Supporting Information

Organocatalytic Asymmetric Synthesis of Axially and Centrally Chiral Heterotriarylmethanes by Friedel-Crafts Reaction

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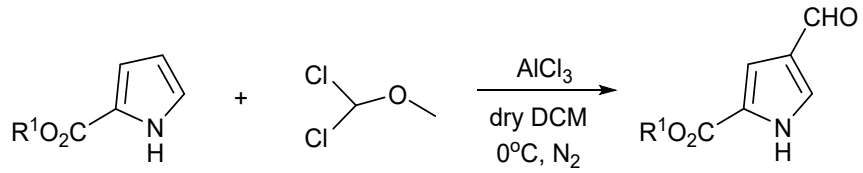
1. General information

All solvents and reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 50 GF254 plates. Flash column chromatography was performed using silica gel (200-300 mesh). Visualization on TLC was achieved by use of UV light (254, 365nm). NMR spectrums were recorded on a Bruker DPX 400 NMR spectrometer at 400 MHz for ^{1}H NMR, 101 MHz for ^{13}C NMR. The solvent used for NMR spectroscopy was $CDCl_3$. Chemical shifts for ^{1}H NMR and ^{13}C NMR spectra were reported as δ in units of parts per million (ppm) downfield from standard tetramethylsilane (0.0), relative to the signal of chloroform-d. Multiplicities were given as s (singlet), d (doublet), t (triplet), dd (doublets of doublet), or m (multiplets). The number of protons (n) for a given resonance is indicated by nH. Coupling constants were reported as a *J* value in hertz. A high resolution mass spectrum (HRMS) was determined by 1290II-6230 TOF using ESI ionization. Infrared spectra were recorded on an ATR-FTIR spectrometer (NICOLET iS10). Optical rotations were reported as follows: $[\alpha]_D^{20}$ (c: g/100 mL, in DCM). Enantiomeric excess was determined by chiral high-performance liquid chromatography (chiral HPLC) using DAICEL CHIRALPAK columns such as IA, AD-H, IE-3, IC-3, and IB-3. The melting point of each compound was determined by melting point meter SGW X-4A. The racemic products employed to determine enantiomeric ratios were prepared by using diphenylphosphate as a catalyst. Optical rotation values were measured with instruments operating at λ = 589 nm, corresponding to the sodium D line at the temperatures indicated. The X-ray source used for the single crystal X-ray diffraction analysis of compound **3b** was GaKα (λ = 1.34139). The thermal ellipsoid was drawn at the 50% probability level.

2. Methods of synthesizing substrates

2.1 Methods of synthesizing 1H-pyrrol-3-yl carbinol 1

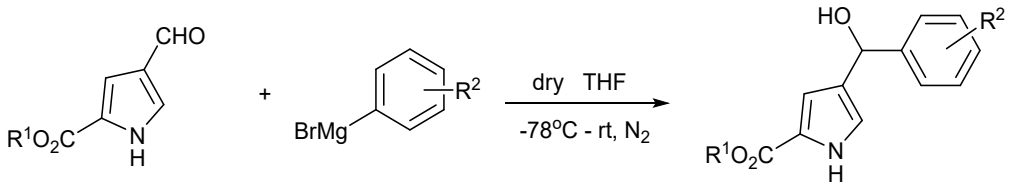
4-(Hydroxy(phenyl)methyl)-1H-pyrrole-2-carboxylate derivatives used in the synthesis of substrates 1 were performed by the following method.[1]



R^1 =Me, Et

S1a **S1b**

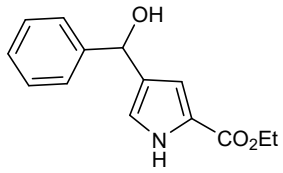
Under a nitrogen atmosphere, 1,1-dichlorodimethyl ether (60 mmol, 1.5 equiv, 6.9 g) was added dropwise to 1H-pyrrole-2-carboxylate derivative (40 mmol, 5.58 g, 1 equiv) and aluminum trichloride (3 equiv, 120 mmol, 16.04 g) dissolved in dry CH_2Cl_2 (80 mL) in a three-neck flask. The reaction mixture was stirred at 0°C for 2 hours. Cold water was slowly added to the mixture in an ice bath until no more gas bubbles evolved. The reaction mixture was then extracted with dichloromethane (3 × 90 mL). The combined organic layer was washed with brine (60 mL) and dried over sodium sulfate. The solution was concentrated under reduced pressure and purified by flash chromatography (PE : EA = 1:8) to obtain **S1b**.



S1b **1**

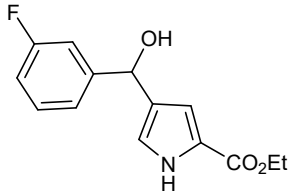
In a three-neck flask, a Grignard reagent (1M in THF, 66 mmol, 3 equiv, 66 mL) was added dropwise to dry THF containing 1H-pyrrole-3-carbaldehyde (20 mL) at -78°C. The mixture was then warmed to room temperature and stirred overnight under a nitrogen atmosphere. After cooling in an ice bath, the resulting mixture was quenched

with a saturated aqueous solution of NH_4Cl (80 mL). The reaction mixture was then extracted with ethyl acetate (3 × 80 mL). The combined organic layer was washed with brine (60 mL) and dried over Na_2SO_4. The solution was concentrated in vacuo and purified by flash chromatography (PE : EA = 1:6) to obtain product **1**.



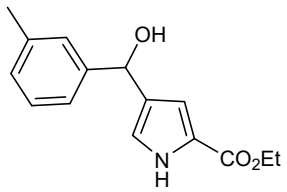
Ethyl 4-(hydroxy(phenyl)methyl)-1H-pyrrole-2-carboxylate (1a)

Yellow solid (2.11g , 86% yield); MP = 102-104 ^oC; ^1H NMR (400 MHz, Chloroform-d) δ 9.87 (s, 1H), 7.33 (d, *J* = 7.0 Hz, 2H), 7.29 -7.17 (m, 3H), 6.75 (d, *J* = 1.8 Hz, 1H), 6.65 (d, *J* = 2.1 Hz, 1H), 5.68 (s, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.55 (s, 1H), 1.23 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-d) δ 161.8, 144.2, 129.5, 128.4, 127.4, 126.4, 122.9, 121.6, 113.9, 70.6, 60.5, 14.4 ppm. HRMS (ESI TOF) m/z: $[M + Na]^+$ calcd for $C_{14}H_{15}NO_3Na$: 268.0945; Found: 268.0952. IR (KBr, cm^{-1}): 3426, 3314, 2970, 2914, 2857, 1682, 1605, 1473, 1106, 1023, 828.



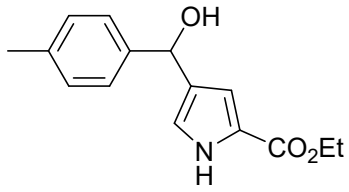
Ethyl 4-((3-fluorophenyl)(hydroxy)methyl)-1H-pyrrole-2-carboxylate (1b)

^1H NMR (400 MHz, Chloroform-d) δ 9.54 (s, 1H), 7.32 – 7.23 (m, 1H), 7.19 – 7.08 (m, 2H), 6.94 (tt, *J* = 8.7, 1.8 Hz, 1H), 6.82 – 6.74 (m, 2H), 5.76 (s, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.87 (s, 1H), 1.31 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-d) δ 171.3, 162.92 (d, *J* = 245.7 Hz), 161.3, 146.6, 129.86 (d, *J* = 8.2 Hz), 129.1, 123.3, 121.9, 121.0, 114.24 (d, *J* = 21.2 Hz), 113.5, 113.20 (d, *J* = 22.1 Hz), 60.5, 53.4, 14.4 ppm. ^{19}F NMR (376 MHz, Chloroform-d) δ -112.92 ppm.



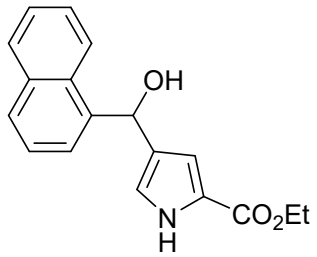
Ethyl 4-(hydroxy(m-tolyl)methyl)-1H-pyrrole-2-carboxylate (1c)

^{1}H NMR (400 MHz, Chloroform-d) δ 9.09 (s, 1H), 7.37 – 7.27 (m, 1H), 7.23 – 7.14 (m, 2H), 7.08 (dd, *J* = 12.4, 6.7 Hz, 2H), 6.83 (dt, *J* = 10.5, 2.2 Hz, 2H), 5.77 (s, 1H), 4.28 (q, 2H), 2.35 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-d) δ 143.9, 138.1, 128.4, 127.0, 123.4, 120.6, 114.2, 113.5, 70.8, 60.4, 31.5, 30.2, 29.7, 21.5, 14.4 ppm.



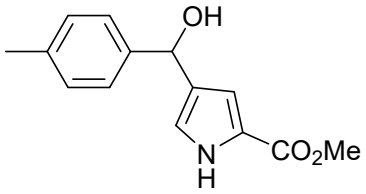
Ethyl 4-(hydroxy(p-tolyl)methyl)-1H-pyrrole-2-carboxylate (1d)

Yellow solid (2.33g, 90% yield); MP = 121-123 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.08 (s, 1H), 7.31 – 7.15 (m, 3H), 7.09 (d, *J* = 7.7 Hz, 2H), 6.74 (dd, *J* = 11.7, 2.5 Hz, 2H), 5.70 (s, 1H), 4.20 (q, 2H), 2.27 (s, 3H), 1.20 (t, *J* = 11.9 Hz, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-d) δ 161.2, 141.0, 137.3, 129.9, 129.2, 126.3, 123.2, 120.7, 113.5, 70.7, 60.4, 31.5, 29.7, 21.1, 14.4 ppm. HRMS (ESI TOF) m/z: [M+ Na] $^{+}$ calcd for $C_{15}H_{17}NO_3Na$: 282.1101; Found: 282.1112. IR (KBr, cm^{-1}): 3406, 3315, 2963, 2910, 2838, 1682, 1605, 1483, 1104, 1006, 847.



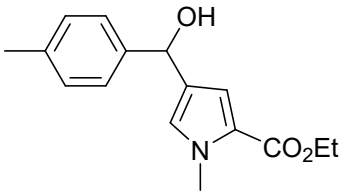
Ethyl 4-(hydroxy(p-tolyl)methyl)-1H-pyrrole-2-carboxylate (1e)

Yellow solid (2.79g , 88% yield); MP = 129-130 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-d) δ 9.35 – 9.24 (m, 1H), 7.88 (d, *J* = 1.8 Hz, 1H), 7.84 – 7.77 (m, 3H), 7.51 – 7.43 (m, 3H), 7.25 (m, 1H), 6.80 (q, *J* = 1.6 Hz, 2H), 5.94 (d, *J* = 2.5 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.29 (t, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-d) δ 161.3, 141.3, 133.3, 132.9, 129.6, 128.3, 128.1, 127.7, 126.2, 125.9, 124.7, 124.7, 123.3, 121.0, 113.7, 70.8, 60.5, 14.4 ppm. HRMS (ESI TOF) m/z: [M+ Na] $^{+}$ calcd for $C_{18}H_{17}FNO_3Na$: 318.1101; Found: 318.1126. IR (KBr, cm-1): 3429, 3315, 2946, 1689, 1580, 1463, 1379, 1209, 1106, 1024, 825.



Methyl 4-(hydroxy(p-tolyl)methyl)-1H-pyrrole-2-carboxylate (1f)

Yellow solid (1.98g, 81% yield); MP = 115-116 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-d) δ 9.24 (s, 1H), 7.50 – 7.24 (m, 2H), 7.15 (d, *J* = 7.8 Hz, 3H), 6.85 – 6.73 (m, 2H), 5.76 (s, 1H), 3.80 (s, 3H), 2.34 (s, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-d) δ 161.7, 141.0, 137.3, 129.9, 129.2, 126.3, 120.9, 113.7, 70.6, 51.5, 31.5, 30.2, 29.7, 21.1 ppm. HRMS (ESI TOF) m/z: [M+ Na] $^{+}$ calcd for $C_{14}H_{15}FNO_3Na$: 268.0944; Found: 268.0932. IR (KBr, cm-1): 3446, 3305, 2981, 1672, 1608, 1565, 1430, 1192, 1017, 792.



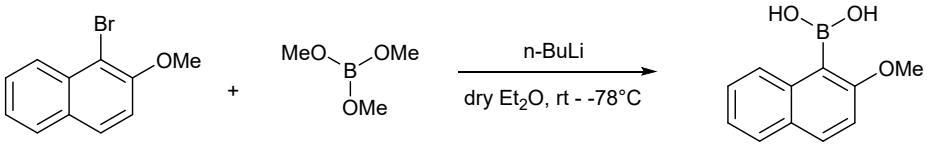
Ethyl 4-(hydroxy(p-tolyl)methyl)-1H-pyrrole-2-carboxylate (1g)

Yellow solid (2.51g , 92% yield); MP = 128-129°C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.42 – 7.19 (m, 3H), 7.16 (d, *J* = 7.8 Hz, 2H), 6.84 (d, *J* = 2.0 Hz, 1H), 6.64 (d, *J* = 2.0 Hz, 1H), 5.71 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 2.34 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-d) δ 161.3, 141.1, 137.2, 129.1, 127.3, 126.2, 115.9, 70.6, 67.1, 59.9, 36.8, 31.5, 30.1, 29.7, 21.2, 14.4 ppm. HRMS (ESI TOF) m/z: [M+ Na] $^{+}$ calcd for $C_{15}H_{17}FNO_3Na$: 282.1101; Found: 282.1152. IR (KBr, cm-1): 3426, 3312, 2952, 1678, 1604, 1506, 1461, 1217, 1014, 832, 736.

2.2 Methods of synthesizing naphthyl-indole substrates 2

2.2.1 Methods of synthesizing boronic acid substrates

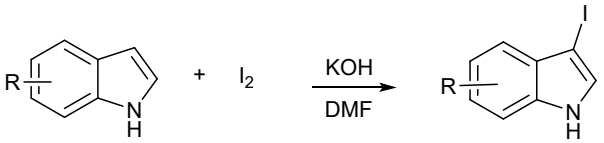
Boronic acid substrates used in the construction of substrates **2** were synthesized by the methods described in the literature.[2]



S2a **S2**

n-Butyllithium (7.0 mL, 2.5 M in hexanes, 18 mmol, 1.13 equiv.) was added dropwise to a stirred solution of 1-bromo-2-methoxynaphthalene derivatives (15.9 mmol, 1 equiv.) in dry Et_2O (60 mL) at -78°C under nitrogen atmosphere. The solution was warmed to room temperature and stirred for 1 h. After this time, the flask was re-cooled to -78°C and trimethylborate (2.3 mL, 21 mmol, 1.32 equiv.) was added drop-wise. The mixture was allowed warm to room temperature overnight (18 h) under nitrogen. 1M HCl (50 mL) was added dropwise and the solution was stirred for an additional 1h. The reaction mixture was evaporated in vacuo and extracted with dichloromethane (3 × 30 mL). The combined organic layer was washed with brine (30 mL) and dried over Na_2SO_4. The solution was concentrated in vacuo and purified by flash chromatography (PE : EA = 1:6) to get **S2**.

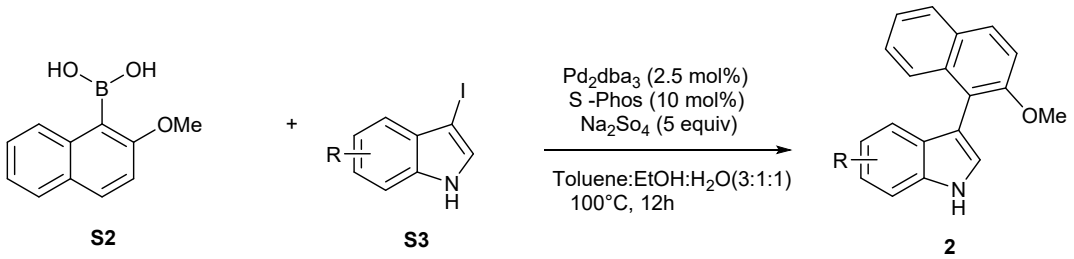
2.2.2 Methods of synthesizing 3-Iodoindole derivatives



S3a **S3**

All 3-iodoindole substrates were synthesized according to the reported literature.[3] A solution of indole **S3a** (17.1 mmol, 1 equiv.) in 30 mL of DMF was treated with KOH (2.39 g, 42.7 mmol, 2.5 equiv.) and allowed to stir at room temperature for 20 min. I_2 (4.38 g, 17.1 mmol, 1 equiv.) was dissolved in 5 mL of DMF and added to the reaction. The resulting solution was stirred for an additional 45 min. The reaction mixture was poured into 400 mL of ice water and the precipitate was collected by filtration, washed with water and dried by azeotropic distillation with toluene to yield 3-iodoindole derivatives **S3**.

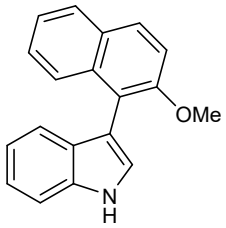
2.2.3 Methods of synthesizing naphthyl-indole substrates



S2 **S3** **2**

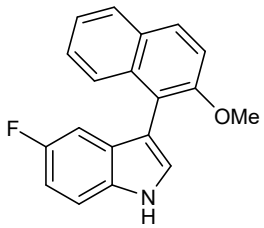
Substrates **2** were prepared according to the general procedure reported by Shi and coworkers.[4] Under nitrogen atmosphere, to the mixture of 3-iodoindole derivatives (10.4 mmol, 1 equiv.), naphthyl boronic acid derivatives (11.4 mmol, 1.1 equiv.), Pd_2dba_3 (238 mg, 2.5 mol%), S-Phos (436 mg, 10 mol%) and Na_2CO_3 (5.6 g, 52 mmol, 5 equiv.) was added the mixed solvent of toluene (60 mL), ethanol (20 mL) and H_2O (20 mL) (3:1:1). Then, the reaction mixture was stirred at 100 ^oC in an oil bath for 12 h. After the completion of the reaction which was indicated by TLC, the reaction mixture was cooled to room temperature, and the reaction mixture was quenched with water and extracted with ethyl acetate. The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. Then, the organic layer was concentrated in

vacuo to give a residue, which was purified by flash column chromatography (petroleum ether/ethyl acetate = 10/1) to afford the desired compounds **2a-2i**. Compounds **2a-2i** were similar with the previously reported work[4].



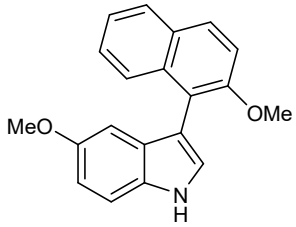
3-(2-methoxynaphthalen-1-yl)-1H-indole (2a)

^{1}H NMR (400 MHz, Chloroform-d) δ 8.15 (s, 1H), 7.87 (d, *J* = 9.0 Hz, 2H), 7.82 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.73 – 7.69 (m, 3H), 7.40 – 7.24 (m, 2H), 7.23 – 7.14 (m, 2H), 7.08 – 7.01 (m, 1H), 3.77 (s, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-d) δ 155.2, 136.1, 134.6, 129.4, 128.9, 128.2, 128.0, 126.2, 126.1, 124.8, 123.6, 122.0, 120.6, 119.7, 118.1, 114.1, 111.3, 110.8, 56.8 ppm.



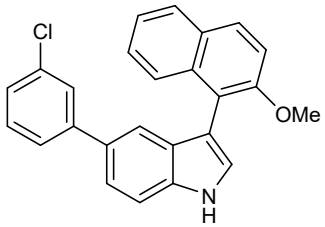
5-fluoro-3-(2-methoxynaphthalen-1-yl)-1H-indole (2b)

^{1}H NMR (400 MHz, Chloroform-d) δ 8.18 (s, 1H), 7.87 (d, *J* = 9.1 Hz, 1H), 7.84 – 7.79 (m, 1H), 7.68 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.37 (d, *J* = 9.0 Hz, 3H), 7.30 (tt, *J* = 6.8, 5.1 Hz, 2H), 7.20 (dd, *J* = 8.6, 3.7 Hz, 1H), 6.97 – 6.87 (m, 1H), 3.78 (s, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-d) δ 158.10 (d, *J* = 234.4 Hz), 155.1, 134.4, 132.6, 129.4, 129.2, 128.64 (d, *J* = 9.9 Hz), 128.1, 126.6, 126.4, 125.7, 123.7, 117.3, 113.8, 111.93 (d, *J* = 9.7 Hz), 111.05 (d, *J* = 4.9 Hz), 110.50 (d, *J* = 26.5 Hz), 105.38 (d, *J* = 23.4 Hz), 56.7 ppm. ^{19}F NMR (376 MHz, Chloroform-d) δ -124.37 ppm.



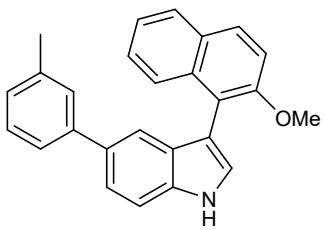
5-methoxy-3-(2-methoxynaphthalen-1-yl)-1H-indole (2c)

^{1}H NMR (400 MHz, Chloroform-d) δ 8.15 (s, 1H), 7.86 (d, *J* = 9.1 Hz, 1H), 7.83 – 7.79 (m, 1H), 7.72 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.37 (d, *J* = 9.1 Hz, 1H), 7.33 – 7.25 (m, 2H), 7.21 – 7.09 (m, 2H), 6.85 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.67 (d, *J* = 2.4 Hz, 1H), 3.77 (s, 3H), 3.63 (s, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-d) δ 155.2, 154.3, 134.5, 131.3, 129.4, 128.9, 128.6, 128.0, 126.2, 126.1, 125.6, 123.7, 118.2, 114.1, 112.5, 112.1, 110.5, 102.1, 56.8, 55.9 ppm.



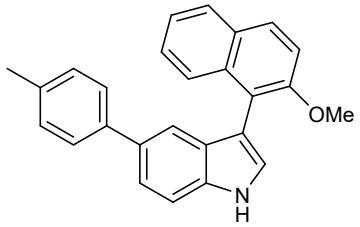
5-(3-chlorophenyl)-3-(2-methoxynaphthalen-1-yl)-1H-indole (2d)

^{1}H NMR (400 MHz, Chloroform-d) δ 8.31 (s, 1H), 7.90 (d, *J* = 9.0 Hz, 1H), 7.84 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.72 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.50 (d, *J* = 1.9 Hz, 1H), 7.42 (d, *J* = 2.6 Hz, 4H), 7.40 – 7.26 (m, 4H), 7.25 – 7.14 (m, 2H), 3.81 (s, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-d) δ 155.3, 144.5, 135.9, 134.6, 134.4, 131.9, 129.8, 129.3, 129.1, 128.7, 128.0, 127.4, 126.3, 126.2, 125.9, 125.6, 123.7, 121.7, 119.1, 117.6, 113.9, 111.7, 111.4, 60.5, 56.8 ppm.



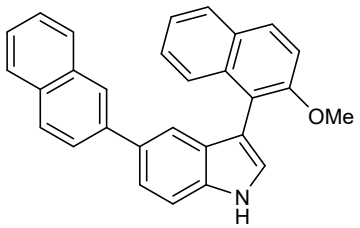
3-(2-methoxynaphthalen-1-yl)-5-(m-tolyl)-1H-indole (2e)

^{1}H NMR (400 MHz, Chloroform-d) δ 8.16 (s, 1H), 7.87 (d, *J* = 9.0 Hz, 1H), 7.84 – 7.79 (m, 1H), 7.74 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.41 – 7.23 (m, 6H), 7.22 – 7.13 (m, 2H), 7.06 – 7.01 (m, 1H), 3.77 (s, 3H), 2.31 (s, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-d) δ 155.3, 142.7, 138.1, 135.7, 134.7, 133.5, 129.4, 129.0, 128.7, 128.5, 128.3, 128.0, 127.1, 126.3, 126.1, 125.4, 124.6, 123.7, 122.0, 119.0, 118.0, 114.0, 111.6, 111.2, 56.8, 21.6 ppm.



3-(2-methoxynaphthalen-1-yl)-5-(p-tolyl)-1H-indole (2f)

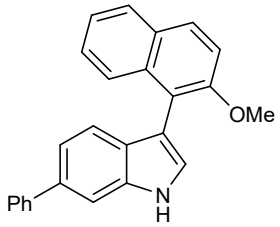
^{1}H NMR (400 MHz, Chloroform-d) δ 8.28 (s, 1H), 7.89 (d, *J* = 9.0 Hz, 1H), 7.83 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.79 – 7.73 (m, 1H), 7.47 – 7.38 (m, 6H), 7.31 (qd, *J* = 8.4, 7.6, 1.4 Hz, 3H), 7.21 (s, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 3.81 (s, 3H), 2.32 (s, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-d) δ 155.3, 139.7, 135.8, 135.5, 134.6, 133.3, 129.3, 128.9, 128.7, 127.9, 127.3, 126.2, 126.0, 125.3, 123.6, 121.9, 118.8, 117.9, 114.0, 111.4, 111.3, 56.8, 21.0 ppm.



3-(2-methoxynaphthalen-1-yl)-5-(naphthalen-2-yl)-1H-indole (2g)

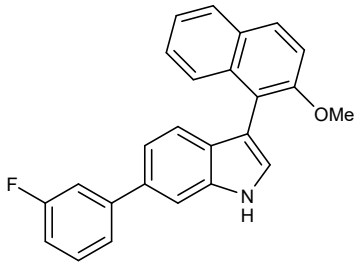
^{1}H NMR (400 MHz, Chloroform-d) δ 8.22 (s, 1H), 7.94 (d, *J* = 1.8 Hz, 1H), 7.88 (d, *J* = 9.0 Hz, 1H), 7.82 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.79 – 7.73 (m, 4H), 7.67 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.62 – 7.52 (m, 2H), 7.38 (dt, *J* = 9.2, 6.4 Hz, 4H), 7.34 – 7.24 (m, 2H), 7.20

– 7.13 (m, 1H), 3.77 (s, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-d) δ 155.3, 140.0, 135.8, 134.7, 133.9, 133.2, 132.2, 129.4, 129.1, 128.8, 128.1, 128.0, 127.7, 126.4, 126.1, 126.0, 125.6, 125.5, 123.7, 122.2, 119.4, 117.9, 114.0, 111.7, 111.3, 60.6, 56.8, 21.2, 14.3 ppm.



3-(2-methoxynaphthalen-1-yl)-6-phenyl-1H-indole (2h)

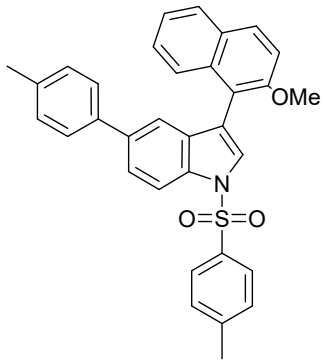
^{1}H NMR (400 MHz, Chloroform-d) δ 8.04 (d, *J* = 2.5 Hz, 1H), 7.88 – 7.77 (m, 2H), 7.72 (d, *J* = 8.6 Hz, 1H), 7.56 – 7.51 (m, 2H), 7.45 – 7.39 (m, 1H), 7.36 – 7.20 (m, 8H), 7.07 (d, *J* = 2.4 Hz, 1H), 3.71 (s, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-d) δ 155.2, 142.4, 136.7, 135.5, 134.7, 129.4, 129.1, 128.8, 128.1, 127.6, 127.5, 126.7, 126.3, 126.1, 125.7, 123.7, 120.9, 119.7, 118.0, 114.0, 110.7, 109.9, 56.7 ppm.



6-(3-fluorophenyl)-3-(2-methoxynaphthalen-1-yl)-1H-indole (2i)

^{1}H NMR (400 MHz, Chloroform-d) δ 8.22 (s, 1H), 7.90 – 7.79 (m, 1H), 7.71 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.42 (t, *J* = 1.1 Hz, 1H), 7.37 (d, *J* = 9.1 Hz, 2H), 7.34 – 7.22 (m, 6H), 7.15 (d, *J* = 2.4 Hz, 2H), 6.95 (dddd, *J* = 8.8, 7.9, 2.7, 1.5 Hz, 1H), 3.76 (s, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-d) δ 163.29 (d, *J* = 244.9 Hz), 155.2, 144.67 (d, *J* = 7.8 Hz), 136.6, 134.6, 134.2, 129.4, 129.1, 128.1, 128.0, 126.3, 125.9, 123.7, 123.0,

120.22 (d, *J* = 146.8 Hz), 117.7, 114.2, 114.0, 113.9, 110.8, 109.9, 60.6, 56.7, 21.2, 14.3 ppm. ^{19}F NMR (376 MHz, Chloroform-d) δ -113.41 ppm.

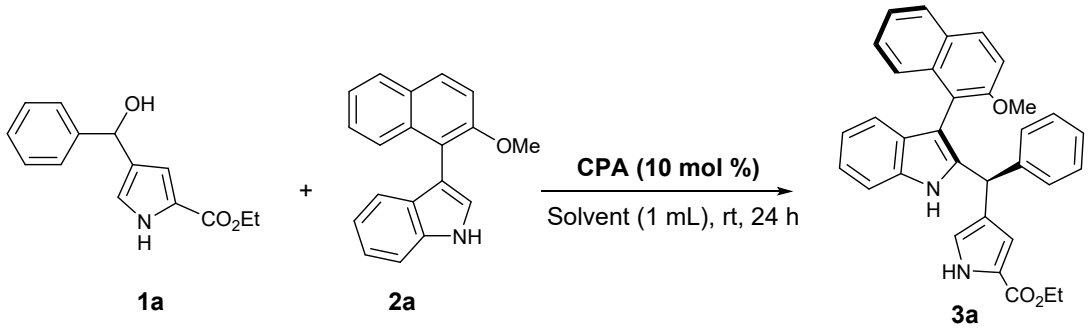


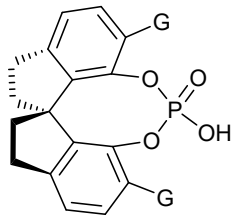
3-(2-methoxynaphthalen-1-yl)-5-(p-tolyl)-1-tosyl-1H-indole (2j)

White solid (2.51g , 85% yield); MP = 152-154 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.12 (d, *J* = 8.6 Hz, 1H), 7.91 (d, *J* = 9.0 Hz, 1H), 7.88 – 7.78 (m, 3H), 7.67 (s, 1H), 7.54 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.39 – 7.29 (m, 4H), 7.28 – 7.20 (m, 4H), 7.10 (d, *J* = 7.8 Hz, 2H), 3.77 (s, 3H), 2.35 (s, 3H), 2.29 (s, 3H) ppm. ^{13}C NMR (101 MHz, Chloroform-d) δ 155.3, 145.0, 138.4, 136.8, 136.7, 135.5, 134.5, 133.9, 132.3, 130.0, 129.9, 129.4, 129.1, 128.1, 127.2, 127.0, 126.9, 126.6, 125.2, 124.1, 123.8, 119.3, 118.1, 115.1, 114.0, 113.7, 56.7, 21.7, 21.0 ppm; HRMS (ESI TOF) m/z: [M+ H] $^{+}$ calcd for $C_{33}H_{28}NO_3S$: 518.1784; Found: 518.1796. IR (KBr, cm-1): 3462, 3263, 2942, 1689, 1609, 1528, 1438, 1205, 1075, 831, 716.

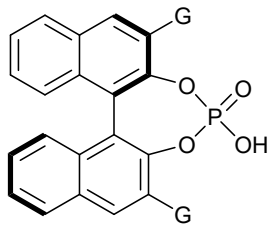
3. Optimization of reaction conditions

Table S1. Optimization of the reaction catalyst [a]

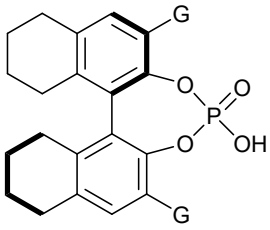




(S) -**4.1**



(R) -**4.2**



(R) -**4.3**

4.1a: G = 3,5-$(tBu)_{2\text{-}4}$-$MeOC_2H_6$
4.1b: G = 2,4,6-$Me_3C_6H_2$
4.1c: G = H
4.1d: G = 9-anthracenyl
4.1e: G = 3,5-$(CH_3)_2C_6H_3$
4.1f: G = 3,5-$(CF_3)_2C_6H_3$
4.1g: G = 1-naphthalene
4.1h: G = Si-Ph_3
4.1i: G = Ph
4.1j: G = 4-NO_2-C_6H_4
4.1k: G = 9-phenanthrenyl

4.2a: G = 3,5-$(tBu)_{2\text{-}4}$-$MeOC_2H_6$
4.2b: G = 2,4,6-$Me_3C_6H_2$
4.2c: G = 1-pyrenyl
4.2d: G = 9-anthracenyl
4.2e: G = 3,5-$(CH_3)_2C_6H_3$
4.2f: G = 3,5-$(CF_3)_2C_6H_3$

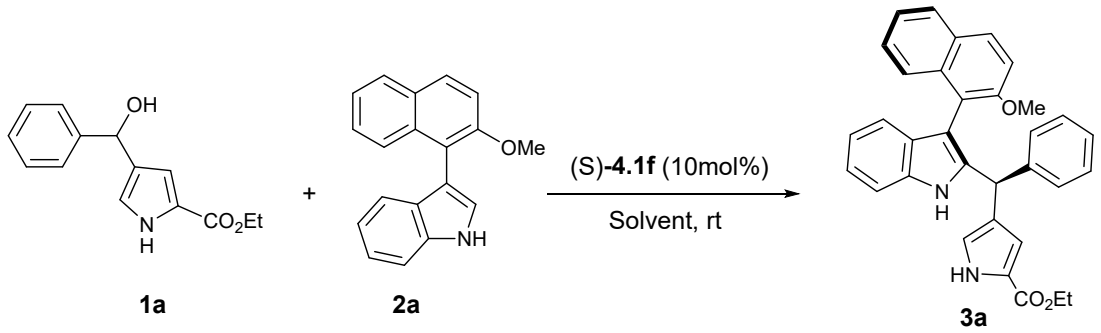
4.3a:G= 2,4,6-i-$Pr_3C_6H_2$
4.3b:G= 3,5-$(CF_3)_2C_6H_3$
4.3c:G= 3,5-$(tBu)_{2\text{-}4}$-$MeOC_6H_2$
4.3d:G= 9-anthraceny

Entry	Cat.	Solvent	Temp(°C)	Yield(%)[b]	dr[c]	ee(%)[d]
1	(*S*)-**4.1a**	DCE	rt	64	82:18	78
2	(*S*)-**4.1b**	DCE	rt	43	83:17	55
3	(*S*)-**4.1c**	DCE	rt	62	86:14	70
4	(*S*)-**4.1d**	DCE	rt	78	80:20	76
5	(*S*)-**4.1e**	DCE	rt	83	75:25	64
6	**(*S*)-4.1f**	**DCE**	**rt**	**82**	**86:14**	**87**
7	(*S*)-**4.1g**	DCE	rt	59	83:17	48
8	(*S*)-**4.1h**	DCE	rt	57	85:15	43
9	(*S*)-**4.1i**	DCE	rt	50	68:32	36
10	(*S*)-**4.1j**	DCE	rt	79	78:22	68
11	(*S*)-**4.1k**	DCE	rt	63	85:15	27

12	(*R*)-**4.2a**	DCE	rt	52	58:42	67
13	(*R*)-**4.2b**	DCE	rt	84	88:12	47
14	(*R*)-**4.2c**	DCE	rt	70	85:15	55
15	(*R*)-**4.2d**	DCE	rt	73	82:18	26
16	(*R*)-**4.2e**	DCE	rt	41	75:25	59
17	(*R*)-**4.2f**	DCE	rt	31	60:40	55
18	(*R*)-**4.3a**	DCE	rt	64	87:13	29
19	(*R*)-**4.3b**	DCE	rt	55	76:24	71
20	(*R*)-**4.3c**	DCE	rt	60	79:21	37
21	(*R*)-**4.3d**	DCE	rt	47	84:16	62

[a] Reaction conditions: 1a (0.06 mmol), 2a (0.05 mmol) and catalyst (10 mol%) in DCE (0.5 mL) at room temperature for 12 h. [b] Isolated yields.[c] Determined by HPLC with C18 column. [d] Determined by chiral HPLC analysis.

Table S2. Optimization of the reaction solvent [a]

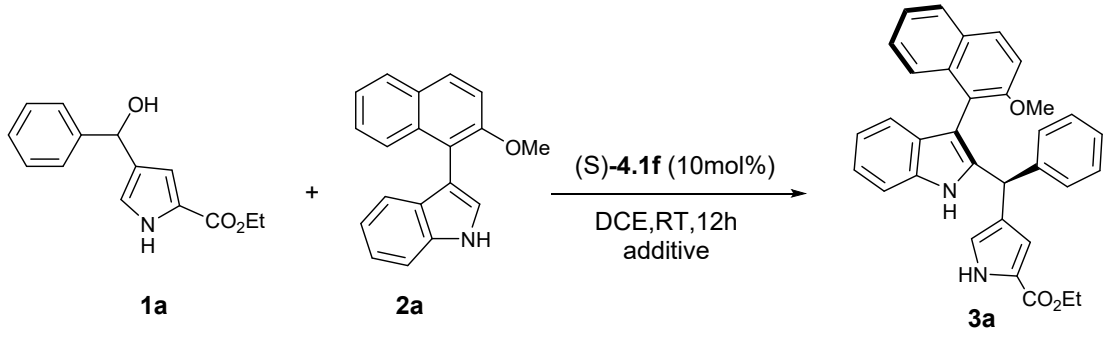


Entry	Solvent	Yield(%)[b]	dr[c]	ee(%)[d]
1	DCM	88	84:16	85
2	DMF	N.R.	--	--

3	Methano	43	73:27	62
4	THF	N.R.	--	--
5	$CHCl_3$	86	83:17	72
6	Et_2O	70	55:45	64
7	EA	63	76:24	78
8	Toluene	77	80:20	60
9	DME	N.R.	--	--
10[e]	DCE	80	86:14	82
11[f]	DCE	73	85:15	78

[a] Reaction conditions: 1a (0.05 mmol), 2a (0.06 mmol) and (*S*)-4.1i (10 mol%) in 0.5 mL solvent at room temperature for 12 h. [b] Isolated yields. [c] Determined by HPLC with C18 column. [d] Determined by chiral HPLC analysis.[e] 1.0 mL DCE. [f] 0.25 mL DCE.

Table S3. Optimization of the reaction additive [a]

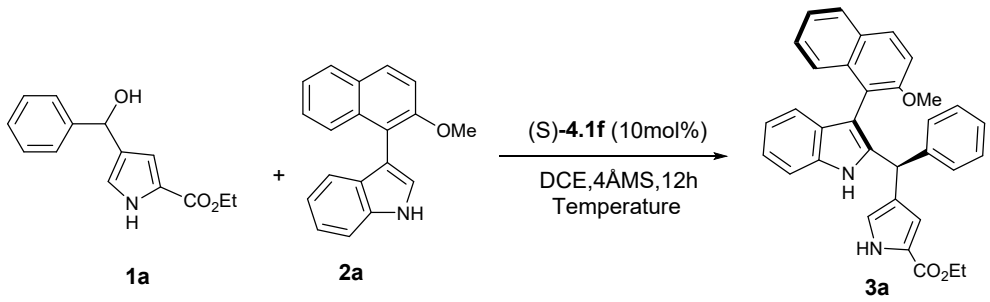


Entry	Additive	Yield(%)[b]	dr[d]	ee(%)[c]
1	3 Å MS	83	88:12	88
2	**4 Å MS**	**85**	**87:13**	**89**

3	5 Å MS	80	85:15	86
4	Na_2SO_4	67	86:14	82
5	$MgSO_4$	72	85:15	80
6	3 ÅMS[e]	87	88:12	84
7	4 Å MS[e]	78	88:12	86
8	5 Å MS[e]	80	86:14	85

[a] Reaction conditions: 1a (0.05 mmol), 2a (0.06 mmol), (*S*)-4.1f (10 mol%) and additive(80 mg) in 0.5 mL solvent for 12 h. [b] Isolated yields. [c] Determined by chiral HPLC analysis.[d] Determined by HPLC with C18 column. [e]120mg

Table S4. Optimization of the reaction temperature and catalyst loading [a]

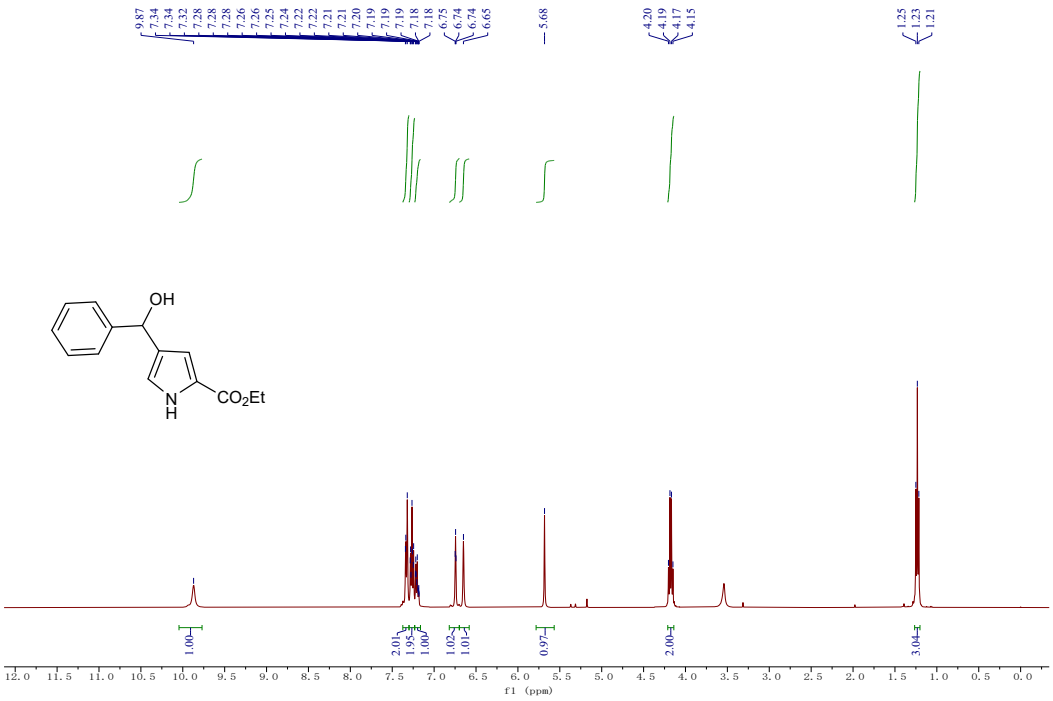


Entry	Temp.(°C)	Yield(%)[b]	dr[c]	ee(%)[d]
1[e]	**-20**	**88**	**85:15**	**92**
2[e]	-10	85	87:13	90
3	0	85	90:10	89
4	10	89	82:18	89
5	rt	84	85:15	86
6	40	55	72:28	63

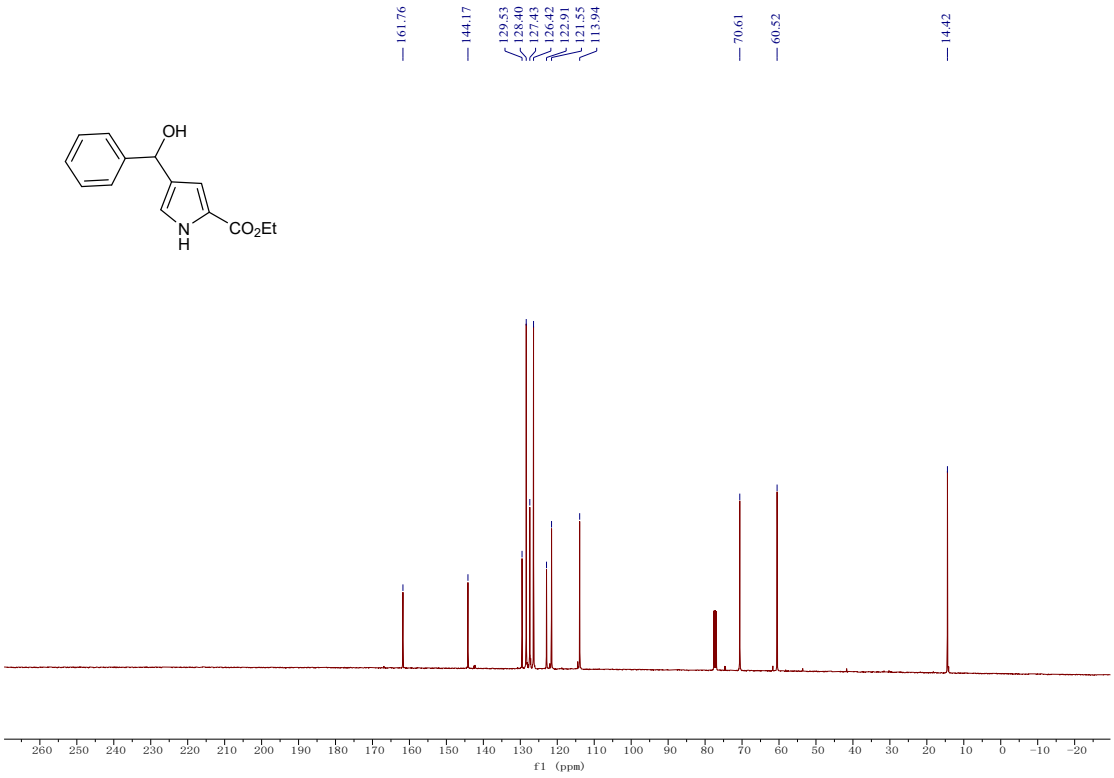
[a] Reaction conditions: **1a** (0.05 mmol), **2a** (0.06 mmol), (*S*)-**4.1f** (10 mol%) and 4 Å MS (80 mg) in 0.5 mL solvent for 12 h. [b] Isolated yields.[c] Determined by HPLC with C18 column. [d] Determined by chiral HPLC analysis. [e] 24 h

4. Copies of 1H NMR, 13C NMR and 19F NMR Spectra

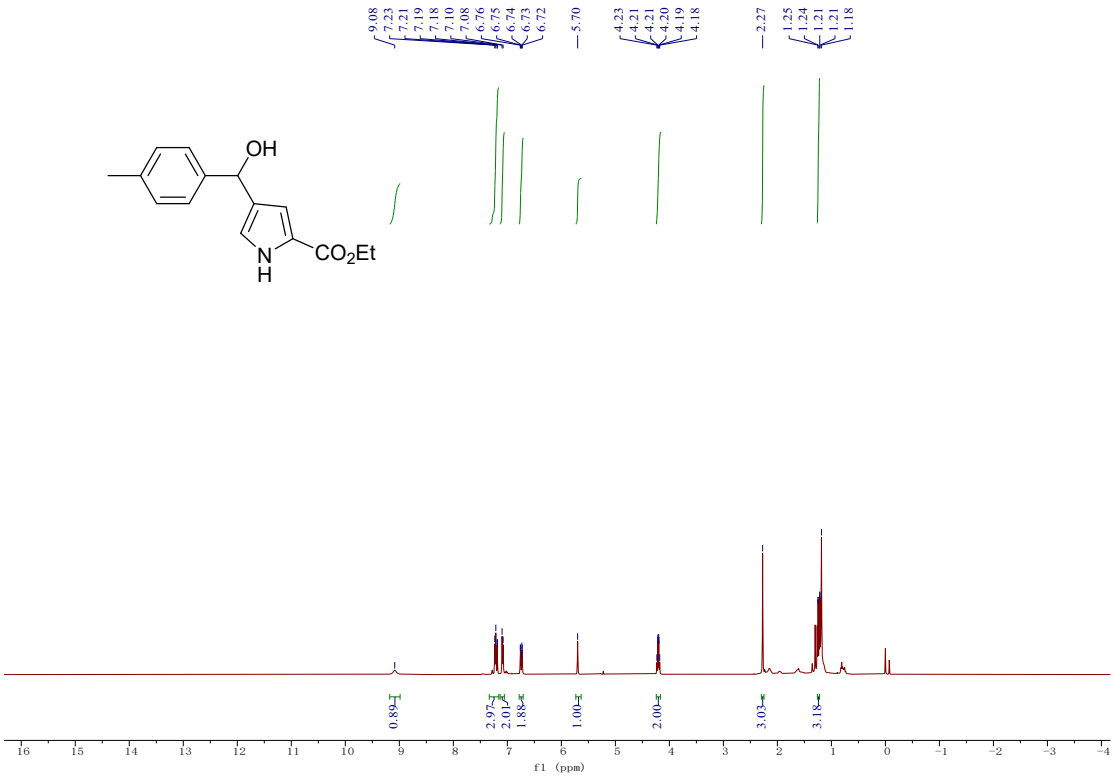
^{1}H NMR (400 MHz, $CDCl_3$) of **1a**



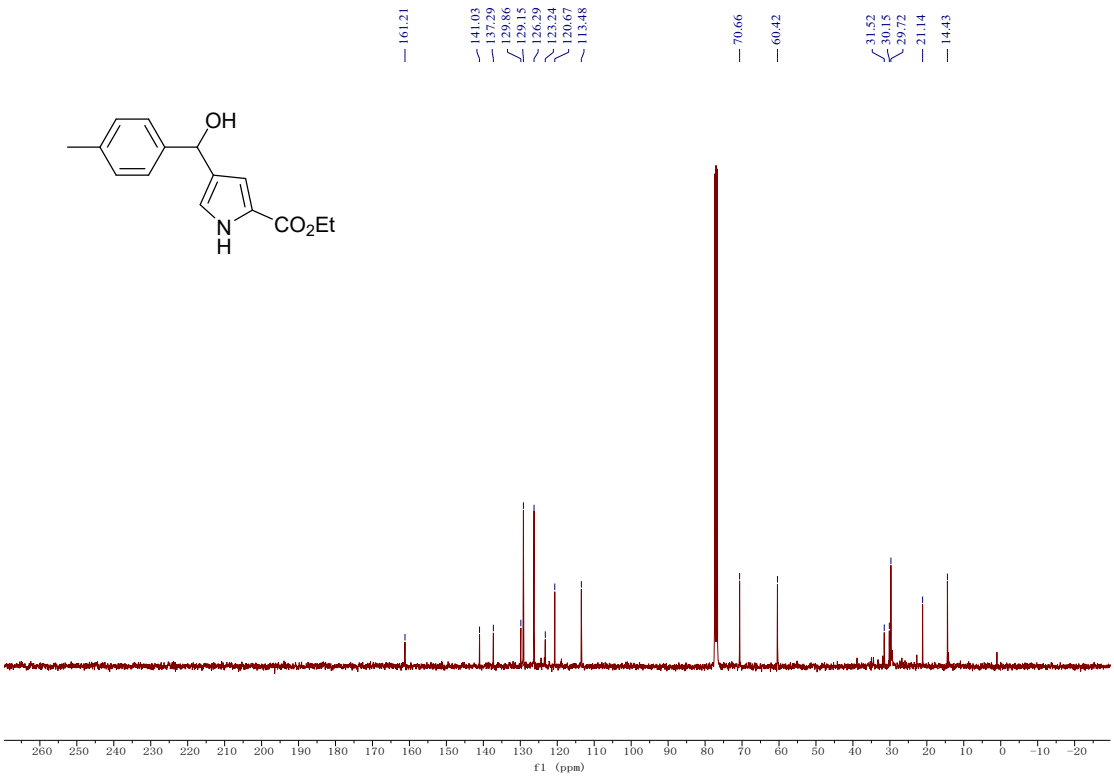
^{13}C NMR (101 MHz, $CDCl_3$) of **1a**



