

**Electronic supplementary information for**

**Pd-catalysed carbonylative annulation of salicylaldehydes with benzyl chlorides using *N*-formylsaccharin as CO surrogate**

**Vinod K. Yadav, Vishnu P. Srivastava, Lal Dhar S. Yadav**

<sup>b</sup> *Green Synthesis Lab, Department of Chemistry, University of Allahabad, Allahabad 211002, India*

\* Corresponding author. Tel.: +91 532 2500652; fax: +91 532 2460533; E-mail address: ldsyadav@hotmail.com  
(L.D.S. Yadav)

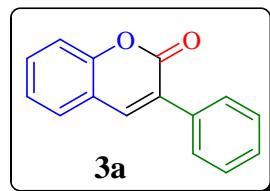
<b>Contents</b>	<b>Page No.</b>
I. General Information	2
II. General procedure for the synthesised compounds	2
III. Spectral data of synthesised compounds	2-9
IV. Copies of <sup>1</sup> H and <sup>13</sup> C NMR spectra of the synthesised compounds	10-27

**I. General Information:** All commercially available reagents were obtained from commercial suppliers and used without further purification. Solvents were purified by the usual methods and stored over molecular sieves. All reactions were performed using oven-dried glass ware under a nitrogen atmosphere. Organic solutions were concentrated using a Buchi rotary evaporator. Column chromatography was carried out over silica gel (Merck 100–200 mesh) and TLC was performed using silica gel GF254 (Merck) plates.  $^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra were recorded on a Bruker AVII spectrometer in  $\text{CDCl}_3$  using TMS as internal reference with chemical shift values being reported in  $\delta$  (ppm). All coupling constants ( $J$ ) are reported in Hertz (Hz). MS (EI) spectra were recorded on double focusing mass spectrometer.

## II. General Procedure for the Synthesis of 3-Arylcoumarins 3.

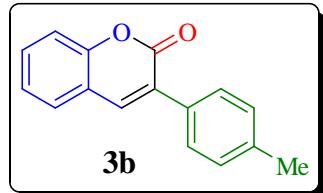
A mixture of salicylaldehyde (1 mmol), benzyl chlorides (1 mmol),  $\text{Na}_2\text{CO}_3$  (3 mmol),  $\text{Pd}(\text{OAc})_2$  (3 mol%), xantphos (5 mol%), *N*-formylsaccharin (2.5 mmol), and DMSO (3 mL) was taken in a flask and stirred at 85 °C for 10-11 h under a nitrogen atmosphere (Table 2). After completion of the reaction (monitored by TLC), water (5 mL) was added and the mixture was extracted with ethyl acetate ( $3 \times 5$  mL). The combined organic phase was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and evaporated under reduced pressure. The resulting crude product was purified by silica gel chromatography using a mixture of hexane/ethyl acetate (4:1) as eluent to afford an analytically pure sample of product **3**. All the compounds **3** are known and were characterized by comparison of their spectral data with those reported in the literature.<sup>1-3</sup> Characterization data of compounds **3** are given below:

## III. Spectral data of synthesised compounds 3

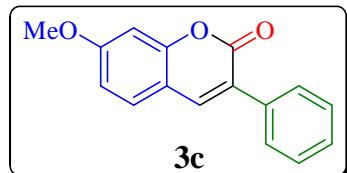


**Compound (3a).**<sup>1</sup> White solid, 87% yield, mp: 140–142 °C (lit.<sup>3</sup> mp 139–141 °C).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.83 (s, 1H), 7.68 (dd,  $J = 8.4, 2.4$  Hz, 2H), 7.58-7.48 (m, 2H), 7.47-7.36 (m, 4H), 7.32 (t,  $J = 7.6, 0.8$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 160.7, 153.6, 139.9,

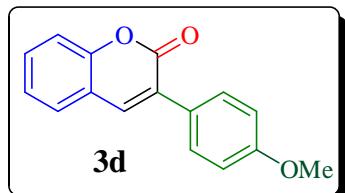
134.6, 131.5, 128.9, 128.6, 127.8, 124.5, 119.7, 116.6; HRMS (EI) calcd for C<sub>15</sub>H<sub>10</sub>O<sub>2</sub>: 222.0681; found 222.0677.



**Compound (3b).**<sup>2</sup> White solid, 89% yield, mp: 158-159 °C (lit.<sup>3</sup> mp 157–158 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.73 (d, *J* = 0.6 Hz, 1H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.46-7.40 (m, 2H), 7.34-7.29 (m, 1H), 7.26 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.20-7.19 (m, 1H), 7.16 (t, *J* = 0.7 Hz, 1H), 2.31 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 153.5, 139.3, 139.0, 131.7, 131.2, 129.3, 128.5, 128.3, 127.8, 124.6, 119.8, 116.4, 21.5; HRMS (EI) calcd for C<sub>16</sub>H<sub>12</sub>O<sub>2</sub>: 236.0837; found 236.0840.

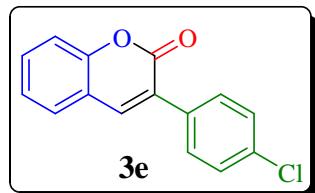


**Compound (3c).**<sup>1</sup> White solid, 90% yield, mp: 121-123 °C (lit.<sup>3</sup> mp 122-124 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.76 (s, 1H), 7.71-7.69 (m, 2H), 7.48-7.39 (m, 3H), 7.30-7.26 (m, 1H), 7.11 (dd, *J* = 9.0, 2.9 Hz, 1H), 6.99 (d, *J* = 2.9 Hz, 1H), 3.83 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 160.8, 156.2, 148.1, 139.7, 134.9, 128.8, 128.6, 128.7, 128.5, 120.0, 119.1, 117.5, 109.9, 55.8; HRMS (EI) calcd for C<sub>16</sub>H<sub>12</sub>O<sub>3</sub>: 252.0786; found 252.0782.

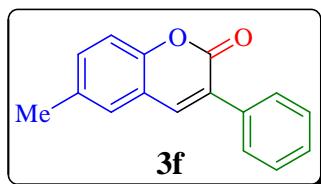


**Compound (3d).**<sup>1</sup> White solid, 91% yield, mp: 141-143 °C (lit.<sup>3</sup> mp 141–142 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.69 (s, 1H), 7.74 (dt, *J* = 9.6, 2.8 Hz, 2H), 7.40 (t, *J* = 1.6 Hz, 2H), 7.26-7.18 (m, 2H), 6.90 (d, *J* = 9.6, 2.8 Hz, 2H), 3.77 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 160.3,

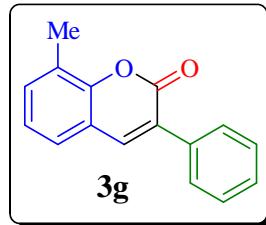
153.2, 138.5, 131.0, 129.8, 127.9, 127.6, 127.1, 124.4, 119.8, 116.4, 113.8, 55.4; HRMS (EI) calcd for C<sub>16</sub>H<sub>12</sub>O<sub>3</sub>: 252.0786; found 252.0783.



**Compound (3e).**<sup>2</sup> Yellow solid, 68% yield, mp: 184-186 °C (lit.<sup>3</sup> mp 184-185 °C). <sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>) δ: 7.80 (s, 1H), 7.68-7.61 (m, 2H), 7.57-7.48 (m, 2H), 7.42-7.38 (m, 2H), 7.42-7.34 (m, 1H), 7.36-7.29 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 160.3, 153.4, 139.9, 134.8, 133.0, 131.6, 129.7, 128.6, 128.0, 127.1, 124.7, 119.5, 116.4; HRMS (EI) calcd for C<sub>15</sub>H<sub>9</sub>ClO<sub>2</sub>: 256.0291; found 256.0295.

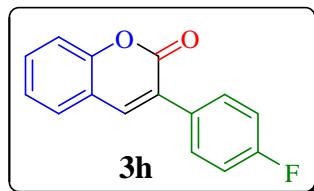


**Compound (3f).**<sup>1</sup> White solid, 92% yield, mp: 142-144 °C (lit.<sup>3</sup> mp 144-145 °C). <sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>) δ: 7.73 (s, 1H), 7.70-7.64 (m, 2H), 7.46-7.39 (m, 3H), 7.33-7.28 (m, 2H), 7.22 (t, J = 2.4 Hz, 1H), 2.40 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 160.9, 151.7, 139.9, 134.8, 134.1, 132.5, 128.9, 128.7, 128.5, 128.3, 127.7, 119.5, 116.3, 20.8; HRMS (EI) calcd for C<sub>16</sub>H<sub>12</sub>O<sub>2</sub>: 236.0837; found 236.0840.

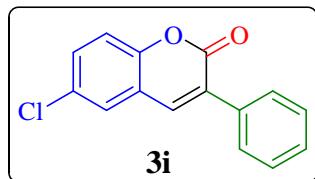


**Compound (3g).**<sup>2</sup> White solid, 89% yield, mp: 113-114 °C (lit.<sup>3</sup> mp 112–114 °C). (<sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>) δ: 7.73 (s, 1H), 7.66 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.45-7.23 (m, 5H), 7.10 (dd,

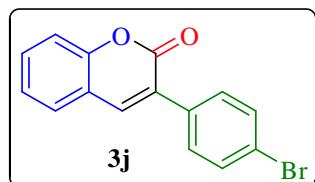
*J* = 8.1, 7.0 Hz, 1H), 2.40 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 160.7, 151.8, 140.3, 134.8, 132.6, 128.6, 128.5, 128.4, 127.9, 125.8, 125.6, 124.0, 119.3, 15.47; HRMS (EI) calcd for C<sub>16</sub>H<sub>12</sub>O<sub>2</sub>: 236.0837; found 236.0841.



