Electronic Supplementary Material (ESI) for Chemical Communications

Catalytic asymmetric cleavage of sp^3 C-N bonds for an access to highly enantioenriched *N*-benzylic sulfonamides

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Supporting information

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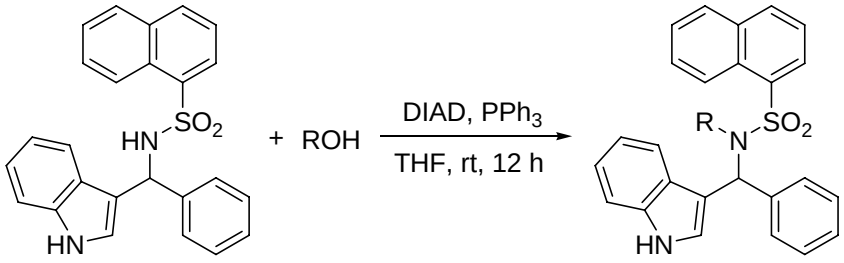
General information

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-400 FT (400 MHz and 100 MHz, respectively) using tetramethylsilane as an internal reference, and chemical shifts (δ) and coupling constants (*J*) were expressed in ppm and Hz, respectively. ^{31}P NMR spectra were recorded on a Bruker AC-400 FT (162 MHz, respectively) with complete proton decoupling, and chemical shifts are reported in ppm from H_3PO_4 resonance as the external standard. High resolution mass spectra (HRMS) were recorded on a LC-TOF spectrometer (Micromass). High pressure liquid chromatography (HPLC) analyses were performed on a Hewlett-Packard 1200 Series instrument equipped with an isostatic pump using a Daicel Chiralpak column (AS, AD, OD or IC, 250 x 4.6 mm) with isopropanol/hexanes as mobile phase, and the UV detection was monitored at 220 or 254 nm. Optical rotations were measured on a Perkin-Elmer 343 Polarimeter with a sodium lamp at λ = 589 nm and reported as $[\alpha]_D^{T\,°C}$ (*c* = g/100 mL, solvent). Melting points were uncorrected.

Racemic *N*-benzylic sulfonamides[1] and chiral phosphoric acids[2] were prepared according to known procedures. The rest of chemicals were purchased from the Sinopharm Chemical Reagent Co., Meryer, Acros, and Alfa Aesar, and used as received.

Preparation of sulfonamides 1s and 1t



1e **1s**, R = Me; **1t**, R = Pr

To a stirred solution of sulfonamide **1e** (413 mg, 1.0 mmol) and triphenylphosphine (315 mg, 1.2 mmol) in tetrahydrofuran (5.0 mL) under nitrogen were added dropwise methanol (or 1-propanol, 1.0 mmol) followed by diisopropyl azodicarboxylate (203 mg, 0.20 mL, 1.0 mmol). The mixture was stirred at room temperature for 12 h, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel, eluting with ethyl acetate/petroleum ether (1:3), to give sulfonamide **1s** (350 mg, 82%) as a white solid or sulfonamide **1t** (245 mg, 54%) as a white solid.

Kinetics studies

The reaction orders for sulfonamide **1a**, benzyl thiol, and phosphoric acid **3a** were determined by an integral method under pseudo-first-order reaction conditions (eqn (1)).[3]

General procedure: To a stirred solution of sulfonamide **1a** (37.6 mg, 0.10 mmol) in 1,2-dichloroethane (10.0 mL) under nitrogen at 25 °C were added benzyl thiol (2.0 ~ 4.0 mmol) and phosphoric acid **3a** (0.0050 ~ 0.025 mmol). The mixture was stirred at 25 °C and samples (0.10 mL) were withdrawn with a syringe at set intervals, filtered through short silica gel column (eluting with ethyl acetate) to remove the phosphoric acid, and concentrated under reduced pressure. The residues were analyzed by HPLC (hypersil column, λ = 220 nm, *n*-hexane/*i*-PrOH = 97/3, flow rate = 1.0

mL/min).

The conversion, C, was calculated using the following equation:

$$C = \frac{\text{Area } (TsNH_2)}{a \cdot \text{Area } (\mathbf{1a}) + \text{Area } (TsNH_2)} \qquad a\text{: response factor} \tag{1}$$

The rate expression for this reaction may be expressed as:

$$r = -\frac{d[\mathbf{1a}]}{dt} = k[\mathbf{1a}]^a[BnSH]^b[\mathbf{3a}]^p \tag{2}$$

Under pseudo-first-order reaction conditions, if [BnSH] >> [**1a**] and **3a** functions as catalyst, equation (2) can be expressed as:

$$r = -\frac{d[\mathbf{1a}]}{dt} = k_{obs}[\mathbf{1a}]^a \tag{3}$$

The observed rate constant (k_{obs}) is defined as:

$$k_{obs} = k[BnSH]^b[\mathbf{3a}]^p \tag{4}$$

The conversion (C) can be expressed as:

$$C = 1 - \frac{[\mathbf{1a}]_t}{[\mathbf{1a}]_o} \tag{5}$$

(a) If the reaction is zero-order for **1a**, a = 0, on integrating equation (3) yields:

$$[\mathbf{1a}]_o - [\mathbf{1a}]_t = C[\mathbf{1a}]_o = k_{obs}t \tag{6}$$

It is linearity between C and t.

(b) If the reaction is first-order for **1a**, a = 1, on integrating equation (3) yields:

$$-\ln\frac{[\mathbf{1a}]_t}{[\mathbf{1a}]_o} = -\ln(1-C) = k_{obs}t \tag{7}$$

It is linearity between -ln(1 - C) and t.

(c) If the reaction is second-order for **1a**, a = 2, on integrating equation (3) yields:

$$\frac{1}{[\mathbf{1a}]_t} - \frac{1}{[\mathbf{1a}]_o} = \frac{1}{1\text{-}C} \cdot \frac{1}{[\mathbf{1a}]_o} - \frac{1}{[\mathbf{1a}]_o} = k_{obs}t \quad (8)$$

It is linearity between 1/(1 - C) and t.

Respectively, draw curves of C – t, -ln(1 - C) – t, and 1/(1 - C) – t (Fig. 1). It is linearity between -ln(1 - C) and t, and therefore, the reaction is first-order for sulfonamide **1a**. The pseudo-first-order rate constant k_{obs} can be obtained by the linear fit of -ln(1 - C) *vs* t.

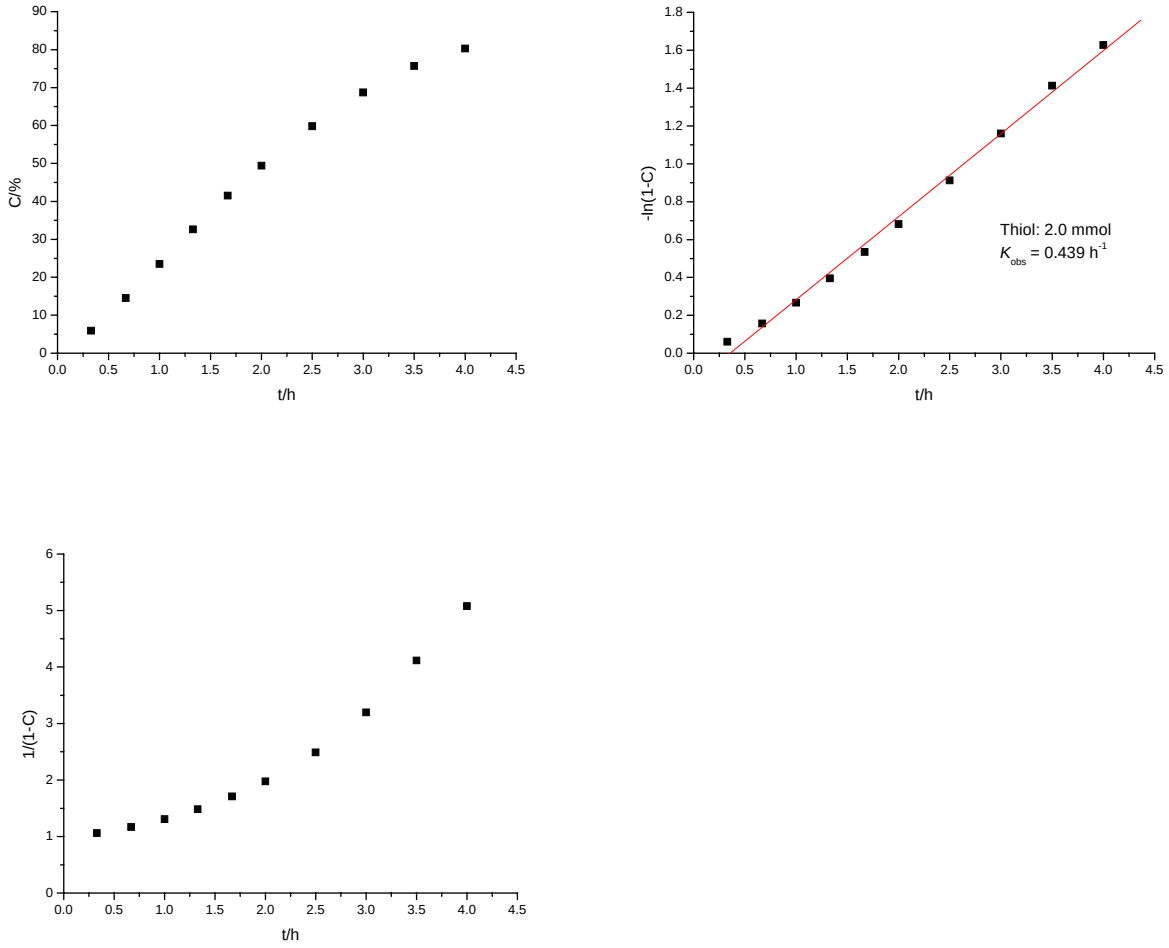


Fig. 1

Thereafter increase the amount of benzyl thiol (Table 1 and Fig. 2), the pseudo-first-order rate constant k_{obs} doesn't increase linearly or exponentially related to the amount of benzyl thiol. Therefore, the reaction is zero-order for benzyl thiol.

Table 1 Kinetic data for the reaction of sulfonamide **1a** with varying amounts of benzyl thiol in the presence of phosphoric acid **3a** at 25 °C

Entry	**1a** (mmol)	Thiol(mmol)	**3a** (mmol)	k_{obs} (h^{-1})
1	0.10	2.0	0.010	0.439
2	0.10	2.5	0.010	0.400
3	0.10	3.0	0.010	0.345
4	0.10	3.5	0.010	0.369
5	0.10	4.0	0.010	0.343

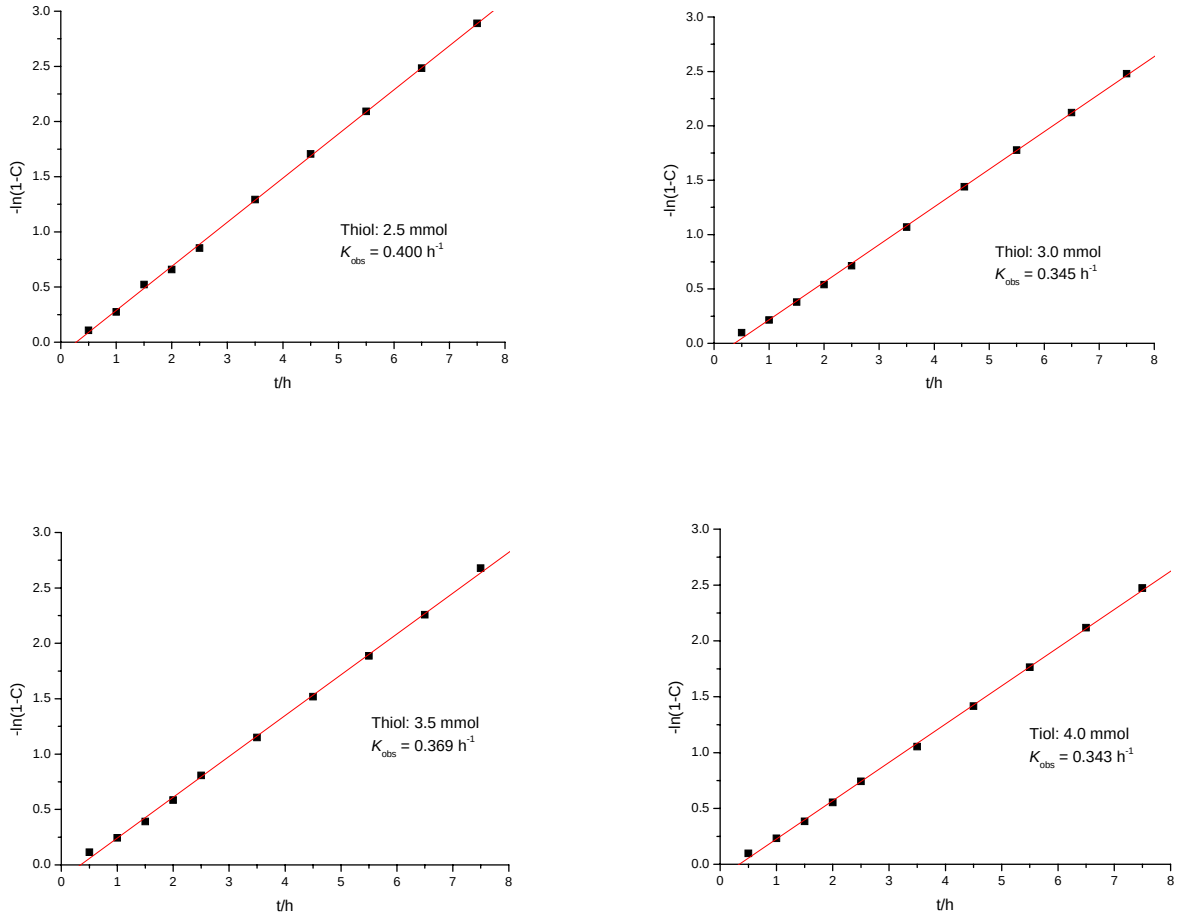


Fig. 2

Varying the amount of phosphoric acid **3a** (Table 2), the plot shows a linear relationship between the pseudo-first-order rate constants and the amounts of phosphoric acid **3a** (Fig. 3), therefore, the reaction is first-order for phosphoric acid **3a**.

Table 2 Kinetic data for the reaction of sulfonamide **1a** with benzyl thiol in the presence of varying

amounts of phosphoric acid **3a** at 25 °C

Entry	**1a** (mmol)	Thiol(mmol)	**3a** (mmol)	k_{obs} (h^{-1})
1	0.10	2.0	0.005	0.115
2	0.10	2.0	0.010	0.234
3	0.10	2.0	0.015	0.333
4	0.10	2.0	0.020	0.422
5	0.10	2.0	0.025	0.548

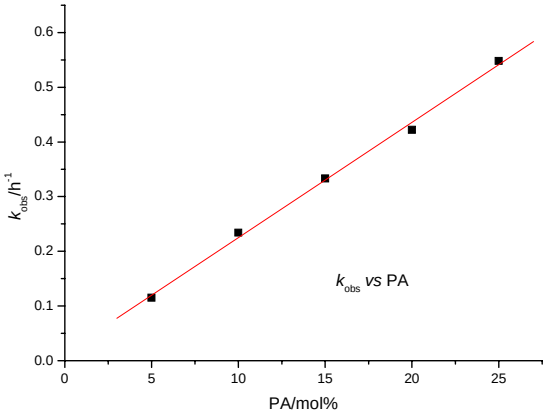


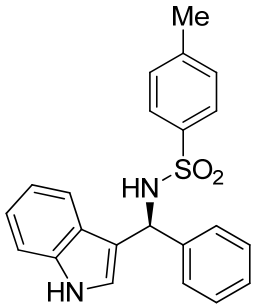
Fig. 3

In summary, the phosphoric acid **3a**-catalyzed reaction of sulfonamide **1a** with benzyl thiol catalyzed is first-order for both sulfonamide **1a** and phosphoric acid **3a**, and zero-order for benzyl thiol. The kinetics equation can be described as: rate = *k* [**1a**] [**3a**].

General procedure for the kinetic resolution of racemic *N*-benzylic sulfonamides with benzyl thiol

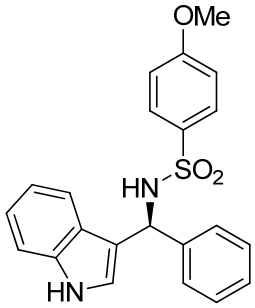
To a stirred solution of racemic sulfonamide **1** (0.10 mmol) in 1,2-dichloroethane (2-20 mL, specified in Tables 1 and 2) under nitrogen at 0 or 25 °C were added a solution of benzyl thiol in 1,2-dichloroethane (0.10 M, 0.70 mL, 0.070 mmol) and phosphoric acid **3b** (or **3c**, 0.010 mmol). The mixture was stirred at the temperature and monitored by HPLC. The mixture was quenched by saturated aqueous sodium bicarbonate (5 mL), and extracted with ethyl acetate (2 × 10 mL). The combined organic layers were washed with water and brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by preparative thin layer chromatography (TLC), eluting with ethyl acetate/petroleum ether (1:3), to recover sulfonamide **1***.

Analytical data for the products



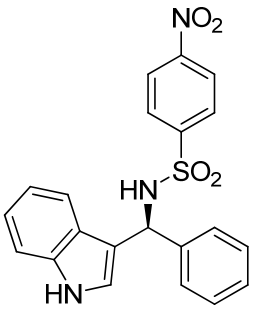
1a*

1a*,[1] white solid; m.p. 174-175 °C; $[\alpha]_D^{20}$ = -17.8° (c = 0.60, $CHCl_3$), in the literature[1a]: $[\alpha]_D^{25}$ = -17.0° (c = 1.0, $CHCl_3$, 94% ee, *S*-enantiomer); ^{1}H NMR (400 MHz, DMSO-*d*6): δ 2.28 (s, 3H), 5.77 (d, *J* = 8.8 Hz, 1H), 6.81 (s, 1H), 6.85-6.95 (m, 1H), 7.00-7.10 (m, 1H), 7.11-7.21 (m, 5H), 7.26-7.35 (m, 4H), 7.52 (d, *J* = 8.4 Hz, 2H), 8.49 (d, *J* = 8.8 Hz, 1H), 10.87 (s, 1H); ^{13}C NMR (100 MHz, DMSO-*d*6): δ 20.9, 54.5, 111.4, 115.7, 118.5, 118.9, 121.2, 123.7, 125.5, 126.4, 126.6, 127.1, 127.9, 128.9, 136.4, 138.8, 141.7, 141.8; HRMS (ESI) calcd for $C_{22}H_{20}N_2NaO_2S^+$ ($M+Na^+$) 399.1138, found 399.1127. The ee was determined to be 98% by HPLC analysis (Chiralpak OD, λ = 254 nm, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min): t_R (minor) = 10.8 min, t_R (major) = 18.0 min.



