

## *Supplementary Information*

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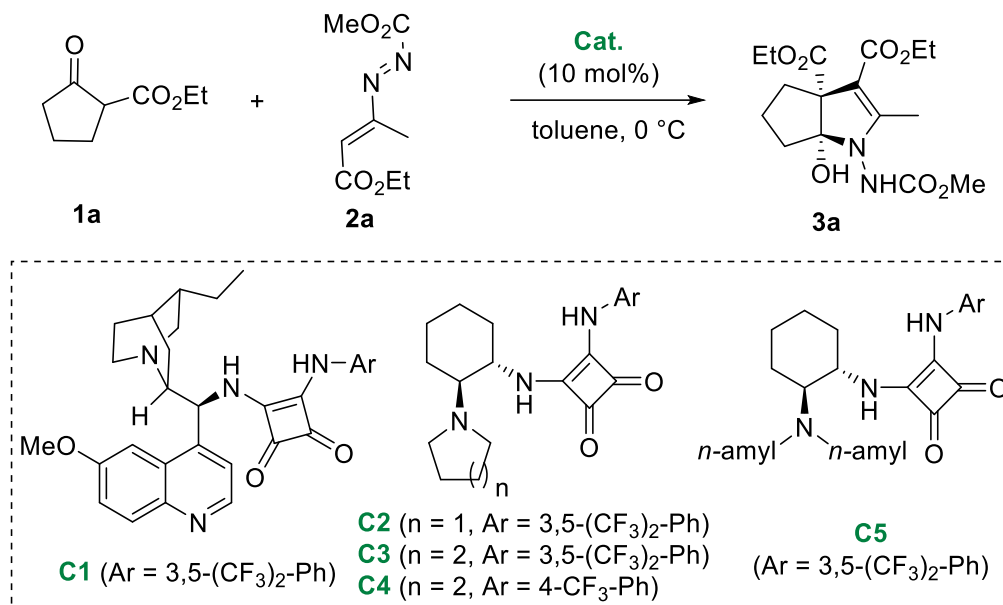
## 1. General Methods

Unless otherwise specified, all reactions were conducted under an inert atmosphere and anhydrous conditions. All the solvents were purified according to the standard procedures. All chemicals which are commercially available were employed without further purification. Thin-layer chromatography (TLC) was performed on silica gel plates (60F - 254) using UV - light (254 nm). Flash chromatography was conducted on silica gel (200–300 mesh).  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded at ambient reported in parts per million (ppm). The data are reported as follows: for  $^1\text{H}$  NMR, chemical shift in ppm from tetramethylsilane with the solvent as internal standard (DMSO  $\delta$  2.50 ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or overlap of non-equivalent resonances), integration; for  $^{13}\text{C}$  NMR, chemical shift in ppm from tetramethylsilane with the solvent as internal indicator (DMSO  $\delta$  39.5 ppm), multiplicity with respect to protons. All high-resolution mass spectra were obtained on a Q-TOF Micro LC/MS System ESI spectrometer to be given in m/z. Enantiomeric excesses values were determined with HPLC (chiral column; mobile phase hexane/*i*-PrOH). Cyclic  $\beta$ -keto esters **1** were employed directly from commercial sources except **1q-1s**<sup>[1]</sup>, **1t**<sup>[2]</sup>, **1x**<sup>[3]</sup>, which prepared according to the literature; azoalkenes **2** were synthesized according to modified literature-reported procedures<sup>[4]</sup>.

## 2. Representative Procedures

### Optimization of the reaction conditions for 3a-3k, 3p-3t, 3a'

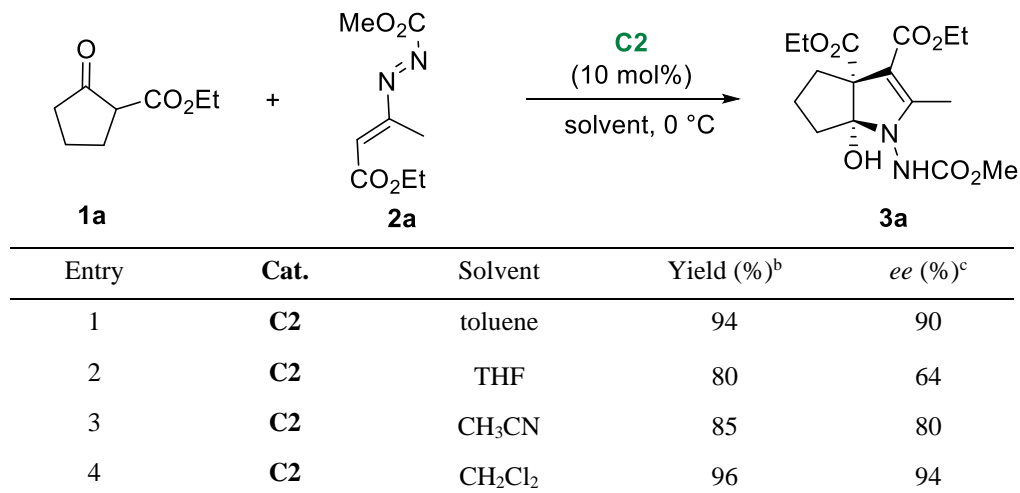
#### 1. Effect of Catalysts (Table S1)



Entry	Cat.	Yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
1	<b>C1</b>	92	88
2	<b>C2</b>	94	90
3	<b>C3</b>	90	52
4	<b>C4</b>	95	32
5	<b>C5</b>	96	<5

a) Reaction conditions: **1a** (0.05 mmol), **2a** (0.06 mmol.), **Cat.** (10 mol%) and toluene (1 mL) at 0 °C for 12 h. b) Isolated yields. c) Determined by chiral HPLC analysis. All dr > 20:1.

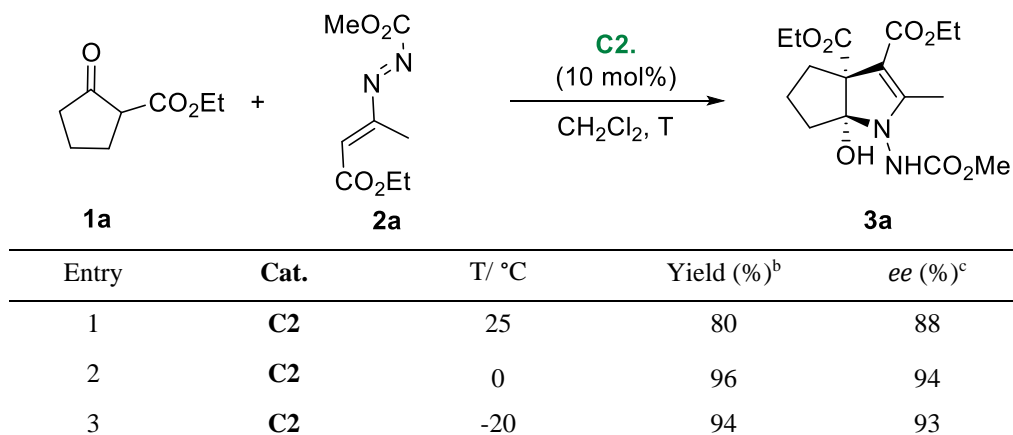
#### 2. Effect of Solvents (Table S2)



Entry	Cat.	Solvent	Yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
1	<b>C2</b>	toluene	94	90
2	<b>C2</b>	THF	80	64
3	<b>C2</b>	CH <sub>3</sub> CN	85	80
4	<b>C2</b>	CH <sub>2</sub> Cl <sub>2</sub>	96	94

a) Reaction conditions: **1a** (0.05 mmol), **2a** (0.06 mmol.), **C2** (10 mol%) and solvent (1 mL) at 0 °C for 12 h. b) Isolated yields. c) Determined by chiral HPLC analysis. All dr > 20:1.

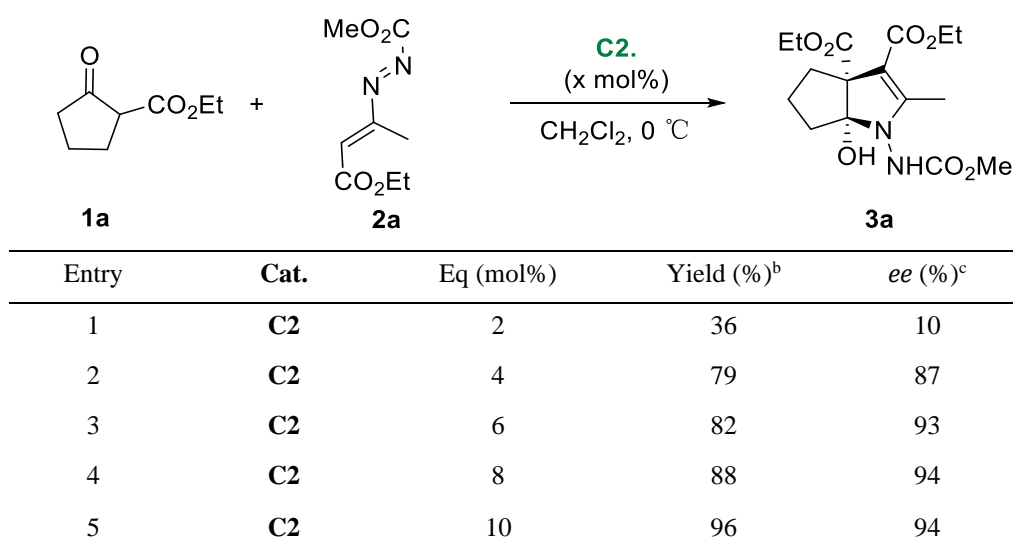
### 3. Effect of more Temperatures (Table S3)



a) Reaction conditions: **1a** (0.05 mmol), **2a** (0.06 mmol.), **C2** (10 mol%) and CH<sub>2</sub>Cl<sub>2</sub> (1 mL), 12 h.

b) Isolated yields. c) Determined by chiral HPLC analysis. All dr > 20:1.

### 5. Effect of the amount of catalyst (Table S4)

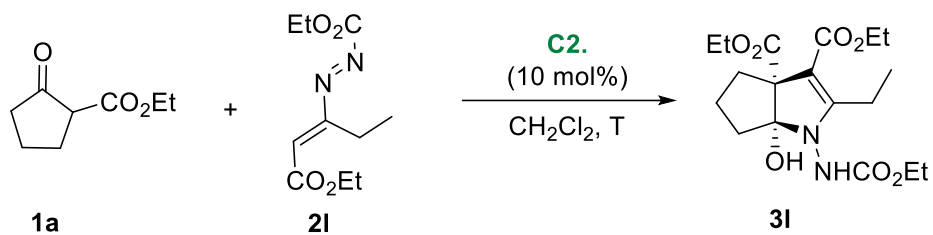


a) Reaction conditions: **1a** (0.05 mmol), **2a** (0.06 mmol.), and CH<sub>2</sub>Cl<sub>2</sub> (1 mL), at 0 °C for 12 h. b)

Isolated yields. c) Determined by chiral HPLC analysis. All dr > 20:1.

## Optimization of the reaction conditions for 3l-3o

### 1. Effect of more Temperatures (Table S5)



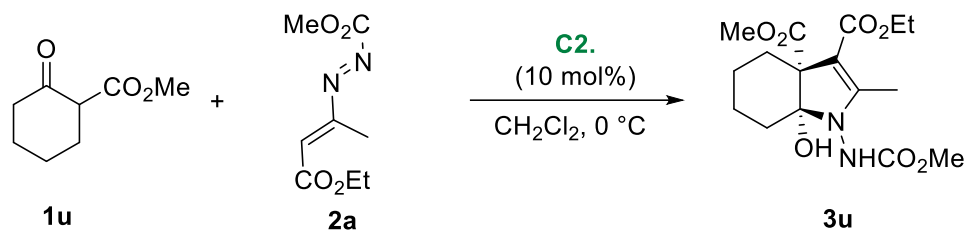
Entry	Cat.	T/ °C	Yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
1	<b>C2</b>	25	83	80
2	<b>C2</b>	0	88	86
3	<b>C2</b>	-20	87	84
4	<b>C2</b>	-40	92	90

a) Reaction conditions: **1a** (0.05 mmol), **2l** (0.06 mmol.), **C2** (10 mol%) and  $\text{CH}_2\text{Cl}_2$  (1 mL), 24 h.

b) Isolated yields. c) Determined by chiral HPLC analysis. All dr > 20:1.

## Optimization of the reaction conditions for 3u-3z

### 1. Effect of additive (Table S6)

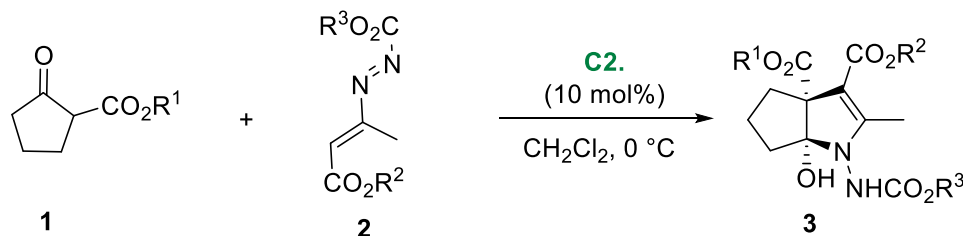


Entry	Cat.	Additive	Yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
1	<b>C2</b>	-	78	32
2	<b>C2</b>	50 mg 3Å MS	89	93
3	<b>C2</b>	50 mg 4Å MS	91	94
4	<b>C2</b>	50 mg 5Å MS	90	94

a) Reaction conditions: **1u** (0.05 mmol), **2a** (0.06 mmol.), **C2** (10 mol%) and CH<sub>2</sub>Cl<sub>2</sub> (1 mL) at 0 °C for 48 h. b) Isolated yields. c) Determined by chiral HPLC analysis. All dr > 20:1.

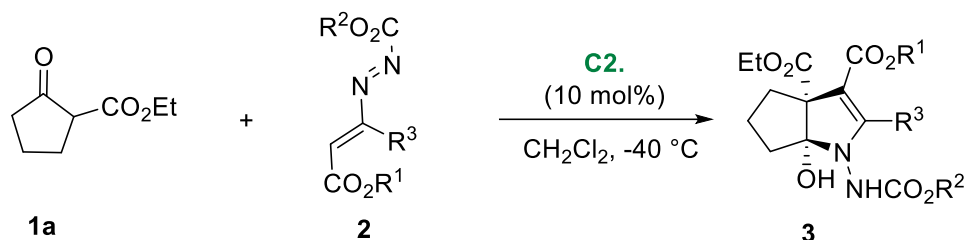
## General Procedures for the synthesis of products 3

### For 3a-3k, 3p-3t, 3a'



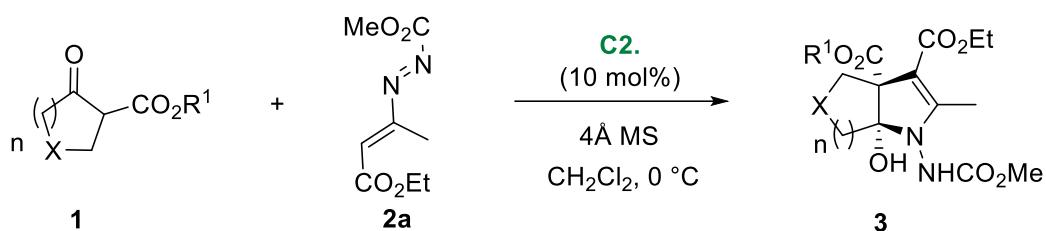
Cyclic  $\beta$ -keto ester **1** (0.20 mmol), and **C2** (10 mol%) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) and azoalkene **2** (0.24 mmol) was added dropwise at 0 °C. The reaction mixture was stirred for 12 h. After the completion of the reaction which was indicated by TLC, the solvents were removed in vacuo and the crude product was separated by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 1.5:1–1:1) to afford the target products **3**.

### For 3l-3o



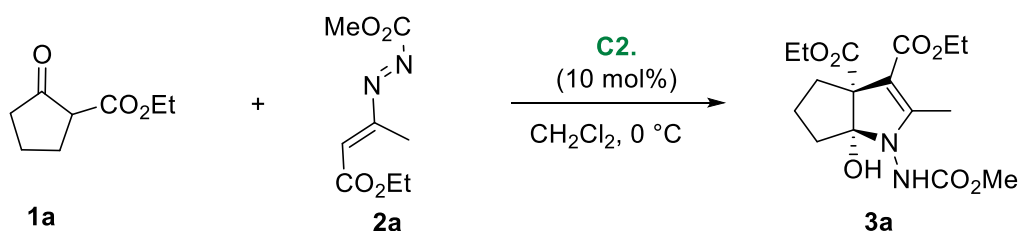
Cyclic  $\beta$ -keto ester **1a** (0.20 mmol), and **C2** (10 mol%) were dissolved in  $\text{CH}_2\text{Cl}_2$  (2 mL) and azoalkene **2** (0.24 mmol) was added dropwise at  $-40\text{ }^\circ\text{C}$ . The reaction mixture was stirred for 12 h. After the completion of the reaction which was indicated by TLC, the solvents were removed in vacuo and the crude product was separated by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 1.5:1–1:1) to afford the target products **3**.

#### For 3u-3z



Cyclic  $\beta$ -keto ester **1** (0.20 mmol), 4 Å MS (50 mg) and **C2** (10 mol%) were dissolved in  $\text{CH}_2\text{Cl}_2$  (2 mL) and azoalkene **2a** (0.24 mmol) was added dropwise at  $0\text{ }^\circ\text{C}$ . The reaction mixture was stirred for 12 h. After the completion of the reaction which was indicated by TLC, the solvents were removed in vacuo and the crude product was separated by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 1.5:1–1:1) to afford the target products **3**.

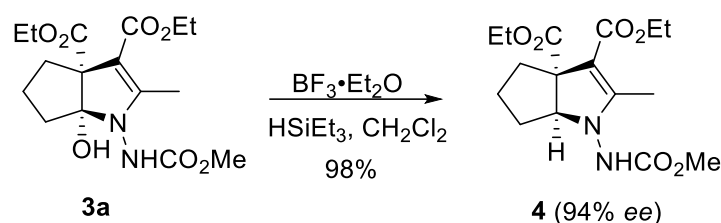
#### Procedure for the gram-scale reaction



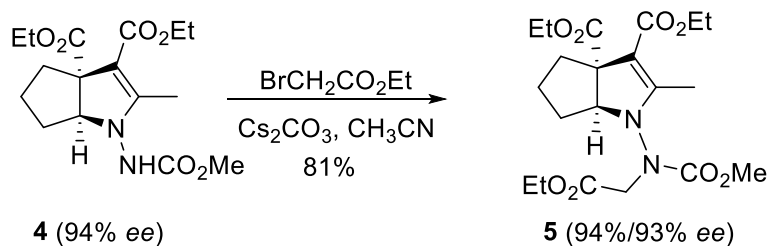
Cyclic  $\beta$ -keto ester **1a** (0.47 g, 3 mmol), and **C2** (10 mol%) were dissolved in

CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and azoalkene **2a** (0.72 g, 3.6 mmol) was added dropwise at 0 °C. The reaction mixture was stirred for 24 h. After the completion of the reaction which was indicated by TLC, the solvents were removed in vacuo and the crude product was separated by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 3:1–1:1) to afford the target products **3a** (0.94 g, 88% yield) as a white solid.

### Derivatization of **3a**, **3c** and **3e** into compounds 4-8



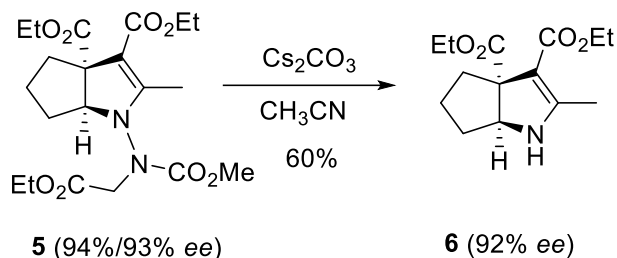
To the solution of compound **3a** (68.4 mg, 0.19 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) was added boron trifluoride ether (41.2 mg, 0.29 mmol) and triethyl silane (33.4 mg, 0.29 mmol) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (1 mL), the reaction mixture was stirred at 20 °C for 4 h. After the completion of the reaction which was indicated by TLC, the reaction mixture was treated with H<sub>2</sub>O and extracted with ethyl acetate and washed with brine. The combined organic layers were dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure. The residue was purified through preparative thin layer chromatography on silica gel (petroleum ether/ethyl acetate = 3:1) to afford pure product **4**.



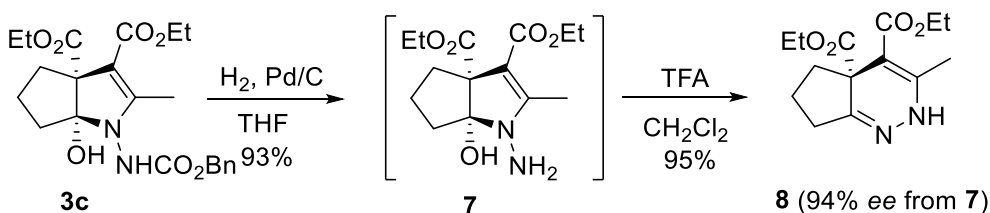
To the solution of compound **4** (64.0 mg, 0.19 mmol) in CH<sub>3</sub>CN (1 mL) was added ethyl 2-bromoacetate (48.1 mg, 0.29 mmol). Then, Cs<sub>2</sub>CO<sub>3</sub> (94.5 mg, 0.29 mmol) was added to the reaction mixture, which was stirred at room temperature for 2 h. After the completion of the reaction which was indicated by TLC, the reaction mixture was



purified through preparative thin layer chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) to afford pure product **5**.



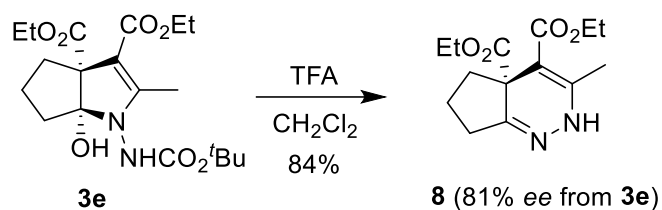
To the solution of compound **5** (65.0 mg, 0.15 mmol) in  $\text{CH}_3\text{CN}$  (1 mL) was added  $\text{Cs}_2\text{CO}_3$  (97.7 mg, 0.3 mmol), the reaction mixture was stirred at 60 °C for 3 day. After the completion of the reaction which was indicated by TLC, the reaction mixture was purified through preparative thin layer chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) to afford pure product **6**.



To the solution of compound **3c** (83.0 mg, 0.19 mmol) in THF (1 mL) was added Pd/C (25 mg) under  $\text{H}_2$ , the reaction mixture was stirred at room temperature overnight. After the completion of the reaction which was indicated by TLC, the reaction mixture was purified through preparative thin layer chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) to afford pure product **7**.

To the solution of compound **7** (53.2 mg, 0.18 mmol) in  $\text{CH}_2\text{Cl}_2$  (1 mL) was added TFA (0.25 mmol), the reaction mixture was stirred at 20 °C for 24 h. After the completion of the reaction which was indicated by TLC, the reaction mixture was treated with  $\text{H}_2\text{O}$  and extracted with ethyl acetate and washed with brine. The combined organic layers were dried with anhydrous  $\text{Na}_2\text{SO}_4$  and the solvent was removed under reduced pressure. The residue was purified through preparative thin layer chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) to afford pure

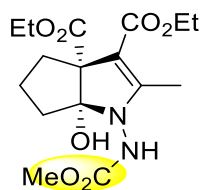
product **8**.



To the solution of compound **3e** (59.7 mg, 0.15 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) was added TFA (0.26 mmol), the reaction mixture was stirred at 20 °C for 6 h. After the completion of the reaction which was indicated by TLC, the reaction mixture was treated with H<sub>2</sub>O and extracted with ethyl acetate and washed with brine. The combined organic layers were dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure. The residue was purified through preparative thin layer chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) to afford pure product **8**.

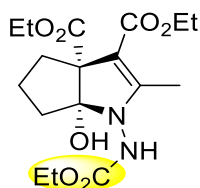
### 3. Characterization of Products

Diethyl (3*aR*,6*aR*)-6*a*-hydroxy-1-((methoxycarbonyl)amino)-2-methyl-4,5,6,6*a*-tetrahydrocyclopenta[*b*]pyrrole-3,3*a*(1*H*)-dicarboxylate **3a**:



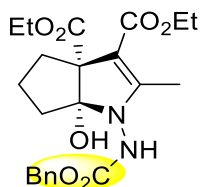
A colorless solid; 68.4 mg; isolated yield = 96%; dr > 20:1; m.p. 87.5 – 87.8°C;  $[\alpha]^{25.2}_D = -11.00$  (c 0.1 EtOAc); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min,  $\lambda = 254$  nm), retention time:  $t_1 = 5.76$  min (minor),  $t_2 = 7.71$  min (major), *ee* = 94%; <sup>1</sup>H NMR (400 MHz, DMSO)  $\delta$  9.32 – 8.82 (m, 1H), 6.49 (s, 1H), 4.11 – 3.95 (m, 4H), 3.64 (s, 3H), 2.68 – 2.60 (m, 1H), 2.08 (s, 3H), 1.99 – 1.62 (m, 5H), 1.11 (t,  $J = 7.1$  Hz, 6H). <sup>13</sup>C NMR (100 MHz, DMSO)  $\delta$  172.2, 165.3, 159.5, 157.9, 104.8, 99.4, 63.3, 60.4, 58.5, 52.7, 38.0, 36.9, 23.0, 14.8, 14.6, 11.8. HRMS (ESI) *m/z* calcd for C<sub>16</sub>H<sub>24</sub>N<sub>2</sub>O<sub>7</sub>Na<sup>+</sup> [M + Na]<sup>+</sup> = 379.1476, found = 379.1486.

Diethyl (3*aR*,6*aR*)-1-((ethoxycarbonyl)amino)-6*a*-hydroxy-2-methyl-4,5,6,6*a*-tetrahydrocyclopenta[*b*]pyrrole-3,3*a*(1*H*)-dicarboxylate **3b**:



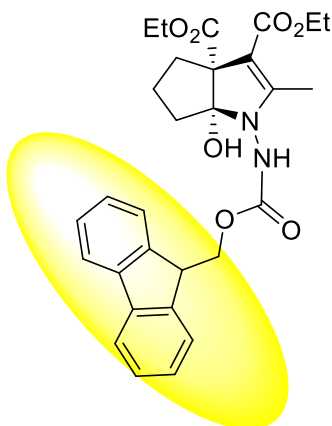
A colorless oil; 66.6 mg; isolated yield = 90%; dr > 20:1;  $[\alpha]_{\text{D}}^{25.2} = 15.38$  (c 0.13 EtOAc); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min,  $\lambda = 254$  nm), retention time:  $t_1 = 5.67$  min (minor),  $t_2 = 7.80$  min (major),  $ee = 91\%$ ;  $^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  9.24 – 8.76 (m, 1H), 6.51 – 6.45 (m, 1H), 4.10 – 3.94 (m, 6H), 2.67 – 2.62 (m, 1H), 2.08 (s, 3H), 1.75 – 1.62 (m, 5H), 1.20 (t,  $J = 7.0$  Hz, 3H), 1.11 (t,  $J = 7.1$  Hz, 6H).  $^{13}\text{C NMR}$  (100 MHz, DMSO)  $\delta$  172.2, 165.3, 159.6, 157.4, 104.7, 99.2, 63.3, 61.5, 60.4, 58.5, 38.0, 36.9, 23.0, 14.9, 14.8, 14.6, 11.8. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{26}\text{N}_2\text{O}_7\text{Na}^+$   $[\text{M} + \text{Na}]^+ = 393.1632$ , found = 393.1636.

Diethyl (3*aR*,6*aR*)-1-(((benzyloxy)carbonyl)amino)-6*a*-hydroxy-2-methyl-4,5,6,6*a*-tetrahydrocyclopenta[*b*]pyrrole-3,3*a*(1*H*)-dicarboxylate **3c**:



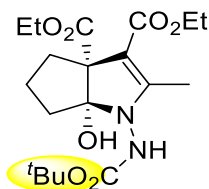
A colorless solid; 83.0 mg; isolated yield = 96%; dr > 20:1; m.p. 84.2 – 84.4°C;  $[\alpha]_{\text{D}}^{25.4} = -10.67$  (c 0.15 EtOAc); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min,  $\lambda = 254$  nm), retention time:  $t_1 = 8.35$  min (minor),  $t_2 = 11.53$  min (major),  $ee = 95\%$ ;  $^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  9.30 – 8.81 (m, 1H), 7.36 – 7.28 (m, 5H), 6.56 – 6.50 (m, 1H), 5.08 – 5.00 (m, 2H), 4.12 – 3.90 (m, 4H), 2.70 – 2.66 (m, 1H), 2.11 (s, 3H), 1.99 – 1.64 (m, 5H), 1.20 (t,  $J = 7.0$  Hz, 3H), 1.02 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C NMR}$  (100 MHz, DMSO)  $\delta$  172.2, 165.3, 159.4, 157.4, 136.9, 129.0, 128.6, 128.3, 104.8, 99.3, 66.8, 63.3, 60.4, 58.5, 38.0, 36.9, 23.0, 14.8, 14.6, 11.8. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_7\text{Na}^+$   $[\text{M} + \text{Na}]^+ = 455.1789$ , found = 455.1794.

Diethyl (3aR,6aR)-1-(((9H-fluoren-9-yl)methoxy)carbonyl)amino)-6a-hydroxy-2-methyl-4,5,6,6a-tetrahydrocyclopenta[*b*]pyrrole-3,3a(1*H*)-dicarboxylate **3d**:



A colorless solid; 98.8 mg; isolated yield = 95%; dr > 20:1; m.p. 140.2 – 140.5°C;  $[\alpha]^{24.5}_D = 9.31$  (c 0.23 EtOAc); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min,  $\lambda = 254$  nm), retention time:  $t_1 = 9.86$  min (minor),  $t_2 = 13.19$  min (major), *ee* = 95%;  $^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  9.57 – 8.68 (m, 1H),  $\delta$  7.91 – 7.33 (m, 8H), 6.47 – 6.29 (m, 1H), 4.65 – 4.05 (m, 4H), 4.00 – 3.95 (m, 3H), 2.65 – 2.51 (m, 1H), 2.06 (s, 3H), 1.96 – 1.60 (m, 5H), 1.14 – 1.09 (m, 6H).  $^{13}\text{C NMR}$  (100 MHz, DMSO)  $\delta$  172.2, 165.3, 159.5, 157.3, 144.0, 141.3, 128.2, 127.6, 125.8, 120.6, 104.8, 99.4, 66.7, 63.3, 60.4, 58.5, 47.1, 38.0, 37.0, 23.1, 14.9, 14.6, 11.8. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{29}\text{H}_{32}\text{N}_2\text{O}_7\text{Na}^+$   $[\text{M} + \text{Na}]^+ = 543.2102$ , found = 543.2110.

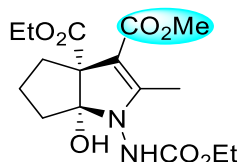
Diethyl (3aR,6aR)-1-((*tert*-butoxycarbonyl)amino)-6a-hydroxy-2-methyl-4,5,6,6a-tetrahydrocyclopenta[*b*]pyrrole-3,3a(1*H*)-dicarboxylate **3e**:



A colorless solid; 59.7 mg; isolated yield = 75%; dr > 20:1; m.p. 76.2 – 76.4°C;  $[\alpha]^{24.6}_D = -5.20$  (c 0.51 EtOAc); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min,  $\lambda = 254$  nm), retention time:  $t_1 = 5.96$  min (minor),  $t_2 = 6.85$  min (major), *ee* = 85%;  $^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  9.97 – 8.45 (m, 1H), 6.48 – 6.36 (m, 1H), 4.11 – 3.95 (m, 4H), 2.64 – 2.62 (m, 1H), 2.07 (s, 3H), 1.99 – 1.61 (m, 5H), 1.41

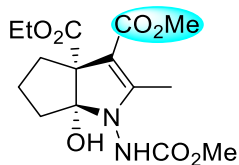
(s, 9H), 1.11 (t,  $J = 7.1$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz, DMSO)  $\delta$  172.2, 165.4, 159.8, 156.4, 104.7, 99.0, 80.4, 63.3, 60.5, 58.5, 38.0, 36.9, 28.3, 23.0, 14.9, 14.6, 11.8. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{30}\text{N}_2\text{O}_7\text{Na}^+$   $[\text{M} + \text{Na}]^+ = 421.1945$ , found = 421.1950.

3a-ethyl 3-methyl (3a*R*,6a*R*)-1-((ethoxycarbonyl)amino)-6a-hydroxy-2-methyl-4,5,6,6a-tetrahydrocyclopenta[*b*]pyrrole-3,3a(1*H*)-dicarboxylate **3f**:



A colorless solid; 68.4 mg; isolated yield = 96%; dr > 20:1; m.p. 78.3 – 78.5°C;  $[\alpha]^{24.6}_{\text{D}} = -7.39$  (c 0.23 EtOAc); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min,  $\lambda = 254$  nm), retention time:  $t_1 = 5.94$  min (minor),  $t_2 = 8.97$  min (major),  $ee = 95\%$ ;  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  9.26 – 8.78 (m, 1H), 6.54 – 6.49 (m, 1H), 4.11 – 3.91 (m, 4H), 3.49 (s, 3H), 2.66 – 2.58 (m, 1H), 2.07 (s, 3H), 1.95 – 1.61 (m, 5H), 1.19 (t,  $J = 7.0$  Hz, 3H), 1.09 (d,  $J = 7.0$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz, DMSO)  $\delta$  172.1, 165.8, 159.7, 157.4, 104.8, 99.0, 63.3, 61.5, 60.4, 50.4, 38.0, 36.9, 23.0, 14.9, 14.6, 11.9. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{16}\text{H}_{24}\text{N}_2\text{O}_7\text{Na}^+$   $[\text{M} + \text{Na}]^+ = 379.1476$ , found = 379.1481.

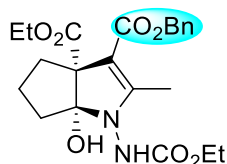
3a-ethyl 3-methyl (3a*R*,6a*R*)-6a-hydroxy-1-((methoxycarbonyl)amino)-2-methyl-4,5,6,6a-tetrahydrocyclopenta[*b*]pyrrole-3,3a(1*H*)-dicarboxylate **3g**:



A colorless solid; 47.9 mg; isolated yield = 70%; dr > 20:1; m.p. 95.3 – 95.7°C;  $[\alpha]^{24.6}_{\text{D}} = 7.95$  (c 0.23 EtOAc); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min,  $\lambda = 254$  nm), retention time:  $t_1 = 6.28$  min (minor),  $t_2 = 9.43$  min (major),  $ee = 93\%$ ;  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  9.33 – 8.83 (m, 1H), 6.52 (s, 1H), 4.14 – 4.08 (m, 2H), 3.63 (s, 3H), 3.50 (s, 3H), 2.66 – 2.58 (m, 1H), 2.07 (s, 3H), 1.73 – 1.62 (m,

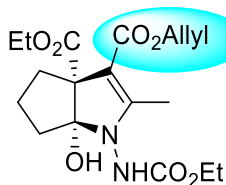
5H), 1.09 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz, DMSO)  $\delta$  172.1, 165.8, 159.7, 157.9, 104.8, 99.2, 63.2, 60.4, 52.7, 50.4, 38.0, 36.9, 23.0, 14.6, 11.9. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{22}\text{N}_2\text{O}_7\text{Na}^+$   $[\text{M} + \text{Na}]^+ = 365.1319$ , found = 365.1328.

3-benzyl 3a-ethyl (3a*R*,6a*R*)-6a-hydroxy-1-((ethoxycarbonyl)amino)-2-methyl-4,5,6,6a-tetrahydrocyclopenta[*b*]pyrrole-3,3a(1*H*)-dicarboxylate **3h**:



A colorless oil; 77.8 mg; isolated yield = 90%; dr > 20:1;  $[\alpha]^{24.7}_{\text{D}} = 10.42$  (c 0.05 EtOAc); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min,  $\lambda = 254$  nm), retention time:  $t_1 = 5.36$  min (minor),  $t_2 = 6.49$  min (major),  $ee = 92\%$ ;  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  9.28 – 8.80 (m, 1H), 7.35 – 7.25 (m, 5H), 6.58 – 5.50 (m, 1H), 5.07 – 5.00 (m, 2H), 4.11 – 3.89 (m, 4H), 2.67 – 2.65 (m, 1H), 2.11 (s, 3H), 1.98 – 1.64 (m, 5H), 1.19 (t,  $J = 7.1$  Hz, 3H), 1.01 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz, DMSO)  $\delta$  172.1, 165.0, 160.3, 157.4, 137.7, 128.7, 128.0, 127.7, 104.9, 98.8, 64.2, 63.3, 61.5, 60.5, 38.1, 37.0, 23.0, 14.9, 14.5, 11.9. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_7\text{Na}^+$   $[\text{M} + \text{Na}]^+ = 455.1789$ , found = 455.1794.

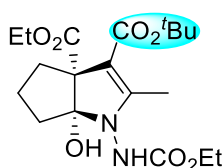
3-allyl 3a-ethyl (3a*R*,6a*R*)-6a-hydroxy-1-((ethoxycarbonyl)amino)-2-methyl-4,5,6,6a-tetrahydrocyclopenta[*b*]pyrrole-3,3a(1*H*)-dicarboxylate **3i**:



A colorless oil; 33.6 mg; isolated yield = 55%; dr > 20:1;  $[\alpha]^{24.8}_{\text{D}} = -2.67$  (c 0.15 EtOAc); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min,  $\lambda = 254$  nm), retention time:  $t_1 = 6.68$  min (minor),  $t_2 = 9.25$  min (major),  $ee = 93\%$ ;  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  9.29 – 8.80 (m, 1H), 6.56 – 6.51 (m, 1H), 5.90 – 5.81 (m, 1H), 5.23 – 5.11 (m, 2H),  $\delta$  4.50 – 4.40 (m, 2H),  $\delta$  4.09 – 3.92 (m, 4H),  $\delta$  2.68 – 2.63 (m,

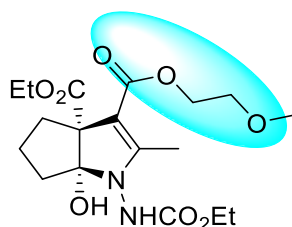
1H), 2.08 (s, 3H), 1.97 – 1.62 (m, 5H), 1.19 (t,  $J = 6.8$  Hz, 3H), 1.09 (t,  $J = 7.0$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz, DMSO)  $\delta$  172.2, 164.9, 160.2, 157.4, 133.9, 116.6, 104.8, 98.8, 63.2, 61.5, 60.5, 38.0, 36.9, 23.0, 14.9, 14.6, 11.9. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{26}\text{N}_2\text{O}_7\text{Na}^+$   $[\text{M} + \text{Na}]^+ = 405.1632$ , found = 405.1638.

3-(*tert*-butyl) 3a-ethyl (3a*R*,6a*R*)-6a-hydroxy-1-((ethoxycarbonyl)amino)-2-methyl-4,5,6,6a-tetrahydrocyclopenta[*b*]pyrrole-3,3a(1*H*)-dicarboxylate **3j**:



A colorless oil; 71.6 mg; isolated yield = 90%; dr > 20:1;  $[\alpha]^{24.8}_{\text{D}} = 1.86$  (c 0.15 EtOAc); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min,  $\lambda = 254$  nm), retention time:  $t_1 = 9.84$  min (major),  $t_2 = 15.1$  min (minor),  $ee = 93\%$ ;  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  9.22 – 8.71 (m, 1H), 6.44 – 6.38 (m, 1H), 4.16 – 4.03 (m, 4H), 2.73 – 2.68 (m, 1H), 2.10 (s, 3H), 2.00 – 1.66 (m, 5H), 1.40 (s, 9H), 1.25 (t,  $J = 7.0$  Hz, 3H), 1.20 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz, DMSO)  $\delta$  172.4, 164.9, 158.6, 157.5, 104.5, 100.7, 78.0, 63.5, 61.4, 60.4, 38.0, 37.0, 28.6, 22.9, 14.9, 14.7, 11.7. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{30}\text{N}_2\text{O}_7\text{Na}^+$   $[\text{M} + \text{Na}]^+ = 421.1945$ , found = 421.1956.

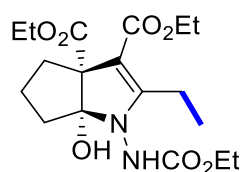
3a-ethyl 3-(2-methoxyethyl) (3a*R*,6a*R*)-1-((ethoxycarbonyl)amino)-6a-hydroxy-2-methyl-4,5,6,6a-tetrahydrocyclopenta[*b*]pyrrole-3,3a(1*H*)-dicarboxylate **3k**:



A colorless oil; 72.0 mg; isolated yield = 90%; dr > 20:1;  $[\alpha]^{24.8}_{\text{D}} = 17.29$  (c 0.17 EtOAc); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min,  $\lambda = 254$  nm), retention time:  $t_1 = 6.93$  min (minor),  $t_2 = 11.15$  min (major),  $ee = 80\%$ ;  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  9.29 – 8.80 (m, 1H), 6.54 – 6.48 (m, 1H), 4.11 – 4.07 (m, 6H), 3.47 – 3.45 (m, 2H), 3.23 (s, 3H), 2.64 – 2.62 (m, 1H), 2.07 (s, 3H), 1.97 – 1.62 (m,

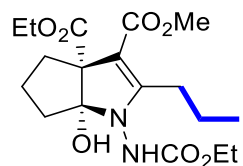
5H), 1.19 (t,  $J = 7.0$  Hz, 3H), 1.11 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz, DMSO)  $\delta$  172.1, 165.2, 159.8, 157.2, 104.8, 99.0, 70.7, 63.3, 61.9, 61.59, 60.4, 58.5, 38.1, 36.8, 23.0, 14.9, 14.6, 11.9. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{28}\text{N}_2\text{O}_8\text{Na}^+$   $[\text{M} + \text{Na}]^+ = 423.1738$ , found = 423.1740.

Diethyl (3*R*,6*aR*)-1-((ethoxycarbonyl)amino)-2-ethyl-6*a*-hydroxy-4,5,6,6*a*-tetrahydrocyclopenta[*b*]pyrrole-3,3*a*(1*H*)-dicarboxylate **3l**:



A colorless oil; 70.7 mg; isolated yield = 92%; dr > 20:1;  $[\alpha]^{25.1}_{\text{D}} = 16.87$  (c 0.15 EtOAc); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min,  $\lambda = 254$  nm), retention time:  $t_1 = 5.12$  min (minor),  $t_2 = 5.86$  min (major),  $ee = 90\%$ ;  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  9.21 – 8.75 (m, 1H), 6.49 – 6.43 (m, 1H), 4.11 – 3.93 (m, 6H), 2.85 – 2.63 (m, 2H), 2.20 – 1.62 (m, 6H), 1.22 – 1.19 (m, 3H), 1.12 (t,  $J = 7.1$  Hz, 6H), 1.05 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz, DMSO)  $\delta$  172.2, 165.1, 164.9, 157.3, 104.9, 98.5, 63.1, 61.3, 60.3, 58.4, 38.2, 36.8, 23.0, 19.0, 14.9, 14.7, 14.5, 12.5. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{28}\text{N}_2\text{O}_7\text{Na}^+$   $[\text{M} + \text{Na}]^+ = 407.1789$ , found = 407.1792.

3*a*-ethyl 3-methyl (3*R*,6*aR*)-1-((ethoxycarbonyl)amino)-6*a*-hydroxy-2-propyl-4,5,6,6*a*-tetrahydrocyclopenta[*b*]pyrrole-3,3*a*(1*H*)-dicarboxylate **3m**:

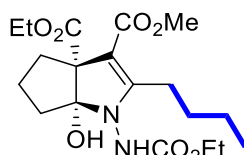


A colorless oil; 69.9 mg; isolated yield = 91%; dr > 20:1;  $[\alpha]^{25.8}_{\text{D}} = 11.14$  (c 0.21 EtOAc); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min,  $\lambda = 254$  nm), retention time:  $t_1 = 6.13$  min (minor),  $t_2 = 8.33$  min (major),  $ee = 94\%$ ;  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  9.18 – 8.72 (m, 1H), 6.49 – 6.43 (m, 1H), 4.15 – 3.86 (m, 4H), 3.49 (s, 3H), 2.82 – 2.58 (m, 2H), 2.02 – 1.46 (m, 8H), 1.21 – 1.17 (m, 3H), 1.09 (t,  $J = 7.1$  Hz, 3H), 0.87 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz, DMSO)  $\delta$  172.1, 165.6,



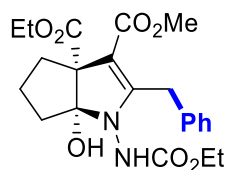
163.5, 157.2, 105.0, 99.6, 63.2, 61.3, 60.3, 50.3, 38.1, 36.9, 27.1, 23.1, 20.9, 14.9, 14.6, 14.0. HRMS (ESI)  $m/z$  calcd for  $C_{18}H_{28}N_2O_7Na^+$   $[M + Na]^+ = 407.1789$ , found = 407.1790.

3a-ethyl 3-methyl (3a*R*,6a*R*)-2-butyl-1-((ethoxycarbonyl)amino)-6a-hydroxy-4,5,6,6a-tetrahydrocyclopenta[*b*]pyrrole-3,3a(1*H*)-dicarboxylate **3n**:



A colorless oil; 71.6 mg; isolated yield = 90%; dr > 20:1;  $[\alpha]^{25.8}_D = 19.46$  (c 0.13 EtOAc); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min,  $\lambda = 254$  nm), retention time:  $t_1 = 5.02$  min (minor),  $t_2 = 6.71$  min (major),  $ee = 93\%$ ;  $^1H$  NMR (400 MHz, DMSO)  $\delta$  9.21 – 8.74 (m, 1H), 6.52 – 6.46 (m, 1H), 4.15 – 3.86 (m, 4H), 3.49 (s, 3H), 2.84 – 2.58 (m, 2H), 2.45 – 1.61 (m, 6H), 1.44 – 1.42 (m, 2H), 1.33 – 1.27 (m, 2H), 1.19 (t,  $J = 6.8$  Hz, 3H), 1.09 (t,  $J = 7.0$  Hz, 3H), 0.86 (t,  $J = 7.2$  Hz, 3H).  $^{13}C$  NMR (100 MHz, DMSO)  $\delta$  172.2, 165.5, 164.0, 157.3, 105.0, 99.2, 63.1, 61.3, 60.3, 50.3, 38.2, 36.9, 29.6, 25.0, 23.1, 22.3, 14.9, 14.6, 14.1. HRMS (ESI)  $m/z$  calcd for  $C_{19}H_{30}N_2O_7Na^+$   $[M + Na]^+ = 421.1945$ , found = 421.1949.

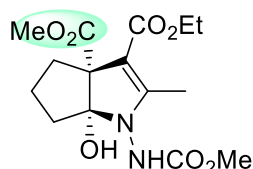
3a-ethyl 3-methyl (3a*R*,6a*R*)-2-benzyl-1-((ethoxycarbonyl)amino)-6a-hydroxy-4,5,6,6a-tetrahydrocyclopenta[*b*]pyrrole-3,3a(1*H*)-dicarboxylate **3o**:



A colorless oil; 82.1 mg; isolated yield = 95%; dr > 20:1;  $[\alpha]^{24.8}_D = -30.83$  (c 0.12 EtOAc); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min,  $\lambda = 254$  nm), retention time:  $t_1 = 7.42$  min (minor),  $t_2 = 9.86$  min (major),  $ee = 90\%$ ;  $^1H$  NMR (400 MHz, DMSO)  $\delta$  9.17 – 8.68 (m, 1H), 7.25 – 7.18 (m, 5H), 6.59 – 6.48 (m, 1H), 4.15 – 3.93 (m, 4H), 3.82 – 3.68 (m, 2H), 3.50 (s, 3H), 2.67 – 2.62 (m, 1H), 2.05 – 1.62 (m, 5H), 1.16 – 1.11 (m, 6H).  $^{13}C$  NMR (100 MHz, DMSO)  $\delta$  172.1, 165.1, 160.3,

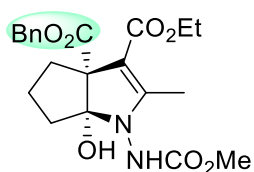
157.4, 137.7, 128.7, 127.9, 127.7, 104.9, 104.7, 98.8, 64.2, 63.3, 61.5, 60.5, 38.1, 37.1, 23.1, 14.9, 14.7, 14.5, 11.9. HRMS (ESI)  $m/z$  calcd for  $C_{22}H_{28}N_2O_7Na^+$   $[M + Na]^+ = 455.1789$ , found = 455.1794.

3-ethyl 3a-methyl (3a*R*,6a*R*)-6a-hydroxy-1-((methoxycarbonyl)amino)-2-methyl-4,5,6,6a-tetrahydrocyclopenta[*b*]pyrrole-3,3a(1*H*)-dicarboxylate **3p**:



A colorless solid; 61.6 mg; isolated yield = 90%; dr > 20:1; m.p. 86.9 – 87.3°C;  $[\alpha]^{25.3}_D = 16.64$  (c 0.22 EtOAc); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min,  $\lambda = 254$  nm), retention time:  $t_1 = 6.44$  min (minor),  $t_2 = 7.69$  min (major), *ee* = 94%;  $^1H$  NMR (400 MHz, DMSO)  $\delta$  9.34 – 8.84 (m, 1H), 6.56 (s, 1H), 4.04 – 3.90 (m, 2H), 3.63 (s, 3H), 3.52 (s, 3H), 2.66 – 2.58 (m, 1H), 2.07 (s, 3H), 1.99 – 1.66 (m, 5H), 1.10 (t,  $J = 7.1$  Hz, 3H).  $^{13}C$  NMR (100 MHz, DMSO)  $\delta$  172.8, 165.3, 159.7, 157.9, 104.7, 99.1, 63.4, 58.5, 52.8, 52.0, 38.2, 36.8, 23.0, 14.9, 11.8. HRMS (ESI)  $m/z$  calcd for  $C_{15}H_{22}N_2O_7Na^+$   $[M + Na]^+ = 365.1319$ , found = 365.1321.

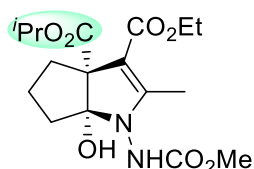
3a-benzyl 3-ethyl (3a*R*,6a*R*)-6a-hydroxy-1-((methoxycarbonyl)amino)-2-methyl-4,5,6,6a-tetrahydrocyclopenta[*b*]pyrrole-3,3a(1*H*)-dicarboxylate **3q**:



A colorless oil; 60.2 mg; isolated yield = 72%; dr > 20:1;  $[\alpha]^{25.2}_D = 21.74$  (c 0.23 EtOAc); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min,  $\lambda = 254$  nm), retention time:  $t_1 = 5.70$  min (minor),  $t_2 = 7.42$  min (major), *ee* = 90%;  $^1H$  NMR (400 MHz, DMSO)  $\delta$  9.37 – 8.87 (m, 1H), 7.34 – 7.29 (m, 5H), 6.64 – 5.89 (m, 1H), 5.18 – 4.91 (m, 2H), 3.96 – 3.84 (m, 2H), 3.59 (s, 3H), 2.71 – 2.64 (m, 1H), 2.08 (s, 3H), 1.80 – 1.64 (m, 5H), 1.03 (t,  $J = 7.1$  Hz, 3H).  $^{13}C$  NMR (100 MHz, DMSO)  $\delta$  172.2,

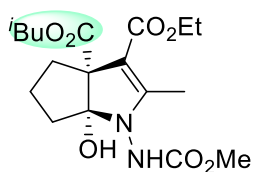
165.3, 159.6, 157.9, 137.1, 128.7, 128.1, 127.9, 104.9, 99.1, 66.0, 63.6, 58.6, 52.7, 38.2, 37.0, 23.1, 14.8, 11.9. HRMS (ESI)  $m/z$  calcd for  $C_{21}H_{26}N_2O_7Na^+$   $[M + Na]^+ = 441.1632$ , found = 441.1640.

