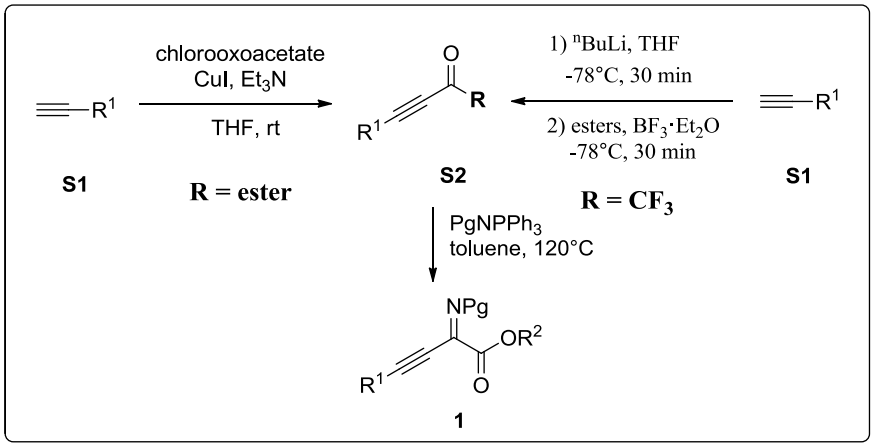
Electronic Supplementary Material (ESI) for ChemComm.

Content

1. General information

The products were purified by column chromatography on silica gel (200-300 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) and Bruker 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, acetone-d_6 δ 2.05) and carbon (chloroform δ 77.16, acetone-d_6 δ 29.84) 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.

2. General procedure for the preparation of β,γ-alkynyl-α-imino esters

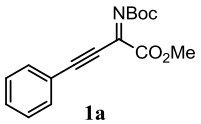


The alkynyl ketoesters (R = ester) were synthesized according to the literature.[1] A two necked round bottomed flask was charged with CuI (0.0571 g, 10 mol%) and THF (7.5 mL, 0.4 M), triethylamine (0.5 mL, 1.2 equiv), alkyne (0.33 mL, 3.0 mmol, 1.0 equiv) and chlorooxoacetate (0.7 mL, 1.5 equiv) were added sequentially and the resulting mixture was stirred at room temperature for 24 hours. The reaction was quenched by saturated $NaHCO_3$ aqueous solution and the aqueous phase was extracted with ethyl acetate. The organic phases were combined, dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 95:5) to give the alkynyl ketoester **S2**.

When R group was CF_3, the alkynyl ketoester was prepared according to the literature.[2] A solution of phenylacetylene (0.33 mL, 3.0 mmol, 1.0 equiv) in anhydrous THF (0.3 M) was cooled to –78 ℃, then ^{n}BuLi (1.3 mL, 3.0 mmol, 2.4 M) in n-Hexane was slowly added within 15 min. The obtained reaction mixture was stirred at –78 ℃ for 0.5 h, and a solution of ethyl 2,2,2-trifiuoroacetate (0.3 mL, 3 mmol) and BF_3 OEt_2 (0.74 mL, 6 mmol) in THF (2 mL) was slowly added at -78 ℃ within 0.5 h. The mixture was allowed to keep at this temperature and stirred for 2 h. After quenching with 1 N hydrochloric acid, the aqueous layer was separated and extracted with Et_2O (10 mL×3). The combined organic layer was washed with brine, dried with anhydrous Na_2SO_4 and concentrated in vacuum. The residue was chromatographed on silica gel column (petroleum ether/ethyl acetate 99:1) to

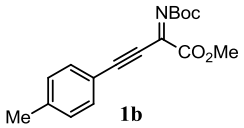
obtain the desired products.

An oven-dried round bottom two-neck flask was added ketoester **S2** (1.0 mmol, 1.0 equiv), *N*-Boc-triphenyliminophosphorane (452.9 mg, 1.2 equiv) or *N*-Cbz-triphenyliminophosphorane (493.7 mg, 1.2 equiv) and toluene (0.1 M). The mixture was heated to 120 ℃ and stirred for 24-72 h. After cooling to room temperature, the mixture was concentrated under vacuum. The residue was purified by silica gel chromatography (petroleum ether/ethyl acetate 10:1-6:1) to give the β,γ-alkynyl-α-imino esters **1**.



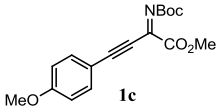
1a

According to the general procedure, **1a** was obtained in 54% yield as a yellow solid, Melting point 55-58 ℃. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.54 (dt, J = 7.2, 1.4 Hz, 2H), 7.49 – 7.43 (m, 1H), 7.38 (dd, J = 8.2, 6.7 Hz, 2H), 3.95 (s, 3H), 1.57 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 161.8, 159.9, 144.6, 133.0, 131.2, 128.8, 120.0, 101.5, 84.4, 81.0, 54.0, 28.2. **HRMS (ESI-TOF)** m/z: $[M+H]^+$Calcd for $C_{16}H_{18}NO_4^+$ 288.1231; Found:288.1227.



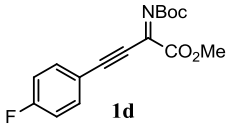
1b

According to the general procedure, **1b** was obtained in 64% yield as a yellow solid, Melting point 43-45 ℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) 7.44 (d, *J* = 7.9 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 3.95 (s, 3H), 2.38 (s, 3H), 1.57 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 161.7, 159.8, 144.5, 141.8, 132.8, 129.5, 116.7, 102.1, 84.1, 80.7, 53.8, 28.1, 21.8. **HRMS (ESI-TOF)** m/z: $[M+H]^+$Calcd for $C_{17}H_{20}NO_4^+$ 302.1387; Found:302.1390.



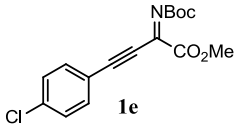
1c

According to the general procedure, **1c** was obtained in 32% yield as a yellow solid, Melting point 41-43 ℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.54 – 7.47 (m, 2H), 6.92 – 6.86 (m, 2H), 3.95 (s, 3H), 3.84 (s, 3H), 1.58 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 161.9, 160.0, 159.7, 144.5, 134.9, 114.4, 111.7, 102.6, 84.0, 80.9, 55.4, 53.8, 28.1. **HRMS (ESI-TOF)** m/z: $[M+H]^+$Calcd for $C_{17}H_{20}NO_5^+$ 318.1336; Found:318.1341.



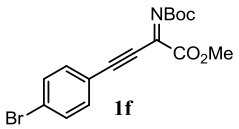
1d

According to the general procedure, **1d** was obtained in 60% yield as a yellow solid, Melting point 37-40 ℃. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.55 (dd, *J* = 8.3, 5.4 Hz, 2H), 7.09 (t, *J* = 8.5 Hz, 2H), 3.96 (s, 3H), 1.57 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.4, 162.8, 160.6 (d, *J* = 186.6 Hz), 144.3, 136.3 (d, *J* = 9.2 Hz), 135.1 (d, *J* = 9.0 Hz), 116.3 (d, *J* = 22.5 Hz), 100.3, 84.2, 80.8, 53.8, 28.1. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -105.47. **HRMS (ESI-TOF)** m/z: $[M+H]^+$Calcd for $C_{16}H_{17}FNO_4^+$ 306.1136; Found: 306.1137.



1e

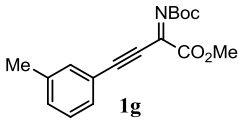
According to the general procedure, **1e** was obtained in 22% yield as a yellow solid, Melting point 44-47 ℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.55 (dd, *J* = 8.3, 5.4 Hz, 2H), 7.09 (t, *J* = 8.5 Hz, 2H), 3.96 (s, 3H), 1.57 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 161.5, 159.7, 144.2, 137.5, 134.0, 129.2, 118.2, 99.9, 84.3, 81.5, 53.9, 28.1. **HRMS (ESI-TOF)** m/z: $[M+H]^+$Calcd for $C_{16}H_{17}ClNO_4^+$: 322.0841; Found: 322.0841.



1f

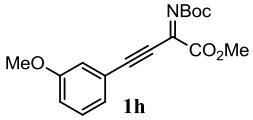
According to the general procedure, **1f** was obtained in 36% yield as a yellow solid. Melting point 50-53 ℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 3.96 (s, 3H), 1.57 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 161.5, 159.6, 144.2, 134.1, 132.1, 125.9, 118.7, 100.0, 84.3, 81.6, 53.9, 28.1. **HRMS (ESI-TOF)** m/z: $[M+H]^+$Calcd for $C_{16}H_{17}BrNO_4^+$: 366.0336;

Found: 366.0332.



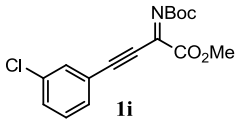
1g

According to the general procedure, **1g** was obtained in 70% yield as a yellow solid. Melting point 46-48 ℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.39 – 7.30 (m, 2H), 7.27 (d, *J* = 5.0 Hz, 2H), 3.95 (s, 3H), 2.34 (s, 3H), 1.58 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 161.7, 159.8, 144.5, 138.5, 133.3, 132.0, 130.0, 128.5, 119.6, 101.8, 84.1, 80.6, 53.8, 28.1, 21.1. **HRMS (ESI-TOF)** m/z: $[M+H]^+$Calcd for $C_{17}H_{20}NO_4^+$: 302.1387; Found:302.1382.



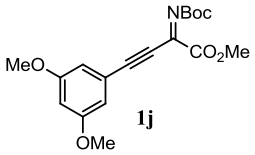
1h

According to the general procedure, **1h** was obtained in 44% yield as a yellow solid. Melting point 44-46 ℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.34 – 7.24 (m, 1H), 7.17 – 7.13 (m, 1H), 7.05 (t, *J* = 2.0 Hz, 1H), 7.01 (ddd, *J* = 8.3, 2.7, 1.0 Hz, 1H), 3.96 (s, 3H), 3.80 (s, 3H), 1.58 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 161.6, 159.7, 159.4, 144.4, 129.8, 125.4, 120.7, 117.8, 117.2, 101.3, 84.2, 80.5, 55.4, 53.8, 28.1. **HRMS (ESI-TOF)** m/z: $[M+H]^+$Calcd for $C_{17}H_{20}NO_5^+$ 318.1336; Found:318.1335.



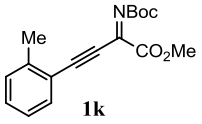
1i

According to the general procedure, **1i** was obtained in 32% yield as a yellow solid. Melting point 45-47 ℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.66 – 7.65 (m, 1H), 7.60 – 7.54 (m, 1H), 7.51 – 7.46 (m, 1H), 7.40 – 7.35 (m, 1H), 3.96 (s, 3H), 1.45 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 168.9, 159.4, 138.5, 134.8, 133.3, 132.1, 131.8, 130.1, 120.7, 118.3, 95.6, 87.3, 79.7, 53.8, 28.2. **HRMS (ESI-TOF)** m/z: $[M+H]^+$Calcd for $C_{16}H_{17}ClNO_4^+$: 322.0841; Found: 322.0846.



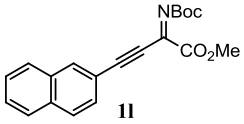
1j

According to the general procedure, **1j** was obtained in 52% yield as a yellow solid. Melting point 69-71 ℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.68 (d, *J* = 2.3 Hz, 2H), 6.55 (t, *J* = 2.3 Hz, 1H), 3.96 (s, 3H), 3.78 (s, 6H), 1.58 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 161.6, 160.6, 159.7, 144.3, 121.0, 110.4, 104.5, 101.4, 84.2, 80.1, 55.5, 53.8, 28.1. **HRMS (ESI-TOF)** m/z: $[M+H]^+$Calcd for $C_{18}H_{22}NO_6^+$: 348.1442; Found: 348.1442.



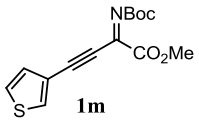
1k

According to the general procedure, **1k** was obtained in 83% yield as a yellow solid. Melting point 30-33 ℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.49 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.36 (td, *J* = 7.6, 1.4 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.19 (td, *J* = 7.5, 1.2 Hz, 1H), 3.96 (s, 3H), 2.51 (s, 3H), 1.57 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 161.7, 159.8, 144.4, 142.5, 134.4, 133.3, 131.1, 129.9, 119.7, 100.8, 84.6, 84.1, 53.8, 28.1, 20.5. **HRMS (ESI-TOF)** m/z: $[M+H]^+$Calcd for $C_{17}H_{20}NO_4^+$: 302.1387; Found:302.1384.



1l

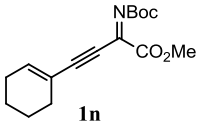
According to the general procedure, **1l** was obtained in 28% yield as a yellow solid. Melting point 72-74 ℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 1.6 Hz, 1H), 7.90 – 7.81 (m, 3H), 7.62 – 7.50 (m, 3H), 3.99 (s, 3H), 1.61 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 161.7, 159.8, 144.4, 134.2, 134.0, 132.6, 128.5, 128.24, 128.20, 128.0, 127.9, 127.1, 117.0, 102.0, 84.2, 81.1, 53.9, 28.1. **HRMS (ESI-TOF)** m/z: $[M+H]^+$Calcd for $C_{20}H_{20}NO_4^+$: 338.1387; Found:338.1386.



1m

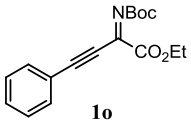
According to the general procedure, **1m** was obtained in 22% yield as a yellow solid. Melting point 37-40 ℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 5.0 Hz, 1H), 7.34 (dd, *J* = 5.1, 3.0 Hz, 1H), 7.19 (d, *J* = 5.0 Hz, 1H), 3.95 (s, 3H),

1.58 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 161.6, 159.8, 144.4, 134.0, 129.9, 126.3, 119.1, 96.8, 84.1, 81.0, 53.8, 28.0. **HRMS (ESI-TOF)** m/z: $[M+H]^+$Calcd for $C_{14}H_{16}NO_4S^+$: 294.0795; Found: 294.0790.



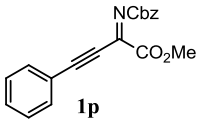
1n

According to the general procedure, **1n** was obtained in 55% yield as a yellow solid. Melting point 45-47 ℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.47 (dt, *J* = 4.3, 2.3 Hz, 1H), 3.91 (s, 3H), 2.26 – 2.12 (m, 4H), 1.55 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 161.8, 159.9, 144.6, 143.3, 119.1, 103.9, 83.8, 79.2, 53.7, 28.1, 28.0, 26.2, 21.8, 20.0. **HRMS (ESI-TOF)** m/z: $[M+H]^+$Calcd for $C_{16}H_{22}NO_4^+$: 292.1544; Found: 292.1539.



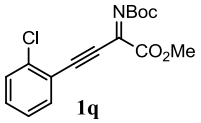
1o

According to the general procedure, **1o** was obtained in 62% yield as a yellow solid. Melting point 58-60 ℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.58 – 7.52 (m, 2H), 7.48 – 7.44 (m, 1H), 7.40 – 7.35 (m, 2H), 4.42 (q, *J* = 7.2 Hz, 2H), 1.58 (s, 9H), 1.41 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 161.2, 159.9, 144.8, 132.8, 131.0, 128.6, 119.9, 101.2, 84.1, 80.9, 63.3, 28.1, 14.0. **HRMS (ESI-TOF)** m/z: $[M+H]^+$Calcd for $C_{17}H_{20}NO_4^+$: 302.1387; Found: 302.1391.



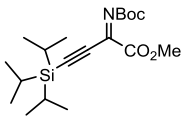
1p

According to the general procedure, **1p** was obtained in 34% yield as a yellow oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.96 – 7.90 (m, 1H), 7.50 – 7.47 (m, 1H), 7.44 – 7.41 (m, 2H), 7.36 – 7.35 (m, 3H), 7.32 – 7.28 (m, 3H), 5.35 (s, 2H), 3.97 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 162.0, 159.6, 134.9, 133.9, 133.8, 133.0, 128.8, 128.60, 128.55, 128.1, 121.2, 87.1, 81.0, 66.9, 53.9. **HRMS (ESI-TOF)** m/z: $[M+H]^+$Calcd for $C_{19}H_{16}NO_4^+$: 322.1074; Found: 322.1070.



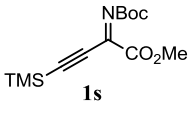
1q

According to the general procedure, **1q** was obtained in 70% yield as a yellow solid. Melting point 43-45 ℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.56 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.45 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.39 (td, *J* = 7.7, 1.7 Hz, 1H), 7.29 (dd, *J* = 7.6, 1.3 Hz, 1H), 3.97 (s, 3H), 1.57 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 161.4, 159.5, 144.0, 137.2, 134.5, 132.0, 129.7, 126.7, 120.2, 97.3, 84.7, 84.3, 53.9, 28.1. **HRMS (ESI-TOF)** m/z: $[M+H]^+$Calcd for $C_{16}H_{17}ClNO_4^+$: 322.0841; Found: 322.0846.



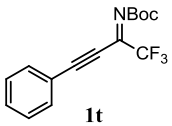
1r

According to the general procedure, **1r** was obtained in 90% yield as a yellow oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 3.90 (s, 3H), 1.54 (s, 9H), 1.10 (s, 21H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 161.4, 159.4, 143.7, 107.9, 96.4, 84.0, 53.7, 28.0, 18.4, 11.0. **HRMS (ESI-TOF)** m/z: $[M+H]^+$Calcd for $C_{19}H_{34}NO_4Si^+$: 368.2252; Found: 368.2248.



1s

According to the general procedure, **1t** was obtained in 38% yield as a yellow oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 3.90 (s, 3H), 1.53 (s, 9H), 0.23 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 161.4, 159.4, 143.9, 109.8, 94.0, 84.0, 53.7, 28.0, -0.9. **HRMS (ESI-TOF)** m/z: $[M+H]^+$Calcd for $C_{13}H_{22}NO_4Si^+$: 284.1313; Found: 284.1312.



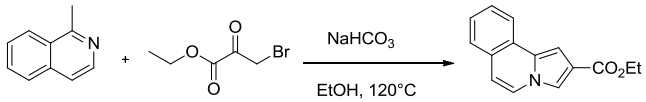
1t

According to the general procedure, **1s** was obtained in 58% yield as a yellow oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.57 – 7.52 (m, 2H), 7.51 – 7.47 (m, 1H), 7.43 – 7.37 (m, 2H), 1.60 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 158.7, 143.0 (d, *J* = 40.9 Hz), 132.8, 131.6, 128.8, 118.9, 118.0 (d, *J* = 278.3 Hz), 102.4,

84.7, 77. 6, 27.9. **^{19}F NMR** (376 MHz, Chloroform-d) δ -72.37. **HRMS (ESI-TOF)** m/z: $[M+H]^+$Calcd for $C_{15}H_{15}F_3NO_2^+$: 298.1050; Found:298.1058. The spectrum mached the literature data.[2]

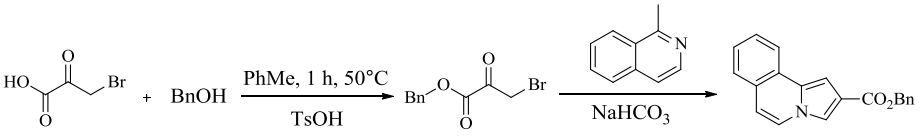
3. General procedure for the pyrrolo[2,1-a]isoquinolines

Procedure A: To a 100 mL dry round-bottom flask was added 1-methylisoquinoline (0.13 mL, 1.0 mmol, 1.0 equiv), ethyl bromopyruvate (0.12 mL, 1.0 mmol, 1.0 equiv), and $NaHCO_3$ (0.168 g, 2.0 equiv) in EtOH (0.1 M). The mixture was stirred at 120 ℃ in an oil bath 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 50:1) to afford the product **2a**, methyl bromopyruvate was subjected instead of ethyl bromopyruvate affording the corresponding product **2b**.



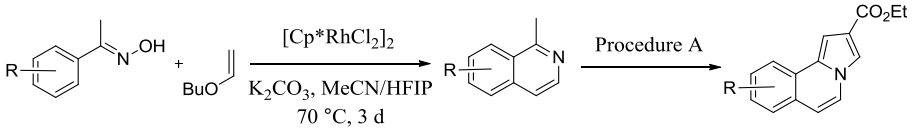
2a

Procedure B: To a solution of 3-bromopyruvic acid (834.8 mg, 5 mmol, 1.0 equiv) and BnOH (0.57 mL, 5.5 mmol, 1.1 equiv) in toluene (10 mL, 0.5 M) was added TsOH (0.1722 g, 20 mol%) and montmorillonite (2.822 g, 10 mmol, 2.0 equiv) and the resulting solution was stirred at 50 ℃ for 1 hour. The resulting reaction mixture was filterated by celite and concentrated under vacuum to yield bromopyruvate as a yellow oil. The crude product was used in next step without further purification. Bromopyruvate was subjected to the subsequent step according to procedure A, affording the corresponding products **2c**-**2d**.

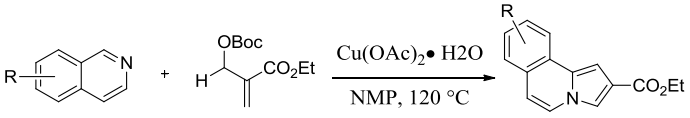


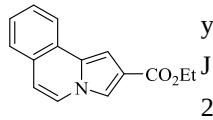
2c

Procedure C: Acetophenone oxime (1.0 mmol), $[Cp^*RhCl_2]_2$ (15.45 mg, 2.5 mol%), K_2CO_3 (276.4 mg, 2.0 mmol) and n-butyl vinyl ether (0.26 mL, 2.0 mmol) were mixed in dry MeCN (5 mL) and then HFIP (0.5 mL) was added. The reaction mixture was stirred at 70 ℃ for 3 days. The mixture was then opened to air and evaporated in vacuum. The residue was subjected to column chromatography on silica gel (petroleum ether/ethyl acetate 15:1), which furnished target the methylisoquinoline.[3] The obtained methylisoquinolines were subjected the next step according to procedure A.

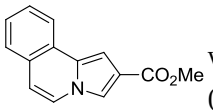


Procedure D: A mixture of isoquinoline (3 mmol), MBH carbonate (230.3 mg, 1 mmol), $Cu(OAc)_2 \cdot H_2O$ (39.9 mg, 20 mol%), and NMP (1 mL, 0.1 M) was stirred at 120 ℃ in air. Upon the consumption of MBH carbonate (monitored by TLC), the mixture was concentrated and the residue was purified by a silica gel flash chromatography (petroleum ether/EtOAc 30:1) to afford the product.[4]

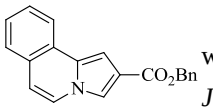




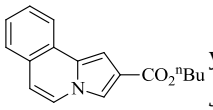
Following the general procedure A, compound **2a** was isolated in 67% yield as a yellow solid. Melting point 82-84 ℃. **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.01 (d, J = 7.9 Hz, 1H), 7.79 (d, J = 1.6 Hz, 1H), 7.67 (d, J = 7.3 Hz, 1H), 7.57 – 7.45 (m, 2H), 7.42 – 7.31 (m, 2H), 6.79 (d, J = 7.4 Hz, 1H), 4.37 (q, J = 7.1 Hz, 2H), 1.40 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 165.2, 130.4, 128.2, 127.2, 126.8, 126.6, 126.5, 124.3, 122.4, 118.9, 118.8, 113.4, 101.2, 60.4, 14.6. **HRMS (ESI-TOF)** m/z: $[M+H]^+$Calcd for $C_{15}H_{14}NO_2^+$ 240.1019; Found: 240.1023.



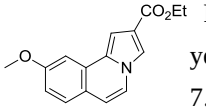
Following the general procedure A, compound **2b** was isolated in 51% yield as a white solid. Melting point 123-125 ℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 1.6 Hz, 1H), 7.66 (d, *J* = 7.4 Hz, 1H), 7.57 – 7.45 (m, 2H), 7.38 (td, *J* = 7.5, 1.2 Hz, 1H), 7.34 – 7.31 (m, 1H), 6.79 (d, *J* = 7.4 Hz, 1H), 3.90 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.6, 130.5, 128.2, 127.2, 126.8, 126.6, 126.5, 124.3, 122.4, 118.9, 118.5, 113.5, 101.2, 51.6. **HRMS (ESI-TOF)** m/z: $[M+H]^+$Calcd for $C_{14}H_{12}NO_2^+$ 226.0863; Found: 226.0865.



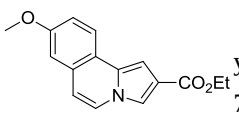
Following the general procedure B, compound **2c** was isolated in 21% yield as a white solid. Melting point 113-114 ℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 1.6 Hz, 1H), 7.63 (d, *J* = 7.4 Hz, 1H), 7.57 – 7.45 (m, 4H), 7.45 – 7.32 (m, 5H), 6.78 (d, *J* = 7.4 Hz, 1H), 5.38 (s, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.9, 136.6, 130.4, 128.7, 128.3, 128.22, 128.18, 127.2, 126.8, 126.6, 126.4, 124.2, 122.4, 119.0, 118.4, 113.5, 101.3, 66.1. **HRMS (ESI-TOF)** m/z: $[M+H]^+$Calcd for $C_{20}H_{16}NO_2^+$ 302.1176; Found: 302.1178.



Following the general procedure B, compound **2d** was isolated in 39% yield as a yellow solid. Melting point 77-79 ℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 1.6 Hz, 1H), 7.64 (d, *J* = 7.4 Hz, 1H), 7.55 – 7.44 (m, 2H), 7.37 (td, *J* = 7.5, 1.3 Hz, 1H), 7.33 – 7.30 (m, 1H), 6.77 (d, *J* = 7.4 Hz, 1H), 4.32 (t, *J* = 6.7 Hz, 2H), 1.76 (dq, *J* = 8.4, 6.7 Hz, 2H), 1.56 – 1.44 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.2, 130.3, 128.1, 127.2, 126.8, 126.5, 126.4, 124.2, 122.4, 118.9, 118.8, 113.3, 101.1, 64.2, 31.0, 19.4, 13.9. **HRMS (ESI-TOF)** m/z: $[M+H]^+$Calcd for $C_{17}H_{18}NO_2^+$ 268.1332; Found: 268.1330.

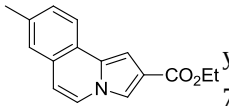


Following the general procedure D, compound **2e** was isolated in 17% yield as a yellow solid. Melting point 129-133 ℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.79 – 7.74 (m, 1H), 7.60 – 7.53 (m, 1H), 7.49 – 7.42 (m, 1H), 7.44 – 7.39 (m, 1H), 7.32 – 7.27 (m, 1H), 6.99 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.77 – 6.71 (m, 1H), 4.42 – 4.32 (m, 1H), 3.95 – 3.91 (m, 3H), 1.44 – 1.38 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.2, 159.6, 130.3, 128.8, 127.7, 122.2, 120.7, 118.8, 118.7, 115.7, 113.1, 104.4, 101.2, 60.3, 55.6, 14.6. **HRMS (ESI-TOF)** m/z: $[M+H]^+$Calcd for $C_{16}H_{16}NO_3^+$ 270.1125; Found: 270.1121.

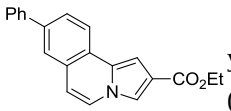


Following the general procedure D, compound **2f** was isolated in 21% yield as a yellow solid. Melting point 114-115 ℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 8.7 Hz, 1H), 7.74 (d, *J* = 1.3 Hz, 1H), 7.65 (d, *J* = 7.4 Hz, 1H), 7.18 (s, 1H), 7.10 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.98 (d, *J* = 2.6 Hz, 1H), 6.72 (d, *J* = 7.3 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.3, 158.4, 130.6, 128.2, 124.8, 124.0, 120.4, 118.9, 118.2, 117.0, 113.1, 109.2, 99.5,

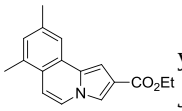
60.3, 55.6, 14.6. **HRMS (ESI-TOF)** m/z: $[M+H]^+$Calcd for $C_{16}H_{16}NO_3^+$ 270.1125; Found: 270.1128.



Following the general procedure C, compound **2g** was isolated in 47% yield as a yellow solid. Melting point 103-105 ℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 8.6 Hz, 1H), 7.72 (d, *J* = 1.7 Hz, 1H), 7.56 (d, *J* = 7.3 Hz, 1H), 7.31 – 7.23 (m, 3H), 4.38 (d, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 1.42 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 165.3, 136.4, 130.6, 129.5, 127.1, 126.9, 124.3, 124.1, 122.4, 118.8, 118.5, 113.3, 100.5, 60.3, 21.5, 14.6. **HRMS (ESI-TOF)** m/z: $[M+H]^+$Calcd for $C_{16}H_{16}NO_2^+$ 254.1176; Found:254.1179.

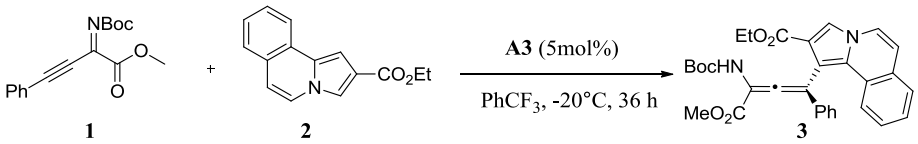


Following the general procedure C, compound **2h** was isolated in 34% yield as a yellow solid. Melting point 93-96 ℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 1.6 Hz, 1H), 7.73 (m, *J*= 7.5 Hz, 2H), 7.67 (m, *J* = 7.5 Hz, 3H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.41 – 7.35 (m, 2H), 6.82 (d, *J* = 7.3 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.1, 140.6, 139.3, 130.2, 129.1, 129.0, 127.6, 127.3, 127.23, 127.20, 125.5, 125.4, 124.6, 122.9, 118.9, 113.5, 101.3, 60.3, 14.6. **HRMS (ESI-TOF)** m/z: $[M+H]^+$Calcd for $C_{21}H_{18}NO_2^+$ 316.1332; Found: 316.1337.



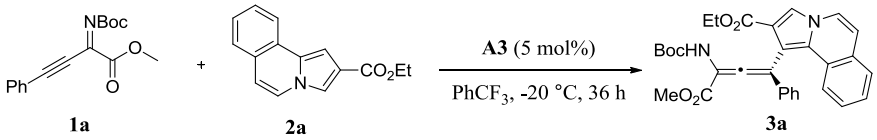
Following the general procedure C, compound **2i** was isolated in 48% yield as a yellow solid. Melting point 116-118 ℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.72 (q, *J* = 1.5 Hz, 1H), 7.65 (s, 1H), 7.56 (dd, *J* = 5.1, 2.7 Hz, 1H), 7.28 (d, *J* = 1.7 Hz, 1H), 7.02 (s, 1H), 6.87 – 6.81 (m, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 2.48 (d, *J* = 2.5 Hz, 3H), 2.43 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.2, 137.6, 134.0, 130.6, 129.3, 126.4, 123.1, 123.0, 120.3, 118.7, 118.3, 109.6, 100.8, 60.2, 21.7, 19.3, 14.6. **HRMS (ESI-TOF)** m/z: $[M+H]^+$Calcd for $C_{17}H_{18}NO_2^+$ 268.1332; Found: 268.1328.

5. General procedure for the asymmetric synthesis of axially chiral allenes



To a 4 mL vial was added β,γ-alkynyl-α-imino ester **1** (0.1 mmol, 1.0 equiv), pyrrolo[2,1-a]isoquinoline **2** (0.12 mmol, 1.2 equiv) and **A3** (0.005 mmol, 5 mol%) in $PhCF_3$ (0.5 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**.

6. Scale-up synthesis of the product 3a

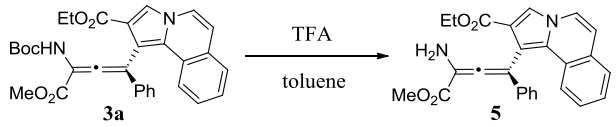


To a 25 mL round-bottom flaskl was added β,γ-alkynyl-α-imino ester (**1a**) (1.0 mmol, 287 mg, 1.0 equiv), pyrrolo[2,1-a]isoquinoline (**2a**) (1.2 mmol, 287 mg,1.2 equiv) and **A3** (0.05 mmol, 5 mol%) in $PhCF_3$ (5 mL). The mixture was stirred at -20 ℃ for 36 h. The solvent was removed by rotovapor and

the residue was directly purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 15:1) to afford the product **3a (**380.1 mg) in 72% yield as a faint yellow solid.

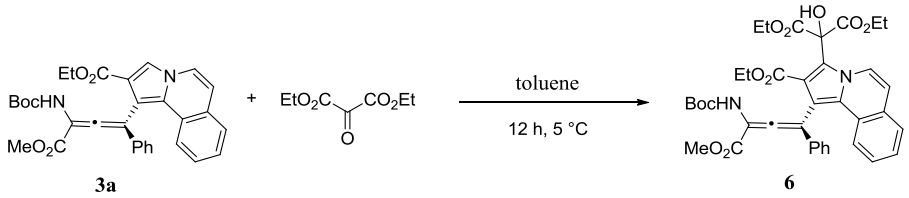
7. Procedure for the late-stage functionalizations of 3a.

a) Procedure for the deprotection of **3a**.



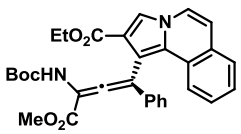
Compound **3a** (26.3 mg, 0.05 mmol) was dissolved in toluene (1.0 mL). Then TFA (2 equiv) was added and the reaction mixture was allowed to stir at 5 ℃. After 1 hour, the reaction was monitored by TLC until **3a** disappeared completely. After that, the reaction mixture was directly purified by column chromatography on silica gel (petroleum ether/ethyl acetate 5:1) to provide product **5** bearing a free amino group as a reddish brown oil (19.2 mg, 90% yield).

b) C3-functionalization of **3a** with ketomalonate.

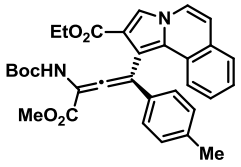


To a solution of **3a** (0.105 mg, 0.2 mmol) in toluene (2.0 mL) was added diethyl ketomalonate (5.0 equiv). The mixture was stirred at 5 ℃ for 12 h. After reaction, the solvent was removed by rotovapor and the residue was directly purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate 6:1) to afford the product **6** as a yellow solid (94.7 mg, 68% yield).

9. Analytical data

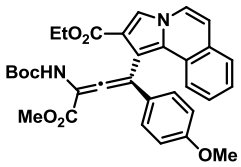


The compound **3a** was prepared according to the general procedure. The product was obtained as a yellow solid (35.6 mg, 68% yield). Melting point 83.8-86.8 ℃. The 97% ee was measured by HPLC using a chiral stationary phase [Daicel IG, *n*-hexane:*i*-PrOH=70:30,1.0 mL/min), t_R =9.838 min (major), t_R =15.413 min (minor)], $[\alpha]_D^{30}$ = -27.2 (c = 0.71, $CHCl_3$). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.50 (d, *J* = 77.1 Hz, 1H), 7.90 (s, 1H), 7.68 (d, *J* = 7.4 Hz, 1H), 7.51 (m, *J* = 7.5 Hz, 3H), 7.39 – 7.27 (m, 3H), 7.25 (m, *J* = 7.9 Hz, 2H), 6.81 (d, *J* = 7.3 Hz, 1H), 6.14 (s, 1H), 4.27 – 4.07 (m, 2H), 3.69 (s, 3H), 1.44 (s, 9H), 1.02 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.9, 164.4, 151.8, 135.4, 128.5, 127.9, 127.7, 127.4, 126.8, 126.4, 126.3, 124.2, 119.6, 113.8, 110.1, 102.5, 80.4, 60.2, 52.9, 28.3, 13.8. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{31}H_{31}N_2O_6^+$ 527.2177; Found: 527.2172.

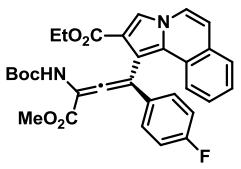


The compound **3b** was prepared according to the general procedure. The product was obtained as a yellow solid (32.4 mg, 60% yield). Melting point 95.2-97.1 ℃. The 96% ee was measured by HPLC using a chiral stationary phase [Daicel IG, *n*-hexane:*i*-PrOH=70:30, 1.0 mL/min), t_R =10.065 min (major), t_R =16.285 min (minor)], $[\alpha]_D^{30}$ = -29.9 (c = 0.65, $CHCl_3$). **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.51 (d, J = 82.7 Hz, 1H), 7.89 (s, 1H), 7.67 (d, J = 7.3 Hz, 1H), 7.52 – 7.46 (m, 1H), 7.42 – 7.28 (m, 4H), 7.11 (d, J = 7.8 Hz, 2H), 6.80 (d, J = 7.3 Hz, 1H), 6.12 (s, 1H), 4.28 – 4.06 (m, 2H), 3.67 (s, 3H), 2.32 (s, 3H), 1.44 (s, 9H), 1.06 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz,

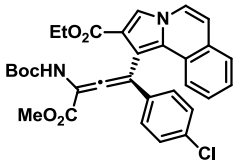
Chloroform-*d*) δ 166.0, 164.5, 151.9, 137.7, 132.5, 129.2, 127.6, 127.4, 126.7, 126.4, 126.3, 124.2, 119.5, 113.8, 110.3, 102.3, 80.3, 60.1, 52.8, 28.4, 21.4, 13.9. **HRMS (ESI-TOF)** m/z : $[M+H]^+$ Calcd for $C_{32}H_{33}N_2O_6^+$ 541.2333; Found:541.2329



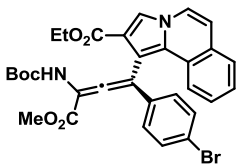
The compound **3c** was prepared according to the general procedure. The product was obtained as a yellow oil (39.0 mg, 70% yield). Melting point 94.1-96.0 ℃. The 94% ee was measured by HPLC using a chiral stationary phase [Daicel IG, *n*-hexane:*i*-PrOH=70:30, 1.0 mL/min), t_R =12.307 min (major), t_R =19.382 min (minor)], $[\alpha]_D^{30}$ = +19.4 (c = 0.65, $CHCl_3$). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.50 (d, *J* = 94.0 Hz, 1H), 7.89 (s, 1H), 7.67 (d, *J* = 7.4 Hz, 1H), 7.52 – 7.46 (m, 1H), 7.46 – 7.40 (m, 2H), 7.32 (m, *J* = 7.2, 6.7 Hz, 2H), 6.82 (m, *J* = 13.5, 7.9 Hz, 3H), 6.12 (s, 1H), 4.28 – 4.06 (m, 2H), 3.77 (s, 3H), 3.67 (s, *J* = 40.9 Hz, 3H), 1.44 (s, 9H), 1.07 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.0, 164.7, 159.5, 152.1, 129.0, 127.8, 127.3, 126.8, 126.4, 126.3, 124.2, 119.5, 114.0, 113.8, 110.4, 102.2, 80.3, 60.2, 55.4, 52.8, 28.4, 13.9. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{32}H_{33}N_2O_7^+$ 557.2283; Found: 557.2284.



The compound **3d** was prepared according to the general procedure. The product was obtained as a yellow oil (32.6 mg, 60% yield). Melting point 73.4-75.4 ℃. The 96% ee was measured by HPLC using a chiral stationary phase [Daicel IG, *n*-hexane:*i*-PrOH=70:30, 1.0 mL/min), t_R =7.408 min (major), t_R =10.288 min (minor)], $[\alpha]_D^{30}$ = -18.3 (c = 0.65, $CHCl_3$). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.47 (d, *J* = 86.2 Hz, 1H), 7.90 (s, 1H), 7.68 (d, *J* = 7.4 Hz, 1H), 7.50 (q, *J* = 7.2, 5.3 Hz, 3H), 7.34 (td, *J* = 7.5, 6.9, 4.3 Hz, 2H), 6.99 (t, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 7.4 Hz, 1H), 6.13 (s, 1H), 4.28 – 4.06 (m, 2H), 3.72 (s, 3H), 1.45 (s, 9H), 1.06 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.80, 163.94, 161.48, 151.81, 131.55, 129.41 (d, *J* = 8.3 Hz), 127.68, 127.36, 126.84, 126.54, 126.23, 124.18, 119.56, 115.44 (d, *J* = 21.8 Hz), 113.87, 112.63, 110.02, 102.55, 80.47, 60.19, 52.94, 28.37, 13.90. **^{19}F NMR** (376 MHz, Acetone-d_6) δ -116.05. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{31}H_{30}FN_2O_6^+$ 545.2083; Found: 545.2078.

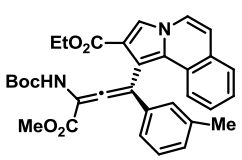


The compound **3e** was prepared according to the general procedure. The product was obtained as a yellow solid (29.1 mg, 52% yield). Melting point 89.4-91.6 ℃. The 96% ee was measured by HPLC using a chiral stationary phase [Daicel IG, *n*-hexane:*i*-PrOH=70:30, 1.0 mL/min), t_R =7.440 min (major), t_R =9.332 min (minor)], $[\alpha]_D^{30}$ =-33.4 (c = 0.58, $CHCl_3$). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.44 (d, *J* = 96.8 Hz, 1H), 7.90 (s, 1H), 7.68 (d, *J* = 7.3 Hz, 1H), 7.58 – 7.48 (m, 1H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.35 – 7.31 (m, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 6.82 (d, *J* = 7.4 Hz, 1H), 6.13 (s, 1H), 4.28 – 4.06 (m, 2H), 3.72 (s, 3H), 1.45 (s, 9H), 1.07 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.7, 164.3, 151.7, 134.1, 133.7, 131.4, 129.0, 128.7, 127.7, 127.4, 126.8, 126.6, 126.2, 124.1, 119.6, 113.9, 112.7, 109.6, 102.7, 80.5, 60.2, 53.0, 29.8, 28.4, 13.9. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{31}H_{30}ClN_2O_6^+$ 561.1787; Found: 561.1788.

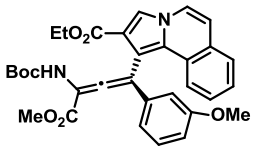


The compound **3f** was prepared according to the general procedure. The product was obtained as a yellow solid (36.2 mg, 60% yield). Melting point 86.4-88.3 ℃. The 96% ee was measured by HPLC using a chiral stationary phase [Daicel IG, *n*-hexane:*i*-PrOH=70:30, 1.0 mL/min), t_R =7.605 min (major), t_R =9.285 min (minor)], $[\alpha]_D^{30}$ = -11.2 (c = 0.72, $CHCl_3$). **^{1}H NMR**

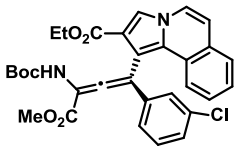
(400 MHz, Chloroform-*d*) δ 8.44 (d, *J* = 99.2 Hz, 1H), 7.89 (s, 1H), 7.68 (d, *J* = 7.4 Hz, 1H), 7.53 – 7.47 (m, 1H), 7.46 – 7.29 (m, 6H), 6.82 (d, *J* = 7.4 Hz, 1H), 6.13 (s, 1H), 4.28 – 4.06 (m, 2H), 3.73 (s, 3H), 1.44 (s, 9H), 1.07 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.7, 164.4, 151.7, 134.6, 131.6, 129.3, 127.4, 126.9, 126.6, 126.2, 124.2, 122.0, 119.6, 113.9, 112.8, 109.5, 102.8, 80.6, 60.2, 53.0, 28.4, 13.9. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{31}H_{30}BrN_2O_6^+$ 605.1282; Found: 605.1280.



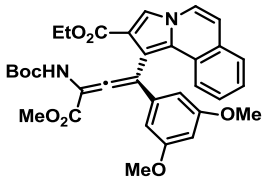
The compound **3g** was prepared according to the general procedure. The product was obtained as a yellow solid (31.3 mg, 58% yield). Melting point 67.6-70.8 ℃. The 97% ee was measured by HPLC using a chiral stationary phase [Daicel IG, *n*-hexane:*i*-PrOH=70:30, 1.0 mL/min), t_R =9.117 min (major), t_R =14.570 min (minor)], $[\alpha]_D^{30}$ =-39.8 (c = 0.63, $CHCl_3$). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.50 (d, *J* = 69.3 Hz, 1H), 7.90 (s, 1H), 7.68 (d, *J* = 7.3 Hz, 1H), 7.55 – 7.47 (m, 1H), 7.39 – 7.24 (m, 4H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 7.3 Hz, 1H), 6.12 (s, 1H), 4.36 – 3.99 (m, 2H), 3.68 (s, 3H), 2.29 (s, 3H), 1.44 (s, 9H), 1.04 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.0, 164.4, 152.0, 137.9, 135.3, 128.8, 128.33, 128.27, 127.7, 127.4, 126.8 126.41, 126.37, 124.9, 124.2, 119.6, 113.8, 110.3, 102.4, 80.4, 60.1, 52.9, 28.4, 21.6, 13.8. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{32}H_{33}N_2O_6^+$ 541.2333; Found: 541.2335.



