

Biocatalytic Domino Reaction: Synthesis of 2H-1-Benzopyran-2-one Derivatives  
using Alkaline Protease from *Bacillus licheniformis*

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## NMR spectra data

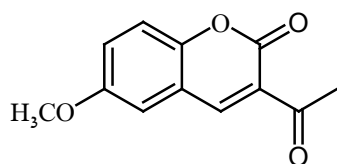
### 3-Benzoyl-6-methoxy-2H-chromen-2-one (3a)<sup>1</sup>

White solid. mp 157-159°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 3.87 (s, 3H), 7.00 (d, J = 3Hz, 1H), 7.21 – 7.27 (m, 1H), 7.35 (d, J = 9Hz, 1H), 7.46 – 7.51 (m, 2H), 7.60 – 7.65 (m, 1H), 7.88 (d, J = 9Hz, 2H), 8.04 (s, 1H)

### Ethyl 6-methoxy-2-oxo-2H-chromene-3-carboxylate (3b)<sup>1</sup>

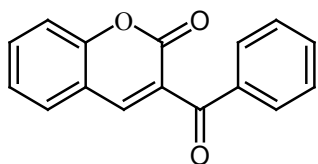
Yellow solid. mp 138-140°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.41 (t, J = 9Hz, 3H), 3.86 (s, 3H), 4.41 (q, J = 9Hz, 2H), 7.00 – 7.01 (m, 1H), 7.23 – 7.31 (m, 2H), 8.49(s, 1H).

### 3-Acetyl-6-methoxy-2H-chromen-2-one (3c)<sup>1</sup>



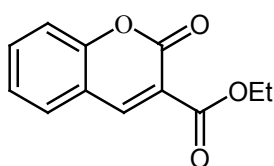
Yellow solid. mp 184-186°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 2.73 (s, 3H), 3.87(s, 3H), 7.04 (s, 1H), 7.22 – 7.28 (m, 2H), 8.47 (s, 1H)

### 3-benzoyl-2H-chromen-2-one (3d)<sup>1</sup>



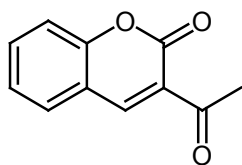
White solid. mp 138 -140°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.33 – 7.42 (m, 2H), 7.46 – 7.51 (m, 2H), 7.60 – 7.68 (m, 3H), 7.88 – 7.96 (m, 2H), 8.09 (s, 1H)

### Ethyl 2-oxo-2H-chromene-3-carboxylate (3e)<sup>1</sup>



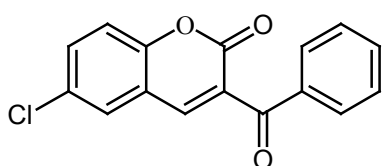
White solid. mp 93-95°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.37 (t, J = 9 Hz, 3H), 4.37 (q, J = 9Hz, 2H), 7.29 – 7.32 (m, 2H), 7.58– 7.61 (m, 2H), 8.50(s, 1H)

### 3-acetyl-2H-chromen-2-one (3f)<sup>1</sup>



White solid. mp 121-123°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 2.73(s, 3H) , 7.33 – 7.39(m, 2H), 7.64 – 7.68(m, 2H), 8.51(s, 1H).

### 3-Benzoyl-6-chloro-2H-chromen-2-one (3g)<sup>1</sup>

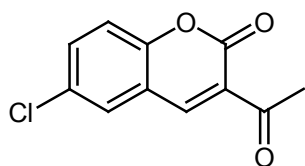


White solid. mp 165-166 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.35 – 7.38 (m, 1H), 7.47 – 7.52(m, 2H), 7.58 – 7.66 (m, 3H), 7.88 (d, J = 9Hz, 2H), 7.98(s, 1H).

### **Ethyl 6-chloro-2-oxo-2H-chromene-3-carboxylate (3h)<sup>1</sup>**

Yellow solid. mp 204-206°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.42 (t, J = 9Hz, 3H), 4.45 (q, J = 9Hz, 2H), 7.28 – 7.34 (m, 1H), 7.60 (d, J = 9Hz, 2H), 8.45 (s, 1H)

### **3-acetyl-6-chloro-2H-chromen-2-one(3i)<sup>1</sup>**



White solid. mp 161-163°C; <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>) δ 2.56 (s, 3H), 7.49 (d, J = 9Hz, 1H), 7.73 – 7.77 (m, 1H), 8.05 – 8.06 (m, 1H), 8.58 (s, 1H)

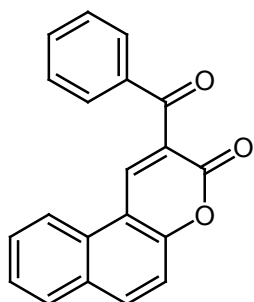
### **3-benzoyl-6-nitro-2H-chromen-2-one(3j)<sup>6</sup>**

Yellow solid. mp 196-198°C; <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>) δ 7.53 – 7.58 (m, 2H), 7.68 – 7.73 (m, 2H), 7.98 (d, J = 9Hz, 2H), 8.49 (dd, J = 3Hz, 3Hz, 1H), 8.55 (s, 1H), 8.81 – 8.82(m, 1H)

### **Ethyl 6-nitro-2-oxo-2H-chromene-3-carboxylate (3k)<sup>4</sup>**

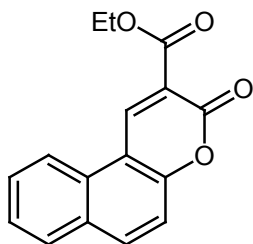
White solid. mp 198-200°C;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.44 (t,  $J = 9\text{Hz}$ , 3H), 4.46 (q,  $J = 9\text{Hz}$ , 2H), 7.52 (d,  $J = 9\text{Hz}$ , 1H), 8.52 (d,  $J = 9\text{Hz}$ , 1H), 8.57 – 8.59 (m, 2H).

