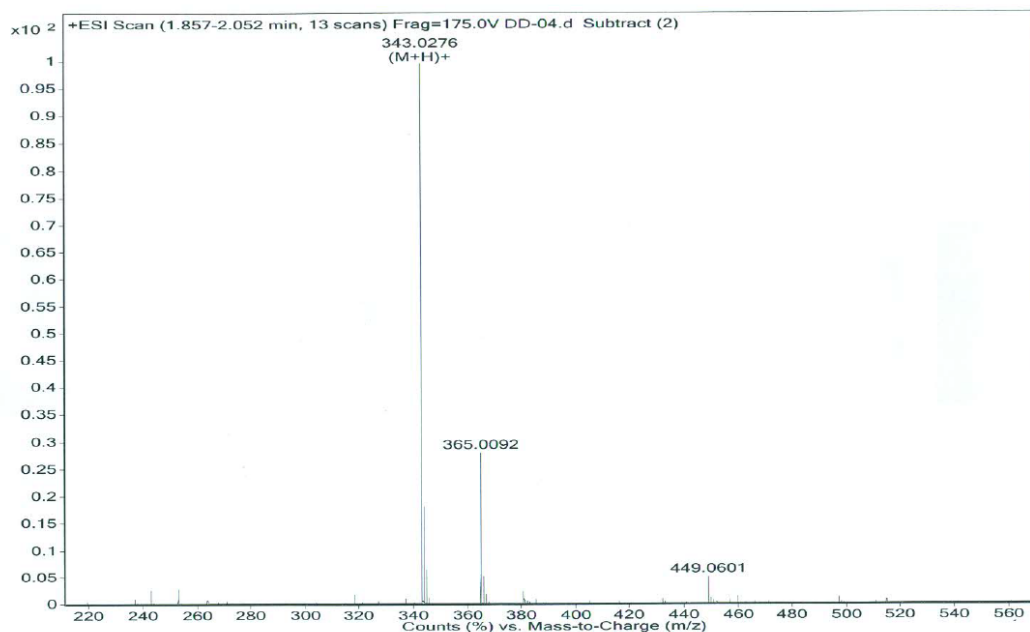
Some Ions Missed 1/23/2015 8:49:15 AM



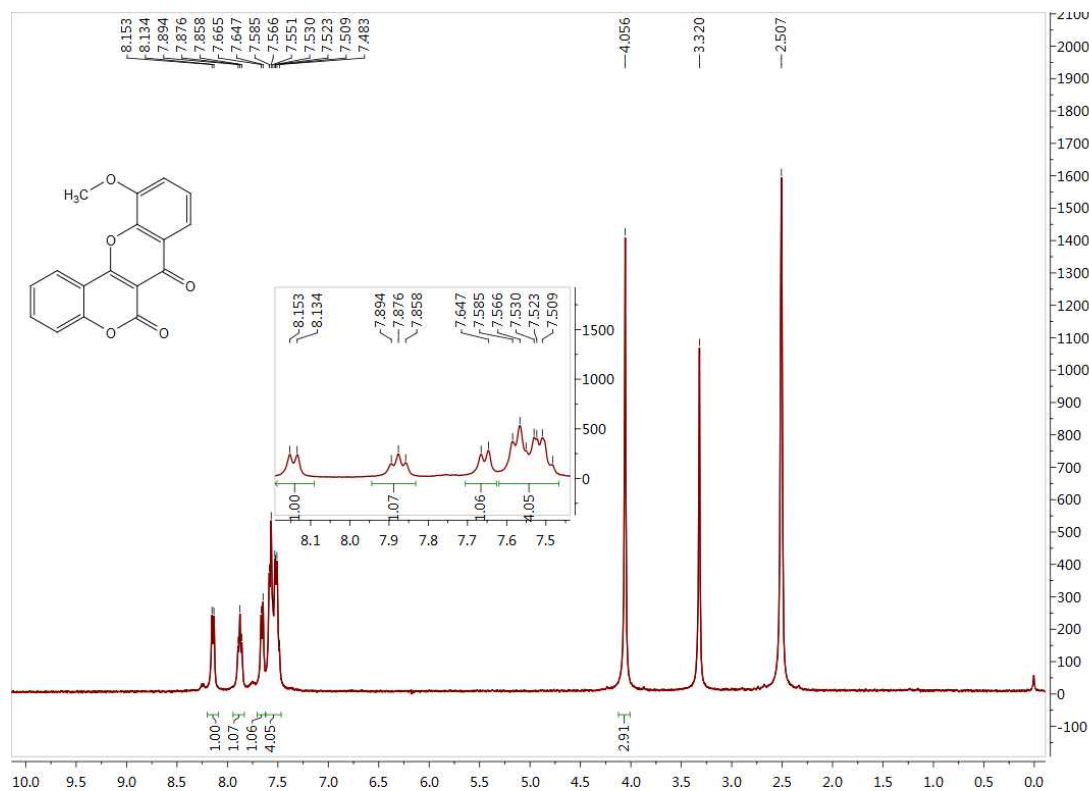
Data for **13-9**: white solid; yield 92%; m.p. > 300 °C;  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$ : 8.55 (s, 1H), 8.39 (dd,  $J = 27.0, 7.7$  Hz, 2H), 8.09 (d,  $J = 7.3$  Hz, 1H), 7.90 (t,  $J = 7.1$  Hz, 1H), 7.56 (m, 2H), 3.42 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz, DMSO)  $\delta$ : 172.39, 165.95, 155.86, 154.33, 154.21, 146.48, 136.67, 127.89, 127.64, 125.52, 125.25, 124.52, 118.65, 117.41, 113.55, 105.80, 43.55; HRMS: calcd for  $\text{C}_{17}\text{H}_{10}\text{O}_6\text{S}$   $[\text{M}+\text{H}]^+$  343.0198, found 343.0276.

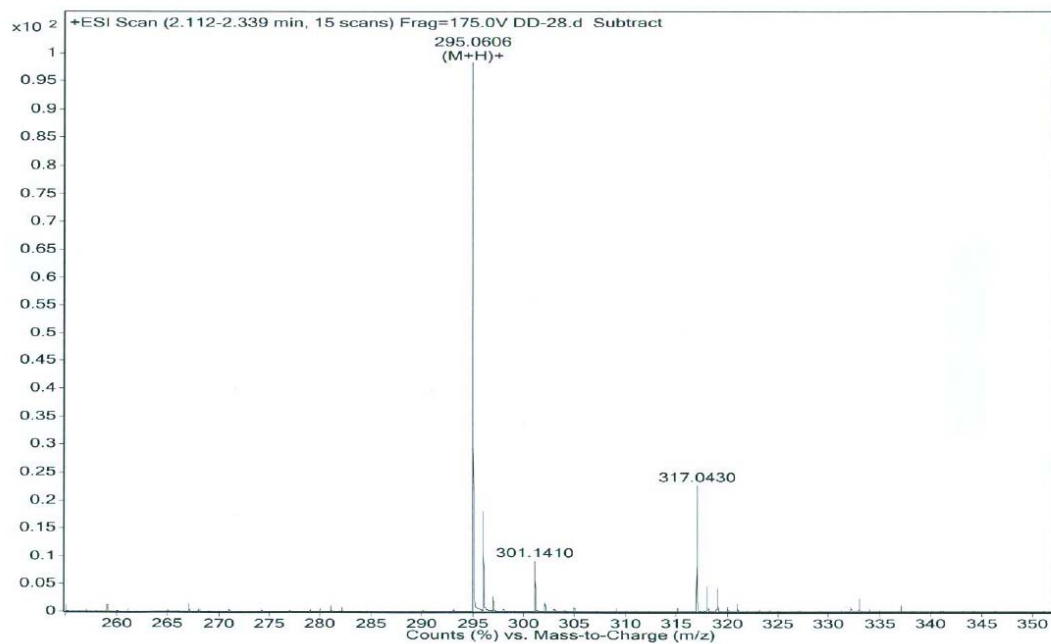
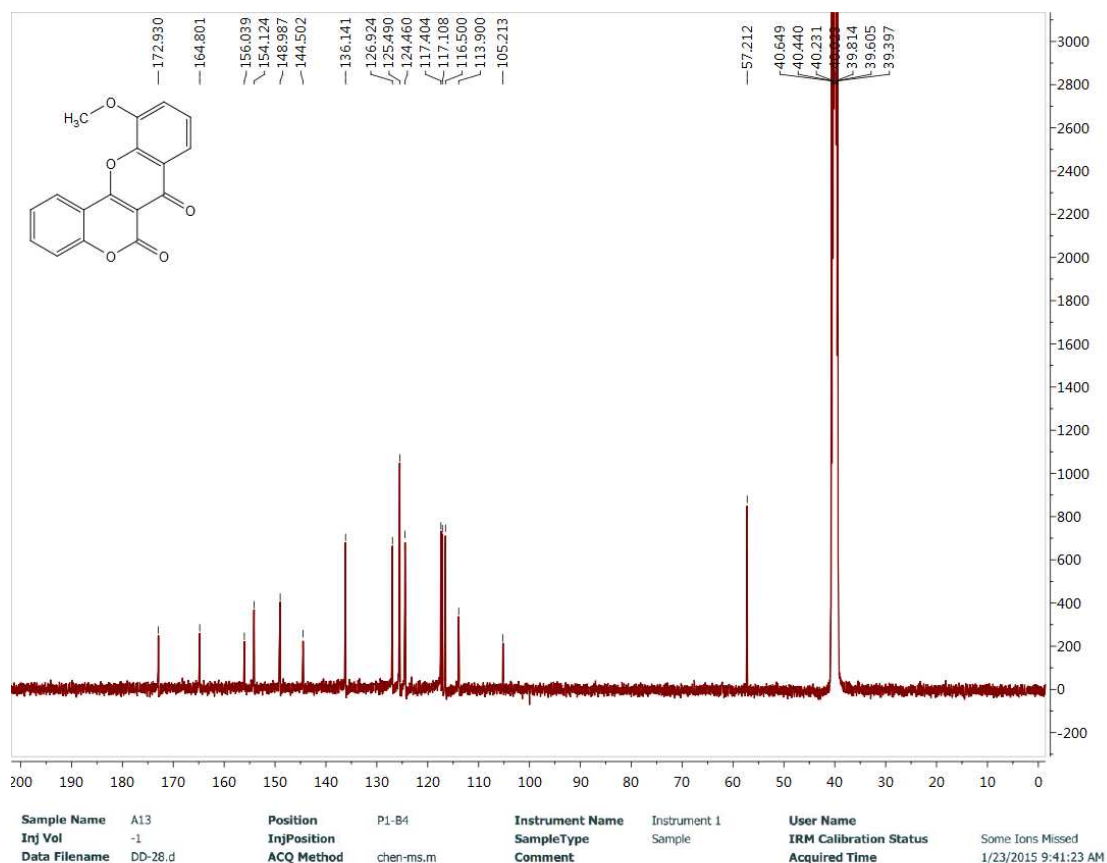


Sample Name	lc/ms	Position	P1-A4	Instrument Name	Instrument 1	User Name
Inj Vol	2	InjPosition		SampleType	Sample	IRM Calibration Status
Data Filename	DD-04.d	ACQ Method	chen-ms.m	Comment		Some Ions Missed
						12/26/2014 8:10:30 AM



