

# Supporting Information

## Rh(III)-Catalyzed C-H Activation/Annulation of Salicylaldehydes

### with Sulfoxonium Ylides for the Synthesis of Chromones

Libo Cai, Xiaoyi Zhu, Jiayi Chen, Aijun Lin\* and Hequan Yao\*

*State Key Laboratory of Natural Medicines (SKLNM) and Department of Medicinal Chemistry,*

*School of Pharmacy, China Pharmaceutical University, Nanjing, 210009, P. R. China*

\*E-mail: ajlin@cpu.edu.cn.

\*E-mail: hyao@cpu.edu.cn, cpuhyao@126.com.

## CONTENT

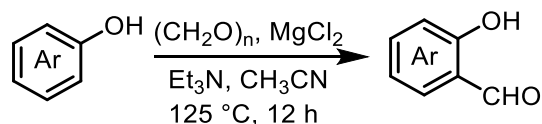
<b>1. General Information</b> .....	<b>2</b>
<b>2. Preparation of Starting Materials</b> .....	<b>3</b>
<b>3. General Experimental Procedures</b> .....	<b>5</b>
<b>4. Mechanistic Experiments</b> .....	<b>6</b>
<b>5. Gram-Scale Experiment and Further Transformation</b> .....	<b>11</b>
<b>5.1 A gram scale experiment of 3aa</b> .....	<b>11</b>
<b>5.2 Synthetic Transformation of 3aa to 10</b> .....	<b>11</b>
<b>5.3 Synthetic Transformation of 3aa to 11</b> .....	<b>12</b>
<b>5.4 Synthetic Transformation of 3aa to 12</b> .....	<b>12</b>
<b>5.5 Synthetic Transformation of 3aa to 13</b> .....	<b>13</b>
<b>5.6 Synthetic Transformation of 3aa to 14</b> .....	<b>13</b>
<b>5.7 Synthetic Transformation of 3aa to 15</b> .....	<b>14</b>
<b>6. Characterization of the Products</b> .....	<b>15</b>
<b>7. References</b> .....	<b>28</b>
<b>8. <sup>1</sup>H and <sup>13</sup>C NMR Spectra of Title Compounds</b> .....	<b>29</b>

## ***1. General Information***

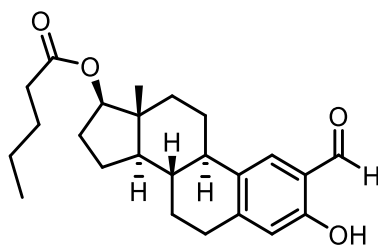
Unless otherwise noted, all chemicals were purchased from commercial suppliers (Adamas, Aladdin, etc) and used without further purification.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were collected on BRUKER (300 or 400 MHz) spectrometer using  $\text{CDCl}_3$  as solvent. Chemical shifts of  $^1\text{H}$  NMR were recorded in parts per million (ppm,  $\delta$ ) relative to tetramethylsilane ( $\delta = 0.00$  ppm) with the solvent resonance as the internal standard ( $\text{CDCl}_3$ :  $\delta = 7.26$  ppm). Data are reported as follows: chemical shift in ppm ( $\delta$ ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz) and integration. Chemical shifts of  $^{13}\text{C}$  NMR were reported in ppm with the solvent as the internal standard ( $\text{CDCl}_3$ :  $\delta = 77.0$  ppm). High Resolution Mass measurement was performed on Agilent QTOF 6520 mass spectrometer with electron spray ionization (ESI and APCI) as the ion source. Melting point (m. p.) was measured on a microscopic melting point apparatus. Flash column chromatography was carried out using commercially available 200-300 mesh under pressure unless otherwise indicated. Gradient flash chromatography was conducted eluting with PE/EA, they are listed as volume/volume ratios.

## 2. Preparation of Starting Materials

Salicylaldehyde substrates were synthesized according to the literature procedure.<sup>1</sup>



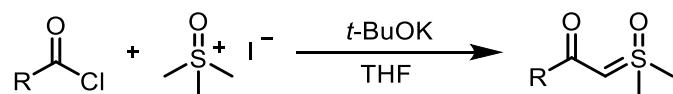
To a mixture of phenol (5.0 mmol), paraformaldehyde (50.0 mmol) and magnesium chloride (13.0 mmol) was added CH<sub>3</sub>CN (20.0 mL), followed by triethylamine (23.0 mmol) at room temperature. The sealed tube was heated at 125 °C for 12 h. 2 N HCl (15.0 mL) was added slowly after cooling to room temperature, and then the mixture extracted with diethyl ether (50.0 mL x 2). The extracts were combined, washed with H<sub>2</sub>O (50.0 mL x 2), brine (50.0 mL), then dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The crude product was purified by flash chromatography on silica gel (PE: EA = 100:1) to afford the corresponding salicylaldehyde substrates.



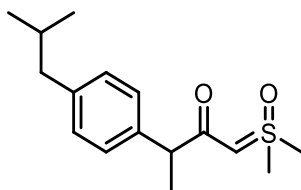
### **(8*S*,9*R*,13*R*,14*R*,17*R*)-2-formyl-3-hydroxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl pentanoate**

Pale yellow solid, **m. p.** 74–75 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 10.78 (s, 1H), 9.81 (s, 1H), 7.41 (s, 1H), 6.69 (s, 1H), 4.78 – 4.66 (m, 1H), 2.97 – 2.79 (m, 2H), 2.33 (t, *J* = 7.5 Hz, 3H), 2.27 – 2.13 (m, 2H), 1.98 – 1.84 (m, 2H), 1.83 – 1.69 (m, 1H), 1.67 – 1.22 (m, 11H), 0.94 (t, *J* = 7.3 Hz, 3H), 0.85 (s, 3H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 196.1, 173.9, 159.2, 147.9, 132.6, 130.6, 119.0, 116.94, 82.2, 49.8, 43.3, 42.9, 38.2, 36.7, 34.3, 30.1, 27.6, 27.2, 26.8, 26.1, 23.2, 22.3, 13.8, 12.1 ppm; **HRMS (ESI) *m/z*** Calcd for [C<sub>24</sub>H<sub>32</sub>O<sub>4</sub>+H]<sup>+</sup> 385.2373, found 385.2374.

Compounds **2a-m** were synthesized according to the literature procedure.<sup>2</sup>



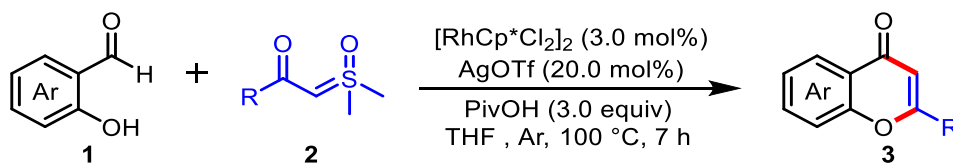
To a stirred solution of potassium *tert*-butoxide (3.0 g, 27.2 mmol) in THF (30.0 mL) was added trimethylsulfoxonium iodide (5.0 g, 20.6 mmol) at room temperature. The resulting mixture was refluxed for 2 h and then cooled to 0 °C, followed by addition of acyl chlorides (7.0 mmol) in THF (5.0 mL). The reaction was allowed to warm to room temperature and stirred for 3 h. Then, the solvent was evaporated and water (15.0 mL) and ethyl acetate (20.0 mL) were added to the resulting mixture. The organic layer was separated and the aqueous layer was washed with ethyl acetate (20 mL x 3) and the organic layers were combined. The organic solution was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and then filtered. After removing the solvent under vacuum, the crude product was purified by flash chromatography over silica gel using EtOAc/MeOH (95:5) to afford the corresponding sulfoxonium ylides.



### **1-(dimethyl(oxo)-16-sulfanylidene)-3-(4-isobutylphenyl)butan-2-one**

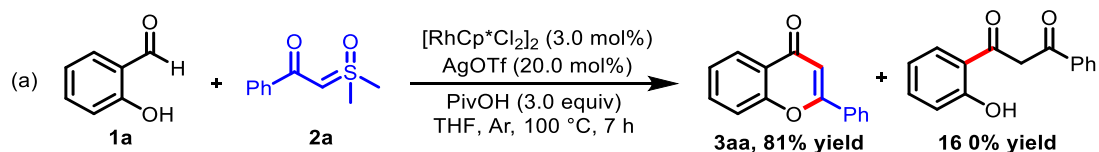
Pale yellow solid, **m. p.** 119–120 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.19 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 4.28 (s, 1H), 3.50 (q, *J* = 7.1 Hz, 1H), 3.34 (d, *J* = 11.5 Hz, 6H), 2.43 (d, *J* = 7.2 Hz, 2H), 1.89 – 1.77 (m, 1H), 1.43 (d, *J* = 7.2 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 6H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 192.3, 140.4, 139.7, 129.1, 127.3, 68.7, 50.1, 45.1, 42.3, 42.1, 30.2, 22.5, 18.4 ppm; **HRMS (ESI)** *m/z* Calcd for [C<sub>16</sub>H<sub>24</sub>O<sub>2</sub>S+H]<sup>+</sup> 281.1570, found 281.1571.

### 3. General Experimental Procedures

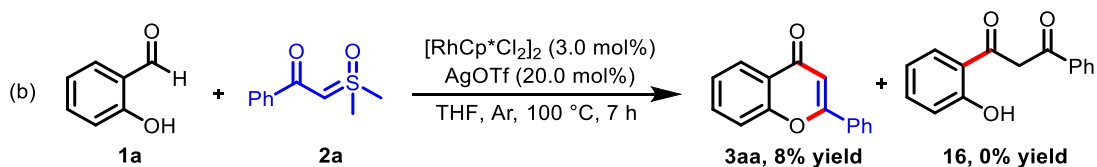


A sealed tube was charged with salicylaldehyde substrates **1** (0.2 mmol),  $[\text{RhCp}^*\text{Cl}_2]_2$  (3.0 mol%), AgOTf (20.0 mol%), PivOH (0.6 mmol), sulfoxonium ylides **2** (0.24 mmol) and 0.5 mL THF. Under an argon atmosphere, the reaction mixture was vigorously stirred at 100 °C (oil temperature) for 7 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through a plug of Celite. The filtrate was washed with  $\text{NaHCO}_3$  and brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The mixture was concentrated in vacuo and purified by flash chromatography on silica gel (PE : EA = 10:1) to afford the desired products **3**.

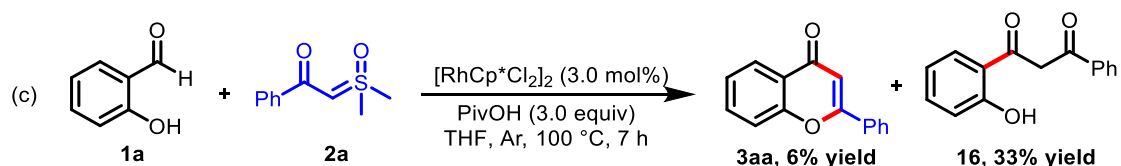
#### 4. Mechanistic Experiments



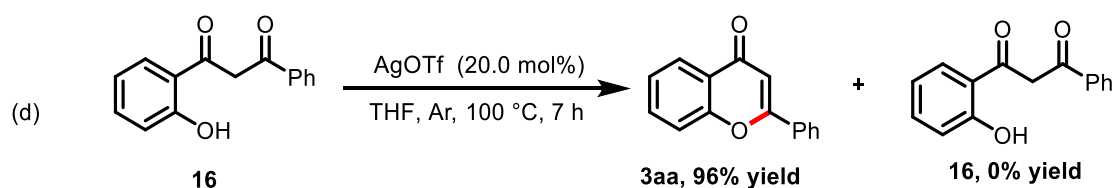
A sealed tube was charged with salicylaldehyde **1a** (0.2 mmol), [RhCp\*Cl<sub>2</sub>]<sub>2</sub> (3.0 mol%), AgOTf (20.0 mol%), PivOH (0.6 mmol), sulfoxonium ylide **2a** (0.24 mmol) and 0.5 mL THF. Under an argon atmosphere, the reaction mixture was vigorously stirred at 100 °C (oil temperature) for 7 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through a plug of Celite. The filtrate was washed with NaHCO<sub>3</sub> and brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The mixture was concentrated in vacuo and purified by flash chromatography on silica gel (PE : EA = 10:1) to afford the desired product **3aa**.



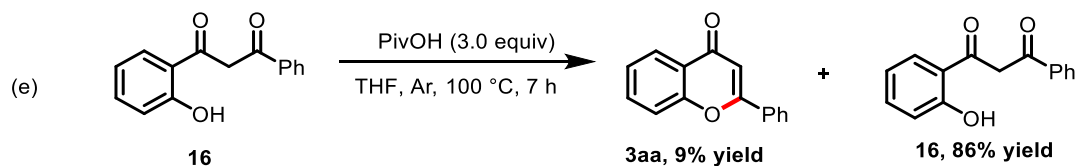
A sealed tube was charged with salicylaldehyde **1a** (0.2 mmol), [RhCp\*Cl<sub>2</sub>]<sub>2</sub> (3.0 mol%), AgOTf (20.0 mol%), sulfoxonium ylide **2a** (0.24 mmol) and 0.5 mL THF. Under an argon atmosphere, the reaction mixture was vigorously stirred at 100 °C (oil temperature) for 7 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through a plug of Celite. The mixture was concentrated in vacuo and purified by flash chromatography on silica gel (PE : EA = 10:1) to afford the desired product **3aa**.



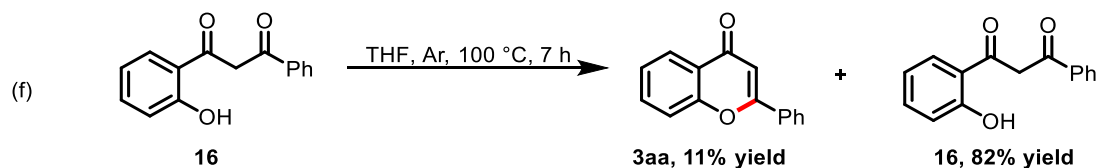
A sealed tube was charged with salicylaldehyde **1a** (0.2 mmol),  $[\text{RhCp}^*\text{Cl}_2]_2$  (3.0 mol%), PivOH (0.6 mmol), sulfoxonium ylide **2a** (0.24 mmol) and 0.5 mL THF. Under an argon atmosphere, the reaction mixture was vigorously stirred at 100 °C (oil temperature) for 7 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through a plug of Celite. The filtrate was washed with  $\text{NaHCO}_3$  and brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The mixture was concentrated in vacuo and purified by flash chromatography on silica gel (PE : EA = 10:1) to afford the desired product **3aa**.



A sealed tube was charged with 1-(2-hydroxyphenyl)-3-phenylpropane-1,3-dione **16** (0.2 mmol), AgOTf (20.0 mol%) and 0.5 mL THF. Under an argon atmosphere, the reaction mixture was vigorously stirred at 100 °C (oil temperature) for 7 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through a plug of Celite. The mixture was concentrated in vacuo and purified by flash chromatography on silica gel (PE : EA = 10:1) to afford the desired product **3aa**.



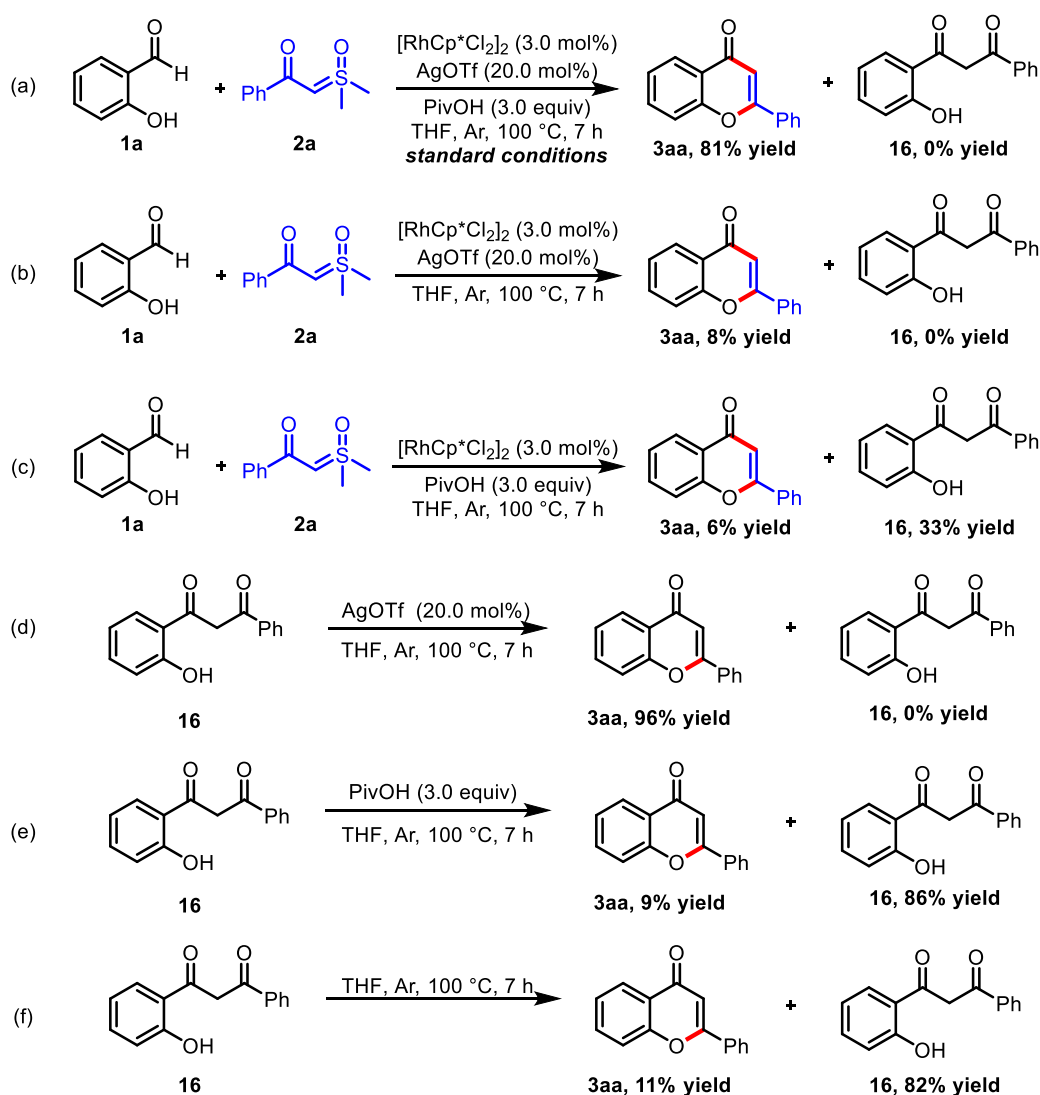
A sealed tube was charged with 1-(2-hydroxyphenyl)-3-phenylpropane-1,3-dione **16** (0.2 mmol), PivOH (0.6 mmol) and 0.5 mL THF. Under an argon atmosphere, the reaction mixture was vigorously stirred at 100 °C (oil temperature) for 7 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through a plug of Celite. The filtrate was washed with NaHCO<sub>3</sub> and brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The mixture was concentrated in vacuo and purified by flash chromatography on silica gel (PE : EA = 100:1) to afford **16**.



A sealed tube was charged with 1-(2-hydroxyphenyl)-3-phenylpropane-1,3-dione **16** (0.2 mmol) and 0.5 mL THF. Under an argon atmosphere, the reaction mixture was vigorously stirred at 100 °C (oil temperature) for 7 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through a plug of Celite. The mixture was concentrated in vacuo and purified by flash chromatography on silica gel (PE : EA = 10:1) to afford the desired product **3aa**.



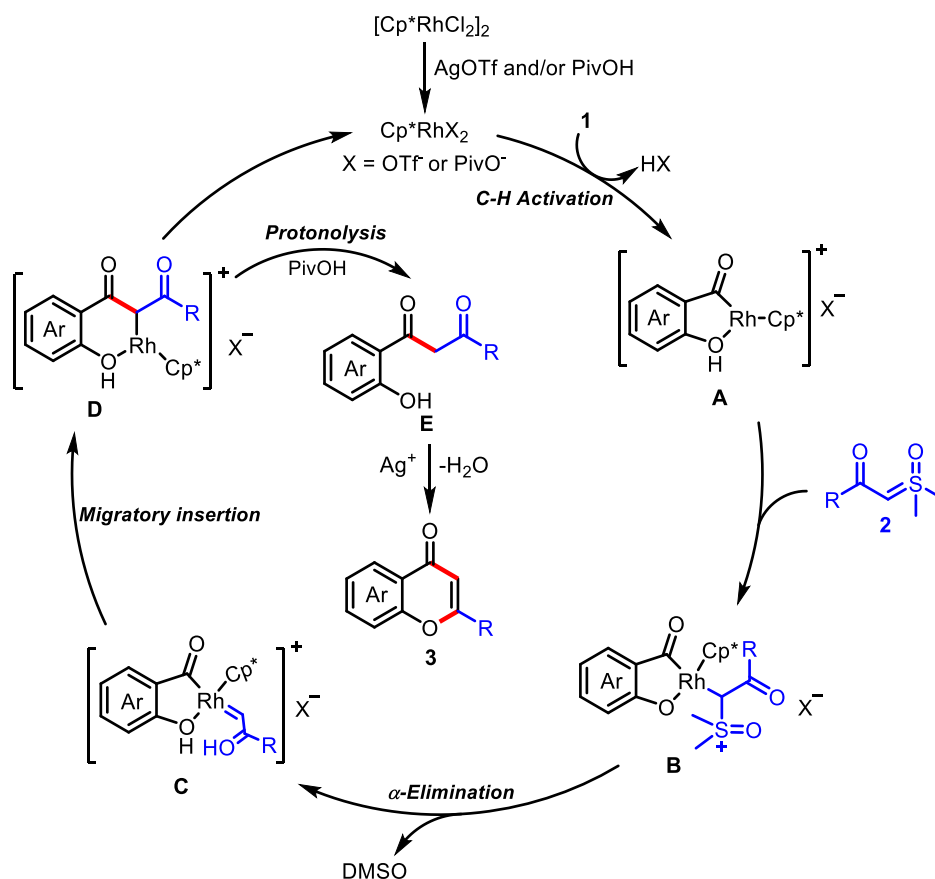
## Control experiments



Chromone **3aa** was obtained in 8% and 6% yields from the reactions, each carried out in the absence of PivOH or AgOTf, respectively (Scheme 2b and 2c). Notably, diketone **16**, a potential reaction intermediate, was formed in 33% yield from the reaction run without AgOTf, which indicated that PivOH took part in the formation of the active  $\text{Cp}^*\text{RhX}_2$  complex and the C-H activation process to generate **16**. Treatment of **16** with AgOTf in THF produced **3aa** in 95% yield (Scheme 2d). Meanwhile, conversion of **16** to **3aa** took place only in 9% yield using PivOH (Scheme 2e). Heating compound **16** directly afforded **3aa** in 11% yield (Scheme 2d). These results suggested that AgOTf played an important role

in the formation of an active  $\text{Cp}^*\text{RhX}_2$  complex and promotion of the intramolecular dehydrative condensation of **16** to yield the desired product **3aa**.

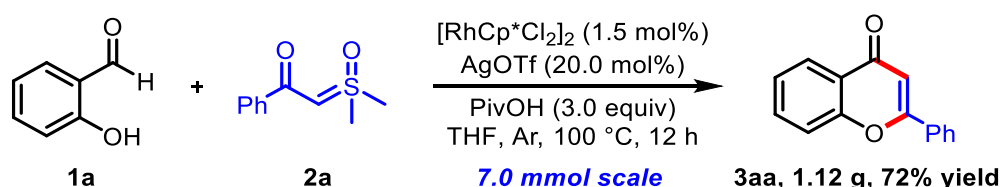
### *Mechanistic hypothesis*



The active  $\text{Cp}^*\text{RhX}_2$  complex is generated from  $[\text{RhCp}^*\text{Cl}_2]_2$ ,  $\text{AgOTf}$  and/or  $\text{PivOH}$  via ligand exchange. After coordination with salicylaldehydes **1** and aldehydic C–H activation, the rhodium catalyst forms metalacyclic intermediate **A**. Then, sulfoxonium ylide **2** attacks the metal center of intermediate **A** to deliver intermediate **B**, which undergoes  $\alpha$ -elimination of  $\text{DMSO}$  to afford the carbene species **C**. Subsequently, migratory insertion of the  $\text{Rh-C}$  bond into the carbene generates the six-membered rhodacyclic intermediate **D**. Protonation of **D** with  $\text{PivOH}$  provides intermediate **E** and regenerates the active  $\text{Cp}^*\text{RhX}_2$  species for the next catalytic cycle. Finally, the silver salt promotes the intramolecular dehydrative condensation of **E** to chromone **3**.

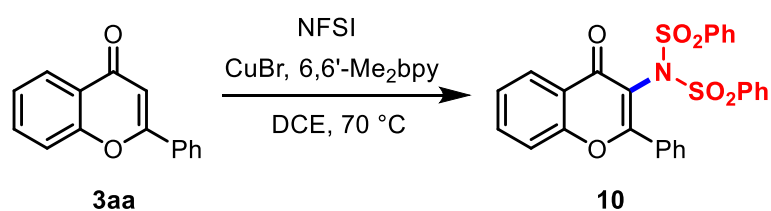
## 5. Gram-Scale Experiment and Further Transformations

### 5.1 A gram scale experiment of **3aa**



A sealed tube was charged with salicylaldehyde **1a** (7.0 mmol),  $[\text{RhCp}^*\text{Cl}_2]_2$  (1.5 mol%), AgOTf (20.0 mol%), PivOH (21.0 mmol), sulfoxonium ylide **2a** (8.4 mmol) and 17.5 mL THF. Under an argon atmosphere, the reaction mixture was vigorously stirred at 100 °C (oil temperature) for 12 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through a plug of Celite. The filtrate was washed with  $\text{NaHCO}_3$  and brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The mixture was concentrated in vacuo and purified by flash chromatography on silica gel (PE : EA = 10:1) to afford the desired product **3aa** (1.12 g, 72% yield).

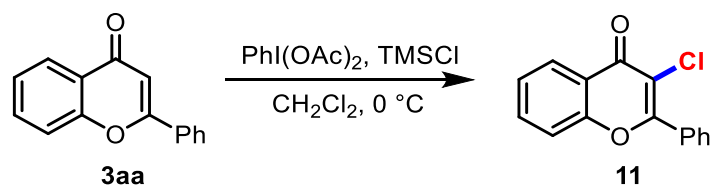
### 5.2 Synthetic Transformation of **3aa** to **10**



A sealed tube was charged with **3aa** (0.2 mmol), NFSI (0.21 mmol) and CuBr (10.0 mol%), 6,6'-Me<sub>2</sub>bpy (12.0 mol%) in DCE (1.0 mL). Under an argon atmosphere, the reaction mixture was stirred at 70 °C for 11 h. The mixture was cooled to room temperature and then additional NFSI (0.21 mmol) and CuBr (10.0 mol%), 6,6'-Me<sub>2</sub>bpy (12.0 mol%) were added to the mixture. The reaction mixture was heated for another 48 h. The mixture was then cooled to room temperature and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford the corresponding product **10** (82.8 mg, 80% yield). <sup>1</sup>H NMR (300

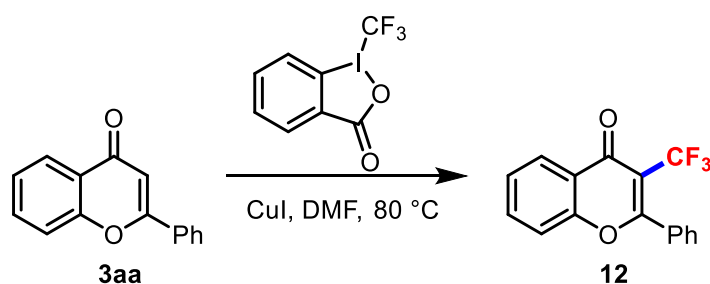
MHz, CDCl<sub>3</sub>)  $\delta$  8.15 -8.13 (m, 1H), 7.91 – 7.89 (m, 2H), 7.90 – 7.81 (m, 4H), 7.75 – 7.72 (m, 1H), 7.55 – 7.52 (m, 3H), 7.46 (t,  $J = 7.0$  Hz, 2H), 7.37 – 7.33 (m, 6H) ppm.

### 5.3 Synthetic Transformation of 3aa to 11<sup>4</sup>



A two neck flask was charged with  $\text{PhI(OAc)}_2$  (0.15 mmol) in anhydrous DCM (0.5 ml), the solution was protected under Ar atmosphere and stirred in  $0\text{ }^\circ\text{C}$ . Then trimethyldilyl chloride (0.3 mmol) was added dropwise and the mixture was stirred in  $0\text{ }^\circ\text{C}$  for 30 min. The **3aa** (0.1 mmol) in anhydrous DCM (0.5 ml) and pyridine (0.4 mmol) was added. The mixture was stirred in  $0\text{ }^\circ\text{C}$  for another 3.5 h. The mixture was concentrated in vacuo and purified by flash chromatography on silica gel by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford the corresponding product **11** (22.3 mg, 87% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.30 (d,  $J = 7.9$  Hz, 1H), 7.97 – 7.83 (m, 2H), 7.78 – 7.66 (m, 1H), 7.61 – 7.40 (m, 5H) ppm.

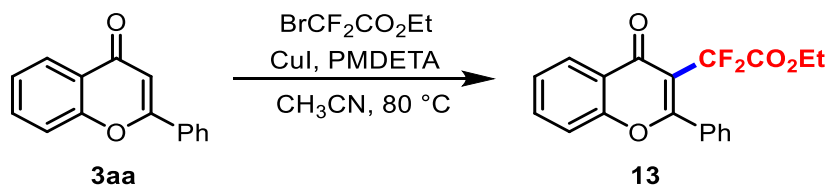
### 5.4 Synthetic Transformation of 3aa to 12<sup>5</sup>



A sealed tube was charged with Togni reagent (0.15 mmol) and  $\text{CuI}$  (10.0 mol%) under Ar atmosphere. Then **3aa** (0.1 mmol) in DMF (0.5 ml) was added. The mixture was heated to  $80\text{ }^\circ\text{C}$  and stirred for 26 h until the complete conversion of **3aa** by TLC detection. The resulting mixture was concentrated in vacuo and the residue was dissolved by DCM. The organic layer was washed with saturated sodium chloride, dried

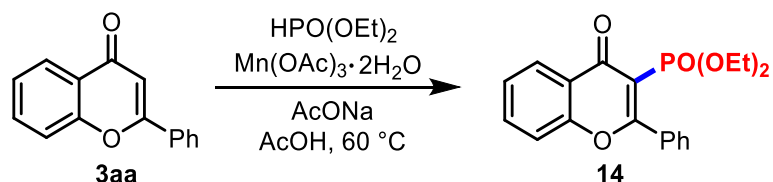
by MgSO<sub>4</sub> and concentrated. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford the corresponding product **12** (14.5 mg, 50 % yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.27 (d, *J* = 7.9 Hz, 1H), 7.78 – 7.69 (m, 1H), 7.64 – 7.43 (m, 7H) ppm.

### 5.5 Synthetic Transformation of **3aa** to **13**<sup>6</sup>



A sealed tube was charged with CuI (10.0 mol%) under Ar atmosphere. Then CH<sub>3</sub>CN (0.5 ml), PMDETA (0.38 mmol), **3aa** (0.25 mmol) and ethyl bromodifluoroacetate (0.75 mmol) was added in subsequence. The mixture was heated to 80 °C for 12 h and then the reaction was cooled to room temperature. The mixture was diluted with EtOAc and filtered with a pad of celite. The filtrate was concentrated in vacuo. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford the corresponding product **13** (44.5 mg, 52 % yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.21 (d, *J* = 8.0 Hz, 1H), 7.70 – 7.65 (m, 3H), 7.62 – 7.42 (m, 5H), 4.36 (q, *J* = 7.2 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H) ppm.

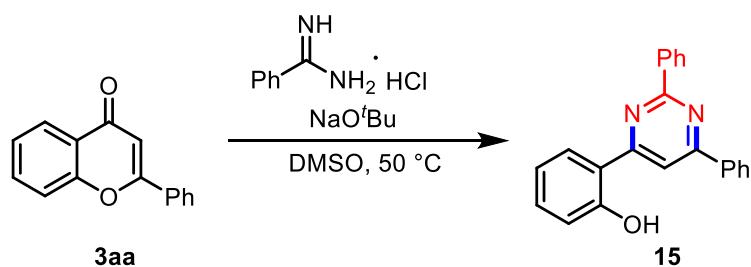
### 5.6 Synthetic Transformation of **3aa** to **14**<sup>7</sup>



To a stirred mixture of **3aa** (0.1 mmol), diethylphosphite (0.4 mmol) in acetic acid (0.4 mL) was added Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O (0.3 mmol) and NaOAc (0.3 mmol) in three portions and the resulting solution was heated at 60 °C for 24 h. Then it was quenched with water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were washed with Na<sub>2</sub>CO<sub>3</sub> and brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The

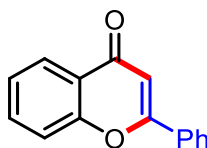
residue was purified by column chromatography to afford the desired compound **14** (19.8 mg, 55 % yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.26 – 8.19 (m, 1H), 7.80 – 7.74 (m, 2H), 7.73 – 7.67 (m, 1H), 7.59 – 7.41 (m, 5H), 4.17 – 3.98 (m, 4H), 1.10 (t,  $J = 7.1$  Hz, 6H) ppm.

### 5.7 Synthetic Transformation of **3aa** to **15**<sup>8</sup>



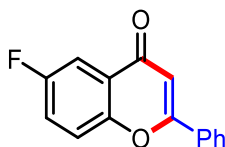
A sealed tube was charged with **3aa** (0.23 mmol, 1.0 equiv), benzamidine hydrochloride (0.29 mmol, 1.25 equiv), sodium *t*-butoxide (0.75 mmol, 3.25 equiv) in anhydrous DMSO (1.0 mL). Under Ar atmosphere, the reaction mixture was stirred at  $50\text{ }^\circ\text{C}$  for 15 min then immediately cooled to room temperature. The saturated ammonium chloride solution was added to the reaction mixture and extracted with EtOAc. The combined organic phase was washed with saturated brine and dried over  $\text{Na}_2\text{SO}_4$ . The solvent was evaporated, and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford the corresponding product **15** (67.9 mg, 91% yield). Yellow solid, **m. p.**  $159\text{--}160\text{ }^\circ\text{C}$ ;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  14.26 (s, 1H), 8.47 (s, 2H), 8.24 (s, 2H), 8.04 (s, 1H), 7.93 (d,  $J = 7.9$  Hz, 1H), 7.55 (s, 6H), 7.41 (t,  $J = 7.7$  Hz, 1H), 7.09 (d,  $J = 8.2$  Hz, 1H), 6.97 (t,  $J = 7.5$  Hz, 1H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  165.1, 165.0, 162.5, 161.1, 137.0, 136.6, 133.4, 131.3, 131.2, 129.0, 128.8, 128.2, 127.4, 126.9, 119.2, 118.9, 117.4, 108.4 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}+\text{H}]^+$  325.1335, found 325.1338.