### 2-benzoyl-3H-benzo[f]chromen-3-one(3l)<sup>2</sup>



Yellow solid. mp 217-219°C;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 – 7.48 (m, 3H), 7.63 (d,  $J = 6\text{Hz}$ , 2H), 7.70 – 7.76 (m, 1H), 7.92 – 7.97 (m, 3H), 8.12 (d,  $J = 9\text{Hz}$ , 1H), 8.27 (d,  $J = 9\text{Hz}$ , 1H), 8.93 (s, 1H)

### ethyl 3-oxo-3H-benzo[f]chromene-2-carboxylate(3m)<sup>3</sup>



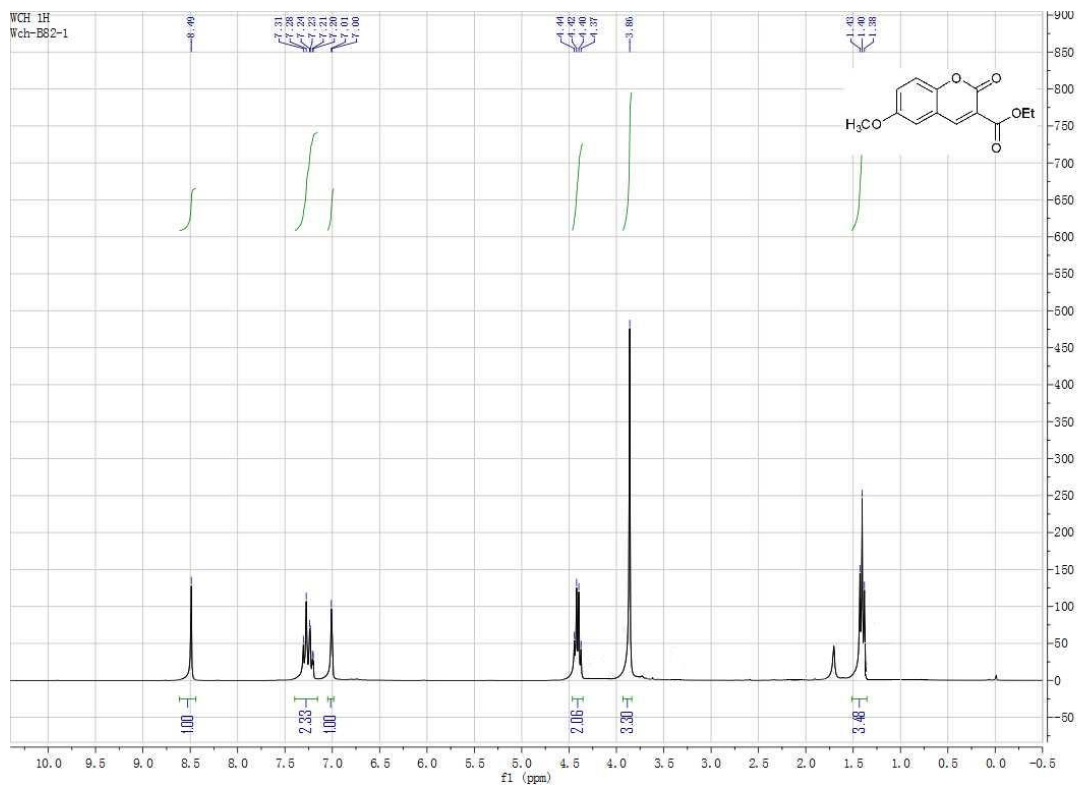
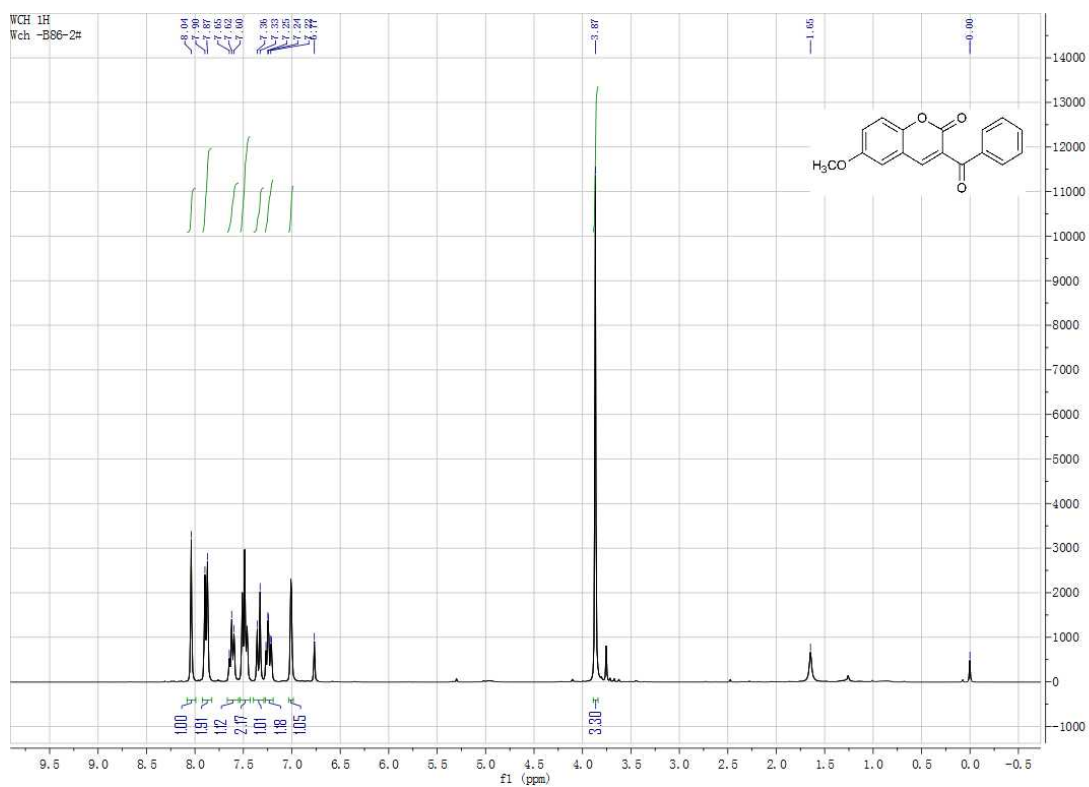
White solid. mp 120 - 122°C;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.46 (t,  $J = 9\text{Hz}$ , 3H), 4.48 (q,  $J = 9\text{Hz}$ , 2H), 7.47 (d,  $J = 9\text{Hz}$ , 1H), 7.59 – 7.64 (m, 1H), 7.72 – 7.77 (m, 1H), 7.92 – 7.94 (m, 1H), 8.10 (d,  $J = 9\text{Hz}$ , 1H), 8.32 (d,  $J = 9\text{Hz}$ , 1H), 9.32 (s, 1H),

