Mantis-shaped bifunctional tridentate HoMPy-PI-NO ligands capable of cooperatively activating both nucleophiles and electrophiles: empowering asymmetric addition reactions

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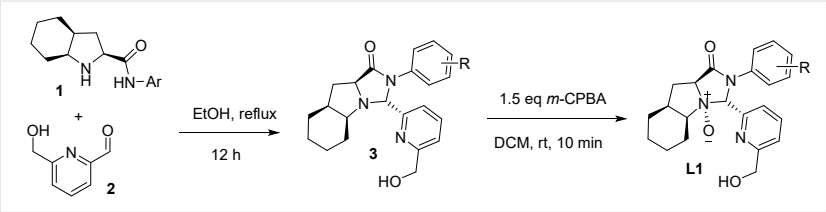
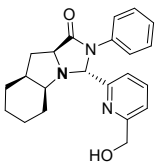
1. General information

Reactions were monitored by thin layer chromatography using UV light to visualize the course of reaction. Purification of reaction products was carried out by flash chromatography. ^{1}H and ^{13}CNMR spectra were obtained using a Bruker DPX-600 spectrometer. ^{1}H NMR chemical shifts are reported in ppm (δ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR chemical shifts are reported in ppm (δ) from tetramethylsilane (TMS) with the solvent resonance as the internal standard. Melting points were measured on an electrothermal digital melting point apparatus.

2. General procedure for preparation of chiral ligands L1

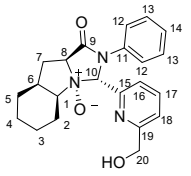


In a sealed tube equipped with a magnetic stirring bar, bicyclic prolinamides **1** (1.2 mmol, 1.2 equiv) and hydroxymethyl picolinaldehyde **2** (1.0 mmol) were added. Then, ethanol (8.0 mL) was added and the reaction was heated with stirring at reflux for 12 h. After completion of the reaction, as indicated by TLC, the aftertreatment residue was purified by flash column chromatography to give the intermediate **3**. In a sealed tube equipped with a magnetic stirring bar, to the intermediate **3** was added 3.0 mL of DCM and *m*-CPBA (1.5 eq). The reaction mixture was stirred at rt for 10 min. After completion of the reaction, as indicated by TLC, the aftertreatment residue was purified by flash column chromatography to furnish the ligand **L1**.

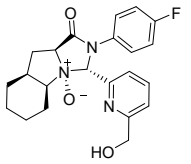


3a: Light yellow solid, yield 85% (308.6 mg), >20:1 dr; ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 1.12-1.19 (m, 1H), 1.26-1.36 (m, 2H), 1.49 (d, J = 13.2 Hz, 1H), 1.62-1.67 (m, 1H), 1.72-1.76 (m, 2H),

1.94-1.96 (m, 1H), 2.12-2.16 (m, 2H), 2.53-2.56 (m, 1H), 3.42-3.46 (m, 1H), 3.81 (br s, 1H), 4.24-4.26 (m, 1H), 4.70 (s, 2H), 6.02 (s, 1H), 7.08-7.17 (m, 3H), 7.27-7.29 (m, 2H), 7.47 (d, J = 7.8 Hz, 2H), 7.63-7.65 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 20.6, 23.2, 24.1, 25.8, 28.5, 38.4, 62.7, 63.5, 64.0, 78.2, 118.6, 120.1, 120.8, 125.1, 129.1, 137.1, 138.0, 157.7, 159.9, 176.4; HRMS (ESI-TOF) m/z: Calcd. for $C_{22}H_{26}N_3O_2$ $[M+H]^+$: 364.2020; Found: 364.2027.

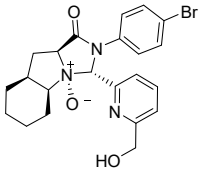


L1a: Light yellow solid, m.p. 162.9-163.3 °C, overall yield 60% (227.4 mg), 20:1 dr; ^{1}H NMR (CD_3OD, 600 MHz) δ: 1.11-1.18 (m, 1H), 1.28-1.41 (m, 2H), 1.48 (d, J = 13.2 Hz, 1H), 1.64-1.71 (m, 1H), 1.75-1.81 (m, 2H), 1.87-1.93 (m, 1H, O-H), 2.20-2.27 (m, 2H), 2.33-2.39 (m, 1H), 3.26-3.32 (m, 1H), 3.80-3.84 (m, 1H, C_1-H), 4.53-4.62 (m, 2H, C_{20}-H), 4.68-4.71 (m, 1H, C_8-H), 6.72 (s, 1H, C_{10}-H), 7.05-7.08 (m, 1H, C_{14}-H), 7.18-7.20 (m, 2H, C_{13}-H), 7.31-7.32 (m, 2H, C_{12}-H), 7.38-7.40 (m, 2H, C_{16}-H, C_{18}-H), 7.69-7.72 (m, 1H, C_{17}-H); ^{13}C NMR (CD_3OD, 150 MHz) δ: 19.8, 23.8, 24.0, 24.5, 27.0 (C_7), 35.7 (C_6), 64.7 (C_{20}), 75.6 (C_1), 84.2 (C_8), 84.3 (C_{10}), 121.3, 122.2, 124.7, 126.5, 128.9 (C_{13}), 135.0 (C_{11}), 137.1 (C_{17}), 150.6 (C_{15}), 161.7 (C_{19}), 169.4 (C_9); IR (KBr) ν 2936, 2860, 1717, 1597, 1498, 1394, 761, 690 cm^{-1}. HRMS (ESI-TOF) m/z: Calcd. for $C_{22}H_{26}N_3O_3$ $[M+H]^+$: 380.1969; Found: 380.1960.

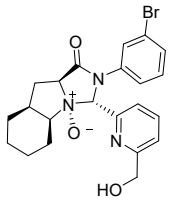


L1b: Light yellow solid, m.p. 170.2-170.9 °C, overall yield 58% (230.3 mg), 17:1 dr; ^{1}H NMR (CD_3OD, 600 MHz) δ: 1.14-1.21 (m, 1H), 1.30-1.43 (m, 2H), 1.50 (d, J = 13.2 Hz, 1H), 1.67-1.73 (m, 1H), 1.79-1.81 (m, 2H), 1.88-1.94 (m, 1H), 2.20-2.25 (m, 1H), 2.29-2.31 (m, 1H), 2.35-2.40 (m, 1H), 3.28-3.33 (m, 1H), 3.80-3.85 (m, 1H), 4.55-4.63 (m, 2H), 4.68-4.71 (m, 1H), 6.69 (s, 1H), 6.94-6.97 (m, 2H), 7.32-7.42 (m, 4H), 7.71-7.73 (m, 1H); ^{13}C NMR (CD_3OD, 150 MHz) δ: 19.7, 23.8, 24.0, 24.5, 26.9, 35.7, 64.7, 75.5, 84.2, 84.5, 115.6 (d, J_{CF} = 22.5 Hz), 121.4, 124.8, 124.9 (d, J_{CF} = 9.2 Hz), 130.2, 131.1 (d, J_{CF} = 3.0 Hz), 137.2, 150.4, 160.8 (d, J_{CF} = 244.5 Hz), 161.8, 169.5;

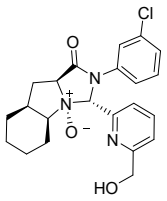
IR (KBr) *v* 2937, 2860, 1718, 1510, 1396, 1230, 837 cm^{-1}. HRMS (ESI-TOF) m/z: Calcd. for $C_{22}H_{25}FN_3O_3$ $[M+H]^+$: 398.1874; Found: 398.1873.



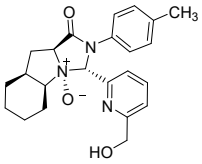
L1c: Light yellow solid, m.p. 185.3-186.0 °C, overall yield 61% (278.8 mg), 17:1 dr; ^1H NMR (CD_3OD, 600 MHz) *δ*: 1.13-1.17 (m, 1H), 1.30-1.36 (m, 2H), 1.49 (d, *J* = 12.6 Hz, 1H), 1.66-1.72 (m, 1H), 1.76-1.81 (m, 2H), 1.88-1.94 (m, 1H), 2.22-2.25 (m, 2H), 2.36-2.41 (m, 1H), 3.28-3.33 (m, 1H), 3.80-3.84 (m, 1H), 4.53-4.61 (m, 2H), 4.67-4.70 (m, 1H), 6.73 (s, 1H), 7.29-7.31 (m, 2H), 7.34-7.37 (m, 2H), 7.41-7.42 (m, 2H), 7.72-7.74 (m, 1H); ^{13}C NMR (CD_3OD, 150 MHz) *δ*: 19.7, 23.8, 23.9, 24.5, 27.0, 35.7, 64.7, 75.5, 84.0, 84.3, 119.4, 121.4, 123.7, 124.9, 132.0, 134.3, 137.2, 150.3, 161.9, 169.4; IR (KBr) *v* 2934, 2858, 1719, 1492, 1386, 1076, 827 cm^{-1}. HRMS (ESI-TOF) m/z: Calcd. for $C_{22}H_{25}BrN_3O_3$ $[M+H]^+$: 458.1074; Found: 458.1074.



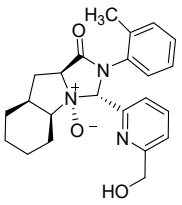
L1d: Light yellow solid, m.p. 158.9-159.4 °C, overall yield 55% (251.4 mg), 17:1 dr; ^1H NMR (CD_3OD, 600 MHz) *δ*: 1.22-1.26 (m, 1H), 1.41-1.45 (m, 2H), 1.58 (d, *J* = 12.6 Hz, 1H), 1.76-1.80 (m, 1H), 1.85-1.91 (m, 2H), 1.98-2.04 (m, 1H), 2.31-2.36 (m, 2H), 2.45-2.51 (m, 1H), 3.38-3.39 (m, 1H), 3.90-3.93 (m, 1H), 4.62-4.71 (m, 2H), 4.77-4.80 (m, 1H), 6.90 (s, 1H), 7.20-7.22 (m, 1H), 7.30-7.33 (m, 1H), 7.51-7.54 (m, 2H), 7.80 (s, 1H), 7.83-7.86 (m, 1H); ^{13}C NMR (CD_3OD, 150 MHz) *δ*: 19.7, 23.7, 23.9, 24.5, 27.1, 35.7, 64.7, 75.4, 83.7, 84.2, 120.1, 121.4, 122.2, 124.6, 127.0, 129.1, 130.4, 136.4, 137.2, 150.2, 161.9, 169.4; IR (KBr) *v* 2932, 2859, 1719, 1591, 1479, 1386, 1076, 1038, 779, 752, 691 cm^{-1}. HRMS (ESI-TOF) m/z: Calcd. for $C_{22}H_{25}BrN_3O_3$ $[M+H]^+$: 458.1064; Found: 458.1053.



L1e: Light yellow solid, m.p. 153.7-154.3 °C, overall yield 52% (214.8 mg), 16:1 dr; ^{1}H NMR (CD_3OD, 600 MHz) δ: 1.22-1.26 (m, 1H), 1.39-1.44 (m, 2H), 1.58 (d, J = 13.2 Hz, 1H), 1.76-1.81 (m, 1H), 1.85-1.91 (m, 2H), 1.98-2.04 (m, 1H), 2.31-2.36 (m, 2H), 2.46-2.51 (m, 1H), 3.37-3.42 (m, 1H), 3.90-3.94 (m, 1H), 4.63-4.71 (m, 2H), 4.77-4.80 (m, 1H), 6.89 (s, 1H), 7.16-7.18 (m, 1H), 7.26-7.29 (m, 1H), 7.35-7.37 (m, 1H), 7.51-7.54 (m, 2H), 7.65-7.66 (m, 1H), 7.83-7.85 (m, 1H); ^{13}C NMR (CD_3OD, 150 MHz) δ: 19.7, 23.7, 23.9, 24.5, 27.1, 35.7, 64.7, 75.4, 83.8, 84.3, 119.6, 121.4, 121.7, 124.8, 126.2, 130.2, 134.4, 136.3, 137.2, 150.3, 161.9, 169.5; IR (KBr) ν 2932, 2859, 1719, 1595, 1483, 1386, 1096, 1076, 1038, 779, 781, 752 cm^{-1}. HRMS (ESI-TOF) m/z: Calcd. for $C_{22}H_{25}ClN_3O_3$ $[M+H]^+$: 414.1576; Found: 414.1562.

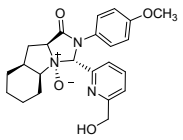


L1f: Light yellow solid, m.p. 154.9-155.7 °C, overall yield 61% (239.7 mg), 18:1 dr; ^{1}H NMR (CD_3OD, 600 MHz) δ: 1.12-1.17 (m, 1H), 1.29-1.42 (m, 2H), 1.49 (d, J = 13.2 Hz, 1H), 1.66-1.72 (m, 1H), 1.76-1.81 (m, 2H), 1.87-1.94 (m, 1H), 2.14 (s, 3H), 2.19-2.25 (m, 1H), 2.28-2.31 (m, 1H), 2.34-2.39 (m, 1H), 3.28-3.31 (m, 1H), 3.80-3.84 (m, 1H), 4.55-4.63 (m, 2H), 4.68-4.71 (m, 1H), 6.67 (s, 1H), 7.00 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 7.37-7.41 (m, 2H), 7.69-7.71 (m, 1H); ^{13}C NMR (CD_3OD, 150 MHz) δ: 19.5, 19.8, 23.8, 24.0, 24.5, 27.0, 35.7, 64.7, 75.6, 84.2, 84.5, 121.2, 122.4, 127.7, 129.4, 132.4, 136.8, 137.1, 150.7, 161.7, 169.4; IR (KBr) ν 2936, 2860, 1719, 1516, 1395, 1076, 1038, 814, 770, 752 cm^{-1}. HRMS (ESI-TOF) m/z: Calcd. for $C_{23}H_{28}N_3O_3$ $[M+H]^+$: 394.2121; Found: 394.2113.

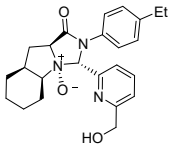


L1g: Light yellow solid, m.p. 147.1-147.6 °C, overall yield 53% (208.3 mg), 16:1 dr; ^{1}H NMR

(CD_3OD, 600 MHz) δ: 1.29-1.35 (m, 1H), 1.38-1.44 (m, 1H), 1.51-1.55 (m, 1H), 1.58-1.64 (m, 1H), 1.76-1.83 (m, 1H), 1.89-1.98 (m, 2H), 2.00 (s, 1H), 2.23 (s, 3H), 2.30-2.35 (m, 1H), 2.40-2.45 (m, 1H), 2.72-2.74 (m, 1H), 3.43-3.44 (m, 1H), 3.94-3.98 (m, 1H), 4.68 (d, J = 15.0 Hz, 1H), 4.76 (d, J = 15.0 Hz, 1H), 4.95-4.97 (m, 1H), 6.85 (s, 1H), 7.13-7.20 (m, 3H), 7.30-7.33 (m, 1H), 7.37-7.40 (m, 1H), 7.47 (d, J = 7.8 Hz, 1H), 7.69-7.71 (m, 1H); ^{13}C NMR (CD_3OD, 150 MHz) δ: 18.0, 19.6, 23.8, 24.2, 24.6, 26.1, 35.8, 64.6, 75.6, 84.3, 86.2, 121.3, 124.6, 125.0, 126.3, 128.3, 131.6, 132.8, 136.4, 136.9, 150.4, 161.4, 168.0; IR (KBr) ν 2930, 2858, 1719, 1495, 1460, 1400, 1078, 1036, 768, 743, 718 cm^{-1}. HRMS (ESI-TOF) m/z: Calcd. for $C_{23}H_{28}N_3O_3$ $[M+H]^+$: 394.2121; Found: 394.2108.

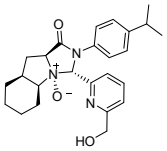


L1h: Light yellow solid, m.p. 180.6-181.3 °C, overall yield 56% (229.0 mg), 15:1 dr; ^1H NMR (CD_3OD, 600 MHz) δ: 1.26-1.31 (m, 1H), 1.38-1.45 (m, 1H), 1.49-1.56 (m, 1H), 1.59 (d, J = 13.2 Hz, 1H), 1.76-1.82 (m, 1H), 1.89 (d, J = 8.4 Hz, 2H), 1.97-2.03 (m, 1H), 2.28-2.34 (m, 1H), 2.42-2.45 (m, 2H), 3.37-3.42 (m, 1H), 3.71 (s, 3H), 3.90-3.94 (m, 1H), 4.66-4.74 (m, 2H), 4.78-4.80 (m, 1H), 6.71 (s, 1H), 6.82-6.84 (m, 2H), 7.24-7.27 (m, 2H), 7.43 (d, J = 7.8 Hz, 1H), 7.50 (d, J = 7.8 Hz, 1H), 7.78-7.81 (m, 1H); ^{13}C NMR (CD_3OD, 150 MHz) δ: 19.8, 23.8, 24.1, 24.6, 26.9, 35.7, 54.5, 64.7, 75.6, 84.1, 84.9, 114.1, 121.3, 124.8, 127.5, 129.1, 137.1, 150.6, 158.6, 161.7, 169.5; IR (KBr) ν 2936, 2860, 1715, 1514, 1458, 1398, 1252, 1034, 835, 801 cm^{-1}. HRMS (ESI-TOF) m/z: Calcd. for $C_{23}H_{28}N_3O_4$ $[M+H]^+$: 410.2074; Found: 410.2065.

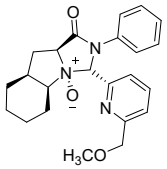


L1i: Light yellow solid, m.p. 156.2-156.9 °C, overall yield 54% (219.8 mg), 16:1 dr; ^1H NMR (CD_3OD, 600 MHz) δ: 1.12-1.15 (m, 3H), 1.22-1.27 (m, 1H), 1.39-1.50 (m, 2H), 1.59 (d, J = 13.2 Hz, 1H), 1.75-1.82 (m, 1H), 1.86-1.91 (m, 2H), 1.97-2.04 (m, 1H), 2.30-2.39 (m, 2H), 2.44-2.49 (m, 1H), 2.53-2.57 (m, 2H), 3.37-3.41 (m, 1H), 3.90-3.94 (m, 1H), 4.64-4.72 (m, 2H), 4.78-4.81 (m, 1H), 6.78 (s, 1H), 7.13 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 9.0 Hz, 2H), 7.47-7.51 (m, 2H), 7.79-

7.82 (m, 1H); ^{13}C NMR (CD_3OD, 150 MHz) δ: 14.5, 19.8, 23.8, 24.0, 24.5, 27.0, 27.9, 35.7, 64.7, 75.6, 84.2, 84.5, 121.3, 122.5, 124.7, 128.3, 132.6, 137.1, 143.1, 150.7, 161.7, 169.4; IR (KBr) v 2963, 2934, 2860, 1719, 1516, 1458, 1395, 1076, 1038, 837, 766, 752 cm^{-1}. HRMS (ESI-TOF) m/z: Calcd. for $C_{24}H_{30}N_3O_3$ $[M+H]^+$: 408.2282; Found: 408.2272.

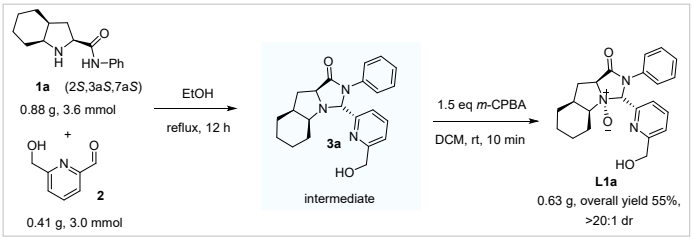


L1j: Light yellow solid, m.p. 150.6-151.2 °C, overall yield 59% (248.4 mg), 20:1 dr; ^{1}H NMR (CD_3OD, 600 MHz) δ: 1.15 (d, J = 6.6 Hz, 6H), 1.23-1.29 (m, 1H), 1.38-1.51 (m, 2H), 1.59 (d, J = 13.2 Hz, 1H), 1.76-1.81 (m, 1H), 1.86-1.91 (m, 2H), 1.97-2.04 (m, 1H), 2.30-2.39 (m, 2H), 2.43-2.49 (m, 1H), 2.79-2.84 (m, 1H), 3.39 (s, 1H), 3.90-3.93 (m, 1H), 4.65-4.73 (m, 2H), 4.78-4.80 (m, 1H), 6.79 (s, 1H), 7.16 (d, J = 7.8 Hz, 2H), 7.32 (d, J = 7.8 Hz, 2H), 7.48-7.51 (m, 2H), 7.80-7.82 (m, 1H); ^{13}C NMR (CD_3OD, 150 MHz) δ: 19.8, 22.8, 23.8, 24.0, 24.5, 27.0, 33.5, 35.7, 64.7, 75.5, 84.2, 84.4, 121.3, 122.4, 124.7, 126.8, 132.6, 137.1, 147.6, 150.7, 161.8, 169.4; IR (KBr) v 2959, 2934, 2864, 1717, 1516, 1458, 1395, 1096, 1076, 1038, 837, 754 cm^{-1}. HRMS (ESI-TOF) m/z: Calcd. for $C_{25}H_{32}N_3O_3$ $[M+H]^+$: 422.2432; Found: 422.2425.



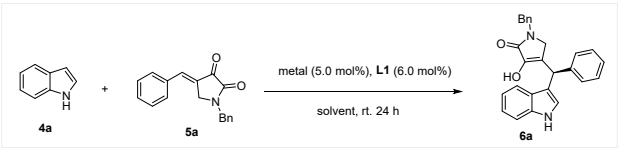
L3a: Light yellow solid, m.p. 145.9-150.6 °C, overall yield 62% (243.7 mg), >20:1 dr; ^{1}H NMR (CD_3OD, 600 MHz) δ: 1.25-1.32 (m, 1H), 1.42-1.52 (m, 2H), 1.61 (d, J = 13.2 Hz, 1H), 1.78-1.84 (m, 1H), 1.89-1.94 (m, 2H), 2.32-1.41 (m, 2H), 2.44-2.50 (m, 1H), 3.38-3.41 (m, 1H), 3.43 (s, 3H), 3.94-3.98 (m, 1H), 4.54 (d, J = 13.8 Hz, 1H), 4.61 (d, J = 13.8 Hz, 1H), 4.76-4.79 (m, 1H), 6.87 (s, 1H), 7.18-7.21 (m, 1H), 7.31-7.34 (m, 2H), 7.44-7.46 (m, 2H), 7.48 (d, J = 7.8 Hz, 1H), 7.55 (d, J = 7.8 Hz, 1H), 7.83-7.86 (m, 1H); ^{13}C NMR (CD_3OD, 150 MHz) δ: 19.7, 23.8, 24.0, 24.5, 27.0, 35.7, 57.7, 74.8, 75.6, 84.2, 84.3, 121.9, 122.2, 125.1, 126.5, 128.9, 135.0, 137.1, 150.7, 159.2, 169.4; HRMS (ESI-TOF) m/z: Calcd. for $C_{23}H_{28}N_3O_3$ $[M+H]^+$: 394.2125; Found: 394.2128.

3. The gram scale synthesis of the ligand L1a



In a sealed tube equipped with a magnetic stirring bar, bicyclic prolinamides **1** (0.88 g, 3.6 mmol) and hydroxymethyl picolinaldehyde **2** (0.41 g, 3.0 mmol) were added. Then, ethanol (16.0 mL) was added and the reaction was heated with stirring at reflux for 12 h. After completion of the reaction, as indicated by TLC, the aftertreatment residue was purified by flash column chromatography to give the intermediate **3**. In a sealed tube equipped with a magnetic stirring bar, to the intermediate **3** was added 6.0 mL of DCM and *m*-CPBA (1.5 eq). The reaction mixture was stirred at rt for 10 min. After completion of the reaction, as indicated by TLC, the aftertreatment residue was purified by flash column chromatography to furnish the ligand **L1a** (0.63 g, overall yield 55%, >20:1 dr).

4. Table S1. Examination of the catalytic reactivity of ligands L[a]

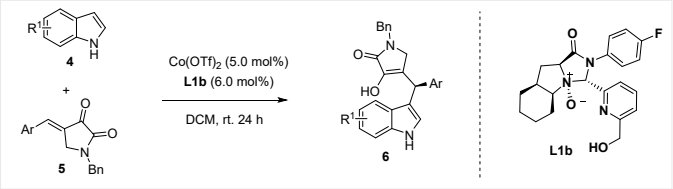


Entry	Metal	Ligand	Solvent	Yield[b] (%)	Ee[c]
1	$Ni(OTf)_2$	**L1a**	DCM	81	76
2	$Ni(OTf)_2$	**L1b**	DCM	90	86
3	$Ni(OTf)_2$	**L1c**	DCM	80	79
4	$Ni(OTf)_2$	**L1d**	DCM	83	80
5	$Ni(OTf)_2$	**L1e**	DCM	84	79
6	$Ni(OTf)_2$	**L1f**	DCM	80	72
7	$Ni(OTf)_2$	**L1g**	DCM	79	51
8	$Ni(OTf)_2$	**L1h**	DCM	81	79
9	$Ni(OTf)_2$	**L1i**	DCM	88	80
10	$Ni(OTf)_2$	**L1j**	DCM	87	80
11	$Zn(OTf)_2$	**L1b**	DCM	81	65
12	$Cu(OTf)_2$	**L1b**	DCM	84	90
13	$Co(OTf)_2$	**L1b**	DCM	90	92
14	$Co(OTf)_2$	**L1b**	$CHCl_3$	87	83
15	$Co(OTf)_2$	**L1b**	DCE	89	90
16	$Co(OTf)_2$	**L1b**	Toluene	88	89
17	$Co(OTf)_2$	**L1b**	THF	<10	-

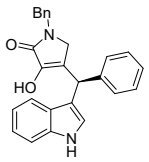
18	$Co(OTf)_2$	**L1b**	CH_3CN	71	64
19[d]	$Co(OTf)_2$	**L1b**	DCM	90	90
20[e]	$Co(OTf)_2$	**L1b**	DCM	86	83

[a] Reaction conditions: metal (5.0 mol %), ligand (6.0 mol %), **4a** (0.30 mmol), and **5a** (0.20 mmol) in 2.0 mL of solvent at rt.
[b] Isolated yield after flash chromatography.
[c] Determined by HPLC analysis.
[d] 1.0 mL of CH_2Cl_2.
[e] 3.0 mL of CH_2Cl_2.

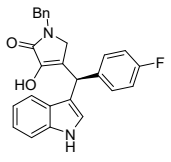
5. Catalytic asymmetric synthesis of compounds 6



In a sealed tube equipped with a stirring bar, to the mixture of $Co(OTf)_2$ (5.0 mol %), **L1b** (6.0 mol %) in 2.0 mL of DCM was added **4** (0.30 mmol), and **5** (0.20 mmol). The reaction mixture was stirred at room temperature for 24 h and was directly loaded onto a silica gel and purified by flash chromatography to give the desired product **6**, using hexane/EtOAc (10/1, v/v) as the eluent.

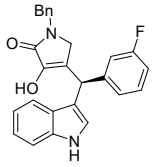


6a: Product in accordance with literature characterization data[7a-g]. 90% yield (70.9 mg), 92% ee; The ee was determined by HPLC analysis using a Chiralpak IA column (60/40 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 10.74 min; τ_{minor} = 20.90 min); ^{1}H NMR (DMSO-d_6, 600 MHz) δ: 3.55-3.65 (m, 2H), 4.48-4.53 (m, 2H), 5.58 (s, 1H), 6.86-6.88 (m, 1H), 6.96 (d, J = 2.4 Hz, 1H), 7.02-7.05 (m, 1H), 7.12 (d, J = 7.2 Hz, 2H), 7.15 (d, J = 7.8 Hz, 1H), 7.18-7.30 (m, 8H), 7.33 (d, J = 8.4 Hz, 1H), 9.52 (br s, 1H), 10.92 (br s, 1H); ^{13}C NMR (DMSO-d_6, 150 MHz) δ: 39.0, 46.0, 48.2, 112.0, 115.6, 118.9, 119.1, 121.6, 123.4, 123.9, 126.8, 126.9, 127.7, 128.5, 128.8, 129.1, 136.9, 138.2, 142.5, 142.8, 167.3.

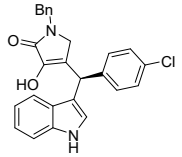


6b: Product in accordance with literature characterization data[7a-g]. 89% yield (73.3 mg), 91% ee;

The ee was determined by HPLC analysis using a Chiralpak IA column (60/40 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 10.28 min; τ_{minor} = 21.02 min); ^{1}H NMR (DMSO-d_6, 600 MHz) δ: 3.55-3.65 (m, 2H), 4.47-4.54 (m, 2H), 5.56 (s, 1H), 6.87-6.89 (m, 1H), 6.96 (s, 1H), 7.03-7.05 (m, 1H), 7.08-7.15 (m, 5H), 7.23-7.30 (m, 5H), 7.33 (d, J = 8.4 Hz, 1H), 9.52 (br s, 1H), 10.93 (br s, 1H); ^{13}C NMR (DMSO-d_6, 150 MHz) δ: 38.3, 46.0, 48.2, 112.1, 115.4 (d, J_{CF} = 21.0 Hz), 115.5, 119.0 (d, J_{CF} = 6.1 Hz), 121.6, 123.1, 123.9, 126.7, 127.6, 127.7, 129.1, 130.2 (d, J_{CF} = 9.0 Hz), 137.0, 138.2, 138.9, 142.6, 161.8 (d, J_{CF} = 240.0 Hz), 167.3.

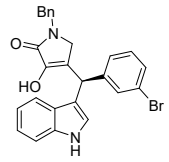


6c: Product in accordance with literature characterization data[7a-g]. 88% yield (72.5 mg), 91% ee; The ee was determined by HPLC analysis using a Chiralpak IA column (60/40 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 9.84 min; τ_{minor} = 18.08 min); ^{1}H NMR (DMSO-d_6, 600 MHz) δ: 3.39-3.48 (m, 2H), 4.28-4.36 (m, 2H), 5.40 (s, 1H), 6.69-6.71 (m, 1H), 6.81-6.87 (m, 4H), 6.91-6.94 (m, 3H), 6.98 (d, J = 7.8 Hz, 1H), 7.01-7.04 (m, 1H), 7.08-7.17 (m, 4H), 9.40 (br s, 1H), 10.77 (br s, 1H); ^{13}C NMR (DMSO-d_6, 150 MHz) δ: 38.8, 46.0, 48.2, 112.1, 113.6 (d, J_{CF} = 21.2 Hz), 114.9, 115.1 (d, J_{CF} = 21.1 Hz), 119.0, 119.1, 121.7, 122.7, 124.0, 124.6, 126.7, 127.7, 129.1, 130.6 (d, J_{CF} = 9.2 Hz), 136.9, 138.1, 142.8, 145.8 (d, J_{CF} = 6.1 Hz), 162.6 (d, J_{CF} = 243.1 Hz), 162.8, 167.3.

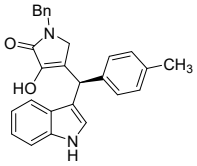


6d: Product in accordance with literature characterization data[7a-g]. 90% yield (77.0 mg), 90% ee; The ee was determined by HPLC analysis using a Chiralpak IA column (60/40 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 10.23 min; τ_{minor} = 20.29 min); ^{1}H NMR (DMSO-d_6, 600 MHz) δ: 3.56-3.65 (m, 2H), 4.46-4.55 (m, 2H), 5.56 (s, 1H), 6.87-6.90 (m, 1H), 6.98 (d, J = 2.4 Hz, 1H), 7.03-7.06 (m, 1H), 7.12-7.15 (m, 3H), 7.22-7.26 (m, 3H), 7.28-7.35 (m, 5H), 9.56 (br s, 1H), 10.95 (br s, 1H); ^{13}C NMR (DMSO-d_6, 150 MHz) δ: 38.5, 46.0, 48.2, 112.1, 115.1, 119.0, 119.1, 121.7, 122.8, 124.0, 126.7, 127.7, 127.8, 128.7, 129.1, 130.3, 131.3, 137.0, 138.1, 141.9,

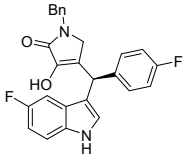
142.7, 167.3.



6e: Product in accordance with literature characterization data[7a-g]. 90% yield (85.0 mg), 90% ee; The ee was determined by HPLC analysis using a Chiralpak IA column (60/40 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 9.86 min; τ_{minor} = 22.15 min); ^{1}H NMR (DMSO-d_6, 600 MHz) δ: 3.58-3.67 (m, 2H), 4.49-4.55 (m, 2H), 5.57 (s, 1H), 6.89-6.91 (m, 1H), 7.01 (s, 1H), 7.04-7.07 (m, 1H), 7.13 (d, J = 7.8 Hz, 2H), 7.19 (d, J = 7.8 Hz, 1H), 7.22-7.27 (m, 3H), 7.29-7.31 (m, 2H), 7.35 (d, J = 8.4 Hz, 1H), 7.39-7.40 (m, 2H), 9.60 (br s, 1H), 10.98 (br s, 1H); ^{13}C NMR (DMSO-d_6, 150 MHz) δ: 38.7, 46.0, 48.3, 112.1, 114.8, 118.9, 119.1, 121.7, 122.1, 122.5, 124.1, 126.7, 127.6, 127.7, 129.1, 129.7, 131.0, 136.9, 138.1, 142.9, 145.7, 162.8, 167.3.

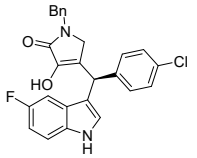


6f: Product in accordance with literature characterization data[7a-g]. 87% yield (71.0 mg), 91% ee; The ee was determined by HPLC analysis using a Chiralpak IA column (60/40 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 10.61 min; τ_{minor} = 21.98 min); ^{1}H NMR (DMSO-d_6, 600 MHz) δ: 2.24 (s, 3H), 3.53-3.64 (m, 2H), 4.47-4.53 (m, 2H), 5.53 (s, 1H), 6.85-6.88 (m, 1H), 6.93 (s, 1H), 7.02-7.04 (m, 1H), 7.07 (d, J = 7.2 Hz, 2H), 7.11-7.14 (m, 5H), 7.21-7.24 (m, 1H), 7.28-7.30 (m, 2H), 7.32 (d, J = 8.4 Hz, 1H), 9.48 (br s, 1H), 10.89 (br s, 1H); ^{13}C NMR (DMSO-d_6, 150 MHz) δ: 21.1, 38.6, 45.9, 48.1, 112.0, 115.7, 118.9, 119.1, 121.5, 123.7, 123.8, 126.9, 127.7, 127.8, 128.4, 129.1, 129.4, 135.7, 136.9, 138.2, 139.8, 142.4, 167.4.

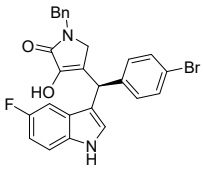


6g: Product in accordance with literature characterization data[7a-g]. 85% yield (73.1 mg), 90% ee; The ee was determined by HPLC analysis using a Chiralpak IA column (60/40 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 8.27 min; τ_{minor} = 13.32 min); ^{1}H NMR (DMSO-d_6,

600 MHz) δ: 3.57-3.67 (m, 2H), 4.49-4.57 (m, 2H), 5.53 (s, 1H), 6.96-6.92 (m, 2H), 7.08-7.14 (m, 5H), 7.22-7.24 (m, 1H), 7.29-7.30 (m, 4H), 7.35-7.36 (m, 1H), 9.58 (br s, 1H), 11.08 (br s, 1H); ^{13}C NMR (DMSO-d_6, 150 MHz) δ: 38.3, 46.0, 48.1, 103.6 (d, J_{CF} = 22.5 Hz), 109.8 (d, J_{CF} = 25.5 Hz), 113.1 (d, J_{CF} = 10.5 Hz), 115.5, 115.6, 115.7 (d, J_{CF} = 4.5 Hz), 122.8, 126.0, 126.9 (d, J_{CF} = 9.0 Hz), 127.7 (d, J_{CF} = 6.2 Hz), 129.0, 130.3 (d, J_{CF} = 7.5 Hz), 133.6, 138.1, 138.6, 142.7, 157.2 (d, J_{CF} = 229.5 Hz), 161.2 (d, J_{CF} = 240.1 Hz), 162.8, 167.3.

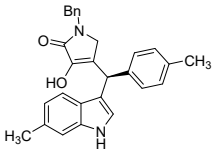


6h: Product in accordance with literature characterization data[7a-g]. 86% yield (76.7 mg), 90% ee; The ee was determined by HPLC analysis using a Chiralpak IA column (60/40 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 8.43 min; τ_{minor} = 13.80 min); ^{1}H NMR (DMSO-d_6, 600 MHz) δ: 3.58-3.67 (m, 2H), 4.48-4.57 (m, 2H), 5.53 (s, 1H), 6.87-6.92 (m, 2H), 7.10 (s, 1H), 7.14 (d, J = 7.2 Hz, 2H), 7.22-7.25 (m, 1H), 7.27-7.31 (m, 4H), 7.34-7.37 (m, 3H), 9.60 (br s, 1H), 11.09 (br s, 1H); ^{13}C NMR (DMSO-d_6, 150 MHz) δ: 38.4, 46.0, 48.2, 103.6 (d, J_{CF} = 24.0 Hz), 109.8 (d, J_{CF} = 25.5 Hz), 113.1 (d, J_{CF} = 9.2 Hz), 115.4 (d, J_{CF} =3.1 Hz), 122.4, 126.1, 126.9 (d, J_{CF} = 9.3 Hz), 127.7, 127.8, 128.8, 129.1, 130.4, 131.4, 133.6, 138.1, 141.5, 142.8, 157.2 (d, J_{CF} = 229.5 Hz), 162.8, 167.2.



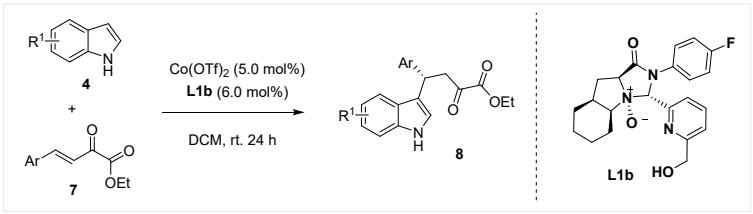
6i: Product in accordance with literature characterization data[7a-g]. 88% yield (86.2 mg), 91% ee; The ee was determined by HPLC analysis using a Chiralpak IA column (60/40 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 8.62 min; τ_{minor} = 13.73 min); ^{1}H NMR (DMSO-d_6, 600 MHz) δ: 3.58-3.67 (m, 2H), 4.48-4.58 (m, 2H), 5.52 (s, 1H), 6.88-6.93 (m, 2H), 7.10 (s, 1H), 7.14 (d, J = 7.2 Hz, 2H), 7.21-7.25 (m, 3H), 7.29-7.31 (m, 2H), 7.35-7.37 (m, 1H), 7.47 (d, J = 7.8 Hz, 2H), 9.61 (br s, 1H), 11.10 (br s, 1H); ^{13}C NMR (DMSO-d_6, 150 MHz) δ: 38.5, 46.0, 48.2, 103.6, 109.8, 113.1, 115.3, 119.9, 122.3, 126.1, 126.9, 127.7, 129.1, 130.8, 131.7, 133.6, 138.1,

141.9, 142.8, 157.2, 162.8, 167.3.

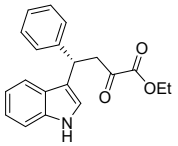


6j: Product in accordance with literature characterization data[7a-g]. 86% yield (72.6 mg), 99% ee; The ee was determined by HPLC analysis using a Chiralpak IC column (60/40 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 7.12 min; τ_{minor} = 9.98 min); ^{1}H NMR (DMSO-d_6, 600 MHz) δ: 3.51-3.62 (m, 2H), 4.45-4.50 (m, 2H), 5.50 (s, 1H), 6.69 (d, J = 8.4 Hz, 1H), 6.83 (s, 1H), 6.99 (d, J = 8.4 Hz, 1H), 7.06 (d, J = 7.2 Hz, 2H), 7.09-7.12 (m, 5H), 7.21-7.25 (m, 1H), 7.28-7.30 (m, 2H), 9.46 (br s, 1H), 10.72 (br s, 1H); ^{13}C NMR (DMSO-d_6, 150 MHz) δ: 21.1, 21.8, 38.6, 45.9, 48.1, 111.8, 115.5, 118.9, 120.7, 123.1, 123.8, 124.8, 127.7, 127.8, 128.3, 129.1, 129.3, 130.6, 135.7, 137.4, 138.2, 139.8, 142.3, 167.4.

6. Catalytic asymmetric synthesis of compounds 8

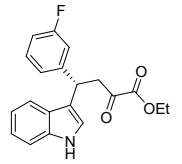


In a sealed tube equipped with a stirring bar, to the mixture of $Co(OTf)_2$ (5.0 mol %), **L1b** (6.0 mol %) in 2.0 mL of DCM was added **4** (0.30 mmol), and **7** (0.20 mmol). The reaction mixture was stirred at room temperature for 24 h and was directly loaded onto a silica gel and purified by flash chromatography to give the desired product **8**, using hexane/EtOAc (10/1, v/v) as the eluent.

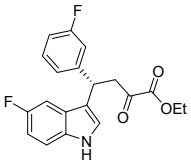


8a: Product in accordance with literature characterization data[7h-n]. 81% yield (52.0 mg), 91% ee; The ee was determined by HPLC analysis using a Chiralpak IA column (95/5 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 41.49 min; τ_{minor} = 32.16 min); ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 1.24-1.26 (m, 3H), 3.57-3.61 (m, 1H), 3.64-3.68 (m, 1H), 4.17-4.22 (m, 2H), 4.90-4.92

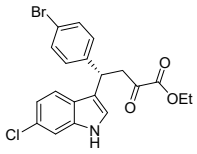
(m, 1H), 6.98 (s, 1H), 7.00-7.02 (m, 1H), 7.12-7.17 (m, 2H), 7.23-7.32 (m, 5H), 7.41 (d, J = 7.8 Hz, 1H), 8.03 (br s, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 13.9, 37.8, 45.6, 62.5, 111.2, 118.3, 119.4, 119.5, 121.6, 122.2, 126.4, 126.6, 127.8, 128.5, 136.5, 143.2, 161.0, 193.1.



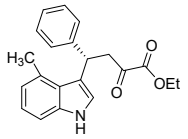
8b: Product in accordance with literature characterization data[7h-n]. 78% yield (52.9 mg), 91% ee; The ee was determined by HPLC analysis using a Chiralpak ID column (95/5 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 19.72 min; τ_{minor} = 16.58 min); ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 1.27-1.29 (m, 3H), 3.55-3.59 (m, 1H), 3.64-3.68 (m, 1H), 4.21-4.25 (m, 2H), 4.90-4.93 (m, 1H), 6.85-6.88 (m, 1H), 6.99-7.05 (m, 3H), 7.12-7.17 (m, 2H), 7.20-7.22 (m, 1H), 7.32 (d, J = 8.4 Hz, 1H), 7.40 (d, J = 7.8 Hz, 1H), 8.06 (br s, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 13.9, 37.4, 45.4, 62.6, 111.3, 113.5 (d, J_{CF} = 21.1 Hz), 114.7 (d, J_{CF} = 21.0 Hz), 117.7, 119.3, 119.7, 121.6, 122.5, 123.5, 126.3, 130.0 (d, J_{CF} = 7.5 Hz), 136.6, 146.0 (d, J_{CF} = 6.2 Hz), 160.9, 162.8 (d, J_{CF} = 244.5 Hz), 192.7.



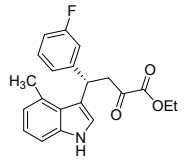
8c: Product in accordance with literature characterization data[7h-n]. 78% yield (55.7 mg), 91% ee; The ee was determined by HPLC analysis using a Chiralpak IA column (95/5 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 35.99 min; τ_{minor} = 28.14 min); ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 1.29-1.31 (m, 3H), 3.53-3.67 (m, 1H), 3.62-3.66 (m, 1H), 4.22-4.27 (m, 2H), 4.82-4.85 (m, 1H), 6.87-6.92 (m, 2H), 6.96-7.02 (m, 2H), 7.11 (s, 2H), 7.22-7.26 (m, 2H), 8.10 (br s, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 13.9, 37.3, 45.3, 62.7, 104.2 (d, J_{CF} = 24.0 Hz), 110.9 (d, J_{CF} = 27.1 Hz), 111.9 (d, J_{CF} = 9.1 Hz), 113.7 (d, J_{CF} = 21.0 Hz), 114.7 (d, J_{CF} = 21.2 Hz), 117.8 (d, J_{CF} = 4.5 Hz), 123.2, 123.4 (d, J_{CF} = 3.2 Hz), 126.6 (d, J_{CF} = 9.2 Hz), 130.1 (d, J_{CF} = 7.5 Hz), 133.1, 145.6 (d, J_{CF} = 7.5 Hz), 157.6 (d, J_{CF} = 234.2 Hz), 160.8, 162.9 (d, J_{CF} = 244.5 Hz), 192.5.



8d: Product in accordance with literature characterization data[7h-n]. 85% yield (73.6 mg), 90% ee; The ee was determined by HPLC analysis using a Chiralpak IE column (95/5 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 21.50 min; τ_{minor} = 29.59 min); ^{1}H NMR ($CDCl_3$, 600 MHz) *δ*: 1.29-1.31 (m, 3H), 3.52-3.56 (m, 1H), 3.61-3.65 (m, 1H), 4.23-4.26 (m, 2H), 4.82-4.84 (m, 1H), 6.99 (d, *J* = 9.0 Hz, 1H), 7.05 (s, 1H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.33 (s, 1H), 7.38 (d, *J* = 7.8 Hz, 2H), 8.04 (br s, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) *δ*: 13.9, 37.0, 45.2, 62.7, 111.2, 118.1, 120.2, 120.5, 122.0, 124.8, 128.7, 129.5, 131.7, 137.0, 142.1, 160.8, 192.5.

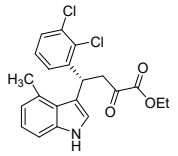


8e: Product in accordance with literature characterization data[7h-n]. 80% yield (53.6 mg), 91% ee; The ee was determined by HPLC analysis using a Chiralpak IA column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 18.27 min; τ_{minor} = 12.69 min); ^{1}H NMR ($CDCl_3$, 600 MHz) *δ*: 1.22-1.25 (m, 3H), 2.50 (s, 3H), 3.47-3.51 (m, 1H), 3.54-3.59 (m, 1H), 4.17-4.21 (m, 2H), 5.27-5.29 (m, 1H), 6.74 (d, *J* = 7.2 Hz, 1H), 6.99-7.02 (m, 2H), 7.12-7.15 (m, 2H), 7.22-7.24 (m, 4H), 8.16 (br s, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) *δ*: 13.9, 20.7, 38.6, 47.5, 62.5, 109.1, 118.5, 121.4, 122.2, 122.4, 125.4, 126.5, 128.0, 128.6, 131.0, 137.0, 144.6, 161.2, 193.2.

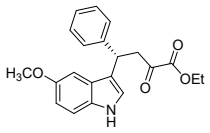


8f: Product in accordance with literature characterization data[7h-n]. 86% yield (60.7 mg), 90% ee; The ee was determined by HPLC analysis using a Chiralpak IA column (95/5 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 27.95 min; τ_{minor} = 22.15 min); ^{1}H NMR ($CDCl_3$, 600 MHz) *δ*: 1.24-1.27 (m, 3H), 2.50 (s, 3H), 3.44-3.48 (m, 1H), 3.55-3.60 (m, 1H), 4.20-4.23 (m, 2H), 5.27-2.30 (m, 1H), 6.76 (d, *J* = 7.2 Hz, 1H), 6.83-6.86 (m, 1H), 6.90 (d, *J* = 10.2 Hz, 1H), 7.01-7.05 (m, 3H), 7.14 (d, *J* = 7.8 Hz, 1H), 7.18-7.22 (m, 1H), 8.18 (br s, 1H); ^{13}C NMR ($CDCl_3$, 150

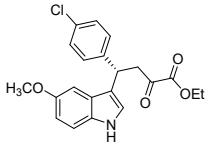
MHz) δ: 13.9, 20.7, 38.2, 47.2, 62.6, 109.2, 113.4 (d, J_{CF} = 21.0 Hz), 114.8 (d, J_{CF} = 21.1 Hz), 117.9, 121.6, 122.1, 122.6, 123.7, 125.2, 130.0 (d, J_{CF} = 7.5 Hz), 130.9, 137.0, 147.4 (d, J_{CF} = 7.5 Hz), 161.0, 162.8 (d, J_{CF} = 244.5 Hz), 192.7.



8g: Product in accordance with literature characterization data[7h-n]. 86% yield (69.3 mg), 90% ee; The ee was determined by HPLC analysis using a Chiralpak IA column (95/5 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 31.11 min; τ_{minor} = 28.64 min); ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 1.27-1.29 (m, 3H), 2.37 (s, 3H), 3.32-3.36 (m, 1H), 3.52-3.56 (m, 1H), 4.23-4.27 (m, 2H), 5.73-5.75 (m, 1H), 6.75 (d, J = 7.2 Hz, 1H), 6.86-6.88 (m, 1H), 6.98-7.04 (m, 3H), 7.16 (d, J = 8.4 Hz, 1H), 7.30-7.32 (m, 1H), 8.15 (br s, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 13.9, 19.8, 36.5, 44.6, 62.6, 109.2, 116.6, 121.6, 122.7, 122.8, 125.3, 127.5, 127.8, 128.8, 131.0, 133.4, 137.2, 144.5, 161.1, 192.5.

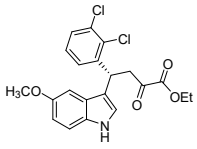


8h: Product in accordance with literature characterization data[7h-n]. 80% yield (56.2 mg), 96% ee; The ee was determined by HPLC analysis using a Chiralpak IE column (95/5 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 47.99 min; τ_{minor} = 38.37 min); ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 1.25-1.27 (m, 3H), 3.56-3.60 (m, 1H), 3.63-3.67 (m, 1H), 3.73 (s, 3H), 4.19-4.23 (m, 2H), 4.84-4.87 (m, 1H), 6.79-6.81 (m, 1H), 6.82 (s, 1H), 6.98 (d, J = 1.2 Hz, 1H), 7.16-7.18 (m, 2H), 7.24-7.27 (m, 2H), 7.32 (d, J = 7.2 Hz, 2H), 7.96 (br s, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 13.9, 37.8, 45.6, 55.8, 62.5, 101.4, 111.9, 112.3, 126.6, 126.9, 127.8, 128.6, 131.7, 143.2, 153.9, 161.0, 193.2.