## 6. Characterization of the Products



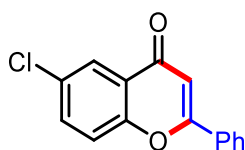
### 2-phenyl-4H-chromen-4-one (3aa)<sup>9</sup>

36.0 mg, 81% yield; White solid, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.24 – 8.18 (m, 1H), 7.94 – 7.84 (m, 2H), 7.72 – 7.62 (m, 1H), 7.59 – 7.44 (m, 4H), 7.43 – 7.35 (m, 1H), 6.80 (s, 1H) ppm.



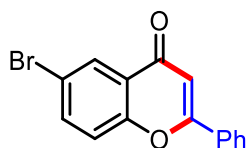
### 6-fluoro-2-phenyl-4H-chromen-4-one (3ba):

40.3 mg, 84% yield; Light yellow solid, **m. p.** 122–123 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.88 (m, 3H), 7.63 – 7.47 (m, 4H), 7.43 – 7.37 (m, 1H), 6.80 (s, 1H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 177.5, 163.6, 159.5 (d, *J* = 246.9 Hz), 152.4, 131.7, 131.4, 129.0, 126.2, 125.1 (d, *J* = 7.1 Hz), 121.8 (d, *J* = 25.5 Hz), 120.1 (d, *J* = 8.1 Hz), 110.6 (d, *J* = 23.7 Hz), 106.8 ppm; **HRMS (ESI)** *m/z* Calcd for [C<sub>15</sub>H<sub>9</sub>FO<sub>2</sub>+H]<sup>+</sup> 241.0659, found 241.0660.



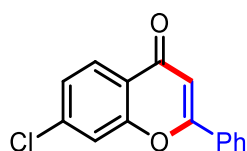
### 6-chloro-2-phenyl-4H-chromen-4-one (3ca):

42.4 mg, 83% yield; White solid, **m. p.** 178–179 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.16 (s, 1H), 7.89 (d, *J* = 7.3 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.59 – 7.47 (m, 4H), 6.80 (s, 1H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 177.1, 163.6, 154.5, 133.9, 131.9, 131.3, 131.2, 129.1, 126.3, 125.1, 124.9, 119.8, 107.4 ppm; **HRMS (ESI)** *m/z* Calcd for [C<sub>15</sub>H<sub>9</sub>ClO<sub>2</sub>+H]<sup>+</sup> 257.0364, found 257.0368.



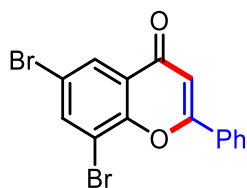
**6-bromo-2-phenyl-4H-chromen-4-one (3da):**

51.7 mg, 86% yield; White solid, **m. p.** 187–188 °C;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.32 (d,  $J = 2.5$  Hz, 1H), 7.93 – 7.83 (m, 2H), 7.80 – 7.71 (m, 1H), 7.52 (d,  $J = 7.0$  Hz, 3H), 7.45 (d,  $J = 8.9$  Hz, 1H), 6.81 (s, 1H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  176.5, 163.1, 154.5, 136.2, 131.4, 130.8, 128.6, 127.8, 125.8, 124.8, 119.5, 118.2, 107.0 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{15}\text{H}_9\text{BrO}_2+\text{H}]^+$  300.9859, found 300.9865.



**7-chloro-2-phenyl-4H-chromen-4-one (3ea):**

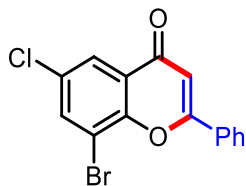
36.3 mg, 71% yield; Light red solid, **m. p.** 150–151 °C;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.16 (d,  $J = 8.5$  Hz, 1H), 7.95 – 7.82 (m, 2H), 7.63 – 7.47 (m, 4H), 7.37 (d,  $J = 8.6$  Hz, 1H), 6.80 (s, 1H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  177.5, 163.5, 156.3, 139.8, 131.8, 131.3, 129.1, 127.1, 126.3, 126.1, 122.5, 118.2, 107.8 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{15}\text{H}_9\text{ClO}_2+\text{H}]^+$  257.0364, found 257.0362.



**6, 8-dibromo-2-phenyl-4H-chromen-4-one (3fa):**

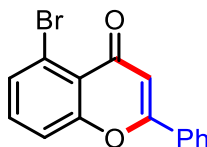
68.3 mg, 90% yield; White solid, **m. p.** 161–162 °C;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.23 (s, 1H), 8.05 – 7.86 (m, 3H), 7.52 (d,  $J = 6.9$  Hz, 3H), 6.82 (s, 1H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  175.9, 163.0, 151.2, 138.8, 131.7, 130.2, 128.7, 127.2, 125.9, 125.4, 118.0, 112.6, 106.5 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{15}\text{H}_8\text{Br}_2\text{O}_2+\text{H}]^+$  378.8964, found 378.8962.





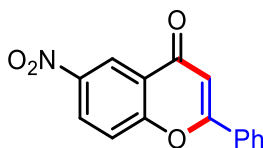
**8-bromo-6-chloro-2-phenyl-4H-chromen-4-one (3ga):**

59.2 mg, 88% yield; Light yellow solid, **m. p.** 174–175 °C; **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 8.14 – 8.04 (m, 1H), 8.01 – 7.91 (m, 2H), 7.90 – 7.81 (m, 1H), 7.53 (d, *J* = 5.5 Hz, 3H), 6.83 (d, *J* = 2.1 Hz, 1H) ppm; **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 176.0, 163.0, 150.8, 136.2, 131.7, 130.8, 130.3, 128.7, 125.9, 125.1, 124.1, 112.4, 106.5 ppm; **HRMS (ESI)** *m/z* Calcd for [C<sub>15</sub>H<sub>8</sub>BrClO<sub>2</sub>+H]<sup>+</sup> 334.9469, found 334.9470.



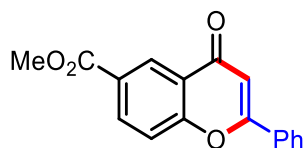
**5-bromo-2-phenyl-4H-chromen-4-one (3ha):**

23.4 mg, 39% yield; Red brown solid, **m. p.** 144–145 °C; **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 7.90 (d, *J* = 5.4 Hz, 2H), 7.64 (d, *J* = 7.2 Hz, 1H), 7.59 – 7.40 (m, 5H), 6.80 (s, 1H) ppm; **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 177.1, 161.7, 157.7, 133.2, 131.9, 131.7, 131.1, 129.1, 126.2, 121.7, 120.4, 118.1, 108.5 ppm; **HRMS (ESI)** *m/z* Calcd for [C<sub>15</sub>H<sub>9</sub>BrO<sub>2</sub>+H]<sup>+</sup> 300.9859, found 300.9864.



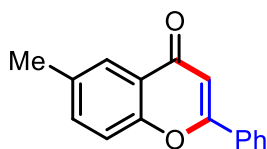
**6-nitro-2-phenyl-4H-chromen-4-one (3ia):**

37.2 mg, 70% yield; Light yellow solid, **m. p.** 182–183 °C; **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 9.09 (s, 1H), 8.53 (d, *J* = 9.1 Hz, 1H), 7.93 (d, *J* = 6.9 Hz, 2H), 7.73 (d, *J* = 9.1 Hz, 1H), 7.57 (d, *J* = 6.4 Hz, 3H), 6.88 (s, 1H). ppm; **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 176.2, 163.7, 158.5, 144.3, 131.9, 130.2, 128.8, 127.6, 125.9, 123.5, 121.9, 119.4, 107.3 ppm; **HRMS (ESI)** *m/z* Calcd for [C<sub>15</sub>H<sub>9</sub>NO<sub>4</sub>+H]<sup>+</sup> 268.0604, found 268.0604.



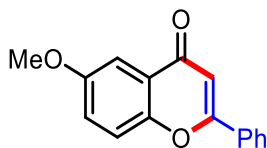
**methyl 4-oxo-2-phenyl-4H-chromene-6-carboxylate (3ja):**

44.8 mg, 80% yield; Light red solid, **m. p.** 184–185 °C;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.88 (s, 1H), 8.34 (d,  $J = 8.5$  Hz, 1H), 7.91 (d,  $J = 7.1$  Hz, 2H), 7.67 – 7.46 (m, 4H), 6.83 (s, 1H), 3.95 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  177.6, 165.7, 163.6, 158.6, 134.4, 131.9, 131.2, 129.1, 128.1, 127.2, 126.3, 123.6, 118.5, 107.8, 52.4 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{17}\text{H}_{12}\text{O}_4+\text{H}]^+$  281.0808, found 281.0809.



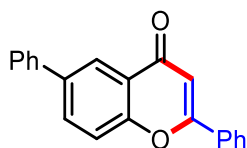
**6-methyl-2-phenyl-4H-chromen-4-one (3ka):**

31.0 mg, 66% yield; White solid, **m. p.** 124–125 °C;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (s, 1H), 7.98 – 7.87 (m, 2H), 7.59 – 7.42 (m, 5H), 6.81 (s, 1H), 2.47 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  178.6, 163.2, 154.6, 135.2, 135.0, 131.9, 131.5, 129.0, 126.3, 125.1, 123.7, 117.8, 107.5, 20.9 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{16}\text{H}_{12}\text{O}_2+\text{H}]^+$  237.0910, found 237.0908.



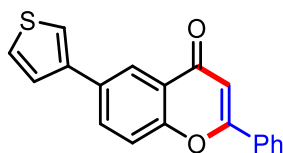
**6-methoxy-2-phenyl-4H-chromen-4-one (3la):**

30.9 mg, 61% yield; Light yellow solid, **m. p.** 154–155 °C;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 (d,  $J = 4.2$  Hz, 2H), 7.68 – 7.44 (m, 5H), 7.29 (d,  $J = 9.2$  Hz, 1H), 6.82 (s, 1H), 3.91 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  178.3, 163.2, 157.0, 151.1, 131.9, 131.5, 129.0, 126.2, 124.6, 123.8, 119.5, 106.8, 104.8, 55.9 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{16}\text{H}_{12}\text{O}_3+\text{H}]^+$  253.0859, found 253.0857.



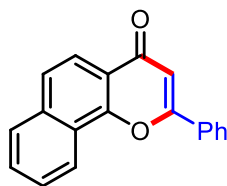
**2, 6-diphenyl-4H-chromen-4-one (3ma):**

50.3 mg, 84% yield; White solid, **m. p.** 150–151 °C;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.48 – 8.39 (m, 1H), 7.98 – 7.86 (m, 3H), 7.73 – 7.33 (m, 9H), 7.90 – 7.79 (m, 1H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  178.4, 163.4, 155.6, 139.3, 138.3, 132.6, 131.7, 131.6, 129.1, 129.0, 127.9, 127.2, 126.3, 124.1, 123.5, 118.6, 107.6 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{21}\text{H}_{14}\text{O}_2+\text{H}]^+$  299.1067, found 299.1065.



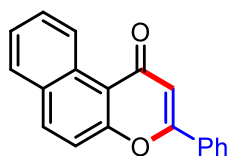
**2-phenyl-6-(thiophen-3-yl)-4H-chromen-4-one (3na):**

46.9 mg, 77% yield; Yellow solid, **m. p.** 196–197 °C;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.39 (s, 1H), 7.90 (d,  $J = 7.4$  Hz, 3H), 7.65 – 7.35 (m, 7H), 6.82 (s, 1H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  178.4, 163.4, 155.3, 140.5, 133.1, 131.9, 131.6, 129.1, 126.7, 126.3, 126.2, 124.1, 122.5, 121.2, 118.6, 107.5 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{19}\text{H}_{12}\text{O}_2\text{S}+\text{H}]^+$  305.0631, found 305.0637.



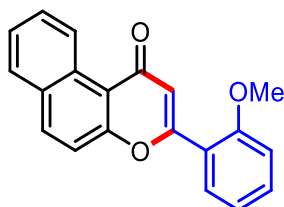
**2-phenyl-4H-benzo[h]chromen-4-one (3oa):**

45.9 mg, 84% yield; Light yellow solid, **m. p.** 143–144 °C;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.57 – 8.47 (m, 1H), 8.17 – 8.08 (m, 1H), 7.98 (s, 2H), 7.92 – 8.84 (m, 1H), 7.78 – 7.62 (m, 3H), 7.61 – 7.49 (m, 3H), 6.92 (d,  $J = 3.4$  Hz, 1H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  178.2, 162.6, 153.5, 136.0, 131.9, 131.5, 129.2, 129.2, 128.2, 127.1, 126.2, 125.3, 124.1, 122.3, 120.7, 120.2, 108.7 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{19}\text{H}_{12}\text{O}_2+\text{H}]^+$  273.0910, found 273.0912.



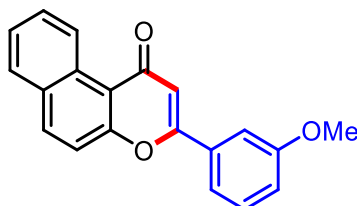
**3-phenyl-1H-benzo[f]chromen-1-one (3pa):**

52.9 mg, 97% yield; White solid, **m. p.** 152–153 °C; **m. p.** 152–153 °C;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  10.08 (d,  $J = 8.6$  Hz, 1H), 8.06 (d,  $J = 9.0$  Hz, 1H), 7.97 – 7.82 (m, 3H), 7.80 – 7.69 (m, 1H), 7.64 – 7.46 (m, 5H), 6.96 (s, 1H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  180.3, 160.7, 157.3, 135.4, 131.4, 130.6, 130.4, 129.2, 129.0, 128.1, 127.2, 126.6, 126.0, 117.5, 117.2, 110.4 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{19}\text{H}_{12}\text{O}_2+\text{H}]^+$  273.0910, found 273.0914.



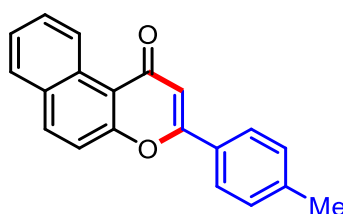
**3-(2-methoxyphenyl)-1H-benzo[f]chromen-1-one (3pb):**

57.2 mg, 95% yield; Light yellow solid, **m. p.** 170–171 °C;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  9.99 (d,  $J = 8.6$  Hz, 1H), 7.92 (d,  $J = 9.0$  Hz, 1H), 7.82 (d,  $J = 8.1$  Hz, 1H), 7.75 (d,  $J = 8.0$  Hz, 1H), 7.69 – 7.57 (m, 1H), 7.52 – 7.39 (m, 2H), 7.38 – 7.27 (m, 1H), 7.21 (s, 1H), 7.03 – 6.94 (m, 1H), 6.90 (d,  $J = 8.3$  Hz, 1H), 3.82 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  180.8, 158.1, 158.0, 157.5, 135.2, 132.3, 130.5, 130.5, 129.1, 129.0, 128.1, 127.2, 126.4, 120.7, 120.2, 117.7, 117.0, 115.6, 111.7, 55.7 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{20}\text{H}_{14}\text{O}_3+\text{H}]^+$  303.1016, found 303.1016.



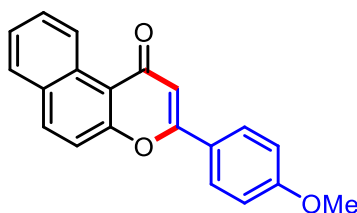
**3-(3-methoxyphenyl)-1H-benzo[f]chromen-1-one (3pc):**

57.4 mg, 95% yield; Light yellow solid, **m. p.** 124–125 °C;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  10.03 (d,  $J = 8.6$  Hz, 1H), 8.02 (d,  $J = 9.0$  Hz, 1H), 7.83 (d,  $J = 8.0$  Hz, 1H), 7.76 – 7.66 (m, 1H), 7.61 – 6.43 (m, 3H), 7.42 – 7.33 (m, 2H), 7.07 – 6.97 (m, 1H), 6.90 (s, 1H), 3.86 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  180.2, 160.5, 160.0, 157.3, 135.4, 132.6, 130.5, 130.4, 130.1, 129.2, 128.1, 127.1, 126.6, 118.4, 117.6, 117.2, 116.9, 111.5, 110.5, 55.5 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{20}\text{H}_{14}\text{O}_3+\text{H}]^+$  303.1016, found 303.1017.



**3-(p-tolyl)-1H-benzof[chromen]-1-one (3pd):**

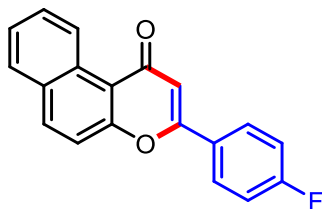
55.1 mg, 96% yield; Light yellow solid, **m. p.** 185–186 °C;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  10.04 (d,  $J = 8.6$  Hz, 1H), 8.00 (d,  $J = 9.0$  Hz, 1H), 7.88 – 7.65 (m, 4H), 7.61 – 7.44 (m, 2H), 7.24 (d,  $J = 7.7$  Hz, 2H), 6.86 (s, 1H), 2.36 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  180.3, 160.9, 157.2, 141.9, 135.3, 130.5, 130.5, 129.7, 129.1, 128.4, 128.1, 127.2, 126.5, 125.9, 117.6, 117.1, 109.7, 21.5 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{20}\text{H}_{14}\text{O}_2+\text{H}]^+$  287.1067, found 287.1065.



**3-(4-methoxyphenyl)-1H-benzof[chromen]-1-one (3pe):**

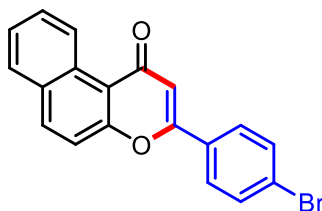
56.7 mg, 94% yield; Light yellow solid, **m. p.** 160–161 °C;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  10.05 (d,  $J = 8.6$  Hz, 1H), 8.00 (d,  $J = 9.0$  Hz, 1H), 7.81 (d,  $J = 8.3$  Hz, 3H), 7.75 – 7.66 (m, 1H), 7.61 – 7.44 (m, 2H), 6.95 (d,  $J = 8.4$  Hz, 2H), 6.82 (s, 1H), 3.82 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  180.2, 162.1, 160.7, 157.1, 135.2, 130.5, 130.5,

129.0, 128.1, 127.6, 127.2, 126.4, 123.5, 117.5, 117.0, 114.4, 108.9, 55.5 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[C_{20}H_{14}O_3+H]^+$  303.1016, found 303.1017.



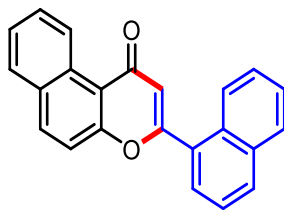
**3-(4-fluorophenyl)-1H-benzo[f]chromen-1-one (3pf):**

45.2 mg, 78% yield; White solid, **m. p.** 193–194 °C;  **$^1H$  NMR** (300 MHz,  $CDCl_3$ )  $\delta$  10.05 (s, 1H), 8.15 – 7.99 (m, 1H), 7.89 (s, 3H), 7.73 (s, 1H), 7.65 – 7.47 (m, 2H), 7.19 (s, 2H), 6.86 (s, 1H) ppm;  **$^{13}C$  NMR** (75 MHz,  $CDCl_3$ )  $\delta$  180.1, 164.6 (d,  $J = 253.0$  Hz), 159.8, 157.2, 135.5, 130.6, 130.4, 129.3, 128.3, 128.2, 127.5 (d,  $J = 3.4$  Hz), 127.1, 126.7, 117.4, 117.1, 116.3 (d,  $J = 22.1$  Hz), 110.1 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[C_{19}H_{11}ClO_2+H]^+$  307.0520, found 307.0522.



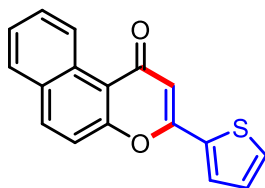
**3-(4-bromophenyl)-1H-benzo[f]chromen-1-one (3pg):**

41.5 mg, 59% yield; White solid, **m. p.** 219–220 °C;  **$^1H$  NMR** (300 MHz,  $CDCl_3$ )  $\delta$  10.05 (d,  $J = 8.7$  Hz, 1H), 8.11 (d,  $J = 9.1$  Hz, 1H), 7.90 (d,  $J = 8.1$  Hz, 1H), 7.85 – 7.72 (m, 3H), 7.70 – 7.55 (m, 4H), 6.94 (s, 1H) ppm;  **$^{13}C$  NMR** (75 MHz,  $CDCl_3$ )  $\delta$  180.1, 159.7, 157.3, 135.7, 132.4, 130.6, 130.4, 130.3, 129.4, 128.2, 127.5, 127.1, 126.7, 126.1, 117.5, 117.2, 110.5 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[C_{19}H_{11}BrO_2+H]^+$  351.0015, found 351.0015.



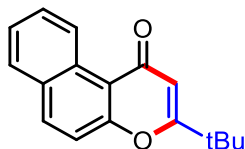
**3-(naphthalen-1-yl)-1H-benzo[f]chromen-1-one (3ph):**

42.9 mg, 67% yield; Light yellow solid, **m. p.** 144–145 °C;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  10.14 (d,  $J = 8.5$  Hz, 1H), 8.23 – 8.08 (m, 2H), 8.03 (d,  $J = 8.2$  Hz, 1H), 7.98 – 7.88 (m, 2H), 7.85 – 7.74 (m, 2H), 7.70 – 7.51 (m, 5H), 6.87 (s, 1H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  180.2, 162.8, 158.0, 135.7, 133.8, 131.5, 130.7, 130.6, 130.5, 130.1, 129.4, 128.8, 128.3, 128.1, 127.5, 127.3, 126.7, 126.6, 125.1, 124.9, 117.7, 117.3, 116.0 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{23}\text{H}_{14}\text{O}_2+\text{H}]^+$  323.1067, found 323.1068.



**3-(thiophen-2-yl)-1H-benzo[f]chromen-1-one (3pi):**

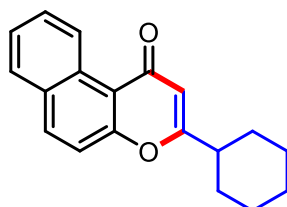
49.4 mg, 89% yield; Brown solid, **m. p.** 154–155 °C;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  10.02 (d,  $J = 8.6$  Hz, 1H), 8.01 (d,  $J = 9.0$  Hz, 1H), 7.83 (d,  $J = 8.0$  Hz, 1H), 7.75 – 7.62 (m, 2H), 7.59 – 7.44 (m, 3H), 7.17 – 7.10 (m, 1H), 6.77 (s, 1H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  179.8, 156.9, 156.6, 135.4, 134.6, 130.6, 130.4, 129.9, 129.2, 128.5, 128.2, 128.1, 127.1, 126.6, 117.4, 117.2, 109.0 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{17}\text{H}_{10}\text{O}_2\text{S}+\text{H}]^+$  279.0474, found 279.0473.



**3-(tert-butyl)-1H-benzo[f]chromen-1-one (3pj):**

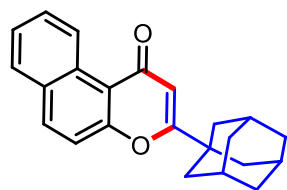
45.8 mg, 91% yield; Brown solid, **m. p.** 105–106 °C;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  10.04 (d,  $J = 8.7$  Hz, 1H), 8.05 (d,  $J = 9.1$  Hz, 1H), 7.87 (d,  $J = 8.0$  Hz, 1H), 7.78 – 7.70

(m, 1H), 7.62 – 7.55 (m, 1H), 7.50 (d,  $J = 9.1$  Hz, 1H), 6.43 (s, 1H), 1.39 (s, 9H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  180.9, 173.2, 157.6, 135.1, 130.5, 130.4, 129.1, 128.1, 127.1, 126.4, 117.6, 116.6, 109.7, 36.0, 27.9 ppm; HRMS (ESI)  $m/z$  Calcd for  $[\text{C}_{17}\text{H}_{16}\text{O}_2+\text{H}]^+$  253.1223, found 253.1224.



**3-cyclohexyl-1H-benzo[f]chromen-1-one (3pk):**

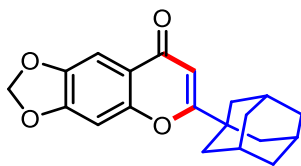
51.8 mg, 93% yield; White solid, **m. p.** 166–167 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  10.04 (d,  $J = 8.6$  Hz, 1H), 8.02 (d,  $J = 9.1$  Hz, 1H), 7.86 (d,  $J = 8.0$  Hz, 1H), 7.77 – 7.67 (m, 1H), 7.62– 7.52 (m, 1H), 7.46 (d,  $J = 9.0$  Hz, 1H), 6.31 (s, 1H), 72.65– 2.47 (m, 1H), 2.07 (d,  $J = 11.0$  Hz, 2H), 1.89 (d,  $J = 12.3$  Hz, 2H), 1.77 (d,  $J = 11.6$  Hz, 1H), 1.58 – 1.19 (m, 5H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  180.7, 170.5, 157.6, 135.1, 130.5, 130.4, 129.0, 128.1, 127.1, 126.4, 117.6, 116.9, 110.8, 42.1, 30.4, 25.9, 25.8 ppm; HRMS (ESI)  $m/z$  Calcd for  $[\text{C}_{19}\text{H}_{18}\text{O}_2+\text{H}]^+$  279.1380, found 279.1375.



**3-((3r,5r,7r)-adamantan-1-yl)-1H-benzo[f]chromen-1-one (3pl):**

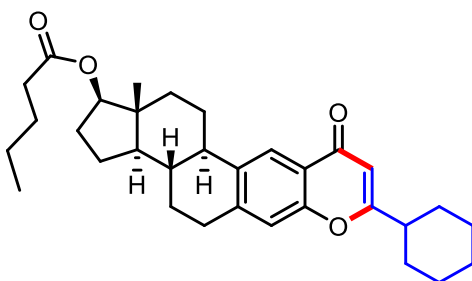
61.6 mg, 93% yield; White solid, **m. p.** 173–174 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  10.04 (d,  $J = 8.6$  Hz, 1H), 8.03 (d,  $J = 9.1$  Hz, 1H), 7.86 (d,  $J = 7.9$  Hz, 1H), 7.76 – 7.67 (m, 1H), 7.62 – 7.53 (m, 1H), 7.49 (d,  $J = 9.0$  Hz, 1H), 6.35 (s, 1H), 2.13 (s, 3H), 1.99 (d,  $J = 2.9$  Hz, 6H), 1.88 – 1.71 (m, 6H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  181.0, 173.0, 157.6, 135.1, 130.5, 130.4, 129.0, 128.1, 127.1, 126.4, 117.6, 116.7, 109.6, 39.6, 37.7, 36.5, 28.0 ppm; HRMS (ESI)  $m/z$  Calcd for  $[\text{C}_{23}\text{H}_{22}\text{O}_2+\text{H}]^+$  331.1693, found 331.1692.





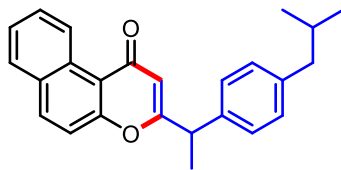
**6-((3*r*,5*r*,7*r*)-adamantan-1-yl)-8*H*-[1,3]dioxolo[4,5-*g*]chromen-8-one (4):**

61.6 mg, 95% yield; White solid, **m. p.** 203–204 °C;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 (s, 1H), 6.86 (s, 1H), 6.14 (s, 1H), 6.09 (s, 2H), 2.12 (s, 3H), 1.94 (s, 6H), 1.87 – 1.70 (m, 6H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  177.6, 174.5, 153.2, 152.0, 145.3, 117.9, 105.4, 101.8, 101.6, 97.3, 39.0, 37.5, 35.9, 27.4 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{20}\text{H}_{20}\text{O}_4+\text{H}]^+$  325.1434, found 325.1434.



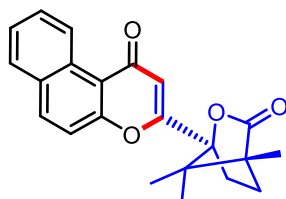
**(1*R*,3*aR*,3*bS*,11*bR*,13*aR*)-8-cyclohexyl-13*a*-methyl-10-oxo-1,2,3,3*a*,3*b*,4,5,10,11*b*,12,13,13*a*-dodecahydrocyclopenta[5,6]naphtho[1,2-*g*]chromen-1-yl pentanoate (5):**

36.0 mg, 37% yield; White solid, **m. p.** 113–114 °C;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 (s, 1H), 7.14 (s, 1H), 6.12 (s, 1H), 4.70 (dd,  $J = 9.1, 7.5$  Hz, 1H), 3.09 – 2.87 (m, 2H), 2.57 – 2.41 (m, 2H), 2.38 – 2.14 (m, 4H), 2.07 – 1.97 (m, 2H), 1.96 – 1.82 (m, 4H), 1.81 – 1.70 (m, 2H), 1.69 – 1.51 (m, 4H), 1.49 – 1.23 (m, 12H), 0.93 (t,  $J = 7.3$  Hz, 3H), 0.83 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  178.9, 174.0, 173.0, 154.7, 144.0, 138.1, 121.8, 121.5, 117.0, 107.5, 82.3, 49.9, 43.9, 42.9, 42.8, 38.1, 36.7, 34.3, 30.4, 29.8, 27.6, 27.2, 26.8, 26.1, 25.9, 25.8, 23.3, 22.3, 13.8, 12.0 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{32}\text{H}_{42}\text{O}_4+\text{H}]^+$  491.3156, found 491.3154.



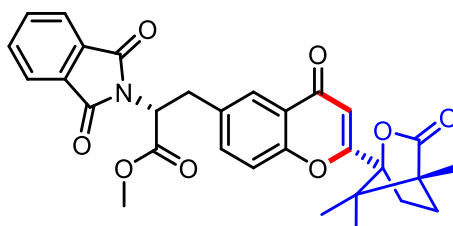
**3-(1-(4-isobutylphenyl)ethyl)-1H-benzo[f]chromen-1-one (6):**

55.7 mg, 78% yield; Light yellow solid, **m. p.** 91–92 °C;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  10.01 (d,  $J = 8.6$  Hz, 1H), 7.99 (d,  $J = 9.1$  Hz, 1H), 7.84 (d,  $J = 8.0$  Hz, 1H), 7.76 – 7.65 (m, 1H), 7.62 – 7.51 (m, 1H), 7.42 (d,  $J = 9.1$  Hz, 1H), 7.24 (d,  $J = 7.0$  Hz, 2H), 7.12 (d,  $J = 7.6$  Hz, 2H), 6.38 (s, 1H), 4.10 – 3.98 (m, 1H), 2.45 (d,  $J = 7.1$  Hz, 2H), 1.93 – 1.77 (m, 1H), 1.69 (d,  $J = 7.2$  Hz, 3H), 0.89 (d,  $J = 6.5$  Hz, 6H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  180.5, 169.1, 157.6, 140.9, 138.3, 135.1, 130.5, 129.6, 129.1, 128.0, 127.3, 127.1, 126.4, 117.6, 116.9, 112.1, 45.0, 43.4, 30.2, 22.4, 18.9 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{25}\text{H}_{24}\text{O}_2+\text{H}]^+$  357.1849, found 357.1844.



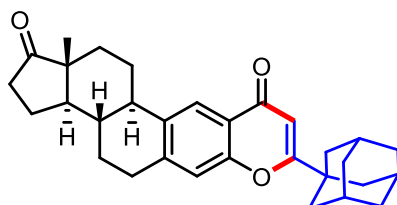
**3-((1S,4R)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptan-1-yl)-1H-benzo[f]chromen-1-one (7):**

49.5 mg, 71% yield; Brown solid, **m. p.** 132–133 °C;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  10.01 (d,  $J = 8.5$  Hz, 1H), 8.10 (d,  $J = 9.0$  Hz, 1H), 7.90 (d,  $J = 7.8$  Hz, 1H), 7.81 – 7.70 (m, 1H), 7.68 – 7.56 (m, 1H), 7.48 (d,  $J = 9.0$  Hz, 1H), 6.72 (s, 1H), 2.78 – 2.63 (m, 1H), 2.20 – 1.98 (m, 2H), 1.91 – 1.77 (m, 1H), 1.18 (d,  $J = 7.0$  Hz, 6H), 0.96 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  179.3, 178.0, 159.6, 157.2, 135.8, 130.7, 130.3, 129.5, 128.2, 127.1, 126.9, 117.3, 117.2, 113.2, 90.3, 55.3, 54.5, 30.7, 28.9, 17.0, 16.8, 10.0 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{22}\text{H}_{20}\text{O}_4+\text{H}]^+$  349.1434, found 349.1435.



**methyl (R)-2-(1,3-dioxoisindolin-2-yl)-3-(4-oxo-2-((1S,4R)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptan-1-yl)-4H-chromen-6-yl)propanoate (8):**

54.1 mg, 51% yield; Brown solid, **m. p.** 63–64 °C;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 (d,  $J = 6.8$  Hz, 1H), 7.75 (d,  $J = 21.5$  Hz, 4H), 7.58 – 7.48 (m, 1H), 7.33 – 7.25 (m, 1H), 6.48 (s, 1H), 5.16 (dd,  $J = 10.3, 4.9$  Hz, 1H), 3.79 (s, 3H), 3.74 – 3.55 (m, 2H), 2.69 – 2.52 (m, 1H), 2.14 – 1.91 (m, 2H), 1.88 – 1.71 (m, 1H), 1.16 (s, 3H), 1.11 (s, 3H) 0.90 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  177.8, 177.0, 168.9, 167.4, 162.2, 154.9, 134.7, 134.5, 134.3, 131.5, 126.0, 123.9, 123.7, 118.2, 110.2, 90.4, 55.3, 54.5, 53.2, 53.1, 34.3, 30.8, 28.8, 17.0, 16.7, 9.9 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{30}\text{H}_{27}\text{NO}_8+\text{H}]^+$  530.1809, found 530.1817.