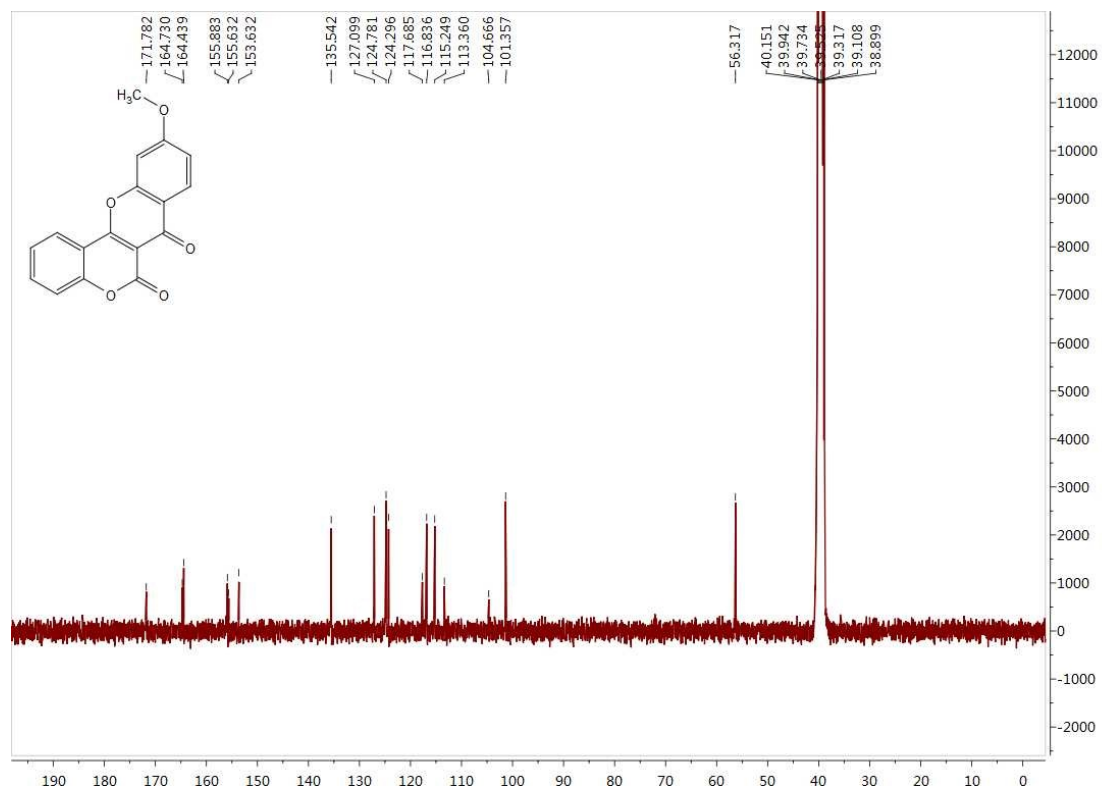
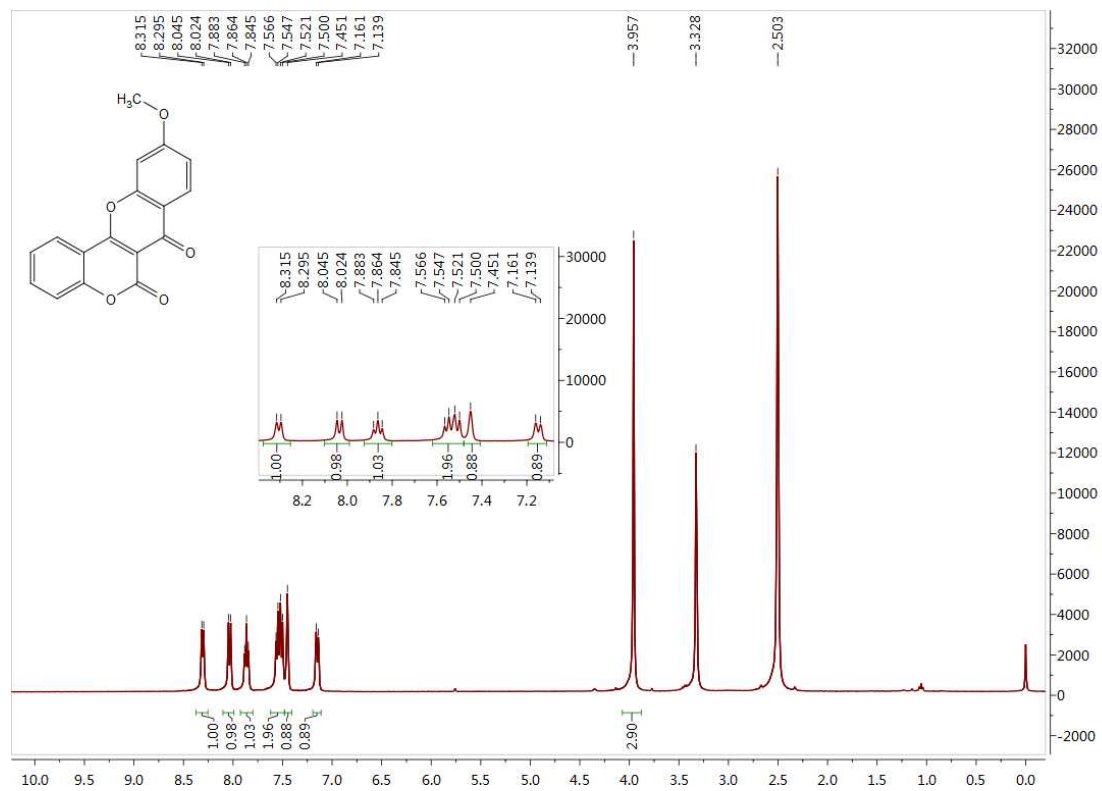
Data for **13-10** <sup>[2]</sup>: white solid; yield 80.0%; m.p. 289-291 °C; <sup>1</sup>H NMR (400 MHz, DMSO) δ: 8.14 (d, *J* = 7.4 Hz, 1H), 7.88 (t, *J* = 7.3 Hz, 1H), 7.66 (d, *J* = 7.5 Hz, 1H), 7.61-7.39 (m, 4H), 4.06 (s, 3H); <sup>13</sup>C NMR (100 MHz, DMSO) δ: 172.93, 164.80, 156.04, 154.12, 148.99, 144.50, 136.14, 126.92, 125.49, 124.46, 117.40, 117.11, 116.50, 113.90, 105.21, 57.21; HRMS: calcd for C<sub>17</sub>H<sub>10</sub>O<sub>5</sub> [M+H]<sup>+</sup> 295.0528, found 295.0606.





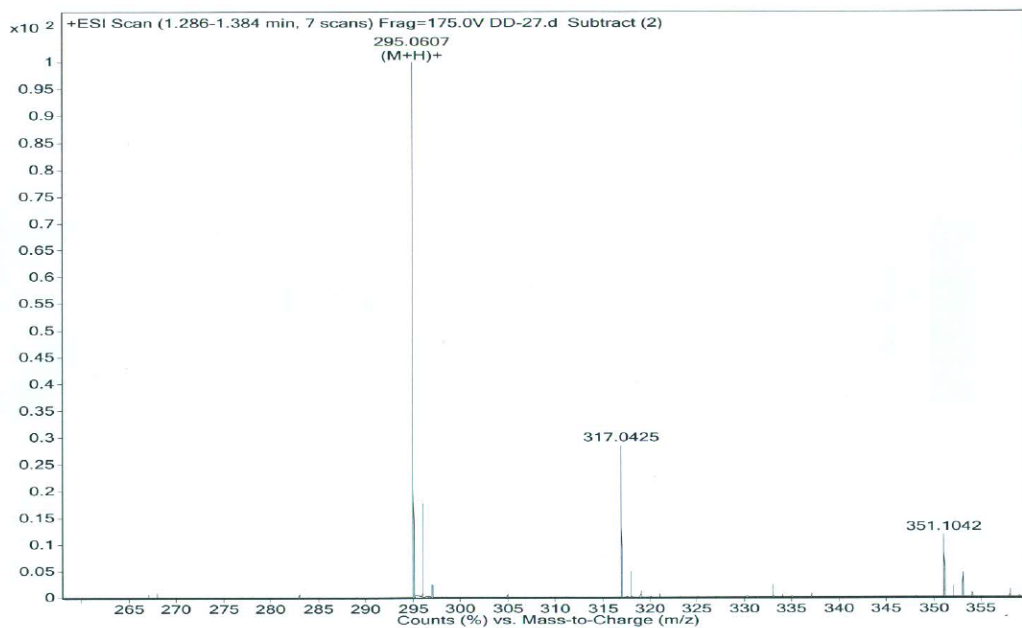
Data for **13-11**: white solid; yield 81%; m.p. 231-232 °C;  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$ : 8.30 (d,  $J$  = 7.7 Hz, 1H), 8.03 (d,  $J$  = 8.8 Hz, 1H), 7.86 (t,  $J$  = 7.6 Hz, 1H), 7.53 (m, 2H), 7.45 (s, 1H), 7.15 (d,  $J$  = 8.5 Hz, 1H), 3.96 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz, DMSO)  $\delta$ : 171.78, 164.73, 164.44, 155.88, 155.63, 153.63, 135.54, 127.10, 124.78, 124.30, 117.68, 116.84, 115.25, 113.36, 104.67, 101.36, 56.32; HRMS: calcd for  $\text{C}_{17}\text{H}_{10}\text{O}_5$   $[\text{M}+\text{H}]^+$  295.0528, found 295.0607.