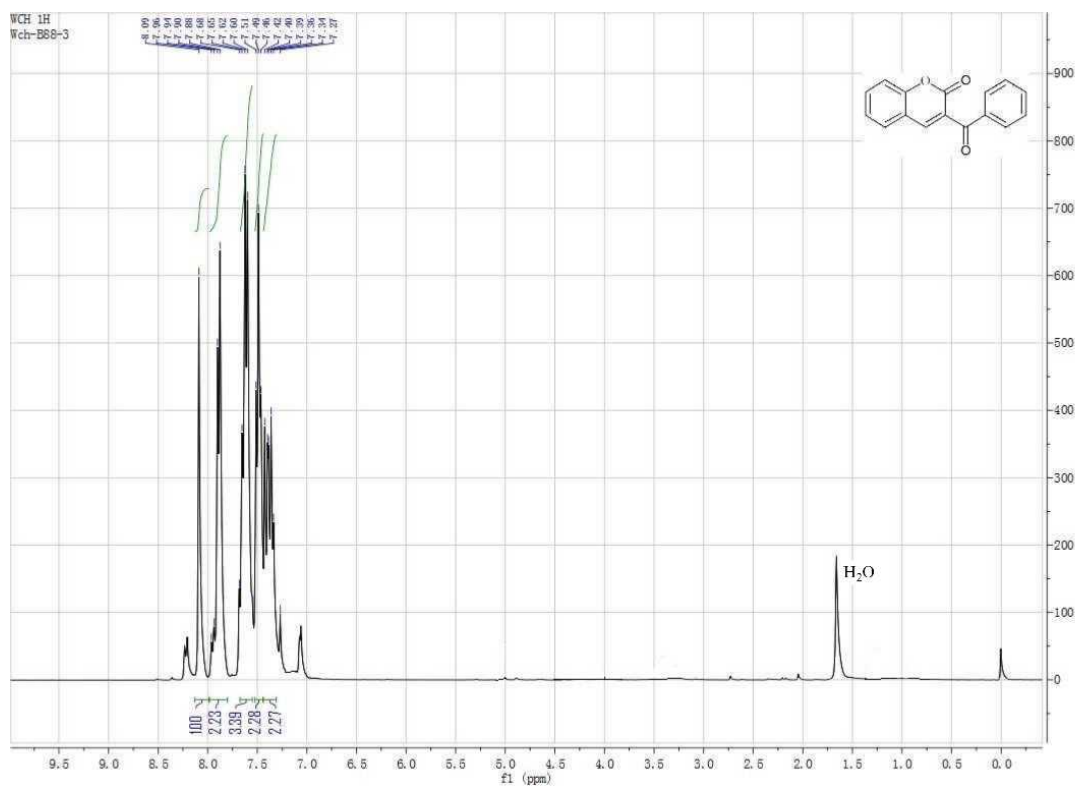
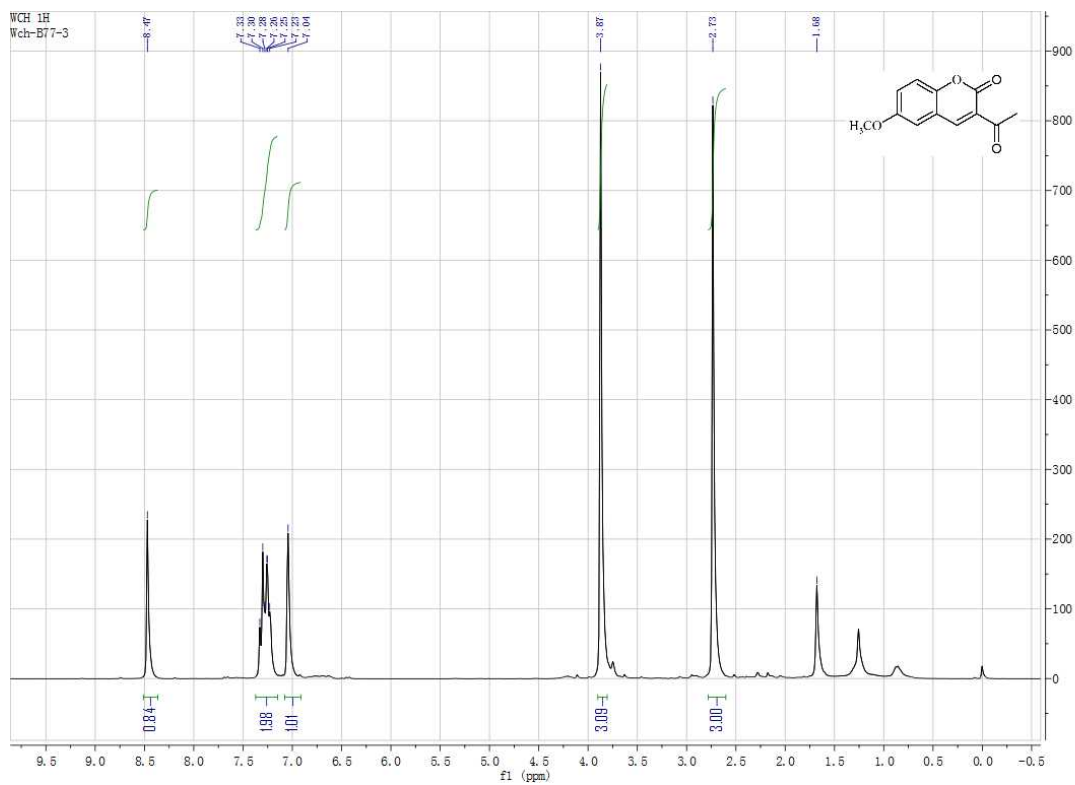
### 2-acetyl-3H-benzo[f]chromen-3-one(3n)<sup>3</sup>

Yellow solid. mp 192 - 193°C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  2.79 (s, 3H), 7.47 (d,  $J = 9\text{Hz}$ , 1H), 7.63 (d,  $J = 9\text{Hz}$ , 1H), 7.72 – 7.77 (m, 1H), 7.93 (d,  $J = 9\text{Hz}$ , 1H), 8.10 (d,  $J = 9\text{Hz}$ , 1H), 8.35 (d,  $J = 6\text{Hz}$ , 1H), 9.30 (s, 1H)