**(3aR,3bS,11bR,13aR)-8-((3R,5R,7R)-adamantan-1-yl)-13a-methyl-2,3,3a,3b,4,5,11b,12,13,13a-decahydrocyclopenta[5,6]naphtho[1,2-g]chromene-1,10-dione (9):**

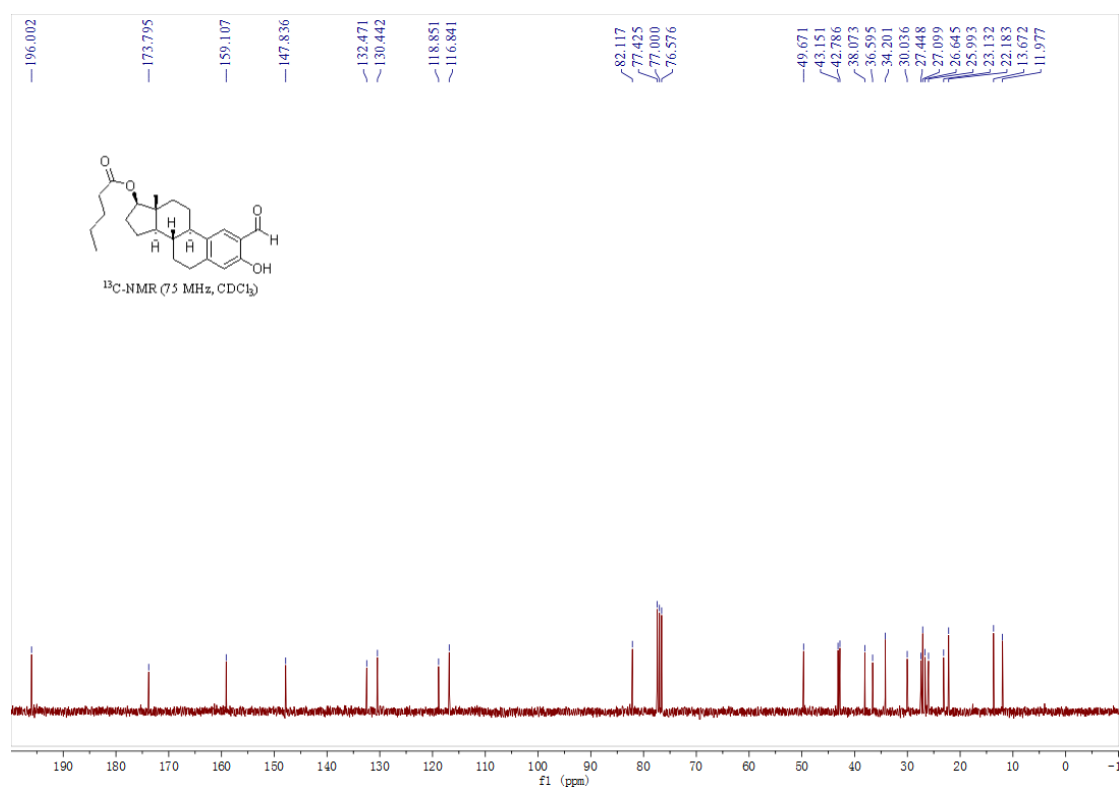
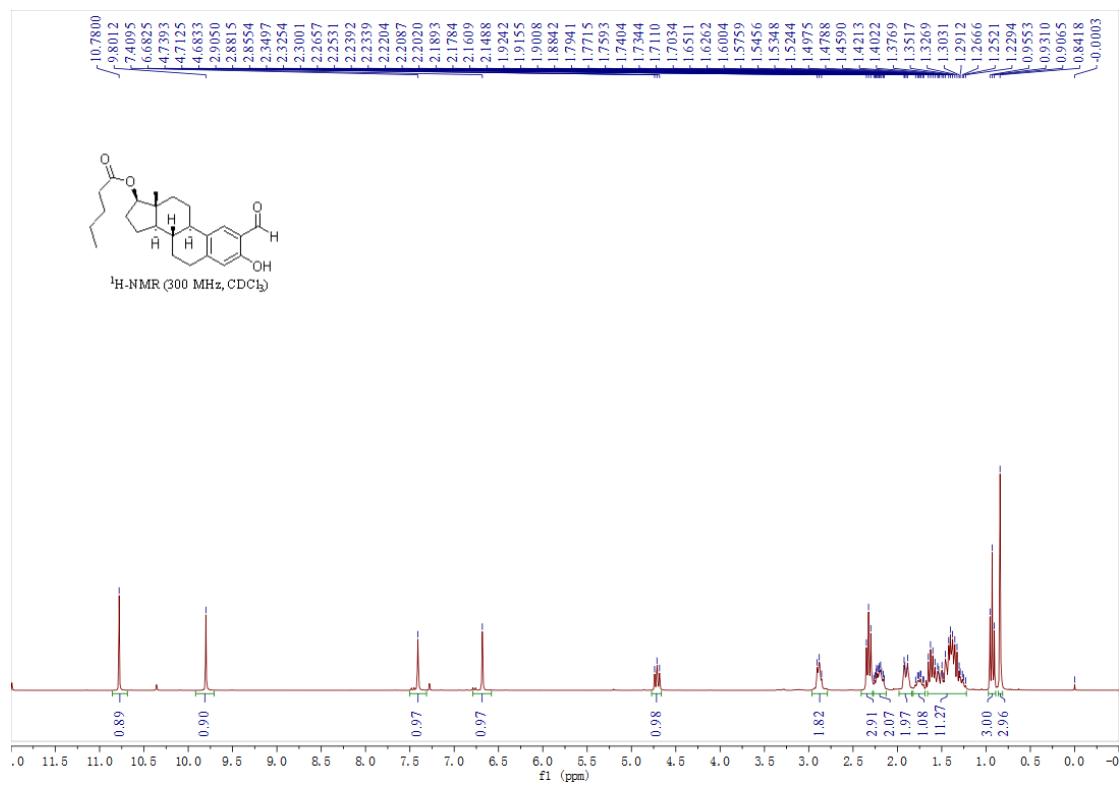
61.0 mg, 67% yield; Light yellow solid, **m. p.** Carbonization;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 (s, 1H), 7.20 (s, 1H), 6.14 (s, 1H), 3.14 – 2.88 (m, 2H), 2.69 – 2.42 (m, 2H), 2.41 – 2.25 (m, 1H), 2.24 – 1.86 (m, 13H), 1.85 – 1.41 (m, 12H), 0.91 (s, 3H) ppm;  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  179.1, 175.4, 154.8, 143.7, 137.5, 121.7, 121.4, 117.1, 106.2, 50.5, 47.9, 44.1, 39.5, 38.1, 37.9, 36.5, 35.8, 31.4, 29.6, 28.0, 26.1, 25.8, 21.6, 13.8 ppm; **HRMS (ESI)**  $m/z$  Calcd for  $[\text{C}_{31}\text{H}_{36}\text{O}_3+\text{H}]^+$  457.2737, found 457.2746.

## 7. References

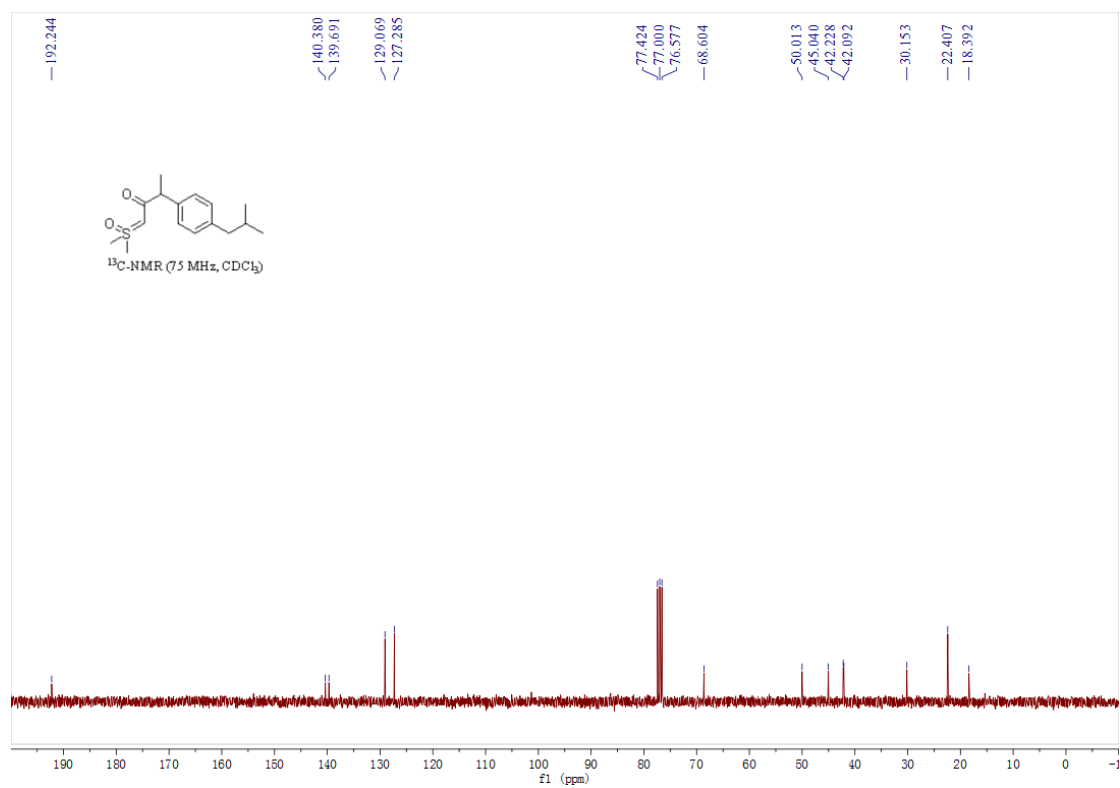
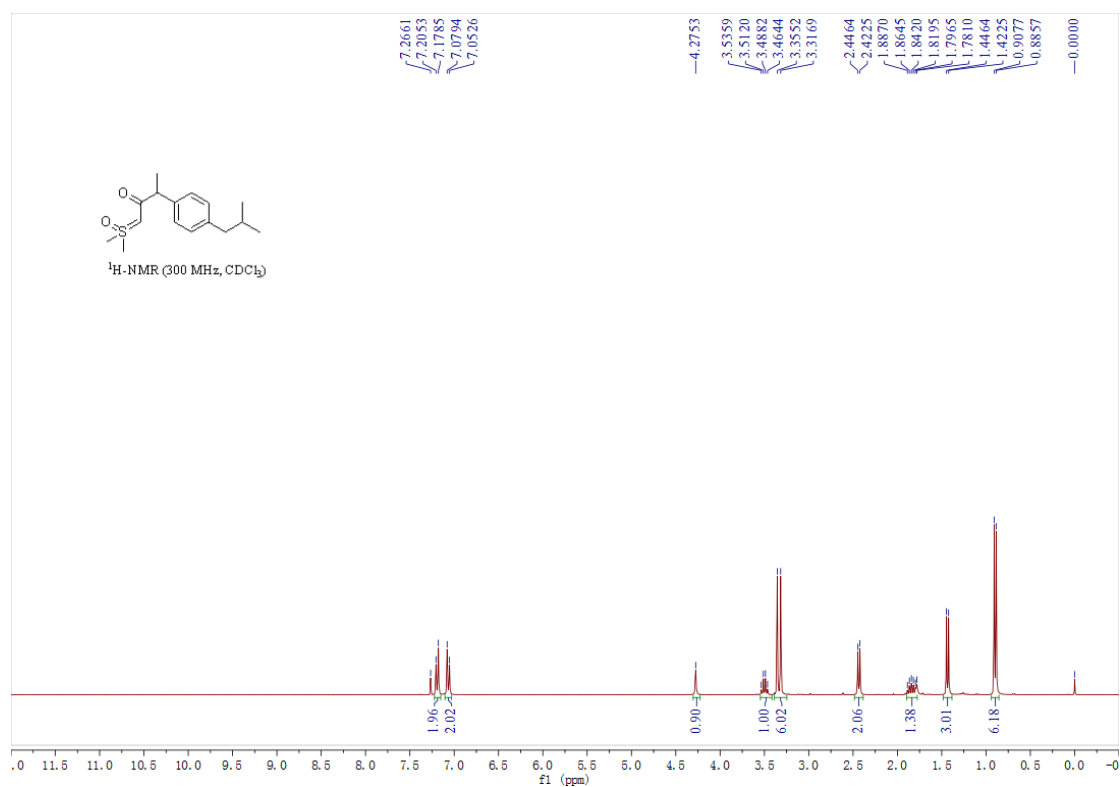
- (1) P. Sun, S. Gao, C. Yang, S. Guo, A. Lin and H Yao, *Org. Lett.*, 2016, **18**, 6464.
- (2) Y. Xu, X. Zhou, G. Zheng and X. Li, *Org. Lett.*, 2017, **19**, 5256.
- (3) T. Kawakami, K. Murakami and K. Itami, *J. Am. Chem. Soc.*, 2015, **137**, 2460.
- (4) H. S. Rho, B.-S. Ko and Y.-S. Ju, *Synthetic Communications*, 2001, **31**, 2101.
- (5) Z. Fang, Y. Ning, P. Mi, P. Liao and X. Bi, *Org. Lett.*, 2014, **16**, 1522.
- (6) X. Wang, S. Zhao, J. Liu, D. Zhu, M. Guo, X. Tang and G. Wang, *Org. Lett.*, 2017, **19**, 4187.
- (7) X.-Q. Pan, J.-P. Zou, G.-L. Zhang and W. Zhang, *Chem. Commun.*, 2010, **46**, 1721.
- (8) D. R. Fandrick, D. Reinhardt, J.-N. Desrosiers, S. Sanyal, K. R. Fandrick, S. Ma, N. Grinberg, H. Lee, J. J. Song and C. H. Senanayake, *Org. Lett.*, 2014, **16**, 2834.
- (9) E. Awuah and A. Capretta, *Org. Lett.*, 2009, **11**, 3210.

## 8. <sup>1</sup>H and <sup>13</sup>C NMR Spectra of Title Compounds

### (8*S*,9*R*,13*R*,14*R*,17*R*)-2-formyl-3-hydroxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl pentanoate

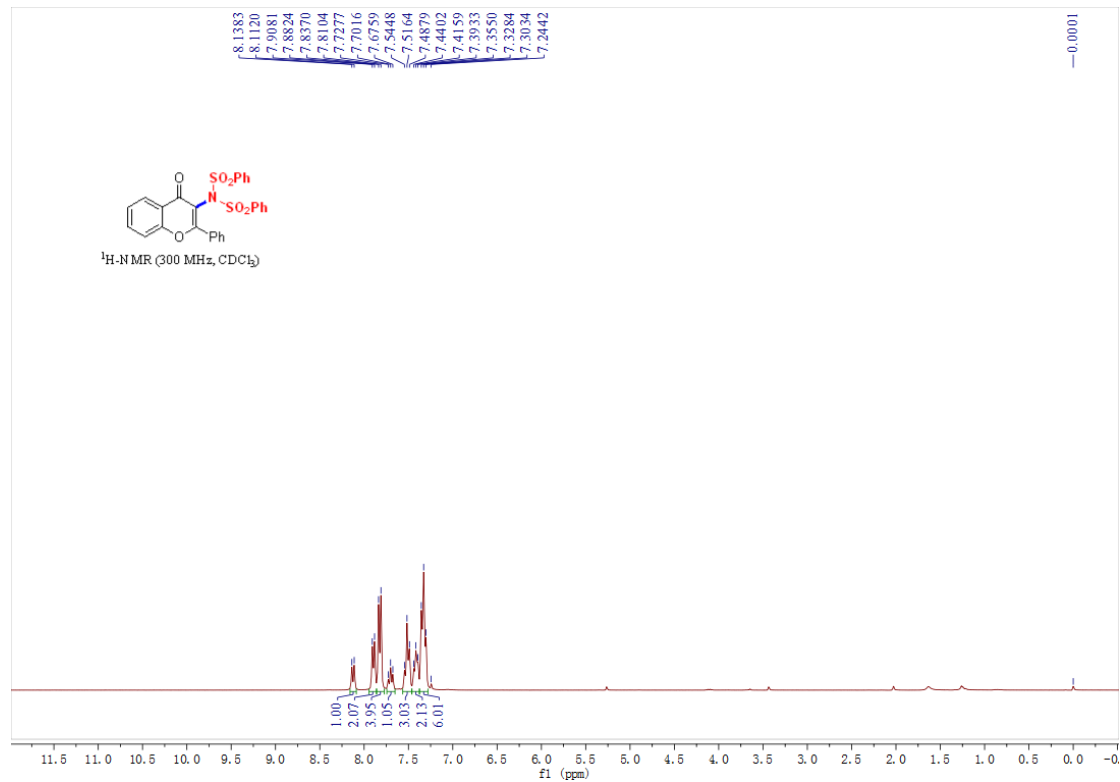


# 1-(dimethyl(oxo)-16-sulfanylidene)-3-(4-isobutylphenyl)butan-2-one

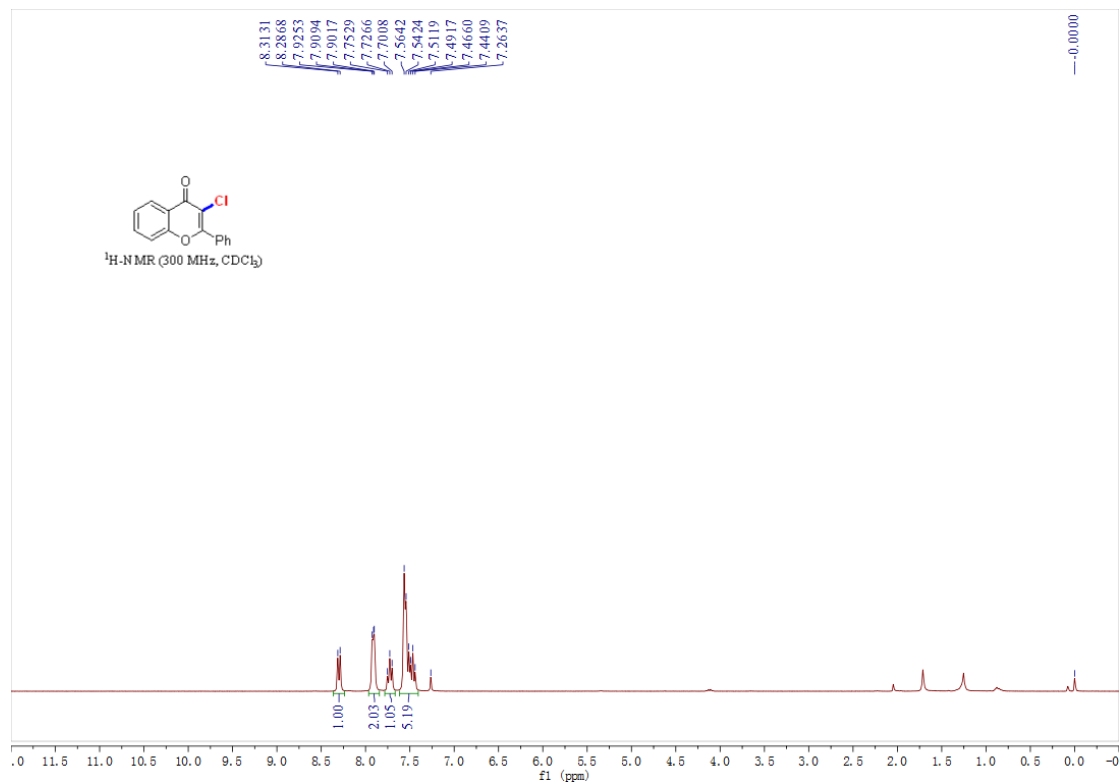


***N*-(4-oxo-2-phenyl-4*H*-chromen-3-yl)-*N*-(phenylsulfonyl)benzenesulfonamide**

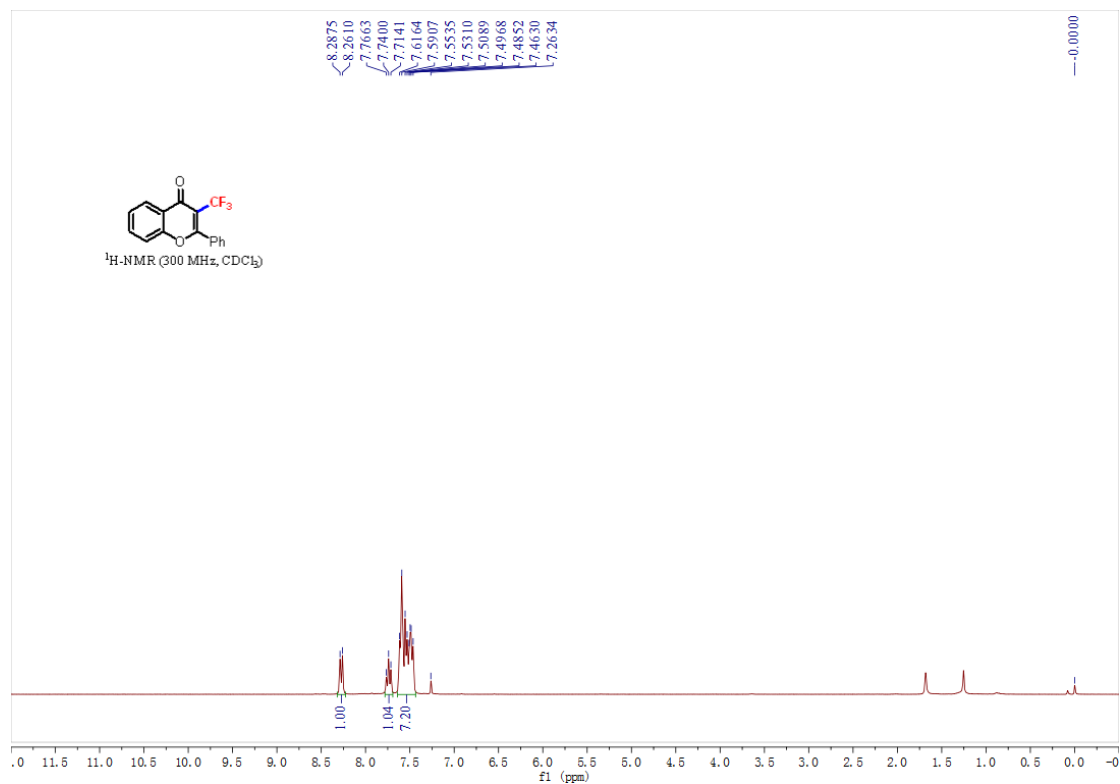
**(10)**



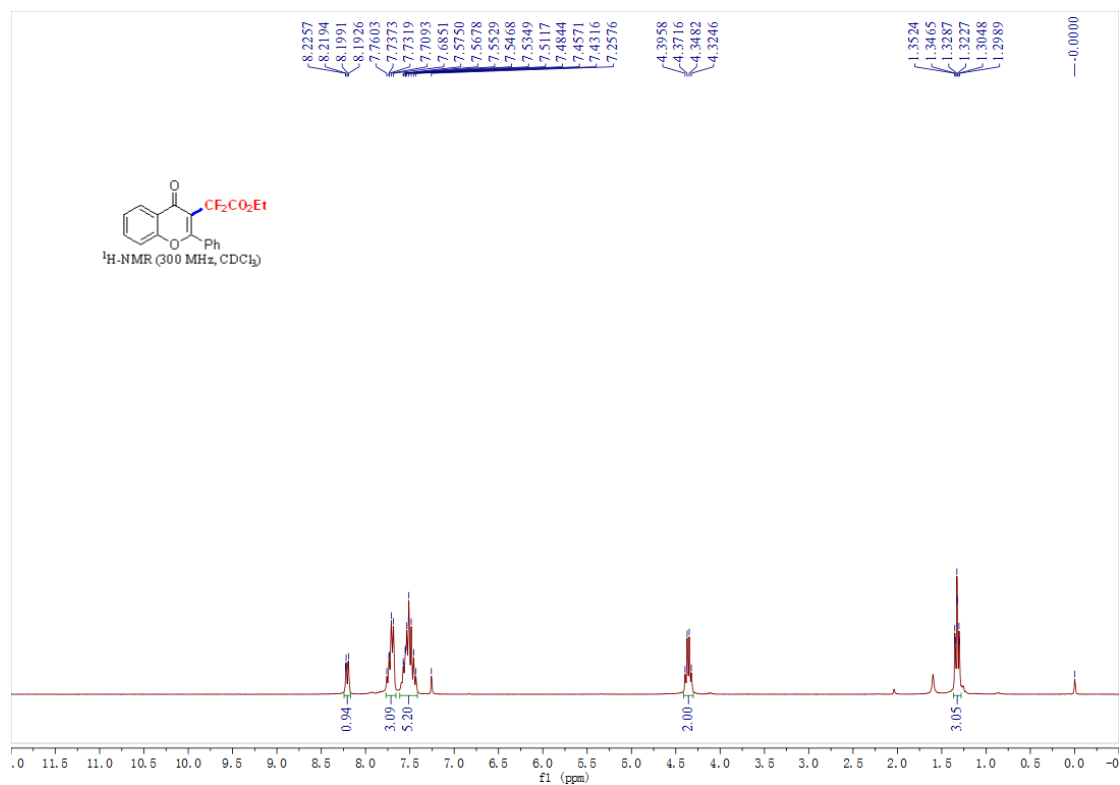
**3-chloro-2-phenyl-4*H*-chromen-4-one (11)**



## 2-phenyl-3-(trifluoromethyl)-4H-chromen-4-one (12)

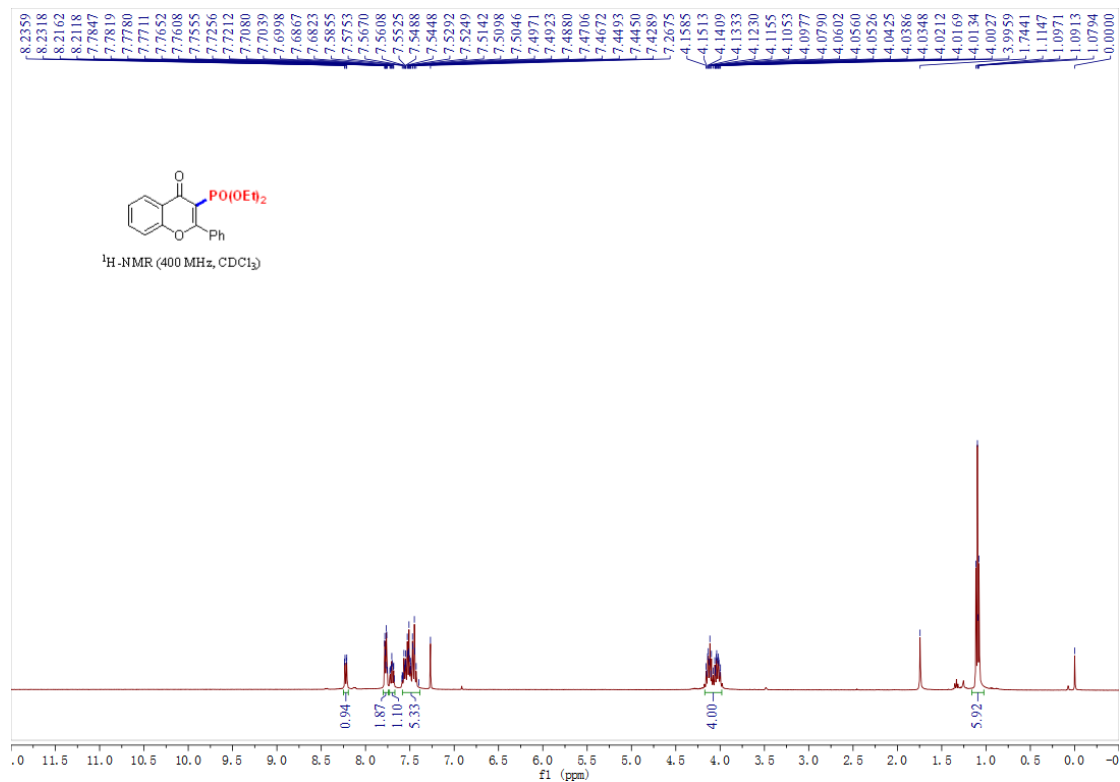


## ethyl 2,2-difluoro-2-(4-oxo-2-phenyl-4H-chromen-3-yl)acetate (13)

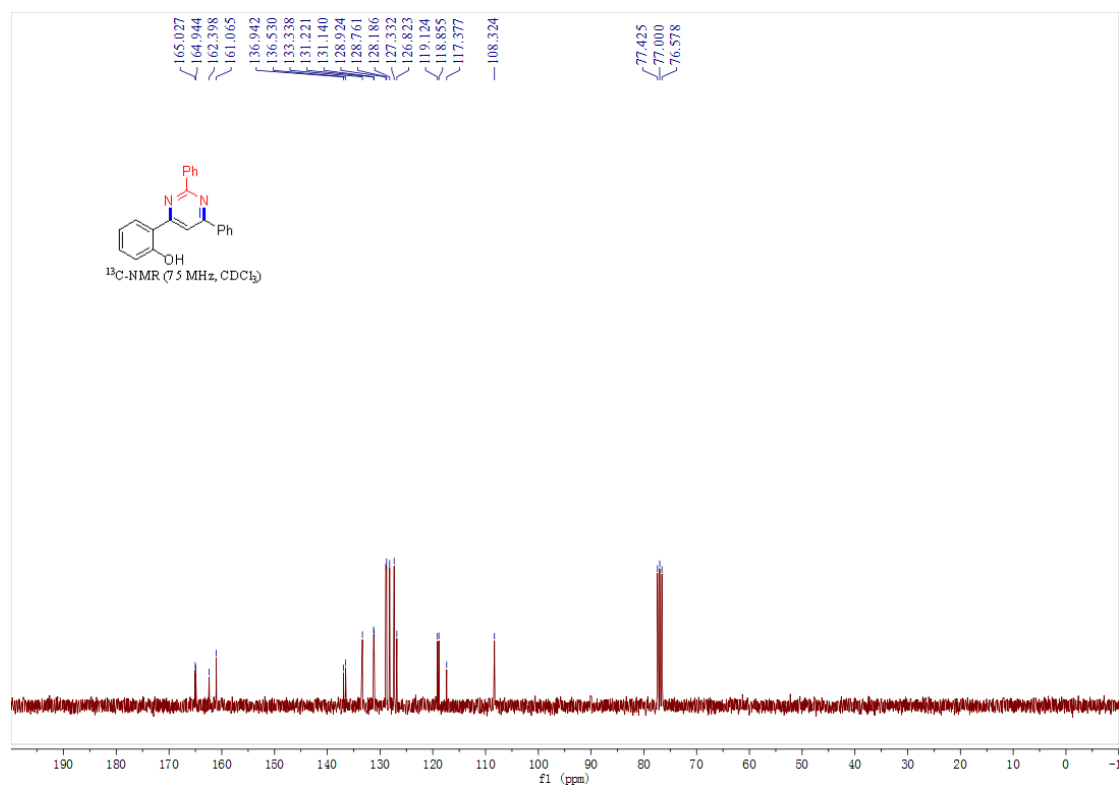
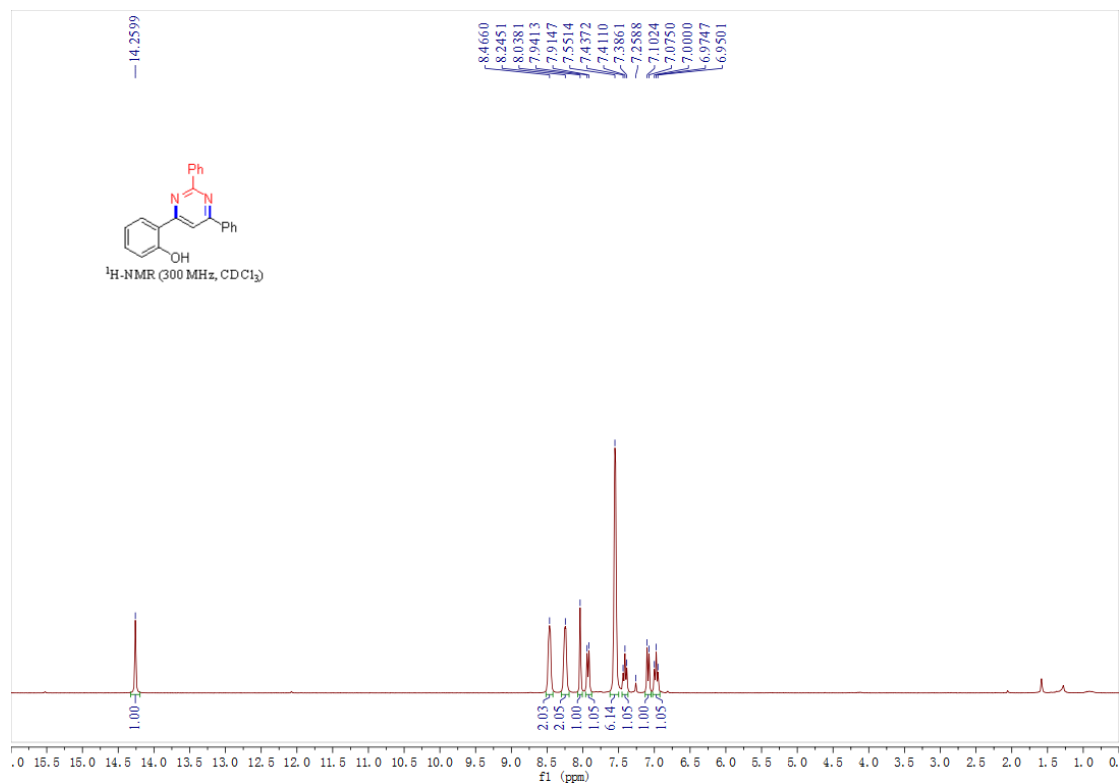




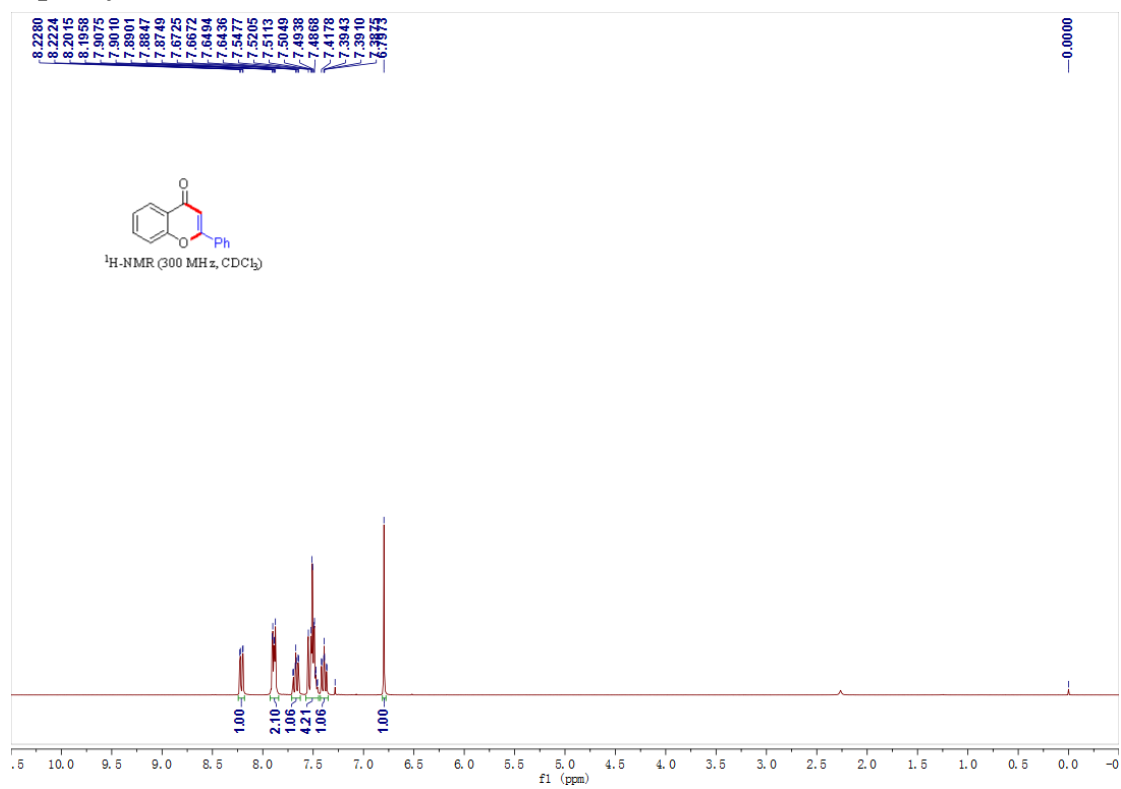
# diethyl (4-oxo-2-phenyl-4H-chromen-3-yl)phosphonate (14)