8i: Product in accordance with literature characterization data[7h-n]. 79% yield (60.8 mg), 92% ee; The ee was determined by HPLC analysis using a Chiralpak ID column (90/10 hexane/*i*-PrOH;

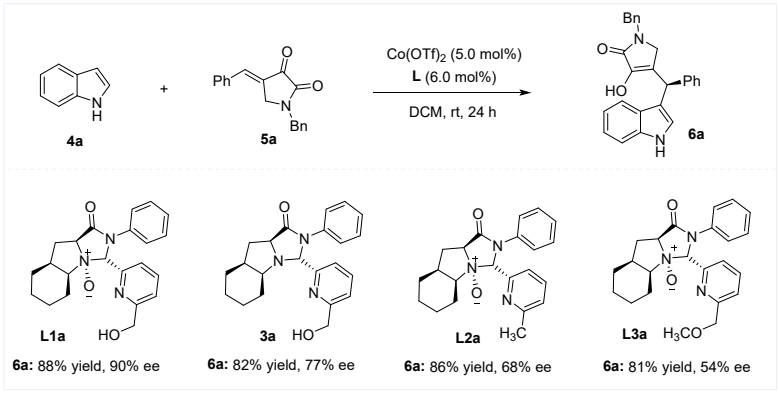
flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 22.96 min; τ_{minor} = 15.81 min); ^{1}H NMR ($CDCl_3$, 600 MHz) *δ*: 1.28-1.30 (m, 3H), 3.53-3.57 (m, 1H), 3.61-3.65 (m, 1H), 3.75 (s, 3H), 4.22-4.25 (m, 2H), 4.82-4.84 (m, 1H), 6.78 (s, 1H), 6.82 (d, *J* = 9.0 Hz, 1H), 7.00 (s, 1H), 7.20-7.26 (m, 5H), 7.96 (br s, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) *δ*: 13.9, 37.1, 45.4, 55.9, 62.6, 101.3, 111.9, 112.4, 117.6, 122.2, 126.7, 128.7, 129.2, 131.7, 132.3, 141.8, 154.0, 160.9, 192.8.

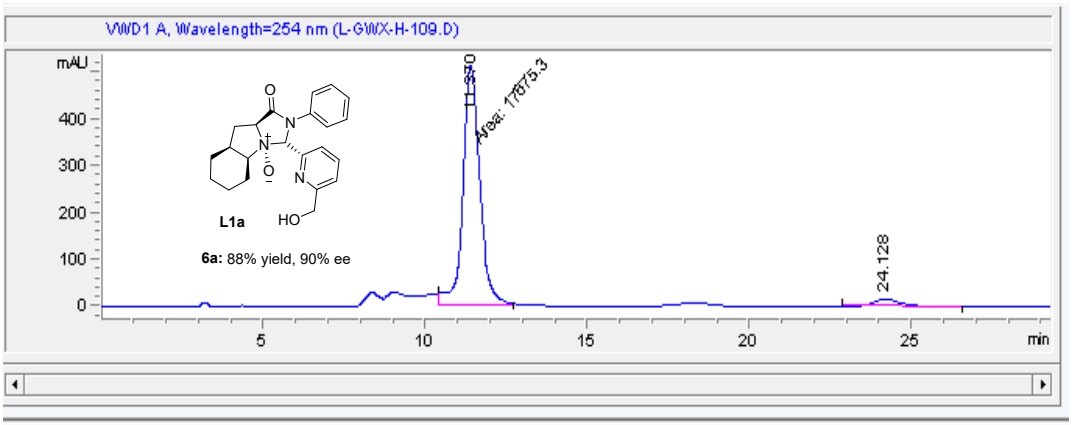


8j: Product in accordance with literature characterization data[7h-n]. 80% yield (67.0 mg), 93% ee; The ee was determined by HPLC analysis using a Chiralpak IA column (85/15 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; τ_{major} = 19.08 min; τ_{minor} = 10.38 min); ^{1}H NMR ($CDCl_3$, 600 MHz) *δ*: 1.29-1.31 (m, 3H), 3.44-3.48 (m, 1H), 3.68-3.72 (m, 1H), 3.77 (s, 3H), 4.24-4.28 (m, 2H), 5.40-5.43 (m, 1H), 6.82 (d, *J* = 9.0 Hz, 1H), 6.85 (s, 1H), 7.03 (s, 1H), 7.05-7.08 (m, 1H), 7.12 (d, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 9.0 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.98 (br s, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) *δ*: 13.9, 35.1, 44.4, 55.9, 62.6, 101.2, 111.9, 112.6, 116.4, 122.7, 126.8, 127.2, 127.3, 128.8, 131.6, 131.9, 133.4, 143.0, 154.1, 160.9, 192.3.

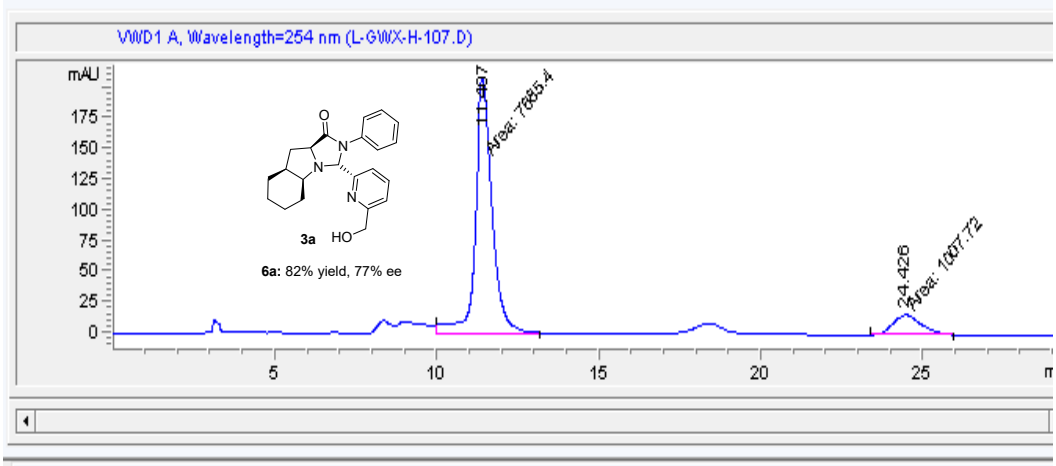
7. Control experiments and HPLC spectra for compound 6a

In a sealed tube equipped with a stirring bar, to the mixture of $Co(OTf)_2$ (5.0 mol %), **L** (6.0 mol %) in 2.0 mL of DCM was added **4a** (0.30 mmol), and **5a** (0.20 mmol). The reaction mixture was stirred at room temperature for 24 h and was directly loaded onto a silica gel and purified by flash chromatography to give the product **6a**, using hexane/EtOAc (10/1, v/v) as the eluent.

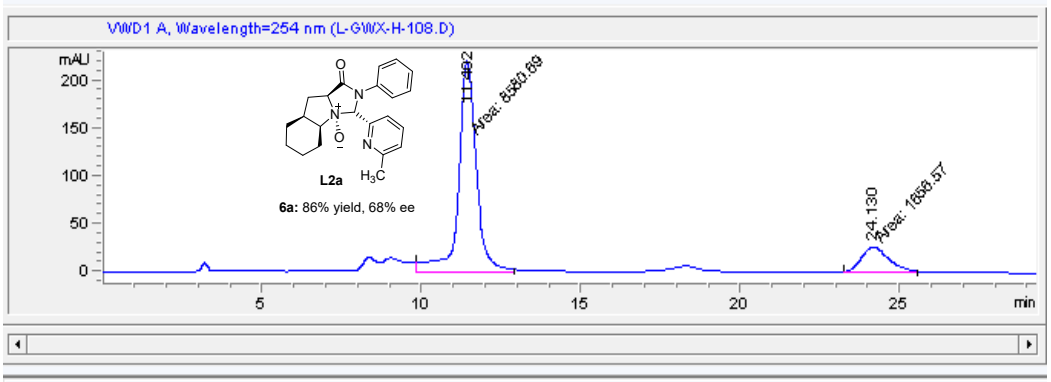




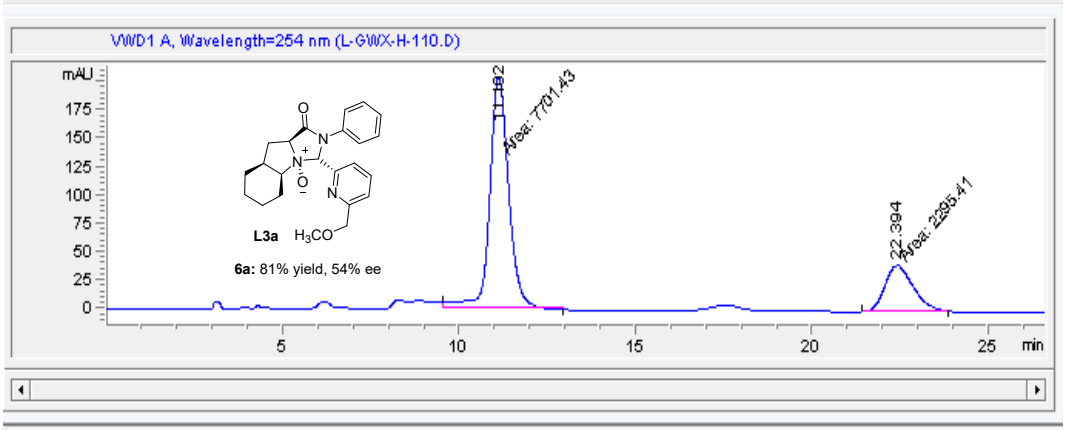
#	Time	Area	Height	Width	Area%	Symmetry
1	11.37	17675.3	510.4	0.5772	94.826	0.751
2	24.128	964.5	15.4	0.9473	5.174	0.683



#	Time	Area	Height	Width	Area%	Symmetry
1	11.407	7685.4	209.4	0.6117	88.408	0.827
2	24.426	1007.7	16.4	1.0242	11.592	0.741



#	Time	Area	Height	Width	Area%	Symmetry
1	11.402	8580.7	220.4	0.649	83.818	0.903
2	24.13	1656.6	26.7	1.0345	16.182	0.674



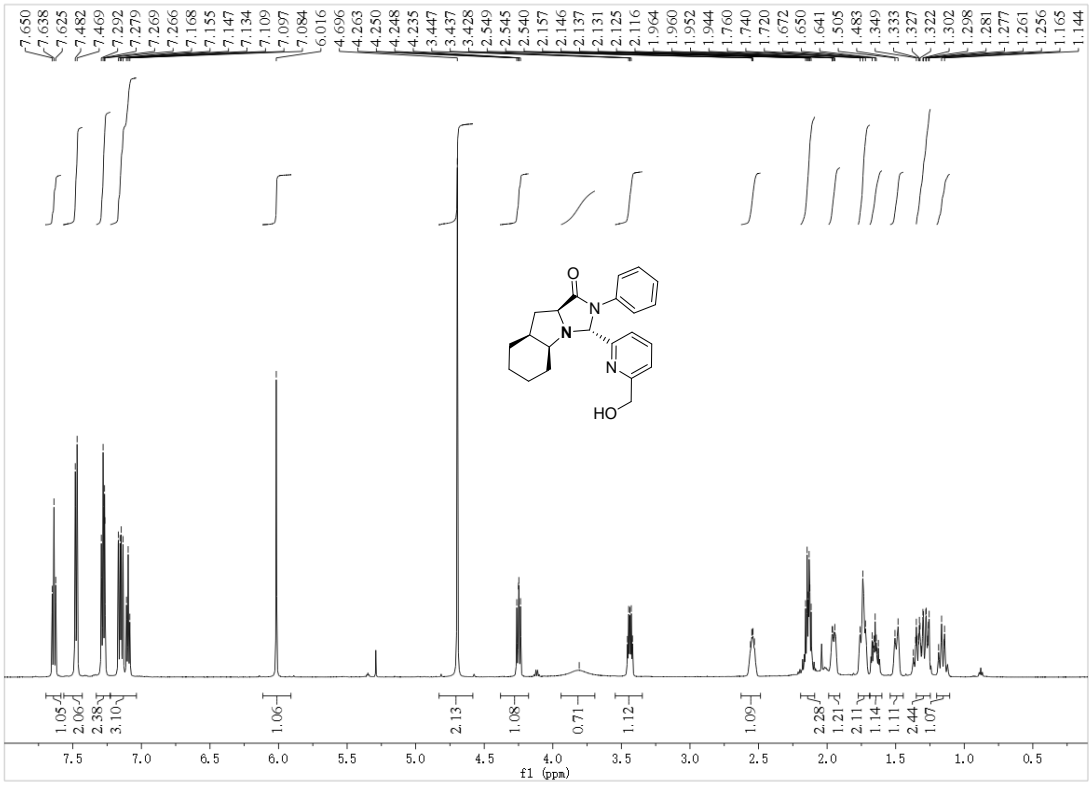
#	Time	Area	Height	Width	Area%	Symmetry
1	11.102	7701.4	204.9	0.6264	77.039	0.904
2	22.394	2295.4	40.8	0.937	22.961	0.727

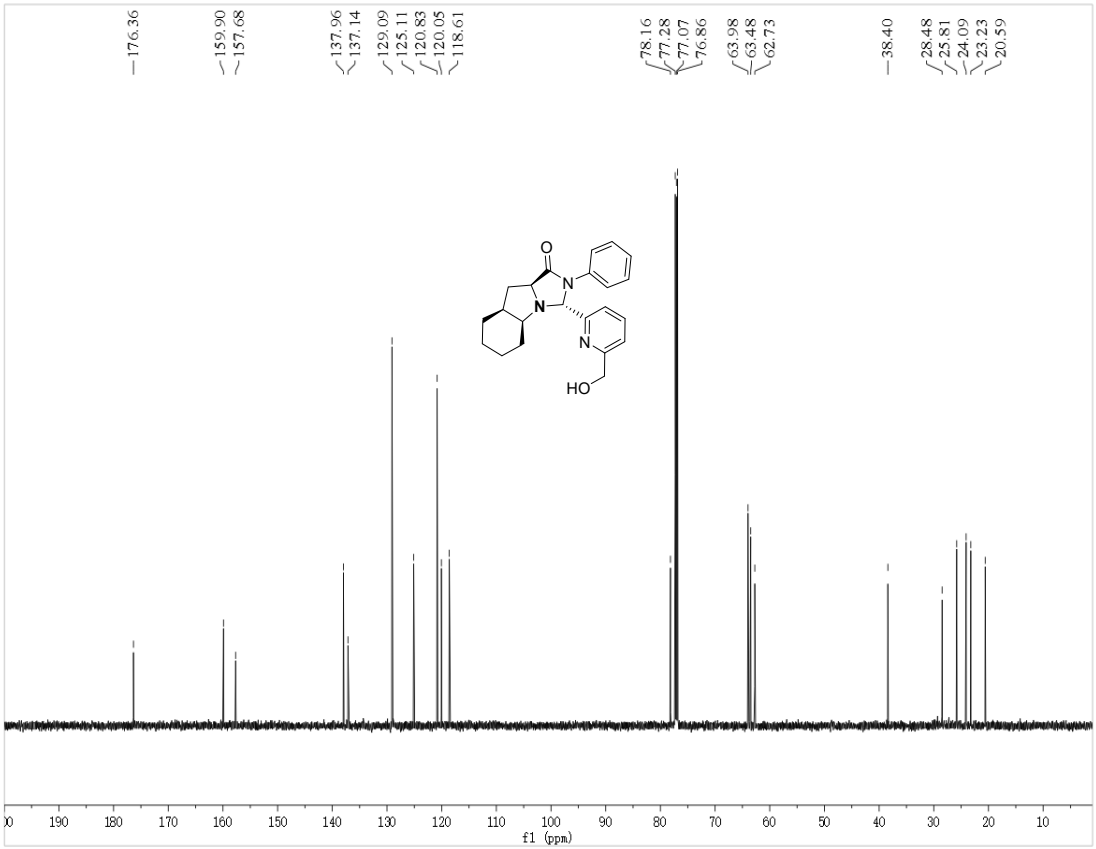
8. References

(a) J. K. Mansaray, Y. Huang, K. Li, X. Sun, Z. Zha and Z. Wang, *Org. Biomol. Chem.*, 2022, **20**, 5510-5514; *(b)* X. Q. Zhu, W. W. Li, L. L. Liu, K. L. Xu, L. J. Peng, M. Zhang, X. L. Liu and W.-J. Zhang, *Adv. Synth. Catal.*, 2025, **367**, e202401348; *(c)* J. Yang, J. Lou, W. Li, X. Q. Zhu, L. Zhao, H. X. Cen and X. L. Liu, *Chem Asian J.*, 2025, **20**, e202500509; *(d)* K. L. Xu, Y. H. Wang, X. R. Wang, P. Hu, B. W. Pan, W. J. Zhang, Z. Y. Chen, Y. Zhou and X. L. Liu, *Chin. J. Chem.*, 2024, **42**, 1474-1480; *(e)* H. X. Cen, L. P. Ding, L. L. Liu, W. D. Pan, X. Q. Zhu, W. W. Li, W. J. Zhang, L. J. Peng and X. L. Liu, *Chin. J. Chem.*, 2025, **43**, 599-606; *(f)* L. L. Yang, D. C. Pan, X. Q. Zhu, D. W. Liu, X. Z. Tang, H. X. Cen, L. J. Peng and X. L. Liu, *New J. Chem.*, 2025, **49**, 5346-5351; *(g)* J. Lou, X. Q. Zhu, D. C. Pan, D. W. Liu, H. X. Jing, X. L. Liu, W. J. Zhang, H. X. Cen and G. D. Deng, *New J. Chem.*, 2025, **49**, 17335-17349; *(h)* Y. H. Wang, P. Hu, X. R. Wang, K. L. Xu, Q. L. Wang, H. J. Wang and X. L. Liu, *Org. Chem. Front.*, 2024, **11**, 1314-1321; *(i)* Y. Liu, D. Shang, X. Zhou, Y. Zhu, L. Lin, X. Liu and X. Feng, *Org. Lett.*, 2010, **12**, 180-183; *(j)* M. Wang, M. Li, L. Zhang, R. Song, D. Yang and J. Lv, *Org. Chem. Front.*, 2022, **9**, 1875-1883; *(k)* S. Yu, Q. Cai, C. Wang, J. Hou, J. Liang, Z. Jiao, C. Yao and Y. M. Li, *J. Org. Chem.*, 2023, **88**, 3046-3053; *(l)* V. Juste-Navarro, E. Marqués-López and R. P. Herrera, *Asian J. Org. Chem.*, 2015, **4**, 884-889; *(m)* Z. Y. Chen, K. L. Xu, X. R. Wang, P. Hu, W. Y. Jiang, Y. F. Dai, L. J. Peng and X. L. Liu, *New J. Chem.*, 2024, **48**, 6670-6675; *(n)* Z. Y. Chen, X. R. Wang, K. L. Xu, P. Hu, Y. P. Tian, H. J. Wang, Y. Zhou and X. L. Liu, *New J. Chem.*, 2024, **48**, 1688-1695.

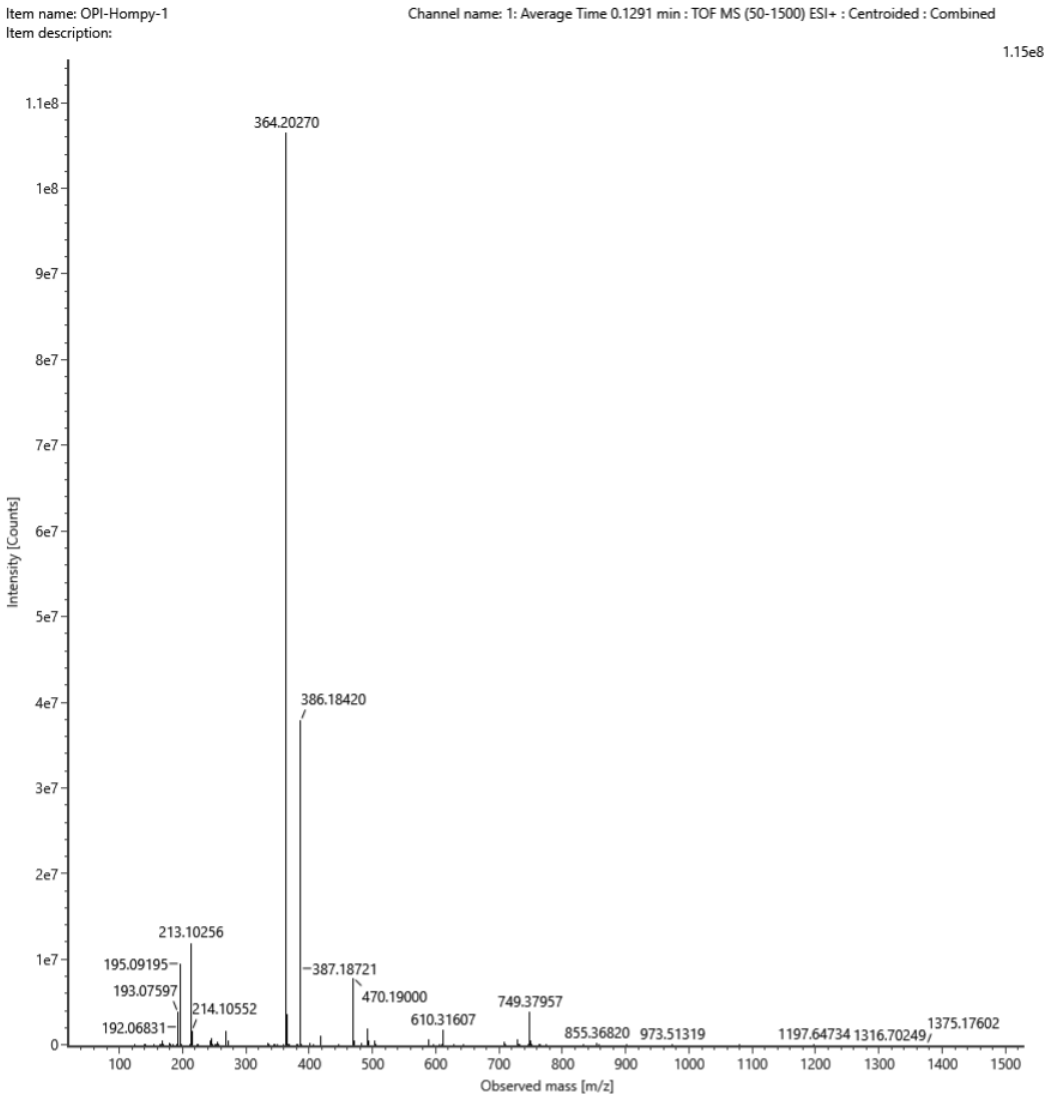
9. The copies of ^{1}H NMR, ^{13}C NMR and HPLC spectra for compounds 3a, L, 6 and 8

^{1}H and ^{13}C NMR of 3a





HRMS of 3a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Item description:
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1.15e8
Intensity [Counts]
Observed mass [m/z]
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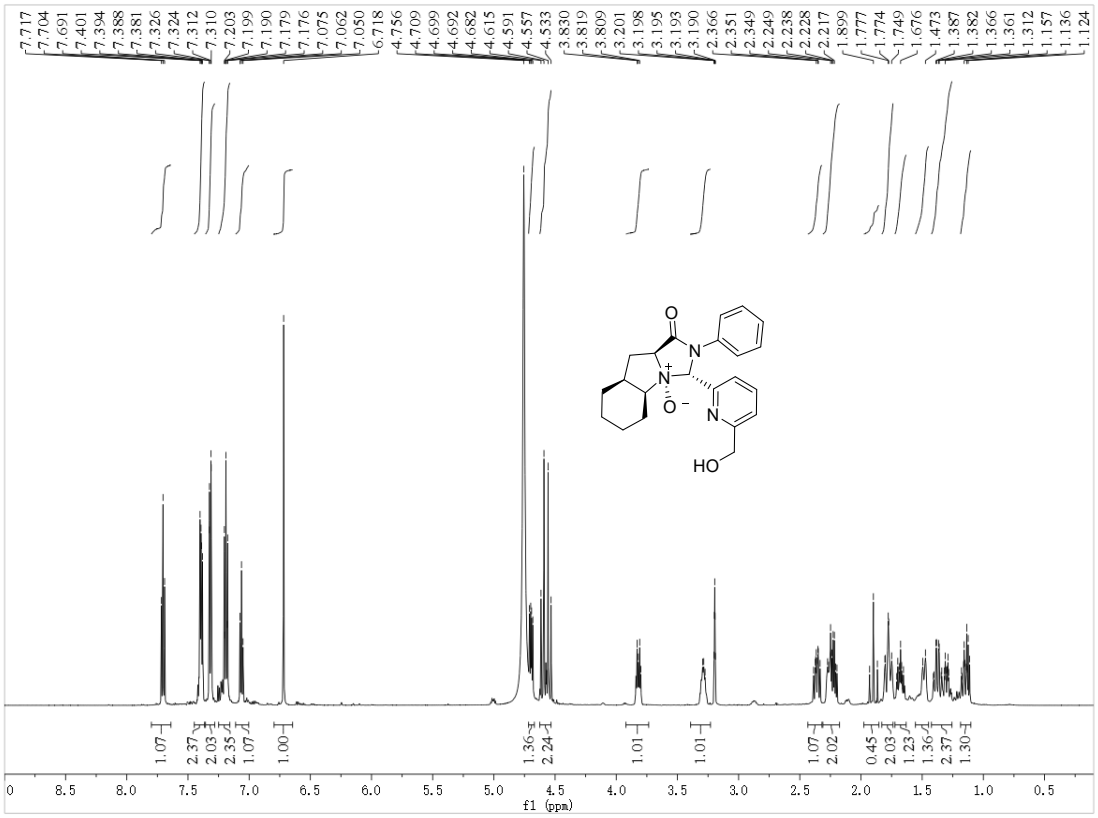
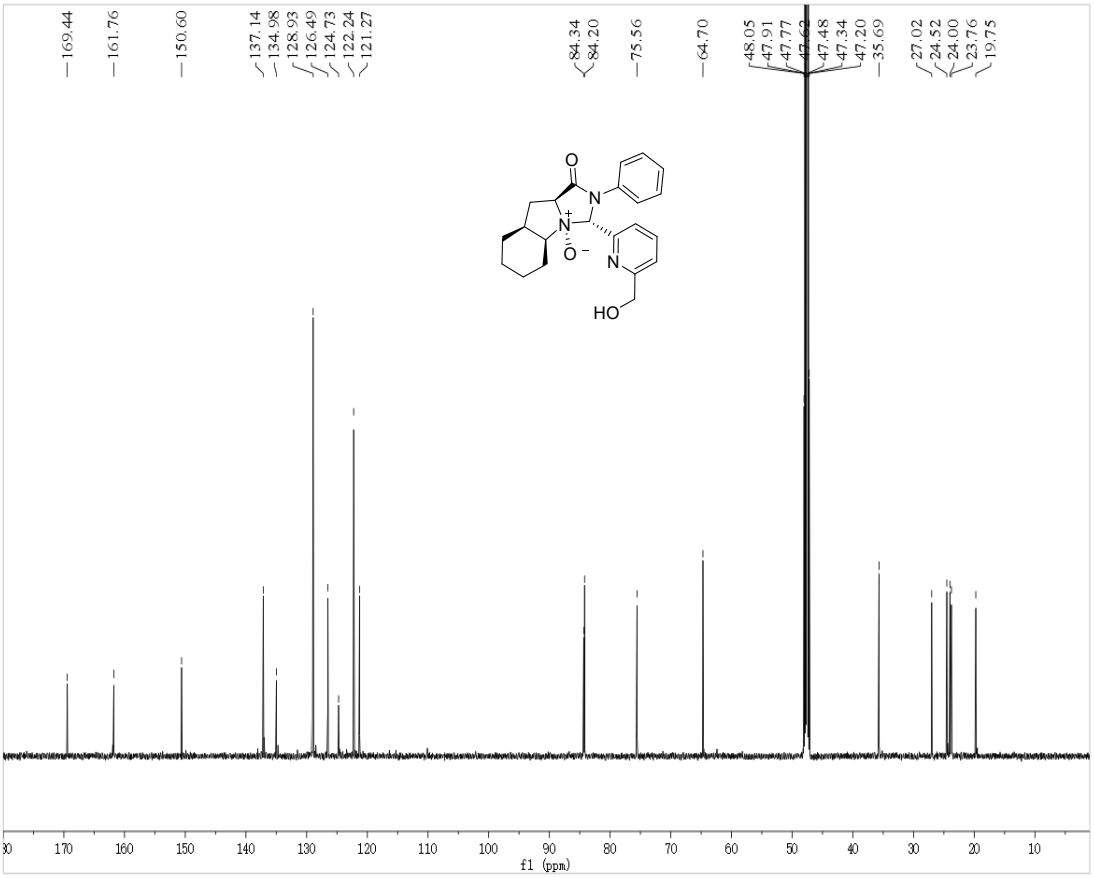
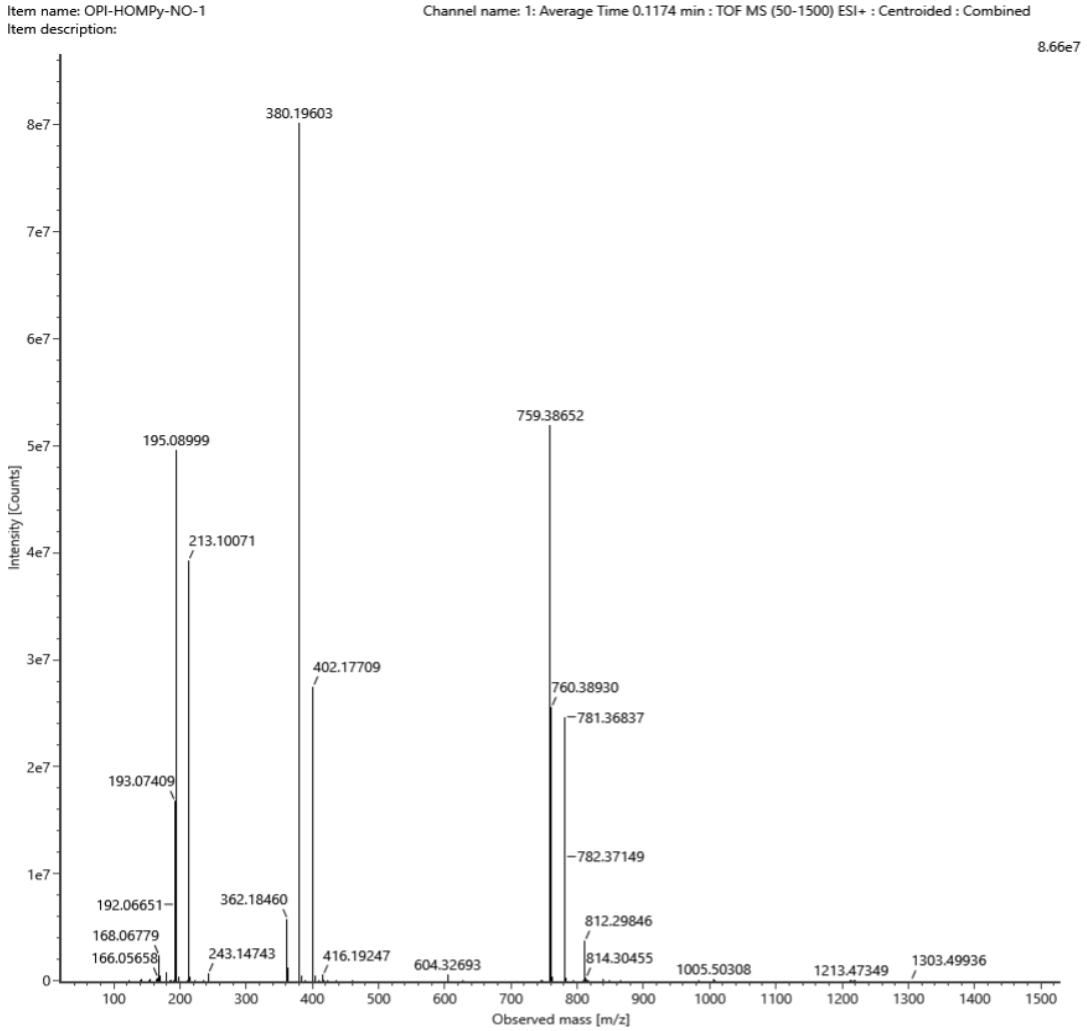
386.18420
213.10256
195.09195
193.07597
214.10552
192.06831
387.18721
470.19000
610.31607
749.37957
855.36820
973.51319
1197.64734
1316.70249
1375.17602