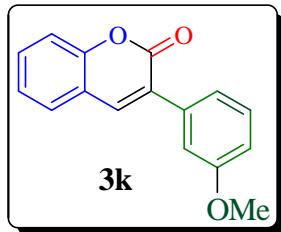
**Compound (3h).**<sup>1</sup> White solid, 59% yield, mp: 153-155 °C (lit.<sup>3</sup> mp 152–154 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.82 (s, 1H), 7.71-7.69 (m, 2H), 7.56-7.54 (m, 2H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.32-7.27 (m, 1H), 7.19-7.10 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 164.3, 161.8, 160.6, 153.5, 139.6, 131.5, 130.8, 130.7, 130.6, 130.3, 127.9, 127.4, 124.5, 119.6, 116.5, 115.7, 115.5. HRMS (EI) calcd for C<sub>15</sub>H<sub>9</sub>FO<sub>2</sub>: 240.0887; found 240.0884.



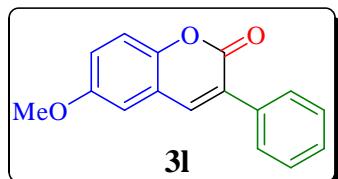
**Compound (3i).**<sup>2</sup> White solid, 61% yield, mp: 198-201 °C (lit.<sup>3</sup> mp 200 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.75 (s, 1H), 7.67 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.58- 7.52 (m, 1H), 7.50-7.40 (m, 4H), 7.32 (d, *J* = 8.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 160.1, 151.8, 138.4, 134.3, 131.3, 129.8, 129.5, 129.1, 128.6, 128.5, 127.0, 120.7, 117.8; HRMS (EI) calcd for C<sub>15</sub>H<sub>9</sub>ClO<sub>2</sub>: 256.0251; found 256.0253.



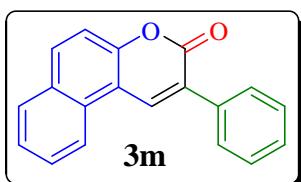
**Compound (3j).**<sup>1</sup> White solid, 67% yield, mp: 195-197 °C (lit.<sup>3</sup> mp 194–196 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.83 (d, *J* = 2.9 Hz, 1H), 7.55 (ddt, *J* = 12.5, 9.2, 5.2 Hz, 6H), 7.45-7.21 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 160.4, 153.5, 140.1, 133.5, 131.8, 131.6, 130.0, 128.0, 127.1, 124.6, 123.3, 119.5, 116.6; HRMS (EI) calcd for C<sub>15</sub>H<sub>9</sub>BrO<sub>2</sub>: 299.9786; found 299.9790.



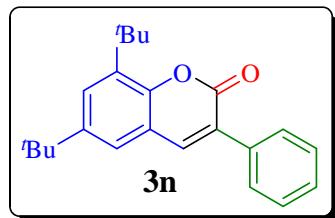
**Compound (3k).**<sup>2</sup> White solid, 91% yield, mp: 79-80 °C (lit.<sup>3</sup> mp 78–79 °C). <sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>) δ: 7.78 (d, *J* = 0.6 Hz, 1H), 7.50-7.41 (m, 2H), 7.32-7.15 (m, 5H), 6.90-6.84 (m, 1H), 3.77 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 159.6, 140.0, 136.1, 131.4, 129.5, 128.3, 127.9, 124.8, 124.6, 120.9, 119.6, 116.6, 114.5, 114.1, 55.4; HRMS (EI) calcd for C<sub>16</sub>H<sub>12</sub>O<sub>3</sub>: 252.0786; found 252.0789.



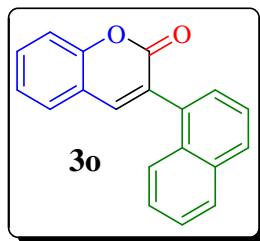
**Compound (3l).**<sup>2</sup> Pale yellow solid, 93% yield, mp: 154-157 °C (lit.<sup>3</sup> mp 155-157 °C). <sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>) δ: 7.68 (d, *J* = 0.6 Hz, 1H), 7.60 (dd, *J* = 8.1, 1.6 Hz, 2H), 7.43- 7.28 (m, 3H), 7.20- 7.12 (m, 1H), 7.02 (dd, *J* = 9.0, 2.9 Hz, 1H), 6.89 (d, *J* = 2.9 Hz, 1H), 3.73 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 160.7, 156.0, 147.8, 139.6, 134.7, 128.8, 128.6, 128.5, 128.4, 119.8, 119.1, 117.2, 109.8, 55.7; HRMS (EI) calcd for C<sub>16</sub>H<sub>12</sub>O<sub>3</sub>: 252.0786; found 252.0782.



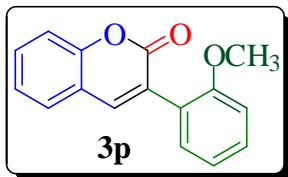
**Compound (3m).**<sup>1</sup> Yellow solid, 69% yield, mp: 180-183 °C (lit.<sup>3</sup> mp 181-182 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.53 (s, 1H), 8.28 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 9.2 Hz, 1H), 7.90 (t, *J* = 6.9 Hz, 1H), 7.85-7.74 (m, 2H), 7.70-7.64 (m, 1H), 7.58 (td, *J* = 7.7, 3.7 Hz, 1H), 7.53-7.38 (m, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 160.6, 153.3, 135.7, 135.2, 132.7, 130.3, 129.2, 129.1, 128.9, 128.6, 128.5, 128.2, 127.3, 126.1, 121.4, 116.7, 113.8; HRMS (EI) calcd for C<sub>19</sub>H<sub>12</sub>O<sub>2</sub>: 272.0837; found 272.0840.



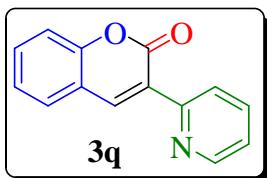
**Compound (3n).**<sup>1</sup> White solid, 90% yield, mp: 141-142 °C (lit.<sup>3</sup> mp 140-141 °C). <sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>) δ: 7.85 (s, 1H), 7.72 (m, 2H), 7.46 (t, *J* = 7.2, 1H), 7.42-7.36 (m, 4H), 1.57 (s, 9H), 1.39 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 160.3, 150.2, 146.7, 141.2, 137.0, 135.1, 128.7, 128.5, 128.3, 127.1, 126.6, 122.6, 119.7, 35.1, 34.7, 31.2, 30.1; HRMS (EI) calcd for C<sub>23</sub>H<sub>26</sub>O<sub>2</sub>: 334.1933; found 334.1935.



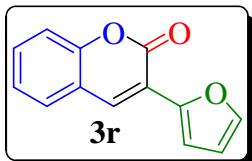
**Compound (3o).**<sup>2</sup> Yellow solid, 56% yield, mp: 155-157 °C (lit.<sup>3</sup> mp 154-156 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.99-7.89 (m, 2H), 7.86-7.80 (m, 1H), 7.85-7.74 (m, 1H), 7.66-7.38 (m, 7H), 7.34-7.30 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 160.8, 153.8, 142.7, 133.6, 132.7, 131.6, 131.6, 129.3, 128.6, 128.3, 127.8, 127.6, 126.5, 126.1, 125.3, 125.0, 124.5, 119.4, 116.7. HRMS (EI) calcd for C<sub>19</sub>H<sub>12</sub>O<sub>2</sub>: 272.0838; found 298.0834.



**Compound (3p).**<sup>2</sup> White solid, 88% yield, mp: 139-141 °C (lit.<sup>3</sup> mp 140-141 °C).  $\delta$ : 7.72 (s, 1H), 7.50-7.48 (m, 2H), 7.40-7.39 (m, 3H), 7.25 (t,  $J=7.2$  Hz, 1H) 7.07-6.96 (m, 2H), 3.85 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 160.5, 157.3, 153.9, 141.9, 131.2, 130.9, 130.4, 128.1, 126.8, 124.5, 124.2, 120.8, 119.8, 116.7, 111.6, 55.9; HRMS (EI) calcd for C<sub>16</sub>H<sub>12</sub>O<sub>3</sub>: 252.0786; found 252.0789.



**Compound (3q).**<sup>2</sup> White solid, 53% yield, mp: 142-144 °C (lit.<sup>4</sup> mp 143-144 °C).  $\delta$ : 8.86-8.71(m, 1H), 8.72 (ddd,  $J = 4.7, 1.7, 0.9$  Hz, 1H), 8.41 (d,  $J = 8.1$  Hz, 1H), 7.76 (tt,  $J = 5.6, 2.8$  Hz, 1H), 7.63 (dd,  $J = 7.7, 1.5$  Hz, 1H), 7.60-7.51 (m, 1H), 7.37 (d,  $J = 8.3$  Hz, 1H), 7.38-7.25 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 160.4, 153.9, 151.3, 149.2, 142.5, 136.7, 132.2, 128.9, 125.2, 124.6, 124.0, 123.5, 119.6, 116.3; HRMS (EI) calcd for C<sub>14</sub>H<sub>9</sub>NO<sub>2</sub>: 223.0633; found 223.0629.



