Atroposelective Synthesis of Axially Chiral Indolizine-pyrroles by Catalytic Asymmetric Paal-Knorr Reaction

Wenyan Zhan,[a] Jiameng Hu,[b] Xiaoyun Chen,[c] Gen Luo,[b,*] Xiaoxiao Song[a,*]

[a] Key Laboratory of Functionalized Molecular Solids, Ministry of Education, Anhui Key Laboratory of Molecule-Based Materials (State Key Laboratory Cultivation Base), College of Chemistry and Materials Science, Anhui Normal University, Wuhu 241002, Anhui, P. R. China

[b] Institutes of Physical Science and Information Technology, Anhui University, Hefei 230601, China

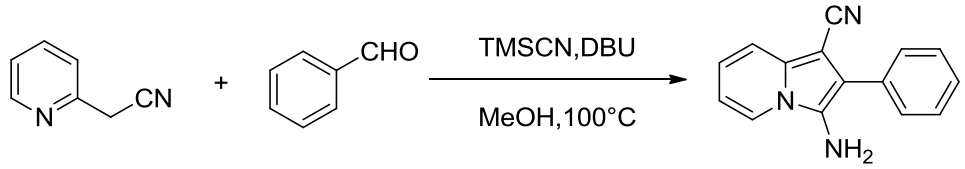
[c] School of Environmental and Chemical Engineering, Jiangsu University of Science and Technology, Zhenjiang, 212003, P. R. China

Content

1. General information

The products were purified by column chromatography on silica gel (300-400 mesh). For thin-layer chromatography (TLC) analysis, silica gel plates (HSGF254) were used. Visualization of the developed TLC plates was performed with ultraviolet irradiation (254 nm) or staining potassium permanganate solution followed by heating using a heat gun. High resolution mass spectra on a Bruker Apex IV RTMS spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AVANCE-400 (400 MHz) /AVANCE-500(500 MHZ) spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.0) or tetramethylsilane (TMS δ 0.00) was used as a reference. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), bs (broad singlet). Coupling constants were reported in Hertz (Hz). Melting points were determined on a SGW X-4 melting apparatus. Analytical HPLC was performed on a Agilent 1200 Series instrument using Daicel Chiralcel® columns as noted. Optical rotation values were measured on a Schmidt Haensch polarimeter. 1,4-Diketones and 3-aminoindolizines were prepared according to the literature procedure.[1-2] The CPA catalysts were purchased from Daicel Chiral technologies(China)CO.,LTD or Bide Pharmatech LTD, which were directly used without additional process. The racemic products were prepared by running reactions with a racemic catalyst.

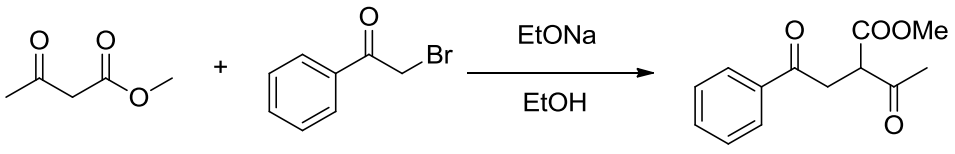
2.General procedure for synthesis of 3-aminoindolizine



1

To a mixture of benzaldehyde (313.1 μL, 2.70 mmol, 1.0 equiv) and pyridine-2-acetonitrile (451.8 μL, 4.05 mmol, 1.5 equiv) in MeOH (10 mL) were added TMSCN (506.7 μL, 4.05 mmol, 1.5 equiv) and DBU (80.6 μL, 0.54 mmol, 0.2 equiv) at rt. After being stirred at 100 °C for 24 h (heating mantle was used), the reaction mixture was cooled down to room temperature and filtered. The filtrate was further purified by silica gel column chromatography (petroleum ether/EtOAc 9:1) to give **1** as a green solid (724.9 mg, 86% yield).

3. General procedure for the preparation of 1,4-diketones

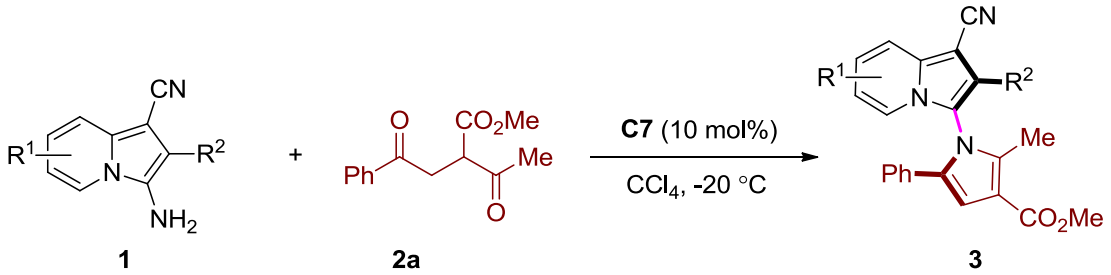


2

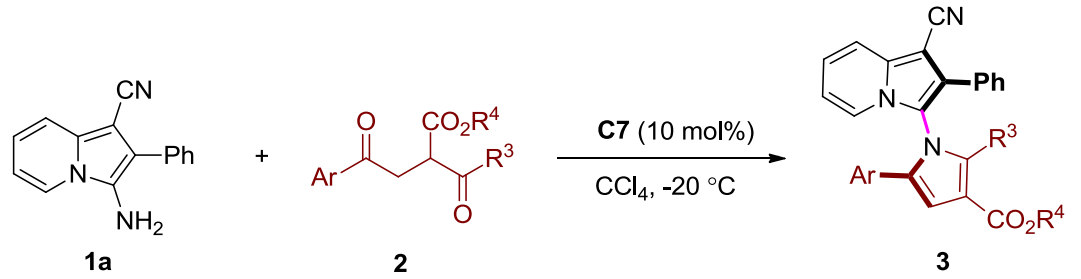
Methyl acetoacetate (1.56 g, 12 mmol) was added dropwise to a stirred suspension of sodium ethoxide (0.68g, 10 mmol) in 15 mL of anhydrous ethanol at room temperature. After 10 min, a solution of 2-bromo-1-phenacylbromide (1.99 g, 10 mmol) in 26 mL of anhydrous ethanol was added dropwise to the reaction mixture. Upon completion of the reaction, which was monitored by TLC, the reaction mixture was quenched with water (20 mL), and extracted with EtOAc (30 mL x

3). The combined organic phases were washed with saturated aqueous ammonium chloride (20 mL), and dried over anhydrous sodium sulfate. The concentrated residue purified by silica gel column chromatography (petroleum ether/EtOAc 15:1) to give compound **2** (2.62 g, 88% yield) as light yellow oil.

4. General procedure for the asymmetric synthesis of axially chiral product

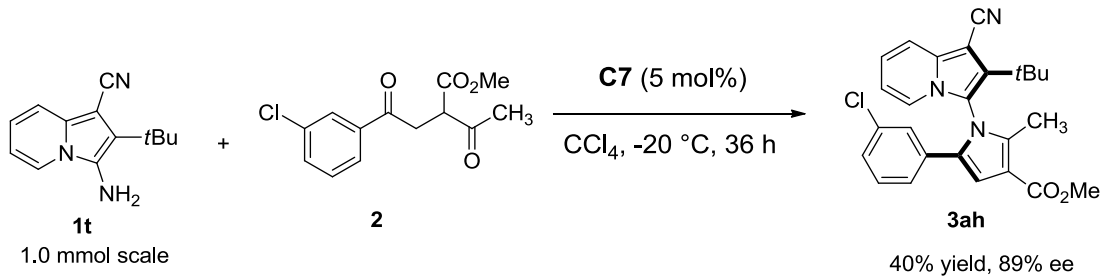


General procedure A: To a 4 mL vial was added 3-aminoindolizine **1** (0.12 mmol, 1.2 equiv), 1,4-diketone **2a** (0.10 mmol, 1.0 equiv) and **C7** (0.01 mmol, 10 mol%) in CCl_4 (1.0 mL). The mixture was stirred at -20 ℃ and monitored by TLC until completion of the reaction. The solvent was removed by rotovapor and the residue was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 15:1) to afford the product **3**.



General procedure B: To a 4 mL vial was added 3-aminoindolizine **1a** (0.10 mmol, 1.0 equiv), 1,4-diketone **2** (0.30 mmol, 3.0 equiv) and **C7** (0.01 mmol, 10 mol%) in CCl_4 (1.0 mL). The mixture was stirred at -20 ℃ and monitored by TLC until completion of the reaction. The solvent was removed by rotovapor and the residue was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 15:1) to afford the product **3**.

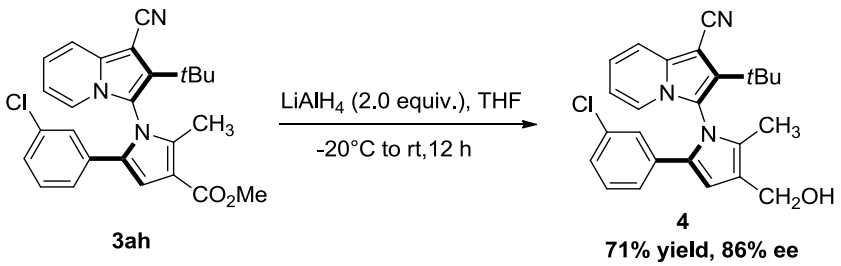
5. Large-scale synthesis of the product 3ah



To a 25 ml round-bottom flask was added 1,4-diketone **2** (3 mmol, 806 mg, 3.0 equiv) and **C7** (0.05 mmol, 5 mol%) in 10 mL CCl_4 with stirring in air at -20 ℃ for 10 min, then 3-aminoindolizine **1t** (1.0 mmol, 213 mg, 1.0 equiv) was added and the mixture was stirred at -20 ℃ for 36 h. The solvent was removed by rotovapor and the residue was directly purified by flash column chromatography on silica gel (petroleum ether/ethylacetate 15:1) to afford the

product **3ah** in 40% yield (180.1 mg) as a white solid.

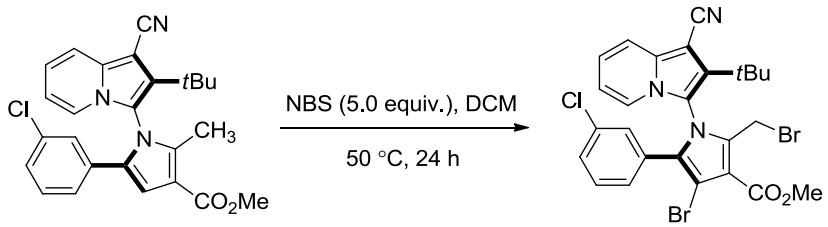
6. Procedure for the late-stage functionalizations of 3ah



3ah **4**

71% yield, 86% ee

To a solution of the **3ah**, $LiAlH_4$ (2.0 equiv.) in THF (1.0 mL) was added portion wise at -20 ℃. The mixture was stirred at room temperature for 12 h. The reaction was quenched with water. The combined organic phases were washed with ethyl acetoacetate and dried over sodium sulfate. Purification of the residue by column chromatography (petroleum ether/EtOAc 15:1) to provide product **4** as a light yellow solid (15.0 mg, 71% yield).

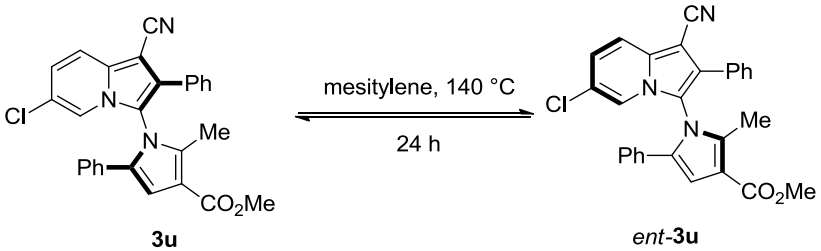


3ah **5**

72% yield, 88% ee

To a solution of the **3ah**, NBS (5.0 equiv.) in CH_2Cl_2 (1.0 mL) was added portionwise at 50 ℃. The mixture was stirred for 24 h. The reaction was quenched with saturated $Na_2S_2O_3$ solution. The combined organic phases were washed with brine and CH_2Cl_2 and dried over sodium sulfate. Purification of the residue by column chromatography (petroleum ether/EtOAc 15:1) to provide product **5** as a light yellow solid (21.1 mg, 72% yield).

7. Racemization experiments

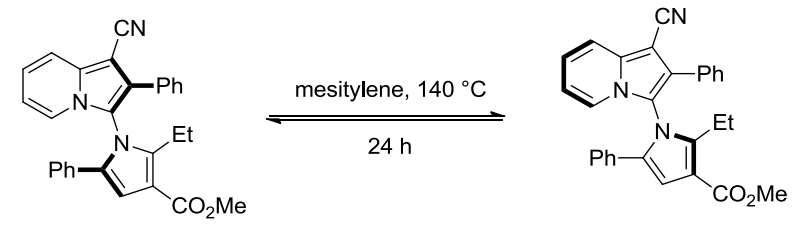


3u ***ent*-3u**

To a 10 mL vial charged with **3u** (0.010 mmol) was added mesitylene (1.0 mL). The reaction solution was stirred at 140 °C. The ee value of **3u** was determined by HPLC at indicated time points.

Time(h)	ee (%)
0	95
1	95
2	95

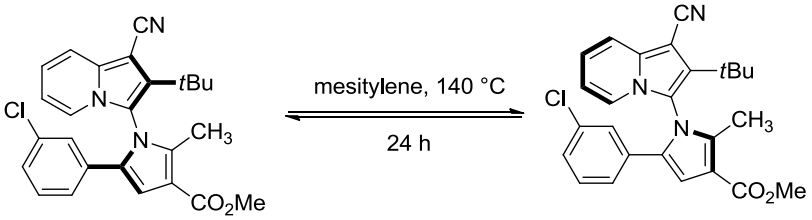
4	95
8	95
16	95
24	95



3ab *ent*-**3ab**

To a 10 mL vial charged with **3ab** (0.010 mmol) was added mesitylene (1.0 mL). The reaction solution was stirred at 140 °C. The ee value of **3ab** was determined by HPLC at indicated time points.

Time(h)	ee (%)
0	91
1	91
2	91
4	91
8	91
16	91
24	91

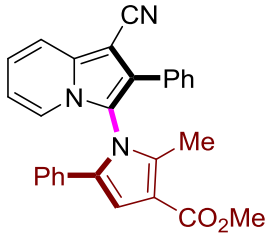


3ah *ent*-**3ah**

To a 10 mL vial charged with **3ah** (0.010 mmol) was added mesitylene (1.0 mL). The reaction solution was stirred at 140 °C. The ee value of **3ah** was determined by HPLC at indicated time points.

Time(h)	ee (%)
0	89
1	89
2	89
4	89
8	89
16	89
24	89

8. Analytical data

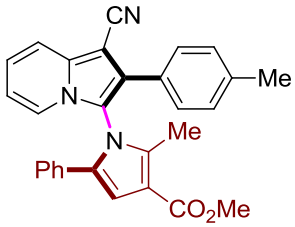


The compound **3a** was prepared according to the general procedure A. The product was obtained as a white solid (21.8 mg, 51% yield,). Melting point: 180-182 ℃. The ee (95%) was measured by HPLC using a chiral stationary phase [Daicel IE, *n*-hexane:*i*-PrOH = 70:30, 1.0 mL/min), t_R =9.070 min (major), t_R =8.320 min (minor)], $[\alpha]_D^{30}$ = +89.0 (c = 0.2, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.67 (m, 1H), 7.43 (d, J = 7.0 Hz, 1H), 7.35 – 7.27 (m, 5H), 7.20 – 7.14 (m, 1H), 7.06 (ddd, J = 14.6, 8.0, 6.4 Hz, 3H), 6.92 (s, 1H), 6.85 – 6.76 (m, 3H), 3.87 (s, 3H), 2.20 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 139.3, 136.3, 134.8, 131.0, 130.1, 129.2, 128.7, 128.6, 128.4, 127.9, 127.7, 126.4, 124.0, 121.8, 118.0, 116.4, 115.3, 114.8, 114.6, 111.1, 80.5, 51.4, 11.6.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{28}H_{22}N_3O_2^+$ 431.1634； Found: 431.1635.

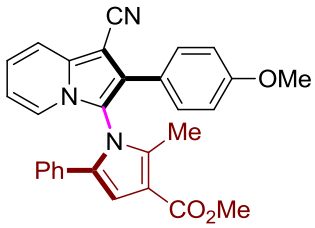


The compound **3b** was prepared according to the general procedure A. The product was obtained as a white solid (22.7 mg, 51% yield,). Melting point: 190-192 ℃. The ee (91%) was measured by HPLC using a chiral stationary phase [Daicel IE, *n*-hexane:*i*-PrOH = 70:30, 1.0 mL/min), t_R =8.268 min (major), t_R =7.537 min (minor)], $[\alpha]_D^{30}$ = +93.0 (c = 0.2, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 9.0 Hz, 1H), 7.39 (d, J = 7.0 Hz, 1H), 7.22 (d, J = 8.2 Hz, 2H), 7.14 (d, J = 8.2 Hz, 3H), 7.10 – 7.01 (m, 3H), 6.93 (s, 1H), 6.90 – 6.85 (m, 2H), 6.75 (td, J = 6.9, 1.2 Hz, 1H), 3.87 (s, 3H), 2.33 (s, 3H), 2.17 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 139.5, 138.7, 136.3, 134.7, 131.1, 130.0, 128.6, 128.5, 127.7, 127.6, 127.2, 126.4, 123.9, 121.7, 117.9, 116.5, 115.0, 114.7, 114.4, 111.0, 80.5, 51.3, 21.4, 11.5.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{29}H_{24}N_3O_2^+$ 446.1863; Found: 446.1862.

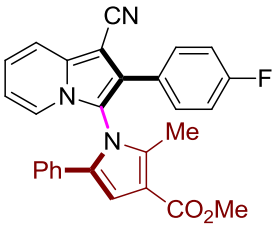


The compound **3c** was prepared according to the general procedure A with 5 mol% **C7**. The product was obtained as a white solid (33.2 mg, 72% yield). Melting point: 212-215 ℃. The ee (93%) was measured by HPLC using a chiral stationary phase [Daicel ID, *n*-hexane:*i*-PrOH = 80:20, 1.0 mL/min), t_R = 13.450 min (major), t_R =15.605 min (minor)], $[\alpha]_D^{30}$ =-52.6 (c = 0.2, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.9 Hz, 1H), 7.39 (d, J = 6.9 Hz, 1H), 7.25 (d, J = 8.8 Hz, 2H), 7.14 (ddd, J = 9.0, 6.8, 1.0 Hz, 1H), 7.10 – 7.01 (m, 1H), 6.93 (s, 1H), 6.88 – 6.82 (m, 4H), 6.75 (td, J = 6.9, 1.2 Hz, 1H), 3.87 (s, 3H), 3.80 (s, 3H), 2.18 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 159.9, 139.4, 136.3, 134.7, 131.1, 129.2, 128.6, 128.3, 127.7, 126.4, 123.8, 122.5, 121.7, 117.8, 116.7, 114.8, 114.7, 114.7, 114.4, 111.1, 80.3, 55.4, 51.4, 11.5.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{29}H_{24}N_3O_3^+$ 462.1812; Found: 462.1811.



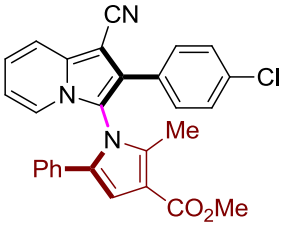
The compound **3d** was prepared according to the general procedure A with 5 mol% **C7**. The product was obtained as a light brown solid (22.4 mg, 50% yield). Melting point: 172-175 ℃. The ee (92%) was measured by HPLC using a chiral stationary phase [Daicel IE, *n*-hexane:*i*-PrOH = 80:20, 1.0 mL/min), t_R =10.038 min (minor), t_R =11.208 min (major)], $[\alpha]_D^{30}$= -83.8 (c = 0.2, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 9.0 Hz, 1H), 7.48 (d, J = 7.0 Hz, 1H), 7.23 – 7.16 (m, 3H), 7.13 – 7.08 (m, 1H), 7.07 – 6.97 (m, 4H), 6.90 (s, 1H), 6.83 (td, J = 6.9, 1.2 Hz, 1H), 6.78 – 6.74 (m, 2H), 3.87 (s, 3H), 2.22 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 139.2, 136.2, 134.9, 131.0, 129.8, 129.7, 128.6, 127.7, 127.6, 126.4, 124.2, 121.8, 118.1, 116.4, 116.2, 115.3, 115.0, 114.7, 111.1, 80.6, 51.4, 11.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -112.18.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{28}H_{21}FN_3O_2^+$ 450.1612; Found: 450.1611.

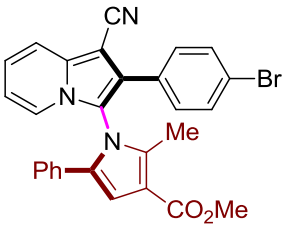


The compound **3e** was prepared according to the general procedure A with 5 mol% **C7**. The product was obtained as a white solid (25.6 mg, 55% yield,). Melting point: 165-166 ℃. The ee (92%) was measured by HPLC using a chiral stationary phase [Daicel IE, *n*-hexane:*i*-PrOH = 70:30, 1.0 mL/min), t_R =7.251min (minor), t_R =8.106min (major)], $[\alpha]_D^{30}$ = +62.3 (c = 0.1, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.68 (m, 1H), 7.48 (d, *J* = 6.9 Hz, 1H), 7.28 (d, *J* = 8.6 Hz, 2H), 7.20 (ddd, *J* = 9.0, 6.7, 1.1 Hz, 1H), 7.15 (d, *J* = 8.6 Hz, 1H), 7.10 (d, *J* = 7.1 Hz, 1H), 7.05 (dd, *J* = 8.3, 6.4 Hz, 2H), 6.91 (s, 1H), 6.83 (td, *J* = 6.9, 1.2 Hz, 1H), 6.80 – 6.74 (m, 1H), 3.88 (s, 3H), 2.21 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 139.1, 136.3, 131.0, 129.5, 129.1, 128.8, 128.7, 128.6, 128.3, 127.8, 127.3, 126.4, 124.3, 121.9, 118.1, 115.4, 115.0, 114.8, 111.2, 80.6, 51.4, 11.6.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{28}H_{21}ClN_3O_2^+$ 466.1317; Found: 466.1324.

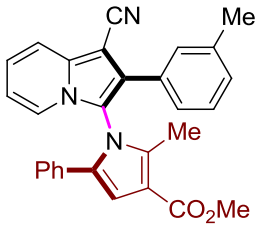


The compound **3f** was prepared according to the general procedure A. The product was obtained as a white solid (36.0 mg, 71% yield). Melting point: 178-181 ℃. The ee (92%) was measured by HPLC using a chiral stationary phase [Daicel IE, *n*-hexane:*i*-PrOH = 70:30, 1.0 mL/min), t_R = 7.942 min (minor), t_R =8.808 min (major)], $[\alpha]_D^{30}$ = -70.2 (c = 0.2, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.70 (m, 1H), 7.48 (dd, *J* = 6.9, 1.2 Hz, 1H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.20 (ddd, *J* = 9.0, 6.7, 1.0 Hz, 1H), 7.09 (q, *J* = 2.5, 1.6 Hz, 2H), 7.07 (d, *J* = 3.4 Hz, 2H), 7.04 (d, *J* = 6.9 Hz, 1H), 6.91 (s, 1H), 6.83 (td, *J* = 6.8, 1.2 Hz, 1H), 6.77 (d, *J* = 7.0 Hz, 2H), 3.87 (s, 3H), 2.21 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 139.1, 136.3, 134.8, 132.4, 130.9, 129.3, 129.1, 128.7, 127.8, 127.3, 126.4, 124.3, 123.1, 121.9, 118.1, 116.1, 115.4, 115.0, 114.8, 111.2, 80.5, 51.4, 11.6.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{28}H_{21}BrN_3O_2^+$ 510.0812; Found: 510.0816.

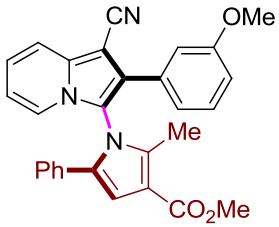


The compound **3g** was prepared according to the general procedure A. The product was obtained as a white solid (33.4 mg, 75% yield). Melting point: 159-161 ℃. The ee (85%) was measured by HPLC using a chiral stationary phase [Daicel ID, *n*-hexane:*i*-PrOH = 90:10, 1.0 mL/min), t_R =14.007 min (major), t_R =15.782 min (minor)], $[\alpha]_D^{30}$ = +46.2 (c = 0.4, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 9.0, 1.1 Hz, 1H), 7.43 (dd, *J* = 7.0, 1.0 Hz, 1H), 7.22 – 7.18 (m, 1H), 7.18 – 7.14 (m, 1H), 7.12 (d, *J* = 1.6 Hz, 1H), 7.10 (s, 1H), 7.09 – 7.06 (m, 3H), 7.04 (d, *J* = 8.7 Hz, 3H), 6.91 (s, 1H), 3.86 (s, 3H), 2.28 (s, 3H), 2.18 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 139.4, 138.8, 136.3, 134.9, 131.1, 130.0, 129.5, 129.0, 128.7, 128.6, 128.6, 127.6, 126.5, 124.9, 123.9, 121.8, 118.0, 116.4, 115.2, 114.7, 114.5, 111.0, 80.7, 51.3, 21.6, 11.6.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{29}H_{24}N_3O_2^+$ 446.1863; Found: 446.1861.

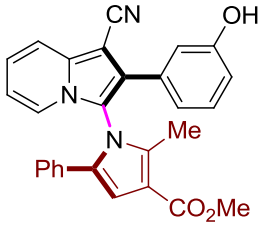


The compound **3h** was prepared according to the general procedure A. The product was obtained as a light pink solid (36.4 mg, 79% yield). Melting point: 163-165 ℃. The ee (92%) was measured by HPLC using a chiral stationary phase [Daicel IE, *n*-hexane:*i*-PrOH = 70:30, 1.0 mL/min), t_R =9.297 min(minor), t_R =10.117 min(major)], $[\alpha]_D^{30}$= 30.0 (c = 0.2, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 9.0 Hz, 1H), 7.43 (d, *J* = 6.9 Hz, 1H), 7.23 (t, *J* = 8.0 Hz, 1H), 7.16 (ddd, *J* = 9.0, 6.8, 1.1 Hz, 1H), 7.12 – 7.00 (m, 3H), 6.95 – 6.90 (m, 2H), 6.87 – 6.82 (m, 3H), 6.81 – 6.74 (m, 2H), 3.86 (s, 3H), 3.67 (s, 3H), 2.19 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 159.9, 139.4, 136.3, 134.7, 131.3, 131.0, 130.2, 128.8, 128.6, 128.2, 127.7, 126.4, 124.0, 121.8, 120.2, 118.0, 115.4, 115.2, 114.8, 114.6, 112.3, 111.1, 80.6, 55.2, 51.3, 11.5.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{29}H_{24}N_3O_3^+$ 462.1812; Found: 462.1807.

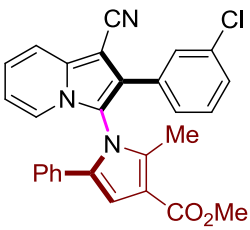


The compound **3i** was prepared according to the general procedure A. The product was obtained as a white solid (23.4 mg, 51% yield). Melting point: 187-193 ℃. The ee (84%) was measured by HPLC using a chiral stationary phase [Daicel IE, *n*-hexane:*i*-PrOH = 90:10, 1.0 mL/min), t_R =30.305 min (minor), t_R =39.530 min (major)], $[\alpha]_D^{30}$ = +29.8 (c = 0.4, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 9.0 Hz, 1H), 7.39 (d, *J* = 7.0 Hz, 1H), 7.22 – 7.12 (m, 2H), 7.11 – 6.96 (m, 3H), 6.90 (s, 1H), 6.86 – 6.80 (m, 5H), 6.77 (td, *J* = 6.9, 1.2 Hz, 1H), 6.30 (s, 1H), 3.85 (s, 3H), 2.19 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 156.5, 139.4, 136.4, 134.8, 131.4, 131.0, 130.6, 128.6, 128.0, 127.7, 126.5, 124.1, 121.8, 120.0, 118.0, 116.5, 116.1, 115.3, 114.8, 114.6, 114.5, 111.1, 80.5, 51.5, 11.6.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{28}H_{22}N_2O_3^+$ 448.1656; Found:448.1649.

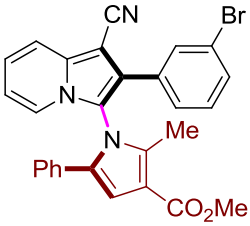


The compound **3j** was prepared according to the general procedure A. The product was obtained as a white solid (31.7 mg, 68% yield,). Melting point:163-166 ℃. The ee (84%) was measured by HPLC using a chiral stationary phase [Daicel ID, *n*-hexane:*i*-PrOH = 90:10, 1.0 mL/min), t_R =16.523 min (major), t_R =18.260 min (minor)], $[\alpha]_D^{30}$ =+68.2 (c = 0.2, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 9.0 Hz, 1H), 7.51 (d, *J* = 7.0 Hz, 1H), 7.27 (d, *J* = 6.5 Hz, 1H), 7.22 (td, *J* = 7.3, 6.8, 2.3 Hz, 2H), 7.15 – 7.09 (m, 2H), 7.08 – 6.99 (m, 3H), 6.90 (s, 1H), 6.85 (td, *J* = 6.9, 1.2 Hz, 1H), 6.77 – 6.71 (m, 2H), 3.87 (s, 3H), 2.22 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 139.1, 136.3, 135.0, 135.0, 131.8, 131.0, 130.3, 128.8, 128.7, 128.0, 127.8, 127.1, 126.6, 126.0, 124.3, 121.9, 118.2, 115.9, 115.7, 115.0, 114.9, 111.2, 80.8, 51.4, 11.6.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{28}H_{21}ClN_3O_2^+$ 466.1317; Found: 466.1310.

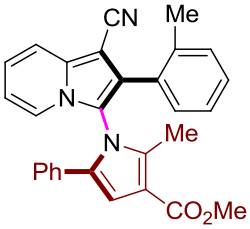


The compound **3k** was prepared according to the general procedure A. The product was obtained as a white solid (35.1 mg, 69% yield). Melting point: 189-193 ℃. The ee (93%) was measured by HPLC using a chiral stationary phase [Daicel IE, *n*-hexane:*i*-PrOH = 90:10, 1.0 mL/min), t_R =22.018 min (minor), t_R =23.965 min (major)], $[\alpha]_D^{30}$ =-57.0 (c = 0.2, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 9.0 Hz, 1H), 7.52 (d, *J* = 7.0 Hz, 1H), 7.45 – 7.38 (m, 1H), 7.26 (s, 1H), 7.24 – 7.19 (m, 1H), 7.16 (t, *J* = 7.8 Hz, 1H), 7.13 – 7.09 (m, 2H), 7.06 (dd, *J* = 8.2, 6.4 Hz, 2H), 6.90 (s, 1H), 6.86 (td, *J* = 6.9, 1.2 Hz, 1H), 6.76 – 6.71 (m, 2H), 3.87 (s, 3H), 2.22 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 139.1, 136.3, 135.1, 132.1, 131.7, 131.0, 130.9, 130.6, 128.7, 127.8, 127.0, 126.6, 126.4, 124.3, 123.1, 121.9, 118.2, 115.8, 115.7, 115.0, 114.9, 111.2, 80.7, 51.4, 11.6.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{28}H_{21}BrN_3O_2^+$510.0812; Found: 510.0805.

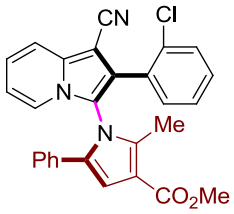


The compound **3l** was prepared according to the general procedure A. The product was obtained as a white solid (28.0 mg, 64% yield,). Melting point:140-145 ℃. The ee (89%) was measured by HPLC using a chiral stationary phase [Daicel ID, *n*-hexane:*i*-PrOH = 90:10, 1.0 mL/min), t_R =15.125 min (major) t_R =16.935 min (minor)], $[\alpha]_D^{30}$ = -26.4 (c = 0.4, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 9.0 Hz, 1H), 7.43 (d, *J* = 7.0 Hz, 1H), 7.23 – 7.18 (m, 1H), 7.18 – 7.14 (m, 1H), 7.12 (d, *J* = 1.4 Hz, 1H), 7.10 (s, 1H), 7.07 (m, 2H), 7.06 – 7.02 (m, 2H), 6.91 (s, 1H), 6.86 – 6.81 (m, 2H), 6.78 (td, *J* = 6.9, 1.2 Hz, 1H), 3.86 (s, 3H), 2.28 (s, 3H), 2.18 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 139.4, 138.8, 136.3, 134.9, 131.2, 130.0, 129.5, 129.0, 128.7, 128.6, 128.3, 127.6, 126.5, 124.9, 123.9, 121.8, 118.0, 116.4, 115.3, 114.7, 114.5, 111.0, 80.7, 51.3, 21.6, 11.6.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{29}H_{24}N3O_2^+$ 446.1863; Found:446.1864.

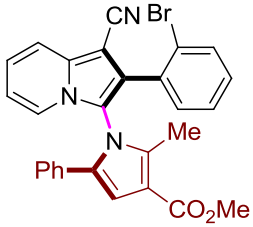


The compound **3m** was prepared according to the general procedure A. The product was obtained as a white solid (36.8 mg, 79% yield). Melting point: 193-196 ℃. The ee (93%) was measured by HPLC using a chiral stationary phase [Daicel ID, *n*-hexane:*i*-PrOH = 80:20, 1.0 mL/min), t_R =11.500 min (major), t_R =12.823 min (minor)], $[\alpha]_D^{30}$ = +73.3 (c = 0.4, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 9.0 Hz, 1H), 7.64 (d, *J* = 7.0 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.25 (d, *J* = 4.7 Hz, 1H), 7.23 – 7.13 (m, 2H), 7.09 (t, *J* = 7.5 Hz, 2H), 7.01 – 6.88 (m, 2H), 6.75 (s, 1H), 6.62 (d, *J* = 7.2 Hz, 2H), 3.84 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 139.6, 135.5, 135.3, 131.6, 131.4, 130.1, 129.9, 128.7, 127.6, 127.1, 126.7, 124.0, 122.0, 118.4, 116.7, 115.5, 114.8, 114.6, 110.7, 83.7, 51.3, 12.0.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{28}H_{21}ClN_3O_2^+$ 466.1317; Found: 466.1302.

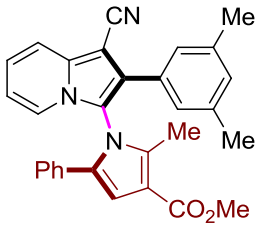


The compound **3n** was prepared according to the general procedure A with 5 mol% **C7**. The product was obtained as a white solid (33.6 mg, 66% yield). Melting point: 178-181 ℃. The ee (90%) was measured by HPLC using a chiral stationary phase [Daicel ID, *n*-hexane:*i*-PrOH = 80:20, 1.0 mL/min), t_R =12.307 min (major), t_R =13.583 min (minor)], $[\alpha]_D^{30}$ =-37.5 (c = 0.4, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 9.0 Hz, 1H), 7.63 (d, *J* = 7.0 Hz, 1H), 7.53 (d, *J* = 8.2 Hz, 1H), 7.34 – 7.27 (m, 1H), 7.18 (d, *J* = 7.1 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 3H), 6.94 (td, *J* = 6.9, 1.2 Hz, 2H), 6.80 (s, 1H), 6.67 – 6.61 (m, 2H), 6.18 (d, *J* = 7.4 Hz, 1H), 3.83 (s, 3H), 2.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 139.8, 135.4, 133.0, 131.8, 130.7, 130.3, 128.8, 127.7, 127.1, 126.5, 124.0, 122.1, 118.4, 116.5, 115.4, 114.9, 114.6, 110.8, 83.9, 51.3, 12.2.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{28}H_{21}BrN_3O_2^+$ 510.0812; Found: 510.0803.

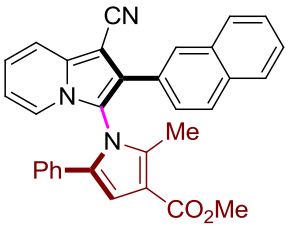


The compound **3o** was prepared according to the general procedure A with 5 mol% **C7**. The product was obtained as a white solid (12.4 mg, 54% yield). Melting point: 163-167 ℃. The ee (90%) was measured by HPLC using a chiral stationary phase [Daicel ID, *n*-hexane:*i*-PrOH = 80:20, 1.0 mL/min), t_R =8.263 min (major), t_R =9.148 min (minor)], $[\alpha]_D^{30}$ = -42.18 (c = 0.2, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.68 (m, 1H), 7.43 (dt, *J* = 7.0, 1.1 Hz, 1H), 7.15 (ddd, *J* = 9.0, 6.8, 1.0 Hz, 1H), 7.12 – 6.98 (m, 3H), 6.93 (d, *J* = 5.4 Hz, 2H), 6.87 – 6.83 (m, 4H), 6.78 (td, *J* = 6.9, 1.2 Hz, 1H), 3.86 (s, 3H), 2.23 (s, 6H), 2.17 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 139.5, 138.5, 136.2, 135.0, 131.2, 130.4, 129.9, 128.9, 128.6, 127.6, 126.5, 125.7, 123.8, 121.8, 117.9, 116.3, 115.2, 114.6, 114.4, 110.9, 80.8, 51.3, 21.5, 11.5.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{30}H_{26}N_3O_2^+$ 460.2020; Found: 460.2015.

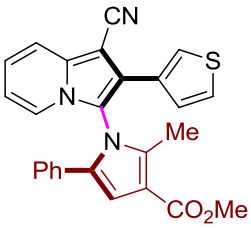


The compound **3p** was prepared according to the general procedure A with 5 mol% **C7**. The product was obtained as a light yellow solid (18.8 mg, 39% yield). Melting point: 183-187 ℃. The ee (95%) was measured by HPLC using a chiral stationary phase [Daicel IE, *n*-hexane:*i*-PrOH = 70:30, 1.0 mL/min), t_R =26.847 min (minor), t_R =44.000 min (major)], $[\alpha]_D^{30}$ =-73.8 (c = 0.2, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (q, *J* = 3.5 Hz, 2H), 7.78 – 7.66 (m, 3H), 7.52 – 7.41 (m, 3H), 7.35 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.19 (ddd, *J* = 9.0, 6.8, 1.1 Hz, 1H), 7.13 – 7.07 (m, 1H), 7.07 – 6.99 (m, 2H), 6.95 (s, 1H), 6.88 – 6.84 (m, 2H), 6.81 (td, *J* = 6.9, 1.2 Hz, 1H), 3.86 (s, 3H), 2.21 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 139.4, 136.4, 134.9, 133.4, 133.0, 131.1, 129.0, 128.7, 128.6, 128.4, 127.7, 127.7, 127.5, 126.9, 126.5, 126.5, 124.9, 124.1, 121.8, 118.0, 116.4, 115.5, 114.9, 114.6, 111.1, 80.8, 51.3, 11.6.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{32}H_{24}N_3O_2^+$482.1863; Found: 482.1858.

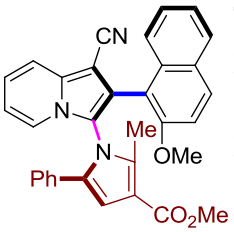


The compound **3q** was prepared according to the general procedure A. The product was obtained as a white solid (33.2 mg, 76% yield). Melting point: 174-179 ℃. The ee (93%) was measured by HPLC using a chiral stationary phase [Daicel IE, *n*-hexane:*i*-PrOH = 70:30, 1.0 mL/min), t_R =8.021 min (minor), t_R =8.730 min (major)], $[\alpha]_D^{30}$ = +32.7 (c = 0.2, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dt, *J* = 9.0, 1.2 Hz, 1H), 7.47 (dd, *J* = 2.9, 1.4 Hz, 1H), 7.38 (d, *J* = 7.0 Hz, 1H), 7.32 (dd, *J* = 5.1, 2.9 Hz, 1H), 7.14 (ddd, *J* = 9.0, 6.8, 1.1 Hz, 1H), 7.11 – 7.00 (m, 3H), 6.98 (s, 1H), 6.95 – 6.88 (m, 2H), 6.76 (td, *J* = 6.9, 1.3 Hz, 1H), 3.89 (s, 3H), 2.17 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 139.3, 136.2, 134.6, 130.9, 130.4, 128.7, 127.8, 126.8, 126.6, 125.8, 124.1, 124.1, 123.8, 121.7, 117.8, 116.8, 115.1, 114.6, 114.5, 111.3, 79.7, 51.4, 11.4.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{26}H_{20}N3O_2S^+$ 438.1271; Found: 438.1281.

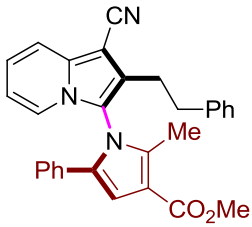


The compound **3r** was prepared according to the general procedure A. The product was obtained as a white solid (28.6 mg, 56% yield). Melting point: 253-257 ℃. The ee (89%) was measured by HPLC using a chiral stationary phase [Daicel ID, *n*-hexane:*i*-PrOH = 70:30, 1 mL/min), t_R =11.690 min (minor), t_R =18.183 min (major)], $[\alpha]_D^{30}$ = -39.3 (c = 0.4, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.83 (m, 2H), 7.77 (d, *J* = 9.2 Hz, 1H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.32 – 7.27 (m, 1H), 7.15 – 7.10 (m, 2H), 7.04 – 6.98 (m, 1H), 6.97 – 6.91 (m, 1H), 6.83 – 6.70 (m, 3H), 6.50 (d, *J* = 8.5 Hz, 1H), 6.47 (s, 1H), 6.34 – 6.26 (m, 2H), 3.83 (s, 3H), 3.67 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 165.4, 140.4, 139.7, 135.9, 135.5, 133.9, 133.1, 132.9, 131.6, 131.5, 131.1, 128.9, 128.5, 128.5, 128.4, 128.2, 127.6, 127.4, 127.3, 127.1, 126.9, 126.9, 125.9, 124.6, 124.4 124.1, 123.9, 123.8, 123.3, 123.2, 123.1, 122.3, 121.9, 118.3, 118.2, 117.7, 117.5, 116.0, 115.6, 114.5, 113.8, 113.8, 113.7, 112.4, 111.9, 111.5, 111.4, 110.5, 110.2, 84.9, 84.8, 55.7, 55.2, 51.2, 51.1, 12.1, 11.7.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{33}H_{26}N_3O_3^+$ 512.1969; Found: 512.1962.

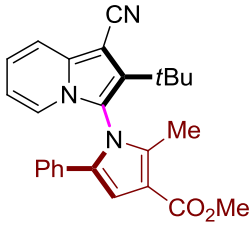


The compound **3s** was prepared according to the general procedure A. The product was obtained as a white solid (25.2 mg, 55% yield). Melting point: 170-175 ℃. The ee (87%) was measured by HPLC using a chiral stationary phase [Daicel IE, *n*-hexane:*i*-PrOH = 70:30, 1.0 mL/min), t_R =8.218 min (minor), t_R =9.210 min (major)], $[\alpha]_D^{30}$ = -72.6 (c = 0.2, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 9.0 Hz, 1H), 7.47 (d, *J* = 6.9 Hz, 1H), 7.25 – 7.18 (m, 4H), 7.16 (dd, *J* = 2.6, 1.7 Hz, 3H), 7.15 – 7.11 (m, 2H), 6.93 (s, 1H), 6.87 – 6.80 (m, 3H), 3.89 (s, 3H), 2.77 (ddd, *J* = 12.9, 10.1, 6.7 Hz, 1H), 2.69 – 2.57 (m, 2H), 2.45 (ddd, *J* = 12.9, 9.4, 5.8 Hz, 1H), 2.07 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 140.7, 139.8, 135.7, 135.5, 131.2, 129.4, 128.8, 128.6, 128.4, 127.8, 126.6, 126.4, 123.6, 121.7, 117.9, 116.2, 116.0, 114.5, 114.3, 110.7, 81.7, 51.4, 34.7, 27.0, 11.3.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{30}H_{26}N_3O_2^+$ 460.2020; Found: 420.2019.

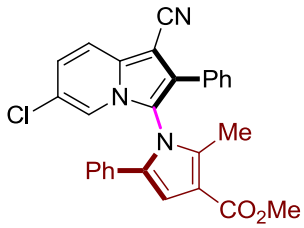


The compound **3t** was prepared according to the general procedure A with 1 mol% **C7**. The product was obtained as a white solid (13.2 mg, 64% yield). Melting point: 169-173 ℃. The ee (86%) was measured by HPLC using a chiral stationary phase [Daicel IE, *n*-hexane:*i*-PrOH = 95:5, 1.0 mL/min), t_R =21.971 min (minor), t_R =23.682 min (major)], $[\alpha]_D^{30}$ = +43.2 (c = 0.2, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 9.0 Hz, 1H), 7.33 (d, *J* = 7.0 Hz, 1H), 7.19 (ddd, *J* = 8.9, 6.7, 1.0 Hz, 1H), 7.15 – 7.03 (m, 3H), 6.94 (s, 1H), 6.83 (td, *J* = 6.8, 1.2 Hz, 1H), 6.77 – 6.69 (m, 2H), 3.88 (s, 3H), 2.24 (s, 3H), 1.08 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 139.7, 137.5, 136.6, 135.8, 131.4, 128.8, 127.7, 126.6, 123.9, 121.5, 117.6, 117.2, 114.5, 114.3, 114.1, 110.6, 81.1, 51.3, 32.9, 29.8, 11.6.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{26}H_{26}N_3O_2^+$ 412.2020; Found: 412.2023.

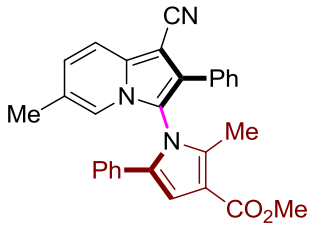


The compound **3u** was prepared according to the general procedure B. The product was obtained as a white solid (19.1 mg, 82% yield). Melting point: 192-197 ℃. The ee (95%) was measured by HPLC using a chiral stationary phase [Daicel IE, *n*-hexane:*i*-PrOH = 90:10, 1.0 mL/min), t_R =14.096 min (minor), t_R =15.431 min (major)], $[\alpha]_D^{30}$ = +33.1 (c = 0.2, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 9.4, 0.9 Hz, 1H), 7.48 – 7.43 (m, 1H), 7.36 – 7.30 (m, 3H), 7.27 – 7.21 (m, 2H), 7.16 – 7.10 (m, 2H), 7.07 (dd, *J* = 8.3, 6.4 Hz, 2H), 6.92 (s, 1H), 6.85 – 6.76 (m, 2H), 3.88 (s, 3H), 2.21 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 139.0, 134.7, 134.2, 130.9, 129.7, 129.3, 129.2, 129.0, 128.7, 127.9, 127.8, 126.5, 125.4, 123.3, 119.6, 118.5, 115.8, 115.7, 115.1, 111.3, 82.1, 51.4, 11.6.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{28}H_{21}ClN_3O_2^+$ 466.1317; Found: 466.1304.

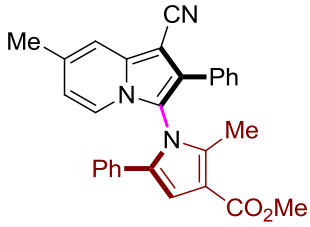


The compound **3v** was prepared according to the general procedure B with 1 mol% **C7**. The product was obtained as a white solid (15.6 mg, 70% yield). Melting point: 178-183 ℃. The ee (94%) was measured by HPLC using a chiral stationary phase [Daicel IG, *n*-hexane:*i*-PrOH = 90:10, 0.5 mL/min), t_R =32.988 min (major), t_R = 40.188 min (minor)], $[\alpha]_D^{30}$ = -30.3 (c = 0.2, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 9.1 Hz, 1H), 7.29 (dd, *J* = 5.3, 1.8 Hz, 3H), 7.25 – 7.14 (m, 3H), 7.12 – 7.07 (m, 1H), 7.06 – 7.00 (m, 3H), 6.91 (s, 1H), 6.83 – 6.77 (m, 2H), 3.88 (s, 3H), 2.24 (s, 3H), 2.21 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 139.4, 135.2, 134.9, 131.2, 130.3, 129.1, 128.6, 128.5, 128.3, 127.8, 127.6, 127.2, 126.5, 124.8, 119.3, 117.4, 116.6, 114.9, 114.7, 110.9, 80.2, 51.4, 18.6, 11.6.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{29}H_{24}N_3O_2^+$ 446.1863; Found: 446.1858.

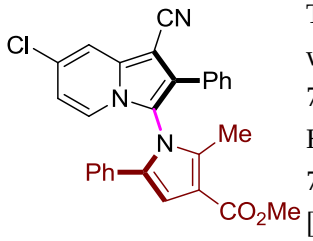


The compound **3w** was prepared according to the general procedure B. The product was obtained as a white solid (12.0 mg, 53% yield). Melting point: 209-211 ℃. The ee (93%) was measured by HPLC using a chiral stationary phase [Daicel IE, *n*-hexane:*i*-PrOH = 70:30, 1.0 mL/min), t_R =8.630 min (minor), t_R =9.805 min (major)], $[\alpha]_D^{30}$ = -38.0 (c = 0.2, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 1.4 Hz, 1H), 7.37 – 7.22 (m, 6H), 7.13 – 6.95 (m, 3H), 6.91 (s, 1H), 6.86 – 6.80 (m, 2H), 6.61 (dd, *J* = 7.1, 1.7 Hz, 1H), 3.87 (s, 3H), 2.40 (d, *J* = 1.1 Hz, 3H), 2.19 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 139.4, 136.9, 135.3, 134.8, 131.1, 130.3, 129.1, 128.6, 128.5, 128.1, 127.8, 127.6, 126.4, 121.3, 117.2, 116.7, 116.4, 114.7, 114.6, 111.0, 79.0, 51.3, 21.4, 11.5.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{29}H_{24}N_3O_2^+$ 446.1863; Found: 446.1867.

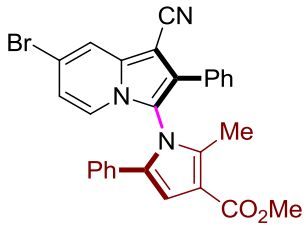


The compound **3x** was prepared according to the general procedure B with 5 mol% **C7**. The product was obtained as a white solid (18.5 mg, 78% yield). Melting point: 168-173 ℃. The ee (94%) was measured by HPLC using a chiral stationary phase [Daicel ID, *n*-hexane:*i*-PrOH = 70:30, 1.0 mL/min), t_R =6.970 min (major), t_R =7.568 min (minor)], $[\alpha]_D^{30}$ = -56.5 (c = 0.2, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 2.1, 0.9 Hz, 1H), 7.38 – 7.31 (m, 4H), 7.30 – 7.22 (m, 2H), 7.15 – 6.99 (m, 3H), 6.92 (s, 1H), 6.85 – 6.81 (m, 2H), 6.74 (dd, *J* = 7.4, 2.1 Hz, 1H), 3.87 (s, 3H), 2.19 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 139.2, 136.0, 134.7, 131.1, 130.9, 129.7, 129.3, 129.0, 129.0, 128.7, 127.9, 127.8, 126.4, 122.5, 116.8, 116.2, 115. 7, 115.6, 115.1, 111.3, 80.9, 51.4, 11.6.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{28}H_{21}ClN_3O_2^+$ 466.1317; Found: 466.1309.

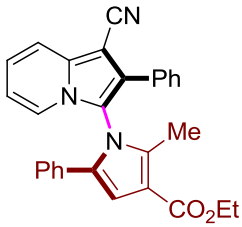


The compound **3y** was prepared according to the general procedure B. The product was obtained as a white solid (20.4 mg, 80% yield). Melting point: 173-179 ℃. The ee (89%) was measured by HPLC using a chiral stationary phase [Daicel ID, *n*-hexane:*i*-PrOH = 80:20, 1.0 mL/min), t_R =9.646 min (major), t_R =10.811 min (minor)], $[\alpha]_D^{30}$ = +33.6(c = 0.2, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 1.9 Hz, 1H), 7.32 (d, *J* = 2.9 Hz, 6H), 7.29 – 7.22 (m, 1H), 7.12 (d, *J* = 7.1 Hz, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.91 (s, 1H), 6.87 – 6.78 (m, 3H), 3.87 (s, 3H), 2.18 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 139.1, 136.4, 134.7, 130.9, 129.7, 129.3, 129.0, 128.9, 128.8, 127.9, 127.8, 126.5, 122.4, 120.2, 118.5, 118.4, 115.7, 115.7, 115.1, 111.3, 80.8, 51.4, 11.6.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{28}H_{21}BrN_3O_2^+$ 510.0812; Found: 510.0804.

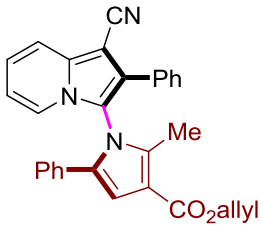


The compound **3z** was prepared according to the general procedure B. The product was obtained as a white solid (18.5 mg, 83% yield). Melting point: 172-175 ℃. The ee (88%) was measured by HPLC using a chiral stationary phase [Daicel IE, *n*-hexane:*i*-PrOH = 80:20, 1.0 mL/min), t_R =10.528 min (minor), t_R =11.865 min (major)], $[\alpha]_D^{30}$ = +94.3 (c = 0.2, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.70 (m, 1H), 7.43 (dt, *J* = 7.0, 1.1 Hz, 1H), 7.34 – 7.23 (m, 5H), 7.17 (ddd, *J* = 9.0, 6.8, 1.1 Hz, 1H), 7.11 – 6.98 (m, 3H), 6.93 (s, 1H), 6.86 – 6.75 (m, 3H), 4.33 (d, *J* = 7.1 Hz, 2H), 2.20 (s, 3H), 1.39 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 134.0, 136.3, 134.7, 131.1, 130.1, 129.2, 128.7, 128.6, 128.4, 127.9, 127.6, 126.4, 124.0, 121.8, 118.0, 116.4, 115.3, 115.1, 114.5, 111.1, 80.6, 60.1, 14.6, 11.6.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{29}H_{24}N_3O_2^+$ 446.1863; Found: 446.1860.

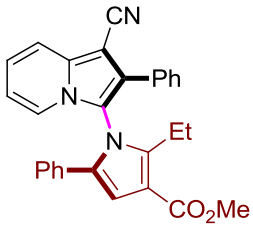


The compound **3aa** was prepared according to the general procedure B. The product was obtained as a light yellow solid (19.2 mg, 84% yield). Melting point: 165-170 ℃. The ee (90%) was measured by HPLC using a chiral stationary phase [Daicel IE-H, *n*-hexane:*i*-PrOH = 80:20, 1.0 mL/min), t_R =10.188 min (minor), t_R =11.212 min (major)], $[\alpha]_D^{30}$ = -61.1(c = 0.2, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 9.0 Hz, 1H), 7.43 (d, *J* = 7.0 Hz, 1H), 7.32 (dt, *J* = 4.8, 2.5 Hz, 3H), 7.29 – 7.21 (m, 3H), 7.17 (ddd, *J* = 9.0, 6.8, 1.1 Hz, 1H), 7.10 – 6.97 (m, 3H), 6.94 (s, 1H), 6.84 – 6.72 (m, 3H), 6.05 (ddt, *J* = 17.3, 10.4, 5.6 Hz, 1H), 5.42 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.28 (dd, *J* = 10.4, 1.4 Hz, 1H), 4.79 (d, *J* = 5.6 Hz, 2H), 2.21 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 139.5, 136.3, 134.9, 132.8, 131.1, 130.1, 129.2, 128.7, 128.6, 128.5, 127.9, 127.7, 126.5, 124.0, 121.8, 118.1, 118.0, 116.4, 115.3, 114.8, 114.6, 111.2, 80.7, 64.9, 11.6.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{30}H_{24}N_3O_2^+$ 458.1863; Found: 458.1856.

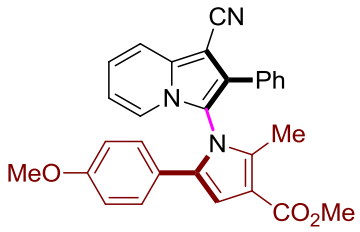


The compound **3ab** was prepared according to the general procedure B. The product was obtained as a white solid (17.8 mg, 80% yield). Melting point: 163-169 ℃. The ee (91%) was measured by HPLC using a chiral stationary phase [Daicel IE, *n*-hexane:*i*-PrOH = 80:20, 1.0 mL/min), t_R =9.325 min (minor), t_R =10.130 min (major)], $[\alpha]_D^{30}$ = +62.0(c = 0.2, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dt, *J* = 9.0, 1.1 Hz, 1H), 7.42 – 7.36 (m, 3H), 7.35 – 7.28 (m, 3H), 7.15 (ddd, *J* = 8.9, 6.8, 1.1 Hz, 1H), 7.11 – 7.02 (m, 3H), 6.99 (s, 1H), 6.90 (dd, *J* = 8.2, 1.6 Hz, 2H), 6.76 (td, *J* = 6.9, 1.2 Hz, 1H), 3.86 (s, 3H), 2.55 (ddq, *J* = 28.9, 14.6, 7.3 Hz, 2H), 0.74 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 145.4, 136.3, 134.5, 131.1, 130.2, 129.3, 128.8, 128.7, 128.2, 127.9, 127.7, 126.4, 124.0, 121.9, 117.9, 116.5, 115.1, 114.5, 114.3, 111.6, 80.7, 51.3, 19.4, 14.0.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{29}H_{24}N_3O_2^+$446.1863; Found: 446.1858.

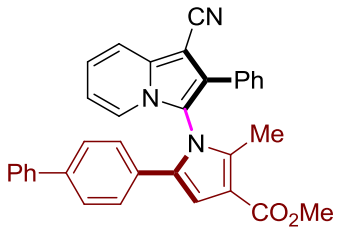


The compound **3ac** was prepared according to the general procedure B. The product was obtained as a white solid (18.7 mg, 81% yield). Melting point: 140-145 ℃. The ee (86%) was measured by HPLC using a chiral stationary phase [Daicel ID, *n*-hexane:*i*-PrOH = 80:20, 1.0 mL/min), t_R =13.637 min (major), t_R =15.035 min (minor)], $[\alpha]_D^{30}$ =+89.2 (c = 0.2, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dt, *J* = 9.0, 1.2 Hz, 1H), 7.41 (dt, *J* = 7.0, 1.1 Hz, 1H), 7.36 – 7.28 (m, 5H), 7.16 (ddd, *J* = 9.0, 6.8, 1.1 Hz, 1H), 6.82 (s, 1H), 6.81 – 6.67 (m, 3H), 6.57 (d, *J* = 8.9 Hz, 2H), 3.86 (s, 3H), 3.68 (s, 3H), 2.18 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 159.2, 138.8, 136.3, 134.7, 130.2, 129.2, 128.7, 128.4, 128.0, 127.9, 124.0, 123.6, 121.8, 118.0, 116.4, 115.3, 114.6, 114.5, 114.0, 110.2, 80.6, 55.3, 51.3, 11.5.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{29}H_{24}N_3O_3^+$ 462.1812; Found: 462.1810.