^{1}H and ^{13}C NMR of L1a

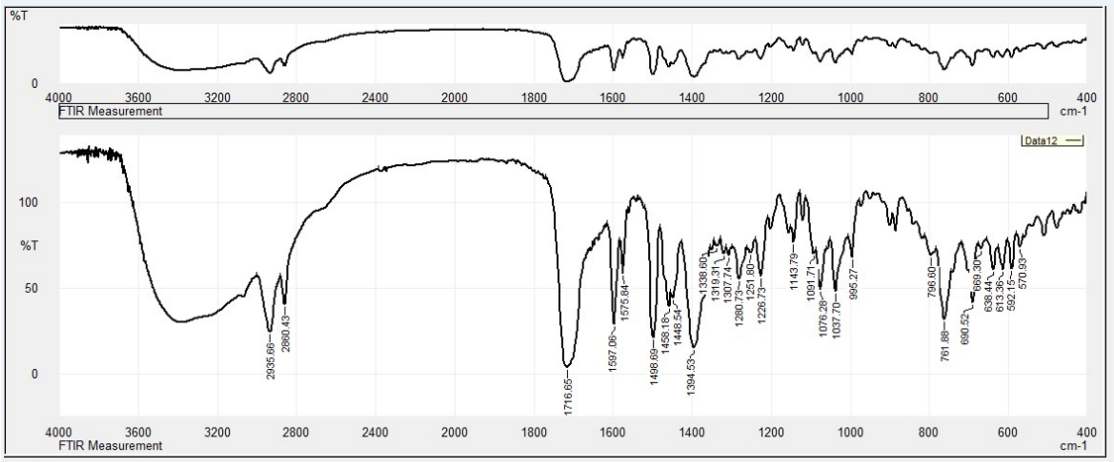




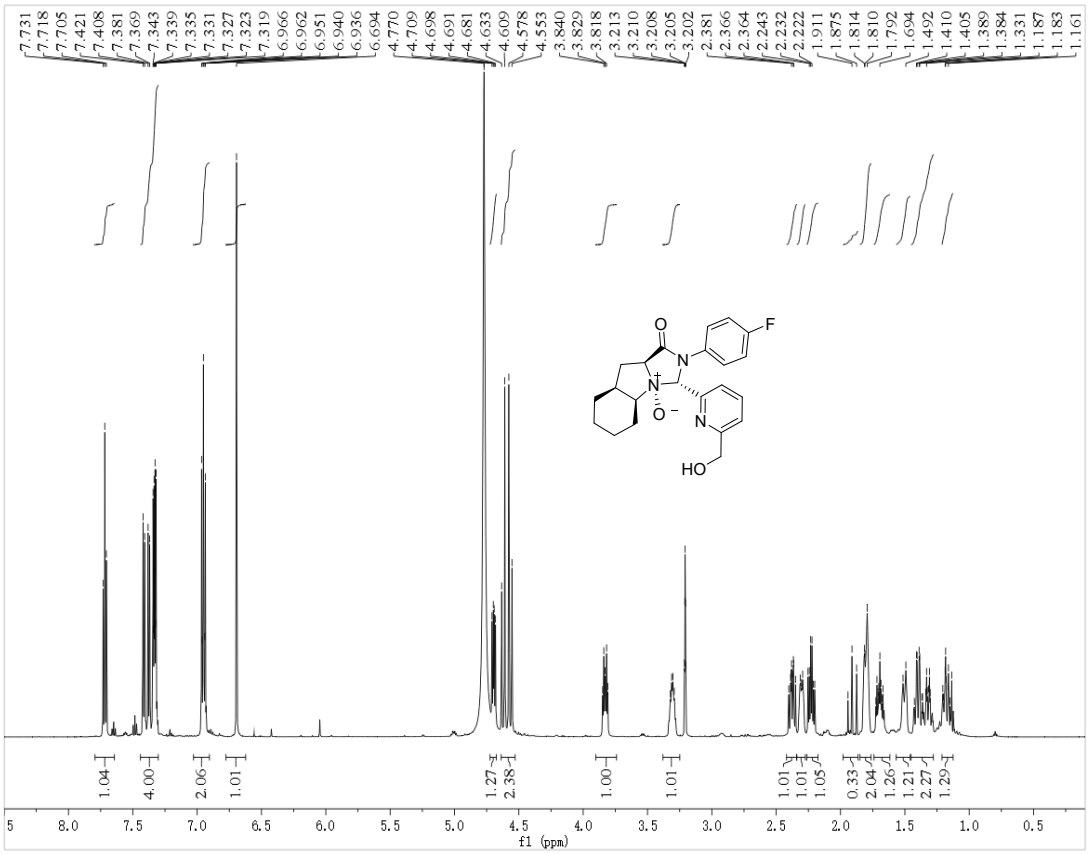
HRMS of L1a

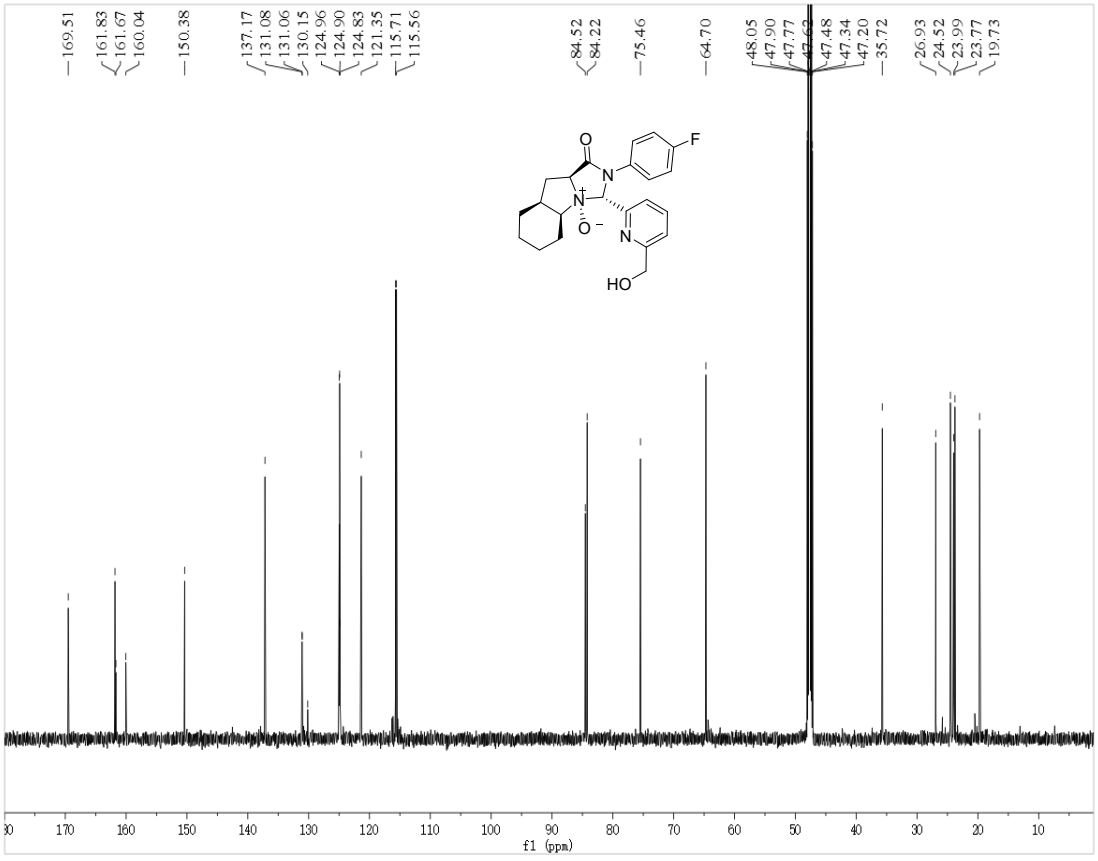


IR of L1a

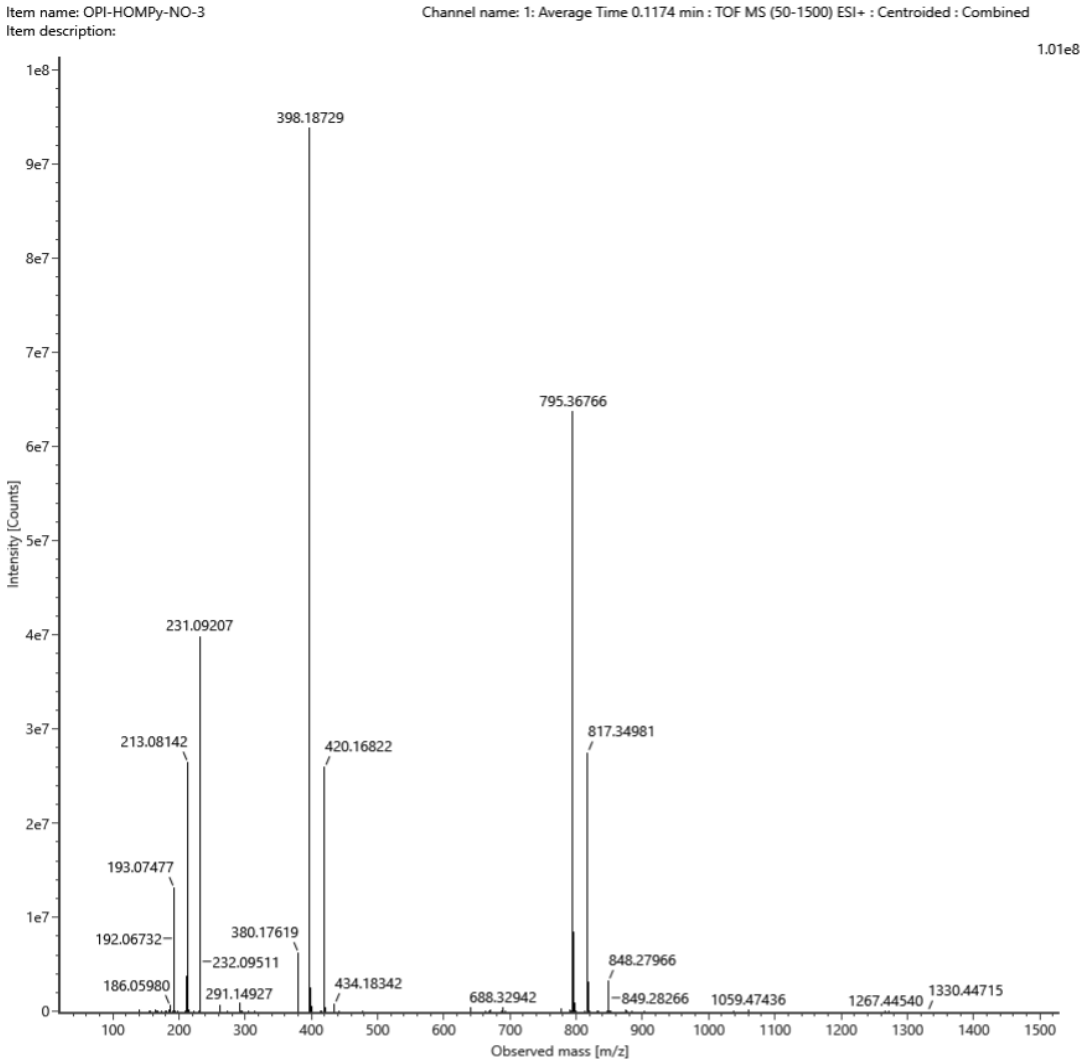


^{1}H and ^{13}C NMR of L1b

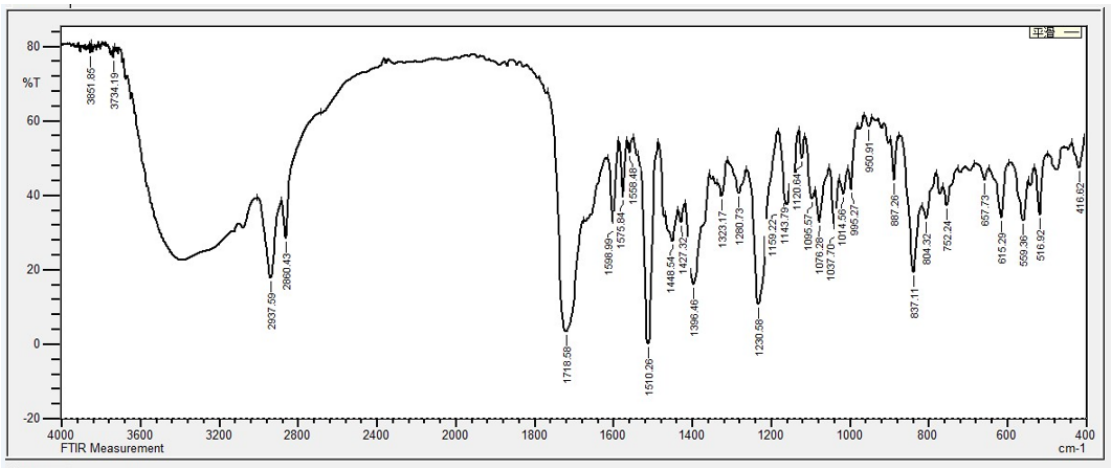




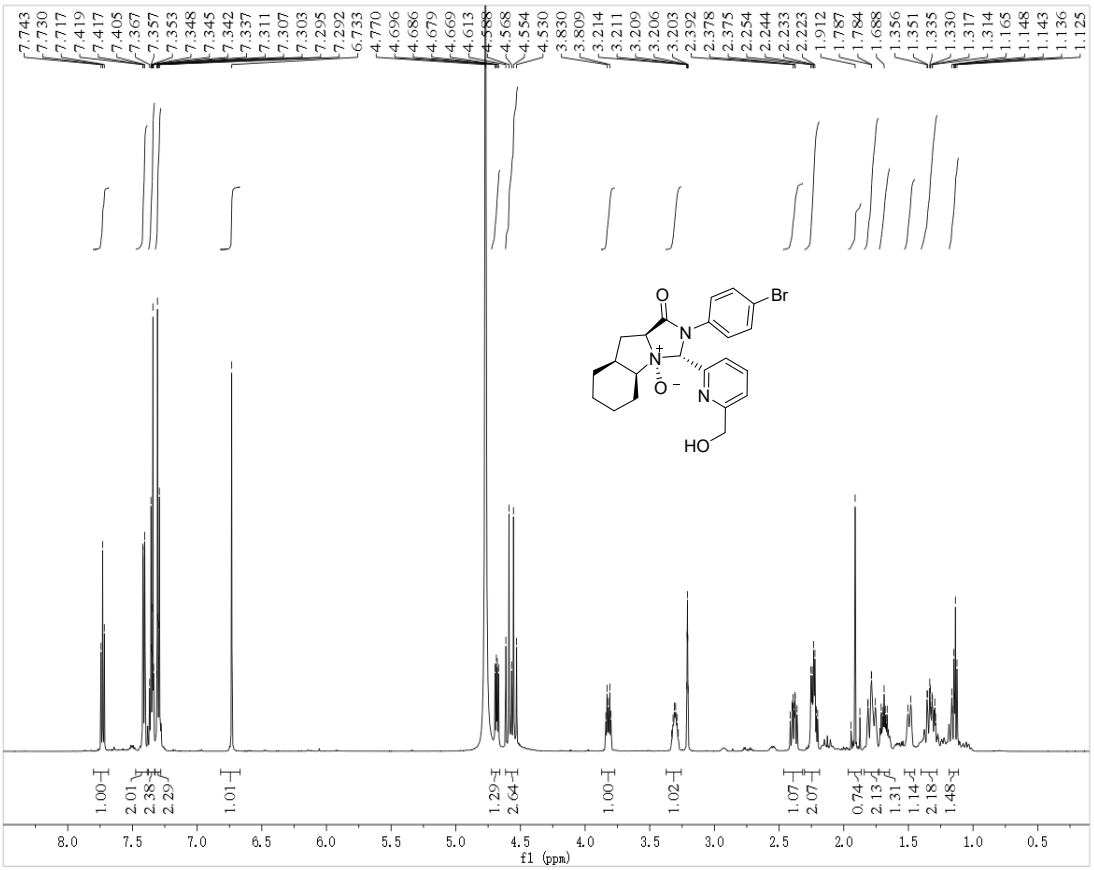
HRMS of L1b

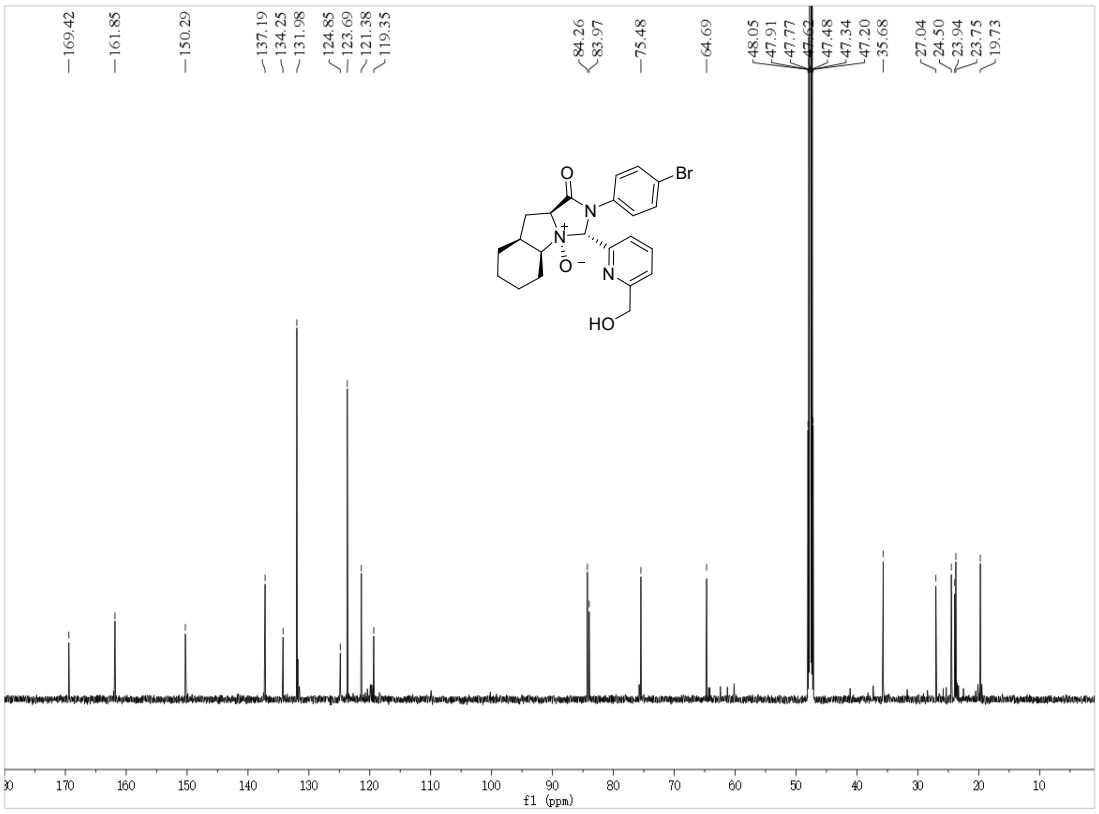


IR of L1b

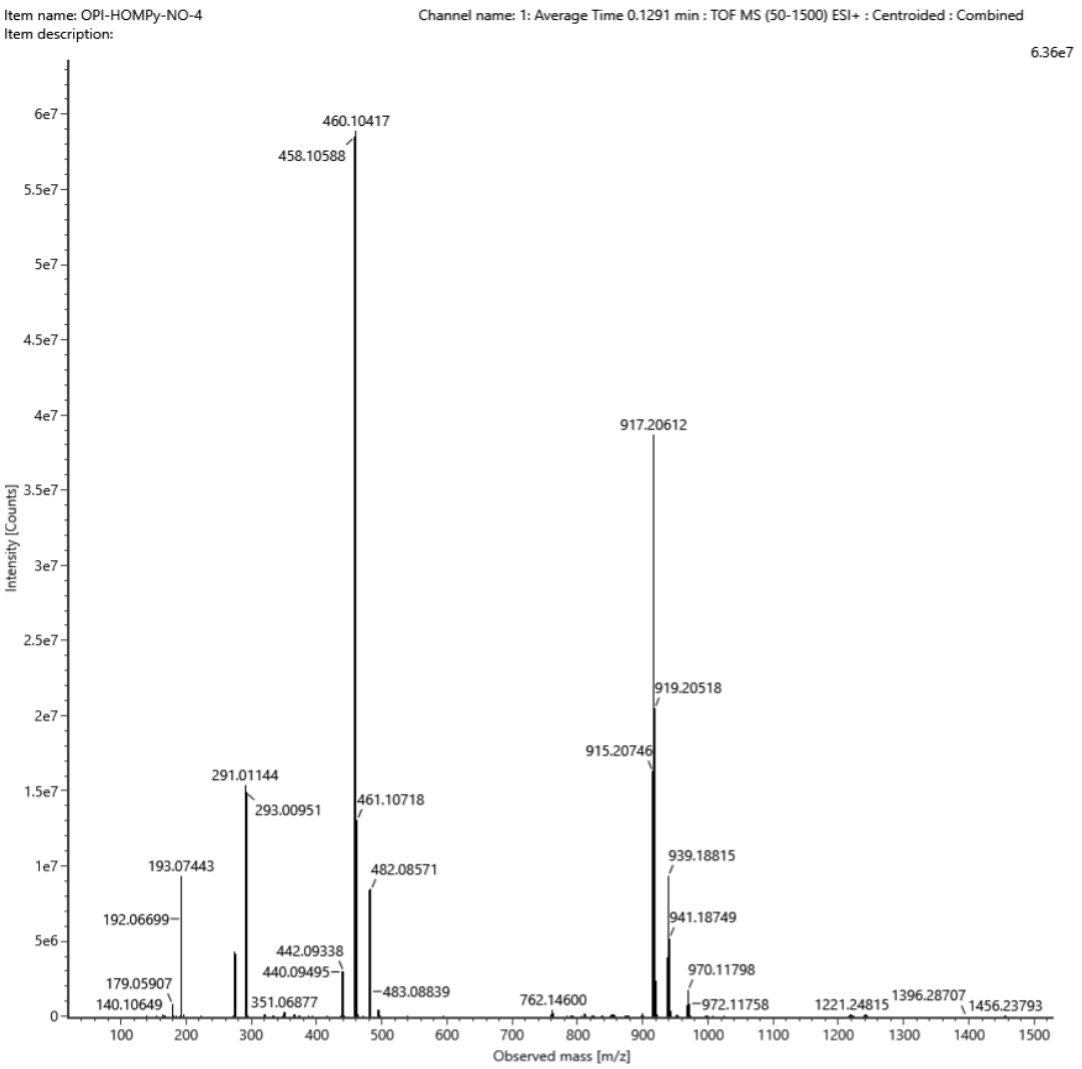


^{1}H and ^{13}C NMR of L1c

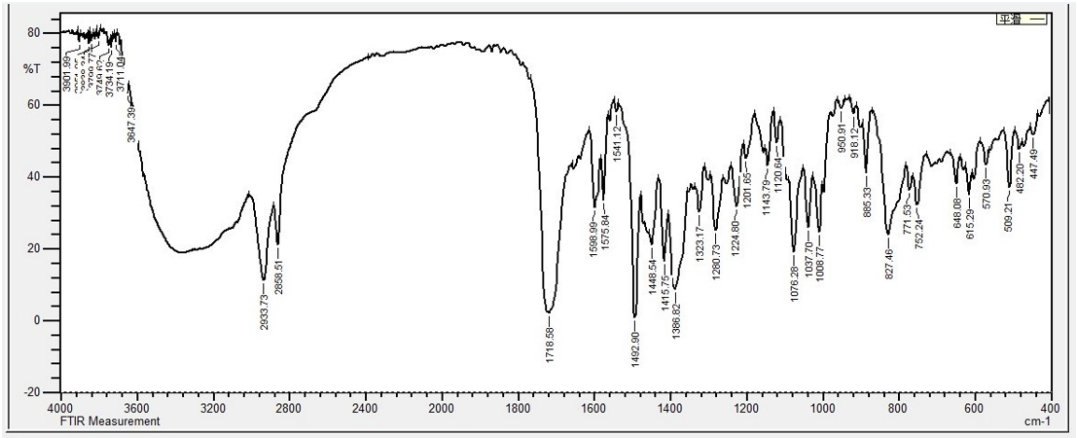




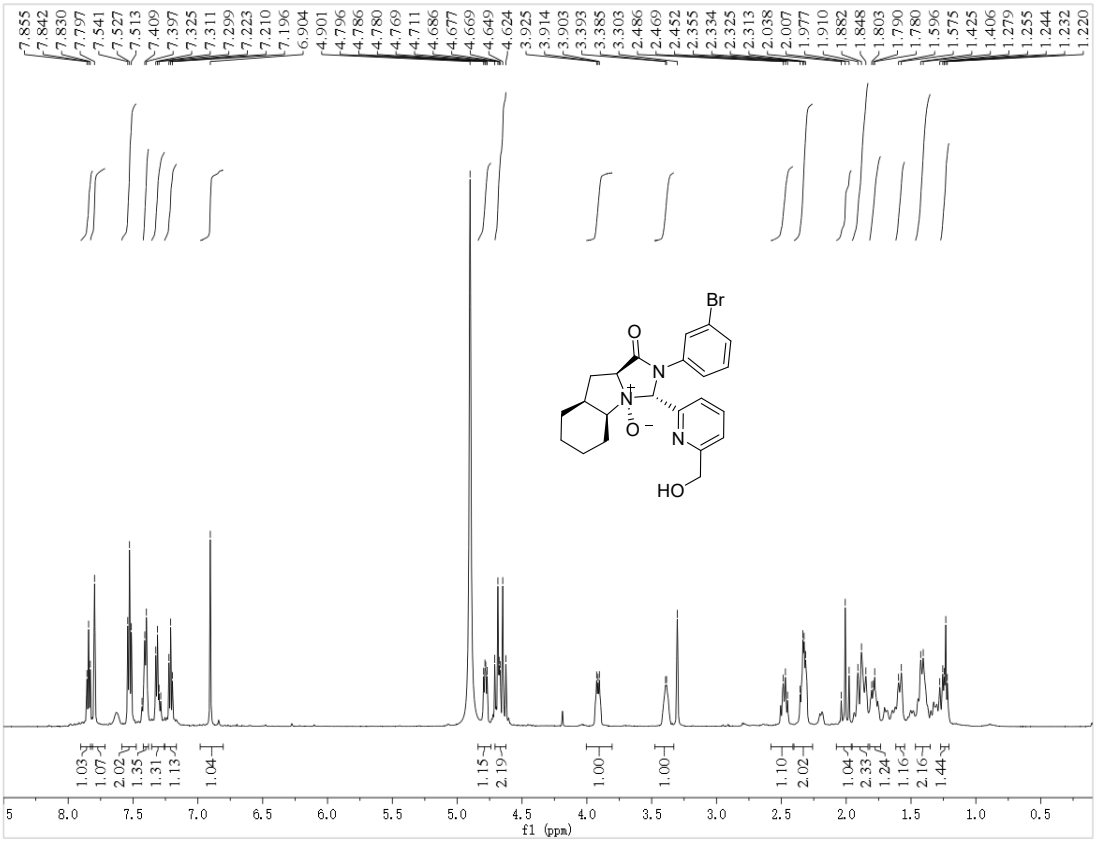
HRMS of L1c

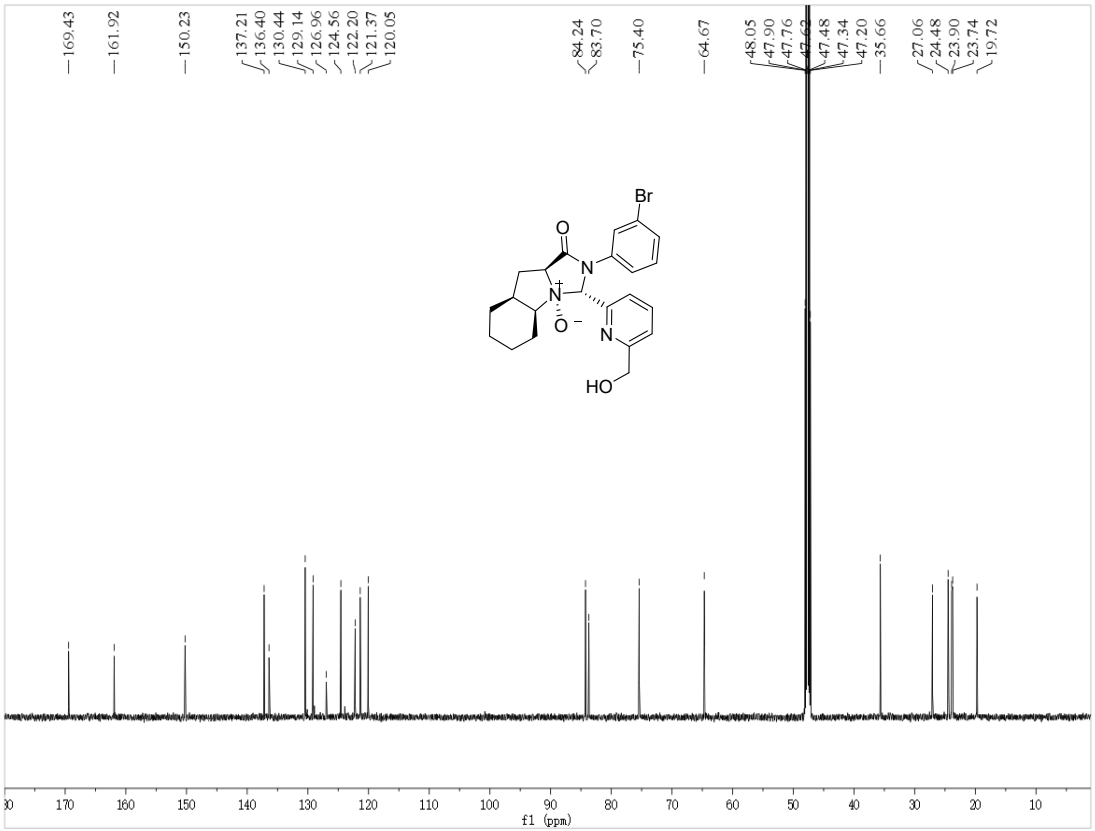


IR of L1c

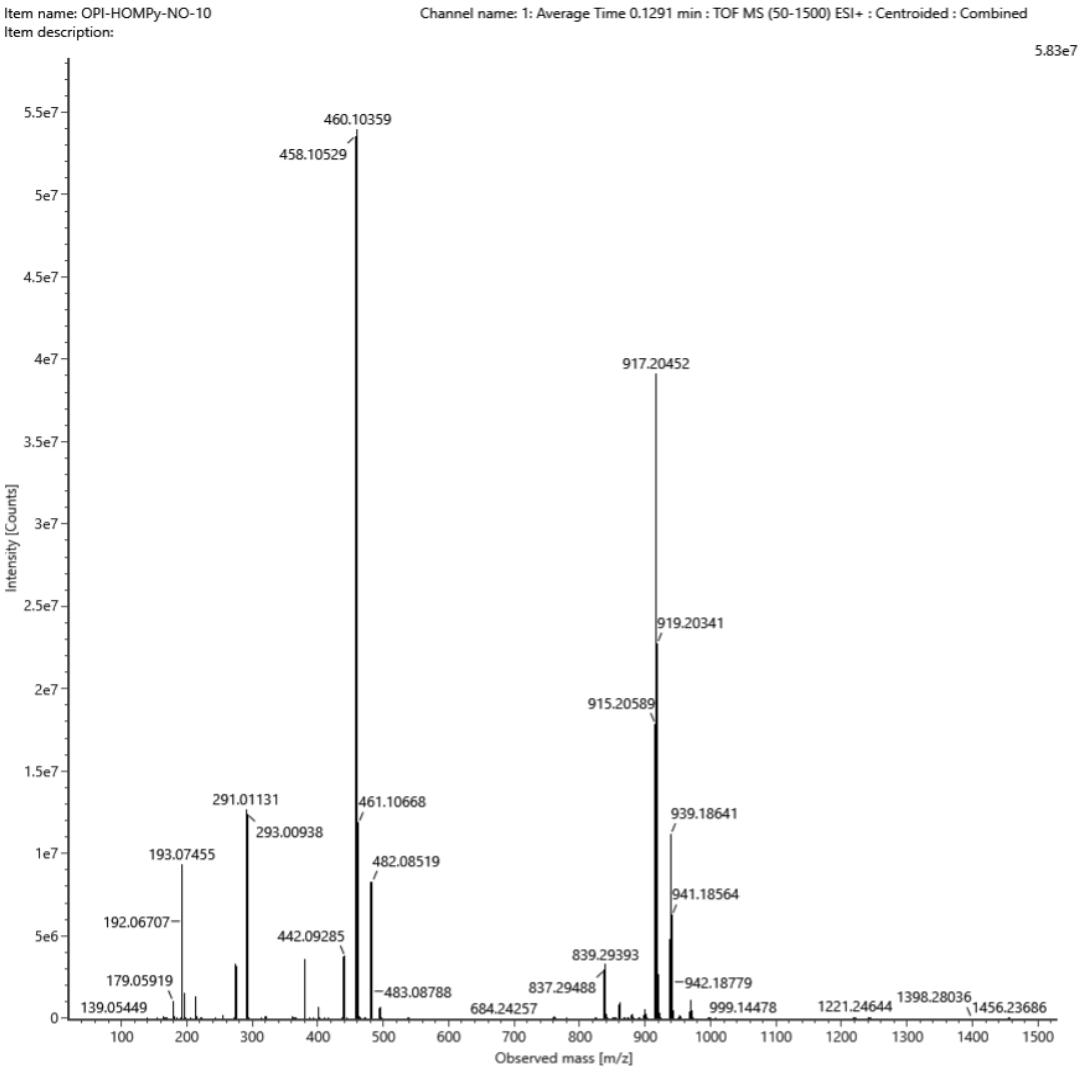


^{1}H and ^{13}C NMR of L1d

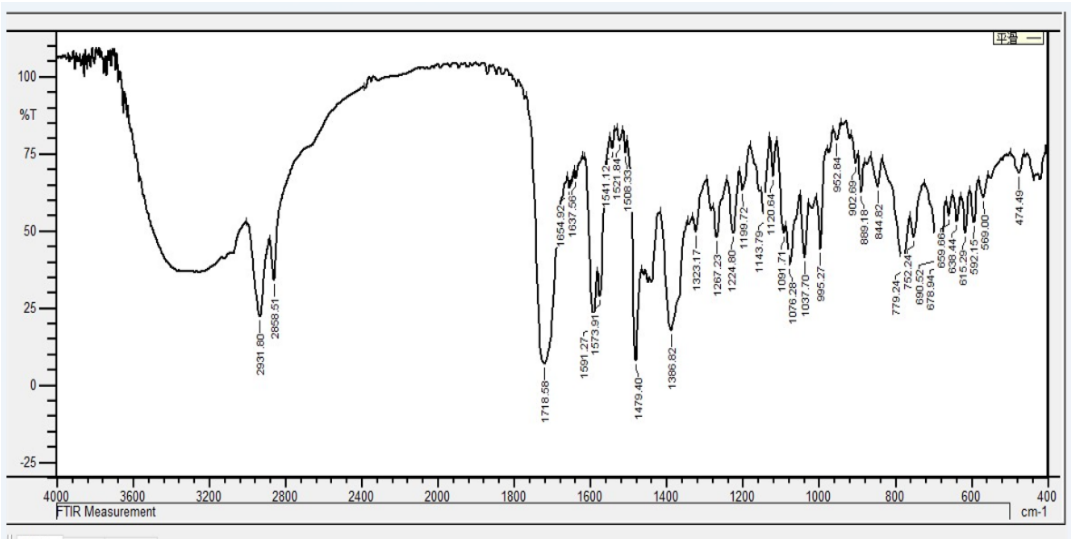




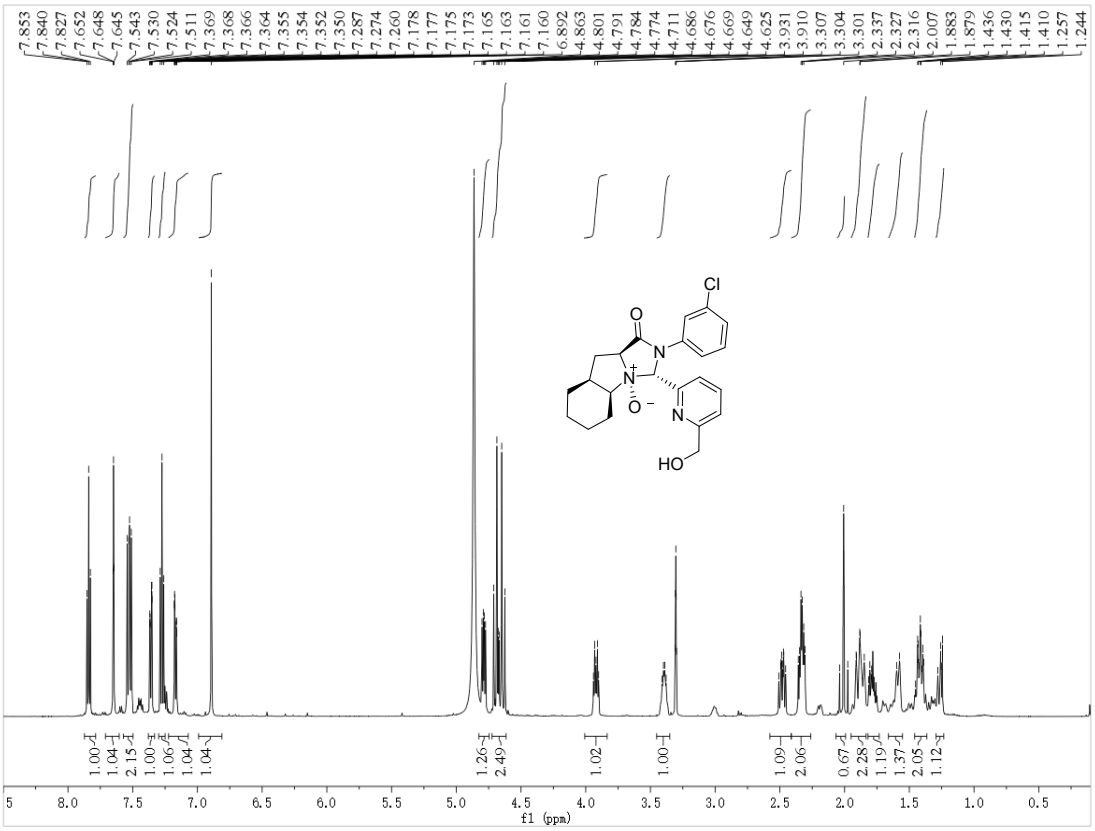
HRMS of L1d

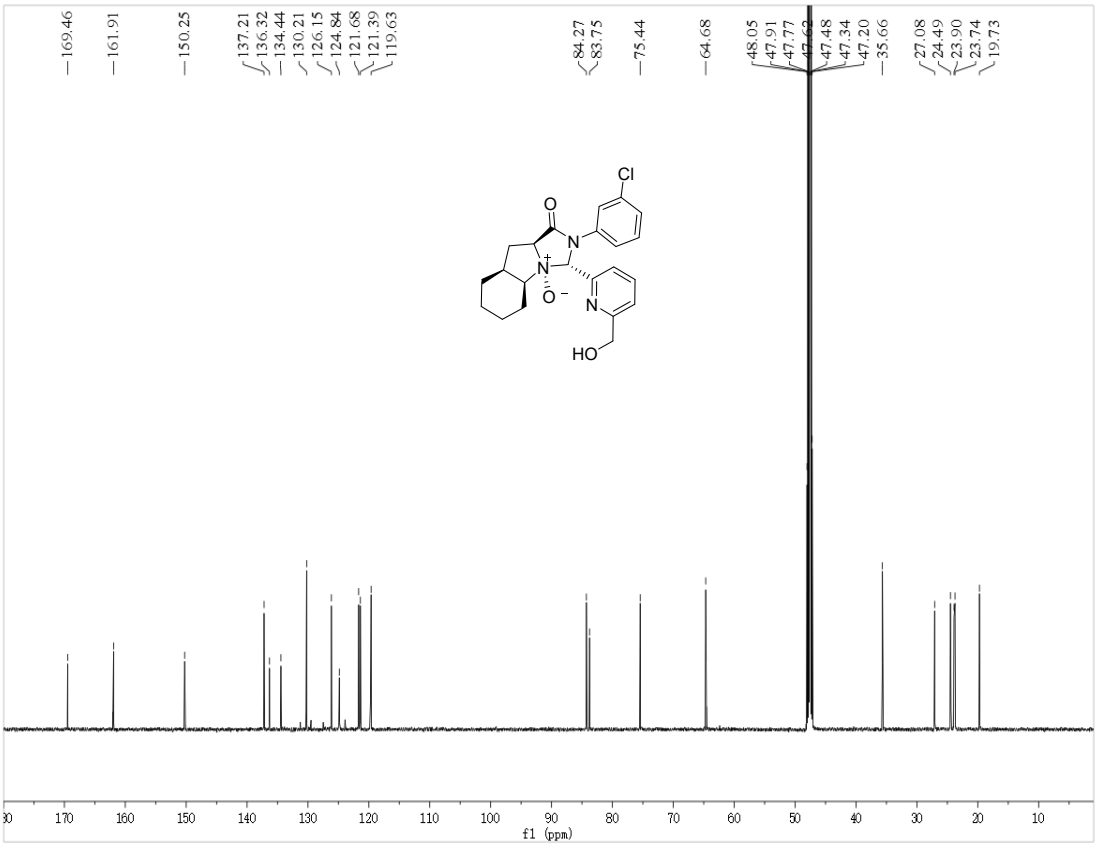


IR of L1d

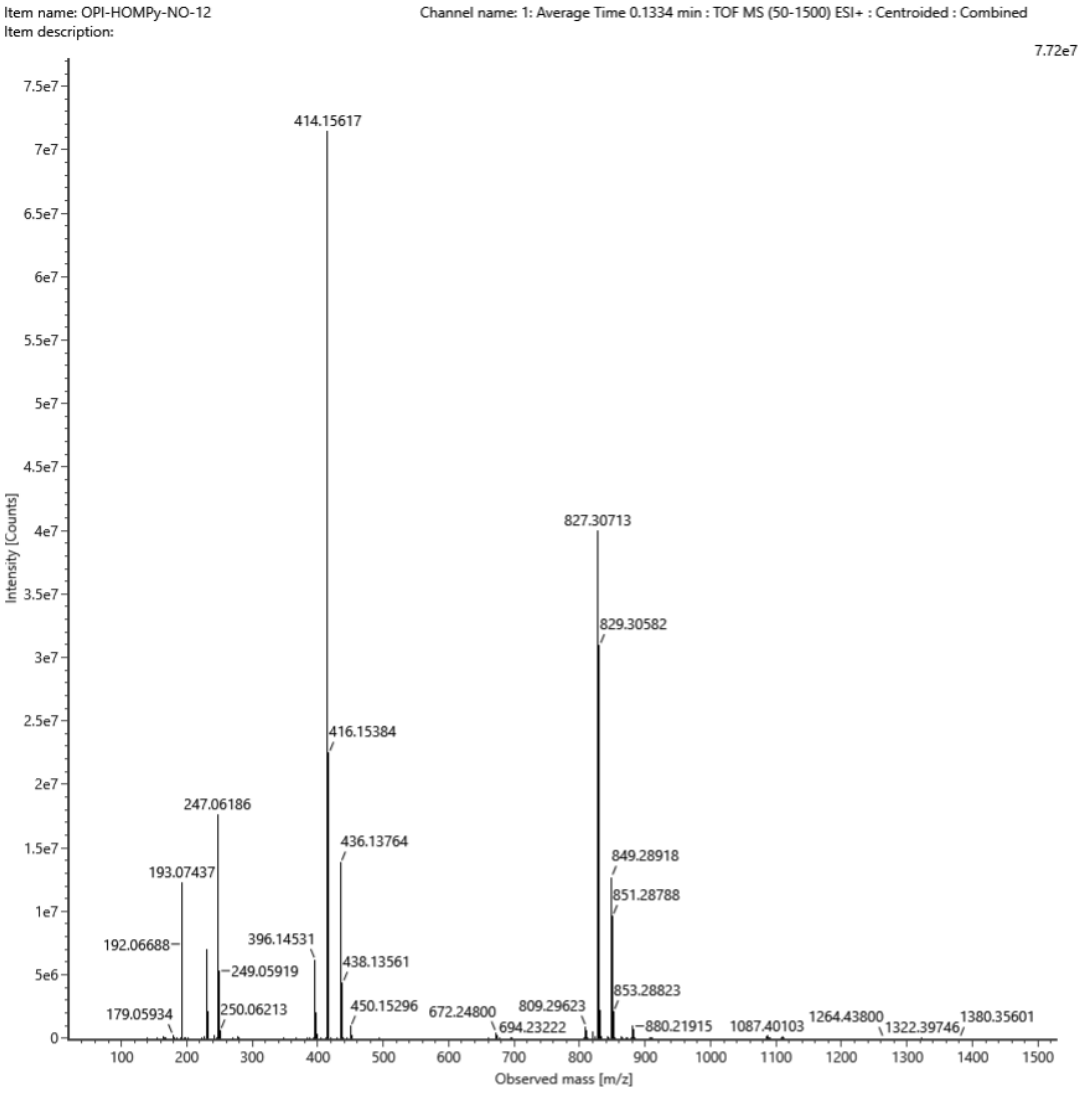


^{1}H and ^{13}C NMR of L1e

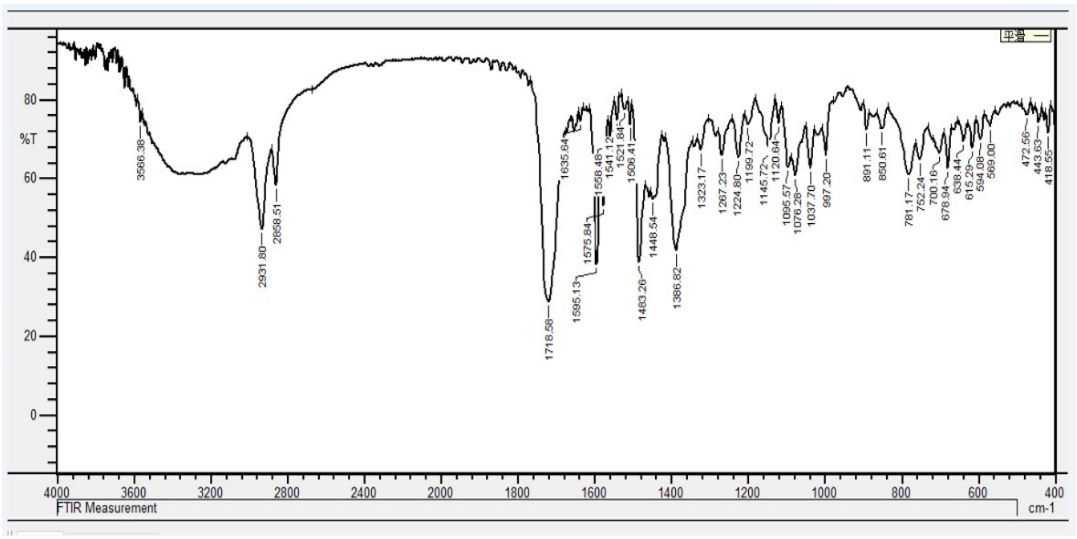




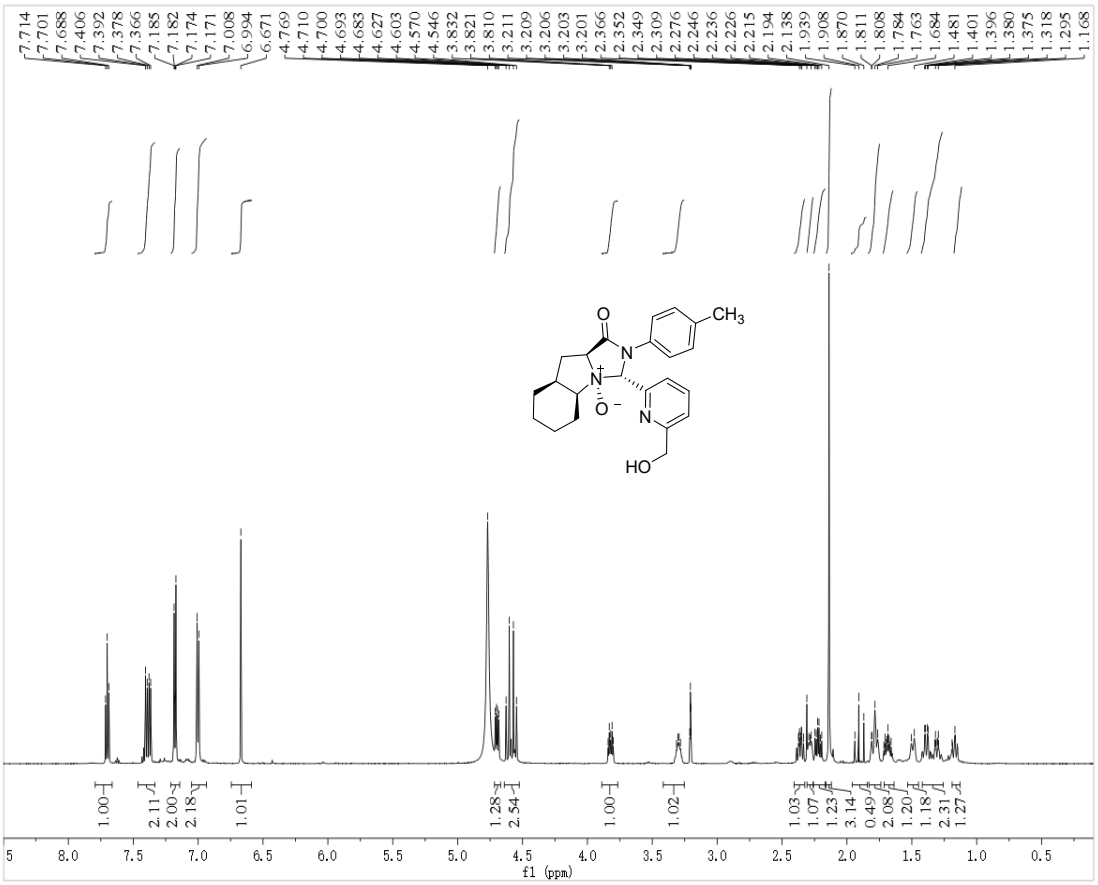
HRMS of L1e

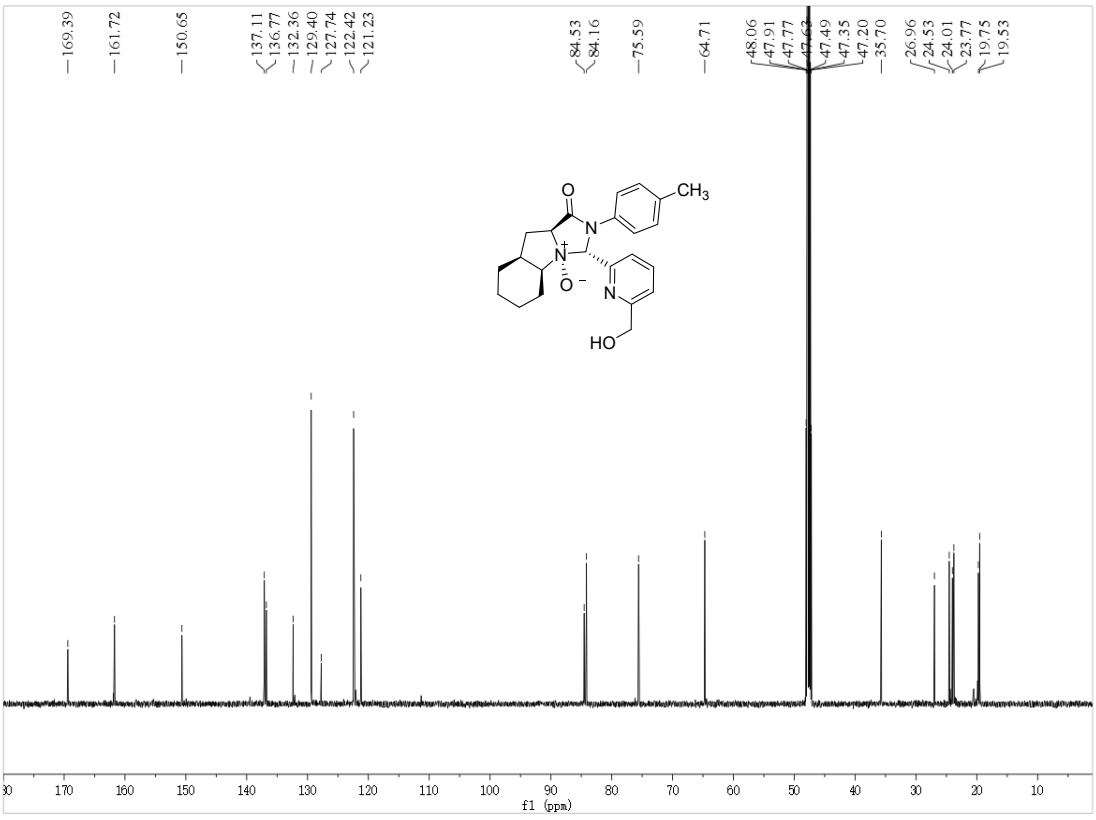


IR of L1e

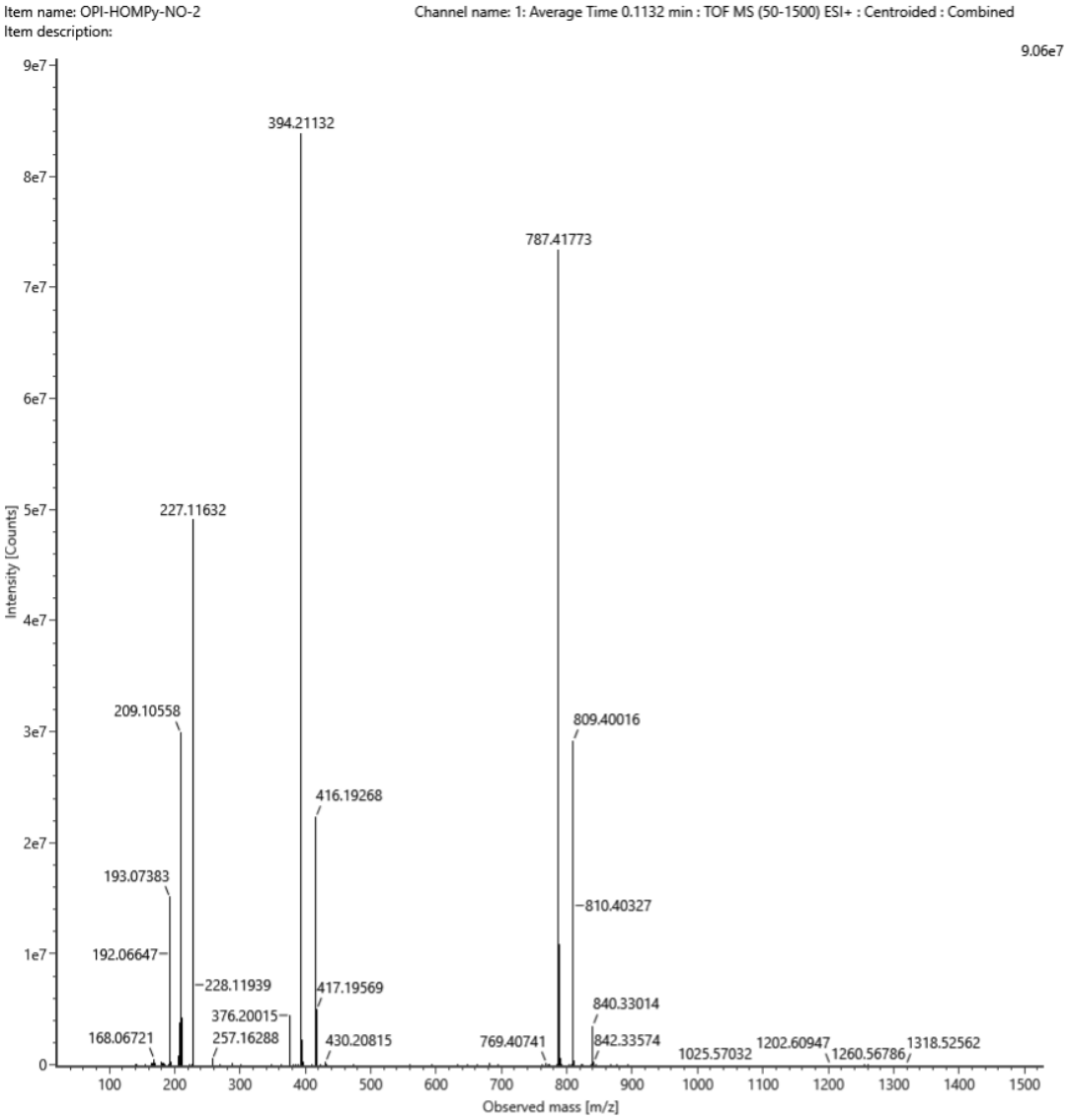


^{1}H and ^{13}C NMR of L1f

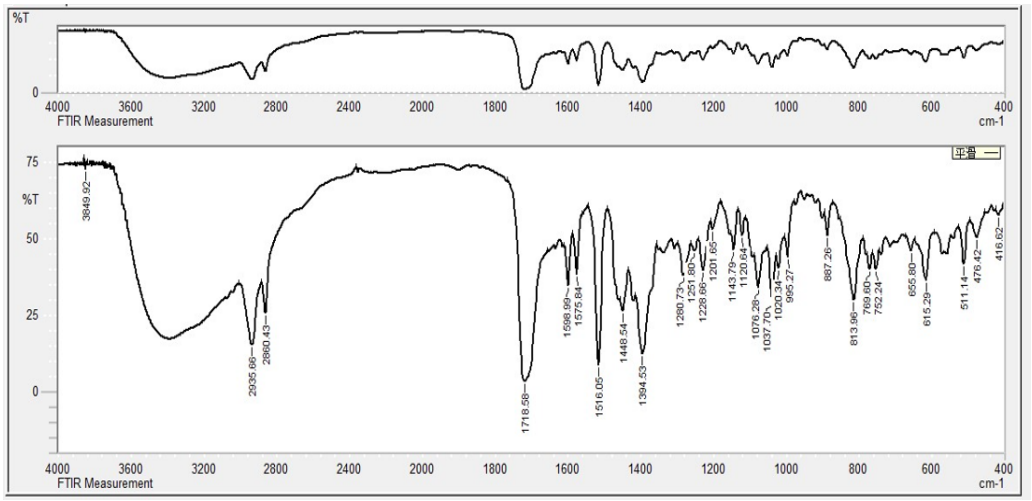




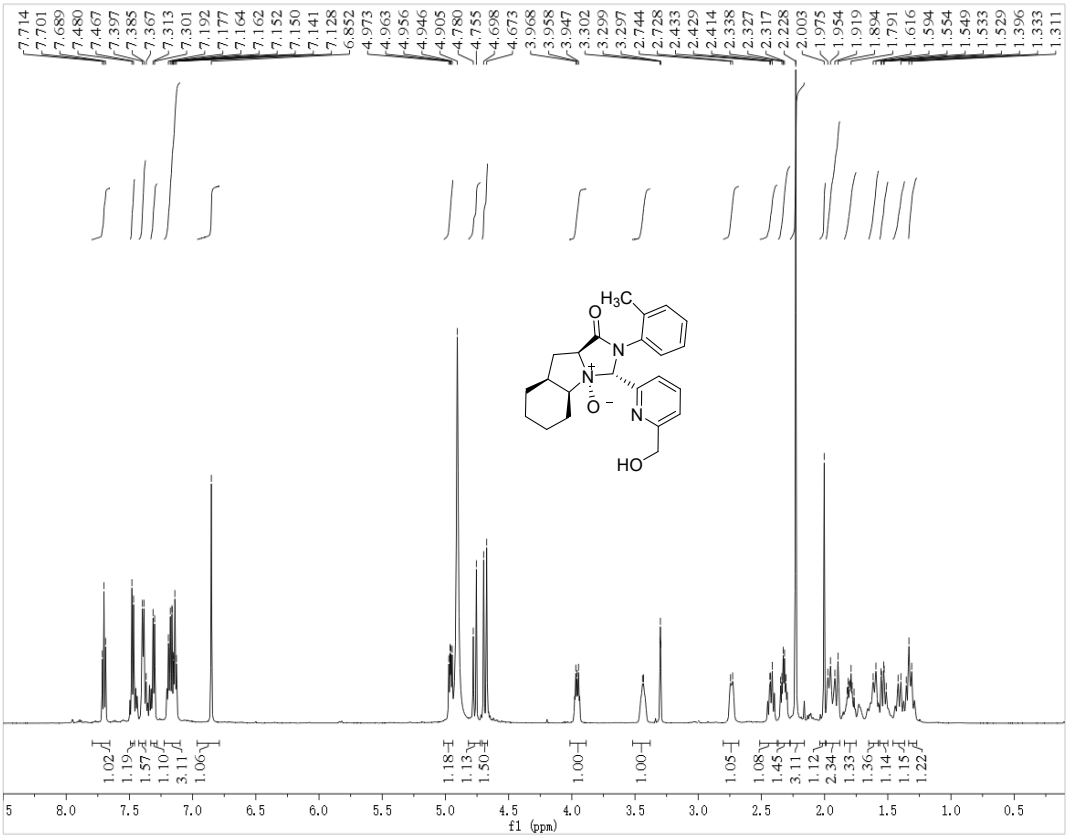
HRMS of L1f

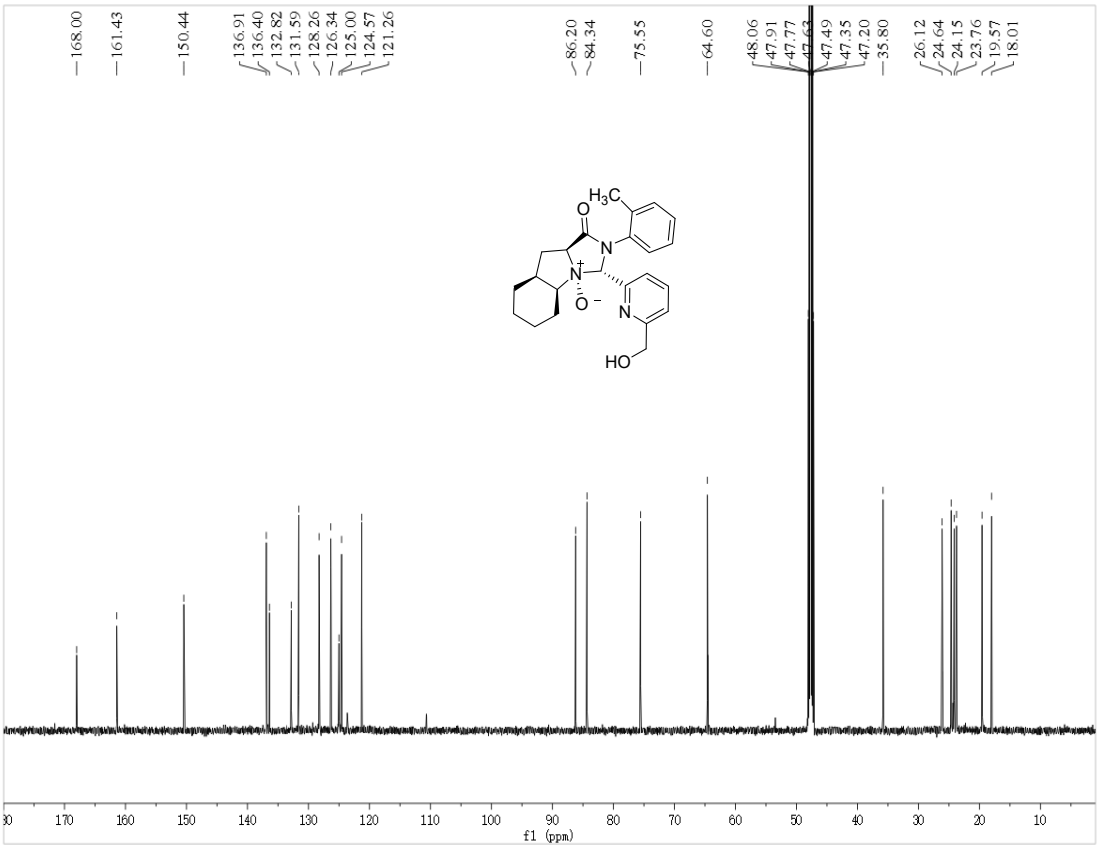


IR of L1f

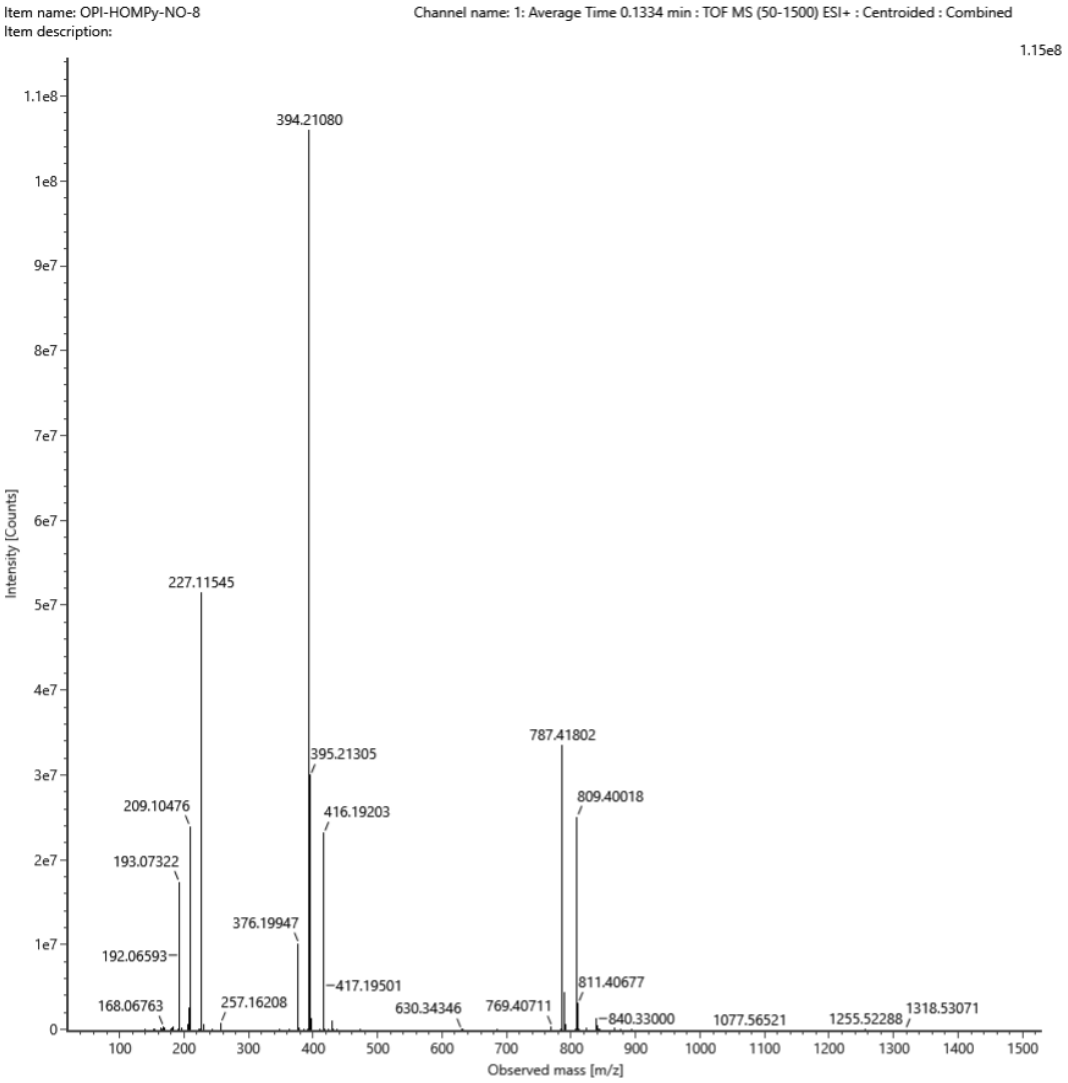


^{1}H and ^{13}C NMR of L1g