The compound **3h** was prepared according to the general procedure. The product was obtained as a yellow solid (35.6 mg, 64% yield). Melting point 67.8-69.2 ℃. The 95% ee was measured by HPLC using a chiral stationary phase [Daicel IG, *n*-hexane:*i*-PrOH=70:30, 1.0 mL/min), t_R =12.210 min (major), t_R =18.113 min (minor)], $[\alpha]_D^{30}$ =-14.4(c = 0.71, $CHCl_3$). **^{1}H NMR** (400 MHz,) δ 8.50 (d, *J* = 71.7 Hz, 1H), 7.89 (s, 1H), 7.67 (d, *J* = 7.3 Hz, 1H), 7.52 – 7.46 (m, 1H), 7.35 – 7.29 (m, 2H), 7.24 – 7.15 (m, 2H), 7.06 (d, *J* = 7.7 Hz, 1H), 6.84 – 6.77 (m, 2H), 6.11 (s, 1H), 4.19 – 4.10 (m, 2H), 3.76 (s, 3H), 3.67 (s, 3H), 1.44 (s, 9H), 1.06 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.9, 164.2, 159.7, 151.9, 136.9, 129.3, 127.7, 127.4, 126.8, 126.4, 126.3, 124.2, 120.4, 119.5, 113.8, 113.5, 110.1, 102.5, 80.4, 60.2, 55.3, 52.9, 28.4, 13.9. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{32}H_{33}N_2O_7^+$ 557.2283; Found: 557.2282.

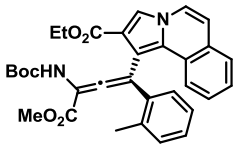


The compound **3i** was prepared according to the general procedure. The product was obtained as a yellow solid (31.4 mg, 56% yield). Melting point 81.4-84.3 ℃. The 94% ee was measured by HPLC using a chiral stationary phase [Daicel IG, *n*-hexane:*i*-PrOH=70:30, 1.0 mL/min), t_R = 8.637 min (major), t_R =10.445 min (minor)], $[\alpha]_D^{30}$ = -30.8 (c = 0.63, $CHCl_3$). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.47 (d, *J* = 90.3 Hz, 1H), 7.90 (s, 1H), 7.69 (d, *J* = 7.3 Hz, 1H), 7.54 – 7.46 (m, 2H), 7.38 – 7.33 (m, 3H), 7.28 – 7.19 (m, 2H), 6.84 (d, *J* = 6.1 Hz, 1H), 6.15 (s, 1H), 4.21 (bs, 2H), 3.73 (s, 3H), 1.44 (s, 9H), 1.05 (bs, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.7, 164.3, 151.7, 137.7, 134.4, 129.7, 127.9, 127.6, 127.5, 126.9, 126.6, 126.2, 125.9, 124.2, 119.7, 113.9, 112.6, 109.2, 103.5, 80.6, 60.3, 53.1, 28.4, 13.9. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{31}H_{30}ClN_2O_6^+$ 561.1787; Found: 561.1791.

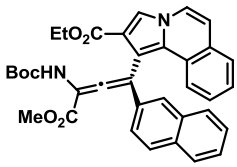


The compound **3j** was prepared according to the general procedure. The product was obtained as a yellow solid (42.2 mg, 72% yield). Melting point 79.3-81.4 ℃. The 96% ee was measured by HPLC using a chiral stationary

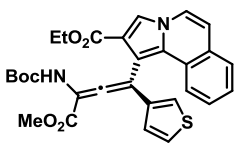
phase [Daicel IG, *n*-hexane:*i*-PrOH=70:30, 1.0 mL/min), t_R =11.313 min (major), t_R =16.722 min (minor)], $[\alpha]_D^{30}$= -27.7 (c = 0.70, $CHCl_3$). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.48 (d, *J* = 70.1 Hz, 1H), 7.88 (s, 1H), 7.66 (d, *J* = 7.3 Hz, 1H), 7.48 (d, *J* = 7.3 Hz, 1H), 7.39 – 7.29 (m, 2H), 6.91 – 6.63 (m, 3H), 6.37 (t, *J* = 2.3 Hz, 1H), 6.12 (s, 1H), 4.21 (bs, 2H), 3.72 (s, 9H), 1.45 (s, 9H), 1.11 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.9, 164.4, 160.7, 151.9, 137.6, 127.6, 127.4, 126.7, 126.4, 126.3, 124.1, 119.5, 113.8, 106.3, 102.4, 99.9, 80.4, 60.1, 55.4, 52.9, 28.3, 14.0. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{33}H_{34}N_2O_8^+$ 587.2388; Found: 587.2383.



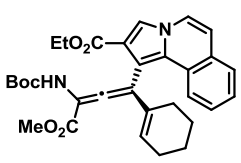
The compound **3k** was prepared according to the general procedure. The product was obtained as a yellow solid (11.3 mg, 21% yield). Melting point 78.7-81.6 ℃. The 95% ee was measured by HPLC using a chiral stationary phase [Daicel IG, *n*-hexane:*i*-PrOH=70:30, 1.0 mL/min), t_R =11.563 min (major), t_R =22.637 min (minor)], $[\alpha]_D^{30}$ =-84.3 (c = 0.23, $CHCl_3$). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.59 – 8.45 (m, 1H), 7.87 (d, *J* = 1.5 Hz, 1H), 7.68 (dd, *J* = 7.3, 1.5 Hz, 1H), 7.55 – 7.50 (m, 1H), 7.37 – 7.32 (m, 2H), 7.28 – 7.23 (m, 2H), 7.19 – 7.10 (m, 2H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.82 (dd, *J* = 7.4, 1.5 Hz, 1H), 6.01 (s, 1H), 4.17 (qt, *J* = 7.2, 2.5 Hz, 2H), 3.65 (s, 3H), 2.64 (s, 3H), 1.40 (s, 9H), 1.06 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 166.1, 164.4, 137.9, 133.9, 131.4, 128.8, 127.94, 127.86, 127.8, 127.4, 126.9, 126.5, 126.4, 126.0, 124.8, 124.3, 119.8, 118.7, 113.8, 112.3, 101.4, 80.4, 60.1, 52.7, 28.3, 22.4, 14.0. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{32}H_{33}N_2O_6^+$541.2333; Found: 541.2331



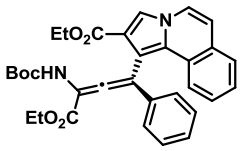
The compound **3l** was prepared according to the general procedure. The product was obtained as a yellow solid (40.9 mg, 71% yield). Melting point 126.4-128.2 ℃. The 96% ee was measured by HPLC using a chiral stationary phase [Daicel IG, *n*-hexane:*i*-PrOH=70:30, 1.0 mL/min),t_R = 11.232 min (major), t_R = 19.642 min (minor)], $[\alpha]_D^{30}$ =-32.3 (c = 0.60, $CHCl_3$). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.52 (d, *J* = 132.1 Hz, 1H), 7.96 (s, 1H), 7.85 – 7.77 (m, 3H), 7.76 – 7.69 (m, 2H), 7.68 – 7.63 (m, 1H), 7.53 – 7.48 (m, 1H), 7.44 – 7.34 (m, 2H), 7.30 (t, *J* = 7.0 Hz, 2H), 6.84 (d, *J* = 7.4 Hz, 1H), 6.17 (s, 1H), 4.23 – 4.03 (m, 2H), 3.71 (d, *J* = 67.5 Hz, 3H), 1.45 (s, 9H), 0.95 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 165.9, 164.3, 151.9, 133.6, 133.3, 133.0, 128.5, 128.1, 127.7, 127.6, 126.8, 126.6, 126.5, 126.3, 126.1, 125.9, 124.2, 119.7, 113.8, 110.1, 102.8, 80.5, 60.2, 52.9, 28.4, 13.9. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{35}H_{33}N_2O_6^+$ 577.2333; Found: 577.2332.



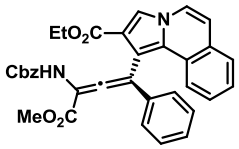
The compound **3m** was prepared according to the general procedure. The product was obtained as a yellow solid (33.0 mg, 62% yield). Melting point 69.6-72.3 ℃. The 95% ee was measured by HPLC using a chiral stationary phase [Daicel IG, *n*-hexane:*i*-PrOH=70:30, 1.0 mL/min), t_R =10.015 min (major), t_R =15.115 min (minor)], $[\alpha]_D^{30}$= -29.4 (c = 0.66, $CHCl_3$). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.54 (d, *J* = 83.6 Hz, 1H), 7.88 (s, 1H), 7.67 (d, *J* = 7.3 Hz, 1H), 7.50 (d, *J* = 7.4 Hz, 1H), 7.41 – 7.30 (m, 3H), 7.28 (dd, *J* = 5.1, 3.0 Hz, 1H), 7.09 (s, 1H), 6.81 (d, *J* = 7.3 Hz, 1H), 6.13 (s, 1H), 4.22 – 4.10 (m, 2H), 3.70 (s, 3H), 1.46 (s, 9H), 1.10 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.8, 164.4, 151.9, 137.5, 127.4, 127.1, 126.8, 126.5, 126.3, 125.6, 124.1, 123.7, 119.4, 113.8, 110.5, 101.6, 80.4, 60.1, 52.9, 28.4, 13.9. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{29}H_{29}N_2O_6S^+$ 533.1741; Found: 533.1740



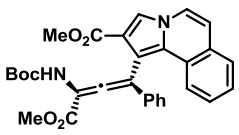
The compound **3n** was prepared according to the general procedure. The product was obtained as a yellow solid (32.3 mg, 61% yield). Melting point 68.6-70.1 ℃. The 93% ee was measured by HPLC using a chiral stationary phase [Daicel IG, *n*-hexane:*i*-PrOH=70:30, 1.0 mL/min), t_R =9.192 min (major), t_R =14.543 min (minor)], $[\alpha]_D^{30}$ = -29.8 (c = 0.65, $CHCl_3$). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.59 (d, *J* = 7.9 Hz, 0.5H), 8.29 (d, *J* = 8.1 Hz, 0.5H), 7.83 (s, 1H), 7.66 – 7.60 (m, 1H), 7.53 – 7.41 (m, 2H), 7.34 (d, *J* = 6.7 Hz, 1H), 6.77 (d, *J* = 7.3 Hz, 1H), 6.00 (s, 1H), 5.59 (s, 1H), 4.44 – 4.15 (m, 2H), 3.76 – 3.60 (m, 3H), 2.78 – 2.23 (m, 2H), 2.01 (s, 2H), 1.77 (q, *J* = 6.0, 5.5 Hz, 2H), 1.61 (dt, *J* = 7.4, 4.0 Hz, 2H), 1.44 (s, 9H), 1.33 (dd, *J* = 9.3, 5.0 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.1, 164.8, 164.4, 152.3, 152.1, 132.6, 131.9, 128.7, 128.4, 128.3, 127.7, 127.4, 127.1, 126.8, 126.6, 126.4, 126.3, 125.5, 124.7, 124.3, 124.0, 119.6, 119.3, 118.6, 113.7, 113.5, 110.5, 110.1, 102.1, 101.8, 80.1, 60.2, 60.0, 52.9, 52.6, 36.7, 28.5, 28.4, 26.8, 26.1, 22.9, 22.3, 14.3, 14.2. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{31}H_{35}N_2O_6^+$ 531.2490; Found: 531.2493.



The compound **3o** was prepared according to the general procedure. The product was obtained as a yellow solid (14.6 mg, 27% yield). Melting point 75.6-77.9 ℃. The 76% ee was measured by HPLC using a chiral stationary phase [Daicel IG, *n*-hexane:*i*-PrOH=70:30, 1.0 mL/min), t_R =10.222 min (major), t_R =12.555 min (minor)], $[\alpha]_D^{30}$ =-66.9 (c = 0.29, $CHCl_3$). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.39 (s, 1H), 7.90 (s, 1H), 7.68 (d, *J* = 7.3 Hz, 1H), 7.52 – 7.47 (m, 3H), 7.35 – 7.27 (m, 4H), 7.25 – 7.20 (m, 1H), 6.81 (d, *J* = 7.4 Hz, 1H), 6.14 (s, 1H), 4.22 – 4.13 (m, 4H), 1.45 (s, 3H), 1.44 (s, 9H), 1.02 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 165.3, 164.4, 156.4, 152.1, 135.5, 128.5, 127.9, 127.7, 127.5, 126.8, 126.44, 126.36, 125.0, 124.2, 119.6, 113.8, 110.2, 102.9, 80.4, 62.0, 60.1, 28.4, 14.4, 13.9. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{32}H_{33}N_2O_6^+$ 540.2333; Found: 540.2333.

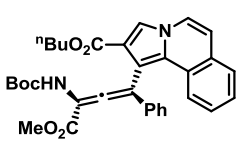


The compound **3p** was prepared according to the general procedure. The product was obtained as a yellow solid (36.4 mg, 65% yield). Melting point 160.2-162.3 ℃. The 97% ee was measured by HPLC using a chiral stationary phase [Daicel IG, *n*-hexane:*i*-PrOH=70:30, 1.0 mL/min), t_R =21.207 min (major), t_R =31.392 min (minor)], $[\alpha]_D^{30}$ = -25.8 (c = 0.68, $CHCl_3$). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.47 (s, 1H), 7.92 (s, 1H), 7.68 (d, *J* = 7.3 Hz, 1H), 7.52 (t, *J* = 6.3 Hz, 3H), 7.42 – 7.21 (m, 10H), 6.83 (d, *J* = 7.3 Hz, 1H), 6.40 (s, 1H), 5.22 – 5.11 (m, 2H), 4.18 (s, 2H), 3.71 (s, 3H), 1.05 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.5, 164.2, 152.8, 136.2, 135.0, 128.54, 128.51, 128.2, 128.0, 127.6, 127.4, 126.8, 126.5, 126.1, 124.8, 124.1, 119.6, 118.9, 113.8, 109.7, 102.2, 67.2, 60.1, 52.9, 13.9. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{34}H_{29}N_2O_6^+$ 561.2020; Found: 561.2021

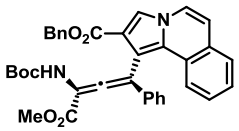


The compound **3q** was prepared according to the general procedure. The product was obtained as a yellow solid (35.8 mg, 70% yield). Melting point 169.9-172.3 ℃. The 92% ee was measured by HPLC using a chiral stationary phase [Daicel IG, *n*-hexane:*i*-PrOH=70:30, 1.0 mL/min), t_R =8.855 min (major), t_R =12.080 min (minor)], $[\alpha]_D^{30}$ = -26.9 (c = 0.72, $CHCl_3$). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.46 (s, 1H), 7.89 (s, 1H), 7.67 (d, *J* = 7.3 Hz, 1H), 7.51 (d, *J* = 7.4 Hz, 3H), 7.32 (q, *J* = 7.6, 6.5 Hz, 4H), 7.26 – 7.22 (m, 1H), 6.81 (d, *J* = 7.4 Hz, 1H), 6.14 (s, 1H), 3.73 (s, 6H), 1.45 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.9, 164.7, 151.8, 135.5, 128.6, 128.1, 127.9, 127.6, 127.4, 126.8, 126.5,

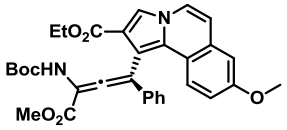
126.3, 124.2, 119.5, 113.9, 113.4, 110.4, 102.5, 80.4, 52.9, 51.4, 28.4. **HRMS (ESI-TOF)** m/z : $[M+H]^+$ Calcd for $C_{30}H_{29}N_2O_6^+$ 513.2020; Found: 513.2023.



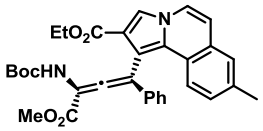
The compound **3r** was prepared according to the general procedure. The product was obtained as a yellow solid (29.6 mg, 53% yield). Melting point 66.0-68.4 ℃. The 93% ee was measured by HPLC using a chiral stationary phase [Daicel IG, *n*-hexane:*i*-PrOH=70:30, 1.0 mL/min), t_R =8.522 min (major), t_R =10.482 min (minor)], $[\alpha]_D^{30}$ = -32.9 (c = 0.59, $CHCl_3$). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.47 (d, *J* = 111.7 Hz, 1H), 7.90 (d, *J* = 1.9 Hz, 1H), 7.68 (d, *J* = 7.3 Hz, 1H), 7.55 – 7.43 (m, 3H), 7.30 (q, *J* = 7.6, 6.8 Hz, 4H), 7.27 – 7.20 (m, 1H), 6.81 (d, *J* = 7.3 Hz, 1H), 6.11 (s, 1H), 4.36 – 3.96 (m, 2H), 3.66 (s, 3H), 1.44 (s, 9H), 1.38 (p, *J* = 7.0 Hz, 2H), 1.09 (s, 2H), 0.76 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-d) δ 165.9, 164.7, 151.9, 135.3, 128.5, 127.9, 127.7, 127.4, 126.8, 126.4, 126.3, 124.2, 119.6, 113.8, 109.8, 102.6, 80.4, 64.3, 52.9, 30.6, 28.4, 19.2, 13.9. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{33}H_{35}N_2O_6^+$ 555.2490; Found: 555.2490.



The compound **3s** was prepared according to the general procedure. The product was obtained as a yellow solid (17.1 mg, 29% yield). Melting point 93.8-95.4 ℃. The 89% ee was measured by HPLC using a chiral stationary phase [Daicel IG, *n*-hexane:*i*-PrOH=70:30, 1.0 mL/min), t_R =12.775 min (major), t_R =14.950 min (minor)], $[\alpha]_D^{30}$ = -57.1 (c = 0.34, $CHCl_3$). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.48 (d, *J* = 139.6 Hz, 1H), 7.92 (s, 1H), 7.67 (d, *J* = 7.4 Hz, 1H), 7.57 – 7.39 (m, 3H), 7.32 (d, *J* = 6.8 Hz, 2H), 7.29 – 7.15 (m, 6H), 7.11 (s, 2H), 6.82 (d, *J* = 7.4 Hz, 1H), 6.11 (s, 1H), 5.46 – 5.02 (m, 2H), 3.61 (s, 3H), 1.43 (s, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 165.9, 164.0, 151.7, 135.2, 128.6, 128.4, 128.0, 127.7, 127.5, 126.8, 126.5, 126.3, 124.2, 119.9, 113.9, 80.5, 65.9, 52.9, 28.4. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{36}H_{33}N_2O_6^+$ 589.2333; Found: 589.2335.

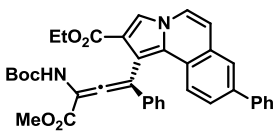


The compound **3t** was prepared according to the general procedure. The product was obtained as a yellow solid (42.0 mg, 76% yield). Melting point 107.4-109.6 ℃. The 90% ee was measured by HPLC using a chiral stationary phase [Daicel IG, *n*-hexane:*i*-PrOH=70:30, 1.0 mL/min), t_R =11.998 min (major), t_R =15.532 min (minor)], $[\alpha]_D^{30}$ = -30.3(c = 0.64, $CHCl_3$). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.41 (s, 1H), 7.85 (s, 1H), 7.66 (d, *J* = 7.4 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 2H), 7.38 – 7.27 (m, 2H), 7.25 – 7.19 (m, 1H), 7.01 – 6.92 (m, 2H), 6.75 (d, *J* = 7.4 Hz, 1H), 6.12 (s, 1H), 4.26 – 4.06 (m, 2H), 3.82 (s, 3H), 3.70 (s, 3H), 1.45 (s, 9H), 1.01 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.9, 164.6, 158.2, 151.9, 135.6, 129.3, 128.5, 127.9, 127.7, 124.7, 120.2, 119.0, 116.4, 113.5, 109.2, 108.3, 102.4, 80.4, 60.1, 55.4, 52.9, 28.4, 13.8. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{32}H_{33}N_2O_7^+$ 557.2283; Found: 557.2282.

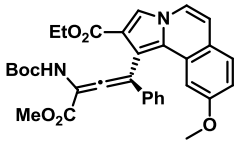


The compound **3u** was prepared according to the general procedure. The product was obtained as a yellow solid (37.8 mg, 70% yield). Melting point 78.4-80.1 ℃. The 93% ee was measured by HPLC using a chiral stationary phase [Daicel IA, *n*-hexane:*i*-PrOH=80:20, 1.0 mL/min), t_R =7.430 min (minor), t_R =8.506 min (major)], $[\alpha]_D^{30}$ = -25.5 (c = 0.76, $CHCl_3$). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.31 (s, 1H), 7.87 (s, 1H), 7.65 (d, *J* = 7.3 Hz, 1H), 7.50 (d, *J* = 7.6 Hz, 2H), 7.35 – 7.27 (m, 3H), 7.25 – 7.11 (m, 2H), 6.75 (d, *J* = 7.4 Hz, 1H), 6.11 (s, 1H), 4.19 (q, *J* = 9.5, 8.7 Hz, 2H), 3.70 (s, 3H), 2.38 (s, 3H), 1.45 (s, 9H), 1.02 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.9, 164.5,

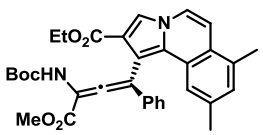
152.0, 136.2, 135.5, 128.5, 127.84, 127.79, 127.7, 127.6, 126.8, 124.2, 123.9, 119.3, 113.7, 109.3, 102.4, 80.4, 60.1, 52.9, 28.4, 21.4, 13.8. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{32}H_{33}N_2O_6^+$ 541.2333; Found: 541.2336.



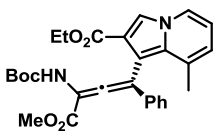
The compound **3v** was prepared according to the general procedure. The product was obtained as a yellow solid (30.1 mg, 50% yield). Melting point 106.9-108.8 ℃. The 91% ee was measured by HPLC using a chiral stationary phase [Daicel IG, *n*-hexane:*i*-PrOH=80:20, 1.0 mL/min), t_R =16.220 min (minor), t_R =18.492 min (major)], $[\alpha]_D^{30}$ = +32.3 (c = 0.60, $CHCl_3$). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.56 (d, *J* = 81.3 Hz, 1H), 7.92 (s, 1H), 7.71 (d, *J* = 7.5 Hz, 2H), 7.60 (d, *J* = 7.7 Hz, 3H), 7.53 (d, *J* = 7.6 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.38 – 7.28 (m, 3H), 7.27 – 7.23 (m, 1H), 6.88 (d, *J* = 7.3 Hz, 1H), 6.15 (s, 1H), 4.26 – 4.11 (m, 2H), 3.71 (s, 3H), 1.45 (s, 9H), 1.03 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.9, 164.7, 152.0, 140.6, 139.1, 135.5, 133.4, 129.0, 128.5, 127.9, 127.7, 127.5, 127.4, 127.1, 125.4, 125.0, 124.6, 119.7, 114.0, 110.4, 102.5, 80.4, 60.2, 52.9, 28.4, 13.8. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{37}H_{35}N_2O_6^+$ 603.2490; Found: 603.2492.



The compound **3w** was prepared according to the general procedure. The product was obtained as a yellow solid (32.8 mg, 59% yield). Melting point 105.6-108.3 ℃. The 95% ee was measured by HPLC using a chiral stationary phase [Daicel IG, *n*-hexane:*i*-PrOH=70:30, 1.0 mL/min), t_R =8.025 min (major), t_R =14.753 min (minor)], $[\alpha]_D^{30}$ = -29.4 (c = 0.66, $CHCl_3$). **^{1}H NMR** (500 MHz, Acetone-d_6) δ 8.12 (s, 1H), 8.00 (d, *J* = 7.3 Hz, 1H), 7.79 (s, 1H), 7.55 (d, *J* = 23.3 Hz, 3H), 7.38 – 7.31 (m, 2H), 7.31 – 7.25 (m, 1H), 6.95 (d, *J* = 7.2 Hz, 3H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.67 (d, *J* = 83.0 Hz, 6H), 1.52 – 1.26 (m, 9H), 1.10 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, Acetone-d_6) δ 165.7, 164.5, 160.0, 153.6, 129.2, 128.8, 128.3, 128.0, 123.5, 122.4, 120.6, 117.0, 116.0, 114.0, 107.8, 80.3, 60.3, 55.5, 52.6, 28.4, 14.3. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{32}H_{33}N_2O_7^+$ 557.2283; Found: 557.2283.

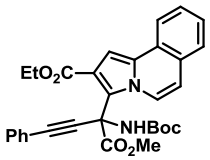


The compound **3x** was prepared according to the general procedure. The product was obtained as a yellow solid (31.6 mg, 57% yield). Melting point 76.8-78.9 ℃. The 87% ee was measured by HPLC using a chiral stationary phase [Daicel IG, *n*-hexane:*i*-PrOH=70:30, 1.0 mL/min), t_R =11.217 min (major), t_R =15.553 min (minor)], $[\alpha]_D^{30}$ = -30.8 (c = 0.63, $CHCl_3$). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.23 – 7.92 (m, 1H), 7.86 (s, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 7.7 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.00 (s, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.14 (s, 1H), 4.21 (q, *J* = 7.4 Hz, 2H), 3.67 (s, 3H), 2.50 (s, 3H), 2.27 (d, *J* = 8.5 Hz, 3H), 1.42 (s, 9H), 1.08 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.9, 164.5, 151.8, 135.5, 133.3, 129.4, 128.4, 127.8, 127.7, 126.4, 124.0, 123.1, 119.1, 118.8, 113.5, 110.0, 102.4, 80.3, 60.1, 52.8, 28.3, 21.8, 19.6, 13.9. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{33}H_{35}N_2O_6^+$ 555.2490; Found: 555.2490.

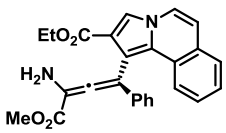


The compound **3y** was prepared according to the general procedure. The product was obtained as a yellow solid (21.1 mg, 43% yield). Melting point 59.7-61.9 ℃. The 90% ee was measured by HPLC using a chiral stationary phase [Daicel IG, *n*-hexane:*i*-PrOH=70:30, 1.0 mL/min), t_R =11.230 min (major), t_R =20.498 min (minor)], $[\alpha]_D^{30}$ = -46.2 (c = 0.42, $CHCl_3$). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.75 (d, *J* = 6.8 Hz, 1H), 7.40 (d, *J* = 7.7 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.24 – 7.18 (m, 1H), 6.46 (dt, *J* = 12.8, 6.7 Hz, 2H), 6.09 (s, 1H), 4.23 – 3.99 (m, 2H), 3.76 (s, 3H), 2.36 (s, 3H), 1.42 (s, 9H), 1.00 (t, *J* =

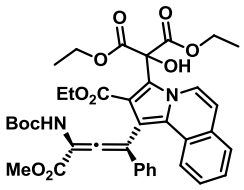
7.2 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.8, 164.6, 152.4, 137.2, 131.6, 131.2, 128.4, 128.3, 127.74, 127.65, 126.9, 123.6, 119.9, 118.9, 117.2, 112.6, 106.8, 102.1, 80.5, 60.1, 52.8, 28.3, 13.8. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{28}H_{31}N_2O_6^+$ 491.2177; Found: 491.2174.



The compound **4a** was prepared according to the general procedure. The product was obtained as a yellow solid . Melting point 73.8-75.8 ℃. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 9.40 (d, *J* = 7.9 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.53 – 7.46 (m, 5H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.37 – 7.28 (m, 3H), 6.90 (d, *J* = 7.9 Hz, 1H), 4.42 – 4.30 (m, 2H), 3.80 (d, *J* = 1.2 Hz, 3H), 1.43 (td, *J* = 7.1, 1.1 Hz, 3H), 1.39 (s, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.4, 165.8, 154.5, 132.0, 130.3, 129.1, 128.5, 127.7, 126.8, 126.7, 126.1, 122.3, 122.1, 116.3, 112.5, 102.9, 87.0, 85.4, 80.3, 60.9, 56.7, 54.2, 28.4, 14.5. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{31}H_{31}N_2O_6^+$ 527.2177; Found: 527.2168.



The compound **5** was prepared according to the general procedure. The product was obtained as reddish brown oil (19.2 mg, 90% yield). Melting point 129.3-130.8 ℃. The 0% ee was measured by HPLC using a chiral stationary phase [Daicel IG, *n*-hexane:*i*-PrOH=70:30, 1.0 mL/min), t_R =11.510 min, t_R =18.767 min]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.95 (s, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 7.4 Hz, 1H), 7.64 – 7.57 (m, 2H), 7.56 – 7.48 (m, 2H), 7.43 – 7.21 (m, 4H), 6.86 (d, *J* = 7.3 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.44 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 184.0, 163.8, 163.4, 1555, 138.8, 130.7, 128.9, 128.3, 128.1, 127.9, 127.5, 127.4, 126.9, 126.1, 124.1, 123.1, 122.9, 120.1, 118.6, 114.2, 113.2, 60.2, 52.3, 14.2. **HRMS (APCI-TOF)** m/z : $[M+Na]^+$ Calcd for $C_{26}H_{22}N_2NaO_4^+$ 449.1472; Found:449.1471.



The compound **6** was prepared according to the general procedure. The product was obtained as a yellow solid (94.7 mg, 68% yield). Melting point 82.4-84.2 ℃. The 88% ee was measured by HPLC using a chiral stationary phase [Daicel AD-H, n-hexane:i-PrOH=80:20, 1.0 mL/min), t_R =13.560 min (minor), t_R =22.088 min (major)], $[\alpha]_D^{30}$ = 27.7 (c = 0.70, $CHCl_3$). **^{1}H NMR** (500 MHz, Acetone-d_6) δ 8.51 (s, 1H), 8.03 (d, *J* = 7.7 Hz, 1H), 7.69 – 7.62 (m, 1H), 7.53 (d, *J* = 7.7 Hz, 2H), 7.43 – 7.31 (m, 4H), 7.30 – 7.25 (m, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 6.92 (s, 1H), 6.28 (s, 1H), 4.41 – 3.97 (m, 6H), 3.68 (s, 3H), 1.43 (s, 9H), 1.23 (t, *J* = 7.1 Hz, 6H), 0.86 (q, *J* = 8.5, 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, Acetone-d_6) δ 169.0, 165.7, 165.6, 153.1, 136.3, 132.0, 129.6, 129.1, 128.7, 128.52, 128.45, 127.7, 127.5, 126.4, 125.8, 124.5, 123.3, 121.4, 113.5, 109.9, 103.7, 80.5, 78.6, 63.4, 61.2, 53.1, 28.4, 14.1, 13.6. **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{38}H_{41}N_2O_{11}^+$ 701.2705; Found:701.2711.

10. X-ray crystallographic analysis

Single crystals suitable for X-ray diffraction experiment were obtained by diffusion method of *n*-hexane/EtOAc containing the corresponding compounds **3p** and **4a**, respectively. The crystal was kept at 300 K during data collection. Date collection was performed at 300 K on Bruker D8 Venture diffractrometer with a CCD area detector, using graphite monochromated Cu *Kα* radiation (λ = 1.54178 Å). Refinements were performed on *F* anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method using SHELXL program in OLEX2 software.

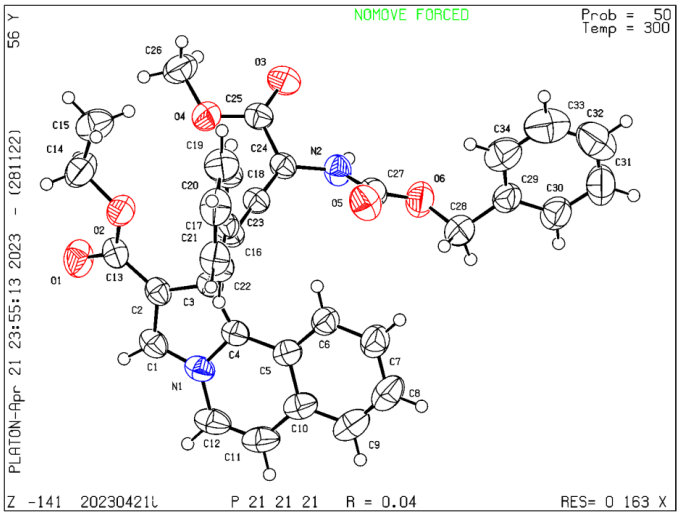


Figure S1. X-ray structure of **3p** at 50% probability level. Flack parameter = 0.13(7).

Bond precision: C-C = 0.0043 A Wavelength=1.54178

Cell: a=9.2858(**6**) b=10.8685(7) c=27.6229(17)
alpha=90 beta=90 gamma=90

Temperature: 300 K

	Calculated	Reported
Volume	2787.8(3)	2787.8(3)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C34 H28 N2 O6	C34 H28 N2 O6
Sum formula	C34 H28 N2 O6	C34 H28 N2 O6
Mr	560.58	560.58
Dx,g cm-3	1.336	1.336
Z	4	4
Mu (mm-1)	0.753	0.753
F000	1176.0	1176.0
F000'	1179.72	
h,k,lmax	11,13,34	11,13,34
Nref	5557[3160]	5556
Tmin,Tmax	0.893,0.914	0.436,0.754
Tmin'	0.893	

Correction method= # Reported T Limits: Tmin=0.436 Tmax=0.754
AbsCorr = MULTI-SCAN

Data completeness= 1.76/1.00 Theta(max)= 72.594

R(reflections)= 0.0430(5006) wR2(reflections)= 0.1124(5556)

S = 1.058 Npar=382

Single crystals suitable for X-ray diffraction experiment were obtained by diffusion method of *n*-hexane/Acetonitrile containing the corresponding compound **4a**. The crystal was kept at 300 K during data collection.

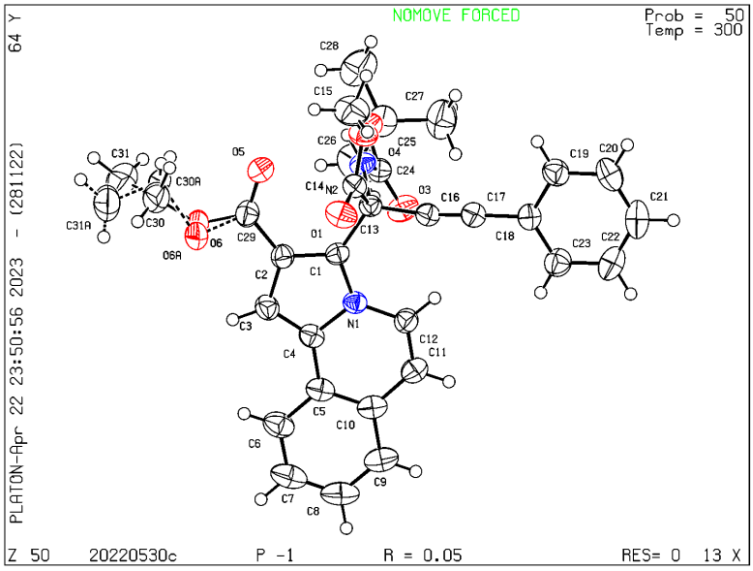


Figure S2. X-ray structure of **4a** (at 50% probability level).

Bond precision: C-C = 0.0025 A Wavelength=0.71073

Cell: a=10.1018(8) b=11.4504(7) c=13.7104(12)
alpha=105.430(3) beta=99.759(3) gamma=108.874(4)

Temperature: 300 K

	Calculated	Reported
Volume	1388.58(19)	1388.58(19)
Space group	P -1	P -1
Hall group	-P1	-P 1
Moiety formula	C31 H30 N2 O6	C31 H30 N2 O6
Sum formula	C31 H30 N2 O6	C31 H30 N2 O6
Mr	526.57	526.57
Dx,g cm-3	1.259	1.259
Z	2	2
Mu (mm-1)	0.088	0.088
F000	556.0	0.088
F000'	556.27	
h,k,lmax	15,17,20	13,15,20
Nref	9737	7152
Tmin,Tmax	0.986,0.989	0.688,0.746
Tmin'	0.986	

Correction method= # Reported T Limits: Tmin=0.688 Tmax=0.746
AbsCorr = MULTI-SCAN

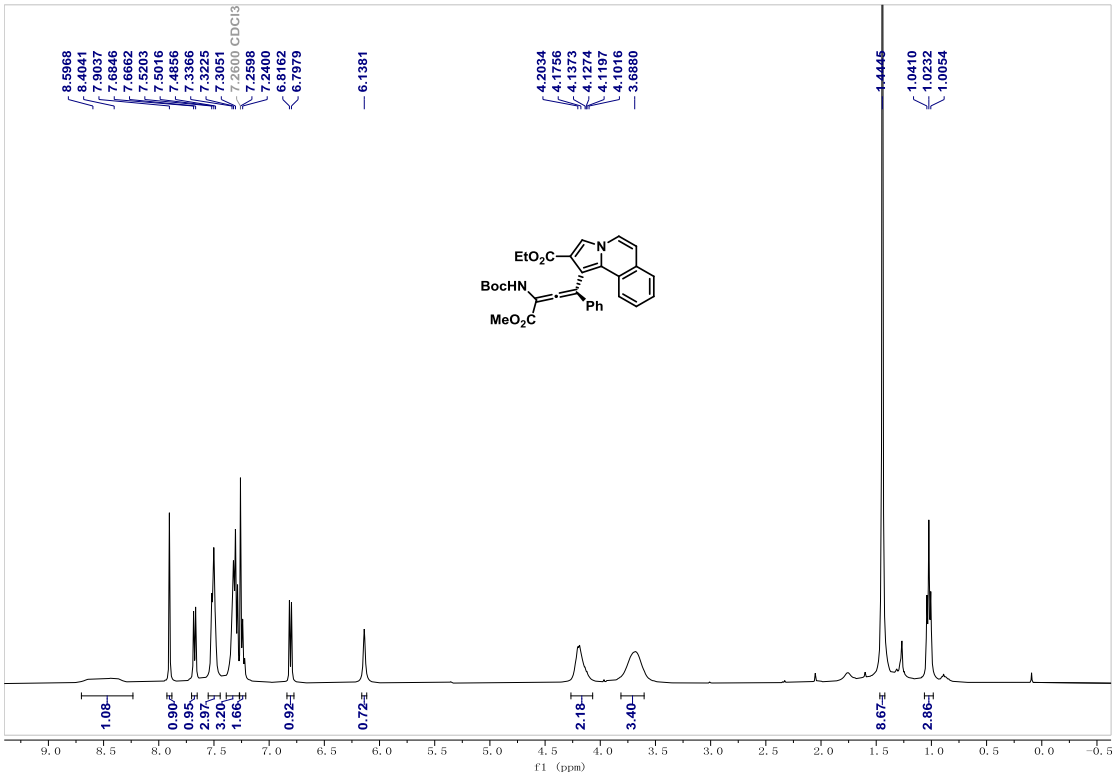
Data completeness= 0.735 Theta(max)= 32.134

R(reflections)= 0.0490(4171) wR2(reflections)= 0.1398(7152)

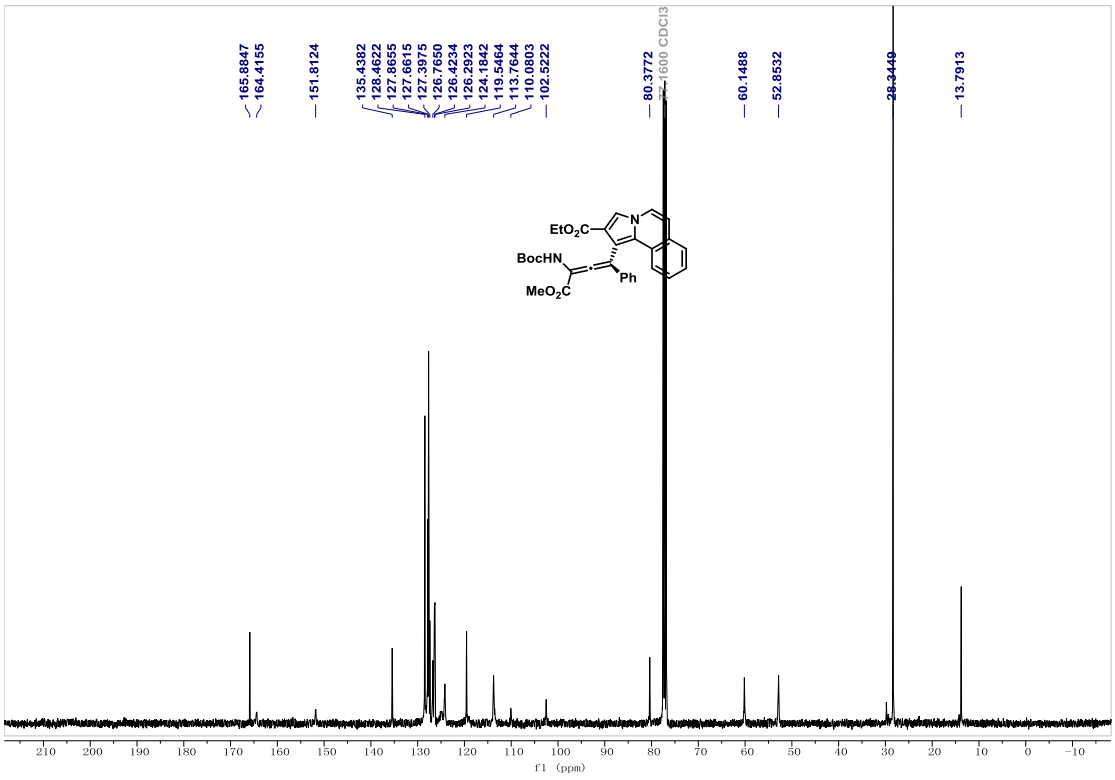
S = 1.022 Npar= 386

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

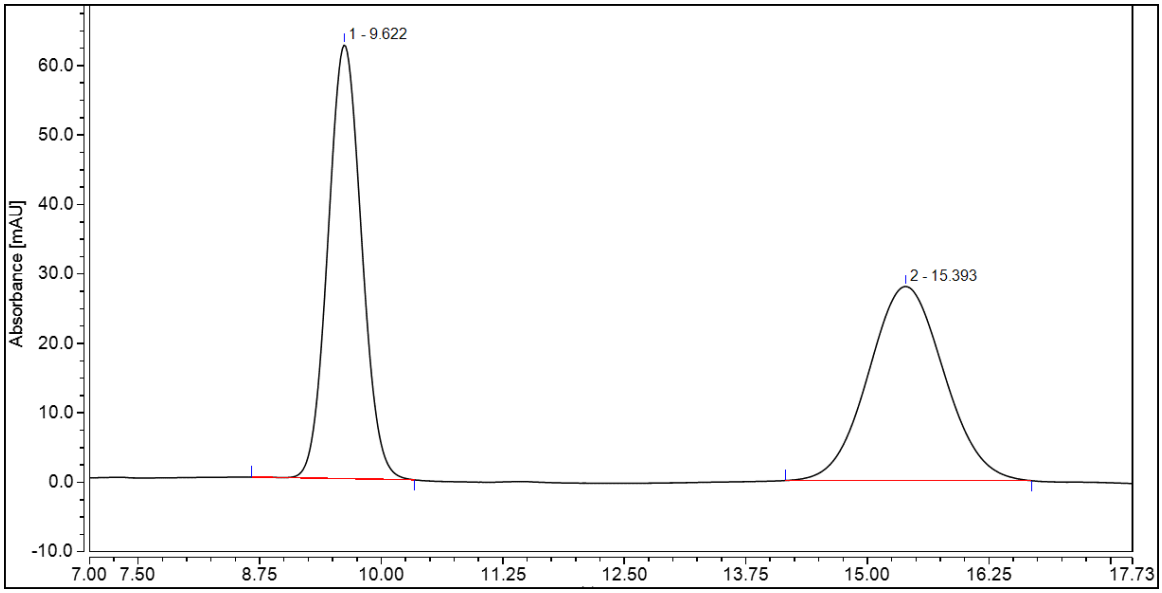
^{1}H NMR of **3a** (400 MHz, $CDCl_3$)