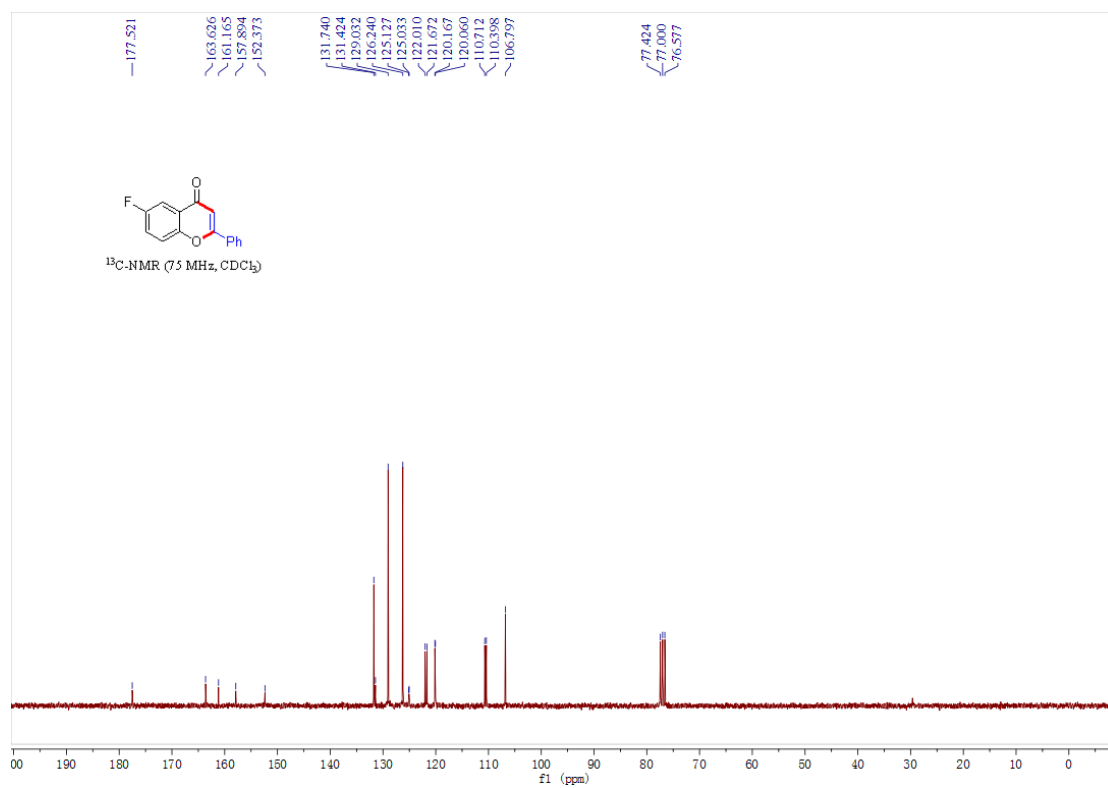
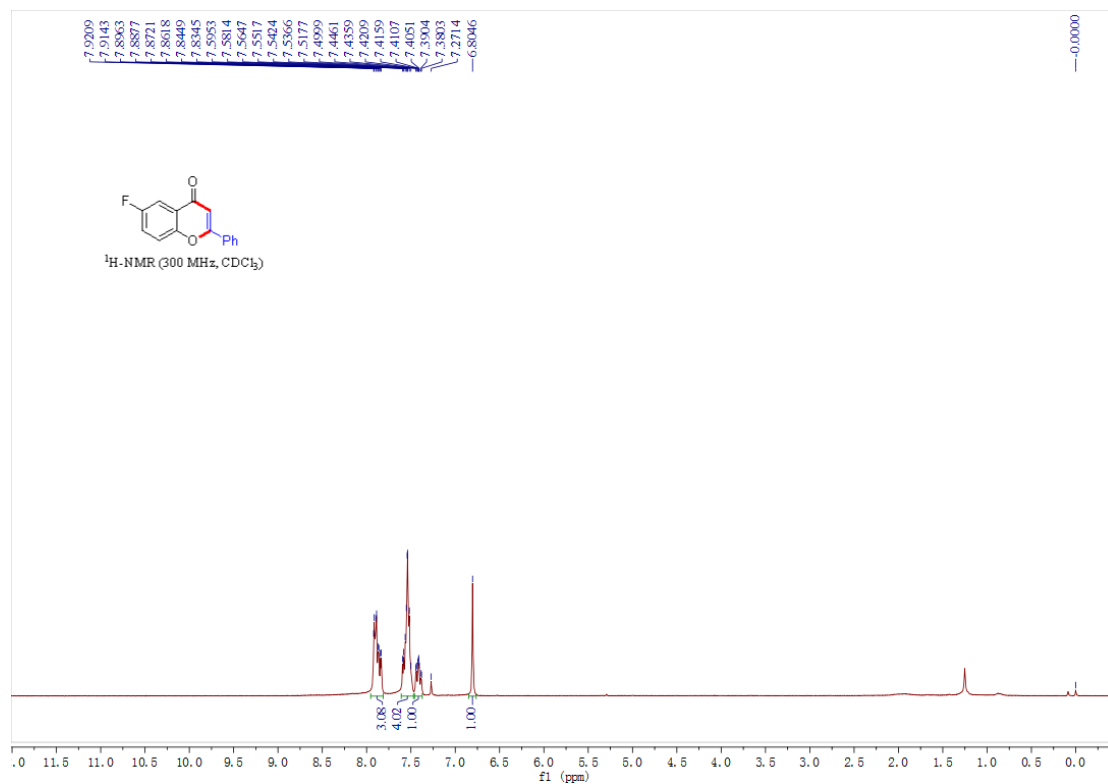
## 2-(2,6-diphenylpyrimidin-4-yl)phenol (15)



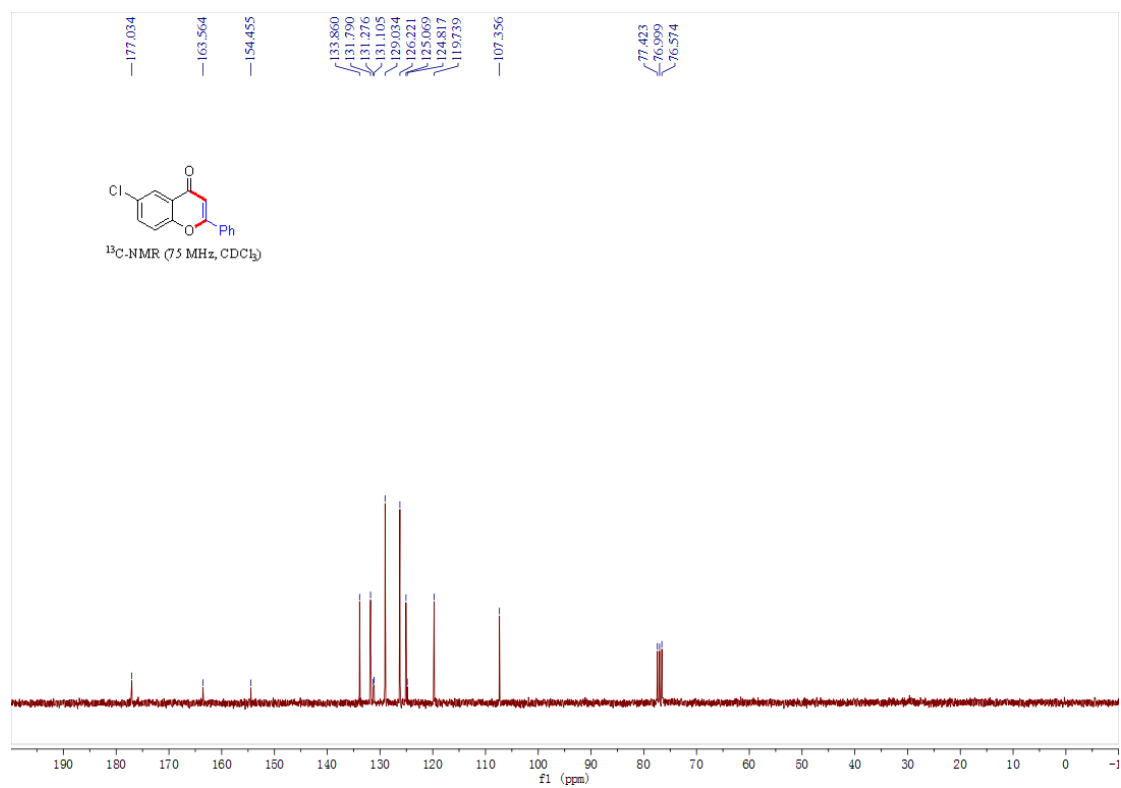
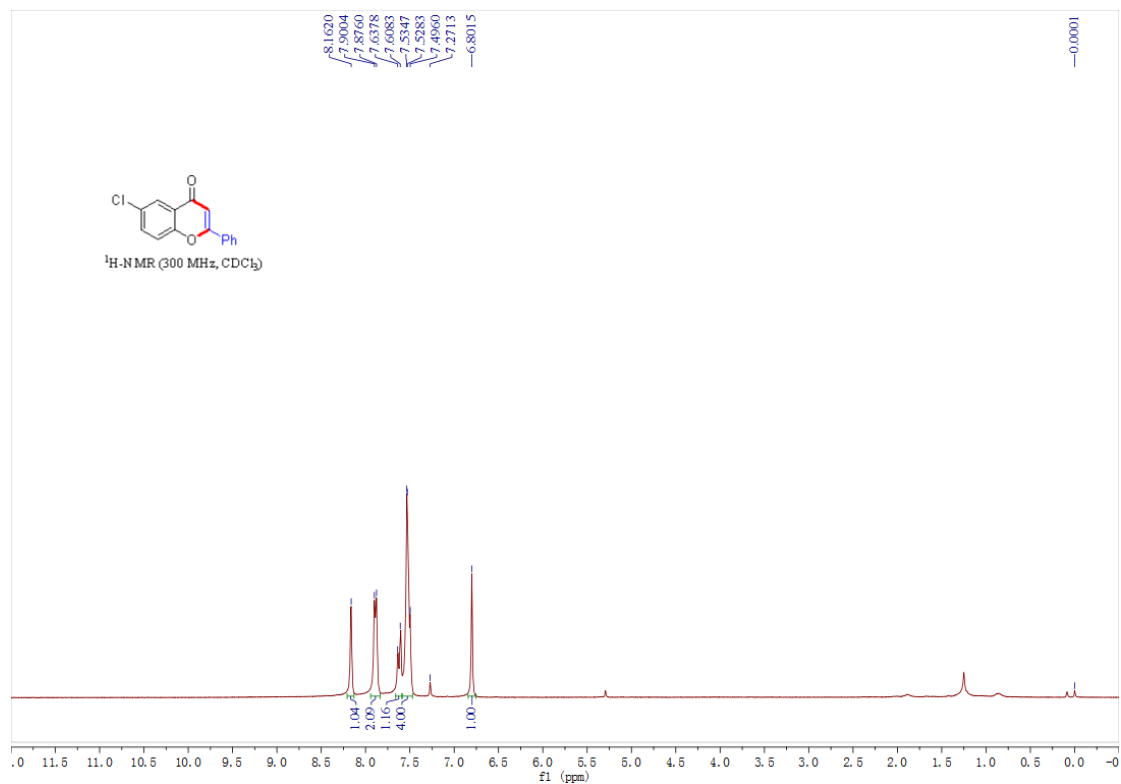
## 2-phenyl-4H-chromen-4-one (3aa)



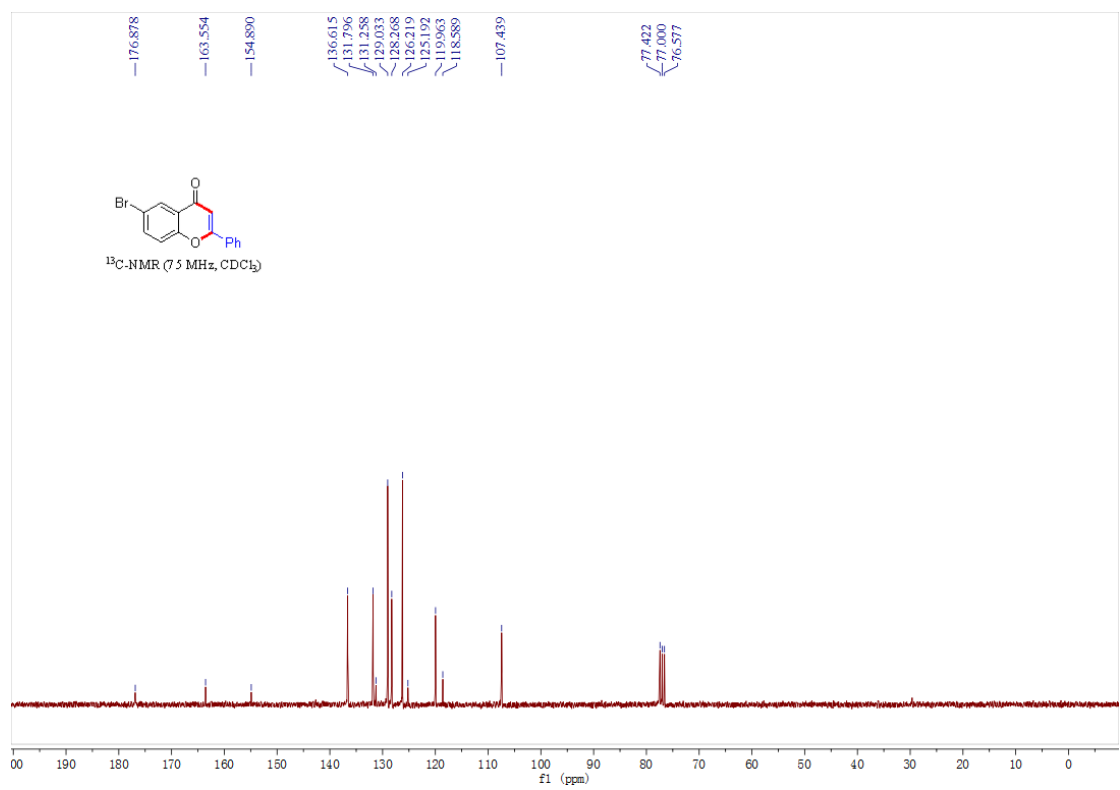
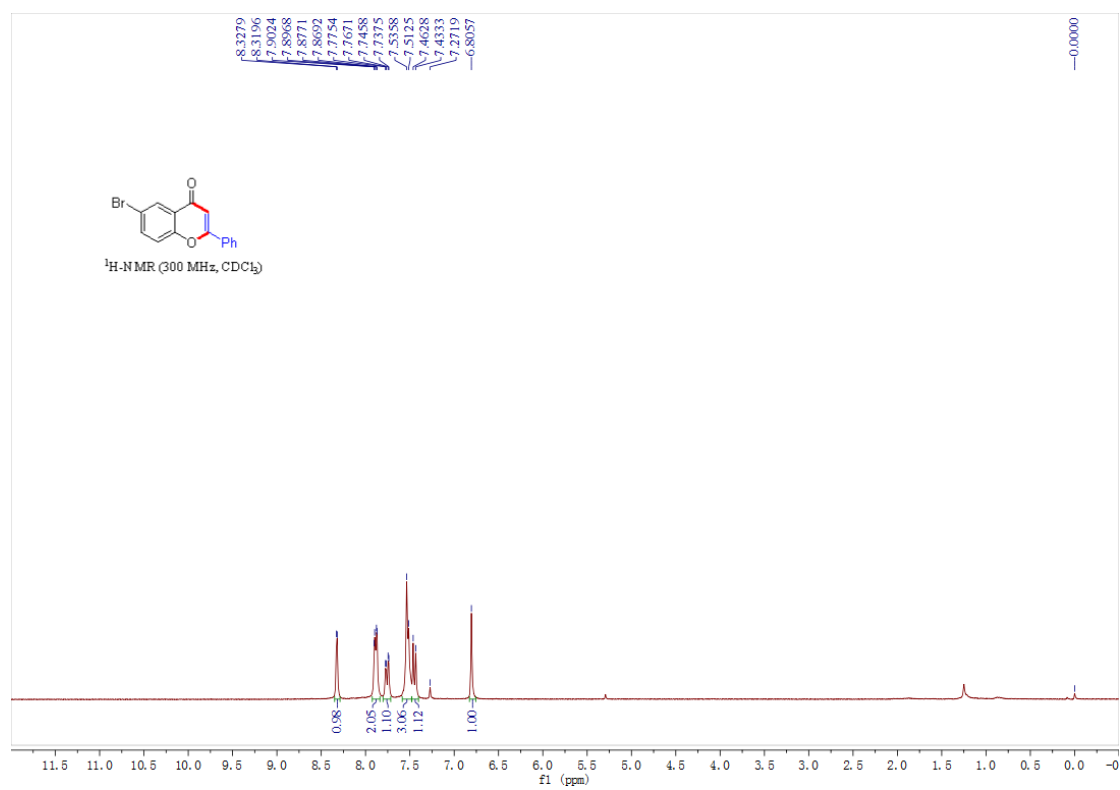
### 6-fluoro-2-phenyl-4H-chromen-4-one (3ba)



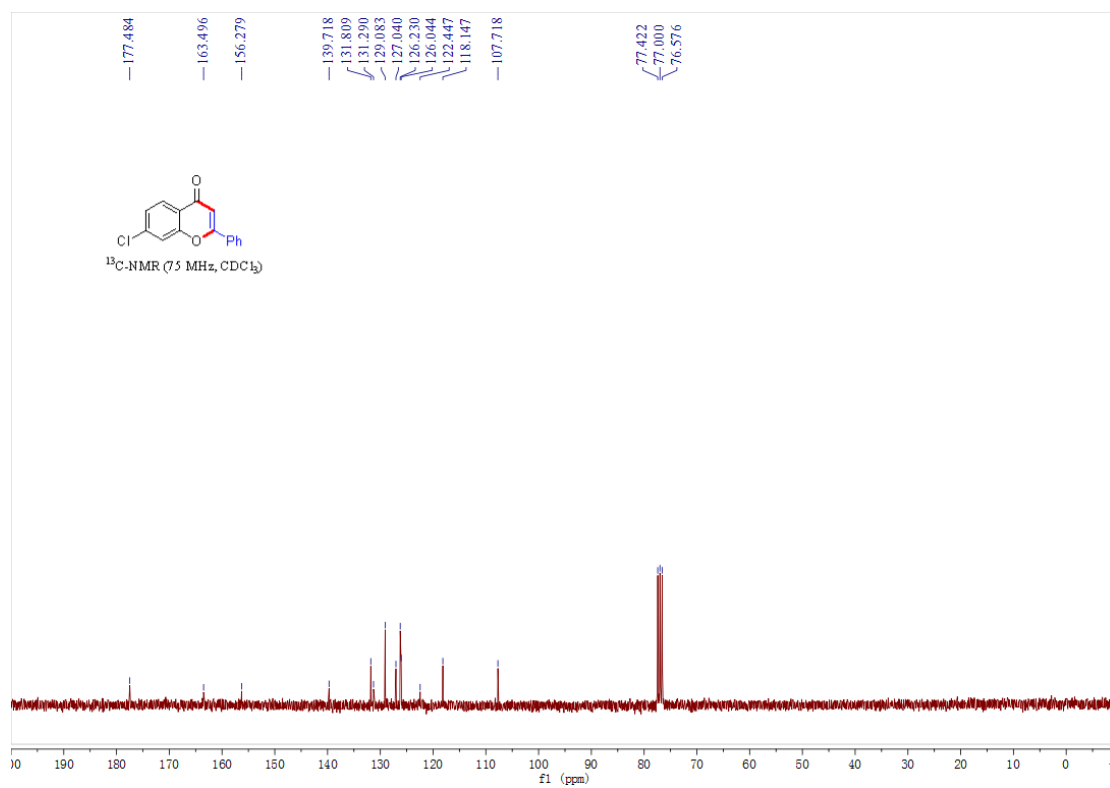
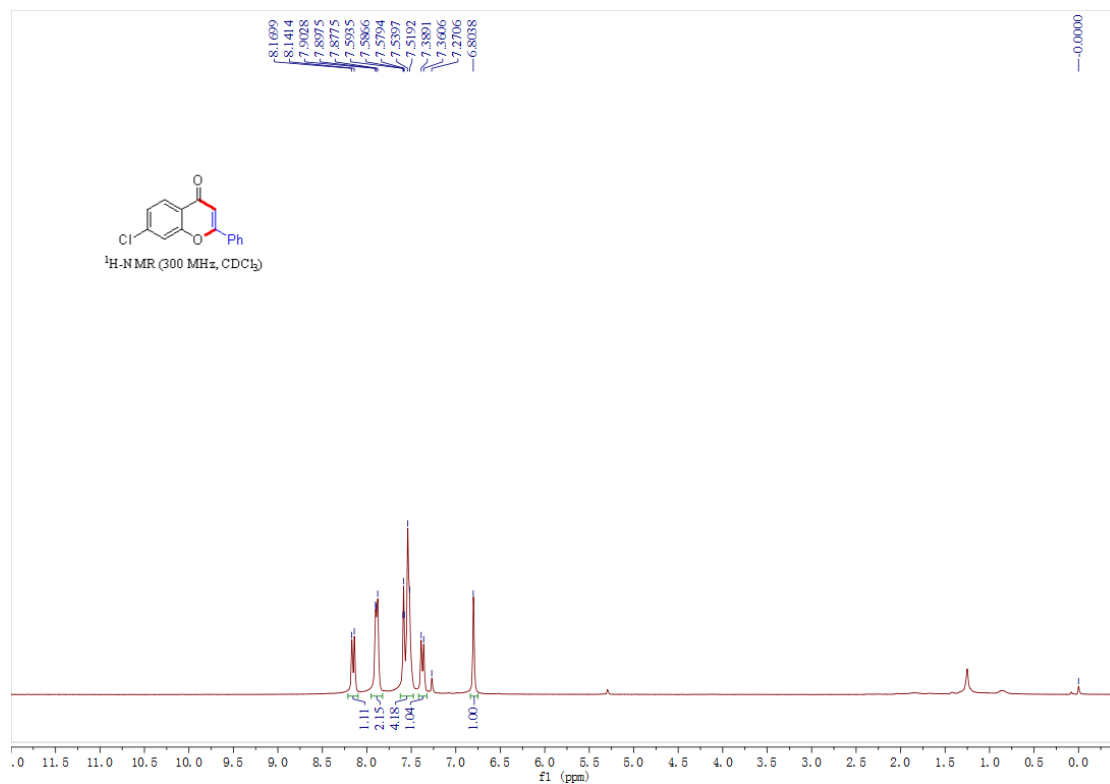
### 6-chloro-2-phenyl-4H-chromen-4-one (3ca)



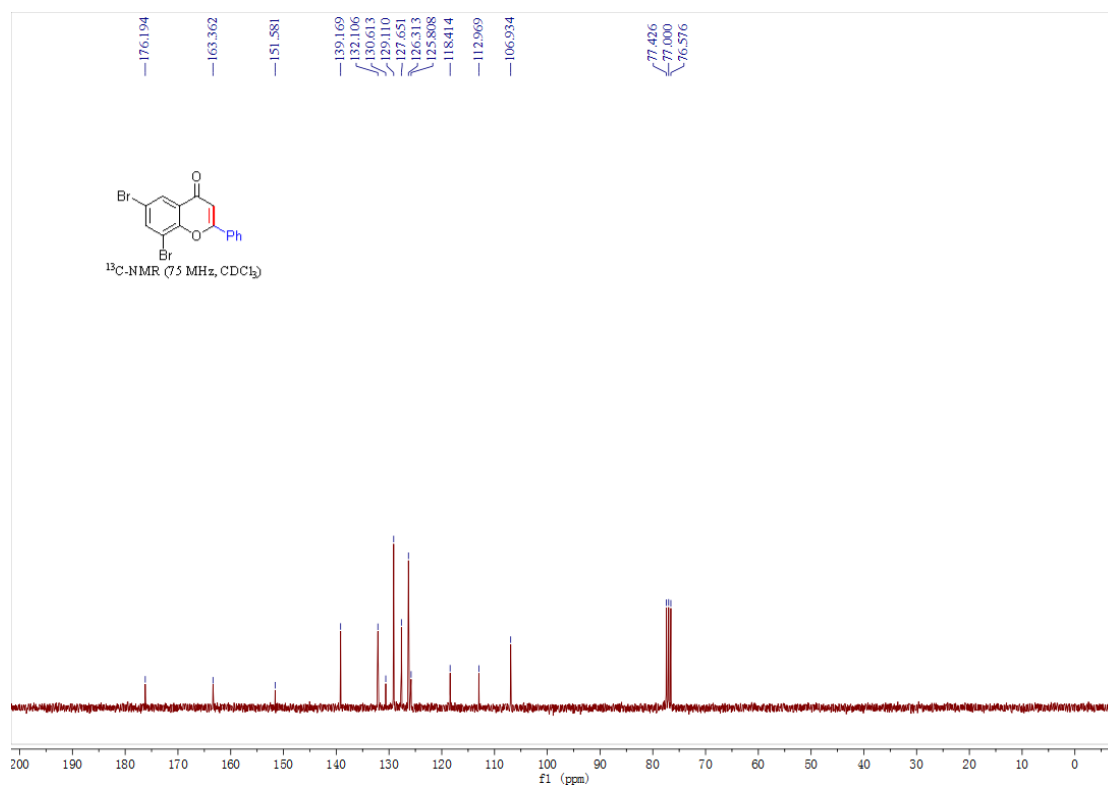
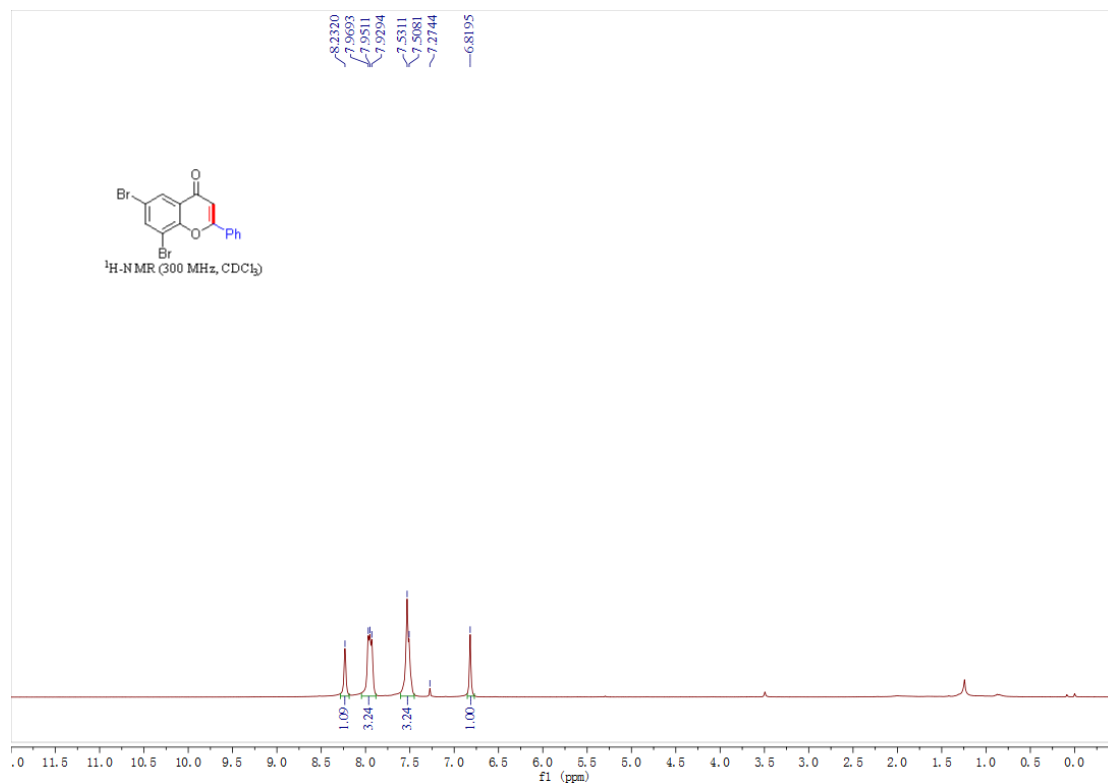
### 6-bromo-2-phenyl-4H-chromen-4-one (3da)



# 7-chloro-2-phenyl-4H-chromen-4-one (3ea)

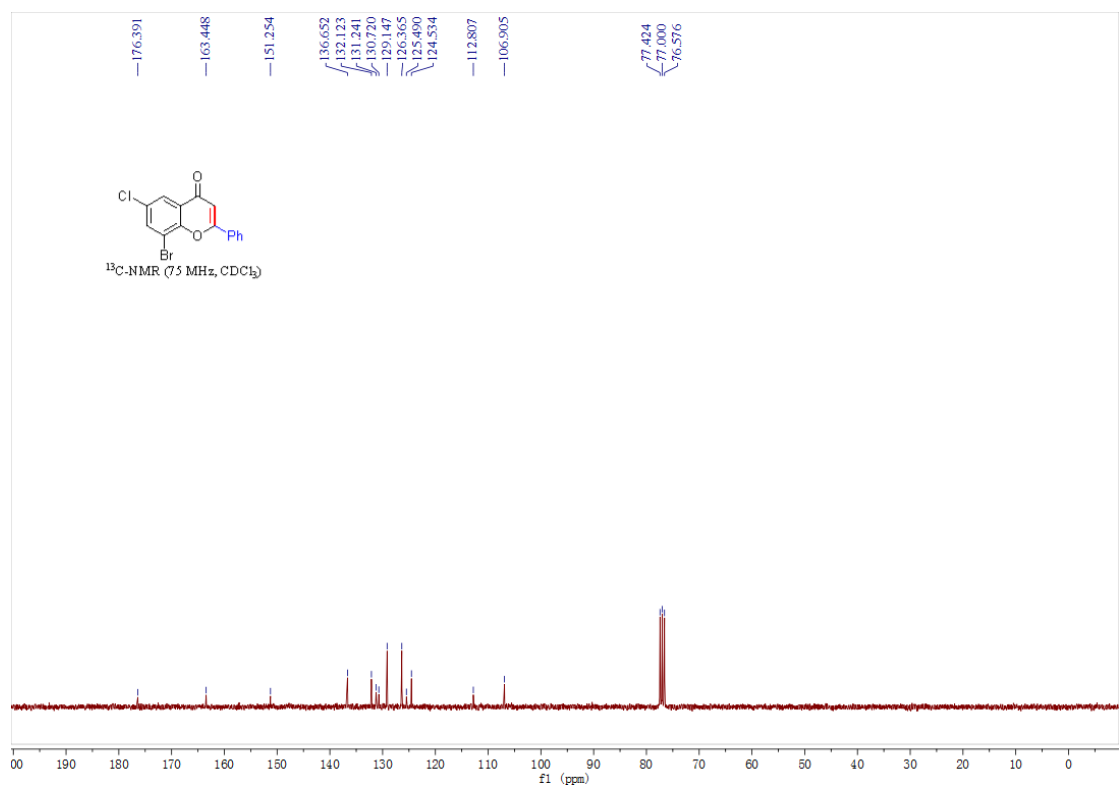
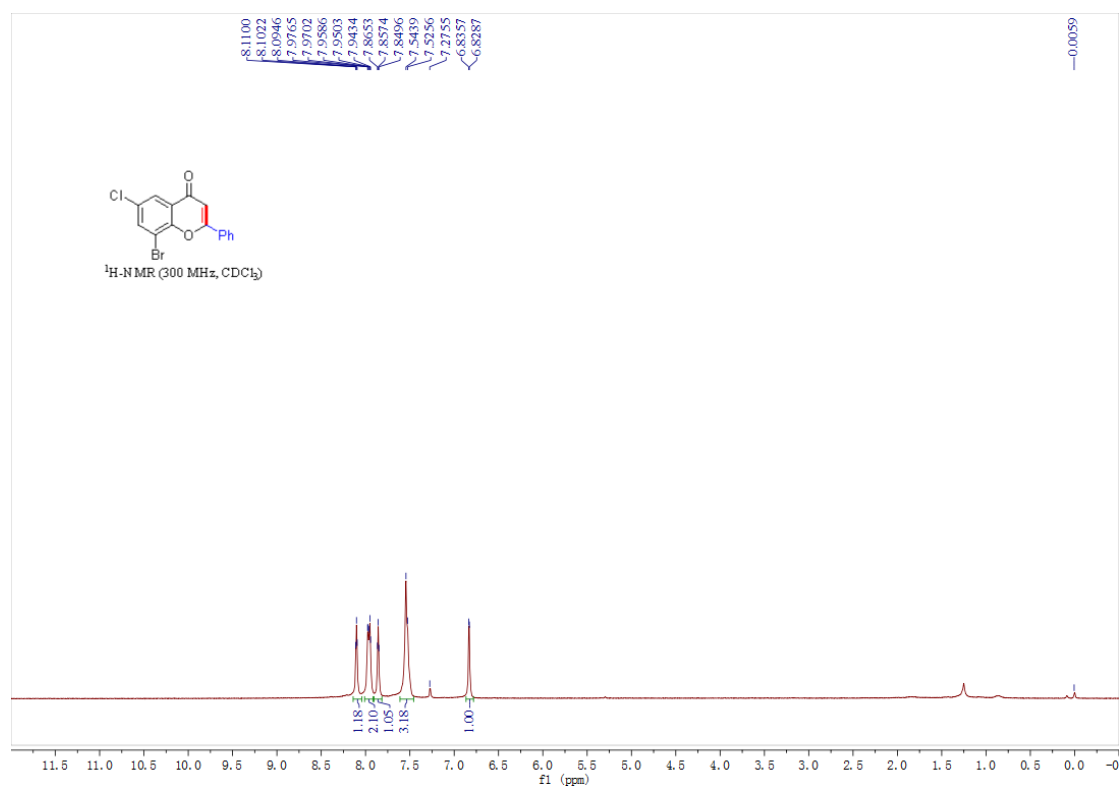


