

# Supporting Information

## The Construction of Chiral 3-Acyl Bicyclopentanes via a RuPHOX/Pd Catalyzed Asymmetric Allylic Substitution Cascade of $\alpha$ - Carbonylamides

Siqi Dong,<sup>a</sup> Shaofeng Xu,<sup>a</sup> Yashi Zou,<sup>a</sup> Zhaodi Li,<sup>a</sup> Kai Xu,<sup>b</sup> Daxu Fu,<sup>\*b</sup> Delong Liu,<sup>\*a</sup> and  
Wanbin Zhang<sup>a,c</sup>

<sup>a</sup> Shanghai Key Laboratory for Molecular Engineering of Chiral Drugs, School of Pharmacy,  
Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, P.R. China.

<sup>b</sup> Shanghai Institute for Biomedical and Pharmaceutical Technologies, 779 Laohumin Road,  
Shanghai 200237, P.R. China.

<sup>c</sup> Frontier Science Center for Transformative Molecules, School of Chemistry and Chemical  
Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, P.R. China.

Supporting information for this article is given via a link at the end of the document.

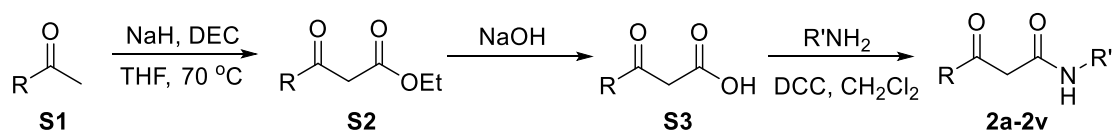
## Table of Contents

1. General Information.....	1
2. Preparation of $\alpha$ -Carbonylamides .....	1
3. Pd-Catalyzed Allylic Substitution Cascade .....	10
4. Mechanism Experiments.....	22
5. Large Scale Reaction and Transformations .....	28
6. NMR Spectra .....	33
7. HPLC Data.....	94
8. X-Ray Crystal Structure Analysis .....	122
9. Calculation Experiment .....	124
10. References.....	153

## 1. General Information

Unless specified otherwise, all reactions were carried out under nitrogen atmosphere using dried glassware. Solvents were dried and distilled according to standard procedures before use. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F254 plates. Compounds were visualized by exposure to UV light. Flash column chromatography was performed with silica gel (100-200 mesh). NMR spectra were recorded on a 400 or 500 MHz spectrometer at ambient temperature, and chemical shifts were given in dimensionless  $\delta$  values and were frequency referenced to tetramethylsilane (TMS) in  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectroscopy. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiple. The coupling constants,  $J$ , are reported in Hertz (Hz). HRMS data were recorded on a Vanquish UHPLC system (ThermoFisher, consisting of a binary pump, a vacuum degasser, an autosampler and a columnoven) & Q Exactive plus Mass spectrometer (ThermoFisher).

## 2. Preparation of $\alpha$ -Carbonylamides



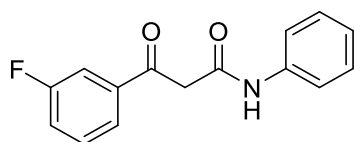
**2a**, **2h** and **2u**, **6** are known compounds.

**Step 1:** To a stirred solution of ketone (20 mmol) in THF (50 mL), was added diethyl carbonate (DEC, 40 mmol) and NaH (100 mmol, 60%). The reaction mixture was heated at reflux at 70 °C overnight. After cooling to room temperature, the reaction mixture was quenched by the addition of ice-cold water and extracted with ethyl acetate (50 mL  $\times$  3). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to obtain the corresponding  $\beta$ -ketoesters **S2** (yields up to 99%).

**Step 2:**  $\beta$ -ketoesters **S2** (20 mmol, 1.0 equiv) and aqueous NaOH (2 M, 20 mL) are stirred for 12 h at room temperature. Upon completion, the reaction mixture was diluted with ethyl acetate (20 mL) and the two phases were separated. The aqueous phase was washed with ethyl acetate (2  $\times$  2 mL), and cooled to 0 °C before it was acidified with aqueous HCl (1 M) to pH 1~2. If a precipitate was observed, the  $\beta$ -ketoacid (**S3**) was filtered, washed with H<sub>2</sub>O, dried under vacuum, and used without further purification (yields up to 90%). Otherwise, the reaction contents were extracted with CH<sub>2</sub>Cl<sub>2</sub> (3  $\times$

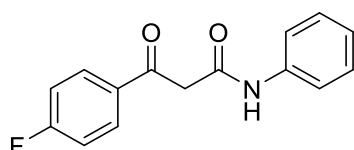
50 mL), and the combined organic extracts were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated (bath set to less than 30 °C) to give the desired  $\beta$ -ketoacids **S3** (yields up to 90%) which were used without further purification.

**Step3:** To a solution of *N*-substituted aniline (10 mmol) in DCM (50 mL) was added **S3** (10 mmol, 1.0 equiv) and DCC (2.06 g, 10 mmol, 1.0 equiv). The reaction mixture was stirred at room temperature until TLC indicated the total consumption of the substrate. The mixture was filtered through a short pad of silica gel, and the filtrate was evaporated to partially remove the solvent. The residue was treated with saturated aqueous NaHCO<sub>3</sub> (50 mL) followed by aqueous HCl (1 M) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (50 mL  $\times$  3). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under vacuum, and the crude product was purified by silica gel flash column chromatography to give the corresponding 3-oxo-*N*-propanamides **2b-2v**.



**2b**

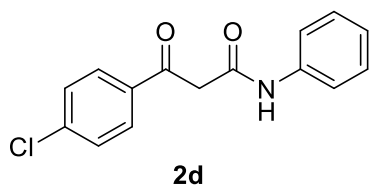
**3-(3-Fluorophenyl)-3-oxo-*N*-phenylpropanamide (2b):** Purified by flash column chromatography (petroleum ether/ethyl acetate = 5/1) to give a white solid (2.0 g, 38%, keto/enol = 10/3). Mp: 108~109 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 9.08 (s, 1H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.62 (dt, *J* = 9.3, 2.1 Hz, 1H), 7.53–7.33 (m, 5H), 7.18 (s, 1H), 7.05 (t, *J* = 7.4 Hz, 1H), 4.01 (s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 195.0, 164.1, 163.5, 138.0 (d, *J* = 6.1 Hz), 137.4, 130.7 (d, *J* = 7.1 Hz), 129.1, 124.8, 124.5 (d, *J* = 3.0 Hz), 121.4 (d, *J* = 22.2 Hz), 120.2, 115.3 (d, *J* = 25.3 Hz), 45.9; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  = -110.8; IR (KBr) (v/cm<sup>-1</sup>): 3321, 3076, 2926, 2853, 1720, 1653, 1644, 1599, 1546, 756, 687; HRMS (ESI) calcd for C<sub>15</sub>H<sub>12</sub>FNNaO<sub>2</sub> (M+Na)<sup>+</sup> 280.0744, found 280.0740.



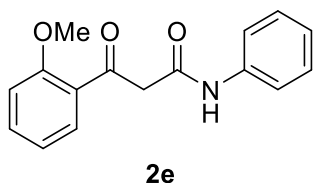
**2c**

**3-(4-Fluorophenyl)-3-oxo-*N*-phenylpropanamide (2c):** Purified by flash column chromatography (petroleum ether/ethyl acetate = 5/1) to give a white solid (1.2 g, 23%). Mp: 130~131 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 9.17 (s, 1H), 8.05 (dd, *J* = 8.7, 5.4 Hz, 2H), 7.55 (d, *J* = 7.9 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.19–7.02 (m, 3H), 4.06 (s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 194.7, 165.2, 163.6, 137.5, 132.5, 131.5 (d, *J* = 10.1 Hz), 129.0, 124.7, 120.2, 116.2 (d, *J* = 22.2 Hz), 45.8; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)

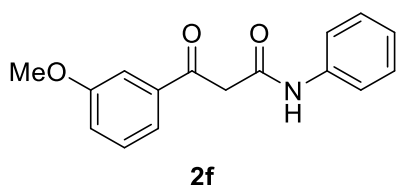
$\delta = -102.4$ ; IR (KBr) ( $\text{v}/\text{cm}^{-1}$ ): 3292, 3070, 2932, 2854, 1680, 1660, 1595, 1534, 1443, 841, 752, 689; HRMS (ESI) calcd for  $\text{C}_{15}\text{H}_{12}\text{FNNaO}_2$  ( $\text{M}+\text{Na}$ ) $^+$  280.0744, found 280.0738.



**3-(4-Chlorophenyl)-3-oxo-N-phenylpropanamide (2d):** Purified by flash column chromatography (petroleum ether/ethyl acetate = 5/1) to give a white solid (1.9 g, 35%, ketone/enolate = 5/1). Mp: 131~132 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 9.17$  (s, 1H), 7.73–7.32 (m, 8H), 7.15 (t,  $J = 7.4$  Hz, 1H), 4.10 (s, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 195.1, 163.4, 141.0, 137.4, 134.3, 130.0, 129.3, 129.0, 128.8, 127.2, 124.7, 120.1, 77.2, 45.7$ ; IR (KBr) ( $\text{v}/\text{cm}^{-1}$ ): 3277, 2929, 2840, 1691, 1651, 1544, 1514, 1420, 825, 748, 689; HRMS (ESI) calcd for  $\text{C}_{15}\text{H}_{12}^{35}\text{ClNaNO}_2$  ( $\text{M}+\text{Na}$ ) $^+$  296.0449, found 296.0445, calcd for  $\text{C}_{15}\text{H}_{12}^{37}\text{ClNaNO}_2$  ( $\text{M}+\text{Na}$ ) $^+$  298.0420, found 298.0412.



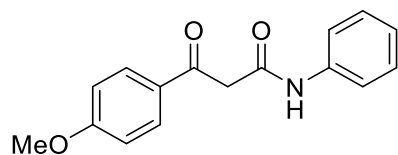
**3-(2-Methoxyphenyl)-3-oxo-N-phenylpropanamide (2e):** Purified by flash column chromatography (petroleum ether/ethyl acetate = 3/1) to give a white solid (2.5 g, 46%). Mp: 117~118 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 9.34$  (s, 1H), 7.77 (dd,  $J = 7.7, 1.8$  Hz, 1H), 7.64–7.58 (m, 2H), 7.56–7.50 (m, 1H), 7.33 (t,  $J = 7.9$  Hz, 2H), 7.15–7.08 (m, 1H), 7.07–6.96 (m, 2H), 4.15 (s, 2H), 3.91 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 198.2, 164.8, 159.0, 137.9, 135.0, 130.7, 129.0, 127.2, 124.3, 120.8, 120.1, 111.7, 55.6, 50.4$ ; IR (KBr) ( $\text{v}/\text{cm}^{-1}$ ): 3307, 3203, 3062, 2932, 2847, 1666, 1660, 1595, 1548, 1446, 1337, 1252, 754, 691; HRMS (ESI) calcd for  $\text{C}_{16}\text{H}_{16}\text{NO}_3$  ( $\text{M}+\text{H}$ ) $^+$  270.1125, found 270.1121.



**3-(3-Methoxyphenyl)-3-oxo-N-phenylpropanamide (2f):** Purified by flash column chromatography (petroleum ether/ethyl acetate = 3/1) to give a white solid (2.6 g, 48%). Mp: 121~122 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 9.35$  (s, 1H), 7.63–7.57 (m, 3H),

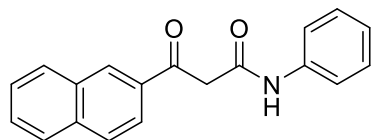


7.55–7.51 (m, 1H), 7.41 (t,  $J = 7.9$  Hz, 1H), 7.34 (t,  $J = 7.9$  Hz, 2H), 7.20–7.10 (m, 2H), 4.10 (s, 2H), 3.86 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 196.2, 164.0, 160.0, 137.6, 137.4, 130.0, 129.0, 124.6, 121.3, 120.9, 120.2, 112.6, 55.5, 45.8$ ; IR (KBr) ( $\text{v}/\text{cm}^{-1}$ ): 3292, 3206, 3059, 2926, 2832, 1687, 1656, 1609, 1544, 1443, 1342, 1342, 1256, 758, 685; HRMS (ESI) calcd for  $\text{C}_{16}\text{H}_{16}\text{NO}_3$  ( $\text{M}+\text{H}$ ) $^+$  270.1125, found 270.1120.



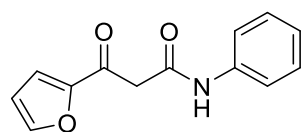
**2g**

**3-(4-Methoxyphenyl)-3-oxo-N-phenylpropanamide (2g):** Purified by flash column chromatography (petroleum ether/ethyl acetate = 3/1) to give a white solid (2.7 g, 46%). Mp: 96~97 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 9.39$  (s, 1H), 8.03 (d,  $J = 8.9$  Hz, 2H), 7.58 (d,  $J = 7.9$  Hz, 2H), 7.33 (t,  $J = 7.9$  Hz, 2H), 7.12 (t,  $J = 7.4$  Hz, 1H), 6.98 (d,  $J = 8.9$  Hz, 2H), 4.06 (s, 2H), 3.90 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 194.6, 164.5, 164.4, 137.8, 131.1, 129.1, 129.0, 124.4, 120.2, 114.1, 55.6, 45.4, 34.0, 25.6, 25.0$ ; IR (KBr) ( $\text{v}/\text{cm}^{-1}$ ): 3319, 3138, 3062, 2930, 2847, 1685, 1538, 1512, 1468, 1350, 1254, 1194, 758, 690; HRMS (ESI) calcd for  $\text{C}_{16}\text{H}_{15}\text{NNaO}_3$  ( $\text{M}+\text{Na}$ ) $^+$  292.0944, found 292.0939.



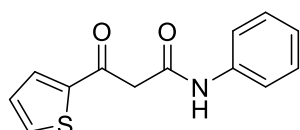
**2i**

**3-(Naphthalen-2-yl)-3-oxo-N-phenylpropanamide (2i):** Purified by flash column chromatography (petroleum ether/ethyl acetate = 3/1) to give a white solid (1.2 g, 40%). Mp: 131~132 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 9.41$  (s, 1H), 8.58 (s, 1H), 8.06 (dd,  $J = 8.6, 1.8$  Hz, 1H), 7.99 (d,  $J = 8.1$  Hz, 1H), 7.91 (dd,  $J = 11.8, 8.3$  Hz, 2H), 7.69–7.50 (m, 5H), 7.35 (t,  $J = 7.9$  Hz, 2H), 7.15 (t,  $J = 7.4$  Hz, 1H), 4.26 (s, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 196.3, 164.0, 137.6, 136.1, 133.4, 132.4, 131.2, 129.9, 129.3, 129.0, 128.9, 127.8, 127.2, 124.6, 123.5, 120.2, 45.7$ ; IR (KBr) ( $\text{v}/\text{cm}^{-1}$ ): 3307, 3138, 3055, 2926, 2851, 1682, 1664, 1603, 1544, 1443, 1337, 1313, 1188, 748, 699; HRMS (ESI) calcd for  $\text{C}_{19}\text{H}_{16}\text{NO}_2$  ( $\text{M}+\text{H}$ ) $^+$  290.1176, found 290.1172.



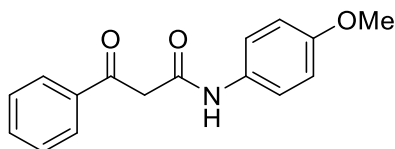
**2j**

**3-(Furan-2-yl)-3-oxo-*N*-phenylpropanamide (2j):** Purified by flash column chromatography (petroleum ether/ethyl acetate = 5/1) to give a white solid (1.1 g, 45%). Mp: 104~106 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 9.17 (s, 1H), 7.56 (s, 1H), 7.47 (d, *J* = 7.5 Hz, 2H), 7.32–7.19 (m, 3H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.49 (dd, *J* = 3.7, 1.7 Hz, 1H), 3.87 (s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 184.1, 163.5, 151.7, 148.1, 137.6, 129.0, 124.6, 120.2, 120.0, 113.0, 45.4; IR (KBr) (v/cm<sup>-1</sup>): 3315, 3139, 2924, 2855, 1682, 1656, 1599, 1546, 1447, 1333, 1248, 752, 694; HRMS (ESI) calcd for C<sub>13</sub>H<sub>11</sub>NNaO<sub>3</sub> (M+Na)<sup>+</sup> 252.0631, found 252.0627.



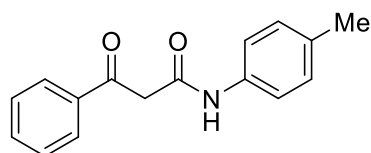
**2k**

**3-Oxo-*N*-phenyl-3-(thiophen-2-yl) propanamide (2k):** Purified by flash column chromatography (petroleum ether/ethyl acetate = 5/1) to give a white solid (0.9 g, 38%). Mp: 129~130 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 9.25 (s, 1H), 7.76 (d, *J* = 3.9 Hz, 1H), 7.66 (d, *J* = 5.0 Hz, 1H), 7.48 (d, *J* = 7.9 Hz, 2H), 7.22 (t, *J* = 7.9 Hz, 2H), 7.12–6.98 (m, 2H), 3.96 (s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 188.7, 163.5, 143.2, 137.6, 136.1, 134.2, 129.0, 128.8, 124.6, 120.2, 46.3; IR (KBr) (v/cm<sup>-1</sup>): 3309, 3206, 3145, 3084, 1656, 1605, 1542, 1496, 1445, 1335, 1240, 756, 692; HRMS (ESI) calcd for C<sub>13</sub>H<sub>11</sub>NNaO<sub>2</sub>S (M+Na)<sup>+</sup> 268.0403, found 268.0398.



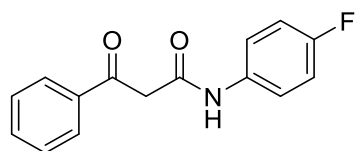
**2l**

***N*-(4-Methoxyphenyl)-3-oxo-3-phenylpropanamide (2l):** Purified by flash column chromatography (petroleum ether/ethyl acetate = 3/1) to give a white solid (1.2 g, 44%). Mp: 120~122 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 9.15 (s, 1H), 8.01 (d, *J* = 7.3 Hz, 2H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.48 (dd, *J* = 16.9, 8.4 Hz, 4H), 6.84 (d, *J* = 8.8 Hz, 2H), 4.08 (s, 2H), 3.77 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 196.5, 163.8, 156.6, 136.1, 134.3, 130.7, 129.0, 128.6, 128.5, 122.0, 114.1, 55.5, 45.5; IR (KBr) (v/cm<sup>-1</sup>): 3286, 3132, 3057, 2937, 2847, 1711, 1652, 1544, 1512, 1462, 1336, 1236, 757, 685; HRMS (ESI) calcd for C<sub>16</sub>H<sub>16</sub>NO<sub>3</sub> (M+H)<sup>+</sup> 270.1125, found 270.1120.



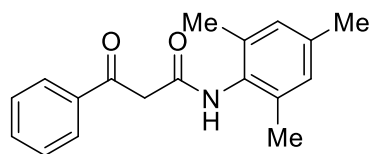
**2m**

**3-Oxo-3-phenyl-N-(p-tolyl) propenamide (2m):** Purified by flash column chromatography (petroleum ether/ethyl acetate = 3/1) to give a white solid (1.9 g, 76%). Mp: 92~93 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.25 (s, 1H), 8.10–8.00 (m, 2H), 7.69–7.61 (m, 1H), 7.56–7.46 (m, 4H), 7.15 (d,  $J$  = 8.1 Hz, 2H), 4.12 (s, 2H), 2.34 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 196.5, 163.7, 136.1, 135.0, 134.3, 134.2, 129.5, 129.0, 128.6, 120.3, 45.6, 20.9; IR (KBr) ( $\text{v}/\text{cm}^{-1}$ ): 3319, 3206, 3053, 2924, 2843, 1680, 1653, 1542, 1512, 1412, 1335, 1265, 756, 687; HRMS (ESI) calcd for  $\text{C}_{16}\text{H}_{16}\text{NO}_2$  ( $\text{M}+\text{H}$ ) $^+$  254.1176, found 254.1172.



**2n**

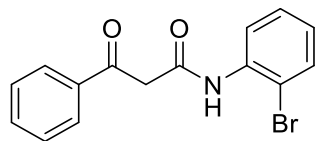
**N-(4-Fluorophenyl)-3-oxo-3-phenylpropanamide (2n):** Purified by flash column chromatography (petroleum ether/ethyl acetate = 5/1) to give a white solid (2.1 g, 0.83 %). Mp: 148~149 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.35 (s, 1H), 8.01 (d,  $J$  = 7.2 Hz, 2H), 7.63 (t,  $J$  = 7.4 Hz, 1H), 7.56–7.46 (m, 4H), 7.00 (t,  $J$  = 8.6 Hz, 2H), 4.09 (s, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 194.7, 166.5 (d,  $J$  = 162.6 Hz), 136.6, 134.5, 133.0, 129.0, 128.6, 122.0, 121.9, 115.7 (d,  $J$  = 22.2 Hz), 45.2;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  = -117.7; IR (KBr) ( $\text{v}/\text{cm}^{-1}$ ): 3266, 3215, 3088, 2953, 2844, 1690, 1662, 1557, 1506, 1410, 1340, 1208, 831, 754, 687; HRMS (ESI) calcd for  $\text{C}_{15}\text{H}_{12}\text{FNNaO}_2$  ( $\text{M}+\text{Na}$ ) $^+$  280.0744, found 280.0739.



**2o**

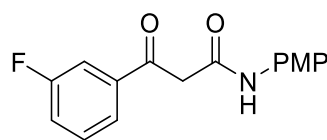
**N-Mesityl-3-oxo-3-phenylpropanamide (2o):** Purified by flash column chromatography (petroleum ether/ethyl acetate = 5/1) to give a white solid (1.4 g, 50%). Mp: 177~178 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.46 (s, 1H), 8.08–8.01 (m, 2H), 7.67–7.56 (m, 1H), 7.55–7.49 (m, 2H), 6.88 (s, 2H), 4.15 (s, 2H), 2.25 (s, 3H), 2.16 (s, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 196.4, 164.3, 137.0, 136.1, 135.0, 134.3, 131.0, 129.0, 128.9, 128.7, 45.4, 20.9, 18.4; IR (KBr) ( $\text{v}/\text{cm}^{-1}$ ): 3211, 3068, 2926, 2843, 1696,

1649, 1592, 1534, 1447, 1342, 1216, 753, 681; HRMS (ESI) calcd for C<sub>18</sub>H<sub>20</sub>NO<sub>2</sub> (M+H)<sup>+</sup> 282.1489, found 282.1484.



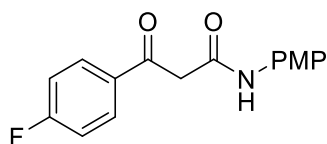
**2p**

***N*-(2-Bromophenyl)-3-oxo-3-phenylpropanamide (2p)**: Purified by flash column chromatography (petroleum ether/ethyl acetate = 3/1) to give a white solid (1.5 g, 47%). Mp: 124~125 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 9.72 (s, 1H), 8.36 (dd, *J* = 8.3, 1.6 Hz, 1H), 8.06 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.60–7.42 (m, 4H), 7.38–7.29 (m, 1H), 4.19 (s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 195.9, 164.0, 136.0, 135.9, 134.4, 132.5, 129.0, 128.6, 128.2, 126.0, 125.5, 122.4, 45.7; IR (KBr) (v/cm<sup>-1</sup>): 3189, 3100, 3026, 2942, 2891, 1688, 1662, 1578, 1538, 1439, 1364, 1210, 754, 745; HRMS (ESI) calcd for C<sub>15</sub>H<sub>13</sub><sup>79</sup>BrNO<sub>2</sub> (M+H)<sup>+</sup> 318.0124, found 318.0121, calcd for C<sub>15</sub>H<sub>13</sub><sup>81</sup>BrNO<sub>2</sub> (M+H)<sup>+</sup> 320.0104, found 320.0097.



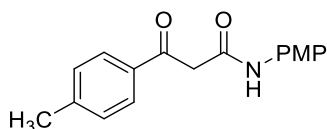
**2q**

**3-(3-Fluorophenyl)-*N*-(4-methoxyphenyl)-3-oxopropanamide (2q)**: Purified by flash column chromatography (petroleum ether/ethyl acetate = 3/1) to give a white solid (0.9 g, 31%, ketone/enolate = 4/1). Mp: 131~132 °C; <sup>1</sup>H NMR (ketone) (400 MHz, CDCl<sub>3</sub>) δ = 9.00 (s, 1H), 7.81 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.71 (dt, *J* = 9.2, 2.2 Hz, 1H), 7.48–7.45 (m, 2H), 7.35 (dd, *J* = 8.2, 2.6 Hz, 1H), 6.88–6.84 (m, 2H), 4.07 (s, 2H), 3.79 (s, 3H); <sup>1</sup>H NMR (enol) (400 MHz, CDCl<sub>3</sub>) δ = 14.10 (s, 1H), 7.52 (d, *J* = 5.4 Hz, 2H), 7.50 (d, *J* = 5.5 Hz, 2H), 7.42 (s, 1H), 7.32 (d, *J* = 2.5 Hz, 1H), 6.89 (d, *J* = 3.9 Hz, 2H), 5.61 (s, 1H), 3.80 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 195.2, 163.2, 162.9 (d, *J* = 231.3 Hz), 156.7, 138.1, 130.7 (d, *J* = 7.1 Hz), 130.5, 124.5, 122.0, 121.4 (d, *J* = 22.2 Hz), 115.3 (d, *J* = 22.2 Hz), 114.2, 55.5, 45.8; <sup>19</sup>F NMR (ketone) (376 MHz, CDCl<sub>3</sub>) δ = -110.9; <sup>19</sup>F NMR (enol) (376 MHz, CDCl<sub>3</sub>) δ = -112.5; IR (KBr) (v/cm<sup>-1</sup>): 3276, 3206, 3063, 2934, 2840, 1702, 1664, 1595, 1541, 1512, 1338, 1238, 759, 685; HRMS (ESI) calcd for C<sub>16</sub>H<sub>15</sub>FNO<sub>3</sub> (M+H)<sup>+</sup> 288.1030, found 288.1028.



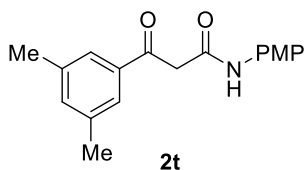
**2r**

**3-(4-Fluorophenyl)-N-(4-methoxyphenyl)-3-oxopropanamide (2r):** Purified by flash column chromatography (petroleum ether/ethyl acetate = 3/1) to give a white solid (1.1 g, 39%). Mp: 149~150 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.03 (s, 1H), 8.07 (dd,  $J$  = 8.7, 5.5 Hz, 2H), 7.46 (d,  $J$  = 9.0 Hz, 2H), 7.18 (t,  $J$  = 8.5 Hz, 2H), 6.86 (d,  $J$  = 8.9 Hz, 2H), 4.06 (s, 2H), 3.79 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 194.8, 166.5 (d,  $J$  = 257.6 Hz), 163.4, 156.6, 132.5, 131.5 (d,  $J$  = 10.1 Hz), 130.6, 121.98, 116.2 (d,  $J$  = 22.2 Hz), 114.2, 55.5, 45.7;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  = -102.7; IR (KBr) ( $\text{v}/\text{cm}^{-1}$ ): 3276, 3209, 3067, 2934, 2835, 1690, 1666, 1595, 1538, 1412, 1238, 1159, 758, 685; HRMS (ESI) calcd for  $\text{C}_{16}\text{H}_{15}\text{FNO}_3$  ( $\text{M}+\text{H}$ ) $^+$  288.1030, found 288.1027.



**2s**

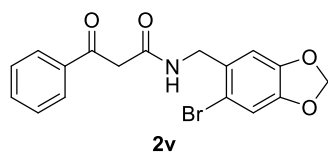
**N-(4-Methoxyphenyl)-3-oxo-3-(p-tolyl) propanamide (2s):** Purified by flash column chromatography (petroleum ether/ethyl acetate = 3/1) to give a white solid (1.8 g, 64%). Mp: 146~147 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.22 (s, 1H), 7.97–7.90 (m, 2H), 7.54–7.45 (m, 2H), 7.31 (d,  $J$  = 8.0 Hz, 2H), 6.89–6.83 (m, 2H), 4.07 (s, 2H), 3.79 (s, 3H), 2.44 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 196.1, 163.9, 156.5, 145.5, 133.7, 130.8, 129.7, 128.8, 122.0, 114.1, 55.5, 45.3, 21.8; IR (KBr) ( $\text{v}/\text{cm}^{-1}$ ): 3284, 3222, 3083, 2965, 2835, 1703, 1652, 1544, 1514, 1412, 1295, 1244, 829, 750; HRMS (ESI) calcd for  $\text{C}_{17}\text{H}_{18}\text{NO}_3$  ( $\text{M}+\text{H}$ ) $^+$  284.1281, found 284.1278.



**2t**

**3-(3,5-Dimethylphenyl)-N-(4-methoxyphenyl)-3-oxopropanamide (2t):** Purified by flash column chromatography (petroleum ether/ethyl acetate = 3/1) to give a white solid (1.1 g, 37%). Mp: 126~127 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.21 (s, 1H), 7.62 (d,  $J$  = 8.1 Hz, 2H), 7.51–7.45 (m, 2H), 6.91–6.82 (m, 3H), 4.07 (s, 2H), 3.79 (s, 3H), 2.39 (s, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 196.7, 164.2, 156.5, 138.6, 136.2, 135.9, 130.9, 126.4, 122.0, 114.1, 55.4, 45.6, 21.2; IR (KBr) ( $\text{v}/\text{cm}^{-1}$ ): 3321, 3136, 3002, 2920, 2859, 1678, 1650, 1605, 1552, 1458, 1336, 1173, 1034, 833; HRMS (ESI) calcd for

C<sub>18</sub>H<sub>20</sub>NO<sub>3</sub> (M+H)<sup>+</sup> 298.1438, found 298.1433.



2v

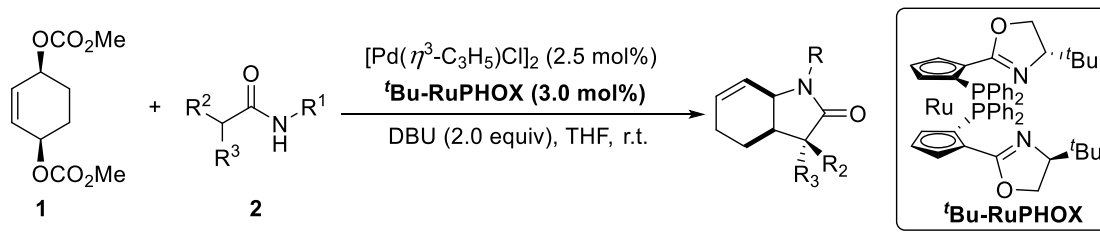
**N-((6-Bromobenzo[*d*][1,3]dioxol-5-yl)methyl)-3-oxo-3-phenylpropanamide (2v):**

Purified by flash column chromatography (DCM/MeOH = 25/1) to give a white solid (0.65 g, 23%, ketone/enolate = 7/1). Mp: 147~148 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 8.00 (q, *J* = 1.7 Hz, 1H), 7.97 (d, *J* = 1.6 Hz, 1H), 7.67 – 7.57 (m, 2H), 7.49 (dd, *J* = 8.4, 7.1 Hz, 2H), 6.99 (d, *J* = 4.1 Hz, 1H), 6.90 (s, 1H), 5.95 (s, 2H), 4.47 (d, *J* = 6.0 Hz, 2H), 3.98 (s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 199.71, 163.81, 150.19, 147.49, 138.39, 132.98, 130.28, 128.89, 128.58, 126.18, 114.66, 112.76, 110.19, 101.82, 45.13, 43.83; HRMS (ESI) calcd for C<sub>17</sub>H<sub>14</sub><sup>79</sup>BrNNaO<sub>4</sub> (M+Na)<sup>+</sup> 397.9998, found 397.9995, calcd for C<sub>17</sub>H<sub>14</sub><sup>81</sup>BrNNaO<sub>4</sub> (M+Na)<sup>+</sup> 399.9978, found 399.9976.

### 3. Pd-Catalyzed Allylic Substitution Cascade

#### 3.1 Reaction conditions screening

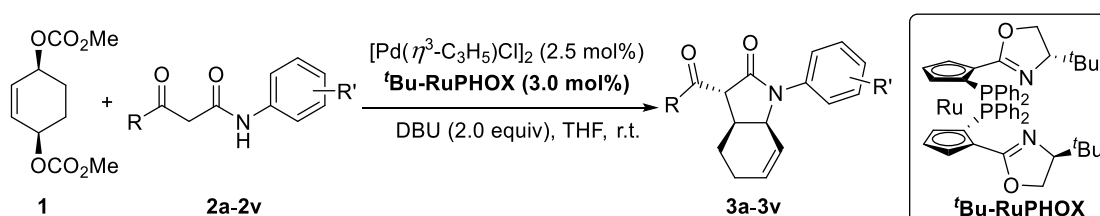
Table S1. Selection of substrates<sup>a</sup>



entry	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	yield% <sup>b</sup>	ee% <sup>c</sup>	Dr <sup>d</sup>
1	Ts	CO <sub>2</sub> Et	H	trace	-	-
2	Ts	CO <sub>2</sub> Et	H	40	-	-
3	Ts	CO <sub>2</sub> Et	H	trace	-	-
4	Bn	CN	H	trace	-	-
5	Ph	Bz	F	98	89	1:1
6	Bn	Bz	F	98	96/93	2:1
7	<sup>t</sup> Bu	Bz	F	trace	-	-
<b>8</b>	<b>Ph</b>	<b>Bz</b>	<b>H</b>	<b>93</b>	<b>97/-</b>	<b>&gt;20:1</b>
9	Bn	Bz	H	47	n.d.	3:1
10 <sup>e</sup>	Ph	Bz	H	78	61	>20:1

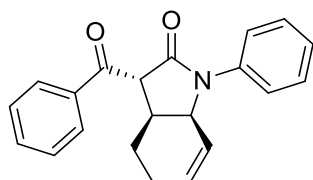
[a] Unless otherwise noted, the reaction of **1** (0.3 mmol) and **2** (0.20 mmol) was conducted using [Pd( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)Cl]<sub>2</sub> (2.5 mol%) and <sup>t</sup>Bu-RuPHOX (3.0 mol%) as the chiral catalyst in the presence of DBU (2.0 equiv) in THF (2.0 mL) under a N<sub>2</sub> atmosphere at 25 °C for 3 h; [b] Isolated yield; [c] Determined by HPLC analysis using a chiral Daicel OD-H and OJ columns; [d] Determined by <sup>1</sup>H NMR spectra; [e] Using the *mono*-<sup>t</sup>Bu-RuPHOX (5.95 mg, 5.5 mol%) as chiral ligand.

#### 3.2 General Procedures for Enantioselective Catalysis



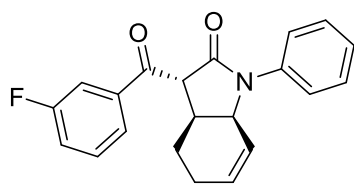
A flame-dried Schlenk tube equipped with a magnetic stirring bar, was charged with a mixture of [Pd( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)Cl]<sub>2</sub> (1.83 mg, 2.5 mol%) and RuPHOX (5.10 mg, 3.0 mol%). After being evacuated and backfilled with nitrogen three times, THF (2 mL) was added

to the Schlenk tube and the mixture was stirred at room temperature under N<sub>2</sub> atmosphere for 1 h. Allylic biscarbonate **1** (51 mg, 0.22 mmol, 1.1 equiv) was added via a syringe followed by the addition of 3-oxo-*N*,3-diphenylpropanamide **2a-2v** (0.2 mmol, 1.0 equiv) and DBU (0.4 mmol, 2.0 equiv). The reaction mixture was allowed to stir under N<sub>2</sub> atmosphere at room temperature for 3 h. THF was evaporated in vacuo and the residue was purified by flash silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to give final products **3a-3v**.



**3a**

**(3R,3aS,7aS)-3-Benzoyl-1-phenyl-1,3,3a,4,5,7a-hexahydro-2H-indol-2-one (3a):** Colorless oil (59 mg, 93%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 8.18–8.09 (m, 2H), 7.63–7.53 (m, 1H), 7.52–7.46 (m, 3H), 7.45 (d, *J* = 1.2 Hz, 1H), 7.37 (dd, *J* = 8.6, 7.2 Hz, 2H), 7.23–7.15 (m, 1H), 5.99 (dtd, *J* = 10.2, 3.8, 1.3 Hz, 1H), 5.76 (dq, *J* = 10.2, 2.3 Hz, 1H), 4.81 (ddd, *J* = 6.7, 3.3, 1.7 Hz, 1H), 4.46 (d, *J* = 5.8 Hz, 1H), 3.31–3.14 (m, 1H), 2.13 (dh, *J* = 7.5, 3.9 Hz, 2H), 1.96–1.82 (m, 1H), 1.78–1.69 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 195.5, 169.7, 137.4, 136.6, 133.6, 131.8, 129.5, 129.0, 128.6, 126.4, 123.7, 123.5, 56.8, 55.3, 34.9, 26.1, 21.8; IR (KBr) (v/cm<sup>-1</sup>): 3059, 3026, 2940, 2863, 1752, 1719, 1682, 1536, 1523, 1397, 1271, 744, 693; HRMS (ESI) calcd for C<sub>21</sub>H<sub>20</sub>NO<sub>2</sub> (M+H)<sup>+</sup> 318.1489, found 318.1485; HPLC: 96% *ee*, chiral stationary column: OD-H, mobile phase: hexane/<sup>i</sup>PrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C, *t*<sub>R</sub> (major) = 11.8 min, *t*<sub>R</sub> (minor) = 21.2 min; [α]<sub>D</sub><sup>25</sup> = +51.20 (*c* 1.0, CH<sub>2</sub>Cl<sub>2</sub>).

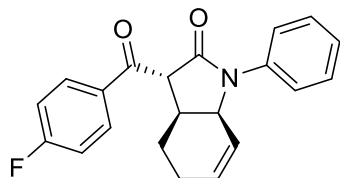


**3b**

**(3S,3aR,7aR)-3-(3-Fluorobenzoyl)-1-phenyl-1,3,3a,4,5,7a-hexahydro-2H-indol-2-one (3b):** Colorless oil (56 mg, 83%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.95 (d, *J* = 7.8 Hz, 1H), 7.82 (ddd, *J* = 9.5, 2.6, 1.6 Hz, 1H), 7.51–7.39 (m, 4H), 7.36–7.18 (m, 3H), 6.06–5.95 (m, 1H), 5.81–5.72 (m, 1H), 4.81 (ddd, *J* = 6.7, 3.3, 1.6 Hz, 1H), 4.39 (d, *J* = 5.9 Hz, 1H), 3.29–3.20 (m, 1H), 2.21–2.07 (m, 2H), 1.92–1.85 (m, 1H), 1.78–1.69 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 194.3 (d, *J* = 2.5 Hz), 168.7, 162.8 (d, *J* = 249.5 Hz), 138.6 (d, *J* = 6.4 Hz), 137.3, 131.8, 130.2 (d, *J* = 7.6 Hz), 129.1, 126.1, 125.5

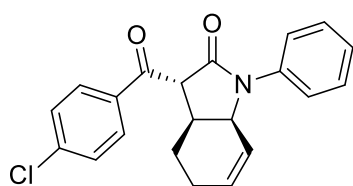


(d,  $J = 3.0$  Hz), 123.7, 123.4, 120.6 (d,  $J = 21.2$ ), 116.1 (d,  $J = 22.2$  Hz), 56.6, 54.8 34.7, 23.3, 22.4;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta = -111.8$ ; IR (KBr) ( $\text{v}/\text{cm}^{-1}$ ): 3303, 3075, 3038, 2933, 1735, 1707, 1556, 1519, 1459, 1418, 1369, 1271, 829; HRMS (ESI) calcd for  $\text{C}_{21}\text{H}_{19}\text{FNO}_2$  ( $\text{M}+\text{H}$ ) $^+$  336.1394, found 336.1390; HPLC: 91% *ee*, chiral stationary column: OJ-H, mobile phase: hexane/ $i$ PrOH = 80/20, 1.0 mL/min, 254 nm, 25 °C,  $t_{\text{R}}$  (major) = 15.0 min,  $t_{\text{R}}$  (minor) = 45.1 min;  $[\alpha]_{\text{D}}^{25} = +31.24$  ( $c$  1.0,  $\text{CH}_2\text{Cl}_2$ ).



**3c**

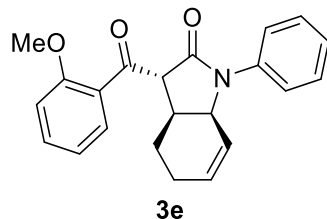
**(3S,3aR,7aR)-3-(4-Fluorobenzoyl)-1-phenyl-1,3,3a,4,5,7a-hexahydro-2H-indol-2-one (3c):** Colorless oil (57 mg, 87%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.22$ – $8.15$  (m, 2H), 7.47–7.33 (m, 4H), 7.23–7.12 (m, 3H), 6.05–5.94 (m, 1H), 5.80–5.70 (m, 1H), 4.81 (ddd,  $J = 6.8, 3.3, 1.7$  Hz, 1H), 4.39 (d,  $J = 5.8$  Hz, 1H), 3.30–3.20 (m, 1H), 2.17–2.10 (m, 2H), 1.91–1.84 (m, 1H), 1.77–1.69 (m, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 193.7, 168.8, 166.1$  (d,  $J = 256.5$  Hz), 137.3, 130.0 (d,  $J = 3.0$  Hz), 132.4 (d,  $J = 9.3$  Hz), 131.8, 129.0, 126.1, 123.7, 123.4, 115.7 (d,  $J = 22.2$  Hz), 56.4, 56.0, 34.6, 23.3, 22.4;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta = -104.1$ ; IR (KBr) ( $\text{v}/\text{cm}^{-1}$ ): 3332, 3075, 3038, 2928, 2851, 1682, 1674, 1601, 1503, 1380, 1281, 1218, 754, 693; HRMS (ESI) calcd for  $\text{C}_{21}\text{H}_{19}\text{FNO}_2$  ( $\text{M}+\text{H}$ ) $^+$  336.1394, found 336.1391; HPLC: 96% *ee*, chiral stationary column: OJ-H, mobile phase: hexane/ $i$ PrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C,  $t_{\text{R}}$  (major) = 35.9 min,  $t_{\text{R}}$  (minor) = 91.7 min;  $[\alpha]_{\text{D}}^{25} = +33.60$  ( $c$  1.0,  $\text{CH}_2\text{Cl}_2$ ).



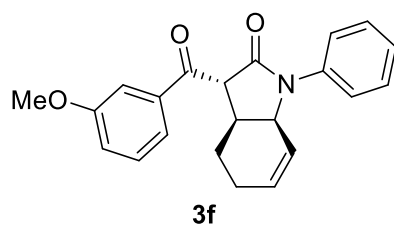
**3d**

**(3S,3aR,7aR)-3-(4-Chlorobenzoyl)-1-phenyl-1,3,3a,4,5,7a-hexahydro-2H-indol-2-one (3d):** Colorless oil (58 mg, 83%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.09$  (d,  $J = 8.6$  Hz, 2H), 7.51–7.33 (m, 6H), 7.24 (d,  $J = 14.6$  Hz, 1H), 6.06–5.96 (m, 1H), 5.82–5.71 (m, 1H), 4.80 (ddd,  $J = 6.8, 3.3, 1.7$  Hz, 1H), 4.38 (d,  $J = 5.8$  Hz, 1H), 3.32–3.18 (m, 1H), 2.23–2.07 (m, 2H), 1.91–1.84 (m, 1H), 1.77–1.70 (m, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 194.2, 168.8, 140.2, 137.3, 134.9, 131.8, 131.0, 129.1, 128.9, 126.1, 123.7, 123.4, 56.4, 56.0, 34.6, 23.3, 22.4$ ; IR (KBr) ( $\text{v}/\text{cm}^{-1}$ ): 3315, 3071, 3034, 2932, 2871, 1703, 1674, 1585, 1510, 1397, 1177, 1090, 821, 752; HRMS (ESI) calcd for  $\text{C}_{21}\text{H}_{19}^{35}\text{ClNO}_2$

(M+H)<sup>+</sup> 352.1099, found 352.1097, calcd for C<sub>21</sub>H<sub>19</sub><sup>37</sup>ClNO<sub>2</sub> (M+H)<sup>+</sup> 354.1070, found 354.1063; HPLC: 94% *ee*, chiral stationary column: OD-H, mobile phase: hexane/<sup>i</sup>PrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C, t<sub>R</sub> (major) = 11.9 min, t<sub>R</sub> (minor) = 24.2 min; [α]<sub>D</sub><sup>25</sup> = +29.20 (*c* 0.5, CH<sub>2</sub>Cl<sub>2</sub>).

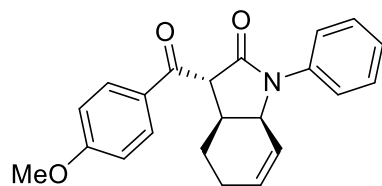


**(3*S*,3*aR*,7*aR*)-3-(2-Methoxybenzoyl)-1-phenyl-1,3,3*a*,4,5,7*a*-hexahydro-2*H*-indol-2-one (3e):** Colorless oil (37 mg, 54%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.64 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.41 (td, *J* = 9.0, 8.5, 1.5 Hz, 3H), 7.33–7.26 (m, 2H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.99–6.89 (m, 2H), 5.94–5.88 (m, 1H), 5.68–5.62 (m, 1H), 4.65 (ddd, *J* = 6.8, 3.3, 1.7 Hz, 1H), 4.55 (d, *J* = 6.2 Hz, 1H), 3.84 (s, 3H), 3.06–2.99 (m, 1H), 2.20–2.00 (m, 2H), 1.89–1.69 (m, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 198.9, 170.4, 158.4, 137.7, 134.0, 131.6, 130.9, 129.0, 128.3, 125.8, 123.7, 123.7, 121.0, 111.5, 59.8, 55.8, 55.7, 35.2, 23.6, 22.5; IR (KBr) (v/cm<sup>-1</sup>): 3356, 3063, 3031, 2924, 2853, 1711, 1704, 1599, 1500, 1463, 1378, 1218, 1017, 756; HRMS (ESI) calcd for C<sub>22</sub>H<sub>22</sub>NO<sub>3</sub> (M+H)<sup>+</sup> 348.1594, found 348.1591; HPLC: 94% *ee*, chiral stationary column: OJ-H, mobile phase: hexane/<sup>i</sup>PrOH = 80/20, 1.0 mL/min, 254 nm, 25 °C, t<sub>R</sub> (major) = 19.5 min, t<sub>R</sub> (minor) = 57.2 min; [α]<sub>D</sub><sup>25</sup> = +45.20 (*c* 1.0, CH<sub>2</sub>Cl<sub>2</sub>).



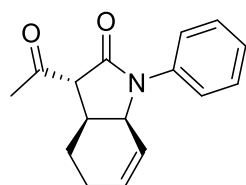
**(3*S*,3*aR*,7*aR*)-3-(3-Methoxybenzoyl)-1-phenyl-1,3,3*a*,4,5,7*a*-hexahydro-2*H*-indol-2-one (3f):** Colorless oil (60 mg, 88%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.73 (d, *J* = 7.8 Hz, 1H), 7.67–7.63 (m, 1H), 7.48–7.35 (m, 5H), 7.21 (d, *J* = 7.3 Hz, 1H), 7.14 (dd, *J* = 7.8, 3.1 Hz, 1H), 6.03–5.96 (m, 1H), 5.79–5.72 (m, 1H), 4.80 (ddd, *J* = 6.8, 3.3, 1.6 Hz, 1H), 4.43 (d, *J* = 5.6 Hz, 1H), 3.87 (s, 3H), 3.24–3.14 (m, 1H), 2.22–2.10 (m, 2H), 1.93–1.85 (m, 1H), 1.79–1.70 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 195.5, 169.2, 159.8, 138.0, 137.4, 131.8, 129.6, 129.0, 126.0, 123.8, 123.5, 122.3, 120.4, 113.3, 56.6, 56.0, 55.5, 35.1, 23.4, 22.5; IR (KBr) (v/cm<sup>-1</sup>): 3319, 3063, 3042, 2922, 2855, 1674, 1642, 1544, 1271, 1179, 1090, 1034, 744; HRMS (ESI) calcd for C<sub>22</sub>H<sub>22</sub>NO<sub>3</sub> (M+H)<sup>+</sup> 348.1594, found 348.1589; HPLC: 98% *ee*, chiral stationary column: OJ-H, mobile

phase: hexane/<sup>i</sup>PrOH = 80/20, 1.0 mL/min, 254 nm, 25 °C,  $t_R$  (major) = 22.4 min,  $t_R$  (minor) = 60.7 min;  $[\alpha]_D^{25} = +47.40$  ( $c$  1.0, CH<sub>2</sub>Cl<sub>2</sub>).



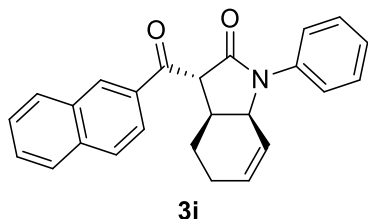
**3g**

**(3S,3aR,7aR)-3-(4-Methoxybenzoyl)-1-phenyl-1,3,3a,4,5,7a-hexahydro-2H-indol-2-one (3g):** Colorless oil (45 mg, 64%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.15–8.09 (m, 2H), 7.45 (dd,  $J$  = 8.6, 1.3 Hz, 2H), 7.40–7.33 (m, 2H), 7.22–7.17 (m, 1H), 6.99–6.94 (m, 2H), 6.02–5.96 (m, 1H), 5.78–5.72 (m, 1H), 4.80 (ddd,  $J$  = 6.8, 3.3, 1.7 Hz, 1H), 4.39 (d,  $J$  = 5.6 Hz, 1H), 3.87 (s, 3H), 3.26–3.17 (m, 1H), 2.19–2.06 (m, 2H), 1.93–1.84 (m, 1H), 1.78–1.73 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 193.8, 169.4, 164.0, 137.5, 131.9, 131.8, 129.6, 129.0, 125.9, 123.8, 123.5, 113.8, 56.2, 56.0, 55.6, 34.9, 23.4, 22.5; IR (KBr) ( $\nu/\text{cm}^{-1}$ ): 3332, 3075, 3030, 2932, 2845, 1703, 1674, 1605, 1493, 1382, 1267, 1169, 1028, 752; HRMS (ESI) calcd for C<sub>22</sub>H<sub>22</sub>NO<sub>3</sub> (M+H)<sup>+</sup> 348.1594, found 348.1590. HPLC: 96% *ee*, chiral stationary column: OD-H, mobile phase: hexane/<sup>i</sup>PrOH = 80/20, 1.0 mL/min, 254 nm, 25 °C,  $t_R$  (major) = 11.9 min,  $t_R$  (minor) = 33.5 min;  $[\alpha]_D^{25} = +29.20$  ( $c$  0.5, CH<sub>2</sub>Cl<sub>2</sub>).

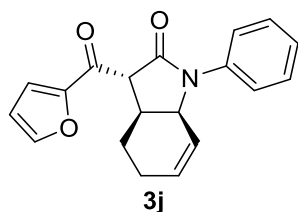


**3h**

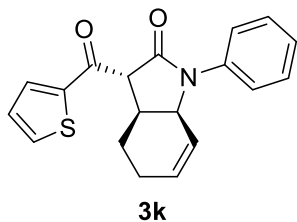
**(3S,3aR,7aR)-3-Acetyl-1-phenyl-1,3,3a,4,5,7a-hexahydro-2H-indol-2-one (3h):** Colorless oil (37 mg, 73%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.45–7.35 (m, 4H), 7.25–7.18 (m, 1H), 5.98–5.92 (m, 1H), 5.69 (dq,  $J$  = 10.2, 2.3 Hz, 1H), 4.67–4.62 (m,  $J$  = 6.5, 3.2, 1.7 Hz, 1H), 3.58 (d,  $J$  = 6.9 Hz, 1H), 3.16–3.08 (m, 1H), 2.46 (s, 3H), 2.13–2.06 (m, 2H), 1.85–1.76 (m, 2H), 1.74–1.76 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 203.4, 168.7, 137.3, 131.6, 129.1, 126.1, 123.6, 123.4, 60.6, 55.9, 32.8, 30.4, 22.9, 21.9; IR (KBr) ( $\nu/\text{cm}^{-1}$ ): 3319, 3079, 3030, 2924, 2847, 1686, 1599, 1510, 1457, 1267, 1090, 1032, 748; HRMS (ESI) calcd for C<sub>16</sub>H<sub>18</sub>NO<sub>2</sub> (M+H)<sup>+</sup> 256.1332, found 256.1329; HPLC: 95% *ee*, chiral stationary column: OJ, mobile phase: hexane/<sup>i</sup>PrOH = 80/20, 1.0 mL/min, 254 nm, 25 °C,  $t_R$  (major) = 14.8 min,  $t_R$  (minor) = 35.4 min;  $[\alpha]_D^{25} = +112.72$  ( $c$  1.0, CH<sub>2</sub>Cl<sub>2</sub>).



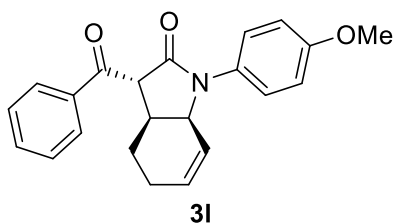
**(3*S*,3*a**R*,7*a**R*)-3-(2-Naphthoyl)-1-phenyl-1,3,3*a*,4,5,7*a*-hexahydro-2*H*-indol-2-one (3i):** Colorless oil (72 mg, 98%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.73 (s, 1H), 8.14 (dd,  $J$  = 8.7, 1.7 Hz, 1H), 8.03 (d,  $J$  = 8.0 Hz, 1H), 7.90 (dd,  $J$  = 14.4, 8.4 Hz, 2H), 7.65–7.53 (m, 2H), 7.50–7.44 (m, 2H), 7.38 (t,  $J$  = 7.9 Hz, 2H), 7.24–7.17 (m, 1H), 6.07–6.00 (m, 1H), 5.83–5.76 (m, 1H), 4.86 (ddd,  $J$  = 6.9, 3.4, 1.7 Hz, 1H), 4.61 (d,  $J$  = 5.5 Hz, 1H), 3.34–3.24 (m, 1H), 2.25–2.09 (m, 2H), 1.97–1.89 (m, 1H), 1.83–1.74 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 195.4, 169.2, 137.4, 135.8, 133.9, 132.5, 132.2, 131.9, 130.0, 129.0, 128.8, 128.4, 127.7, 126.8, 126.0, 124.5, 123.8, 123.5, 56.6, 56.0, 35.1, 23.5, 22.6; IR (KBr) (v/cm<sup>-1</sup>): 3344, 3067, 3030, 2930, 2867, 1700, 1672, 1601, 1542, 1455, 1370, 1277, 1175, 746; HRMS (ESI) calcd for C<sub>25</sub>H<sub>22</sub>NO<sub>2</sub> (M+H)<sup>+</sup> 368.1645, found 368.1642; HPLC: 94% *ee*, chiral stationary column: OJ-H, mobile phase: hexane/<sup>i</sup>PrOH = 80/20, 1.0 mL/min, 254 nm, 25 °C,  $t_R$  (major) = 23.1 min,  $t_R$  (minor) = 44.4 min;  $[\alpha]_D^{25}$  = +1.28 (*c* 0.5, CH<sub>2</sub>Cl<sub>2</sub>).



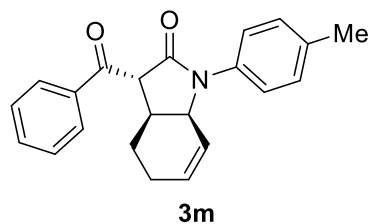
**(3*S*,3*a**R*,7*a**R*)-3-(Furan-2-carbonyl)-1-phenyl-1,3,3*a*,4,5,7*a*-hexahydro-2*H*-indol-2-one (3j):** Colorless oil (48 mg, 78%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.67 (d,  $J$  = 1.6 Hz, 1H), 7.50–7.34 (m, 5H), 7.23–7.16 (m, 1H), 6.59 (dd,  $J$  = 3.6, 1.7 Hz, 1H), 6.03–5.95 (m, 1H), 5.75 (dq,  $J$  = 10.2, 2.2 Hz, 1H), 4.82–4.76 (m, 1H), 4.25 (d,  $J$  = 6.7 Hz, 1H), 3.28–3.19 (m, 1H), 2.25–2.06 (m, 2H), 1.92–1.84 (m, 1H), 1.79–1.70 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 184.0, 169.0, 152.4, 147.5, 137.5, 131.5, 129.1, 125.9, 123.5, 123.5, 120.0, 112.7, 56.2, 56.1, 34.4, 23.1, 22.1; IR (KBr) (v/cm<sup>-1</sup>): 3340, 3063, 3042, 2928, 2855, 1753, 1716, 1702, 1680, 1540, 1337, 1173, 756; HRMS (ESI) calcd for C<sub>19</sub>H<sub>18</sub>NO<sub>3</sub> (M+H)<sup>+</sup> 308.1281, found 308.1277; HPLC: 96% *ee*, chiral stationary column: OJ-H, mobile phase: hexane/<sup>i</sup>PrOH = 70/30, 1.0 mL/min, 254 nm, 25 °C,  $t_R$  (major) = 26.9 min,  $t_R$  (minor) = 93.2 min;  $[\alpha]_D^{25}$  = +65.12 (*c* 0.5, CH<sub>2</sub>Cl<sub>2</sub>).



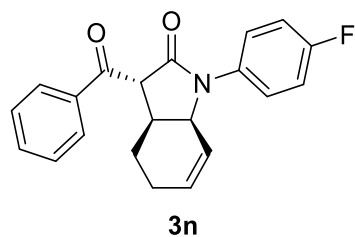
**(3*S*,3*aR*,7*aR*)-1-Phenyl-3-(Thiophene-2-carbonyl)-1,3,3*a*,4,5,7*a*-hexahydro-2*H*-indol-2-one (3k):** Colorless oil (52 mg, 81%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.00 (dd,  $J$  = 3.9, 1.1 Hz, 1H), 7.71 (dd,  $J$  = 5.0, 1.1 Hz, 1H), 7.48–7.42 (m, 2H), 7.41–7.34 (m, 2H), 7.23–7.16 (m, 2H), 6.03–5.97 (m, 1H), 5.79–5.73 (m, 1H), 4.84–4.79 (m, 1H), 4.23 (d,  $J$  = 5.7 Hz, 1H), 3.29–3.21 (m, 1H), 2.20–2.13 (m, 2H), 1.92–1.84 (m, 1H), 1.80–1.71 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 187.9, 168.7, 143.9, 137.4, 135.1, 134.8, 131.8, 129.0, 128.5, 126.0, 123.7, 123.4, 57.7, 56.1, 34.7, 23.3, 22.4; IR (KBr) ( $\nu/\text{cm}^{-1}$ ): 3352, 3063, 3010, 2926, 2859, 1698, 1645, 1538, 1508, 1463, 1263, 746; HRMS (ESI) calcd for C<sub>19</sub>H<sub>18</sub>NO<sub>2</sub>S (M+H)<sup>+</sup> 324.1053, found 324.1049; HPLC: 94% *ee*, chiral stationary column: OJ-H, mobile phase: hexane/*i*PrOH = 80/20, 1.0 mL/min, 254 nm, 25 °C,  $t_R$  (major) = 30.3 min,  $t_R$  (minor) = 89.9 min;  $[\alpha]_D^{25}$  = +38.88 ( $c$  0.25, CH<sub>2</sub>Cl<sub>2</sub>).



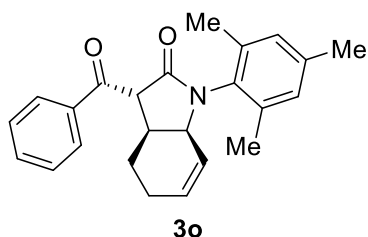
**(3*S*,3*aR*,7*aR*)-3-Benzoyl-1-(4-methoxyphenyl)-1,3,3*a*,4,5,7*a*-hexahydro-2*H*-indol-2-one (3l):** Colorless solid (57 mg, 82%). Mp 105~106 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.06–8.03 (m, 2H), 7.52–7.46 (m, 1H), 7.43–7.36 (m, 2H), 7.25–7.20 (m, 2H), 6.84–6.78 (m, 2H), 5.94–5.86 (m, 1H), 5.62–5.56 (m, 1H), 4.60 (ddd,  $J$  = 5.2, 3.6, 1.7 Hz, 1H), 4.33 (d,  $J$  = 5.1 Hz, 1H), 3.69 (s, 3H), 3.10–3.02 (m, 1H), 2.13–1.98 (m, 2H), 1.84–1.58 (m, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 195.8, 169.2, 157.9, 136.5, 133.6, 131.7, 130.2, 129.5, 128.6, 126.0, 123.6, 114.3, 56.6, 56.4, 55.5, 35.2, 23.6, 22.7; IR (KBr) ( $\nu/\text{cm}^{-1}$ ): 3336, 3079, 3039, 2934, 2843, 1710, 1668, 1514, 1273, 1177, 1040, 746; HRMS (ESI) calcd for C<sub>22</sub>H<sub>22</sub>NO<sub>3</sub> (M+H)<sup>+</sup> 348.1594, found 348.1591; HPLC: 97% *ee*, chiral stationary column: OJ-H, mobile phase: hexane/*i*PrOH = 80/20, 1.0 mL/min, 254 nm, 25 °C,  $t_R$  (major) = 20.8 min,  $t_R$  (minor) = 61.2 min;  $[\alpha]_D^{25}$  = +50.68 ( $c$  1.0, CH<sub>2</sub>Cl<sub>2</sub>).



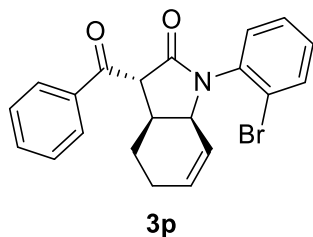
**(3S,3aR,7aR)-3-Benzoyl-1-(p-tolyl)-1,3,3a,4,5,7a-hexahydro-2H-indol-2-one (3m):** Colorless oil (50 mg, 75%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.16–8.11 (m, 2H), 7.59 (t,  $J$  = 7.4 Hz, 1H), 7.49 (t,  $J$  = 7.7 Hz, 2H), 7.31 (d,  $J$  = 8.4 Hz, 2H), 7.17 (d,  $J$  = 8.1 Hz, 2H), 6.02–5.95 (m, 1H), 5.73 (dq,  $J$  = 10.2, 2.4 Hz, 1H), 4.75 (ddd,  $J$  = 6.7, 3.3, 1.7 Hz, 1H), 4.43 (d,  $J$  = 5.6 Hz, 1H), 3.23–3.16 (m, 1H), 2.32 (s, 3H), 2.17–2.09 (m, 2H), 1.92–1.70 (m, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 195.7, 169.1, 136.6, 135.9, 134.8, 133.6, 131.6, 129.6, 129.5, 128.6, 123.9, 123.6, 56.4, 56.1, 35.0, 23.5, 22.5, 21.0; IR (KBr) (v/cm<sup>-1</sup>): 3344, 3067, 3037, 2932, 2861, 1704, 1678, 1607, 1516, 1441, 1384, 1279, 1218, 823; HRMS (ESI) calcd for C<sub>22</sub>H<sub>22</sub>NO<sub>2</sub> (M+H)<sup>+</sup> 332.1645, found 332.1640; HPLC: 98% *ee*, chiral stationary column: OJ-H, mobile phase: hexane/<sup>i</sup>PrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C,  $t_R$  (major) = 22.8 min,  $t_R$  (minor) = 68.6 min;  $[\alpha]_D^{25}$  = +43.84 (*c* 1.0, CH<sub>2</sub>Cl<sub>2</sub>).



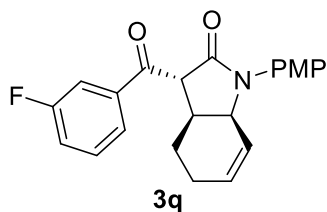
**(3S,3aR,7aR)-3-Benzoyl-1-(4-fluorophenyl)-1,3,3a,4,5,7a-hexahydro-2H-indol-2-one (3n):** Colorless oil (58 mg, 86%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.08–8.02 (m, 2H), 7.55–7.48 (m, 1H), 7.42 (t,  $J$  = 7.7 Hz, 2H), 7.34–7.28 (m, 2H), 6.99 (t,  $J$  = 8.6 Hz, 2H), 5.98–5.90 (m, 1H), 5.65–5.58 (m, 1H), 4.66 (ddd,  $J$  = 6.8, 3.4, 1.7 Hz, 1H), 4.35 (d,  $J$  = 5.2 Hz, 1H), 3.14–3.04 (m, 1H), 2.16–1.98 (m, 2H), 1.85–1.77 (m, 1H), 1.69–1.62 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 196.5, 169.4, 160.6 (d,  $J$  = 246.4 Hz), 136.4, 133.7, 133.3 (d,  $J$  = 4.0 Hz), 132.1, 129.4, 128.6, 126.0 (d,  $J$  = 9.1 Hz), 123.2, 115.9 (d,  $J$  = 23.2 Hz), 56.5, 56.2, 35.1, 23.5, 22.6; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  = -115.57; IR (KBr) (v/cm<sup>-1</sup>): 3356, 3071, 3023, 2932, 2853, 1707, 1668, 1512, 1451, 1380, 1248, 1208, 1028, 748; HRMS (ESI) calcd for C<sub>21</sub>H<sub>19</sub>FNO<sub>2</sub> (M+H)<sup>+</sup> 336.1394, found 336.1391; HPLC: 96% *ee*, chiral stationary column: OJ-H, mobile phase: hexane/<sup>i</sup>PrOH = 90/10, 1.0 mL/min, 254 nm, 25 °C,  $t_R$  (major) = 28.2 min,  $t_R$  (minor) = 75.5 min;  $[\alpha]_D^{25}$  = +44.92 (*c* 1.0, CH<sub>2</sub>Cl<sub>2</sub>).



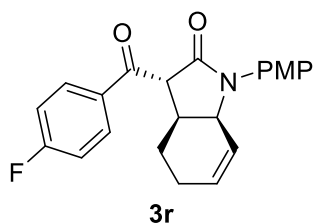
**(3*S*,3*aR*,7*aR*)-3-Benzoyl-1-mesityl-1,3,3*a*,4,5,7*a*-hexahydro-2*H*-indol-2-one (3o):** Colorless oil (63 mg, 88%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.09–8.05 (m, 2H), 7.54–7.47 (m, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 6.80 (s, 2H), 5.95–5.87 (m, 1H), 5.34–5.28 (m, 1H), 4.62–4.56 (m, 1H), 4.28 (d, *J* = 2.3 Hz, 1H), 2.97–2.88 (m, 1H), 2.18 (s, 3H), 2.14 (s, 3H), 2.10 (s, 3H), 2.08–1.93 (m, 2H), 1.87–1.80 (m, 1H), 1.69–1.78 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 196.4, 168.8, 137.9, 137.3, 136.3, 135.9, 133.6, 132.0, 131.3, 129.5, 129.4, 129.2, 128.6, 123.2, 58.5, 55.7, 36.8, 24.9, 23.7, 21.0, 18.9, 17.9; IR (KBr) ( $\nu$ /cm<sup>-1</sup>): 3340, 3033, 2922, 2853, 2859, 1700, 1672, 1597, 1516, 1449, 1396, 1218, 1179, 687; HRMS (ESI) calcd for C<sub>24</sub>H<sub>26</sub>NO<sub>2</sub> (M+H)<sup>+</sup> 360.1958, found 360.1955; HPLC: 94% *ee*, chiral stationary column: IA, mobile phase: hexane/<sup>i</sup>PrOH = 95.0/5.0, 1.0 mL/min, 254 nm, 25 °C, *t<sub>R</sub>* (major) = 18.5 min, *t<sub>R</sub>* (minor) = 21.5 min;  $[\alpha]_D^{25}$  = +83.92 (*c* 1.0, CH<sub>2</sub>Cl<sub>2</sub>).



**(3*S*,3*aR*,7*aR*)-3-Benzoyl-1-(2-bromophenyl)-1,3,3*a*,4,5,7*a*-hexahydro-2*H*-indol-2-one (3p):** Colorless solid (78 mg, 98%). Mp: 125–126 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.64–7.52 (m, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.32 (td, *J* = 7.7, 1.5 Hz, 1H), 7.26–7.13 (m, 2H), 6.00 (dt, *J* = 9.2, 3.7 Hz, 1H), 5.47–5.38 (m, 1H), 4.76 (t, *J* = 5.0 Hz, 1H), 4.34 (d, *J* = 3.7 Hz, 1H), 3.23–3.02 (m, 1H), 2.24–2.03 (m, 2H), 1.89–1.75 (m, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 195.1, 168.9, 136.3, 136.0, 133.6, 133.5, 132.2, 130.4, 129.6, 129.5, 128.5, 128.1, 123.3, 123.1, 57.2, 56.4, 36.0, 23.1; IR (KBr) ( $\nu$ /cm<sup>-1</sup>): 3311, 3067, 3030, 2930, 2859, 1700, 1670, 1510, 1475, 1390, 1216, 1036, 839; HRMS (ESI) calcd for C<sub>21</sub>H<sub>19</sub><sup>79</sup>BrNO<sub>2</sub> (M+H)<sup>+</sup> 396.0594, found 396.0592, calcd for C<sub>21</sub>H<sub>19</sub><sup>81</sup>BrNO<sub>2</sub> (M+H)<sup>+</sup> 398.0574, found 398.0570; HPLC: 94% *ee*, chiral stationary column: OD-H, mobile phase: hexane/<sup>i</sup>PrOH = 90.0/10.0, 1.0 mL/min, 254 nm, 25 °C, *t<sub>R</sub>* (major) = 12.5 min, *t<sub>R</sub>* (minor) = 19.1 min;  $[\alpha]_D^{25}$  = +59.80 (*c* 1.0, CH<sub>2</sub>Cl<sub>2</sub>).