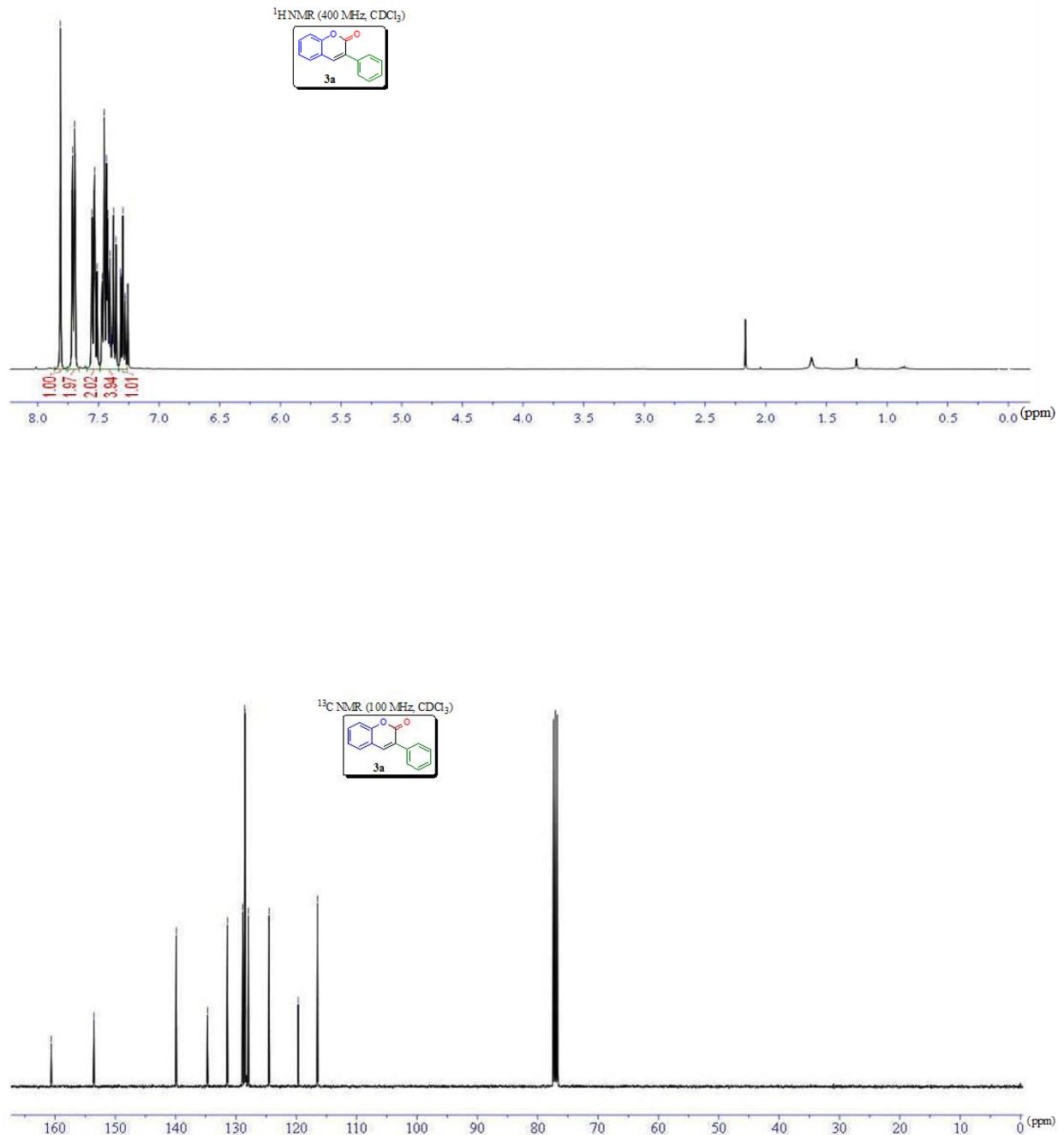
**Compound (3r).**<sup>2</sup> White solid, 58% yield, mp: 83-84 °C (lit.<sup>5</sup> mp 81-83 °C).  $\delta$ : 8.10 (s, 1H), 7.60 (dd,  $J = 7.7, 1.4$  Hz, 1H), 7.51-7.45 (m, 2H), 7.40-7.31 (m, 2H), 7.34-7.25 (m, 1H), 6.58 (dd,  $J = 3.4, 1.8$  Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 158.1, 152.7, 147.6, 143.3, 133.9,

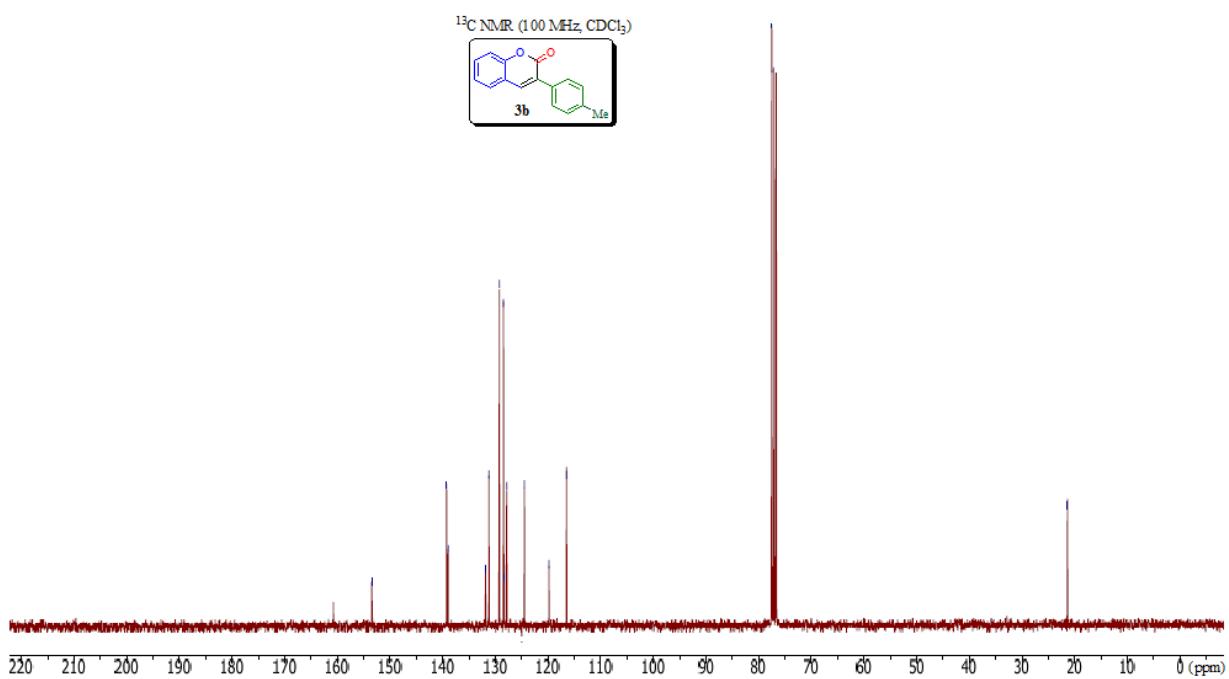
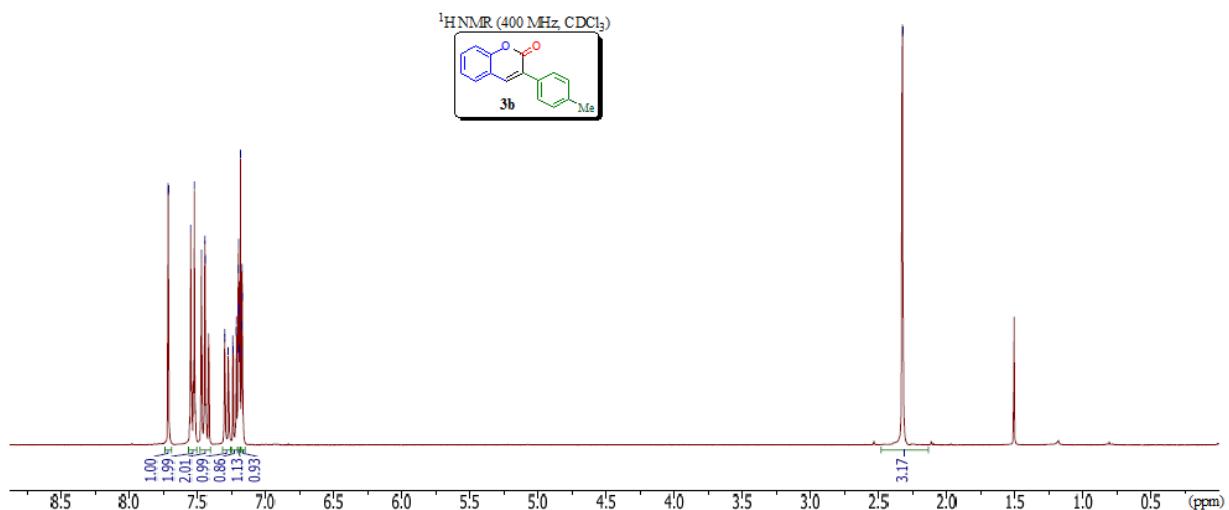
131.2, 127.8, 124.7, 119.4, 118.2, 116.5, 112.8, 112.5; HRMS (EI) calcd for C<sub>13</sub>H<sub>8</sub>O<sub>3</sub>: 212.0473; found 212.0475.