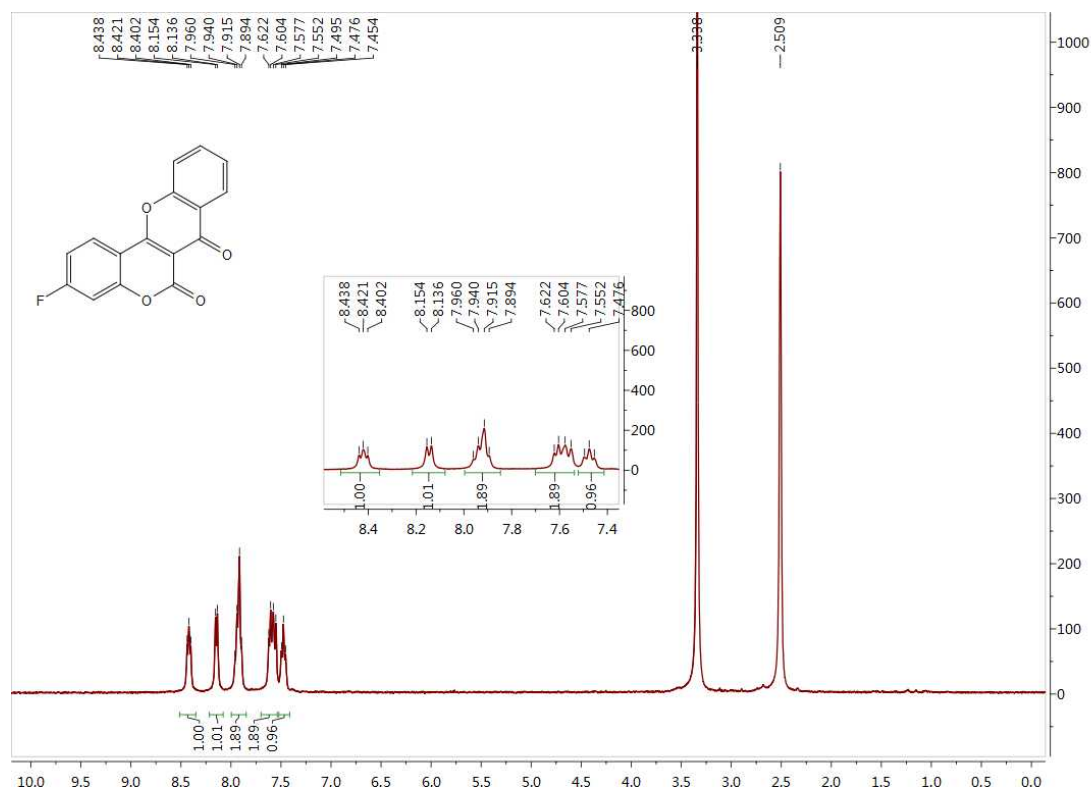


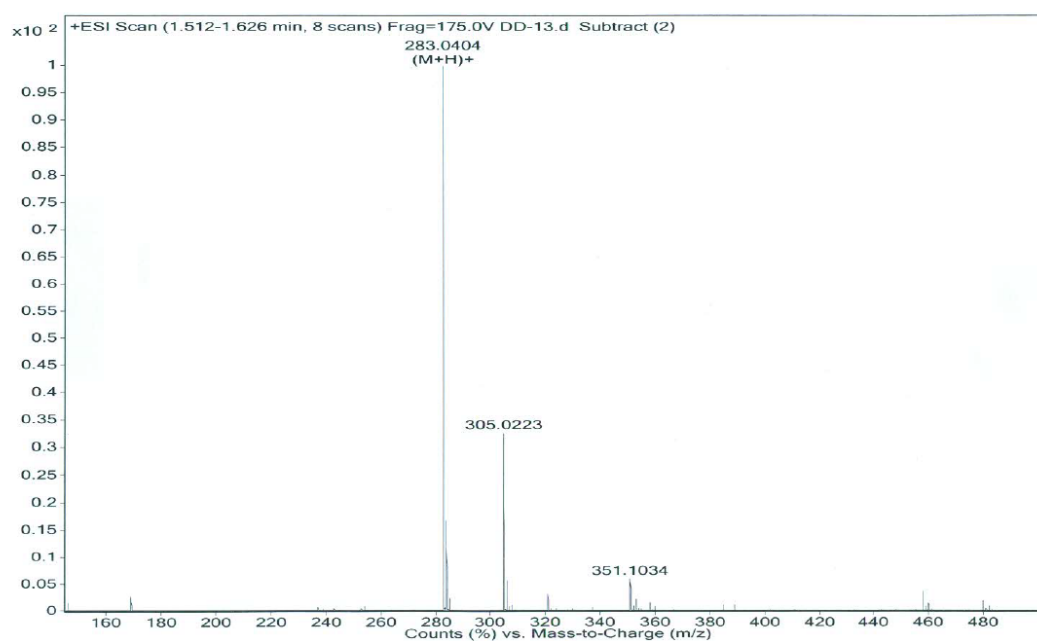
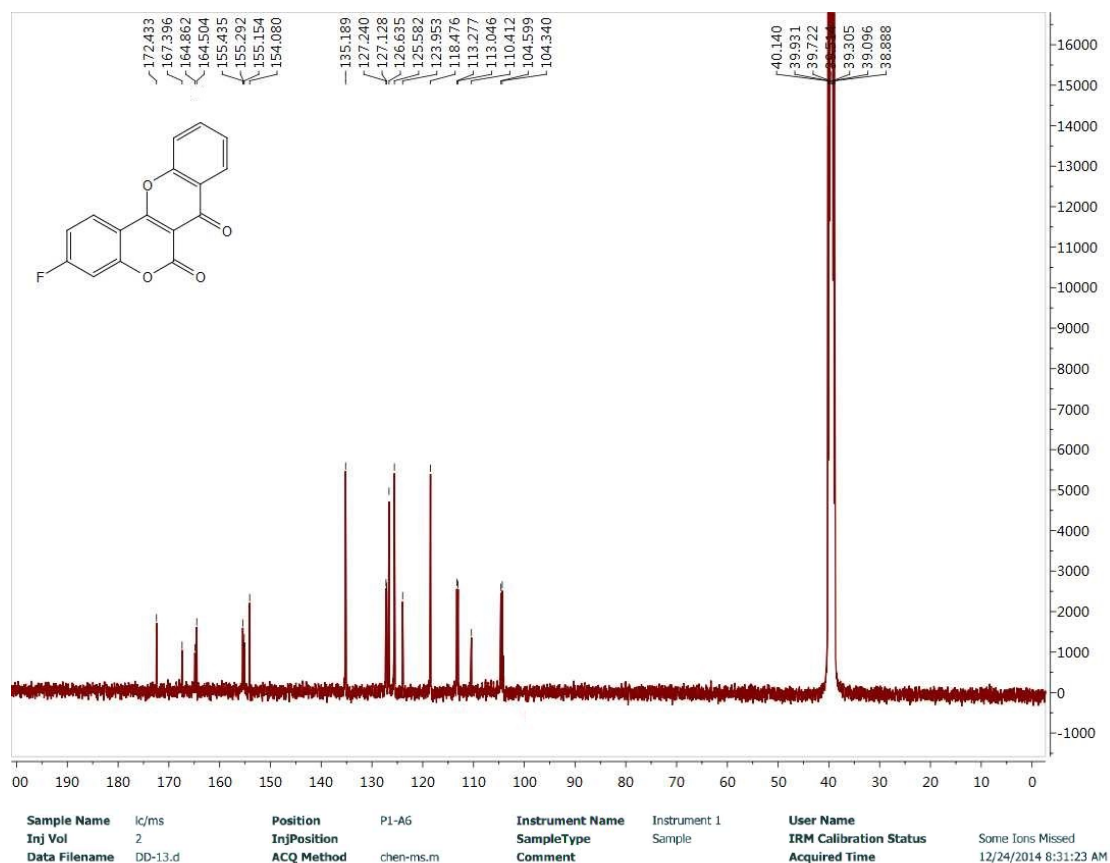


Sample Name	lc/ms	Position	P1-A3	Instrument Name	Instrument 1	User Name	
Inj Vol	2	InjPosition		SampleType	Sample	IRM Calibration Status	Some Ions Missed
Data Filename	DD-27.d	ACQ Method	chen-ms.m	Comment		Acquired Time	12/24/2014 8:20:01 AM

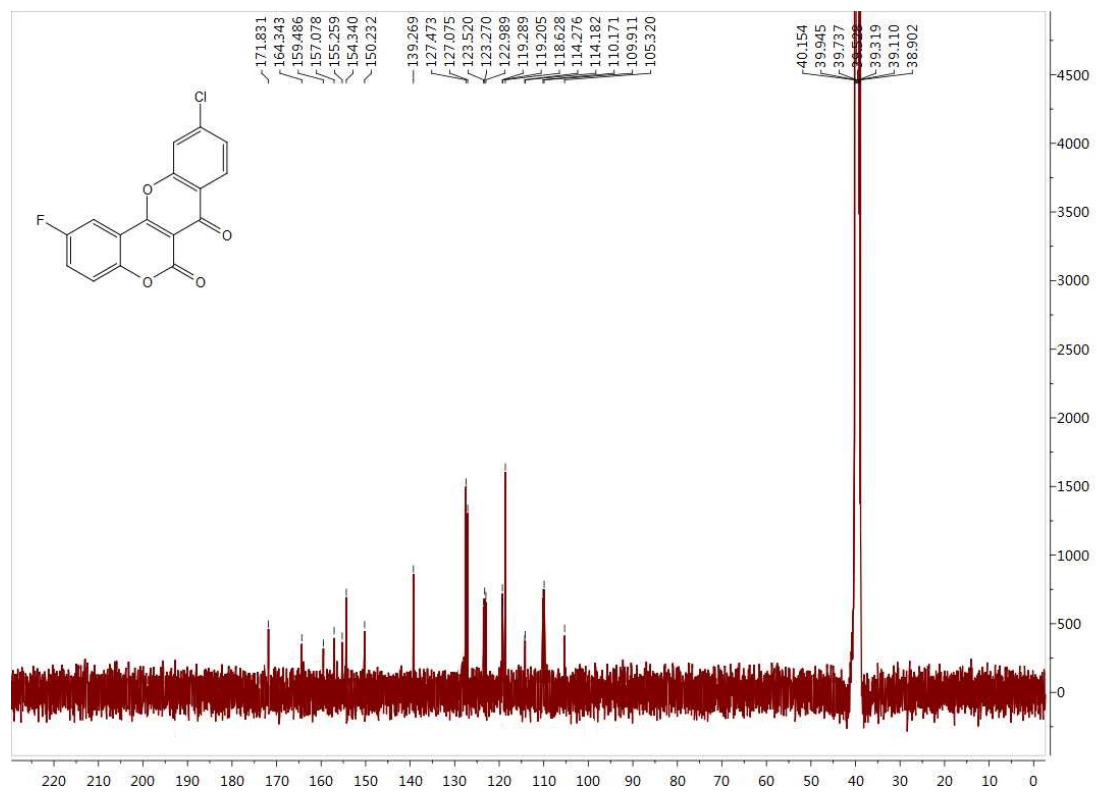
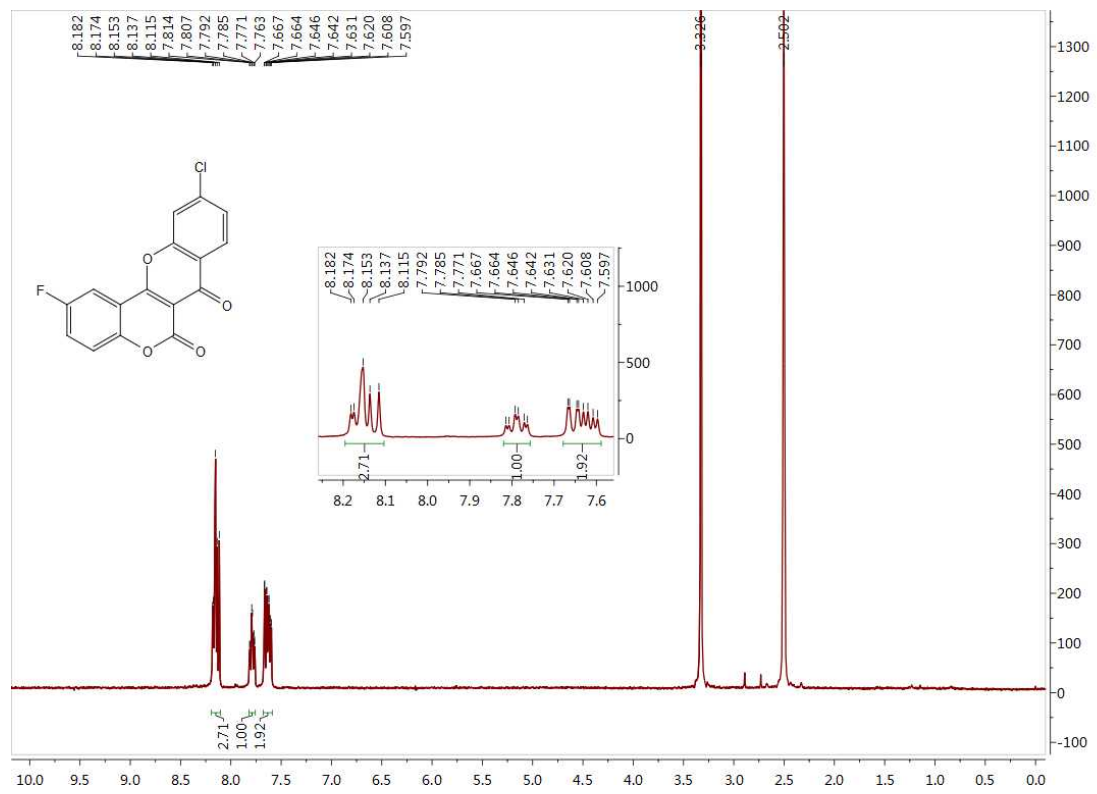


Data for **13-12**: white solid; yield 90%; m.p. > 300 °C;  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$ : 8.42(m,  $J = 7.6$  Hz, 1H), 8.15 (d,  $J = 7.5$  Hz, 1H), 7.93 (q,  $J = 8.3$  Hz, 2H), 7.59 (dd,  $J = 19.6$  Hz, 8.6 Hz, 2H), 7.48 (t,  $J = 8.2$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz, DMSO)  $\delta$ : 172.43, 167.40, 164.86, 164.50, 155.44, 155.22 (d), 154.08, 135.19, 127.18 (d), 126.63, 125.58, 123.95, 118.48, 113.16 (d), 110.41, 104.47 (d); HRMS: calcd for  $\text{C}_{16}\text{H}_7\text{FO}_4$   $[\text{M}+\text{H}]^+$  283.0328, found 283.0404.