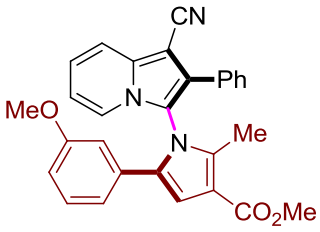


The compound **3ad** was prepared according to the general procedure B. The product was obtained as a white solid (13.0 mg, 51% yield,). Melting point: 204-207 ℃. The ee (94%) was measured by HPLC using a chiral stationary phase [Daicel OD-H, *n*-hexane:*i*-PrOH = 70:30, 1.0 mL/min), t_R =6.830 min (major), t_R =8.553 min (minor)], $[\alpha]_D^{30}$ = +33.6 (c = 0.2, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.71 (m, 1H), 7.46 (ddd, *J* = 8.5, 7.2, 1.4 Hz, 3H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.35 – 7.28 (m, 8H), 7.18 (ddd, *J* = 8.9, 6.8, 1.1 Hz, 1H), 6.98 (s, 1H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.80 (td, *J* = 6.9, 1.2 Hz, 1H), 3.88 (s, 3H), 2.20 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 140.2, 140.2, 139.5, 136.4, 134.4, 130.2, 130.0, 129.3, 128.9, 128.8, 128.5, 127.9, 127.6, 127.3, 126.9, 126.7, 124.1, 121.9, 118.1, 116.4, 115.3, 115.0, 114.7, 111.2, 80.8, 51.4, 11.6.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{34}H_{26}N_3O_2^+$ 508.2020; Found: 508.2016.

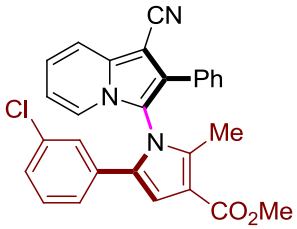


The compound **3ae** was prepared according to the general procedure B. The product was obtained as a light green solid (19.8 mg, 86% yield). Melting point: 177-180 ℃. The ee (89%) was measured by HPLC using a chiral stationary phase [Daicel IE, *n*-hexane:*i*-PrOH = 90:10, 1.0 mL/min), t_R =22.883 min (minor), t_R =24.880 min (major)], $[\alpha]_D^{30}$ = -164.6 (c = 0.1, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 9.0 Hz, 1H), 7.44 (d, *J* = 7.0 Hz, 1H), 7.31 (t, *J* = 3.0 Hz, 5H), 7.18 (ddd, *J* = 9.0, 6.8, 1.1 Hz, 1H), 6.96 (t, *J* = 8.0 Hz, 1H), 6.92 (s, 1H), 6.80 (td, *J* = 6.9, 1.2 Hz, 1H), 6.64 (ddd, *J* = 8.3, 2.6, 0.9 Hz, 1H), 6.44 (ddd, *J* = 7.7, 1.7, 1.0 Hz, 1H), 6.35 (dd, *J* = 2.5, 1.6 Hz, 1H), 3.87 (s, 3H), 3.46 (s, 3H), 2.19 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 159.6, 139.4, 136.3, 134.7, 132.3, 130.1, 129.7, 129.2, 128.7, 128.4, 127.9, 124.0, 121.9, 118.8, 118.0, 116.3, 115.3, 114.8, 114.6, 114.0, 111.2, 111.2, 80.6, 55.0, 51.4, 11.5.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{29}H_{24}N_3O_3^+$ 462.1812; Found: 462.1806.

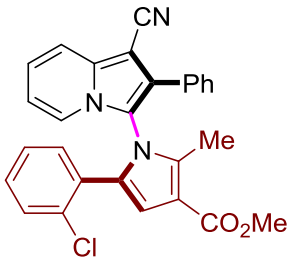


The compound **3af** was prepared according to the general procedure B. The product was obtained as a white solid (16.1 mg, 68% yield). Melting point: 165-171 ℃. The ee (88%) was measured by HPLC using a chiral stationary phase [Daicel IE, *n*-hexane:*i*-PrOH = 90:10, 1.0 mL/min), t_R =19.043 min (minor), t_R =20.550 min (major)], $[\alpha]_D^{30}$ = +111.4 (c = 0.2, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dt, *J* = 9.0, 1.2 Hz, 1H), 7.42 (dt, *J* = 7.0, 1.1 Hz, 1H), 7.33 (dd, *J* = 5.1, 1.9 Hz, 3H), 7.23 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.21 – 7.17 (m, 1H), 7.06 (ddd, *J* = 8.1, 2.2, 1.0 Hz, 1H), 6.99 – 6.88 (m, 2H), 6.87 – 6.75 (m, 2H), 6.54 (dt, *J* = 7.9, 1.2 Hz, 1H), 3.87 (s, 3H), 2.25 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 139.9, 136.4, 134.4, 133.4, 132.7, 130.0, 129.8, 129.3, 128.8, 128.8, 127.9, 127.7, 127.1, 124.1, 124.0, 121.6, 118.1, 116.2, 115.0, 114.9, 114.8, 111.8, 80.8, 51.4, 11.6.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{28}H_{21}ClN_3O_2^+$ 466.1317; Found: 466.1310.

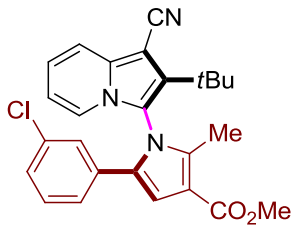


The compound **3ag** was prepared according to the general procedure B. The product was obtained as a white solid (7.2mg, 32% yield). Melting point: 197-199 ℃. The ee (25%) was measured by HPLC using a chiral stationary phase [Daicel IE, *n*-hexane:*i*-PrOH = 70:30, 1.0 mL/min), t_R =7.490min (major), t_R =8.116 min (minor)], $[\alpha]_D^{30}$ = +95.0(c = 0.1, $CHCl_3$).

^{1}H NMR(400 MHz, $CDCl_3$) δ 7.71 – 7.59 (m, 1H), 7.32 (dd, J = 5.1, 2.0 Hz, 2H), 7.18 (ddd, J = 9.1, 6.7, 1.1 Hz, 1H), 7.10 (dd, J = 8.0, 1.3 Hz, 1H), 7.07 – 6.93 (m, 3H), 6.86 (td, J = 6.9, 1.1 Hz, 1H), 6.77 (s, 1H), 6.72 (td, J = 7.5, 1.3 Hz, 1H), 6.22 (dd, J = 7.7, 1.6 Hz, 1H), 3.89 (s, 3H), 2.40 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 138.8, 136.4, 134.1, 132.1, 131.7, 130.3, 129.8, 129.5, 129.2, 129.1, 128.6, 128.3, 128.1, 126.2, 124.0, 122.7, 117.9, 116.3, 115.0, 114.5, 114.0, 113.3, 80.4, 51.4, 11.9.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{28}H_{21}ClN_3O_2^+$ 466.1317; Found: 466.1329.

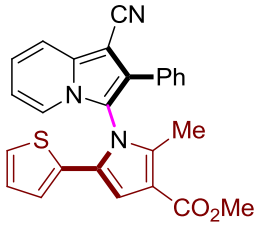


The compound **3ah** was prepared according to the general procedure B with 5 mol% **C7**. The product was obtained as a white solid (11.6 mg, 52% yield). Melting point: 145-149 ℃. The ee (89%) was measured by HPLC using a chiral stationary phase [Daicel IG, *n*-hexane:*i*-PrOH = 90:10, 1.0 mL/min), t_R =9.736 min (minor), t_R =10.951 min (major)], $[\alpha]_D^{30}$ = -171.2 (c = 0.2, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 9.0 Hz, 1H), 7.33 – 7.24 (m, 1H), 7.20 (dd, *J* = 9.0, 6.7 Hz, 1H), 7.13 – 7.08 (m, 1H), 7.04 – 6.96 (m, 2H), 6.91 (s, 1H), 6.83 (td, *J* = 6.9, 1.2 Hz, 1H), 6.48 (dt, *J* = 7.8, 1.3 Hz, 1H), 3.88 (s, 3H), 2.24 (s, 3H), 1.12 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 140.4, 137.6, 136.7, 134.7, 134.1, 133.0, 130.0, 127.6, 126.8, 124.1, 123.9, 121.3, 117.7, 117.0, 114.7, 114.5, 113.6, 111.4, 81.2, 51.4, 32.9, 29.9, 11.6.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{26}H_{25}ClN_3O_2^+$ 446.1630; Found: 446.1623.

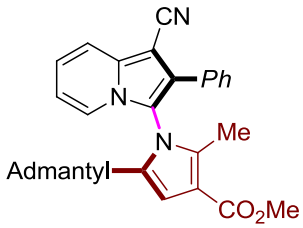


The compound **3ai** was prepared according to the general procedure B. The product was obtained as a light green solid (13.0 mg, 59% yield). Melting point: 180-182 ℃. The ee (96%) was measured by HPLC using a chiral stationary phase [Daicel IE, *n*-hexane:*i*-PrOH = 80:20, 1.0 mL/min), t_R =12.080 min (minor), t_R =13.595 min (major)], $[\alpha]_D^{30}$ =+71.1 (c = 0.2, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 9.0 Hz, 1H), 7.42 – 7.36 (m, 3H), 7.36 – 7.26 (m, 3H), 7.21 (ddd, *J* = 9.0, 6.8, 1.1 Hz, 1H), 7.03 (s, 1H), 6.99 (dd, *J* = 5.1, 1.1 Hz, 1H), 6.83 – 6.74 (m, 2H), 6.61 (dd, *J* = 3.7, 1.2 Hz, 1H), 3.85 (s, 3H), 2.12 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 139.4, 136.6, 132.3, 123.0, 129.6, 129.3, 128.8, 128.0, 127.5, 124.9, 124.3, 123.7, 122.0, 118.0, 116.3, 114.8, 114.7, 114.1, 110.6, 81.0, 51.4, 11.4.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{26}H_{20}N_3O_2S^+$438.1271; Found: 438.1273.

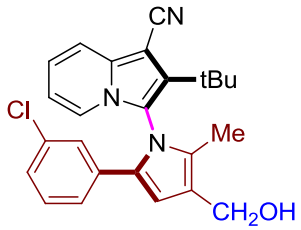


The compound **3aj** was prepared according to the general procedure B. The product was obtained as a white solid (12.3 mg, 50% yield). Melting point: 136-140 ℃. The ee (86%) was measured by HPLC using a chiral stationary phase [Daicel IE, *n*-hexane:*i*-PrOH = 95:5, 1.0 mL/min), t_R =24.921 min (minor), t_R =26.977 min (major)], $[\alpha]_D^{30}$ = +21.2 (c = 0.2, $CHCl_3$).

^{1}H NMR (400 MHz, CDCl3) δ 7.78 (d, J = 8.9 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.40 – 7.31 (m, 3H), 7.25 – 7.15 (m, 1H), 7.06 (dt, J = 6.9, 1.1 Hz, 1H), 6.84 (td, J = 6.9, 1.2 Hz, 1H), 6.50 (s, 1H), 3.86 (s, 3H), 2.14 (s, 3H)，δ 1.58 (s, 3H), 1.51 (d, J = 12.6 Hz, 6H), 1.35 (d, J = 12.3 Hz, 3H), 1.24 – 1.15 (m, 3H).

^{13}C NMR (100 MHz, CDCl3) δ 165.8, 144.3, 139.1, 136.3, 130.9, 129.3, 128.8, 127.8, 127.7, 124.1, 122.2, 117.9, 116.8, 116.6, 114.5, 113.5, 108.2, 80.4, 51.3, 41.1, 36.4, 34.4, 28.3, 11.1.

HRMS (ESI-TOF) m/z : [M+H]+Calcd for $C_{32}H_{30}N_3O_2^+$ 490.2489; Found: 490.2482.

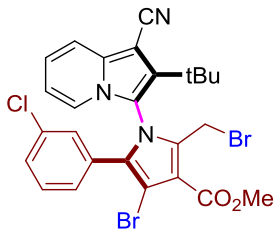


The compound **4** was prepared according to the general procedure. The product was obtained as a light-yellow solid (21.0 mg, 71% yield). Melting point: 250-255 ℃. The ee (86%) was measured by HPLC using a chiral stationary phase [Daicel IG, *n*-hexane:*i*-PrOH = 70:30, 1.0 mL/min), t_R =4.766 min (major), t_R =5.500 min (minor)], $[\alpha]_D^{30}$ = -105.1 (c = 0.2, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 9.0 Hz, 1H), 7.31 (d, *J* = 6.9 Hz, 1H), 7.17 (ddd, *J* = 8.9, 6.7, 1.1 Hz, 1H), 7.09 – 7.03 (m, 1H), 6.98 (t, *J* = 7.9 Hz, 1H), 6.92 (s, 1H), 6.79 (td, *J* = 6.8, 1.2 Hz, 1H), 6.63 (s, 1H), 6.46 (dt, *J* = 7.9, 1.4 Hz, 1H), 4.63 (s, 2H), 1.95 (s, 3H), 1.14 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 136.5, 134.6, 133.9, 133.7, 131.4, 129.9, 126.8, 126.4, 123.9, 123.4, 122.3, 121.7, 117.5, 117.3, 114.9, 114.1, 110.9, 80.8, 57.9, 32.9, 29.9, 9.98.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{25}H_{25}ClN_3O^+$ 418.1681; Found: 418.1687.



The compound **5** was prepared according to the general procedure. The product was obtained as a white solid (21.6 mg, 72% yield). Melting point: 175-180 ℃. The ee (88%) was measured by HPLC using a chiral stationary phase [Daicel IG, *n*-hexane:*i*-PrOH = 70:30, 1.0 mL/min), t_R =4.945 min (minor), t_R =5.851 min (major)], $[\alpha]_D^{30}$ = -23.4 (c = 0.2, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.9 Hz, 1H), 7.49 (d, *J* = 7.0 Hz, 1H), 7.22 (dd, *J* = 5.0, 2.9 Hz, 2H), 7.11 (t, *J* = 7.9 Hz, 1H), 7.01 (t, *J* = 1.9 Hz, 1H), 6.92 – 6.87 (m, 1H), 6.84 – 6.78 (m, 1H), 4.85 (d, *J* = 10.8 Hz, 1H), 4.33 (d, *J* = 10.8 Hz, 1H), 3.98 (s, 3H), 1.15 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 138.4, 137.6, 137.1, 135.6, 134.4, 130.6, 129.8, 129.7, 129.5, 127.5, 124.7, 122.7, 117.4, 116.6, 116.1, 114.0, 110.9, 100.3, 81.7, 52.0, 33.0, 29.8, 21.1.

HRMS (ESI-TOF) m/z : $[M+H]^+$Calcd for $C_{26}H_{23}Br_2ClN_3O_2^+$ 601.9840; Found: 601.9852.

9. X-ray crystallographic analysis

Single crystals suitable for X-ray diffraction experiment were obtained by diffusion method of *n*-hexane/DCM containing the corresponding compound **5**. Date collection was performed at 296.00 K on Bruker D8 Venture diffractrometer with a CCD area detector, using graphite monochromated Cu *Kα* radiation (λ = 1.54178 Å).

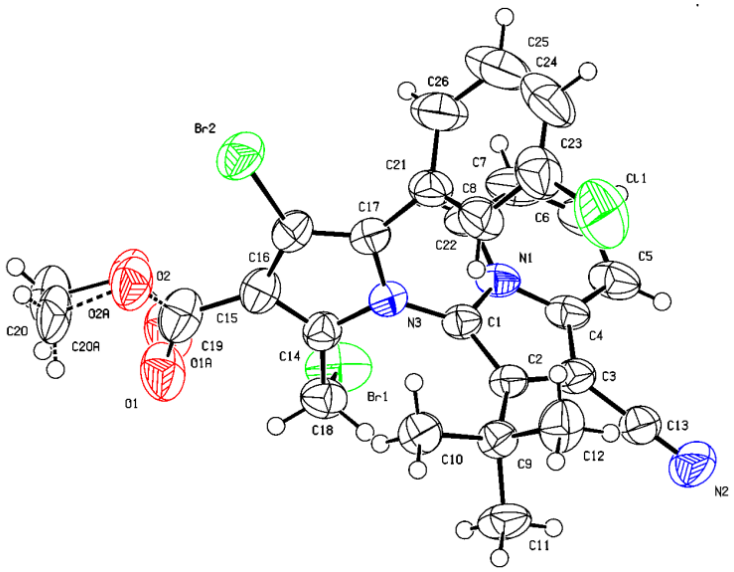


Figure S1. X-ray structure of **5** (ellipsoid contour at 50% probability).

Datablock: 20240509d

Bond precision: C-C = 0.0089 A Wavelength= 1.54178
Cell: a= 9.9201 (4) b= 12.9585 (5) c= 20.1488 (7)
alpha=90 beta= 90 gamma=90
Temperature: 296 K

	Calculated	Reported
Volume	2590.12 (17)	2590.12 (17)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C26 H22 Br2 C1 N3 O2	C26 H22 Br2 C1 N3 O2
Sum formula	C26 H22 Br2 C1 N3 O2	C26 H22 Br2 C1 N3 O2
Mr	603.72	603.73
Dx,g cm-3	1.548	1.548
Z	4	4
Mu (mm-1)	5.146	5.146
F000	1208.0	1208.0
F000’	1206.57	
h,k,lmax	12,16,24	12,16,24
Nref	5150 [2916]	5083
Tmin,Tmax	0.455,0.512	0.283,0.754
Tmin’	0.344	

Correction method= # Reported T Limits: Tmin=0.283 Tmax=0.754
AbsCorr = MULTI-SCAN
Data completeness= 1.74/0.99 Theta(max)= 72.539
R(reflections)= 0.0473 (4832) wR2(reflections)= 0.1287(5083)
S = 1.051 Npar= 341

10. Theoretical calculation on the rotational barriers of products

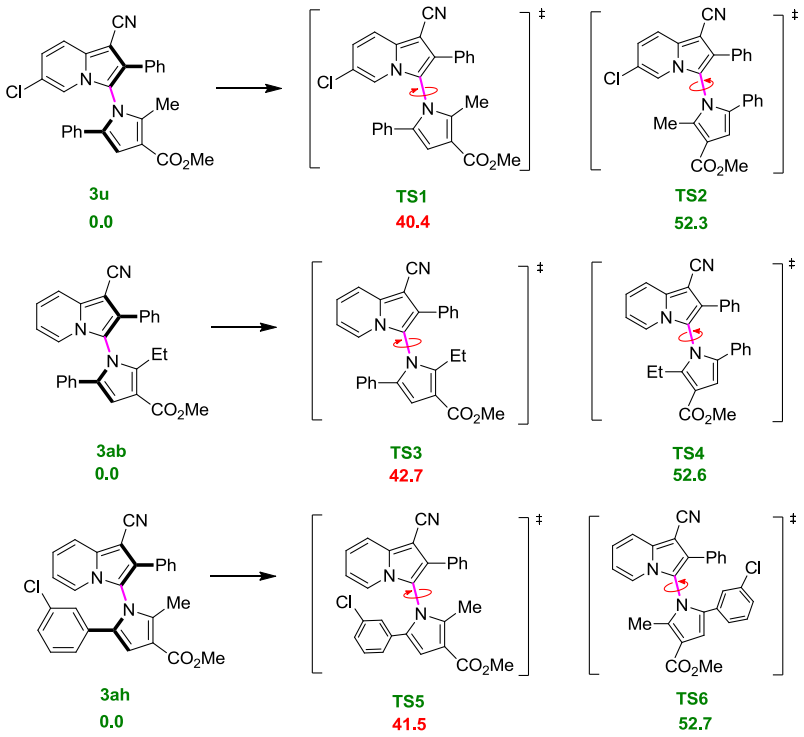


Figure S2. Computational analysis of axial chiral isomerization process calculated at the level of M06-2X/6-311+G(d,p) (SMD, mesitylene)//M06-2X/6-31G(d). The relative free energies are given in kcal/mol.

Optimized Cartesian Coordinates

Optimized Cartesian coordinates and their corresponding single-point energies (*E*(SCRF), a.u.) calculated at the M06-2X/6-311+G(d,p) (SMD, mesitylene)//M06-2X/6-31G(d) level as well as the imaginary frequency (IF, cm^{-1}) of transition states.

54 (the number of atoms involved in the molecule)

TS1, *E*(SCRF) = -2026.21774849 a.u., IF = *i*25.4299 cm^{-1}

C	1.450255000	-2.439722000	0.224986000
C	2.431419000	-0.471517000	-0.694889000
C	3.622419000	-1.113687000	-0.777855000
C	3.802226000	-2.434524000	-0.274285000
C	2.704964000	-3.094829000	0.185350000
C	0.159355000	-2.905395000	0.404174000
C	-0.739091000	-1.814323000	0.240658000
C	0.034486000	-0.656725000	0.102920000
H	2.262700000	0.478265000	-1.168472000
H	4.777150000	-2.903905000	-0.326298000
H	2.741875000	-4.133282000	0.496033000
N	1.365058000	-1.070005000	-0.041556000
C	-0.171173000	-4.270115000	0.616136000
N	-0.410976000	-5.388803000	0.803084000
C	-2.168335000	-2.064712000	-0.038382000

C	-2.714950000	-1.598479000	-1.238696000
C	-2.953061000	-2.844826000	0.814313000
C	-4.039202000	-1.874317000	-1.560765000
H	-2.096999000	-1.009572000	-1.911338000
C	-4.277418000	-3.120320000	0.489457000
H	-2.527900000	-3.223336000	1.739581000
C	-4.825557000	-2.630684000	-0.693719000
H	-4.455720000	-1.502328000	-2.491561000
H	-4.881460000	-3.720492000	1.162372000
H	-5.859251000	-2.846721000	-0.944584000
N	-0.345934000	0.714110000	0.196894000
C	0.464586000	1.846314000	-0.091708000
C	-1.676429000	1.150894000	0.278799000
C	-0.369086000	2.888952000	-0.375815000
C	-1.703060000	2.460635000	-0.156634000
H	-0.067379000	3.913214000	-0.544343000
C	1.852113000	2.035686000	0.368696000
C	2.293830000	1.455955000	1.563815000
C	2.720111000	2.872438000	-0.342669000
C	3.588513000	1.682711000	2.017550000
H	1.618320000	0.821630000	2.131732000
C	4.009711000	3.105855000	0.121413000
H	2.382239000	3.319309000	-1.273912000
C	4.452393000	2.504481000	1.297640000
H	3.921055000	1.219965000	2.941563000
H	4.675828000	3.748295000	-0.445923000
H	5.463734000	2.676518000	1.651247000
C	-2.751528000	0.478323000	1.084852000
H	-3.185105000	1.245433000	1.729423000
H	-3.562595000	0.056074000	0.490305000
H	-2.328221000	-0.302234000	1.715911000
C	-2.839901000	3.387916000	-0.244500000
O	-2.737808000	4.549166000	-0.567605000
O	-4.021822000	2.811981000	0.052024000
C	-5.145276000	3.686061000	-0.037549000
H	-5.244575000	4.074460000	-1.053368000
H	-6.011313000	3.082761000	0.230413000
H	-5.031703000	4.526375000	0.650700000
Cl	4.938556000	-0.325235000	-1.591973000

54

TS2, *E*(SCRF) = -1853.68807079 a.u., IF = *i*14.3368 cm^{-1}

C	0.770749000	-2.791681000	-0.428034000
C	2.625762000	-1.375069000	0.069679000
C	3.462089000	-2.434255000	-0.050887000
C	2.992790000	-3.716117000	-0.465783000
C	1.649648000	-3.887537000	-0.608400000
C	-0.599608000	-2.693615000	-0.256028000
C	-0.929149000	-1.333481000	0.004845000
C	0.245597000	-0.592663000	-0.155882000

H	2.932006000	-0.439107000	0.503107000
H	3.693933000	-4.532135000	-0.590893000
H	1.212223000	-4.856472000	-0.823537000
N	1.294538000	-1.501617000	-0.287386000
C	-1.482633000	-3.806942000	-0.257099000
N	-2.178195000	-4.733734000	-0.276785000
N	0.426388000	0.812682000	-0.267909000
C	-0.626894000	1.726893000	-0.033542000
C	1.630704000	1.536511000	-0.302198000
C	-0.069348000	2.936249000	0.262926000
C	1.338293000	2.822914000	0.104676000
C	-1.999976000	1.558723000	-0.548003000
C	-2.188124000	1.005208000	-1.820376000
C	-3.094158000	2.098390000	0.130679000
C	-3.455580000	0.968191000	-2.388820000
H	-1.333237000	0.611222000	-2.363274000
C	-4.360577000	2.062892000	-0.443038000
H	-2.949580000	2.521663000	1.120353000
C	-4.546967000	1.494121000	-1.700683000
H	-3.589887000	0.536180000	-3.375892000
H	-5.206660000	2.471583000	0.100874000
H	-5.537349000	1.464374000	-2.144056000
C	-2.210448000	-0.985492000	0.659142000
C	-2.168924000	-0.415755000	1.937178000
C	-3.441371000	-1.347934000	0.110174000
C	-3.344122000	-0.186004000	2.642090000
H	-1.207567000	-0.156603000	2.372861000
C	-4.616391000	-1.114446000	0.817863000
H	-3.477541000	-1.797593000	-0.877577000
C	-4.571891000	-0.531735000	2.081535000
H	-3.300775000	0.255843000	3.632938000
H	-5.569627000	-1.388758000	0.377048000
H	-5.490947000	-0.354743000	2.631582000
H	-0.606501000	3.864617000	0.396592000
C	2.833189000	1.166173000	-1.141792000
H	3.754919000	0.981697000	-0.582655000
H	2.627130000	0.294031000	-1.763529000
C	2.234329000	3.998131000	0.083268000
O	1.830453000	5.124601000	-0.027995000
O	3.577830000	3.748517000	0.120166000
C	4.092747000	3.004363000	1.216665000
H	3.444492000	2.162714000	1.480629000
H	5.073868000	2.635817000	0.914664000
H	4.204639000	3.657990000	2.087225000
Cl	5.129747000	-2.233143000	0.392707000
H	3.036955000	2.008649000	-1.806210000

57

TS3, *E*(SCRF) = -1433.40998199 a.u., IF = *i*26.6802 cm^{-1}

C	1.711091000	-2.610106000	-0.120940000

C	2.816970000	-0.693047000	-0.994617000
C	3.956489000	-1.411862000	-1.149402000
C	4.036852000	-2.761134000	-0.697506000
C	2.908188000	-3.359431000	-0.226510000
C	0.395537000	-2.988620000	0.087692000
C	-0.422384000	-1.828270000	-0.003855000
C	0.424903000	-0.726273000	-0.129103000
H	2.698275000	0.285374000	-1.420106000
H	4.962748000	-3.316389000	-0.794846000
H	2.866548000	-4.410211000	0.039392000
N	1.720387000	-1.227805000	-0.333097000
C	-0.028338000	-4.332004000	0.262359000
N	-0.346063000	-5.436342000	0.417626000
C	-1.881116000	-1.947468000	-0.179733000
C	-2.482637000	-1.373639000	-1.305889000
C	-2.658655000	-2.696208000	0.707335000
C	-3.850161000	-1.505680000	-1.513125000
H	-1.871266000	-0.809655000	-2.005053000
C	-4.027812000	-2.829917000	0.495053000
H	-2.191987000	-3.159015000	1.572283000
C	-4.627315000	-2.228102000	-0.608405000
H	-4.310272000	-1.047426000	-2.382886000
H	-4.626072000	-3.405630000	1.194061000
H	-5.695796000	-2.330599000	-0.769974000
N	0.128921000	0.660186000	0.047912000
C	0.956337000	1.750863000	-0.334209000
C	-1.174053000	1.161319000	0.247045000
C	0.149186000	2.824693000	-0.567449000
C	-1.178686000	2.461999000	-0.222645000
H	0.477280000	3.833197000	-0.776899000
C	2.377262000	1.894697000	0.027601000
C	2.873011000	1.312916000	1.200612000
C	3.226002000	2.694786000	-0.746344000
C	4.199100000	1.503143000	1.572469000
H	2.212026000	0.707252000	1.815389000
C	4.549514000	2.888134000	-0.366228000
H	2.844092000	3.146154000	-1.658172000
C	5.043958000	2.286451000	0.789574000
H	4.572180000	1.041115000	2.481231000
H	5.198826000	3.506260000	-0.978694000
H	6.079135000	2.432420000	1.080815000
C	-2.195102000	0.597816000	1.210568000
H	-2.784193000	1.462553000	1.517974000
H	-2.908683000	-0.088238000	0.758591000
C	-2.262487000	3.458155000	-0.268874000
O	-2.086934000	4.620164000	-0.557557000
O	-3.482698000	2.952482000	-0.002795000
C	-4.544342000	3.903025000	-0.064475000
H	-4.615006000	4.327858000	-1.068018000

H	-5.449204000	3.350875000	0.184666000
H	-4.375989000	4.712497000	0.649009000
H	4.786212000	-0.944563000	-1.665608000
C	-1.559838000	-0.008965000	2.465817000
H	-0.921974000	0.727217000	2.965282000
H	-2.348320000	-0.306165000	3.163018000
H	-0.953073000	-0.891965000	2.253386000

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TS4, *E*(SCRF) = -1433.39375358 a.u., IF = *i*18.4778 cm^{-1}

C	0.697508000	3.147042000	-0.175217000
C	-1.661593000	2.961611000	0.091346000
C	-1.787482000	4.308827000	-0.000168000
C	-0.655940000	5.129022000	-0.287989000
C	0.575805000	4.549919000	-0.327992000
C	1.783933000	2.323001000	0.066711000
C	1.309947000	0.992425000	0.240629000
C	-0.058910000	1.004443000	-0.036497000
H	-2.458562000	2.330124000	0.441367000
H	-0.771936000	6.201260000	-0.394647000
H	1.490215000	5.123973000	-0.433482000
N	-0.447274000	2.341462000	-0.163963000
C	3.116696000	2.795629000	0.200097000
N	4.193864000	3.214616000	0.290445000
N	-0.910997000	-0.112223000	-0.299183000
C	-0.388710000	-1.425886000	-0.240010000
C	-2.309686000	-0.197965000	-0.130057000
C	-1.392014000	-2.260652000	0.155384000
C	-2.588825000	-1.495921000	0.244594000
C	0.870451000	-1.844527000	-0.876410000
C	1.318624000	-1.205367000	-2.038424000
C	1.559684000	-2.964923000	-0.404378000
C	2.457256000	-1.659437000	-2.693089000
H	0.769004000	-0.352167000	-2.425783000
C	2.692078000	-3.422254000	-1.067870000
H	1.223585000	-3.451312000	0.506685000
C	3.150665000	-2.766634000	-2.208201000
H	2.799274000	-1.152425000	-3.590207000
H	3.228074000	-4.283781000	-0.681587000
H	4.041003000	-3.119184000	-2.719342000
C	2.158486000	-0.049311000	0.854908000
C	1.700185000	-0.720762000	1.994417000
C	3.452233000	-0.295351000	0.388950000
C	2.512830000	-1.647104000	2.637086000
H	0.702179000	-0.511027000	2.369988000
C	4.263979000	-1.220704000	1.036471000
H	3.812637000	0.222104000	-0.494935000
C	3.796004000	-1.902392000	2.156700000
H	2.147438000	-2.163841000	3.519389000
H	5.263322000	-1.412781000	0.658742000

H	4.431819000	-2.624320000	2.659920000
H	-1.340501000	-3.338715000	0.214016000
C	-3.289003000	0.694455000	-0.875303000
H	-4.039118000	1.142009000	-0.211571000
H	-2.745505000	1.508498000	-1.353097000
C	-3.917935000	-2.114262000	0.437945000
O	-4.136367000	-3.277690000	0.230080000
O	-4.937415000	-1.286136000	0.818000000
C	-4.756999000	-0.459802000	1.961558000
H	-3.810465000	0.086933000	1.930359000
H	-5.590962000	0.242678000	1.965338000
H	-4.794133000	-1.066733000	2.871724000
H	-2.754307000	4.750643000	0.208710000
C	-3.998457000	-0.077460000	-1.998414000
H	-4.674753000	-0.838536000	-1.607068000
H	-4.588033000	0.618049000	-2.603197000
H	-3.264023000	-0.561779000	-2.647732000

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TS5, *E*(SCRF) = -1853.71210094 a.u., IF = *i*24.0576 cm^{-1}

C	-1.131175000	2.687611000	-0.331614000
C	-2.171351000	0.864383000	-1.456760000
C	-3.244720000	1.641848000	-1.741701000
C	-3.338176000	2.970829000	-1.232926000
C	-2.270108000	3.495325000	-0.571395000
C	0.157037000	2.988095000	0.079026000
C	0.928497000	1.792009000	0.052435000
C	0.053878000	0.742749000	-0.242951000
H	-2.021505000	-0.099482000	-1.908326000
H	-4.218031000	3.571185000	-1.433495000
H	-2.229960000	4.529437000	-0.246827000
N	-1.169969000	1.319190000	-0.610177000
C	0.614538000	4.300090000	0.370557000
N	0.960324000	5.379049000	0.616705000
C	2.404322000	1.858366000	0.032883000
C	3.091155000	1.319091000	-1.060050000
C	3.118770000	2.537181000	1.023042000
C	4.475552000	1.421925000	-1.139918000
H	2.531851000	0.809958000	-1.840555000
C	4.503686000	2.639571000	0.940635000
H	2.588292000	2.972657000	1.865072000
C	5.185848000	2.077055000	-0.135693000
H	4.999346000	0.994517000	-1.989212000
H	5.050428000	3.162038000	1.719117000
H	6.266451000	2.158337000	-0.197471000
N	0.234596000	-0.667257000	-0.103194000
C	-0.647670000	-1.688010000	-0.546904000
C	1.456284000	-1.271971000	0.219051000
C	0.078374000	-2.837810000	-0.677234000
C	1.391659000	-2.583425000	-0.212474000

H	-0.318624000	-3.816875000	-0.906346000
C	-2.107023000	-1.697185000	-0.349049000
C	-2.677630000	-1.039605000	0.746236000
C	-2.928252000	-2.438087000	-1.207151000
C	-4.051128000	-1.099675000	0.938642000
H	-2.056866000	-0.476220000	1.435973000
C	-4.299169000	-2.497700000	-0.986678000
H	-2.485156000	-2.946893000	-2.058255000
C	-4.878099000	-1.819540000	0.083094000
H	-4.929327000	-3.069873000	-1.660168000
H	-5.947563000	-1.848148000	0.257718000
C	2.450811000	-0.729474000	1.205423000
H	3.397124000	-0.414754000	0.763647000
H	2.023603000	0.103192000	1.762887000
C	2.393654000	-3.652729000	-0.099912000
O	2.198593000	-4.795544000	-0.445709000
O	3.567632000	-3.232508000	0.410465000
C	4.563097000	-4.248079000	0.521274000
H	4.796474000	-4.660134000	-0.462788000
H	5.436355000	-3.760111000	0.951431000
H	4.214158000	-5.056334000	1.167491000
H	-4.005446000	1.241098000	-2.400495000
Cl	-4.753061000	-0.249696000	2.289116000
H	2.670021000	-1.538254000	1.904923000

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TS6, *E*(SCRF) = -1853.69386106 a.u., IF = *i*17.3059 cm^{-1}

C	0.206250000	3.231874000	0.299824000
C	2.490511000	2.602552000	0.038420000
C	2.878737000	3.883370000	0.252501000
C	1.923333000	4.883196000	0.607961000
C	0.600277000	4.561777000	0.589149000
C	-1.009134000	2.664136000	-0.044733000
C	-0.797744000	1.289311000	-0.347479000
C	0.535959000	1.006371000	-0.043917000
H	3.152271000	1.846131000	-0.345899000
H	2.247258000	5.896303000	0.815747000
H	-0.183073000	5.295861000	0.744241000
N	1.170574000	2.221455000	0.222815000
C	-2.221836000	3.394575000	-0.163364000
N	-3.196989000	4.016141000	-0.242093000
N	1.180708000	-0.256912000	0.093973000
C	0.532796000	-1.466527000	-0.245754000
C	2.547434000	-0.531699000	0.256521000
C	1.494050000	-2.407770000	-0.474551000
C	2.754365000	-1.829190000	-0.171280000
C	-0.857468000	-1.799580000	0.117165000
C	-1.361718000	-1.358535000	1.345795000
C	-1.610678000	-2.681559000	-0.659899000
C	-2.619003000	-1.778044000	1.754335000

H	-0.779149000	-0.693746000	1.975468000
C	-2.863319000	-3.099101000	-0.224962000
H	-1.220610000	-3.013622000	-1.616813000
C	-3.384209000	-2.646961000	0.984027000
H	-3.450270000	-3.772735000	-0.841186000
H	-4.364672000	-2.957108000	1.327470000
C	-1.792181000	0.535782000	-1.143151000
C	-1.412000000	0.047563000	-2.398671000
C	-3.125170000	0.428961000	-0.740962000
C	-2.345669000	-0.564524000	-3.226416000
H	-0.379229000	0.154561000	-2.719781000
C	-4.056985000	-0.185475000	-1.571829000
H	-3.427287000	0.814981000	0.228745000
C	-3.670497000	-0.686145000	-2.812448000
H	-2.040525000	-0.938703000	-4.198969000
H	-5.088555000	-0.272877000	-1.245405000
H	-4.401664000	-1.161364000	-3.459131000
H	1.320842000	-3.458661000	-0.658822000
C	3.466619000	0.197098000	1.210134000
H	4.321726000	0.692519000	0.742232000
H	2.921279000	0.932172000	1.802514000
C	3.990047000	-2.630355000	-0.057494000
O	3.988373000	-3.830517000	0.003402000
O	5.164144000	-1.935412000	0.048172000
C	5.503304000	-1.048025000	-1.008876000
H	4.646871000	-0.444689000	-1.327317000
H	6.294509000	-0.399107000	-0.631295000
H	5.880564000	-1.615789000	-1.865191000
H	3.876865000	-0.547156000	1.895929000
H	3.919257000	4.140731000	0.095716000
Cl	-3.254295000	-1.194912000	3.272118000

3u, *E*(SCRF) = -1853.76877123 a.u.

C	-0.694022000	-2.769449000	-0.702757000
C	1.451785000	-2.458789000	0.377241000
C	1.602125000	-3.808568000	0.441330000
C	0.614036000	-4.690764000	-0.084535000
C	-0.517702000	-4.170784000	-0.644110000
C	-1.708621000	-1.928854000	-1.170353000
C	-1.293184000	-0.583114000	-0.978786000
C	-0.039395000	-0.633799000	-0.396545000
H	2.162478000	-1.741433000	0.768847000
H	0.775558000	-5.760500000	-0.025066000
H	-1.300709000	-4.805161000	-1.044863000
N	0.319385000	-1.952944000	-0.212403000
C	-2.914404000	-2.397117000	-1.757462000
N	-3.893744000	-2.806564000	-2.223440000
C	-2.056783000	0.648685000	-1.226346000
C	-3.427358000	0.685496000	-0.951371000

C	-1.409384000	1.813197000	-1.657225000
C	-4.138100000	1.871526000	-1.101254000
H	-3.929575000	-0.208427000	-0.593913000
C	-2.123805000	2.996190000	-1.804008000
H	-0.344207000	1.789890000	-1.874802000
C	-3.488626000	3.028739000	-1.522981000
H	-5.199972000	1.892292000	-0.877498000
H	-1.613482000	3.894216000	-2.137885000
H	-4.044359000	3.954596000	-1.635303000
N	0.755887000	0.402987000	0.104881000
C	0.314727000	1.342780000	1.046615000
C	1.959292000	0.811174000	-0.444746000
C	1.261294000	2.326265000	1.103849000
C	2.298728000	1.993053000	0.184179000
H	1.252915000	3.191198000	1.751577000
C	-0.983548000	1.222853000	1.724500000
C	-1.436612000	0.005169000	2.245496000
C	-1.806701000	2.350311000	1.816055000
C	-2.695295000	-0.084816000	2.829066000
H	-0.797591000	-0.873412000	2.197926000
C	-3.059483000	2.261277000	2.412639000
H	-1.469721000	3.285691000	1.379012000
C	-3.510633000	1.042215000	2.912665000
H	-3.037833000	-1.035626000	3.225418000
H	-3.692837000	3.141308000	2.466768000
H	-4.494148000	0.969006000	3.366233000
C	2.625349000	0.026659000	-1.528879000
H	3.122308000	0.703489000	-2.223432000
H	3.392721000	-0.648145000	-1.132033000
H	1.892224000	-0.572193000	-2.077766000
C	3.500924000	2.815640000	0.002960000
O	3.695045000	3.871623000	0.558181000
O	4.387704000	2.265532000	-0.854916000
C	5.569921000	3.037005000	-1.057710000
H	6.102218000	3.173042000	-0.113908000
H	6.176517000	2.470592000	-1.762922000
H	5.320537000	4.019060000	-1.465363000
Cl	3.025125000	-4.467891000	1.182025000

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3ab, *E*(SCRF) = -1433.47496555 a.u.

C	1.922176000	2.519517000	-0.331424000
C	0.013618000	3.045239000	1.057648000
C	0.523723000	4.281550000	1.301657000
C	1.753992000	4.681625000	0.701498000
C	2.443916000	3.813091000	-0.096550000
C	2.368176000	1.396960000	-1.036572000
C	1.381775000	0.378721000	-0.918880000
C	0.358238000	0.905558000	-0.153763000
H	-0.902120000	2.653943000	1.483986000

H	2.143882000	5.674903000	0.892947000
H	3.392080000	4.073924000	-0.553955000
N	0.691543000	2.189863000	0.224289000
C	3.593881000	1.349618000	-1.752224000
N	4.604552000	1.333655000	-2.320353000
C	1.453927000	-1.016517000	-1.378120000
C	2.670342000	-1.704783000	-1.318956000
C	0.299846000	-1.696856000	-1.786144000
C	2.728987000	-3.052523000	-1.656314000
H	3.564442000	-1.189938000	-0.980677000
C	0.363274000	-3.044356000	-2.121074000
H	-0.649268000	-1.168874000	-1.839342000
C	1.576825000	-3.726312000	-2.053419000
H	3.676560000	-3.578774000	-1.598700000
H	-0.537649000	-3.562540000	-2.434590000
H	1.623716000	-4.779649000	-2.312259000
N	-0.789779000	0.276534000	0.348497000
C	-0.742764000	-0.869424000	1.153633000
C	-2.074274000	0.461583000	-0.137971000
C	-2.008333000	-1.380659000	1.201847000
C	-2.846960000	-0.550853000	0.401526000
H	-2.333016000	-2.248865000	1.757304000
C	0.519194000	-1.386132000	1.701144000
C	1.472710000	-0.545180000	2.286496000
C	0.794364000	-2.753412000	1.590222000
C	2.681836000	-1.061309000	2.738950000
H	1.263607000	0.516806000	2.392029000
C	1.999187000	-3.269398000	2.054439000
H	0.071515000	-3.397934000	1.098584000
C	2.948558000	-2.424154000	2.623556000
H	3.415622000	-0.398573000	3.187024000
H	2.204916000	-4.330332000	1.951399000
H	3.894841000	-2.824176000	2.974229000
C	-4.273818000	-0.831318000	0.202216000
O	-4.869172000	-1.745279000	0.723316000
O	-4.869101000	0.035255000	-0.647907000
C	-6.253906000	-0.216674000	-0.877046000
H	-6.811483000	-0.165712000	0.060596000
H	-6.586243000	0.559224000	-1.565350000
H	-6.393808000	-1.206923000	-1.315791000
H	-0.013930000	4.951107000	1.961700000
C	-2.410169000	1.565684000	-1.096706000
H	-2.980213000	1.130661000	-1.922367000
H	-1.481028000	1.961584000	-1.522276000
C	-3.235583000	2.703335000	-0.480741000
H	-2.682798000	3.226648000	0.303829000
H	-3.494353000	3.437061000	-1.249364000
H	-4.159741000	2.310525000	-0.052841000

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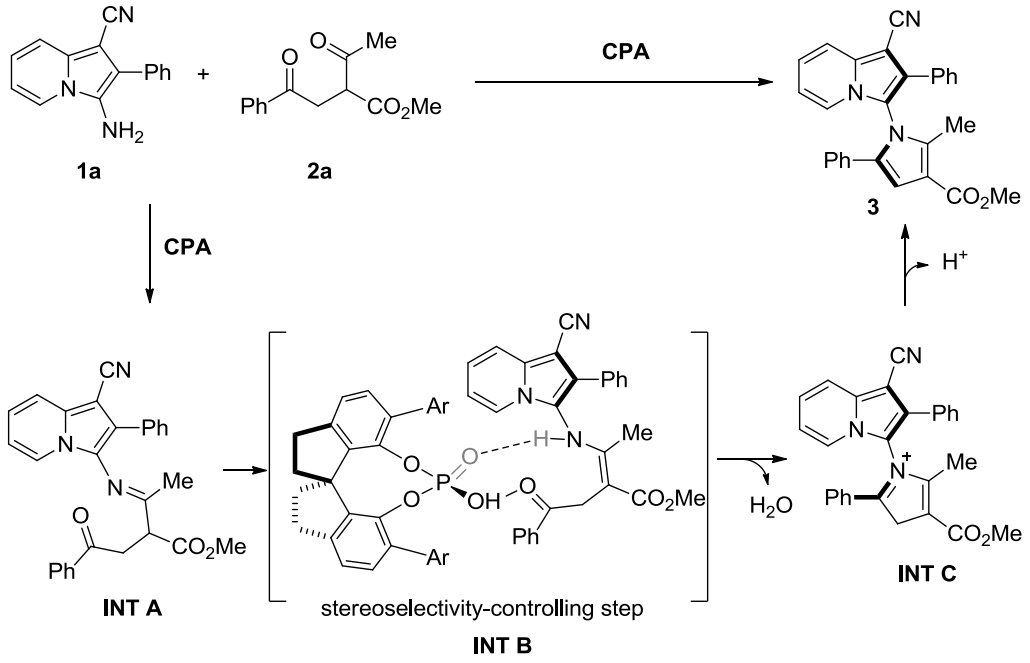
3ah, *E*(SCRF) = -1853.77514137 a.u.

C	-1.464054000	2.640412000	0.646955000
C	0.401381000	3.125210000	-0.815608000
C	-0.086982000	4.375118000	-1.031624000
C	-1.284713000	4.801063000	-0.385513000
C	-1.962955000	3.946934000	0.437276000
C	-1.903699000	1.532166000	1.378527000
C	-0.950776000	0.488986000	1.219097000
C	0.043428000	0.983559000	0.395736000
H	1.296398000	2.720873000	-1.273250000
H	-1.657496000	5.804149000	-0.558725000
H	-2.884702000	4.229028000	0.934225000
N	-0.271075000	2.277725000	0.032131000
C	-3.088401000	1.519257000	2.161799000
N	-4.062996000	1.530028000	2.789647000
C	-1.028790000	-0.896084000	1.706888000
C	-2.258543000	-1.562650000	1.715939000
C	0.130171000	-1.586675000	2.082601000
C	-2.325389000	-2.900588000	2.090221000
H	-3.158055000	-1.038456000	1.406514000
C	0.058406000	-2.924105000	2.453698000
H	1.088560000	-1.072952000	2.081891000
C	-1.168770000	-3.585076000	2.454766000
H	-3.283633000	-3.410448000	2.087686000
H	0.962468000	-3.450725000	2.743250000
H	-1.222794000	-4.630345000	2.743223000
N	1.140272000	0.323704000	-0.174436000
C	1.042562000	-0.846760000	-0.936984000
C	2.463231000	0.570784000	0.142866000
C	2.312765000	-1.317096000	-1.118642000
C	3.207898000	-0.426539000	-0.458058000
H	2.603002000	-2.189221000	-1.686971000
C	-0.250711000	-1.416477000	-1.337470000
C	-1.286205000	-0.608752000	-1.820145000
C	-0.464088000	-2.790894000	-1.190205000
C	-2.514013000	-1.181841000	-2.120677000
H	-1.142166000	0.458070000	-1.962328000
C	-1.695445000	-3.348376000	-1.514440000
H	0.329387000	-3.407110000	-0.779480000
C	-2.736643000	-2.547139000	-1.974164000
H	-1.856950000	-4.413766000	-1.385353000
H	-3.707704000	-2.965690000	-2.213955000
C	4.664685000	-0.605537000	-0.469390000
O	5.232408000	-1.544083000	-0.977376000
O	5.321574000	0.400408000	0.148114000
C	6.740653000	0.258524000	0.161041000
H	7.129049000	0.222725000	-0.858992000
H	7.121497000	1.132827000	0.687003000
H	7.028492000	-0.658849000	0.679095000

H	0.444598000	5.037651000	-1.703514000
C	2.850378000	1.723760000	1.011351000
H	3.703770000	1.450340000	1.631310000
H	2.016900000	2.014869000	1.657661000
H	3.147104000	2.597547000	0.419883000
Cl	-3.806193000	-0.160495000	-2.697736000

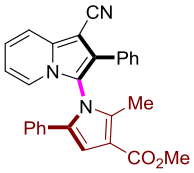
11. Proposed reaction pathway

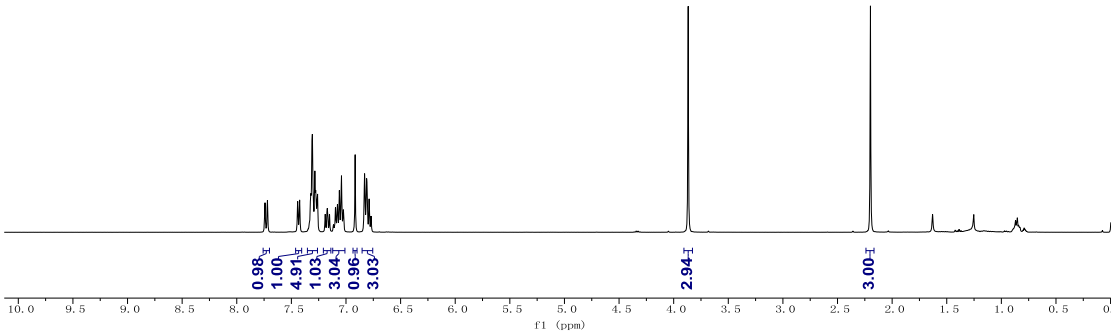
On the basis of previous related studies, a proposed mechanism of this transformation was illustrated. The condensation of 3-aminoindolizine **1a** with 1,4-diketone **2a** in the presence of CPA catalyst gave rise to iminoketone intermediate **INT A**, which subsequent tautomerized into its emamine type **INT B**. Dual H-bond activation of CPA with **INT B**, which was concerned as the enantio-determining step, resulted in the dehydrative cyclization and the generation of **INT C**. Finally, deprotonation and aromation of **INT C** promoted the formation of the desired product **3**.