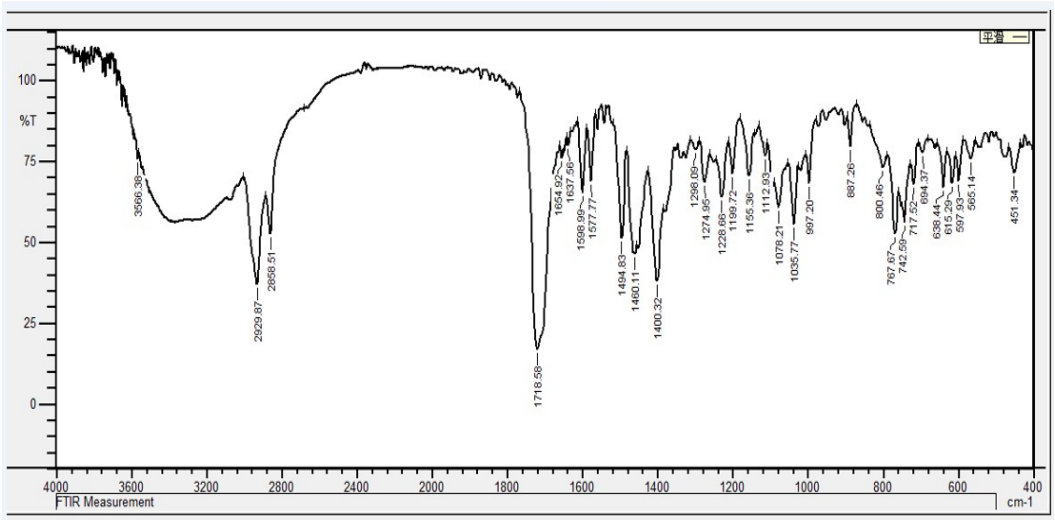




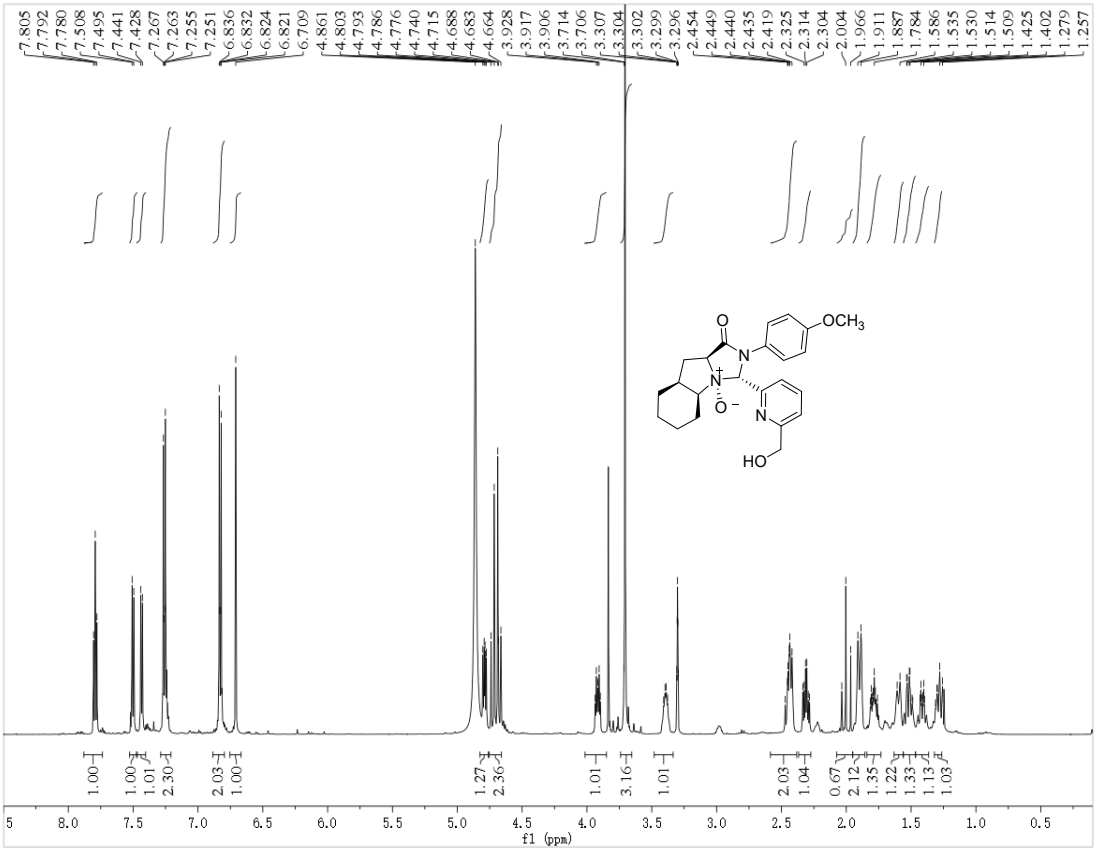
HRMS of L1g

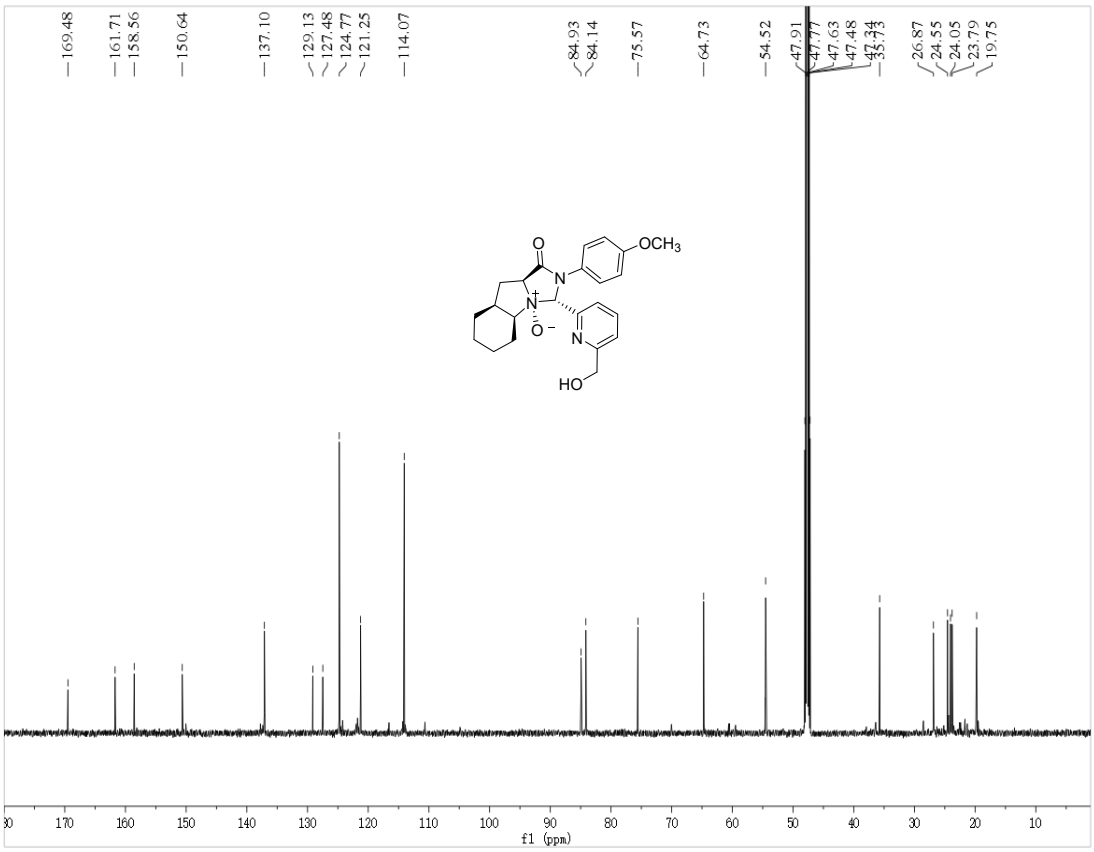


IR of L1g

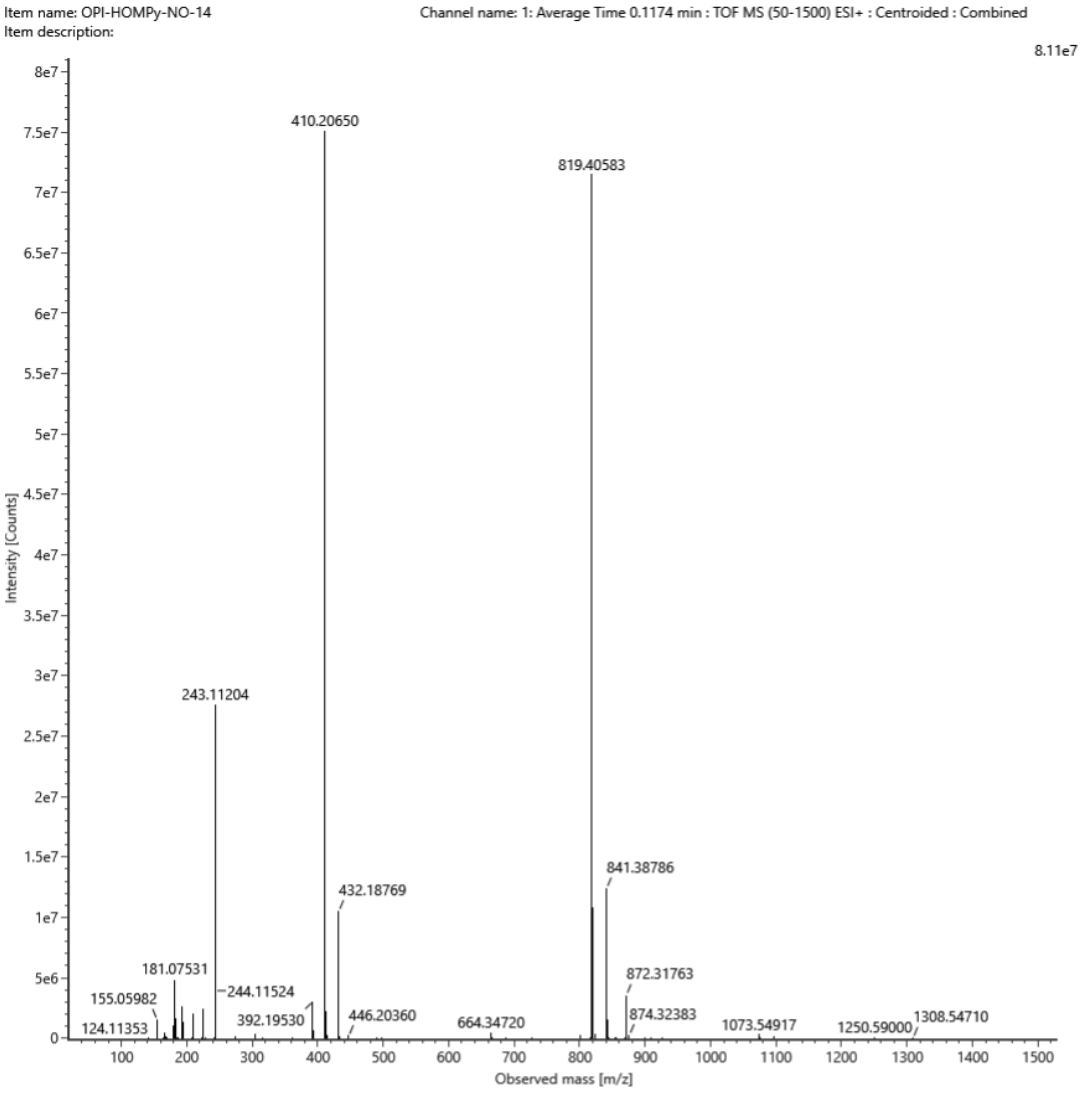


^{1}H and ^{13}C NMR of L1h

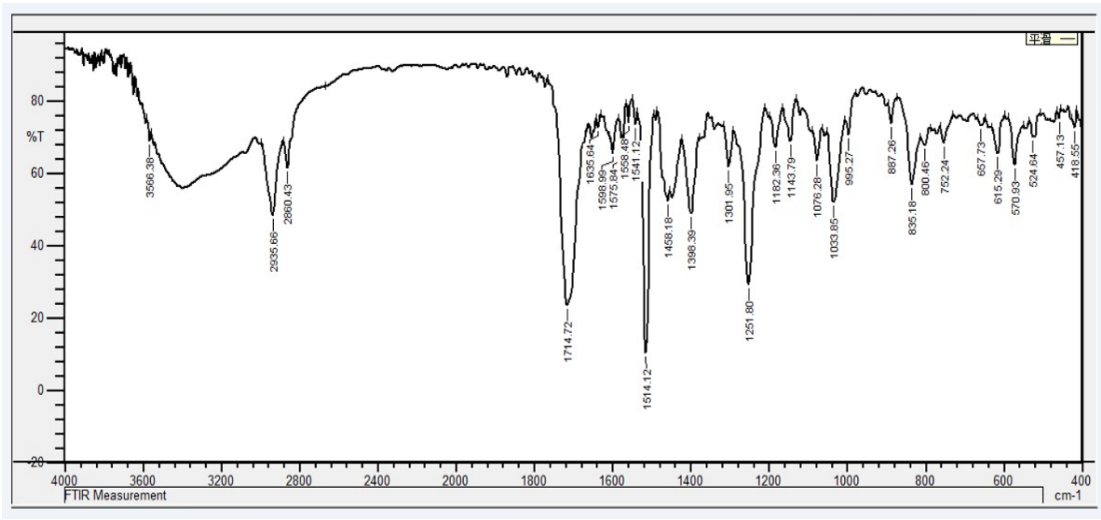




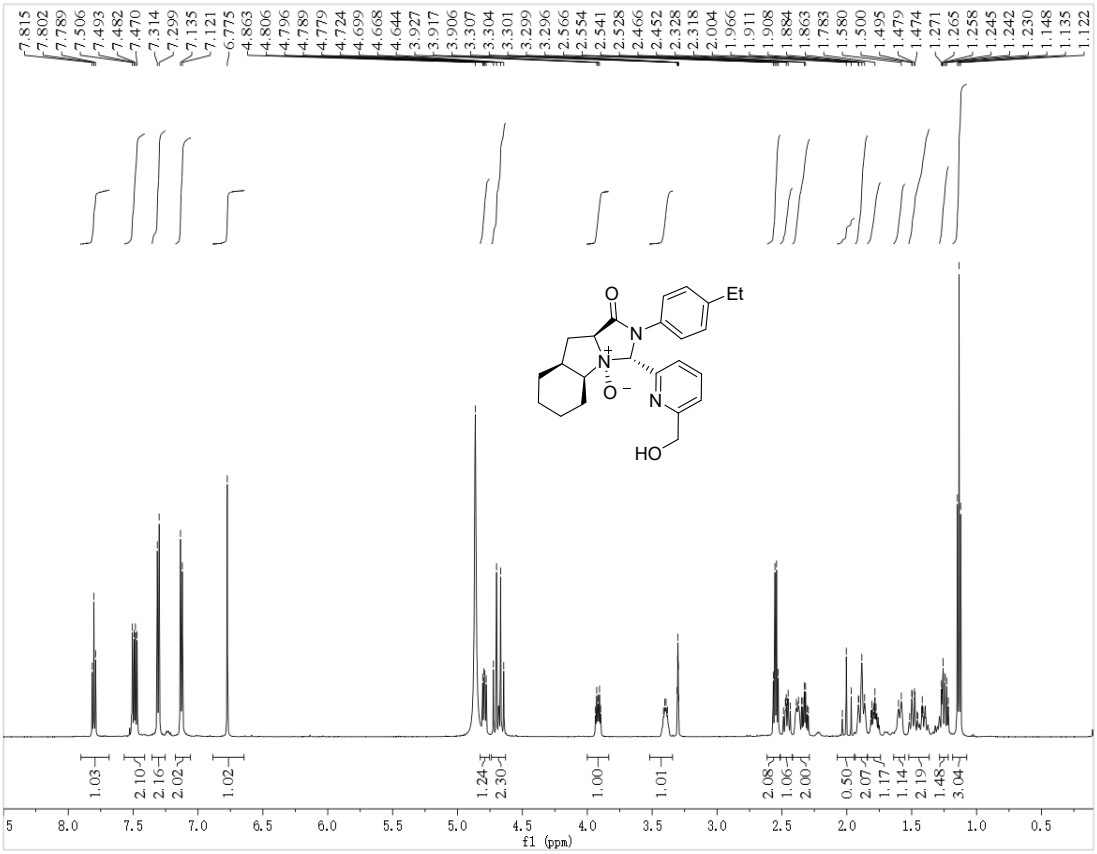
HRMS of L1h

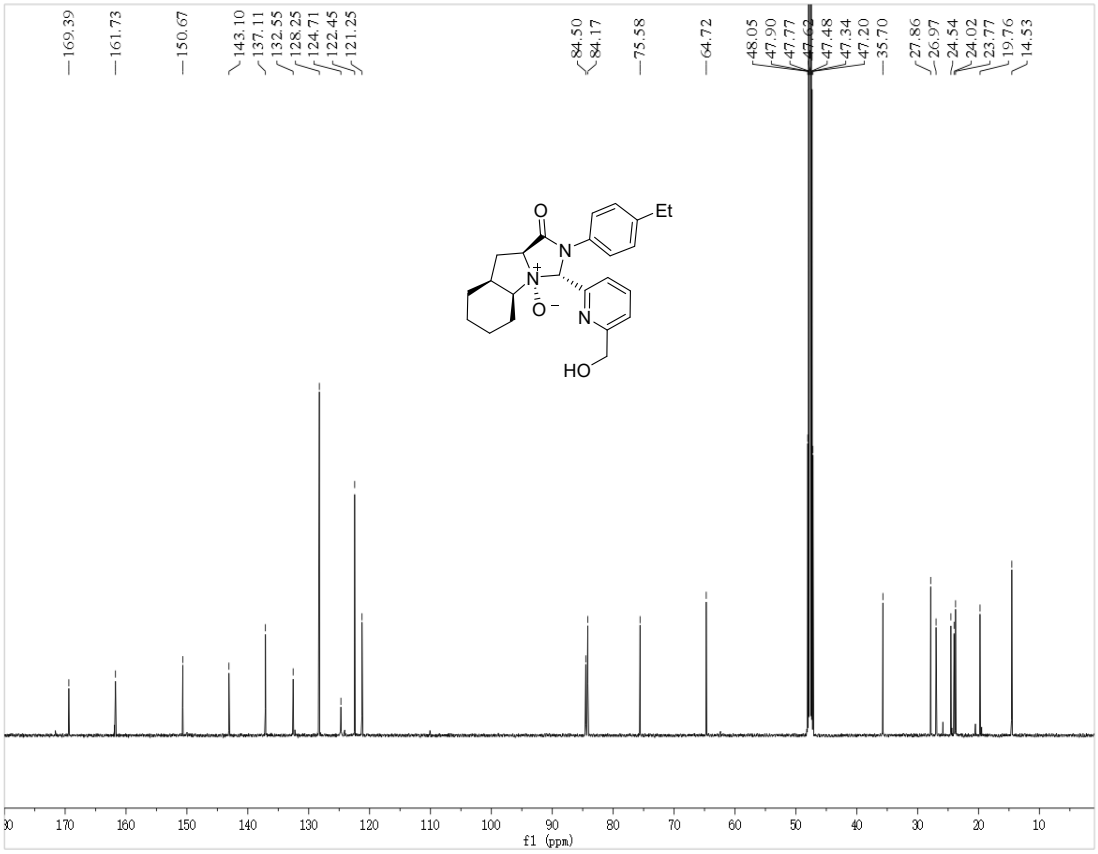


IR of L1h

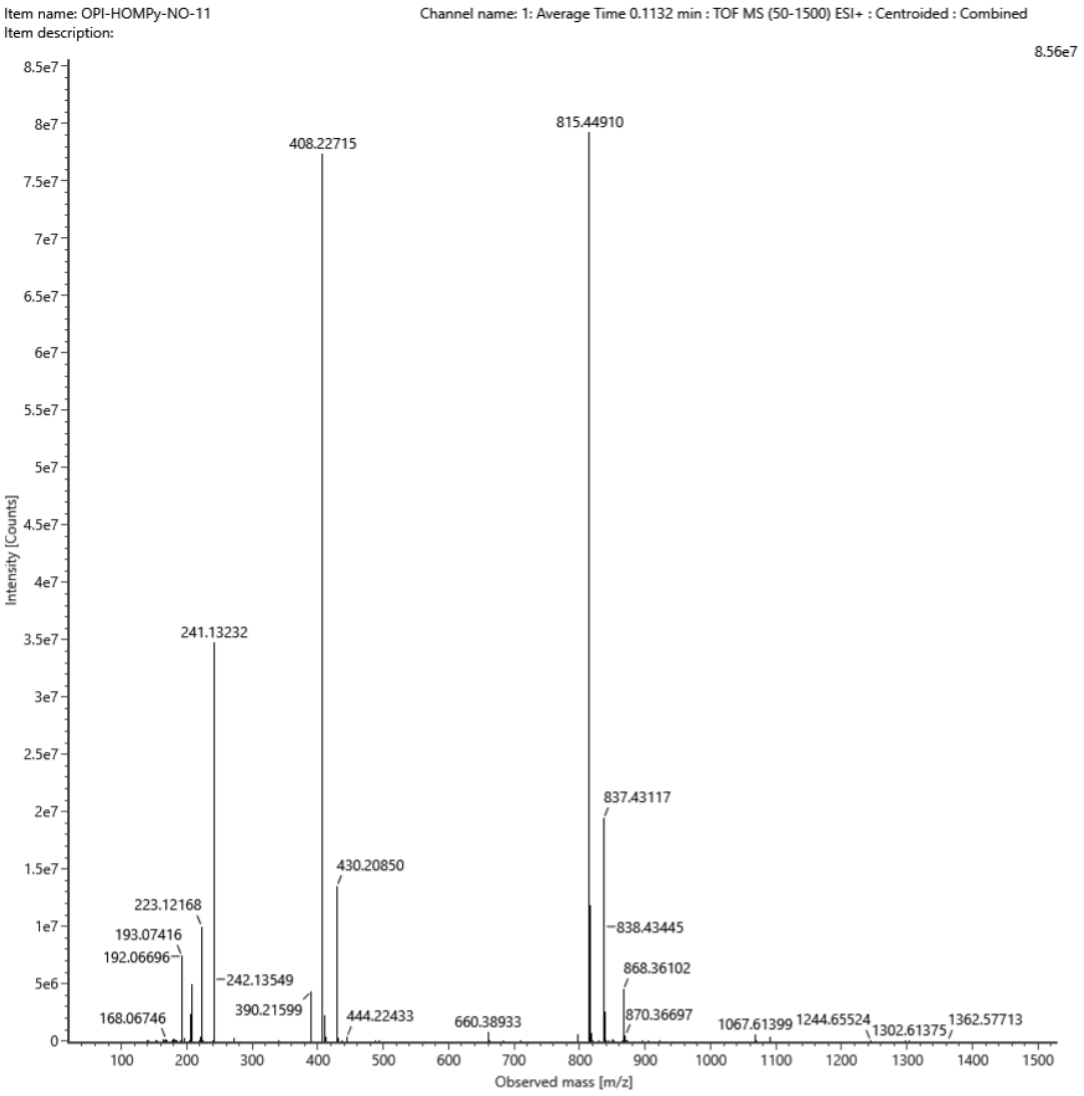


^{1}H and ^{13}C NMR of L1i

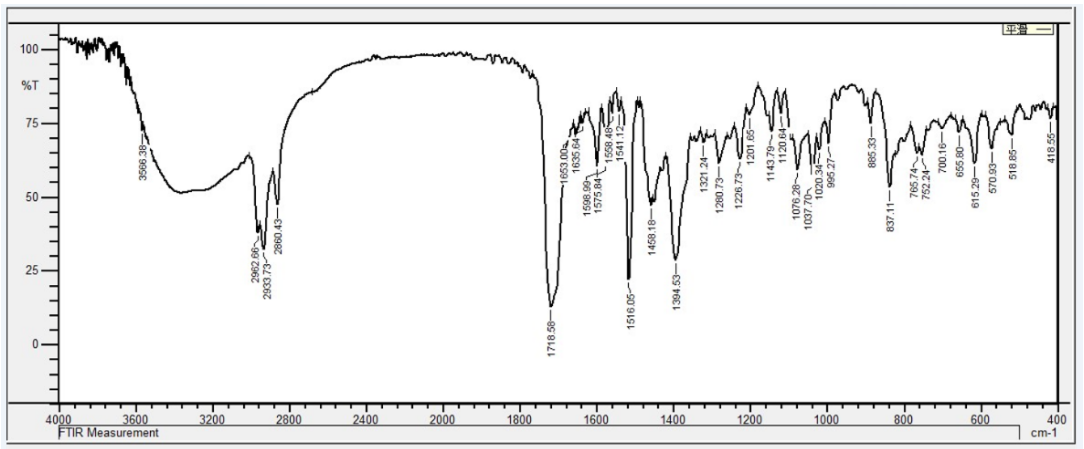




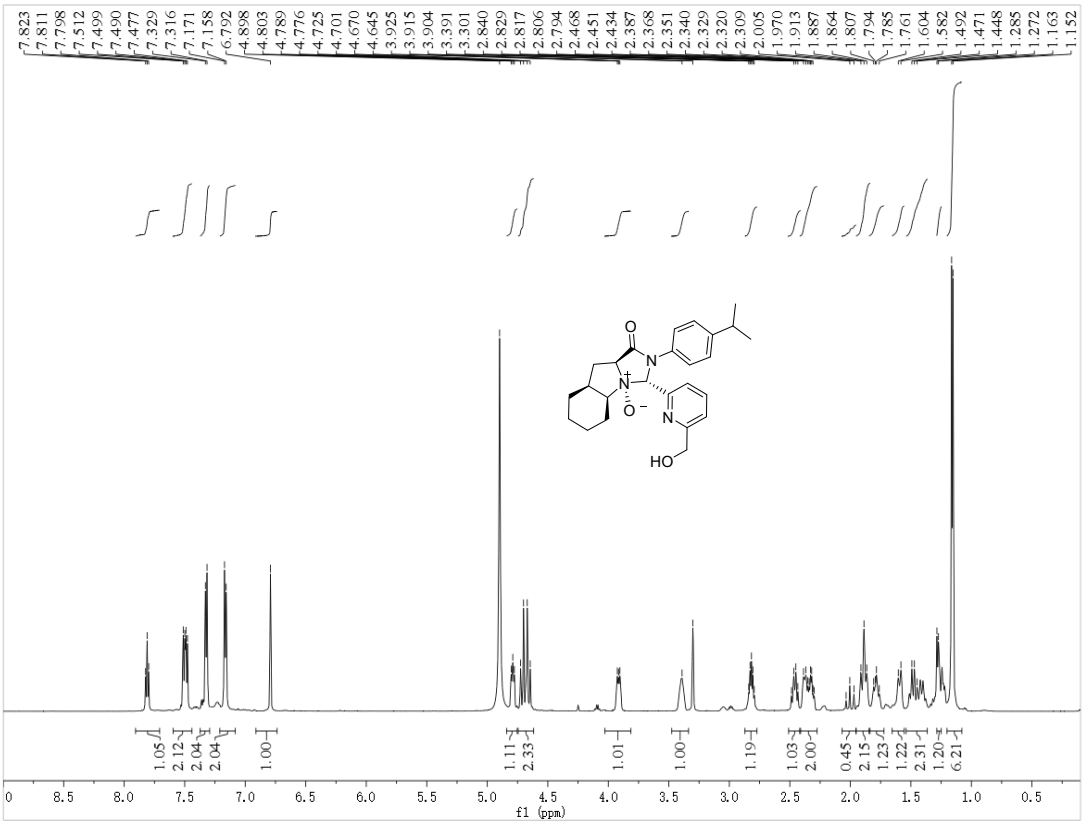
HRMS of L1i

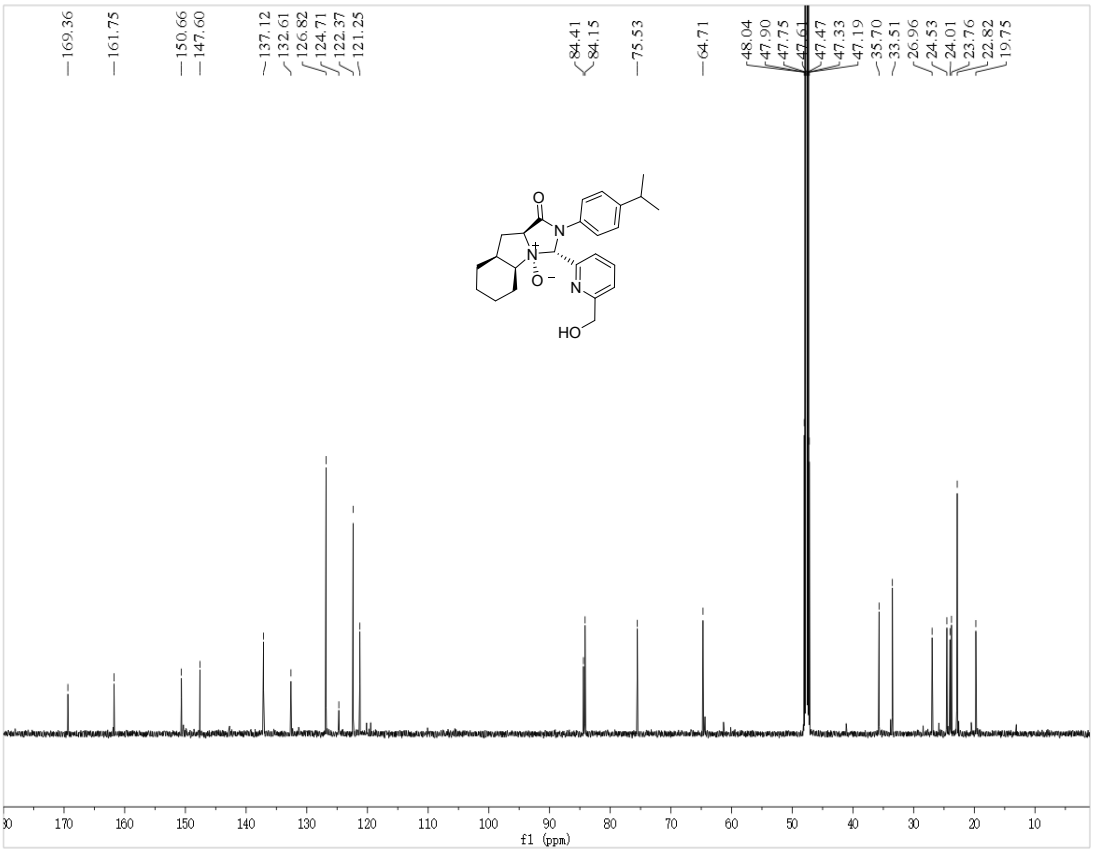


IR of L1i

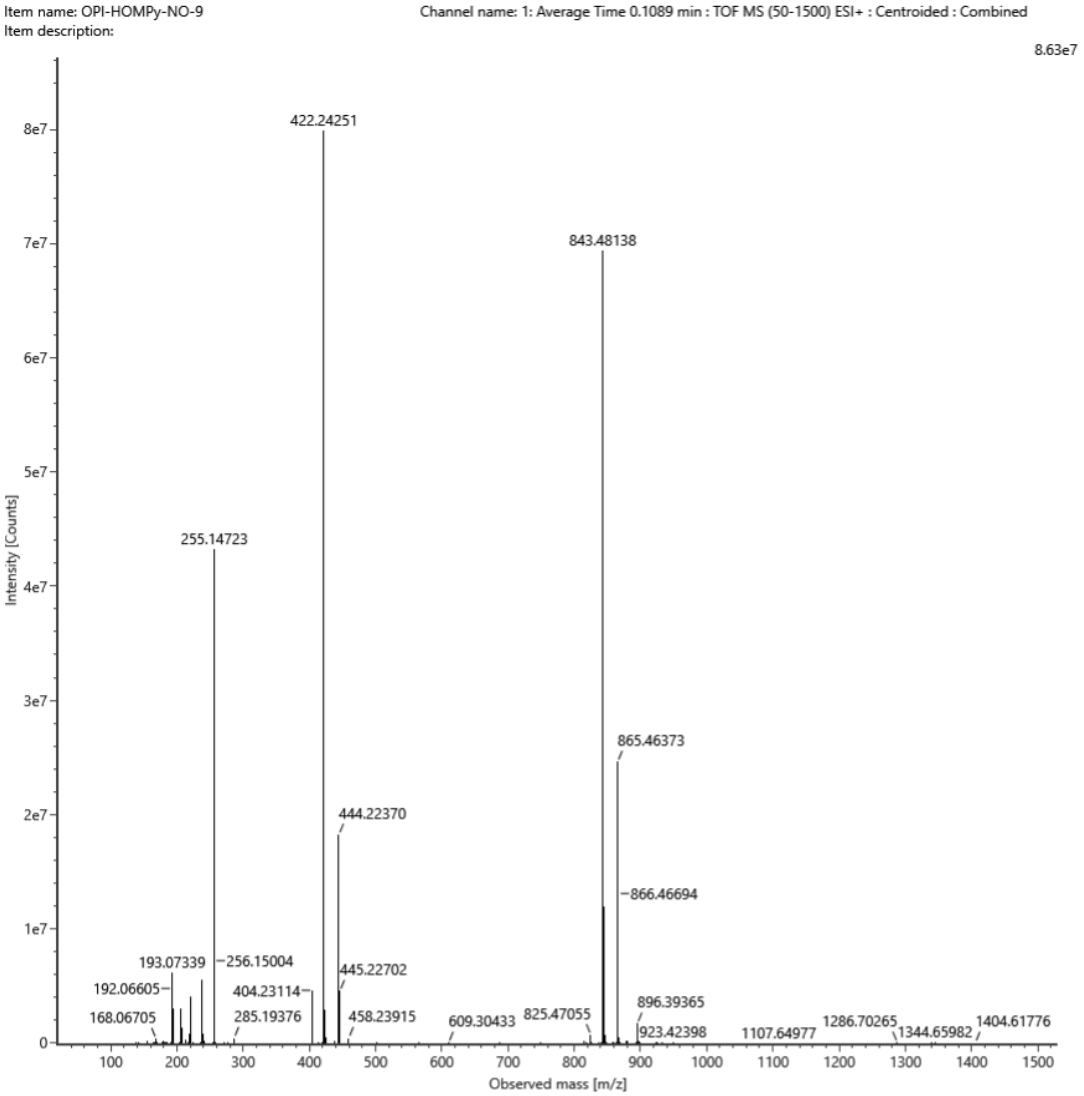


^{1}H and ^{13}C NMR of L1j

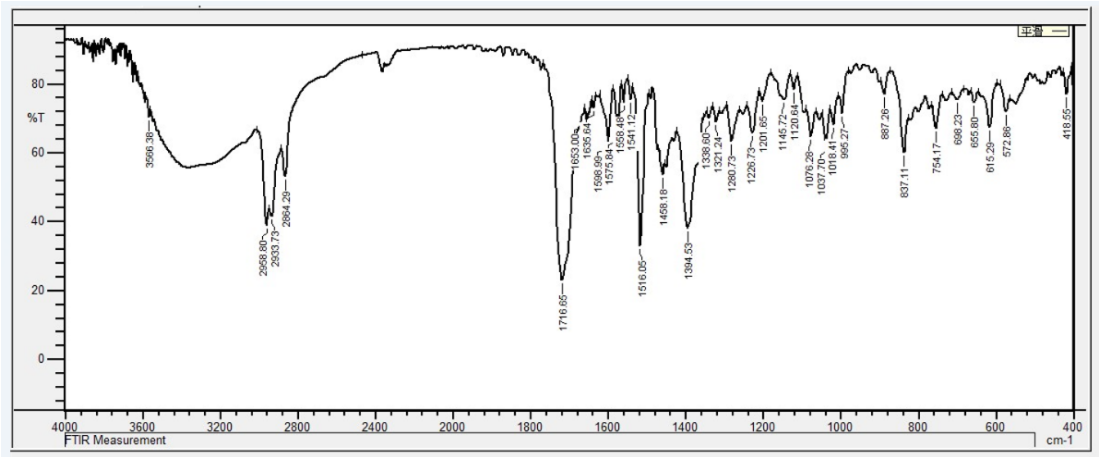




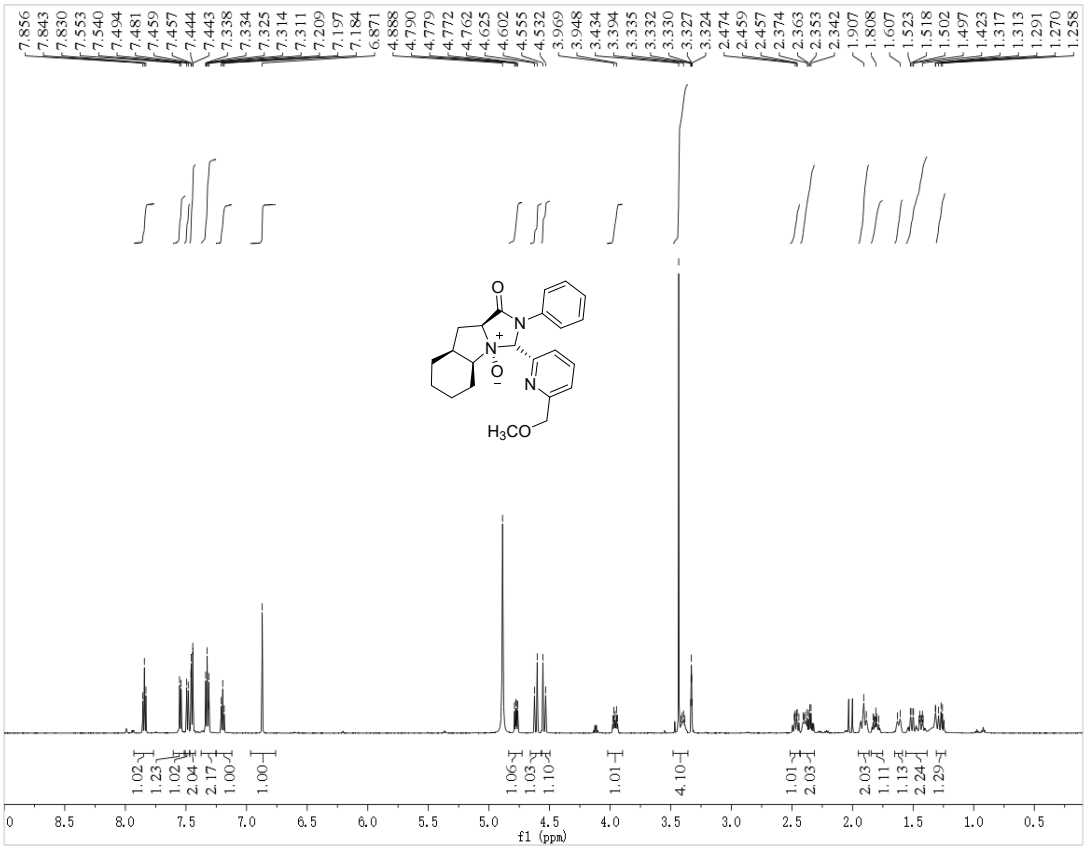
HRMS of L1j

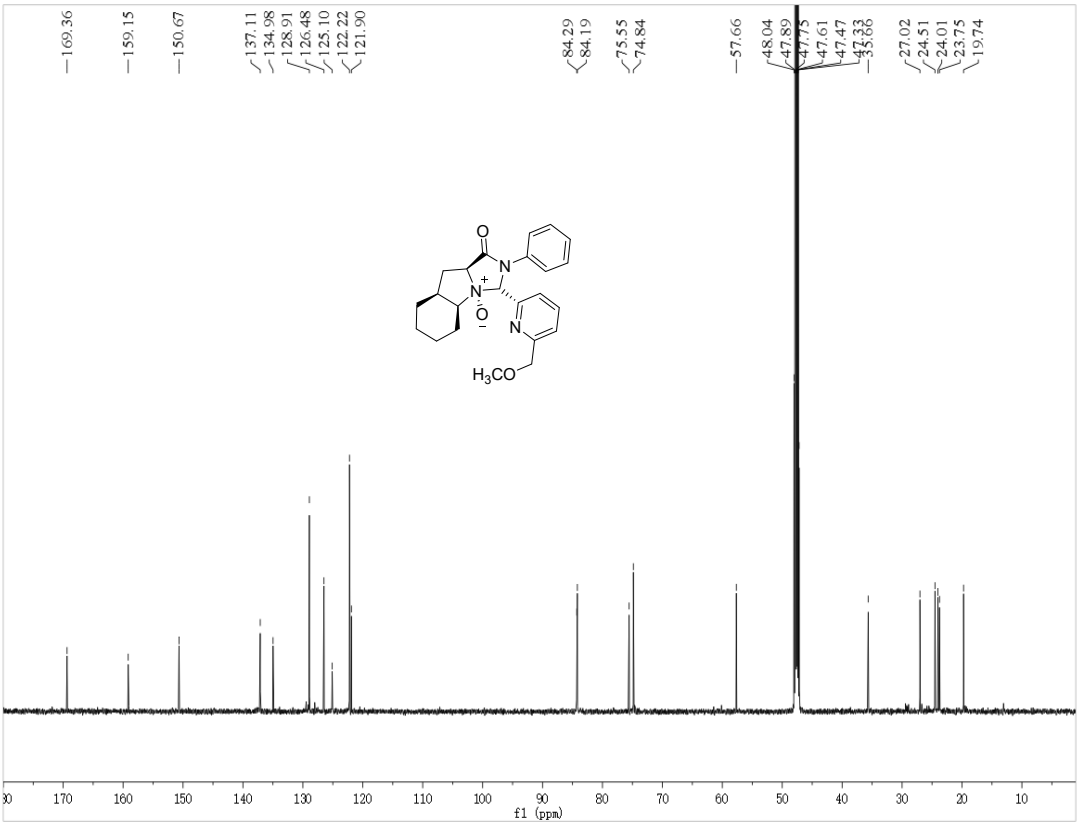


IR of L1j

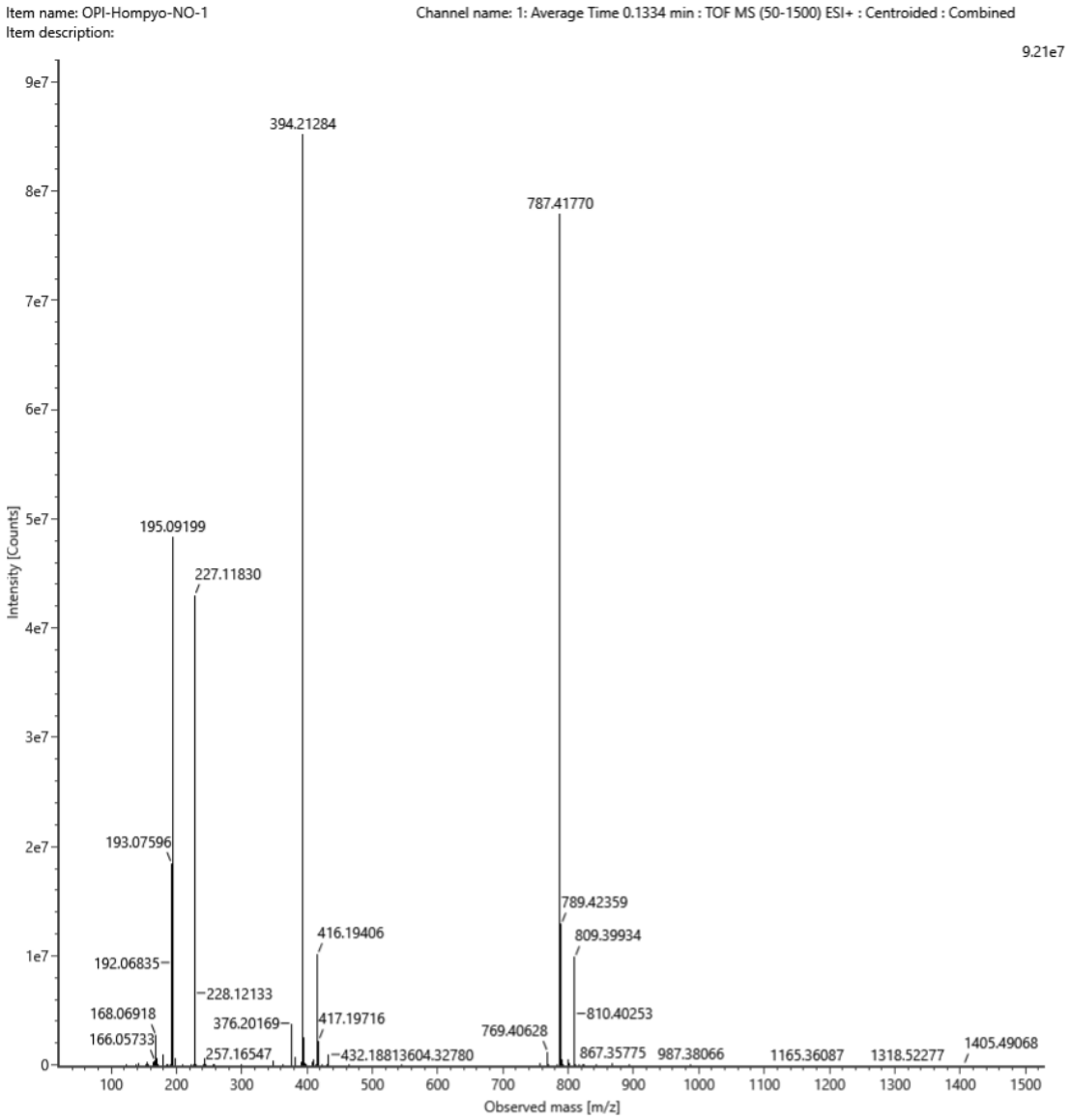


^{1}H and ^{13}C NMR of L3a





HRMS of L3a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Item description:
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9.21e7
Intensity [Counts]
Observed mass [m/z]
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227.11830
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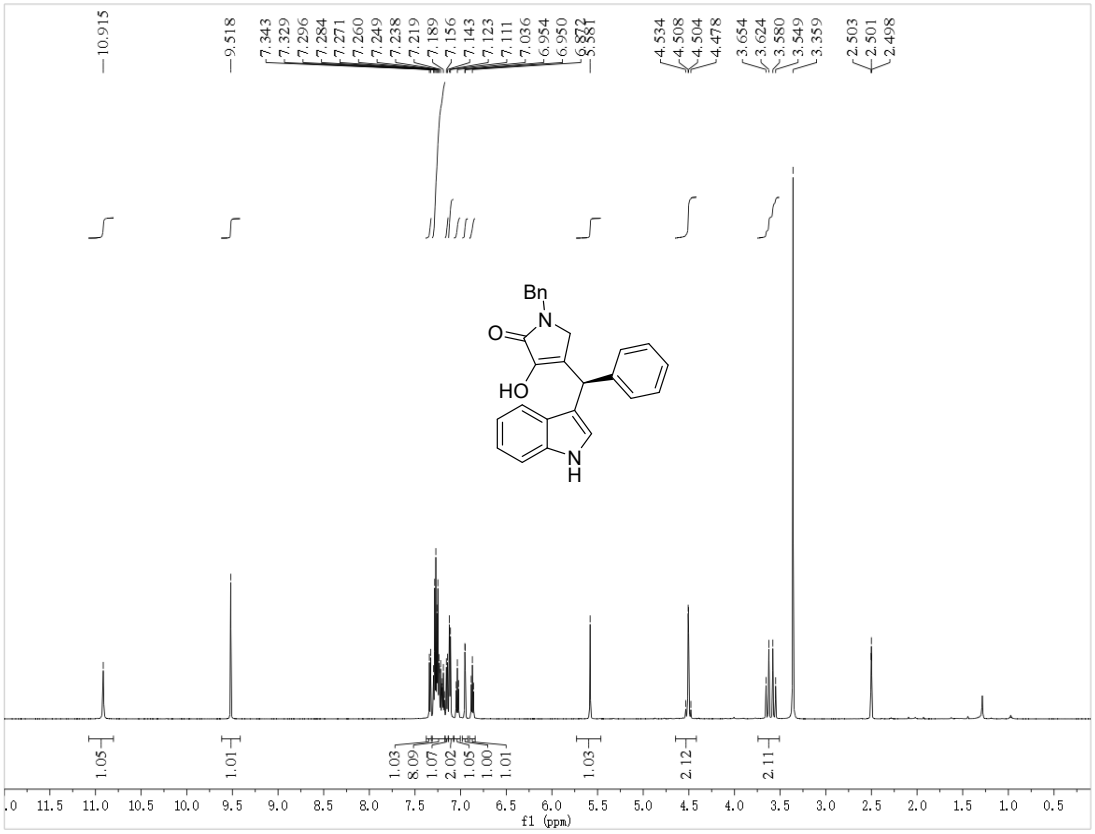
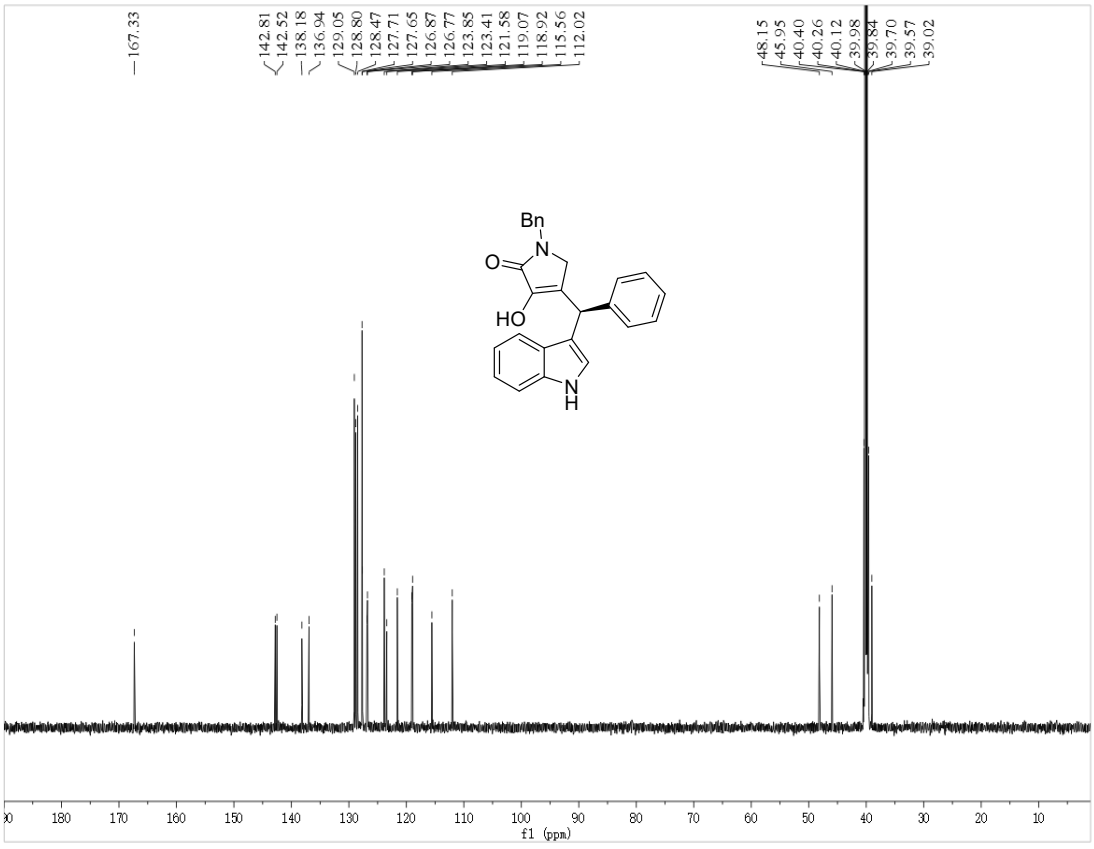
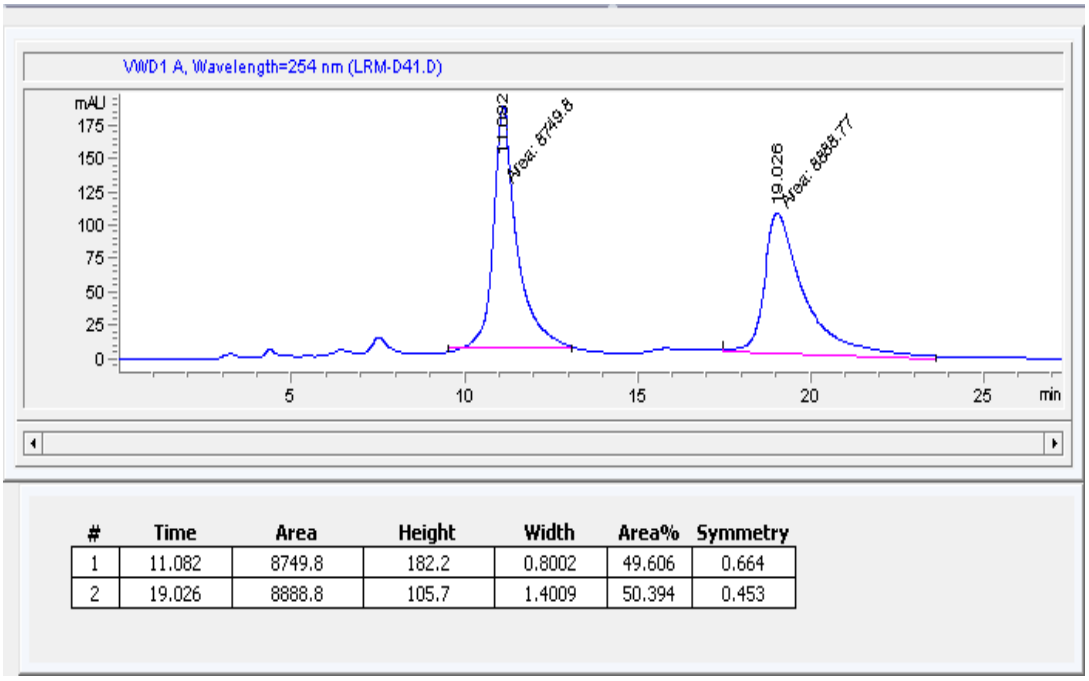
^{1}H and ^{13}C NMR of 6a