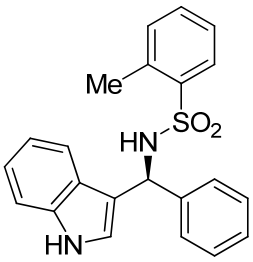
1b*

1b*, white solid; m.p. 103-104 °C; $[\alpha]_D^{20}$ = -24.6° (c = 0.62, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-*d*6): δ 3.75 (s, 3H), 5.74 (d, *J* = 8.8 Hz, 1H), 6.79 (s, 1H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.85-6.94 (m, 1H), 7.01-7.09 (m, 1H), 7.10-7.21 (m, 3H), 7.25-7.37 (m, 4H), 7.54 (d, *J* = 8.8 Hz, 2H), 8.40 (d, *J* = 8.8 Hz, 1H), 10.86 (s, 1H); ^{13}C NMR (100 MHz, DMSO-*d*6): δ 54.5, 55.5, 111.4, 113.7, 115.7, 118.5, 118.9, 121.2, 123.6, 125.5, 126.6, 127.1, 127.9, 128.4, 133.4, 136.4, 141.7, 161.6; HRMS (ESI) calcd for $C_{22}H_{20}N_2NaO_3S^+$ ($M+Na^+$) 415.1087, found 415.1073. The ee was determined to be 97% by HPLC analysis (Chiralpak IC, λ = 254 nm, *n*-hexane/*i*-PrOH = 65/35, flow rate = 1.0 mL/min): t_R (minor) = 17.3 min, t_R (major) = 23.8 min.



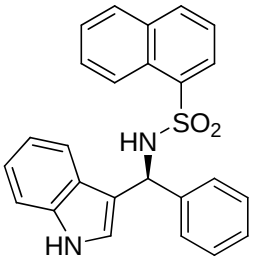
1c*

1c*,[4] yellow solid; m.p. 145-146 °C; $[\alpha]_D^{20}$ = -15.0° (c = 0.54, $CHCl_3$), in the literature[4]: $[\alpha]_D^{20}$ = -14.9° (c = 1.4, $CHCl_3$, 94% ee, *S*-enantiomer); ^{1}H NMR (400 MHz, DMSO-*d*6): δ 5.84 (d, *J* = 7.6 Hz, 1H), 6.82 (s, 1H), 6.86-6.96 (m, 1H), 6.96-7.07 (m, 1H), 7.09-7.19 (m, 3H), 7.22-7.29 (m, 3H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 9.2 Hz, 2H), 8.01 (d, *J* = 8.8 Hz, 2H), 8.95 (d, *J* = 7.6 Hz, 1H), 10.88 (s, 1H); ^{13}C NMR (100 MHz, DMSO-*d*6): δ 54.8, 111.4, 114.8, 118.6, 118.9, 121.3, 123.4, 124.1, 125.3, 126.9, 127.2, 127.7, 128.0, 136.3, 140.7, 146.9, 148.6; HRMS (ESI) calcd for $C_{21}H_{18}N_3O_4S^+$ ($M+H^+$) 408.1013, found 408.1004. The ee was determined to be 94% by HPLC analysis (Chiralpak AD, λ = 254 nm, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min): t_R (minor) = 13.6 min, t_R (major) = 23.3 min.



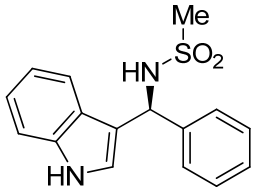
1d*

1d*,[5] white solid; m.p. 139-140 °C; $[\alpha]_D^{20}$ = -21.9° (c = 0.52, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-*d*6): δ 2.41 (s, 3H), 5.69 (d, *J* = 9.2 Hz, 1H), 6.82 (s, 1H), 6.86-6.94 (m, 1H), 7.02-7.10 (m, 1H), 7.10-7.23 (m, 5H), 7.25 (d, *J* = 6.8 Hz, 2H), 7.31-7.37 (m, 3H), 7.81 (d, *J* = 8.0 Hz, 1H), 8.65 (d, *J* = 9.2 Hz, 1H), 10.89 (s, 1H); ^{13}C NMR (100 MHz, DMSO-*d*6): δ 19.8, 54.2, 111.4, 115.6, 115.7, 118.5, 118.8, 121.2, 123.7, 125.5, 125.7, 126.7, 126.9, 127.8, 128.6, 132.0, 136.4, 136.5, 139.3, 141.6; HRMS (ESI) calcd for $C_{22}H_{20}N_2NaO_2S^+$ ($M+Na^+$) 399.1138, found 399.1127. The ee was determined to be 99% by HPLC analysis (Chiralpak AD, λ = 254 nm, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min): t_R (minor) = 11.5 min, t_R (major) = 20.4 min.



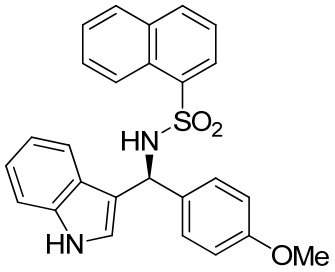
1e*

1e*, white solid; m.p. 167-168 °C; $[\alpha]_D^{20}$ = -57.9° (c = 0.62, $CHCl_3$); ^1H NMR (400 MHz, DMSO-*d*6): δ 5.74 (d, *J* = 8.8 Hz, 1H), 6.66 (s, 1H), 6.78-6.86 (m, 1H), 6.91-7.05 (m, 4H), 7.09-7.13 (m, 2H), 7.23-7.32 (m, 2H), 7.38-7.46 (m, 1H), 7.54-7.62 (m, 2H), 7.93 (d, *J* = 9.2 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 7.2 Hz, 1H), 8.68 (d, *J* = 10.0 Hz, 1H), 8.88 (d, *J* = 9.2 Hz, 1H), 10.80 (s, 1H); ^{13}C NMR (100 MHz, DMSO-*d*6): δ 54.4, 111.3, 115.5, 118.4, 118.8, 121.2, 123.7, 124.0, 125.0, 125.4, 126.4, 126.5, 126.7, 127.3, 127.4, 127.5, 128.4, 128.5, 133.3, 133.6, 136.3, 136.4, 141.2; HRMS (EI) calcd for $C_{25}H_{20}N_2O_2S$ (M) 412.1245, found 412.1284. The ee was determined to be 99% by HPLC analysis (Chiralpak IC, λ = 254 nm, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min): t_R (minor) = 10.9 min, t_R (major) = 17.6 min.



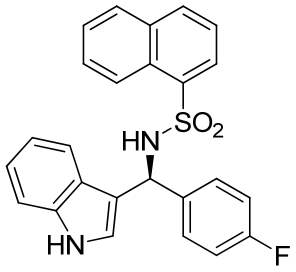
1f*

1f*, white solid; m.p. 145-146 °C; $[\alpha]_D^{20}$ = -14.1° (c = 0.60, $CHCl_3$); ^1H NMR (400 MHz, DMSO-*d*6): δ 2.59 (s, 3H), 5.87 (d, *J* = 9.2 Hz, 1H), 6.94-6.72 (m, 1H), 7.06-7.13 (m, 2H), 7.23-7.31 (m, 1H), 7.34-7.41 (m, 3H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 1H), 8.13 (d, *J* = 9.2 Hz, 1H), 11.00 (s, 1H); ^{13}C NMR (100 MHz, DMSO-*d*6): δ 41.3, 54.4, 111.6, 115.9, 118.7, 119.0, 121.4, 123.6, 125.5, 127.1, 127.2, 128.3, 136.5, 142.3; HRMS (ESI) calcd for $C_{16}H_{17}N_2O_2S^+$ ($M+H^+$) 301.1005, found 301.0999. The ee was determined to be 99% by HPLC analysis (Chiralpak IC, λ = 254 nm, *n*-hexane/*i*-PrOH = 83/17, flow rate = 1.0 mL/min): t_R (minor) = 28.7 min, t_R (major) = 24.7 min.



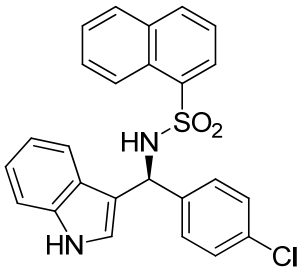
1g*

1g*, white solid; m.p. 101-102 °C; $[\alpha]_D^{20}$ = -66.4° (c = 0.50, $CHCl_3$); ^1H NMR (400 MHz, DMSO-*d*6): δ 3.60 (s, 3H), 5.68 (d, *J* = 9.2 Hz, 1H), 6.46 (d, *J* = 8.8 Hz, 2H), 6.70 (s, 1H), 6.79-6.87 (m, 1H), 6.98 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 6.8 Hz, 1H), 7.23-7.33 (m, 2H), 7.39-7.47 (m, 1H), 7.54-7.61 (m, 2H), 7.93 (d, *J* = 9.6 Hz, 1H), 8.00-8.08 (m, 2H), 8.67 (d, *J* = 10.0 Hz, 1H), 8.78 (d, *J* = 9.2 Hz, 1H), 10.79 (s, 1H); ^{13}C NMR (100 MHz, DMSO-*d*6): δ 54.0, 54.9, 111.3, 112.7, 115.8, 118.4, 118.9, 121.1, 123.6, 124.1, 125.1, 125.4, 126.4, 127.3, 127.6, 127.9, 128.4, 128.5, 133.2, 133.3, 133.6, 136.4, 136.4, 157.7; HRMS (ESI) calcd for $C_{26}H_{22}N_2NaO_3S^+$ ($M+Na^+$) 465.1243, found 465.1243. The ee was determined to be 99% by HPLC analysis (Chiralpak OD, λ = 254 nm, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min): t_R (minor) = 12.5 min, t_R (major) = 14.9 min.



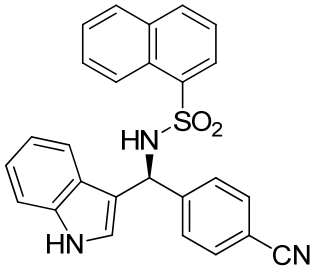
1h*

1h*, white solid; m.p. 187-188 °C; $[\alpha]_D^{20}$ = -66.2° (c = 0.65, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-*d*6): δ 5.74 (d, *J* = 9.2 Hz, 1H), 6.64-6.71 (m, 3H), 6.82-6.90 (m, 1H), 6.99-7.05 (m, 1H), 7.09 (dd, *J* = 8.8, 5.6 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.41-7.49 (m, 1H), 7.54-7.62 (m, 2H), 7.93 (d, *J* = 9.6 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 7.2 Hz, 1H), 8.65 (d, *J* = 9.6 Hz, 1H), 8.89 (d, *J* = 9.2 Hz, 1H), 10.84 (s, 1H); ^{13}C NMR (100 MHz, DMSO-*d*6): δ 53.8, 111.4, 113.9 ($^2J_{CF}$ = 21.2 Hz), 115.4, 118.5, 118.9, 121.3, 123.7, 124.1, 125.0, 125.4, 126.4, 127.3, 127.5, 128.5, 128.6, 128.7 ($^3J_{CF}$ = 8.0 Hz), 133.3, 133.6, 136.2, 136.4, 137.1 ($^4J_{CF}$ = 2.9 Hz), 160.6 ($^1J_{CF}$ = 241 Hz); HRMS (EI) calcd for $C_{25}H_{19}FN_2O_2S$ (M) 430.1151, found 430.1178. The ee was determined to be 98% by HPLC analysis (Chiralpak IC, λ = 254 nm, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min): t_R (minor) = 17.9 min, t_R (major) = 15.8 min.



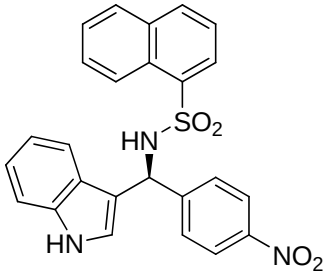
1i*

1i*, white solid; m.p. 174-175 °C; $[\alpha]_D^{20}$ = -83.2° (c = 0.68, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-*d*6): δ 5.73 (d, *J* = 9.2 Hz, 1H), 6.68 (s, 1H), 6.82-6.89 (m, 1H), 6.91 (d, *J* = 8.4 Hz, 2H), 7.00-7.06 (m, 1H), 7.08 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.41-7.49 (m, 1H), 7.55-7.62 (m, 2H), 7.94 (d, *J* = 9.2 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 8.08 (d, *J* = 7.6 Hz, 1H), 8.65 (d, *J* = 10.0 Hz, 1H), 8.92 (d, *J* = 8.8 Hz, 1H), 10.86 (s, 1H); ^{13}C NMR (100 MHz, DMSO-*d*6): δ 53.8, 111.4, 115.0, 118.6, 118.8, 121.3, 123.8, 124.1, 124.9, 125.4, 126.4, 127.2, 127.4, 127.5, 128.5, 128.7, 131.0, 133.4, 133.6, 136.1, 136.4, 140.0; HRMS (EI) calcd for $C_{25}H_{19}ClN_2O_2S$ (M) 446.0856, found 446.0890. The ee was determined to be 97% by HPLC analysis (Chiralpak IC, λ = 254 nm, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min): t_R (minor) = 18.1 min, t_R (major) = 15.3 min.



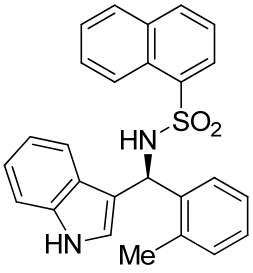
1j*

1j*, white solid; m.p. 128-129 °C; $[\alpha]_D^{20}$ = -85.5° (c = 0.60, $CHCl_3$); ^1H NMR (400 MHz, DMSO-*d*6): δ 5.81 (d, *J* = 9.2 Hz, 1H), 6.66 (s, 1H), 6.84-6.92 (m, 1H), 7.01-7.09 (m, 1H), 7.24-7.33 (m, 5H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.42-7.50 (m, 1H), 7.57-7.62 (m, 2H), 7.93 (d, *J* = 9.6 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 8.11 (d, *J* = 6.0 Hz, 1H), 8.64 (d, *J* = 10.0 Hz, 1H), 9.04 (d, *J* = 9.2 Hz, 1H), 10.92 (s, 1H); ^{13}C NMR (100 MHz, DMSO-*d*6): δ 54.1, 109.2, 111.5, 114.3, 118.6, 118.7, 118.8, 121.5, 123.8, 123.9, 124.2, 124.9, 125.3, 126.5, 127.4, 127.5, 127.6, 128.5, 128.9, 131.1, 133.5, 135.8, 136.4, 146.3; HRMS (EI) calcd for $C_{26}H_{19}N_3O_2S$ (M) 437.1198, found 437.1208. The ee was determined to be 99% by HPLC analysis (Chiralpak IC, λ = 254 nm, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min): t_R (minor) = 91.7 min, t_R (major) = 80.5 min.



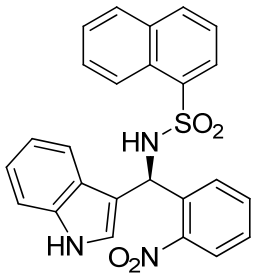
1k*

1k*, yellow solid; m.p. 202-203 °C; $[\alpha]_D^{20}$ = -91.1° (c = 0.72, $CHCl_3$); ^1H NMR (400 MHz, DMSO-*d*6): δ 5.84 (d, *J* = 8.0 Hz, 1H), 6.69 (s, 1H), 6.83-6.91 (m, 1H), 7.00-7.08 (m, 1H), 7.27-7.37 (m, 4H), 7.43-7.50 (m, 1H), 7.52-7.62 (m, 2H), 7.67 (d, *J* = 8.8 Hz, 2H), 7.87 (d, *J* = 7.6 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 8.11 (d, *J* = 7.2 Hz, 1H), 8.61 (d, *J* = 8.0 Hz, 1H), 9.07 (d, *J* = 8.8 Hz, 1H), 10.93 (s, 1H); ^{13}C NMR (100 MHz, DMSO-*d*6): δ 53.8, 111.5, 114.1, 118.7, 121.5, 122.3, 123.8, 124.0, 124.2, 124.8, 125.3, 126.5, 127.4, 127.5, 127.8, 128.4, 129.0, 133.5, 135.7, 136.2, 145.8, 148.5; HRMS (EI) calcd for $C_{25}H_{19}N_3O_4S$ (M) 457.1096, found 457.1122. The ee was determined to be 99% by HPLC analysis (Chiralpak OD, λ = 254 nm, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min): t_R (minor) = 16.8 min, t_R (major) = 19.2 min.



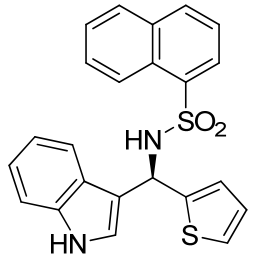
1l*

1l*, white solid; m.p. 109-110 °C; $[\alpha]_D^{20}$ = -88.1° (c = 0.54, $CHCl_3$); ^1H NMR (400 MHz, DMSO-*d*6): δ 2.06 (s, 3H), 5.97 (d, *J* = 8.8 Hz, 1H), 6.41 (s, 1H), 6.65-6.71 (m, 1H), 6.81-6.88 (m, 3H), 7.00-7.08 (m, 1H), 7.23-7.31 (m, 3H), 7.38-7.46 (m, 1H), 7.55-7.63 (m, 2H), 7.94 (d, *J* = 7.2 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 7.2 Hz, 1H), 8.73 (d, *J* = 7.6 Hz, 1H), 8.86 (d, *J* = 8.4 Hz, 1H), 10.81 (s, 1H); ^{13}C NMR (100 MHz, DMSO-*d*6): δ 18.5, 50.4, 111.5, 114.5, 118.5, 118.6, 121.3, 124.0, 124.3, 125.0, 125.1, 125.8, 126.3, 126.4, 126.5, 127.3, 127.6, 128.1, 128.6, 129.4, 133.3, 133.6, 133.7, 136.4, 139.1; HRMS (EI) calcd for $C_{26}H_{22}N_2O_2S$ (M) 426.1402, found 426.1414. The ee was determined to be 99% by HPLC analysis (Chiralpak IC, λ = 254 nm, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min): t_R (minor) = 14.4 min, t_R (major) = 17.3 min.



1m*

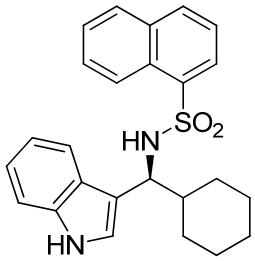
1m*, yellow solid; m.p. 177-178 °C; $[\alpha]_D^{20}$ = -107.9° (c = 0.72, $CHCl_3$); ^1H NMR (400 MHz, DMSO-*d*6): δ 6.44-6.49 (m, 2H), 6.84-6.72 (m, 1H), 7.05-7.21 (m, 3H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.44-7.51 (m, 1H), 7.57-7.65 (m, 4H), 7.95 (d, *J* = 9.2 Hz, 1H), 8.06 (d, *J* = 7.2 Hz, 2H), 8.66 (d, *J* = 9.2 Hz, 1H), 9.16 (d, *J* = 8.8 Hz, 1H), 10.94 (s, 1H); ^{13}C NMR (100 MHz, DMSO-*d*6): δ 48.9, 111.6, 113.6, 118.5, 118.8, 121.6, 123.5, 124.3, 124.4, 124.8, 125.6, 126.7, 127.4, 127.6, 127.9, 128.5, 128.7, 129.0, 132.4, 133.6, 133.7, 135.2, 135.5, 136.4, 147.1; HRMS (EI) calcd for $C_{25}H_{19}N_3O_4S$ (M) 457.1096, found 457.1114. The ee was determined to be 99% by HPLC analysis (Chiralpak IC, λ = 254 nm, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min): t_R (minor) = 10.4 min, t_R (major) = 14.5 min.