### 6, 8-dibromo-2-phenyl-4H-chromen-4-one (3fa)

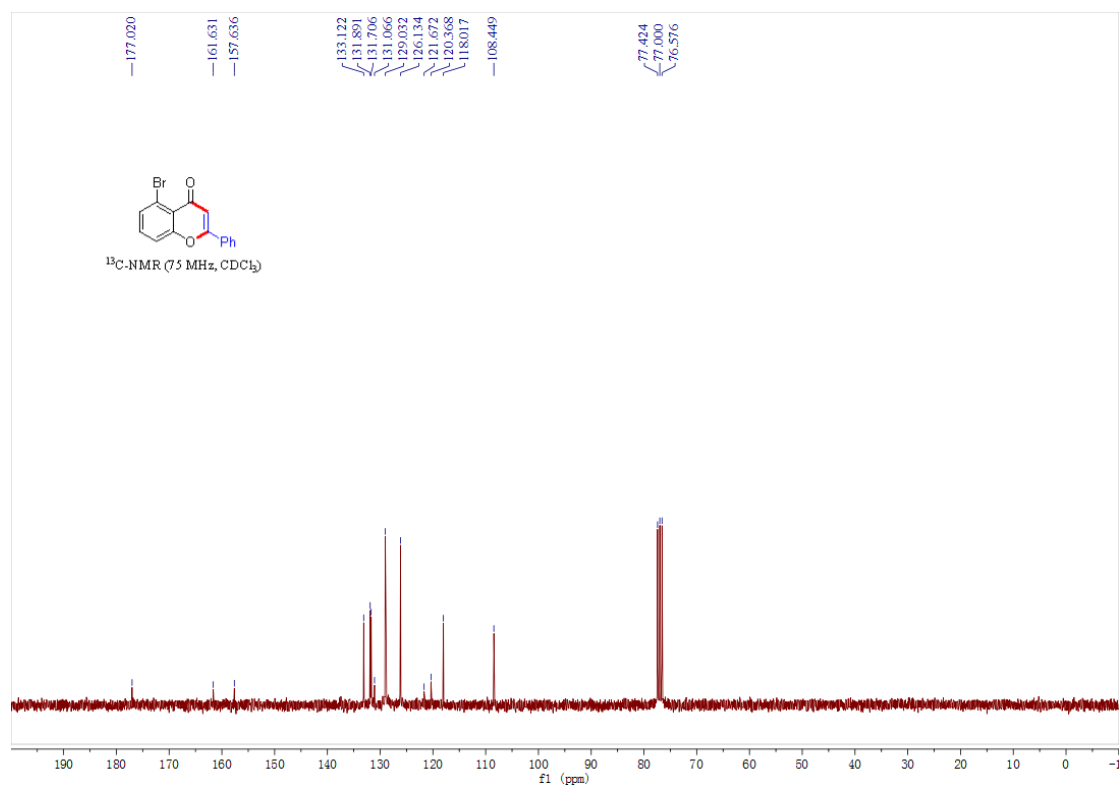
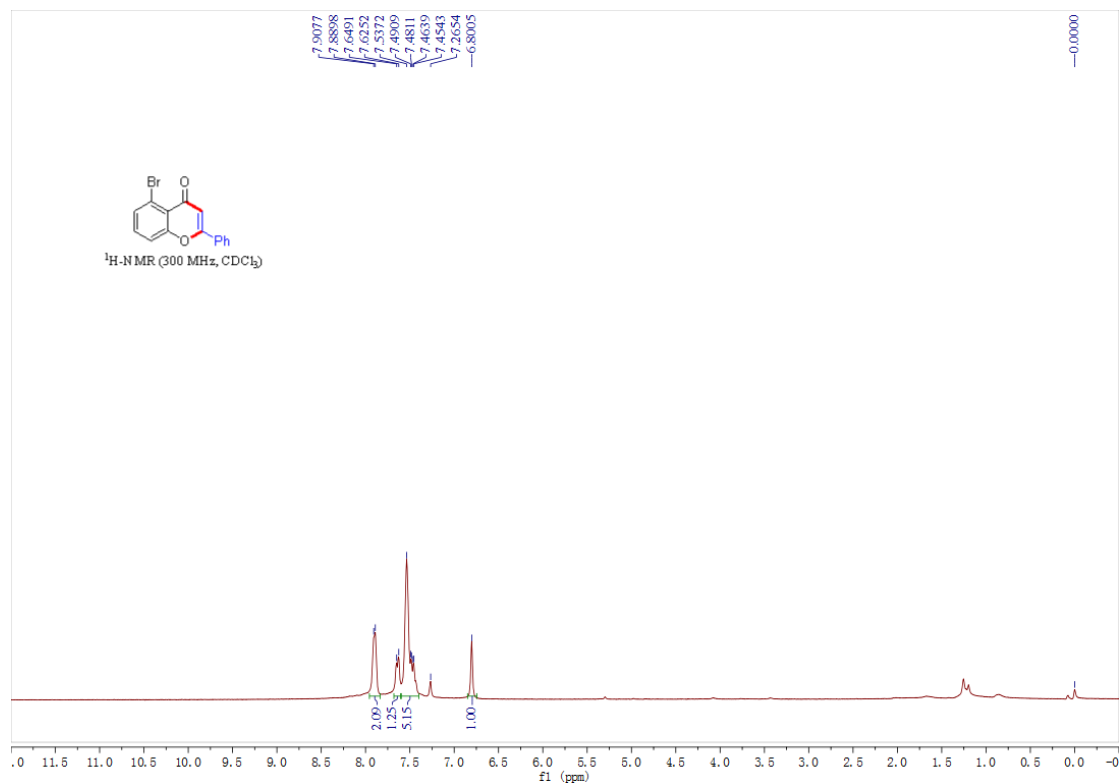




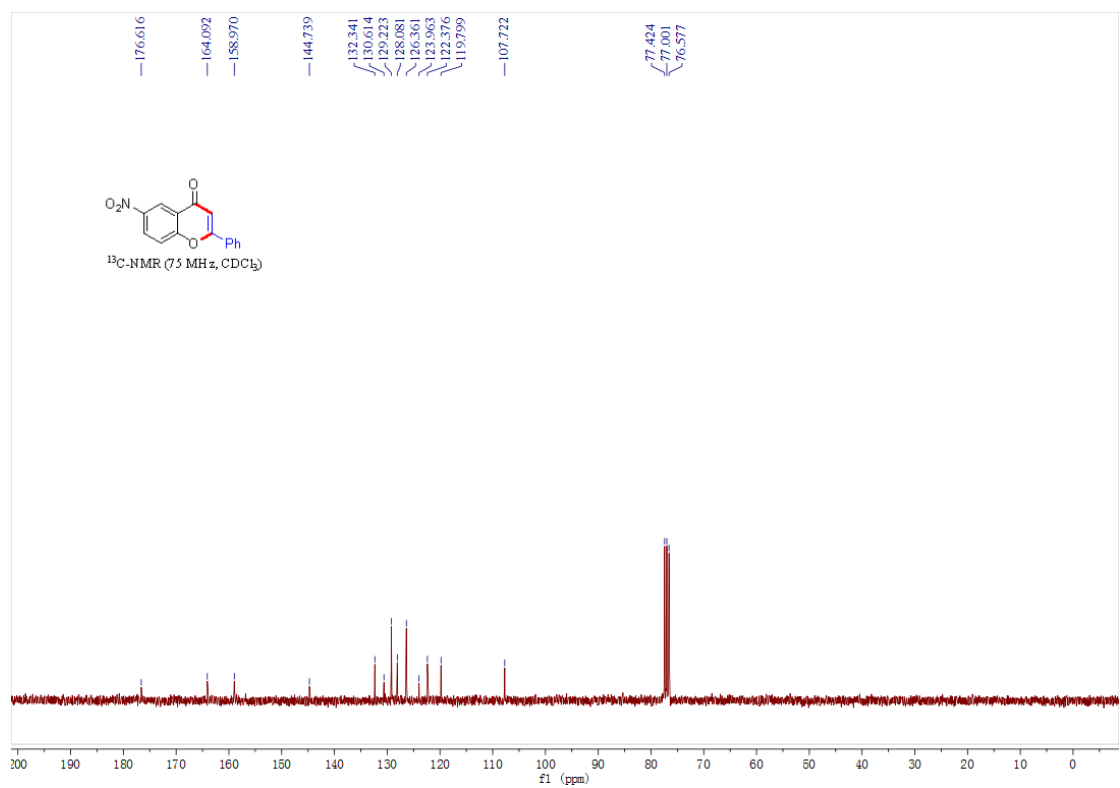
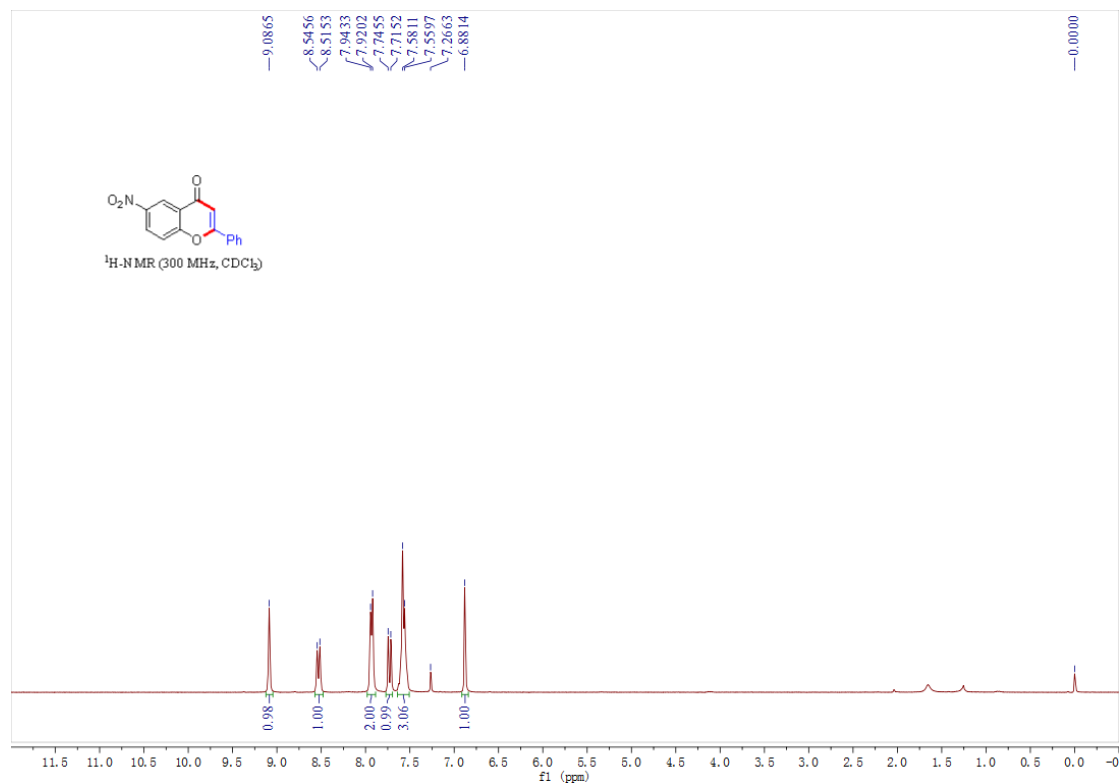
# 8-bromo-6-chloro-2-phenyl-4H-chromen-4-one (3ga)



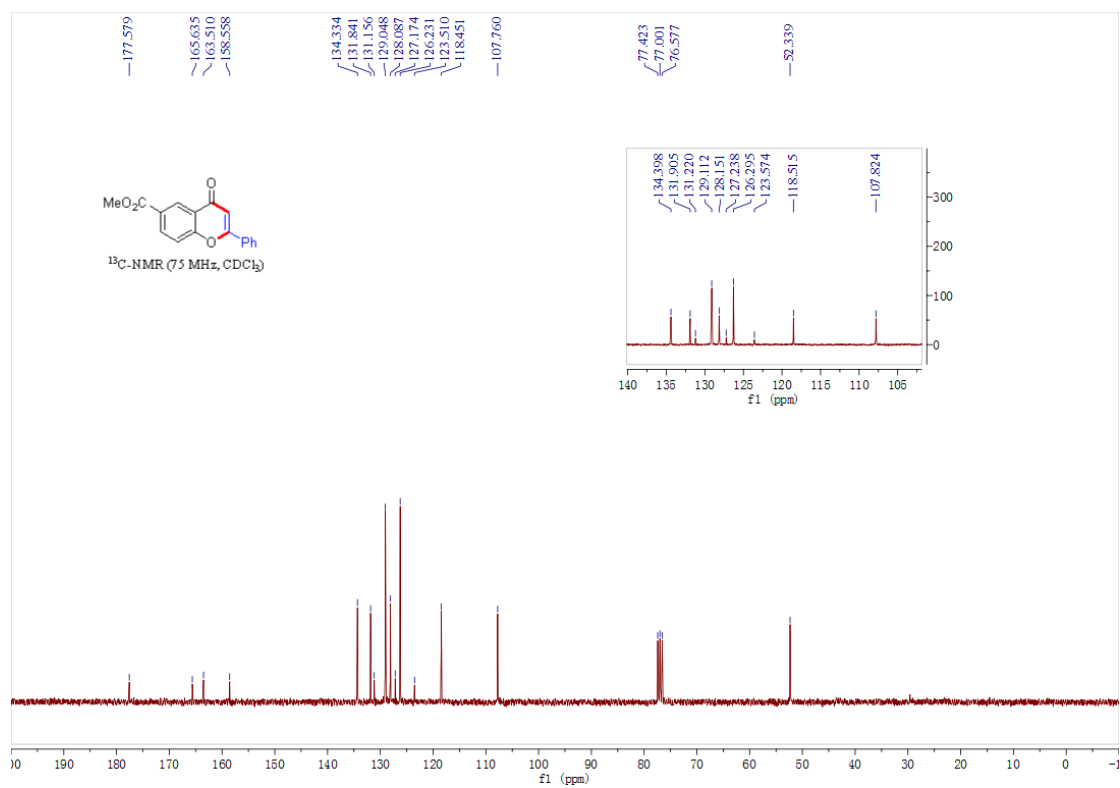
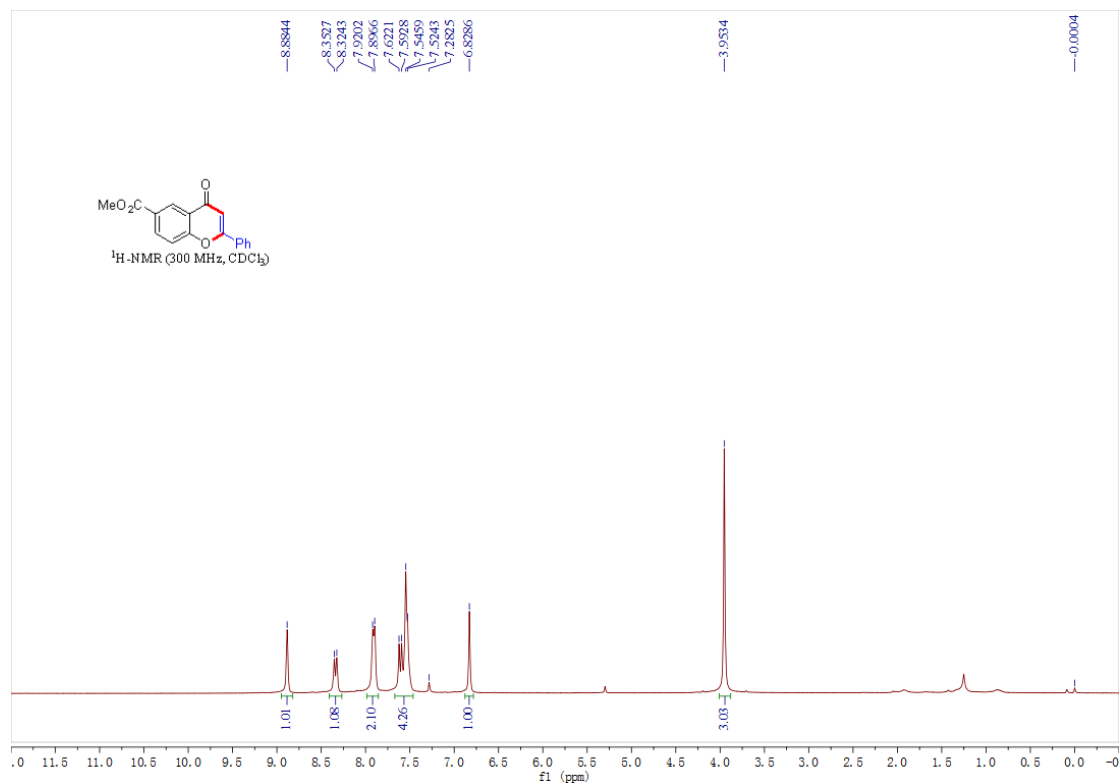
### 5-bromo-2-phenyl-4H-chromen-4-one (3ha)



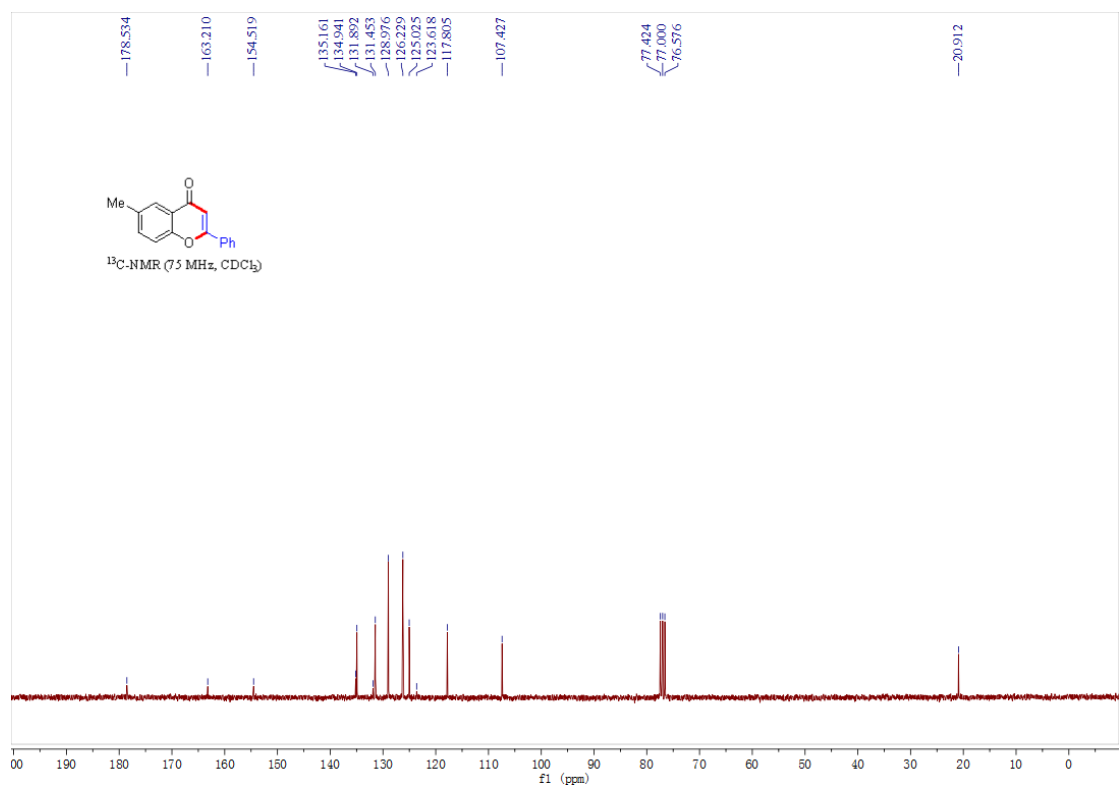
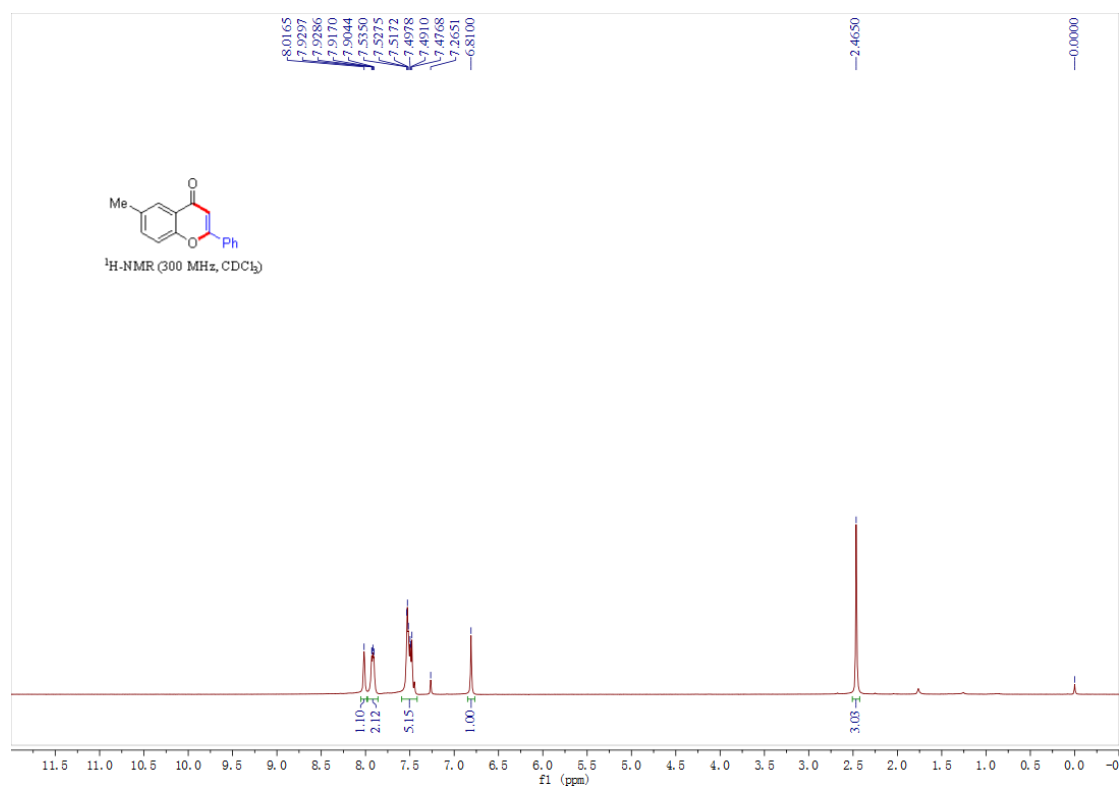
### 6-nitro-2-phenyl-4H-chromen-4-one (3ia)



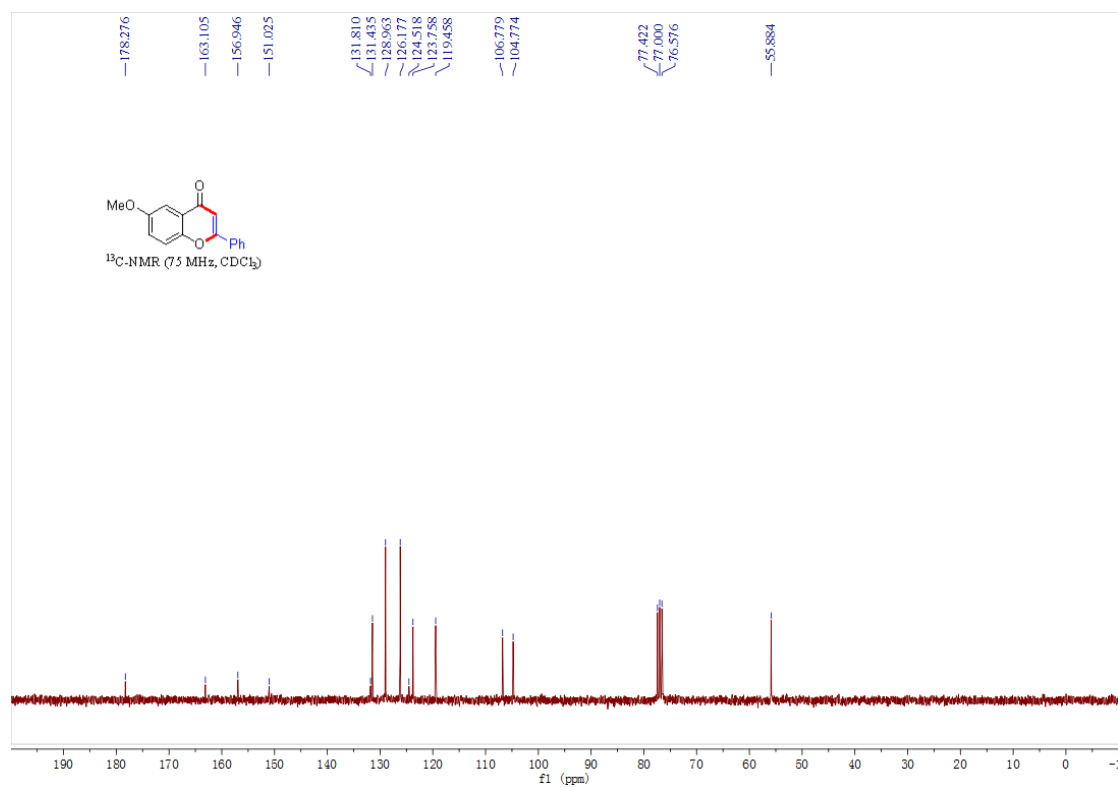
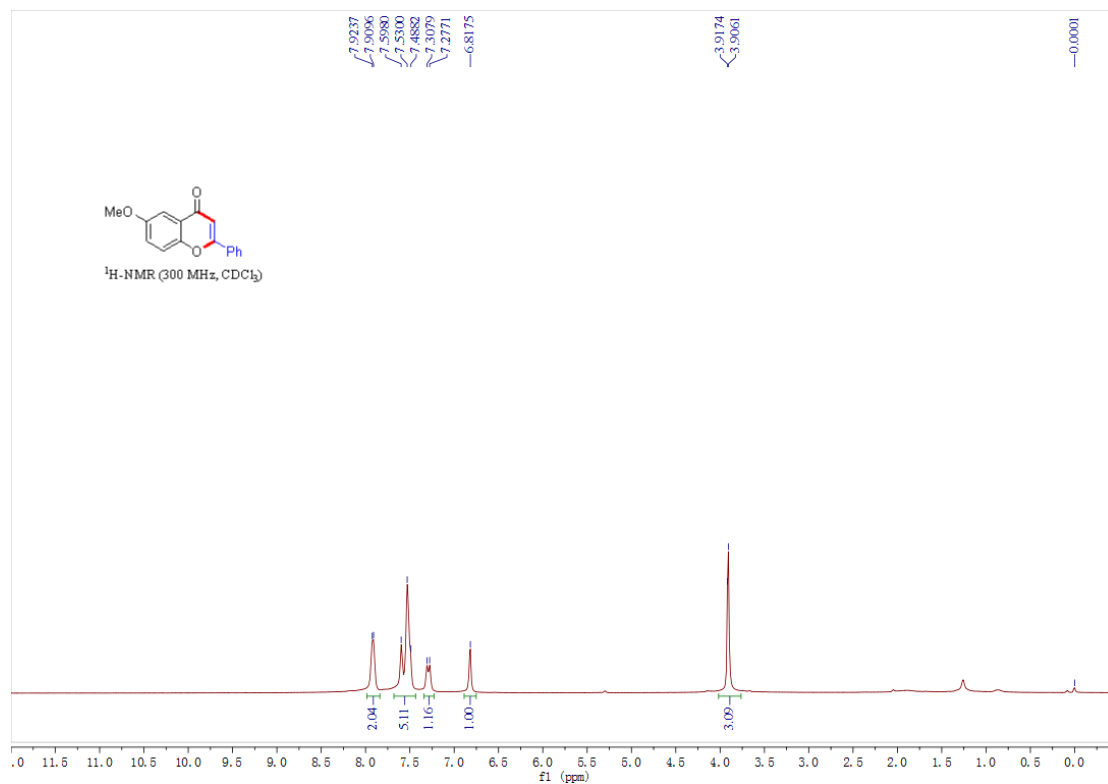
# methyl 4-oxo-2-phenyl-4H-chromene-6-carboxylate (3ja)



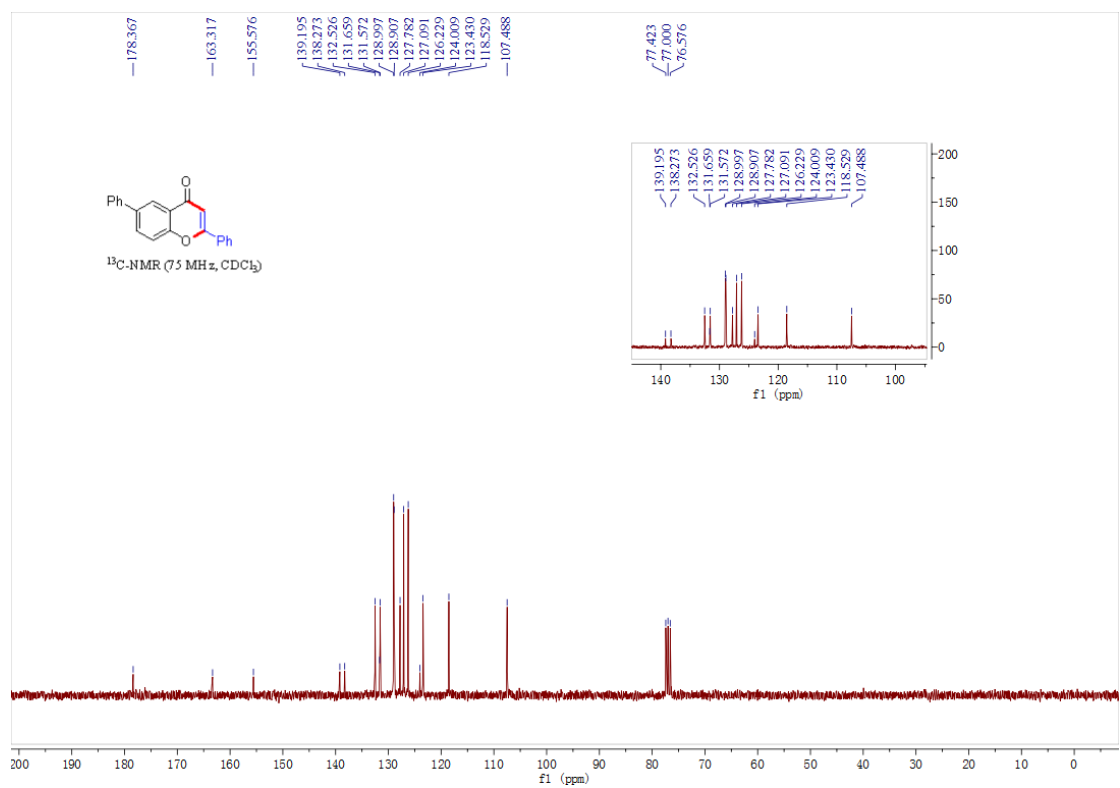
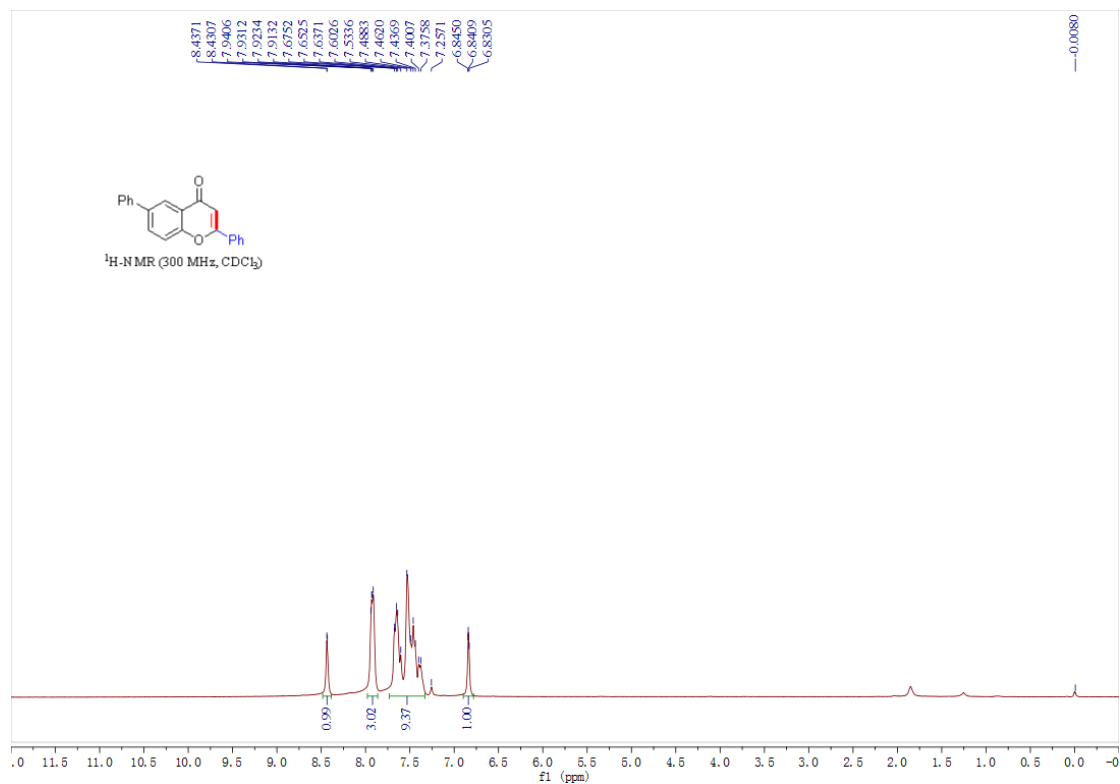
# 6-methyl-2-phenyl-4H-chromen-4-one (3ka)



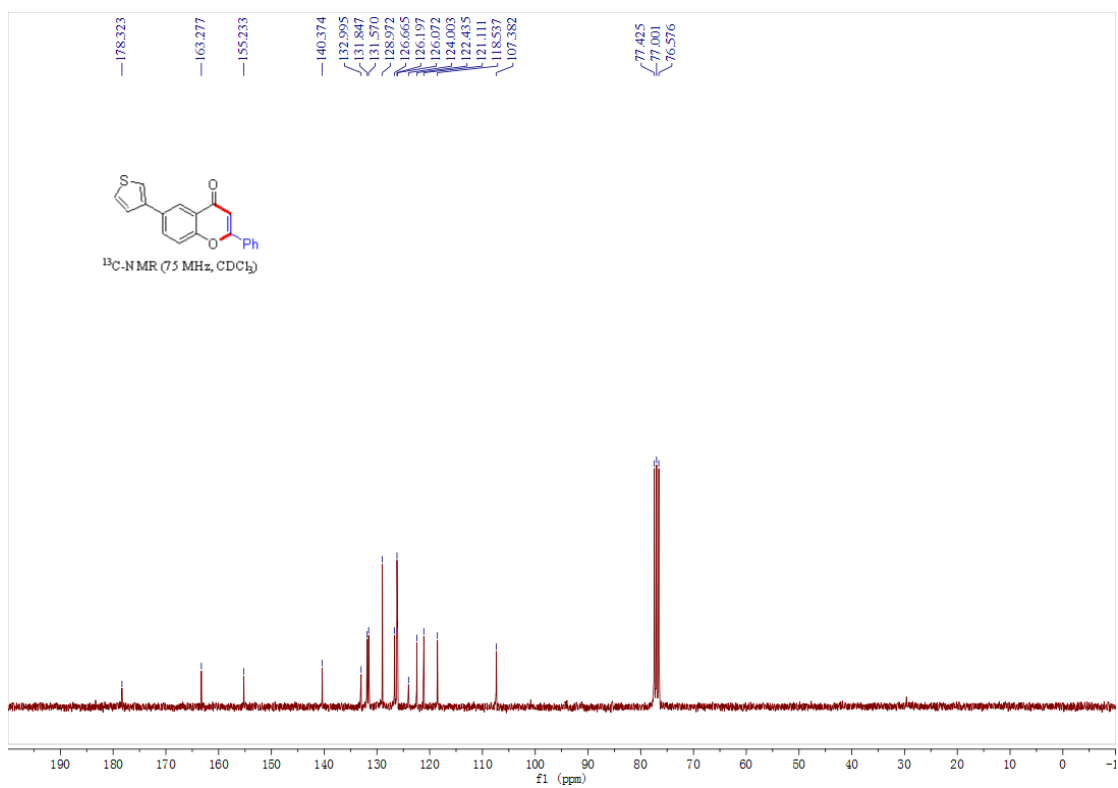
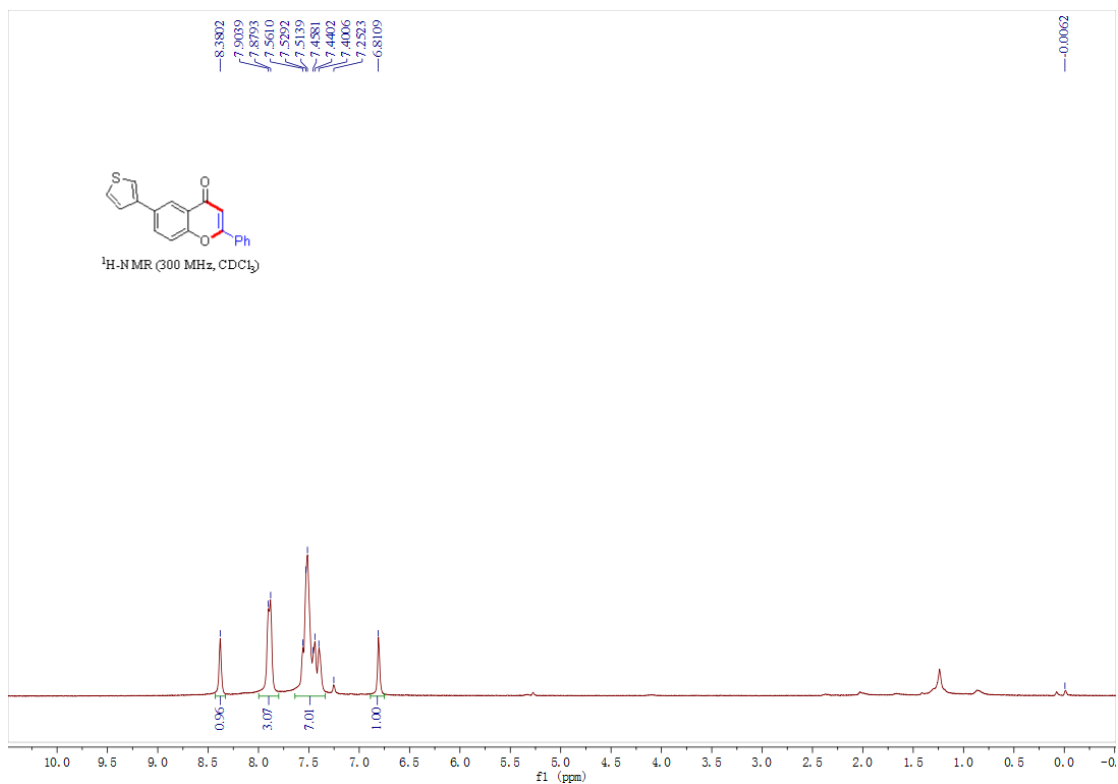
### 6-methoxy-2-phenyl-4H-chromen-4-one (3la)