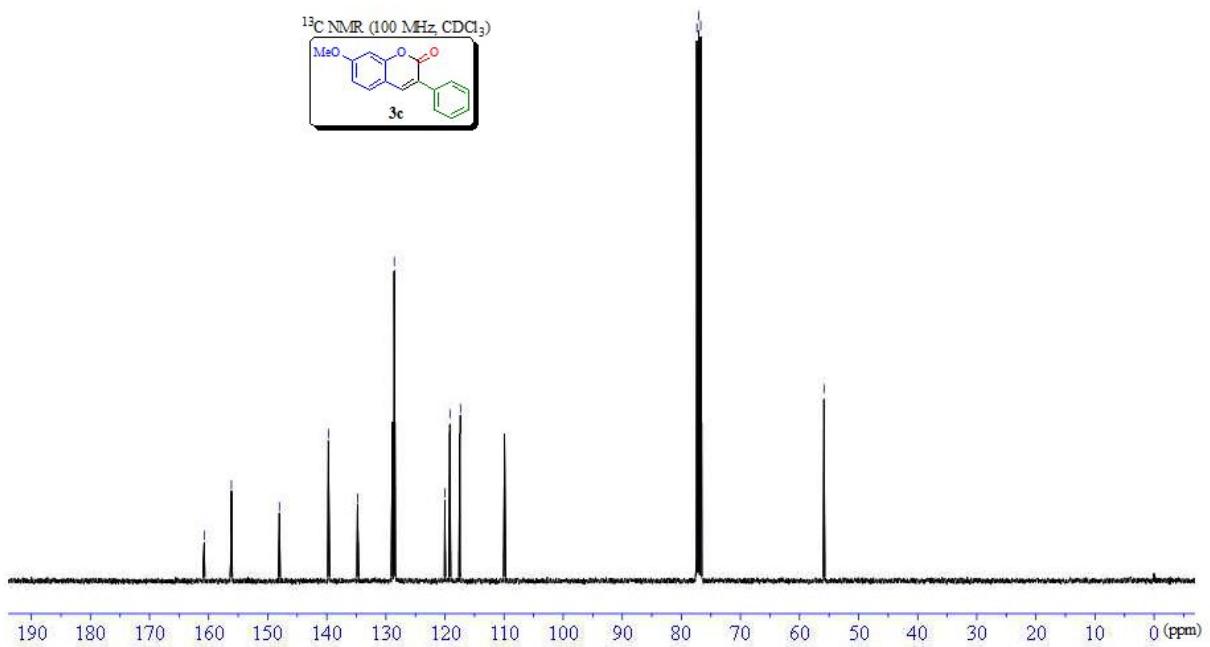
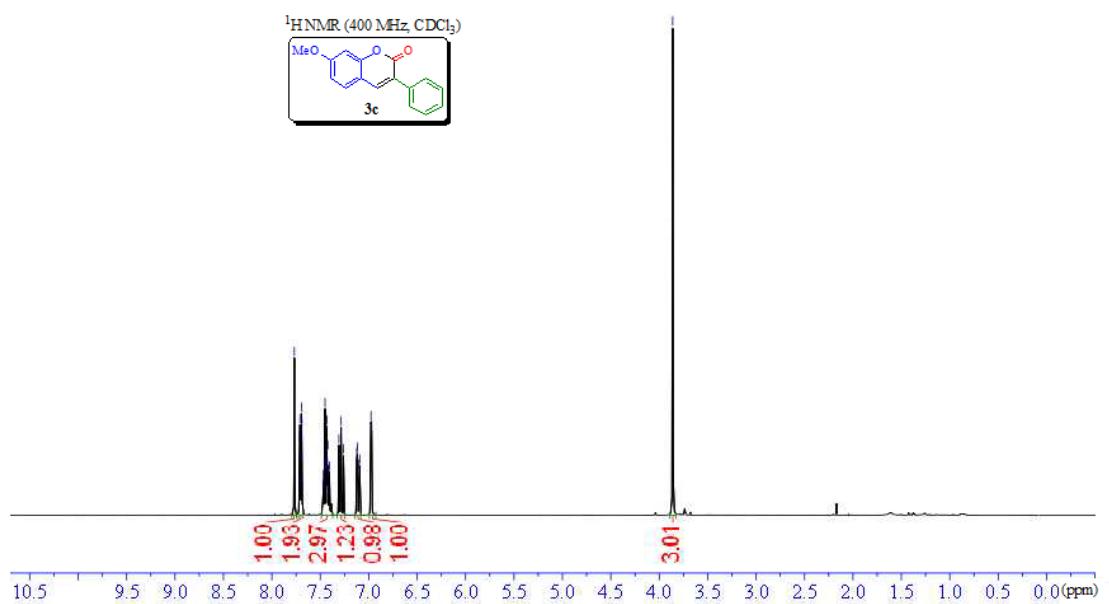
## References

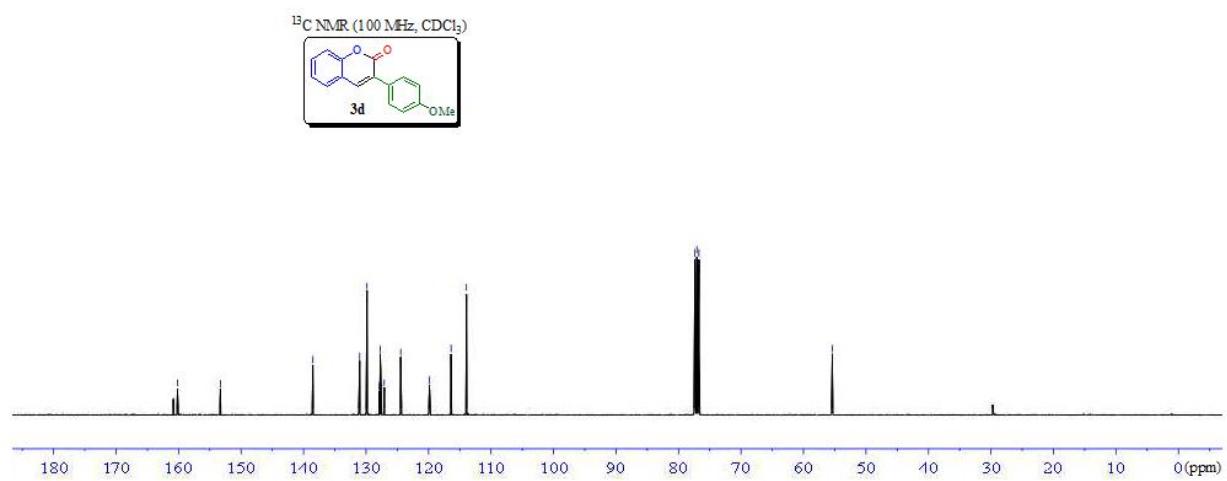
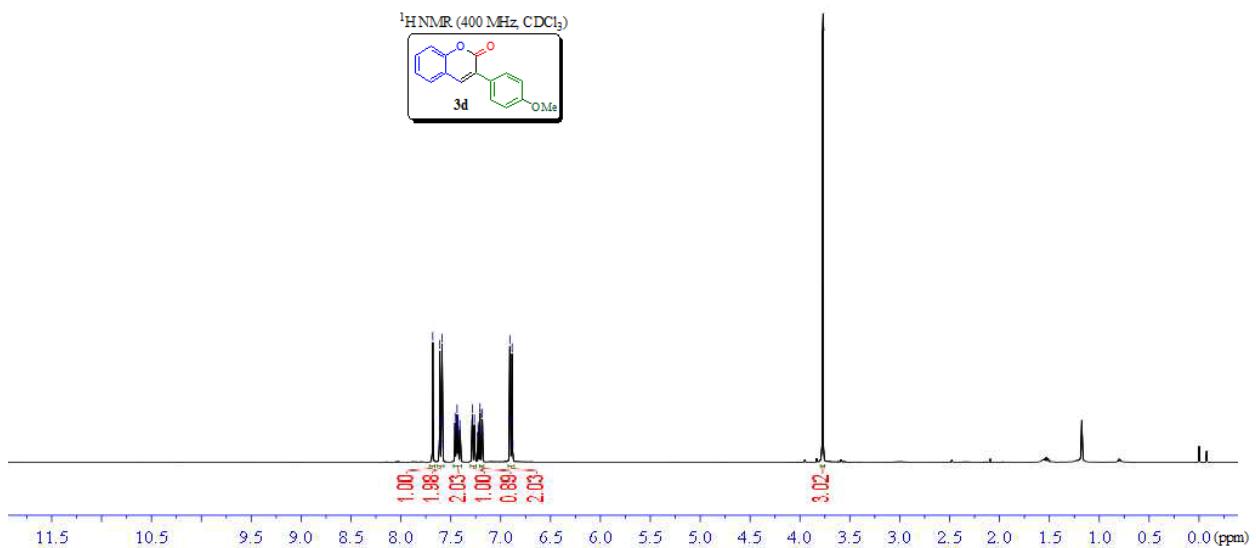
1. J. Liu, X. Zhang, L. Shi, M. Liu, Y. Yue, F. Li and K. Zhuo *Chem. Commun.*, 2014, **50**, 9887.
2. W. Xiao-Feng, W. Lipeng, J. Ralf, N. Helfried, and B. Matthias, *Chem. Eur. J.*, 2013, **19**, 12245.
3. Y. Jiang, W. Chen, and W. Lu, *S Tetrahedron*, 2013, **69**, 3669.
4. T. Yu, S. Yang, J. Meng, Y. Zhao, H. Zhang, D. Fan, X. Han, Z. Liu, *Inorg. Chem. Commun.* 2011, **14**, 159.
5. J. Meng, M. Shen, D. Fu, Z. Gao, R. Wang, H. Wang, and T. Matsuura, *Synthesis*, 1990, 719.