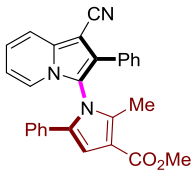
12. Copies of NMR spectra and HPLC measurements of the products

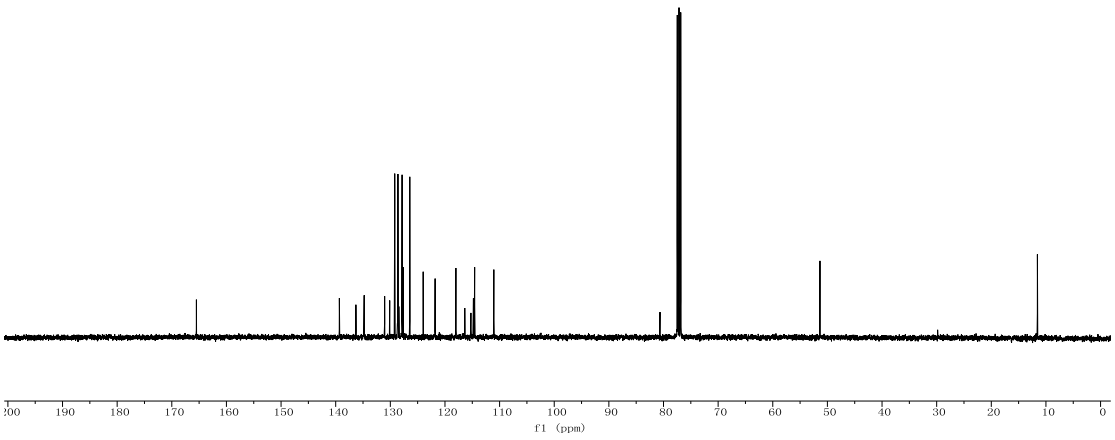
^{1}H NMR of **3a** (400 MHz, $CDCl_3$)



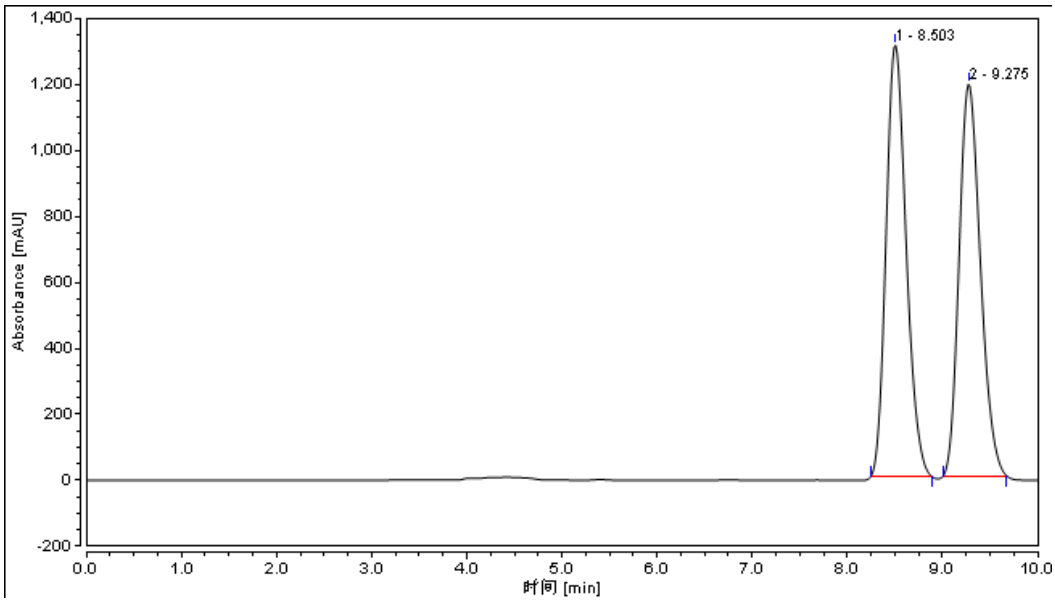


^{13}C NMR of **3a** (100 MHz, $CDCl_3$)



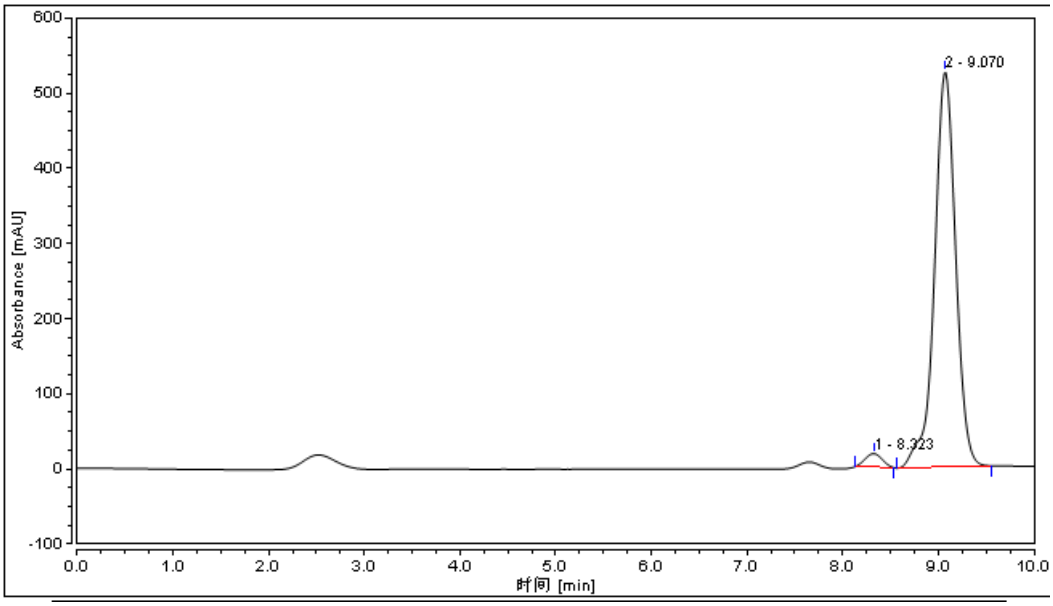


HPLC analysis: rac-**3a**



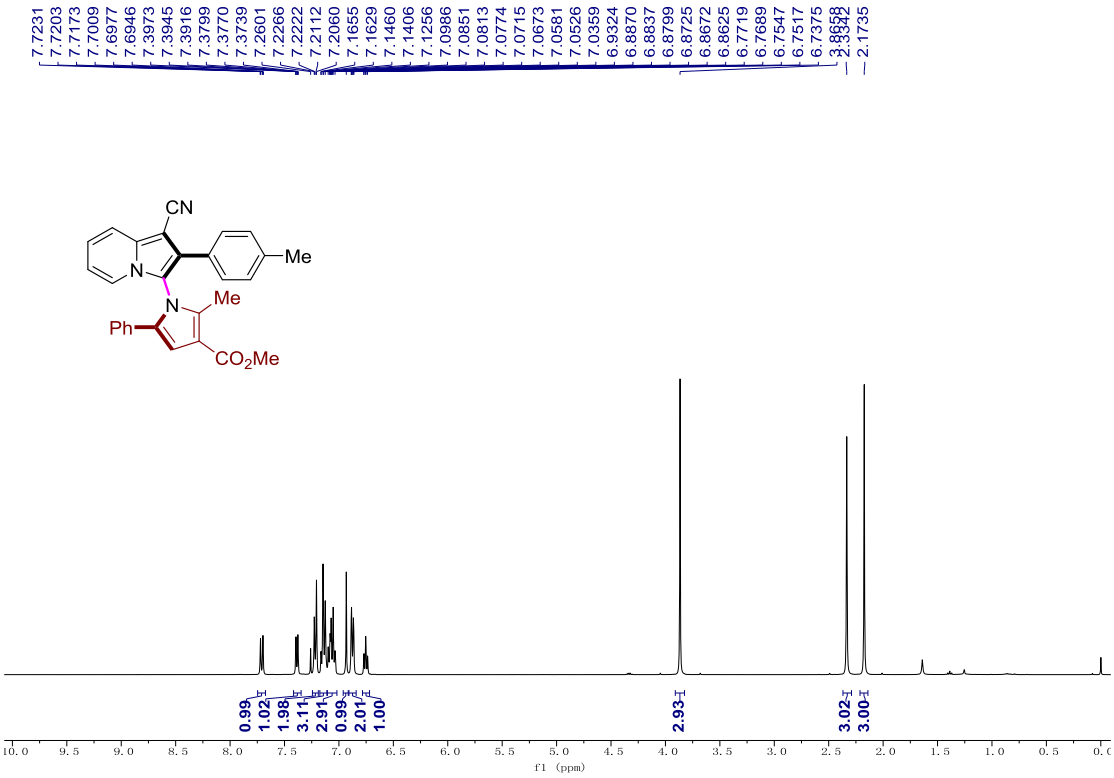
Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	8.503	319.500	1310.031	50.90
2	9.275	308.257	1188.979	49.10

Enantioenriched **3a**

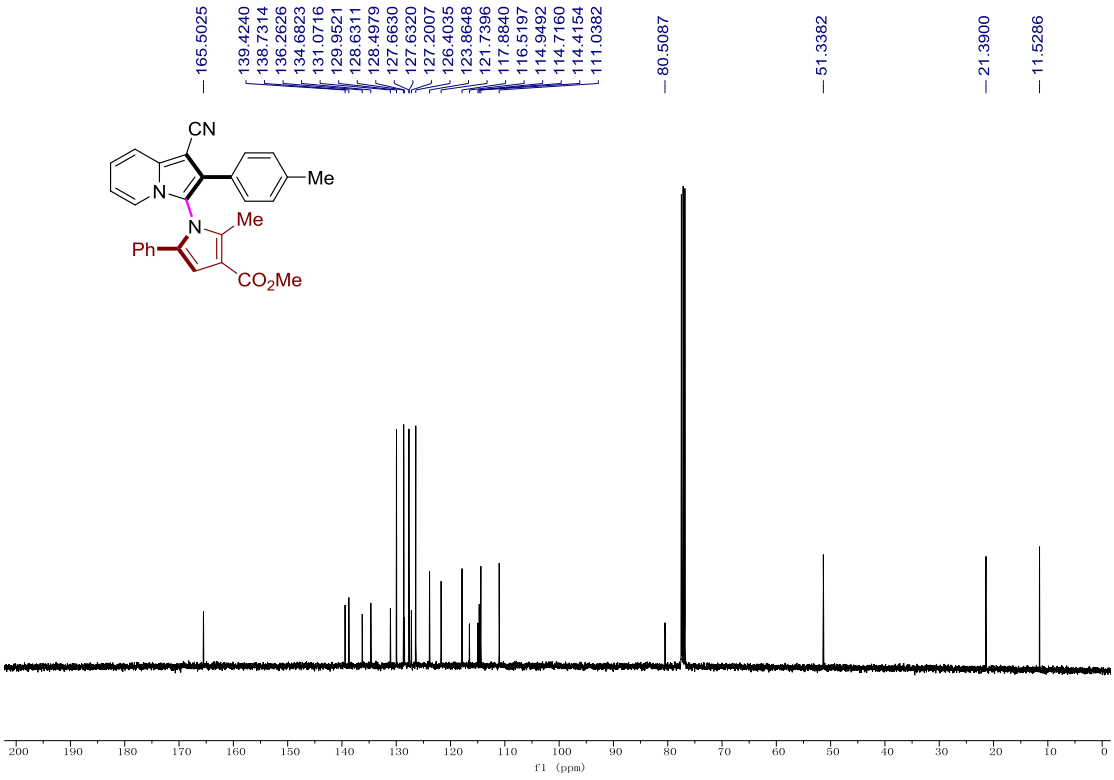


Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	8.320	3.436	16.978	2.59
2	9.070	129.242	505.340	97.41

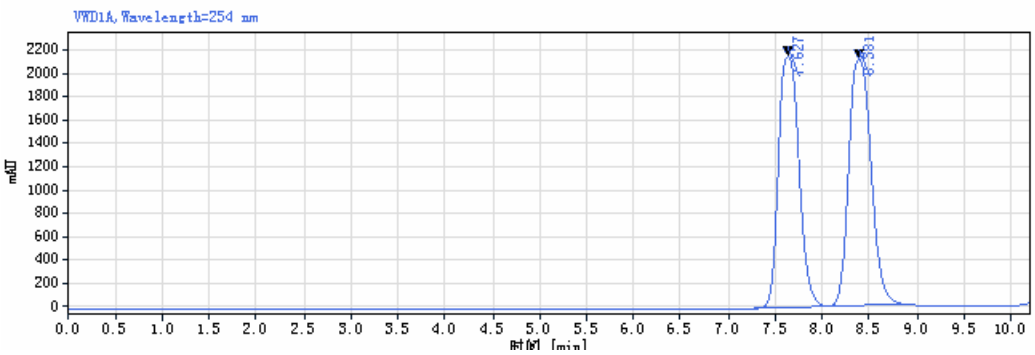
^{1}H NMR of **3b** (400 MHz, $CDCl_3$)



^{13}C NMR of **3b** (100 MHz, $CDCl_3$)

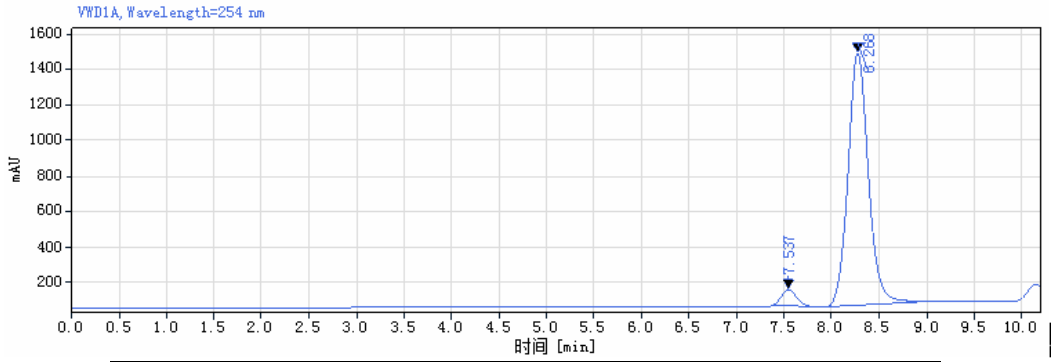


HPLC analysis: rac-**3b**



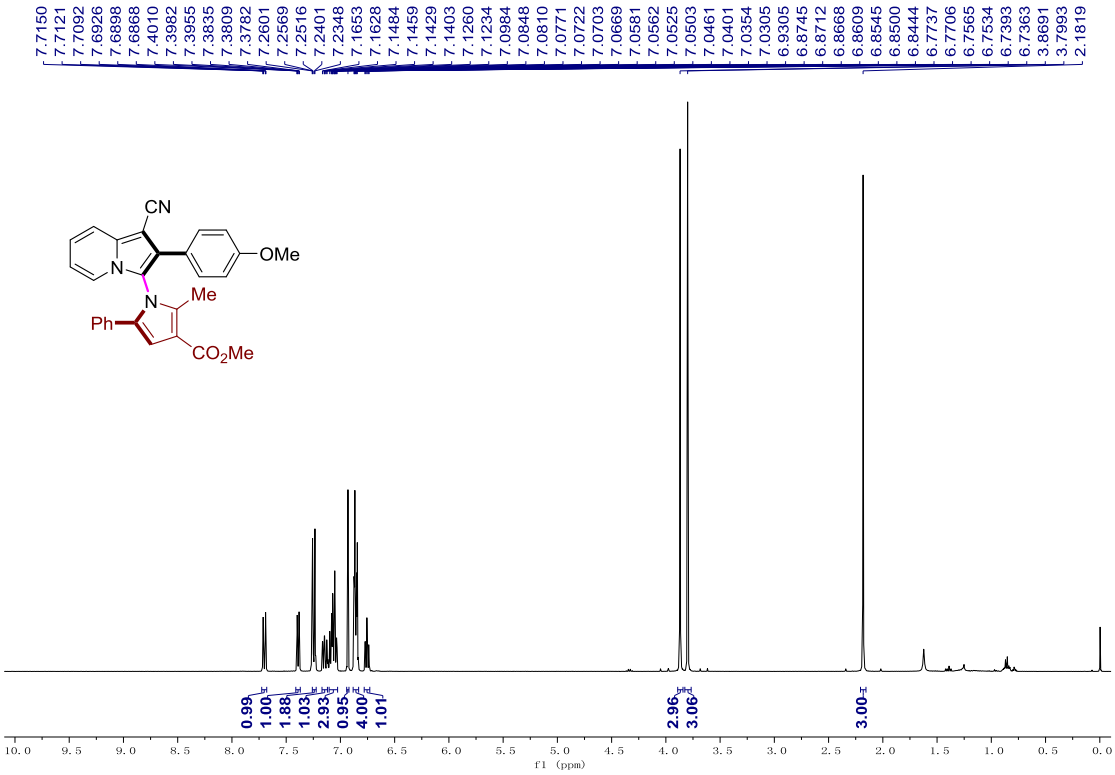
Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	7.627	32450.56	2145.33	48.39
2	8.381	34609.57	2106	51.61

Enantioenriched **3b**

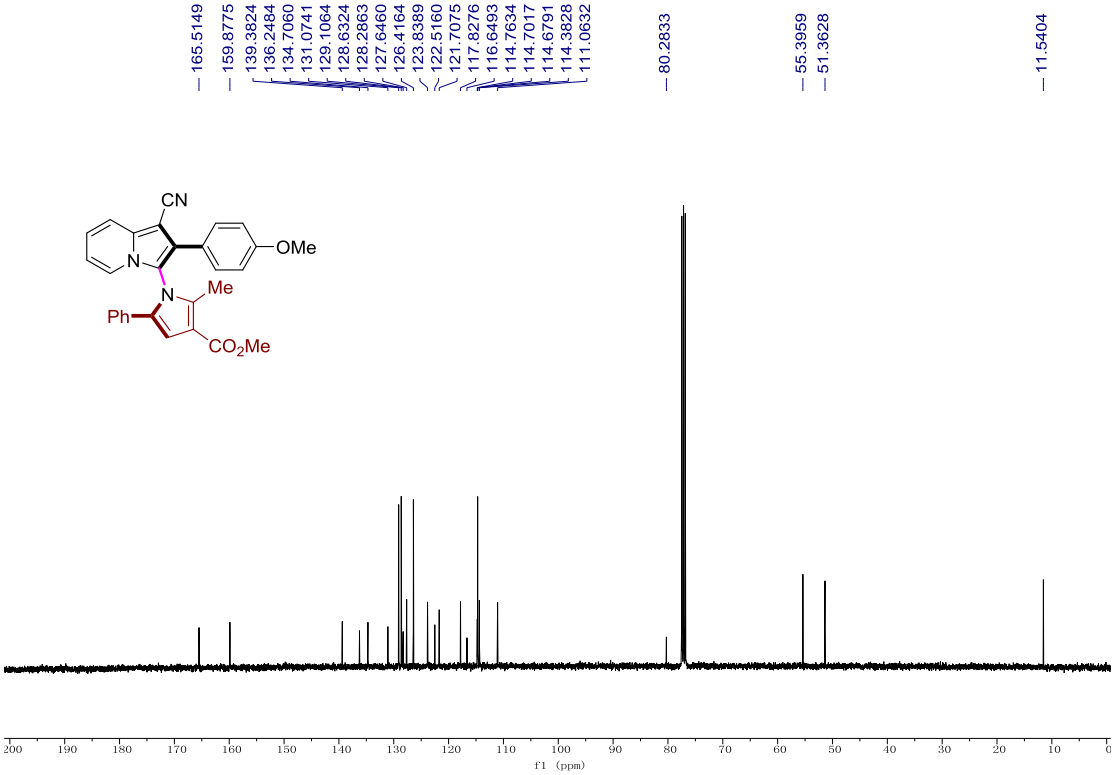


Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	7.537	975.87	87.95	4.43
2	8.268	21075	1415.45	95.57

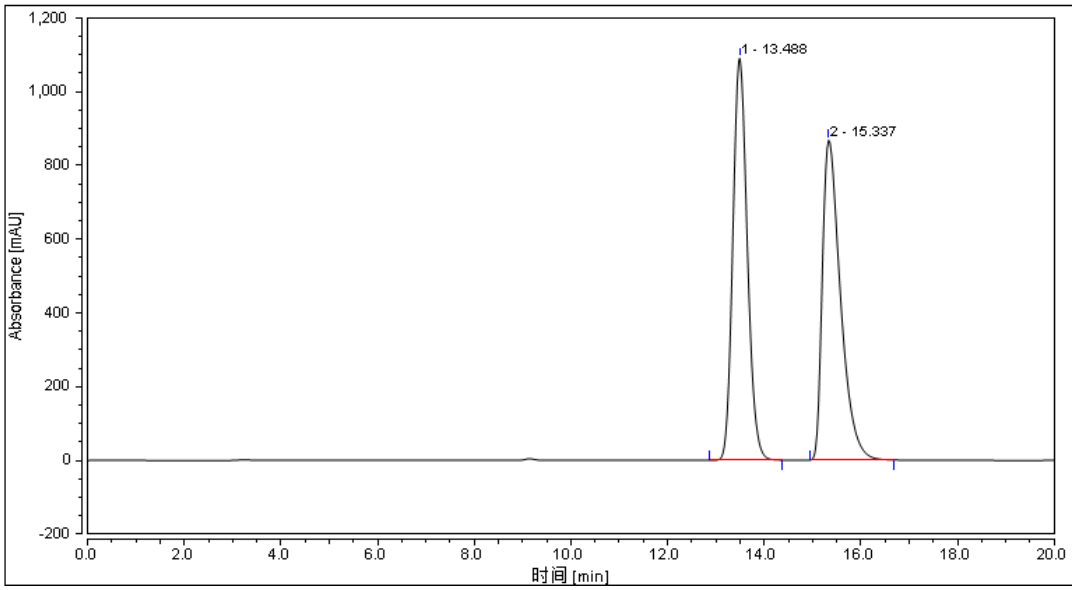
^{1}H NMR of **3c** (400 MHz, $CDCl_3$)



^{13}C NMR of **3c** (100 MHz, $CDCl_3$)

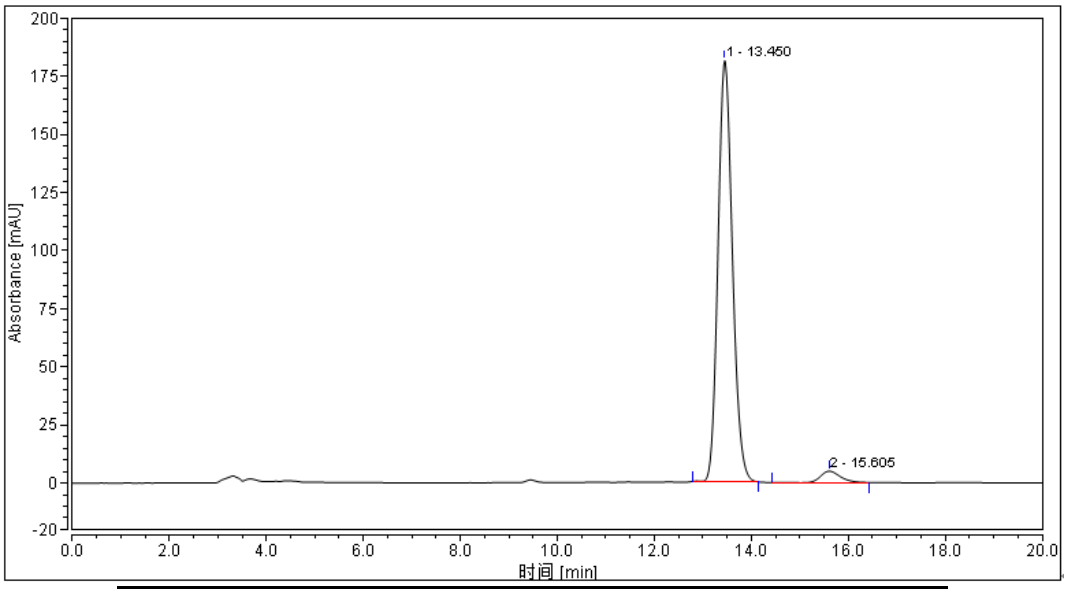


HPLC analysis: rac-**3c**



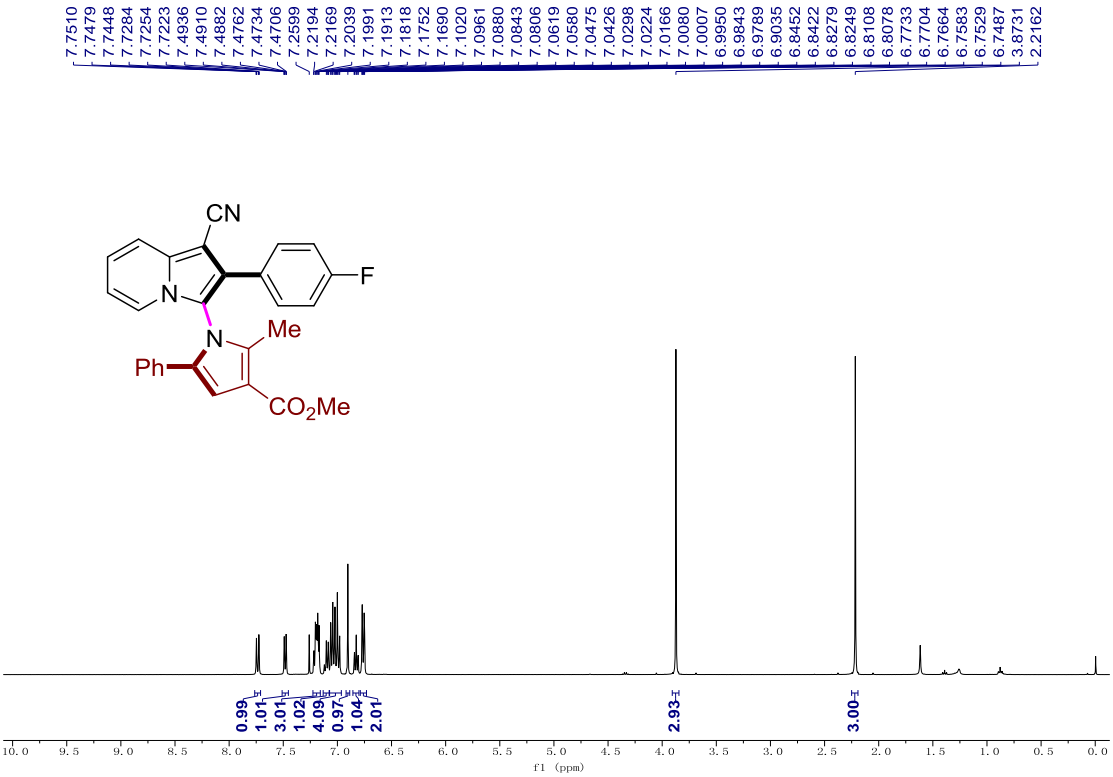
Peak	RetTime	Area	Height	Area
	min	mAU*min	mAU	%
1	13.488	377.253	1090.015	49.93
2	15.337	378.250	868.920	50.07

Enantioenriched **3c**

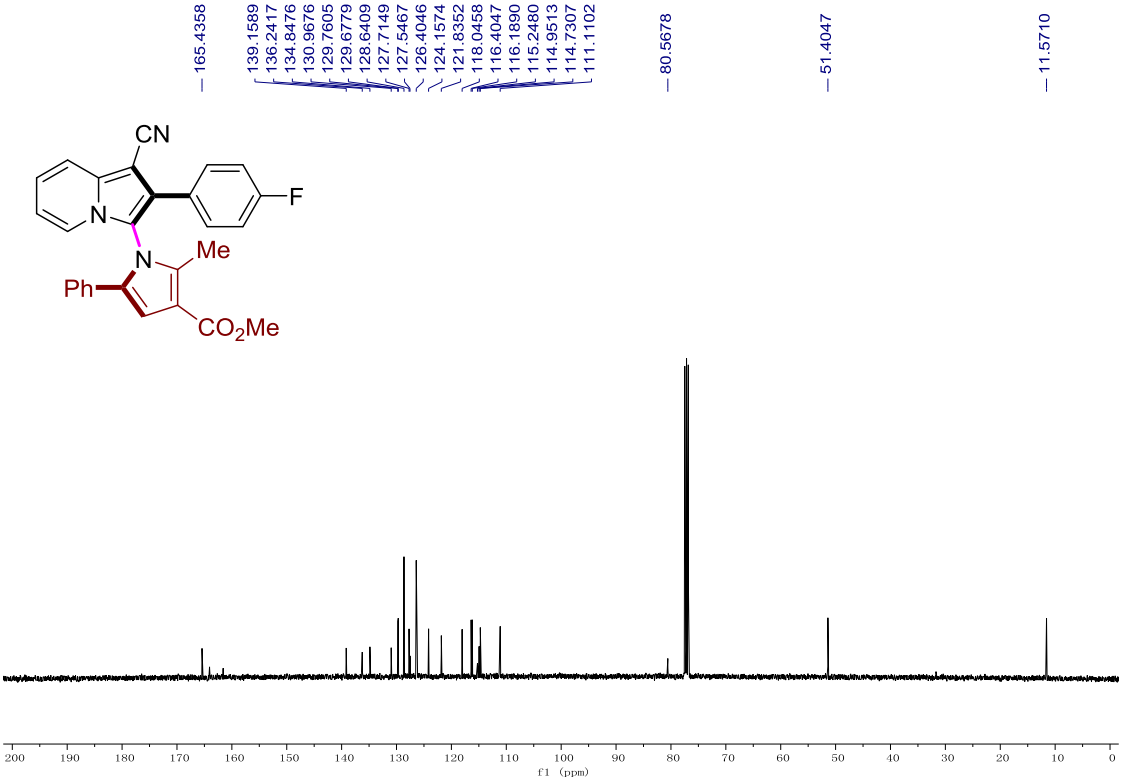


Peak	RetTime	Area	Height	Area
	min	mAU*min	mAU	%
1	13.450	62.347	181.160	96.51
2	15.605	2.255	4.919	3.49

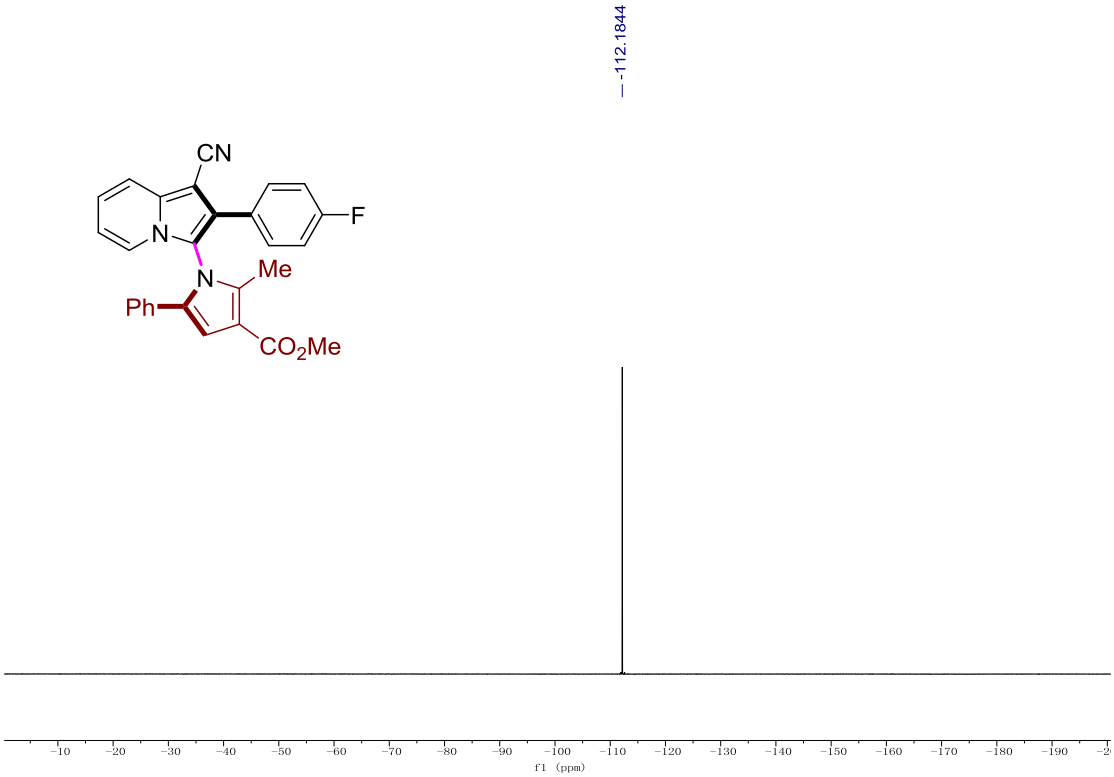
^{1}H NMR of **3d** (400 MHz, $CDCl_3$)



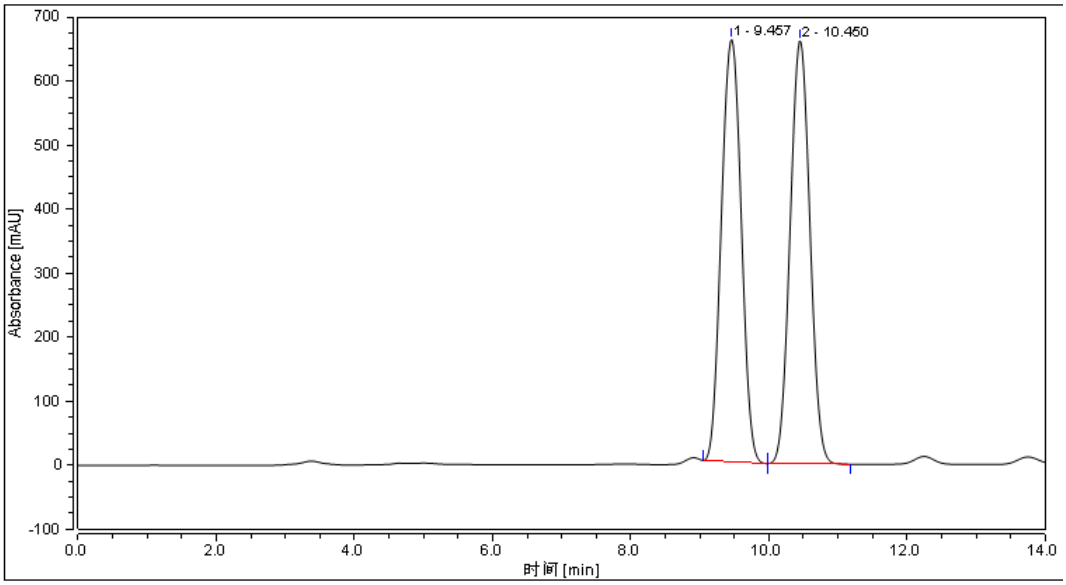
^{13}C NMR of **3d** (100 MHz, $CDCl_3$)



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

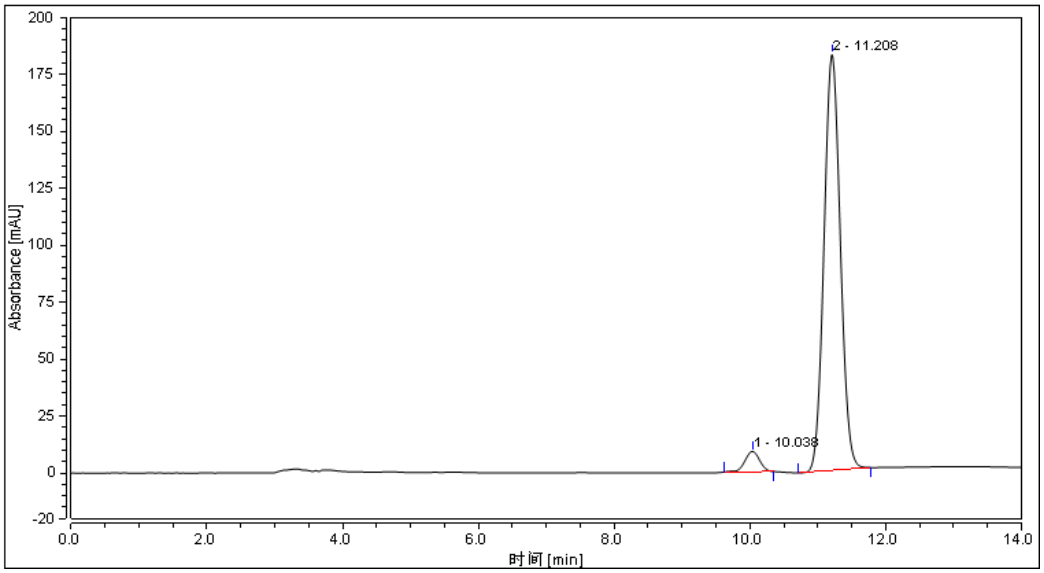


HPLC analysis:rac-**3d**



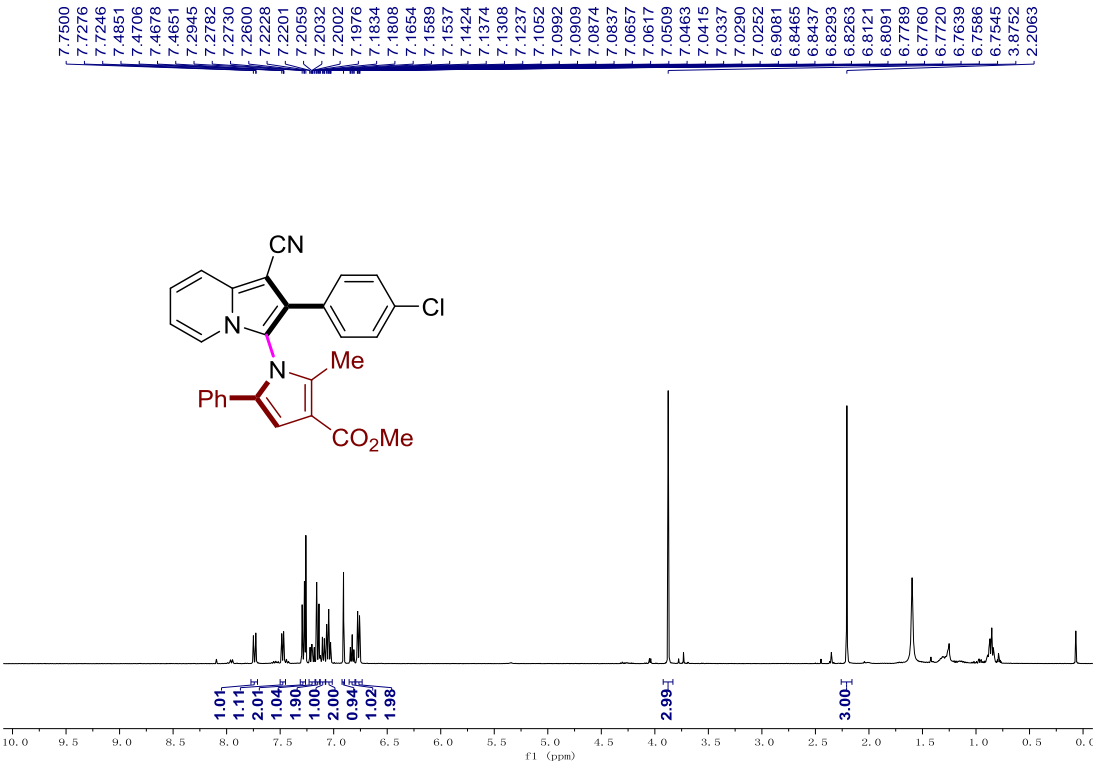
Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	9.457	219.440	659.988	50.02
2	10.450	219.264	661.486	49.98

Enantioenriched **3d**

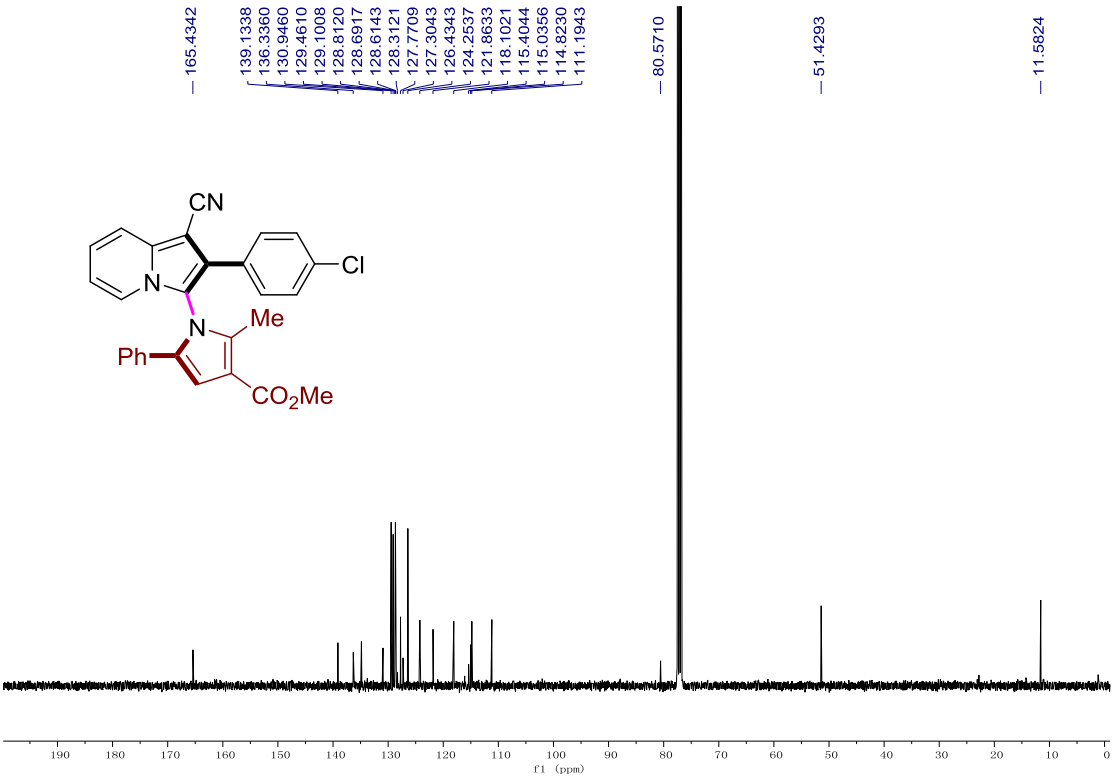


Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	10.038	2.224	8.935	4.20
2	11.208	50.688	182.511	95.80

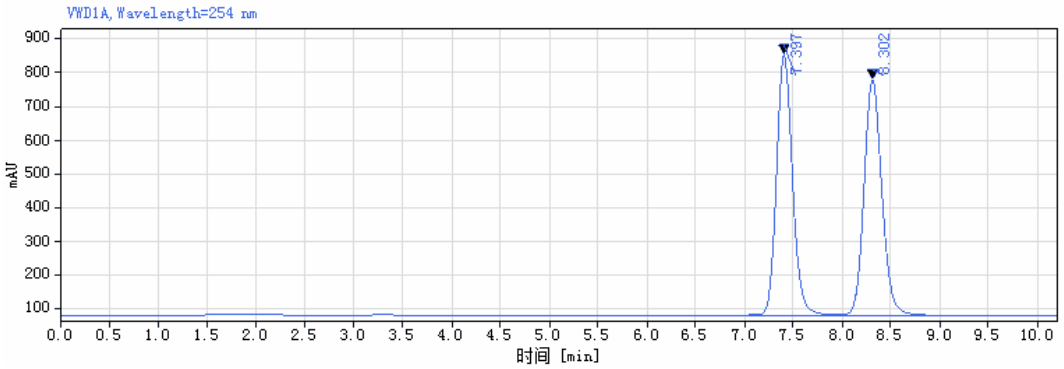
^{1}H NMR of **3e** (400 MHz, $CDCl_3$)



^{13}C NMR of **3e** (100 MHz, $CDCl_3$)

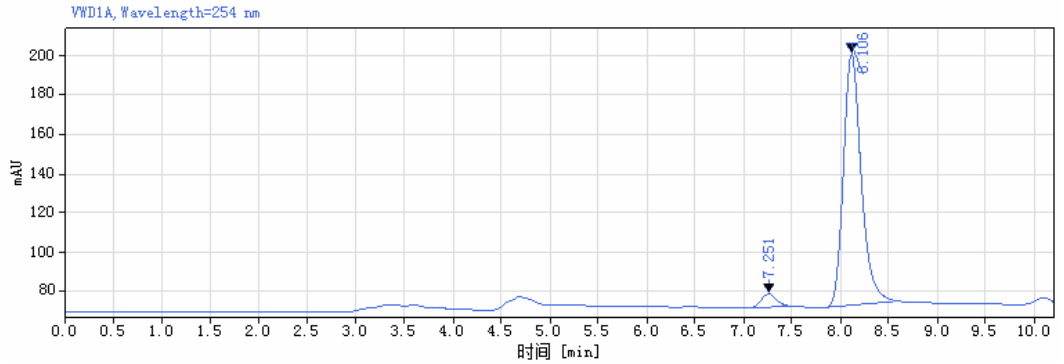


HPLC analysis: rac-**3e**



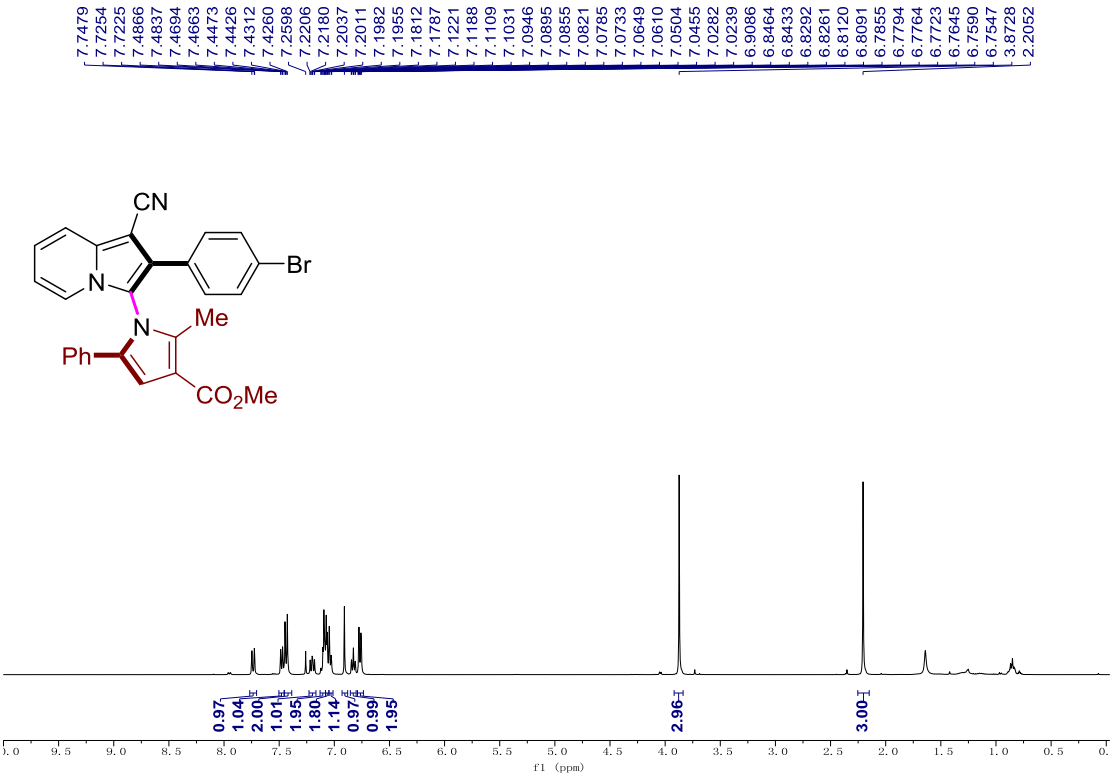
Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	7.397	8884.19	774.17	49.76
2	8.302	8968.13	699.31	50.24

Enantioenriched **3e**

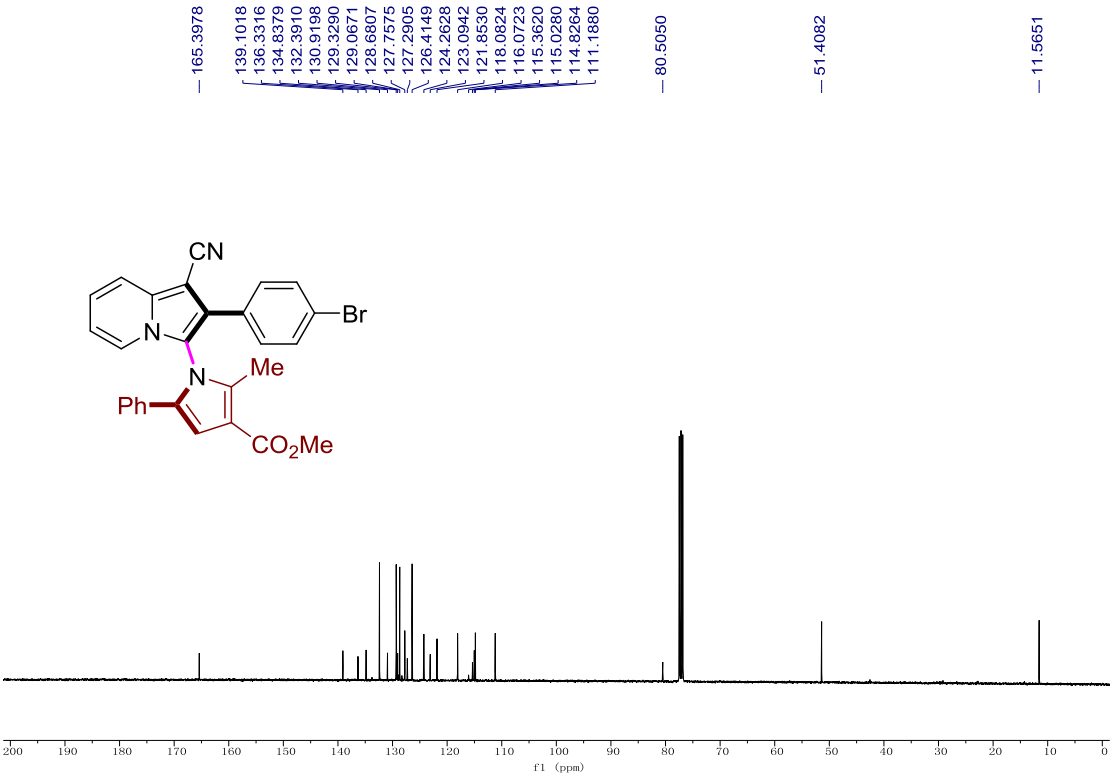


Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	7.251	73.39	6.67	4.29
2	8.106	1636.57	127.97	95.71

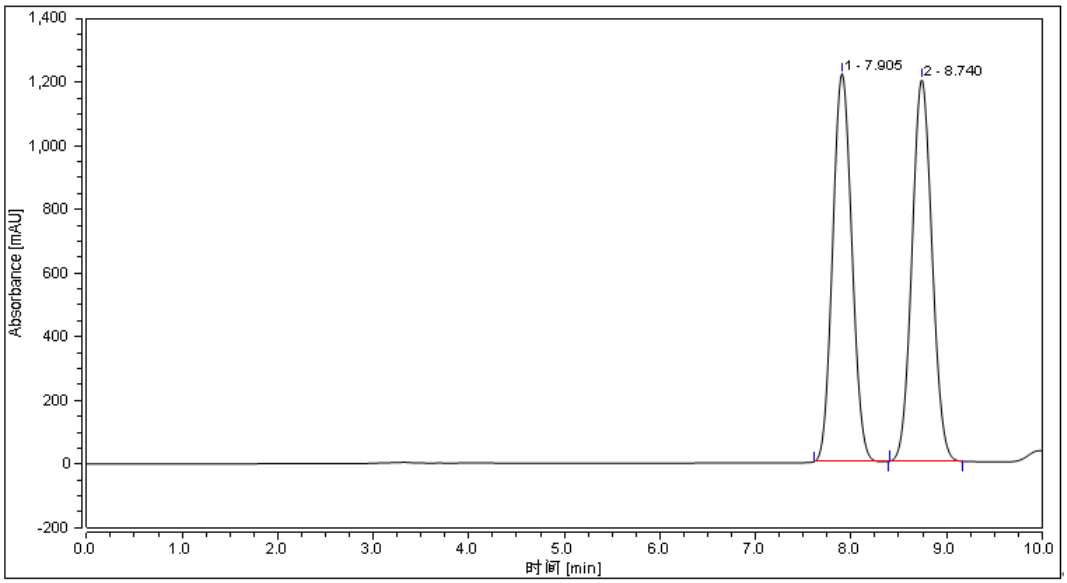
^{1}H NMR of **3f** (400 MHz, $CDCl_3$)



^{13}C NMR of **3f** (100 MHz, $CDCl_3$)

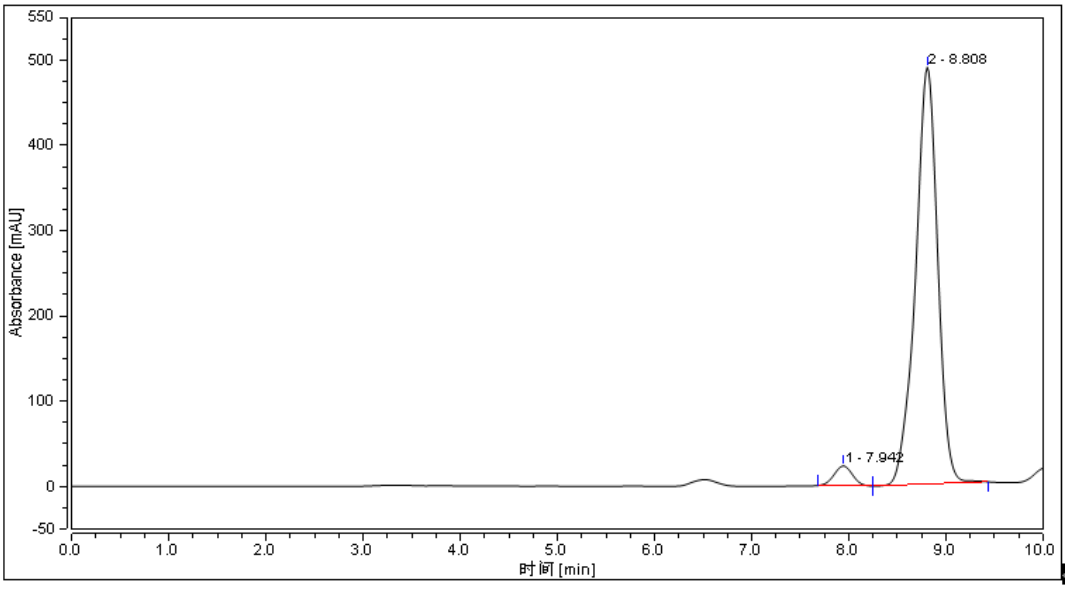


HPLC analysis: rac-**3f**



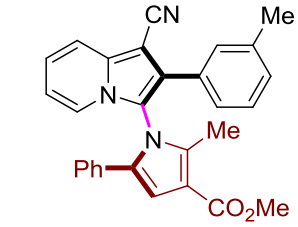
Peak	RetTime	Area	Height	Area
	min	mAU*min	mAU	%
1	7.905	282.902	1218.868	49.25
2	8.740	291.490	1198.792	50.75

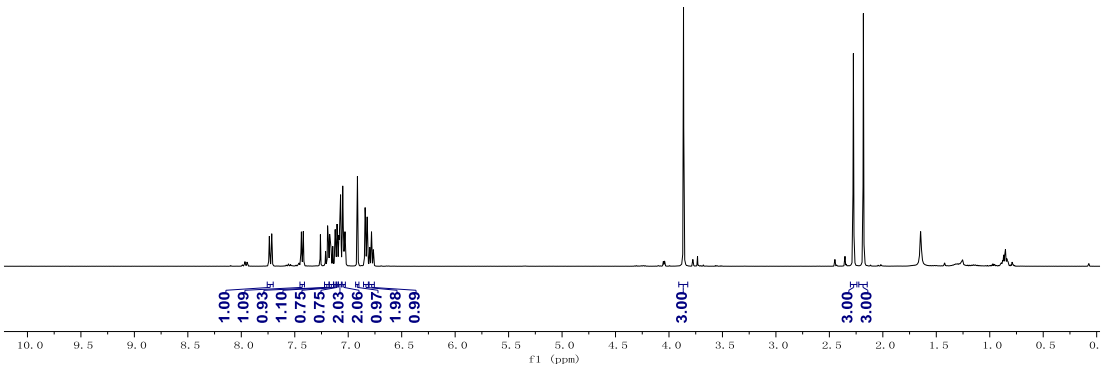
Enantioenriched **3f**



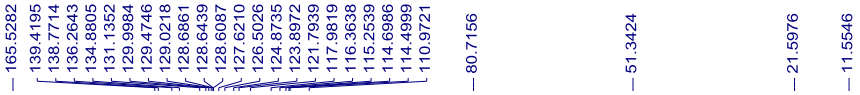
Peak	RetTime	Area	Height	Area
	min	mAU*min	mAU	%
1	7.942	5.103	23.219	3.80
2	8.808	129.361	489.101	96.20

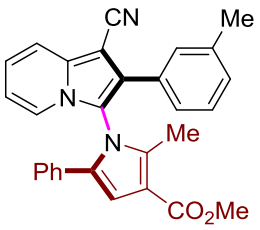
^{1}H NMR of **3g** (400 MHz, $CDCl_3$)

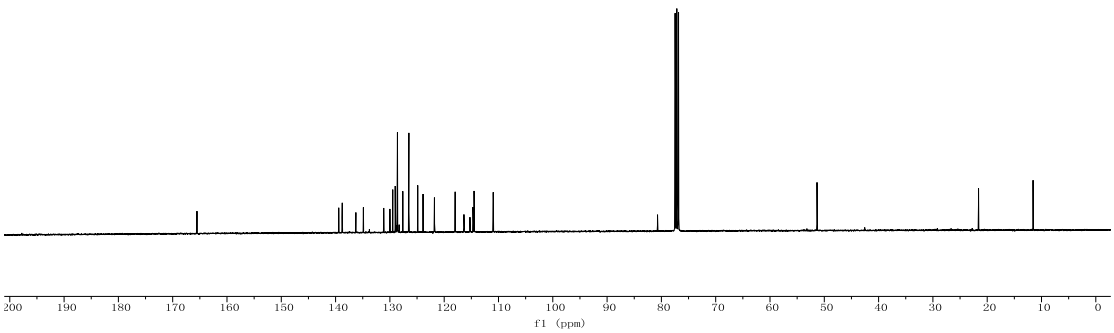




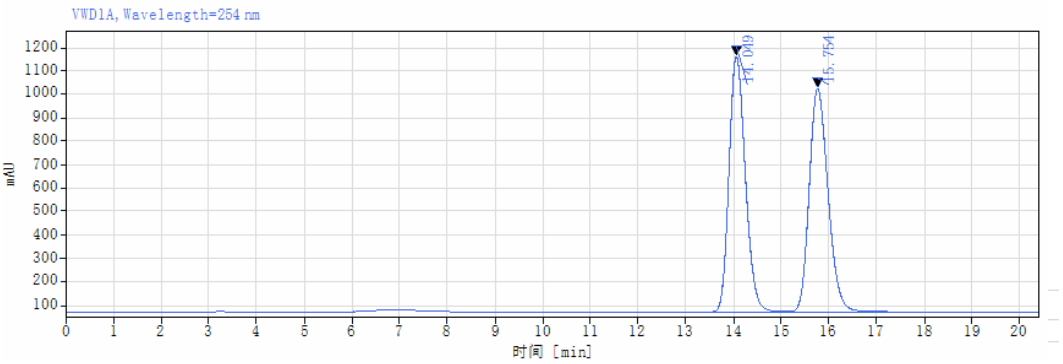
^{13}C NMR of **3g** (100 MHz, $CDCl_3$)





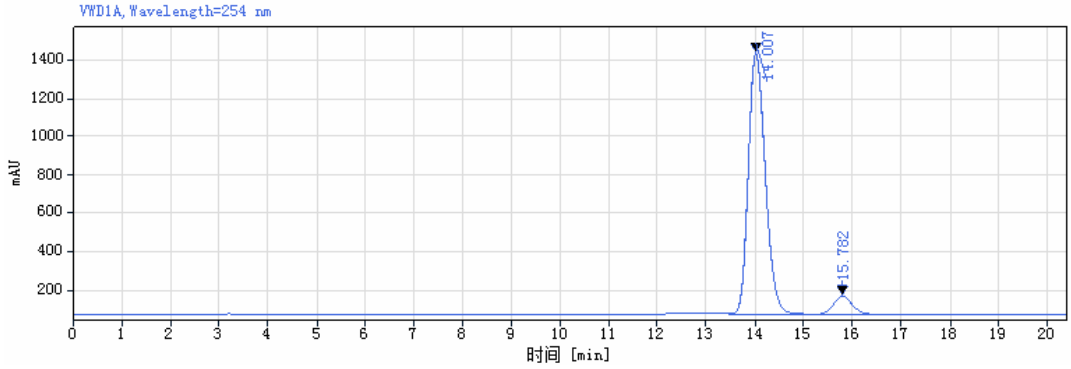


HPLC analysis: rac-**3g**



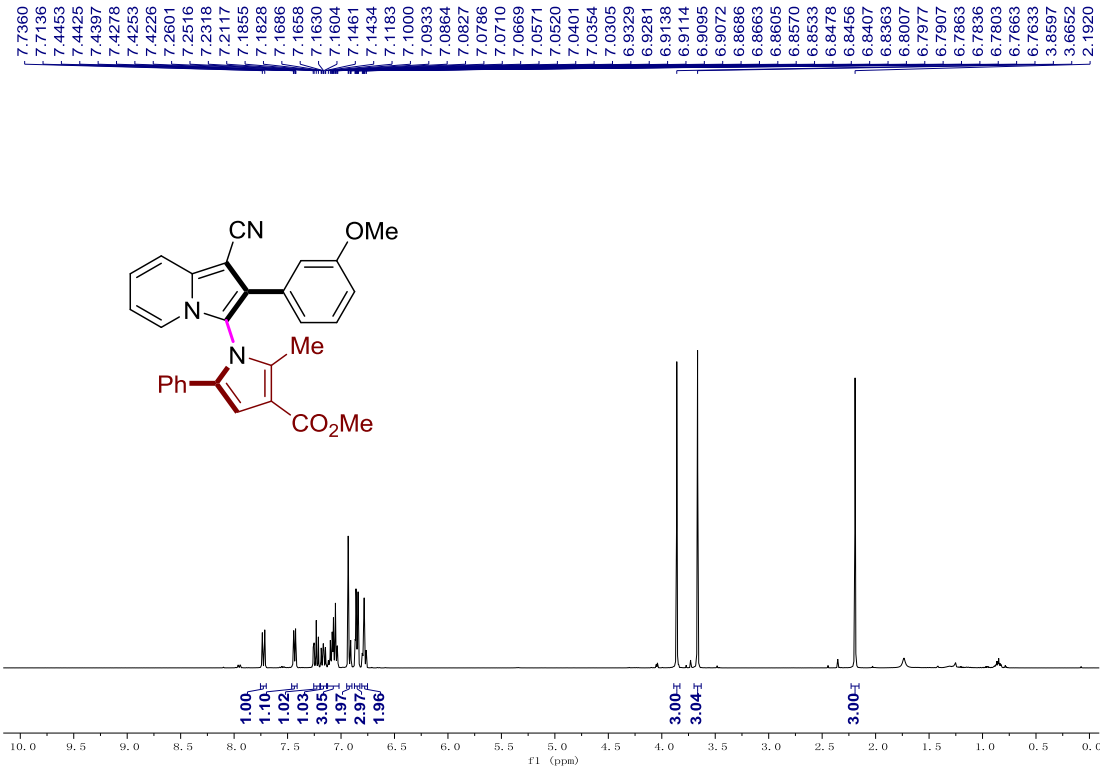
Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	14.049	26032.36	1091.00	49.79
2	15.754	26248.53	954.87	50.21

Enantioenriched **3g**

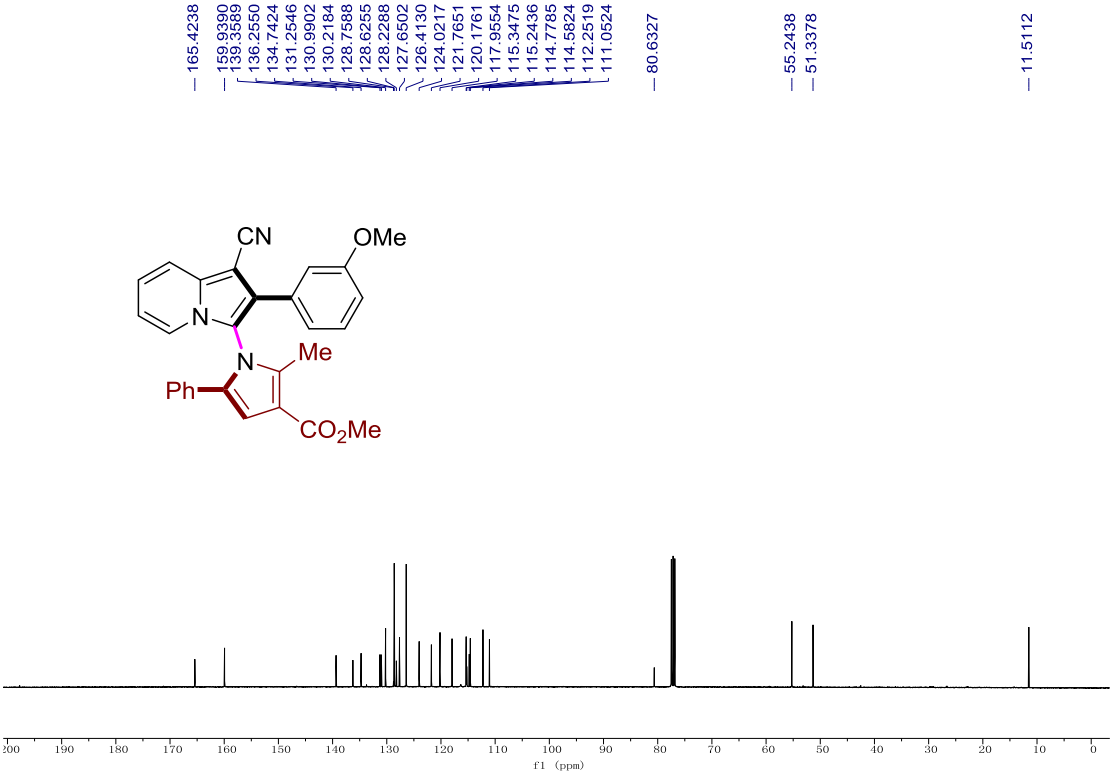


Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	14.007	33204.3	1364.71	92.71
2	15.782	2610.35	94.81	7.29