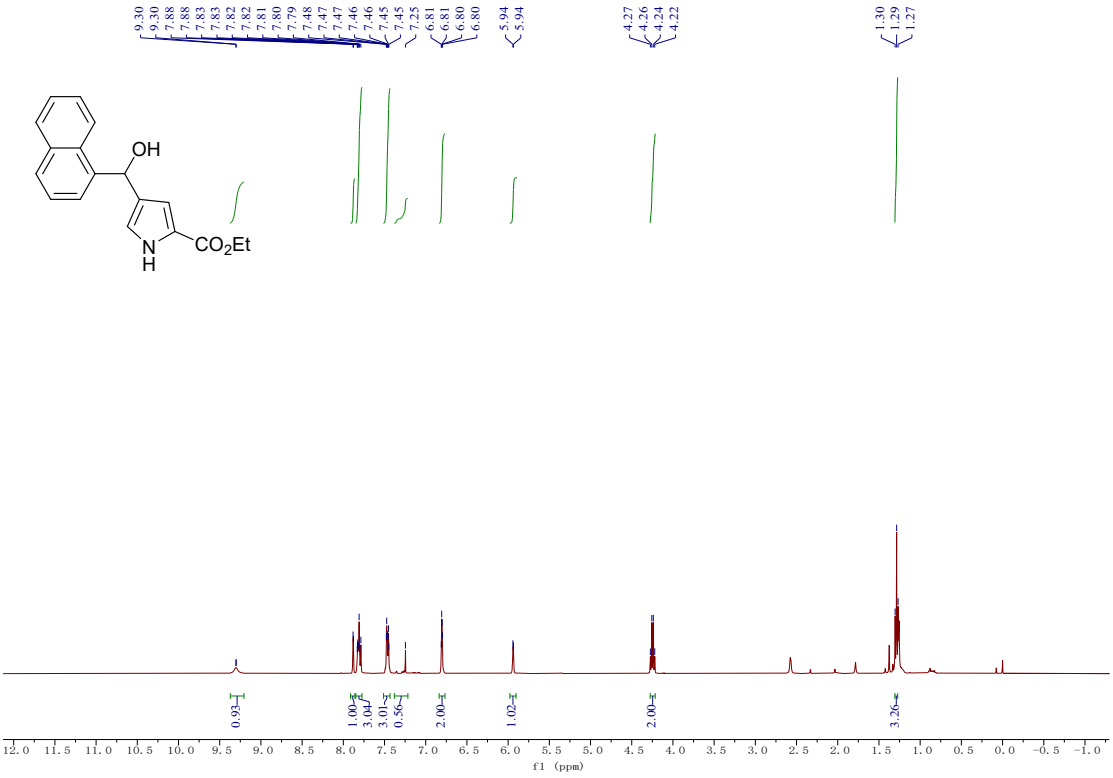
^{1}H NMR (400 MHz, $CDCl_3$) of **1d**



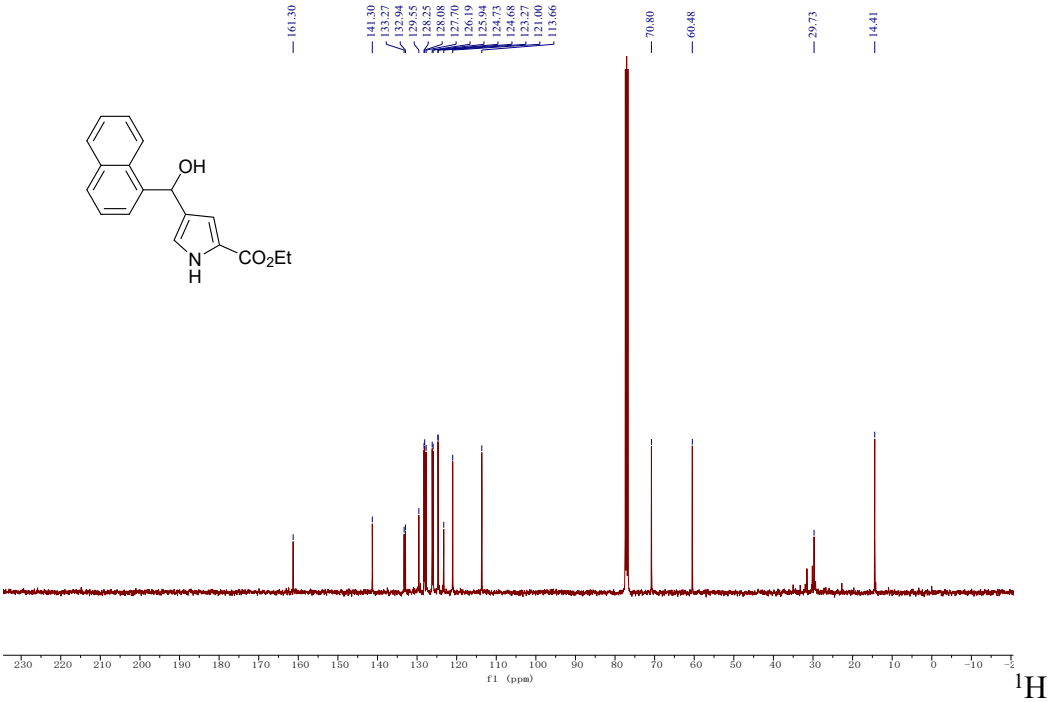
^{13}C NMR (101 MHz, $CDCl_3$) of **1d**



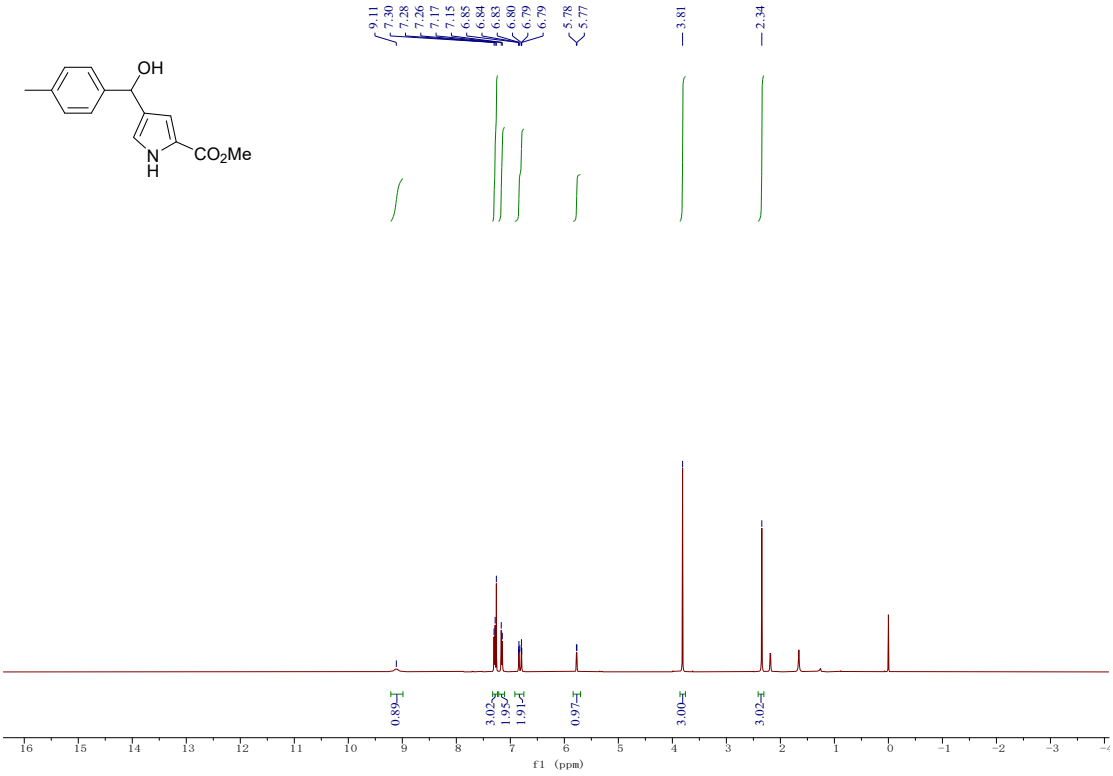
^{1}H NMR (400 MHz, $CDCl_3$) of **1e**



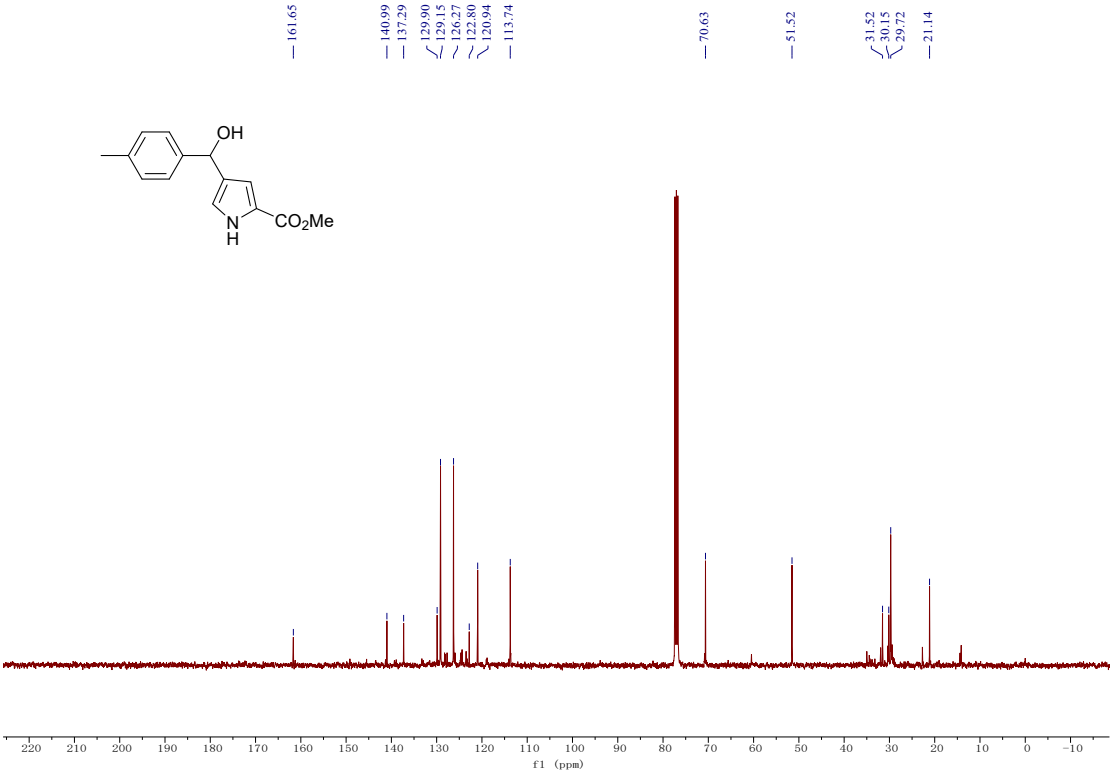
^{13}C NMR (101 MHz, $CDCl_3$) of **1e**



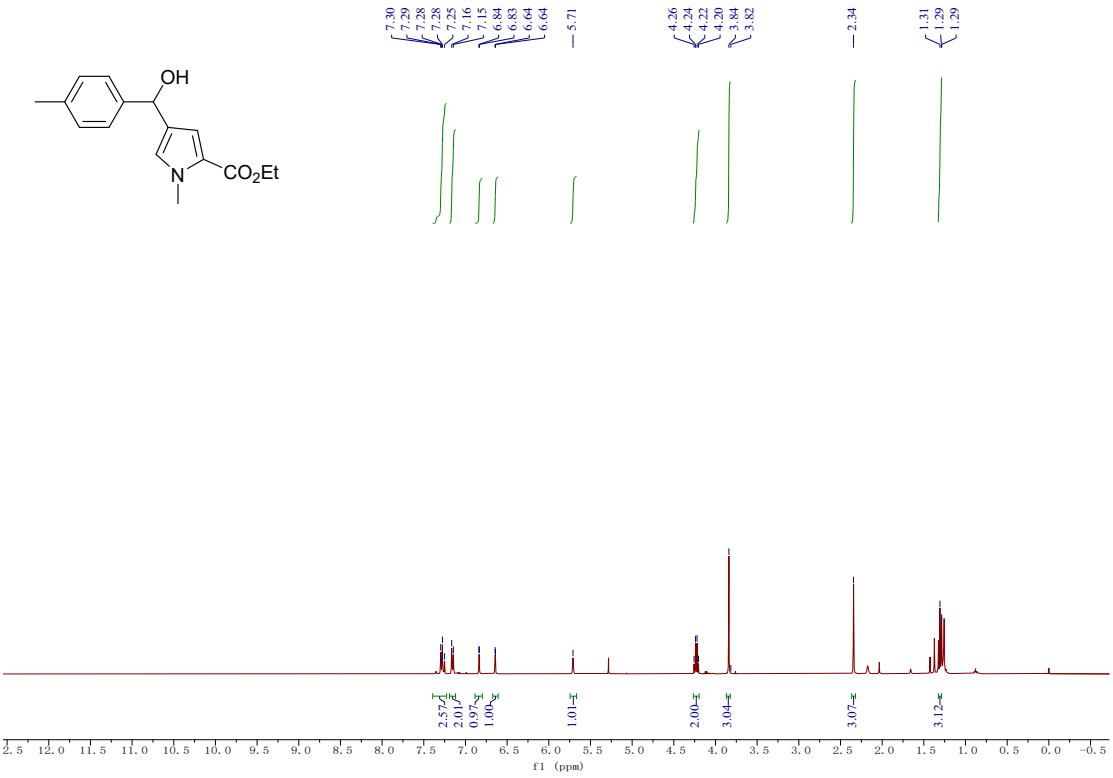
^{1}H NMR (400 MHz, $CDCl_3$) of **1f**



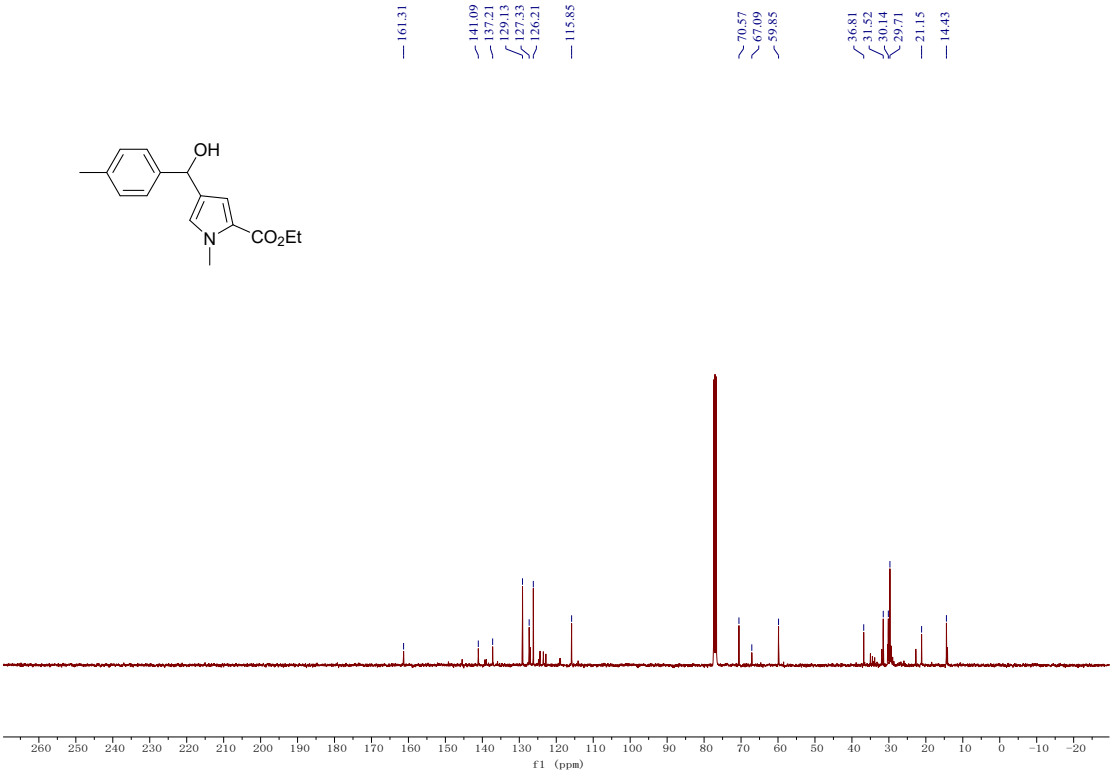
^{13}C NMR (101 MHz, $CDCl_3$) of **1f**



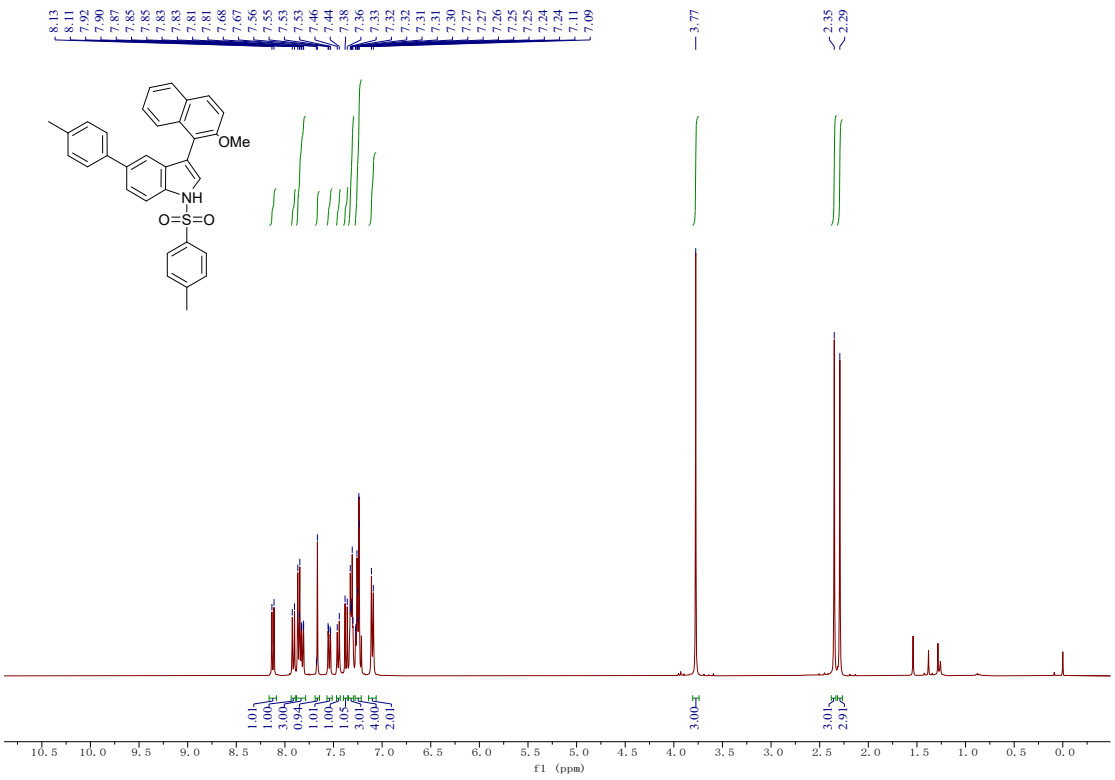
^{1}H NMR (400 MHz, $CDCl_3$) of **1g**



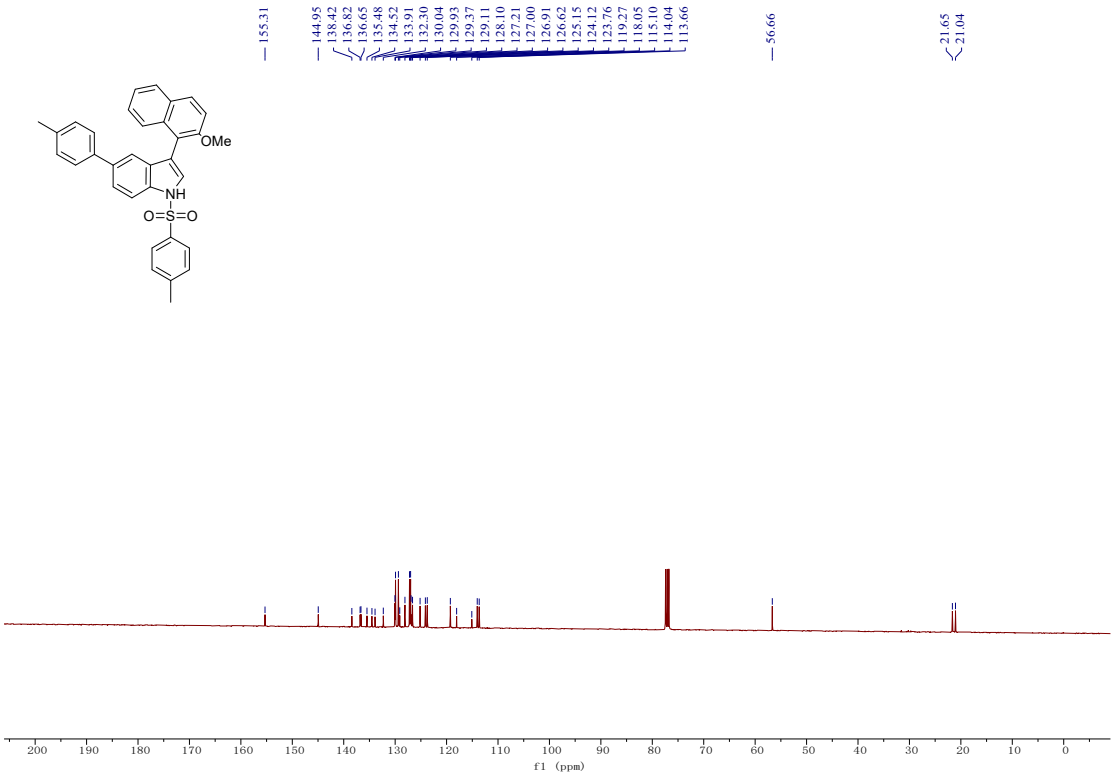
^{13}C NMR (101 MHz, $CDCl_3$) of **1g**



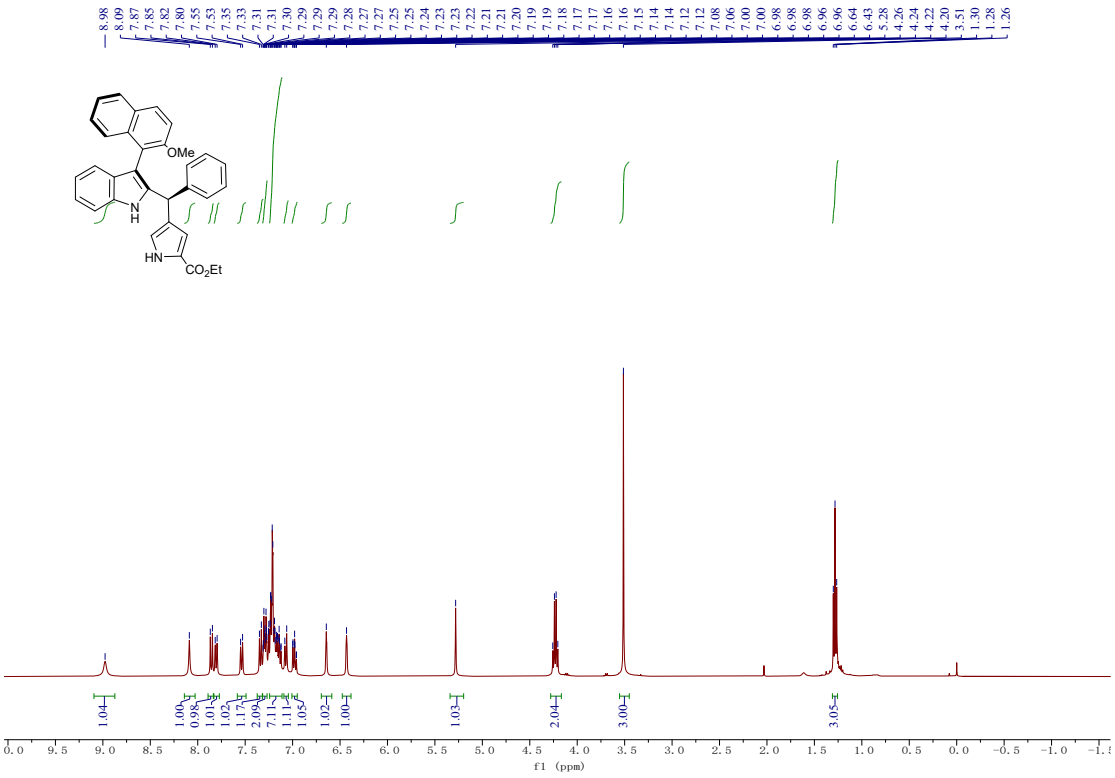
^{1}H NMR (400 MHz, $CDCl_3$) of **2j**



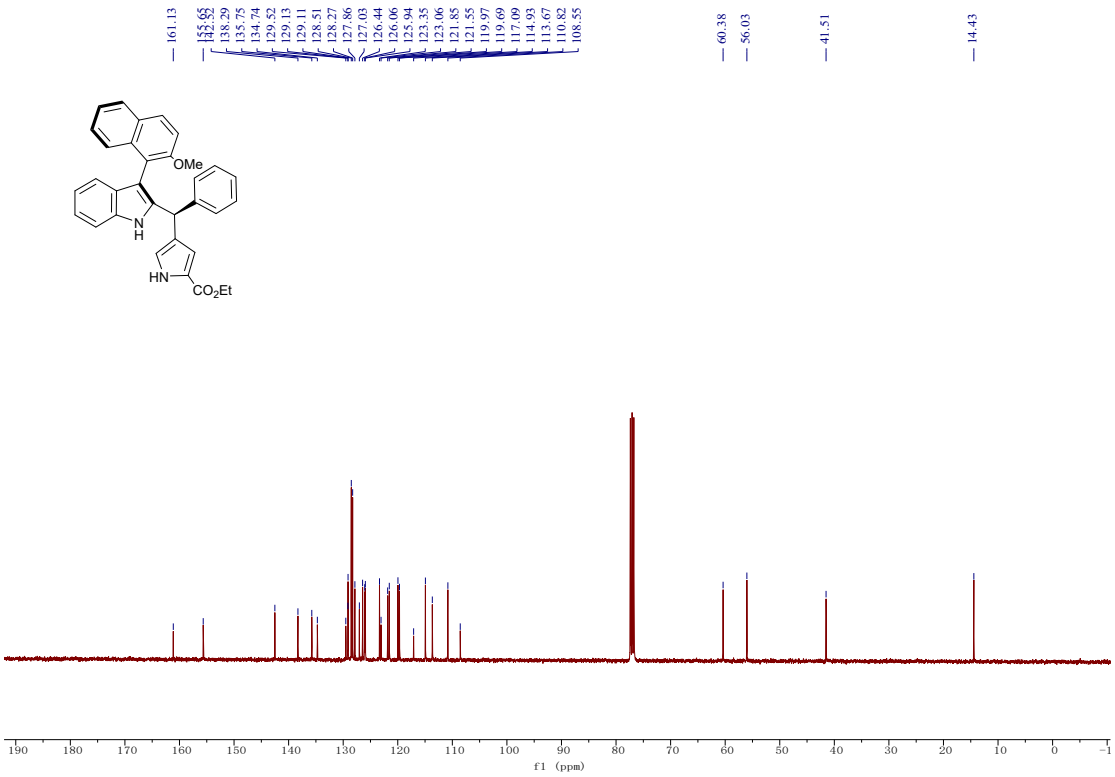
^{13}C NMR (101 MHz, $CDCl_3$) of **2j**



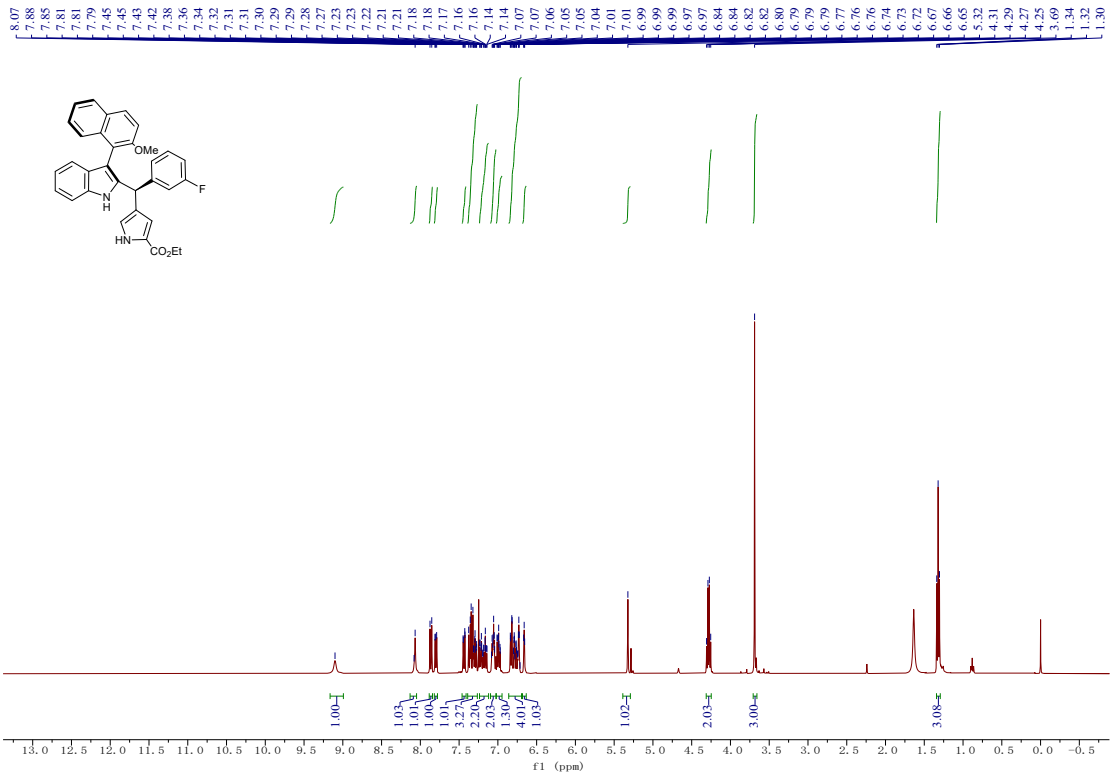
^{1}H NMR (400 ^{1}H NMR (400 MHz, $CDCl_3$) of **3a**



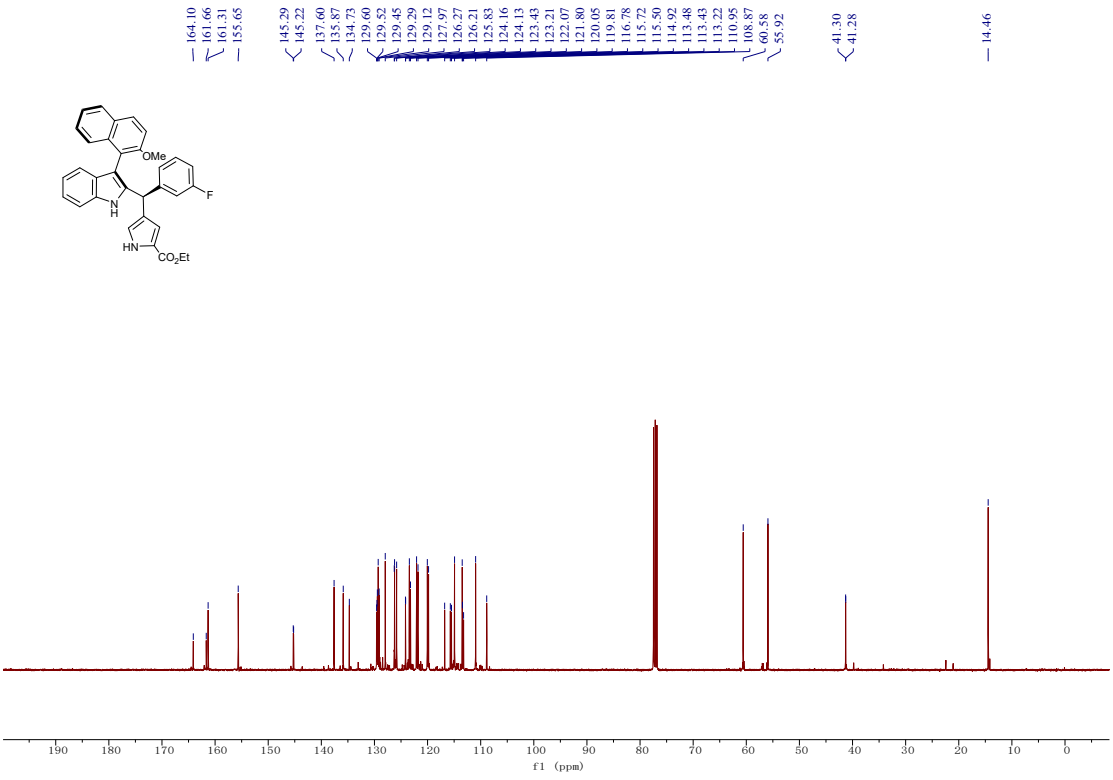
^{13}C NMR (101 MHz, $CDCl_3$) of **3a**



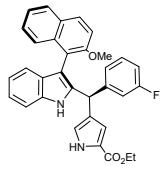
^{1}H NMR (400 MHz, $CDCl_3$) of **3b**



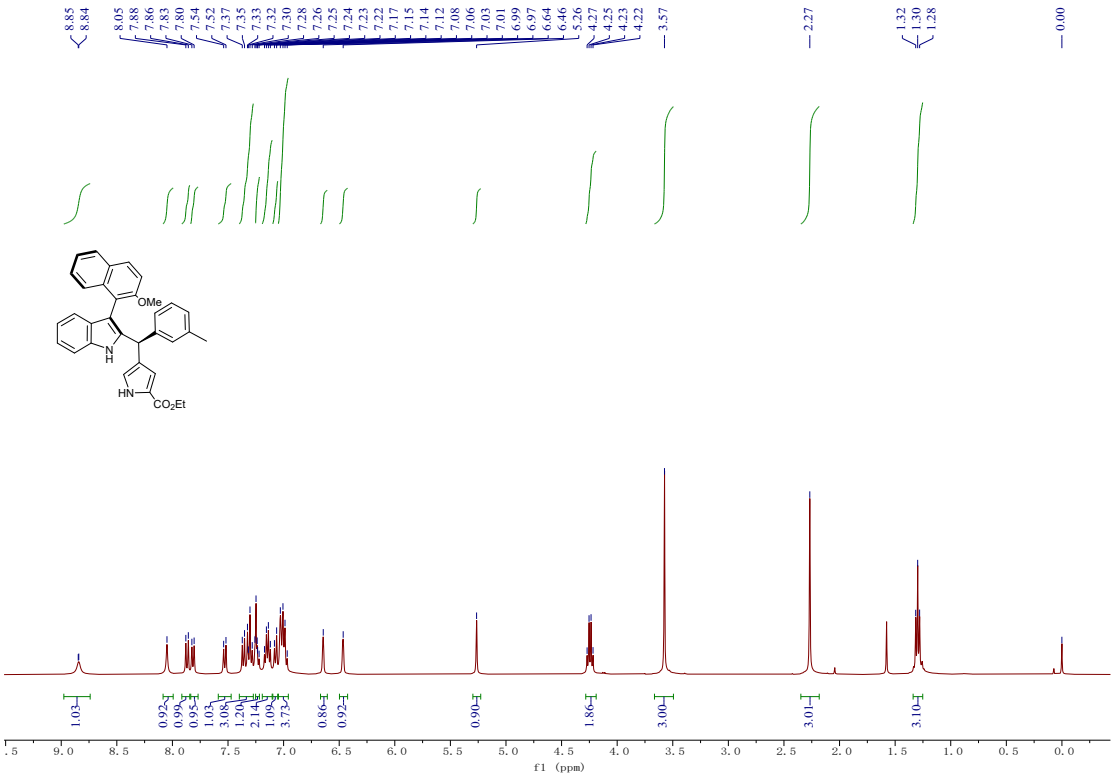
^{13}C NMR (101 MHz, $CDCl_3$) of **3b**



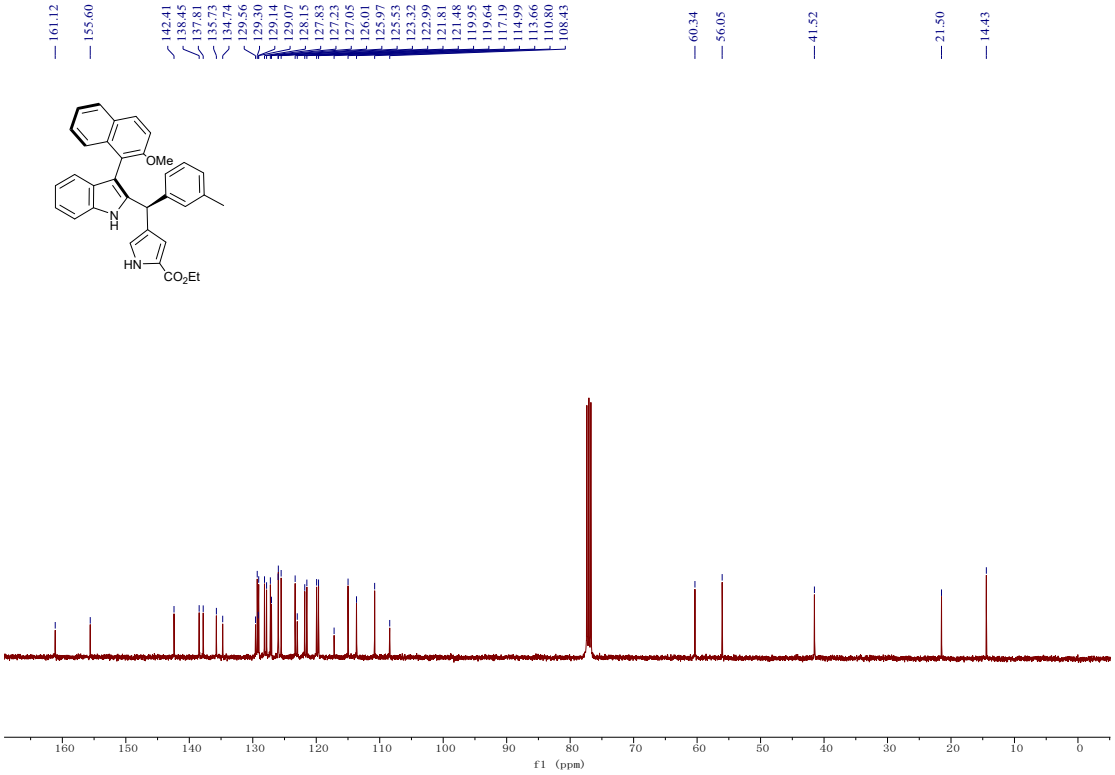
^{19}F NMR (376 MHz, $CDCl_3$) of **3b**



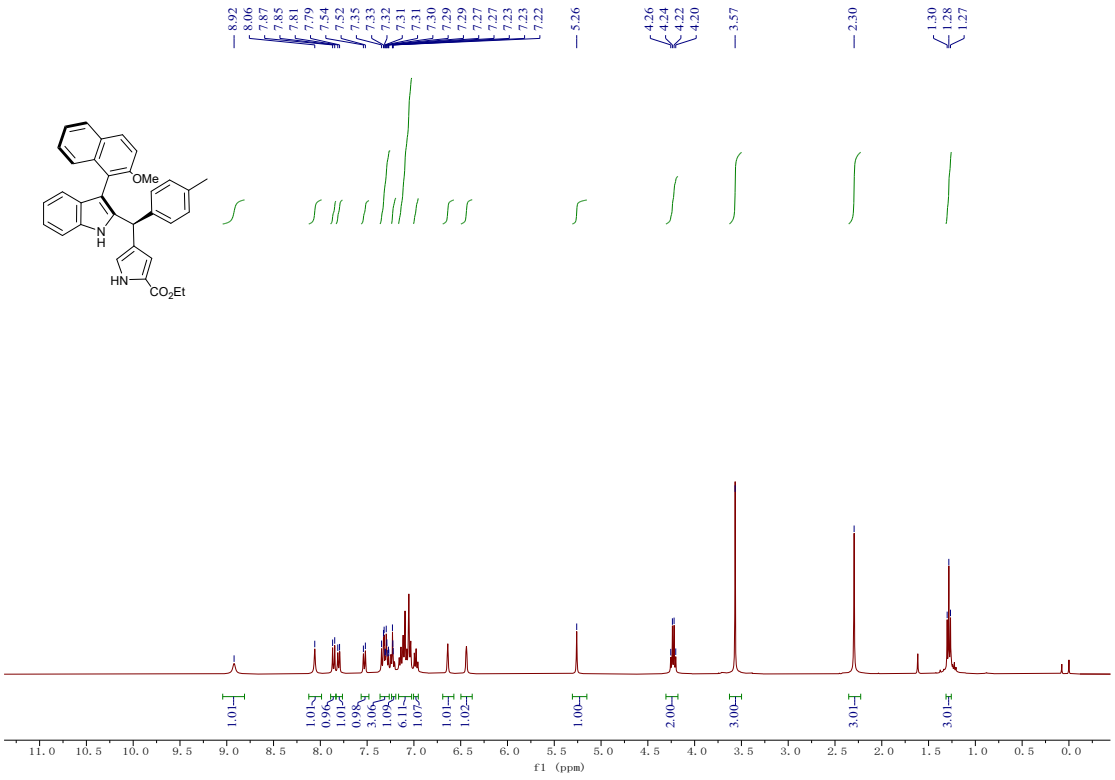
^{1}H NMR (400 MHz, $CDCl_3$) of **3c**



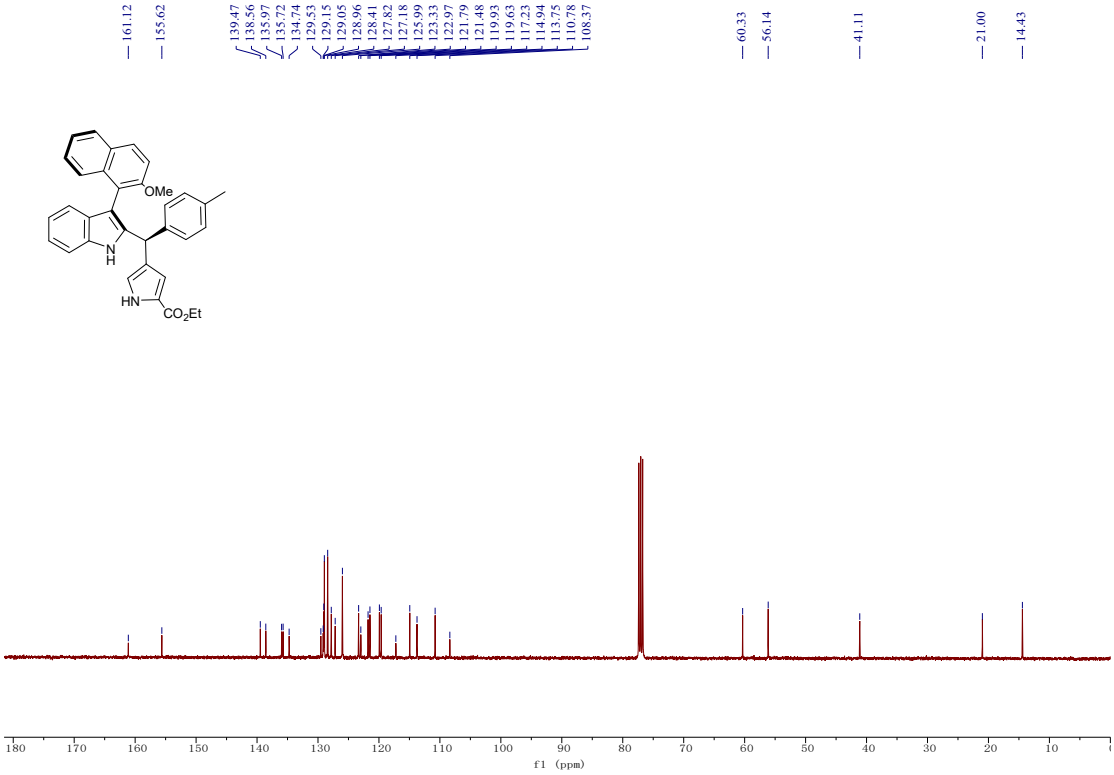
^{13}C NMR (101 MHz, $CDCl_3$) of **3c**



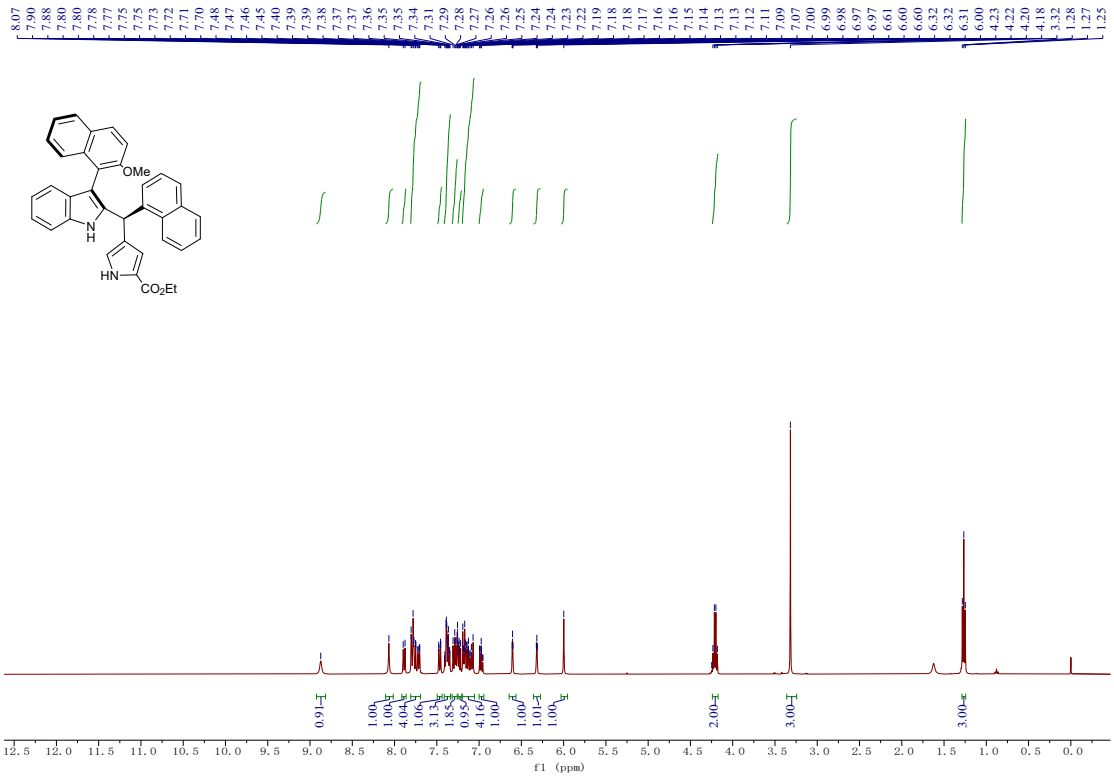
^{1}H NMR (400 MHz, $CDCl_3$) of **3d**



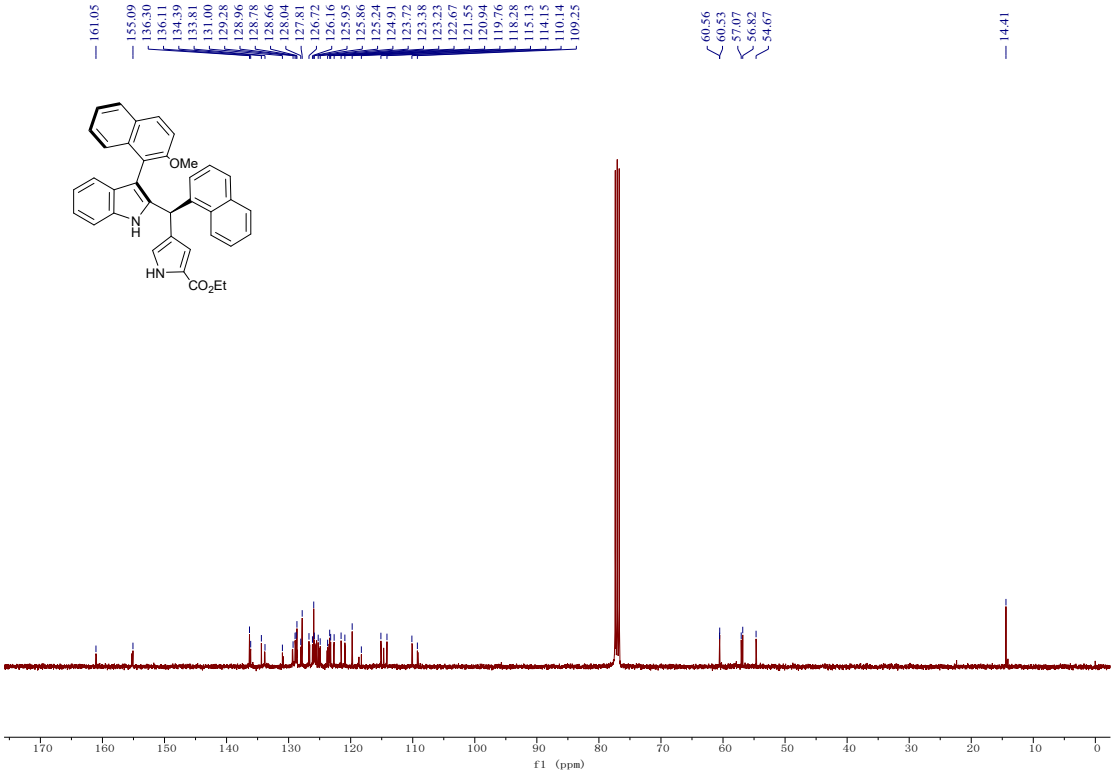
^{13}C NMR (101 MHz, $CDCl_3$) of **3d**



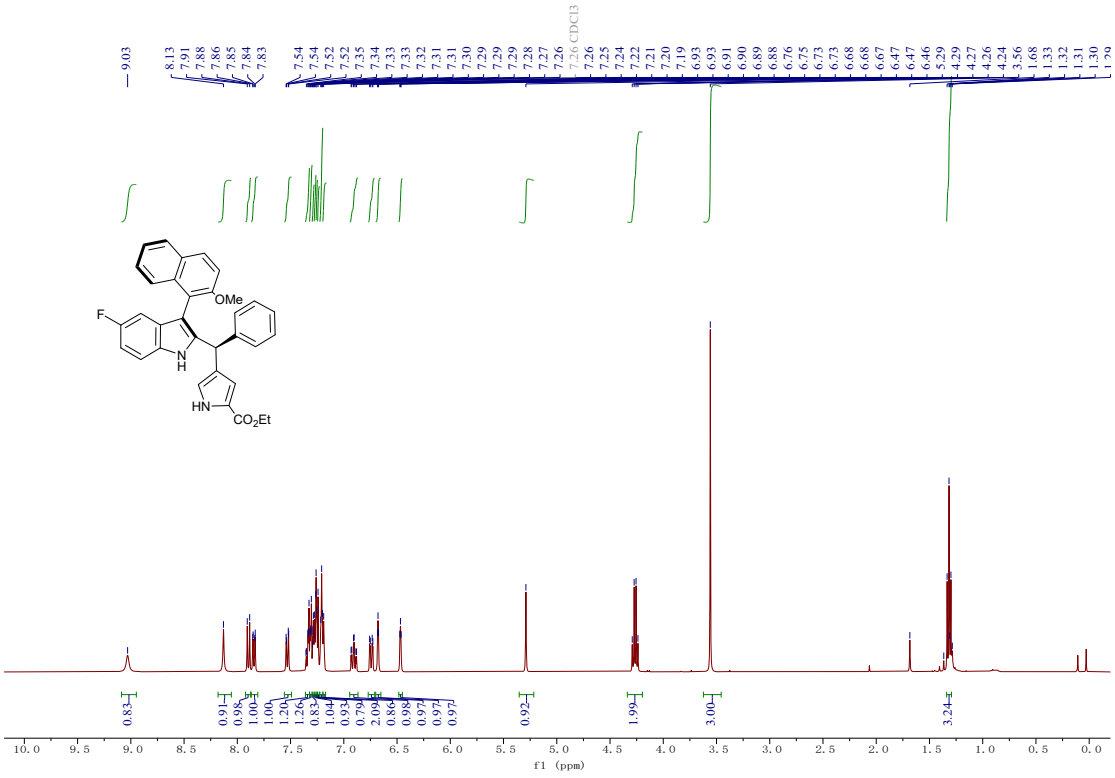
^{1}H NMR (400 MHz, $CDCl_3$) of **3e**



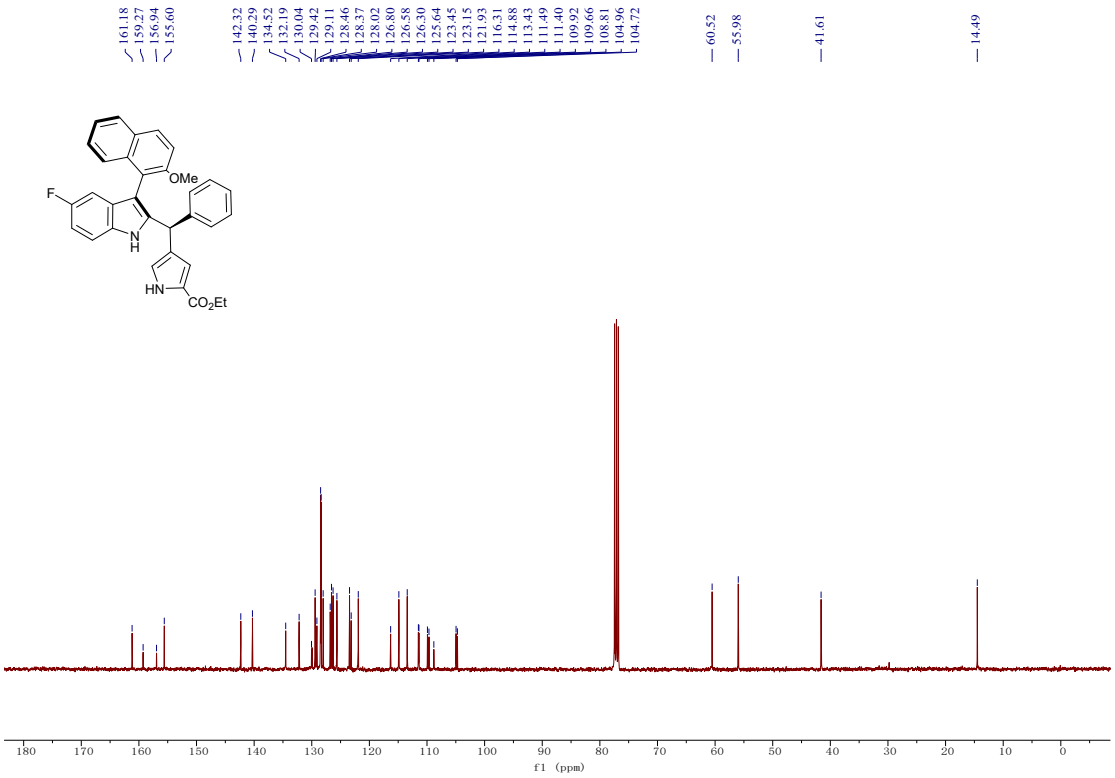
^{13}C NMR (101 MHz, $CDCl_3$) of **3e**