## 2, 6-diphenyl-4*H*-chromen-4-one (3ma)

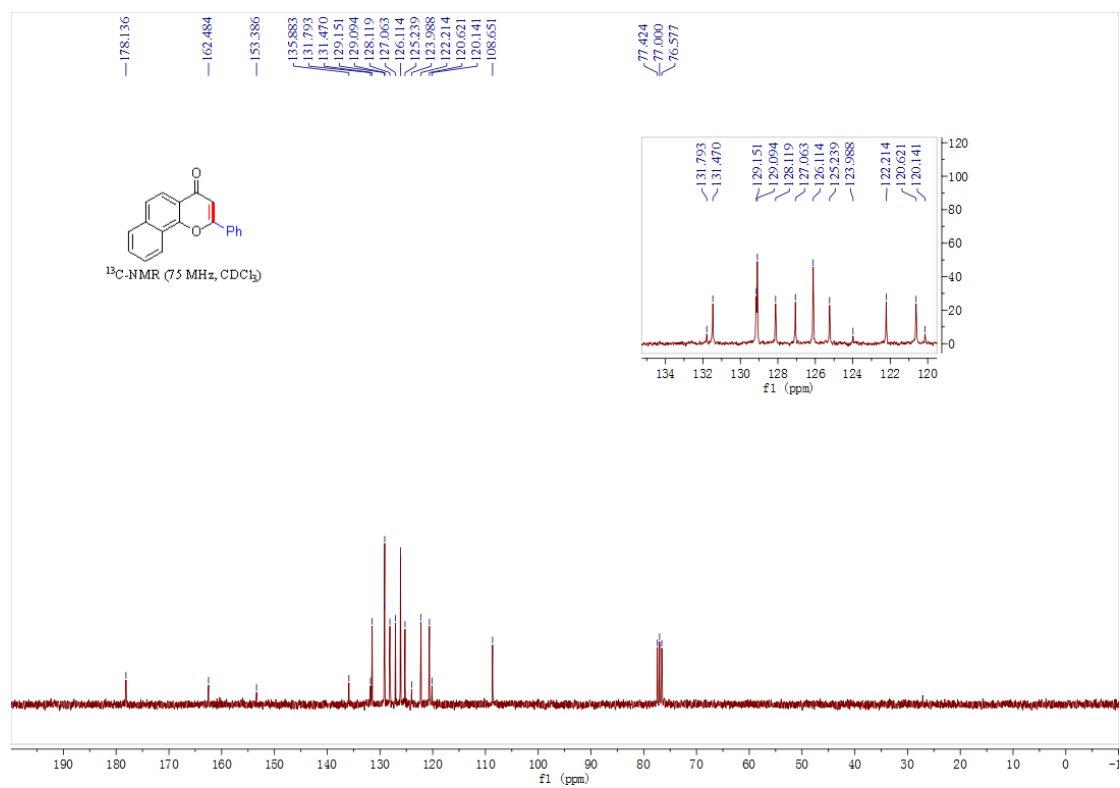
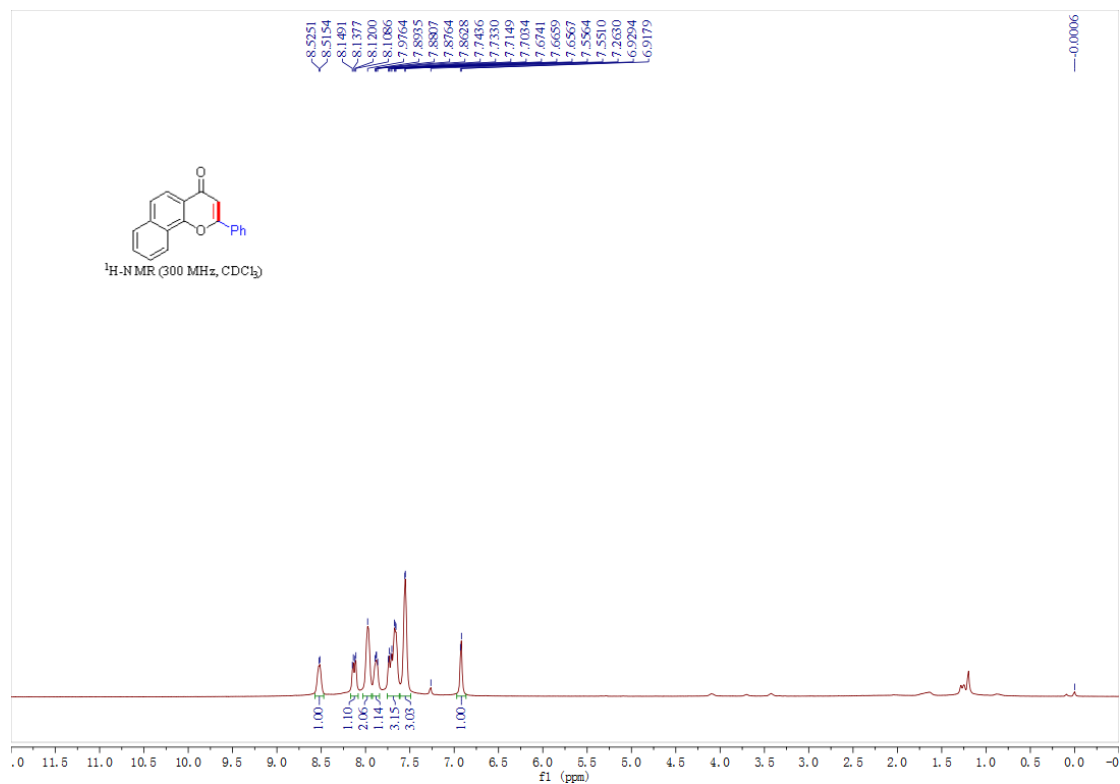


## 2-phenyl-6-(thiophen-3-yl)-4H-chromen-4-one (3na)

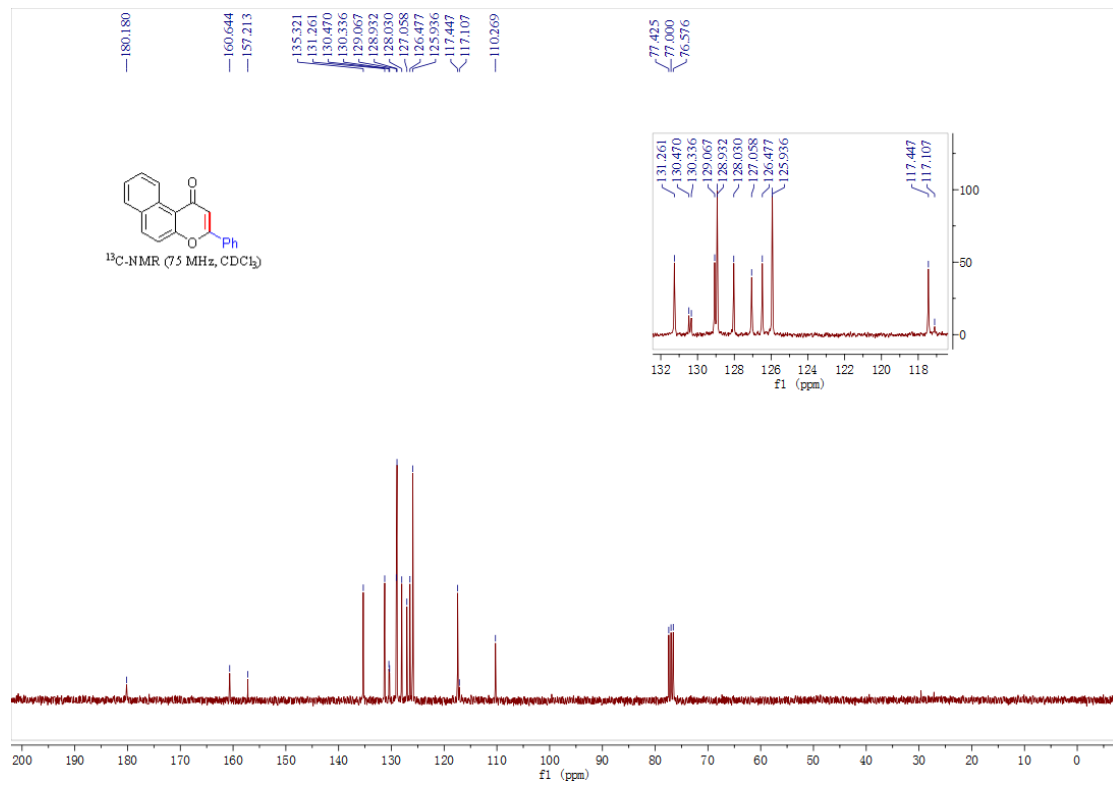
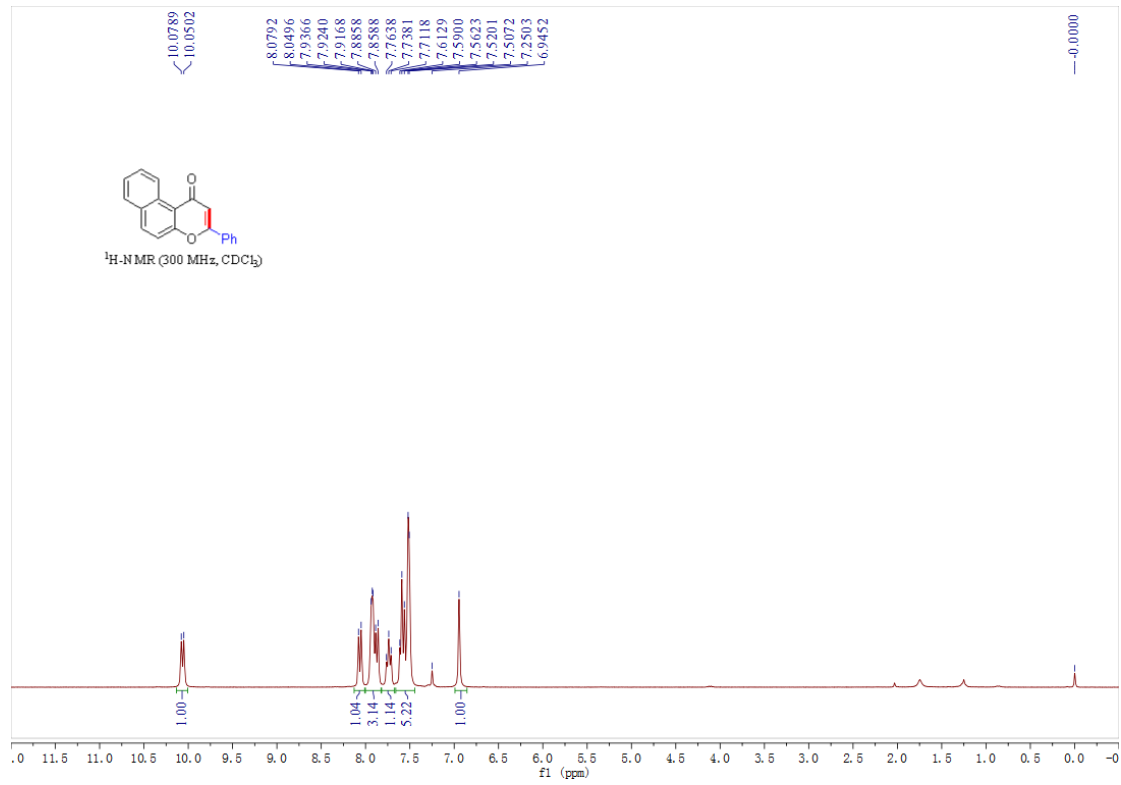




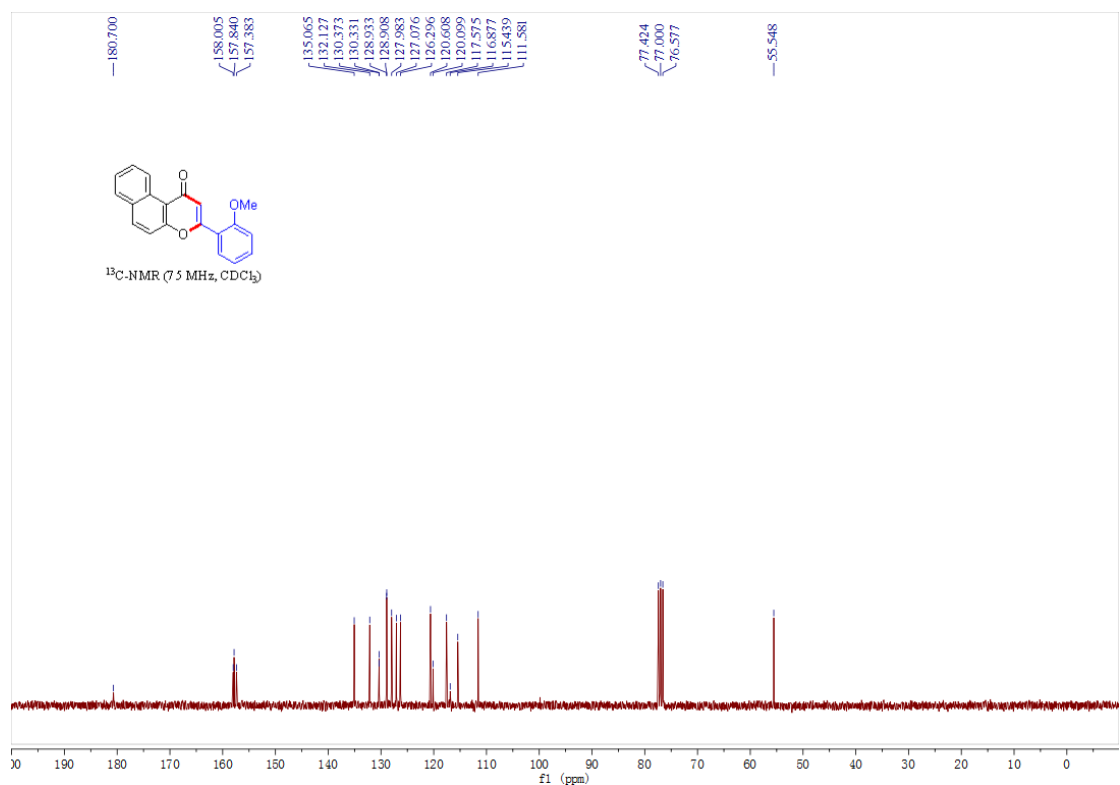
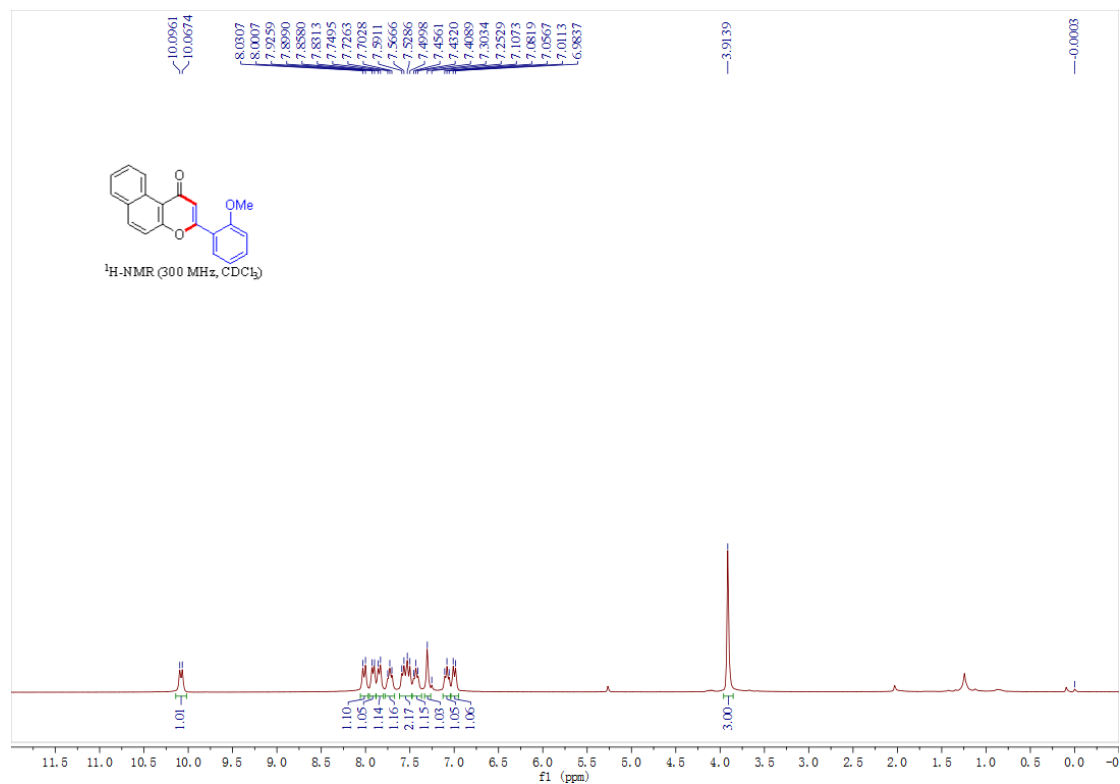
## 2-phenyl-4*H*-benzo[*h*]chromen-4-one (30a)



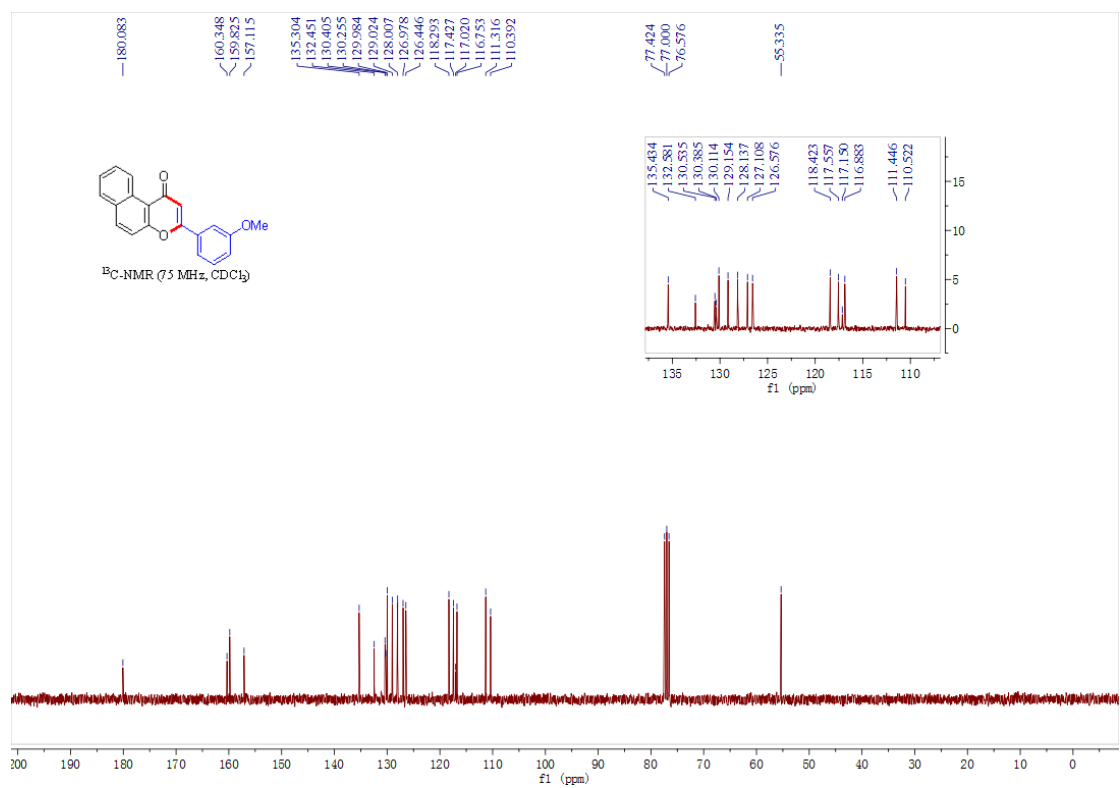
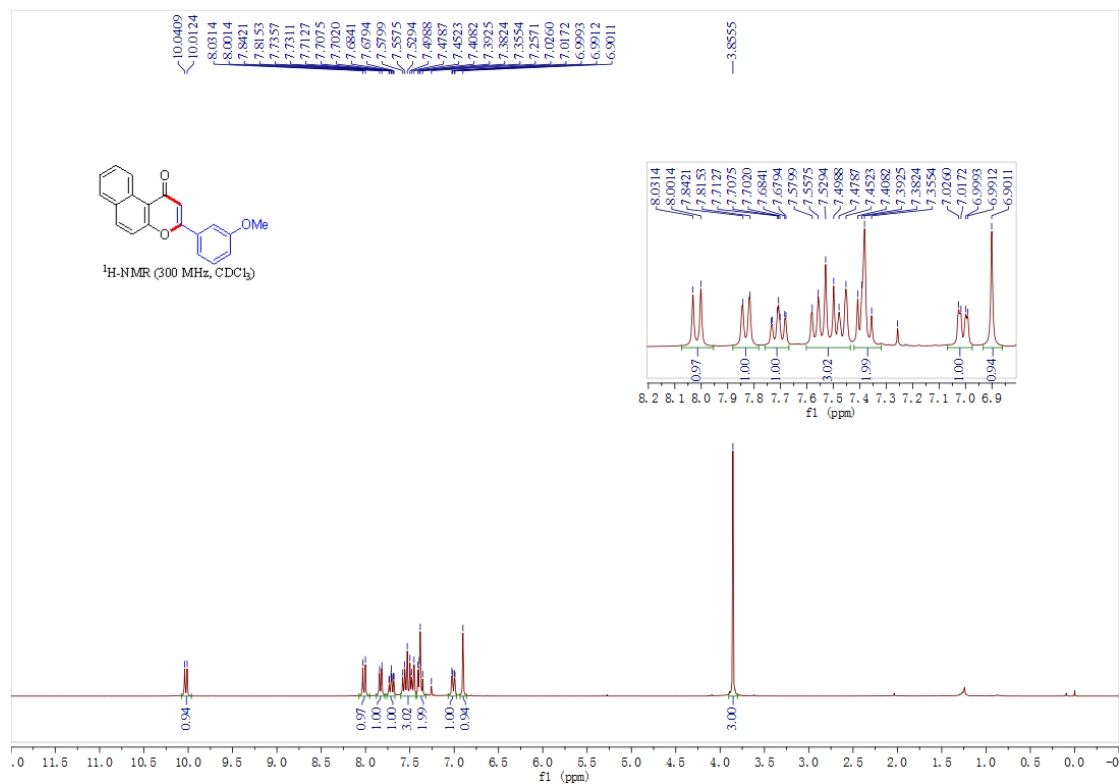
### 3-phenyl-1*H*-benzo[*f*]chromen-1-one (3pa)



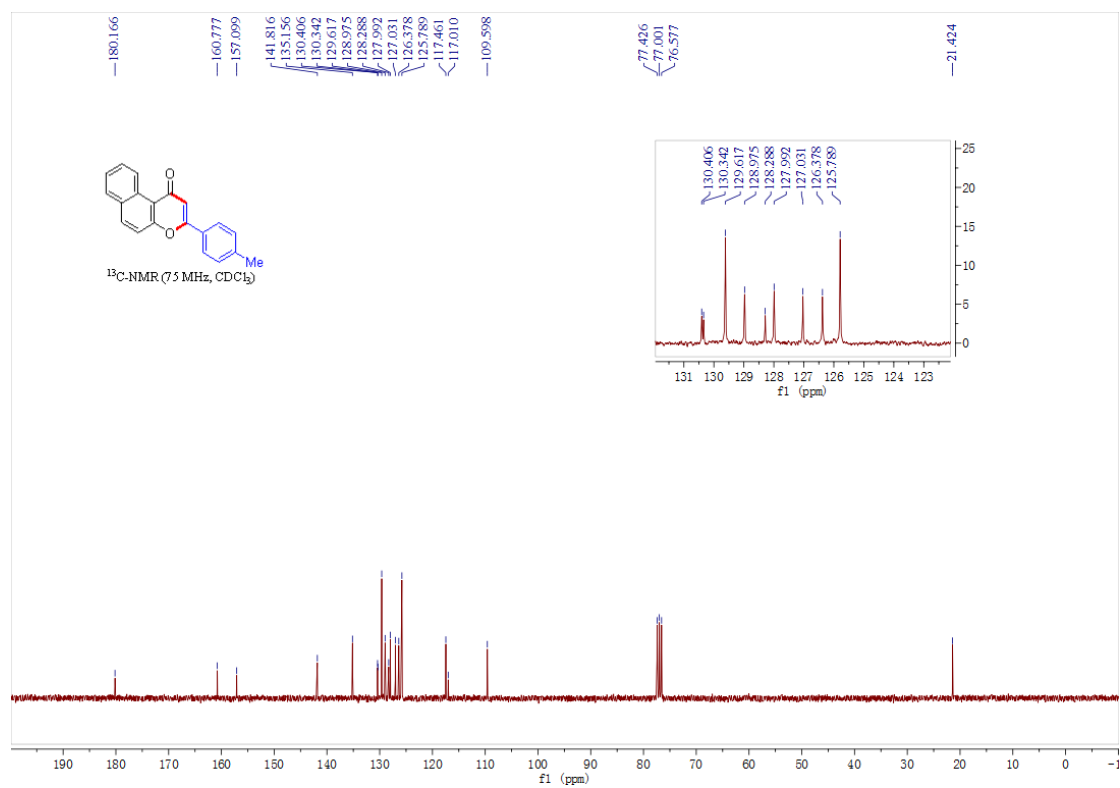
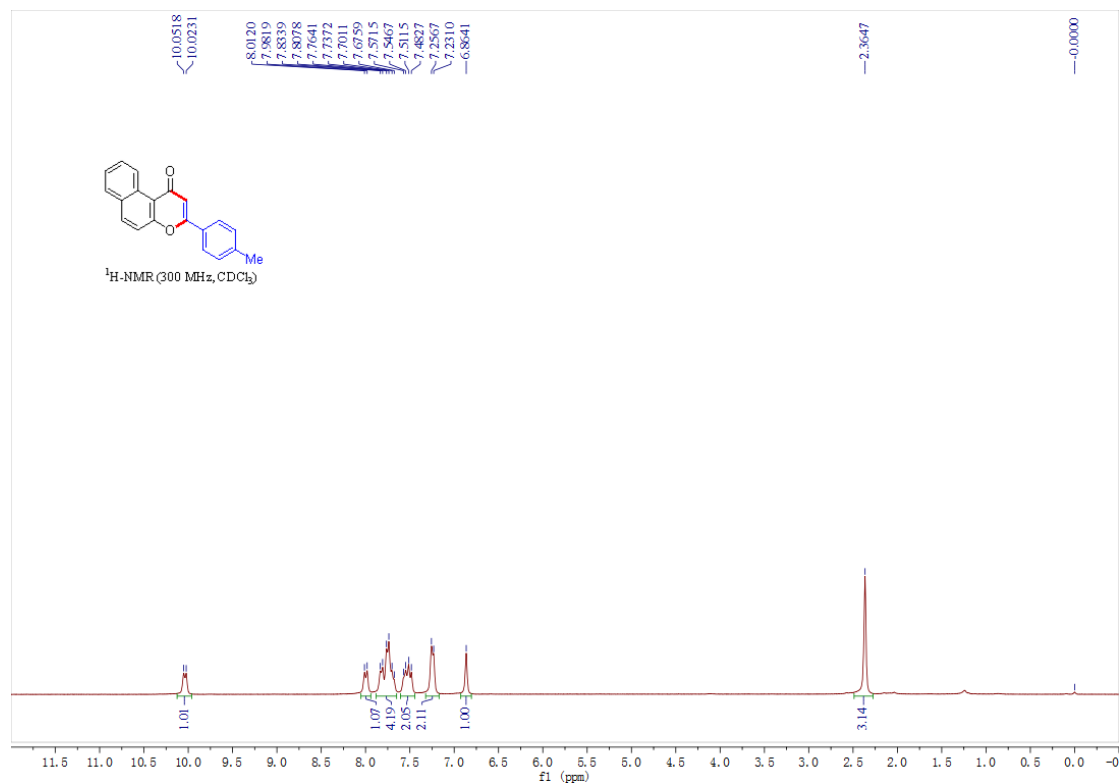
### 3-(2-methoxyphenyl)-1H-benzo[f]chromen-1-one (3pb)



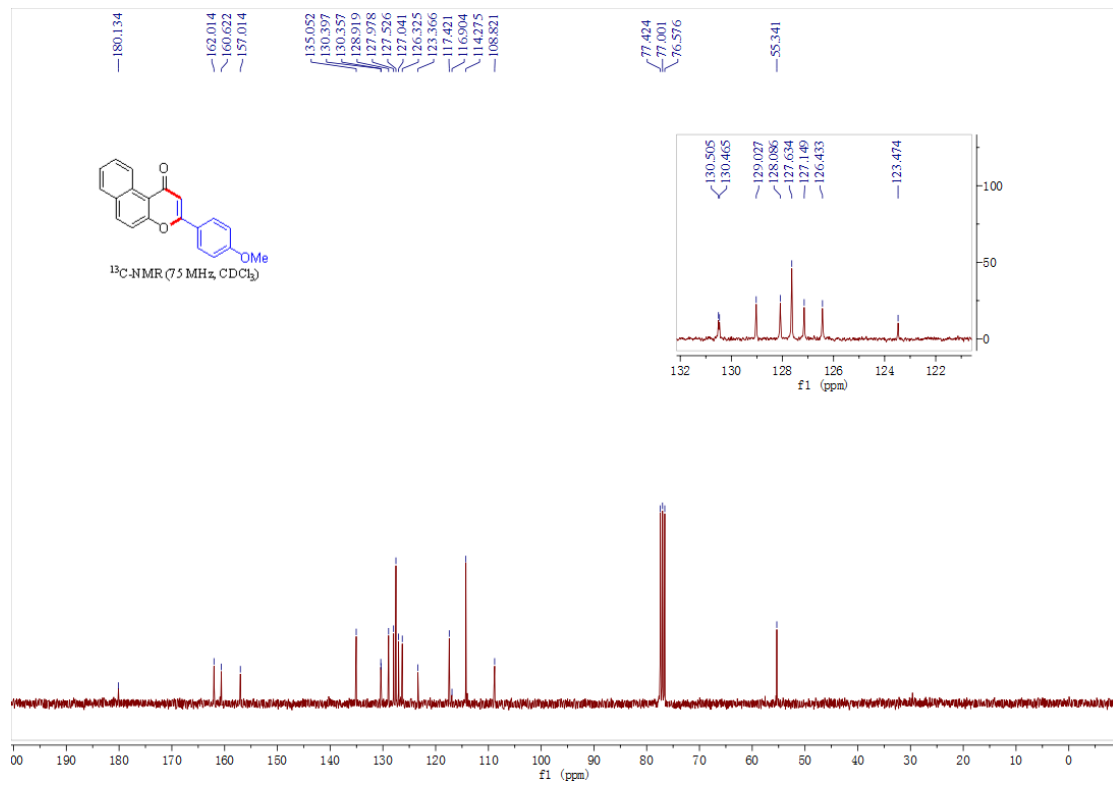
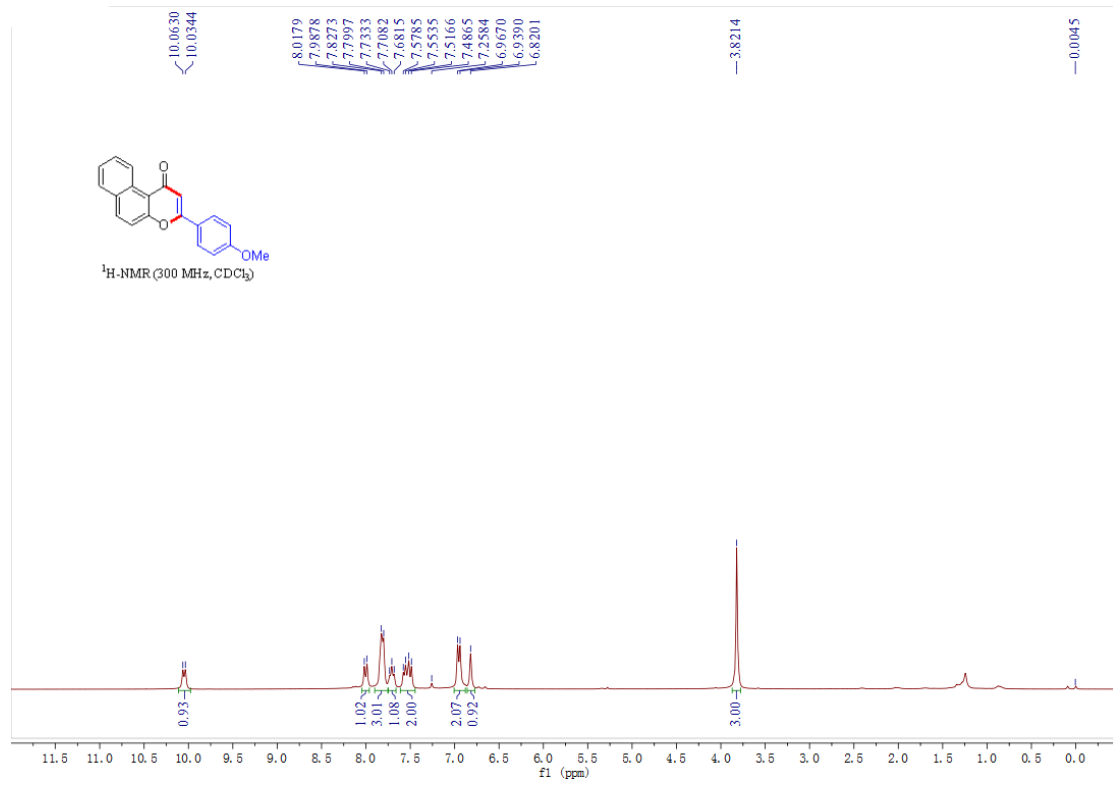
### 3-(3-methoxyphenyl)-1H-benzo[f]chromen-1-one (3pc)