1n*

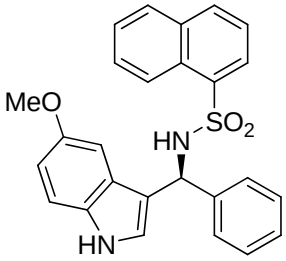
1n*, yellow solid; m.p. 85-86 °C; $[\alpha]_D^{20}$ = -84.2° (c = 0.70, $CHCl_3$); ^1H NMR (400 MHz, DMSO-*d*6): δ 6.02 (d, *J* = 8.8 Hz, 1H), 6.65-6.69 (m, 2H), 6.77-6.85 (m, 1H), 6.96-7.03 (m, 2H), 7.17 (dd, *J* = 4.4, 2.0 Hz, 1H), 7.23-7.28 (m, 2H), 7.41-7.49 (m, 1H), 7.55-7.63 (m, 2H), 7.97 (d, *J* = 9.6 Hz, 1H), 8.07 (d, *J* = 7.6 Hz, 2H), 8.69 (d, *J* = 9.6 Hz, 1H), 9.03 (d, *J* = 8.8 Hz, 1H), 10.83 (s, 1H); ^{13}C NMR (100 MHz, DMSO-*d*6): δ 49.9, 111.3, 115.1, 118.5, 118.8, 121.1, 123.6, 124.1, 124.9, 125.0, 125.1, 126.0, 126.5, 127.4, 127.6, 128.3, 128.6, 133.4, 133.6, 136.1, 136.4, 146.8; HRMS (ESI) calcd for $C_{23}H_{18}N_2NaO_2S_2^+$ ($M+Na^+$) 441.0702, found 441.0700. The ee was determined to be 92% by HPLC analysis (Chiralpak IC, λ = 254 nm, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0

mL/min): t_R (minor) = 31.0 min, t_R (major) = 33.6 min.



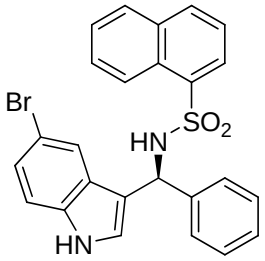
1o*

1o*, white solid; m.p. 89-90 °C; $[\alpha]_D^{20}$ = -223.3° (c = 0.62, $CHCl_3$); ^1H NMR (400 MHz, DMSO-*d*6): δ 0.67-0.71 (m, 2H), 0.87-1.03 (m, 3H), 1.21-1.26 (m, 1H), 1.38-1.56 (m, 3H), 1.61-1.71 (m, 1H), 1.77-1.84 (m, 1H), 4.31 (m, 1H), 6.73-6.81 (m, 1H), 6.88-6.94 (m, 2H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.22-7.30 (m, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.48-7.57 (m, 2H), 7.84-7.91 (m, 3H), 8.18 (d, *J* = 8.8 Hz, 1H), 8.65 (d, *J* = 8.0 Hz, 1H), 10.52 (s, 1H); ^{13}C NMR (100 MHz, DMSO-*d*6): δ 25.4, 25.9, 29.5, 42.4, 55.9, 110.9, 114.4, 118.1, 118.6, 120.5, 123.0, 123.8, 125.0, 125.6, 126.2, 127.0, 127.5, 127.9, 128.4, 132.8, 133.4, 135.7, 136.7; HRMS (EI) calcd for $C_{25}H_{26}N_2O_2S$ (M) 418.1715, found 418.1686. The ee was determined to be 90% by HPLC analysis (Chiralpak OD, λ = 254 nm, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min): t_R (minor) = 11.3 min, t_R (major) = 17.7 min.



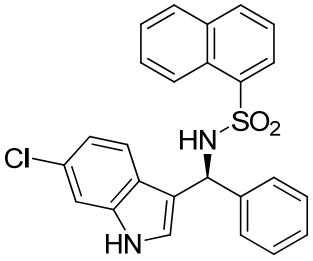
1p*

1p*, white solid; m.p. 91-92 °C; $[\alpha]_D^{20}$ = -75.7° (c = 0.50, $CHCl_3$); ^1H NMR (400 MHz, DMSO-*d*6): δ 3.58 (s, 3H), 5.73 (d, *J* = 8.8 Hz, 1H), 6.62 (s, 1H), 6.66 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.87 (d, *J* = 2.4 Hz, 1H), 6.93-6.98 (m, 3H), 7.11-7.17 (m, 3H), 7.37-7.45 (m, 1H), 7.53-7.62 (m, 2H), 7.91 (d, *J* = 7.6 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 7.6 Hz, 1H), 8.67 (d, *J* = 8.4 Hz, 1H), 8.86 (d, *J* = 9.6 Hz, 1H), 10.65 (s, 1H); ^{13}C NMR (100 MHz, DMSO-*d*6): δ 54.4, 55.2, 100.9, 111.2, 112.0, 115.2, 124.0, 124.4, 125.0, 125.8, 126.4, 126.8, 127.3, 127.4, 127.5, 128.3, 128.5, 131.4, 133.3, 133.6, 136.5, 141.2, 152.9; HRMS (EI) calcd for $C_{26}H_{22}N_2O_3S$ (M) 442.1351, found 442.1352. The ee was determined to be 99% by HPLC analysis (Chiralpak IC, λ = 254 nm, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min): t_R (minor) = 15.7 min, t_R (major) = 19.9 min.



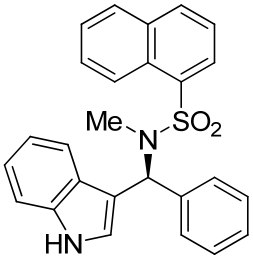
1q*

1q*, white solid; m.p. 193-194 °C; $[\alpha]_D^{20}$ = -13.3° (c = 0.68, $CHCl_3$); ^1H NMR (400 MHz, DMSO-*d*6): δ 5.73 (d, *J* = 9.2 Hz, 1H), 6.72 (s, 1H), 6.94-7.01 (m, 3H), 7.08-7.14 (m, 3H), 7.22 (d, *J* = 8.8 Hz, 1H), 7.40-7.47 (m, 2H), 7.52-7.61 (m, 2H), 7.91 (d, *J* = 7.6 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 8.05 (d, *J* = 7.6 Hz, 1H), 8.65 (d, *J* = 8.0 Hz, 1H), 8.90 (d, *J* = 9.2 Hz, 1H), 11.00 (s, 1H); ^{13}C NMR (100 MHz, DMSO-*d*6): δ 54.0, 111.3, 113.4, 115.2, 121.2, 123.7, 124.0, 124.9, 125.5, 126.4, 126.6, 126.7, 127.1, 127.3, 127.4, 127.5, 128.5, 128.6, 133.4, 133.5, 135.0, 136.1, 140.8; HRMS (EI) calcd for $C_{25}H_{19}BrN_2O_2S$ (M) 490.0351, found 490.0403. The ee was determined to be 99% by HPLC analysis (Chiralpak IC, λ = 254 nm, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min): t_R (minor) = 12.7 min, t_R (major) = 15.5 min.



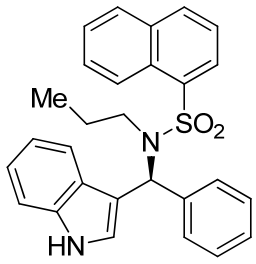
1r*

1r*, white solid; m.p. 198-199 °C; $[\alpha]_D^{20}$ = -46.9° (c = 0.62, $CHCl_3$); ^1H NMR (400 MHz, DMSO-*d*6): δ 5.73 (d, *J* = 9.2 Hz, 1H), 6.71 (s, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.92-7.00 (m, 3H), 7.09-7.12 (m, 2H), 7.26 (d, *J* = 8.4 Hz, 1H), 7.31 (s, 1H), 7.38-7.47 (m, 1H), 7.53-7.61 (m, 2H), 7.92 (d, *J* = 9.6 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 7.2 Hz, 1H), 8.66 (d, *J* = 9.6 Hz, 1H), 8.91 (d, *J* = 9.2 Hz, 1H), 10.93 (s, 1H); ^{13}C NMR (100 MHz, DMSO-*d*6): δ 54.2, 111.0, 115.8, 118.8, 120.2, 124.0, 124.2, 124.9, 125.0, 126.0, 126.4, 126.6, 126.8, 127.3, 127.4, 127.5, 128.4, 128.5, 133.3, 133.5, 136.2, 136.7, 140.8; HRMS (ESI) calcd for $C_{25}H_{19}ClN_2NaO_2S^+$ ($M+Na^+$) 469.0748, found 469.0742. The ee was determined to be 99% by HPLC analysis (Chiralpak IC, λ = 254 nm, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min): t_R (minor) = 21.0 min, t_R (major) = 18.6 min.



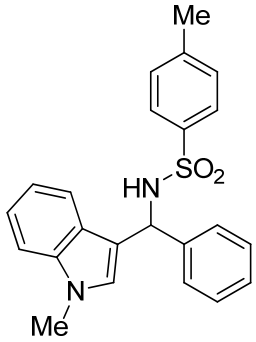
1s*

1s*, white solid; m.p. 79-80 °C; $[\alpha]_D^{20}$ = -26.6° (c = 0.62, $CHCl_3$); ^1H NMR (400 MHz, DMSO-*d*6): δ 2.74 (s, 3H), 6.64 (s, 1H), 6.78-6.86 (m, 1H), 6.88 (s, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 7.02-7.09 (m, 1H), 7.16-7.26 (m, 5H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.53-7.64 (m, 3H), 8.06 (d, *J* = 8.0 Hz, 1H), 8.13 (d, *J* = 7.2 Hz, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 8.61 (d, *J* = 8.4 Hz, 1H), 11.10 (s, 1H); ^{13}C NMR (100 MHz, DMSO-*d*6): δ 31.0, 57.4, 111.6, 111.7, 118.8, 121.3, 124.4, 124.7, 125.7, 125.9, 126.0, 126.8, 127.2, 127.6, 127.7, 127.8, 128.1, 128.9, 129.6, 133.9, 134.1, 134.6, 136.3, 139.3; HRMS (ESI) calcd for $C_{26}H_{22}N_2NaO_2S^+$ ($M+Na^+$) 449.1294, found 449.1292. The ee was determined to be 98% by HPLC analysis (Chiralpak OD, λ = 254 nm, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min): t_R (minor) = 16.5 min, t_R (major) = 9.6 min.



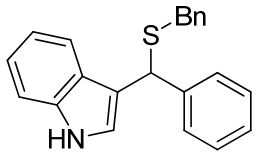
1t*

1t*, white solid; m.p. 85-86 °C; $[\alpha]_D^{20}$ = -40.2° (c = 0.70, $CHCl_3$); ^1H NMR (400 MHz, DMSO-*d*6): δ 0.33 (t, *J* = 7.4 Hz, 3H), 0.70-0.92 (m, 2H), 3.29-3.34 (m, 2 H), 6.63 (s, 1H), 6.81-6.88 (m, 1H), 6.93 (s, 1H), 7.02-7.07 (m, 2H), 7.13-7.21 (m, 5H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.47-7.56 (m, 1H), 7.59-7.68 (m, 2H), 8.03 (d, *J* = 7.6 Hz, 1H), 8.16 (d, *J* = 7.6 Hz, 2H), 8.73 (d, *J* = 8.0 Hz, 1H), 11.04 (s, 1H); ^{13}C NMR (100 MHz, DMSO-*d*6): δ 10.9, 23.0, 47.3, 58.1, 111.6, 112.3, 118.7, 118.8, 121.3, 124.3, 124.8, 125.7, 126.1, 126.8, 127.1, 127.7, 127.8, 127.9, 128.0, 128.9, 129.5, 133.8, 134.0, 135.5, 136.2, 139.9; HRMS (ESI) calcd for $C_{28}H_{26}N_2NaO_2S^+$ ($M+Na^+$) 477.1607, found 477.1595. The ee was determined to be 99% by HPLC analysis (Chiralpak OD, λ = 254 nm, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min): t_R (minor) = 11.8 min, t_R (major) = 20.0 min.



1u

1u,[6] white solid; m.p. 171-172 °C; ^1H NMR (400 MHz, DMSO-*d*6): δ 2.28 (s, 3H), 3.62 (s, 3H), 5.74 (d, *J* = 8.8 Hz, 1H), 6.73 (s, 1H), 6.89-6.97 (m, 1H), 7.07-7.21 (m, 6H), 7.25-7.36 (m, 4H), 7.47 (d, *J* = 8.4 Hz, 2H), 8.47 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-*d*6): δ 20.8, 32.2, 54.3, 109.6, 114.8, 118.6, 119.1, 121.3, 125.8, 126.4, 126.6, 127.0, 127.9, 128.0, 128.8, 136.7, 138.7, 141.4, 141.8; The ee was determined to be 15% by HPLC analysis (Chiralpak OD, λ = 254 nm, *n*-hexane/*i*-PrOH = 85/15, flow rate = 1.0 mL/min): t_R (minor) = 9.9 min, t_R (major) = 16.5 min.



2a

2a, yellow solid; m.p. 88-89 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.54-3.65 (m, 2H), 5.21 (s, 1H), 6.98 (s, 1H), 7.01-7.07 (m, 1H), 7.12-7.33 (m, 10H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.90 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 36.9, 45.6, 111.5, 116.8, 119.9, 120.0, 122.6, 123.7, 126.6, 127.2, 127.4, 128.7, 128.8, 128.9, 129.4, 136.8, 138.7, 141.8; HRMS (ESI) calcd for $C_{22}H_{19}NNaS^{+}$ ($M+Na^{+}$) 352.1130, found 352.1130.

References

1 (*a*) Y.-Q. Wang, J. Song, R. Hong, H. Li and L. Deng, *J. Am. Chem. Soc*., 2006, **128**, 8156; (*b*) Q. Kang, Z.-A. Zhao and S.-L. You, *J. Am. Chem. Soc*., 2007, **129**, 1484; (*c*) F.-L. Sun, X.-J. Zheng, Q. Gu, Q.-L. He and S.-L. You, *Eur. J. Org. Chem*., 2010, 45.

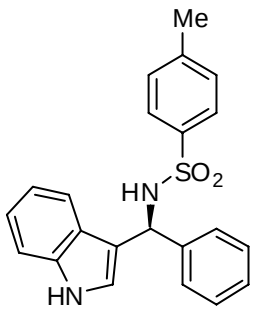
2 (*a*) J. Jacques and C. Fouquey, *Org. Synth.*, 1989, **67**, 1; (*b*) D. Uraguchi and M. Terada, *J. Am. Chem. Soc.*, 2004, **126**, 5356.

3 For examples, see: (*a*) M.-L. Wang, W.-H. Chen and F.-S. Wang, *J. Mol. Catal. A: Chem.*, 2005, **236**, 65; (*b*) M.-L. Wang and V. Rajendran, *J. Mol. Catal. A: Chem.*, 2006, **244**, 237.

4 Y.-X. Jia, J.-H. Xie, H.-F. Duan, L.-X. Wang and Q.-L. Zhou, *Org. Lett*., 2006, **8**, 1621.

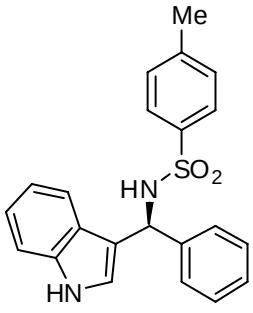
5 Y. Qian, G. Ma, A. Lv, H.-L. Zhu, J. Zhao and V. H. Rawal, *Chem. Commun*., 2010, **46**, 3004.

6 I. Alonso, J. Esquivias, R. G. Arrayás and J. C. Carretero, *J. Org. Chem.*, 2008, **73**, 6401.



1a*

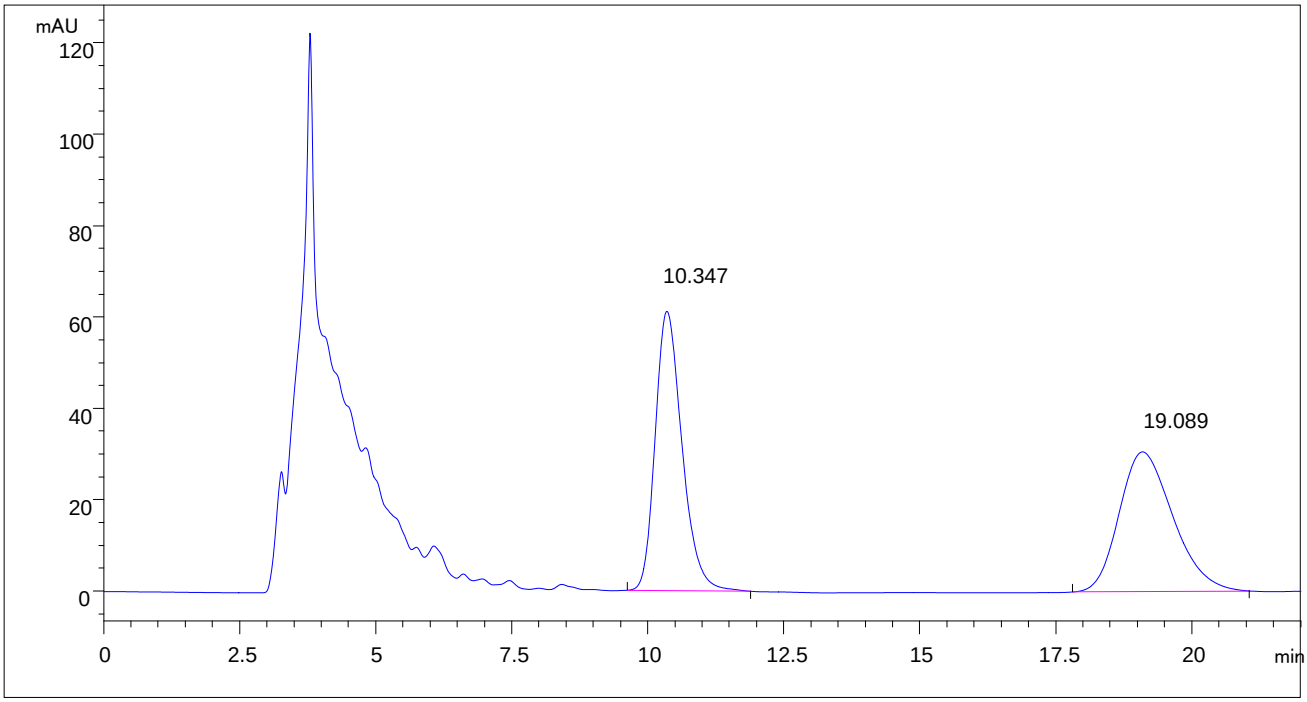
^{1}H NMR (400 MHz, DMSO-*d6*)