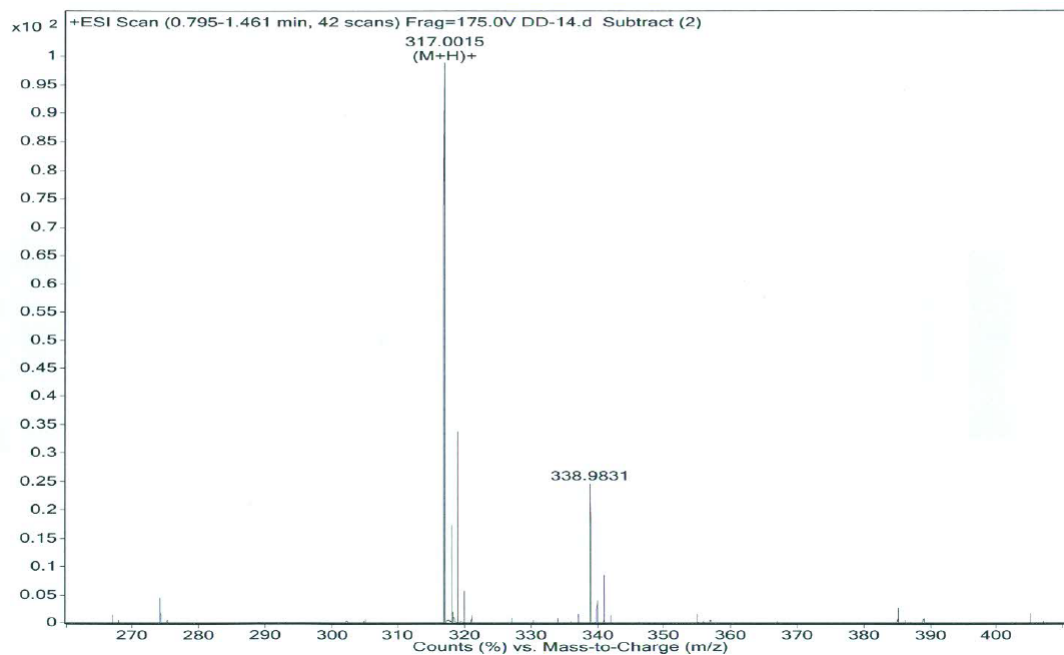




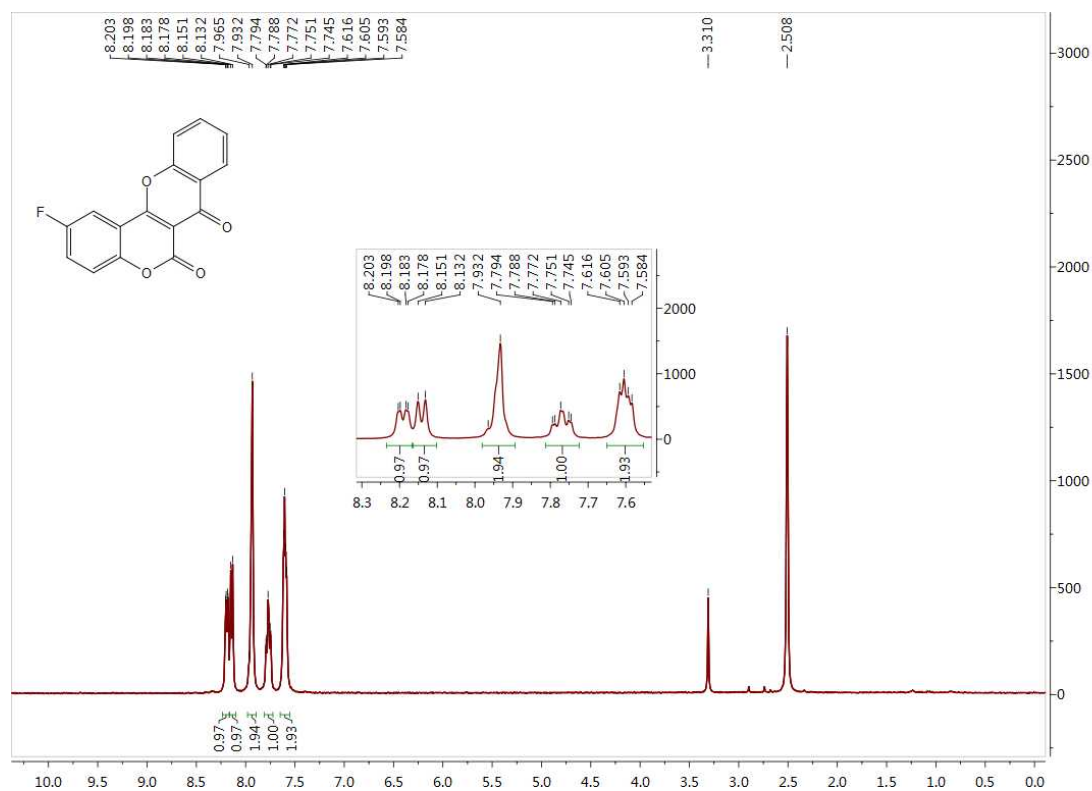
Data for **13-13**: white solid; yield 95%; m.p. > 300 °C; <sup>1</sup>H NMR (400 MHz, DMSO) δ: 8.20-8.10 (m, 3H), 7.79 (td, *J* = 8.7 Hz, 3.0 Hz, 1H), 7.63 (m, 2H); <sup>13</sup>C NMR (100 MHz, DMSO) δ: 171.83, 164.34, 159.49, 157.08, 155.26, 154.34, 150.23, 139.27, 127.27 (d), 124.19-121.88 (t), 119.25 (d), 118.63, 114.23 (d), 110.04 (d), 105.32; HRMS: calcd for C<sub>16</sub>H<sub>6</sub>ClFO<sub>4</sub> [M+H]<sup>+</sup> 316.9939, found 317.0015.

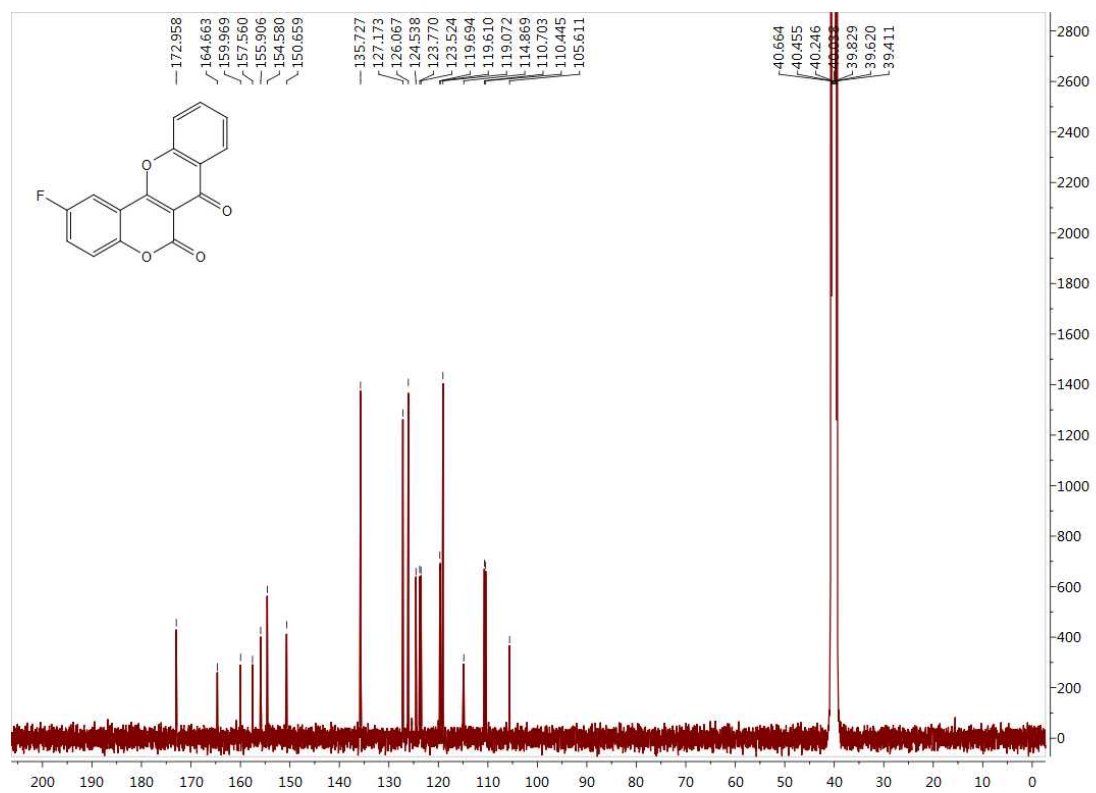


Sample Name	A5	Position	P1-A5	Instrument Name	Instrument 1	User Name	
Inj Vol	-1	InjPosition		SampleType	Sample	IRM Calibration Status	Some Ions Missed
Data Filename	DD-14.d	ACQ Method	chen-ms.m	Comment		Acquired Time	1/23/2015 9:03:27

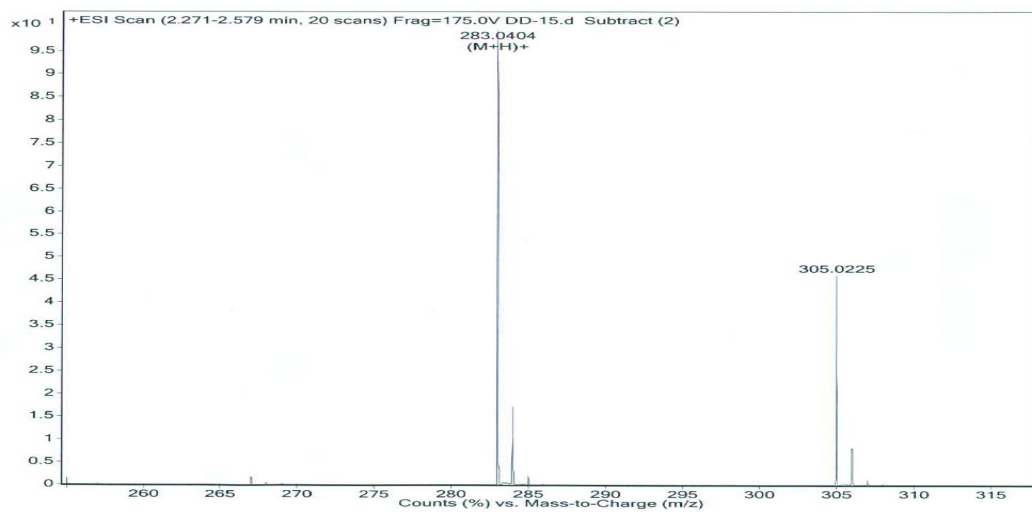


Data for **13-14**: white solid; yield 90%; m.p. 296-298 °C;  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$ : 8.19 (dd,  $J = 8.1$  Hz, 2.2 Hz, 1H), 8.14 (d,  $J = 7.8$  Hz, 1H), 7.94 (bs, 2H), 7.77 (td,  $J = 8.8$  Hz, 2.6 Hz, 1H), 7.60 (dd,  $J = 8.8$  Hz, 4.2 Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz, DMSO)  $\delta$ : 172.96, 164.66, 159.97, 157.56, 155.91, 154.58, 150.66, 135.73, 127.17, 126.07, 124.54, 123.65 (d), 119.65 (d), 119.07, 114.87, 110.57 (d), 105.61; HRMS: calcd for  $\text{C}_{16}\text{H}_7\text{FO}_4$   $[\text{M}+\text{H}]^+$  283.0328, found 283.0404.