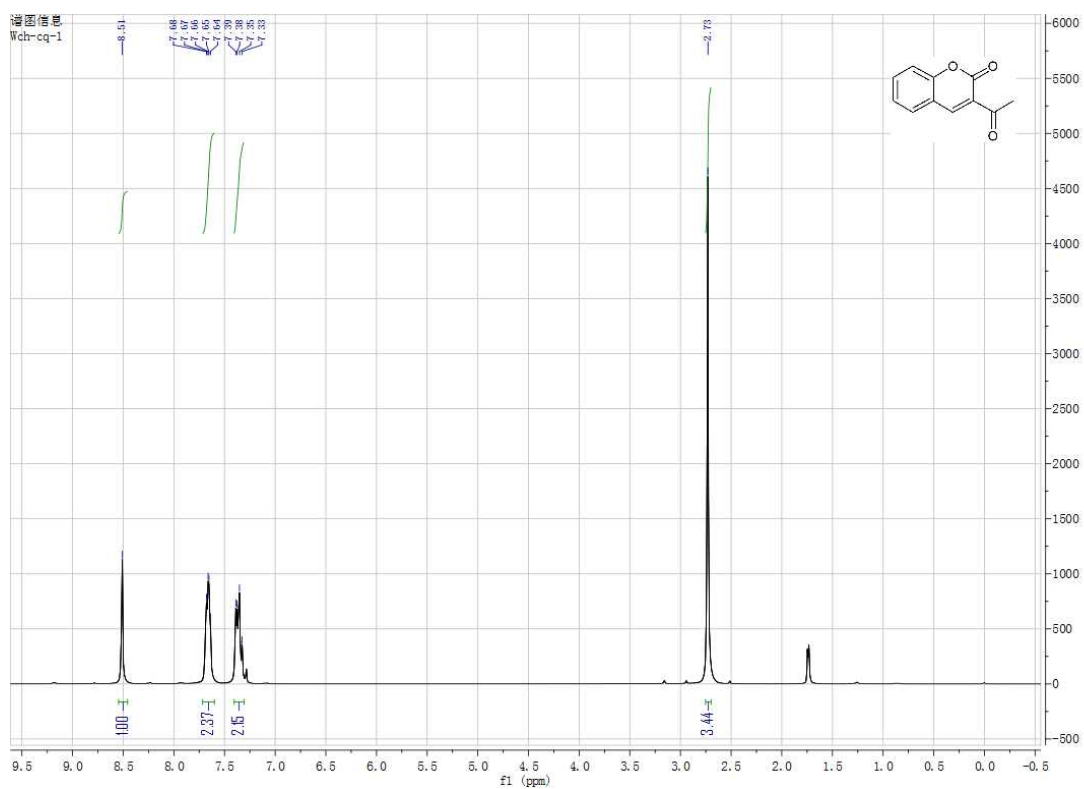
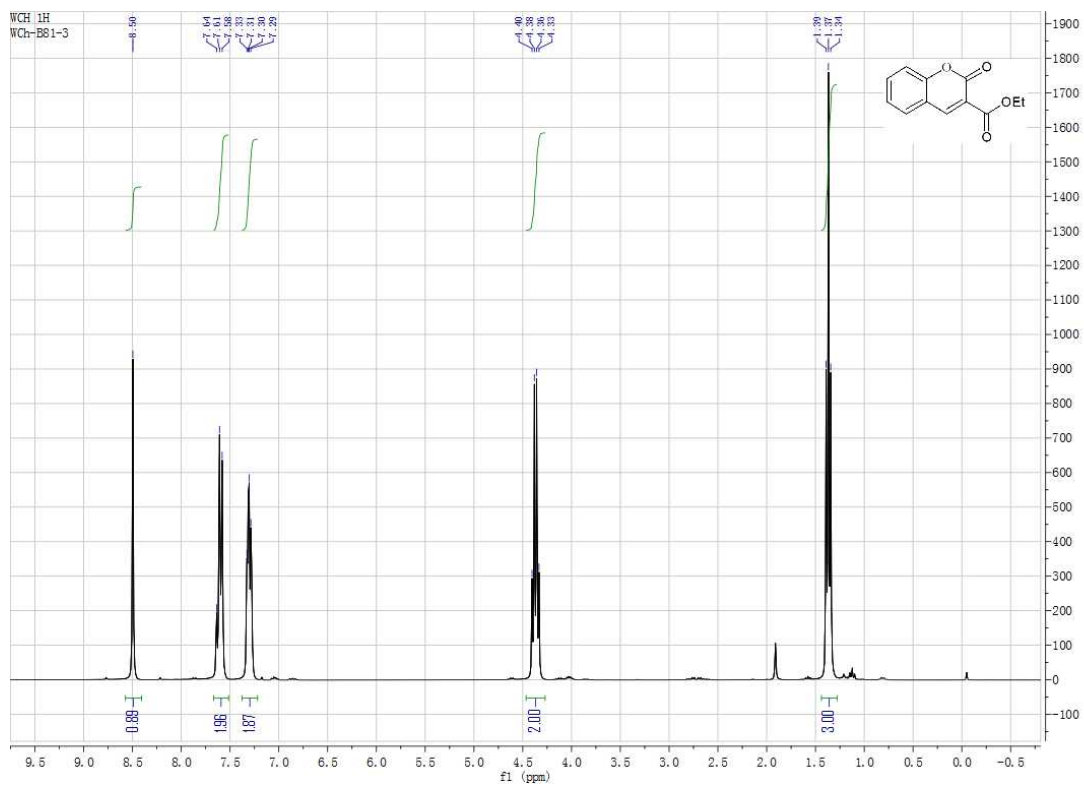
**ethyl 2-hydroxy-2-methyl-2H-chromene-3-carboxylate(4)<sup>5</sup>**

