

## *Supplementary Information for*

### **Organocatalytic Asymmetric Intramolecular [3+2] Cycloaddition: A**

#### **Straightforward Approach to Access Multiply Substituted**

#### **Hexahydrochromeno[4,3-b]pyrrolidine Derivatives in High Optical Purity**

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**General data:** NMR spectra were recorded on a Bruker-400 MHz spectrometer. Optical rotations were measured on a Perkin-Elmer 241 Polarimeter at  $\lambda = 589$  nm (sodium D line). HRMS (Micromass GCT-MS) spectra were recorded on P-SIMS-Gly of Bruker Daltonics Inc. Infrared spectra were recorded on a Nicolet MX-1E FT-IR spectrometer. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. HPLC analysis was performed on Waters-Breeze (2487 Dual  $\lambda$  Absorbance Detector and 1525 Binary HPLC Pump). Chiralpak AS, AD, OD and IA columns were purchased from Daicel Chemical Industries, Ltd. Toluene was refluxed with sodium and benzophenone and distilled prior to use. Petroleum ether and ethyl acetate for column chromatography were distilled before use. The relative and absolute configuration of **3d** was assigned by the X-ray analysis.

**Materials:** All starting materials were purchased from Acros, Alfa Aesar, Aldrich and used directly

**The preparation of chiral phosphoric acid 4g:** Chiral catalyst was prepared on the base of the literature procedures.<sup>1</sup>

**General Procedure for the synthesis of aldehyde substrates.** Different substituted 2-hydroxybenzaldehydes, (*E*)-ethyl 4-bromobut-2-enoate or (*E*)-methyl 4-bromobut-2-enoate and  $K_2CO_3$  were dissolved in DMF. After the reaction system was heated at 70 °C under argon for 4 hours, it was filtrated and then added  $H_2O$ . The mixture was extracted with EtOAc (20 ml X 3). The combined organic phases were washed with  $H_2O$  and saturated NaCl, and dried over anhydrous

Na<sub>2</sub>SO<sub>4</sub>. After removal of solvent under reduced pressure, the residue was purified through flash column chromatography on a silica gel (eluent: petroleum ether: ethyl acetate) to give the pure products.

**(E)-Ethyl 4-(2-formylphenoxy)but-2-enoate (1a).** 67% yield (Flash column chromatography eluent, petroleum ether / ethyl acetate = 80: 1 to 10: 1); yellow solid, mp: 66-68 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 1.31 (t, *J*= 7.1 Hz, 3H), 4.20 (q, *J*= 7.1 Hz, 2H), 4.82 (q, *J*= 2.0 Hz, 2H), 6.19-6.24 (m, 1H), 6.94 (d, *J*= 8.4 Hz, 1H), 7.05-7.13 (m, 2H), 7.52-7.57 (m, 1H), 7.87 (dd, *J*<sub>1</sub>= 1.8 Hz, *J*<sub>2</sub>= 15.3 Hz, 1H), 10.56 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz) δ (ppm): 14.59, 61.12, 67.29, 112.94, 121.85, 122.98, 129.25, 136.28, 141.51, 189.66; IR (KBr): γ 3399, 2986, 2874, 1714, 1688, 1663, 1600, 1479, 1438, 1379, 1305, 1249, 1183, 1075, 1041, 969, 946, 850, 769, 682, 661, 614 cm<sup>-1</sup>; HRMS (Micromass GCT-MS EI) exact mass calcd for (C<sub>13</sub>H<sub>14</sub>O<sub>4</sub>)<sup>+</sup> requires m/z 234.0892, found m/z 234.0891.

**(E)-Ethyl 4-(4-chloro-2-formylphenoxy)but-2-enoate (1b).** 67% yield (Flash column chromatography eluent, petroleum ether / ethyl acetate / CH<sub>2</sub>Cl<sub>2</sub>= 30: 1: 1); white solid, mp: 64-66 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 1.26 (t, *J*= 7.1 Hz, 3H), 4.16 (q, *J*= 7.1 Hz, 2H), 4.77 (q, *J*= 2.0 Hz, 2H), 6.11-6.16 (m, 1H), 6.85 (d, *J*= 8.9 Hz, 1H), 7.00-7.06 (m, 1H), 7.44 (dd, *J*<sub>1</sub>= 2.7 Hz, *J*<sub>2</sub>= 17.7 Hz, 1H), 10.43 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz) δ (ppm): 14.58, 61.19, 67.68, 114.61, 123.27, 126.42, 127.61, 128.77, 135.76, 140.96, 159.00, 166.02, 188.28; IR (KBr): γ 3408, 2986, 2908, 2869, 1719, 1684, 1594, 1482, 1437, 1307, 1272, 1183, 1127, 1040, 975, 844, 680 cm<sup>-1</sup>; HRMS (Micromass GCT-MS EI) exact mass calcd for (C<sub>13</sub>H<sub>13</sub>ClO<sub>4</sub>)<sup>+</sup> requires m/z 268.0502, found m/z 268.0506.

**(E)-Ethyl 4-(2-formyl-4-methoxyphenoxy)but-2-enoate (1c).** 72% yield (Flash column chromatography eluent, petroleum ether / ethyl acetate= 70: 1 to 40: 1); yellow solid, mp: 83-85 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 1.30 (t, *J*= 7.1 Hz, 3H), 3.80 (s, 3H), 4.20 (q, *J*= 7.1 Hz, 2H), 4.78 (q, *J*= 2.0 Hz, 2H), 6.19 (d, *J*= 15.7 Hz, 1H), 6.90 (d, *J*= 9.0 Hz, 1H), 7.05-7.13 (m, 2H), 7.35 (d, *J*= 3.0 Hz, 1H), 10.51 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz) δ (ppm): 14.22, 55.84, 60.71, 67.64, 110.72, 114.52, 122.48, 123.37, 125.47, 141.48, 154.18, 155.01, 165.83, 189.05; IR (KBr): γ 3438, 2981, 2874, 1720, 1677, 1616, 1496, 1450, 1285, 1214, 1184, 1087, 1035, 942, 873, 817, 728, 647 cm<sup>-1</sup>; HRMS (Micromass GCT-MS EI) exact mass calcd for (C<sub>14</sub>H<sub>16</sub>O<sub>5</sub>)<sup>+</sup> requires m/z 264.0998, found m/z 264.0991.

**(E)-Ethyl 4-(2-formyl-5-methoxyphenoxy)but-2-enoate (1d).** 78% yield (Flash column

chromatography eluent, petroleum ether / ethyl acetate= 70: 1 to 40: 1); yellow solid, mp: 91-93 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 1.31 (t, *J*= 7.1 Hz, 3H), 3.86 (s, 3H), 4.20 (q, *J*= 7.1 Hz, 2H), 4.78 (q, *J*= 2.1 Hz, 2H), 6.19-6.24 (m, 1H), 6.40 (d, *J*= 2.2 Hz, 1H), 6.57-6.60 (m, 1H), 7.05-7.11 (m, 1H), 7.84 (d, *J*= 8.7 Hz, 1H), 10.37 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz) δ (ppm): 14.21, 55.71, 60.73, 66.86, 99.06, 106.34, 119.29, 122.59, 130.94, 140.99, 161.89, 165.80, 166.08, 187.83; IR (KBr): γ 3426, 3072, 2856, 1719, 1671, 1607, 1505, 1427, 1282, 1201, 1172, 1123, 1084, 1039, 957, 882, 811, 647 cm<sup>-1</sup>; HRMS (Micromass GCT-MS EI) exact mass calcd for (C<sub>14</sub>H<sub>16</sub>O<sub>5</sub>)<sup>+</sup> requires m/z 264.0998, found m/z 264.0994.

**(E)-Ethyl 4-(2-formyl-6-methoxyphenoxy)but-2-enoate (1e).** 78% yield (Flash column chromatography eluent, petroleum ether / ethyl acetate= 40: 1 to petroleum ether / ethyl acetate / CH<sub>2</sub>Cl<sub>2</sub>= 30: 1: 1); white solid, mp: 56-58 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 1.25 (t, *J*= 7.1 Hz, 3H), 3.84 (s, 3H), 4.15 (q, *J*= 7.1 Hz, 2H), 4.76 (q, *J*= 1.9 Hz, 2H), 6.15-6.20 (m, 1H), 7.00-7.06 (m, 1H), 7.10-7.11 (m, 1H), 7.36-7.39 (m, 1H), 10.38 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz) δ (ppm): 14.61, 56.49, 60.95, 72.89, 118.53, 119.82, 122.67, 124.95, 130.23, 142.57, 151.16, 153.18, 166.39, 190.16; IR (KBr): γ 3434, 2986, 2904, 1711, 1660, 1586, 1482, 1433, 1305, 1270, 1178, 1073, 1044, 961, 922, 843, 786, 744 cm<sup>-1</sup>; HRMS (Micromass GCT-MS EI) exact mass calcd for (C<sub>14</sub>H<sub>16</sub>O<sub>5</sub>)<sup>+</sup> requires m/z 264.0998, found m/z 264.0996.

**(E)-Ethyl 4-(2-ethoxy-6-formylphenoxy)but-2-enoate (1f).** 78% yield (Flash column chromatography eluent, petroleum ether / ethyl acetate = 70: 1 to 40: 1); white solid, mp: 52-53 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 1.28-1.32 (m, 3H), 1.44-1.48 (m, 3H), 4.07-4.13 (m, 2H), 4.19-4.25 (m, 2H), 4.83-4.85 (m, 2H), 6.21-6.26 (m, 2H), 7.06-7.15 (m, 3H), 7.39-7.43 (m, 1H), 10.43 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz) δ (ppm): 14.24, 14.82, 60.56, 64.75, 72.48, 119.22, 119.35, 122.25, 124.47, 129.88, 142.39, 151.03, 152.07, 166.05, 189.88; IR (KBr): γ 3413, 2986, 2899, 1718, 1697, 1659, 1585, 1480, 1400, 1304, 1279, 1209, 1178, 1065, 958, 924, 869, 782, 746 cm<sup>-1</sup>; HRMS (Micromass GCT-MS EI) exact mass calcd for (C<sub>15</sub>H<sub>18</sub>O<sub>5</sub>)<sup>+</sup> requires m/z 278.1154, found m/z 278.1146.

**(E)-Ethyl 4-(2-fluoro-6-formylphenoxy)but-2-enoate (1g).** 89% yield (Flash column chromatography eluent, petroleum ether / ethyl acetate= 70: 1 to 10: 1); white solid, mp: 67-68 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 1.31 (t, *J*= 7.1 Hz, 3H), 4.20 (q, *J*= 7.1 Hz, 2H), 4.91-4.93 (m, 2H), 6.20-6.25 (m, 1H), 7.03-7.14 (m, 1H), 7.32-7.38 (m, 1H), 7.62-7.64 (m, 1H), 10.43 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz) δ (ppm): 14.22, 60.71, 72.79 (d, *J*= 7.4 Hz), 122.84, 122.91 (d, *J*=

19.3 Hz), 123.82 (d,  $J= 3.3$  Hz), 124.06 (d,  $J= 7.3$  Hz), 130.17 (d,  $J= 1.6$  Hz), 141.23, 148.51 (d,  $J= 10.7$  Hz), 154.84 (d,  $J= 247.6$  Hz), 165.79, 188.46 (d,  $J= 3.3$  Hz); IR (KBr):  $\gamma$  3430, 2986, 2874, 1722, 1690, 1481, 1382, 1303, 1270, 1180, 1078, 1035, 960, 927, 791, 779, 735, 681  $\text{cm}^{-1}$ ; HRMS (Micromass GCT-MS EI) exact mass calcd for  $(\text{C}_{13}\text{H}_{13}\text{FO}_4)^+$  requires  $m/z$  252.0798, found  $m/z$  252.0792.

**(E)-Methyl 4-(2-formylphenoxy)but-2-enoate (1h).** 60% yield (Flash column chromatography eluent, petroleum ether / ethyl acetate = 10: 1 to petroleum ether / ethyl acetate /  $\text{CH}_2\text{Cl}_2$  =15: 1); white solid, mp: 65-66 °C;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 3.73 (s, 3H), 4.78-4.80 (m, 2H), 6.15-6.20 (m, 1H), 6.79 (d,  $J= 8.4$  Hz, 1H), 7.00-7.10 (m, 2H), 7.47-7.52 (m, 1H), 7.80-7.83 (m, 1H), 10.50 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz)  $\delta$  (ppm): 52.19, 67.25, 98.77, 112.94, 121.86, 122.54, 125.57, 129.28, 136.28, 141.86, 160.53, 166.61, 189.61; IR (KBr):  $\gamma$  3426, 2951, 2861, 2766, 1719, 1683, 1599, 1494, 1442, 1390, 1312, 1239, 1165, 1108, 1017, 960, 849, 769, 739, 662, 612  $\text{cm}^{-1}$ ; HRMS (Micromass GCT-MS EI) exact mass calcd for  $(\text{C}_{12}\text{H}_{12}\text{O}_4)^+$  requires  $m/z$  220.0736, found  $m/z$  220.0731.

**General Procedure for the organocatalytic enantioselectivity intramolecular [3+2] reaction.**

Aldehyde (0.24 mmol), amine (0. 20 mmol), 400mg 3Å MS and catalyst (0.02 mmol) were dissolved in toluene (1 mL), the reaction mixture was stirred at 25 °C for 72 hours. Then filtrate and added the saturated  $\text{NaHCO}_3$  to the reaction mixture, extract with  $\text{CH}_2\text{Cl}_2$  (10 ml X 3), dry with anhydrous  $\text{Na}_2\text{SO}_4$  and rotary evaporate the solvent. The mixture was purified through flash column chromatography on a silica gel (eluent: petroleum ether: ethyl acetate) to give the pure products.

**(2S,3S,3aS,9bS)-3-Ethyl-2-methyl-2-phenyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-b]pyrrole-2,3-dicarboxylate (3a).** 33.2 mg (This template reaction was carried out at 0.1 mmol scale and flash column chromatography eluent, petroleum ether to petroleum ether / ethyl acetate = 15: 1), 94% yield; yellow solid; mp: 76-78°C;  $[\alpha]_D^{20} = -7.95^\circ$  ( $c = 0.088$ , EtOAc);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 1.35 (t,  $J= 7.2$  Hz, 3H), 2.52-2.62 (m, 1H), 3.21 (d,  $J= 11.6$  Hz, 1H), 3.31 (s, 1H), 3.63 (s, 3H), 3.68 (bs, 1H), 4.07 (dd,  $J_1= 10.2$  Hz,  $J_2= 11.6$  Hz, 1H), 4.17-4.32 (m, 2H), 4.50 (dd,  $J_1= 4.2$  Hz,  $J_2= 10.1$  Hz, 1H), 6.82-6.84 (m, 1H), 6.92-6.96 (m, 1H), 7.15-7.20 (m, 1H), 7.28-7.32 (m, 1H), 7.35-7.40 (m, 2H), 7.48-7.50 (m, 1H), 7.93-7.96 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz)  $\delta$  (ppm): 14.20, 49.46, 53.18, 58.78, 60.74, 61.52, 68.99, 77.62, 116.09, 120.32, 124.42, 124.93, 127.44, 127.80, 128.24, 128.72, 143.09, 153.24, 171.83, 172.19; IR (KBr):  $\gamma$  3448, 3284, 2960, 17336, 1610, 1489, 1456, 1253, 1179, 1092, 1036, 989, 837, 756, 699  $\text{cm}^{-1}$ ; HRMS (Micromass GCT-MS EI)

exact mass calcd for  $(C_{22}H_{23}NO_5)^+$  requires  $m/z$  381.1576, found  $m/z$  381.1575; Enantiomeric excess: 91%, determined by HPLC (Daicel Chirapak AD-H, hexane/ isopropanol = 90: 10, flow rate 1.0 mL/min):  $T_R$  = 9.55 min (major),  $T_R$  = 10.78 min (minor).

**(2S,3S,3aS,9bS)-3-Ethyl-2-methyl-2-(2-chlorophenyl)-1,2,3,3a,4,9b-hexahydrochromeno[4,3-b]pyrrole-2,3-dicarboxylate (3b).** 73.5 mg (Flash column chromatography eluent, petroleum ether / ethyl acetate = 10: 1), 89% yield;  $[\alpha]_D^{20}$  = +105.62° (c = 1.070, EtOAc);  $^1H$ -NMR ( $CDCl_3$ , 400 MHz)  $\delta$  (ppm): 1.26 (t,  $J$  = 7.1 Hz, 3H), 2.65-2.68 (m, 1H), 3.61 (d,  $J$  = 12.1 Hz, 1H), 3.64 (s, 3H), 3.74 (bs, 1H), 4.12-4.23 (m, 3H), 4.53 (dd,  $J_1$  = 4.2 Hz,  $J_2$  = 10.0 Hz, 1H), 6.83 (dd,  $J_1$  = 1.0 Hz,  $J_2$  = 8.2 Hz, 1H); 6.88-6.92 (m, 1H), 7.14-7.18 (m, 2H), 7.29-7.35 (m, 3H), 7.42-7.44 (m, 1H), 7.99 (dd,  $J_1$  = 1.8 Hz,  $J_2$  = 7.8 Hz, 1H);  $^{13}C$  NMR ( $CDCl_3$ , 101 MHz)  $\delta$  (ppm): 14.15, 46.10, 53.48, 55.01, 58.75, 61.50, 68.90, 76.33, 115.97, 120.37, 124.48, 124.60, 126.48, 128.62, 131.39, 134.81, 139.63, 153.06, 170.34, 172.92; IR (KBr):  $\gamma$  3448, 3287, 2929, 1739, 1609, 1458, 1330, 1266, 1176, 1038, 984, 848, 758, 747  $cm^{-1}$ ; HRMS (Micromass GCT-MS EI) exact mass calcd for  $(C_{22}H_{22}ClNO_5)^+$  requires  $m/z$  415.1187, found  $m/z$  415.1181; Enantiomeric excess: 87%, determined by HPLC (Daicel Chirapak AD-H, hexane/ isopropanol = 90: 10, flow rate 1.0 mL/min):  $T_R$  = 12.16 min (major),  $T_R$  = 20.42 min (minor).

**(2S,3S,3aS,9bS)-3-Ethyl-2-methyl-2-(3-chlorophenyl)-1,2,3,3a,4,9b-hexahydrochromeno[4,3-b]pyrrole-2,3-dicarboxylate (3c).** 71.2 mg (Flash column chromatography eluent, petroleum ether / ethyl acetate = 15: 1), 86% yield; white solid, mp: 103-105 °C;  $[\alpha]_D^{20}$  = -13.54° (c = 0.128, EtOAc);  $^1H$ -NMR ( $CDCl_3$ , 400 MHz)  $\delta$  (ppm): 1.36 (t,  $J$  = 7.1 Hz, 3H), 2.51-2.61 (m, 1H), 3.14 (d,  $J$  = 11.7 Hz, 1H), 3.31 (d,  $J$  = 12.5 Hz, 1H), 3.60 (d,  $J$  = 11.7 Hz, 1H), 3.64 (s, 3H), 4.07 (dd,  $J_1$  = 10.2 Hz,  $J_2$  = 11.5 Hz, 1H), 4.18-4.32 (m, 2H), 4.50 (dd,  $J_1$  = 4.2 Hz,  $J_2$  = 10.2 Hz, 1H), 6.83 (dd,  $J_1$  = 0.8 Hz,  $J_2$  = 8.2 Hz, 1H); 6.92-6.96 (m, 1H), 7.16-7.20 (m, 1H), 7.26-7.33 (m, 2H), 7.46-7.48 (m, 1H), 7.82-7.85 (m, 1H), 7.99 (t,  $J$  = 1.6 Hz, 1H);  $^{13}C$  NMR ( $CDCl_3$ , 101 MHz)  $\delta$  (ppm): 14.17, 49.27, 53.37, 58.88, 60.76, 61.66, 68.89, 77.21, 116.14, 120.38, 124.12, 124.90, 125.90, 127.67, 129.50, 134.21, 145.25, 153.23, 171.33, 171.79; IR (KBr):  $\gamma$  3296, 2986, 1739, 1597, 1570, 1488, 1458, 1432, 1371, 1250, 1207, 1181, 1036, 995, 833, 759, 698  $cm^{-1}$ ; HRMS (Micromass GCT-MS EI) exact mass calcd for  $(C_{22}H_{22}ClNO_5)^+$  requires  $m/z$  415.1187, found  $m/z$  415.1192; Enantiomeric excess: 92%, determined by HPLC (Daicel Chirapak OD-H, hexane/ isopropanol = 85: 15, flow rate 1.0 mL/min):  $T_R$  = 6.32 min (minor),  $T_R$  = 10.01 min (major).

**(2S,3S,3aS,9bS)-3-Ethyl-2-methyl-2-(4-chlorophenyl)-1,2,3,3a,4,9b-hexahydrochromeno[4,3-b]**

**pyrrole-2,3-dicarboxylate (3d).** 66.4 mg (Flash column chromatography eluent, petroleum ether / ethyl acetate = 15: 1), 80% yield; white solid, mp: 129-130 °C;  $[\alpha]_D^{20} = -5.76^\circ$  (c = 0.110, EtOAc);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 1.34 (t,  $J = 7.1$  Hz, 3H), 2.51-2.61 (m, 1H), 3.12 (d,  $J = 11.6$  Hz, 1H), 3.30 (d,  $J = 12.0$  Hz, 1H), 3.59 (d,  $J = 11.6$  Hz, 1H), 3.63 (s, 3H), 4.06 (dd,  $J_1 = 10.2$  Hz,  $J_2 = 11.6$  Hz, 1H), 4.17-4.31 (m, 2H), 4.49 (dd,  $J_1 = 4.2$  Hz,  $J_2 = 10.2$  Hz, 1H), 6.83 (dd,  $J_1 = 0.8$  Hz,  $J_2 = 8.2$  Hz, 1H); 7.16-7.20 (m, 1H), 7.32-7.35 (m, 2H), 7.45-7.47 (m, 1H), 7.88-7.92 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz)  $\delta$  (ppm): 14.20, 49.42, 53.31, 58.87, 60.89, 61.64, 68.92, 77.19, 116.15, 120.37, 124.15, 124.86, 128.36, 128.83, 128.99, 133.80, 141.66, 153.23, 171.46, 171.89; IR (KBr):  $\gamma$  3448, 3309, 2926, 1729, 1611, 1492, 1455, 1332, 1254, 1176, 1089, 979, 838, 770  $\text{cm}^{-1}$ ; HRMS (Micromass GCT-MS EI) exact mass calcd for  $(\text{C}_{22}\text{H}_{22}\text{ClNO}_5)^+$  requires m/z 415.1187, found m/z 415.1181; Enantiomeric excess: 90%, determined by HPLC (Daicel Chirapak OD-H, hexane/ isopropanol = 85: 15, flow rate 1.0 mL/min):  $T_R = 6.69$  min (minor),  $T_R = 9.31$  min (major).

**(2S,3S,3aS,9bS)-3-Ethyl-2-methyl-2-(2-fluorophenyl)-1,2,3,3a,4,9b-hexahydrochromeno[4,3-b] pyrrole-2,3-dicarboxylate (3e).** 74.5 mg (Flash column chromatography eluent, petroleum ether / ethyl acetate = 15: 1), 93% yield;  $[\alpha]_D^{20} = +16.67^\circ$  (c = 0.990, EtOAc);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 1.29 (t,  $J = 7.1$  Hz, 3H), 2.42-2.52 (m, 1H), 3.26 (dd,  $J_1 = 1.8$  Hz,  $J_2 = 11.9$  Hz, 1H), 3.44 (s, 1H), 3.69 (bs, 4H), 4.11-4.27 (m, 3H), 4.54 (dd,  $J_1 = 4.2$  Hz,  $J_2 = 10.2$  Hz, 1H), 6.83 (dd,  $J_1 = 0.9$  Hz,  $J_2 = 8.2$  Hz, 1H), 6.90-6.94 (m, 1H), 7.06-7.19 (m, 3H); 7.28-7.32 (m, 1H), 7.40-7.42 (m, 1H), 8.01-8.05 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz)  $\delta$  (ppm): 14.22, 48.39, 53.33, 58.38, 58.94, 61.28, 69.19, 74.03 (d,  $J = 2.4$  Hz), 116.07, 116.29 (d,  $J = 22.8$  Hz), 120.35, 123.84 (d,  $J = 3.3$  Hz), 124.29, 124.76, 128.09 (d,  $J = 3.4$  Hz), 128.73, 129.87 (d,  $J = 8.6$  Hz), 129.99 (d,  $J = 11.3$  Hz), 153.25, 161.46 (d,  $J = 247.0$  Hz), 171.11, 172.01; IR (KBr):  $\gamma$  3443, 3289, 2929, 1741, 1579, 1479, 1460, 1334, 1303, 1262, 1173, 1033, 979, 823, 763, 747  $\text{cm}^{-1}$ ; HRMS (Micromass GCT-MS EI) exact mass calcd for  $(\text{C}_{22}\text{H}_{22}\text{FNO}_5)^+$  requires m/z 399.1482, found m/z 399.1477; Enantiomeric excess: 94%, determined by HPLC (Daicel Chirapak OD-H, hexane/ isopropanol = 85: 15, flow rate 1.0 mL/min):  $T_R = 7.82$  min (minor),  $T_R = 13.65$  min (major).

**(2S,3S,3aS,9bS)-3-Ethyl-2-methyl-2-(3-fluorophenyl)-1,2,3,3a,4,9b-hexahydrochromeno[4,3-b] pyrrole-2,3-dicarboxylate (3f).** 65.1 mg (Flash column chromatography eluent, petroleum ether / ethyl acetate = 15: 1), 82% yield; white solid, mp: 64-66 °C;  $[\alpha]_D^{20} = -11.04^\circ$  (c = 0.154, EtOAc);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 1.36 (t,  $J = 7.2$  Hz, 3H), 2.51-2.61 (m, 1H), 3.15 (d,  $J = 11.6$  Hz, 1H), 3.61 (d,  $J = 11.1$  Hz, 1H), 3.64 (s, 3H), 4.07 (dd,  $J_1 = 10.2$  Hz,  $J_2 = 11.6$  Hz, 1H), 4.20-4.30

(m, 2H), 4.50 (dd,  $J_1 = 4.2$  Hz,  $J_2 = 10.2$  Hz, 1H), 6.83 (dd,  $J_1 = 0.9$  Hz,  $J_2 = 8.2$  Hz, 1H), 6.92-6.96 (m, 1H), 6.97-7.02 (m, 1H), 7.16-7.20 (m, 1H); 7.31-7.36 (m, 1H), 7.46-7.48 (m, 1H), 7.70-7.74 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz)  $\delta$  (ppm): 14.18, 49.33, 53.33, 58.87, 60.78, 61.65, 68.90, 77.27, 114.59 (d,  $J = 1.4$  Hz), 114.81, 116.14, 120.38, 123.24 (d,  $J = 2.8$  Hz), 124.14, 124.89, 128.82, 129.65 (d,  $J = 8.0$  Hz), 145.84 (d,  $J = 7.0$  Hz), 153.23, 162.77 (d,  $J = 243.6$  Hz), 171.36, 171.85; IR (KBr):  $\gamma$  3296, 2951, 1740, 1609, 1591, 1491, 1454, 1250, 1202, 1169, 1036, 995, 831, 755, 688  $\text{cm}^{-1}$ ; HRMS (Micromass GCT-MS EI) exact mass calcd for  $(\text{C}_{22}\text{H}_{22}\text{FNO}_5)^+$  requires  $m/z$  399.1482, found  $m/z$  399.1490; Enantiomeric excess: 90%, determined by HPLC (Daicel Chirapak OD-H, hexane/ isopropanol = 85: 15, flow rate 1.0 mL/min):  $T_R = 6.13$  min (minor),  $T_R = 9.92$  min (major).