HPLC of 6a



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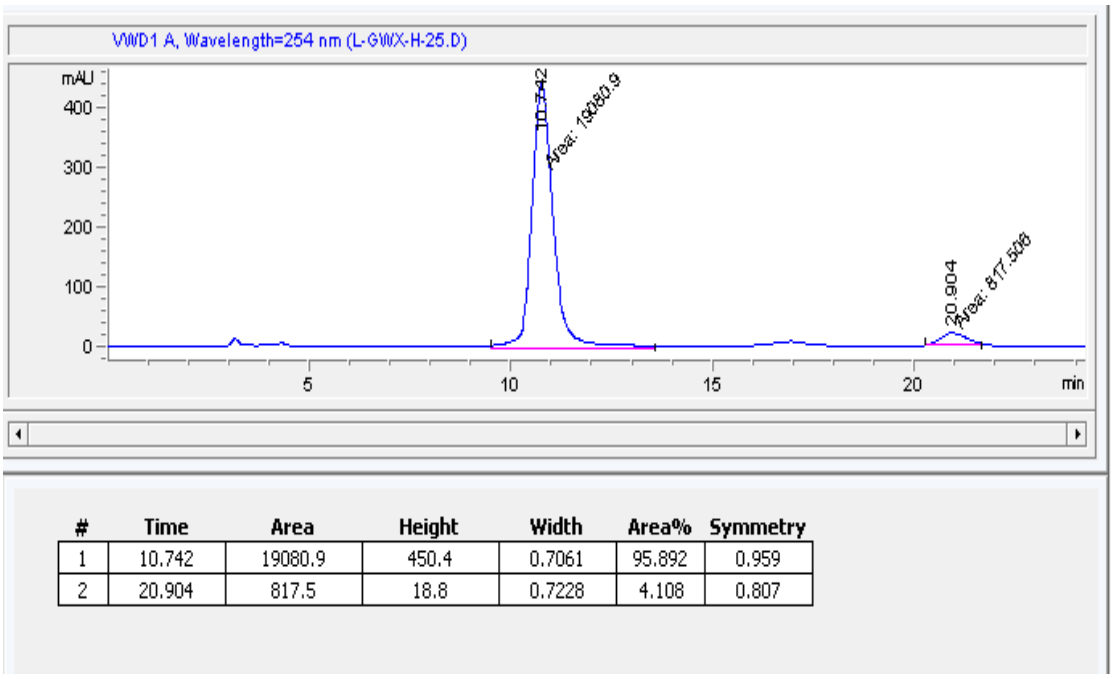

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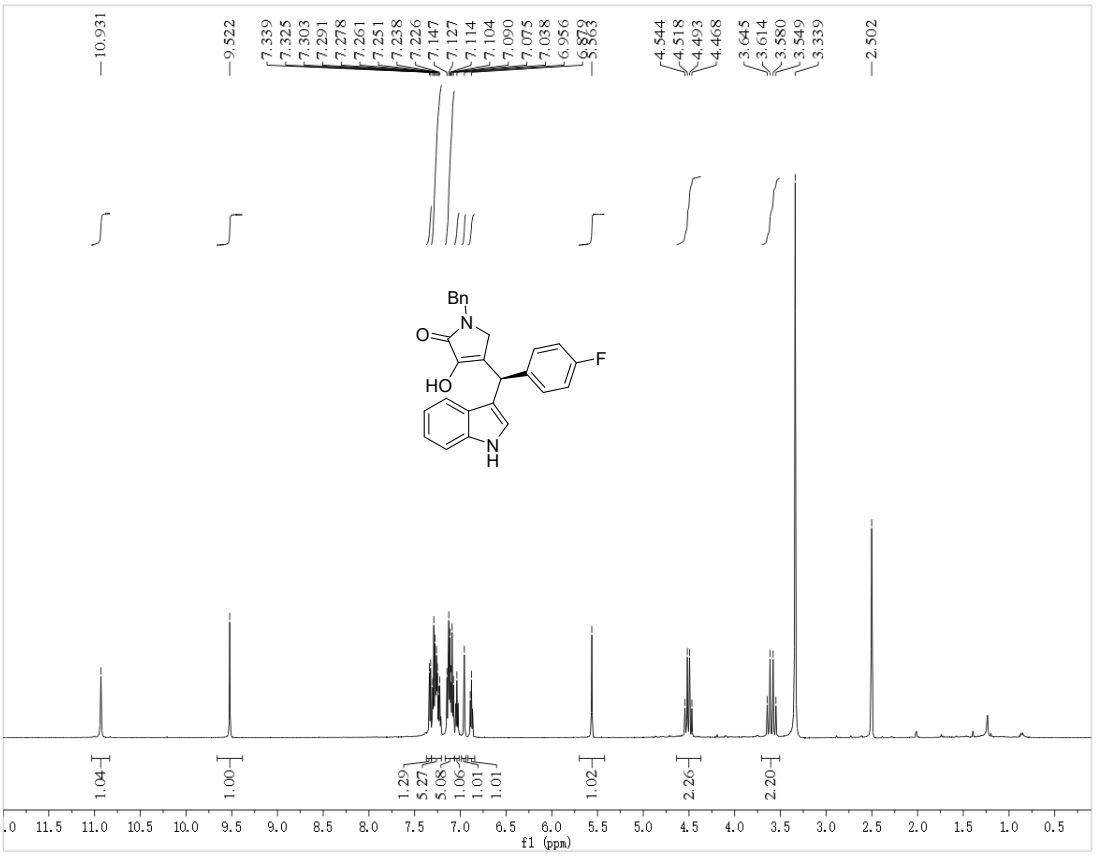
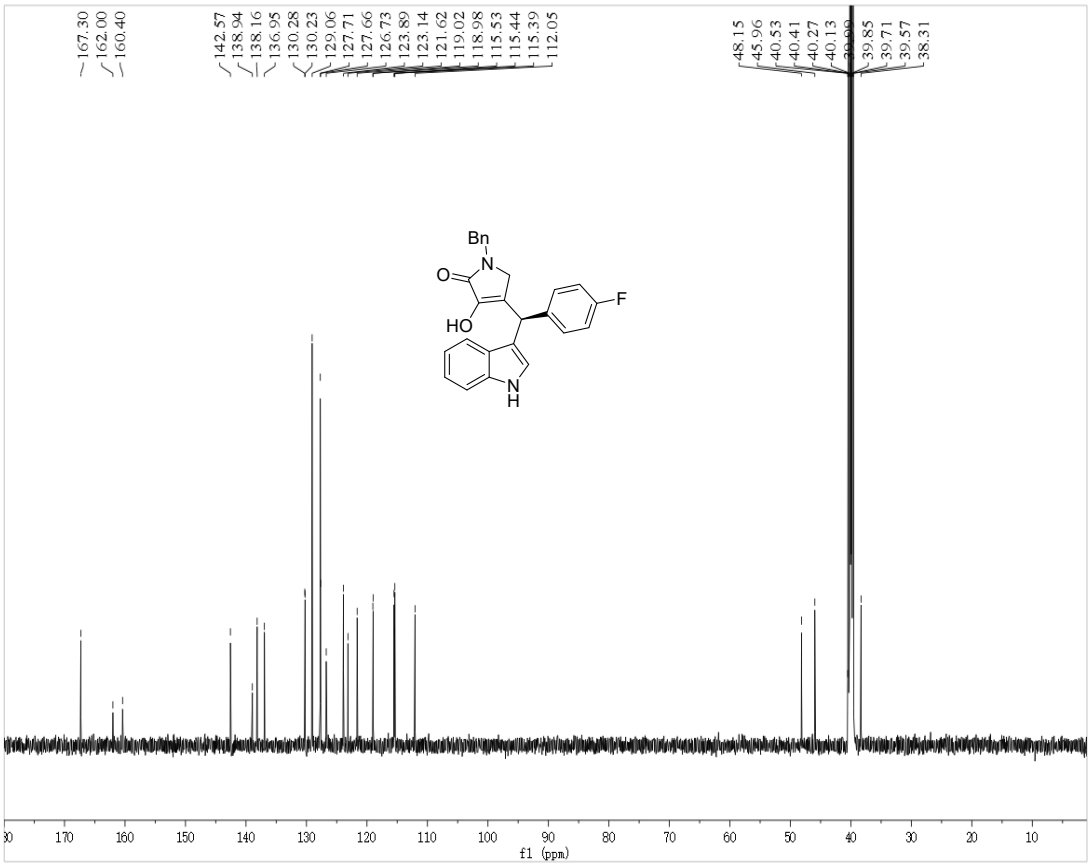
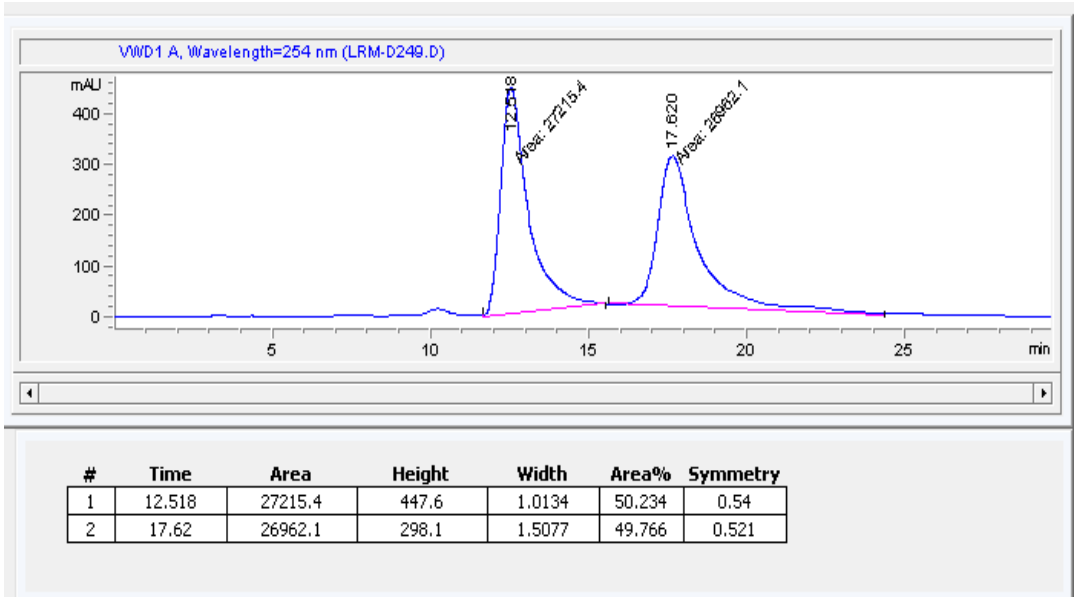
2	20.904	817.5	18.8	0.7228	4.108	0.807

^{1}H and ^{13}C NMR of 6b





HPLC of 6b



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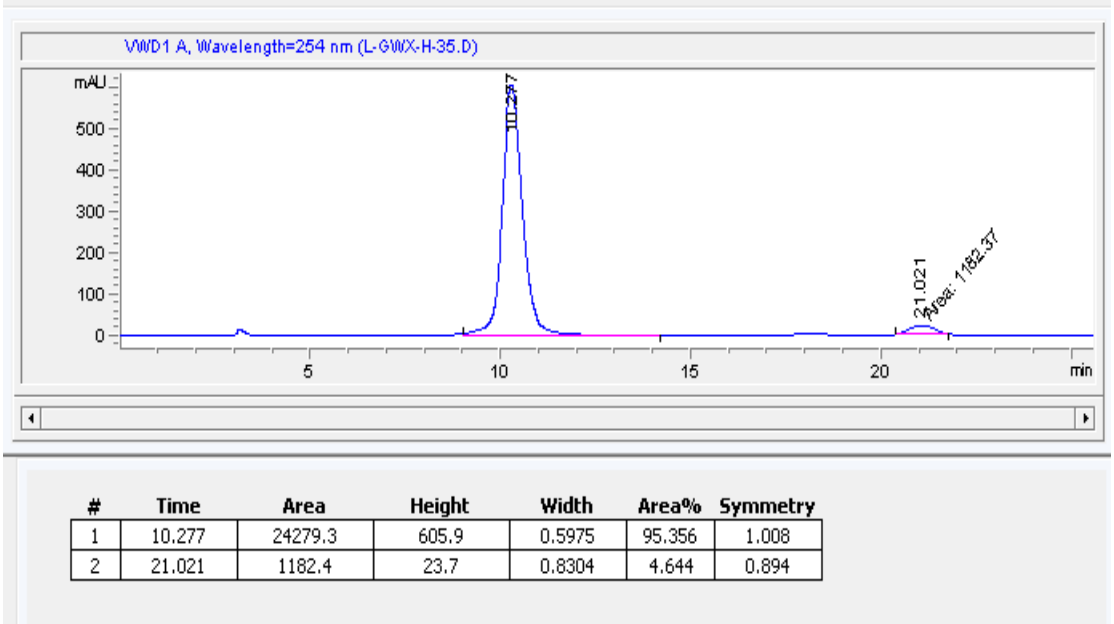

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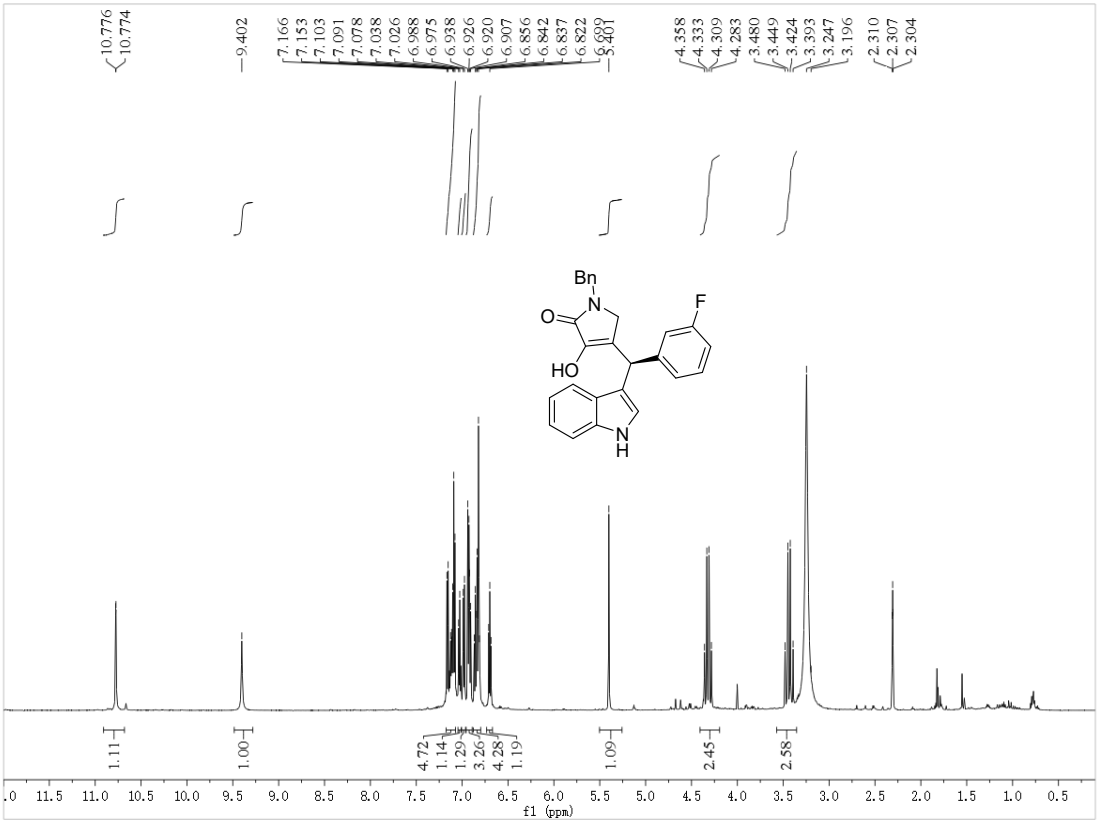
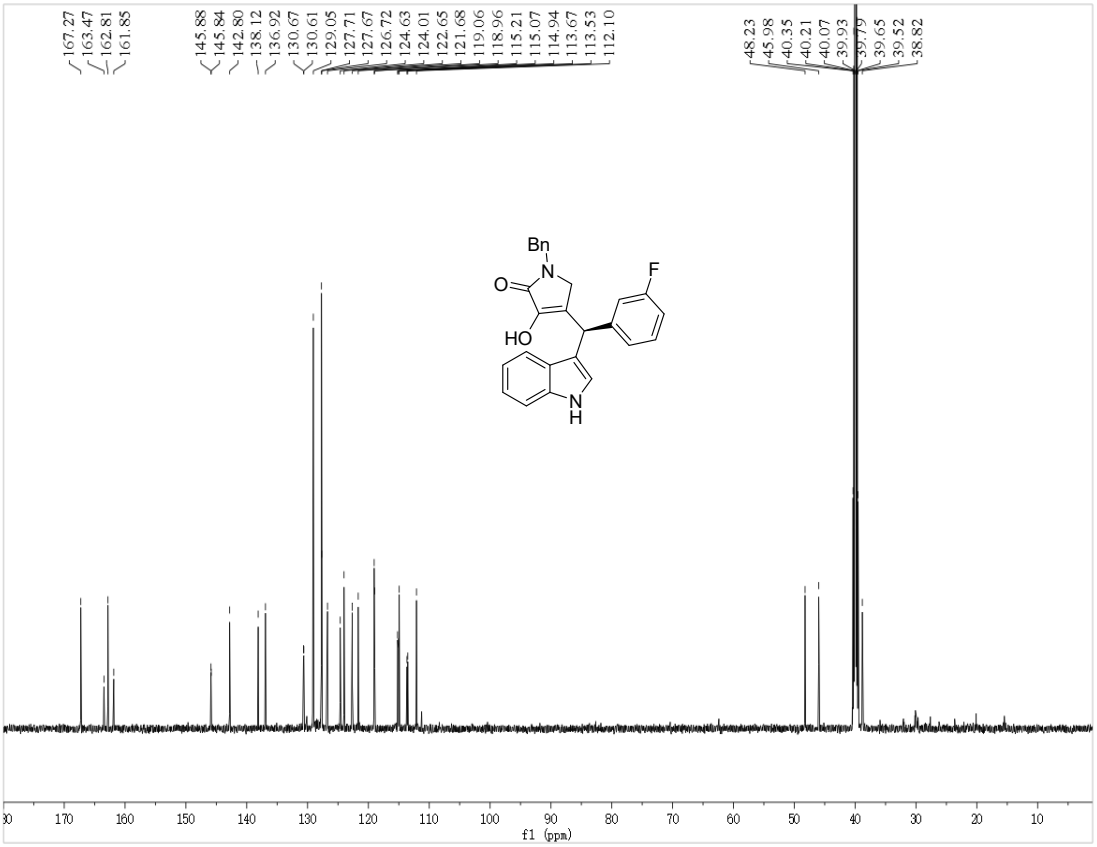
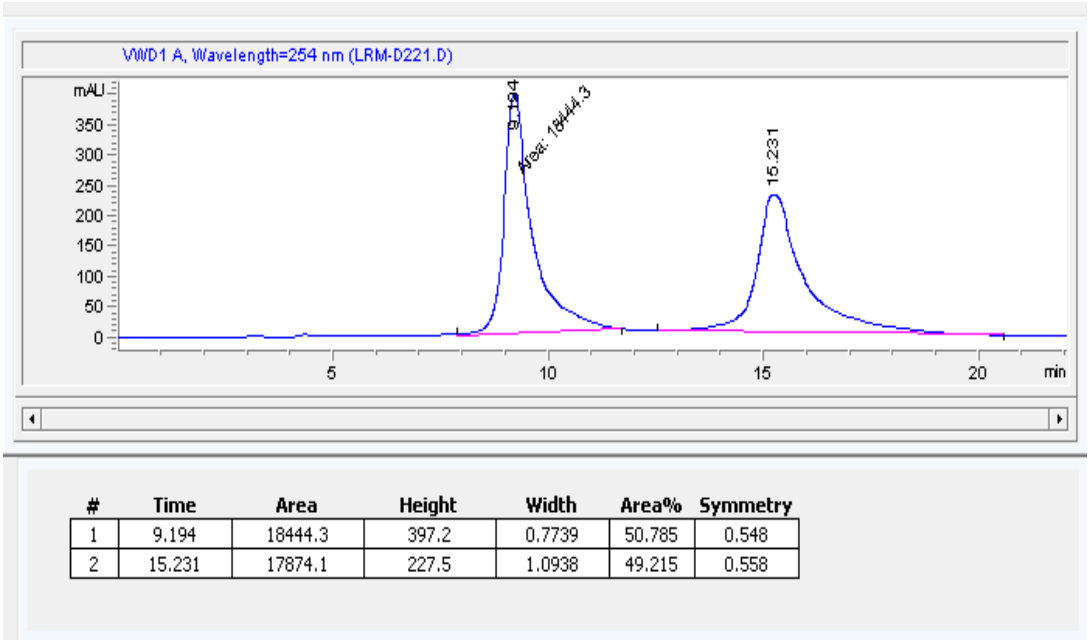
^{1}H and ^{13}C NMR of 6c





HPLC of 6c



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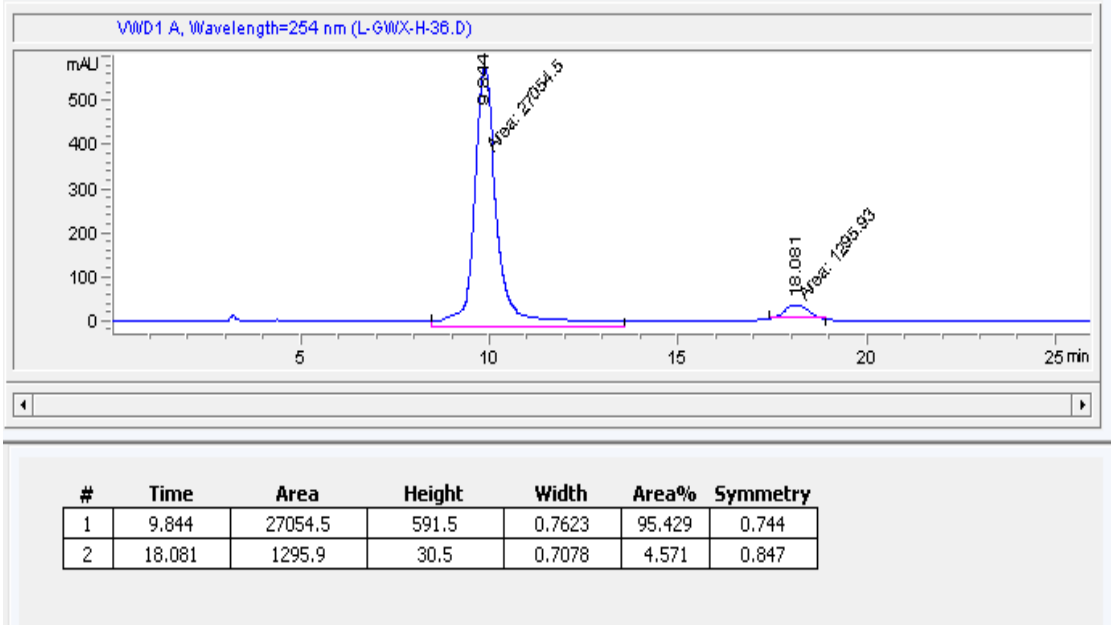

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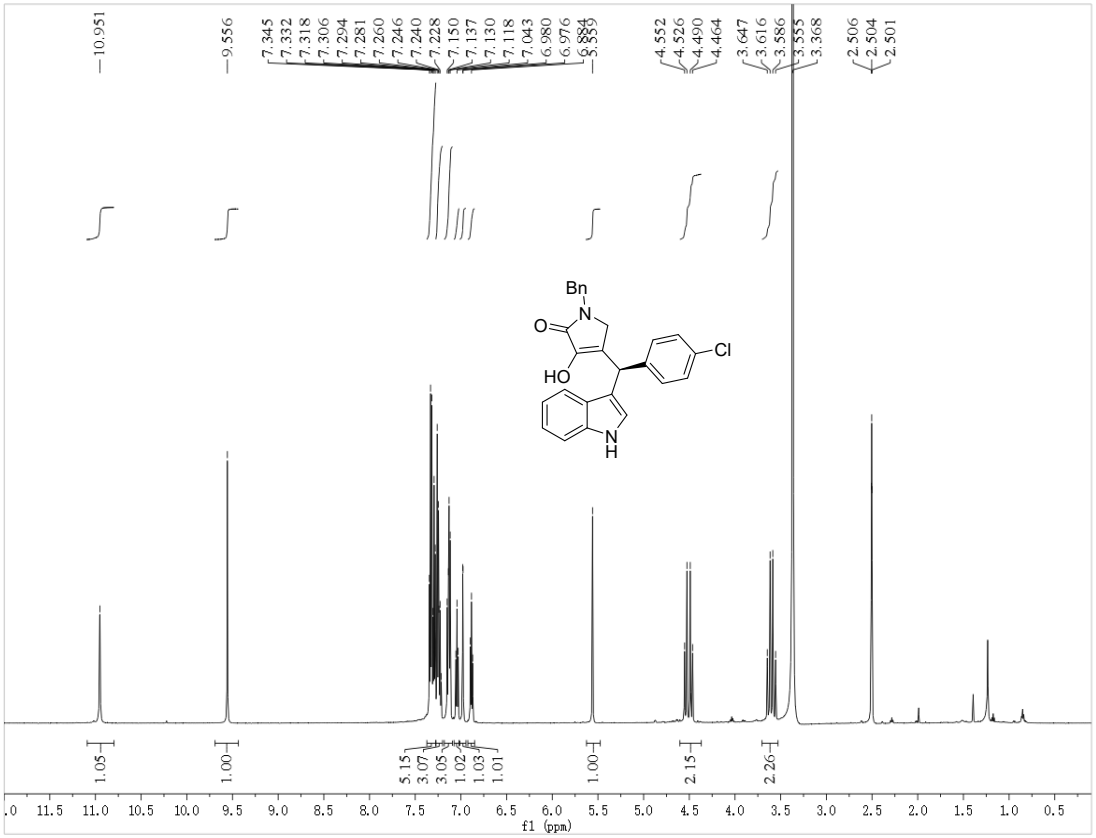
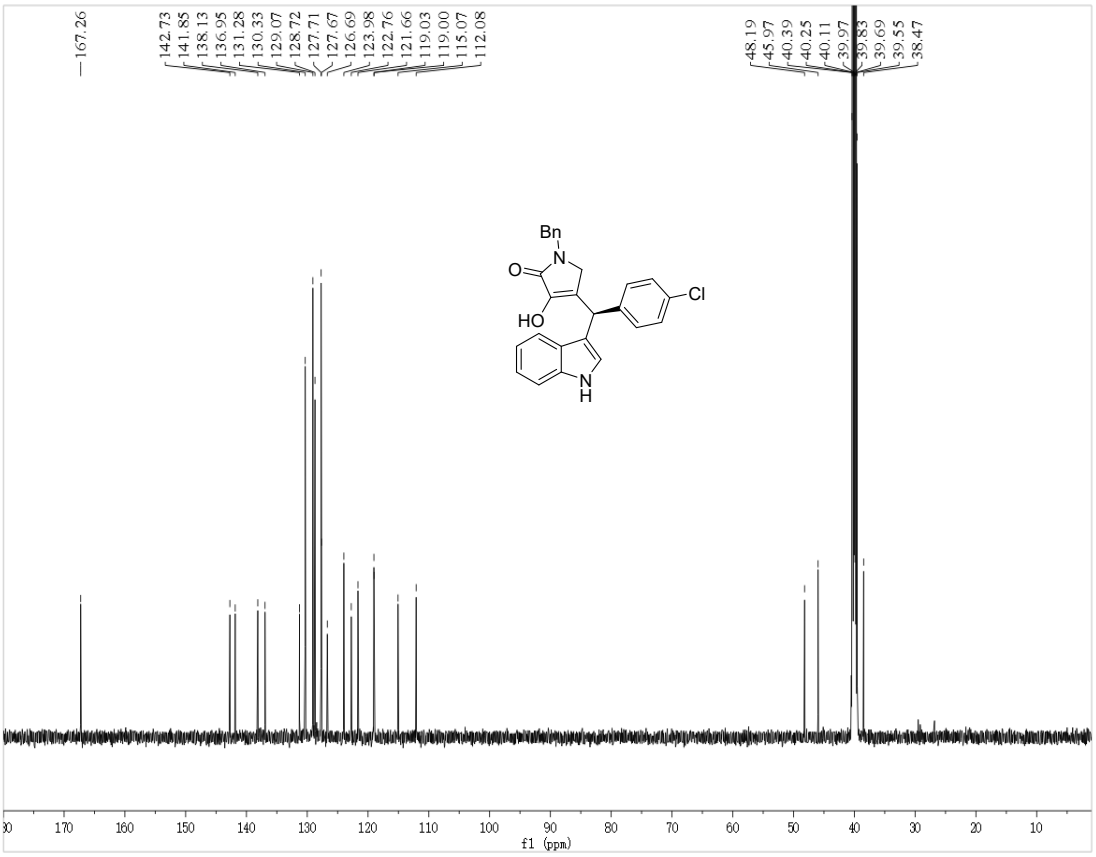
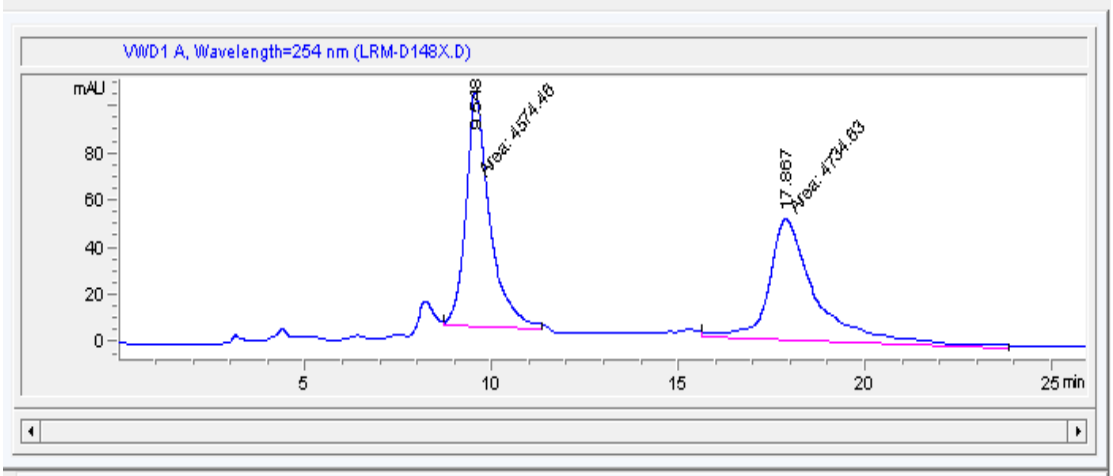
^{1}H and ^{13}C NMR of 6d

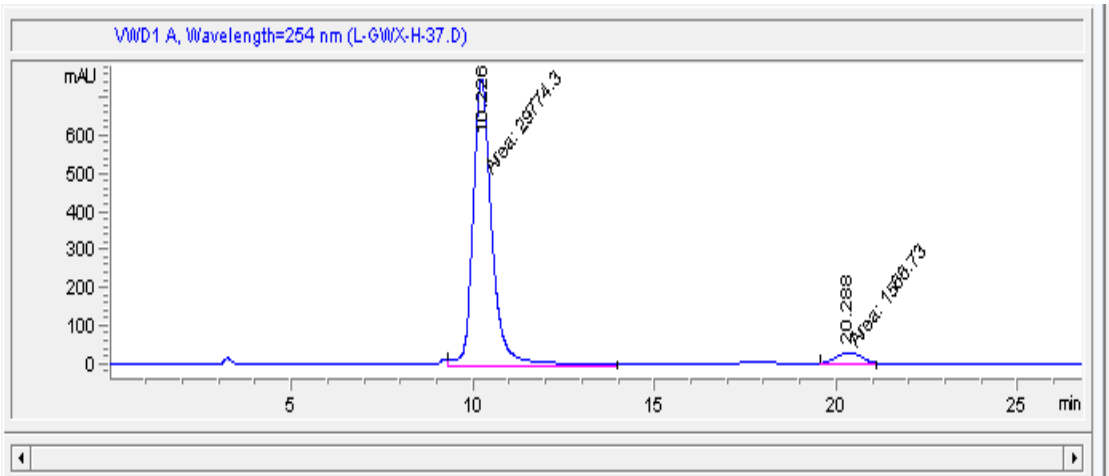




HPLC of 6d

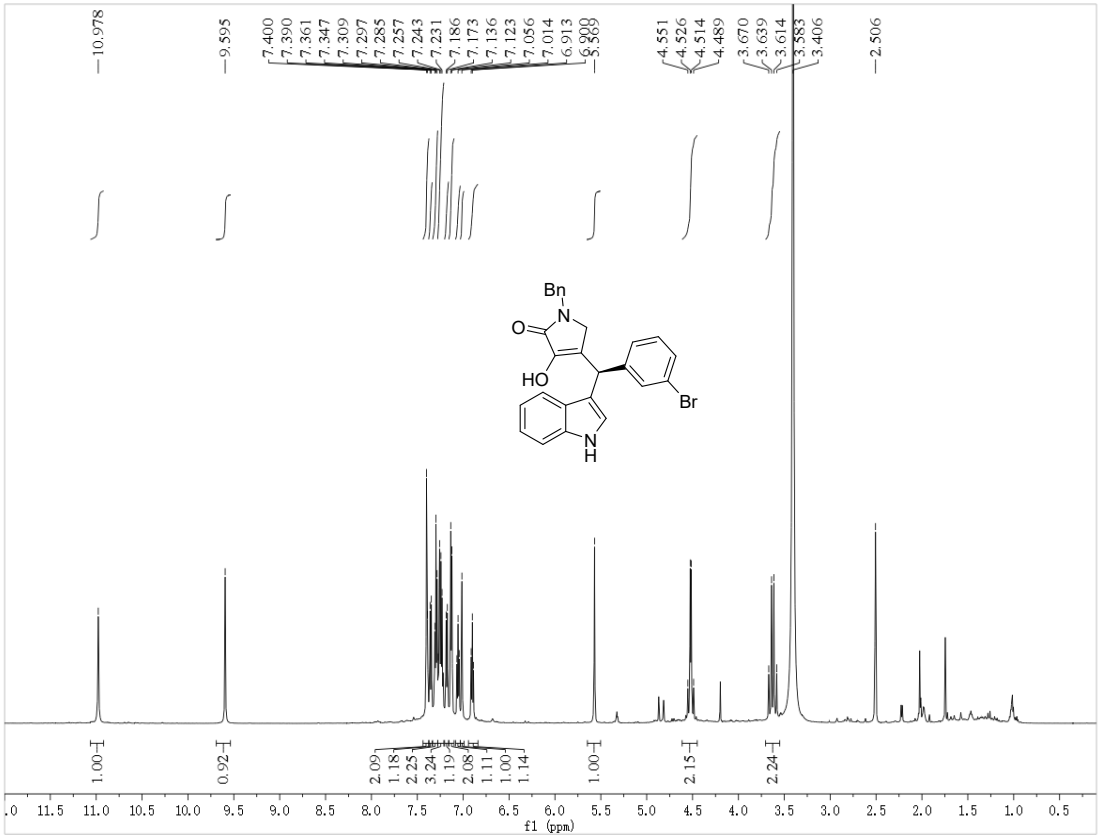


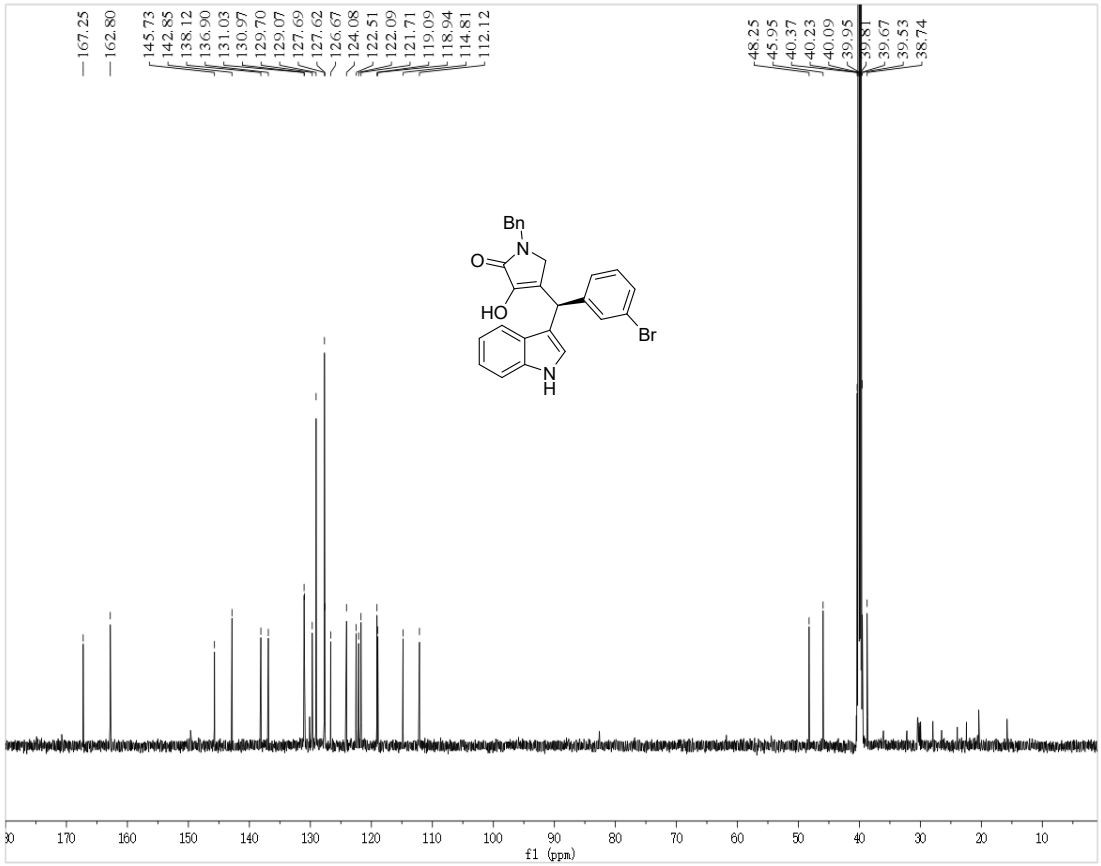
#	Time	Area	Height	Width	Area%	Symmetry
1	9.548	4574.5	100.6	0.7577	49.140	0.664
2	17.867	4734.6	51.6	1.5286	50.860	0.533



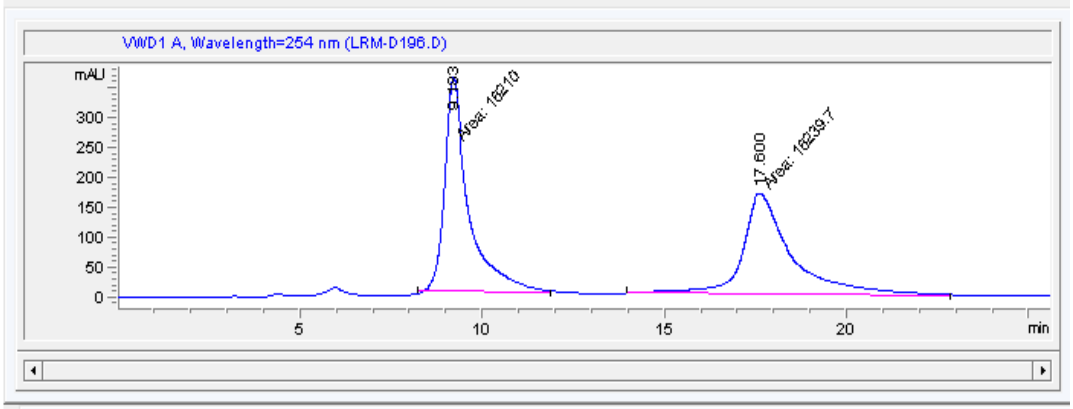
#	Time	Area	Height	Width	Area%	Symmetry
1	10.226	29774.3	759.1	0.6538	95.001	0.82
2	20.288	1566.7	30.6	0.854	4.999	0.889

^{1}H and ^{13}C NMR of 6e

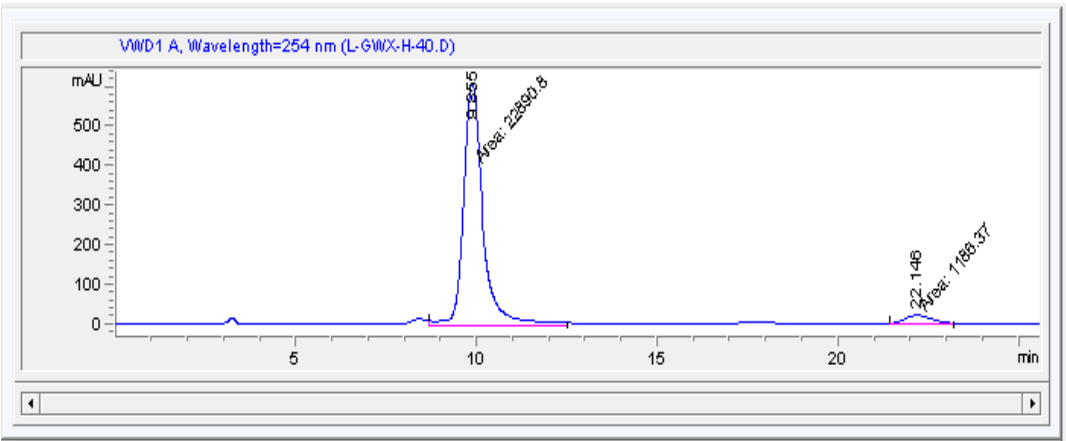




HPLC of 6e

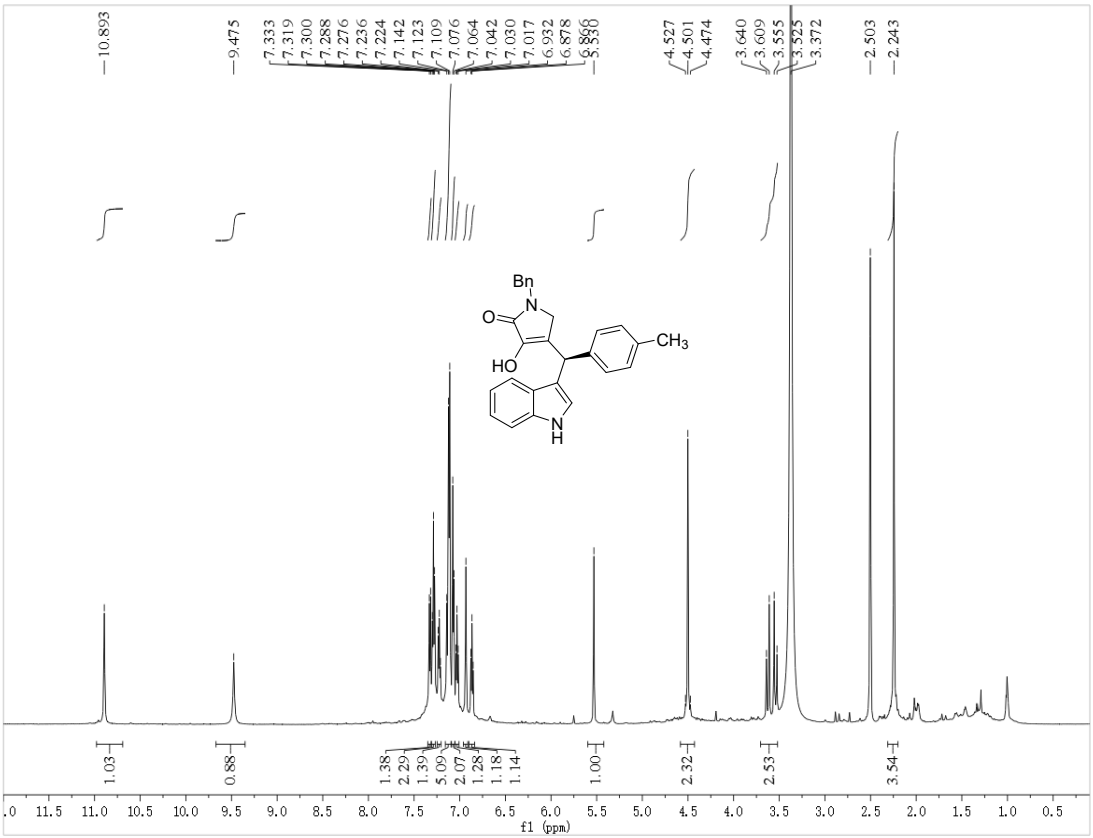


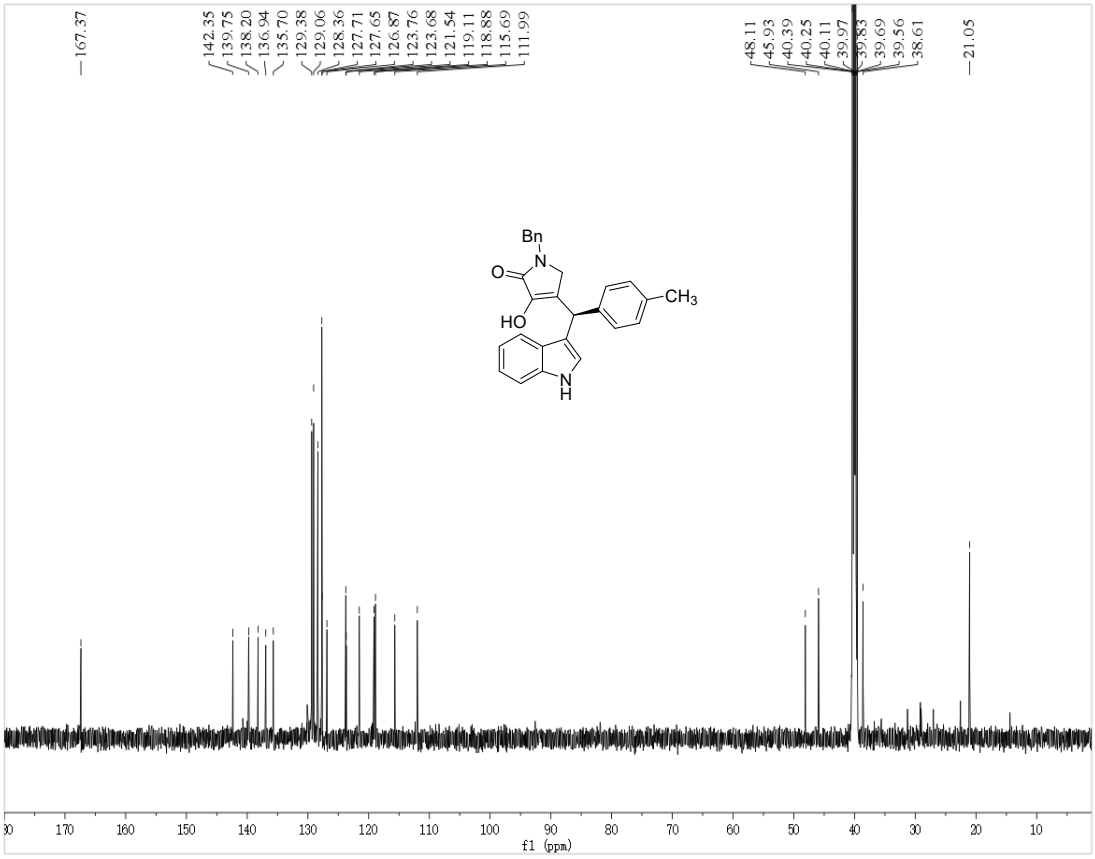
#	Time	Area	Height	Width	Area%	Symmetry
1	9.183	16210	358.1	0.7545	49.954	0.531
2	17.6	16239.7	169.1	1.6009	50.046	0.526