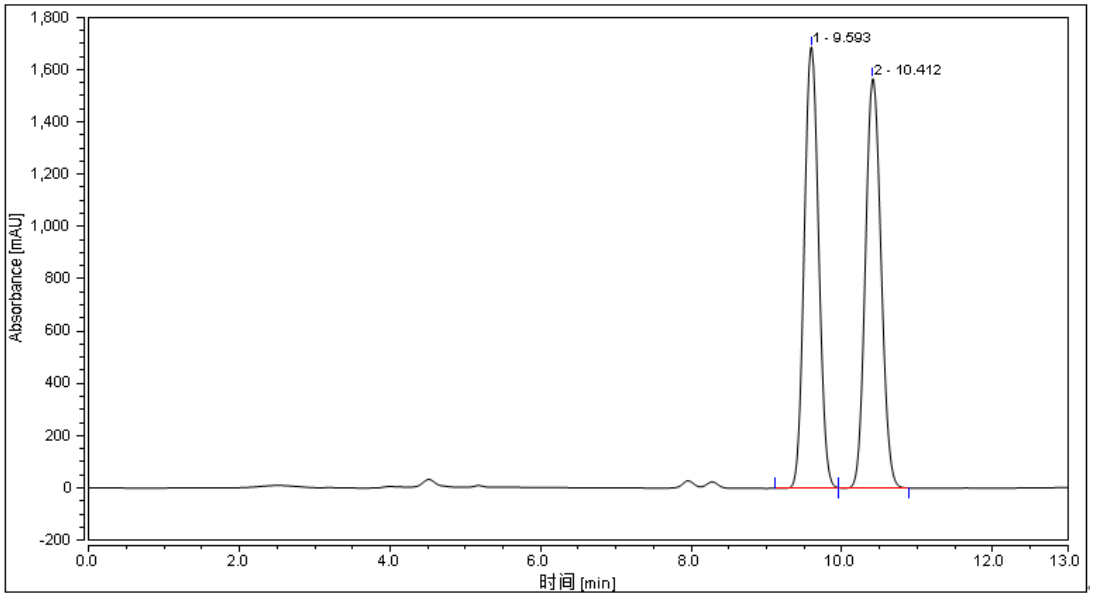
^{1}H NMR of **3h** (400 MHz, $CDCl_3$)



^{13}C NMR of **3h** (100 MHz, $CDCl_3$)

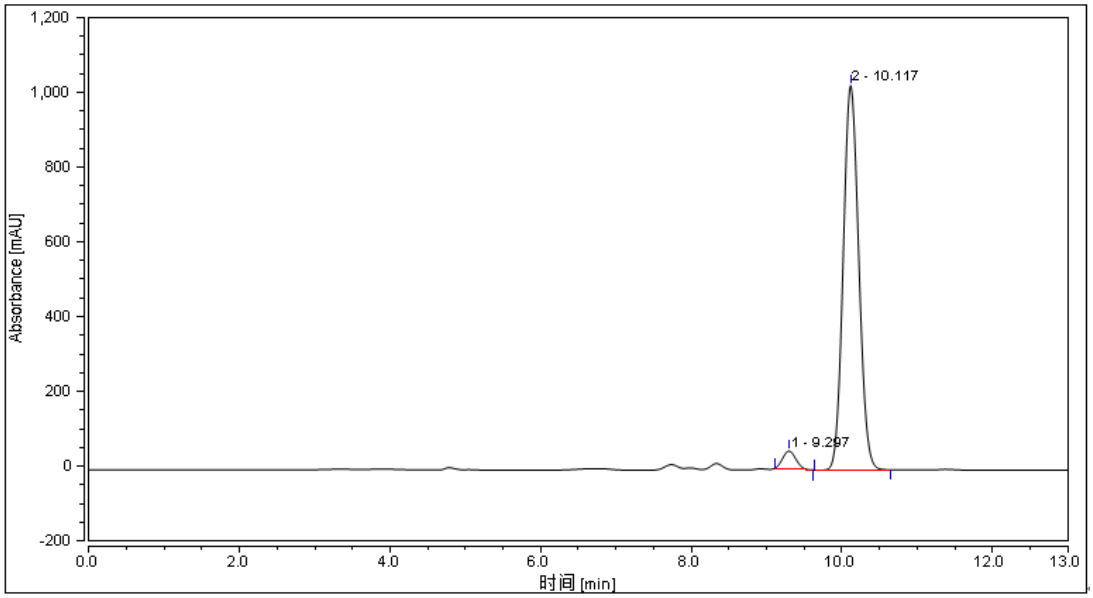


HPLC analysis: rac-**3h**



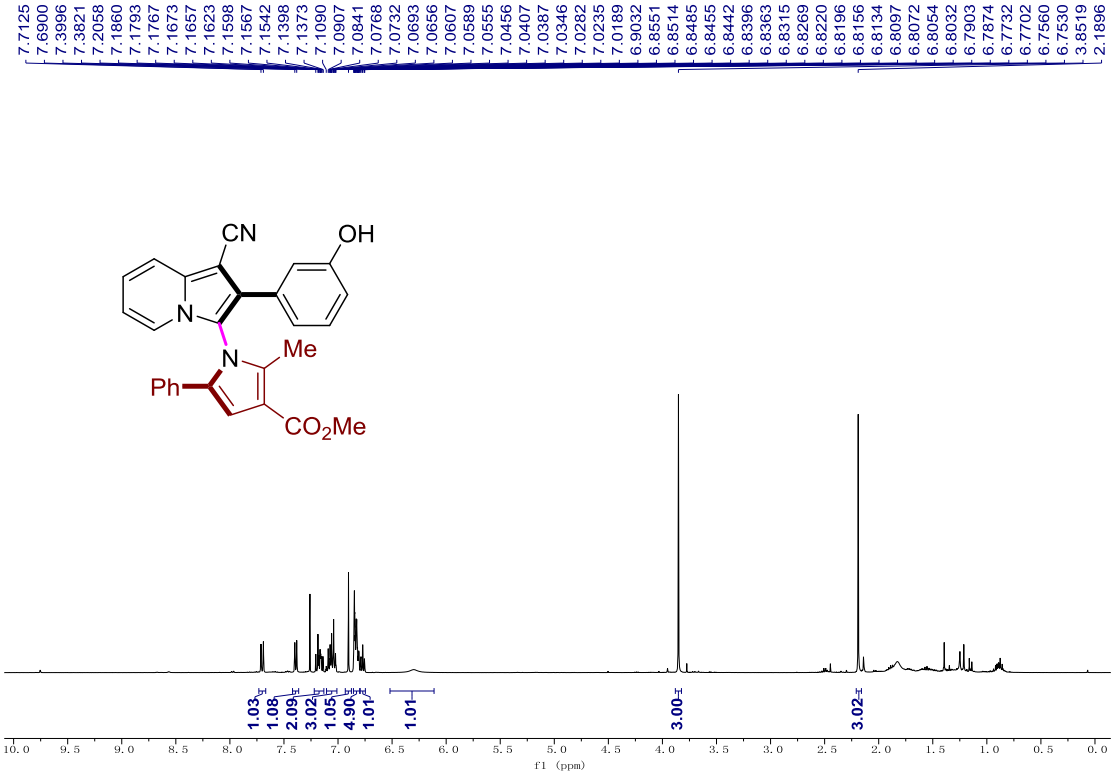
Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	9.593	372.729	1687.657	49.74
2	10.412	376.687	1565.839	50.26

Enantioenriched **3h**

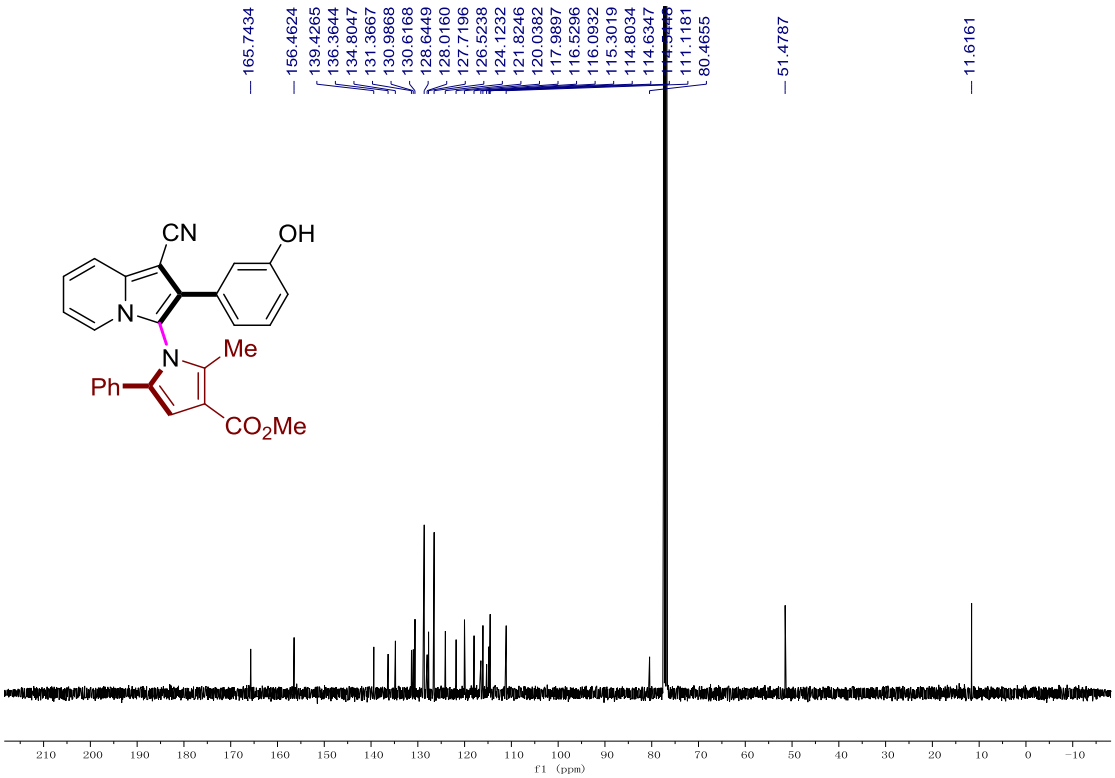


Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	9.297	9.867	48.219	3.87
2	10.117	245.405	1028.383	96.13

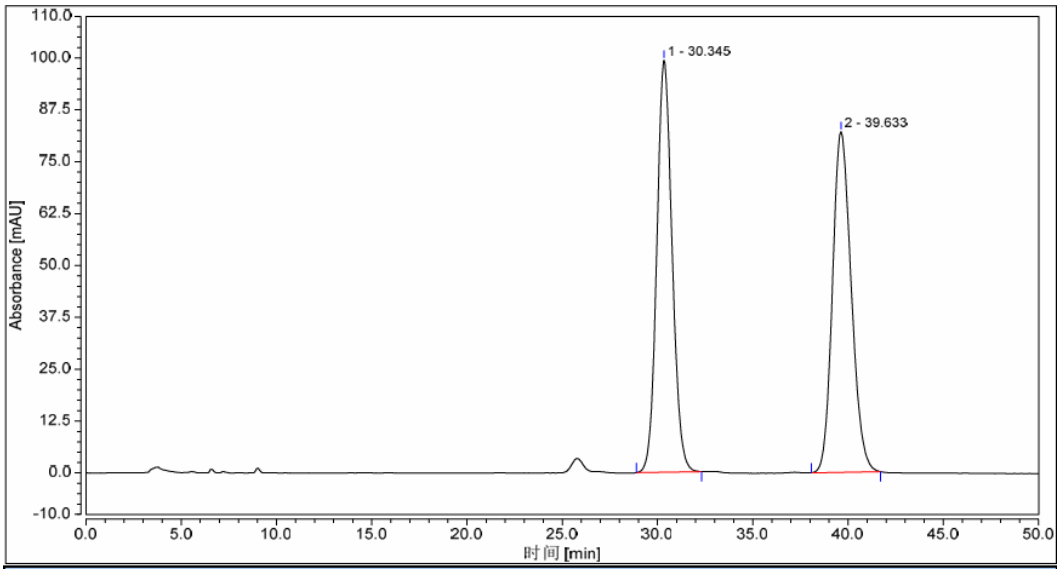
^{1}H NMR of **3i** (400 MHz, $CDCl_3$)



^{13}C NMR of **3i** (100 MHz, $CDCl_3$)

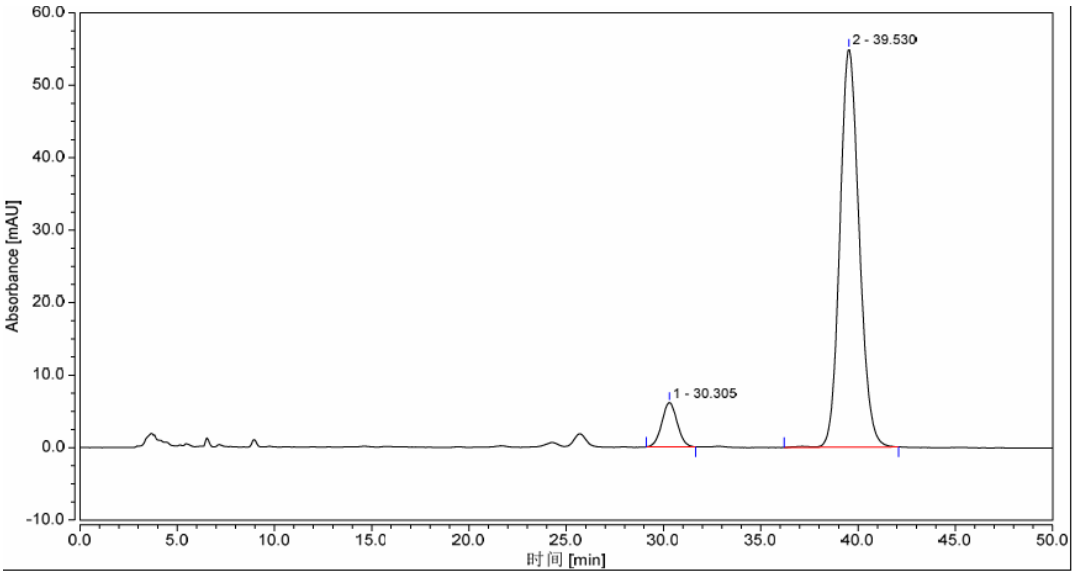


HPLC analysis: rac-**3i**



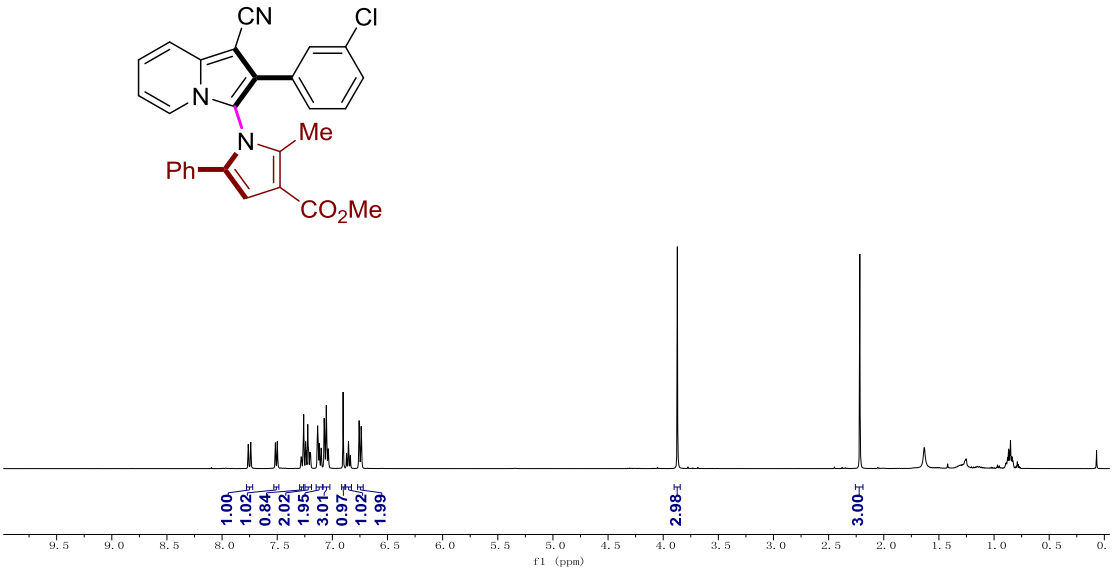
Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	30.345	92.665	99.319	49.69
2	39.633	93.828	82.132	50.31

Enantioenriched **3i**

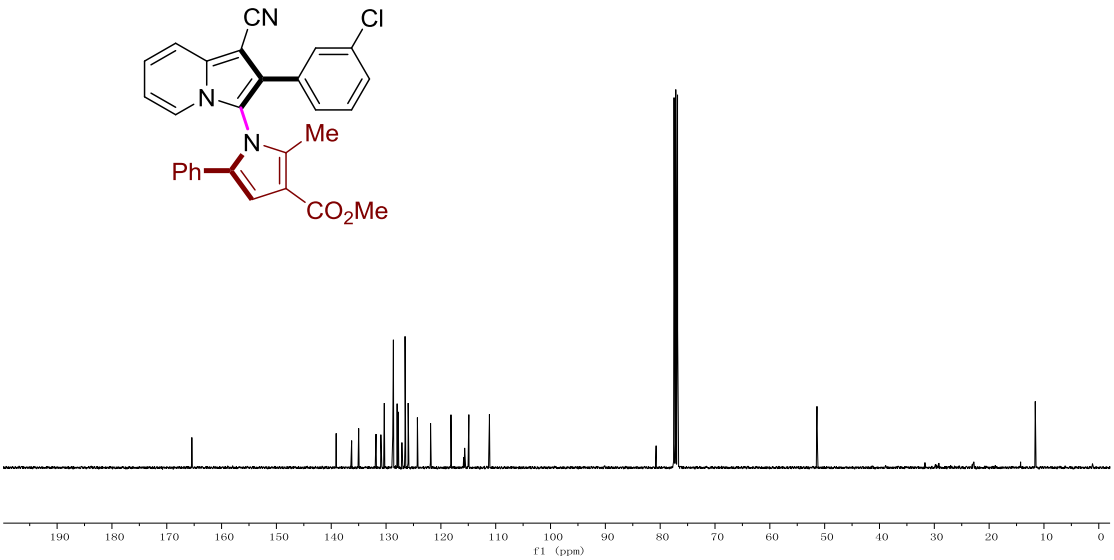


Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	30.305	5.610	6.141	8.14
2	39.530	63.299	54.968	91.86

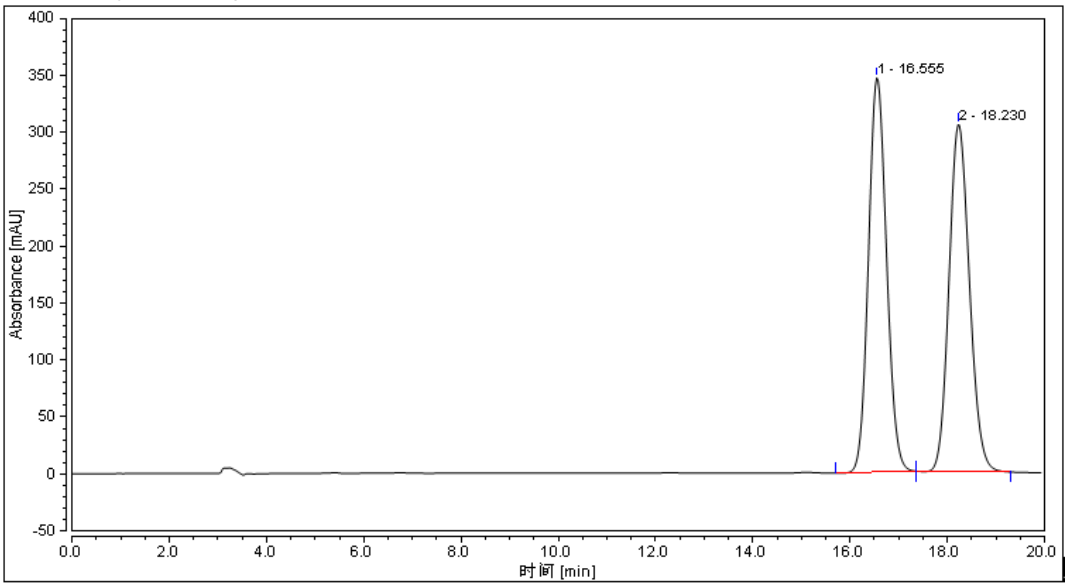
^{1}H NMR of **3j** (400 MHz, $CDCl_3$)



^{13}C NMR of **3j** (100 MHz, $CDCl_3$)

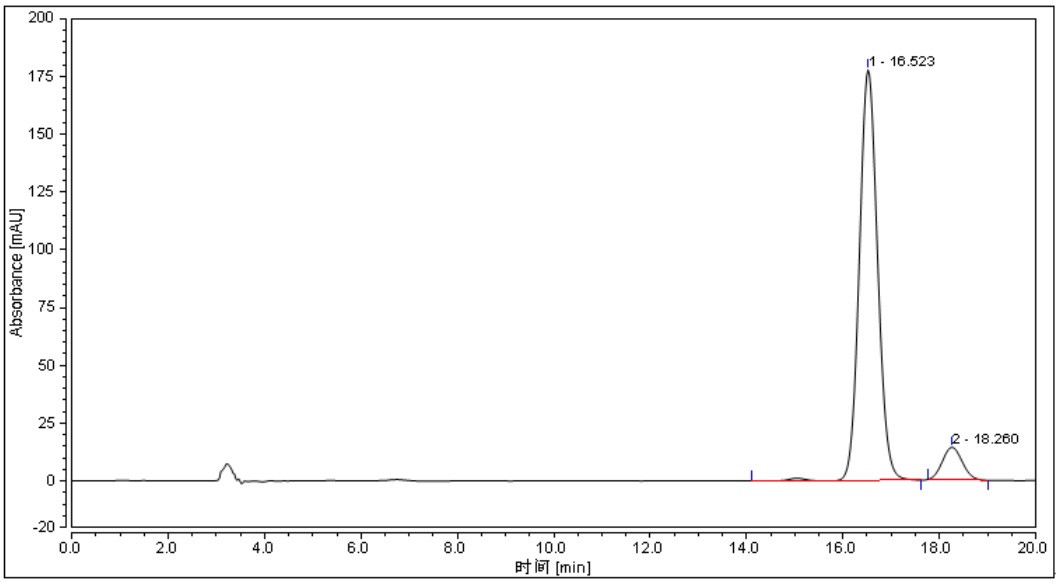


HPLC analysis: rac-**3j**



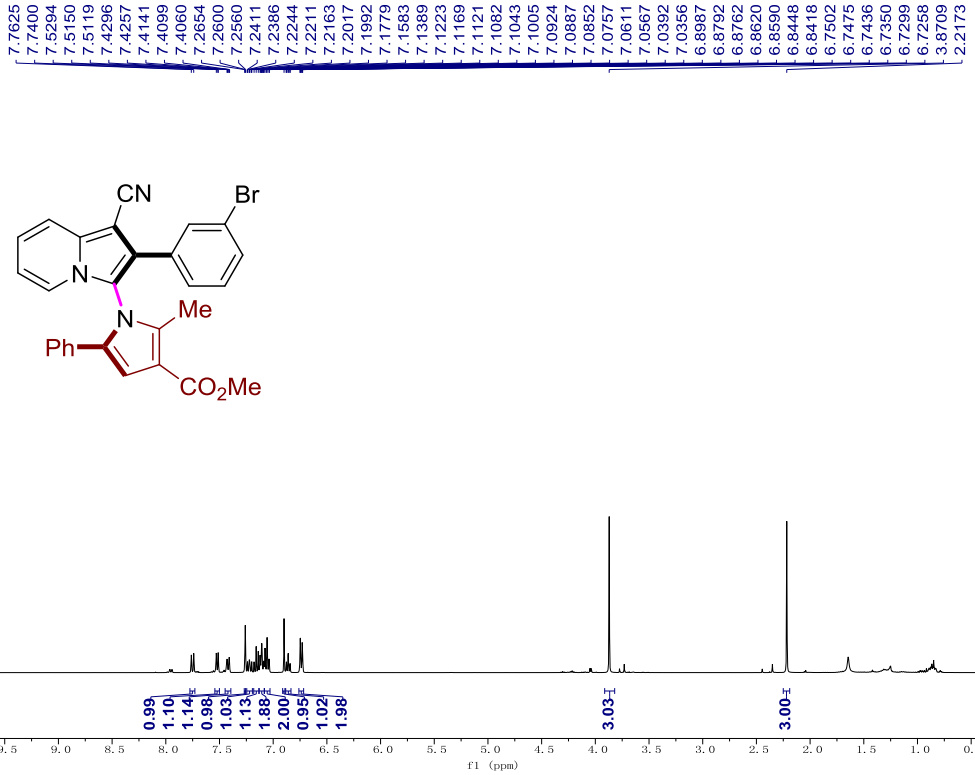
Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	16.555	148.832	346.468	50.09
2	18.230	148.288	305.134	49.91

Enantioenriched **3j**

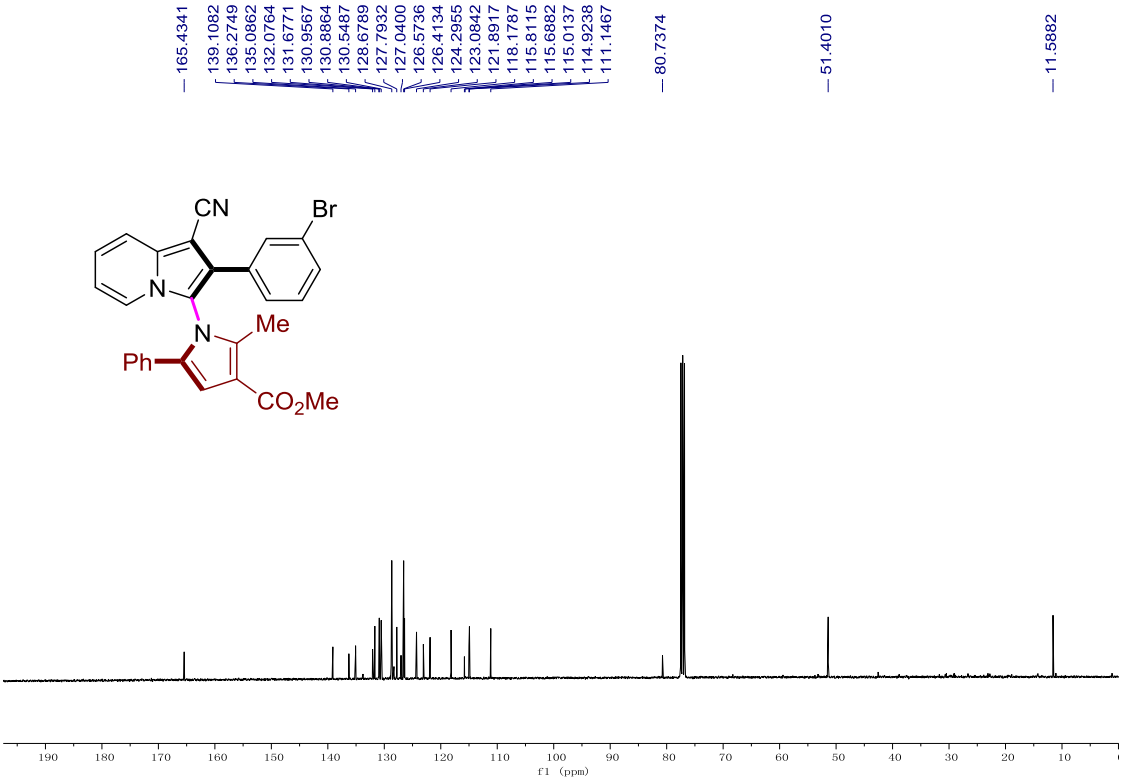


Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	16.523	77.740	177.561	92.09
2	18.260	6.681	14.053	7.91

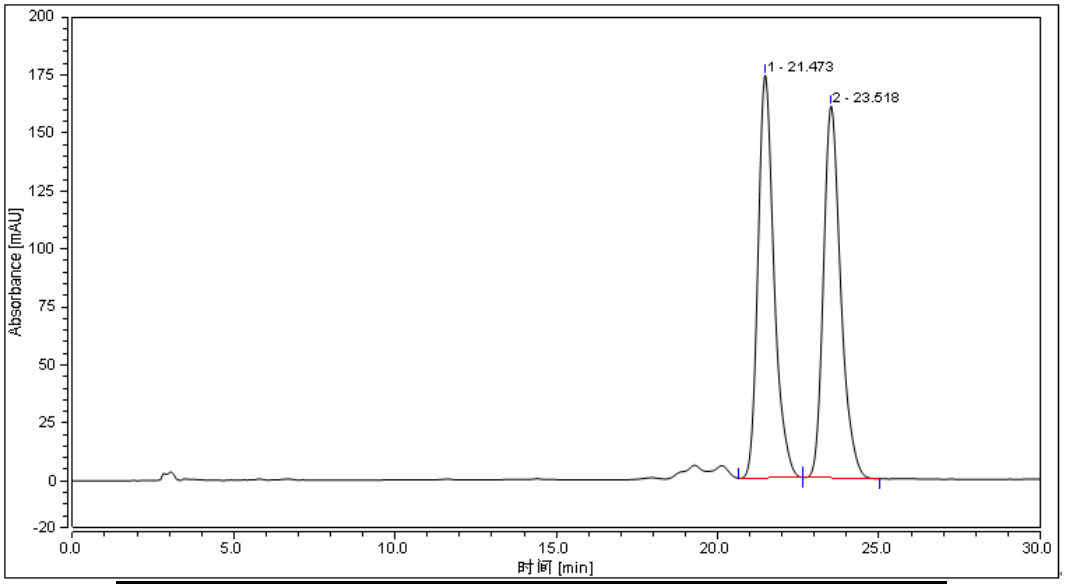
^{1}H NMR of **3k** (400 MHz, $CDCl_3$)



^{13}C NMR of **3k** (100 MHz, $CDCl_3$)

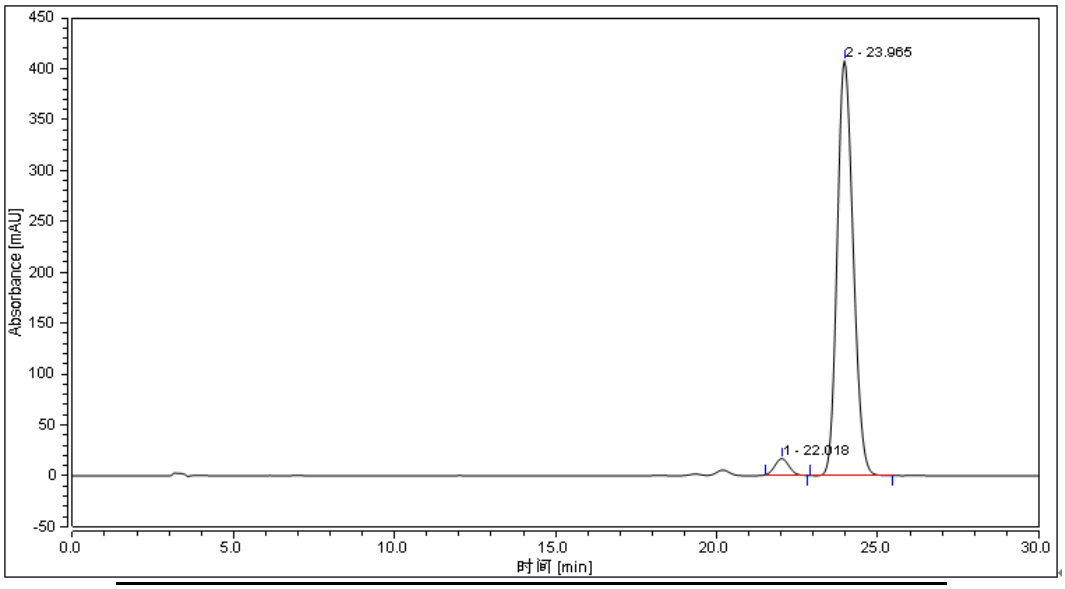


HPLC analysis: rac-**3k**



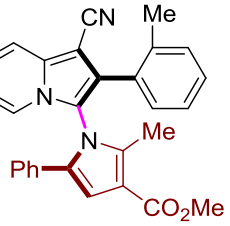
Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	21.473	99.908	173.734	50.10
2	23.518	99.508	160.474	49.90

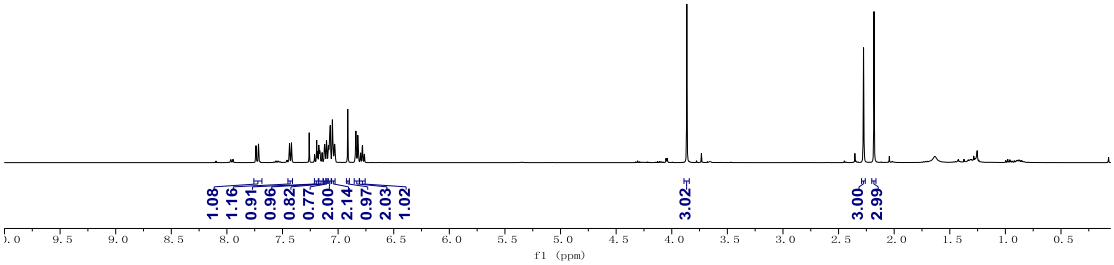
Enantioenriched **3k**



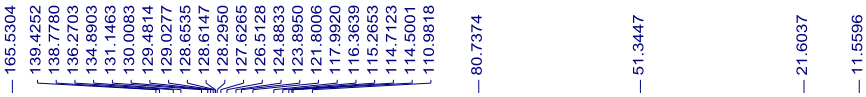
Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	22.018	8.043	16.093	3.33
2	23.965	233.567	408.058	96.67

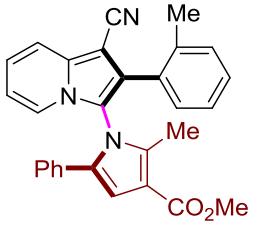
^{1}H NMR of **3l** (400 MHz, $CDCl_3$)



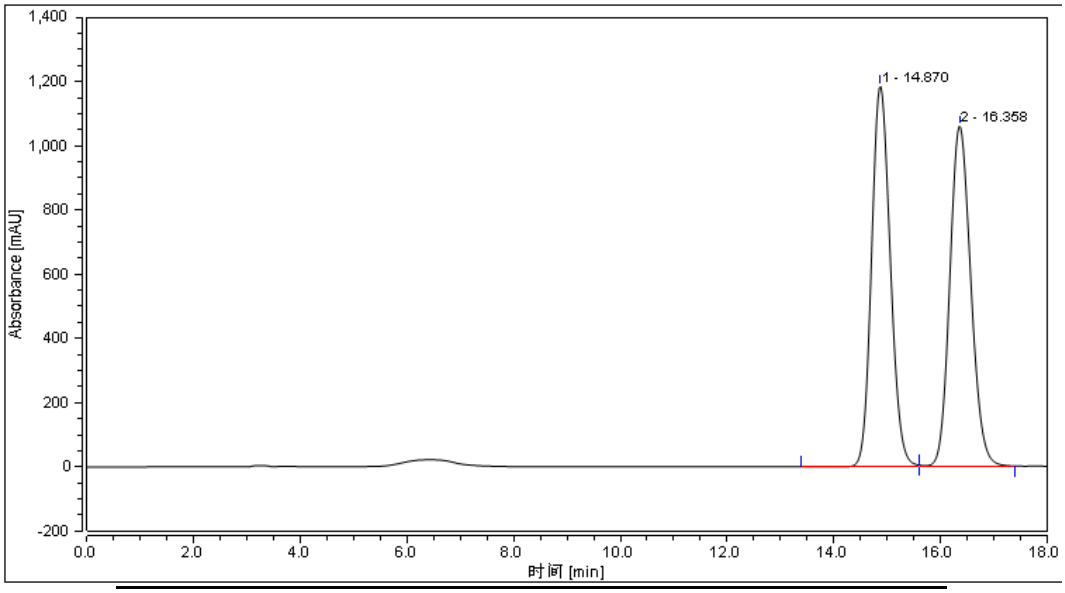


^{13}C NMR of **3l** (100 MHz, $CDCl_3$)



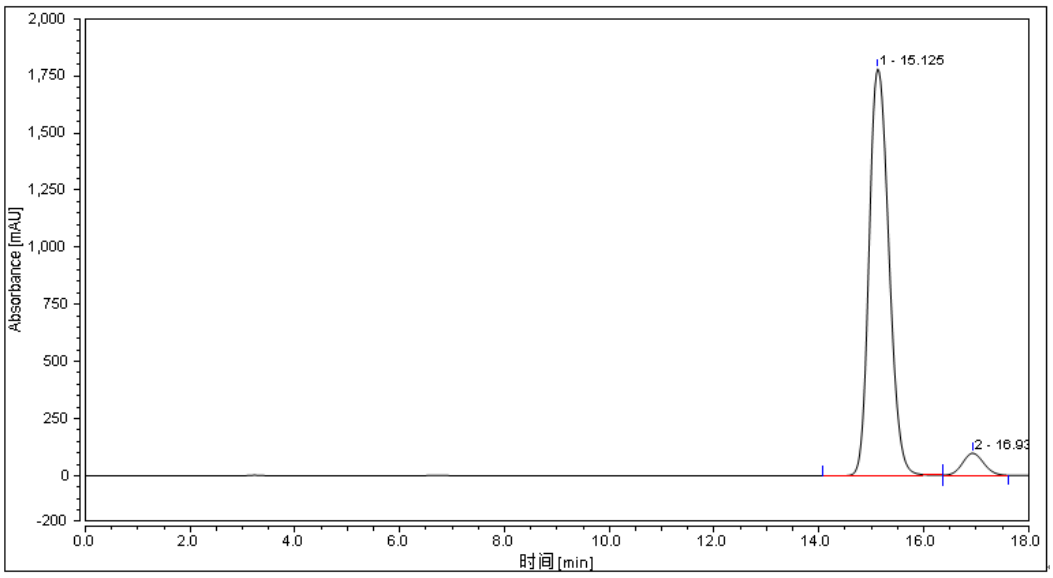


HPLC analysis: rac-**3l**



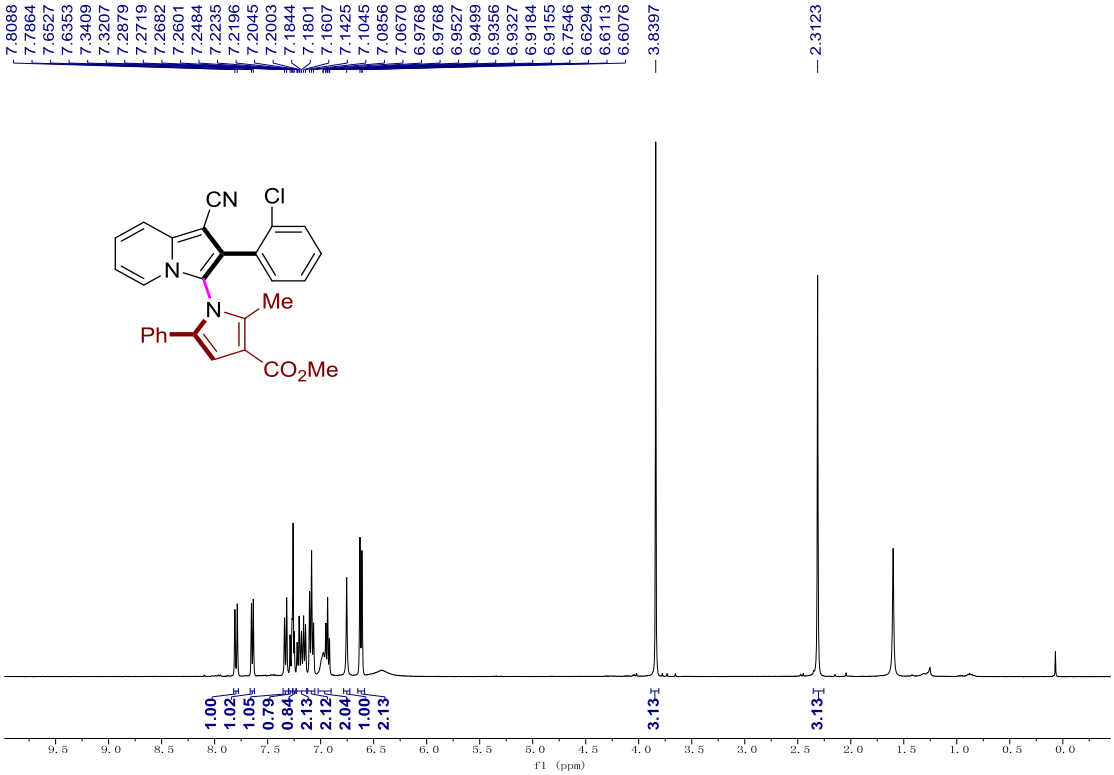
Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	14.870	480.297	1185.372	49.89
2	16.358	482.351	1059.948	50.11

Enantioenriched **3l**

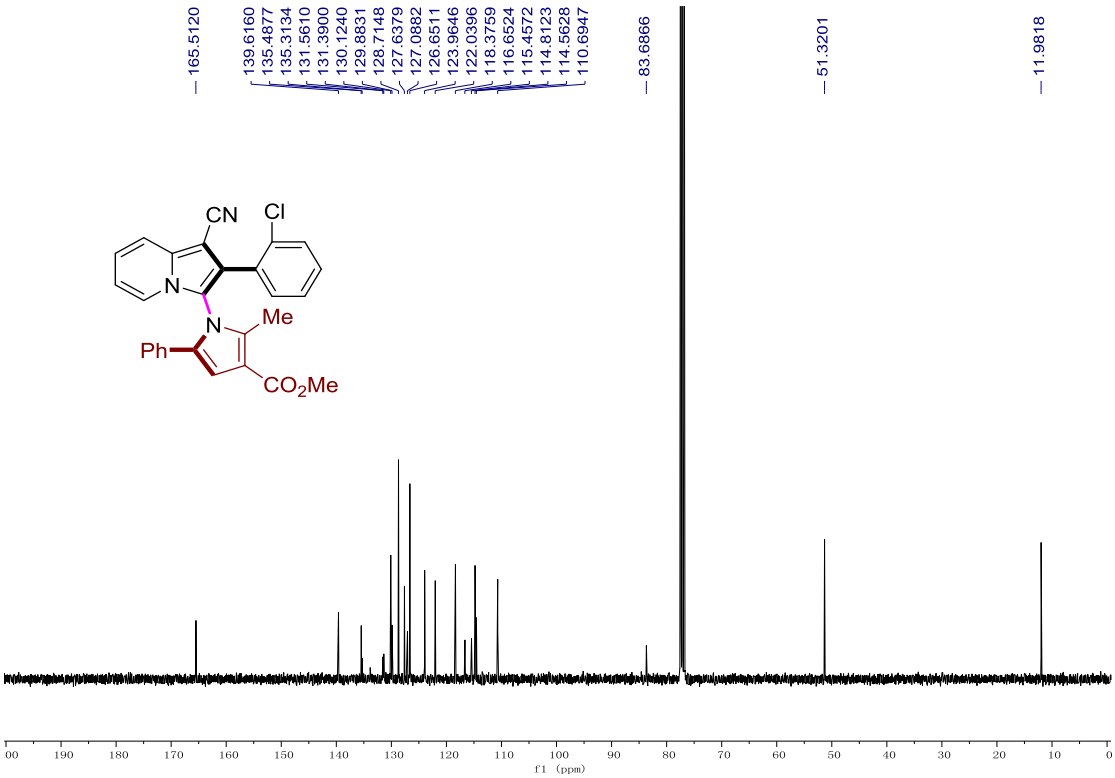


Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	15.125	776.391	1780.047	94.52
2	16.935	45.033	96.424	5.48

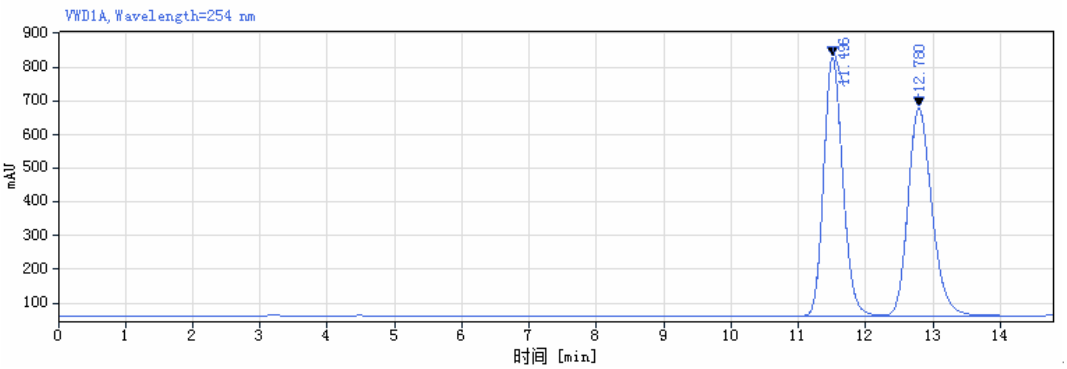
^{1}H NMR of **3m** (400 MHz, $CDCl_3$)



^{13}C NMR of **3m** (100 MHz, $CDCl_3$)

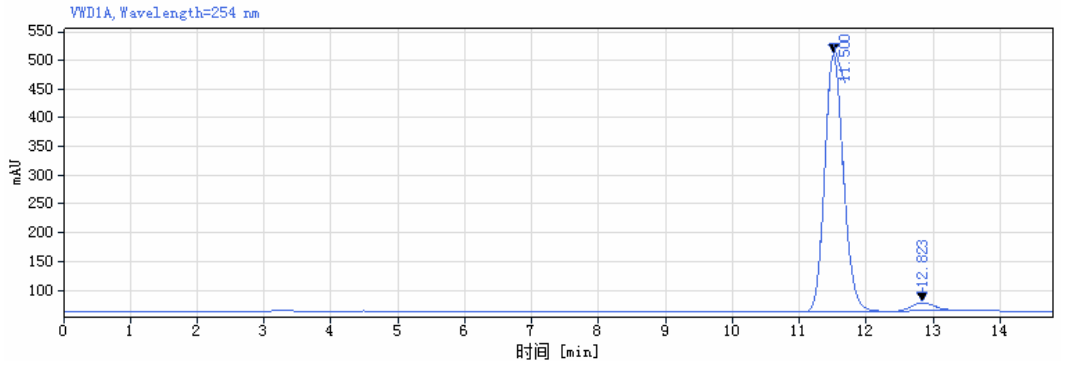


HPLC analysis: rac-**3m**



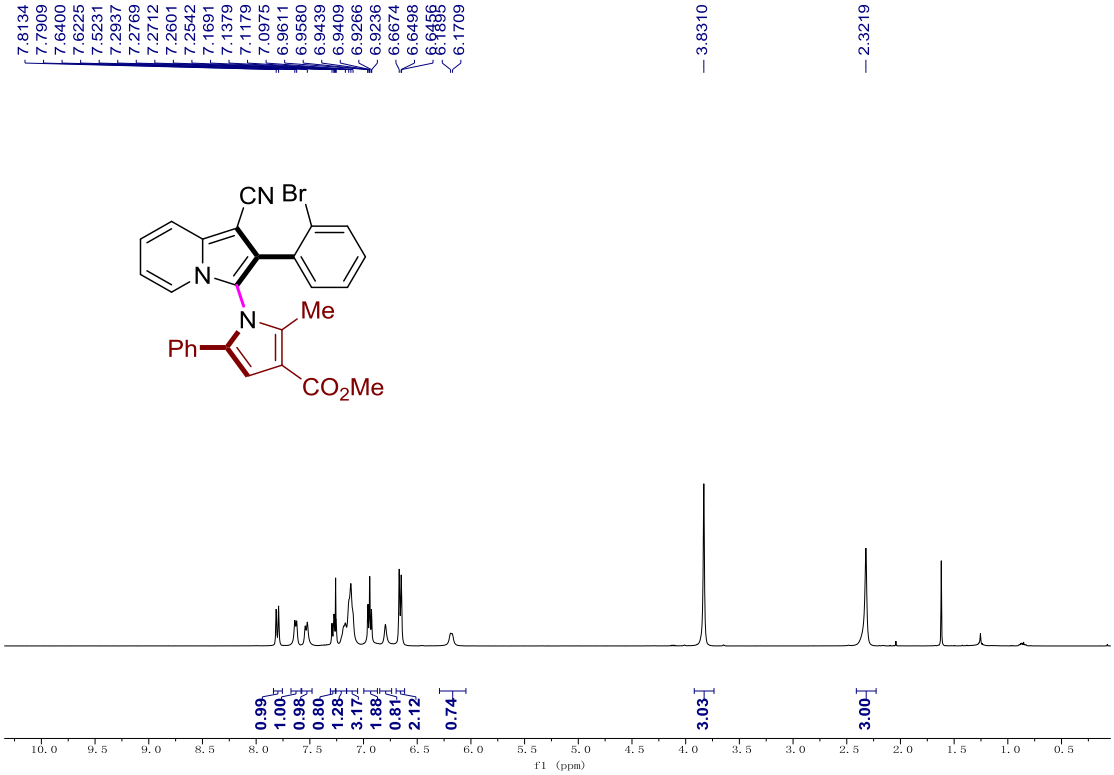
Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	11.496	15119.03	765.57	49.87
2	12.78	15197.4	616.39	50.13

Enantioenriched **3m**

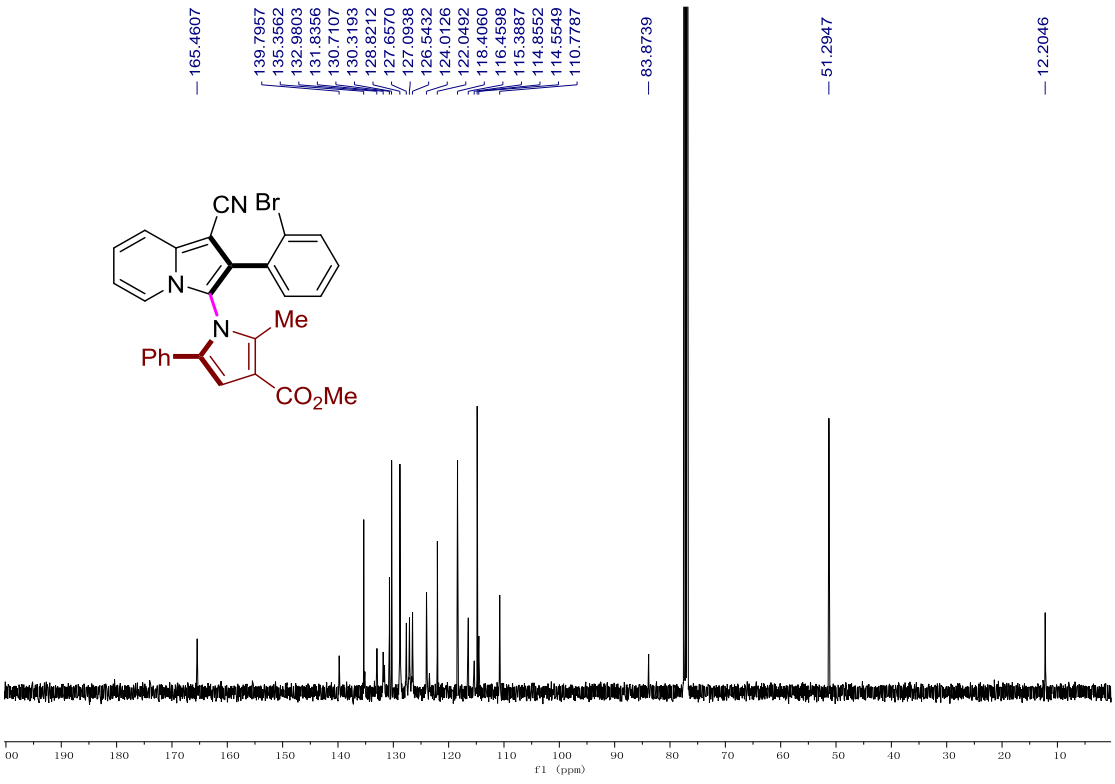


Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	11.5	8751.47	447.89	96.34
2	12.823	332.2	13.87	3.66

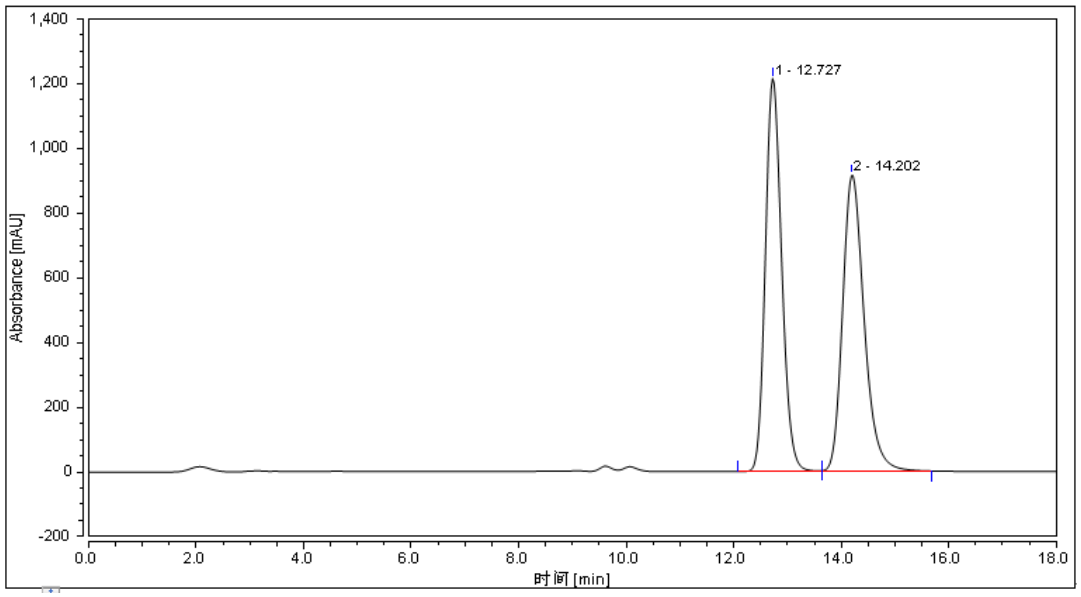
^{1}H NMR of **3n** (400 MHz, $CDCl_3$)



^{13}C NMR of **3n** (100 MHz, $CDCl_3$)

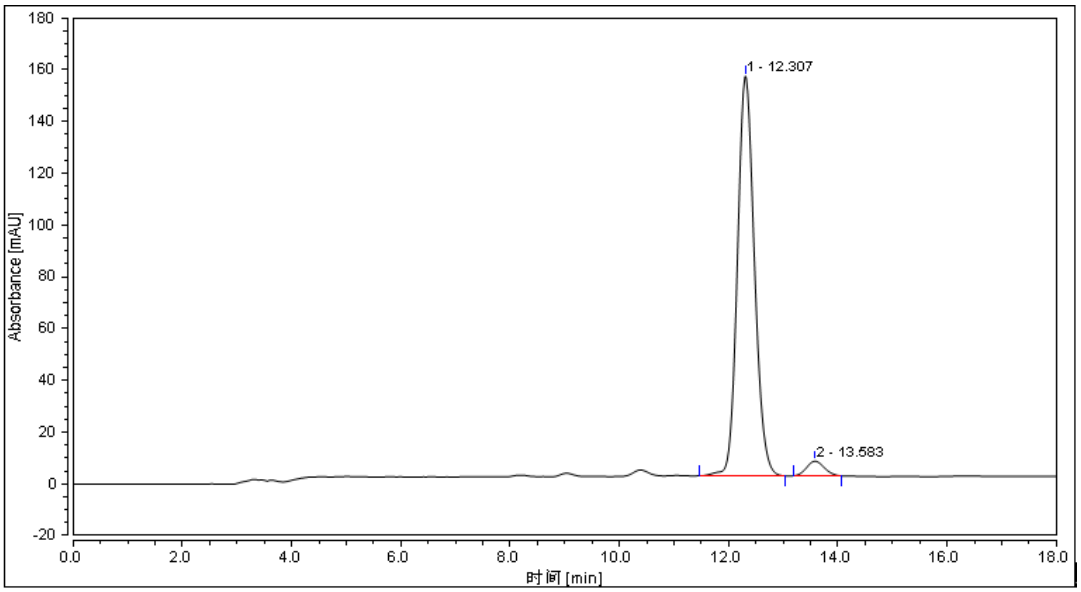


HPLC analysis: rac-**3n**



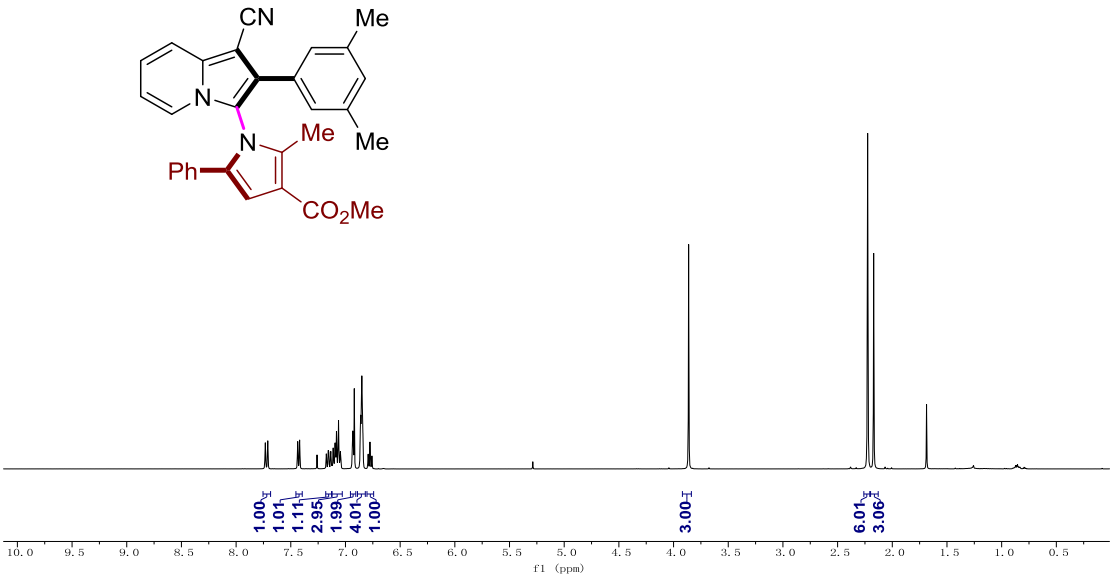
Peak	RetTime	Area	Height	Area
	min	mAU*min	mAU	%
1	12.727	424.412	1213.815	50.12
2	14.202	422.362	914.559	49.88