1a*

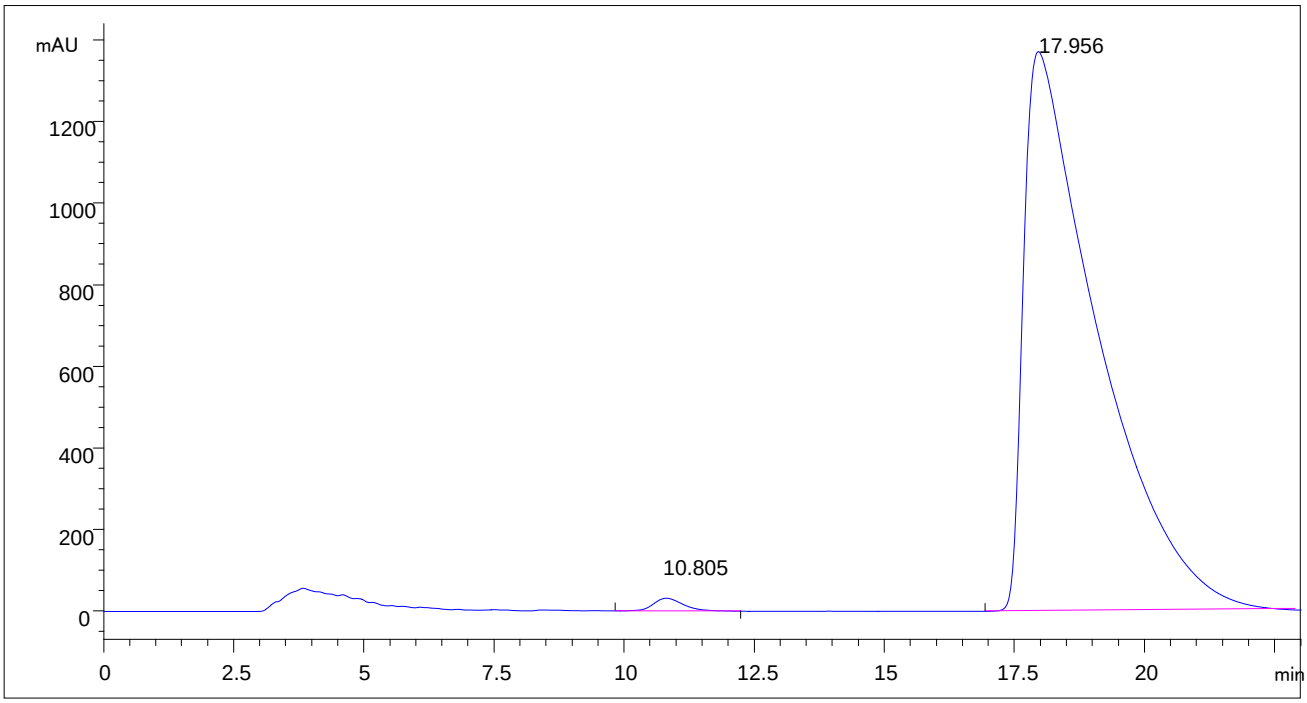
^{13}C NMR (100 MHz, DMSO-*d6*)

Racemic **1a**

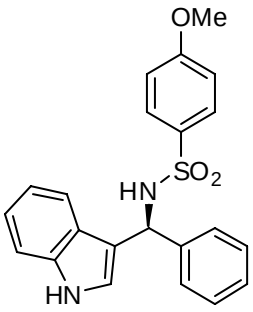


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	10.347	2103.6	61.2	0.528	0.726	49.911
2	19.089	2111.1	30.6	1.0645	0.736	50.089

Chiral **1a***

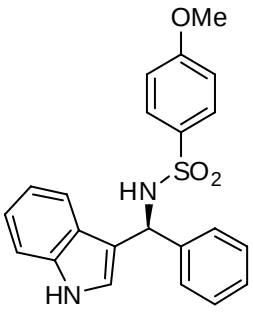


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	10.805	1329.4	31.9	0.6302	0.767	0.959
2	17.956	137245	1371.7	1.393	0.226	99.041



1b*

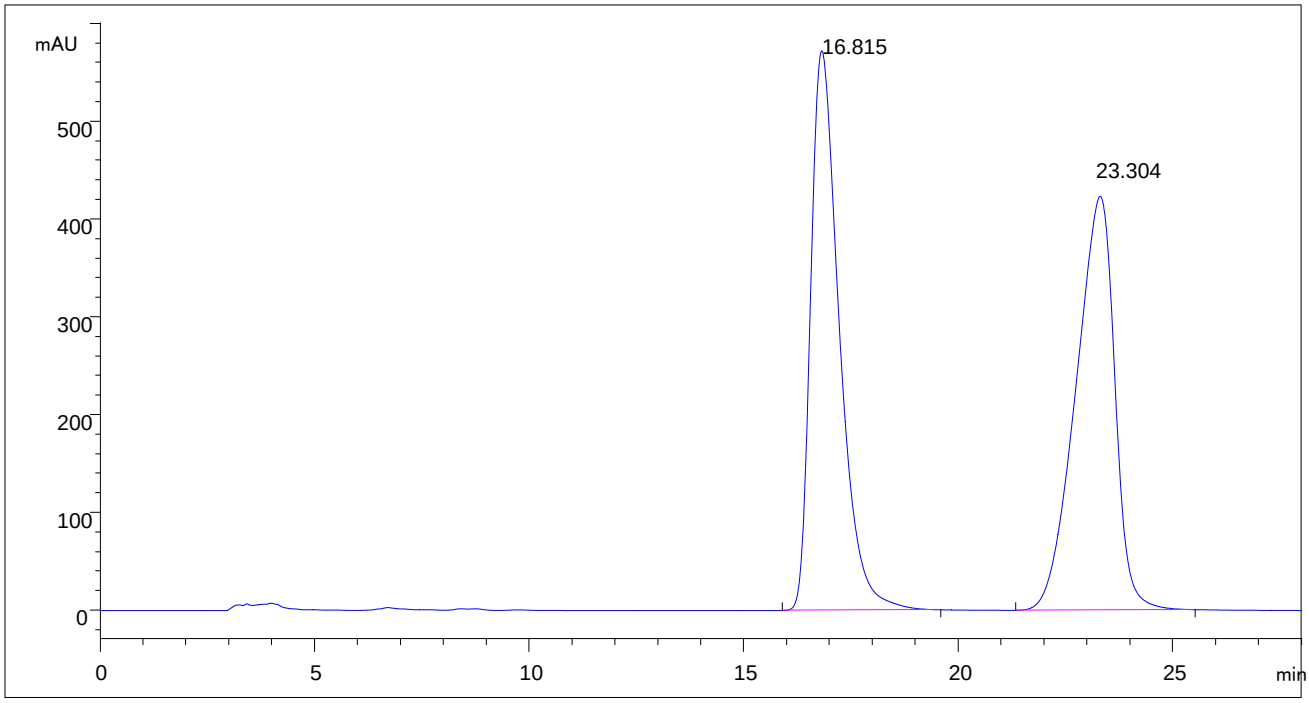
^{1}H NMR (400 MHz, DMSO-*d6*)



1b*

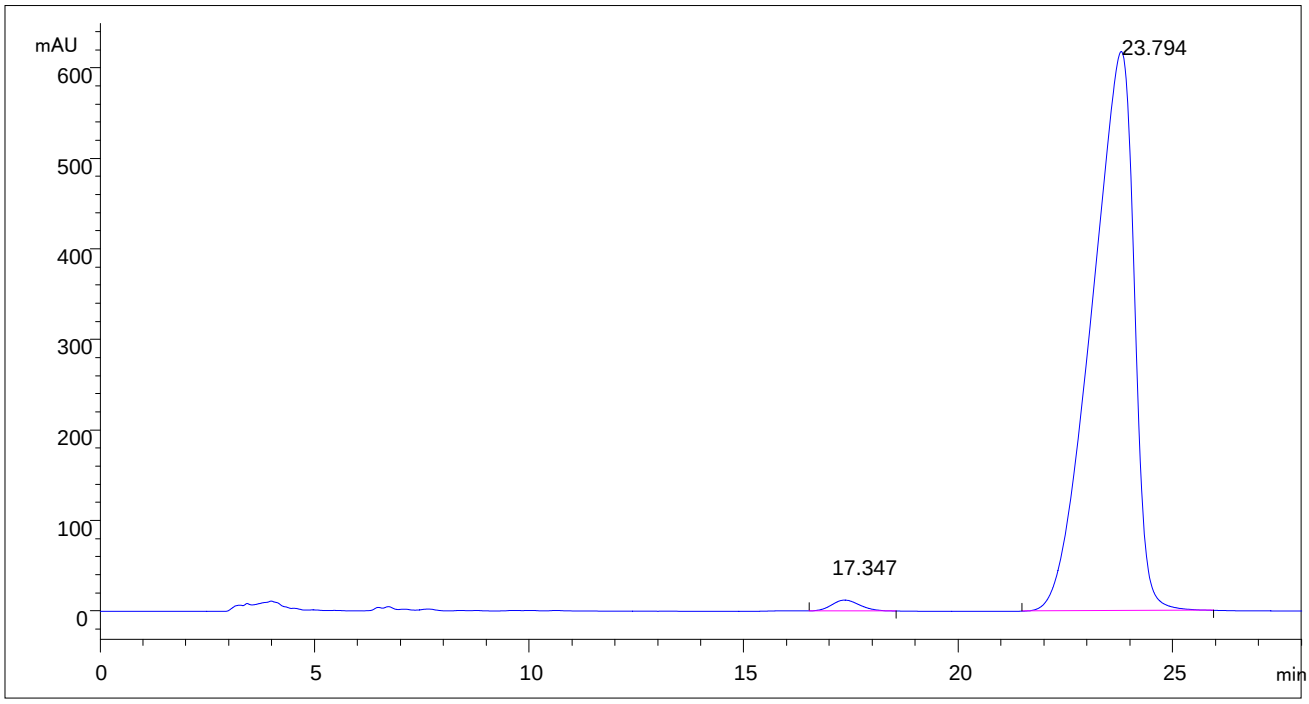
^{13}C NMR (100 MHz, DMSO-*d6*)

Racemic **1b**

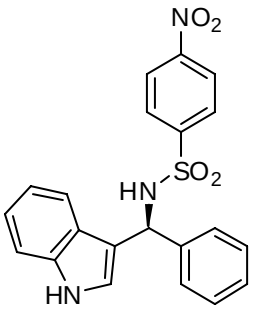


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	16.815	26636.4	572.2	0.7091	0.583	49.967
2	23.304	26672	423	0.9656	1.595	50.033

Chiral **1b***

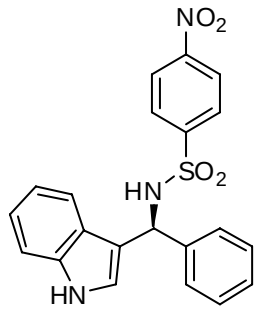


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	17.347	546.1	12	0.6852	0.805	1.270
2	23.794	42446.4	618	1.0678	2.194	98.730



1c*

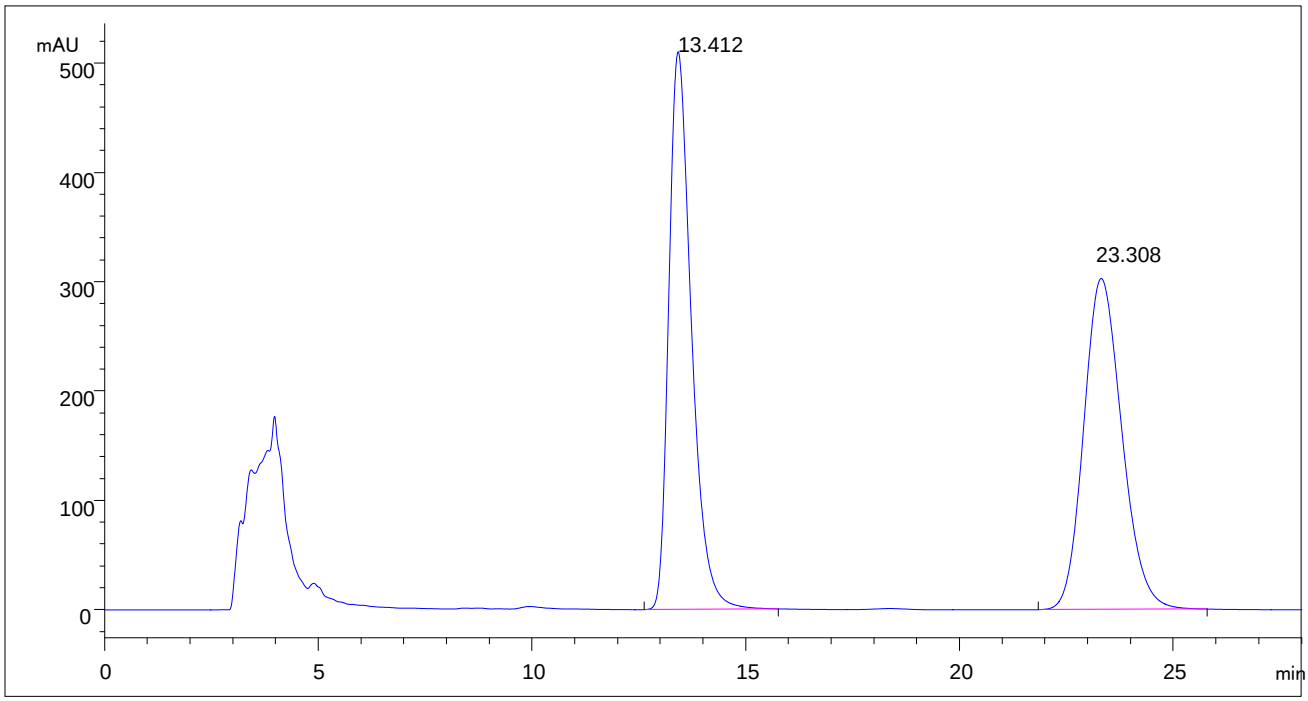
^{1}H NMR (400 MHz, DMSO-*d6*)



1c*

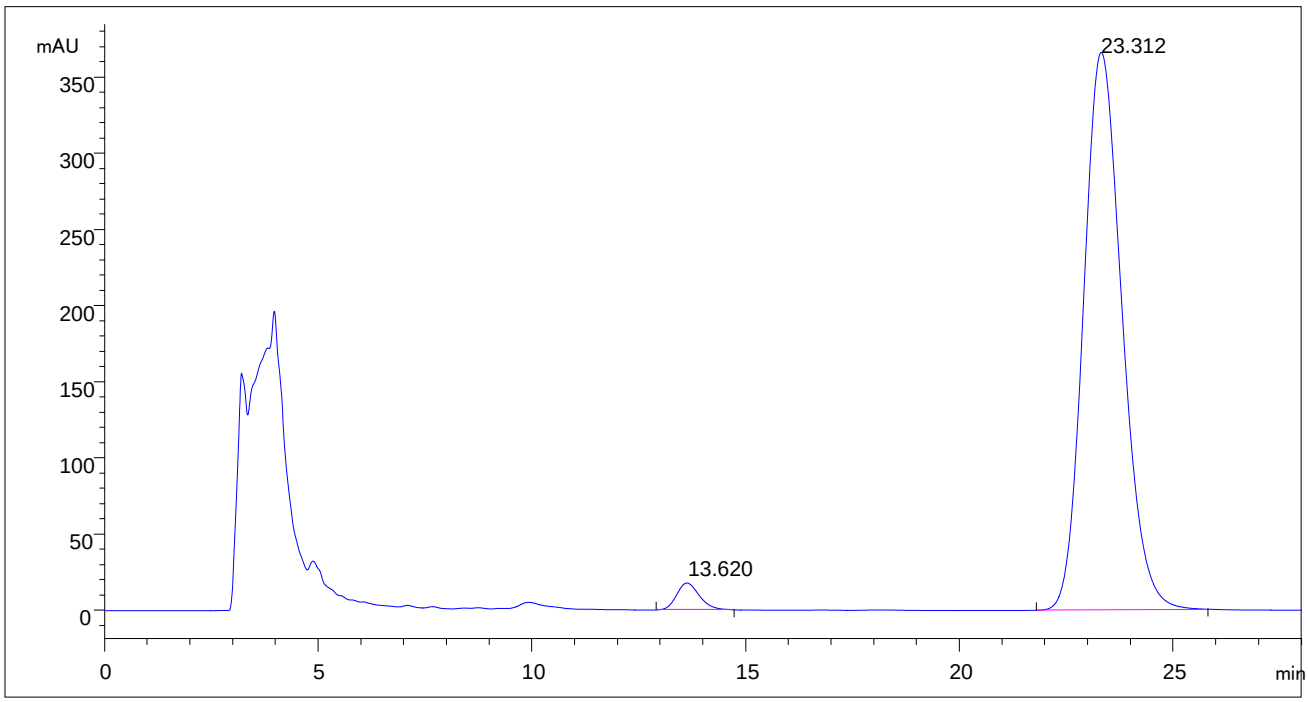
^{13}C NMR (100 MHz, DMSO-*d6*)

Racemic **1c**

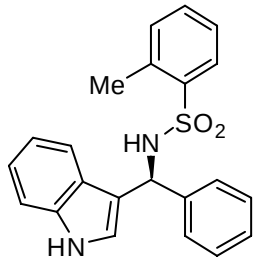


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	13.412	18798.1	510.4	0.5622	0.651	49.966
2	23.308	18823.7	302.9	0.9623	0.808	50.034

Chiral **1c***

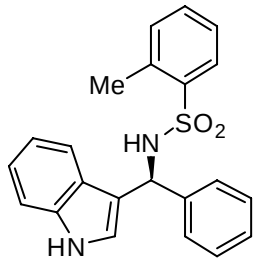


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	13.62	661.6	17.7	0.5733	0.785	2.807
2	23.312	22911.8	366.1	0.9689	0.806	97.193



1d*

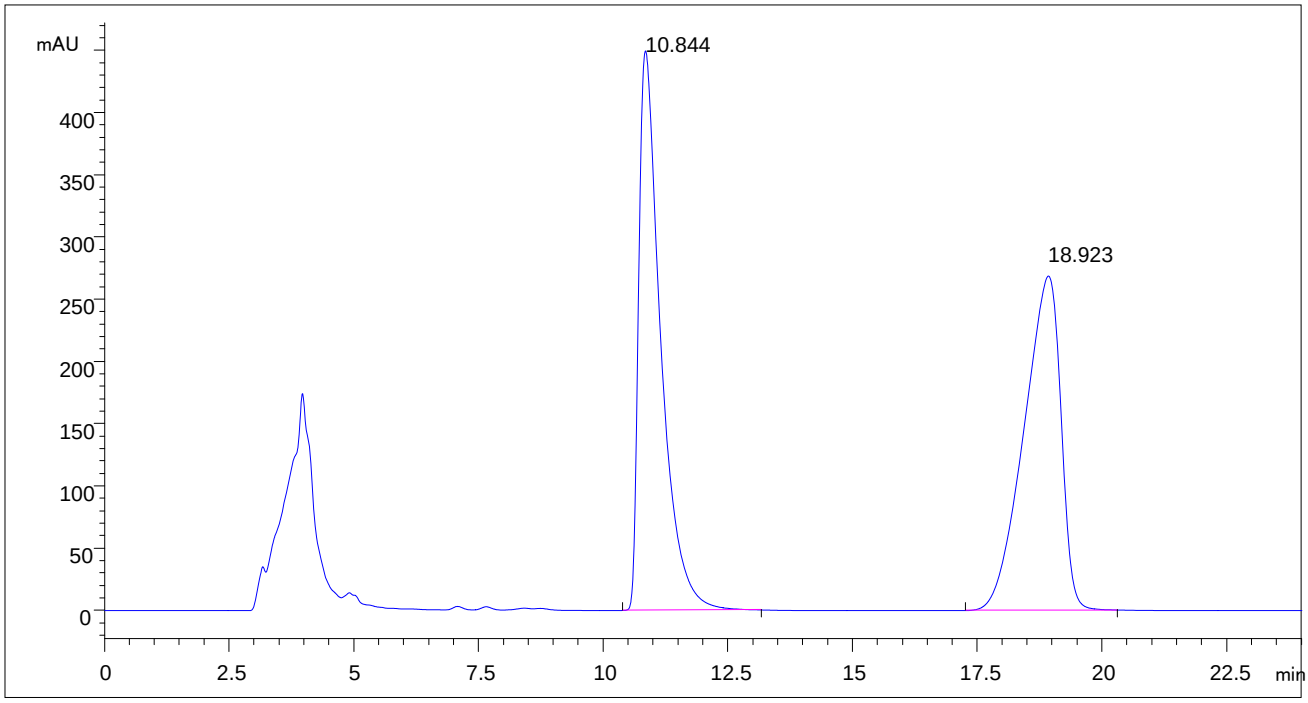
^{1}H NMR (400 MHz, DMSO-*d6*)