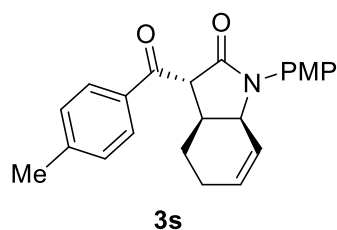
**(3S,3aR,7aR)-3-(3-Fluorobenzoyl)-1-(4-methoxyphenyl)-1,3,3a,4,5,7a-hexahydro-2H-indol-2-one (3q):** Colorless oil (61 mg, 84%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.87 (d,  $J$  = 7.8 Hz, 1H), 7.77–7.72 (m, 1H), 7.44–7.35 (m, 1H), 7.24–7.18 (m, 3H), 6.85–6.79 (m, 2H), 5.96–5.89 (m, 1H), 5.65–5.58 (m, 1H), 4.62 (ddd,  $J$  = 6.8, 3.3, 1.7 Hz, 1H), 4.27 (d,  $J$  = 5.3 Hz, 1H), 3.71 (s, 3H), 3.15–3.07 (m, 1H), 2.14–1.98 (m, 2H), 1.83–1.76 (m, 1H), 1.69–1.62 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 194.5 (d,  $J$  = 2.3 Hz), 168.7, 162.8 (d,  $J$  = 248.5 Hz), 157.9, 138.6 (d,  $J$  = 6.4 Hz), 131.7, 130.2 (d,  $J$  = 7.6 Hz), 130.02, 126.0, 125.4 (d,  $J$  = 2.9 Hz), 123.6, 120.6 (d,  $J$  = 22.2 Hz), 116.1 (d,  $J$  = 22.2 Hz), 114.3, 56.8, 56.4, 55.5, 35.0, 29.7, 23.5, 22.6; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  = –112.0; IR (KBr) (v/cm<sup>–1</sup>): 3340, 3071, 3031, 2924, 2853, 1696, 1681, 1587, 1514, 1443, 1392, 1271, 1032, 748; HRMS (ESI) calcd for C<sub>22</sub>H<sub>21</sub>FNO<sub>3</sub> (M+H)<sup>+</sup> 366.1500, found 366.1496; HPLC: 95% *ee*, chiral stationary column: OJ-H, mobile phase: hexane/<sup>i</sup>PrOH = 80/20, 1.0 mL/min, 254 nm, 25 °C,  $t_R$  (major) = 16.6min,  $t_R$  (minor) = 58.7 min;  $[\alpha]_D^{25}$  = +38.52 (*c* 1.0, CH<sub>2</sub>Cl<sub>2</sub>).



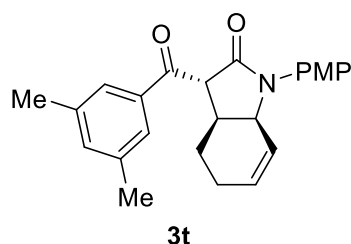
**(3S,3aR,7aR)-3-(4-Fluorobenzoyl)-1-(4-methoxyphenyl)-1,3,3a,4,5,7a-hexahydro-2H-indol-2-one(3r):** Colorless solid (70 mg, 96%). Mp: 146~147 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.15–8.08 (m, 2H), 7.23–7.18 (m, 2H), 7.12–7.04 (m, 2H), 6.85–6.80 (m, 2H), 5.95–5.89 (m, 1H), 5.64–5.59 (m, 1H), 4.64–4.59(m, 1H), 4.27 (d,  $J$  = 5.1 Hz, 1H), 3.71 (s, 3H), 3.17–3.08 (m, 1H), 2.11–2.02 (m, 2H), 1.82–1.75 (m, 1H), 1.68–1.59 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 193.9, 168.9, 166.1 (d,  $J$  = 257.6 Hz), 157.9, 133.0 (d,  $J$  = 2.9 Hz), 132.4 (d,  $J$  = 9.1 Hz), 131.8, 130.1, 125.9, 123.6, 115.7 (d,  $J$  = 22.2 Hz), 114.3, 56.7, 56.5, 55.5, 34.9, 23.6, 22.6; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  = –104.37; IR (KBr) (v/cm<sup>–1</sup>): 3368, 3067, 3051, 2926, 2849, 1696, 1676, 1599, 1514, 1455, 1392, 1252, 1034, 833; HRMS (ESI) calcd for C<sub>22</sub>H<sub>21</sub>FNO<sub>3</sub> (M+H)<sup>+</sup> 366.1500, found 366.1496; HPLC: 99% *ee*, chiral stationary column: OJ-H, mobile phase: hexane/<sup>i</sup>PrOH = 80/20, 1.0 mL/min, 254 nm, 25 °C,  $t_R$  (major) = 24.8min,  $t_R$  (minor) =



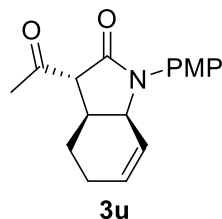
69.9 min;  $[\alpha]_D^{25} = +23.78$  (c 0.5 CH<sub>2</sub>Cl<sub>2</sub>).



**(3S,3aR,7aR)-1-(4-Methoxyphenyl)-3-(4-methylbenzoyl)-1,3,3a,4,5,7a-hexahydro-2H-indol-2-one (3s):** Colorless oil (65 mg, 90%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta = 7.98$ – $7.93$  (m, 2H),  $7.26$ – $7.20$  (m, 4H),  $6.86$ – $6.79$  (m, 2H),  $5.95$ – $5.89$  (m, 1H),  $5.64$ – $5.59$  (m, 1H),  $4.63$ – $4.58$  (m, 1H),  $4.30$  (d,  $J = 5.1$  Hz, 1H),  $3.72$  (s, 3H),  $3.11$ – $3.03$  (m, 1H),  $2.34$  (s, 3H),  $2.10$ – $2.02$  (m, 2H),  $1.83$ – $1.76$  (m, 1H),  $1.69$ – $1.61$  (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta = 195.3$ ,  $169.3$ ,  $157.8$ ,  $144.4$ ,  $134.1$ ,  $131.6$ ,  $130.2$ ,  $129.5$ ,  $129.2$ ,  $126.0$ ,  $123.7$ ,  $114.3$ ,  $56.5$ ,  $56.4$ ,  $55.4$ ,  $35.2$ ,  $23.6$ ,  $22.7$ ,  $21.6$ ; IR (KBr) (v/cm<sup>-1</sup>): 3323, 3034, 3010, 2924, 2857, 1700, 1676, 1599, 1510, 1445, 1394, 1250, 1040, 837; HRMS (ESI) calcd for C<sub>23</sub>H<sub>24</sub>NO<sub>3</sub> (M+H)<sup>+</sup> 362.1751, found 362.1747; HPLC: 96% *ee*, chiral stationary column: OJ-H, mobile phase: hexane/<sup>i</sup>PrOH = 80/20, 1.0 mL/min, 254 nm, 25 °C,  $t_R$  (major) = 21.4 min,  $t_R$  (minor) = 42.5 min;  $[\alpha]_D^{25} = +39.24$  (c 1.0, CH<sub>2</sub>Cl<sub>2</sub>).



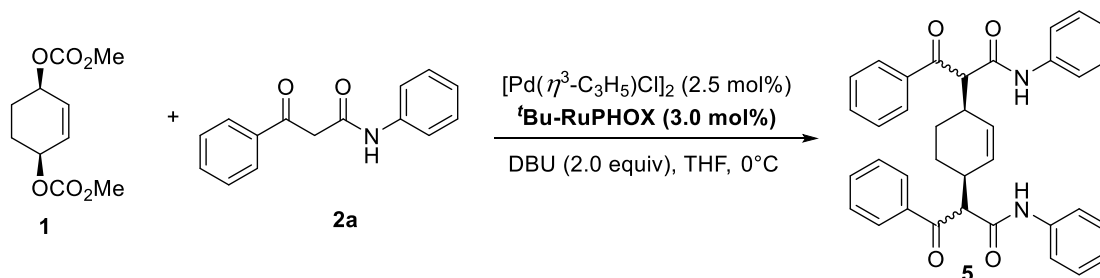
**(3S,3aR,7aR)-3-(3,5-Dimethylbenzoyl)-1-(4-methoxyphenyl)-1,3,3a,4,5,7a-hexahydro-2H-indol-2-one (3t):** Colorless solid (59 mg, 78%). Mp: 116–117 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta = 7.73$  (s, 2H),  $7.34$ – $7.28$  (m, 2H),  $7.22$  (s, 1H),  $6.93$ – $6.87$  (m, 2H),  $6.03$ – $5.97$  (m, 1H),  $5.72$ – $5.67$  (m, 1H),  $4.72$ – $4.67$  (m, 1H),  $4.38$  (d,  $J = 4.9$  Hz, 1H),  $3.79$  (s, 3H),  $3.16$ – $3.09$  (m, 1H),  $2.38$  (s, 6H),  $2.18$ – $2.09$  (m, 2H),  $1.90$ – $1.83$  (m, 1H),  $1.77$ – $1.69$  (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta = 196.2$ ,  $169.4$ ,  $157.8$ ,  $138.2$ ,  $136.8$ ,  $135.2$ ,  $131.6$ ,  $130.3$ ,  $127.1$ ,  $126.0$ ,  $123.7$ ,  $114.3$ ,  $56.7$ ,  $56.4$ ,  $55.4$ ,  $35.4$ ,  $23.7$ ,  $22.7$ ,  $21.2$ ; IR (KBr) (v/cm<sup>-1</sup>): 3332, 3136, 3030, 2928, 2847, 1702, 1674, 1512, 1457, 1252, 1026, 828; HRMS (ESI) calcd for C<sub>24</sub>H<sub>26</sub>NO<sub>3</sub> (M+H)<sup>+</sup> 376.1907, found 376.1903; HPLC: 99% *ee*, chiral stationary column: OJ-H, mobile phase: hexane/<sup>i</sup>PrOH = 80/20, 1.0 mL/min, 254 nm, 25 °C,  $t_R$  (major) = 11.5 min,  $t_R$  (minor) = 20.4 min;  $[\alpha]_D^{25} = +50.52$  (c 1.0, CH<sub>2</sub>Cl<sub>2</sub>).



**(3R,3aS,7aS)-3-Acetyl-1-(4-Methoxyphenyl)-1,3,3a,4,5,7a-hexahydro-2H-indol-2-one (3u):** Colorless solid (39 mg, 69%). Mp: 137~139 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.23–7.17 (m, 2H), 6.90–6.76 (m, 2H), 5.95–5.82 (m, 1H), 5.59–5.52 (m, 1H), 4.50–4.41 (m, 1H), 3.73 (s, 3H), 3.47 (d, *J* = 6.4 Hz, 1H), 3.10–2.95 (m, 1H), 2.38 (s, 3H), 2.02 (dd, *J* = 6.0, 3.9 Hz, 2H), 1.80–1.67 (m, 1H), 1.74–1.68 (m, 1H), 1.64–1.56 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 202.5, 167.7, 156.9, 130.5, 129.0, 124.8, 122.6, 113.4, 59.7, 55.3, 54.5, 31.9, 29.3, 22.1, 21.1; IR (KBr) (ν/cm<sup>-1</sup>): 3360, 2969, 2926, 2849, 1684, 1508, 1561, 1406, 1258, 1246, 1105, 811, 740; HRMS (ESI) calcd for C<sub>17</sub>H<sub>20</sub>NO<sub>3</sub> (M+H)<sup>+</sup> 286.1438, found 286.1436; HPLC: 96% *ee*, chiral stationary column: OJ-H, mobile phase: hexane/<sup>i</sup>PrOH = 80/20, 1.0 mL/min, 254 nm, 25 °C, *t*<sub>R</sub> (major) = 18.4 min, *t*<sub>R</sub> (minor) = 39.0 min; [α]<sub>D</sub><sup>25</sup> = +41.40 (*c* 1.0, CH<sub>2</sub>Cl<sub>2</sub>).

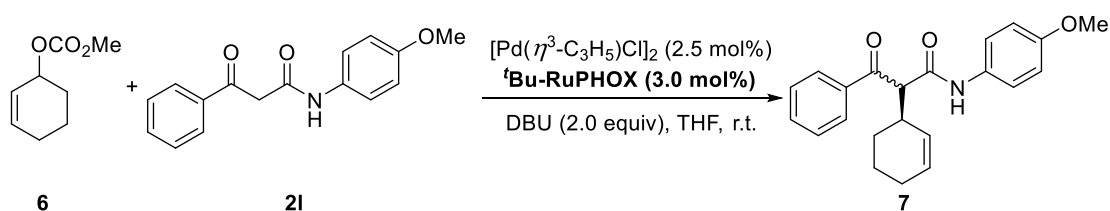
## 4. Mechanism Experiments

### 4.1 Procedure for synthesis of 5



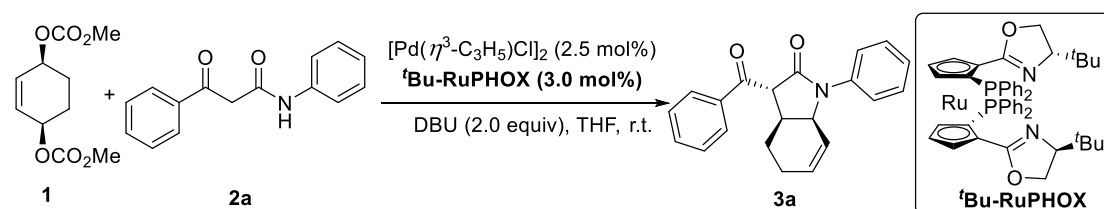
A flame-dried Schlenk tube equipped with a magnetic stirring bar, was charged with a mixture of  $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}]_2$  (1.83 mg, 2.5 mol%) and RuPHOX (5.10 mg, 3.0 mol%). After being evacuated and backfilled with nitrogen three times, THF (2 mL) was added to the Schlenk tube and the mixture was stirred at room temperature under  $\text{N}_2$  atmosphere for 1 h. Allylic biscarbonate **1** (51 mg, 0.22 mmol, 1.1 equiv) was added via a syringe followed by the addition of 3-oxo-*N*,3-diphenylpropanamide **2a** (0.2 mmol, 1.0 equiv) and DBU (0.4 mmol, 2.0 equiv). The reaction mixture was allowed to stir under  $\text{N}_2$  atmosphere at 0 °C overnight. THF was evaporated in vacuo and the residue was purified by flash silica gel column chromatography (petroleum ether/ethyl acetate = 3/1) to give colorless solid **5** (23 mg, 22%). Mp: 215~216 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.54 (d,  $J$ =13.0 Hz, 1H), 8.47 (d,  $J$ =4.5 Hz, 1H), 7.99 (t,  $J$ =7.7 Hz, 4H), 7.66–7.54 (m, 2H), 7.48 (dd,  $J$  = 14.5, 7.9 Hz, 8H), 7.31–7.24 (m, 4H), 7.08 (d,  $J$  = 7.7 Hz, 2H), 5.93–5.67 (m, 1H), 5.67–5.45 (m, 1H), 4.52–4.31 (m, 2H), 3.05 (s, 2H), 1.92–1.68 (m, 4H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 200.0, 199.8, 199.2, 198.8, 171.0, 165.3, 165.1, 152.1, 137.4, 137.4, 137.3, 137.3, 136.7, 136.7, 136.6, 136.6, 134.3, 134.2, 134.2, 132.4, 132.1, 131.7, 131.6, 131.1, 131.0, 130.6, 130.4, 130.0, 129.9, 129.9, 129.4, 129.0, 128.9, 128.9, 128.9, 128.8, 128.8, 128.71, 128.66, 128.4, 128.3, 128.2, 128.1, 127.9, 127.3, 126.6, 125.6, 125.6, 124.8, 124.5, 124.5, 124.4, 123.5, 121.2, 120.0, 119.8, 119.8, 119.8, 119.3, 62.1, 61.0, 60.9, 60.8, 60.6, 60.3, 38.9, 38.8, 38.1, 37.7, 29.6, 24.5, 24.4, 23.5, 23.2, 20.9, 14.1; HRMS (ESI) calcd for  $\text{C}_{36}\text{H}_{32}\text{N}_2\text{NaO}_4$  ( $\text{M}+\text{Na}$ ) $^+$  579.2254, found 579.2248.

### 4.2 Procedure for synthesis of 7



A flame-dried Schlenk tube equipped with a magnetic stirring bar, was charged with a mixture of  $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}]_2$  (1.83 mg, 2.5 mol%) and RuPHOX (5.10 mg, 3.0 mol%). After being evacuated and backfilled with nitrogen three times, THF (2 mL) was added to the Schlenk tube and the mixture was stirred at room temperature under  $\text{N}_2$  atmosphere for 1 h. Allylic carbonate **6** (34 mg, 0.22 mmol, 1.1 equiv) was added via a syringe followed by the addition of **21** (54mg, 0.2 mmol, 1.0 equiv) and DBU (0.4 mmol, 2.0 equiv). The reaction mixture was allowed to stir under  $\text{N}_2$  atmosphere at room temperature for 3 h. THF was evaporated in vacuo and the residue was purified by flash silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to give colorless oil **7** (64 mg, 93%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.41 (d,  $J$  = 17.4 Hz, 1H), 8.03 (d,  $J$  = 6.6 Hz, 2H), 7.60 (d,  $J$  = 9.6 Hz, 1H), 7.44 (dd,  $J$  = 28.1, 7.9 Hz, 4H), 6.81 (d,  $J$  = 8.7 Hz, 2H), 5.72–5.64 (m, 1H), 5.39–5.30 (m, 1H), 4.36 (dd,  $J$  = 10.4, 3.1 Hz, 1H), 3.74 (s, 3H), 3.05 (q,  $J$  = 7.7, 6.2 Hz, 1H), 2.03–1.90 (m, 2H), 1.82–1.68 (m, 2H), 1.53 (d,  $J$  = 34.4 Hz, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 200.6, 200.2, 165.4, 165.2, 156.5, 156.4, 137.1, 134.1, 134.1, 130.7, 130.3, 129.9, 128.9, 128.8, 128.7, 127.2, 126.6, 121.6, 121.5, 114.0, 61.7, 61.5, 55.4, 39.8, 39.5, 27.5, 26.6, 24.9, 24.8, 20.8, 20.7; HPLC: 96% ee (major), 1.2:1 dr, chiral stationary column: IE, mobile phase: hexane/*i*PrOH = 90/10, 1.0 mL/min, 254 nm, 40 °C,  $t_{\text{R}}$  (major) = 25.2 min,  $t_{\text{R}}$  (minor) = 21.0 min.

### 4.3 Control experiments: variation of ee/dr over time

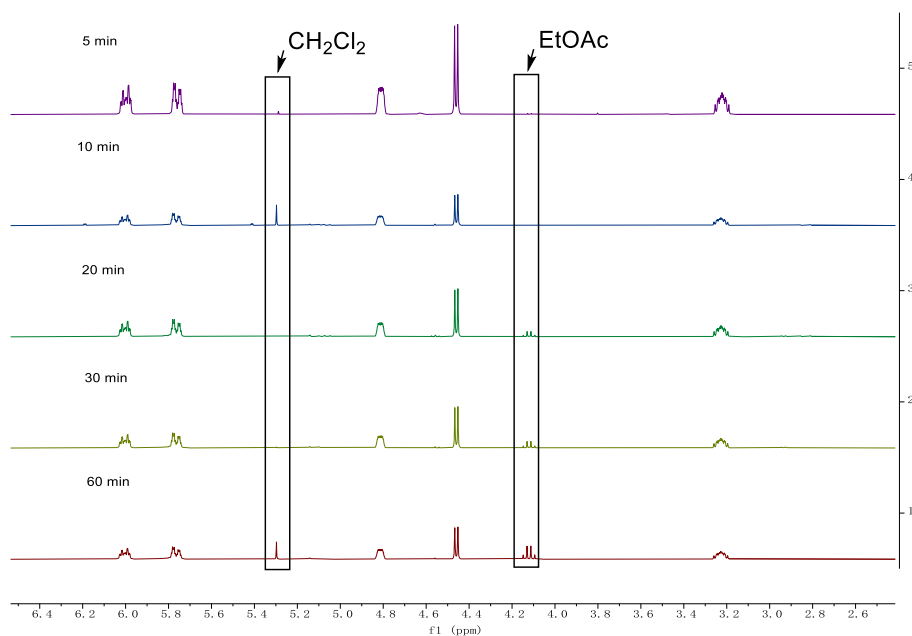
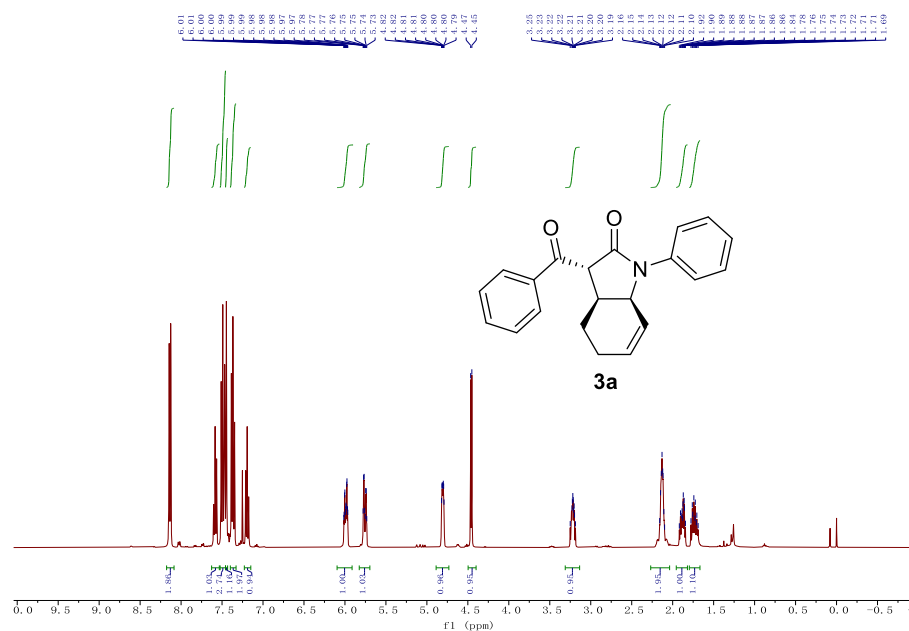


time / min	5	10	20	30	60
ee / %	96	96	96	96	96
dr	>20:1	>20:1	>20:1	>20:1	>20:1

A flame-dried Schlenk tube equipped with a magnetic stirring bar, was charged with a mixture of  $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}]_2$  (9.15 mg, 2.5 mol%) and RuPHOX (25.50 mg, 3.0 mol%). After being evacuated and backfilled with nitrogen three times, THF (10 mL) was added to the Schlenk tube and the mixture was stirred at room temperature under  $\text{N}_2$  atmosphere for 1 h. Allylic biscarbonate **1** (253 mg, 1.1 mmol, 1.1 equiv) was added via a syringe followed by the addition of 3-oxo-*N*,3-diphenylpropanamide **2a** (239 mg, 1 mmol) and DBU (2 mmol, 2.0 equiv). The reaction mixture was sampled at a suitable

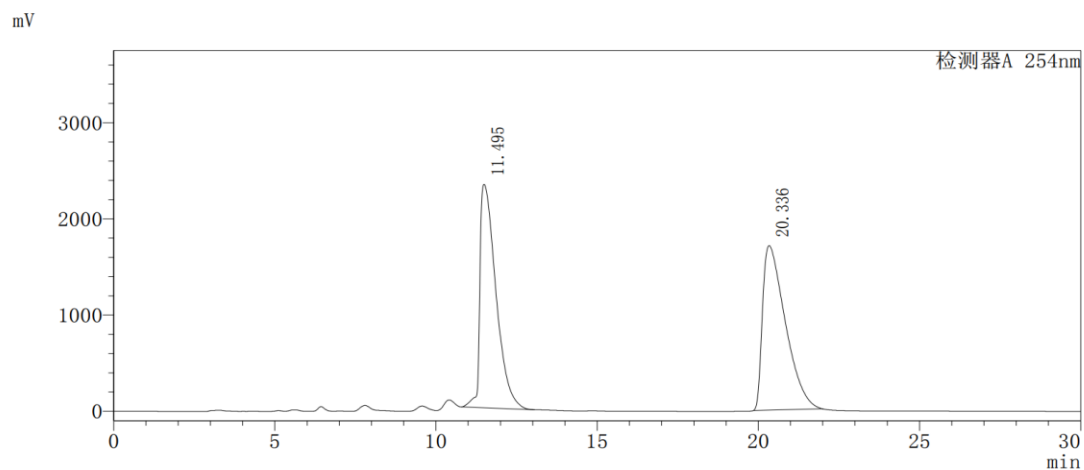
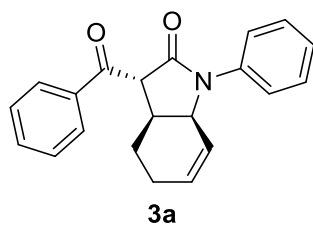
time and the solvent was evaporated in vacuo. The residue was purified by flash silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to give **3a**. Ees were determined by chiral HPLC and drs were determined by  $^1\text{H}$  NMR.

### NMR spectra of the crude product **3a** sampled at different time



It was observed that only one set of peaks were shown in the above Figure. We therefore can conclude almost one pair of enantiomers exist, illustrating that  $>20:1$  drs being obtained for **3a** sampled at different time.

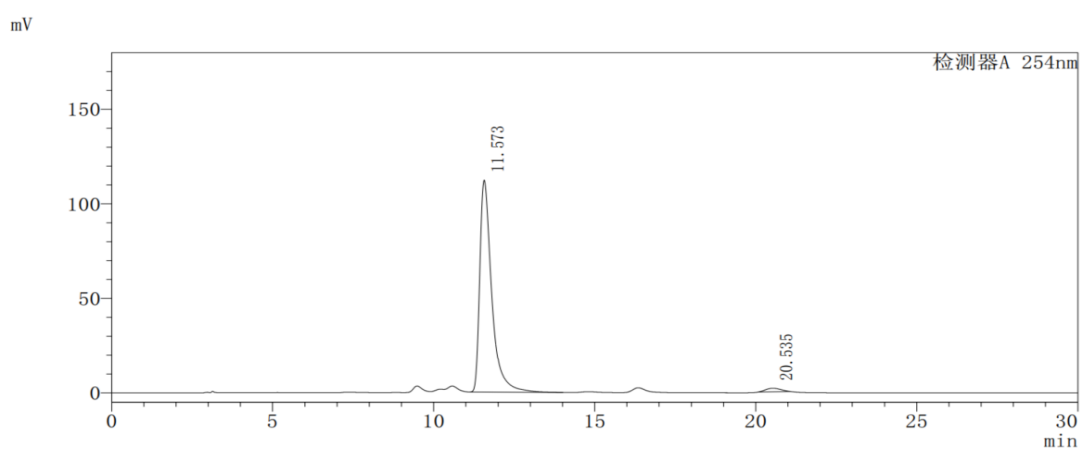
### HPLC analysis for 3a sampled at different time



PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %
1	11.495	80244428	48.768
2	20.336	84297169	51.232
Total		164541597	100.0

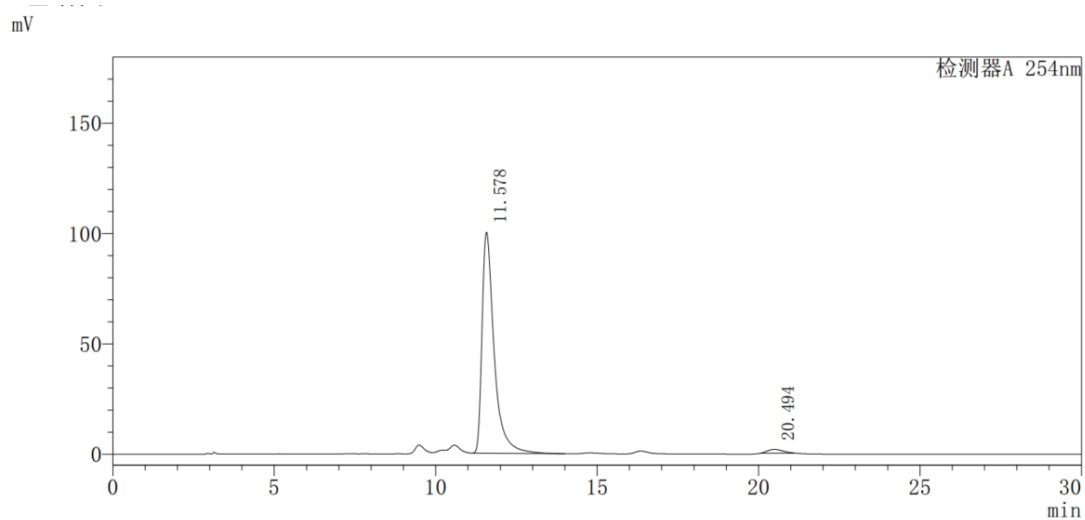
5 min:



PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %	Ee %
1	11.573	2896918	97.909	96
2	20.535	61868	2.091	
Total		2958786	100.0	

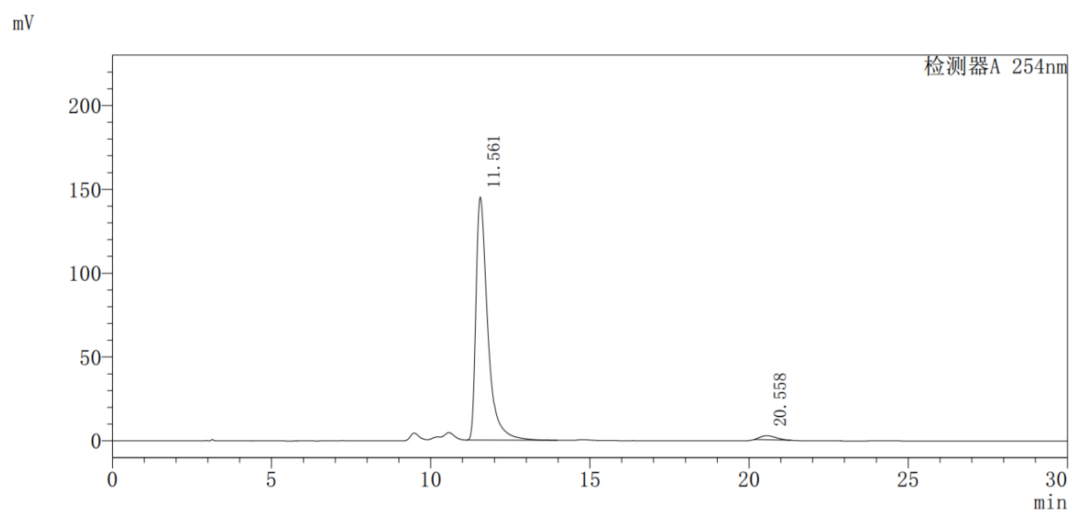
10 min:



PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %	Ee %
1	11.578	2609861	97.964	96
2	20.494	54232	2.036	
Total		2664093	100.0	

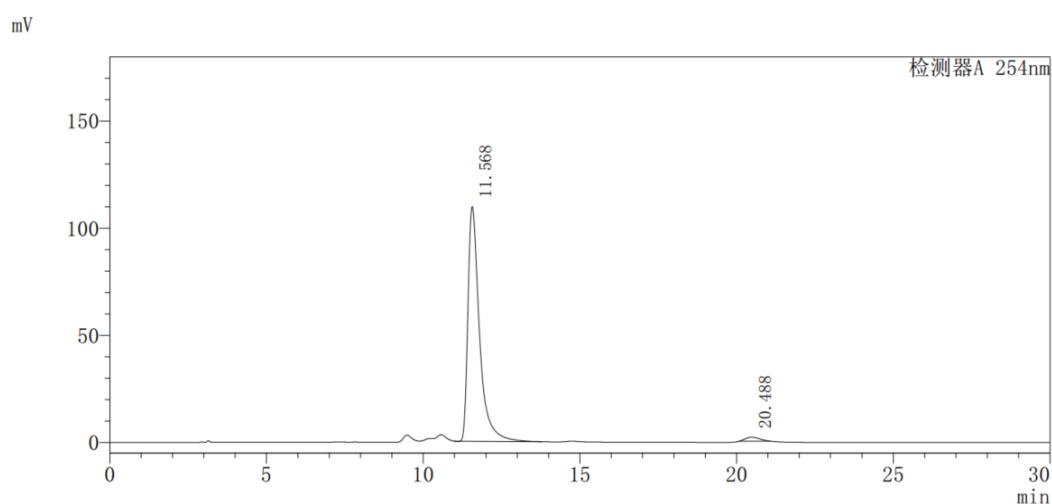
20 min:



PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %	Ee %
1	11.561	3721990	97.820	96
2	20.558	82939	2.180	
Total		3804930	100.0	

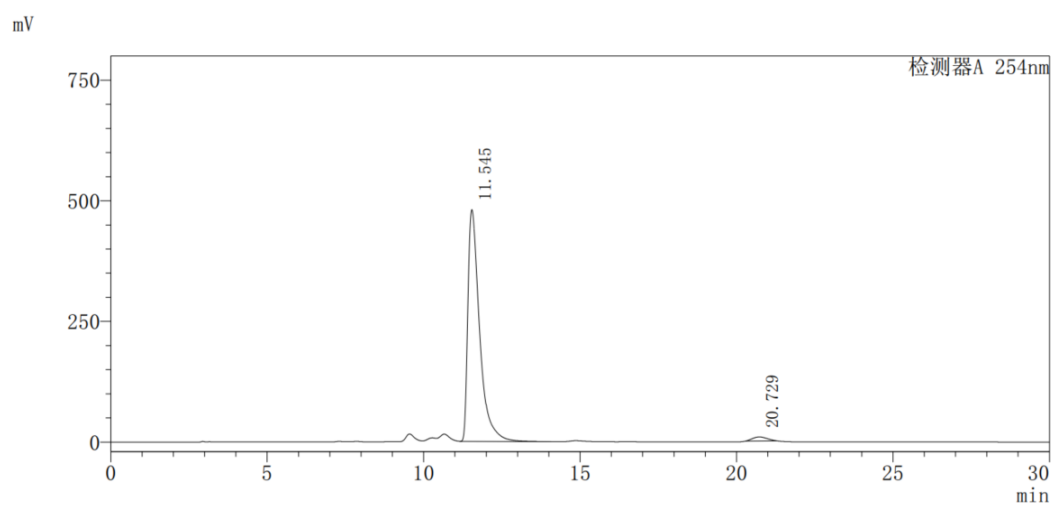
30 min:



PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %	Ee %
1	11.568	2806583	97.922	96
2	20.488	59563	2.078	
Total		2866145	100.0	

60 min:



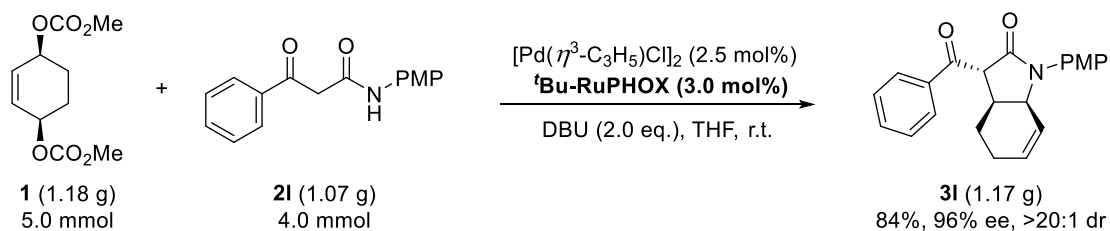
PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %	Ee %
1	11.545	12507313	97.883	96
2	20.729	270502	2.117	
Total		12777815	100.0	



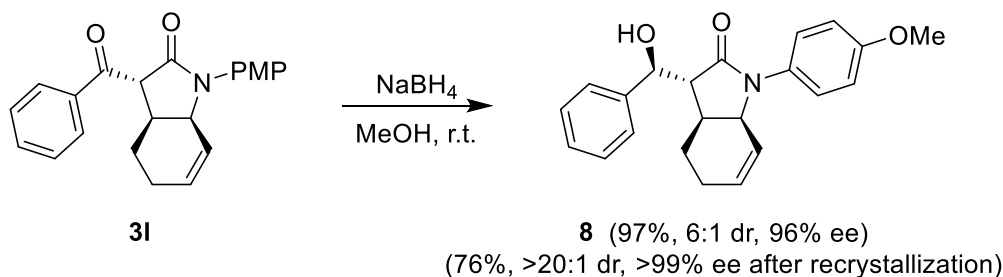
## 5. Large Scale Reaction and Transformations

### 5.1 Large-Scale Synthesis of **3I**



A flame-dried Schlenk tube equipped with a magnetic stirring bar, was charged with a mixture of  $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}]_2$  (36.6 mg, 2.5 mol%) and RuPHOX (133.0 mg, 3.0 mol%). After being evacuated and backfilled with nitrogen three times, THF (40 mL) was added to the Schlenk tube and the mixture was stirred at room temperature under  $\text{N}_2$  atmosphere for 1 h. Allylic biscarbonate **1** (5.0 mmol, 1.18 g) was added via a syringe followed by the addition of **2I** (4.0 mmol, 1.07 g) and DBU (4.0 mmol, 1.21 g). The reaction mixture was allowed to stir under  $\text{N}_2$  atmosphere at room temperature for 3 h. THF was evaporated in vacuo and the residue was purified by flash silica gel column chromatography (petroleum ether/ethyl acetate = 3/1) to give product **3I** as white solid (1.17 g, 84%). HPLC: 96% ee, chiral stationary column: OJ-H, mobile phase: hexane/*i*PrOH = 80/20, 1.0 mL/min, 254 nm, 25 °C,  $t_{\text{R}}$  (major) = 20.3 min,  $t_{\text{R}}$  (minor) = 60.5 min.

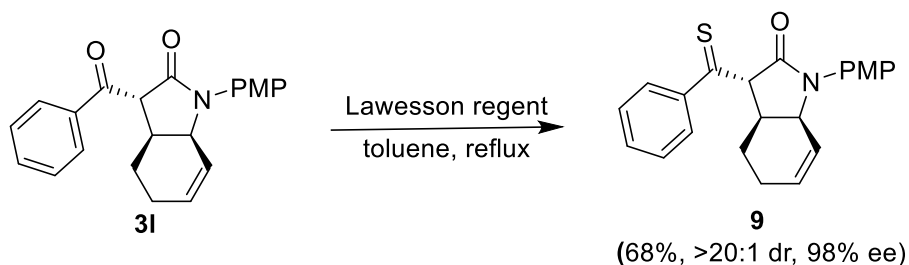
### 5.2 Procedure for synthesis of **8**



A tube equipped with a magnetic stirring bar, was charged with **3I** (70 mg, 0.2 mmol) in MeOH (2 mL). Then the temperature was reduced to 0 °C. To the mixture was added  $\text{NaBH}_4$  (30 mg, 0.8 mmol, 4.0 equiv) in portion. The reaction was then warmed to room temperature. After stirring at the same temperature for 6 h, the solvent was removed under reduced pressure and the residue was treated with ethyl acetate (3 mL) and water (1 mL). The organic layer was concentrated under vacuum, the residue was purified by flash silica gel column chromatography (petroleum ether/ethyl acetate = 2/1) to give **8** as a white solid (97%, 6:1 dr, 96% ee), which can be recrystallized from petroleum ether/ethyl acetate (5/1) to give the highly enantioenriched **8** (52 mg, 74%). Mp:

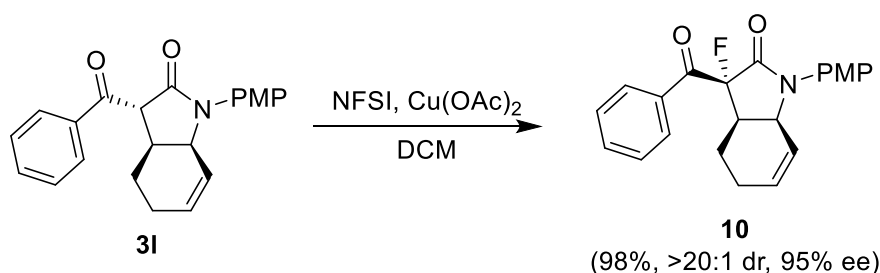
99~101 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 7.41 (d, *J* = 7.1 Hz, 1H), 7.39–7.29 (m, 2H), 7.25 (d, *J* = 8.4 Hz, 1H), 6.90 (d, *J* = 9.0 Hz, 1H), 5.90–5.75 (m, 1H), 5.53 (dt, *J* = 10.2, 2.4 Hz, 1H), 4.15 (dd, *J* = 7.5, 2.4 Hz, 1H), 3.80 (s, 2H), 2.95 (dd, *J* = 7.7, 3.8 Hz, 1H), 2.57 (qd, *J* = 7.2, 4.2 Hz, 1H), 2.01–1.79 (m, 1H), 1.71–1.46 (m, 1H), 1.23–1.02 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 174.1, 157.7, 141.7, 131.0, 130.2, 128.4, 127.5, 125.9, 125.4, 123.8, 114.4, 72.4, 56.9, 55.5, 52.4, 31.7, 23.4, 21.7; IR (KBr) (v/cm<sup>-1</sup>): 2962, 2930, 2853, 1678, 1714, 1678, 1526, 1455, 1271, 1090, 1046, 815; HRMS (ESI) calcd for C<sub>22</sub>H<sub>24</sub>NO<sub>3</sub> (M+H)<sup>+</sup> 350.1751, found 350.1751; HPLC: 99% *ee* (major), >20:1 *dr*, chiral stationary column: OD, mobile phase: hexane/<sup>i</sup>PrOH = 80.0/20.0, 1.0 mL/min, 254 nm, 25 °C, *t<sub>R</sub>* (major) = 14.7 min, *t<sub>R</sub>* (minor) = 7.9 min; [α]<sub>D</sub><sup>25</sup> = +32.28 (*c* 1.0, CH<sub>2</sub>Cl<sub>2</sub>).

### 5.3 Procedure for synthesis of **9**



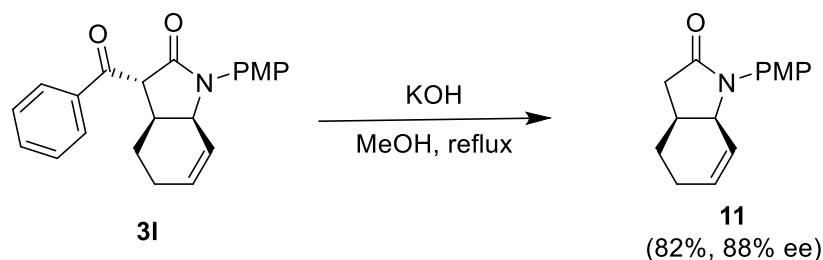
A flame-dried Schlenk tube equipped with a magnetic stirring bar, was charged with a mixture of **31** (70 mg, 0.2mmol, 1.0 equiv) and lawesson's reagent (24.3 mg, 0.06mmol, 0.6 equiv). After being evacuated and backfilled with nitrogen three times, dry toluene (2 mL) was added to the Schlenk tube and the mixture was heated to reflux under N<sub>2</sub> atmosphere for 24 h. Then the mixture was cooled to room temperature and the solvent was removed under vacuum. The residue was purified by flash silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) to give products **9** as a white solid (49 mg, 68%). Mp: 178~179 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 8.17 (d, *J* = 8.2 Hz, 2H), 7.70–7.61 (m, 1H), 7.55 (t, *J* = 7.2 Hz, 2H), 7.29–7.24 (m, 2H), 7.01 (dd, *J* = 9.0, 3.3 Hz, 2H), 6.17–6.01 (m, 1H), 5.61–5.46 (m, 1H), 4.95 (d, *J* = 2.9 Hz, 1H), 4.93 (d, *J* = 4.9 Hz, 1H), 3.85 (s, 3H), 3.04–2.81 (m, 1H), 2.22 (dd, *J* = 18.3, 4.7 Hz, 1H), 2.16–2.06 (m, 1H), 2.00–1.83 (m, 1H), 1.77–1.67 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 198.2, 197.0, 159.3, 136.5, 133.7, 133.0, 132.7, 129.6, 128.7, 128.4, 122.5, 114.7, 67.4, 65.2, 55.5, 38.8, 24.2, 23.4; IR (KBr) (v/cm<sup>-1</sup>): 2960, 2931, 3380, 1718, 1704, 1680, 1544, 1510, 1461, 1254, 1027, 805; HRMS (ESI) calcd for C<sub>22</sub>H<sub>22</sub>NO<sub>2</sub>S (M+H)<sup>+</sup> 364.1366, found 364.1366; HPLC: 98% *ee*, chiral stationary column: IA, mobile phase: hexane/<sup>i</sup>PrOH = 85/15, 1.0 mL/min, 254 nm, 25 °C, *t<sub>R</sub>* (major) = 38.3 min, *t<sub>R</sub>* (minor) = 42.2 min; [α]<sub>D</sub><sup>25</sup> = +67.88 (*c* 1.0, CH<sub>2</sub>Cl<sub>2</sub>).

#### 5.4 Procedure for synthesis of **10**



In a Schlenk tube equipped with a magnetic stirring bar, **31** (35 mg, 0.1 mmol, 1.0 equiv), NFSI (35mg, 0.11 mmol, 1.1 equiv) and Cu(OAc)<sub>2</sub> (1.03 mg, 5 mol%) were dissolved in CHCl<sub>2</sub> (1 mL). The reaction was stirred at room temperature for 6 h. CHCl<sub>2</sub> was evaporated under vacuum and the residue was purified by flash silica gel column chromatography (petroleum ether/ethyl acetate = 3/1) to give products **10** as colorless solid (36 mg, 98%). Mp: 160~161 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 8.10 (d, *J* = 8.0 Hz, 2H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 8.9 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 5.96–6.03 (m, 1H), 5.73–5.65 (m, 1H), 4.73–4.79 (m, 1H), 3.82 (s, 3H), 3.14–2.99(m, 1H), 2.13–1.92 (m, 2H), 1.72–1.59 (m, 1H), 1.57–1.46 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 194.1 (d, *J* = 23.2 Hz), 165.9 (d, *J* = 18.2 Hz), 135.2, 133.9, 132.7, 129.4 (d, *J* = 5.1 Hz), 128.9, 128.6, 126.7, 121.9, 114.5, 103.4, 101.9, 55.5, 53.8, 42.2 (d, *J* = 17.17 Hz, 2H), 23.5, 20.3; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ = –153.3; IR (KBr) (v/cm<sup>-1</sup>): 3053, 2960, 2926, 2847, 2859, 1724, 1684, 1601, 1514, 1447, 1435, 1402, 1258, 766, 752; HRMS (ESI) calcd for C<sub>22</sub>H<sub>21</sub>FNO<sub>3</sub> (M+H)<sup>+</sup> 366.1500, found 366.1496; HPLC: 95% *ee*, chiral stationary column: IA, mobile phase: hexane/<sup>i</sup>PrOH = 85/15, 1.0 mL/min, 254 nm, 25 °C, *t*<sub>R</sub> (major) = 35.8 min, *t*<sub>R</sub> (minor) = 41.7 min; [α]<sub>D</sub><sup>25</sup> = +20.44 (1.0, CH<sub>2</sub>Cl<sub>2</sub>).

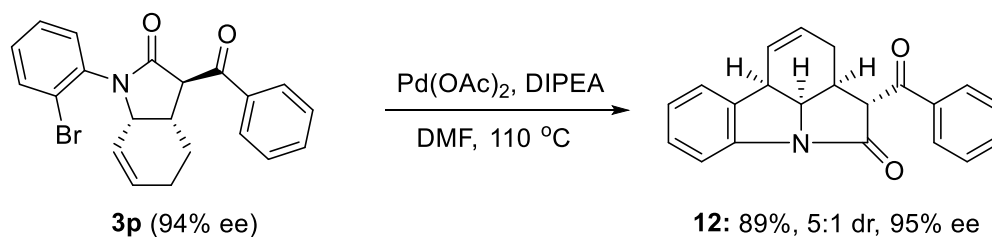
#### 5.5 Procedure for synthesis of **11**



A Schlenk tube equipped with a magnetic stirring bar, **31** (35 mg, 0.1 mmol, 1.0 equiv) and KOH (11mg, 0.2 mmol, 2.0 equiv) were dissolved in MeOH (1 mL), and the mixture was heated to reflux under N<sub>2</sub> atmosphere for 48 h. Then the mixture was cooled to room temperature and the solvent was removed under vacuum. The residue was purified by flash silica gel column chromatography (petroleum ether/ethyl acetate

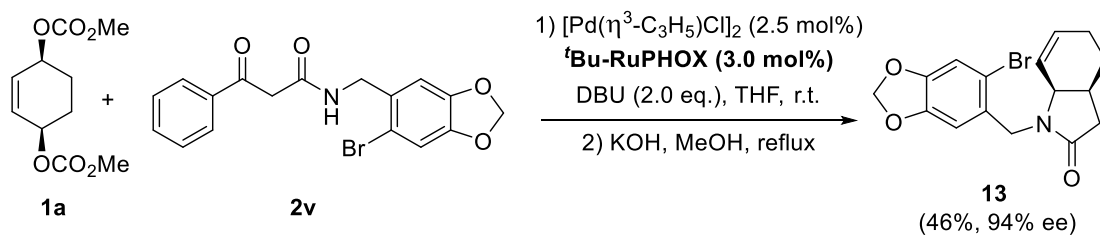
= 2/1) to give products **11** as colorless oil (20 mg, 82%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 7.29 (d, *J* = 9.0 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 5.99–5.94 (m, 1H), 5.72–5.62 (m, 1H), 4.51–4.47 (m, 1H), 3.82 (s, 3H), 2.72–2.65 (m, 2H), 2.41 (q, *J* = 9.1 Hz, 1H), 2.19–2.04 (m, 2H), 1.84–1.78 (m, 1H), 1.73–1.66 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 173.8, 157.6, 131.6, 130.5, 126.0, 125.9, 123.6, 114.4, 57.6, 55.5, 36.8, 31.0, 29.7, 24.1, 22.4; IR (KBr) (ν/cm<sup>-1</sup>): 2972, 2930, 1700, 1647, 1536, 1510, 1455, 1346, 1030, 800; HRMS (ESI) calcd for C<sub>15</sub>H<sub>18</sub>NO<sub>2</sub> (M+H)<sup>+</sup> 244.1332, found 244.1331; HPLC: 88% *ee*, chiral stationary column: OZ, mobile phase: hexane/<sup>i</sup>PrOH = 80/20, 1.0 mL/min, 210 nm, 25 °C, *t*<sub>R</sub> (major) = 21.70 min, *t*<sub>R</sub> (minor) = 15.41 min; [α]<sub>D</sub><sup>25</sup> = +67.00 (*c* 0.5, CH<sub>2</sub>Cl<sub>2</sub>).

### 5.6 Procedure for synthesis of **12**



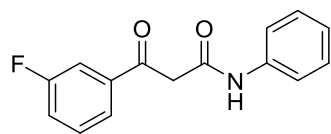
A flame-dried Schlenk tube equipped with a magnetic stirring bar, was charged with a mixture of Pd(OAc)<sub>2</sub> (2.25 mg, 5 mol%) and dppb (52 mg, 10 mol%). After being evacuated and backfilled with nitrogen three times, DMF (2 mL) was added to the Schlenk tube and the mixture was stirred at room temperature under N<sub>2</sub> atmosphere for 1 h. DIPEA (52 mg, 0.4 mmol, 2.0 equiv) was added via a syringe followed by the addition of **3p** (70 mg, 0.2 mmol, 1.0 equiv). The reaction mixture was allowed to stir under N<sub>2</sub> atmosphere at 110 °C for 12 h. DMF was evaporated under vacuum and the residue was purified by flash silica gel column chromatography (petroleum ether/ethyl acetate = 3/1) to give product **12** as a white solid (56 mg, 89%). Mp: 185~187 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 8.23 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.65–7.49 (m, 4H), 7.21 (t, *J* = 7.3 Hz, 2H), 7.12–7.02 (m, 1H), 5.97–5.89 (m, 1H), 5.87–5.79 (m, 1H), 5.31–5.22 (m, 1H), 4.33 (s, 1H), 3.87 (dd, *J* = 9.7, 4.9 Hz, 1H), 3.10 (ddd, *J* = 10.5, 7.1, 5.3 Hz, 1H), 2.40–2.29 (m, 1H), 1.99–1.89 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 193.6, 167.6, 138.6, 137.6, 135.6, 133.9, 129.6, 128.7, 128.0, 127.3, 125.5, 125.2, 124.9, 115.3, 65.7, 62.5, 38.0, 35.9, 25.0; IR (KBr) (ν/cm<sup>-1</sup>): 3071, 3038, 2928, 2851, 1716, 1702, 1670, 1601, 1538, 1510, 1394, 1034, 804, 766; HRMS (ESI) calcd for C<sub>21</sub>H<sub>18</sub>NO<sub>2</sub> (M+H)<sup>+</sup> 316.1332, found 316.1330; HPLC: 95% *ee* (major), 5:1 *dr*, chiral stationary column: IC, mobile phase: hexane/<sup>i</sup>PrOH = 85.0/15.0, 1.0 mL/min, 254 nm, 25 °C, *t*<sub>R</sub> (major) = 18.7 min, *t*<sub>R</sub> (minor) = 26.7 min; [α]<sub>D</sub><sup>25</sup> = +145.20 (*c* 1.0, CH<sub>2</sub>Cl<sub>2</sub>);

### 5.7 Procedure for synthesis of **13**

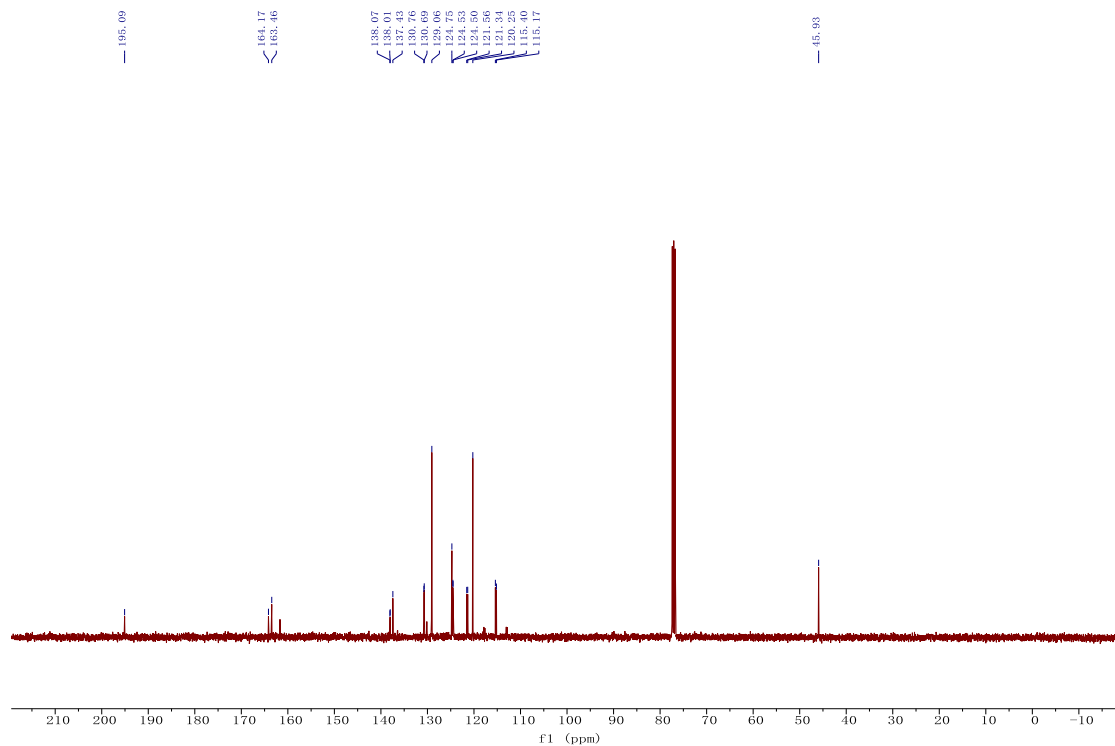
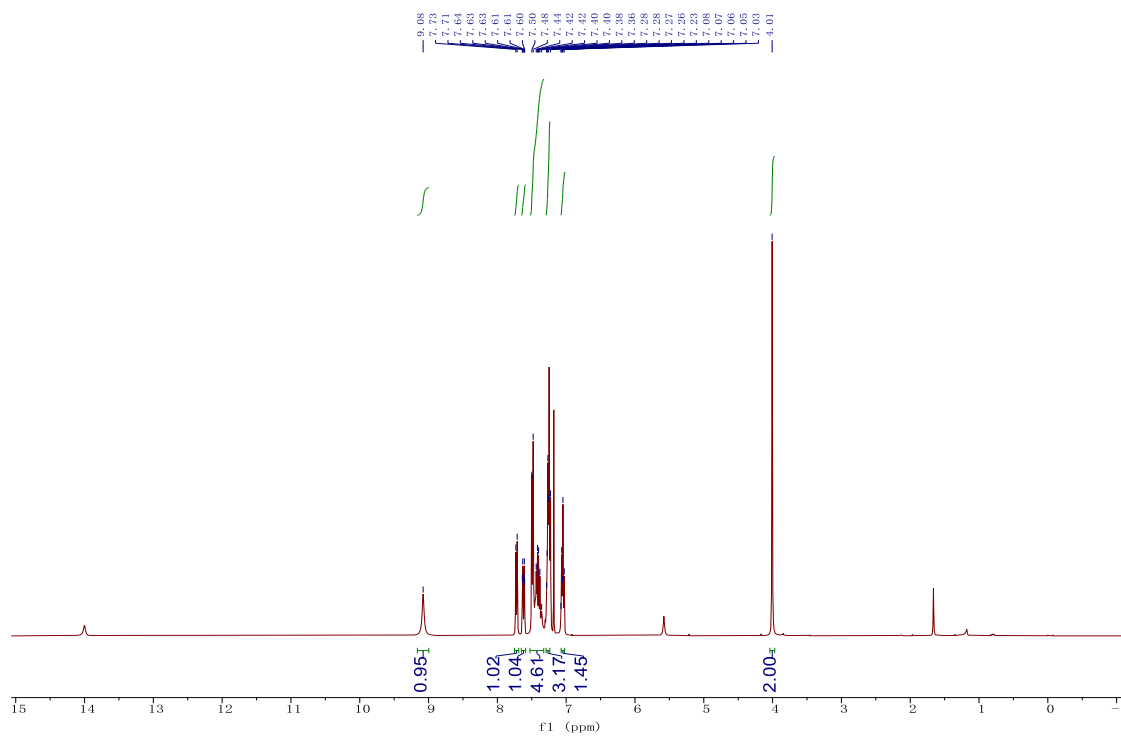


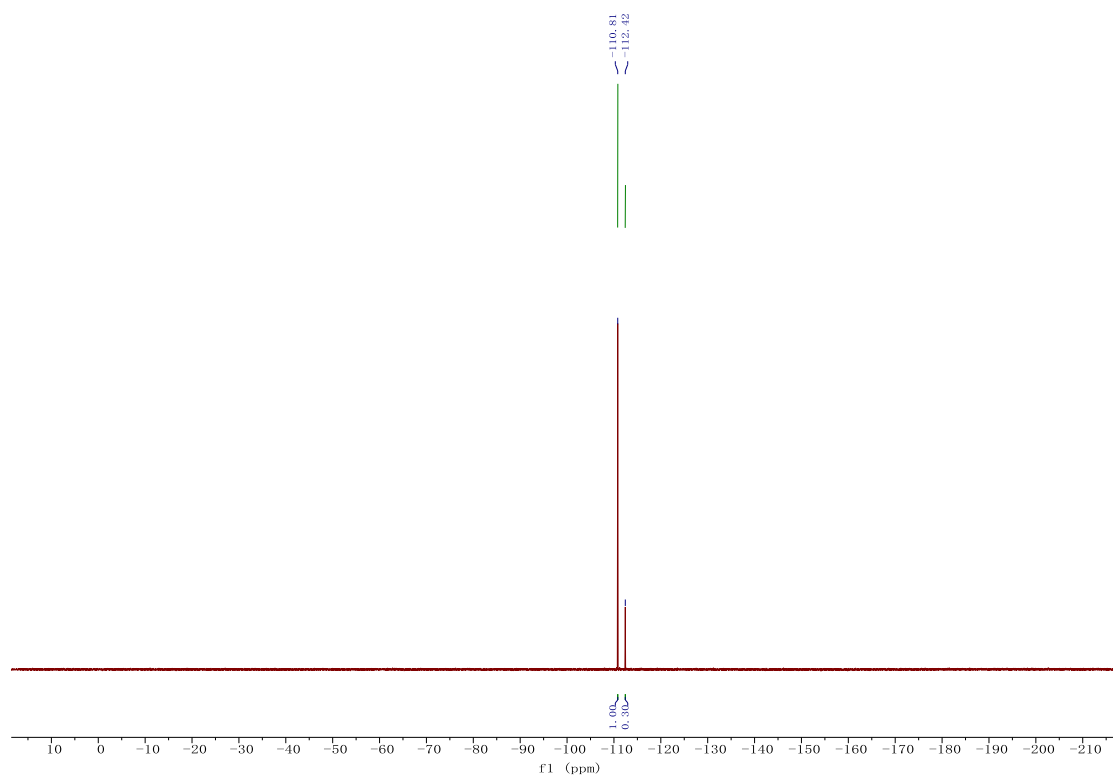
A flame-dried Schlenk tube equipped with a magnetic stirring bar, was charged with a mixture of  $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}]_2$  (3.66 mg, 2.5 mol%) and RuPHOX (10.20 mg, 3.0 mol%). After being evacuated and backfilled with nitrogen three times, THF (4 mL) was added to the Schlenk tube and the mixture was stirred at room temperature under  $\text{N}_2$  atmosphere for 1 h. Allylic biscarbonate **1** (108 mg, 0.44 mmol, 1.1 equiv) was added via a syringe followed by the addition of **2v** (0.4 mmol, 1.0 equiv) and DBU (0.8 mmol, 2.0 equiv). The reaction mixture was allowed to stir under  $\text{N}_2$  atmosphere at room temperature for 3 h. THF was evaporated under vacuum and the residue was purified by flash silica gel column chromatography (petroleum ether/ethyl acetate = 3/1) to give **3v**. Then, to a Schlenk tube equipped with a magnetic stirring bar, was added KOH (56.11 mg, 1 mmol, 5.0 equiv), **3v** and MeOH (2 mL). The mixture was then heated to reflux under an  $\text{N}_2$  atmosphere for 48 h. Then the mixture was cooled to room temperature and the solvent was removed under reduced pressure. The residue was purified by a flash silica gel column chromatography (petroleum ether/ethyl acetate = 2/1) to give product **13** as white solid (64 mg, 46%). Mp: 85~86 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 6.95 (s, 1H), 6.73 (s, 1H), 5.93 (s, 3H), 5.75–5.66 (m, 1H), 4.74 (d,  $J$  = 15.6 Hz, 1H), 4.24 (d,  $J$  = 15.6 Hz, 1H), 3.84–3.46 (m, 2H), 2.46 (s, 1H), 2.25 (dd,  $J$  = 15.2, 4.7 Hz, 1H), 2.12–2.02 (m, 1H), 2.02–1.92 (m, 1H), 1.75–1.56 (m, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 175.3, 149.6, 132.6, 130.2, 123.2, 113.5, 112.6, 108.7, 101.7, 54.4, 44.0, 36.3, 31.0, 23.5, 22.2; IR (KBr) ( $\nu/\text{cm}^{-1}$ ): 3361, 2964, 2922, 2855, 1702, 1686, 1510, 1481, 1261, 817, 746; HRMS (ESI) calcd for  $\text{C}_{16}\text{H}_{17}^{79}\text{BrNO}_3$  ( $\text{M}+\text{H}$ ) $^+$  350.0386, found 350.0385, calcd for  $\text{C}_{16}\text{H}_{17}^{81}\text{BrNO}_3$  ( $\text{M}+\text{H}$ ) $^+$  352.0366, found 352.0363; HPLC: 94% ee, chiral stationary column: AD, mobile phase: hexane/ $i$ PrOH = 80.0/20.0, 1.0 mL/min, 210 nm, 25 °C,  $t_R$  (major) = 13.8 min,  $t_R$  (minor) = 10.1 min;  $[\alpha]_D^{25} = +2.80$  ( $c$  0.5,  $\text{CH}_2\text{Cl}_2$ ).