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

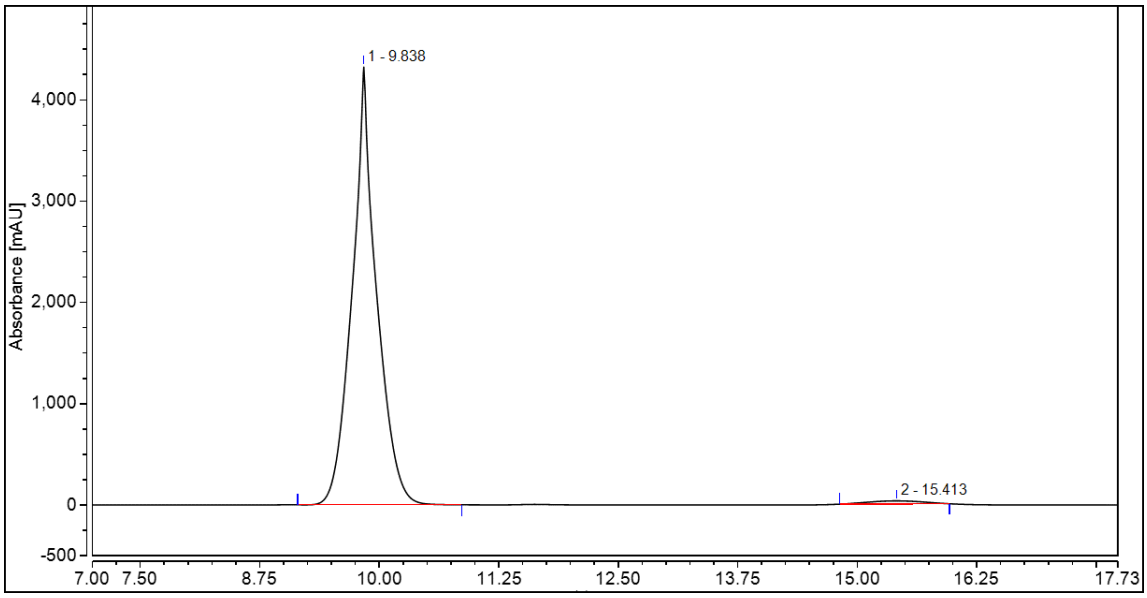


HPLC analysis: rac-**3a**



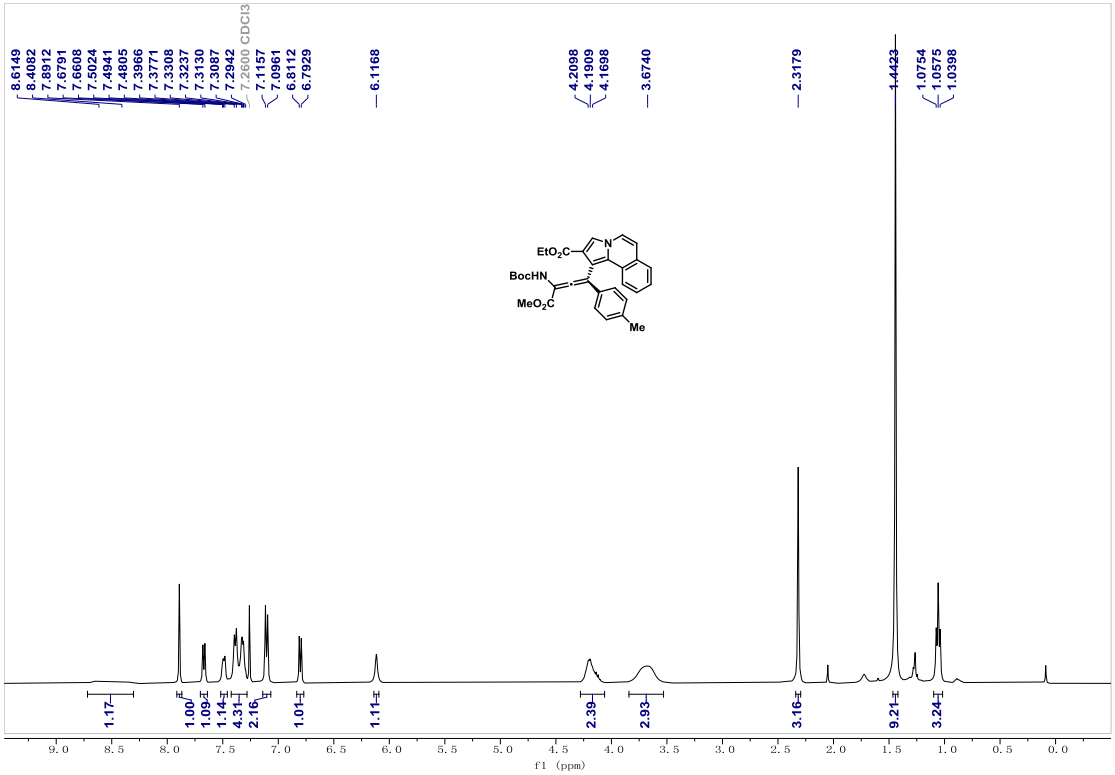
Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	9.622	25.027	62.451	49.85	69.08
2	15.393	25.178	27.953	50.15	30.92

Enantioenriched **3a**

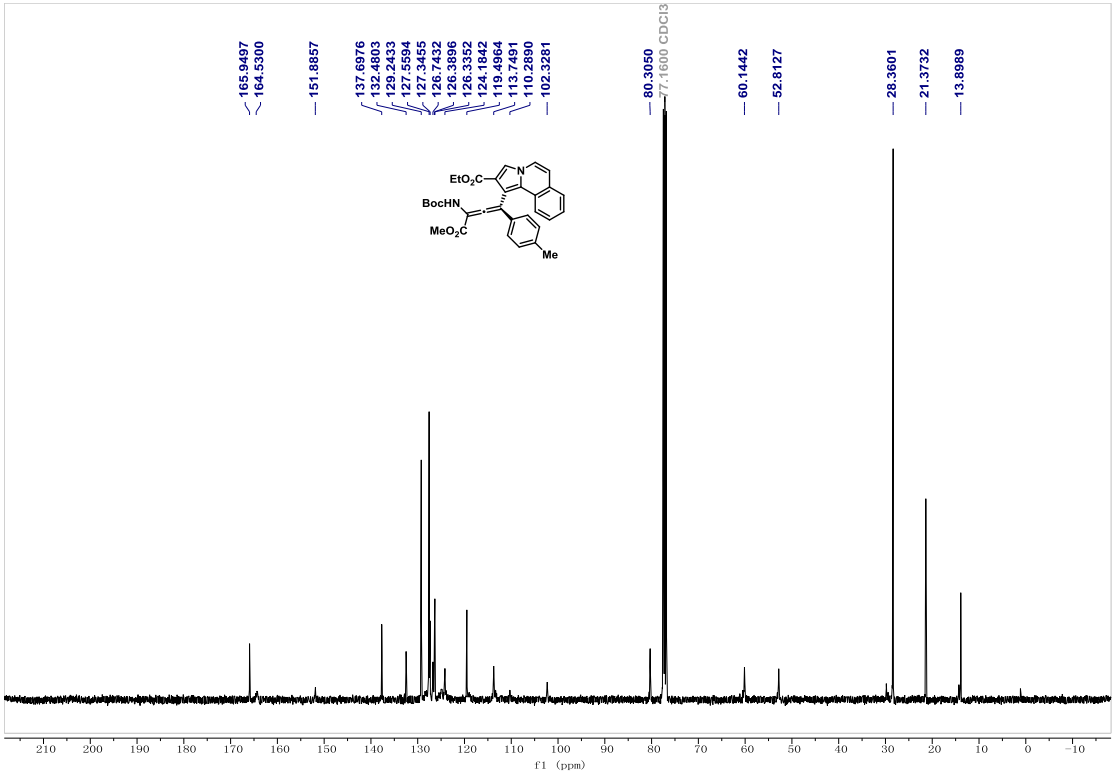


Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	9.838	1270.847	4321.901	98.45	99.30
2	15.413	20.000	30.291	1.55	0.70

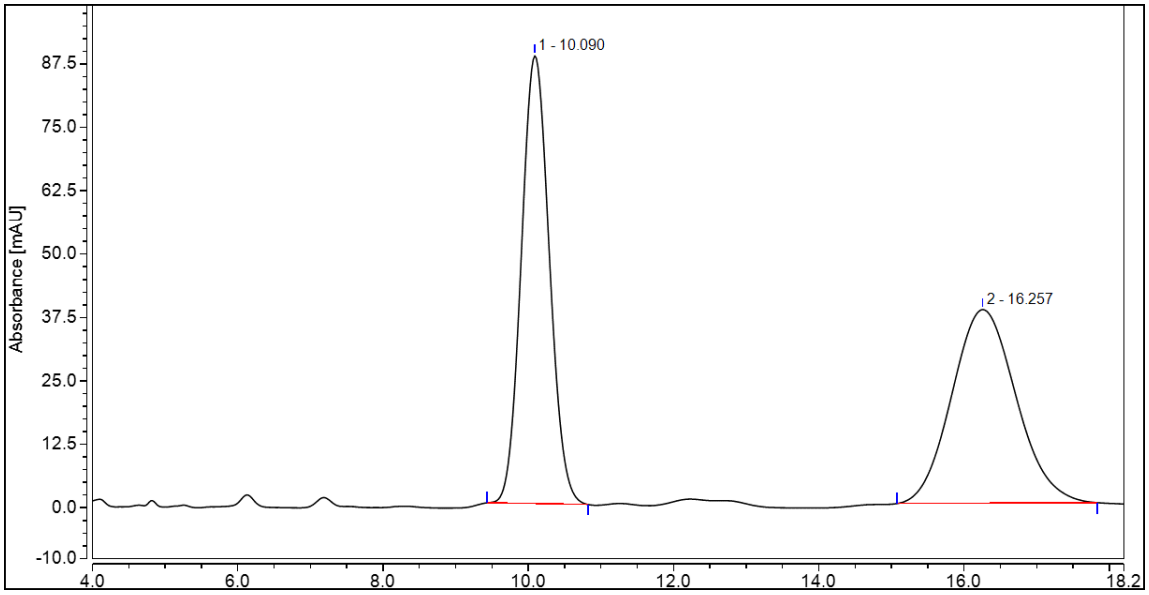
^{1}H NMR of **3b** (400 MHz, $CDCl_3$)



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

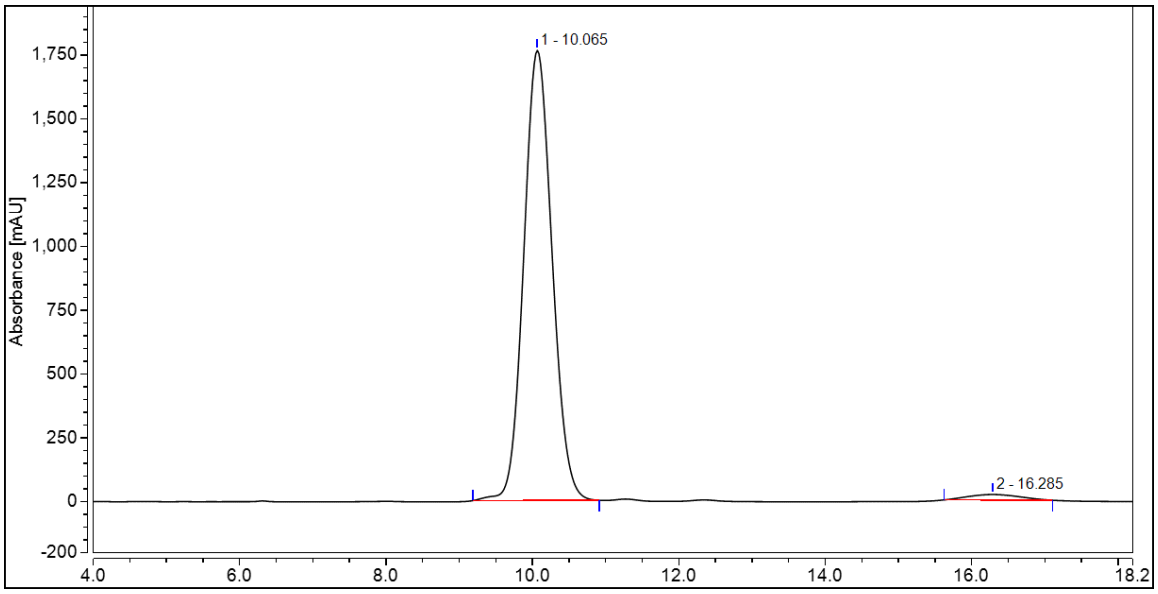


HPLC analysis: rac-**3b**



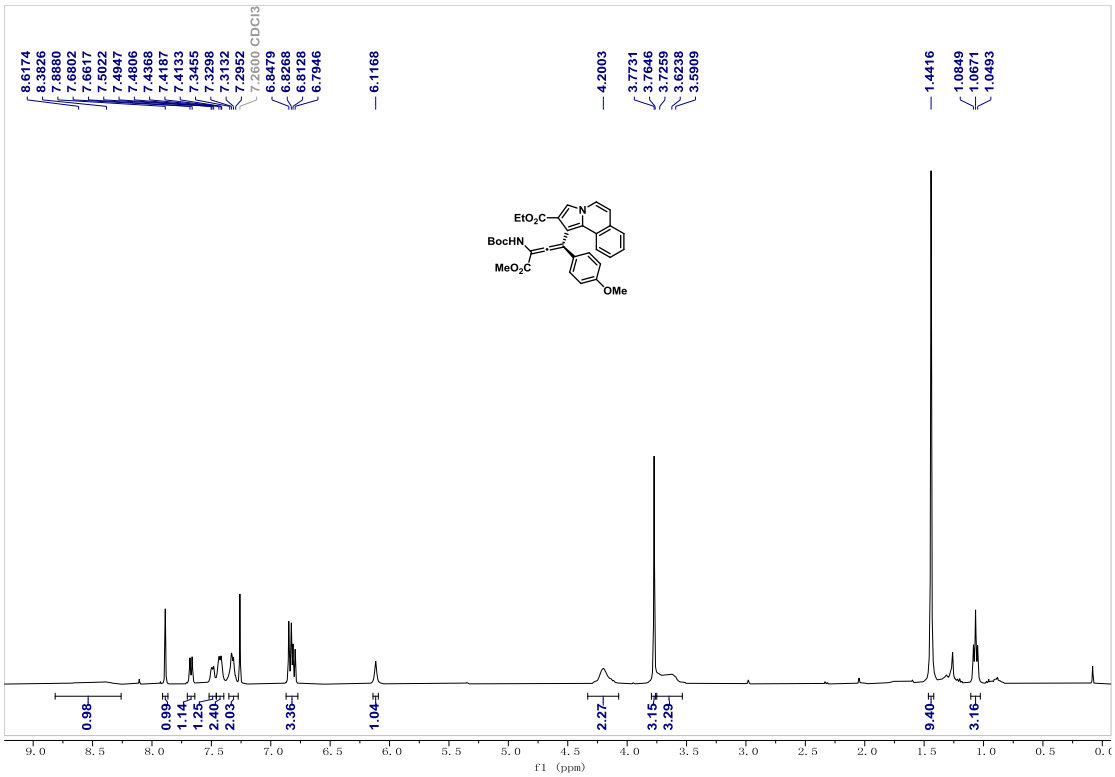
Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	10.090	39.481	88.298	50.22	69.82
2	16.257	39.142	38.162	49.78	30.18

Enantioenriched **3b**

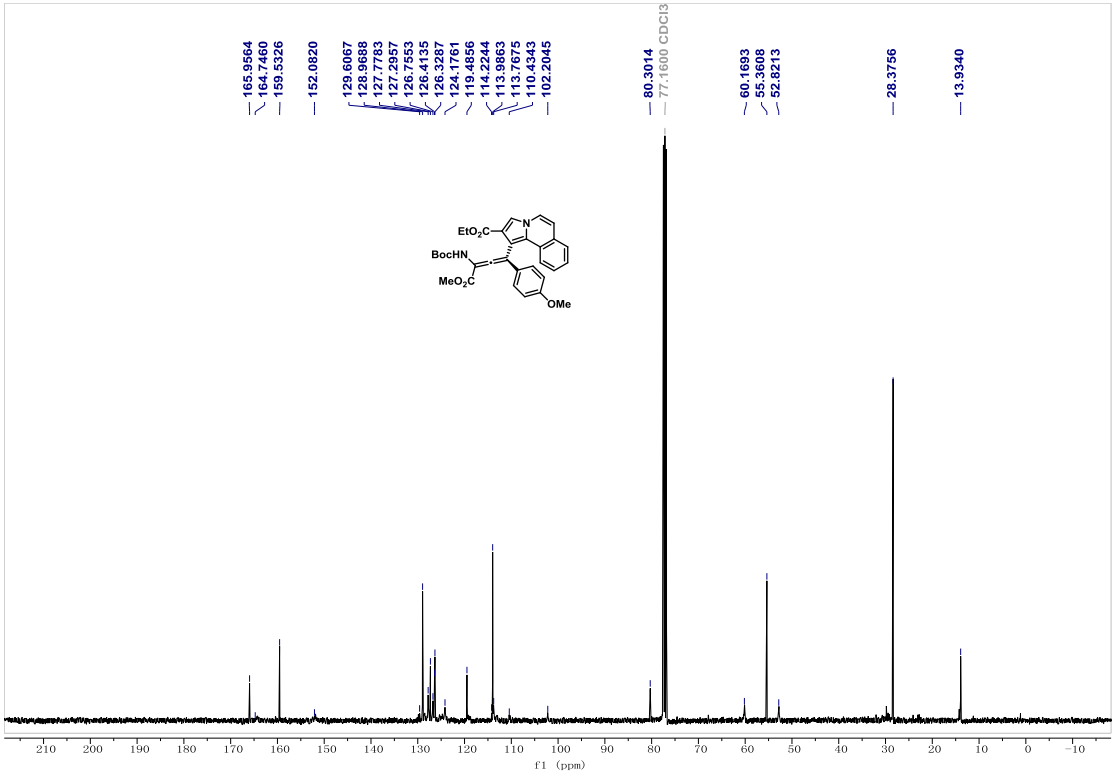


Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	10.065	790.652	1763.457	97.80	98.79
2	16.285	17.757	21.613	2.20	1.21

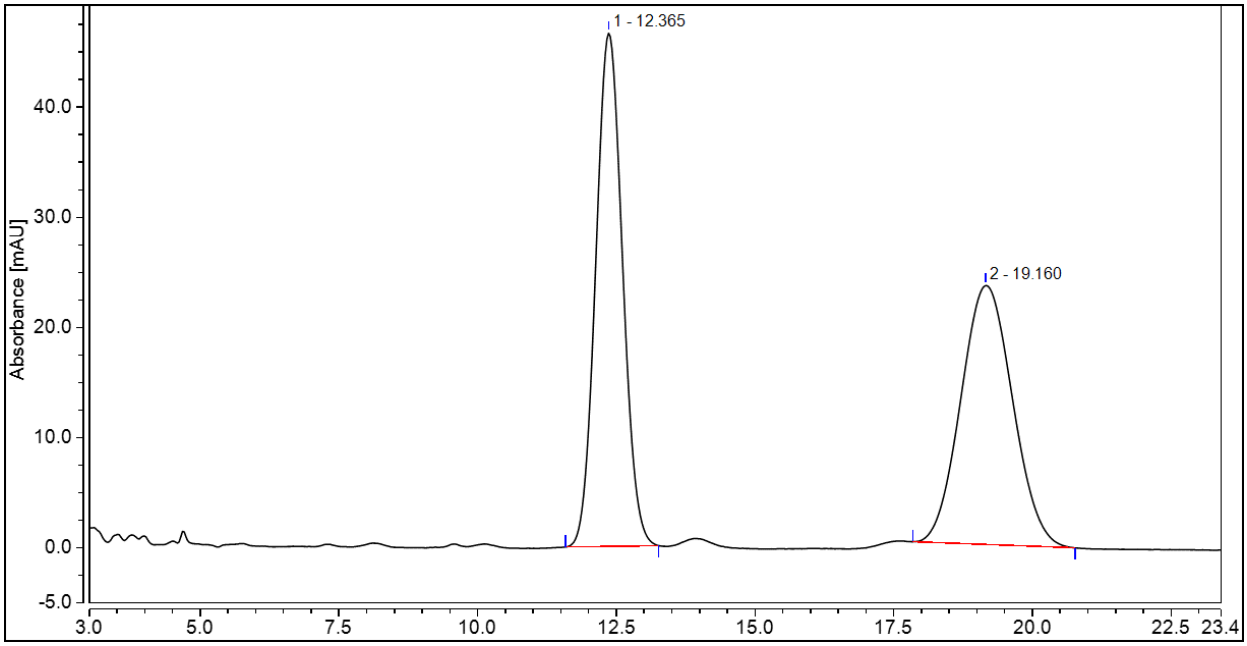
^{1}H NMR of **3c** (400 MHz, $CDCl_3$)



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

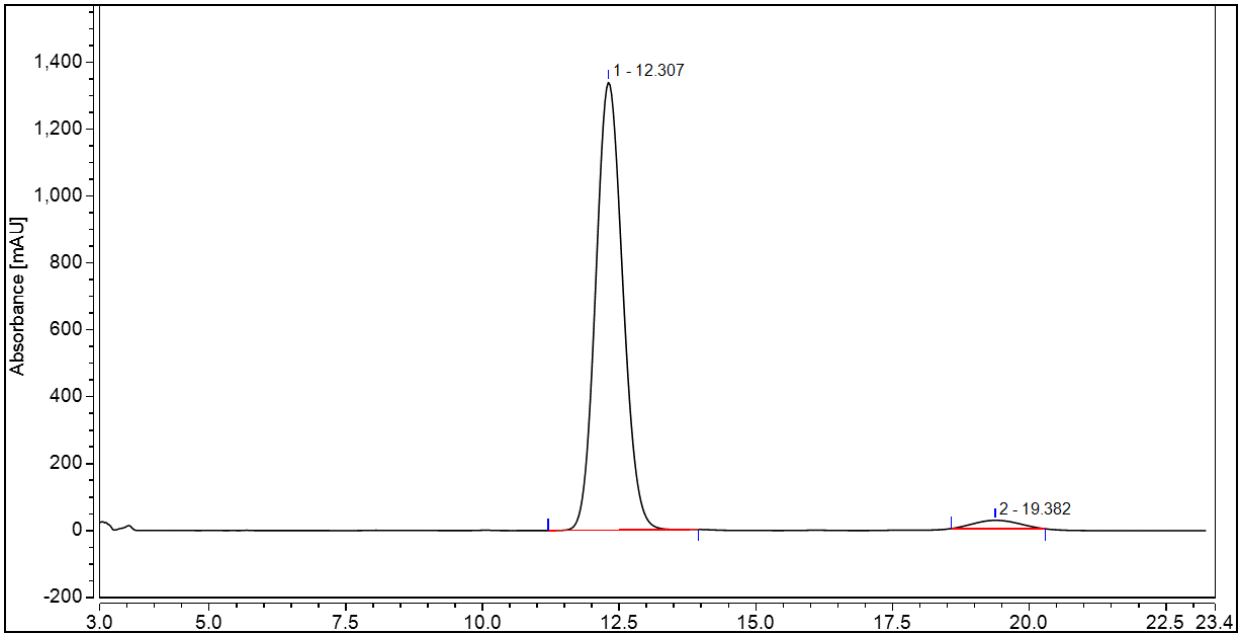


HPLC analysis: rac-**3c**



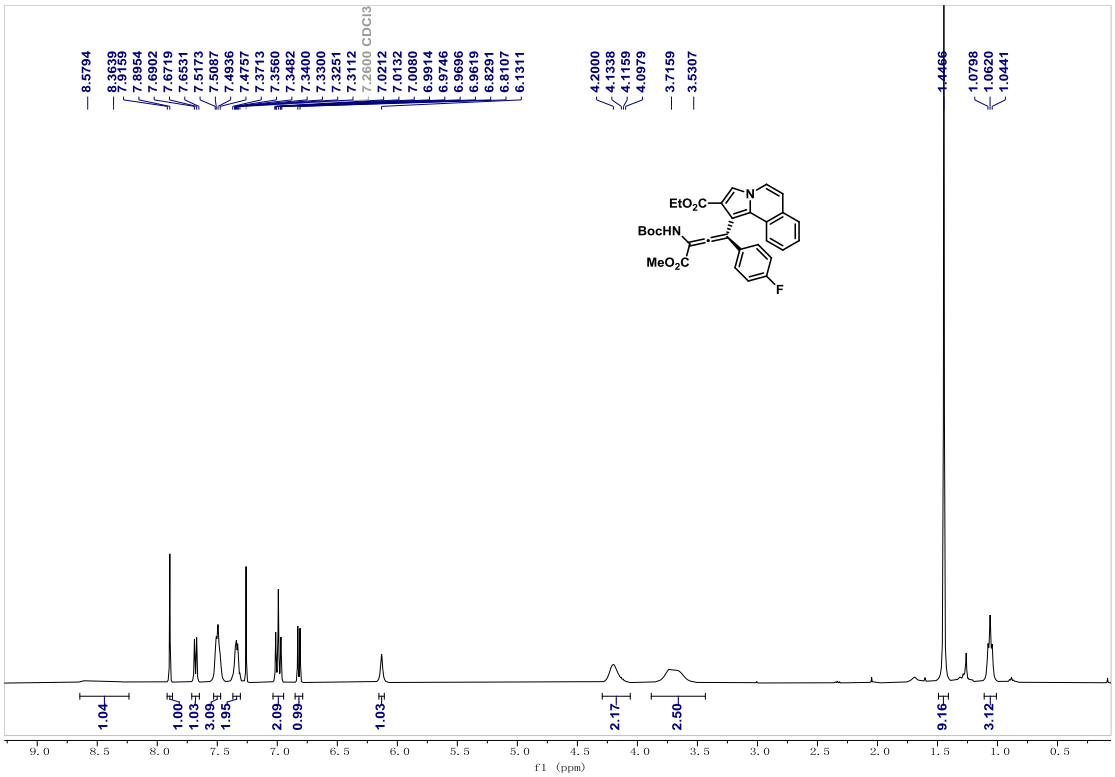
Peak	RetTime min	Area mAU*min	Height mAU	Area %	Height %
1	12.365	26.037	46.602	50.65	66.46
2	19.160	25.371	23.519	49.35	33.54

Enantioenriched **3c**

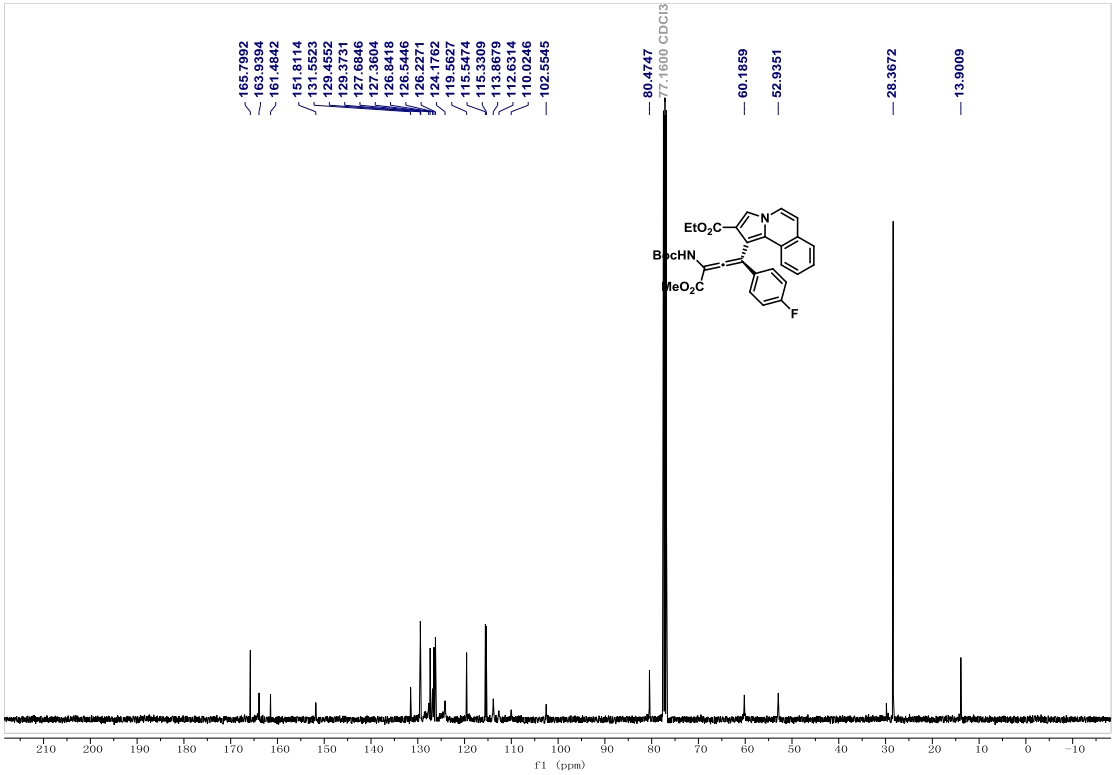


Peak	RetTime min	Area mAU*min	Height mAU	Area %	Height %
1	12.307	767.421	1339.192	97.00	98.17
2	19.382	23.739	24.983	3.00	1.83

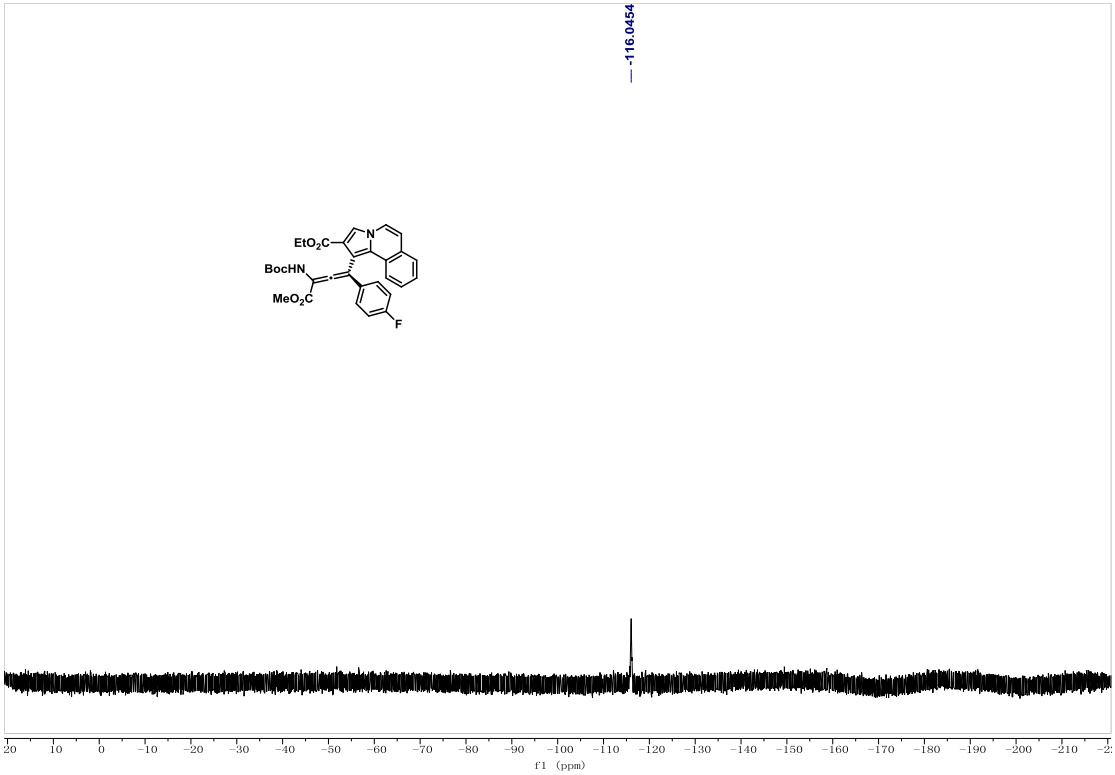
^{1}H NMR of **3d** (400 MHz, $CDCl_3$)



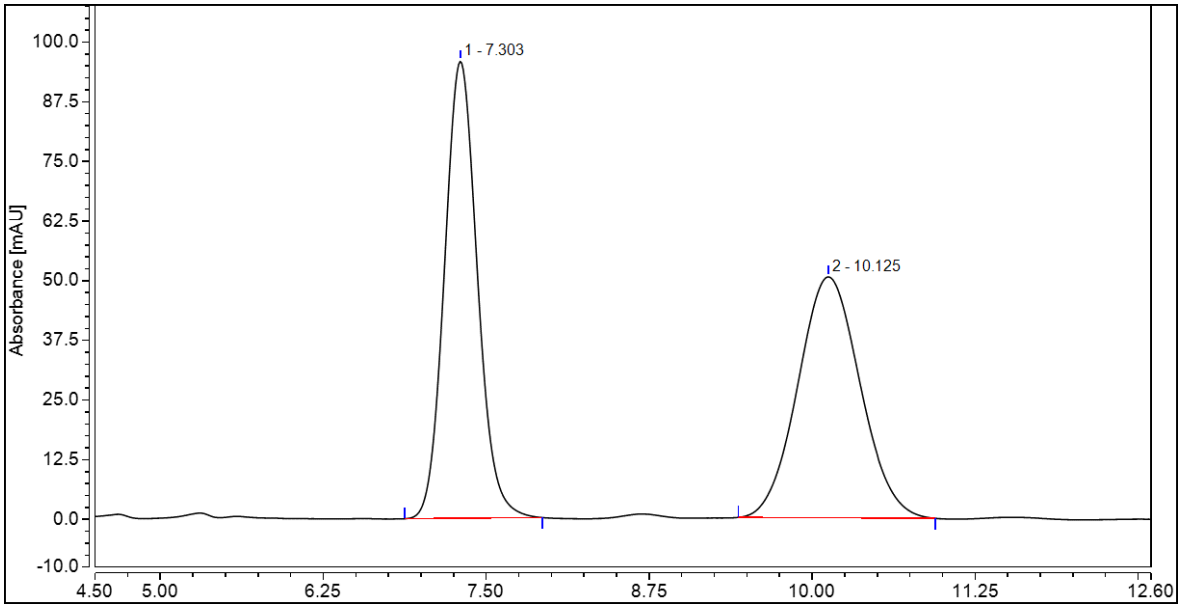
^{13}C NMR of **3d** (101 MHz, $CDCl_3$)



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

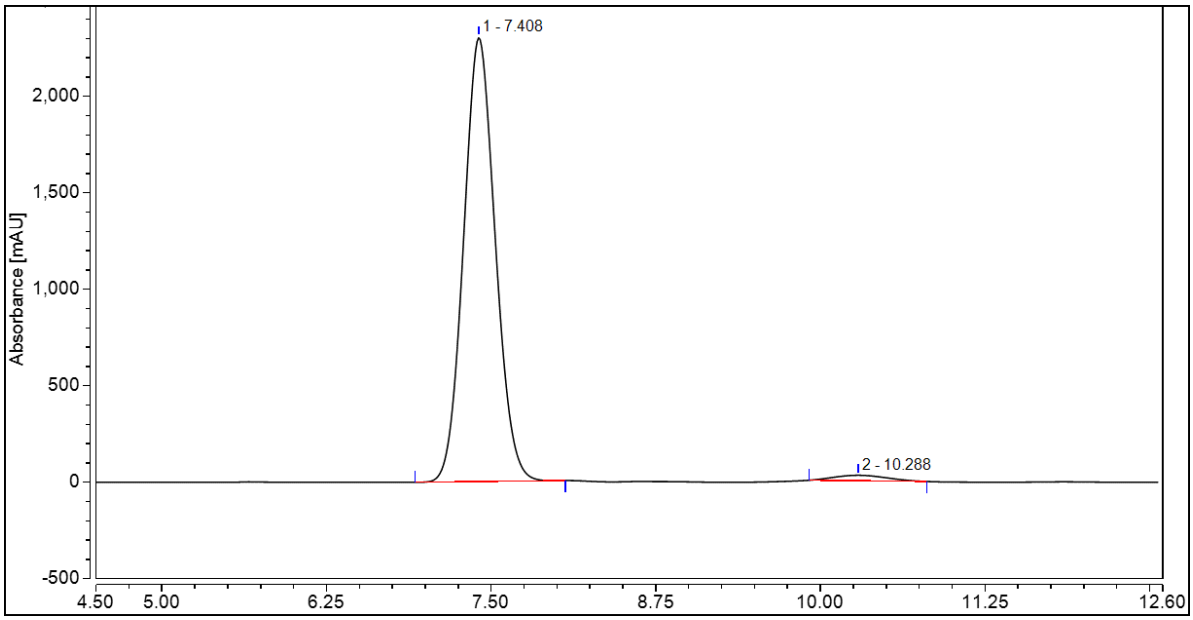


HPLC analysis: rac-**3d**



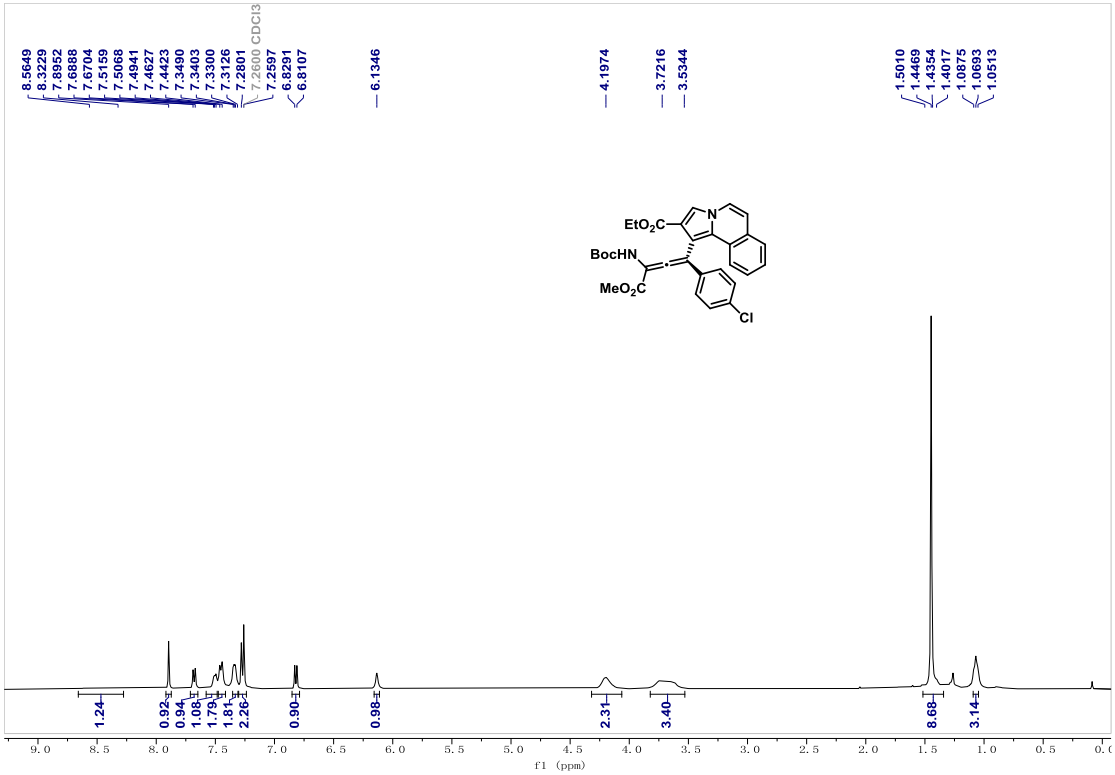
Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	7.303	27.976	95.723	50.03	65.47
2	10.125	27.944	50.480	49.97	34.53

Enantioenriched **3d**

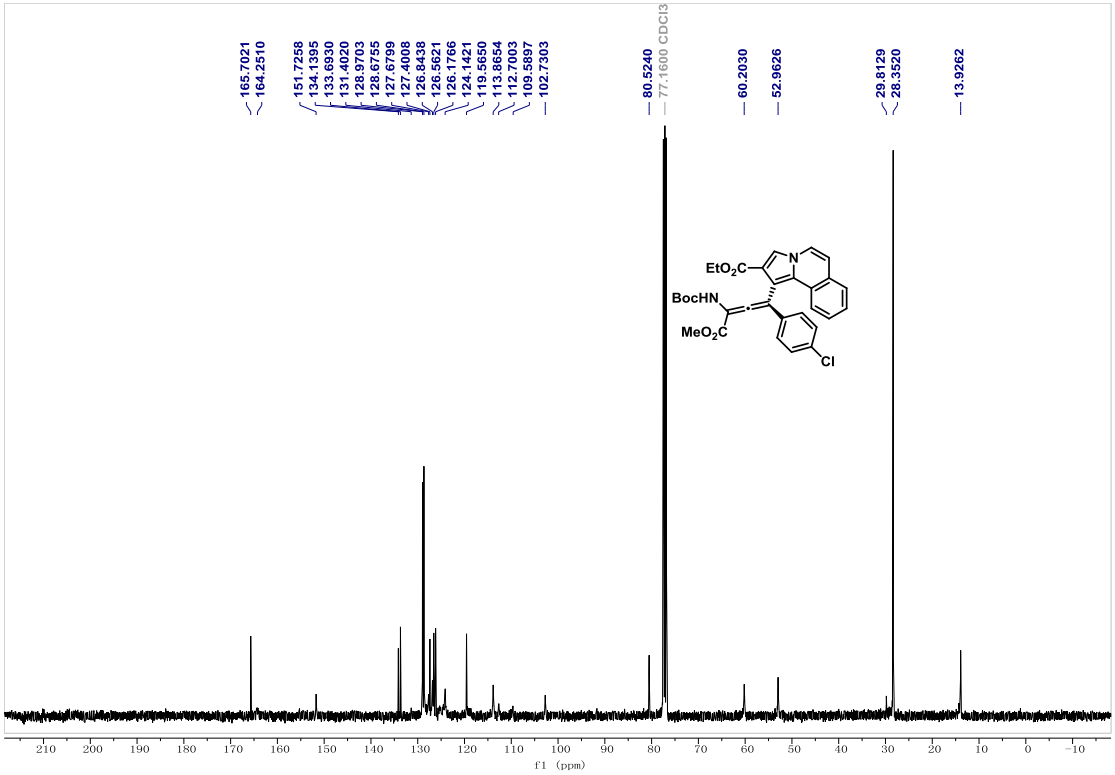


Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	7.408	640.098	2300.420	97.98	98.78
2	10.288	13.180	28.498	2.02	1.22

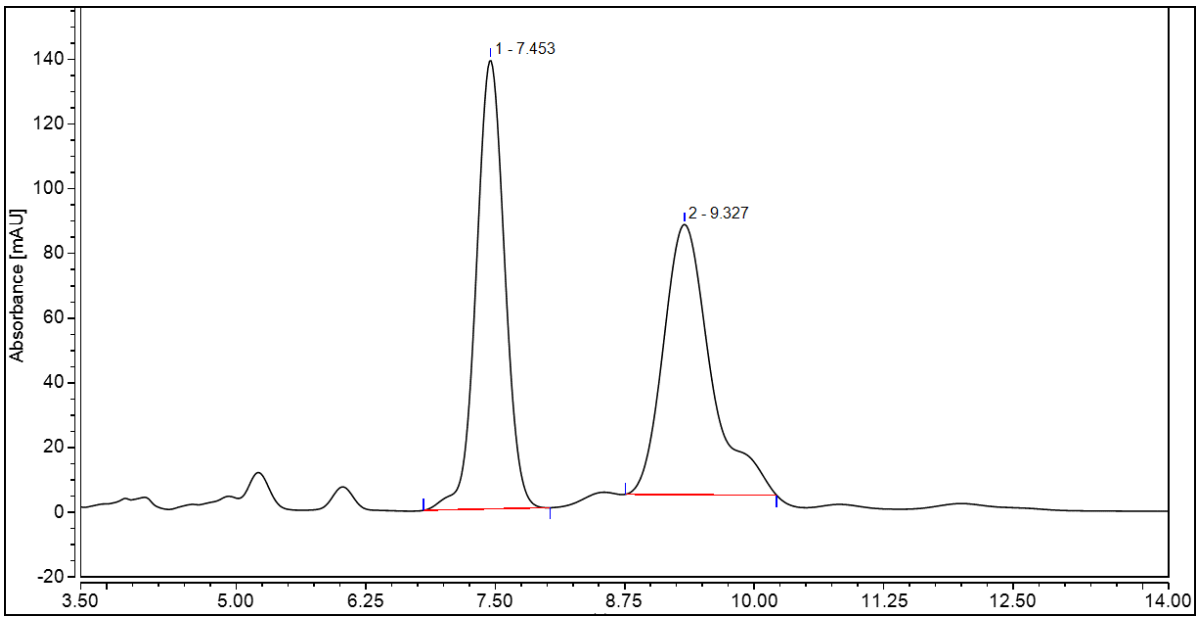
^{1}H NMR of **3e** (400 MHz, $CDCl_3$)



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

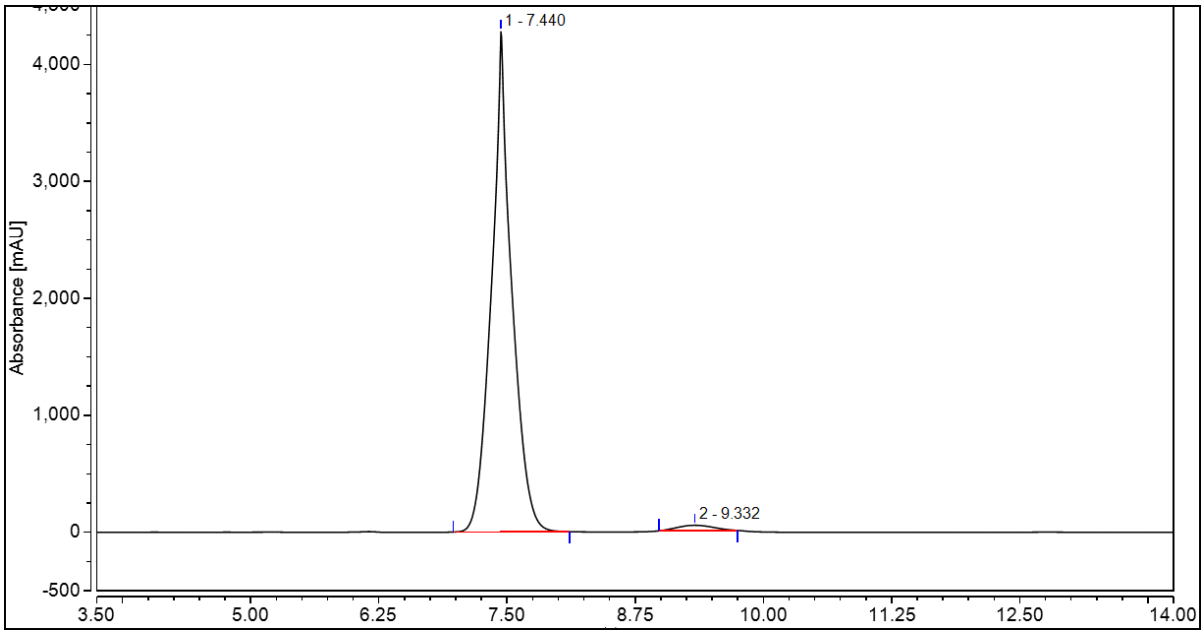


HPLC analysis: rac-**3e**



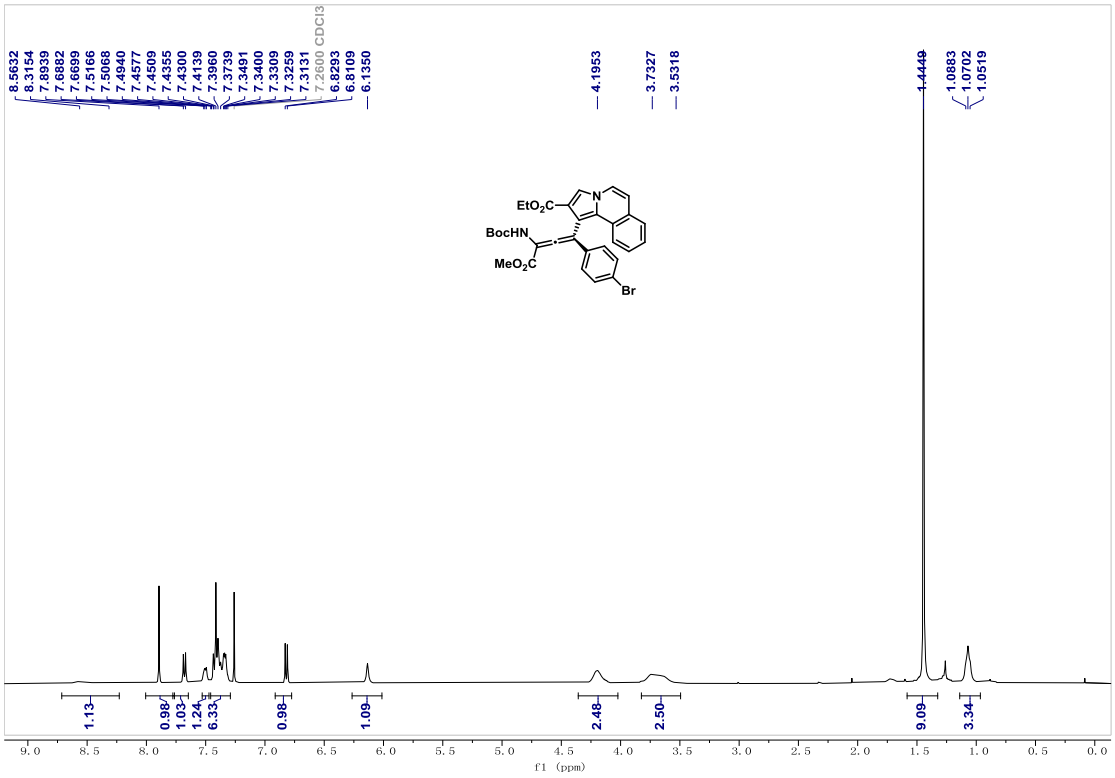
Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	7.453	44.091	138.781	49.91	62.42
2	9.327	44.250	83.552	50.09	37.58