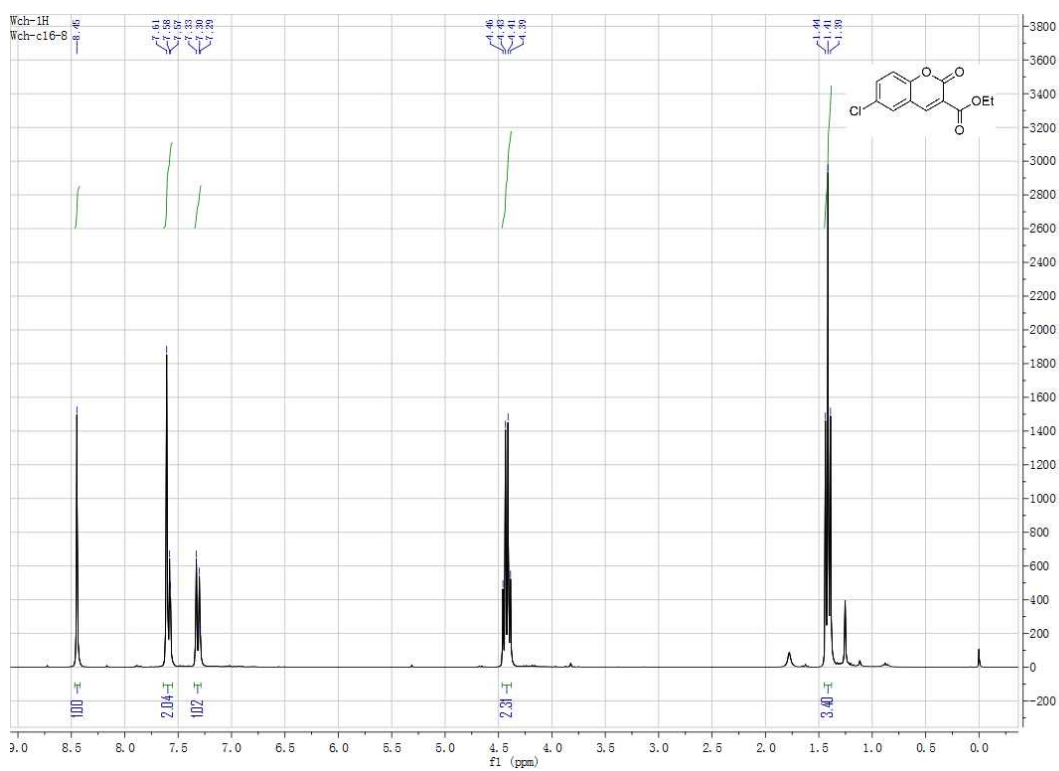
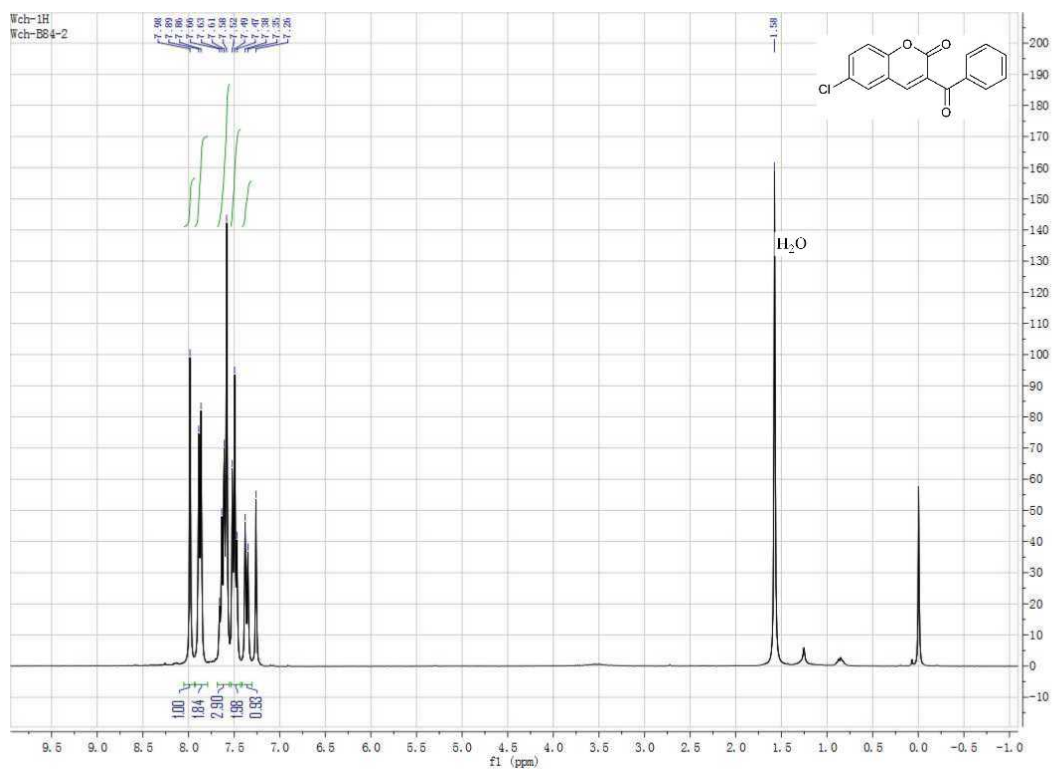
Yellow solid. mp 85-87°C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.38 (t,  $J = 9\text{Hz}$ , 3H), 1.96 (s, 3H), 3.80 (s, 1H), 4.31 (q,  $J = 9\text{Hz}$ , 2H), 6.96 – 7.01 (m, 2H), 7.26 – 7.35 (m, 2H), 7.58 (s, 1H).