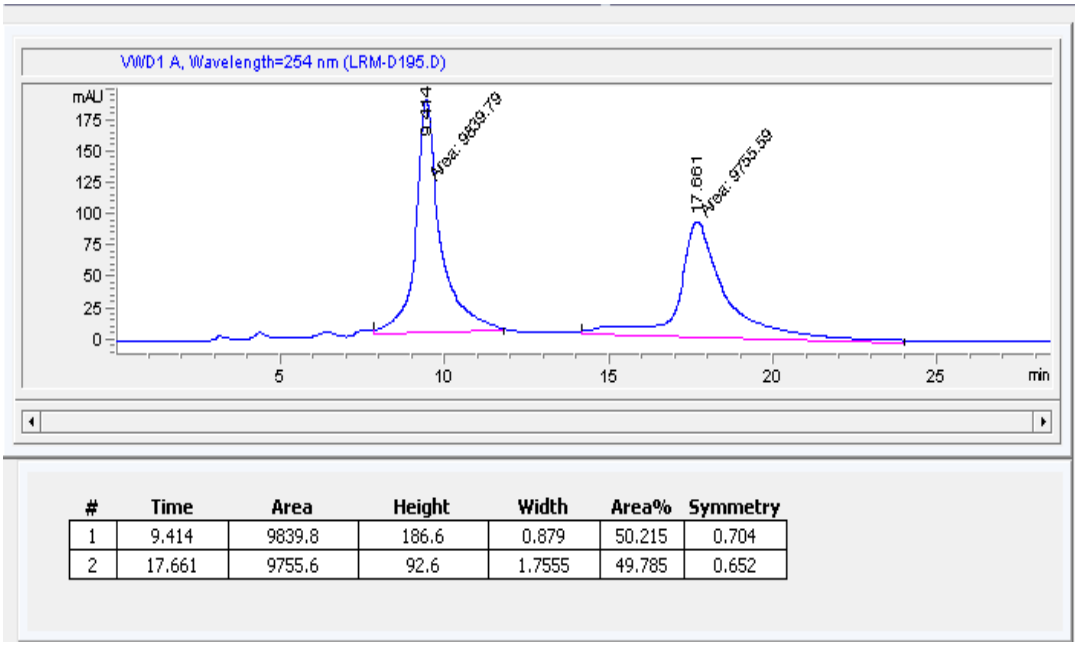
#	Time	Area	Height	Width	Area%	Symmetry
1	9.855	22890.8	614.4	0.621	95.073	0.721
2	22.146	1186.4	22.3	0.8868	4.927	0.769

^{1}H and ^{13}C NMR of 6f

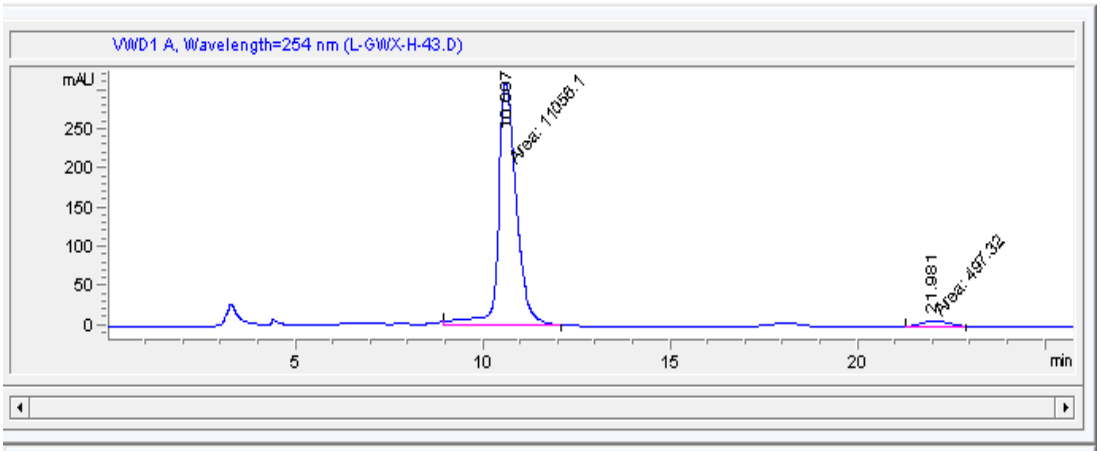




HPLC of 6f

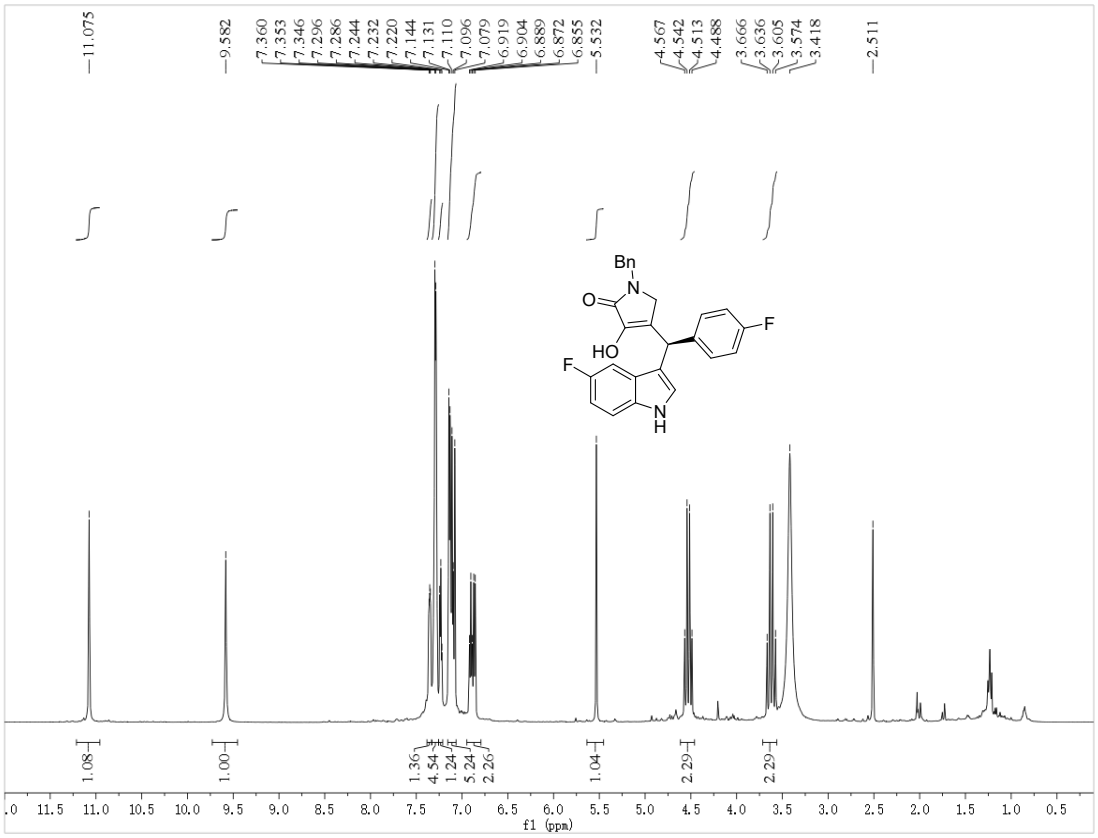


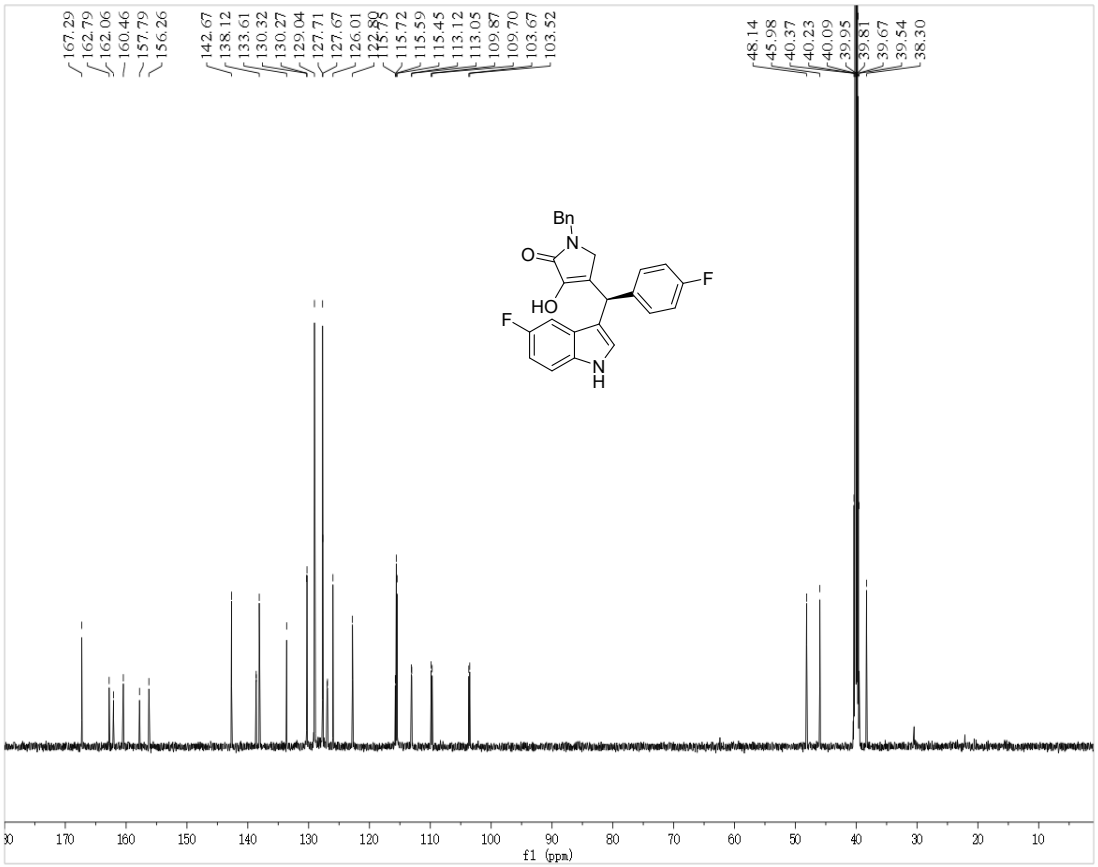
#	Time	Area	Height	Width	Area%	Symmetry
1	9.414	9839.8	186.6	0.879	50.215	0.704
2	17.661	9755.6	92.6	1.7555	49.785	0.652



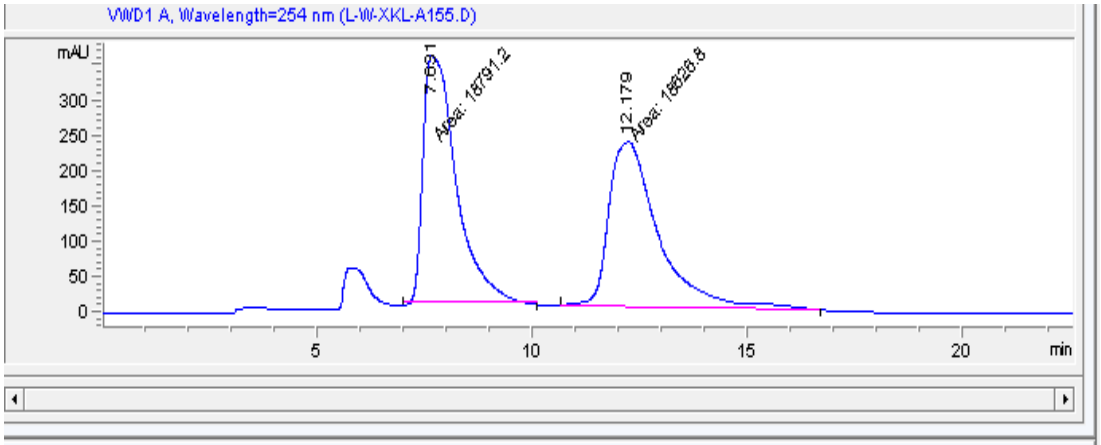
#	Time	Area	Height	Width	Area%	Symmetry
1	10.607	11056.1	312.1	0.5904	95.695	0.839
2	21.981	497.3	8.9	0.9347	4.305	0.776

^{1}H and ^{13}C NMR of 6g

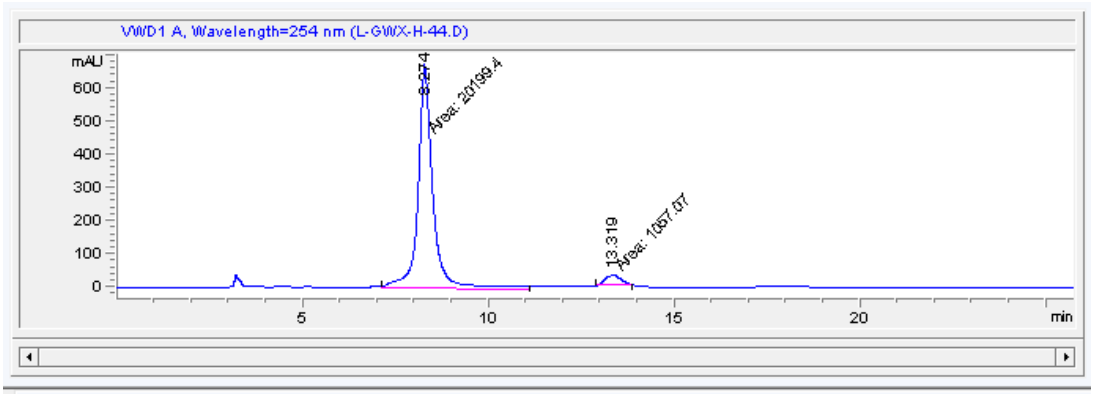




HPLC of 6g

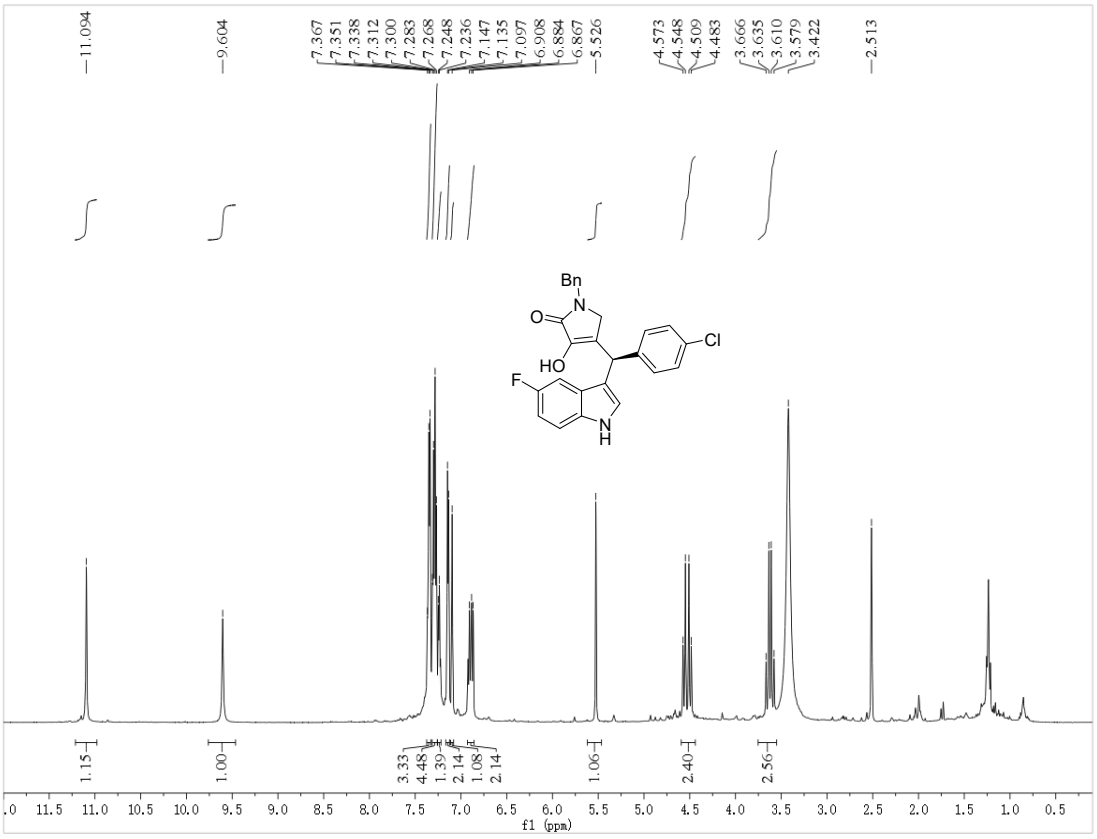


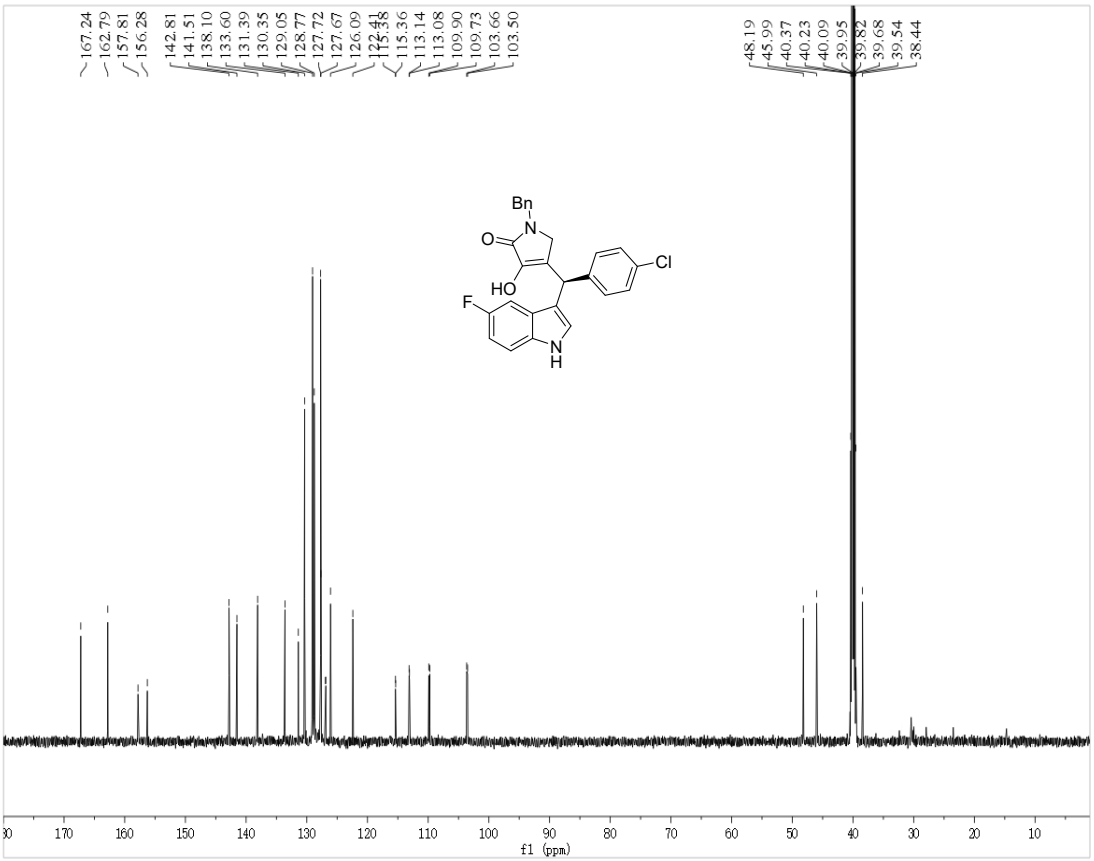
#	Time	Area	Height	Width	Area%	Symmetry
1	7.631	18791.2	352.1	0.8896	50.220	0.356
2	12.179	18626.8	233.4	1.3304	49.780	0.591



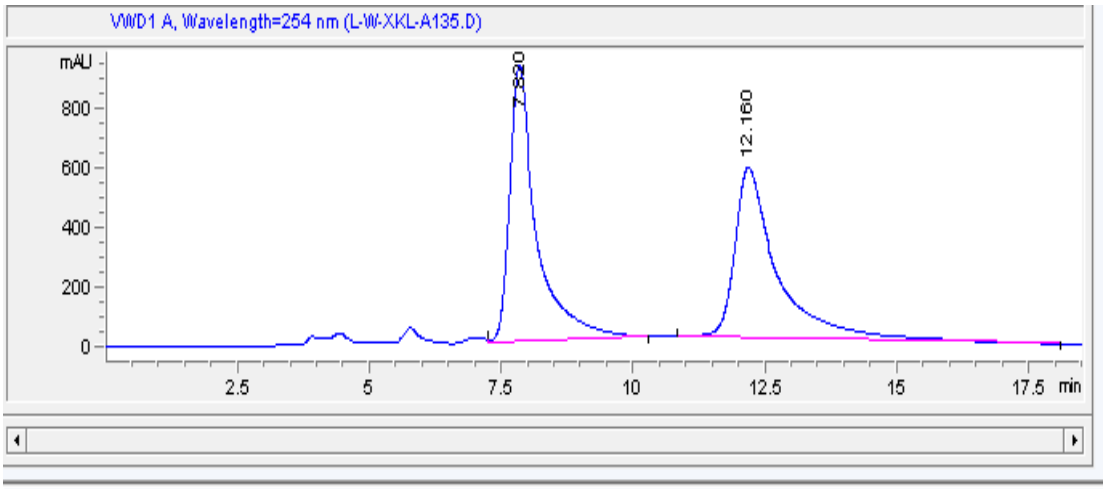
#	Time	Area	Height	Width	Area%	Symmetry
1	8.274	20199.4	677.5	0.4969	95.027	0.77
2	13.319	1057.1	33.9	0.5193	4.973	0.796

^{1}H and ^{13}C NMR of 6h

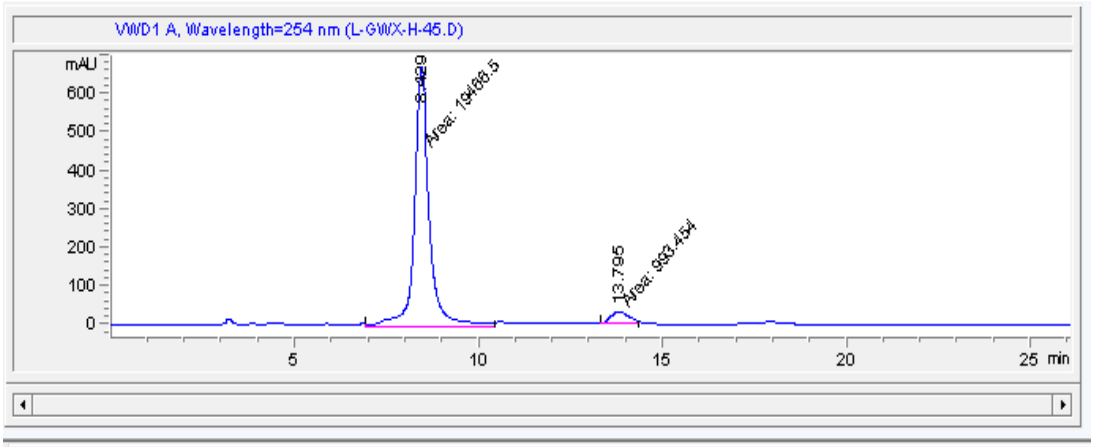




HPLC of 6h

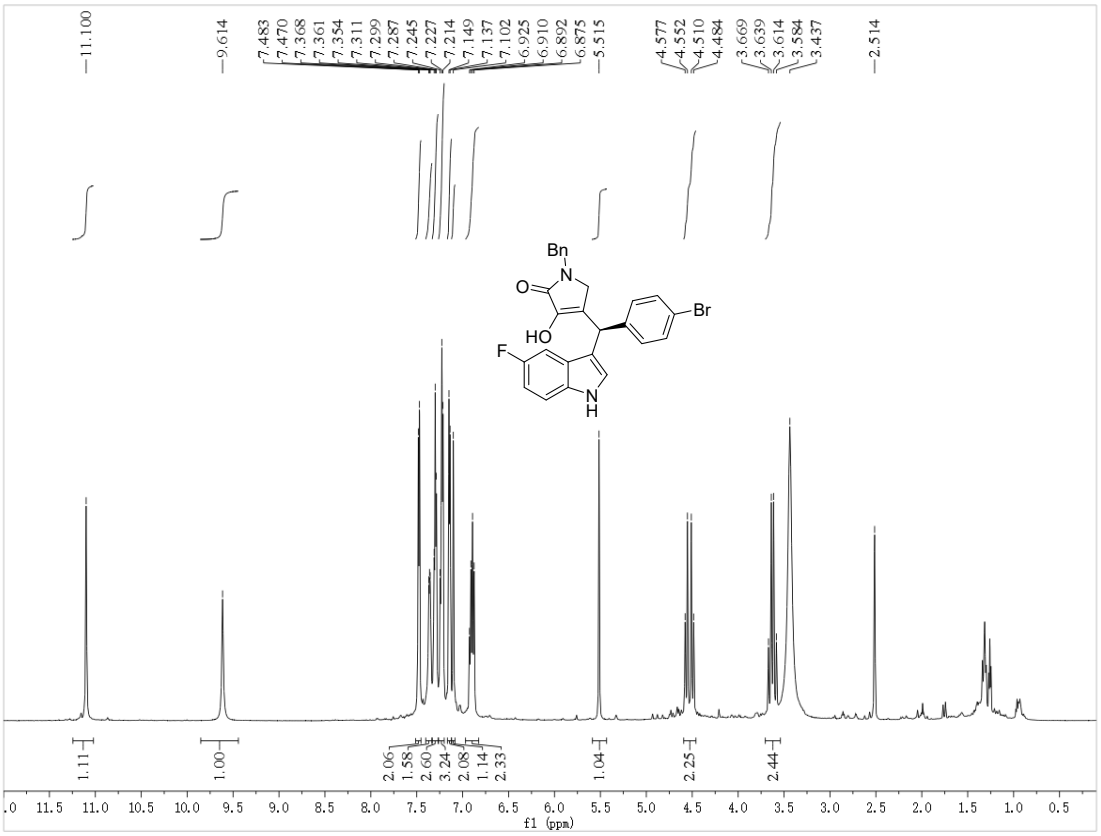


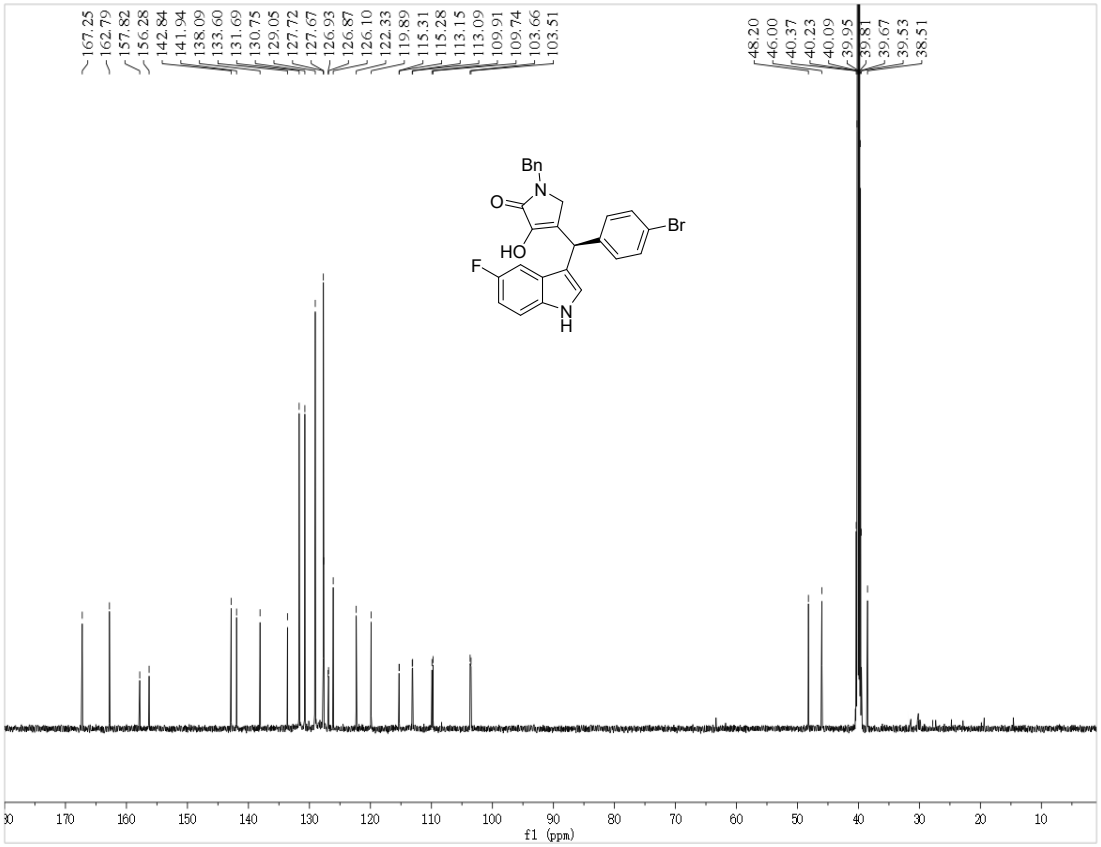
#	Time	Area	Height	Width	Area%	Symmetry
1	7.82	33770	930.7	0.5163	50.850	0.482
2	12.16	32640.4	573.5	0.794	49.150	0.412



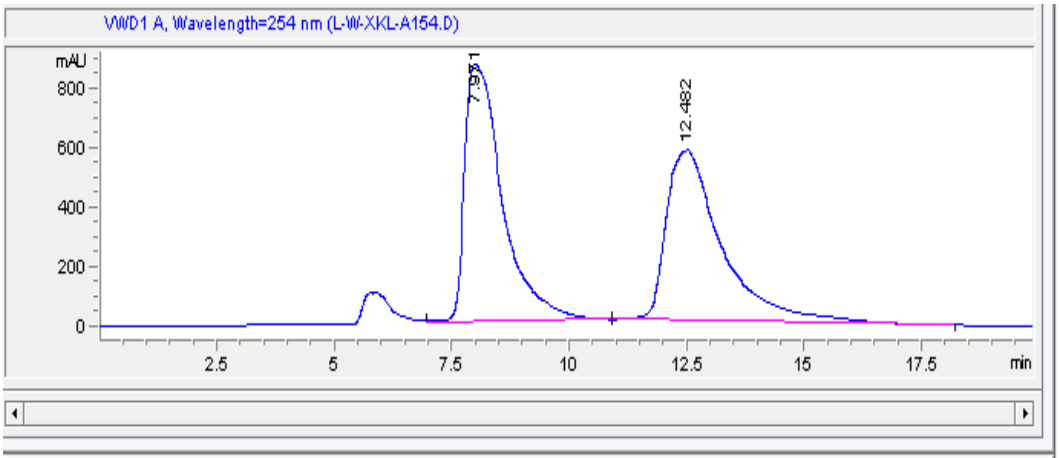
#	Time	Area	Height	Width	Area%	Symmetry
1	8.429	19466.5	673.5	0.4817	95.144	0.826
2	13.795	993.5	30	0.5516	4.856	0.777

^{1}H and ^{13}C NMR of 6i

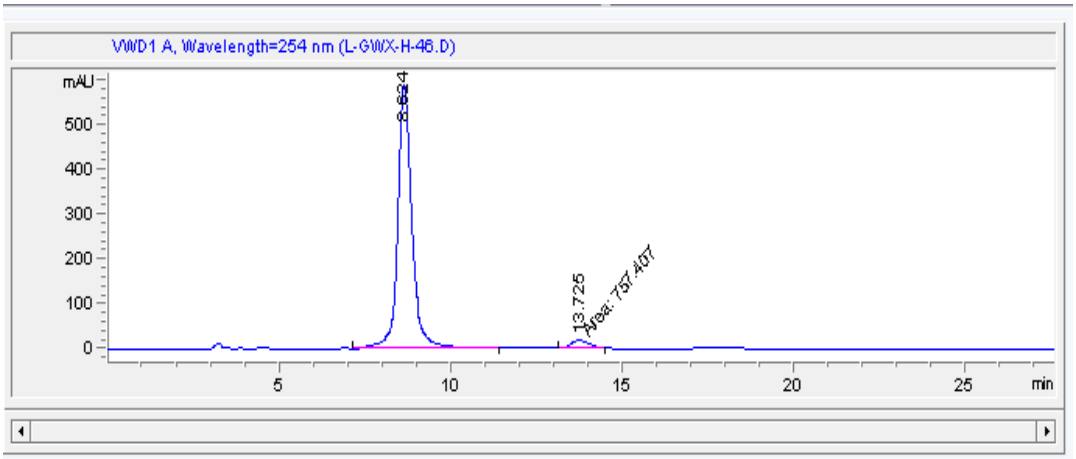




HPLC of 6i

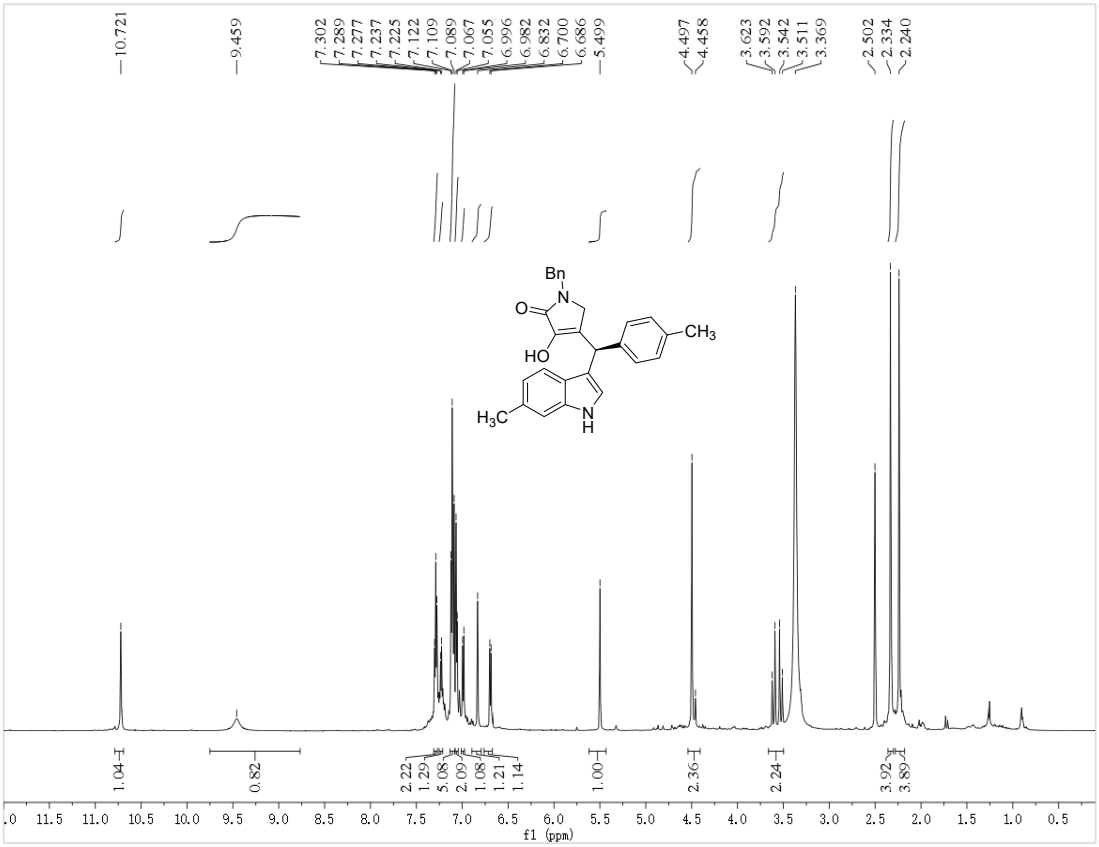


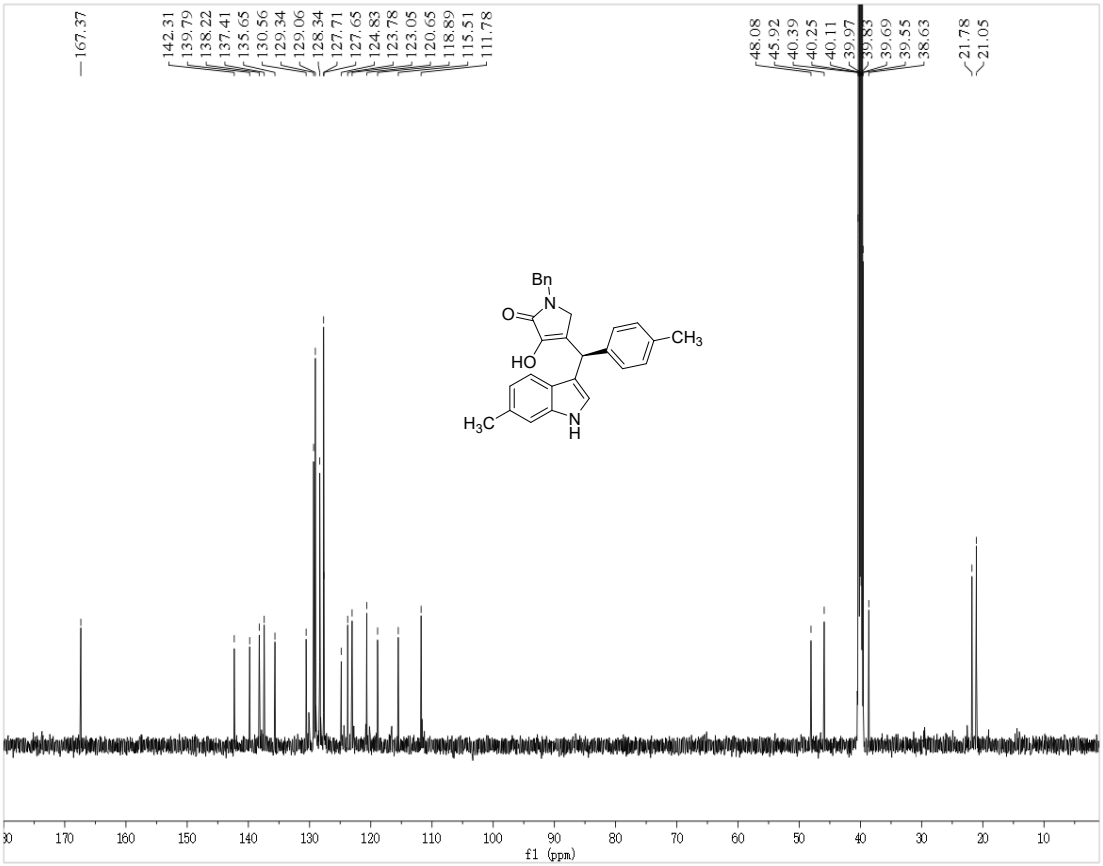
#	Time	Area	Height	Width	Area%	Symmetry
1	7.971	48632.4	868.9	0.851	50.655	0.356
2	12.482	47374.7	573.5	1.2207	49.345	0.515



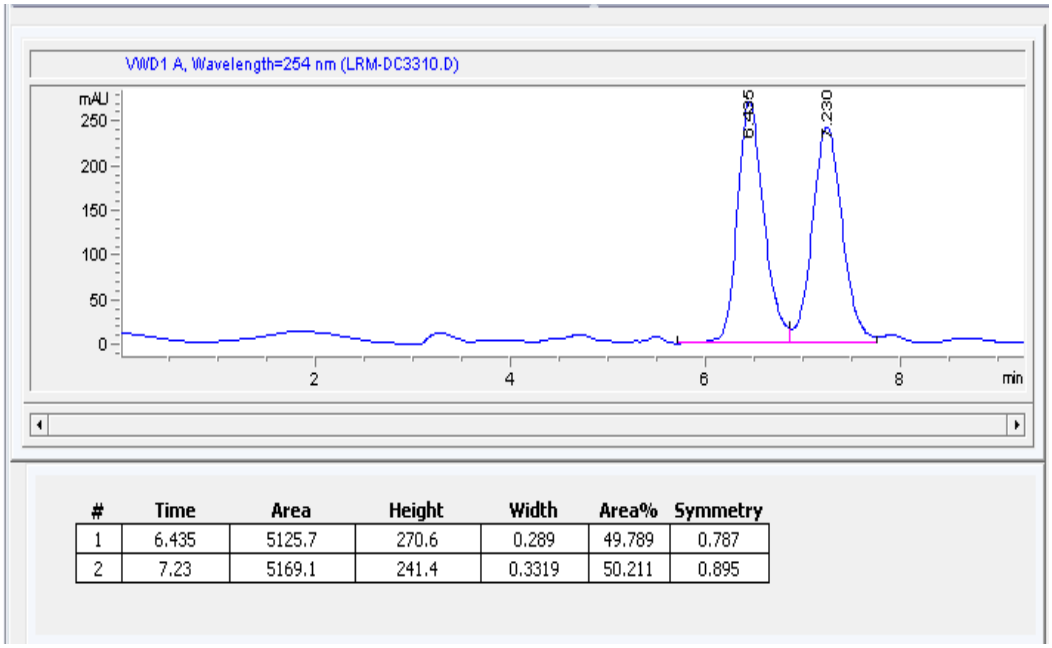
#	Time	Area	Height	Width	Area%	Symmetry
1	8.624	16565	588.1	0.4166	95.628	0.768
2	13.725	757.4	19.5	0.6465	4.372	0.79

^{1}H and ^{13}C NMR of 6j

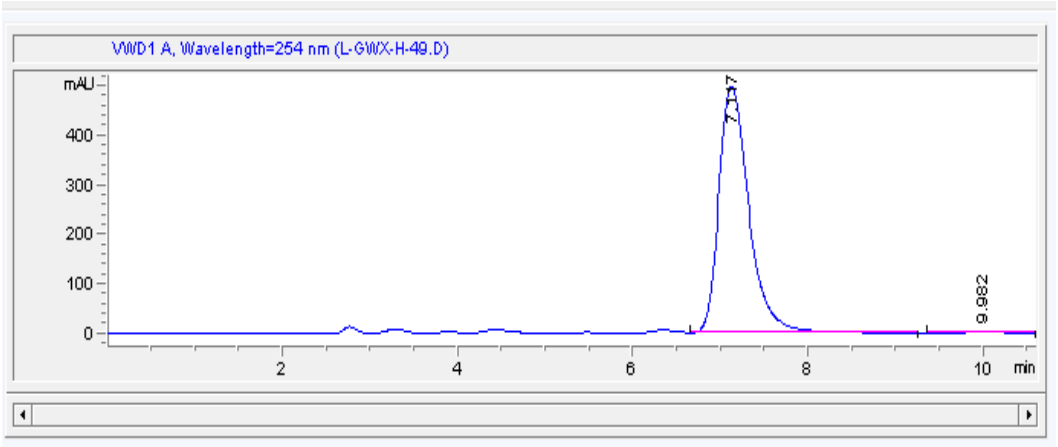




HPLC of 6j

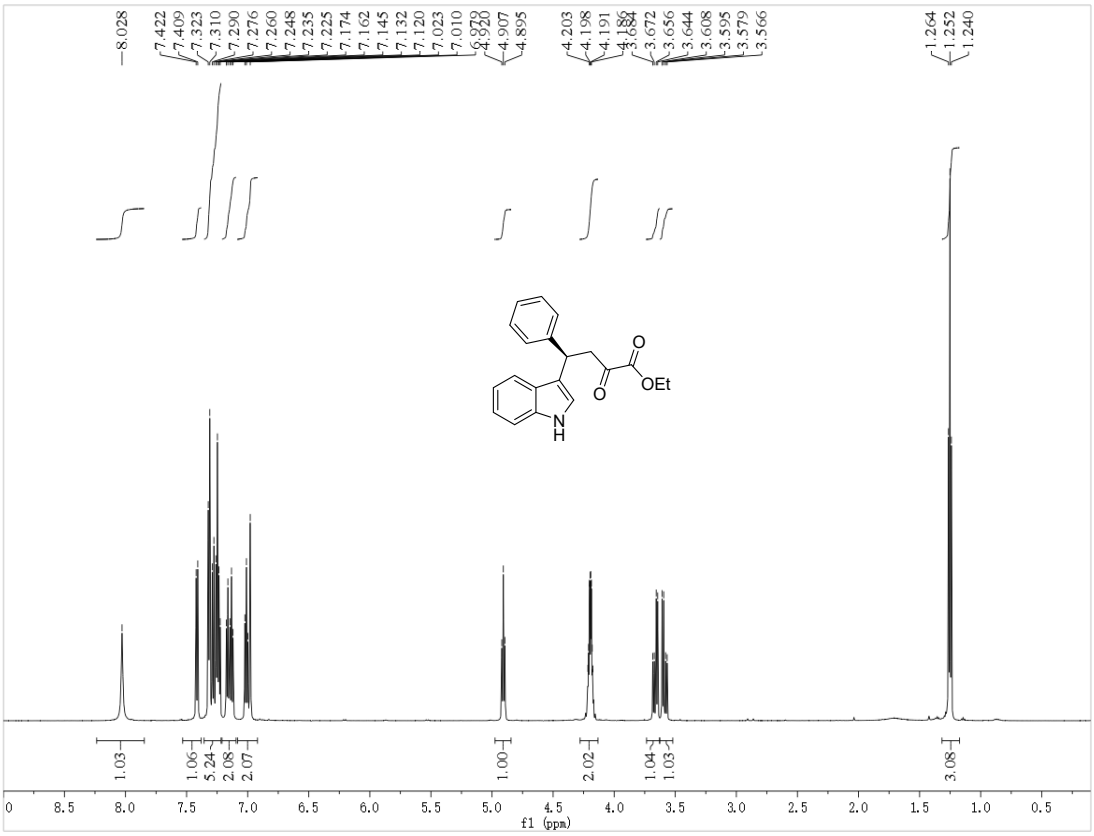


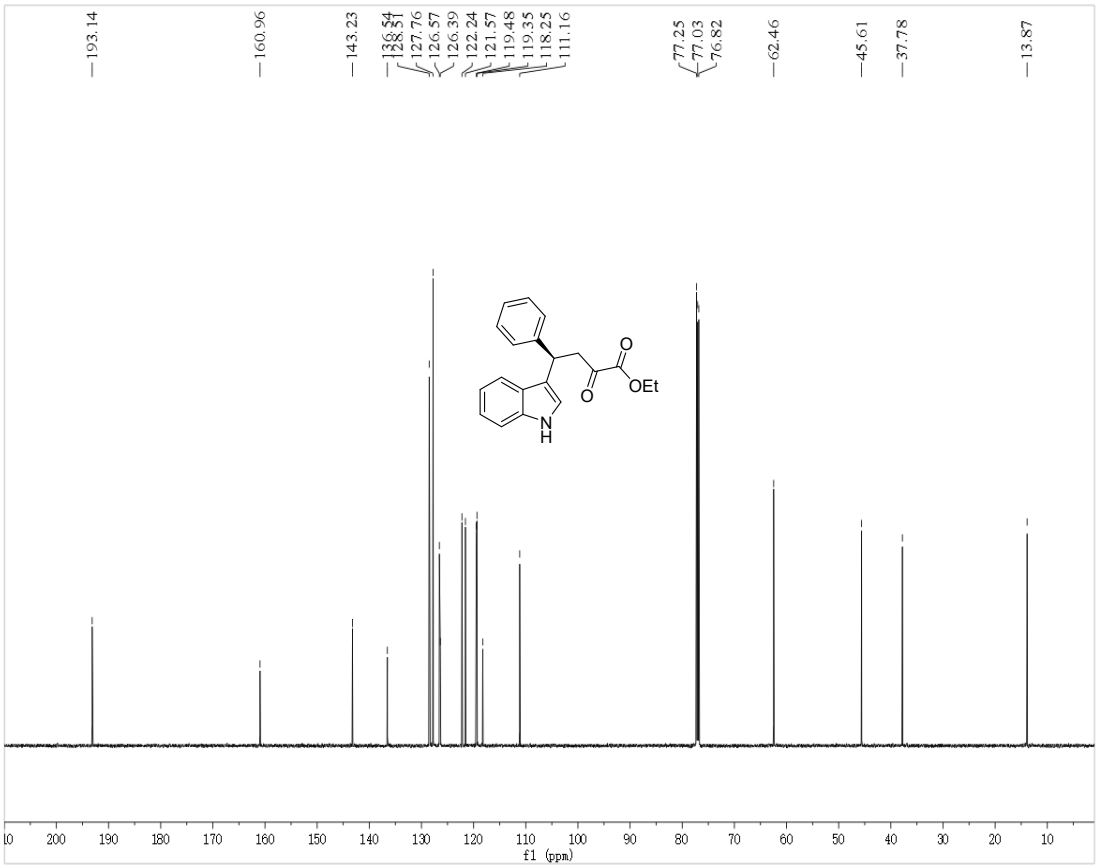
#	Time	Area	Height	Width	Area%	Symmetry
1	6.435	5125.7	270.6	0.289	49.789	0.787
2	7.23	5169.1	241.4	0.3319	50.211	0.895