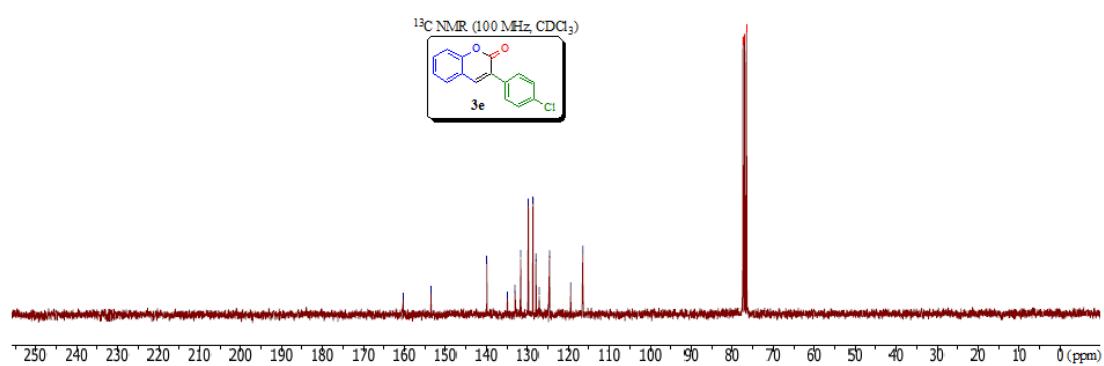
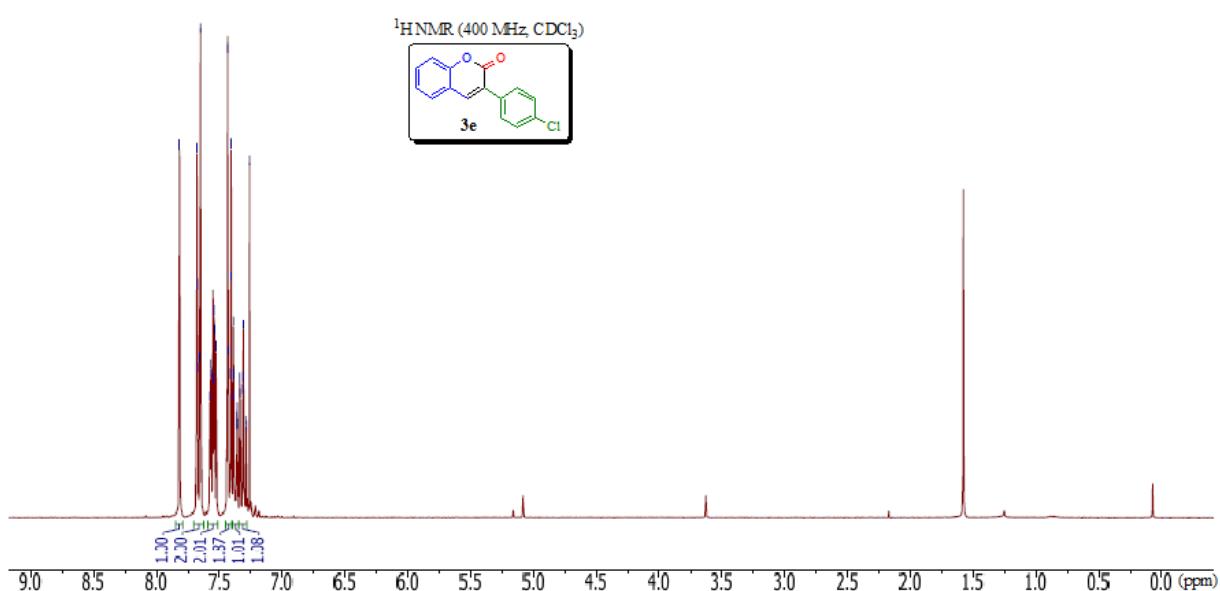
**IV. Copies of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the synthesised compounds.**

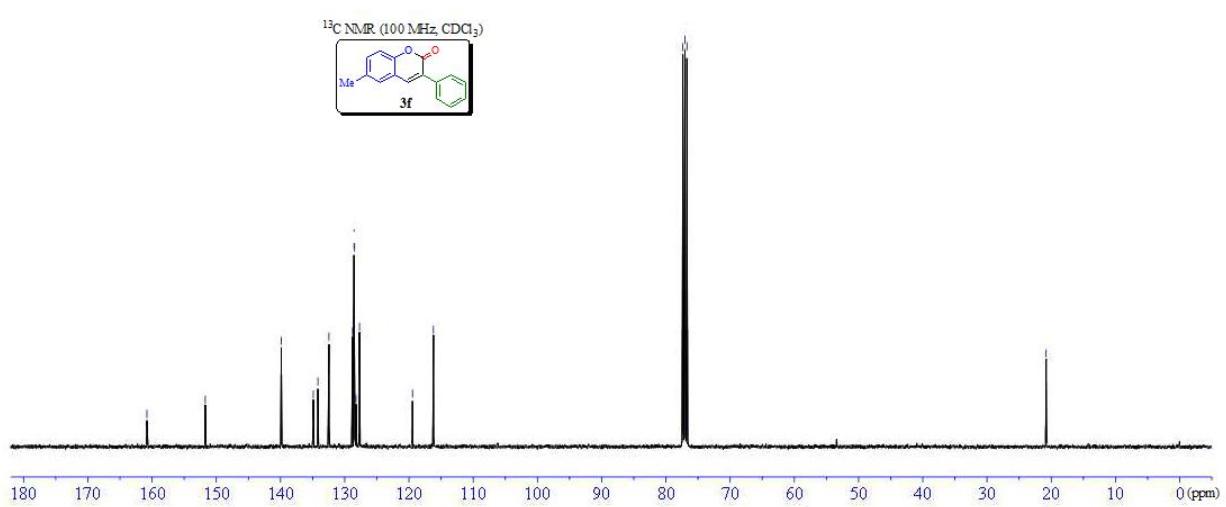
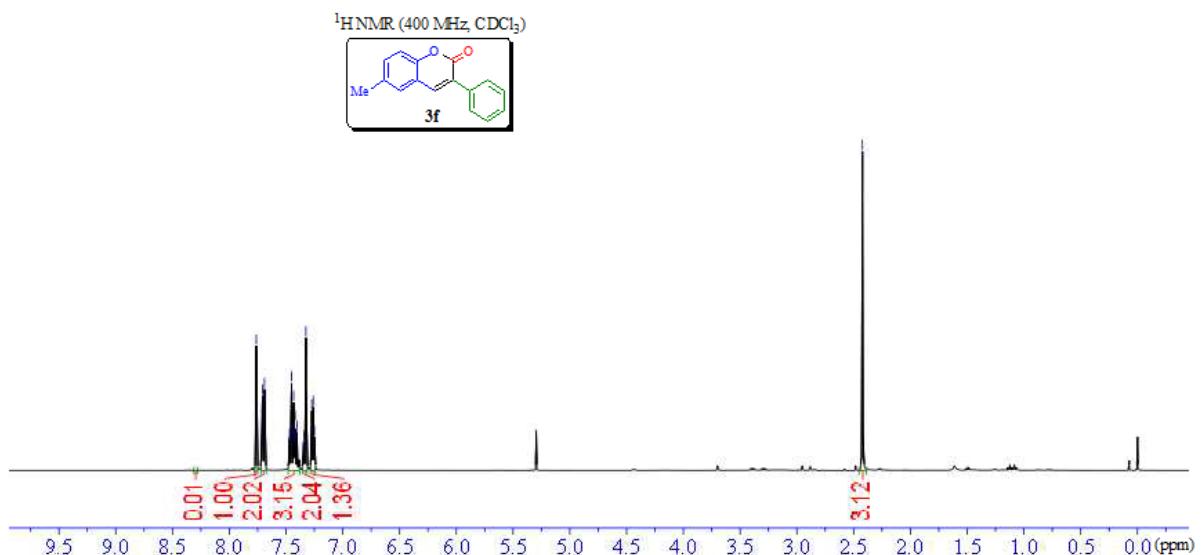


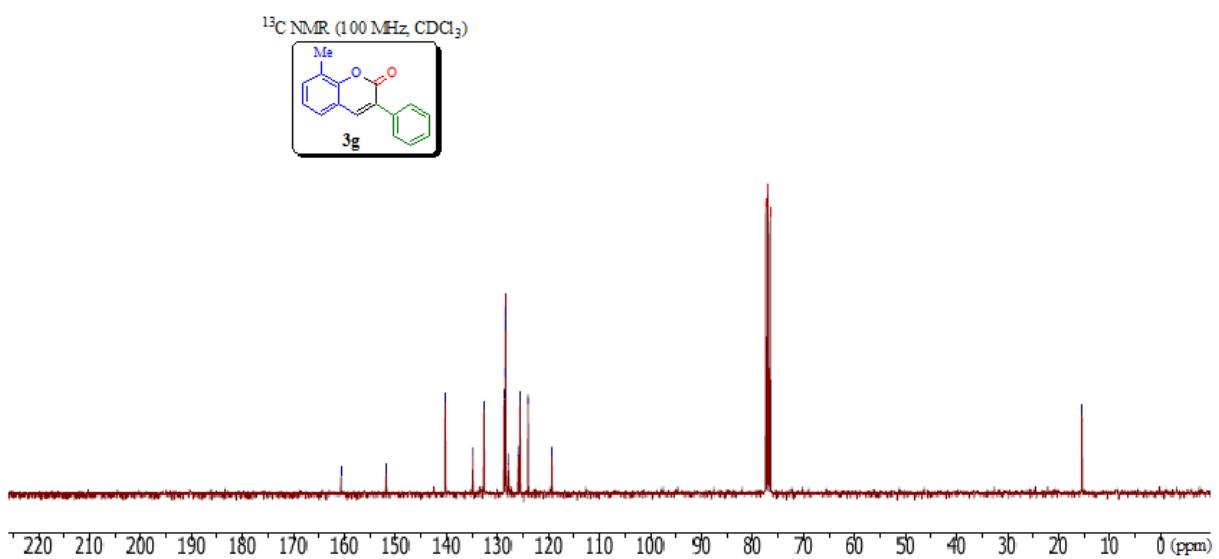
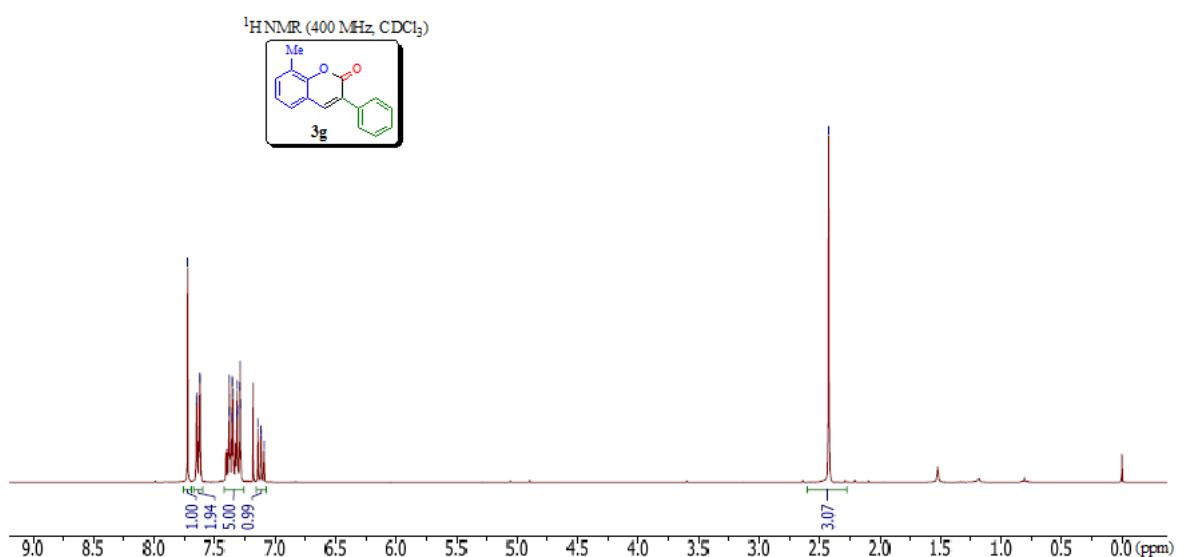