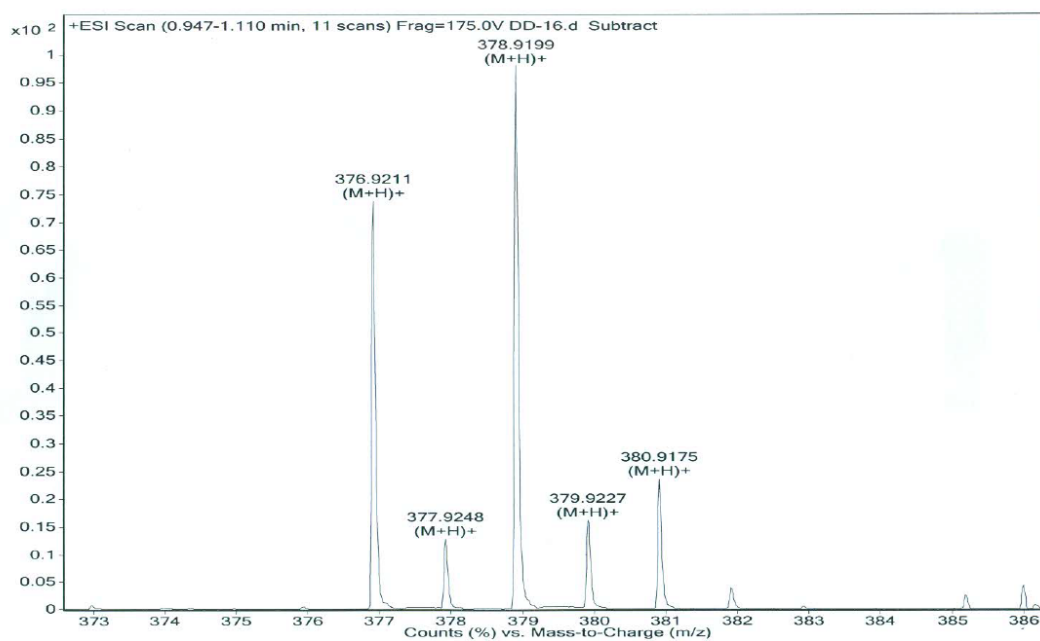
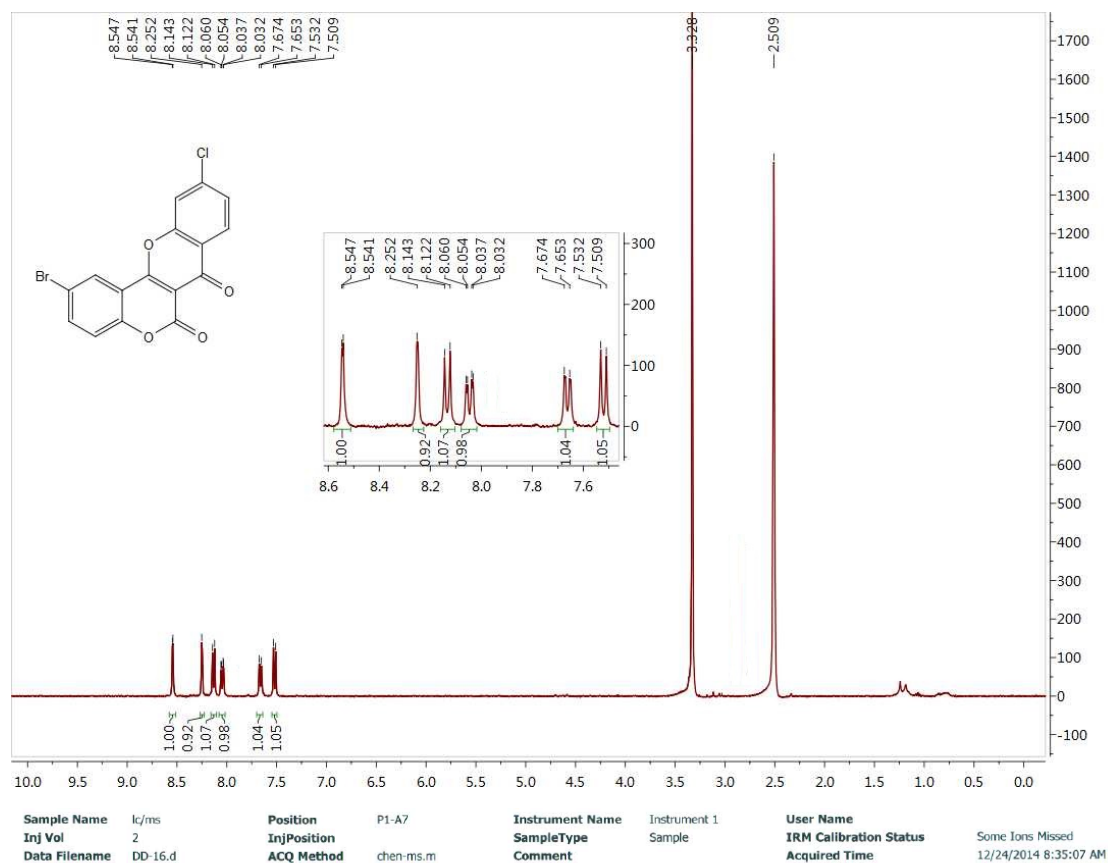




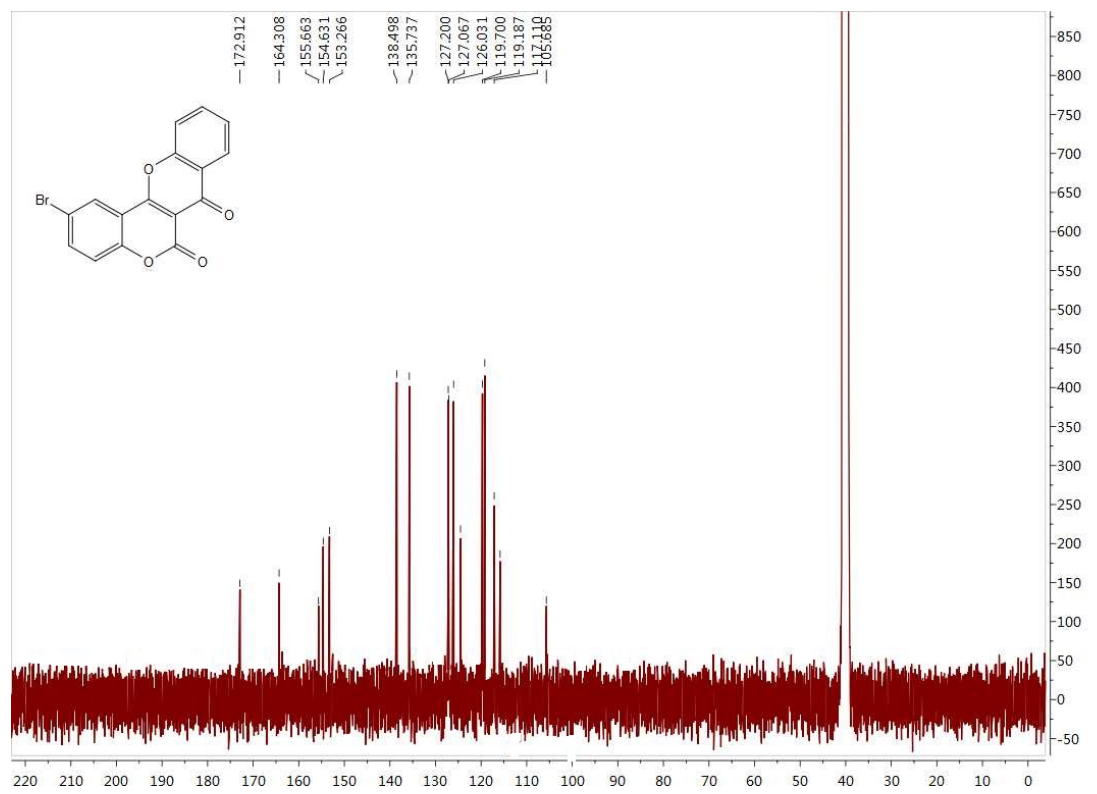
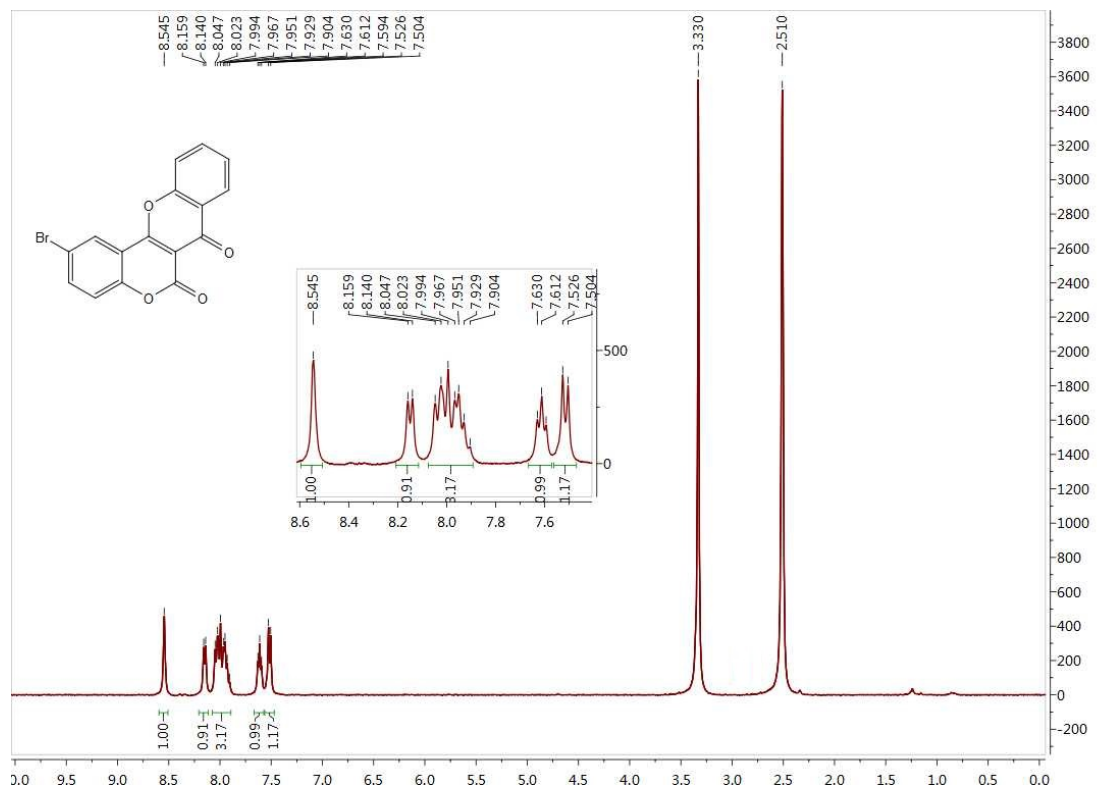
Sample Name	A6	Position	P1-A6	Instrument Name	Instrument 1	User Name	
Inj Vol	-1	InjPosition		SampleType	Sample	IRM Calibration Status	Some Ions Missed
Data Filename	DD-15.d	ACQ Method	chen-ms.m	Comment		Acquired Time	1/23/2015 9:08:11 AM



Data for **13-15**: white solid; yield 93%; m.p. > 300 °C;  $^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$ : 8.54 (d,  $J = 2.1$  Hz, 1H), 8.25 (s, 1H), 8.13 (d,  $J = 8.5$  Hz, 1H), 8.05 (dd,  $J = 8.9$  Hz, 2.2 Hz, 1H), 7.66 (dd,  $J = 8.5$  Hz, 1.7 Hz, 1H), 7.52 (d,  $J = 8.8$  Hz, 1H); HRMS: calcd for  $\text{C}_{16}\text{H}_6\text{BrClO}_4$   $[\text{M}+\text{H}]^+$  376.9138, found 376.9211.

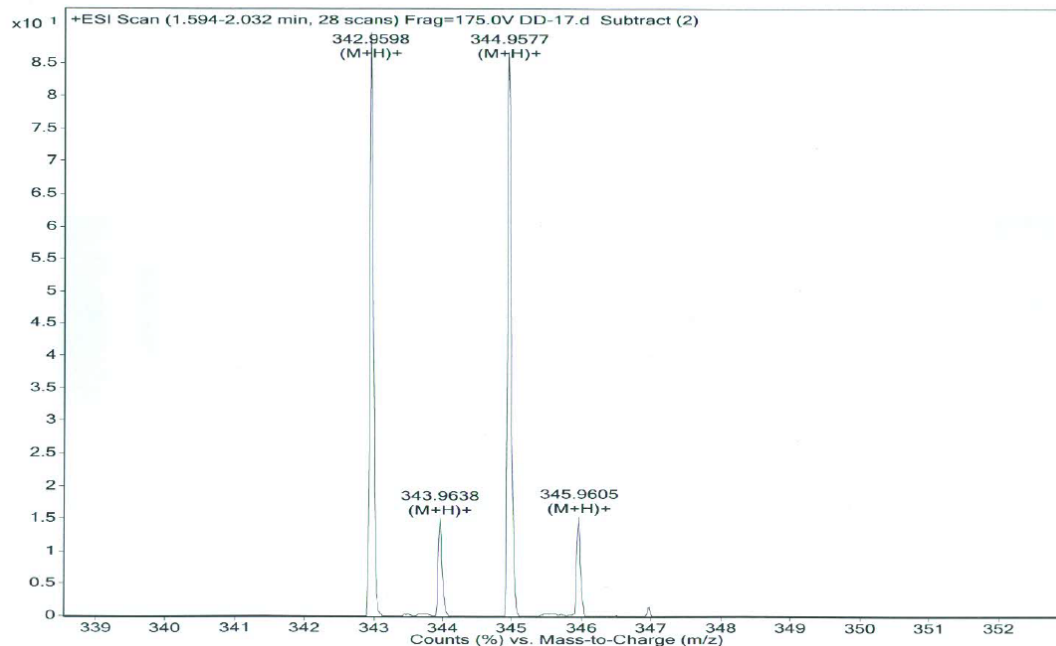


Data for **13-16**: white solid; yield 91%; m.p. > 300 °C;  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$ : 8.54 (s, 1H), 8.15 (d,  $J = 7.5$  Hz, 1H), 8.06-7.87 (m, 3H), 7.61 (t,  $J = 7.1$  Hz, 1H), 7.52 (d,  $J = 8.6$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz, DMSO)  $\delta$ : 172.91, 164.31, 155.66, 154.63, 153.27, 138.50, 135.74, 127.20, 127.07, 126.03, 124.52, 119.70, 119.19, 117.11, 115.82, 105.69; HRMS: calcd for  $\text{C}_{16}\text{H}_7\text{BrO}_4$   $[\text{M}+\text{H}]^+$  342.9528, found 342.9598.