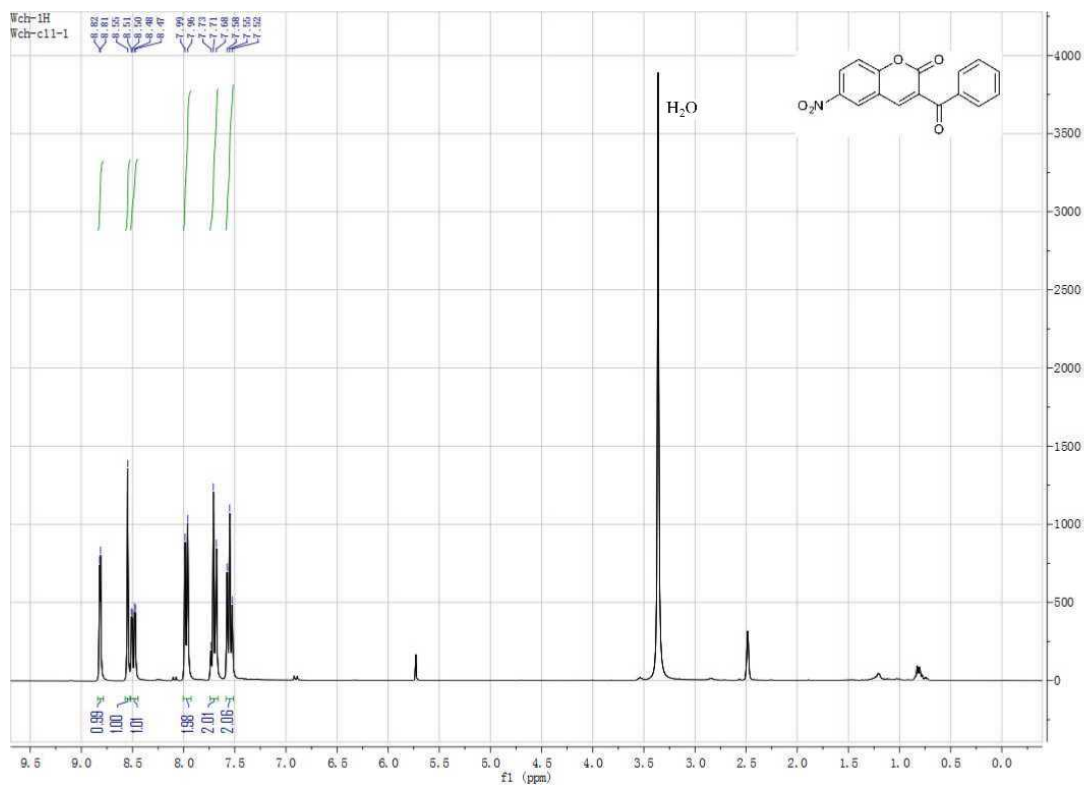
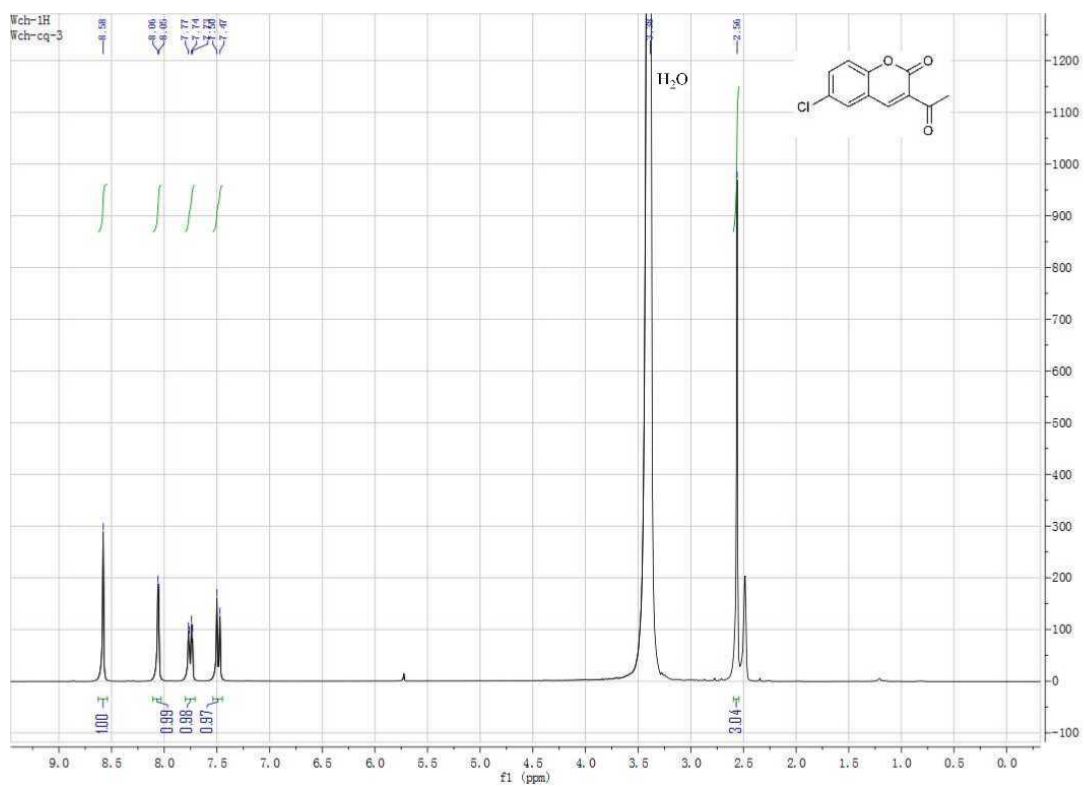