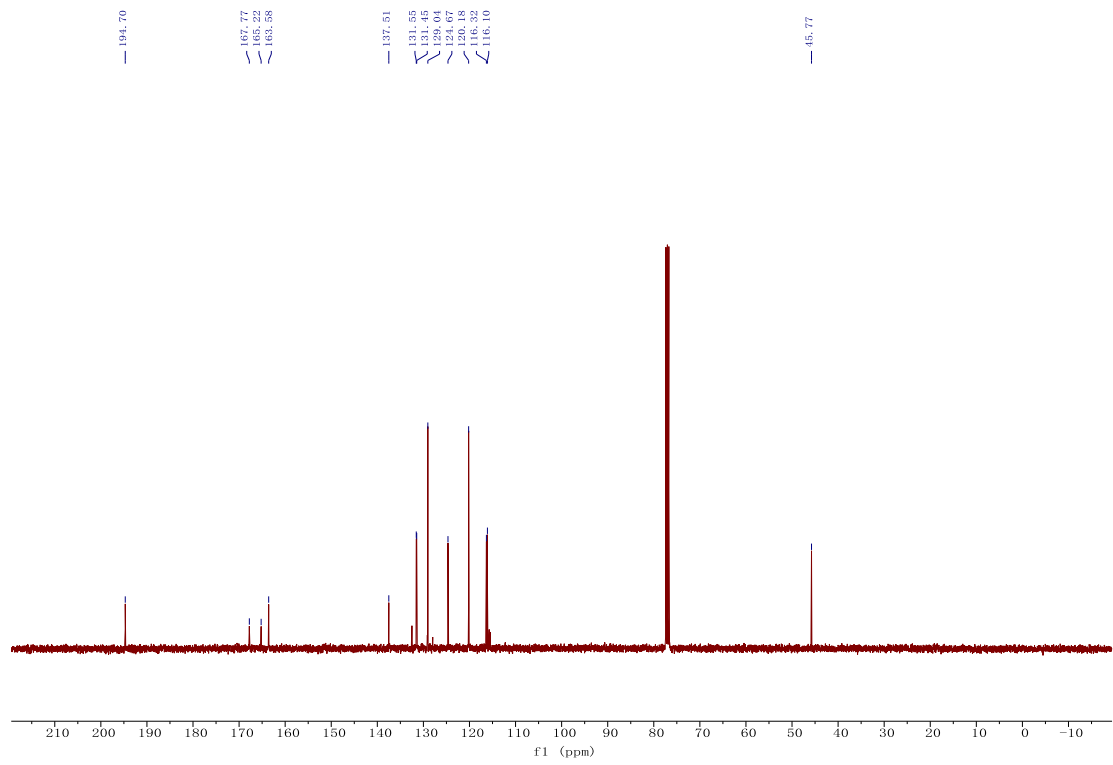
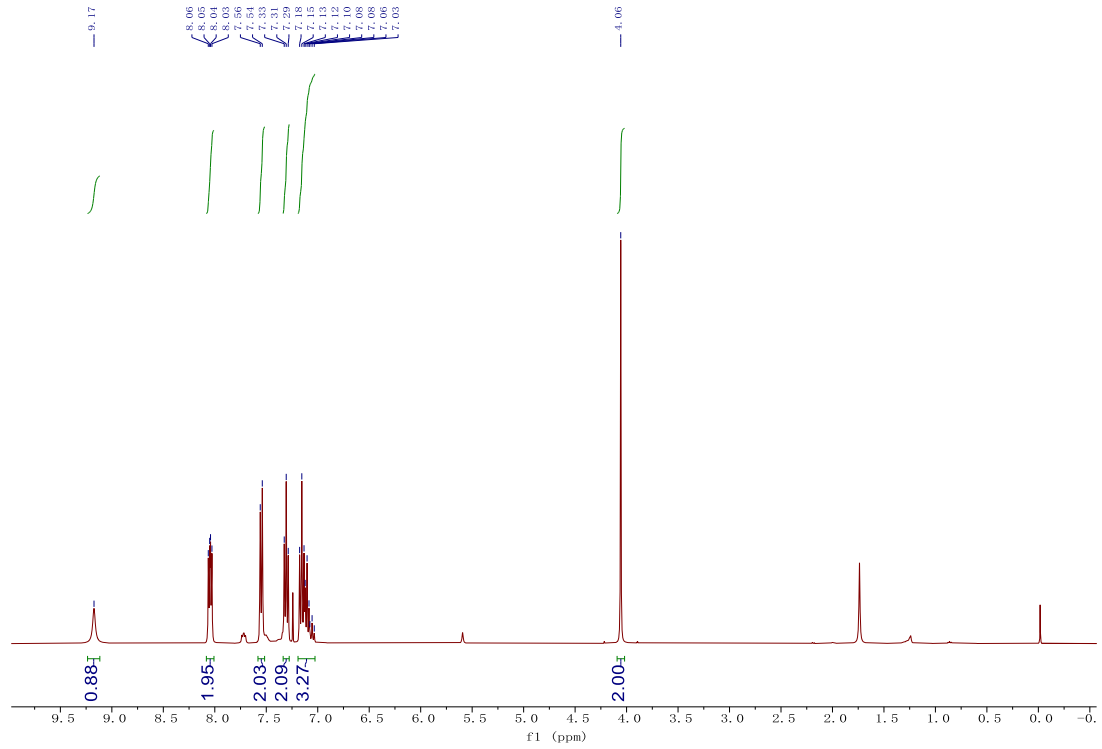
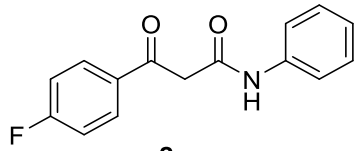
## 6. NMR Spectra



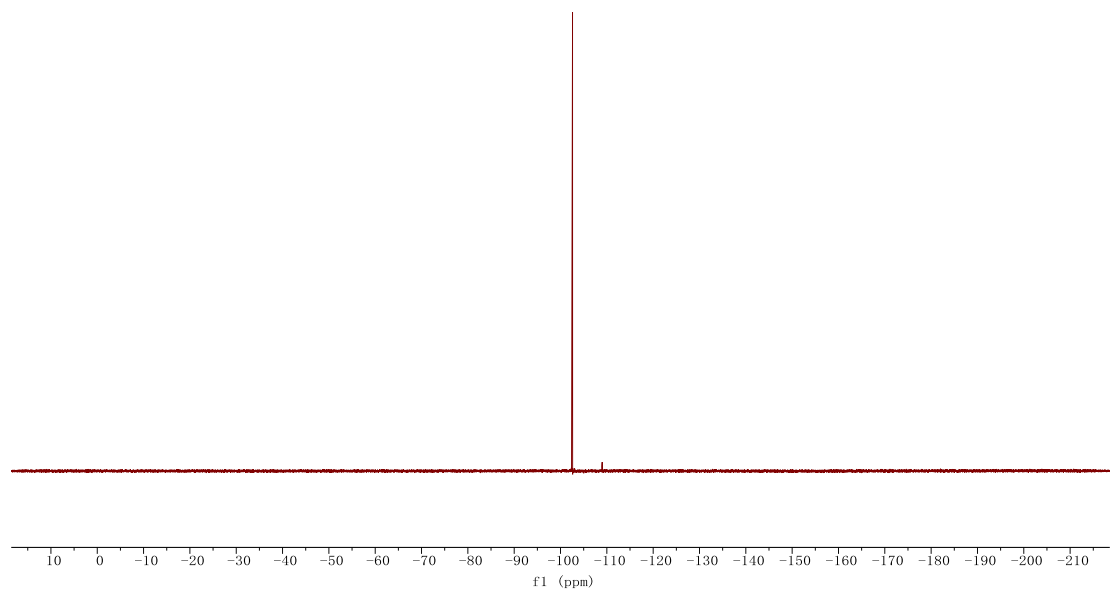
**2b**

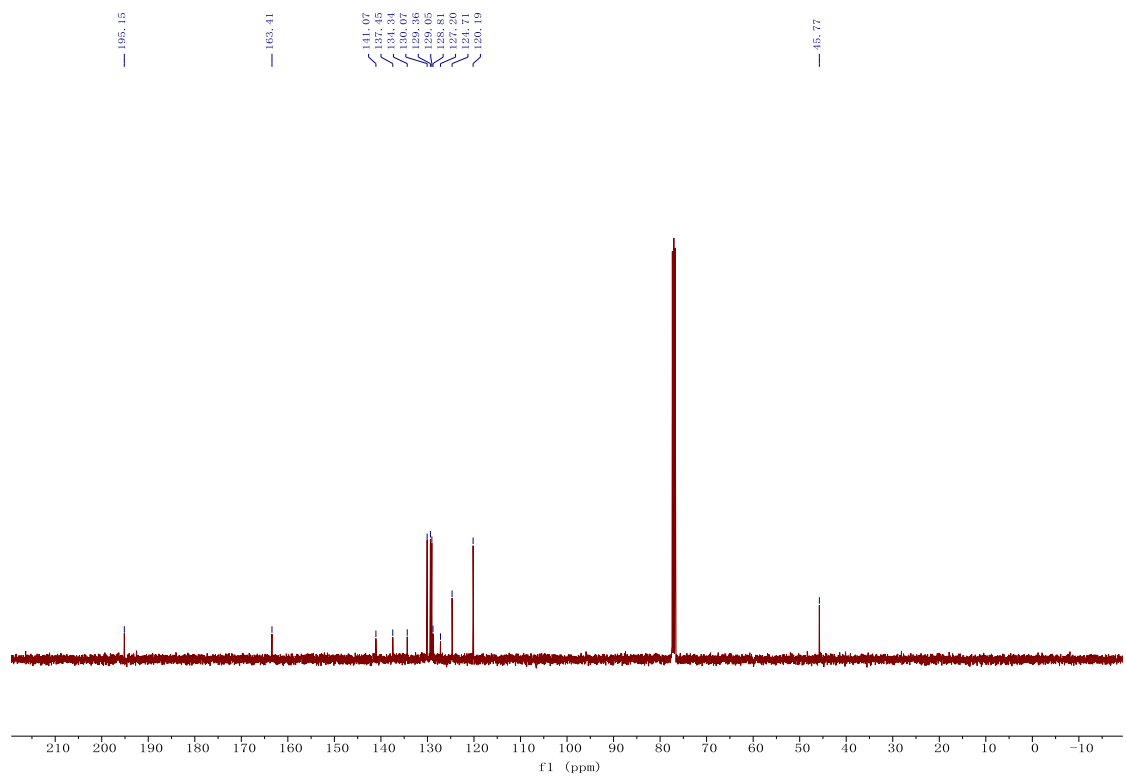
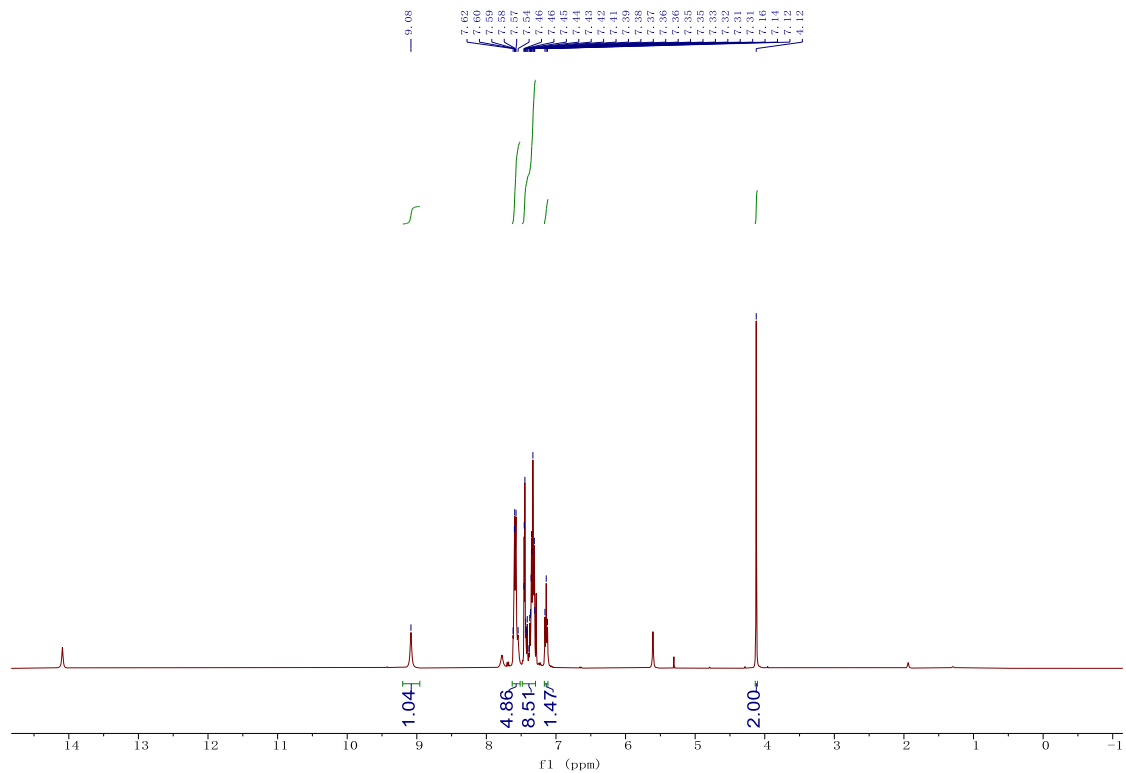
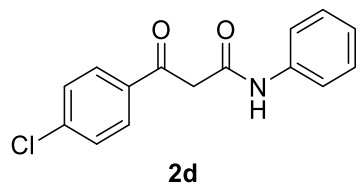


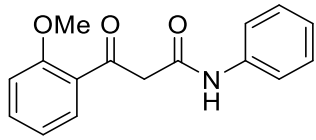




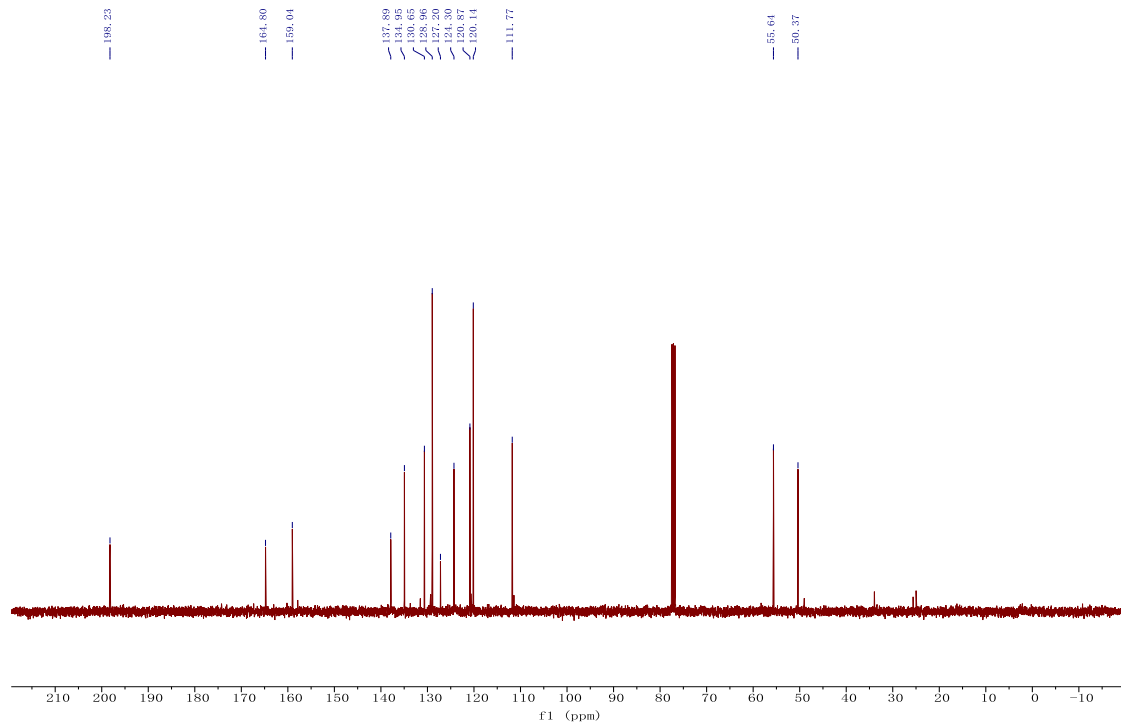
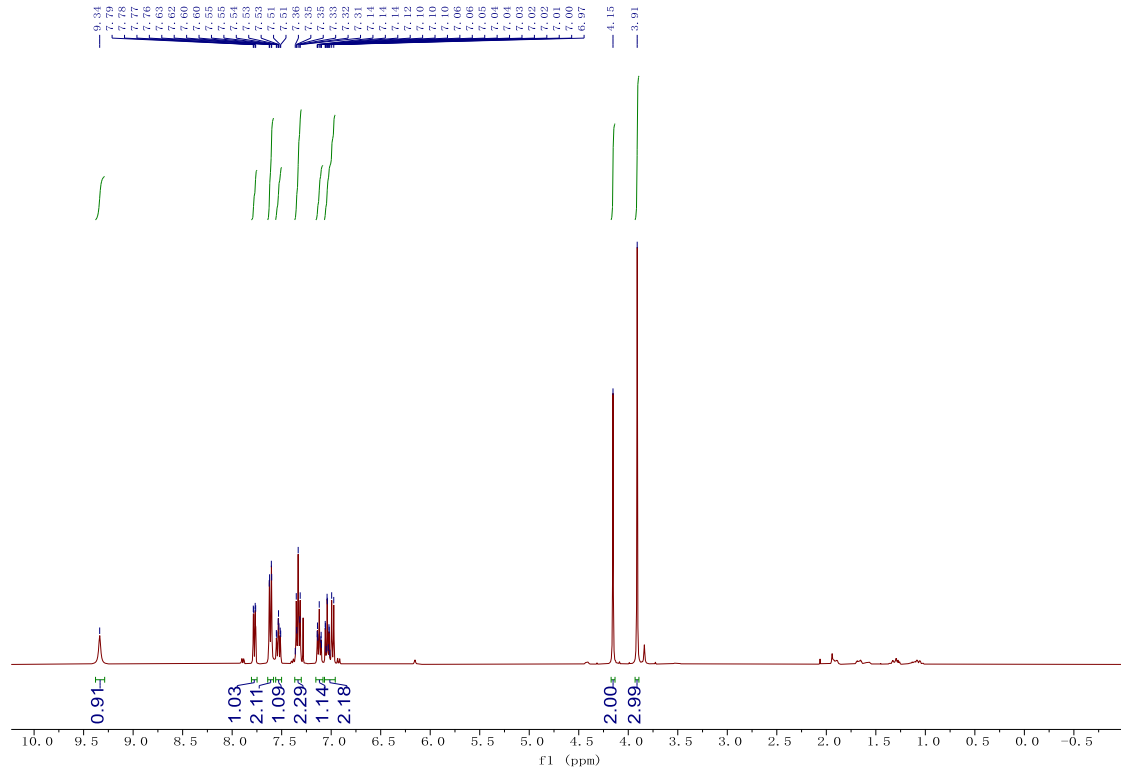


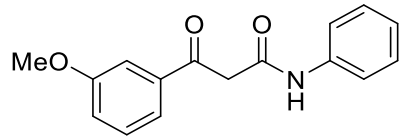




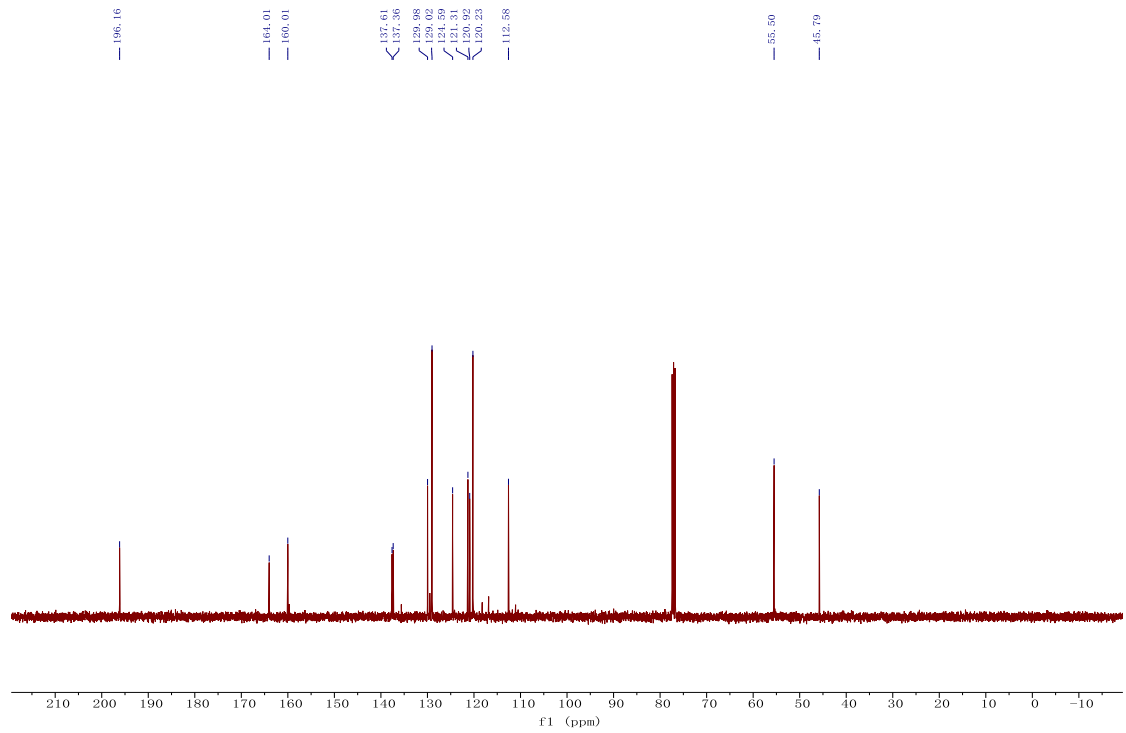
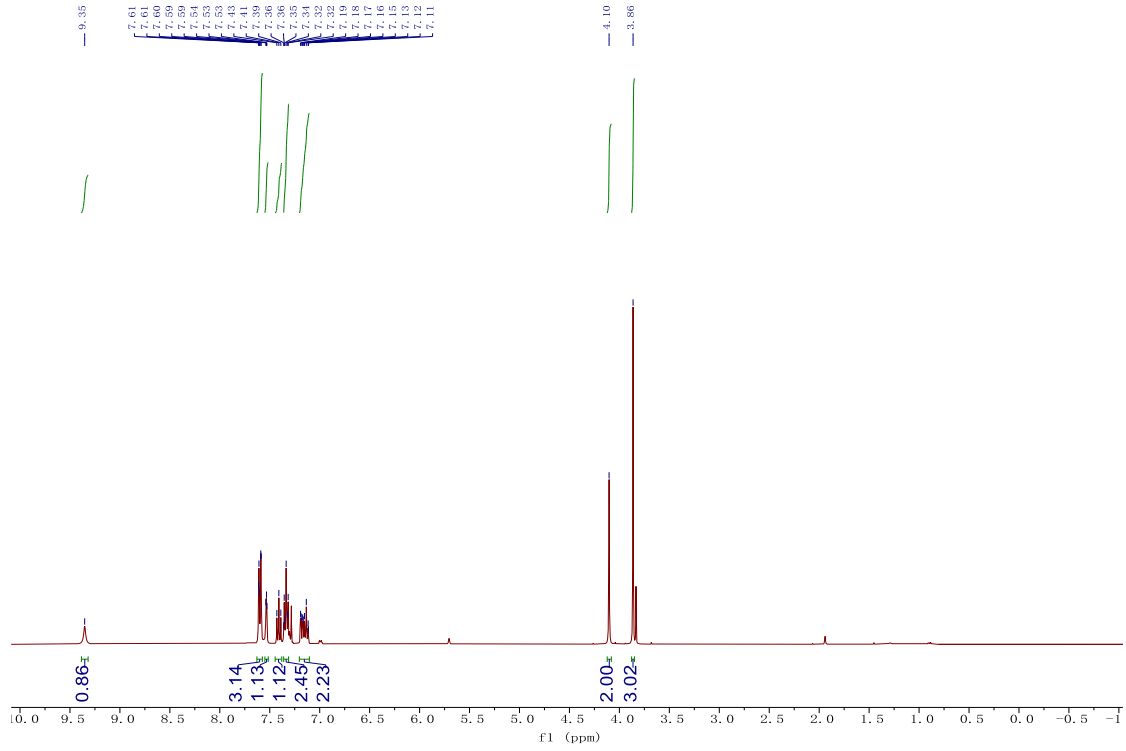


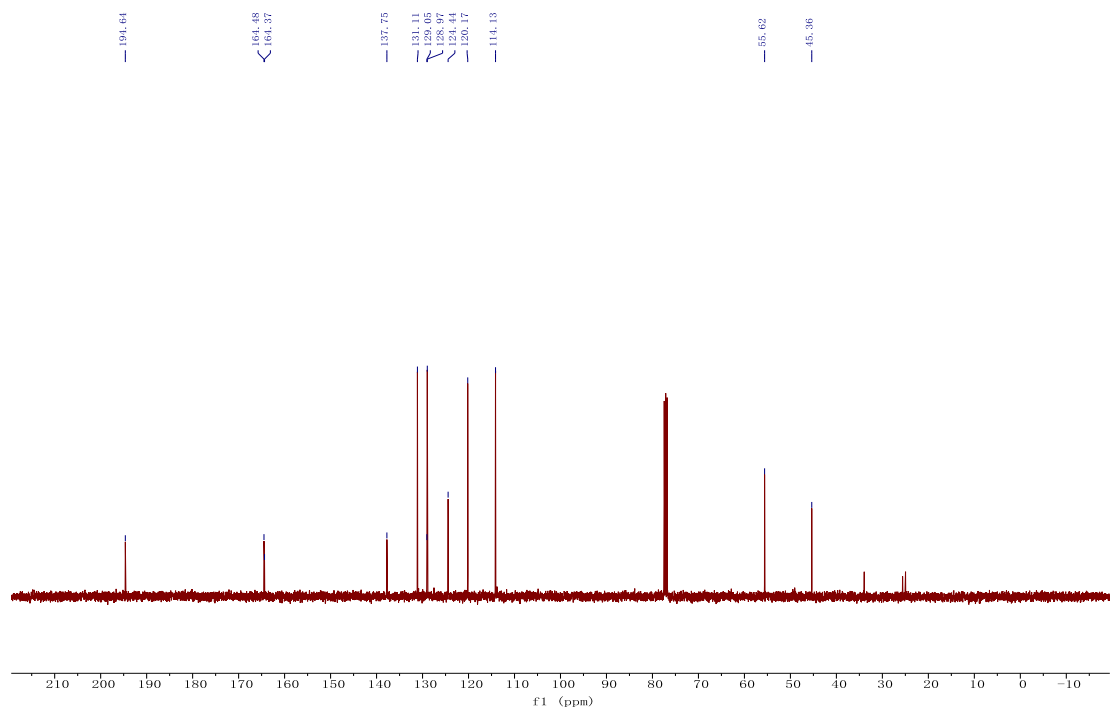
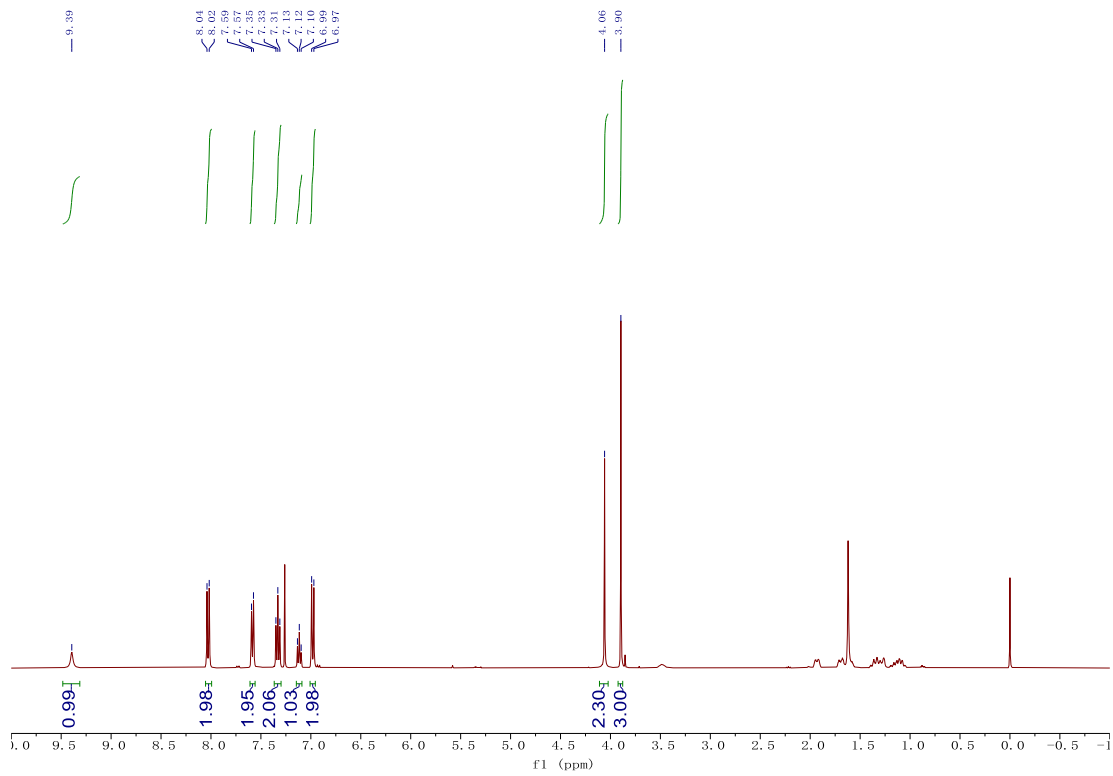
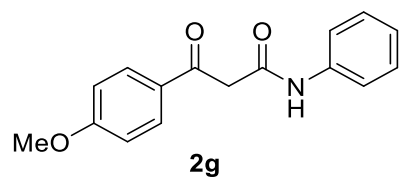
**2e**

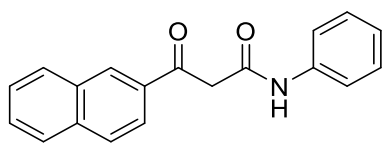




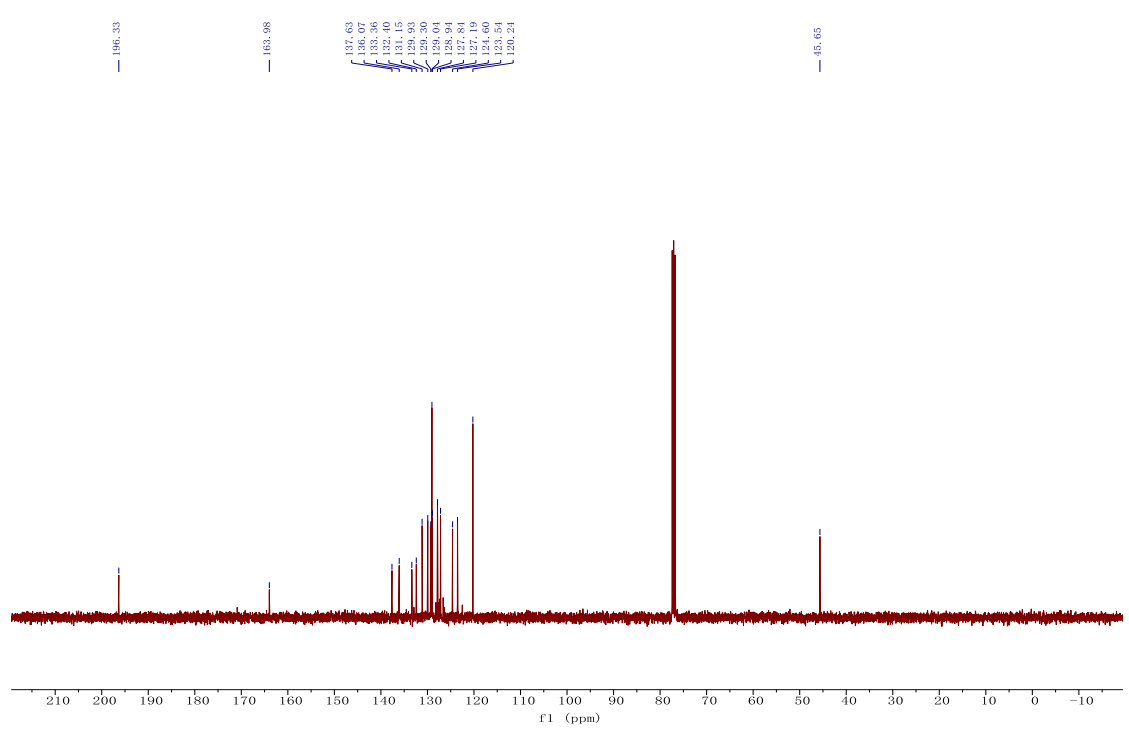
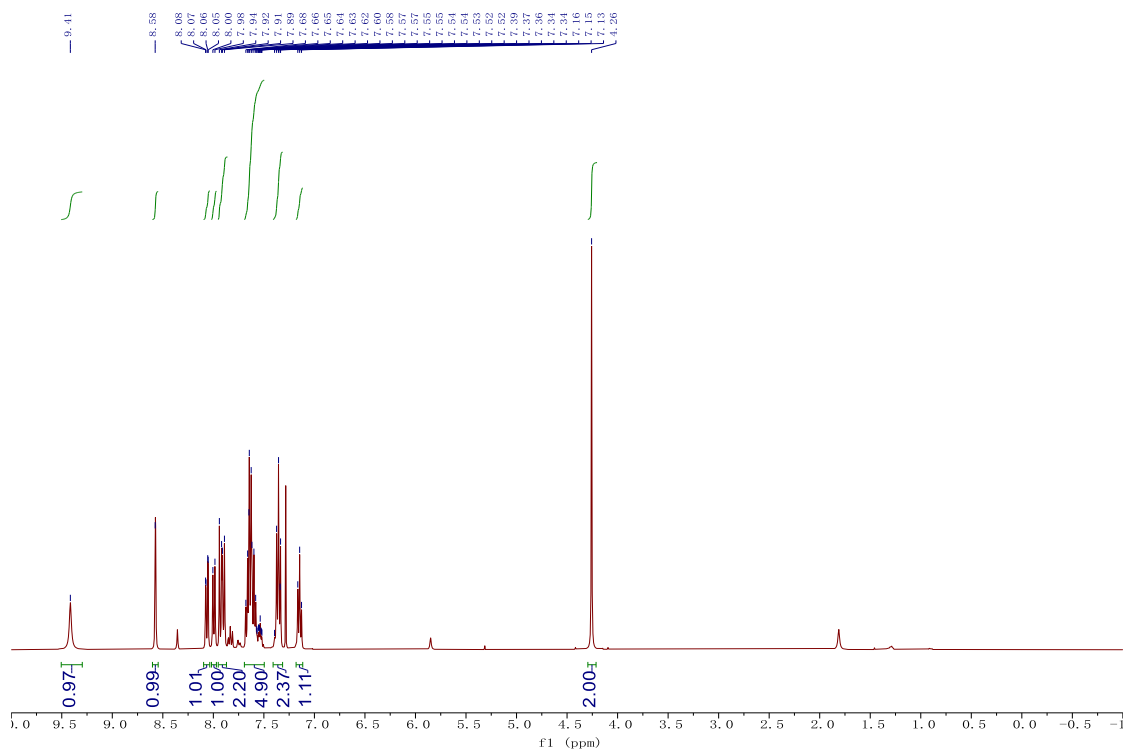
**2f**

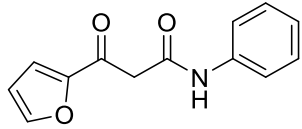




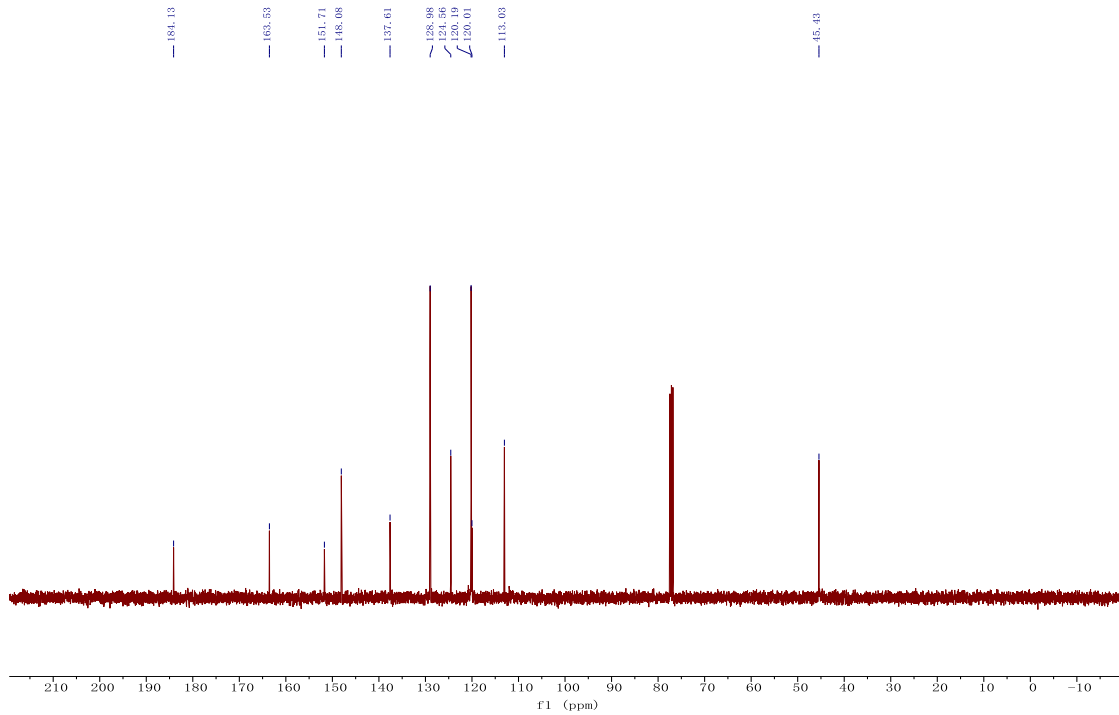
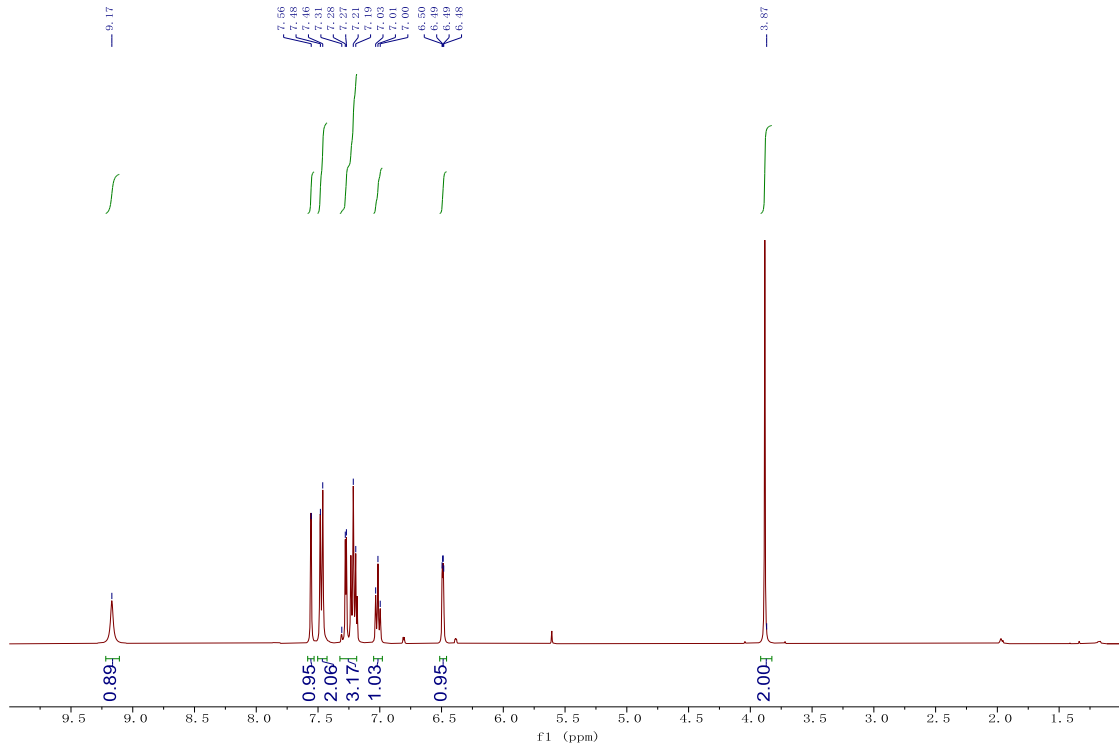


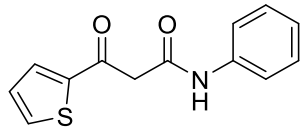
**2i**



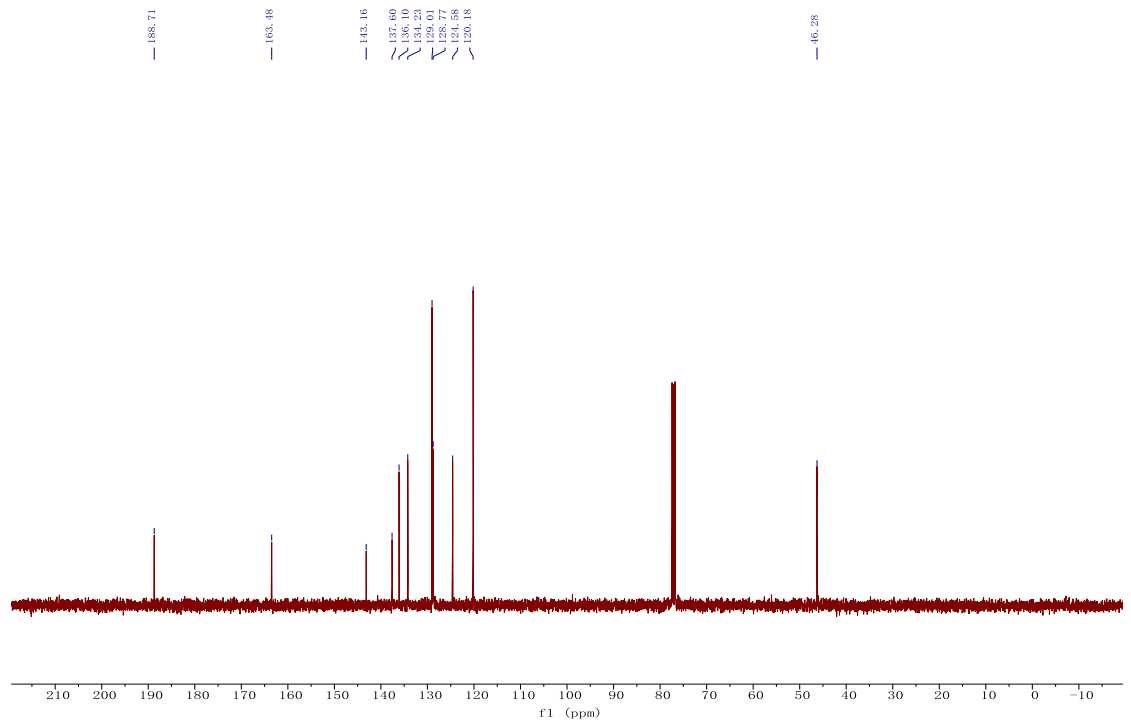
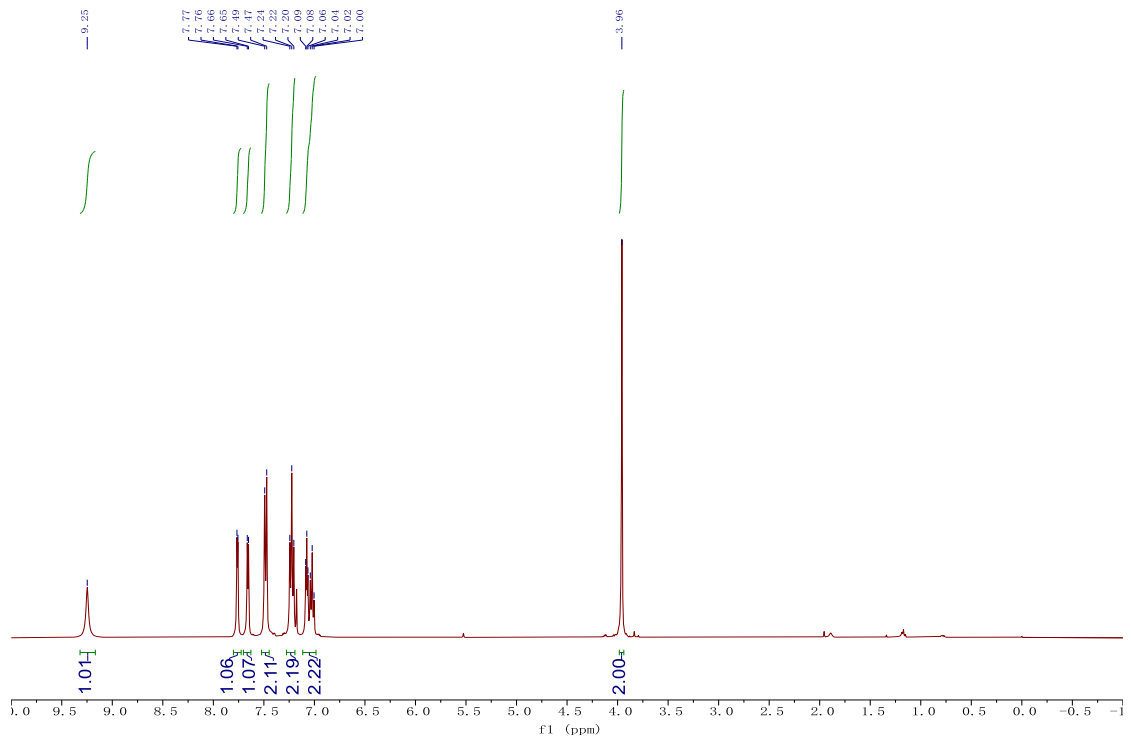


2j

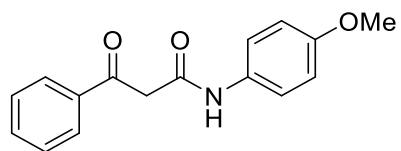




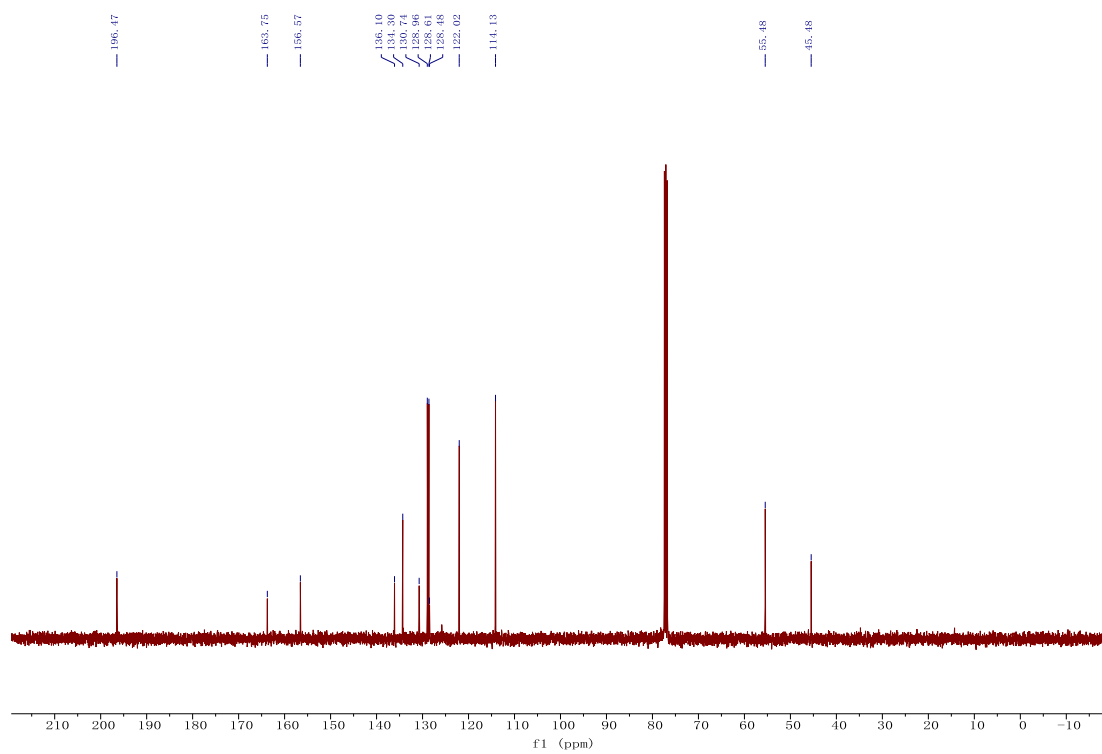
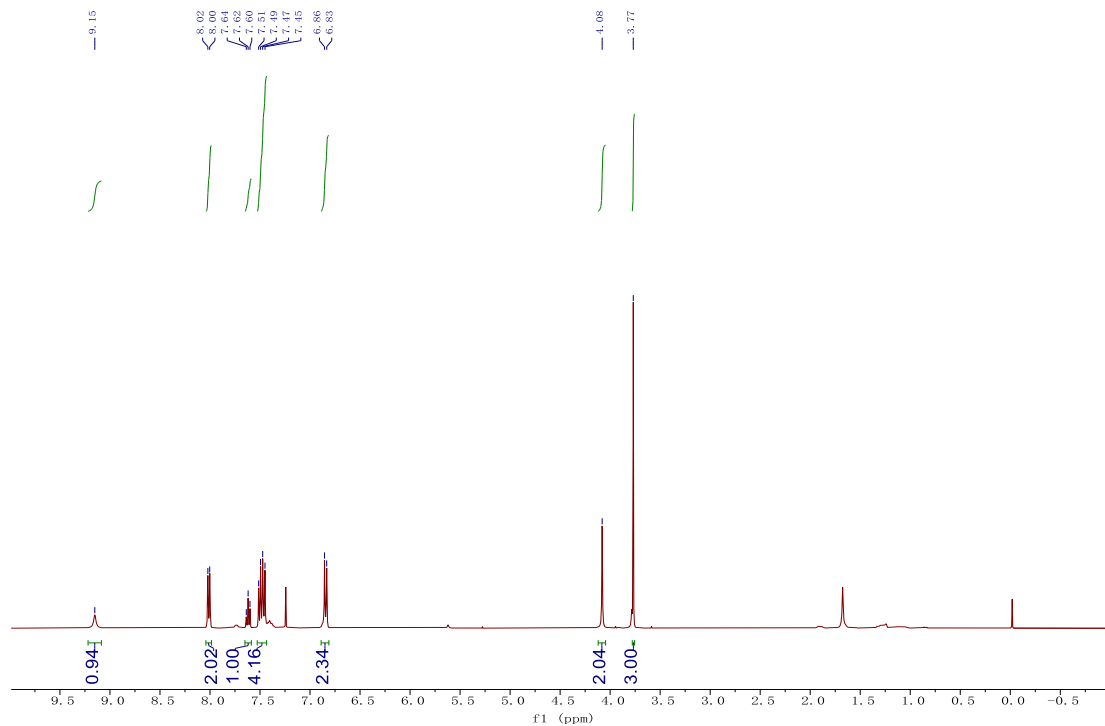
**2k**

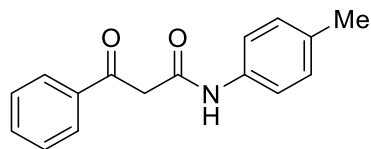




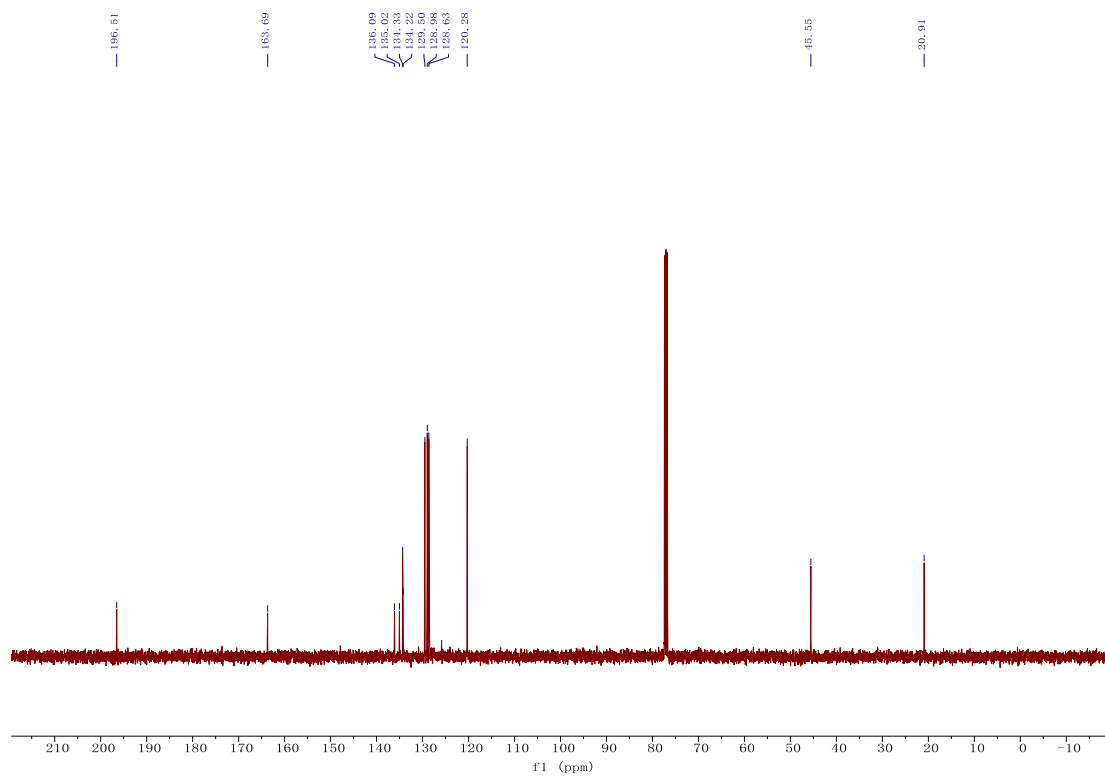
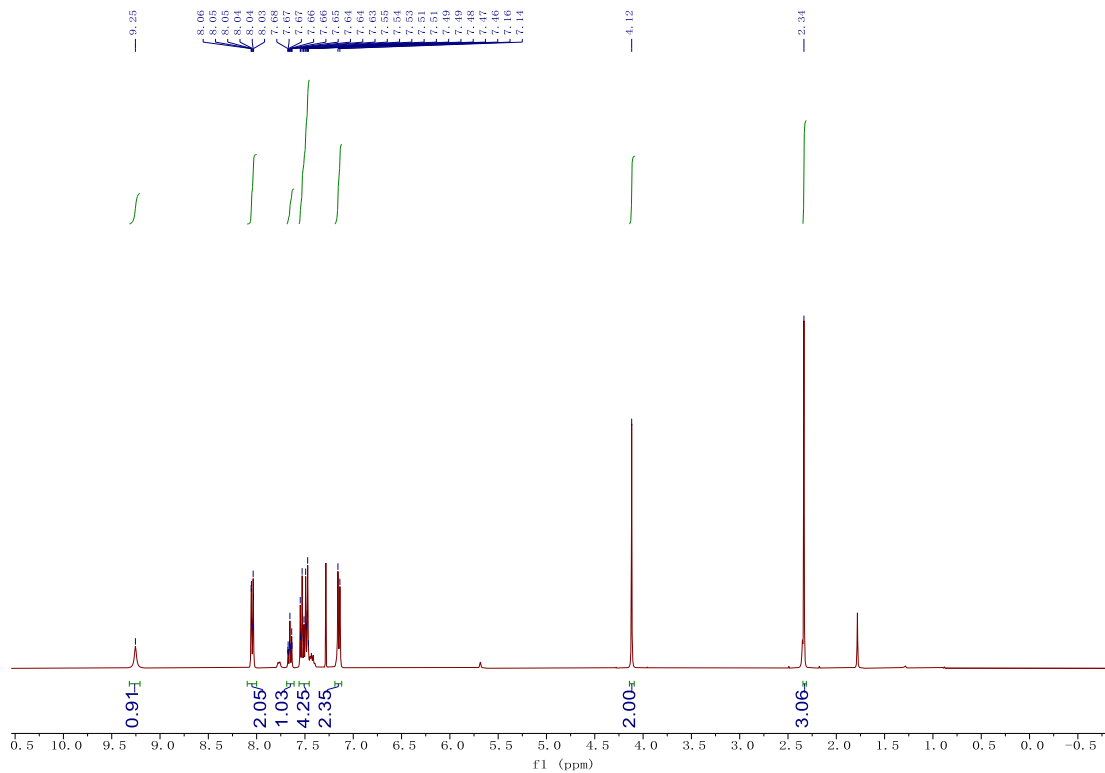


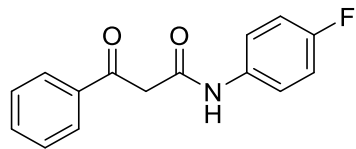
21



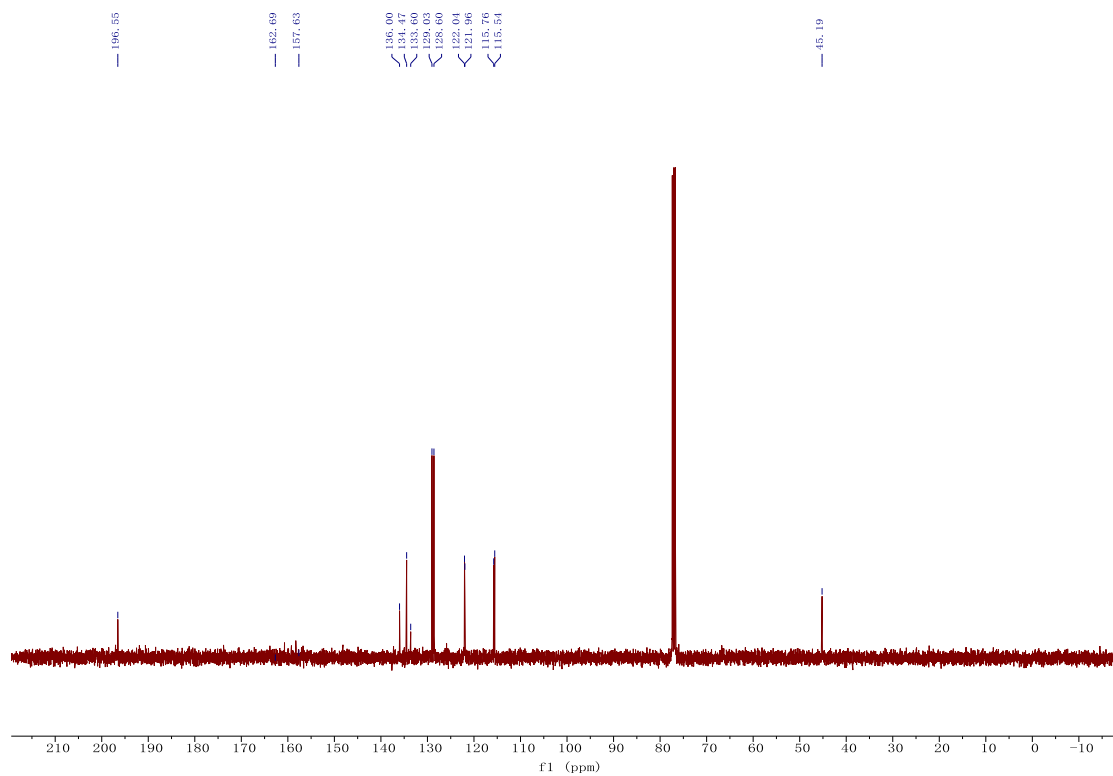
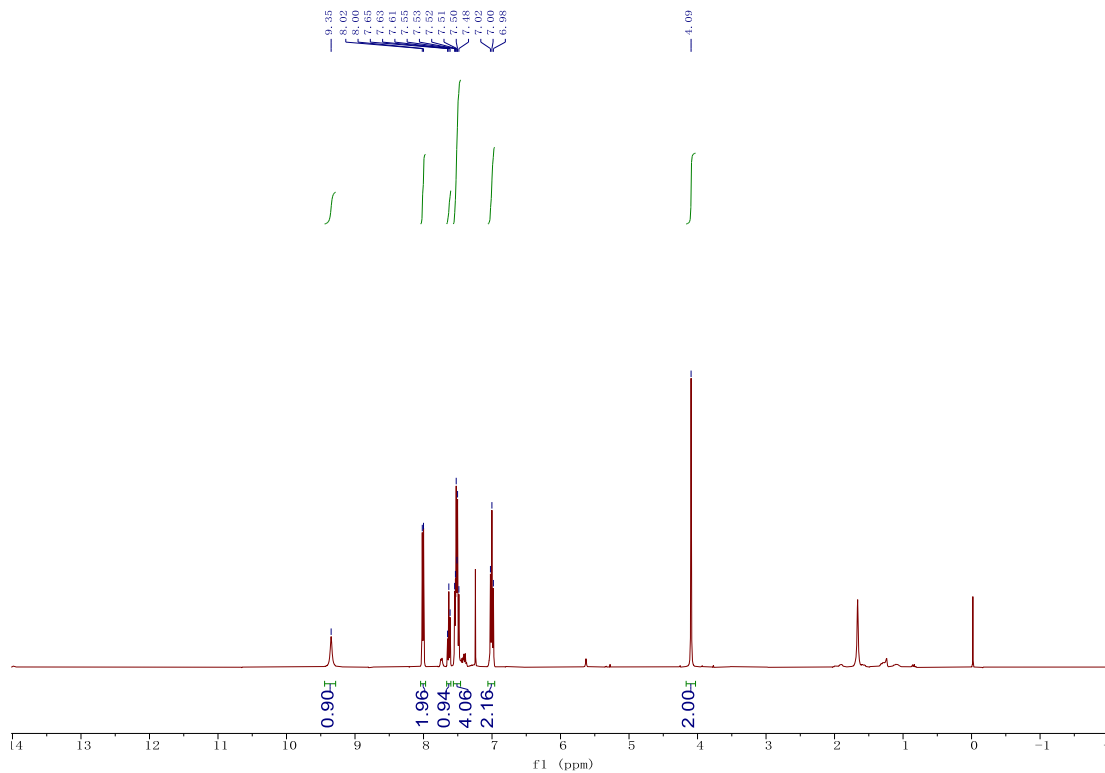


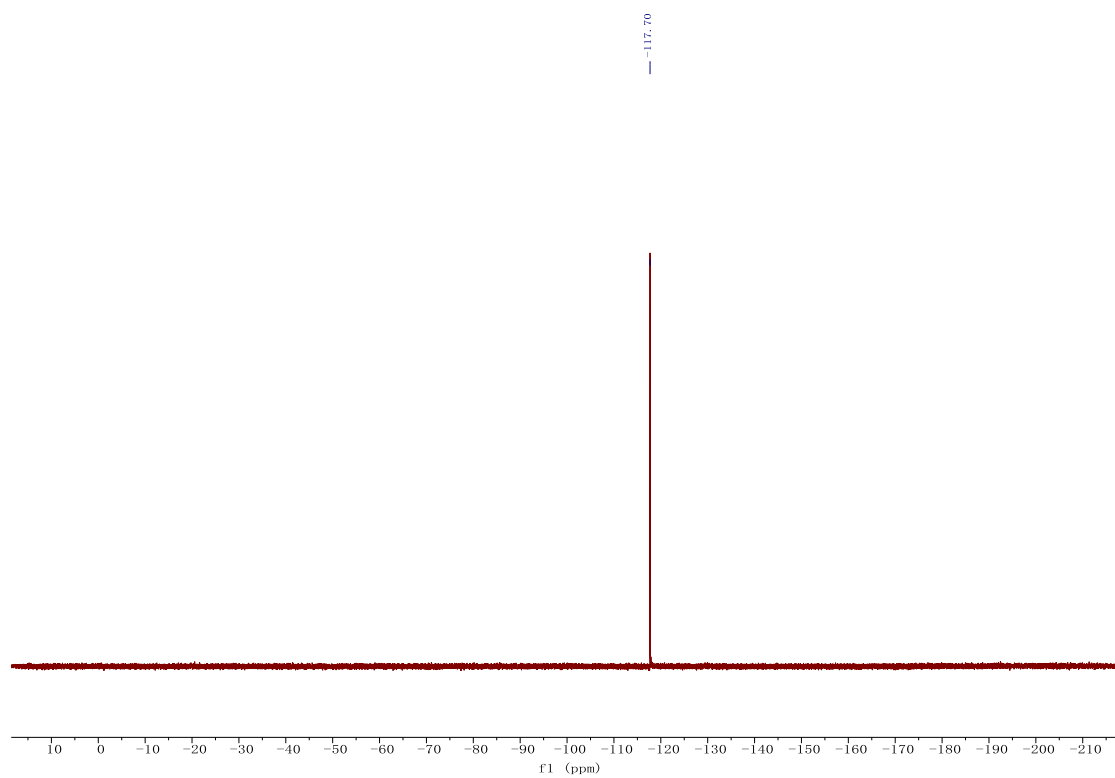
2m

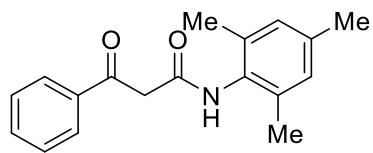




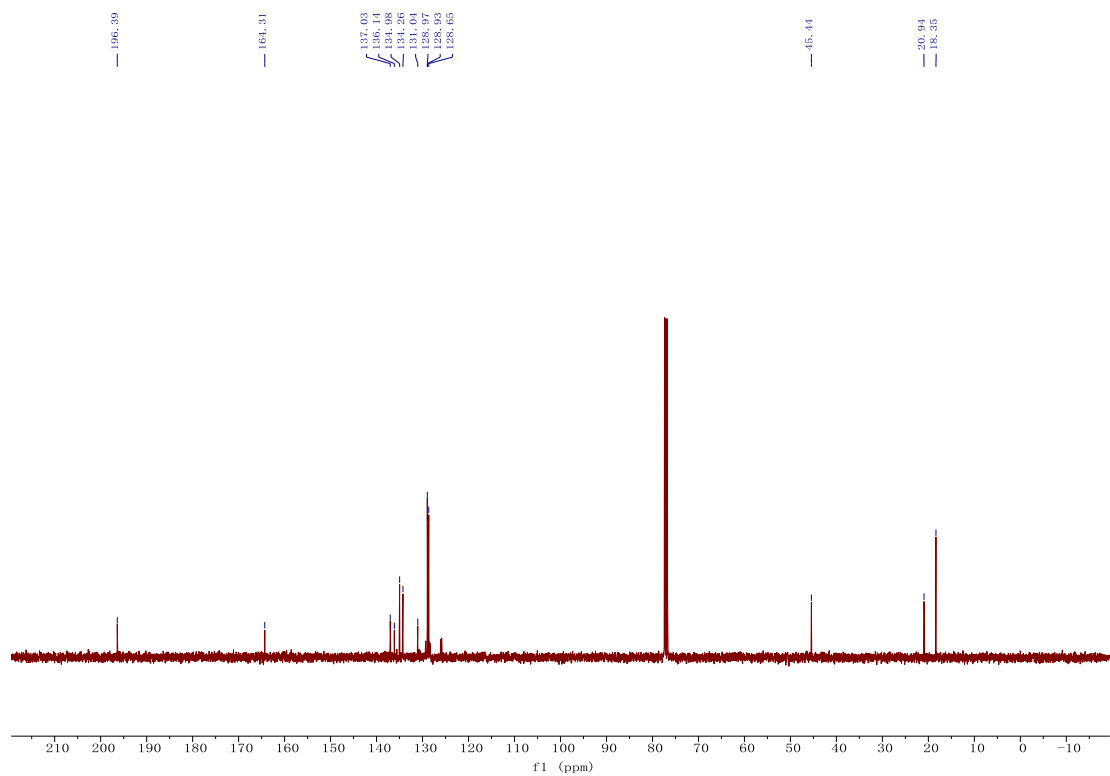
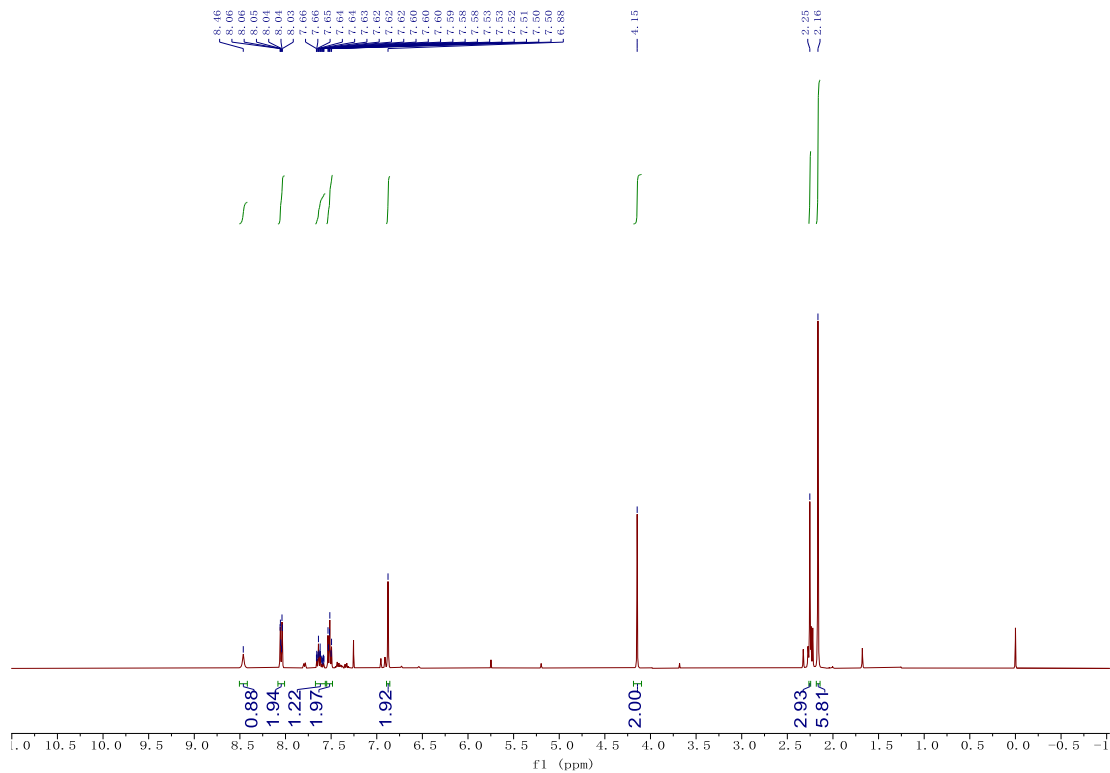
**2n**

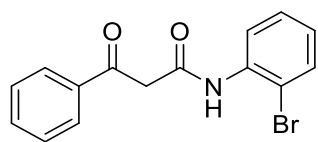




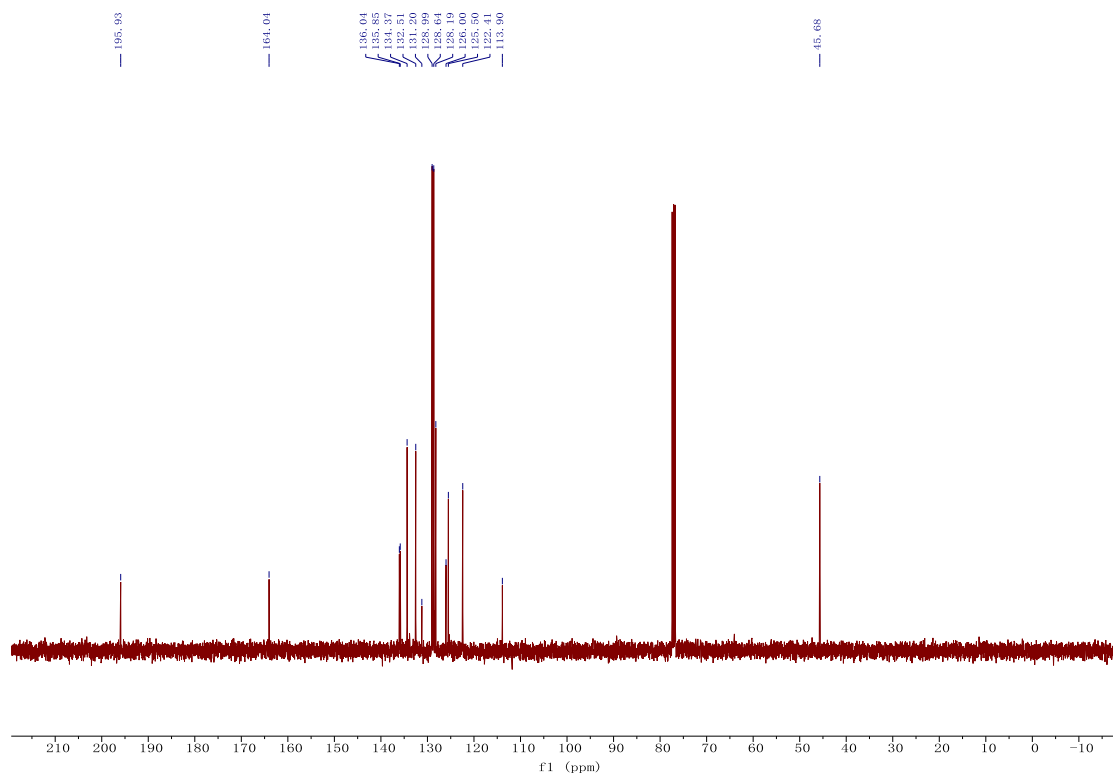
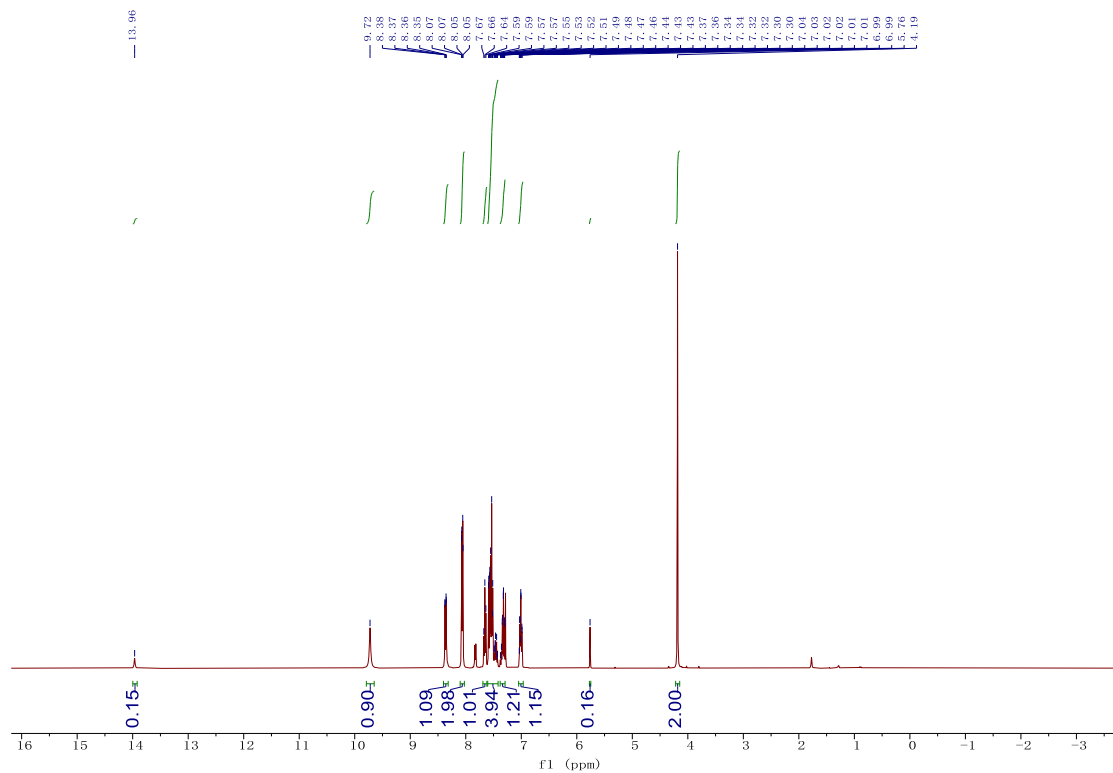