Enantioenriched **3e**

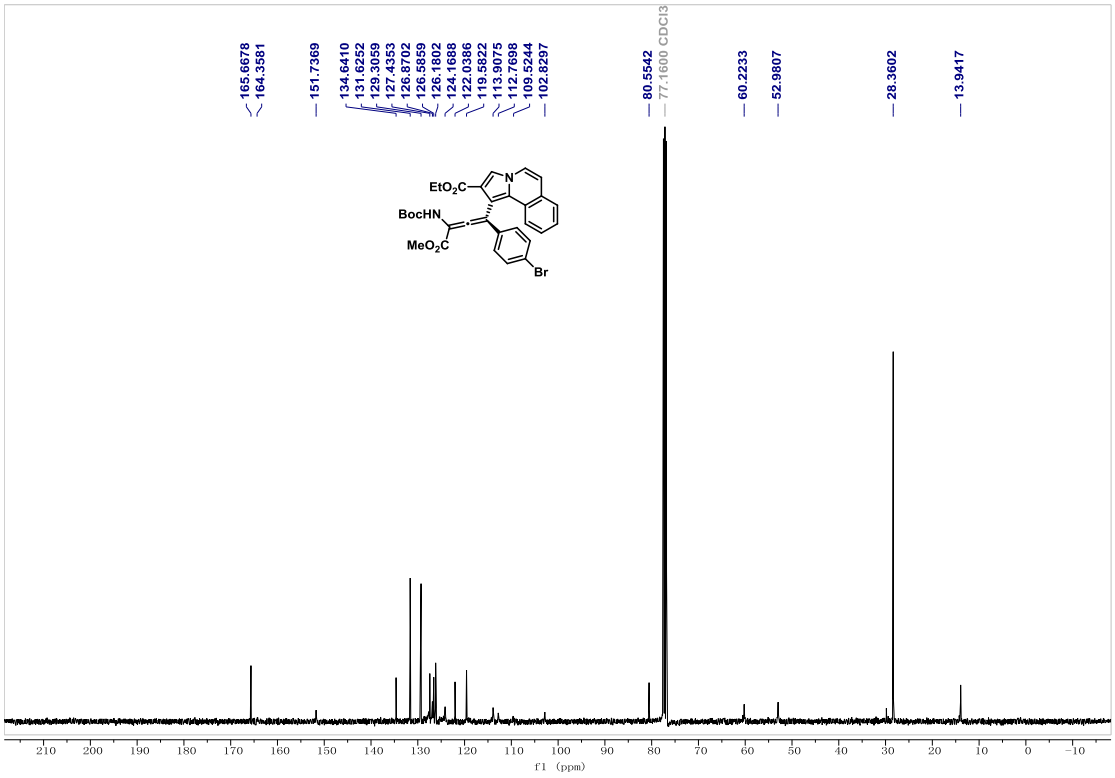


Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	7.440	972.805	4276.012	98.11	98.93
2	9.332	18.761	46.139	1.89	1.07

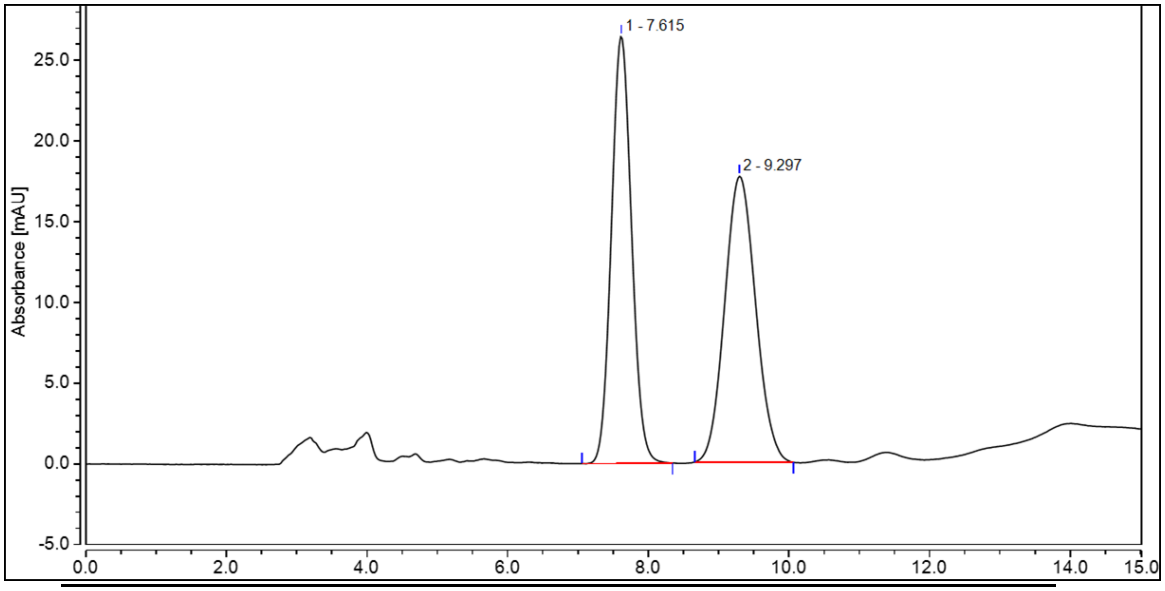
^{1}H NMR of **3f** (400 MHz, $CDCl_3$)



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

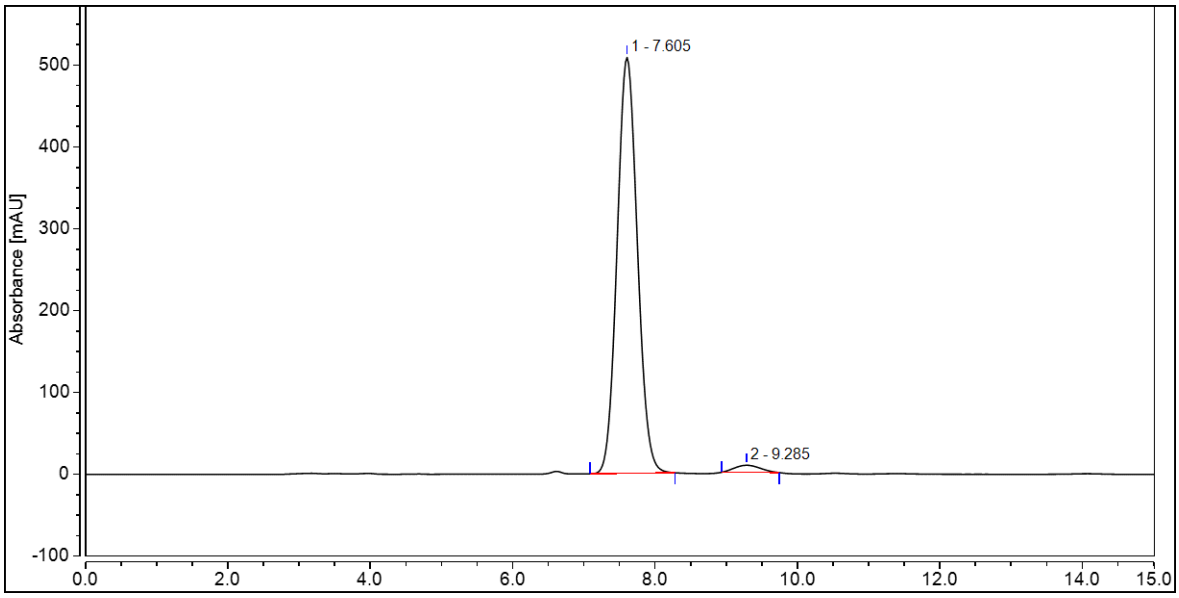


HPLC analysis: rac-**3f**



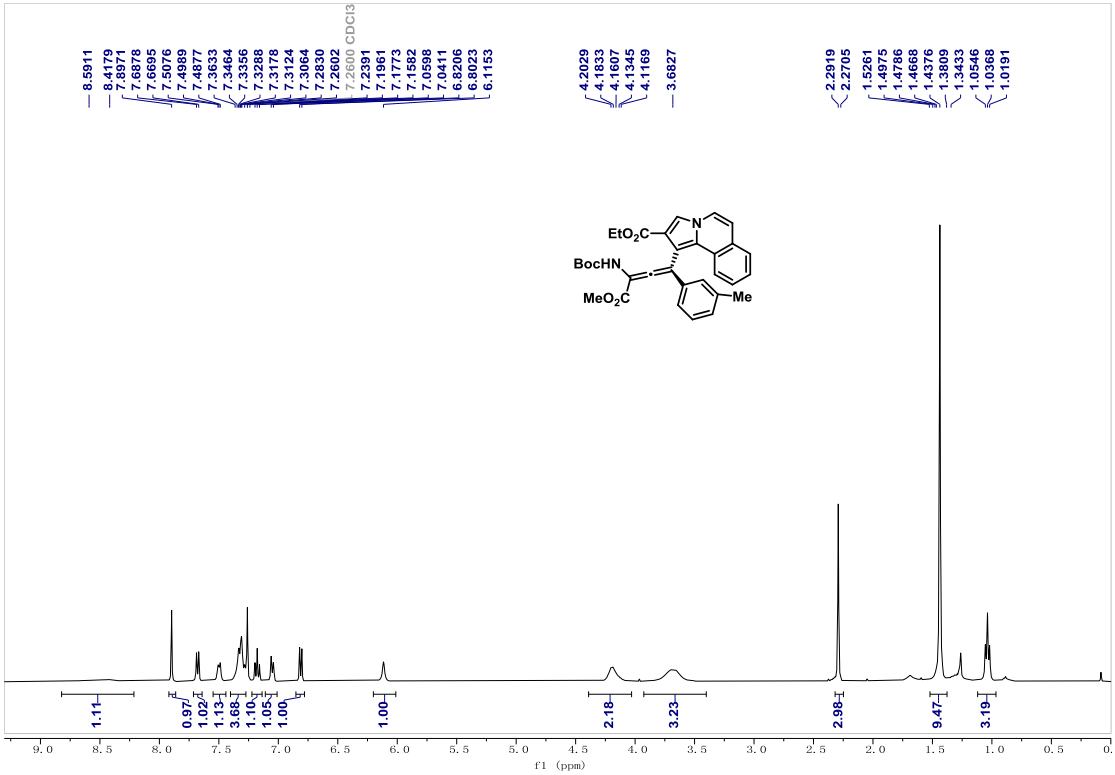
Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	7.615	8.807	26.480	49.38	59.92
2	9.297	9.028	17.714	50.62	40.08

Enantioenriched **3f**

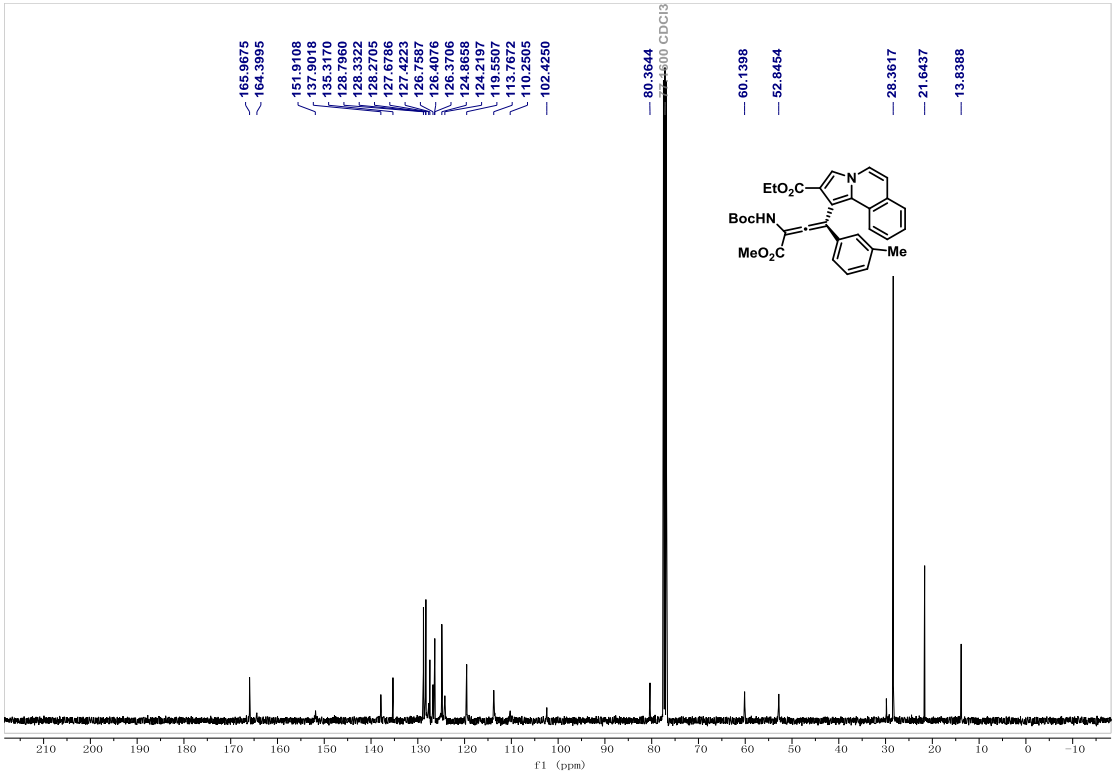


Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	7.605	167.717	508.396	97.86	98.32
2	9.285	3.662	8.705	2.14	1.68

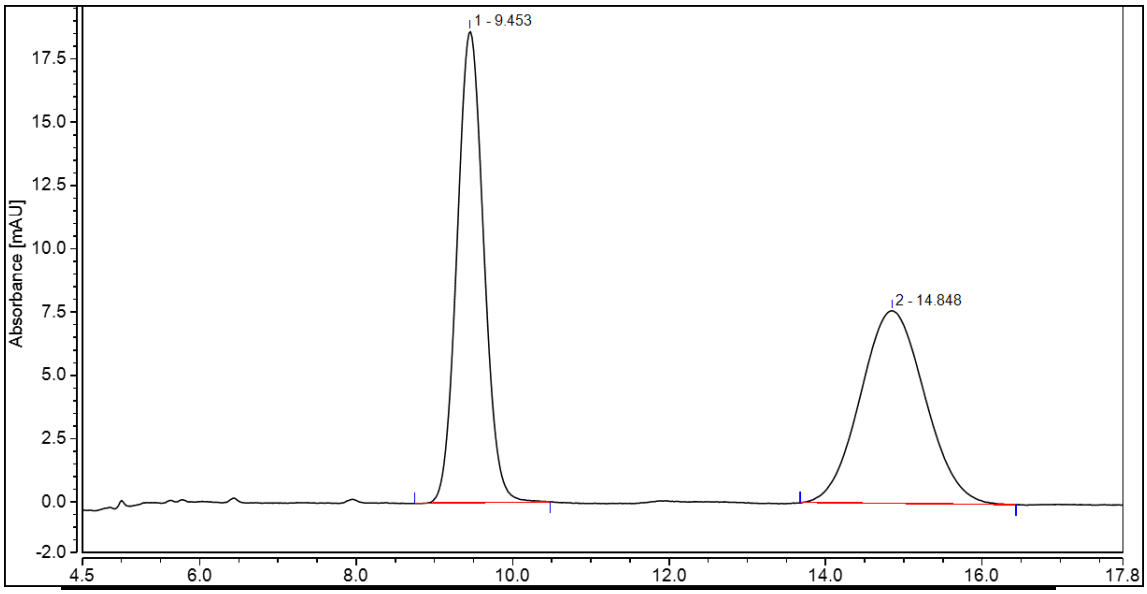
^{1}H NMR of **3g** (400 MHz, $CDCl_3$)



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

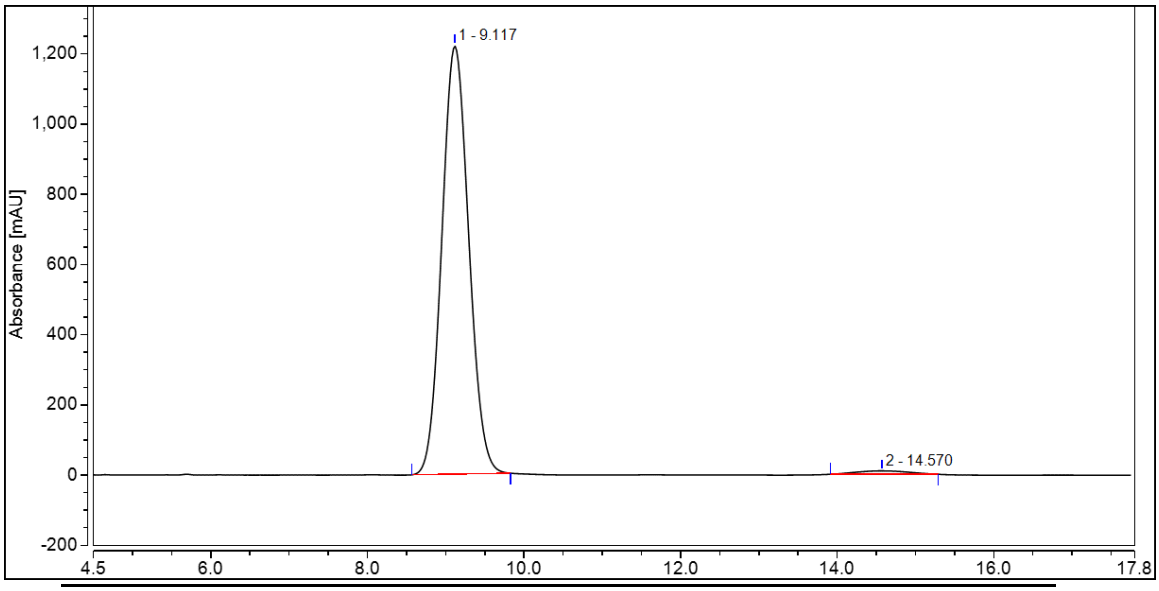


HPLC analysis: rac-**3g**



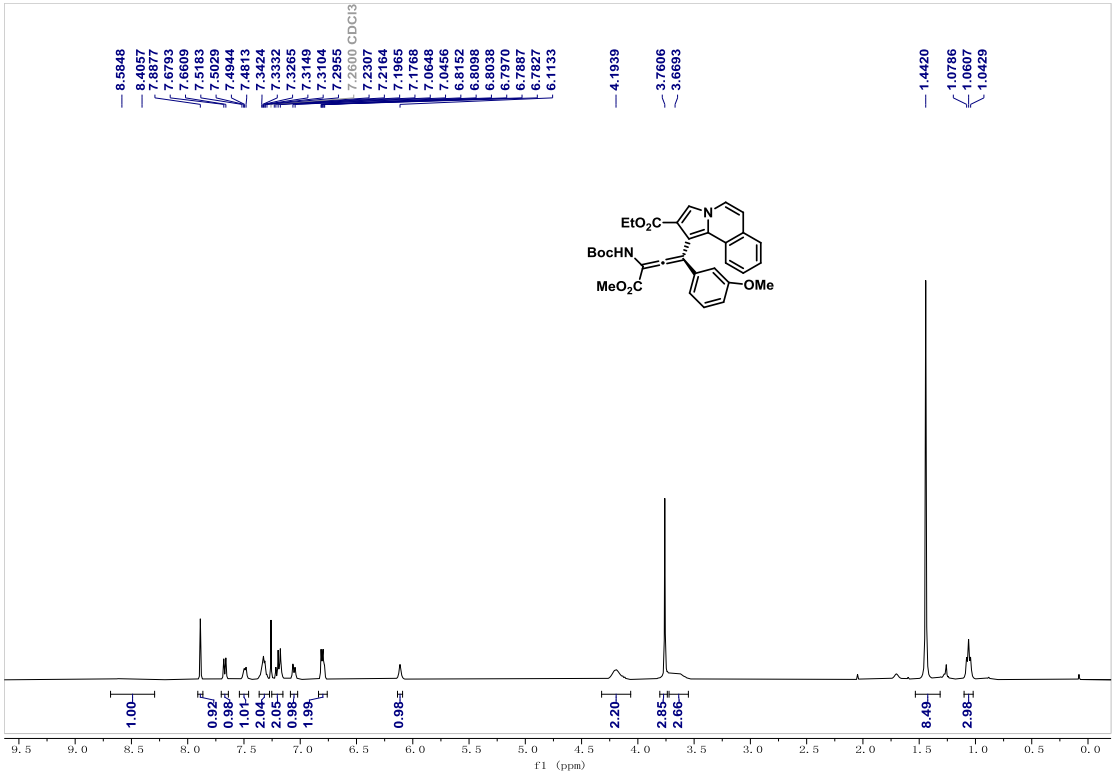
Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	9.453	7.362	18.625	50.31	70.98
2	14.848	7.271	7.616	49.69	29.02

Enantioenriched **3g**

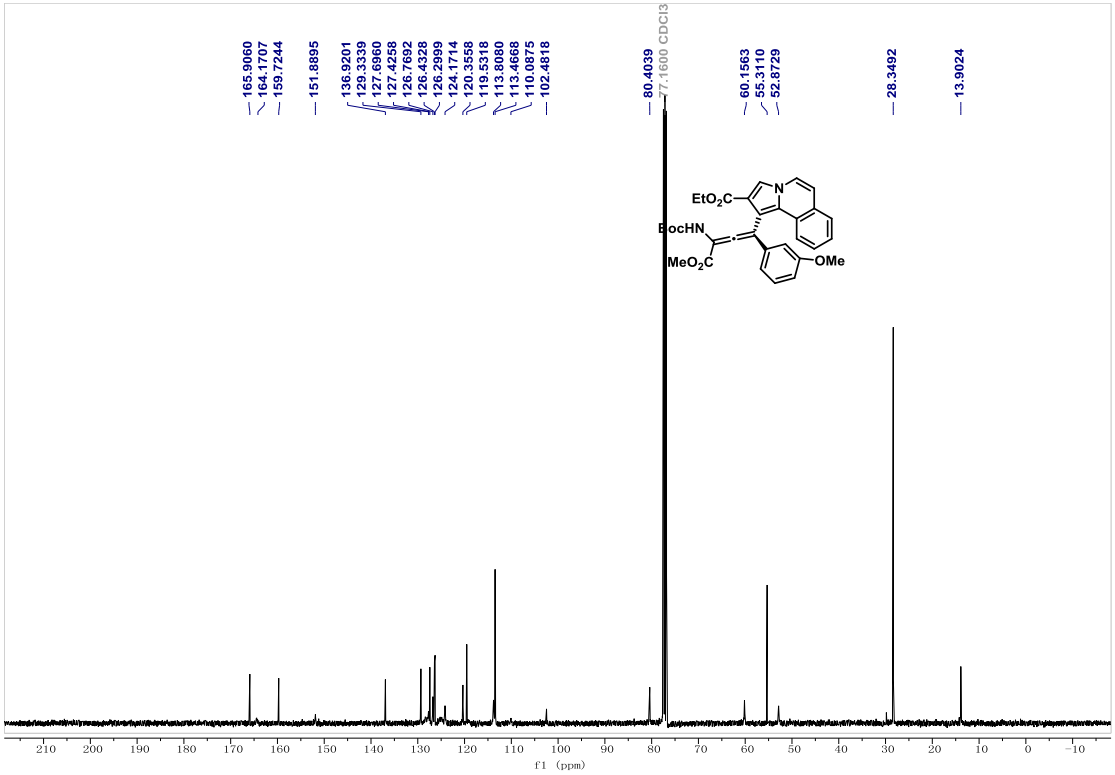


Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	9.117	485.553	1219.586	98.47	99.21
2	14.570	7.523	9.709	1.53	0.79

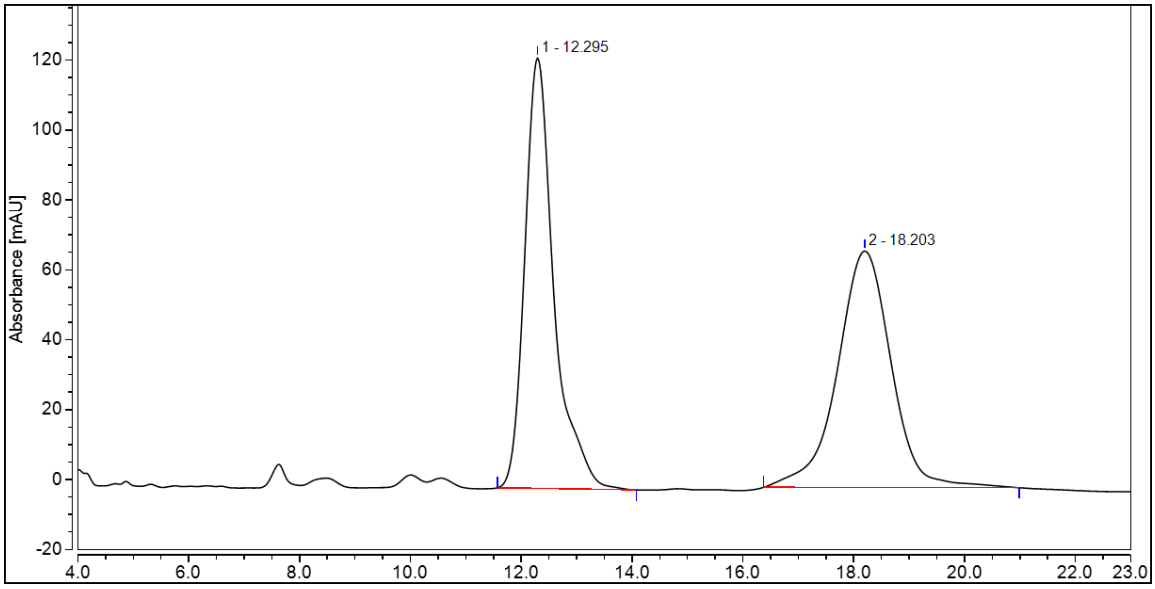
^{1}H NMR of **3h** (400 MHz, $CDCl_3$)



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

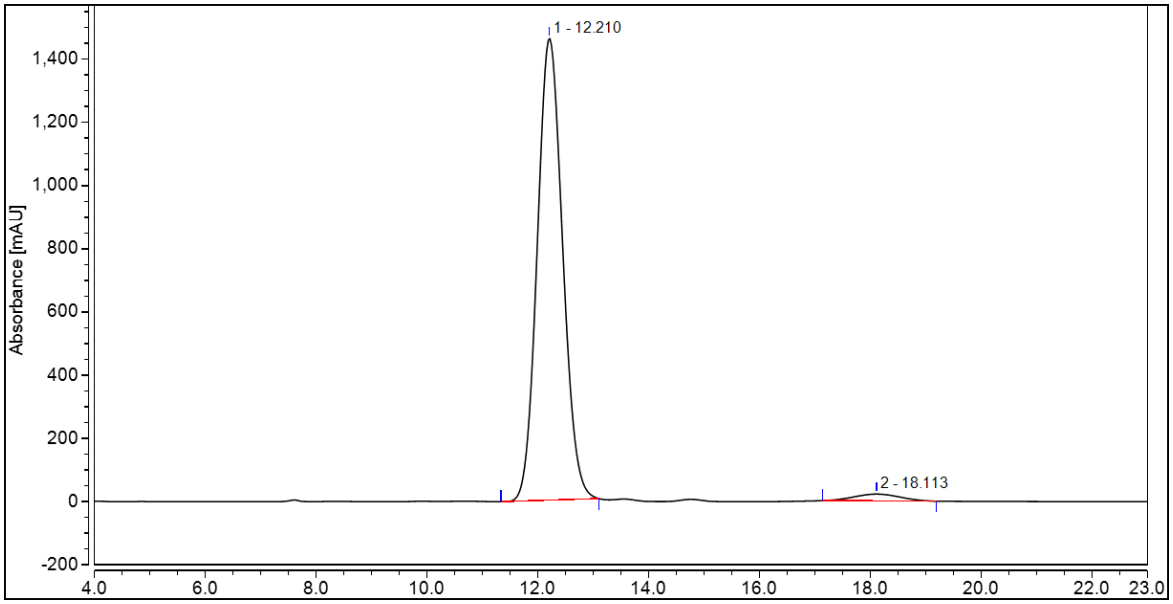


HPLC analysis: rac-**3h**



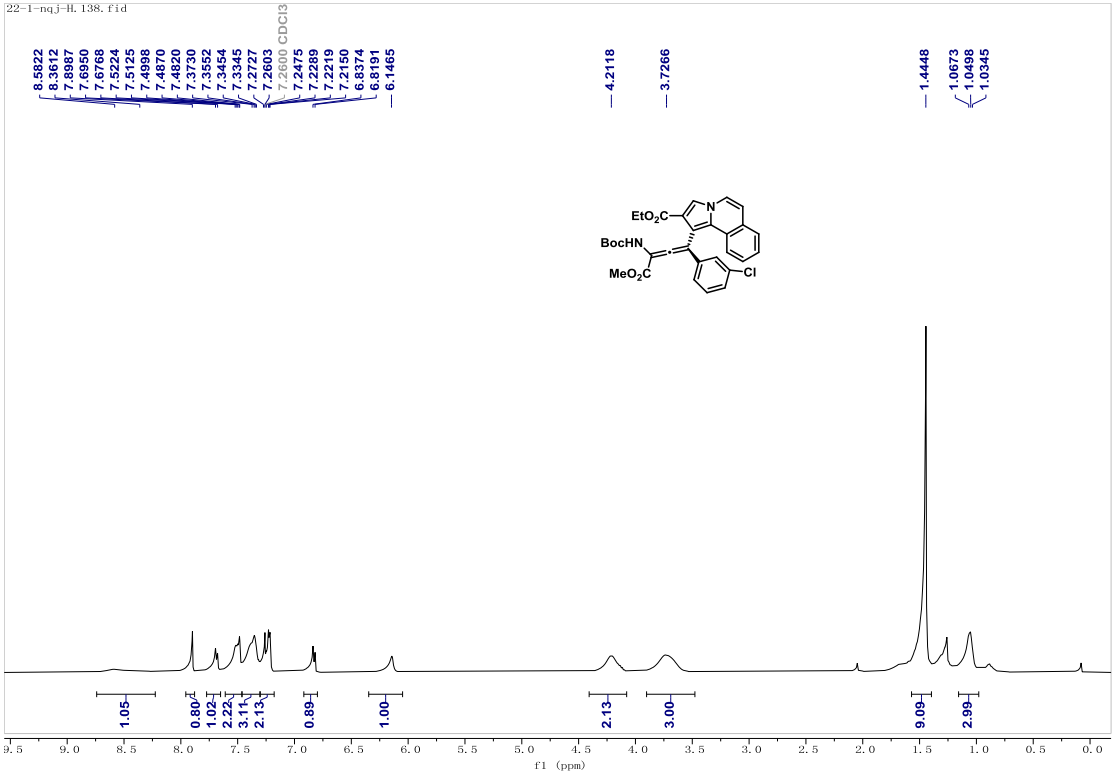
Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	12.295	74.942	123.201	49.69	64.56
2	18.203	75.874	67.635	50.31	35.44

Enantioenriched **3h**

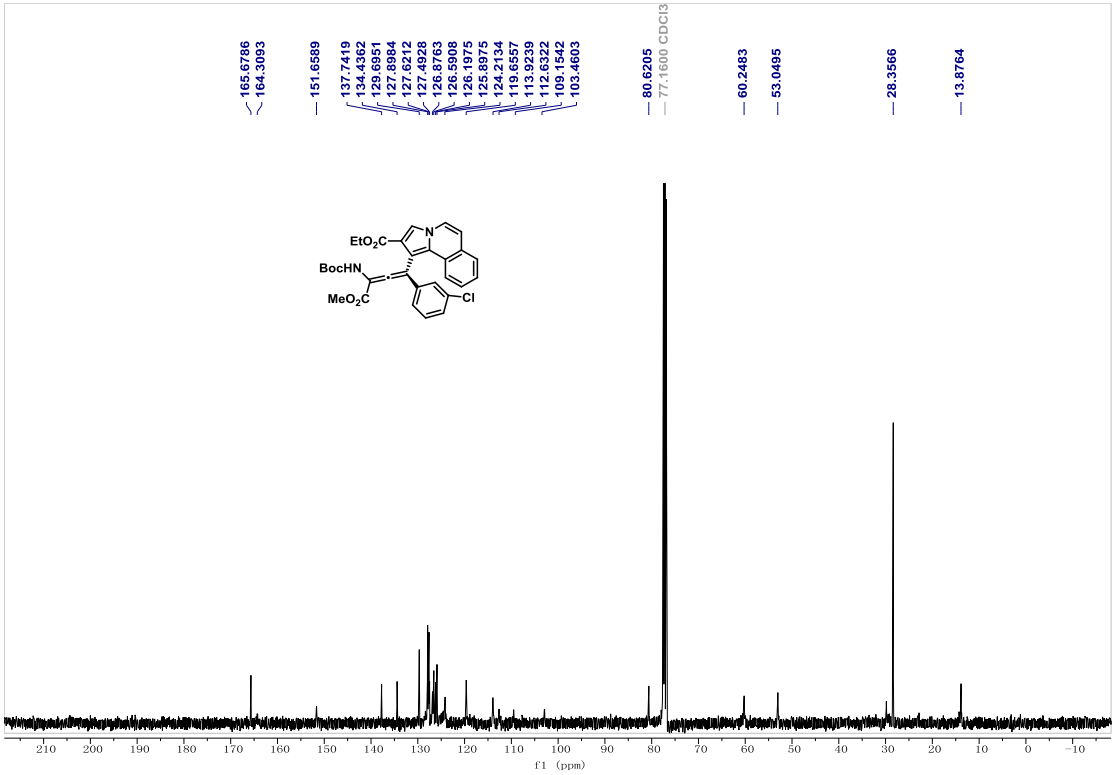


Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	12.210	773.686	1462.097	97.41	98.55
2	18.113	20.589	21.474	2.59	1.45

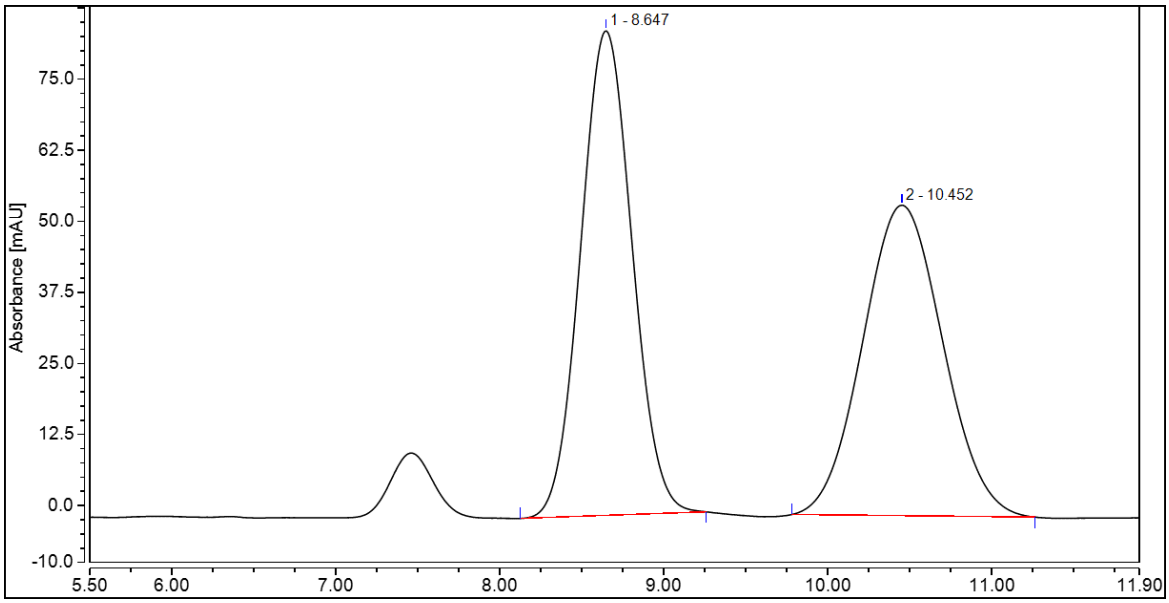
^{1}H NMR of **3i** (400 MHz, $CDCl_3$)



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

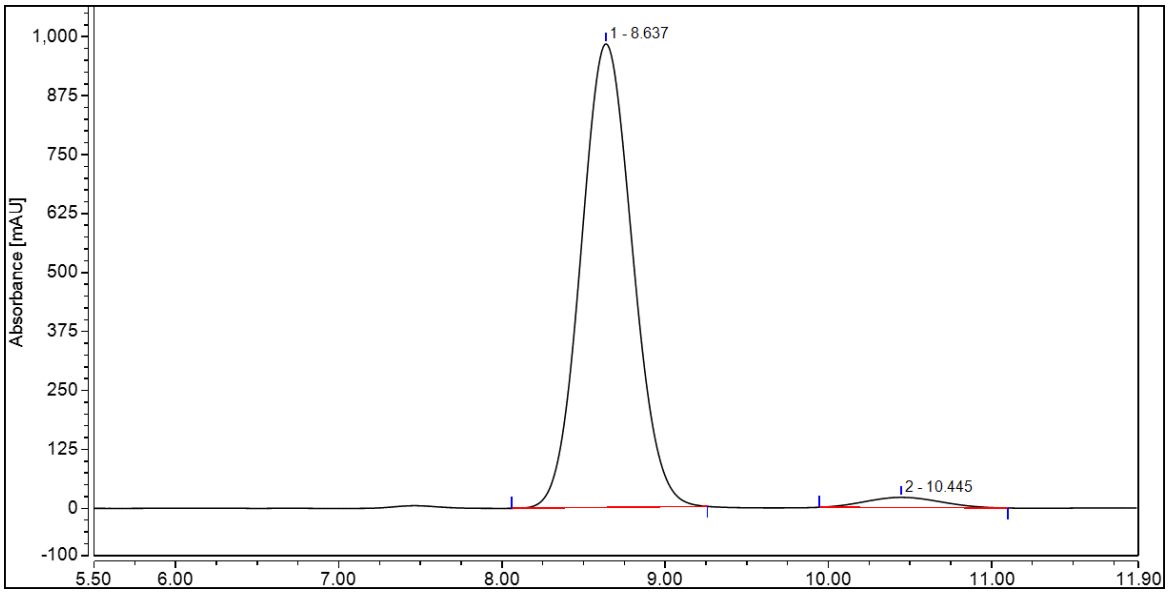


HPLC analysis: rac-**3i**



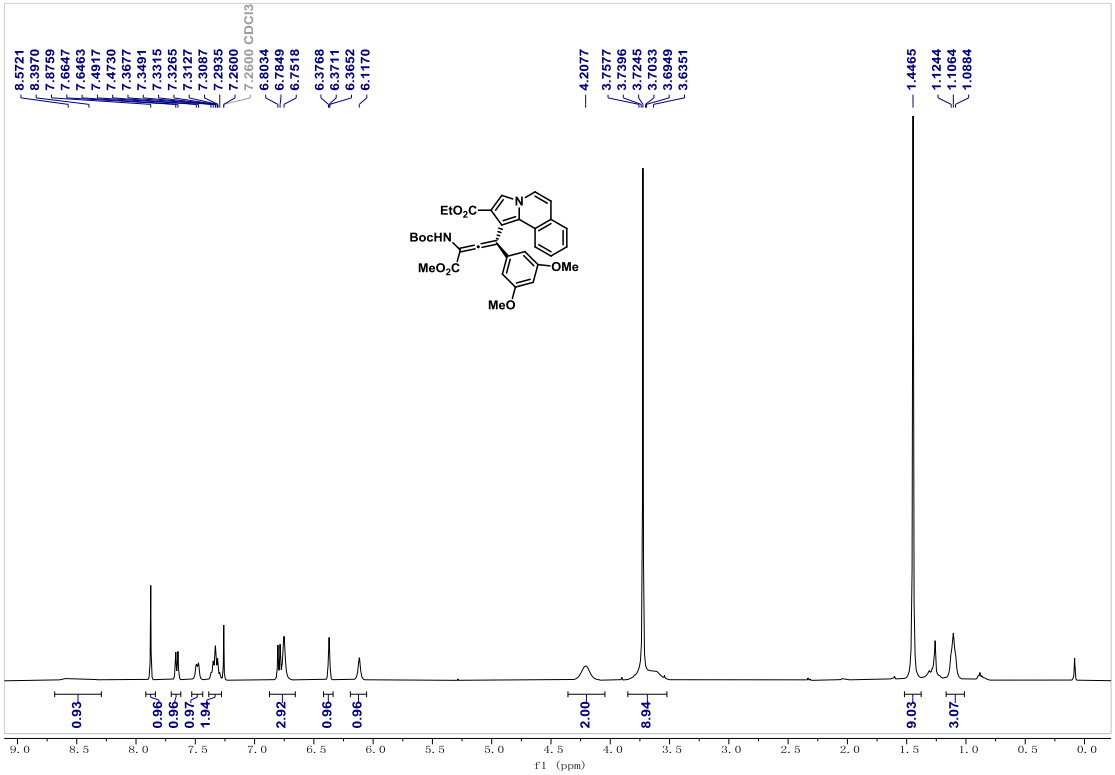
Peak	RetTime min	Area mAU*min	Height mAU	Area %	Height %
1	8.647	31.035	85.256	50.08	60.95
2	10.452	30.940	54.618	49.92	39.05

Enantioenriched **3i**

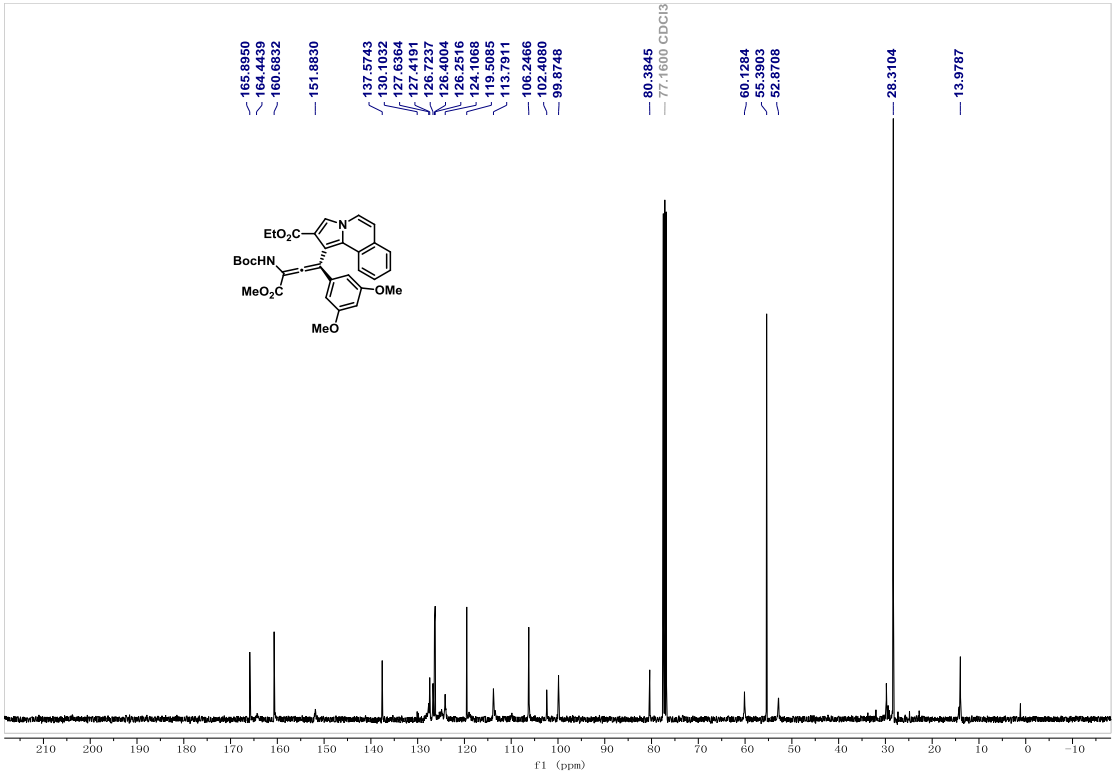


Peak	RetTime min	Area mAU*min	Height mAU	Area %	Height %
1	8.637	359.356	982.973	96.87	97.84
2	10.445	11.607	21.692	3.13	2.16