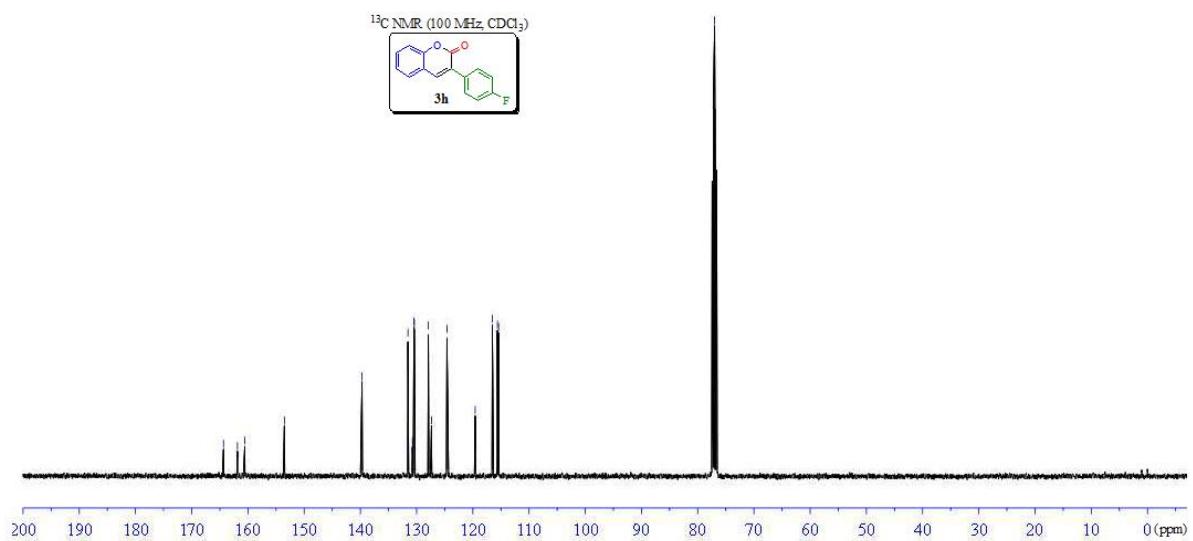
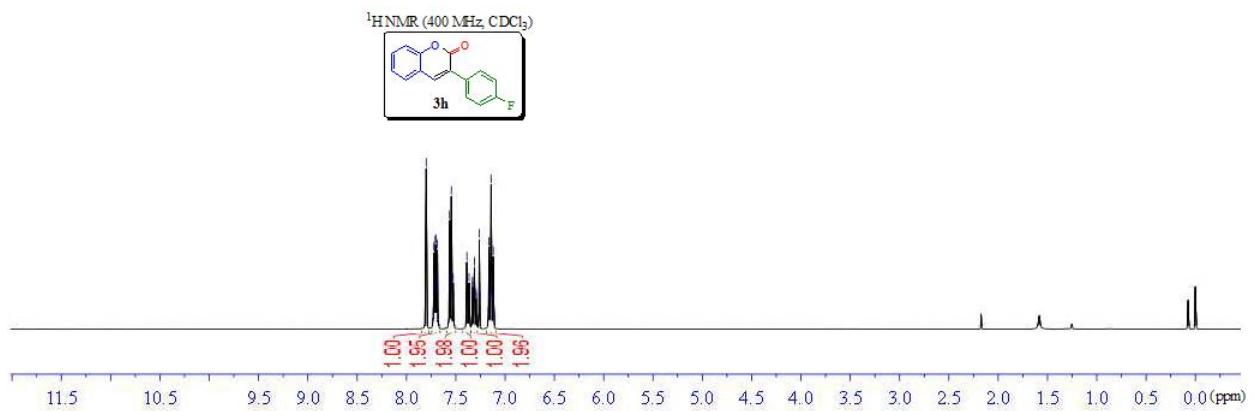


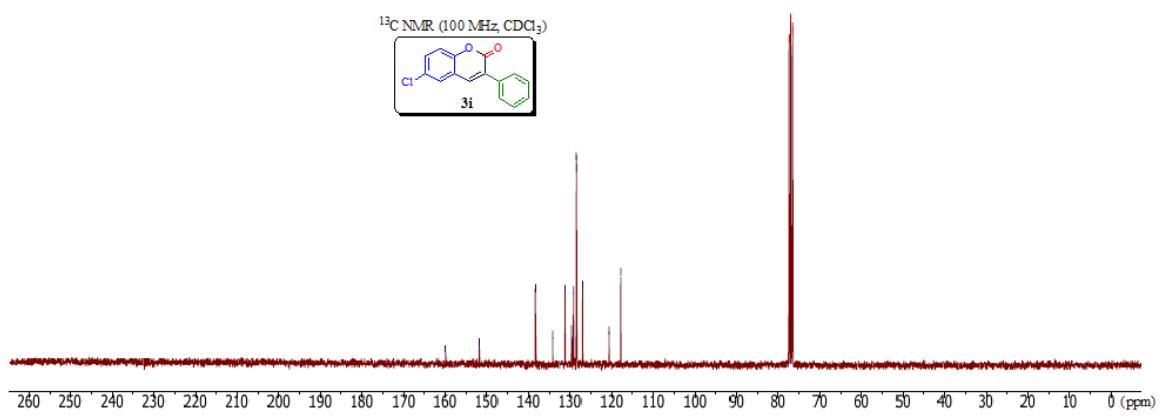
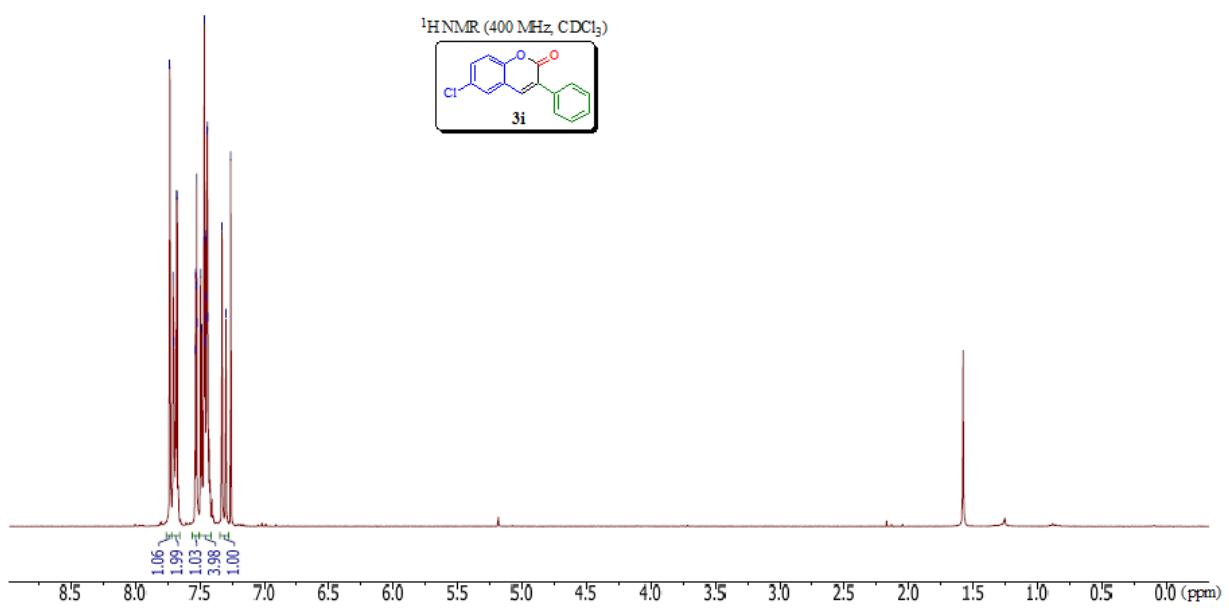


