

## Supporting Information

### Peroxy Mediated Csp2-Csp3 Dehydrogenative Coupling: Regioselective Functionalization of Coumarins and Coumarin-3-carboxylic acids

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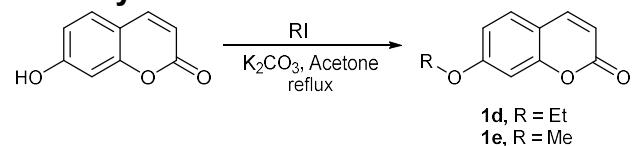
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**1 General remarks:** The following includes general experimental procedures, specific details for representative reactions, isolation and spectroscopic information for the compounds. All reagents were commercially available and used as received. Coumarins **1d**, **1i** and **1j** and coumarin-3-carboxylic acid derivatives were synthesized following the procedures described in the literature.<sup>1</sup> The reactions were carried out in an oil bath using Microwave Vials (2-5 ml). Column chromatography was carried out on silica gel (230–400 mesh). TLC was conducted on silica gel 250 micron, F254 plates. <sup>1</sup>H NMR spectra were recorded at room temperature on Bruker 300, 400 and 500 MHz spectrometers, using CDCl<sub>3</sub> as solvent. Chemical shifts are reported in ppm with TMS as an internal standard (TMS: δ 0.0 ppm). <sup>13</sup>C NMR spectra are referenced from the solvent central peak (77.23 ppm). Chemical shifts are given in ppm. Elemental analyses (CHN) were recorded on a Thermo Finnigan Flash EA 1112 elemental analyzer.

## 2 General experimental details

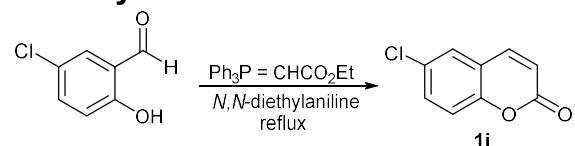
### 2-1 Synthesis of coumarins

#### 2-1-1 Synthesis of coumarins **1d** and **1e**



A suspension of 7-hydroxycoumarin (1.0 mmol), EtI or MeI (1.5 equiv.) and anhydrous K<sub>2</sub>CO<sub>3</sub> (2 equiv.) in anhydrous N,N-dimethylformamide (10 mL) was stirred at rt for 24 h. The solution was diluted with EtOAc (20 mL) and the organic phase washed with H<sub>2</sub>O (3 × 10 mL), dried over anhydrous MgSO<sub>4</sub> and concentrated in vacuo to give 7-alkoxycoumarins **1d** or **1e** as white solids, respectively.<sup>1</sup>

#### 2-1-2 Synthesis of coumarin **1i**

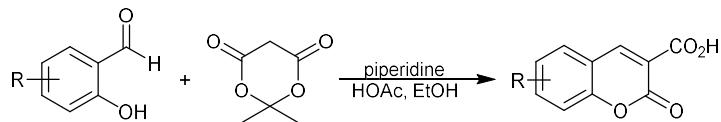


6-chloro-2*H*-chromen-2-one **1i** was synthesized by the Wittig reaction of 6-chloro-2-hydroxybenzaldehyde with the Wittig reagent, ethyl(triphenylphosphoranylidene)acetate in *N,N*'-diethylaniline under reflux. 6-chloro-2-hydroxybenzaldehyde (1 mmol) and ethyl(triphenylphosphoranylidene)acetate (1.2 mmol) were dissolved in *N,N*'-diethylaniline (15 ml) and the resulting mixture was stirred at reflux for 4 h. The solvent was removed under reduced pressure and the resulting brown oil was purified by column chromatography on silica gel with n-hexane/ethyl acetate (8/2 v/v).<sup>2</sup>

<sup>1</sup> (a) A. Sánchez-Recillas, G. Navarrete-Vázquez, S. Hidalgo-Figueroa, M. Y. Ríos, M. Ibarra-Barajas, S. Estrada-Soto, *Eur. J. Med. Chem.*, **2014**, 77, 400; (b) F. Plisson, X.-C. Huang, H. Zhang, Z. Khalil, R. J. Capon, *Chem. An Asian J.*, **2012**, 7, 1616.

<sup>2</sup> D. Maes, M. Eugenia Riveiro, C. Shayo, C. Davio, S. Debenedetti, N. De Kimpe, *Tetrahedron*, **2008**, 64, 4438.

## 2-2 Synthesis of coumarin-3-carboxylic acids



Salicylaldehyde (26 mmol), Meldrum's acid (26 mmol) were dissolved in absolute ethanol (10 mL). Catalytic amounts of piperidine (2 drops) and glacial acetic acid (2 drops) were added and the reaction mixture was heated at reflux and monitored by TLC. Upon completion, the mixture was cooled to room temperature and the coumarin-3-carboxylic acids were obtained by filtration and dried under vacuum. The products were used without further purification.<sup>3</sup>

## 2-3 General procedure for direct functionalization of coumarins

### 2-3-1 Procedure I

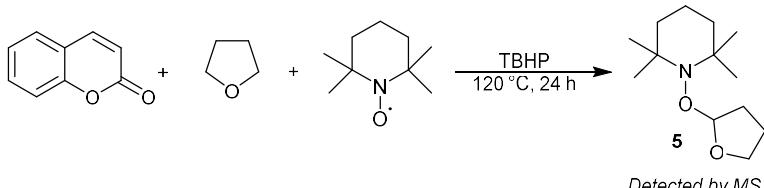
A vial equipped with a stir bar was charged with coumarin (29.2 mg, 0.2 mmol, 1 equiv), ether (0.4 mL), TBHP (tert-butyl hydroperoxide 70 wt % in water, 0.8 mmol, 4 equiv). Then the vial was capped and the resulting mixture was heated in an oil bath at 120 °C for 24 h. The reaction mixture was cooled to room temperature. Then the reaction mixture was quenched with a saturated solution of Na<sub>2</sub>SO<sub>3</sub> for removal of excess TBHP and extracted with ethyl acetate. The combined organic layer was dried over MgSO<sub>4</sub> and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel with n-hexane/ethyl acetate (9/1 v/v) as eluent to provide the desired product.

### 2-3-2 Procedure II (scale up process)

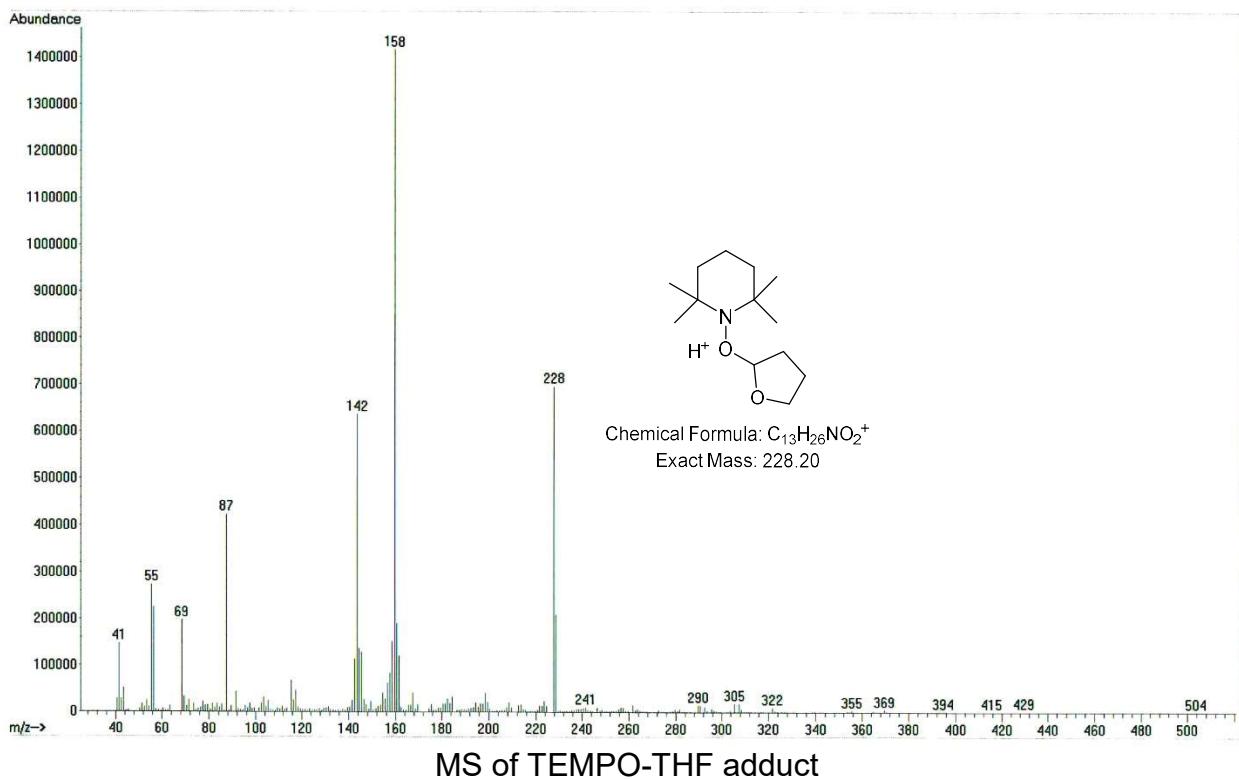
Into a dry 10-mL vial equipped with a magnetic stirring bar were added coumarin (292 mg, 2.0 mmol, 1 equiv), ether (4.0 mL), TBHP (tert-butyl hydroperoxide 70 wt % in water, 8.0 mmol, 4 equiv). Then the vial was capped and the resulting mixture was heated in an oil bath at 120 °C for 24 h. The reaction mixture was cooled to room temperature. Then the reaction mixture was quenched with a saturated solution of Na<sub>2</sub>SO<sub>3</sub> for removal of excess TBHP and extracted with ethyl acetate. The combined organic layer was dried over MgSO<sub>4</sub> and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel with n-hexane/ethyl acetate (9/1 v/v) as eluent to provide the desired product.

<sup>3</sup> M. Li, J. L. Petersen, J. M. Hoover, *Org. Lett.*, **2017**, *19*, 638.

### 3 Radical trapping experiment

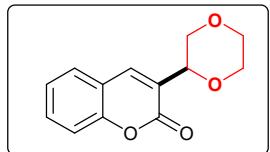


A vial equipped with a stir bar was charged with coumarin (29.2 mg, 0.2 mmol, 1 equiv), THF (0.4 mL), TBHP (tert-butyl hydroperoxide 70 wt % in water, 0.8 mmol, 4 equiv) and 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO) (0.4 mmol, 2.0 equiv). Then the vial was capped and the resulting mixture was heated in an oil bath at 120 °C for 24 h. While no desired product **3k** was found, the TEMPO-THF adduct **5** was detected.



### 4 Compounds characterization data

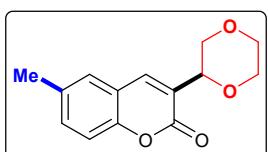
#### **3-(1,4-Dioxan-2-yl)-2H-chromen-2-one 3a<sup>4</sup>**



Colorless solid, isolated yield 70% (33 mg), mp 80-81 °C (ref.<sup>4</sup>, 80.1-80.8 °C); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.81 (s, 1H), 7.46-7.42 (m, 2H), 7.28-7.19 (m, 2H), 4.70-4.67 (m, 1H), 4.21-4.17 (m, 1H), 3.95-3.82 (m, 2H), 3.78-3.71 (m, 1H), 3.66-3.58 (m, 1H), 3.21-3.14 (m, 1H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 159.9, 153.1, 139.2, 131.5, 128.0, 126.0, 124.6, 119.0, 116.4, 72.7, 70.9, 67.2, 66.4 ppm. CHN analysis [%]: Anal. Calcd for C<sub>13</sub>H<sub>12</sub>O<sub>4</sub>: C, 67.23; H, 5.21. Found: C, 67.54; H, 5.35.

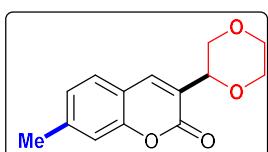
<sup>4</sup> C. Wang, X. Mi, Q. Li, Y. Li, M. Huang, J. Zhang, Y. Wu, *Tetrahedron*, **2015**, *71*, 6689.

### 3-(1,4-Dioxan-2-yl)-6-methyl-2H-chromen-2-one 3b<sup>5</sup>



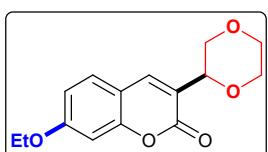
Colorless solid, isolated yield 78% (38 mg), mp 115-116 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.79 (s, 1H), 7.30-7.25 (m, 2H), 7.19-7.17 (m, 1H), 4.74 (m, 1H), 4.23 (dd, J = 11.2, 2.3 Hz, 1H), 3.95-3.91 (m, 2H), 3.82-3.78 (m, 1H), 3.66 (td, J = 11.2, 4.0 Hz, 1H), 3.20 (t, J = 11.2 Hz, 1H), 2.38 (s, 3H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 160.2, 151.3, 139.2, 134.3, 132.6, 127.8, 125.9, 118.8, 116.2, 72.8, 71.0, 67.3, 66.4, 20.8 ppm. CHN analysis [%]: Anal. Calcd for C<sub>14</sub>H<sub>14</sub>O<sub>4</sub>: C, 68.28; H, 5.73. Found: C, 68.57; H, 5.86.

### 3-(1,4-Dioxan-2-yl)-7-methyl-2H-chromen-2-one 3c



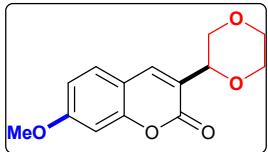
Colorless solid, isolated yield 82% (40 mg), mp 126-127 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.75 (s, 1H), 7.29 (d, J = 7.8 Hz, 1H), 7.04 (s, 1H), 7.02 (d, J = 8.4 Hz, 1H), 4.67 (d, J = 9.6 Hz, 1H), 4.17 (dd, J = 11.2, 2.6 Hz, 1H), 3.91-3.82 (m, 2H), 3.75-3.72 (m, 1H), 3.63-3.57 (m, 1H), 3.16 (dd, J = 11.2, 9.7 Hz, 1H), 2.36 (s, 3H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 159.1, 152.3, 141.8, 138.2, 126.7, 124.7, 123.8, 115.6, 115.6, 71.7, 70.0, 66.3, 65.4, 20.7 ppm. IR: 3062, 2965, 2850, 1701, 1616, 1452, 1372, 1102, 1031, 801 cm<sup>-1</sup>. MS m/z 246 (M<sup>+</sup>, 90%), 202 (80), 187 (30), 174 (28), 160 (100), 132 (45). CHN analysis [%]: Anal. Calcd for C<sub>14</sub>H<sub>14</sub>O<sub>4</sub>: C, 68.28; H, 5.73. Found: C, 68.54; H, 5.83.

### 3-(1,4-Dioxan-2-yl)-7-ethoxy-2H-chromen-2-one 3d



Colorless solid, isolated yield 64% (35 mg), mp 117-119 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.77 (s, 1H), 7.35 (d, J = 8.7 Hz, 1H), 6.82-6.74 (m, 2H), 4.70 (dd, J = 9.0, 1.2 Hz, 1H), 4.19 (dd, J = 11.2, 2.4 Hz, 1H), 4.06 (q, J = 6.9 Hz, 2H), 3.96-3.89 (m, 2H), 3.80-3.77 (m, 1H), 3.69-3.61 (m, 1H), 3.25-3.18 (m, 1H), 1.42 (t, J = 6.9 Hz, 3H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 162.1, 160.3, 155.1, 139.4, 128.9, 122.3, 113.3, 112.6, 101.0, 72.7, 71.1, 67.3, 66.4, 64.2, 14.6 ppm. IR: 2973, 2855, 1697, 1606, 1438, 1229, 1115, 928 cm<sup>-1</sup>. MS m/z 276 (M<sup>+</sup>, 95%), 232 (40), 217 (17), 204 (20), 190 (100), 134 (90). CHN analysis [%]: Anal. Calcd for C<sub>15</sub>H<sub>16</sub>O<sub>5</sub>: C, 65.21; H, 5.84. Found: C, 65.51; H, 5.97.