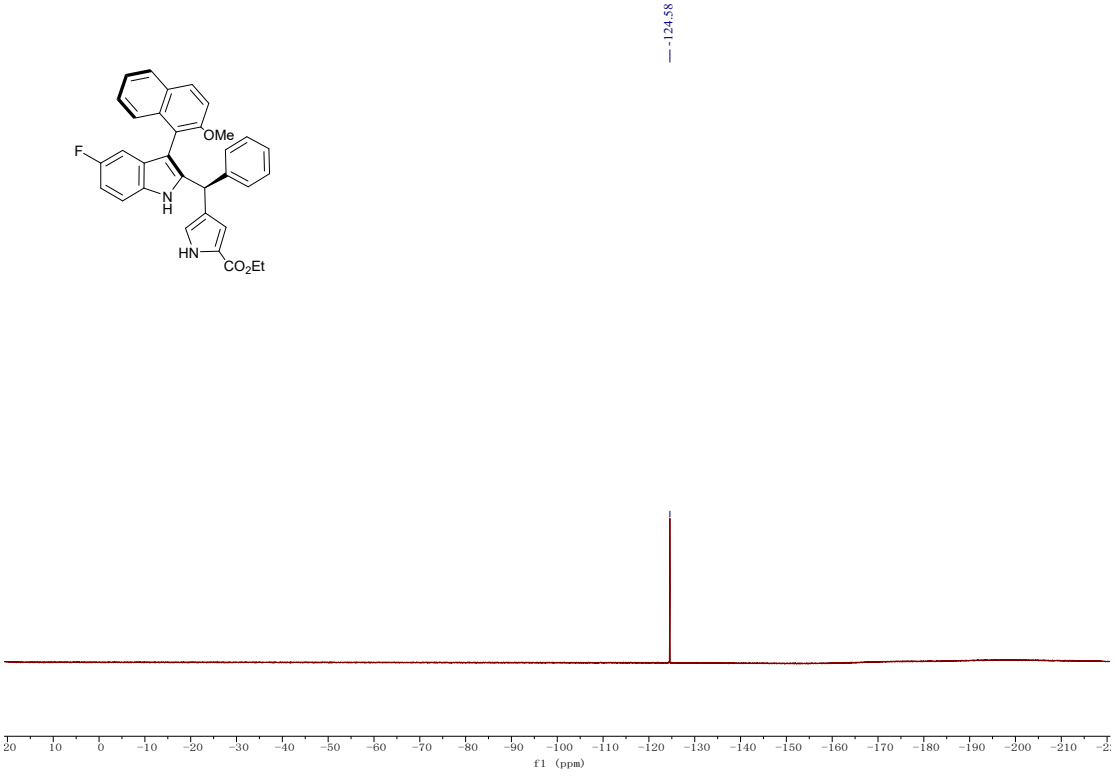
^{1}H NMR (400 MHz, $CDCl_3$) of **3f**



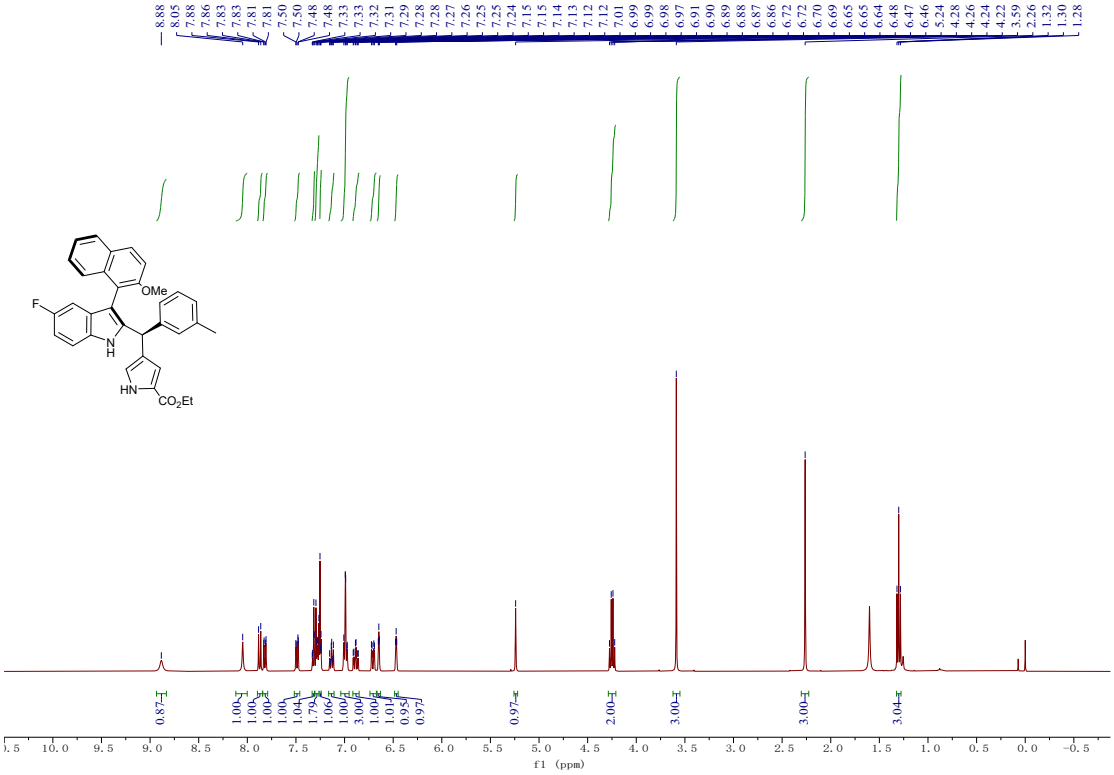
^{13}C NMR (101 MHz, $CDCl_3$) of **3f**



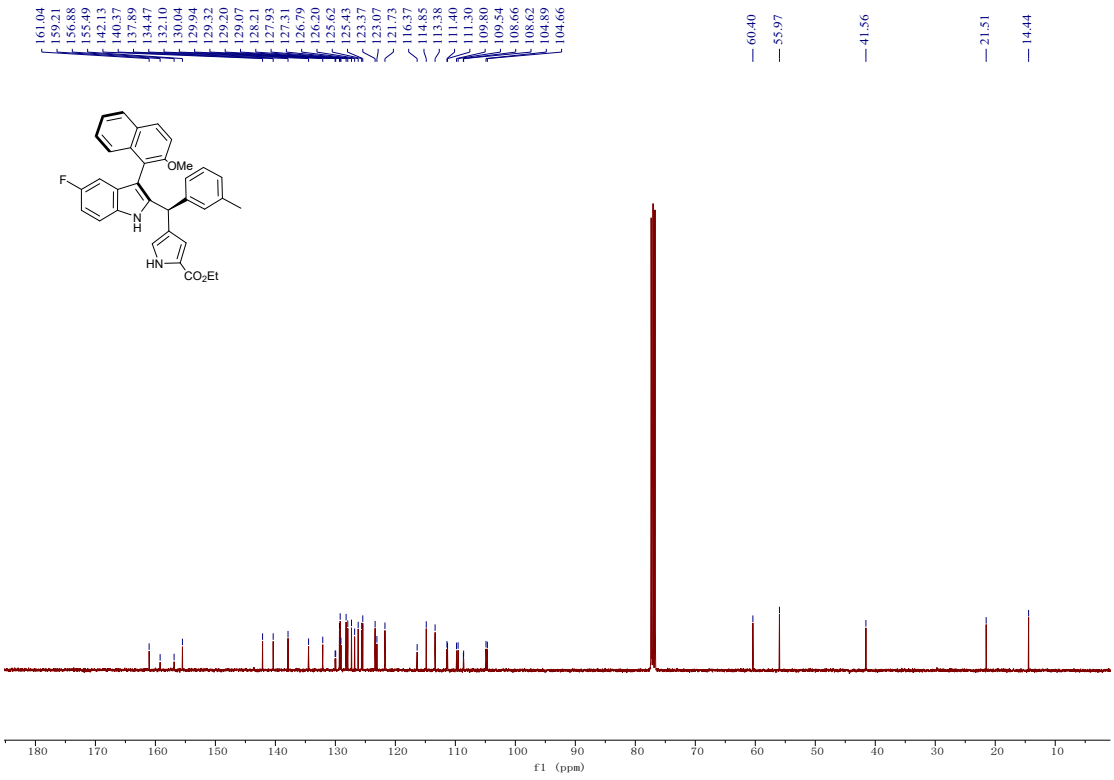
^{19}F NMR (376 MHz, $CDCl_3$) of **3f**



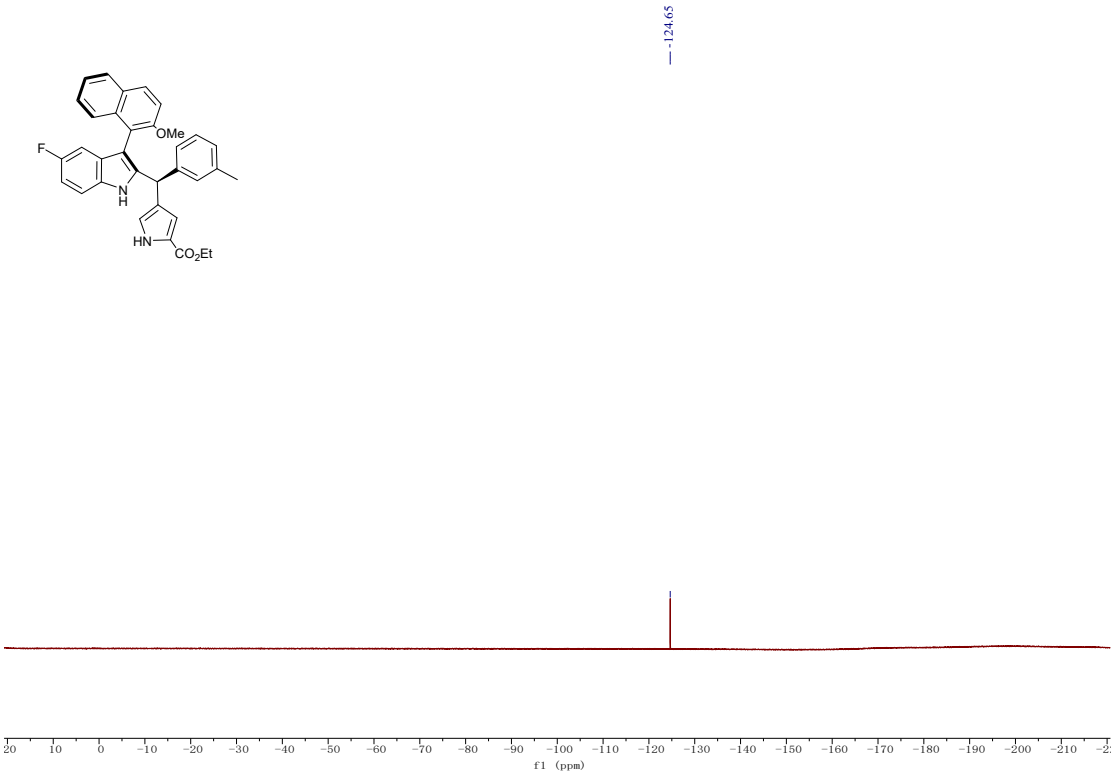
^{1}H NMR (400 MHz, $CDCl_3$) of **3g**



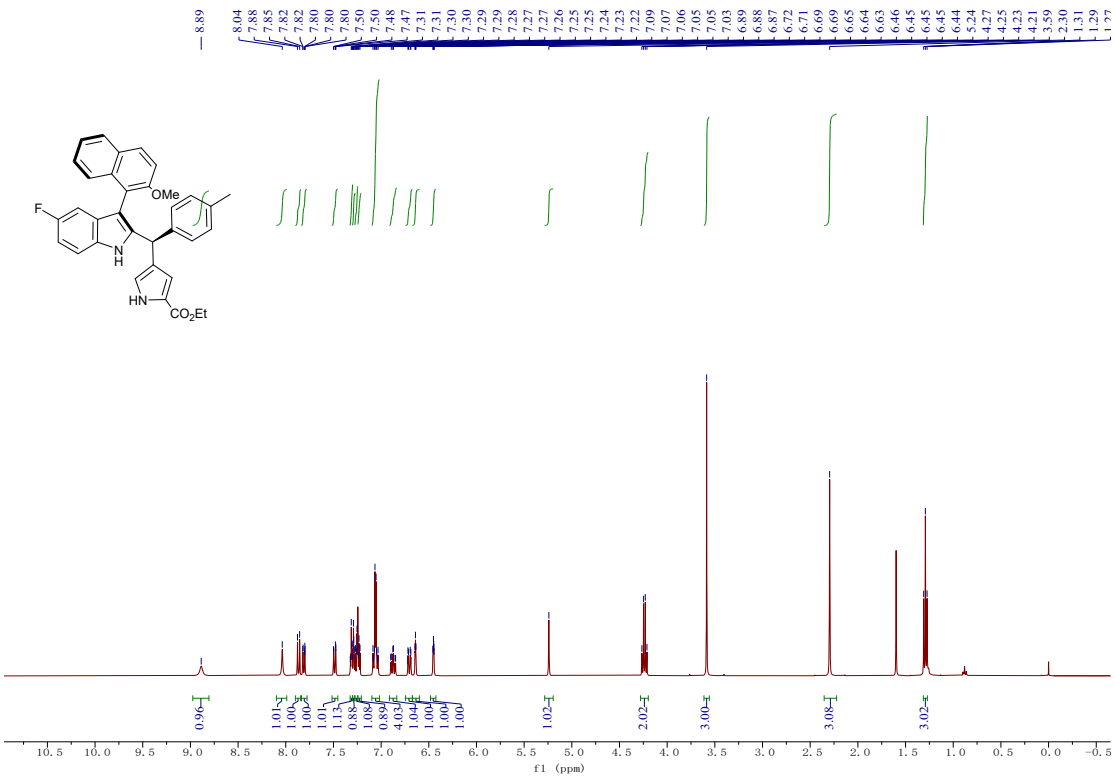
^{13}C NMR (101 MHz, $CDCl_3$) of **3g**



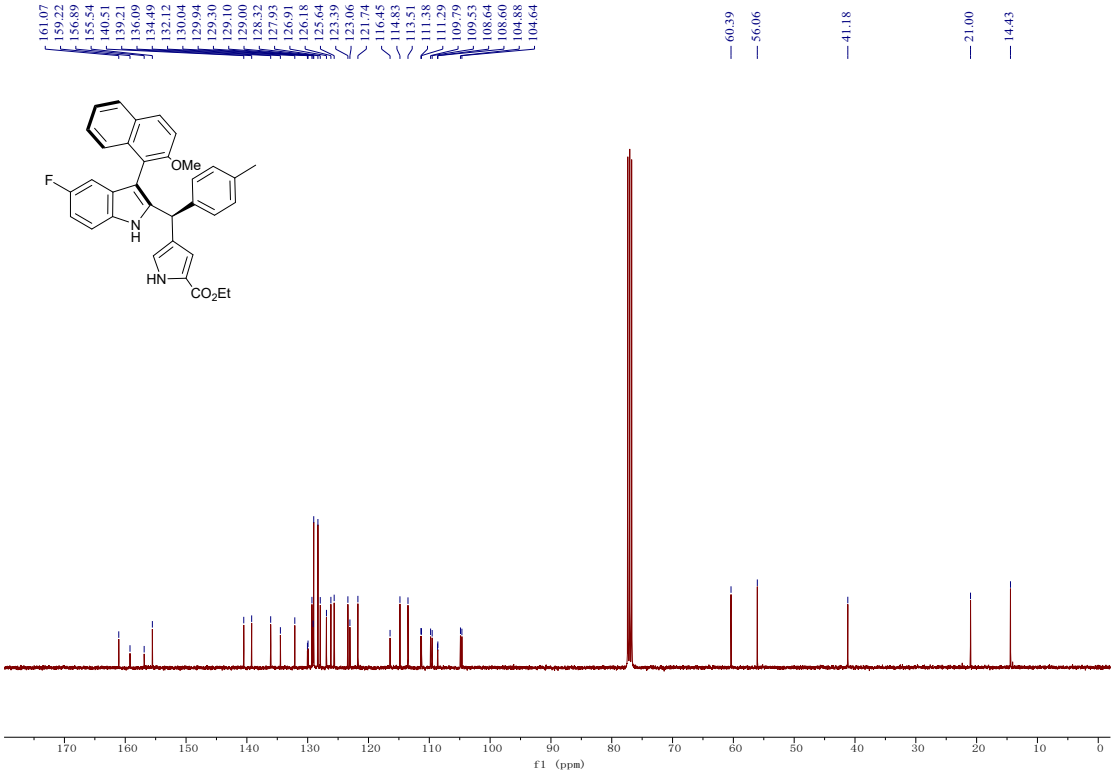
^{19}F NMR (376 MHz, $CDCl_3$) of **3g**



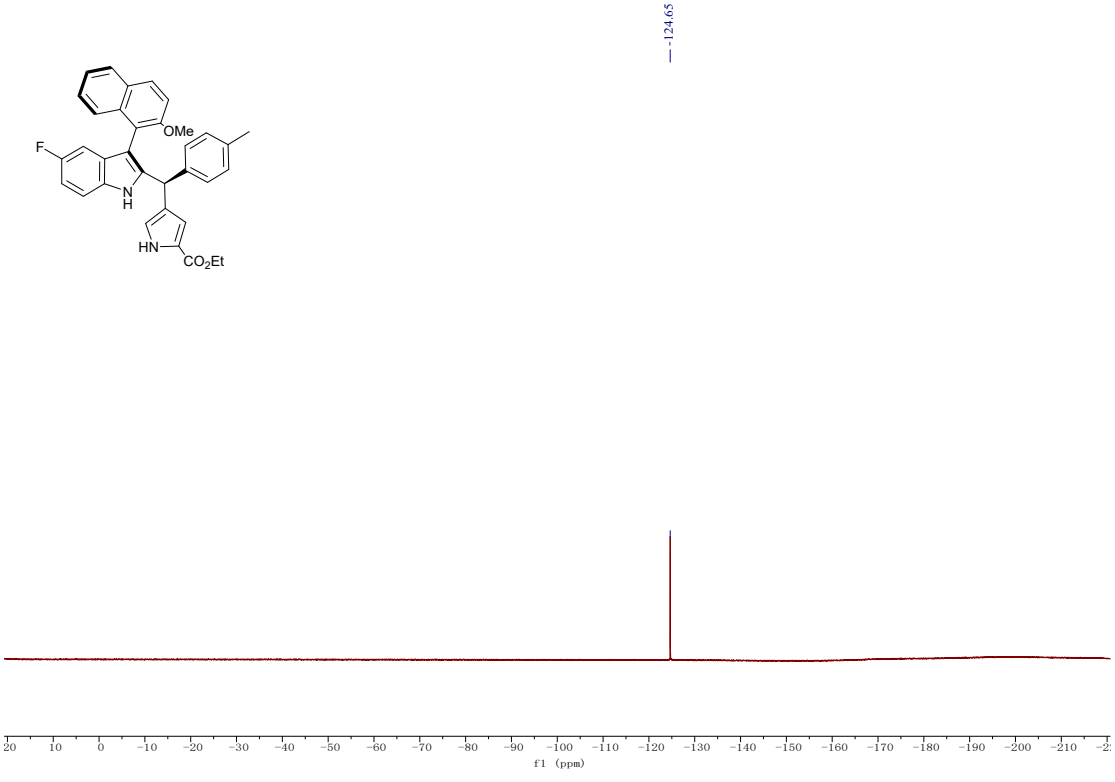
^{1}H NMR (400 MHz, $CDCl_3$) of **3h**



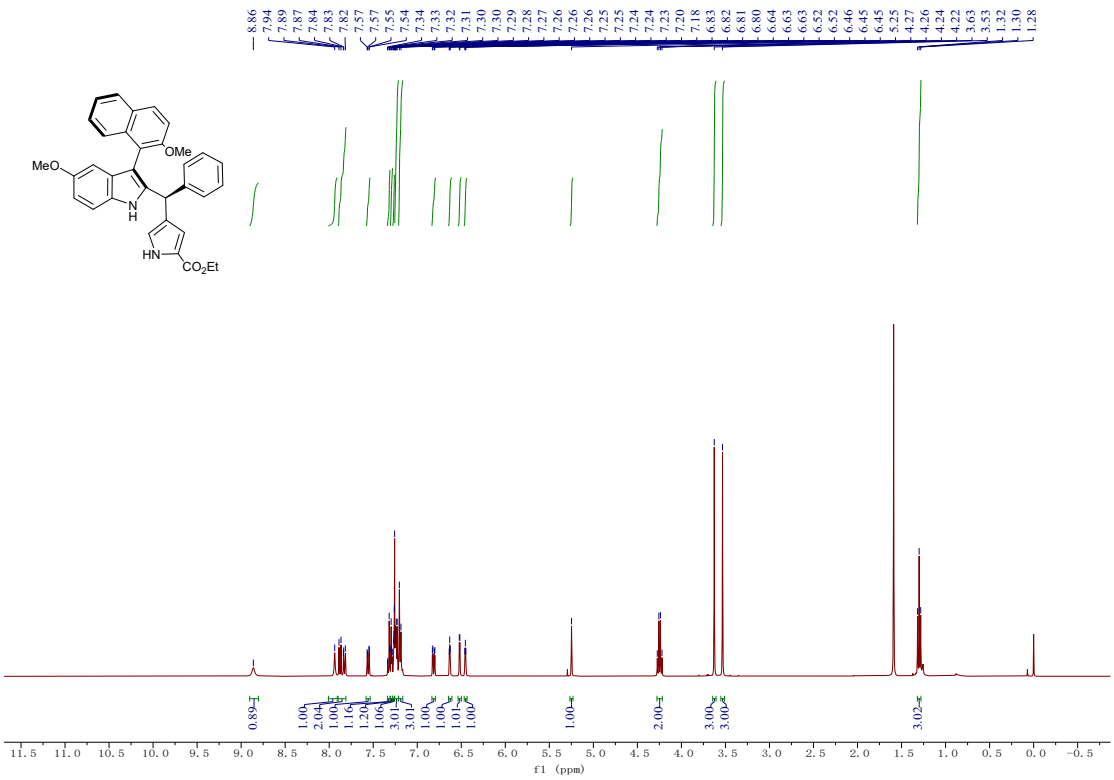
^{13}C NMR (101 MHz, $CDCl_3$) of **3h**



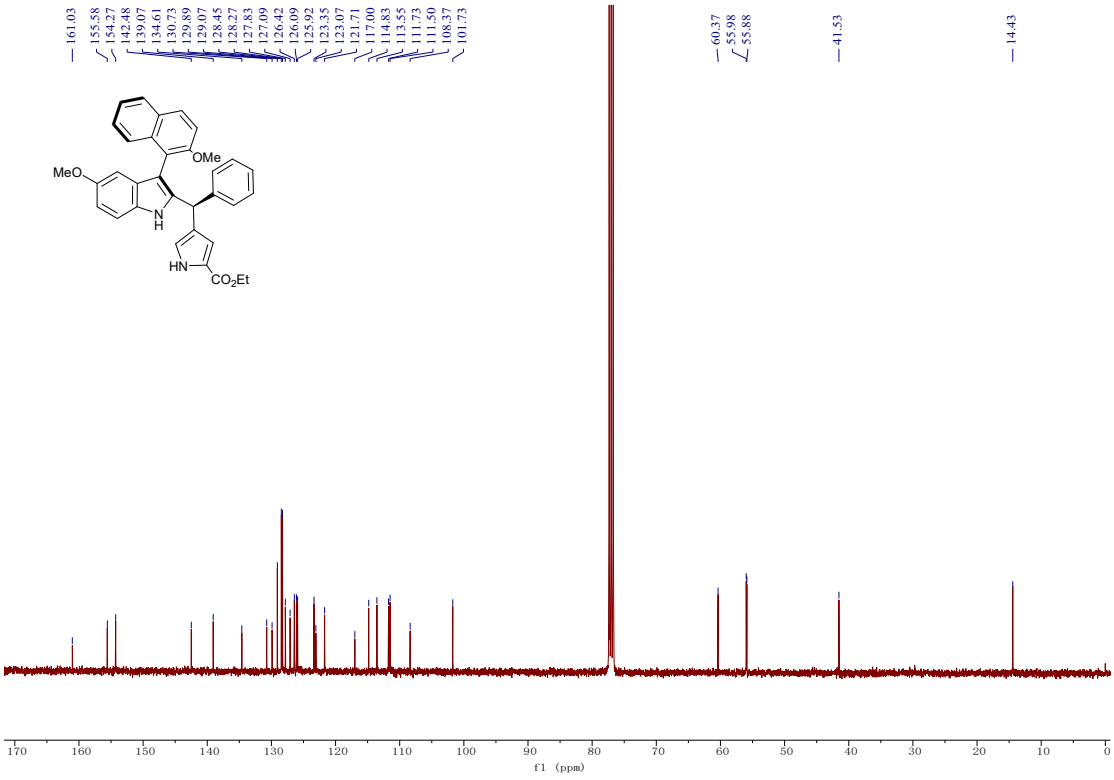
^{19}F NMR (376 MHz, $CDCl_3$) of **3h**



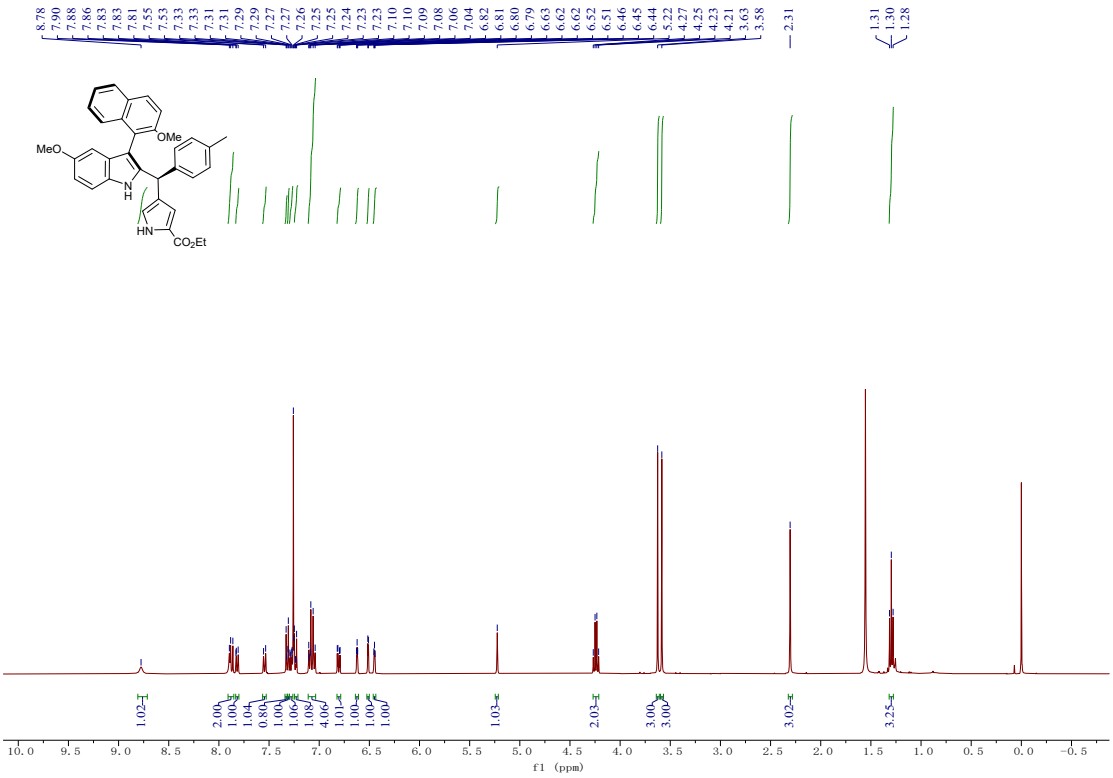
^{1}H NMR (400 MHz, $CDCl_3$) of **3i**



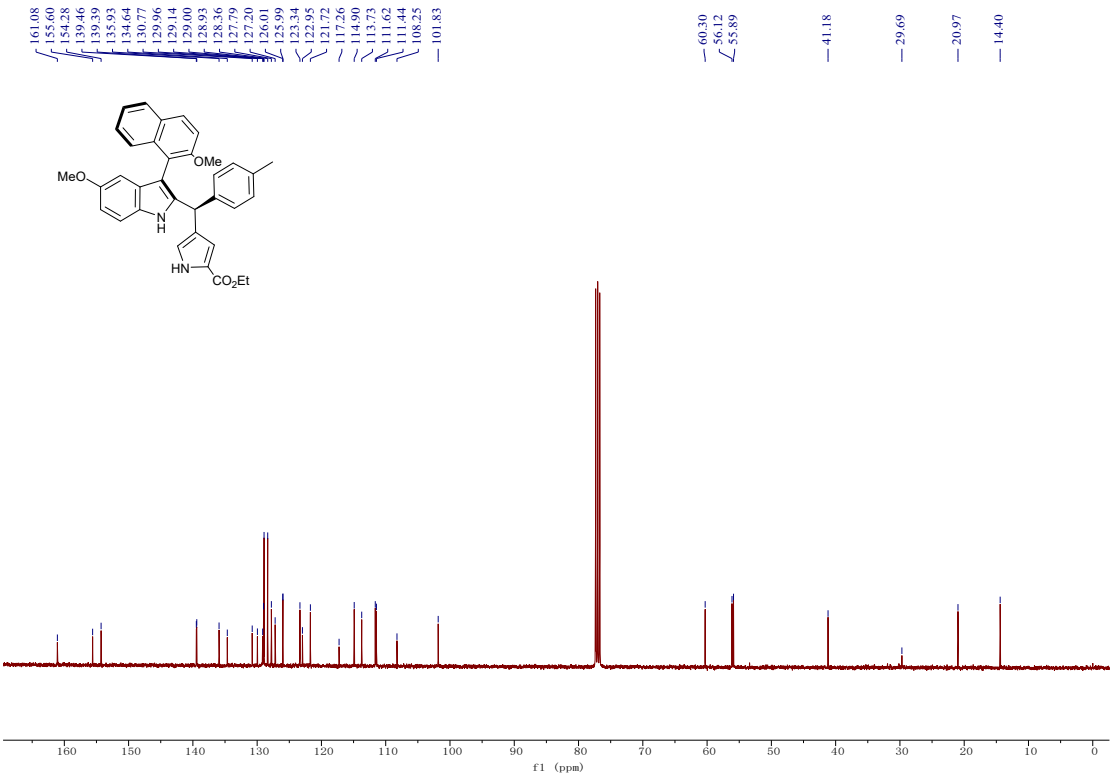
^{13}C NMR (101 MHz, $CDCl_3$) of **3i**



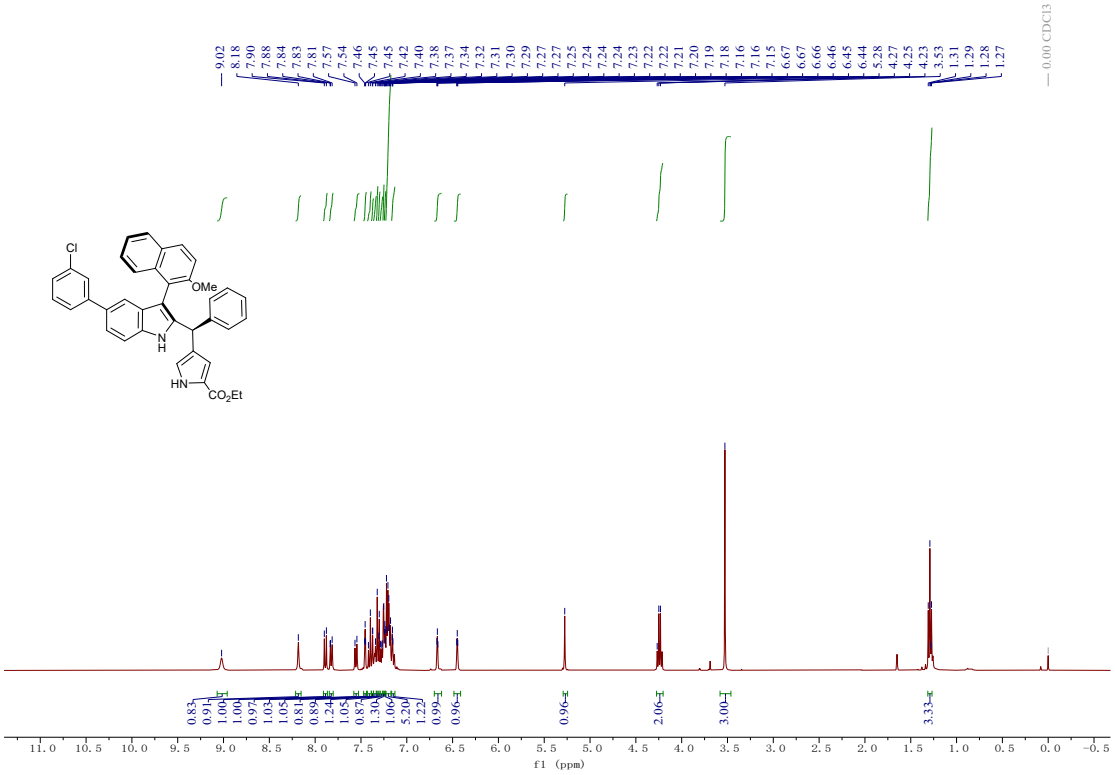
^{1}H NMR (400 MHz, $CDCl_3$) of **3j**



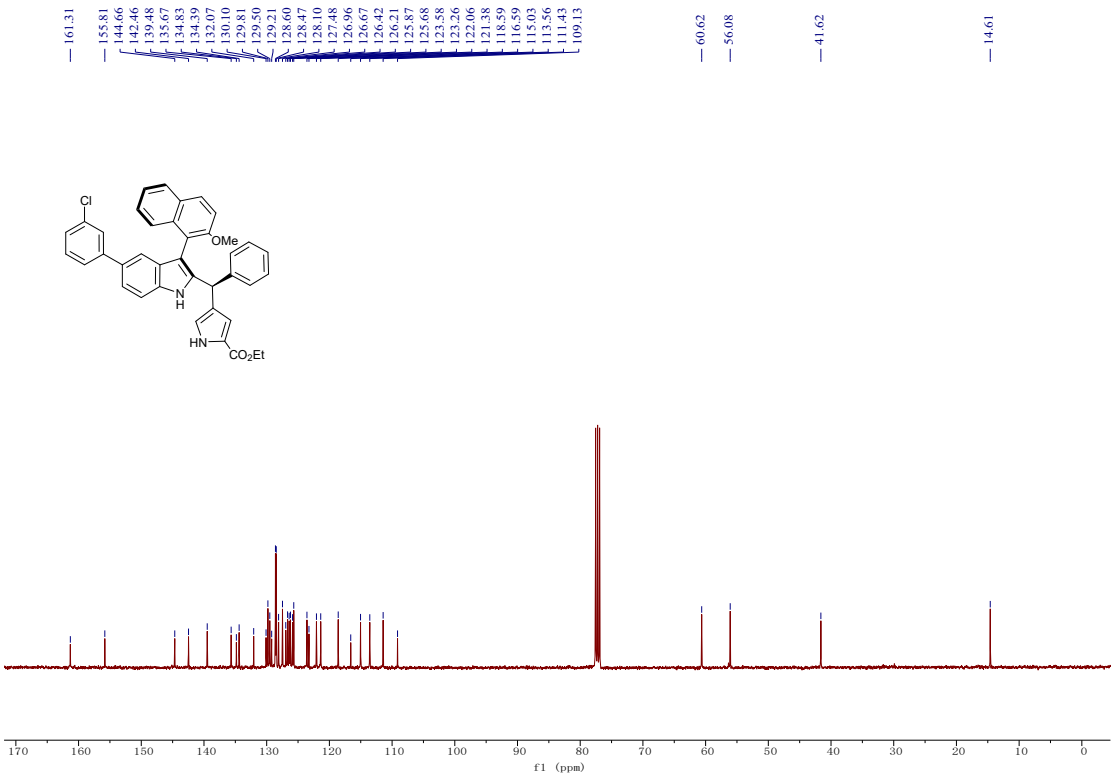
^{13}C NMR (101 MHz, $CDCl_3$) of **3j**



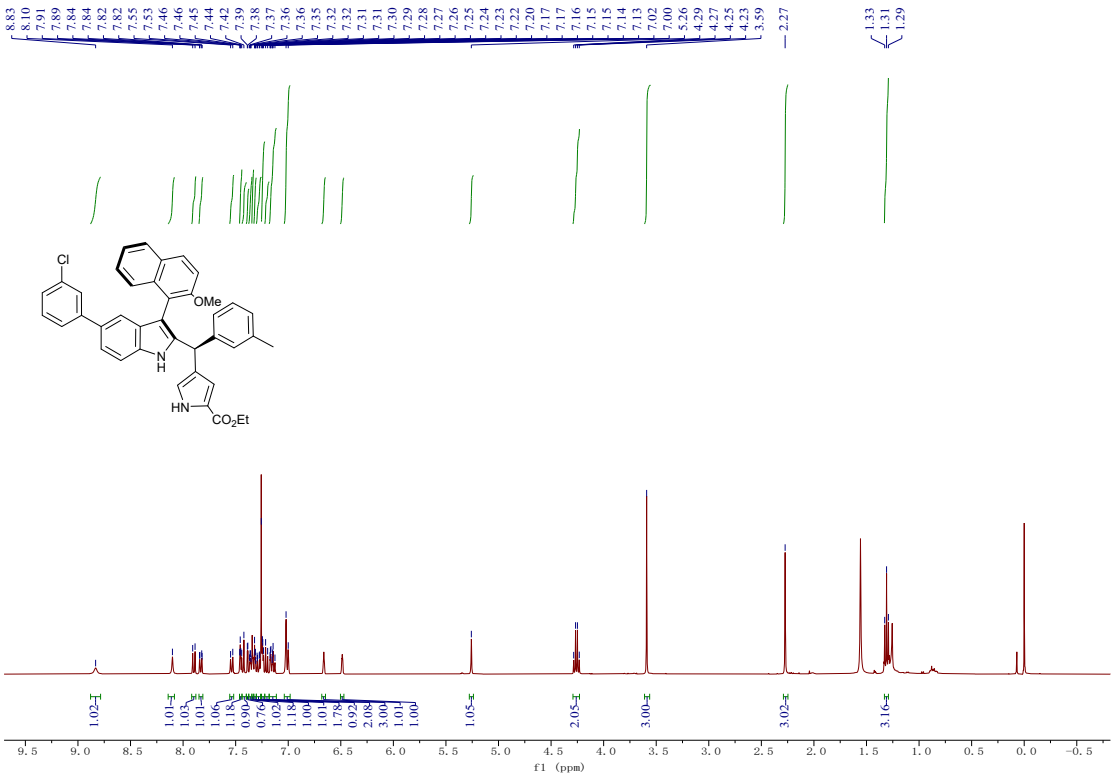
^{1}H NMR (400 MHz, $CDCl_3$) of **3k**



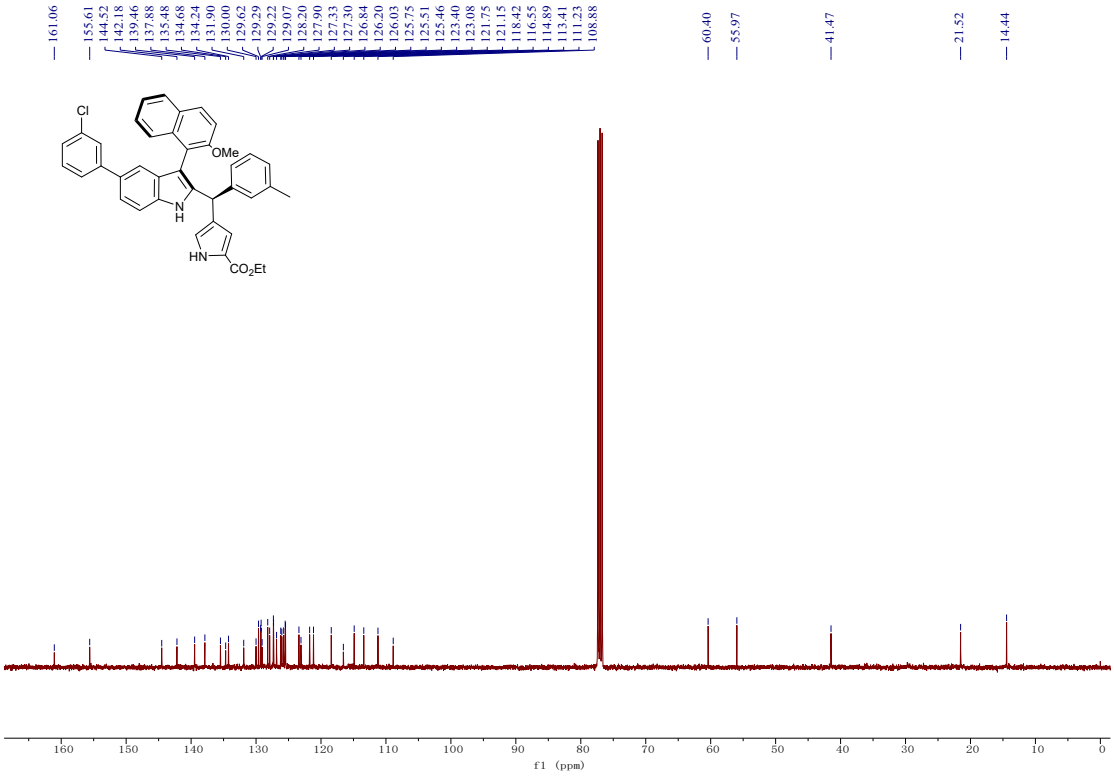
^{13}C NMR (101 MHz, $CDCl_3$) of **3k**



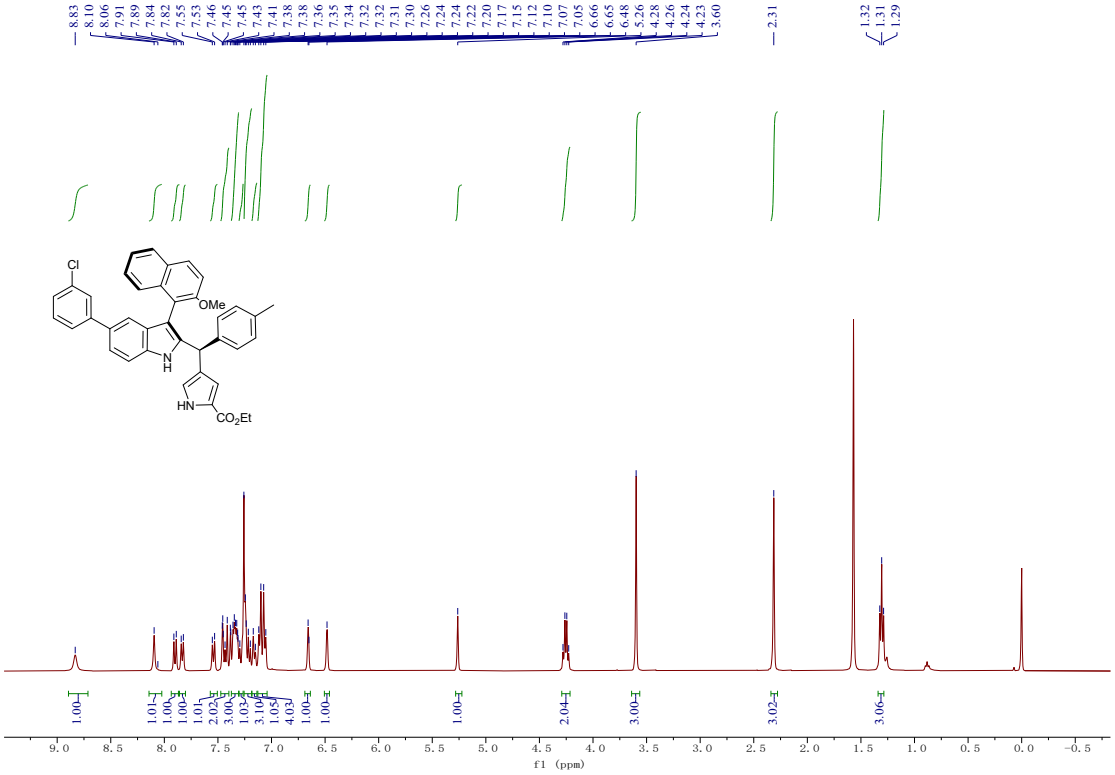
^{1}H NMR (400 MHz, $CDCl_3$) of **3l**



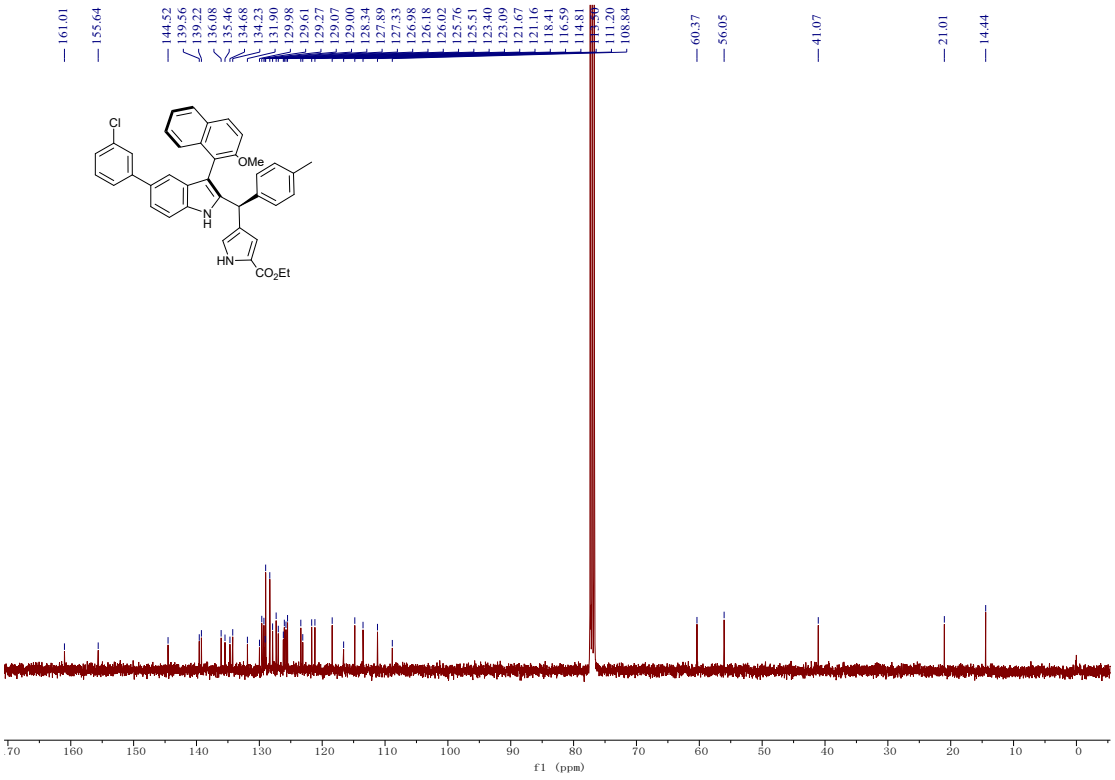
^{13}C NMR (101 MHz, $CDCl_3$) of **3l**



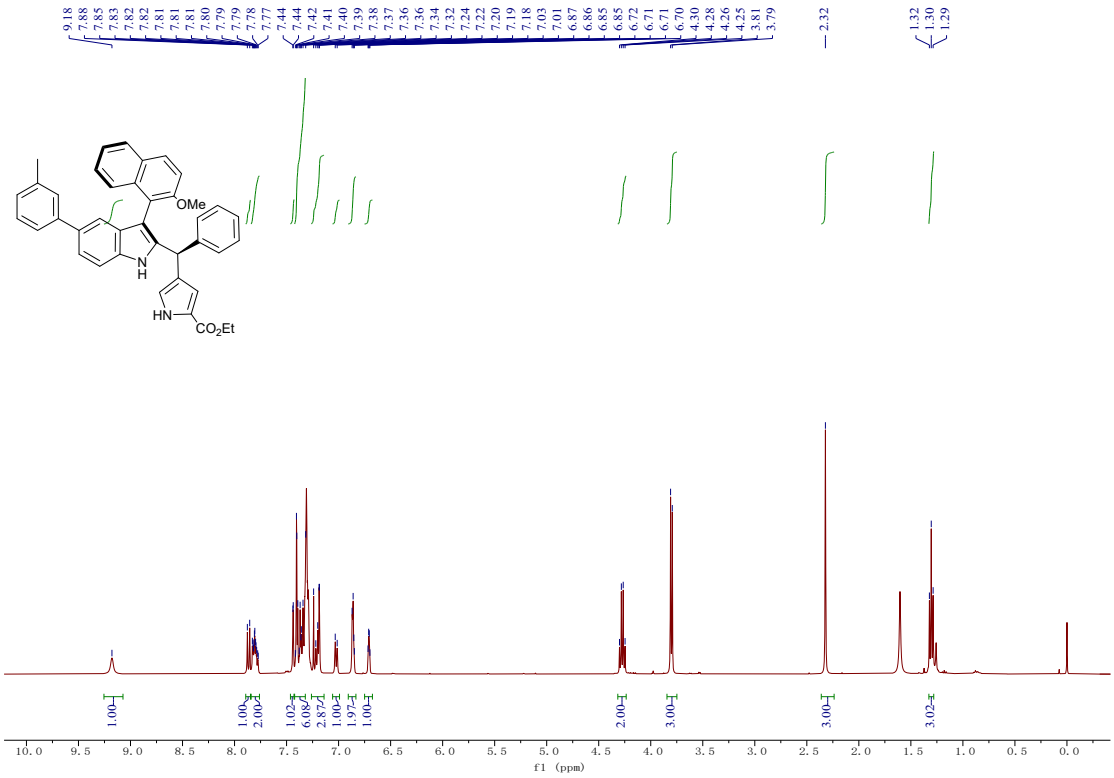
^{1}H NMR (400 MHz, $CDCl_3$) of **3m**



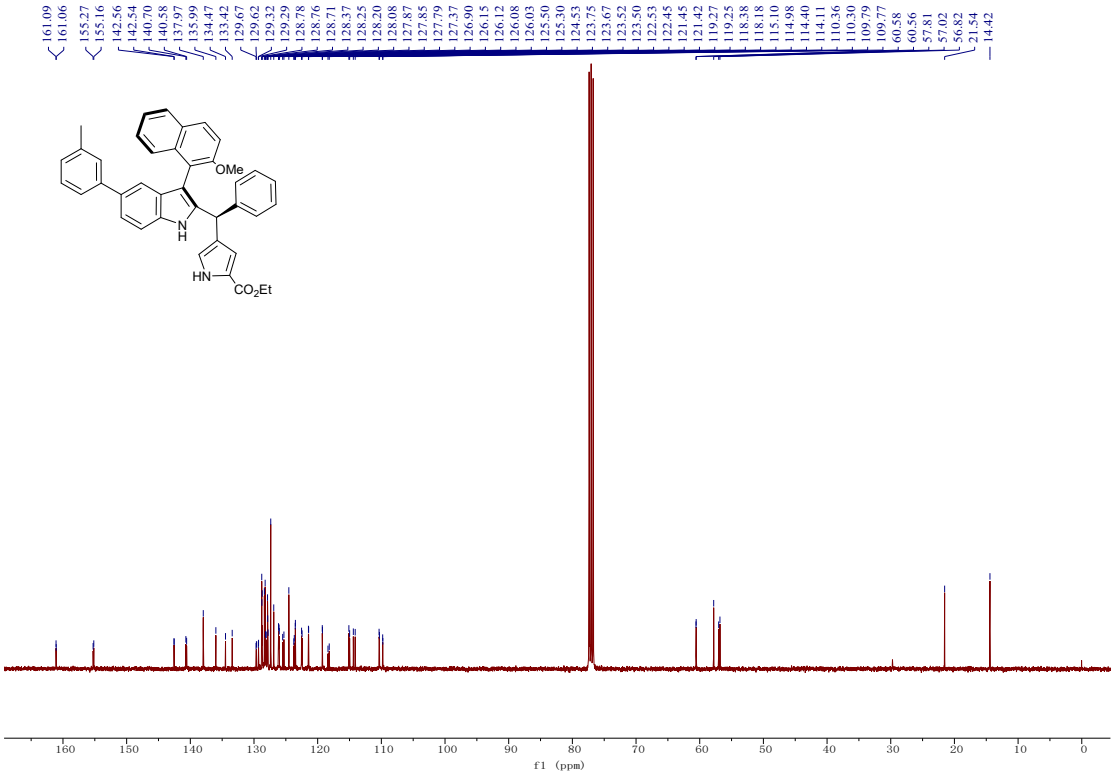
^{13}C NMR (101 MHz, $CDCl_3$) of **3m**