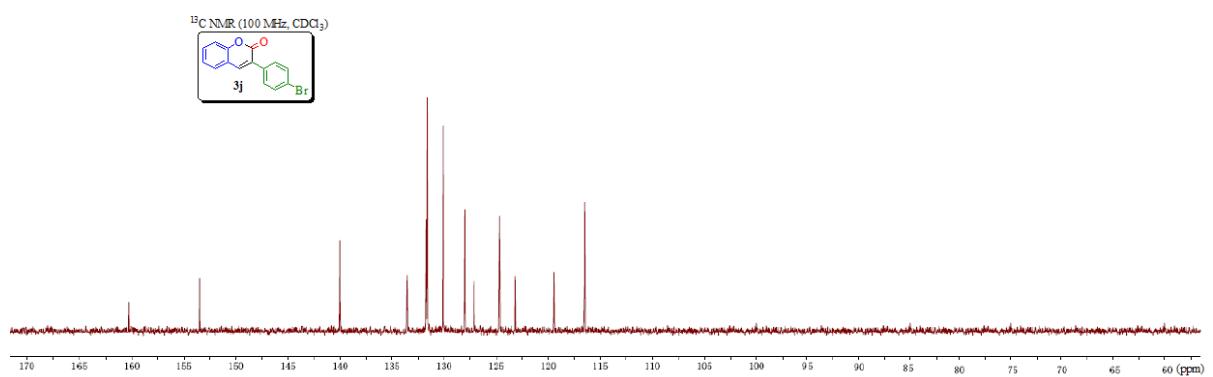
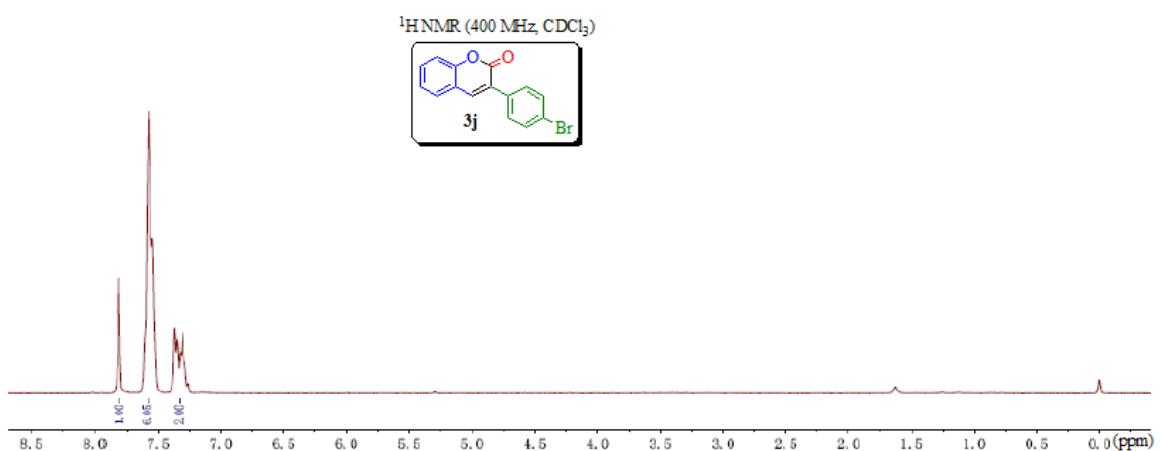




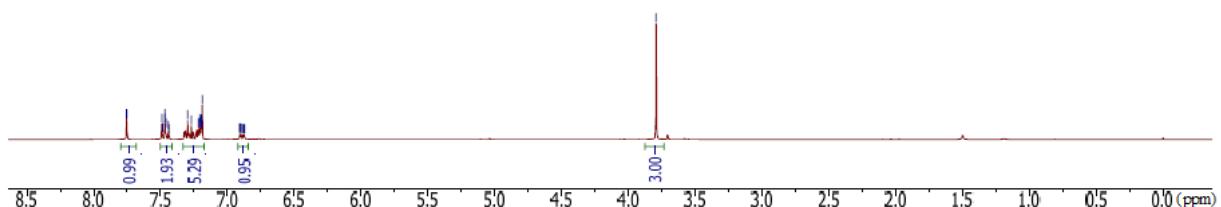
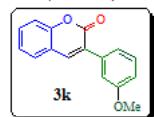




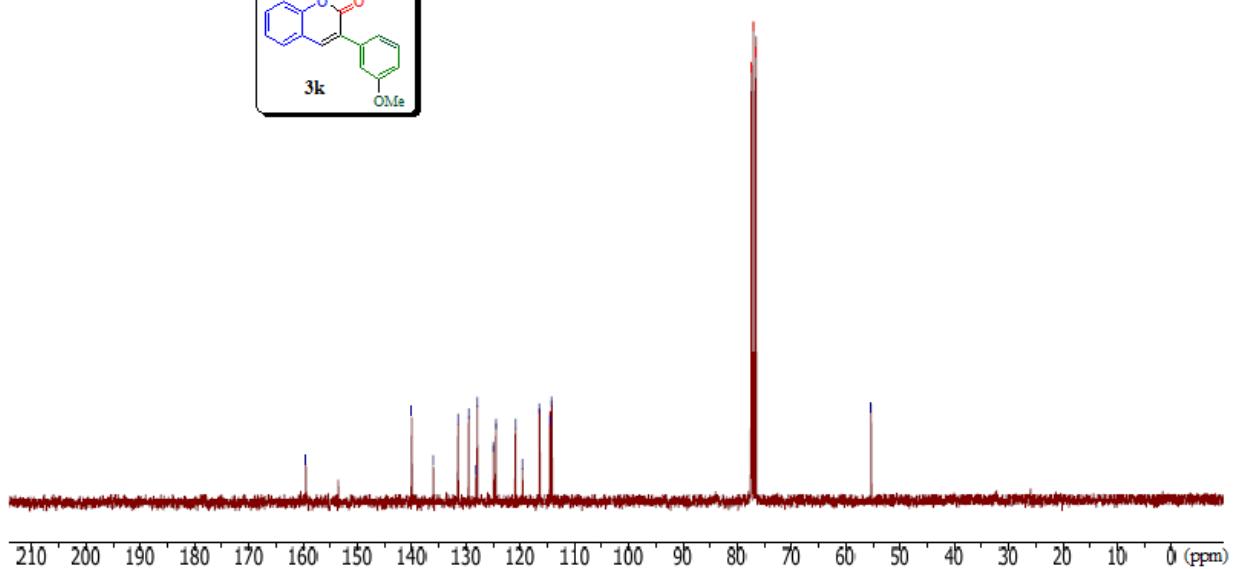
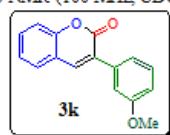


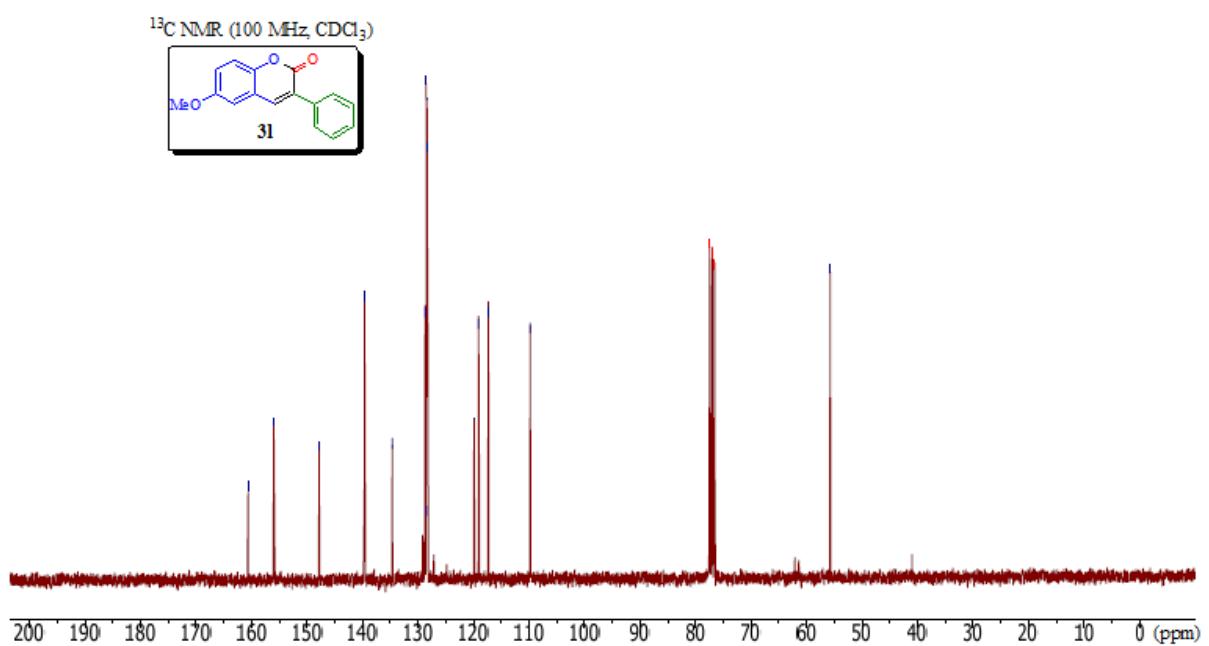
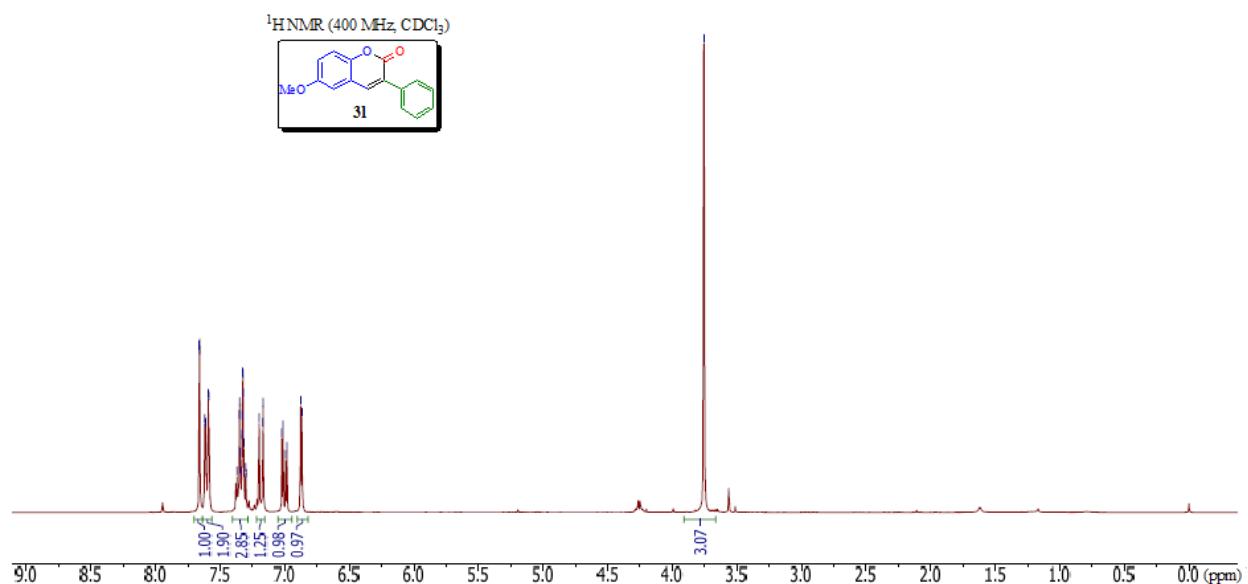