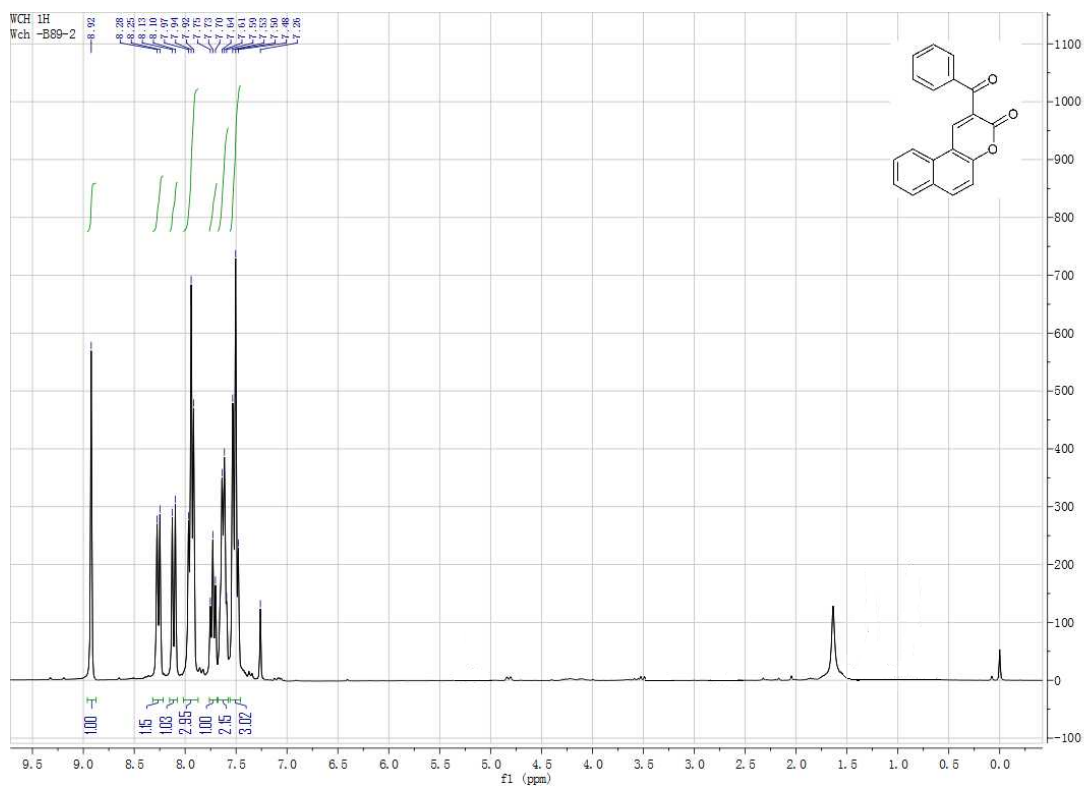
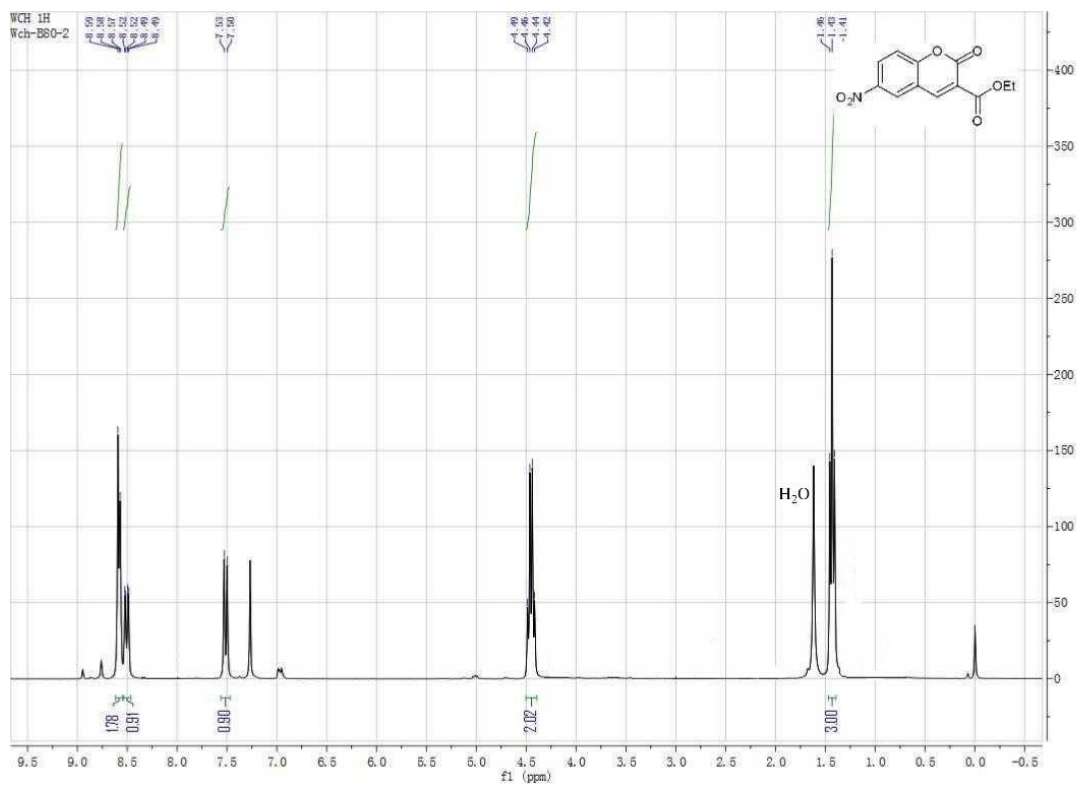