Enantioenriched **3n**

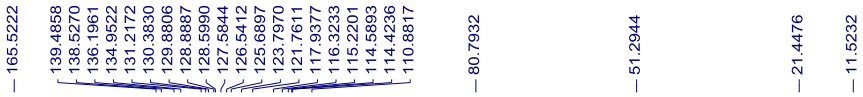


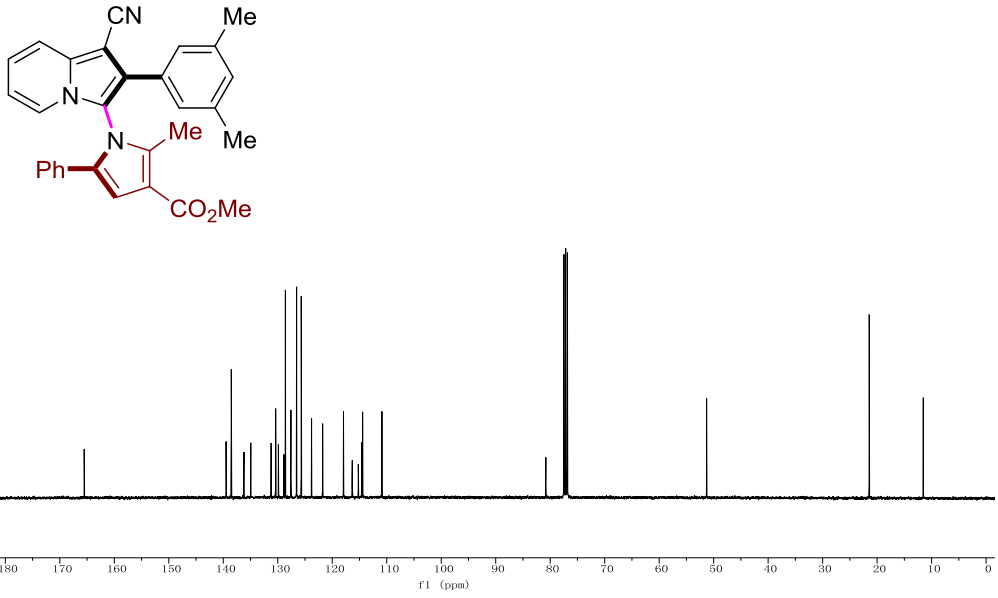
Peak	RetTime	Area	Height	Area
	min	mAU*min	mAU	%
1	12.307	55.671	154.521	93.31
2	13.583	2.132	5.690	3.69

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

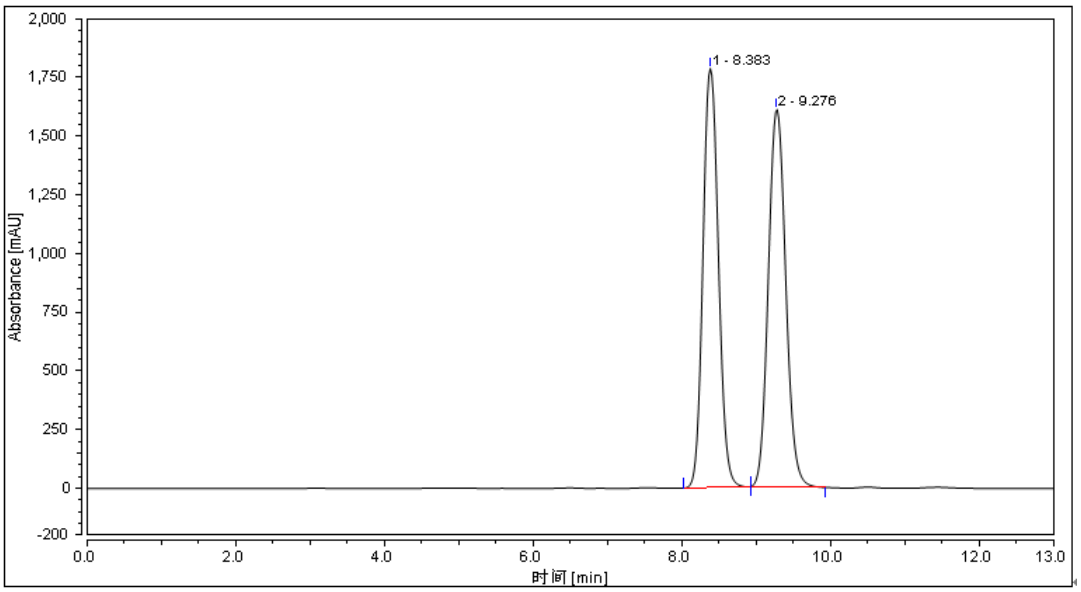


^{13}C NMR of **3o** (100 MHz, $CDCl_3$)



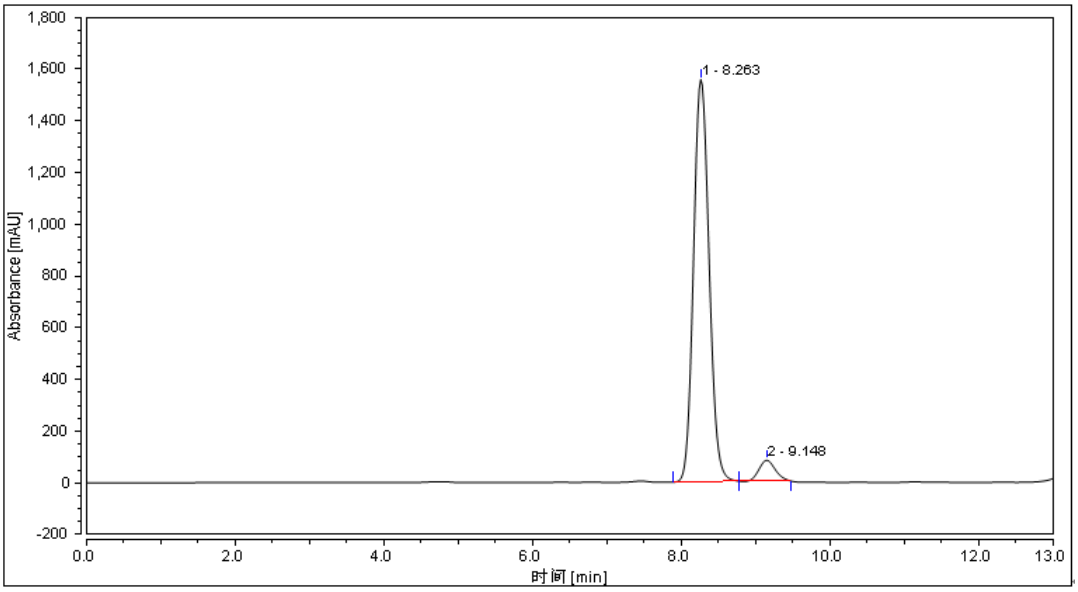


HPLC analysis: rac-**3o**



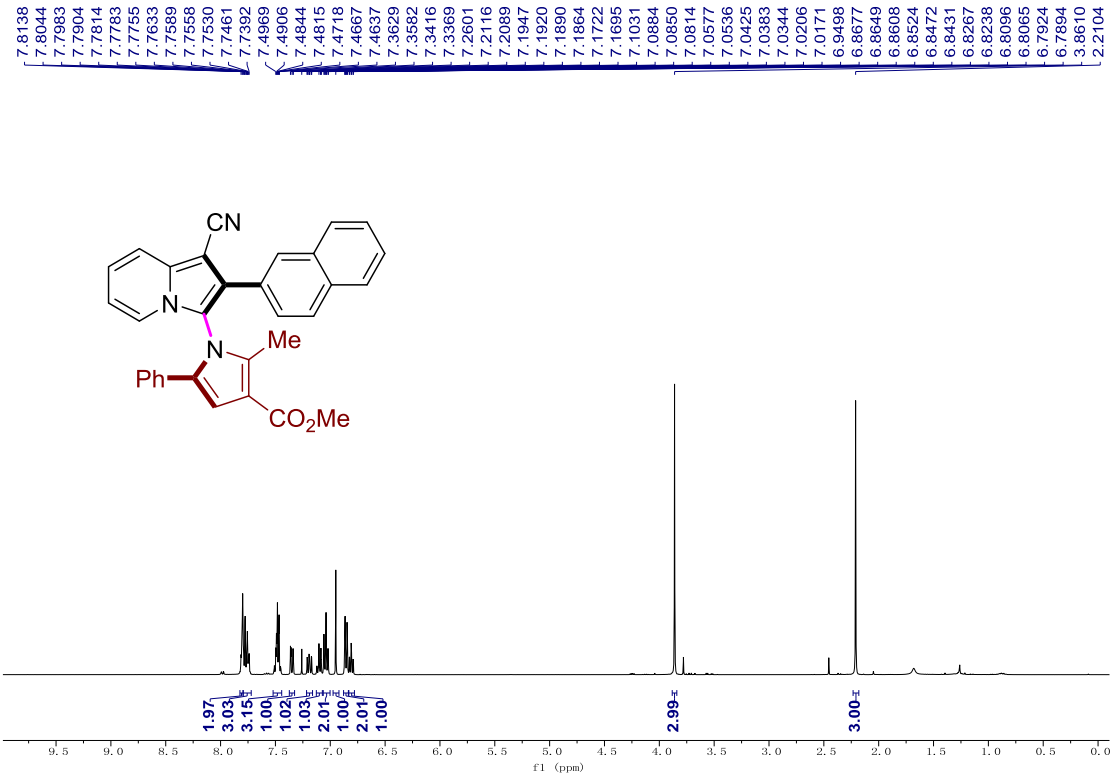
Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	8.383	429.402	1785.561	49.59
2	9.276	436.491	1608.785	50.41

Enantioenriched **3o**

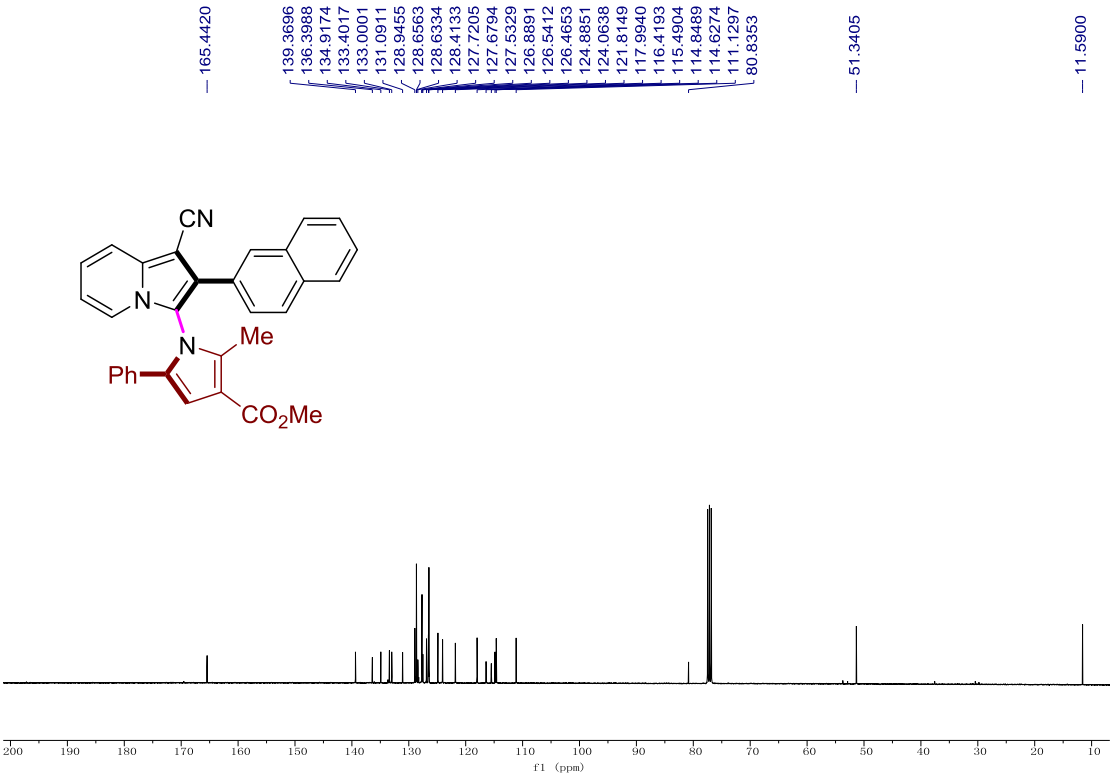


Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	8.263	376.587	1556.039	94.89
2	9.148	20.270	80.195	5.11

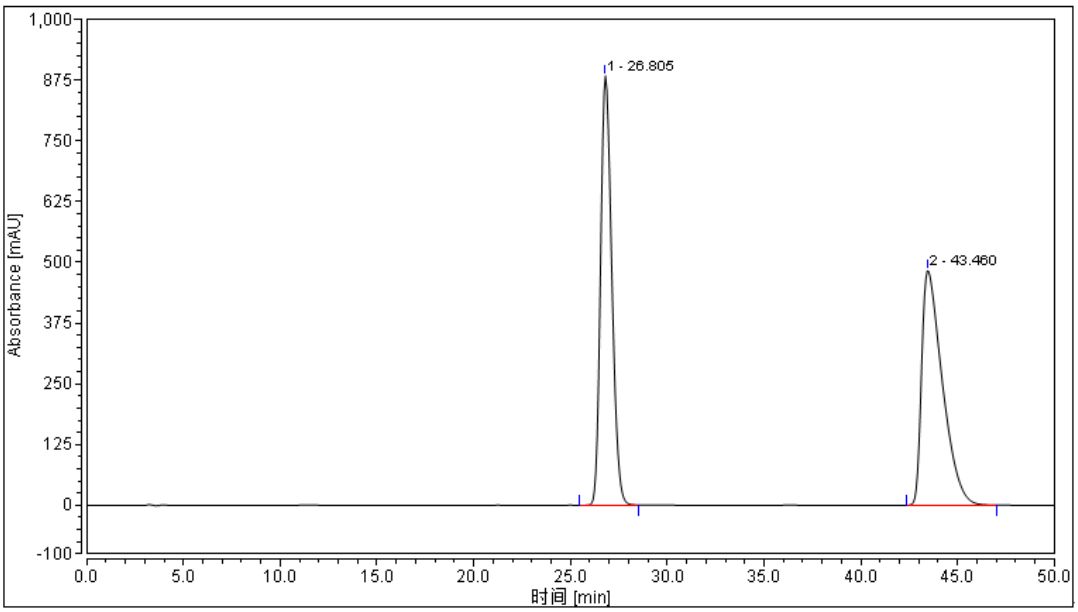
^{1}H NMR of **3p** (400 MHz, $CDCl_3$)



^{13}C NMR of **3p** (100 MHz, $CDCl_3$)

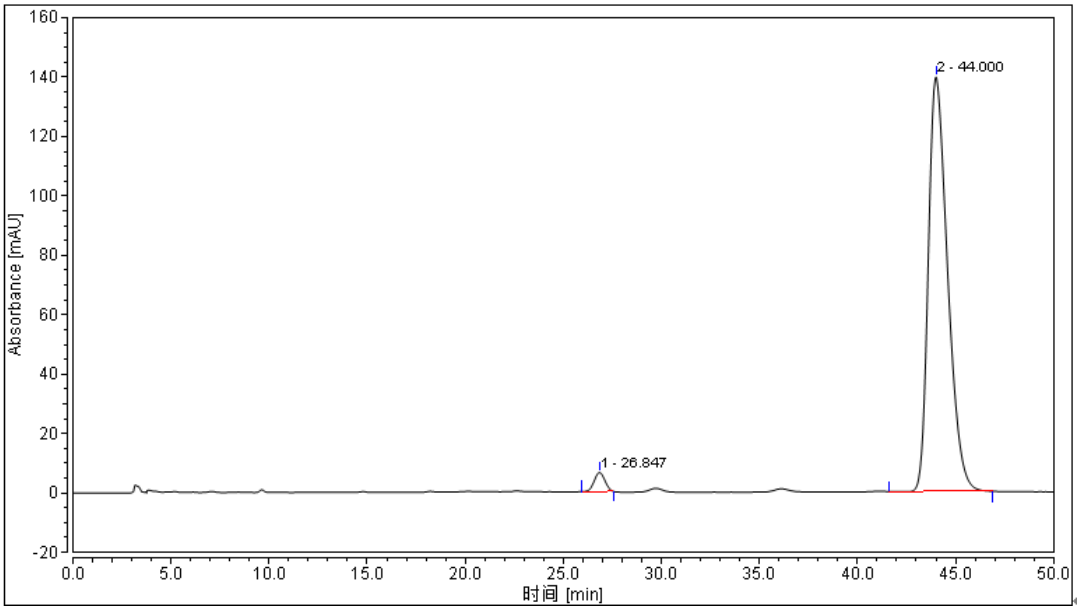


HPLC analysis: rac-**3p**



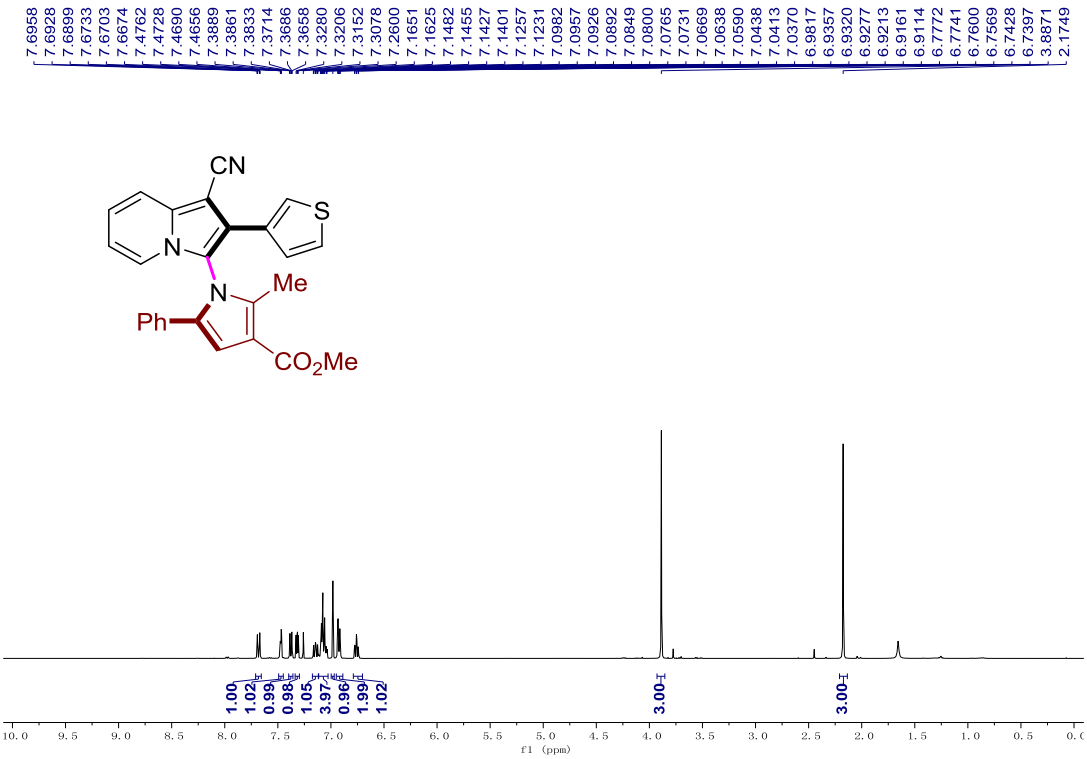
Peak	RetTime	Area	Height	Area
	min	mAU*min	mAU	%
1	26.805	592.854	883.234	49.74
2	43.460	599.139	483.214	50.26

Enantioenriched **3p**

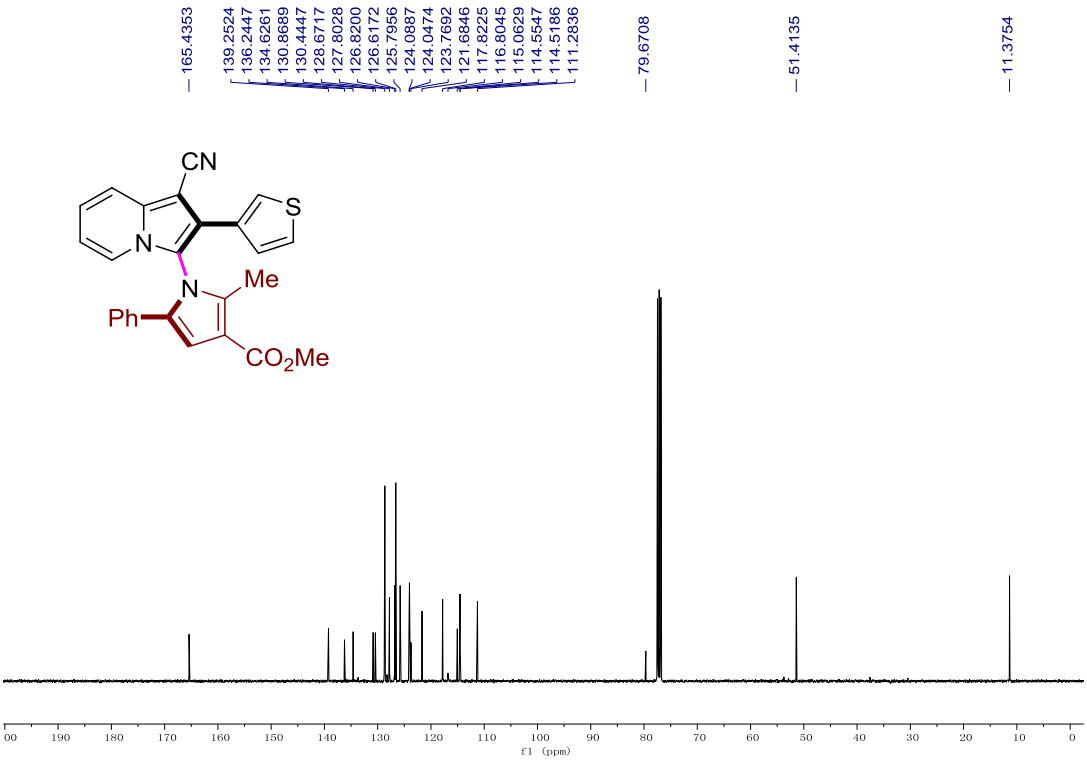


Peak	RetTime	Area	Height	Area
	min	mAU*min	mAU	%
1	26.847	4.046	6.433	2.49
2	44.000	158.745	139.574	97.51

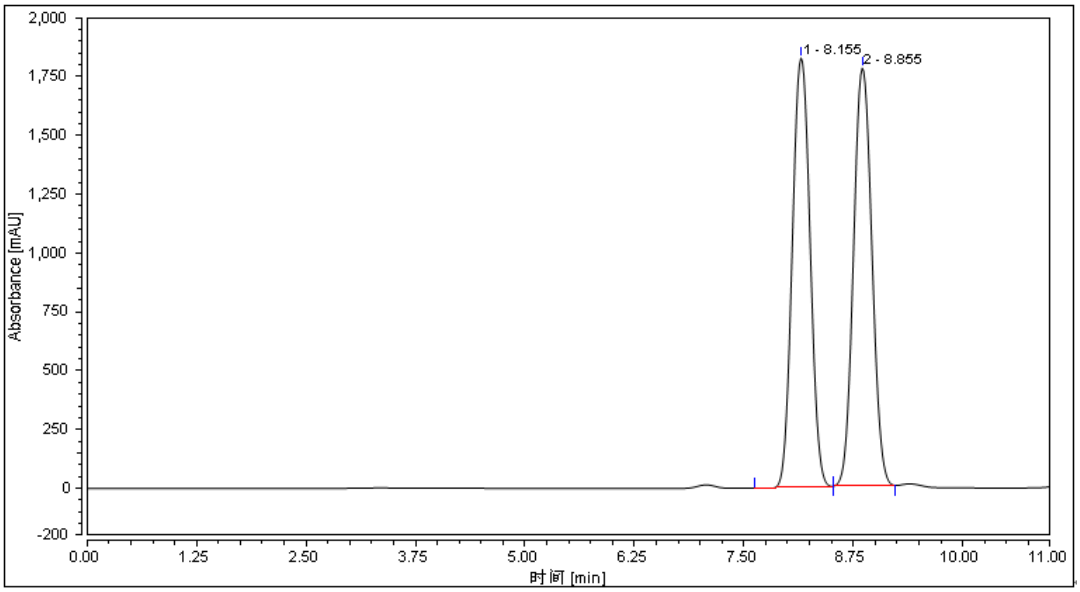
^{1}H NMR of **3q** (400 MHz, $CDCl_3$)



^{13}C NMR of **3q** (100 MHz, $CDCl_3$)

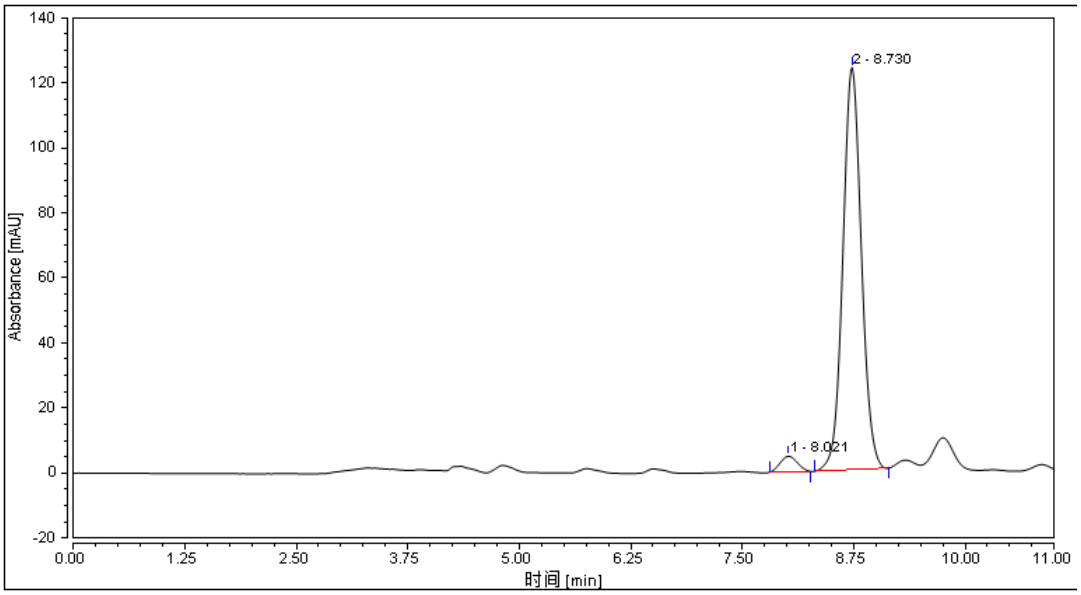


HPLC analysis: rac-**3q**



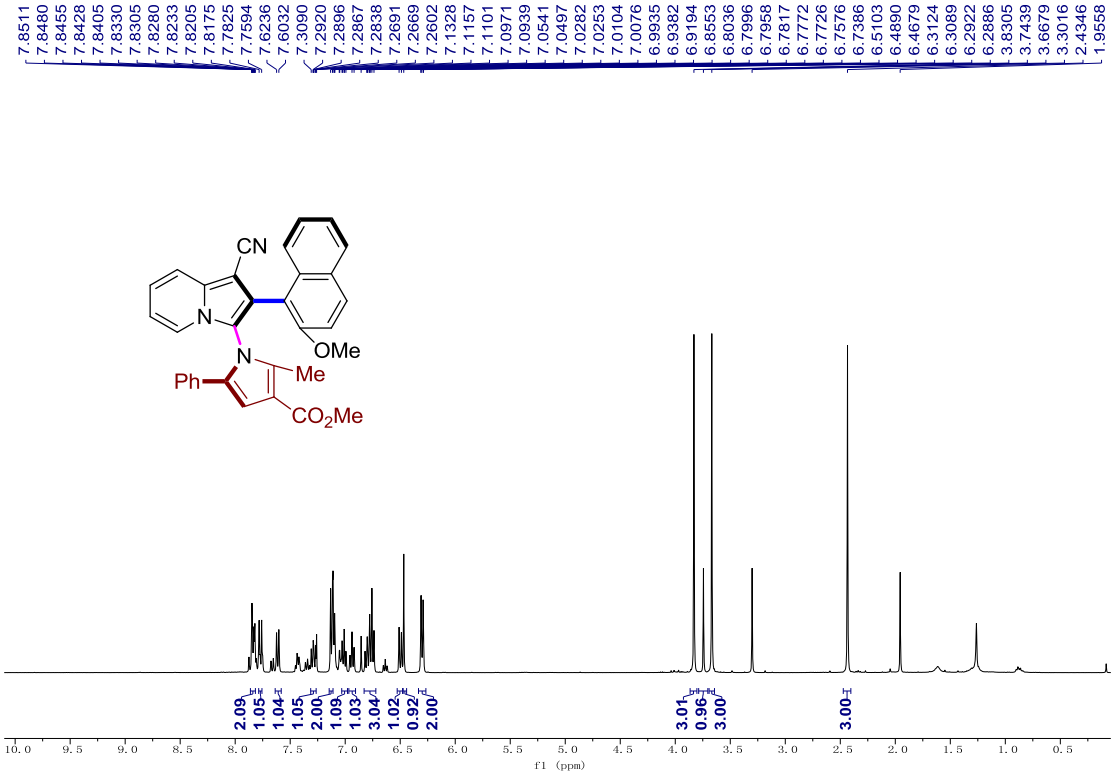
Peak	RetTime	Area	Height	Area
	min	mAU*min	mAU	%
1	8.155	428.061	1824.883	49.76
2	8.855	432.208	1777.057	50.24

Enantioenriched **3q**

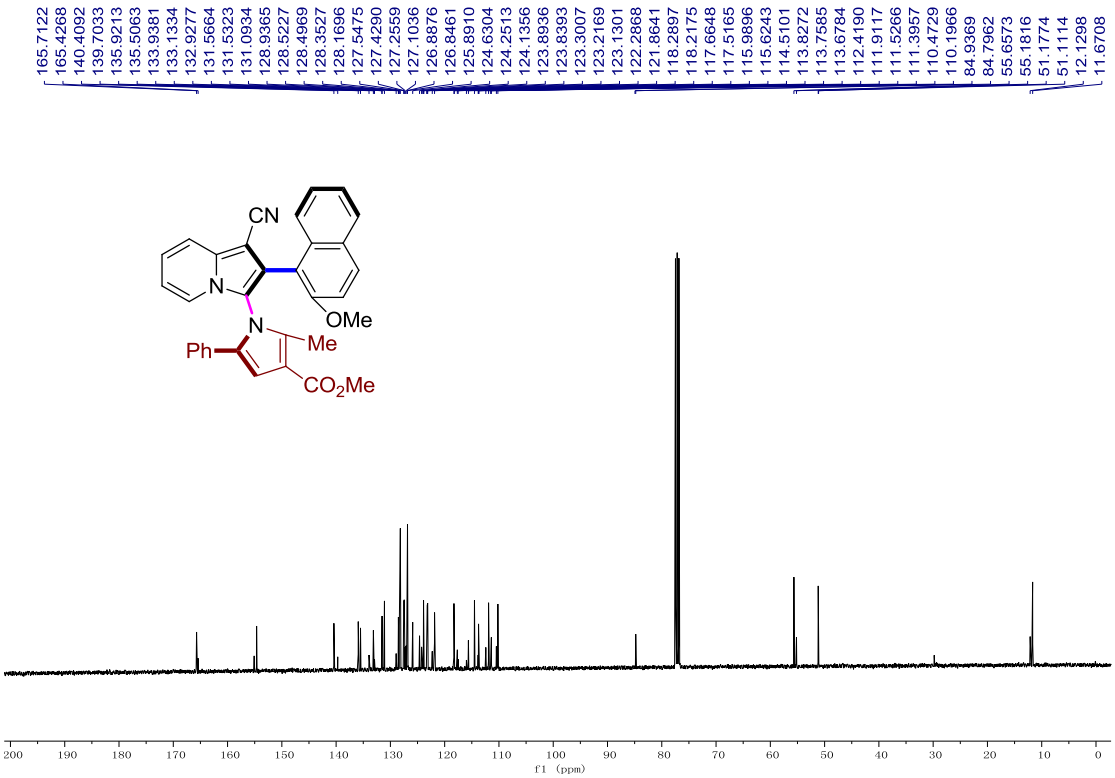


Peak	RetTime	Area	Height	Area
	min	mAU*min	mAU	%
1	8.021	1.065	4.803	3.46
2	8.730	29.710	123.735	96.54

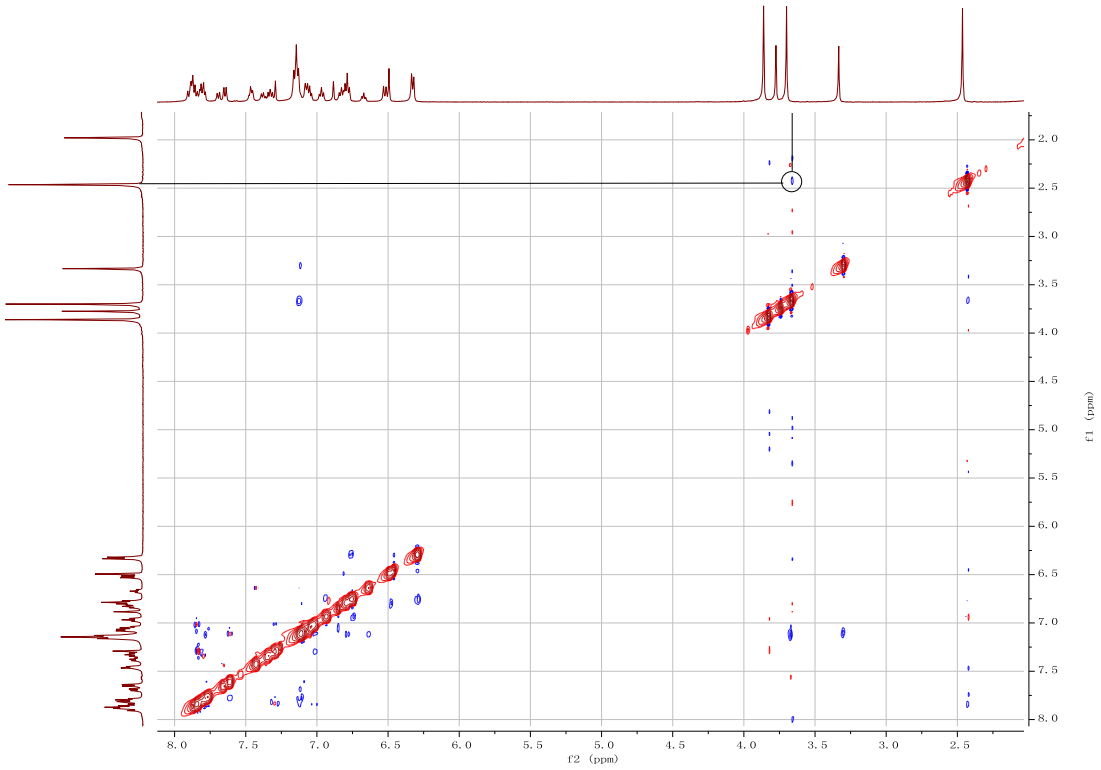
^{1}H NMR of **3r** (400 MHz, $CDCl_3$)



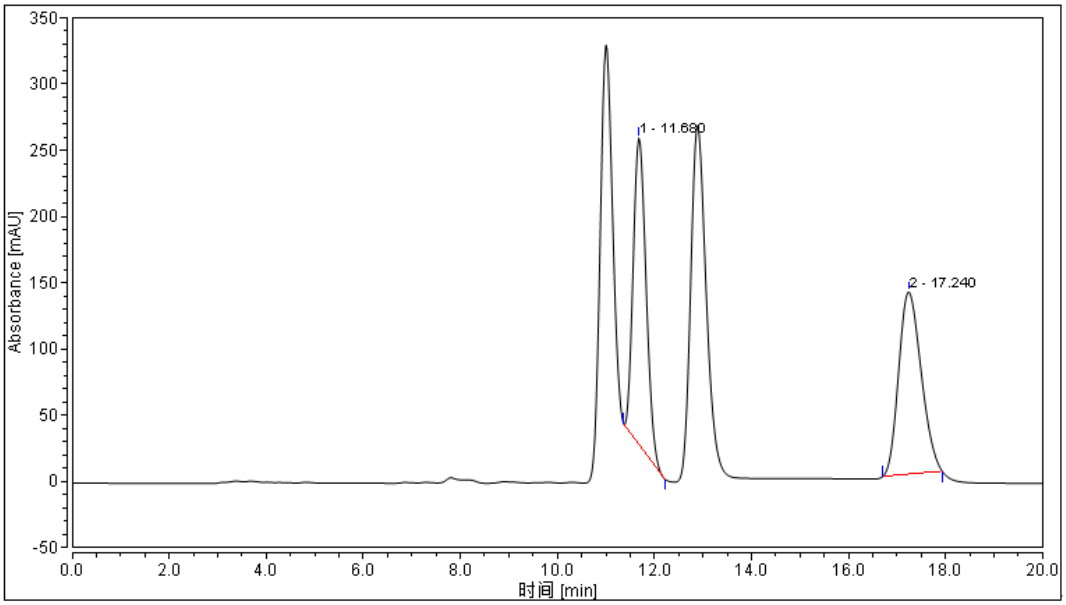
^{13}C NMR of **3r** (100 MHz, $CDCl_3$)



NOESY of **3r** (500 MHz, $CDCl_3$)

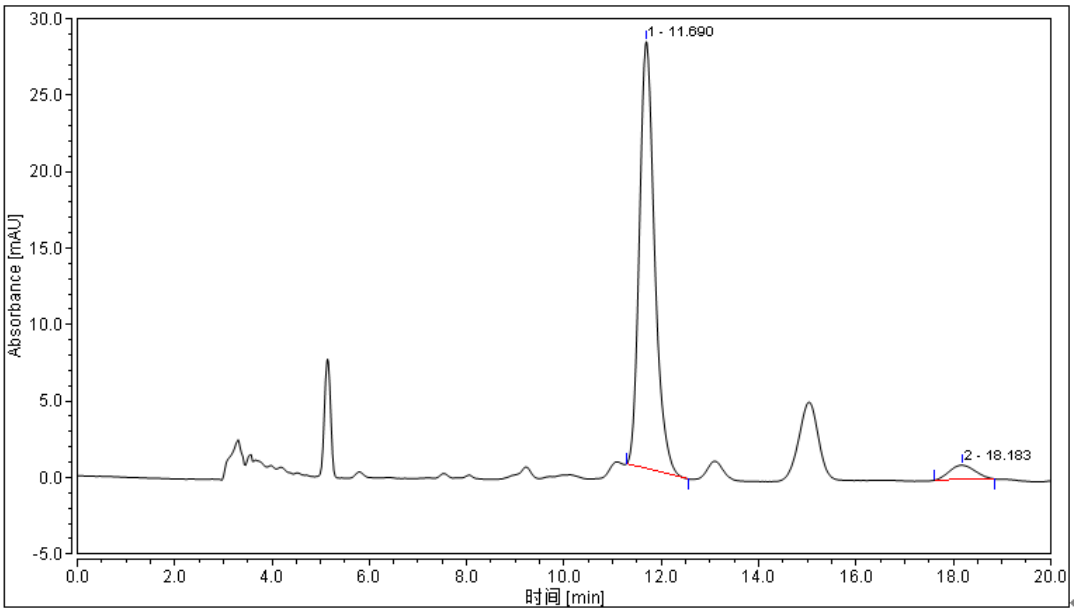


HPLC analysis: rac-**3r**



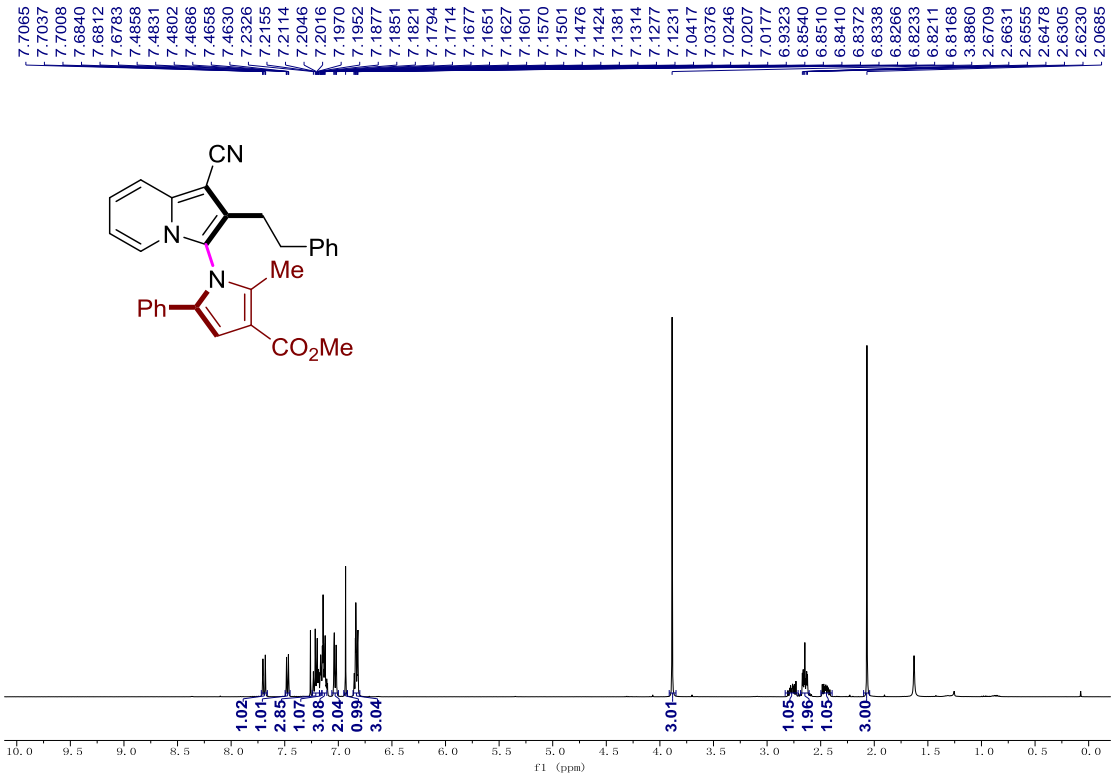
Peak	RetTime	Area	Height	Area
	min	mAU*min	mAU	%
1	11.680	70.910	231.737	50.66
2	17.240	69.054	131.538	49.34

Enantioenriched **3r**

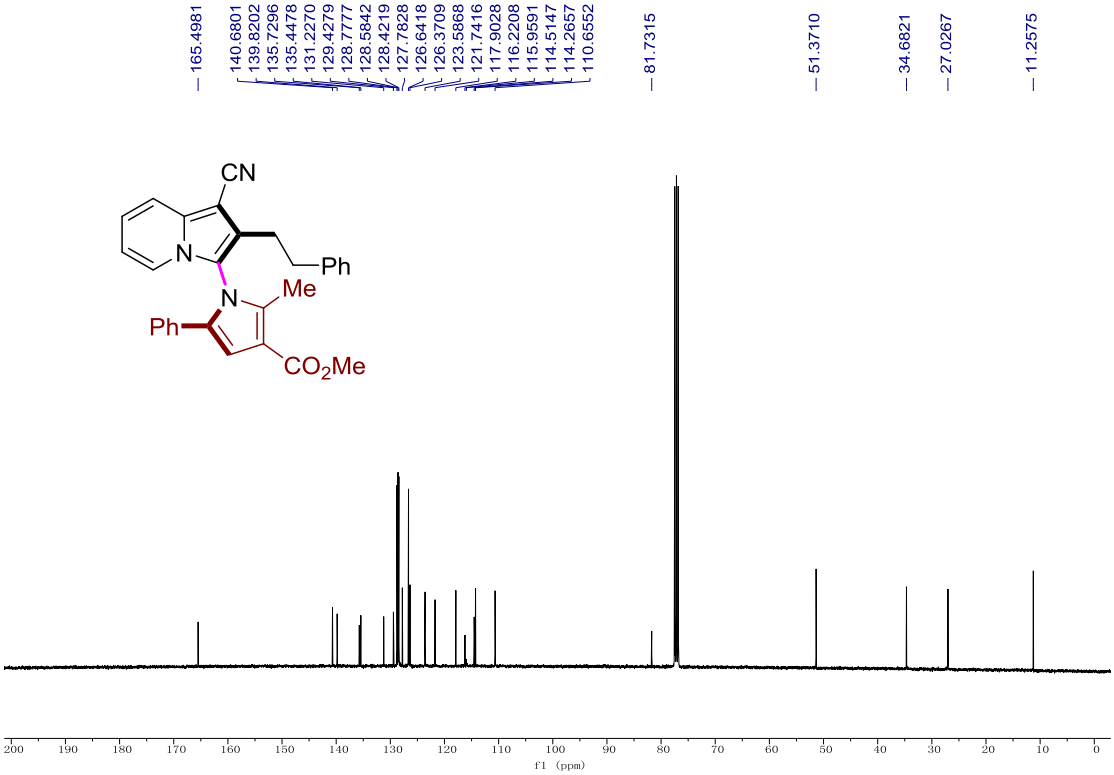


Peak	RetTime	Area	Height	Area
	min	mAU*min	mAU	%
1	11.690	10.098	27.910	94.59
2	18.183	0.578	0.951	5.41

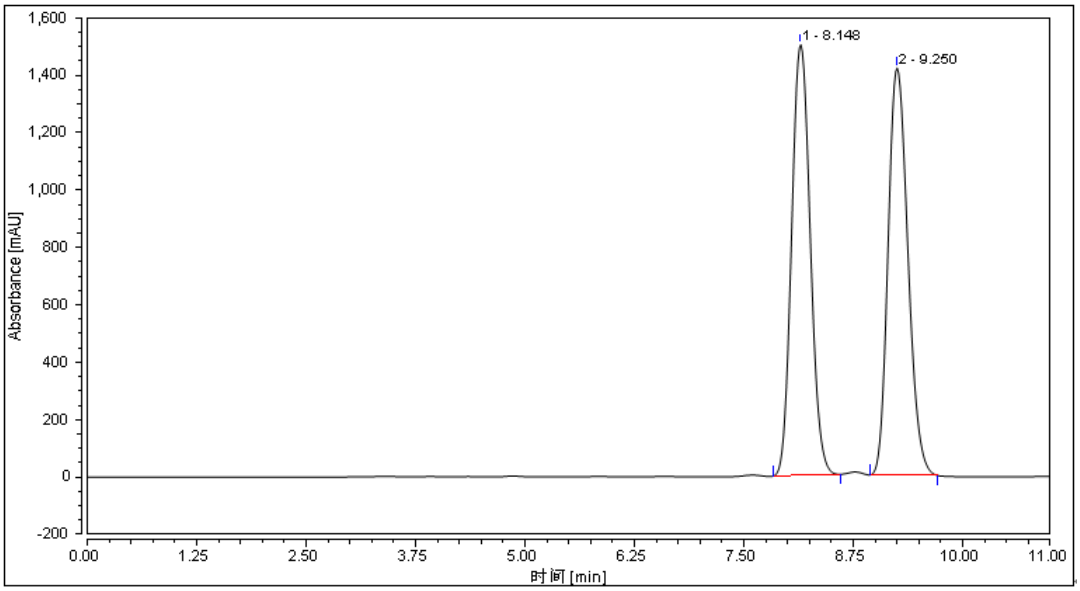
^{1}H NMR of **3s** (400 MHz, $CDCl_3$)



^{13}C NMR of **3s** (100 MHz, $CDCl_3$)

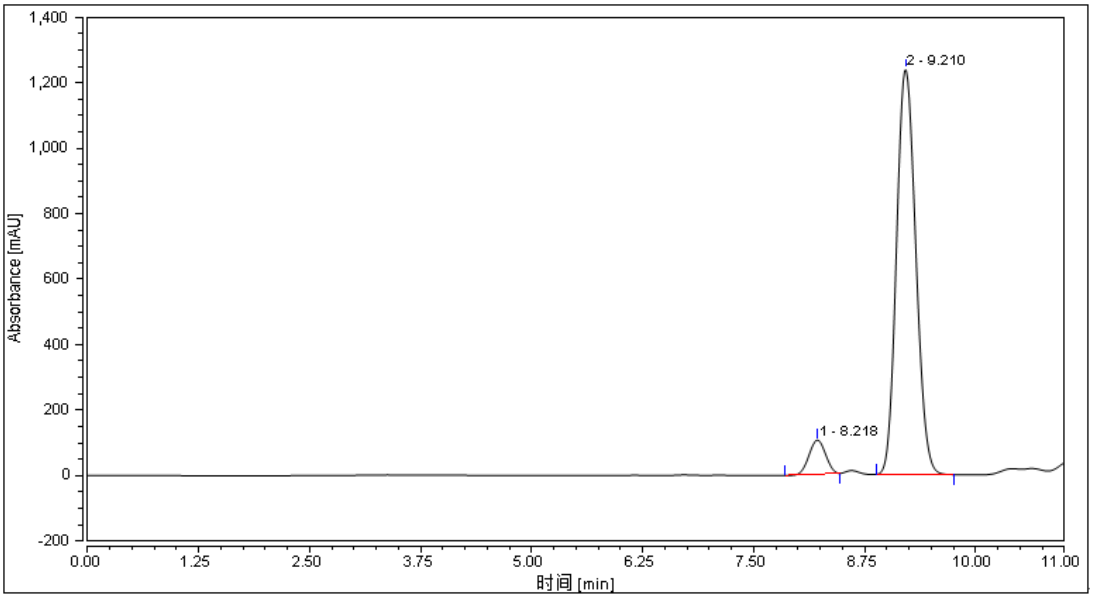


HPLC analysis: rac-**3s**



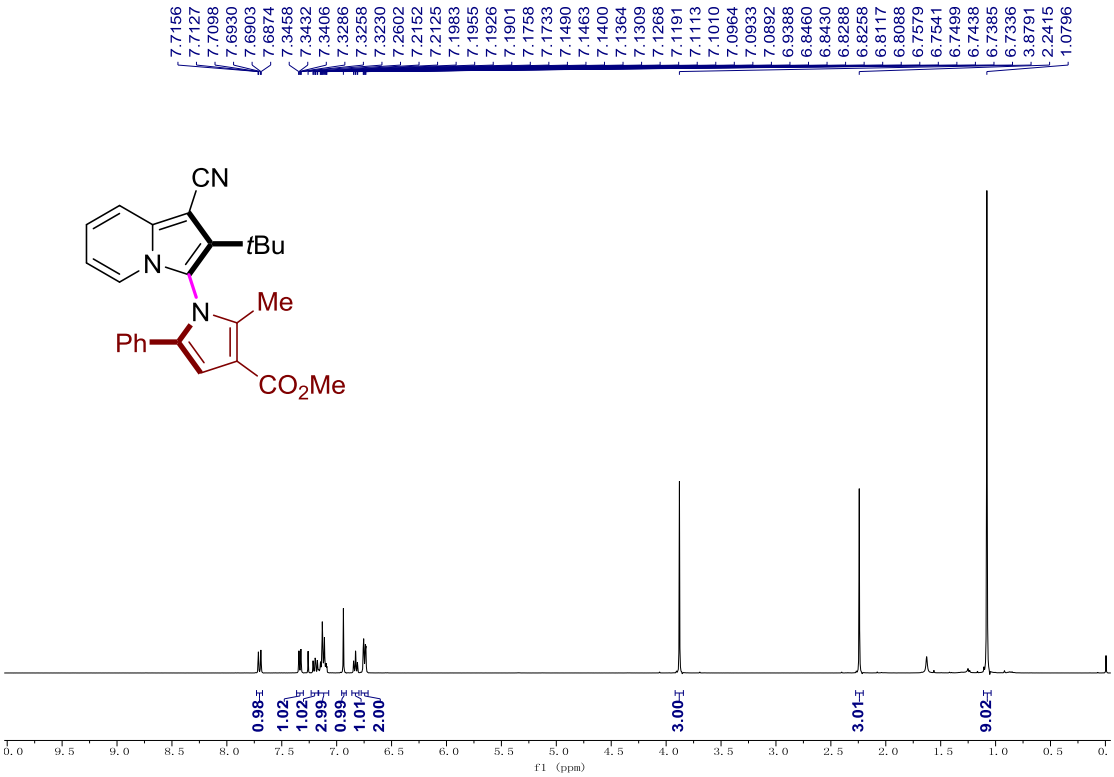
Peak	RetTime	Area	Height	Area
	min	mAU*min	mAU	%
1	8.148	369.777	1501.244	49.86
2	9.250	371.805	1419.169	50.14

Enantioenriched **3s**

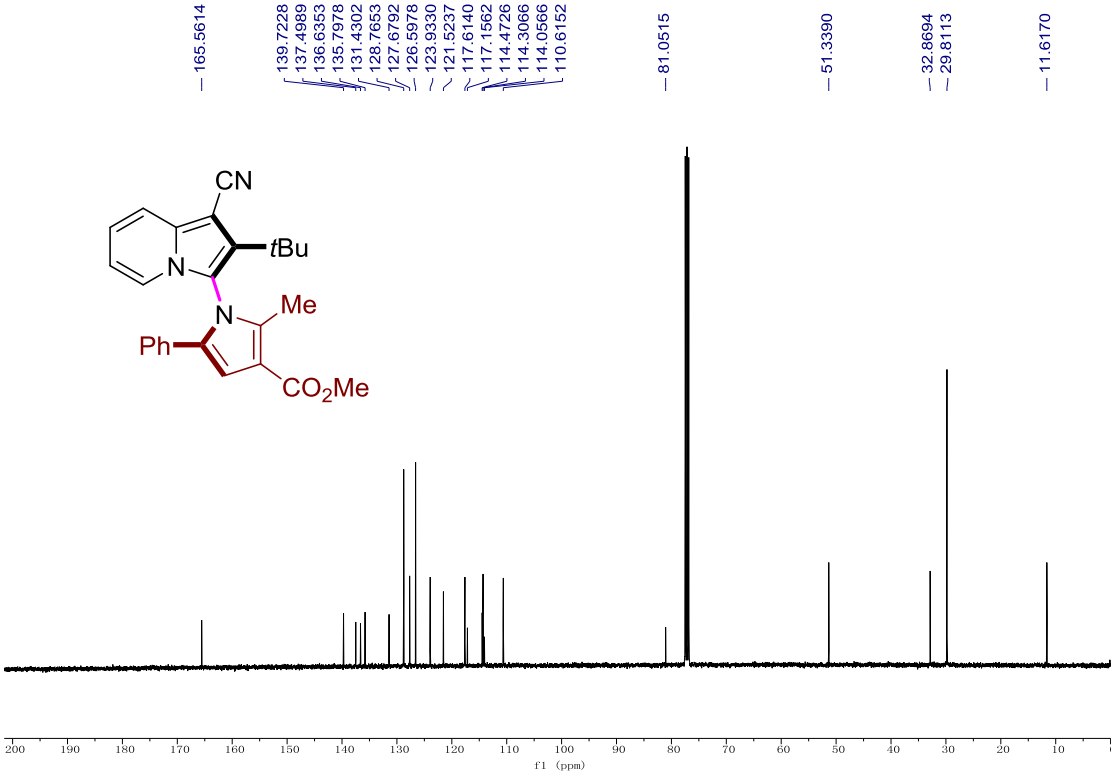


Peak	RetTime	Area	Height	Area
	min	mAU*min	mAU	%
1	8.218	22.539	104.449	6.75
2	9.210	311.307	1238.902	93.25

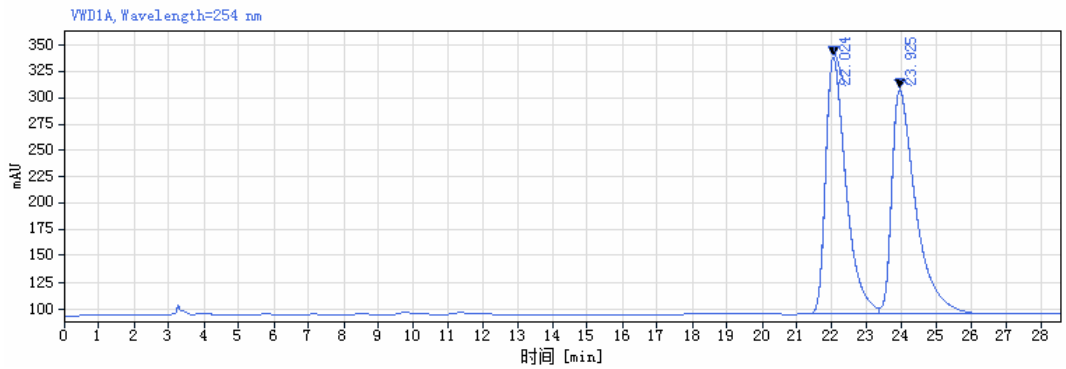
^{1}H NMR of **3t** (400 MHz, $CDCl_3$)



^{13}C NMR of **3t** (100 MHz, $CDCl_3$)