**(2*S*,3*S*,3*aS*,9*bS*)-3-Ethyl-2-methyl-2-(4-fluorophenyl)-1,2,3,3*a*,4,9*b*-hexahydrochromeno[4,3-*b*]pyrrole-2,3-dicarboxylate (3g).** 67 mg (Flash column chromatography eluent, petroleum ether / ethyl acetate = 15: 1), 84% yield; white solid, mp: 124-126 °C;  $[\alpha]_D^{20} = -8.46^\circ$  ( $c = 0.134$ , EtOAc);  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 1.35 (t,  $J = 7.1$  Hz, 3H), 2.52-2.61 (m, 1H), 3.14 (d,  $J = 11.6$  Hz, 1H), 3.31 (d,  $J = 11.4$  Hz, 1H), 3.59 (bs, 1H), 3.63 (s, 3H), 4.07 (dd,  $J_1 = 10.2$  Hz,  $J_2 = 11.6$  Hz, 1H), 4.17-4.32 (m, 2H), 4.49 (dd,  $J_1 = 4.2$  Hz,  $J_2 = 10.1$  Hz, 1H), 6.83 (dd,  $J_1 = 0.8$  Hz,  $J_2 = 8.2$  Hz, 1H); 6.92-6.96 (m, 1H), 7.02-7.08 (m, 2H), 7.16-7.20 (m, 1H), 7.46-7.48 (m, 2H), 7.91-7.96 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz)  $\delta$  (ppm): 14.19, 49.48, 53.24, 58.81, 60.99, 61.60, 68.93, 77.17, 115.00 (d,  $J = 21.3$  Hz), 116.14, 120.36, 124.22, 124.87, 128.80, 129.29 (d,  $J = 8.0$  Hz), 138.80 (d,  $J = 3.0$  Hz), 153.24, 162.43 (d,  $J = 245.3$  Hz), 171.66, 171.98; IR (KBr):  $\gamma$  3438, 3277, 2921, 1735, 1610, 1509, 1489, 1461, 1255, 1088, 1038, 994, 848, 815, 758  $\text{cm}^{-1}$ ; HRMS (Micromass GCT-MS EI) exact mass calcd for  $(\text{C}_{22}\text{H}_{22}\text{FNO}_5)^+$  requires  $m/z$  399.1482, found  $m/z$  399.1489; Enantiomeric excess: 91%, determined by HPLC (Daicel Chirapak OD-H, hexane/ isopropanol = 85: 15, flow rate 1.0 mL/min):  $T_R = 6.18$  min (minor),  $T_R = 14.41$  min (major).

**(2*S*,3*S*,3*aS*,9*bS*)-3-Ethyl-2-methyl-2-(4-methoxyphenyl)-1,2,3,3*a*,4,9*b*-hexahydrochromeno[4,3-*b*]pyrrole-2,3-dicarboxylate (3h).** 53.3 mg (Flash column chromatography eluent, petroleum ether / ethyl acetate = 15: 1), 65% yield; colorless oil;  $[\alpha]_D^{20} = -1.13^\circ$  ( $c = 0.800$ , EtOAc);  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 1.34 (t,  $J = 7.2$  Hz, 3H), 2.50-2.60 (m, 1H), 3.16 (d,  $J = 11.6$  Hz, 1H), 3.62 (s, 1H), 3.67 (bs, 1H), 3.81 (s, 3H), 4.07 (dd,  $J_1 = 10.2$  Hz,  $J_2 = 11.6$  Hz, 1H), 4.16-4.31 (m, 2H), 4.49 (dd,  $J_1 = 4.2$  Hz,  $J_2 = 10.1$  Hz, 1H), 6.83 (dd,  $J_1 = 0.9$  Hz,  $J_2 = 8.2$  Hz, 1H), 6.88-6.95 (m, 3H), 7.15-7.19 (m, 1H), 7.47-7.49 (m, 1H); 7.84-7.88 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz)  $\delta$

(ppm): 14.21, 49.52, 53.12, 55.27, 58.74, 60.85, 61.47, 69.01, 77.34, 113.56, 116.08, 120.30, 124.48, 124.92, 128.62, 128.69, 135.09, 153.26, 159.23, 172.03, 172.25; IR (KBr):  $\gamma$  3451, 3272, 2926, 1738, 1611, 1579, 1510, 1486, 1460, 1246, 1180, 1025, 991, 846, 756  $\text{cm}^{-1}$ ; HRMS (Micromass GCT-MS EI) exact mass calcd for  $(\text{C}_{23}\text{H}_{25}\text{NO}_6)^+$  requires  $m/z$  411.1682, found  $m/z$  411.1679; Enantiomeric excess: 81%, determined by HPLC (Daicel Chirapak OD-H, hexane/ isopropanol = 70: 30, flow rate 1.0 mL/min):  $T_R = 7.36$  min (minor),  $T_R = 15.04$  min (major).

**(2S,3S,3aS,9bS)-3-Ethyl-2-methyl-8-chloro-2-phenyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-b]pyrrole-2,3-dicarboxylate (5a).** 49.7 mg (Flash column chromatography eluent, petroleum ether / ethyl acetate = 4: 1), 60% yield; colorless oil;  $[\alpha]_D^{20} = -7.09^\circ$  ( $c = 0.094$ , EtOAc);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 1.35 (t,  $J = 7.1$  Hz, 3H), 2.48-2.57 (m, 1H), 3.20 (d,  $J = 11.6$  Hz, 1H), 3.28 (d,  $J = 8.7$  Hz, 1H), 3.59 (d,  $J = 7.9$  Hz, 1H), 3.63 (s, 3H), 4.04 (dd,  $J_1 = 10.2$  Hz,  $J_2 = 11.6$  Hz, 1H), 4.18-4.32 (m, 2H), 4.49 (dd,  $J_1 = 4.3$  Hz,  $J_2 = 10.2$  Hz, 1H), 6.75 (d,  $J = 8.7$  Hz, 1H), 7.10-7.13 (m, 1H), 7.28-7.32 (m, 1H), 7.35-7.40 (m, 2H), 7.47 (dd,  $J_1 = 1.1$  Hz,  $J_2 = 2.6$  Hz, 1H), 7.92-7.94 (m, 2H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 101 MHz)  $\delta$  (ppm): 14.20, 49.07, 53.25, 58.48, 60.54, 61.60, 69.07, 77.54, 117.48, 124.86, 125.20, 125.77, 127.39, 127.90, 128.29, 128.60, 142.82, 151.85, 171.69, 172.00; IR (KBr):  $\gamma$  3292, 2981, 1738, 1600, 1483, 1432, 1373, 1255, 1205, 1182, 1101, 1035, 991, 817, 745, 701  $\text{cm}^{-1}$ ; HRMS (Micromass GCT-MS EI) exact mass calcd for  $(\text{C}_{22}\text{H}_{22}\text{ClNO}_5)^+$  requires  $m/z$  415.1187, found  $m/z$  415.1186; Enantiomeric excess: 53%, determined by HPLC (Daicel Chirapak IA-H, hexane/ isopropanol = 95: 5, flow rate 1.0 mL/min):  $T_R = 10.54$  min (minor),  $T_R = 11.30$  min (major).

**(2S,3S,3aS,9bS)-3-Ethyl-2-methyl-8-methoxy-2-phenyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-b]pyrrole-2,3-dicarboxylate (5b).** 45.8 mg (Flash column chromatography eluent, petroleum ether / ethyl acetate = 15: 1), 56% yield; colorless oil;  $[\alpha]_D^{20} = -12.14^\circ$  ( $c = 0.626$ , EtOAc);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 1.35 (t,  $J = 7.2$  Hz, 3H), 2.50-2.60 (m, 1H), 3.20 (d,  $J = 11.6$  Hz, 1H), 3.30 (s, 1H), 3.63 (bs, 4H), 3.81 (s, 3H), 4.01 (dd,  $J_1 = 10.2$  Hz,  $J_2 = 11.6$  Hz, 1H), 4.17-4.32 (m, 2H), 4.45 (dd,  $J_1 = 4.2$  Hz,  $J_2 = 10.1$  Hz, 1H), 6.74-6.75 (m, 2H), 7.05-7.06 (m, 1H), 7.28-7.32 (m, 1H), 7.36-7.40 (m, 2H); 7.94-7.96 (m, 2H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 101 MHz)  $\delta$  (ppm): 14.20, 49.62, 53.19, 55.90, 58.99, 60.75, 61.51, 68.65, 77.56, 109.71, 114.74, 116.77, 124.77, 127.42, 127.82, 128.25, 143.03, 147.09, 153.50, 171.82, 172.20; IR (KBr):  $\gamma$  3296, 2956, 1732, 1601, 1492, 1432, 1370, 1256, 1203, 1036, 997, 861, 817, 737, 699  $\text{cm}^{-1}$ ; HRMS (Micromass GCT-MS EI) exact mass calcd for  $(\text{C}_{23}\text{H}_{25}\text{NO}_6)^+$  requires  $m/z$  411.1682, found  $m/z$  411.1675; Enantiomeric excess: 68%,



determined by HPLC (Daicel Chirapak AD-H, hexane/ isopropanol = 90: 10, flow rate 1.0 mL/min):  $T_R = 18.53$  min (minor),  $T_R = 21.65$  min (major).

**(2S,3S,3aS,9bS)-3-Ethyl-2-methyl-7-methoxy-2-phenyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-b]pyrrole-2,3-dicarboxylate (5c).** 34.6 mg (Flash column chromatography eluent, petroleum ether / ethyl acetate = 10: 1), 42% yield; colorless oil;  $[\alpha]_D^{20} = -13.06^\circ$  (c = 0.444, EtOAc);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 1.35 (t,  $J = 7.1$  Hz, 3H), 2.47-2.57 (m, 1H), 3.19 (d,  $J = 11.6$  Hz, 1H), 3.24 (s, 1H), 3.57 (d,  $J = 11.7$  Hz, 1H), 3.62 (s, 3H), 3.76 (s, 3H), 4.04 (dd,  $J_1 = 10.2$  Hz,  $J_2 = 11.6$  Hz, 1H), 4.17-4.32 (m, 2H), 4.48 (dd,  $J_1 = 4.2$  Hz,  $J_2 = 10.1$  Hz, 1H), 6.41 (d,  $J = 2.4$  Hz, 1H), 6.51 (dd,  $J_1 = 2.5$  Hz,  $J_2 = 8.4$  Hz, 1H), 7.27-7.31 (m, 1H), 7.35-7.39 (m, 3H); 7.93-7.96 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz)  $\delta$  (ppm): 14.20, 49.92, 53.16, 55.34, 58.48, 60.62, 61.49, 69.08, 77.69, 101.66, 106.47, 116.90, 125.60, 127.43, 127.77, 128.21, 143.15, 154.30, 160.25, 171.84, 172.23; IR (KBr):  $\gamma$  3296, 2956, 1738, 1622, 1579, 1508, 1443, 1373, 1322, 1257, 1159, 1036, 856, 793, 699, 635  $\text{cm}^{-1}$ ; HRMS (Micromass GCT-MS EI) exact mass calcd for  $(\text{C}_{23}\text{H}_{25}\text{NO}_6)^+$  requires m/z 411.1682, found m/z 411.1675; Enantiomeric excess: 90%, determined by HPLC (Daicel Chirapak OD-H, hexane/ isopropanol = 95: 5, flow rate 1.0 mL/min):  $T_R = 10.30$  min (major),  $T_R = 13.52$  min (minor).

**(2S,3S,3aS,9bS)-3-Ethyl-2-methyl-6-methoxy-2-phenyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-b]pyrrole-2,3-dicarboxylate (5d).** 44 mg (Flash column chromatography eluent, petroleum ether / ethyl acetate = 8: 1), 54% yield; colorless oil;  $[\alpha]_D^{20} = -11.29^\circ$  (c = 0.558, EtOAc);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 1.34 (t,  $J = 7.1$  Hz, 3H), 2.55-2.64 (m, 1H), 3.21 (d,  $J = 11.6$  Hz, 1H), 3.30 (s, 1H), 3.62 (s, 3H), 3.69 (d,  $J = 19.8$  Hz, 1H), 3.87 (s, 3H), 4.13 (dd,  $J_1 = 10.2$  Hz,  $J_2 = 16.7$  Hz, 1H), 4.16-4.32 (m, 2H), 4.64 (dd,  $J_1 = 4.2$  Hz,  $J_2 = 10.1$  Hz, 1H), 6.82-6.84 (m, 1H), 6.89-6.93 (m, 1H), 7.12-7.15 (m, 2H), 7.27-7.31 (m, 1H); 7.35-7.39 (m, 2H), 7.93-7.96 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz)  $\delta$  (ppm): 14.18, 49.23, 53.17, 55.93, 58.66, 60.80, 61.52, 69.49, 77.53, 110.92, 116.94, 120.17, 125.10, 127.44, 127.80, 128.23, 142.28, 143.06, 147.96, 171.84, 172.06; IR (KBr):  $\gamma$  3430, 3292, 2929, 1738, 1581, 1486, 1460, 1254, 1208, 1179, 1085, 1070, 1023, 993, 853, 740, 701  $\text{cm}^{-1}$ ; HRMS (Micromass GCT-MS EI) exact mass calcd for  $(\text{C}_{23}\text{H}_{25}\text{NO}_6)^+$  requires m/z 411.1682, found m/z 411.1676; Enantiomeric excess: 70%, determined by HPLC (Daicel Chirapak AD-H, hexane/ isopropanol = 97: 3, flow rate 1.0 mL/min):  $T_R = 30.68$  min (major),  $T_R = 56.82$  min (minor).

**(2S,3S,3aS,9bS)-3-Ethyl-2-methyl-6-ethoxy-2-phenyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-b]**

**pyrrole-2,3-dicarboxylate (5e).** 64.4 mg (Flash column chromatography eluent, petroleum ether / ethyl acetate = 10: 1), 76% yield; colorless oil;  $[\alpha]_D^{20} = -9.85^\circ$  ( $c = 0.088$ , EtOAc);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 1.34 (t,  $J = 7.1$  Hz, 3H), 1.45 (t,  $J = 7.0$  Hz, 3H), 2.54-2.64 (m, 1H), 3.21 (d,  $J = 11.6$  Hz, 1H), 3.30 (s, 1H), 3.62 (s, 3H), 3.66 (bs, 1H), 4.06-4.16 (m, 3H), 4.18-4.31 (m, 2H), 4.64 (dd,  $J_1 = 4.2$  Hz,  $J_2 = 10.1$  Hz, 1H), 6.81-6.90 (m, 2H), 7.11-7.14 (m, 1H), 7.27-7.31 (m, 1H), 7.35-7.39 (m, 2H), 7.93-7.96 (m, 2H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 101 MHz)  $\delta$  (ppm): 14.20, 14.82, 49.25, 53.16, 58.77, 60.84, 61.51, 64.33, 69.44, 77.56, 112.38, 116.92, 120.10, 125.22, 127.45, 127.79, 128.23, 142.58, 143.10, 147.24, 171.84, 172.09; IR (KBr):  $\gamma$  3434, 3292, 2977, 1739, 1716, 1579, 1457, 1335, 1250, 1183, 1087, 1063, 984, 850, 754, 725, 702  $\text{cm}^{-1}$ ; HRMS (Micromass GCT-MS EI) exact mass calcd for  $(\text{C}_{24}\text{H}_{27}\text{NO}_6)^+$  requires  $m/z$  425.1838, found  $m/z$  425.1843; Enantiomeric excess: 78%, determined by HPLC (Daicel Chirapak AD-H, hexane/ isopropanol = 90: 10, flow rate 1.0 mL/min):  $T_R = 10.50$  min (major),  $T_R = 12.84$  min (minor).

**(2S,3S,3aS,9bS)-3-Ethyl-2-methyl-6-fluoro-2-phenyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-b]**

**pyrrole-2,3-dicarboxylate (5f).** 50.6 mg (Flash column chromatography eluent, petroleum ether / ethyl acetate = 10: 1), 63% yield; white solid; mp: 89-91  $^\circ\text{C}$ ;  $[\alpha]_D^{20} = -9.06^\circ$  ( $c = 0.114$ , EtOAc);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 1.35 (t,  $J = 7.1$  Hz, 3H), 2.53-2.63 (m, 1H), 3.23 (d,  $J = 11.6$  Hz, 1H), 3.32 (s, 1H), 3.63 (s, 3H), 3.68 (bs, 1H), 4.12 (dd,  $J_1 = 10.2$  Hz,  $J_2 = 11.7$  Hz, 1H), 4.18-4.33 (m, 2H), 4.62 (dd,  $J_1 = 4.3$  Hz,  $J_2 = 10.2$  Hz, 1H), 6.84-6.89 (m, 1H), 6.97-7.02 (m, 1H), 7.26-7.29 (m, 1H), 7.30-7.32 (m, 1H); 7.35-7.40 (m, 2H), 7.92-7.95 (m, 2H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 101 MHz)  $\delta$  (ppm): 14.19, 49.11, 53.24, 58.37 (d,  $J = 3.1$  Hz), 60.59, 61.62, 69.53, 77.45, 115.45 (d,  $J = 18.1$  Hz), 120.00, 120.02 (d,  $J = 3.3$  Hz), 126.86 (d,  $J = 1.6$  Hz), 127.40, 127.89, 128.28, 141.24 (d,  $J = 10.2$  Hz), 142.85, 151.25 (d,  $J = 243.6$  Hz), 171.76, 171.96; IR (KBr):  $\gamma$  3305, 2956, 2844, 1737, 1579, 1480, 1468, 1430, 1382, 1334, 1274, 1255, 1172, 1068, 983, 848, 785, 739, 698  $\text{cm}^{-1}$ ; HRMS (Micromass GCT-MS EI) exact mass calcd for  $(\text{C}_{22}\text{H}_{22}\text{FNO}_5)^+$  requires  $m/z$  399.1482, found  $m/z$  399.1485; Enantiomeric excess: 68%, determined by HPLC (Daicel Chirapak OD-H, hexane/ isopropanol = 95: 5, flow rate 1.0 mL/min):  $T_R = 8.97$  min (minor),  $T_R = 36.44$  min (major).

**(2S,3S,3aS,9bS)-Dimethyl-2-phenyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-b]pyrrole-2,3-dicar**

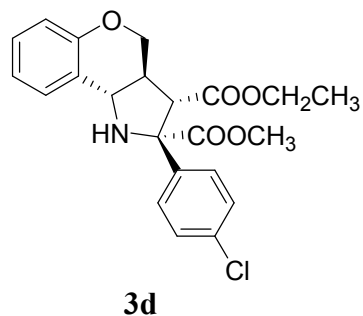
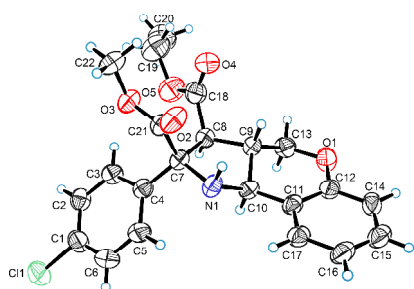
**boxylate (5g).** 46 mg (Flash column chromatography eluent, petroleum ether / ethyl acetate = 10: 1), 84% yield; white solid; mp: 124-126  $^\circ\text{C}$ ;  $[\alpha]_D^{20} = -2.77^\circ$  ( $c = 0.108$ , EtOAc);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 2.52-2.61 (m, 1H), 3.23 (d,  $J = 11.6$  Hz, 1H), 3.32 (s, 1H), 3.63 (s, 3H), 3.68 (bs, 1H), 3.80 (s, 3H), 4.05 (dd,  $J_1 = 10.2$  Hz,  $J_2 = 11.6$  Hz, 1H), 4.49 (dd,  $J_1 = 4.2$  Hz,  $J_2 = 10.1$  Hz, 1H),

6.81-6.83 (m, 1H), 6.91-6.95 (m, 1H), 7.15-7.19 (m, 1H), 7.28-7.32 (m, 1H), 7.36-7.40 (m, 2H), 7.48-7.50 (m, 1H), 7.93-7.96 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz)  $\delta$  (ppm): 49.46, 52.52, 53.28, 58.79, 60.55, 68.90, 77.78, 116.10, 120.33, 124.36, 124.92, 127.42, 127.86, 128.28, 128.74, 142.99, 153.24, 171.79, 172.71; IR (KBr):  $\gamma$  3460, 3279, 2956, 1735, 1611, 1581, 1490, 1455, 1432, 1254, 1182, 1036, 989, 843, 761, 701  $\text{cm}^{-1}$ ; HRMS (Micromass GCT-MS EI) exact mass calcd for  $(\text{C}_{21}\text{H}_{21}\text{NO}_5)^+$  requires  $m/z$  367.1420, found  $m/z$  367.1416; Enantiomeric excess: 74%, determined by HPLC (Daicel Chirapak AD-H, hexane/ isopropanol = 90: 10, flow rate 1.0 mL/min):  $T_R$  = 9.89 min (major),  $T_R$  = 11.22 min (minor).

### References:

1. (a) Chen, X. H.; Wei, Q.; Luo, S. W.; Xiao, H.; Gong, L. Z. *J. Am. Chem. Soc.* **2009**, *131*, 13819. Other group had also been reported this catalyst, see: (b) Storer, R. I.; Carrera, D. E.; Ni, Y.; MacMillan, D.W. C. *J. Am. Chem. Soc.* **2006**, *128*, 84. (c) Reuping, M.; Sugiono, E.; Azap, C.; Theissmann, T.; Bolte, M. *Org. Lett.* **2005**, *7*, 3781. (d) Hoffman, S.; Seayad, A. M.; List, B. *Angew. Chem.Int. Ed.* **2005**, *44*, 7424.

### X-ray single crystal data for **3d** :

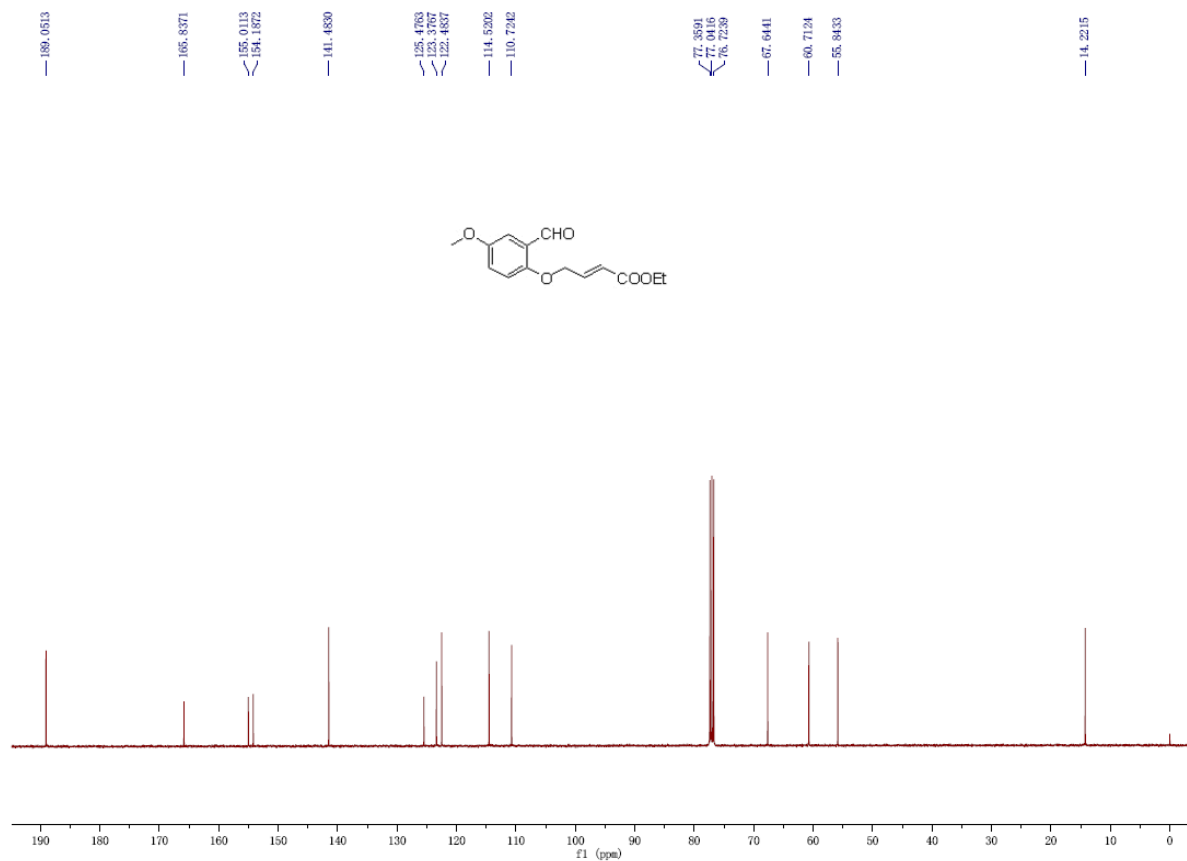
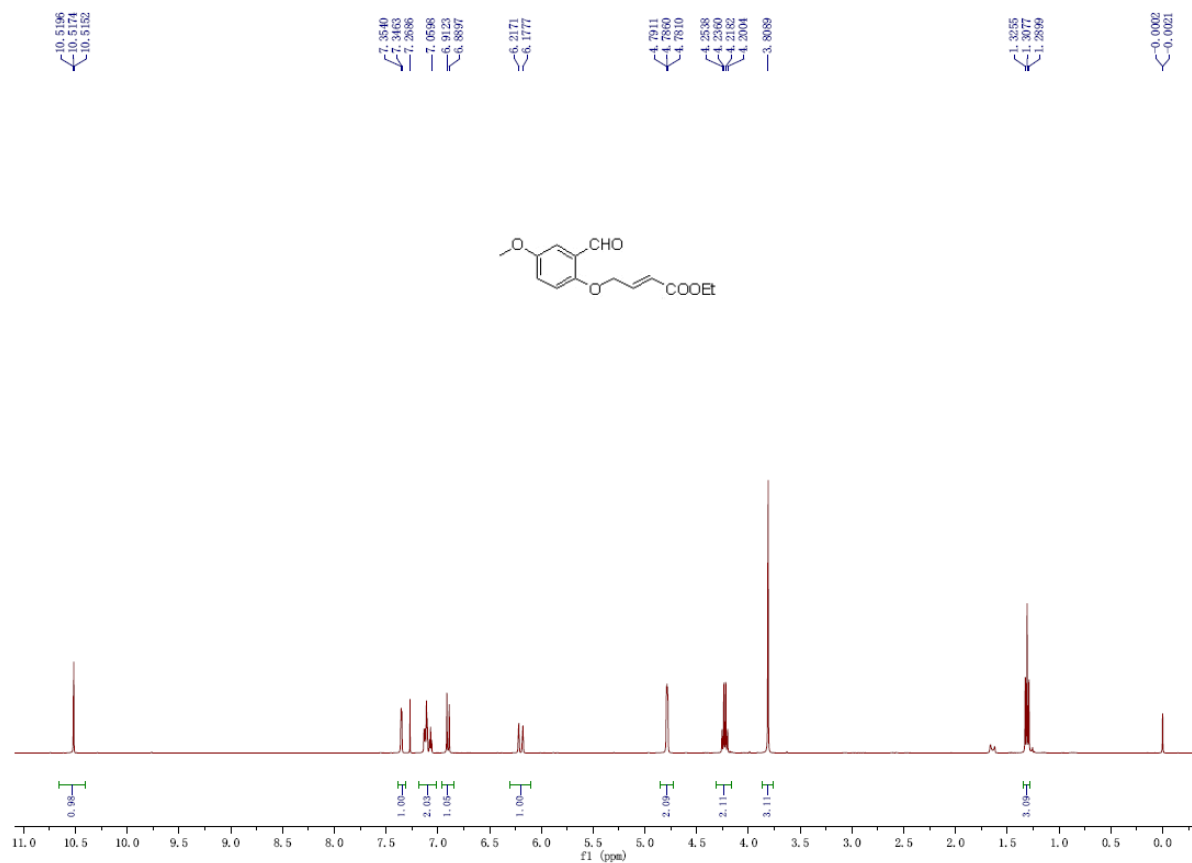