3-ethyl 3*a*-isopropyl (3*aR*,6*aR*)-6*a*-hydroxy-1-((methoxycarbonyl)amino)-2-methyl-4,5,6,6*a*-tetrahydrocyclopenta[*b*]pyrrole-3,3*a*(1*H*)-dicarboxylate **3r**:



A colorless oil; 66.6 mg; isolated yield = 90%;  $dr > 20:1$ ;  $[\alpha]^{24.8}_D = 14.06$  (c 0.18 EtOAc); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min,  $\lambda = 254$  nm), retention time:  $t_1 = 4.87$  min (minor),  $t_2 = 6.48$  min (major),  $ee = 92\%$ ;  $^1H$  NMR (400 MHz, DMSO)  $\delta$  9.30 – 8.78 (m, 1H), 6.40 (s, 1H), 4.85 – 4.81 (m, 1H), 4.02 – 3.91 (m, 2H), 3.62 (s, 3H), 2.67 – 2.62 (m, 1H), 2.07 (s, 3H), 1.74 – 1.62 (m, 5H), 1.14 – 1.08 (m, 9H).  $^{13}C$  NMR (100 MHz, DMSO)  $\delta$  171.6, 165.3, 159.2, 157.9, 104.8, 99.6, 67.6, 63.1, 58.5, 52.7, 37.9, 37.0, 22.1, 21.9, 14.8, 11.8. HRMS (ESI)  $m/z$  calcd for  $C_{17}H_{26}N_2O_7Na^+$   $[M + Na]^+ = 393.1632$ , found = 393.1634.

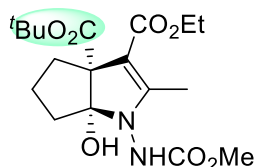
3-ethyl 3*a*-isobutyl (3*aR*,6*aR*)-6*a*-hydroxy-1-((methoxycarbonyl)amino)-2-methyl-4,5,6,6*a*-tetrahydrocyclopenta[*b*]pyrrole-3,3*a*(1*H*)-dicarboxylate **3s**:



A colorless oil; 52.2 mg; isolated yield = 68%;  $dr > 20:1$ ;  $[\alpha]^{25.3}_D = 7.05$  (c 0.23 EtOAc); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min,  $\lambda = 254$  nm), retention time:  $t_1 = 4.85$  min (minor),  $t_2 = 6.89$  min (major),  $ee = 93\%$ ;  $^1H$  NMR (400 MHz, DMSO)  $\delta$  9.33 - 8.83 (m, 1H), 6.47 (s, 1H), 4.02 - 3.81 (m, 4H), 3.63 (s, 3H), 2.67 - 2.62 (m, 1H), 2.07 (s, 3H), 1.99 - 1.97 (m, 1H), 1.81 - 1.62 (m, 5H), 1.11 (t,  $J = 7.1$  Hz, 3H), 0.84 - 0.83 (m, 6H).  $^{13}C$  NMR (100 MHz, DMSO)  $\delta$  172.1, 165.3,

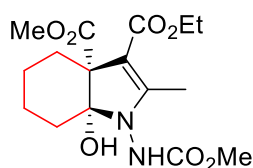
159.4, 157.9, 104.8, 99.4, 70.5, 63.5, 58.5, 52.7, 38.1, 36.8, 27.7, 23.1, 19.4, 14.8, 11.9.  
HRMS (ESI)  $m/z$  calcd for  $C_{18}H_{28}N_2O_7Na^+$   $[M + Na]^+$  = 407.1789, found = 407.1791.

3a-(tert-butyl) 3-ethyl (3a*R*,6a*R*)-6a-hydroxy-1-((methoxycarbonyl)amino)-2-methyl-4,5,6,6a-tetrahydrocyclopenta[*b*]pyrrole-3,3a(1*H*)-dicarboxylate **3t**:



A colorless oil; 53.8 mg; isolated yield = 70%; dr > 20:1;  $[\alpha]^{24.8}_D = 15.81$  (c 0.16 EtOAc); HPLC (IC column, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min,  $\lambda = 254$  nm), retention time:  $t_1 = 5.08$  min (minor),  $t_2 = 5.49$  min (major),  $ee = 84\%$ ;  $^1H$  NMR (400 MHz, DMSO)  $\delta$  8.85 - 8.44 (m, 1H), 6.53 - 6.39 (m, 1H), 4.04 - 3.90 (m, 2H), 3.52 (s, 3H), 2.64 - 2.59 (m, 1H), 2.07 (s, 3H), 1.98 - 1.90 (m, 1H), 1.75 - 1.61 (m, 4H), 1.42 (s, 9H), 1.10 (t,  $J = 7.1$  Hz, 3H).  $^{13}C$  NMR (100 MHz, DMSO)  $\delta$  171.1, 165.4, 159.0, 157.9, 104.9, 99.9, 79.5, 63.7, 58.5, 52.7, 37.9, 37.0, 28.1, 23.1, 14.9, 11.8. HRMS (ESI)  $m/z$  calcd for  $C_{18}H_{28}N_2O_7Na^+$   $[M + Na]^+$  = 407.1789, found = 407.1791.

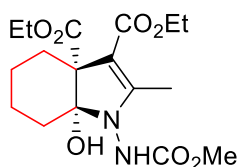
3-ethyl 3a-methyl (3a*R*,7a*R*)-7a-hydroxy-1-((methoxycarbonyl)amino)-2-methyl-1,4,5,6,7,7a-hexahydro-3a*H*-indole-3,3a-dicarboxylate **3u**:



A colorless oil; 64.8 mg; isolated yield = 91%; dr > 20:1;  $[\alpha]^{25.4}_D = 20.29$  (c 0.17 EtOAc); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min,  $\lambda = 254$  nm), retention time:  $t_1 = 7.54$  min (minor),  $t_2 = 11.60$  min (major),  $ee = 91\%$ ;  $^1H$  NMR (400 MHz, DMSO)  $\delta$  8.88 - 8.40 (m, 1H), 5.87 (s, 1H), 4.09 - 3.95 (m, 2H), 3.63 (s, 3H), 3.53 (s, 3H), 2.47 - 2.44 (m, 1H), 2.05 (s, 3H), 1.79 - 1.36 (m, 7H), 1.14 (t,  $J = 7.1$  Hz, 3H).  $^{13}C$  NMR (100 MHz, DMSO)  $\delta$  172.7, 165.5, 157.5, 157.3, 105.2, 94.2,

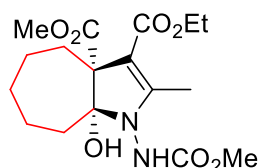
58.8, 57.3, 52.5, 51.6, 34.1, 30.3, 21.4, 20.7, 14.8, 12.3. HRMS (ESI)  $m/z$  calcd for  $C_{16}H_{24}N_2O_7Na^+$   $[M + Na]^+ = 379.1476$ , found = 379.1476.

Diethyl (3a*R*,7a*R*)-7a-hydroxy-1-((methoxycarbonyl)amino)-2-methyl-1,4,5,6,7,7a-hexahydro-3a*H*-indole-3,3a-dicarboxylate **3v**:



A colorless oil; 66.6 mg; isolated yield = 90%; dr > 20:1;  $[\alpha]^{25.6}_D = 15.25$  (c 0.24 EtOAc); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min,  $\lambda = 254$  nm), retention time:  $t_1 = 6.58$  min (minor),  $t_2 = 10.84$  min (major),  $ee = 93\%$ ;  $^1H$  NMR (400 MHz, DMSO)  $\delta$  8.78 – 8.33 (m, 1H), 5.73 (s, 1H), 4.06 – 3.95 (m, 4H), 3.63 (s, 3H), 2.45 – 2.28 (s, 1H), 2.05 (s, 3H), 1.80 – 1.76 (m, 1H), 1.64 – 1.46 (m, 6H), 1.66 – 1.11 (m, 6H).  $^{13}C$  NMR (100 MHz, DMSO)  $\delta$  172.0, 165.5, 157.2, 157.2, 105.9, 94.3, 60.1, 58.9, 57.2, 52.7, 34.5, 30.4, 21.6, 21.0, 14.7, 14.5, 12.3. HRMS (ESI)  $m/z$  calcd for  $C_{17}H_{26}N_2O_7Na^+$   $[M + Na]^+ = 393.1632$ , found = 393.1637.

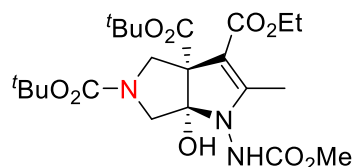
3-ethyl 3a-methyl (3a*R*,8a*R*)-8a-hydroxy-1-((methoxycarbonyl)amino)-2-methyl-4,5,6,7,8,8a-hexahydrocyclohepta[*b*]pyrrole-3,3a(1*H*)-dicarboxylate **3w**:



A colorless oil; 60.7 mg; isolated yield = 82%; dr > 20:1;  $[\alpha]^{25.6}_D = 6.51$  (c 0.35 EtOAc); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min,  $\lambda = 254$  nm), retention time:  $t_1 = 6.46$  min (minor),  $t_2 = 8.99$  min (major),  $ee = 86\%$ ;  $^1H$  NMR (400 MHz, DMSO)  $\delta$  8.88 (s, 1H),  $\delta$  6.03 – 6.01 (m, 1H), 4.09 – 3.95 (m, 2H), 3.66 – 3.59 (m, 3H), 3.51 – 3.48 (m, 3H), 2.33 – 2.23 (m, 1H), 2.14 (s, 3H), 1.99 – 1.78 (m, 3H), 1.55 – 1.24 (m, 6H), 1.12 (d,  $J = 7.1$  Hz, 3H).  $^{13}C$  NMR (100 MHz, DMSO)  $\delta$  172.8, 165.4, 160.3, 157.2, 122.9, 98.0, 63.9, 60.0, 58.7, 51.7, 35.7, 31.8, 30.8, 28.2,

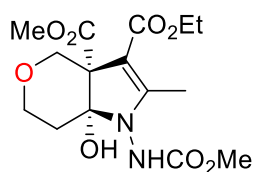
23.8, 14.8, 12.2. HRMS (ESI)  $m/z$  calcd for  $C_{17}H_{26}N_2O_7Na^+$   $[M + Na]^+ = 393.1632$ , found = 393.1637.

3a,5-di-*tert*-butyl 3-ethyl (3a*S*,6a*S*)-6a-hydroxy-1-((methoxycarbonyl)amino)-2-methyl-6,6a-dihydropyrrolo[3,4-*b*]pyrrole-3,3a,5(1*H*,4*H*)-tricarboxylate **3x**:



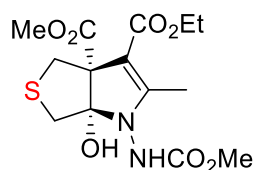
A colorless oil; 82.5 mg; isolated yield = 85%;  $dr > 20:1$ ;  $[\alpha]^{24.8}_D = 8.25$  (c 0.24 EtOAc); HPLC (IC column, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min,  $\lambda = 254$  nm), retention time:  $t_1 = 5.25$  min (minor),  $t_2 = 11.02$  min (major),  $ee = 85\%$ ;  $^1H$  NMR (400 MHz, DMSO)  $\delta$  9.33 – 8.95 (m, 1H), 7.03 (s, 1H), 4.14 – 4.03 (m, 4H), 3.68 (s, 3H), 3.31 – 3.28 (m, 2H), 2.09 (s, 3H), 1.43 – 1.40 (m, 18H), 1.21 - 1.19 (m, 3H).  $^{13}C$  NMR (100 MHz, DMSO)  $\delta$  169.5, 169.2, 165.0, 158.5, 157.5, 101.9, 92.6, 72.5, 64.1, 60.3, 59.2, 57.3, 52.7, 51.8, 30.4, 21.8, 14.7, 12.1. HRMS (ESI)  $m/z$  calcd for  $C_{22}H_{35}N_3O_9Na^+$   $[M + Na]^+ = 508.2266$ , found = 508.2266.

3-ethyl 3a-methyl (3a*S*,7a*R*)-7a-hydroxy-1-((methoxycarbonyl)amino)-2-methyl-1,6,7,7a-tetrahydropyrano[4,3-*b*]pyrrole-3,3a(4*H*)-dicarboxylate **3y**:



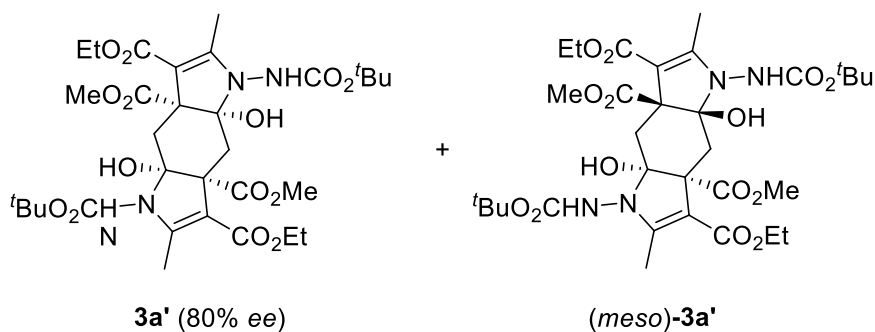
A colorless oil; 46.5 mg; isolated yield = 65%;  $dr > 20:1$ ;  $[\alpha]^{25.8}_D = 11.60$  (c 0.15 EtOAc); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min,  $\lambda = 254$  nm), retention time:  $t_1 = 13.5$  min (minor),  $t_2 = 16.5$  min (major),  $ee = 60\%$ ;  $^1H$  NMR (400 MHz, DMSO)  $\delta$  9.07 – 8.60 (m, 1H), 6.20 (s, 1H), 4.35 – 4.91 (m, 4H), 3.79 – 3.74 (m, 1H), 3.62 (s, 3H), 3.56 (s, 3H), 2.92 – 2.89 (m, 1H), 2.06 (s, 3H), 1.70 – 1.68 (m, 2H), 1.12 (t,  $J = 7.1$  Hz, 3H).  $^{13}C$  NMR (100 MHz, DMSO)  $\delta$  171.1, 165.2, 158.5, 157.4, 102.0, 92.6, 72.5, 64.1, 59.1, 57.4, 52.6, 51.8, 30.5, 14.7, 12.2. HRMS (ESI)  $m/z$  calcd for  $C_{15}H_{22}N_2O_8Na^+$   $[M + Na]^+ = 381.1268$ , found = 381.1272.

3-ethyl 3a-methyl (3a*S*,6a*S*)-6a-hydroxy-1-((methoxycarbonyl)amino)-2-methyl-6,6a-dihydro-1*H*-thieno[3,4-*b*]pyrrole-3,3a(4*H*)-dicarboxylate **3z**:



A colorless oil; 46.8 mg; isolated yield = 65%; dr > 20:1;  $[\alpha]_{\text{D}}^{26.1} = 15.93$  (c 0.15 EtOAc); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min,  $\lambda = 254$  nm), retention time:  $t_1 = 6.77$  min (minor),  $t_2 = 9.21$  min (major),  $ee = 75\%$ ;  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  9.46–8.95 (m, 1H), 7.12 (s, 1H), 4.06–3.93 (m, 2H), 3.83–3.80 (m, 1H), 3.63 (s, 3H), 3.55 (s, 3H), 3.16–3.07 (s, 1H), 2.90–2.86 (m, 2H), 2.11 (s, 3H), 1.12 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz, DMSO)  $\delta$  171.4, 165.0, 161.1, 157.7, 107.0, 98.3, 67.2, 58.8, 52.8, 52.4, 42.7, 41.1, 14.8, 12.1. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{20}\text{N}_2\text{O}_7\text{SNa}^+ [\text{M} + \text{Na}]^+ = 388.0883$ , found = 388.0887.

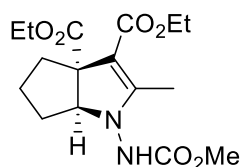
3,7-diethyl 3a,7a-dimethyl (3a*R*,4a*R*,7a*R*,8a*R*)-1,5-bis((*tert*-butoxycarbonyl)amino)-4a,8a-dihydroxy-2,6-dimethyl-4a,5,8,8a-tetrahydropyrrolo[2,3-*f*]indole-3,3a,7,7a(1*H*,4*H*)-tetracarboxylate **3a'**:



A colorless solid; 86.9 mg; isolated yield = 61%; dr = 9:1; m.p. 290.8 – 291.1°C;  $[\alpha]_{\text{D}}^{25.9} = 42.73$  (c 0.11 EtOAc); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min,  $\lambda = 254$  nm), retention time: minor product:  $t_1 = 18.54$  min (minor),  $t_2 = 23.56$  min (major),  $ee = 80\%$ ;  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  8.44–7.98 (m, 2H), 7.30–5.78 (m, 2H), 4.06–3.98 (m, 4H), 3.60–3.51 (m, 6H), 3.07–2.73 (m, 2H), 2.35–2.25 (m, 1H), 2.08–1.98 (m, 6H), 1.59–1.56 (m, 1H), 1.43–1.39 (m, 18H), 1.15–1.14 (d,  $J = 6.0$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz, DMSO)  $\delta$  165.1, 159.0, 156.8, 155.2, 100.6,

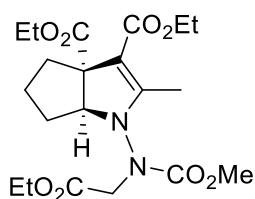
92.6, 81.4, 58.8, 57.1, 52.6, 28.3, 27.9, 14.8, 12.2. HRMS (ESI)  $m/z$  calcd for  $C_{32}H_{48}N_4O_{14}Na^+$   $[M + Na]^+ = 735.3059$ , found = 735.3058.

Diethyl (3a*R*,6a*S*)-1-((methoxycarbonyl)amino)-2-methyl-4,5,6,6a-tetrahydrocyclopenta[*b*]pyrrole-3,3a(1*H*)-dicarboxylate 4:



A colorless oil; 64.0 mg; isolated yield = 98%; dr > 20:1;  $[\alpha]^{20.0}_D = -8.01$  (c 0.35 EtOAc); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min,  $\lambda = 254$  nm), retention time:  $t_1 = 6.24$  min (minor),  $t_2 = 11.46$  min (major),  $ee = 94\%$ ;  $^1H$  NMR (400 MHz, DMSO)  $\delta$  9.52 (s, 1H), 4.09– 3.95 (m, 5H), 3.63 (s, 3H), 2.42– 2.38 (m, 1H), 2.03 (s, 3H), 1.89– 1.55 (m, 5H), 1.15 – 1.10 (m, 6H).  $^{13}C$  NMR (100 MHz, DMSO)  $\delta$  174.5, 165.3, 161.3, 157.0, 100.5, 60.8, 60.7, 58.5, 56.5, 52.7, 36.8, 32.1, 24.4, 14.8, 14.5, 11.9. HRMS (ESI)  $m/z$  calcd for  $C_{16}H_{24}N_2O_6Na^+$   $[M + Na]^+ = 363.1527$ , found = 363.1533.

Diethyl (3a*R*,6a*S*)-1-((2-ethoxy-2-oxoethyl)(methoxycarbonyl)amino)-2-methyl-4,5,6,6a-tetrahydrocyclopenta[*b*]pyrrole-3,3a(1*H*)-dicarboxylate 5:

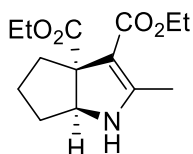


A colorless oil; 65.0 mg; isolated yield = 81%; dr = 2:3;  $[\alpha]^{20.0}_D = 1.77$  (c 0.15 EtOAc); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min,  $\lambda = 254$  nm), major product:  $t_1 = 12.20$  min (minor),  $t_2 = 13.73$  min (major),  $ee = 93\%$ ; minor product:  $t_1 = 14.93$  min (minor),  $t_2 = 17.00$  min (major),  $ee = 94\%$ ;  $^1H$  NMR (400 MHz, DMSO)  $\delta$  4.41 – 4.33 (m, 1H), 4.15 – 4.07 (m, 4H), 4.06 – 3.96 (m, 4H), 3.67 – 3.64 (m, 3H), 2.41 – 2.27 (m, 1H), 2.08 – 2.05 (m, 3H), 1.91 – 1.56 (m, 5H), 1.22 – 1.09 (m, 9H).  $^{13}C$  NMR (100 MHz, DMSO)  $\delta$  174.4, 169.0, 165.4, 161.1, 159.7, 156.8, 102.5,



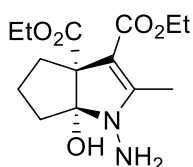
75.3, 72.8, 61.4, 60.9, 58.9, 54.0, 50.6, 36.6, 34.2, 24.5, 14.7, 14.4, 11.9. HRMS (ESI)  $m/z$  calcd for  $C_{20}H_{30}N_2O_8Na^+$   $[M + Na]^+ = 449.1894$ , found = 449.1899.

Diethyl (3*aR*,6*aS*)-2-methyl-4,5,6,6*a*-tetrahydrocyclopenta[*b*]pyrrole-3,3*a*(1*H*)-dicarboxylate **6**:



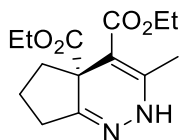
A colorless oil; 24.4 mg; isolated yield = 60%;  $dr > 20:1$ ;  $[\alpha]^{20.0}_D = 1.67$  (c 0.21 EtOAc); HPLC (ID column, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min,  $\lambda = 254$  nm), retention time:  $t_1 = 12.50$  min (minor),  $t_2 = 14.61$  min (major),  $ee = 92\%$ ;  $^1H$  NMR (400 MHz, DMSO)  $\delta$  6.24 (s, 1H), 4.63 - 4.64 (s, 1H), 4.08 - 3.98 (m, 4H), 2.33 - 2.25 (m, 1H), 1.85 - 1.82 (m, 1H), 1.75 (s, 3H), 1.56 - 1.39 (m, 2H), 1.26 - 1.24 (m, 2H), 1.15 - 1.10 (m, 6H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  174.2, 172.4, 170.8, 89.6, 78.8, 66.4, 63.0, 61.0, 33.3, 33.3, 24.1, 15.2, 14.0, 13.8. HRMS (ESI)  $m/z$  calcd for  $C_{14}H_{21}NO_4Na^+$   $[M + Na]^+ = 290.1363$ , found = 290.1363.

Diethyl (3*aR*,6*aR*)-1-amino-6*a*-hydroxy-2-methyl-4,5,6,6*a*-tetrahydrocyclopenta[*b*]pyrrole-3,3*a*(1*H*)-dicarboxylate **7**:



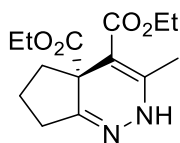
A colorless oil; 53.2 mg; isolated yield = 93%;  $dr > 20:1$ ;  $^1H$  NMR (400 MHz, DMSO)  $\delta$  5.99 (s, 1H), 4.24 (s, 2H), 4.09 - 3.88 (m, 4H), 2.66 - 2.58 (m, 1H), 2.15 (s, 3H), 1.69 - 1.58 (m, 5H), 1.13 - 1.08 (m, 6H).  $^{13}C$  NMR (100 MHz, DMSO)  $\delta$  172.6, 165.5, 162.02, 104.5, 96.0, 63.0, 60.2, 57.8, 37.2, 37.1, 22.8, 15.0, 14.6, 12.8. HRMS (ESI)  $m/z$  calcd for  $C_{14}H_{22}N_2O_5Na^+$   $[M + Na]^+ = 321.1421$ , found = 321.1425.

Diethyl (*R*)-3-methyl-2,5,6,7-tetrahydro-4*aH*-cyclopenta[*c*]pyridazine-4,4*a*-dicarboxylate **8 (from 7)**:



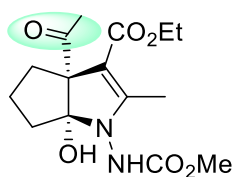
A colorless oil; 47.5 mg; isolated yield = 95%;  $[\alpha]^{20.0}_D = 23.5$  (c 0.1 EtOAc); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min,  $\lambda = 254$  nm), retention time:  $t_1 = 5.24$  min (minor),  $t_2 = 5.81$  min (major), *ee* = 94%;  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  10.07 (s, 1H), 4.05 – 3.96 (m, 4H), 2.80 – 2.78 (m, 1H), 2.49 – 2.41 (m, 2H), 2.15 (s, 3H), 1.86 – 1.64 (m, 3H), 1.16 (t,  $J = 7.1$  Hz, 3H), 1.11 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz, DMSO)  $\delta$  172.2, 166.9, 153.6, 146.7, 92.5, 60.9, 59.1, 49.2, 38.4, 29.4, 19.6, 17.1, 14.7, 14.4. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{20}\text{N}_2\text{O}_4\text{Na}^+$   $[\text{M} + \text{Na}]^+ = 303.1315$ , found = 303.1320.

Diethyl (*R*)-3-methyl-2,5,6,7-tetrahydro-4a*H*-cyclopenta[*c*]pyridazine-4,4a-dicarboxylate **8** (from **3e**):



A colorless oil; 35.3 mg; isolated yield = 84%;  $[\alpha]^{20.0}_D = 10.75$  (c 0.2 EtOAc); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min,  $\lambda = 254$  nm), retention time:  $t_1 = 5.31$  min (minor),  $t_2 = 5.95$  min (major), *ee* = 81%;  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  10.07 (s, 1H), 4.05 – 3.96 (m, 4H), 2.80 – 2.78 (m, 1H), 2.49 – 2.41 (m, 2H), 2.15 (s, 3H), 1.86 – 1.64 (m, 3H), 1.16 (t,  $J = 7.1$  Hz, 3H), 1.11 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz, DMSO)  $\delta$  172.2, 166.9, 153.6, 146.7, 92.5, 60.9, 59.1, 49.2, 38.4, 29.4, 19.6, 17.1, 14.7, 14.4. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{20}\text{N}_2\text{O}_4\text{Na}^+$   $[\text{M} + \text{Na}]^+ = 303.1315$ , found = 303.1320

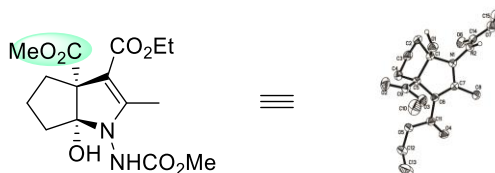
Ethyl(3a*R*,6a*R*)-3a-acetyl-6a-hydroxy-1-((methoxycarbonyl)amino)-2-methyl-1,3a,4,5,6,6a-hexahydrocyclopenta[*b*]pyrrole-3-carboxylate **S1**:



A colorless oil; 49.6 mg; isolated yield = 76%; dr > 20:1;  $[\alpha]^{24.8}_D = 14.01$  (c 0.15 EtOAc); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min,  $\lambda = 254$  nm), retention time:  $t_1 = 6.44$  min (major),  $t_2 = 10.87$  min (minor),  $ee = 40\%$ ;  $^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  9.49 - 9.08 (m, 1H), 6.68 (s, 1H), 4.02 - 3.97 (m, 2H), 3.64 (s, 3H), 2.64 - 2.59 (m, 1H), 2.14 (s, 3H), 2.00 (s, 3H), 1.55 - 1.24 (m, 5H), 1.11 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C NMR}$  (100 MHz, DMSO)  $\delta$  206.8, 165.5, 160.9, 157.8, 104.8, 99.6, 67.0, 58.7, 52.7, 38.4, 34.1, 28.5, 22.6, 14.8, 12.1. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{22}\text{N}_2\text{O}_6\text{Na}^+$   $[\text{M} + \text{Na}]^+ = 349.1370$ , found = 349.1372.

## 4. X-ray Single Crystal Data for Compound 3p and (*meso*)-3a'

3p

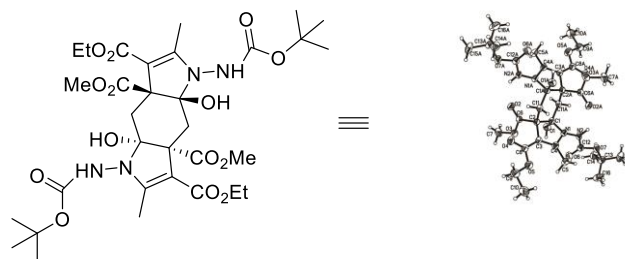


CCDC: 2253282

Table S7 Crystal data and structure refinement for 3p.

Identification code	20230358_auto
Empirical formula	C <sub>15</sub> H <sub>22</sub> N <sub>2</sub> O <sub>7</sub>
Formula weight	342.34
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
a/Å	8.24888(18)
b/Å	8.64551(16)
c/Å	24.3498(5)
α/°	90
β/°	90
γ/°	90
Volume/Å <sup>3</sup>	1736.52(6)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.309
μ/mm <sup>-1</sup>	0.884
F(000)	728.0
Crystal size/mm <sup>3</sup>	0.13 × 0.12 × 0.1
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	7.26 to 140.8
Index ranges	-10 ≤ h ≤ 9, -10 ≤ k ≤ 9, -29 ≤ l ≤ 29
Reflections collected	18852
Independent reflections	3330 [R <sub>int</sub> = 0.0328, R <sub>sigma</sub> = 0.0223]
Data/restraints/parameters	3330/3/240
Goodness-of-fit on F <sup>2</sup>	1.027
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0427, wR <sub>2</sub> = 0.1130
Final R indexes [all data]	R <sub>1</sub> = 0.0454, wR <sub>2</sub> = 0.1160
Largest diff. peak/hole / e Å <sup>-3</sup>	0.24/-0.20
Flack parameter	-0.05(10)

(*meso*)-**3a'**



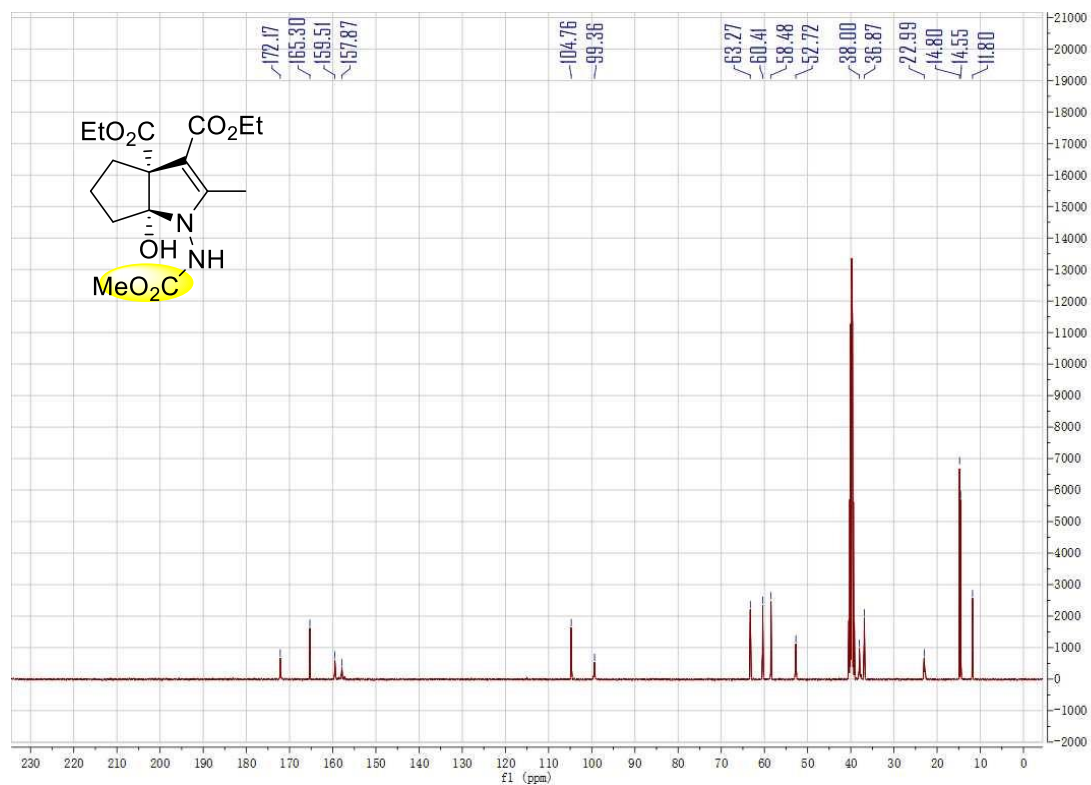
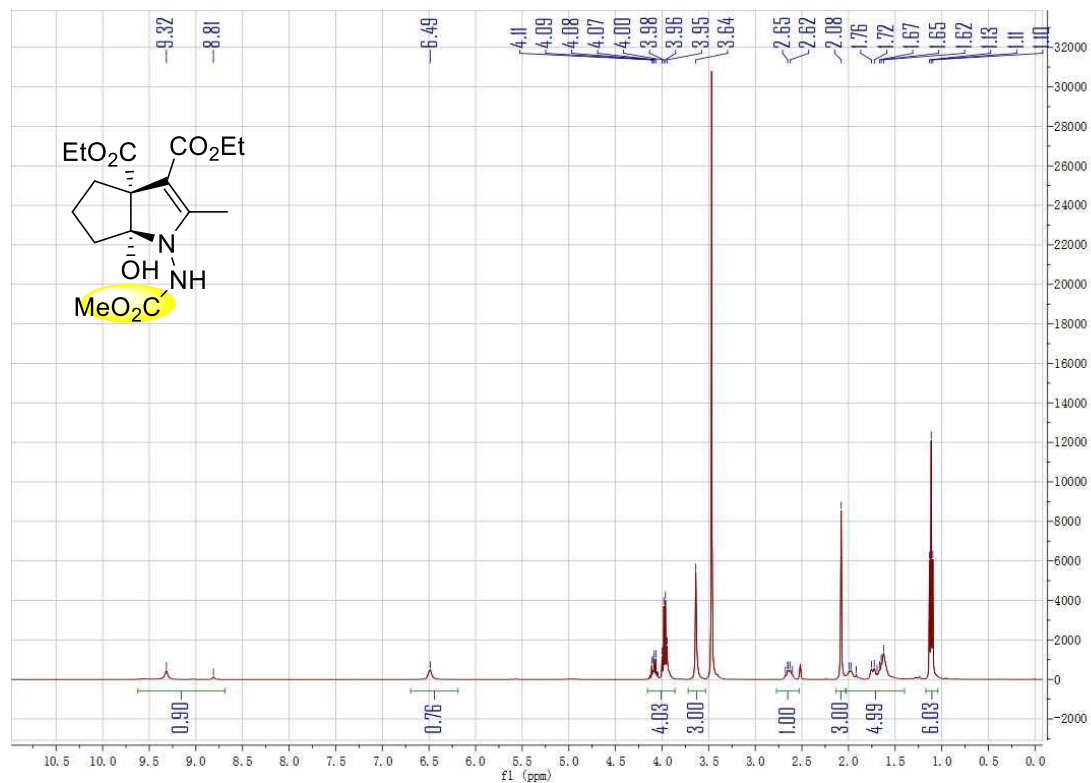
CCDC: 2253283

Table S8 Crystal data and structure refinement for 20230339.

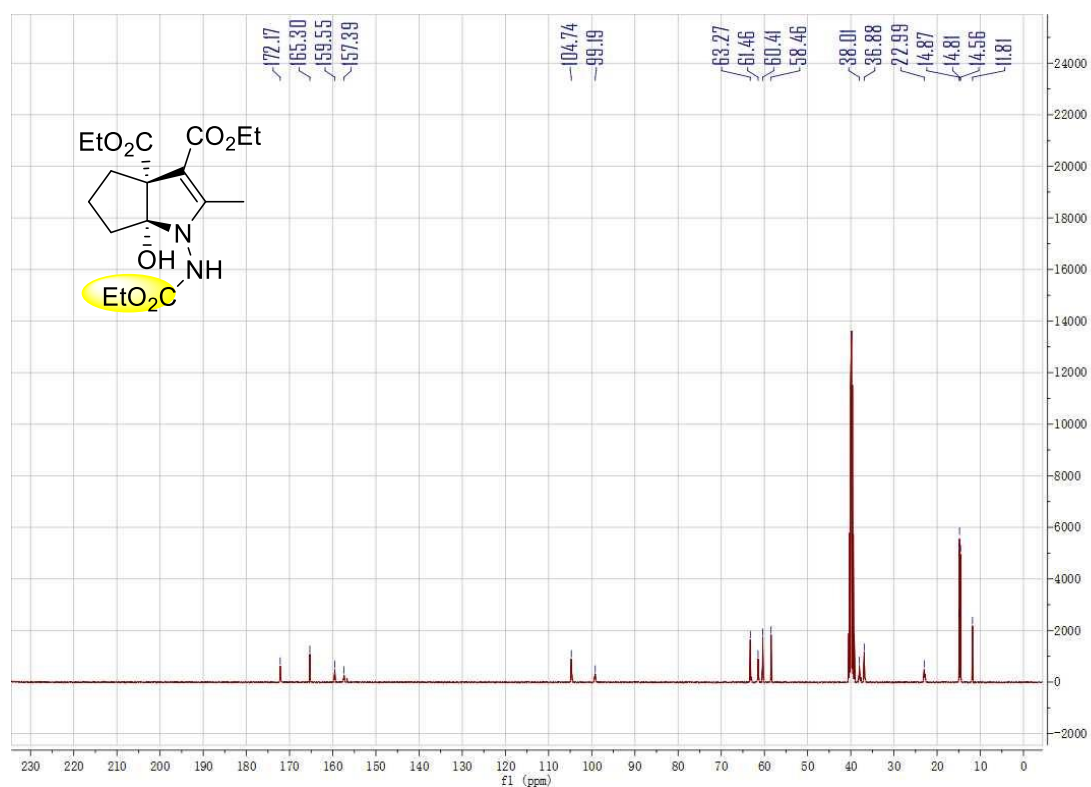
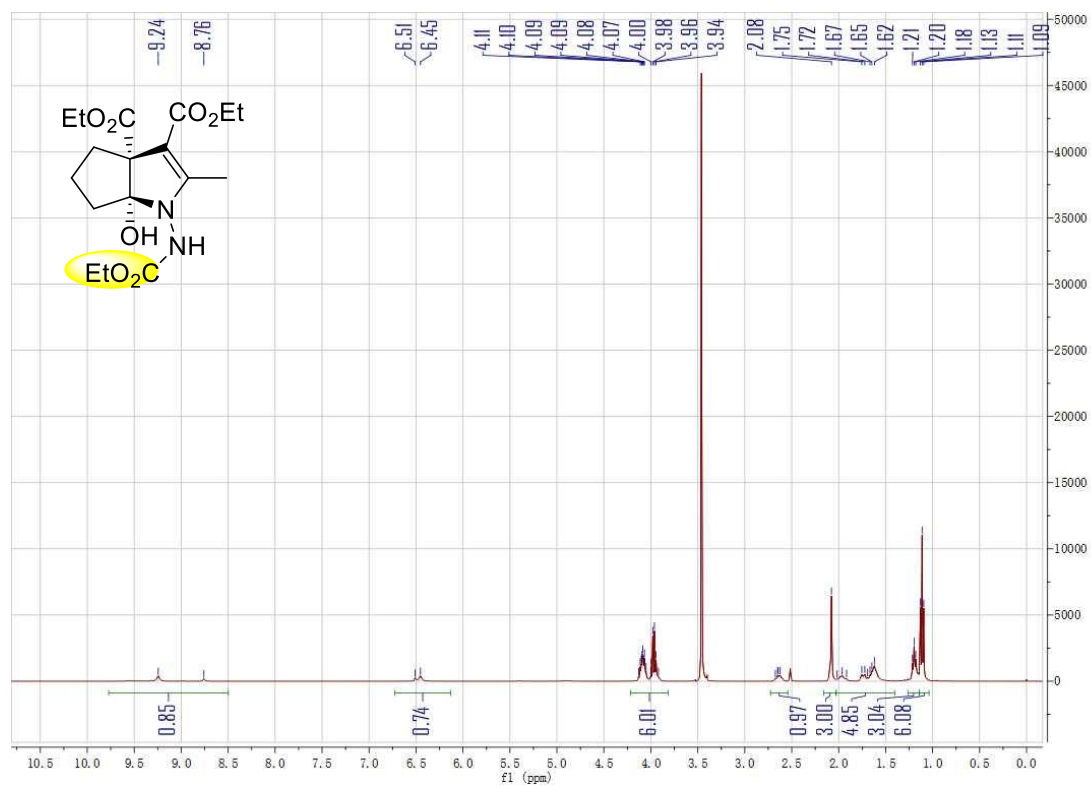
Identification code	20230339
Empirical formula	C <sub>32</sub> H <sub>48</sub> N <sub>4</sub> O <sub>14</sub>
Formula weight	712.74
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.4928(9)
b/Å	9.8026(9)
c/Å	11.3802(8)
α/°	102.528(7)
β/°	110.036(8)
γ/°	102.007(8)
Volume/Å <sup>3</sup>	924.02(15)
Z	1
ρ <sub>calc</sub> /cm <sup>3</sup>	1.281
μ/mm <sup>-1</sup>	0.850
F(000)	380.0
Crystal size/mm <sup>3</sup>	0.15 × 0.12 × 0.1
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	8.71 to 143.166
Index ranges	-11 ≤ h ≤ 11, -10 ≤ k ≤ 11, -13 ≤ l ≤ 12
Reflections collected	6573
Independent reflections	3435 [R <sub>int</sub> = 0.0265, R <sub>sigma</sub> = 0.0456]
Data/restraints/parameters	3435/14/246
Goodness-of-fit on F <sup>2</sup>	1.060
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0544, wR <sub>2</sub> = 0.1335
Final R indexes [all data]	R <sub>1</sub> = 0.0750, wR <sub>2</sub> = 0.1674
Largest diff. peak/hole / e Å <sup>-3</sup>	0.22/-0.23

# 5. NMR Spectra

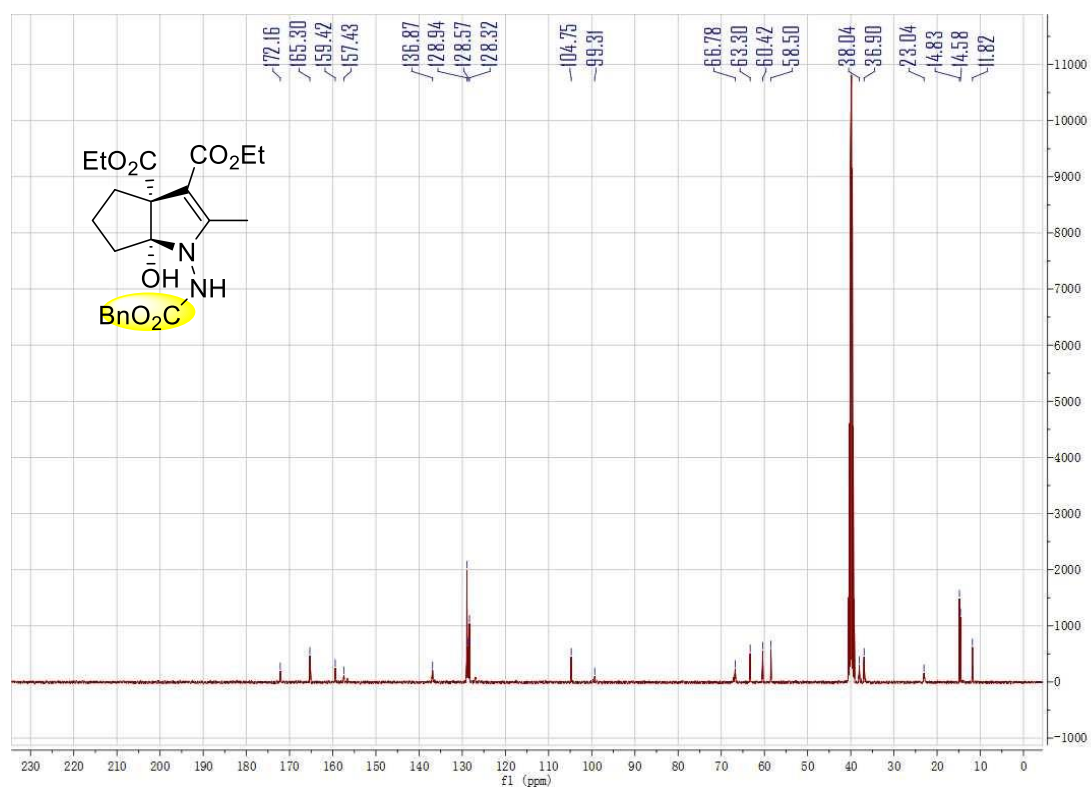
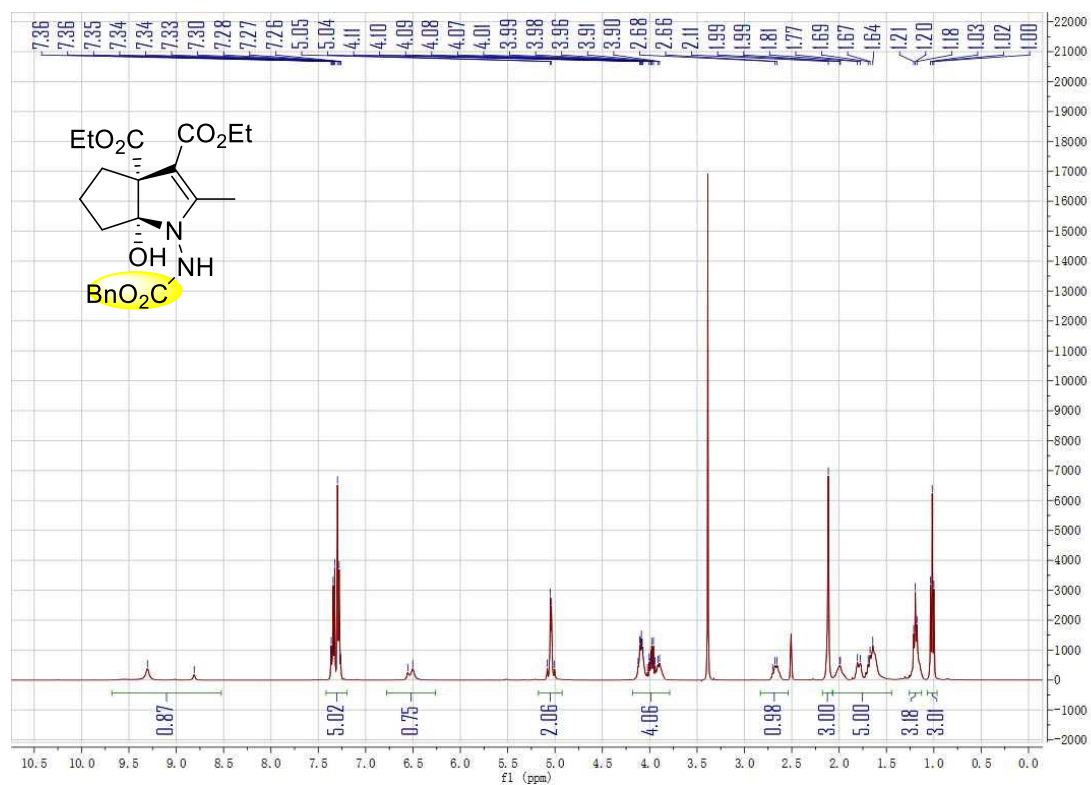
3a



3b

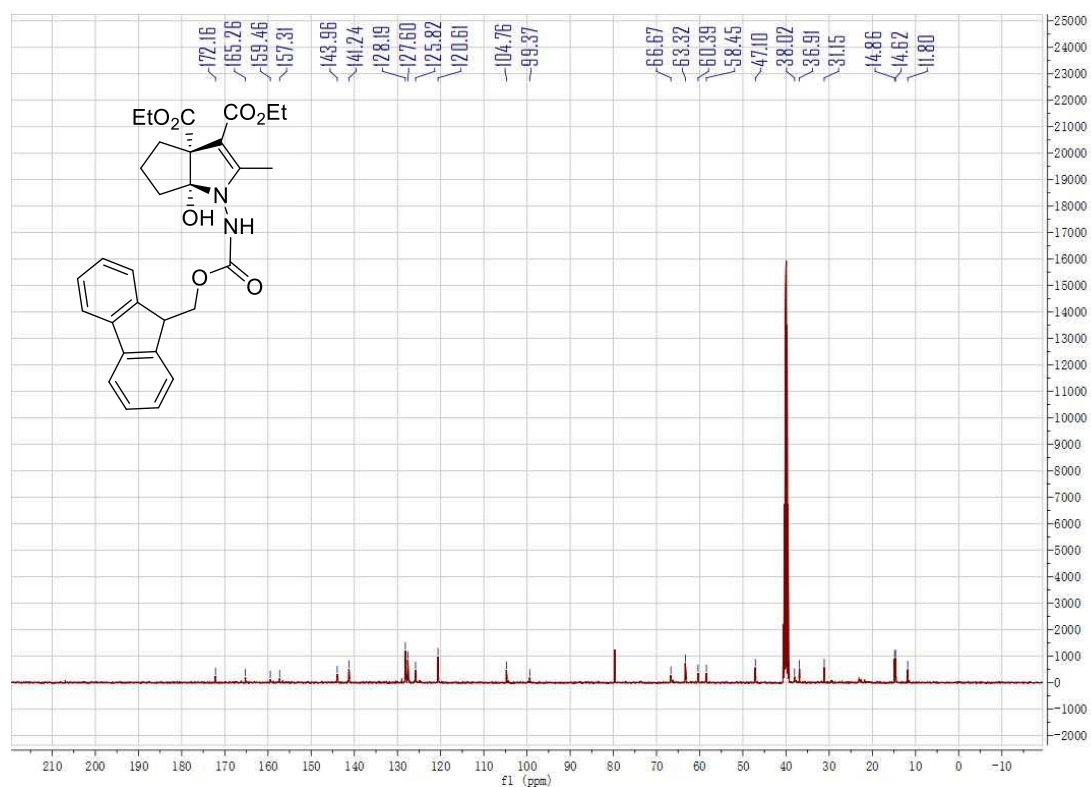
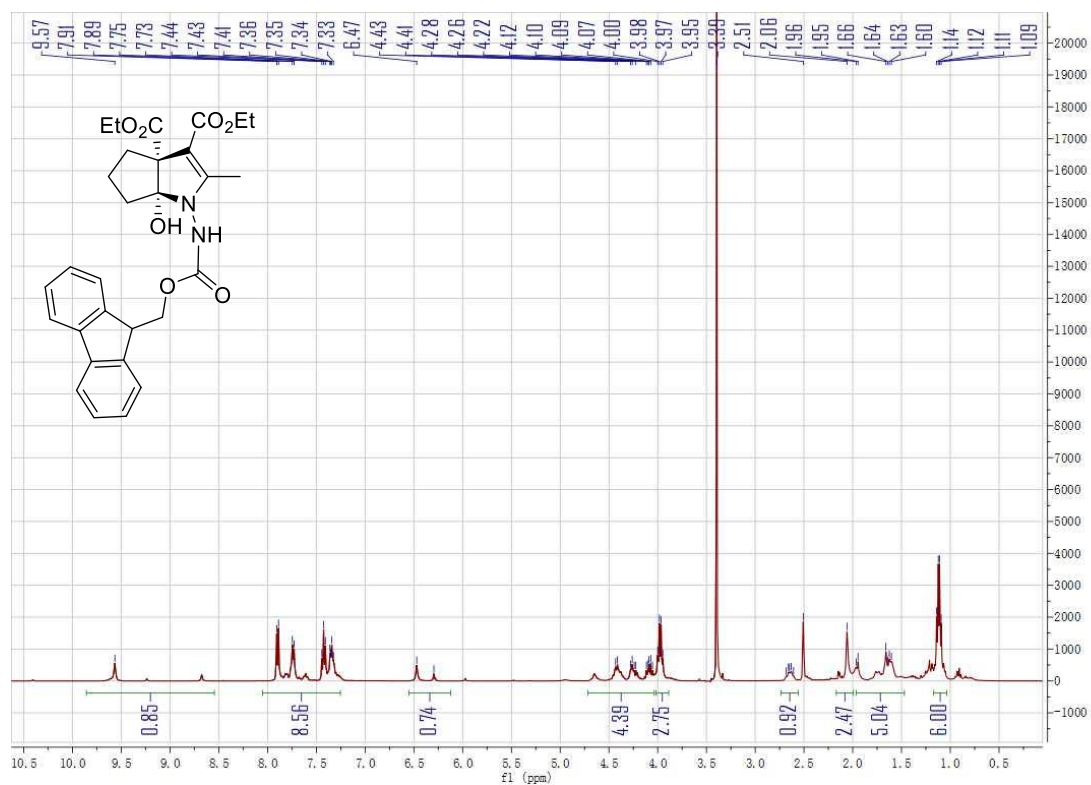