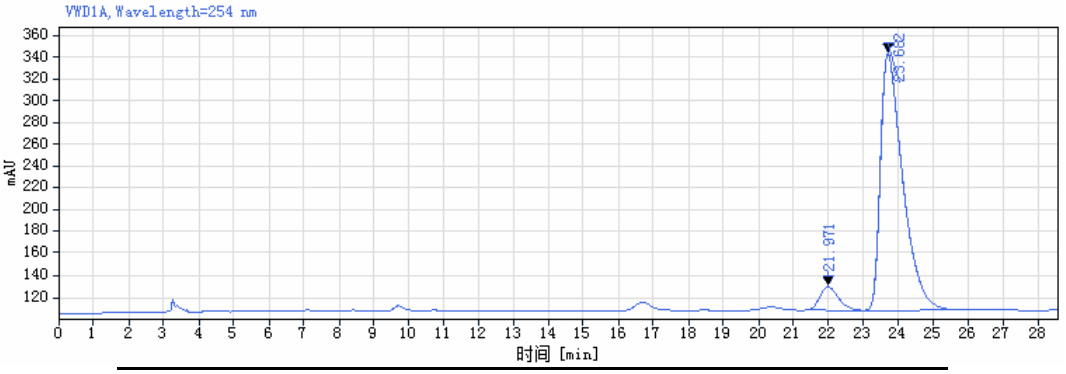


HPLC analysis: rac-**3t**



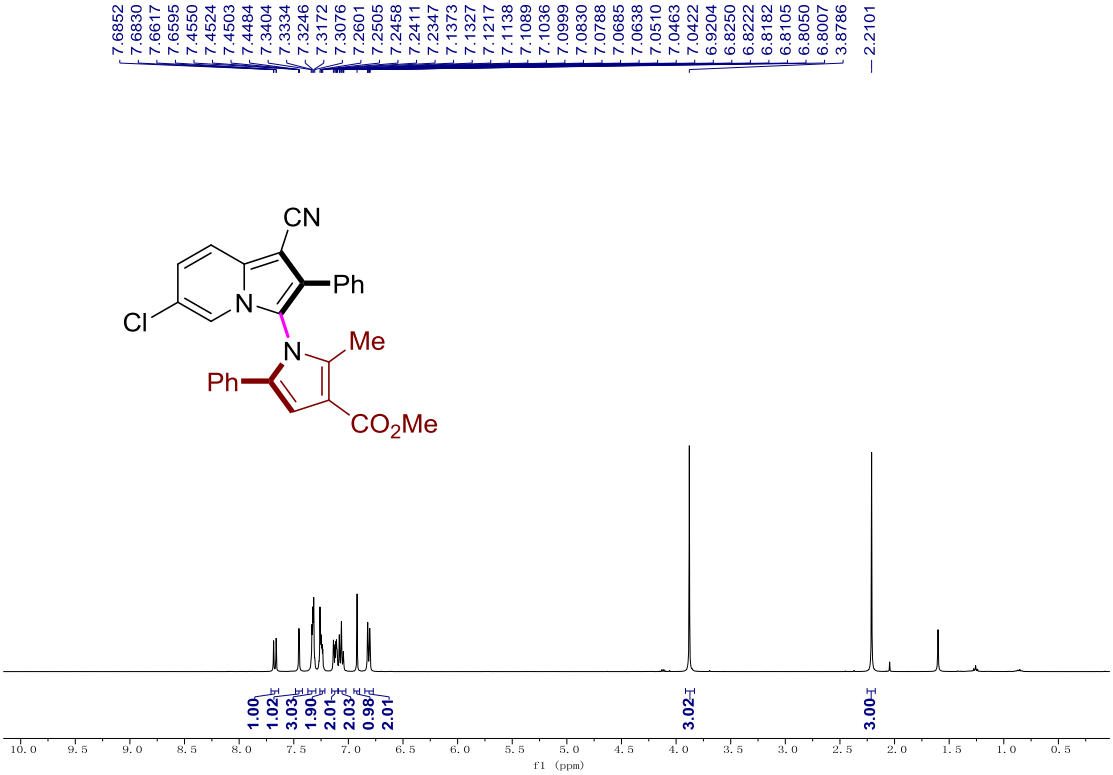
Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	22.024	9859.83	242.85	49.34
2	23.925	10121.8	212.14	50.66

Enantioenriched **3t**

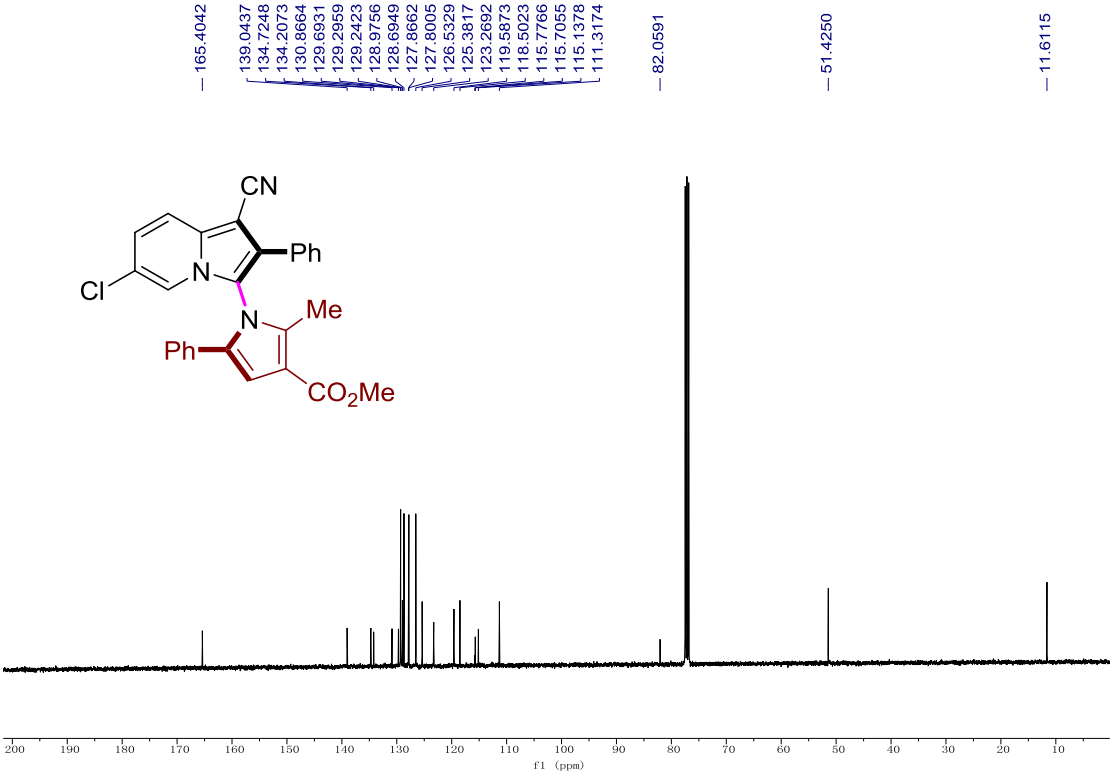


Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	21.971	792.44	21.48	7.06
2	23.682	10431.43	235.21	92.94

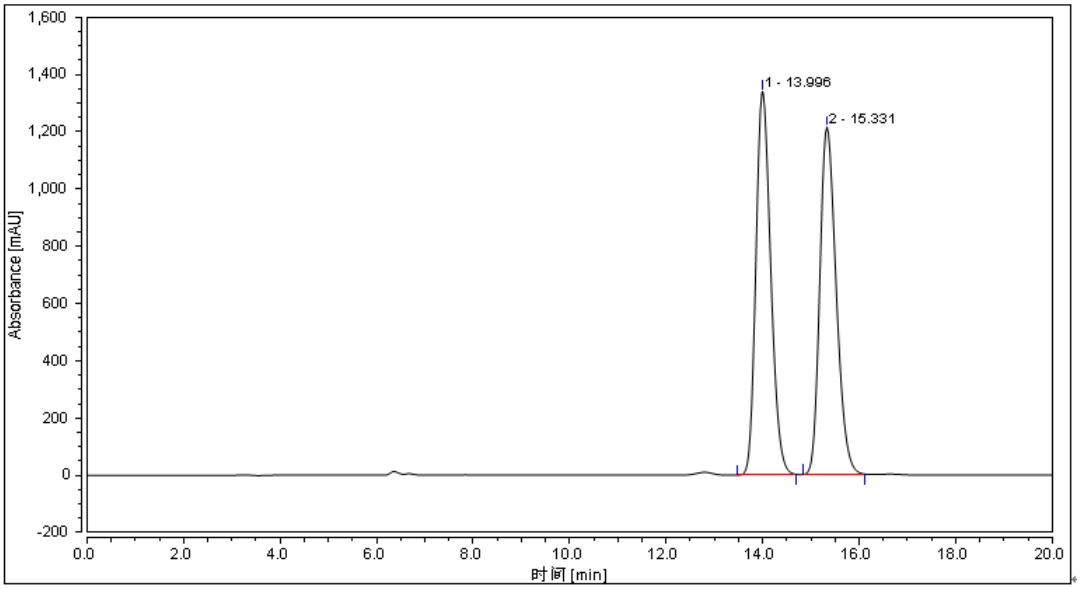
^{1}H NMR of **3u** (400 MHz, $CDCl_3$)



^{13}C NMR of **3u** (100 MHz, $CDCl_3$)

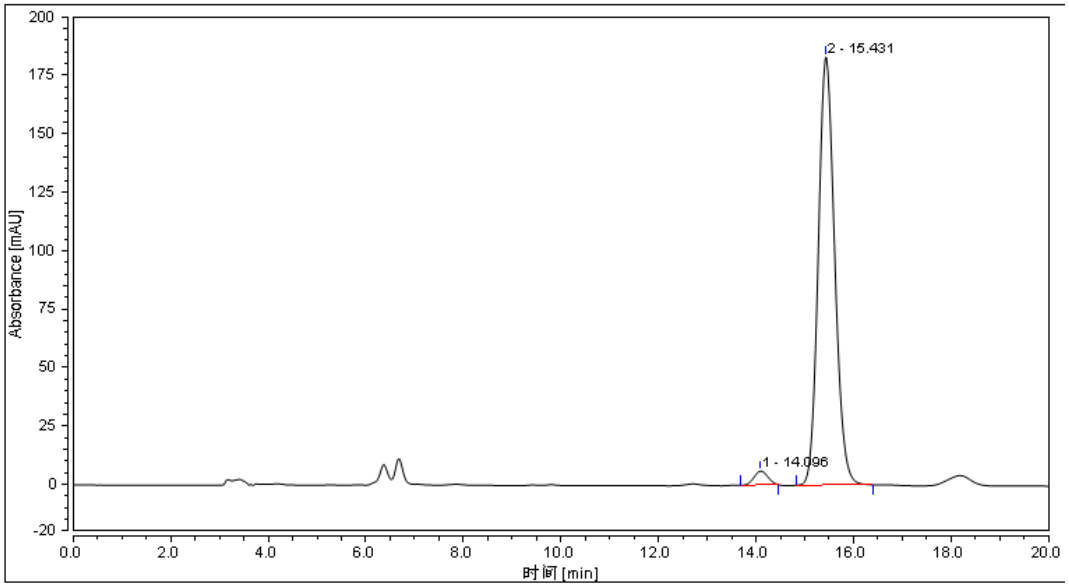


HPLC analysis: rac-**3u**



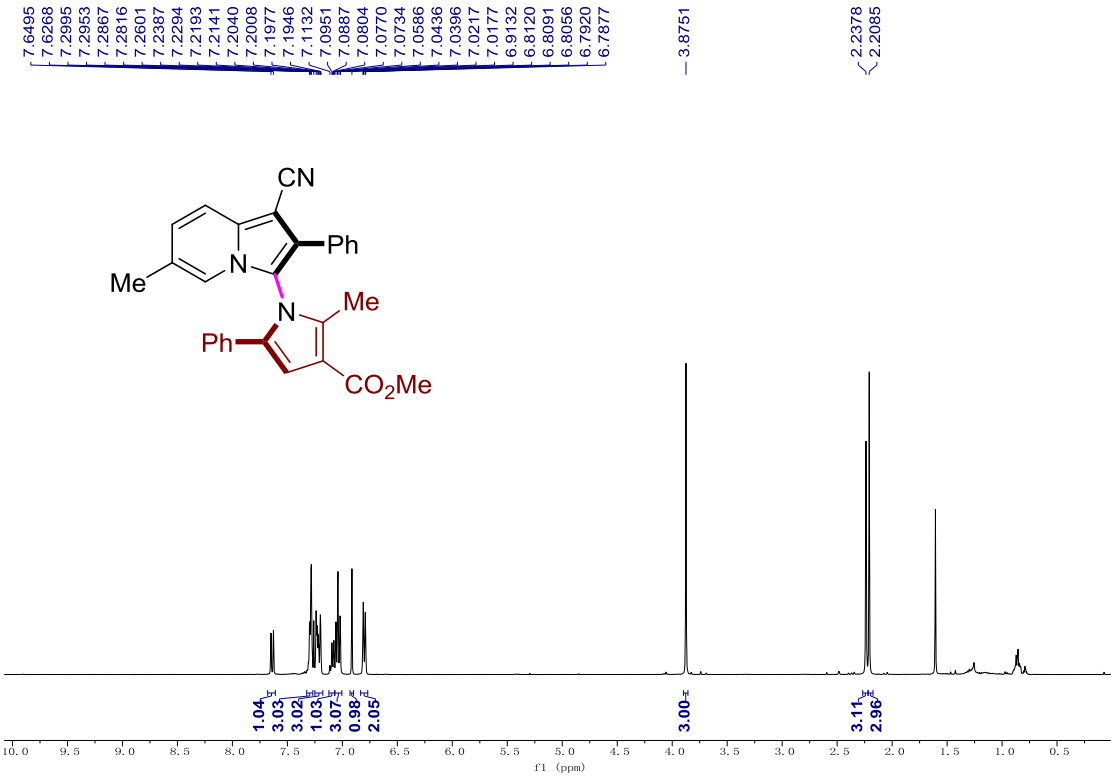
Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	13.996	476.066	1338.962	50.01
2	15.331	475.805	1213.238	49.99

Enantioenriched **3u**

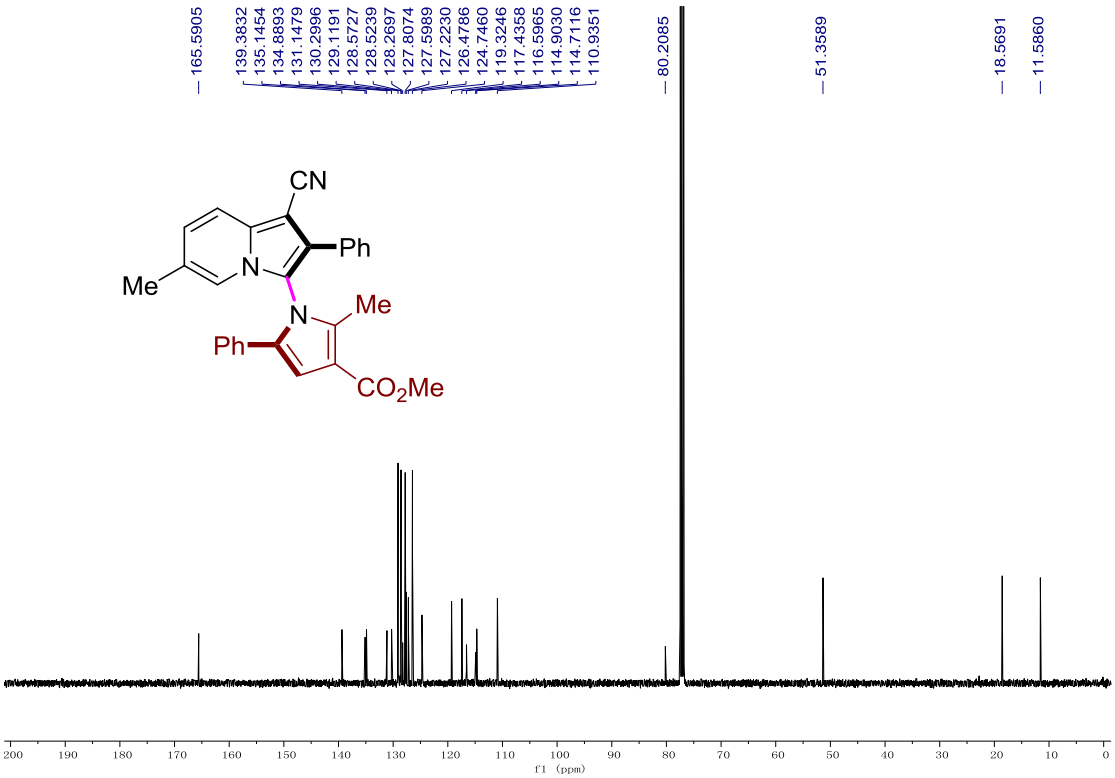


Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	14.096	1.984	6.006	2.71
2	15.431	71.267	183.168	97.29

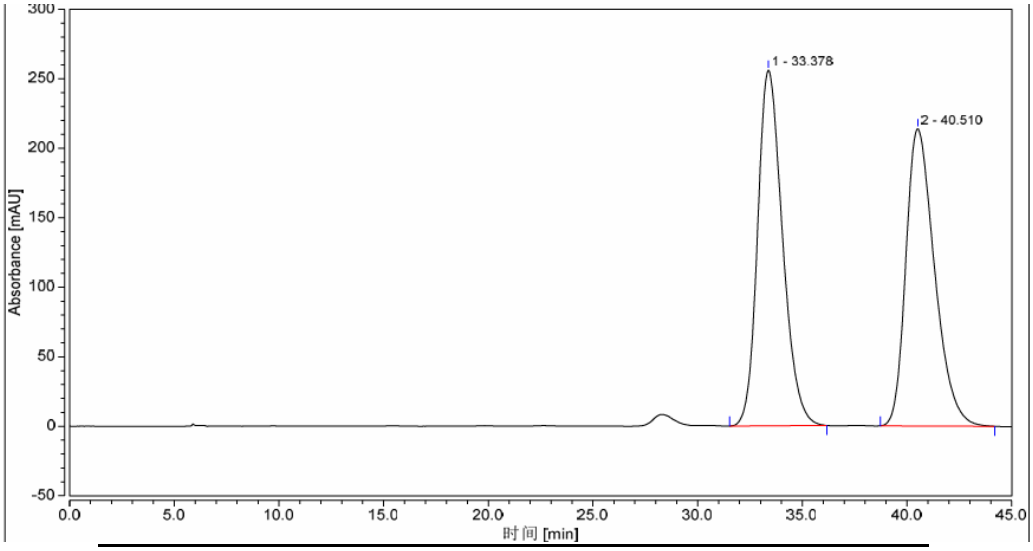
^{1}H NMR of **3v** (400 MHz, $CDCl_3$)



^{13}C NMR of **3v** (100 MHz, $CDCl_3$)

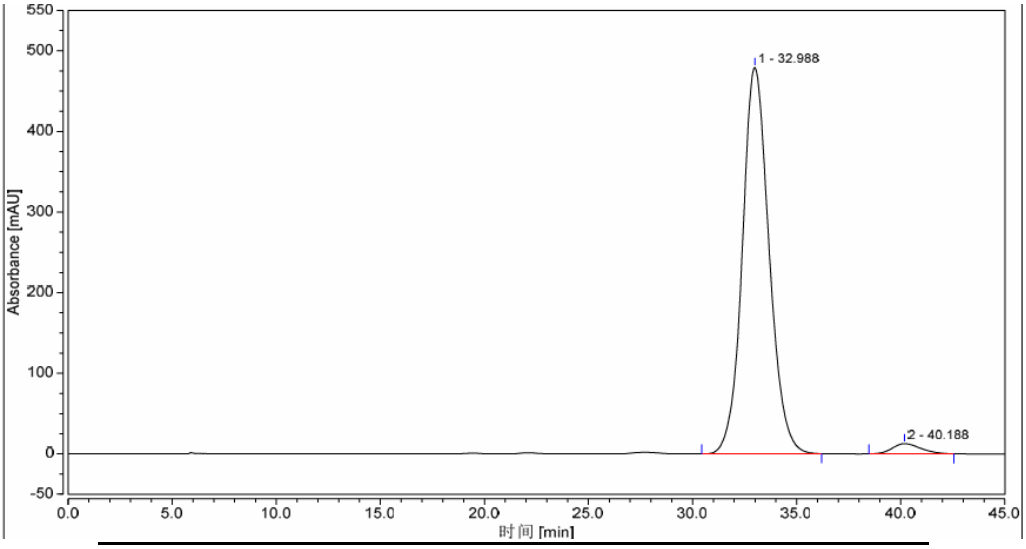


HPLC analysis: rac-**3v**



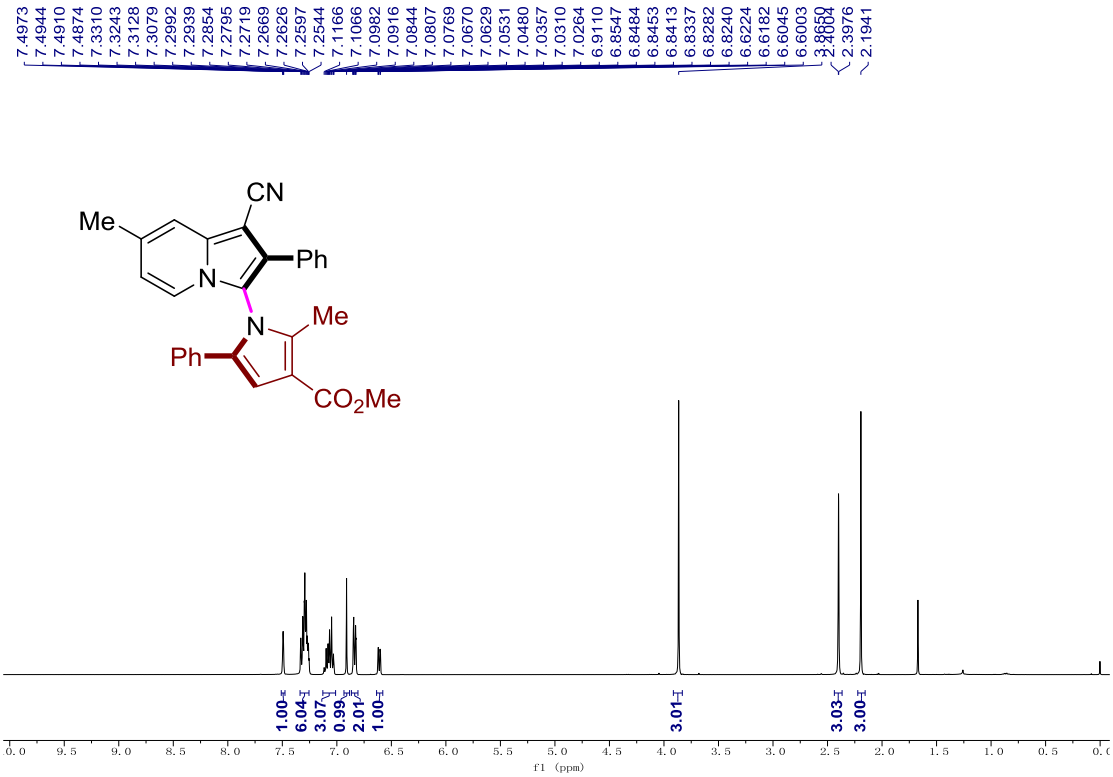
Peak	RetTime	Area	Height	Area
	min	mAU*min	mAU	%
1	33.378	352.881	256.016	50.96
2	40.510	339.590	213.922	49.04

Enantioenriched **3v**

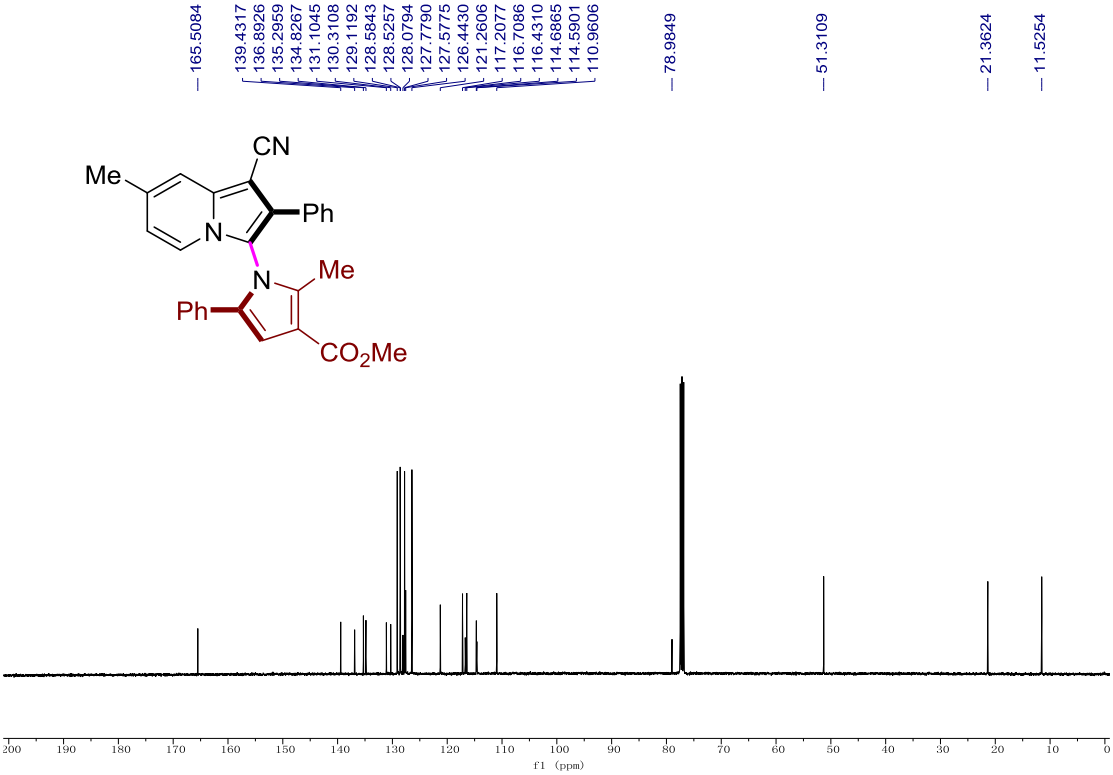


Peak	RetTime	Area	Height	Area
	min	mAU*min	mAU	%
1	32.988	708.650	478.541	97.18
2	40.188	20.544	12.689	2.82

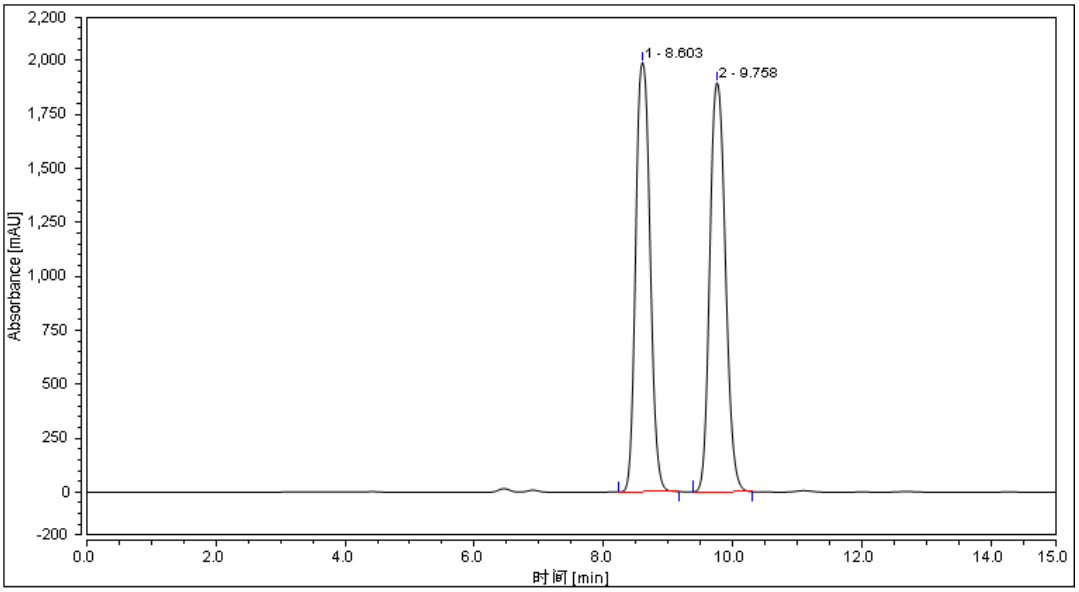
^{1}H NMR of **3w** (400 MHz, $CDCl_3$)



^{13}C NMR of **3w** (100 MHz, $CDCl_3$)

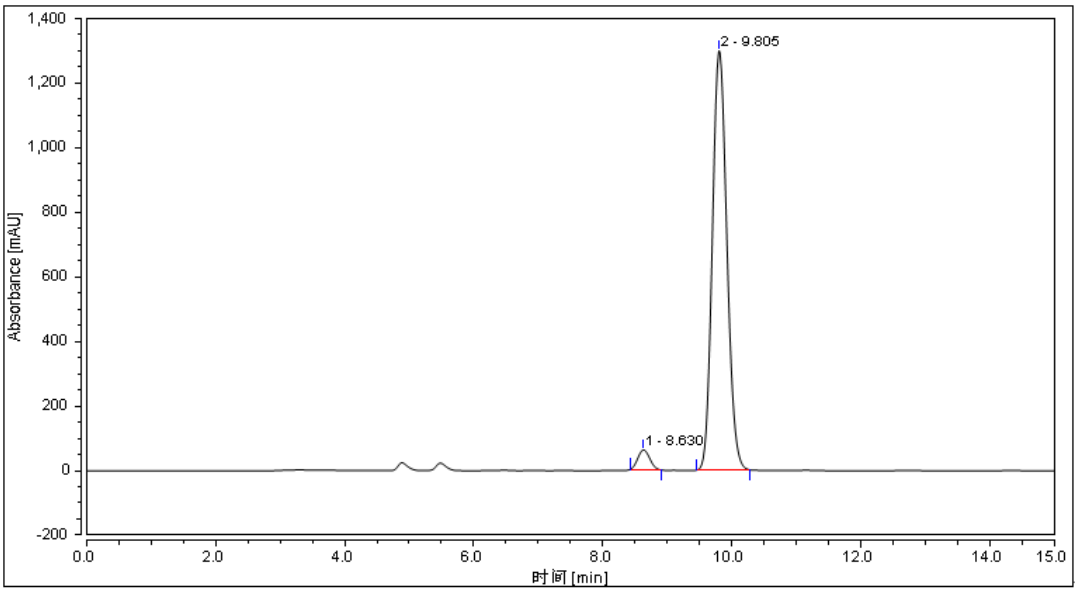


HPLC analysis: rac-**3w**



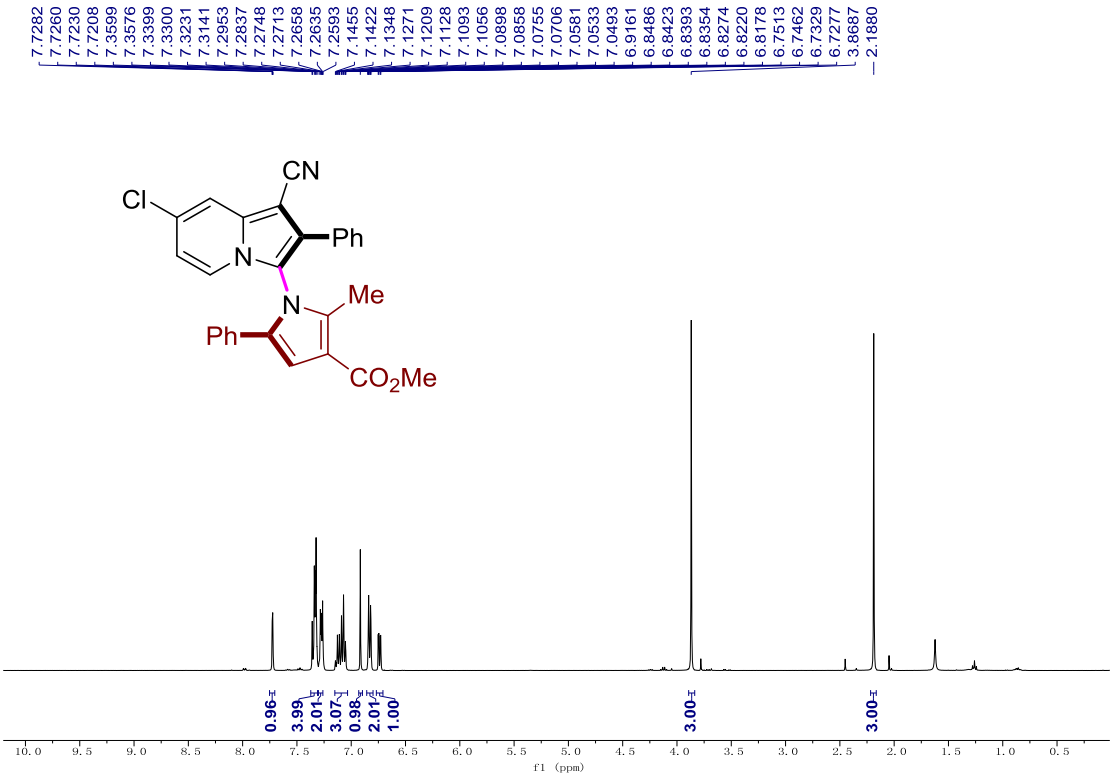
Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	8.603	512.052	1989.567	49.10
2	9.758	530.742	1897.058	50.90

Enantioenriched **3w**

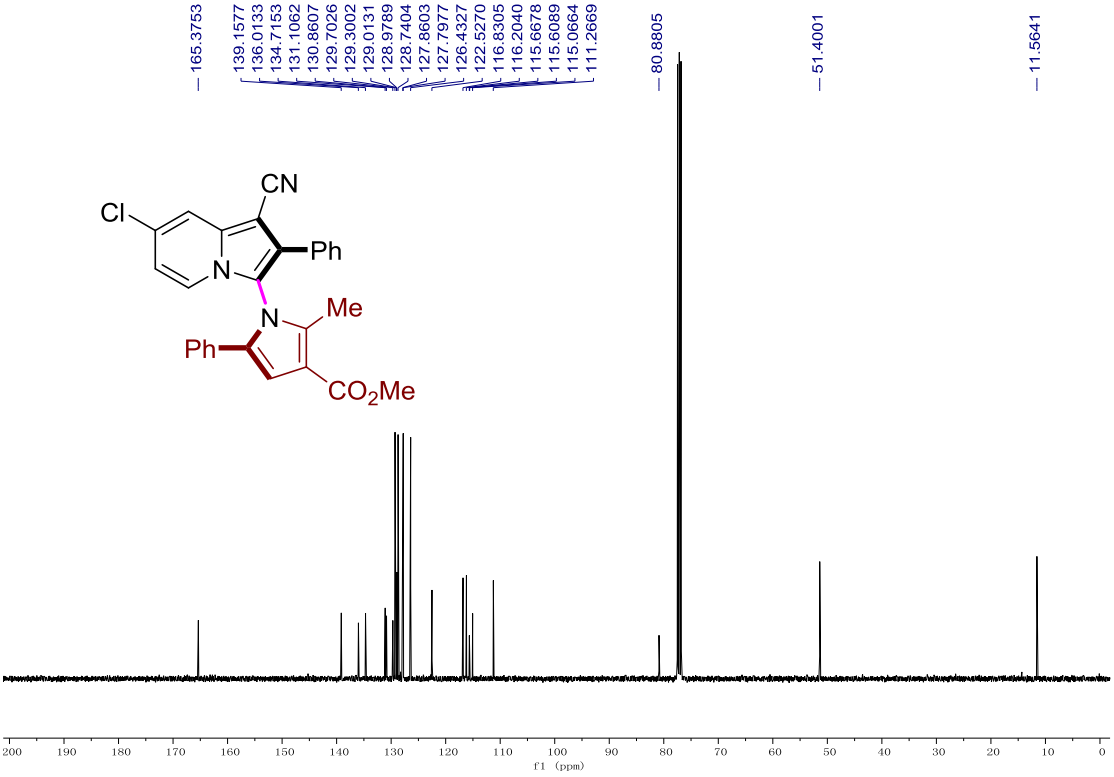


Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	8.630	13.026	61.246	3.71
2	9.805	338.524	1298.134	96.29

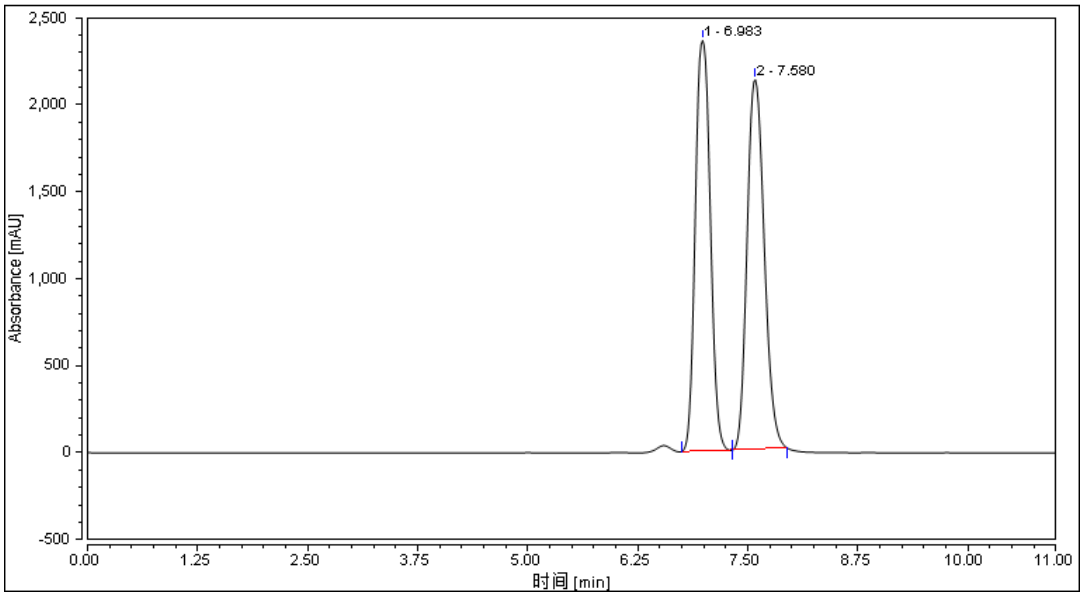
^{1}H NMR of **3x** (400 MHz, $CDCl_3$)



^{13}C NMR of **3x** (100 MHz, $CDCl_3$)

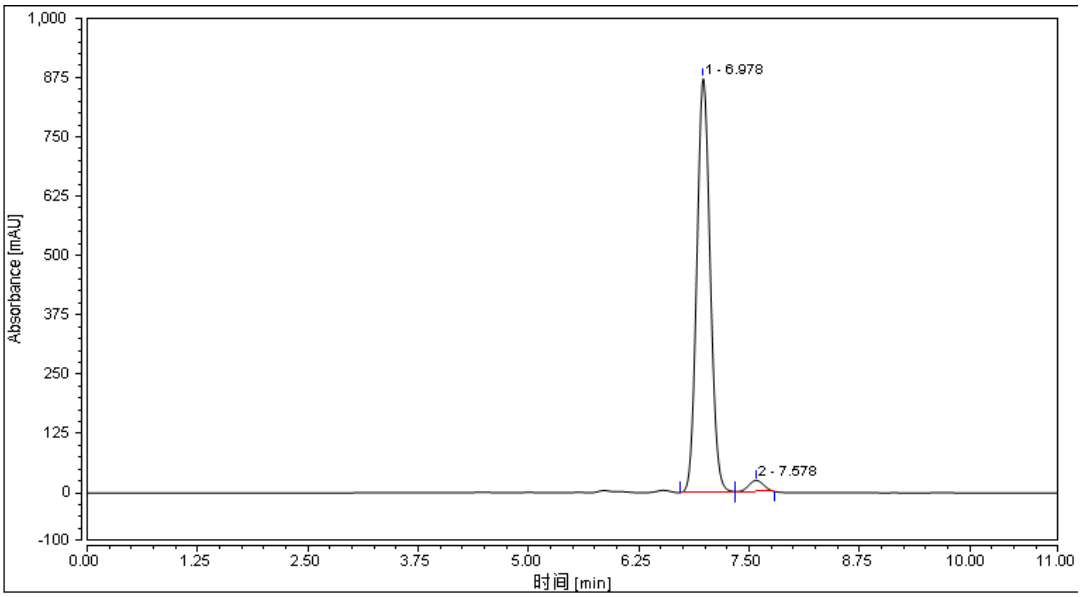


HPLC analysis: rac-**3x**



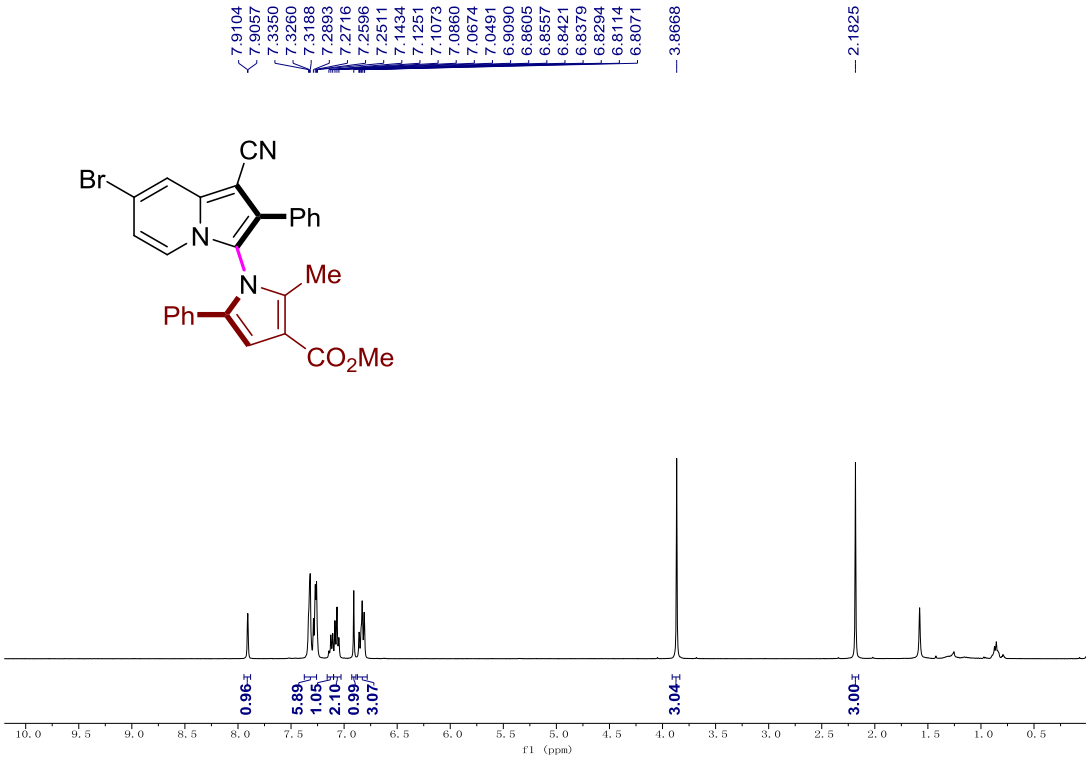
Peak	RetTime	Area	Height	Area
	min	mAU*min	mAU	%
1	6.983	466.608	2360.957	49.31
2	7.580	479.629	2126.426	50.69

Enantioenriched **3x**

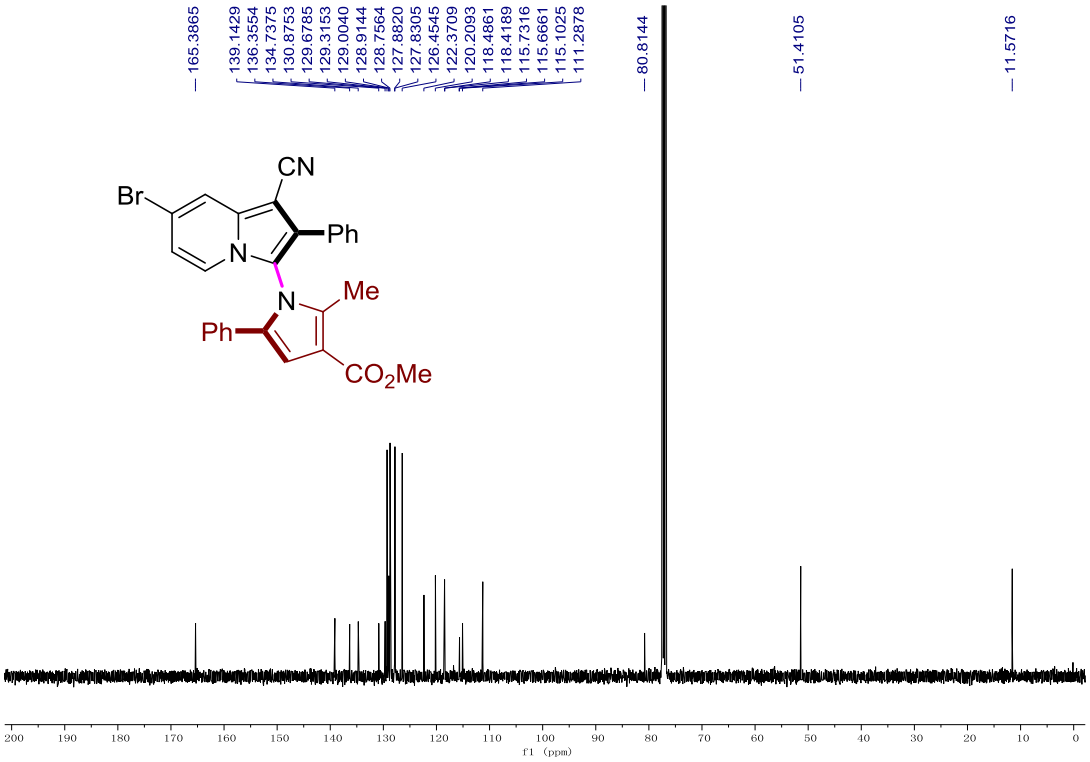


Peak	RetTime	Area	Height	Area
	min	mAU*min	mAU	%
1	6.970	139.973	783.087	96.89
2	7.568	4.499	22.315	3.11

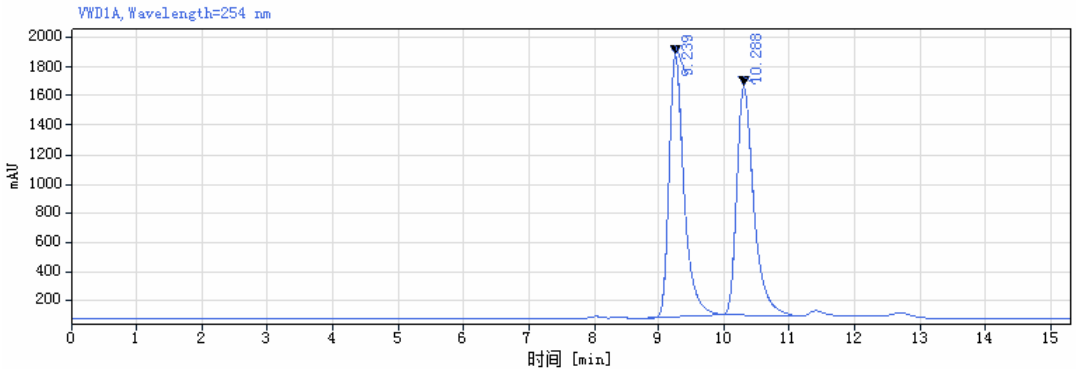
^{1}H NMR of **3y** (400 MHz, $CDCl_3$)



^{13}C NMR of **3y** (100 MHz, $CDCl_3$)

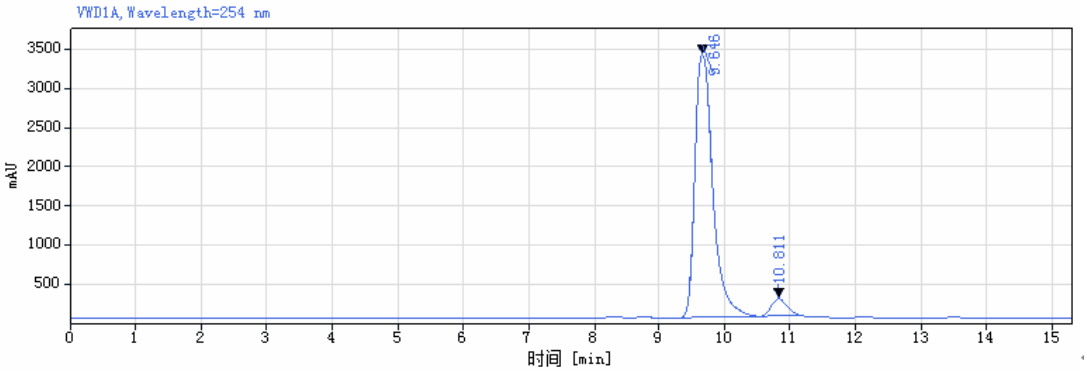


HPLC analysis: rac-**3y**



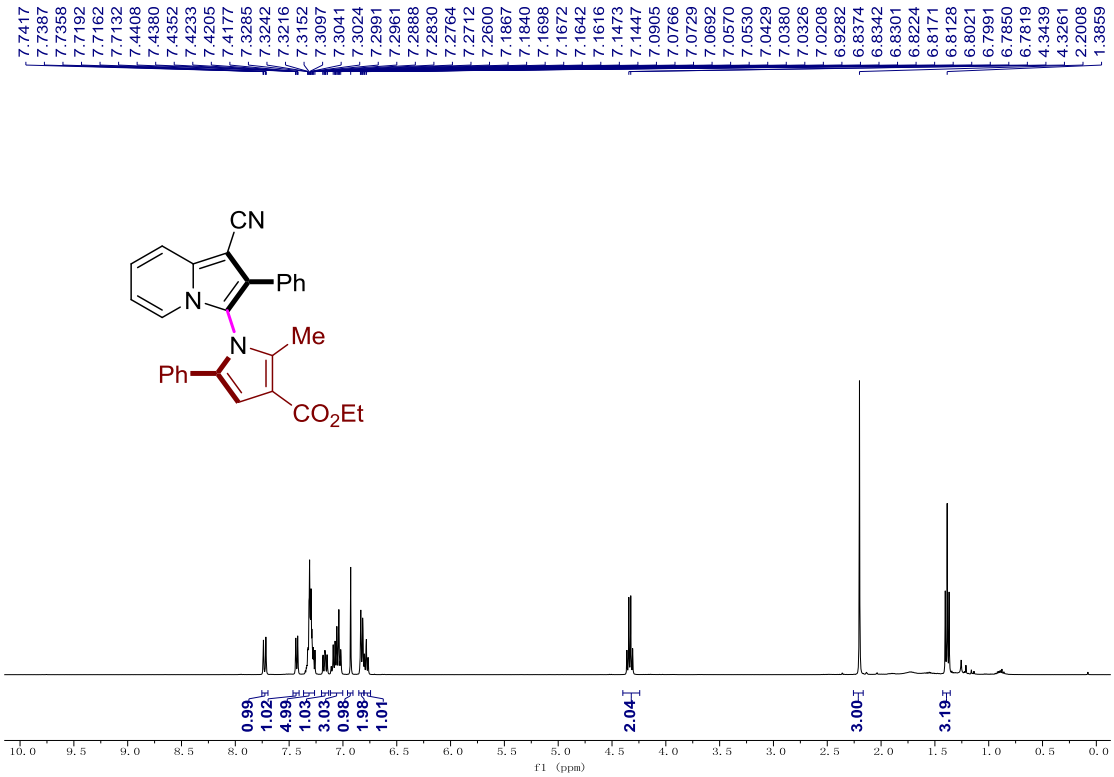
Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	9.239	28383.95	1782.35	50.1
2	10.288	28267.77	1577.01	49.9

Enantioenriched **3y**

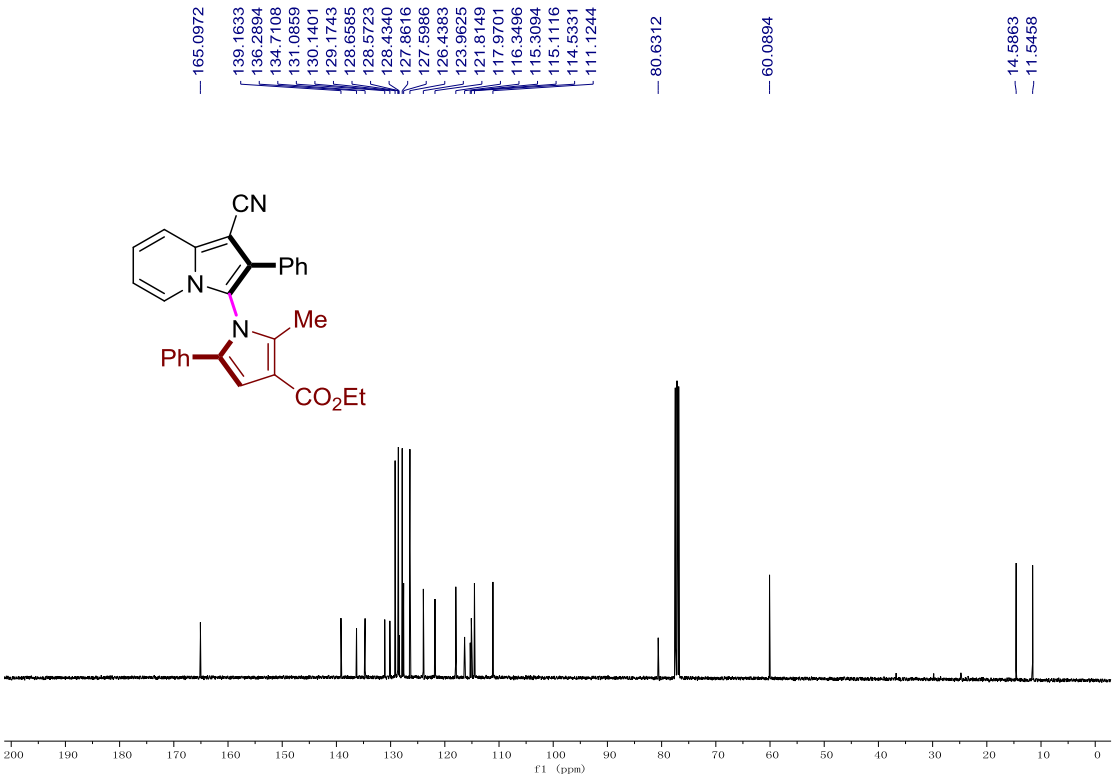


Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	9.646	63635.68	3343.04	94.7
2	10.811	3562.61	214.95	5.3

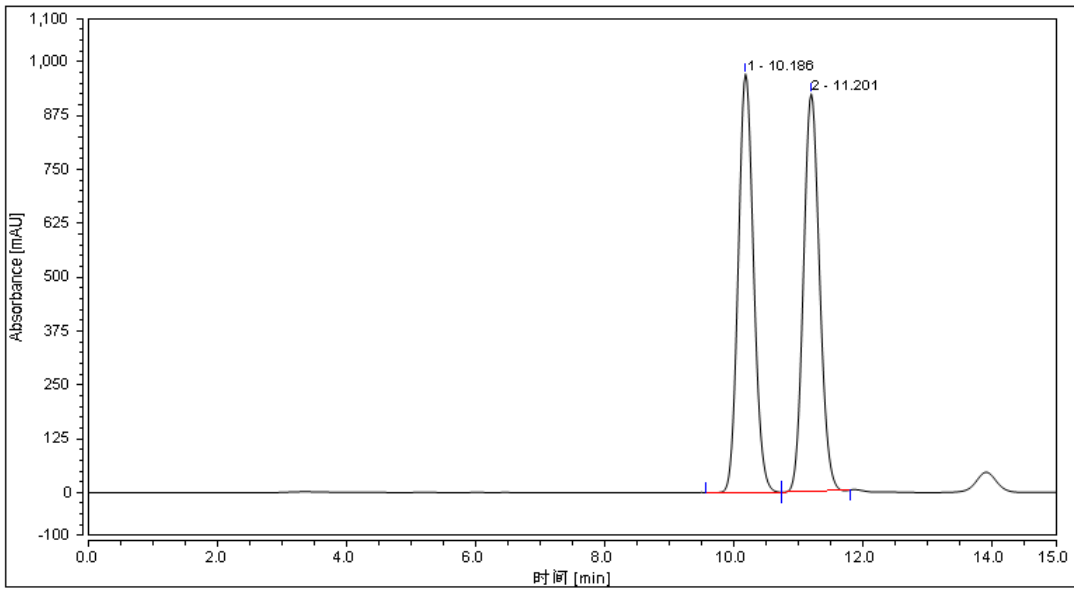
^{1}H NMR of **3z** (400 MHz, $CDCl_3$)



^{13}C NMR of **3z** (100 MHz, $CDCl_3$)

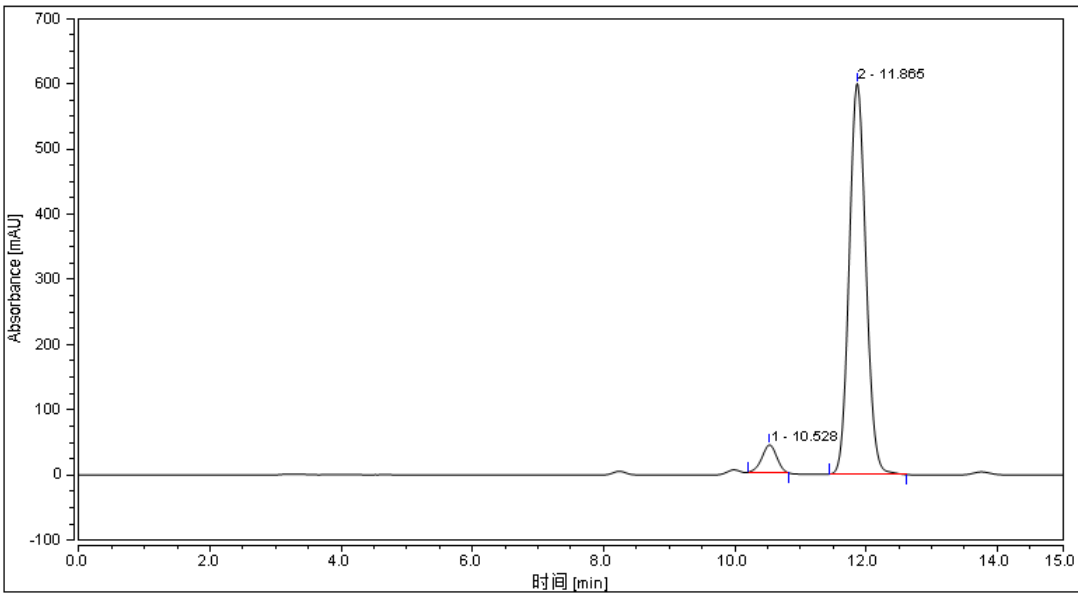


HPLC analysis: rac-**3z**



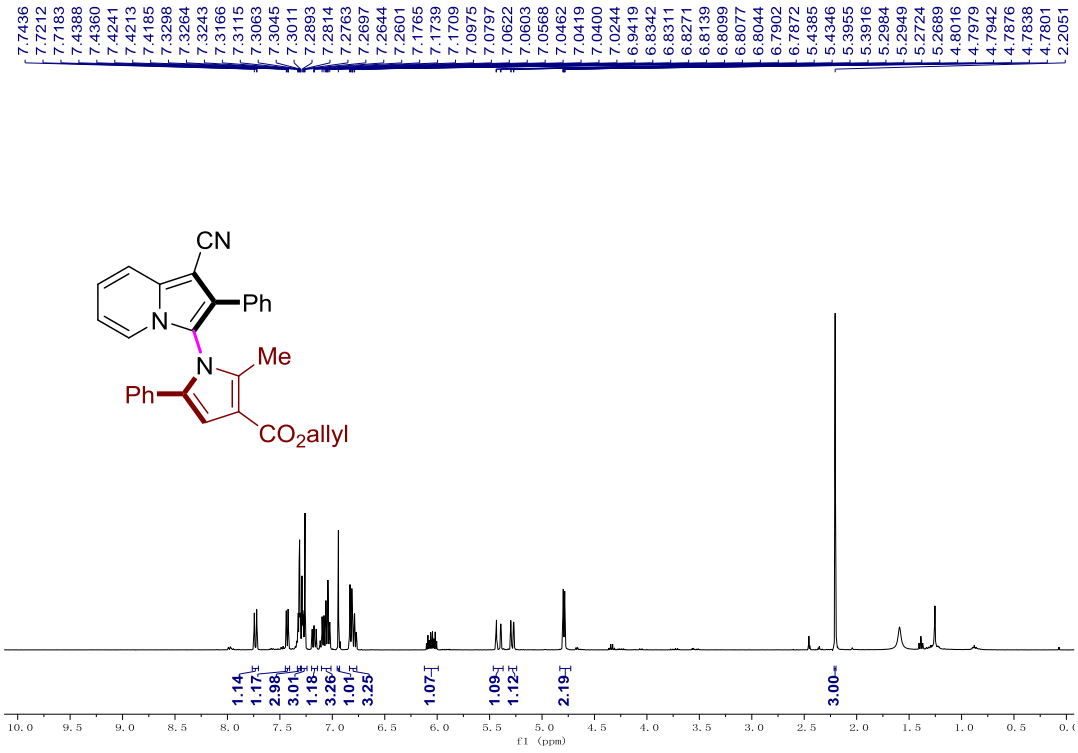
Peak	RetTime	Area	Height	Area
	min	mAU*min	mAU	%
1	10.186	268.003	971.689	50.19
2	11.201	265.932	922.788	49.81