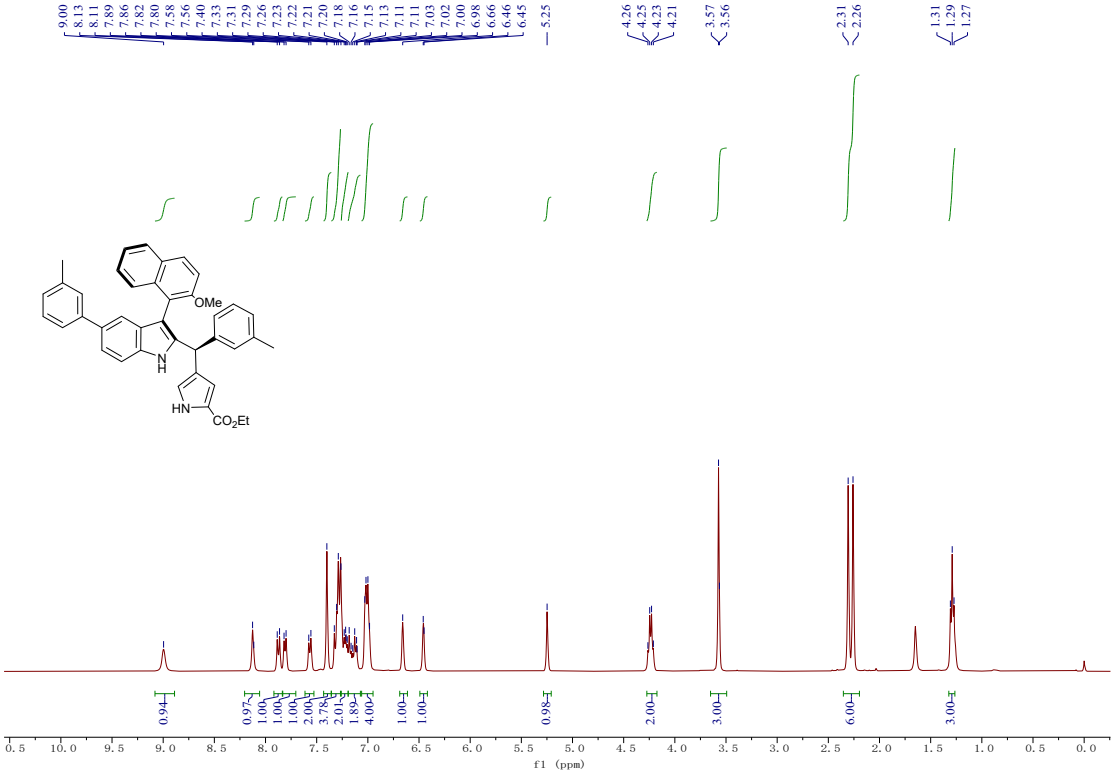
^{1}H NMR (400 MHz, $CDCl_3$) of **3n**



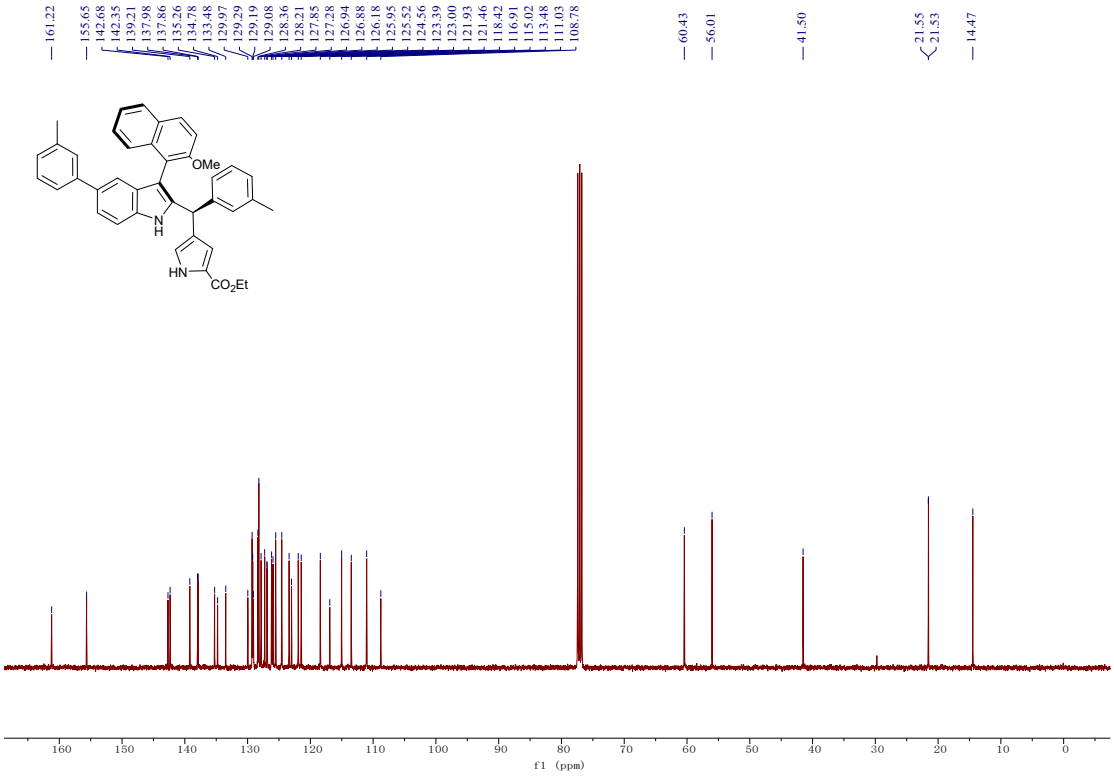
^{13}C NMR (101 MHz, $CDCl_3$) of **3n**



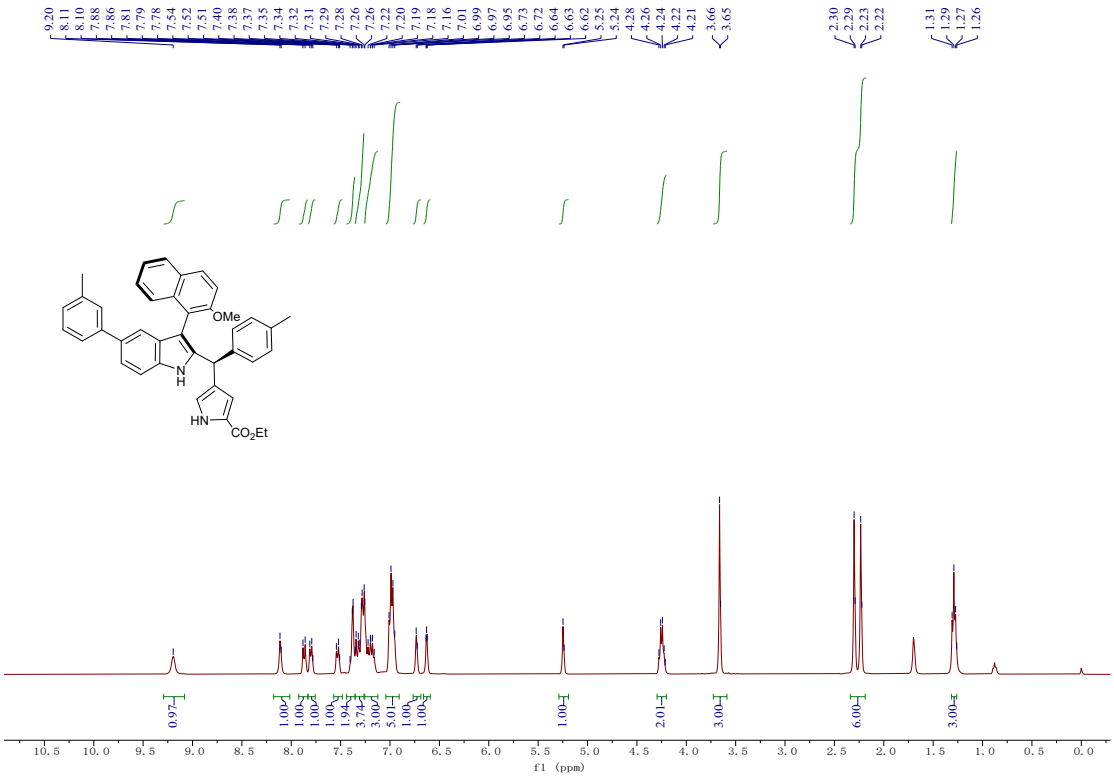
^{1}H NMR (400 MHz, $CDCl_3$) of **3o**



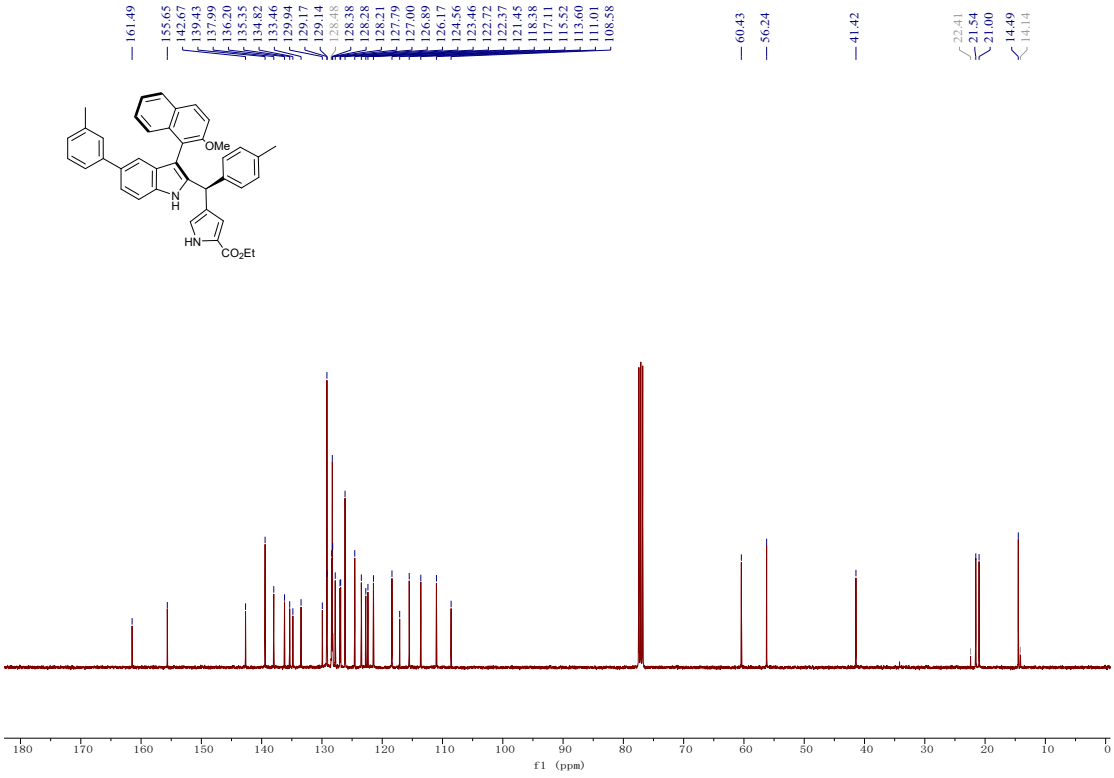
^{13}C NMR (101 MHz, $CDCl_3$) of **3o**



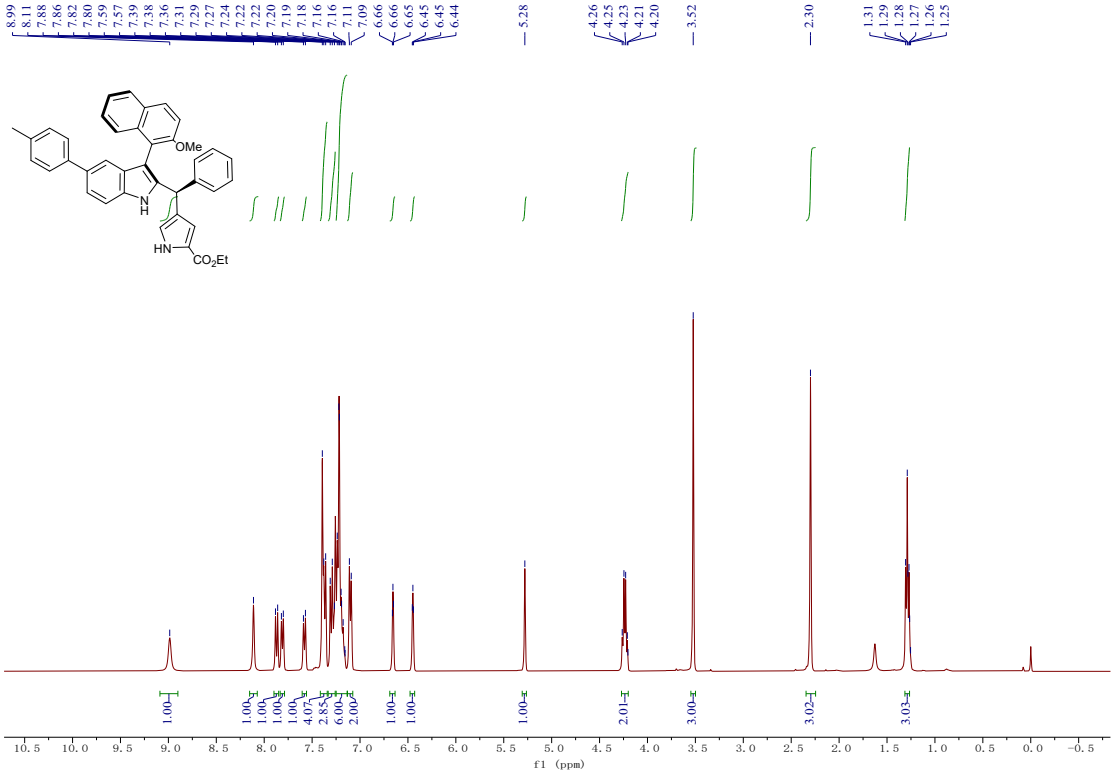
^{1}H NMR (400 MHz, $CDCl_3$) of **3p**



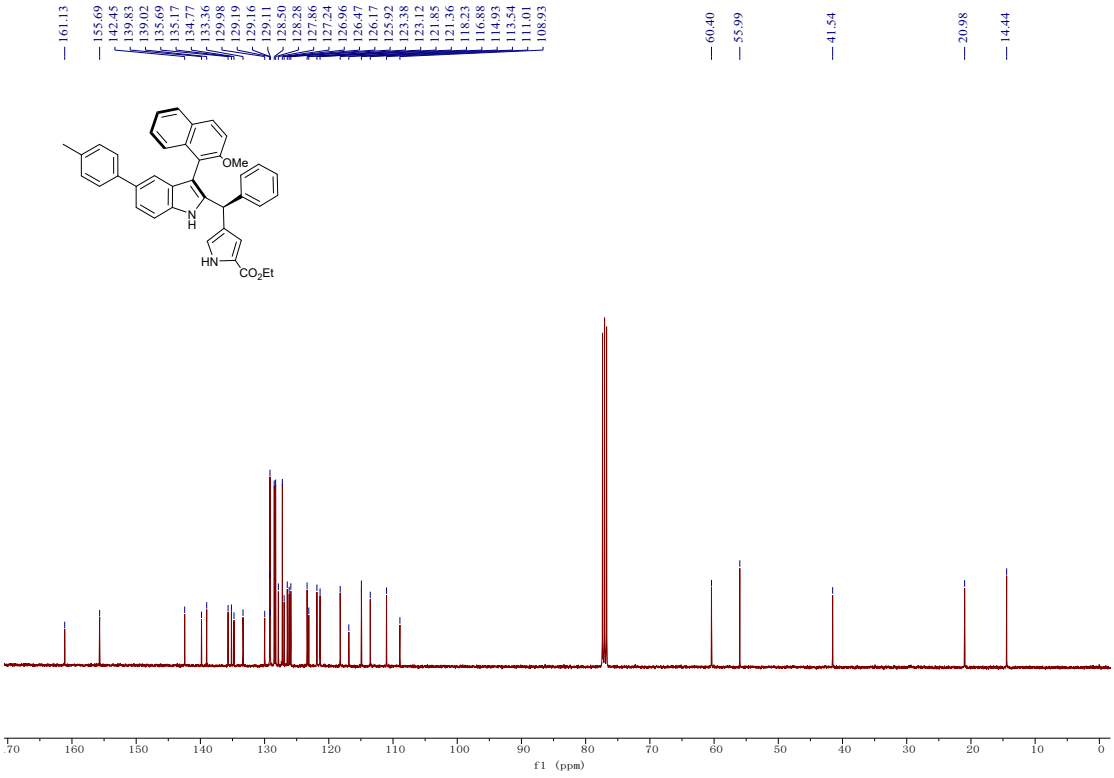
^{13}C NMR (101 MHz, $CDCl_3$) of **3p**



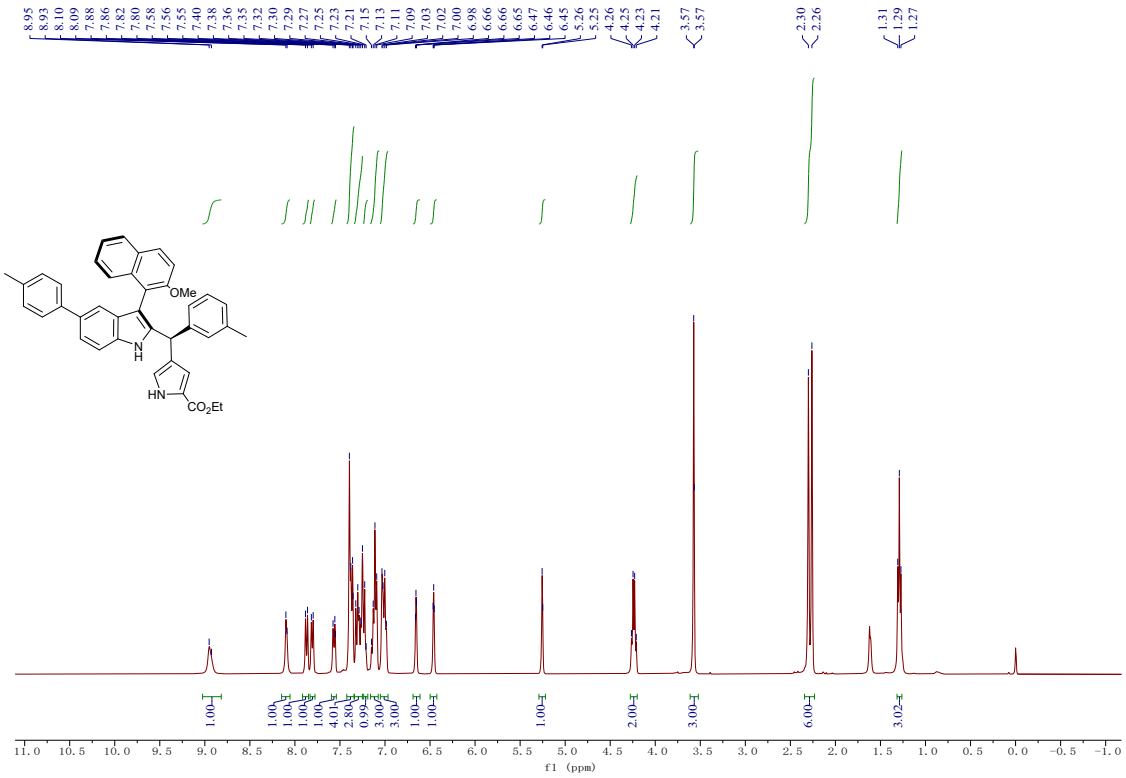
^{1}H NMR (400 MHz, $CDCl_3$) of **3q**



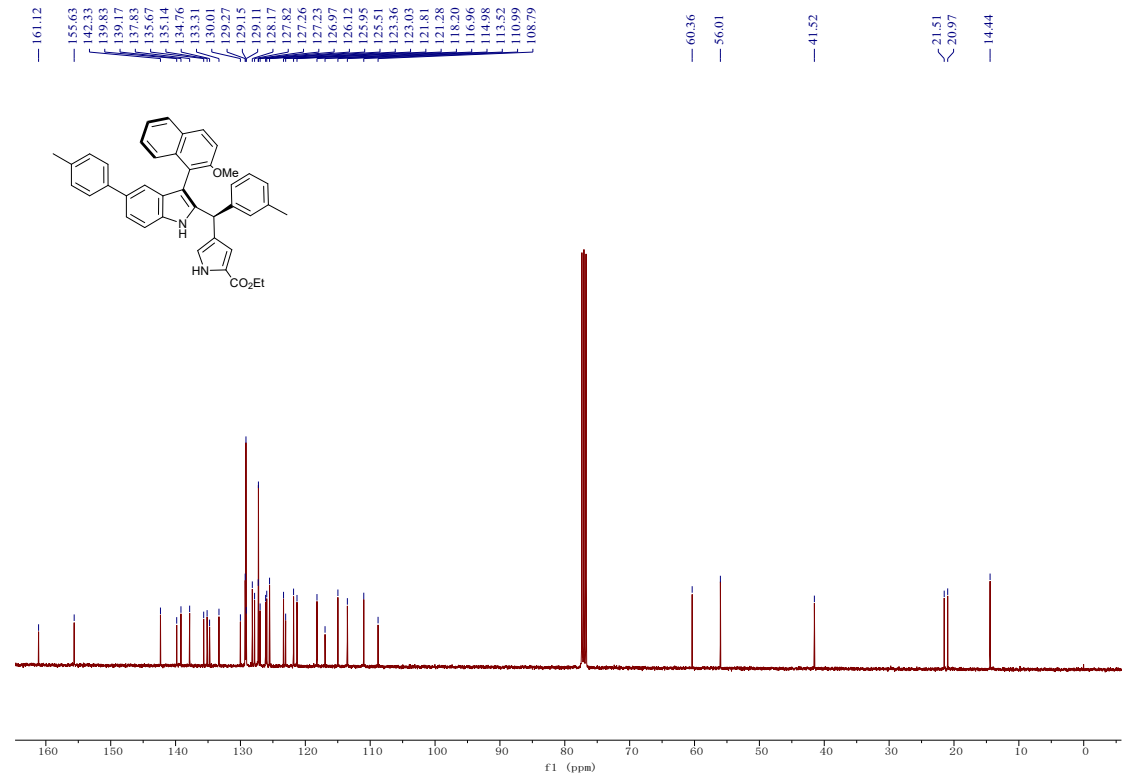
^{13}C NMR (101 MHz, $CDCl_3$) of **3q**



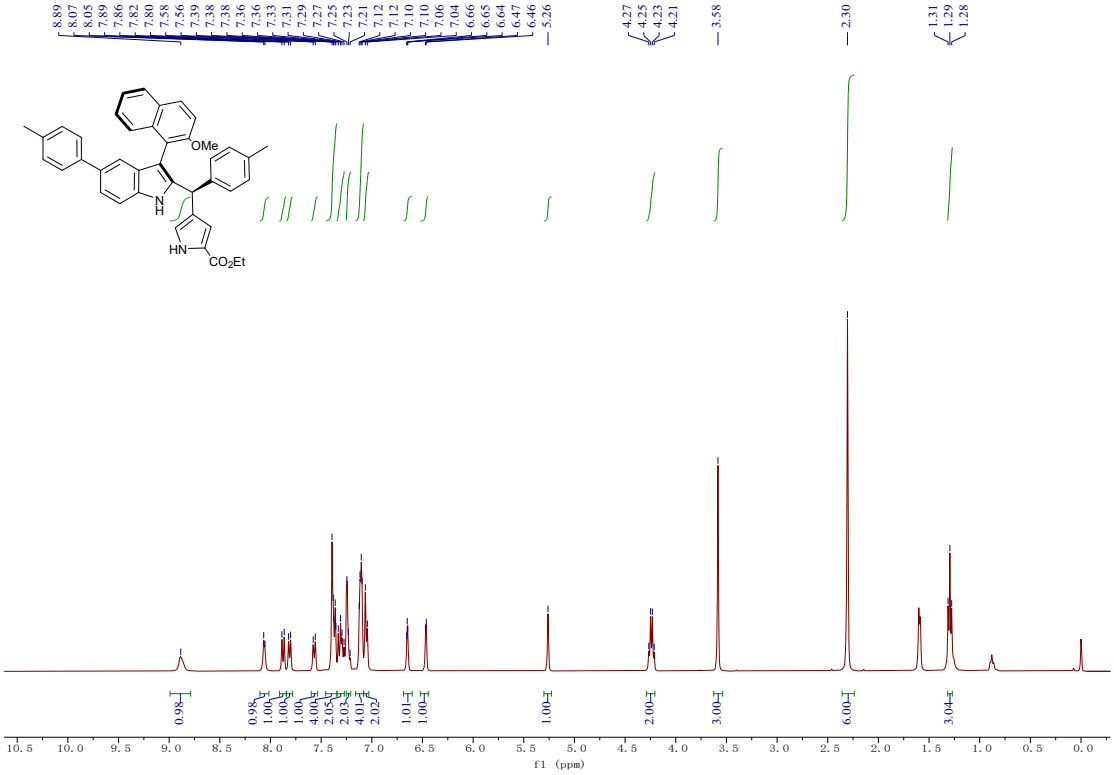
^{1}H NMR (400 MHz, $CDCl_3$) of **3r**



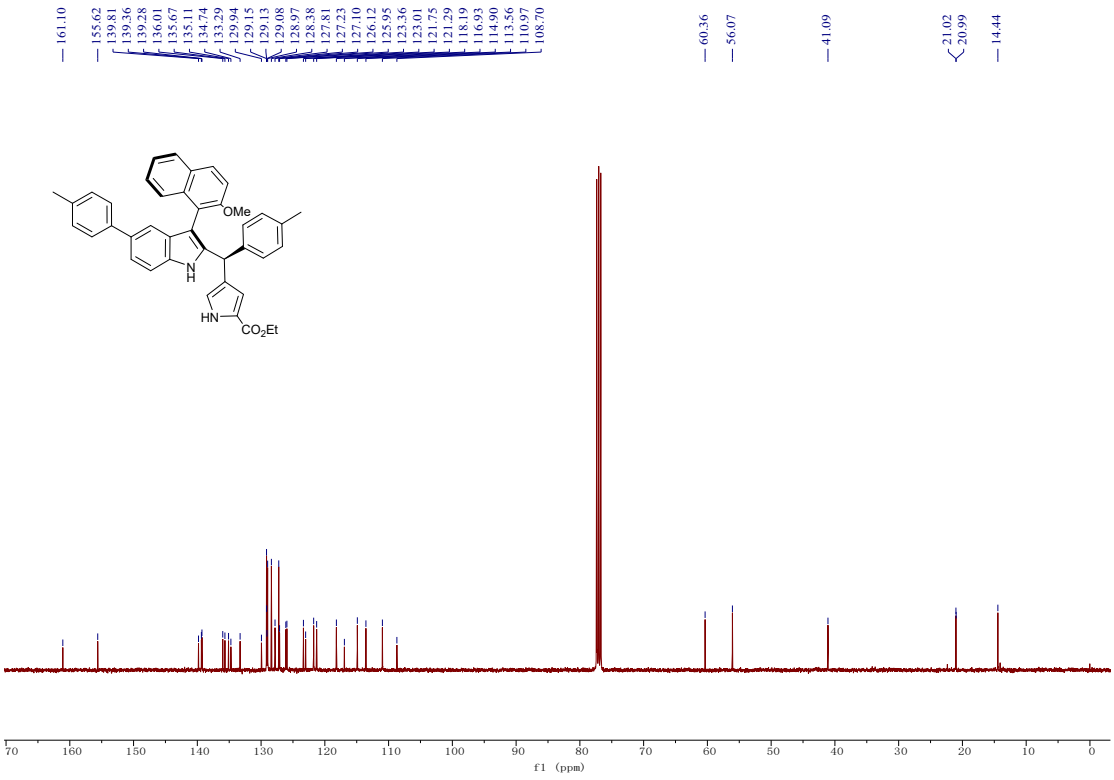
^{13}C NMR (101 MHz, $CDCl_3$) of **3r**



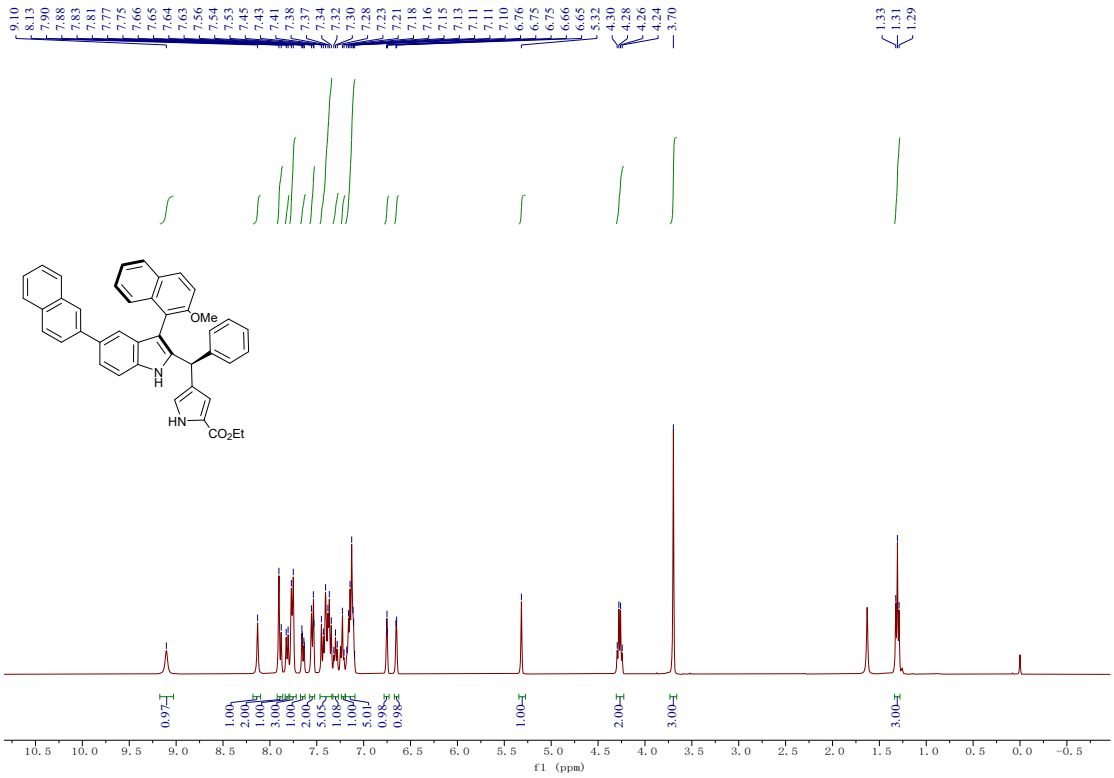
^{1}H NMR (400 MHz, $CDCl_3$) of **3s**



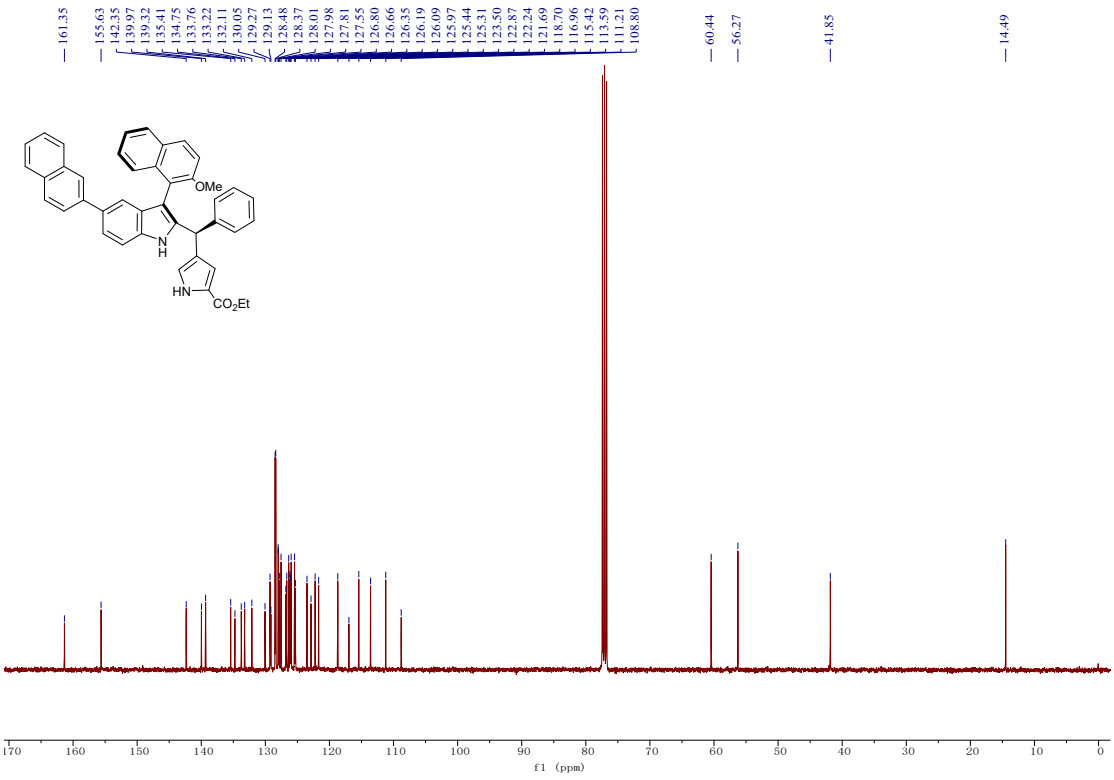
^{13}C NMR (101 MHz, $CDCl_3$) of **3s**



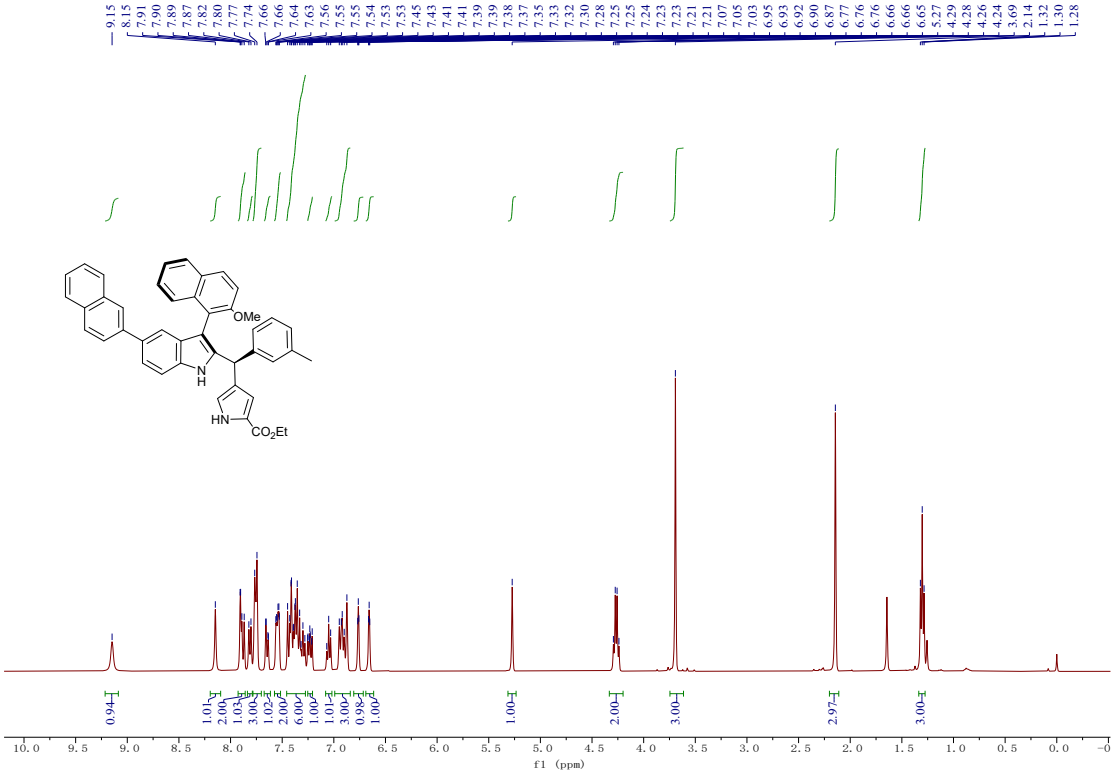
^{1}H NMR (400 MHz, $CDCl_3$) of **3t**



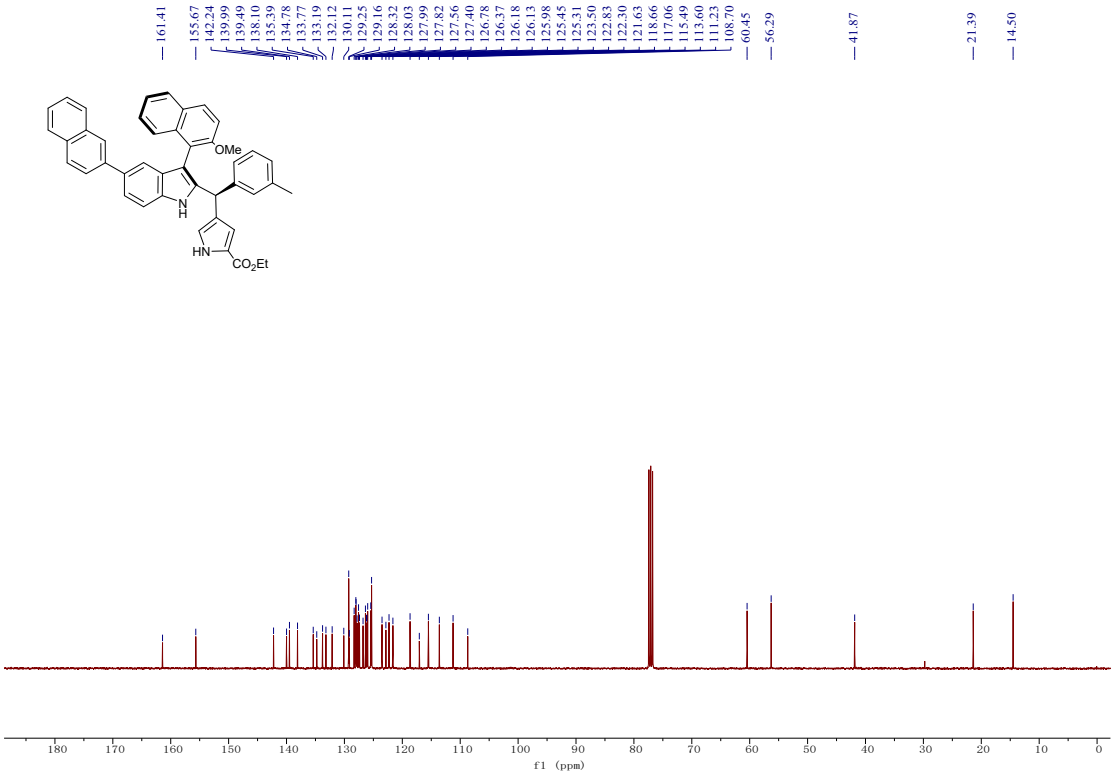
^{13}C NMR (101 MHz, $CDCl_3$) of **3t**



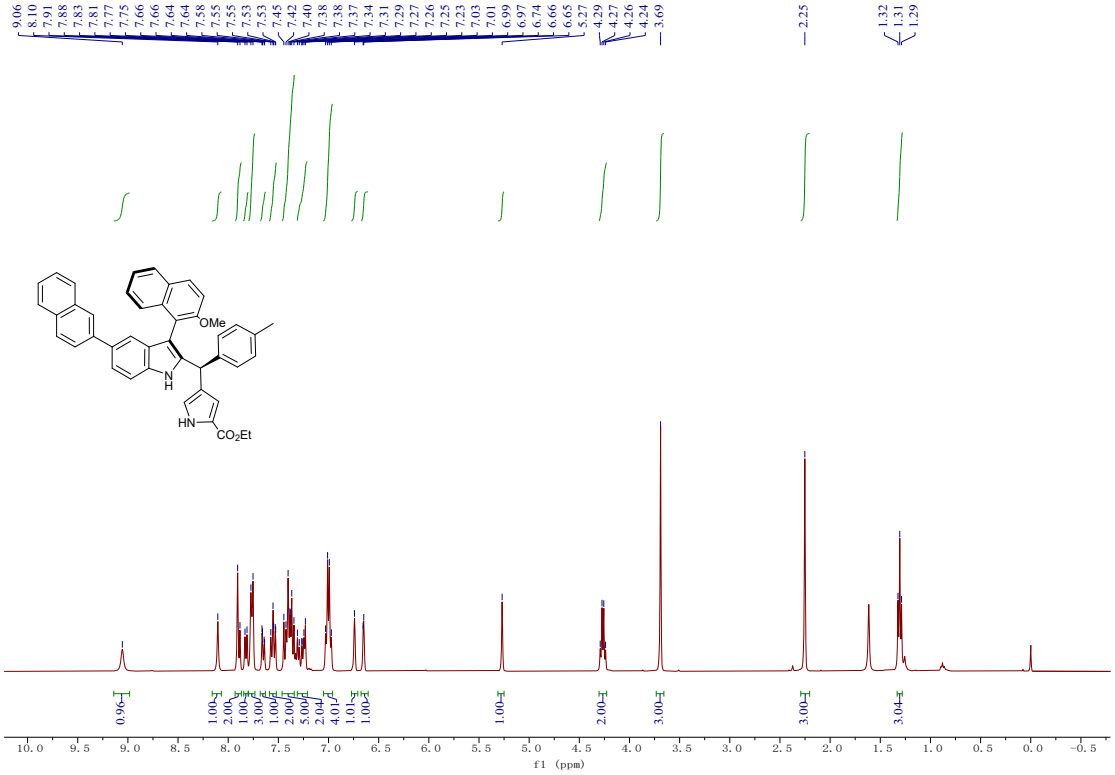
^{1}H NMR (400 MHz, $CDCl_3$) of **3u**



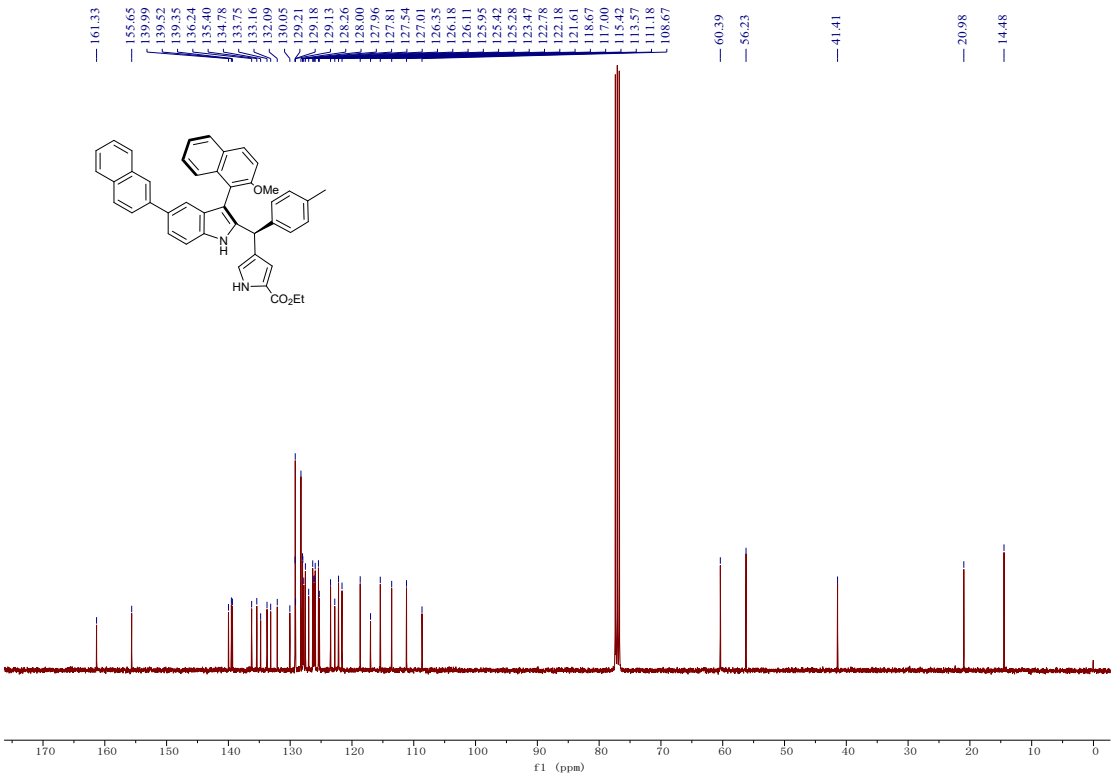
^{13}C NMR (101 MHz, $CDCl_3$) of **3u**



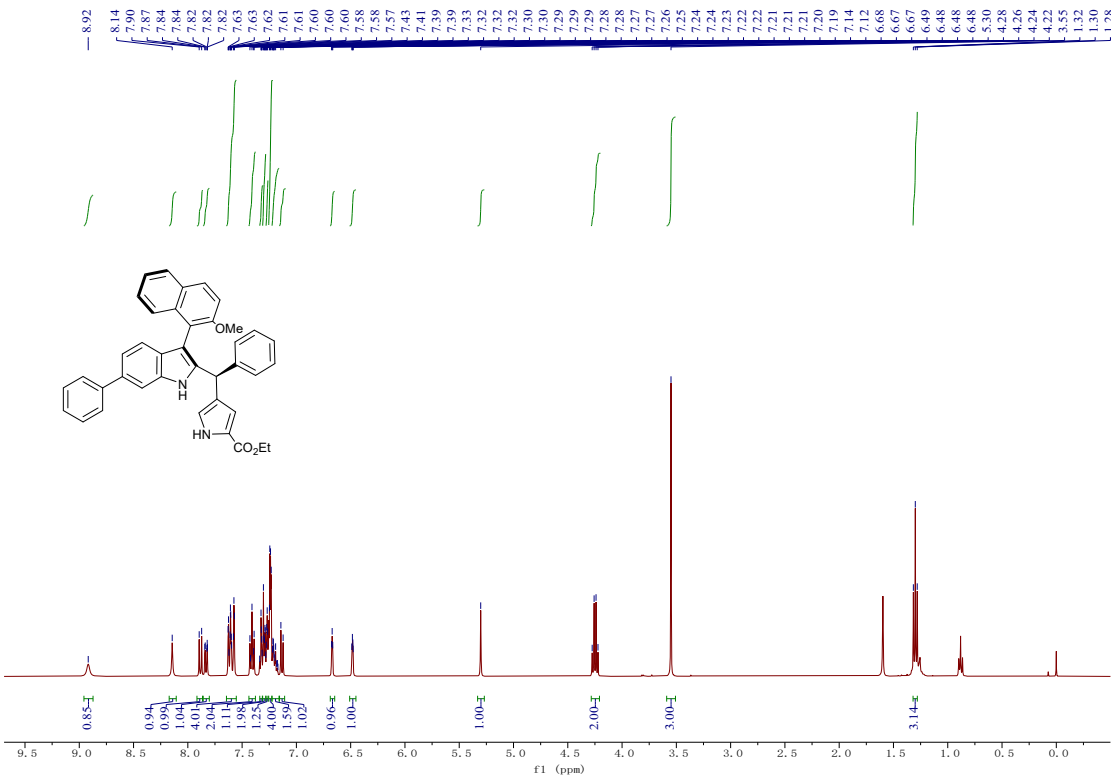
^{1}H NMR (400 MHz, $CDCl_3$) of **3v**



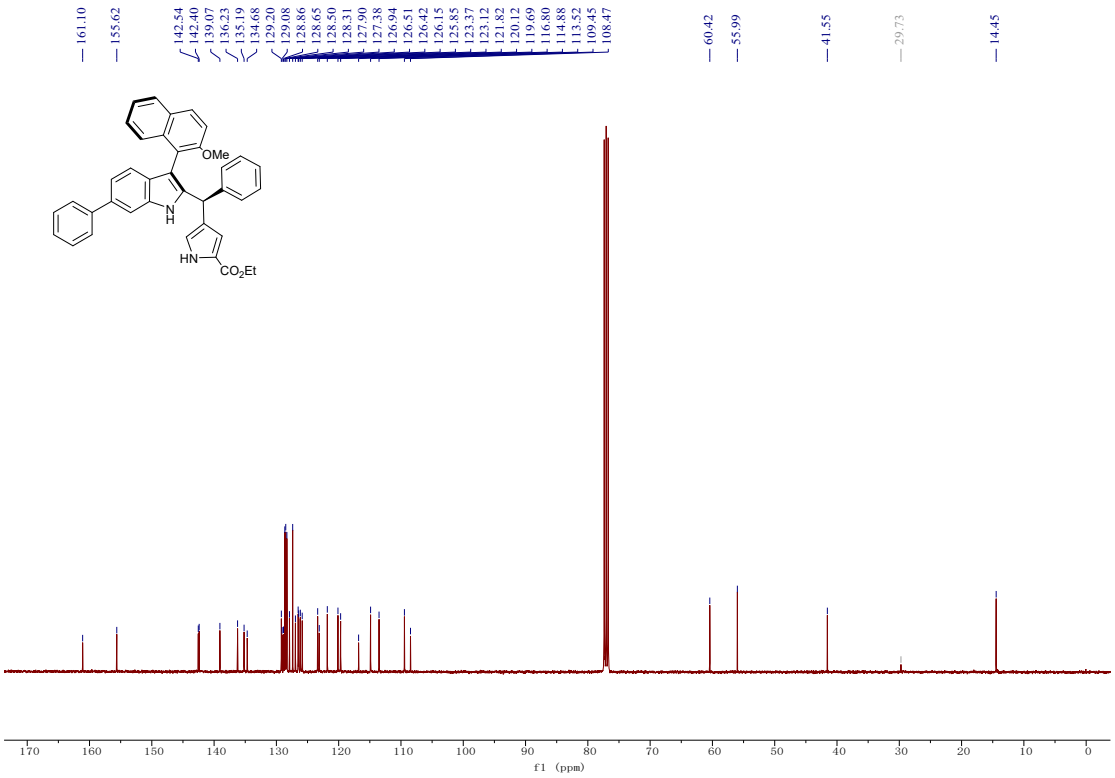
^{13}C NMR (101 MHz, $CDCl_3$) of **3v**