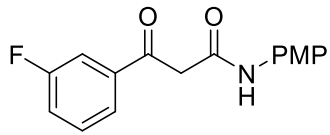
2o





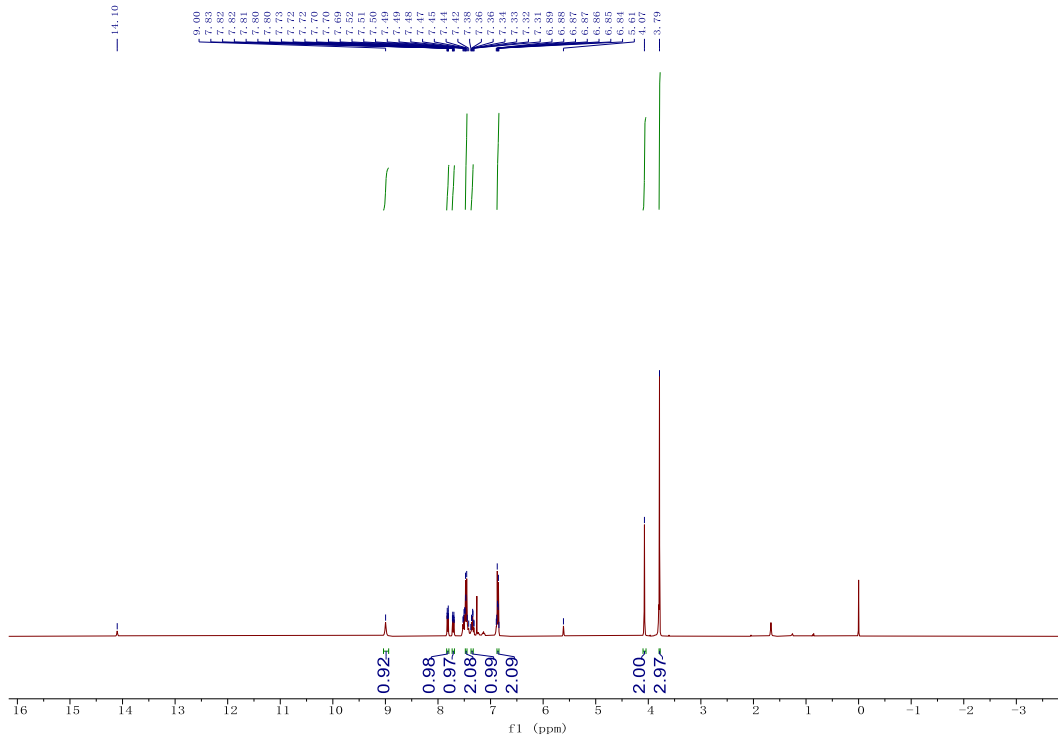
**2p**



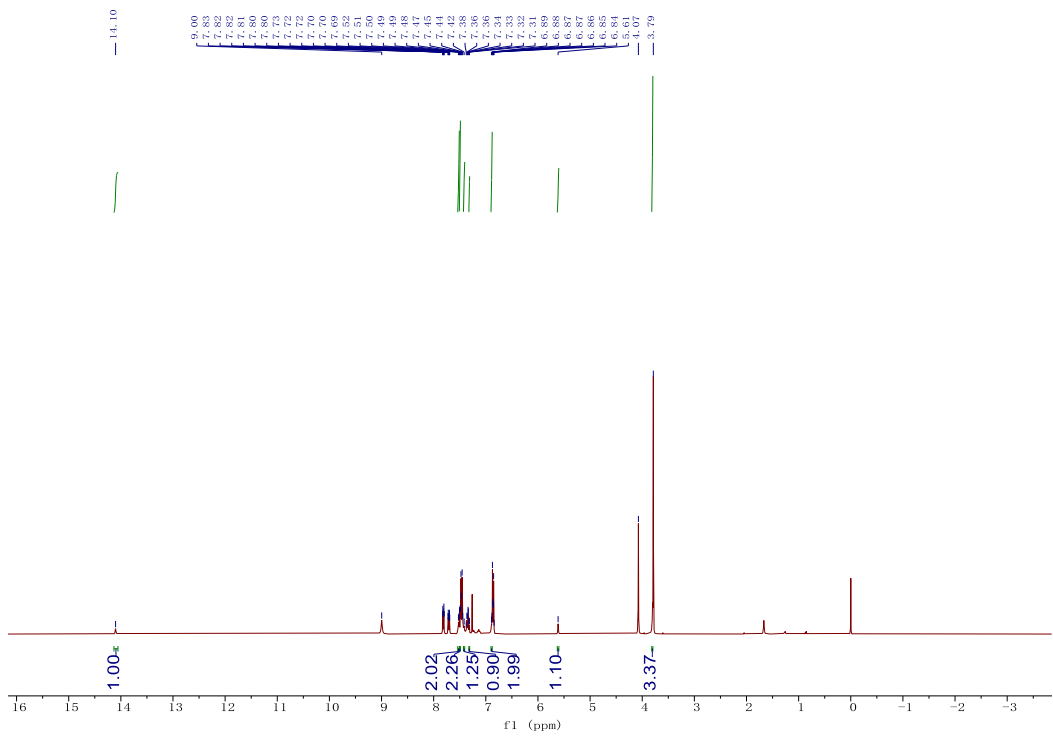


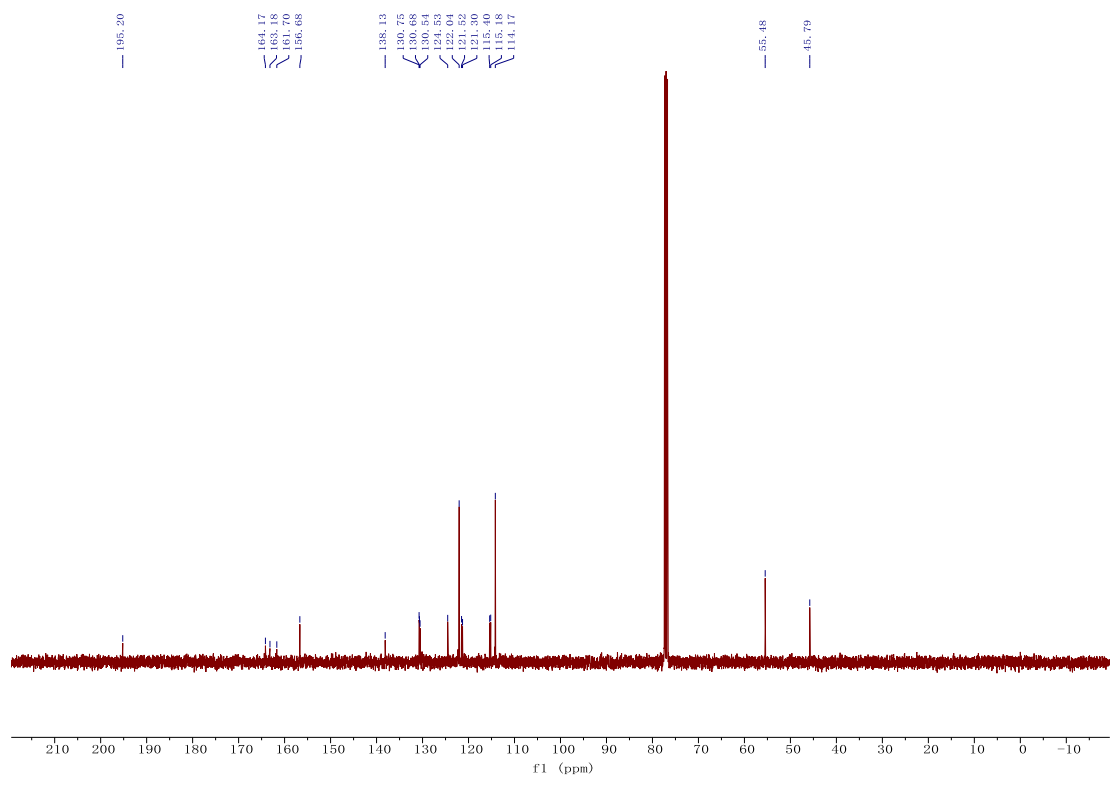
**2q**

Analysis for ketone:



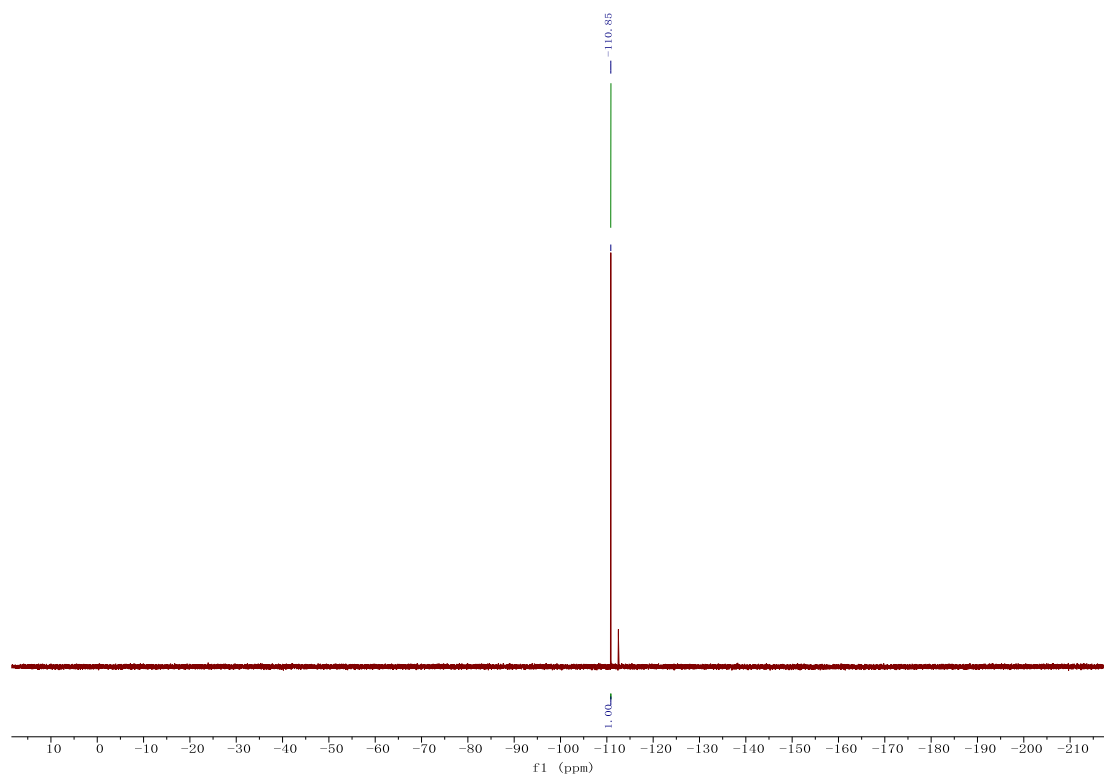
Analysis for enol:



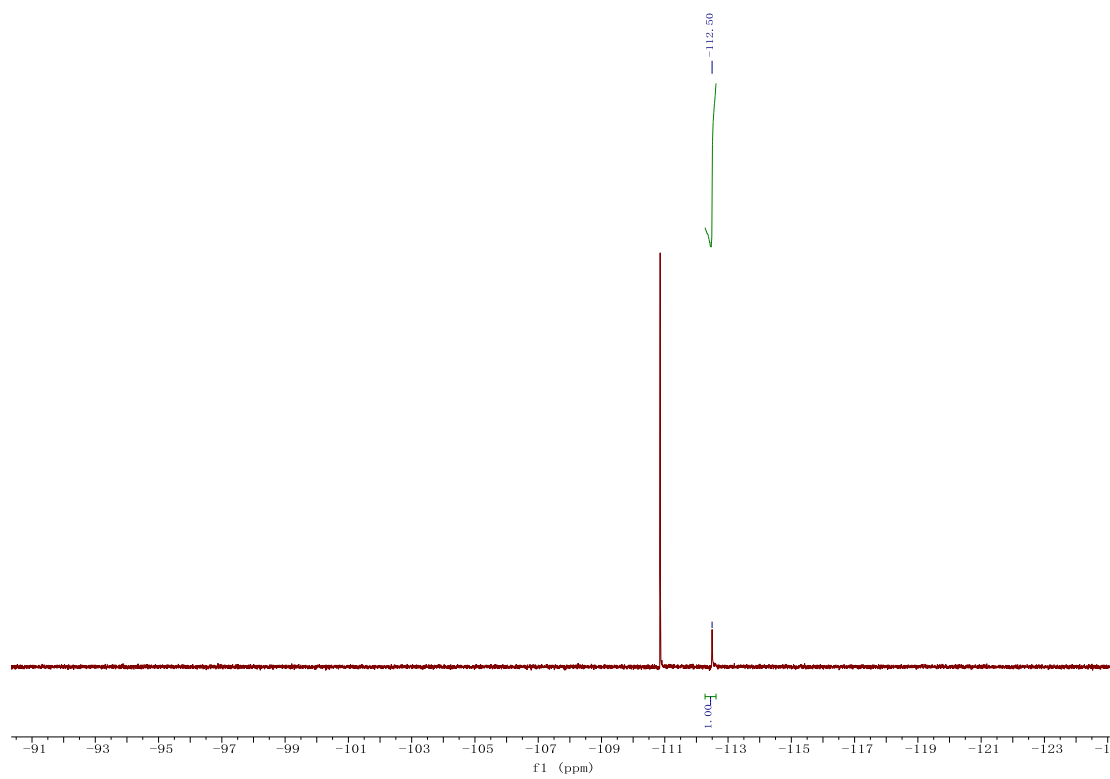


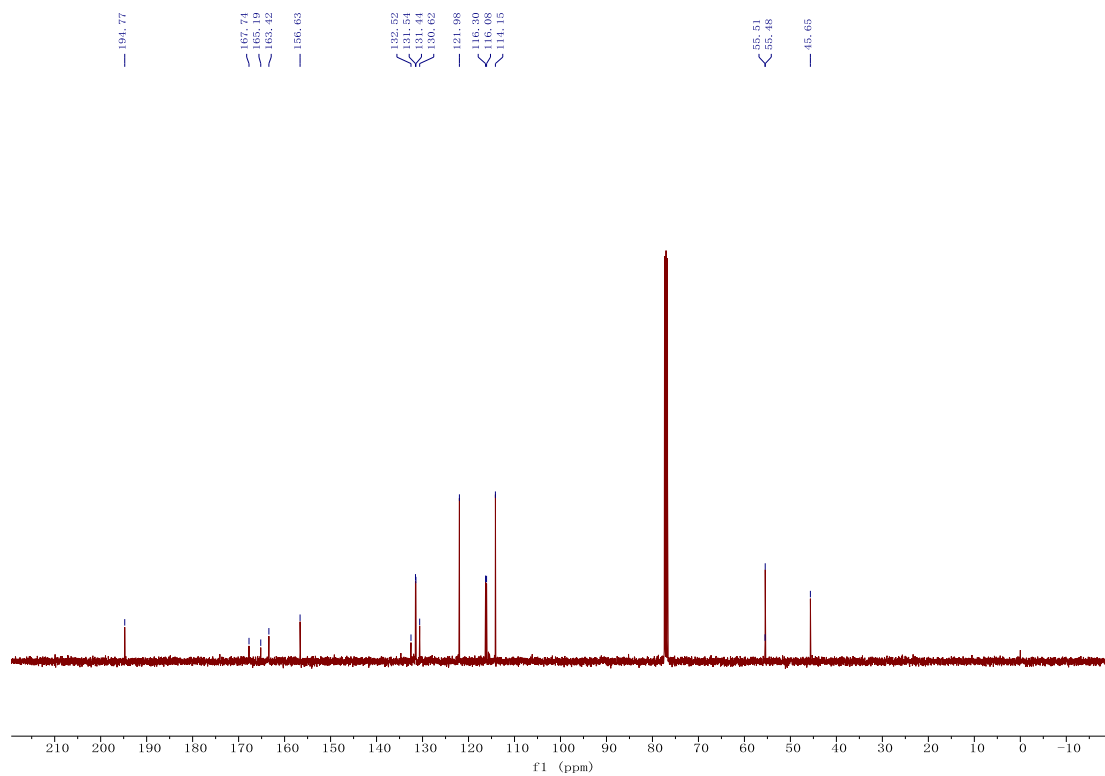
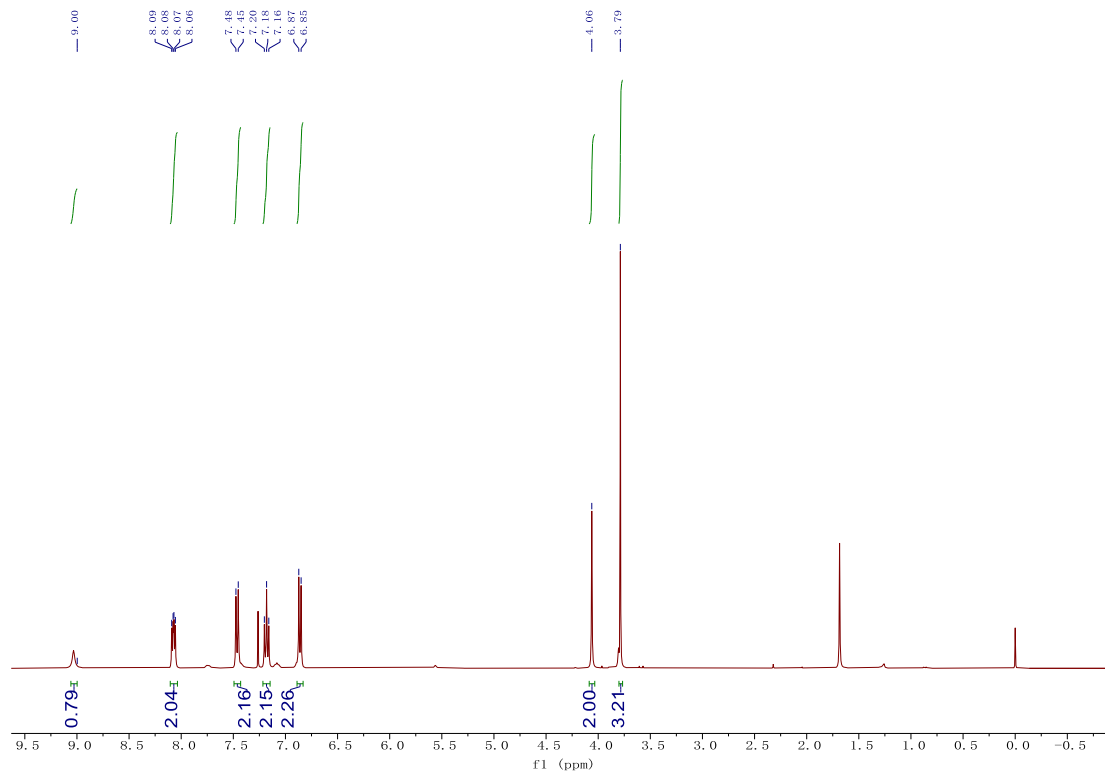
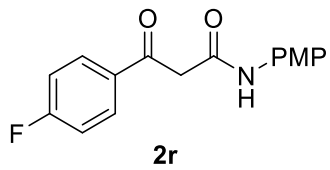


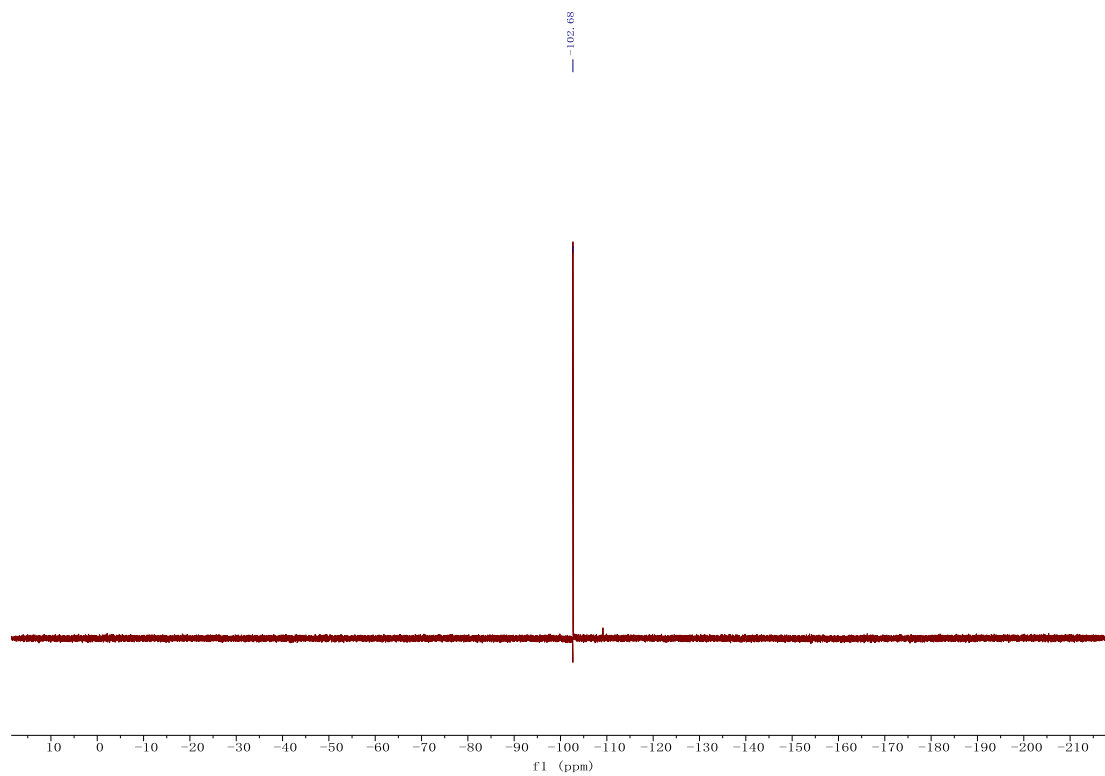
Analysis for ketone:

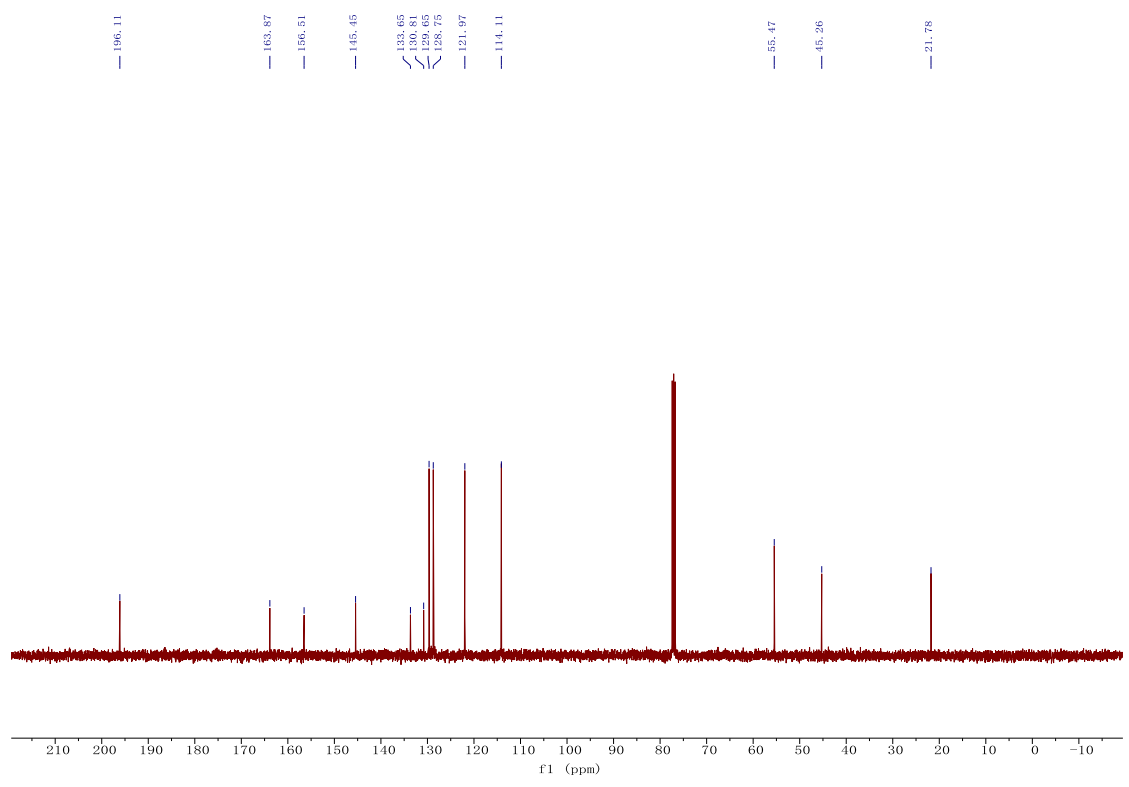
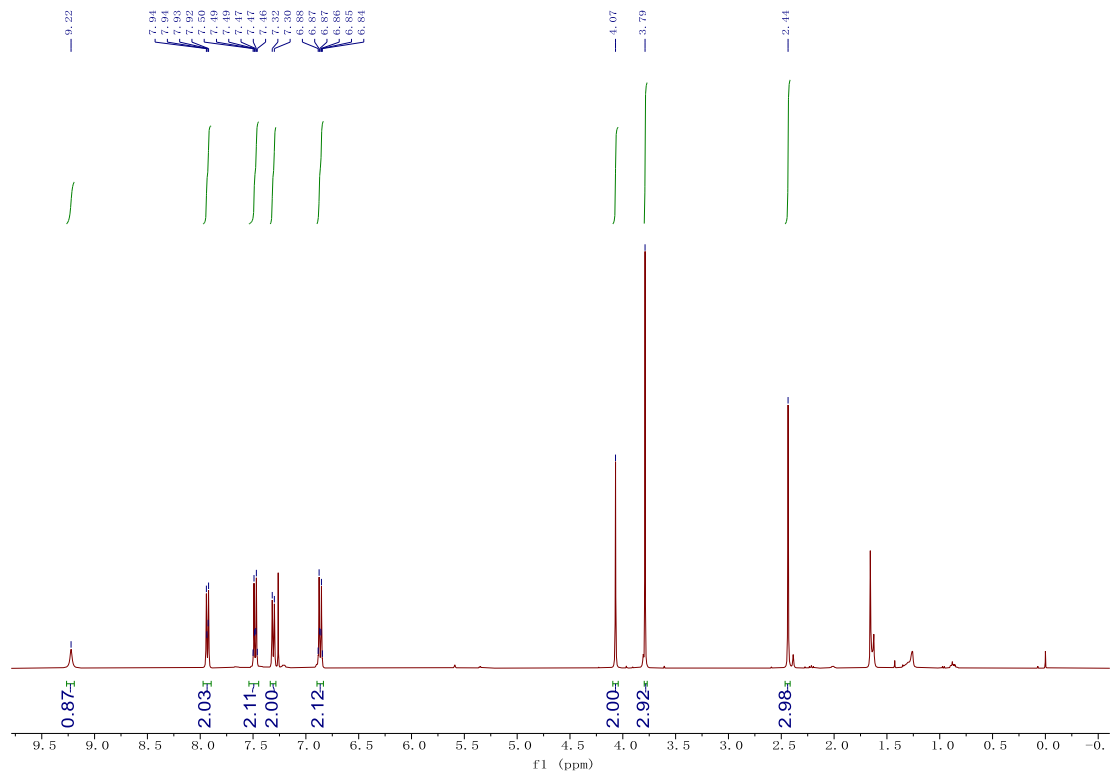
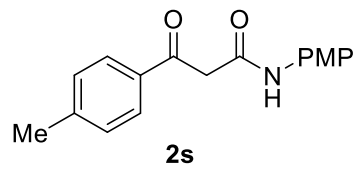


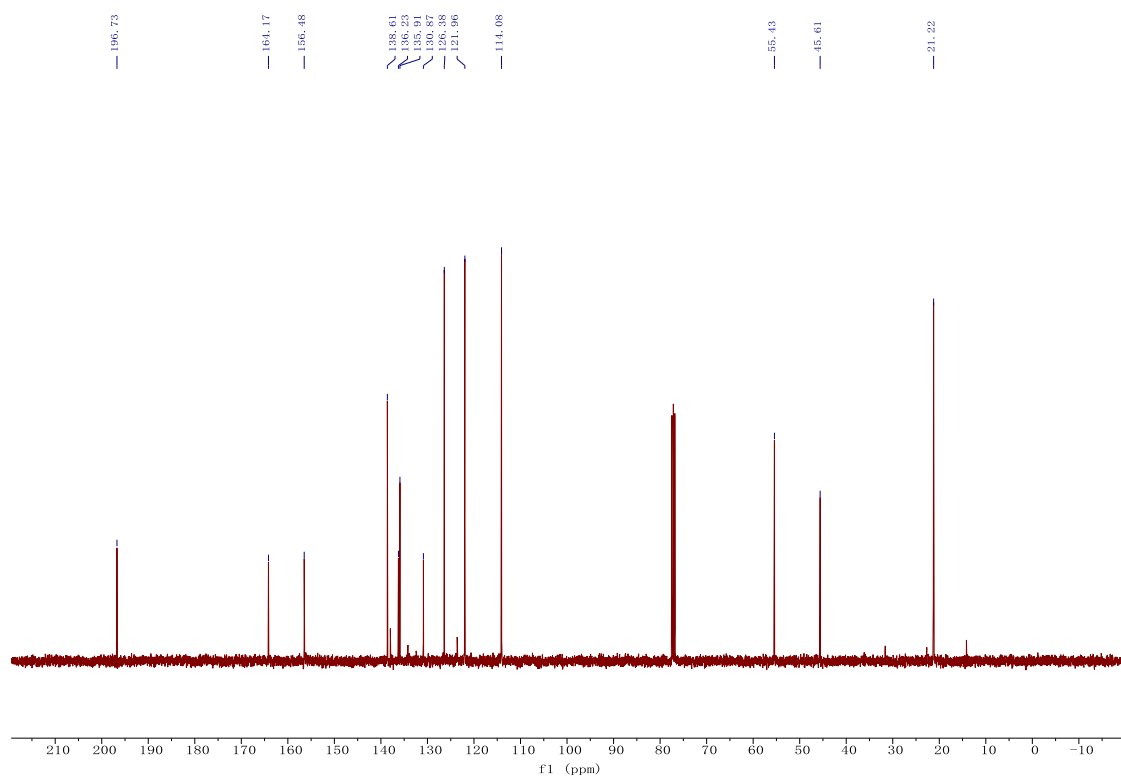
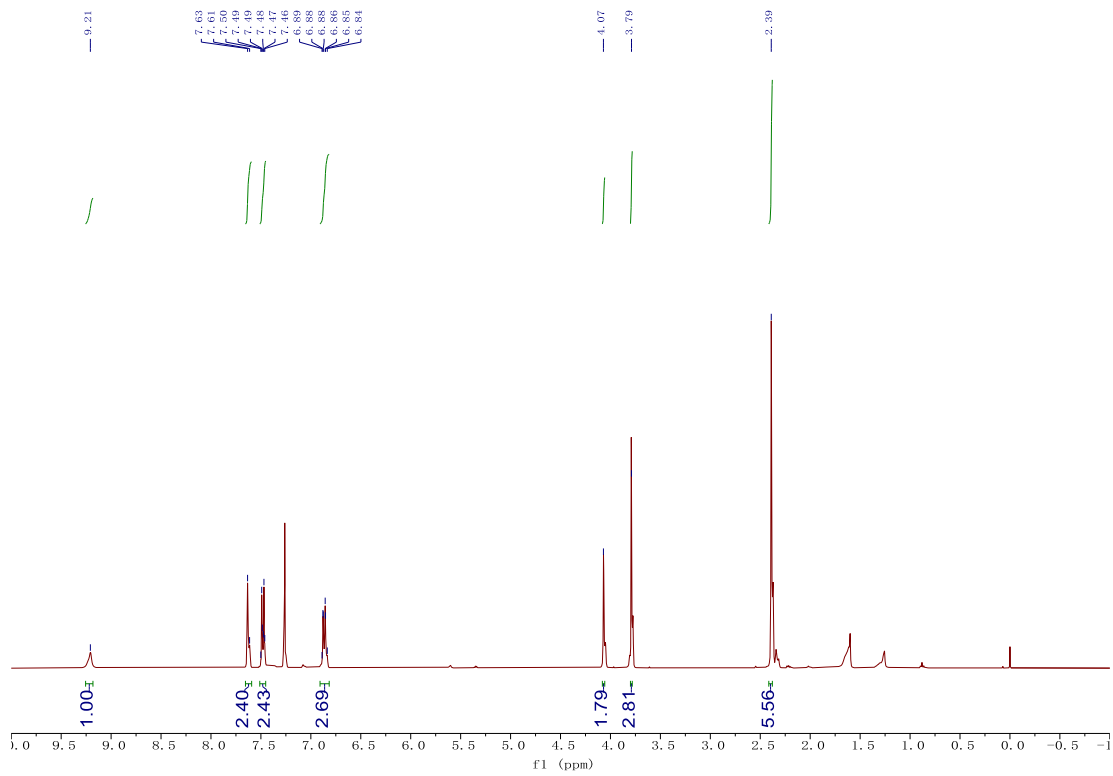
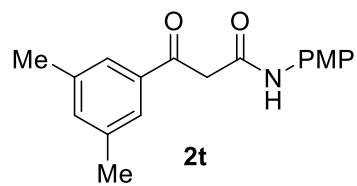
Analysis for enol:

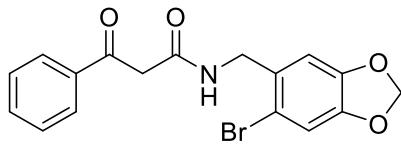




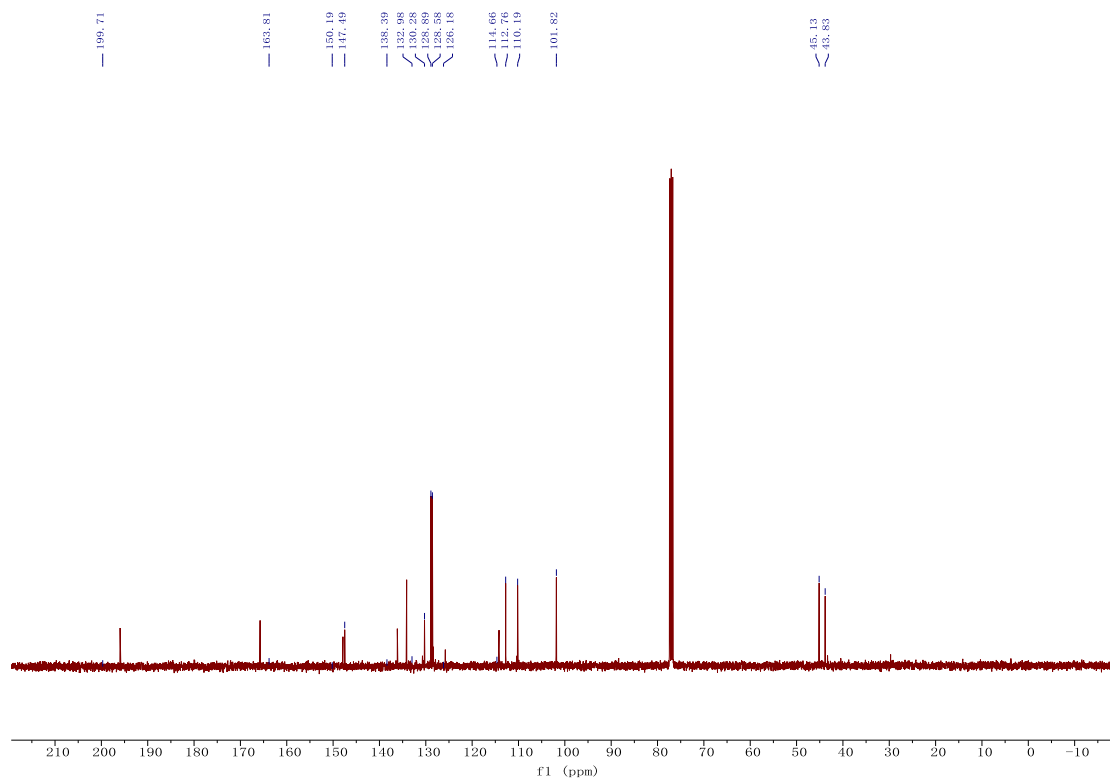
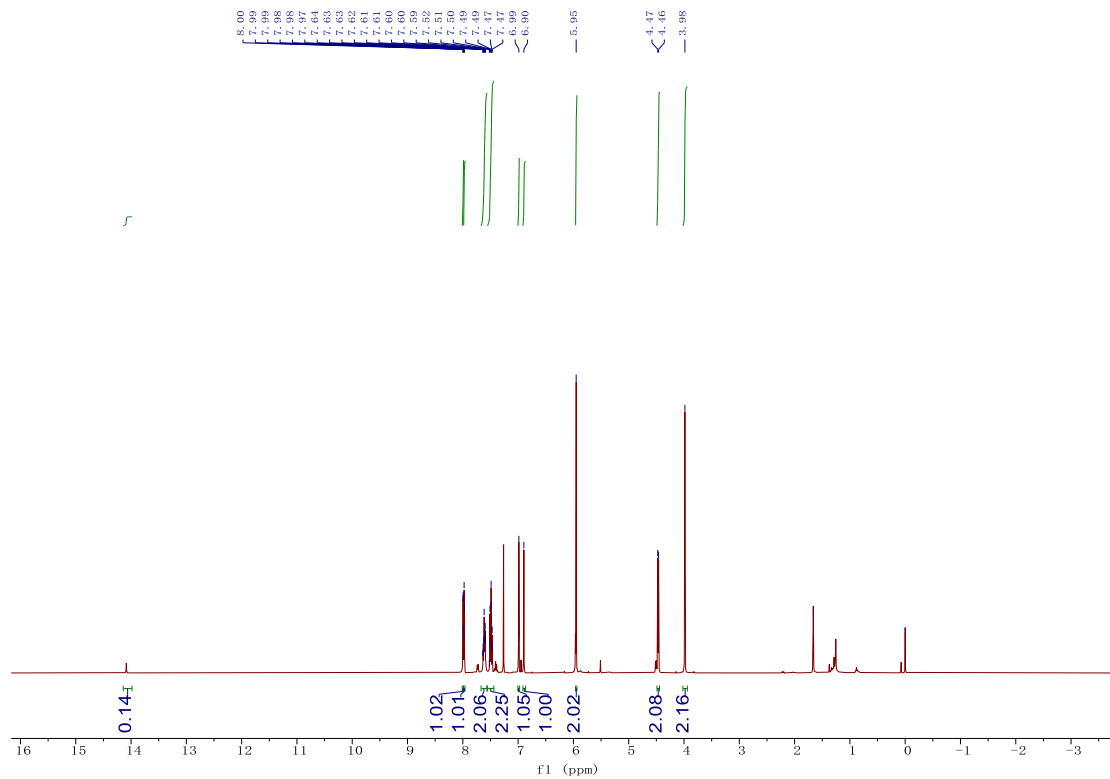


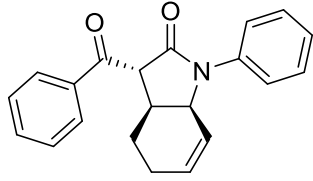




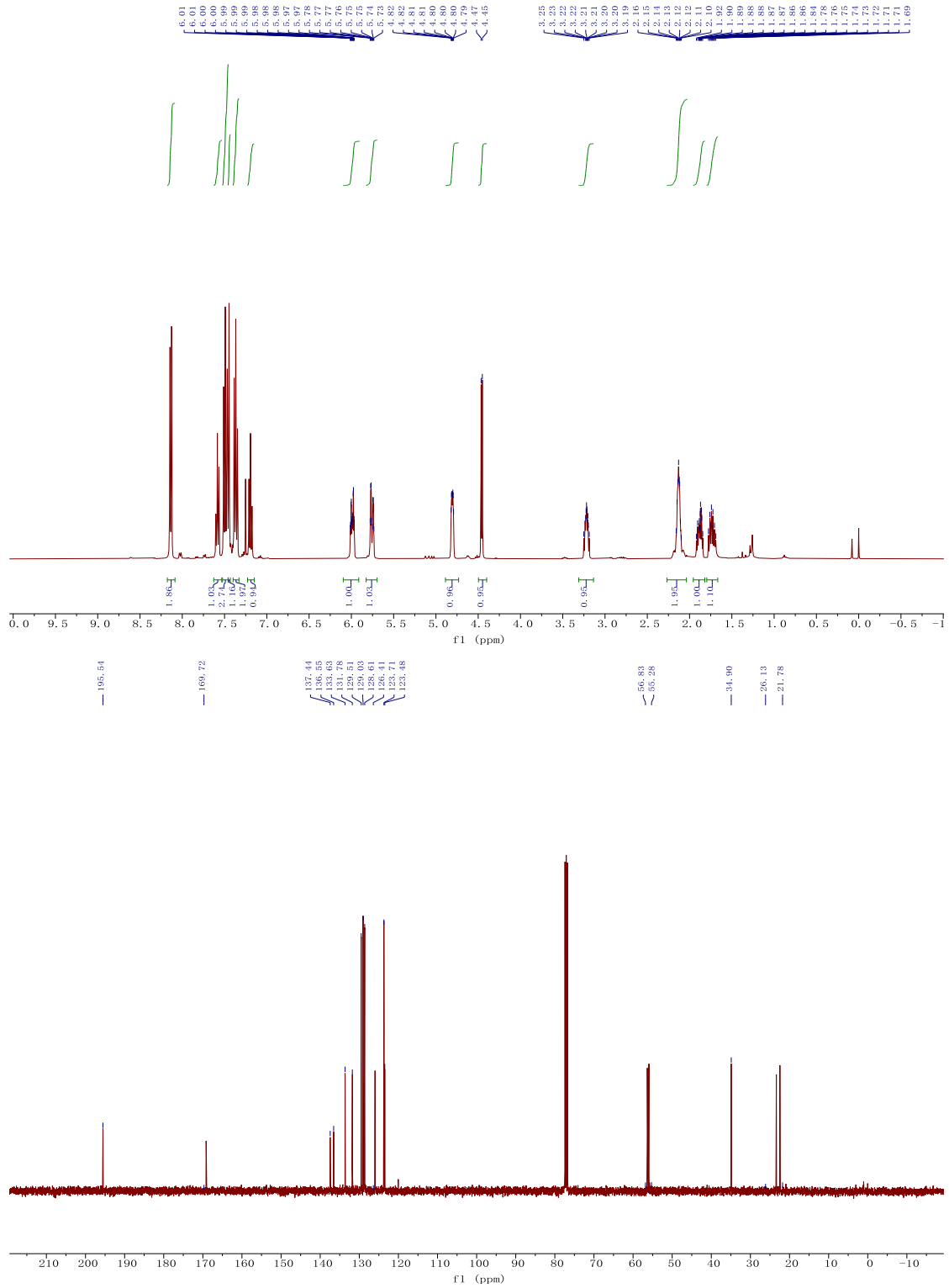


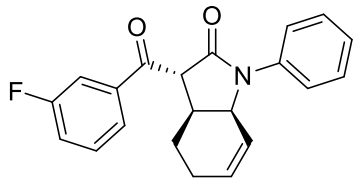
2v



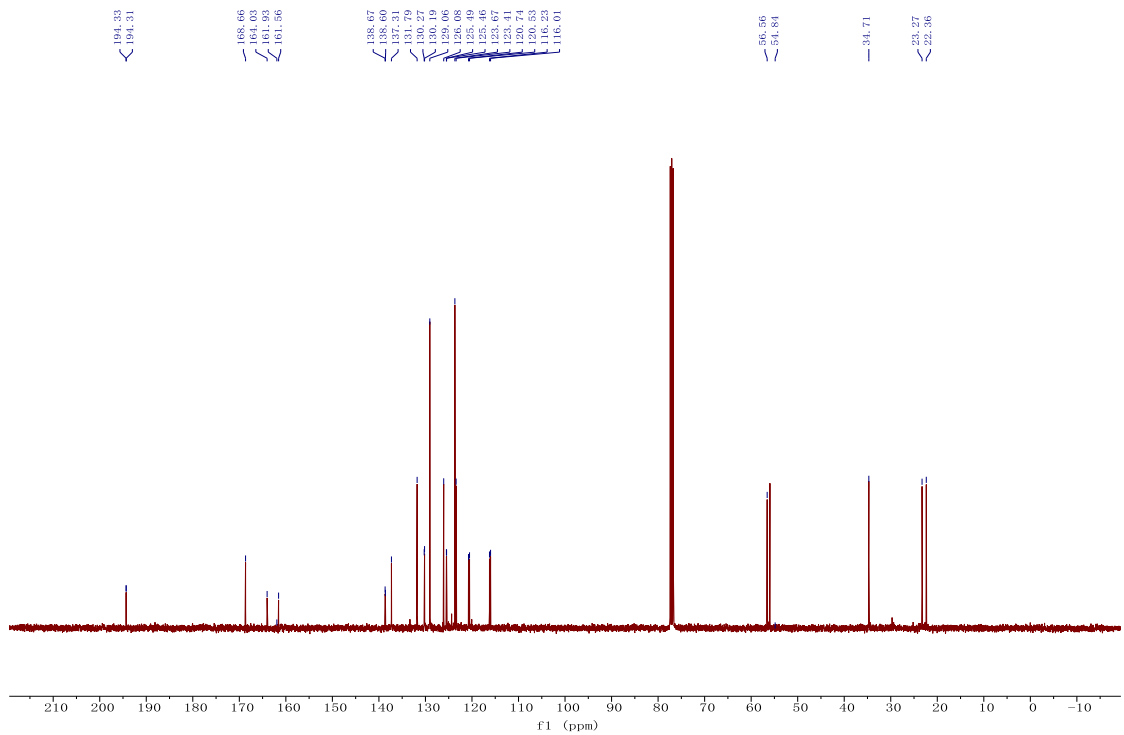
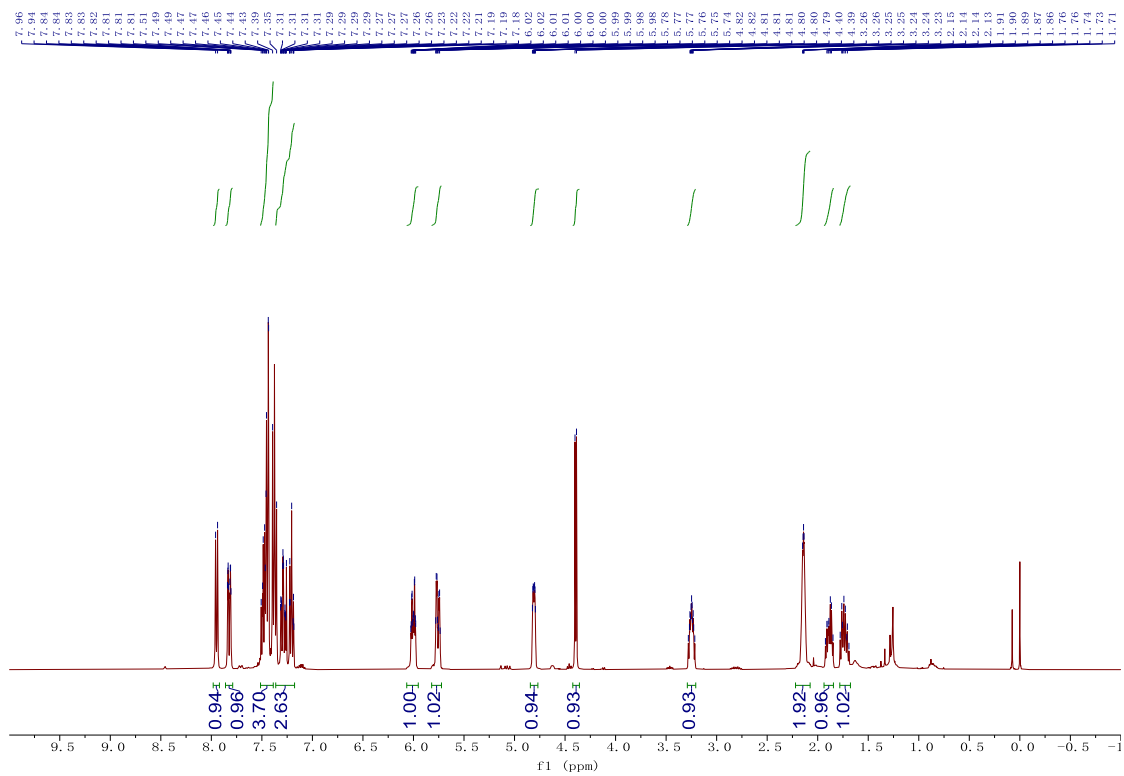


**3a**

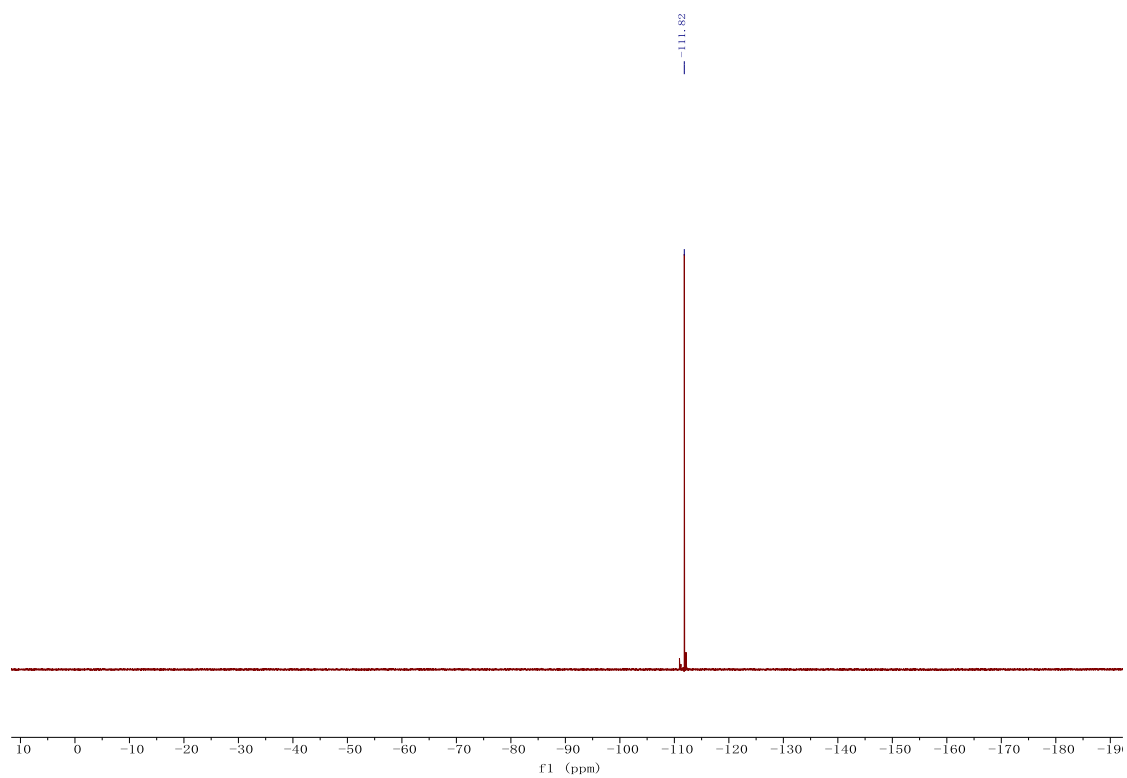


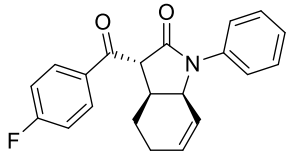


**3b**

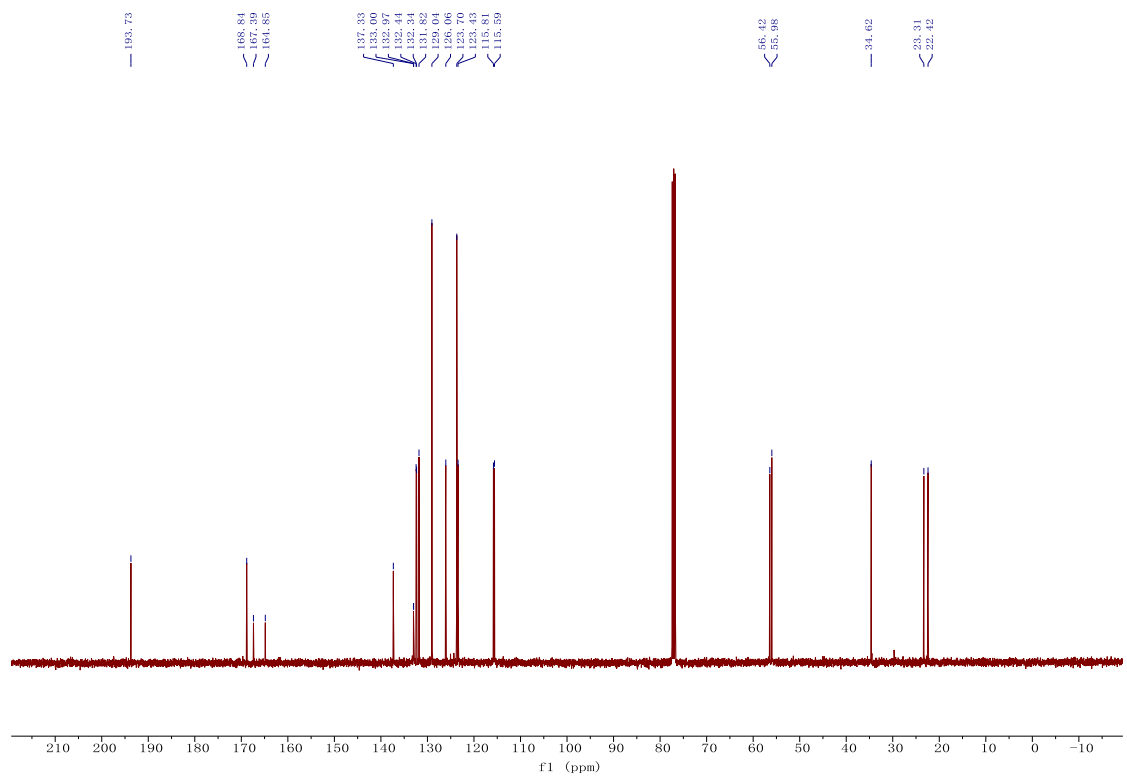
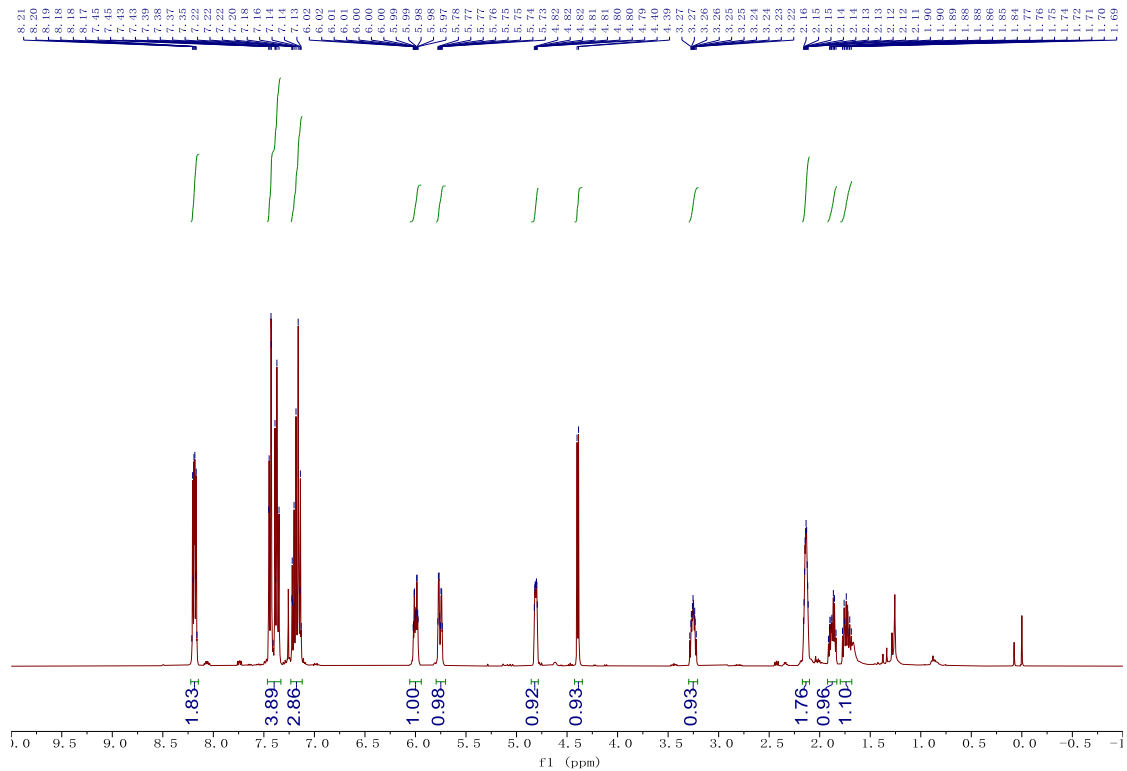


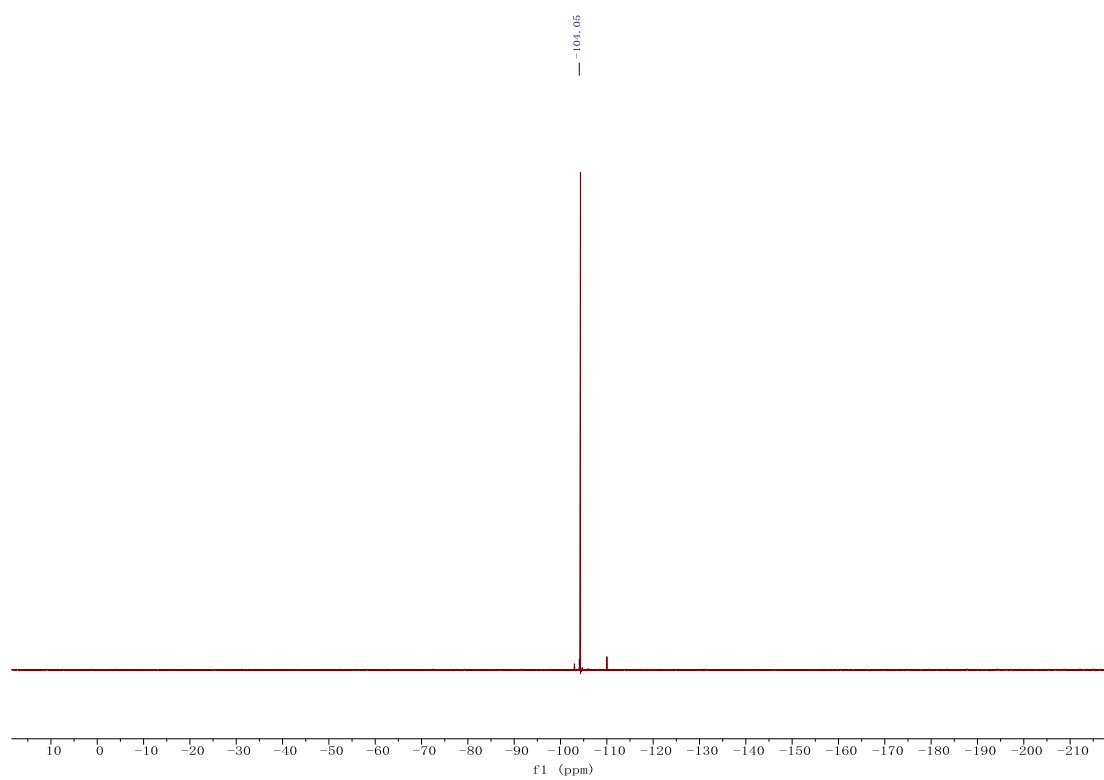


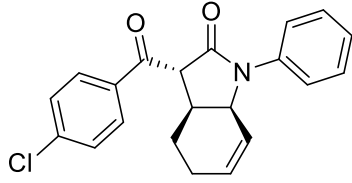




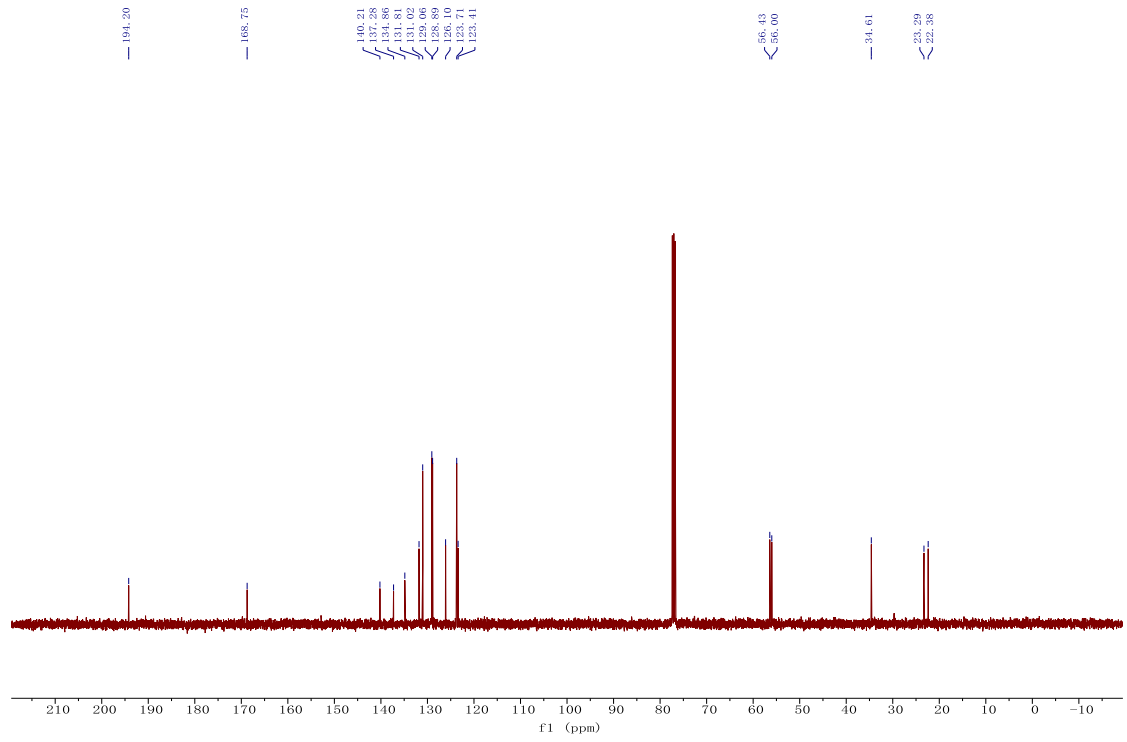
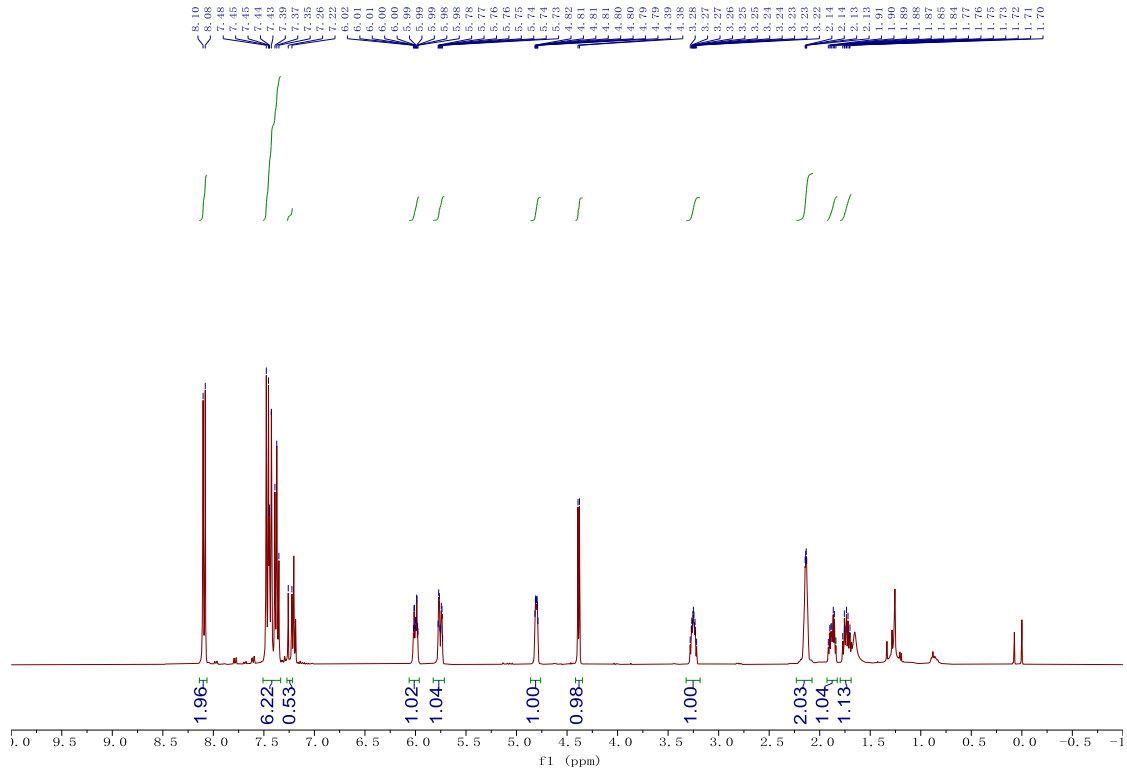
**3c**



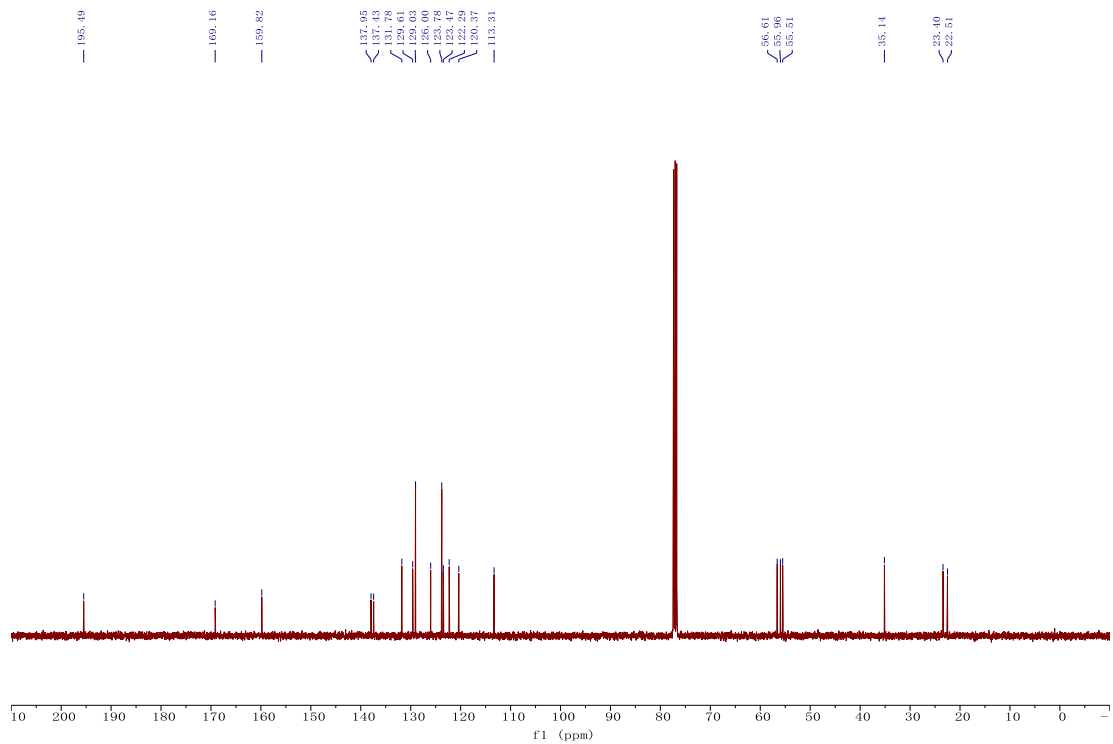
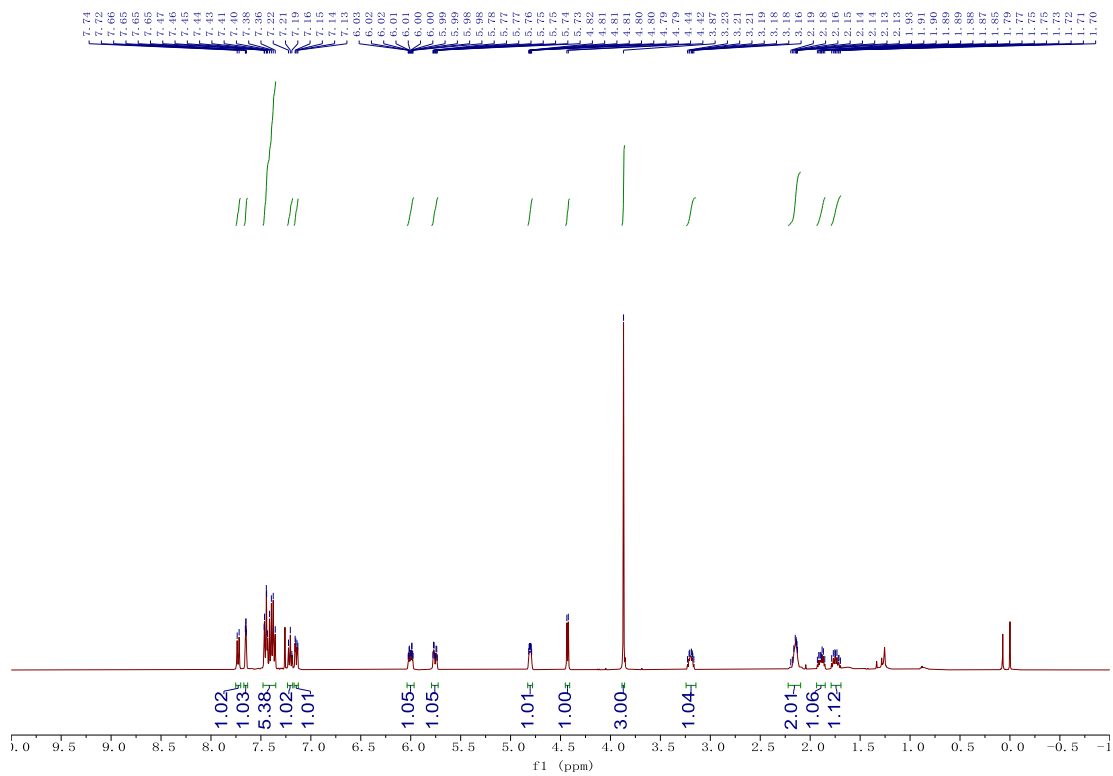
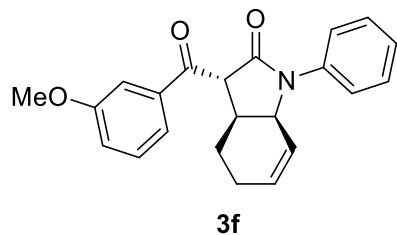


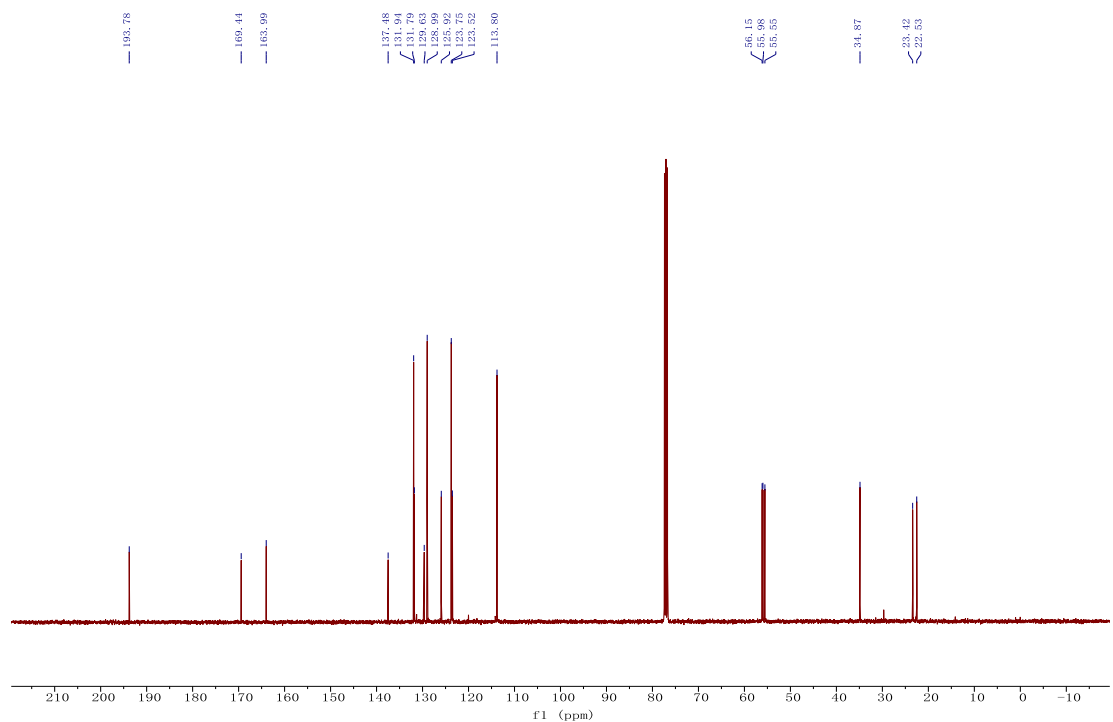
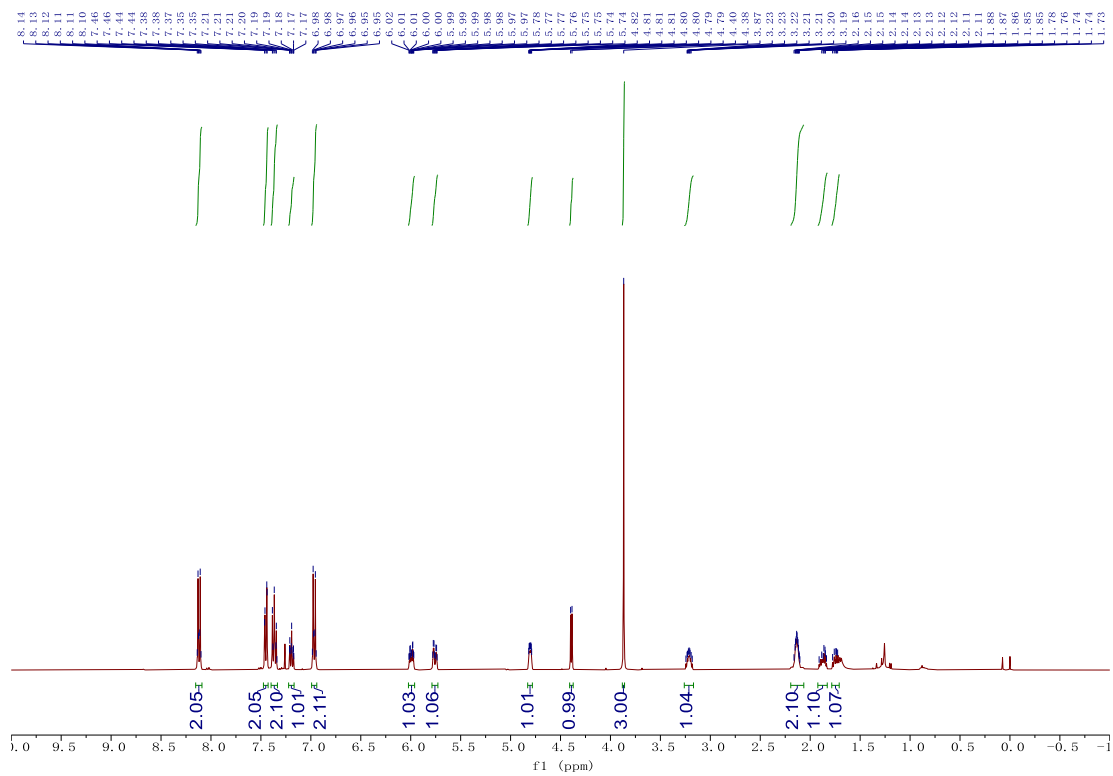
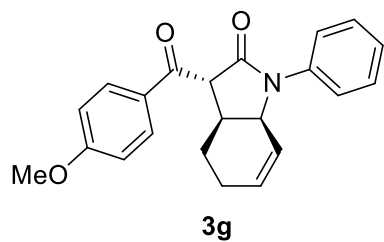