3c

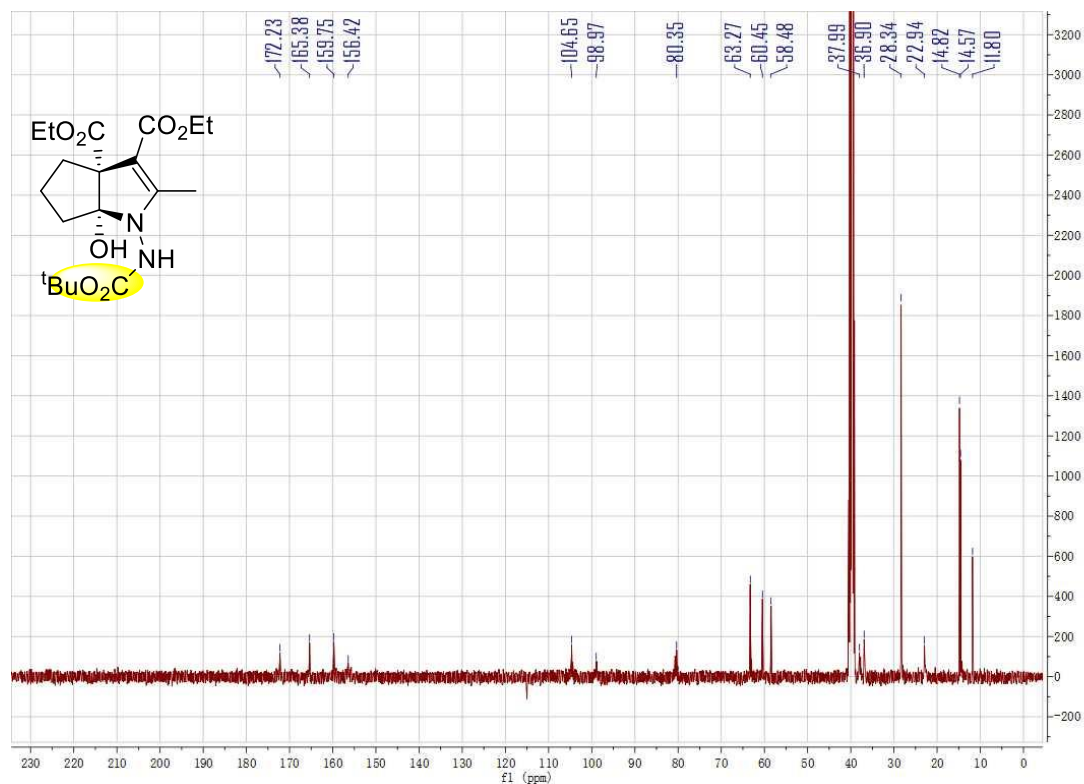
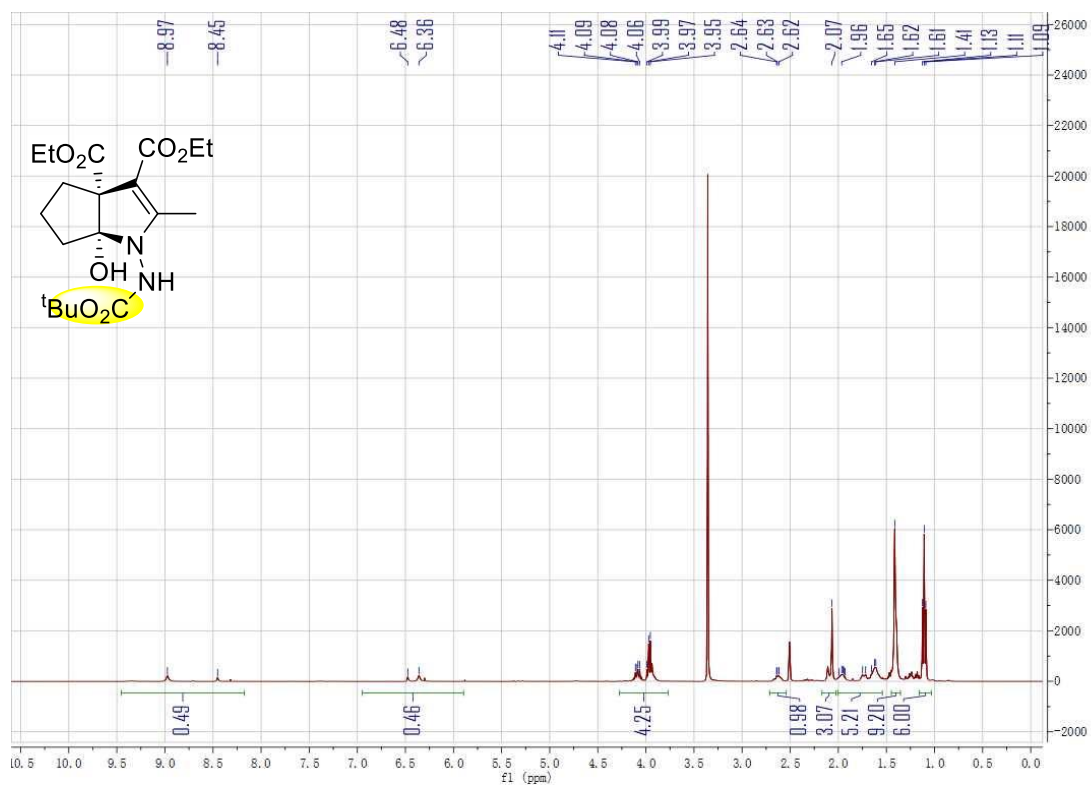




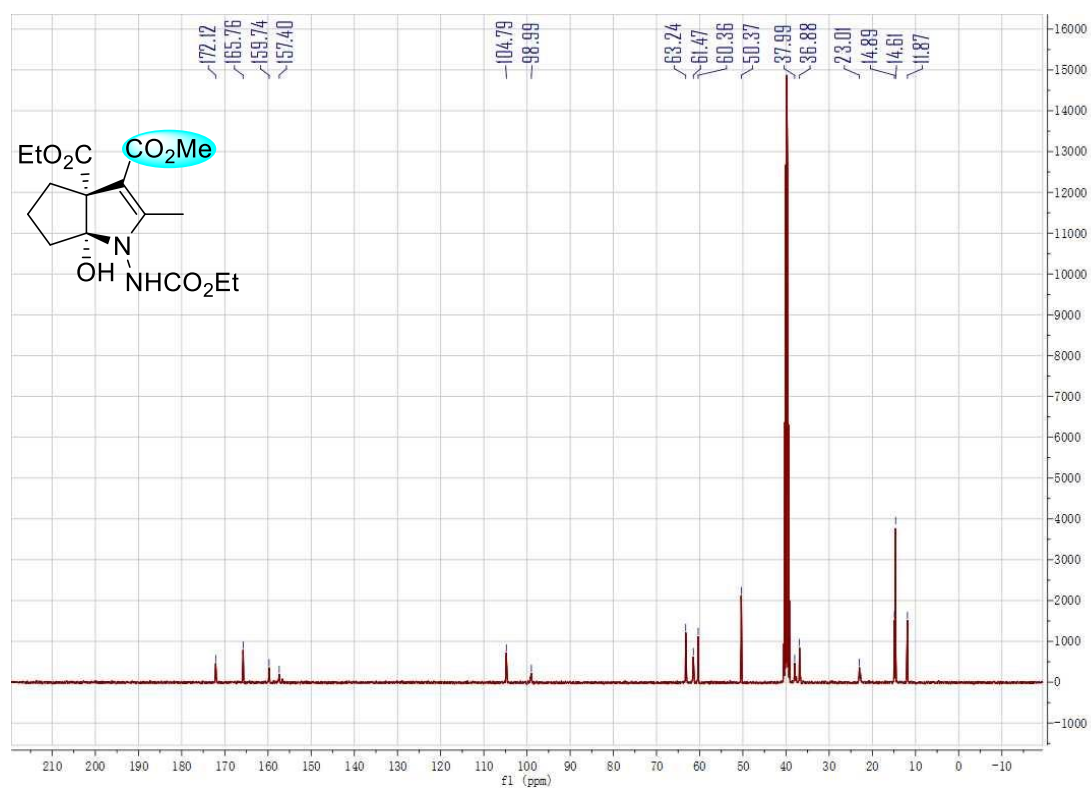
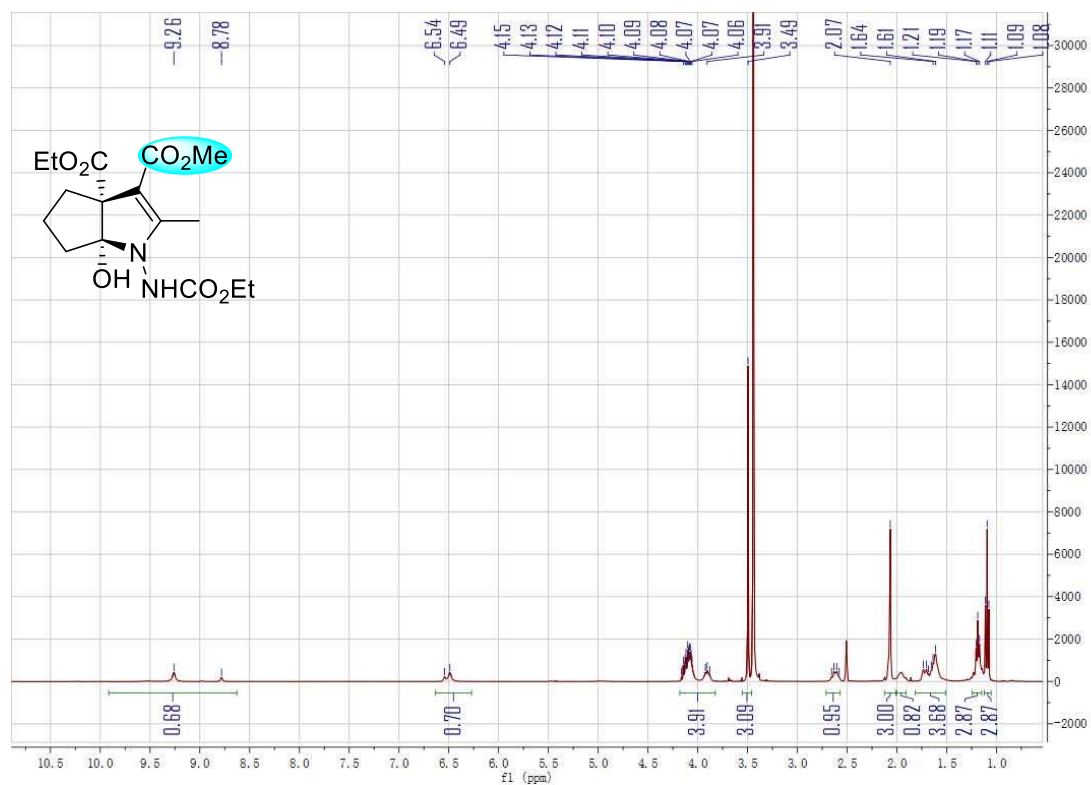
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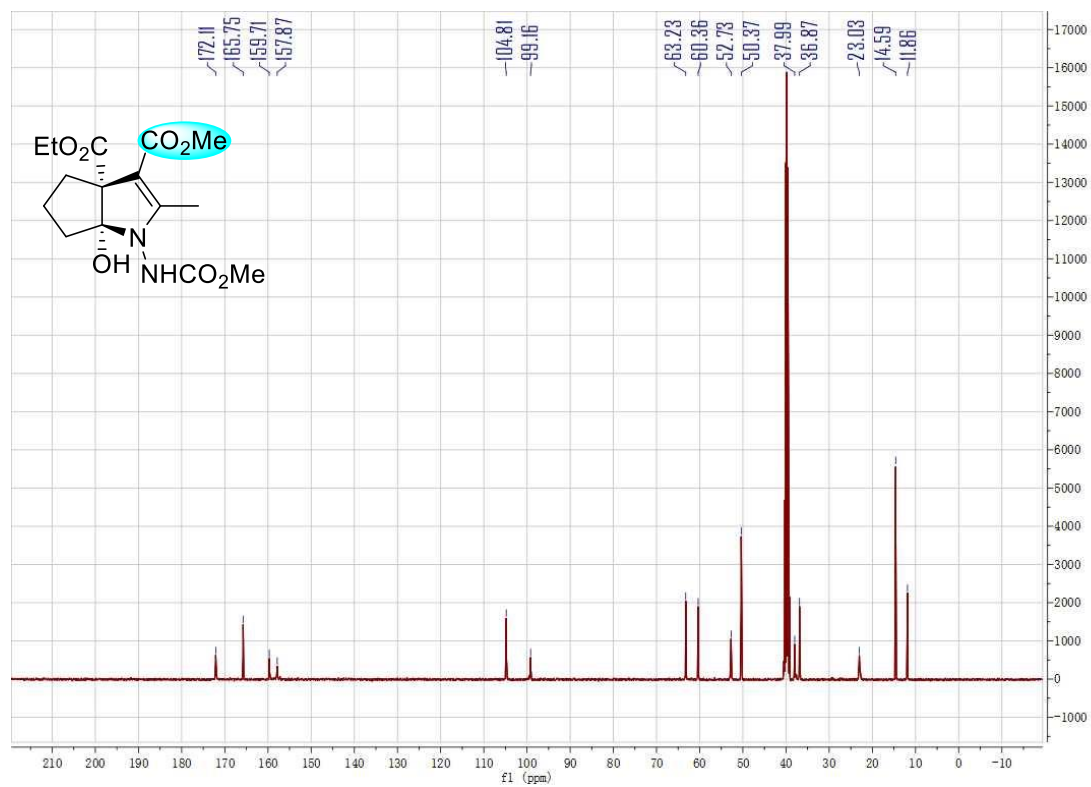
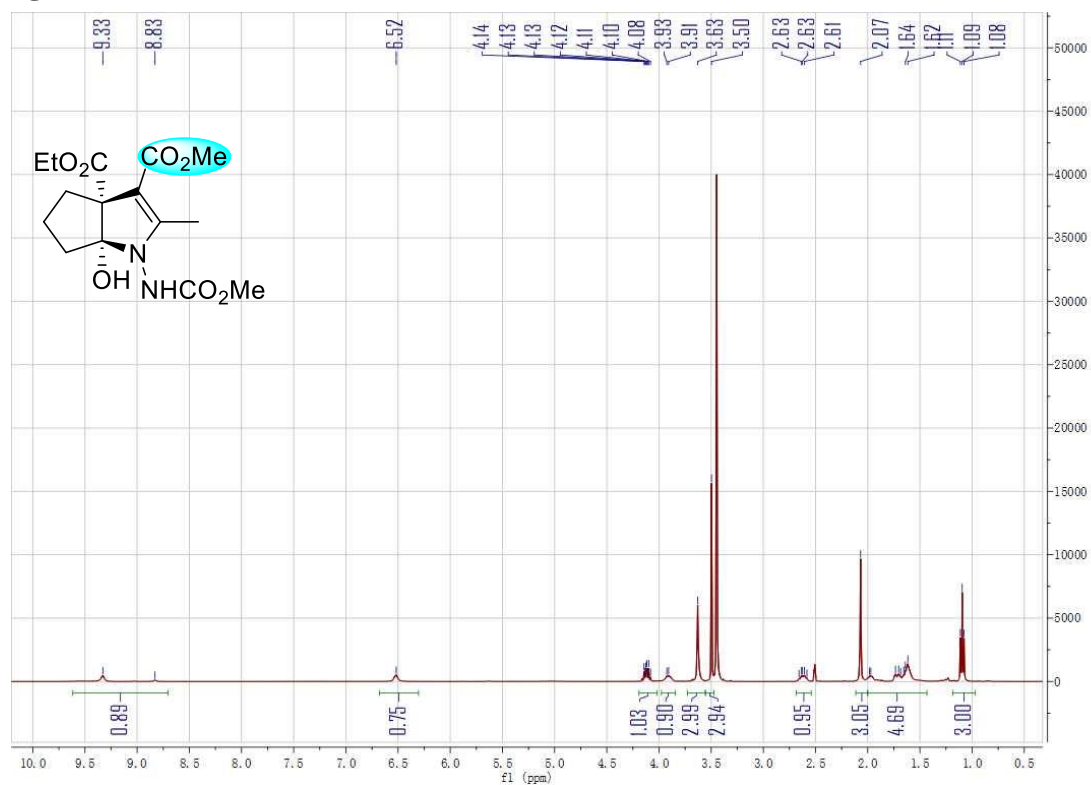
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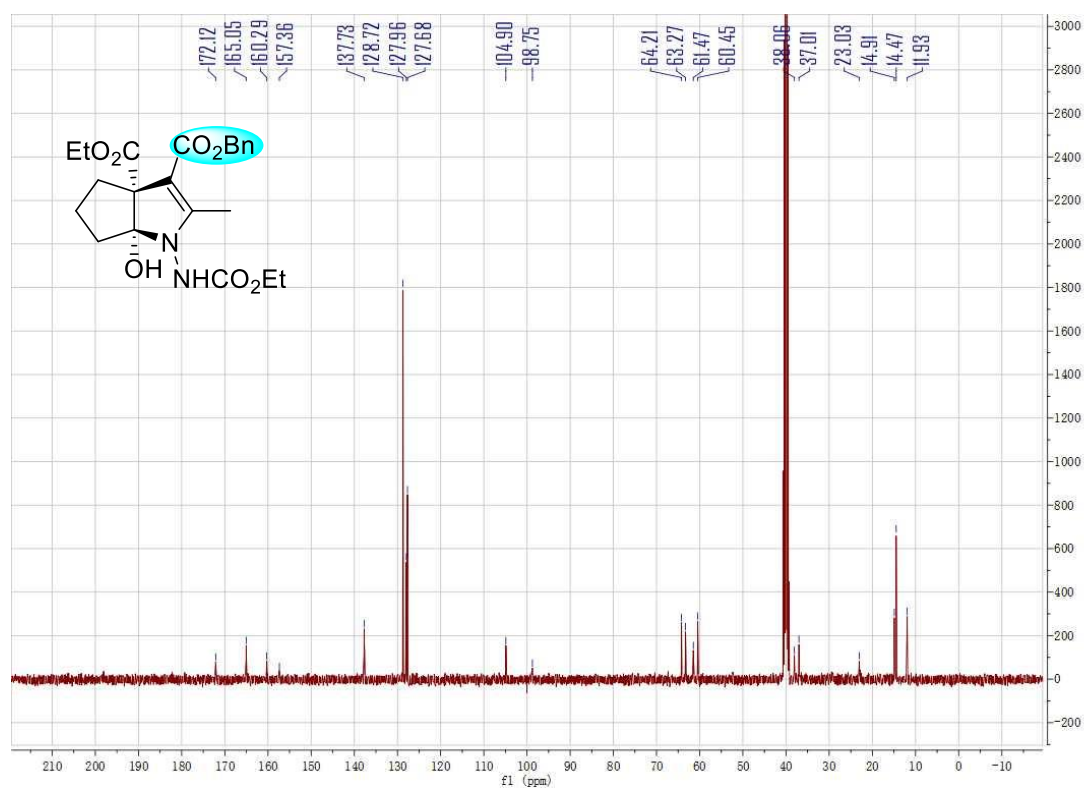
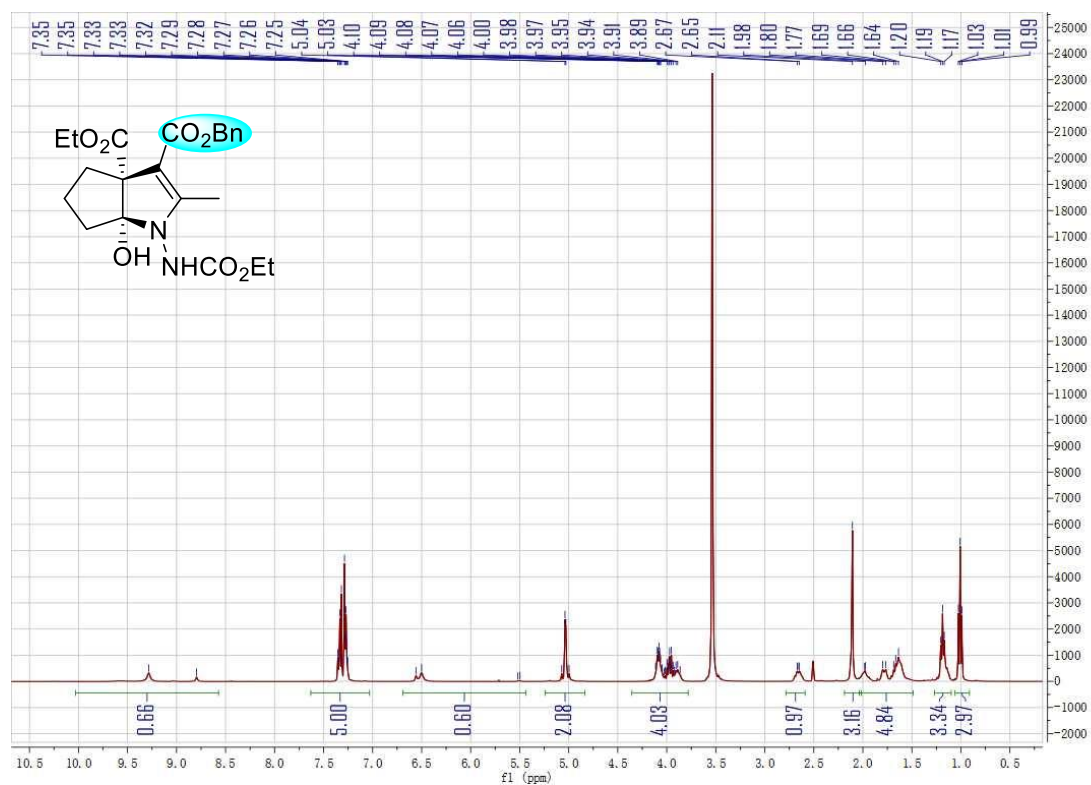
3f



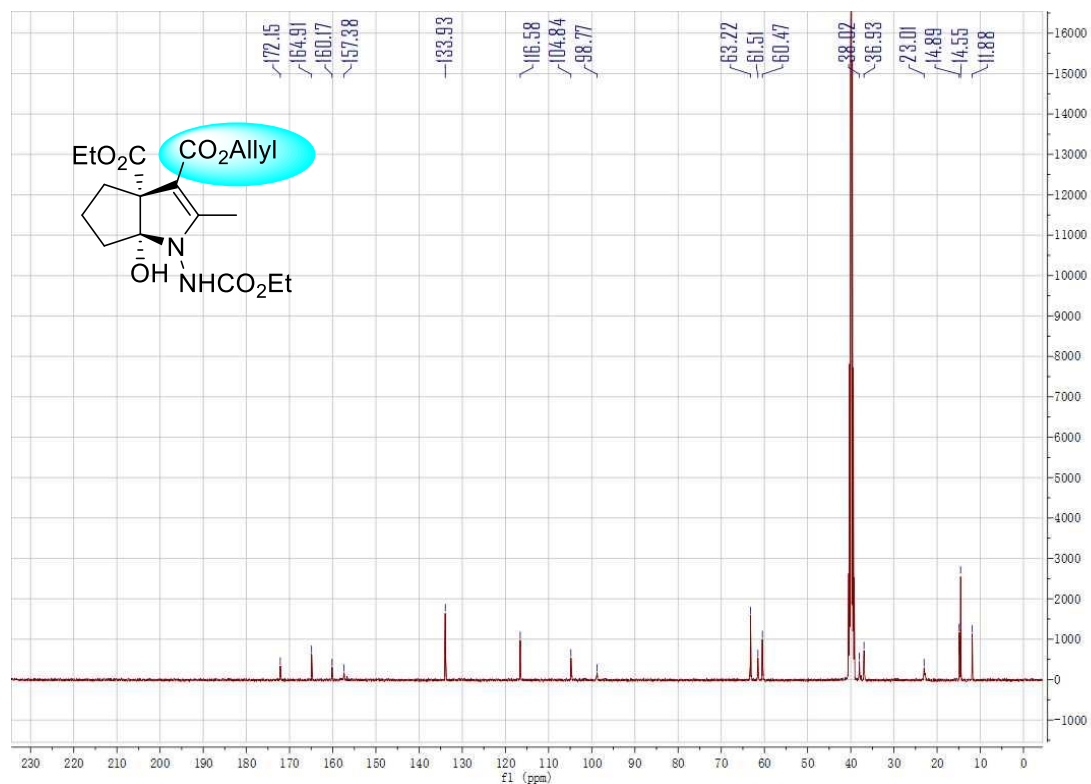
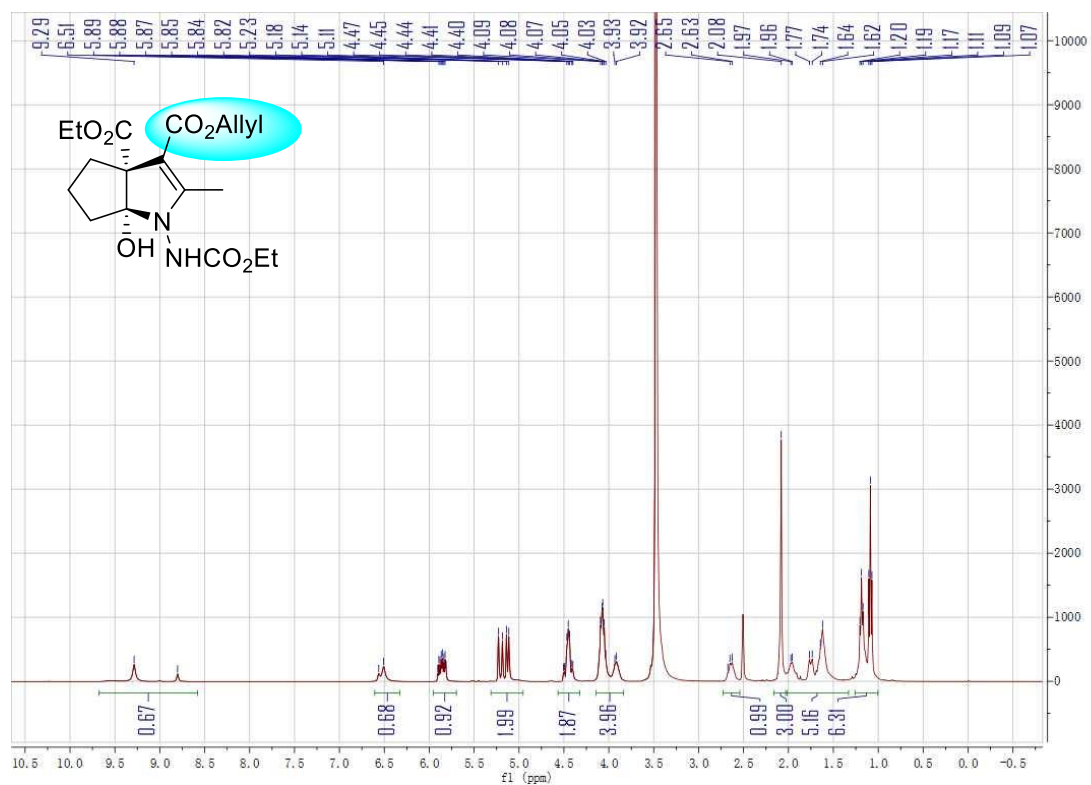
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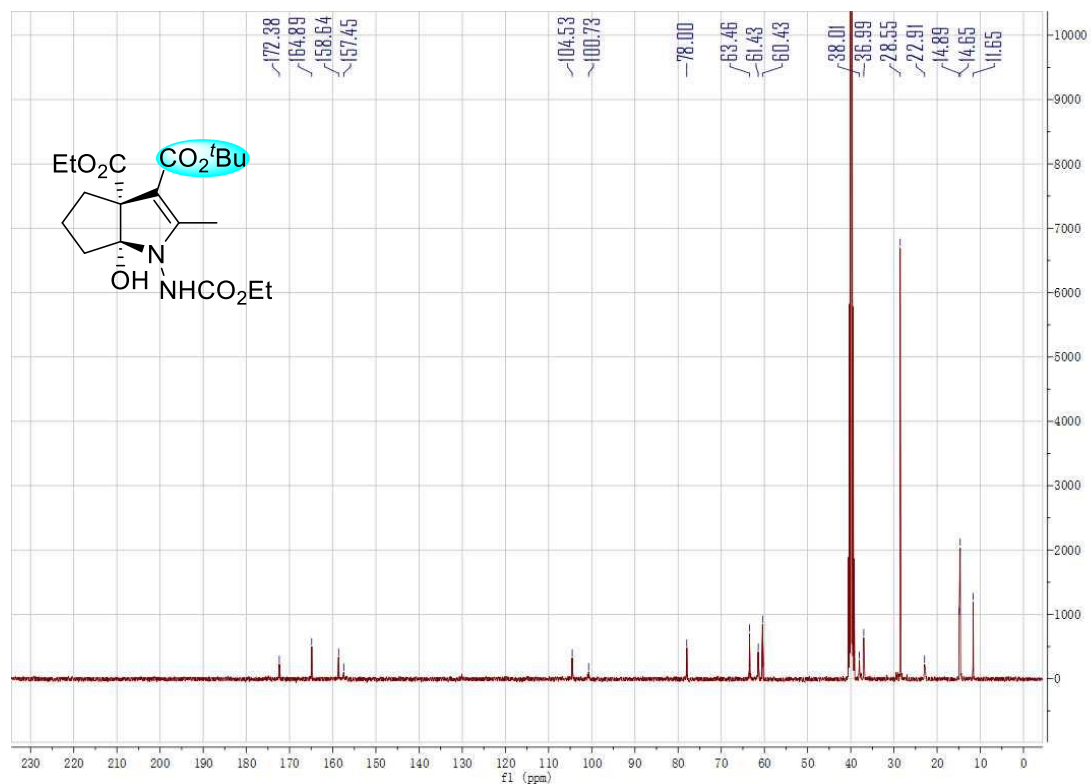
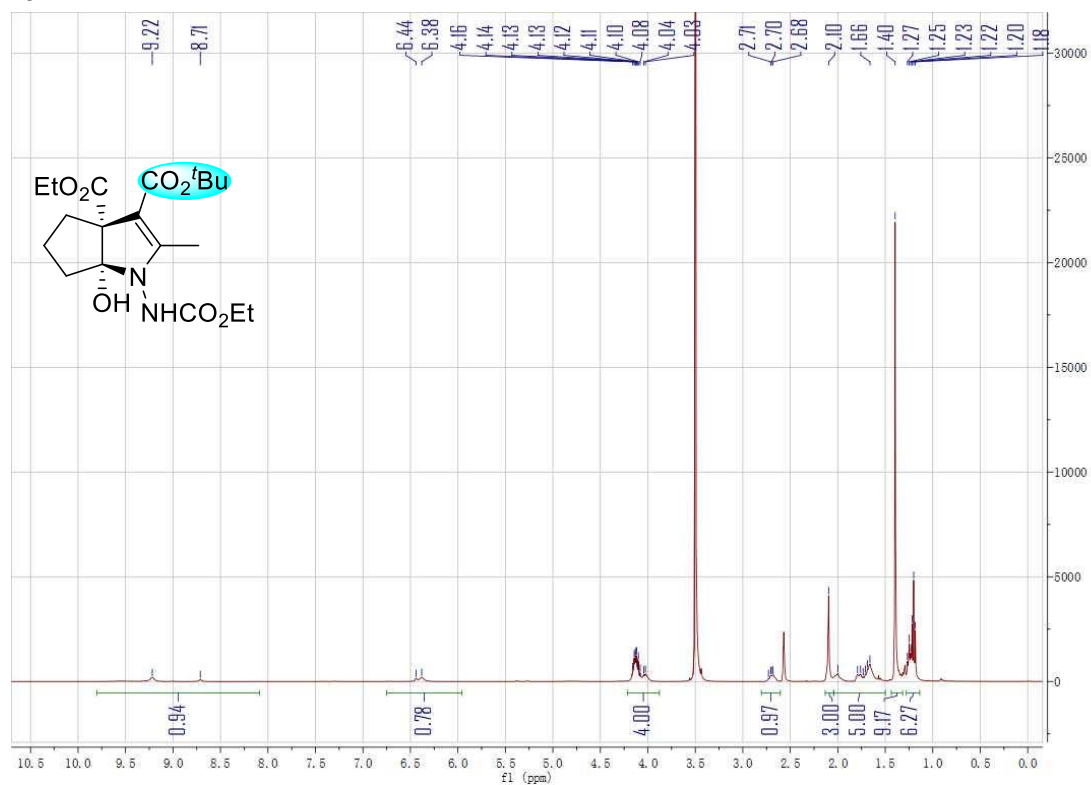
3h



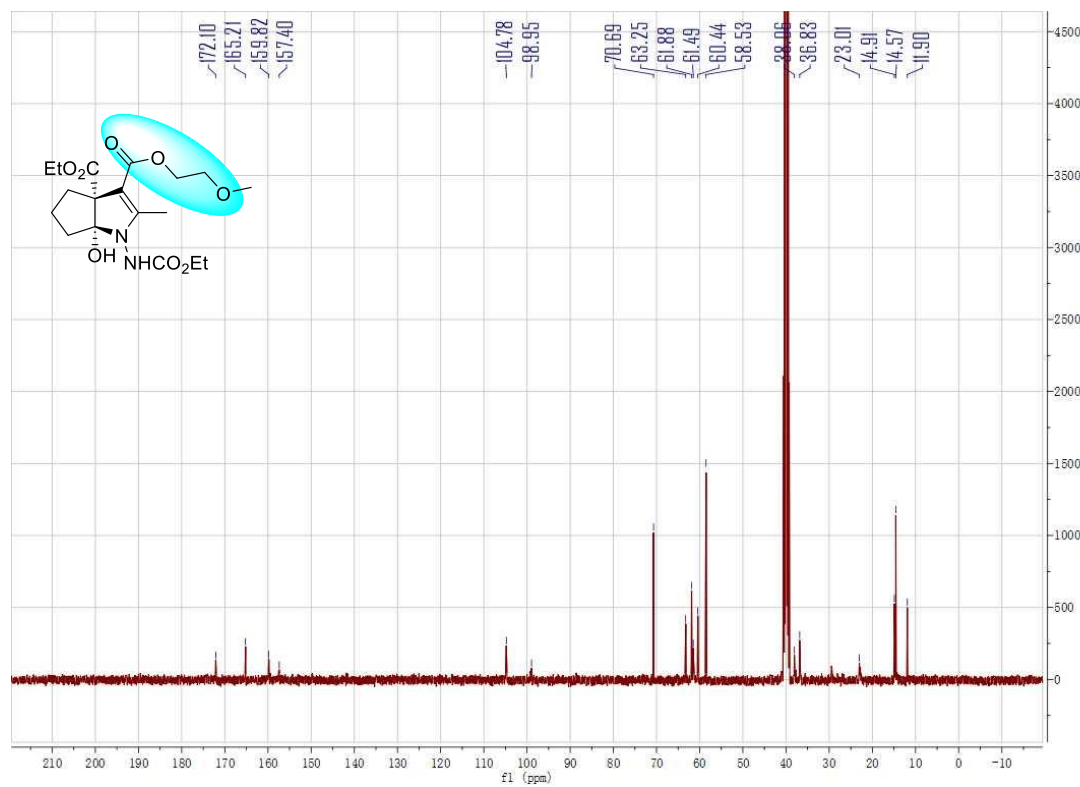
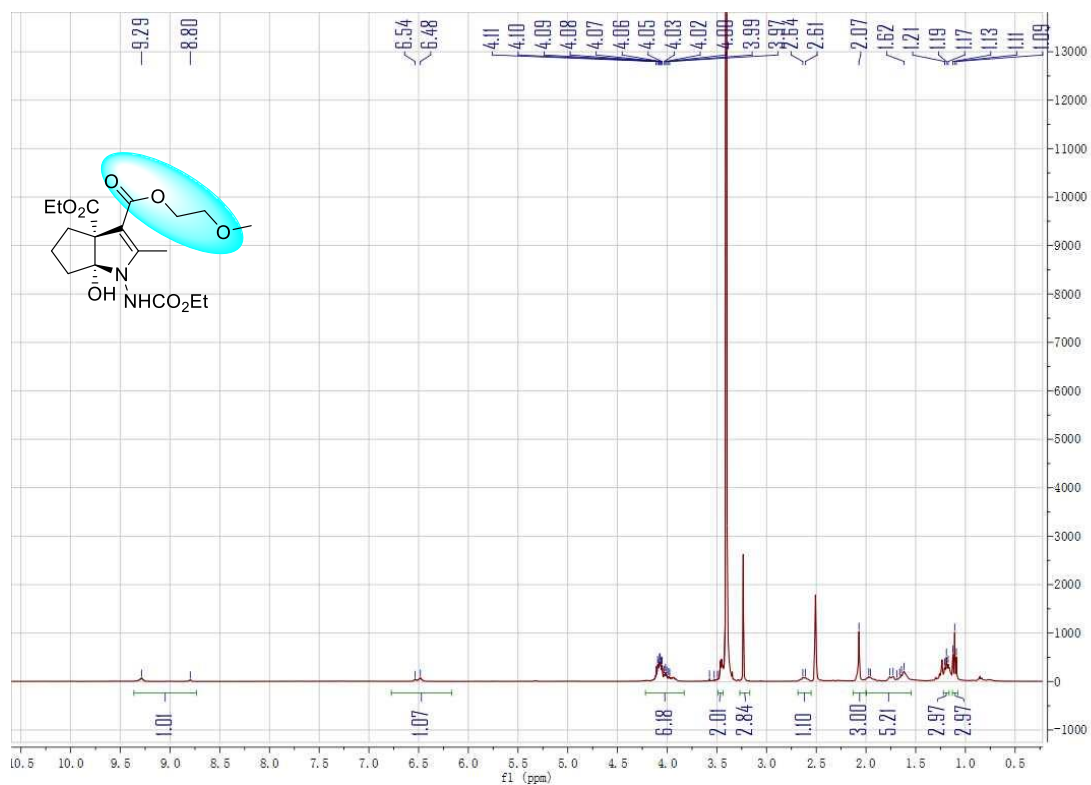
3i



3j

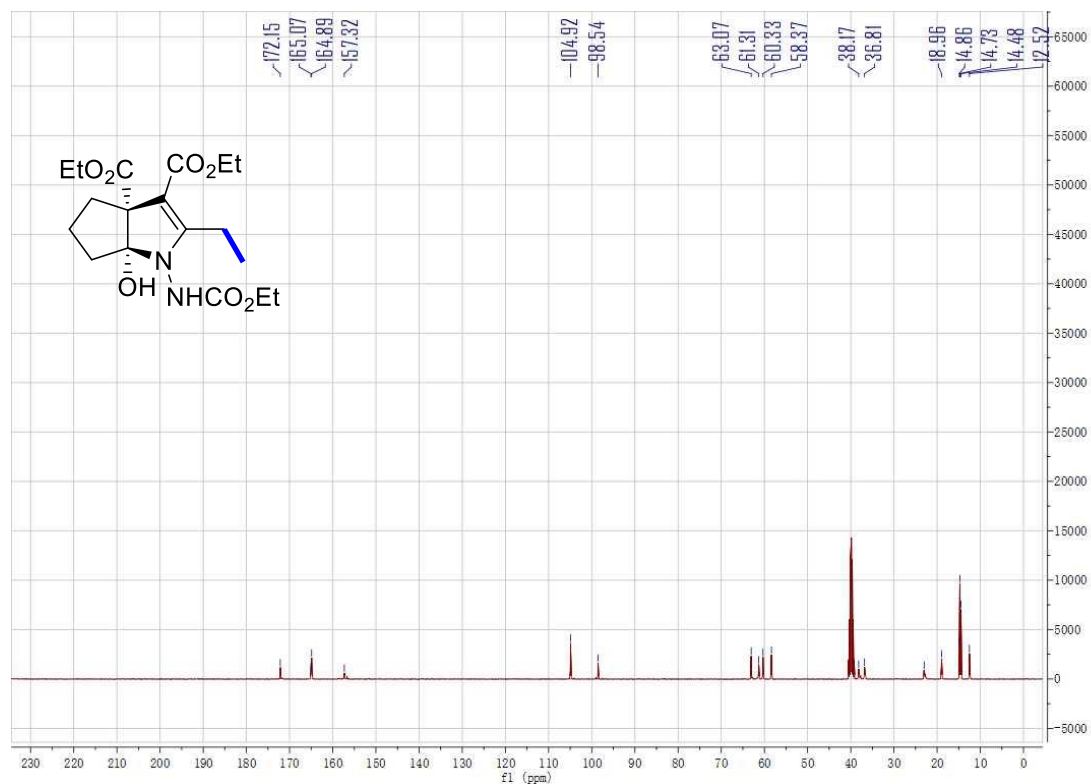
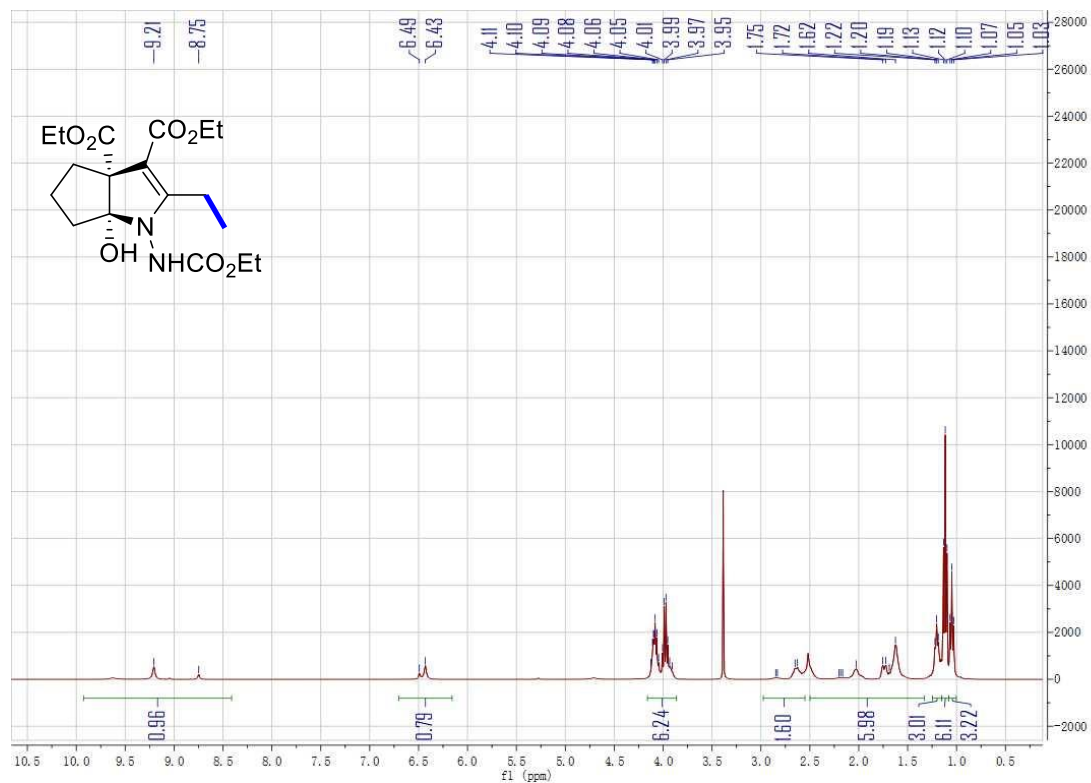


3k

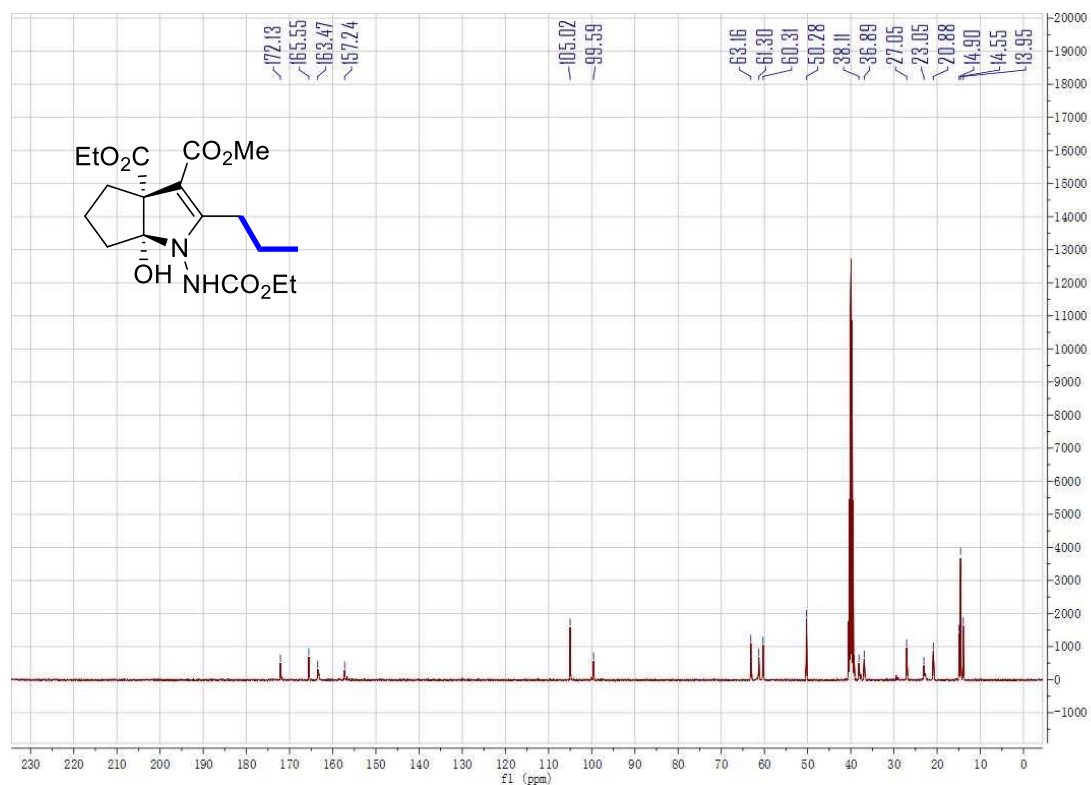
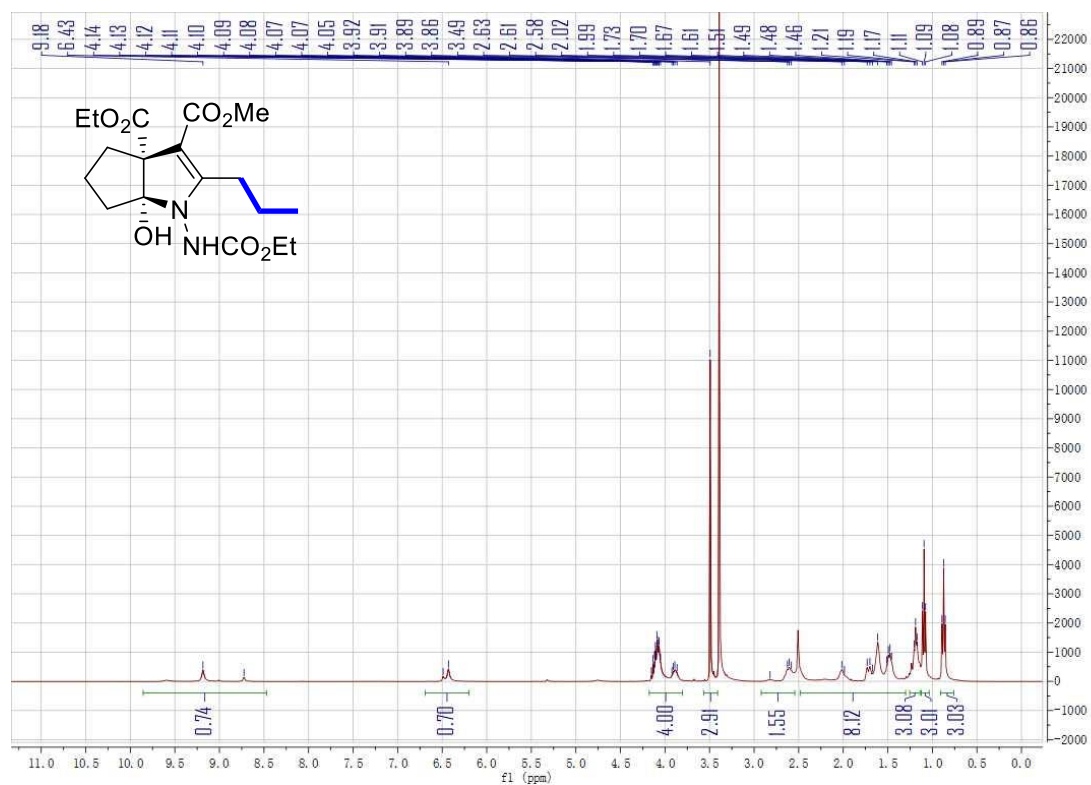