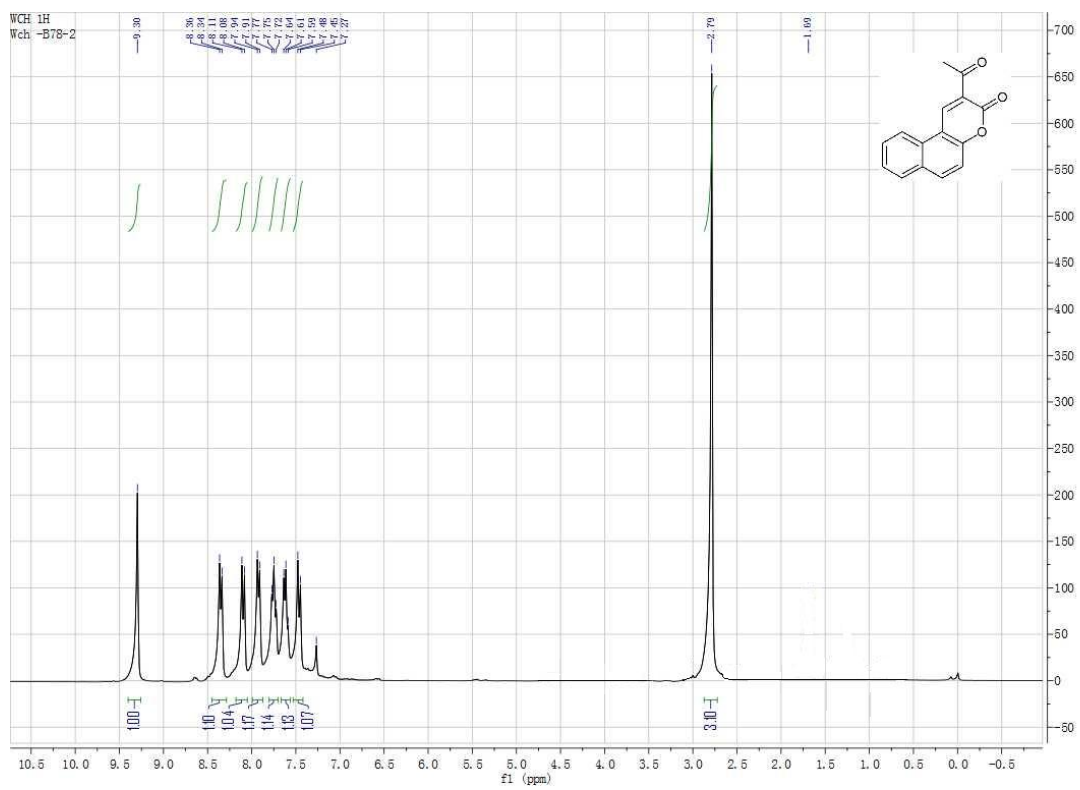
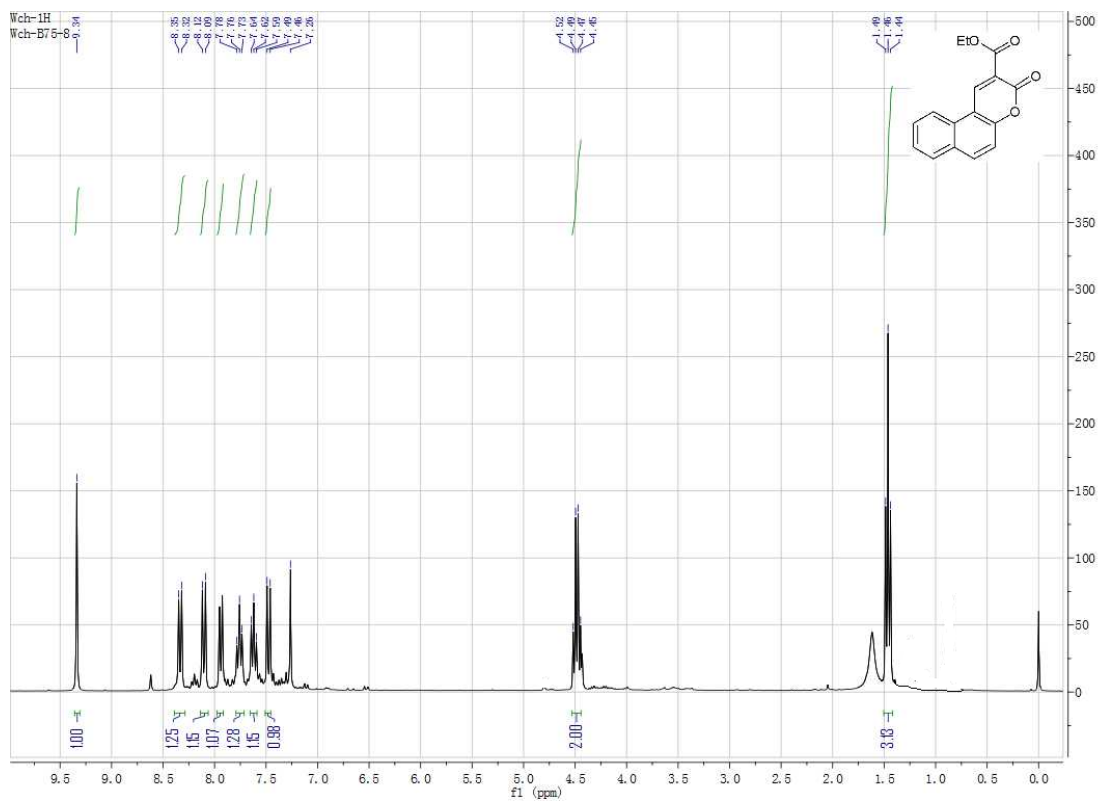


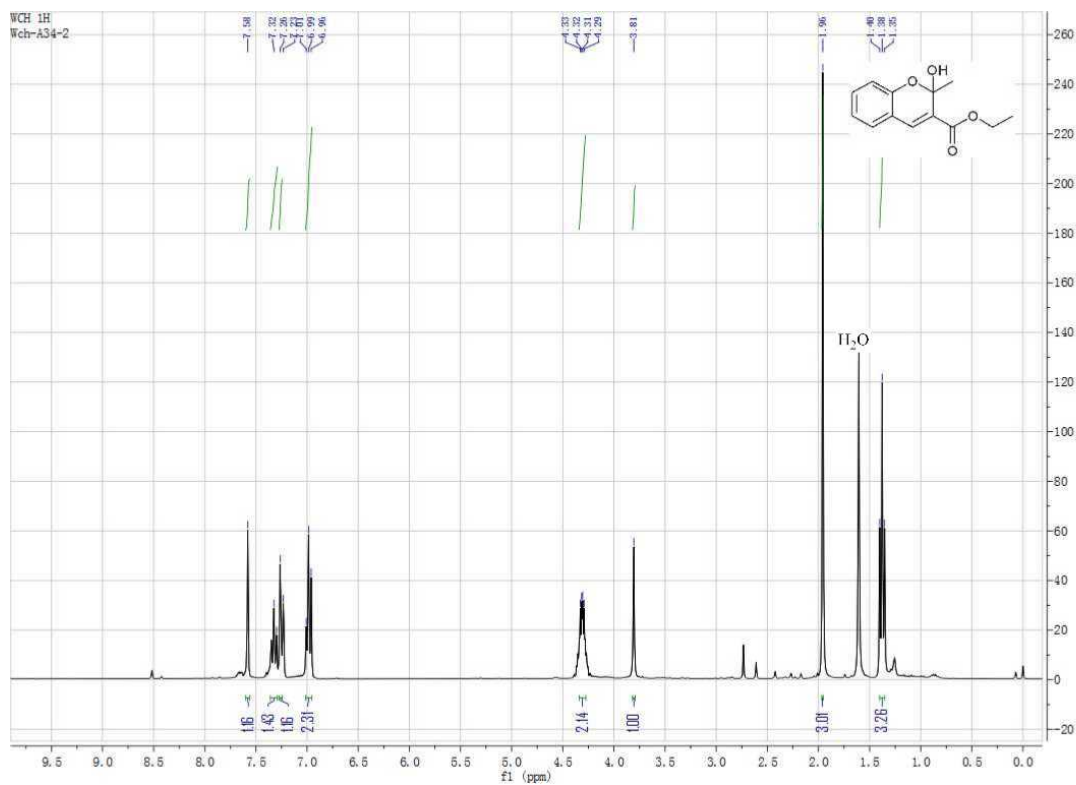












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