### 3-(1,4-Dioxan-2-yl)-7-methoxy-2H-chromen-2-one 3e

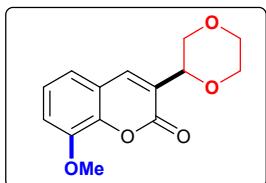


Colorless solid, isolated yield 74% (39 mg), mp 150-152 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.80 (s, 1H), 7.37 (d, J = 8.6 Hz, 1H), 6.84-6.77 (m, 2H), 4.74-4.71 (m, 1H), 4.20 (dd, J = 11.2, 2.4 Hz, 1H), 3.96-3.90 (m, 2H), 3.84 (s, 3H), 3.81-3.77 (m, 1H), 3.69-3.61 (m, 1H), 3.21 (dd, J = 11.0, 9.7 Hz, 1H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 162.6, 160.3, 155.0, 139.4, 128.9, 122.4, 112.8, 112.7, 100.5, 72.6, 71.1, 67.3, 66.4, 55.8 ppm. IR: 2970, 2845, 1702, 1609, 1432, 1199, 1117, 934 cm<sup>-1</sup>. MS m/z 262 (M<sup>+</sup>, 80%), 218 (35), 203

<sup>5</sup> B. Niu, W. Zhao, Y. Ding, Z. Bian, C. U. Pittman Jr, A. Zhou, H. Ge, *J. Org. Chem.*, **2015**, *80*, 7251.

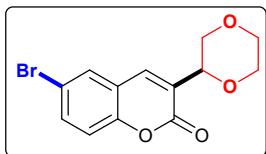
(15), 177 (100), 151 (40), 133 (30). CHN analysis [%]: Anal. Calcd for C<sub>14</sub>H<sub>14</sub>O<sub>5</sub>: C, 64.12; H, 5.38. Found: C, 64.44; H, 5.50.

### 3-(1,4-Dioxan-2-yl)-8-methoxy-2H-chromen-2-one 3f



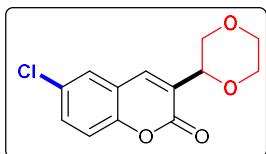
Colorless solid, isolated yield 56% (29 mg), mp 116-118 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.85 (d, J = 1.3 Hz, 1H) 7.20 (t, J = 8.0 Hz, 1H), 7.10-7.05 (m, 2H), 4.79 (d, J = 8.4, 1H), 4.27 (dd, J = 11.2, 2.6 Hz, 1H), 3.96-3.93 (m, 2H), 3.96 (s, 3H), 3.83-3.80 (m, 1H), 3.71-3.67 (m, 1H), 3.23 (dd, J = 11.2, 9.6 Hz, 1H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 159.4, 147.1, 142.9, 139.3, 126.4, 124.4, 119.7, 119.4, 113.4, 72.7, 71.0, 67.3, 66.4, 56.3 ppm. IR: 2916, 2850, 1703, 1607, 1576, 1475, 1271, 1105, 733 cm<sup>-1</sup>. MS m/z 262 (M<sup>+</sup>, 100%), 218 (60), 203 (37), 176 (77), 148 (18), 133 (20). CHN analysis [%]: Anal. Calcd for C<sub>14</sub>H<sub>14</sub>O<sub>5</sub>: C, 64.12; H, 5.38. Found: C, 64.40; H, 5.49.

### 6-Bromo-3-(1,4-Dioxan-2-yl)-2H-chromen-2-one 3h<sup>5</sup>



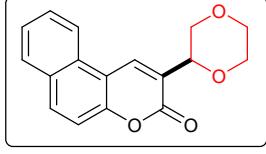
Colorless solid, isolated yield 60% (33 mg), mp 127-128 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.78 (s, 1H), 7.63 (d, J = 2.3 Hz, 1H), 7.58 (dd, J = 8.7, 2.3 Hz, 1H), 7.20 (d, J = 8.7 Hz, 1H), 4.77-4.73 (m, 1H), 4.25 (dd, J = 11.2, 2.6 Hz, 1H), 3.99-3.89 (m, 2H), 3.83-3.80 (m, 1H), 3.68 (td, J = 11.2, 3.7 Hz, 1H), 3.20 (dd, J = 11.2, 9.7 Hz, 1H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 159.2, 152.0, 137.8, 134.2, 130.3, 127.5, 120.6, 118.3, 117.2, 72.7, 70.9, 67.3, 66.4 ppm. CHN analysis [%]: Anal. Calcd for C<sub>13</sub>H<sub>11</sub>BrO<sub>4</sub>: C, 50.19; H, 3.56. Found: C, 50.46; H, 3.66.

### 6-chloro-3-(1,4-dioxan-2-yl)-2H-chromen-2-one 3i



Colorless solid, isolated yield 73% (39 mg), mp 145-146 °C ;<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.81 (s, 1H), 7.49 (d, J = 2.0 Hz, 1H), 7.46 (dd, J = 10.0, 2.0 Hz, 1H), 7.27 (d, J = 10.0 Hz, 1H), 4.78-4.75 (m, 1H), 4.26 (dd, J = 11.2, 2.2 Hz, 1H), 4.00-3.90 (m, 2H), 3.84-3.81 (m, 1H), 3.69 (td, J = 11.8, 3.7 Hz, 1H), 3.24-3.20 (m, J = 11.2, 9.6 Hz, 1H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 159.2, 151.5, 137.8, 131.3, 129.8, 127.5, 127.1, 120.0, 117.9, 72.6, 70.9, 67.2, 66.3 ppm. IR: 2966, 2918, 1703, 1604, 1251, 1177, 932 cm<sup>-1</sup>. MS m/z 266 (M<sup>+</sup>, 100%), 222 (65), 180 (50), 152 (45), 89 (30). CHN analysis [%]: Anal. Calcd for C<sub>13</sub>H<sub>11</sub>ClO<sub>4</sub>: C, 58.55; H, 4.16. Found: C, 58.90; H, 4.28.

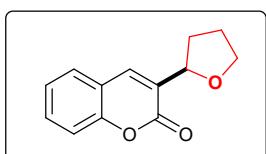
### 2-(1,4-dioxan-2-yl)-3H-benzo[f]chromen-3-one 3j



Yellow solid, isolated yield 78% (44 mg), mp 159-160 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.65 (s, 1H), 8.34 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 9.0 Hz, 1H), 7.91 (d, J = 8.1 Hz, 1H), 7.70-7.67 (m, 1H), 7.59-7.55 (m, 1H), 7.45 (d, J = 9.0 Hz, 1H) 4.87 (dd, J = 9.6, 1.2 Hz, 1H), 4.34 (dd, J = 11.3, 2.7 Hz, 1H), 4.10-3.97 (m, 2H), 3.87 (m, 1H), 3.75 (td, J = 11.4, 3.3 Hz, 1H), 3.30 (dd, J = 11.2, 10 Hz, 1H)

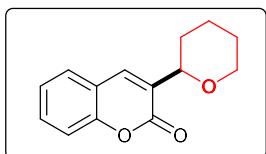
ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.9, 152.8, 134.8, 132.7, 130.3, 129.1, 128.9, 128.1, 126.0, 125.0, 121.8, 116.6, 113.2, 72.9, 71.0, 67.3, 66.4 ppm. IR: 2966, 2854, 1693, 1571, 1511, 1112, 920  $\text{cm}^{-1}$ . MS  $m/z$  282 ( $M^+$ , 100%), 238 (50), 196 (80), 168 (80), 139 (60). CHN analysis [%]: Anal. Calcd for  $\text{C}_{17}\text{H}_{14}\text{O}_4$ : C, 72.33; H, 5.00. Found: C, 72.69; H, 5.13.

### **3-(Tetrahydrofuran-2-yl)-2H-chromen-2-one 3k<sup>4</sup>**



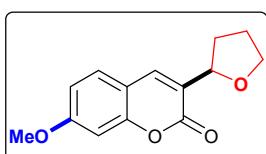
Yellow oil, isolated yield 68% (30 mg);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.78 (s, 1H), 7.48-7.43 (m, 2H), 7.31-7.22 (m, 2H), 4.94 (t,  $J = 6.6$  Hz, 1H), 4.13-3.90 (m, 2H), 2.52-2.43 (m, 1H), 2.03-1.86 (m, 2H), 1.80-1.69 (m, 1H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  160.6, 153.1, 136.5, 131.0, 130.9, 127.8, 124.5, 119.2, 116.4, 76.0, 67.0, 32.2, 25.7 ppm. CHN analysis [%]: Anal. Calcd for  $\text{C}_{13}\text{H}_{12}\text{O}_3$ : C, 72.21; H, 5.59. Found: C, 71.96; H, 5.50.

### **3-(Tetrahydro-2H-pyran-2-yl)-2H-chromen-2-one 3l<sup>4</sup>**



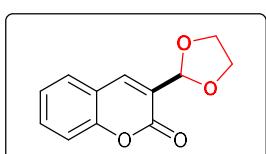
Colorless oil, isolated yield 63% (28 mg);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.82 (s, 1H), 7.47 (t,  $J = 7.6$  Hz, 2H), 7.31 (d,  $J = 8.1$  Hz, 1H), 7.25 (t,  $J = 7.6$  Hz, 1H), 4.46 (d,  $J = 11.0$  Hz, 1H), 4.18 (dt,  $J = 11.2, 1.9$  Hz, 1H), 3.65 (td,  $J = 11.2, 2.6$  Hz, 1H), 2.21 (d,  $J = 12.5$  Hz, 1H), 1.92-1.90 (m, 1H), 1.73-1.58 (m, 3H), 1.30-1.24 (m, 1H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  160.3, 153.1, 137.4, 130.9, 131.0, 127.9, 124.4, 119.5, 116.4, 74.6, 69.1, 32.2, 26.0, 23.6 ppm. CHN analysis [%]: Anal. Calcd for  $\text{C}_{14}\text{H}_{14}\text{O}_3$ : C, 73.03; H, 6.13. Found: C, 72.72; H, 5.98.

### **7-Methoxy-3-(tetrahydrofuran-2-yl)-2H-chromen-2-one 3m<sup>4</sup>**



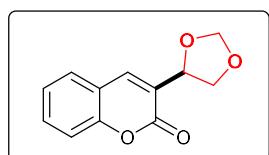
Colorless oil, isolated yield 77% (38 mg);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.72 (s, 1H), 7.36 (d,  $J = 8.4$  Hz, 1H), 6.83-6.81 (m, 2H), 4.96-4.91 (t,  $J = 6.3$  Hz, 1H), 4.12-4.05 (m, 1H), 3.93-3.89 (m, 1H), 3.84 (s, 3H), 2.52-2.41 (m, 1H), 1.99-1.89 (m, 2H), 1.78-1.71 (m, 1H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  162.2, 160.9, 154.8, 136.7, 128.7, 127.4, 112.9, 112.6, 100.5, 75.9, 68.9, 55.8, 32.3, 25.7 ppm. CHN analysis [%]: Anal. Calcd for  $\text{C}_{14}\text{H}_{14}\text{O}_4$ : C, 68.28; H, 5.73. Found: C, 68.53; H, 5.83

### **3-(1,3-Dioxolan-2-yl)-2H-chromen-2-one 3n<sup>4</sup>**



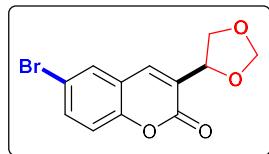
Colorless solid, isolated yield 35% (15 mg), mp 66-67 °C (ref 1, 66.6–67.2 °C);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.96 (s, 1H), 7.58-7.52 (m, 2H), 7.35-7.27 (m, 2H), 5.94 (s, 1H), 4.17-4.05 (m, 4H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.9, 153.9, 139.8, 132.2, 128.5, 124.6, 118.7, 116.7, 99.0, 64.5 ppm. CHN analysis [%]: Anal. Calcd for  $\text{C}_{12}\text{H}_{10}\text{O}_4$ : C, 66.05; H, 4.62. Found: C, 66.28; H, 4.73.

### 3-(1,3-Dioxolan-4-yl)-2H-chromen-2-one 3n'



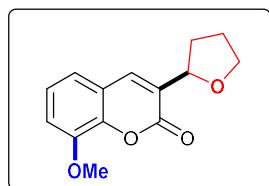
Colorless solid, isolated yield 35% (16 mg), mp 82-84 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.77 (s, 1H), 7.46-7.42 (m, 2H), 7.27-7.19 (m, 2H), 5.10 (s, 1H), 5.02-4.99 (m, 1H), 4.98 (s, 1H), 4.28 (dd,  $J$  = 8.6, 7.2 Hz, 1H), 3.73 (dd,  $J$  = 8.6, 5.4 Hz, 1H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.5, 152.1, 136.5, 130.4, 127.0, 126.9, 123.6, 117.9, 115.5, 94.7, 71.4, 69.5 ppm. IR: 2959, 2848, 1712, 1603, 1258, 1083, 1015, 941, 793. MS  $m/z$  218 ( $M^+$ , 1%), 172 (100), 149 (50), 130 (40), 102 (20). CHN analysis [%]: Anal. Calcd for  $\text{C}_{12}\text{H}_{10}\text{O}_4$ : C, 66.05; H, 4.62. Found: C, 66.36; H, 4.76.

### 6-Bromo-3-(1,3-dioxolan-4-yl)-2H-chromen-2-one 3o



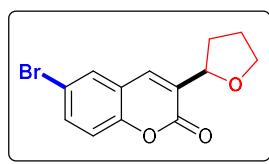
Colorless solid, isolated yield 30% (18 mg), mp 111-113 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.75 (s, 1H), 7.63 (s, 1H), 7.58 (d,  $J$  = 8.7 Hz, 1H), 7.20 (d,  $J$  = 8.7 Hz, 1H), 5.21 (s, 1H), 5.05-5.03 (m, 1H), 5.03 (s, 1H), 4.33 (t,  $J$  = 7.8 Hz, 1H), 3.79 (dd,  $J$  = 8.4, 5.4 Hz, 1H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  158.8, 150.9, 135.2, 133.1, 129.3, 128.3, 119.4, 117.3, 116.2, 94.7, 71.3, 69.4 ppm. IR: 2860, 1713, 1475, 1166, 1074, 926, 811. MS  $m/z$  296 ( $M^+$ , 1%), 252 (100), 210 (30), 182 (10), 115 (17), 89 (15). CHN analysis [%]: Anal. Calcd for  $\text{C}_{12}\text{H}_9\text{BrO}_4$ : C, 48.51; H, 3.05. Found: C, 48.81; H, 3.17.