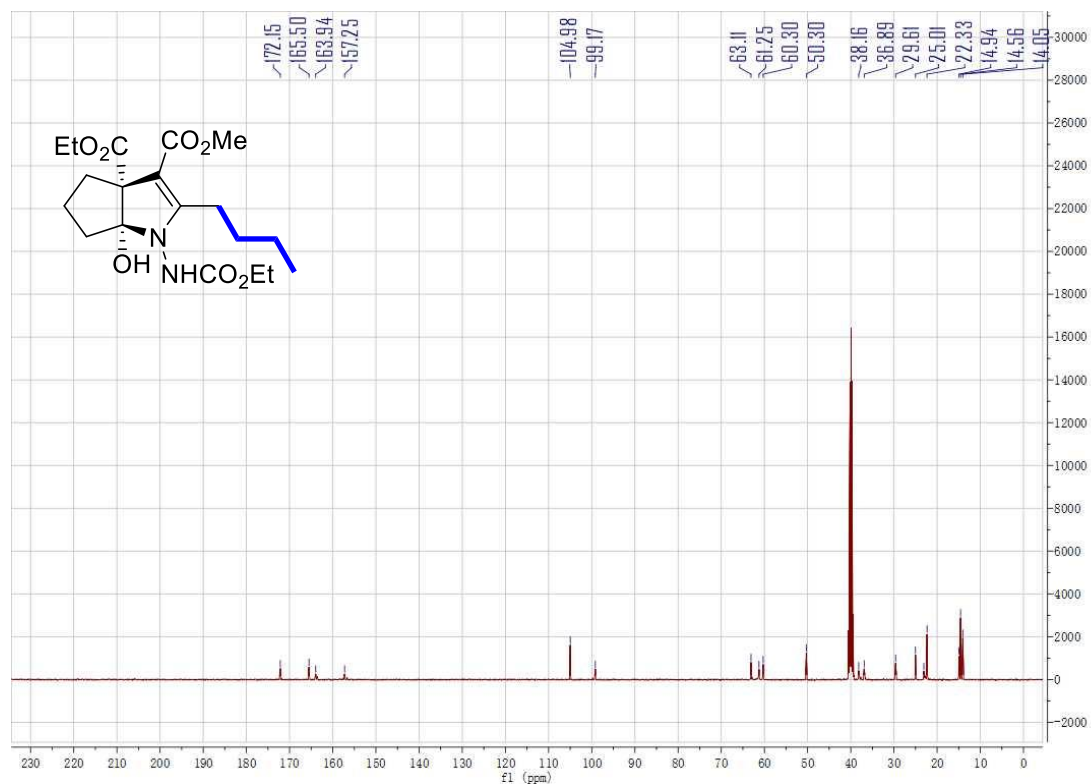
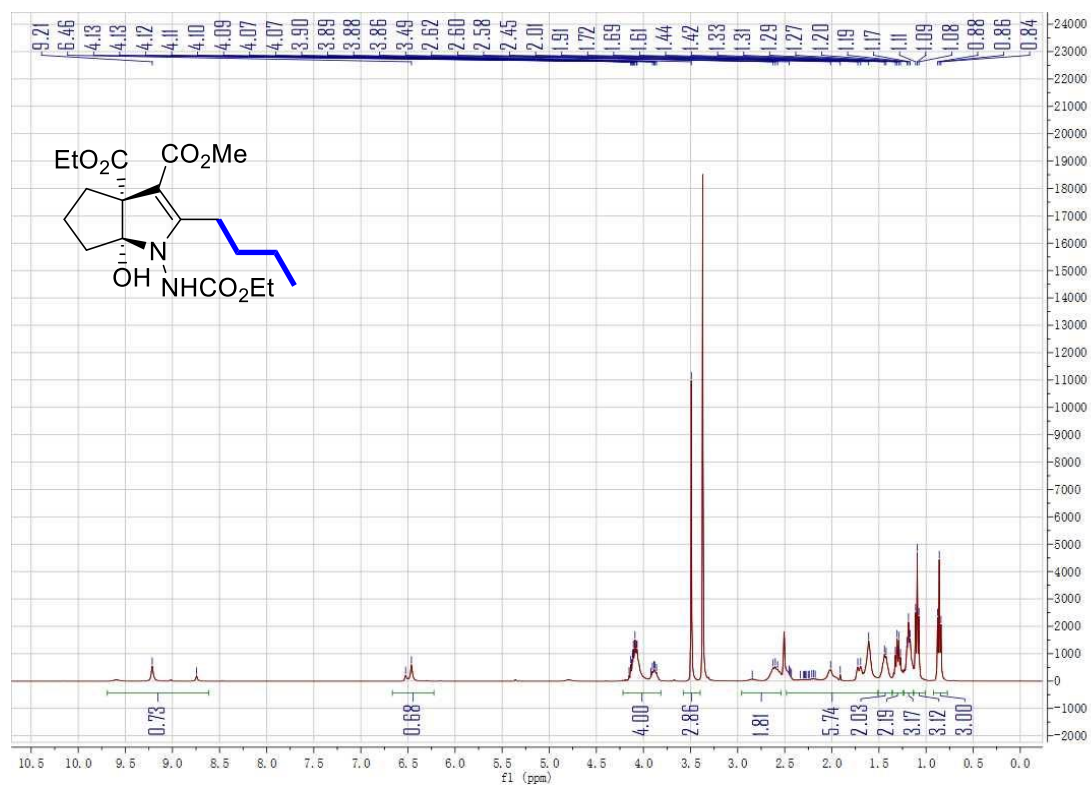
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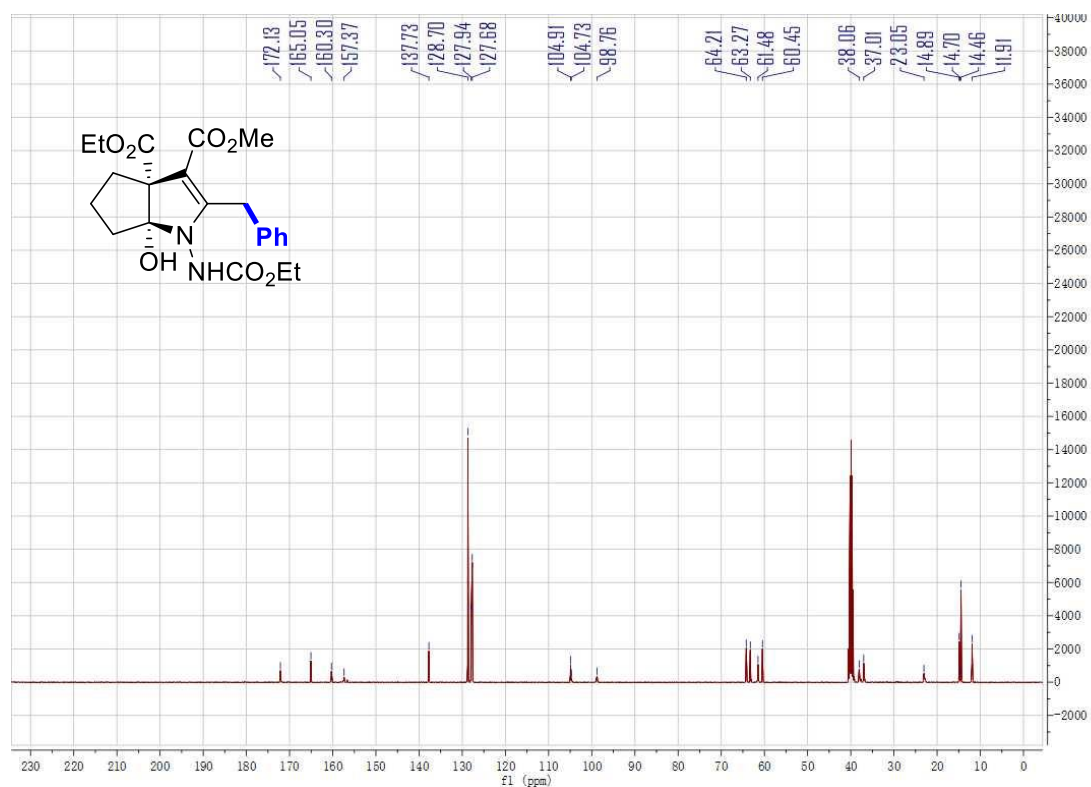
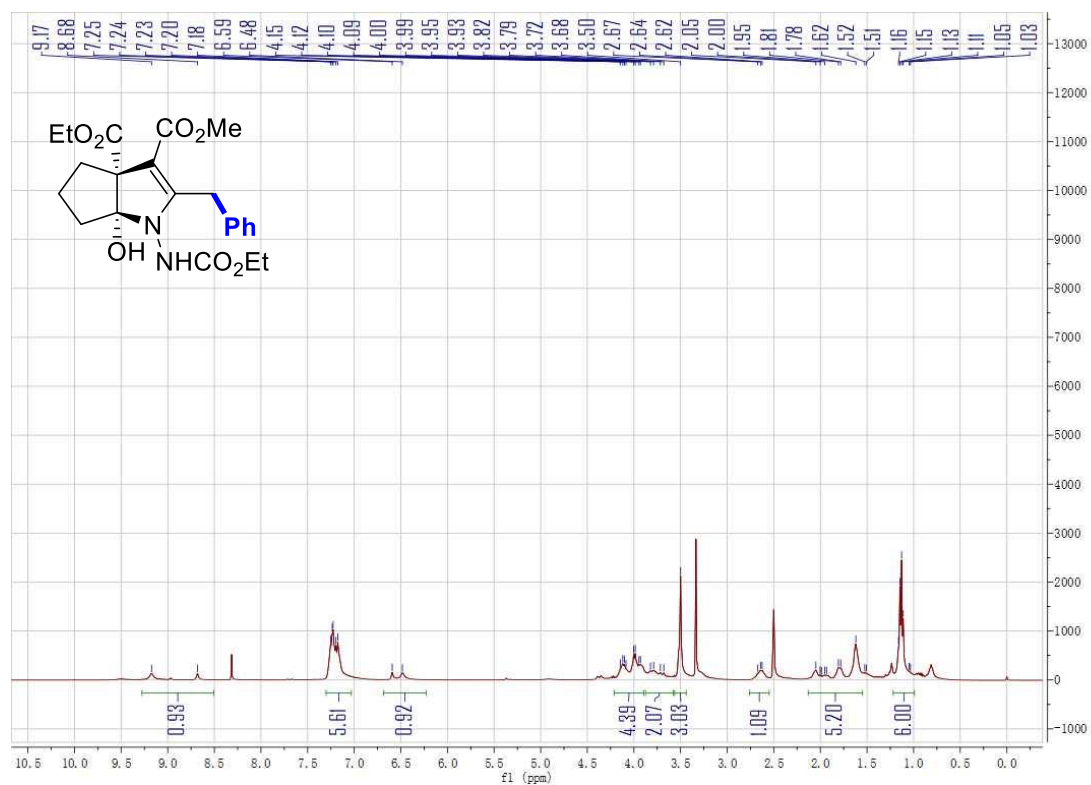
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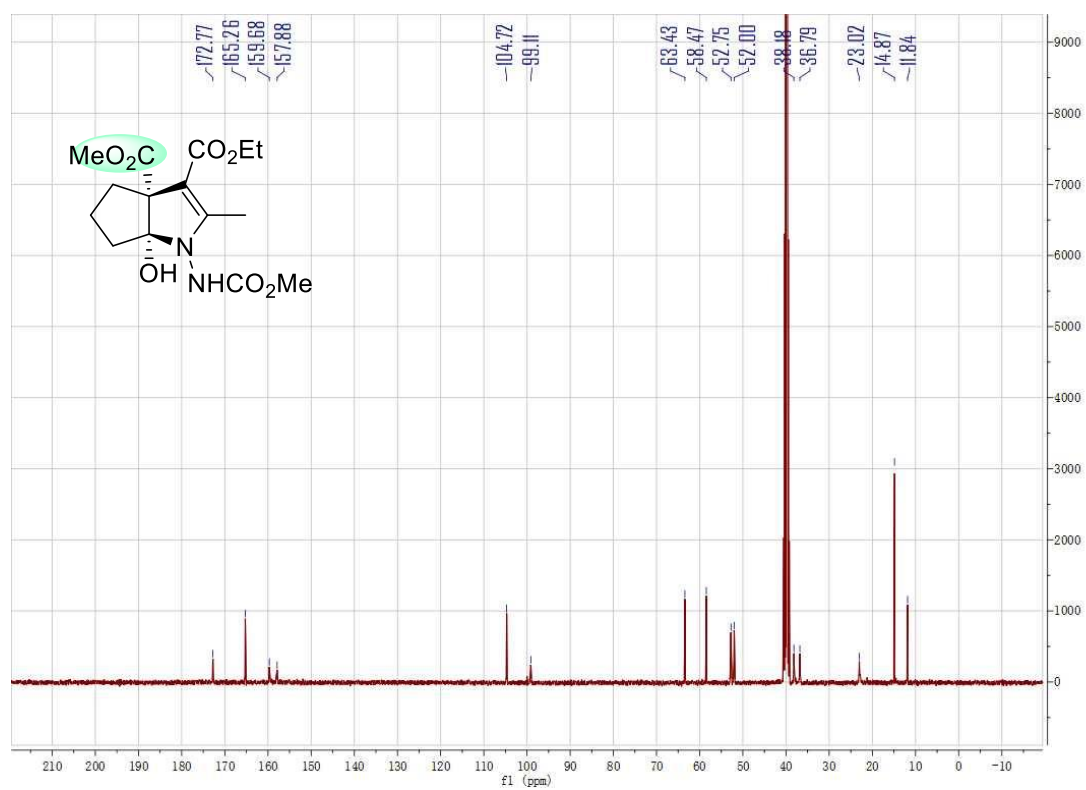
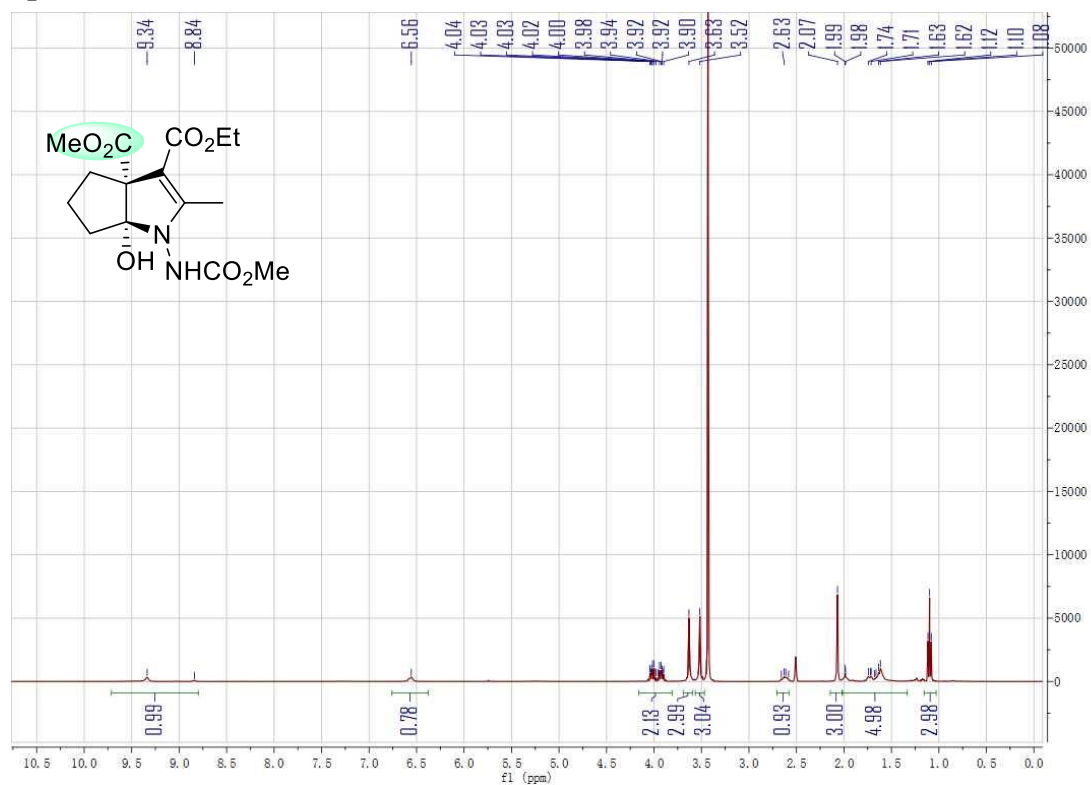
3n



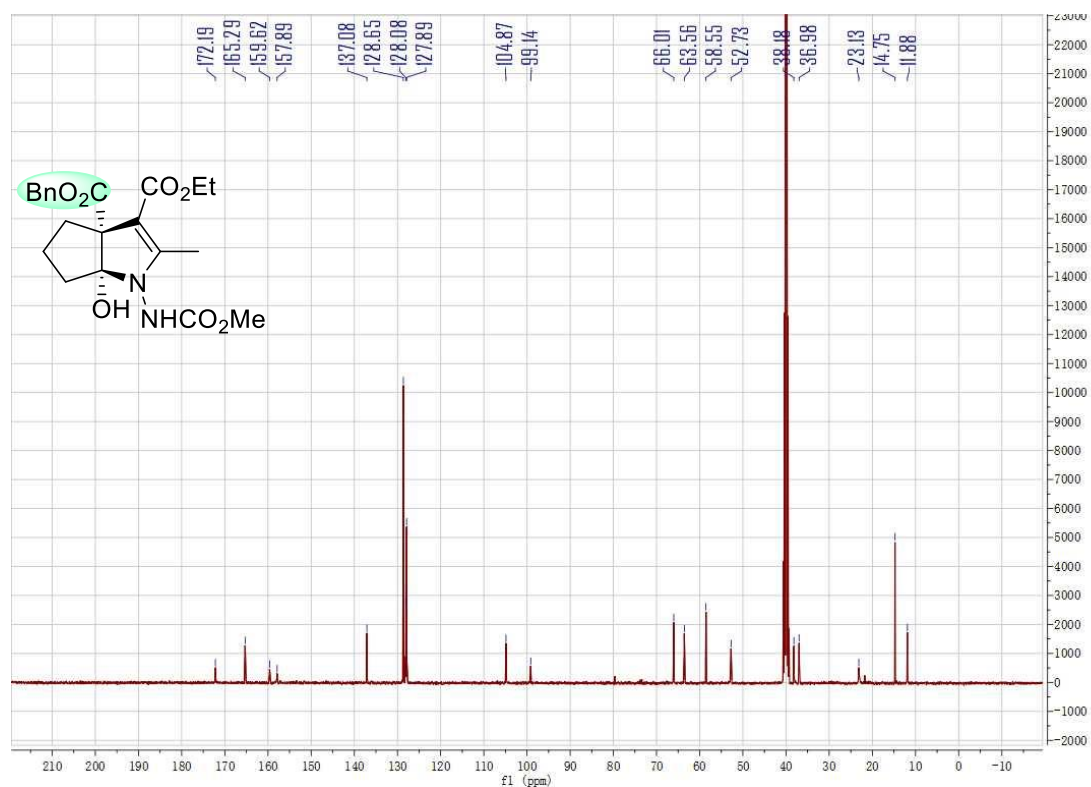
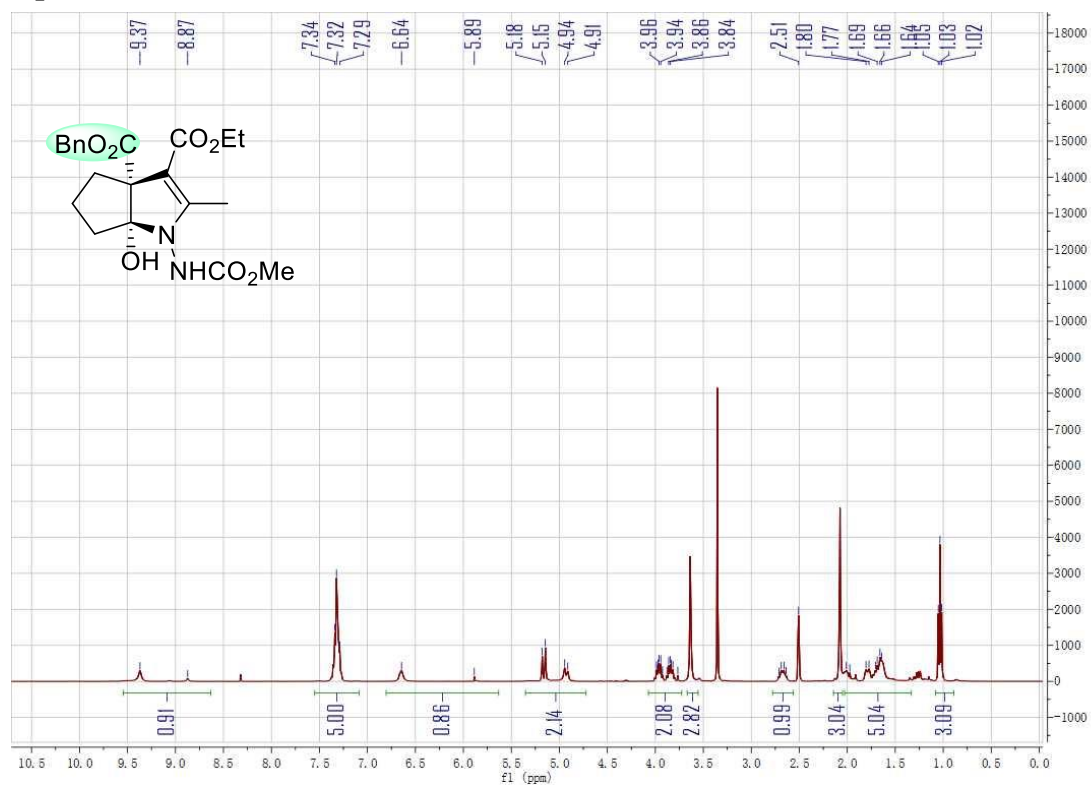
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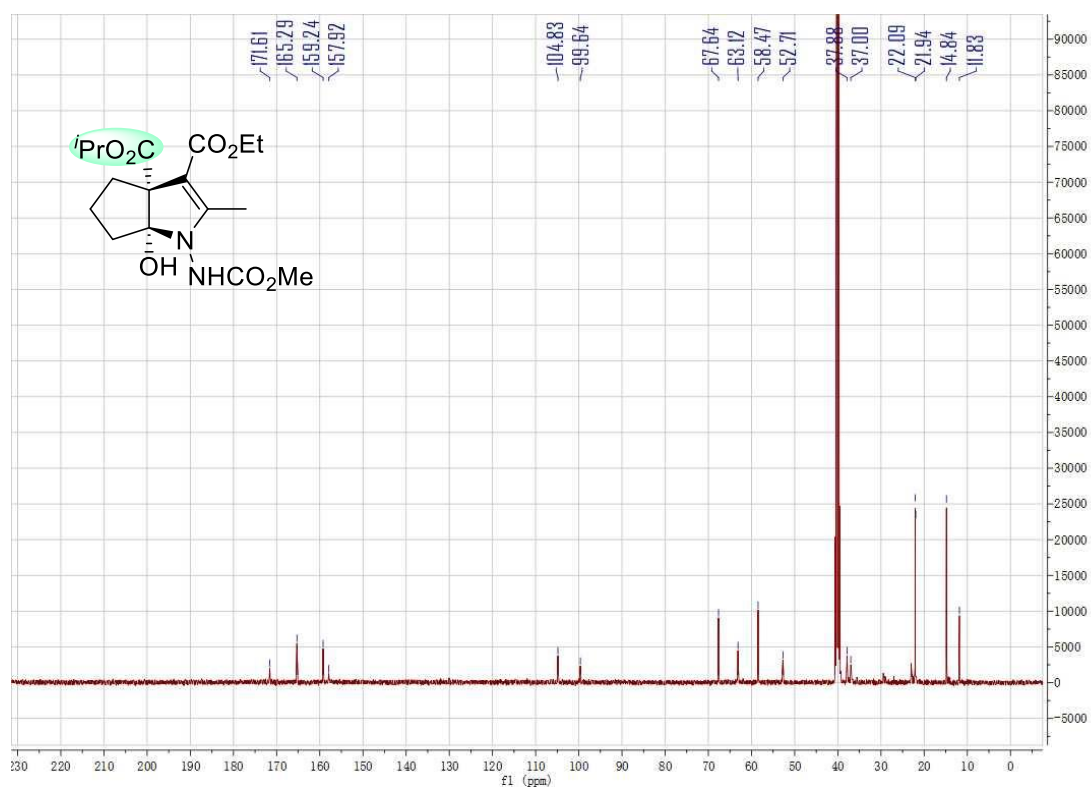
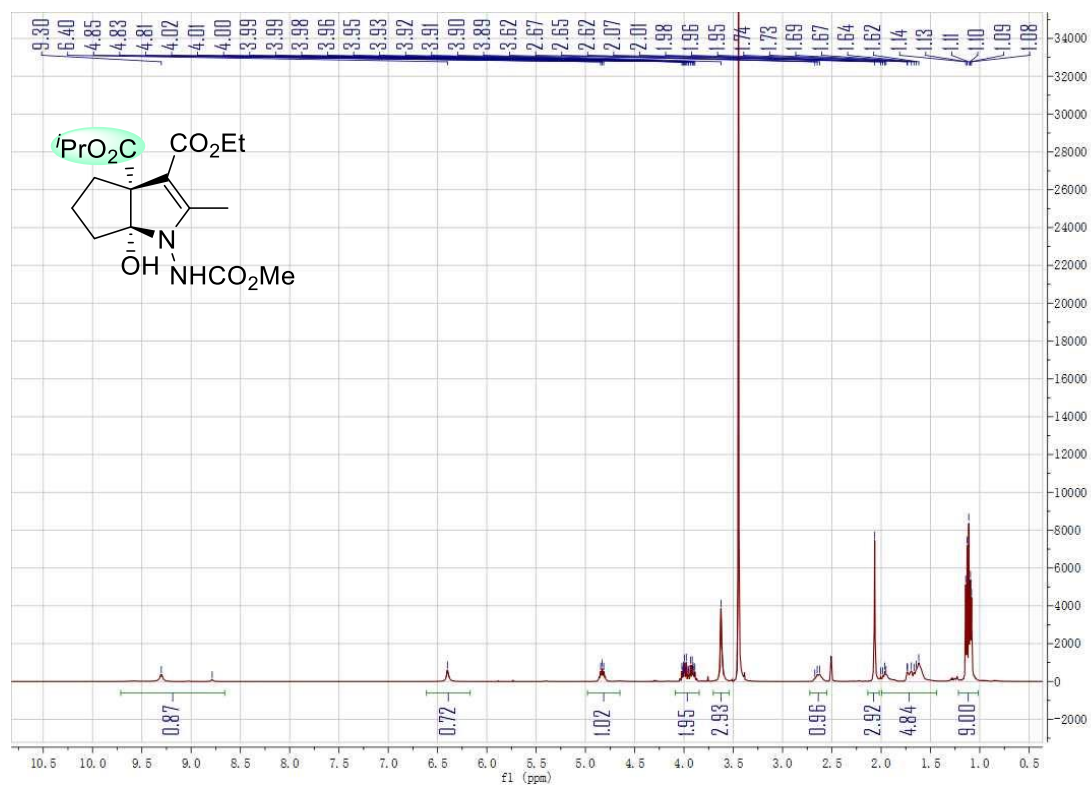
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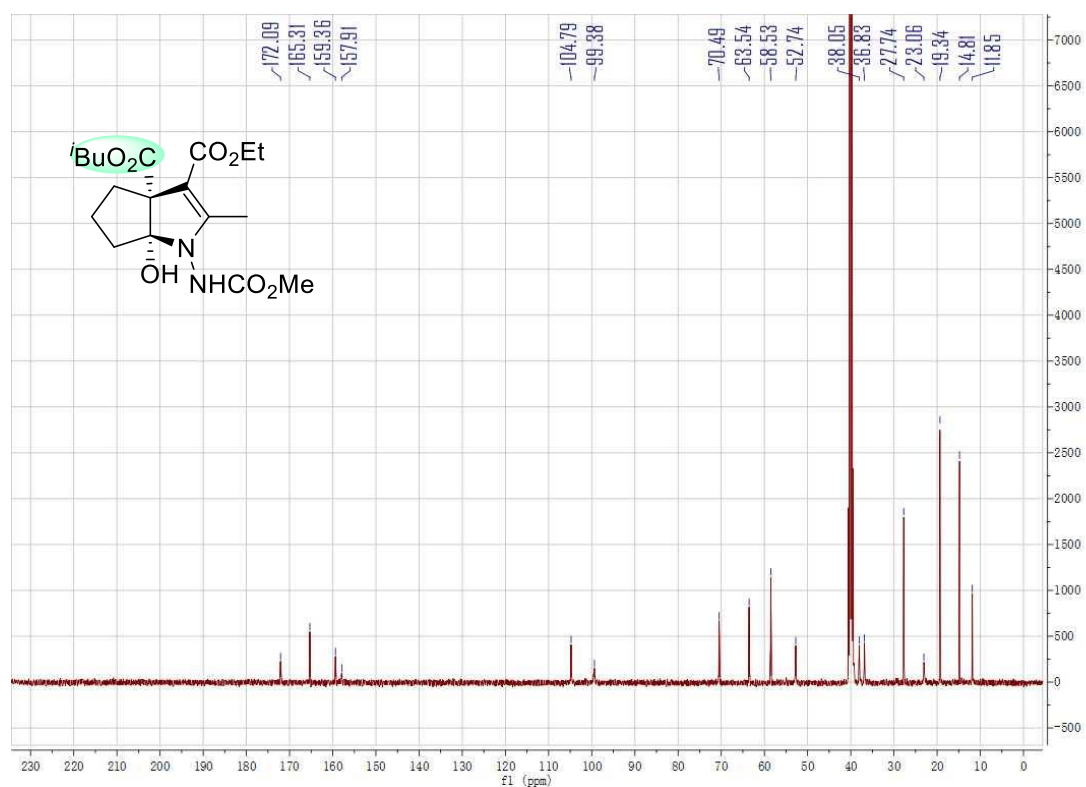
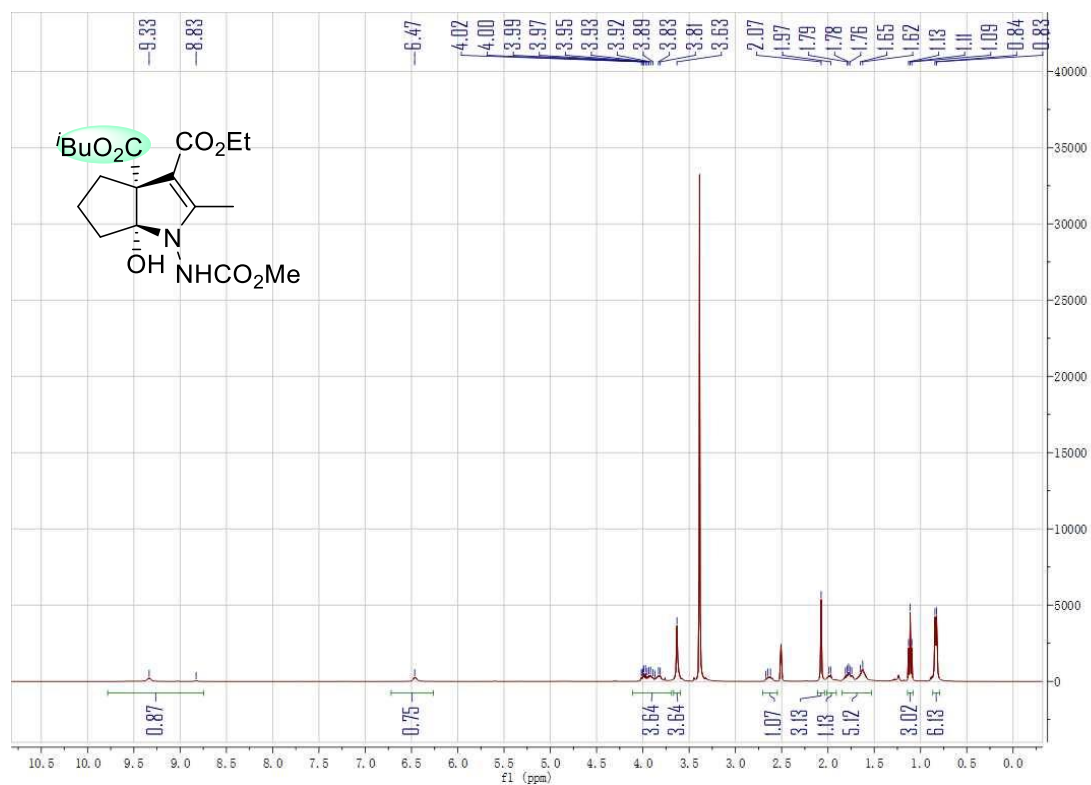
3q



3r

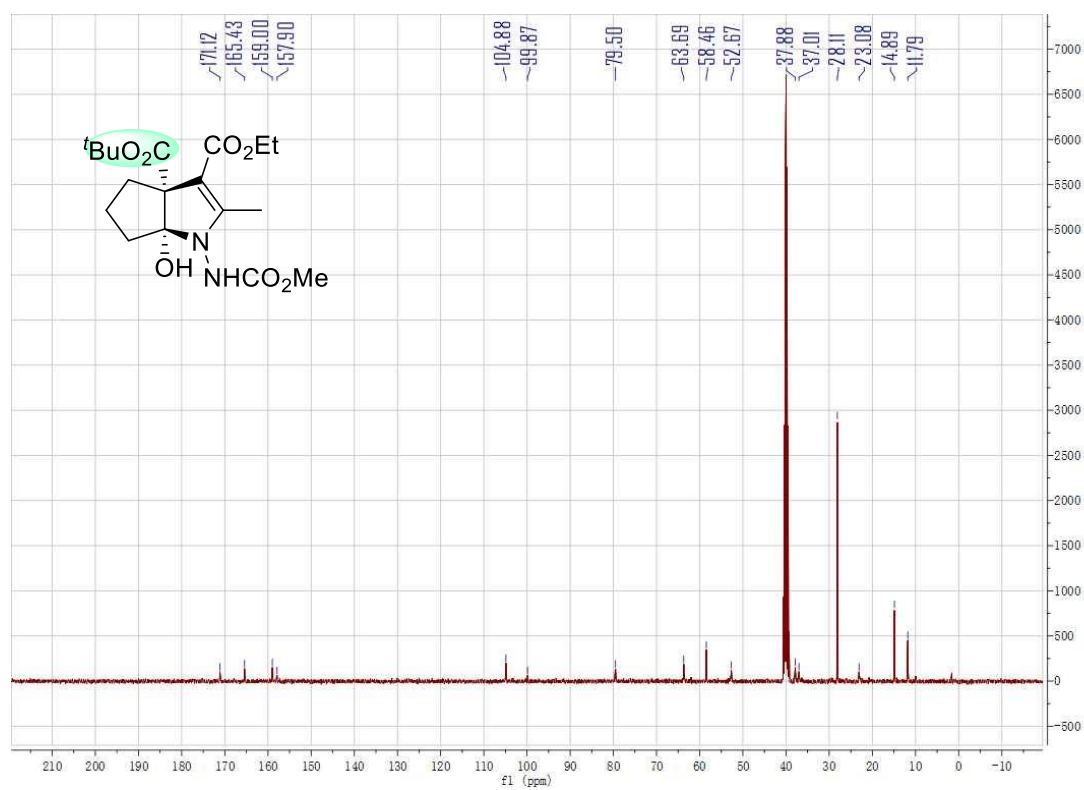
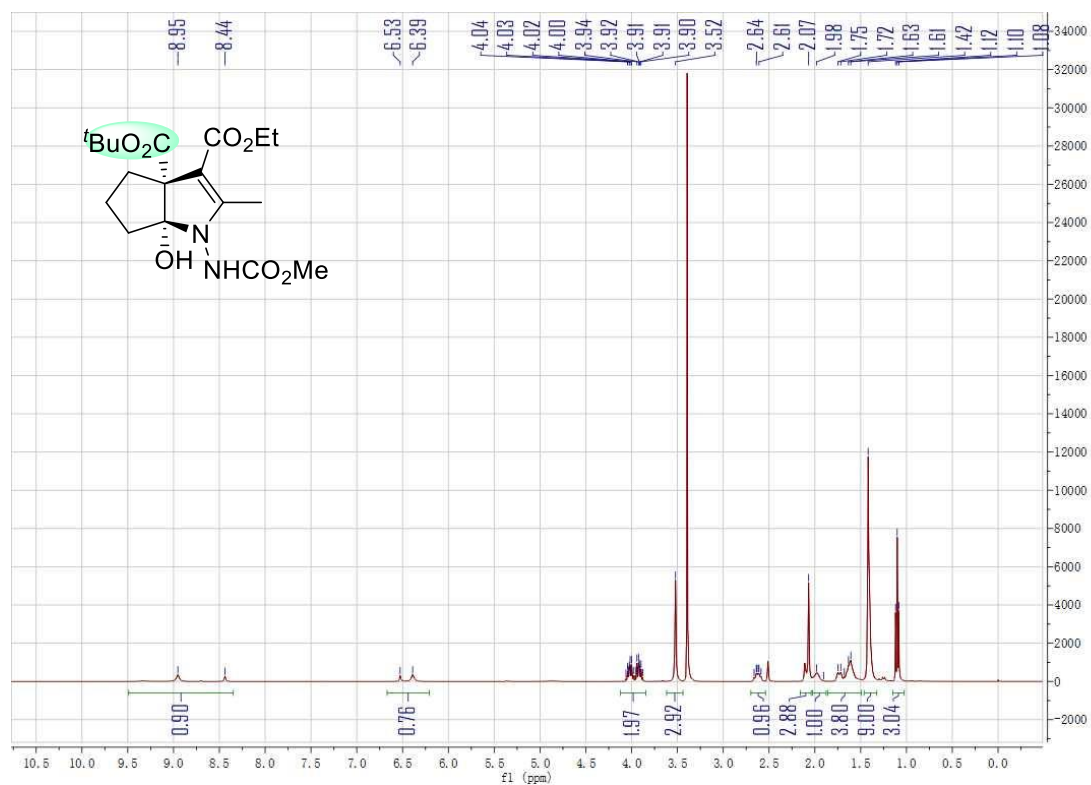


3s

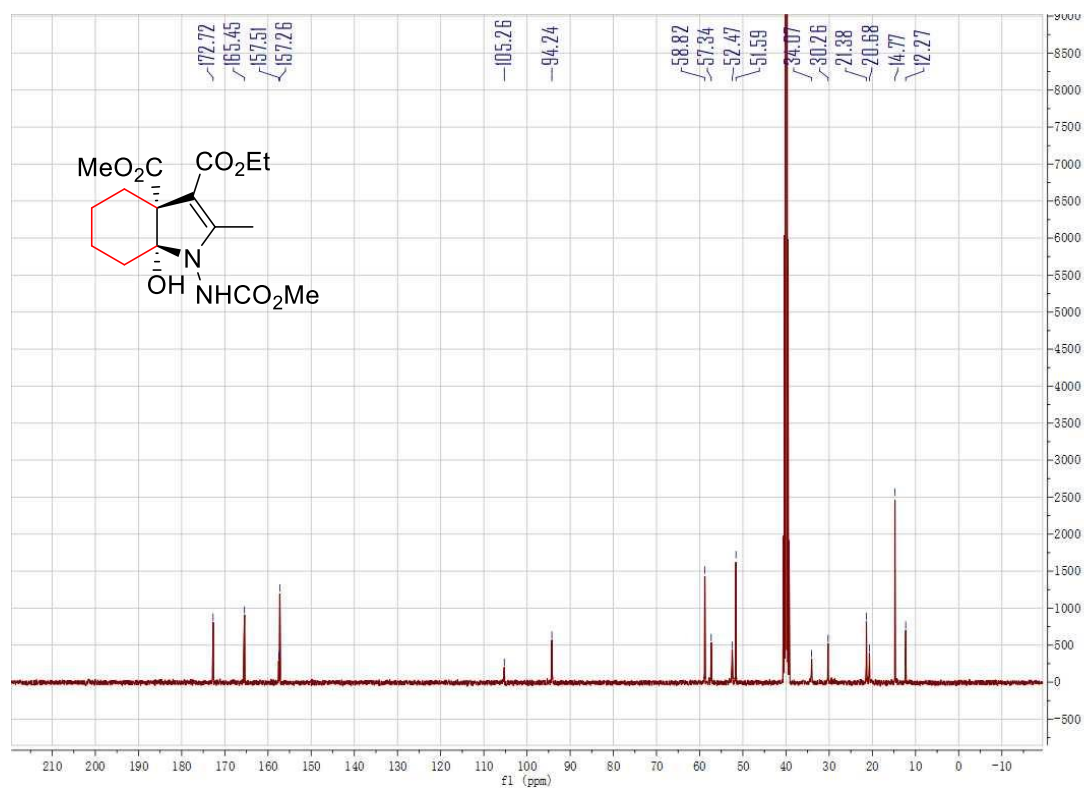
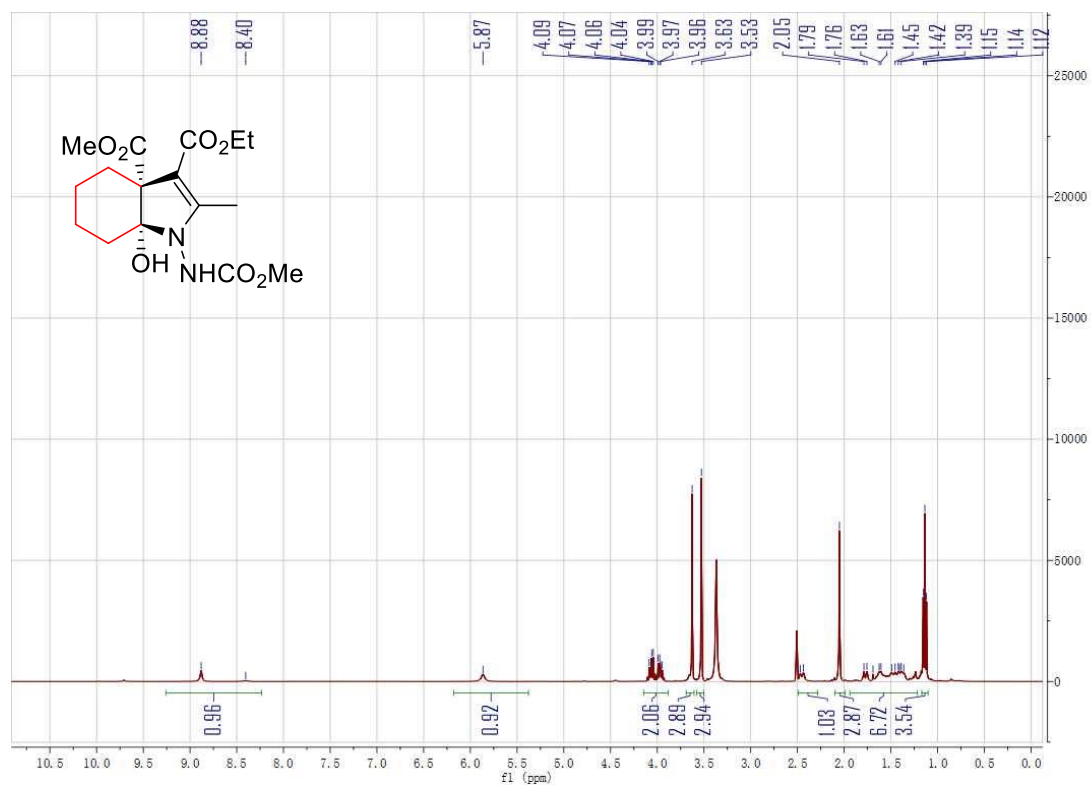