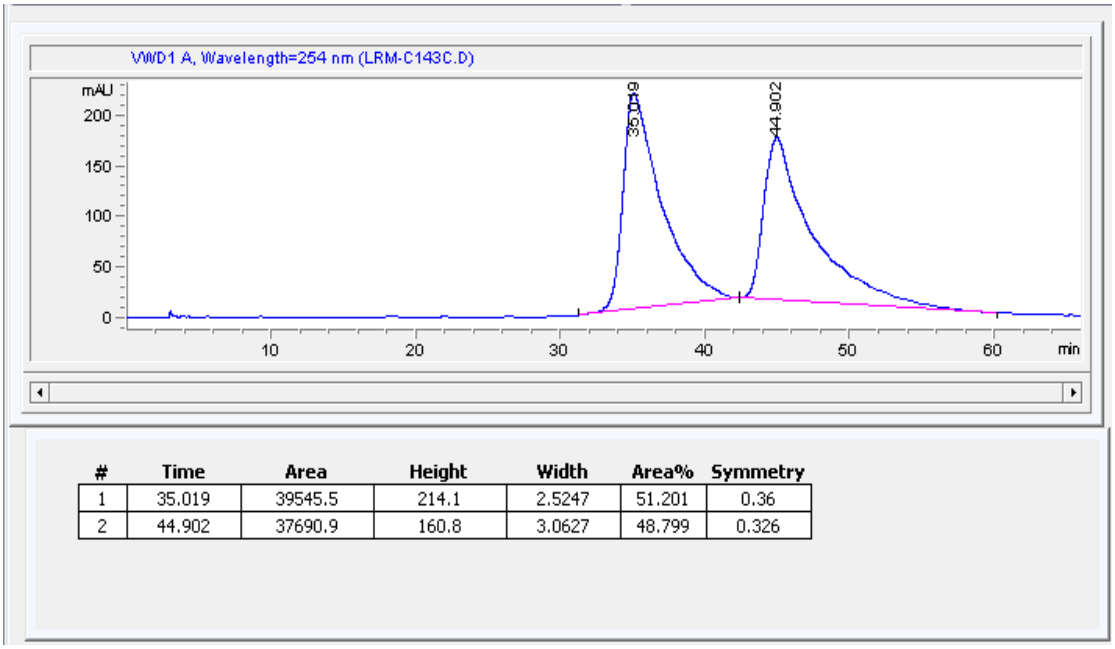
#	Time	Area	Height	Width	Area%	Symmetry
1	7.117	11872.5	497.7	0.3633	99.259	0.678
2	9.982	88.7	4.2	0.3176	0.741	0.816

^{1}H and ^{13}C NMR of 8a

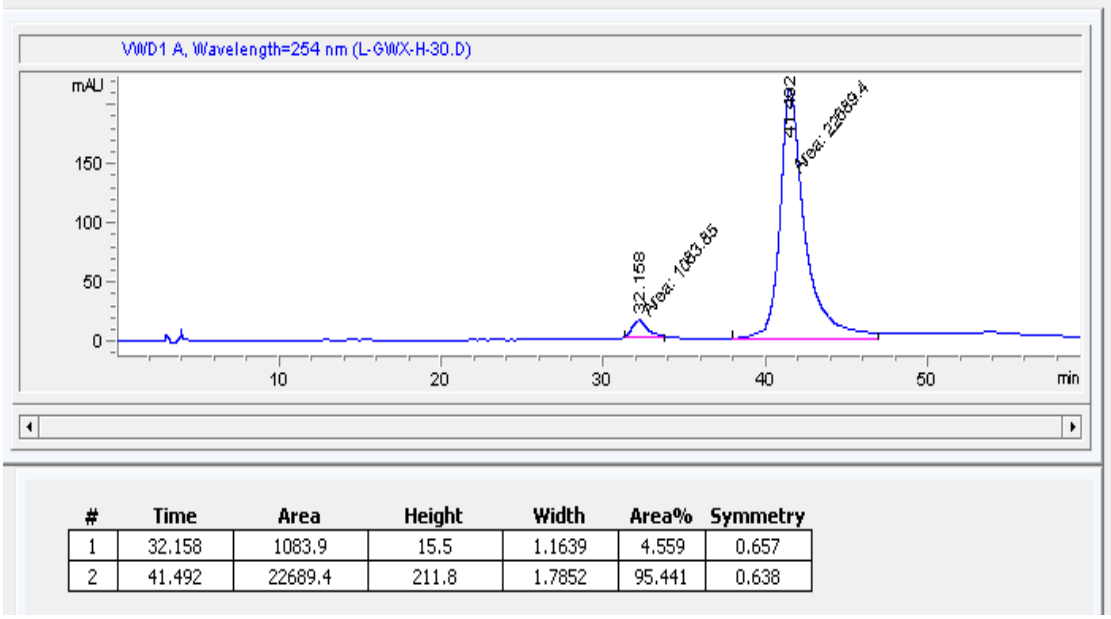




HPLC of 8a

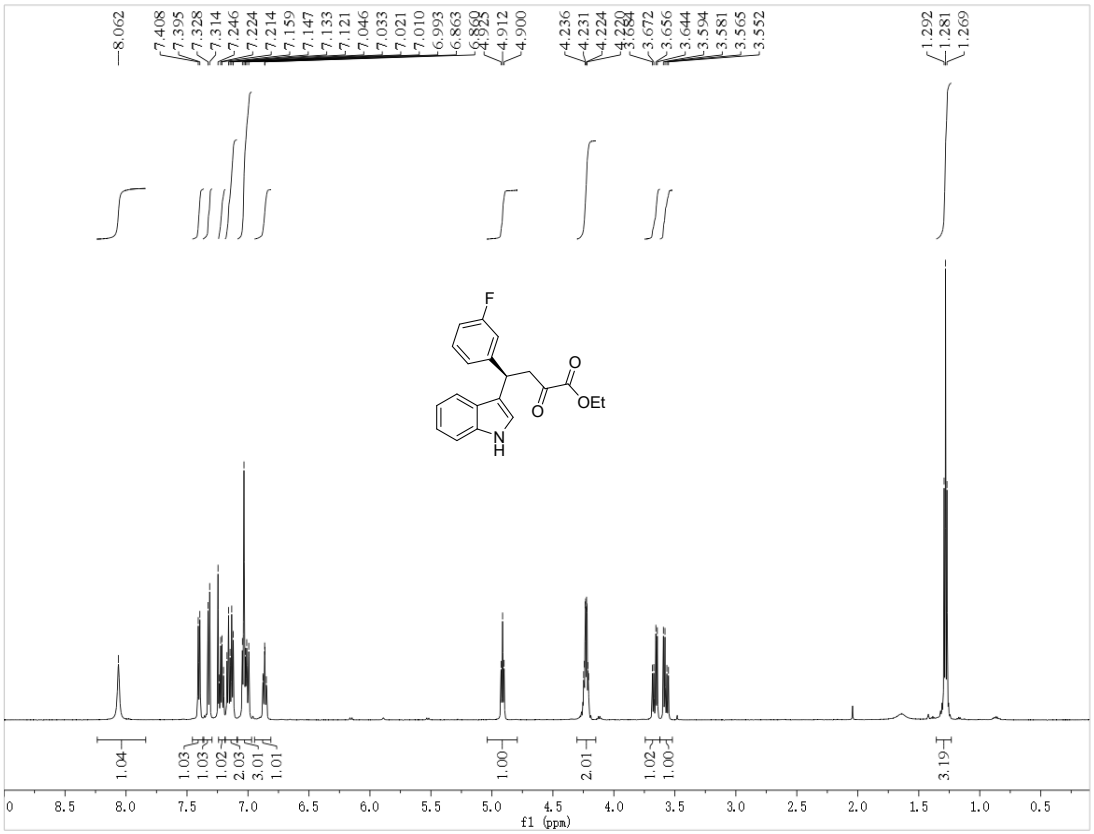


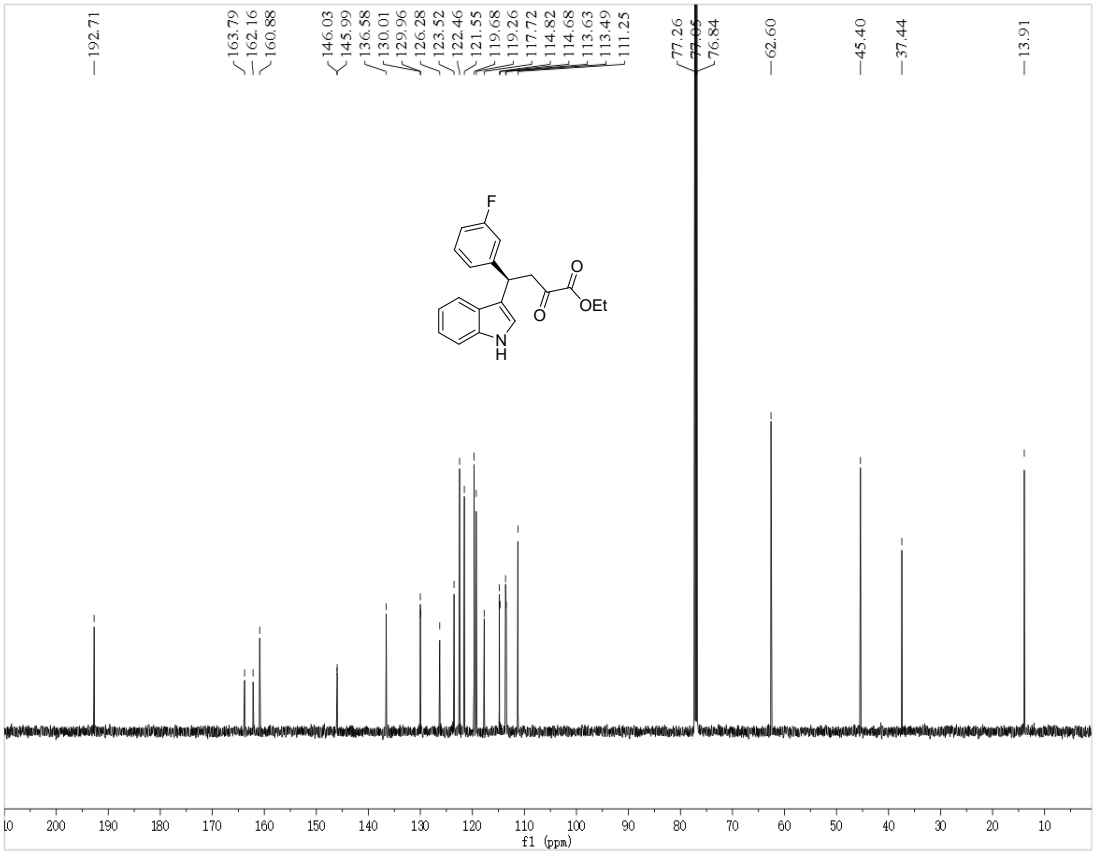
#	Time	Area	Height	Width	Area%	Symmetry
1	35.019	39545.5	214.1	2.5247	51.201	0.36
2	44.902	37690.9	160.8	3.0627	48.799	0.326



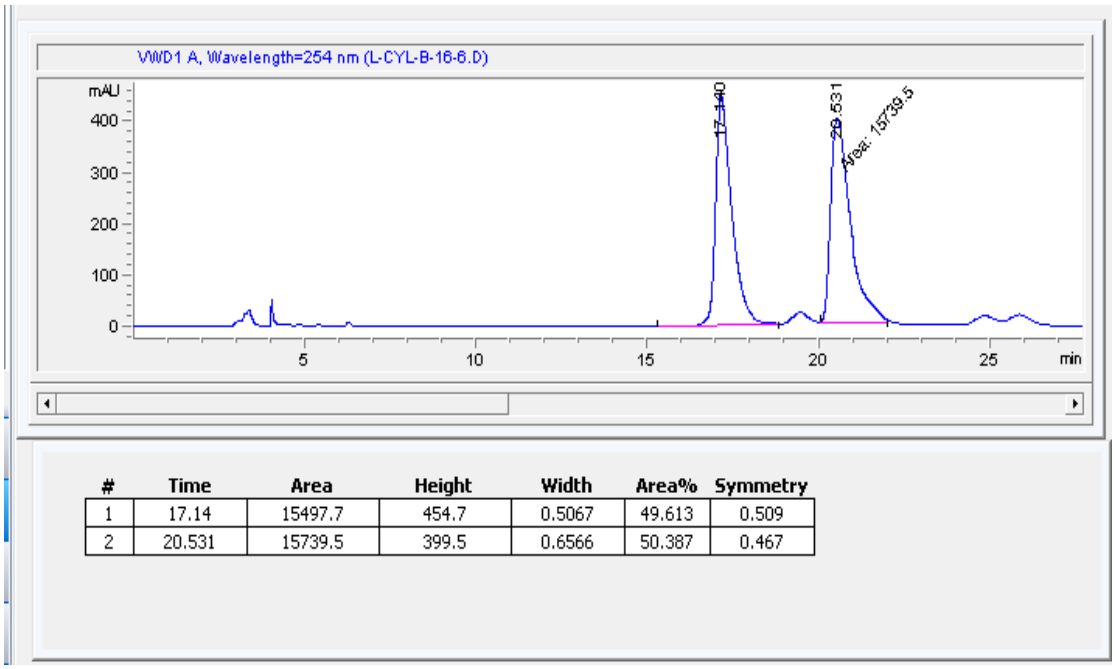
#	Time	Area	Height	Width	Area%	Symmetry
1	32.158	1083.9	15.5	1.1639	4.559	0.657
2	41.492	22689.4	211.8	1.7852	95.441	0.638

^{1}H and ^{13}C NMR of 8b

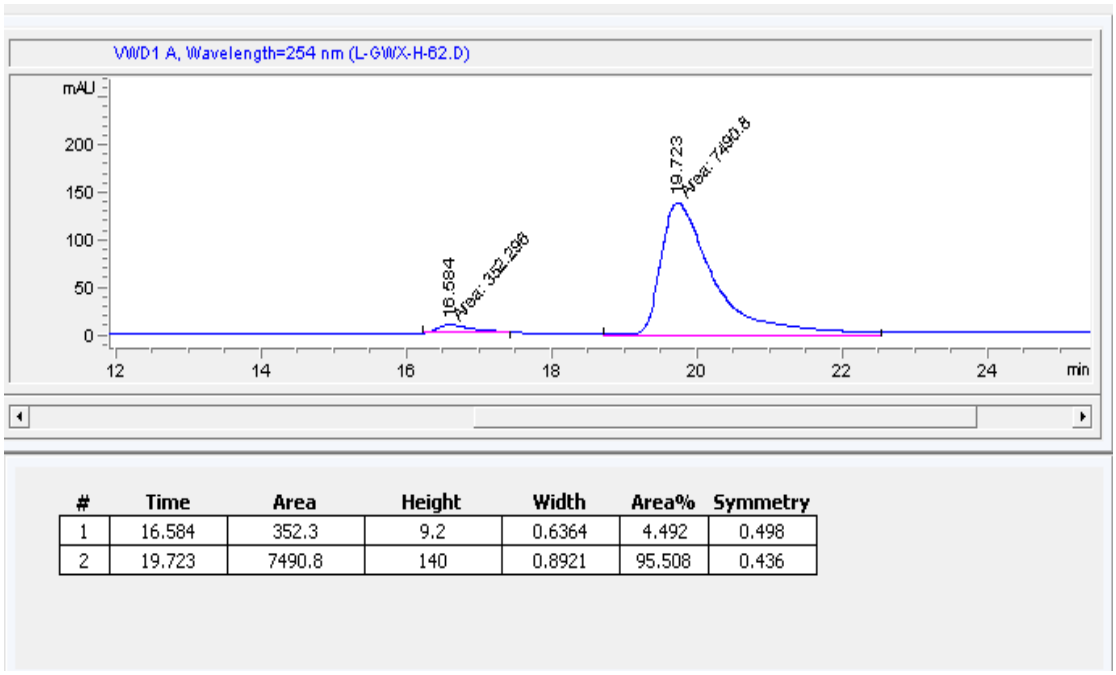




HPLC of 8b

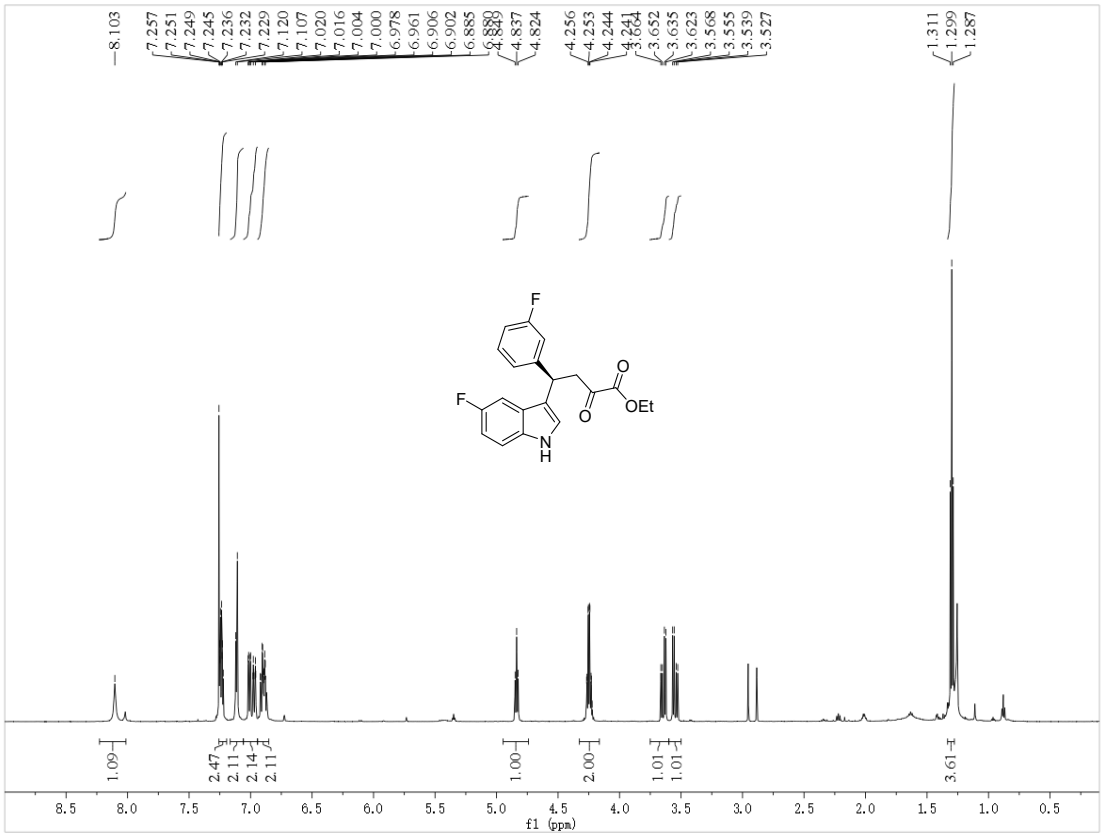


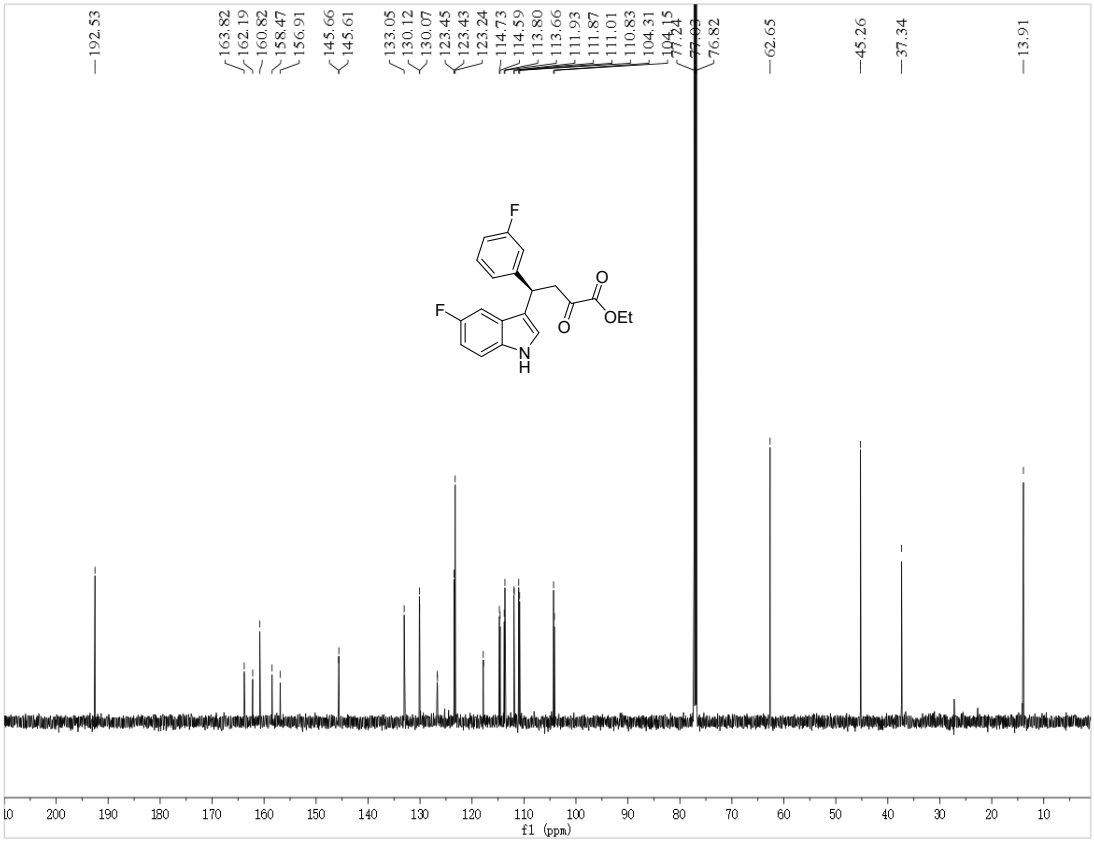
#	Time	Area	Height	Width	Area%	Symmetry
1	17.14	15497.7	454.7	0.5067	49.613	0.509
2	20.531	15739.5	399.5	0.6566	50.387	0.467



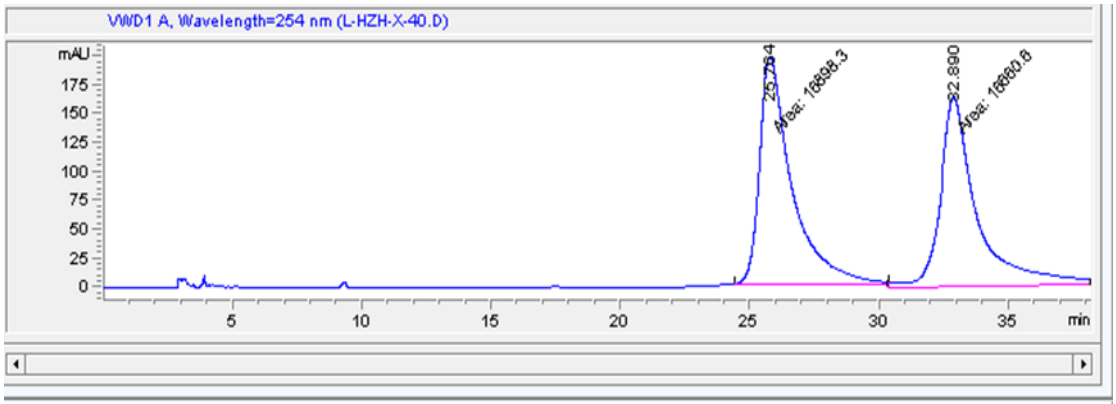
#	Time	Area	Height	Width	Area%	Symmetry
1	16.584	352.3	9.2	0.6364	4.492	0.498
2	19.723	7490.8	140	0.8921	95.508	0.436

^{1}H and ^{13}C NMR of 8c

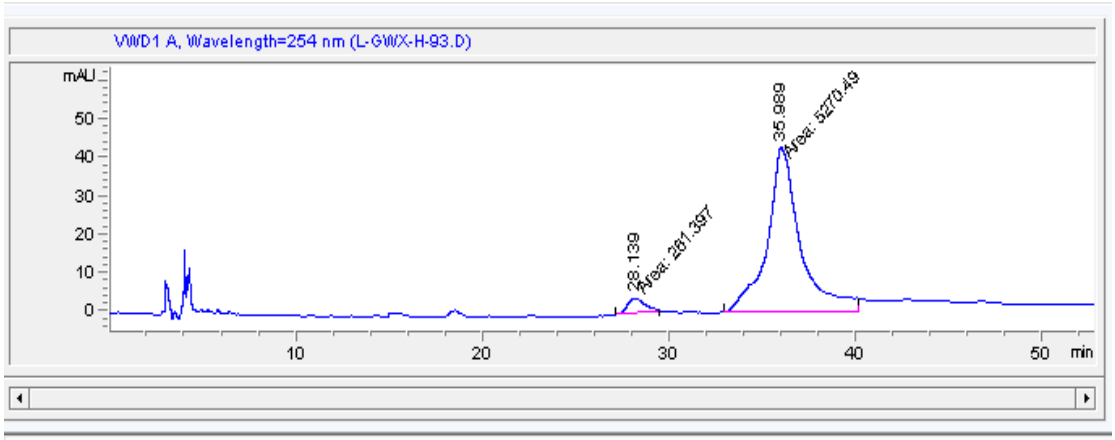




HPLC of 8c

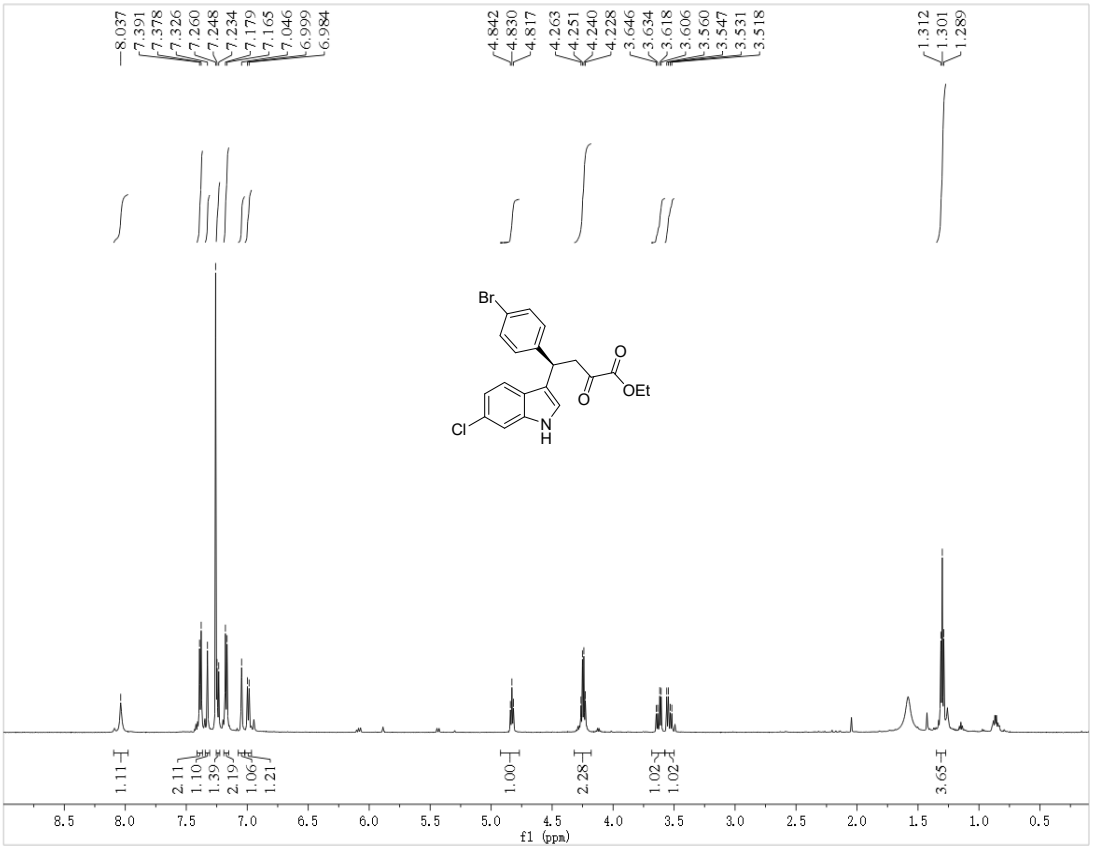


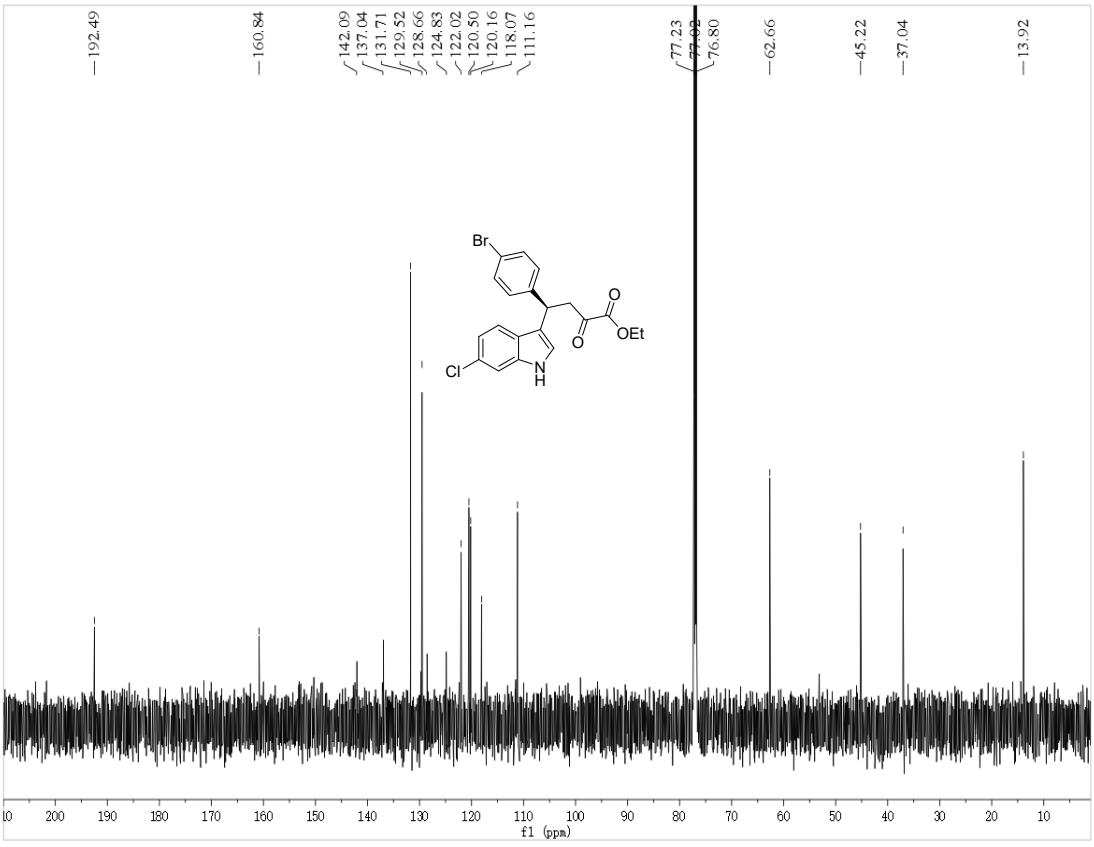
#	Time	Area	Height	Width	Area%	Symmetry
1	25.764	16898.3	197.3	1.4274	50.354	0.45
2	32.89	16660.6	164.3	1.6904	49.646	0.579



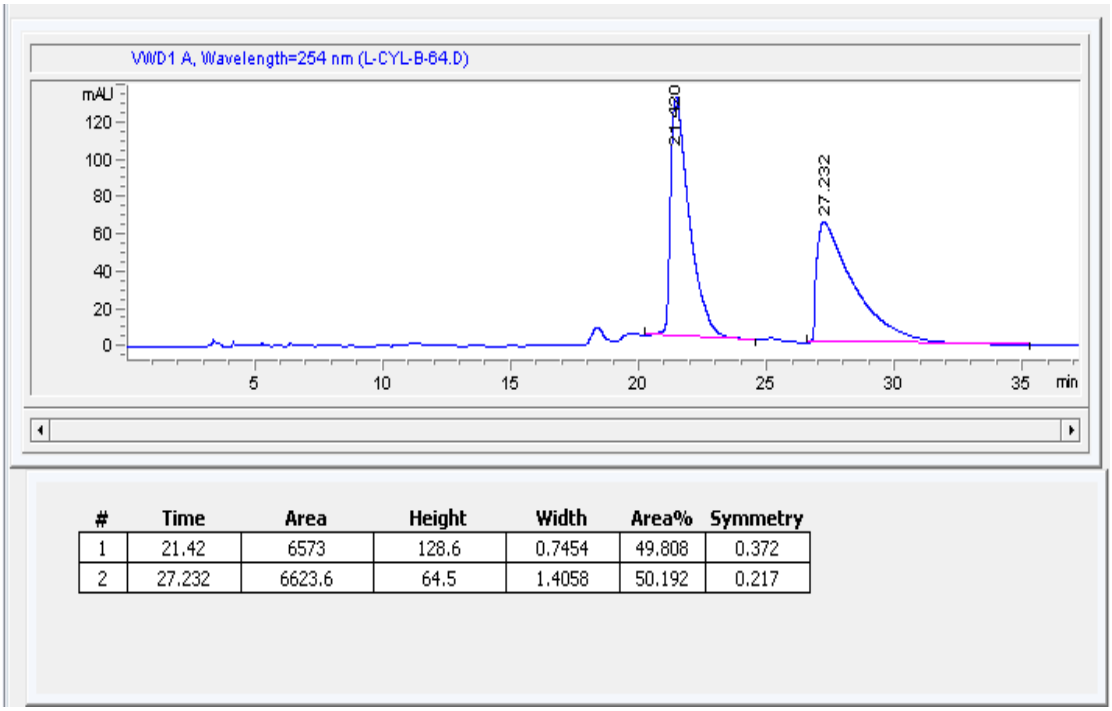
#	Time	Area	Height	Width	Area%	Symmetry
1	28.139	261.4	3.8	1.1318	4.725	0.567
2	35.989	5270.5	42.6	2.0635	95.275	0.697

^{1}H and ^{13}C NMR of 8d

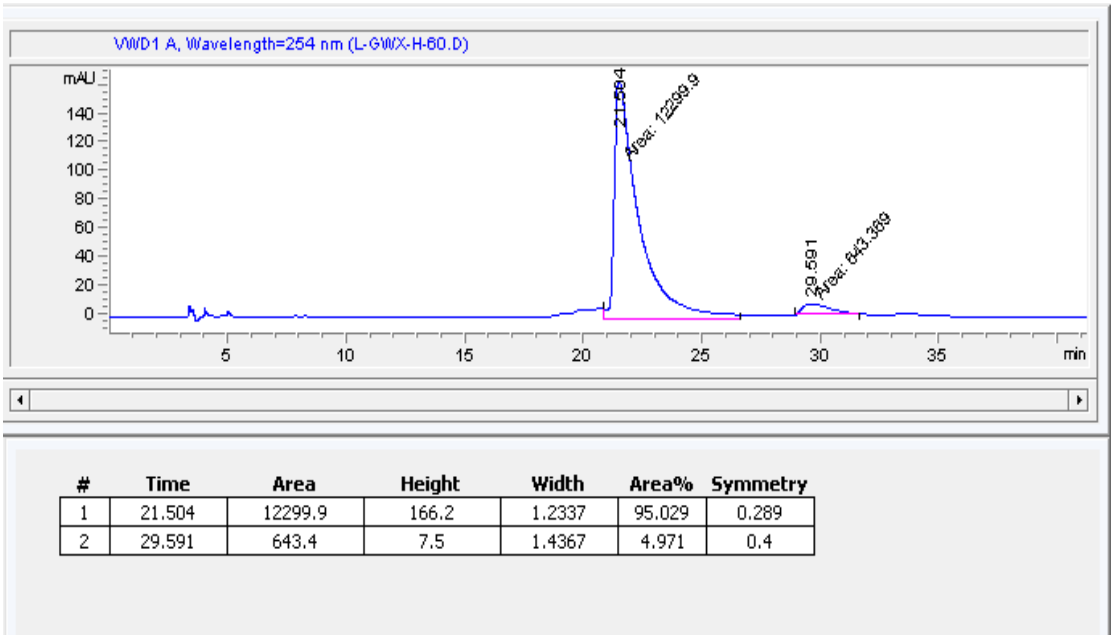




HPLC of 8d

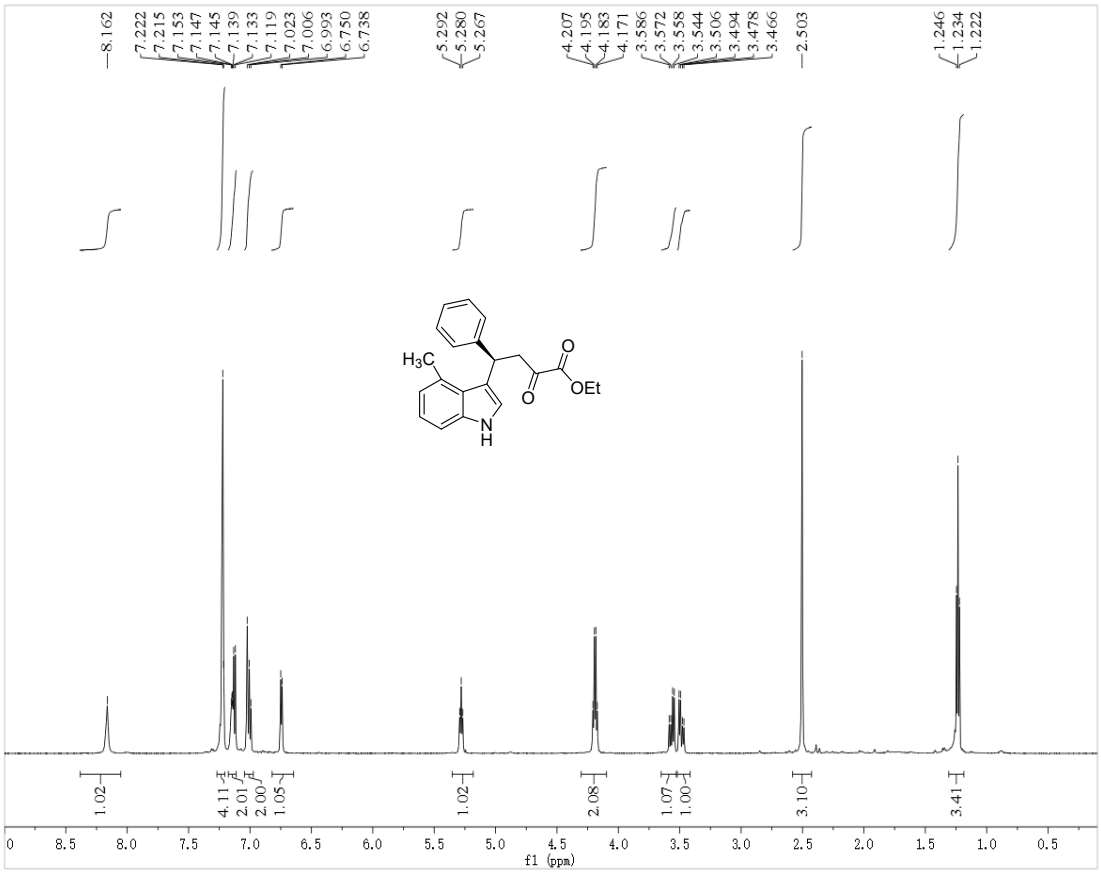


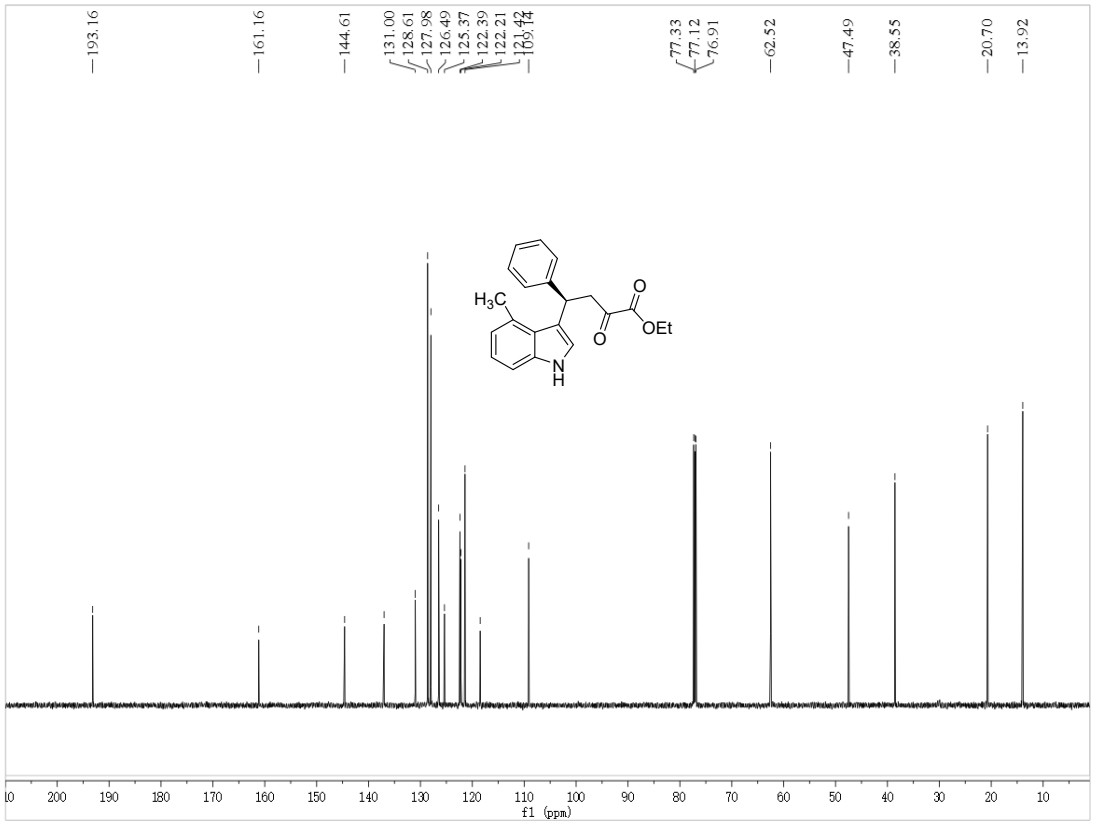
#	Time	Area	Height	Width	Area%	Symmetry
1	21.42	6573	128.6	0.7454	49.808	0.372
2	27.232	6623.6	64.5	1.4058	50.192	0.217



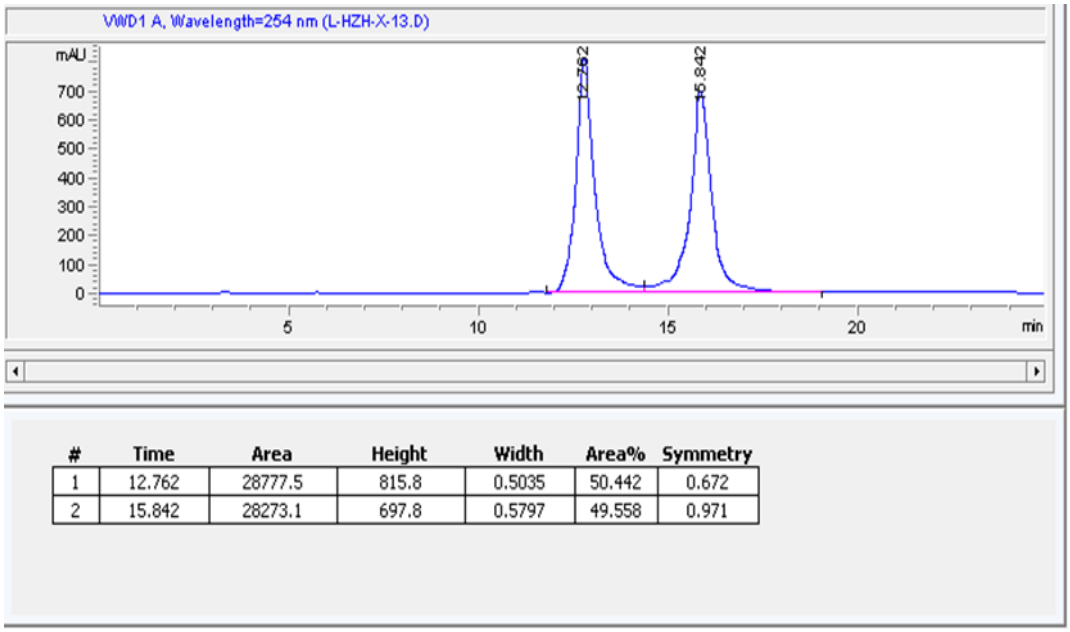
#	Time	Area	Height	Width	Area%	Symmetry
1	21.504	12299.9	166.2	1.2337	95.029	0.289
2	29.591	643.4	7.5	1.4367	4.971	0.4

^{1}H and ^{13}C NMR of 8e

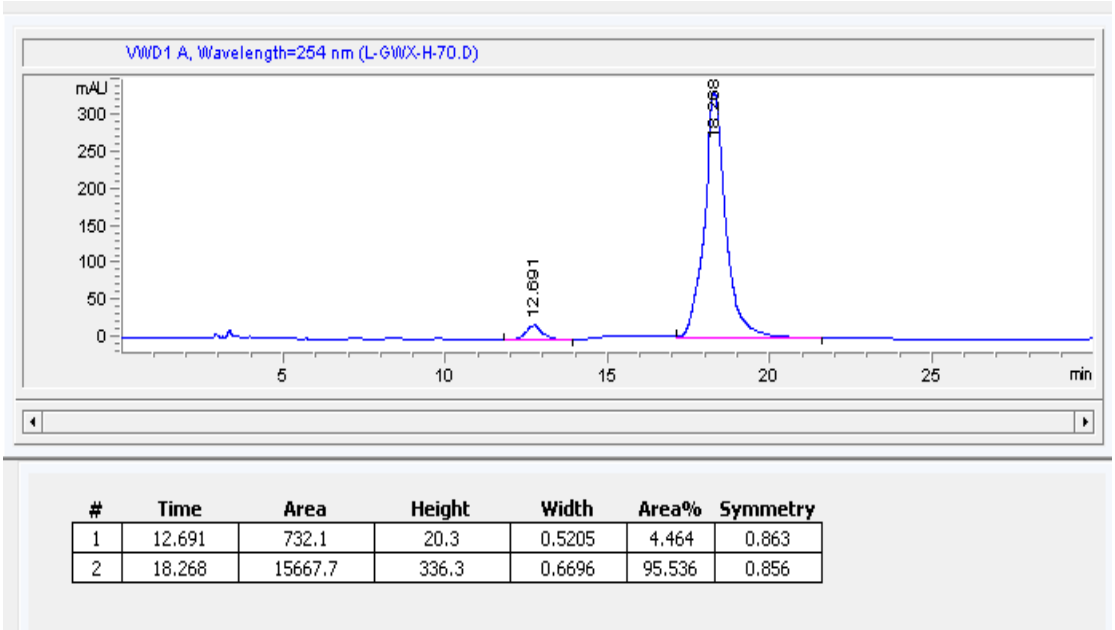




HPLC of 8e

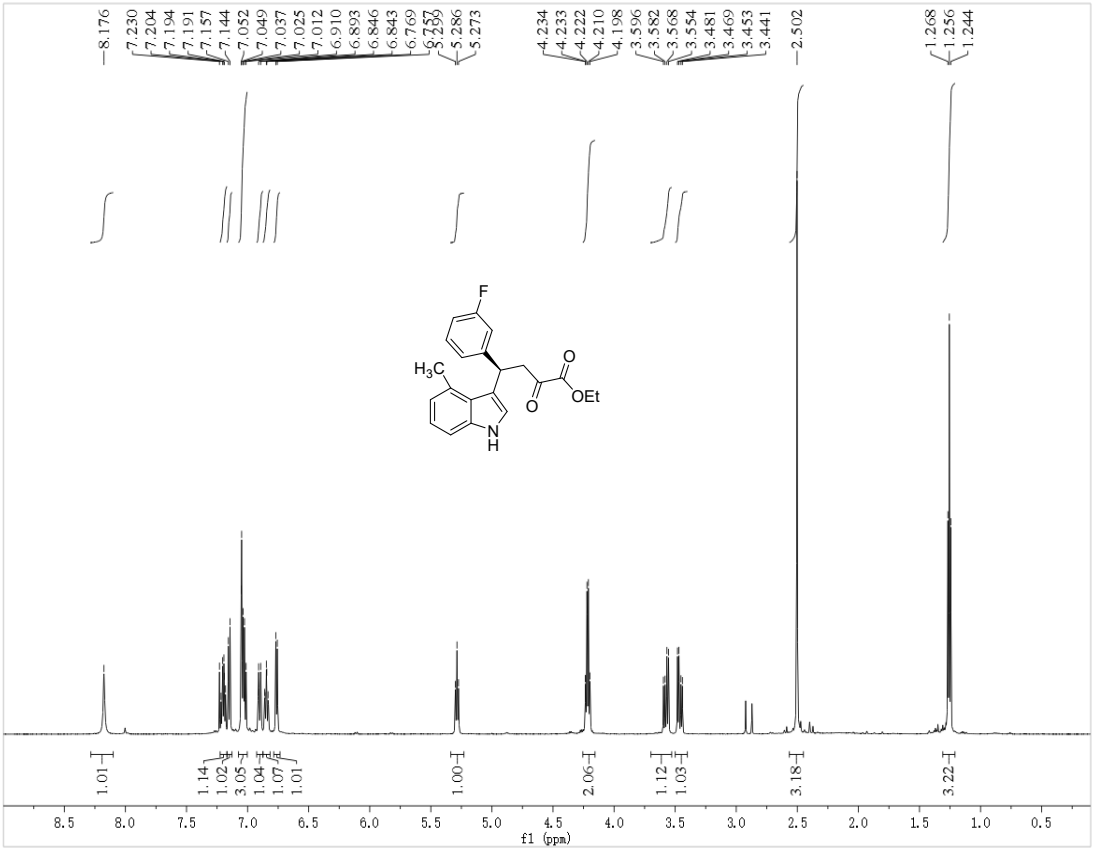


#	Time	Area	Height	Width	Area%	Symmetry
1	12.762	28777.5	815.8	0.5035	50.442	0.672
2	15.842	28273.1	697.8	0.5797	49.558	0.971



#	Time	Area	Height	Width	Area%	Symmetry
1	12.691	732.1	20.3	0.5205	4.464	0.863
2	18.268	15667.7	336.3	0.6696	95.536	0.856