**3d**



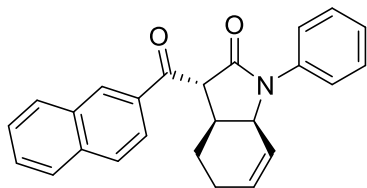




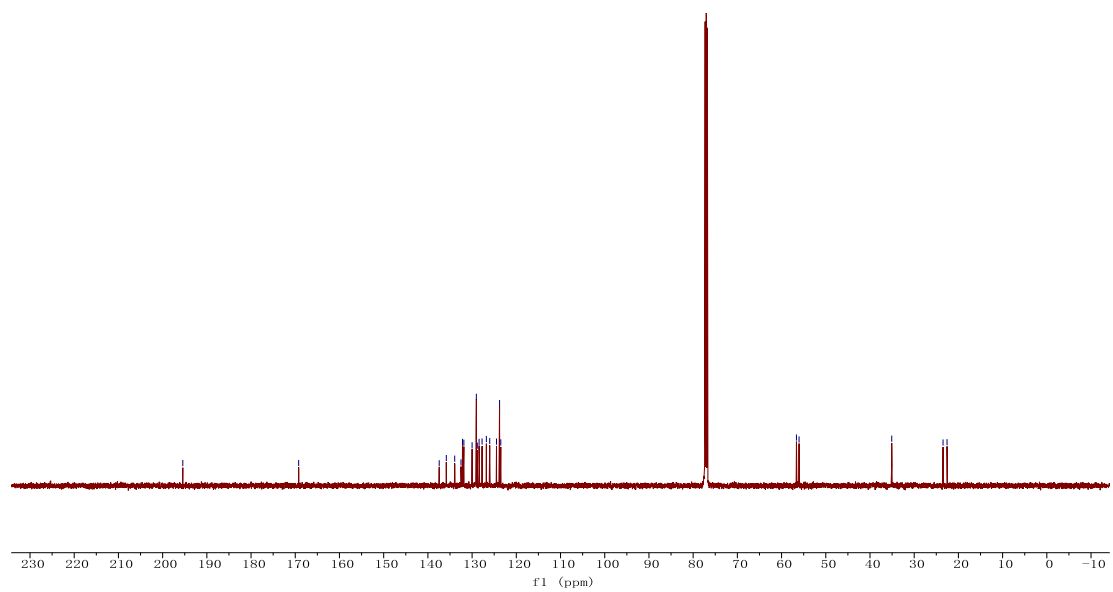
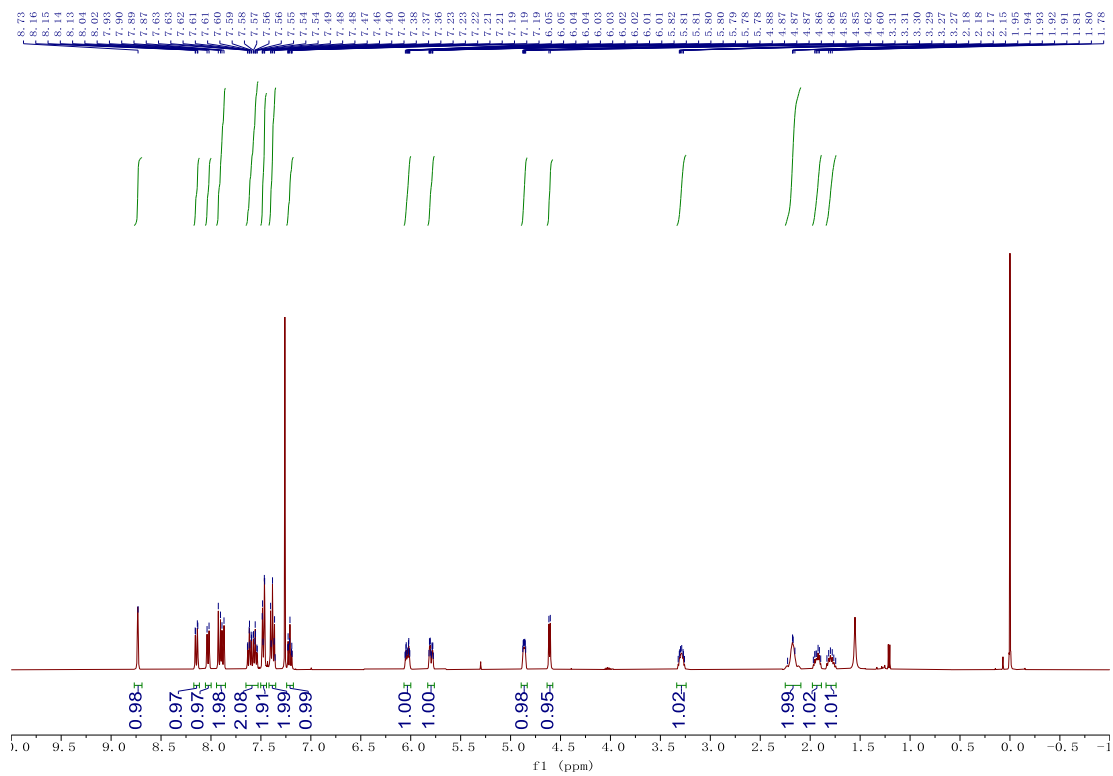


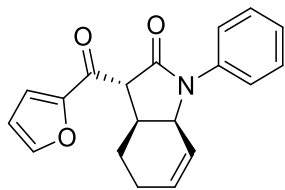




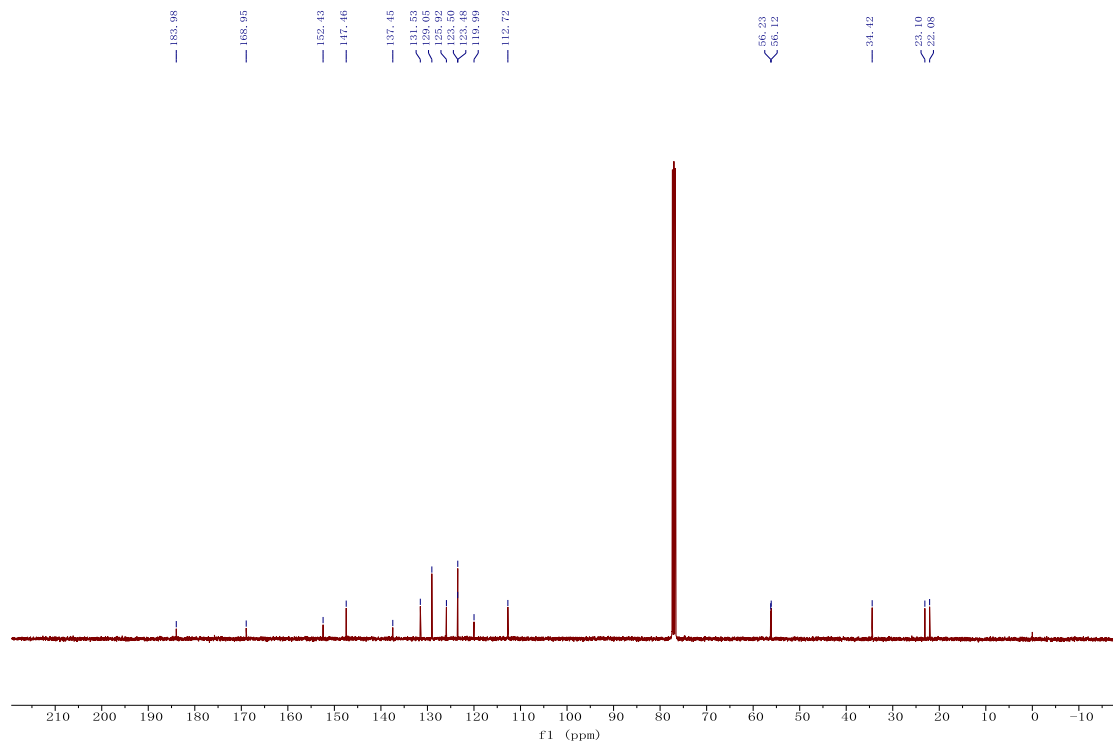
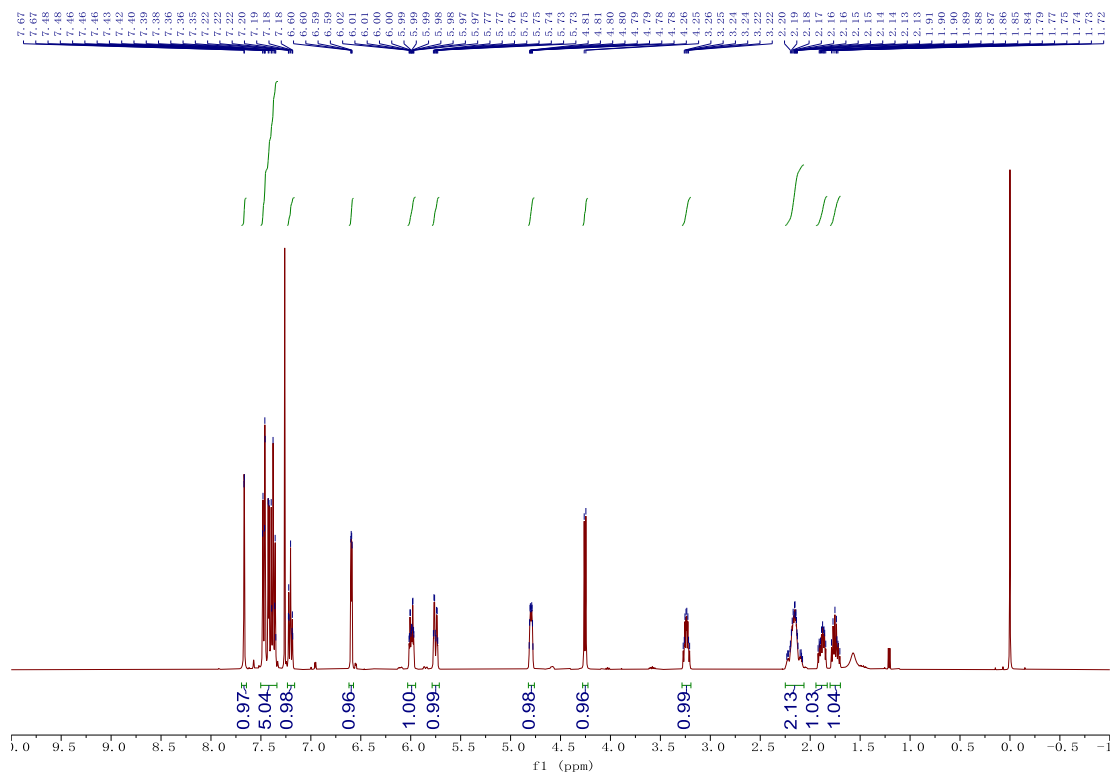


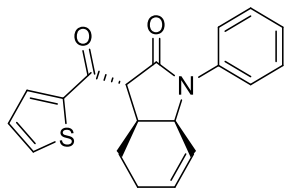
**3i**



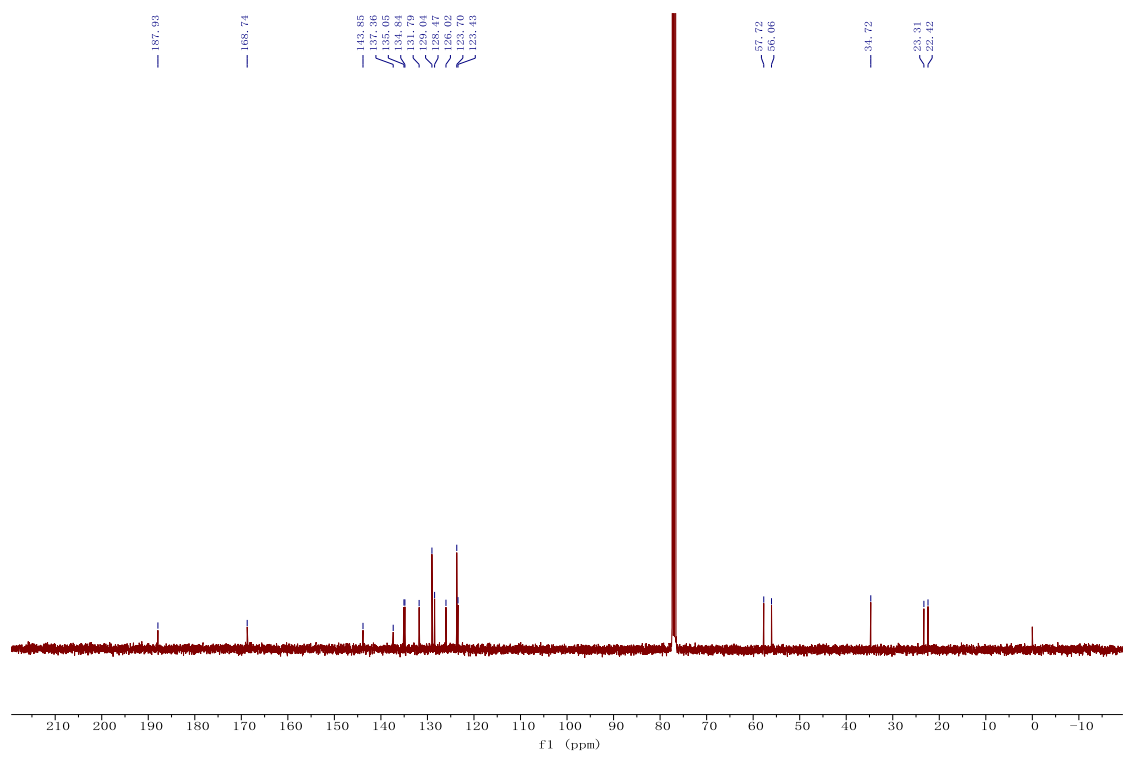
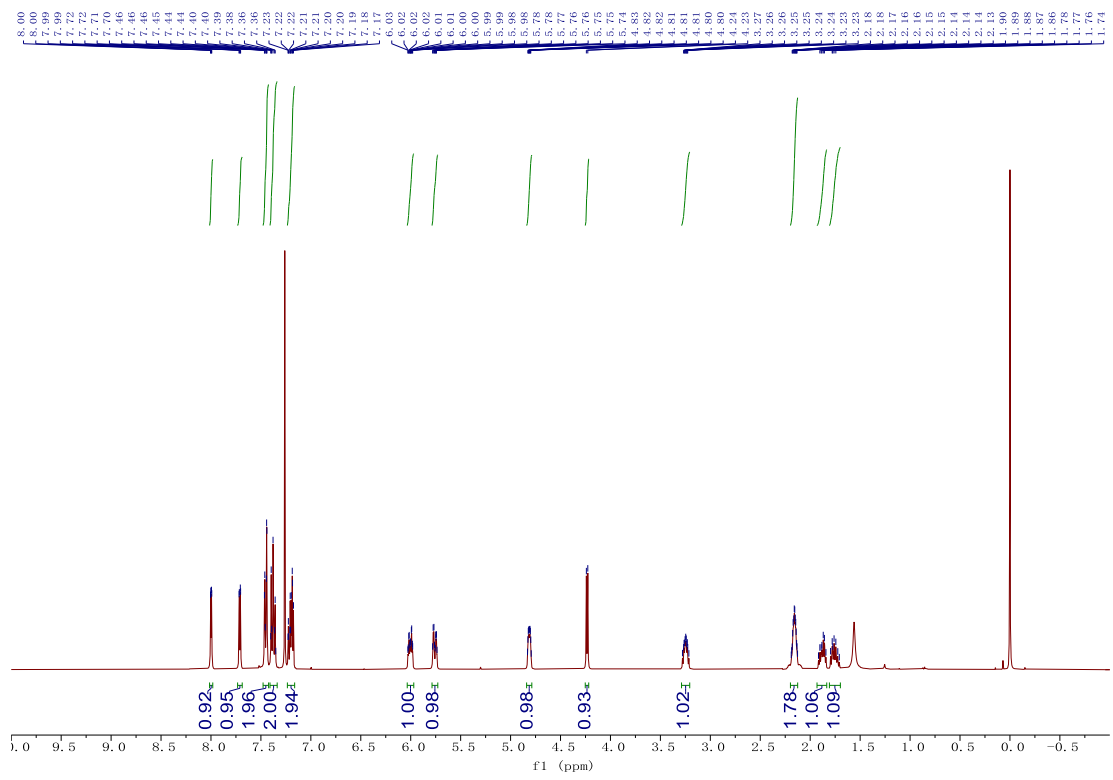


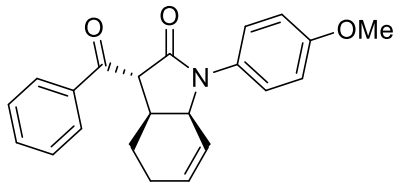
3j



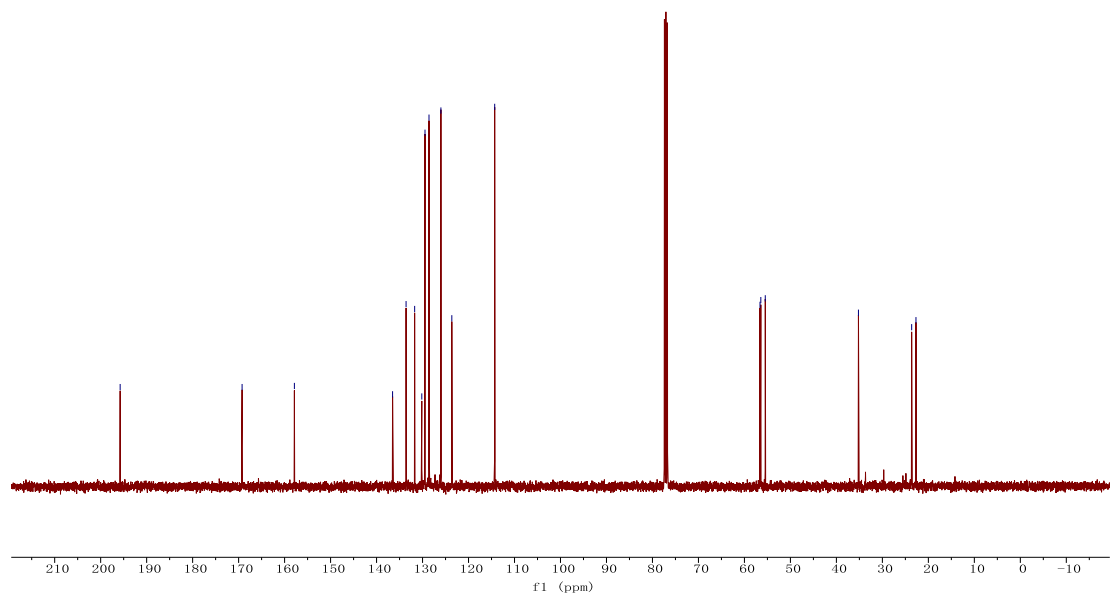
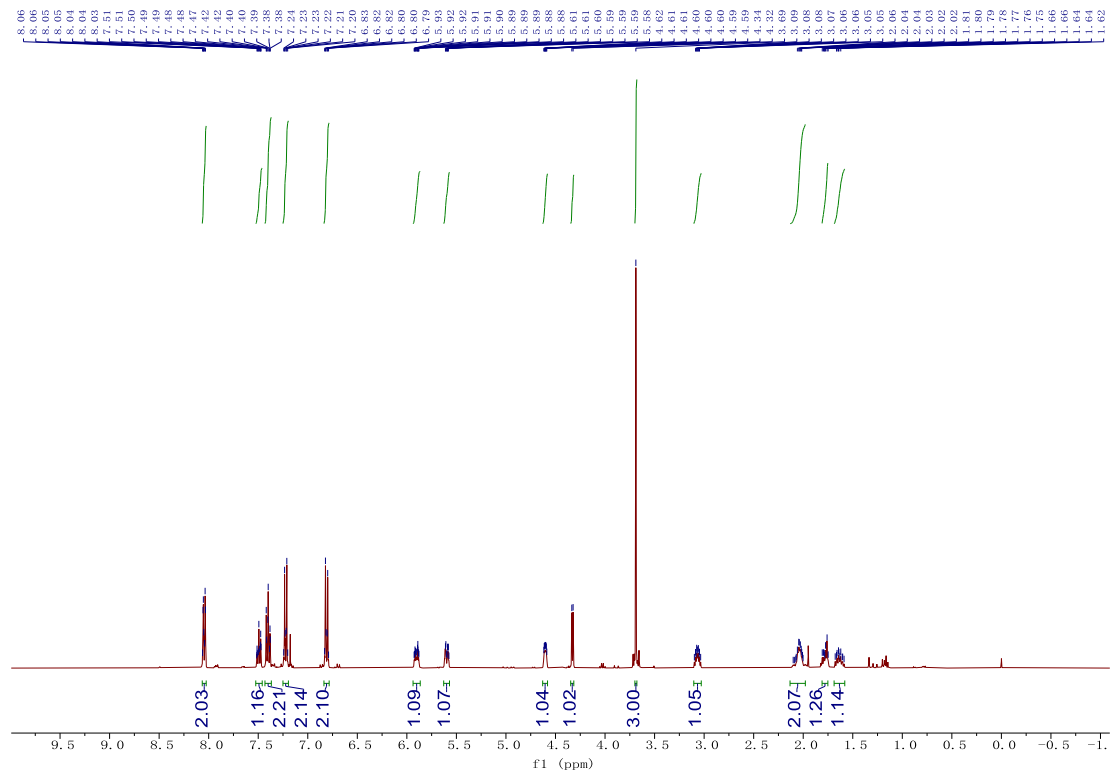


**3k**

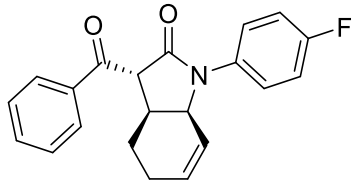




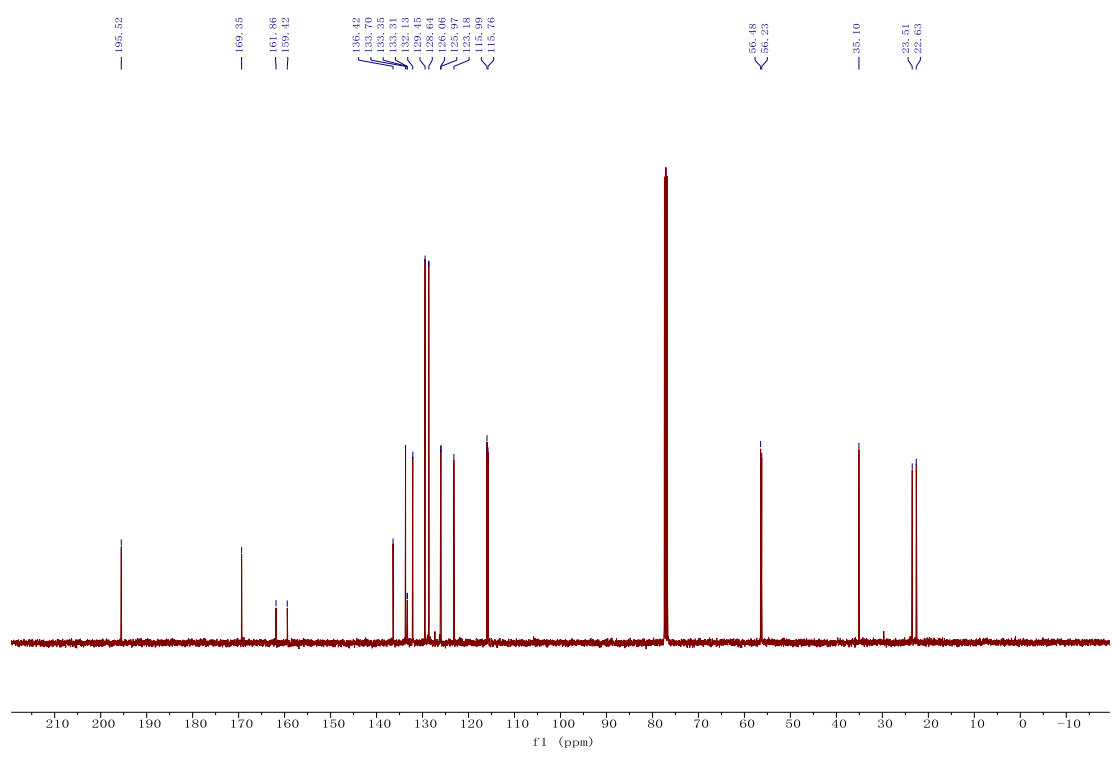
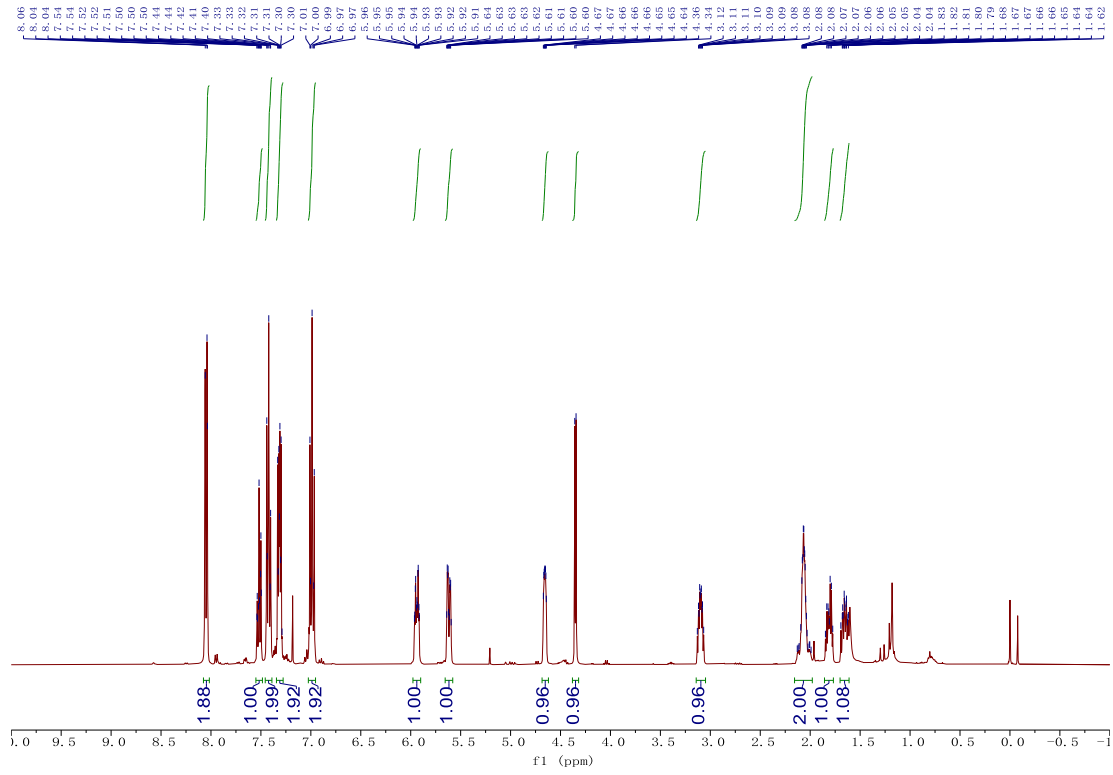
31

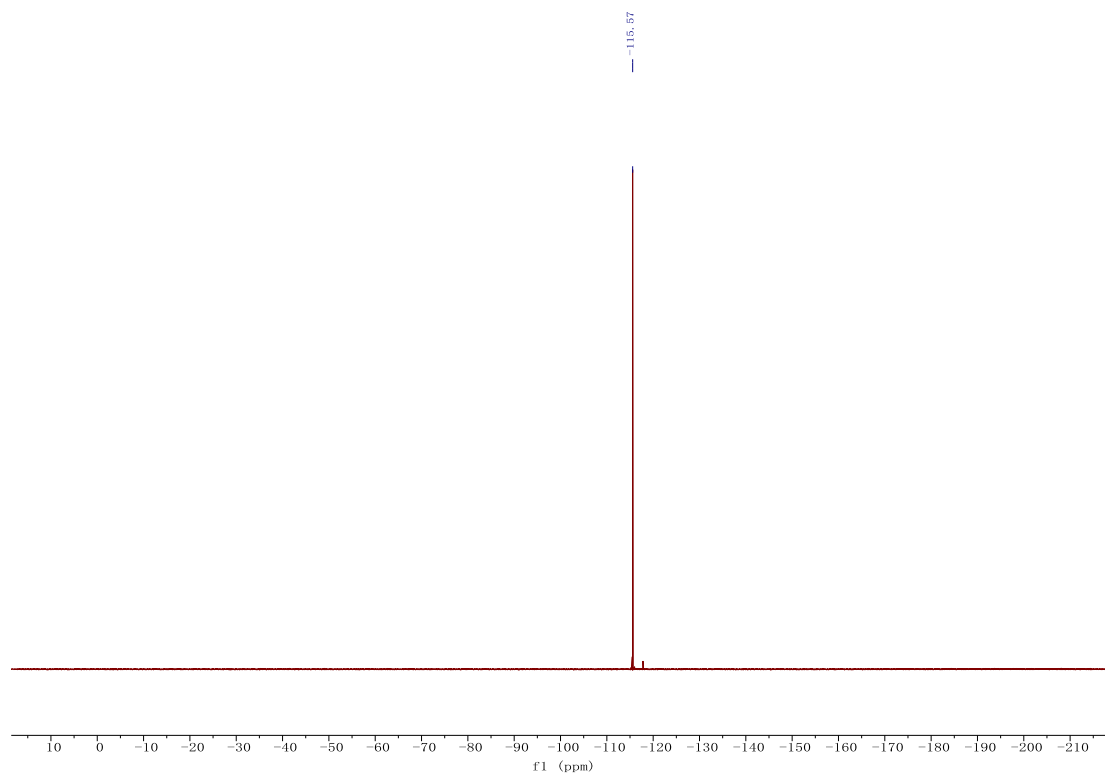






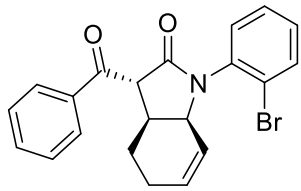
**3n**



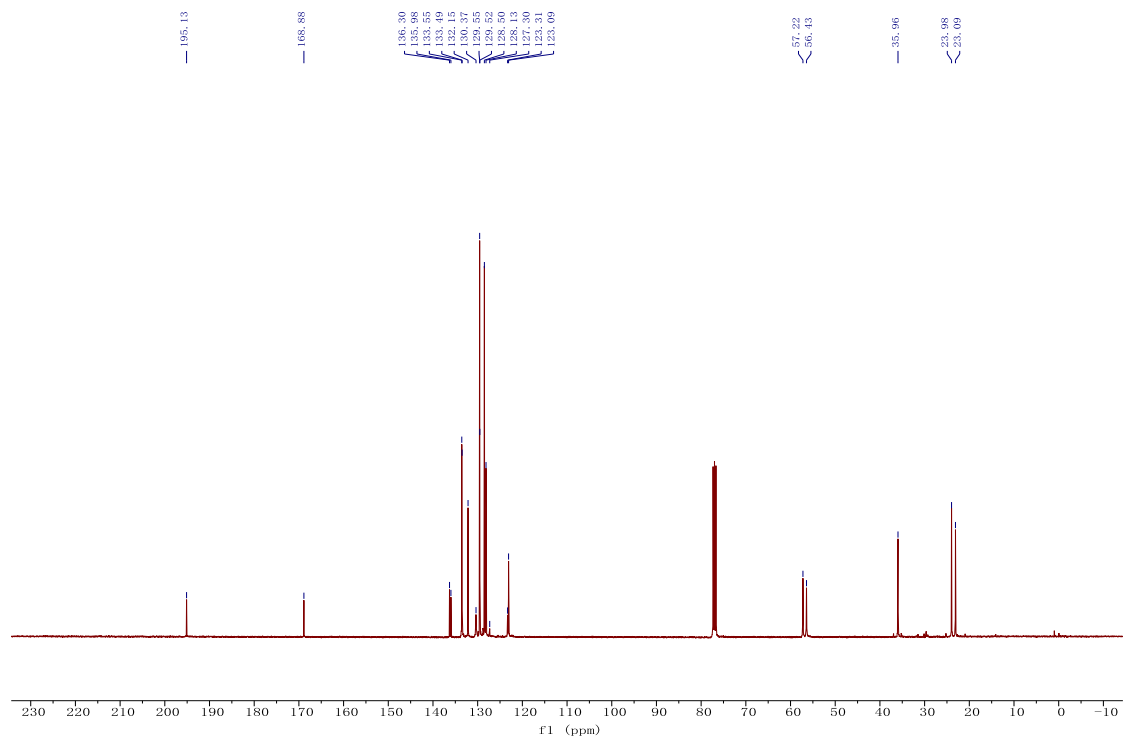
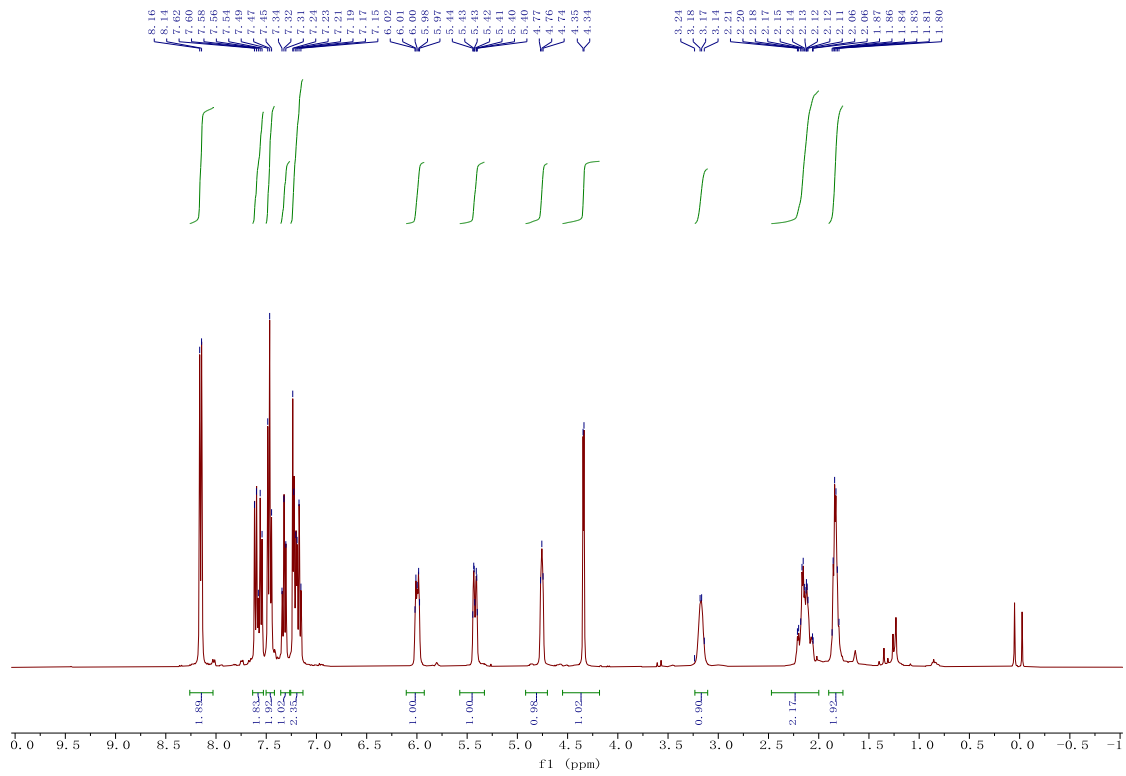




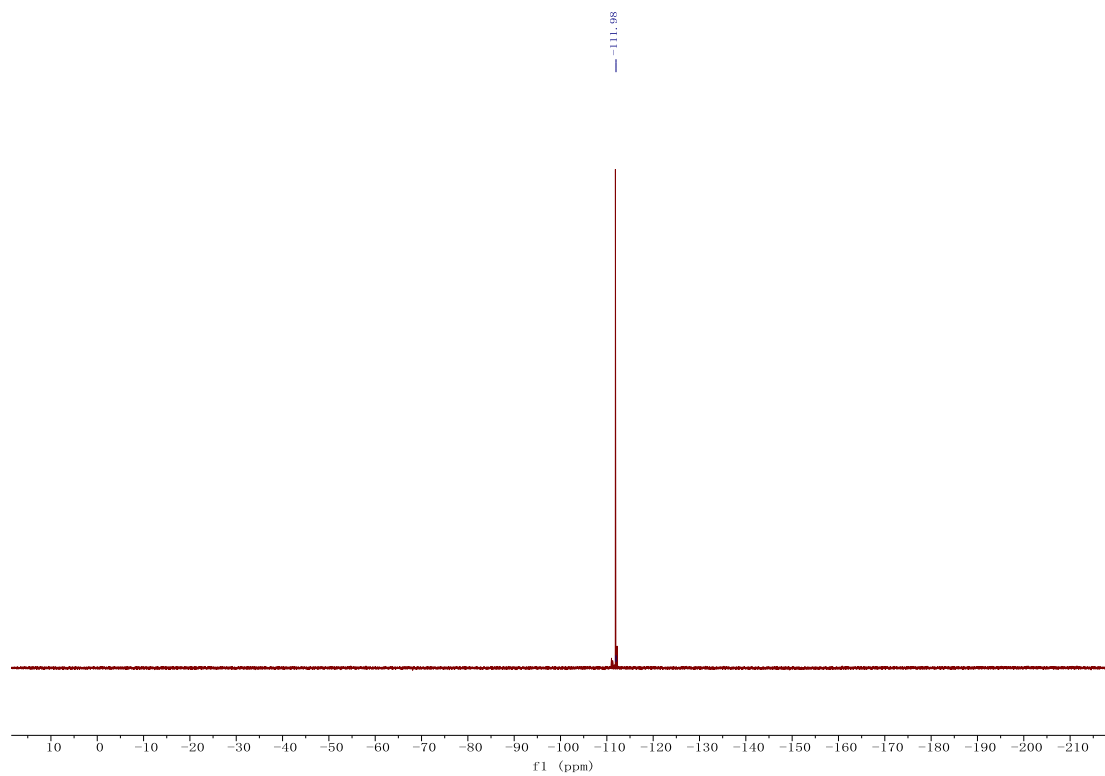


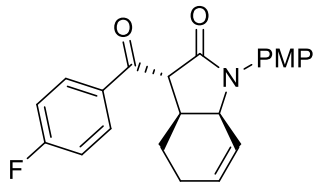


**3p**

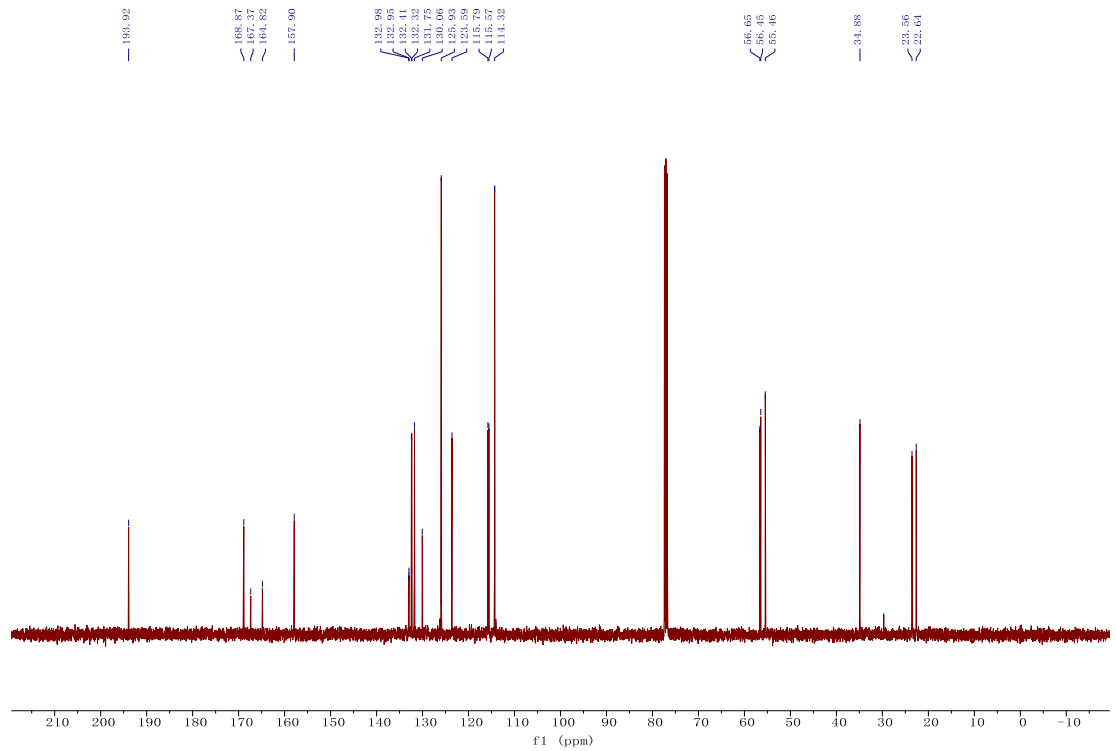
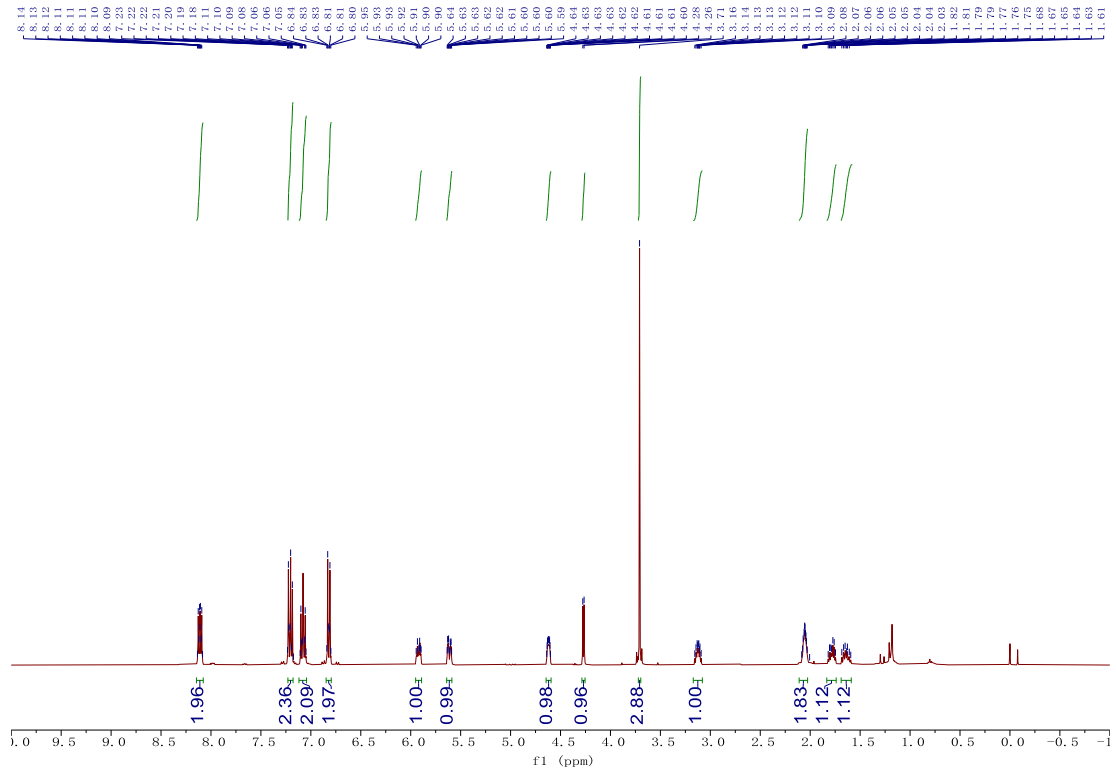


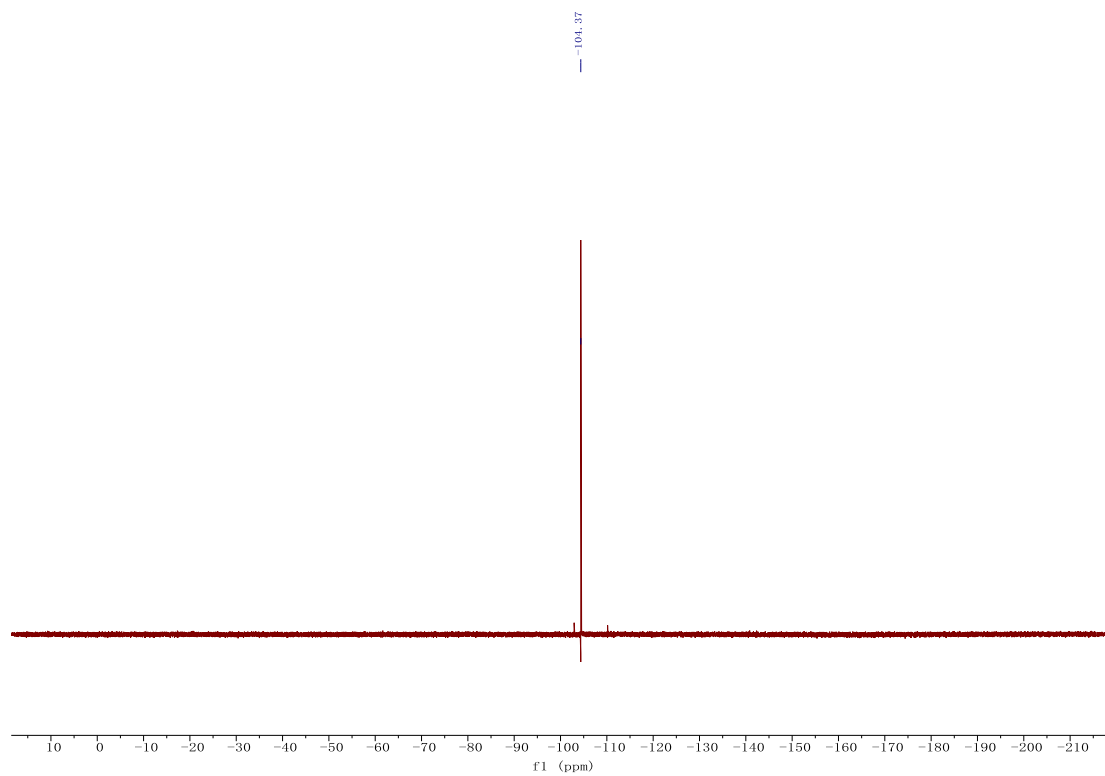


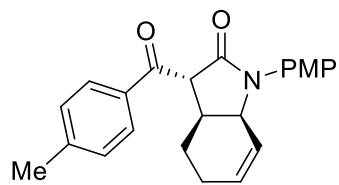




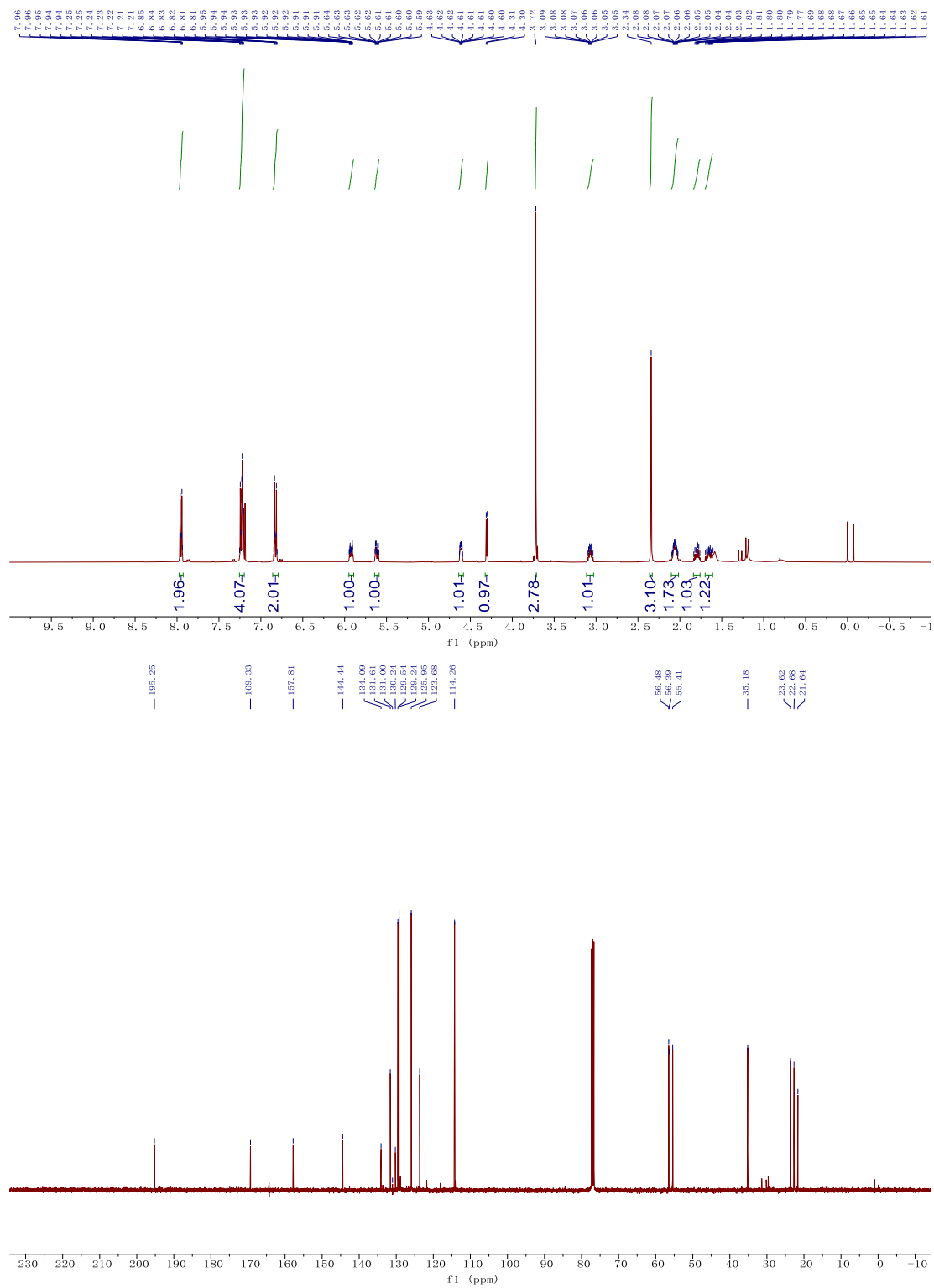
**3r**

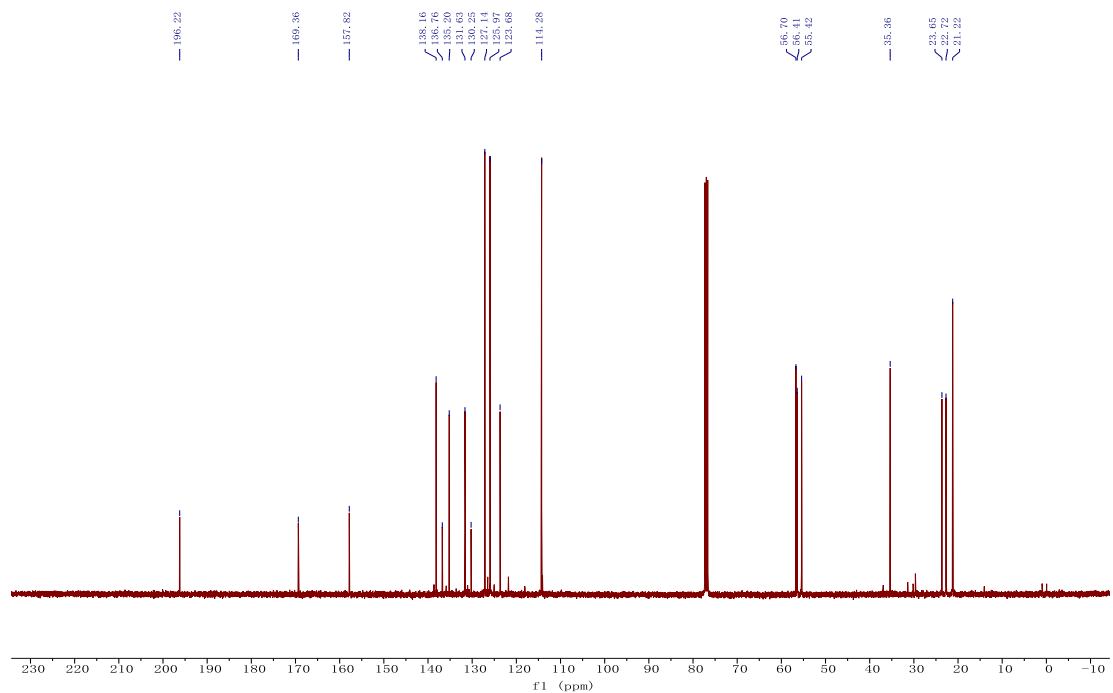
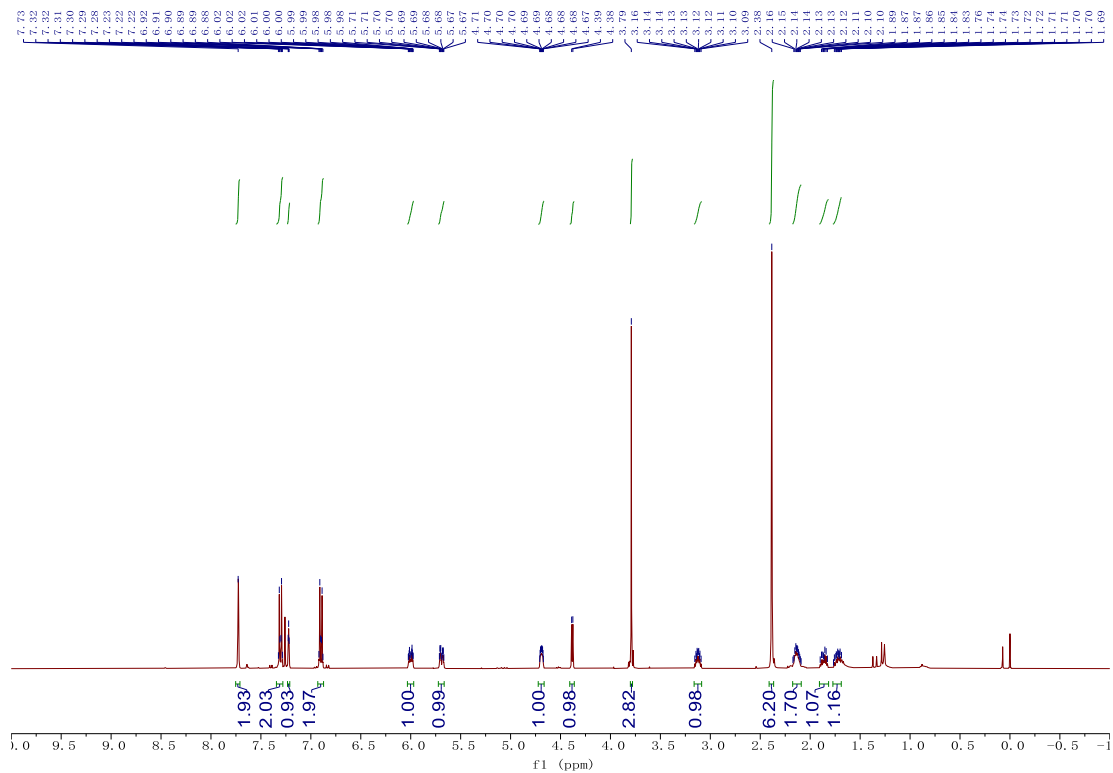
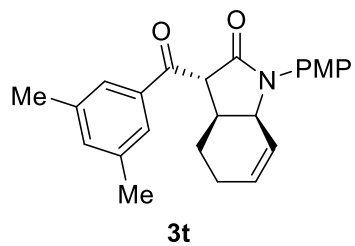


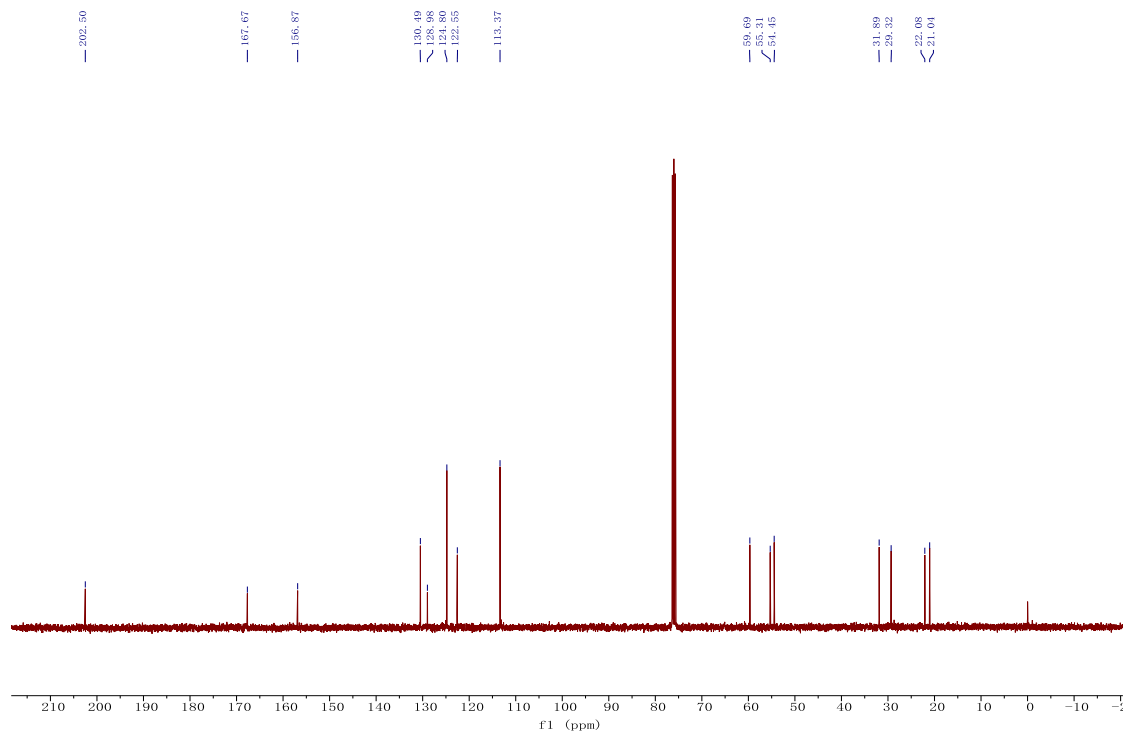
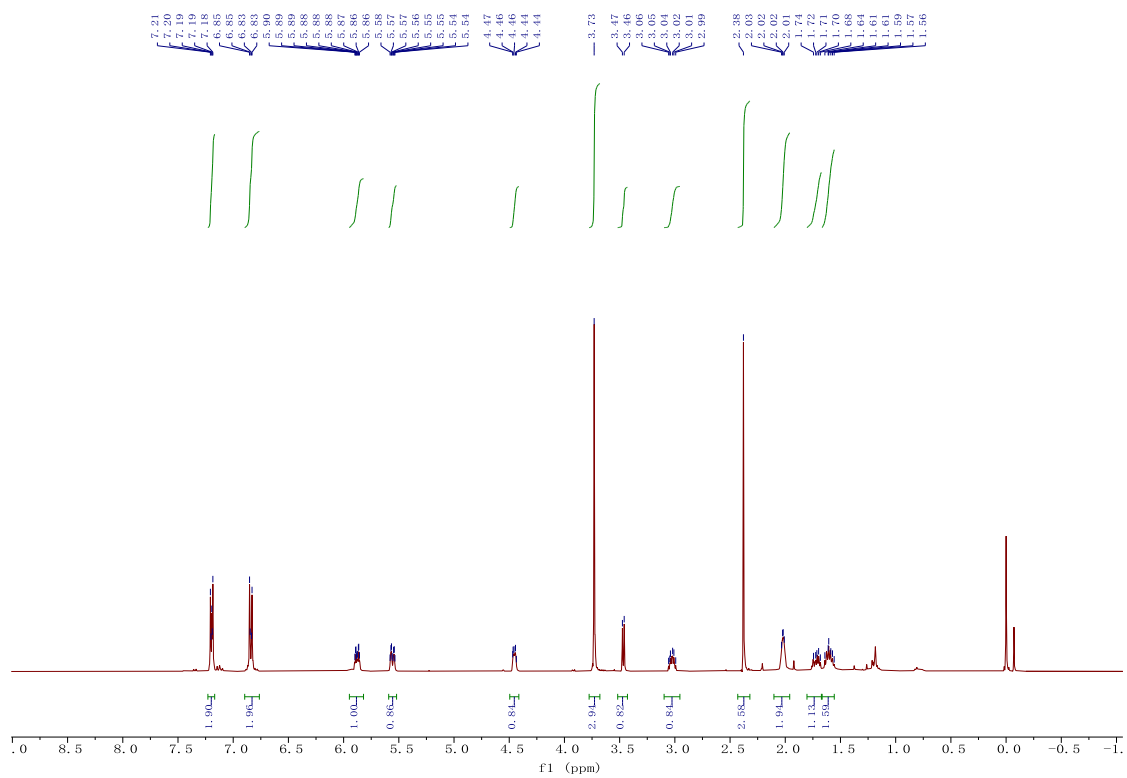
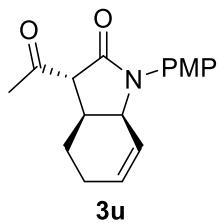




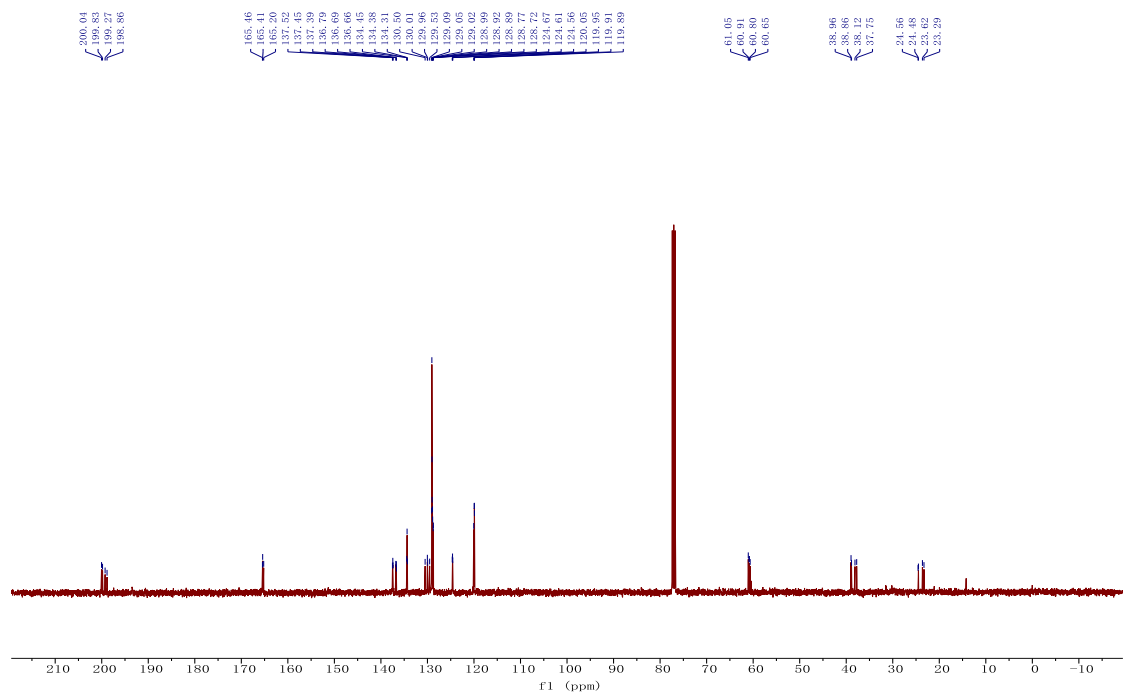
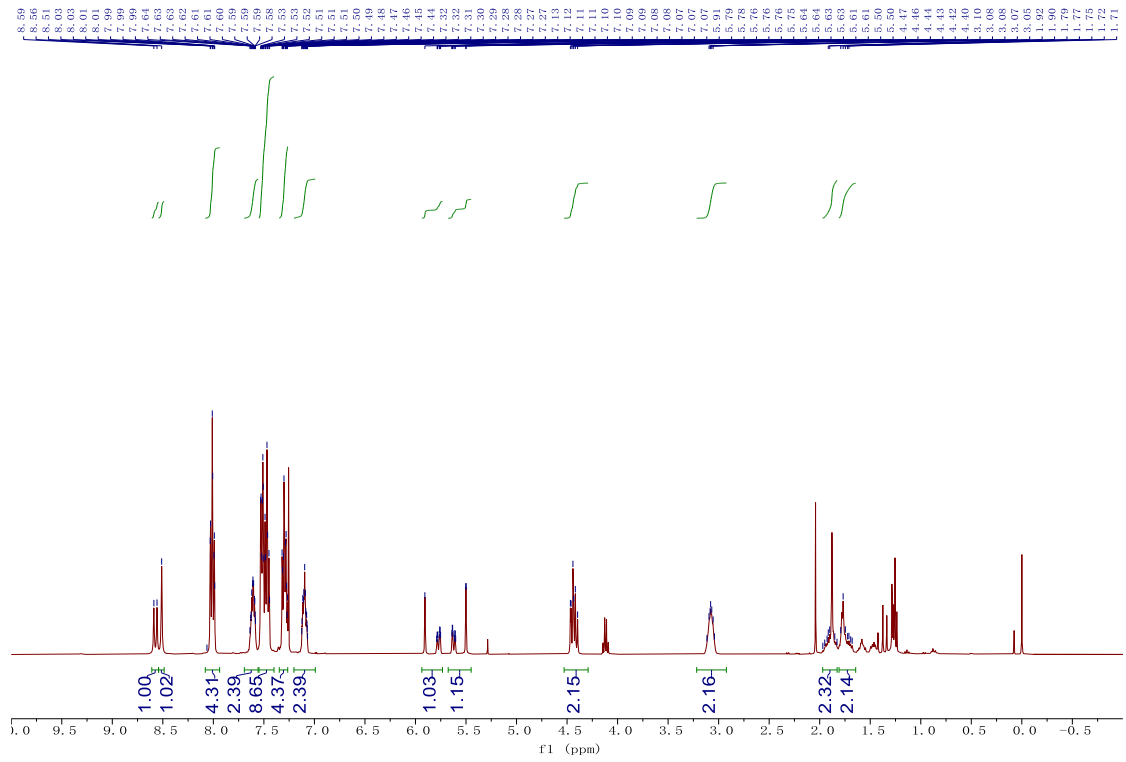
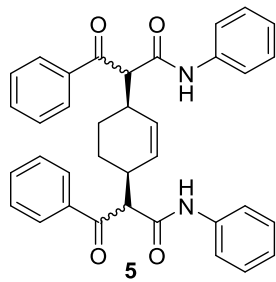
**3s**