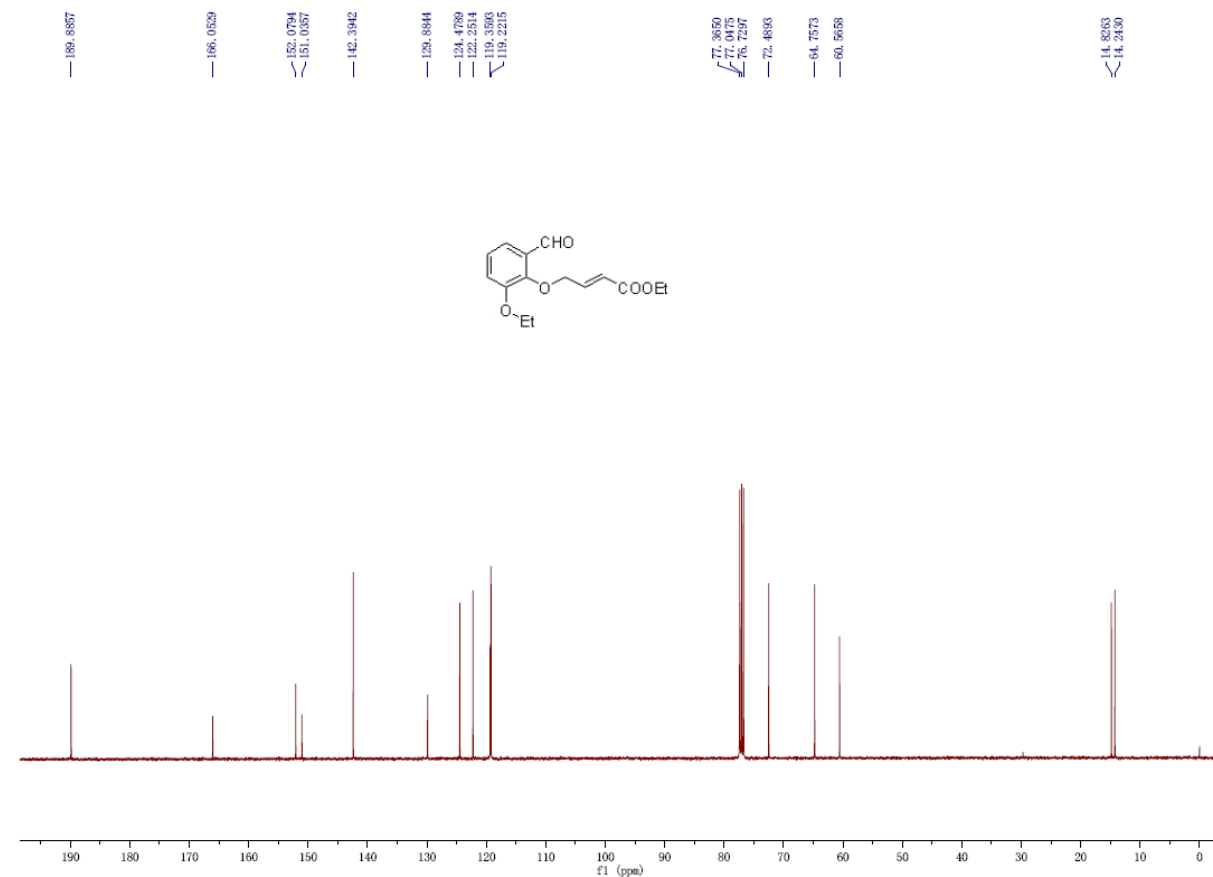
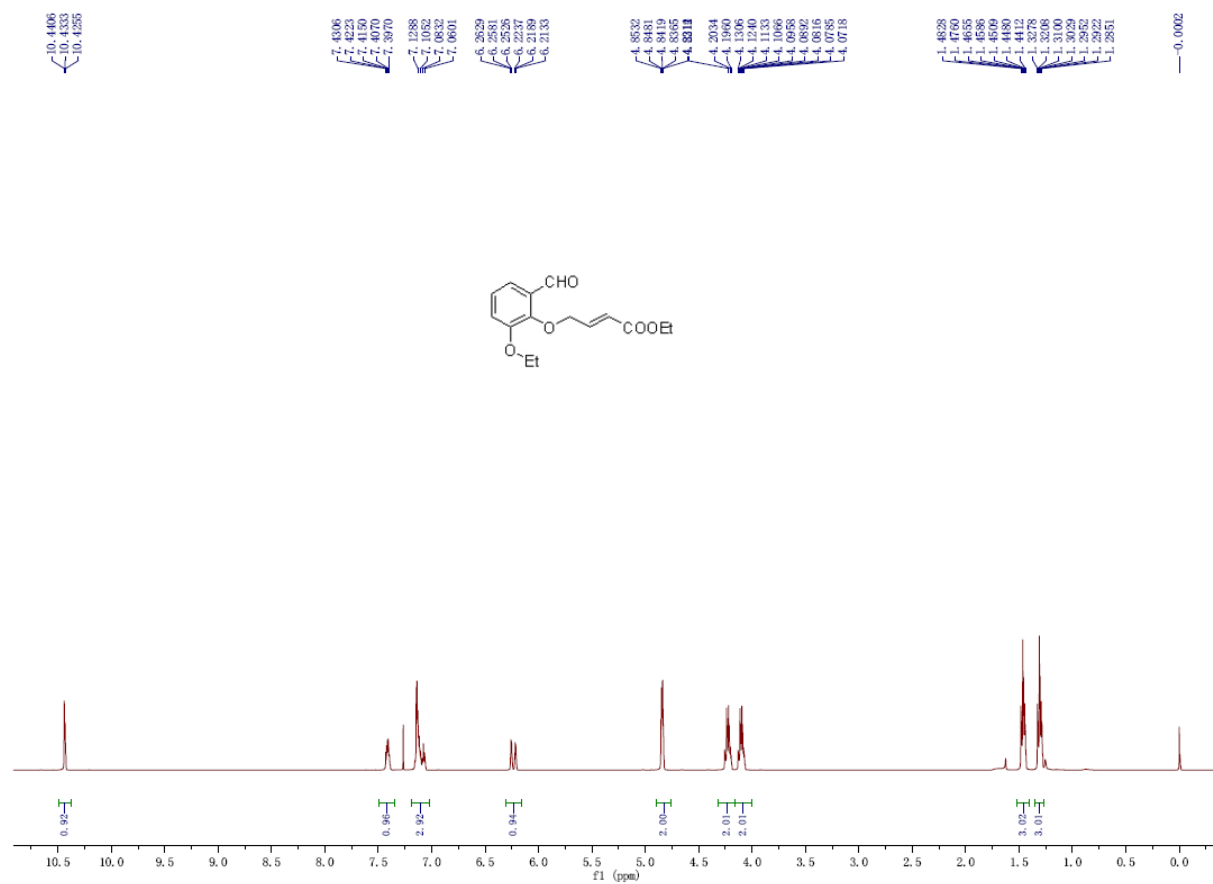
X-ray crystal structure of **3d** with ellipsoids set at 45% probability. Hydrogen atoms are omitted for clarity.

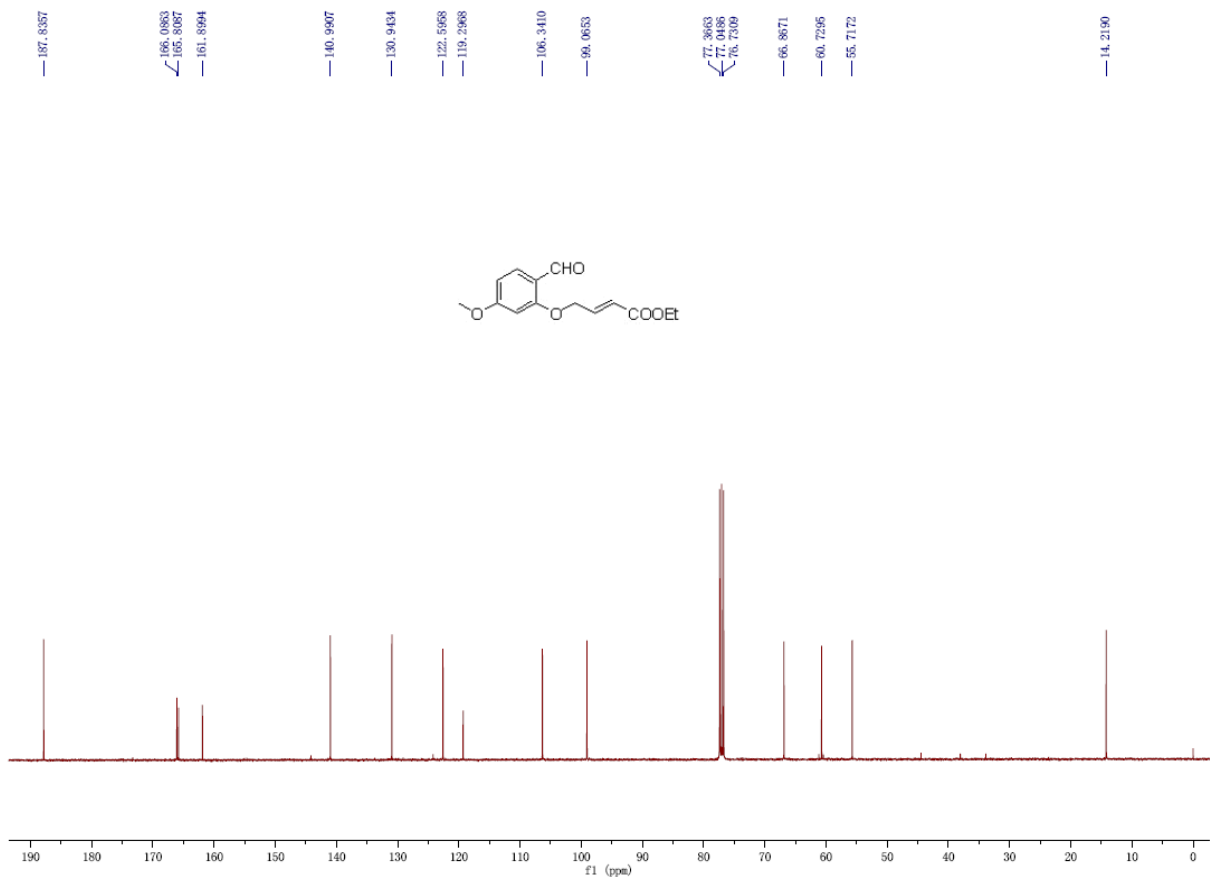
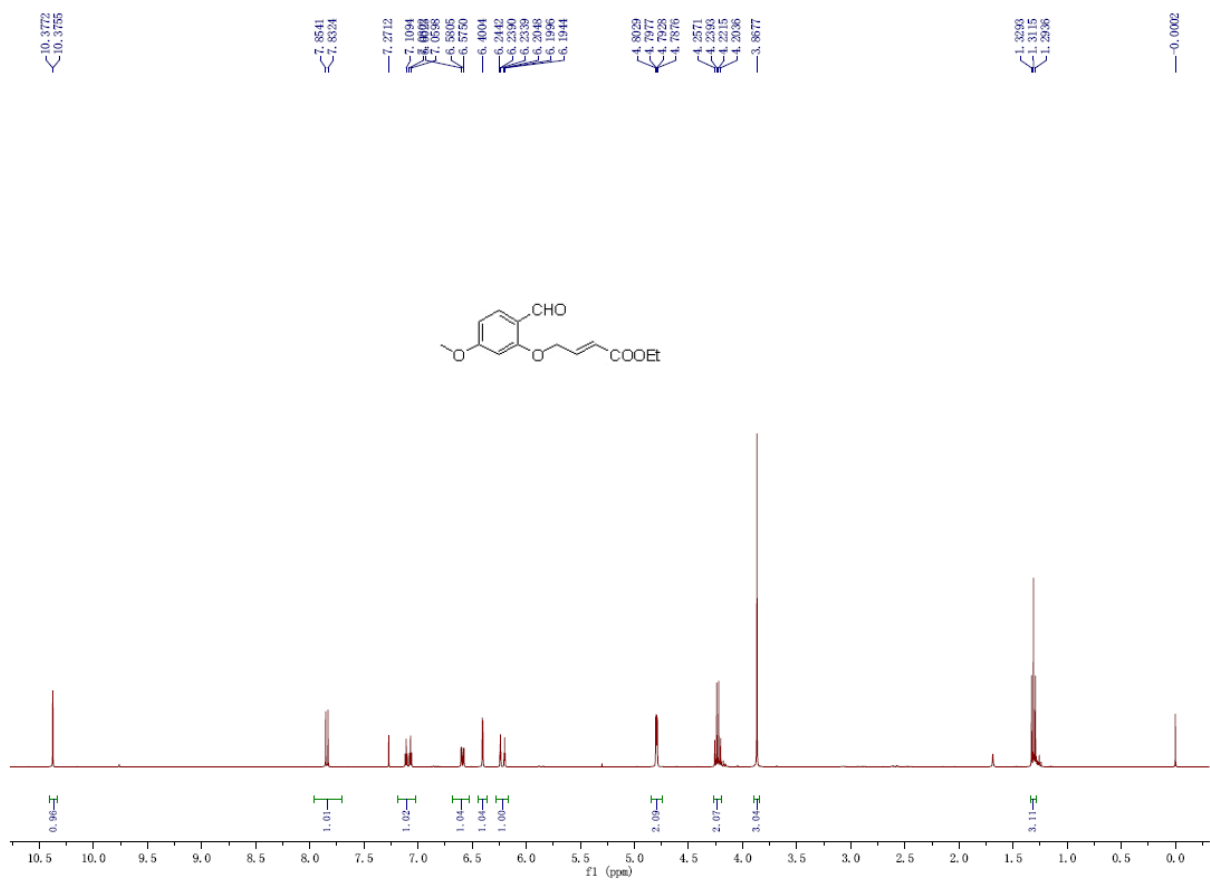
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Z	2
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b, Å	6.8695(13)
c, Å	15.6735(17)
$\alpha$ , °	90.00
$\beta$ , °	92.706
$\gamma$ , °	90.00
V, Å <sup>3</sup>	1033.6(2)
T, K	291
$\rho$ , g/cm <sup>3</sup>	1.336

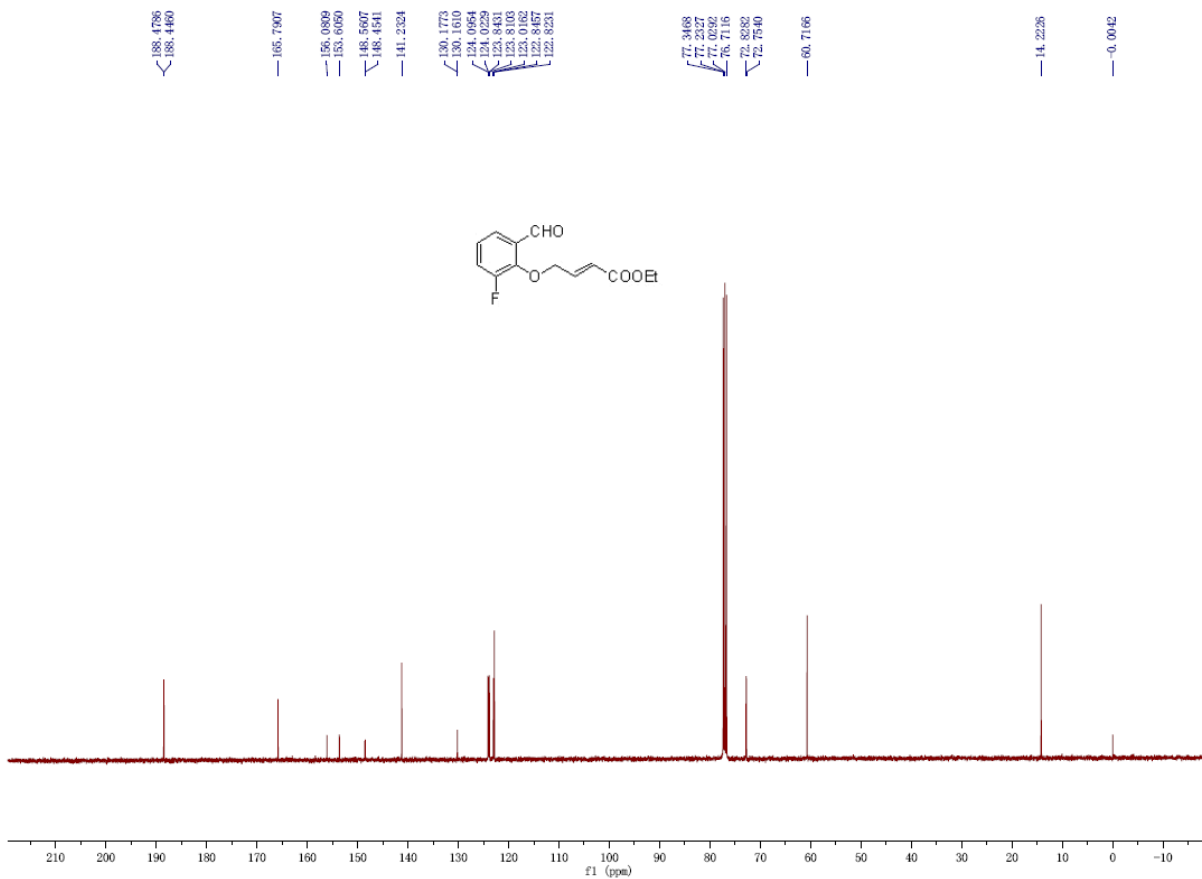
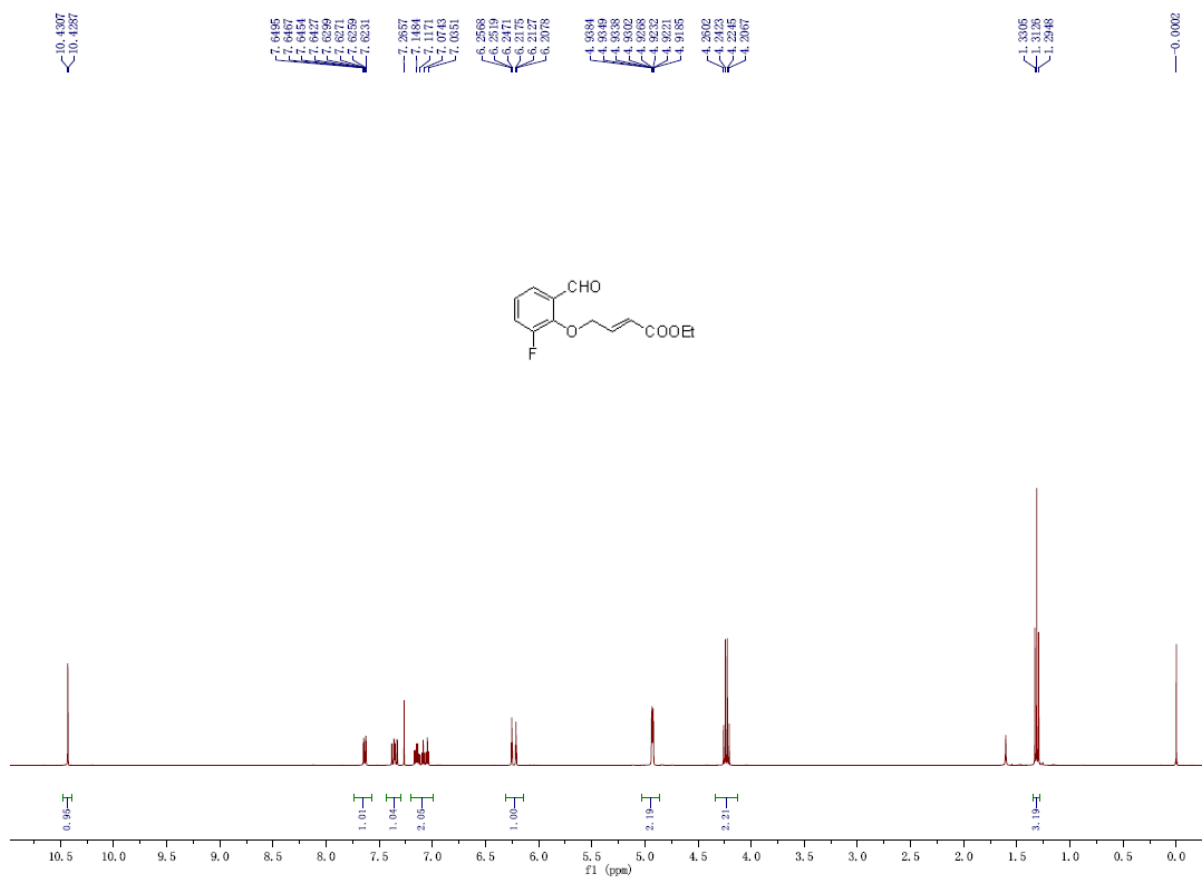
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### Selected NMR and HPLC spectra

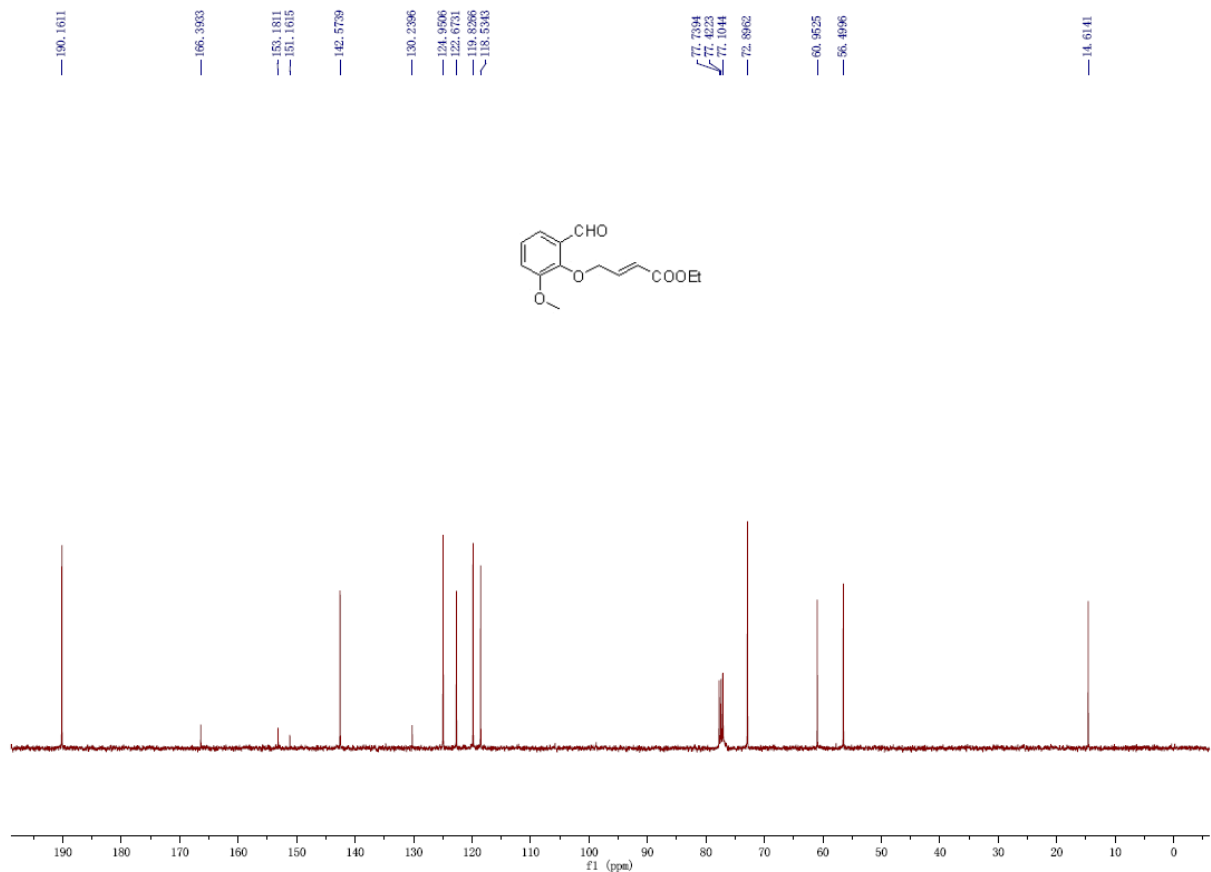
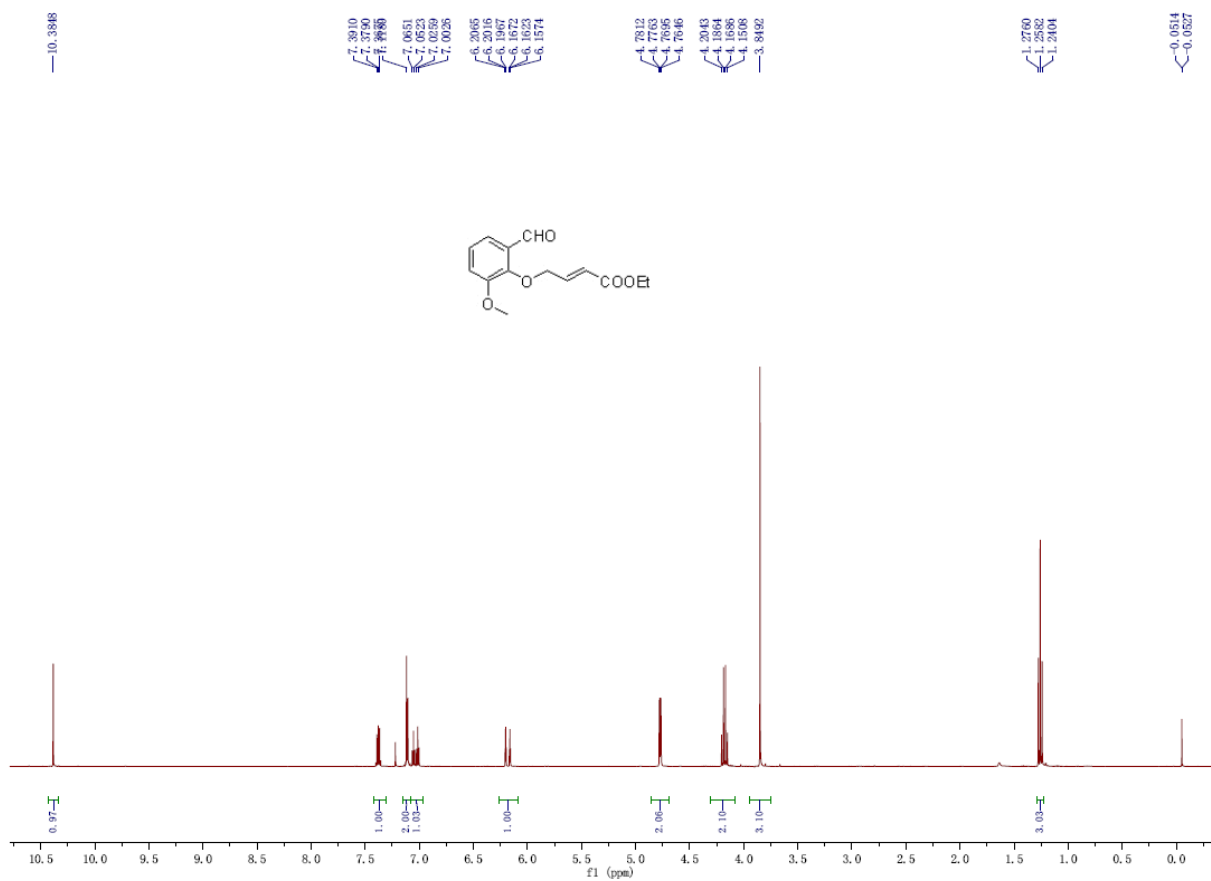