### 8-Methoxy-3-(tetrahydrofuran-2-yl)-2H-chromen-2-one 3p



Colorless solid, isolated yield 67% (33 mg), mp 109-111 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.76 (d,  $J$  = 1.4 Hz, 1H), 7.18 (t,  $J$  = 8.0 Hz, 1H), 7.06-7.01 (m, 2H), 4.95 (td,  $J$  = 7.0, 1.3 Hz, 1H), 4.12-4.06 (m, 1H), 3.96-3.90 (m, 1H), 3.92 (s, 3H), 2.55-2.47 (m, 1H), 2.04-1.86 (m, 2H), 1.78-1.70 (m, 1H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  158.9, 146.1, 141.7, 135.4, 130.3, 123.2, 118.9, 118.3, 111.8, 74.9, 67.9, 55.2, 31.2, 24.6 ppm. IR: 2960, 1708, 1475, 1260, 1017, 795  $\text{cm}^{-1}$ . MS  $m/z$  246 ( $M^+$ , 33%), 218 (77), 203 (100), 176 (33), 149 (33). CHN analysis [%]: Anal. Calcd for  $\text{C}_{14}\text{H}_{14}\text{O}_4$ : C, 68.28; H, 5.73. Found: C, 67.96; H, 5.58.

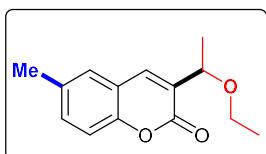
### 6-Bromo-3-(tetrahydrofuran-2-yl)-2H-chromen-2-one 3q<sup>6</sup>



Colorless solid, isolated yield 63% (37 mg), mp 110-112 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.71 (d,  $J$  = 1.3 Hz, 1H), 7.61 (d,  $J$  = 2.3 Hz, 1H), 7.55 (dd,  $J$  = 8.7, 2.3 Hz, 1H), 7.19 (d,  $J$  = 8.7 Hz, 1H), 4.92 (td,  $J$  = 7.6, 1.3 Hz, 1H), 4.11-4.05 (m, 1H), 3.96-3.91 (m, 1H), 2.55-2.46 (m, 1H), 2.05-1.86 (m, 2H), 1.78-1.69 (m, 1H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  158.8, 150.9, 134.1, 132.6, 131.4, 129.1, 119.8, 117.2, 115.9, 74.9, 67.9, 31.2, 24.7 ppm. CHN analysis [%]: Anal. Calcd for  $\text{C}_{13}\text{H}_{11}\text{BrO}_3$ : C, 52.91; H, 3.76. Found: C, 53.23; H, 3.90.

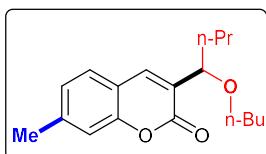
<sup>6</sup> L. Dian, H. Zhao, D. Zhang-Negrierie, Y. Du, *Adv. Synth. Catal.*, **2016**, 358, 2422.

### **3-(1-Ethoxyethyl)-6-methyl-2H-chromen-2-one 3s<sup>5</sup>**



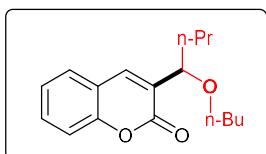
Colorless oil, isolated yield 56% (26 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.66 (s, 1H) 7.24-7.22 (m, 2H), 7.16-7.14 (m, 1H), 4.53 (qd, J = 6.4, 1.0 Hz, 1H), 3.45 (qd, J = 7.0, 2.0 Hz, 2H), 2.33 (s, 3H), 1.35 (d, J = 6.4 Hz, 3H), 1.18 (t, J = 7.0 Hz, 3H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 160.1, 150.3, 136.1, 133.1, 131.1, 130.5, 126.7, 118.1, 115.2, 71.2, 63.7, 20.6, 19.8, 14.5 ppm. CHN analysis [%]: Anal. Calcd for C<sub>14</sub>H<sub>16</sub>O<sub>3</sub>: C, 72.39; H, 6.94. Found: C, 72.63; H, 7.03.

### **3-(1-Butoxybutyl)-7-methyl-2H-chromen-2-one 3t**



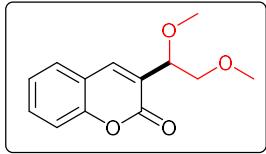
Colorless oil, isolated yield 51% (29 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.63 (s, 1H) 7.30 (d, J = 7.9 Hz, 1H), 7.05 (s, 1H), 7.01 (dd, J = 7.9, 1.0 Hz, 1H), 4.37 (dd, J = 7.1, 3.6 Hz, 1H), 3.38 (dt, J = 9.3, 6.5 Hz, 1H), 3.27 (dt, J = 9.3, 6.5 Hz, 1H), 2.36 (s, 3H), 1.71-1.62 (m, 1H), 1.54-1.30 (m, 7H), 0.86 (t, J = 7.3 Hz, 3H), 0.85 (t, J = 7.3 Hz, 3H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 160.1, 152.2, 141.1, 136.5, 128.4, 126.4, 124.5, 115.9, 115.5, 75.1, 68.5, 36.9, 31.0, 20.7, 18.3, 17.8, 12.9, 12.8 ppm. IR: 2957, 2869, 1715, 1620, 1458, 1090, 809 cm<sup>-1</sup>. MS m/z 288 (M<sup>+</sup>, 1%), 245 (25), 216 (45), 189 (100), 129 (70), 73 (75). CHN analysis [%]: Anal. Calcd for C<sub>18</sub>H<sub>24</sub>O<sub>3</sub>: C, 74.97; H, 8.39. Found: C, 75.30; H, 8.56.

### **3-(1-Butoxybutyl)-2H-chromen-2-one 3u<sup>6</sup>**



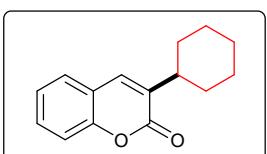
Colorless oil, isolated yield 45% (25 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.67 (s, 1H) 7.44-7.40 (m, 2H), 7.25-7.18 (m, 2H), 4.40 (dd, J = 7.6, 3.4, 1H), 3.40 (dt, J = 9.3, 6.5 Hz, 1H), 3.30 (dt, J = 9.3, 6.5 Hz, 1H), 1.73-1.64 (m, 1H), 1.56-1.44 (m, 4H), 1.40-1.29 (m, 3H), 0.86 (t, J = 7.3 Hz, 3H), 0.85 (t, J = 7.3 Hz, 3H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): 160.9, 153.1, 137.5, 131.0, 130.8, 127.7, 124.3, 119.3, 116.4, 76.1, 69.6, 37.9, 32.0, 19.4, 18.8, 13.9 ppm. CHN analysis [%]: Anal. Calcd for C<sub>17</sub>H<sub>22</sub>O<sub>3</sub>: C, 74.42; H, 8.08. Found: C, 74.73; H, 8.23.

### **3-(1,2-dimethoxyethyl)-2H-chromen-2-one 3v**



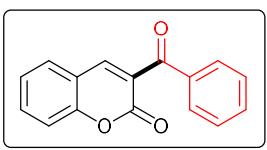
Colorless solid, isolated yield 68% (32 mg), mp 70-75 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.81 (s, 1H), 7.52-7.49 (m, 2H), 7.32 (d, J = 8.0 Hz, 1H), 7.29-7.25 (m, 1H), 4.59 (dd, J = 5.7, 1.8 Hz, 1H), 3.66 (dd, J = 10.5, 1.8 Hz, 1H), 3.54 (dd, J = 10.5, 5.7 Hz, 1H), 3.43 (s, 3H), 3.37 (s, 3H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 160.6, 153.3, 139.5, 131.4, 128.0, 125.9, 124.4, 119.1, 116.4, 77.4, 73.7, 59.2, 57.8 ppm. IR: 3053, 2939, 1697, 1604, 1453, 1099, 752 cm<sup>-1</sup>. MS m/z 234 (M<sup>+</sup>, 1%), 203 (12), 189 (100), 159 (10), 89 (8). CHN analysis [%]: Anal. Calcd for C<sub>13</sub>H<sub>14</sub>O<sub>4</sub>: C, 66.66; H, 6.02. Found: C, 66.90; H, 6.12.

### **3-cyclohexyl-2H-chromen-2-one 3w<sup>4</sup>**



Colorless solid, isolated yield 60% (27 mg), mp 80-85 °C (ref.<sup>4</sup>, 69.3-70.1 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.47-7.44 (m, 3H), 7.30 (d, J = 8.5 Hz, 1H), 7.27-7.24 (m, 1H), 2.78 (tt, J = 11.7, 3.1 Hz, 1H), 2.00-1.97 (m, 2H), 1.87-1.85 (m, 2H), 1.79-1.77 (m, 1H), 1.50-1.41 (m, 2H), 1.35-1.23 (m, 3H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 161.6, 152.8, 136.4, 134.9, 130.5, 127.4, 124.2, 119.7, 116.3, 38.3, 32.2, 26.6, 26.2 ppm. CHN analysis [%]: Anal. Calcd for C<sub>15</sub>H<sub>16</sub>O<sub>2</sub>: C, 78.92; H, 7.06. Found: C, 79.20; H, 7.19.

### **3-Benzoyl-2H-chromen-2-one 4<sup>7</sup>**

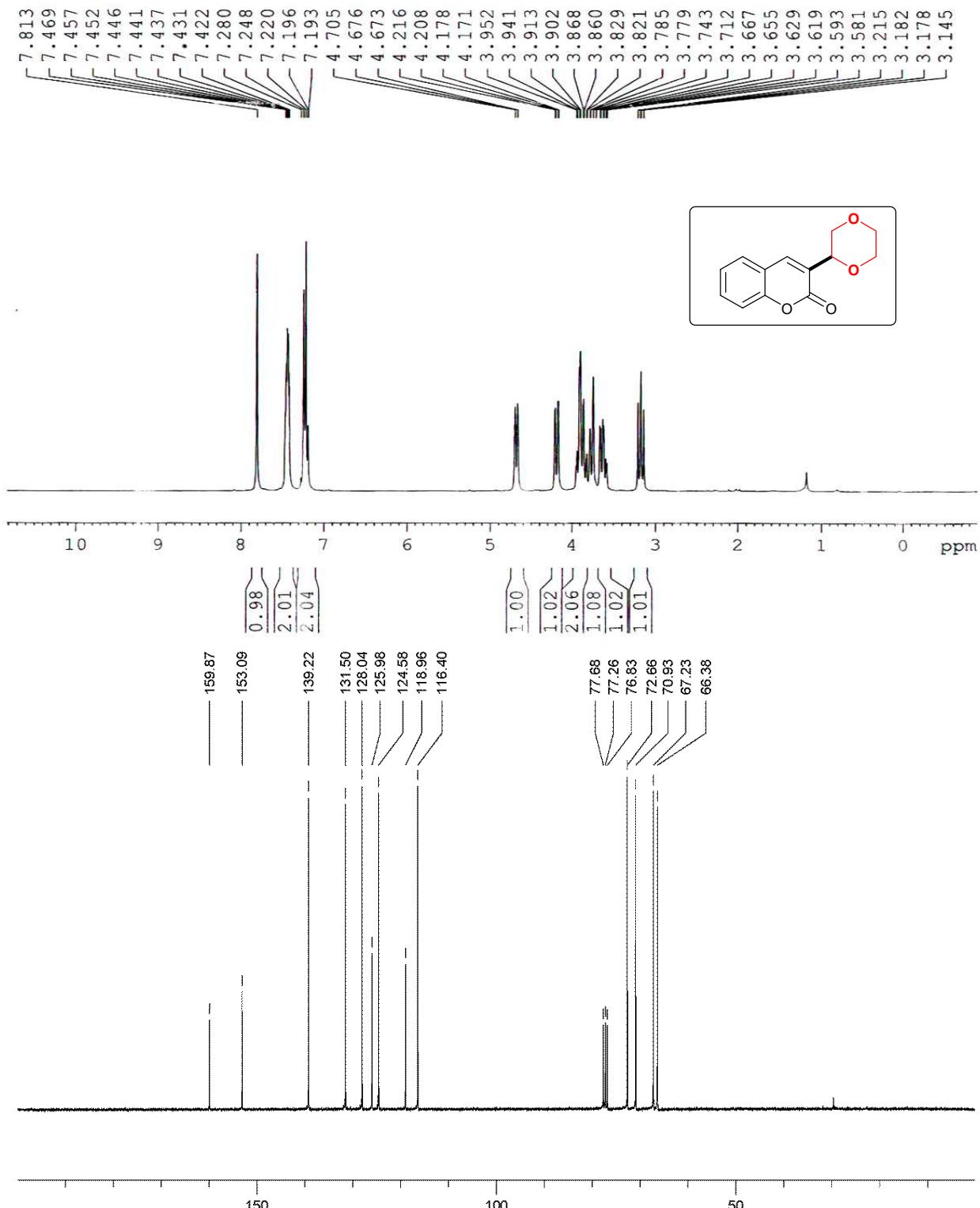


Colorless solid, isolated yield 45% (23 mg), mp 132-133°C (Ref<sup>7</sup>, 131-133); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.09 (s, 1H), 7.89 (d, J = 8.1 Hz, 2H), 7.58-7.66 (m, 3H), 7.31-7.49 (m, 4H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 191.5, 158.3, 154.7, 145.3, 136.2, 133.8, 133.6, 129.5, 129.1, 128.5, 127.0, 124.9, 118.1, 116.9 ppm. CHN analysis [%]: Anal. Calcd for C<sub>16</sub>H<sub>10</sub>O<sub>3</sub>: C, 76.79; H, 4.03. Found: C, 76.50; H, 3.92.

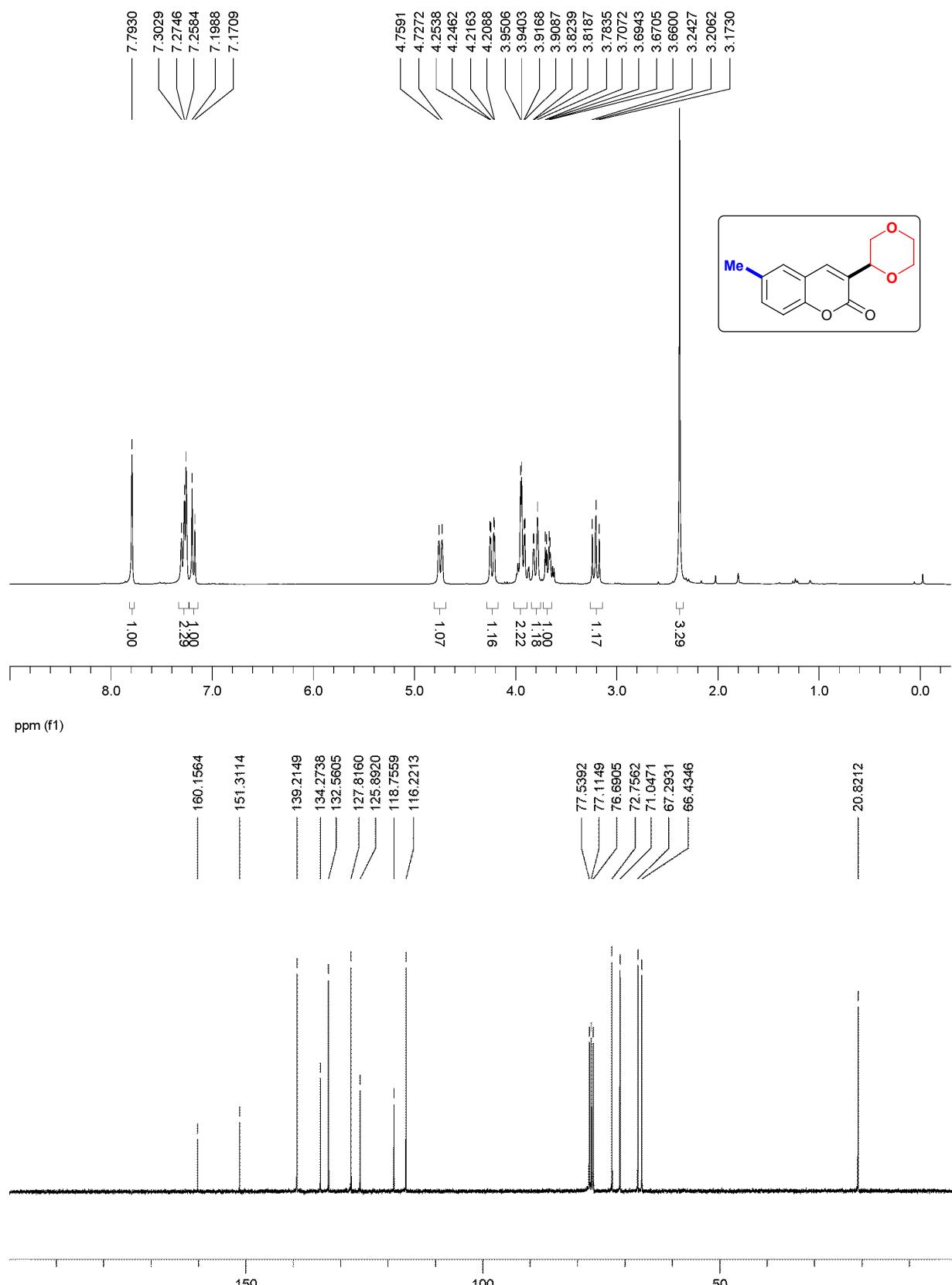
<sup>7</sup> F. Jafarpour, M. Abbasnia, *J. Org. Chem.*, **2016**, *81*, 11982.