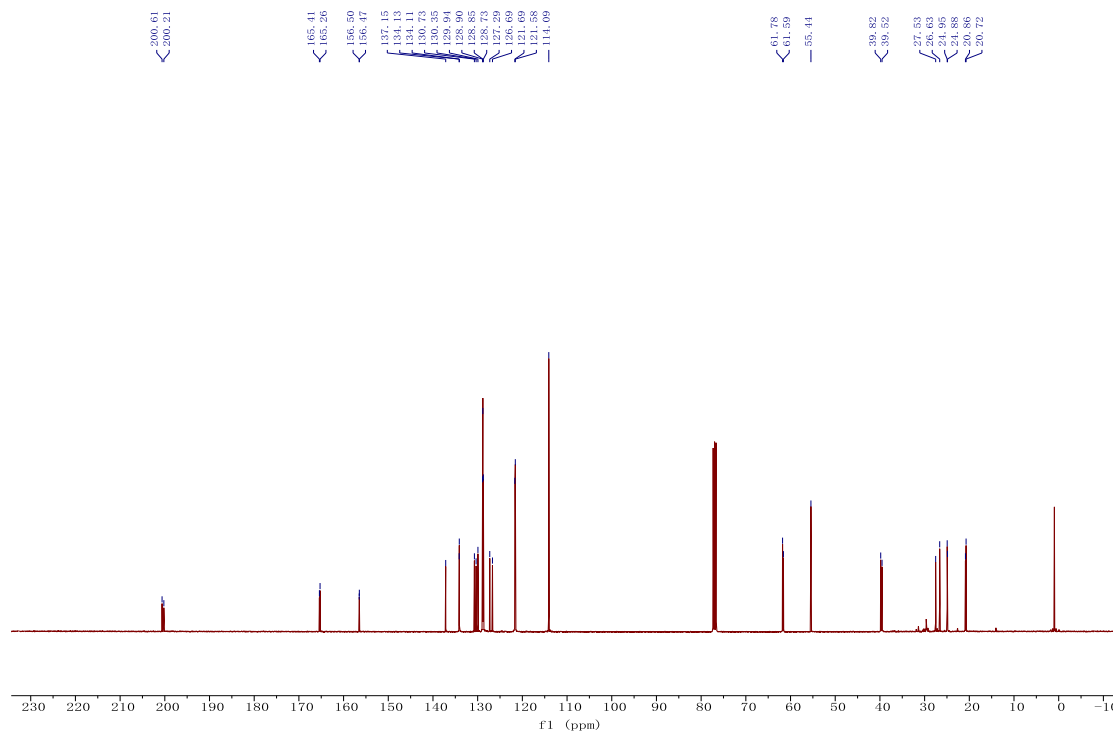
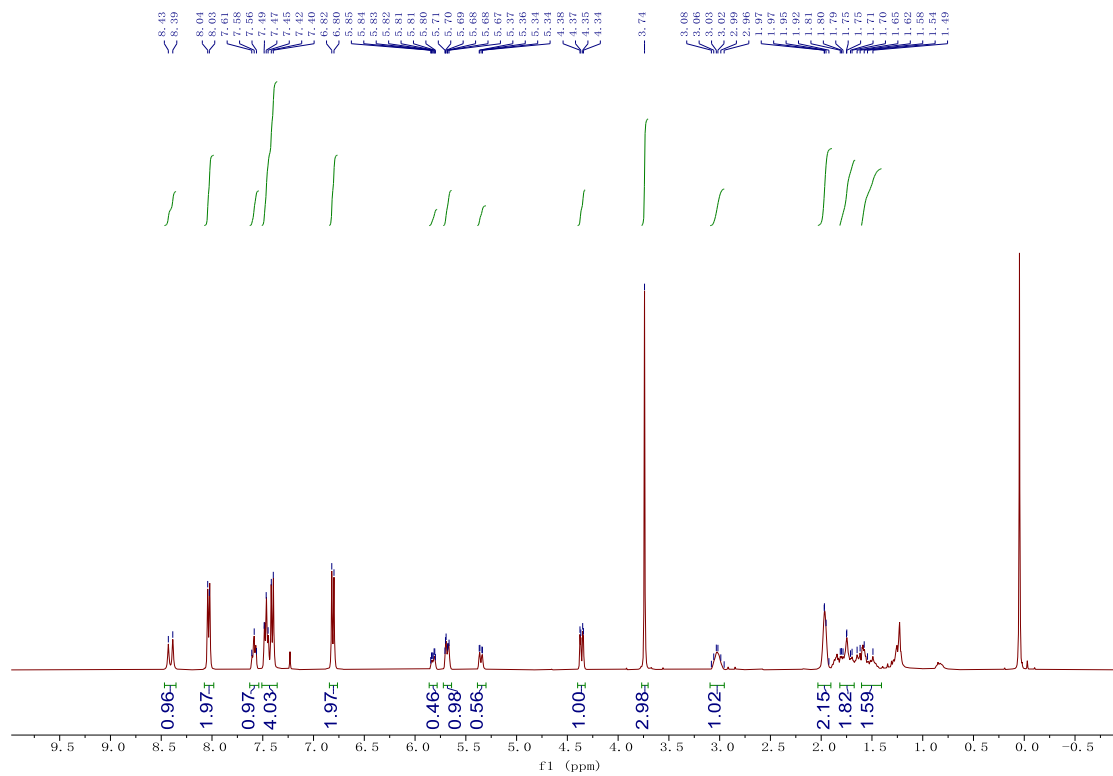
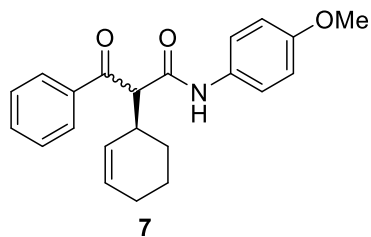


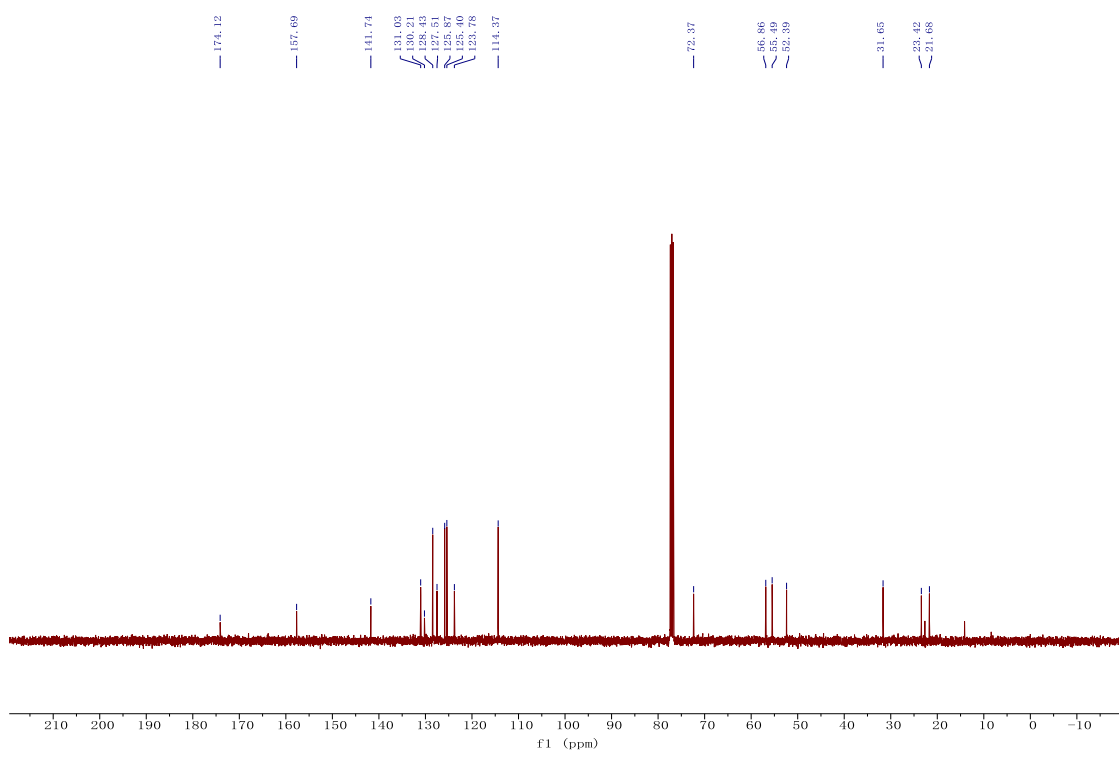
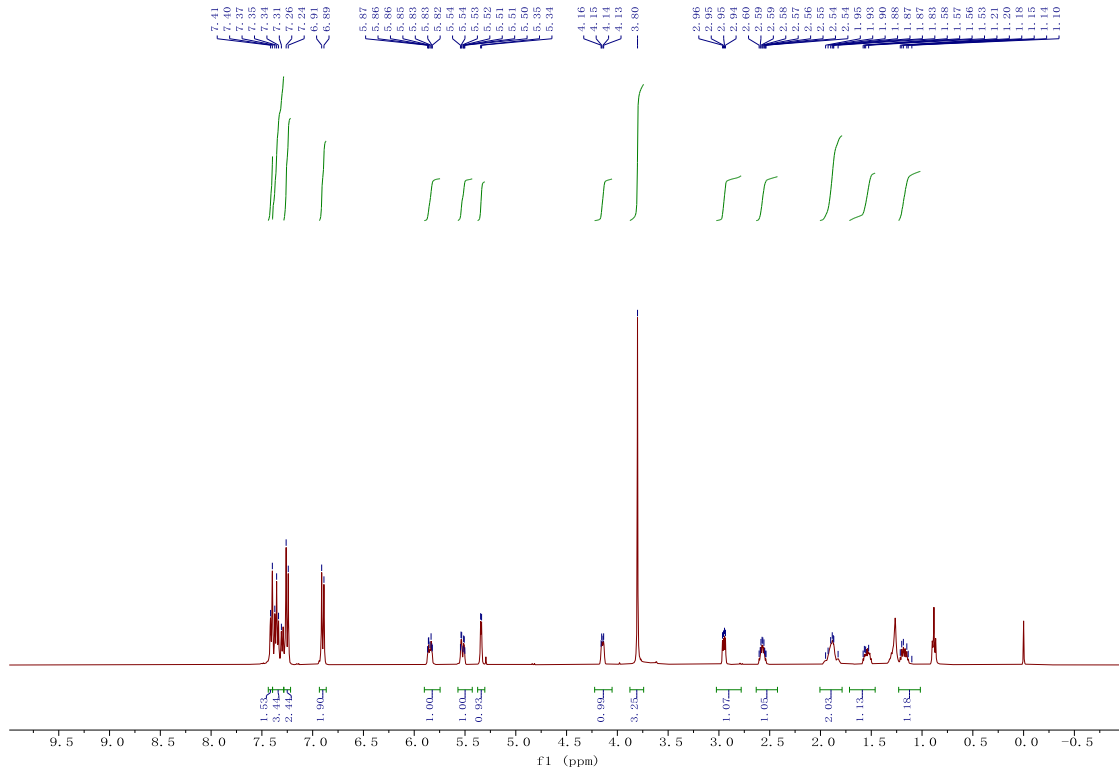
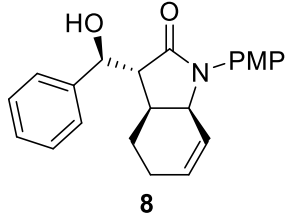


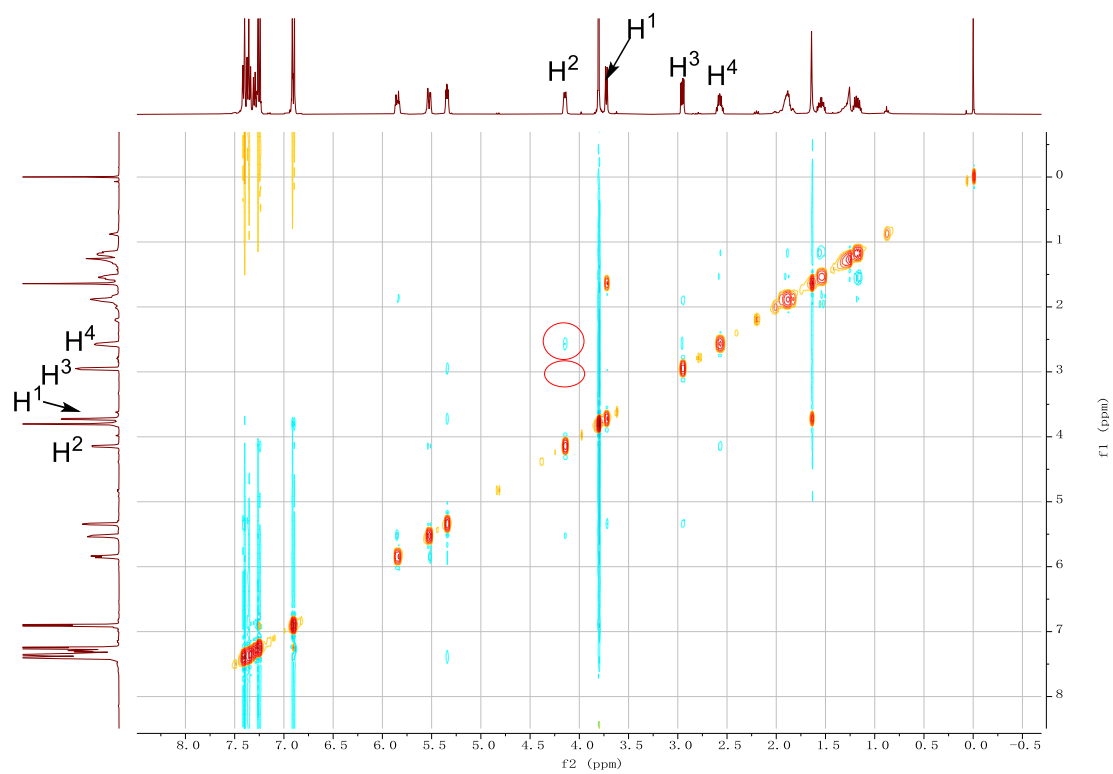
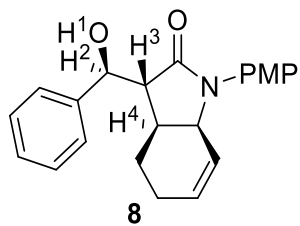




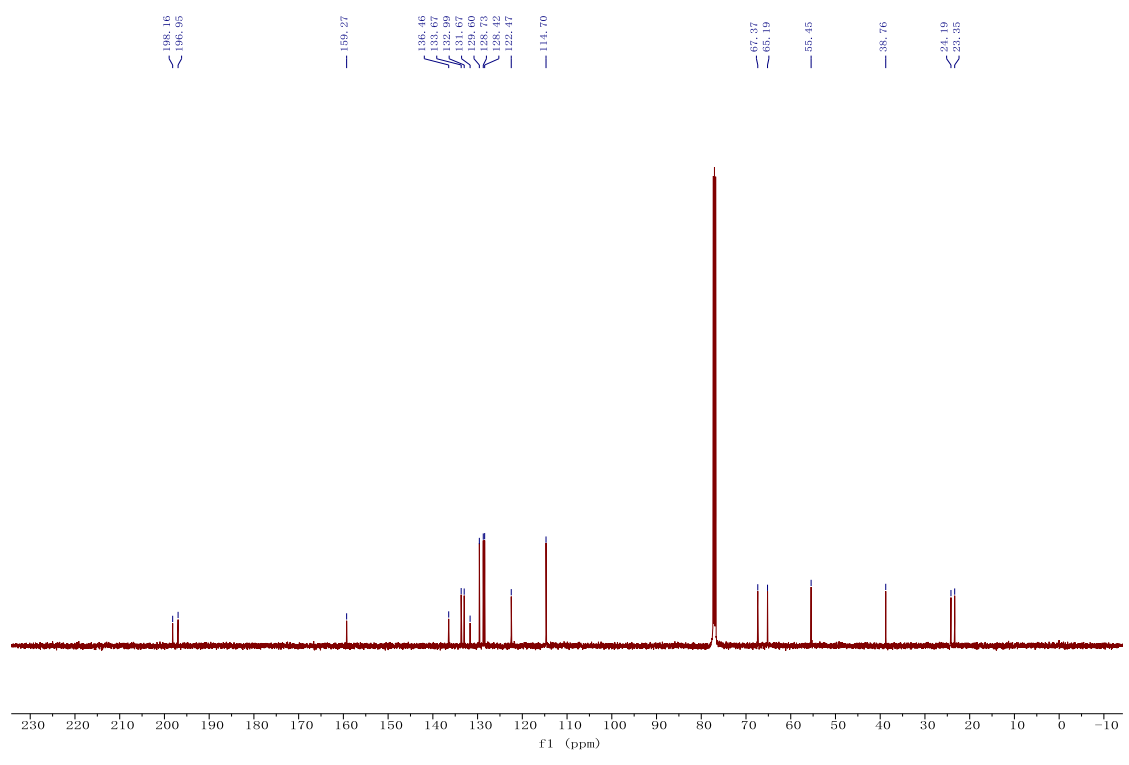
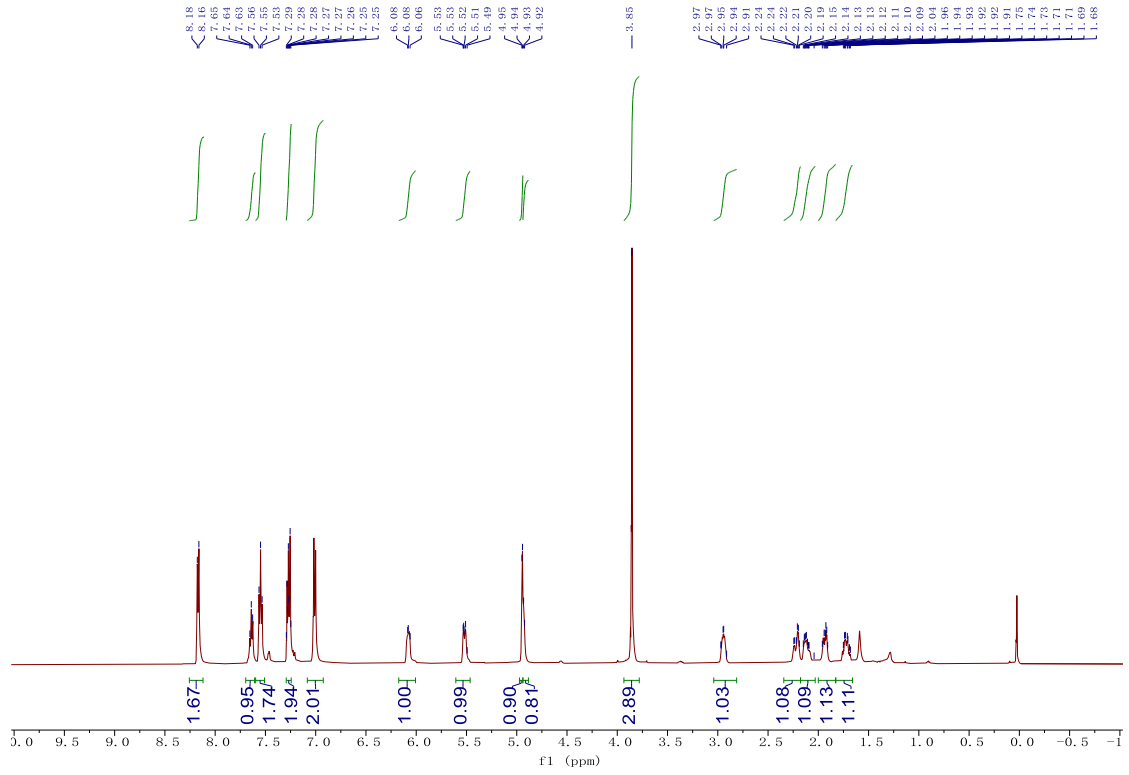
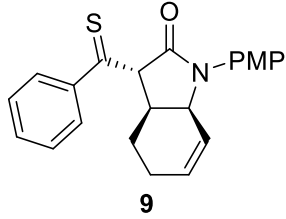


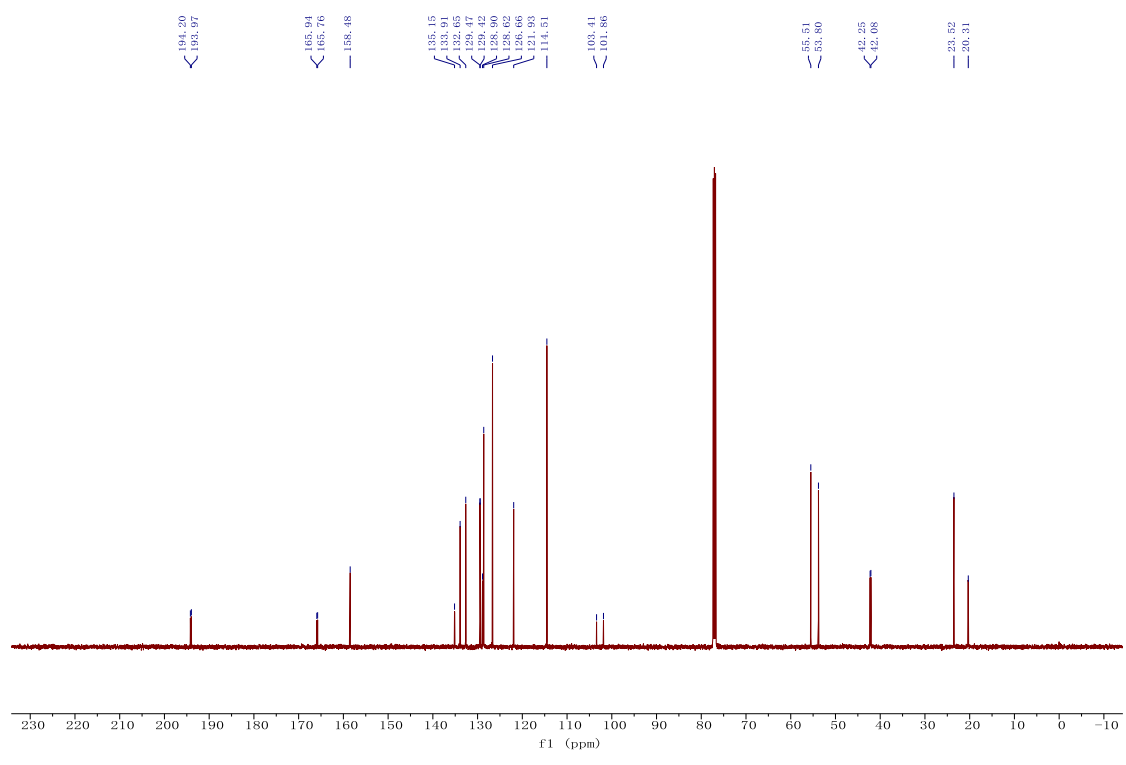
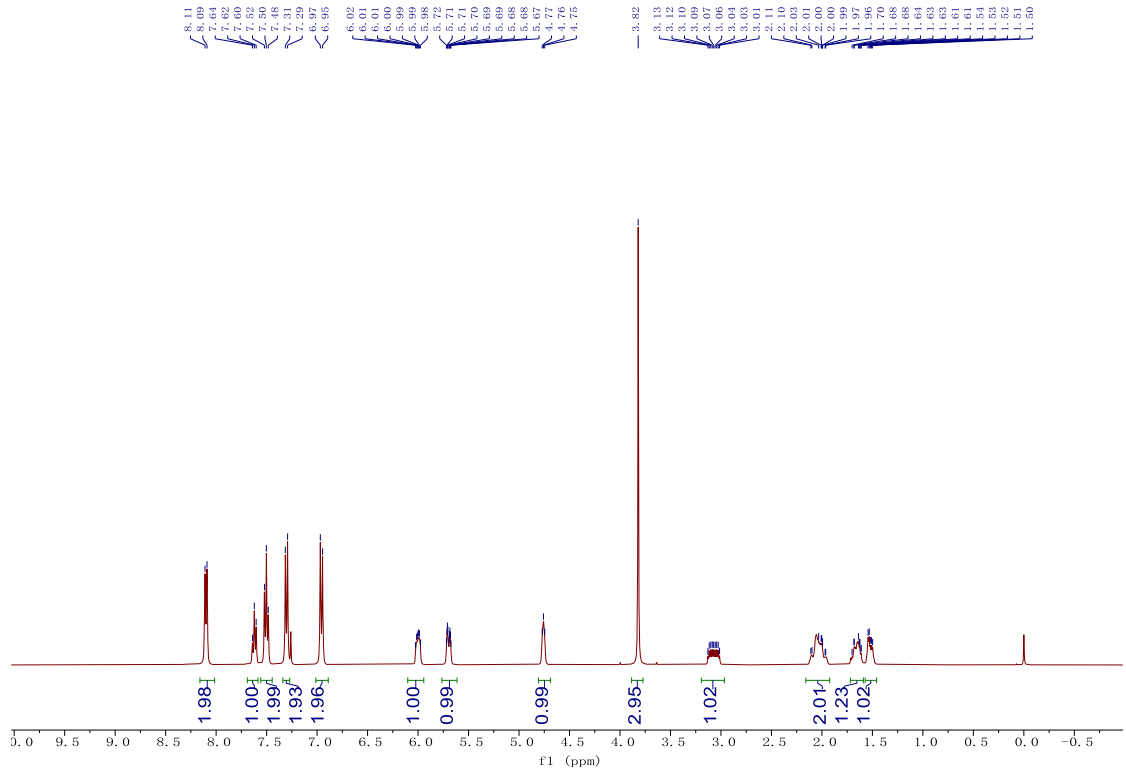
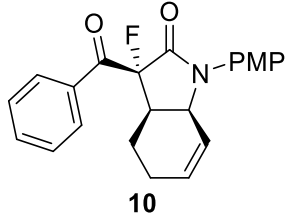


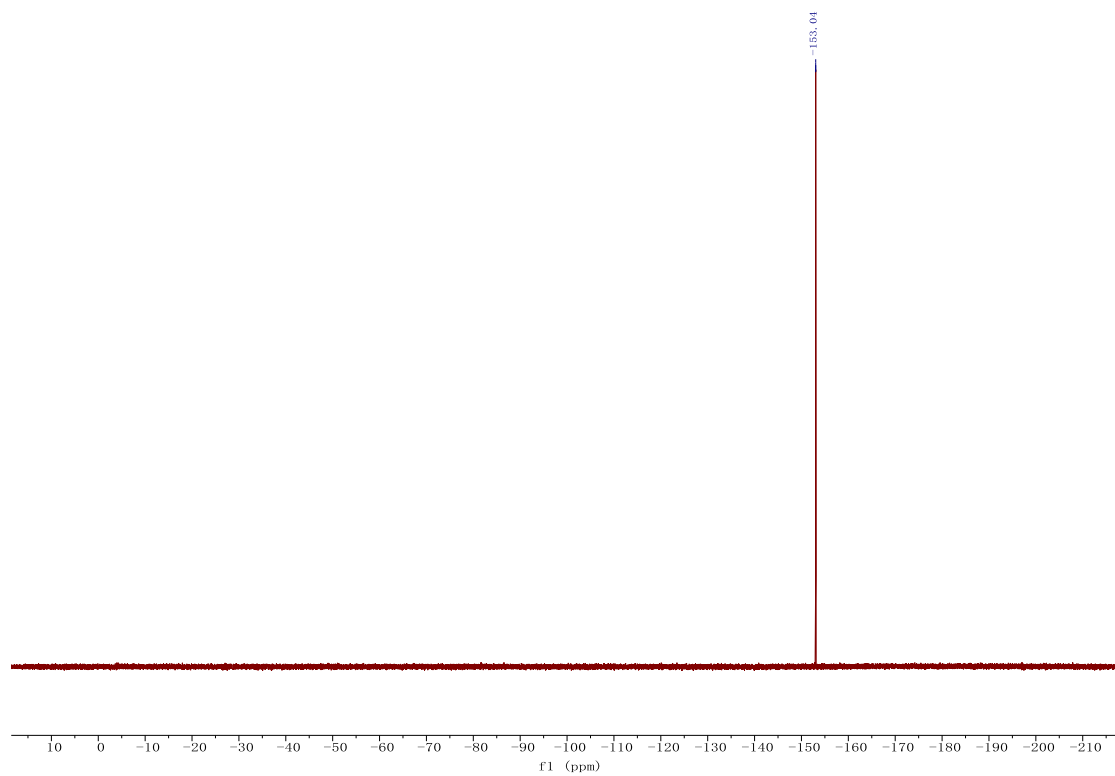




From the NOESY spectrum of **8**, the H<sup>2</sup> atom shows NOE interactions relative to the H atoms of H<sup>4</sup>, but no interactions relative to H<sup>3</sup> atom, which indicates the H<sup>2</sup> and H<sup>4</sup> group are *cis*-configuration.



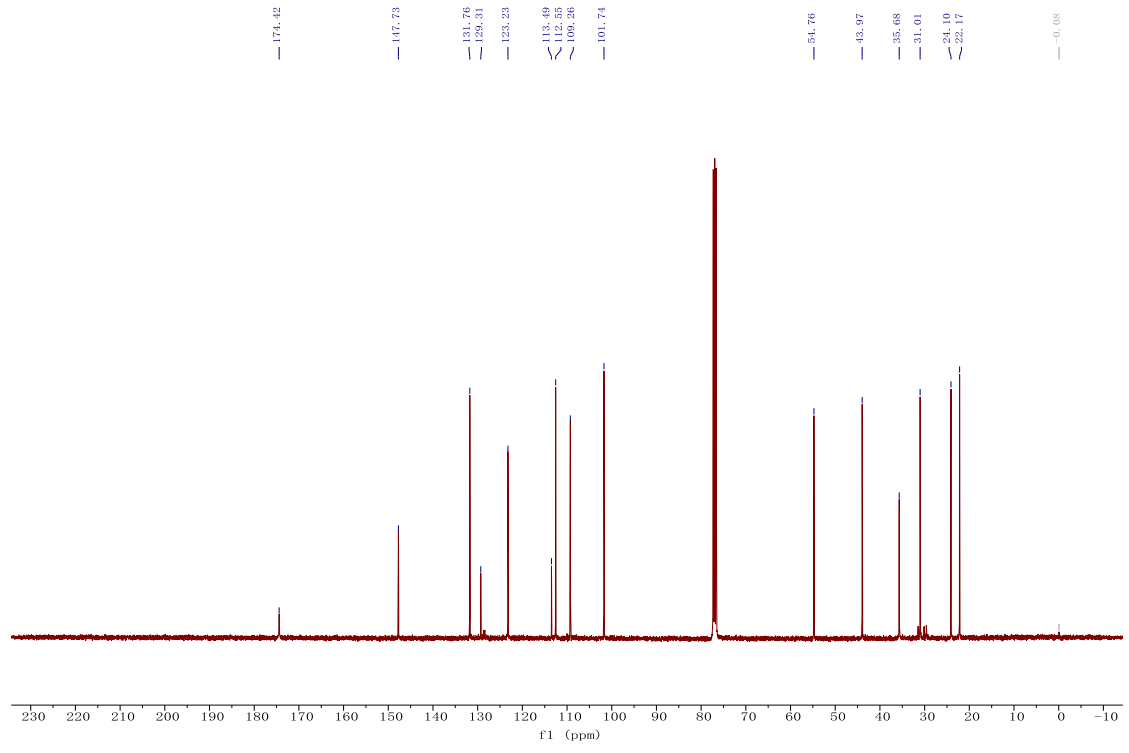
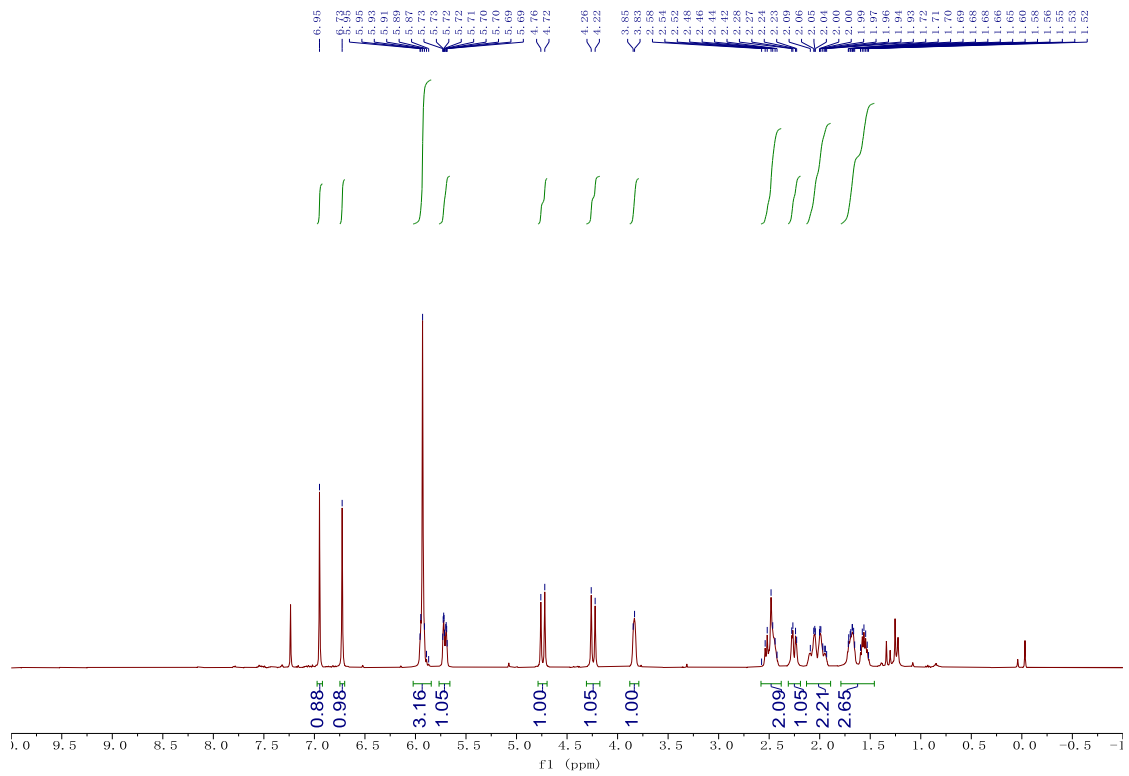
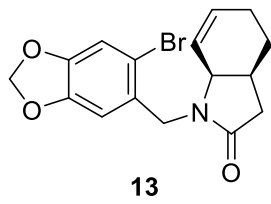




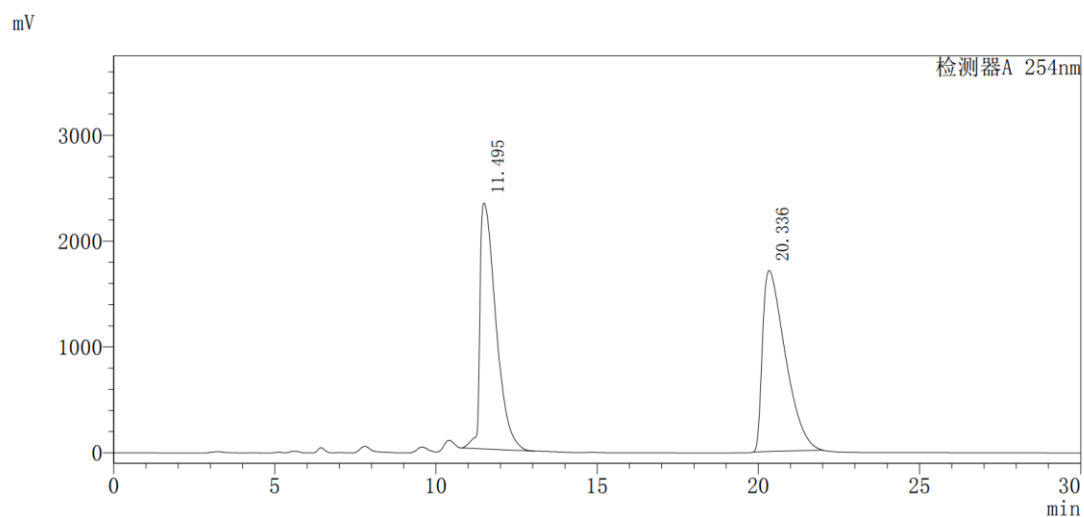
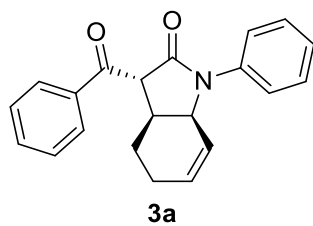






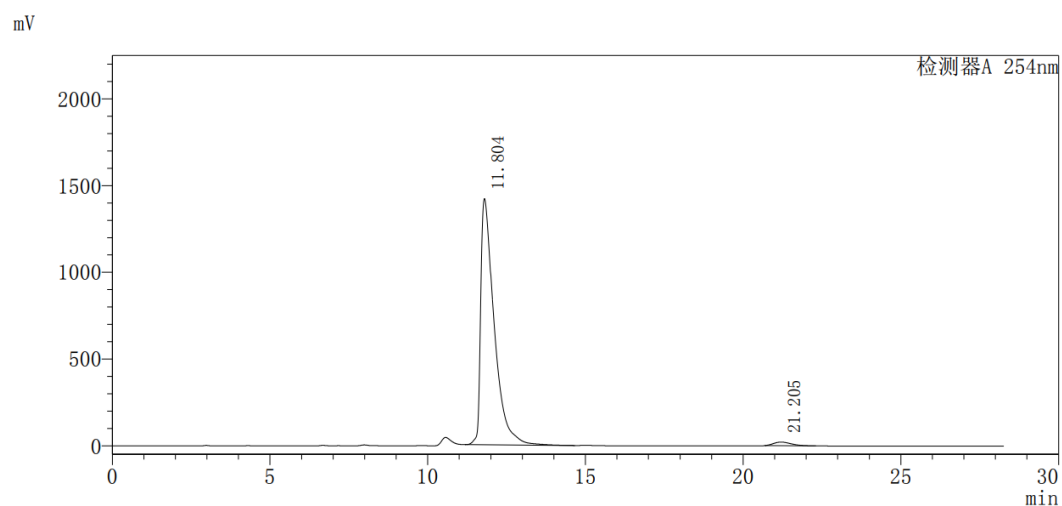


## 7. HPLC Data



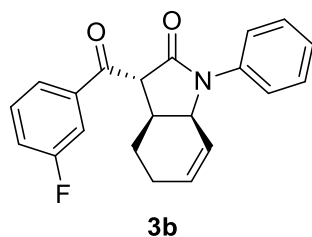
PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %
1	11.495	80244428	48.768
2	20.336	84297169	51.232
Total		164541597	100.0



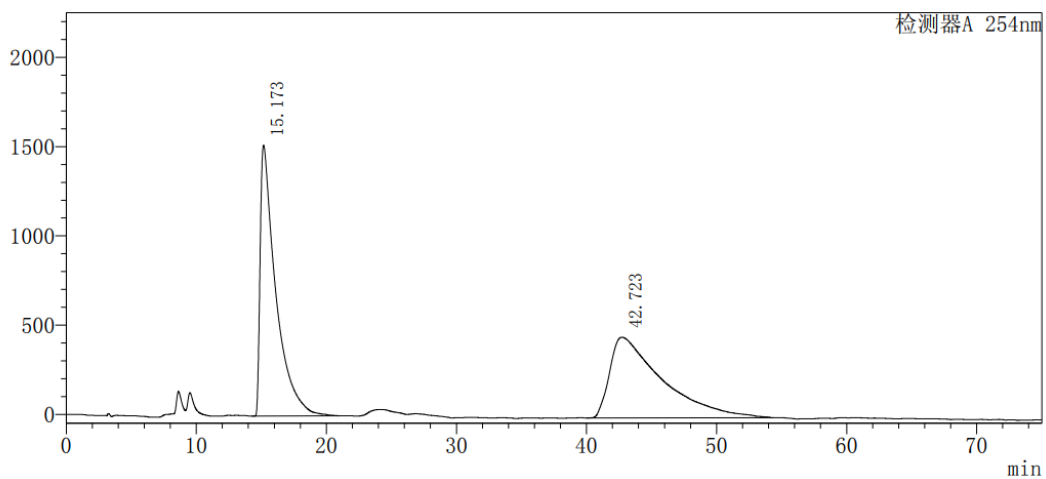
PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %	Ee %
1	11.804	41924600	98.099	96
2	21.205	812472	1.901	
Total		42737072	100.0	



<色谱图>

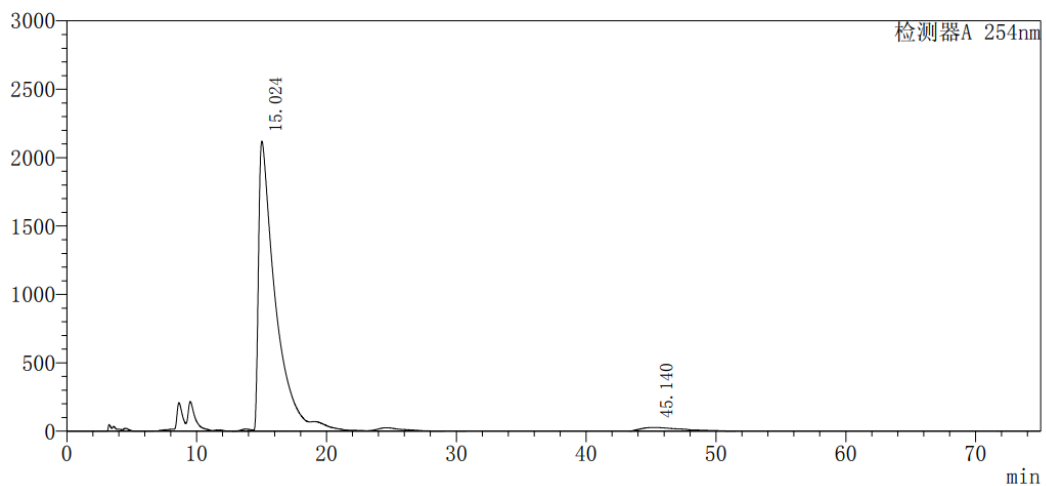
mV



PDA Ch1 254nm

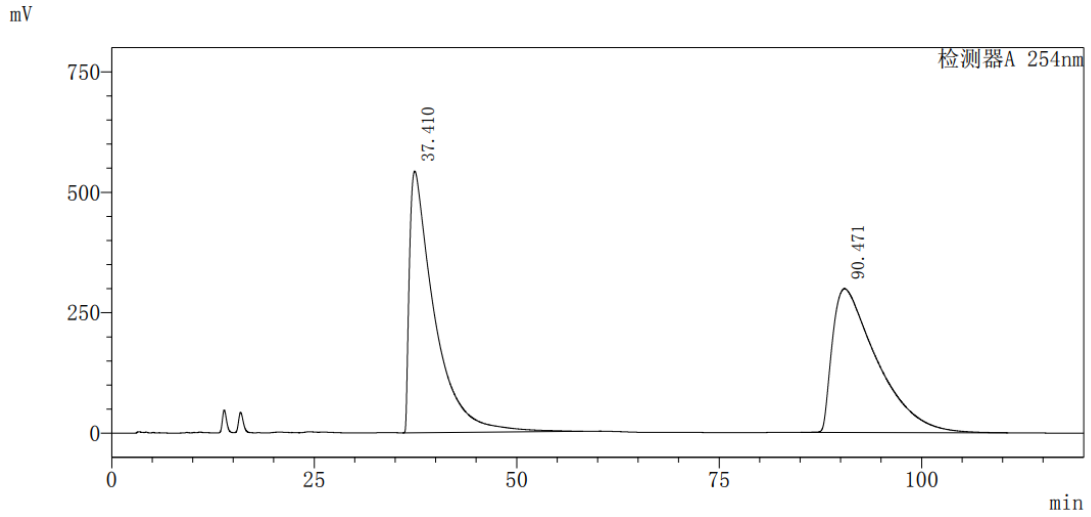
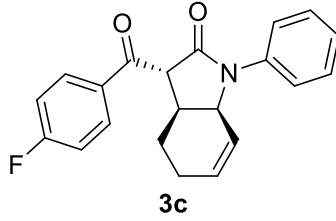
Peak #	Ret. Time	Area	Conc %
1	15.173	126682962	50.083
2	42.723	126265429	49.917
Total		252948391	100.0

mV



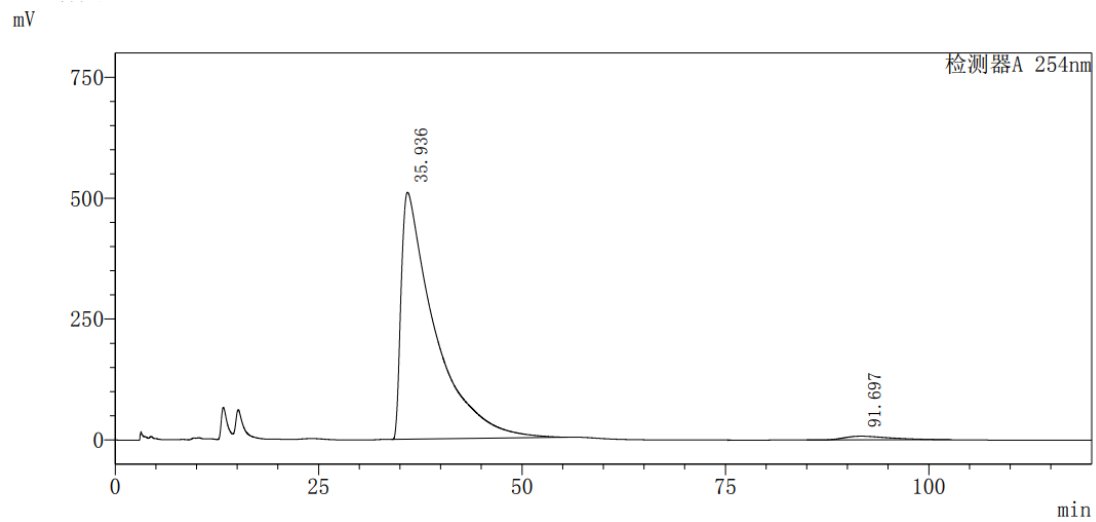
PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %	Ee %
1	15.024	193601047	95.591	91
2	45.140	8929627	4.409	
Total		202530674	100.0	



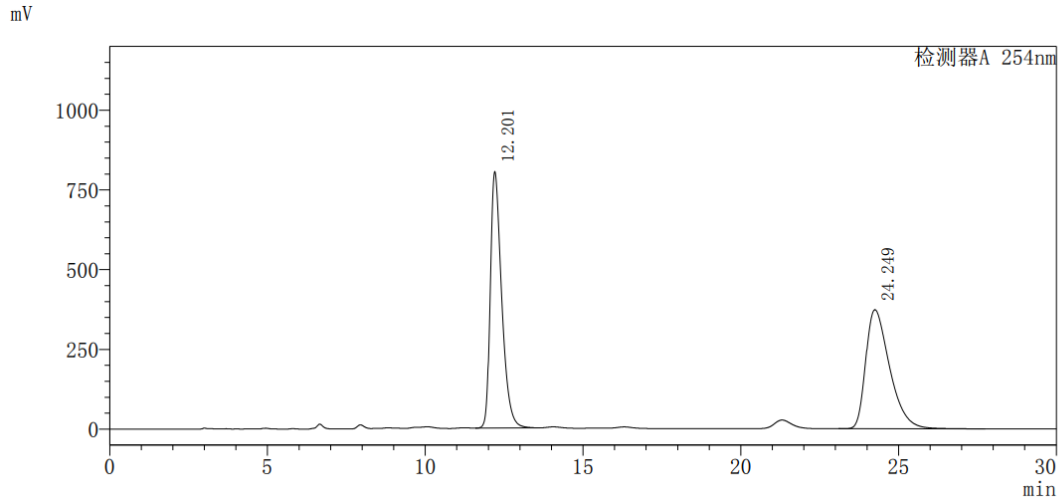
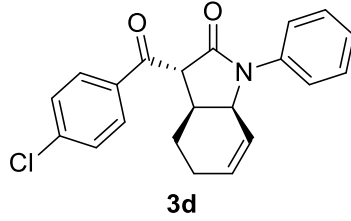
PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %
1	37.410	116825858	50.504
2	90.471	114495771	49.496
Total		231321629	100.0



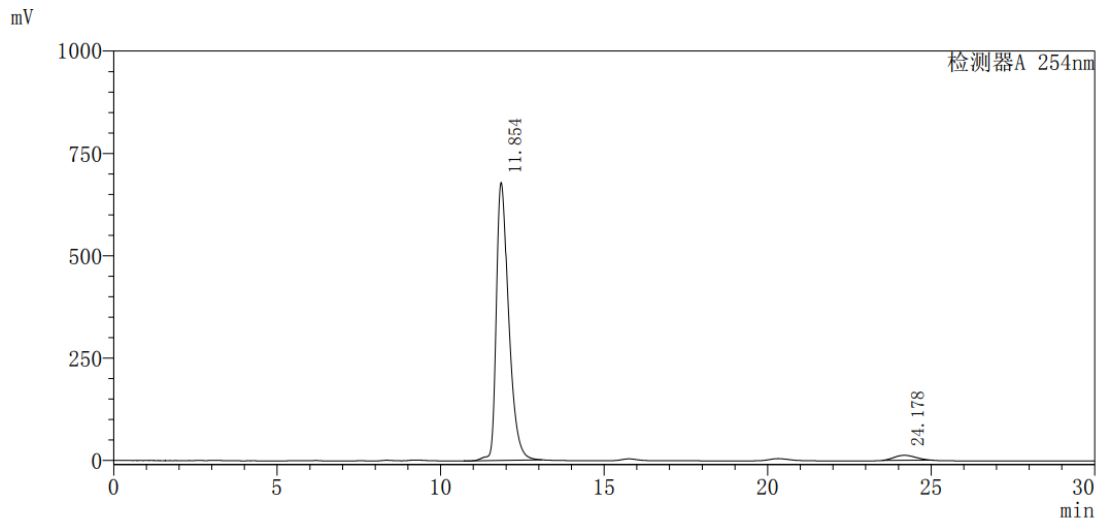
PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %	Ee %
1	35.936	146048569	97.974	96
2	91.697	3020786	2.026	
Total		149069355	100.0	

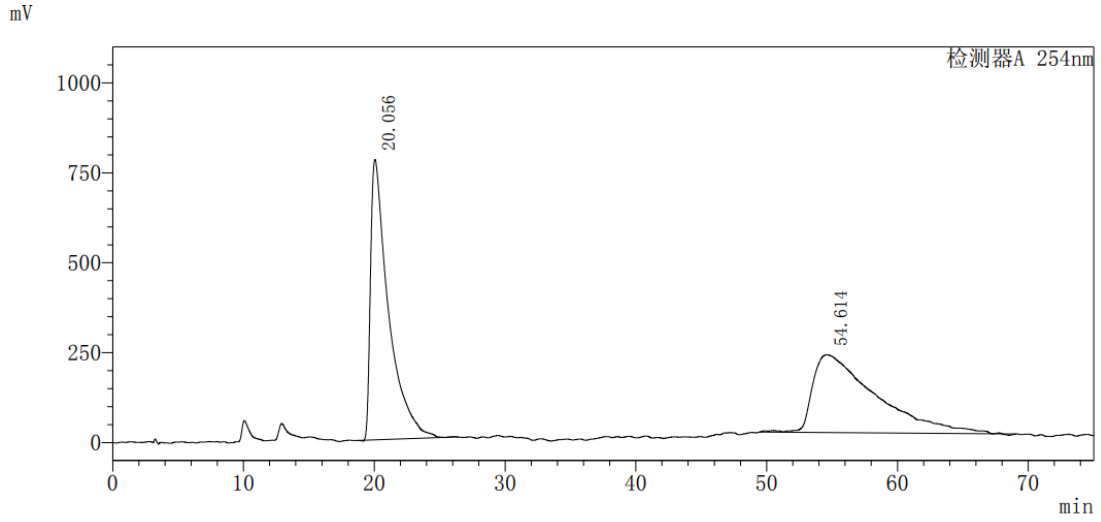
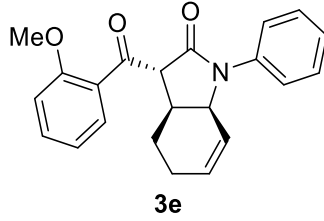


PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %
1	12.201	20027215	50.567
2	24.249	19578304	49.433
Total		39605519	100.0

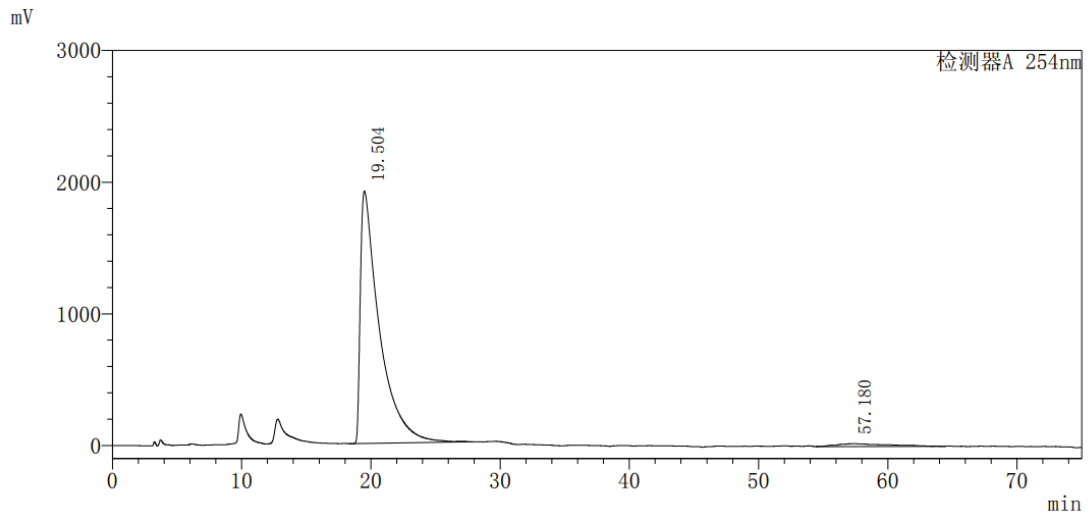


Peak #	Ret. Time	Area	Conc %	Ee %
1	11.854	17714349	96.923	94
2	24.178	562442	3.077	
Total		18276791	100.0	



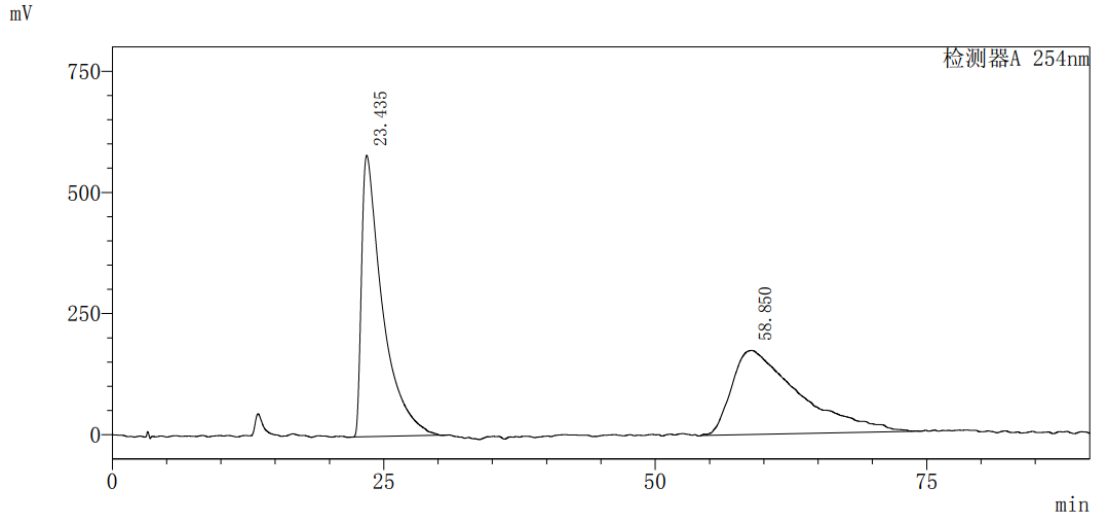
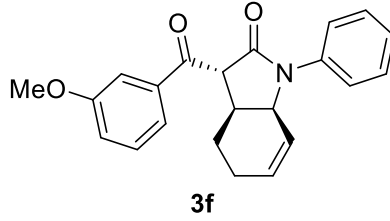
PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %
1	20.056	74549757	50.512
2	54.614	73038154	49.488
Total		147587911	100



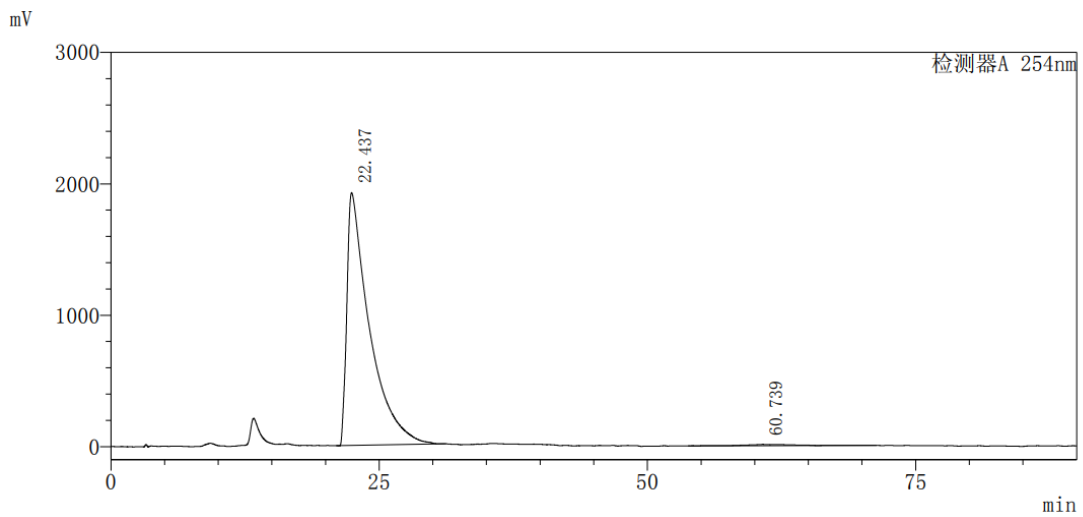
PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %	Ee %
1	19.504	196126260	96.951	94
2	57.180	6168546	3.049	
Total		202294806	100.0	



PDA Ch1 254nm

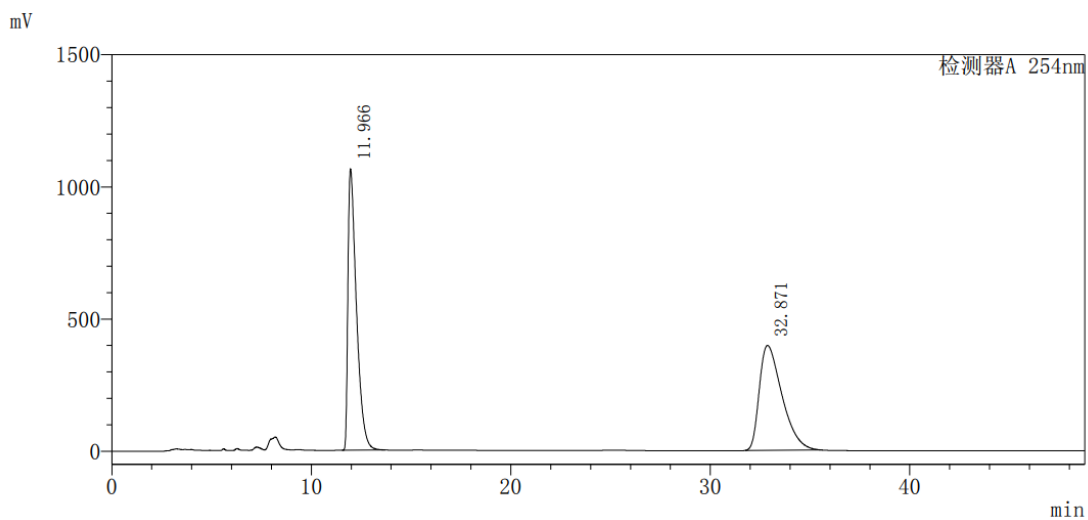
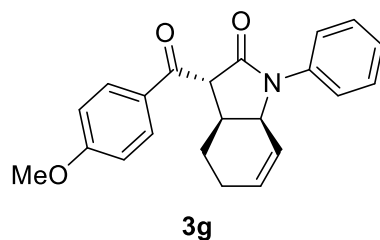
Peak #	Ret. Time	Area	Conc %
1	23.435	77616480	50.965
2	58.850	74676792	49.035
Total		152293273	100.0



PDA Ch1 254nm

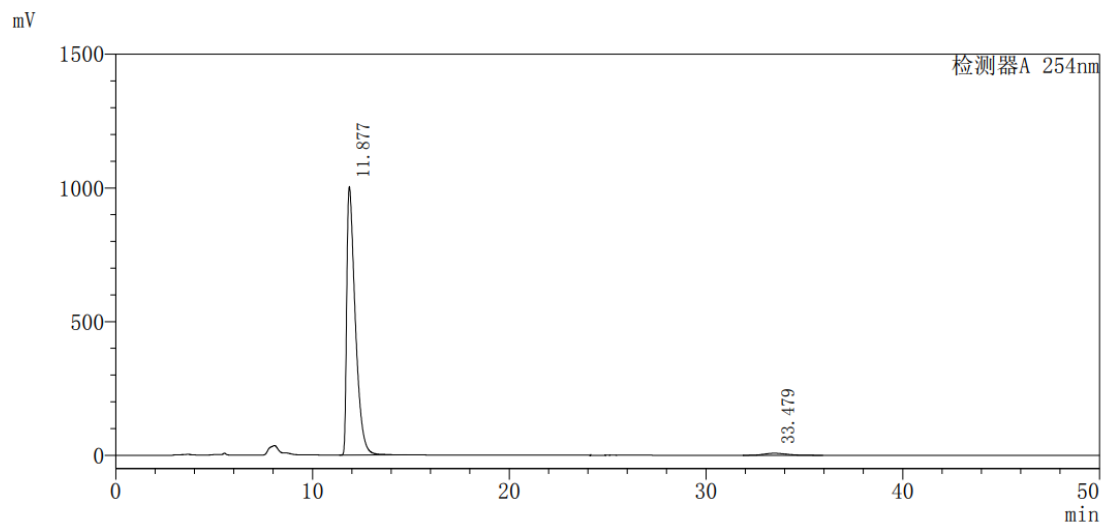
Peak #	Ret. Time	Area	Conc %	Ee %
1	22.437	280592380	98.952	98
2	60.739	2970431	1.048	
Total		283562811	100.0	





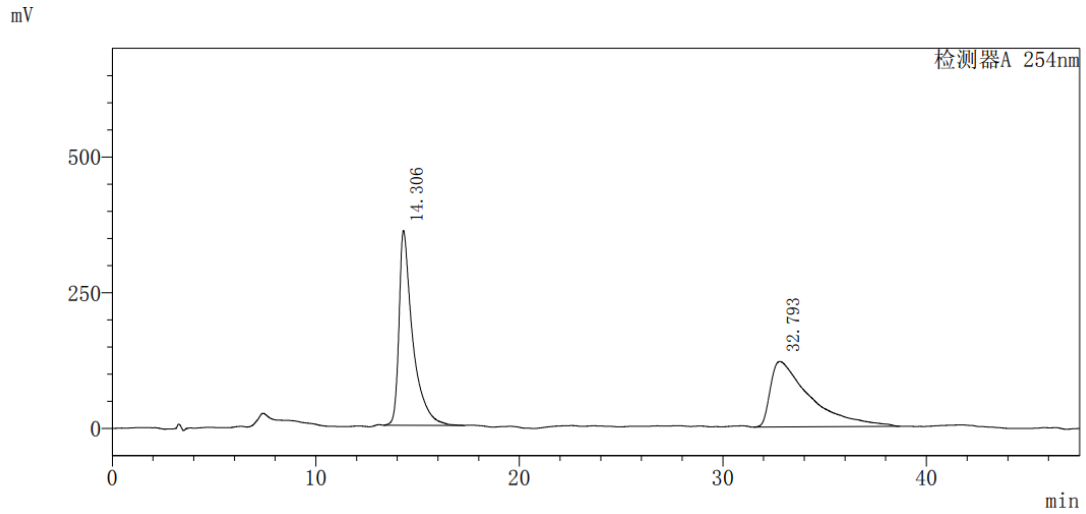
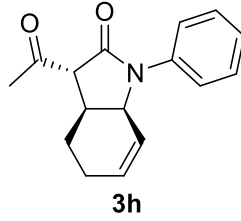
PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %
1	11.966	31565229	50.204
2	32.871	31308549	49.796
Total		62873778	100.0



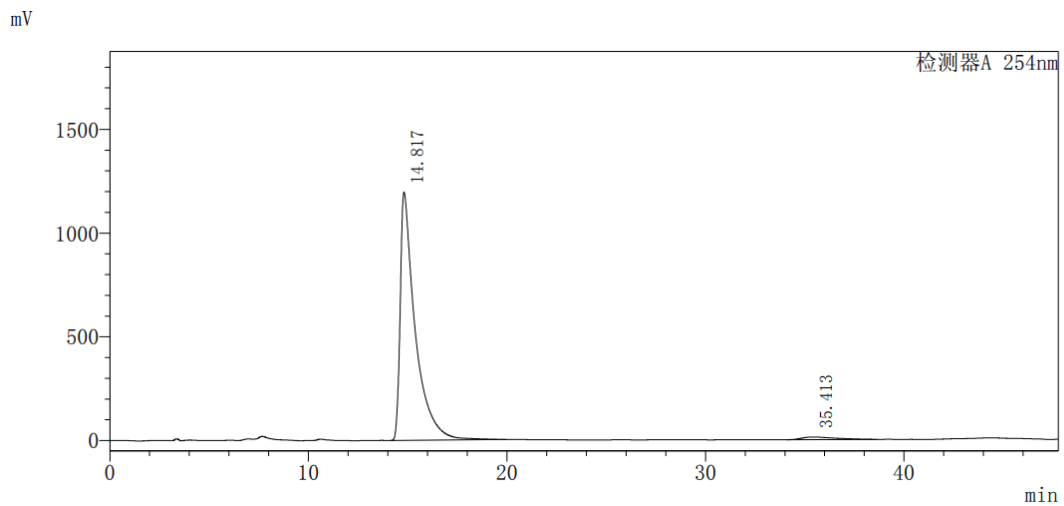
PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %	Ee %
1	11.877	30333910	98.090	96
2	33.479	590525	1.910	
Total		30924435	100.0	



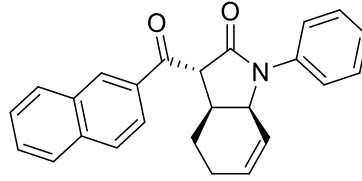
PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %
1	14.306	16710655	50.477
2	32.793	16394805	49.523
Total		33105460	100.0

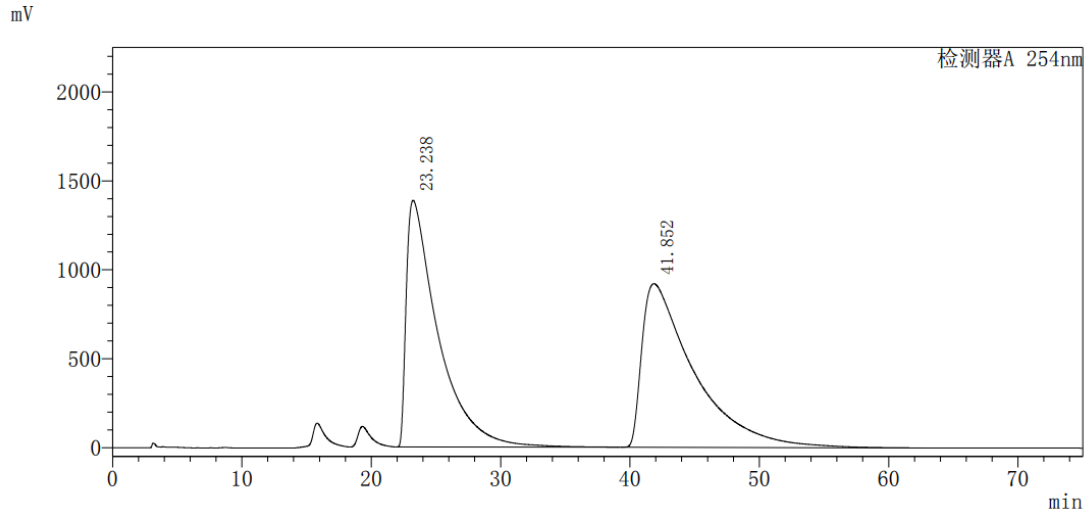


PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %	Ee %
1	14.817	62598860	97.690	95
2	35.413	1480430	2.310	
Total		64079289	100.0	

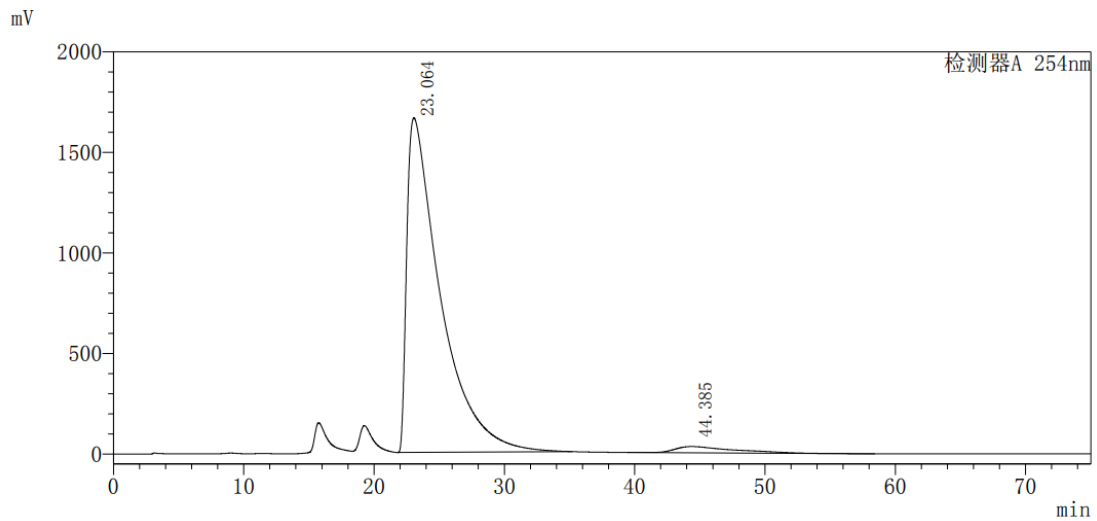


**3i**



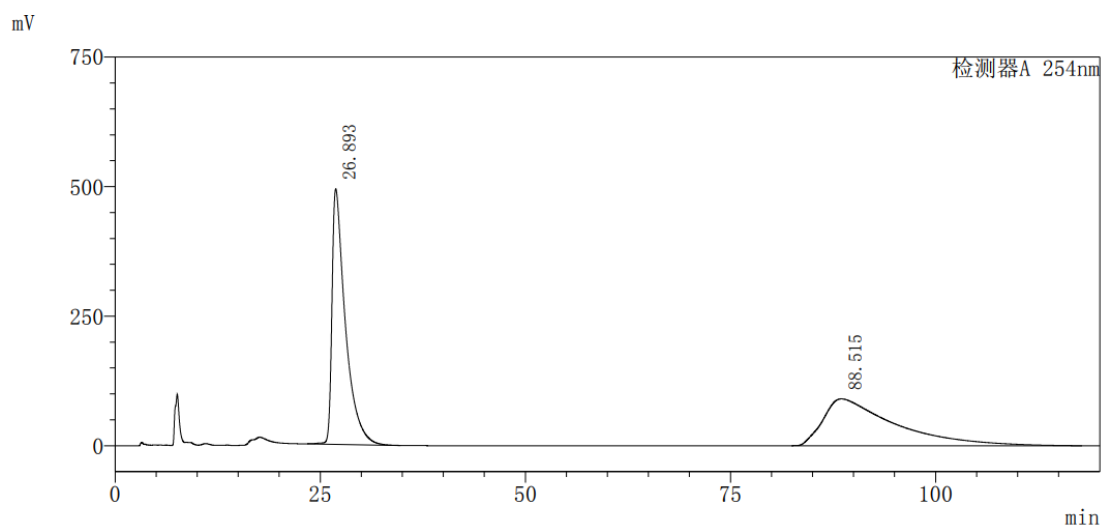
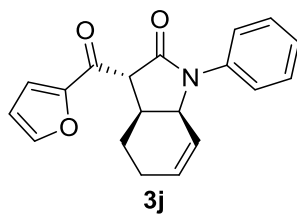
PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %
1	23.238	236929829	47.863
2	41.852	258088066	52.137
Total		495017895	100.0