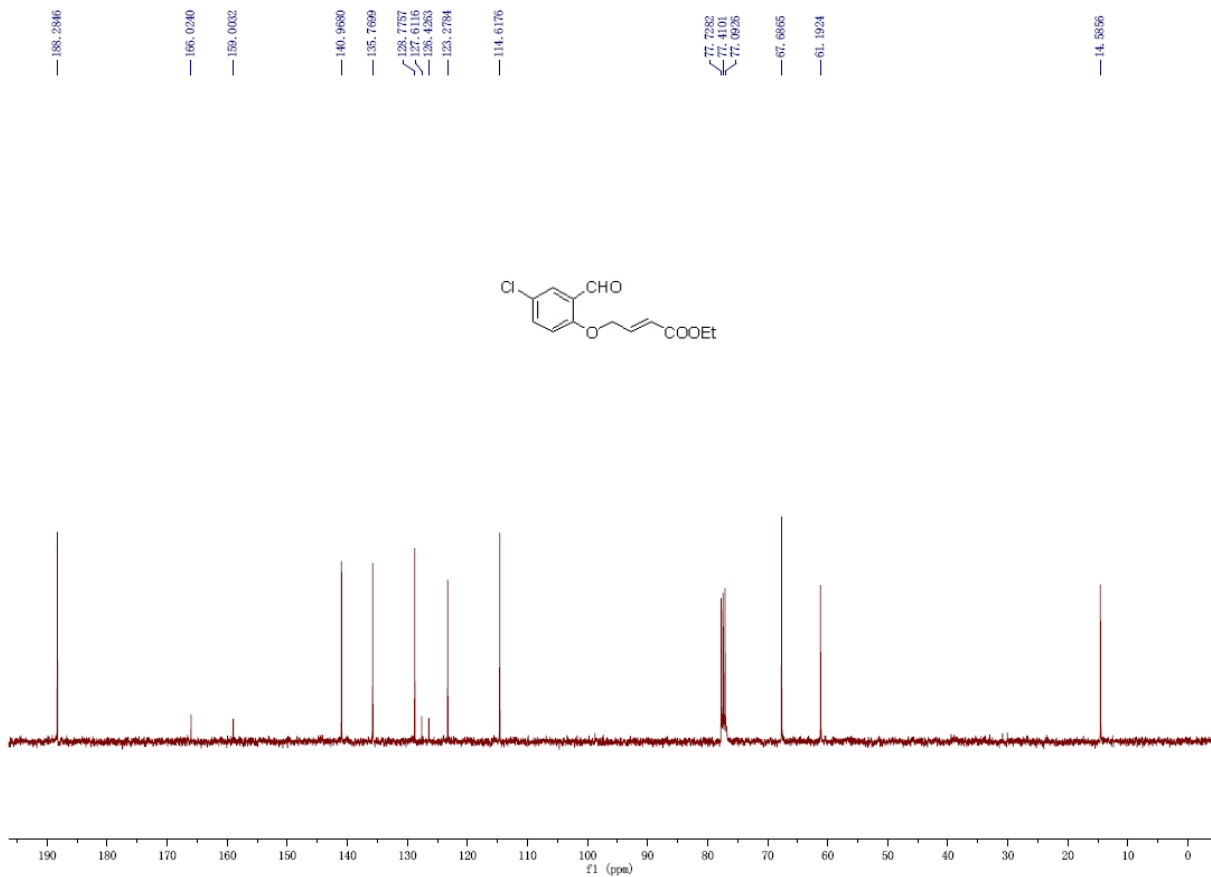
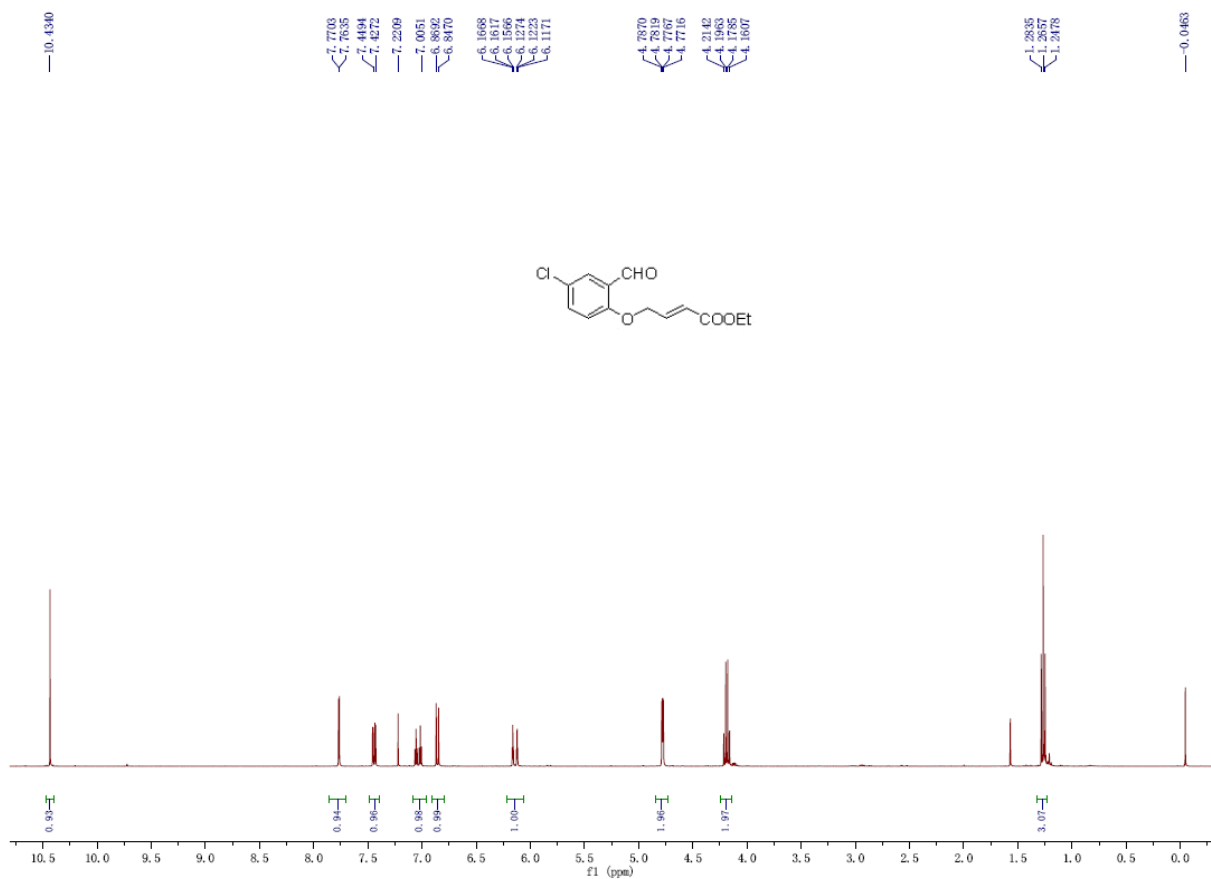


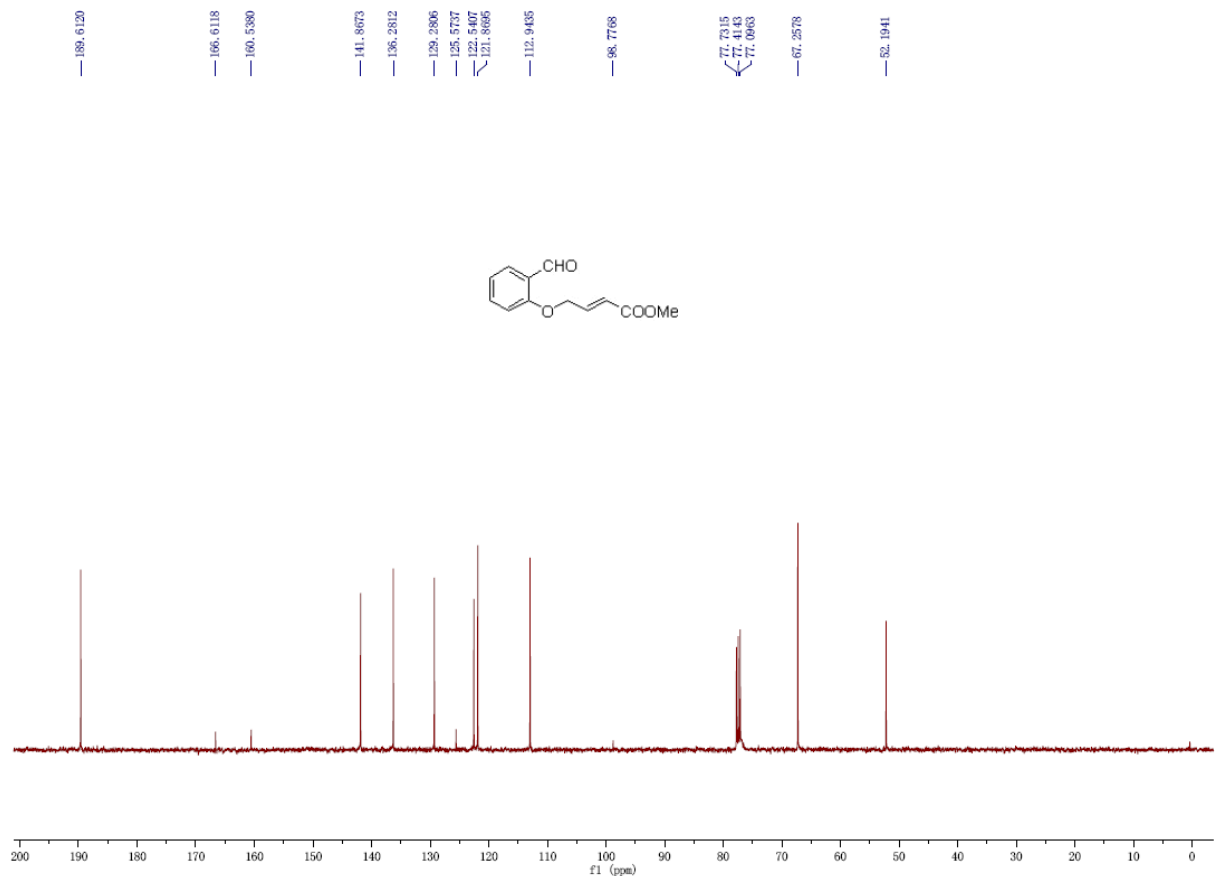
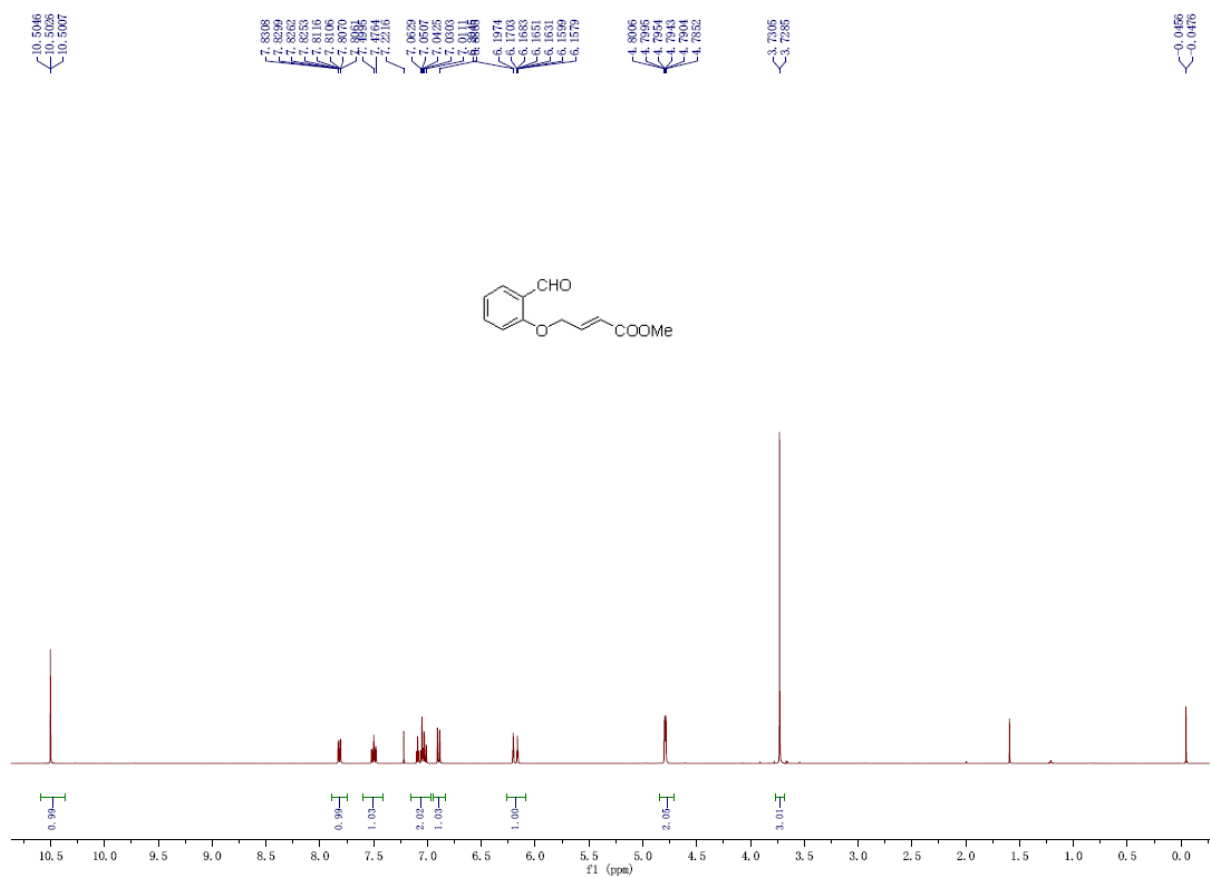


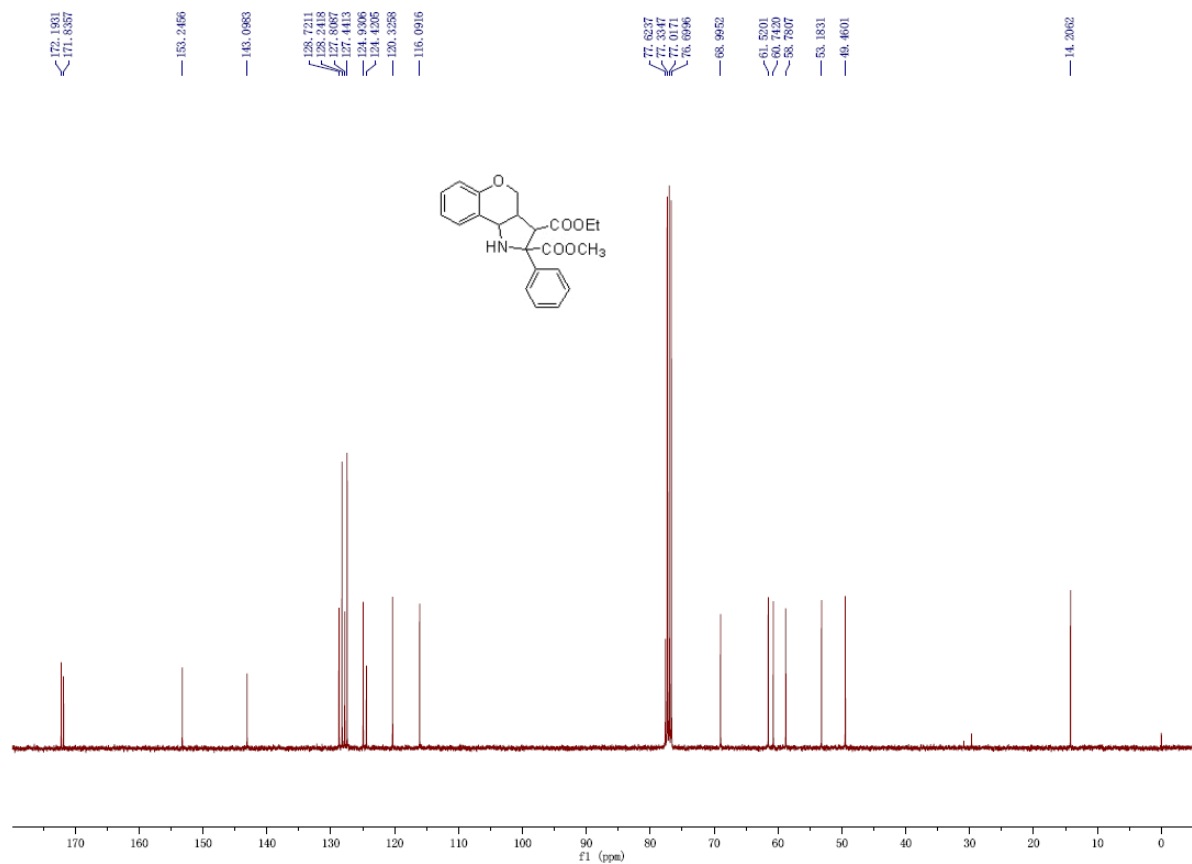
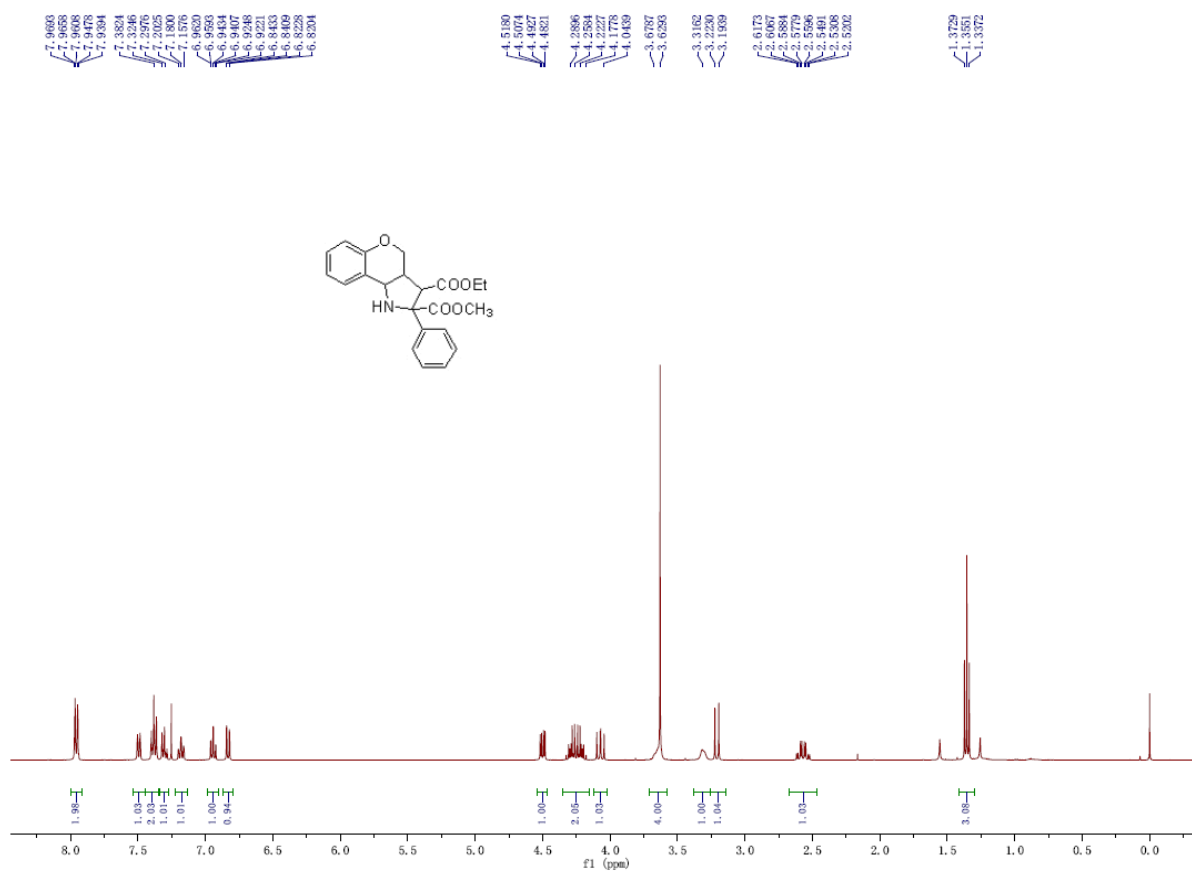


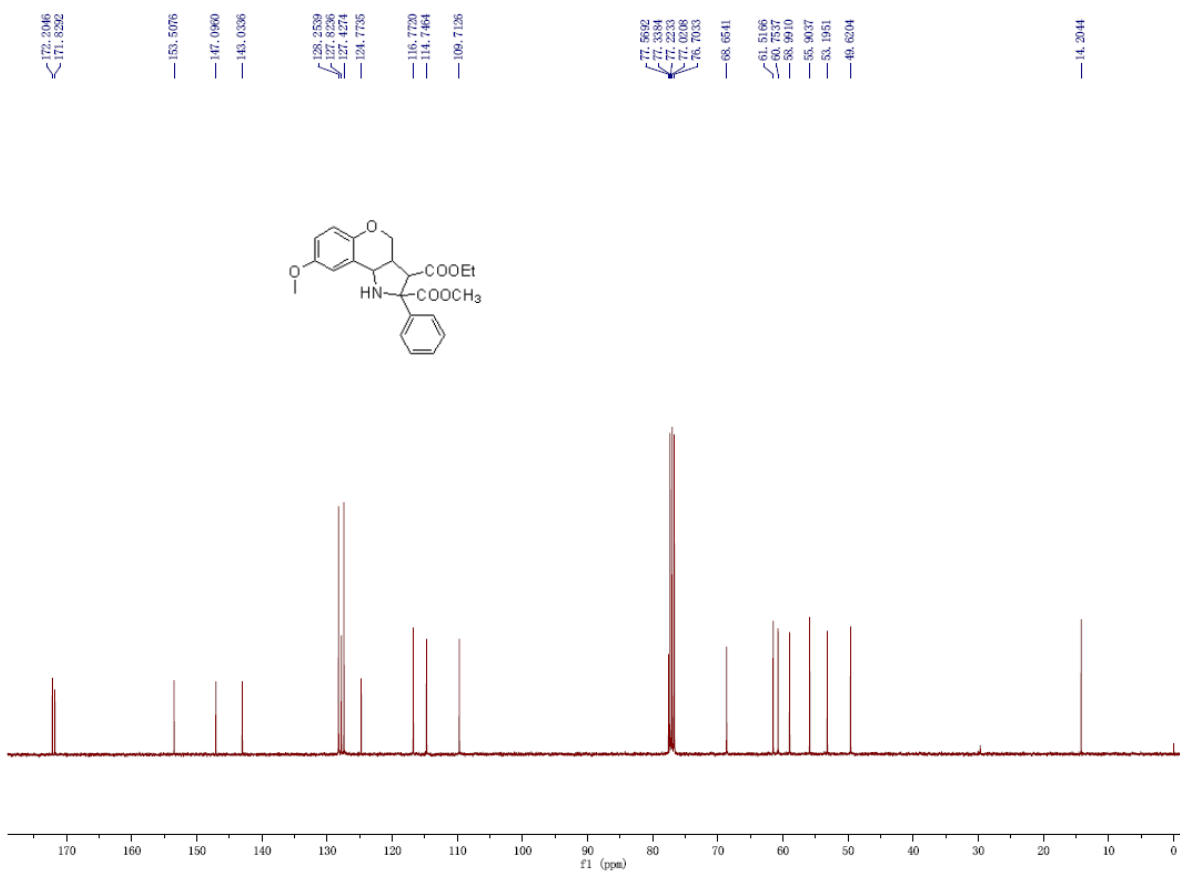
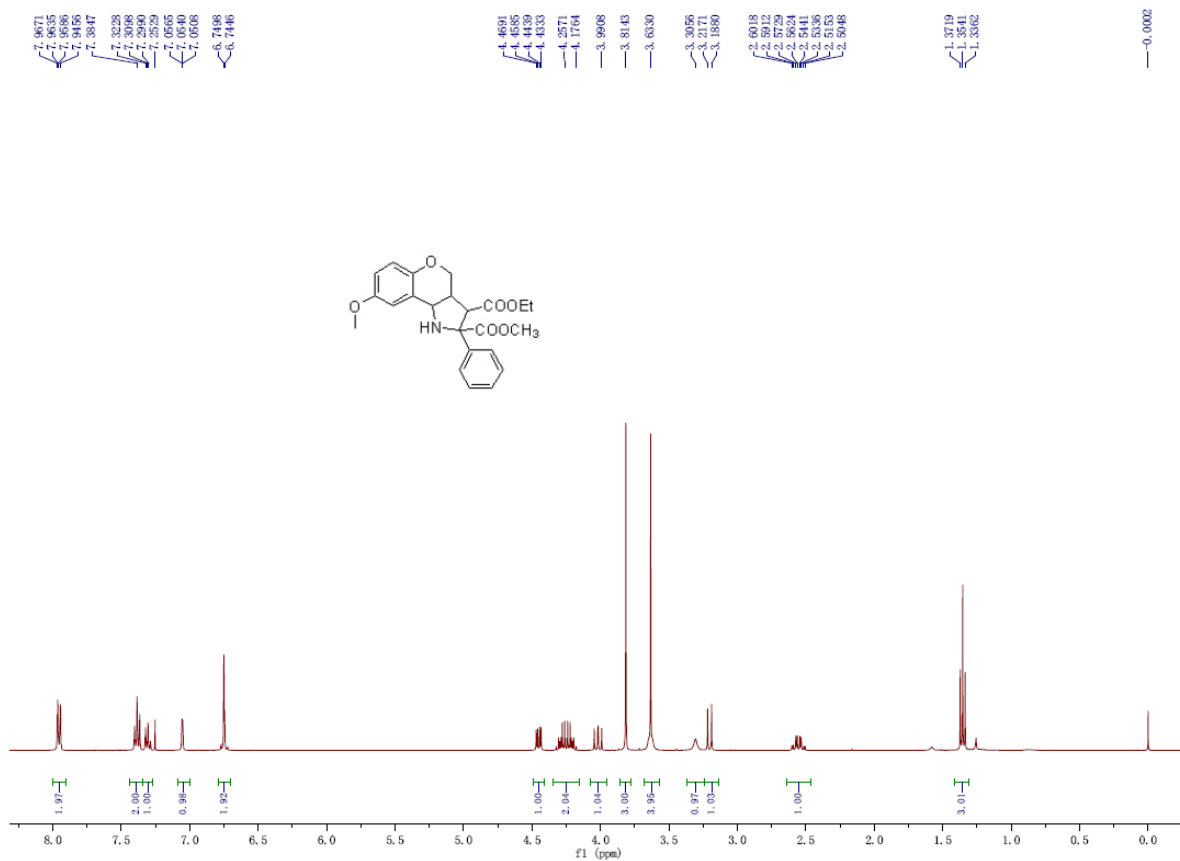


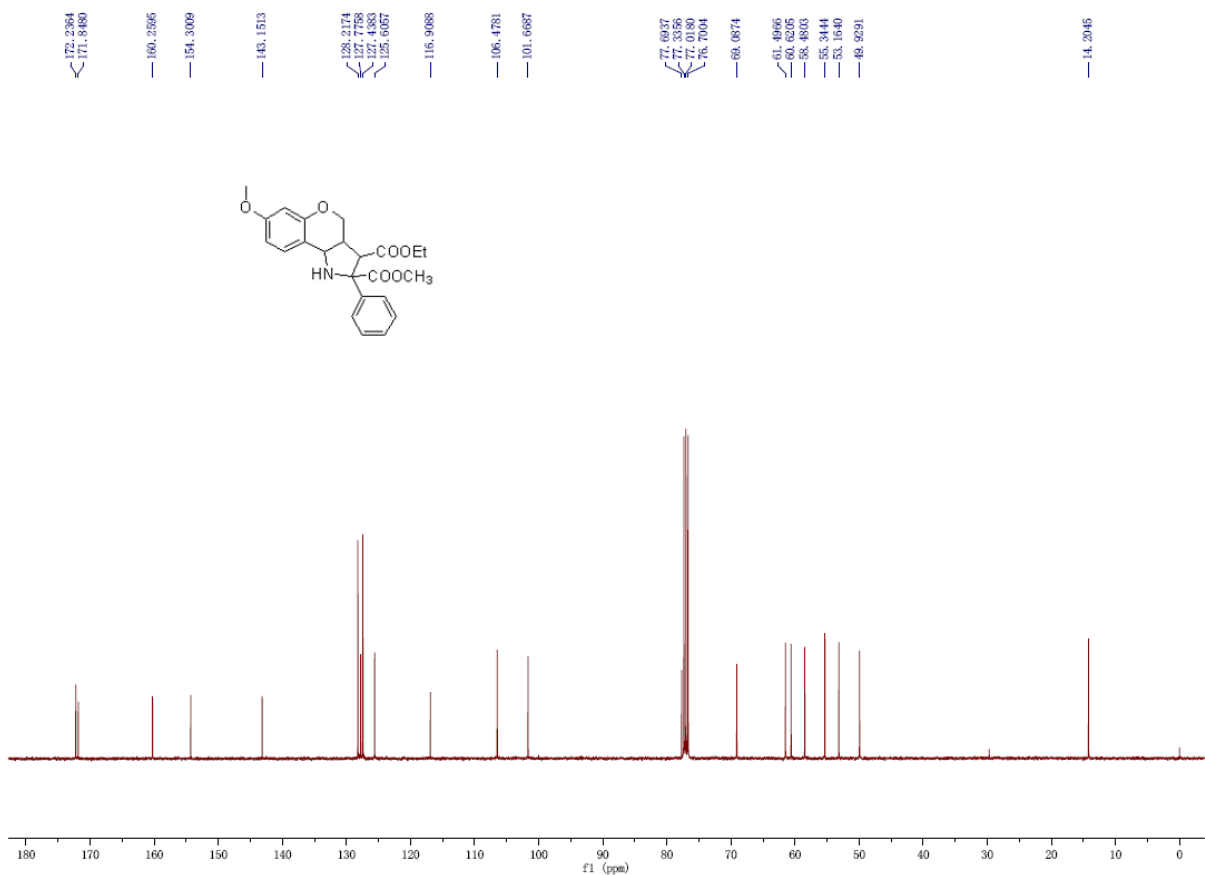
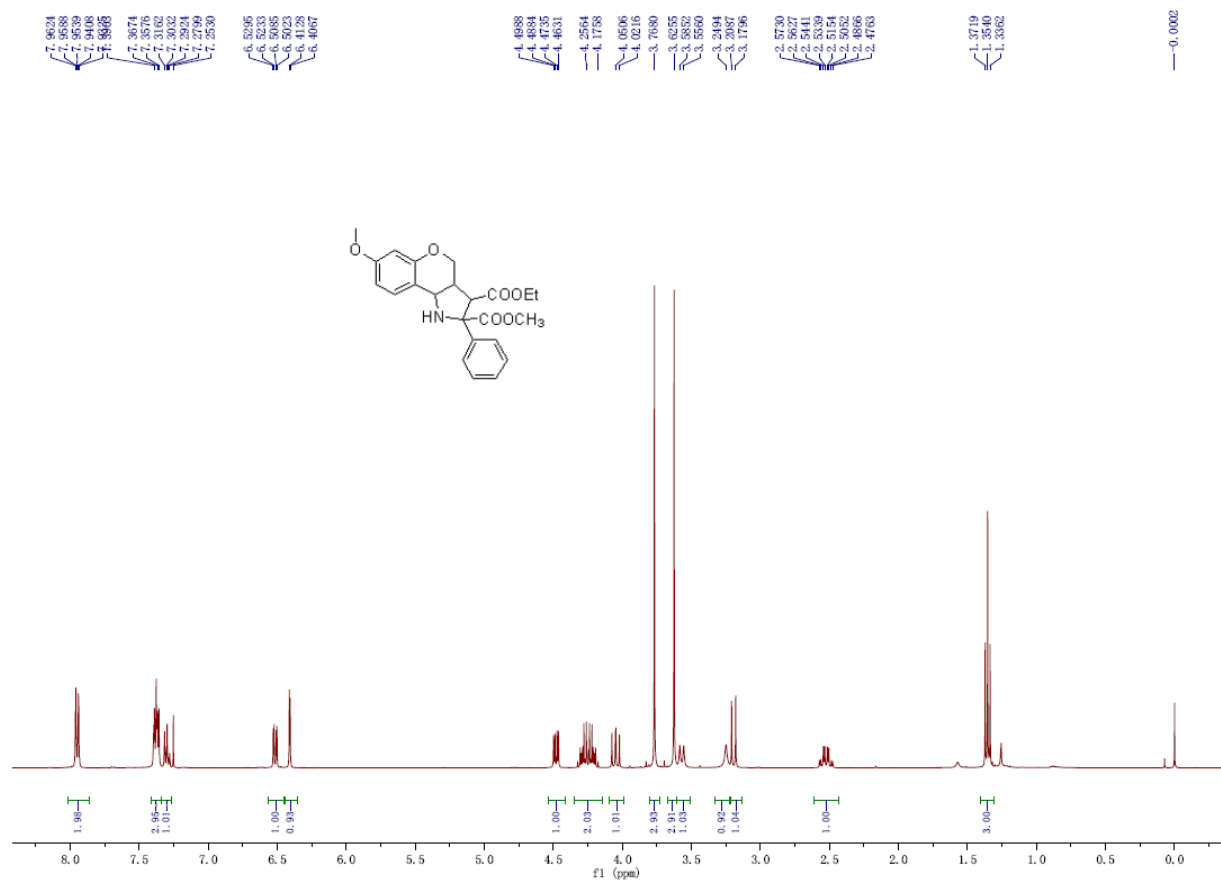