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

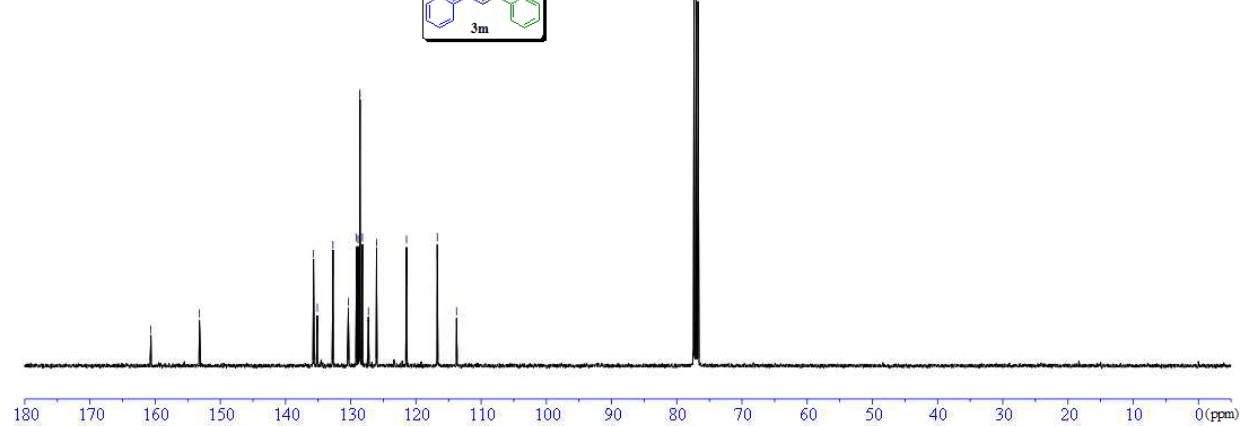
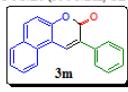
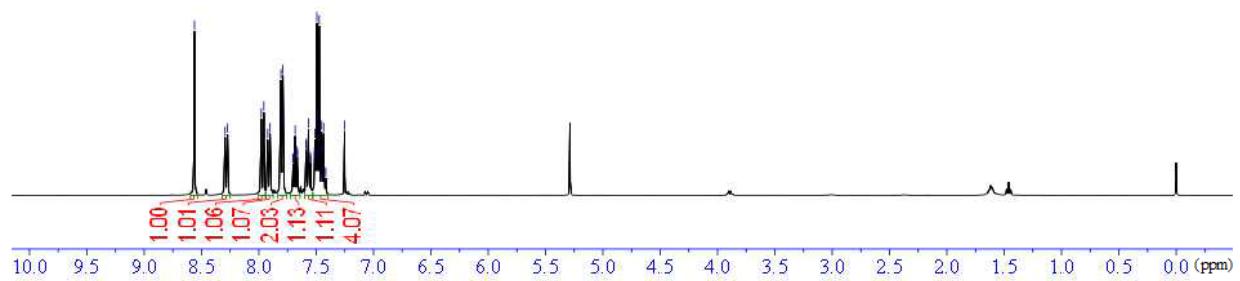
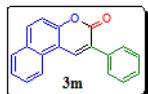


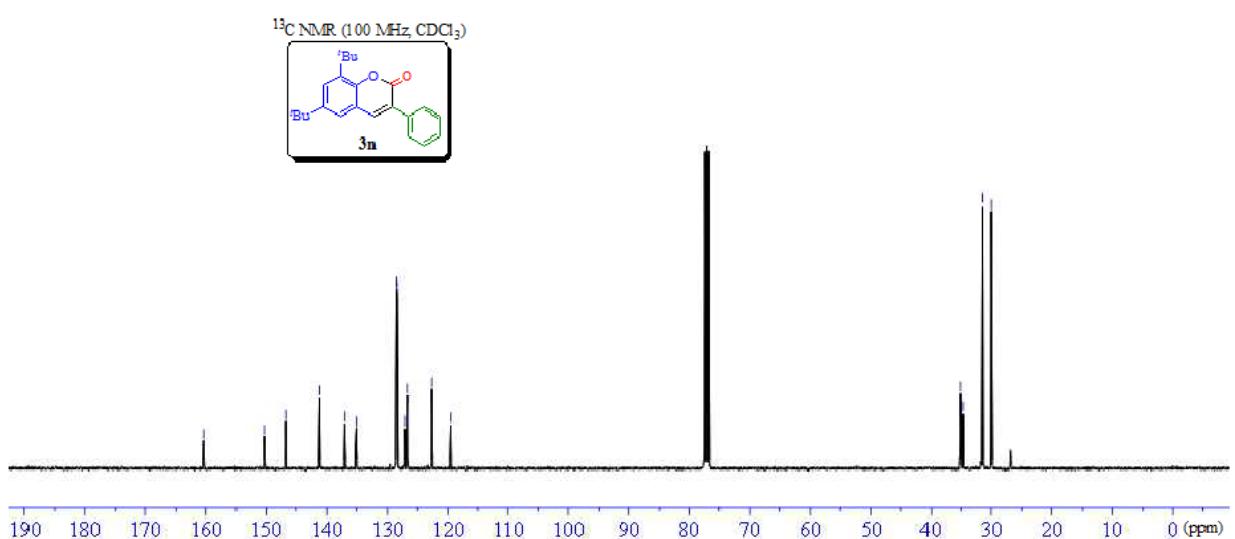
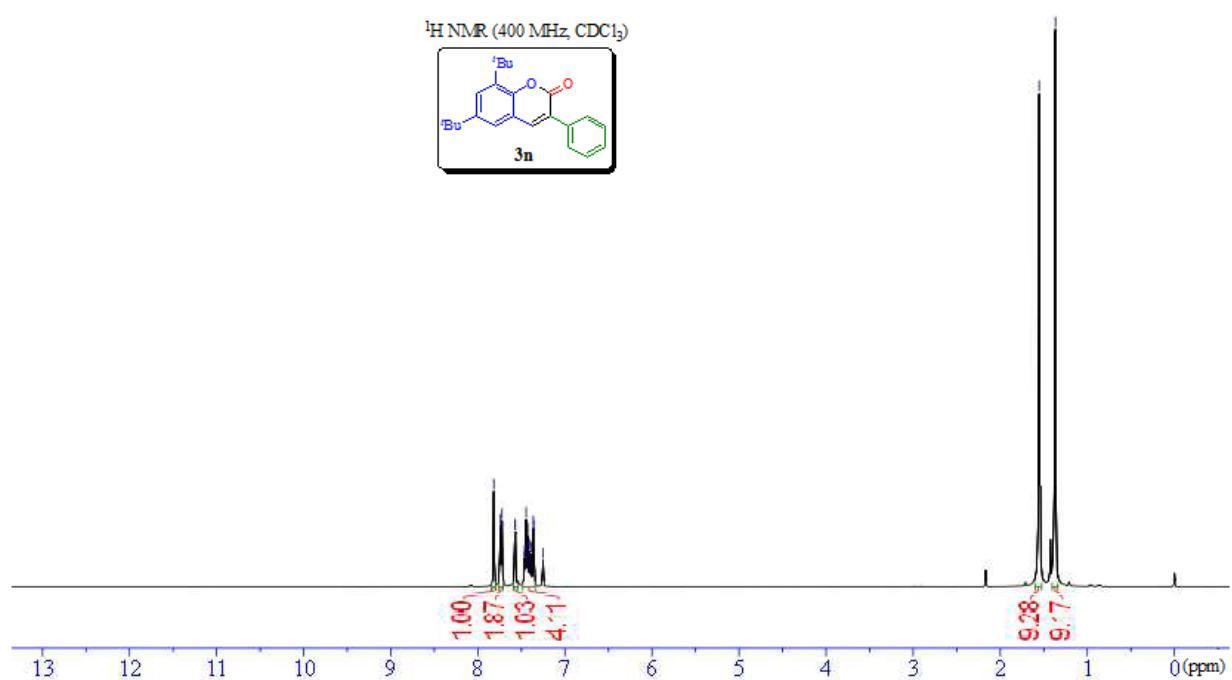
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



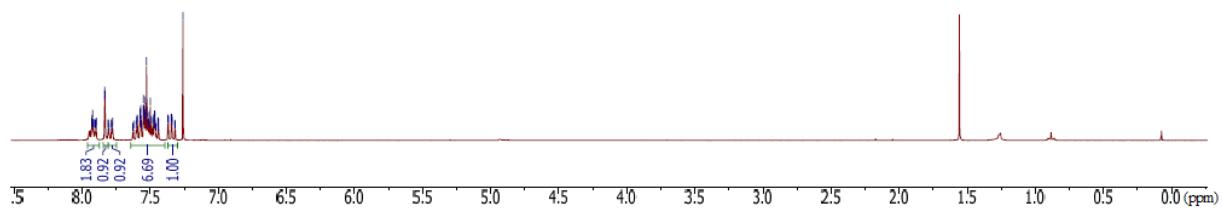
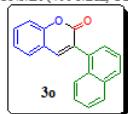


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)





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



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