Enantioenriched **3z**

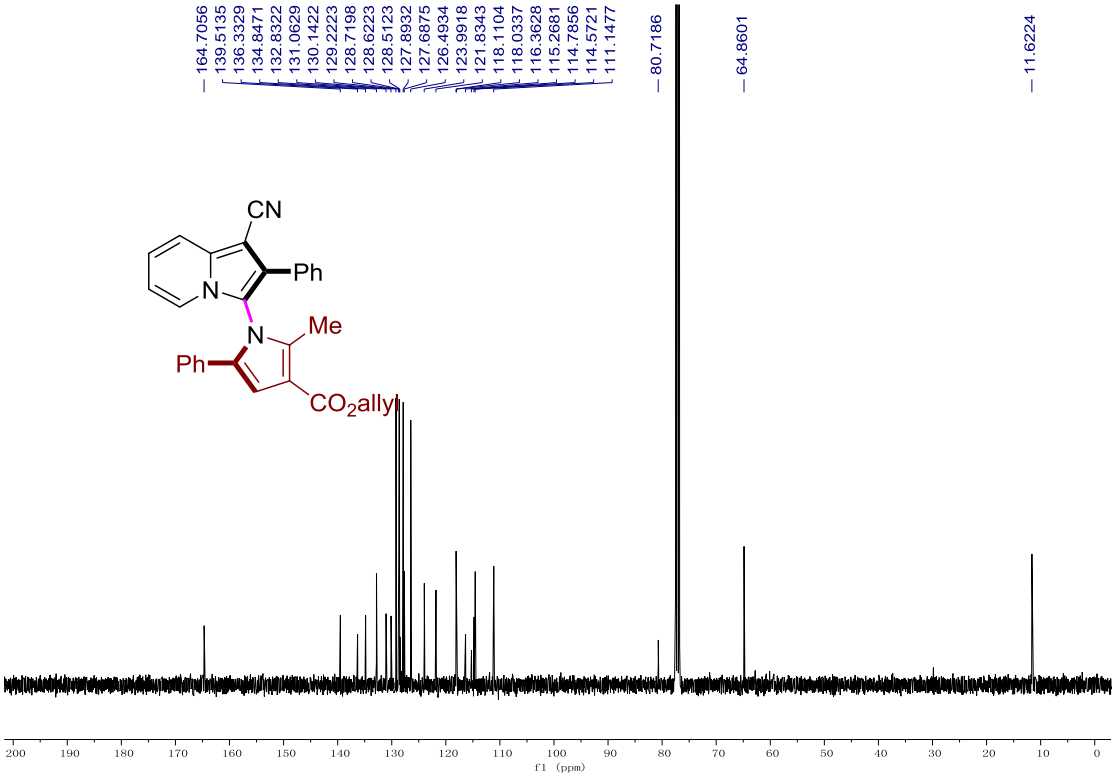


Peak	RetTime	Area	Height	Area
	min	mAU*min	mAU	%
1	10.528	11.119	42.432	5.92
2	11.865	176.670	599.539	94.08

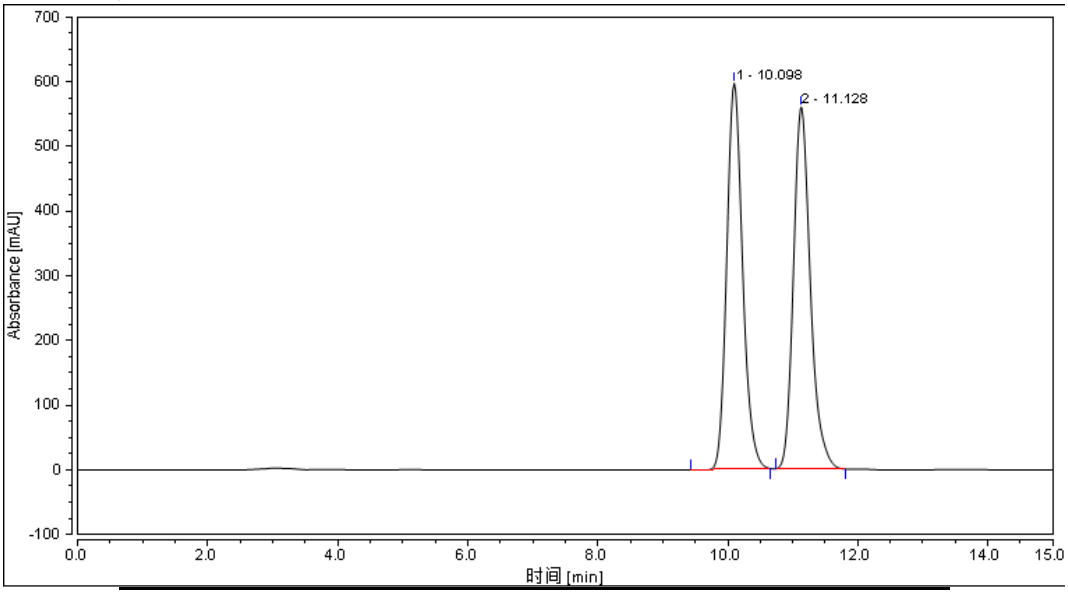
^{1}H NMR of **3aa** (400 MHz, $CDCl_3$)



^{13}C NMR of **3aa** (100 MHz, $CDCl_3$)

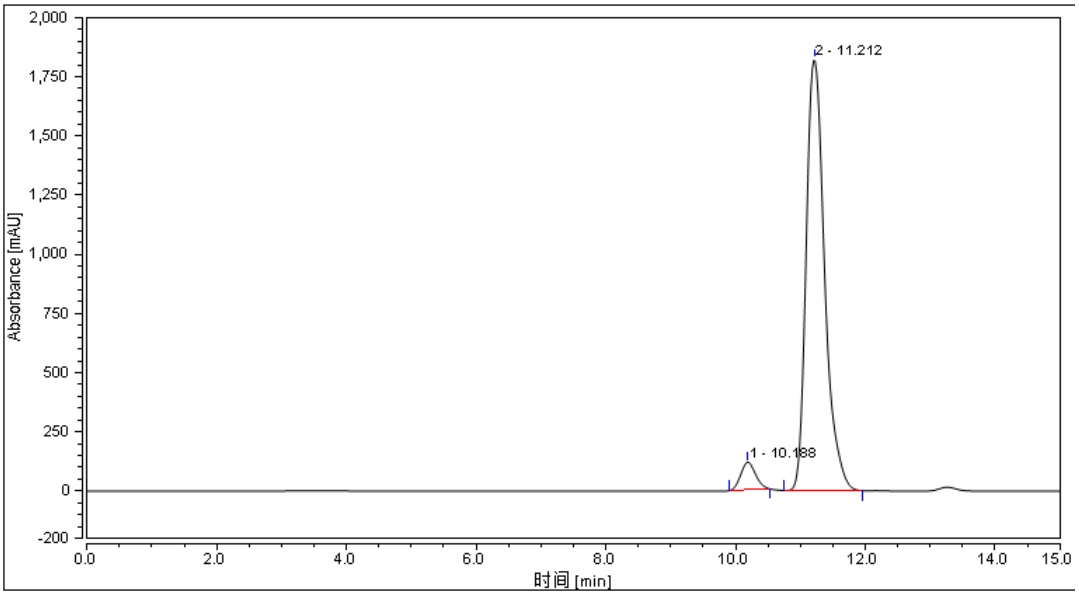


HPLC analysis: rac-**3aa**



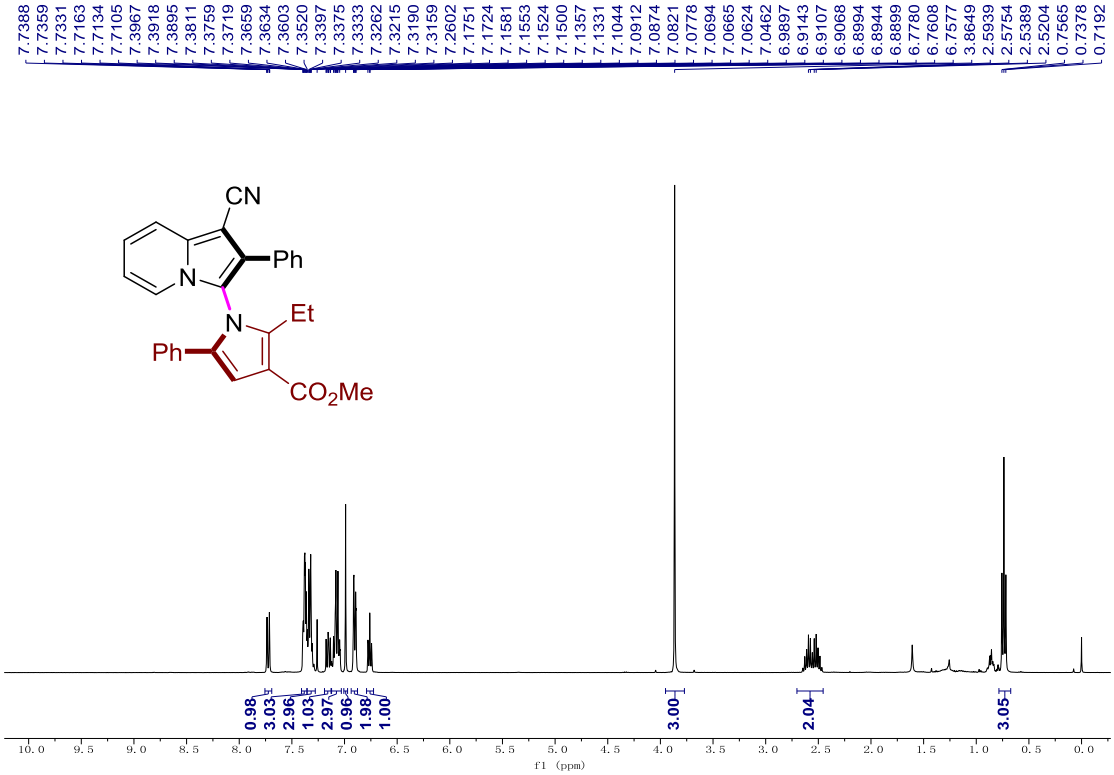
Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	10.098	168.147	596.689	49.95
2	11.128	168.507	559.237	50.05

Enantioenriched **3aa**

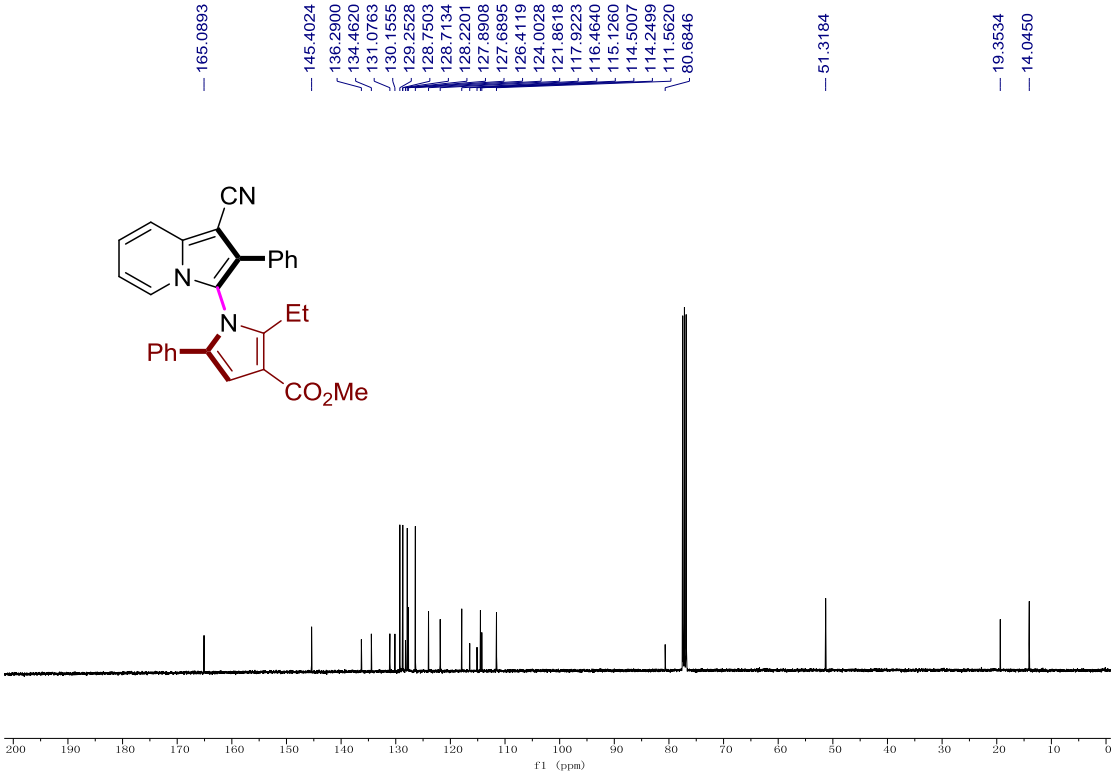


Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	10.188	30.716	116.540	4.88
2	11.212	599.213	1820.046	95.12

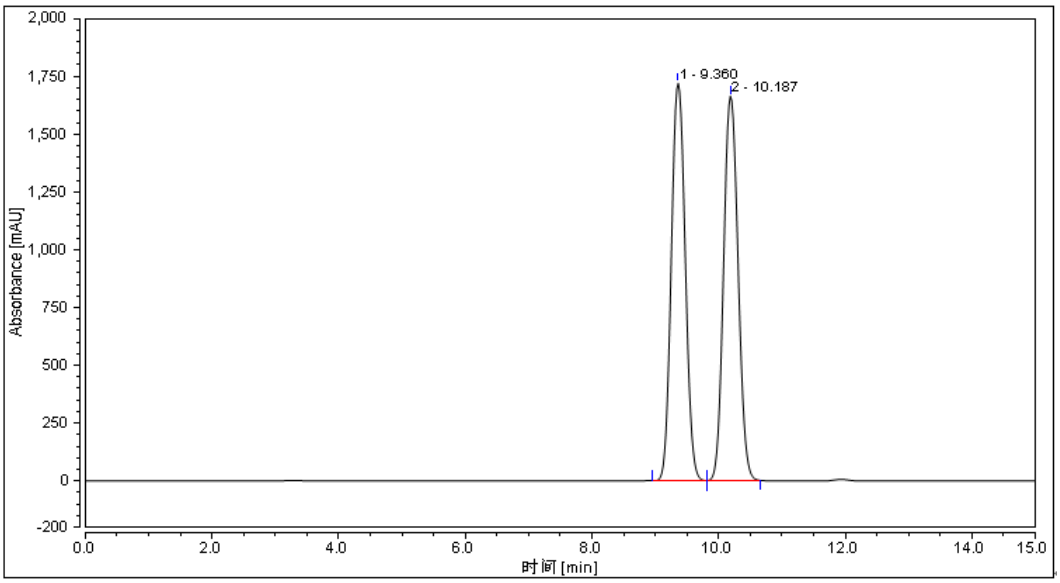
^{1}H NMR of **3ab** (400 MHz, $CDCl_3$)



^{13}C NMR of **3ab** (100 MHz, $CDCl_3$)

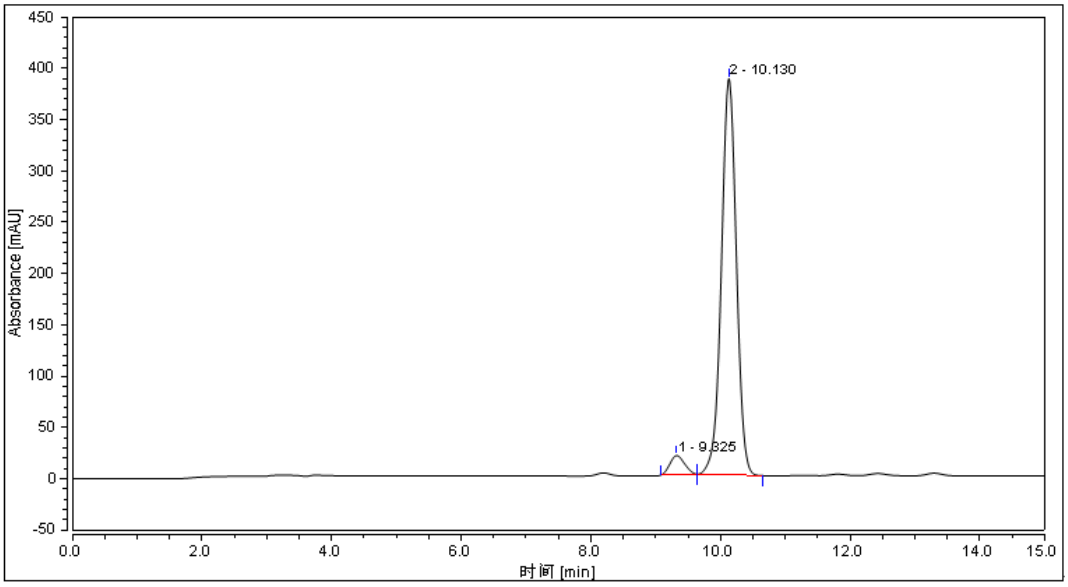


HPLC analysis: rac-**3ab**



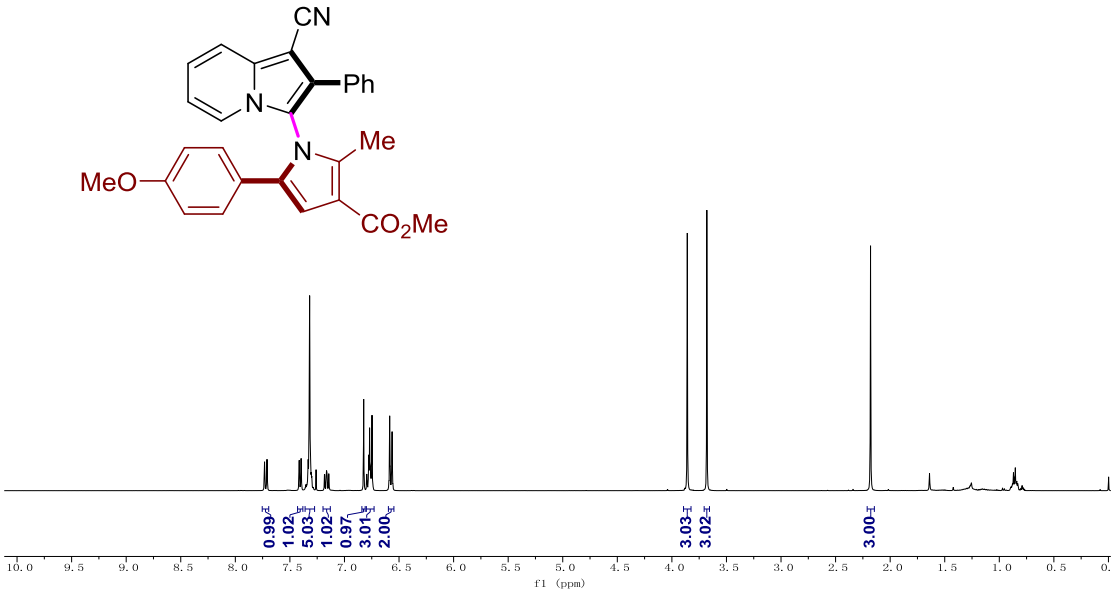
Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	9.360	436.802	1718.820	49.84
2	10.187	439.548	1663.215	50.16

Enantioenriched **3ab**

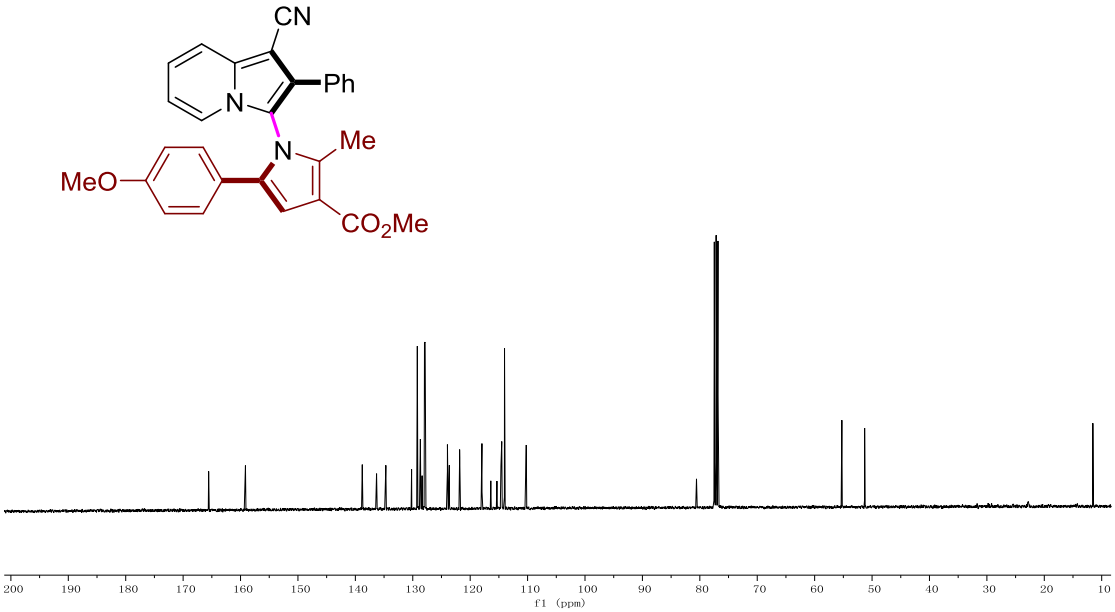


Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	9.325	4.923	18.795	4.54
2	10.130	103.514	386.591	95.46

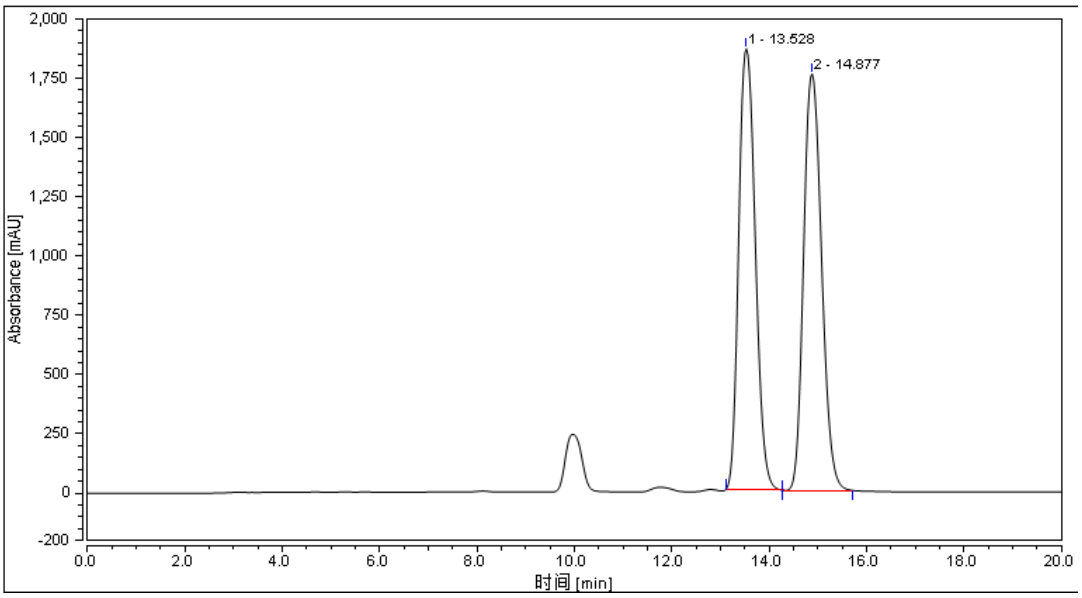
^{1}H NMR of **3ac** (400 MHz, $CDCl_3$)



^{13}C NMR of **3ac** (100 MHz, $CDCl_3$)

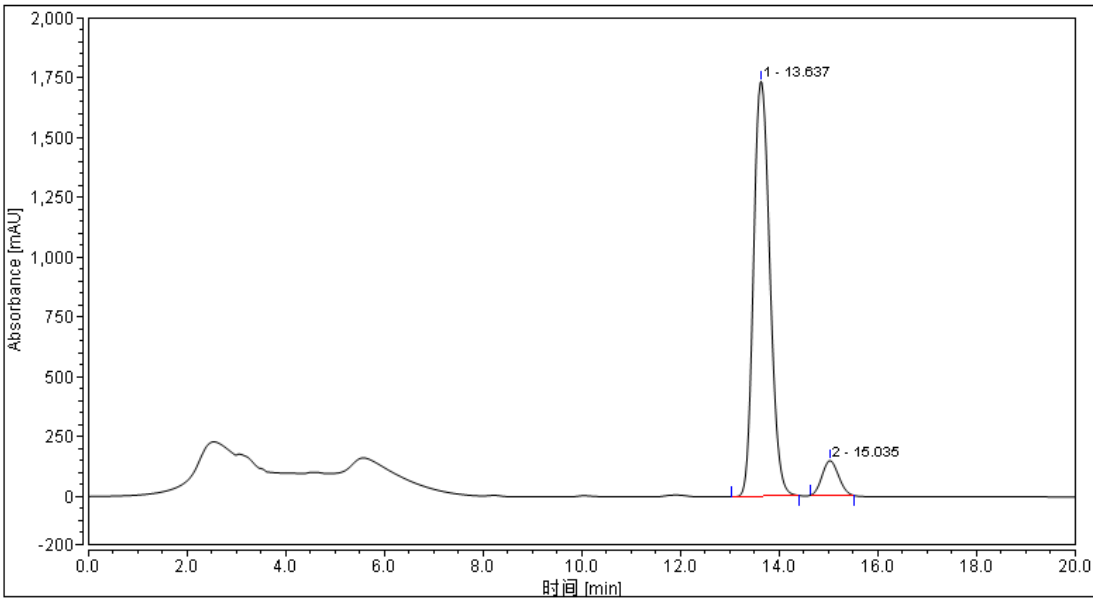


HPLC analysis: rac-**3ac**



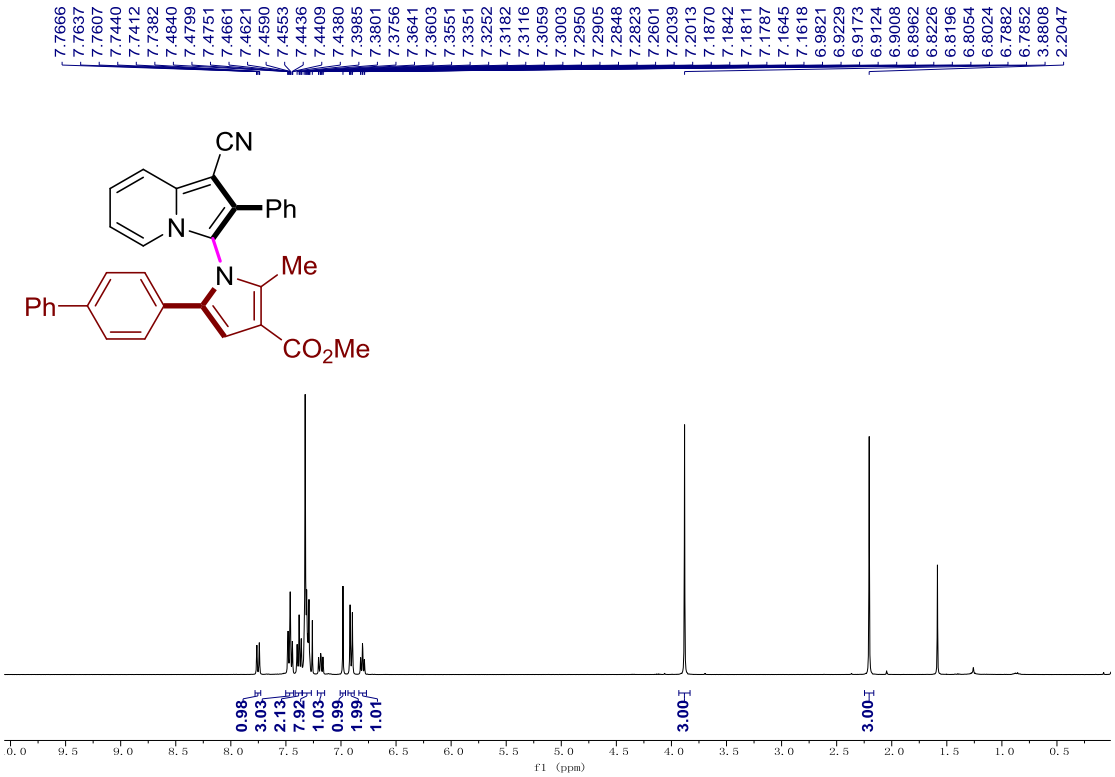
Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	13.528	733.559	1860.391	49.43
2	14.877	750.405	1756.816	50.57

Enantioenriched **3ac**

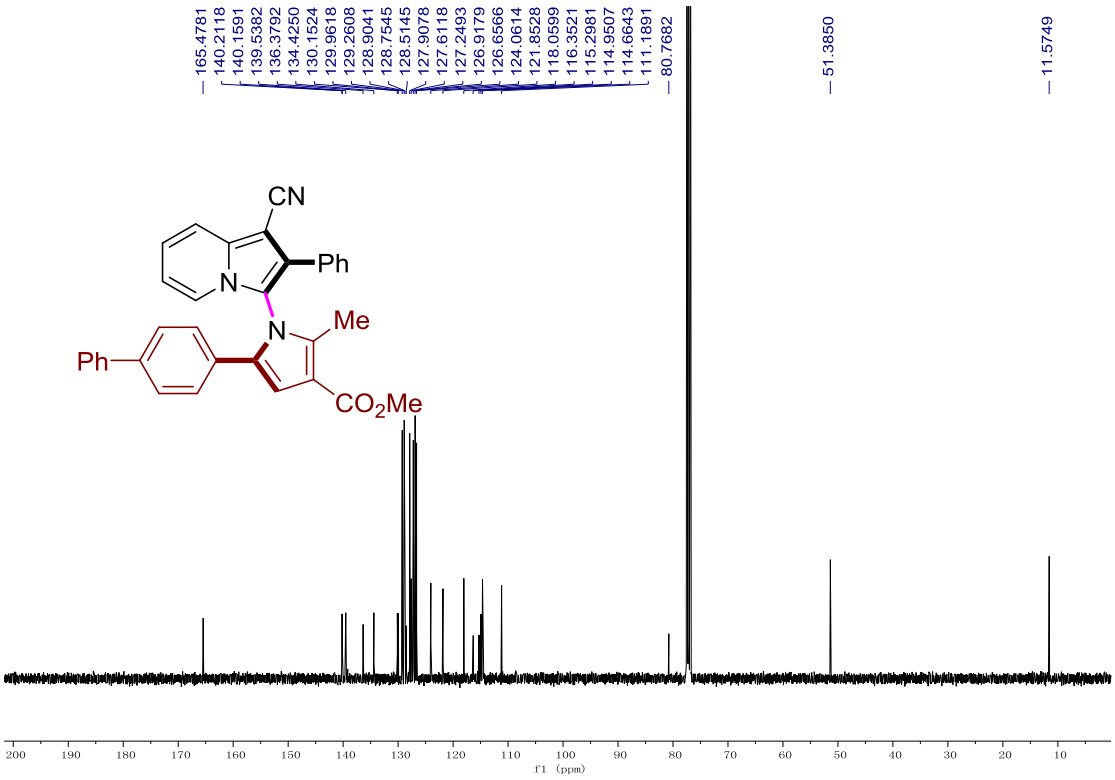


Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	13.637	664.565	1733.655	92.29
2	15.035	55.535	144.719	7.71

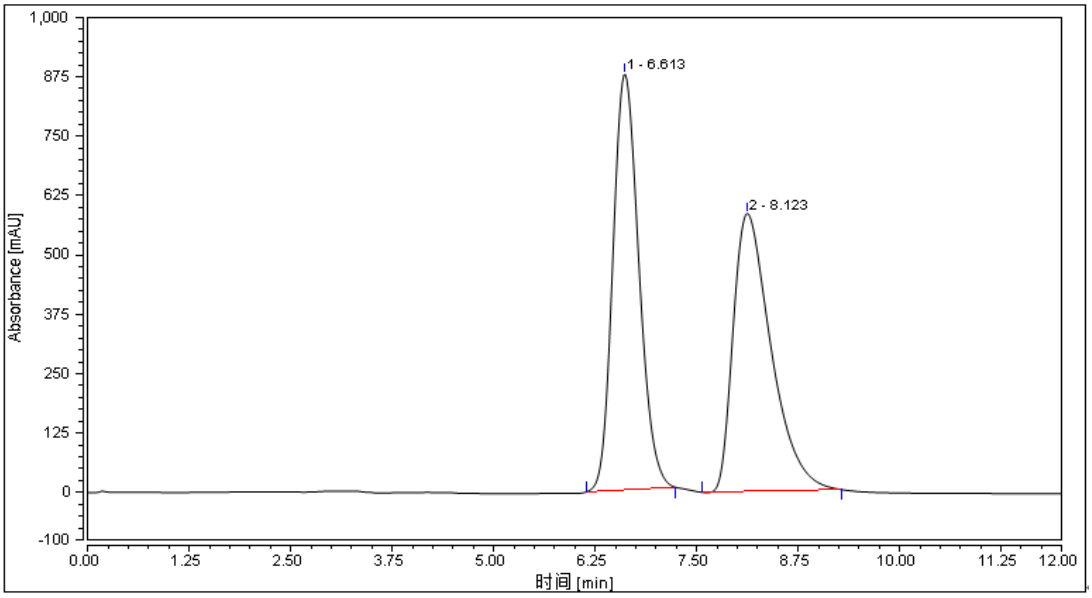
^{1}H NMR of **3ad** (400 MHz, $CDCl_3$)



^{13}C NMR of **3ad** (100 MHz, $CDCl_3$)

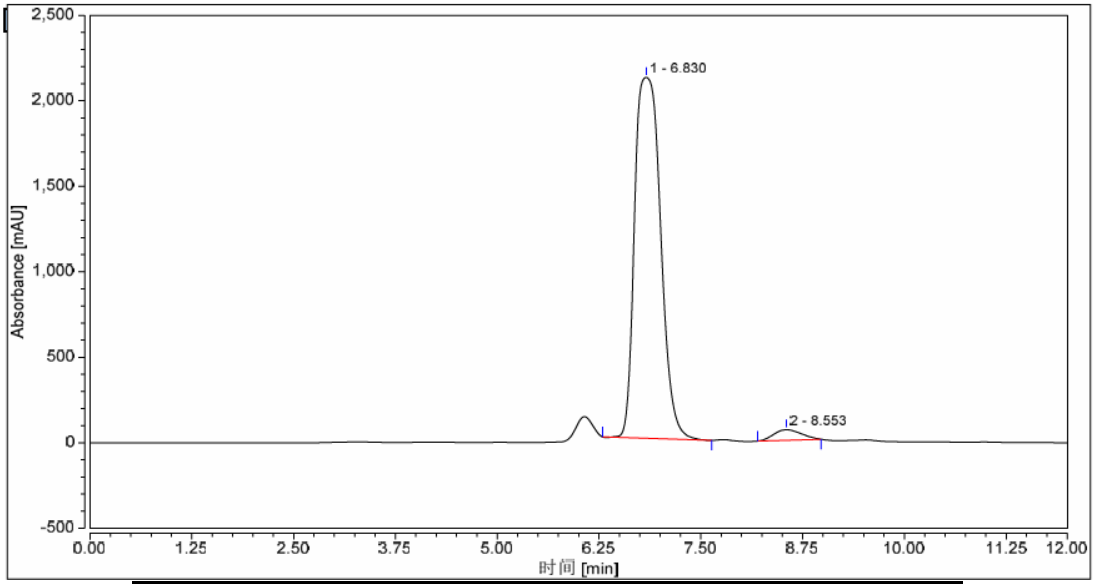


HPLC analysis: rac-**3ad**



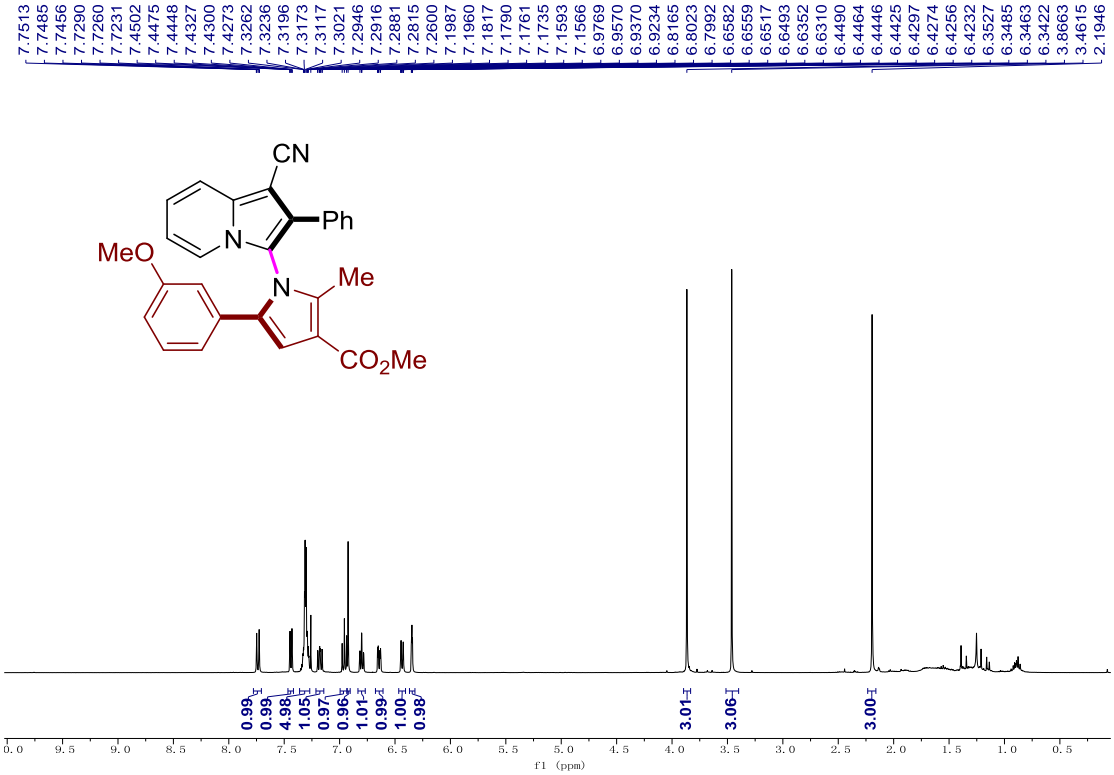
Peak	RetTime	Area	Height	Area
	min	mAU*min	mAU	%
1	6.613	324.484	875.481	50.68
2	8.123	315.742	585.101	49.32

Enantioenriched **3ad**

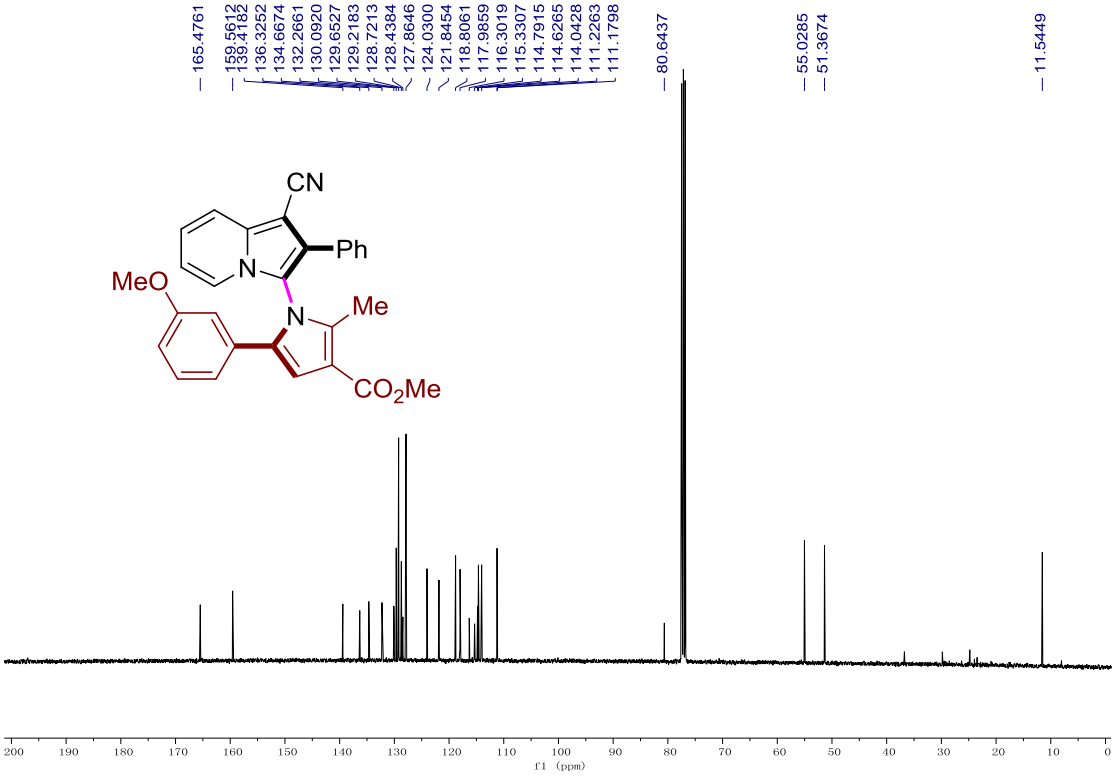


Peak	RetTime	Area	Height	Area
	min	mAU*min	mAU	%
1	6.830	780.206	2110.879	96.99
2	8.553	24.251	61.853	3.01

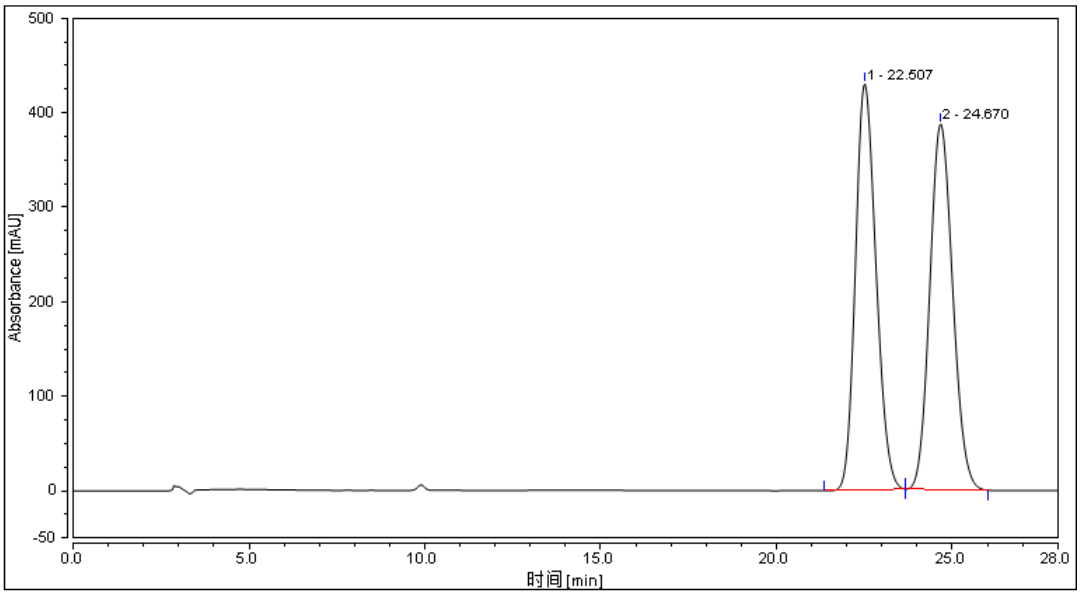
^{1}H NMR of **3ae** (400 MHz, $CDCl_3$)



^{13}C NMR of **3ae** (100 MHz, $CDCl_3$)

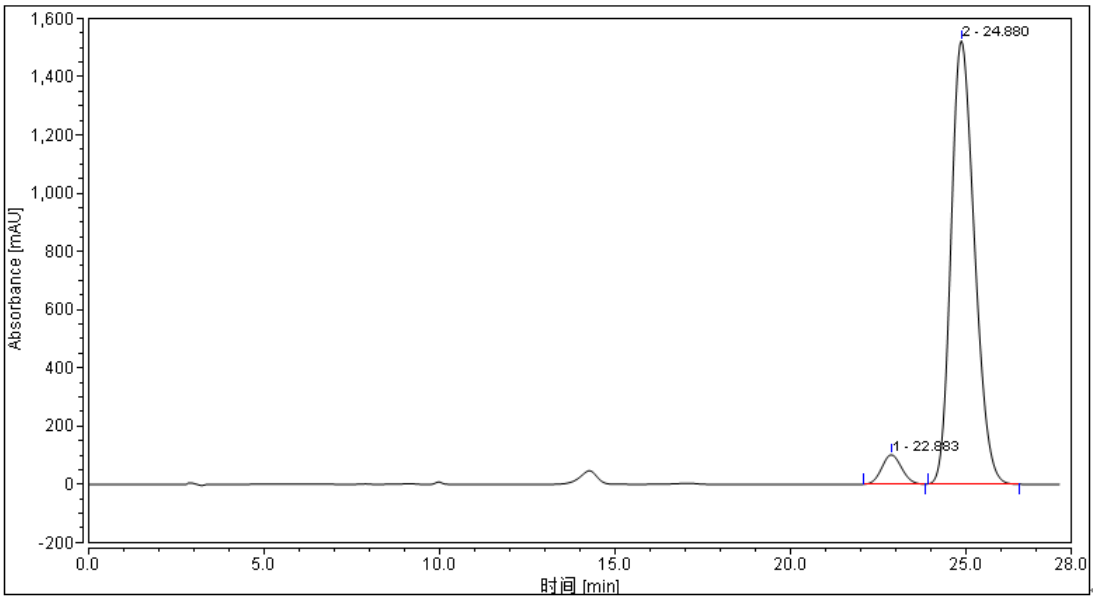


HPLC analysis: rac-**3ae**



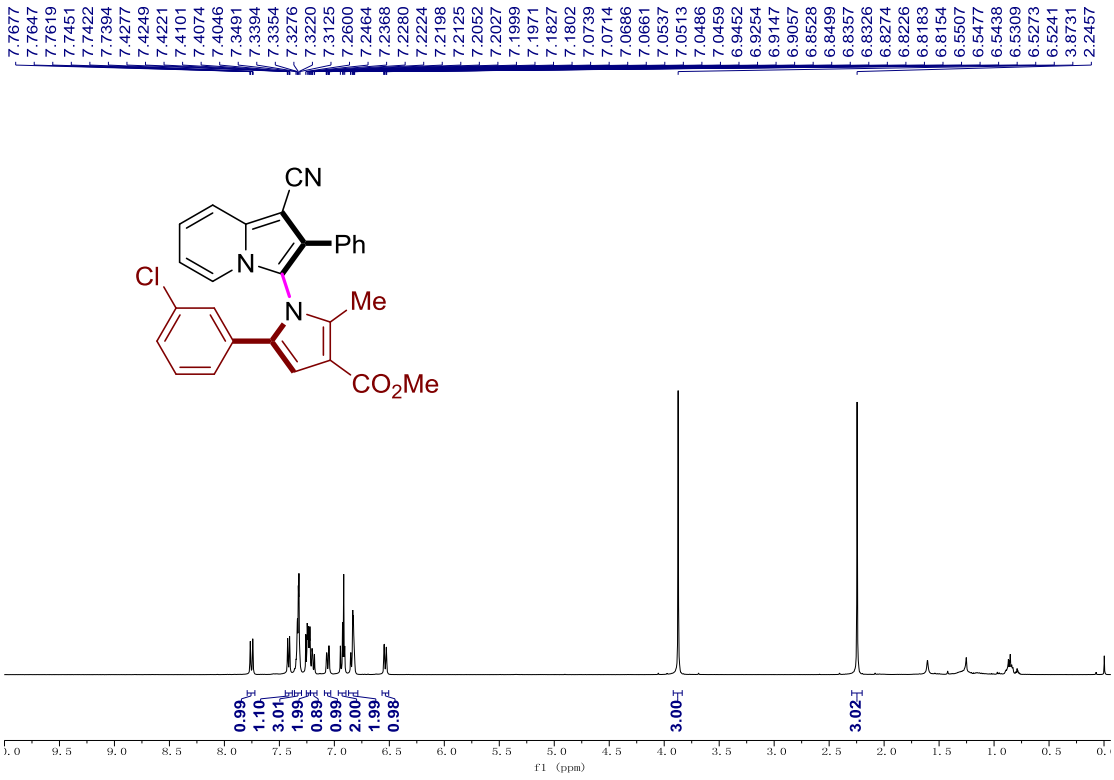
Peak	RetTime	Area	Height	Area
	min	mAU*min	mAU	%
1	22.507	291.538	430.042	50.00
2	24.670	291.582	387.276	50.00

Enantioenriched **3ae**

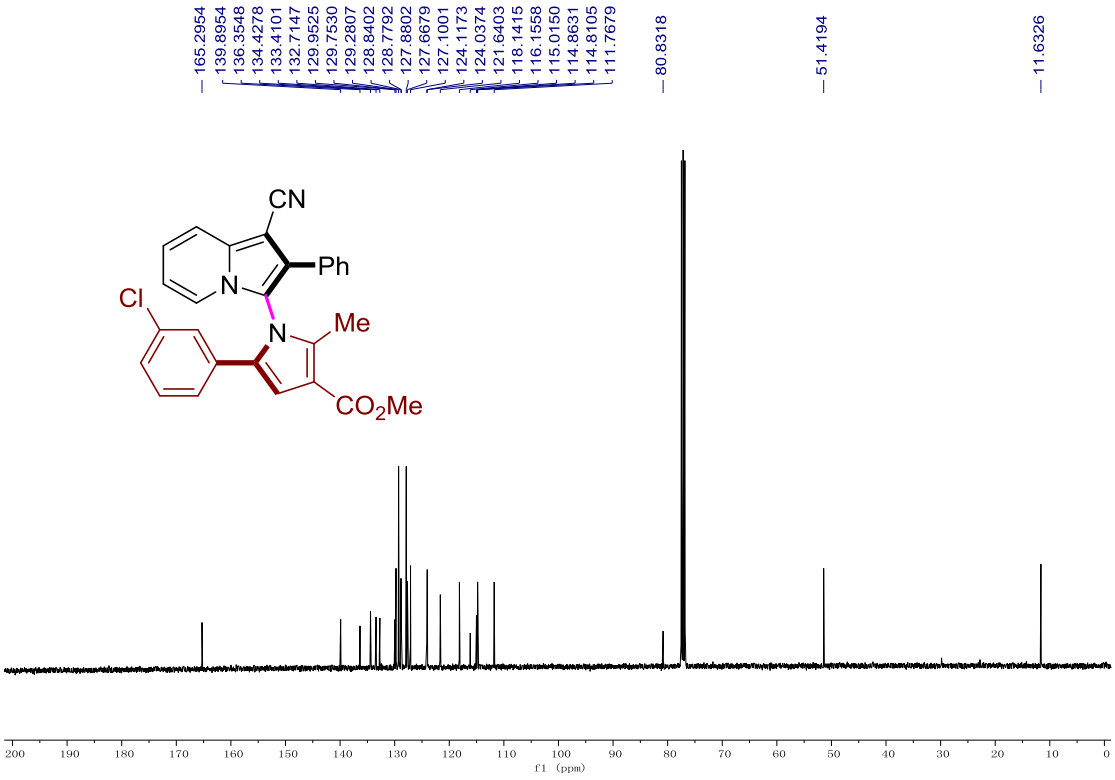


Peak	RetTime	Area	Height	Area
	min	mAU*min	mAU	%
1	22.883	66.254	100.827	5.33
2	24.880	1176.073	1522.062	94.67

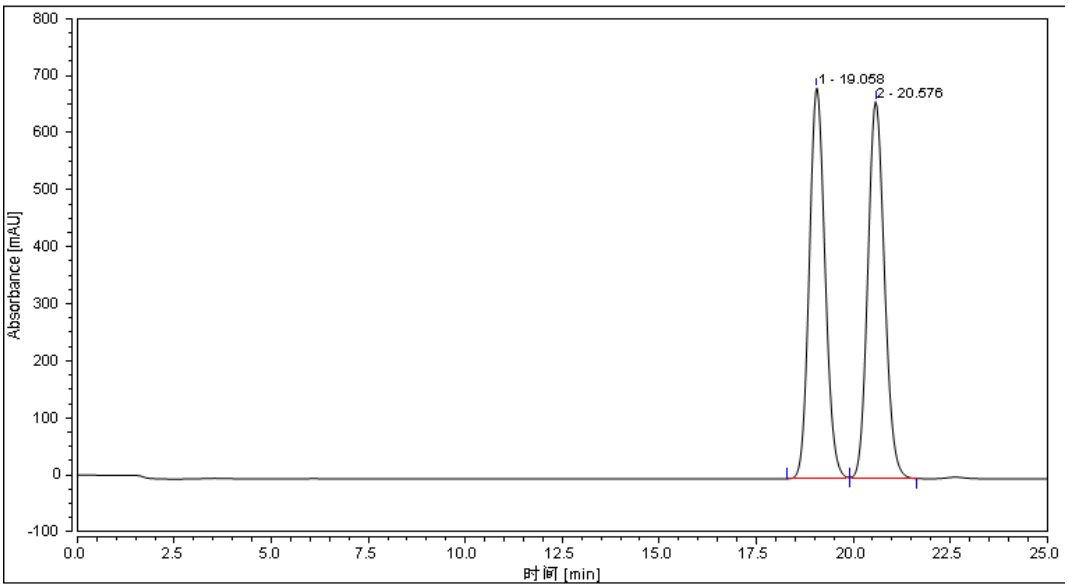
^{1}H NMR of **3af** (400 MHz, CDCl3)



^{13}C NMR of **3af** (100 MHz, $CDCl_3$)