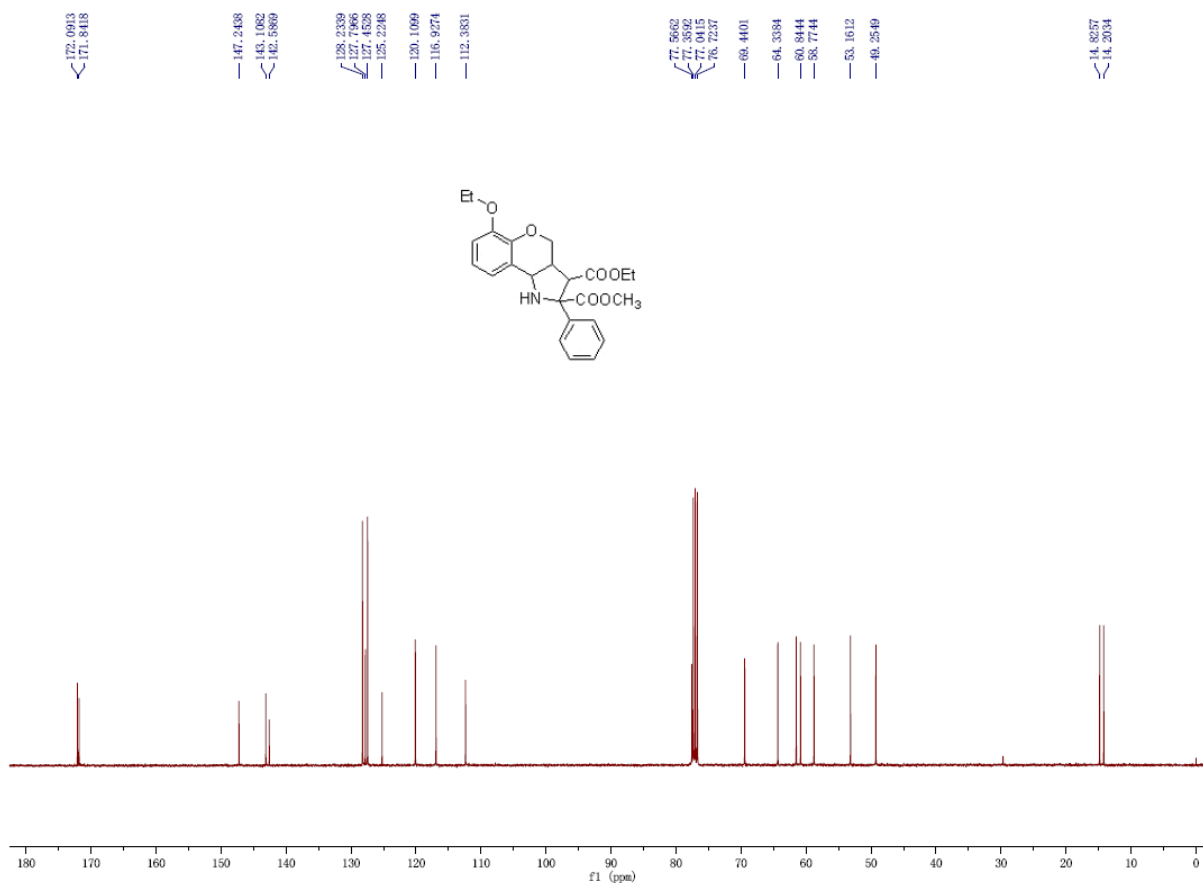
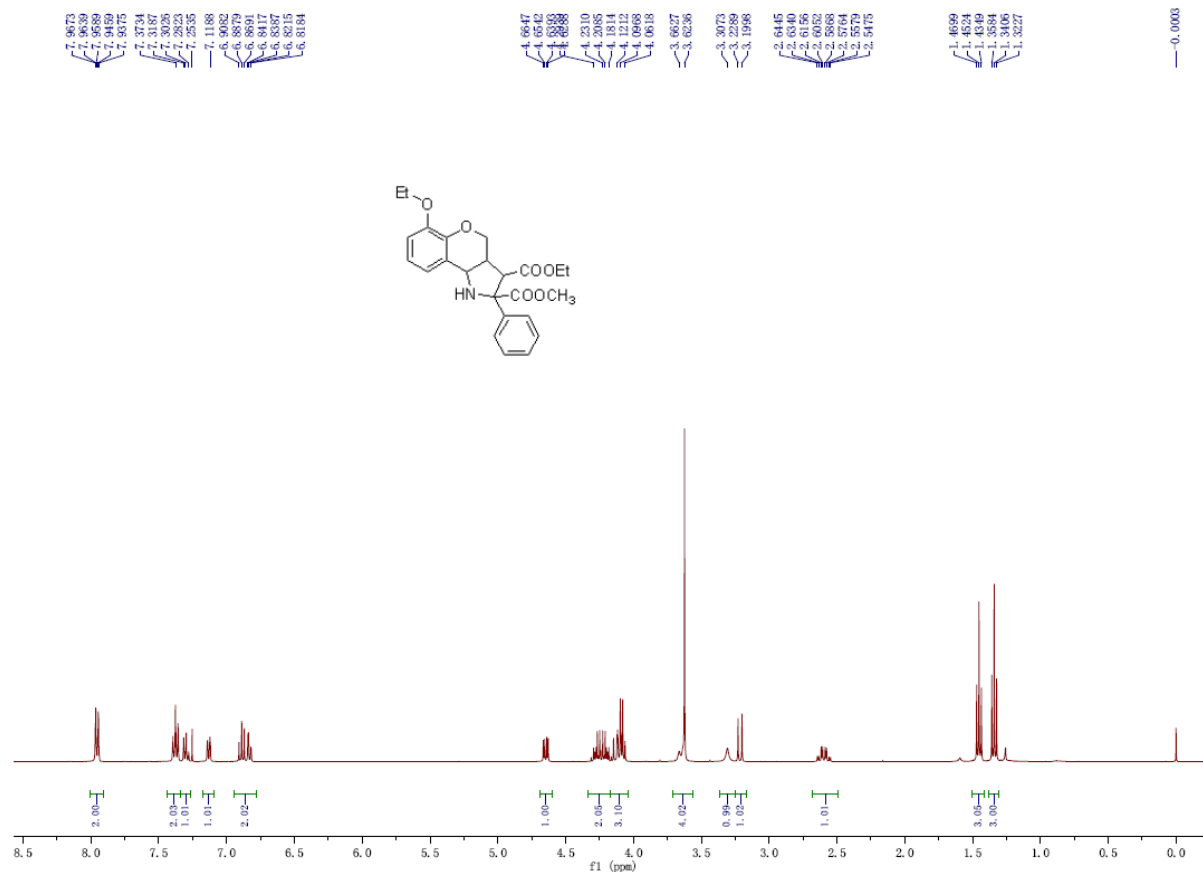


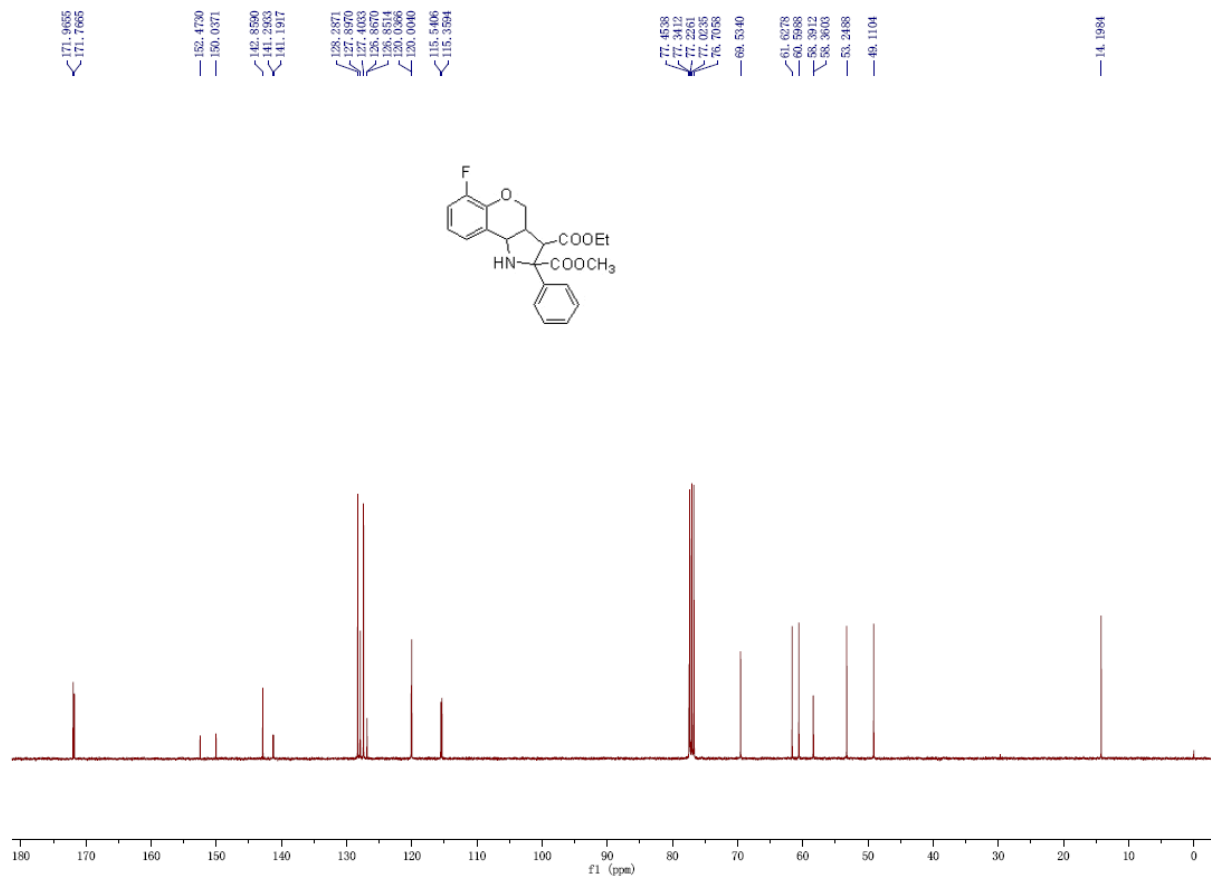
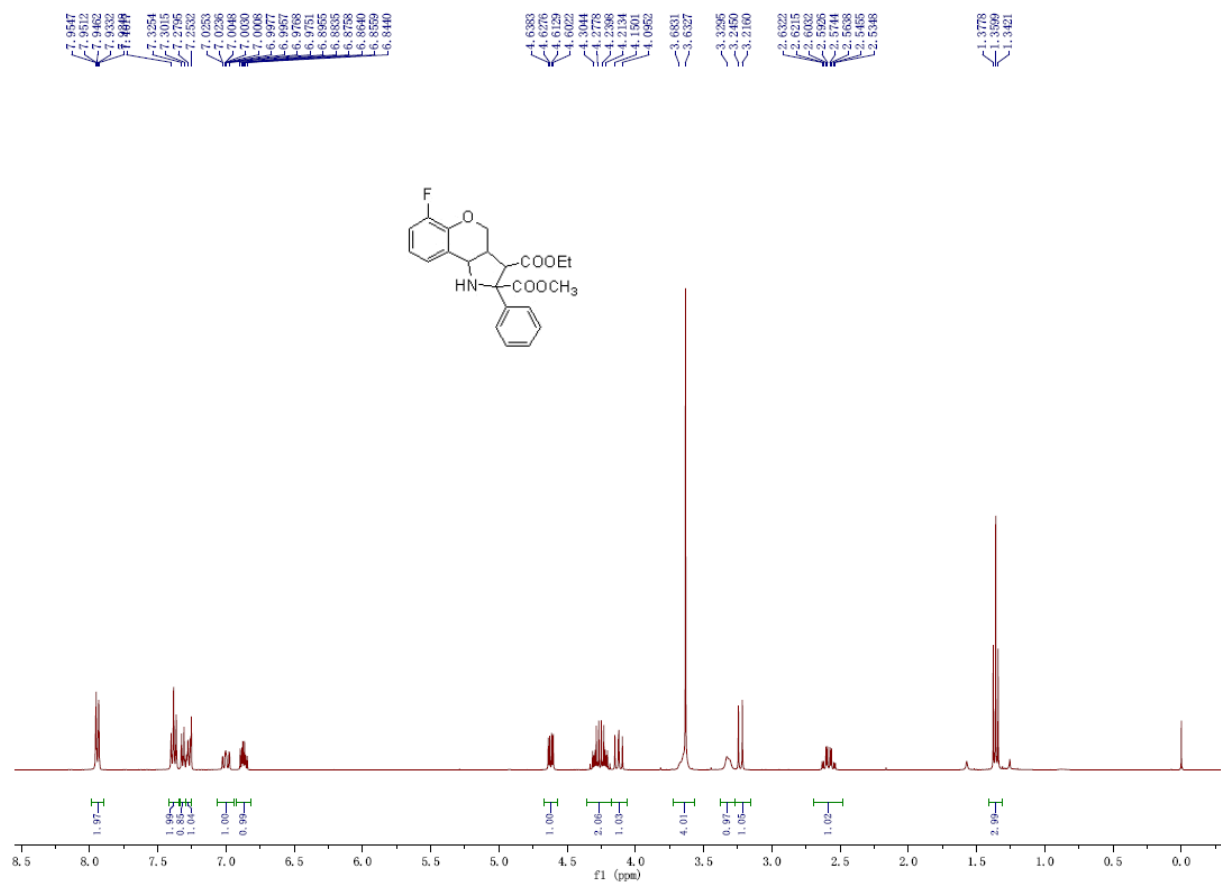




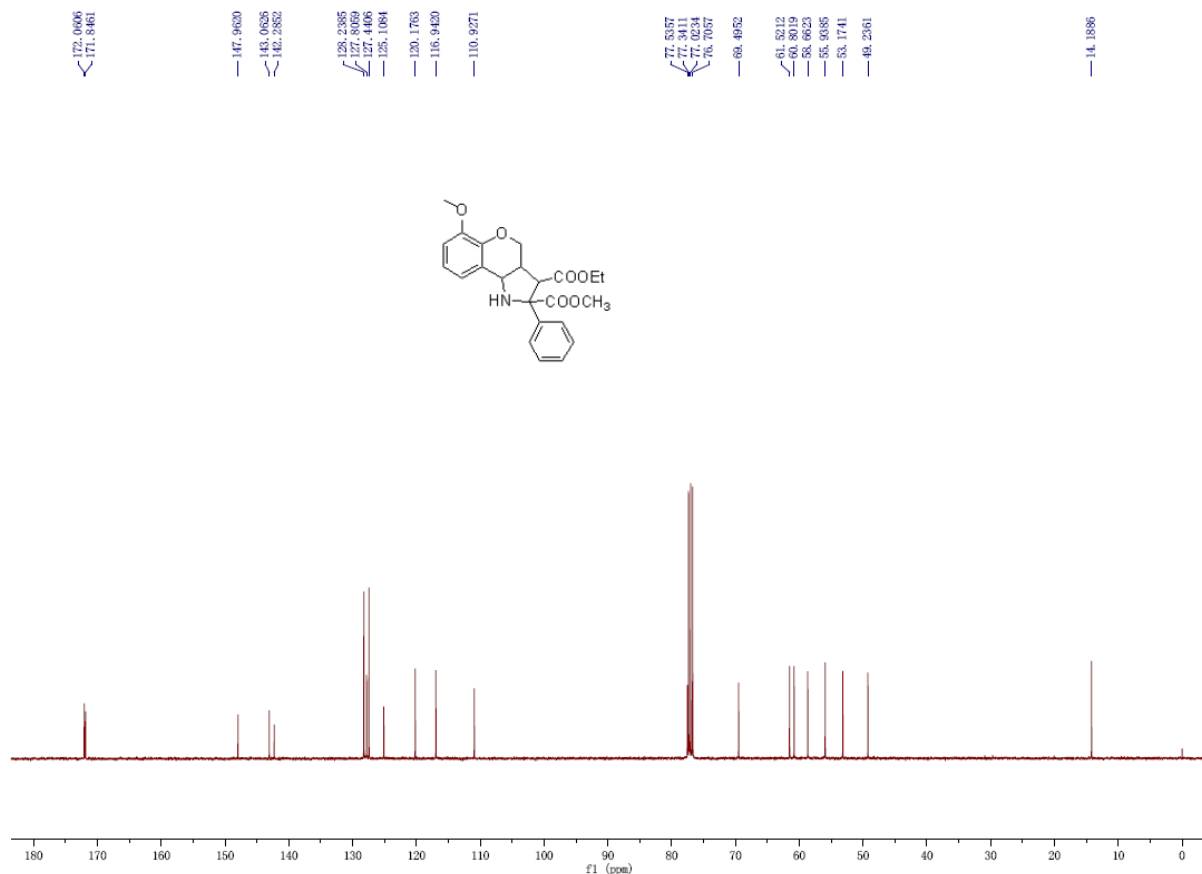
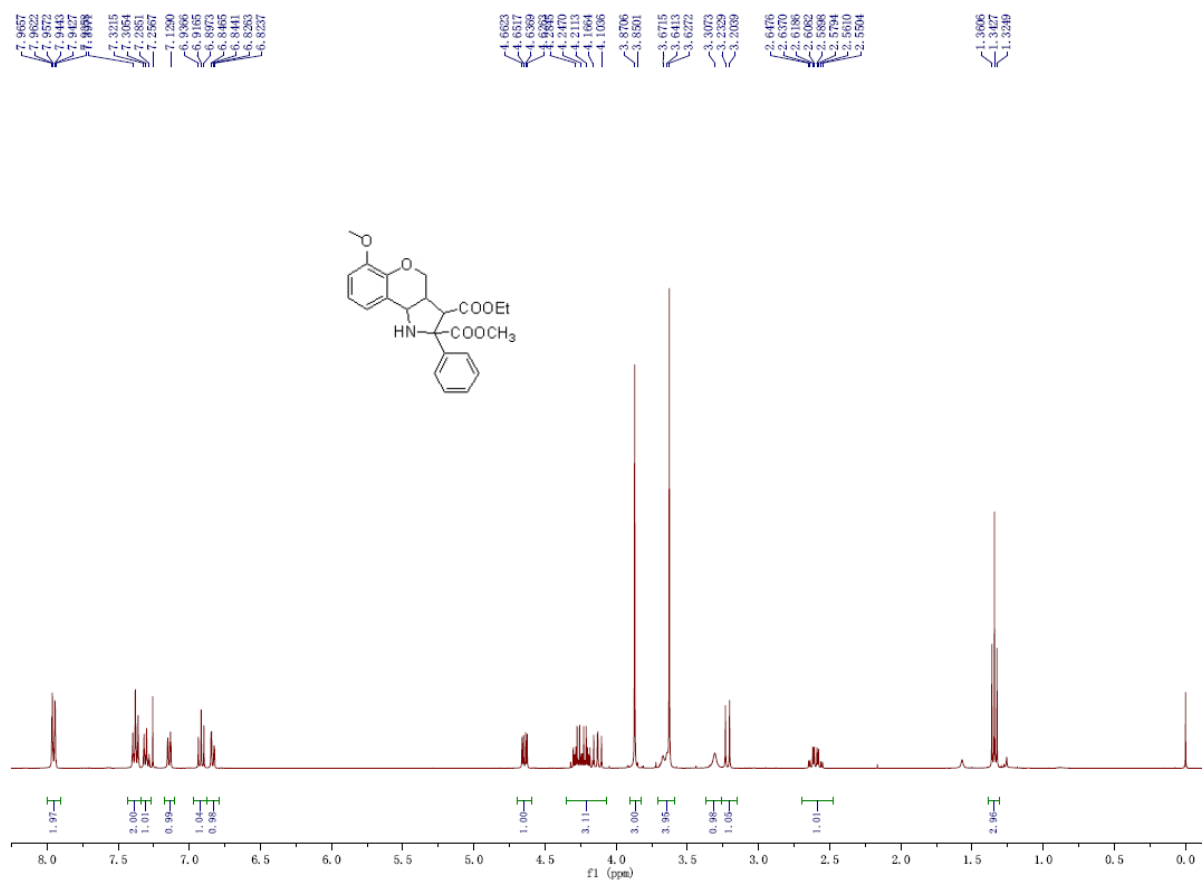


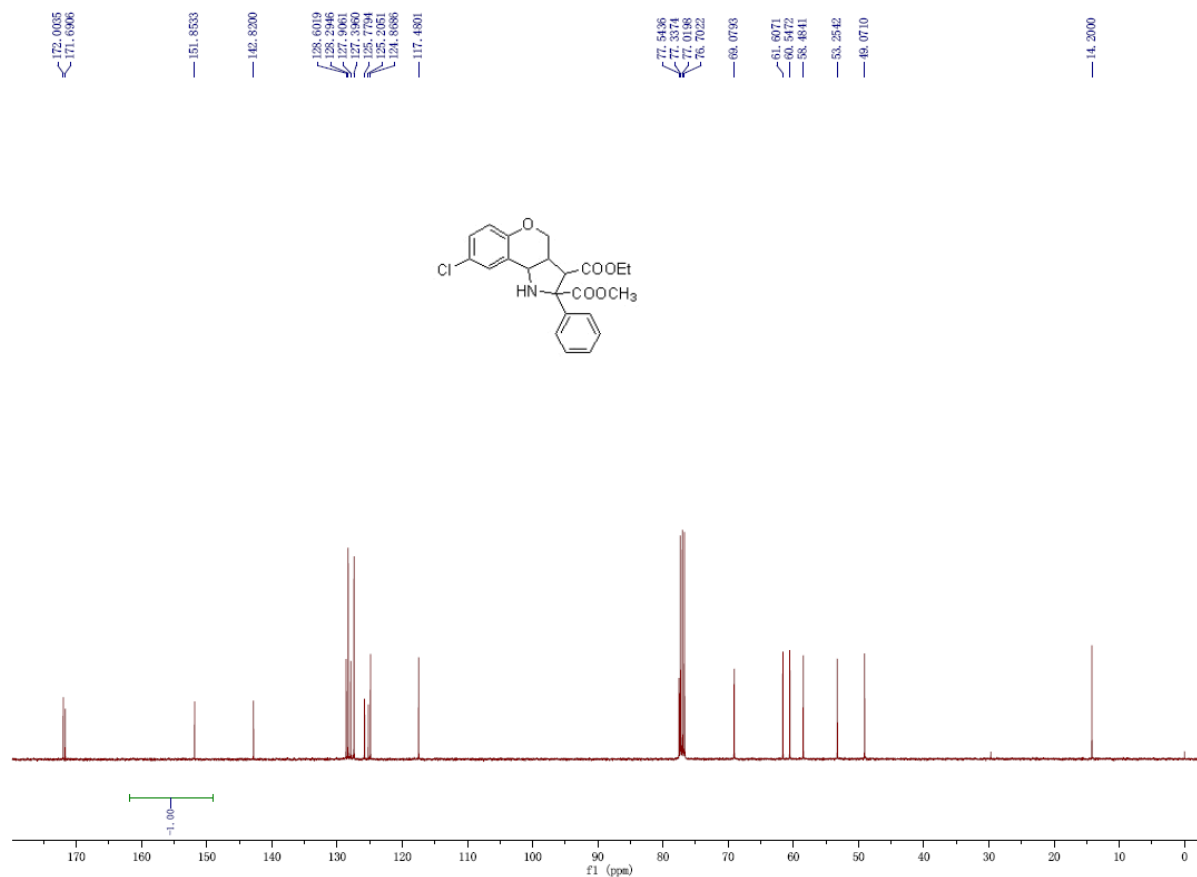
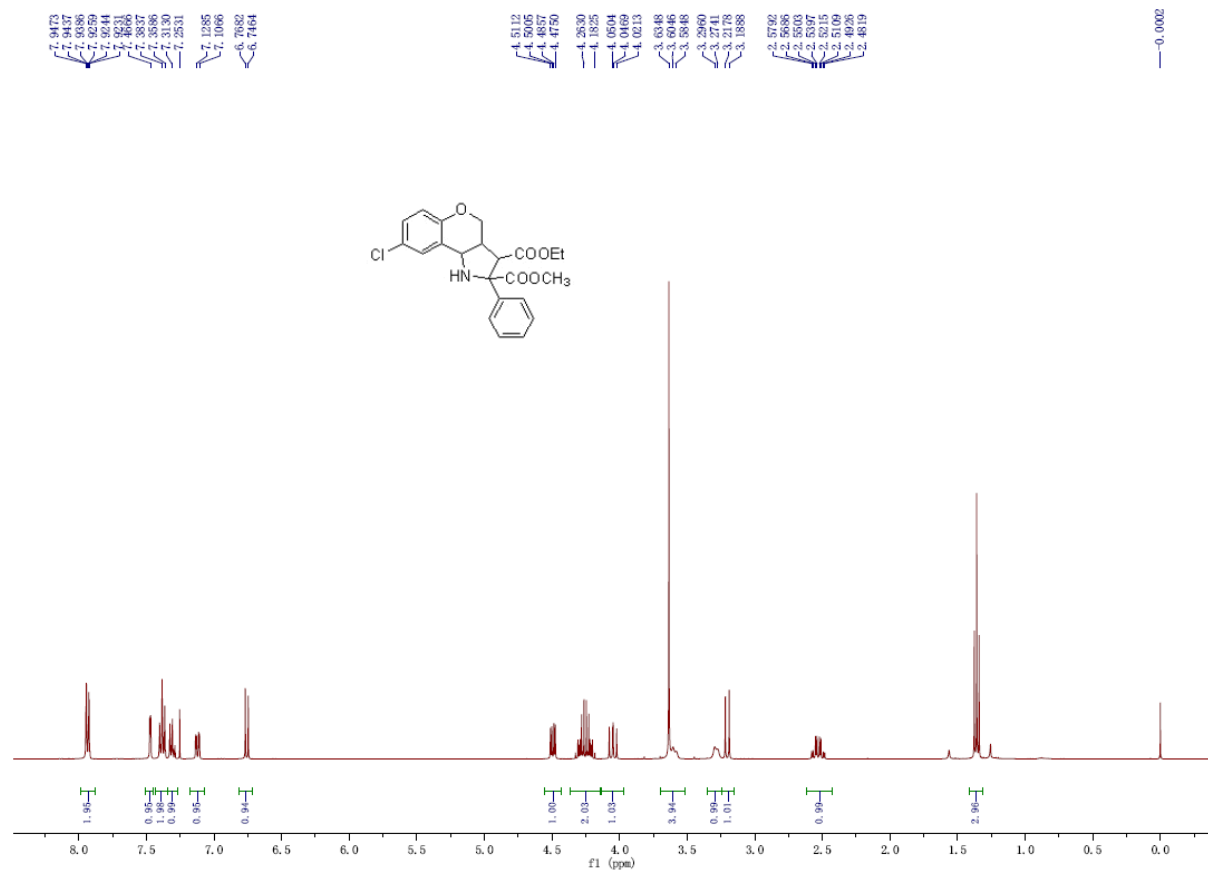