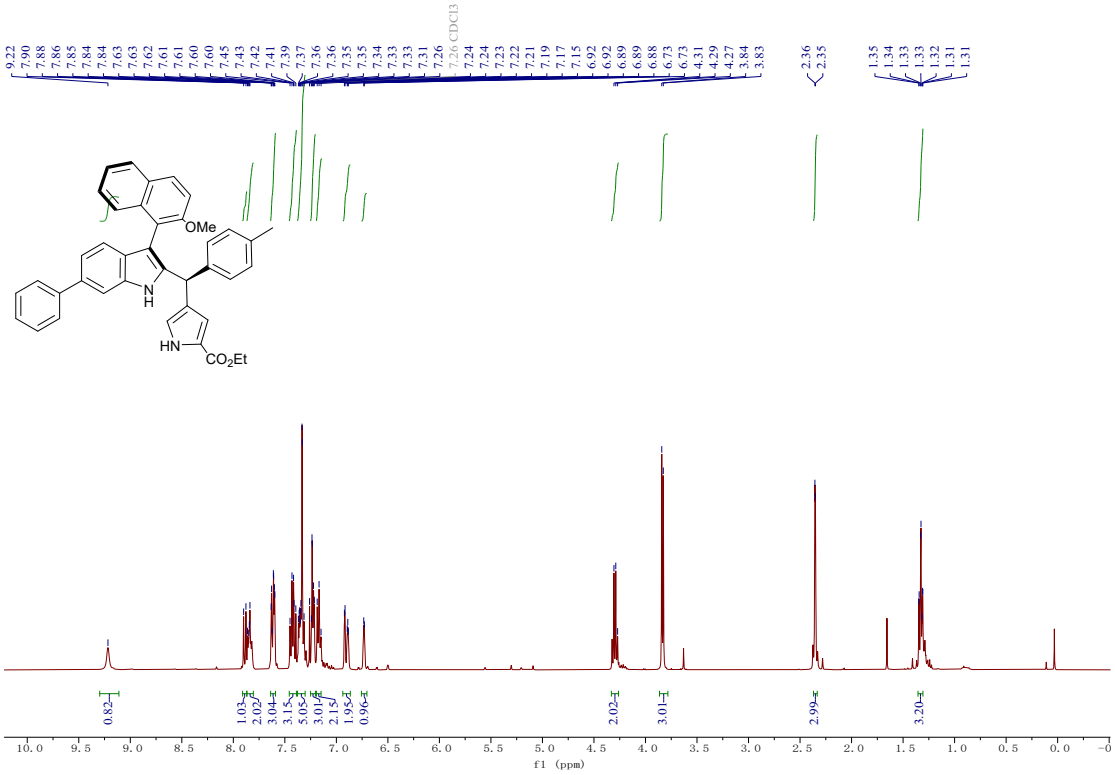
^{1}H NMR (400 MHz, $CDCl_3$) of **3w**



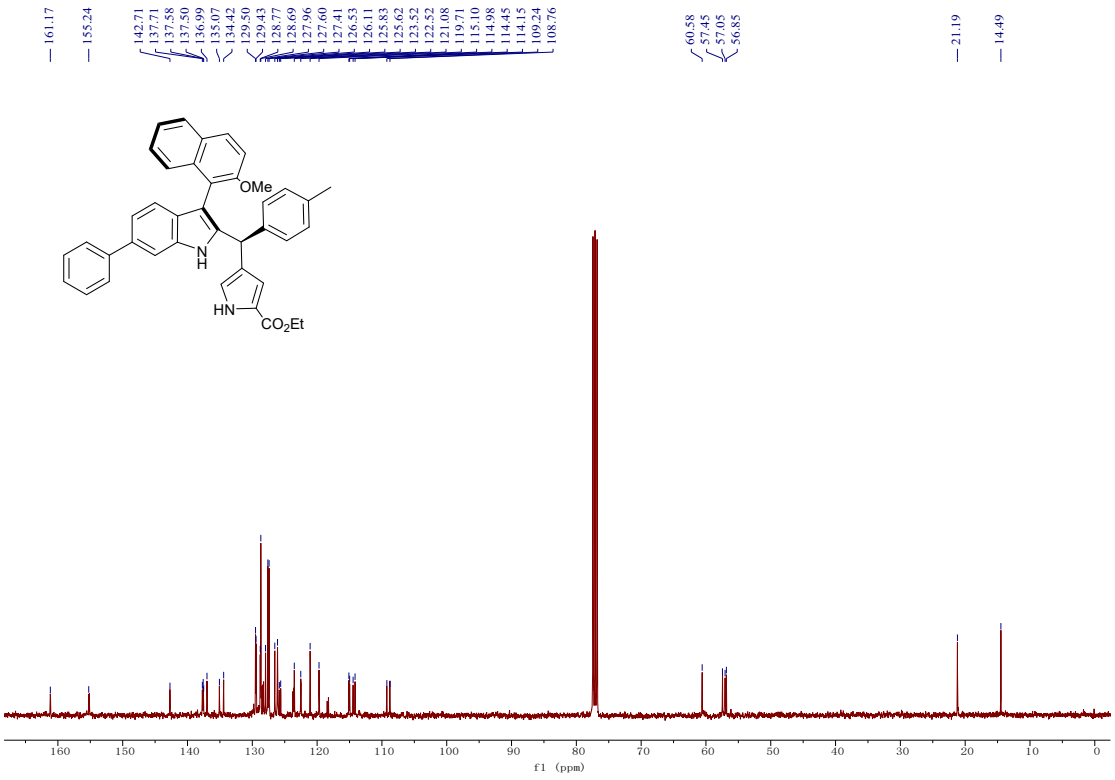
^{13}C NMR (101 MHz, $CDCl_3$) of **3w**



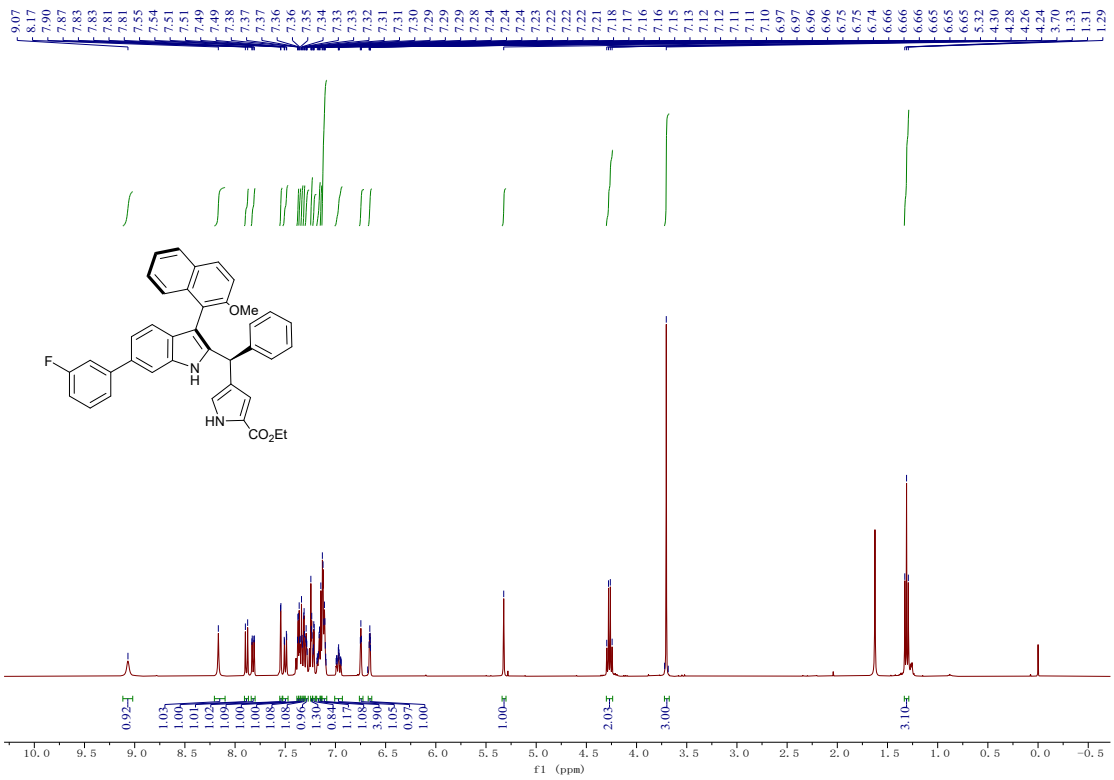
^{1}H NMR (400 MHz, $CDCl_3$) of **3x**



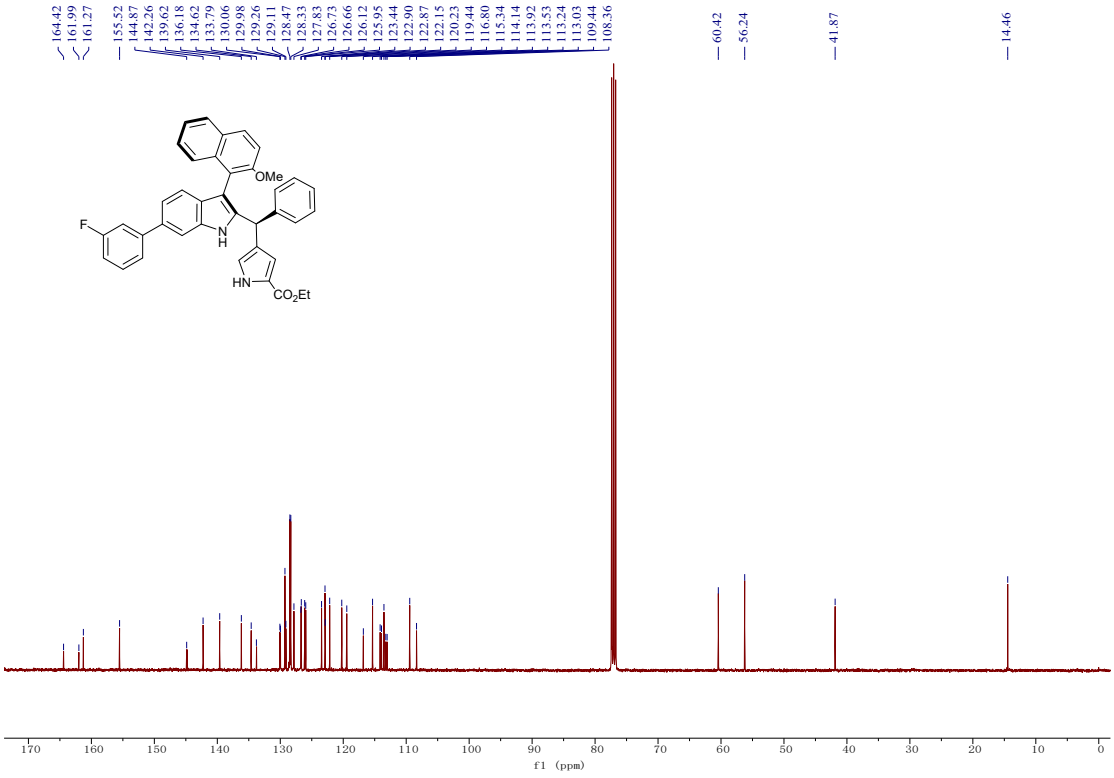
^{13}C NMR (101 MHz, $CDCl_3$) of **3x**



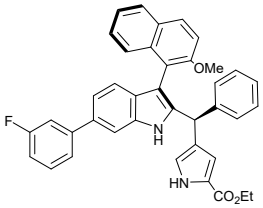
^{1}H NMR (400 MHz, $CDCl_3$) of **3y**



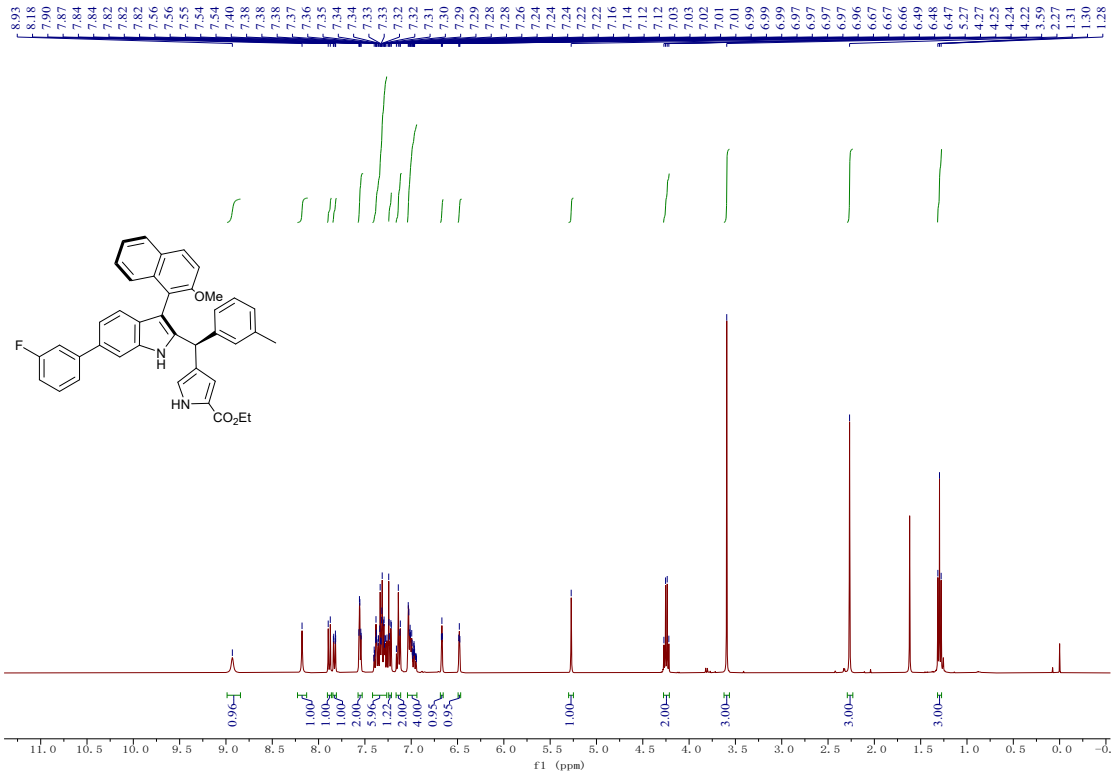
^{13}C NMR (101 MHz, $CDCl_3$) of **3y**



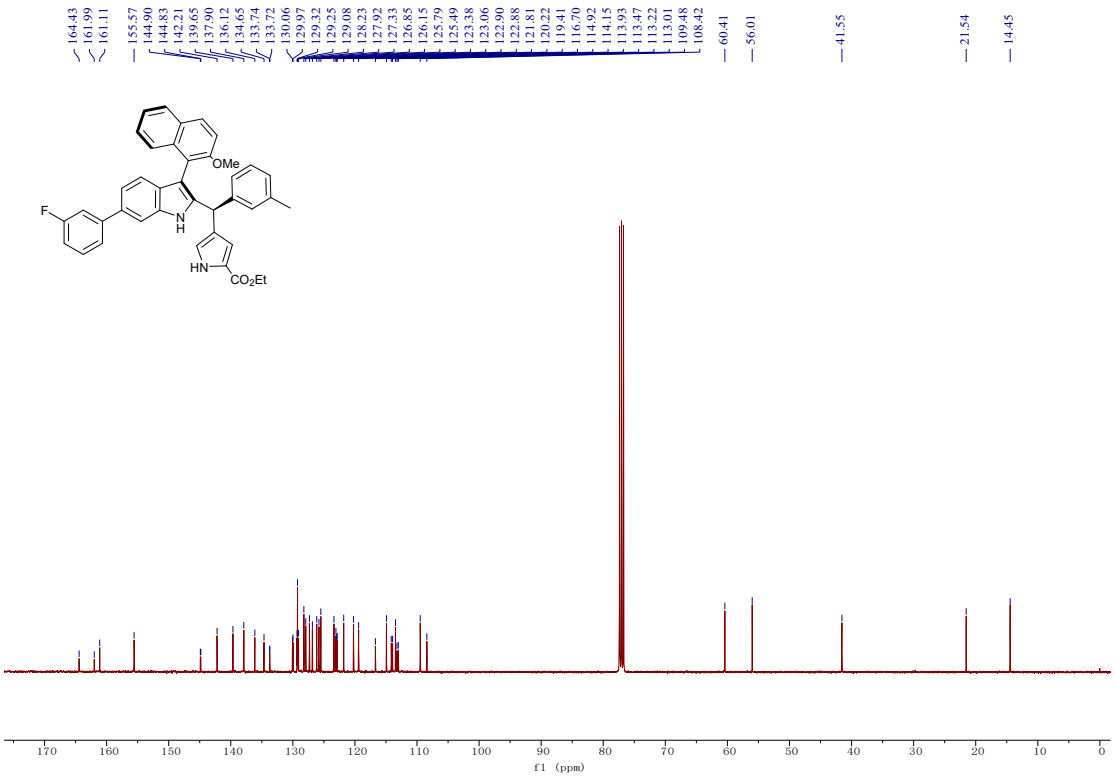
^{19}F NMR (376 MHz, $CDCl_3$) of **3y**



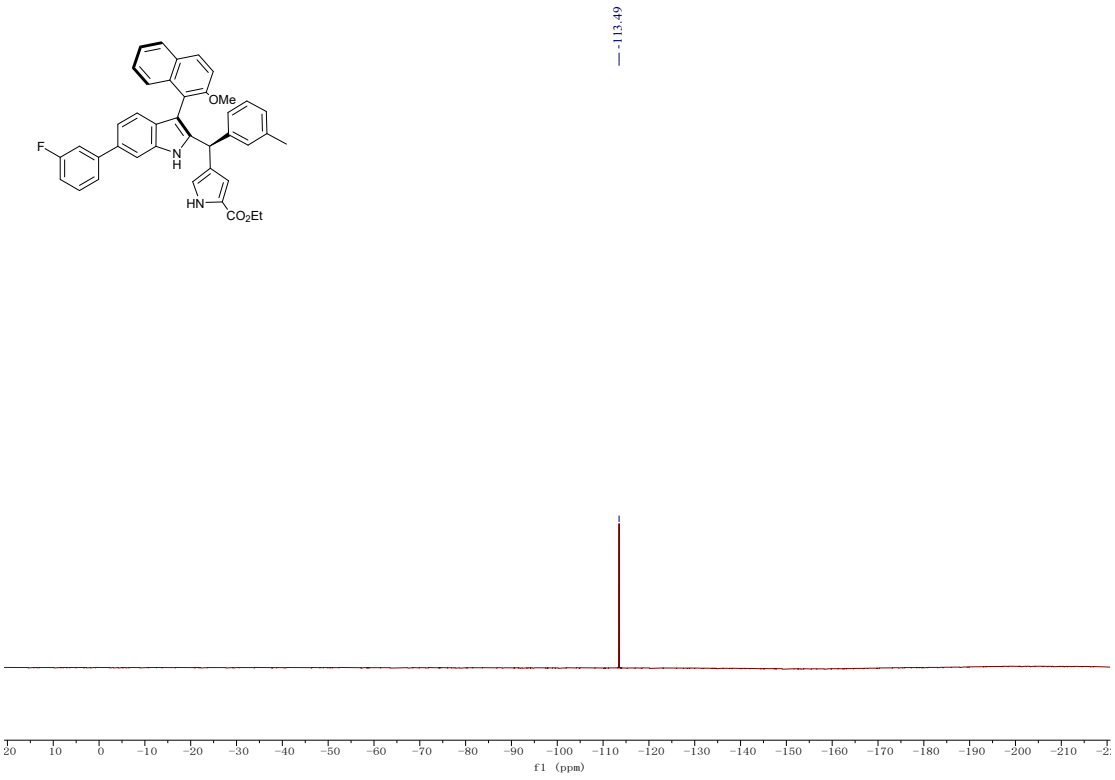
^{1}H NMR (400 MHz, $CDCl_3$) of **3z**



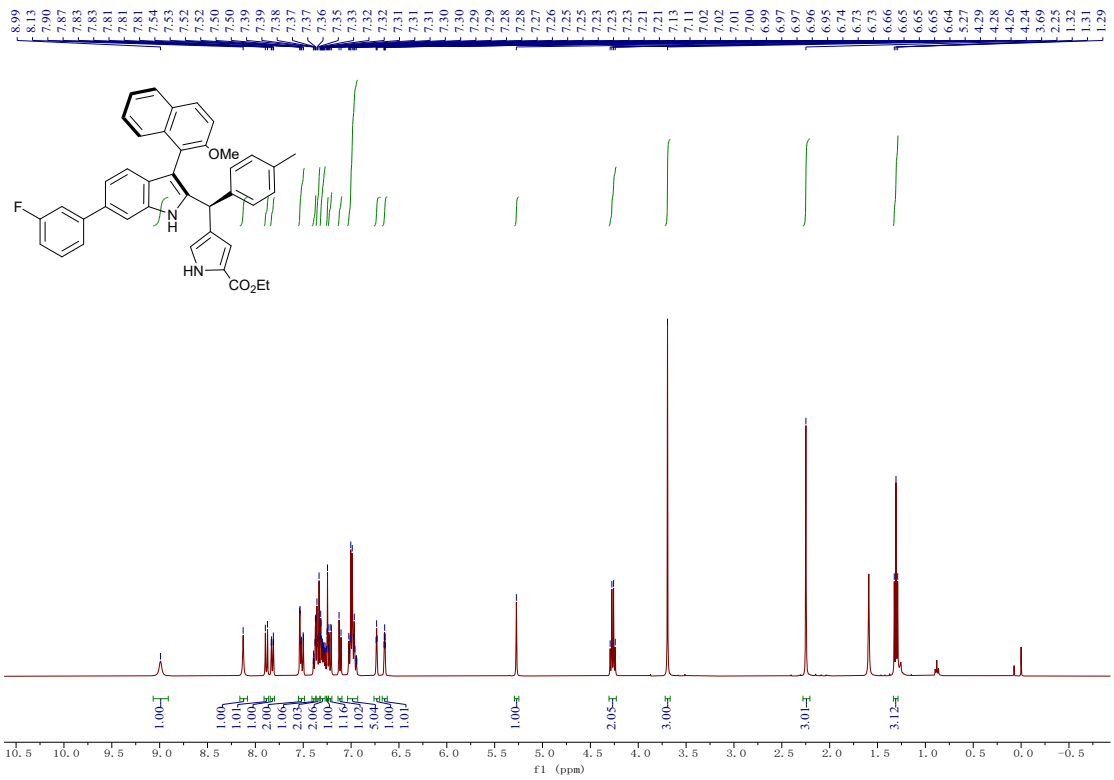
^{13}C NMR (101 MHz, $CDCl_3$) of **3z**



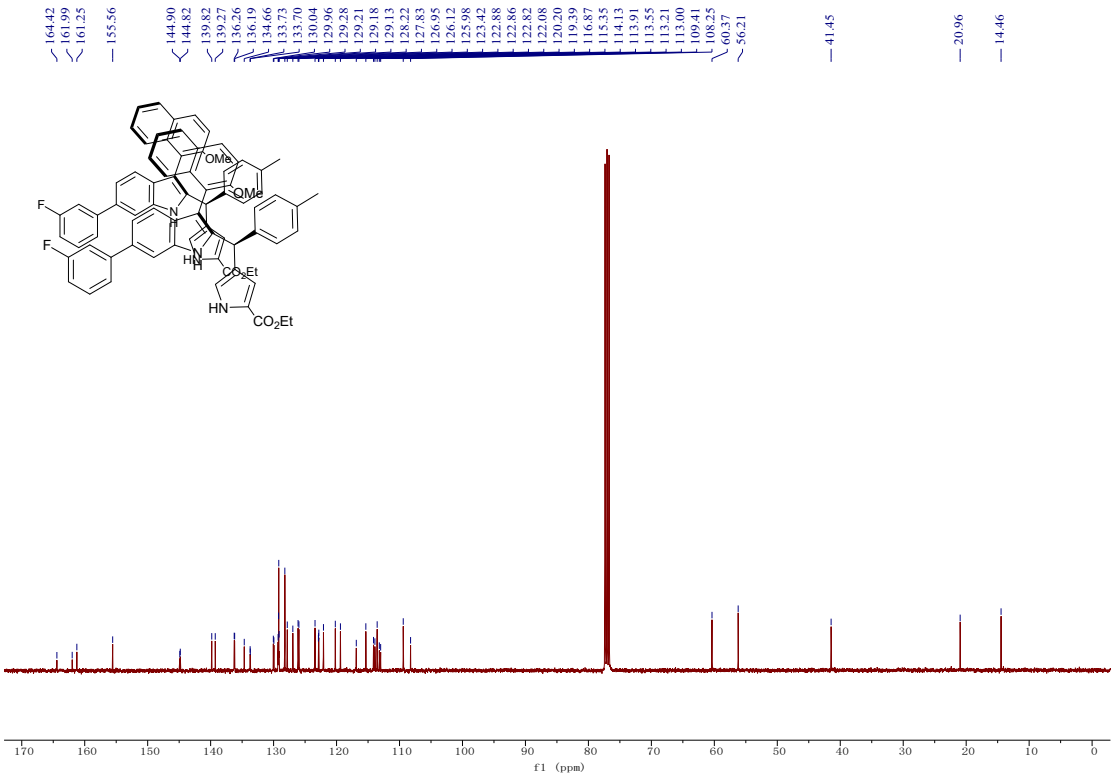
^{19}F NMR (376 MHz, CDCl3) of **3z**



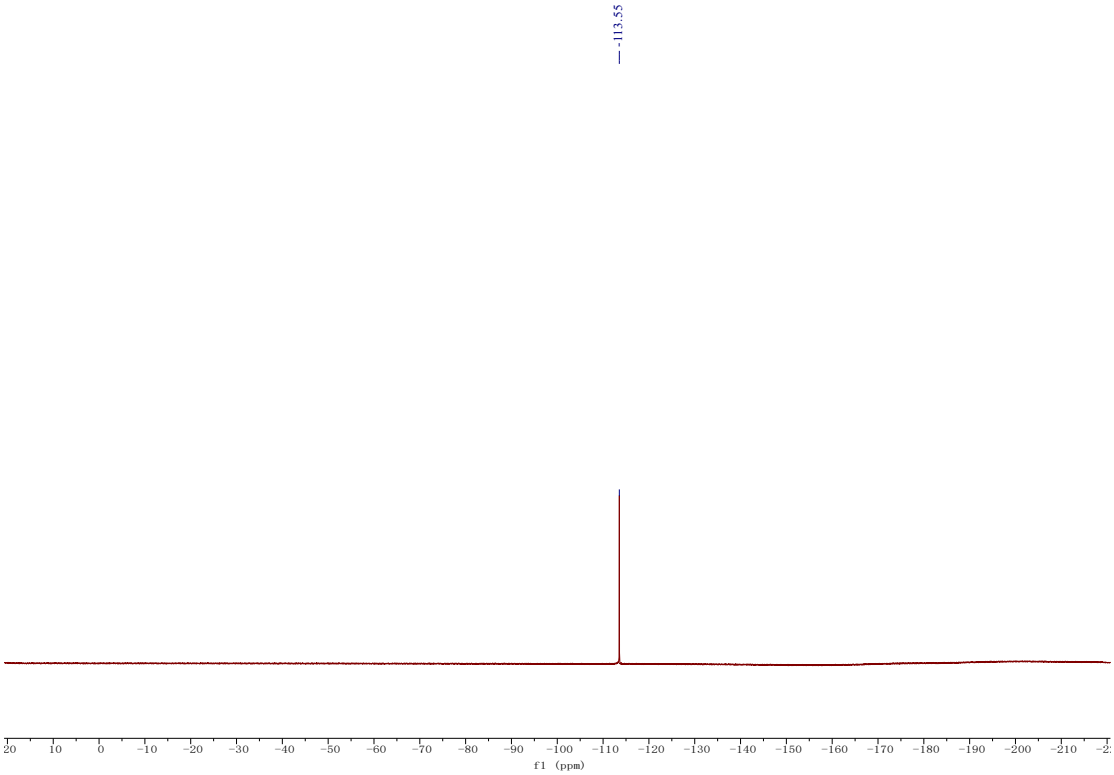
^{1}H NMR (400 MHz, $CDCl_3$) of **3za**



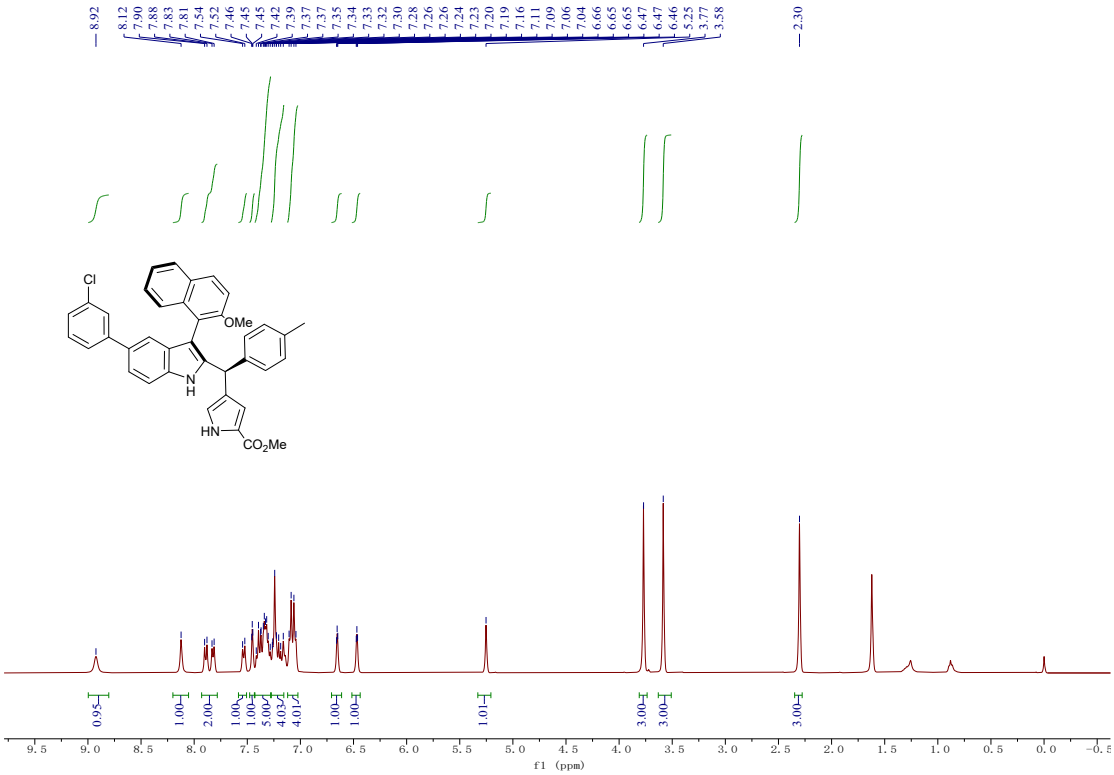
^{13}C NMR (101 MHz, $CDCl_3$) of **3za**



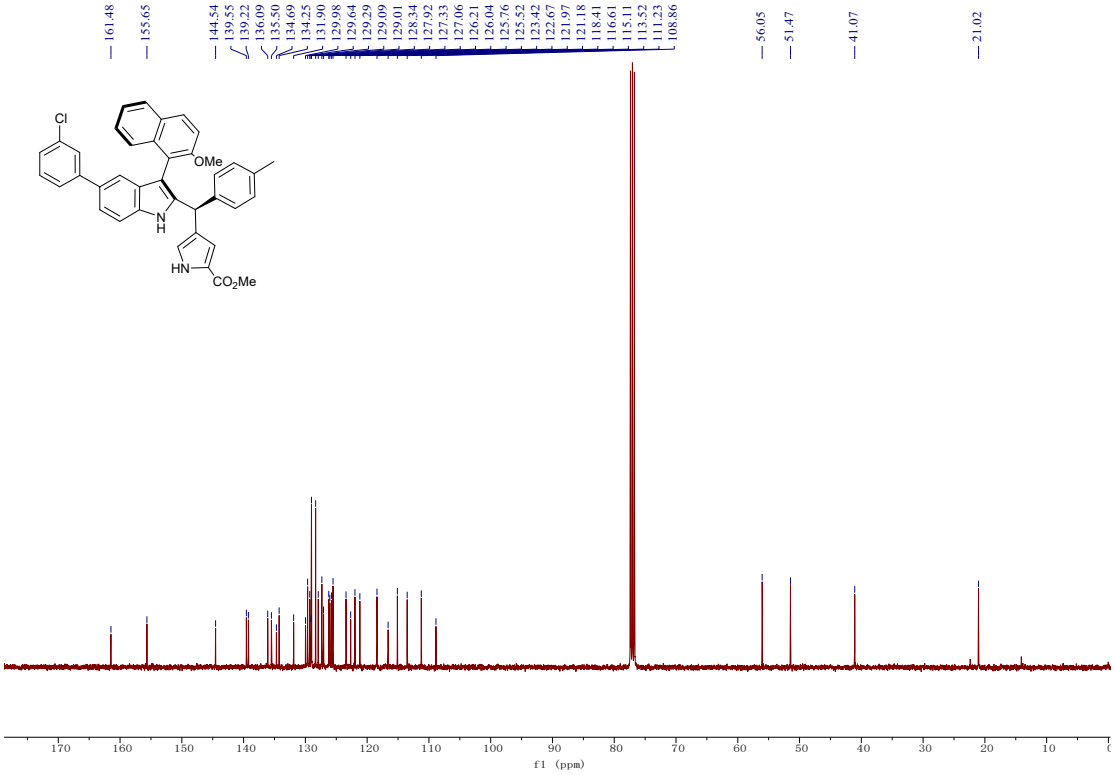
^{19}F NMR (376 MHz, $CDCl_3$) of **3za**



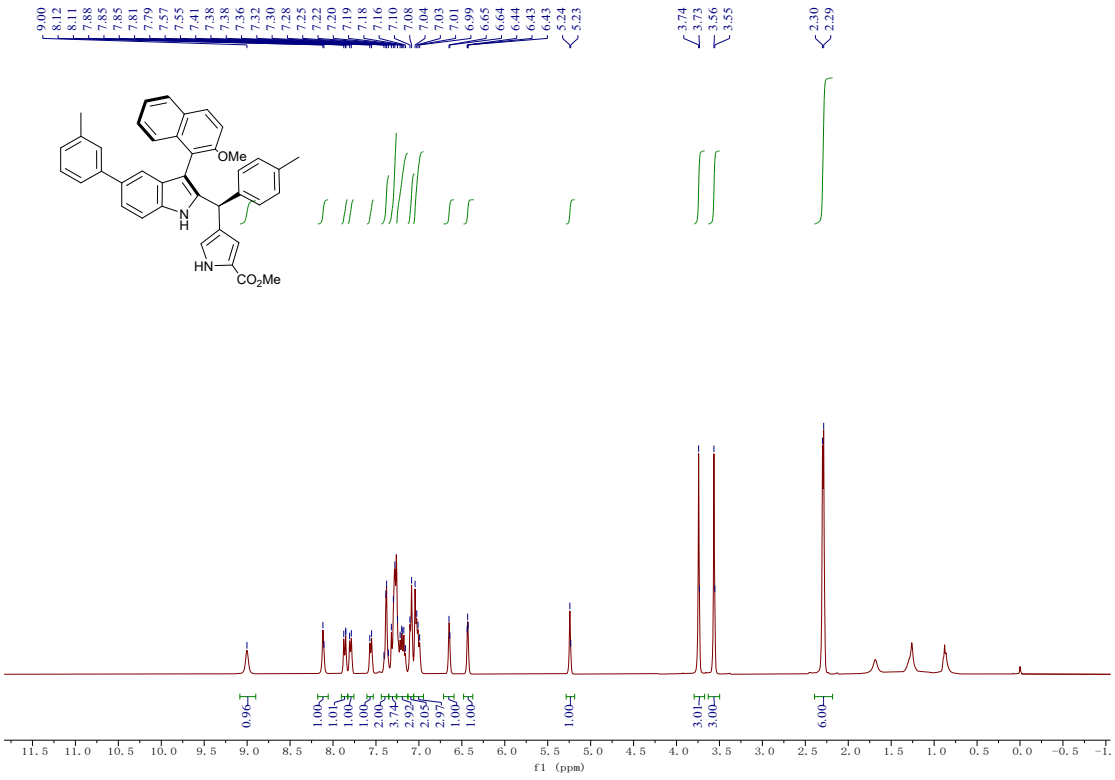
^{1}H NMR (400 MHz, $CDCl_3$) of **3zb**



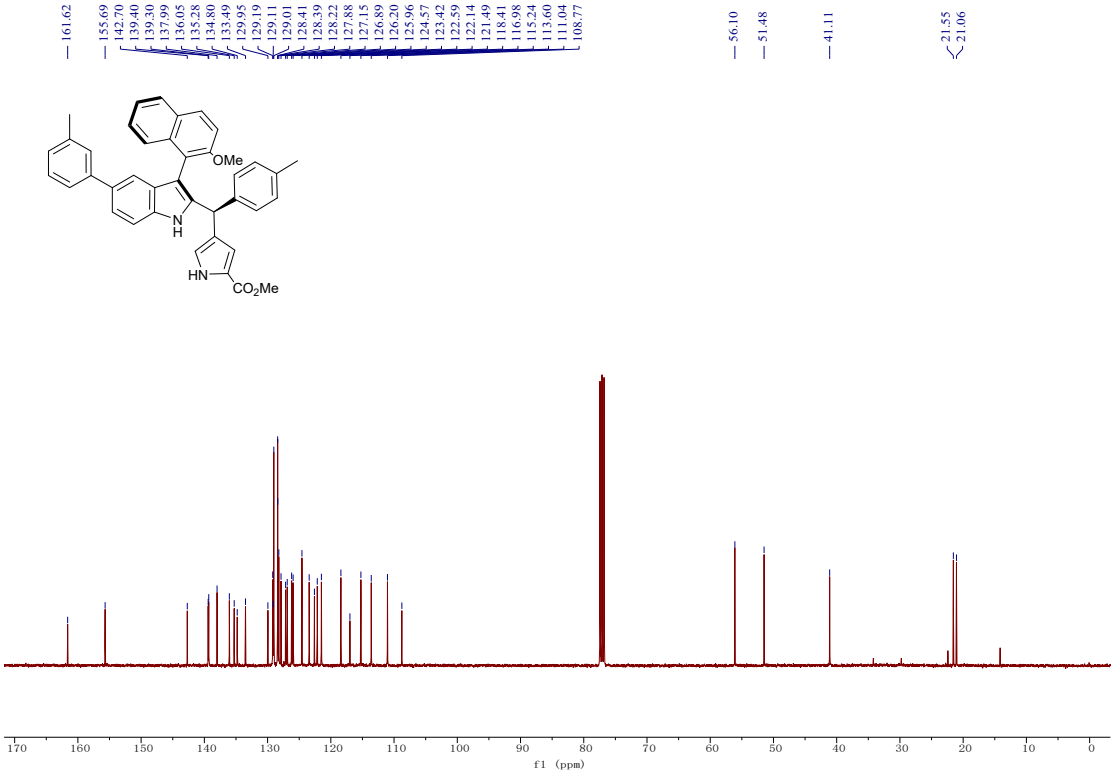
^{13}C NMR (101 MHz, $CDCl_3$) of **3zb**



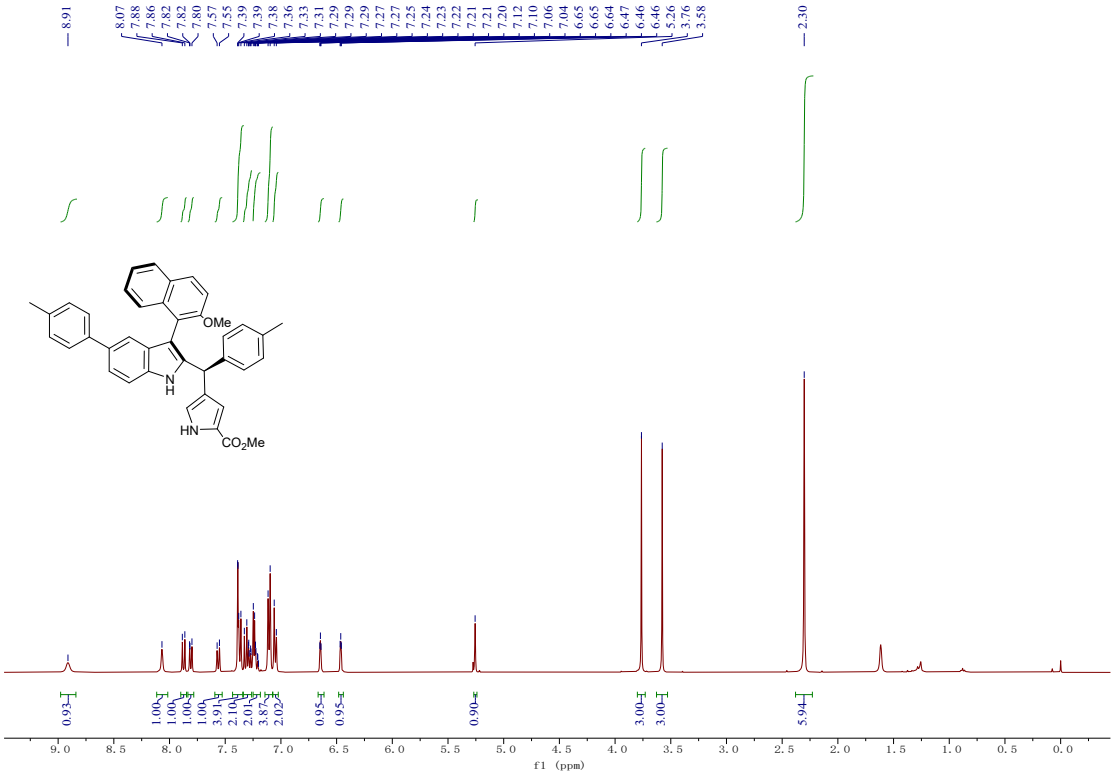
^{1}H NMR (400 MHz, $CDCl_3$) of **3zc**



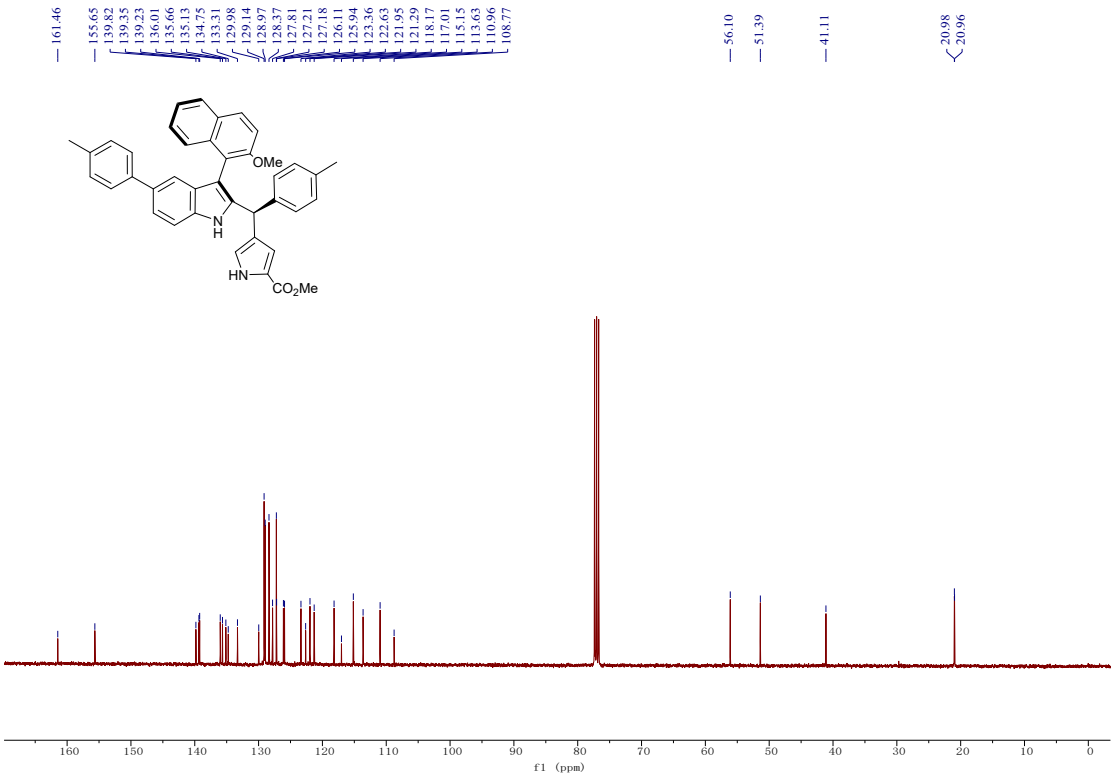
^{13}C NMR (101 MHz, $CDCl_3$) of **3zc**



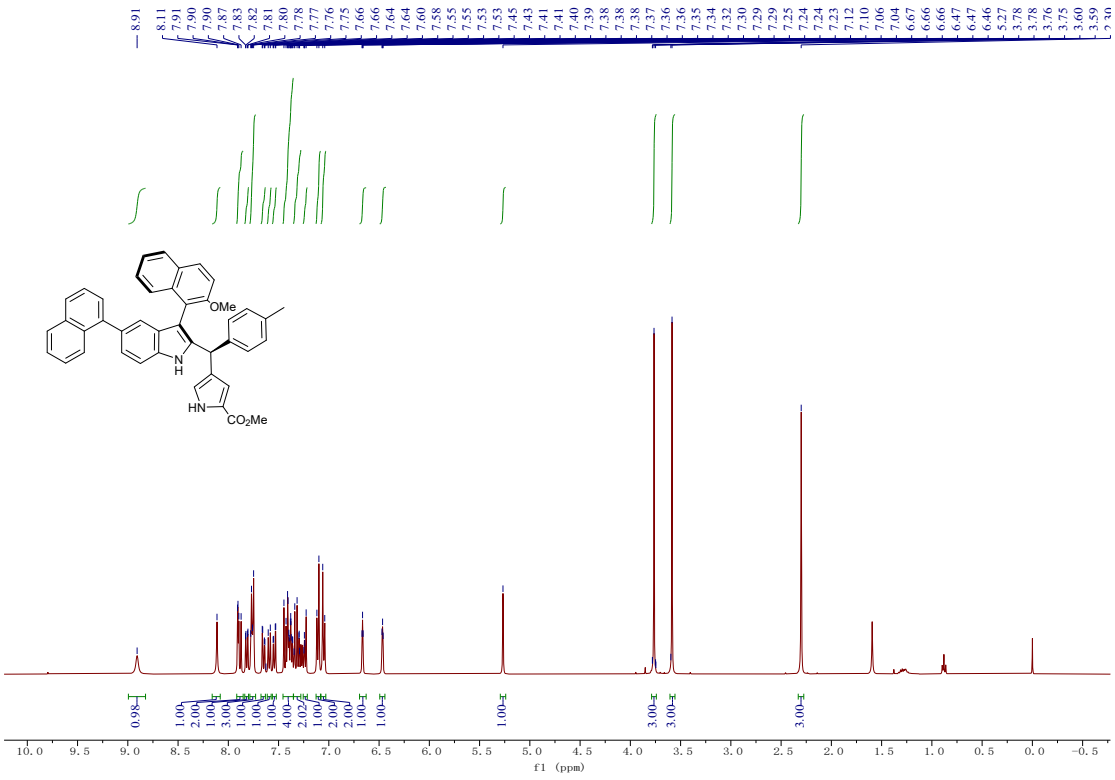
^{1}H NMR (400 MHz, $CDCl_3$) of **3zd**



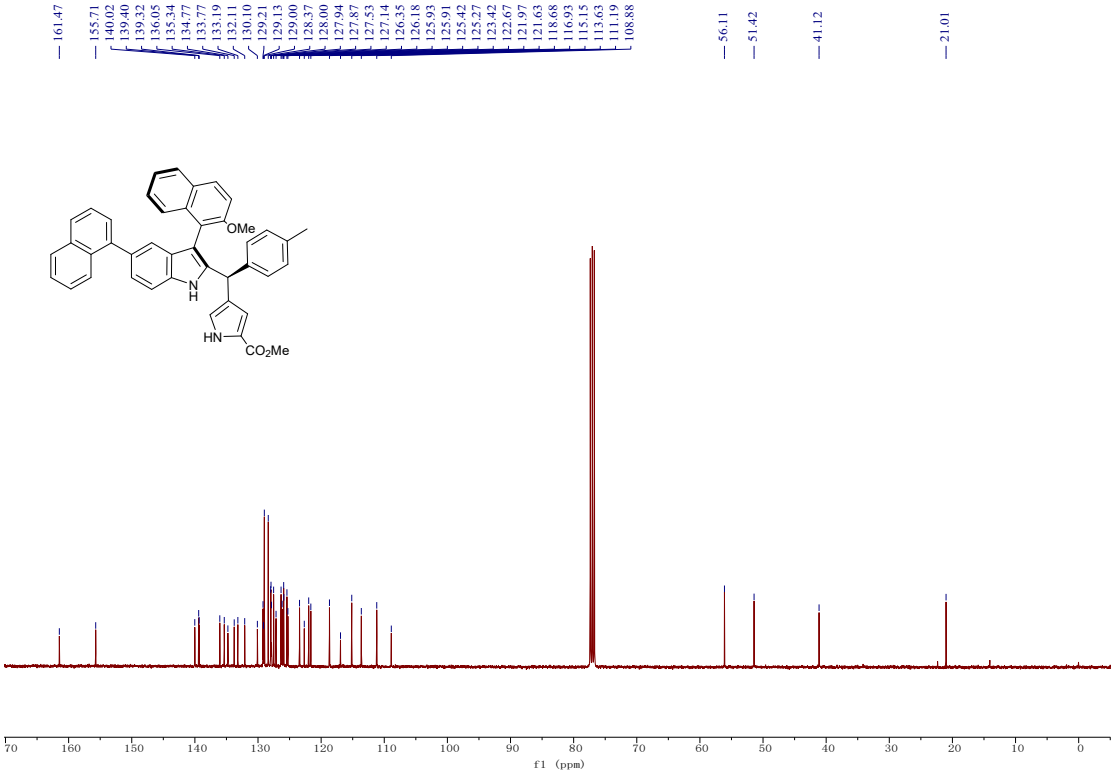
^{13}C NMR (101 MHz, $CDCl_3$) of **3zd**



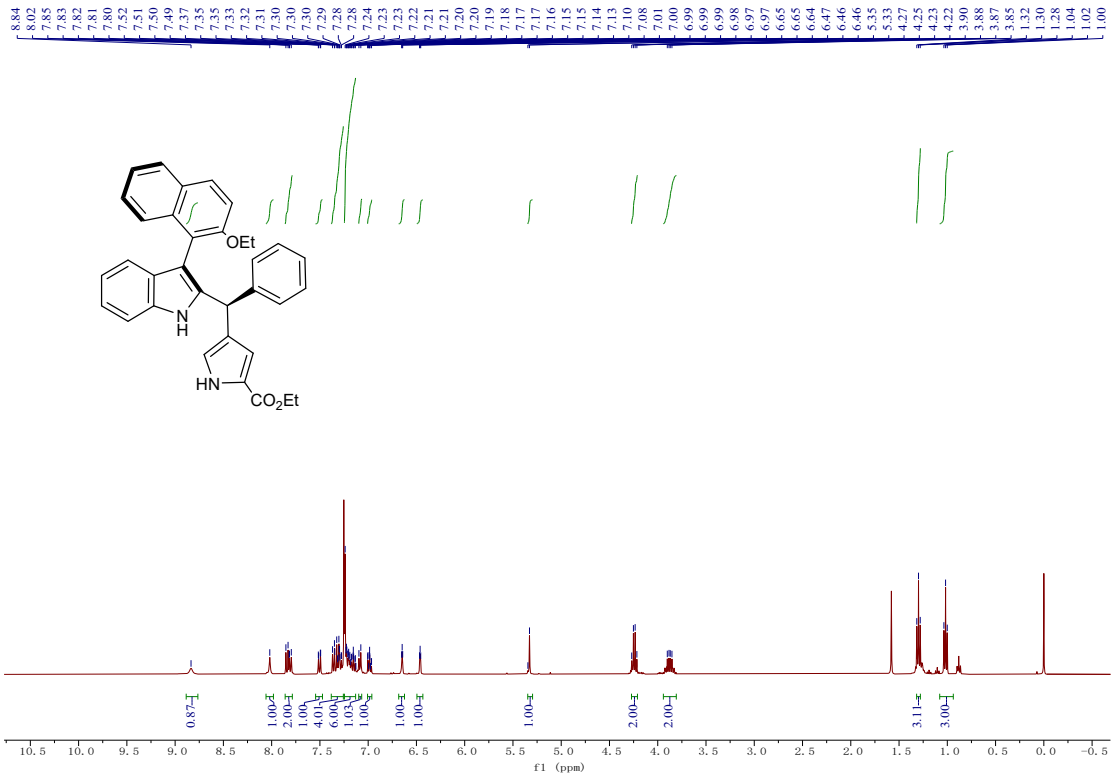
^{1}H NMR (400 MHz, $CDCl_3$) of **3ze**



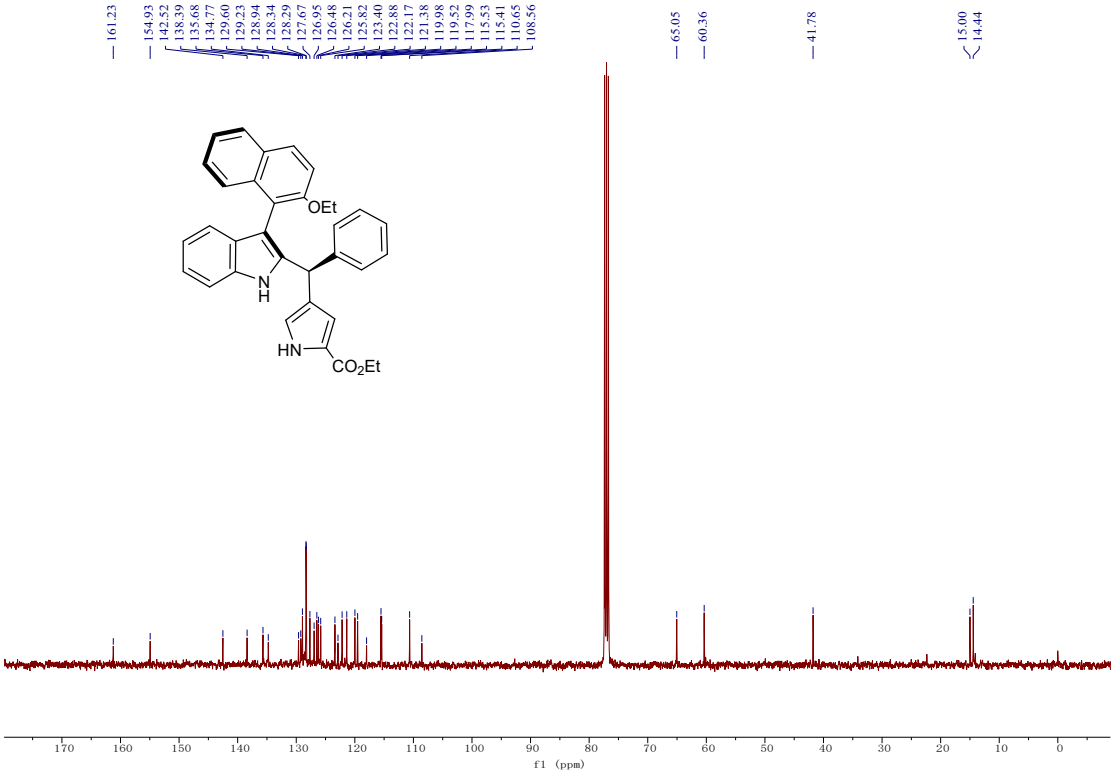
^{13}C NMR (101 MHz, $CDCl_3$) of **3ze**



^{1}H NMR (400 MHz, $CDCl_3$) of **3zf**

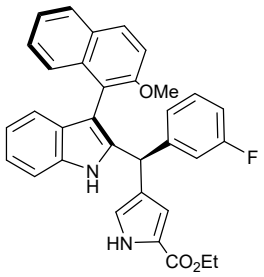


^{13}C NMR (101 MHz, $CDCl_3$) of **3zf**



5. X-Ray Single Crystal Data for Product (*S*)-3b

Single crystals of **3b** were obtained by placing **3b** in a mixed solution of isopropyl alcohol and diethyl ether (volume ratio 1:10) and allowing it to stand at room temperature for a week. The absolute configuration of product **3b** was determined by X-ray diffraction analysis of a single crystal (using a Bruker APEX-II CCD diffractometer). The X-ray data have been deposited at the Cambridge Crystallographic Data Center (CCDC 2431878). The stereochemistry of other products was assumed by analogy.