1d*

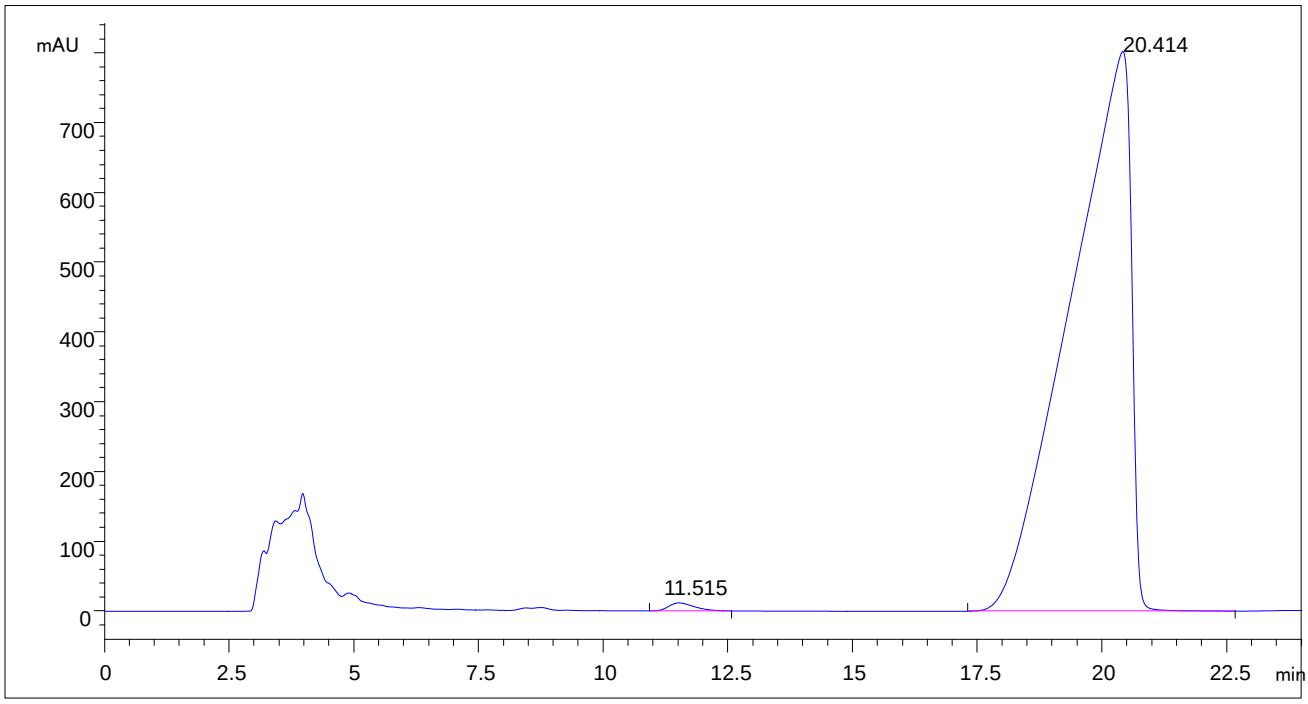
^{13}C NMR (100 MHz, DMSO-*d6*)

Racemic **1d**

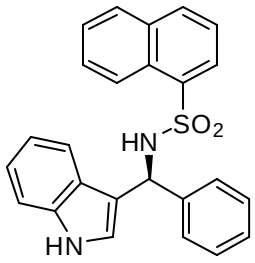


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	10.844	13865.3	449.6	0.4559	0.402	50.030
2	18.923	13848.5	268.6	0.8011	1.921	49.970

Chiral **1d***

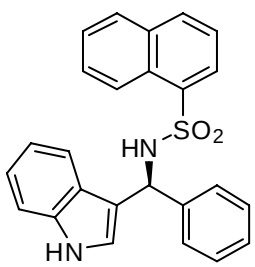


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	11.515	411.9	11.4	0.553	0.625	0.603
2	20.414	67884.2	801.9	1.1434	6.018	99.397



1e*

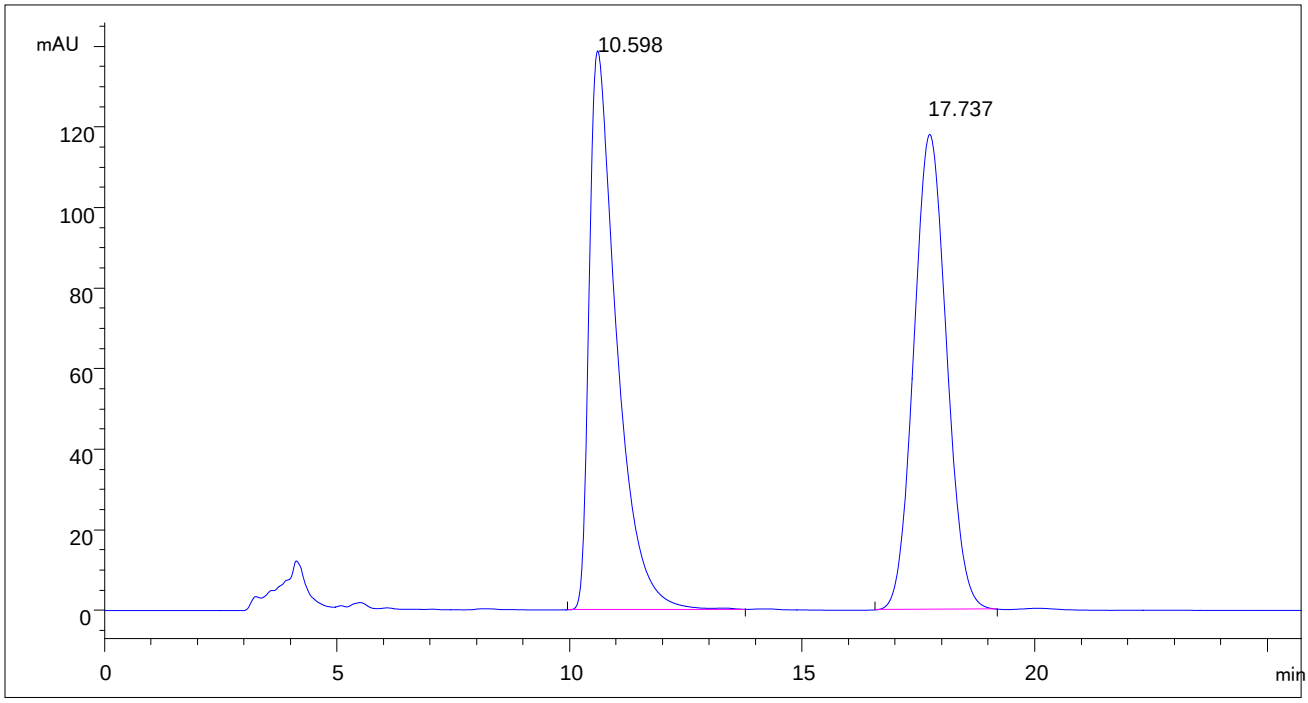
^{1}H NMR (400 MHz, DMSO-*d6*)



1e*

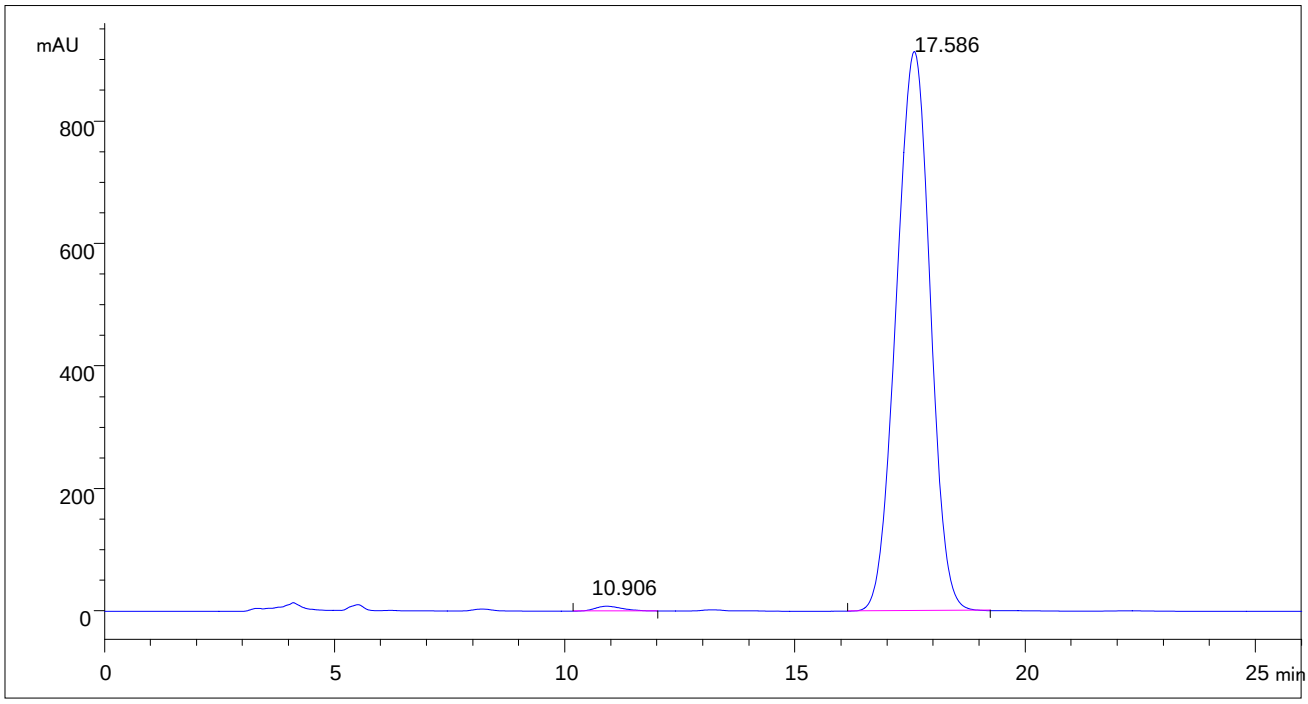
^{13}C NMR (100 MHz, DMSO-*d6*)

Racemic **1e**

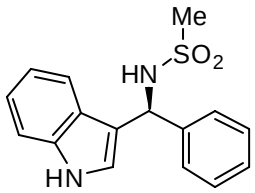


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	10.598	5726	138.8	0.6876	0.425	49.747
2	17.737	5784.4	118	0.7642	0.91	50.253

Chiral **1e***

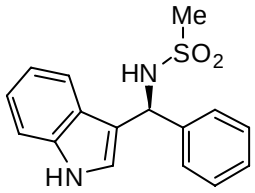


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	10.906	336.5	8	0.638	0.692	0.714
2	17.586	46785.1	913.4	0.8087	1.085	99.286



1f*

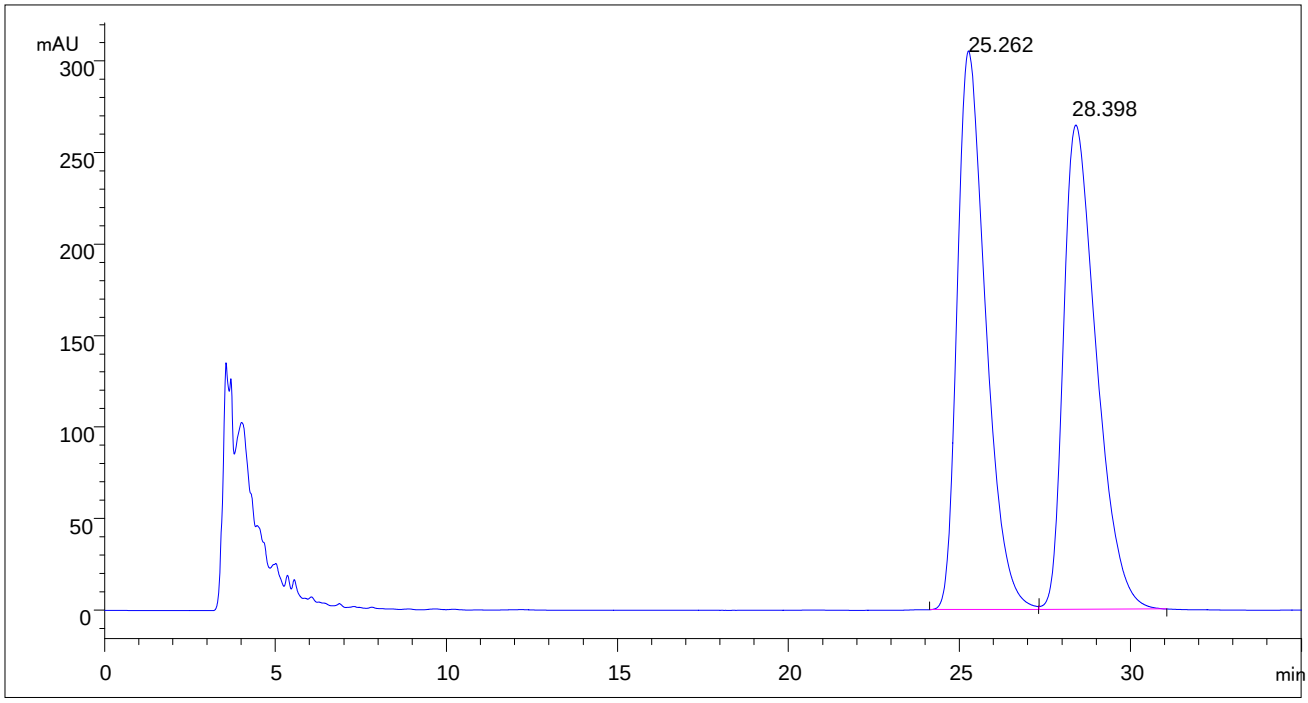
^{1}H NMR (400 MHz, DMSO-*d6*)



1f*

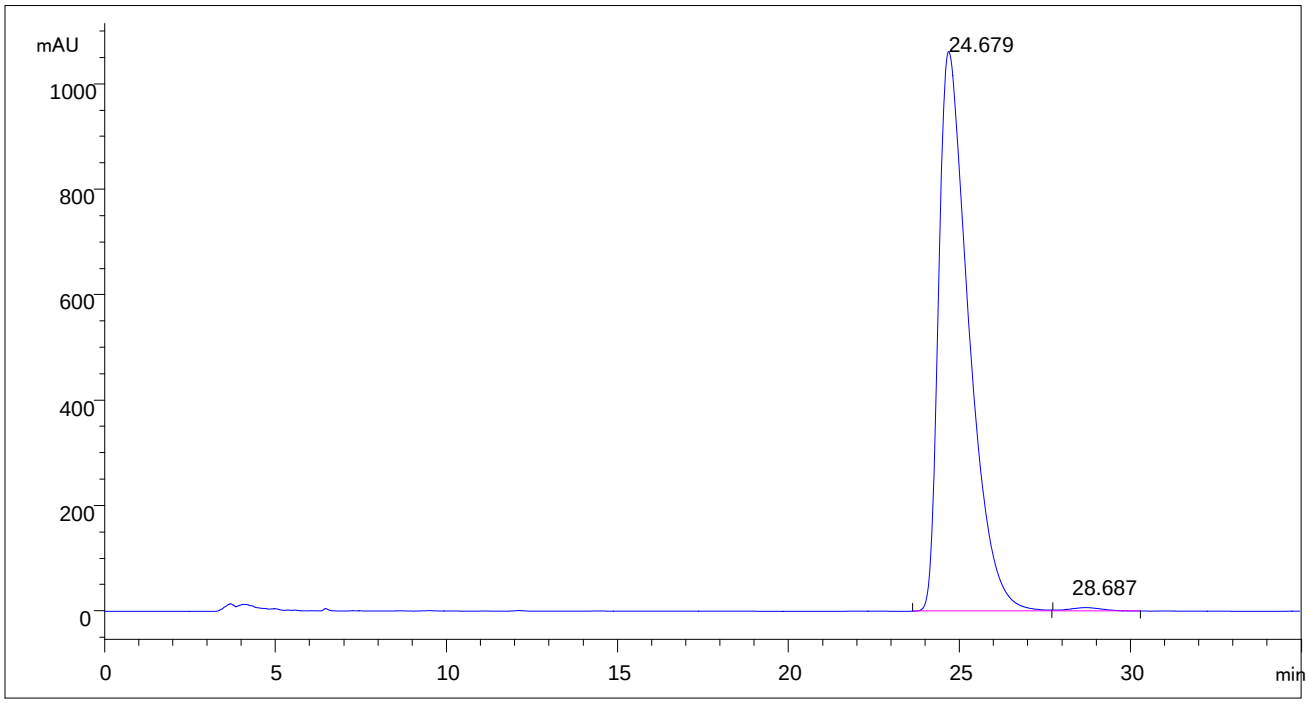
^{13}C NMR (100 MHz, DMSO-*d6*)

Racemic **1f**

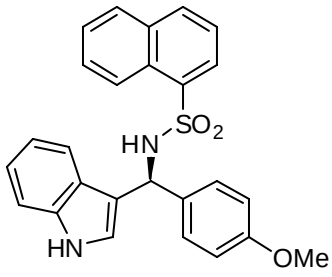


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	25.262	17708.8	305.4	0.8773	0.618	49.961
2	28.398	17736.5	264.7	1.0233	0.561	50.039

Chiral **1f***

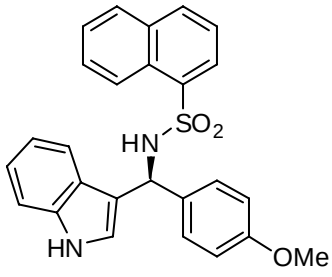


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	24.679	65190.4	1061.6	0.9217	0.463	99.294
2	28.687	463.8	6.6	1.0092	0.97	0.706