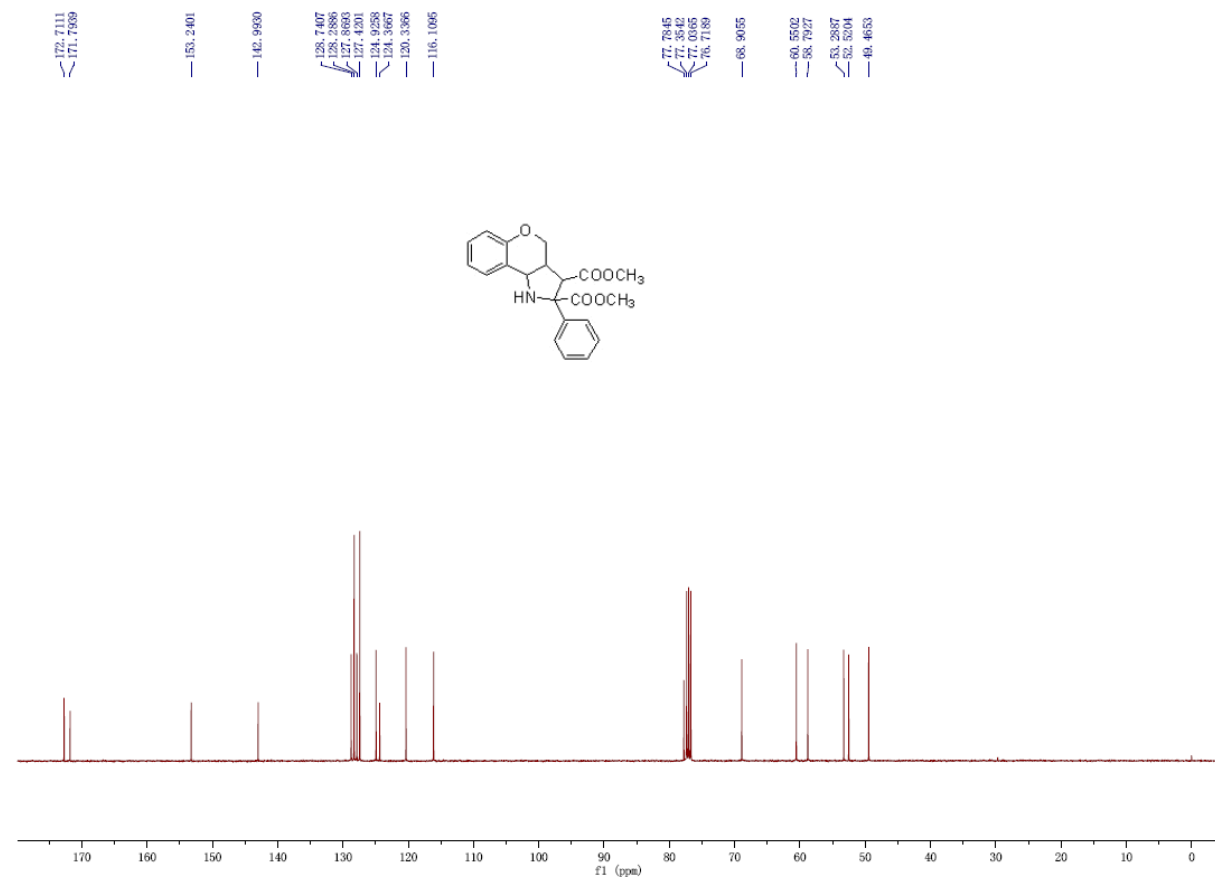
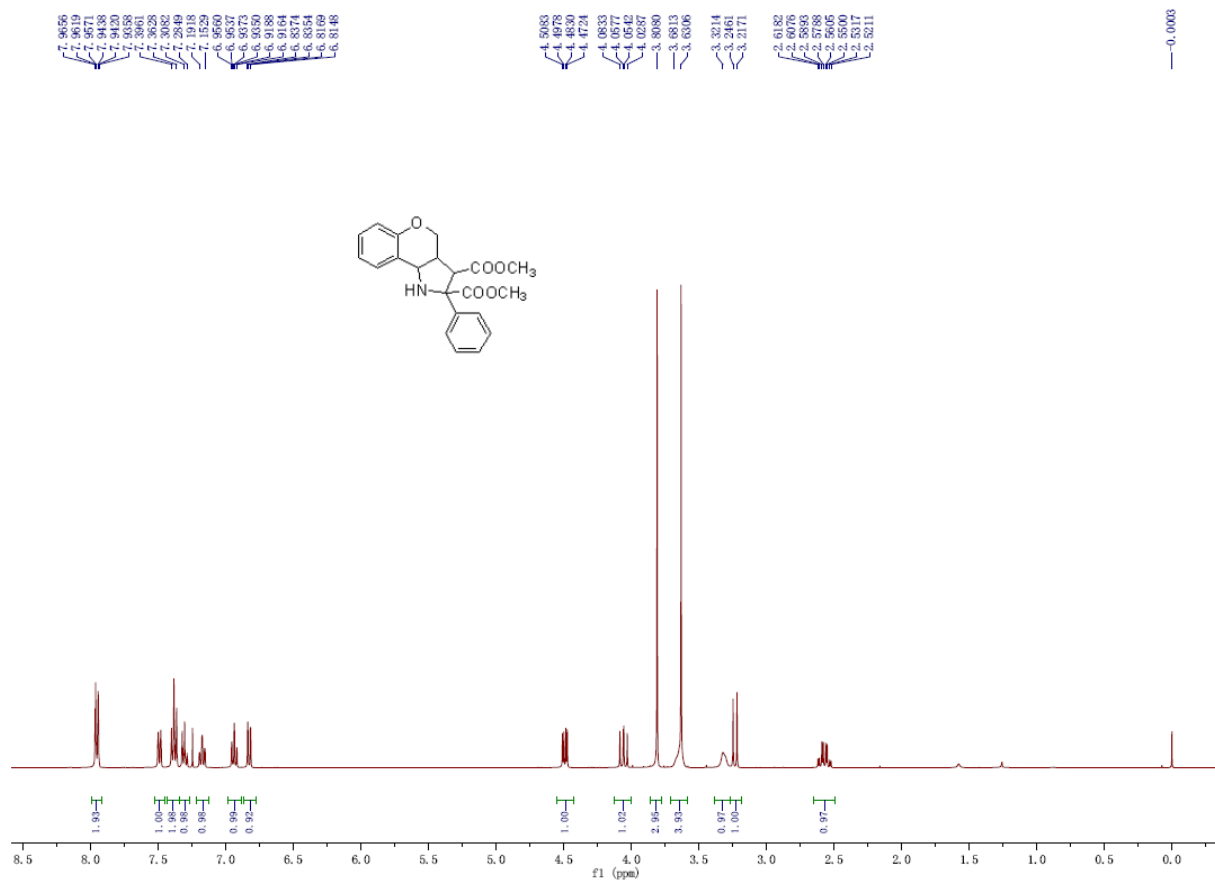


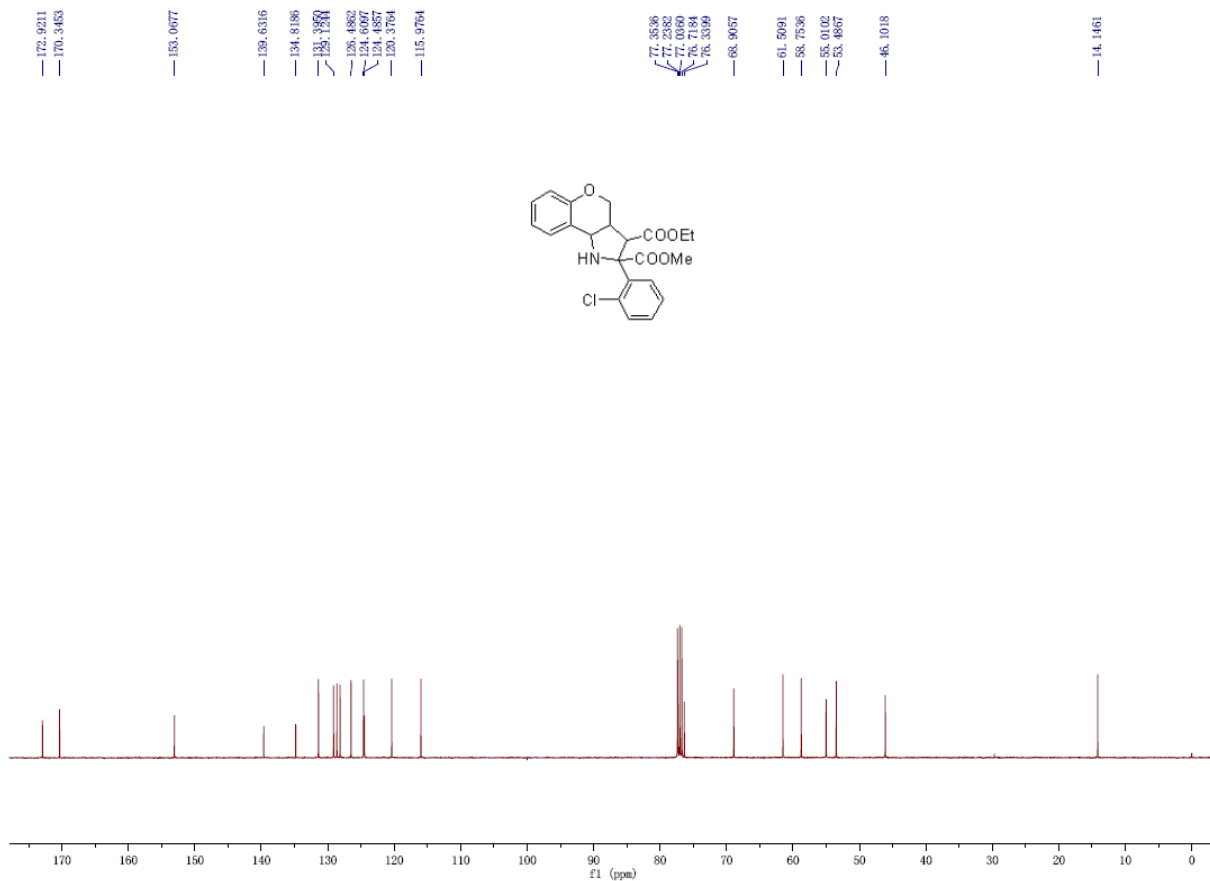
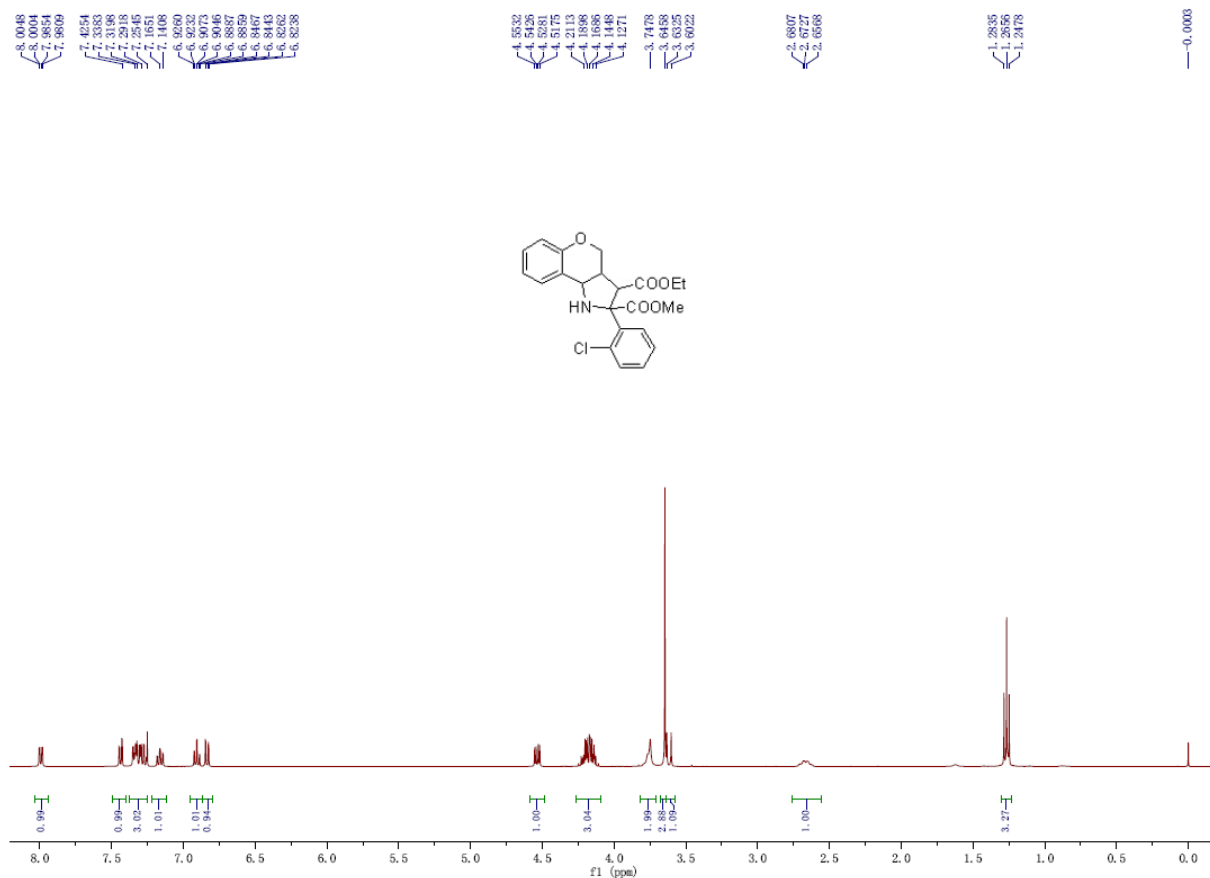


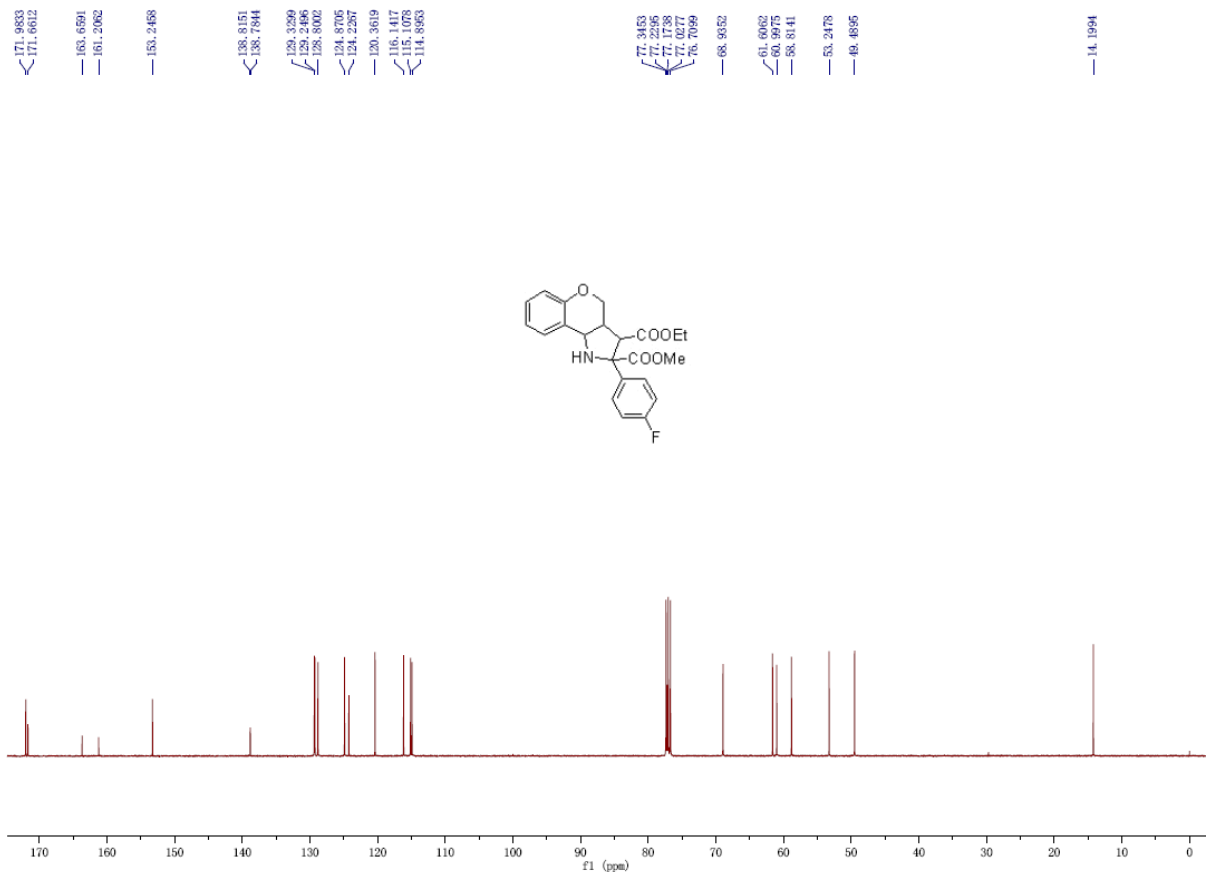
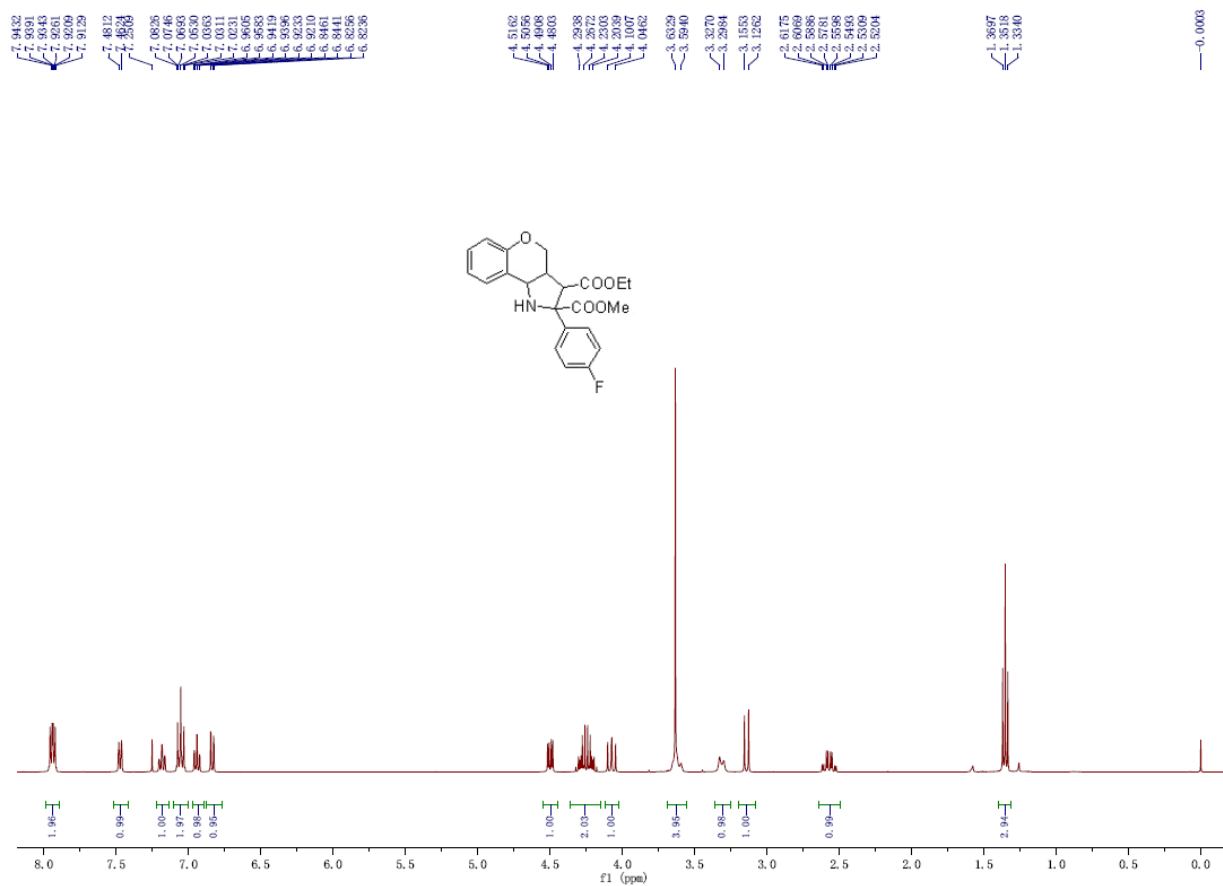


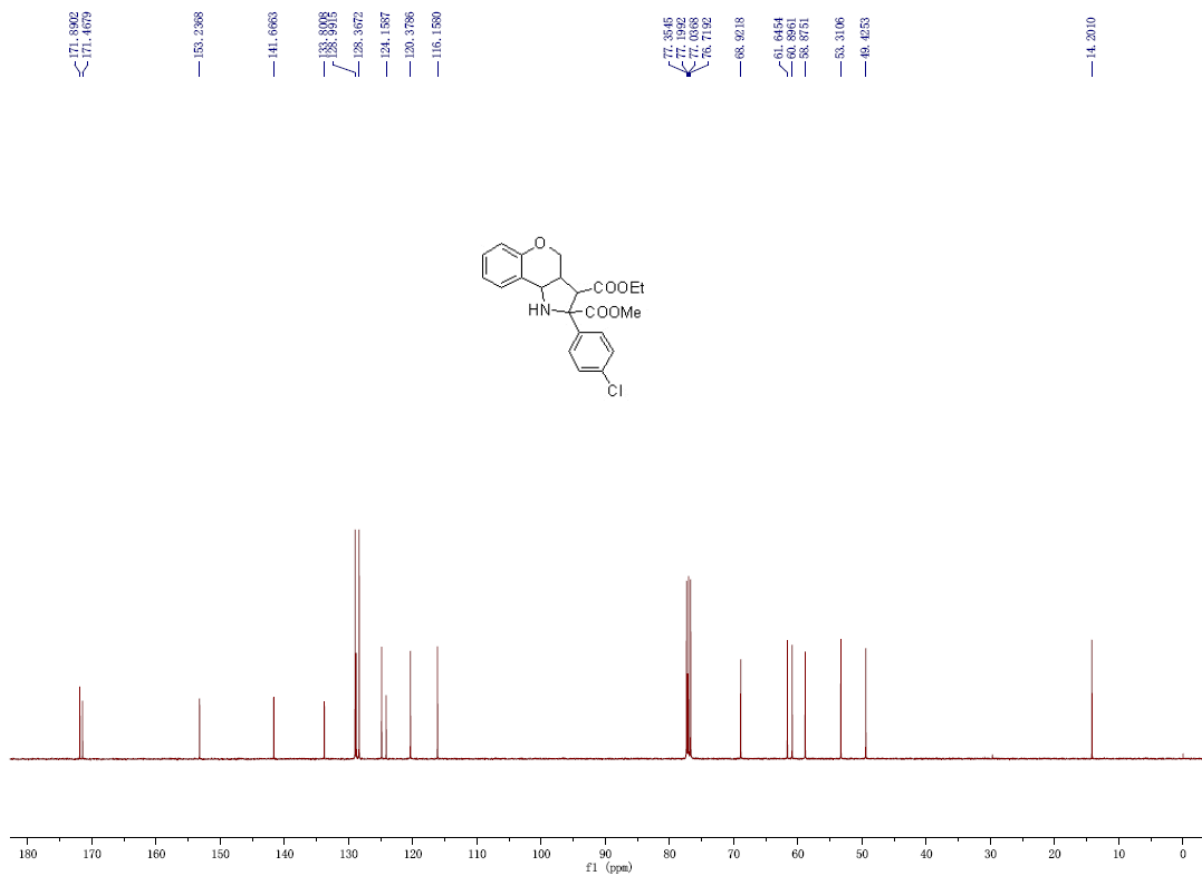
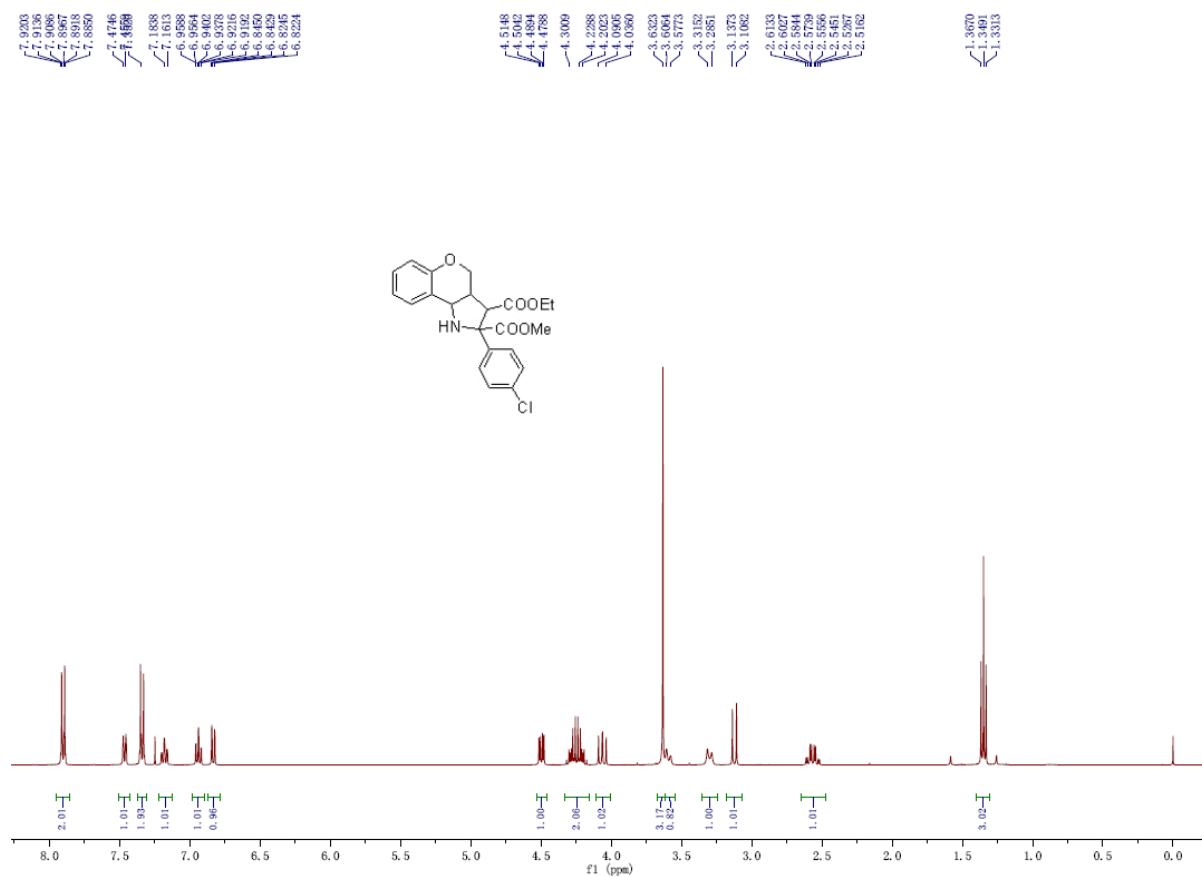