3b

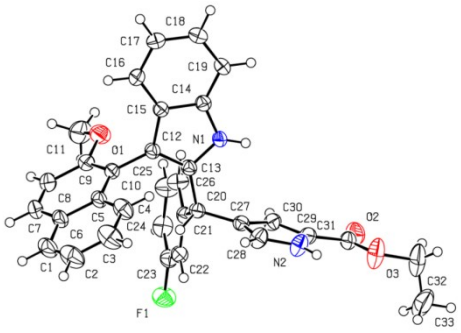
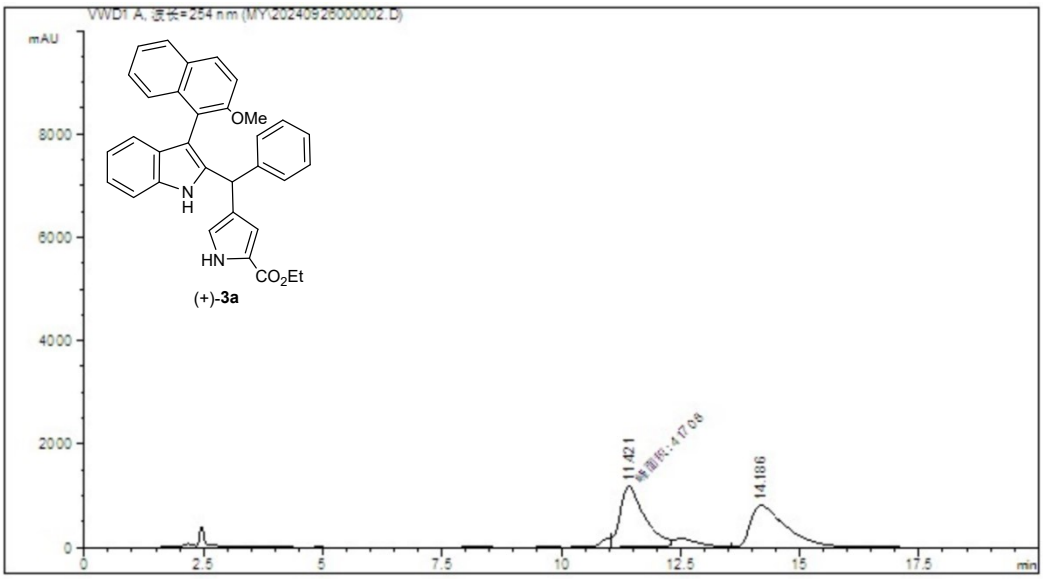


Table 1 Crystal data and structure refinement for 240918_my0918_F1_TSCl (3b).

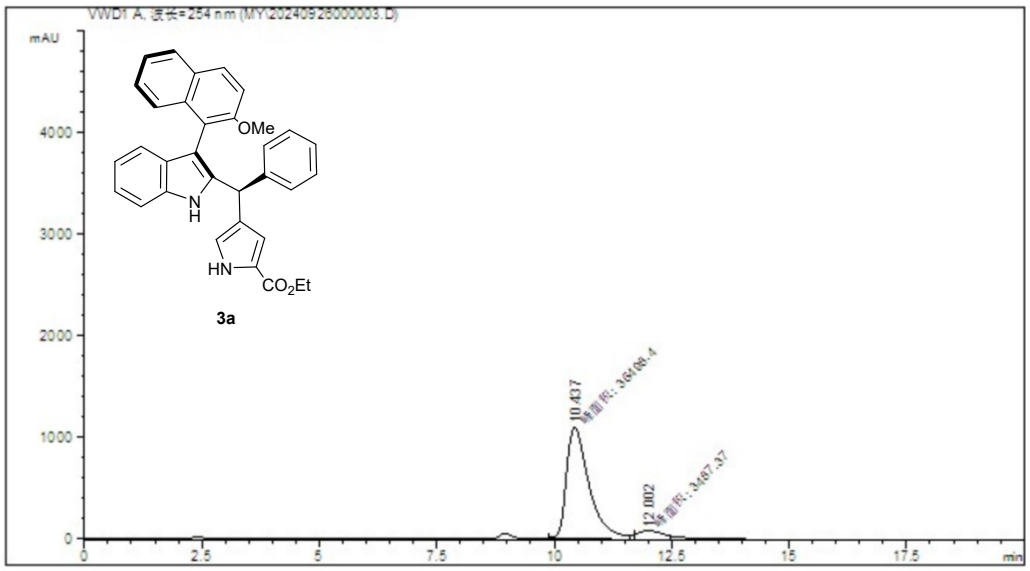
Identification code	240918_my0918_F1_TSCl
Empirical formula	$C_{33.5}H_{27.5}Cl_{1.5}FN_2O_3$
Formula weight	578.25
Temperature/K	170.00
Crystal system	monoclinic
Space group	C2
a/Å	11.5056(7)
b/Å	13.8298(8)
c/Å	18.2204(11)
α/°	90
β/°	98.022(2)
γ/°	90
Volume/Å^3	2870.9(3)
Z	4
ρ_{calc}g/cm^3	1.338

μ/mm^{-1}	1.295
F(000)	1204.0
Crystal size/mm^3	0.16 × 0.08 × 0.06
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	8.528 to 121.602
Index ranges	$-14 \leq h \leq 14$, $-18 \leq k \leq 17$, $-23 \leq l \leq 23$
Reflections collected	47692
Independent reflections	6564 [R_{int} = 0.0378, R_{sigma} = 0.0276]
Data/restraints/parameters	6564/47/401
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0470, wR_2 = 0.1264
Final R indexes [all data]	R_1 = 0.0494, wR_2 = 0.1294
Largest diff. peak/hole / e $Å^{-3}$	0.38/-0.46
Flack parameter	0.097(8)

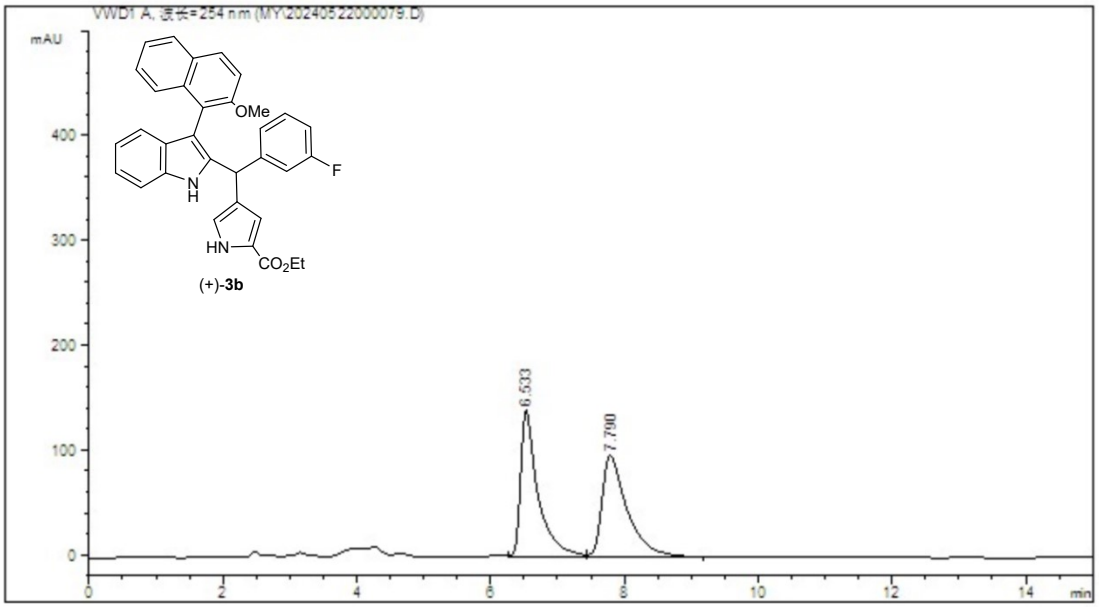
6. Copies of HPLC Spectra



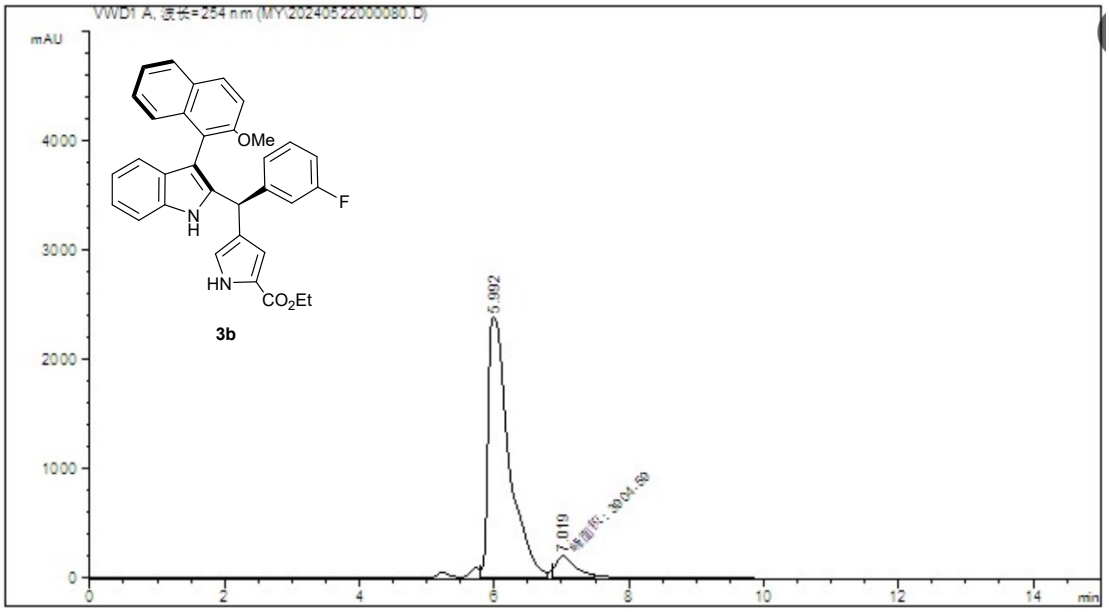
#	[min]		[min]	mAU	*s	[mAU	]	%
1	11.421	MM	0.5896	4.17080e4		1179.05383		49.7632
2	14.186	VV	0.7481	4.21049e4		817.23376		50.2368



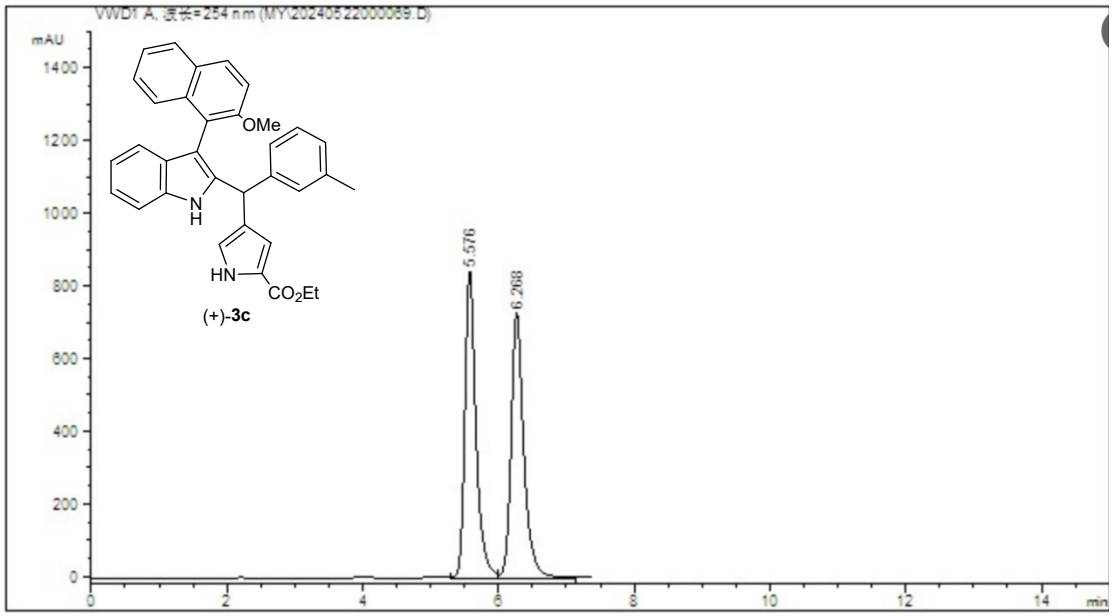
#	[min]		[min]	mAU	*s	[mAU	]	%
1	10.437	MM	0.5575	3.64984e4		1091.19482		91.2785
2	12.002	MM	0.6306	3487.36743		92.16611		8.7215



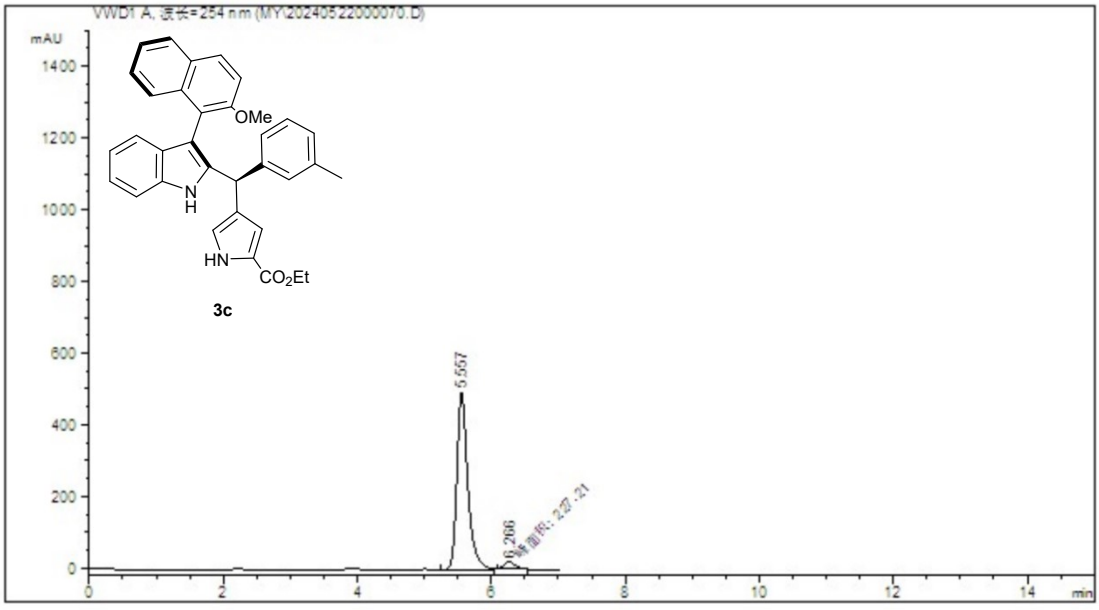
#	[min]		[min]	mAU	*s	[mAU	]	%
1	6.533	VV	0.2607	2551.73145		139.97327		50.1499
2	7.790	VB	0.3801	2536.48047		96.76948		49.8501



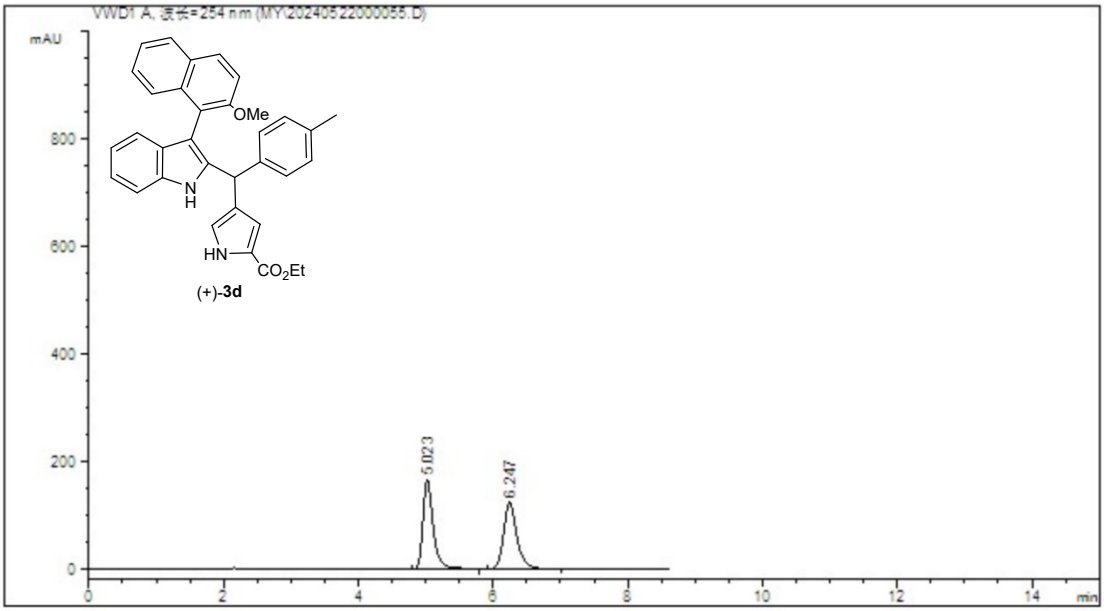
#	[min]		[min]	mAU	*s	[mAU	]	%
1	5.992	VV	0.3202	5.12830e4		2376.80786		92.9249
2	7.019	MM	0.3293	3904.59229		197.64270		7.0751



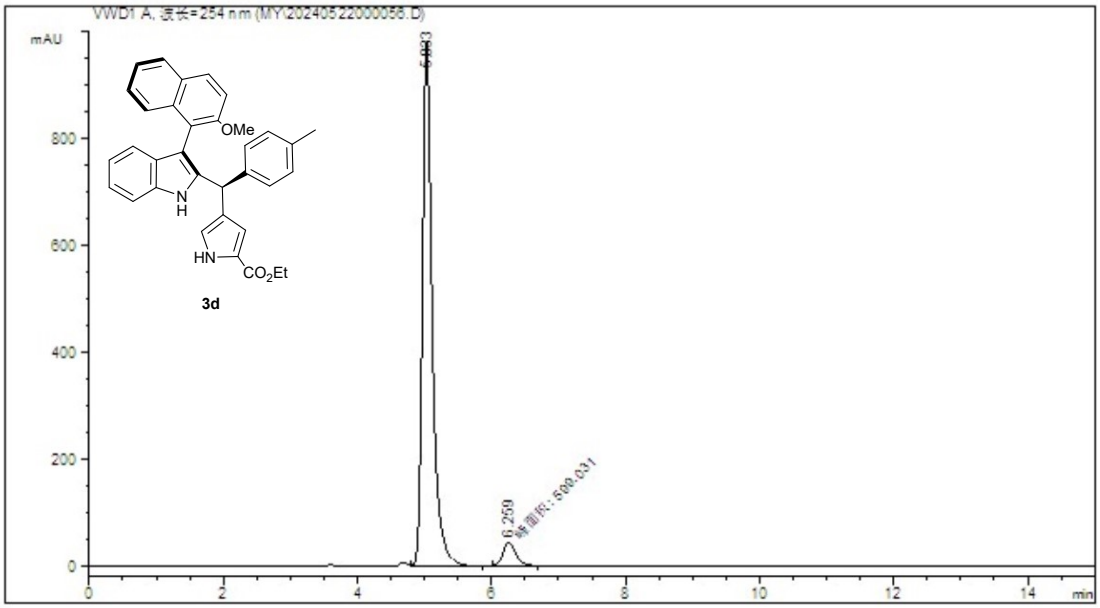
#	[min]		[min]	mAU	*s	[mAU]	%
1	5.576	VV	0.1707	9632.70605	845.72693	50.2093	
2	6.268	VB	0.1937	9552.39453	728.71234	49.7907	



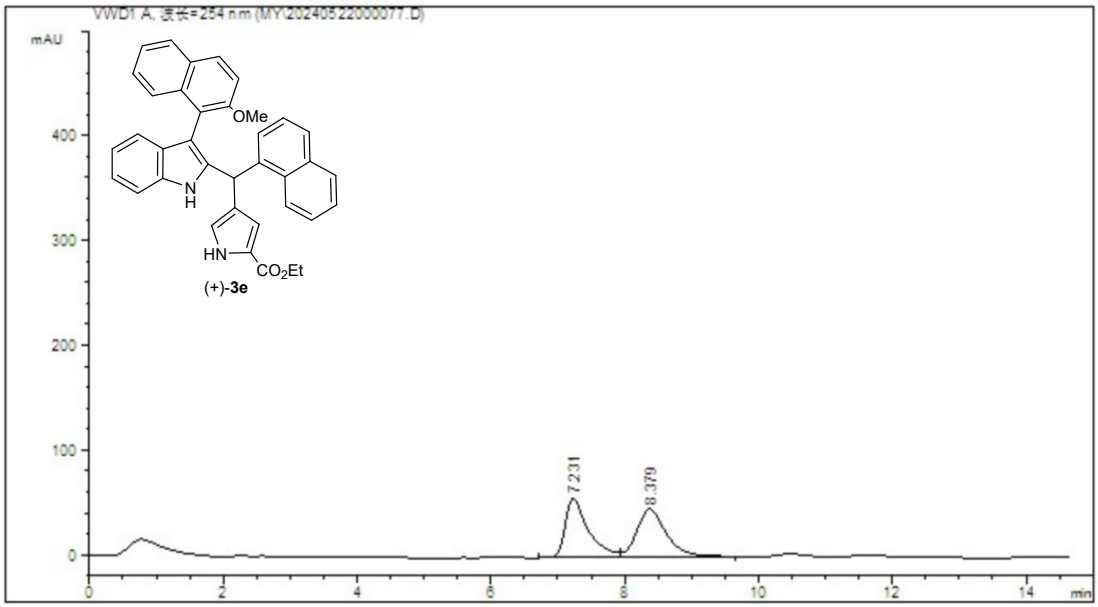
#	[min]		[min]	mAU	*s	[mAU]	%
1	5.557	VV	0.1707	5612.30957	492.90076	96.1091	
2	6.266	MM	0.1978	227.21002	19.14566	3.8909	



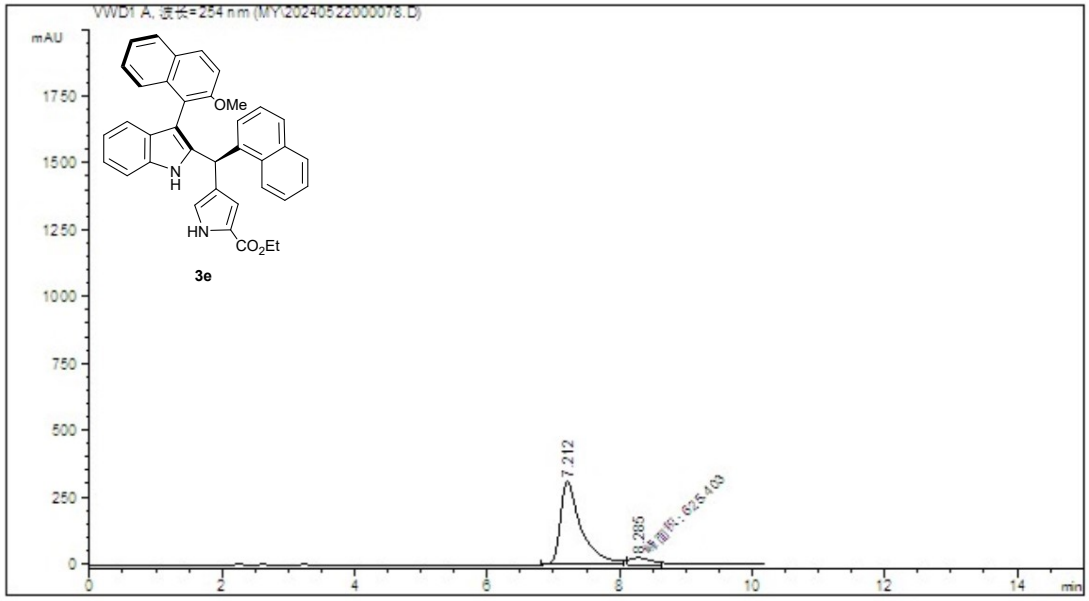
#	[min]		[min]	mAU	*s	[mAU]	%
1	5.023	VB	0.1619	1817.39429		166.97023	50.6889
2	6.247	BV	0.2120	1767.99390		124.67907	49.3111



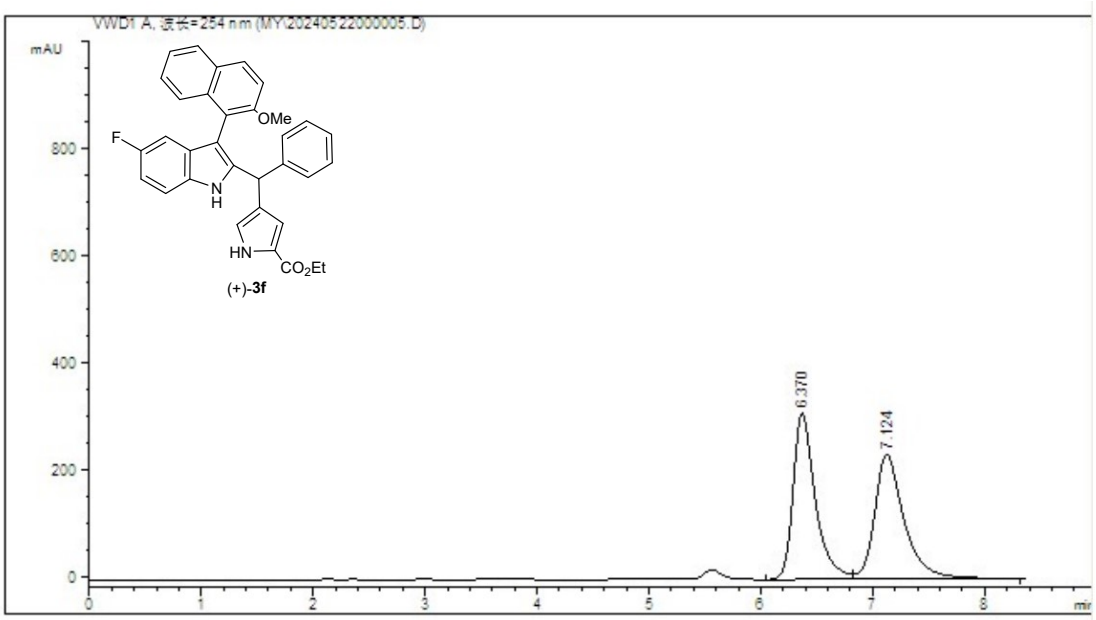
#	[min]		[min]	mAU	*s	[mAU]	%
1	5.033	VB	0.1531	1.00612e4		981.34180	94.3807
2	6.259	MM	0.2237	599.03058		44.64022	5.6193



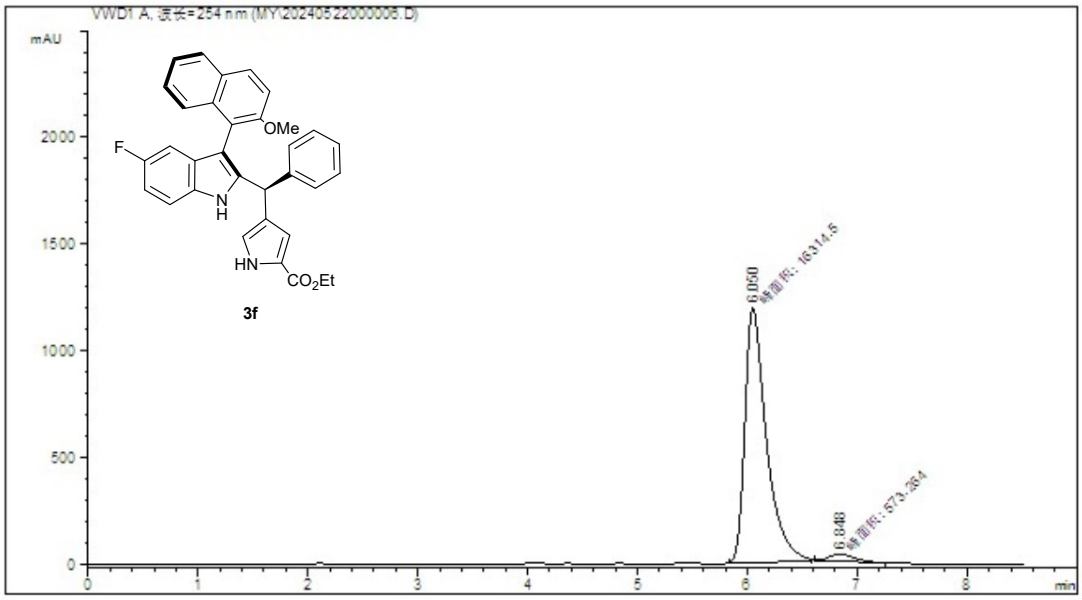
#	[min]		[min]	mAU	*s	[mAU]	%
1	7.231	BV	0.3453	1361.51025	56.78263	48.8248	
2	8.379	VB	0.4637	1427.05054	46.02361	51.1752	



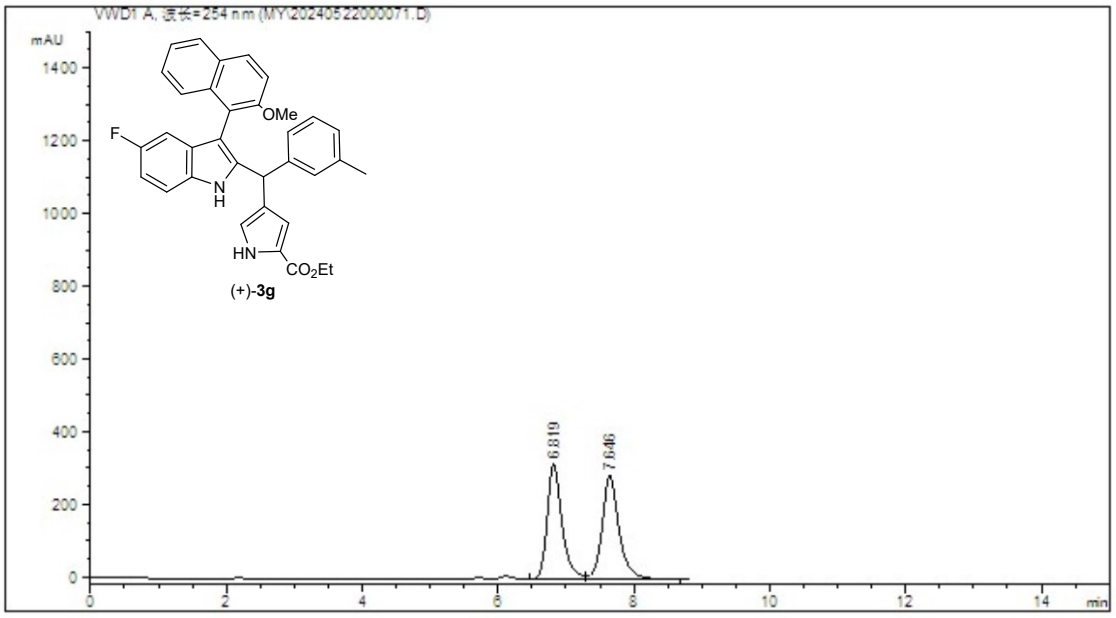
#	[min]		[min]	mAU	*s	[mAU]	%
1	7.212	BV	0.3133	6791.59180	310.67813	91.5680	
2	8.285	MM	0.3823	625.40320	27.26495	8.4320	



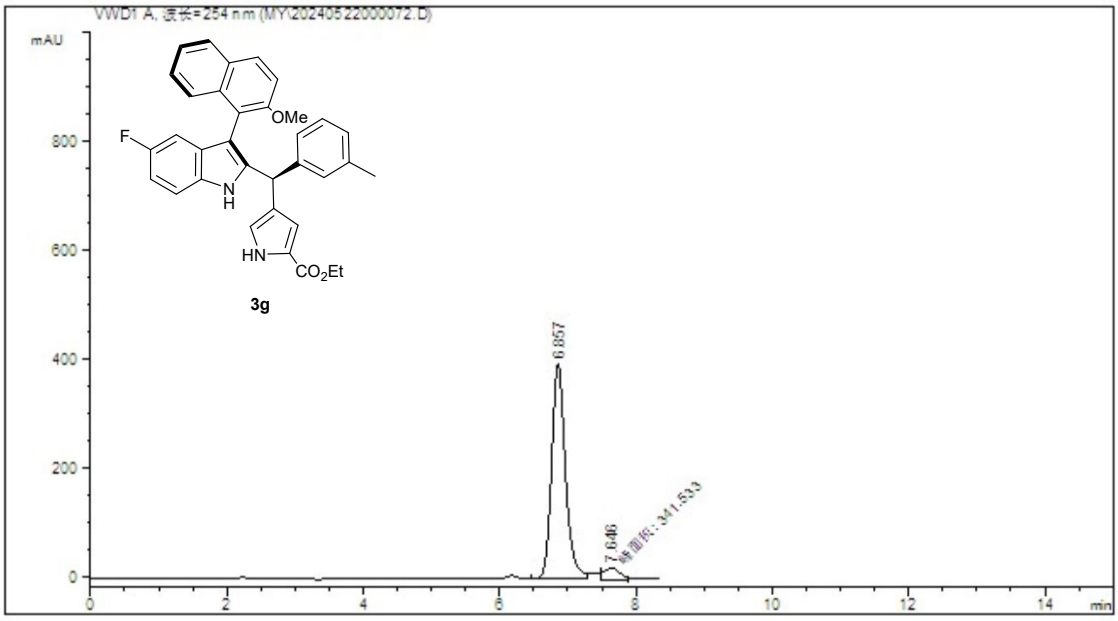
#	[min]		[min]	mAU	*s	[mAU	]	%
1	6.370	BV	0.2047	4289.09912		310.71088		50.0645
2	7.124	VB	0.2694	4278.04443		233.15057		49.9355



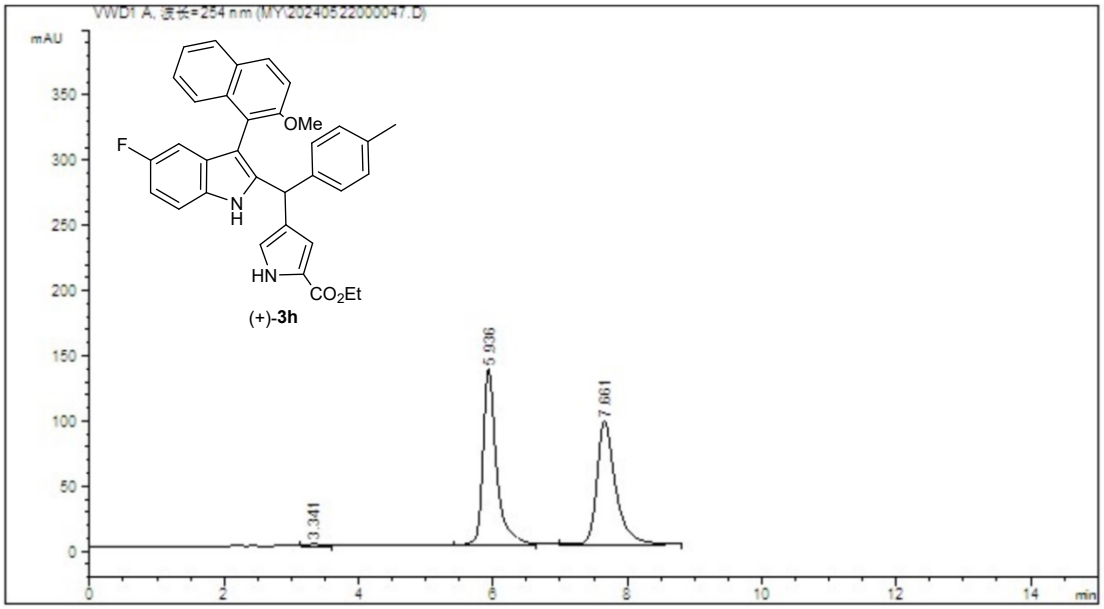
#	[min]		[min]	mAU	*s	[mAU	]	%
1	6.050	MM	0.2274	1.63145e4		1195.80151		96.6054
2	6.848	MM	0.2676	573.26428		35.70073		3.3946



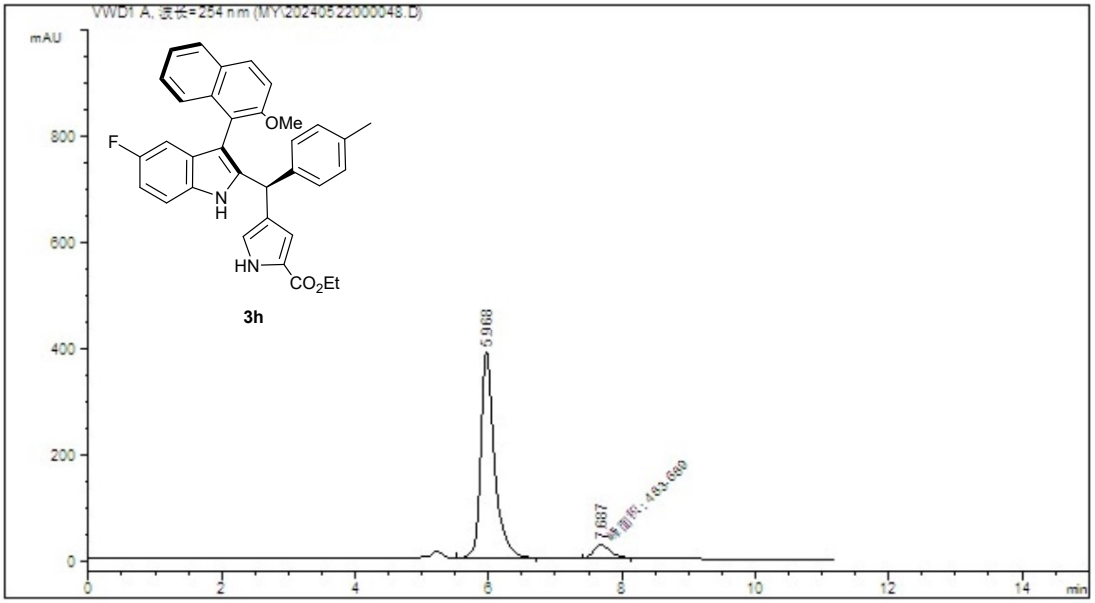
#	[min]		[min]	mAU	*s	[mAU	]	%
1	6.819	VV	0.2285	4820.85156	316.81741			49.3878
2	7.646	VB	0.2580	4940.37012	284.43918			50.6122



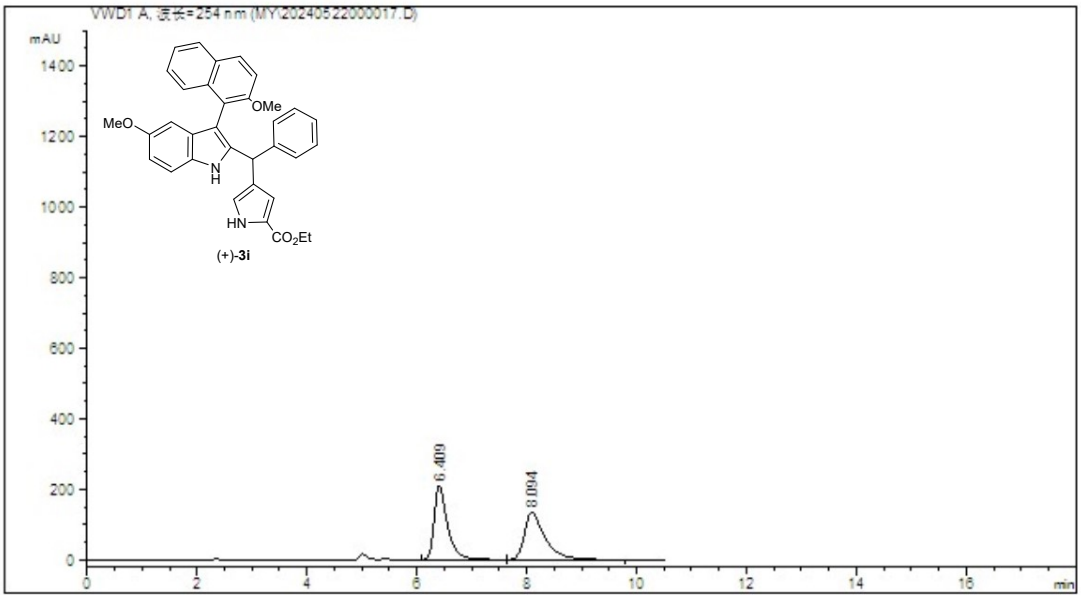
1	6.857	VV	0.2125	5571.95605	395.33994		94.2245
2	7.646	MM	0.2651	341.53290	21.47031		5.7755



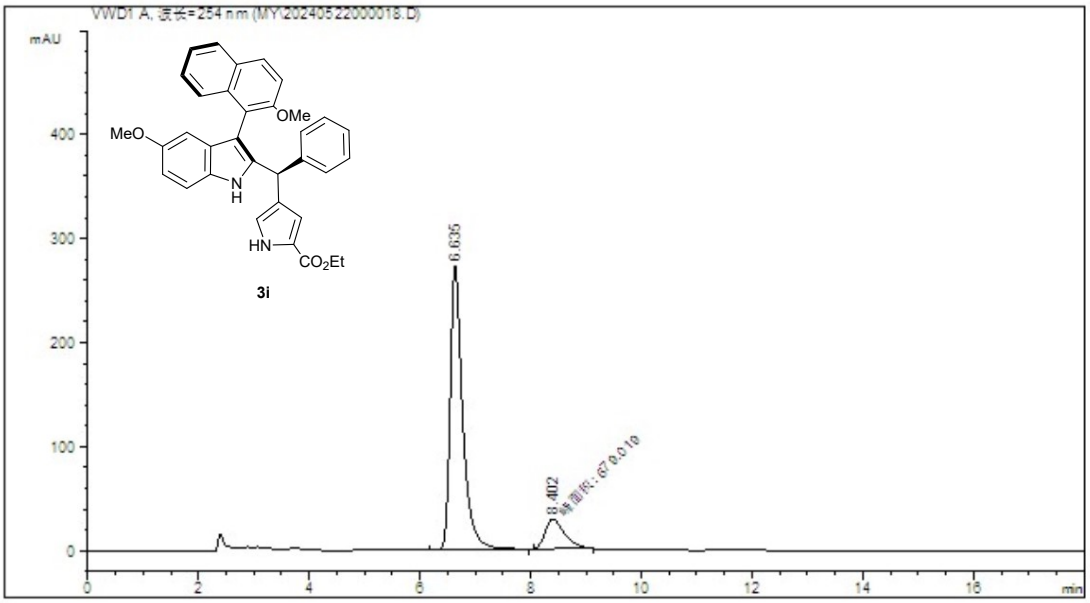
#	[min]		[min]	mAU	*s	[mAU	]	%
1	3.341	VV	0.1714	21.69770		1.85456		0.5746
2	5.936	VV	0.2073	1911.41492		135.05780		50.6156
3	7.661	VB	0.2853	1843.22510		94.69310		48.8099



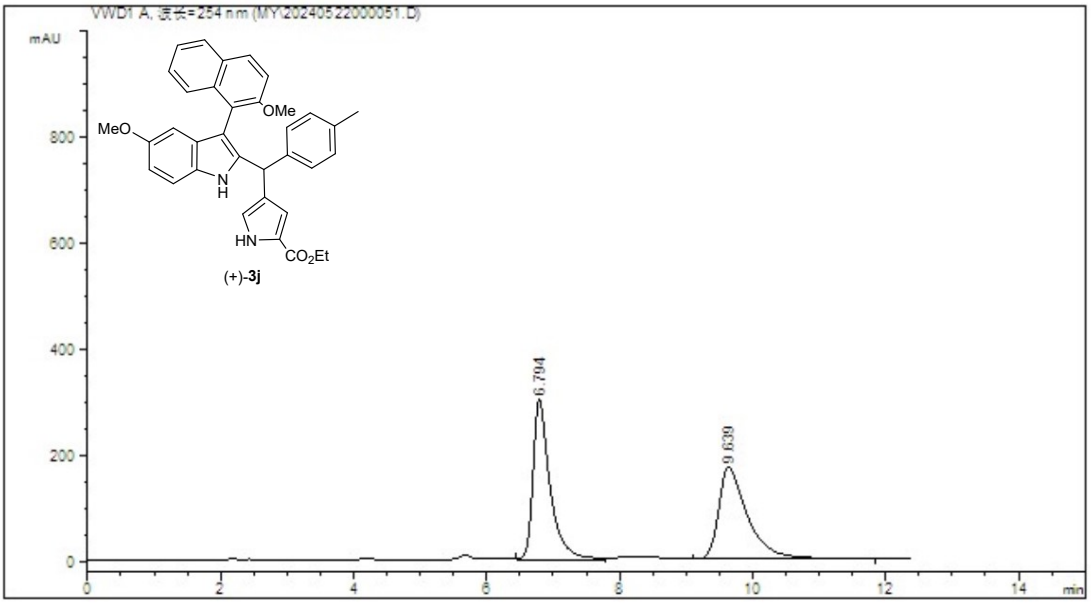
#	[min]		[min]	mAU	*s	[mAU	]	%
1	5.968	VB	0.2112	5579.91895		388.49460		92.0231
2	7.687	MM	0.3049	483.68915		26.44122		7.9769



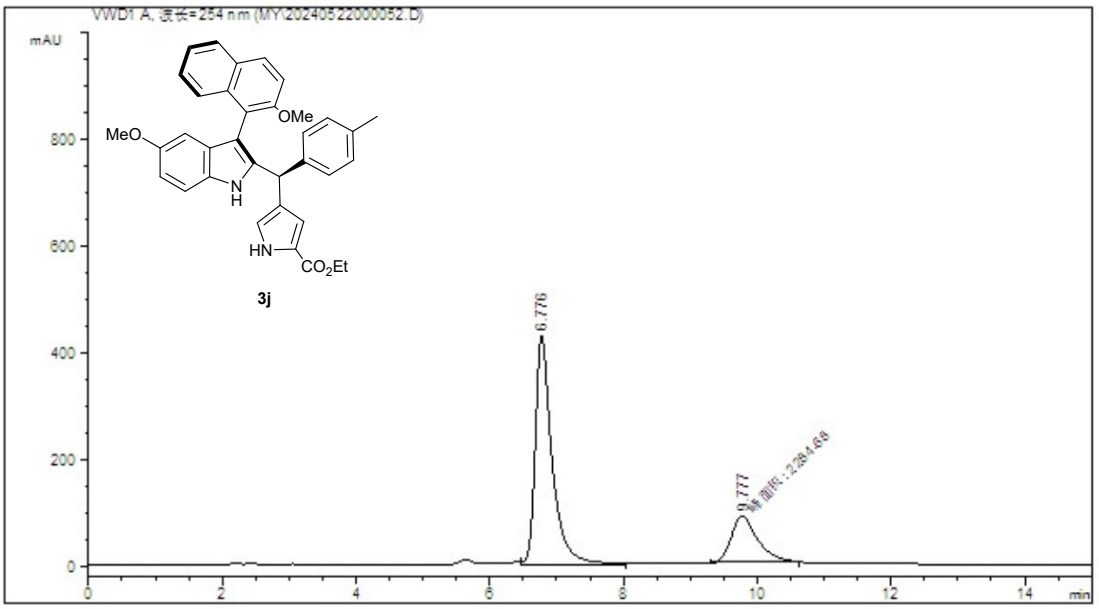
#	[min]		[min]	mAU	*s	[mAU	]	%
1	6.409	VV	0.2524	3612.97388	210.76662			50.2307
2	8.094	VB	0.3847	3579.79175	135.15311			49.7693



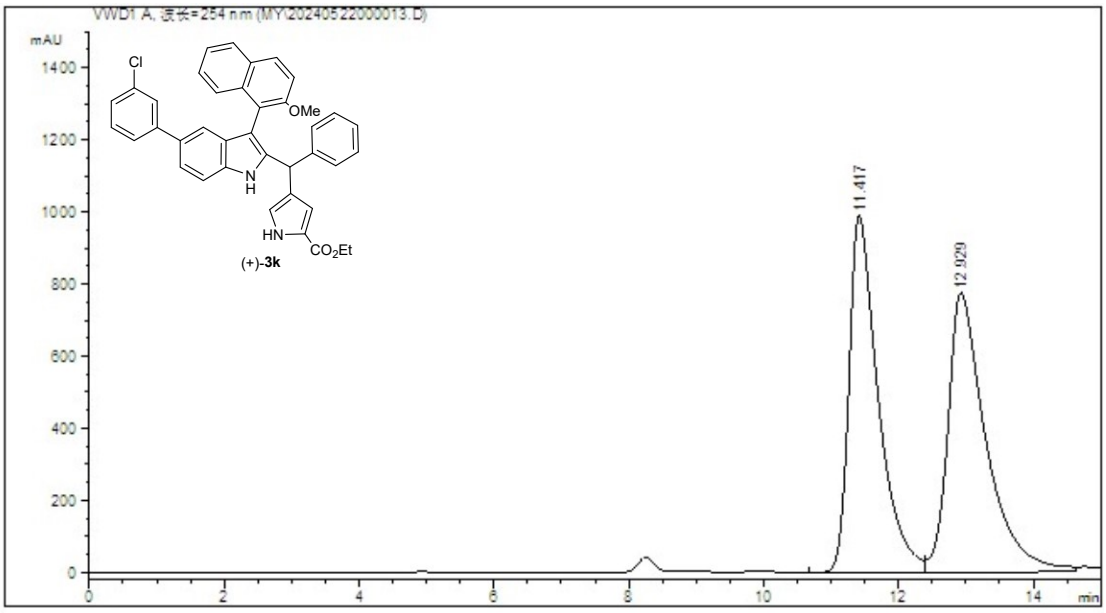
#	[min]		[min]	mAU	*s	[mAU	]	%
1	6.635	BV	0.2327	4334.03125	273.78888			86.4550
2	8.402	MM	0.3940	679.01923	28.72114			13.5450