1g*

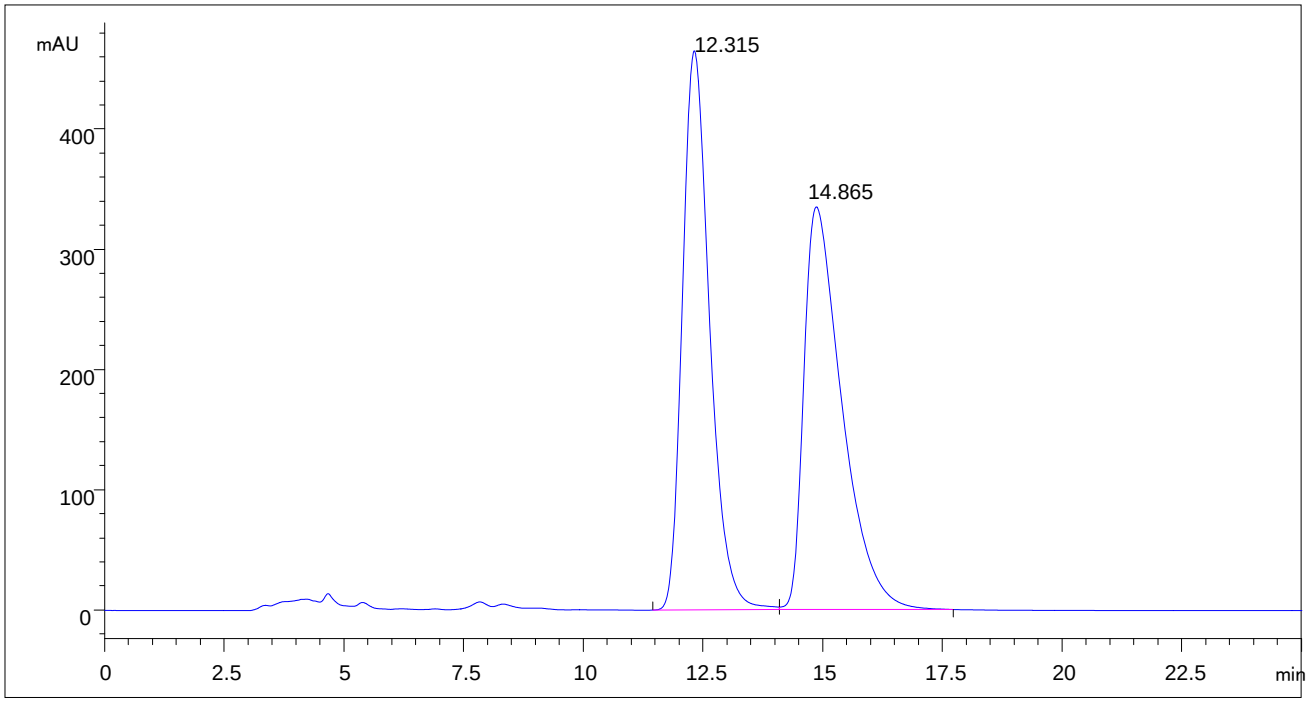
^{1}H NMR (400 MHz, DMSO-*d6*)



1g*

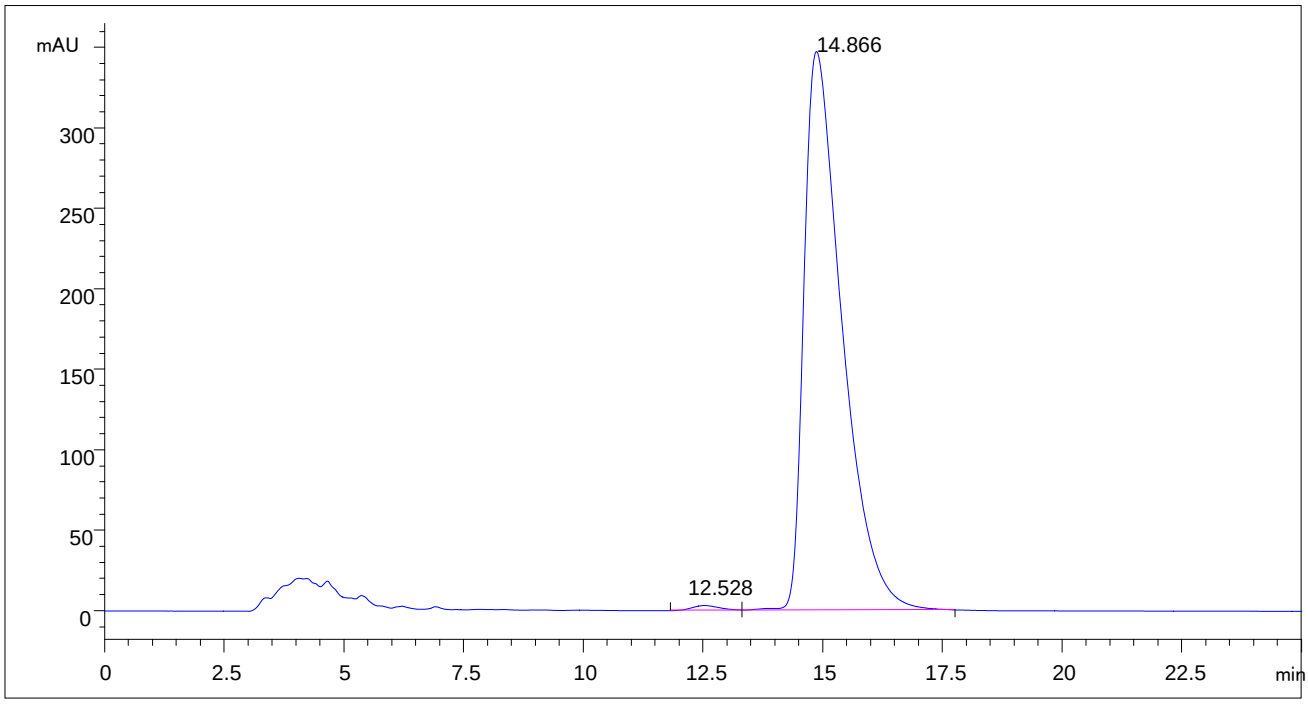
^{13}C NMR (100 MHz, DMSO-*d6*)

Racemic **1g**

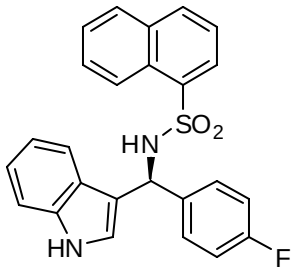


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	12.315	18436.2	465	0.6082	0.713	49.878
2	14.865	18526.3	335.1	0.827	0.455	50.122

Chiral **1g***

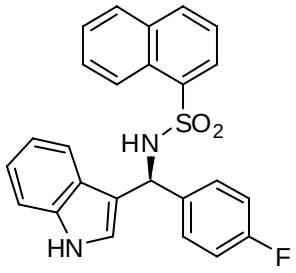


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	12.528	128.6	3.1	0.6159	0.768	0.662
2	14.866	19288.7	347.2	0.8315	0.452	99.338



1h*

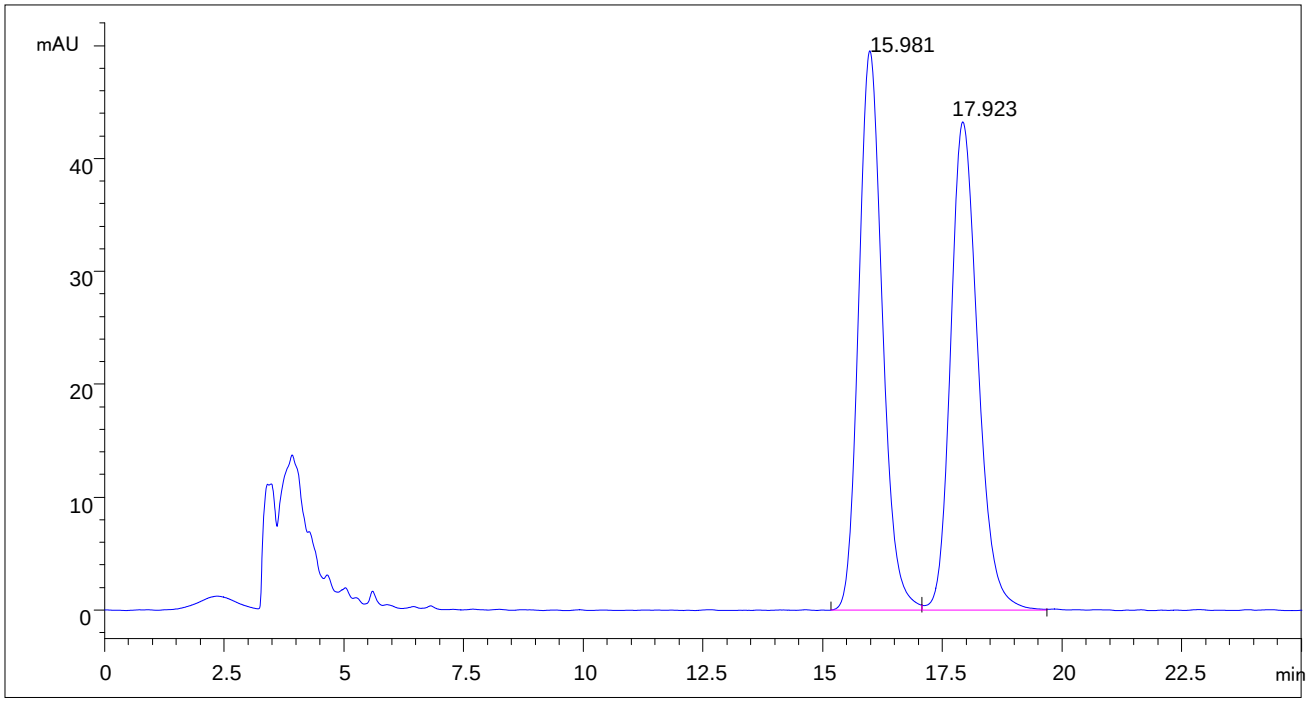
^{1}H NMR (400 MHz, DMSO-*d6*)



1h*

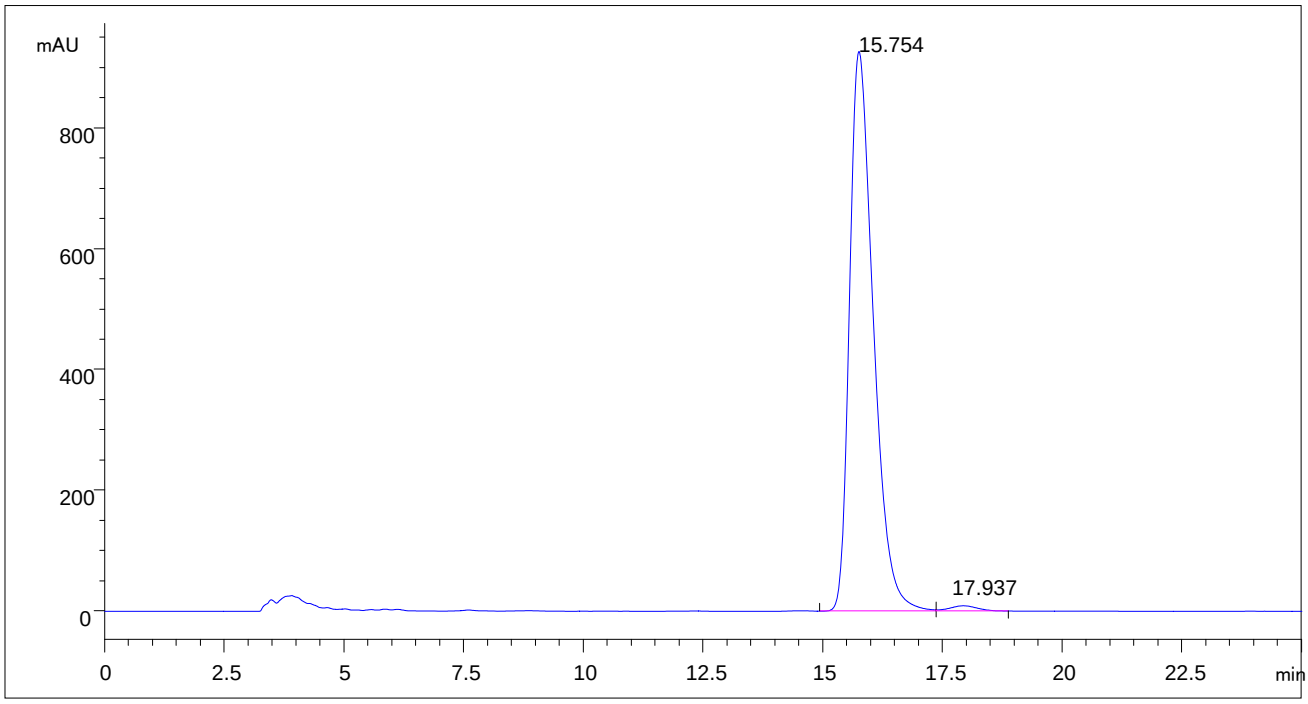
^{13}C NMR (100 MHz, DMSO-*d6*)

Racemic **1h**

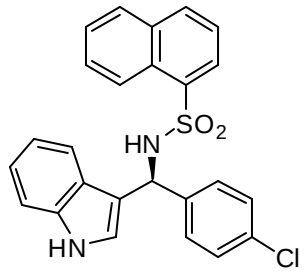


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	15.981	1711.3	49.6	0.5754	0.845	49.997
2	17.923	1711.5	43.3	0.6592	0.774	50.003

Chiral **1h***

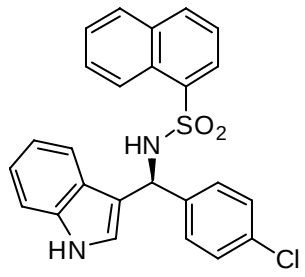


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	15.754	32072.3	926.9	0.5274	0.611	98.876
2	17.937	364.7	8.9	0.6161	0.95	1.124



1i*

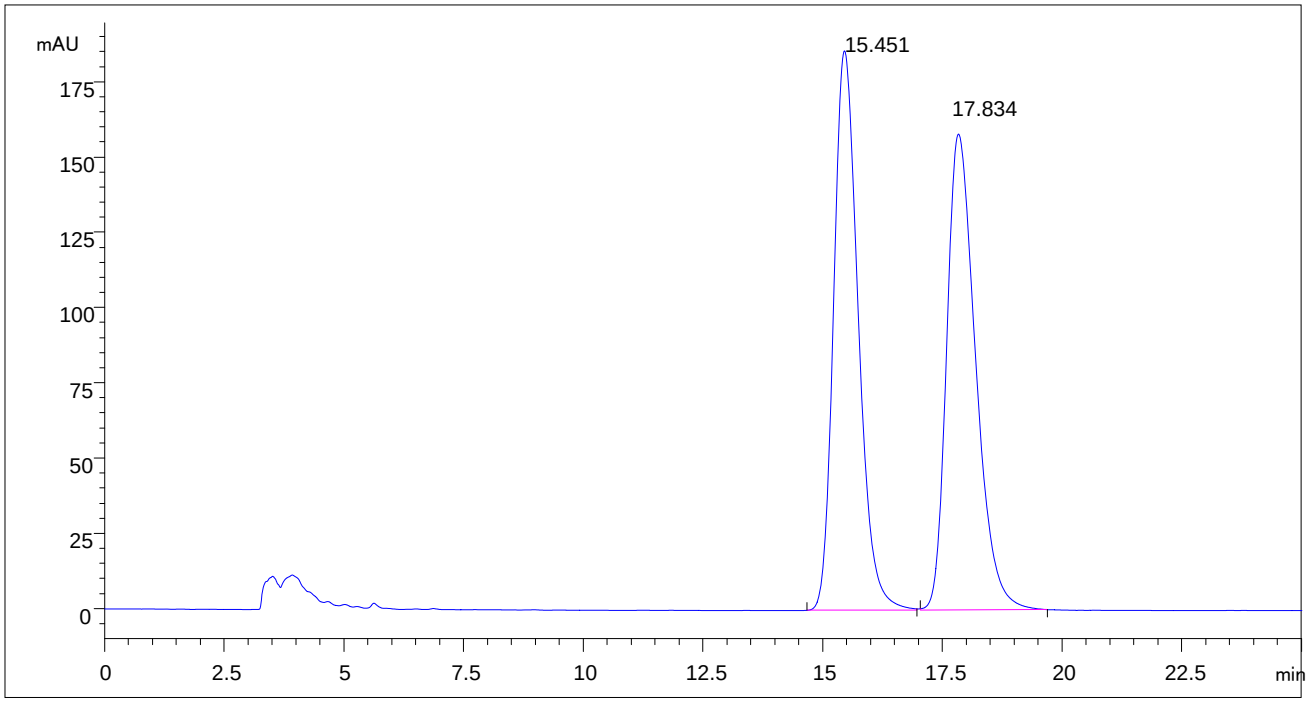
^{1}H NMR (400 MHz, DMSO-*d6*)



1i*

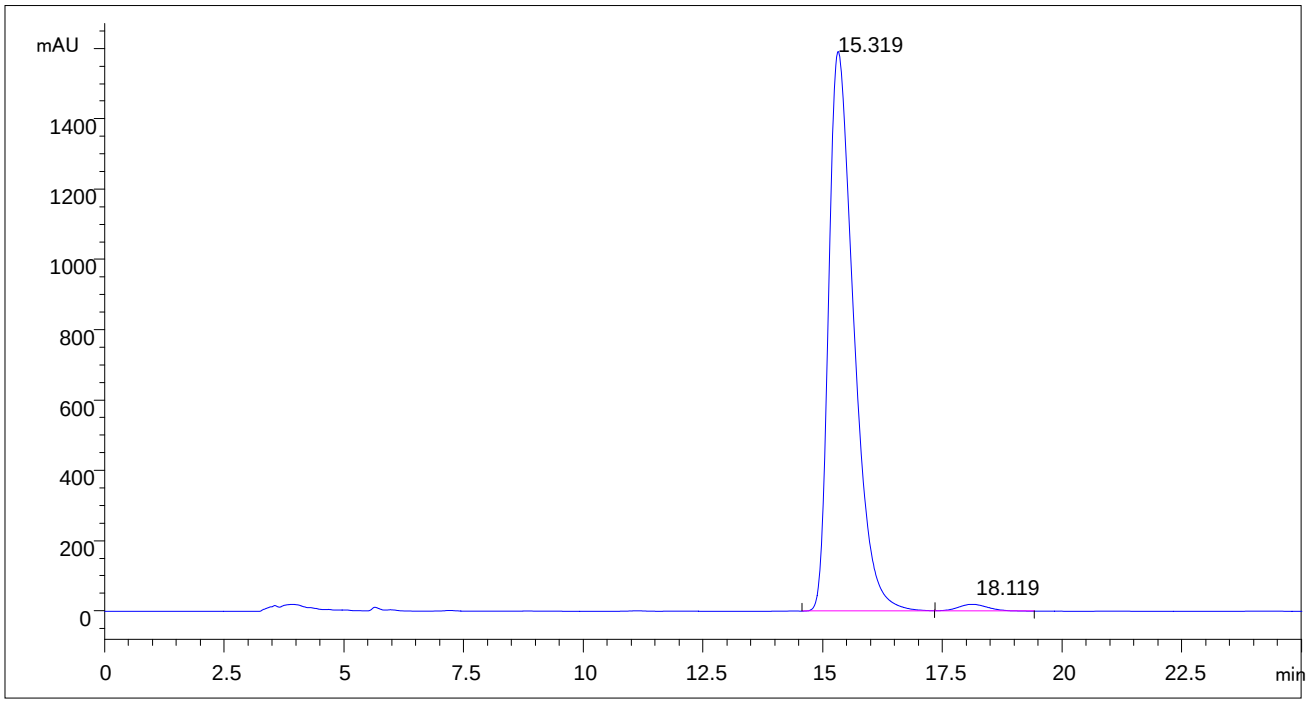
^{13}C NMR (100 MHz, DMSO-*d6*)