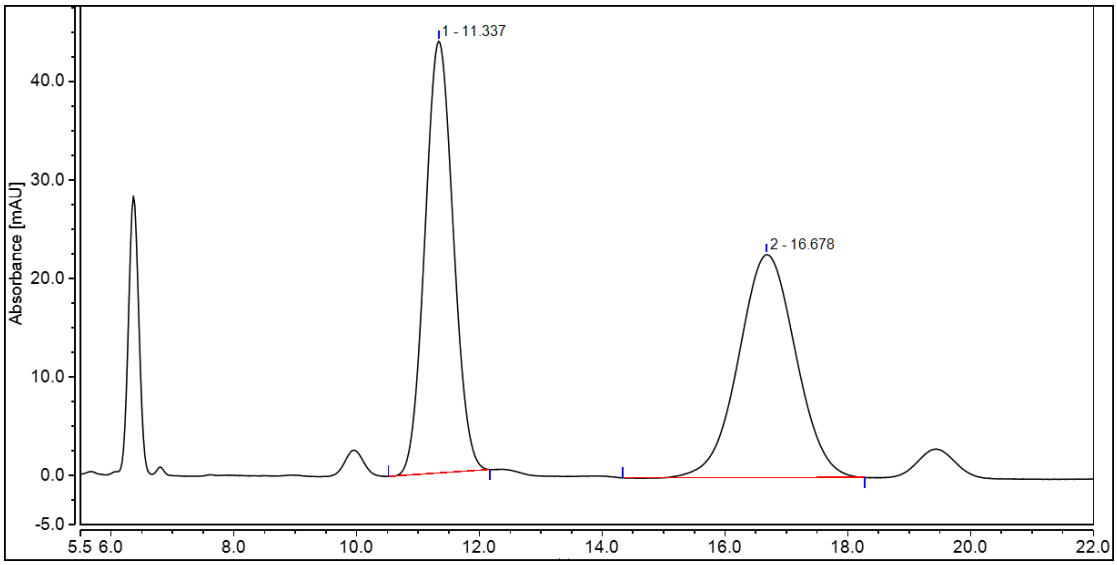
^{1}H NMR of **3j** (400 MHz, $CDCl_3$)



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

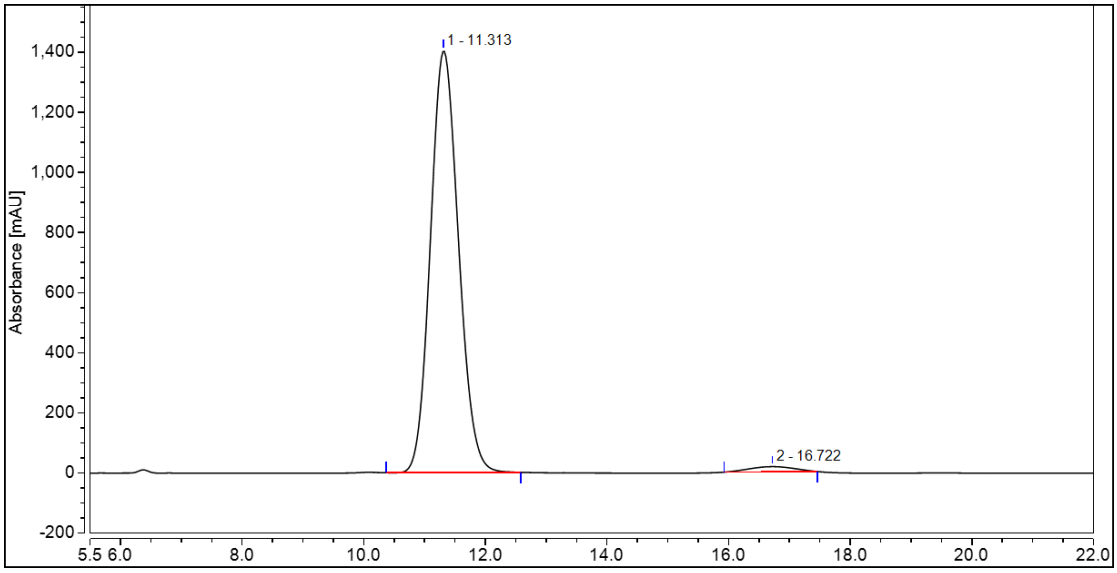


HPLC analysis: rac-**3j**



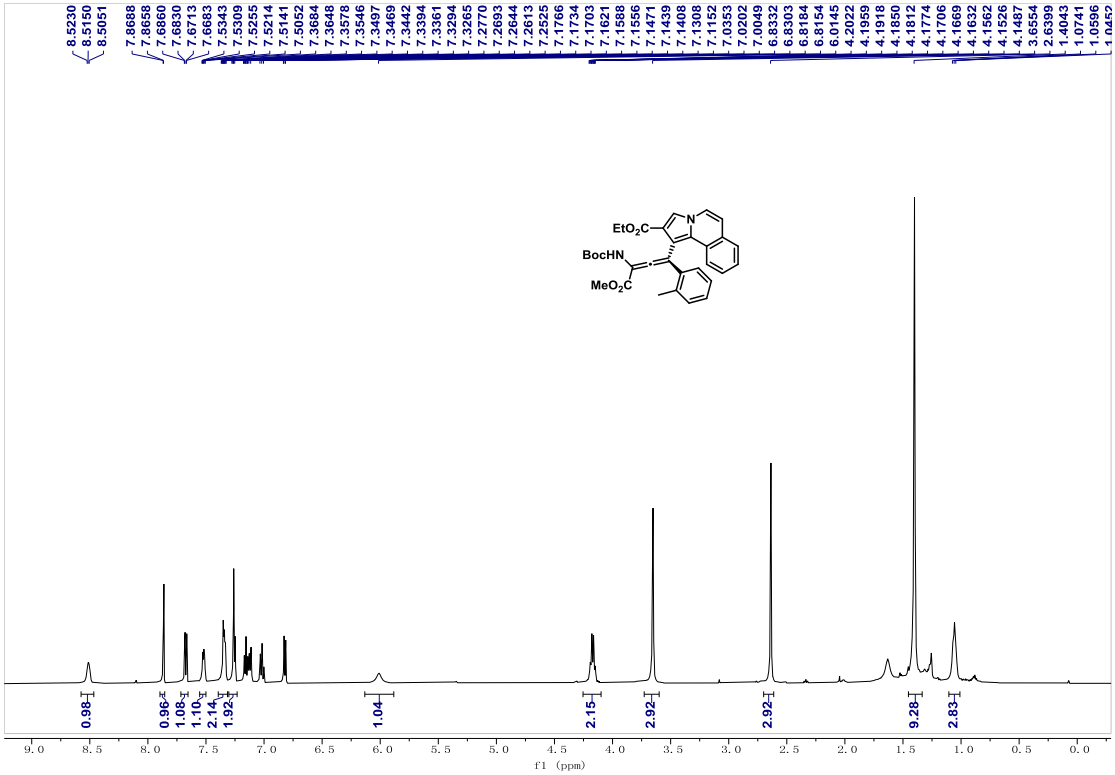
Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	11.337	23.458	43.860	49.05	65.96
2	16.678	24.370	22.638	50.95	34.04

Enantioenriched **3j**

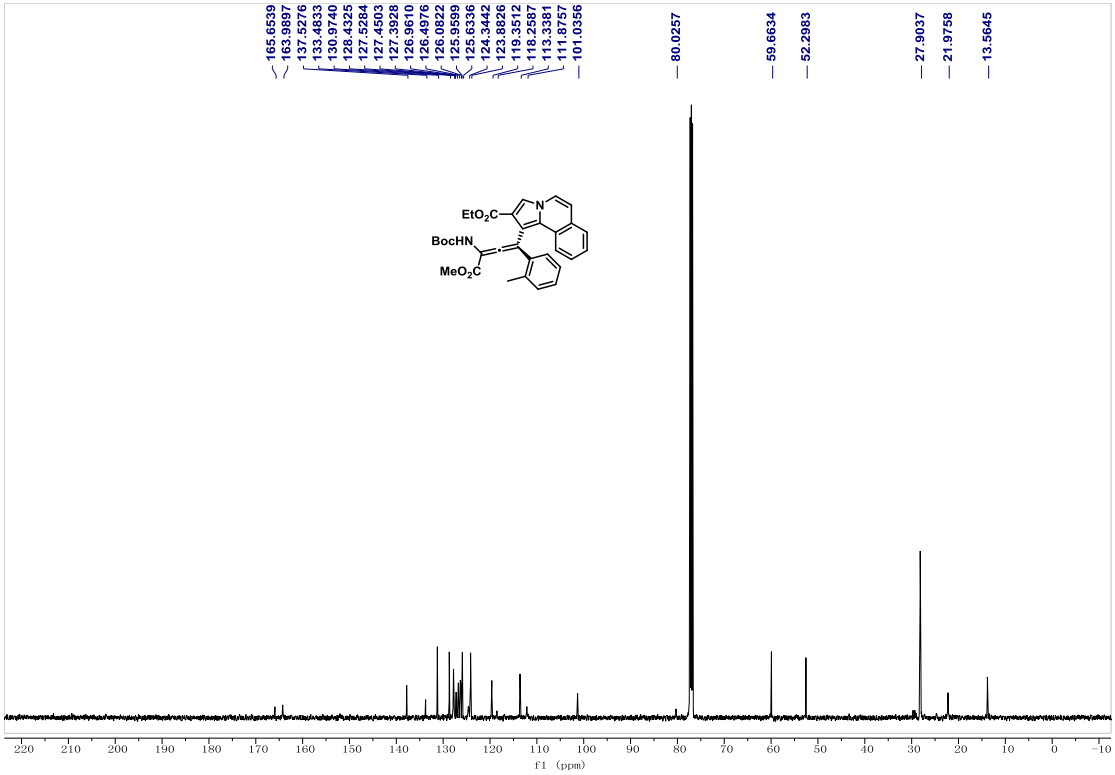


Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	11.313	751.252	1403.323	98.07	98.78
2	16.722	14.755	17.334	1.93	1.22

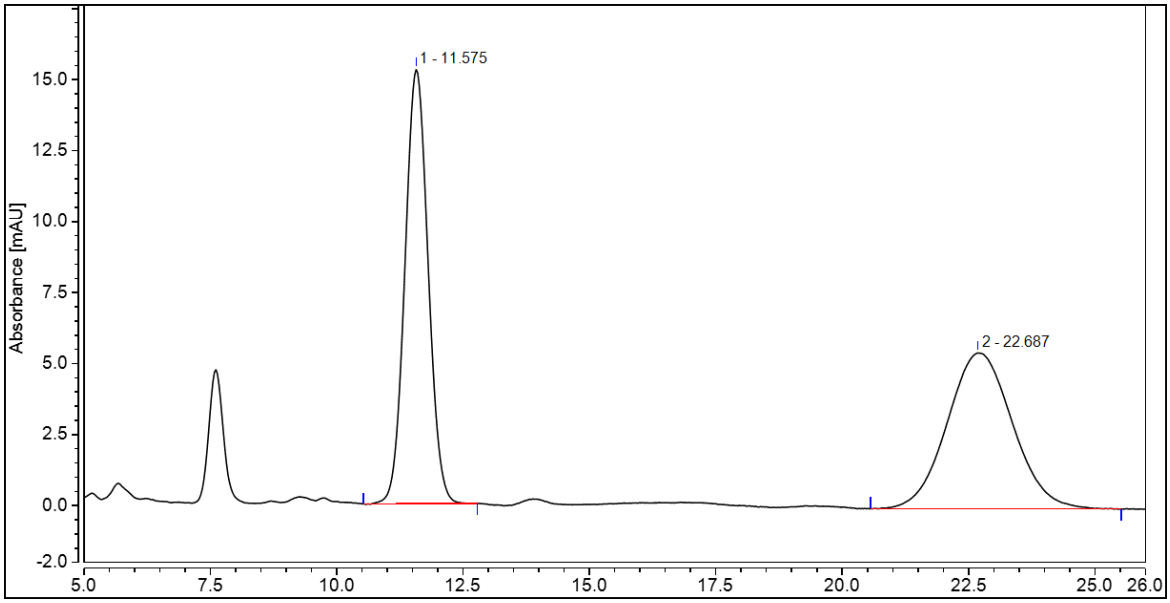
^{1}H NMR of **3k** (500 MHz, $CDCl_3$)



^{13}C NMR of **3k** (126 MHz, $CDCl_3$)

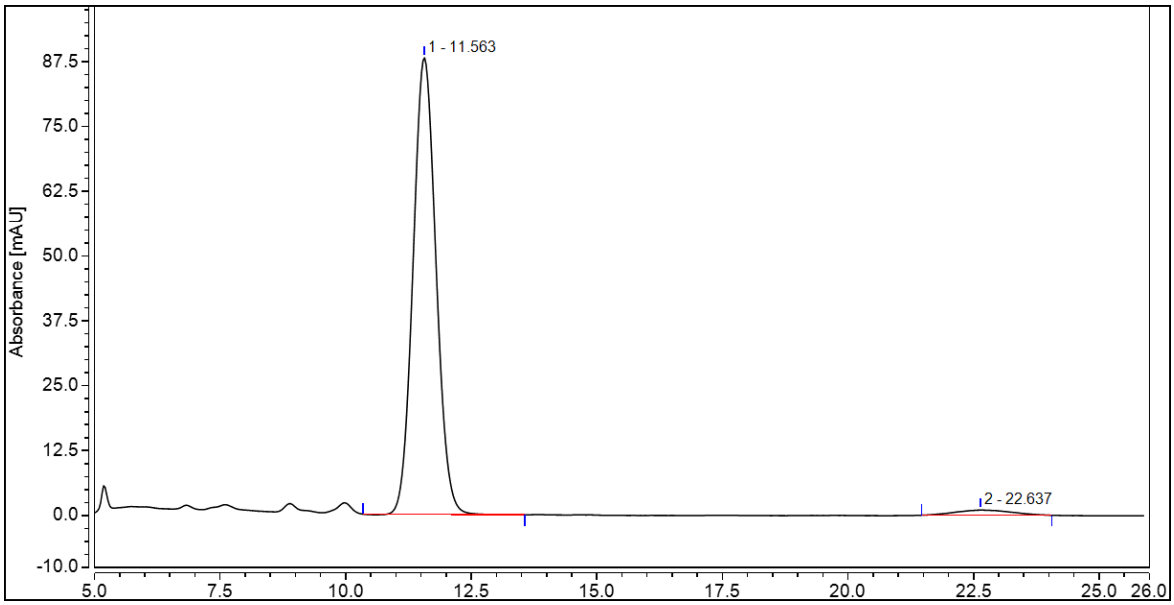


HPLC analysis: rac-**3k**



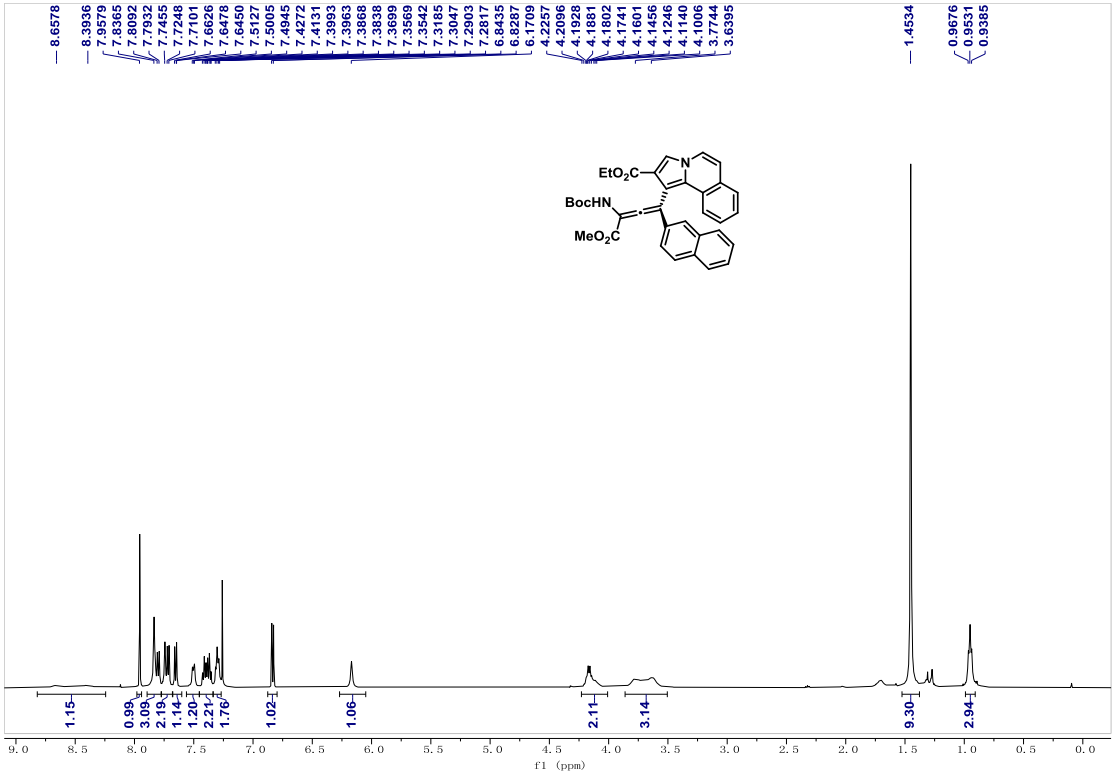
Peak	RetTime min	Area mAU*min	Height mAU	Area %	Height %
1	11.575	8.128	15.297	49.70	73.58
2	22.687	8.226	5.494	50.30	26.42

Enantioenriched **3k**

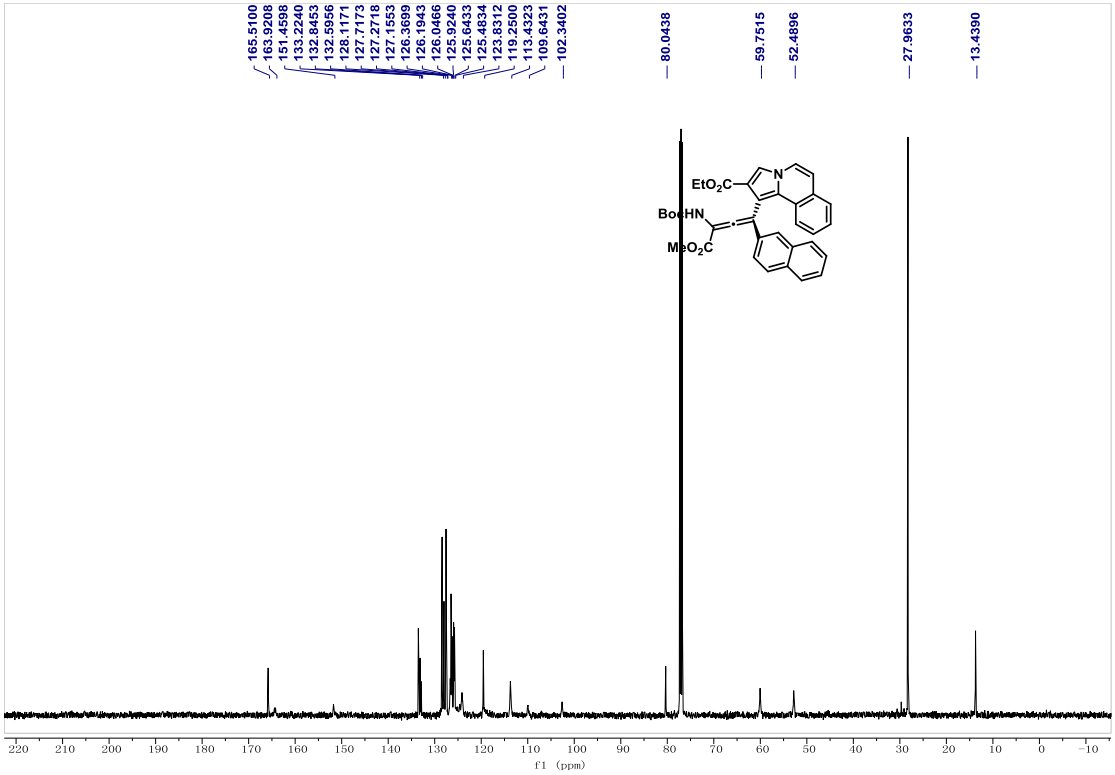


Peak	RetTime min	Area mAU*min	Height mAU	Area %	Height %
1	11.563	46.524	88.122	97.30	98.88
2	22.637	1.293	0.999	2.70	1.12

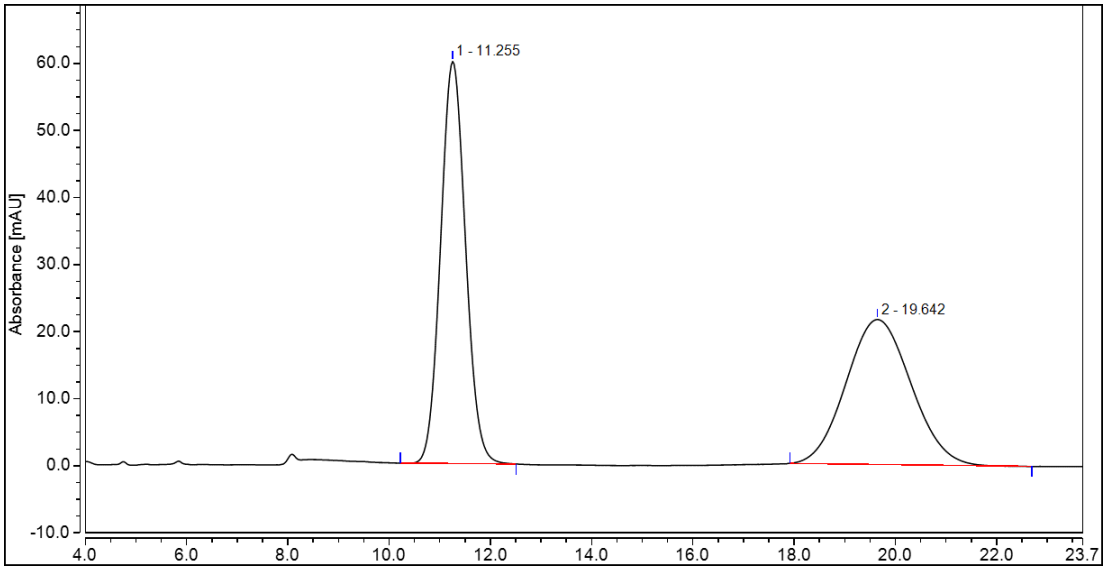
^{1}H NMR of **3l** (500 MHz, $CDCl_3$)



^{13}C NMR of **3l** (126 MHz, $CDCl_3$)

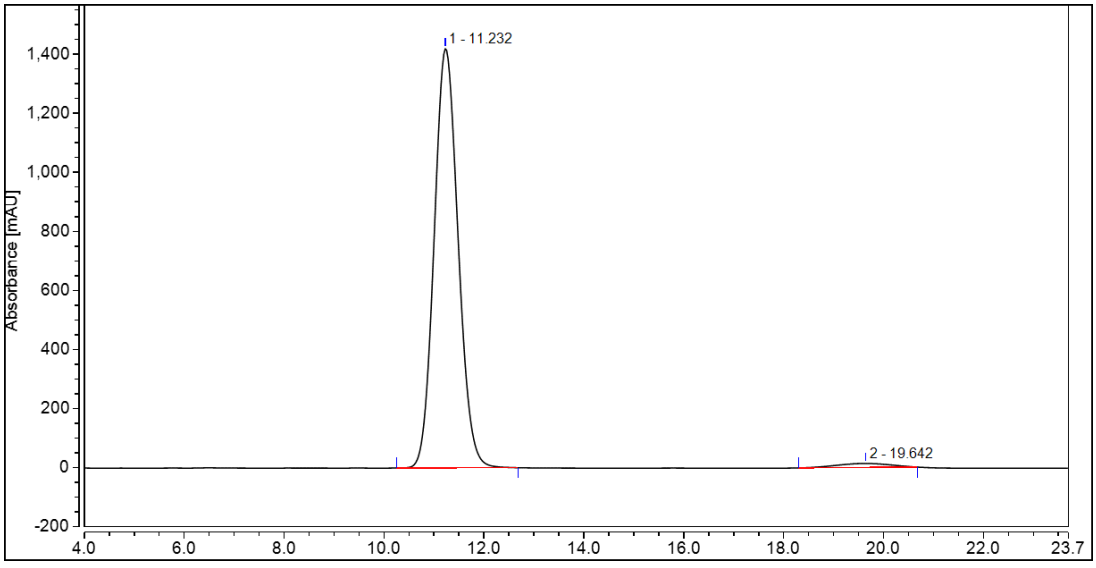


HPLC analysis:rac-**3l**



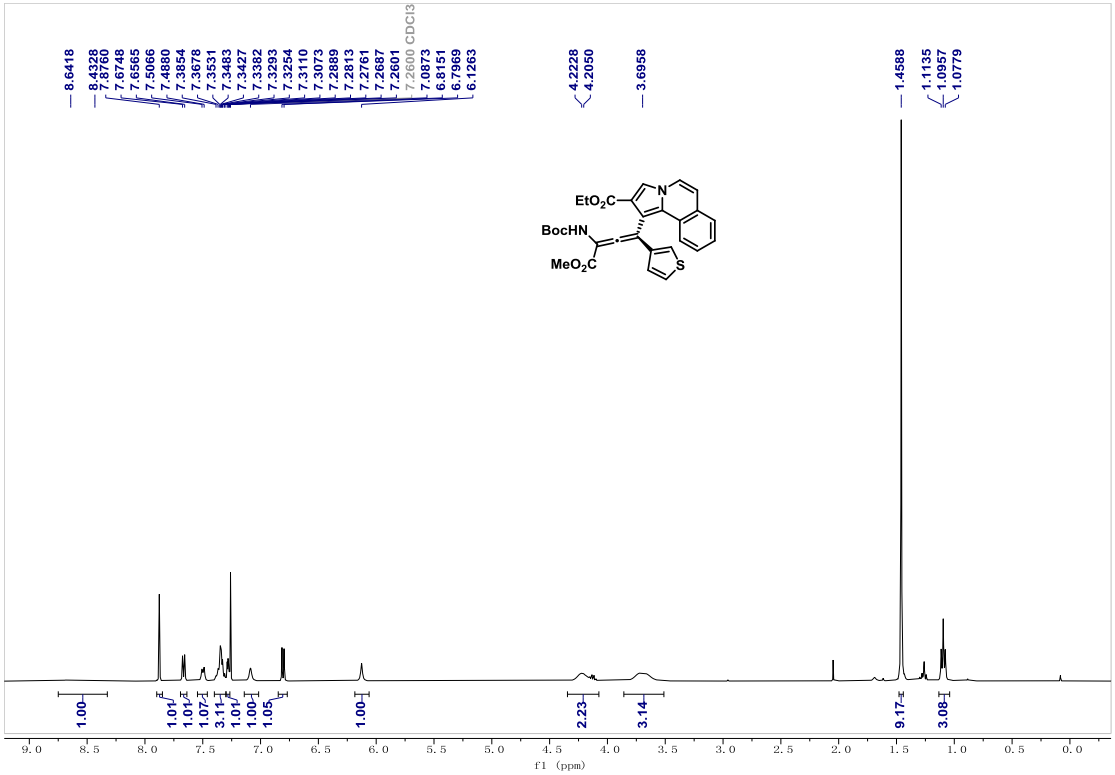
Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	11.255	34.194	59.975	51.55	73.50
2	19.642	32.136	21.622	48.45	26.50

Enantioenriched **3l**

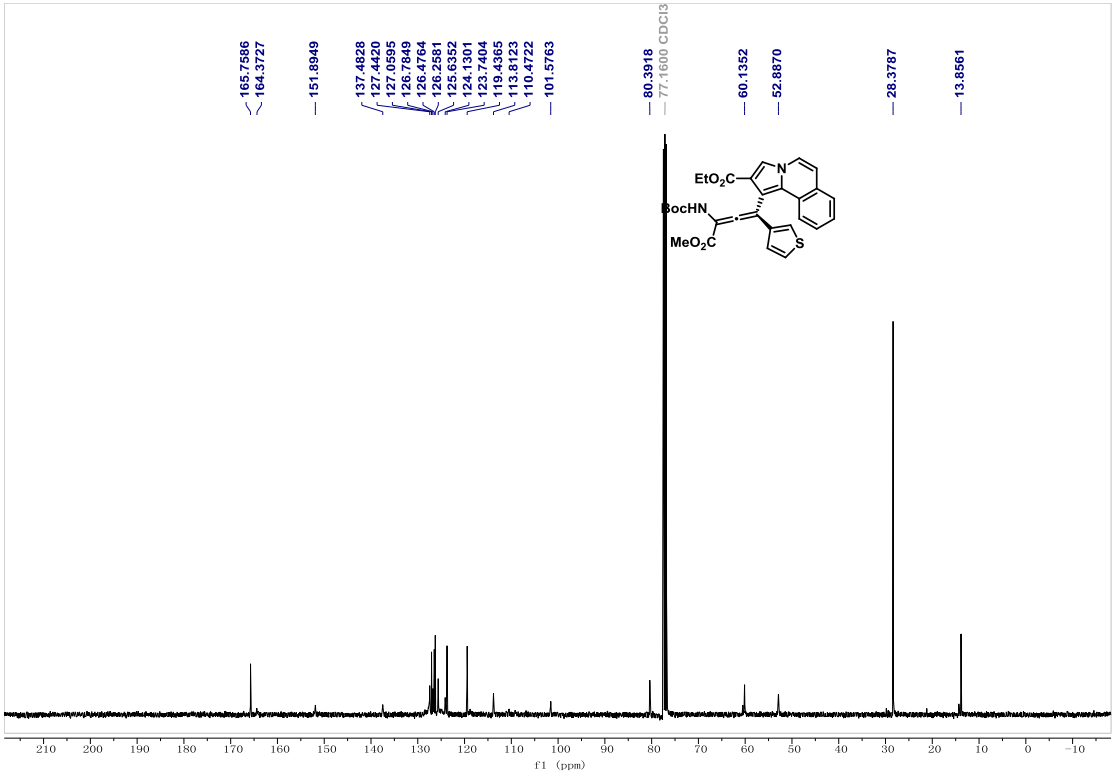


Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	11.232	787.755	1420.100	97.90	99.06
2	19.642	16.925	13.506	2.10	0.94

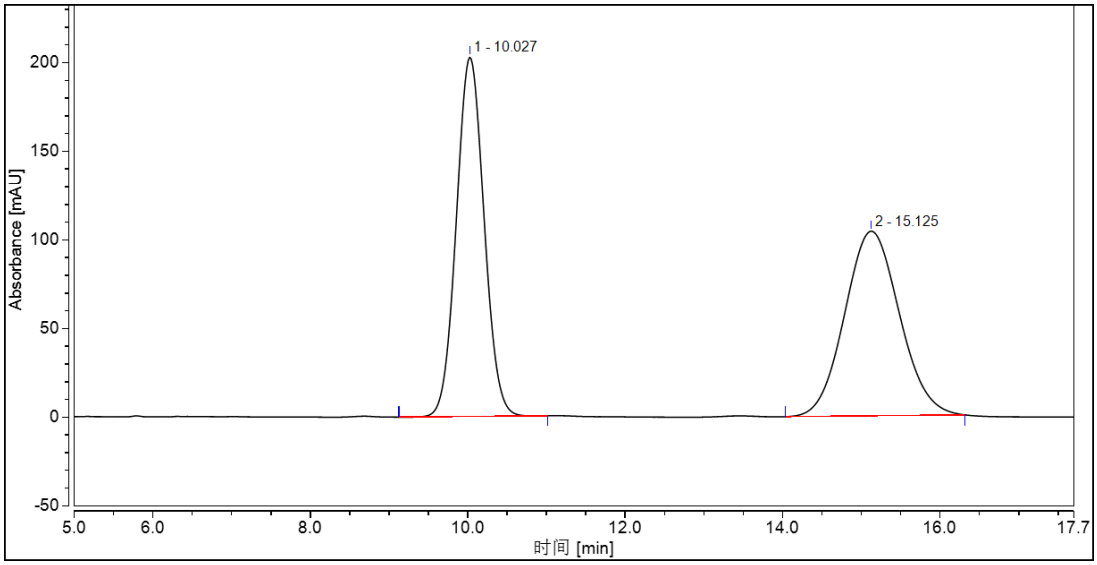
^{1}H NMR of **3m** (400 MHz, $CDCl_3$)



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

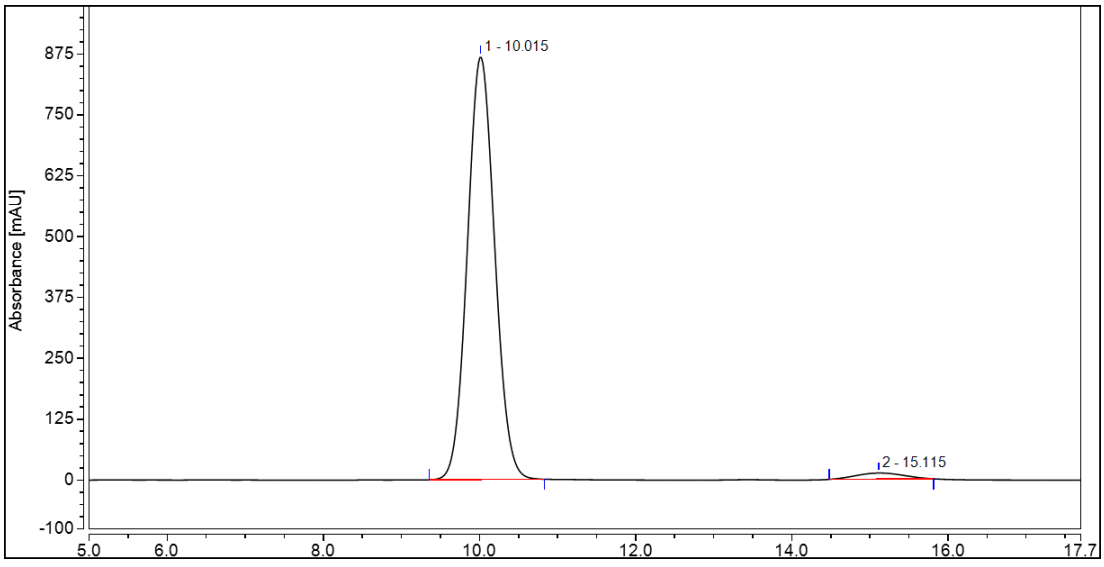


HPLC analysis: rac-**3m**



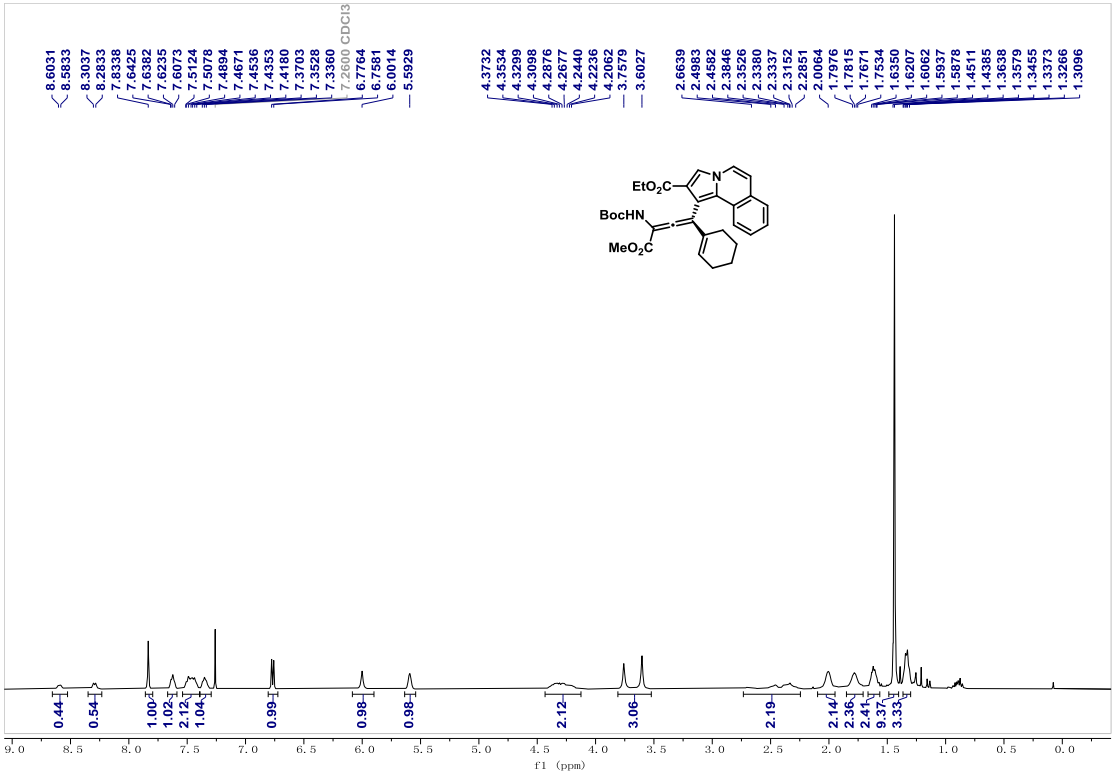
Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	10.027	82.650	202.725	49.62	66.05
2	15.125	83.929	104.213	50.38	33.95

Enantioenriched **3m**

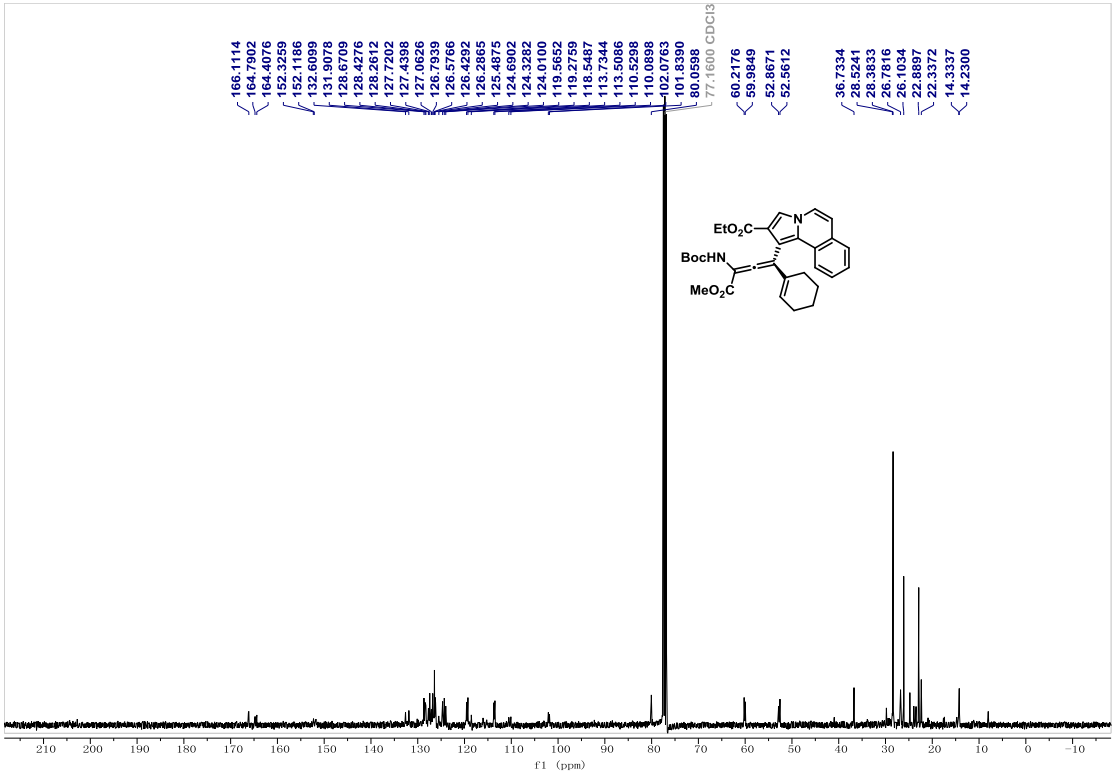


Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	10.015	352.205	868.560	97.55	98.57
2	15.115	8.831	12.608	2.45	1.43

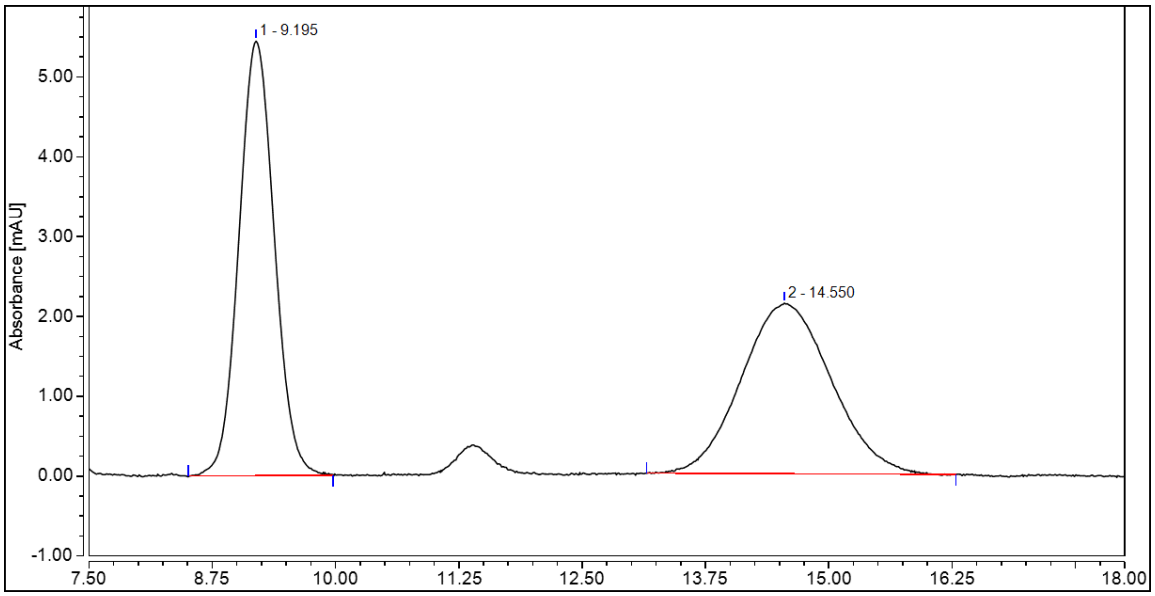
^{1}H NMR of **3n** (400 MHz, $CDCl_3$)