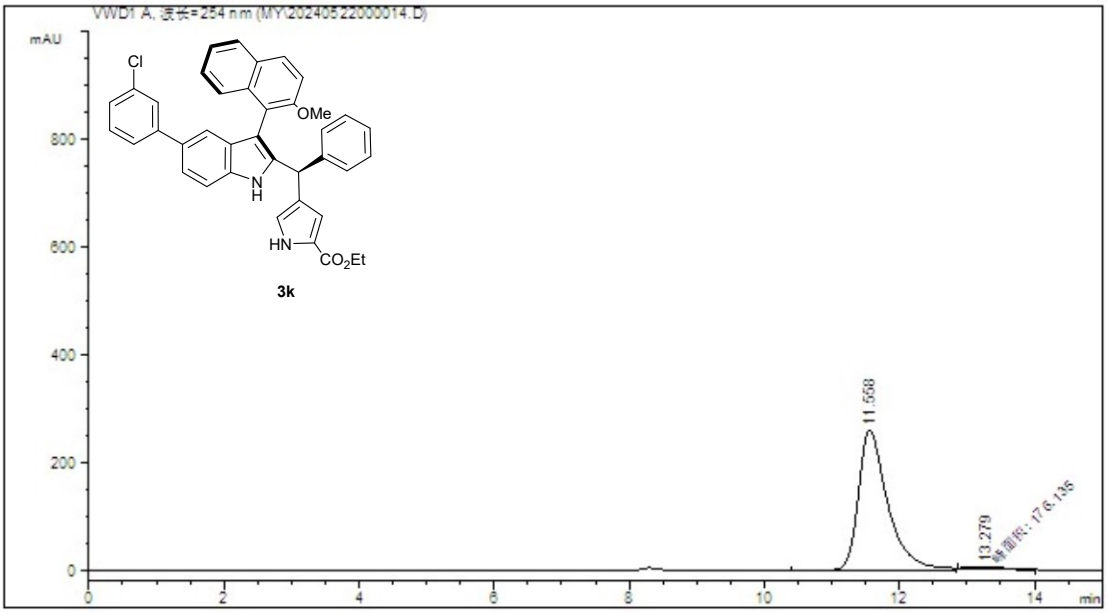
#	[min]		[min]	mAU	*s	[mAU]	%
1	6.794	VV	0.2595	5340.23730		300.90601	50.2462
2	9.639	VB	0.4410	5287.89795		173.02003	49.7538



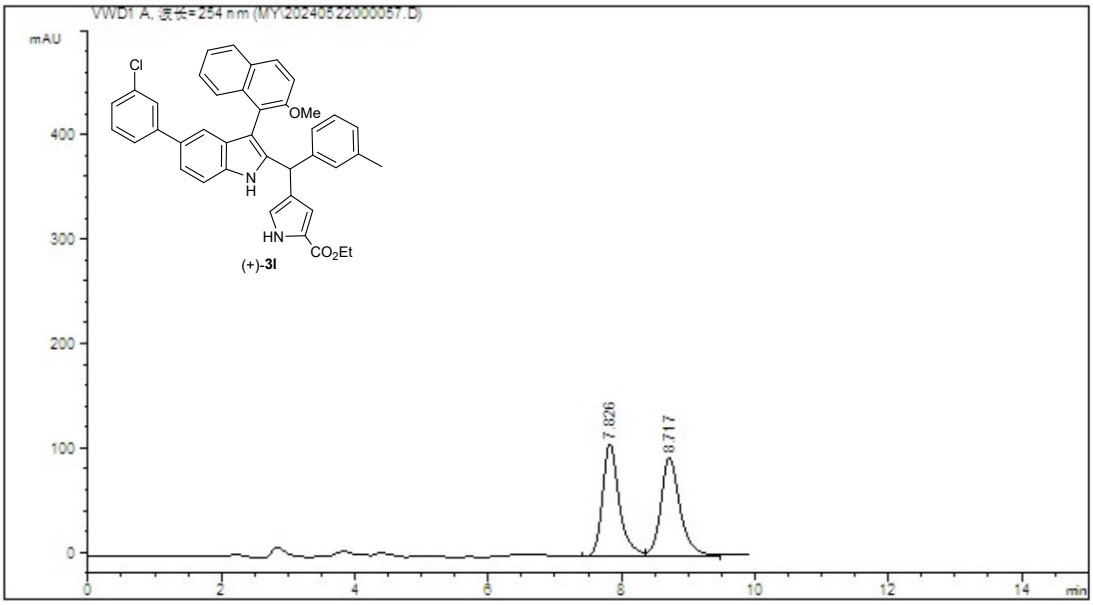
#	[min]		[min]	mAU	*s	[mAU]	%
1	6.776	VB	0.2542	7455.35498		427.86319	76.5434
2	9.777	MM	0.4457	2284.68311		85.43123	23.4566



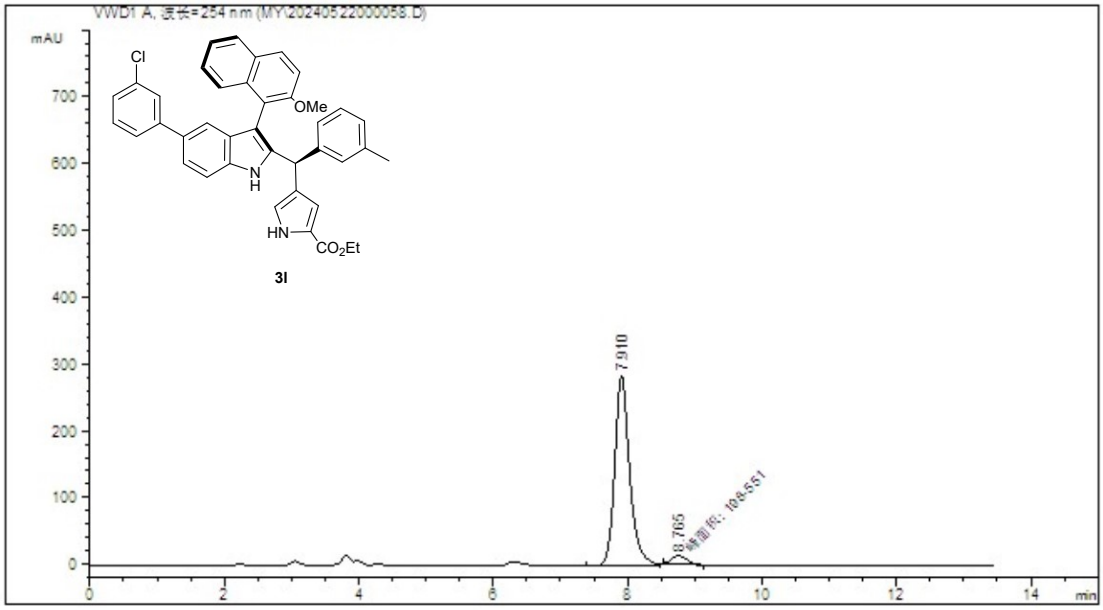
#	[min]		[min]	mAU	*s	[mAU]	%
1	11.417	VV	0.4383	2.96043e4		988.19812	49.4572
2	12.929	VB	0.5649	3.02541e4		774.58813	50.5428



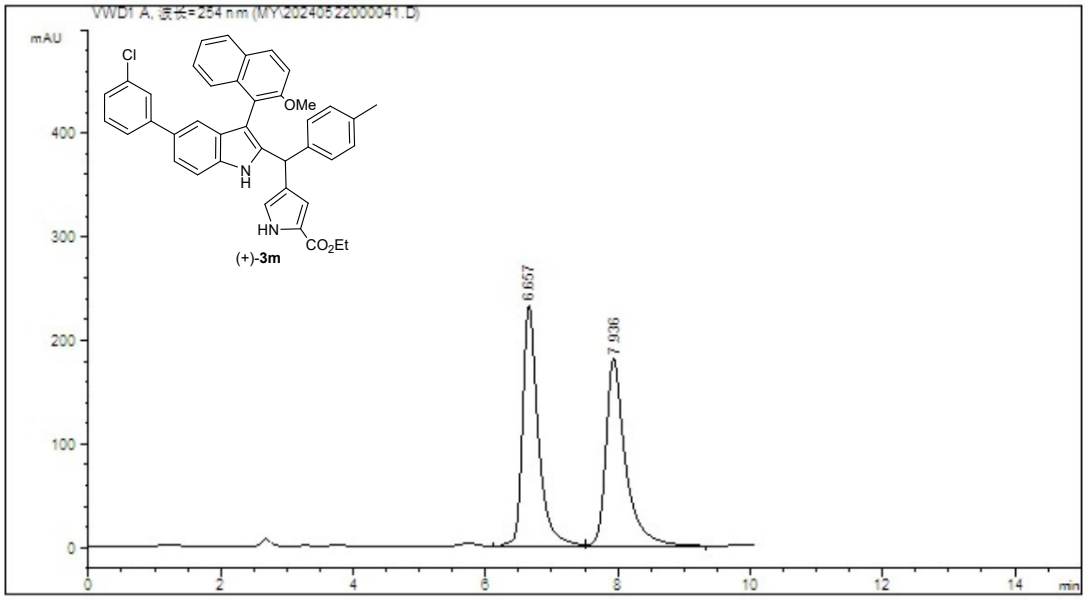
#	[min]		[min]	mAU	*s	[mAU]	%
1	11.558	BV	0.4447	7844.81543		260.37408	97.8041
2	13.279	MM	0.6154	176.13470		4.77037	2.1959



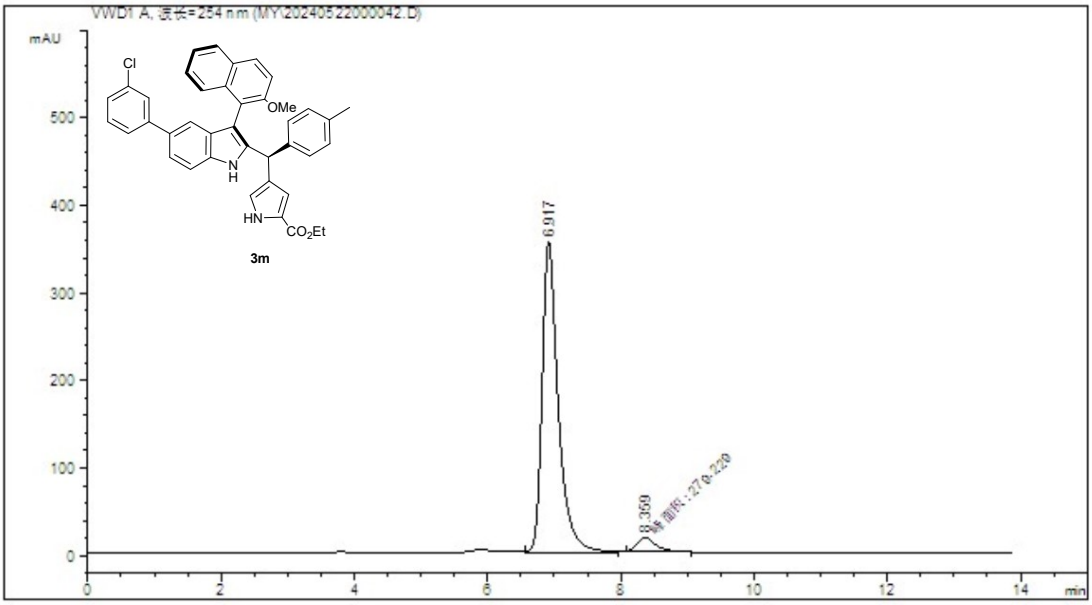
#	[min]		[min]	mAU	*s	[mAU]	%
1	7.826	VV	0.2634	1907.00562	108.41856	49.9849	
2	8.717	VB	0.3037	1908.15942	94.62911	50.0151	



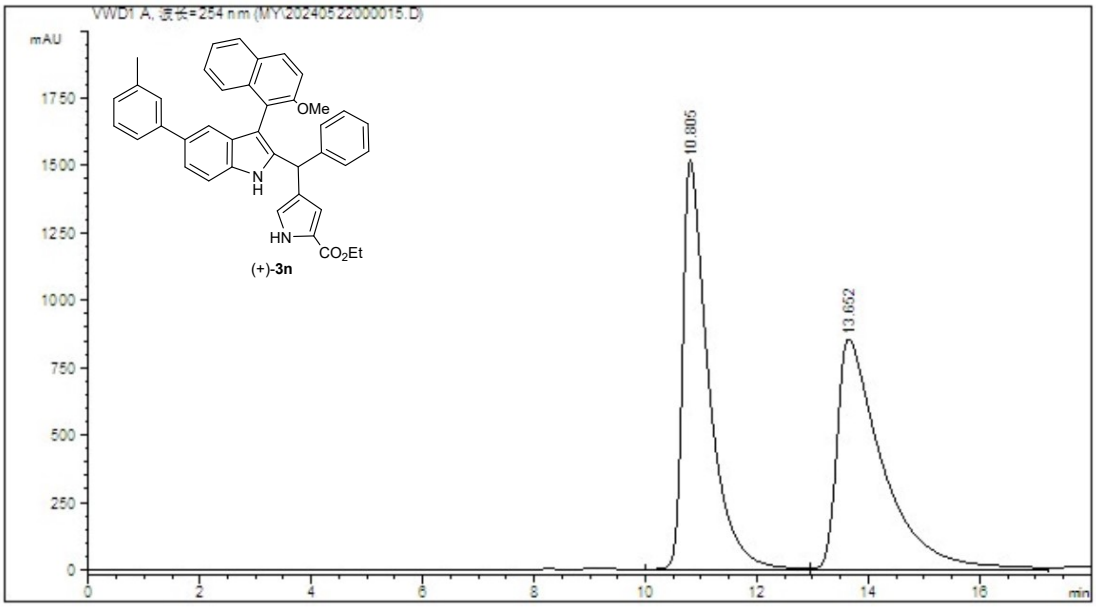
#	[min]		[min]	mAU	*s	[mAU]	%
1	7.910	VV	0.2319	4409.01660	284.31638	95.6908	
2	8.765	MM	0.2667	198.55054	12.40960	4.3092	



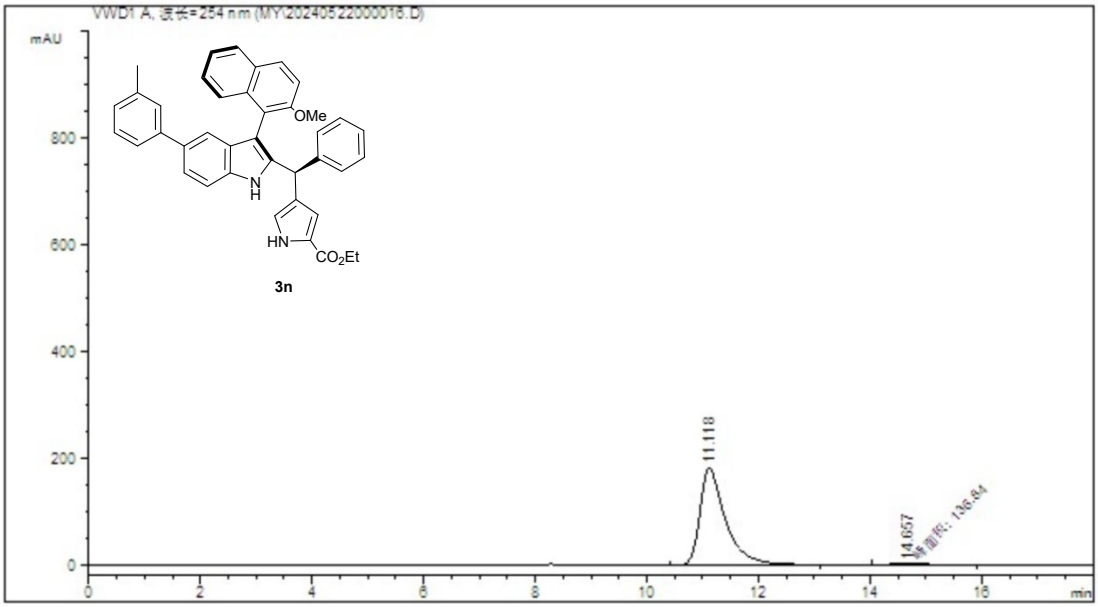
#	[min]		[min]	mAU	*s	[mAU	]	%
1	6.657	VV	0.2448	3834.23437		232.56035		50.7253
2	7.936	VB	0.3012	3724.57983		180.99062		49.2747



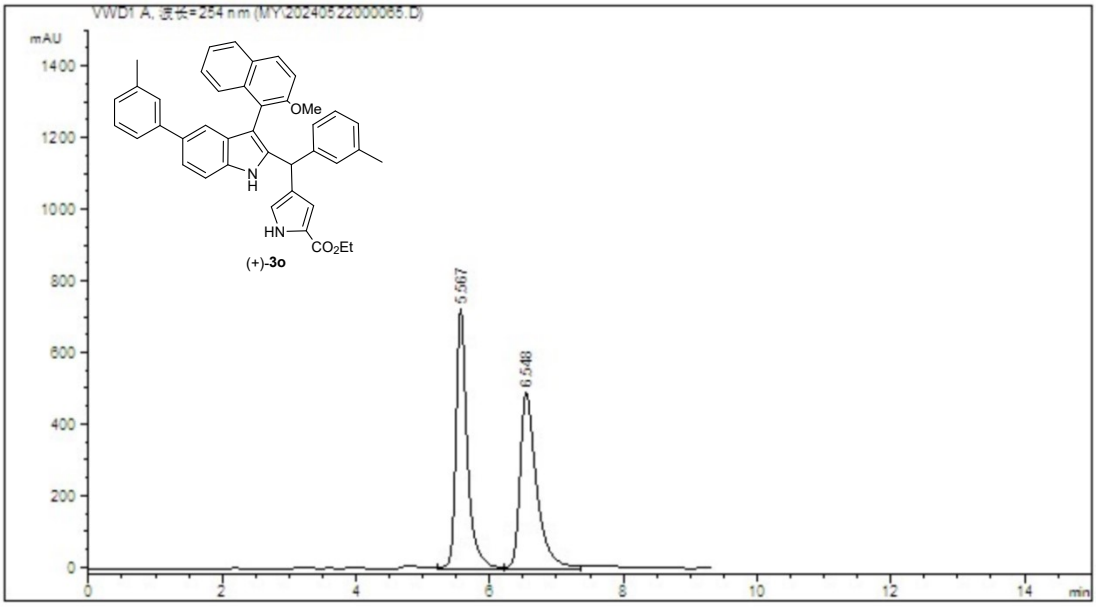
#	[min]		[min]	mAU	*s	[mAU	]	%
1	6.917	VB	0.2511	6001.43506		355.08371		95.5541
2	8.359	MM	0.3009	279.22928		15.46826		4.4459



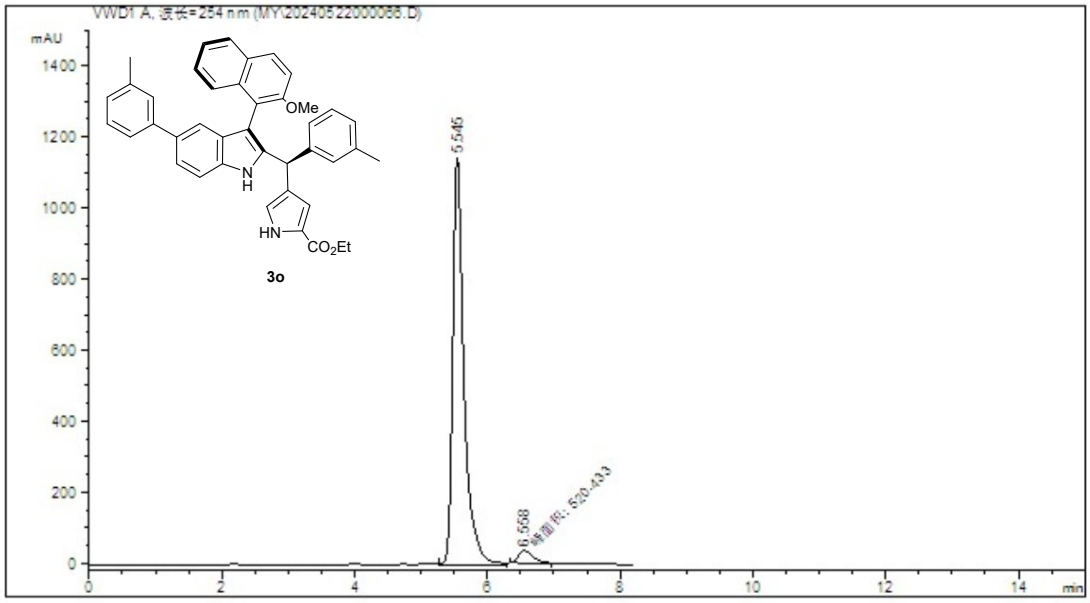
#	[min]		[min]	mAU	*s	[mAU	]	%
1	10.805	VV	0.4655	4.90694e4		1519.69031		50.1559
2	13.652	VB	0.8069	4.87643e4		856.55963		49.8441



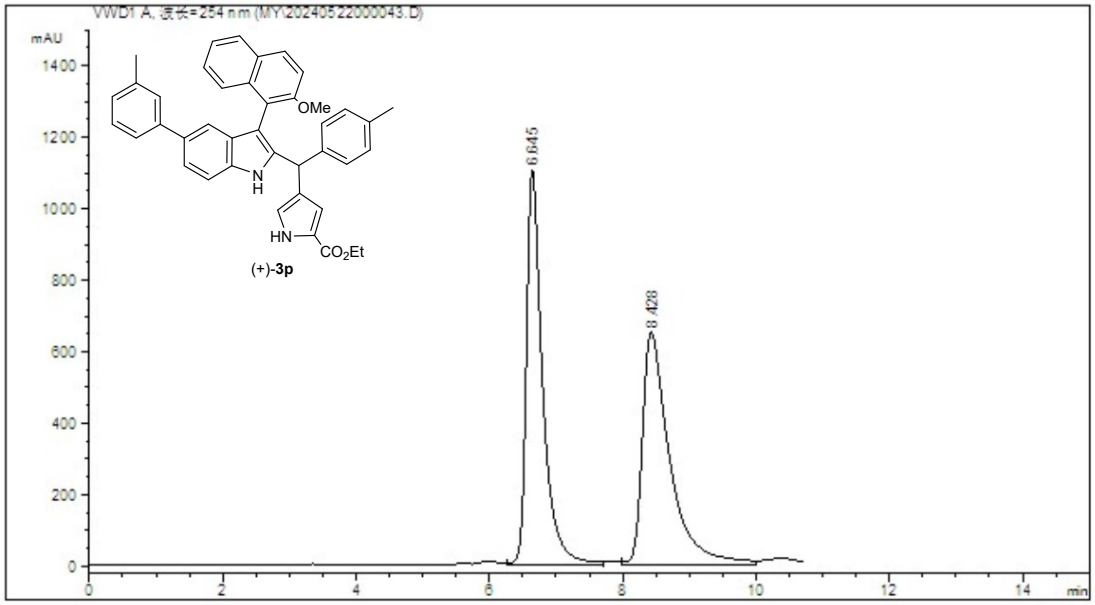
#	[min]		[min]	mAU	*s	[mAU	]	%
1	11.118	BB	0.4652	5789.84570		181.58888		97.6911
2	14.657	MM	0.9858	136.84032		2.31345		2.3089



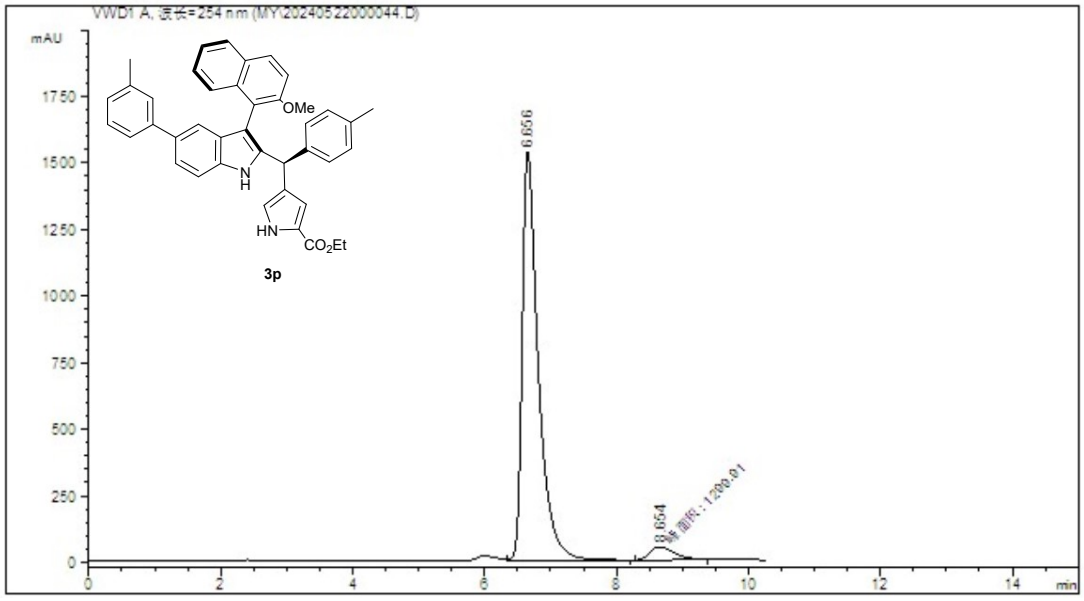
#	[min]		[min]	mAU	*s	[mAU]	%
1	5.567	VV	0.1740	8552.01172		725.05981	50.1182
2	6.548	VV	0.2526	8511.66797		492.51593	49.8818



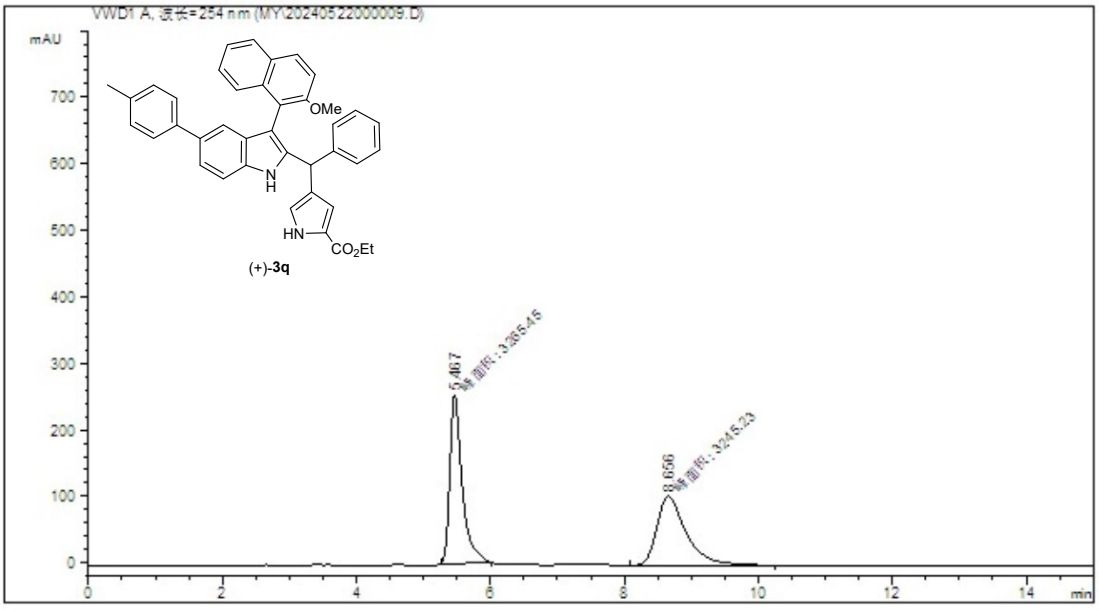
#	[min]		[min]	mAU	*s	[mAU]	%
1	5.545	VV	0.1752	1.34676e4		1143.96814	96.2794
2	6.558	MM	0.2515	520.43311		34.48179	3.7206



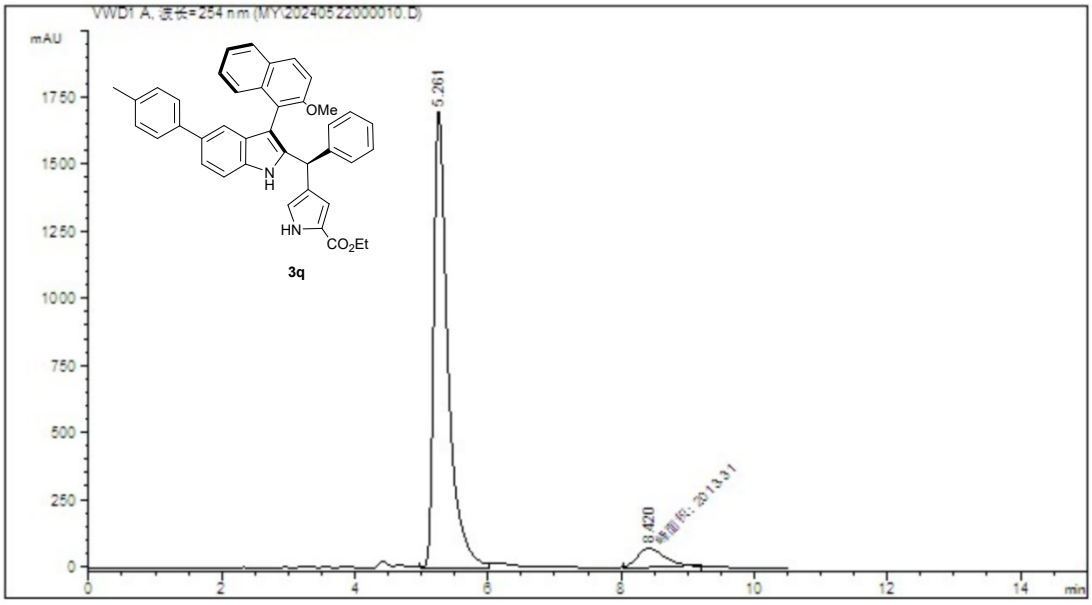
#	[min]		[min]	mAU	*s	[mAU]	%
1	6.645	VV	0.2458	1.85671e4		1103.59399	50.0183
2	8.428	VV	0.4098	1.85535e4		650.75891	49.9817



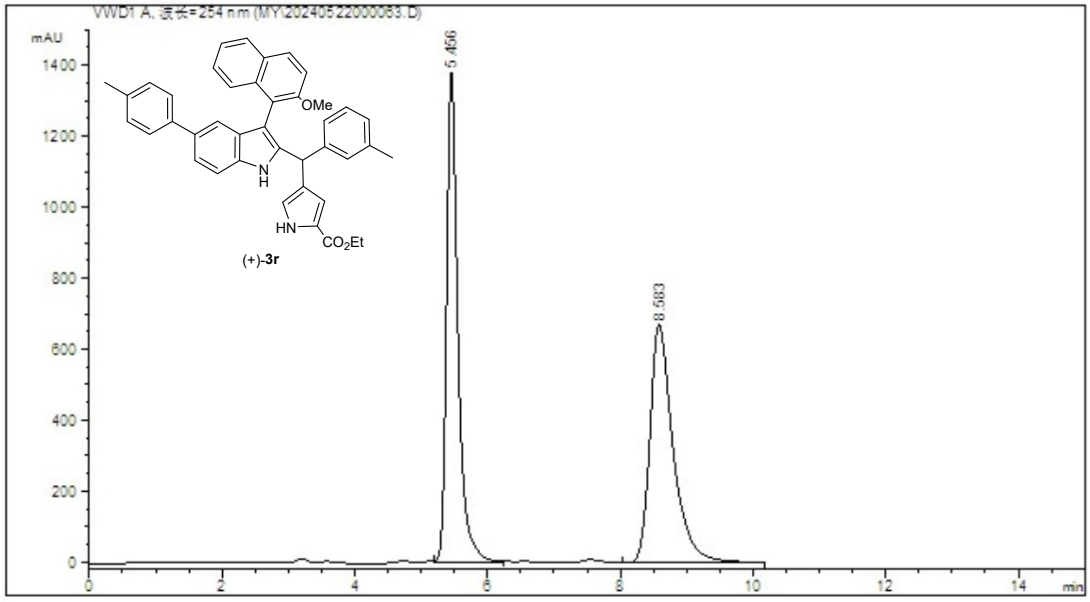
#	[min]		[min]	mAU	*s	[mAU]	%
1	6.656	VV	0.2508	2.63302e4		1537.16211	95.2953
2	8.654	MM	0.4337	1299.91357		49.95850	4.7047



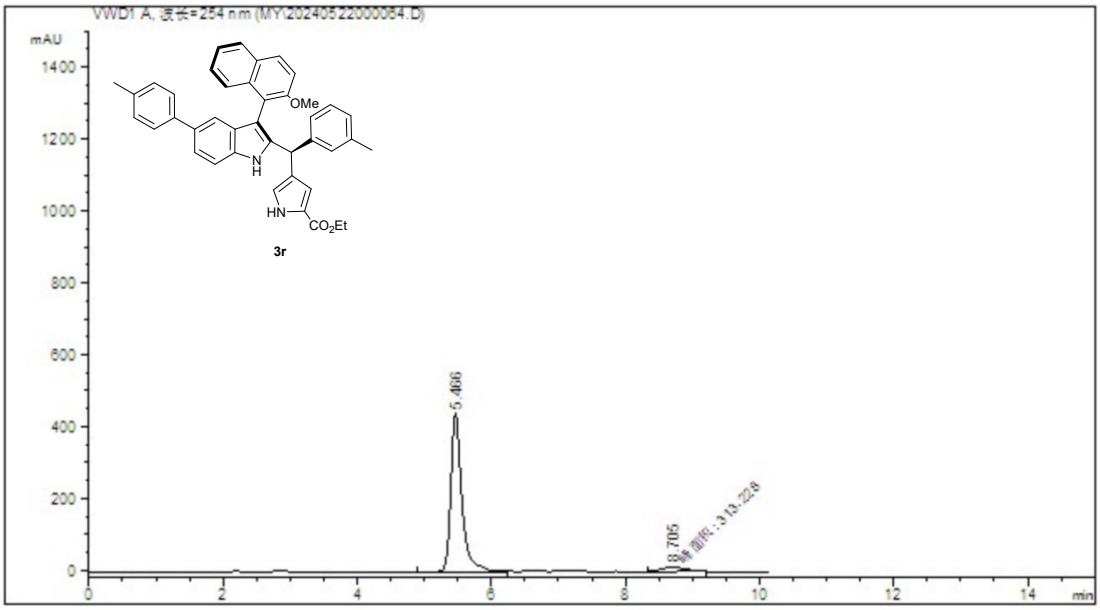
#	[min]		[min]	mAU	*s	[mAU]	%
1	5.467	MM	0.2148	3265.44946	253.37117	50.1553
2	8.656	MM	0.5158	3245.23022	104.86482	49.8447



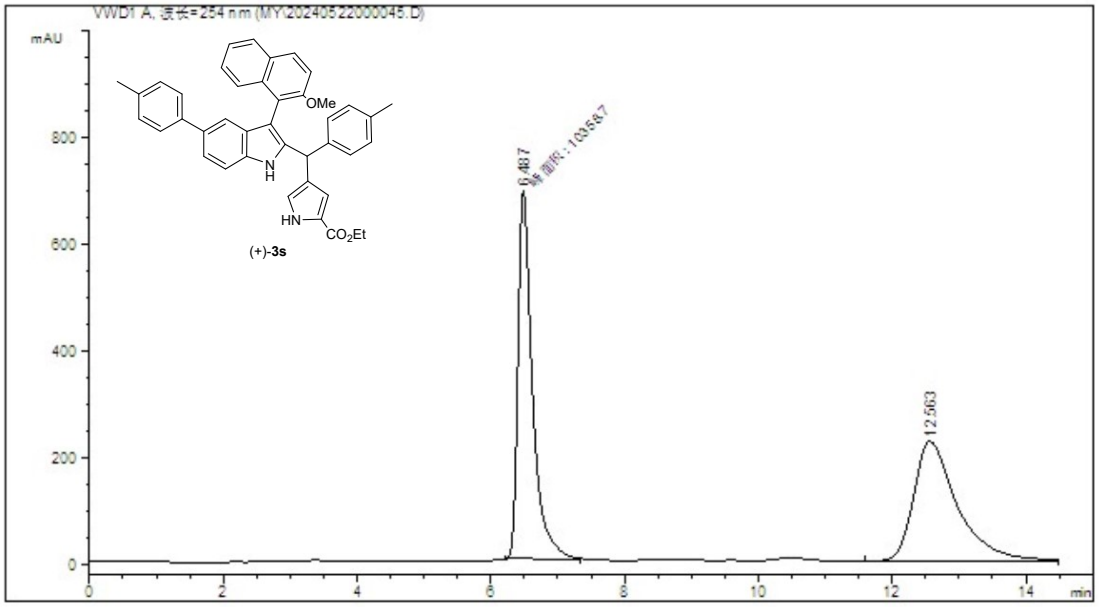
#	[min]		[min]	mAU	*s	[mAU]	%
1	5.261	VV	0.2189	2.51450e4	1702.90662	92.5868
2	8.420	MM	0.4718	2013.30591	71.11877	7.4132



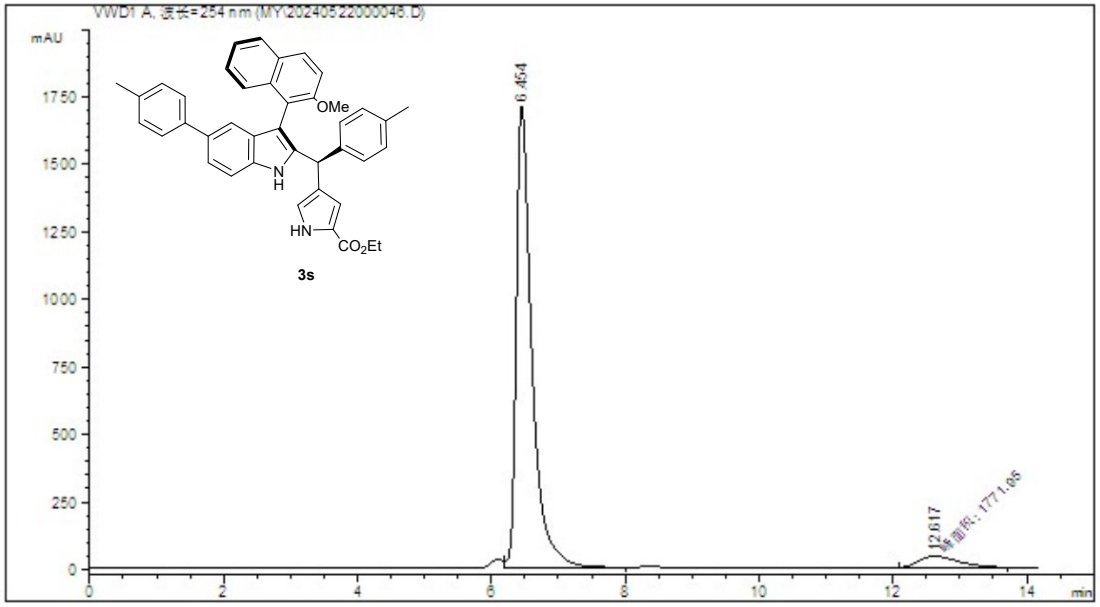
#	[min]		[min]	mAU	*s	[mAU]	%
1	5.456	VB	0.1786	1.65008e4		1381.70605	50.3402
2	8.583	VBA	0.3608	1.62778e4		669.64618	49.6598



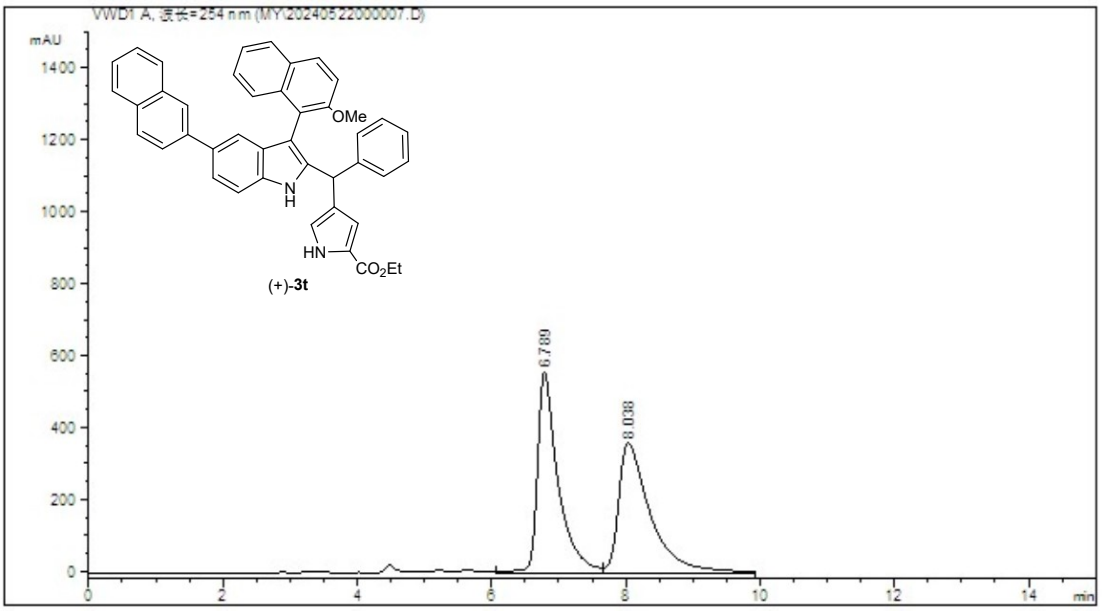
#	[min]		[min]	mAU	*s	[mAU]	%
1	5.466	VB	0.1699	5025.78906		439.15656	94.1332
2	8.705	MM	0.3835	313.22781		13.61135	5.8668



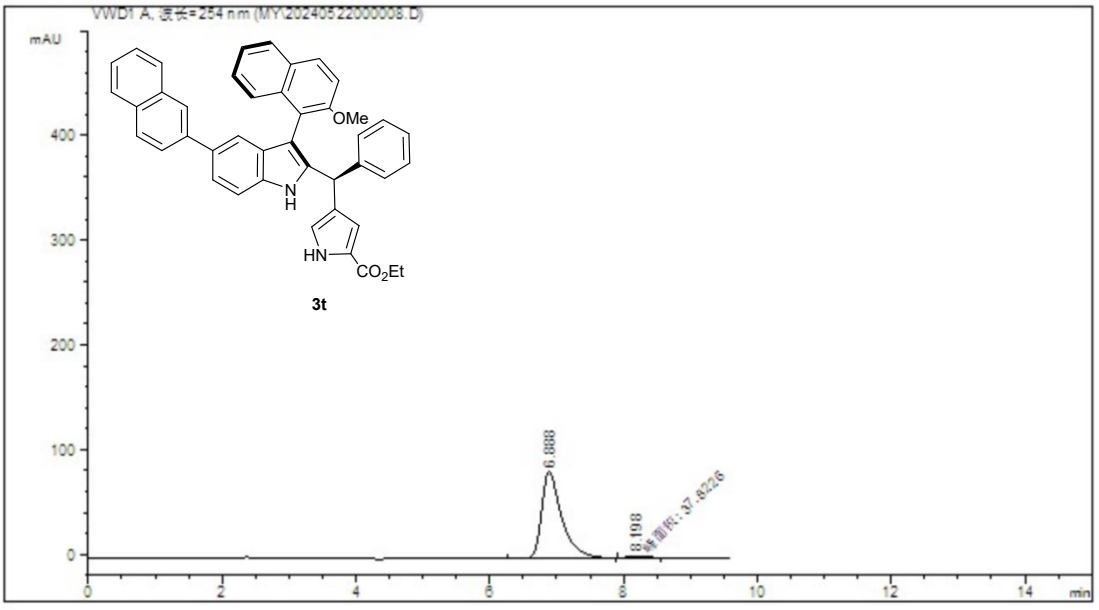
#	[min]		[min]	mAU	*s	[mAU	]	%
1	6.487	MM	0.2507	1.03587e4		688.71466		49.7775
2	12.563	BBA	0.6869	1.04513e4		225.87254		50.2225



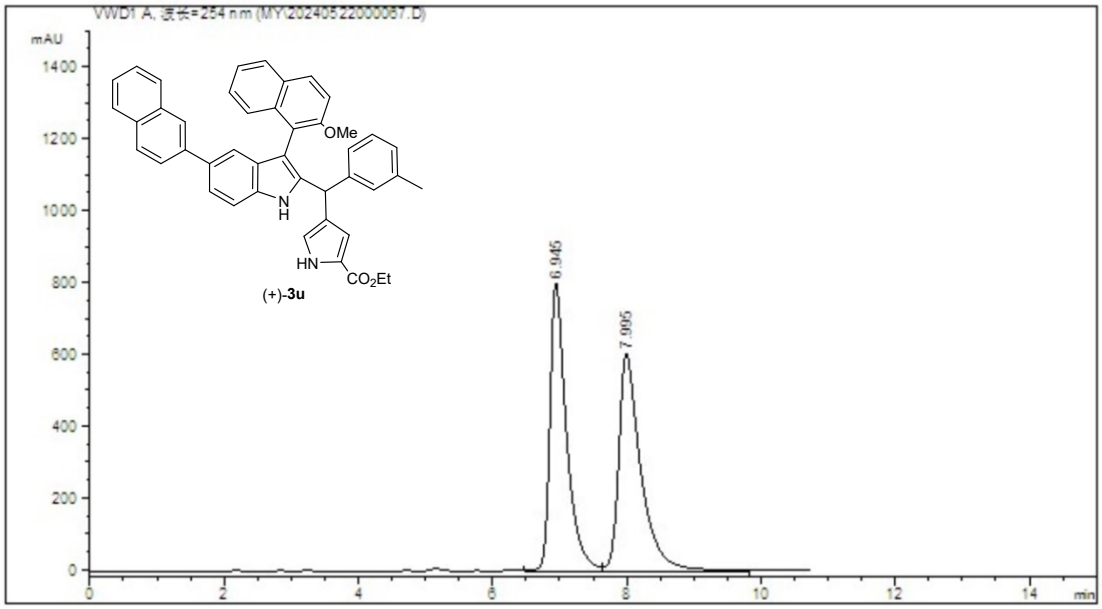
#	[min]		[min]	mAU	*s	[mAU	]	%
1	6.454	VV	0.2412	2.79543e4		1713.93213		94.0391
2	12.617	MM	0.6895	1771.95166		42.83247		5.9609



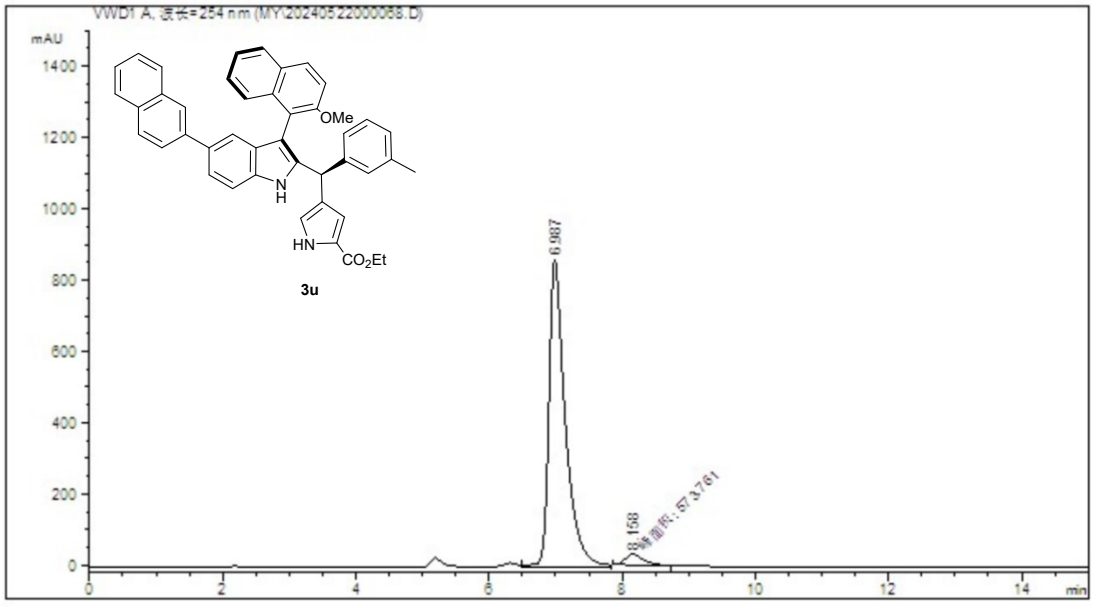
#	[min]		[min]	mAU	*s	[mAU]	%
1	6.789	VV	0.3065	1.19717e4		559.21002	50.0431
2	8.038	VBA	0.4805	1.19510e4		361.30957	49.9569



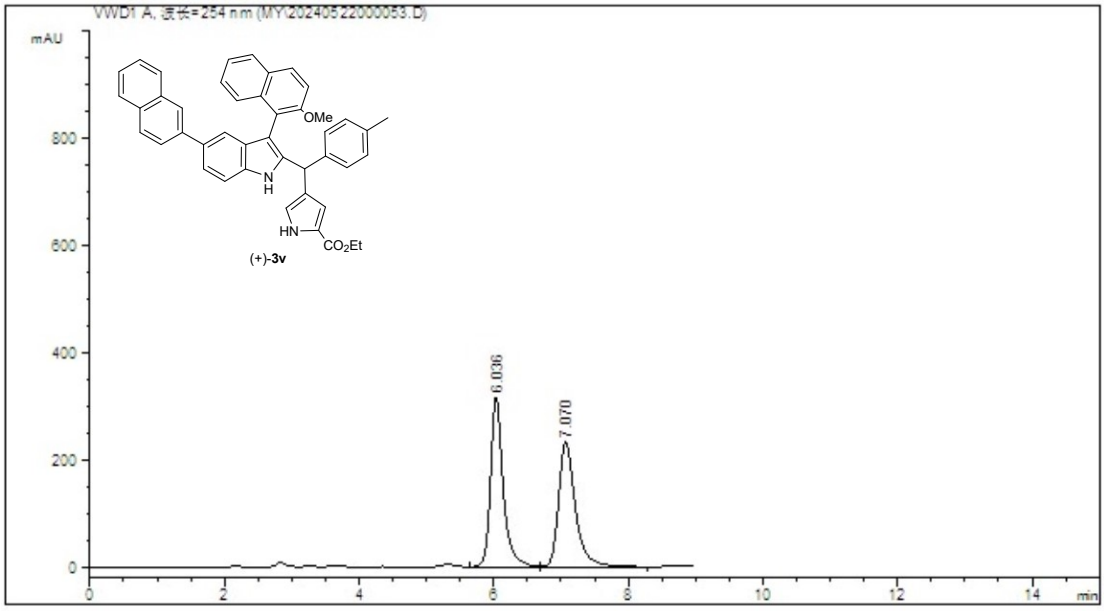
#	[min]		[min]	mAU	*s	[mAU]	%
1	6.888	BB	0.3142	1773.25452		83.19477	97.9116
2	8.198	MM	0.3554	37.82264		1.77376	2.0884



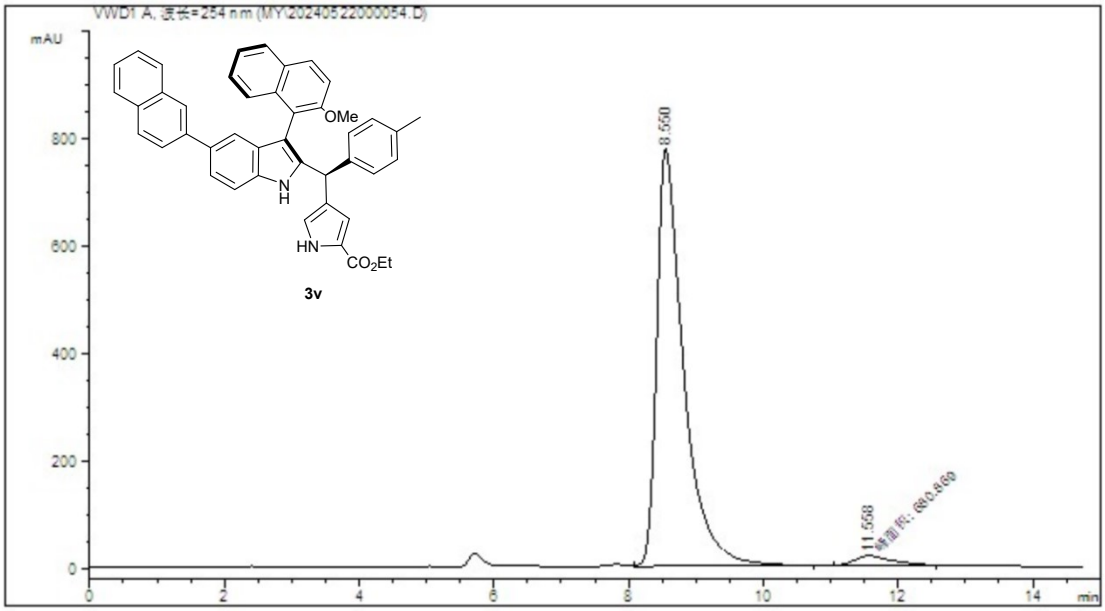
#	[min]		[min]	mAU	*s	[mAU]	%
1	6.945	VV	0.2491	1.37154e4		801.78009	49.6706
2	7.995	VV	0.3303	1.38973e4		605.75421	50.3294