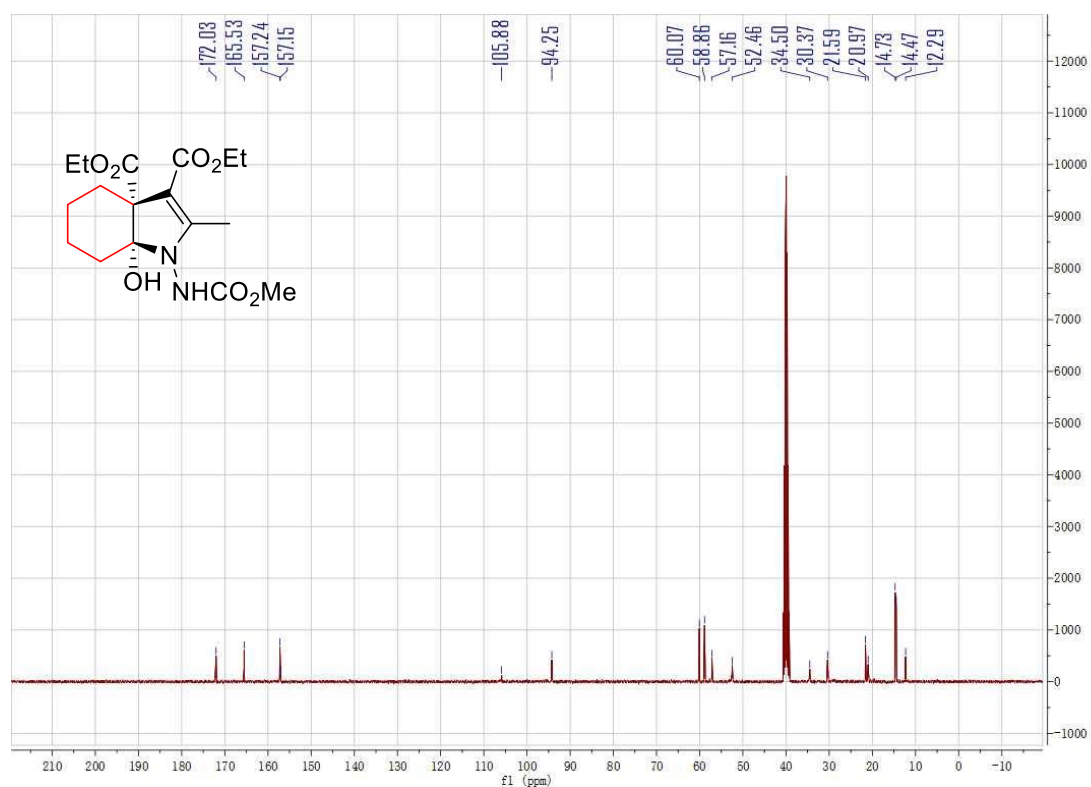
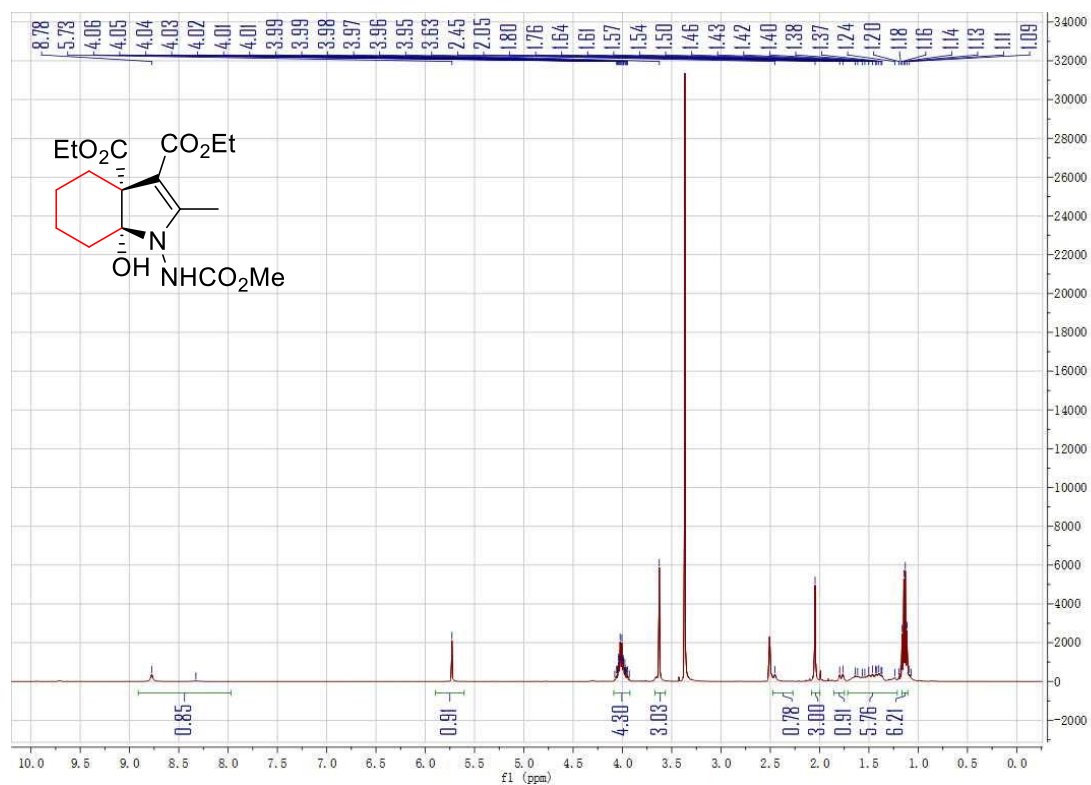
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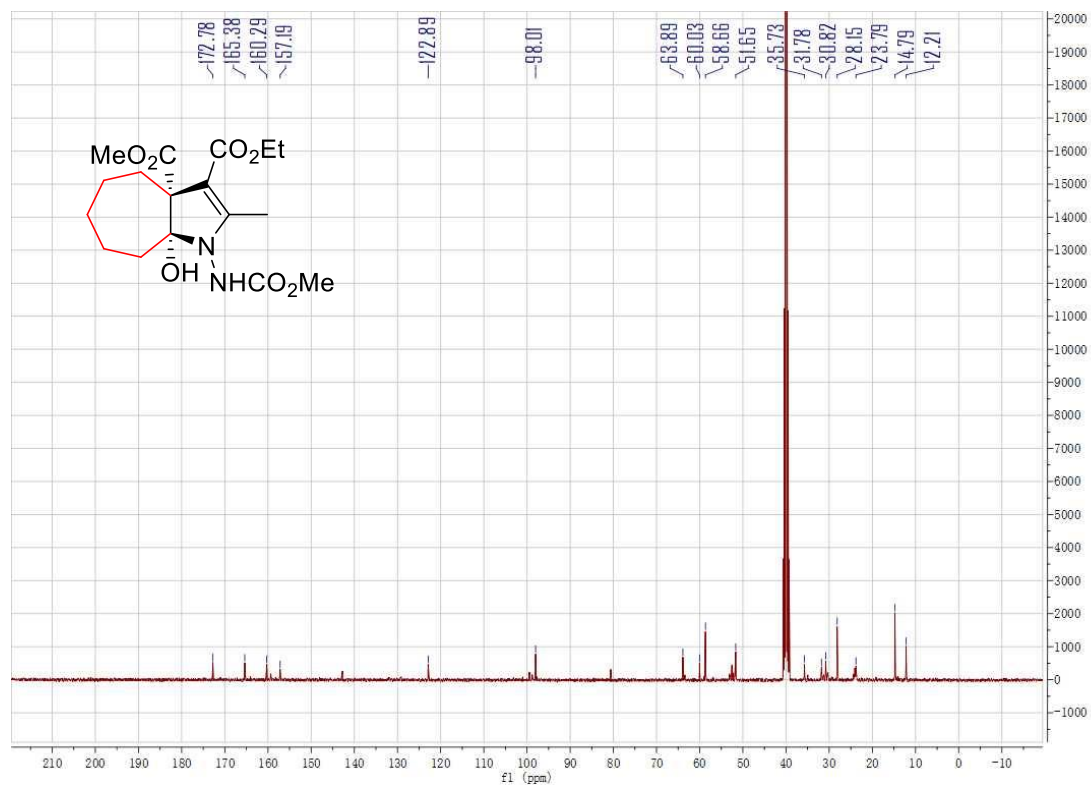
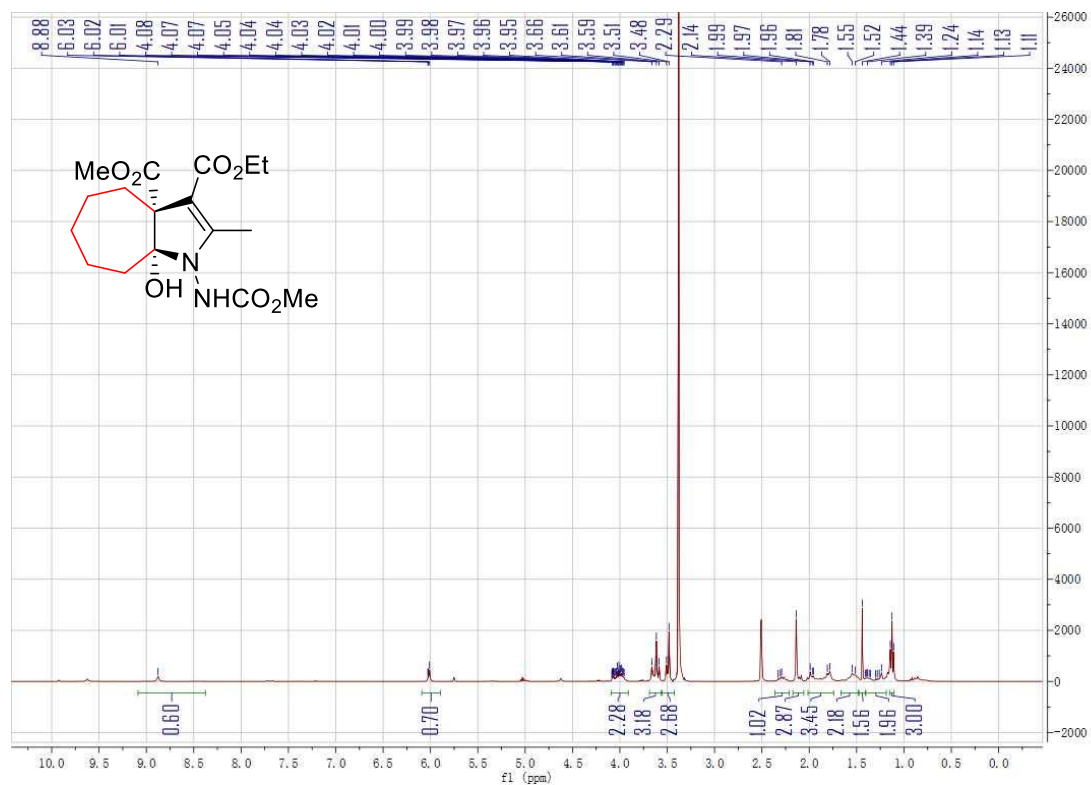
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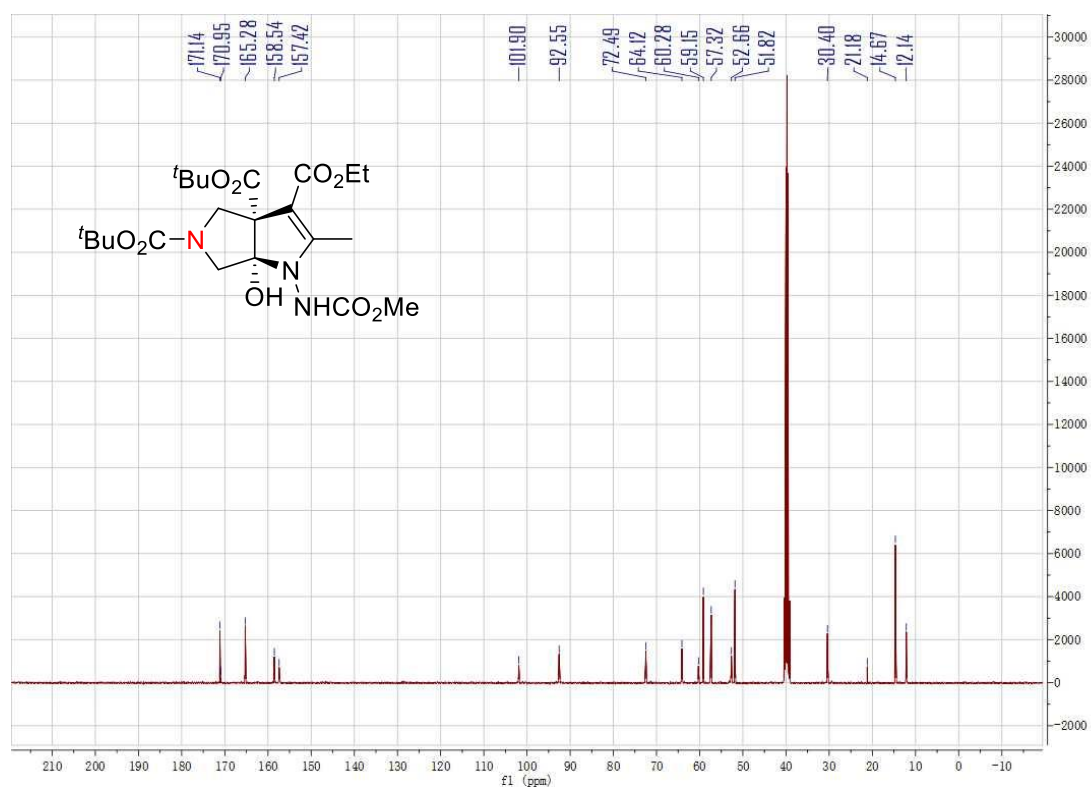
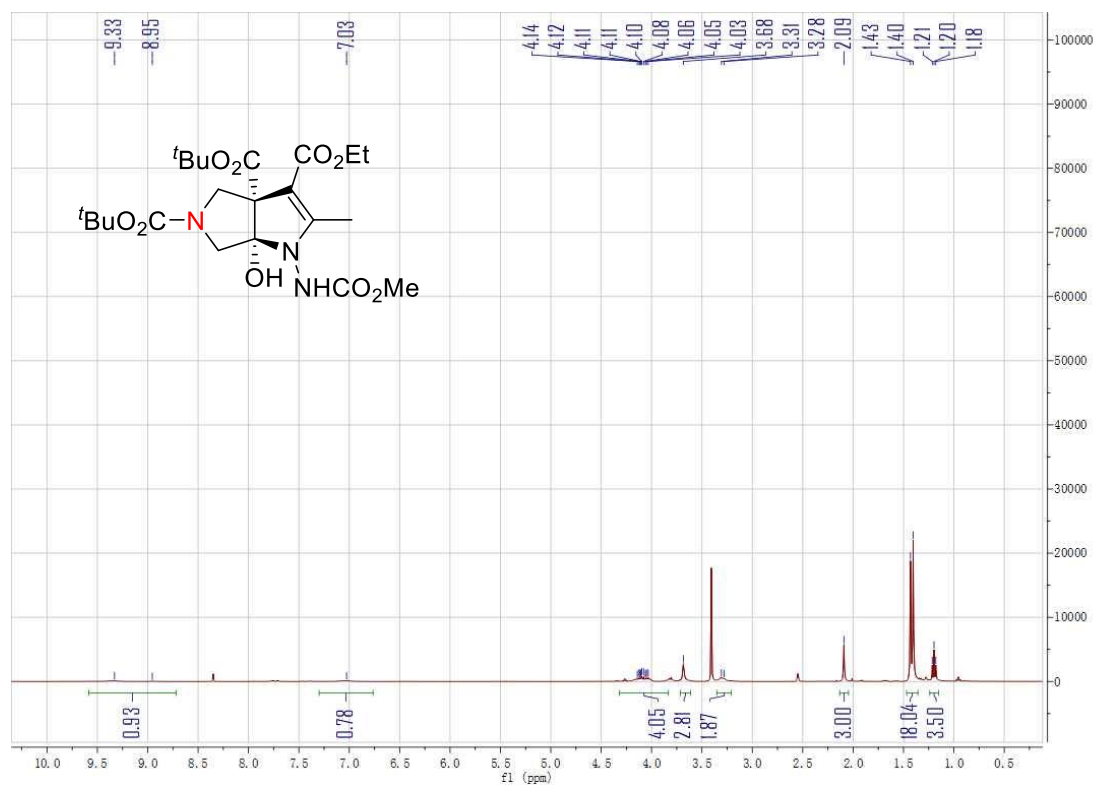
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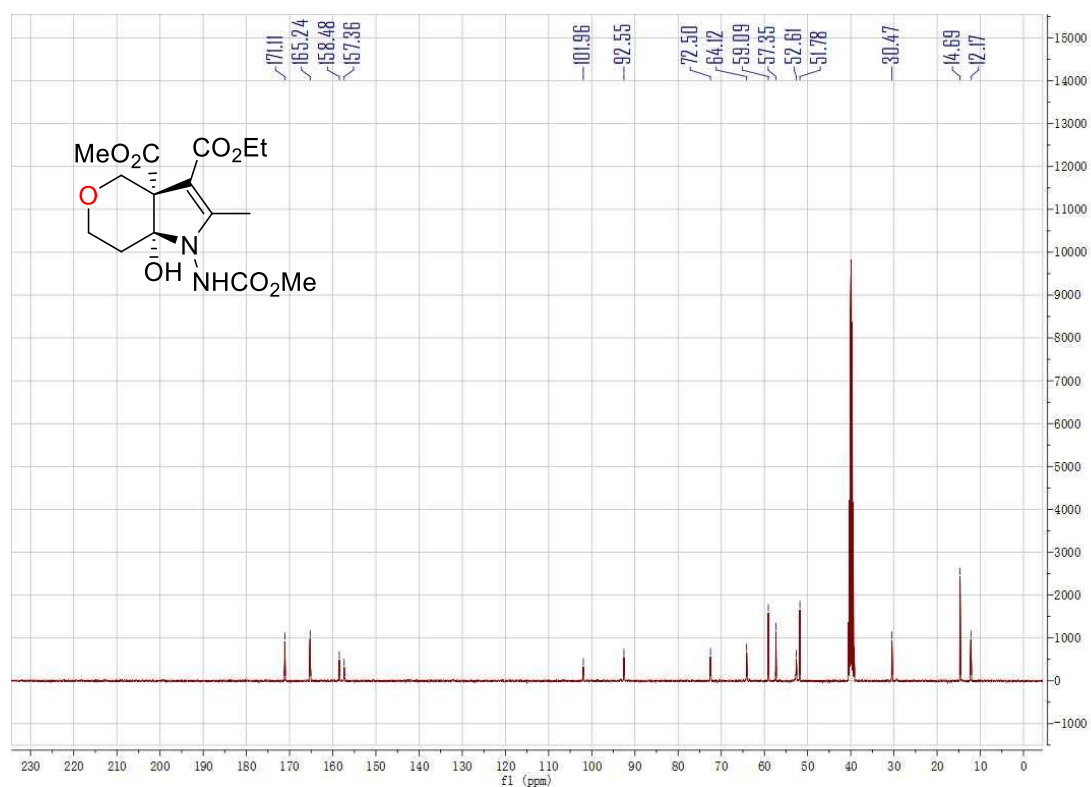
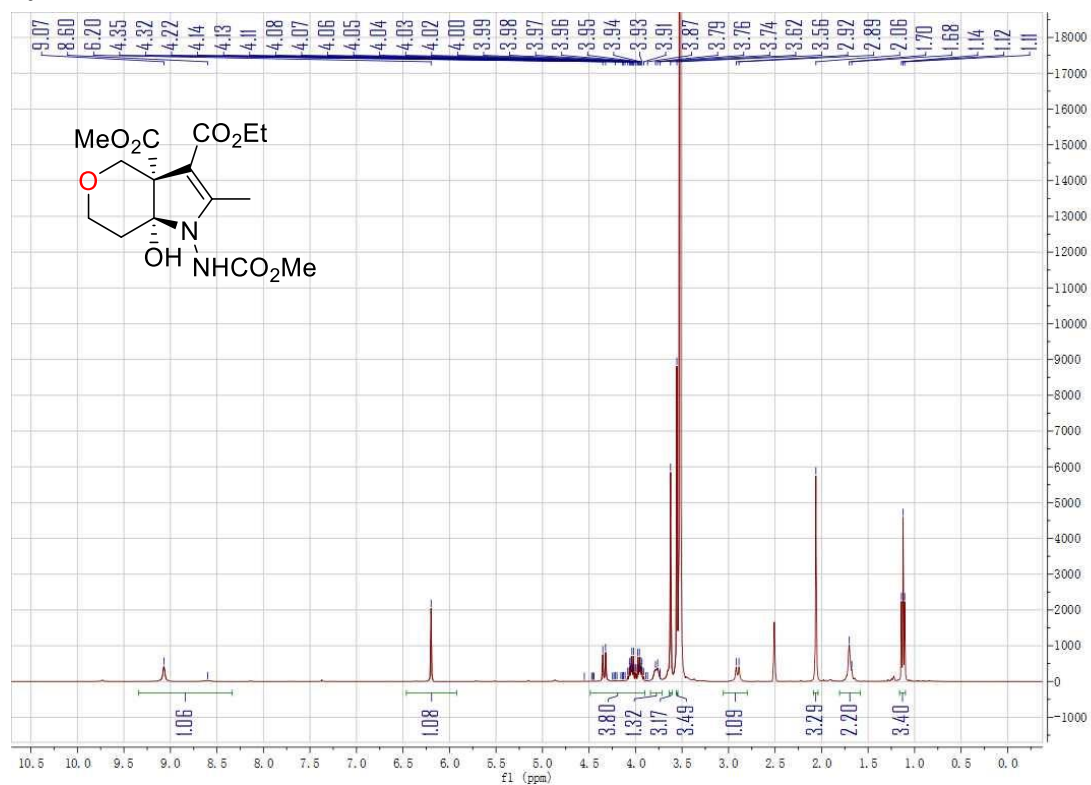
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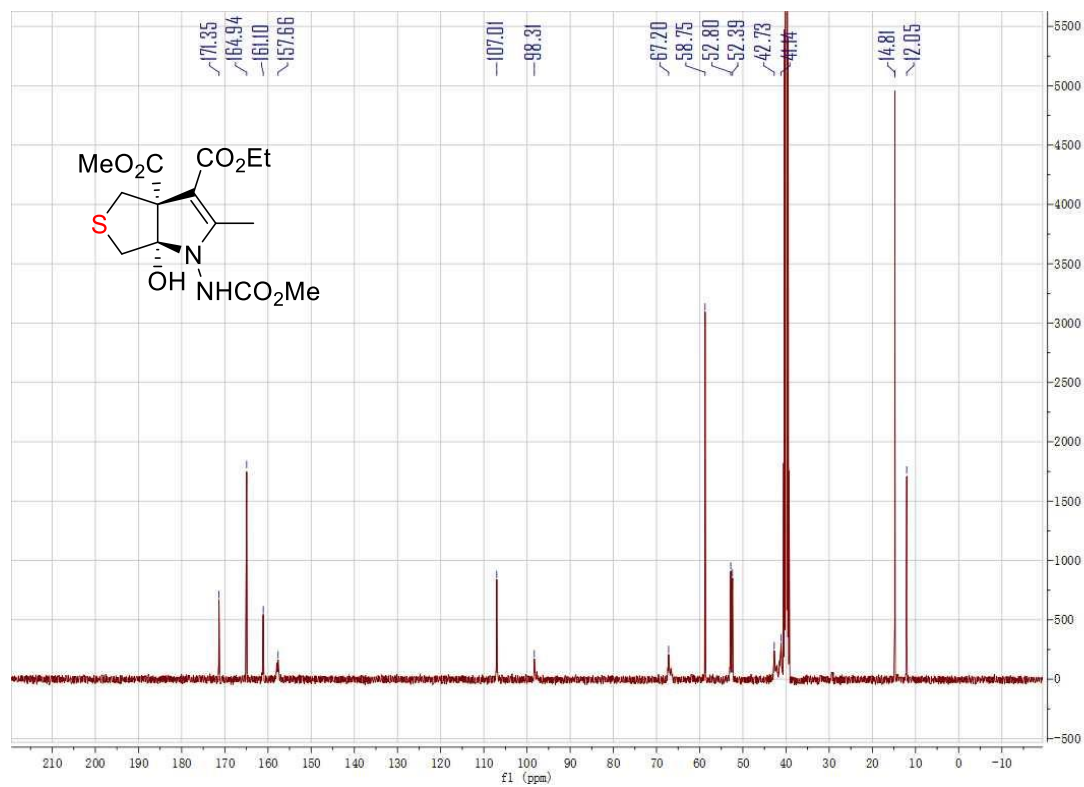
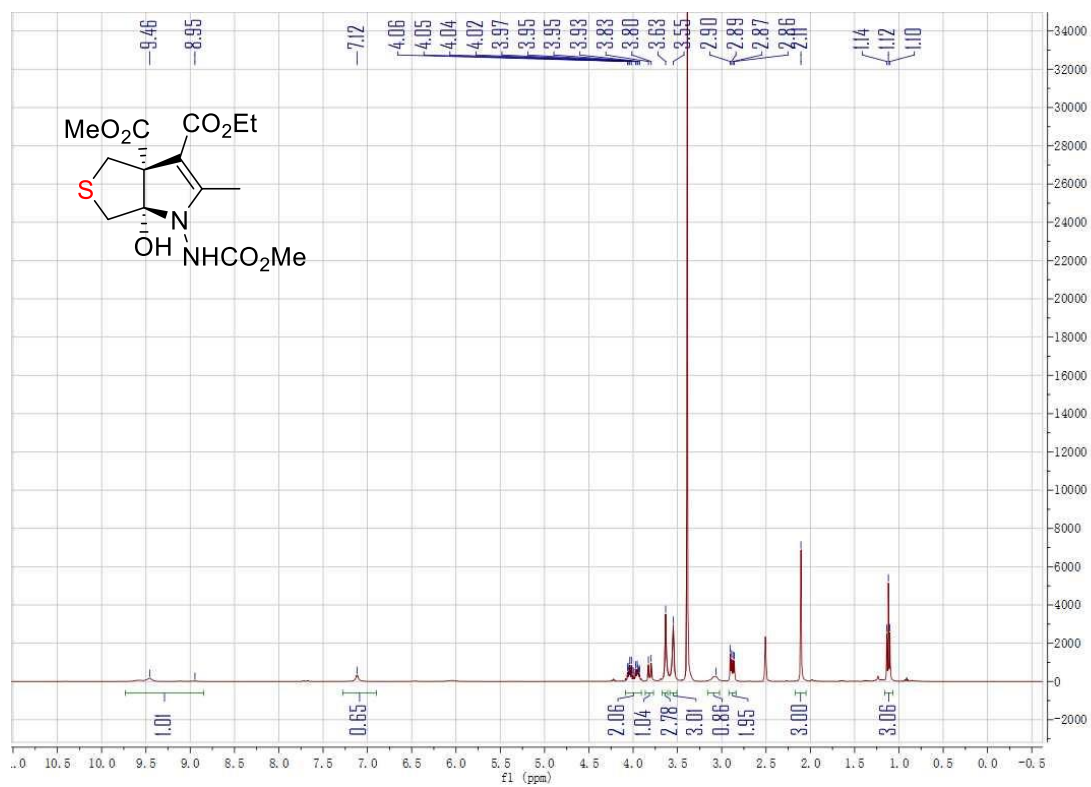
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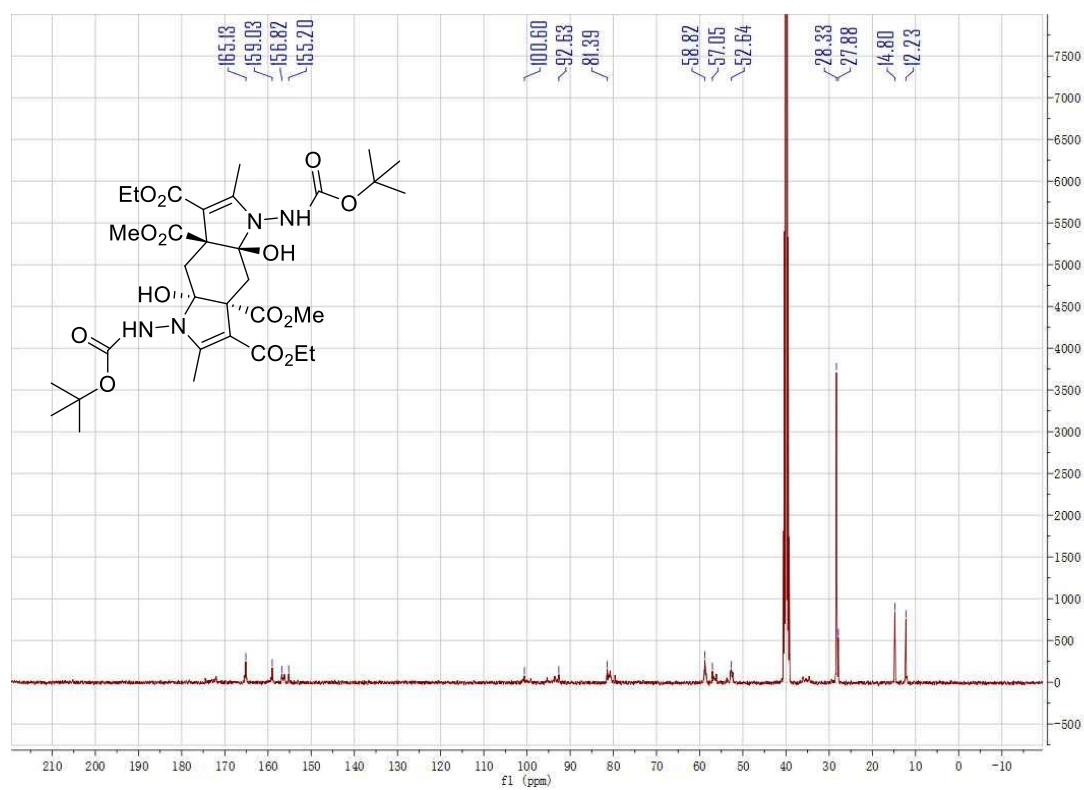
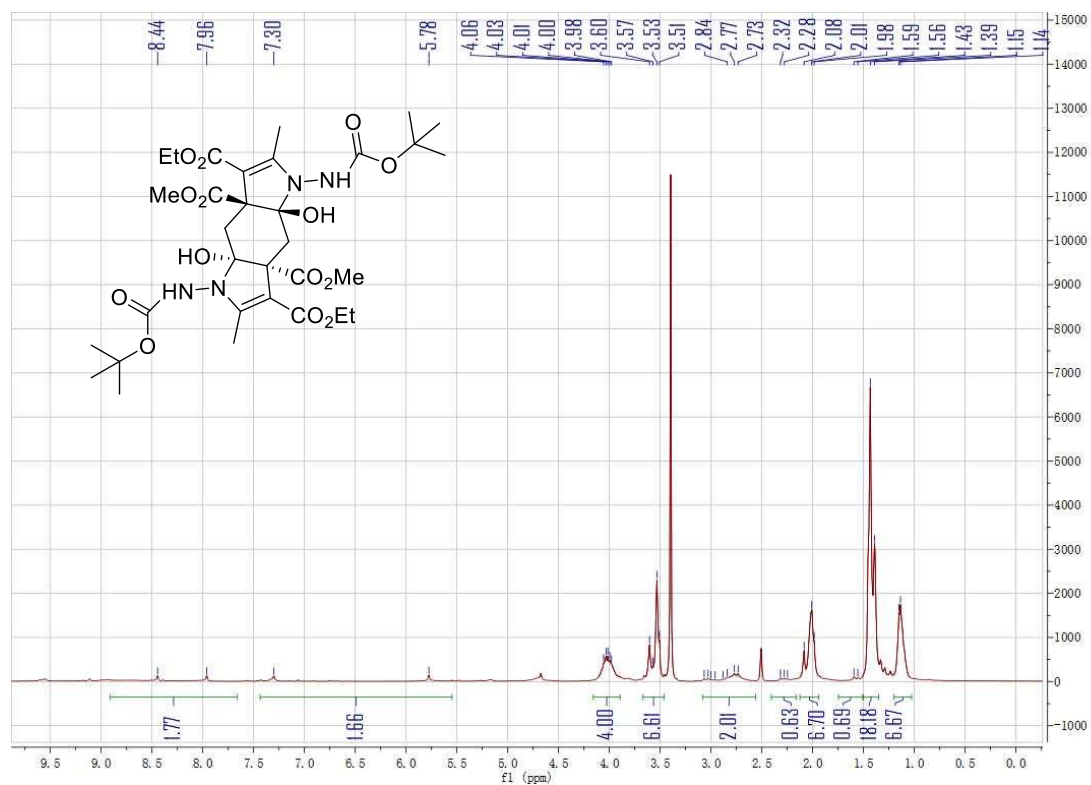
3y



3z

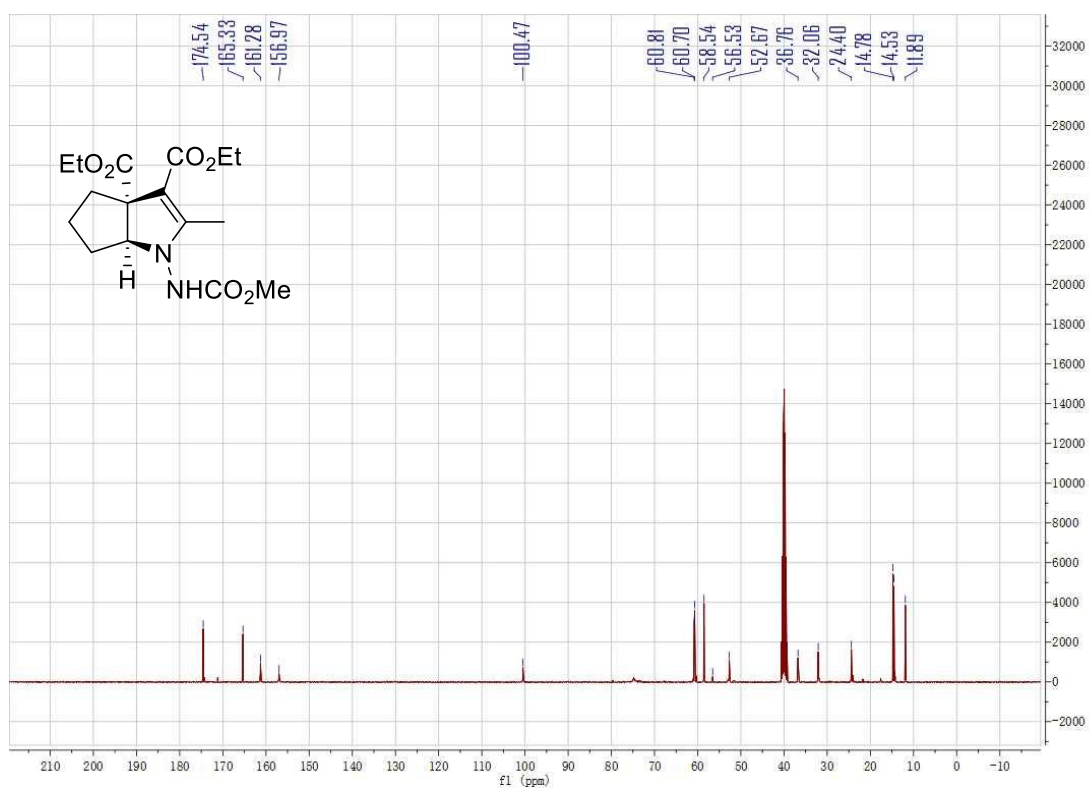
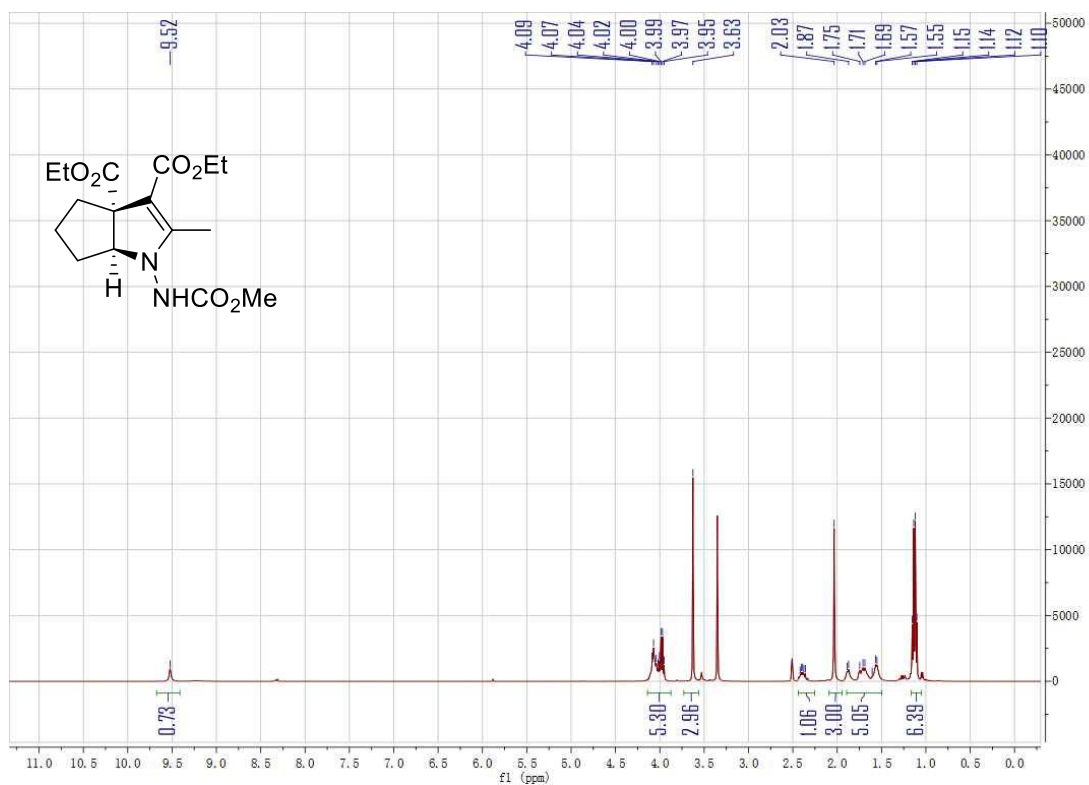


(*meso*)-**3a'** (dr = 9:1)

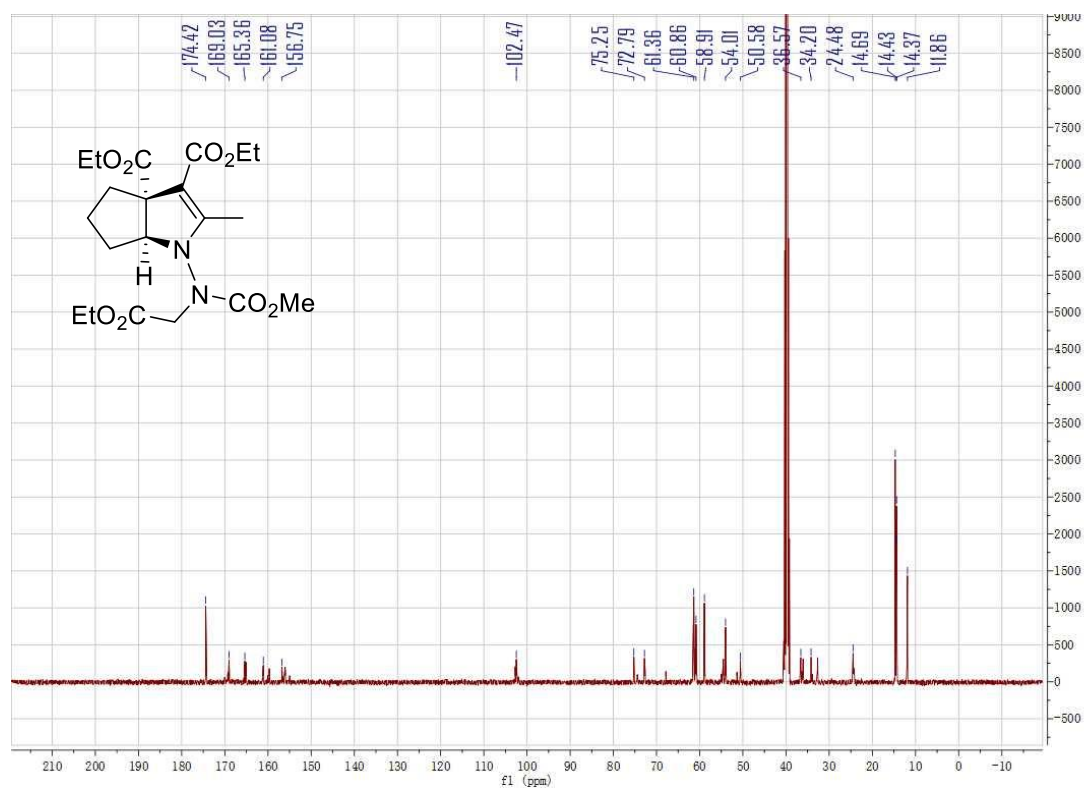
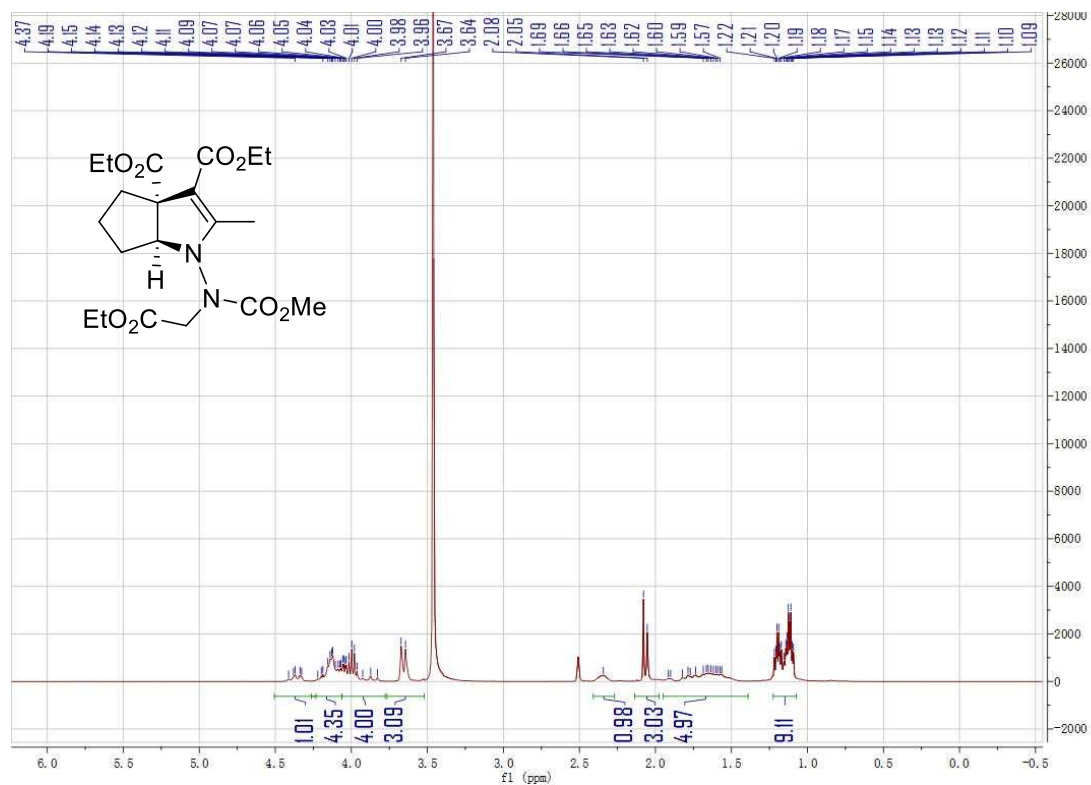




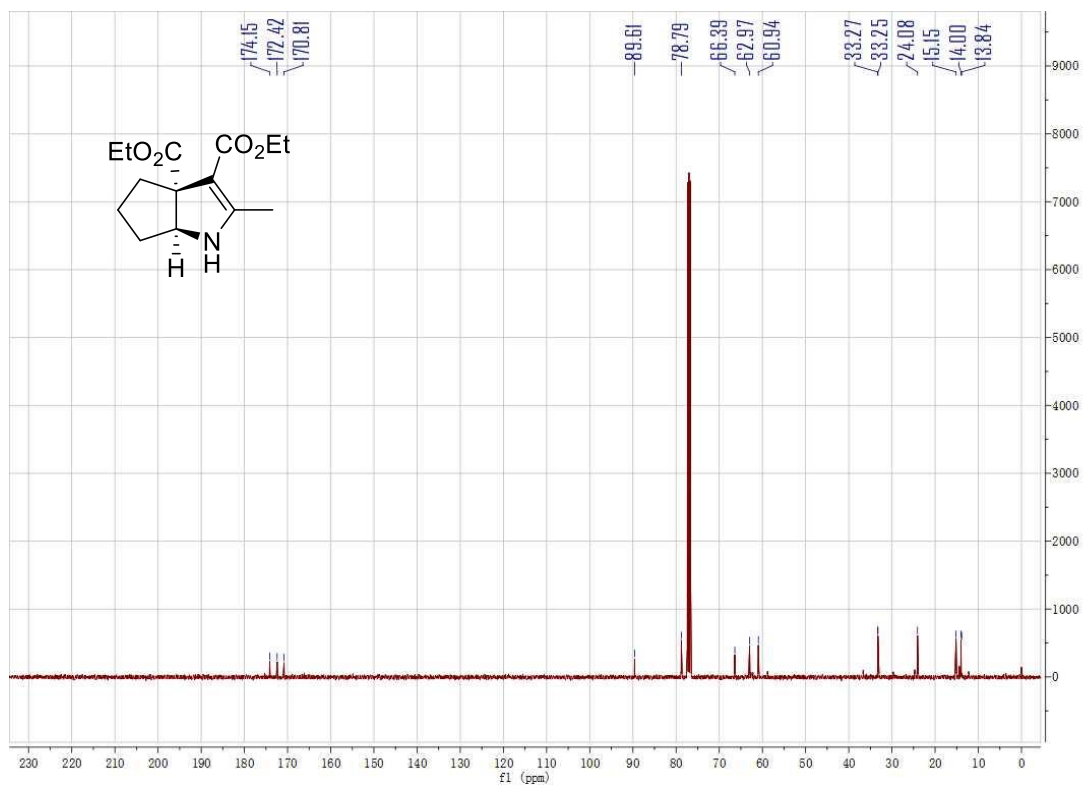
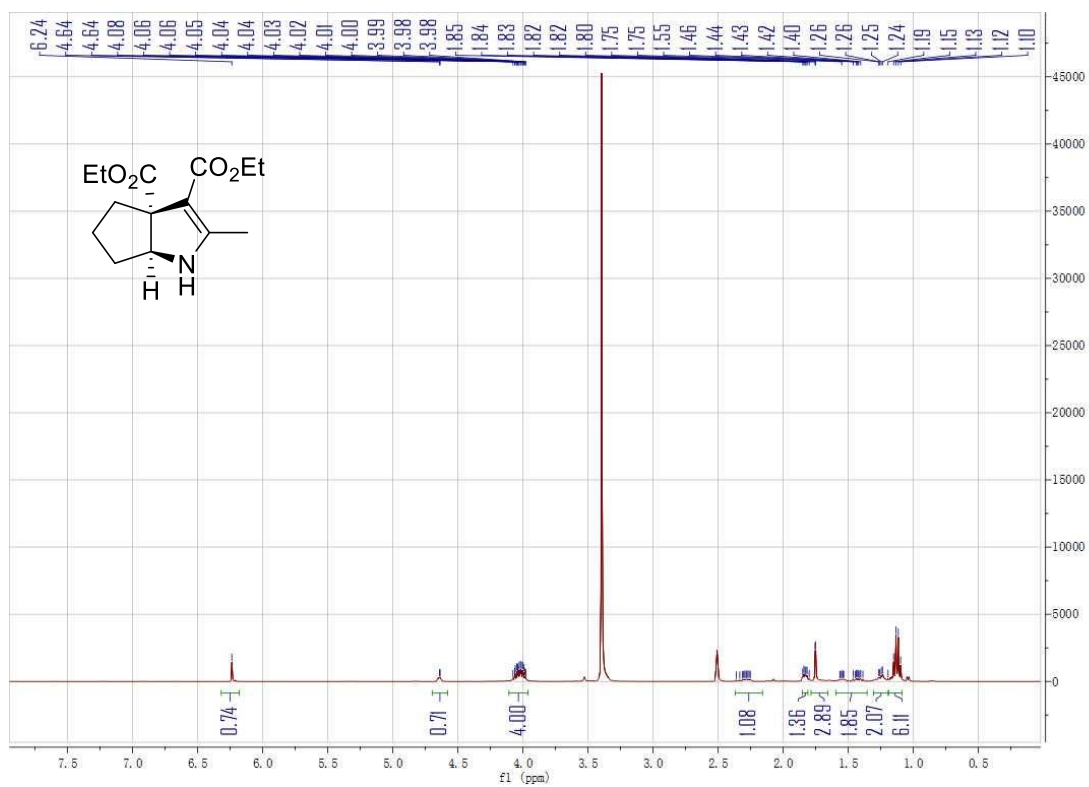
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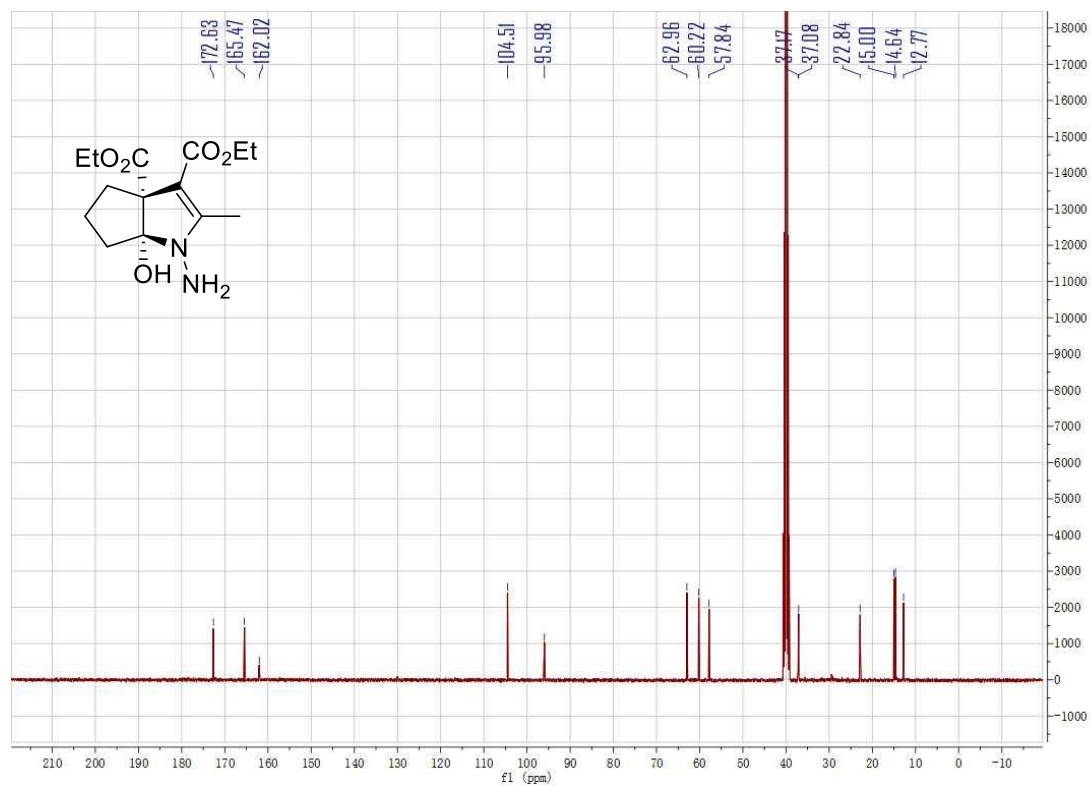
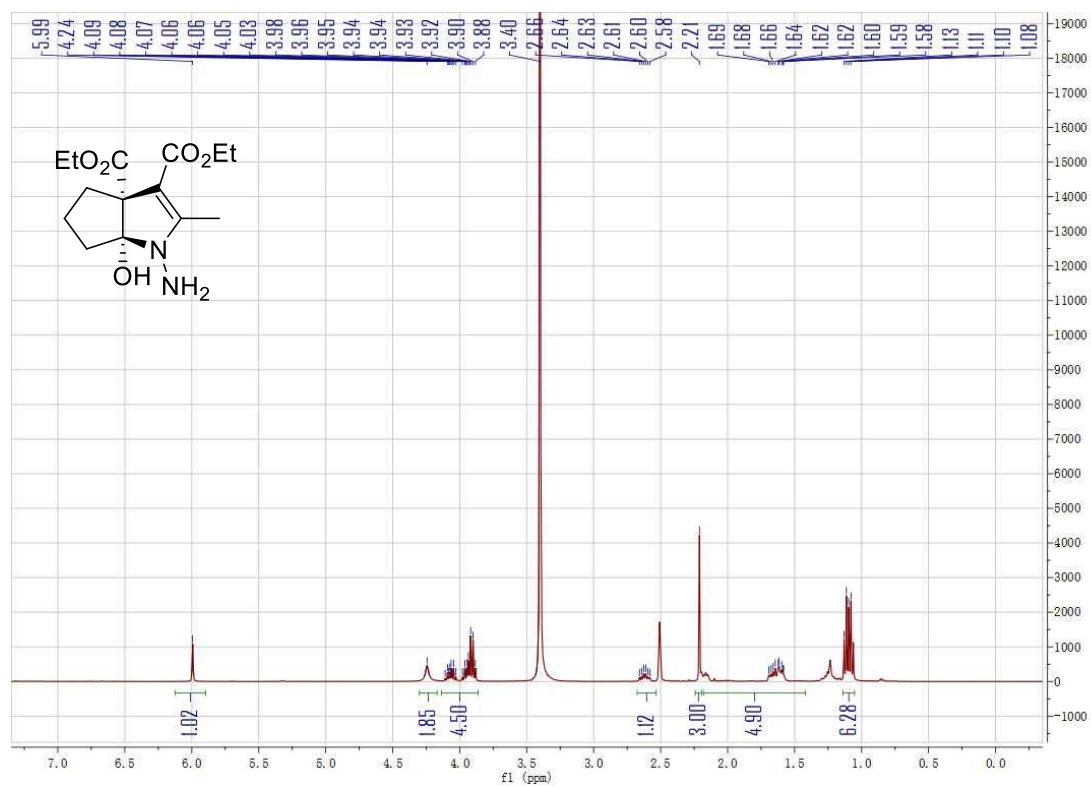
5 (dr = 2:3)



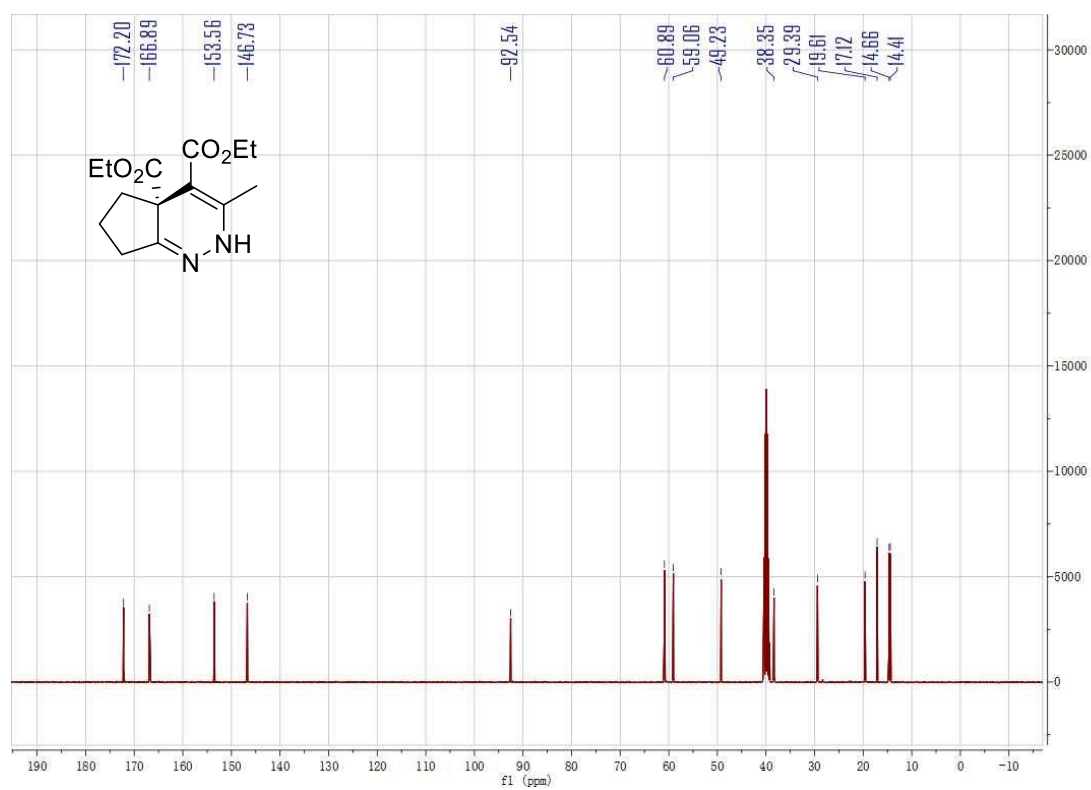
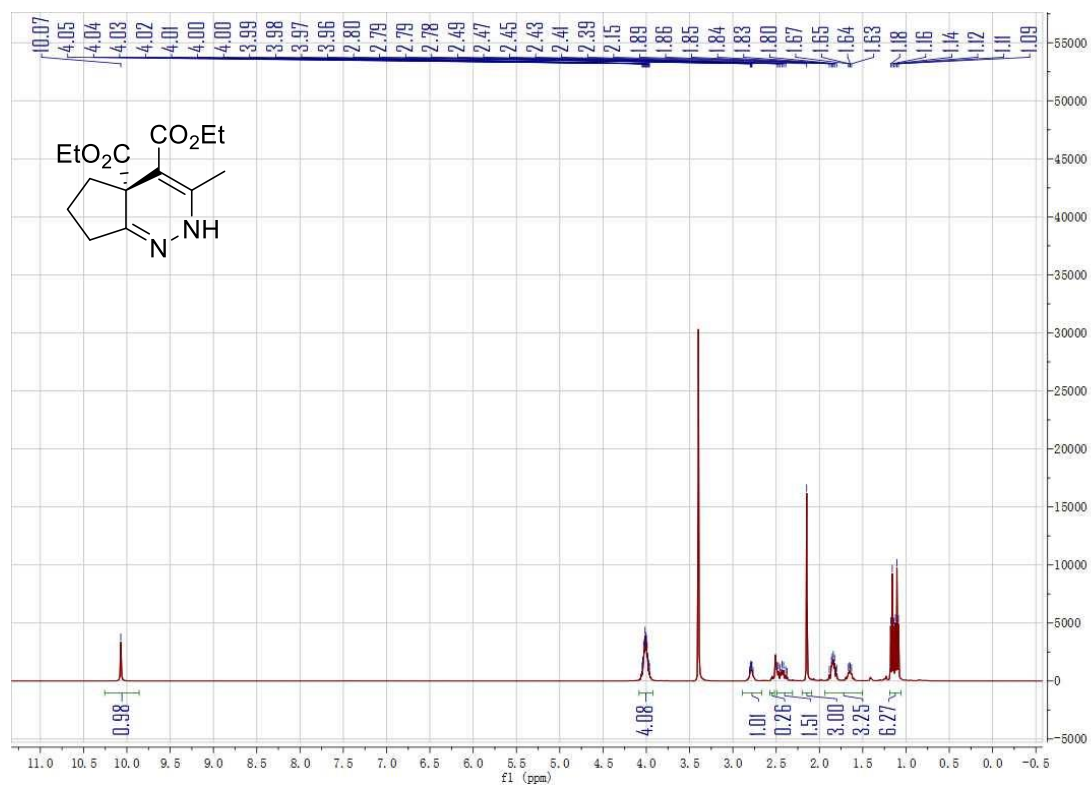
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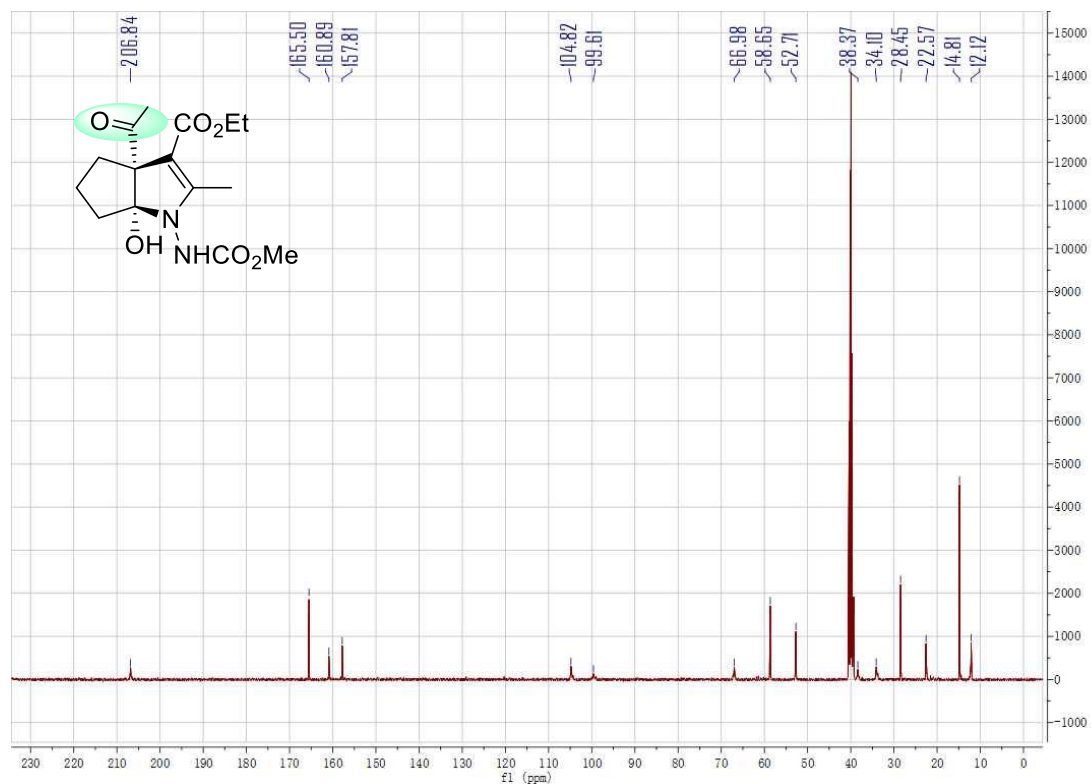
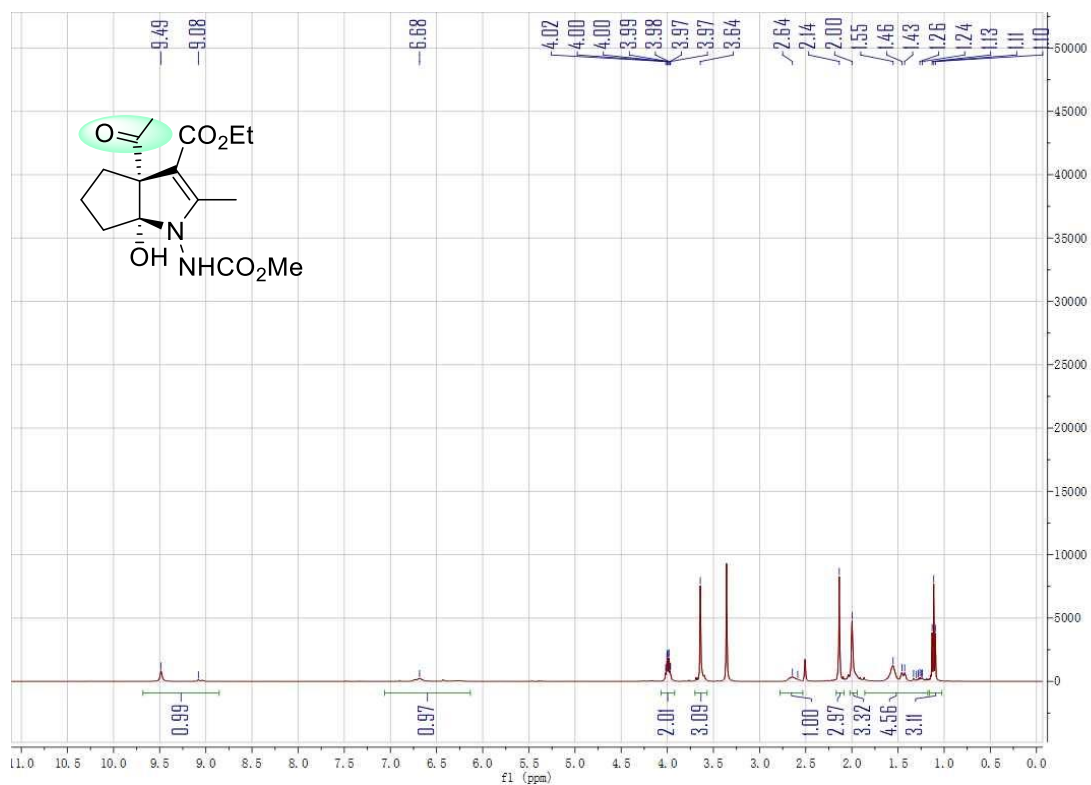
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8