## 5 Copies of $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra

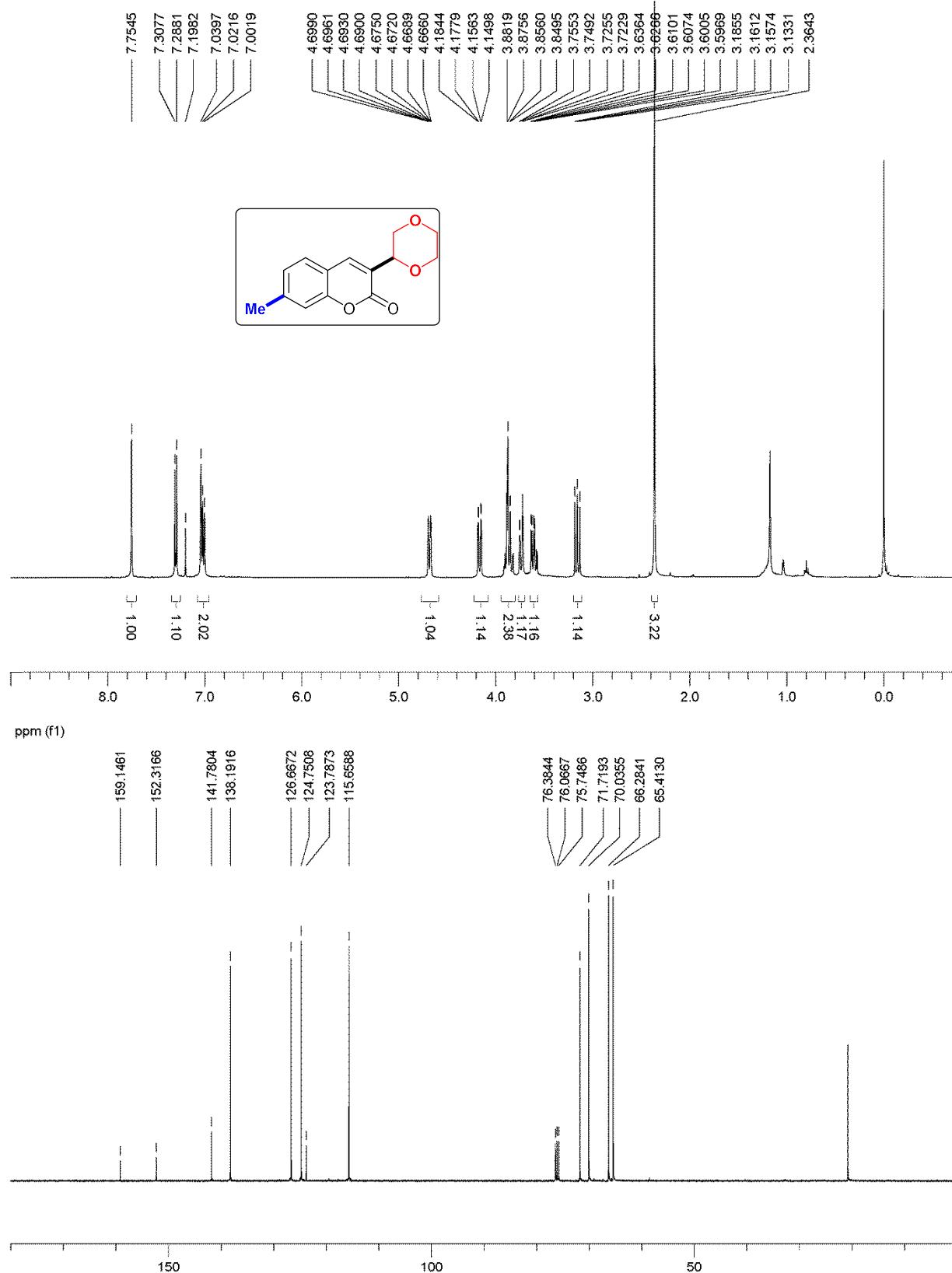
Compound 3a



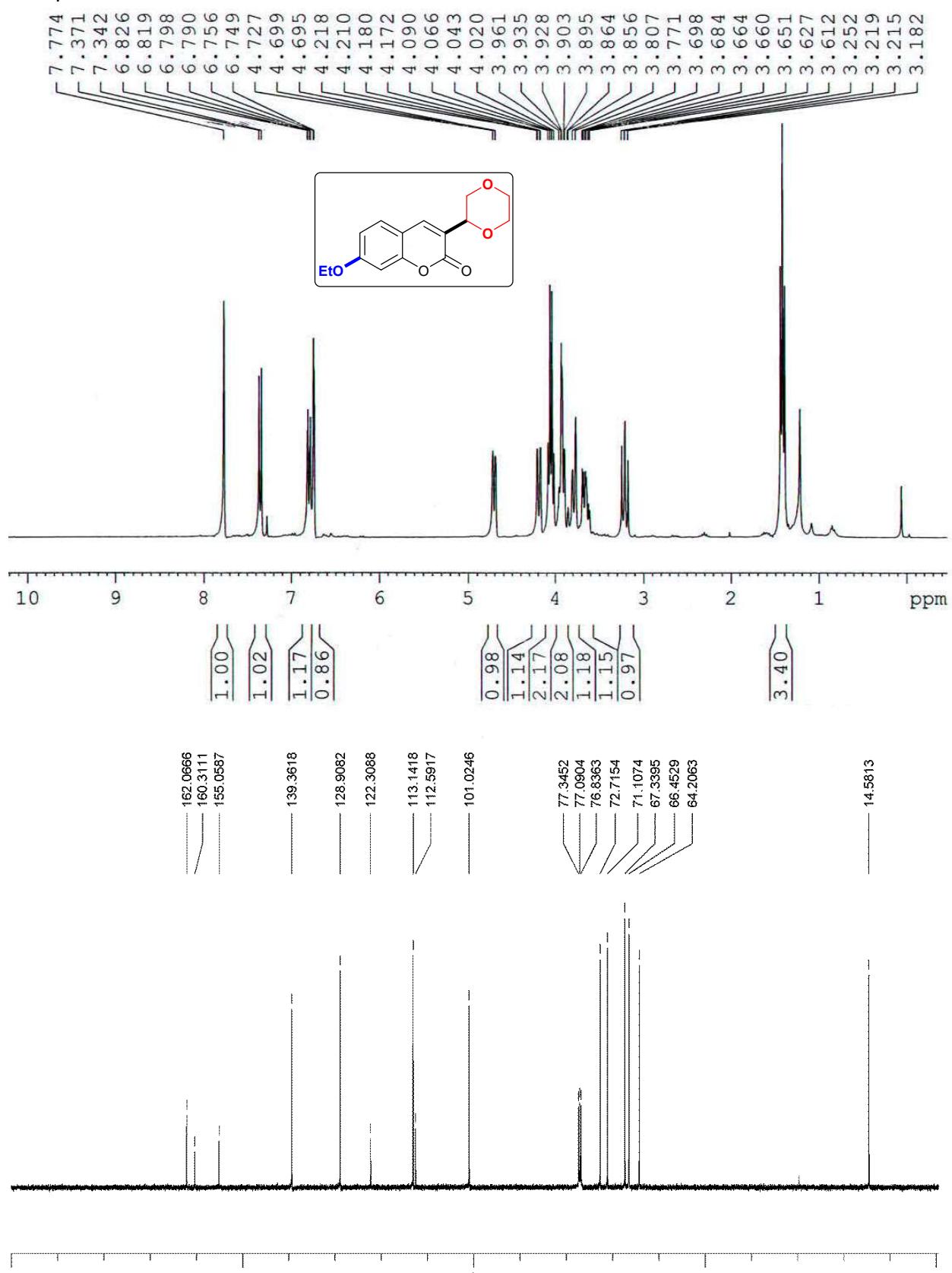
## Compound 3b



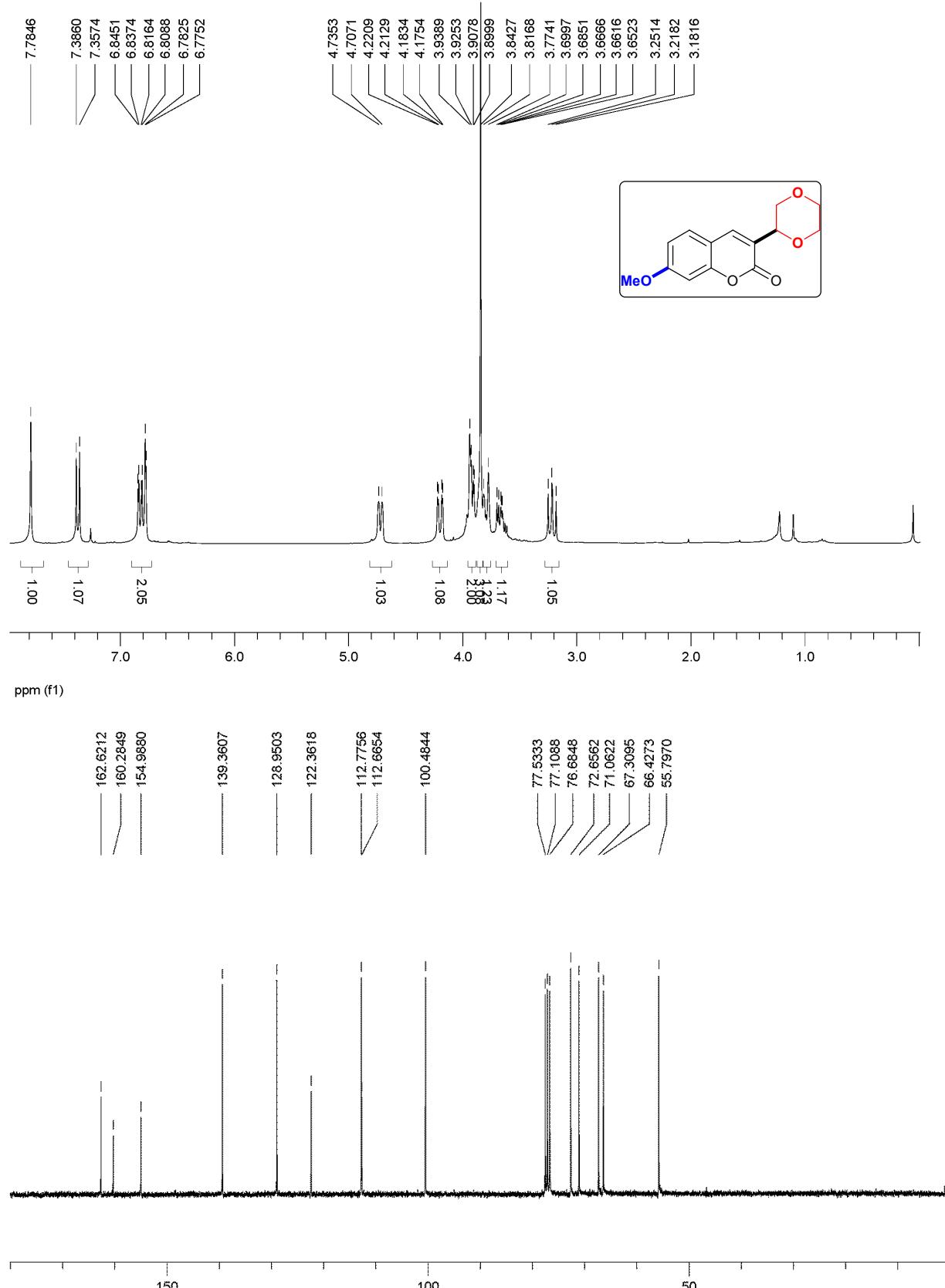
**Compound 3c**



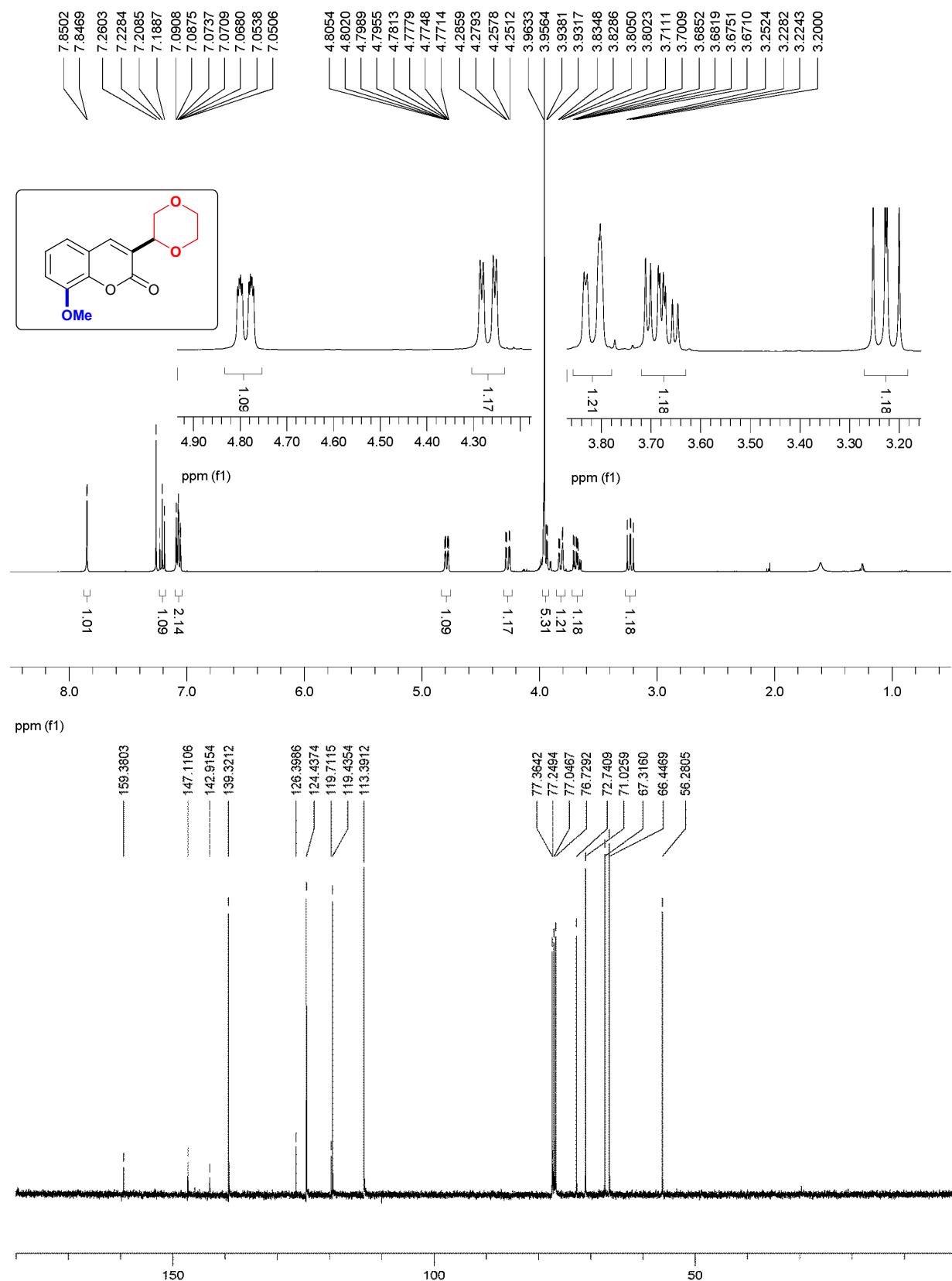