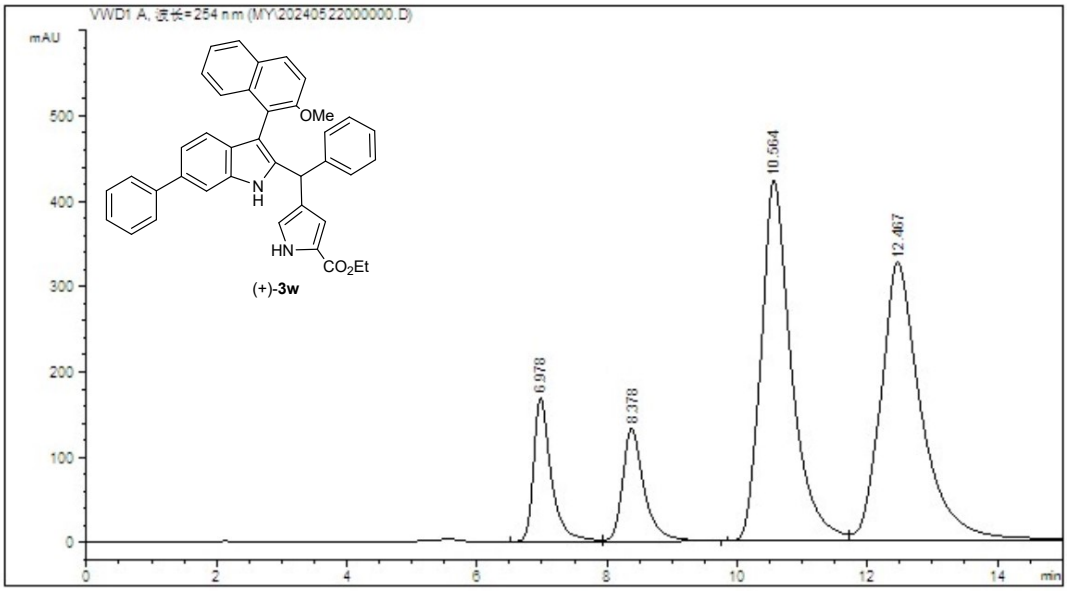
#	[min]		[min]	mAU	*s	[mAU]	%
1	6.987	VV	0.2470	1.46677e4		859.93134	96.2355
2	8.158	MM	0.3225	573.76099		29.65424	3.7645



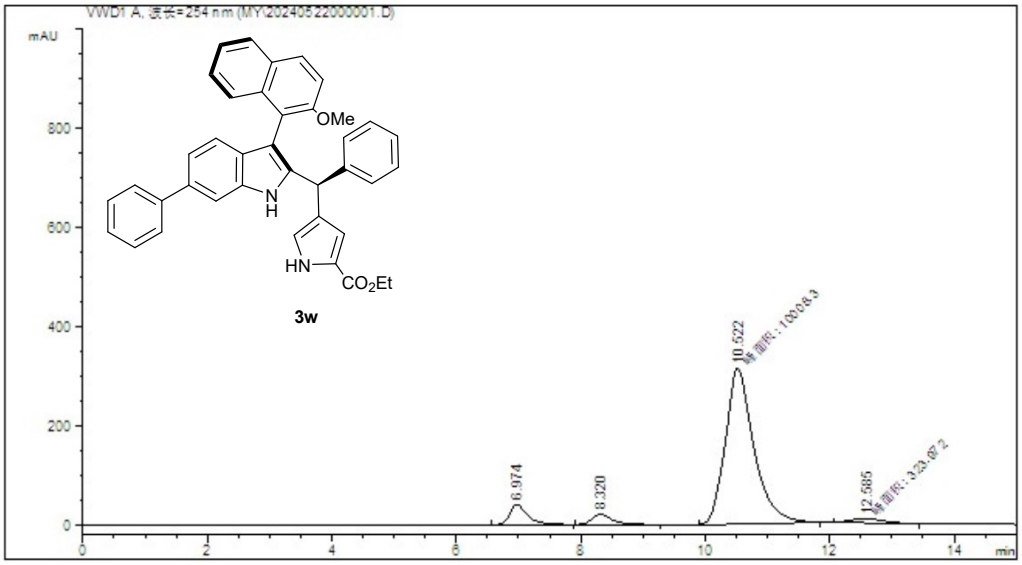
#	[min]		[min]	mAU	*s	[mAU]	%
1	6.036	VV	0.1964	4183.91553		316.59283	50.3790
2	7.070	VV	0.2657	4120.96533		233.37425	49.6210



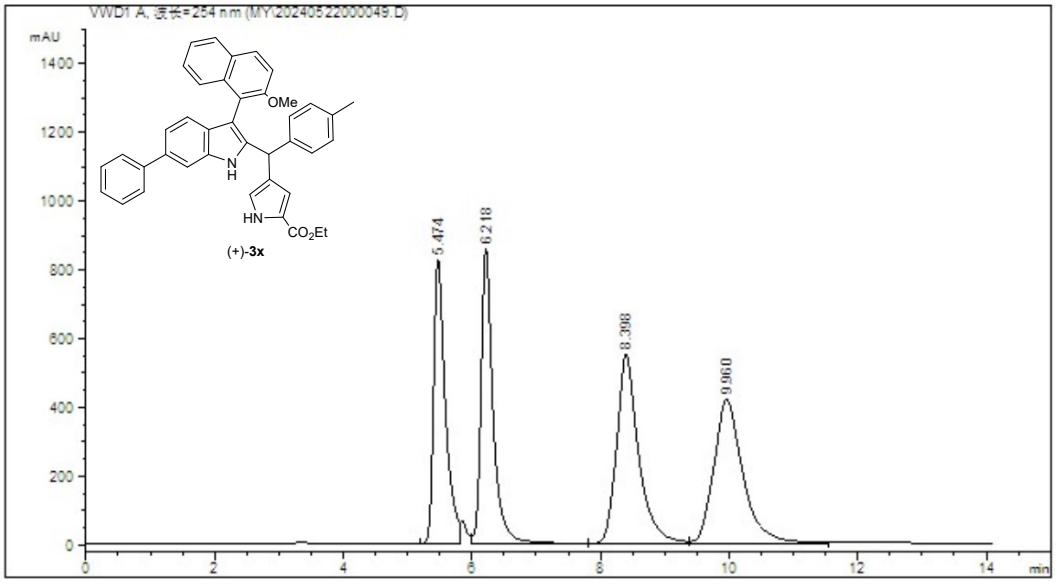
#	[min]		[min]	mAU	*s	[mAU]	%
1	8.550	VB	0.3974	2.14629e4		774.88409	96.9252
2	11.558	MM	0.6372	680.86920		17.80779	3.0748



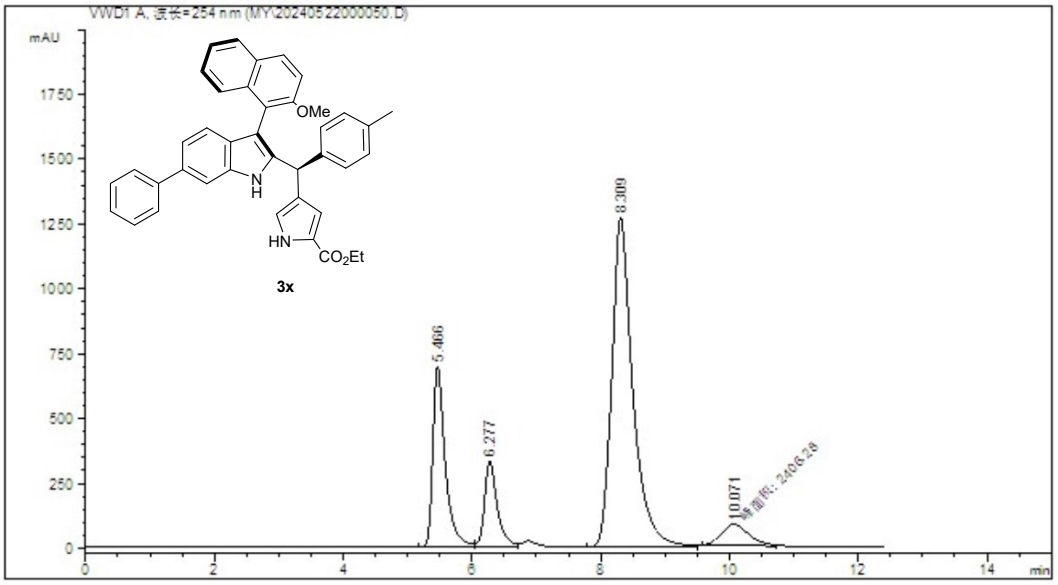
#	[min]		[min]	mAU	*s	[mAU]	%
1	6.978	VV	0.2771	3158.61450		168.40199	9.3382
2	8.378	VB	0.3391	3035.80640		132.25969	8.9751
3	10.564	BV	0.4633	1.36798e4		422.86896	40.4432
4	12.467	VB	0.6067	1.39504e4		326.18692	41.2434



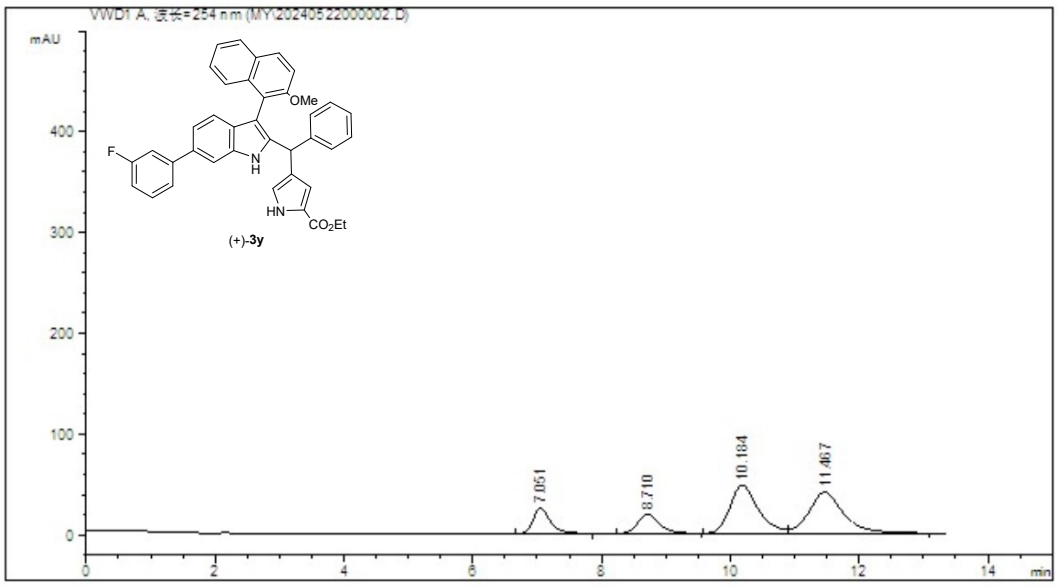
#	[min]		[min]	mAU	*s	[mAU]	%
1	6.974	BB	0.2956	824.44287		41.02570	7.0802
2	8.320	BB	0.3347	487.57346		21.48322	4.1872
3	10.522	MM	0.5307	1.00083e4		314.29877	85.9503
4	12.585	MM	0.6037	323.97229		8.94362	2.7822



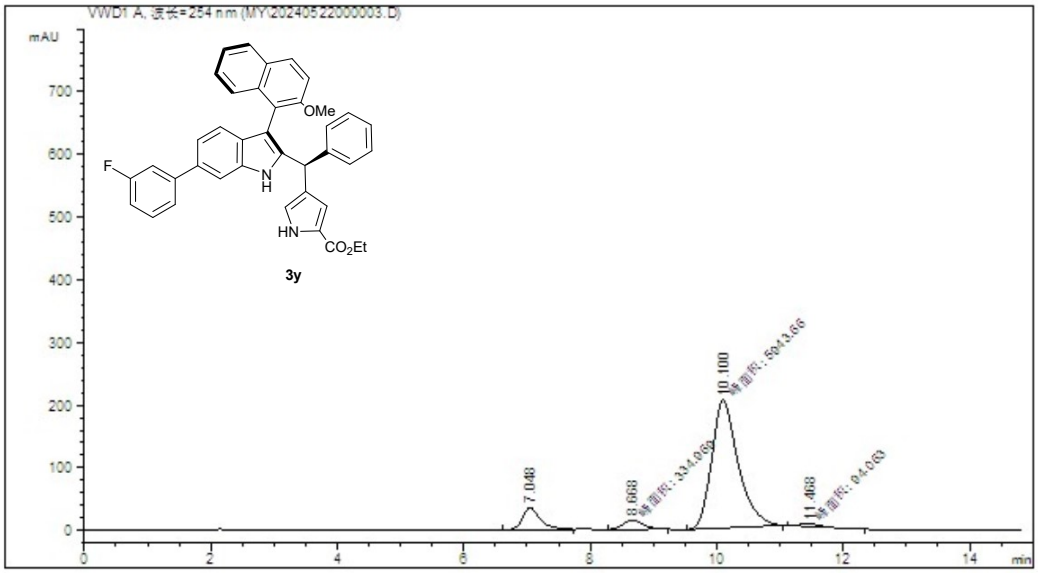
#	[min]		[min]	mAU	*s	[mAU]	%
1	5.474	VV	0.1875	1.05114e4		827.68774	21.8460
2	6.218	VV	0.1916	1.12025e4		858.10303	23.2823
3	8.398	VV	0.3376	1.31031e4		552.98395	27.2323
4	9.960	VV	0.4523	1.32990e4		420.15280	27.6394



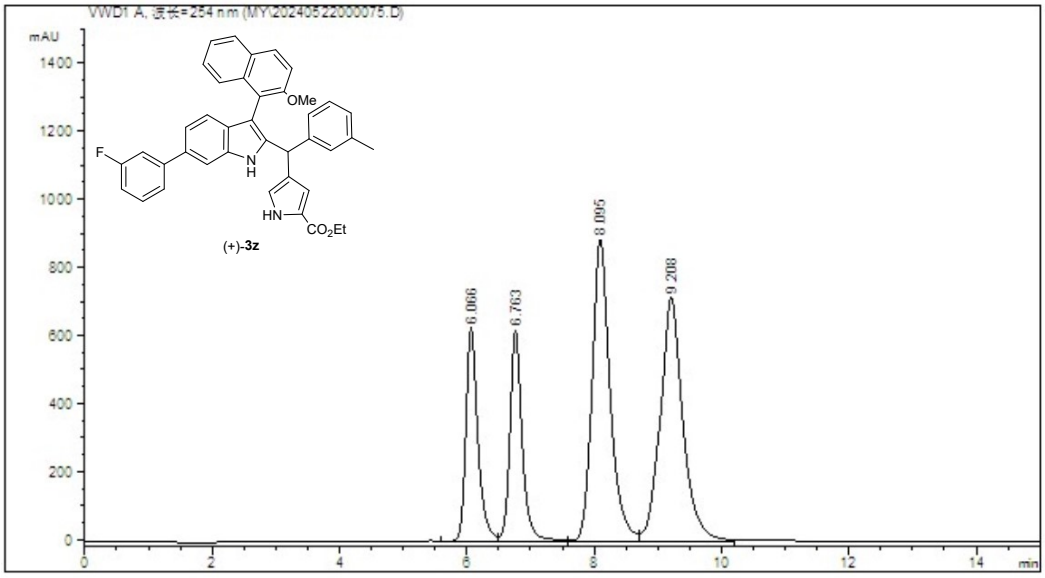
#	[min]		[min]	mAU	*s	[mAU]	%
1	5.466	VV	0.1979	9298.89453		696.71228	20.6055
2	6.277	VV	0.2045	4576.93652		332.01553	10.1421
3	8.309	BV	0.3263	2.88462e4		1269.30151	63.9204
4	10.071	MM	0.4980	2406.27783		80.53552	5.3321



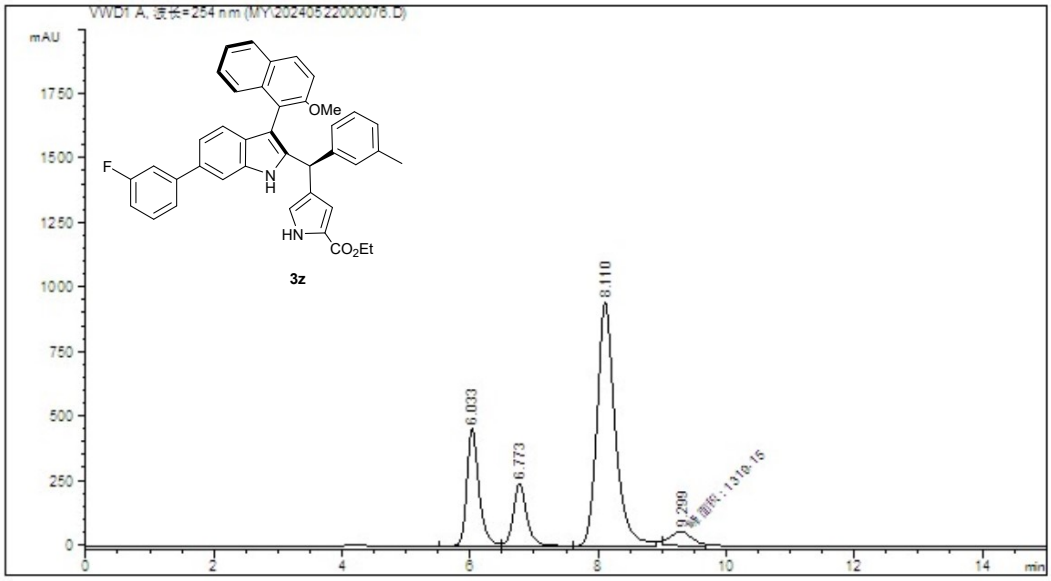
#	[min]		[min]	mAU	*s	[mAU]	%
1	7.051	BB	0.2753	474.58795		25.50977	11.9697
2	8.710	BB	0.3550	458.53296		19.25534	11.5648
3	10.184	BV	0.4528	1476.59912		48.29753	37.2417
4	11.467	VB	0.5489	1555.18811		41.26519	39.2238



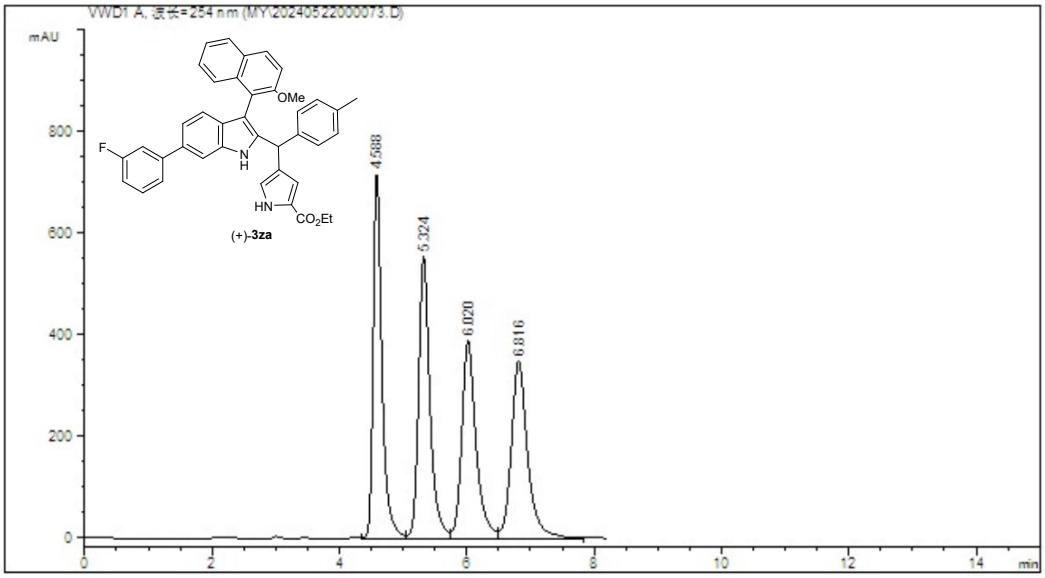
#	[min]		[min]	mAU	*s	[mAU]	%
1	7.048	BV	0.2864	707.03088		35.93025	9.9867
2	8.668	MM	0.3691	334.96912		15.12659	4.7314
3	10.100	MM	0.4841	5943.65869		204.61276	83.9533
4	11.468	MM	0.3955	94.06300		3.96395	1.3286



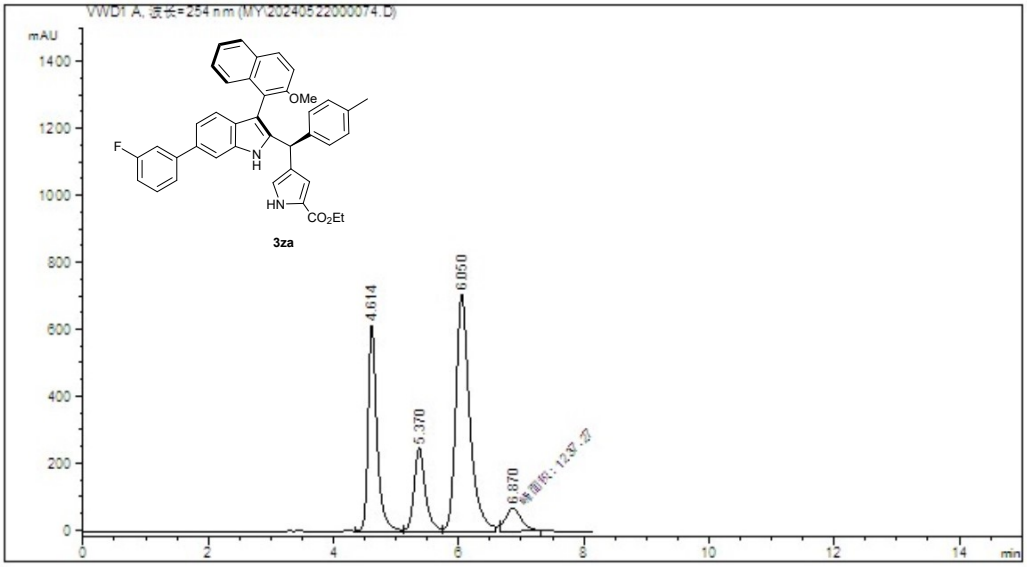
#	[min]		[min]	mAU	*s	[mAU	]	%
1	6.066	VV	0.1975	8289.38086		628.57996		15.9371
2	6.763	VV	0.2010	8397.34766		622.83313		16.1446
3	8.095	VV	0.2872	1.74520e4		889.43494		33.5530
4	9.208	VV	0.3549	1.78745e4		717.08948		34.3653



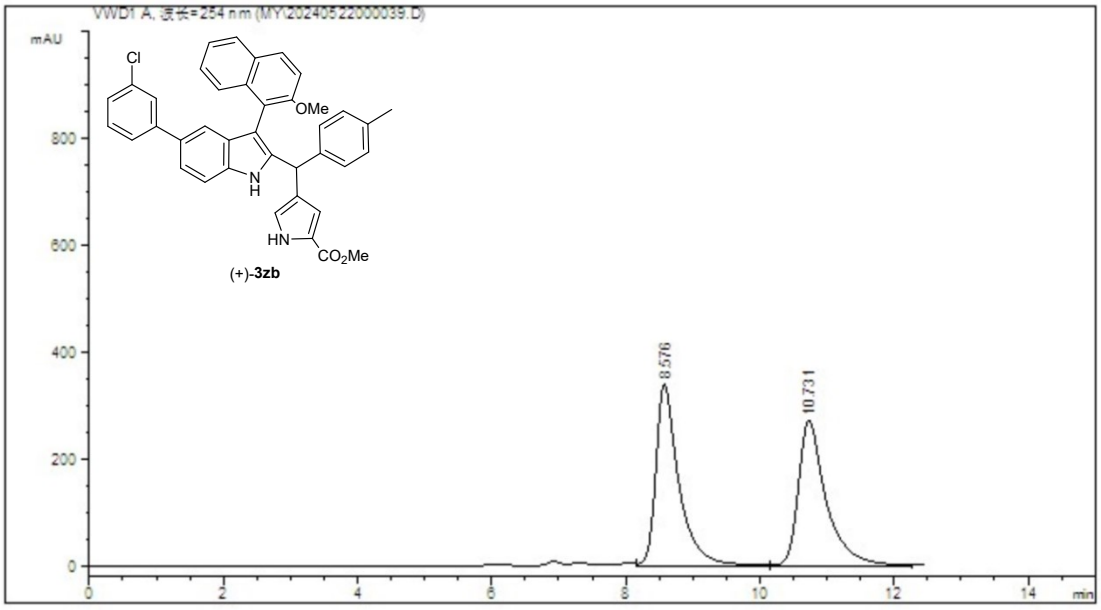
#	[min]		[min]	mAU	*s	[mAU	]	%
1	6.033	VV	0.1996	6035.75391		456.00613		20.4259
2	6.773	VV	0.2170	3569.91455		244.40172		12.0811
3	8.110	VV	0.2878	1.86247e4		946.43854		63.0288
4	9.299	MM	0.3928	1319.15405		55.97678		4.4642



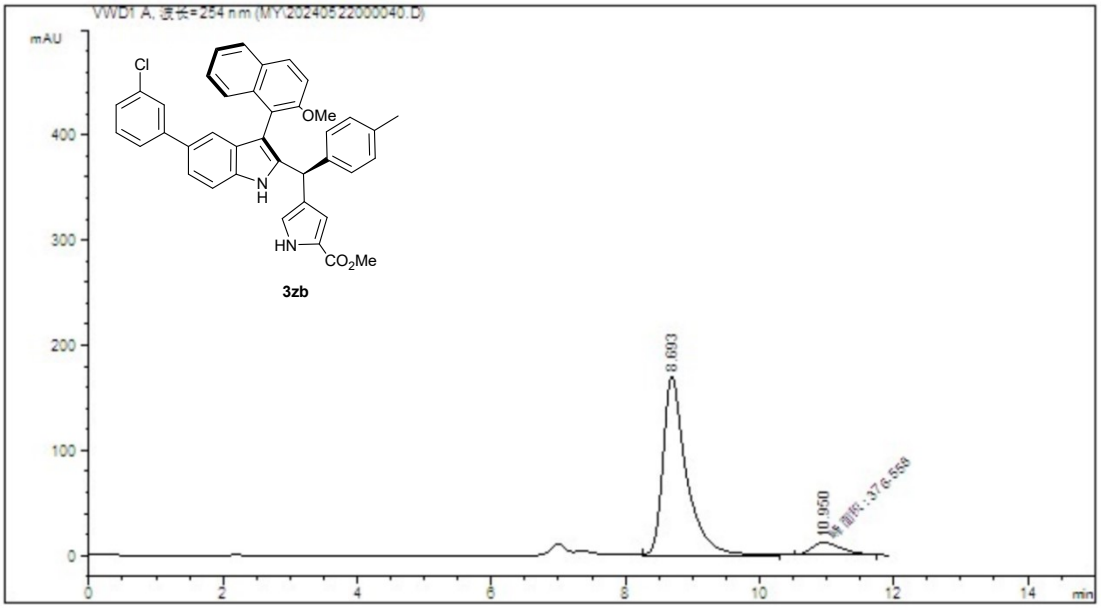
#	[min]		[min]	mAU	*s	[mAU]	%
1	4.588	VV	0.1446	6917.62305	717.23407	26.4892	
2	5.324	VV	0.1858	6900.88525	554.94250	26.4251	
3	6.020	VV	0.2307	6055.82568	389.99277	23.1892	
4	6.816	VV	0.2635	6240.50684	349.76535	23.8964	



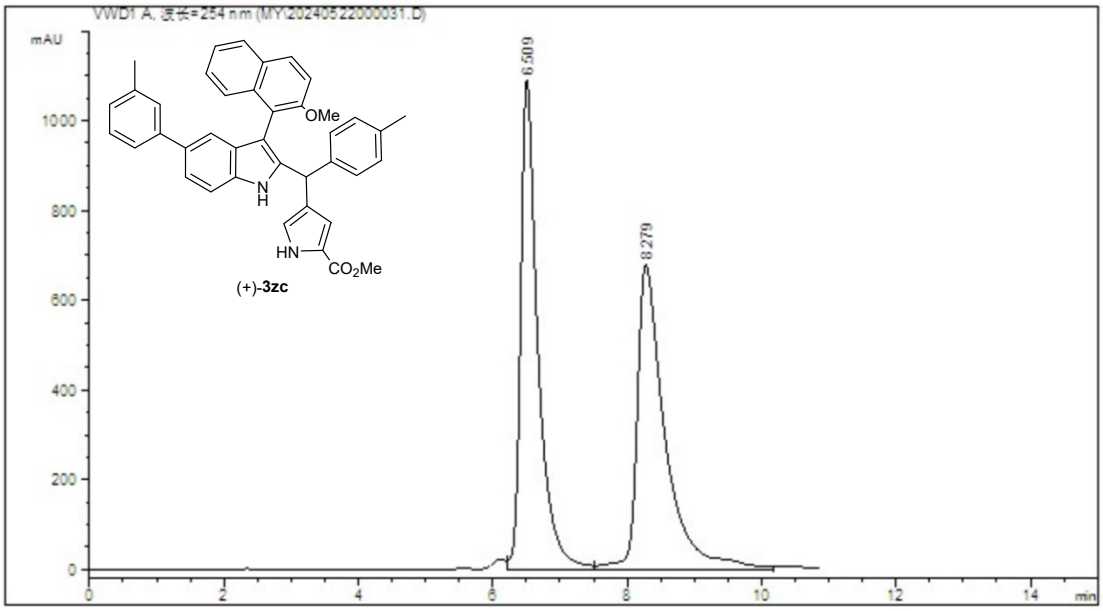
#	[min]		[min]	mAU	*s	[mAU]	%
1	4.614	VV	0.1481	6137.72852	616.94421	28.4977	
2	5.370	VV	0.1884	3167.02222	250.26498	14.7046	
3	6.050	VV	0.2292	1.09956e4	707.96912	51.0529	
4	6.870	MM	0.2952	1237.26929	69.85566	5.7447	



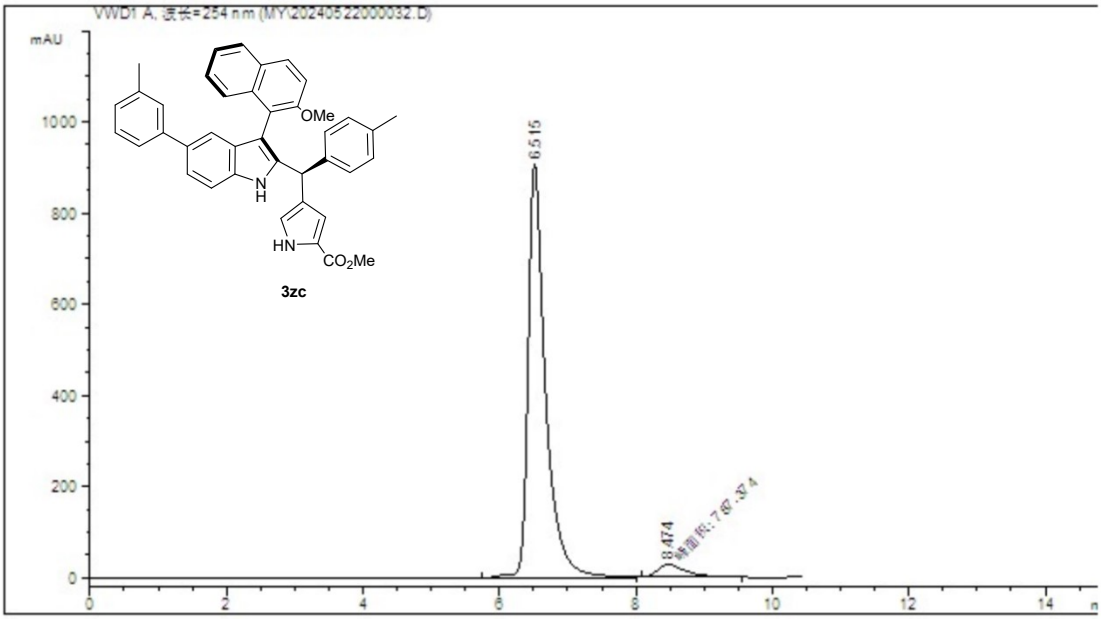
#	[min]		[min]	mAU	*s	[mAU]	%
1	8.576	VV	0.3481	8215.85840	340.90417	50.7466	
2	10.731	VB	0.4259	7974.10938	272.45724	49.2534	



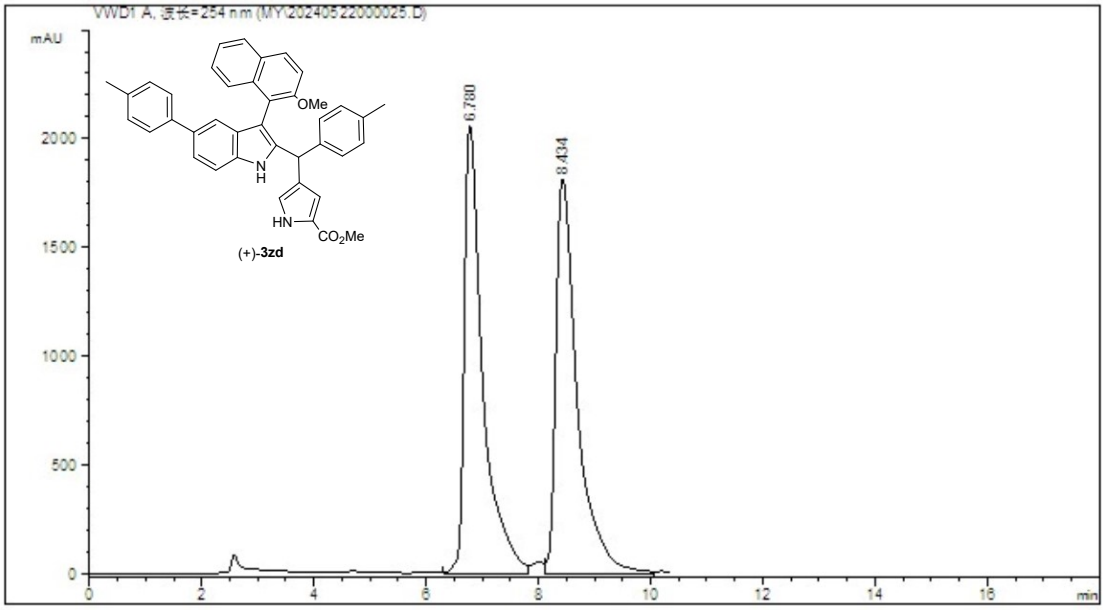
#	[min]		[min]	mAU	*s	[mAU]	%
1	8.693	VB	0.3516	4138.62646	170.53734	91.6602	
2	10.950	MM	0.5120	376.55795	12.25847	8.3398	



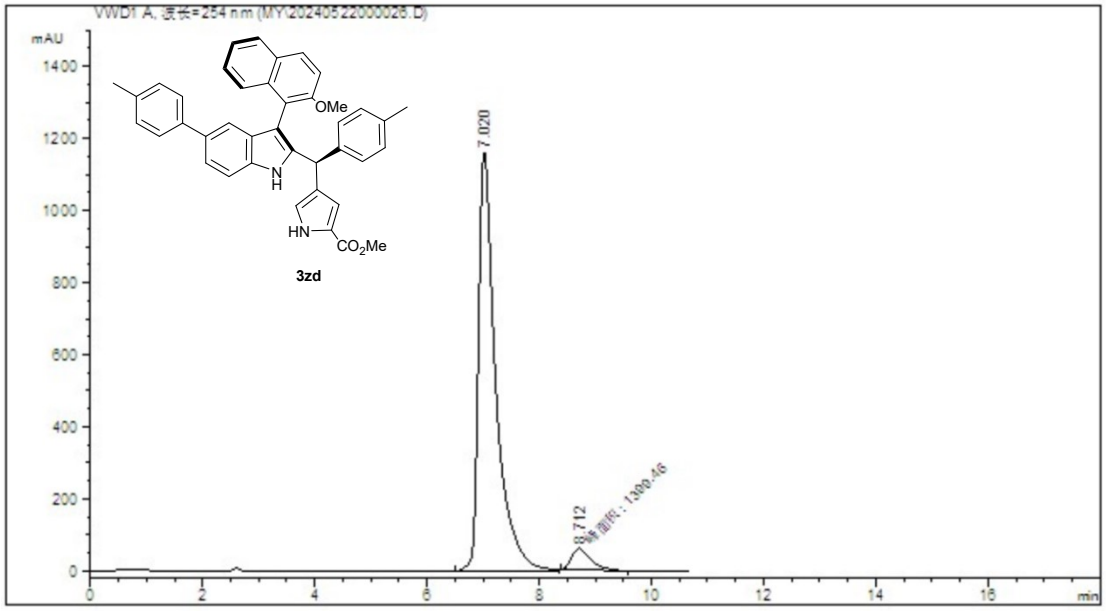
#	[min]		[min]	mAU	*s	[mAU]	%
1	6.509	VV	0.2591	1.94679e4	1091.44788	49.7329
2	8.279	VB	0.4134	1.96770e4	679.86969	50.2671



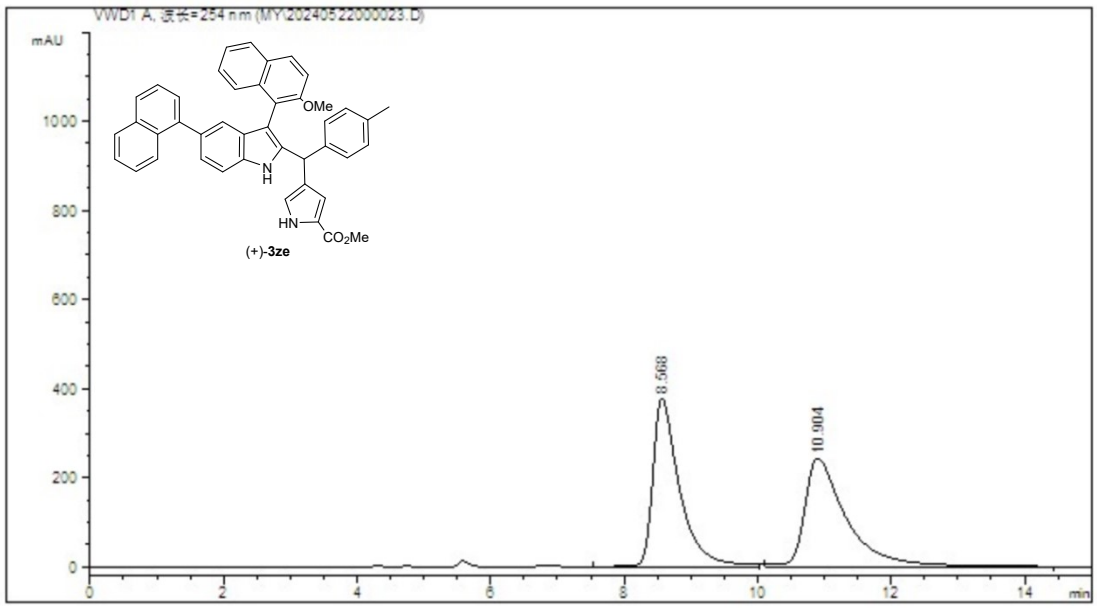
#	[min]		[min]	mAU	*s	[mAU]	%
1	6.515	VV	0.2599	1.61509e4	908.12793	95.3515
2	8.474	MM	0.4825	787.37415	27.19666	4.6485



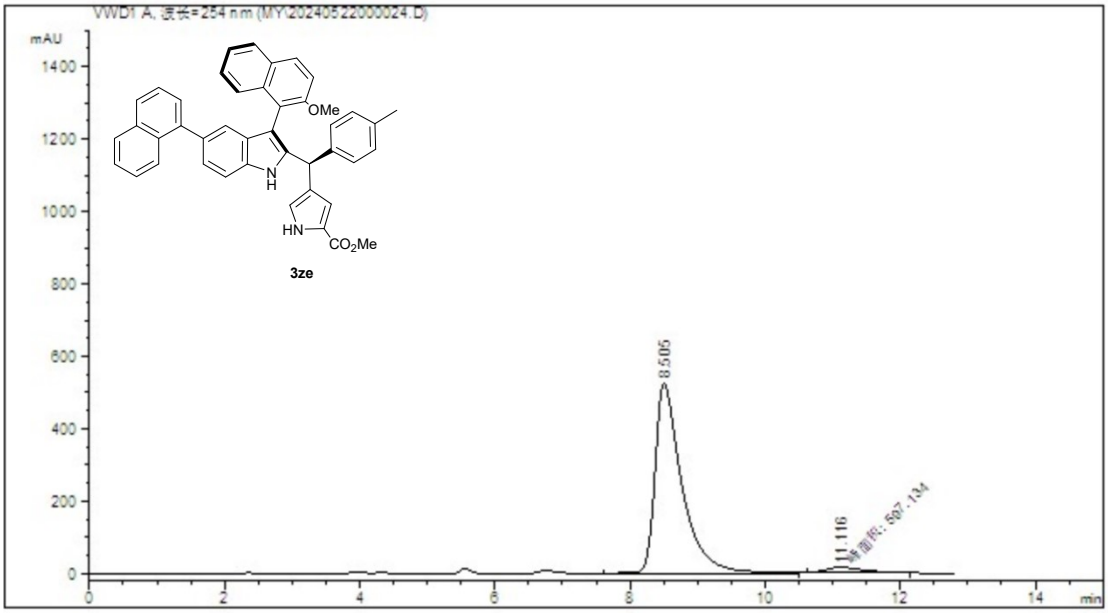
#	[min]		[min]	mAU	*s	[mAU]	%
1	6.780	VV	0.3358	4.74453e4		2058.71069	49.6145
2	8.434	VV	0.3988	4.81826e4		1813.37317	50.3855



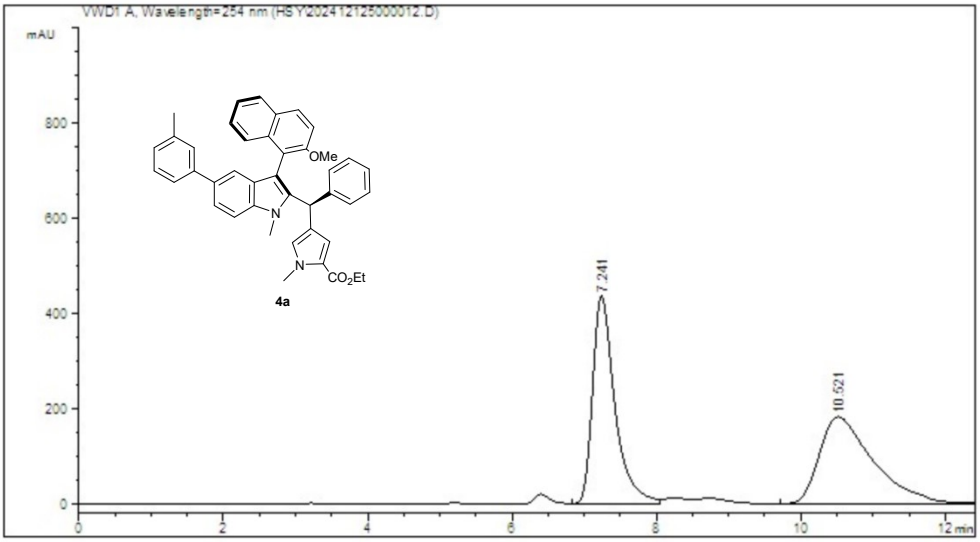
#	[min]		[min]	mAU	*s	[mAU]	%
1	7.020	VV	0.3139	2.50269e4		1161.82141	94.7043
2	8.712	MM	0.3918	1399.45911		59.53061	5.2957



#	[min]		[min]	mAU	*s	[mAU]	%
1	8.568	VB	0.4068	1.05999e4		378.45004	49.8680
2	10.904	BB	0.6298	1.06560e4		243.58430	50.1320



#	[min]		[min]	mAU	*s	[mAU]	%
1	8.505	BB	0.4029	1.46305e4		526.37091	96.0786
2	11.116	MM	0.6653	597.13397		14.96006	3.9214

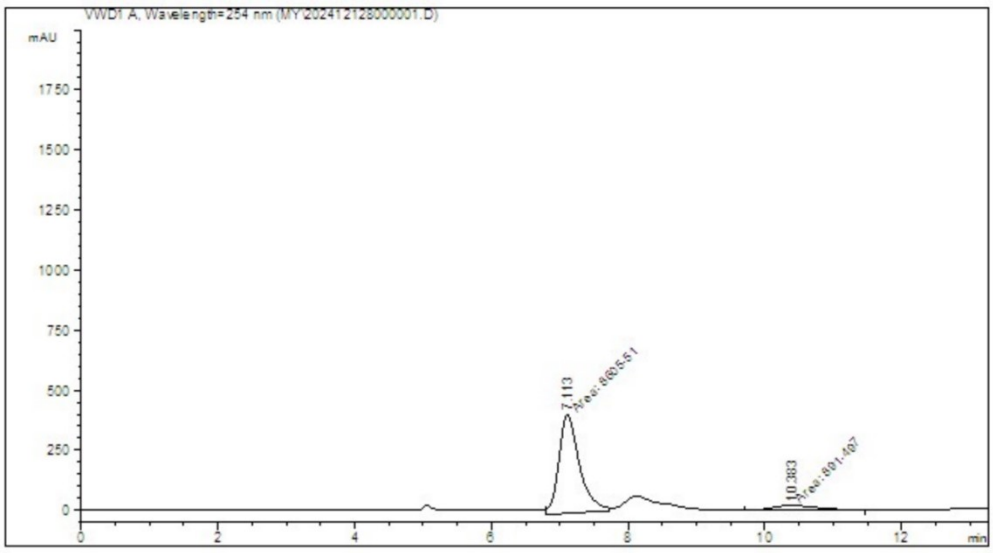



```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   7.241 VV    0.3244 9416.25000  436.54391  49.5612
   2  10.521 BBA   0.7591 9582.97949  183.09856  50.4388
```

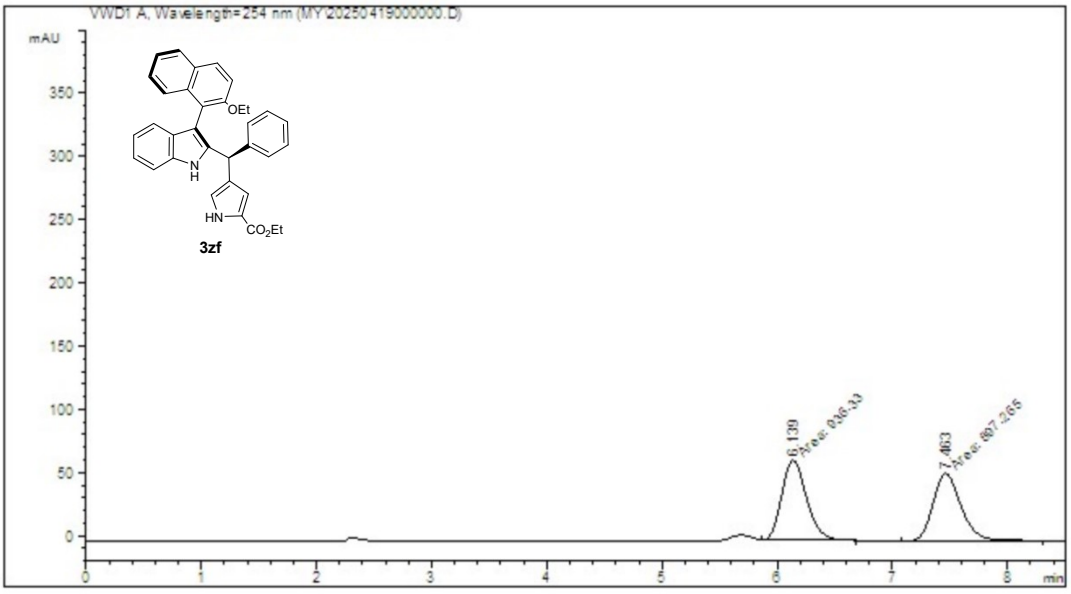



```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   7.113 MM    0.3505 8605.50879  409.15839  90.6129
   2  10.383 MM    0.7615  891.49750   19.51092   9.3871
```

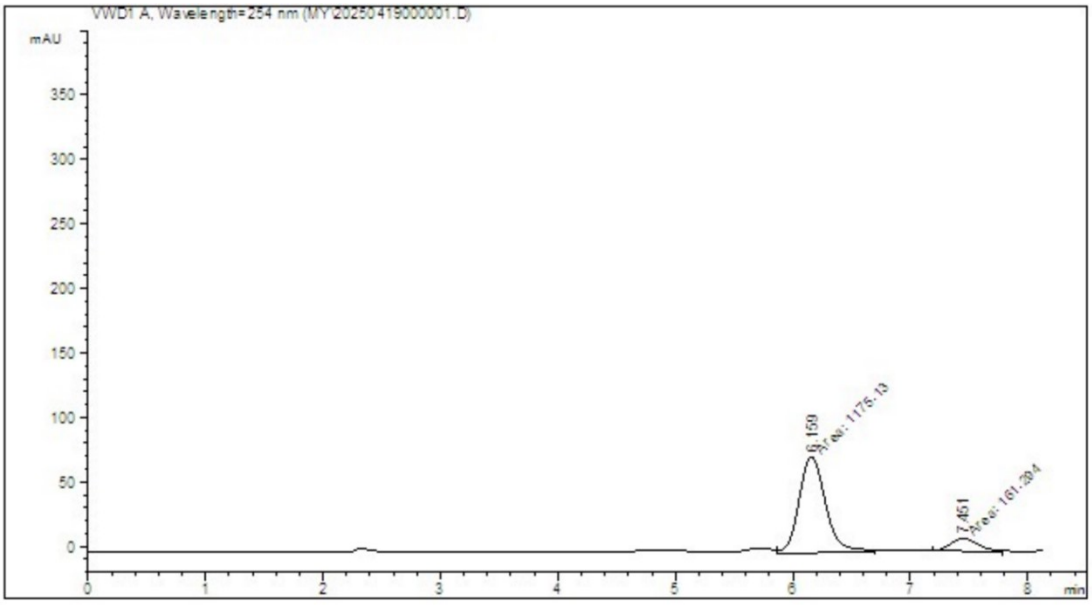



```
================================================================================
                            Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   6.139 MM    0.2484  936.33014   62.82299  51.0653
   2   7.463 MM    0.2801  897.26483   53.39255  48.9347
```




```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   6.159 MM    0.2627 1175.13269   74.54086  87.9309
   2   7.451 MM    0.2746  161.29445    9.79115  12.0691
```

7. References

(1)(a) D. M. Bailey, R. E. *J*ohnson, N. F. Albertson, *Org. Synth.* **1971**, *51*, 100; (b) D. O. A. Garrido, G. Buldain, M. I. O*J*ea, B. Frydman, *J. Org. Chem.* **1988**, *53*, 403–407; (c) K. Bera, C. Schneider, *Chem. Eur. J.* **2016**, *22*, 7074 – 7078; (d) K. Bera, C. Schneider, *Org. Lett.* **2016**, *18*, 5660 – 5663.

(2) (a) A. B. Castillo, B. F. Perandones, E. Zangrando, S. Gladiali, C. Godard, C. Claver, *J. Organomet. Chem.* **2013**, *743*, 31-36. (b) B. A. Sweetman, P. J. Guiry, *Tetrahedron.* **2018**, *74*, 5567-5581. (c) C. Pan, Z.-Z. Zhu, M. Zhang, Z. Gu, *Angew. Chem., Int. Ed*., **2017**, *56*, 4777-4781.

(3) (a) *J*. S. Oakdale, D. L. Boger, *Org. Lett.* **2010**, *12*, 1132-1134. (b) B. Witulski, N. Buschmann, U. Bergsträsser, *Tetrahedron.,* **2000**, *56*, 8473-8480.

(4) F. *J*iang, K.W. Chen, P. Wu, Y.-C. Zhang, Y. *J*iao, F. Shi, *Angew. Chem., Int. Ed*.,**2019**, *58*, 15104-15110.