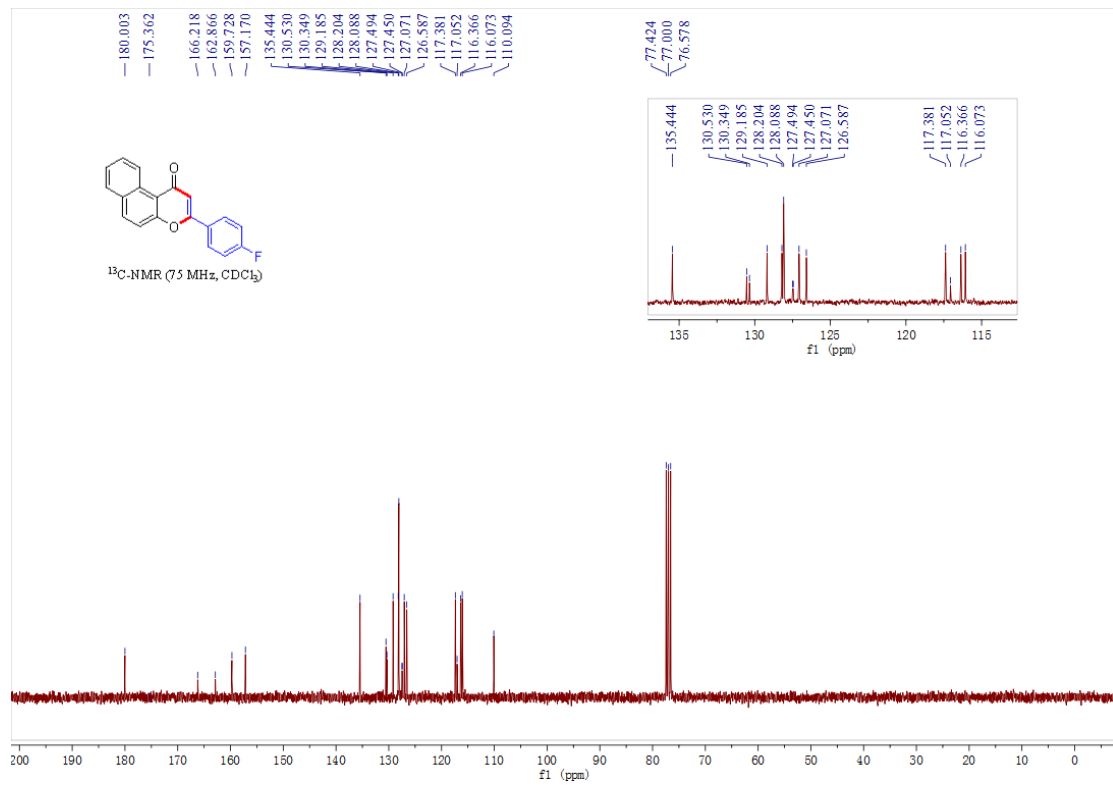
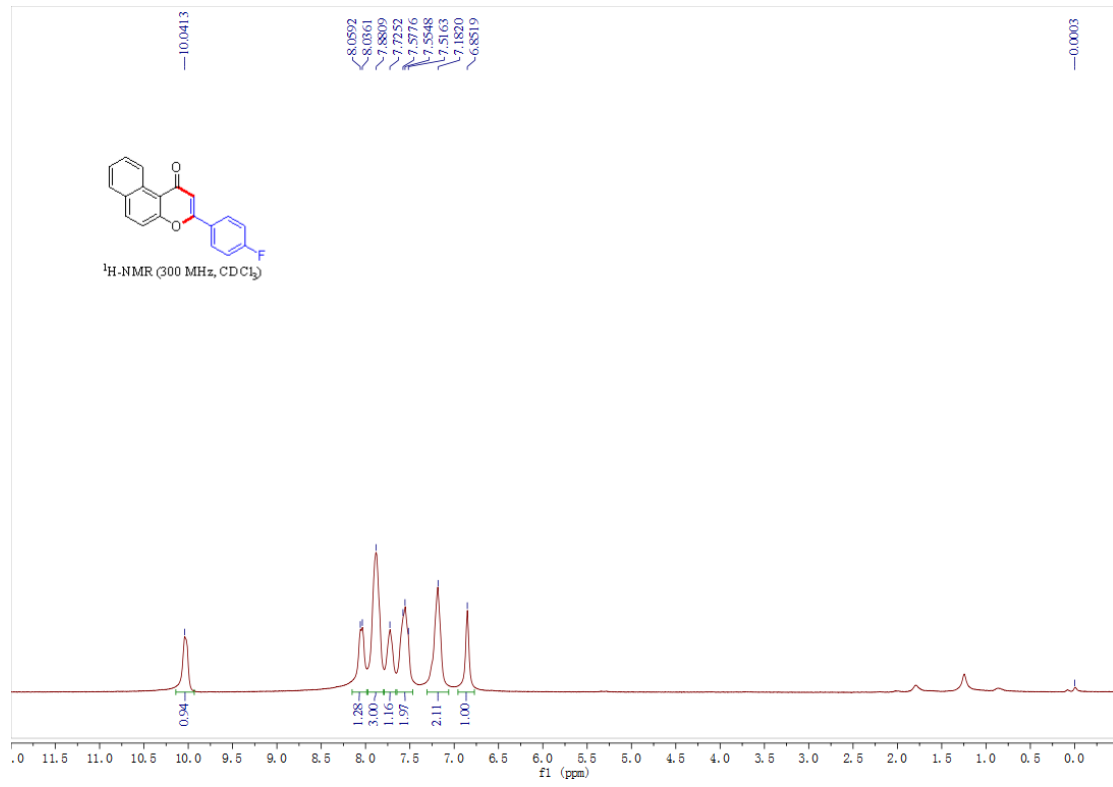
### 3-(p-tolyl)-1H-benzo[f]chromen-1-one (3pd)



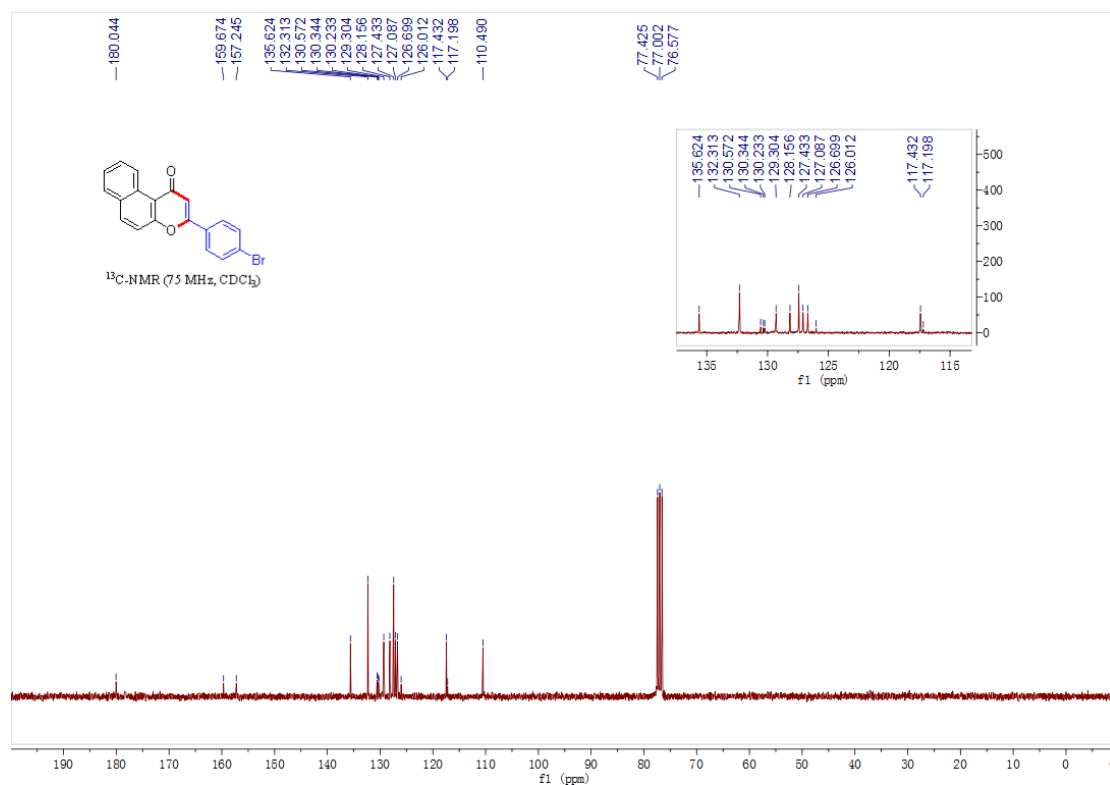
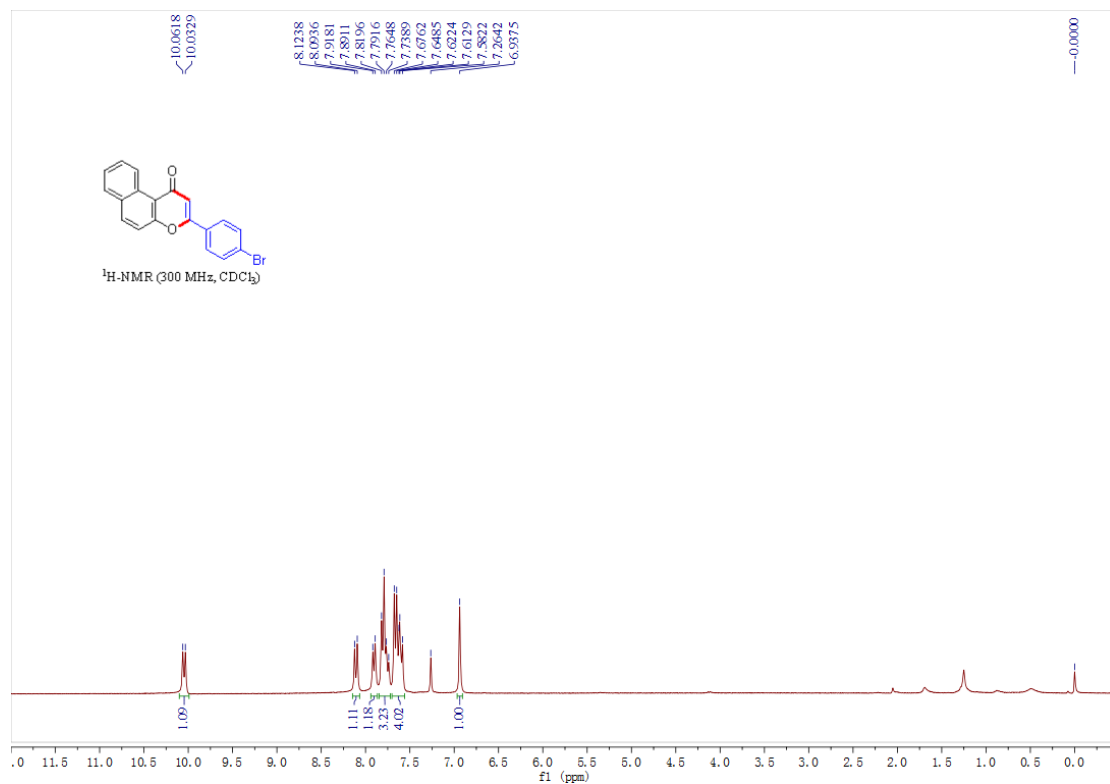
### 3-(4-methoxyphenyl)-1H-benzo[f]chromen-1-one (3pe)



### 3-(4-fluorophenyl)-1H-benzof[*f*]chromen-1-one (3pf)

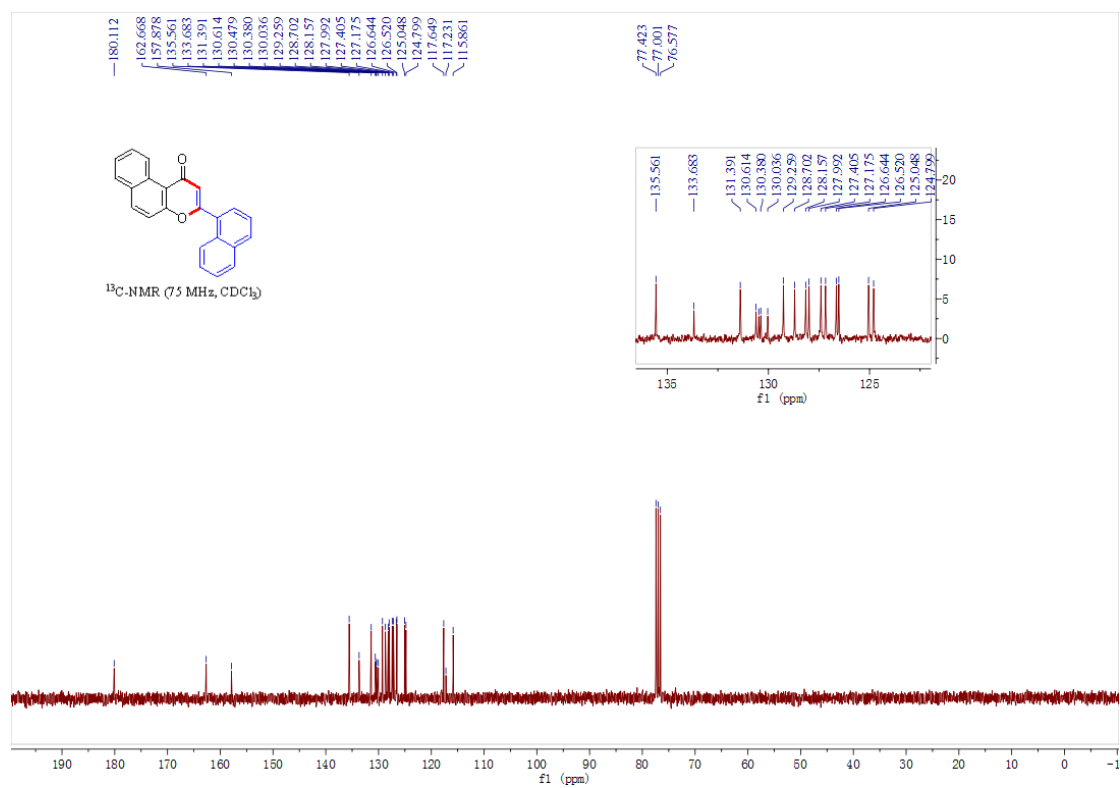
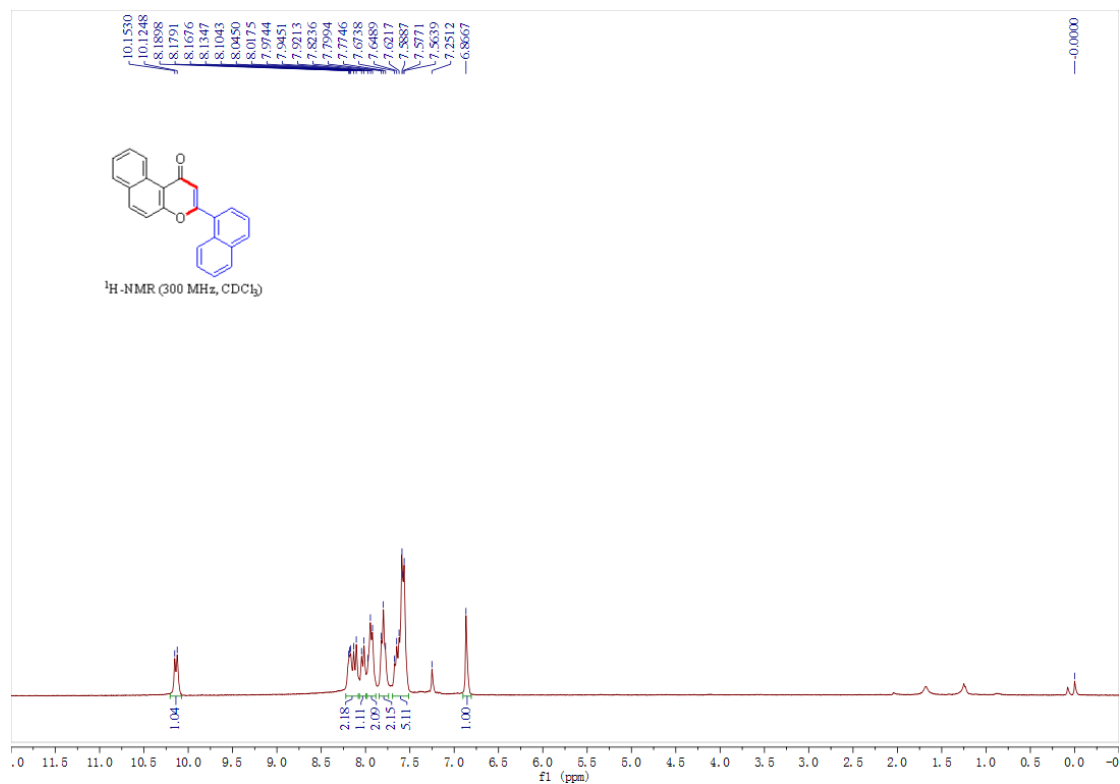


### 3-(4-bromophenyl)-1H-benzo[f]chromen-1-one (3pg)

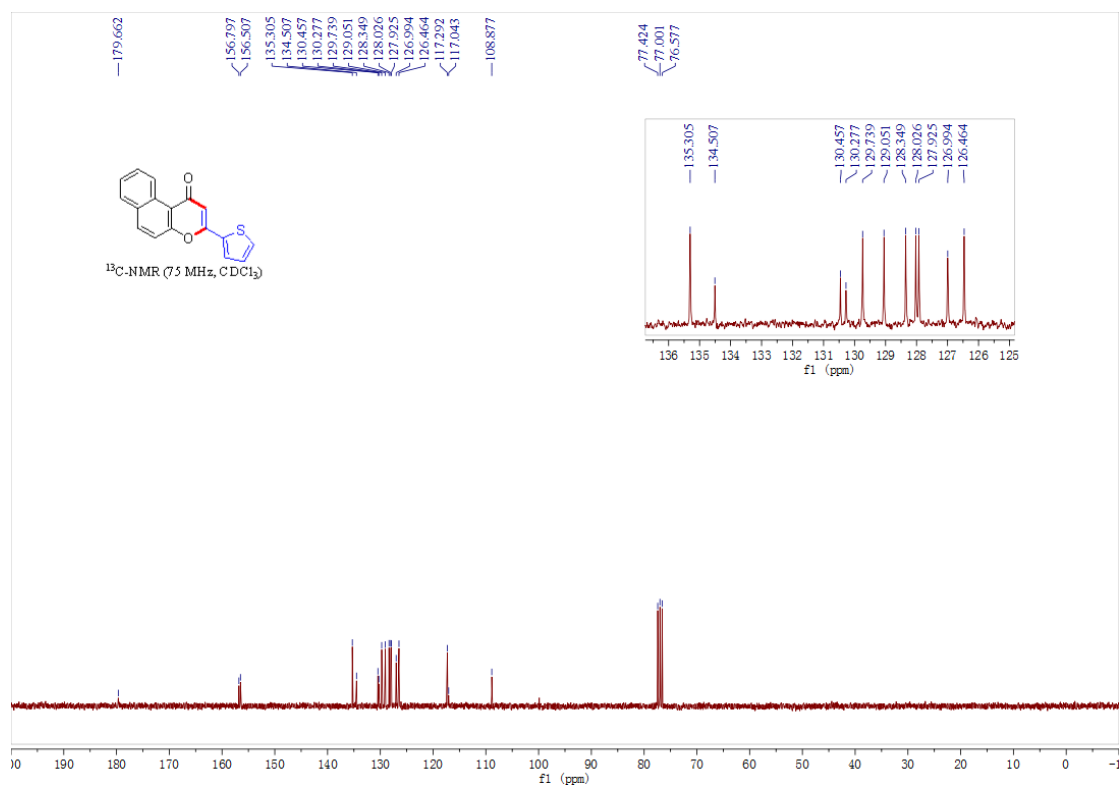
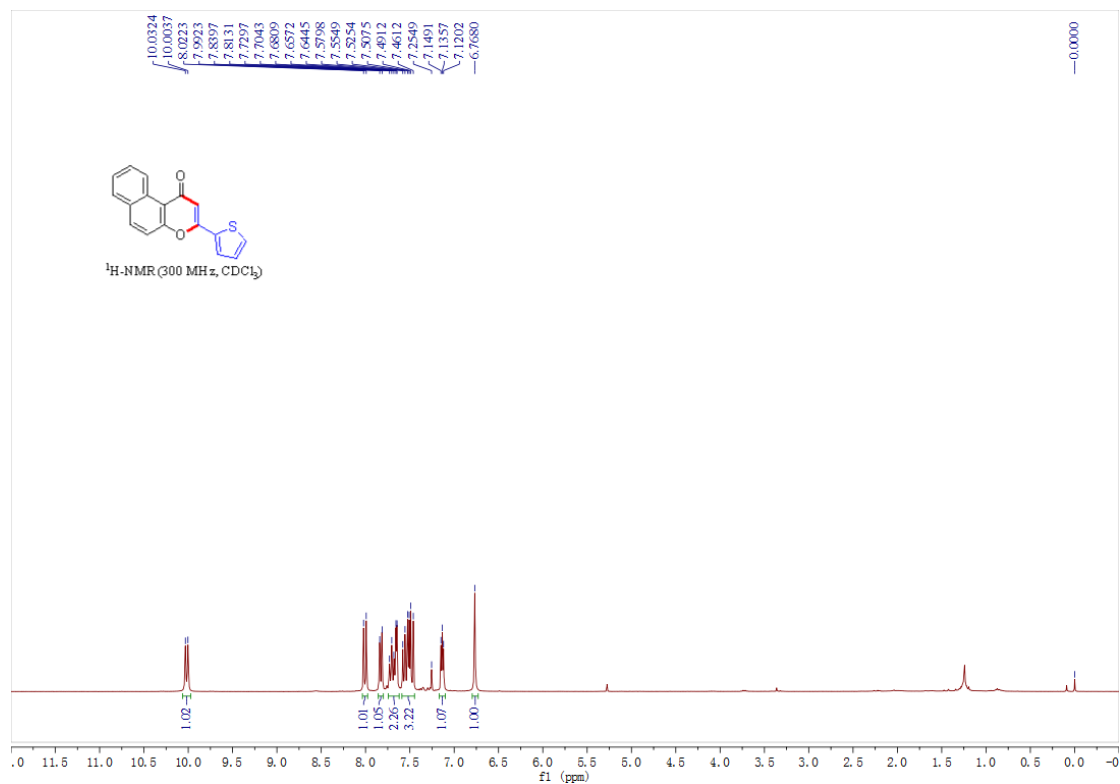




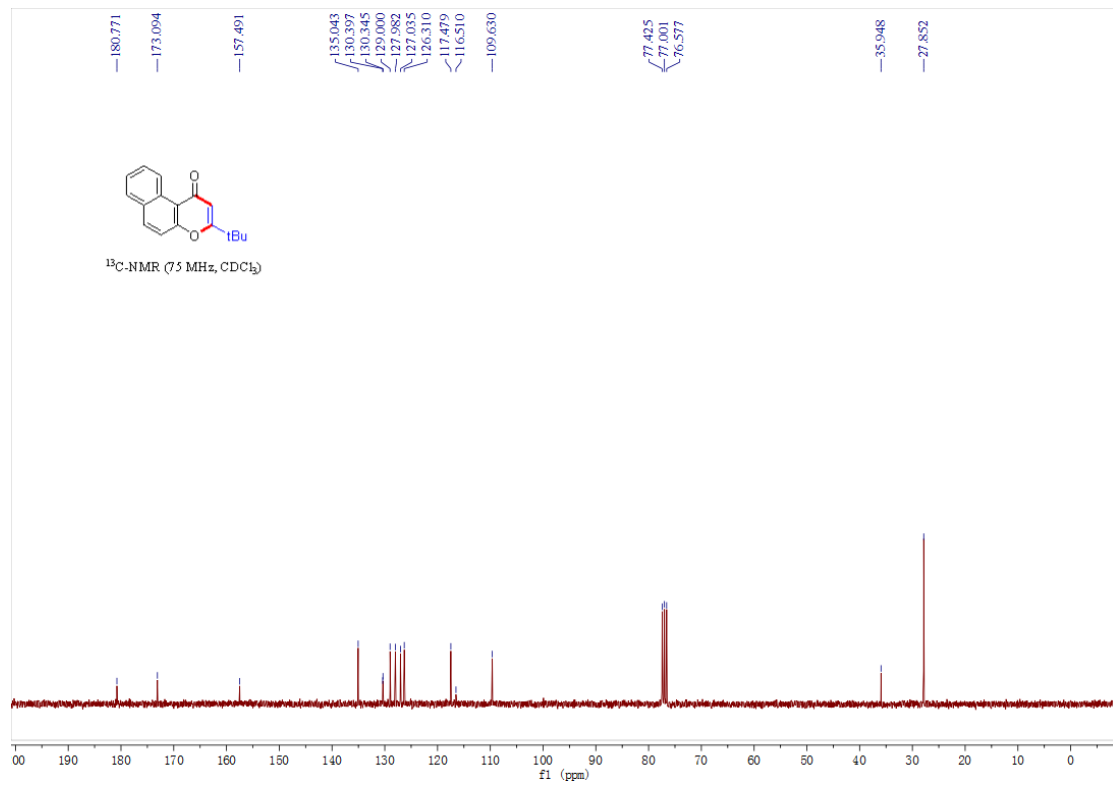
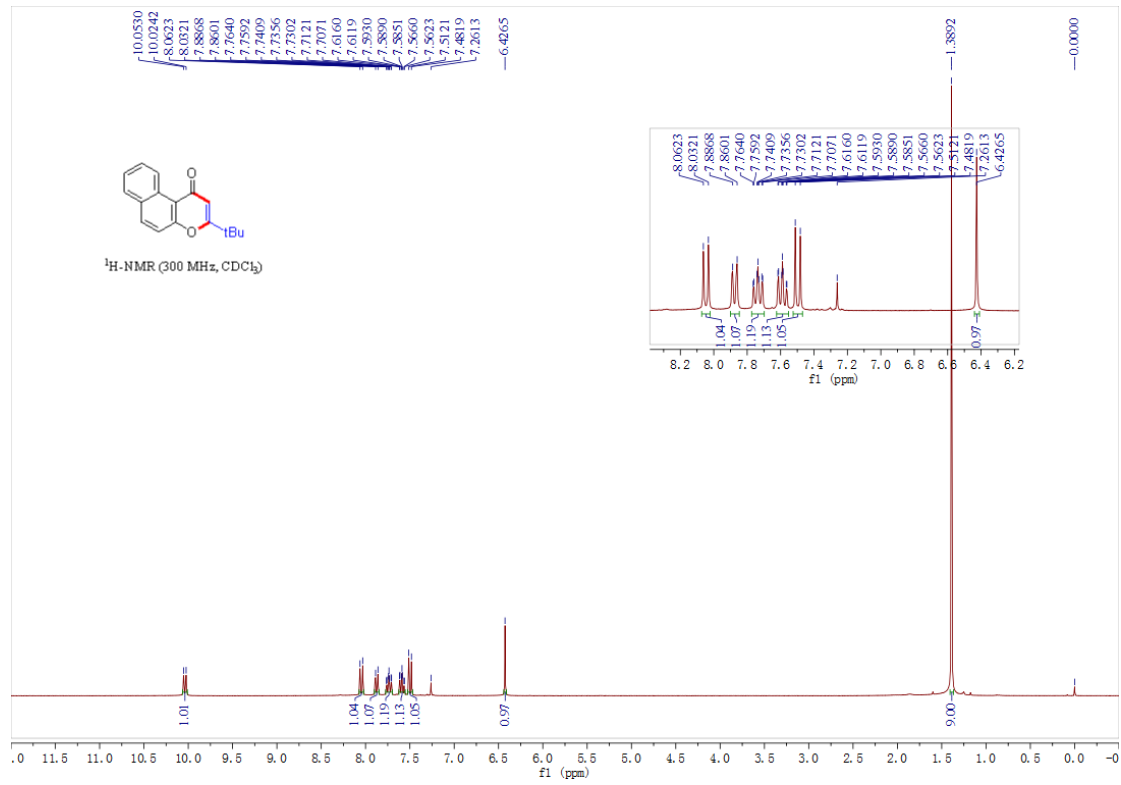
### 3-(naphthalen-1-yl)-1H-benzo[*f*]chromen-1-one (3ph)



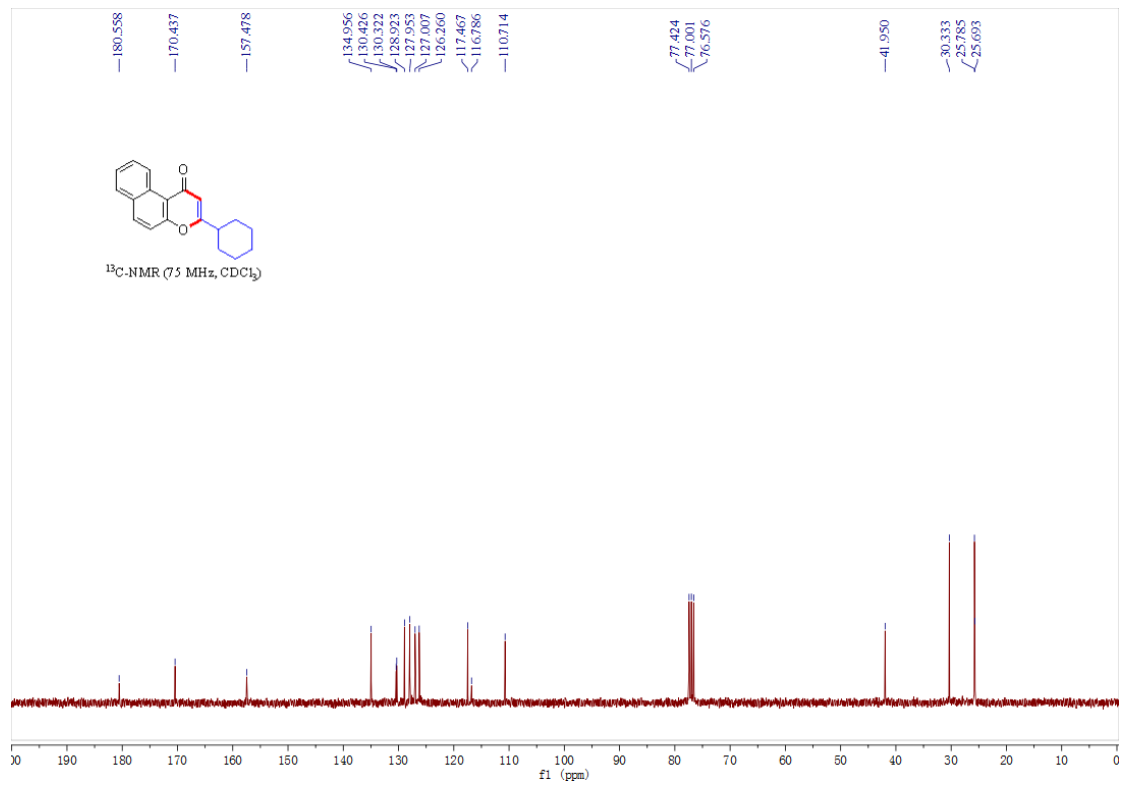
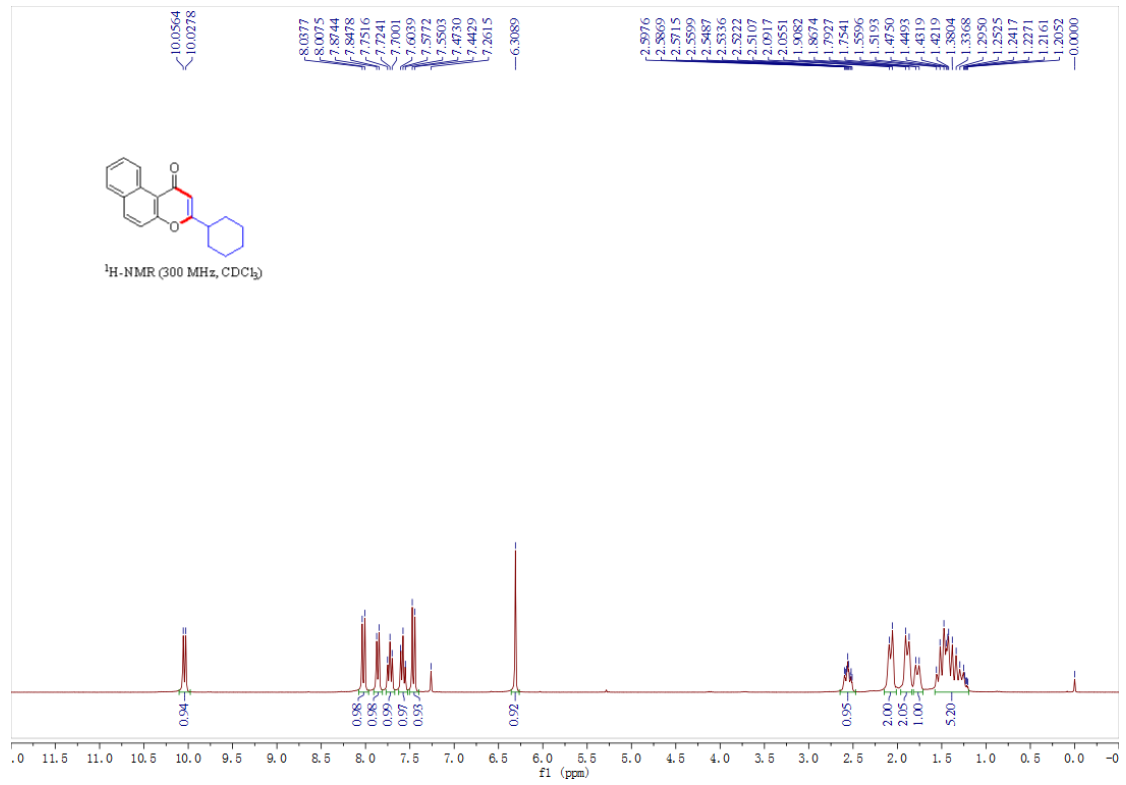
### 3-(thiophen-2-yl)-1*H*-benzo[*f*]chromen-1-one (3pi)