**Compound 3d**



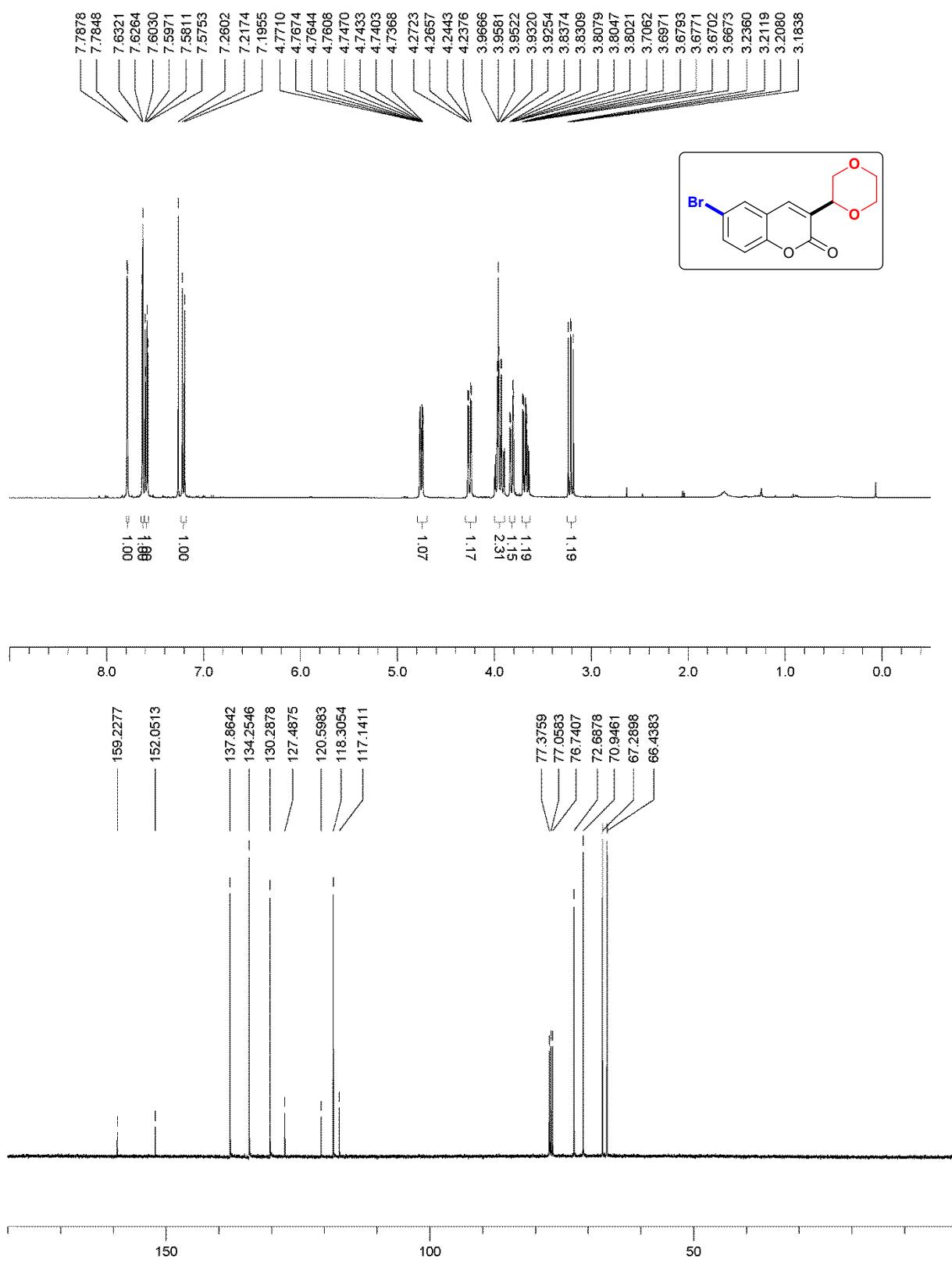
## Compound 3e



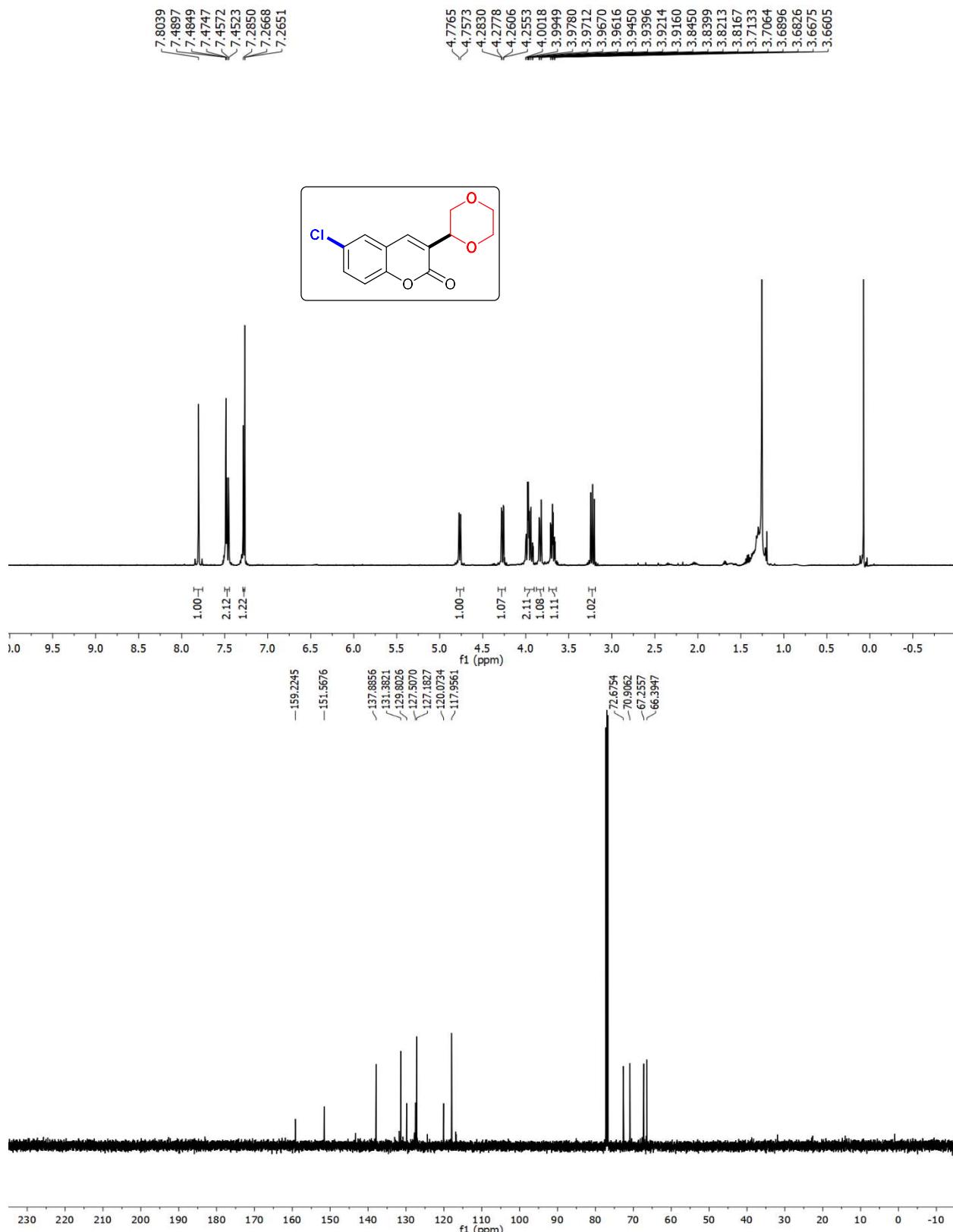
**Compound 3f**



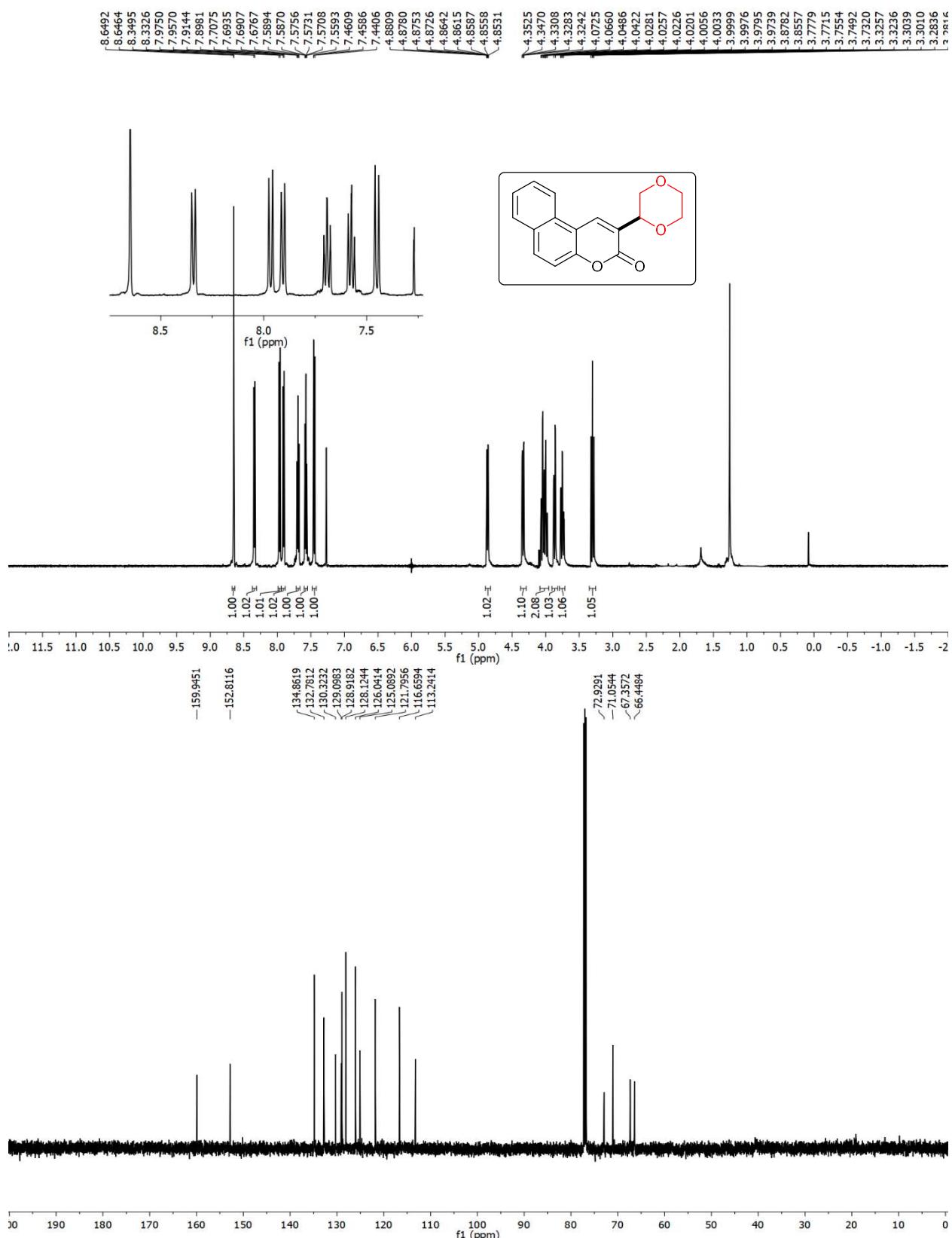
## Compound 3h



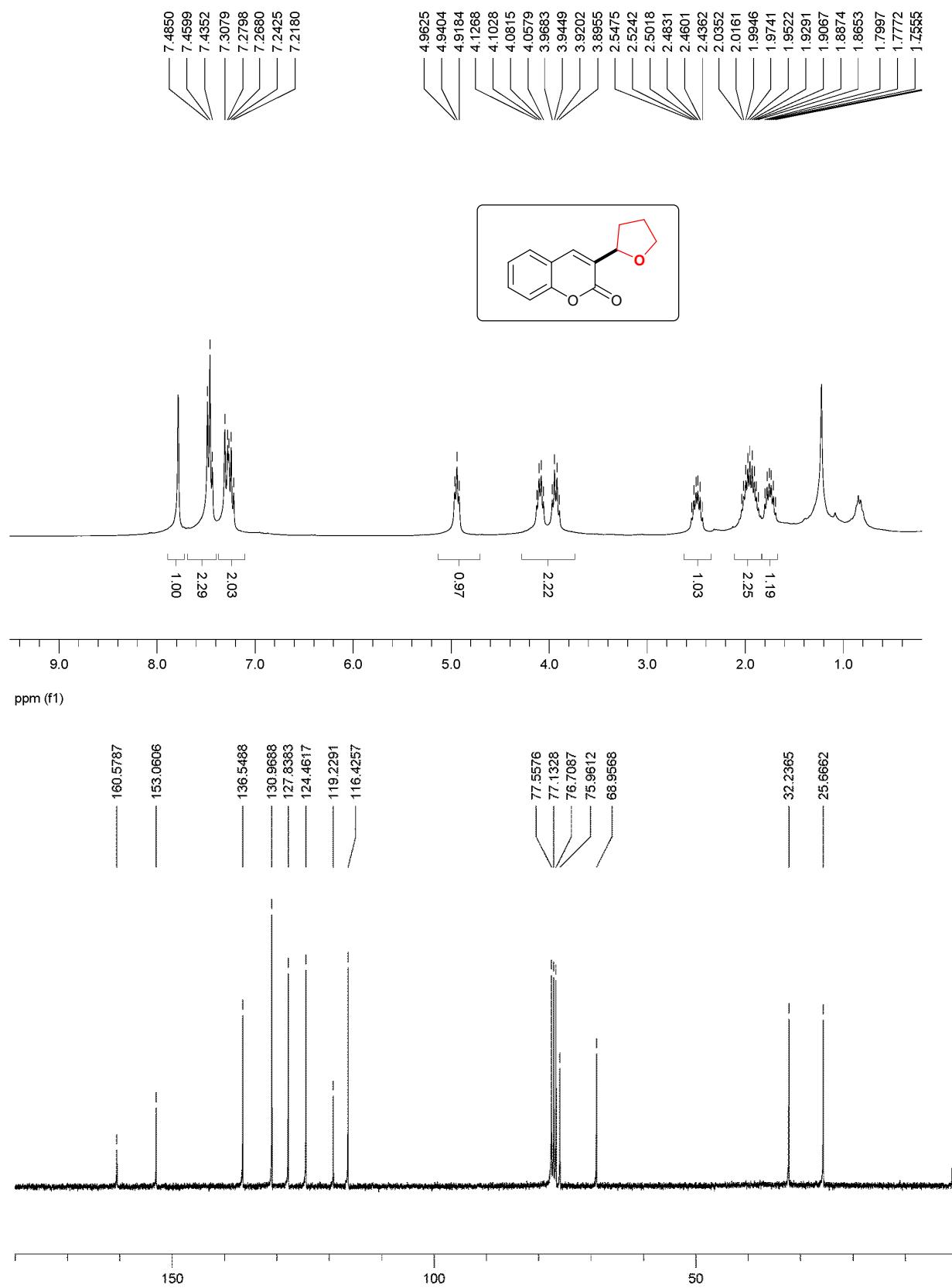
**Compound 3i**



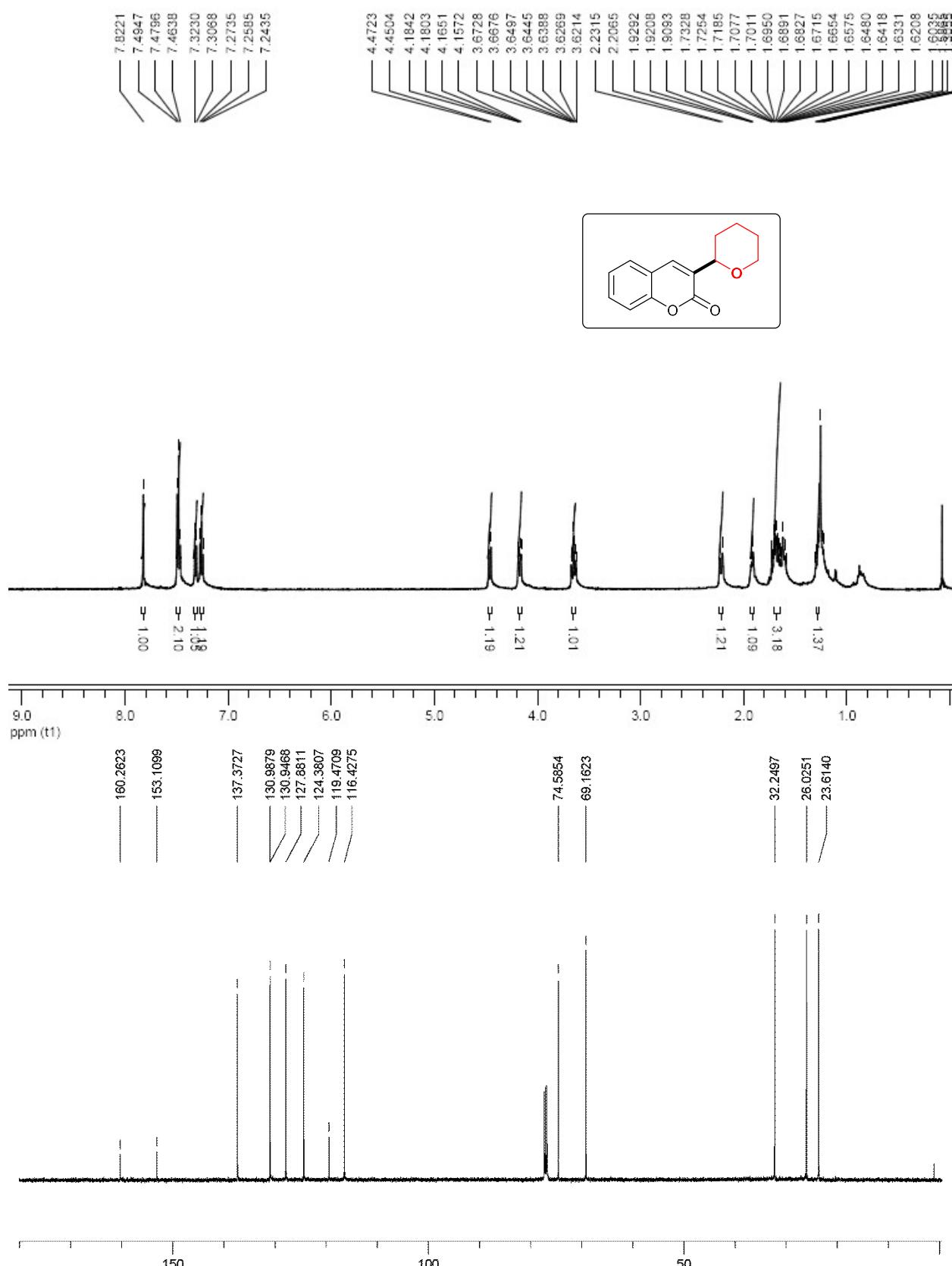