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

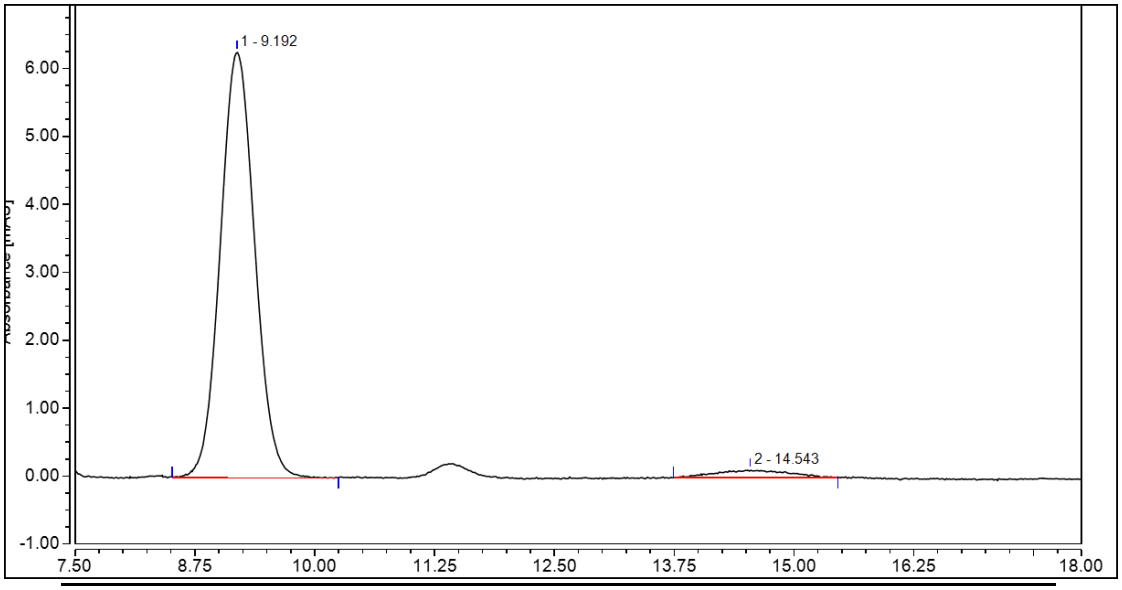


HPLC analysis: rac-**3n**



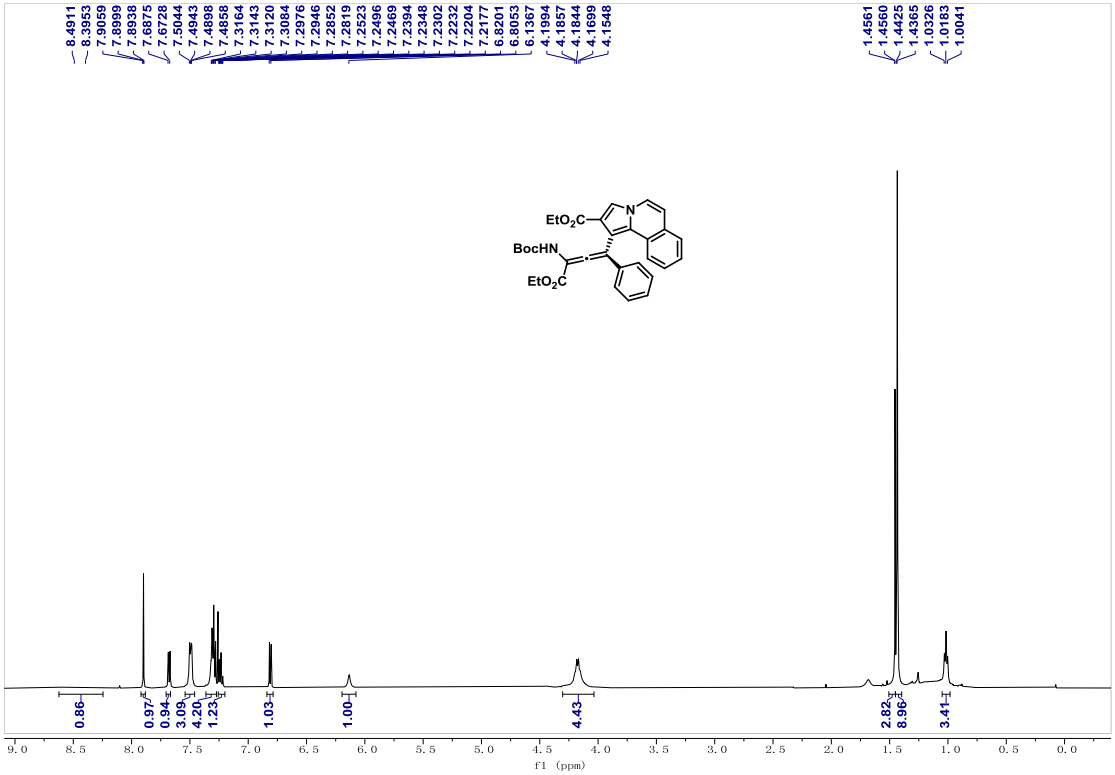
Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	9.195	2.269	5.443	50.21	71.81
2	14.550	2.250	2.137	49.79	28.19

Enantioenriched **3n**

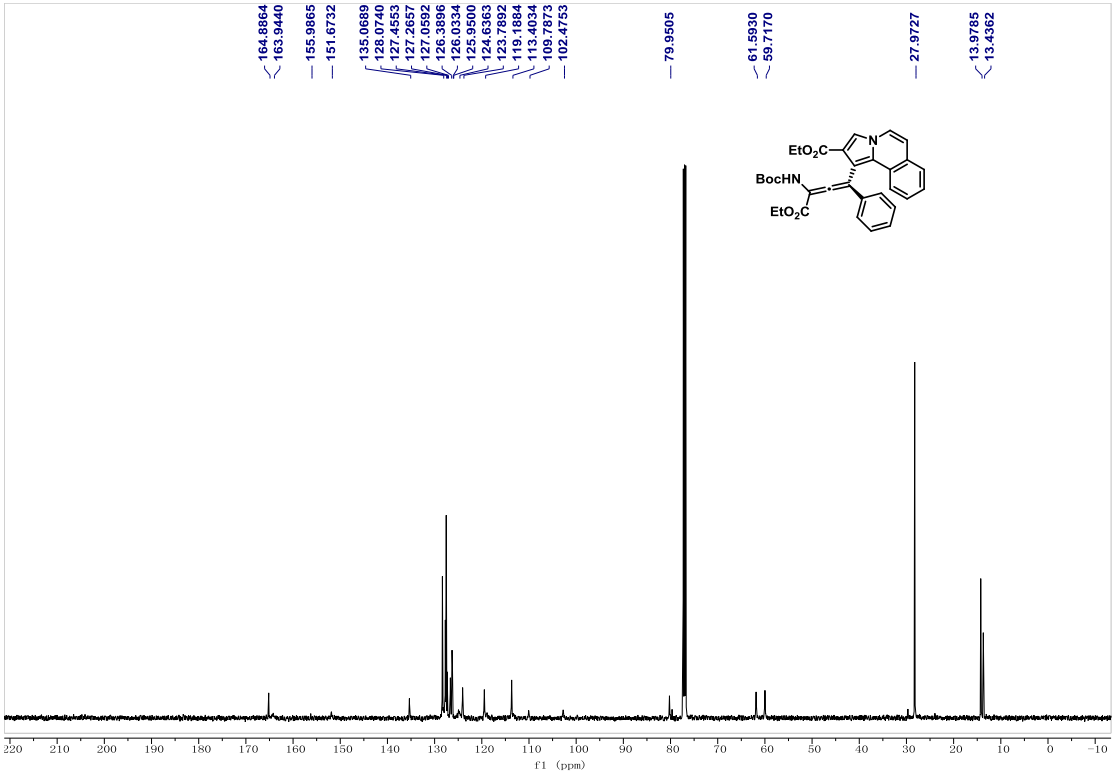


Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	9.192	2.611	6.274	96.57	98.20
2	14.543	0.093	0.115	3.43	1.80

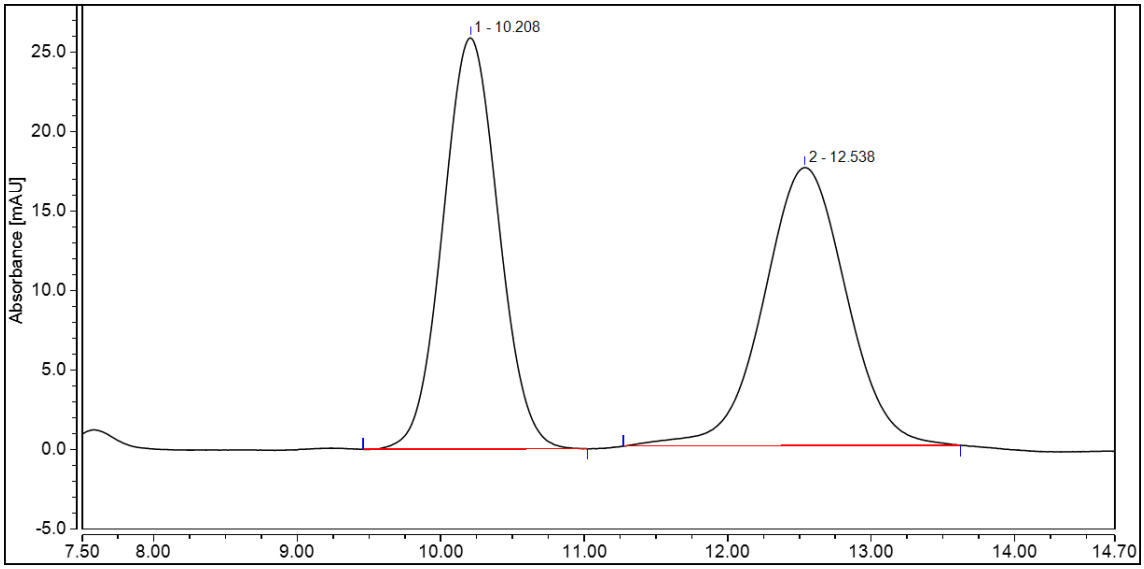
^{1}H NMR of **3o** (500MHz, $CDCl_3$)



^{13}C NMR of **3o** (126 MHz, $CDCl_3$)

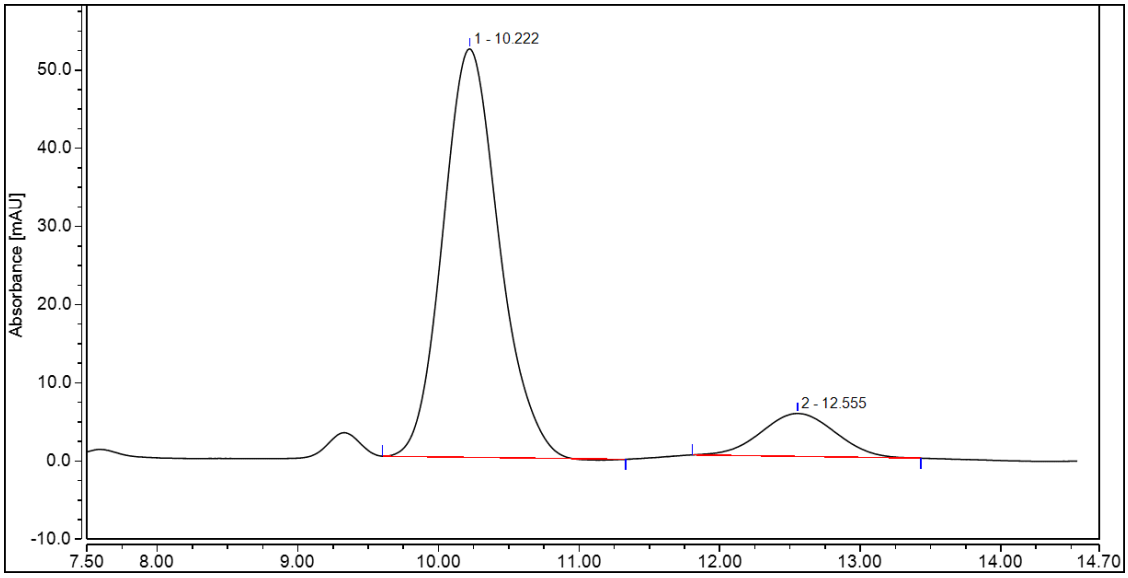


HPLC analysis: rac-**3o**



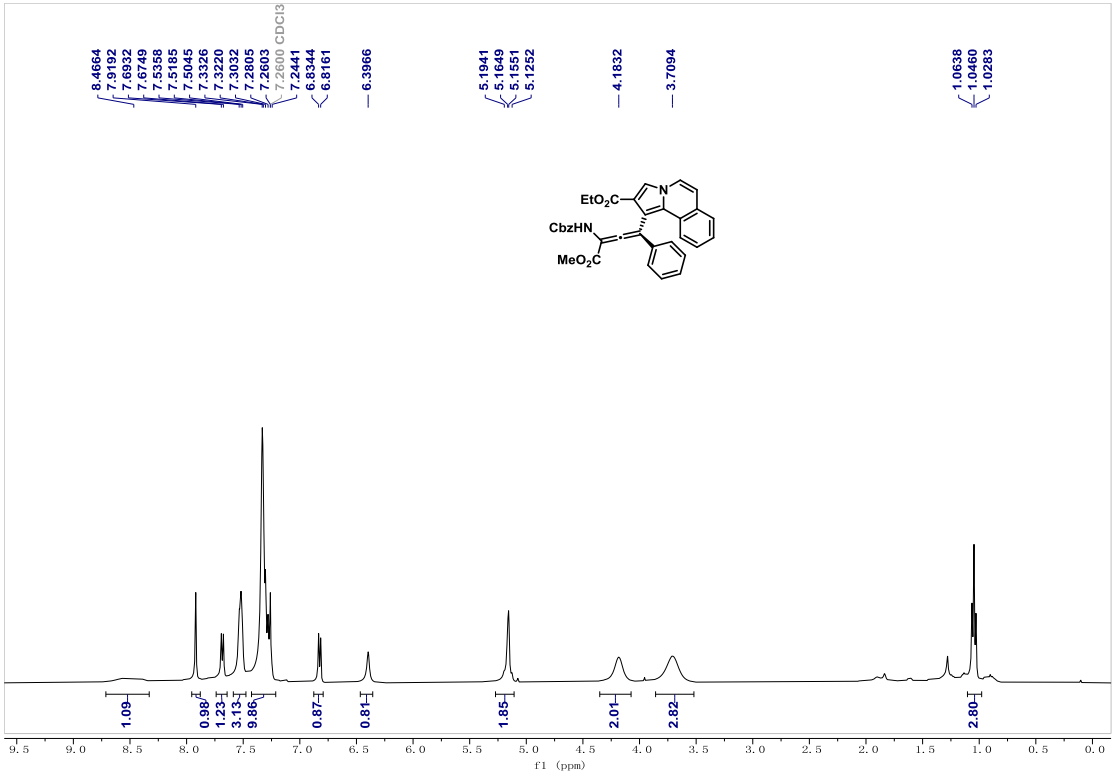
Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	10.208	11.639	25.870	49.90	59.66
2	12.538	11.685	17.491	50.10	40.34

Enantioenriched **3o**

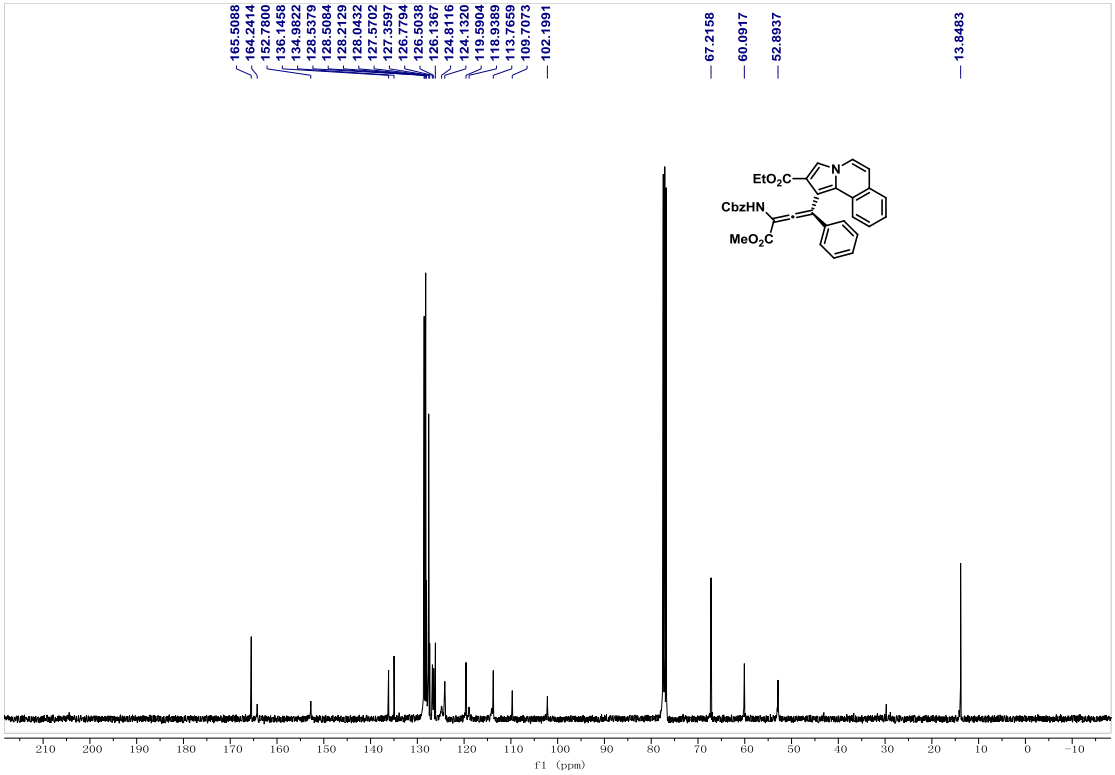


Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	10.222	24.240	52.260	87.79	90.47
2	12.555	3.371	5.505	12.21	9.53

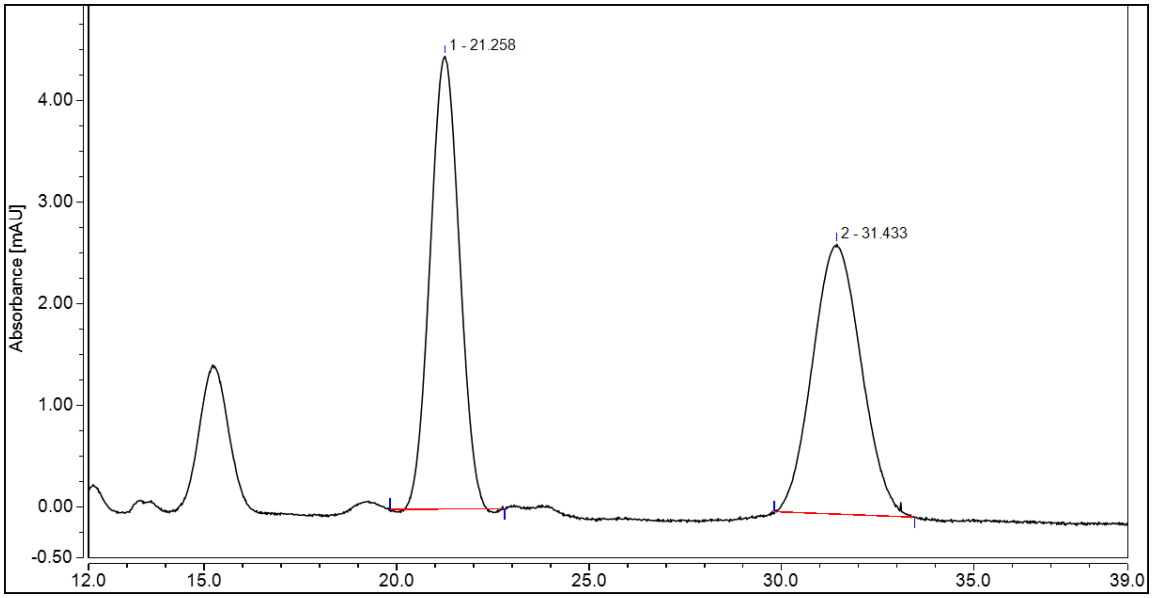
^{1}H NMR of **3p** (400 MHz, $CDCl_3$)



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

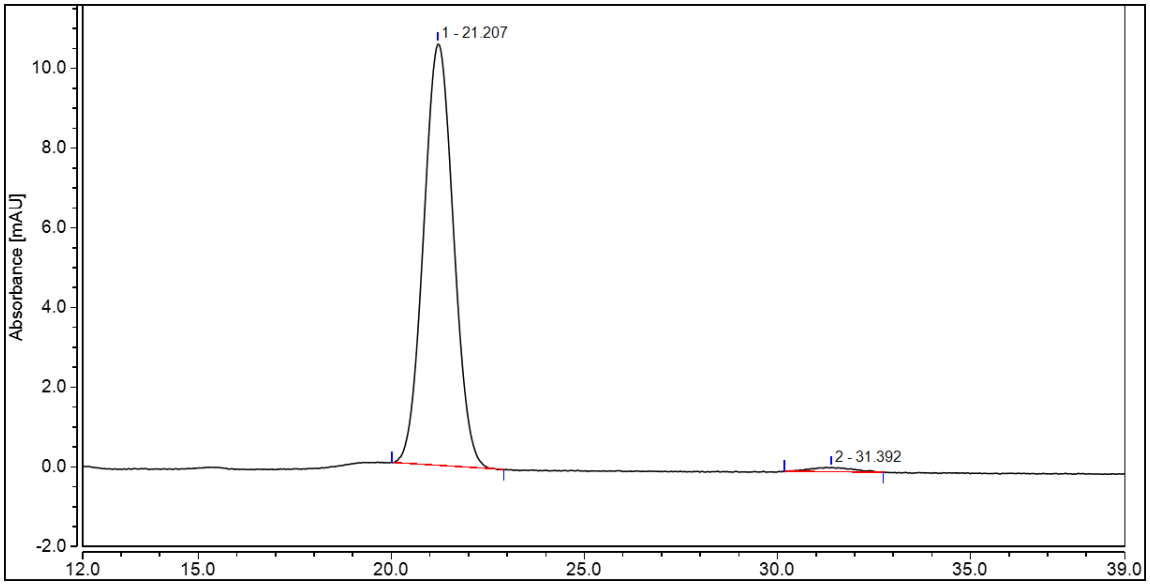


HPLC analysis: rac-**3p**



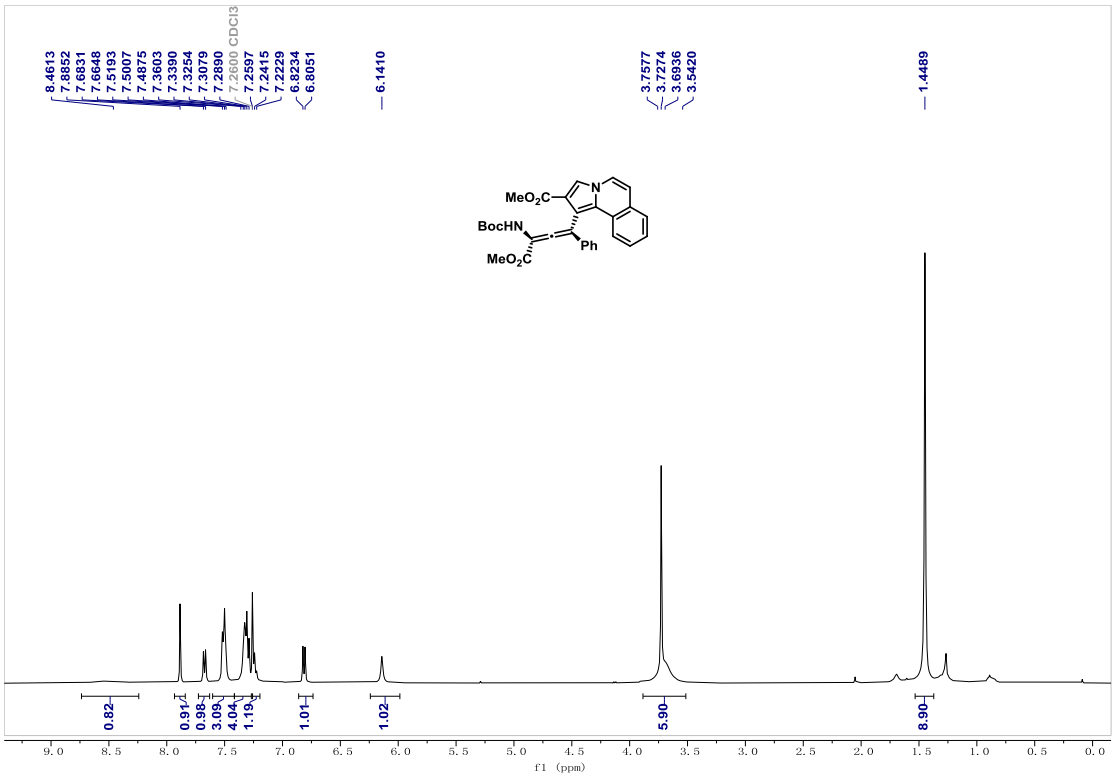
Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	21.258	3.922	4.455	50.27	62.64
2	31.433	3.879	2.657	49.73	37.36

Enantioenriched **3p**

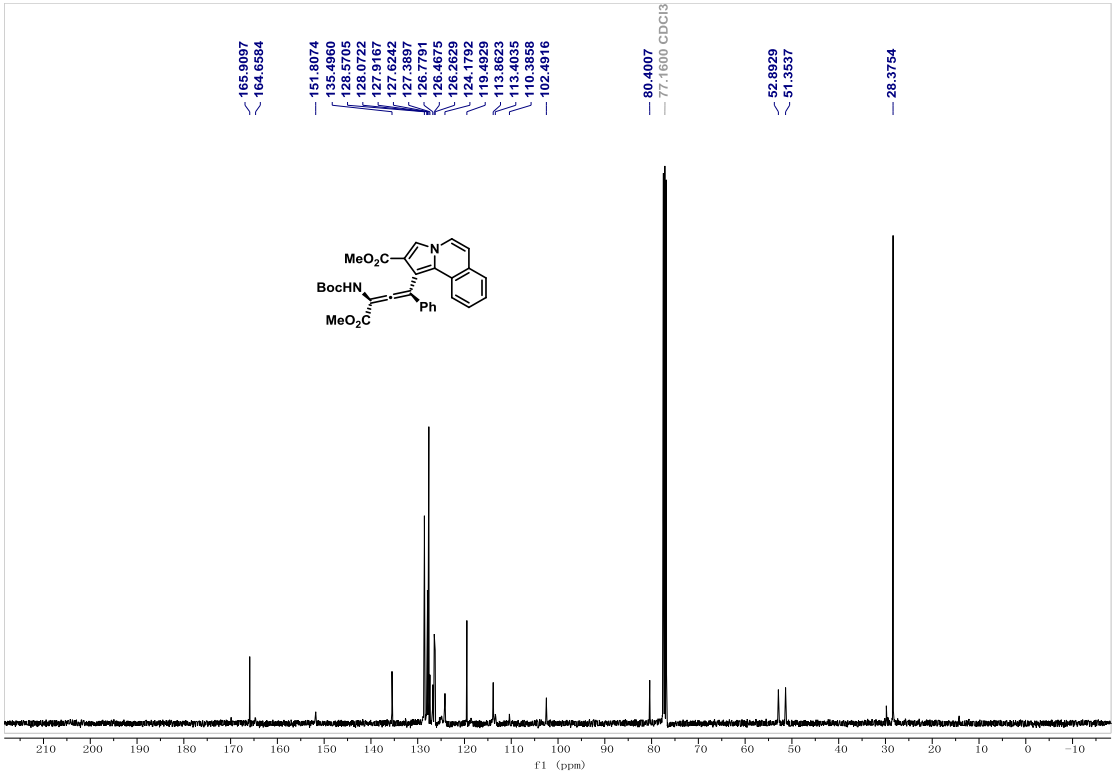


Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	21.207	9.484	10.587	98.56	98.91
2	31.392	0.138	0.117	1.44	1.09

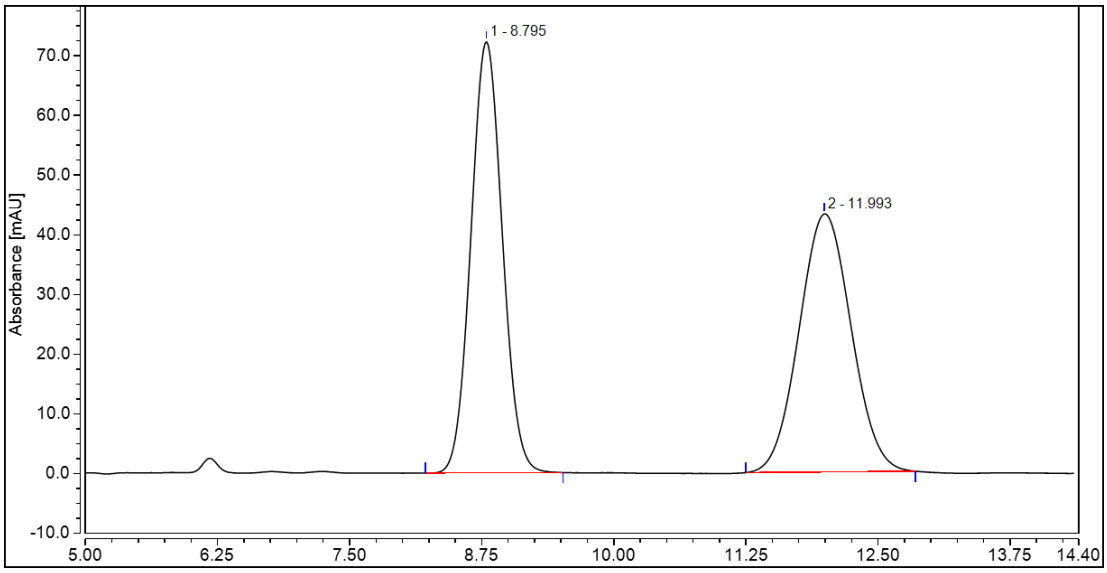
^{1}H NMR of **3q** (400 MHz, $CDCl_3$)



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

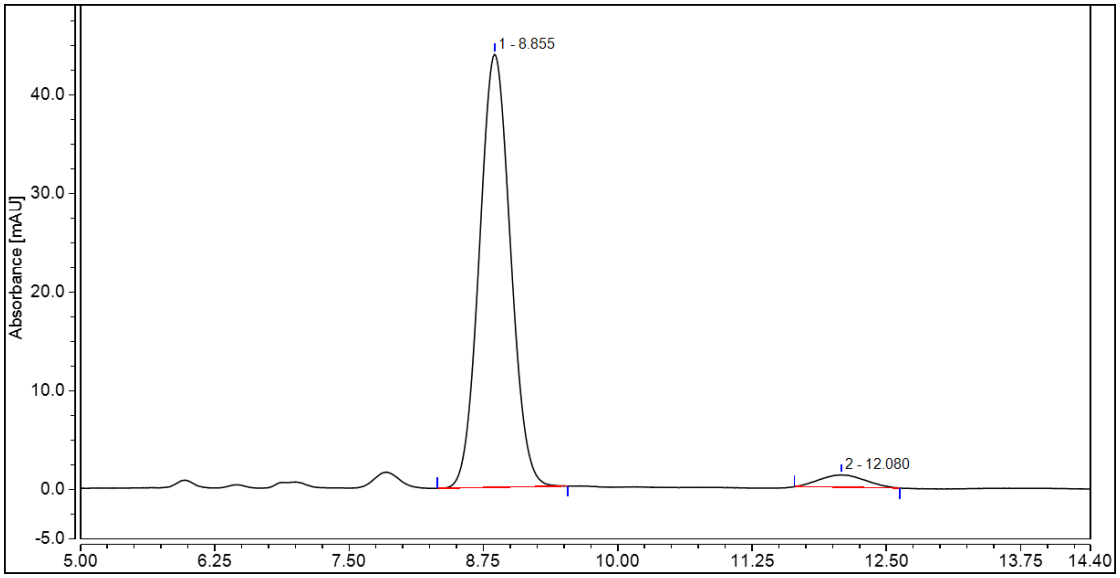


HPLC analysis: rac-**3q**



Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	8.795	24.847	72.213	50.17	62.55
2	11.993	24.676	43.235	49.83	37.45

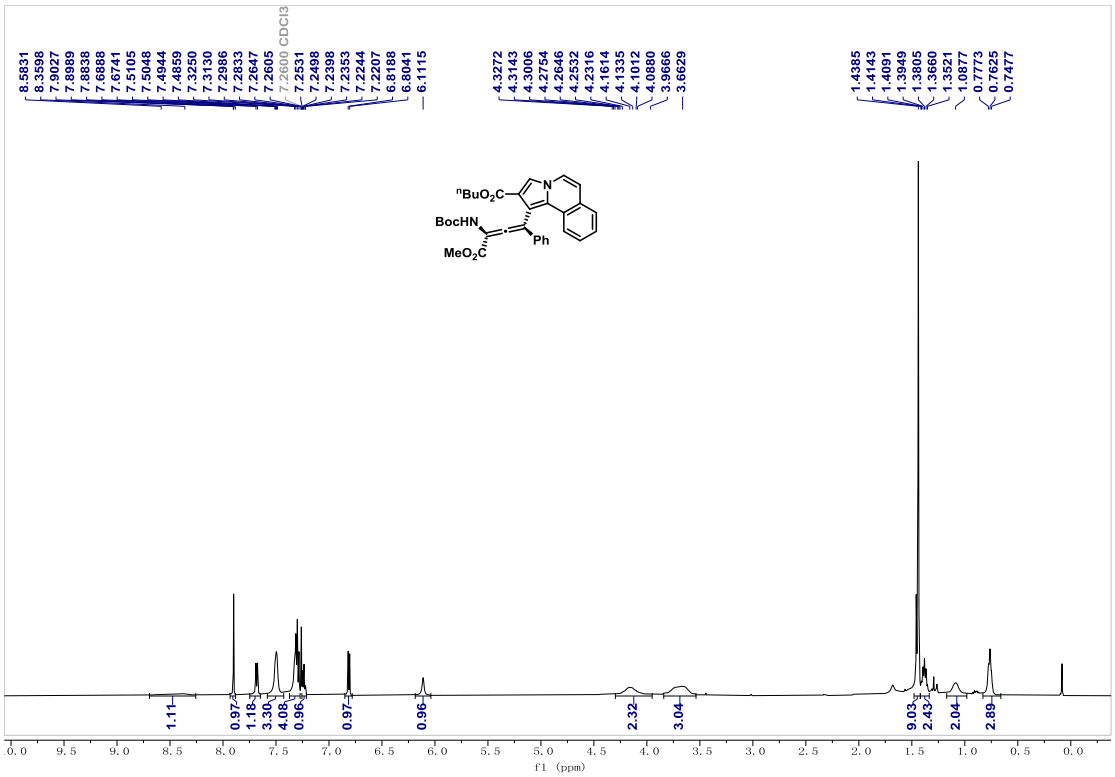
Enantioenriched **3q**



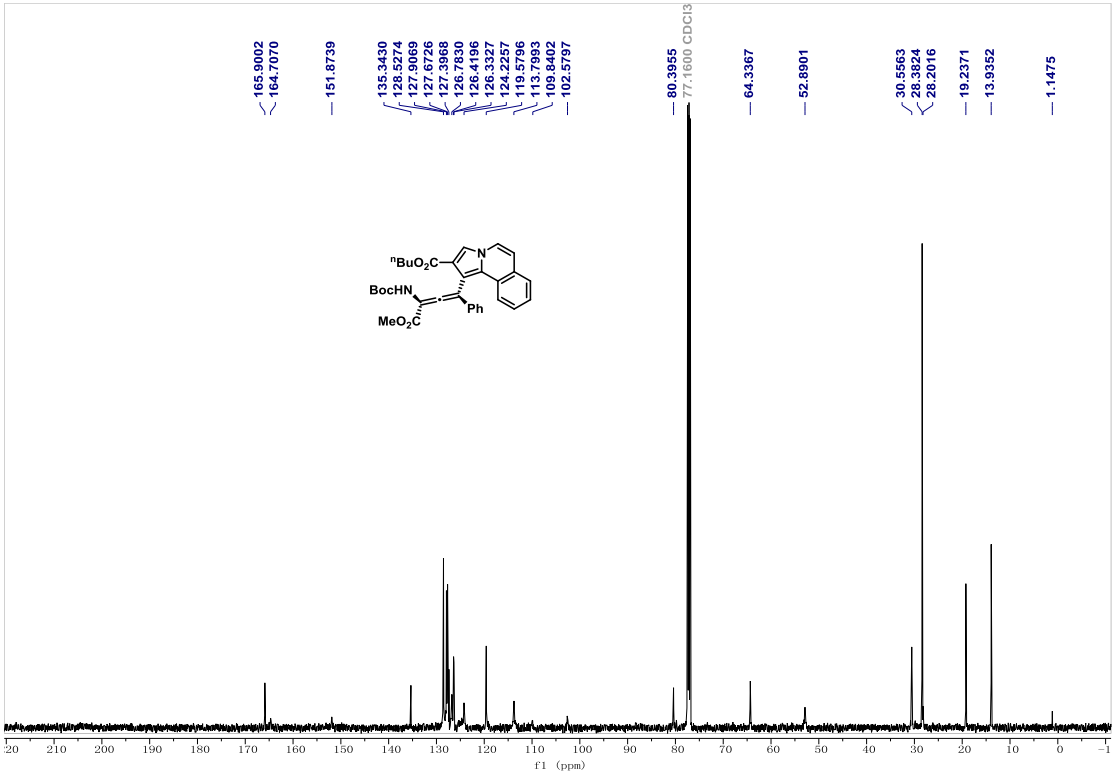
Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	8.855	14.697	43.895	96.01	97.24
2	12.080	0.611	1.244	3.99	2.76

-

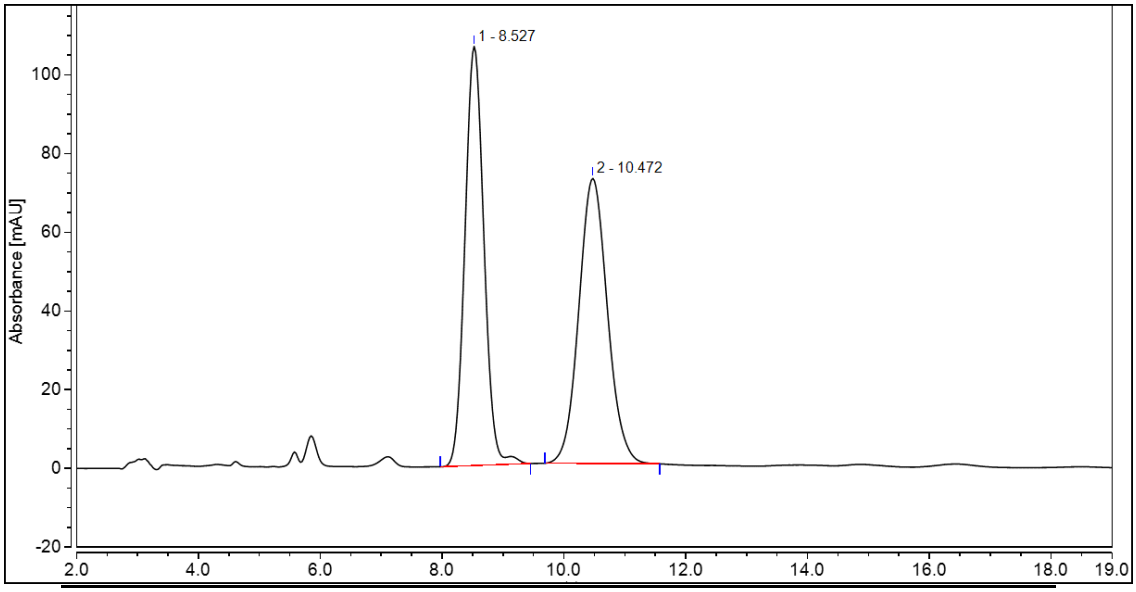
^{1}H NMR of **3r** (500 MHz, $CDCl_3$)



^{13}C NMR of **3r** (126 MHz, $CDCl_3$)

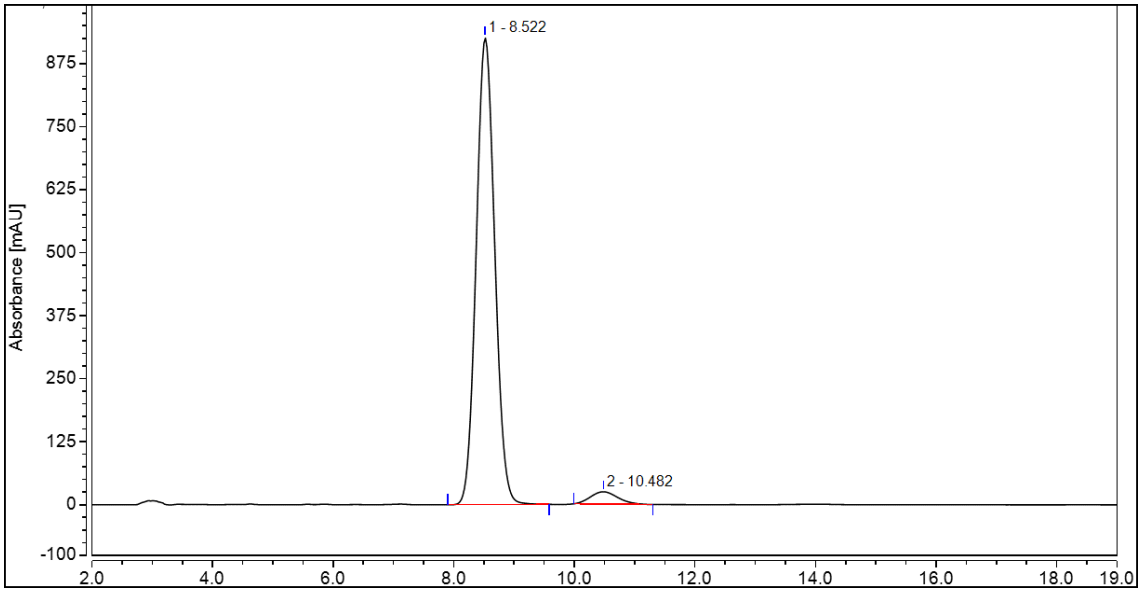


HPLC analysis: rac-**3r**



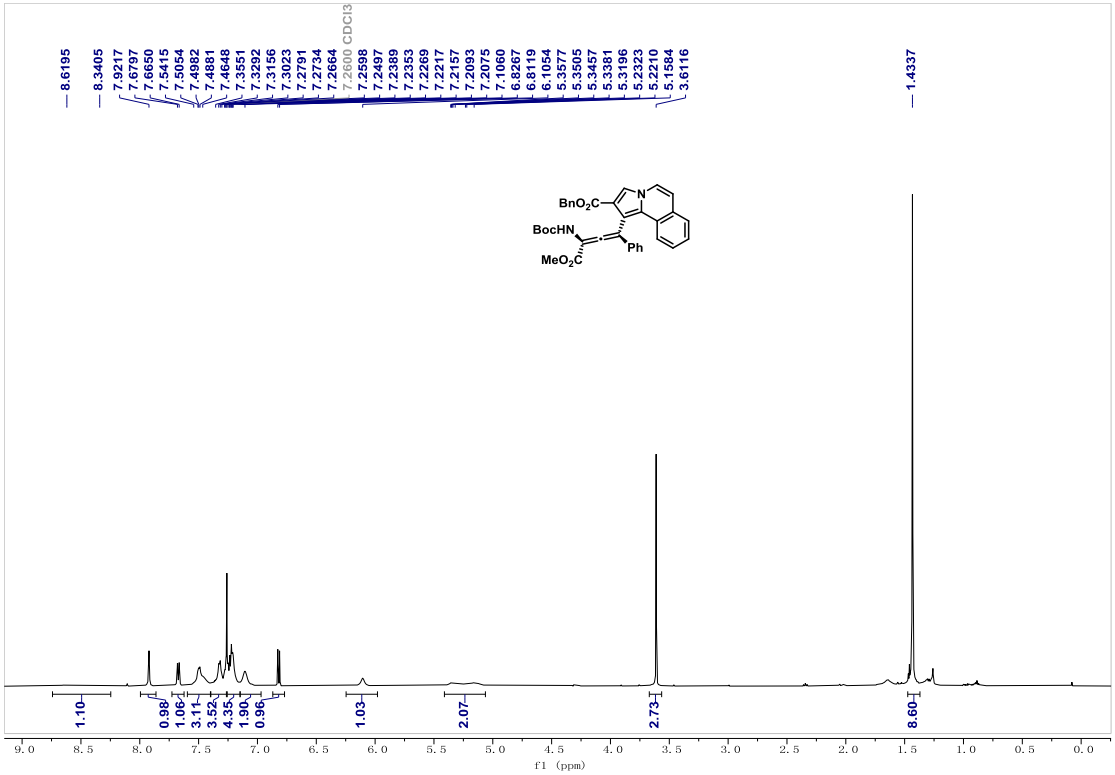
Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	8.527	38.437	106.558	49.43	59.52
2	10.472	39.318	72.460	50.57	40.48

Enantioenriched **3r**

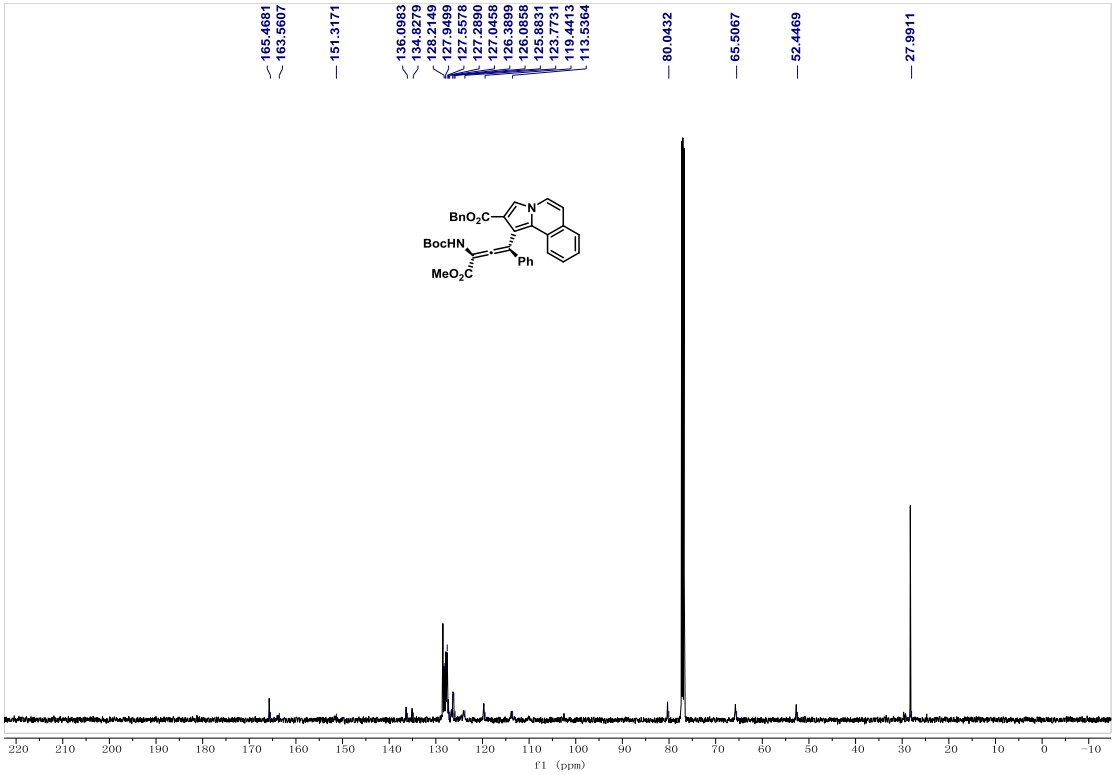


Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	8.522	329.723	925.694	96.26	97.43
2	10.482	12.797	24.395	3.74	2.57