Racemic **1i**

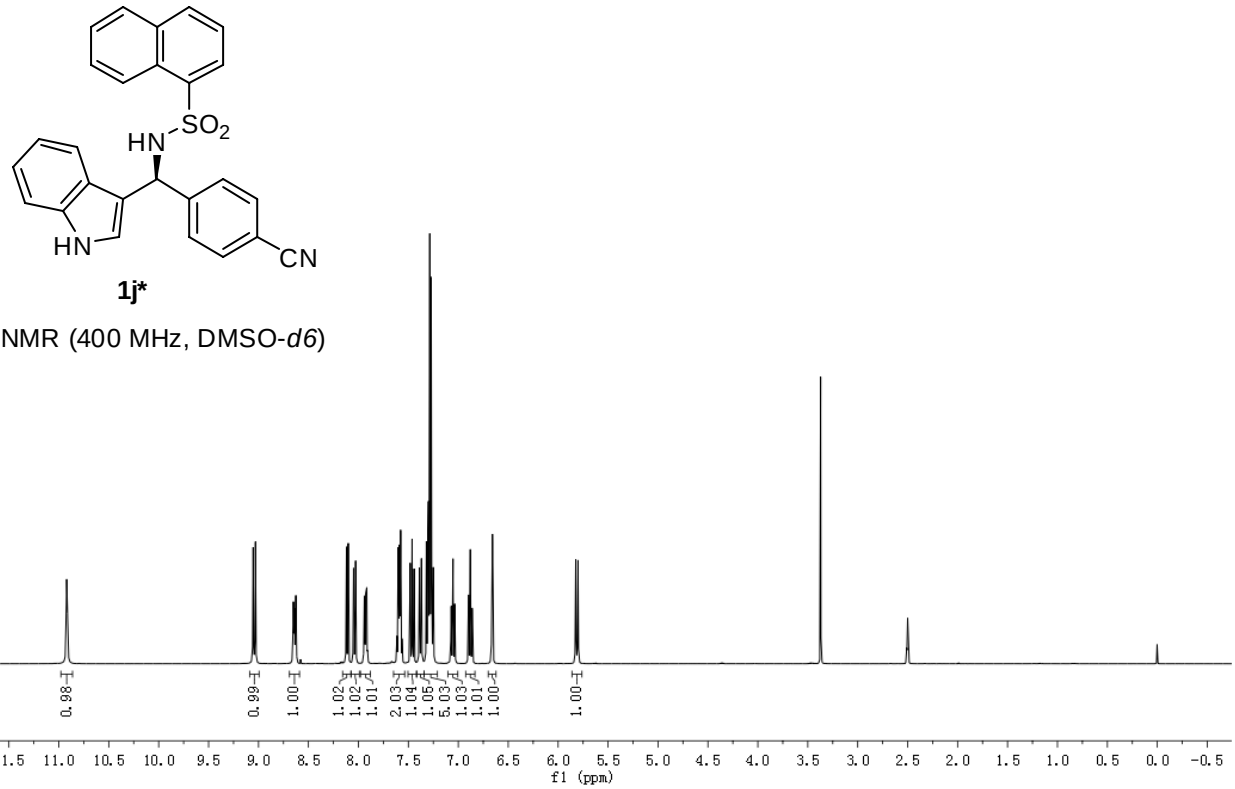


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	15.451	6641.9	185.9	0.5523	0.734	49.961
2	17.834	6652.2	158.1	0.6496	0.648	50.039

Chiral **1i***

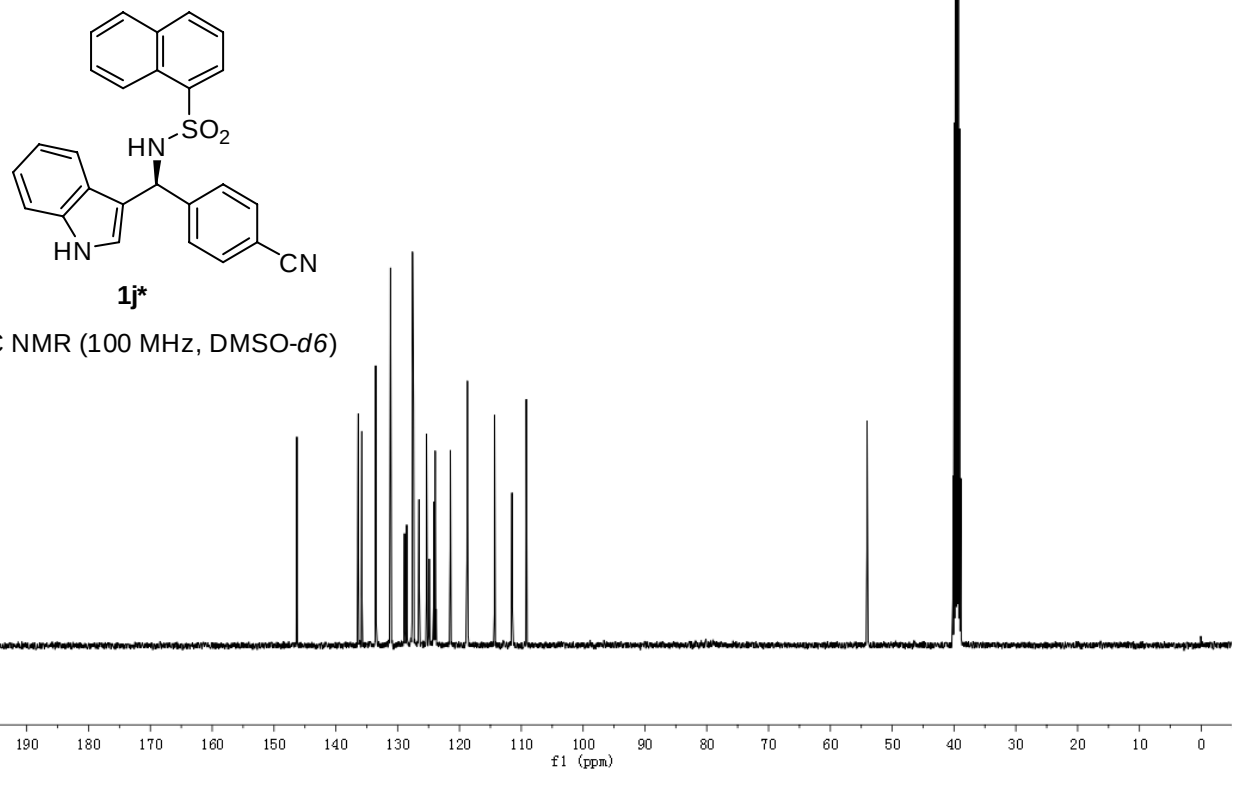


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	15.319	58062	1592.2	0.5565	0.564	98.508
2	18.119	879.2	19.6	0.6914	0.868	1.492



1j*

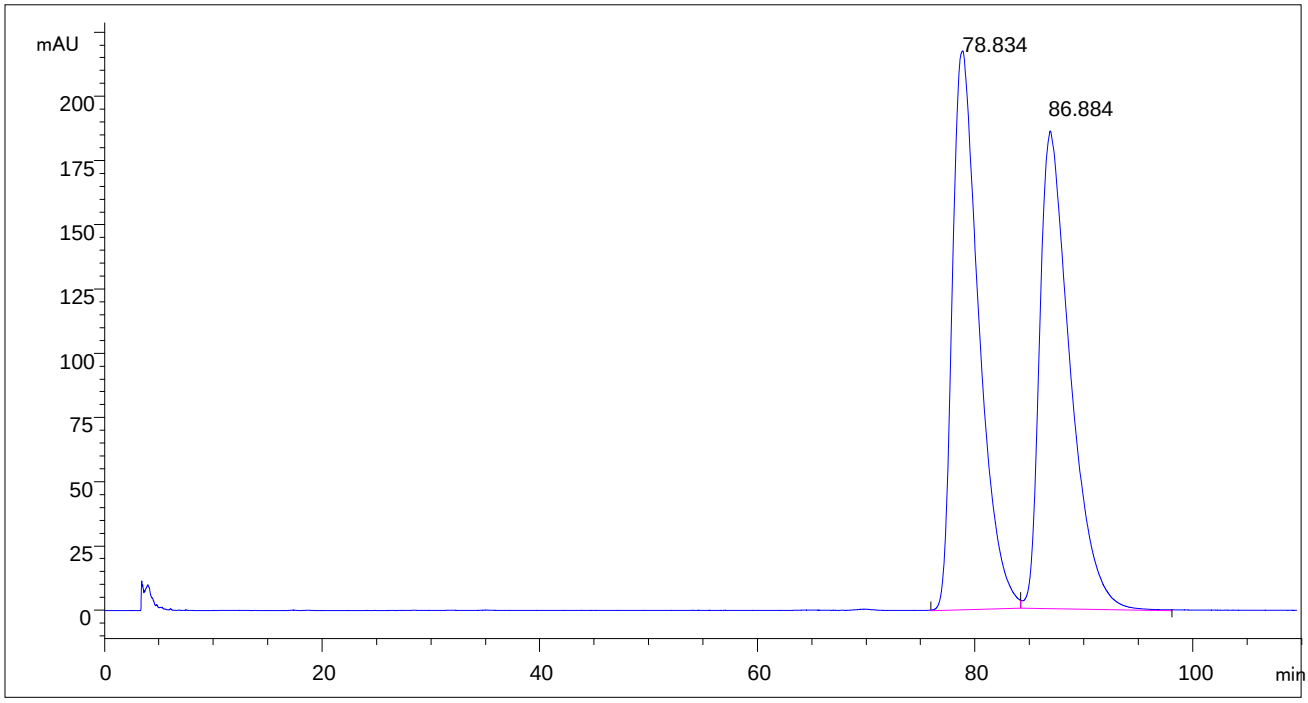
^{1}H NMR (400 MHz, DMSO-*d6*)



1j*

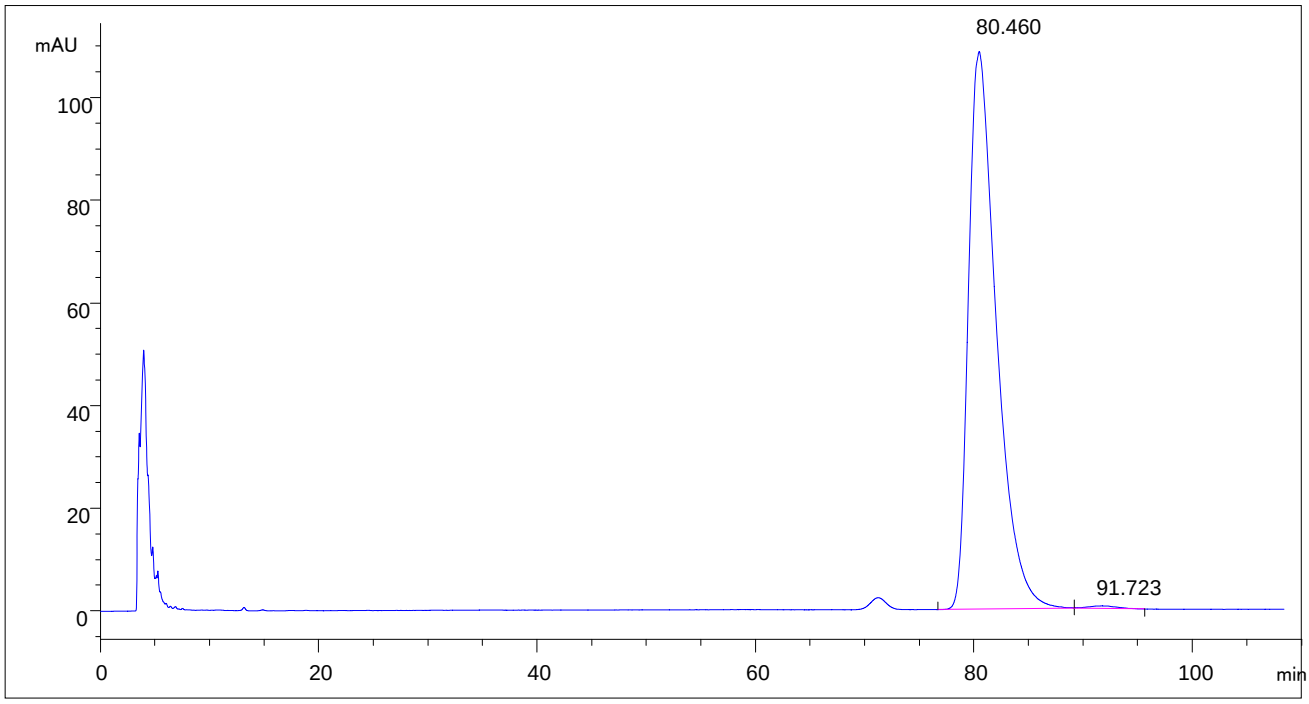
^{13}C NMR (100 MHz, DMSO-*d6*)

Racemic **1j**

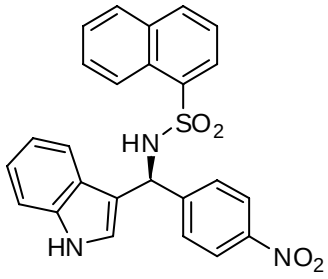


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	78.834	37212.2	217.7	2.8493	0.601	50.535
2	86.884	36424.1	186.1	3.262	0.51	49.465

Chiral **1j***

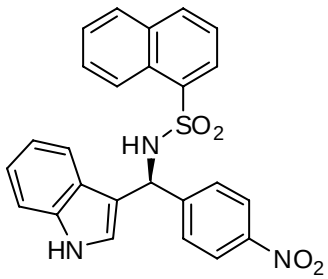


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	80.46	195359.9	108.7	2.9697	0.59	99.435
2	91.723	110	5.7E-1	3.2288	0.947	0.565



1k*

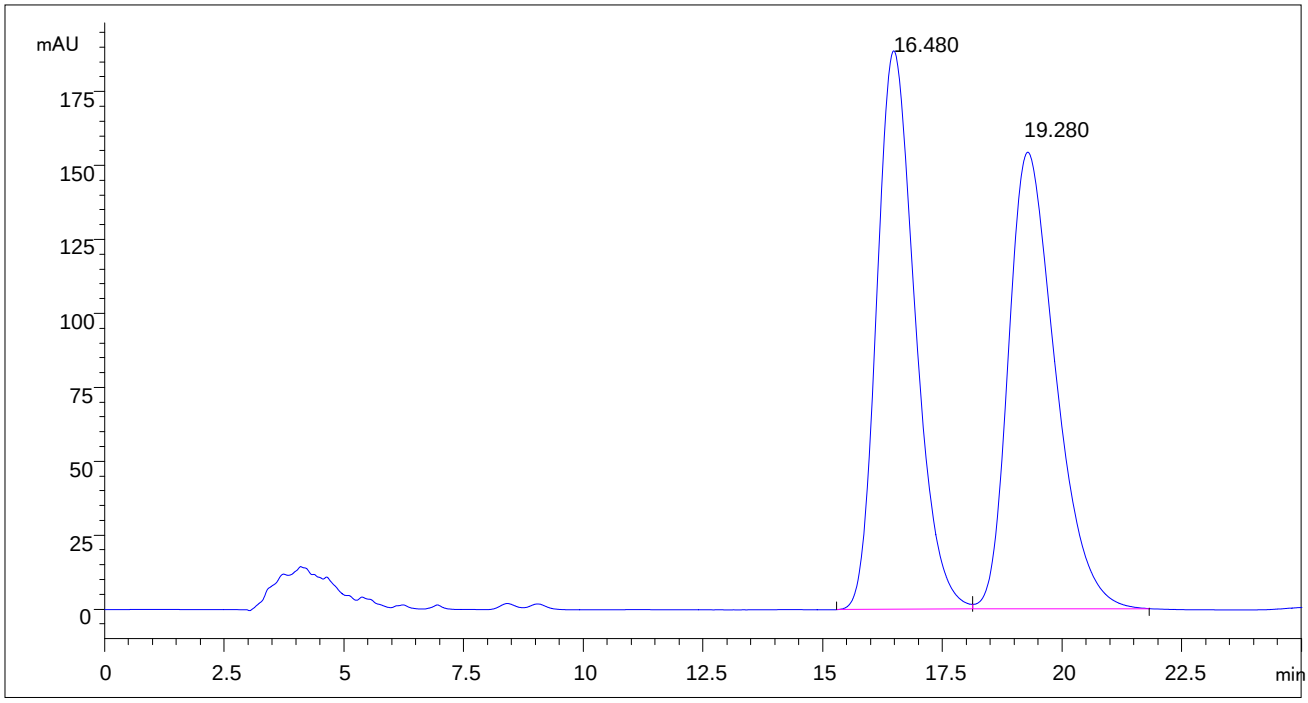
^{1}H NMR (400 MHz, DMSO-*d6*)



1k*

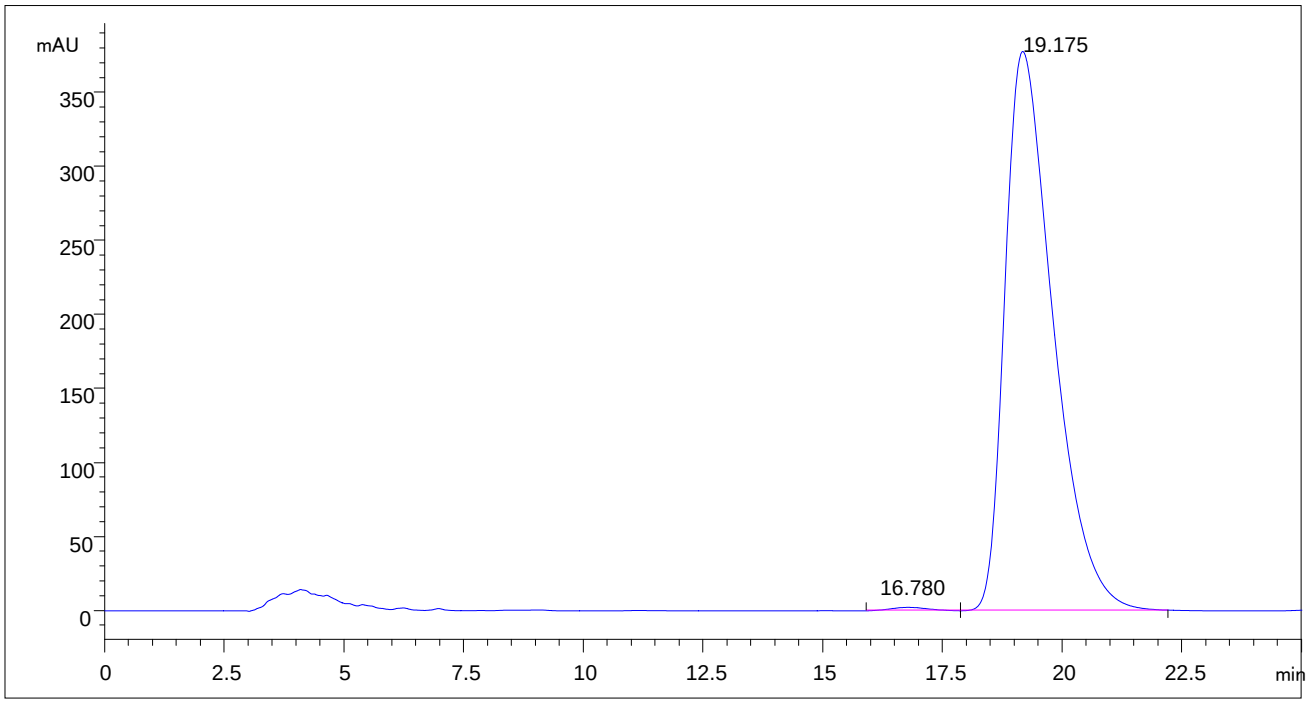
^{13}C NMR (100 MHz, DMSO-*d6*)