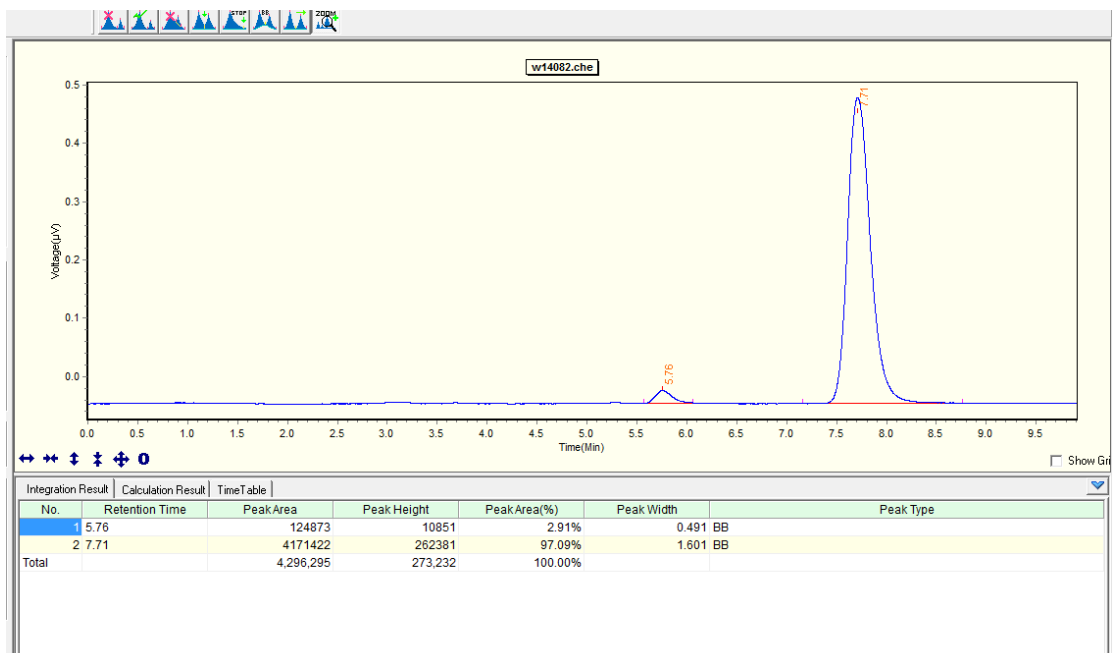
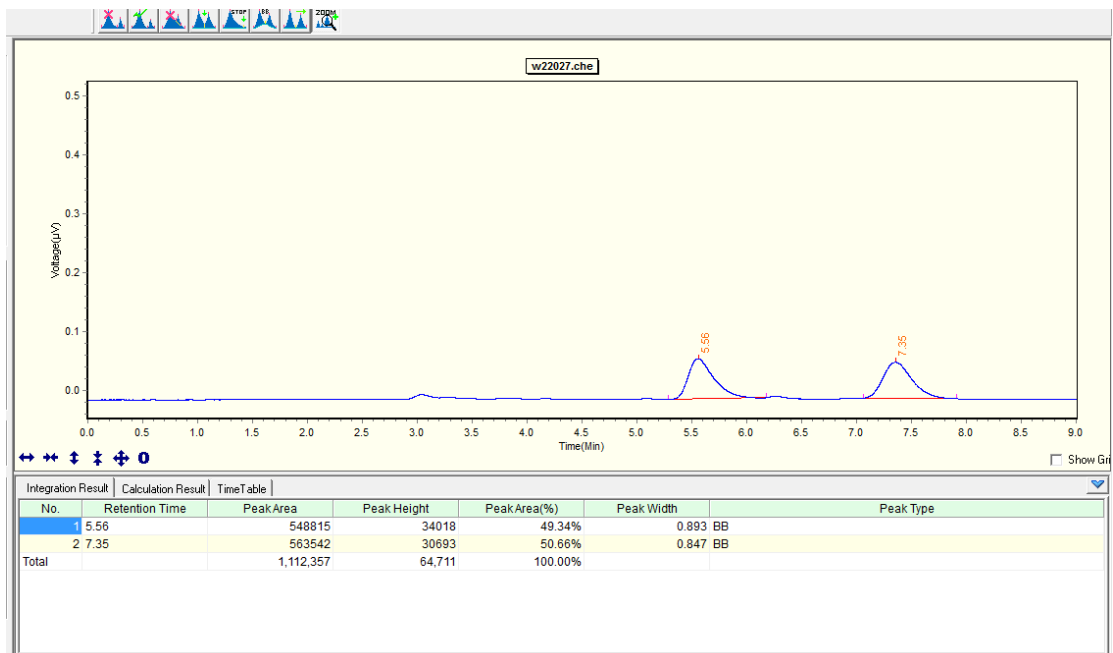
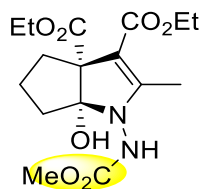


S1

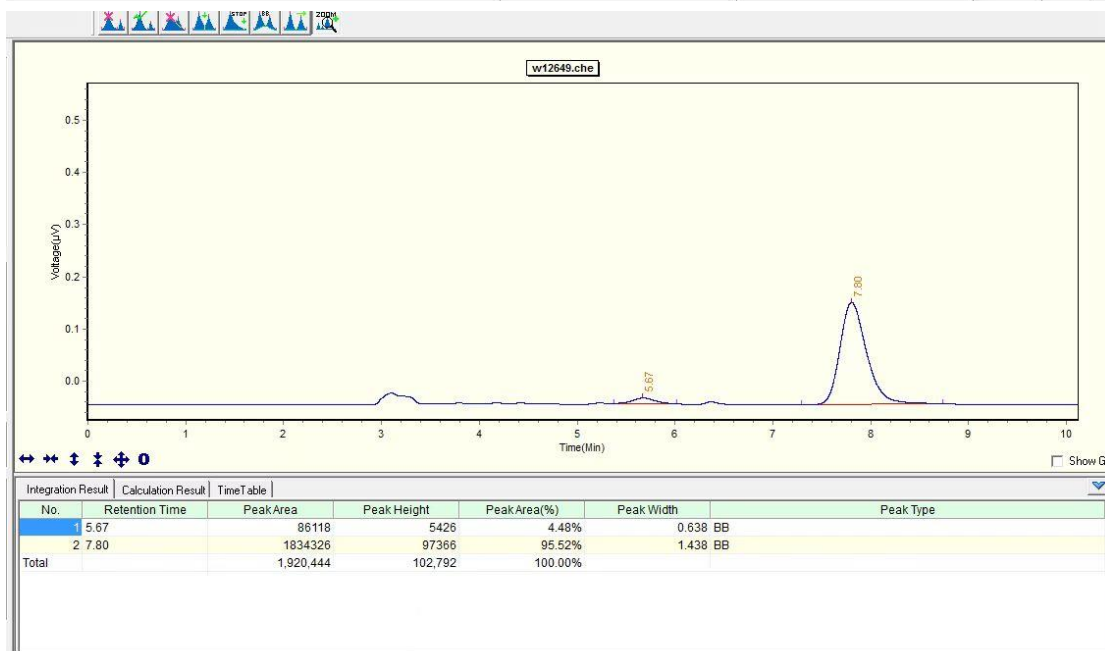
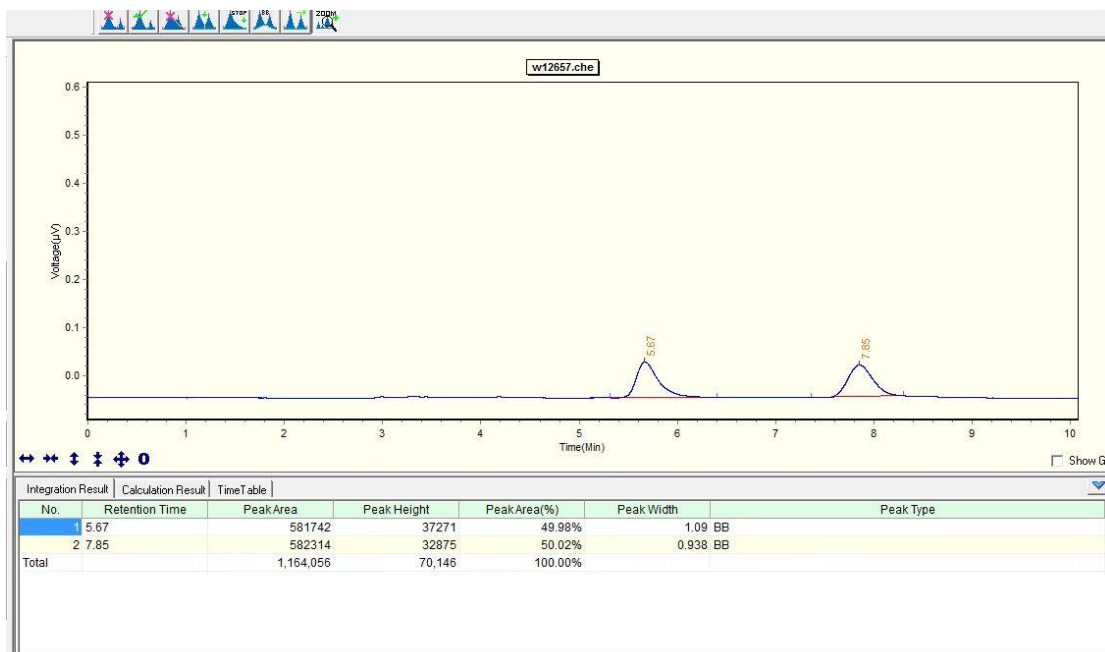
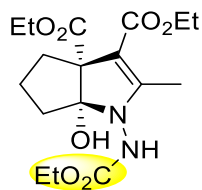


## 6. HPLC Spectra

3a

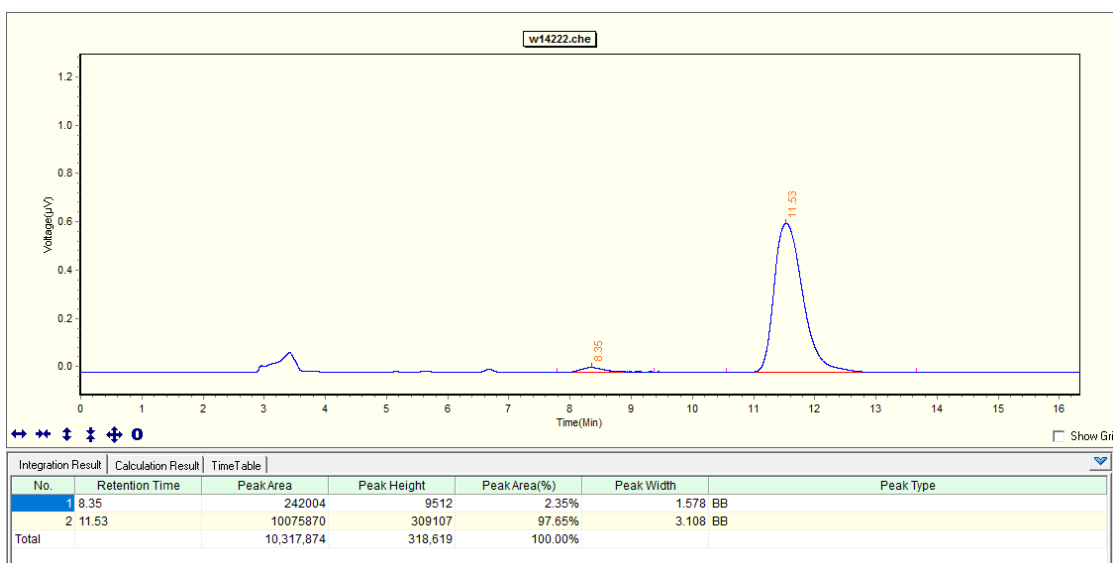
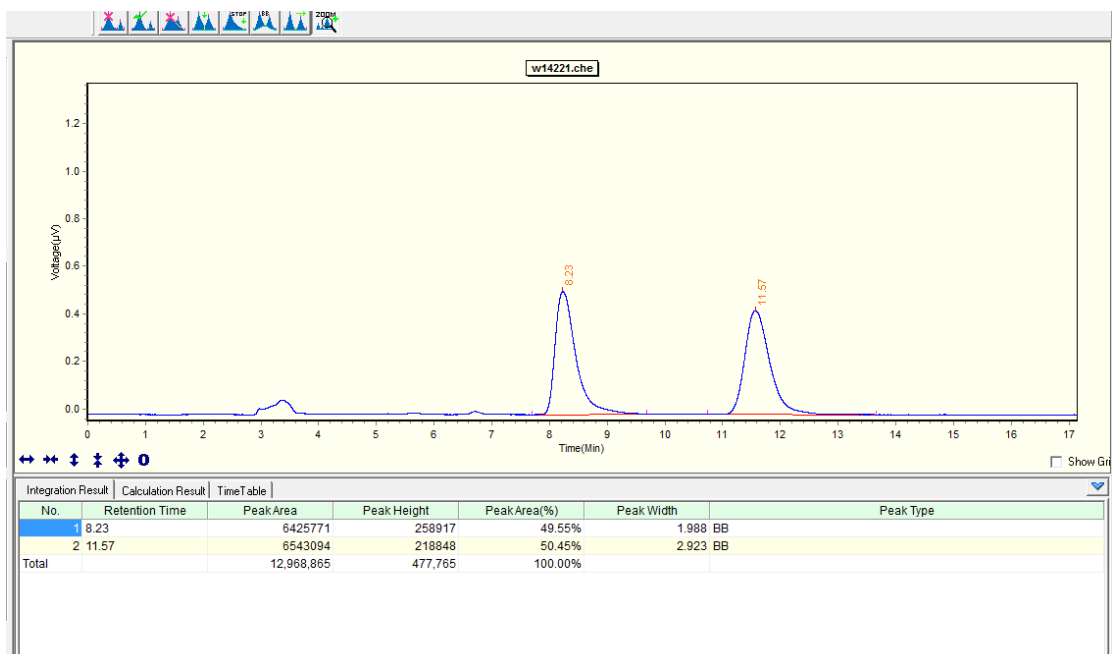
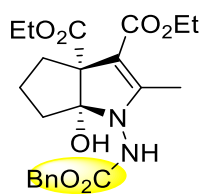


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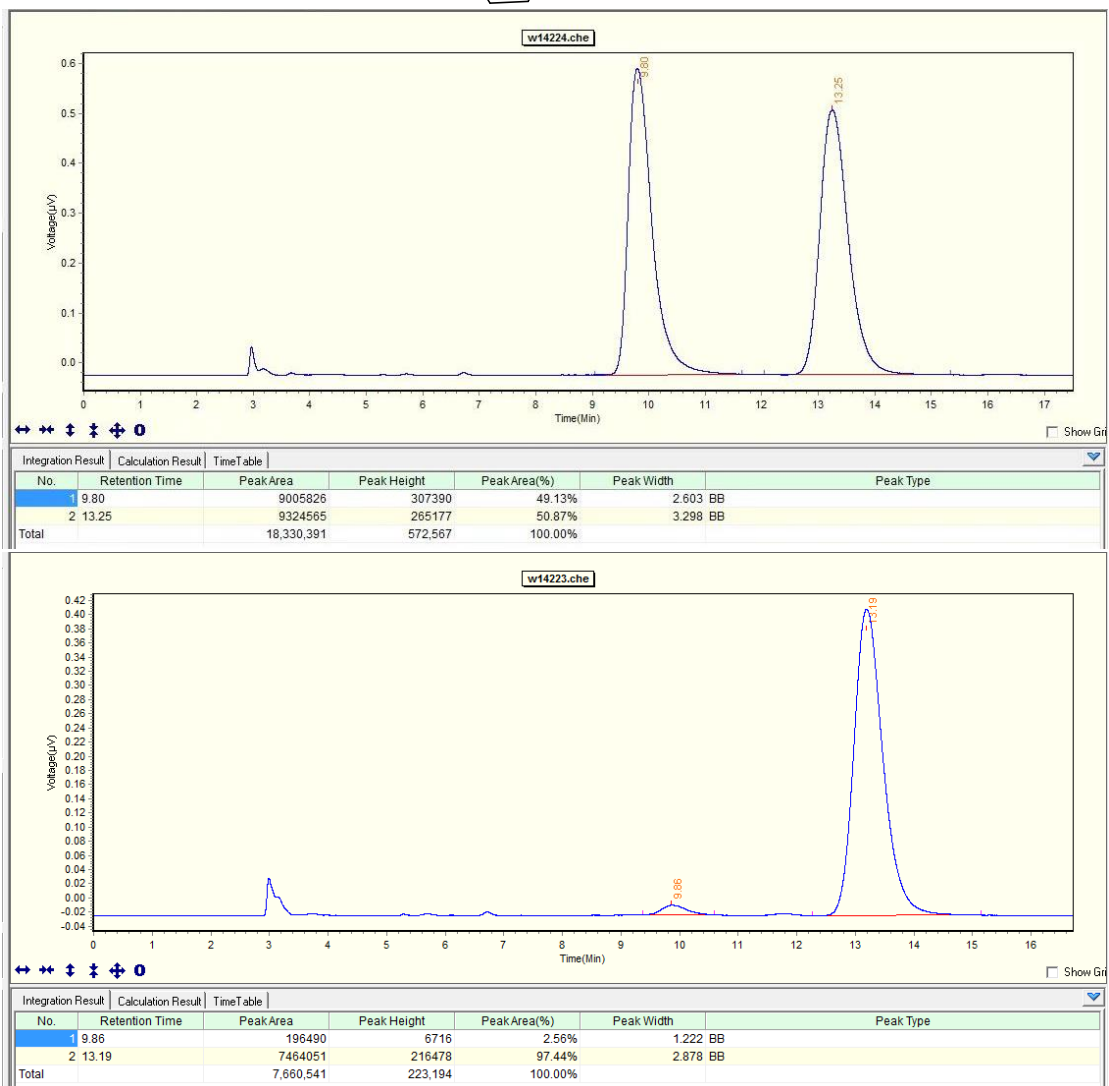
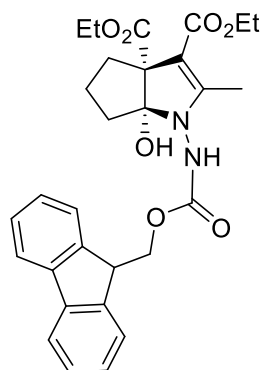




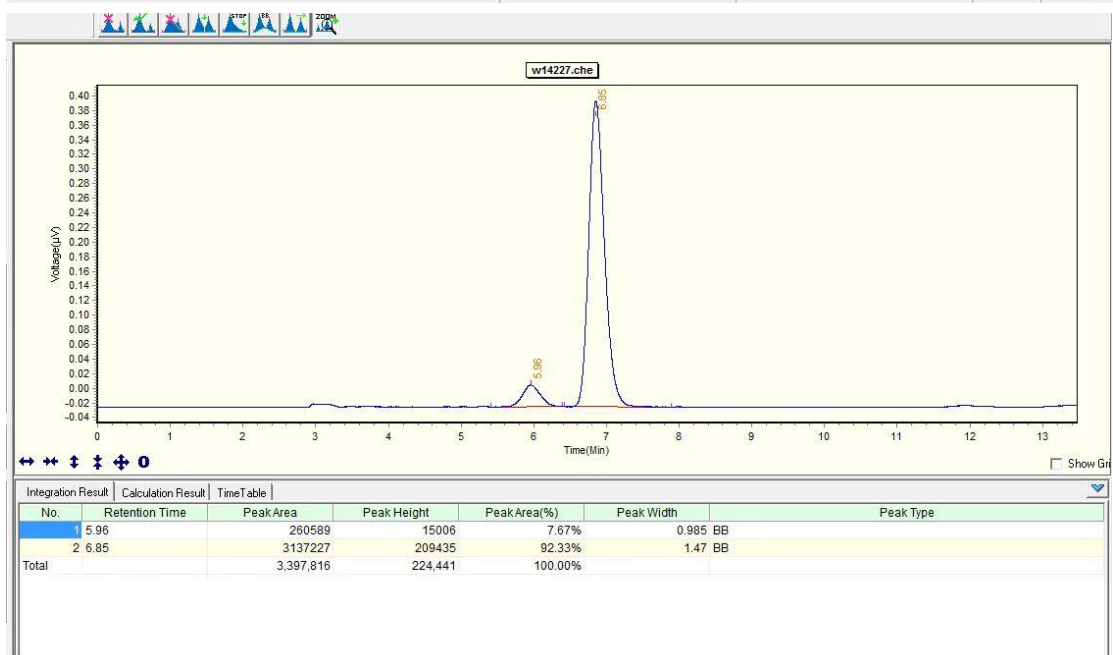
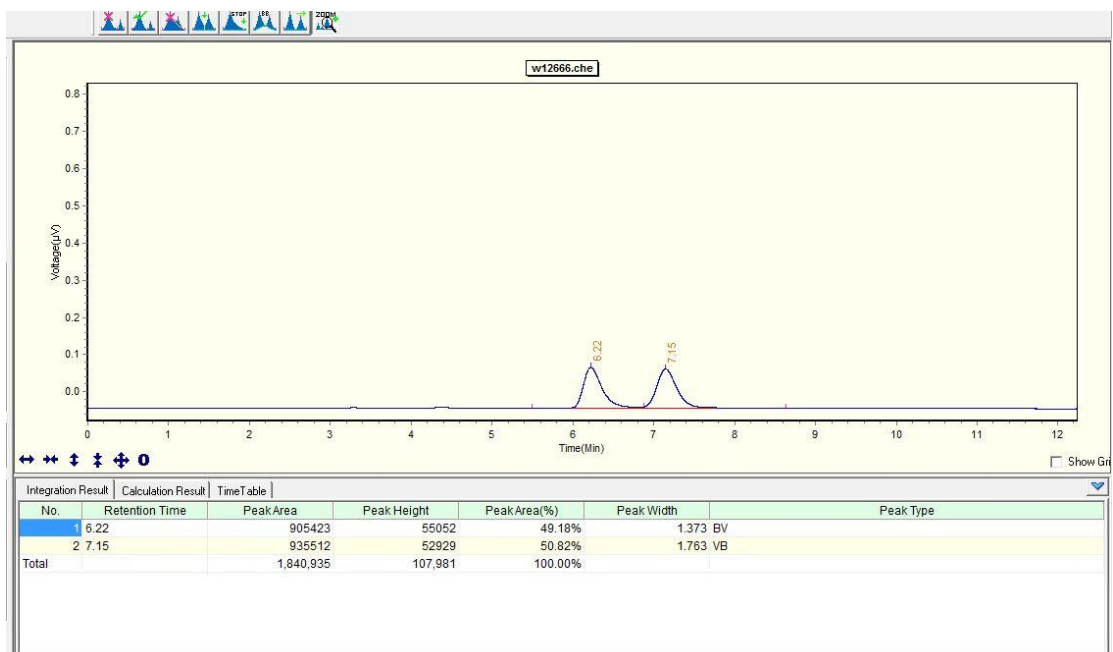
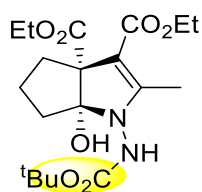
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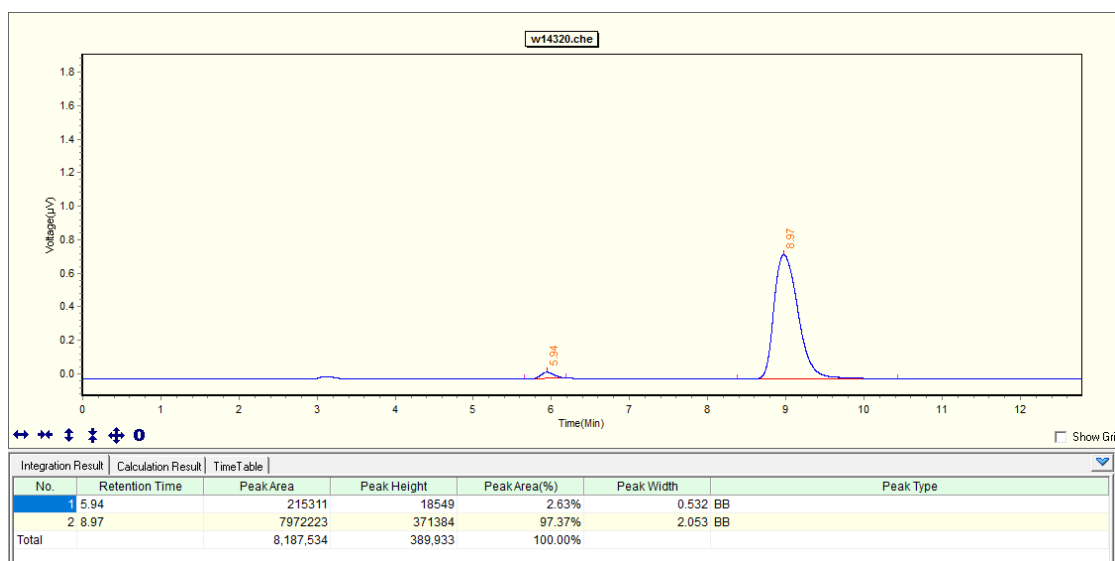
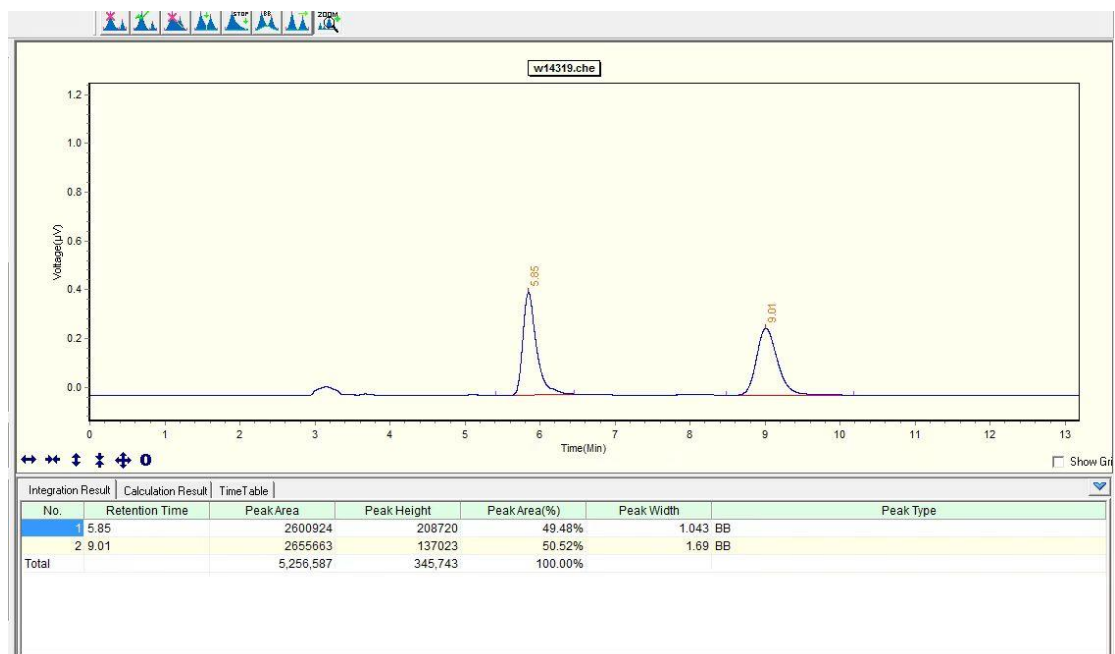
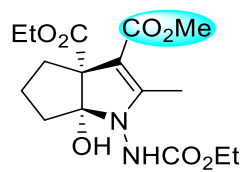
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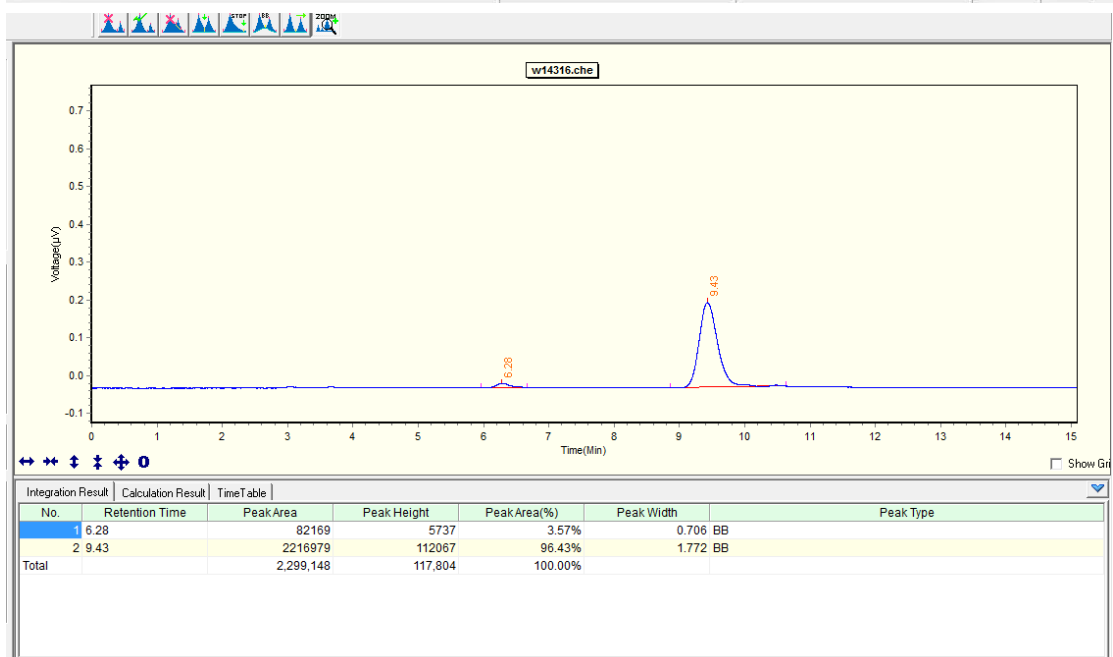
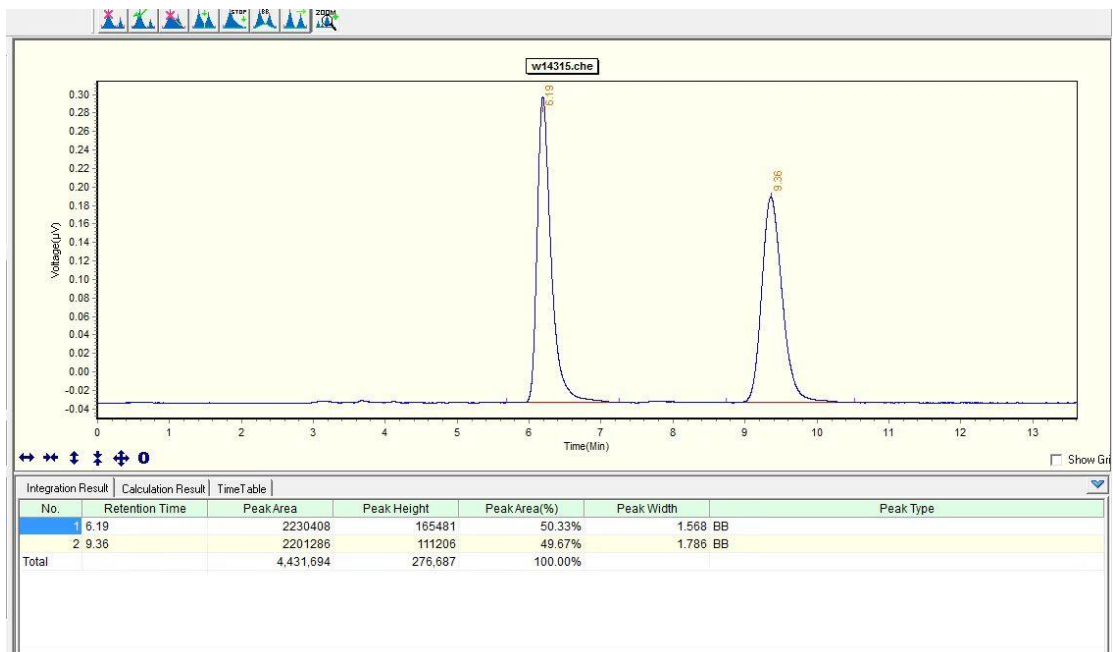
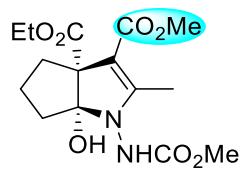
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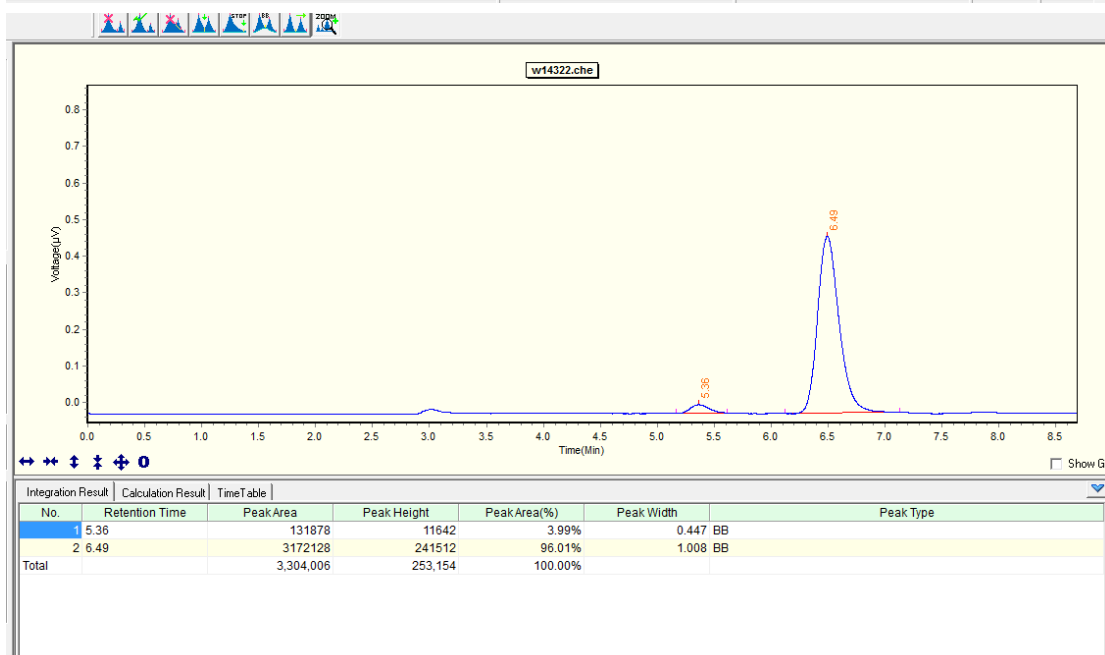
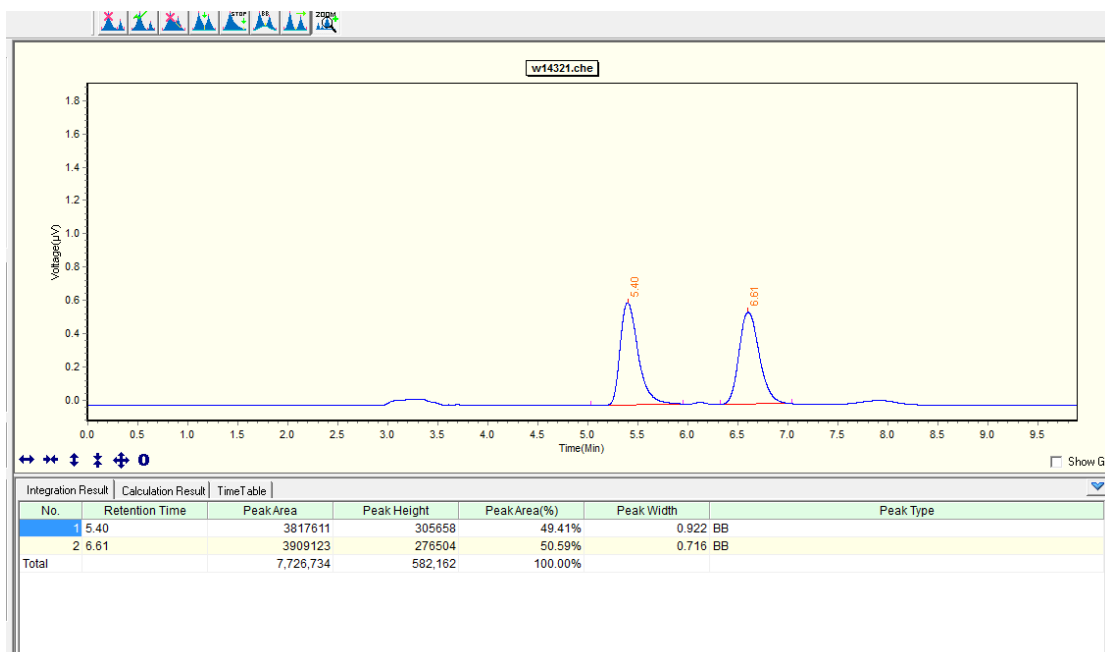
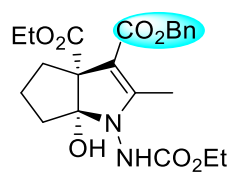
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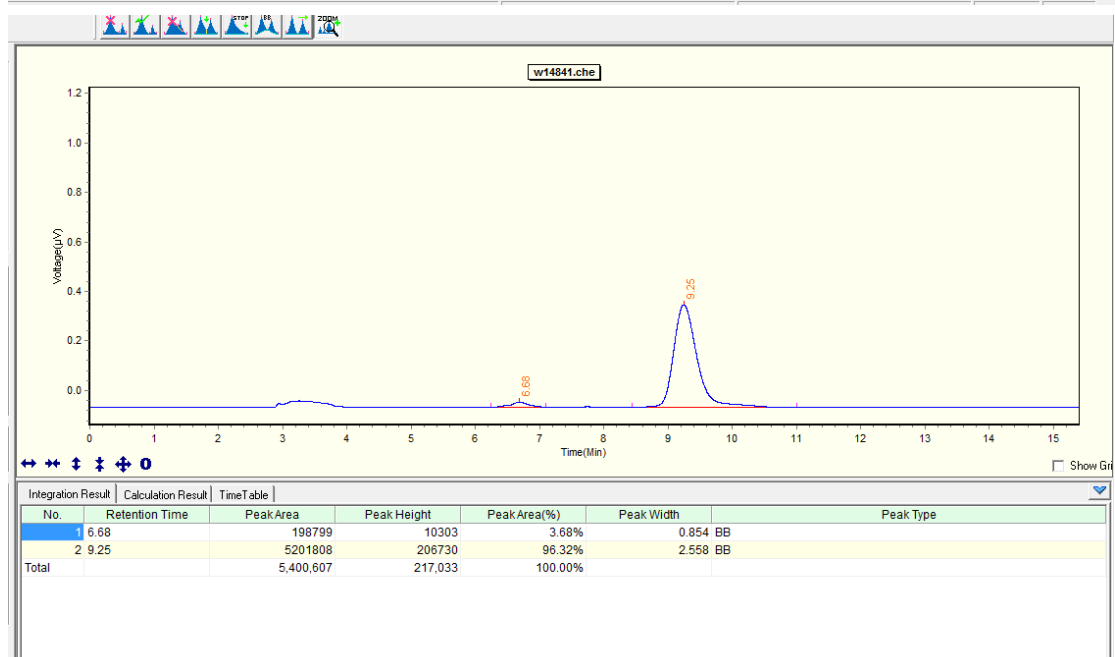
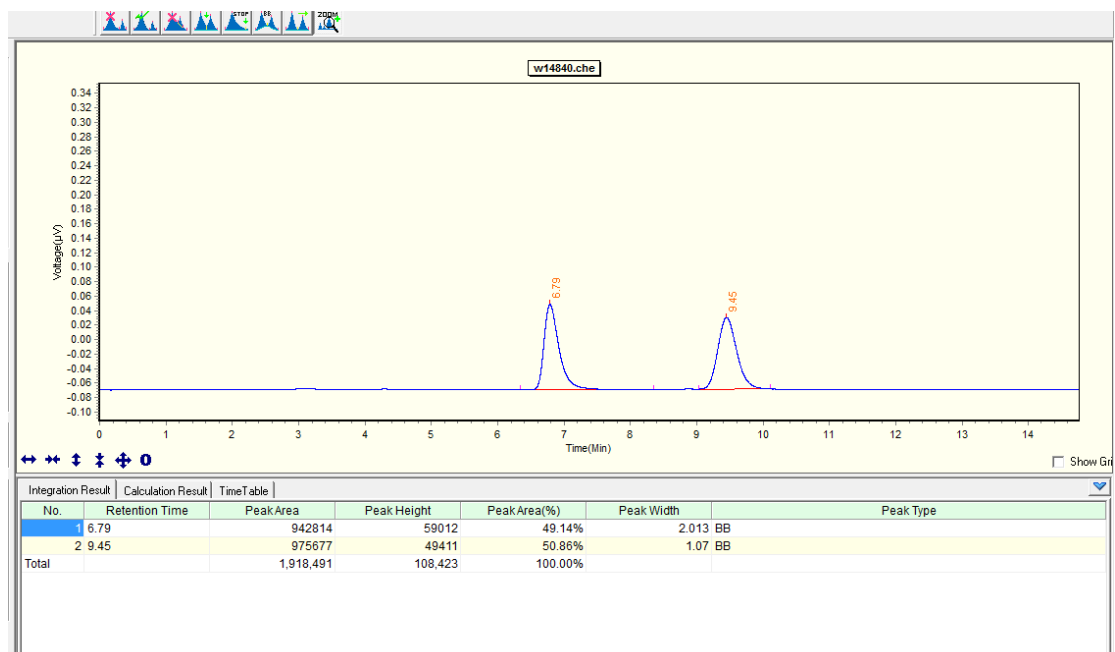
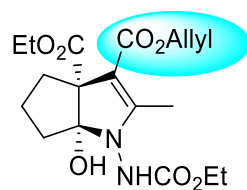
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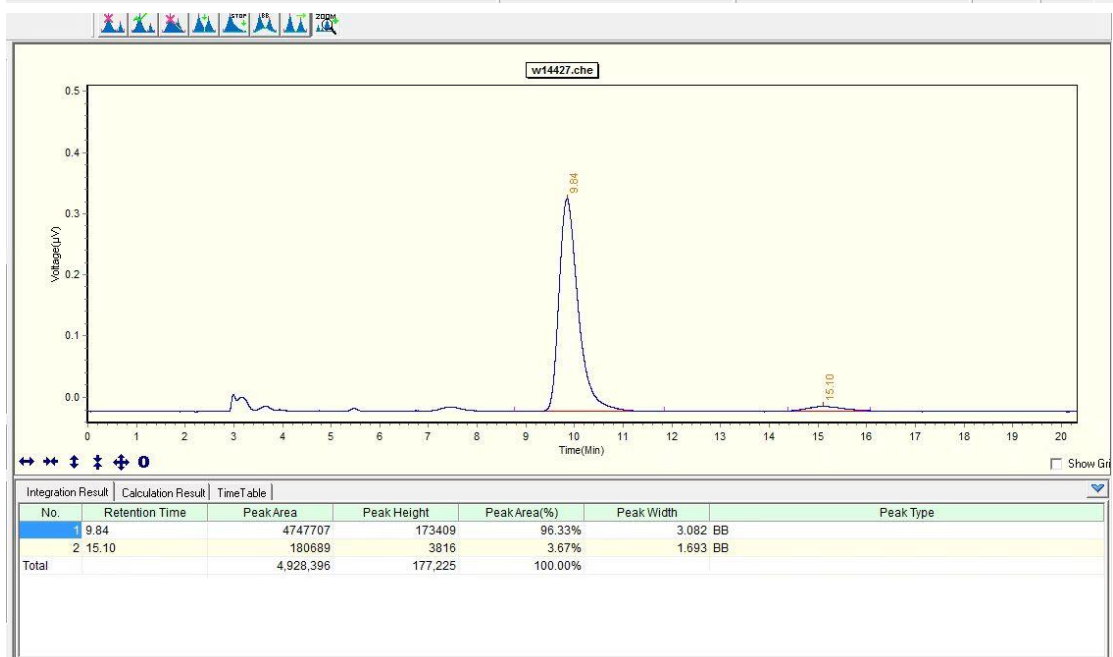
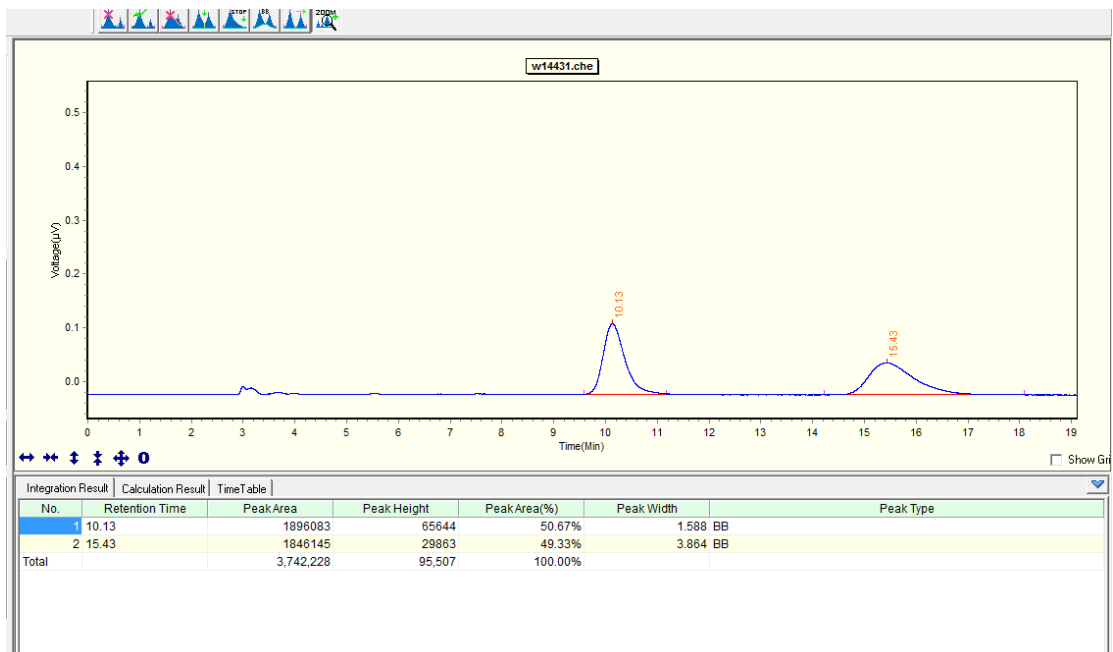
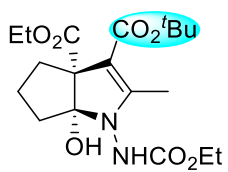
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3i

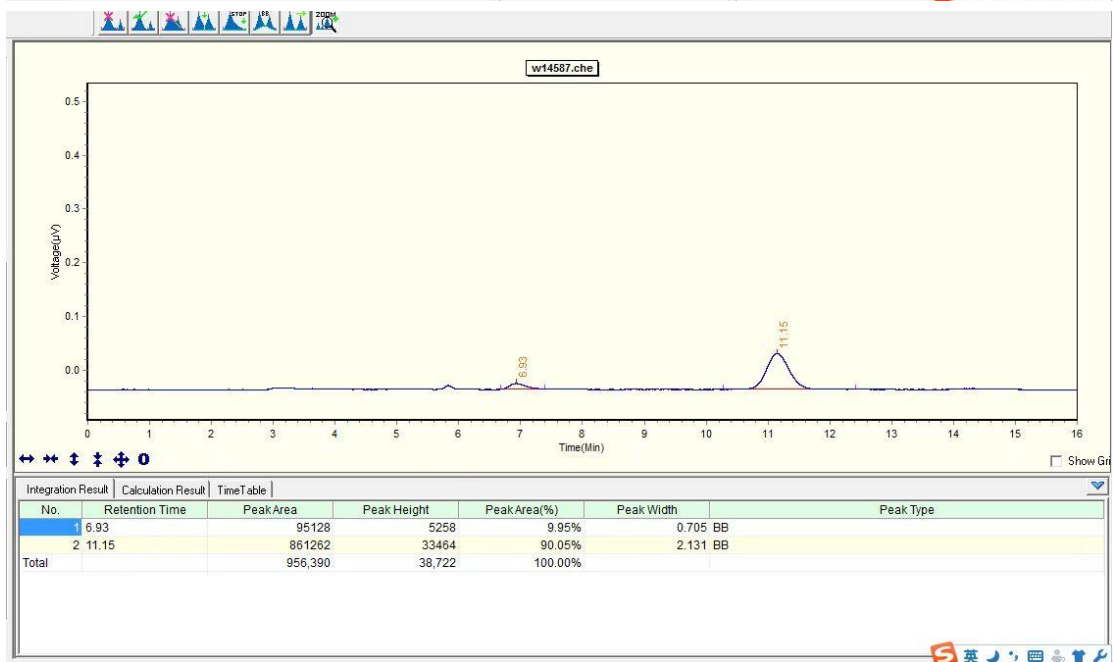
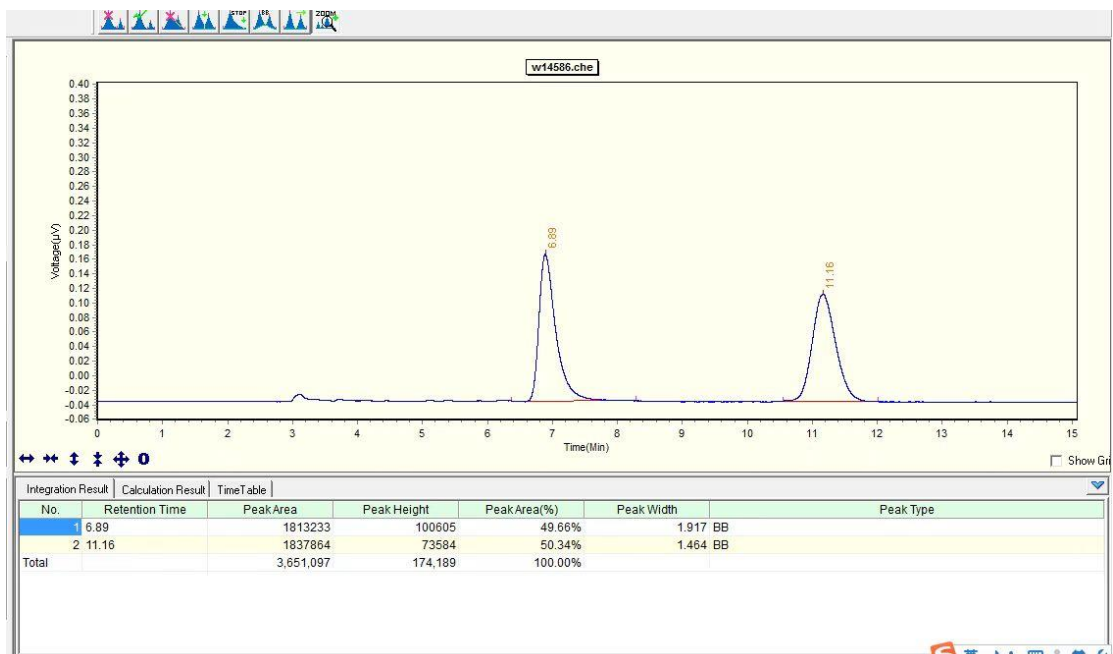
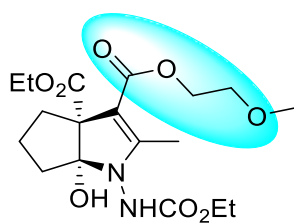