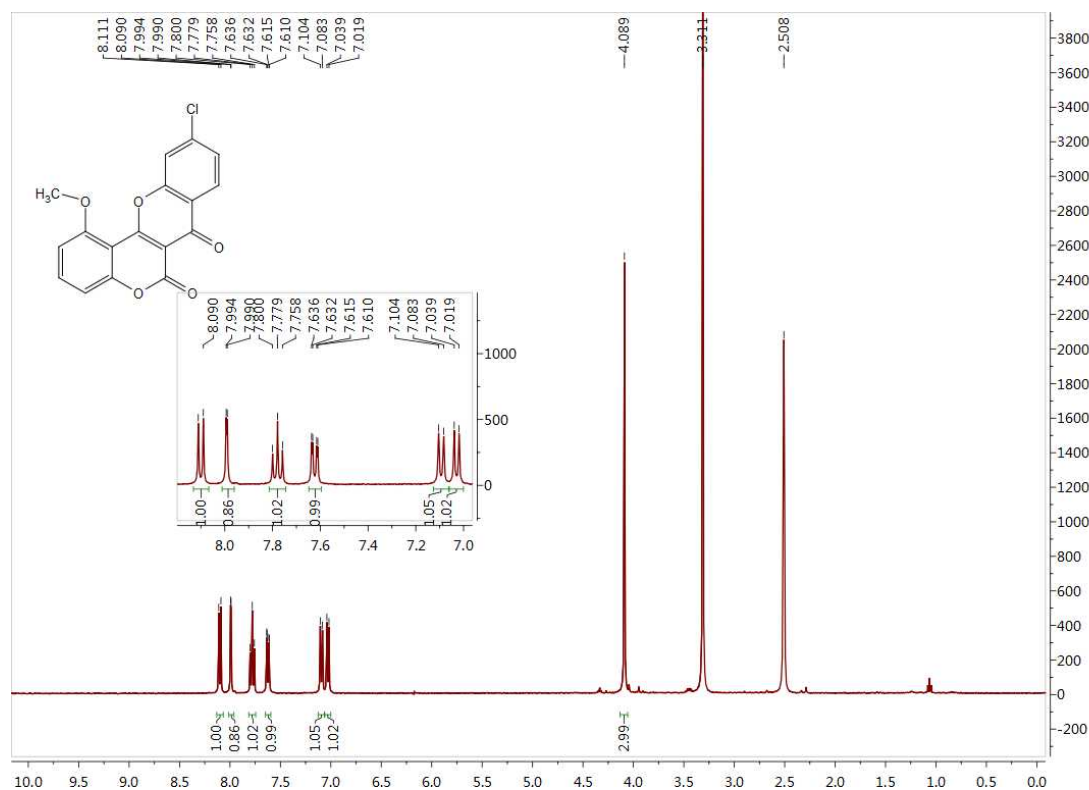




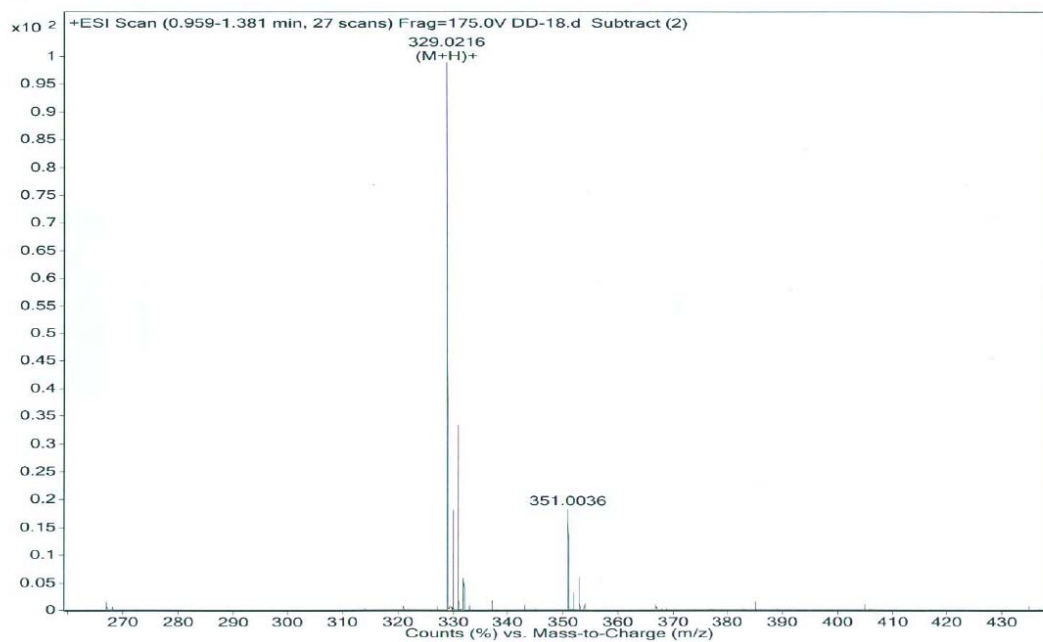
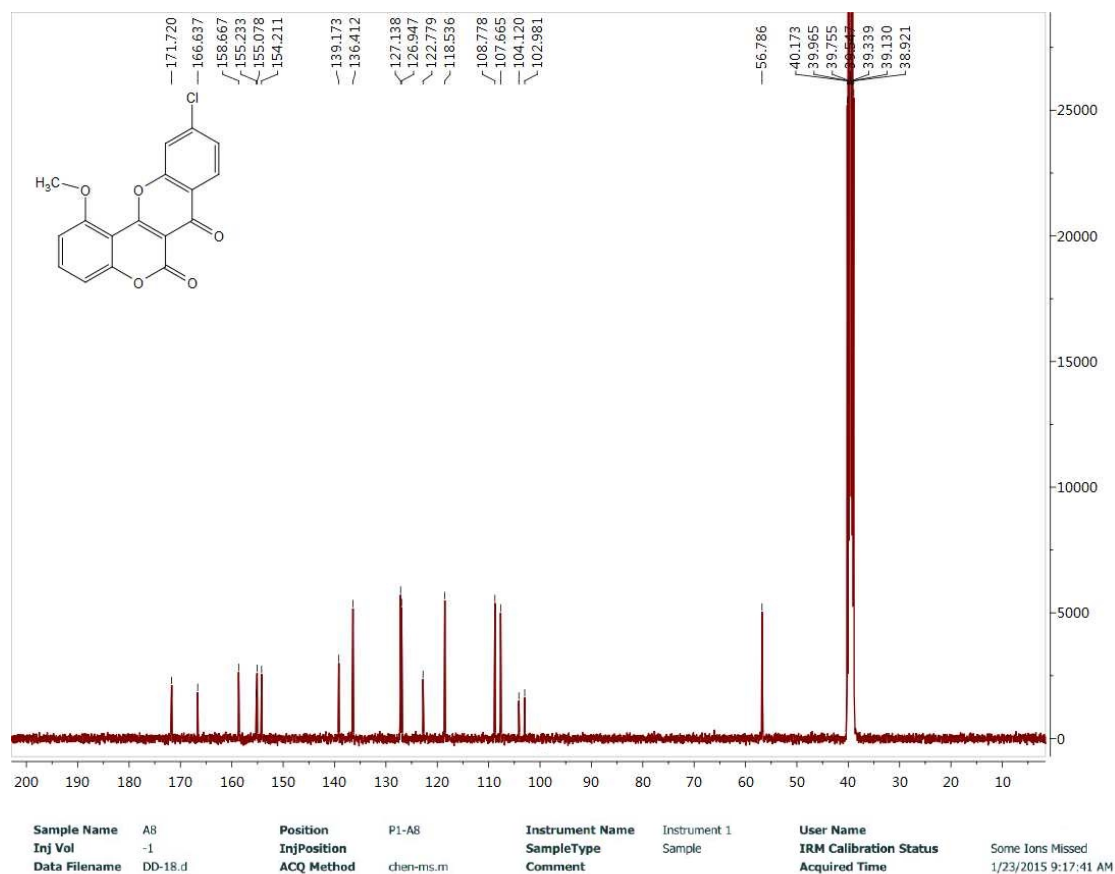
Sample Name	A7	Position	P1-A7	Instrument Name	Instrument 1	User Name	
Inj Vol	-1	InjPosition		SampleType	Sample	IRM Calibration Status	Some Ions Missed
Data Filename	DD-17.d	ACQ Method	chen-ms.m	Comment		Acquired Time	1/23/2015 9:12:56 AM



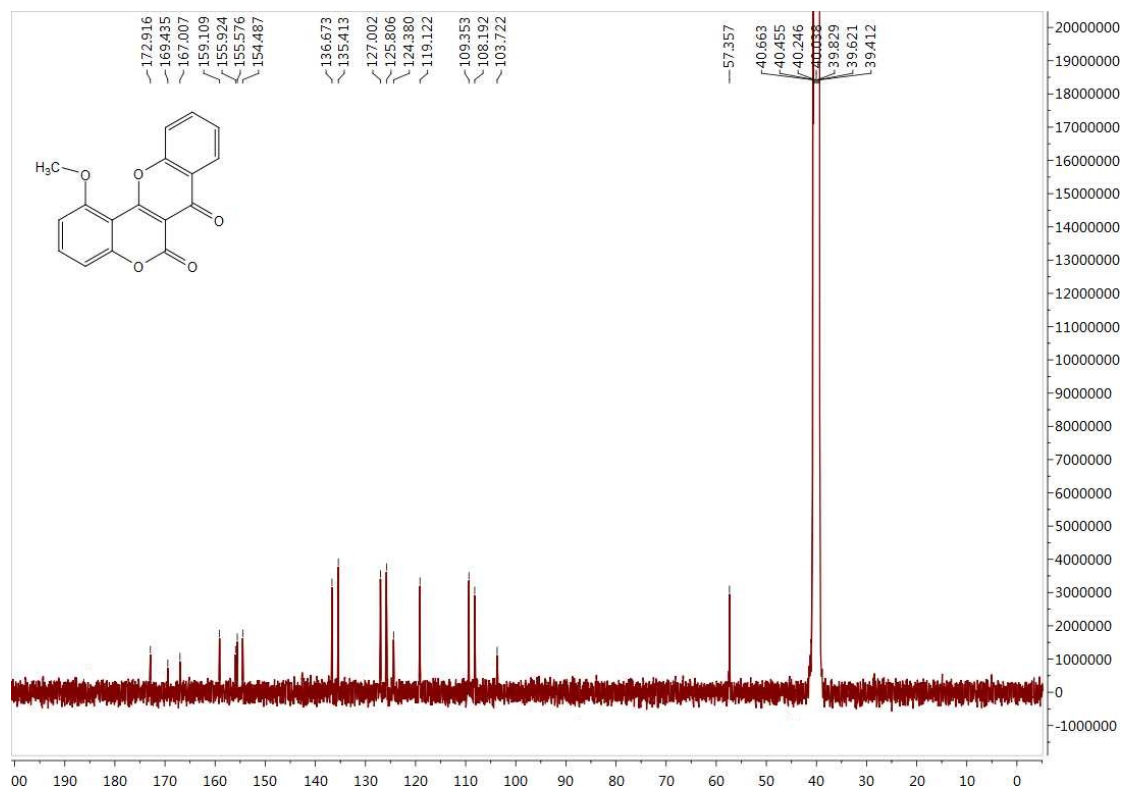
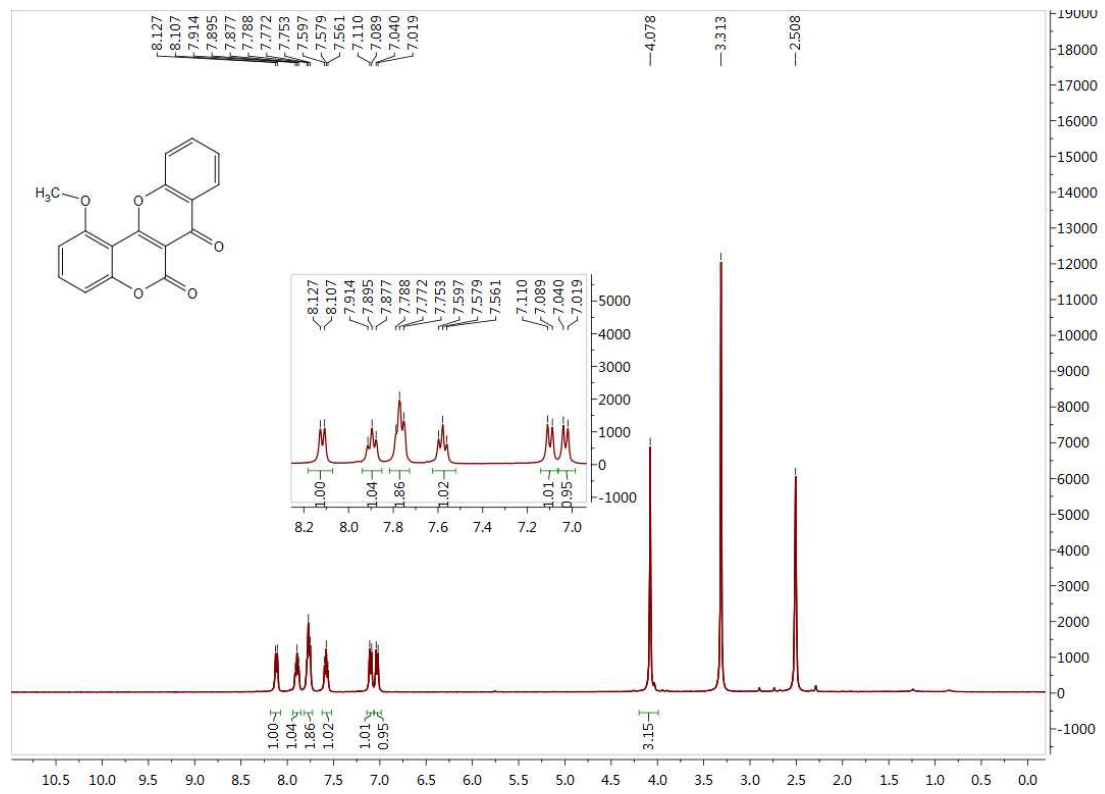
Data for **13-17**: white solid; yield 89%; m.p. 282-284 °C; <sup>1</sup>H NMR (400 MHz, DMSO) δ: 8.10 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 1.8 Hz, 1H), 7.78 (t, *J* = 8.4 Hz, 1H), 7.62 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 7.03 (d, *J* = 8.2 Hz, 1H), 4.09 (s, 3H); <sup>13</sup>C NMR (100 MHz, DMSO) δ: 171.72, 166.64, 158.67, 155.23, 155.08, 154.21, 139.17, 136.41, 127.14, 126.95, 122.78, 118.54, 108.78, 107.67, 104.12, 102.98, 56.79; HRMS: calcd for C<sub>17</sub>H<sub>9</sub>ClO<sub>5</sub> [M+H]<sup>+</sup> 329.0139, found 329.0216.