## Compound 3j



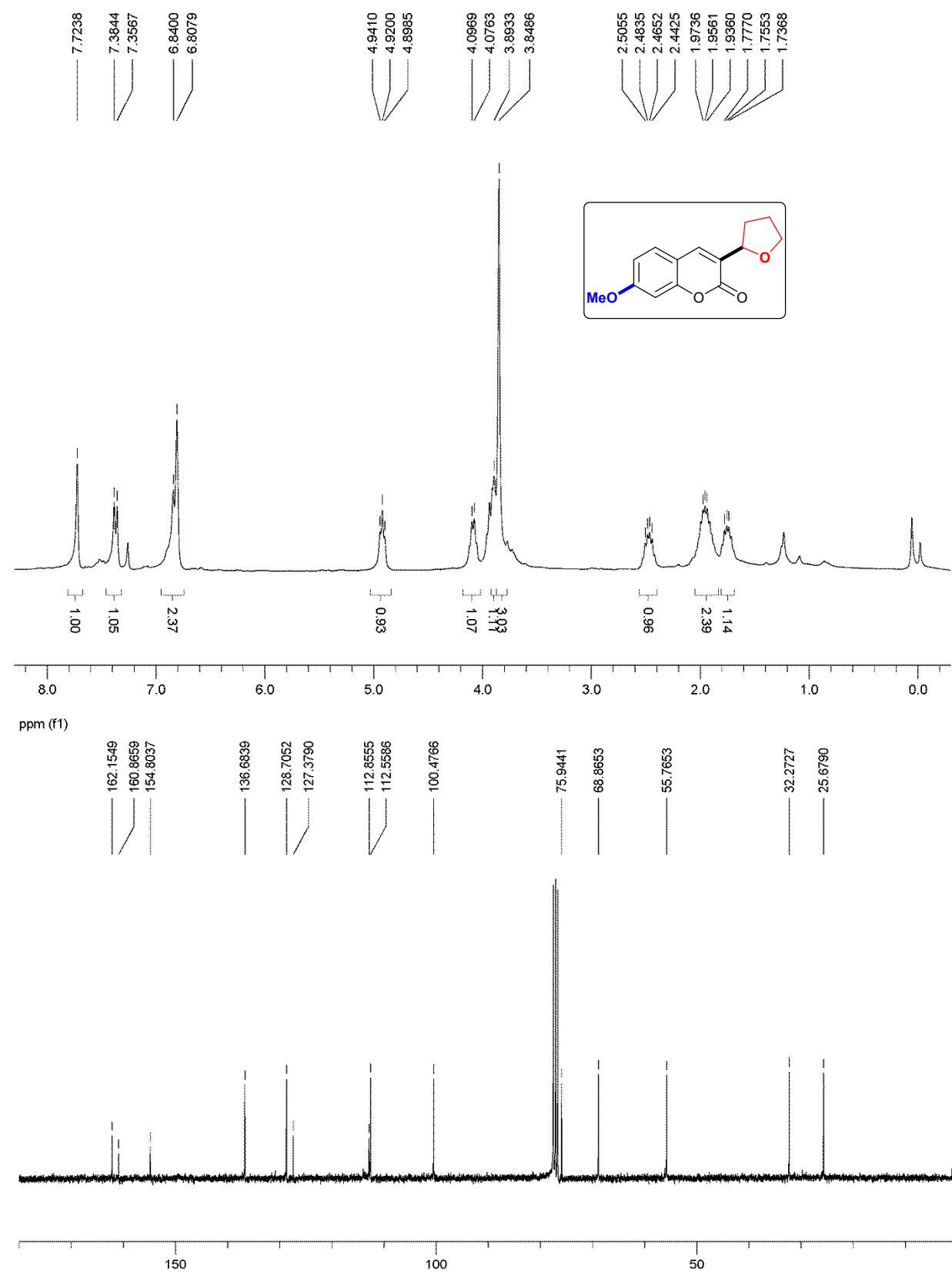
**Compound 3k**



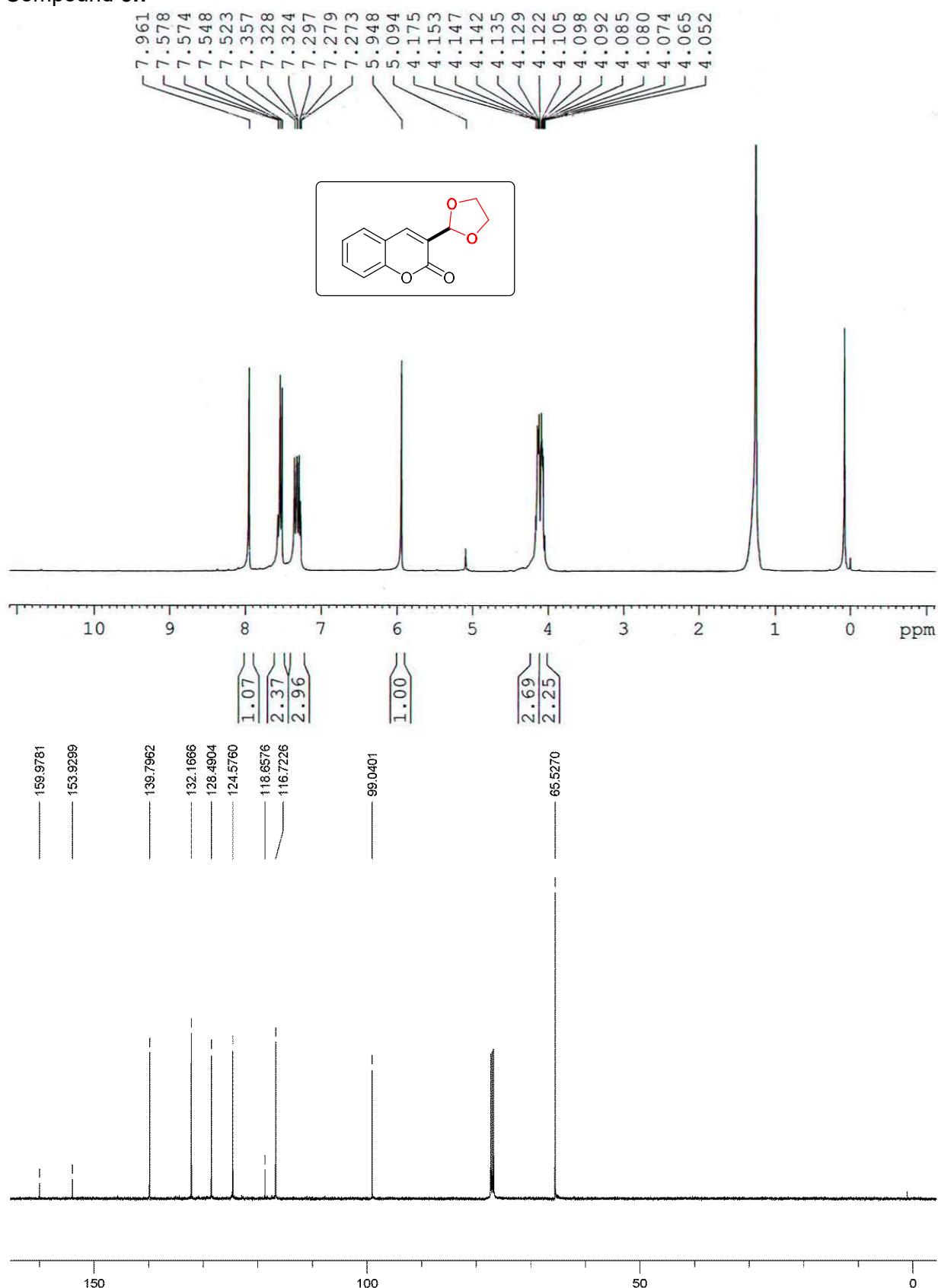
**Compound 3l**



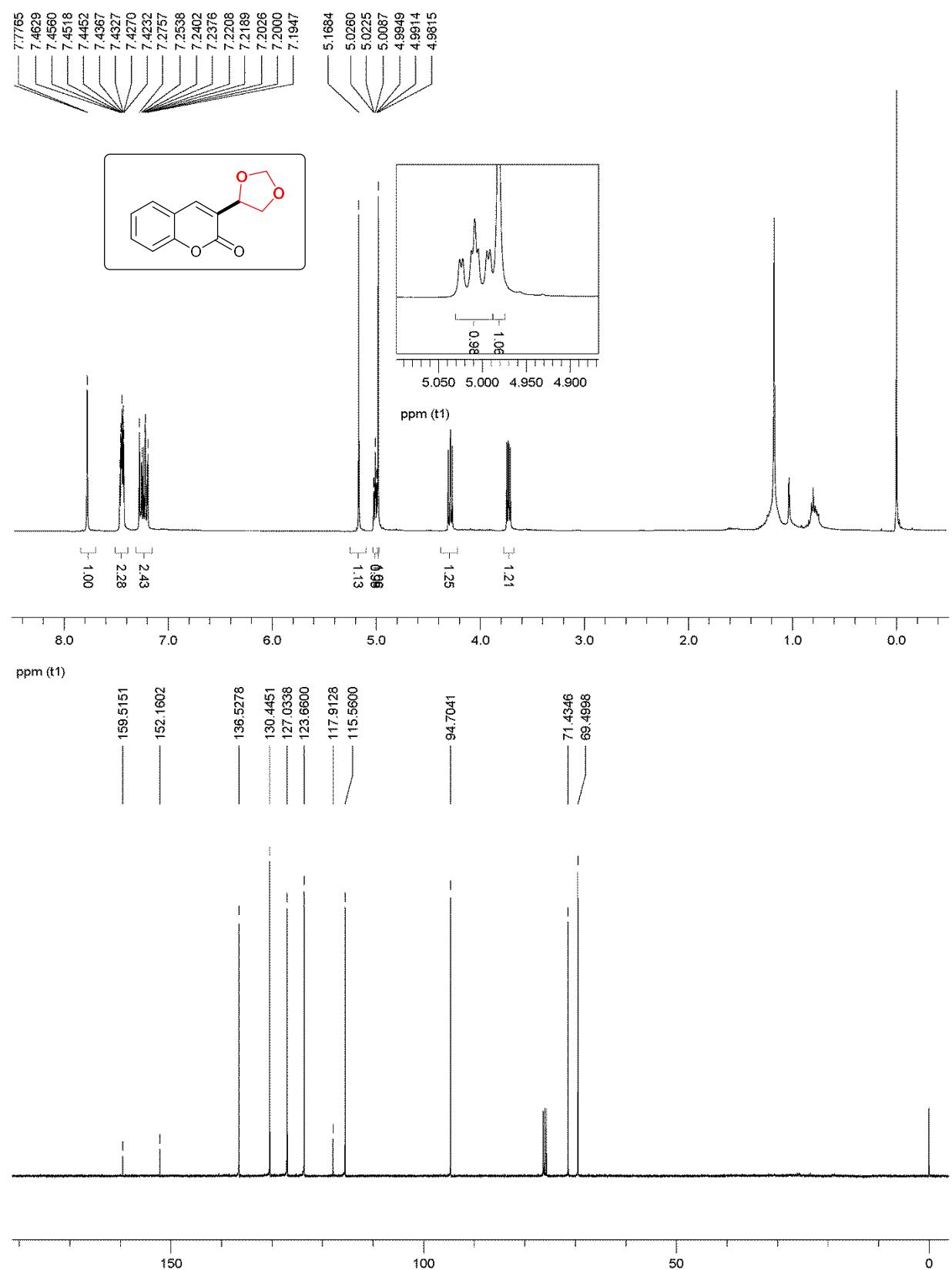
**Compound 3m**



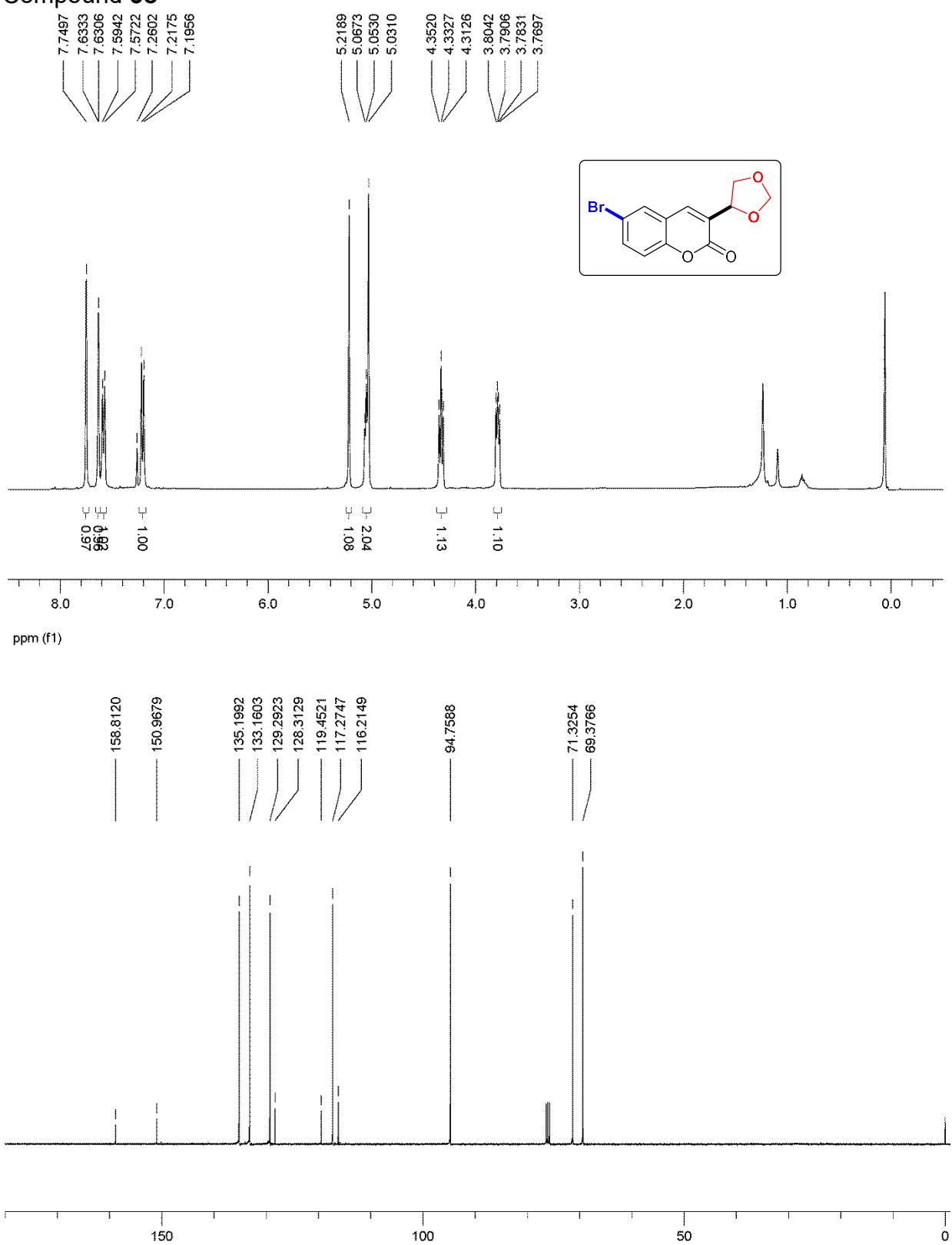
**Compound 3n**



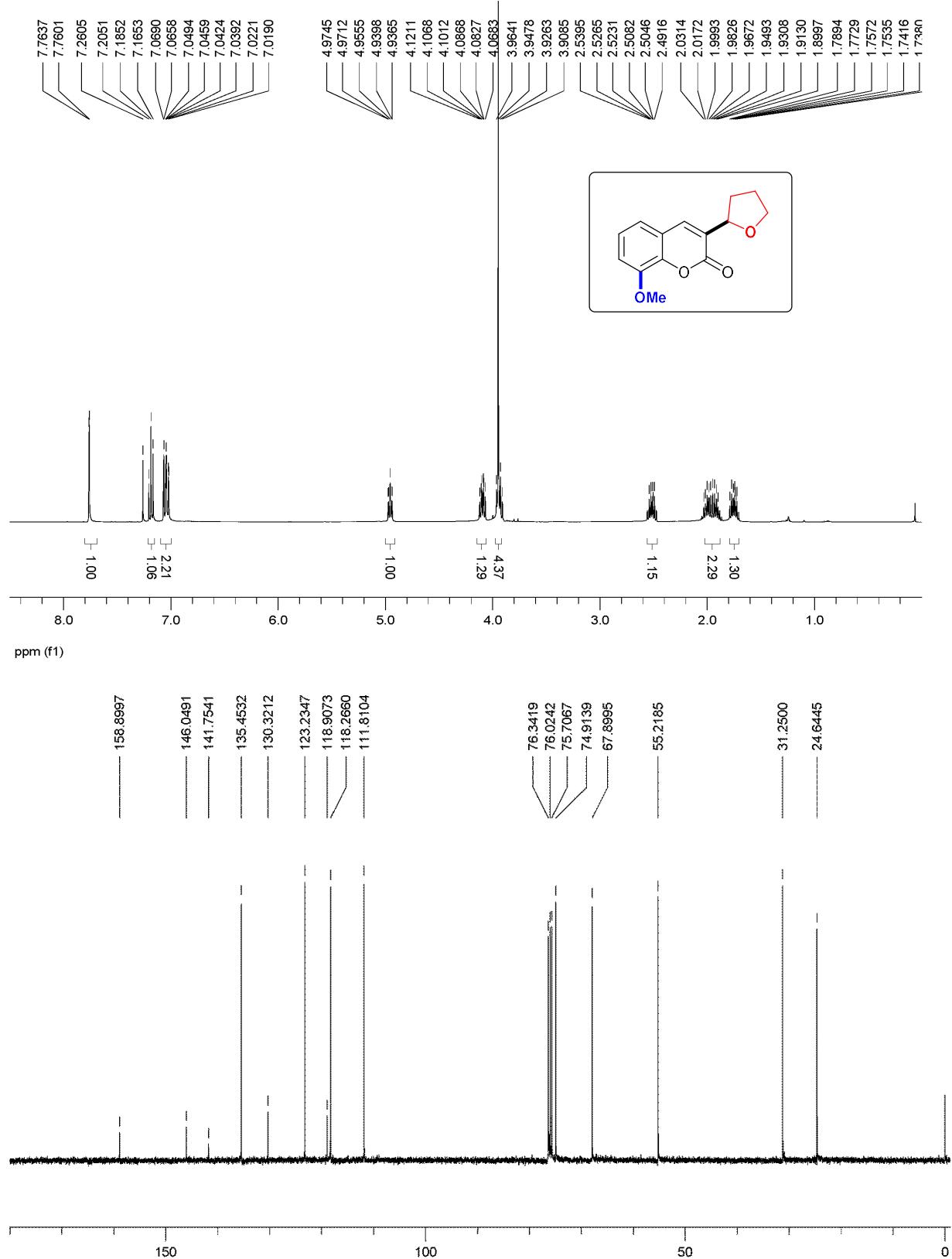
## Compound 3n'