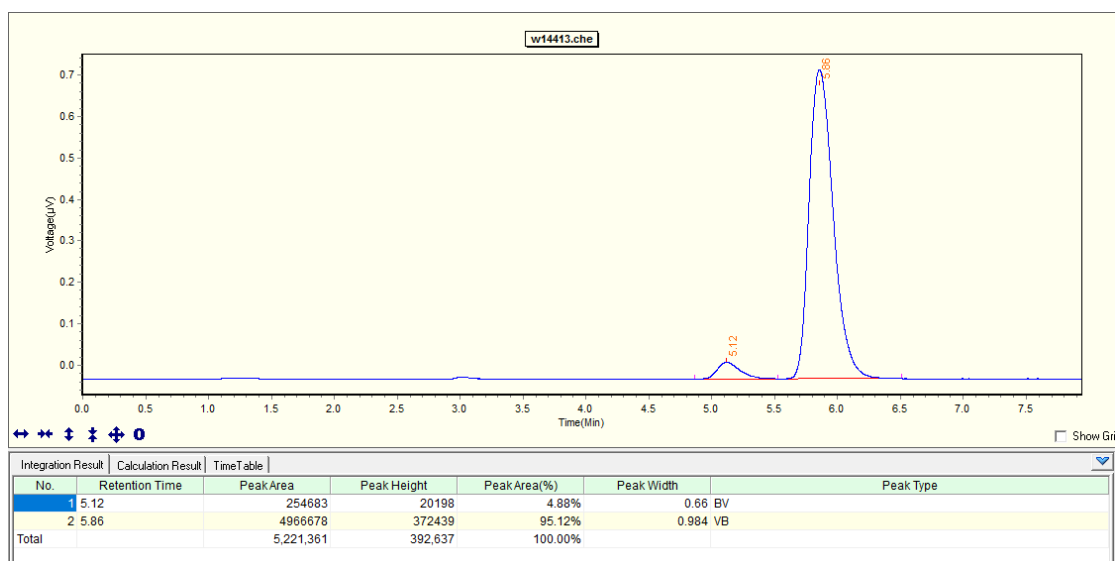
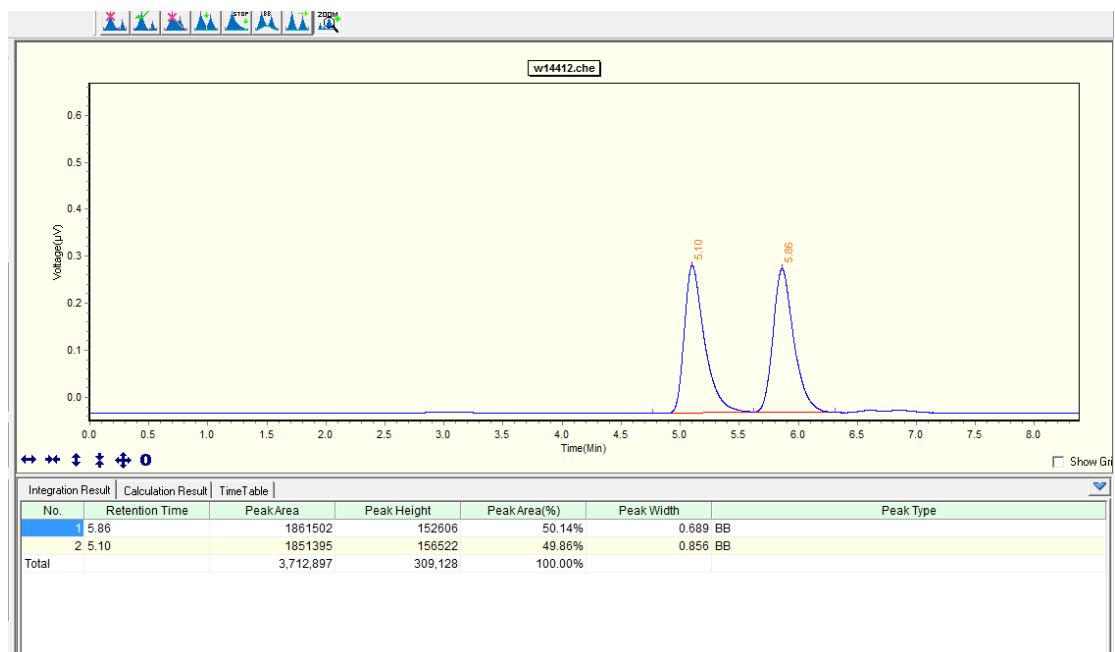
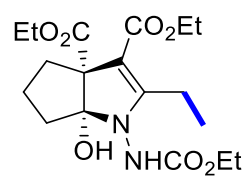
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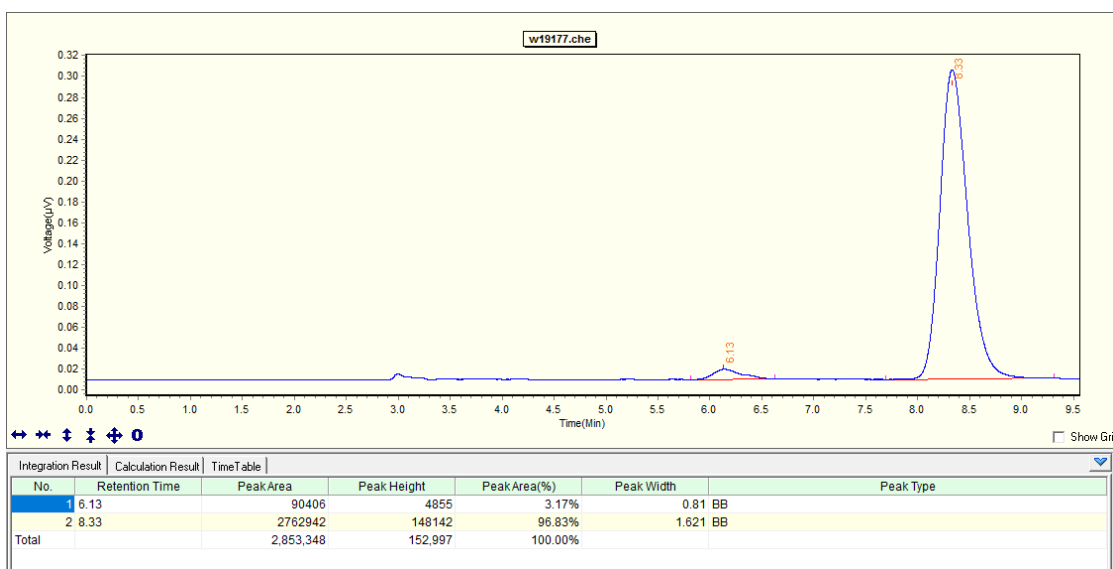
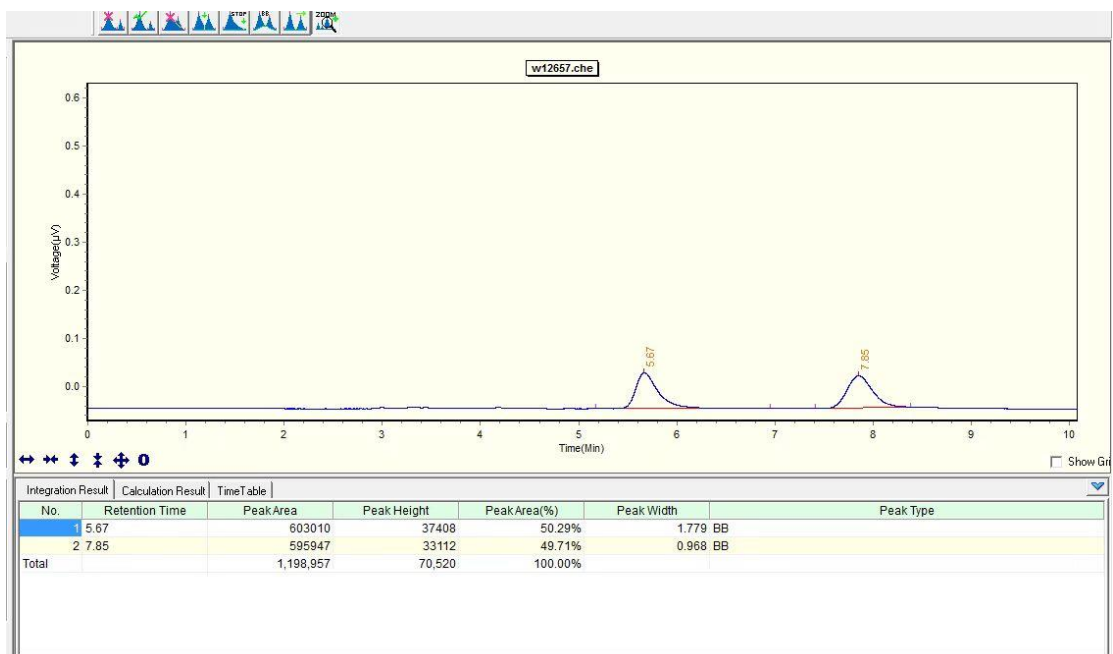
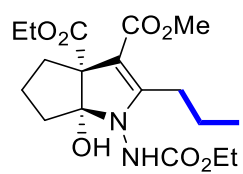


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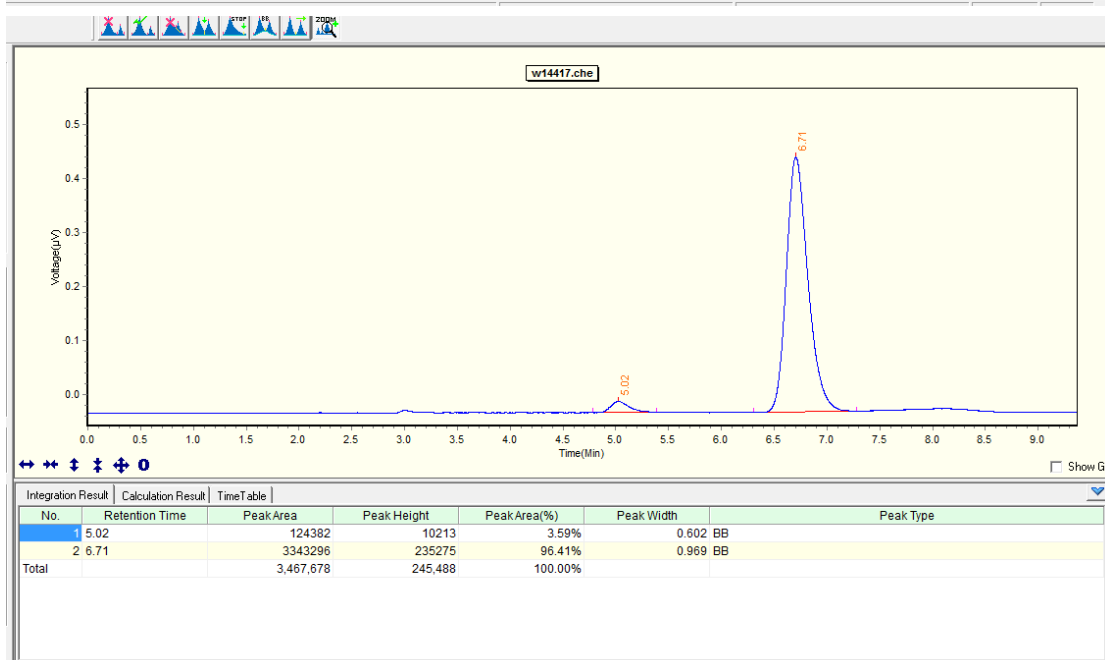
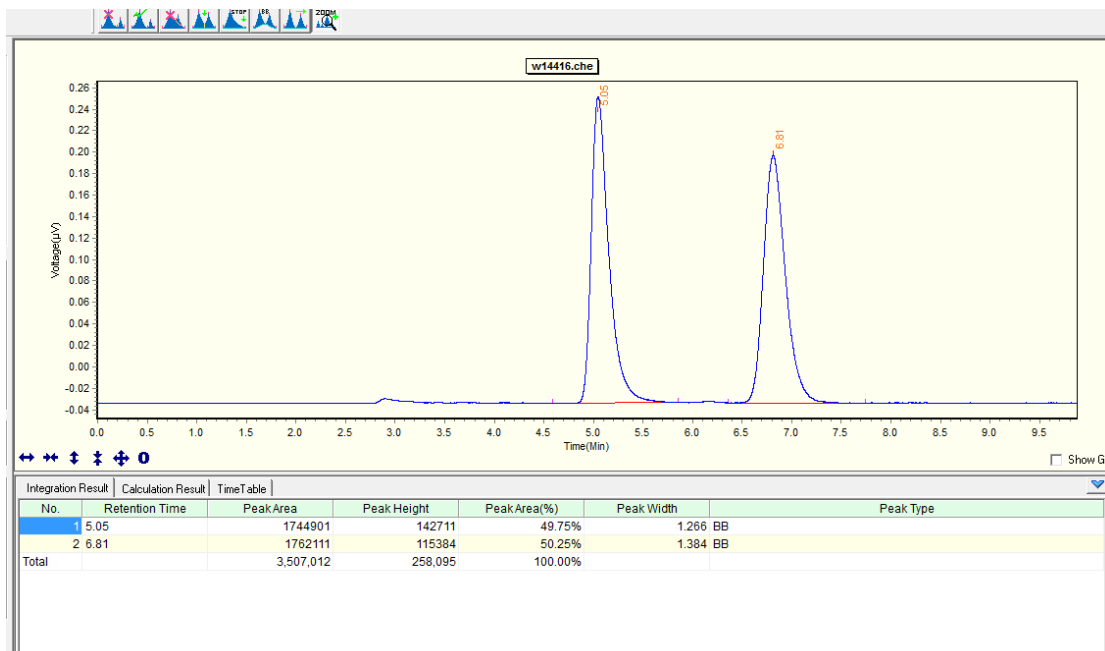
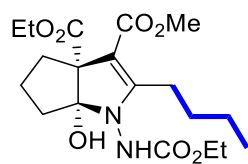




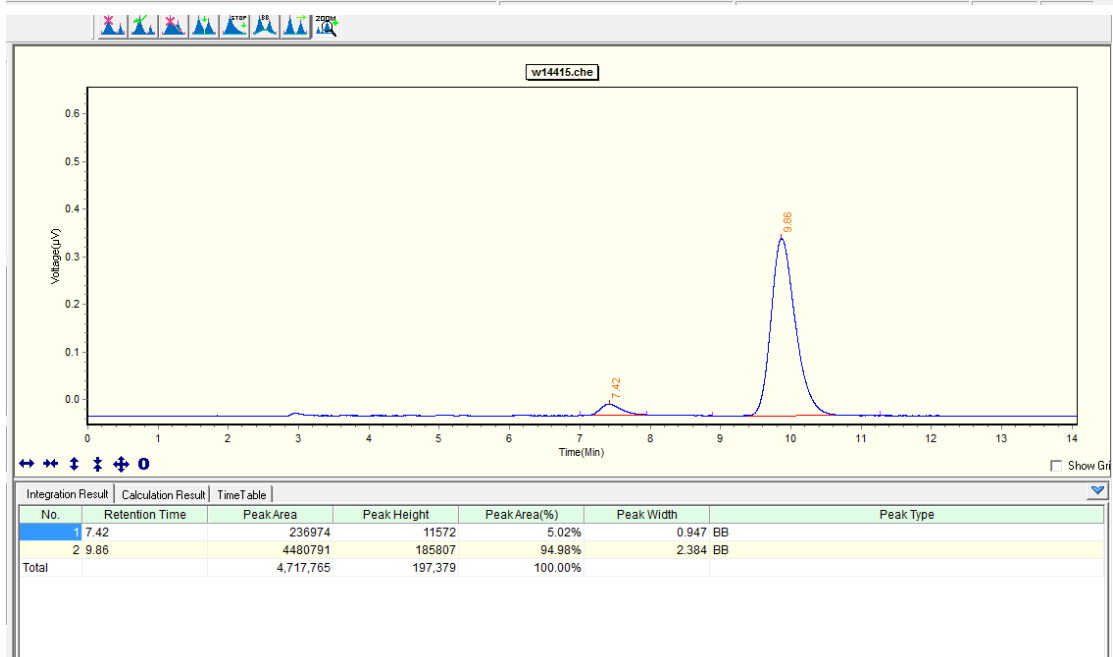
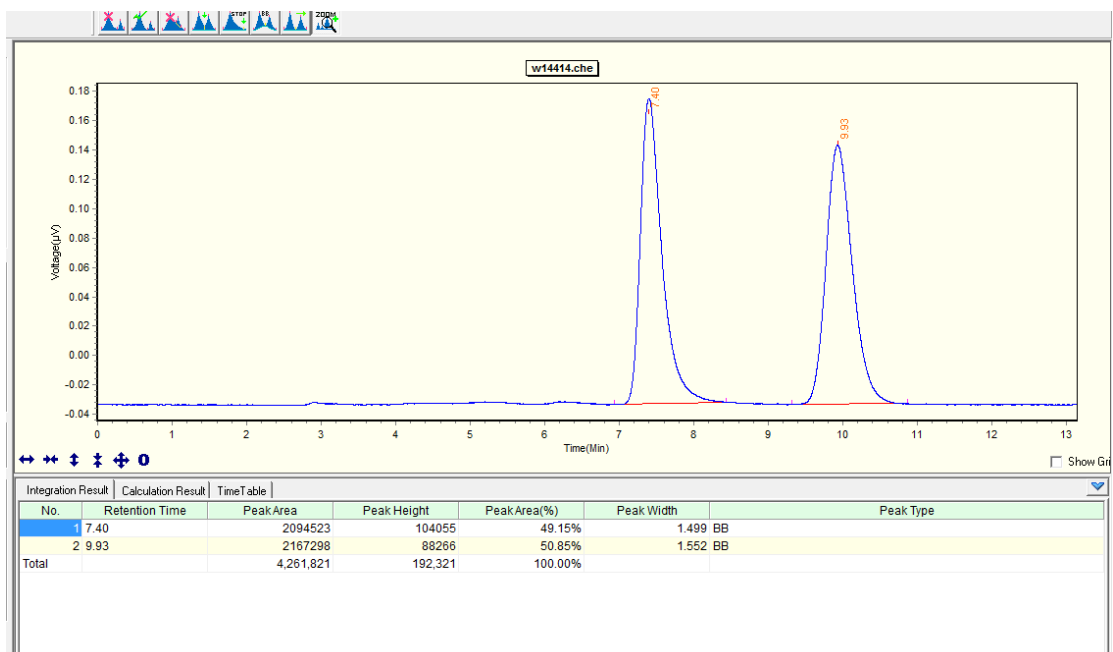
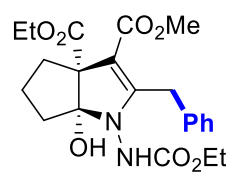
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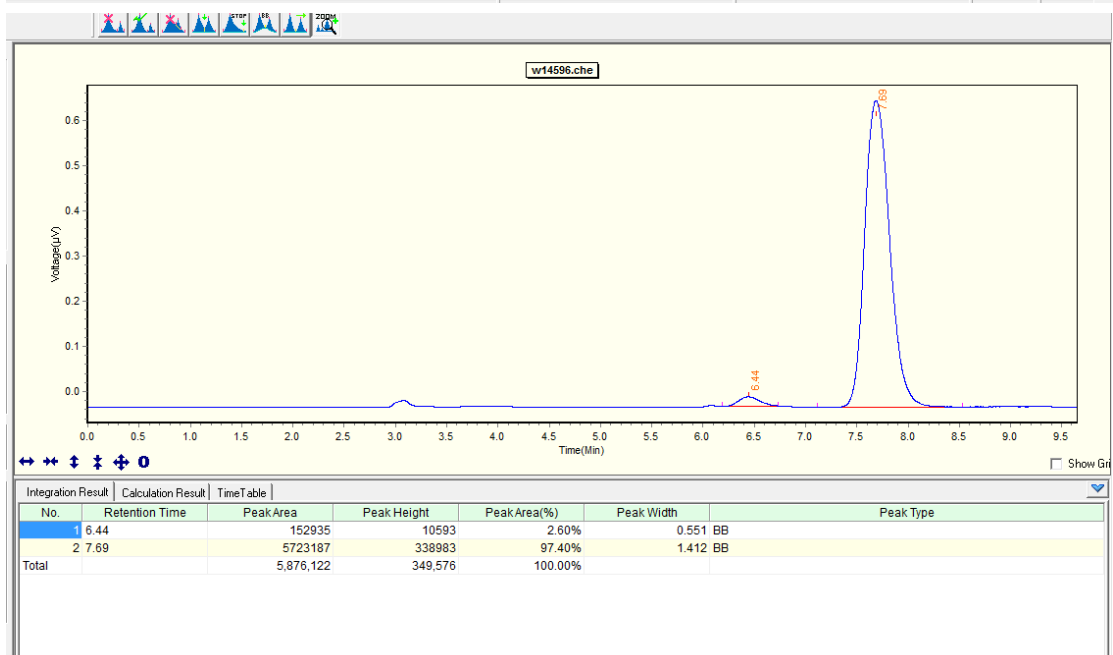
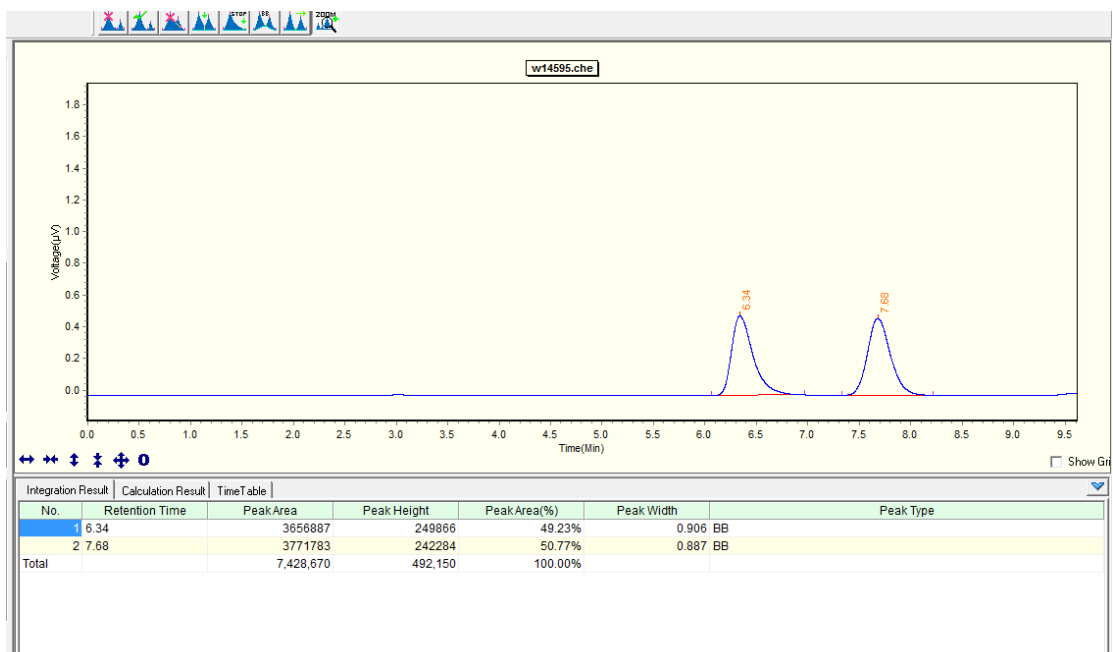
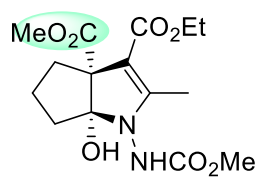
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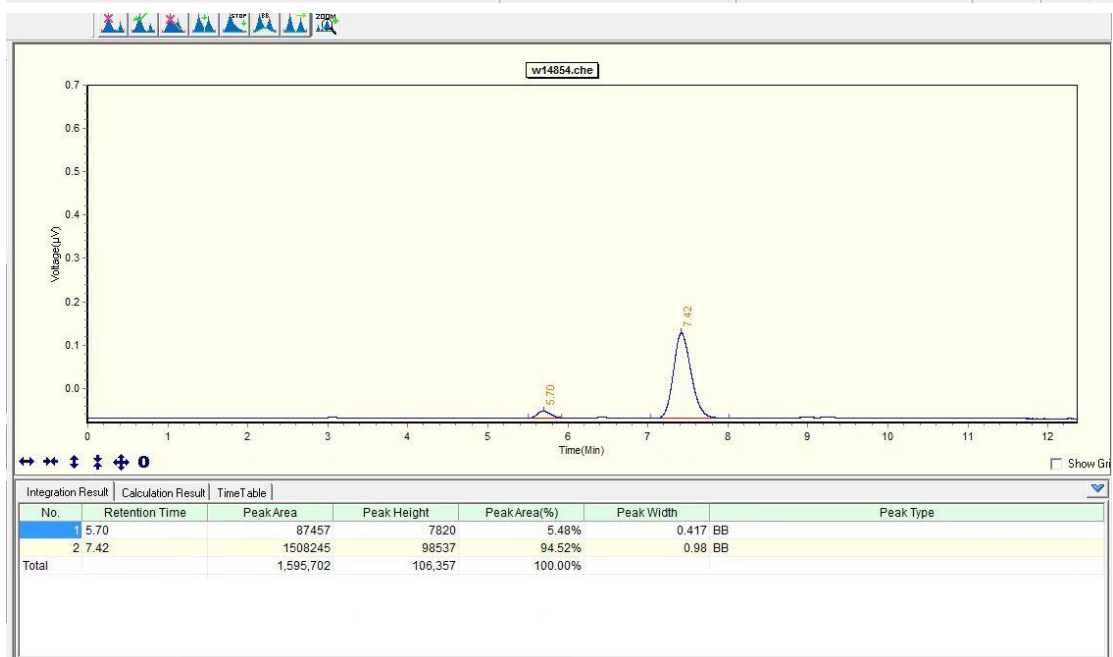
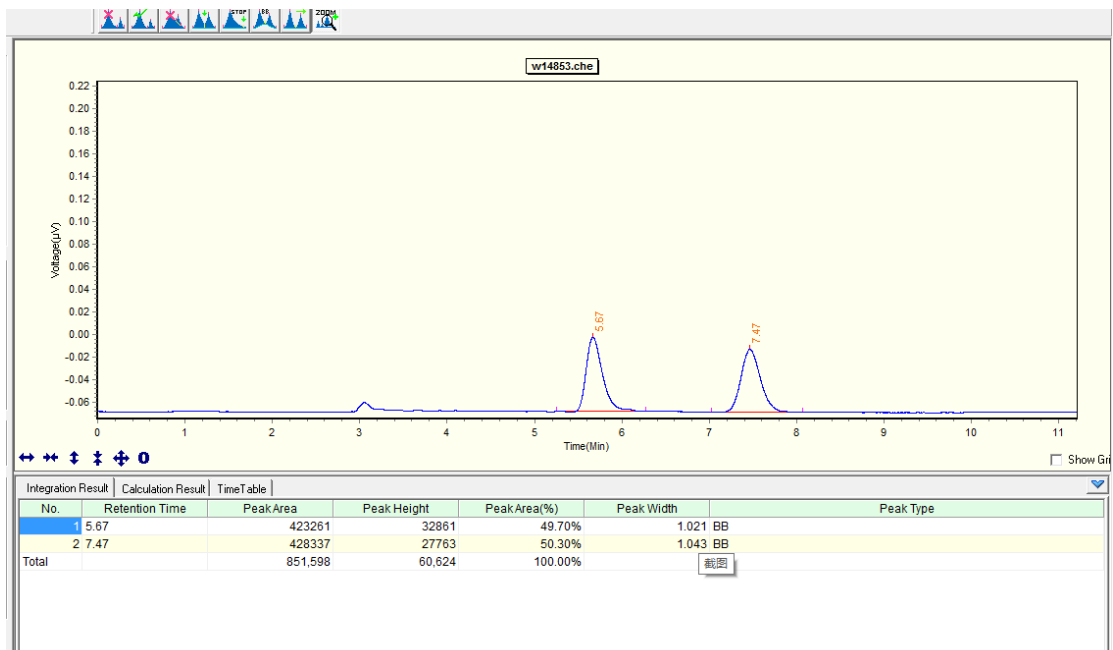
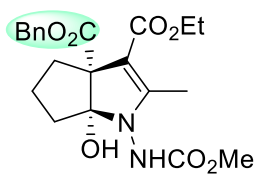
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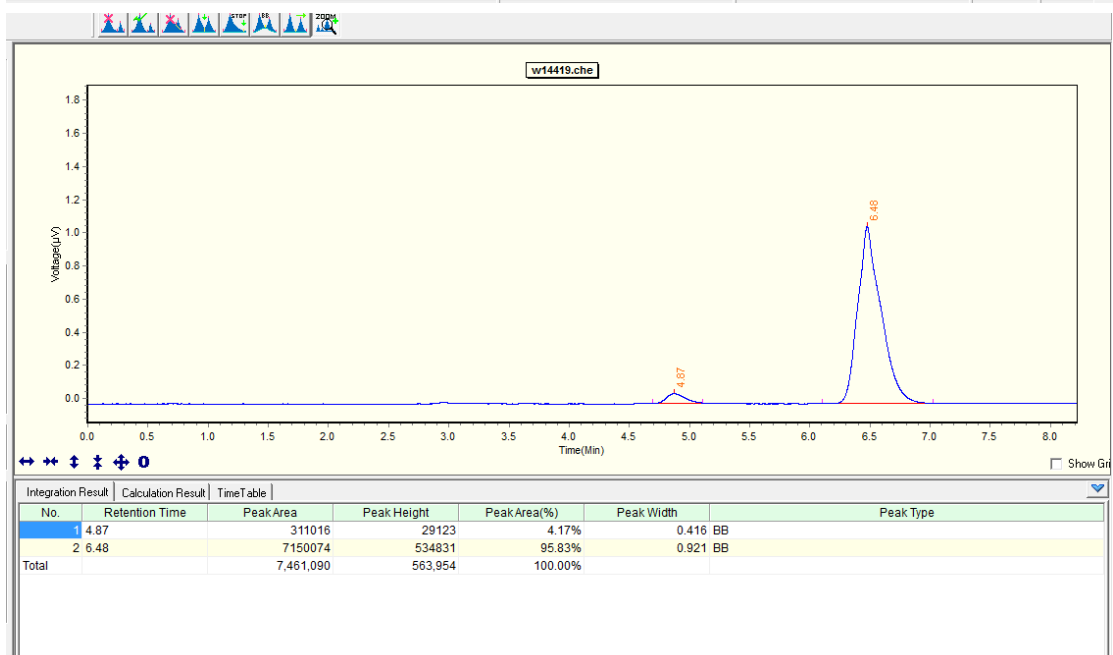
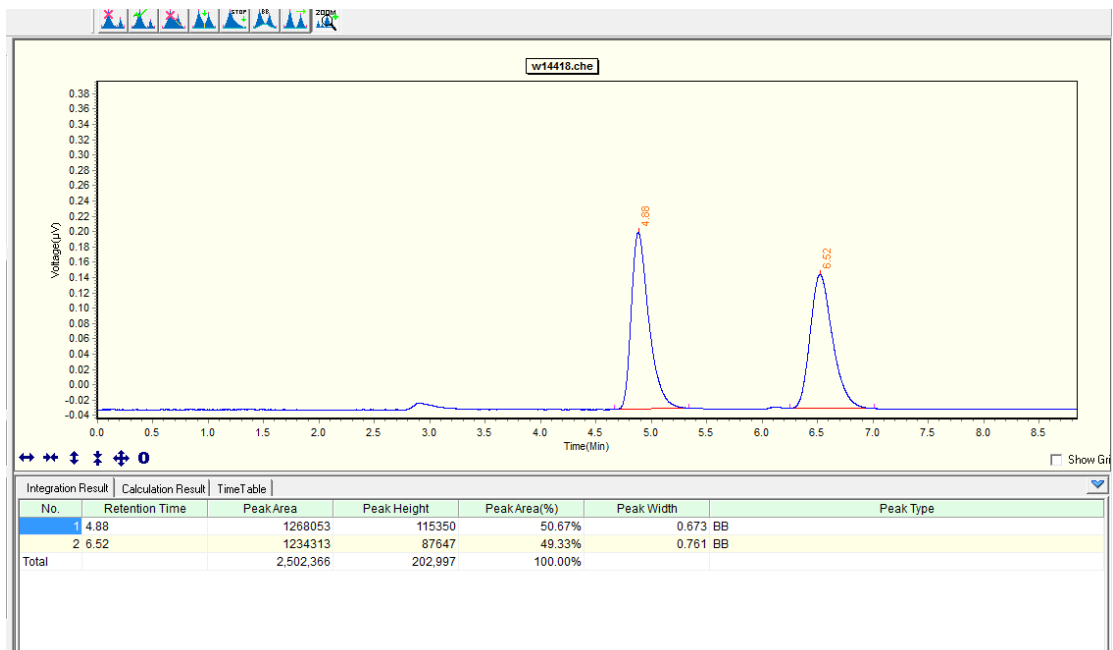
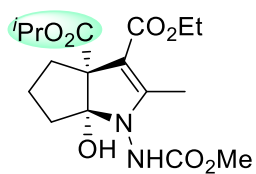
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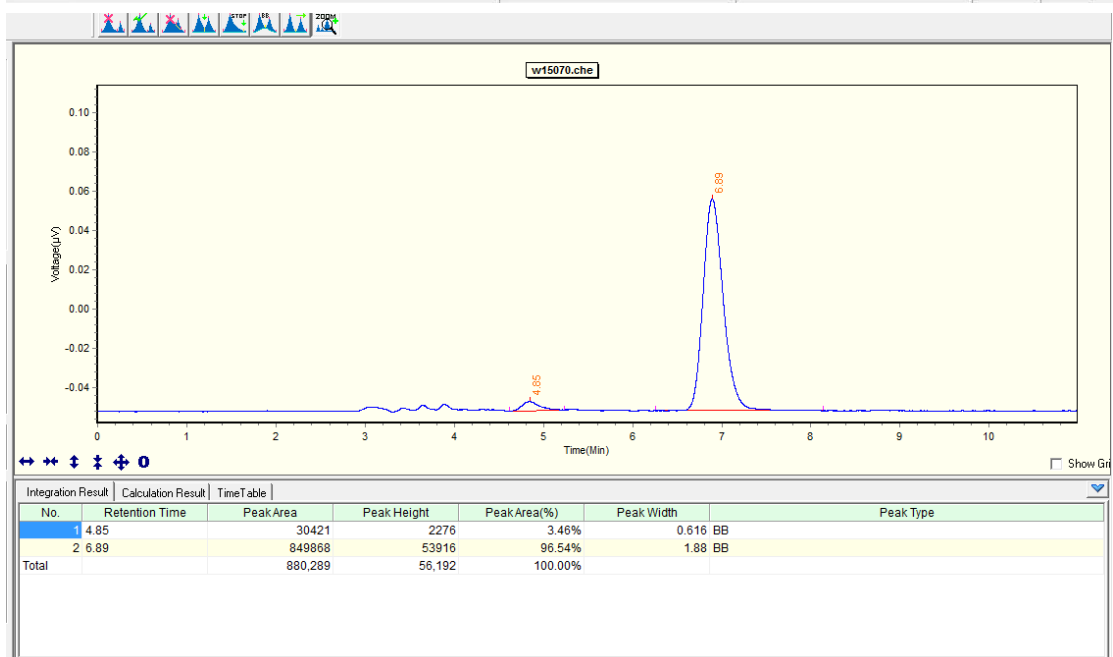
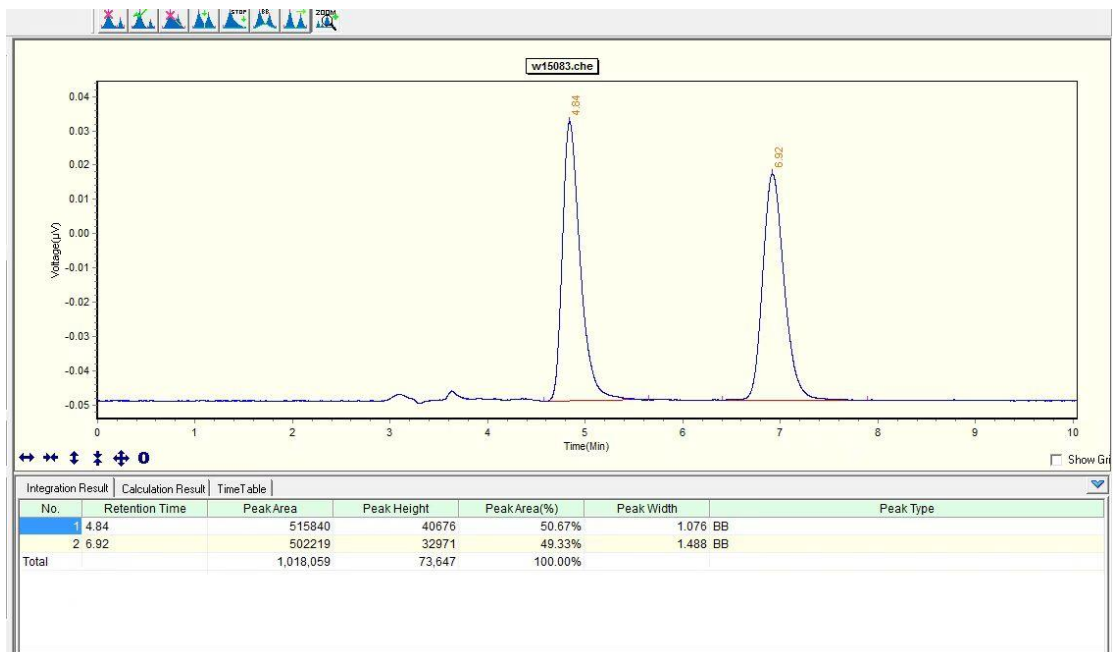
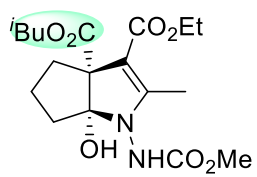


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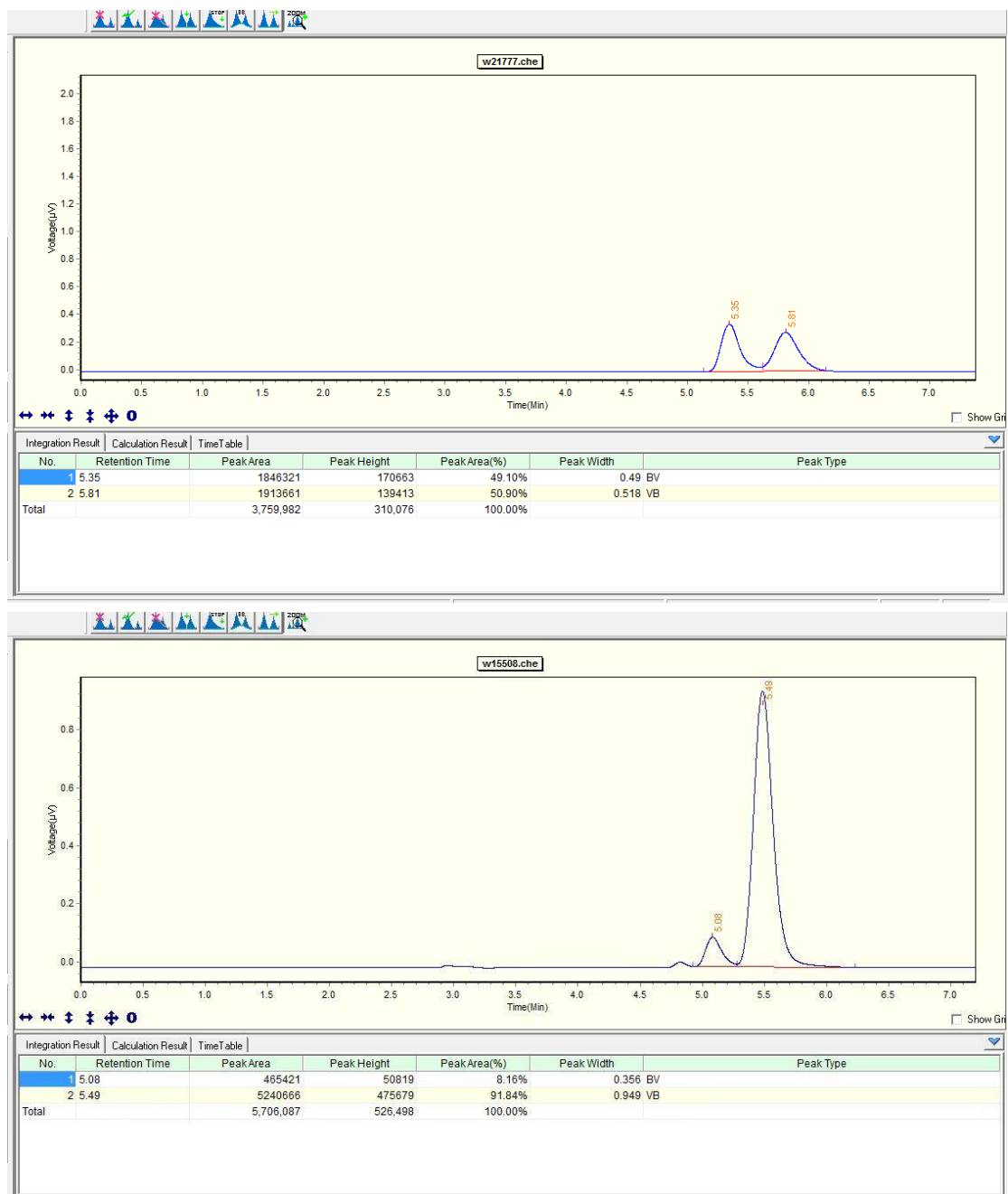
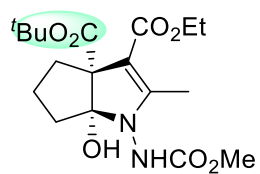