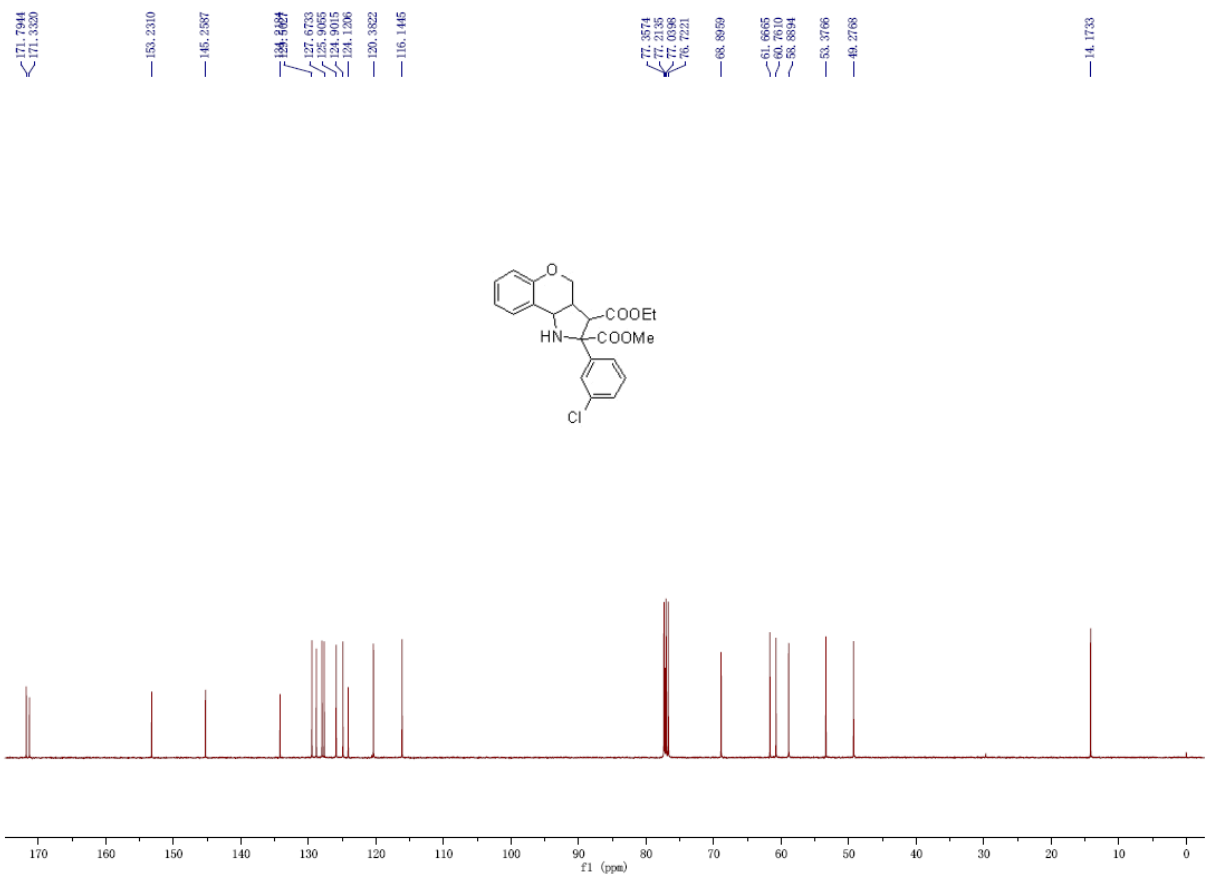
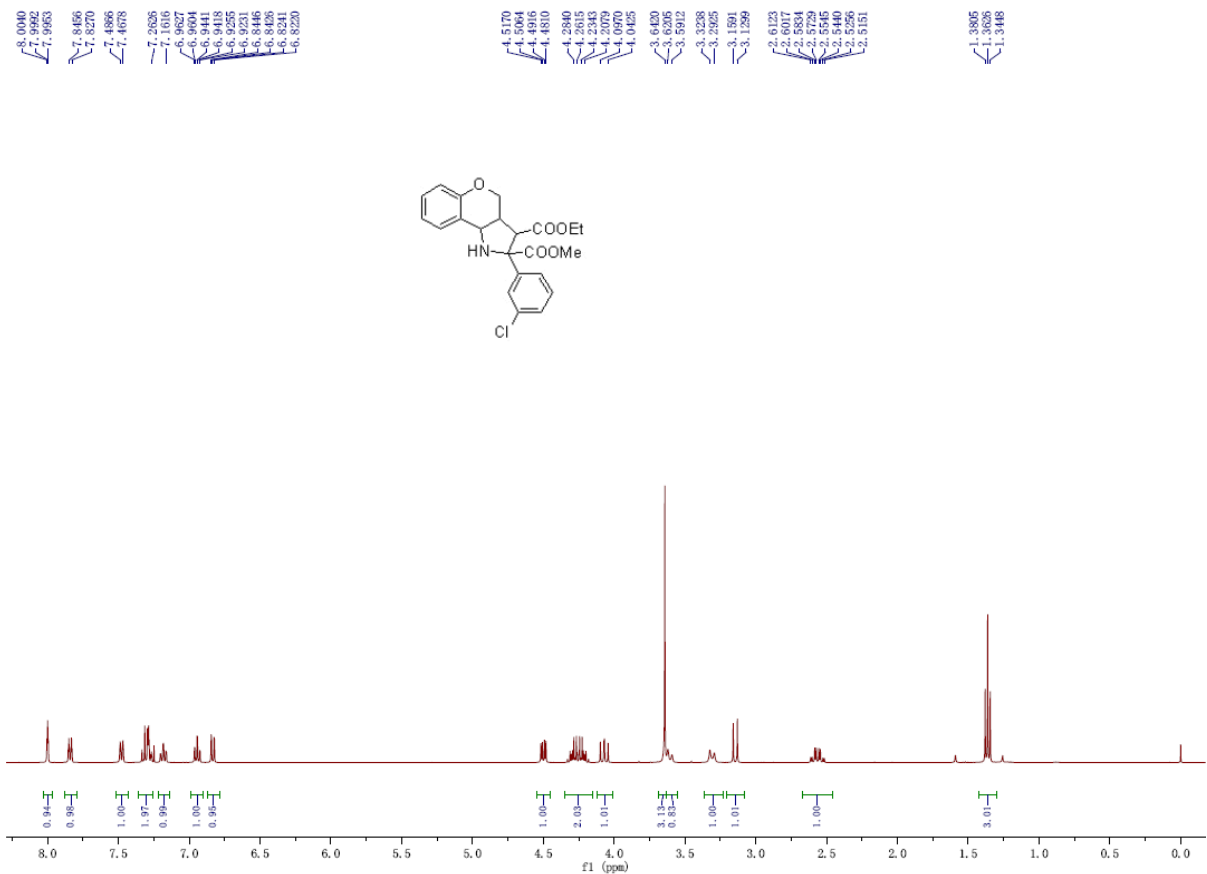


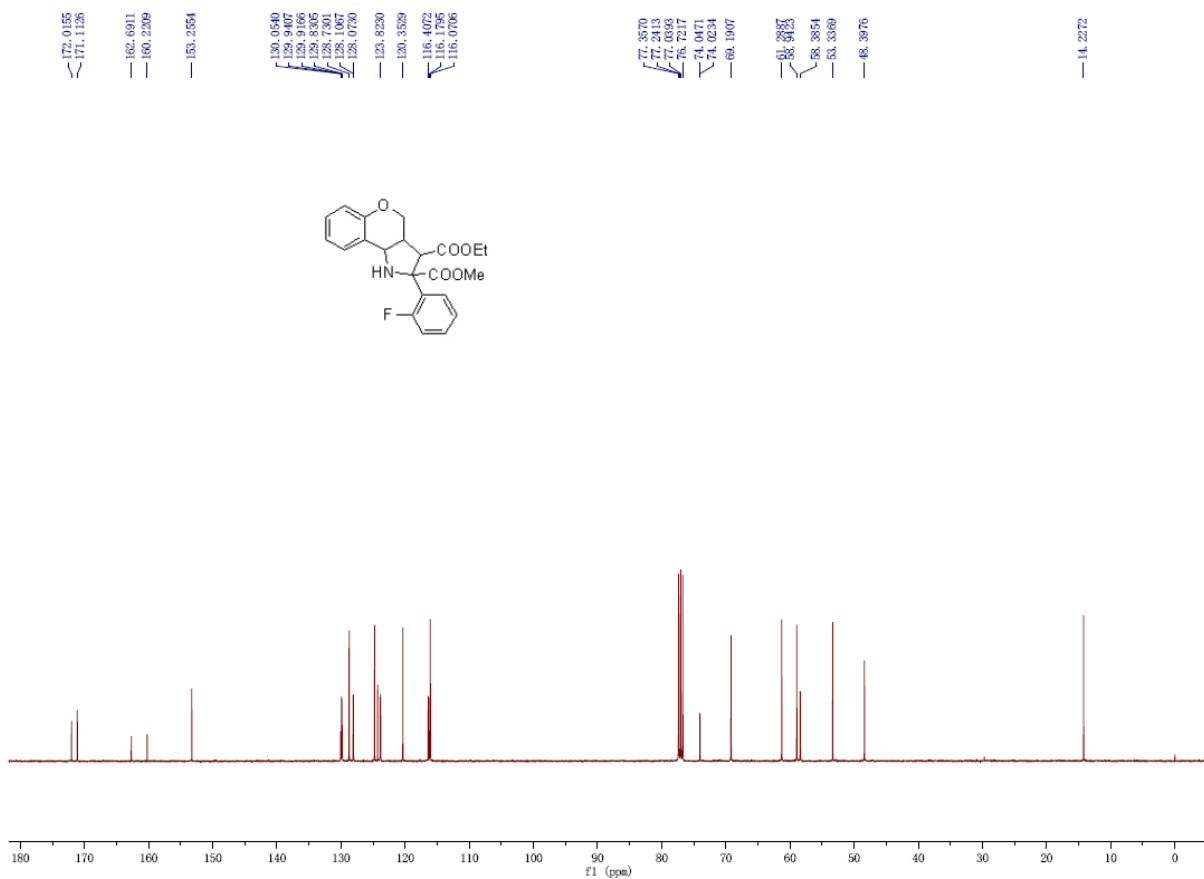
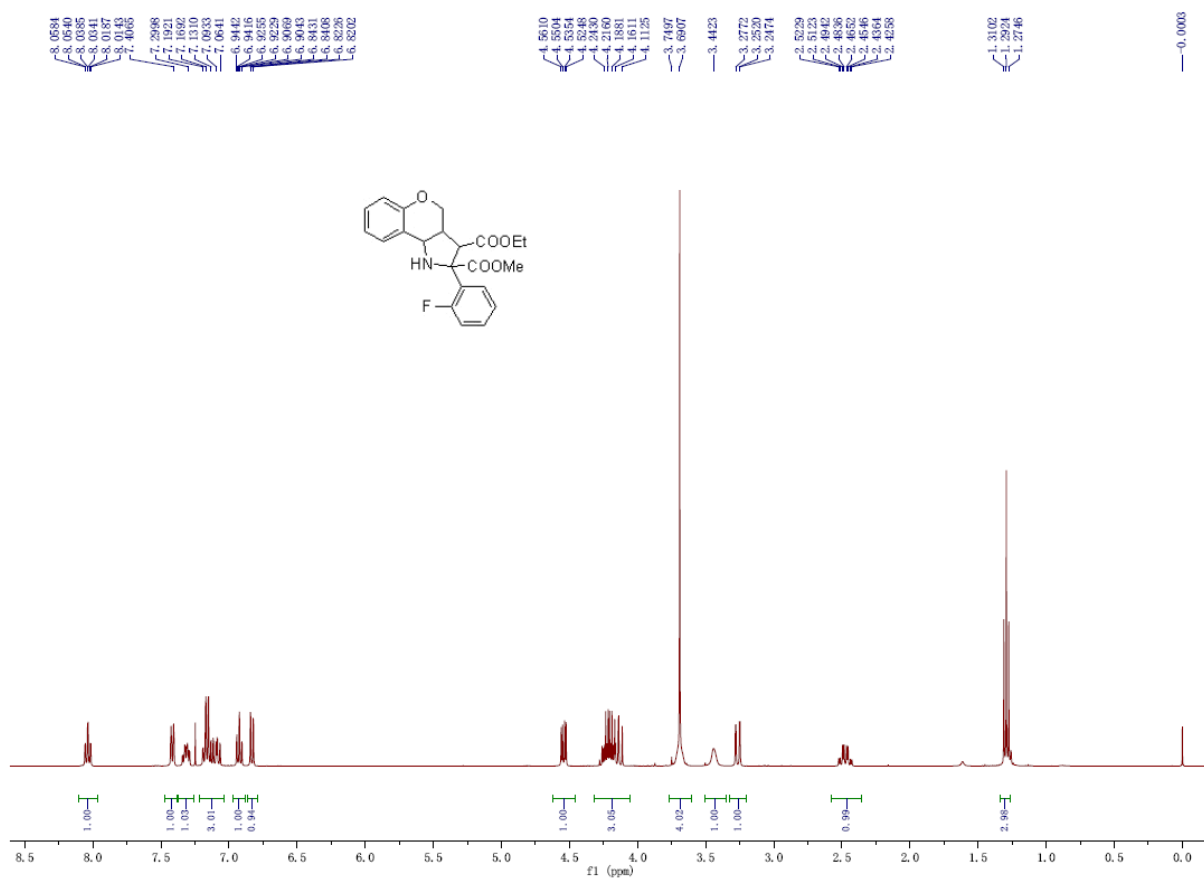




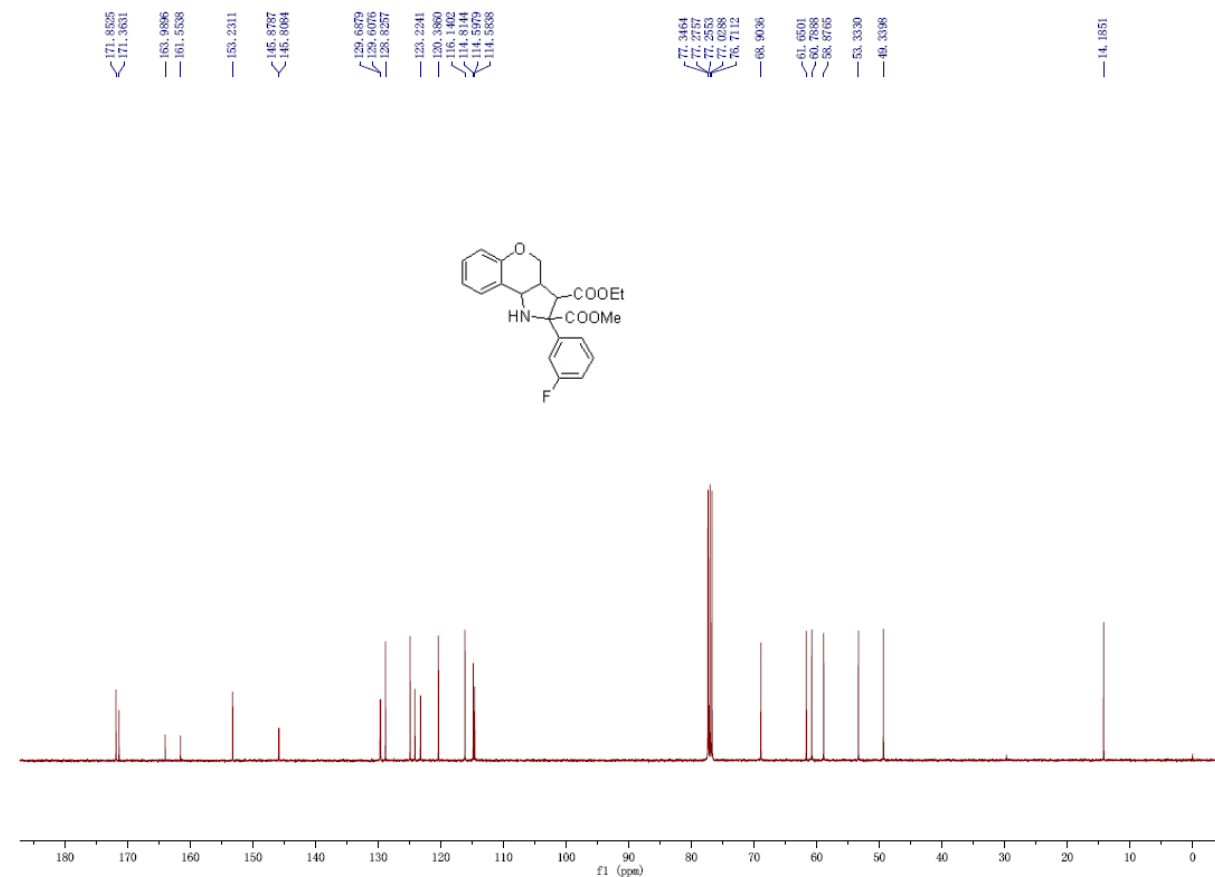
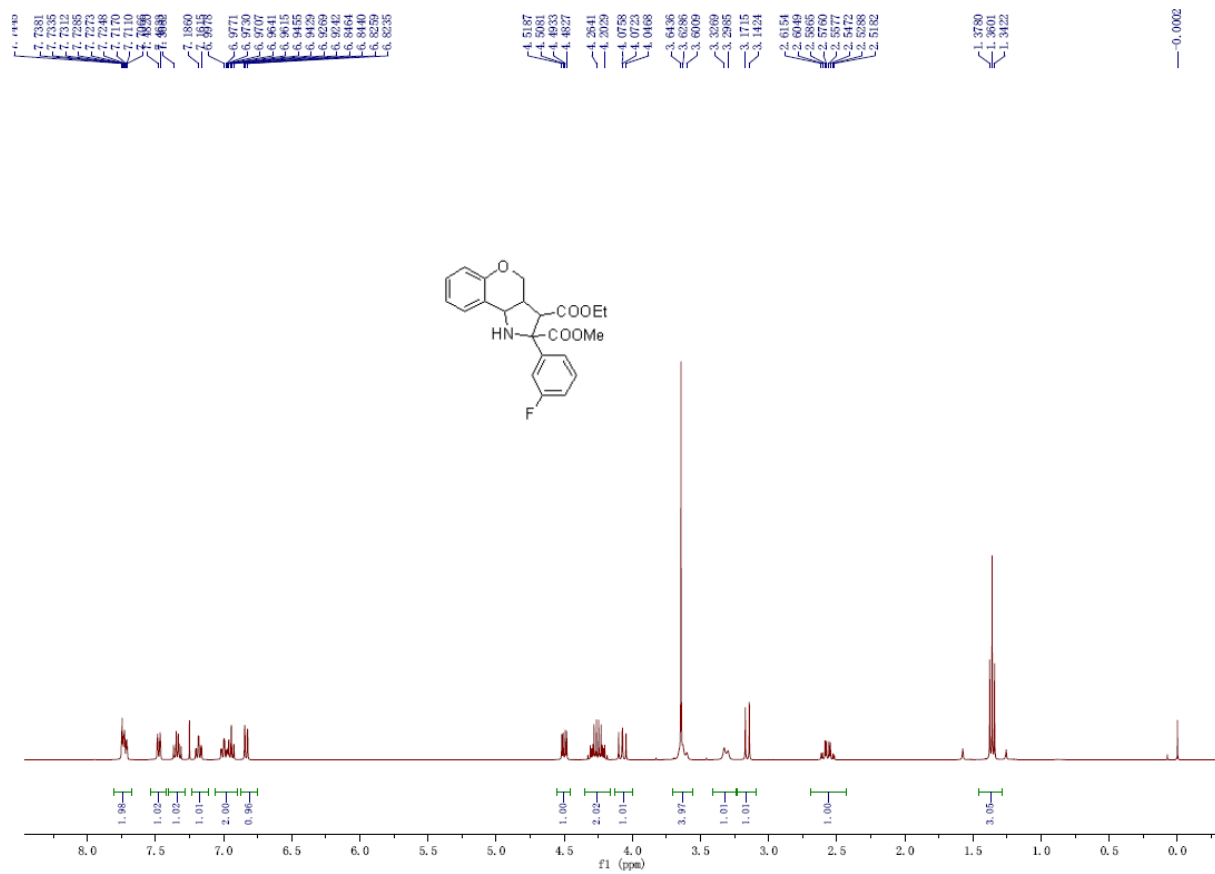


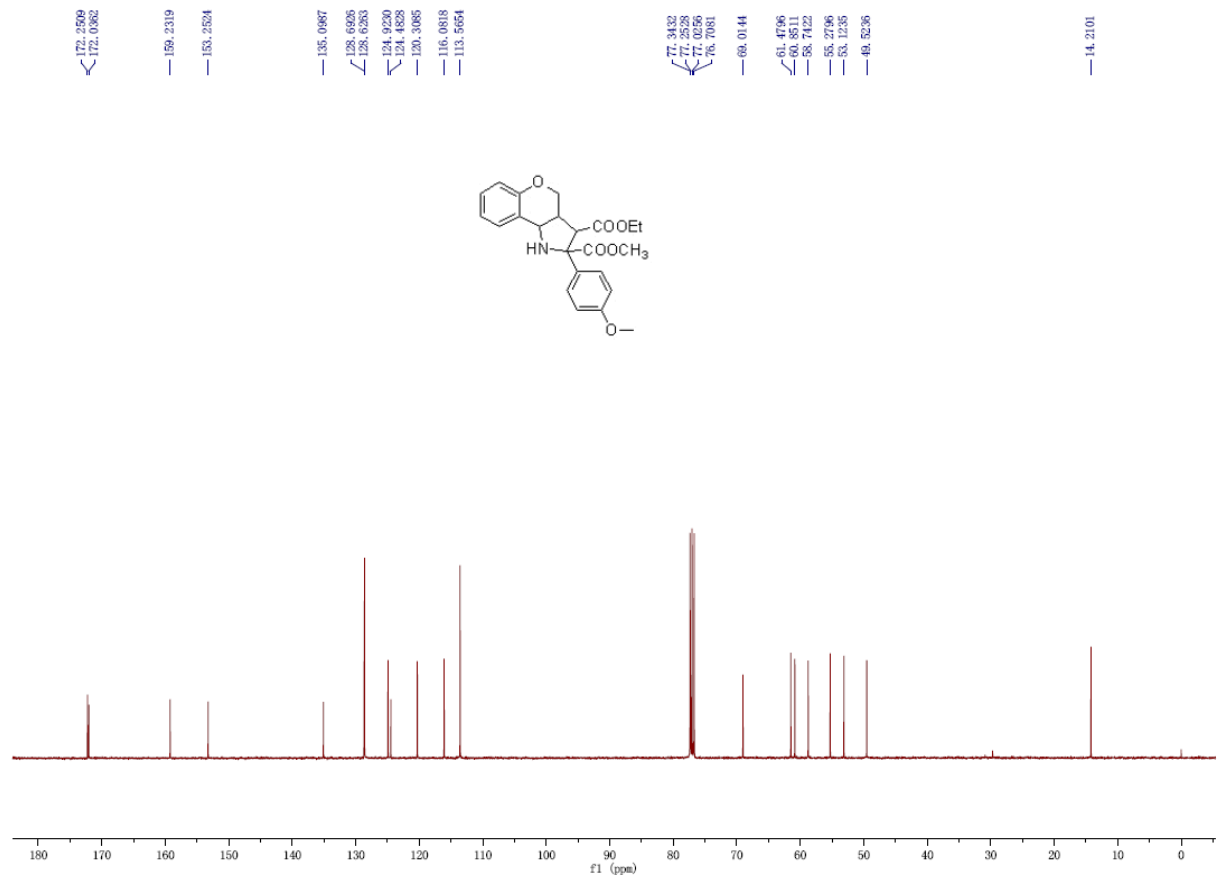
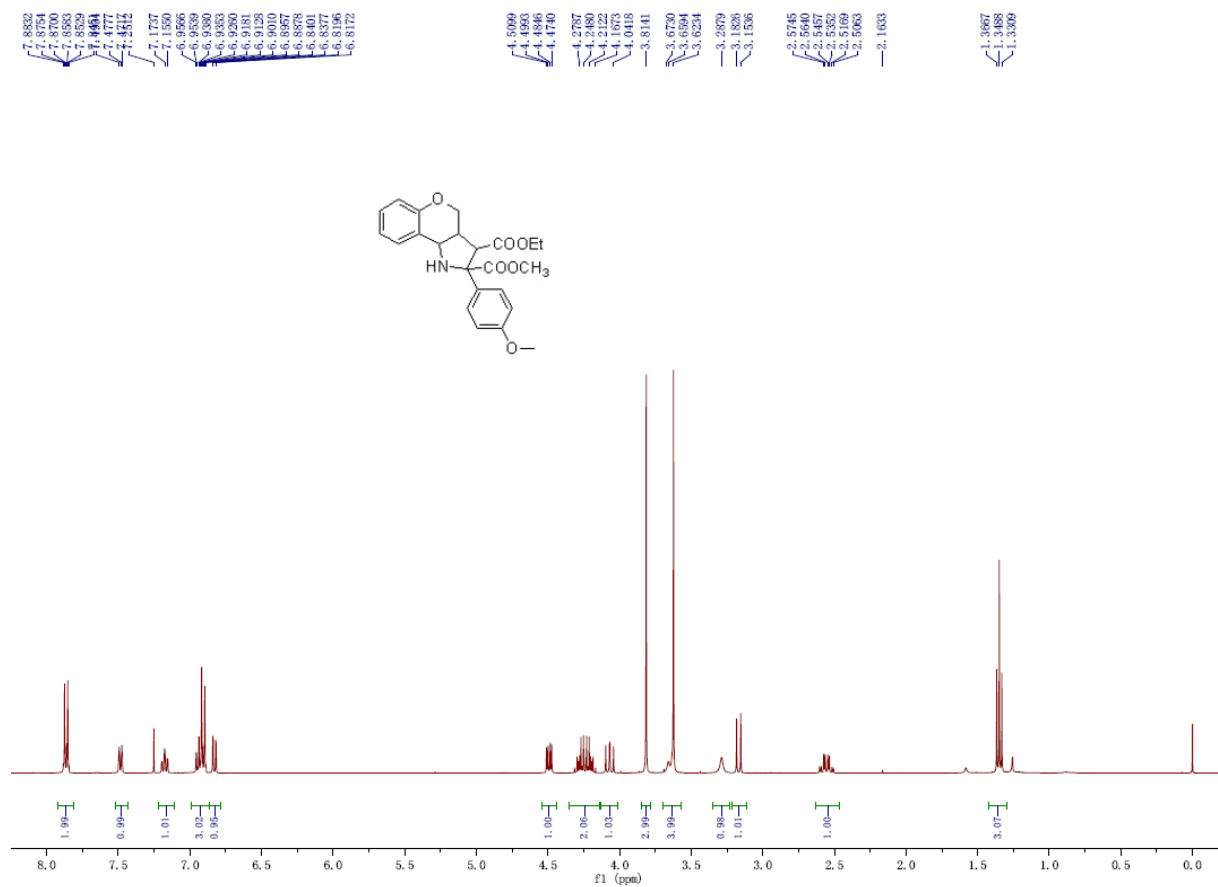


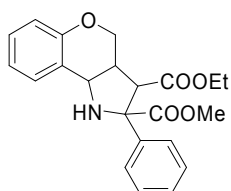










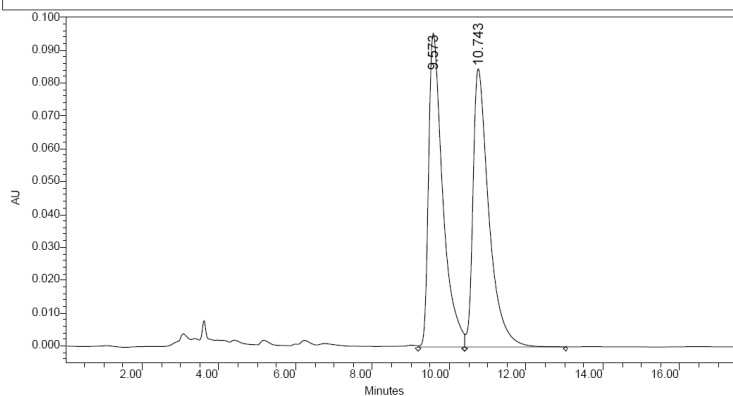


USTC

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 Reported by User: System

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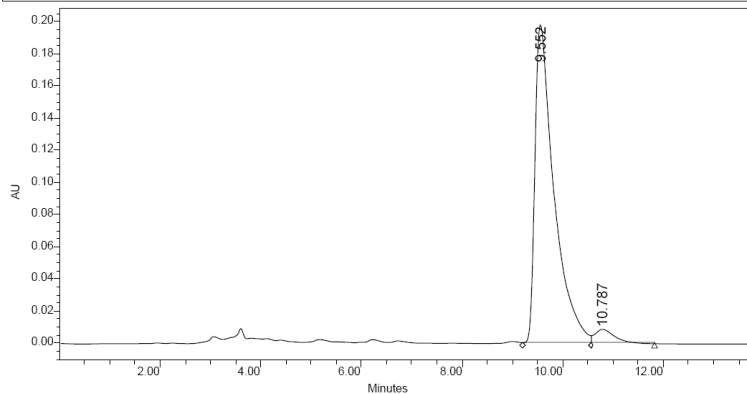
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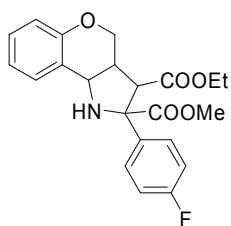
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Run Time:	120.00 Minutes	Sample Set Name:			



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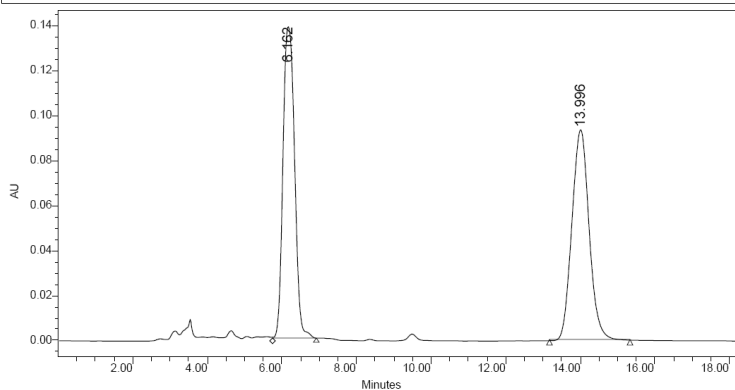