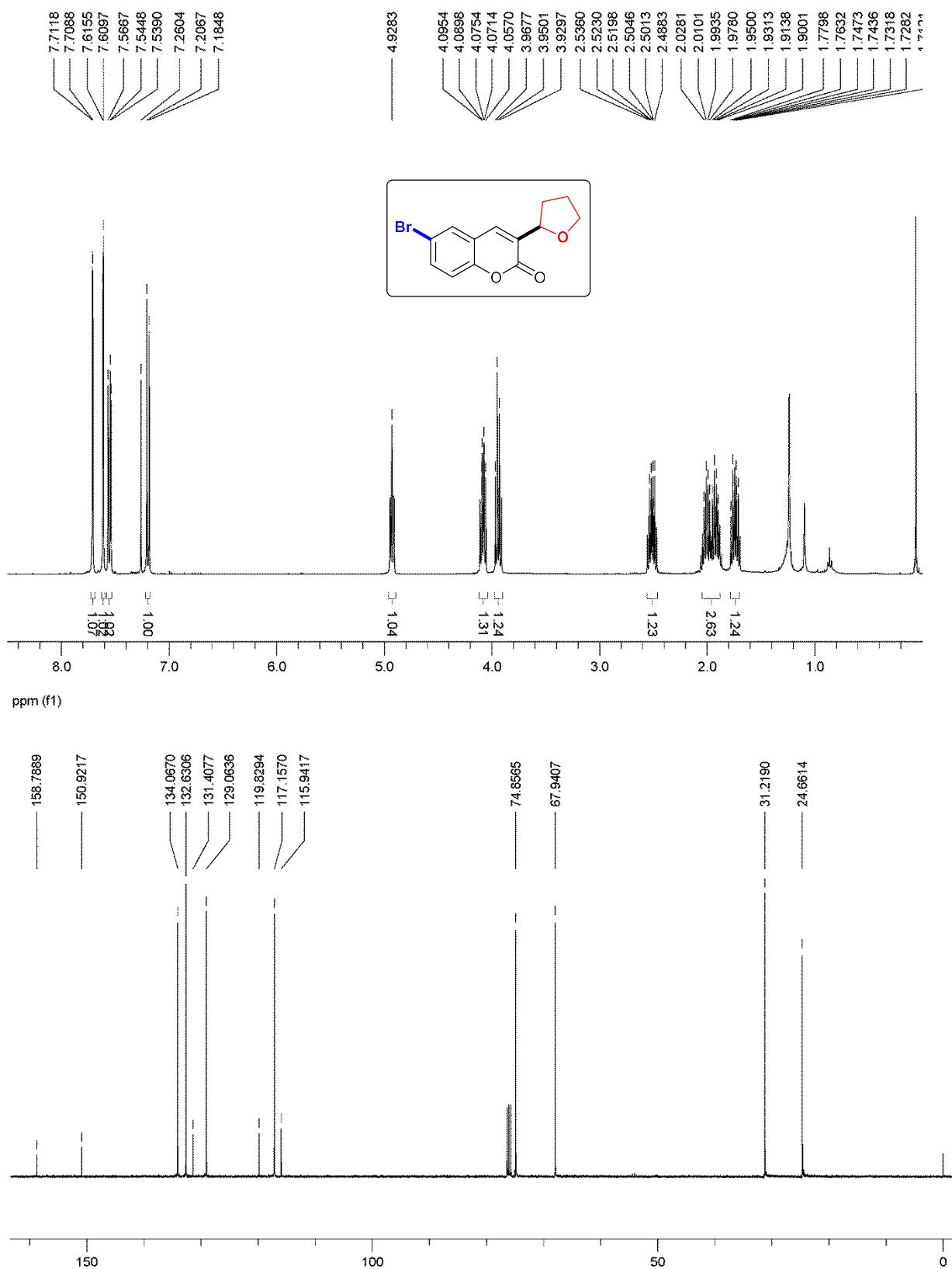
**Compound 3o**



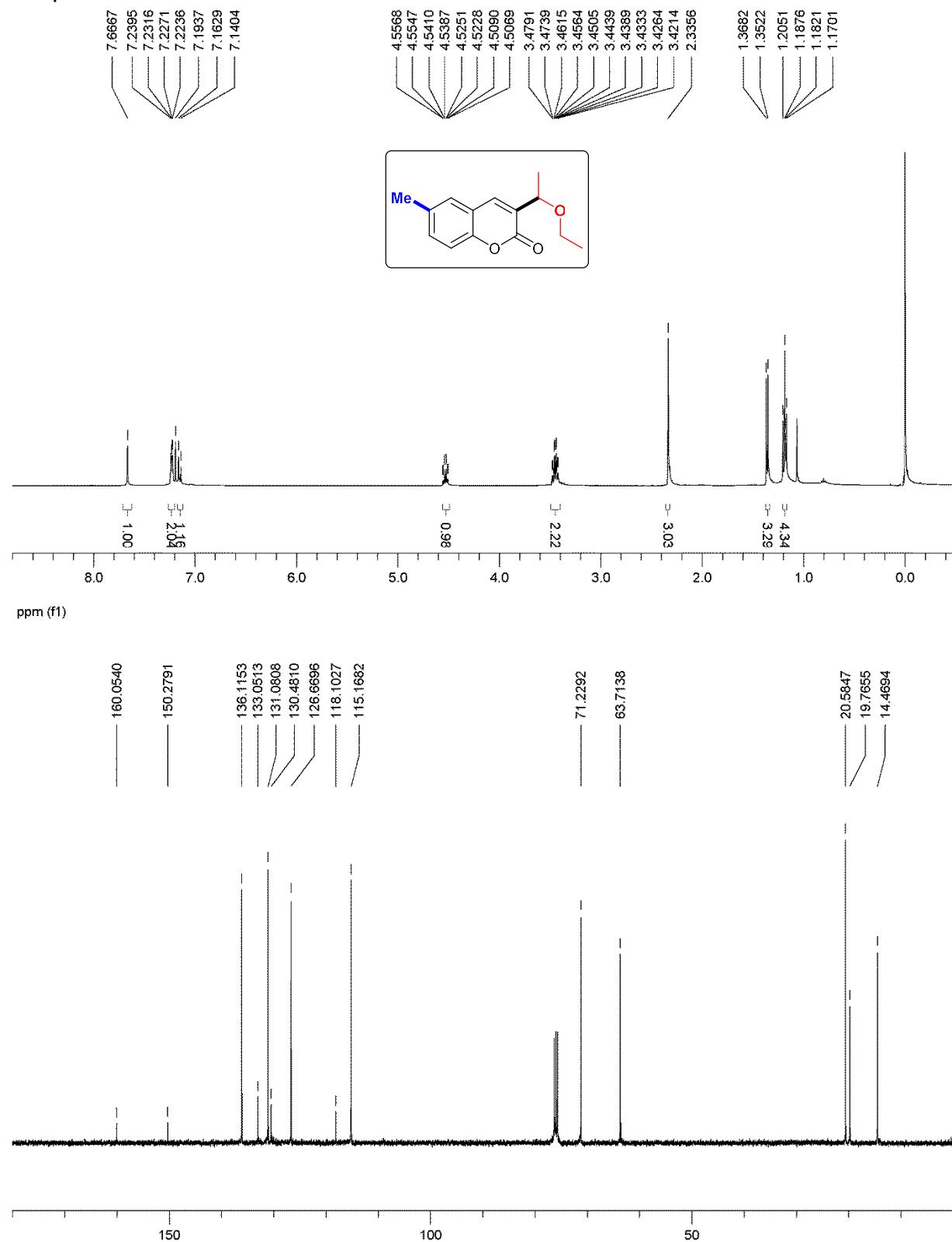
**Compound 3p**



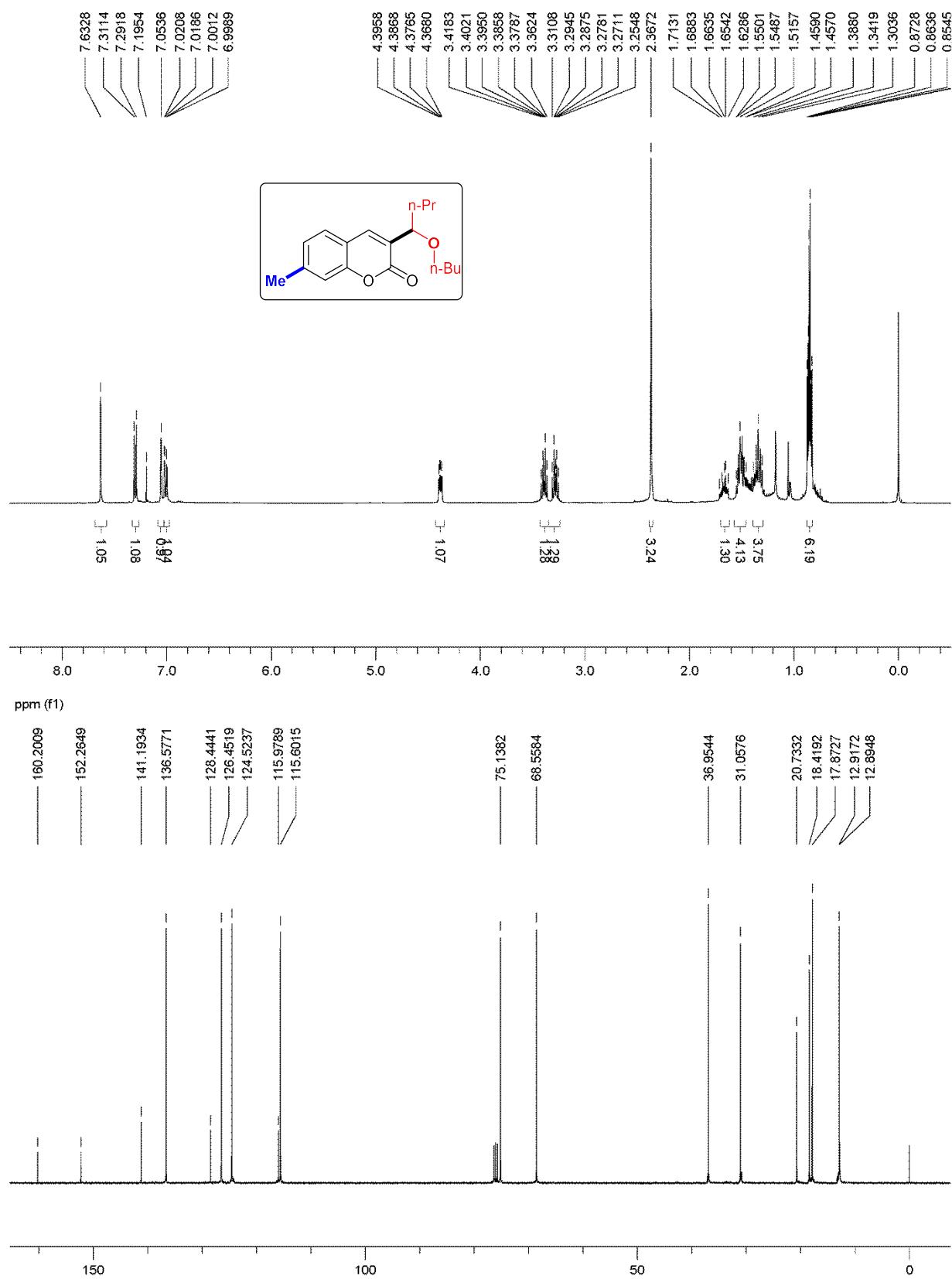
**Compound 3q**



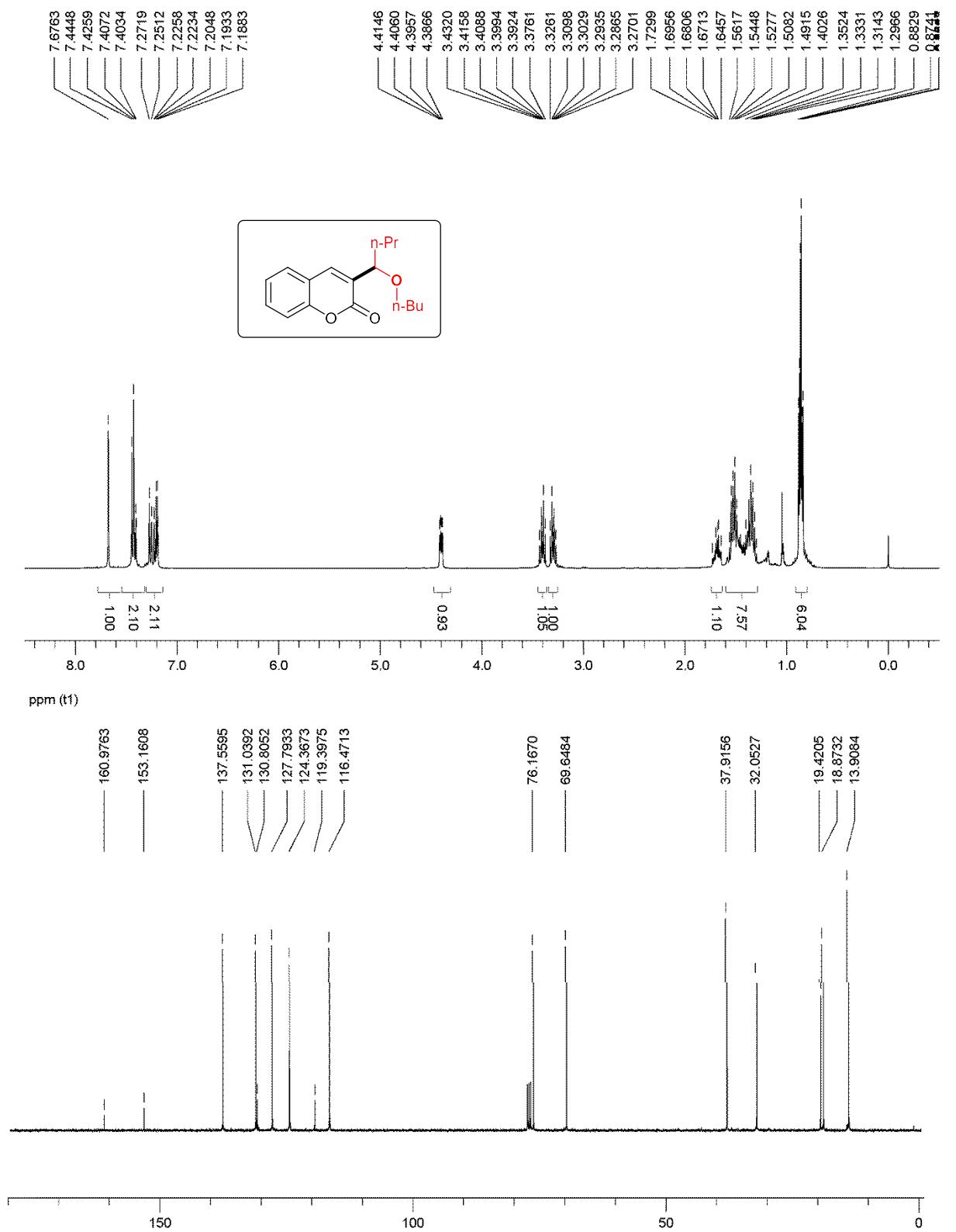