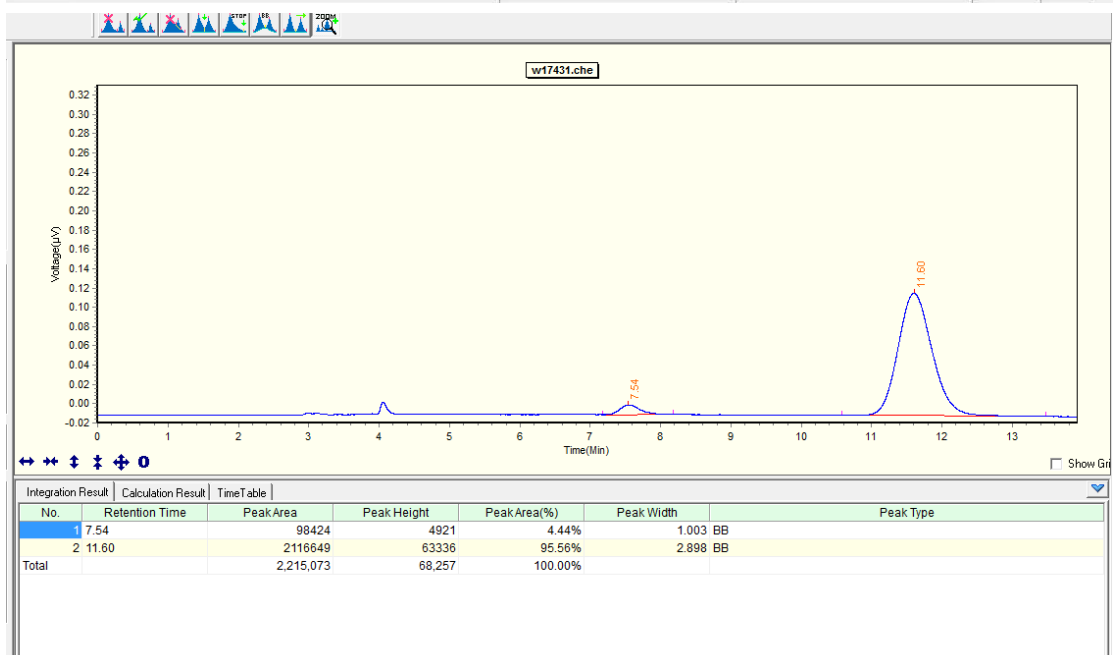
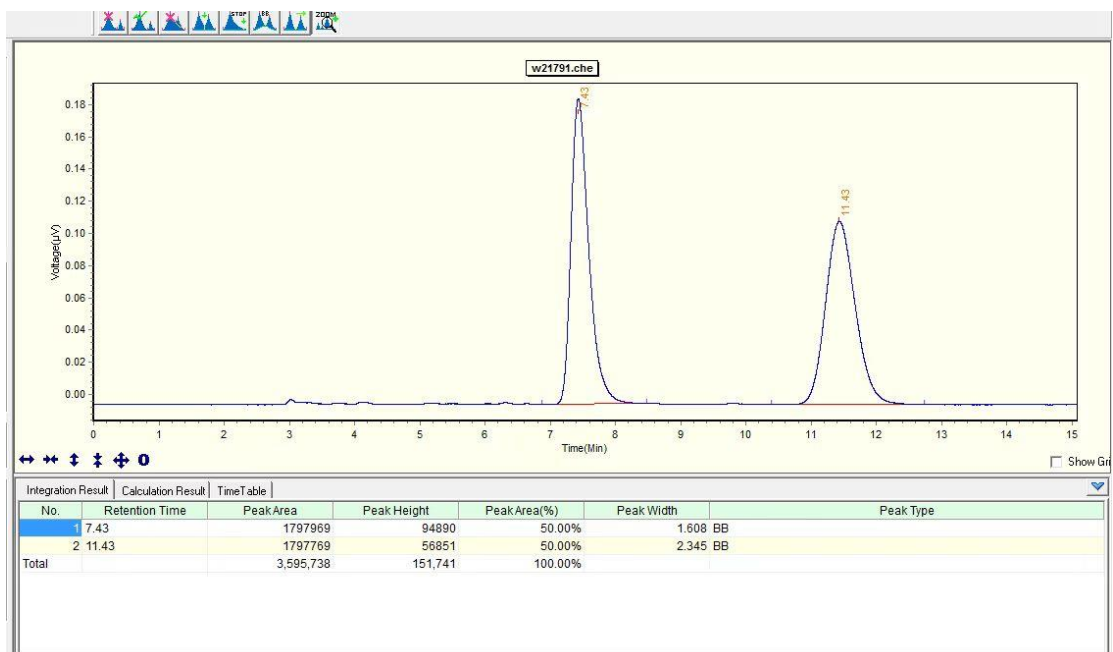
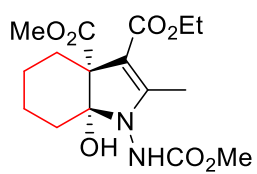
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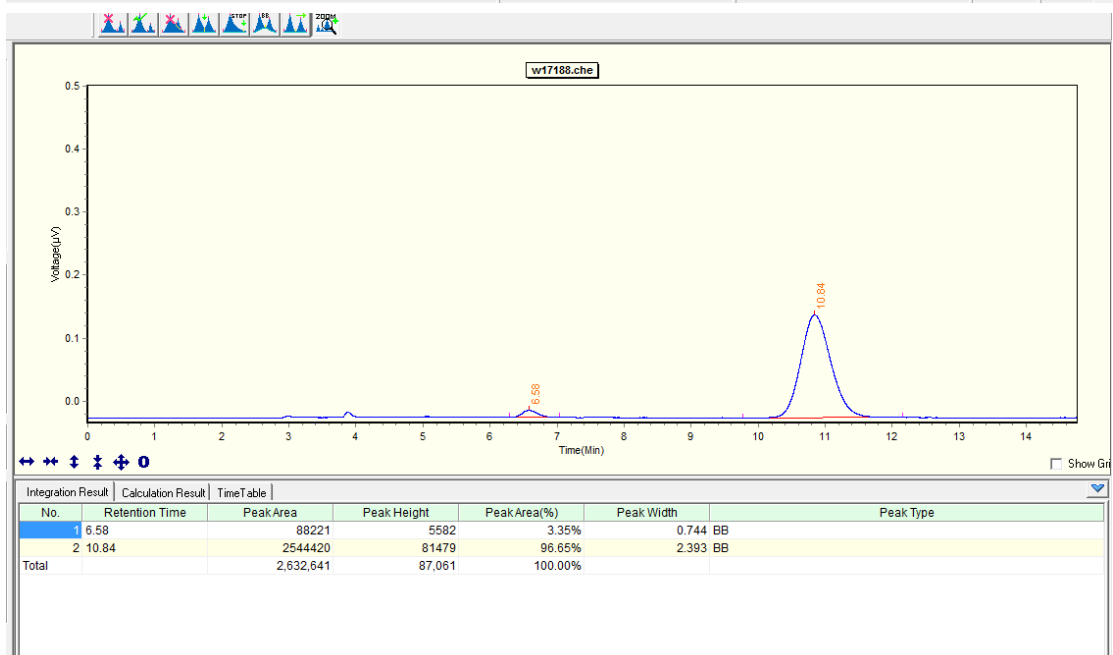
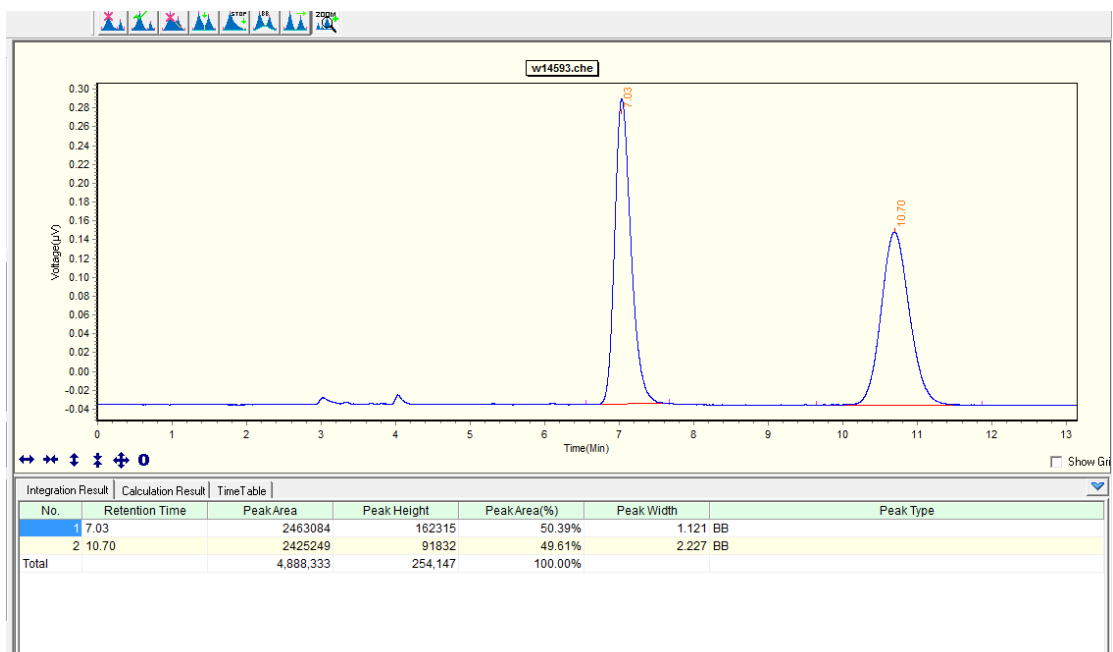
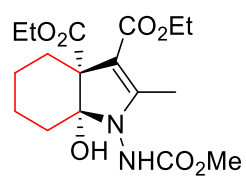
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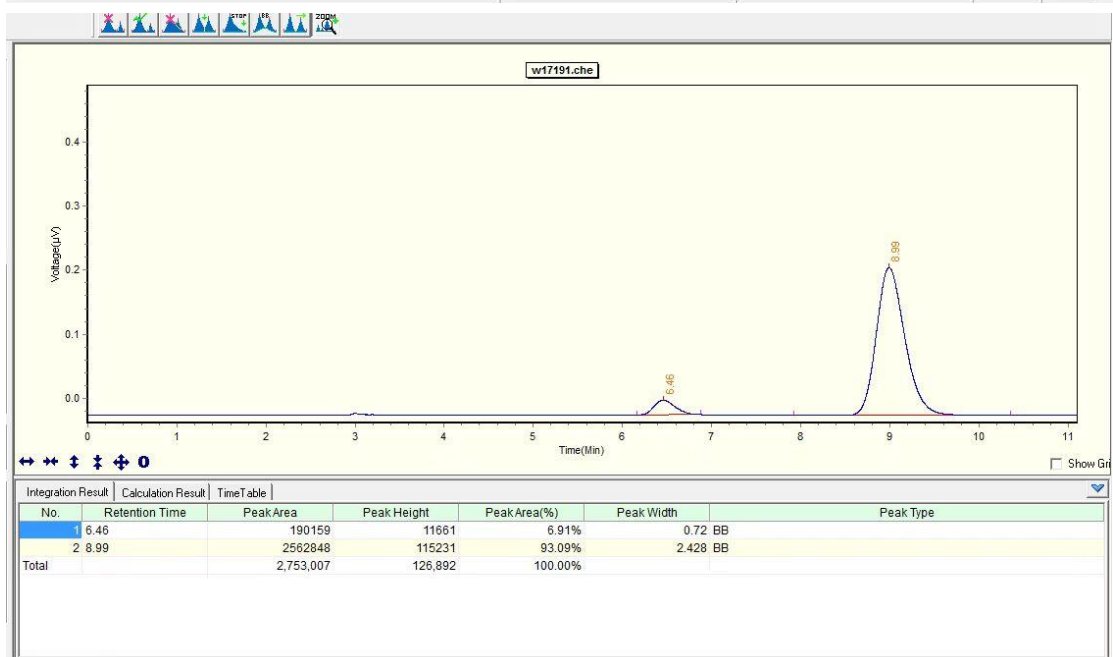
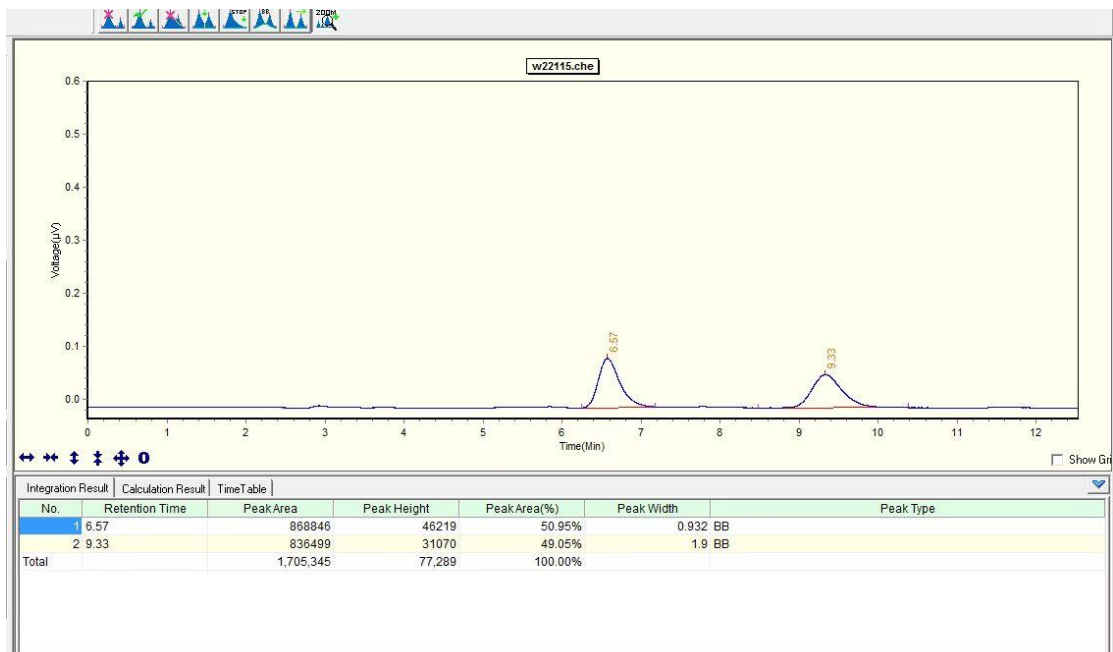
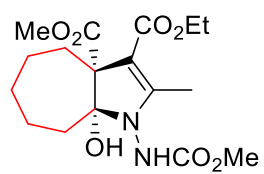
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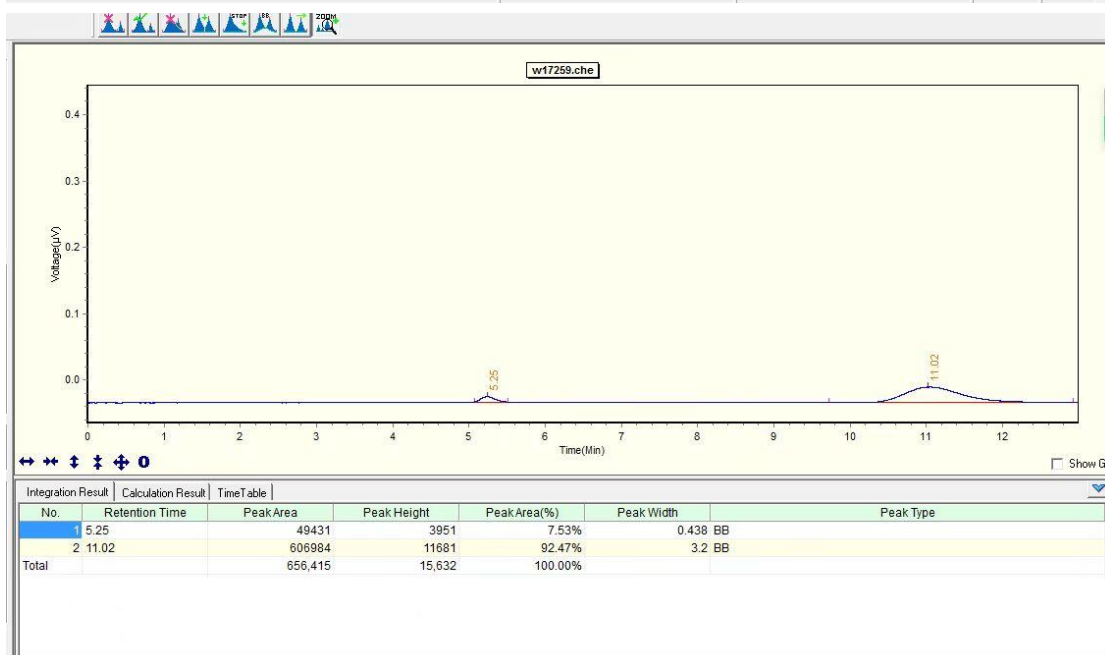
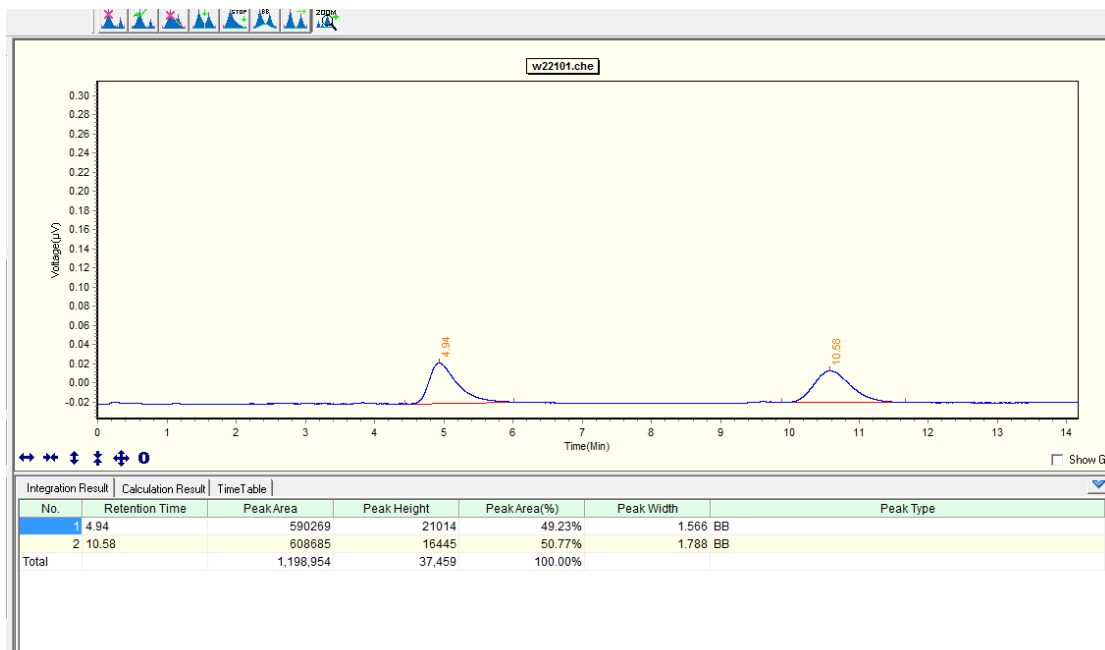
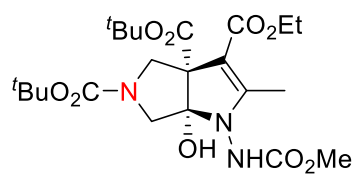
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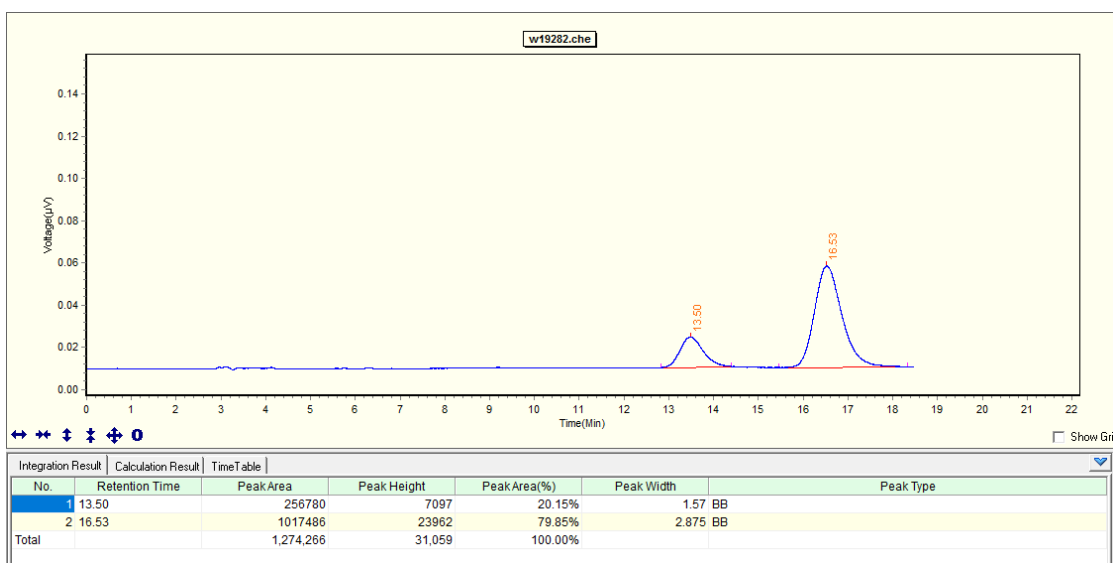
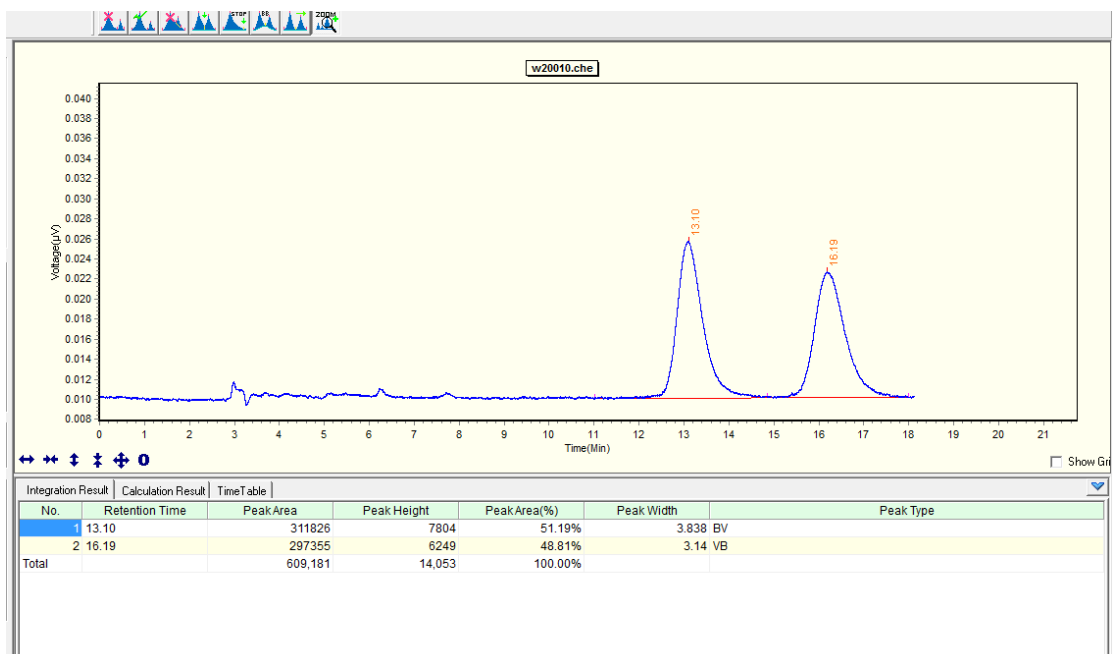
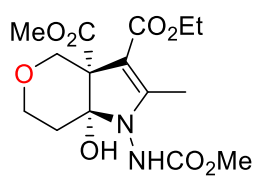
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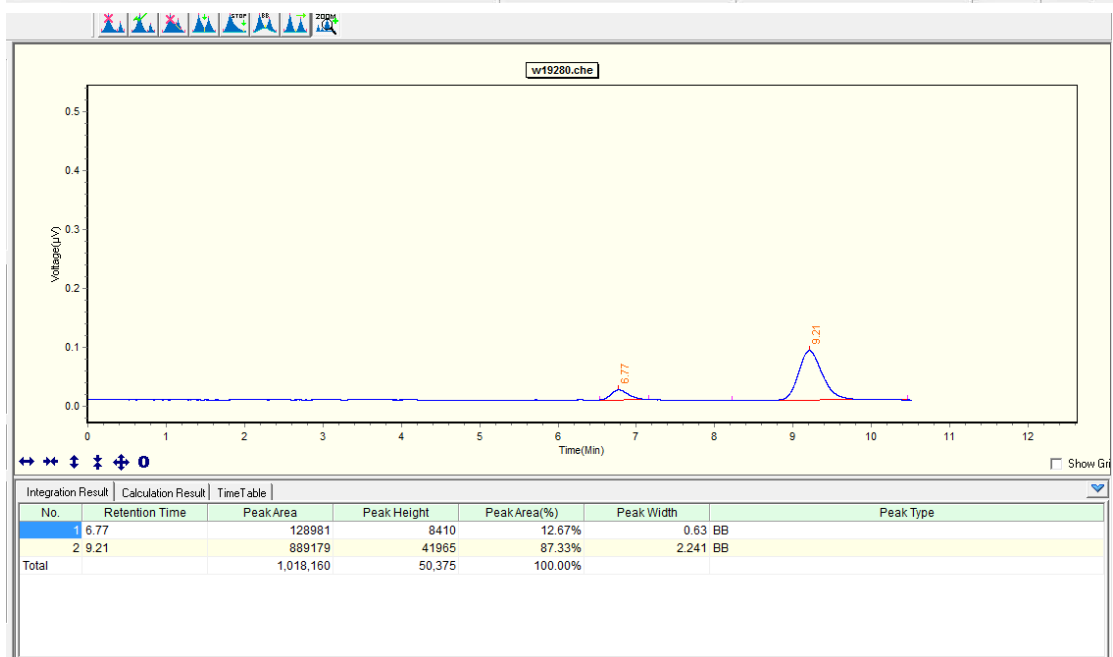
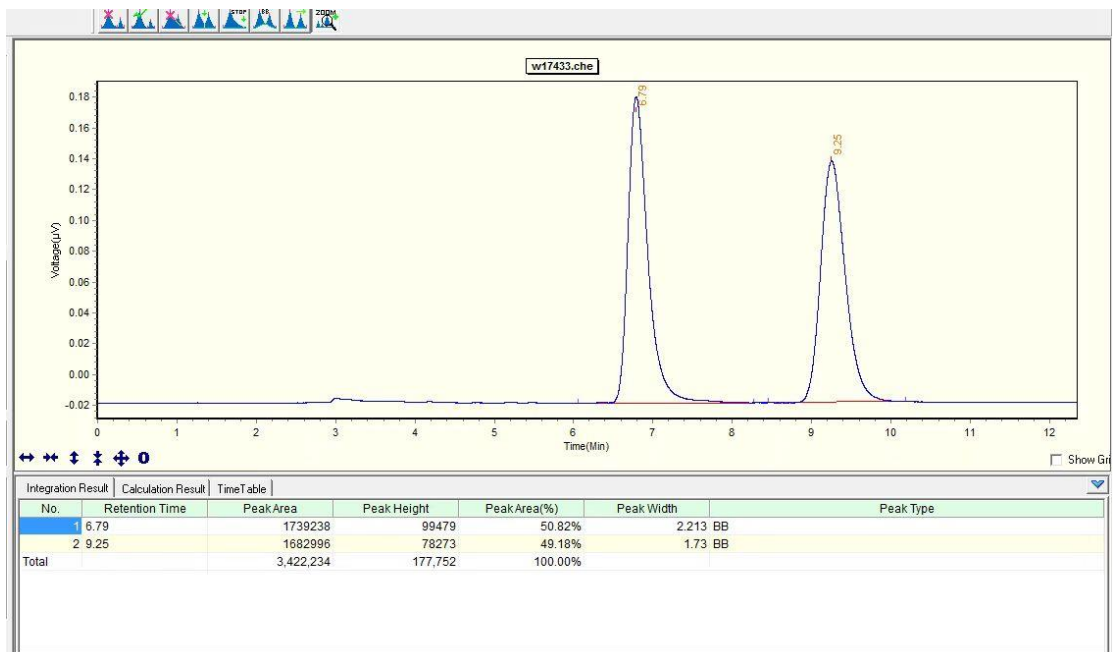
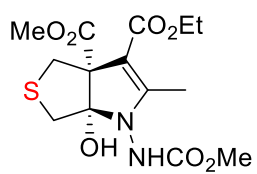
3x



3y

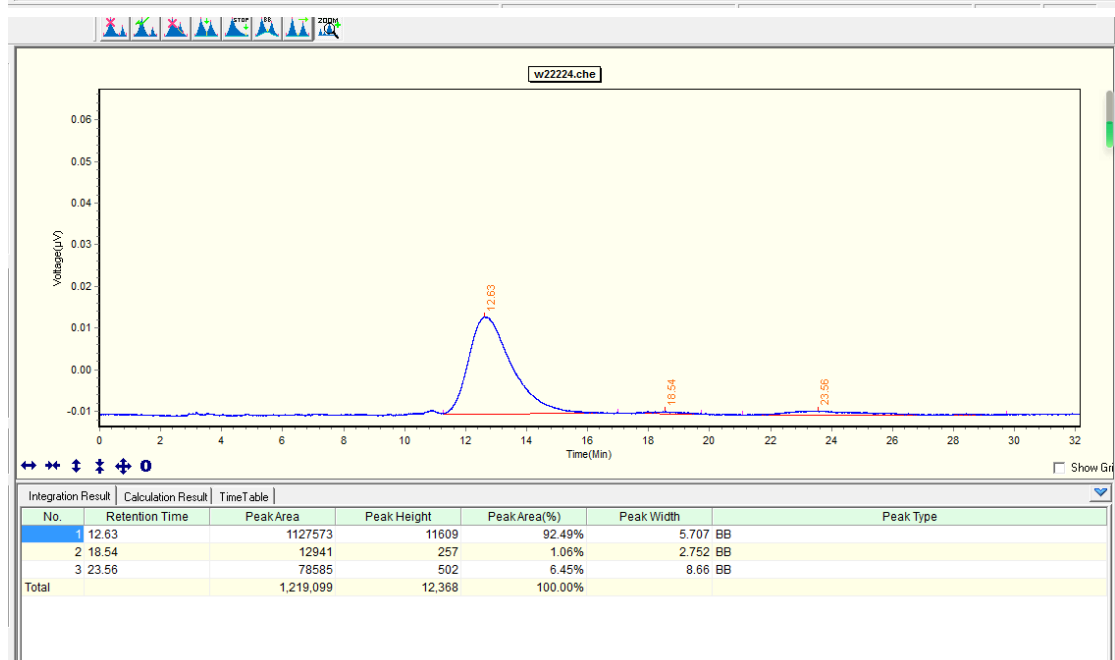
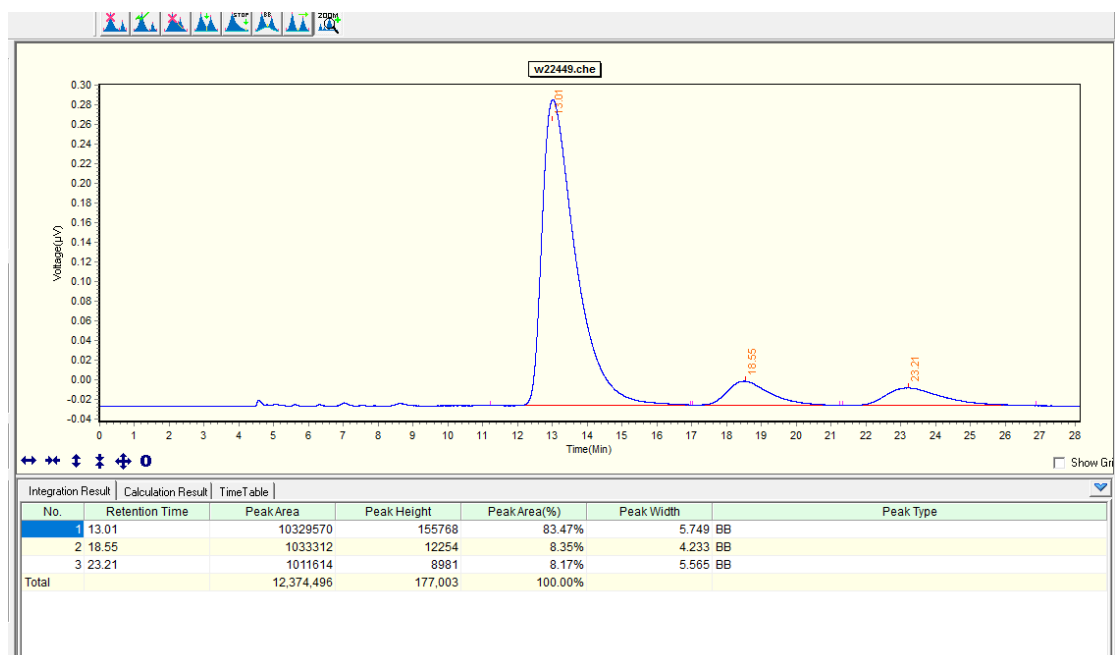
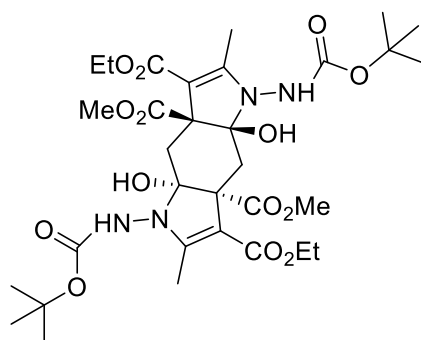


3z

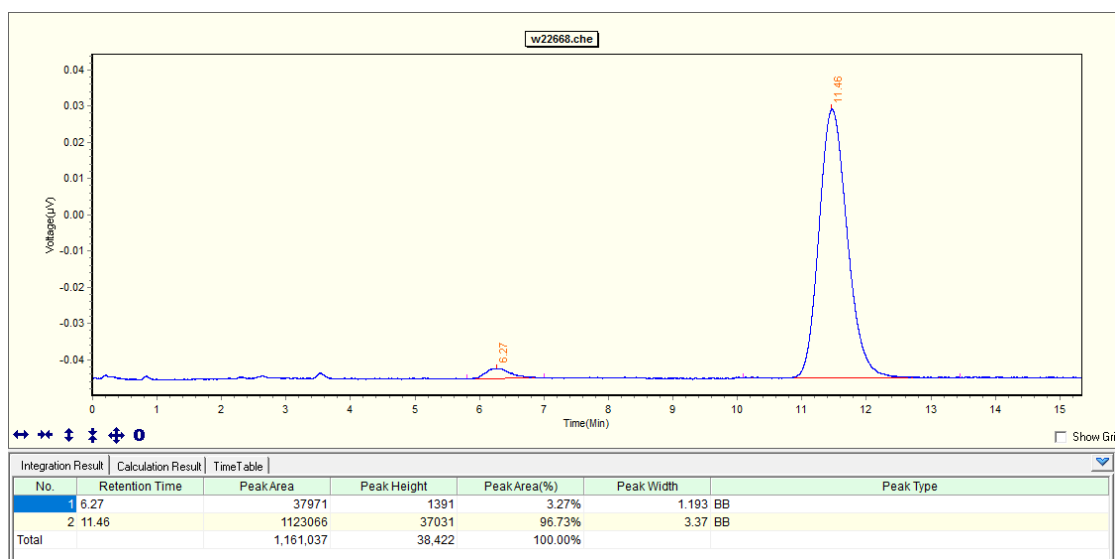
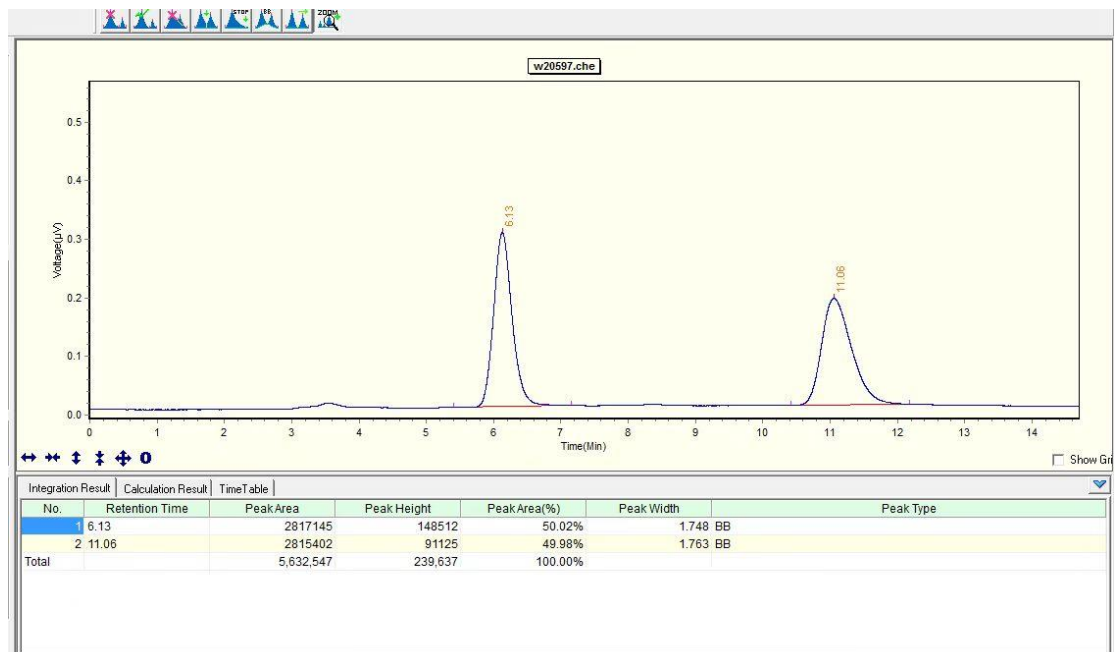
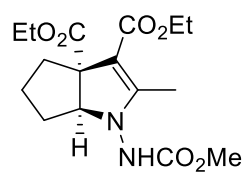




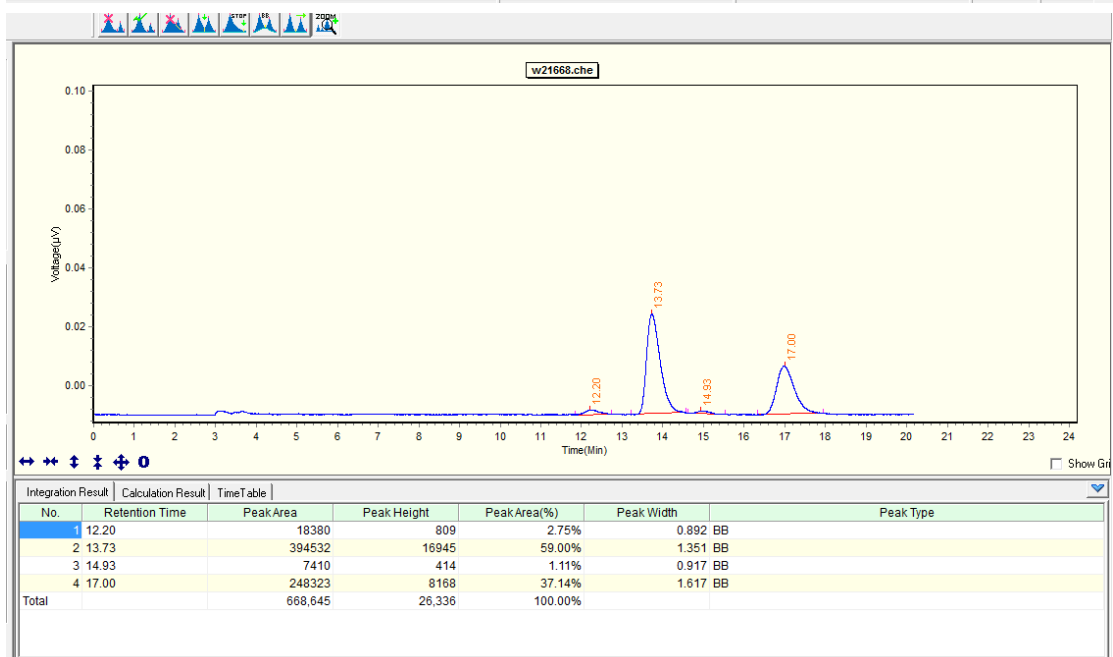
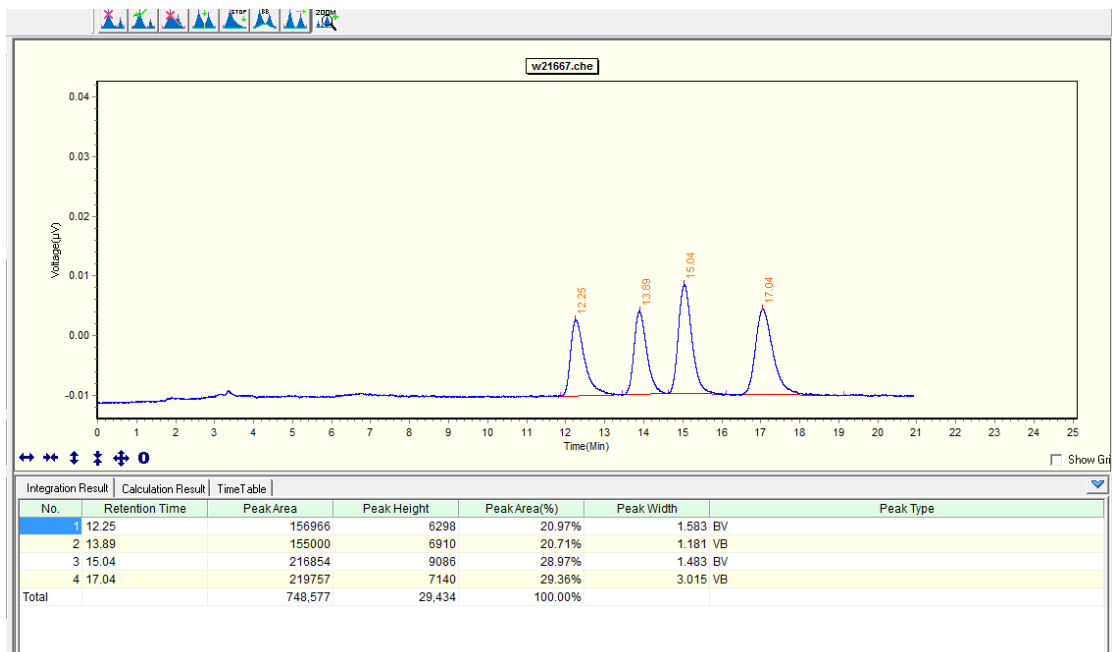
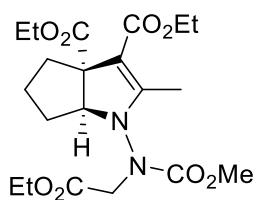
(*meso*)-**3a'** and **3a'** (dr = 9:1)



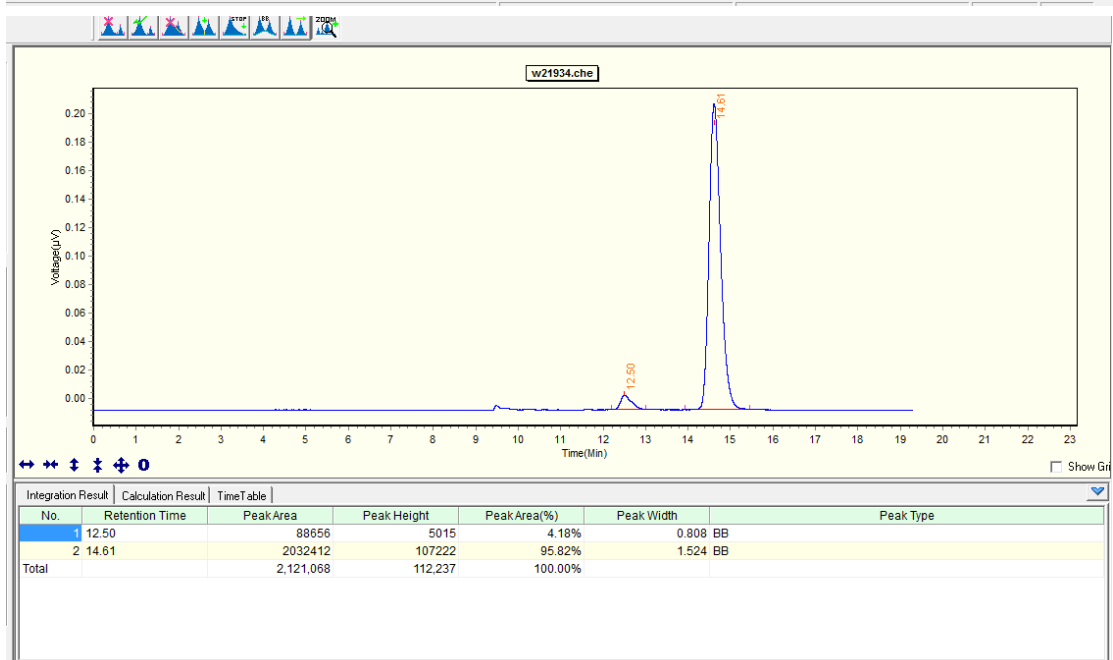
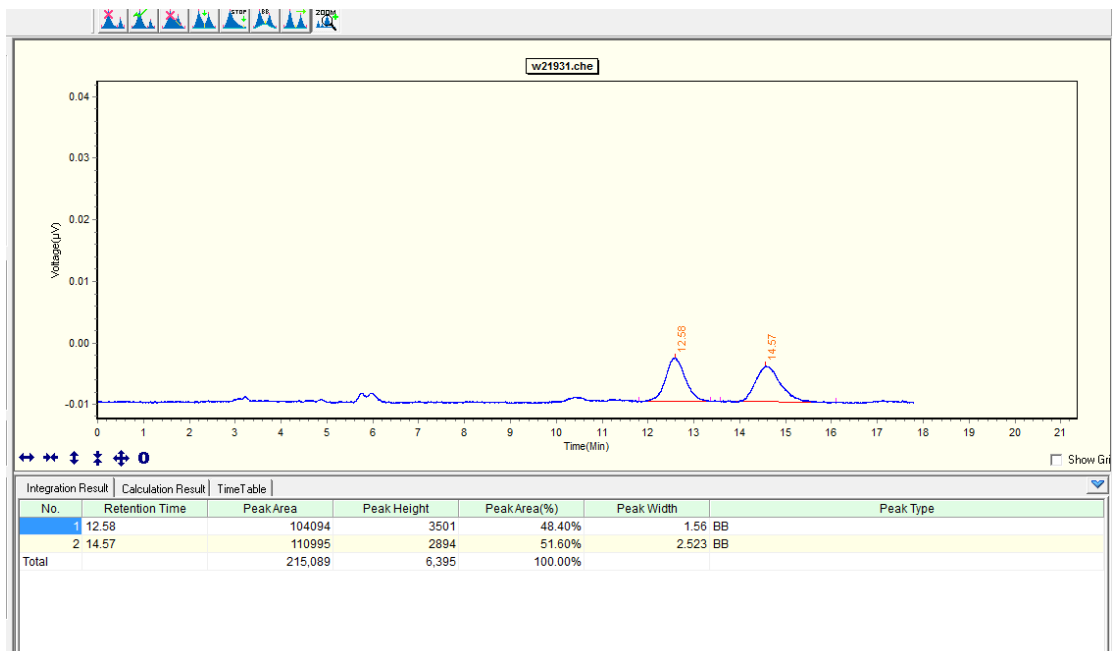
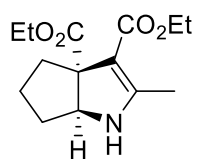
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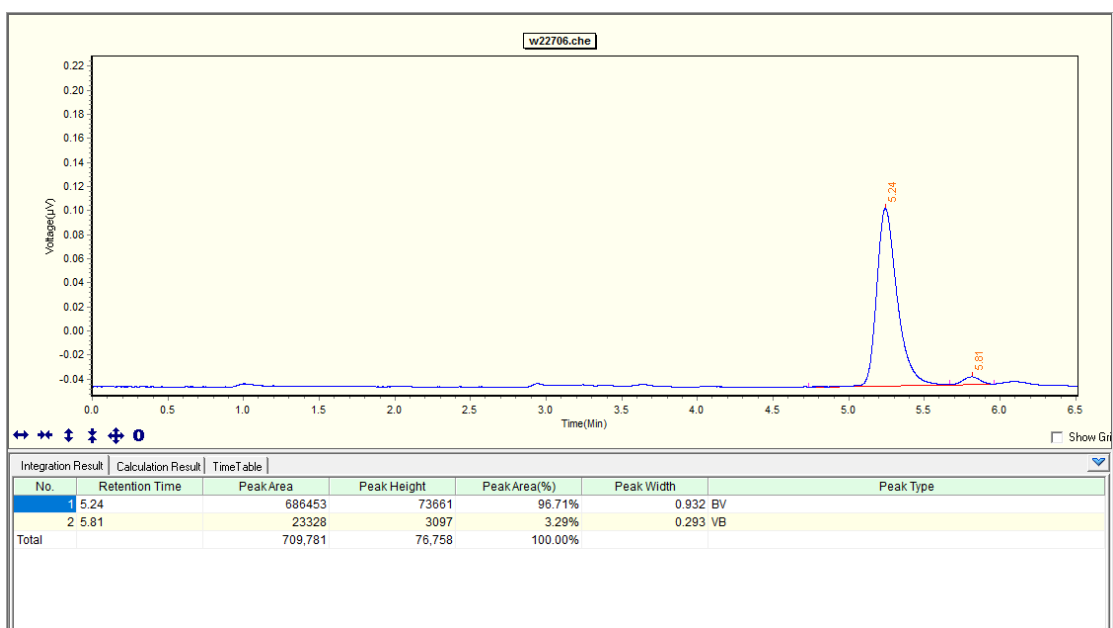
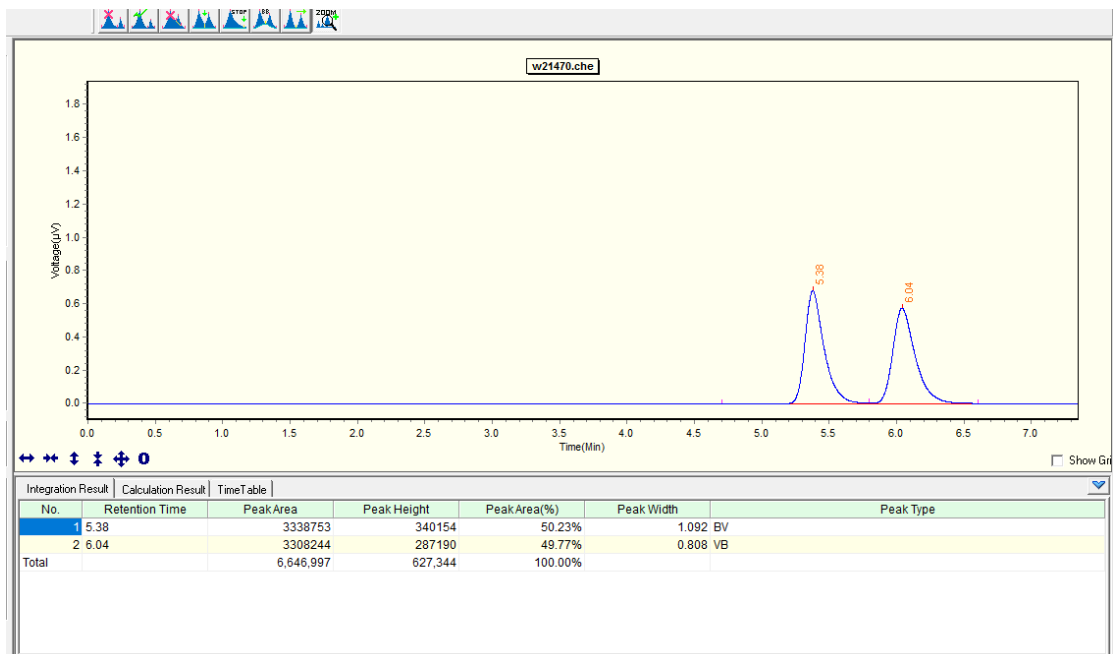
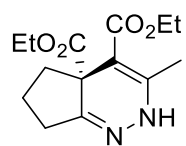
5 (dr = 2:3)



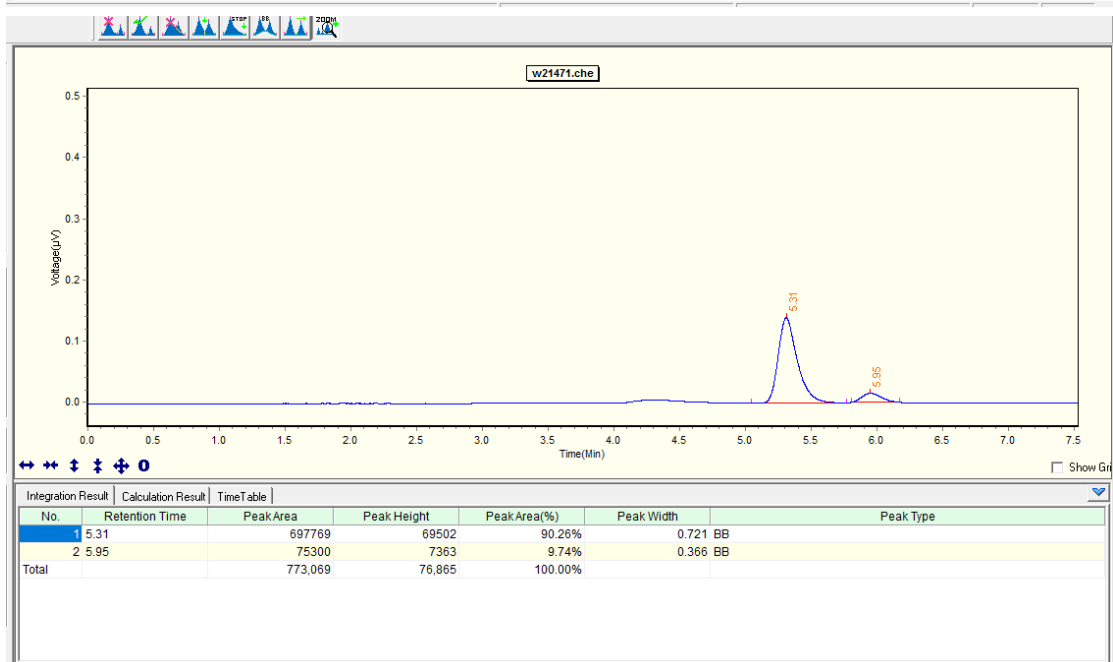
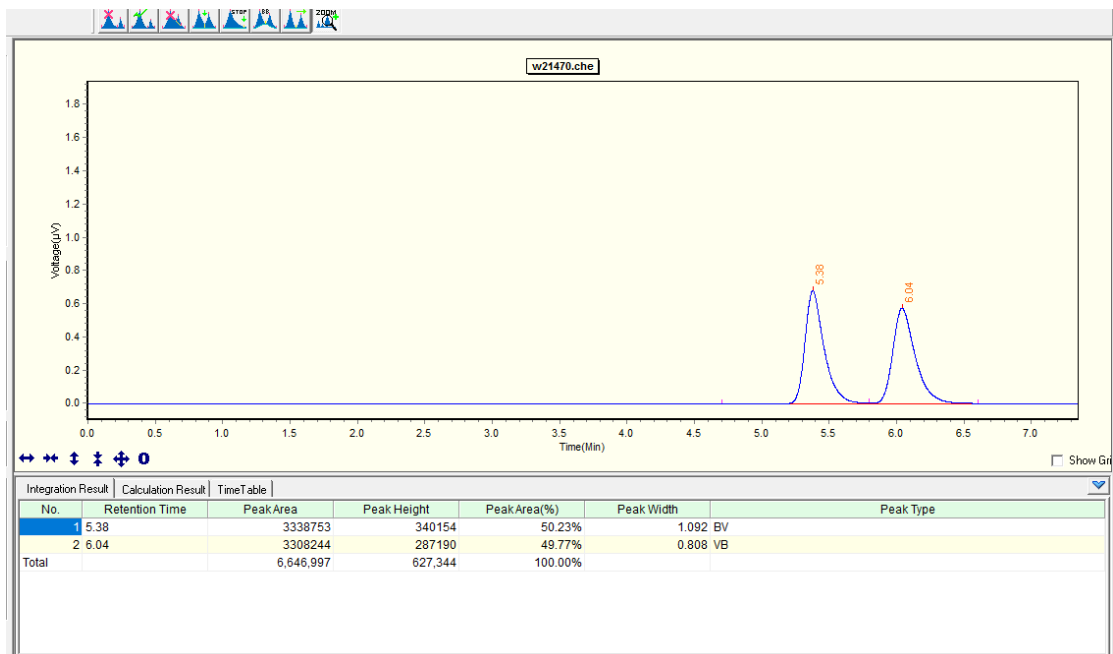
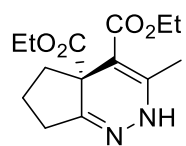
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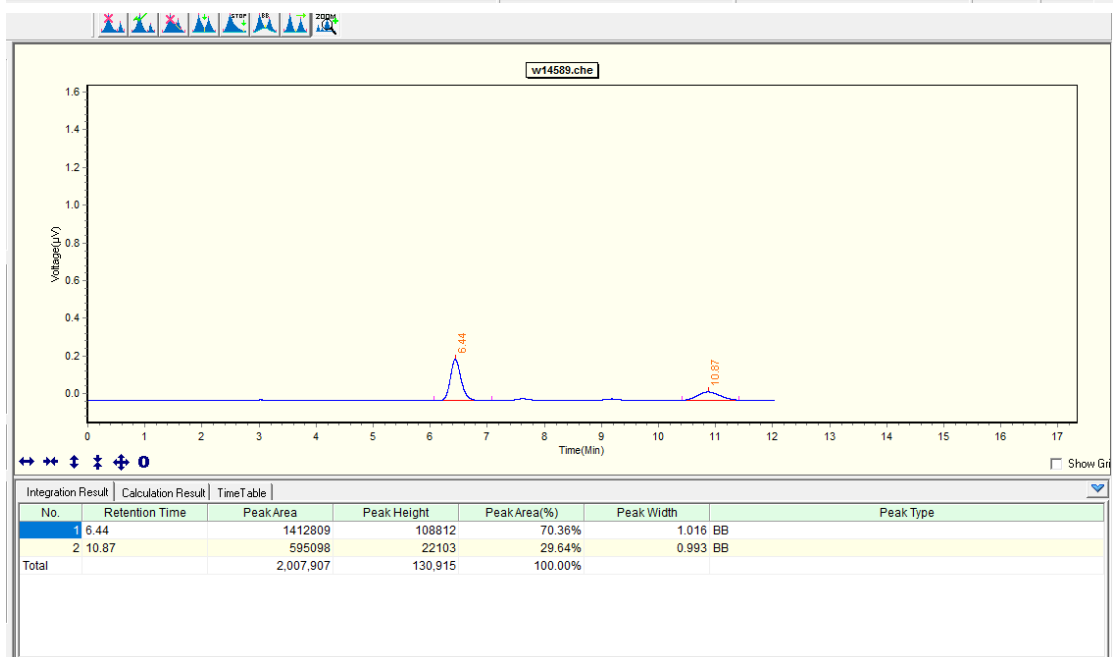
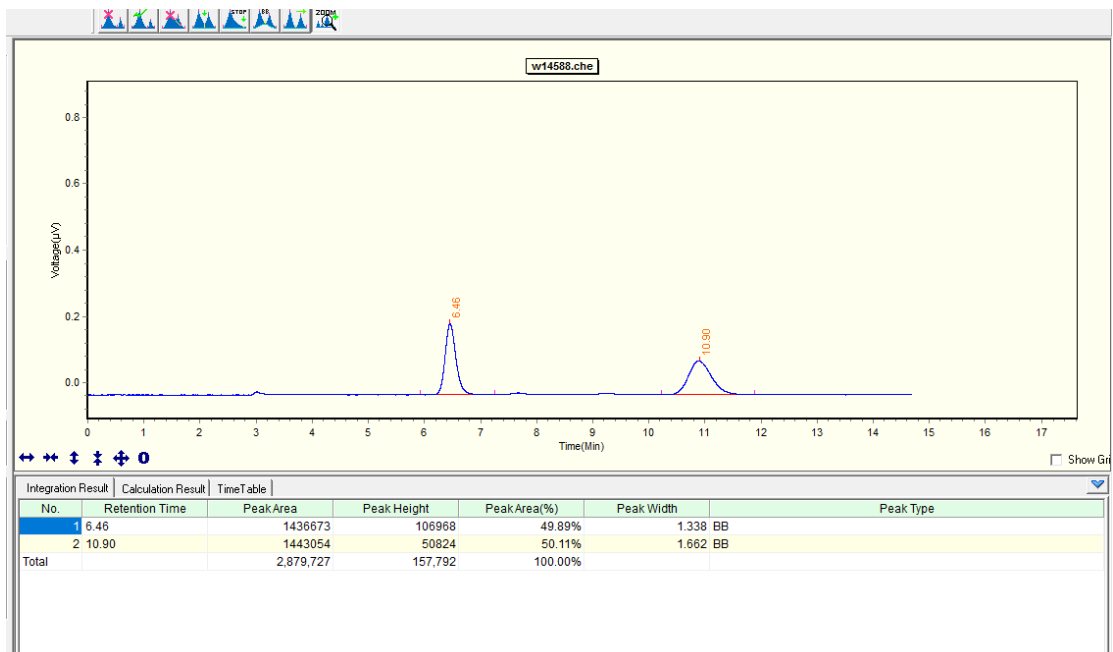
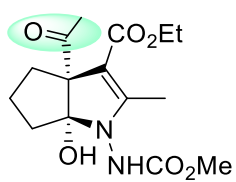
8 from 7



8 from 3e



S1



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