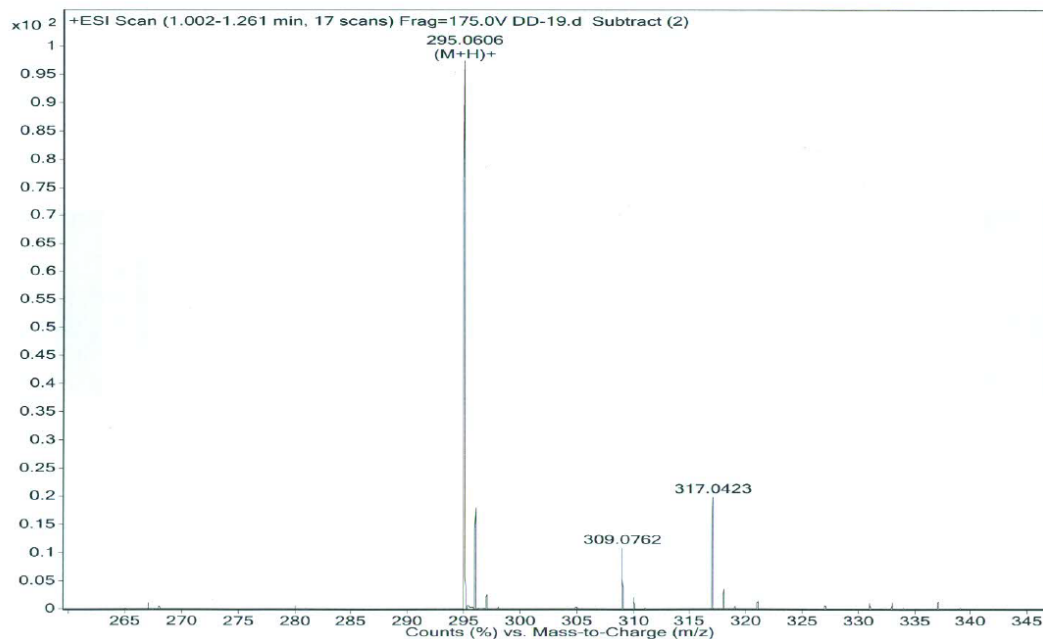




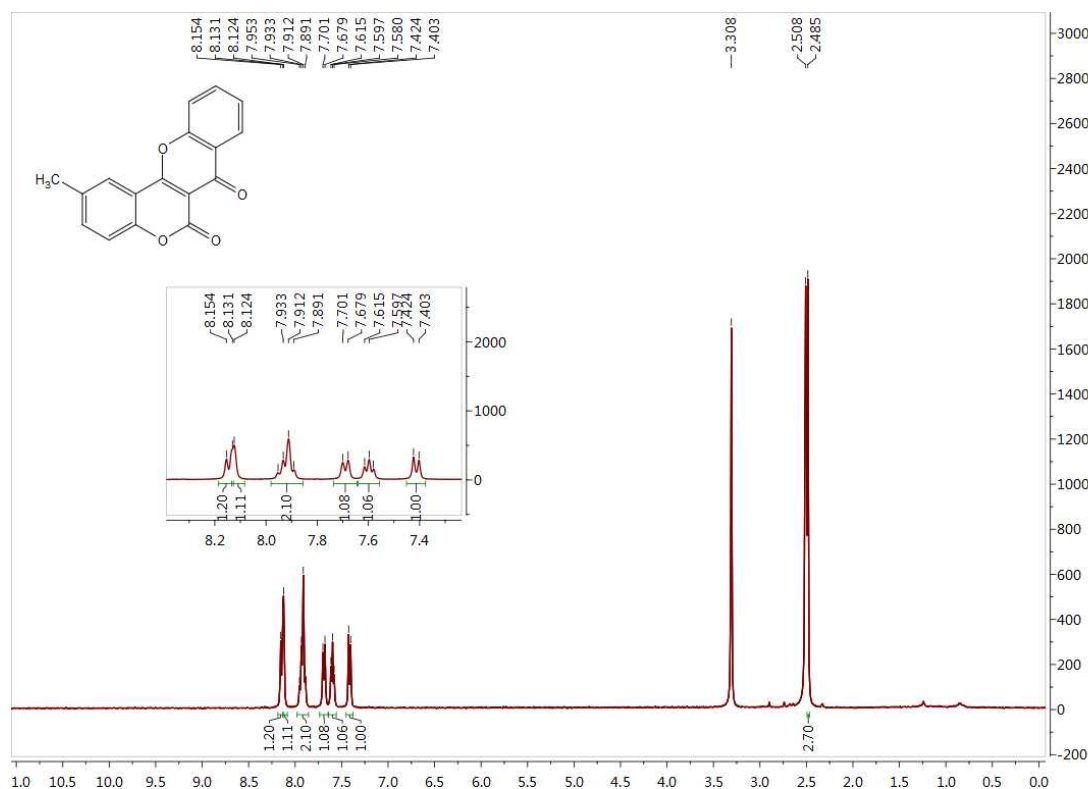
Data for **13-18**: white solid; yield 90.0%; m.p. 291-293 °C;  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$ : 8.12 (d,  $J = 7.7$  Hz, 1H), 7.90 (t,  $J = 7.4$  Hz, 1H), 7.77 (t,  $J = 7.0$  Hz, 2H), 7.58 (t,  $J = 7.3$  Hz, 1H), 7.10 (d,  $J = 8.4$  Hz, 1H), 7.03 (d,  $J = 8.3$  Hz, 1H), 4.08 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz, DMSO)  $\delta$ : 172.92, 169.44, 167.00, 159.11, 155.92, 155.58, 154.49, 136.67, 135.41, 127.00, 125.80, 124.38, 119.12, 109.35, 108.19, 103.72, 57.36; HRMS: calcd for  $\text{C}_{17}\text{H}_{10}\text{O}_5$   $[\text{M}+\text{H}]^+$  295.0528, found 295.0606.

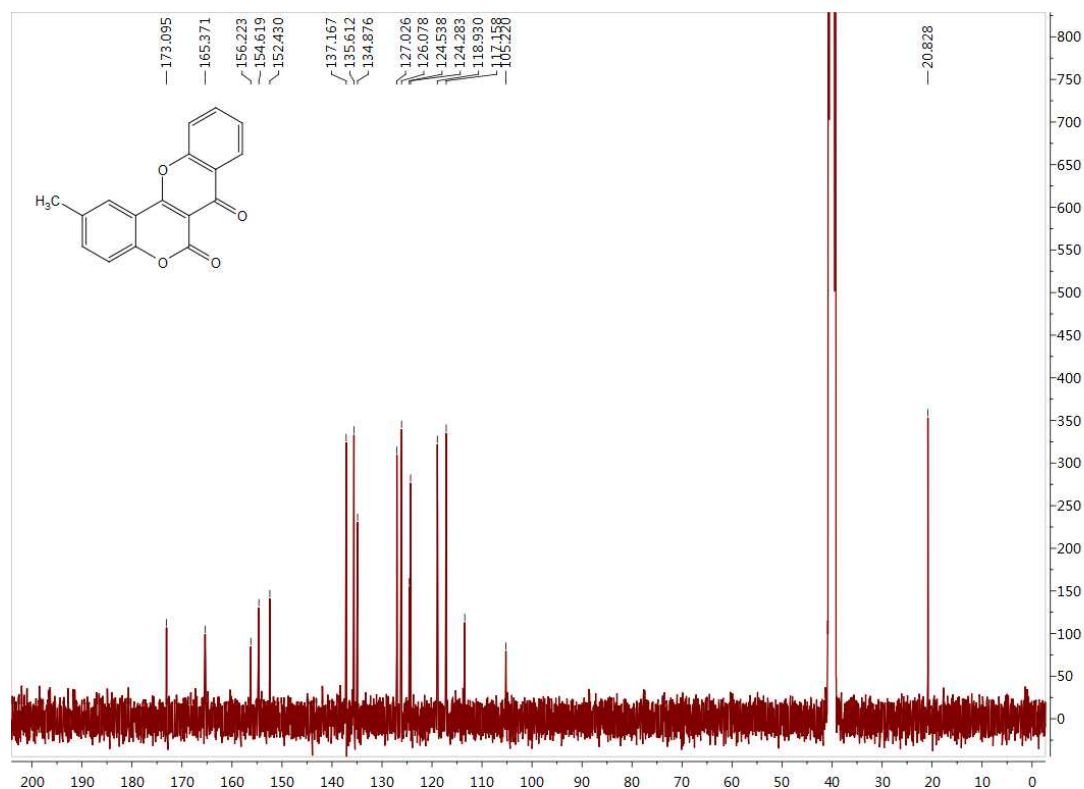


Sample Name	A9	Position	P1-A9	Instrument Name	Instrument 1	User Name	
Inj Vol	-1	InjPosition		SampleType	Sample	IRM Calibration Status	Some Ions Missed
Data Filename	DD-19.d	ACQ Method	chen-ms.m	Comment		Acquired Time	1/23/2015 9:22:26 AM