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Project Name: linan  
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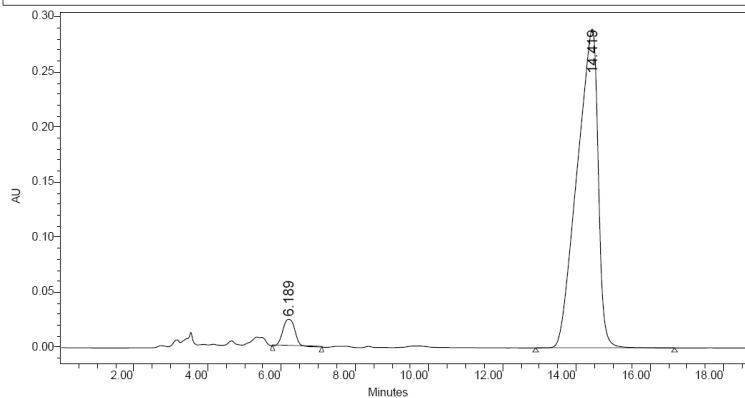
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USTC

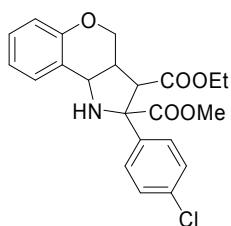
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*Breeze*

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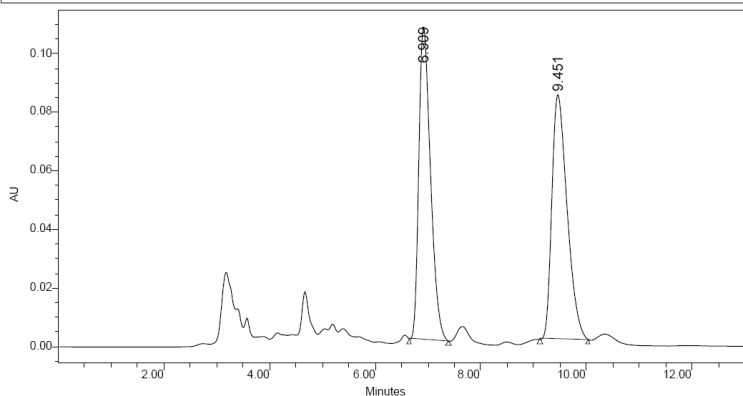


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*Breeze*

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Injection Volume:	20.00 ul	Channel Name:	2487Channel 1		
Run Time:	90.00 Minutes	Sample Set Name:			



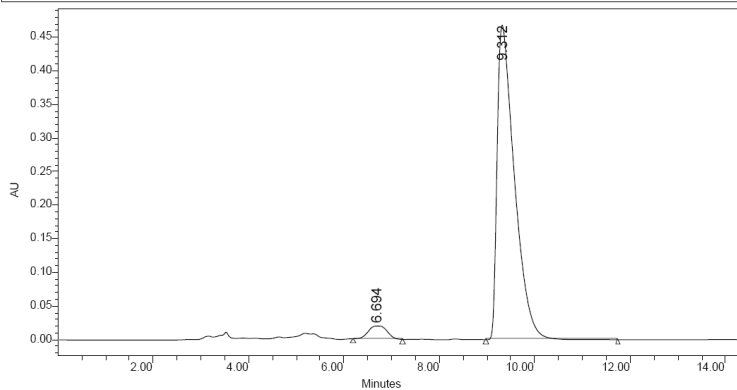
RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1 6.909	1641691	49.45	107285	56.19
2 9.451	1678309	50.55	83650	43.81

USTC

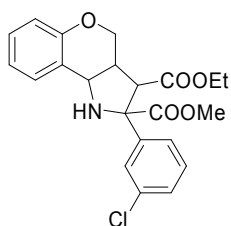
Project Name: linan  
 Reported by User: System

*Breeze*

SAMPLE INFORMATION					
Sample Name:	LN-10-10-od15%	Acquired By:	System		
Sample Type:	Unknown	Date Acquired:	10/13/2009 4:53:30 PM		
Vial:	1	Acq. Method:	linanmethod15%		
Injection #:	4	Date Processed:	10/13/2009 5:09:34 PM		
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1		
Run Time:	120.00 Minutes	Sample Set Name:			



RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1 6.694	529055	4.29	19437	3.99
2 9.312	11794633	95.71	468099	96.01

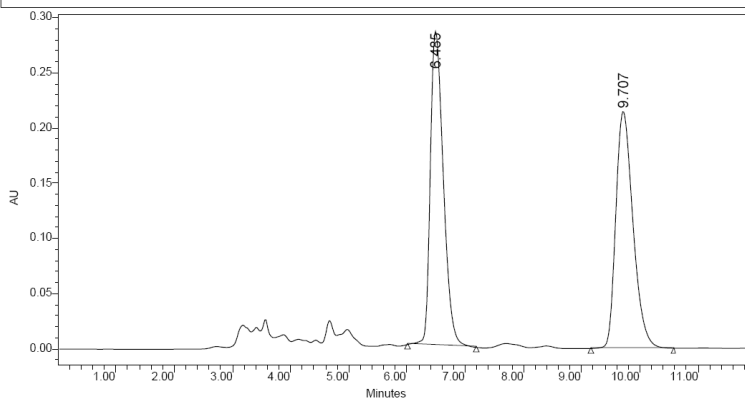


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Project Name: linan  
 Reported by User: System

*Breeze*

SAMPLE INFORMATION			
Sample Name:	LN-10-11-rac-od15%	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	9/22/2009 11:50:36 AM
Vial:	1	Acq. Method:	linanmethod15%
Injection #:	10	Date Processed:	9/22/2009 12:04:05 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	90.00 Minutes	Sample Set Name:	



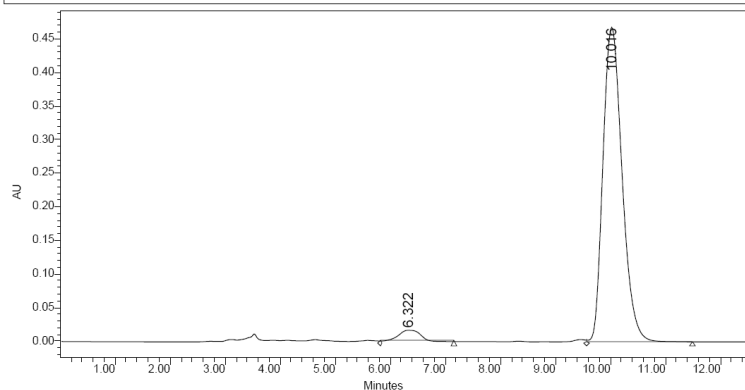
	RT (min)	Area (V <sup>2</sup> sec)	% Area	Height (V)	% Height
1	6.485	4436064	50.16	284821	57.01
2	9.707	4408367	49.84	214814	42.99

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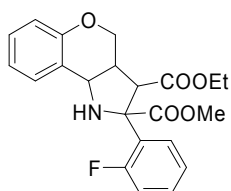
Project Name: linan  
 Reported by User: System

*Breeze*

SAMPLE INFORMATION			
Sample Name:	LN-10-11-od15%	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	10/13/2009 2:42:29 PM
Vial:	1	Acq. Method:	linanmethod15%
Injection #:	3	Date Processed:	10/13/2009 2:58:04 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V <sup>2</sup> sec)	% Area	Height (V)	% Height
1	6.322	481657	4.10	16858	3.48
2	10.016	11269834	95.90	468031	96.52

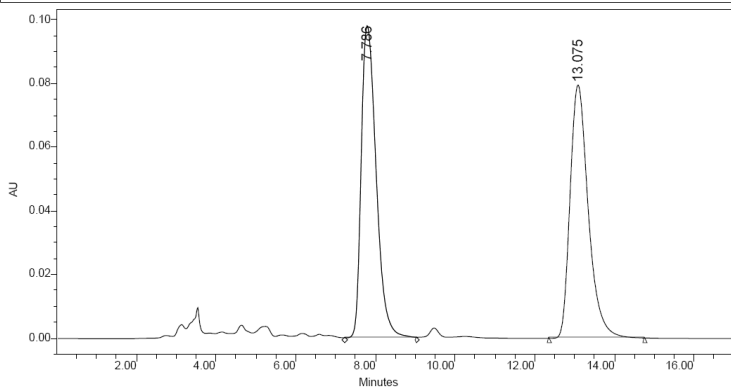


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Project Name: linan  
 Reported by User: System

*Breeze*

SAMPLE INFORMATION					
Sample Name:	LN-10-15-rac-od15%	Acquired By:	System		
Sample Type:	Unknown	Date Acquired:	10/13/2009 2:57:41 PM		
Vial:	1	Acq. Method:	linanmethod15%		
Injection #:	4	Date Processed:	10/13/2009 3:15:49 PM		
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1		
Run Time:	120.00 Minutes	Sample Set Name:			



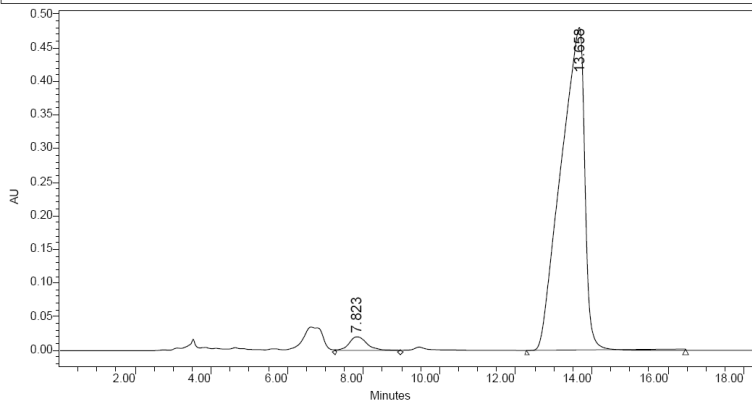
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.786	2560481	50.29	98047	55.22
2	13.075	2530764	49.71	79523	44.78

USTC

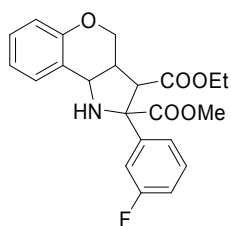
Project Name: linan  
 Reported by User: System

*Breeze*

SAMPLE INFORMATION					
Sample Name:	LN-10-15-od15%	Acquired By:	System		
Sample Type:	Unknown	Date Acquired:	10/13/2009 2:09:32 PM		
Vial:	1	Acq. Method:	linanmethod15%		
Injection #:	1	Date Processed:	10/13/2009 2:43:23 PM		
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1		
Run Time:	120.00 Minutes	Sample Set Name:			



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.823	682236	3.17	20416	4.07
2	13.658	20861083	96.83	480714	95.93

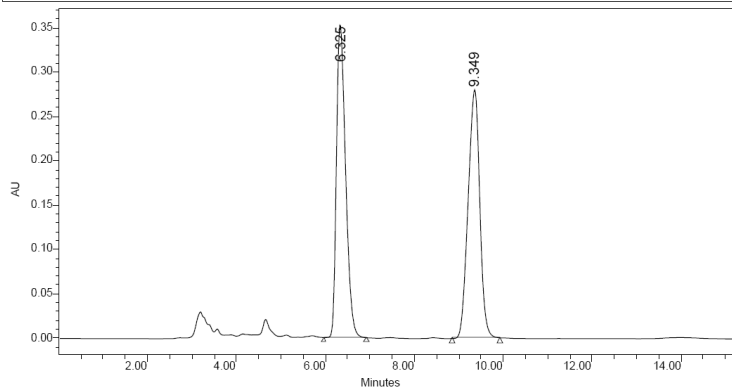


USTC

Project Name: linan  
 Reported by User: System

*Breeze*

SAMPLE INFORMATION			
Sample Name:	LN-10-16-rac-od15%	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	9/22/2009 9:23:56 AM
Vial:	1	Acq. Method:	linanmethod15%
Injection #:	1	Date Processed:	9/22/2009 9:40:17 AM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	90.00 Minutes	Sample Set Name:	



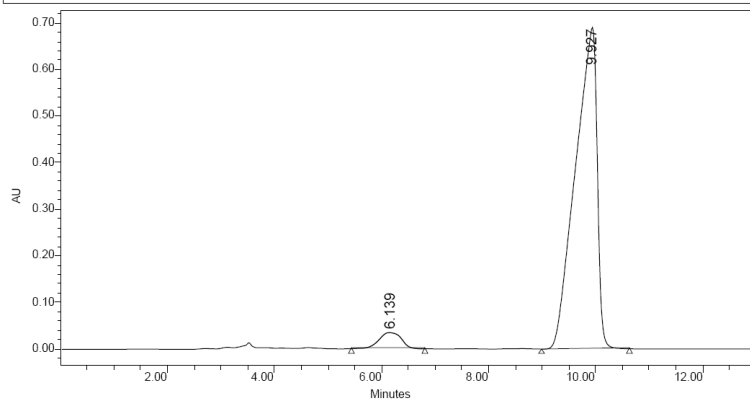
RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1 6.325	5055105	49.75	354100	55.81
2 9.349	5106408	50.25	280336	44.19

USTC

Project Name: linan  
 Reported by User: System

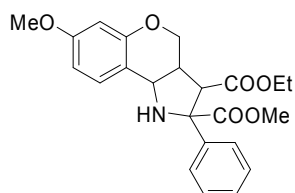
*Breeze*

SAMPLE INFORMATION			
Sample Name:	LN-10-16-od15%	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	10/13/2009 2:28:46 PM
Vial:	1	Acq. Method:	linanmethod15%
Injection #:	2	Date Processed:	10/13/2009 2:42:53 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1 6.139	1016410	4.97	34691	4.78
2 9.927	19438530	95.03	691088	95.22



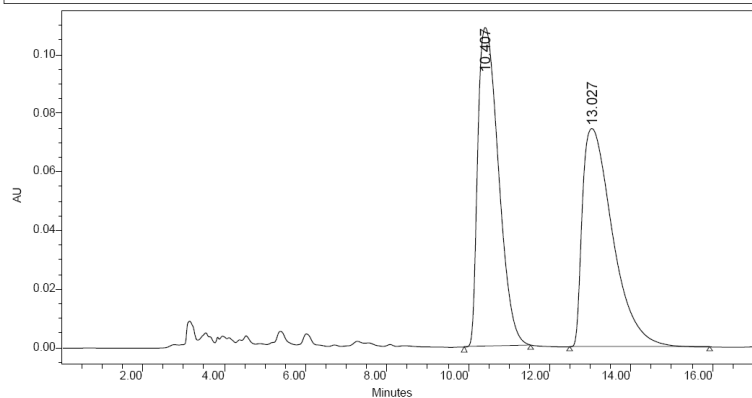


USTC

Project Name: linan  
 Reported by User: System

*Breeze*

SAMPLE INFORMATION					
Sample Name:	LN-10-21-rac-od5%	Acquired By:	System		
Sample Type:	Unknown	Date Acquired:	10/13/2009 7:42:31 PM		
Vial:	1	Acq. Method:	linanmethod5%		
Injection #:	3	Date Processed:	10/13/2009 8:00:17 PM		
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1		
Run Time:	120.00 Minutes	Sample Set Name:			



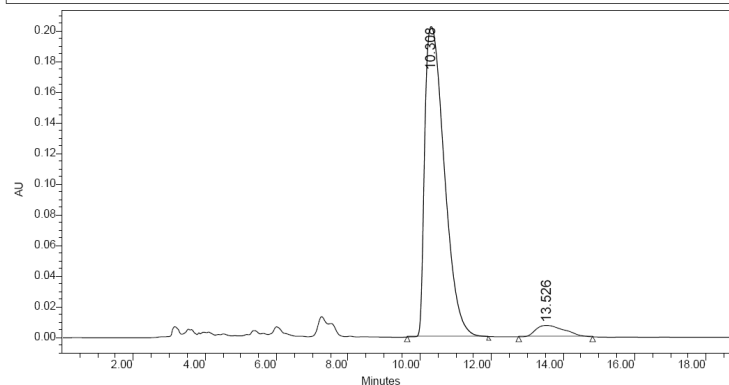
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	10.407	3837893	49.87	108814	59.36
2	13.027	3858183	50.13	74509	40.64

USTC

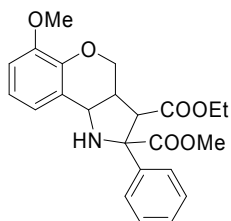
Project Name: linan  
 Reported by User: System

*Breeze*

SAMPLE INFORMATION					
Sample Name:	LN-10-21-od5%	Acquired By:	System		
Sample Type:	Unknown	Date Acquired:	10/13/2009 6:37:57 PM		
Vial:	1	Acq. Method:	linanmethod5%		
Injection #:	1	Date Processed:	10/13/2009 6:58:51 PM		
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1		
Run Time:	120.00 Minutes	Sample Set Name:			



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	10.308	7659960	94.86	202203	96.45
2	13.526	415063	5.14	7449	3.55

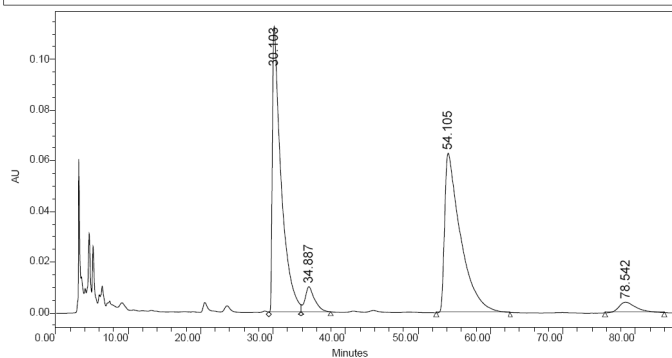


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Project Name: linan  
 Reported by User: System

Breeze

SAMPLE INFORMATION			
Sample Name:	LN-10-24-rac-ad3%	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	9/23/2009 5:25:41 PM
Vial:	1	Acq. Method:	linanmethod3%
Injection #:	1	Date Processed:	10/12/2009 11:38:18 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



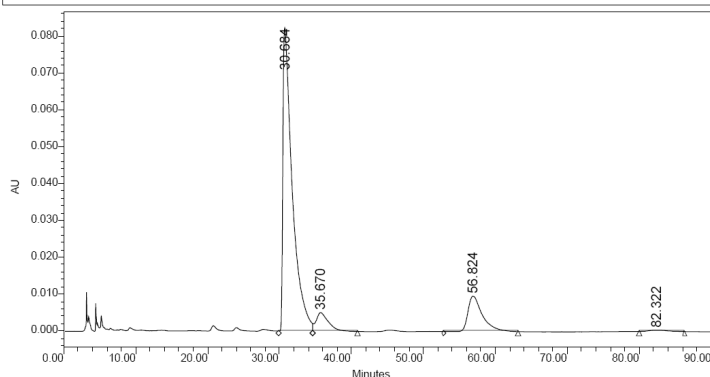
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	30.103	9504115	45.76	112812	59.37
2	34.887	914221	4.40	10005	5.27
3	54.105	9635614	46.39	62992	33.15
4	78.542	716558	3.45	4204	2.21

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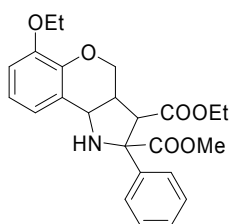
Project Name: linan  
 Reported by User: System

Breeze

SAMPLE INFORMATION			
Sample Name:	LN-10-24-ad3%	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	10/12/2009 10:05:18 PM
Vial:	1	Acq. Method:	linanmethod3%
Injection #:	1	Date Processed:	10/12/2009 11:36:44 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	30.684	7478777	78.84	82359	84.55
2	35.670	605054	6.38	5128	5.26
3	56.824	1343364	14.16	9578	9.83
4	82.322	58887	0.62	343	0.35

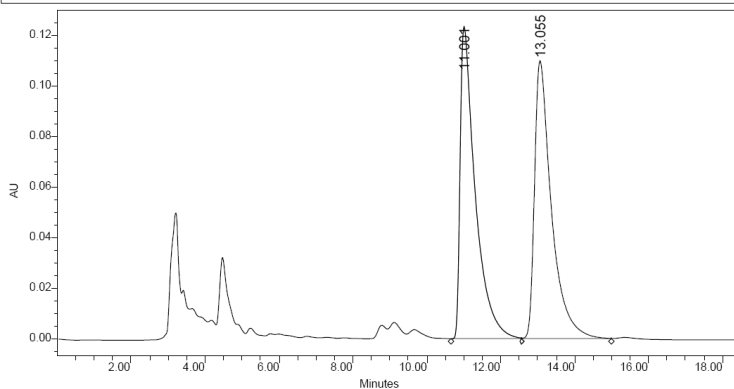


USTC

Project Name: linan  
 Reported by User: System

*Breeze*

SAMPLE INFORMATION					
Sample Name:	LN-10-25-rac-ad10%	Acquired By:	System		
Sample Type:	Unknown	Date Acquired:	9/23/2009 12:59:24 PM		
Vial:	1	Acq. Method:	linanmethod10%		
Injection #:	1	Date Processed:	10/12/2009 8:17:51 PM		
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1		
Run Time:	90.00 Minutes	Sample Set Name:			



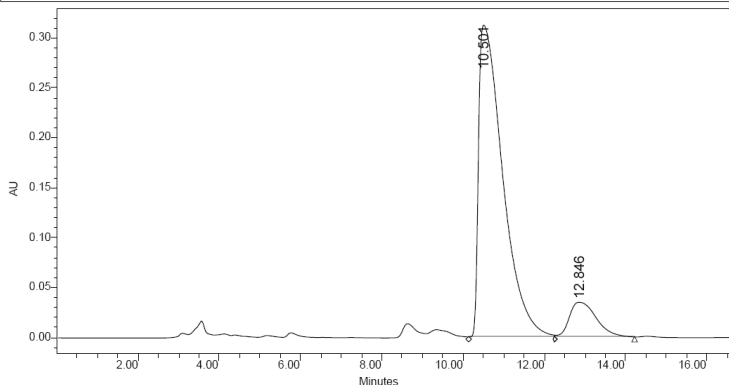
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	11.001	3538920	49.89	123798	52.87
2	13.055	3555218	50.11	110348	47.13

USTC

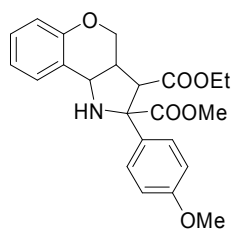
Project Name: linan  
 Reported by User: System

*Breeze*

SAMPLE INFORMATION					
Sample Name:	LN-10-25-ad10%	Acquired By:	System		
Sample Type:	Unknown	Date Acquired:	10/12/2009 9:37:38 PM		
Vial:	1	Acq. Method:	linanmethod10%		
Injection #:	6	Date Processed:	10/12/2009 9:54:55 PM		
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1		
Run Time:	120.00 Minutes	Sample Set Name:			



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	10.501	12942036	88.87	312835	89.92
2	12.846	1621154	11.13	35074	10.08

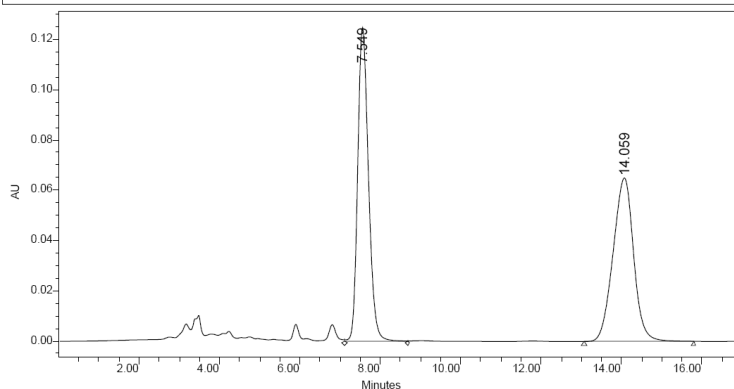


USTC

Project Name: linan  
 Reported by User: System

Breeze

SAMPLE INFORMATION					
Sample Name:	LN-10-31-rac-od30%	Acquired By:	System		
Sample Type:	Unknown	Date Acquired:	9/21/2009 4:43:34 PM		
Vial:	1	Acq. Method:	LN100%A		
Injection #:	6	Date Processed:	9/22/2009 10:00:33 AM		
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1		
Run Time:	90.00 Minutes	Sample Set Name:			



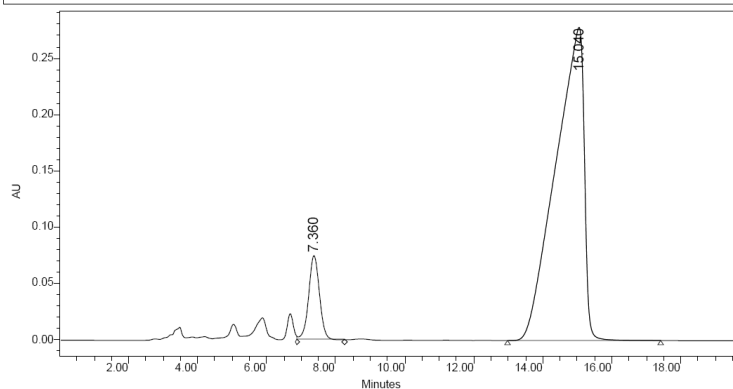
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.549	2320810	50.17	124772	65.73
2	14.059	2305034	49.83	65065	34.27

USTC

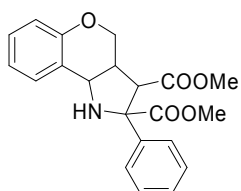
Project Name: linan  
 Reported by User: System

Breeze

SAMPLE INFORMATION					
Sample Name:	LN-10-31-od30%	Acquired By:	System		
Sample Type:	Unknown	Date Acquired:	10/13/2009 1:29:26 PM		
Vial:	1	Acq. Method:	LN100%A		
Injection #:	2	Date Processed:	10/13/2009 1:49:42 PM		
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1		
Run Time:	120.00 Minutes	Sample Set Name:			



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.360	1673889	9.48	75157	21.28
2	15.040	15987336	90.52	278010	78.72

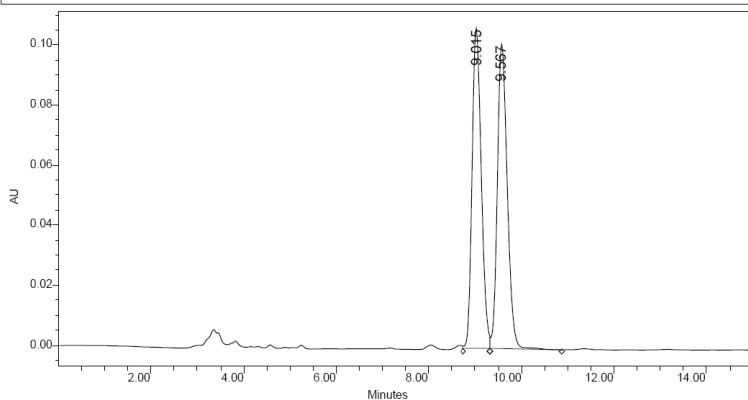


USTC

Project Name: linan  
 Reported by User: System

Breeze

SAMPLE INFORMATION			
Sample Name:	In-6-12-ad10%	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	5/6/2008 7:27:09 PM
Vial:	1	Acq. Method:	linanmethod10%
Injection #:	1	Date Processed:	5/6/2008 7:44:43 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	60.00 Minutes	Sample Set Name:	



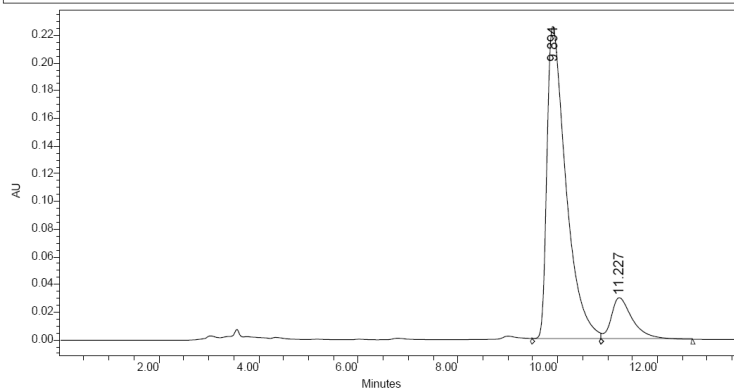
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	9.015	1489410	49.46	107074	51.30
2	9.567	1522221	50.54	101655	48.70

USTC

Project Name: linan  
 Reported by User: System

Breeze

SAMPLE INFORMATION			
Sample Name:	LN-10-37-ad10%	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	11/3/2009 11:29:11 AM
Vial:	1	Acq. Method:	linanmethod10%
Injection #:	1	Date Processed:	11/3/2009 11:43:31 AM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	9.894	6006308	86.94	226192	88.24
2	11.227	901942	13.06	30139	11.76