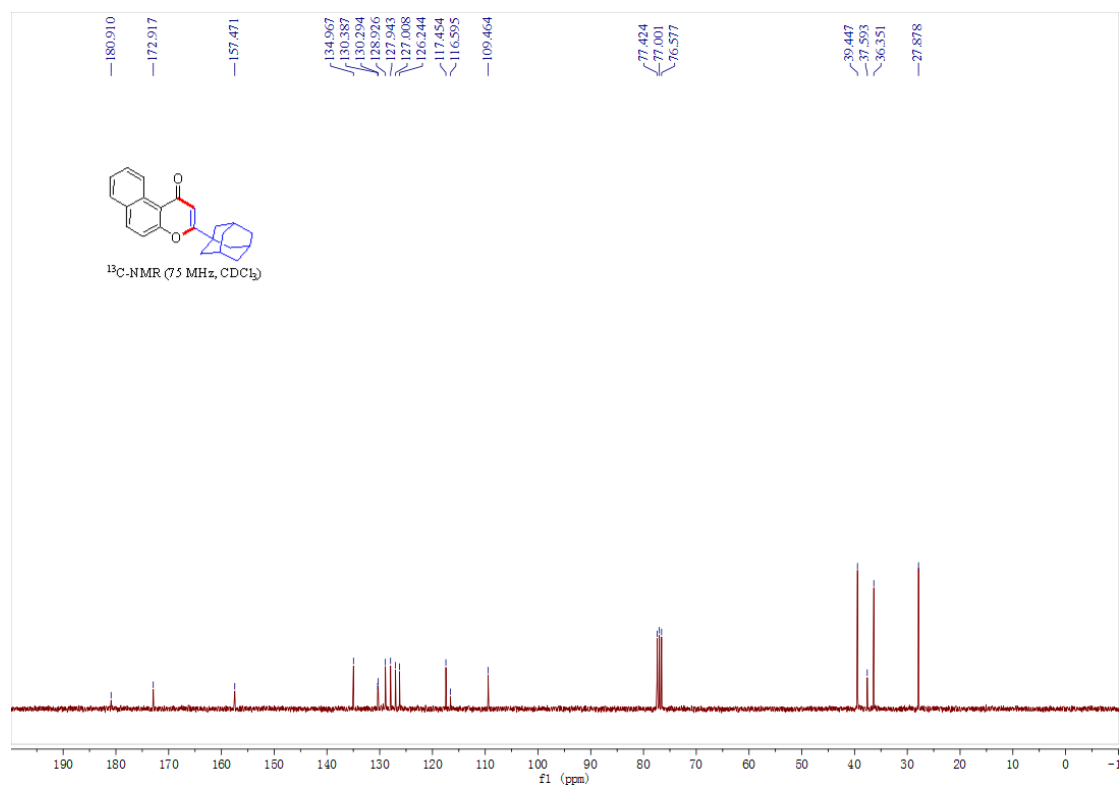
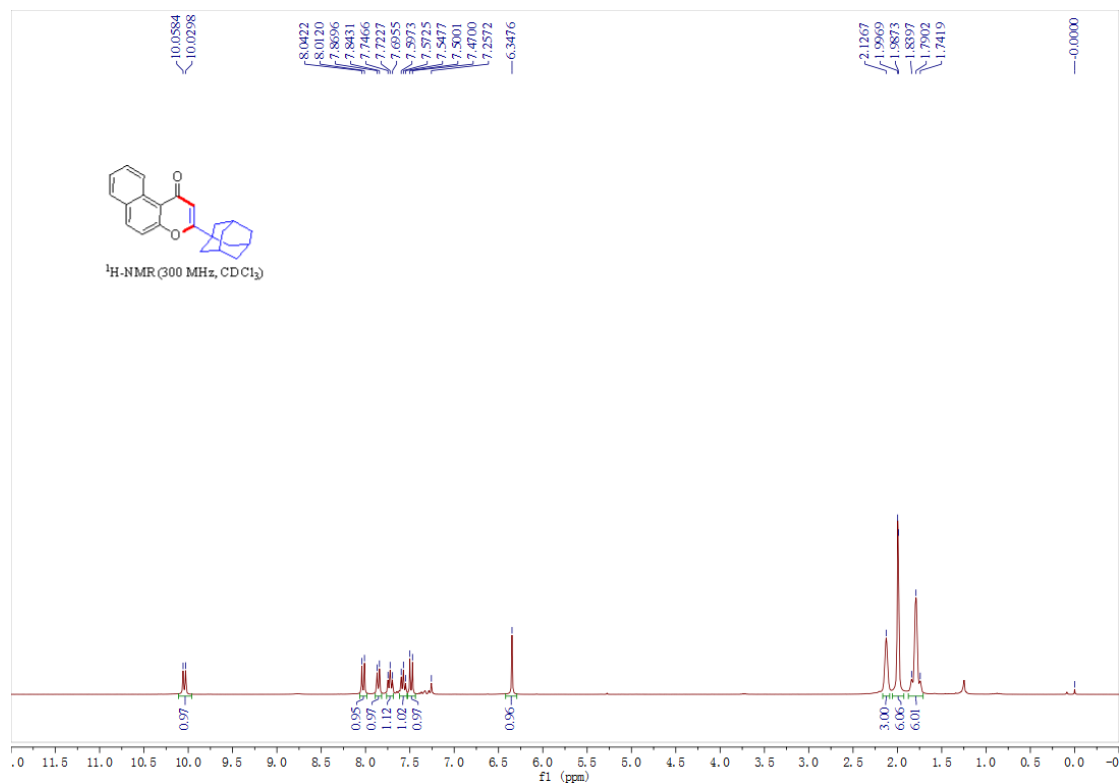
### 3-(tert-butyl)-1H-benzo[f]chromen-1-one (3pj)



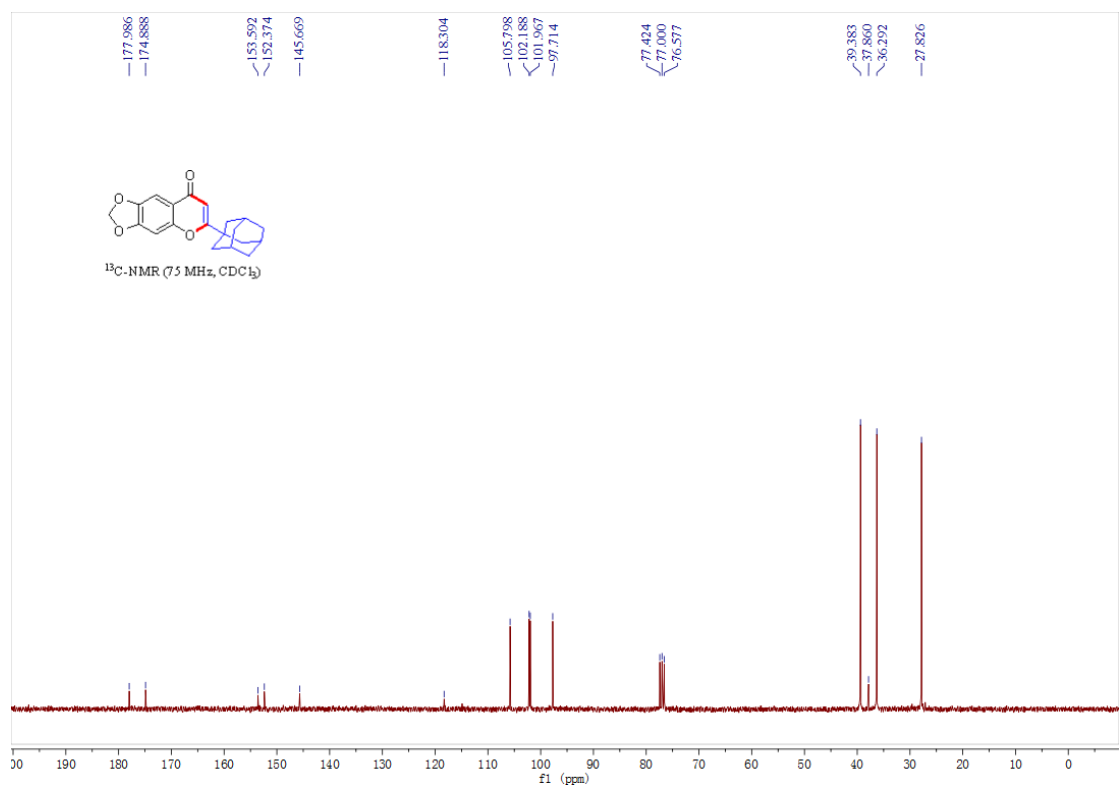
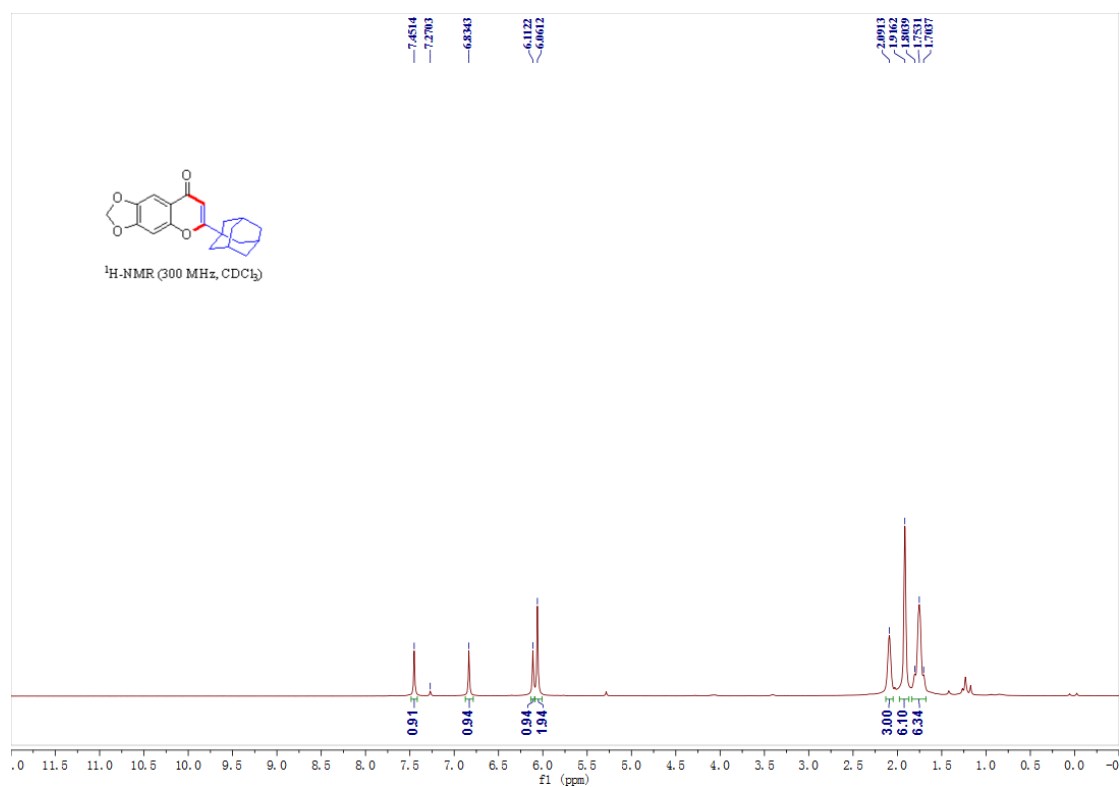
### 3-cyclohexyl-1H-benzo[f]chromen-1-one (3pk)



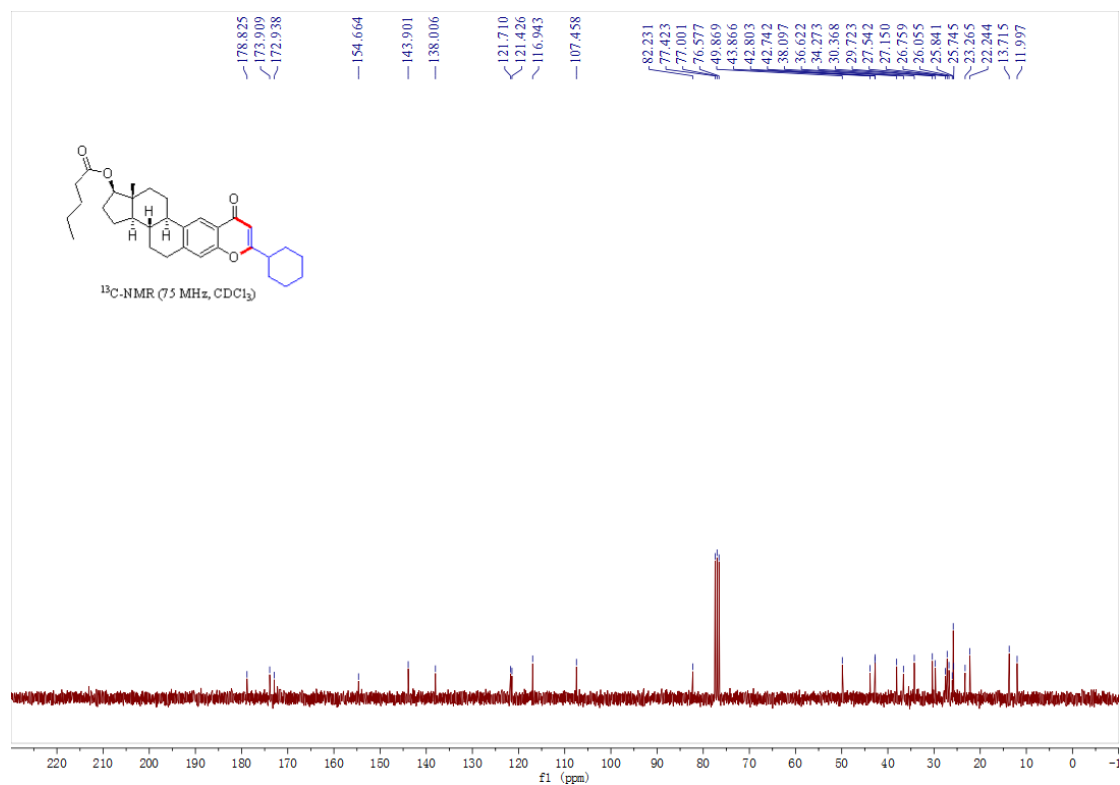
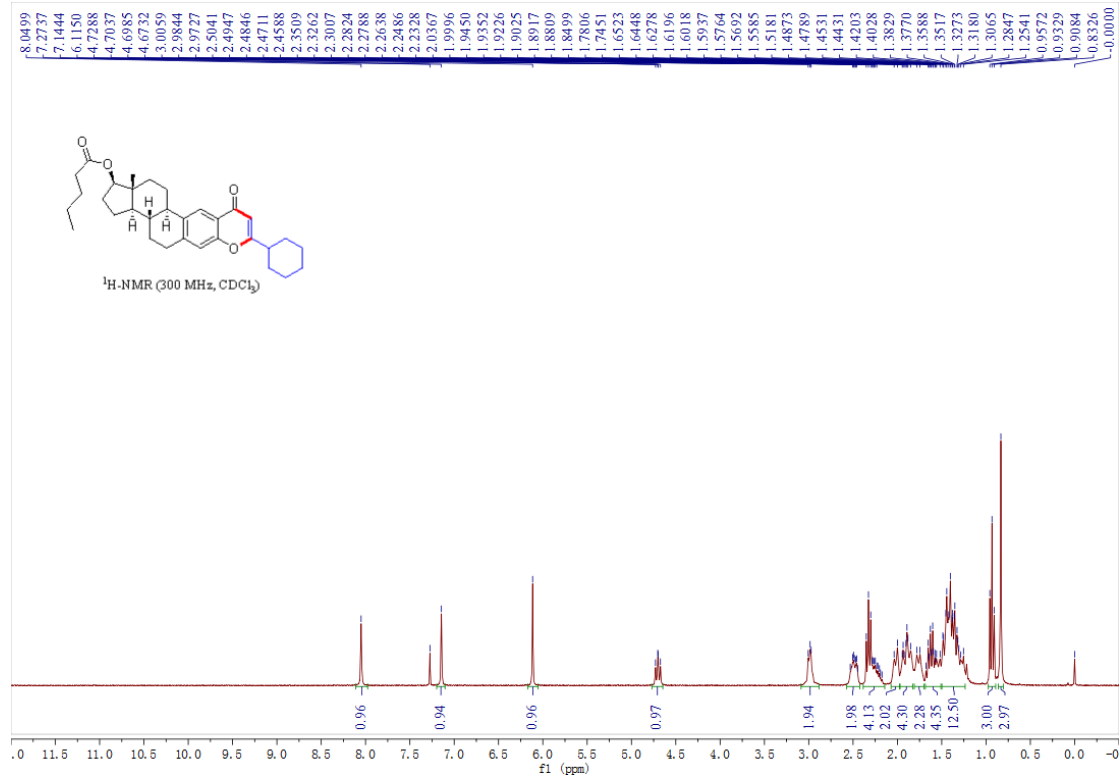
**3-((3*r*,5*r*,7*r*)-adamantan-1-yl)-1*H*-benzo[*f*]chromen-1-one (3pl)**



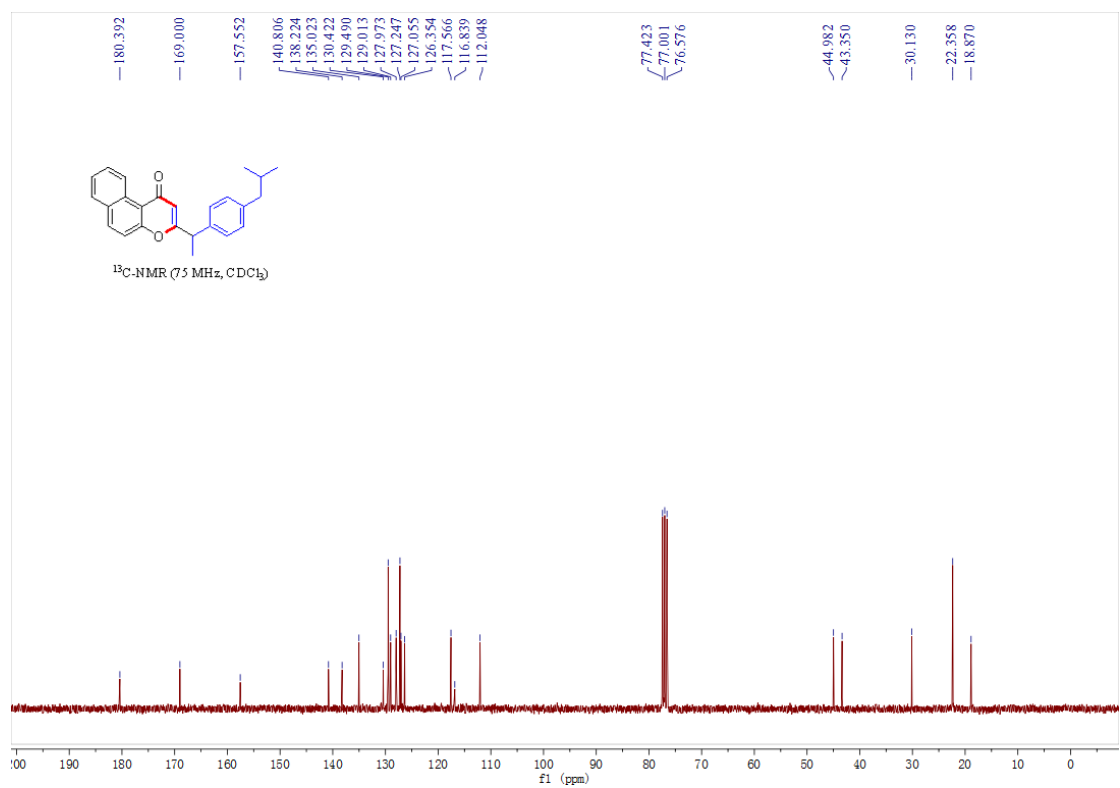
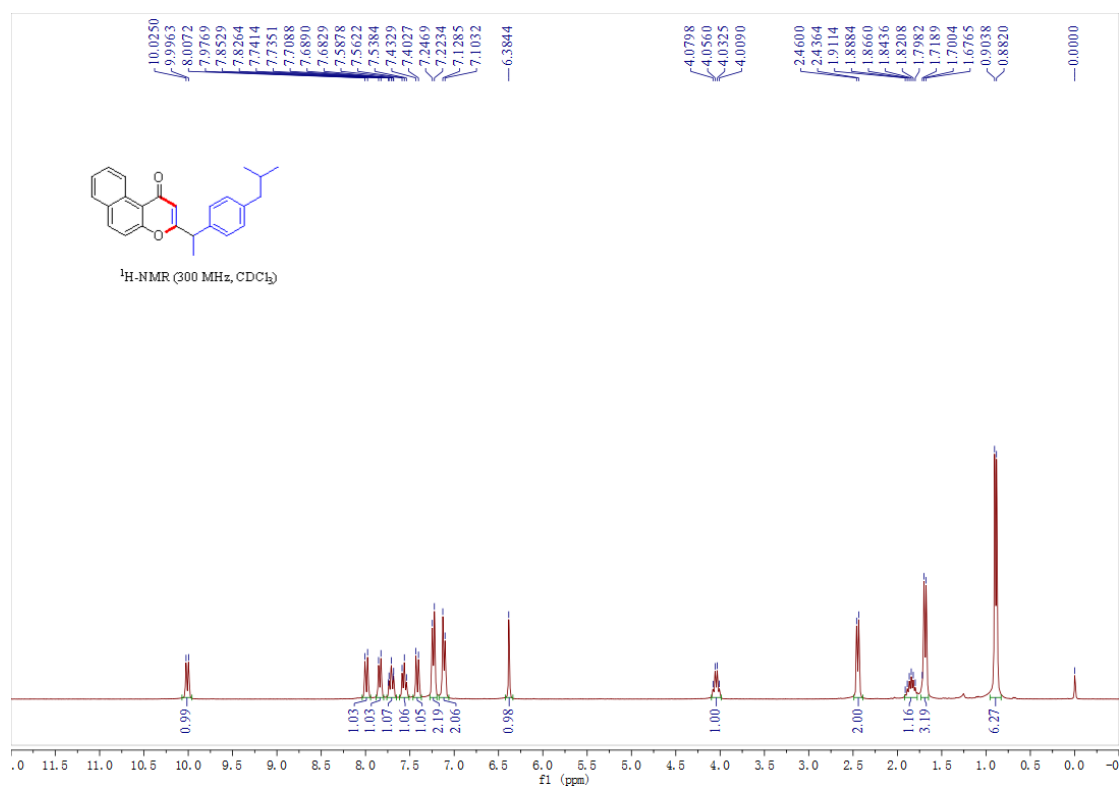
**6-((3*r*,5*r*,7*r*)-adamantan-1-yl)-8*H*-[1,3]dioxolo[4,5-*g*]chromen-8-one (4)**



**(1*R*,3*aR*,3*bS*,11*bR*,13*aR*)-8-cyclohexyl-13*a*-methyl-10-oxo-1,2,3,3*a*,3*b*,4,5,10,11*b*,12,13,13*a*-dodecahydrocyclopenta[5,6]naphtho[1,2-*g*]chromen-1-yl pentanoate (5)**

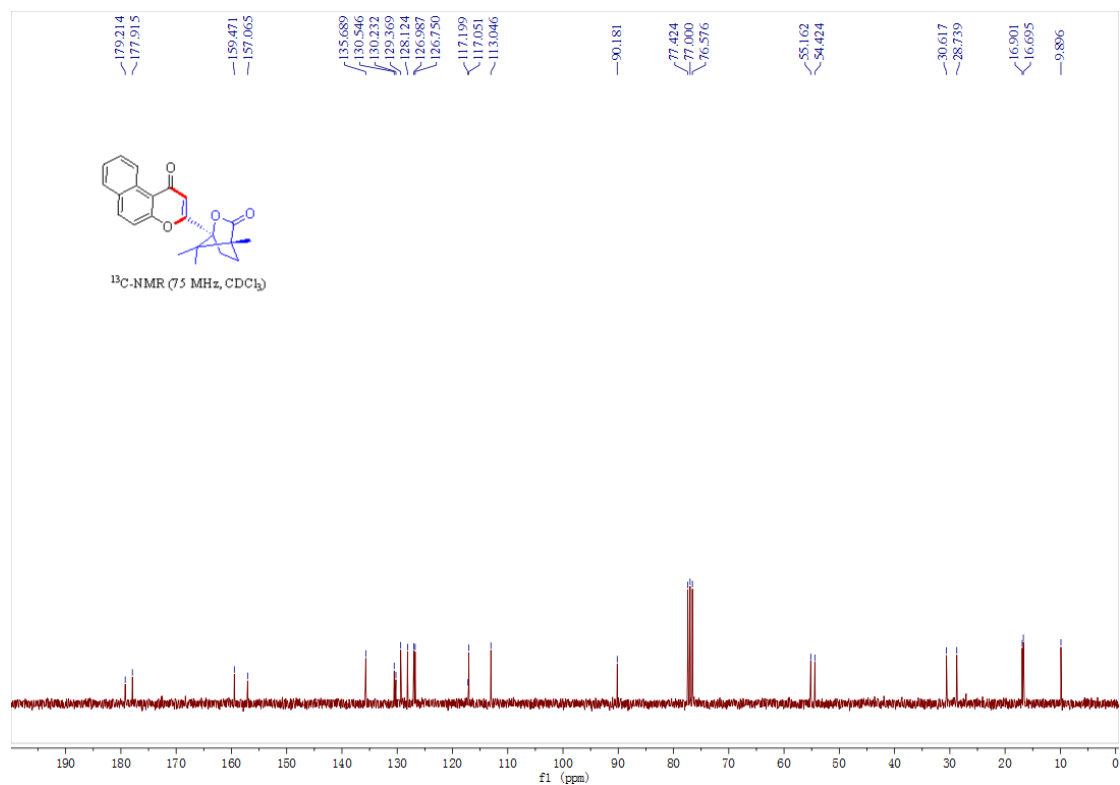
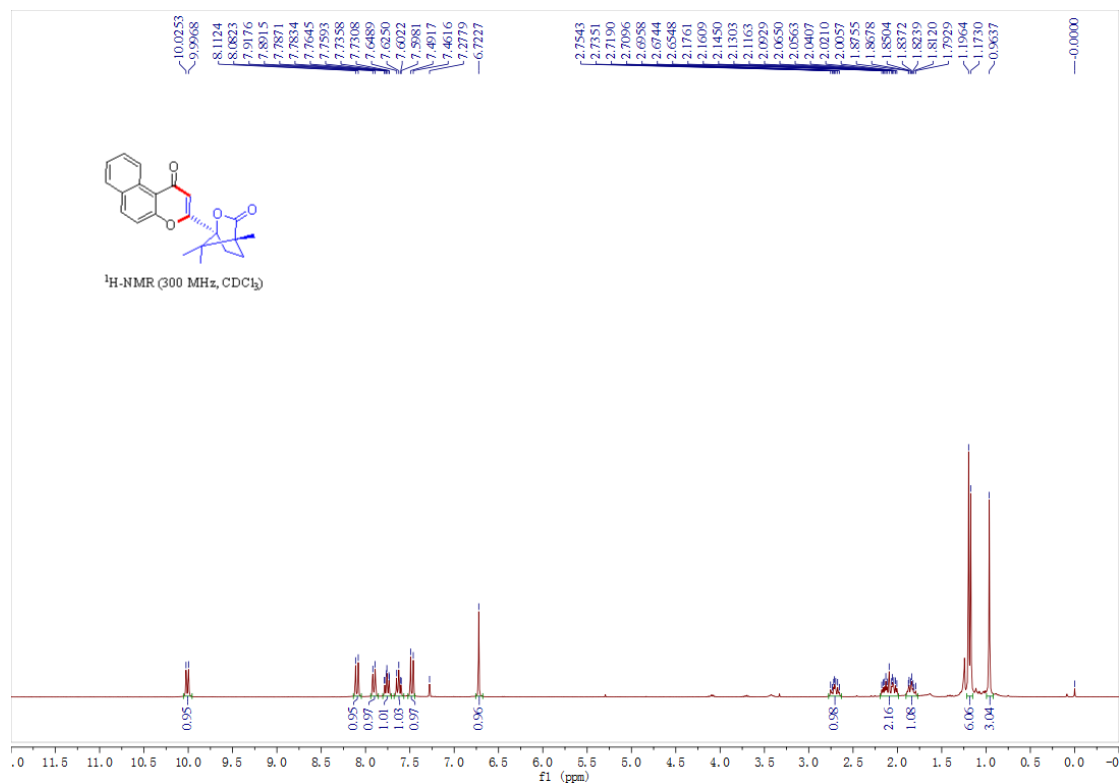


### 3-(1-(4-isobutylphenyl)ethyl)-1H-benzo[f]chromen-1-one (6)

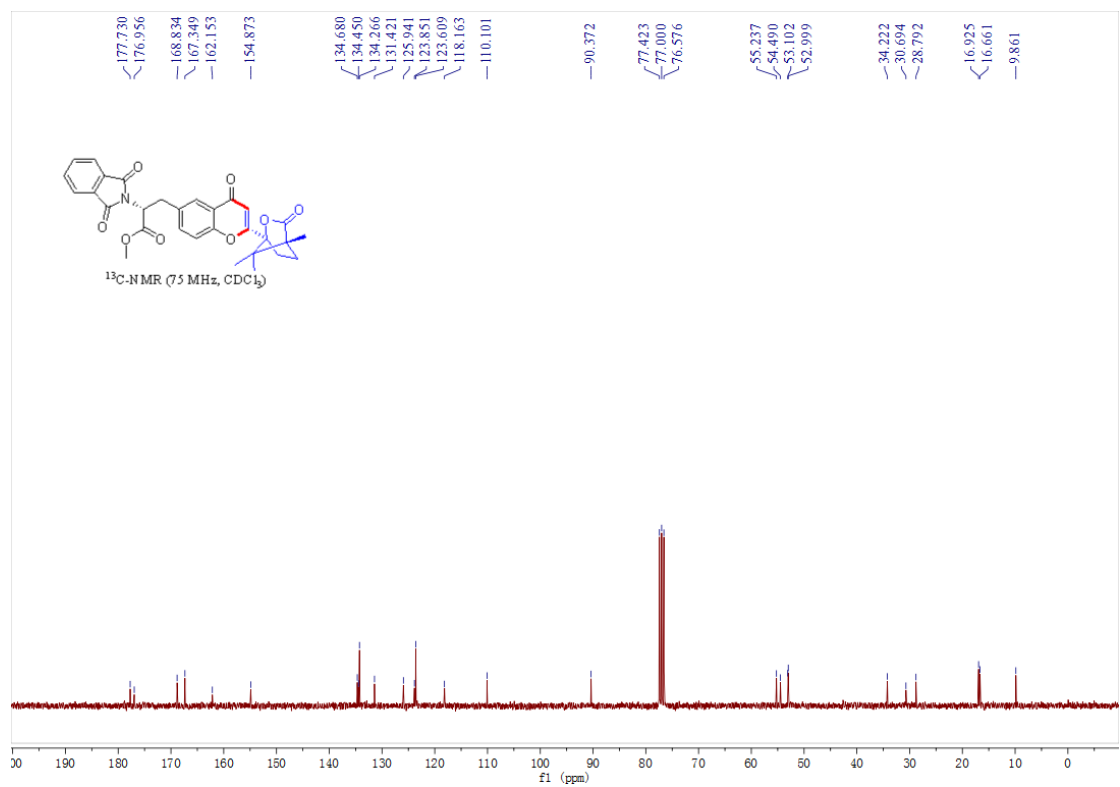
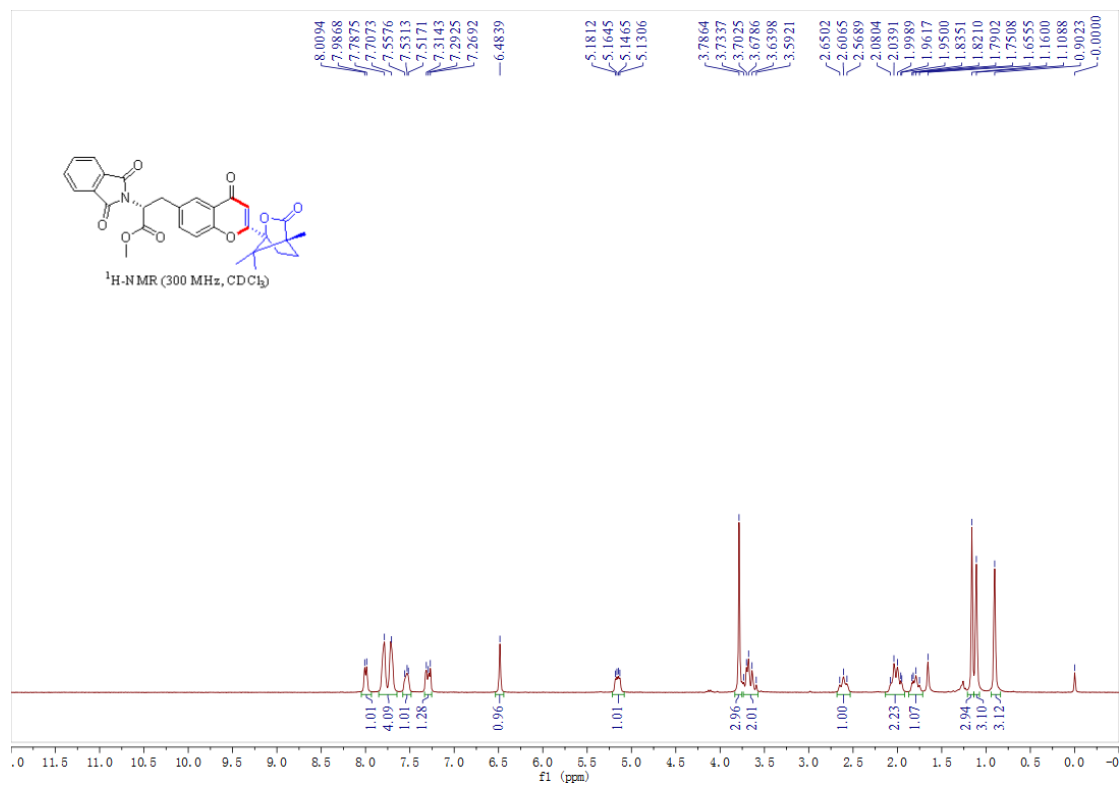




**3-((1*S*,4*R*)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptan-1-yl)-1*H*-benzo[*f*]chromen-1-one (7)**



**methyl (*R*)-2-(1,3-dioxoisindolin-2-yl)-3-(4-oxo-2-((1*S*,4*R*)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptan-1-yl)-4*H*-chromen-6-yl)propanoate (**8**)**



**(3*aR*,3*bS*,11*bR*,13*aR*)-8-((3*R*,5*R*,7*R*)-adamantan-1-yl)-13*a*-methyl  
2,3,3*a*,3*b*,4,5,11*b*,12,13,13*a*-decahydrocyclopenta[5,6]naphtho[1,2-*g*]chromene-  
1,10-dione (9)**