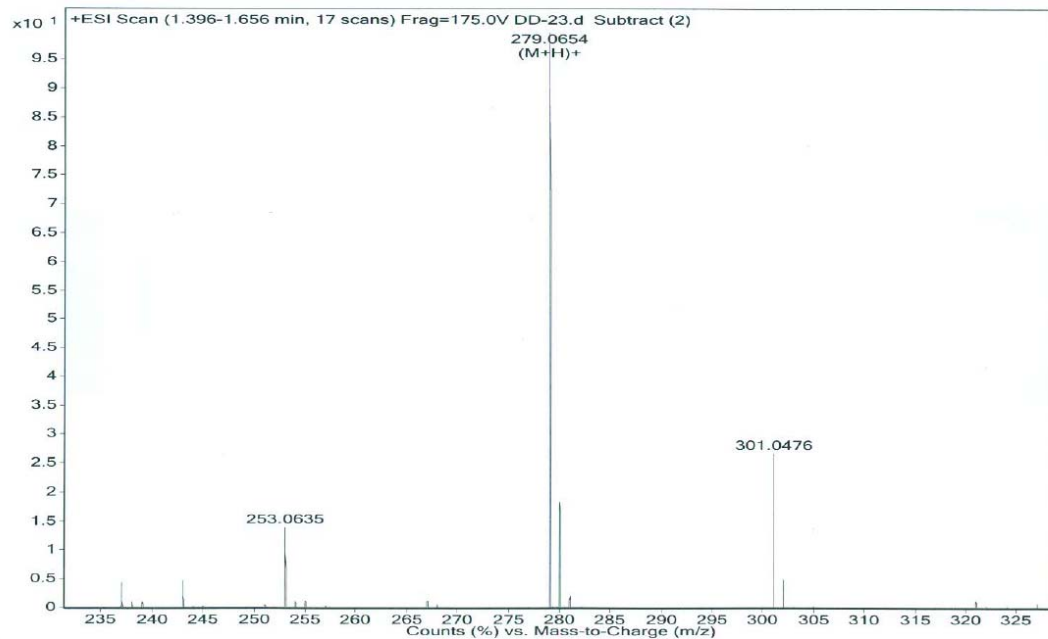


Data for **13-19**: white solid; yield 95%; m.p. 296-298 °C; <sup>1</sup>H NMR (400 MHz, DMSO) δ: 8.14 (d, *J* = 9.5 Hz, 1H), 8.12 (s, 1H), 7.92 (q, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 8.6 Hz, 1H), 7.60 (t, *J* = 6.9 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 1H), 2.48 (s, 3H); <sup>13</sup>C NMR (100 MHz, DMSO) δ: 173.09, 165.37, 156.22, 154.62, 152.43, 137.17, 135.61, 134.88, 127.03, 126.08, 124.54, 124.28, 118.93, 117.16, 113.45, 105.22, 20.83; HRMS: calcd for C<sub>17</sub>H<sub>10</sub>O<sub>4</sub> [M+H]<sup>+</sup> 279.0579, found 279.0654.

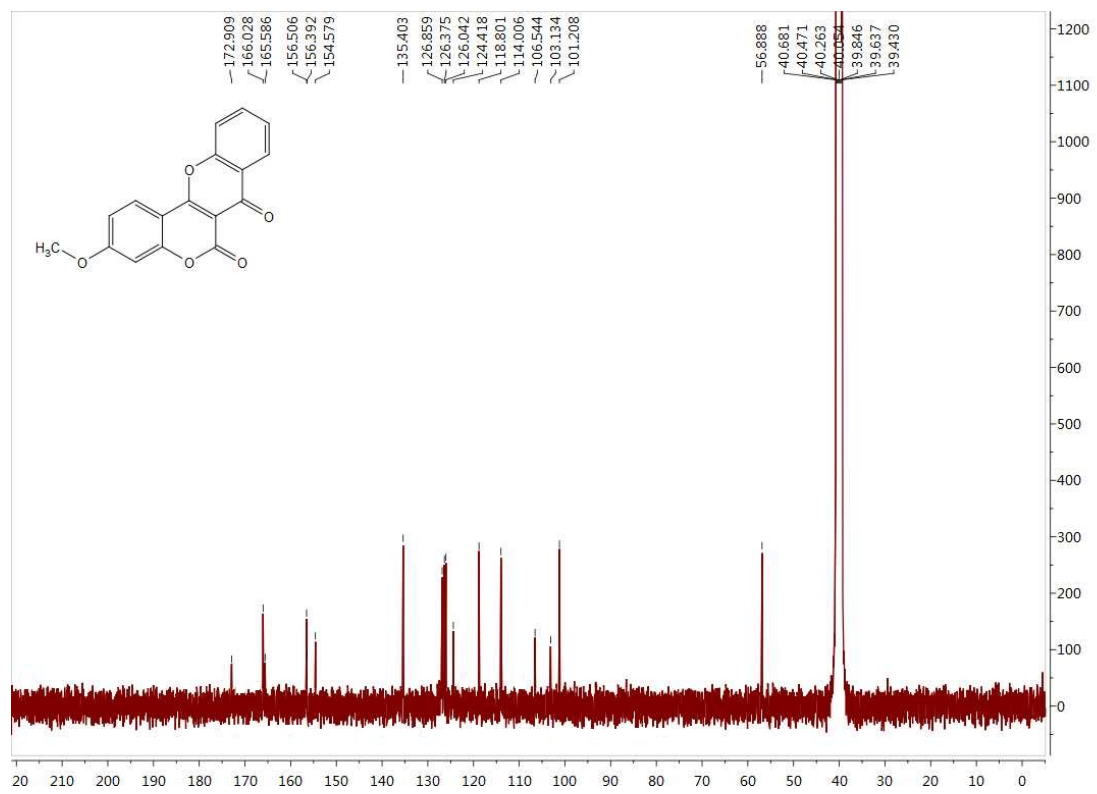
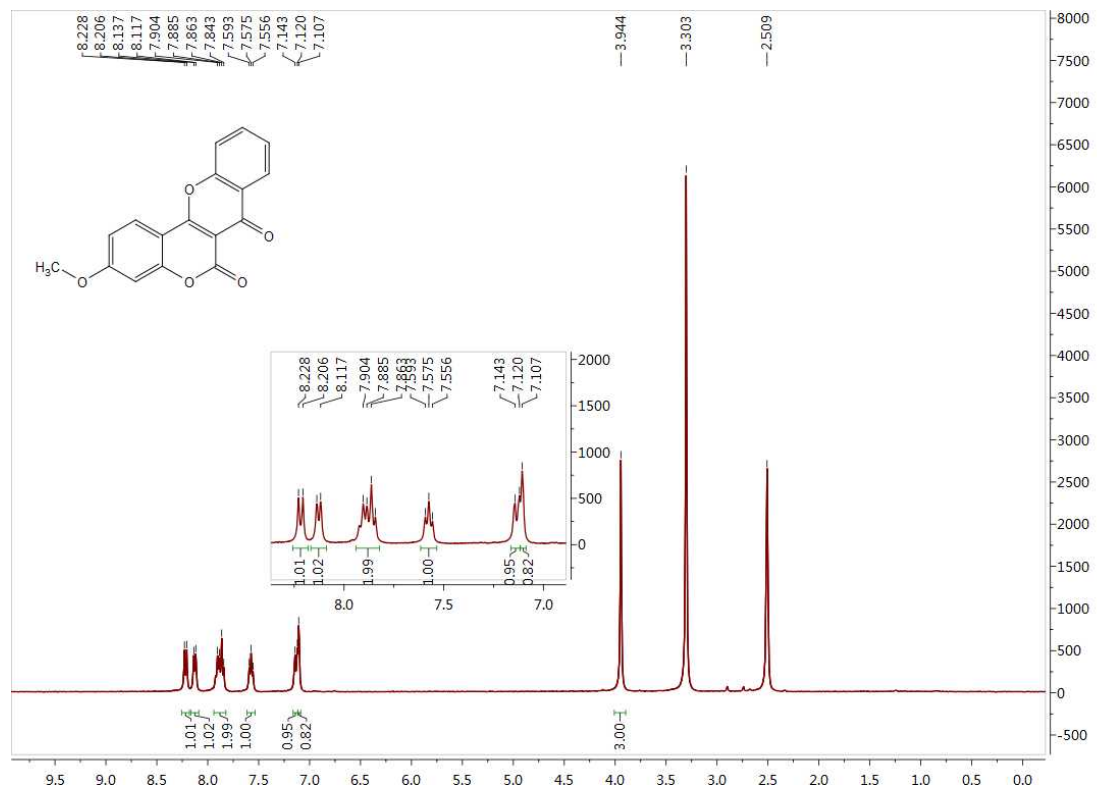




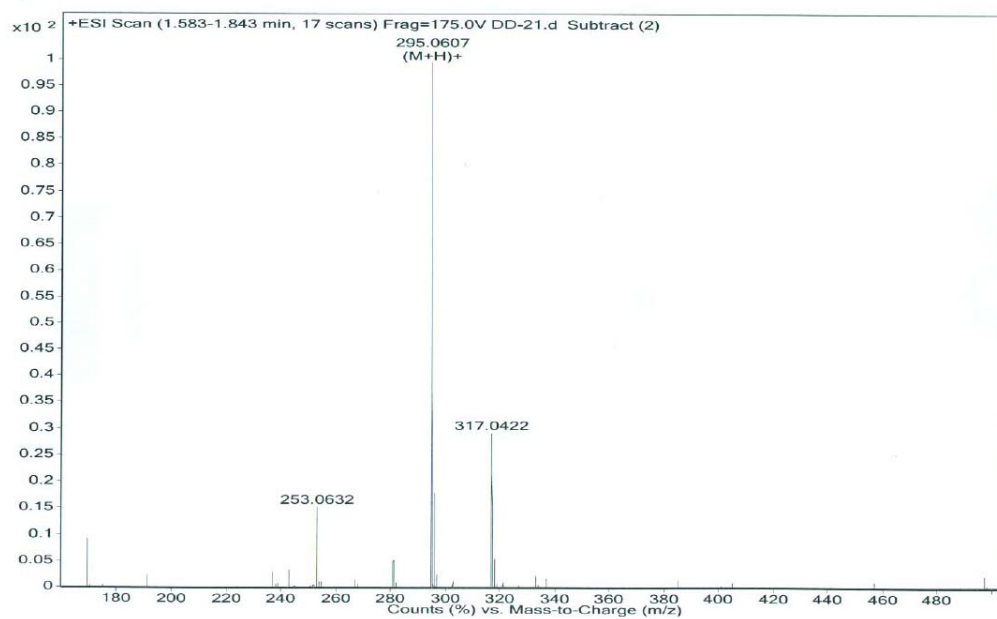
Sample Name	A11	Position	P1-B2	Instrument Name	Instrument 1	User Name	
Inj Vol	-1	InjPosition		SampleType	Sample	IRM Calibration Status	Some Ions Missed
Data Filename	DD-23.d	ACQ Method	chen-ms.m	Comment		Acquired Time	1/23/2015 9:31:53 AM



Data for **13-20**: white solid; yield 89%; m.p. 290-293 °C;  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$ : 8.22 (d,  $J$  = 8.8 Hz, 1H), 8.13 (d,  $J$  = 7.7 Hz, 1H), 7.87 (m, 2H), 7.57 (t,  $J$  = 7.3 Hz, 1H), 7.13 (d,  $J$  = 9.1 Hz, 1H), 7.11 (s, 1H), 3.94 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz, DMSO)  $\delta$ : 172.91, 166.03, 165.59, 156.51, 156.39, 154.58, 135.40, 126.86, 126.38, 126.04, 124.42, 118.80, 114.01, 106.54, 103.13, 101.21, 56.89; HRMS: calcd for  $\text{C}_{17}\text{H}_{10}\text{O}_5$   $[\text{M}+\text{H}]^+$  295.0528, found 295.0607.



Sample Name	A10	Position	P1-B1	Instrument Name	Instrument 1	User Name	
Inj Vol	-1	InjPosition		SampleType	Sample	IRM Calibration Status	Some Ions Missed
Data Filename	DD-21.d	ACQ Method	chen-ms.m	Comment		Acquired Time	1/23/2015 9:27:09 AM



## References

- [1] B. Liu, L. G. Xie, X. H. Xu, Y. H. Li, *Youji Huaxue*, 2011, **31**(12), 2067-2073.
- [2] M. Yoshida, K. Saito, Y. Fujino, T. Doi, *Tetrahedron*, 2014, **70**, 3452-3458.