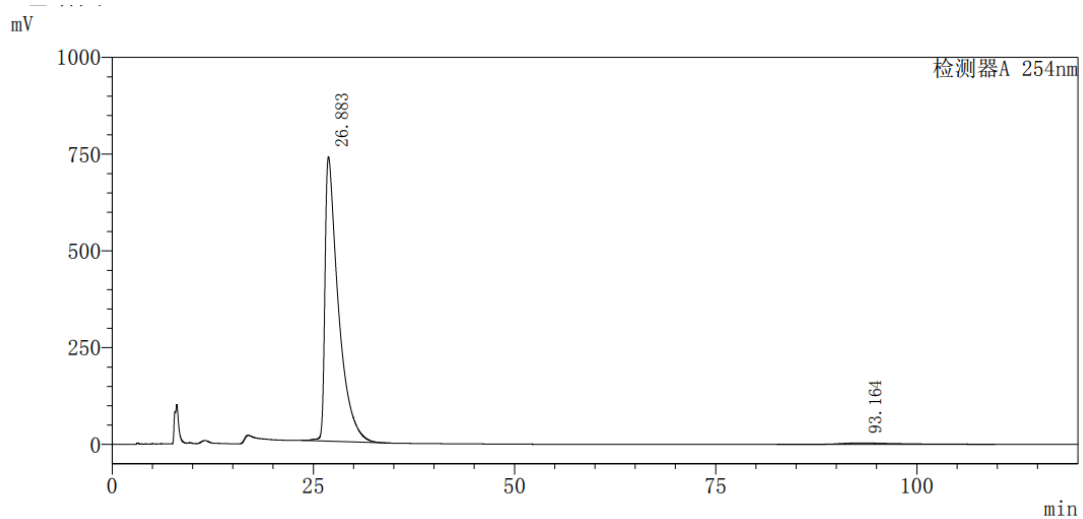
PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %	Ee %
1	23.064	298034514	96.868	94
2	44.385	9637003	3.132	
Total		307671516	100.0	



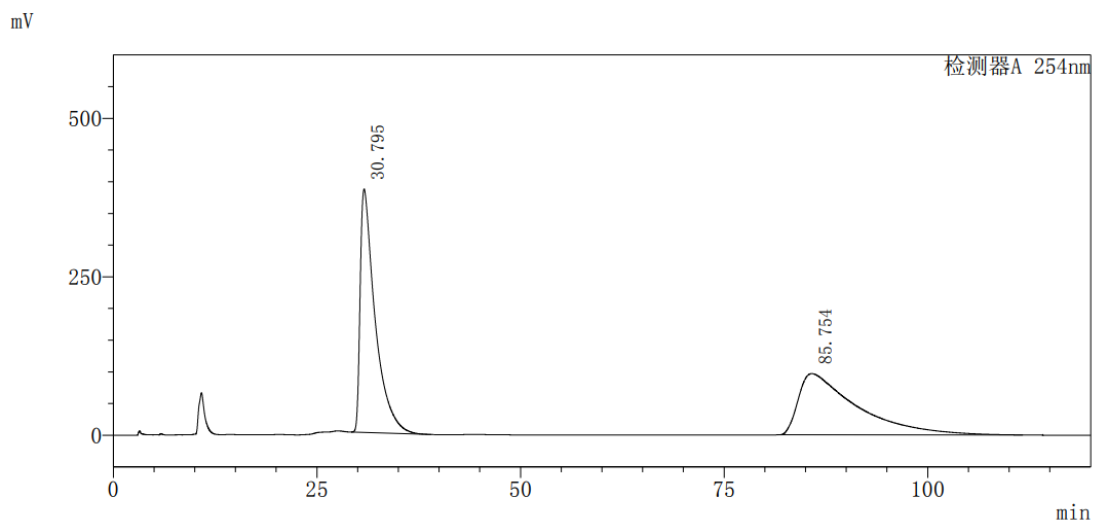
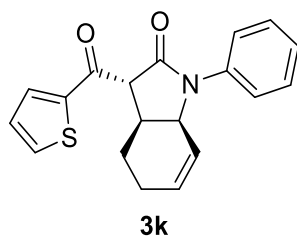
PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %
1	26.893	55929278	50.555
2	88.515	54700704	49.445
Total		110629981	100.0



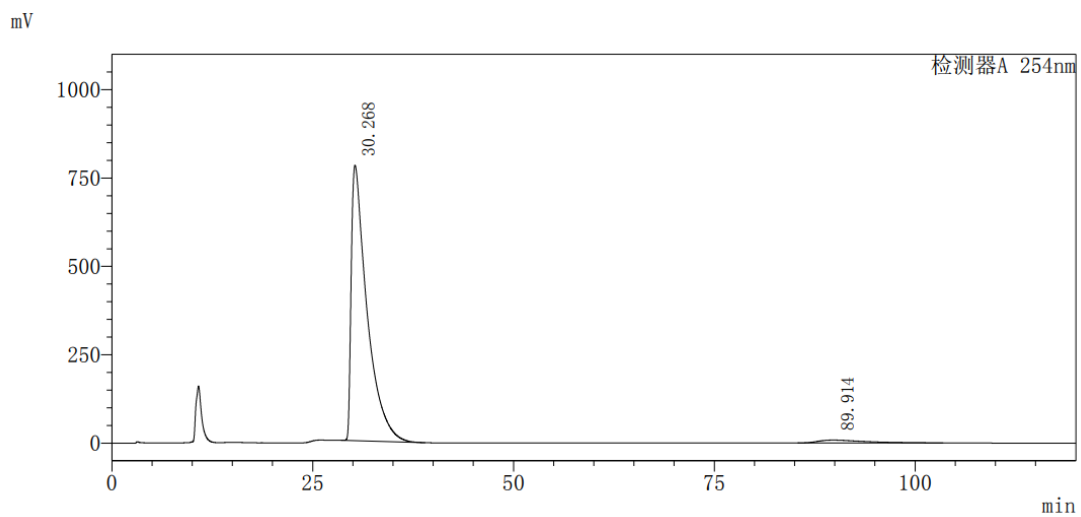
PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %	Ee %
1	26.883	85321767	98.115	96
2	93.164	1639500	1.885	
Total		86961268	100.0	



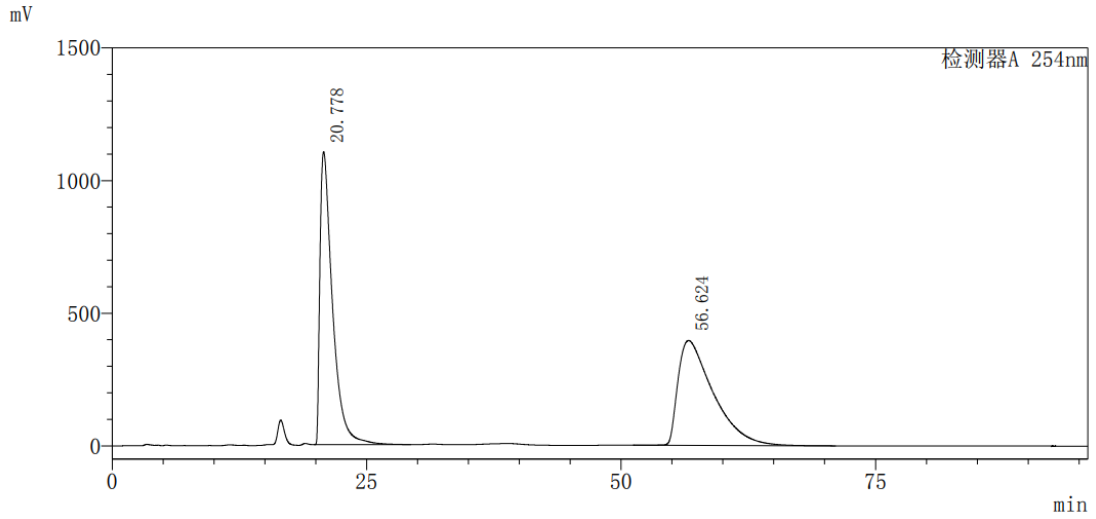
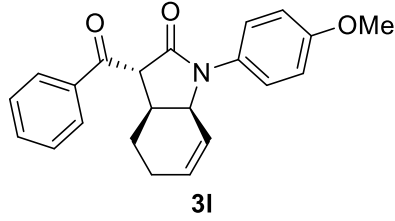
PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %
1	30.795	48961409	50.404
2	85.754	48175603	49.596
Total		97137012	100.0



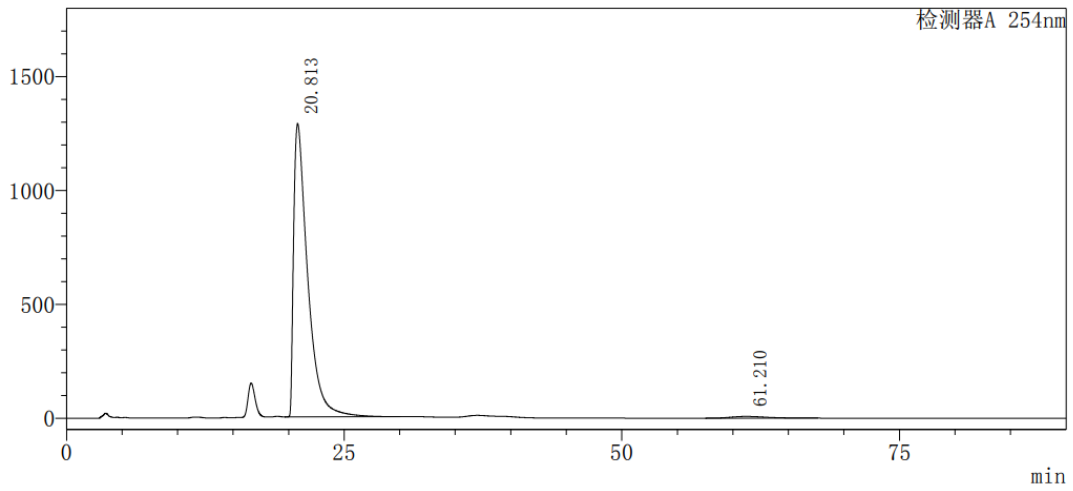
PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %	Ee %
1	30.268	106335844	96.956	94
2	89.914	3338142	3.044	
Total		109673986	100.0	



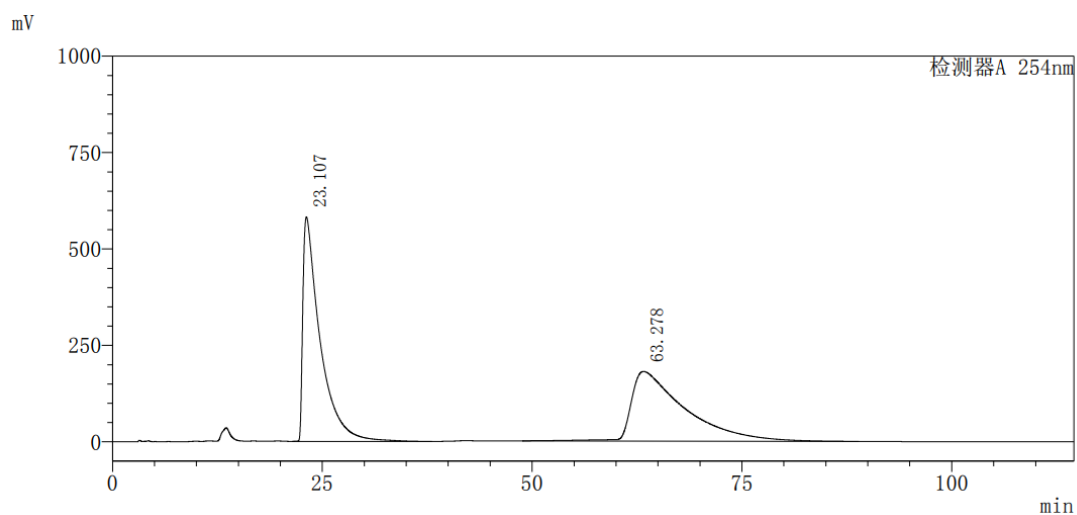
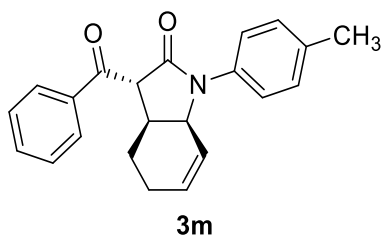
PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %
1	20.778	94816732	49.851
2	56.624	95383666	50.149
Total		190200398	100



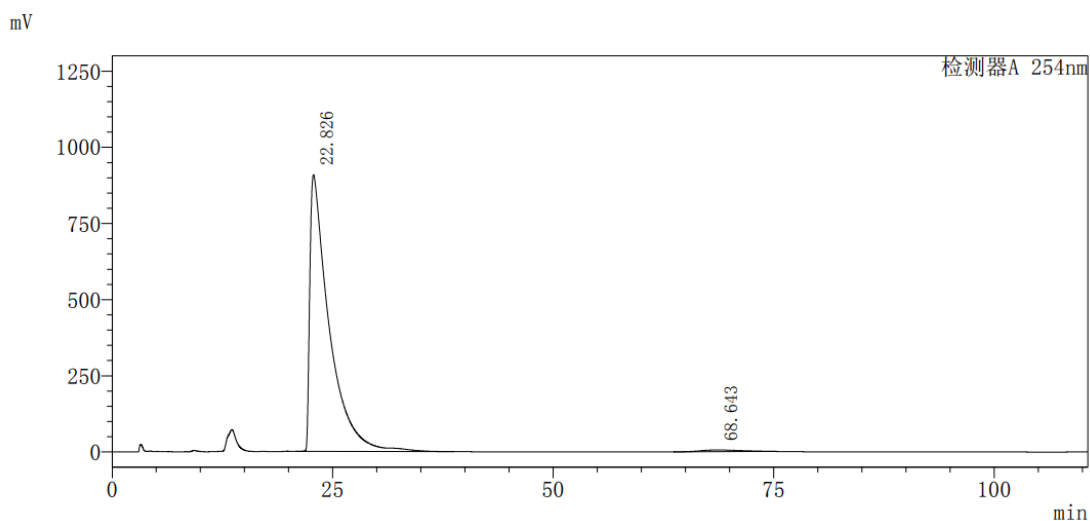
PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %	Ee %
1	20.813	113734511	98.536	97
2	61.210	1689303	1.464	
Total		115423814	100	



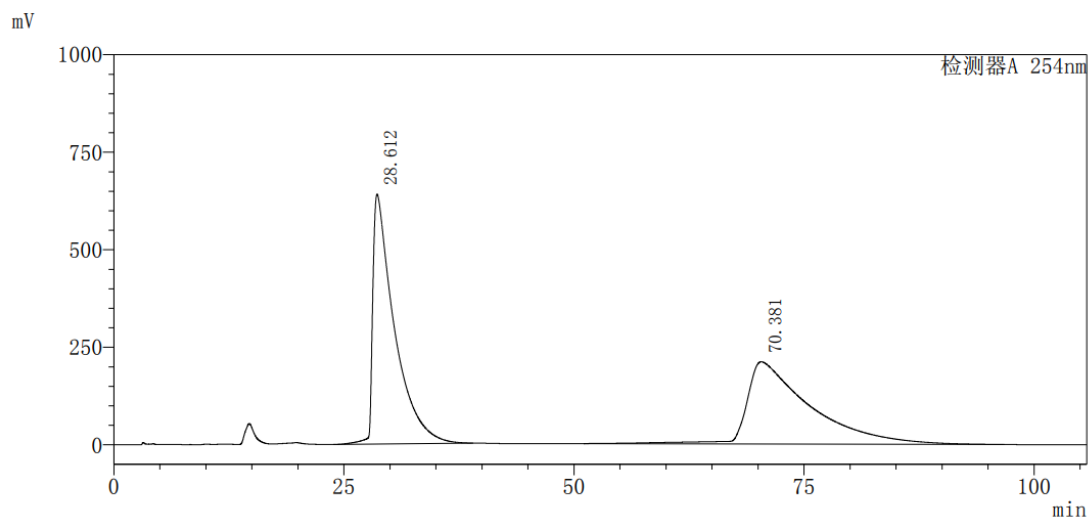
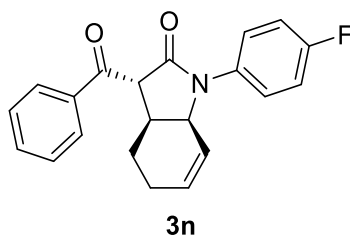
PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %
1	23.107	83236222	51.029
2	63.278	79879754	48.971
Total		163115976	100



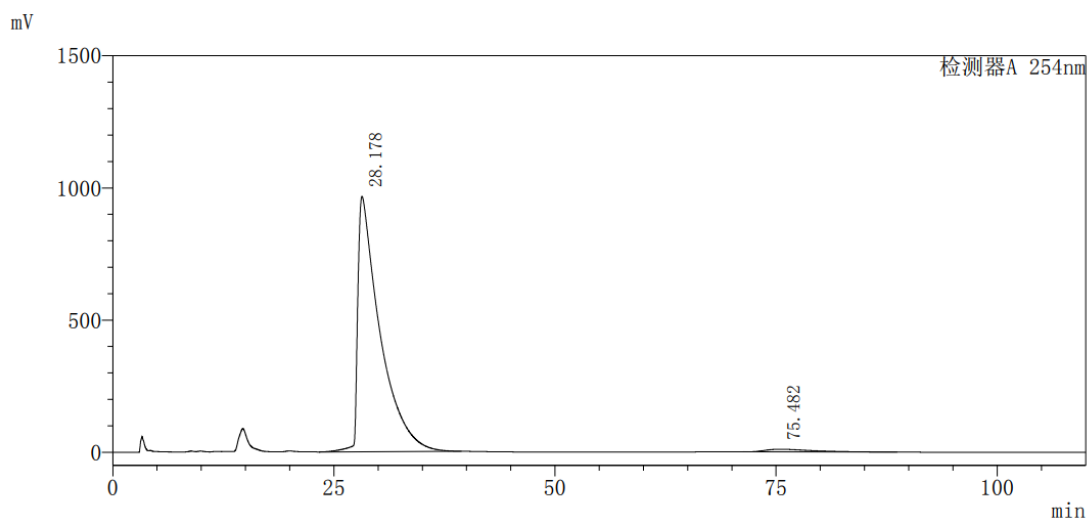
PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %	Ee %
1	22.826	138824302	98.750	98
2	68.643	1757005	1.250	
Total		140581306	100.0	



PDA Ch1 254nm

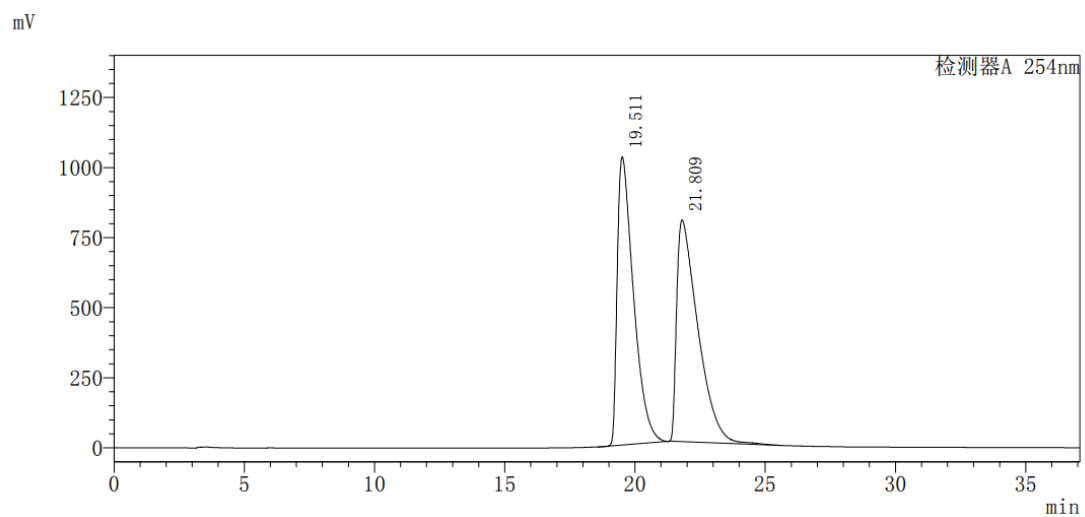
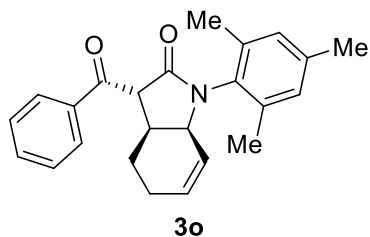
Peak #	Ret. Time	Area	Conc %
1	28.612	104367070	50.990
2	70.381	100314449	49.010
Total		204681519	100.0



PDA Ch1 254nm

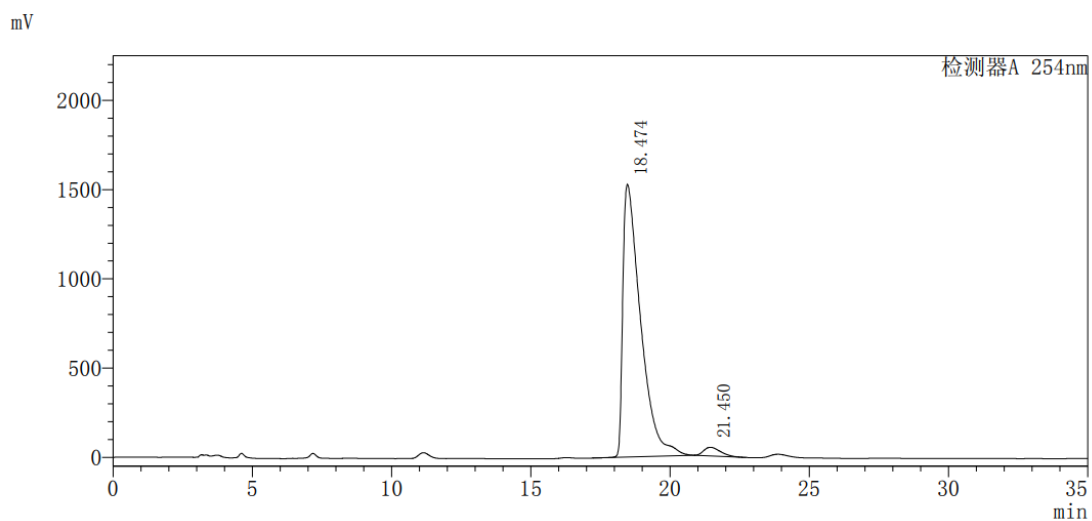
Peak #	Ret. Time	Area	Conc %	Ee %
1	28.178	168465567	97.795	96
2	75.482	3797706	2.205	
Total		172263272	100.0	





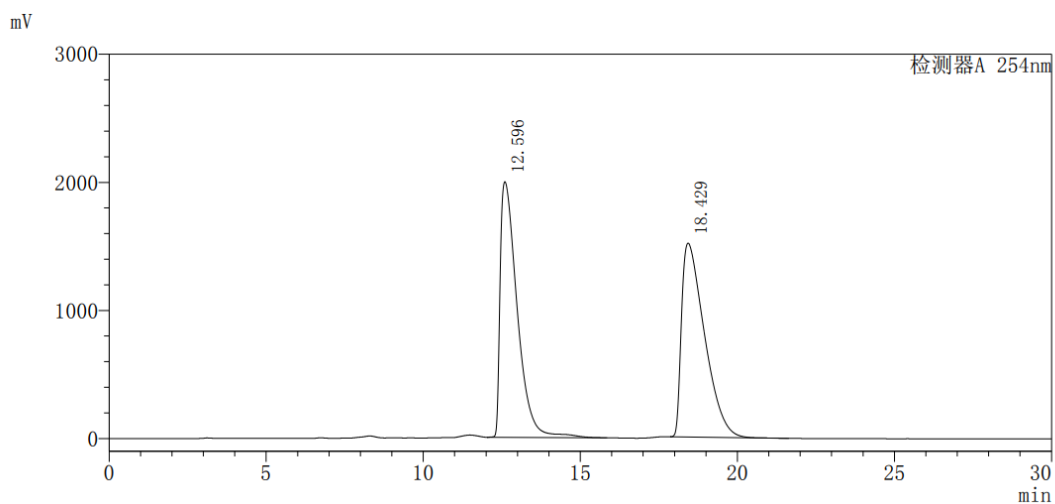
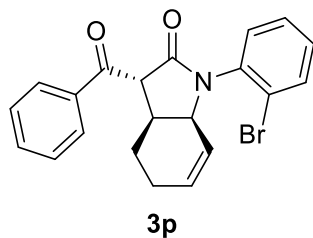
PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %
1	19.511	44593317	49.851
2	21.809	44860443	50.149
Total		89453760	100.0



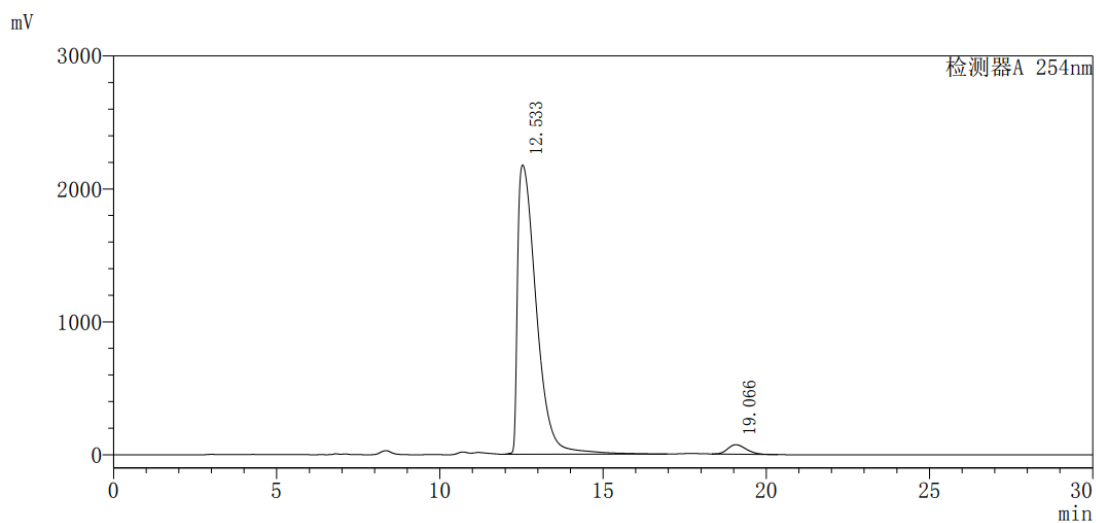
PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %	Ee %
1	18.474	67804317	97.081	94
2	21.450	2038432	2.919	
Total		69842748	100.0	



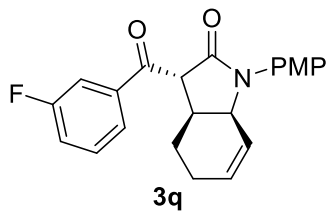
PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %
1	12.596	75437304	49.497
2	18.429	76970711	50.503
Total		152408015	100.0



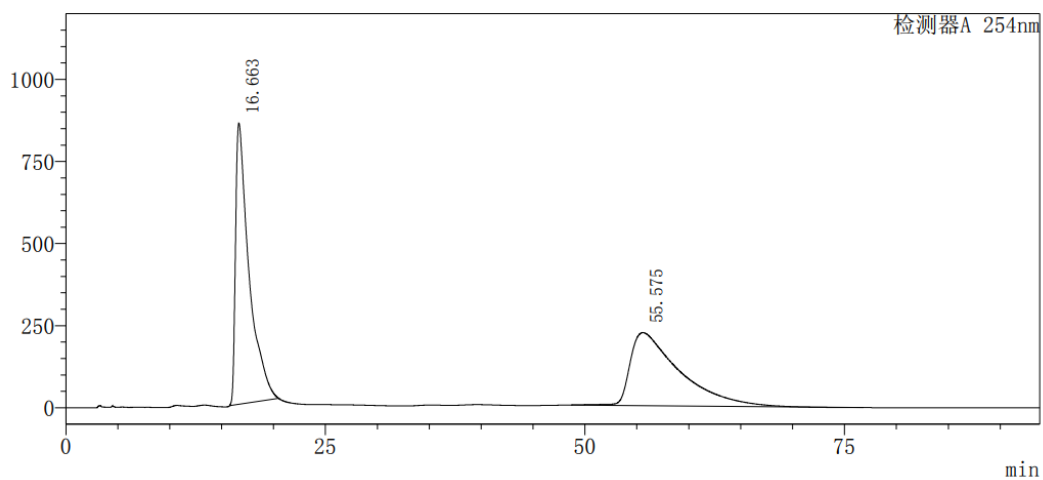
PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %	Ee %
1	12.533	86963396	96.878	94
2	19.066	2802924	3.122	
Total		89766319	100.0	



<色谱图>

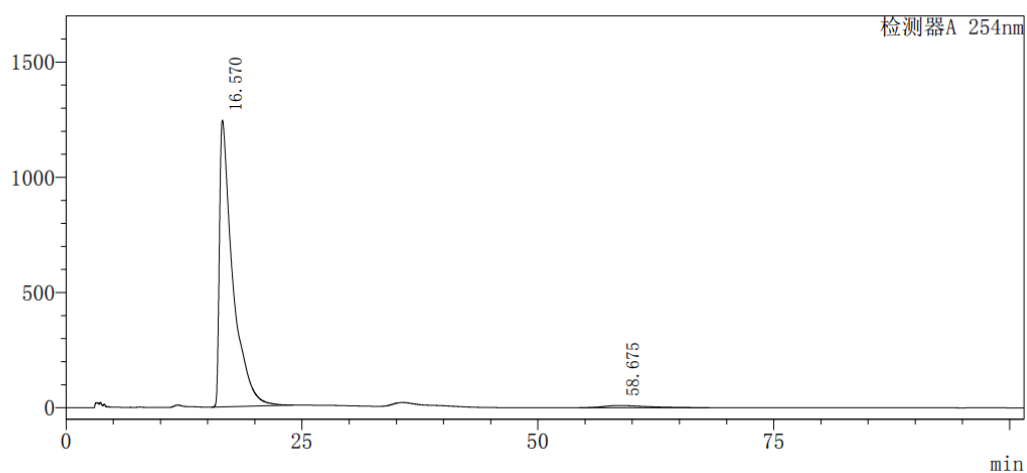
mV



PDA Ch1 254nm

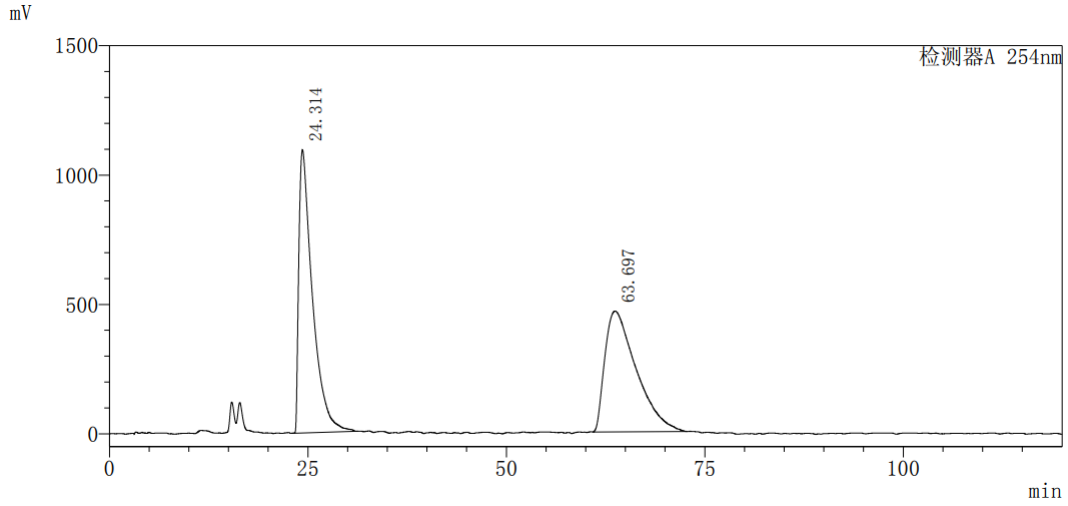
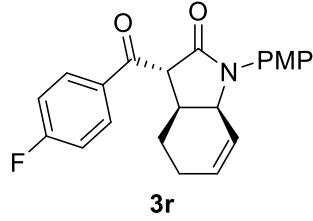
Peak #	Ret. Time	Area	Conc %
1	16.663	77261605	51.260
2	55.575	73461983	48.740
Total		150723589	100.0

mV



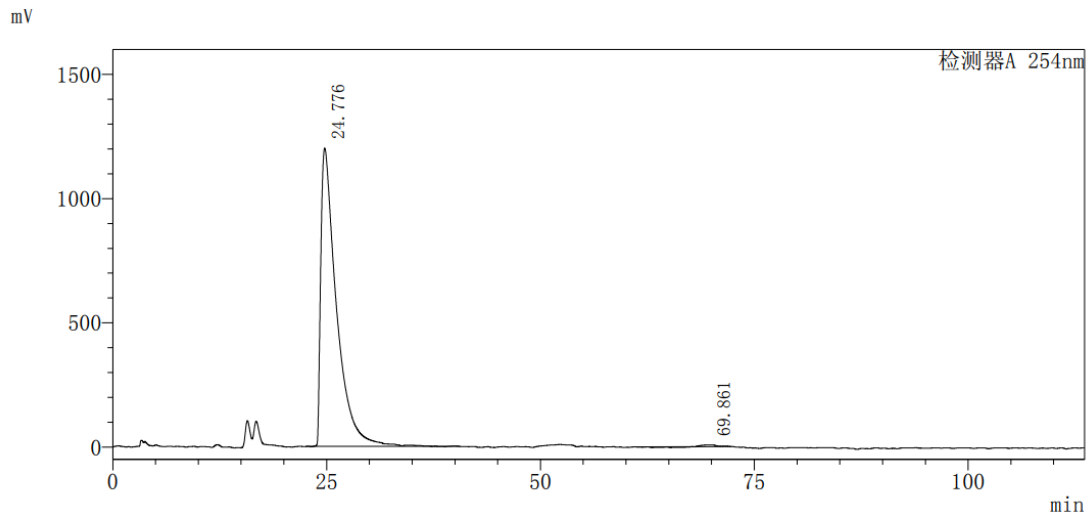
PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %	Ee %
1	16.570	122018386	97.612	95
2	58.675	2985415	2.388	
Total		125003801	100.0	



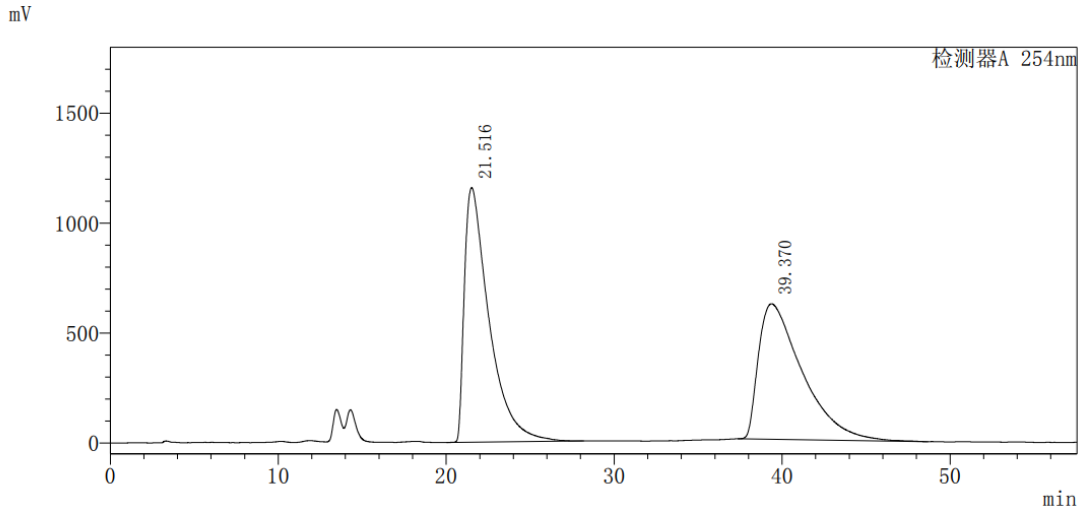
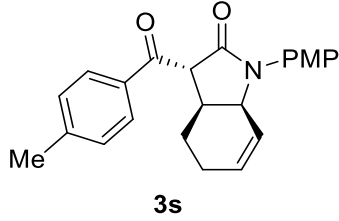
PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %
1	24.314	130499501	50.372
2	63.697	128570211	49.628
Total		259069713	100.0



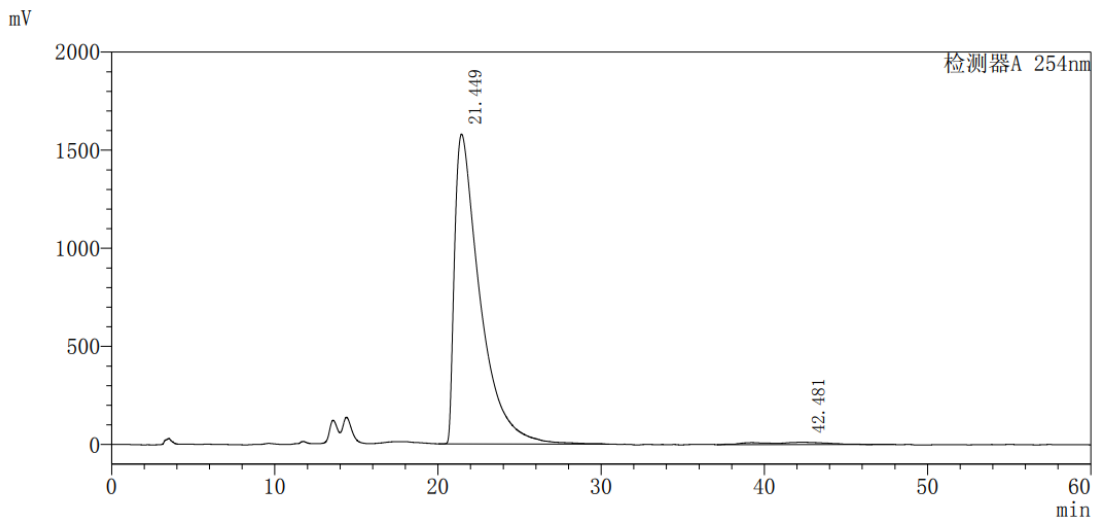
PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %	Ee %
1	24.776	153469977	99.838	99
2	69.861	249678	0.162	
Total		153719656	100.0	



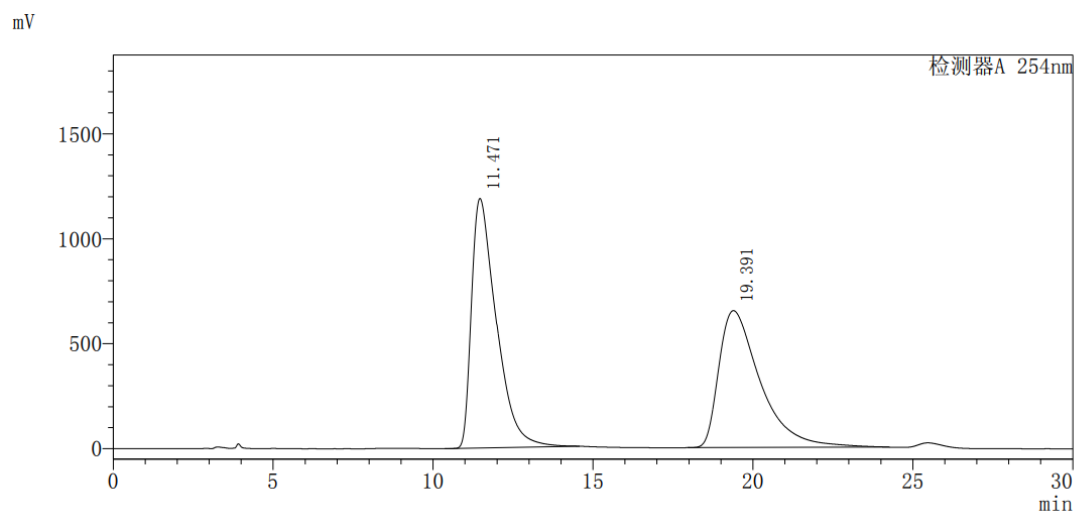
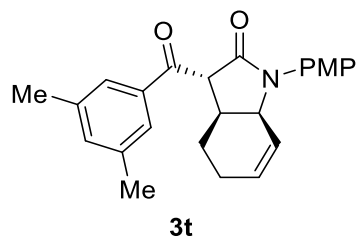
PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %
1	21.516	118505471	51.381
2	39.370	112134000	48.619
Total		230639470	100.0



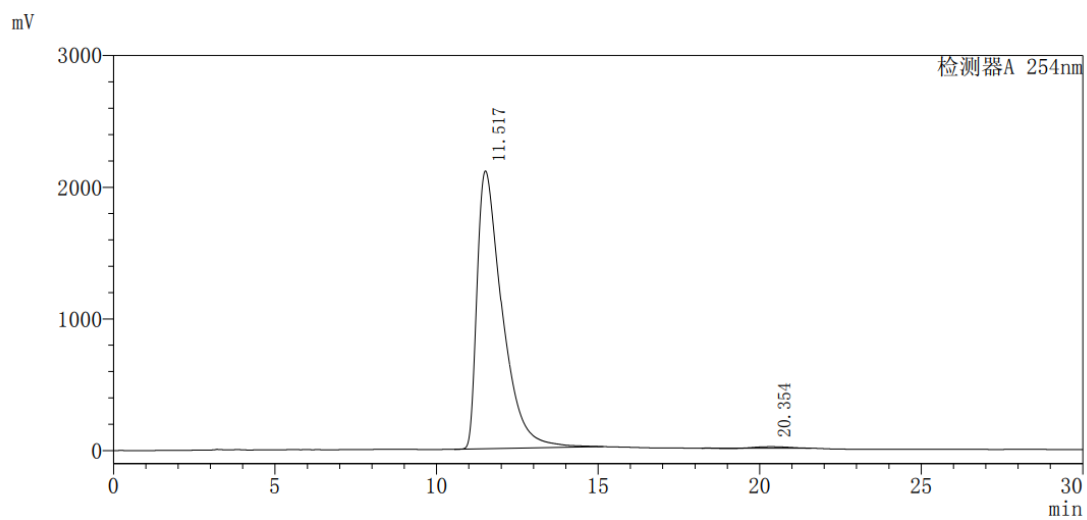
PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %	Ee %
1	21.449	171319008	98.041	96
2	42.481	3423404	1.959	
Total		174742412	100.0	



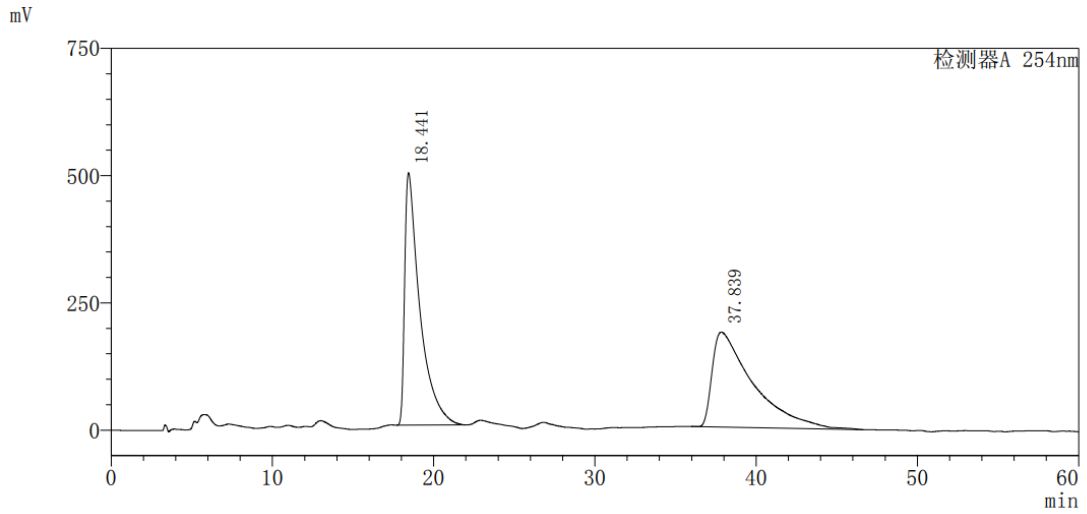
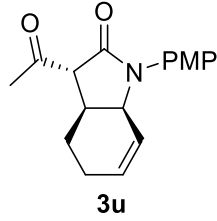
PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %
1	11.471	64143345	52.086
2	19.391	59005568	47.914
Total		123148913	100.0



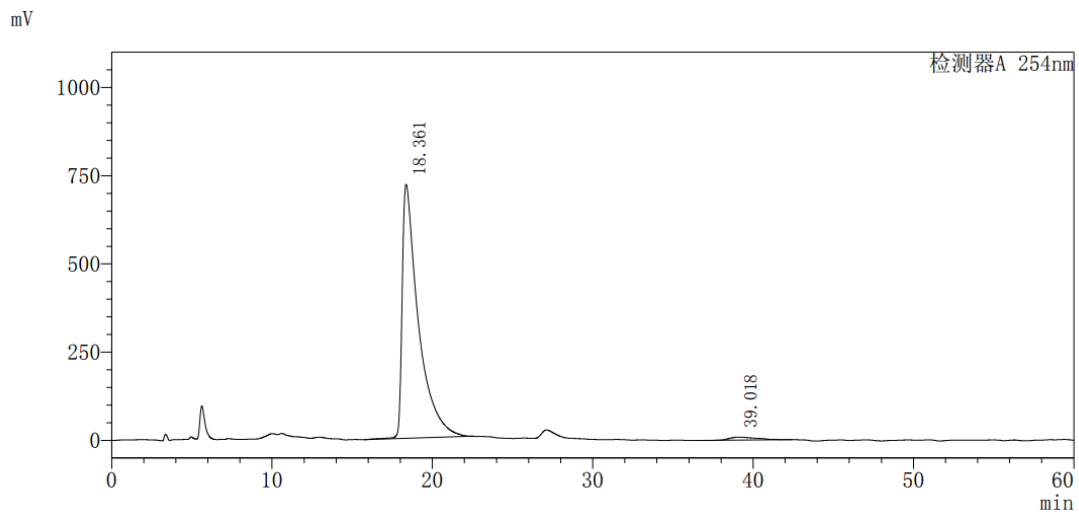
PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %	Ee %
1	11.517	114098724	99.378	99
2	20.354	713900	0.622	
Total		114812625	100.0	



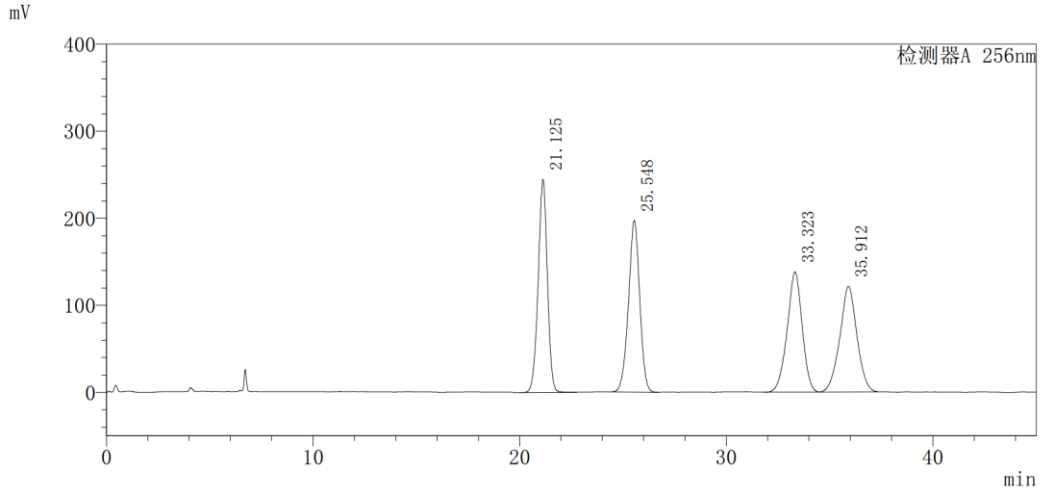
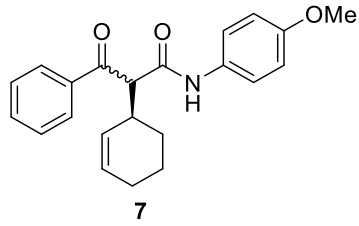
PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %
1	18.441	32364515	49.599
2	37.839	32887450	50.401
Total		65251965	100.0



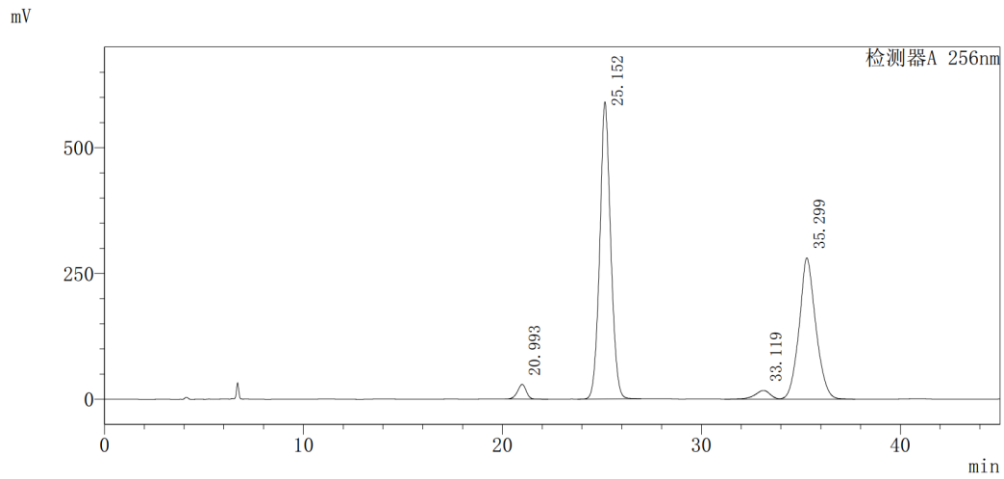
PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %	Ee %
1	18.361	50608044	97.915	96
2	39.018	1077534	2.085	
Total		51685578	100.0	



PDA Ch1 254nm

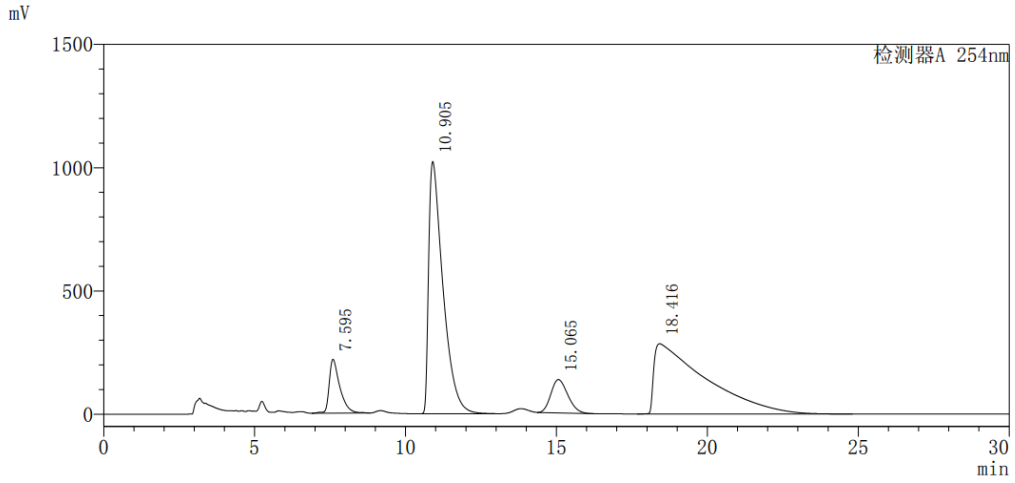
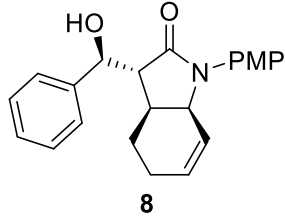
Peak #	Ret. Time	Area	Conc %
1	21.125	7537064	25.978
2	25.548	7522768	25.929
3	33.323	6973610	24.036
4	35.912	6979677	24.057
Total		29013120	100.0



PDA Ch1 254nm

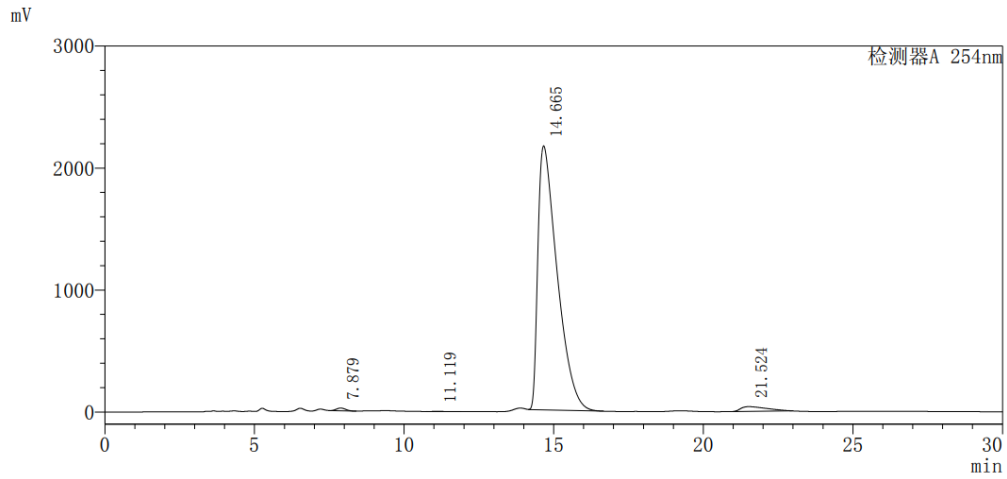
Peak #	Ret. Time	Area	Conc %	Ee %
1	20.993	896641	2.200	96
2	25.152	22575071	55.379	
3	33.119	927064	2.274	89
4	35.299	16365883	40.147	
Total		40764659	100.0	





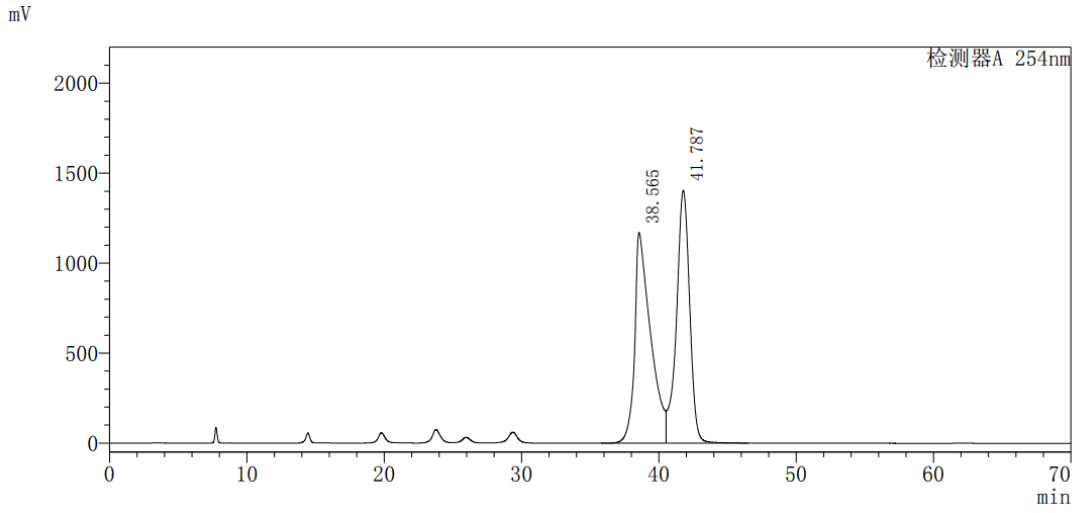
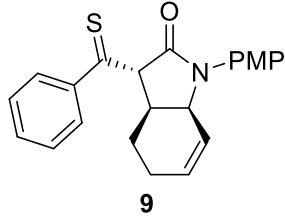
PDA Ch1 210nm

Peak #	Ret. Time	Area	Conc %
1	7.595	5372025	6.833
2	10.905	33786221	42.973
3	15.065	5290693	6.729
4	18.416	34173277	43.465
Total		78622216	100.0



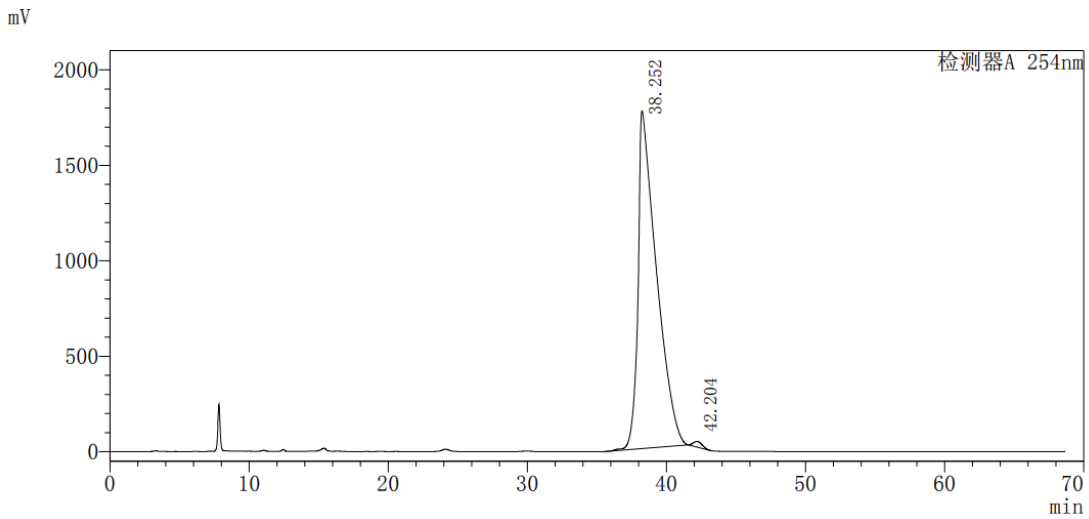
PDA Ch1 210nm

Peak #	Ret. Time	Area	Conc %	Ee %
1	7.879	480282	0.482	99
2	11.119	39354	0.040	
3	14.665	96789268	97.153	
4	21.524	2316615	2.325	
Total		99625520	100.0	



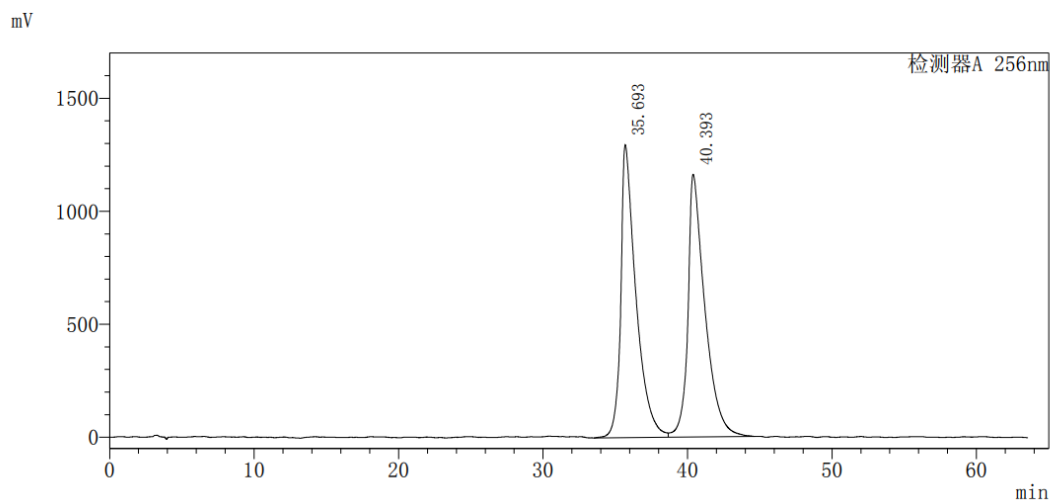
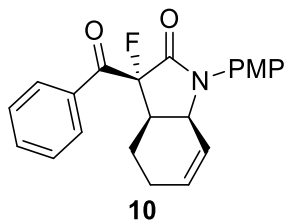
PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %
1	38.565	94697259	50.093
2	41.787	94346451	49.907
Total		189043710	100.0



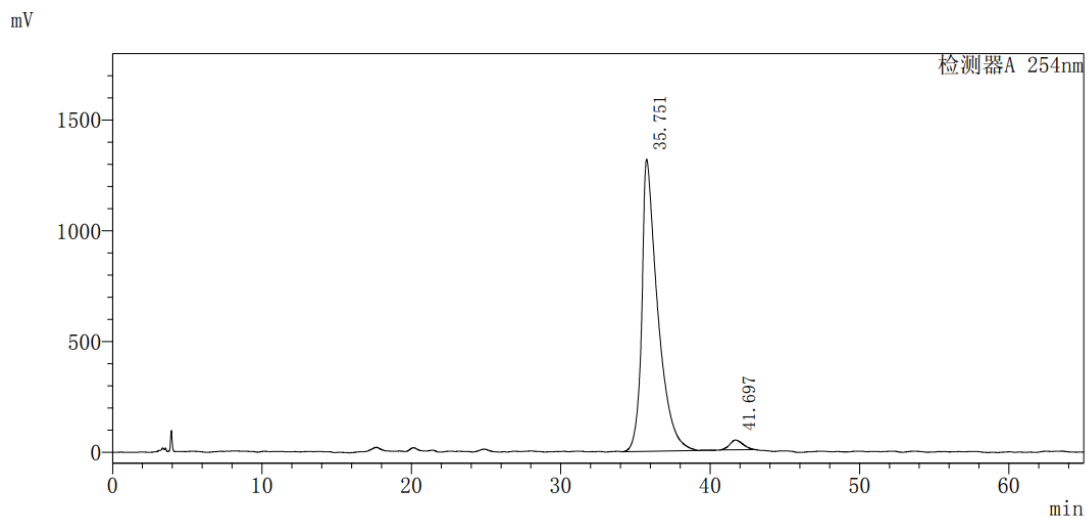
PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %	Ee %
1	38.252	163214984	99.210	98
2	42.204	1300206	0.790	
Total		164515191	100.0	



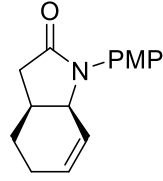
PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %
1	35.693	95071838	49.948
2	40.393	95271497	50.052
Total		190343335	100.0

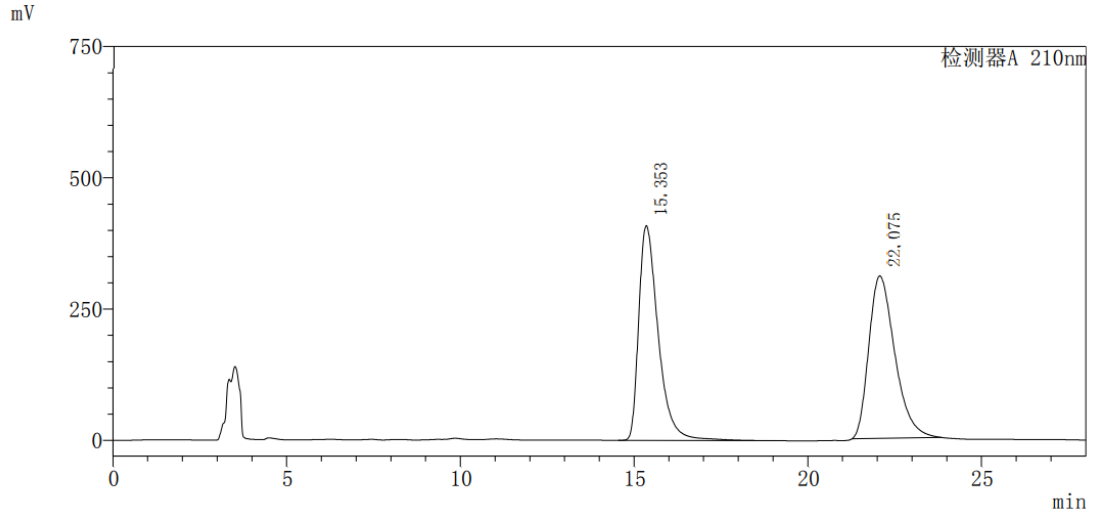


PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %	Ee %
1	35.751	97921162	97.278	95
2	41.697	2740286	2.722	
Total		100661448	100.0	

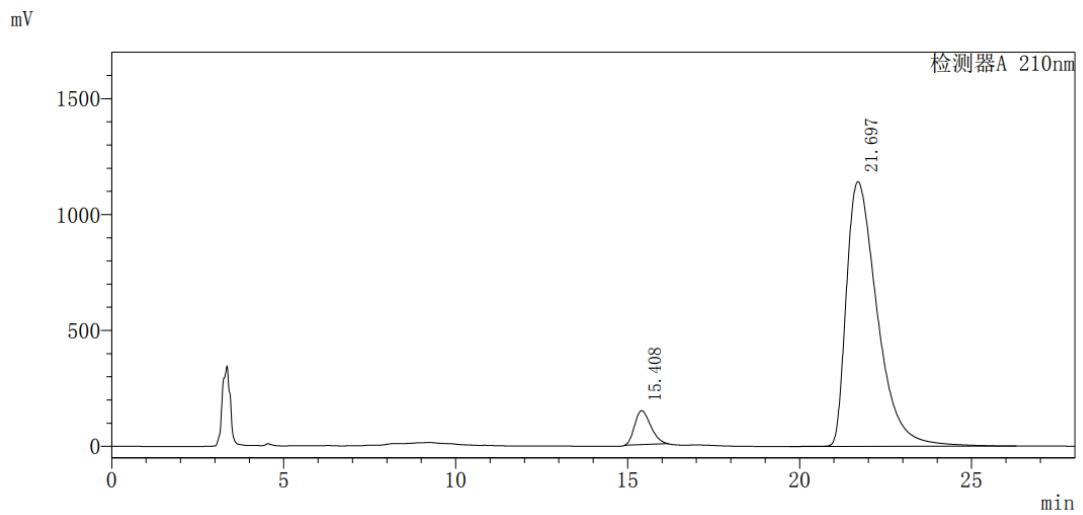


11



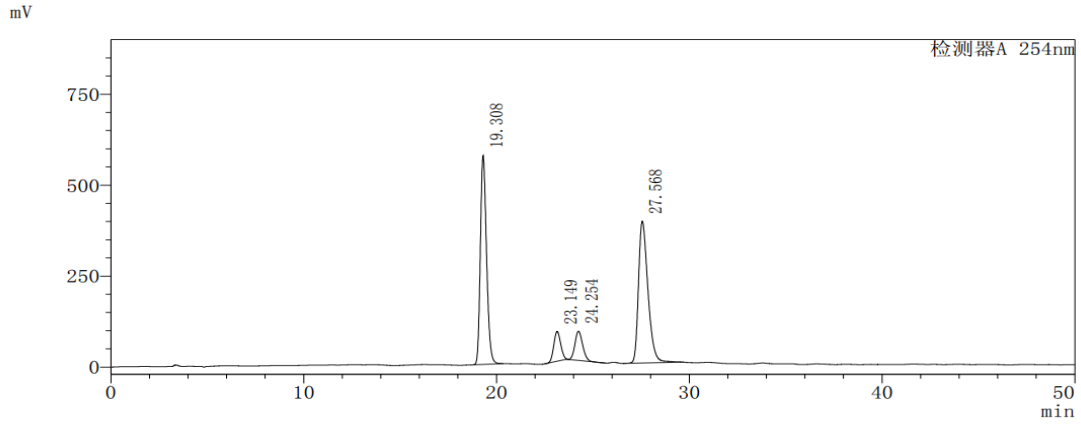
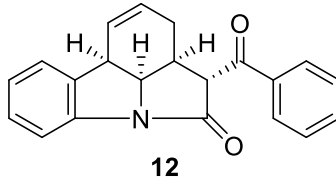
PDA Ch1 210nm

Peak #	Ret. Time	Area	Conc %
1	15.353	15975230	49.821
2	22.075	16089835	50.179
Total		32065065	100.0



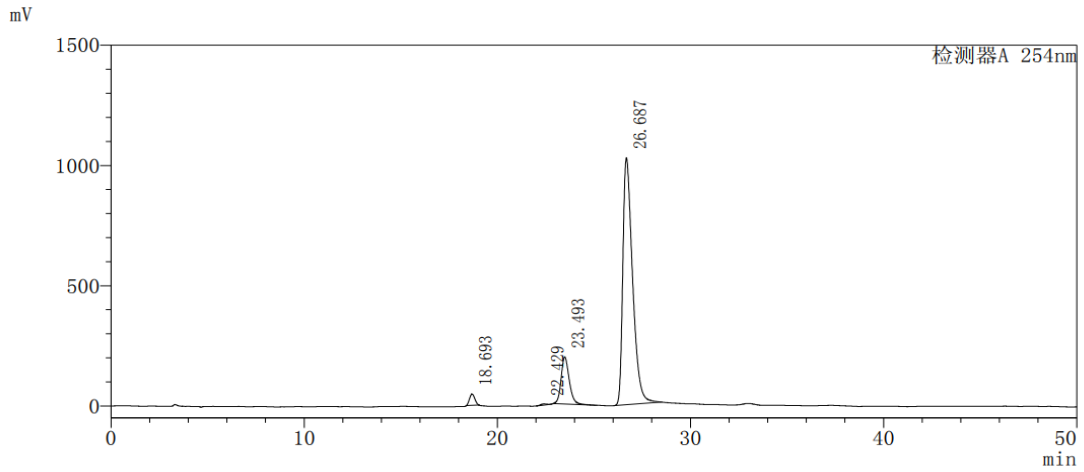
PDA Ch1 210nm

Peak #	Ret. Time	Area	Conc %	Ee %
1	15.408	4759066	6.250	88
2	21.697	71383838	93.750	
Total		76142904	100.0	



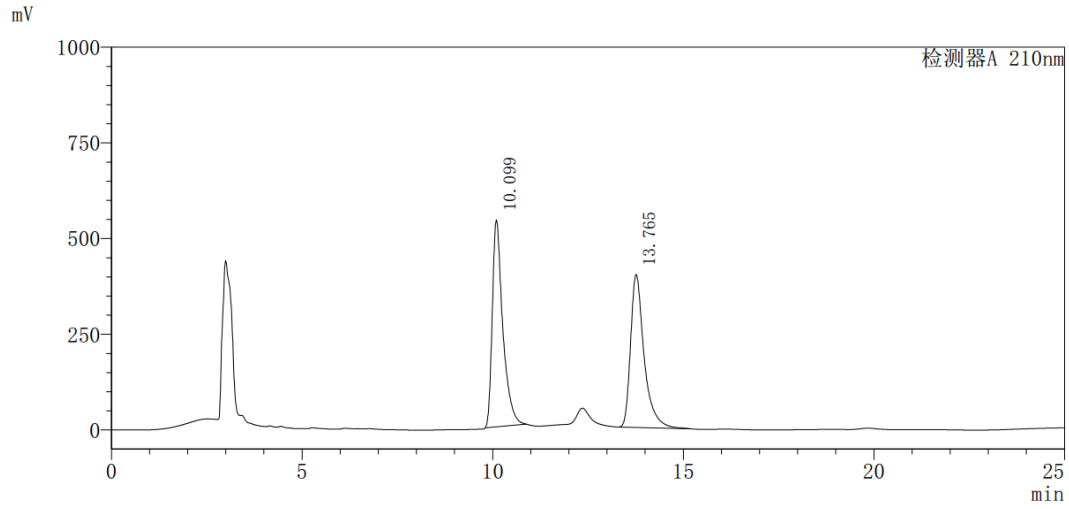
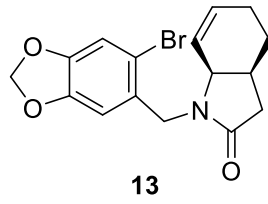
PDA Ch1 254nm

Peak #	Ret. Time	Area	Conc %
1	19.308	12804098	42.177
2	23.149	2010659	6.623
3	24.254	2221759	7.319
4	27.568	13321597	43.882
Total		30358113	100.0



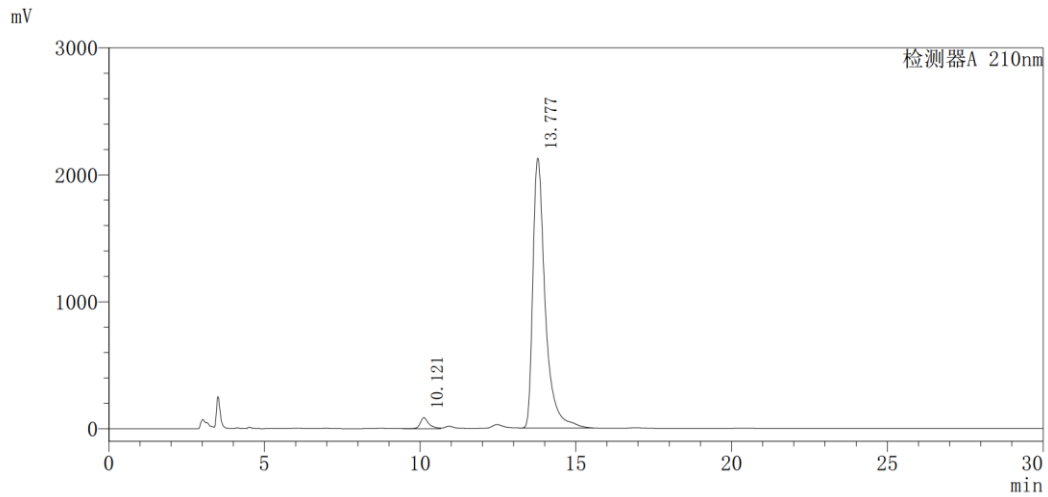
PDA Ch1 254nm

Peak#	Ret. Time	Area	Conc %	Ee %
1	18.693	887068	2.082	95
2	22.429	97797	0.230	
3	23.493	5721941	13.429	
4	26.687	35902226	84.260	
Total		42609032	100.0	



PDA Ch1 210nm

Peak #	Ret. Time	Area	Conc %
1	10.099	10338096	51.154
2	13.765	9865300	48.846
Total		20203396	100.0

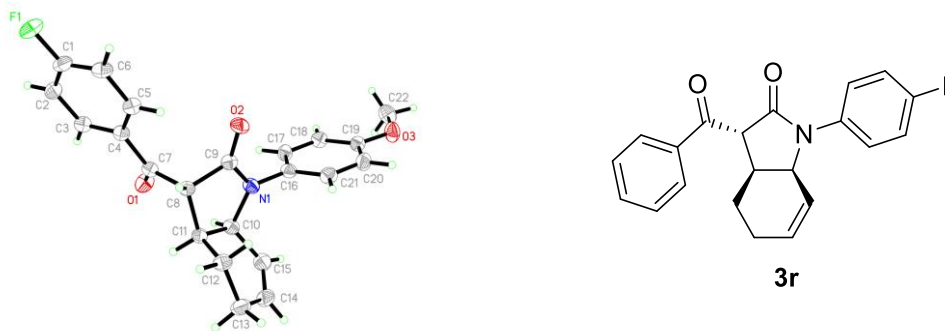


PDA Ch1 210nm

Peak #	Ret. Time	Area	Conc %	Ee %
1	10.121	1732402	2.864	94
2	13.777	58758609	97.136	
Total		60491011	100.0	

## 8. X-Ray Crystal Structure Analysis

X-Ray crystallography data for **3r** (CDCC: 2224422): A colorless crystal suitable for X-ray crystallography was obtained from a *n*-hexane/dichloromethane solution at room temperature under air.