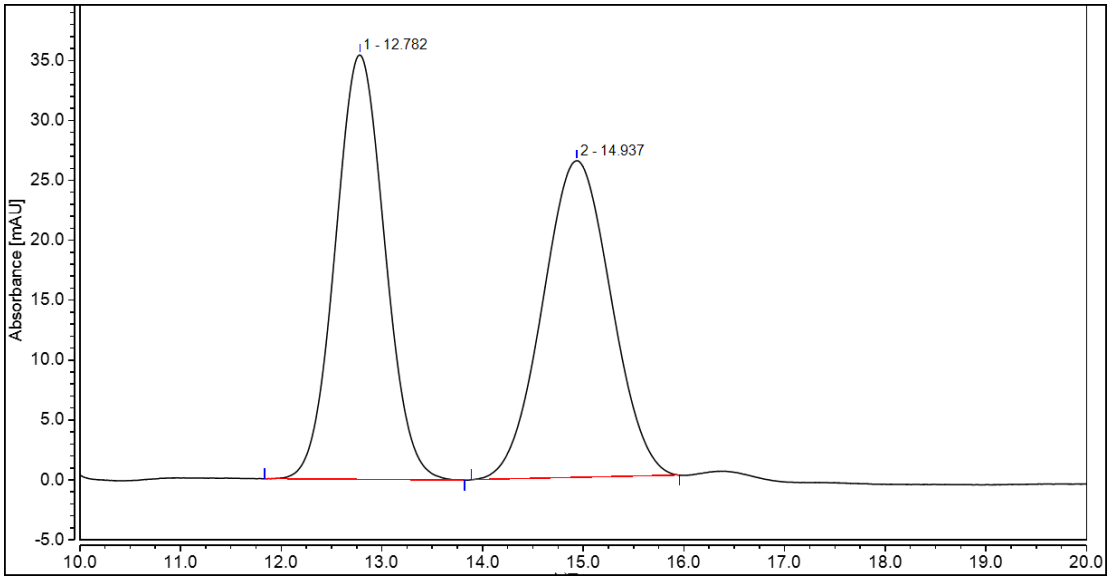
^{1}H NMR of **3s** (500 MHz, $CDCl_3$)



^{13}C NMR of **3s** (126 MHz, $CDCl_3$)

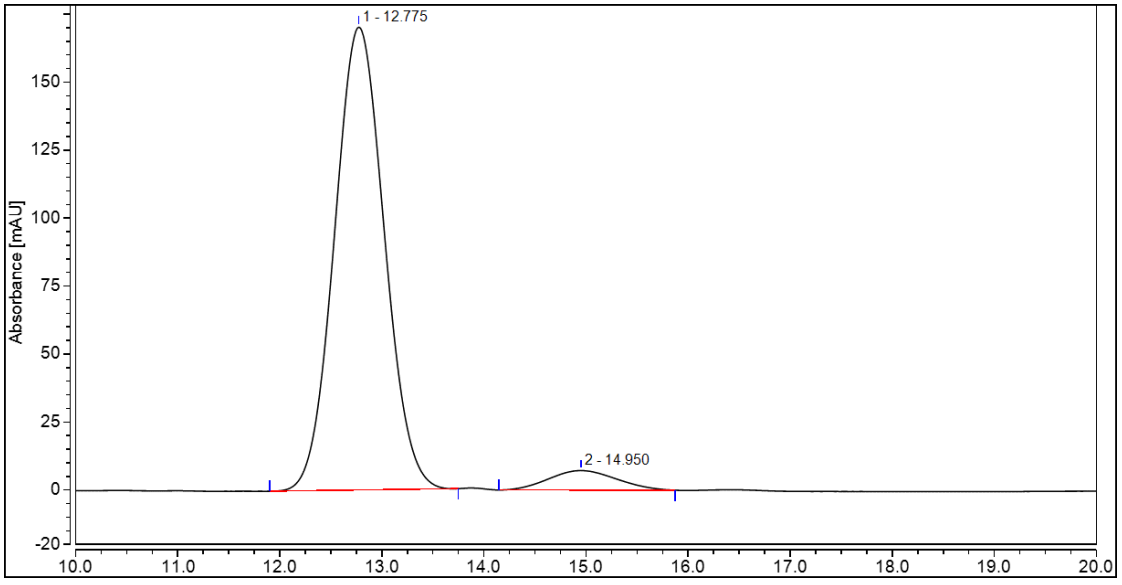


HPLC analysis: rac-**3s**



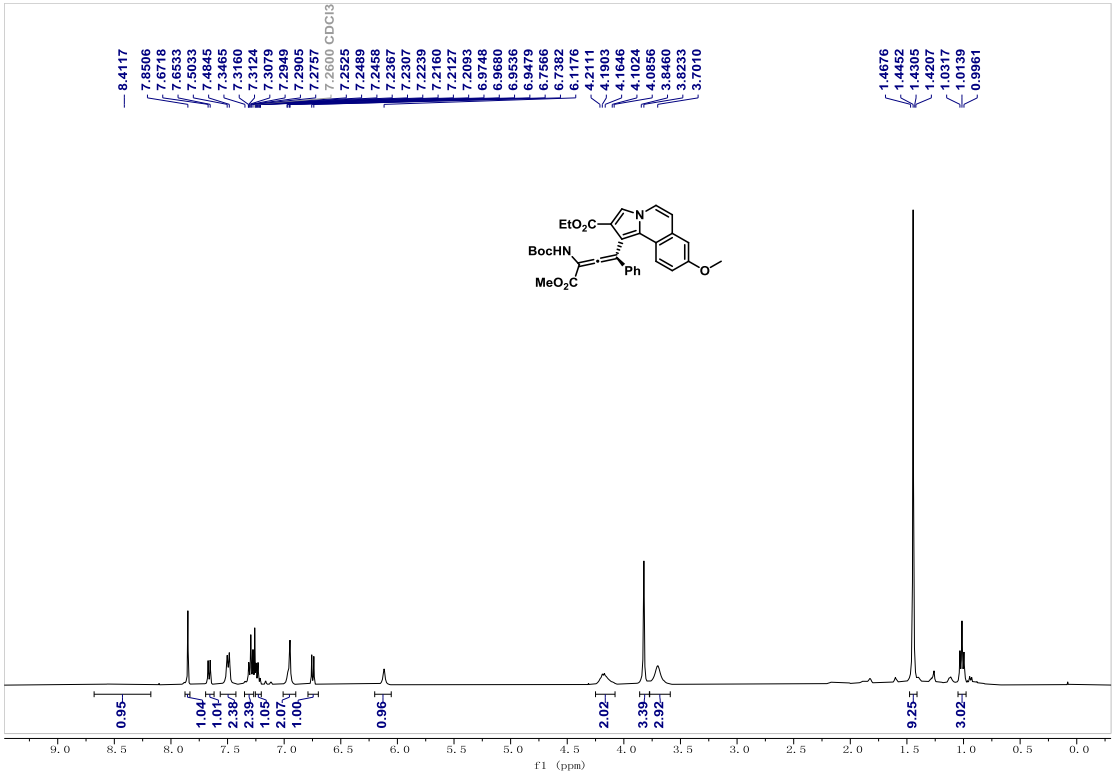
Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	12.782	20.198	35.432	49.31	57.28
2	14.937	20.765	26.426	50.69	42.72

Enantioenriched **3s**

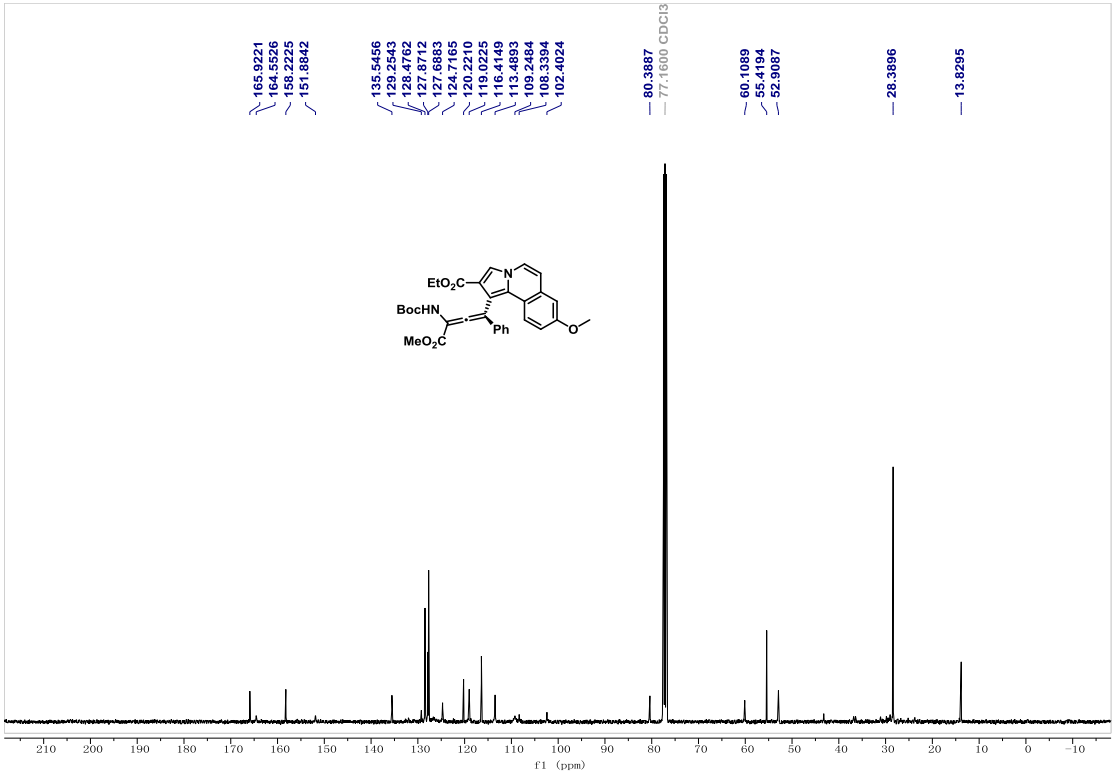


Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	12.775	96.196	170.250	94.55	95.95
2	14.950	5.547	7.186	5.45	4.05

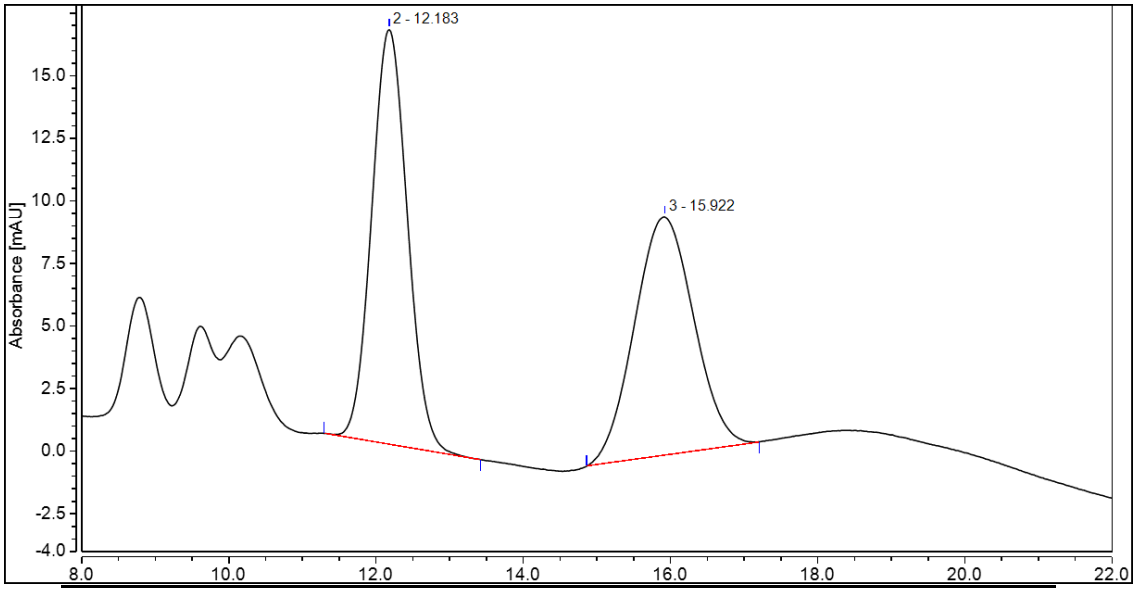
^{1}H NMR of **3t** (400 MHz, $CDCl_3$)



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

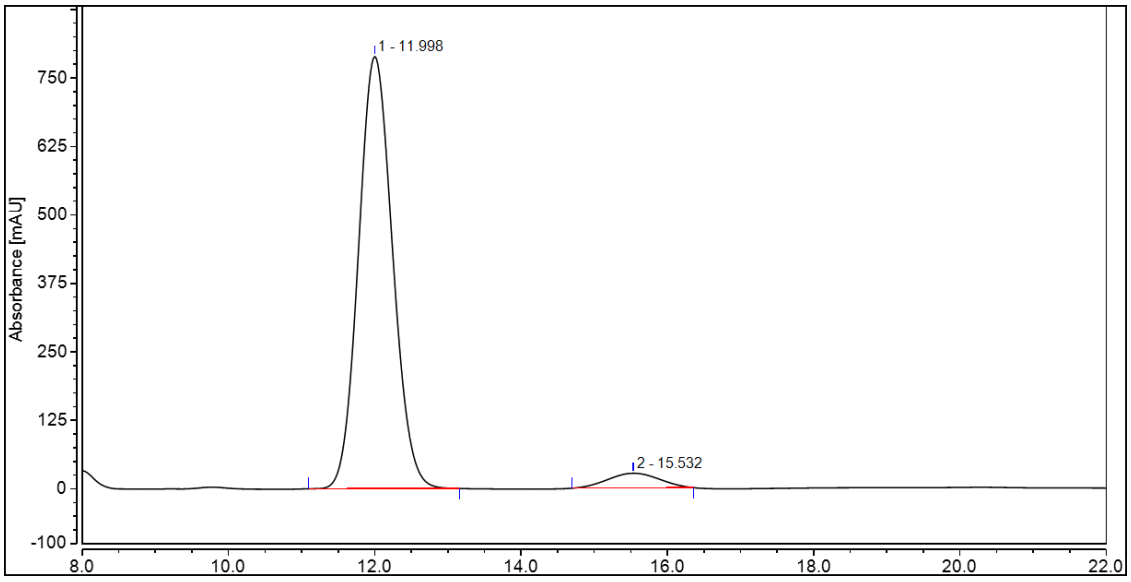


HPLC analysis: rac-**3t**



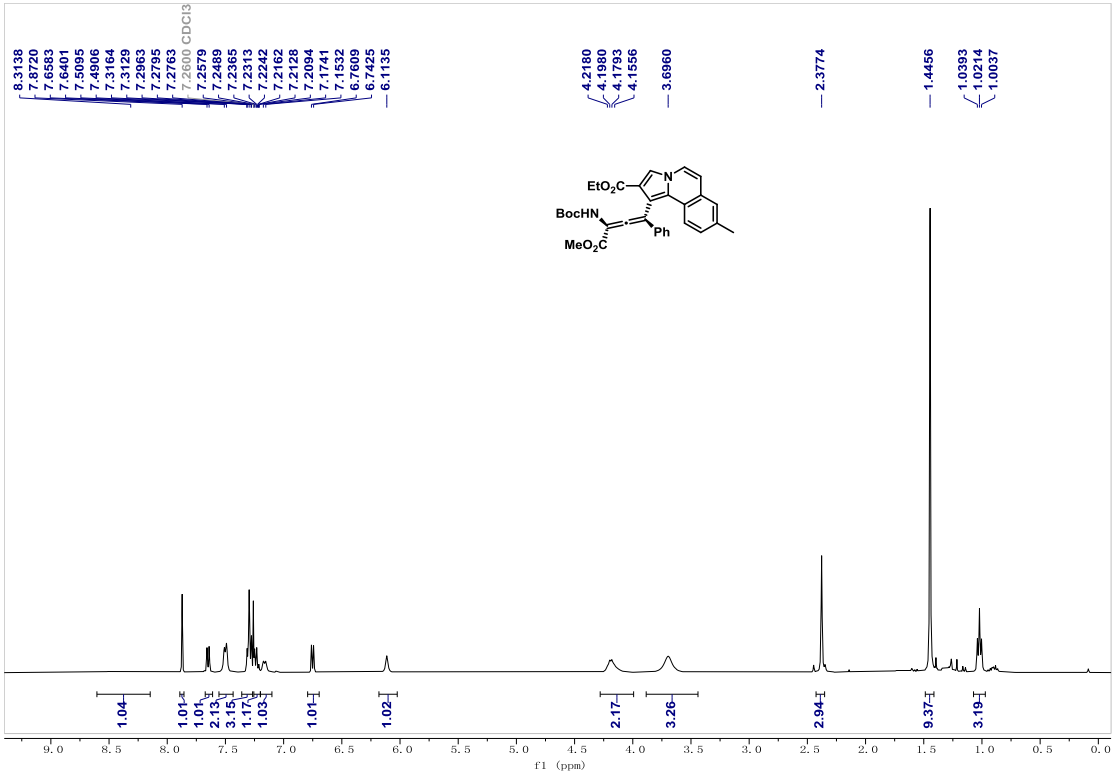
Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	12.183	9.322	16.567	51.24	63.49
2	15.922	8.871	9.526	48.76	36.51

Enantioenriched **3t**

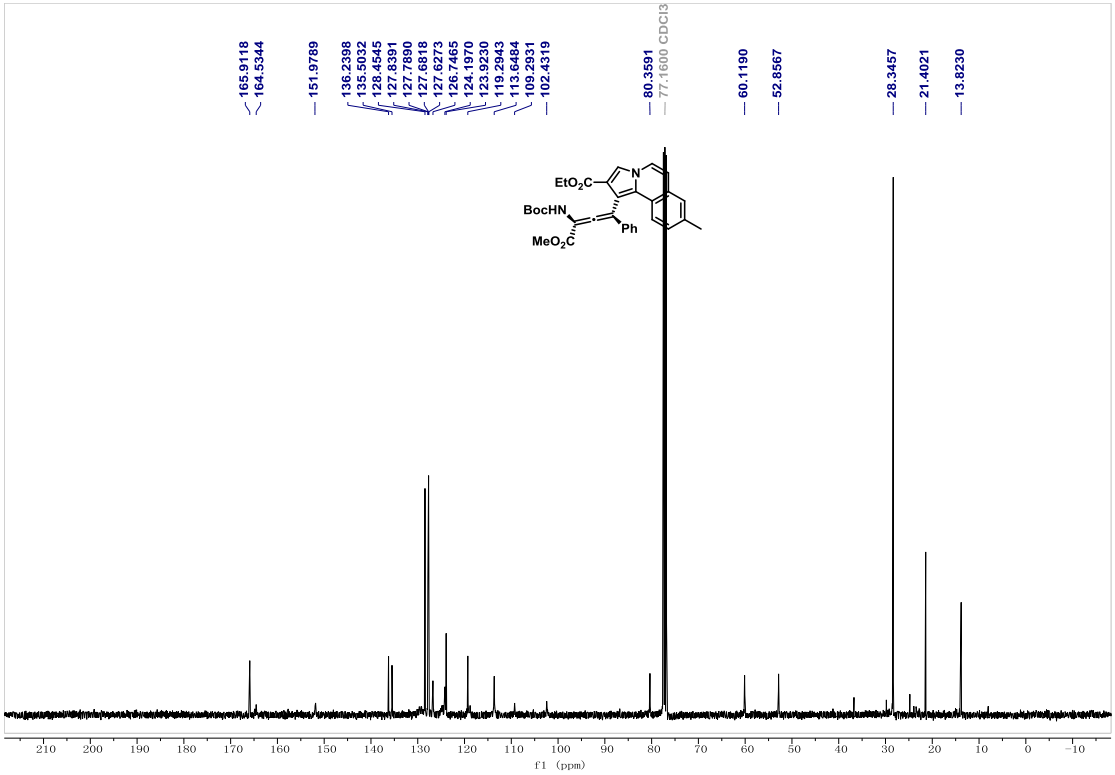


Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	11.998	425.352	789.036	95.09	96.71
2	15.532	21.948	26.873	4.91	3.29

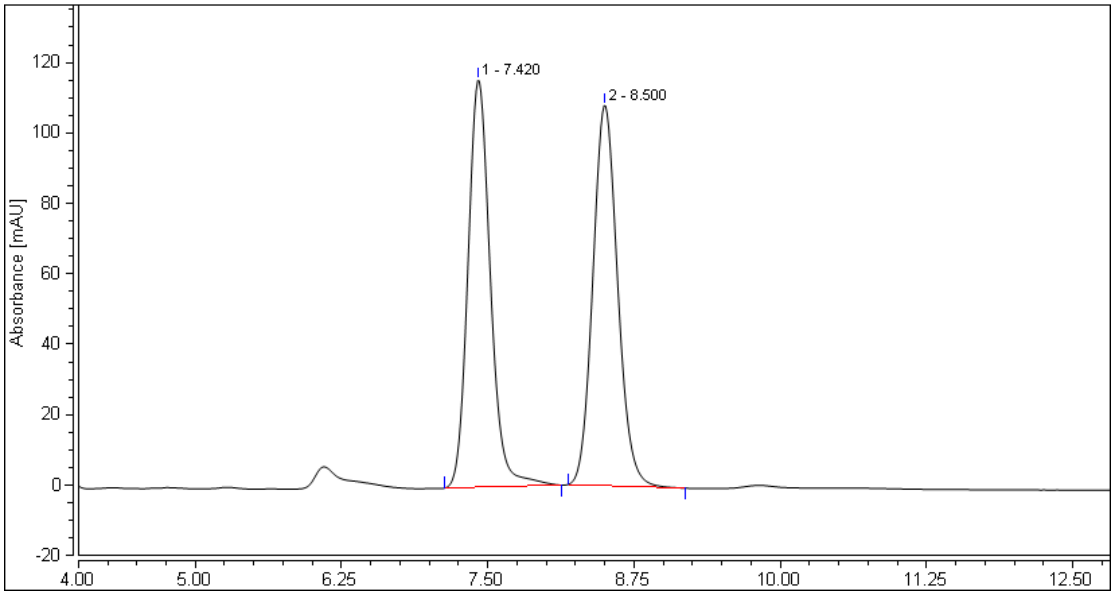
^{1}H NMR of **3u** (400 MHz, $CDCl_3$)



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

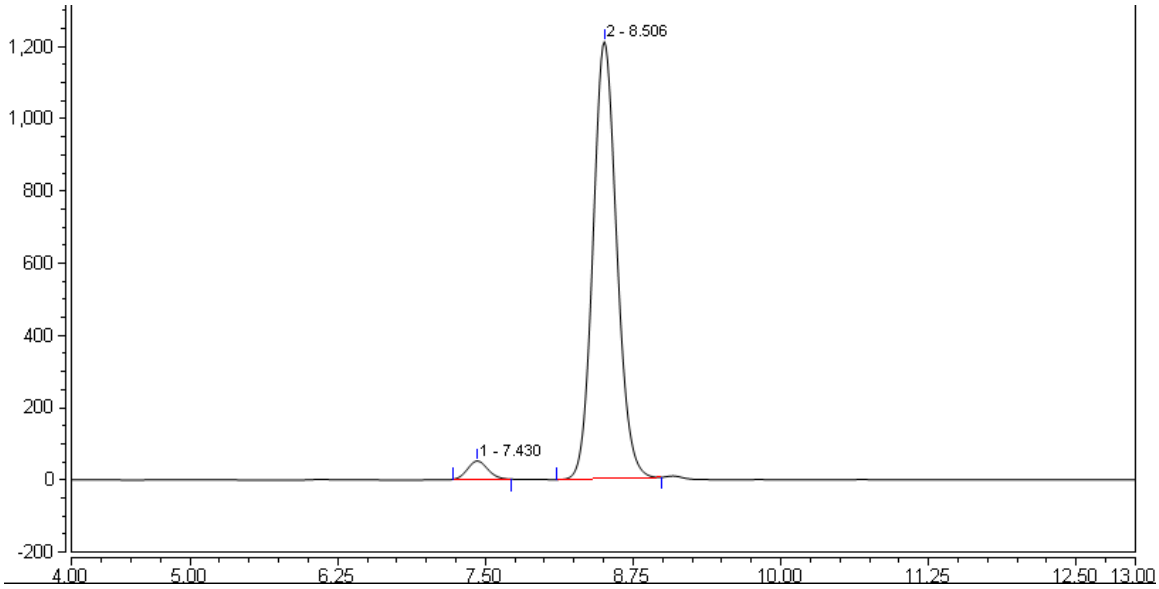


HPLC analysis: rac-**3u**



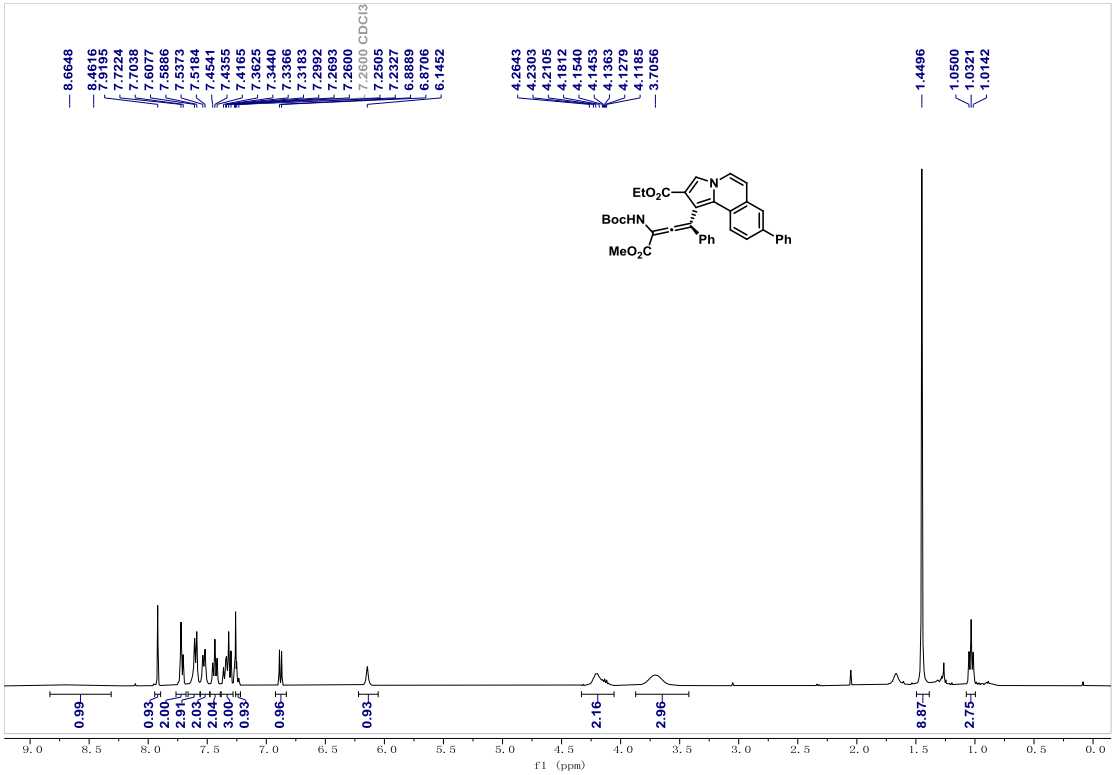
Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	7.420	25.692	115.766	49.23	51.71
2	8.500	26.497	108.114	50.77	48.29

Enantioenriched **3u**

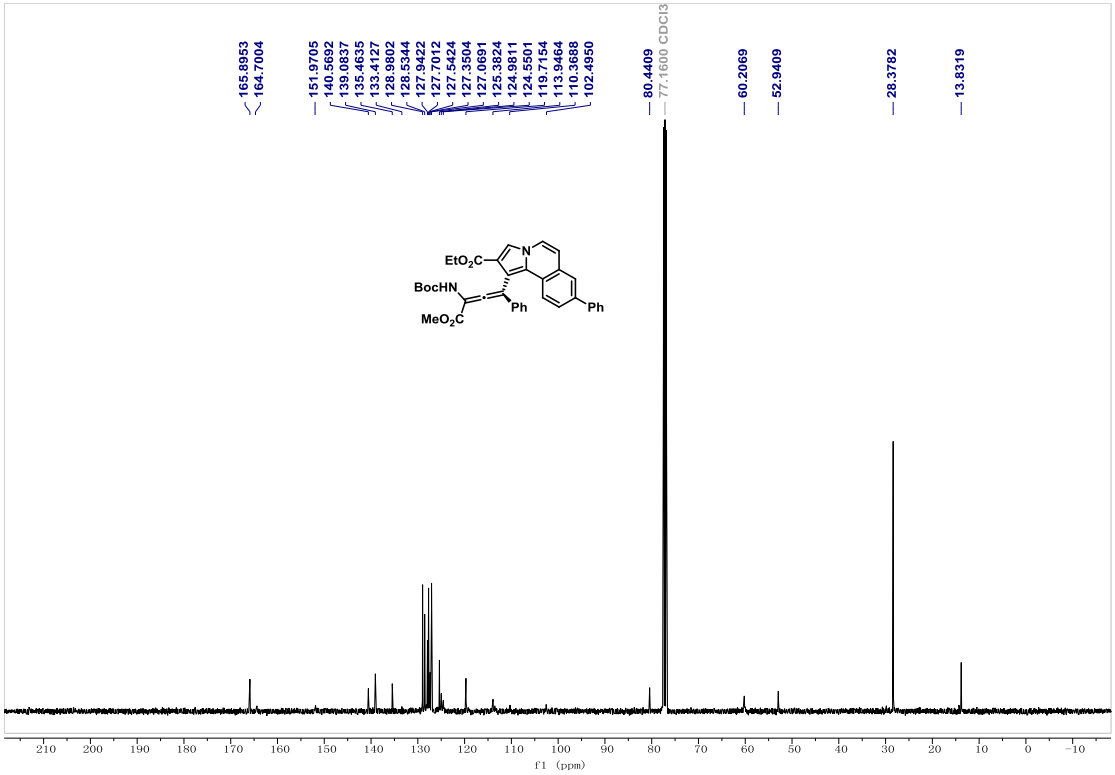


Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	7.430	10.013	50.587	3.44	4.01
2	8.506	281.285	1210.553	96.56	95.99

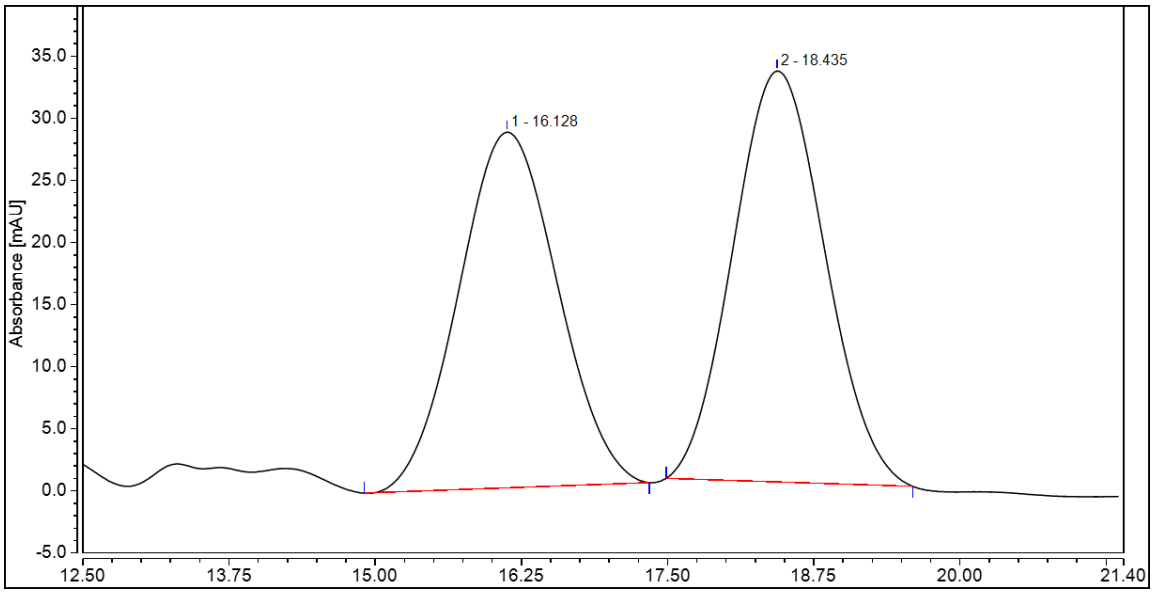
^{1}H NMR of **3v** (400 MHz, $CDCl_3$)



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

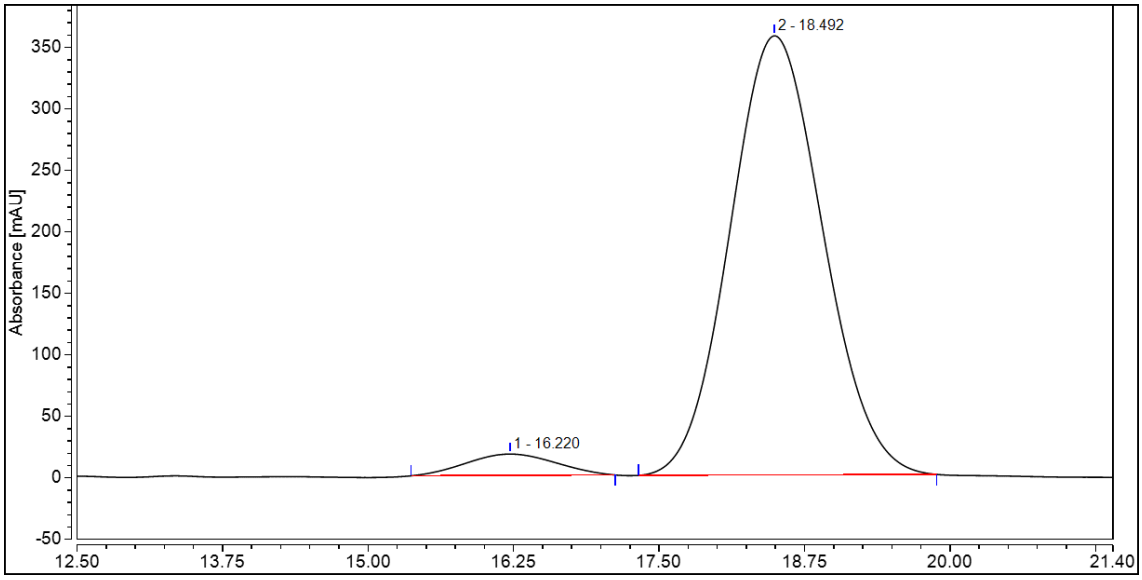


HPLC analysis: rac-**3v**



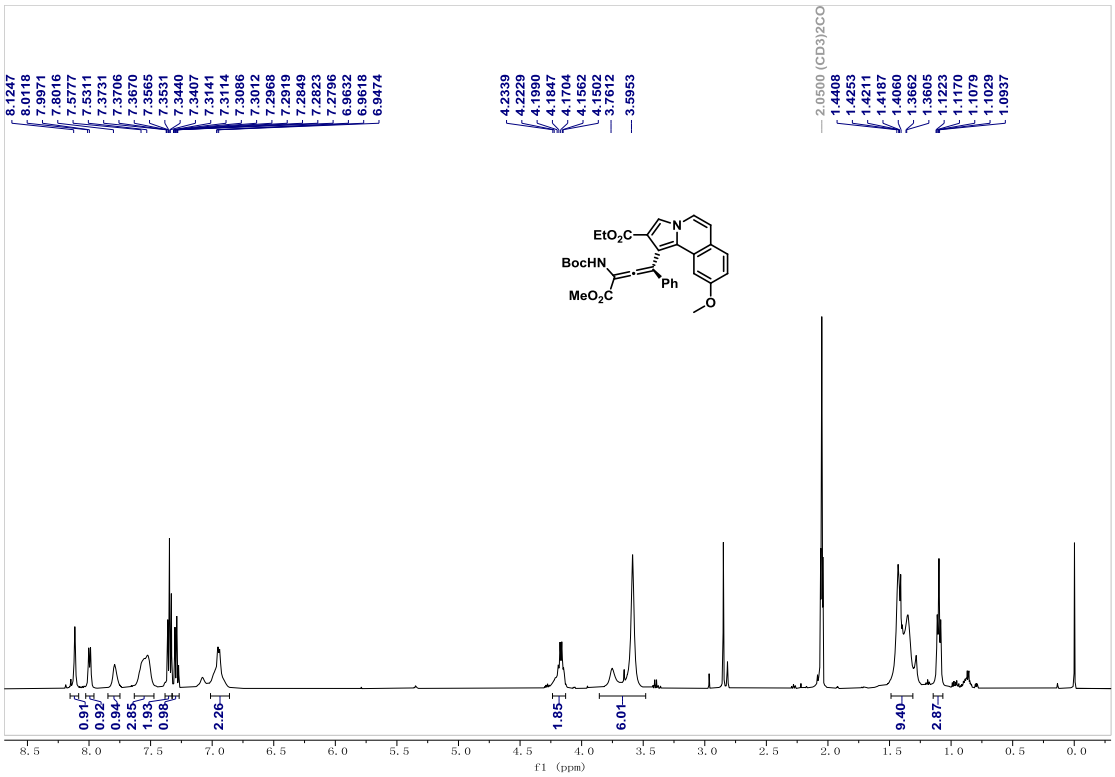
Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	16.128	27.991	28.642	48.21	46.39
2	18.435	30.075	33.094	51.79	53.61

Enantioenriched **3v**

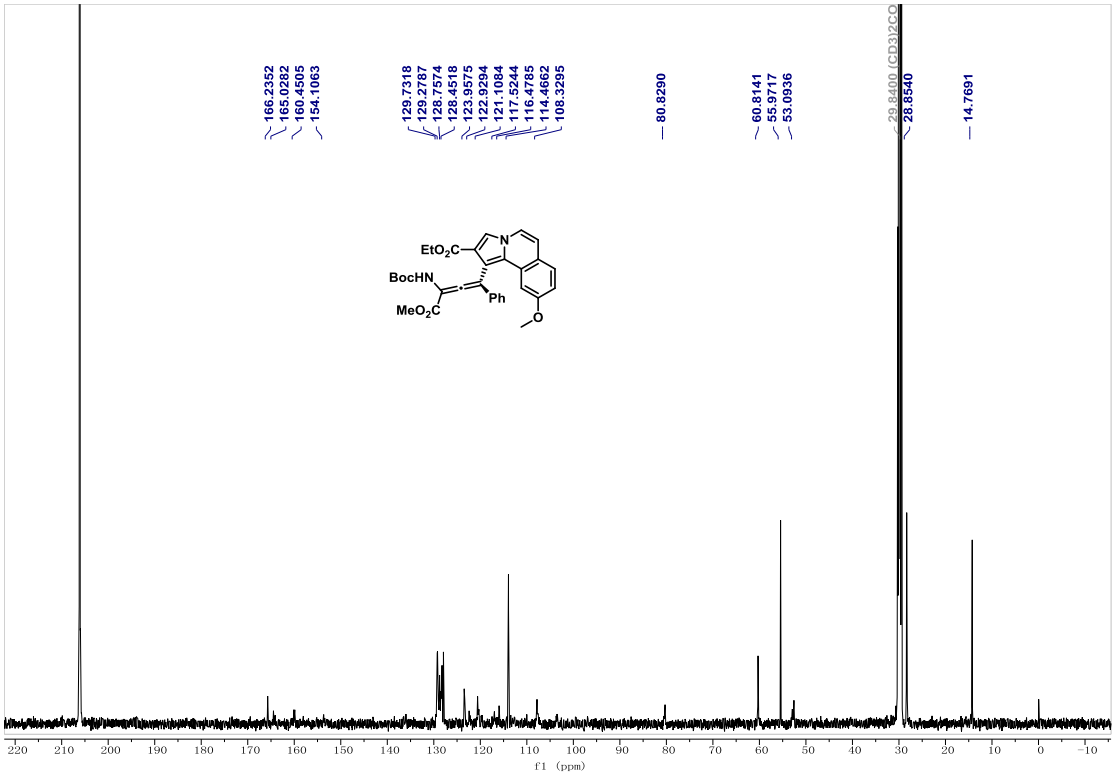


Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	16.220	15.409	17.347	4.45	4.63
2	18.492	330.757	357.104	95.55	95.37

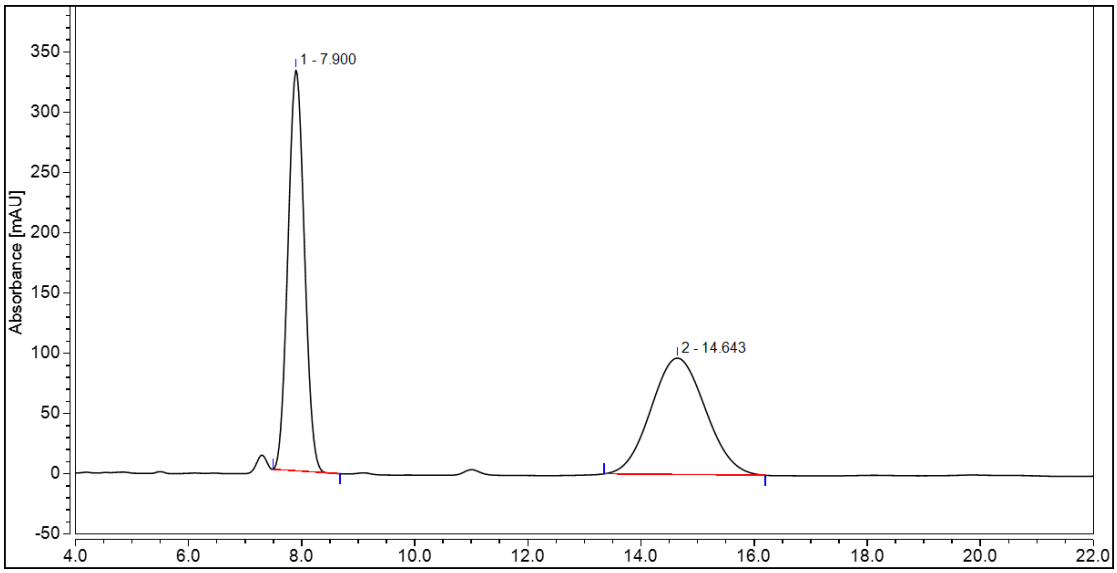
^{1}H NMR of **3w** (500 MHz, Acetone-d_6)



^{13}C NMR of **3w** (126 MHz, Acetone-d_6)