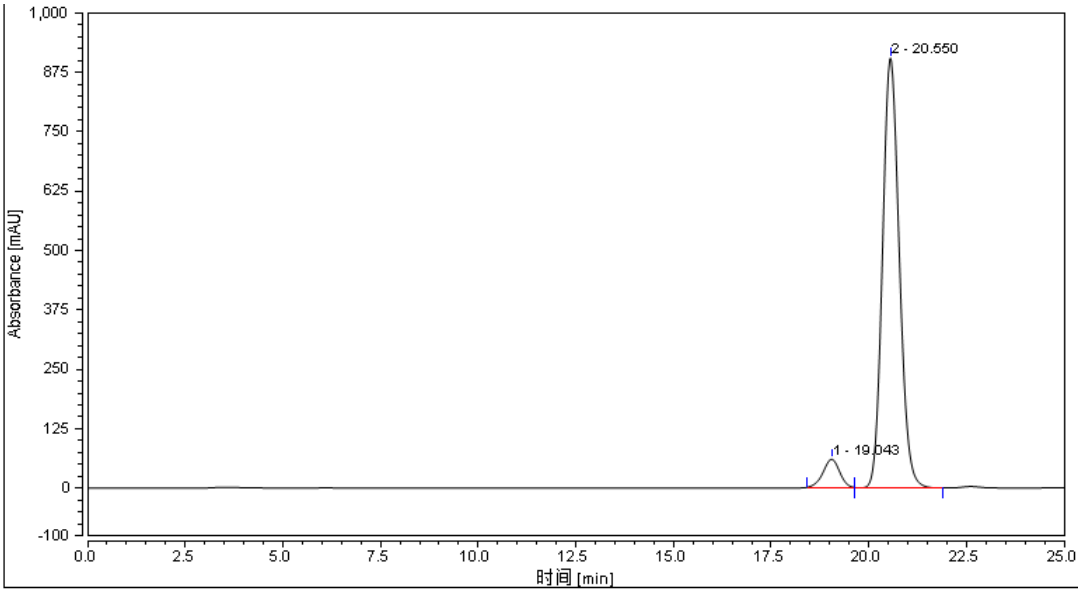


HPLC analysis: rac-**3af**



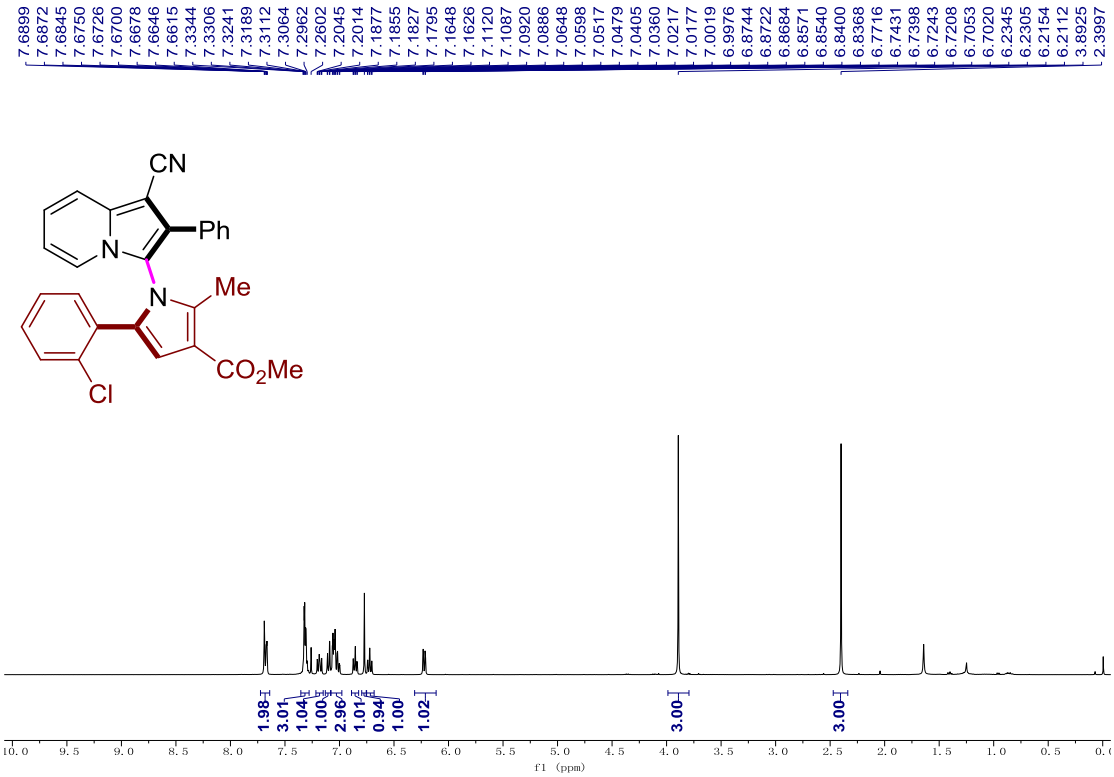
Peak	RetTime	Area	Height	Area
	min	mAU*min	mAU	%
1	19.058	321.714	683.926	49.49
2	20.576	328.365	660.045	50.51

Enantioenriched **3af**

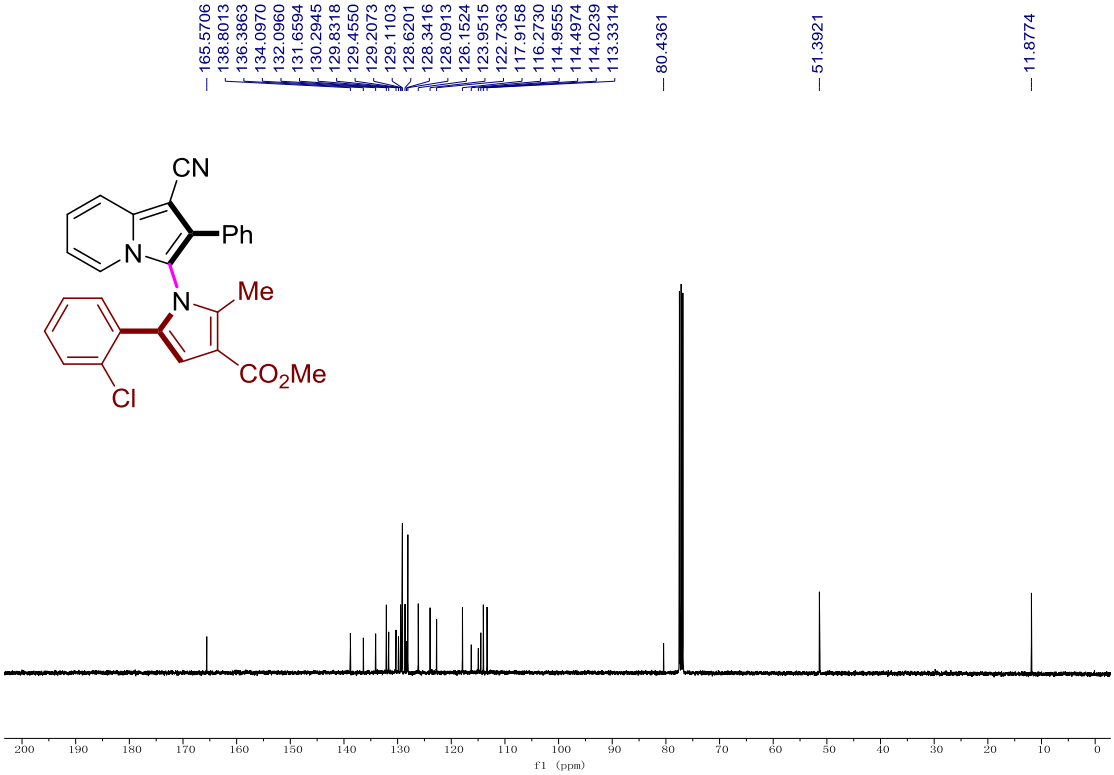


Peak	RetTime	Area	Height	Area
	min	mAU*min	mAU	%
1	19.043	28.997	59.324	6.06
2	20.550	449.503	904.040	93.94

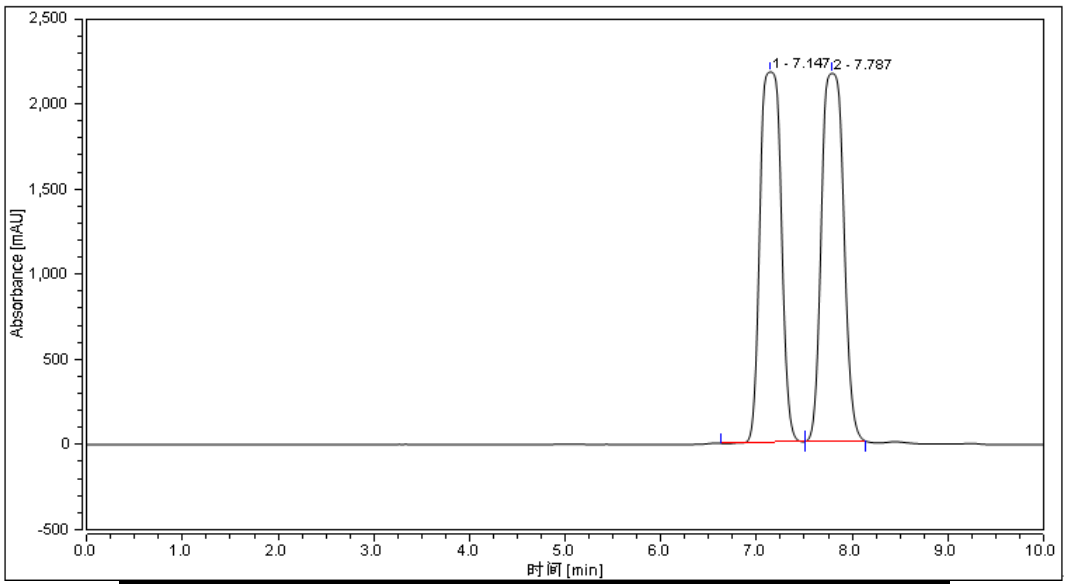
^{1}H NMR of **3ag** (400 MHz, $CDCl_3$)



^{13}C NMR of **3ag** (100 MHz, $CDCl_3$)

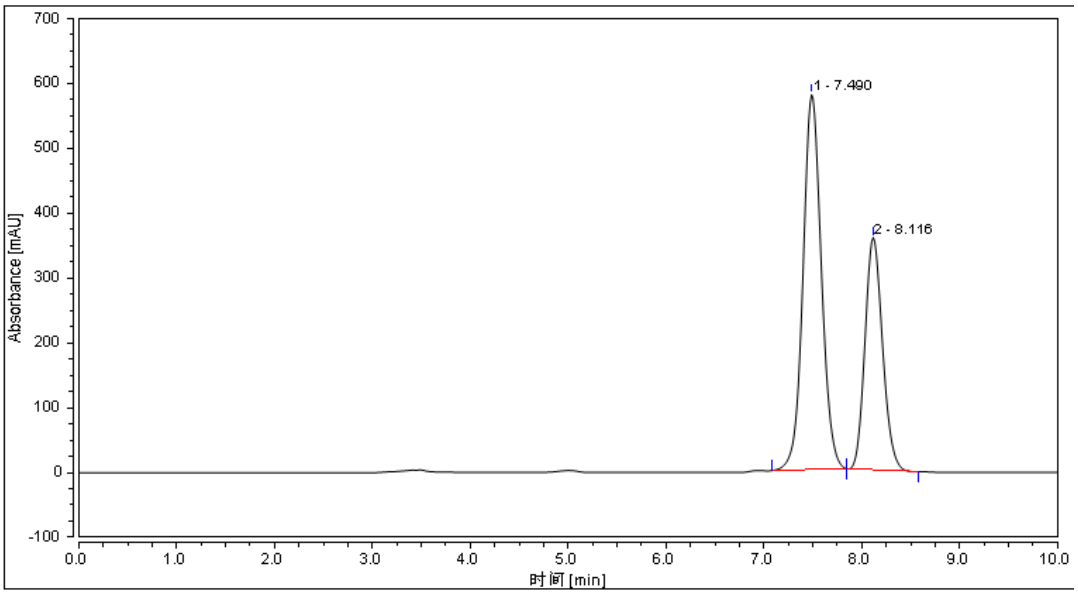


HPLC analysis: rac-**3ag**



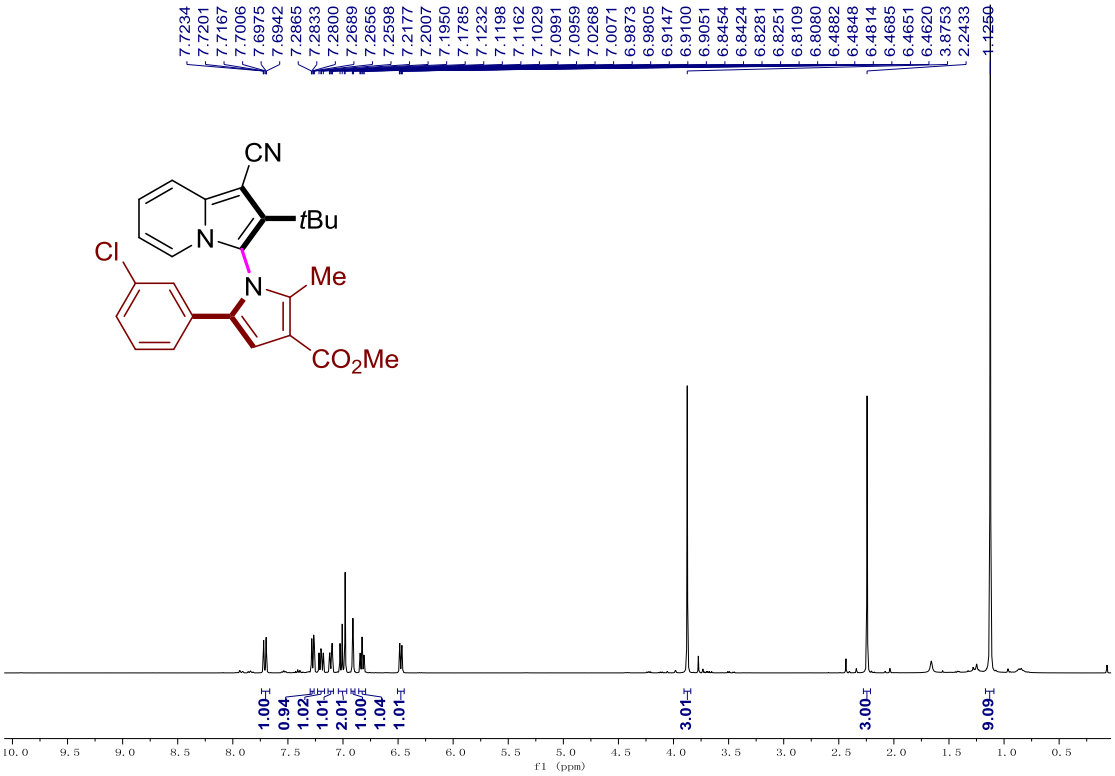
Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	7.147	553.634	2174.462	48.88
2	7.787	579.037	2161.215	51.12

Enantioenriched **3ag**

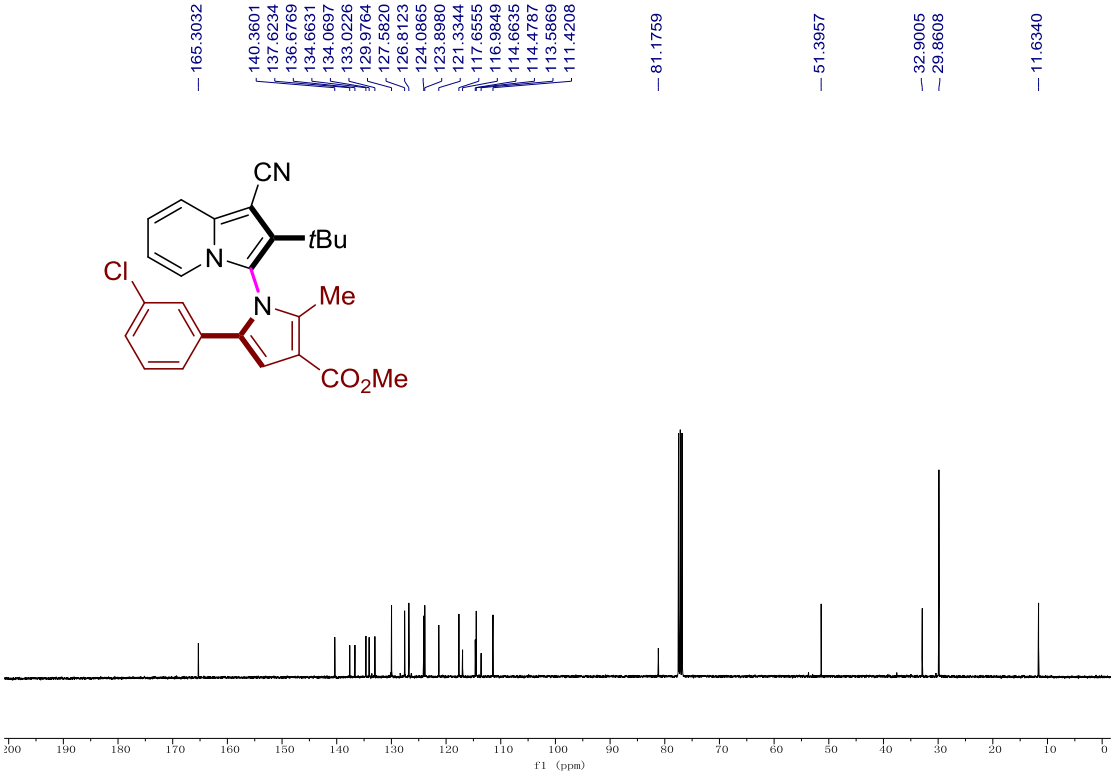


Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	7.490	125.320	578.423	62.81
2	8.116	74.198	358.079	37.19

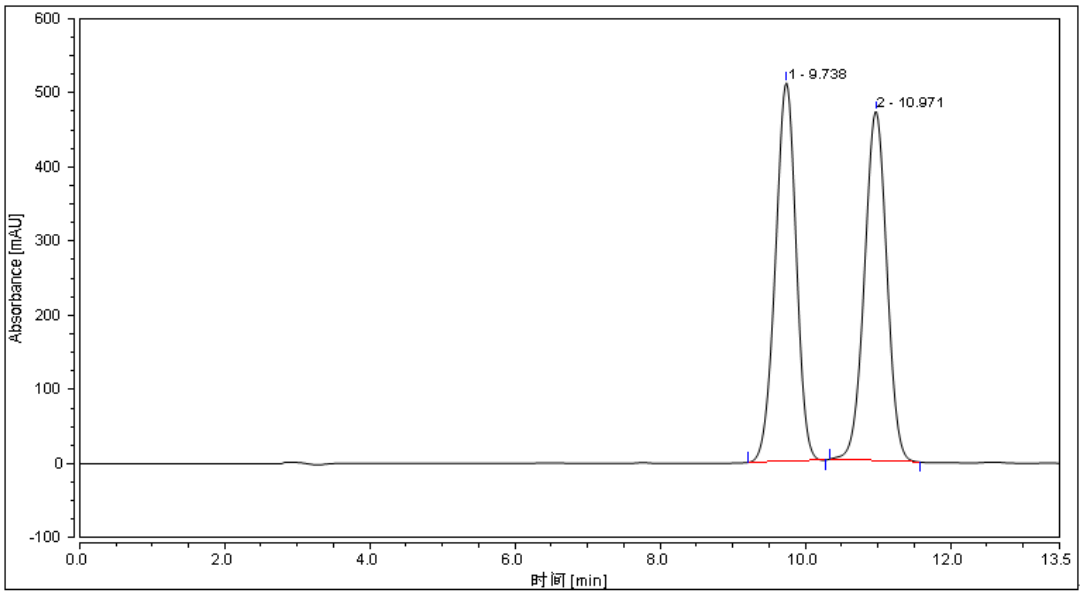
^{1}H NMR of **3ah** (400 MHz, $CDCl_3$)



^{13}C NMR of **3ah** (100 MHz, $CDCl_3$)

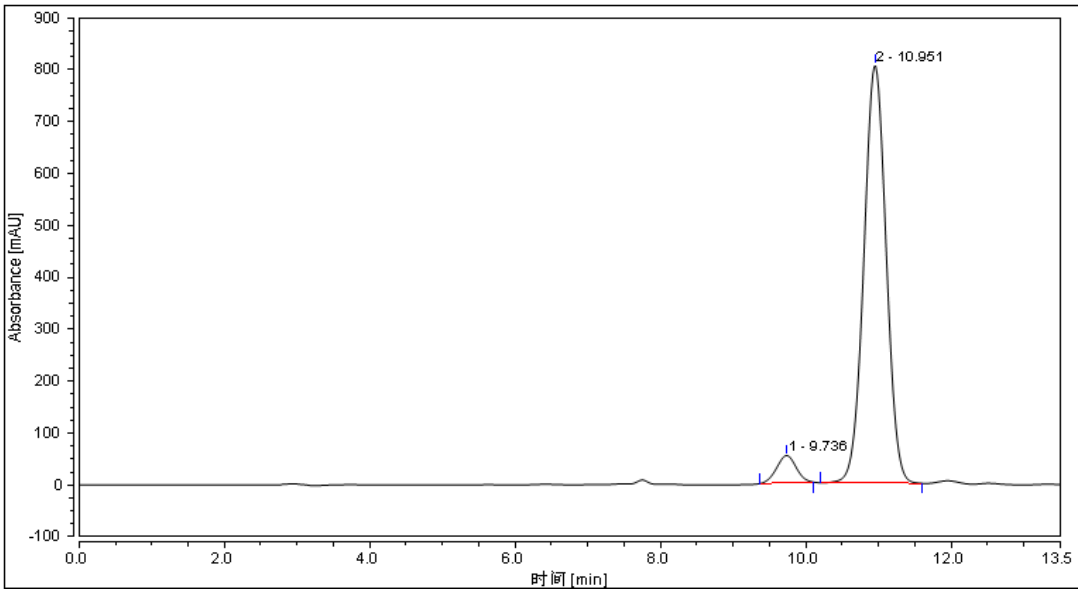


HPLC analysis: rac-**3ah**



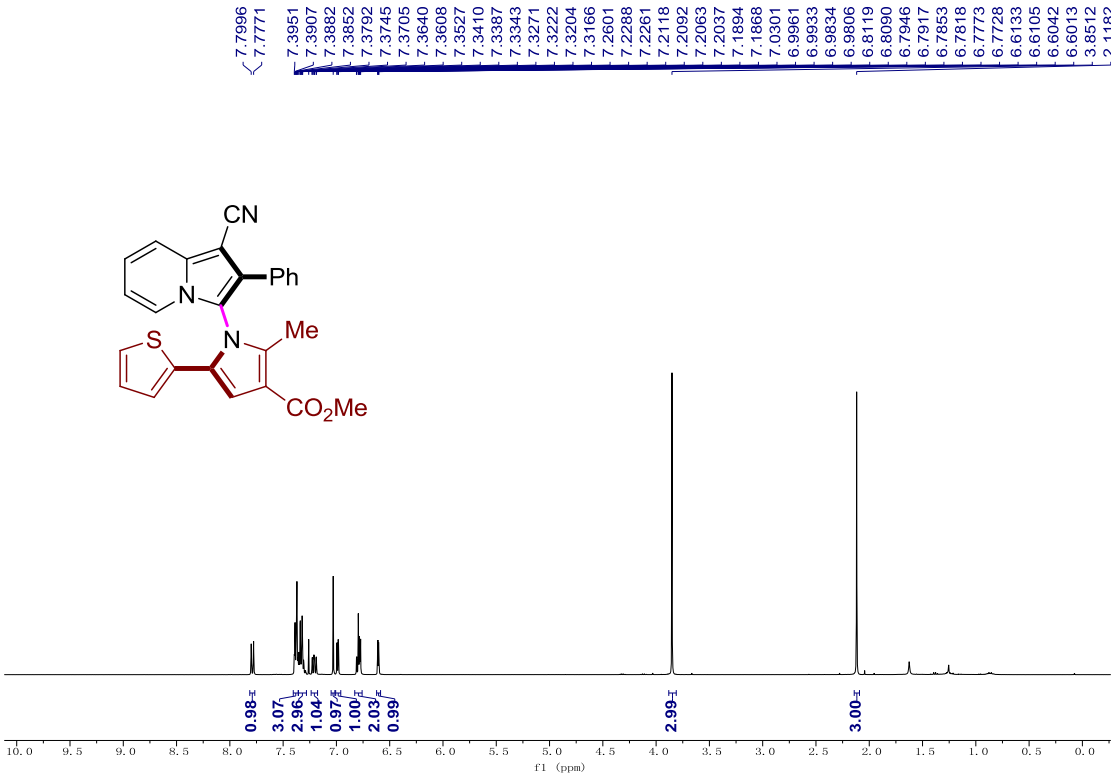
Peak	RetTime	Area	Height	Area
	min	mAU*min	mAU	%
1	9.738	168.563	510.159	50.14
2	10.971	167.620	470.818	49.86

Enantioenriched **3ah**

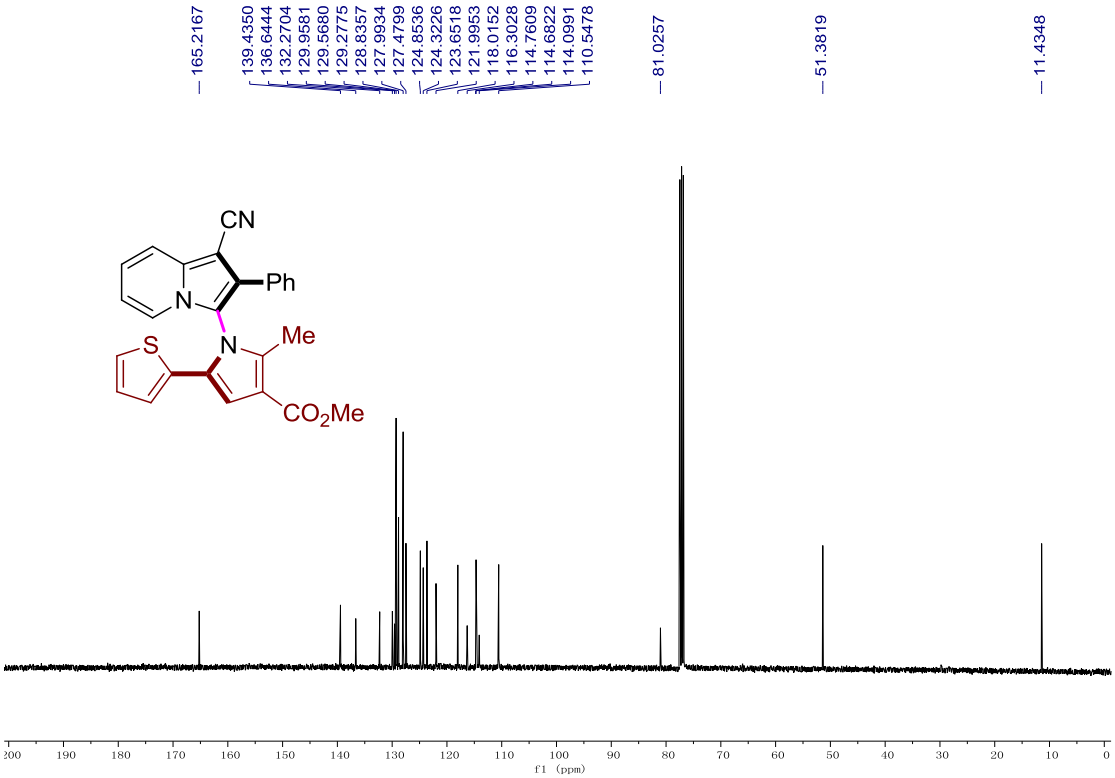


Peak	RetTime	Area	Height	Area
	min	mAU*min	mAU	%
1	9.736	16.384	52.671	5.42
2	10.951	285.903	805.126	94.58

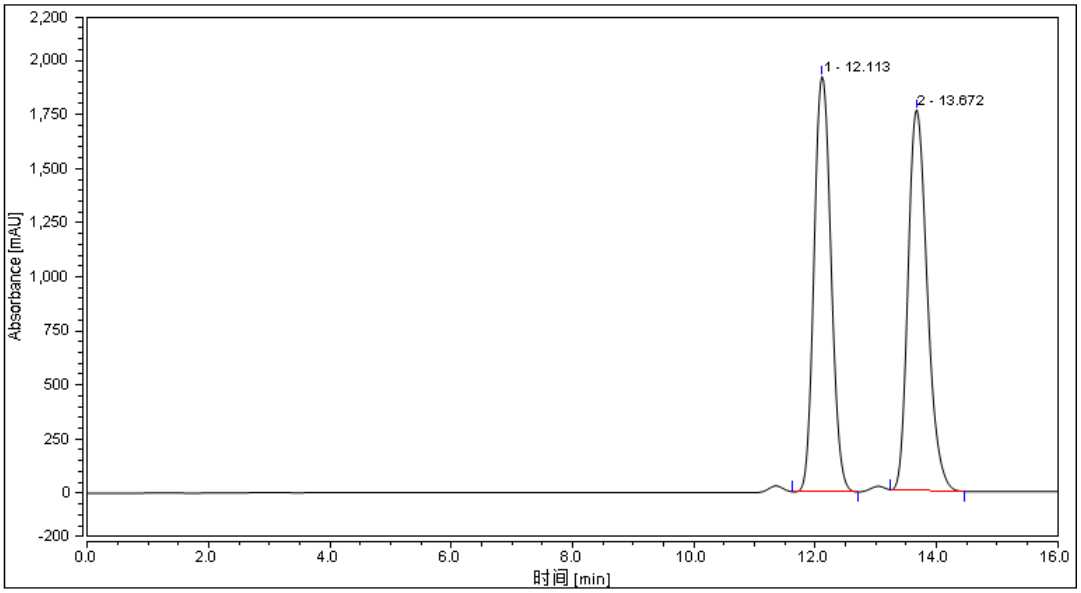
^{1}H NMR of **3ai** (400 MHz, $CDCl_3$)



^{13}C NMR of **3ai** (100 MHz, $CDCl_3$)

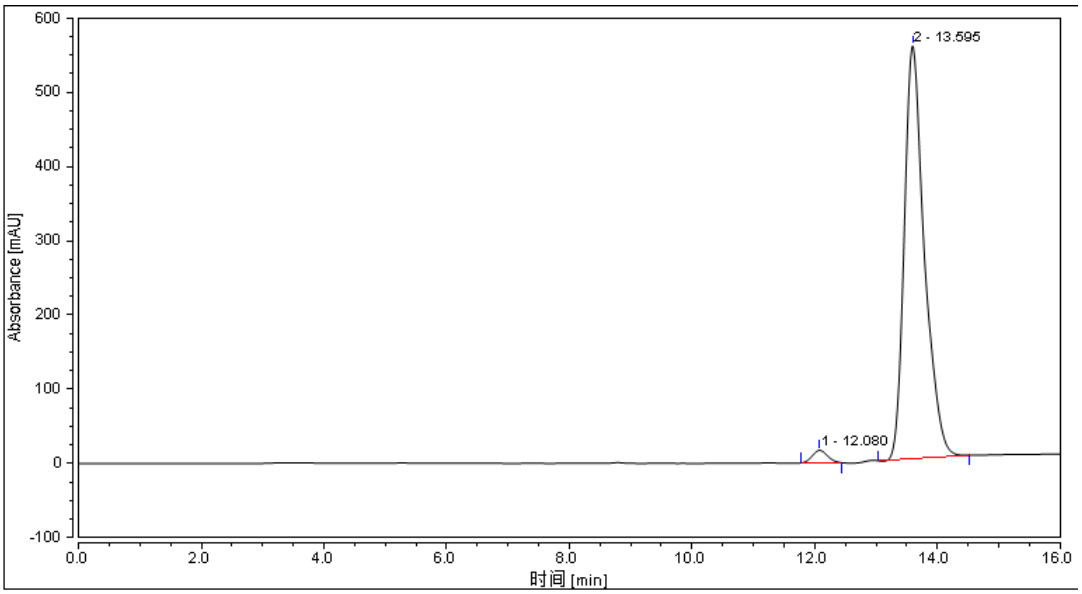


HPLC analysis: rac-**3ai**



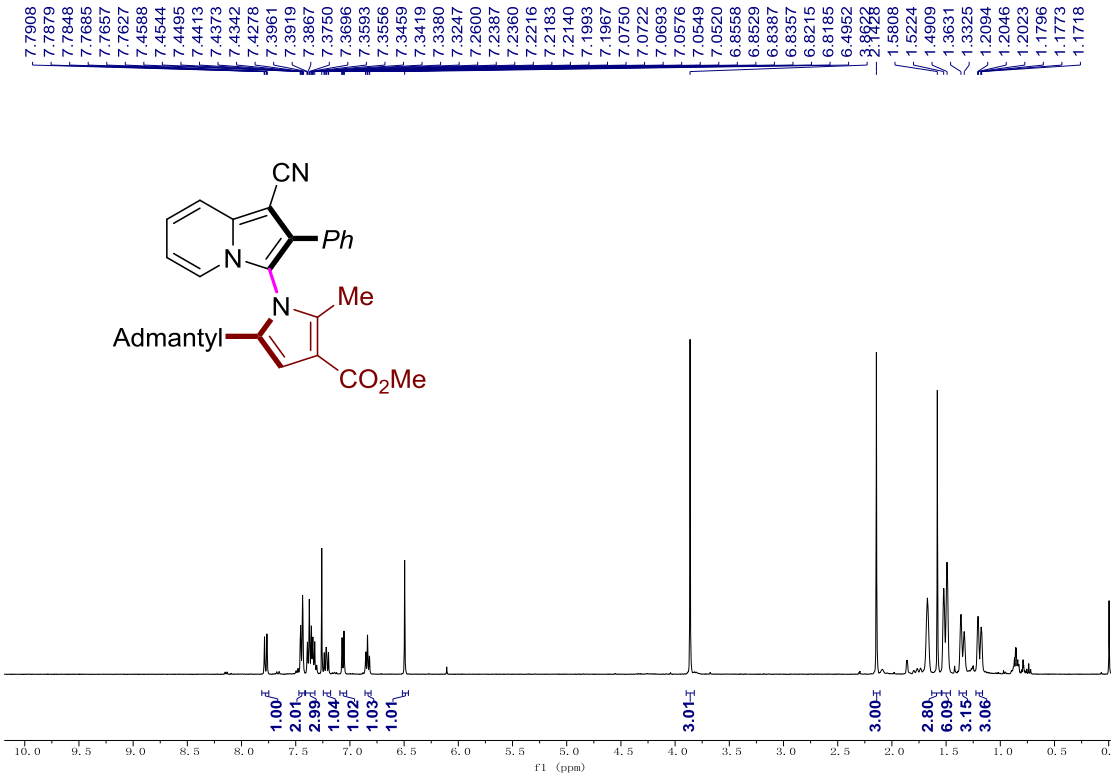
Peak	RetTime	Area	Height	Area
	min	mAU*min	mAU	%
1	12.113	622.059	1920.675	49.17
2	13.672	643.113	1759.724	50.83

Enantioenriched **3ai**

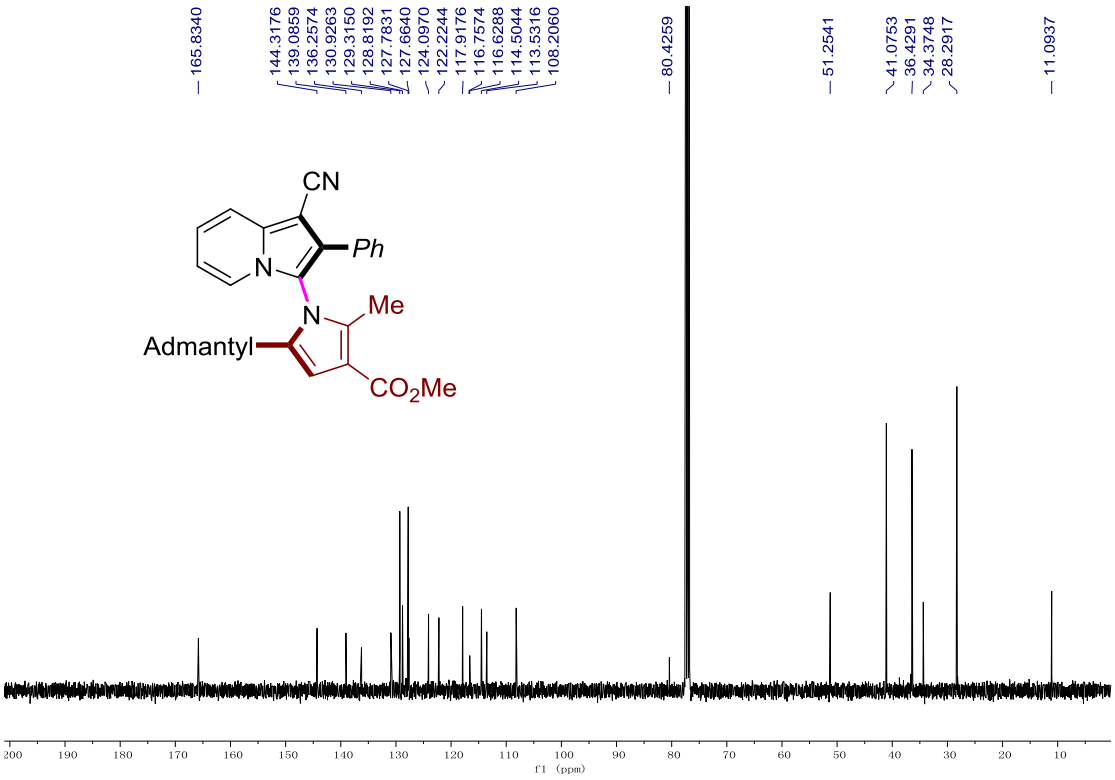


Peak	RetTime	Area	Height	Area
	min	mAU*min	mAU	%
1	12.080	4.812	16.825	2.23
2	13.595	210.561	556.375	97.77

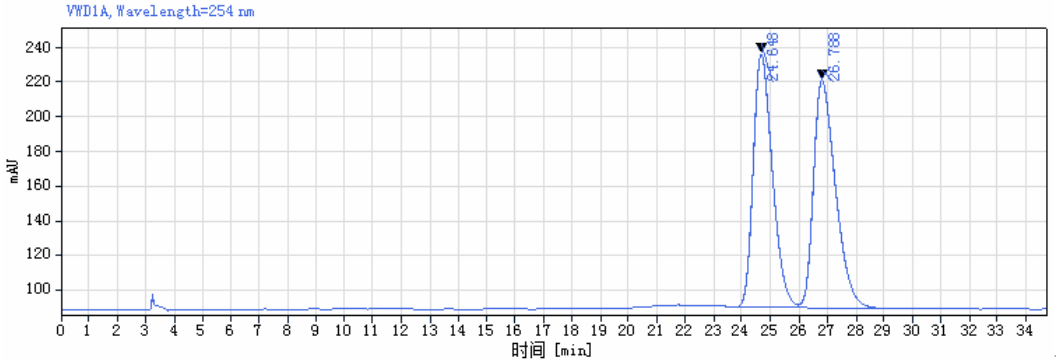
^{1}H NMR of **3aj** (400 MHz, $CDCl_3$)



^{13}C NMR of **3aj** (100 MHz, $CDCl_3$)

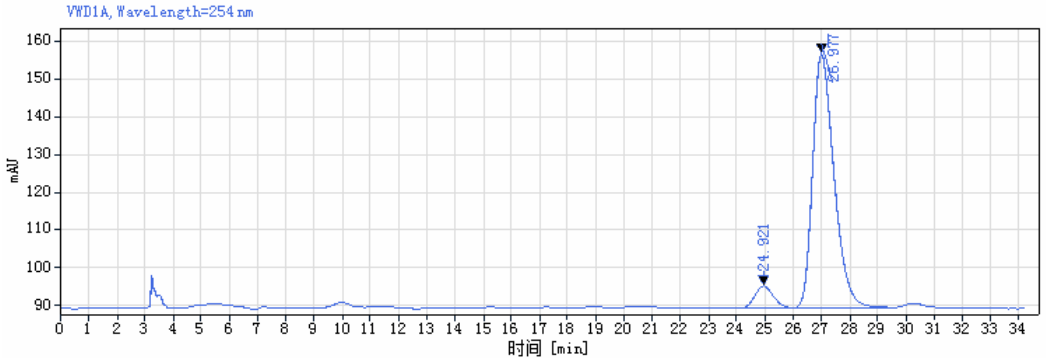


HPLC analysis: rac-**3aj**



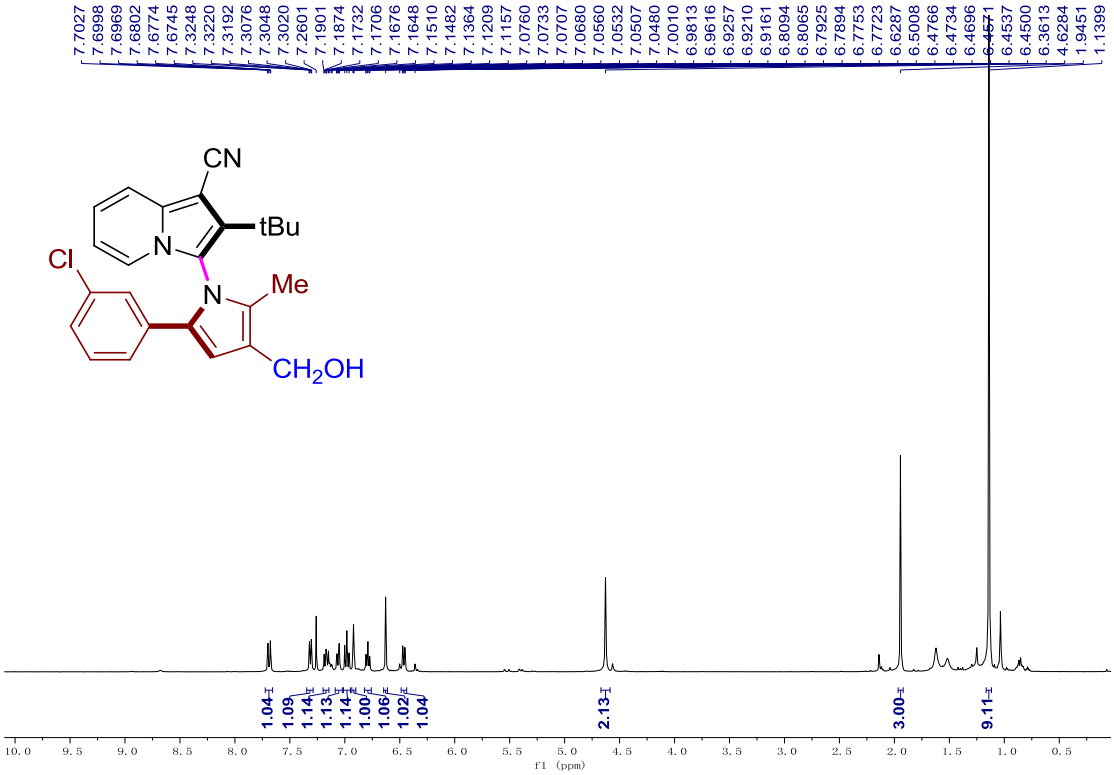
Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	24.648	6845.94	146.37	49.15
2	26.788	7082.46	131.52	50.85

Enantioenriched **3aj**

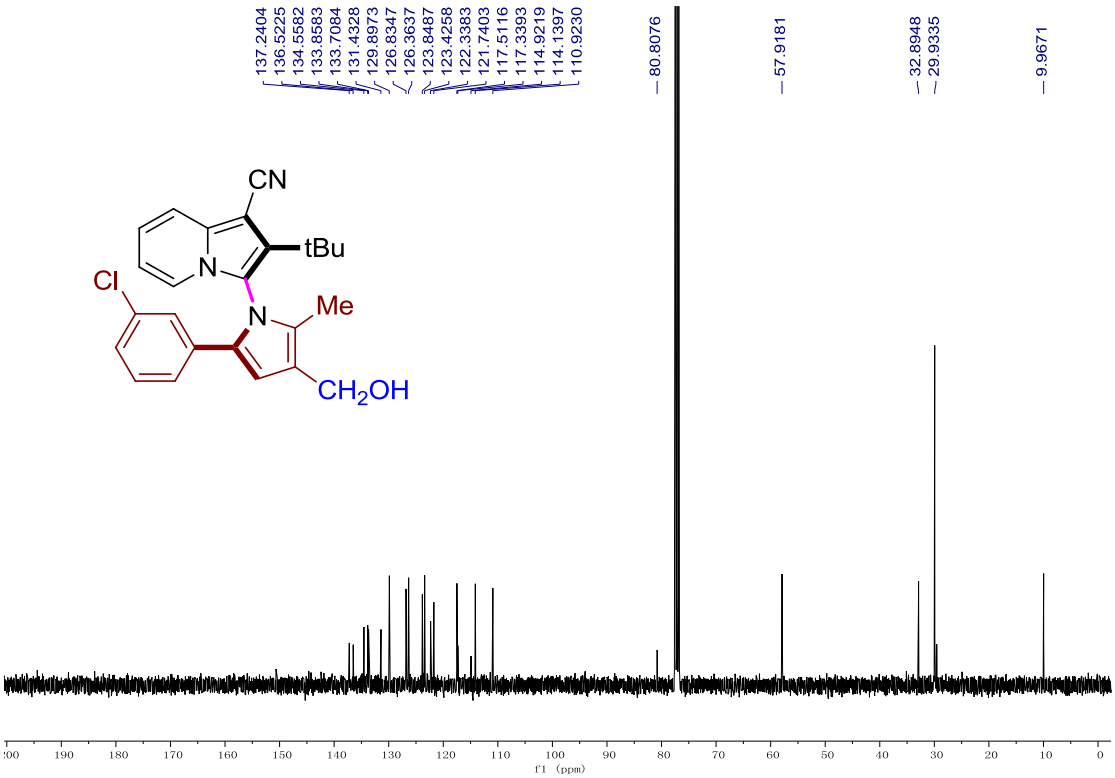


Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	24.921	262.42	5.83	6.93
2	26.977	3523.75	67.21	93.07

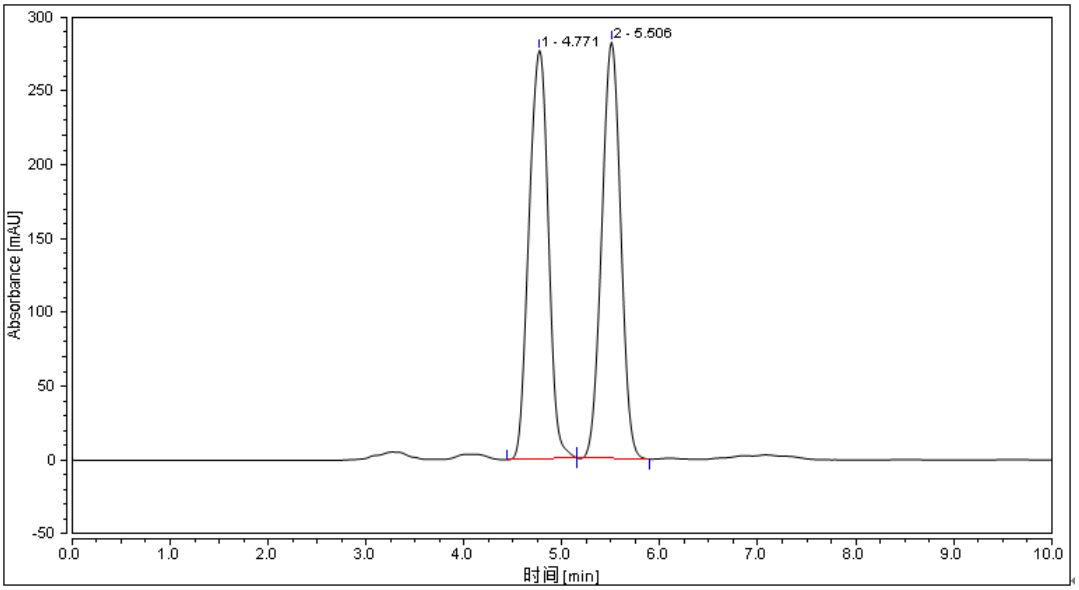
^{1}H NMR of **4** (400 MHz, $CDCl_3$)



^{13}C NMR of **4** (100 MHz, $CDCl_3$)

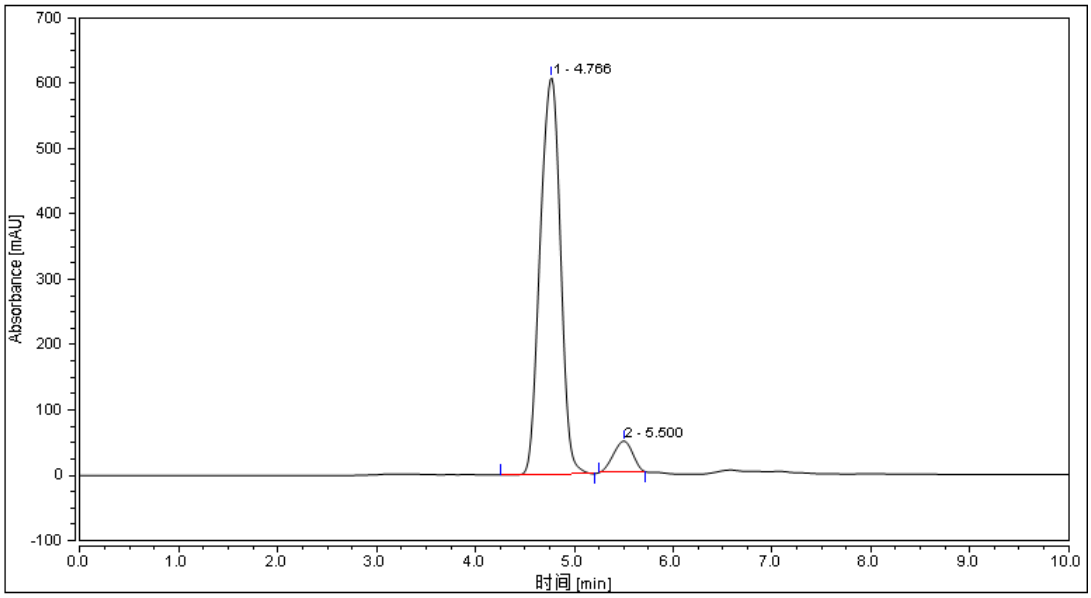


HPLC analysis: rac-**4**



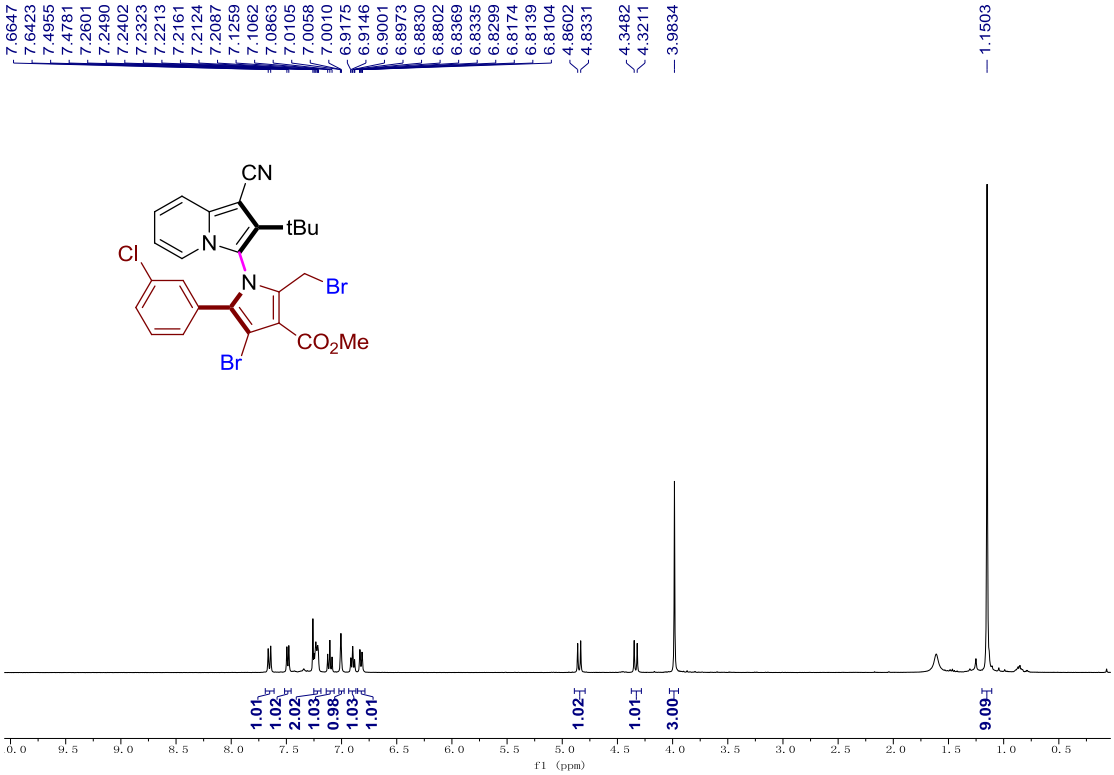
Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	4.771	63.297	276.884	50.08
2	5.506	63.102	282.097	49.92

Enantioenriched **4**

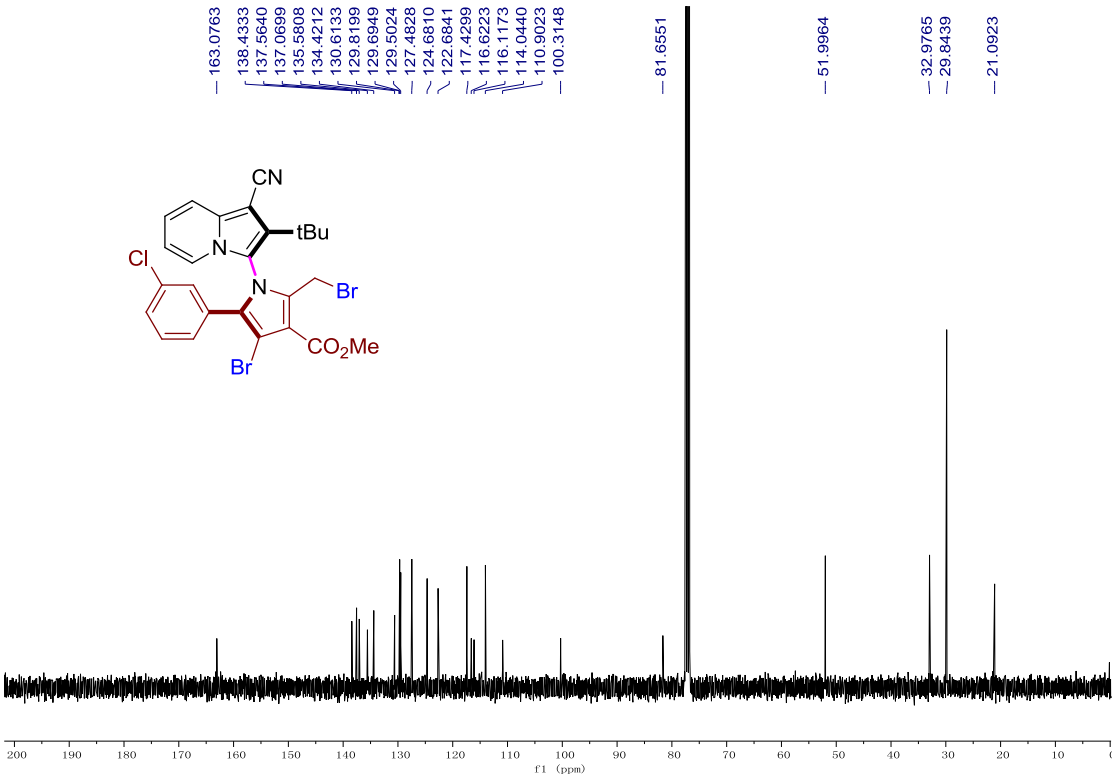


Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	4.766	144.322	607.298	93.10
2	5.500	10.694	47.303	6.90

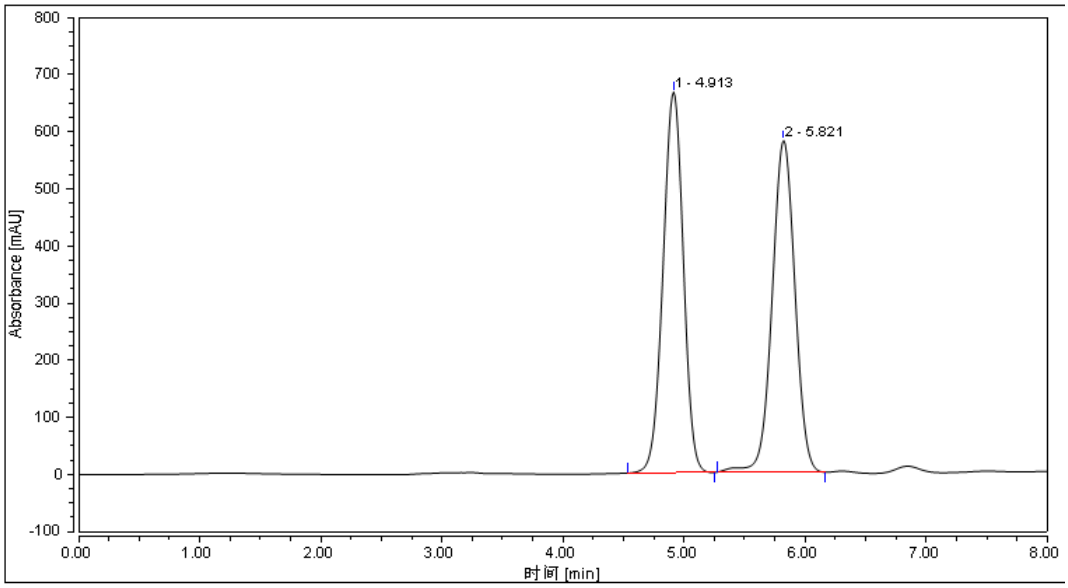
^{1}H NMR of **5** (400 MHz, $CDCl_3$)



^{13}C NMR of **5** (100 MHz, $CDCl_3$)

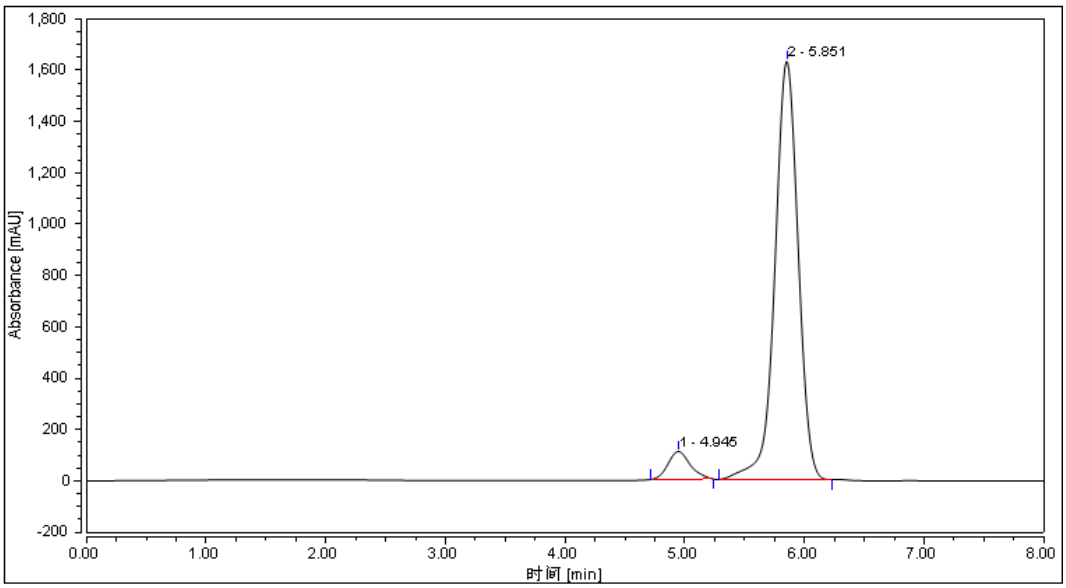


HPLC analysis: rac-**5**



Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	4.913	129.222	666.902	50.52
2	5.821	126.549	580.923	49.48

Enantioenriched **5**



Peak	RetTime min	Area mAU*min	Height mAU	Area %
1	4.945	23.285	108.486	5.97
2	5.851	366.762	1630.457	94.03

13. Reference

1. Hu, W.; Zhang, C.; Huang, J.; Guo, Y.; Fu, Z.; Huang, W., Access to Highly Functionalized Indanes from Arynes and α,γ-Diketo Esters. *Org. Lett.* **2019,** *21*, 941-945.
2. Nam, S.; Kim, I., Cu-Catalyzed Ullmann-Type Double C–N Coupling Approach to 5-Aryl-5H-indolizino[3,2-b]indoles. *J. Org. Chem.* **2023,** *88*, 745-754.