**Figure 1** The ORTEP drawing (50% probability for thermal ellipsoids) of **3r**

Bond precision:	C-C = 0.0029 Å	Wavelength=1.54178	
Cell:	a=5.7149 (9)	b=15.8503 (10)	c=19.6731 (19)
	alpha=90	beta=90	gamma=90
Temperature:	173 K		
	Calculated	Reported	
Volume	1782.1 (3)	1782.0 (3)	
Space group	P 21 21 21	P 21 21 21	
Hall group	P 2ac 2ab	P 2ac 2ab	
Moiety formula	C22 H20 F N O3	C22 H20 F N O3	
Sum formula	C22 H20 F N O3	C22 H20 F N O3	
Mr	365.39	365.39	
Dx, g cm <sup>-3</sup>	1.362	1.362	
Z	4	4	
Mu (mm <sup>-1</sup> )	0.802	0.802	
F000	768.0	768.0	
F000'	770.49		
h, k, lmax	6, 19, 23	6, 19, 23	
Nref	3255 [ 1907]	3237	
Tmin, Tmax	0.838, 0.866	0.574, 0.753	
Tmin'	0.838		
Correction method= # Reported T Limits: Tmin=0.574 Tmax=0.753			
AbsCorr = MULTI-SCAN			
Data completeness=	1.70/0.99	Theta(max)= 68.203	
R(reflections)=	0.0339 ( 3130)	wR2(reflections)=	
S =	1.059	0.0883 ( 3237)	
	Npar= 245		





## 9. Calculation Experiment

### 1. Computational Details

Density functional theory (DFT) calculations were performed using Gaussian 09<sup>1</sup> to investigate the mechanism of the reaction. Geometry optimizations and single-point energies were carried out at B3LYP-D3/6-31G(d,p) (SDD for Ru and Pd)<sup>2-9</sup> level of theory, and SMD<sup>10</sup> continuum model (THF) were used to introduce the solvent effects.

### Coordinates and Geometries of the optimized structures

**Table S1.** Energy of species involved in this work

B3LYP-D3/6-31G(d,p) (SDD for Ru and Pd), THF, 298.15 K, G09 D.01		
Species	Single Point Energy	Gibbs Free Energy
II	-1246.085541	-1245.725345
II'	-1246.08539	-1245.72637
(S)-3a	-1016.979238	-1016.67436
(R)-3a	-1016.985007	-1016.681401
IM-I'	-4208.593344	-4207.469439
IM-I	-4208.594313	-4207.468941
TS-I'	-4208.571286	-4207.448041
TS-I	-4208.581086	-4207.458213
IM-II'	-4208.621655	-4207.495517
IM-II	-4208.627615	-4207.502532
PdL+	-3191.602841	-3190.806561

### II

0 1

C	-2.13245000	4.85549400	-0.71057300
C	-2.45153800	3.55155900	-1.09498800
C	-1.62037200	2.49162500	-0.73497200
C	-0.46423400	2.72797300	0.02880400
C	-0.16032400	4.04419000	0.42311600
C	-0.98331900	5.10059400	0.04917200
H	-2.77757400	5.67989900	-1.00024900
H	-3.34783300	3.35750900	-1.67607900
H	-1.89590200	1.48528600	-1.02705800
H	0.72995100	4.21817300	1.01770800
H	-0.73405900	6.11417800	0.34851100
C	0.44933100	1.64069200	0.47686300

C	0.34284400	0.24154900	-0.12811700
H	-0.32784500	0.23797600	-0.98419200
O	1.28875600	1.85467000	1.35387500
C	1.67700300	-0.28919500	-0.68792500
O	1.70306700	-0.83534900	-1.78825000
N	2.74071000	-0.17577100	0.15894800
C	4.06482900	-0.62328100	-0.01303900
C	4.98961500	-0.26884600	0.98476600
C	4.48864900	-1.40455600	-1.10049500
C	6.31468000	-0.68652000	0.89733500
H	4.66168400	0.33495900	1.82748900
C	5.82106500	-1.81503100	-1.17267100
H	3.78136200	-1.67544900	-1.87094700
C	6.74085300	-1.46364600	-0.18334500
H	7.01501300	-0.40261300	1.67766400
H	6.13832500	-2.41855100	-2.01866700
H	7.77435700	-1.78943900	-0.25203500
H	2.56426000	0.40216000	0.97829300
C	-1.61357700	-2.33780600	-0.46421500
C	-2.87004500	-2.04452800	0.35115400
C	-2.71761800	-0.81661300	1.21157100
C	-1.53945300	-0.24946900	1.48568100
C	-0.21728400	-0.75604700	0.95588100
C	-0.36549800	-2.19097900	0.41415700
H	-3.10679000	-2.91058000	0.97934300
H	-1.57333900	-1.63505300	-1.30323600
H	-1.67627100	-3.34364700	-0.89001900
H	-0.44284800	-2.86967800	1.27251500
H	0.52263700	-2.49075600	-0.14742500
O	-3.94843500	-1.83418200	-0.60576200
H	-1.51222700	0.63688000	2.11625900
H	-3.63272400	-0.40080900	1.62785200
C	-5.24762500	-2.09297600	-0.31895700
O	-6.08080900	-1.80623100	-1.15288600
C	-5.59045400	-2.75023600	0.99909500
H	-5.20674200	-2.18512600	1.85292000
H	-5.16420000	-3.75804900	1.04732400
H	-6.67559600	-2.82038100	1.06920300
H	0.51028100	-0.75144400	1.77657200

## II'

0 1

C	-1.59827300	5.28055500	0.50473800
C	-1.83630900	4.14277800	1.27786800

C	-1.17242200	2.95005200	0.99291500
C	-0.26519300	2.88284000	-0.07864500
C	-0.03787800	4.03561900	-0.85438800
C	-0.69541200	5.22497700	-0.56291300
H	-2.11435800	6.20887400	0.73199500
H	-2.53846400	4.18205900	2.10494300
H	-1.37612500	2.07985700	1.60526400
H	0.66078400	3.97685100	-1.68173300
H	-0.50823100	6.10920000	-1.16473000
C	0.46006100	1.63952000	-0.45986200
C	0.33456100	0.36965100	0.38187800
H	-0.21989900	0.54971800	1.30029400
O	1.15272200	1.60994400	-1.47932800
C	1.69576100	-0.17774400	0.86016100
O	1.83563700	-0.53906500	2.02614500
N	2.64240600	-0.29100800	-0.11585400
C	3.95027400	-0.80632400	-0.03016900
C	4.74845800	-0.70851700	-1.18335900
C	4.47514500	-1.41279500	1.12278500
C	6.04848300	-1.20626000	-1.18438900
H	4.34225000	-0.24006000	-2.07660400
C	5.78087300	-1.90645200	1.10470900
H	3.86540700	-1.48691500	2.01151600
C	6.57514800	-1.80949900	-0.03891400
H	6.65048900	-1.12137500	-2.08458900
H	6.17724500	-2.37278000	2.00247300
H	7.58937500	-2.19717400	-0.03910300
H	2.38774200	0.14380300	-1.00005400
C	-2.63911200	-1.32421500	-1.51433600
C	-2.93008400	-2.38872900	-0.45641100
C	-1.71189200	-2.72313200	0.35976800
C	-0.59681800	-1.98668400	0.34809200
C	-0.43324100	-0.71440500	-0.45016100
C	-1.79760700	-0.18818500	-0.92885000
H	-3.31191400	-3.30041100	-0.92406500
H	-2.10048900	-1.80198700	-2.34233500
H	-3.58123900	-0.94091100	-1.91865000
H	-2.33311300	0.25319600	-0.07997700
H	-1.66099600	0.60205600	-1.67317000
O	-3.92448500	-1.88525700	0.49491900
H	0.25000300	-2.30675700	0.95041300
H	-1.77240600	-3.61417400	0.98005200
C	-5.25858500	-2.01934700	0.29750400
O	-6.00670900	-1.48010700	1.08626500

C	-5.74870600	-2.85384400	-0.86443900
H	-5.35380500	-2.49766400	-1.82000800
H	-5.44166900	-3.89817800	-0.74396000
H	-6.83709600	-2.80308400	-0.88134100
H	0.18895700	-0.93037600	-1.33116500

**(S)-3a**

0 1

C	5.72971300	-0.70609700	-0.01721700
C	4.98868400	-0.40200600	-1.16056300
C	3.59438600	-0.39031800	-1.10893000
C	2.92632600	-0.68198100	0.09144200
C	3.68381700	-0.98617000	1.23663600
C	5.07341400	-0.99880400	1.18335800
H	6.81504600	-0.71589500	-0.05979800
H	5.49506300	-0.17568700	-2.09406600
H	3.03810500	-0.15229700	-2.00826800
H	3.15957600	-1.20810300	2.15993200
H	5.64777500	-1.23527100	2.07422400
C	1.43439700	-0.67503700	0.22404700
C	0.57867100	-0.30841800	-0.99215300
H	1.04810300	-0.70446100	-1.89384400
O	0.90035400	-0.95379400	1.28975700
C	-0.79346200	-0.96980500	-0.84511400
O	-1.01554900	-2.16381900	-0.98486800
N	-1.71753200	0.00399300	-0.54569700
C	-3.07527700	-0.25586100	-0.22154000
C	-3.42677000	-1.39975600	0.51222000
C	-4.07586700	0.64627700	-0.61129600
C	-4.76222100	-1.63758700	0.83244700
H	-2.65503800	-2.09251800	0.82087900
C	-5.40807000	0.40346900	-0.27553900
H	-3.81952900	1.53266200	-1.18120800
C	-5.75986100	-0.74002800	0.44355800
H	-5.02083900	-2.52694700	1.40013800
H	-6.17176900	1.11141600	-0.58456300
H	-6.79794900	-0.92836900	0.70074000
C	1.38350700	2.43227800	0.79772600
C	0.07182600	2.30867700	1.52159100
C	-1.04428400	1.83245200	0.96589000
C	-1.13287600	1.36127200	-0.46578000
C	0.23606800	1.20121900	-1.16836400
C	1.24088700	2.27395800	-0.72470100
H	2.08375500	1.69289000	1.20760200

H	1.83842200	3.40630600	1.01815100
H	0.88638600	3.22626700	-1.13734600
H	2.21777500	2.08300800	-1.17947000
H	-1.75805400	2.05317100	-1.04026900
H	-1.96180600	1.75725700	1.54542000
H	0.06331100	1.33196400	-2.24133200
H	0.05791000	2.61116200	2.56754200

**(R)-3a**

0 1

C	5.20092200	-1.87964600	0.82330700
C	3.97246200	-1.80754700	1.48367500
C	2.91640500	-1.08921000	0.92359400
C	3.08024000	-0.44107300	-0.31123000
C	4.31741900	-0.52885300	-0.97323800
C	5.37189200	-1.23894300	-0.40862200
H	6.02296300	-2.43552700	1.26524000
H	3.83514500	-2.31351300	2.43467400
H	1.96082700	-1.06563900	1.43241500
H	4.43149600	-0.02906500	-1.92930400
H	6.32578700	-1.29586300	-0.92467900
C	1.99100900	0.34499300	-0.96236300
C	0.71834400	0.65974200	-0.17121700
H	0.98239800	0.83223600	0.87888200
O	2.11538700	0.76141200	-2.10759300
C	-0.28211200	-0.50897900	-0.16566100
O	0.00150900	-1.69497900	-0.05625100
N	-1.54383800	0.02155400	-0.28841500
C	-2.74682200	-0.73142100	-0.19868000
C	-2.84280100	-1.84089800	0.65566500
C	-3.86364300	-0.34661600	-0.95538300
C	-4.03799000	-2.55416400	0.73710600
H	-1.98452500	-2.14293200	1.24077400
C	-5.05732500	-1.06119500	-0.85695500
H	-3.80165500	0.50274000	-1.62687800
C	-5.15129400	-2.16962000	-0.01347700
H	-4.09874300	-3.41180400	1.40104200
H	-5.91331500	-0.75060900	-1.44905200
H	-6.08073700	-2.72637700	0.05900300
C	0.17068800	3.44050300	1.22774700
C	-1.15061500	2.91304400	1.72183700
C	-1.91766000	2.06466400	1.03020500
C	-1.53869200	1.50598400	-0.32253200
C	-0.09143800	1.83300600	-0.73814900

C	0.34715400	3.22688200	-0.28268300
H	0.98235800	2.94967000	1.78524000
H	0.25936600	4.50704300	1.46845500
H	-0.26053400	3.96648300	-0.81849800
H	1.38770100	3.39855500	-0.57828900
H	-2.24434700	1.85182600	-1.08305200
H	-2.86466500	1.71829500	1.43914200
H	-0.02360700	1.77165800	-1.82770900
H	-1.48108000	3.24655900	2.70456900

**IM-I'**

1 1

C	5.36743400	3.76339900	-2.70936700
C	5.37777200	4.01149800	-1.18417300
C	5.67067900	5.06342500	-3.46396900
C	4.20788100	4.86067500	-0.64554200
H	6.33834400	4.45361100	-0.90862800
N	5.21652500	2.73647000	-0.43454500
H	6.61009700	5.51448000	-3.12441100
H	5.75829400	4.86999300	-4.53787900
H	4.87358300	5.80418600	-3.32978400
O	3.35290000	3.89013000	0.03431300
H	3.60591300	5.34770200	-1.41294500
H	4.52321700	5.59791700	0.09680400
C	4.05809100	2.75326800	0.14375000
C	3.39651100	1.68695900	0.88776100
C	3.82820000	0.31194300	1.07756200
C	2.12193800	1.84319000	1.53321100
C	2.80902700	-0.34675400	1.84574900
P	5.43001900	-0.38055000	0.56965800
C	1.76976600	0.59420500	2.11995100
H	1.53981400	2.75282400	1.55717500
H	2.83189600	-1.37804900	2.16918200
C	5.05563300	-1.89012300	-0.39124100
C	6.18229100	-0.95019800	2.13928300
H	0.86192800	0.38900100	2.66966700
C	5.22105500	-1.86379500	-1.78432100
C	4.56998400	-3.05094900	0.22810100
C	5.90636600	-0.28370900	3.34353400
C	7.12970700	-1.98716800	2.12334000
C	4.88453900	-2.98061800	-2.55170800
H	5.60907900	-0.97034700	-2.26569200
C	4.24021600	-4.16668300	-0.54212700
H	4.44953200	-3.08673000	1.30528200

C	6.56288200	-0.65882400	4.51731500
H	5.18039300	0.52312700	3.37167600
C	7.78012500	-2.35834800	3.30061000
H	7.35234200	-2.51123400	1.19870800
C	4.39179800	-4.13212500	-1.93146600
H	5.01315600	-2.95319900	-3.62969100
H	3.86407700	-5.06207800	-0.05647400
C	7.49895700	-1.69565300	4.49862200
H	6.33953800	-0.14123300	5.44570200
H	8.50565400	-3.16641400	3.28132100
H	4.13505700	-5.00305500	-2.52735700
H	8.00707000	-1.98655200	5.41330900
H	6.18741400	3.06044600	-2.90181300
C	4.06624300	3.11160500	-3.19164600
H	3.87975800	2.16660000	-2.67387100
H	3.20220200	3.76640500	-3.03088100
H	4.11954700	2.90086200	-4.26478200
Pd	6.70033200	1.22082500	-0.49027800
C	8.48988800	2.37510500	-1.27387400
C	8.59178500	1.02333400	-1.61130400
H	8.48037300	0.72594100	-2.65313600
C	8.48094600	0.03601100	-0.59183300
H	8.41437800	-1.00953700	-0.87990900
H	8.91970400	0.21948200	0.38860900
Ru	1.97202900	0.31947200	-0.08939000
H	8.81973200	2.73287500	-0.29941900
H	8.39101000	3.12332500	-2.05393300
C	-2.83658500	2.62966900	1.37637800
C	-2.80638200	2.26518300	-0.12484000
C	-3.71943400	3.86268300	1.60202800
C	-2.07898000	3.27390500	-1.03775400
H	-3.83452200	2.11361200	-0.46652300
N	-2.02634300	1.01677500	-0.34723900
H	-4.71498100	3.72640200	1.16793000
H	-3.84289500	4.05752200	2.67243600
H	-3.27658500	4.76100100	1.15487700
O	-0.82836300	2.60090300	-1.39071600
H	-1.82093300	4.21970500	-0.56076600
H	-2.62099800	3.46795200	-1.96666600
C	-0.95322600	1.32091100	-0.99725200
C	0.17166100	0.45683900	-1.35088700
C	0.41112600	-0.93226600	-0.98960600
C	1.29409500	0.90961100	-2.12425800
C	1.67678500	-1.30226900	-1.55965700

P	-0.75600800	-2.02781700	-0.11095500
C	2.21187500	-0.17290800	-2.25045300
H	1.41081700	1.90389800	-2.53024300
H	2.14145800	-2.27545700	-1.48456700
C	0.17727300	-2.71782100	1.30670900
C	-0.98302300	-3.42610600	-1.27481500
H	3.15805500	-0.14317500	-2.77180000
C	-0.14243500	-2.27216600	2.59797000
C	1.21347000	-3.64683300	1.13135800
C	-0.96318800	-3.20905600	-2.66155900
C	-1.31501300	-4.69842200	-0.78153000
C	0.57891800	-2.73629000	3.70015700
H	-0.95236600	-1.56113800	2.73695600
C	1.92612300	-4.11486300	2.23571300
H	1.46355600	-4.00402600	0.13823300
C	-1.25456700	-4.25461500	-3.53979300
H	-0.72109400	-2.22846200	-3.06058100
C	-1.60308000	-5.74012800	-1.66430600
H	-1.34394900	-4.87943900	0.28871300
C	1.61370800	-3.65803500	3.51995200
H	0.32718000	-2.38514500	4.69656400
H	2.72610000	-4.83514600	2.09257500
C	-1.57316200	-5.52141500	-3.04418100
H	-1.23228000	-4.07687300	-4.61106600
H	-1.85295100	-6.72179500	-1.27243000
H	2.17006300	-4.02533400	4.37741400
H	-1.79911400	-6.33335400	-3.72905300
H	-3.31066600	1.77635900	1.87770100
C	-1.43473300	2.80317300	1.97285000
H	-0.83009300	1.90386000	1.82461300
H	-0.90466200	3.65159900	1.52366500
H	-1.49751300	2.99265100	3.04970900
Pd	-2.69860400	-0.88451800	0.36046300
C	-11.97524400	-0.97246500	-1.46202800
C	-11.11570300	0.00844900	-1.96513900
C	-9.76866300	0.01427400	-1.60368200
C	-9.26322200	-0.96242300	-0.73035300
C	-10.13604700	-1.94127200	-0.22952200
C	-11.48147100	-1.94884800	-0.59171000
H	-13.02421000	-0.97456200	-1.74550000
H	-11.49622300	0.77337400	-2.63616800
H	-9.12098900	0.79303300	-1.98941000
H	-9.73747900	-2.69146700	0.44567700
H	-12.14535900	-2.71319900	-0.19708000



C	-7.81842400	-1.02574200	-0.31777900
C	-6.81645700	-0.11962800	-1.01061800
H	-7.02418000	-0.13507100	-2.08815000
O	-7.46258900	-1.85489200	0.51711600
C	-6.91651300	1.36969600	-0.55317800
O	-6.18414800	2.18623600	-1.17016900
N	-7.71788400	1.53084900	0.49738900
C	-7.91090200	2.76751300	1.10334100
C	-8.63409900	2.75297700	2.32319000
C	-7.47972200	4.03646400	0.63164200
C	-8.90337500	3.91822500	3.03436800
H	-8.97839600	1.78901900	2.69025100
C	-7.75809500	5.20091500	1.35135200
H	-6.92630900	4.07863600	-0.29654500
C	-8.46495200	5.15974500	2.55616100
H	-9.45995700	3.86015700	3.96738900
H	-7.41287300	6.15680500	0.96140600
H	-8.67308600	6.07179400	3.10918400
C	-4.68032100	-3.07083900	-0.37403700
C	-4.00685500	-2.55746100	0.88679000
C	-4.50624300	-1.36225300	1.46986000
C	-4.87616000	-0.34209800	0.58967000
C	-5.33814900	-0.56442600	-0.83940400
C	-4.99257300	-1.97088400	-1.41022600
H	-5.61312400	-3.54463600	-0.04278600
H	-4.06702900	-3.84941000	-0.83799100
H	-4.11310900	-1.86234600	-2.05572600
H	-5.80708400	-2.31137600	-2.05832000
H	-5.11617400	0.62790100	1.01333100
H	-4.39212800	-1.15611100	2.53181400
H	-4.80899400	0.17613300	-1.44856300
H	-3.59189500	-3.31352400	1.55036000

## IM-I

11

C	5.23751400	3.69746600	-2.92462300
C	5.28266200	4.02772400	-1.41498100
C	5.49025400	4.96050300	-3.75675400
C	4.11184500	4.88353600	-0.89194700
H	6.24126100	4.50027400	-1.18763800
N	5.15990300	2.79127200	-0.59574500
H	6.42626700	5.45204900	-3.46799800
H	5.55540200	4.70975400	-4.82036600
H	4.67892400	5.68903800	-3.64256500

O	3.27584200	3.92797200	-0.16777400
H	3.49576600	5.33844700	-1.66738300
H	4.42988900	5.64807800	-0.17870700
C	4.00343800	2.81083900	-0.01323000
C	3.36462300	1.76511900	0.77710000
C	3.82590400	0.41073500	1.03196900
C	2.09385000	1.92830200	1.42564100
C	2.82657000	-0.22724900	1.84263900
P	5.43464000	-0.27750900	0.53598800
C	1.76954000	0.70532000	2.07865200
H	1.50034200	2.83086100	1.41482500
H	2.87453400	-1.24134500	2.21400300
C	5.08482200	-1.82924000	-0.36631900
C	6.20829800	-0.78521300	2.11664300
H	0.87100400	0.51085000	2.64725100
C	5.25734300	-1.85705000	-1.75845900
C	4.61778500	-2.97345600	0.29714600
C	5.93368100	-0.08937700	3.30427700
C	7.16946800	-1.80980700	2.12144600
C	4.94956600	-3.01159200	-2.48086700
H	5.62603600	-0.97579400	-2.27611400
C	4.31850600	-4.12756900	-0.42773800
H	4.48671100	-2.96669600	1.37358800
C	6.60425000	-0.42413100	4.48245100
H	5.19796100	0.70895000	3.31710900
C	7.83450600	-2.14002500	3.30256600
H	7.39028800	-2.35674800	1.20977300
C	4.47983100	-4.14765300	-1.81630700
H	5.08324500	-3.02494200	-3.55849200
H	3.95818700	-5.01041900	0.09184300
C	7.55359400	-1.44894200	4.48450000
H	6.38113000	0.11534600	5.39834500
H	8.57052900	-2.93877600	3.29899400
H	4.24658500	-5.04791300	-2.37725300
H	8.07234600	-1.70830200	5.40270600
H	6.06666400	3.00151300	-3.10370700
C	3.93908500	2.99217200	-3.33557200
H	3.79555700	2.06642200	-2.77102400
H	3.06204300	3.63004100	-3.17705400
H	3.96598800	2.73480200	-4.39946600
Pd	6.66797500	1.30079200	-0.60206800
C	8.42050600	2.45446000	-1.45880800
C	8.54743300	1.09136900	-1.73920900
H	8.42759900	0.74784400	-2.76583800

C	8.46967500	0.14557500	-0.67806300
H	8.41988300	-0.91214000	-0.92187900
H	8.91671400	0.37822600	0.28814600
Ru	1.96025000	0.30895400	-0.11137900
H	8.75738200	2.86224400	-0.50677700
H	8.29103700	3.16481000	-2.26922100
C	-2.86498500	2.72619500	1.12592400
C	-2.87232000	2.13832800	-0.30295500
C	-3.87086800	3.88025900	1.21860700
C	-2.22765700	3.02892000	-1.38319400
H	-3.90396700	1.89310300	-0.56836400
N	-2.04141800	0.90391200	-0.37573500
H	-4.86614000	3.55273200	0.90055200
H	-3.94198300	4.24767900	2.24783400
H	-3.57080600	4.72672000	0.58806900
O	-0.94296000	2.38172600	-1.65607600
H	-2.02098800	4.05209800	-1.06921100
H	-2.79430300	3.03724200	-2.31783500
C	-0.99929500	1.16192600	-1.09330100
C	0.15010800	0.30280900	-1.37148200
C	0.42743200	-1.04434700	-0.89684400
C	1.25435100	0.71642100	-2.18971600
C	1.69966000	-1.42756200	-1.44447700
P	-0.70866400	-2.08828900	0.07877100
C	2.20150000	-0.34570900	-2.23110700
H	1.33997900	1.67305700	-2.68447600
H	2.18904500	-2.37912500	-1.29182800
C	0.27933000	-2.73070500	1.48086800
C	-1.00706800	-3.52771400	-1.01648600
H	3.14296200	-0.33663100	-2.76087400
C	0.02543900	-2.22442000	2.76474800
C	1.29727600	-3.67870300	1.30002800
C	-1.02204800	-3.37042300	-2.41120600
C	-1.35314900	-4.76920600	-0.45871500
C	0.79391400	-2.64601700	3.85177900
H	-0.77070200	-1.49963100	2.91001200
C	2.05838100	-4.10297100	2.38986000
H	1.49434100	-4.08577800	0.31429400
C	-1.36341800	-4.44521700	-3.23442500
H	-0.76923100	-2.41405400	-2.85921600
C	-1.68993100	-5.84061400	-1.28699100
H	-1.35543300	-4.90339100	0.61866900
C	1.81220000	-3.58478200	3.66489300
H	0.59264900	-2.24748600	4.84179300

H	2.84495500	-4.83699700	2.24275200
C	-1.69600000	-5.68151100	-2.67540400
H	-1.36840200	-4.31398000	-4.31252100
H	-1.94980000	-6.79851600	-0.84595200
H	2.40636800	-3.91821900	4.51073100
H	-1.96030200	-6.51631200	-3.31779900
H	-3.21775200	1.92136000	1.78247900
C	-1.46246800	3.12324200	1.60026200
H	-0.77814800	2.27018700	1.56149500
H	-1.03756800	3.93113900	0.99308700
H	-1.49663200	3.47769100	2.63596900
Pd	-2.62456700	-0.91200900	0.58621100
C	-11.79909300	-0.85566100	-2.17440000
C	-11.26810900	-0.58403200	-0.91123800
C	-9.88782800	-0.47109800	-0.73503600
C	-9.02412900	-0.62219600	-1.83335100
C	-9.56860800	-0.88535800	-3.10235700
C	-10.94483000	-1.00626000	-3.27246900
H	-12.87401600	-0.94669900	-2.30515700
H	-11.93000200	-0.45507800	-0.05947900
H	-9.48754400	-0.22712700	0.24439200
H	-8.89158700	-0.99310900	-3.94351100
H	-11.35432200	-1.21531400	-4.25690700
C	-7.53136500	-0.51168300	-1.71804100
C	-6.90347100	-0.40029400	-0.33328200
H	-7.41635400	-1.06829800	0.36307300
O	-6.83662300	-0.50650000	-2.73003900
C	-7.07110900	1.07711200	0.17214600
O	-6.40921000	1.94753600	-0.45164300
N	-7.84615800	1.17265000	1.24882900
C	-8.09800700	2.39589000	1.86608600
C	-8.72194700	2.33219200	3.13765700
C	-7.82669200	3.69157000	1.35267200
C	-9.03928800	3.47748400	3.86195900
H	-8.94845600	1.34652900	3.53769400
C	-8.15301400	4.83532000	2.08453200
H	-7.35927800	3.77450800	0.38127500
C	-8.75530800	4.74668900	3.34269900
H	-9.51454300	3.38153000	4.83594300
H	-7.93168100	5.81308000	1.66053800
H	-9.00117400	5.64349400	3.90504900
C	-4.63371500	-3.15875600	0.26881600
C	-3.86860200	-2.51629700	1.41260400
C	-4.32452700	-1.26040800	1.89806300

C	-4.77024800	-0.34171200	0.93997200
C	-5.39062300	-0.72683400	-0.39073100
C	-5.03749600	-2.17190600	-0.84767900
H	-5.52617900	-3.62266100	0.71449000
H	-4.04448300	-3.97274200	-0.16405400
H	-4.19942900	-2.10399800	-1.55012100
H	-5.86882700	-2.59468300	-1.41726400
H	-4.95819100	0.67492400	1.26462300
H	-4.11359800	-0.93525200	2.91460000
H	-5.00454300	-0.03652100	-1.14473600
H	-3.39484900	-3.19636600	2.11768400

**TS-I'**

1 1

C	5.97299300	3.10216800	-2.72787300
C	5.89326000	3.46476500	-1.22759600
C	6.46310400	4.30599000	-3.54207300
C	4.79505300	4.48163400	-0.85357700
H	6.87452900	3.81619800	-0.89942600
N	5.52030700	2.27945500	-0.41011000
H	7.42272100	4.68040200	-3.16726600
H	6.59734500	4.02948500	-4.59280800
H	5.74464900	5.13321800	-3.51051100
O	3.77866700	3.67290600	-0.18440600
H	4.31808100	4.97226500	-1.70257500
H	5.13845800	5.23398200	-0.13936900
C	4.32949000	2.47317900	0.06039800
C	3.48840200	1.54712100	0.80793200
C	3.71684200	0.13684600	1.08045400
C	2.20908200	1.90141600	1.35786600
C	2.57100300	-0.34166900	1.80428100
P	5.24324900	-0.78478500	0.72840900
C	1.65536800	0.74189100	1.96971500
H	1.75439100	2.87980000	1.30574300
H	2.43092100	-1.35062900	2.16518700
C	4.73538000	-2.26834100	-0.21225700
C	5.77231300	-1.40011400	2.37205500
H	0.69794000	0.68665100	2.46795800
C	5.06094800	-2.35326800	-1.57417900
C	3.99436500	-3.29606200	0.39065400
C	5.47519800	-0.67680700	3.53769900
C	6.56550000	-2.55607100	2.45775700
C	4.63456000	-3.44748600	-2.33001500
H	5.64144100	-1.56241500	-2.04164100

C	3.57528700	-4.38955600	-0.36722600
H	3.73841800	-3.24304400	1.44362100
C	5.95269100	-1.11590700	4.77418500
H	4.86732700	0.22123000	3.48773900
C	7.03760300	-2.99007700	3.69682100
H	6.80463900	-3.12366100	1.56340000
C	3.89122600	-4.46555600	-1.72719700
H	4.88716000	-3.50626200	-3.38460400
H	2.99999400	-5.18095800	0.10339700
C	6.73180900	-2.27242800	4.85655000
H	5.71178600	-0.55465100	5.67230400
H	7.64190700	-3.89056600	3.75555900
H	3.56420300	-5.31944700	-2.31327100
H	7.09850400	-2.61390600	5.82002700
H	6.72799500	2.30962900	-2.80540700
C	4.64988200	2.54523400	-3.26615900
H	4.32574400	1.67391300	-2.69005900
H	3.85175900	3.29575300	-3.23270900
H	4.76233000	2.23469500	-4.31002000
Pd	6.79902000	0.59352100	-0.26506300
C	8.78151400	1.50175600	-0.88871100
C	8.75362400	0.13612700	-1.18262900
H	8.70865000	-0.18045100	-2.22376700
C	8.42236700	-0.79723000	-0.15937200
H	8.25815400	-1.83611000	-0.43227100
H	8.78135200	-0.63755800	0.85699400
Ru	1.95548900	0.32333300	-0.20958800
H	9.05353500	1.85437100	0.10518900
H	8.84335200	2.22842600	-1.69257100
C	-2.53869100	3.52517100	0.60330000
C	-2.42006800	2.99909200	-0.84445800
C	-3.24642700	4.88565100	0.61753400
C	-1.46242100	3.79440100	-1.75944700
H	-3.42291800	2.95643000	-1.27776800
N	-1.84155900	1.63129700	-0.87595800
H	-4.22080600	4.83604700	0.12020500
H	-3.41946500	5.21889500	1.64458900
H	-2.64850500	5.65612400	0.11570200
O	-0.32706100	2.89663200	-1.95193700
H	-1.08063700	4.71866000	-1.32402100
H	-1.88967000	4.00308100	-2.74337900
C	-0.69155200	1.69723900	-1.45449900
C	0.29620100	0.63556000	-1.63392600
C	0.27687900	-0.73562900	-1.14349800

C	1.52997700	0.83539600	-2.34059800
C	1.50532600	-1.34596100	-1.57365100
P	-1.11108700	-1.54909200	-0.26762700
C	2.26845200	-0.38146800	-2.30071600
H	1.83638500	1.75949300	-2.80811500
H	1.80235400	-2.36806800	-1.38350400
C	-0.34136800	-2.35218000	1.19295300
C	-1.53407200	-2.93762000	-1.39234000
H	3.24116700	-0.54976500	-2.73994500
C	-0.60290000	-1.81225700	2.46158500
C	0.51141500	-3.46036400	1.07999900
C	-1.38306400	-2.81179200	-2.78260900
C	-2.13451900	-4.09579700	-0.87036700
C	-0.00343700	-2.35826900	3.59872600
H	-1.27610900	-0.96435100	2.55539800
C	1.10321400	-4.00888200	2.21851900
H	0.71027100	-3.89732000	0.10738000
C	-1.81226300	-3.83345800	-3.63229300
H	-0.92922600	-1.92093600	-3.20658700
C	-2.55982200	-5.11463500	-1.72376100
H	-2.26370000	-4.20646200	0.20202000
C	0.85159800	-3.45676800	3.47825600
H	-0.21126500	-1.93152300	4.57566500
H	1.76126100	-4.86744400	2.12302200
C	-2.39962500	-4.98683600	-3.10608300
H	-1.68439100	-3.72742000	-4.70584700
H	-3.01703800	-6.00736600	-1.30684800
H	1.31229600	-3.88781000	4.36241300
H	-2.73133200	-5.78065900	-3.76895200
H	-3.17749900	2.80734100	1.13136600
C	-1.18776900	3.56864200	1.32837200
H	-0.71035300	2.58386800	1.33658200
H	-0.49818100	4.28199400	0.86105500
H	-1.32533400	3.88354800	2.36821100
Pd	-2.80609000	-0.04493000	0.11213400
C	-10.18676300	-4.33808900	-1.11014900
C	-9.65264700	-3.45315900	-2.04845300
C	-8.96536400	-2.31301900	-1.62738500
C	-8.79638000	-2.04656500	-0.25830800
C	-9.33477100	-2.95072100	0.67563300
C	-10.02690300	-4.08250900	0.25644000
H	-10.72543800	-5.22208500	-1.44001800
H	-9.77168100	-3.64763000	-3.11050900
H	-8.55901700	-1.64236400	-2.37557900

H	-9.19703300	-2.74313500	1.73136400
H	-10.44158200	-4.76747100	0.99068600
C	-8.03448000	-0.86278700	0.28086500
C	-7.53861500	0.21652000	-0.68200100
H	-7.99937800	0.06704500	-1.65707200
O	-7.82027300	-0.78851200	1.48536600
C	-7.98312300	1.62262500	-0.20291600
O	-8.94727200	2.17353000	-0.76993400
N	-7.20504200	2.04495900	0.79816600
C	-7.14672800	3.34809700	1.25803800
C	-6.34801300	3.58224600	2.40611600
C	-7.74629200	4.47970700	0.64508700
C	-6.15405500	4.86515300	2.91205500
H	-5.89008500	2.72385200	2.89089900
C	-7.54098800	5.76031500	1.15927400
H	-8.37615900	4.32296300	-0.22128400
C	-6.74656400	5.97112100	2.29145500
H	-5.53729900	5.00405100	3.79739200
H	-8.01371700	6.60837200	0.66765200
H	-6.59781600	6.97293900	2.68477300
C	-5.08677800	-2.00448800	0.14264600
C	-4.31882900	-1.15415400	1.13769900
C	-4.63502800	0.23799100	1.26873000
C	-5.25175400	0.93190500	0.21716100
C	-5.98237500	0.19922900	-0.90066000
C	-5.42290400	-1.22633600	-1.14398600
H	-5.99921900	-2.36827800	0.62822200
H	-4.50327000	-2.89273800	-0.12090100
H	-4.50260000	-1.13353100	-1.73404400
H	-6.13230600	-1.79624600	-1.75347200
H	-5.07016900	1.98915800	0.11241100
H	-4.30682900	0.79334300	2.14512600
H	-5.82920200	0.77958500	-1.81792400
H	-3.96643600	-1.67389000	2.02721100

## TS-I

11

C	5.79251200	3.09910200	-3.02685900
C	5.79433800	3.52415500	-1.54069800
C	6.20317100	4.27777200	-3.91742400
C	4.69343100	4.52569400	-1.13901700
H	6.78323200	3.91365700	-1.28766800
N	5.50306900	2.36426900	-0.65652700
H	7.17187300	4.69146900	-3.61450300



H	6.28434400	3.95913200	-4.96158000
H	5.46429600	5.08664600	-3.87868000
O	3.72976900	3.71095600	-0.40208800
H	4.16600100	4.98549500	-1.97480800
H	5.05433900	5.30256500	-0.46021900
C	4.32849200	2.53798100	-0.13937900
C	3.54985600	1.61287500	0.67383600
C	3.84084300	0.22386700	0.99349200
C	2.28025000	1.94505900	1.25919000
C	2.74052100	-0.26382100	1.77909600
P	5.38314700	-0.65745100	0.60900200
C	1.79337200	0.79376600	1.93997300
H	1.79027700	2.90530400	1.19103400
H	2.64765700	-1.26362700	2.18033000
C	4.88987200	-2.20813400	-0.22041600
C	6.02839300	-1.15719500	2.24985200
H	0.85604300	0.72594700	2.47340400
C	5.12079400	-2.34171700	-1.59738300
C	4.25430800	-3.24187100	0.48317500
C	5.74077100	-0.40143200	3.39672500
C	6.90383300	-2.25178100	2.34397400
C	4.70071000	-3.49126400	-2.26947200
H	5.62448500	-1.54572900	-2.13887100
C	3.84204800	-4.39098900	-0.19167700
H	4.07881500	-3.15175800	1.54997200
C	6.31162900	-0.74618700	4.62371100
H	5.07163000	0.45132200	3.33970200
C	7.46985400	-2.59129000	3.57295400
H	7.13580900	-2.84371700	1.46350100
C	4.06000900	-4.51562200	-1.56718200
H	4.87956300	-3.58879700	-3.33617900
H	3.35060400	-5.18868500	0.35655700
C	7.17462000	-1.84058500	4.71460500
H	6.07798600	-0.15990300	5.50766100
H	8.14005700	-3.44341500	3.63834900
H	3.73830000	-5.41240600	-2.08847700
H	7.61539700	-2.10799700	5.67044800
H	6.56047300	2.31985600	-3.11617000
C	4.45265200	2.49237200	-3.46242000
H	4.17957300	1.63985200	-2.83352700
H	3.64139300	3.22815700	-3.41448300
H	4.51154100	2.14000000	-4.49748900
Pd	6.83997600	0.72654100	-0.52098400
C	8.74844100	1.68078200	-1.27266700

C	8.76235500	0.30455900	-1.51666700
H	8.67953800	-0.05306600	-2.54206700
C	8.51868800	-0.60040500	-0.44498100
H	8.38432300	-1.65455100	-0.67157100
H	8.91914000	-0.38666900	0.54565300
Ru	2.02425100	0.29499400	-0.22586600
H	9.05647800	2.07937400	-0.30711700
H	8.74410800	2.37944400	-2.10327900
C	-2.56412600	3.34510100	0.70257800
C	-2.48724300	2.76261000	-0.72591700
C	-3.35355600	4.65973500	0.70302500
C	-1.61275700	3.55602100	-1.72254500
H	-3.50588100	2.65250100	-1.10744800
N	-1.84732600	1.42305600	-0.72412800
H	-4.35331400	4.52637100	0.27575500
H	-3.47866200	5.03321200	1.72374600
H	-2.84056700	5.43882600	0.12593700
O	-0.45134900	2.69660500	-1.94038300
H	-1.24925400	4.51315300	-1.34616700
H	-2.09896900	3.70487700	-2.68977200
C	-0.73656700	1.50734600	-1.37157500
C	0.27821400	0.47315300	-1.56257700
C	0.33850000	-0.87088700	-1.00537000
C	1.45864500	0.67552600	-2.35458600
C	1.55927600	-1.46225000	-1.48035400
P	-0.95913800	-1.68578800	-0.00053400
C	2.24087200	-0.51272900	-2.30152600
H	1.69802800	1.57950200	-2.89572100
H	1.90413800	-2.46217300	-1.25498300
C	-0.07551900	-2.39098300	1.44799100
C	-1.40280800	-3.14358900	-1.02442000
H	3.19004200	-0.66925200	-2.79419900
C	-0.29787800	-1.80851000	2.70493200
C	0.81796200	-3.46691000	1.33747100
C	-1.33083600	-3.09204500	-2.42546000
C	-1.94745700	-4.28190500	-0.40633300
C	0.37976700	-2.27868500	3.83193900
H	-1.00086000	-0.98498200	2.79587000
C	1.48665200	-3.94145100	2.46661400
H	0.99206600	-3.93550700	0.37485600
C	-1.78331800	-4.16786900	-3.19243000
H	-0.92198700	-2.21661200	-2.92159100
C	-2.39617000	-5.35462500	-1.17747100
H	-2.01532600	-4.33398400	0.67638800

C	1.27365800	-3.34603500	3.71379800
H	0.20315000	-1.81752600	4.79937400
H	2.17341100	-4.77728800	2.37320100
C	-2.31526400	-5.30079200	-2.57168500
H	-1.71841100	-4.11939100	-4.27570400
H	-2.81035200	-6.23148300	-0.68807400
H	1.79527800	-3.71916700	4.59043100
H	-2.66584100	-6.13624100	-3.17060500
H	-3.12924100	2.61316400	1.29140800
C	-1.18258000	3.49725600	1.35200800
H	-0.64665600	2.54296700	1.37277100
H	-0.56124700	4.22939300	0.82243000
H	-1.28527500	3.84646000	2.38502000
Pd	-2.68932200	-0.23350000	0.39806100
C	-12.13862400	-2.40959800	-1.04987000
C	-11.51410700	-1.83643900	0.06100100
C	-10.23926700	-1.28289000	-0.05886800
C	-9.57583900	-1.29297100	-1.29651100
C	-10.21609000	-1.86496500	-2.40852600
C	-11.48633700	-2.42237200	-2.28717700
H	-13.13019800	-2.84312800	-0.95268100
H	-12.02109200	-1.81790900	1.02145800
H	-9.77628200	-0.83245800	0.81158000
H	-9.69729700	-1.86376200	-3.36161000
H	-11.96935700	-2.86619900	-3.15322300
C	-8.20118200	-0.72738000	-1.48640800
C	-7.41423900	-0.27845900	-0.25866600
H	-7.56816100	-1.00173400	0.54996500
O	-7.71321800	-0.65421600	-2.60904300
C	-7.92028300	1.10216800	0.24216900
O	-8.84489800	1.68364900	-0.35439400
N	-7.20086100	1.47670600	1.31159400
C	-7.12223600	2.78385500	1.77438800
C	-6.37379500	2.99140500	2.95918200
C	-7.64345100	3.93311000	1.12672700
C	-6.14826400	4.26896200	3.46636200
H	-5.97688100	2.11873500	3.47092100
C	-7.41093900	5.20821000	1.64395800
H	-8.23455200	3.80054300	0.22979800
C	-6.66346600	5.39347300	2.81147000
H	-5.57003800	4.38849700	4.37988500
H	-7.82382300	6.07110500	1.12554200
H	-6.49204700	6.39105800	3.20614800
C	-4.93679300	-2.24991400	0.67220100

C	-4.13353400	-1.31183300	1.55636400
C	-4.48955200	0.07636800	1.58036300
C	-5.21144200	0.65044000	0.52255200
C	-5.89191700	-0.19313000	-0.54993500
C	-5.27252800	-1.60563800	-0.68270100
H	-5.86196900	-2.52575600	1.20108200
H	-4.38371300	-3.18012000	0.50634000
H	-4.34793300	-1.53497500	-1.26897800
H	-5.95505900	-2.24543200	-1.25048500
H	-5.11956000	1.71465500	0.35709400
H	-4.17222700	0.71494700	2.40202600
H	-5.78381700	0.32364500	-1.50834900
H	-3.73751300	-1.74506400	2.47373900

### IM-II'

1 1

C	6.10891800	3.47535400	-1.92048800
C	6.11198200	3.43900700	-0.37509000
C	6.67201500	4.80935500	-2.42573800
C	5.11252200	4.39104300	0.31259300
H	7.12971800	3.62570600	-0.02341100
N	5.67681800	2.10873200	0.12707800
H	7.66791600	5.00635400	-2.01274900
H	6.75604200	4.79954400	-3.51723400
H	6.02353900	5.65086800	-2.15531800
O	4.05570600	3.50581300	0.79277900
H	4.65197000	5.12483800	-0.34899200
H	5.53917600	4.89831200	1.18163400
C	4.51759600	2.24905900	0.68865500
C	3.62953200	1.21883800	1.20853300
C	3.75906000	-0.22664800	1.10323600
C	2.39660300	1.50301900	1.89101100
C	2.60221900	-0.79866500	1.73635600
P	5.19376300	-1.12000100	0.43581100
C	1.77582700	0.26358800	2.21517100
H	2.01513700	2.48959500	2.10886600
H	2.39522200	-1.85556100	1.83513500
C	4.55348800	-2.25192000	-0.84979100
C	5.72734400	-2.19837400	1.81907800
H	0.83014500	0.14534500	2.72458300
C	4.83347800	-1.98152600	-2.19720300
C	3.76025400	-3.35914800	-0.51396700
C	5.53092500	-1.80369700	3.15163100
C	6.42218900	-3.38796400	1.54573600

C	4.31227600	-2.80259300	-3.19960200
H	5.45132600	-1.12693900	-2.45913000
C	3.24638900	-4.17990100	-1.51775500
H	3.53902800	-3.57848300	0.52440000
C	6.00973300	-2.59862700	4.19501100
H	4.99963900	-0.88510100	3.38084600
C	6.89687600	-4.17817400	2.59289900
H	6.58087000	-3.70459400	0.51935100
C	3.51858100	-3.90161700	-2.86073700
H	4.52992900	-2.58676800	-4.24147800
H	2.63022900	-5.03300800	-1.25055300
C	6.69090100	-3.78646300	3.91859500
H	5.84587800	-2.28974400	5.22330600
H	7.42544800	-5.10104900	2.37226400
H	3.11721900	-4.54277300	-3.64004500
H	7.05878400	-4.40486400	4.73206300
H	6.79380600	2.67796400	-2.23677400
C	4.72928800	3.17226100	-2.51769200
H	4.35499100	2.20110900	-2.18095800
H	3.99234000	3.93698100	-2.24643400
H	4.78527300	3.14853400	-3.61111200
Pd	6.82567600	0.36376200	-0.23225900
C	8.85006600	1.26597800	-0.71461300
C	8.70397300	0.02592600	-1.34131100
H	8.59761400	-0.01086400	-2.42462400
C	8.33688700	-1.11352400	-0.57032700
H	8.08376600	-2.03410000	-1.08911800
H	8.74220300	-1.24305200	0.43283300
Ru	1.97296100	0.40544800	-0.00429900
H	9.18648100	1.33284700	0.31899800
H	8.94218800	2.16766700	-1.31187000
C	-2.24307800	3.45357300	1.86931000
C	-2.20083100	3.42583200	0.32371600
C	-2.81529700	4.78522700	2.36948400
C	-1.17237300	4.37147900	-0.33320400
H	-3.20819200	3.62842100	-0.04522700
N	-1.77733400	2.09174400	-0.16295400
H	-3.80313300	4.98200800	1.94031700
H	-2.91784300	4.77249500	3.45987900
H	-2.16143300	5.62809600	2.11280400
O	-0.11688800	3.47781100	-0.79581800
H	-0.72010100	5.09693700	0.34451800
H	-1.57610100	4.89303700	-1.20612600
C	-0.61418500	2.21932300	-0.69636800

C	0.27489700	1.17083100	-1.19913400
C	0.17302100	-0.27659000	-1.06142900
C	1.49100500	1.46581400	-1.90434700
C	1.33138000	-0.83180200	-1.70760200
P	-1.23681900	-1.19102700	-0.30121800
C	2.13485700	0.23460200	-2.21634300
H	1.84798100	2.45719800	-2.14200600
H	1.56342400	-1.88420300	-1.78839800
C	-0.42479400	-2.40753100	0.82154600
C	-1.80517400	-2.21621400	-1.72504600
H	3.07147200	0.12412300	-2.74375500
C	-0.60454200	-2.22034400	2.20059200
C	0.34980400	-3.48912800	0.37554500
C	-1.80479400	-1.68439300	-3.02552100
C	-2.40722300	-3.46607800	-1.50419600
C	0.00271900	-3.07967500	3.11966300
H	-1.22339200	-1.39685700	2.54790500
C	0.94746300	-4.35418000	1.29350900
H	0.48326700	-3.66178000	-0.68711900
C	-2.38736600	-2.38999700	-4.08022200
H	-1.35581000	-0.71364100	-3.21699400
C	-2.98852600	-4.16921700	-2.56081700
H	-2.42413500	-3.89184200	-0.50551900
C	0.78208600	-4.14736400	2.66674100
H	-0.14151700	-2.92102500	4.18464400
H	1.54221100	-5.19080700	0.93757700
C	-2.98221200	-3.63401800	-3.85154700
H	-2.37546000	-1.96694700	-5.08103300
H	-3.44977600	-5.13492200	-2.37305300
H	1.24791900	-4.82287700	3.37862100
H	-3.43708200	-4.18108900	-4.67231400
H	-2.93858900	2.65326800	2.15438300
C	-0.88193000	3.14186700	2.50361700
H	-0.50202700	2.17227200	2.16896900
H	-0.13619600	3.90802100	2.25909800
H	-0.96837700	3.10892900	3.59512400
Pd	-2.92346800	0.23181700	0.35106600
C	-9.64260600	-4.97616900	0.09678500
C	-9.36197000	-4.24574300	-1.05972200
C	-8.91703900	-2.92625100	-0.96417700
C	-8.74444400	-2.32467400	0.29311500
C	-9.03017700	-3.07049100	1.45066700
C	-9.47620300	-4.38456000	1.35433600
H	-9.99017200	-6.00262700	0.02060600

H	-9.49007300	-4.70151800	-2.03716900
H	-8.70230600	-2.37615700	-1.87333900
H	-8.89132200	-2.59785000	2.41719800
H	-9.69435300	-4.95055700	2.25542000
C	-8.24731300	-0.92177700	0.47247700
C	-7.91110700	-0.08451600	-0.76396700
H	-8.61732500	-0.32977900	-1.55938100
O	-8.11726200	-0.44704000	1.59439800
C	-8.09221700	1.39701100	-0.41810600
O	-9.16454700	1.96079000	-0.24808500
N	-6.85003500	1.97623500	-0.35699700
C	-6.63042500	3.33367300	-0.00716900
C	-7.29304000	3.89889000	1.09132300
C	-5.74401300	4.11645700	-0.76064700
C	-7.07044300	5.23505200	1.42528300
H	-7.97971200	3.28912000	1.66620100
C	-5.51950900	5.44939500	-0.41333300
H	-5.23941900	3.68529400	-1.61937500
C	-6.18279900	6.01548200	0.67856800
H	-7.58817500	5.66528000	2.27798700
H	-4.82944000	6.04658800	-1.00291100
H	-6.00942200	7.05390200	0.94545300
C	-5.26333300	-1.84814600	0.24323600
C	-4.73458600	-0.67274700	1.04359000
C	-5.00928500	0.67341200	0.69615100
C	-5.73636600	1.03711800	-0.60186400
C	-6.44476900	-0.15464300	-1.29746900
C	-5.65284200	-1.46450800	-1.18884400
H	-6.12992000	-2.27025500	0.76780000
H	-4.52150900	-2.65355400	0.20439900
H	-4.73528500	-1.33581300	-1.77619500
H	-6.21386200	-2.27952300	-1.65860000
H	-5.04745600	1.50213900	-1.31249300
H	-5.11024000	1.41551800	1.48762300
H	-6.52197100	0.09925000	-2.36046700
H	-4.59526900	-0.88718500	2.10530700

## IM-II

11

C	5.94856600	3.32703100	-2.56846900
C	6.08258900	3.48168300	-1.03634300
C	6.42205600	4.60096600	-3.27899600
C	5.11365400	4.48859700	-0.38608100
H	7.11956600	3.73347500	-0.80030400

N	5.73337300	2.21419400	-0.34022200
H	7.44207800	4.87139500	-2.98250100
H	6.41413600	4.45870400	-4.36446300
H	5.77052400	5.45422300	-3.05697400
O	4.12286600	3.64563200	0.27765300
H	4.58256800	5.13009900	-1.08946800
H	5.59139600	5.10170400	0.38217100
C	4.61438700	2.39561300	0.28800000
C	3.79852000	1.41563000	0.99304400
C	3.98189900	-0.02561700	1.07691500
C	2.59612200	1.74651000	1.70708000
C	2.89055800	-0.54485900	1.85325700
P	5.40404500	-0.95745300	0.43746100
C	2.04798800	0.54267600	2.23403900
H	2.18893400	2.74051200	1.82254300
H	2.73897800	-1.58397900	2.10811600
C	4.72776800	-2.29544400	-0.61048100
C	6.09394800	-1.79602700	1.91377300
H	1.13963100	0.46124700	2.81278800
C	4.86757300	-2.20014600	-2.00314800
C	4.04683800	-3.38814400	-0.05396200
C	5.96315800	-1.22884300	3.19071400
C	6.84883700	-2.96994200	1.75281600
C	4.31342600	-3.17726700	-2.83233500
H	5.40374300	-1.35937200	-2.43519300
C	3.50186400	-4.36649000	-0.88597400
H	3.93675600	-3.47468300	1.02150600
C	6.56556200	-1.83919200	4.29296000
H	5.38998100	-0.31768800	3.33195600
C	7.44668000	-3.57527600	2.85823700
H	6.96093600	-3.41750200	0.76976700
C	3.62944400	-4.26062200	-2.27412800
H	4.42101800	-3.09550000	-3.90989900
H	2.97593300	-5.21024500	-0.44963500
C	7.30546400	-3.01256700	4.12994100
H	6.45242400	-1.39733600	5.27866600
H	8.02009000	-4.48807400	2.72547400
H	3.20256700	-5.02376100	-2.91824700
H	7.76993500	-3.48713700	4.98928600
H	6.62865700	2.51123800	-2.84425900
C	4.53371700	2.92261700	-3.00035100
H	4.22064300	1.99712200	-2.50979300
H	3.79820300	3.70066600	-2.76600500
H	4.49965400	2.75638700	-4.08207300



Pd	6.90133400	0.46257000	-0.58155900
C	8.83803000	1.33754300	-1.37794100
C	8.67954000	0.01877400	-1.81184700
H	8.47268800	-0.17086000	-2.86427600
C	8.42761000	-1.01076200	-0.86063400
H	8.15841200	-2.00012400	-1.22037600
H	8.93125100	-0.99024400	0.10533300
Ru	2.11136300	0.38844500	0.00328000
H	9.26538200	1.55671700	-0.40044400
H	8.84142700	2.14793700	-2.09989700
C	-2.15395200	3.36228400	1.81508500
C	-2.18161000	3.21546000	0.27547200
C	-2.73012100	4.71636200	2.24428200
C	-1.21783000	4.14039300	-0.50030400
H	-3.21254800	3.35401000	-0.06053400
N	-1.72864900	1.86131300	-0.12133000
H	-3.74331100	4.86200700	1.85683200
H	-2.77429400	4.78394500	3.33662900
H	-2.11049200	5.54968900	1.89086700
O	-0.15826400	3.24661700	-0.95342300
H	-0.75601400	4.92424300	0.10211400
H	-1.68043700	4.58688200	-1.38527300
C	-0.59733000	1.98478900	-0.72075700
C	0.31172900	0.92752700	-1.16740600
C	0.29077800	-0.49637000	-0.86088000
C	1.46996900	1.19026900	-1.97440900
C	1.43955100	-1.07321900	-1.50442900
P	-1.04506600	-1.38960600	0.04356400
C	2.15924600	-0.03988500	-2.17973600
H	1.76016000	2.16076900	-2.34924800
H	1.71051800	-2.11937000	-1.48371600
C	-0.13338600	-2.37281200	1.30698600
C	-1.54057800	-2.64550400	-1.21197300
H	3.06816300	-0.16983200	-2.75009100
C	-0.27899500	-1.98976600	2.64902200
C	0.69188900	-3.46288000	0.99349200
C	-1.54633800	-2.33004900	-2.58084100
C	-2.07369800	-3.87835400	-0.79891400
C	0.40754900	-2.66842400	3.65907900
H	-0.93340000	-1.15753200	2.89626400
C	1.36741100	-4.14904700	2.00414000
H	0.80367100	-3.78231800	-0.03720300
C	-2.06068800	-3.23259200	-3.51421400
H	-1.15367100	-1.37745400	-2.92443600

C	-2.58515400	-4.77883100	-1.73465400
H	-2.08802900	-4.13825600	0.25554400
C	1.23225200	-3.74991600	3.33760700
H	0.28938600	-2.36043700	4.69412700
H	1.99898200	-4.99561800	1.75047500
C	-2.58068800	-4.45982800	-3.09513900
H	-2.05452000	-2.97471200	-4.56974600
H	-2.98900600	-5.72983000	-1.39847300
H	1.75815300	-4.28619800	4.12242100
H	-2.98072200	-5.16078500	-3.82210500
H	-2.81771900	2.57268600	2.19083100
C	-0.75811200	3.12484900	2.40458600
H	-0.36365000	2.14977500	2.10602400
H	-0.04768700	3.89708800	2.08520500
H	-0.79670600	3.15042900	3.49908200
Pd	-2.79481200	0.01183300	0.57228100
C	-12.32283300	-2.84064000	0.12816900
C	-11.49881700	-2.12402500	0.99935400
C	-10.32512600	-1.53447200	0.52909400
C	-9.96943600	-1.65155400	-0.82455800
C	-10.81205400	-2.36413900	-1.69589200
C	-11.97772500	-2.95892700	-1.22285400
H	-13.23308800	-3.30361700	0.49912700
H	-11.77094800	-2.02190500	2.04587900
H	-9.71073300	-0.95598300	1.20803600
H	-10.53148900	-2.44297600	-2.74109300
H	-12.61851200	-3.51364800	-1.90227400
C	-8.72504400	-1.04754400	-1.38847900
C	-7.66632500	-0.49348200	-0.43183600
H	-7.65075500	-1.10896000	0.47399200
O	-8.53766300	-1.01424100	-2.59881300
C	-7.99420700	0.93592500	0.03227700
O	-9.09762000	1.35411900	0.36339400
N	-6.82496400	1.64925300	0.01544600
C	-6.71695200	3.00564200	0.42288000
C	-7.35081600	3.45822800	1.58803600
C	-5.96405400	3.90107200	-0.35066300
C	-7.23350100	4.79574200	1.96827600
H	-7.93940100	2.76546800	2.17708100
C	-5.84573500	5.23484600	0.04159400
H	-5.48613300	3.55600100	-1.26185300
C	-6.48095900	5.68877400	1.20085800
H	-7.72964700	5.13844300	2.87192200
H	-5.26130400	5.92066500	-0.56524000

H	-6.39084700	6.72817800	1.50248100
C	-5.11647400	-2.06617100	0.47067100
C	-4.59226600	-0.90298100	1.29628000
C	-4.86570300	0.44851700	0.95403200
C	-5.63511700	0.82686500	-0.31436400
C	-6.26404800	-0.37848500	-1.05198200
C	-5.41900500	-1.65496200	-0.97459300
H	-6.03131000	-2.45911800	0.94208700
H	-4.40033000	-2.89482600	0.47433100
H	-4.47315900	-1.48202600	-1.50359300
H	-5.93799300	-2.46309700	-1.50306300
H	-5.00418900	1.40125400	-0.99697500
H	-4.93068000	1.19054500	1.75059400
H	-6.40307300	-0.10173000	-2.10094600
H	-4.44725300	-1.13009500	2.35456600

**PdL+**

1 1

C	3.66134400	3.57675300	-2.01781500
C	3.72588900	3.52462500	-0.47427400
C	4.19111000	4.92172200	-2.53011800
C	2.75040400	4.46588000	0.26194300
H	4.75602500	3.71505600	-0.16296400
N	3.32135900	2.18746500	0.03634500
H	5.20028400	5.12524400	-2.15428500
H	4.23206600	4.92357300	-3.62418100
H	3.54493800	5.75348000	-2.22632200
O	1.72908200	3.57008900	0.79518800
H	2.24978000	5.19340000	-0.37726700
H	3.21391100	4.97973900	1.10794600
C	2.19191500	2.31678400	0.65849800
C	1.33515000	1.27875500	1.21582500
C	1.47219300	-0.16626900	1.10856300
C	0.12803700	1.55482000	1.94496000
C	0.34524600	-0.74506900	1.78849700
P	2.88315100	-1.04286400	0.37311200
C	-0.47179500	0.31231000	2.29502600
H	-0.25159600	2.53950200	2.17263900
H	0.15134900	-1.80311300	1.89858300
C	2.20215300	-2.20330400	-0.86548700
C	3.52535800	-2.09525900	1.72808900
H	-1.39608100	0.18757200	2.83984700
C	2.42109800	-1.95355400	-2.22850300
C	1.43920600	-3.31476900	-0.47780700

C	3.37688800	-1.71407900	3.07017300
C	4.26902000	-3.24452400	1.41276100
C	1.86597700	-2.79631200	-3.19391700
H	3.01697500	-1.09781600	-2.53310800
C	0.89037500	-4.15635100	-1.44531500
H	1.26669000	-3.52009700	0.57282300
C	3.95634100	-2.48154900	4.08302000
H	2.80805900	-0.82655700	3.32991100
C	4.84349800	-4.00752100	2.42921900
H	4.38956800	-3.54955700	0.37751900
C	1.09888800	-3.89679200	-2.80317300
H	2.03589900	-2.59512500	-4.24757300
H	0.29626700	-5.01184800	-1.13928400
C	4.68848100	-3.62801400	3.76567500
H	3.83141800	-2.18341200	5.11990700
H	5.41038000	-4.89901900	2.17697400
H	0.66937400	-4.55406000	-3.55352600
H	5.13588500	-4.22399500	4.55564900
H	4.34010300	2.79041500	-2.37084900
C	2.26345100	3.26581300	-2.56605100
H	1.91544700	2.28466000	-2.23012800
H	1.52754900	4.01658500	-2.25549300
H	2.27797800	3.25854000	-3.66113200
Pd	4.46161800	0.45454500	-0.38945200
C	6.44719600	1.36979300	-0.99501600
C	6.26523000	0.13363700	-1.61988800
H	6.08718700	0.10370900	-2.69400600
C	5.95591000	-1.01215800	-0.83258700
H	5.67464800	-1.93188800	-1.33802500
H	6.43097600	-1.14430400	0.13911700
Ru	-0.35459600	0.44852400	0.06707300
H	6.84896800	1.43040300	0.01546500
H	6.49799500	2.27682800	-1.58894200
C	-4.34015300	3.84739400	1.96967000
C	-4.31781000	3.75621800	0.42649000
C	-4.77211500	5.24797000	2.42046700
C	-3.21643800	4.57985600	-0.27762800
H	-5.30756300	4.03561800	0.05322200
N	-4.02248800	2.37136200	-0.00421200
H	-5.74225500	5.52433100	1.99221200
H	-4.86020900	5.29194700	3.51099100
H	-4.04330700	6.00999900	2.11896900
O	-2.27586200	3.57668900	-0.75570100
H	-2.67043800	5.26275300	0.37559500

H	-3.59061500	5.12971800	-1.14556500
C	-2.87152100	2.36737500	-0.58442600
C	-2.06922700	1.23711400	-1.08133200
C	-2.20476200	-0.21315400	-0.91870600
C	-0.86831400	1.48315800	-1.83460900
C	-1.07546500	-0.80002900	-1.59047900
P	-3.60519200	-1.18009900	-0.14175200
C	-0.26228000	0.23468300	-2.14475700
H	-0.49650900	2.46111400	-2.10091000
H	-0.87352300	-1.85902700	-1.66255200
C	-2.71217800	-2.36552800	0.97177400
C	-4.08488700	-2.25578500	-1.56860000
H	0.65516300	0.09231100	-2.69737900
C	-2.82906700	-2.15878000	2.35500400
C	-1.94604300	-3.44861400	0.51424400
C	-3.99210500	-1.80054000	-2.89432000
C	-4.67946000	-3.50683900	-1.32606300
C	-2.17296900	-2.99425100	3.26176000
H	-3.44150000	-1.33578600	2.71555000
C	-1.30335000	-4.29520100	1.41998700
H	-1.85590100	-3.64138900	-0.54923700
C	-4.46234200	-2.58547000	-3.95027000
H	-3.55181900	-0.83120100	-3.10857100
C	-5.14166900	-4.29169200	-2.38234300
H	-4.77467400	-3.87272000	-0.30747100
C	-1.40753000	-4.06632100	2.79509800
H	-2.27044500	-2.81584500	4.32908100
H	-0.72119300	-5.13548400	1.05208800
C	-5.03401500	-3.83504100	-3.69968700
H	-4.37898300	-2.21859600	-4.96979400
H	-5.58904800	-5.26022200	-2.17570200
H	-0.90677600	-4.72685900	3.49736600
H	-5.39620200	-4.44610500	-4.52150800
H	-5.10634000	3.12931400	2.29535000
C	-3.00750800	3.42967200	2.60541200
H	-2.72790600	2.41471600	2.30672900
H	-2.19431500	4.10931400	2.32351600
H	-3.08360400	3.44918300	3.69796200
Pd	-4.89473300	0.44304200	0.57780900

## 10. References

- [1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, H. P. H. X. Li, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, D.01 ed., Gaussian, Inc., Wallingford CT, **2013**.
- [2] R. Ditchfield, W. J. Hehre, J. A. Pople, *J. Chem. Phys.*, **1971**, *54*, 724.
- [3] M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees, J. A. Pople, *J. Chem. Phys.*, **1982**, *77*, 3654.
- [4] M. S. Gordon, J. S. Binkley, J. A. Pople, W. J. Pietro, W. J. Hehre, *J. Am. Chem. Soc.* **1982**, *104*, 2797.
- [5] P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta*, **1973**, *28*, 213.
- [6] W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.*, **1972**, *56*, 2257.
- [7] D. Andrae, U. Häußermann, M. Dolg, H. Stoll, H. Preuß, *Theor. Chim. Acta*, **1990**, *77*, 123.
- [8] J. M. L. Martin, A. Sundermann, *J. Chem. Phys.*, **2001**, *114*, 3408.
- [9] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.*, **2010**, *132*, 154104.
- [10] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem B*, **2009**, *113*, 6378.