^{1}H and ^{13}C NMR of 8f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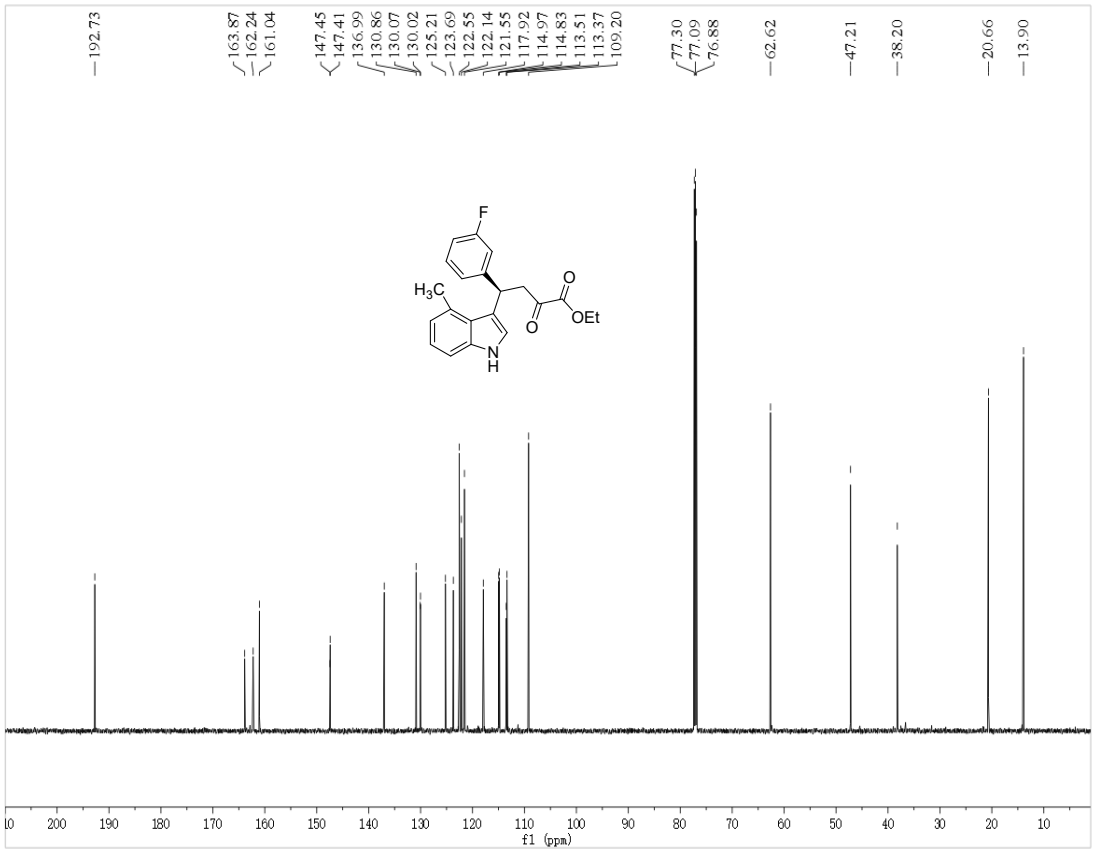
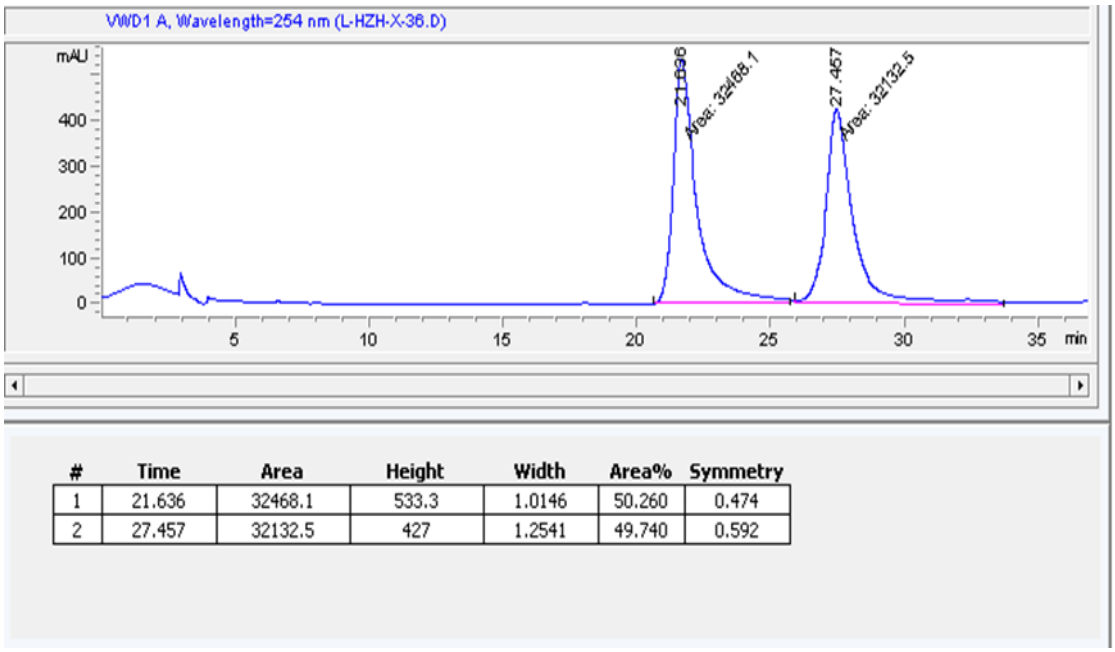
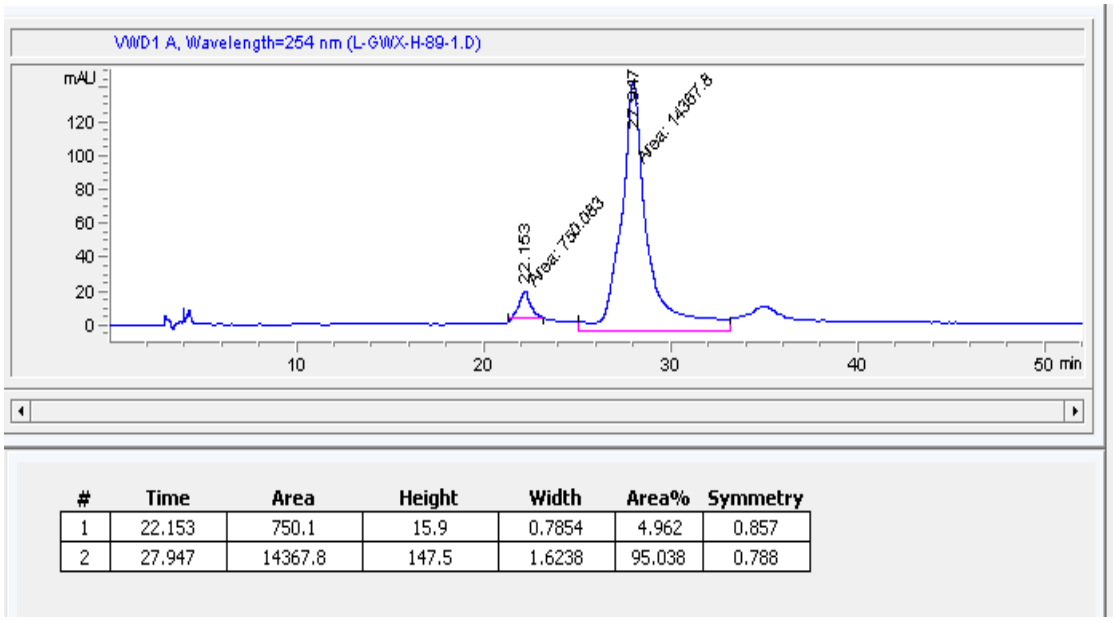
7.230
7.204
7.194
7.191
7.157
7.144
7.052
7.049
7.037
7.025
7.012
6.910
6.893
6.846
6.843
6.769
5.286
5.273
4.234
4.233
4.222
4.210
4.198
3.596
3.582
3.568
3.554
3.481
3.469
3.453
3.441
2.502
1.268
1.256
1.244
F
H3C
O
O
OEt
N
H
1.01
1.14
1.02
3.05
1.04
1.07
1.01
1.00
2.06
1.12
1.03
3.18
3.22
f1 (ppm)


192.73
163.87
162.24
161.04
147.45
147.41
136.99
130.86
130.07
130.02
125.21
123.69
122.55
122.14
121.55
117.92
114.97
114.83
113.51
113.37
109.20
77.30
77.09
76.88
62.62
47.21
38.20
20.66
13.90
F
H3C
O
O
OEt
N
H
f1 (ppm)

HPLC of 8f

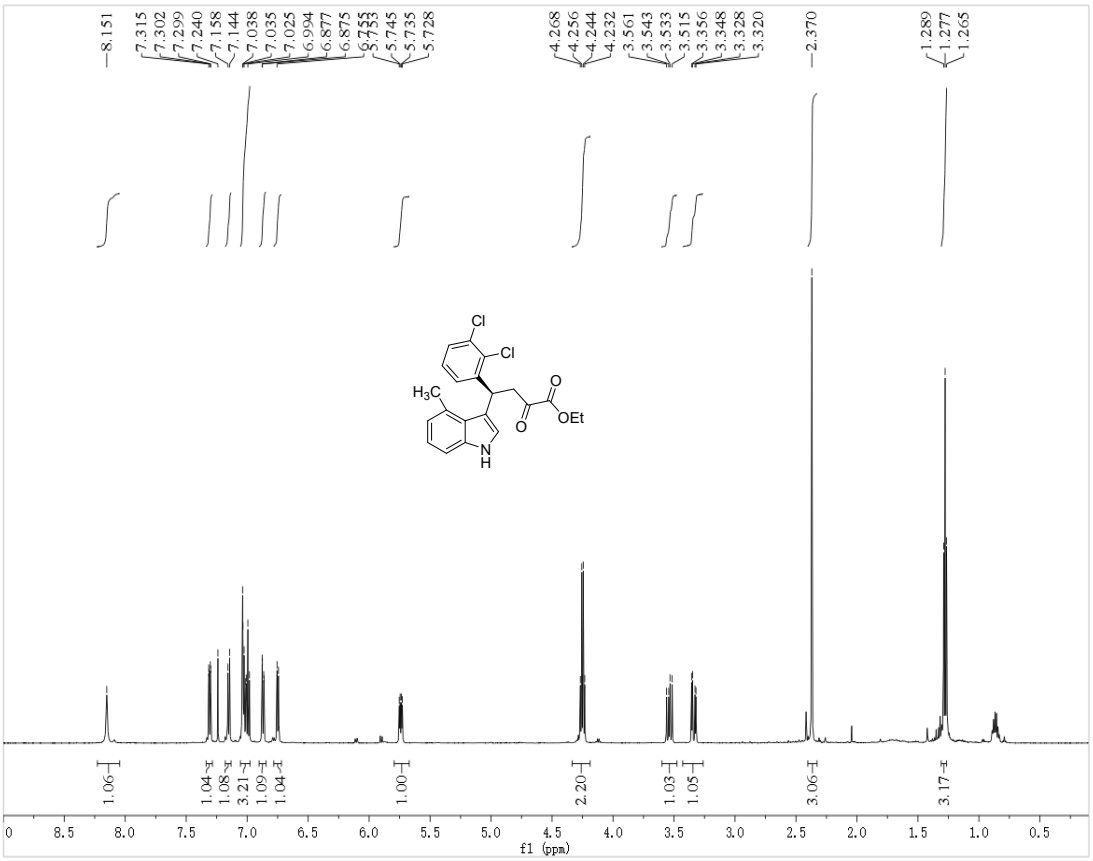


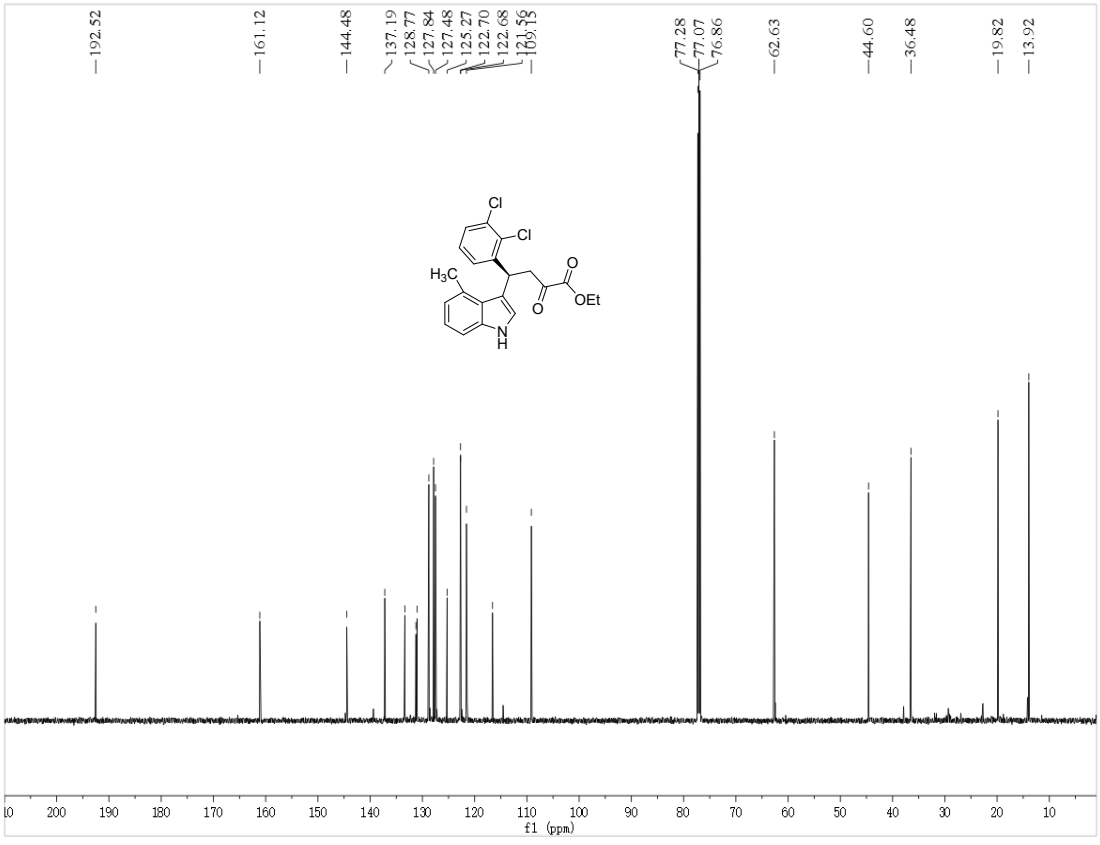
#	Time	Area	Height	Width	Area%	Symmetry
1	21.636	32468.1	533.3	1.0146	50.260	0.474
2	27.457	32132.5	427	1.2541	49.740	0.592



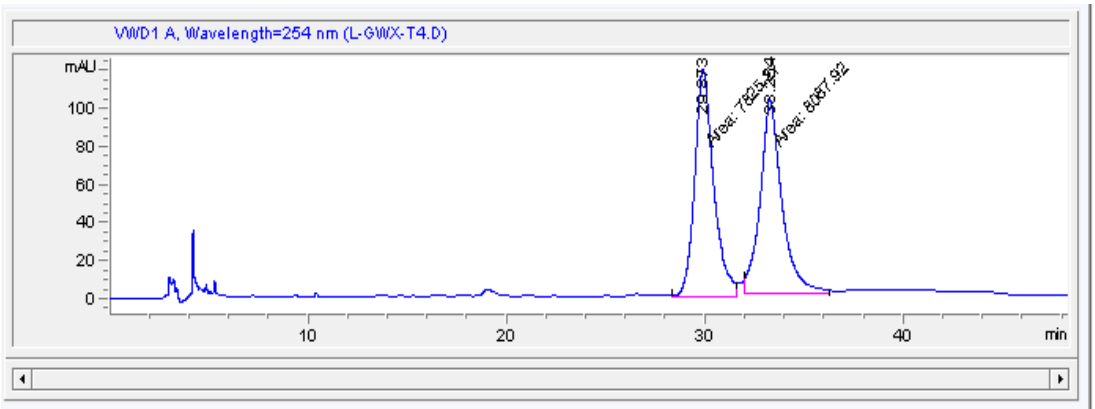
#	Time	Area	Height	Width	Area%	Symmetry
1	22.153	750.1	15.9	0.7854	4.962	0.857
2	27.947	14367.8	147.5	1.6238	95.038	0.788

^{1}H and ^{13}C NMR of 8g

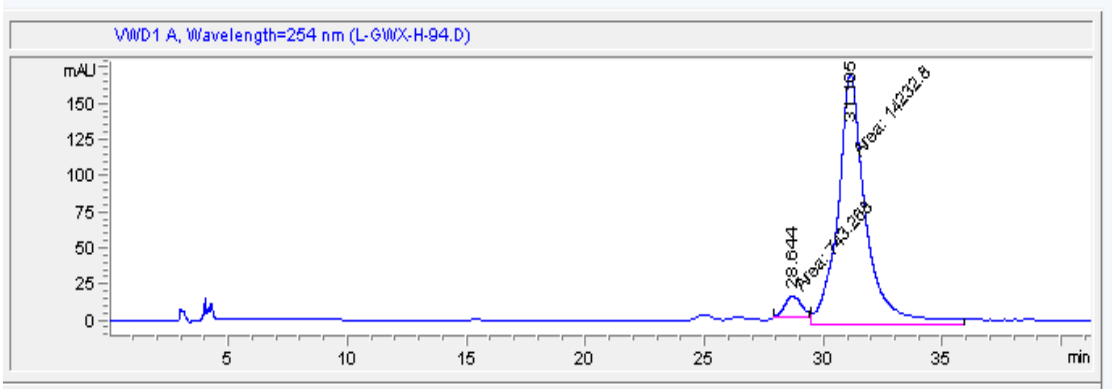

8.151
7.315
7.302
7.299
7.240
7.158
7.144
7.038
7.035
7.025
6.994
6.877
6.875
5.745
5.735
5.728
4.268
4.256
4.244
4.232
3.561
3.543
3.533
3.515
3.356
3.348
3.328
3.320
2.370
1.289
1.277
1.265
Cl
Cl
H3C
O
O
OEt
N
H
1.06
1.04
1.08
3.21
1.09
1.04
1.00
2.20
1.03
1.05
3.06
3.17
f1 (ppm)


192.52
161.12
144.48
137.19
128.77
127.84
127.48
125.27
122.70
122.68
77.28
77.07
76.86
62.63
44.60
36.48
19.82
13.92
Cl
Cl
H3C
O
O
OEt
N
H
f1 (ppm)

HPLC of 8g

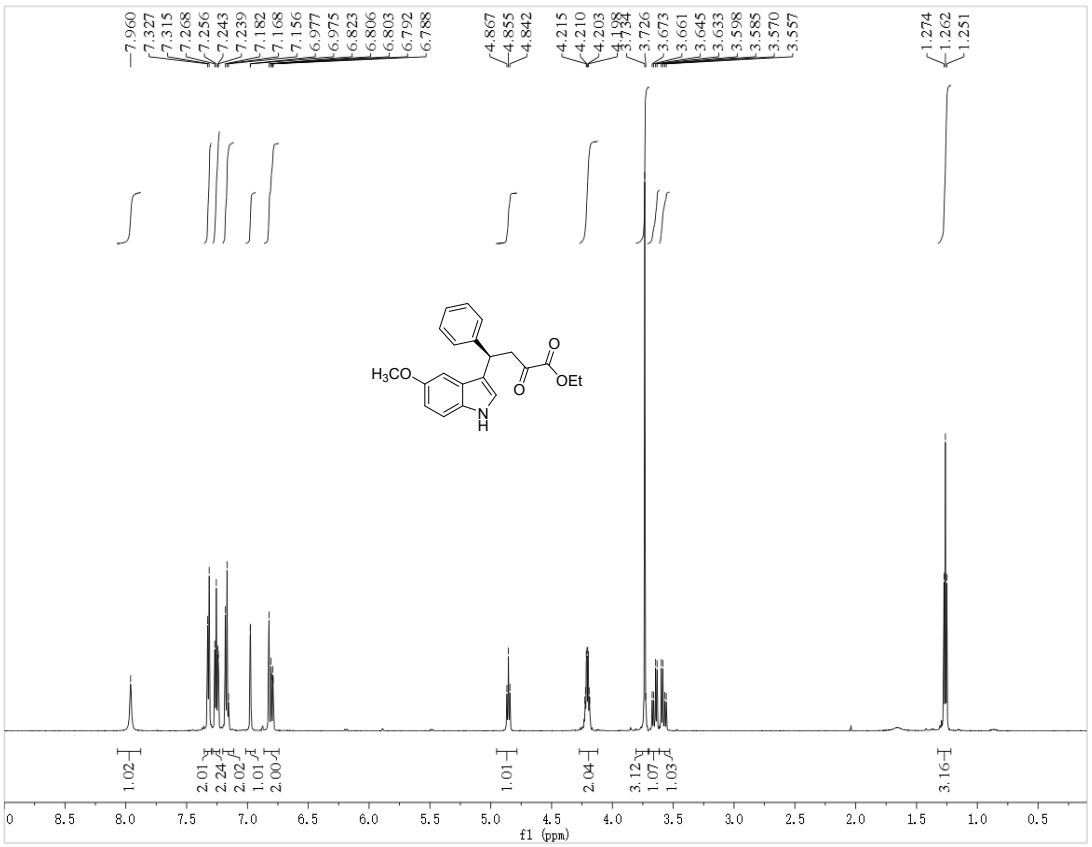


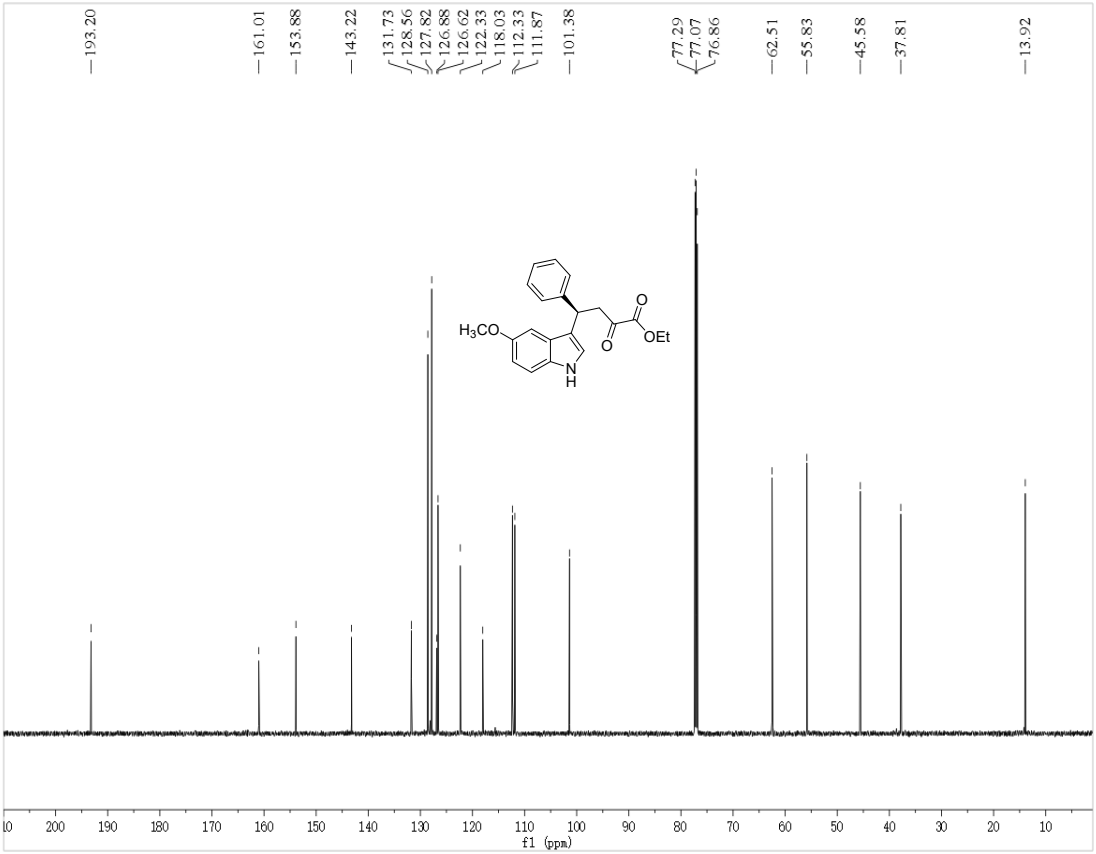
#	Time	Area	Height	Width	Area%	Symmetry
1	29.873	7825.3	119.7	1.0898	49.175	0.738
2	33.254	8087.9	102.5	1.3145	50.825	0.799



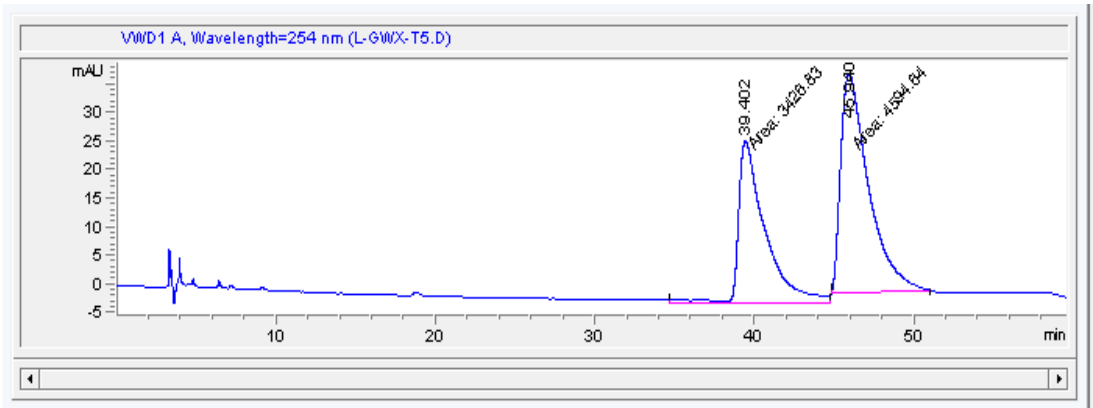
#	Time	Area	Height	Width	Area%	Symmetry
1	28.644	743.3	14.8	0.8372	4.963	0.837
2	31.105	14232.8	174.2	1.362	95.037	0.761

^{1}H and ^{13}C NMR of 8h

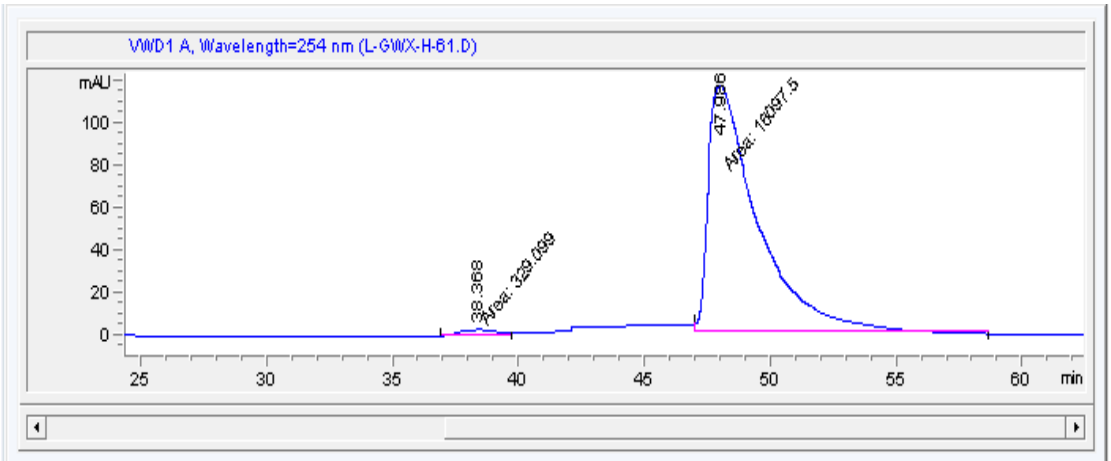

7.960
7.327
7.315
7.268
7.256
7.243
7.239
7.182
7.168
7.156
6.977
6.975
6.823
6.806
6.803
6.792
6.788
4.867
4.855
4.842
4.215
4.210
4.203
4.198
3.734
3.726
3.673
3.661
3.645
3.633
3.598
3.585
3.570
3.557
1.274
1.262
1.251
H3CO
O
O
OEt
N
H
1.02
2.01
2.24
2.02
1.01
2.00
1.01
2.04
3.12
1.07
1.03
3.16
f1 (ppm)


193.20
161.01
153.88
143.22
131.73
128.56
127.82
126.88
126.62
122.33
118.03
112.33
111.87
101.38
77.29
77.07
76.86
62.51
55.83
45.58
37.81
13.92
H3CO
O
O
OEt
N
H
f1 (ppm)

HPLC of 8h

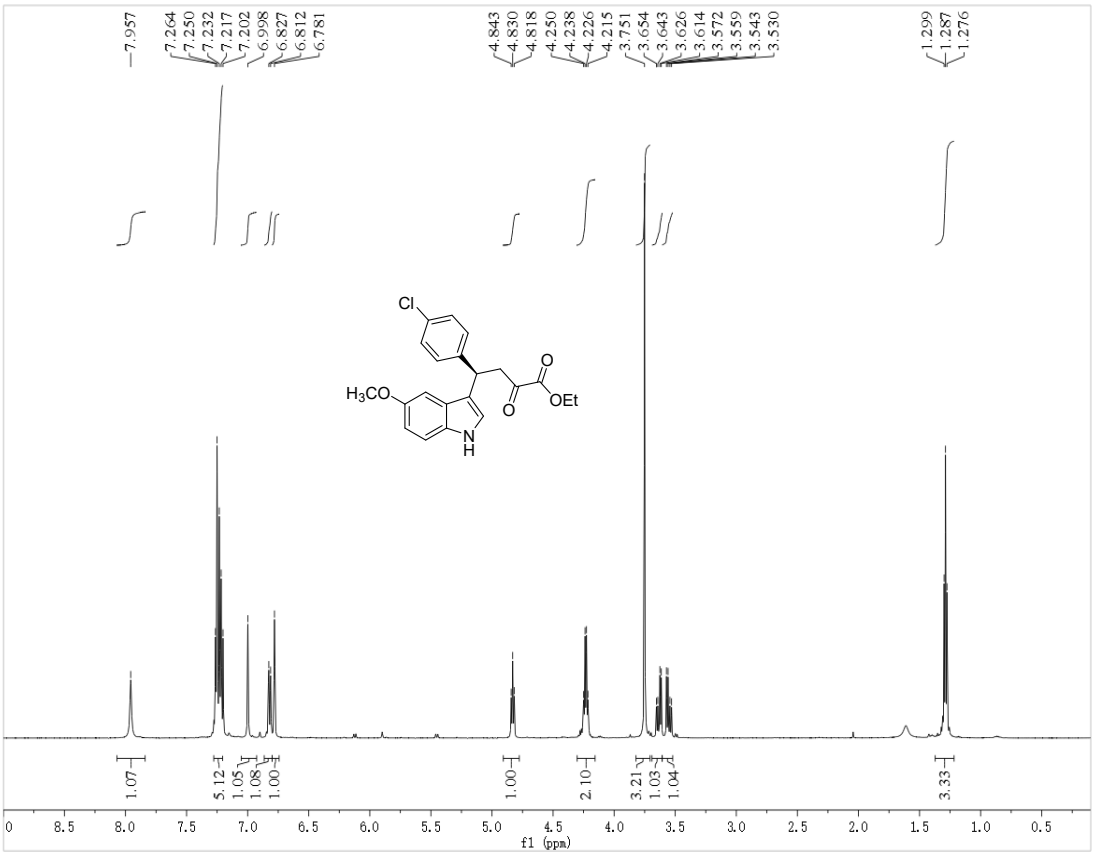


#	Time	Area	Height	Width	Area%	Symmetry
1	39.402	3426.8	28.6	1.9989	42.721	0.375
2	45.94	4594.6	38.4	1.9968	57.279	0.419



#	Time	Area	Height	Width	Area%	Symmetry
1	38.368	329.1	3	1.8591	2.003	0.904
2	47.986	16097.5	116.6	2.3005	97.997	0.308

^{1}H and ^{13}C NMR of 8i


7.957
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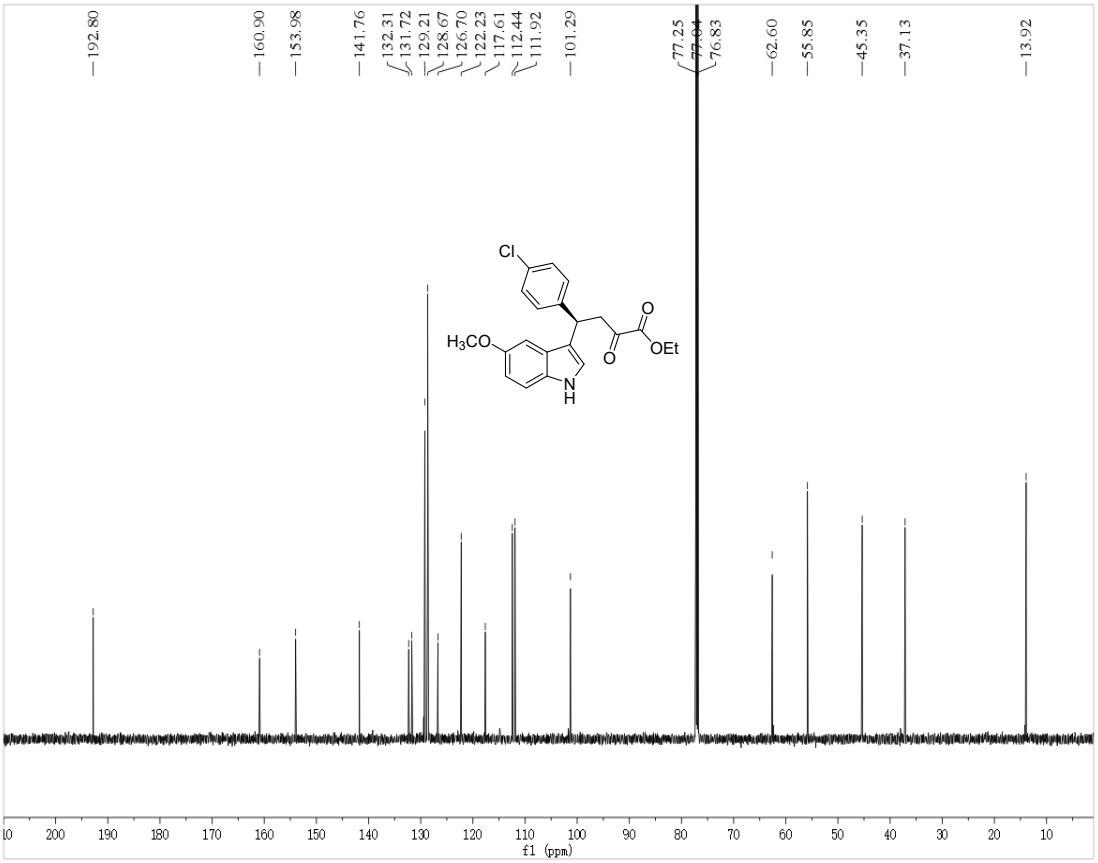
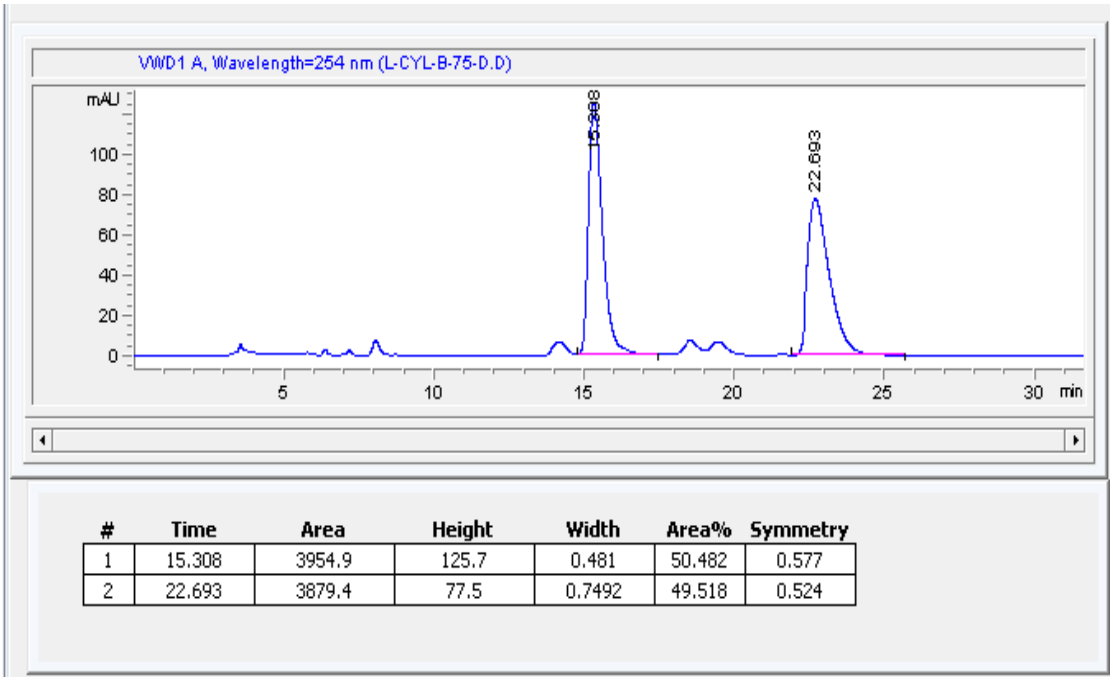
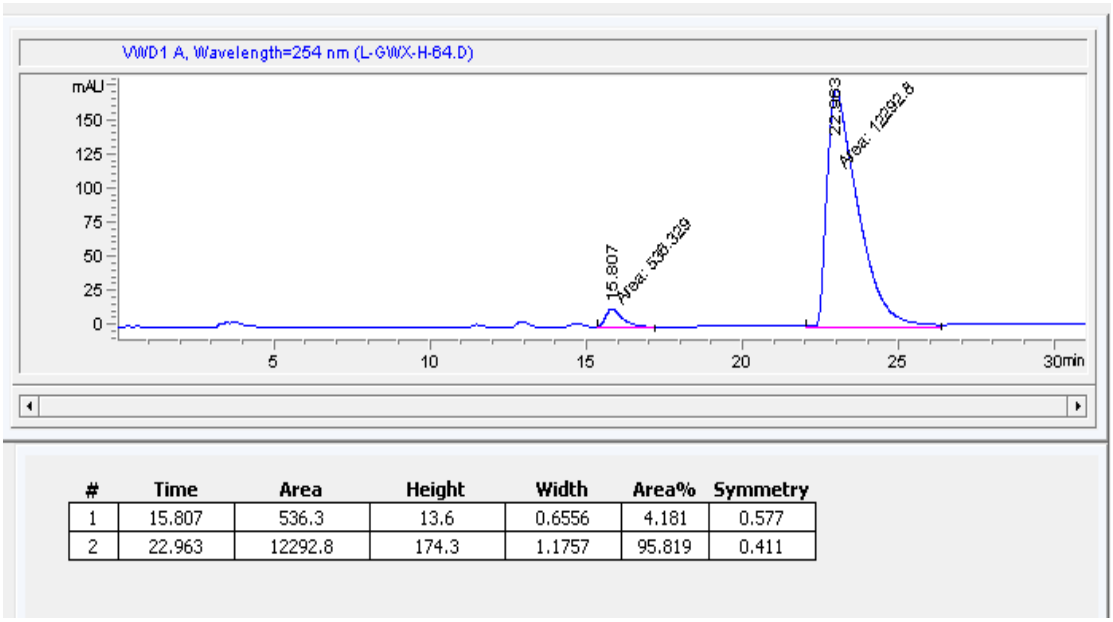
7.250
7.232
7.217
7.202
6.998
6.827
6.812
6.781
4.843
4.830
4.818
4.250
4.238
4.226
4.215
3.751
3.654
3.643
3.626
3.614
3.572
3.559
3.543
3.530
1.299
1.287
1.276
Cl
H3CO
O
O
OEt
N
H
1.07
5.12
1.05
1.08
1.00
1.00
2.10
3.21
1.03
1.04
3.33
f1 (ppm)


192.80
160.90
153.98
141.76
132.31
131.72
129.21
128.67
126.70
122.23
117.61
112.44
111.92
101.29
77.25
77.04
76.83
62.60
55.85
45.35
37.13
13.92
Cl
H3CO
O
O
OEt
N
H
f1 (ppm)

HPLC of 8i

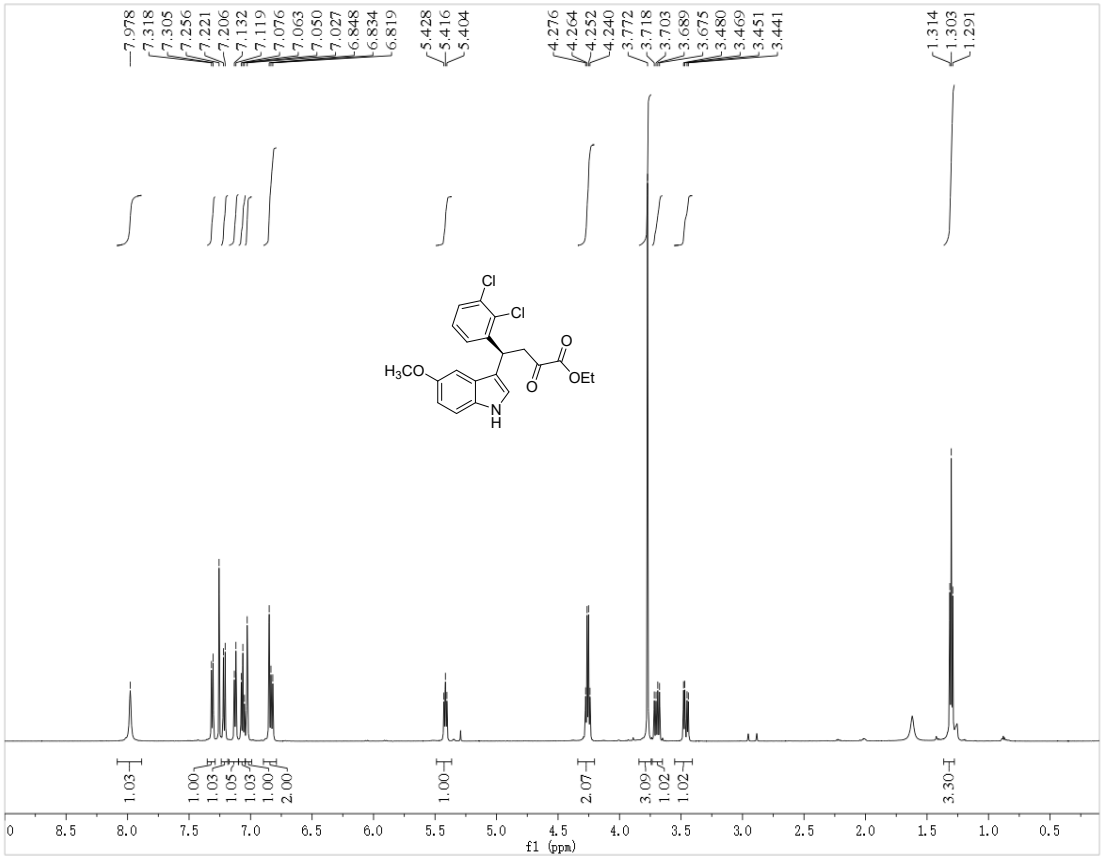


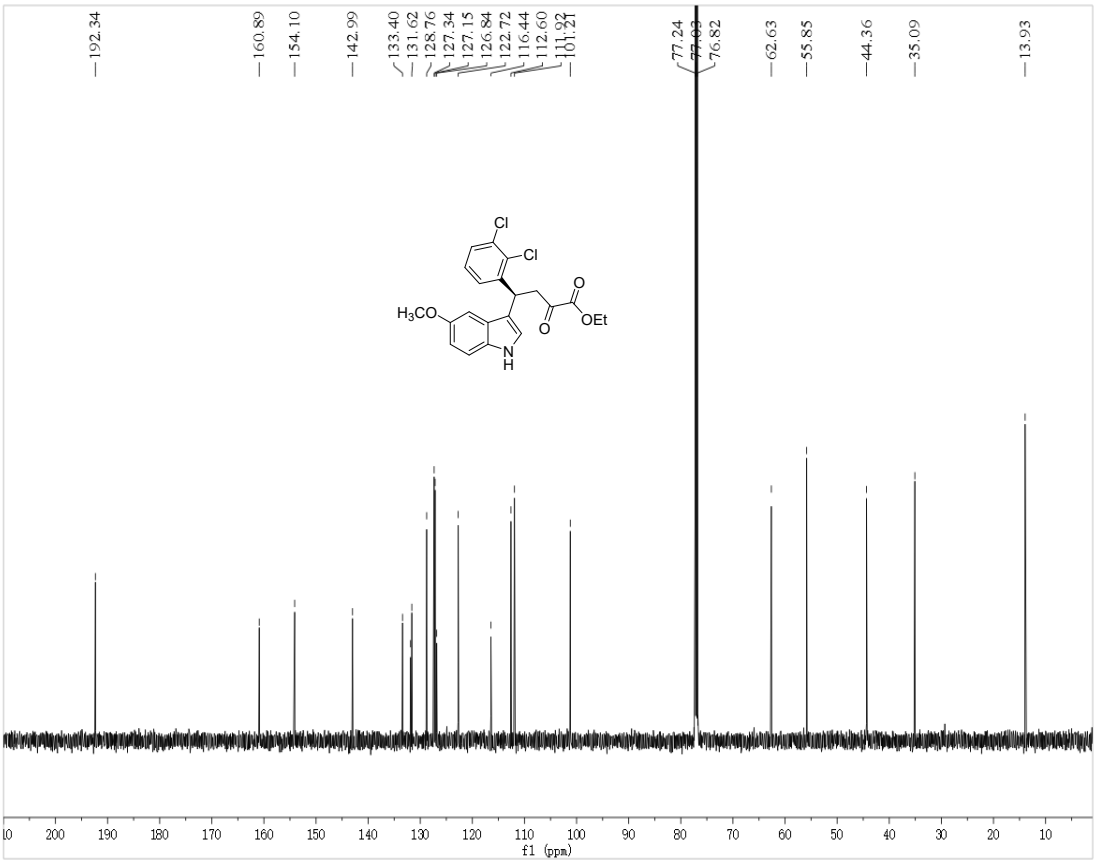
#	Time	Area	Height	Width	Area%	Symmetry
1	15.308	3954.9	125.7	0.481	50.482	0.577
2	22.693	3879.4	77.5	0.7492	49.518	0.524



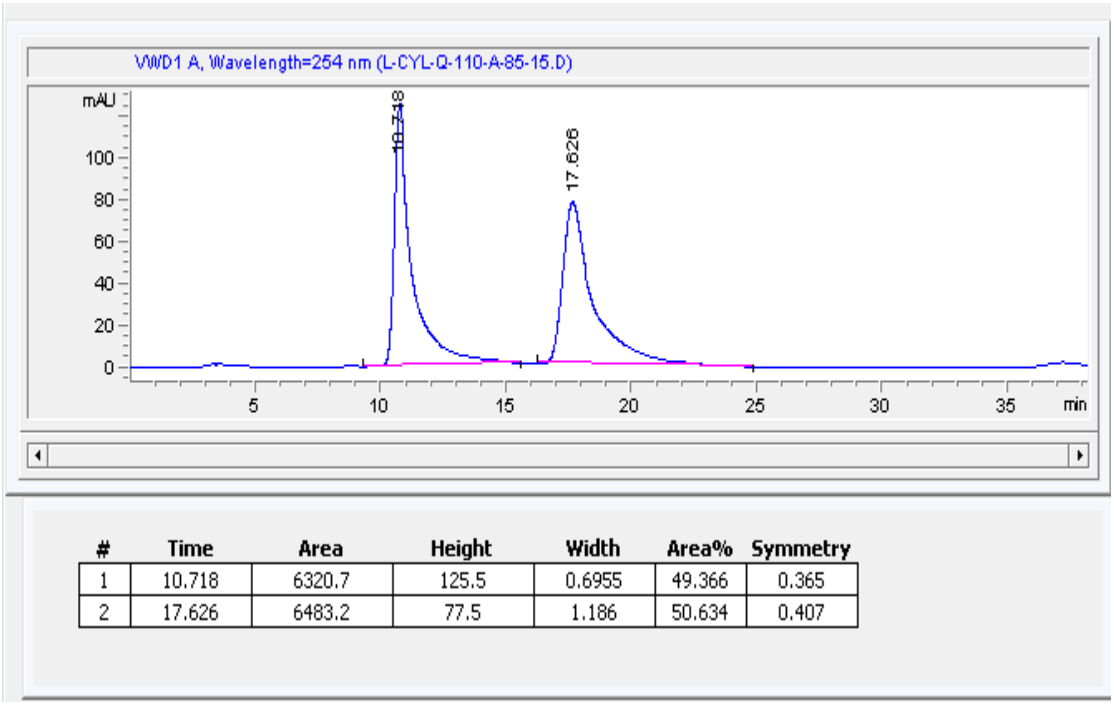
#	Time	Area	Height	Width	Area%	Symmetry
1	15.807	536.3	13.6	0.6556	4.181	0.577
2	22.963	12292.8	174.3	1.1757	95.819	0.411

^{1}H and ^{13}C NMR of 8j

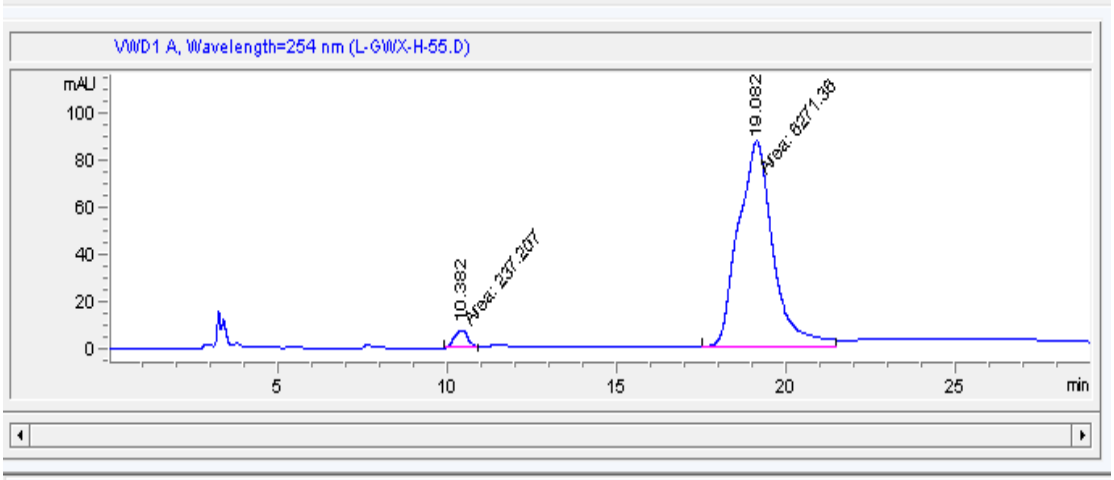




HPLC of 8j



#	Time	Area	Height	Width	Area%	Symmetry
1	10.718	6320.7	125.5	0.6955	49.366	0.365
2	17.626	6483.2	77.5	1.186	50.634	0.407



#	Time	Area	Height	Width	Area%	Symmetry
1	10.382	237.2	7.7	0.5136	3.645	1.051
2	19.082	6271.4	87.8	1.1906	96.355	1.008