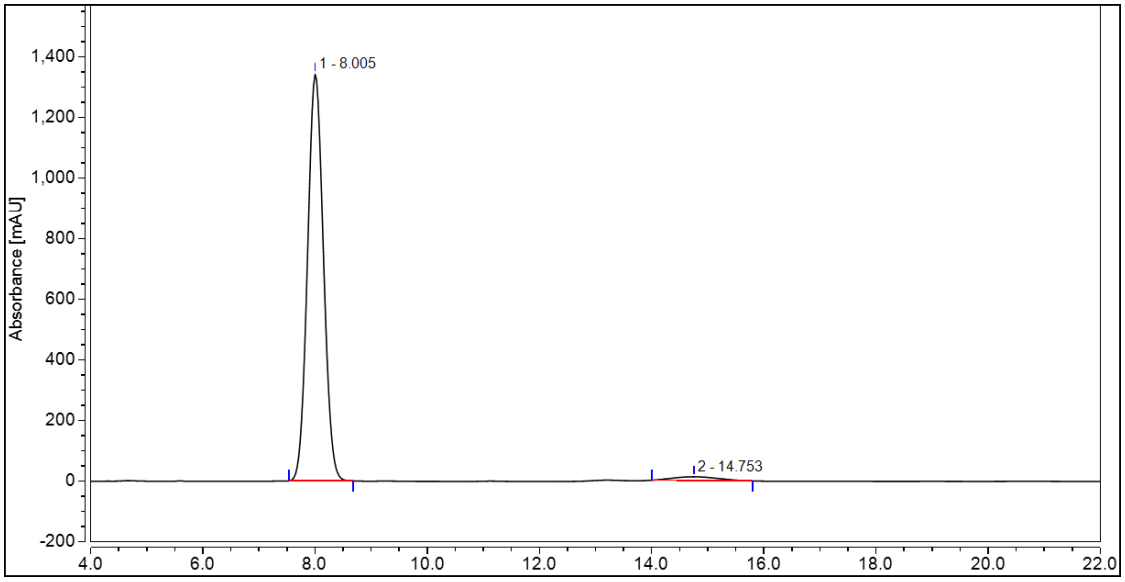


HPLC analysis: rac-**3w**



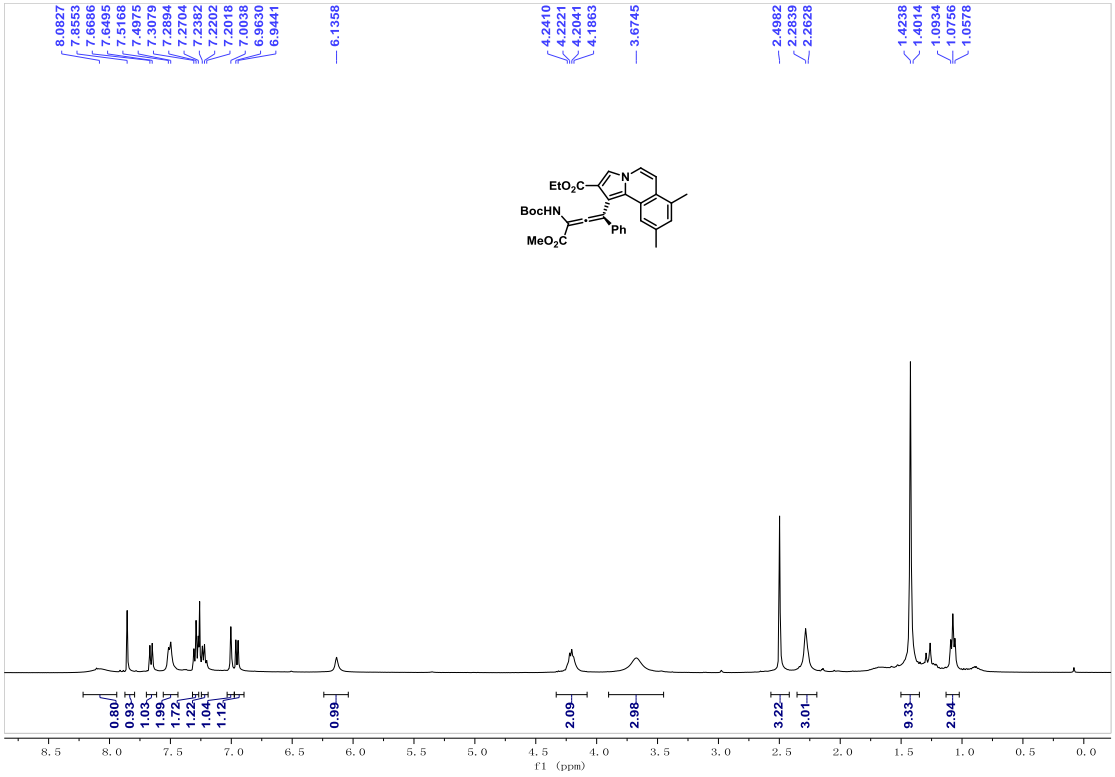
Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	7.900	111.767	332.362	50.92	77.49
2	14.643	107.726	96.532	49.08	22.51

Enantioenriched **3w**

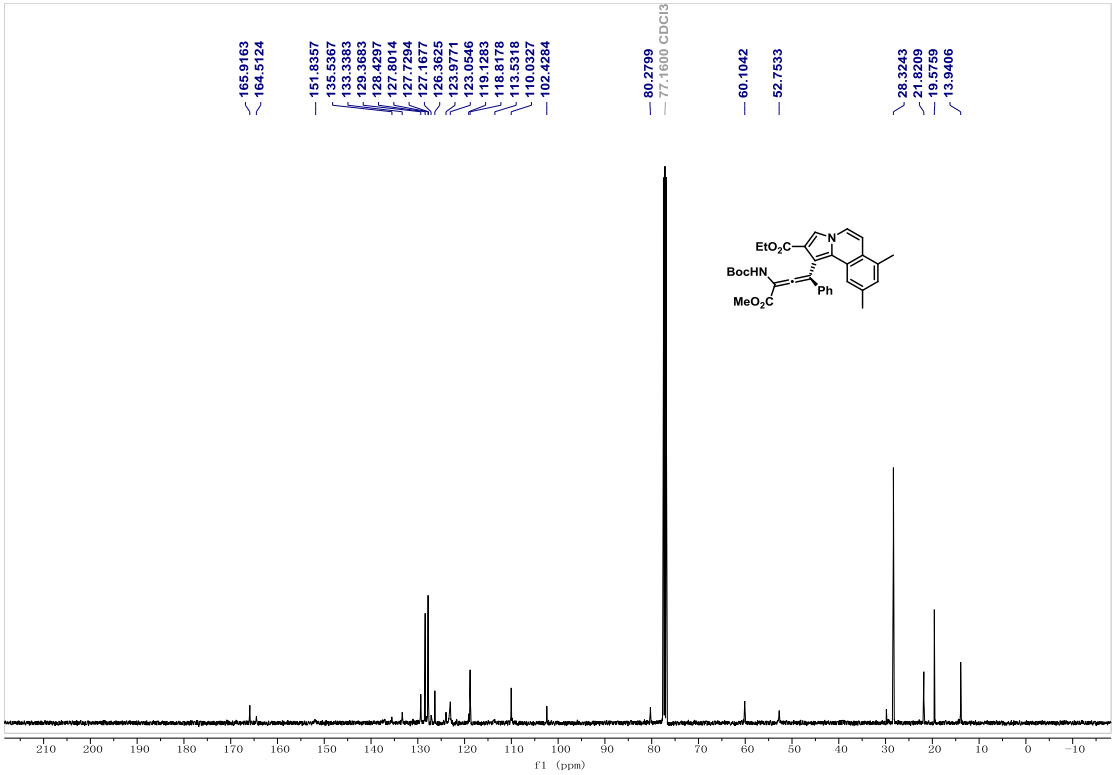


Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	8.005	441.301	1342.270	97.44	99.09
2	14.753	11.612	12.294	2.56	0.91

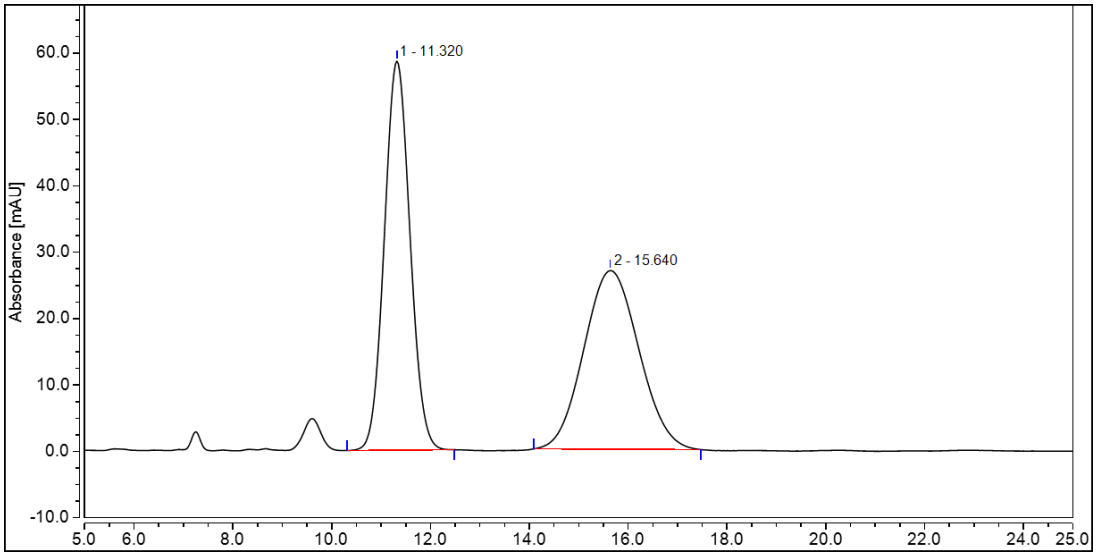
^{1}H NMR of **3x** (400 MHz, $CDCl_3$)



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

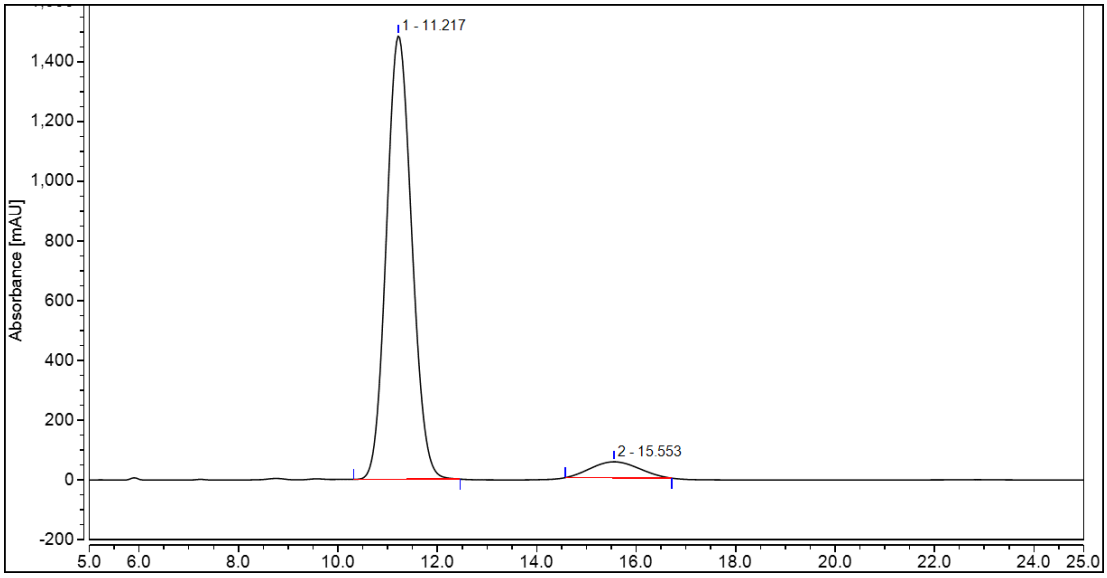


HPLC analysis: rac-**3x**



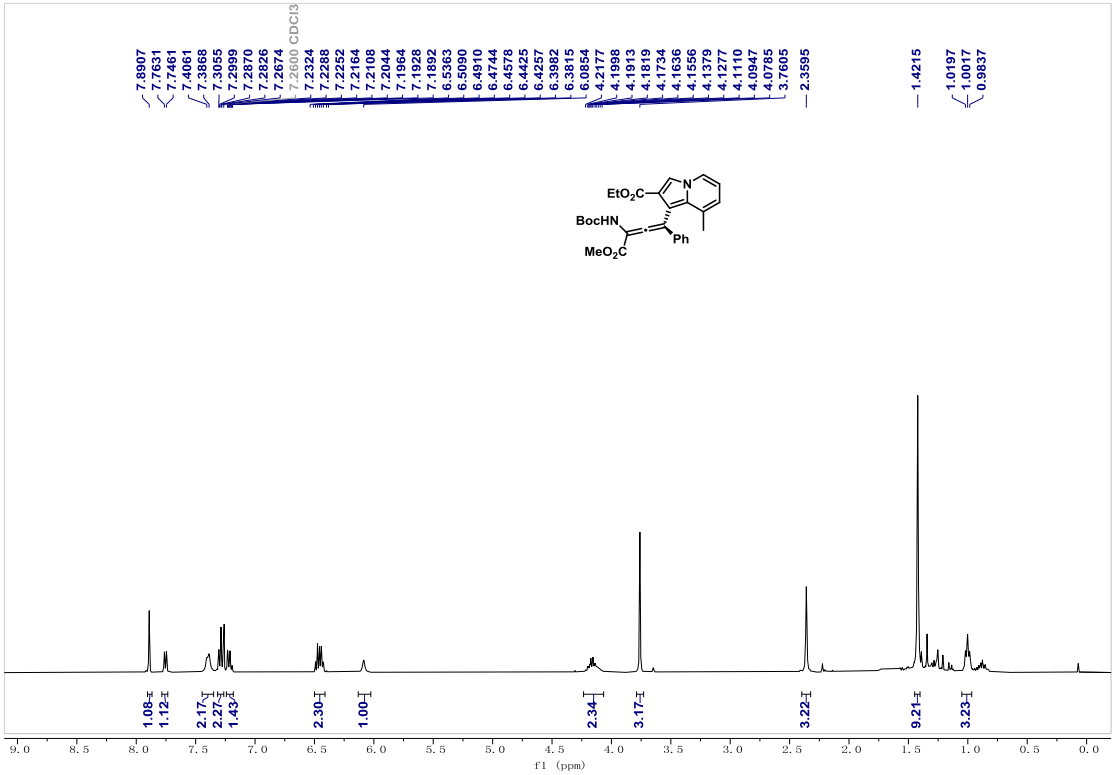
Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	11.320	35.239	58.619	50.39	68.53
2	15.640	34.696	26.913	49.61	31.47

Enantioenriched **3x**

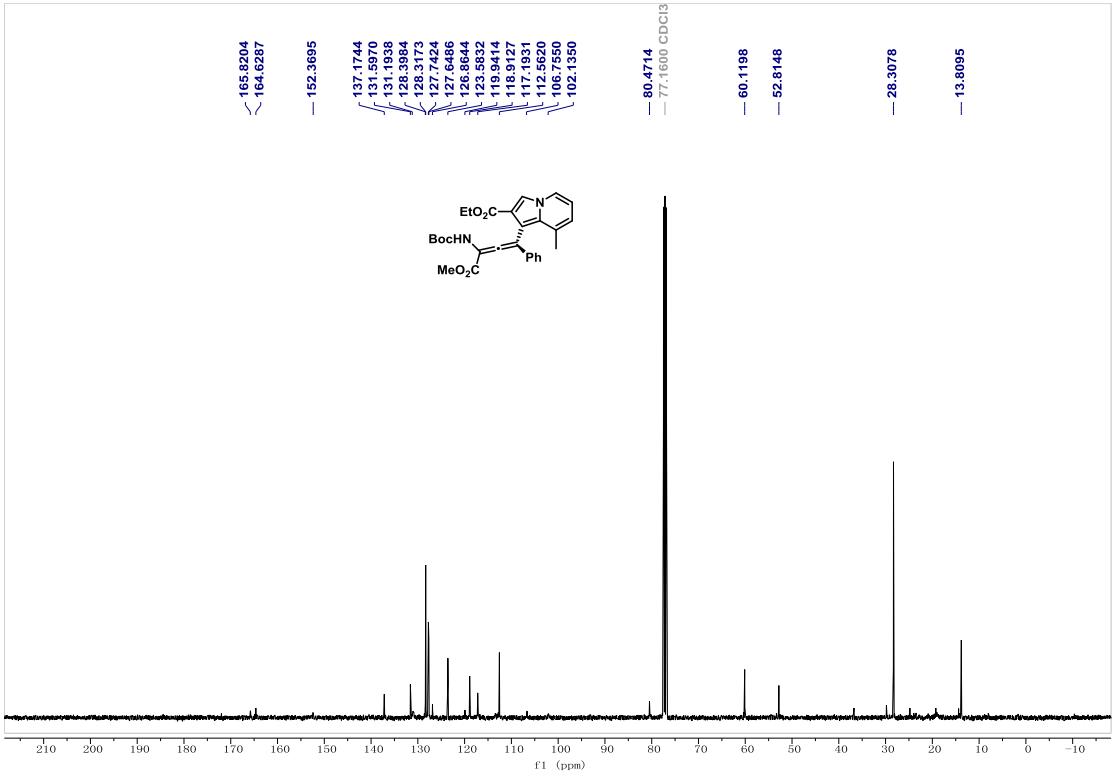


Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	11.217	876.364	1484.678	93.58	96.51
2	15.553	60.077	53.686	6.42	3.49

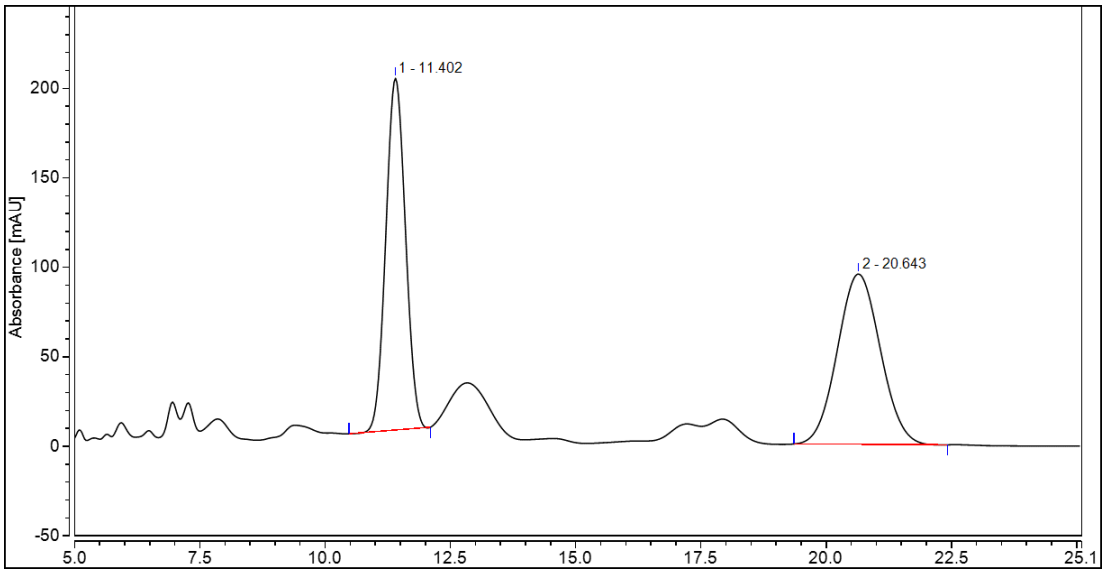
^{1}H NMR of **3y** (400 MHz, $CDCl_3$)



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

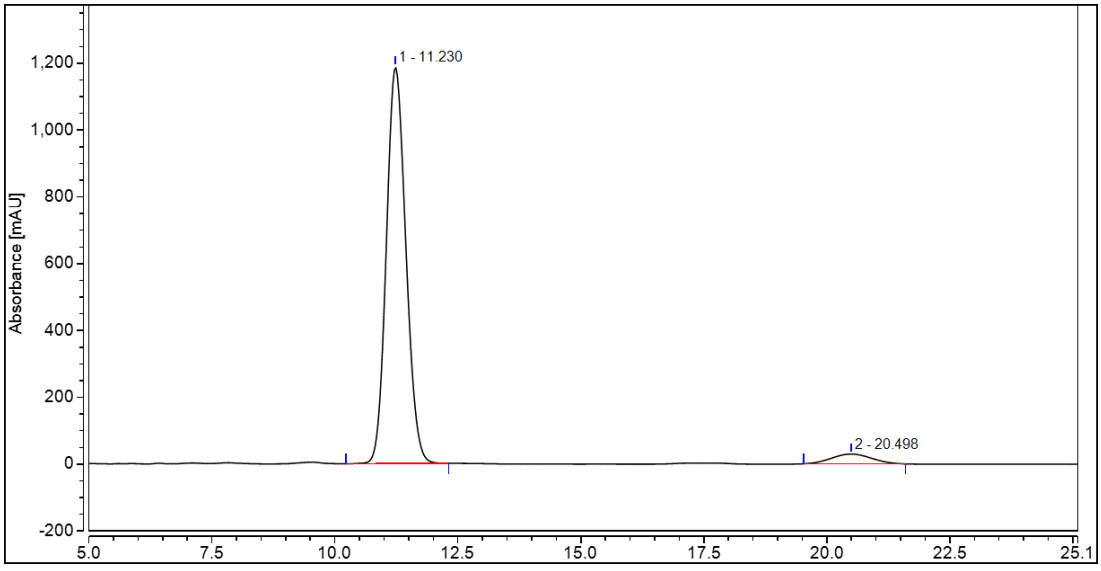


HPLC analysis: rac-**3y**



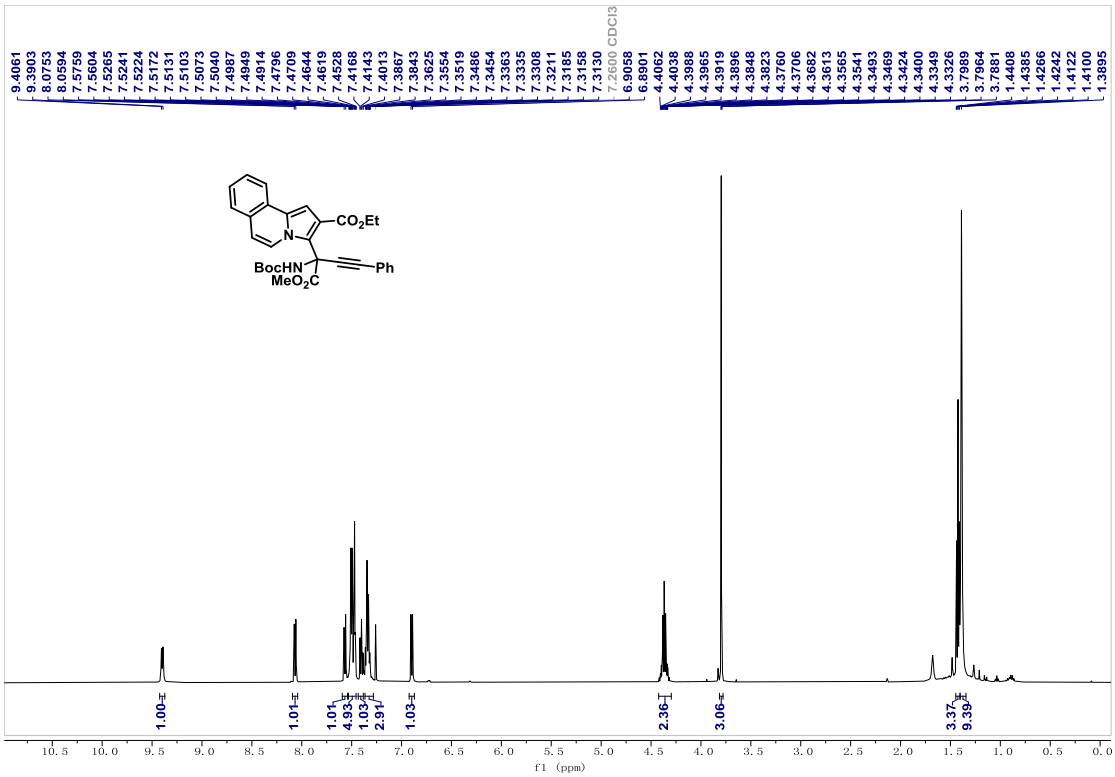
Peak	RetTime min	Area mAU*min	Height mAU	Area %	Height %
1	11.402	89.319	196.566	48.59	67.39
2	20.643	94.520	95.136	51.41	32.61

Enantioenriched **3y**

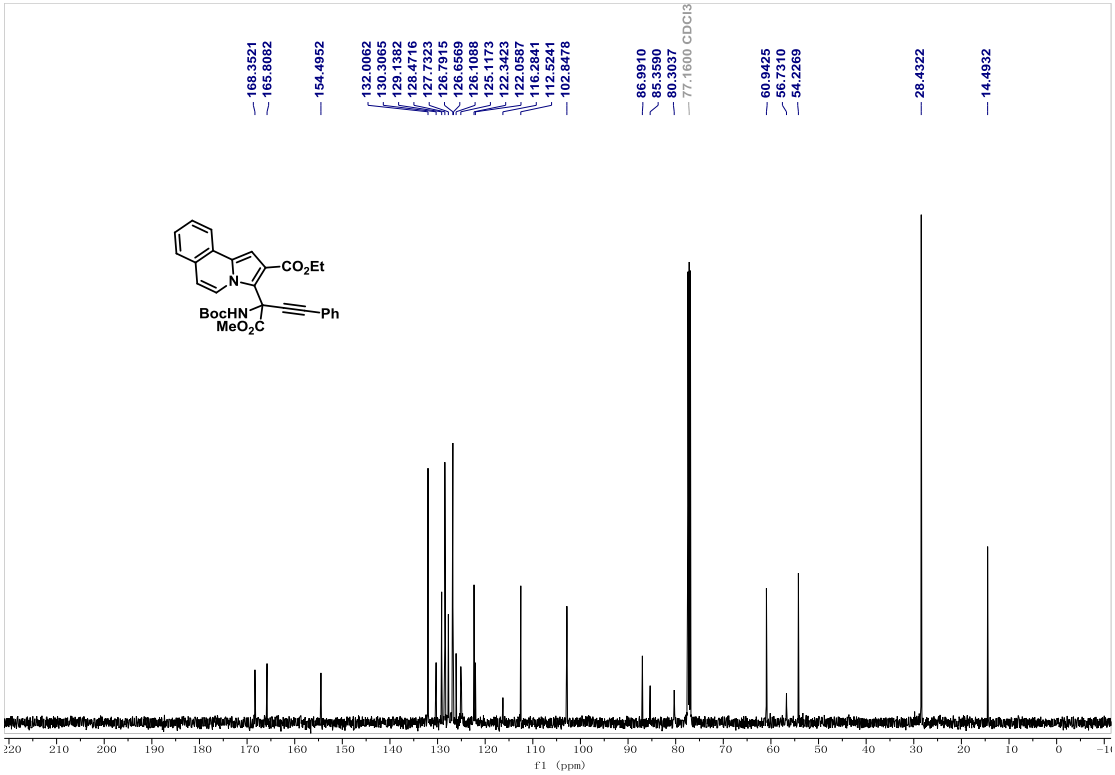


Peak	RetTime min	Area mAU*min	Height mAU	Area %	Height %
1	11.230	545.289	1186.512	95.19	97.59
2	20.498	27.582	29.285	4.81	2.41

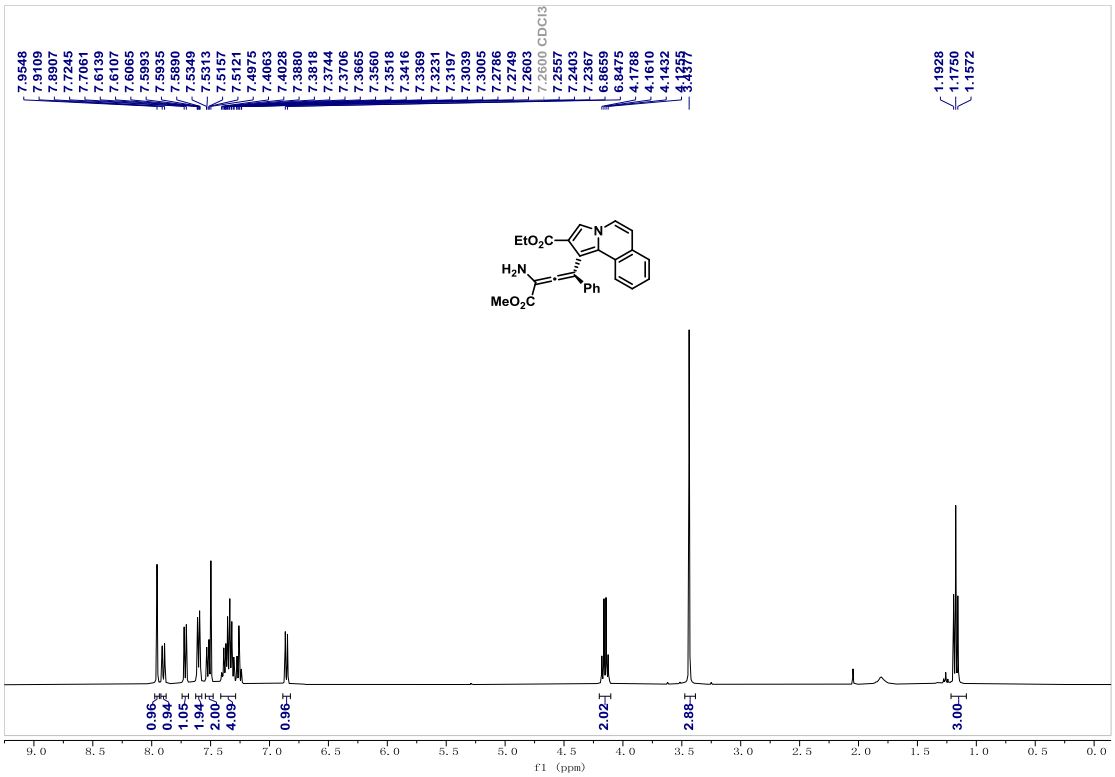
^{1}H NMR of **4a** (400 MHz, $CDCl_3$)



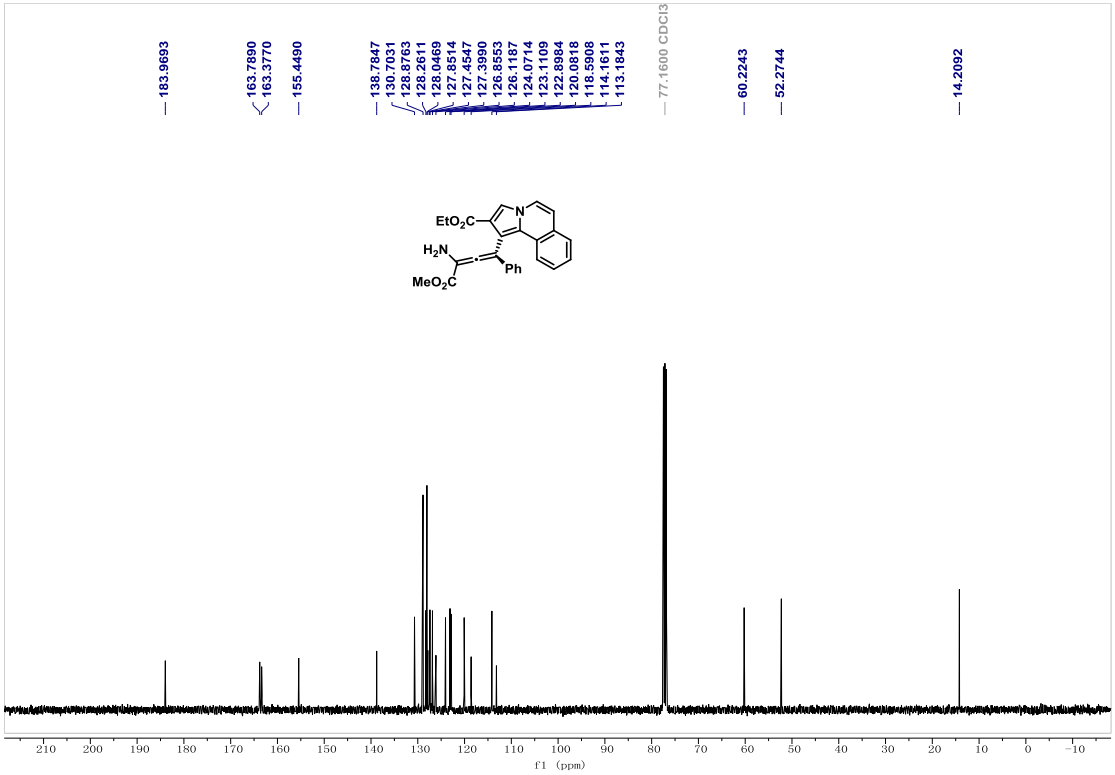
^{13}C NMR of **4a** (101 MHz, $CDCl_3$)



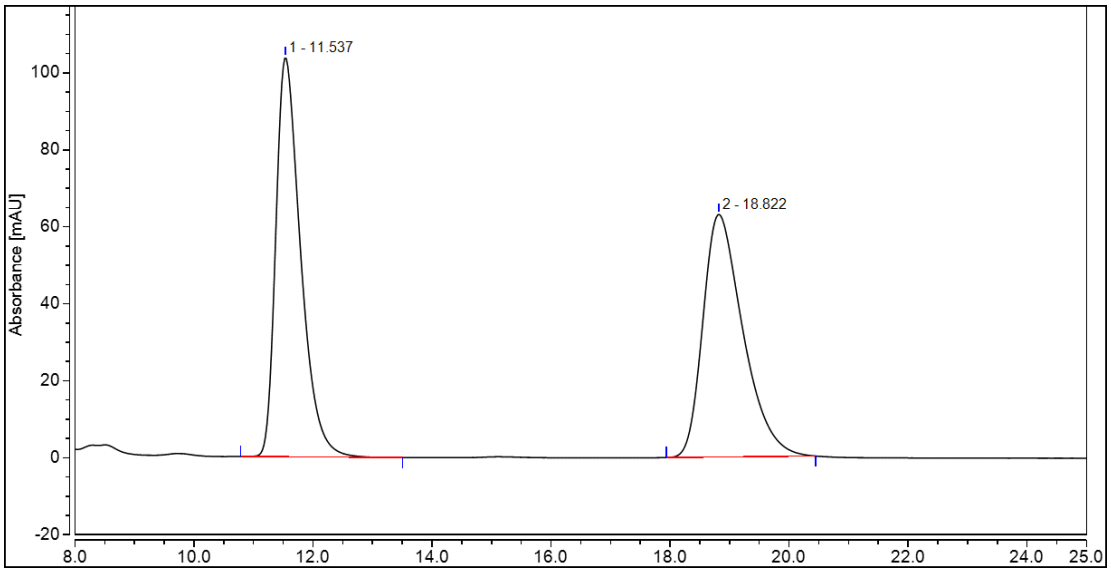
^{1}H NMR of **5** (400 MHz, $CDCl_3$)



^{13}C NMR of **5** (101 MHz, $CDCl_3$)

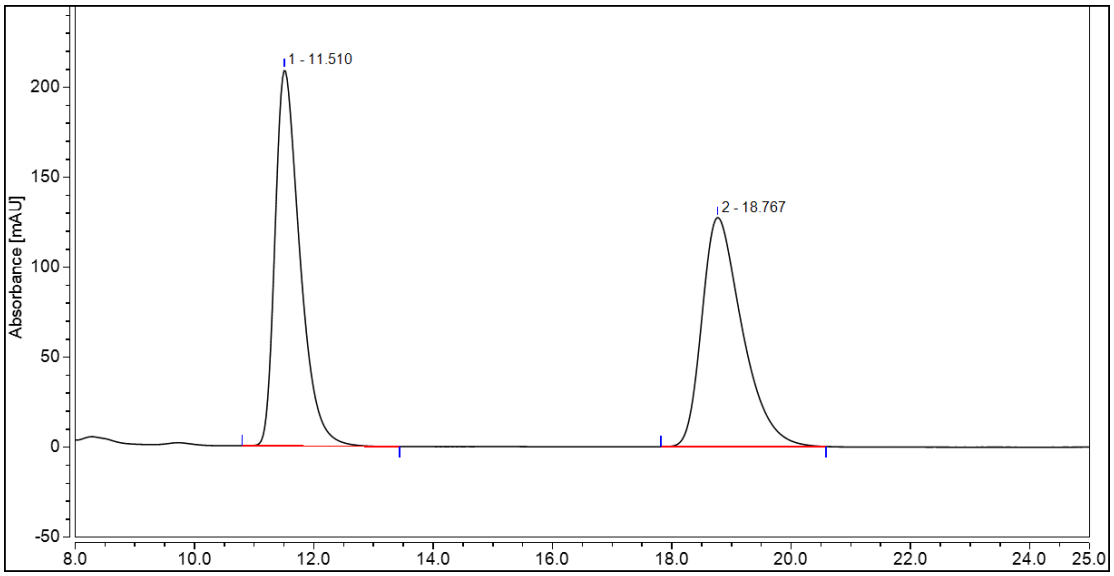


HPLC analysis: rac-**5**



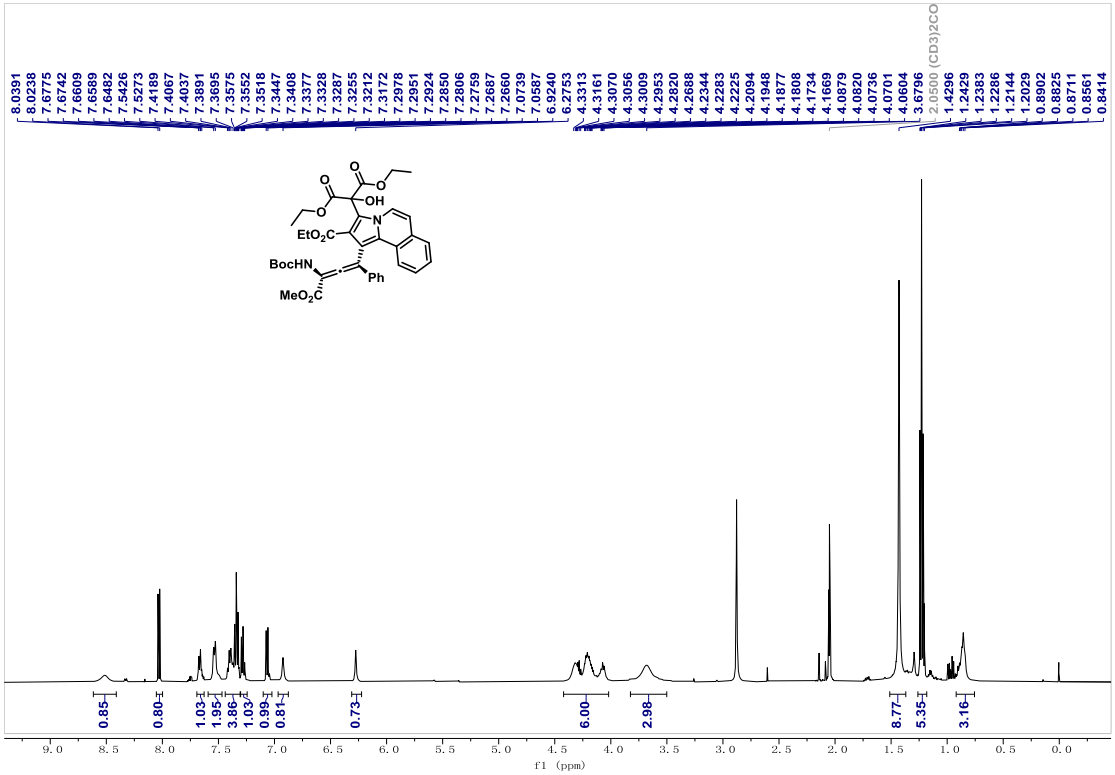
Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	11.537	50.018	103.818	50.45	62.21
2	18.822	49.123	63.066	49.55	37.79

Enantioenriched **5**

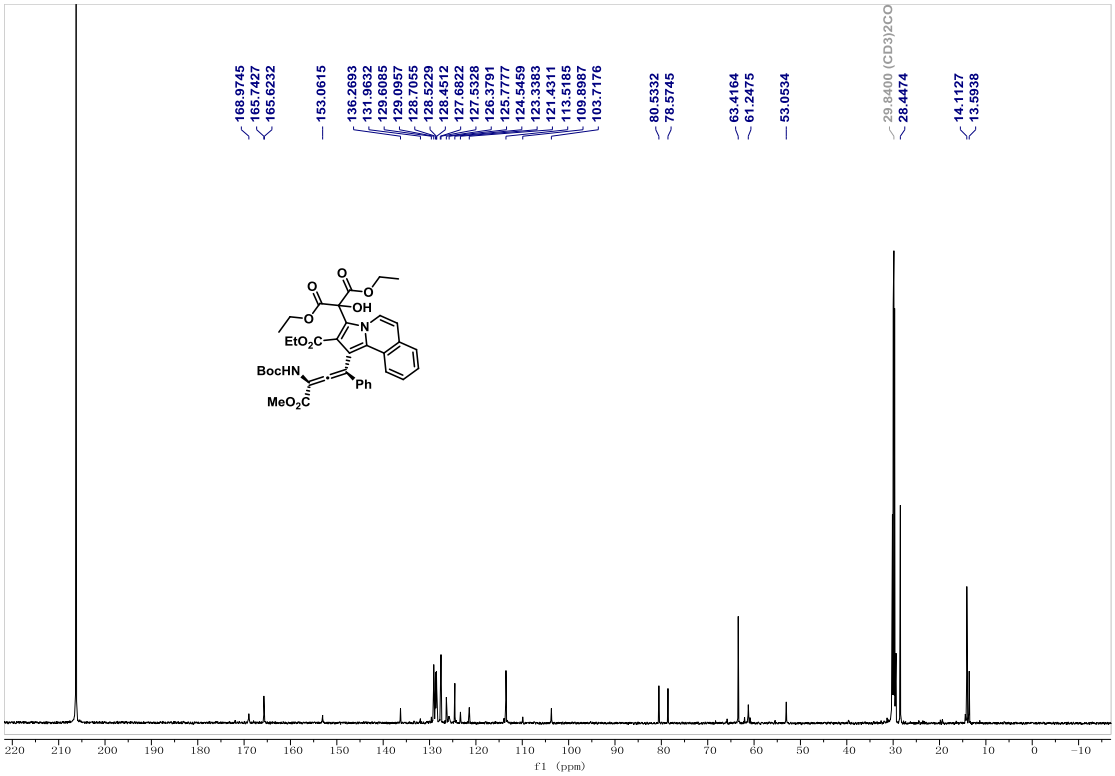


Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	11.510	100.701	208.946	50.28	62.13
2	18.767	99.587	127.340	49.72	37.87

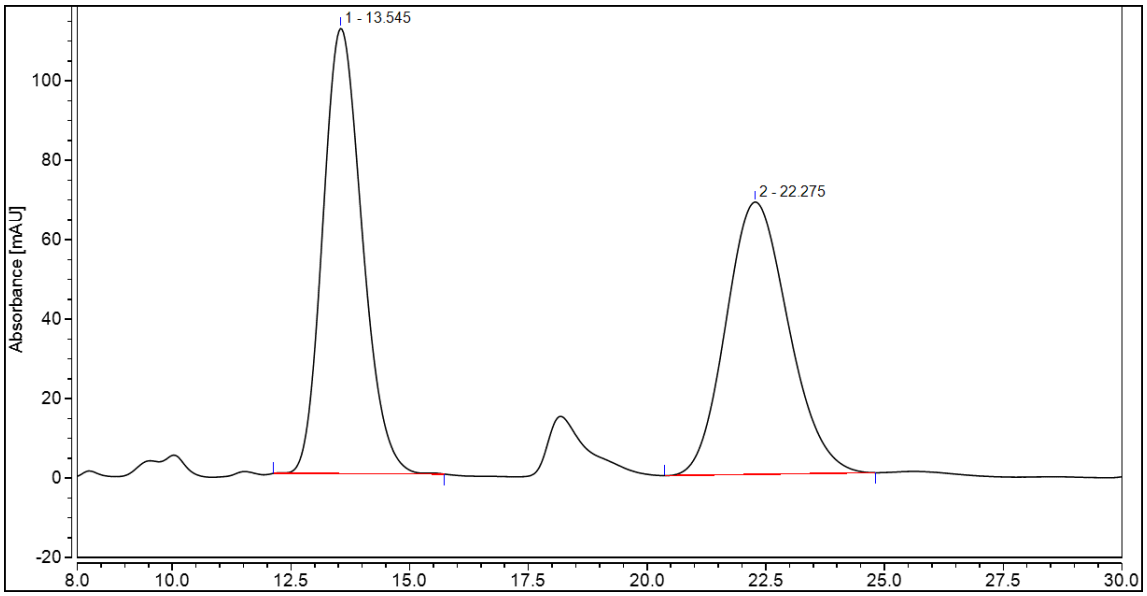
^{1}H NMR of **6** (500 MHz, Acetone-d_6)



^{13}C NMR of **6** (126 MHz, Acetone-d_6)

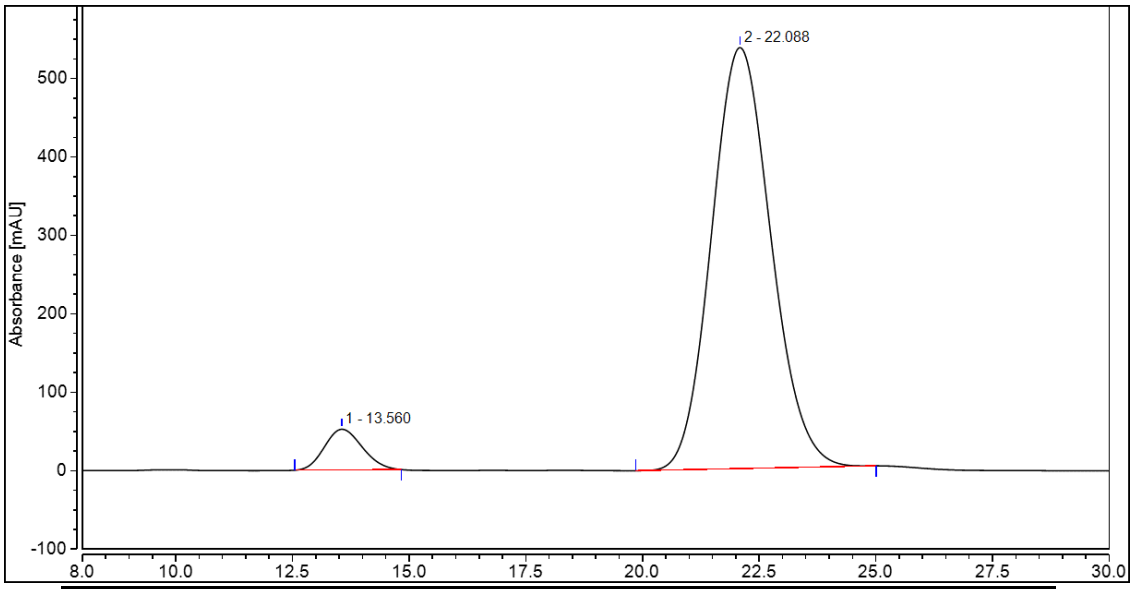


HPLC analysis: rac-**6**



Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	13.545	107.881	112.103	50.77	62.05
2	22.275	104.611	68.577	49.23	37.95

Enantioenriched **6**



Peak	RetTime	Area	Height	Area	Height
	min	mAU*min	mAU	%	%
1	13.560	48.811	51.884	5.80	8.81
2	22.088	793.170	536.914	94.20	91.19

12. Reference

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