**Compound 3s**



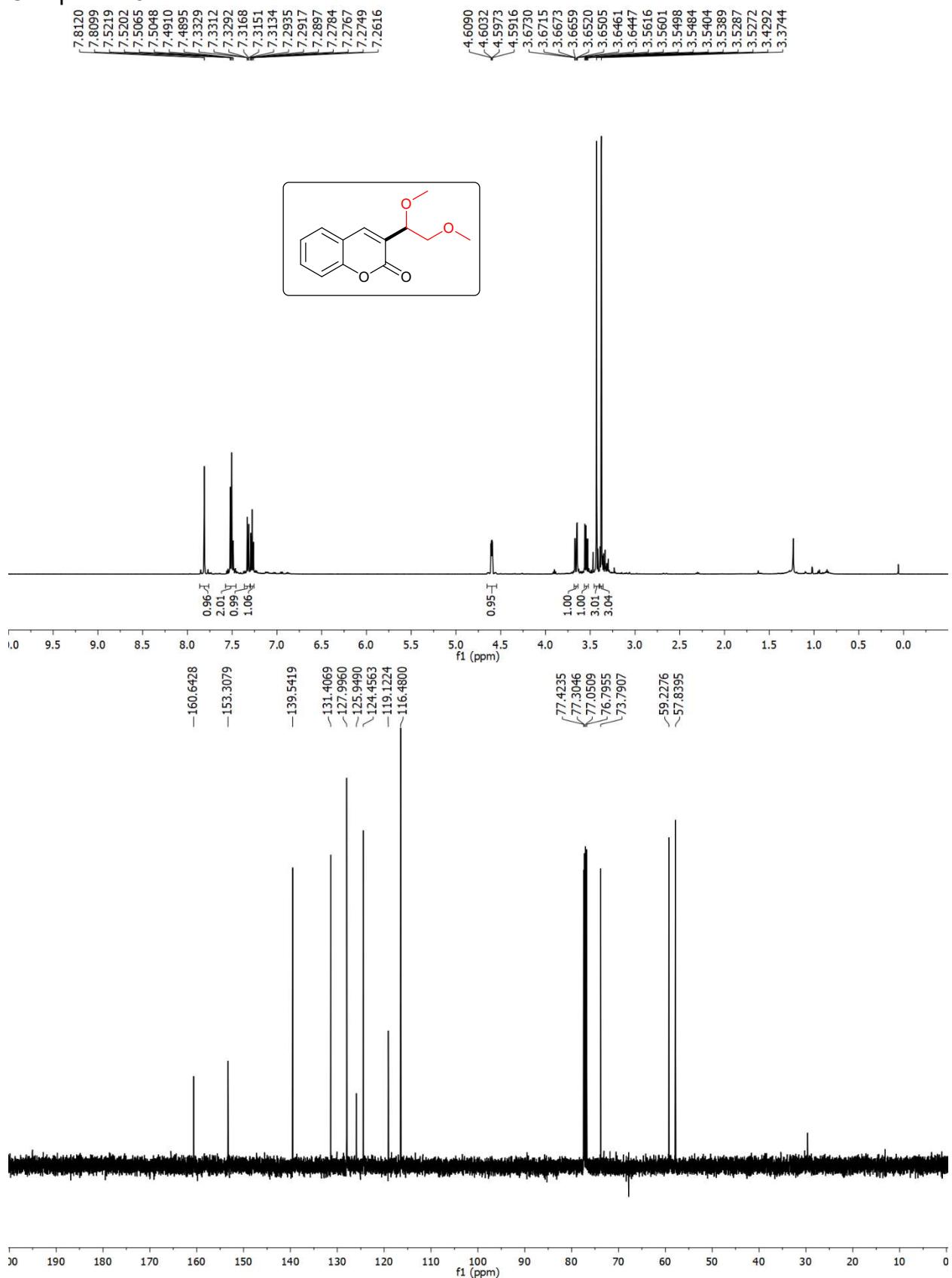
**Compound 3t**



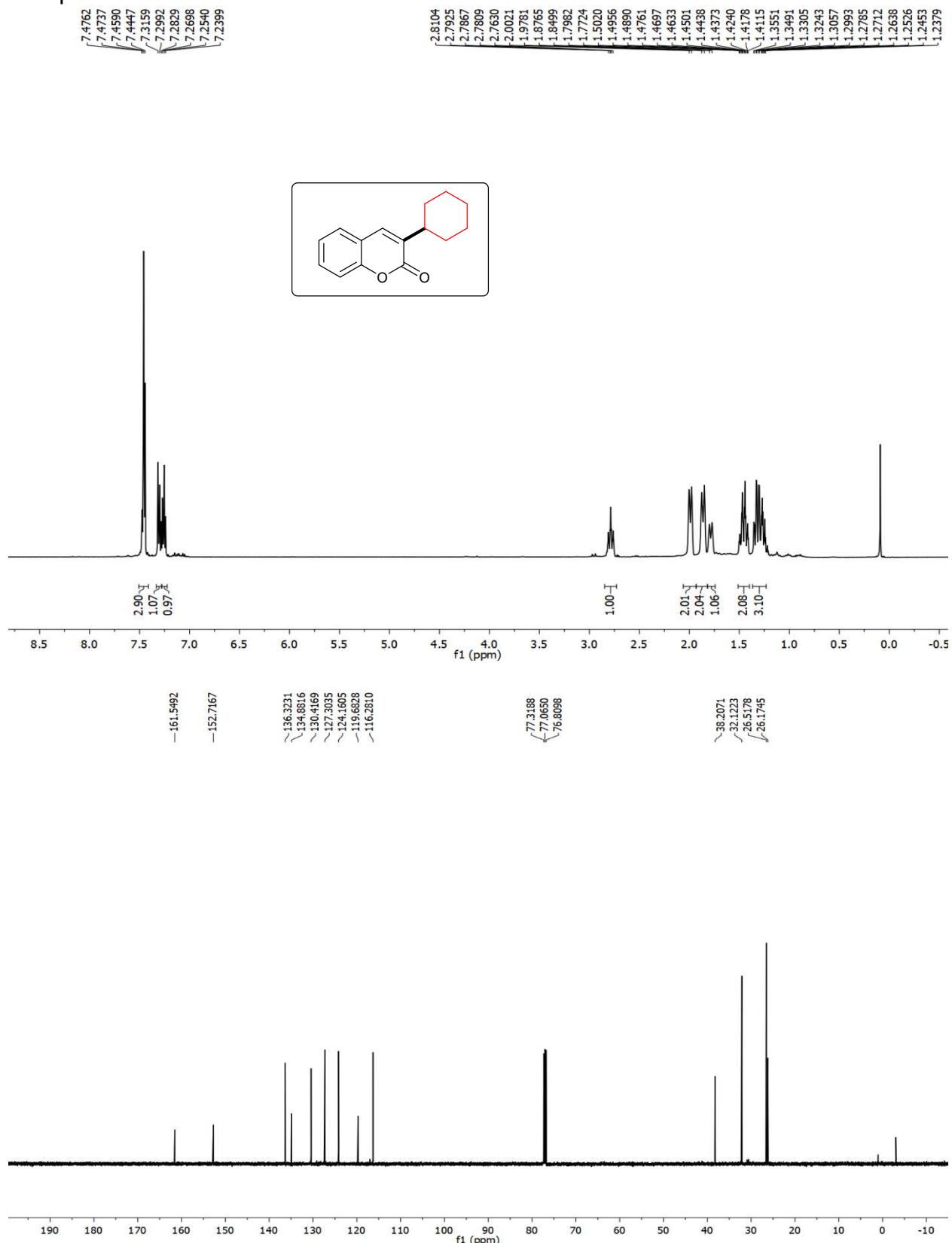
**Compound 3u**



## Compound 3v



**Compound 3w**



**Compound 4**