Racemic **1k**

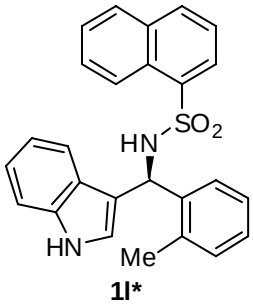


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	16.48	10518	188.9	0.8607	0.747	49.925
2	19.28	10549.5	154.5	1.0397	0.657	50.075

Chiral **1k***

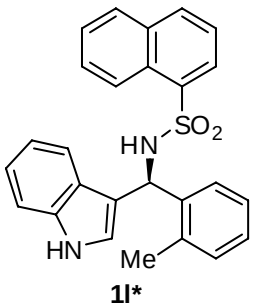


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	16.78	123	2.3	0.7036	0.882	0.462
2	19.175	26475.6	377.7	1.0683	0.547	99.538



1l*

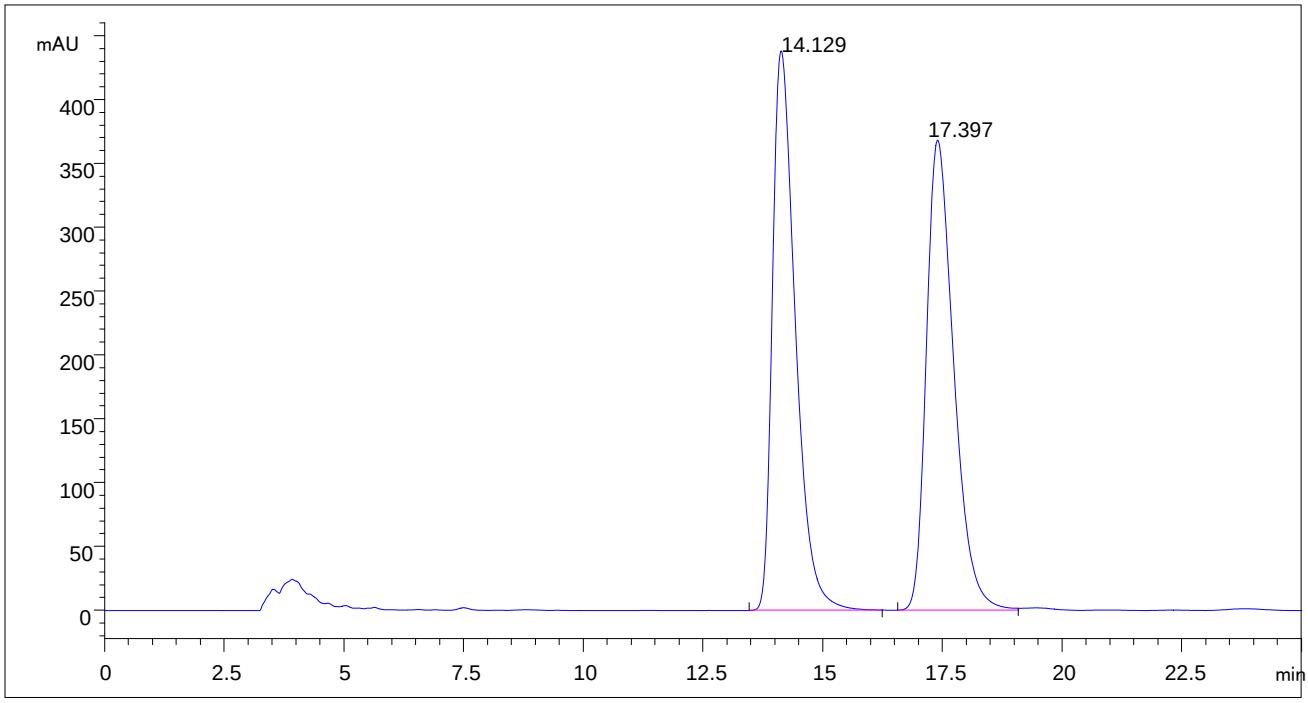
^{1}H NMR (400 MHz, DMSO-*d6*)



1l*

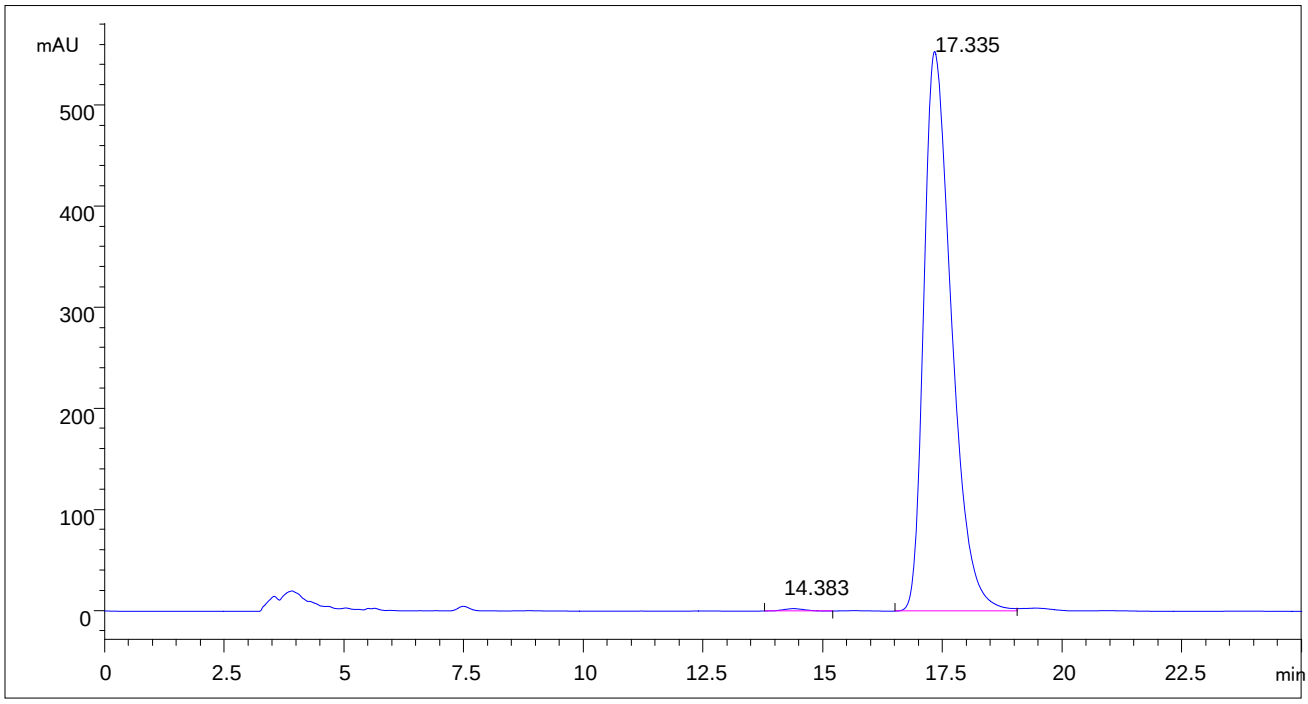
^{13}C NMR (100 MHz, DMSO-*d6*)

Racemic **1l**

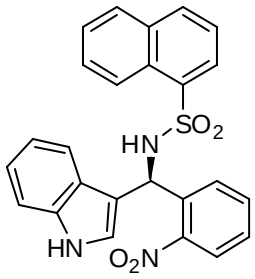


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	14.129	14630.1	438.3	0.5074	0.568	50.013
2	17.397	14622.7	368.1	0.6076	0.647	49.987

Chiral **1l***

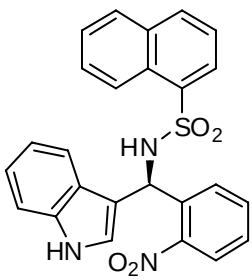


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	14.383	76.3	2.4	0.4822	0.937	0.341
2	17.335	22321.3	553.5	0.616	0.596	99.659



1m*

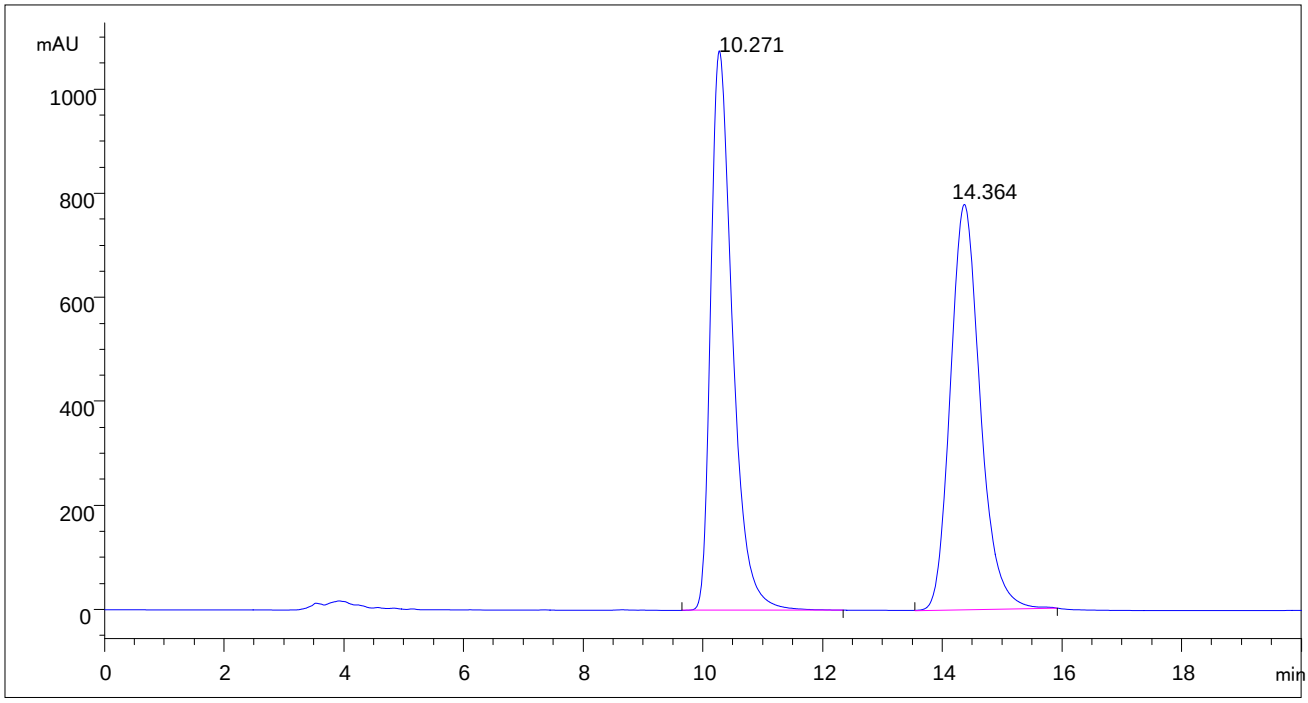
^{1}H NMR (400 MHz, DMSO-*d6*)



1m*

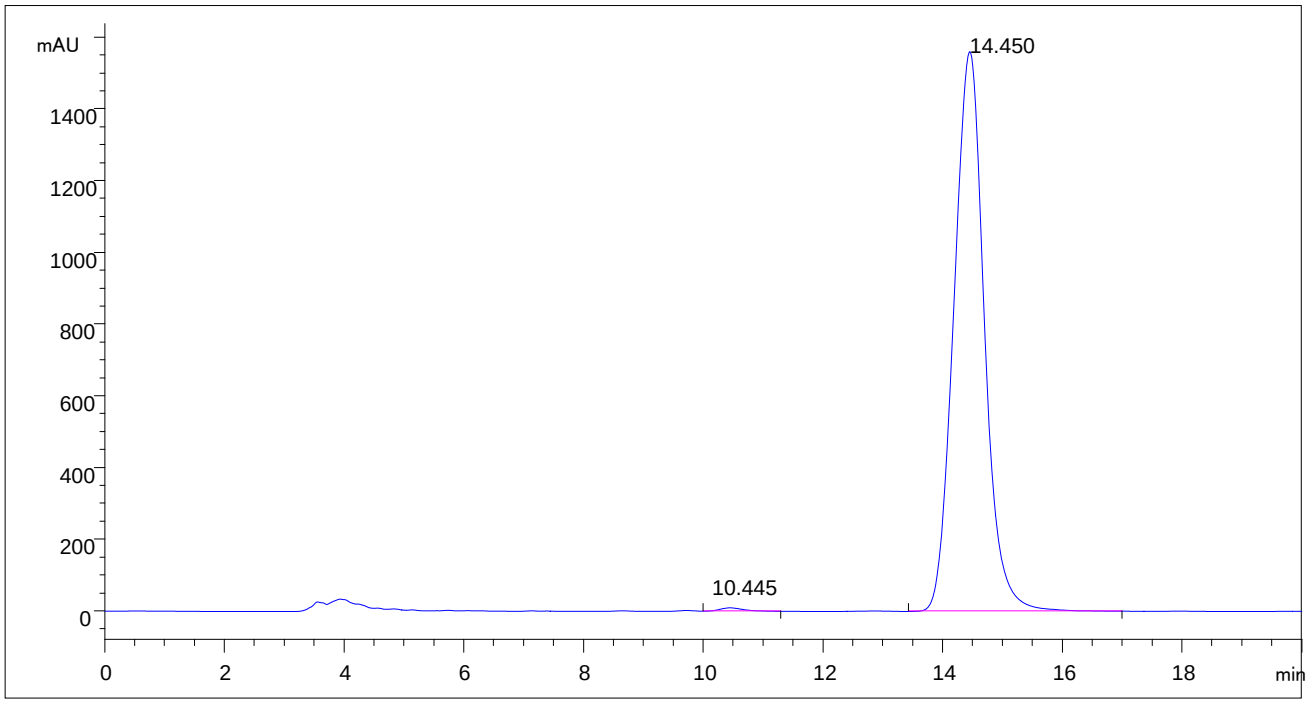
^{13}C NMR (100 MHz, DMSO-*d6*)

Racemic **1m**

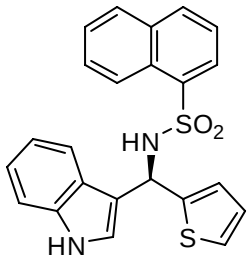


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	10.271	27207.5	1075.3	0.3855	0.605	50.151
2	14.364	27043.7	779.7	0.5781	0.843	49.849

Chiral **1m***



Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	10.445	271.6	9.7	0.4264	0.713	0.490
2	14.45	55185.2	1560.5	0.5465	1.004	99.510

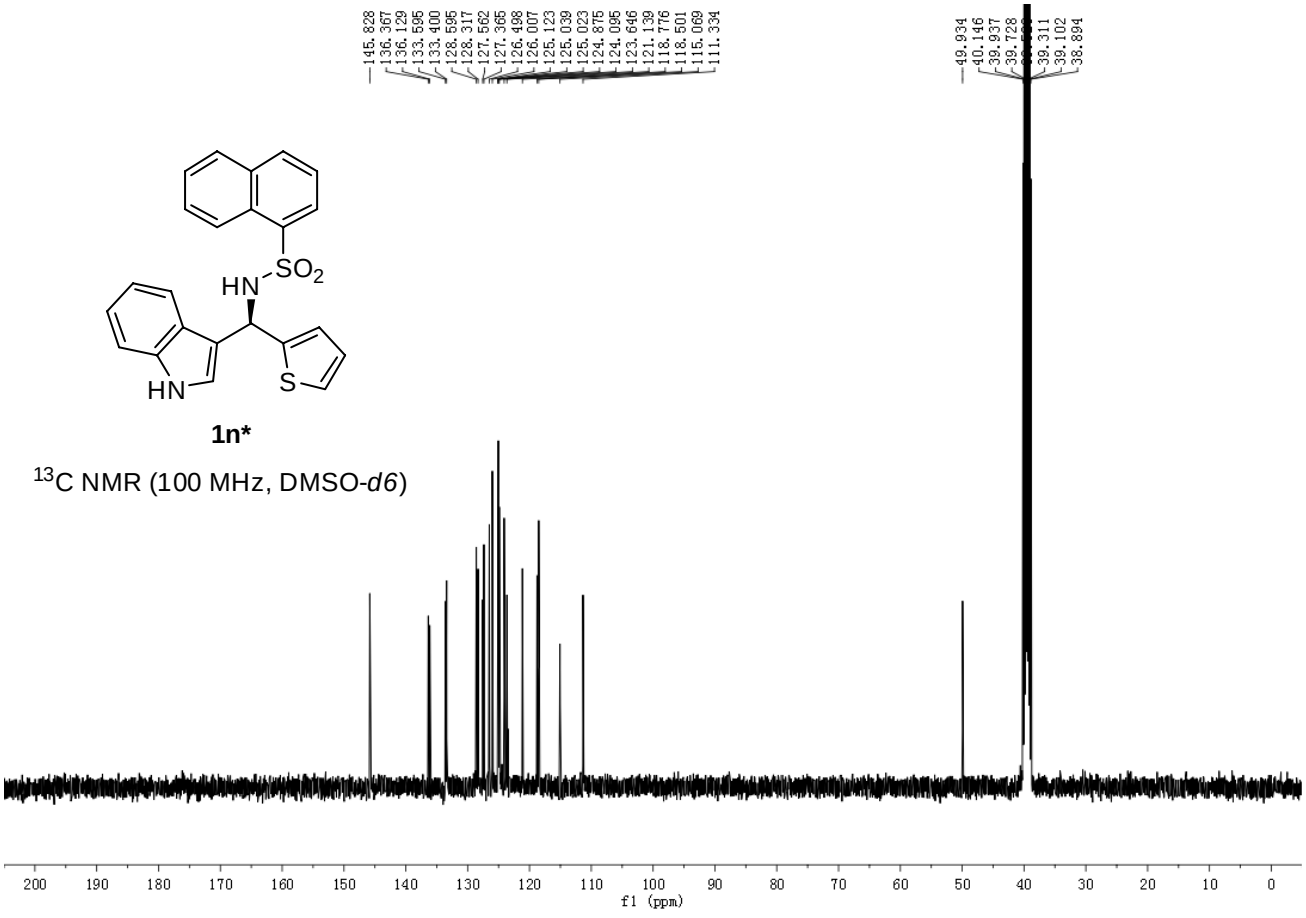


1n*

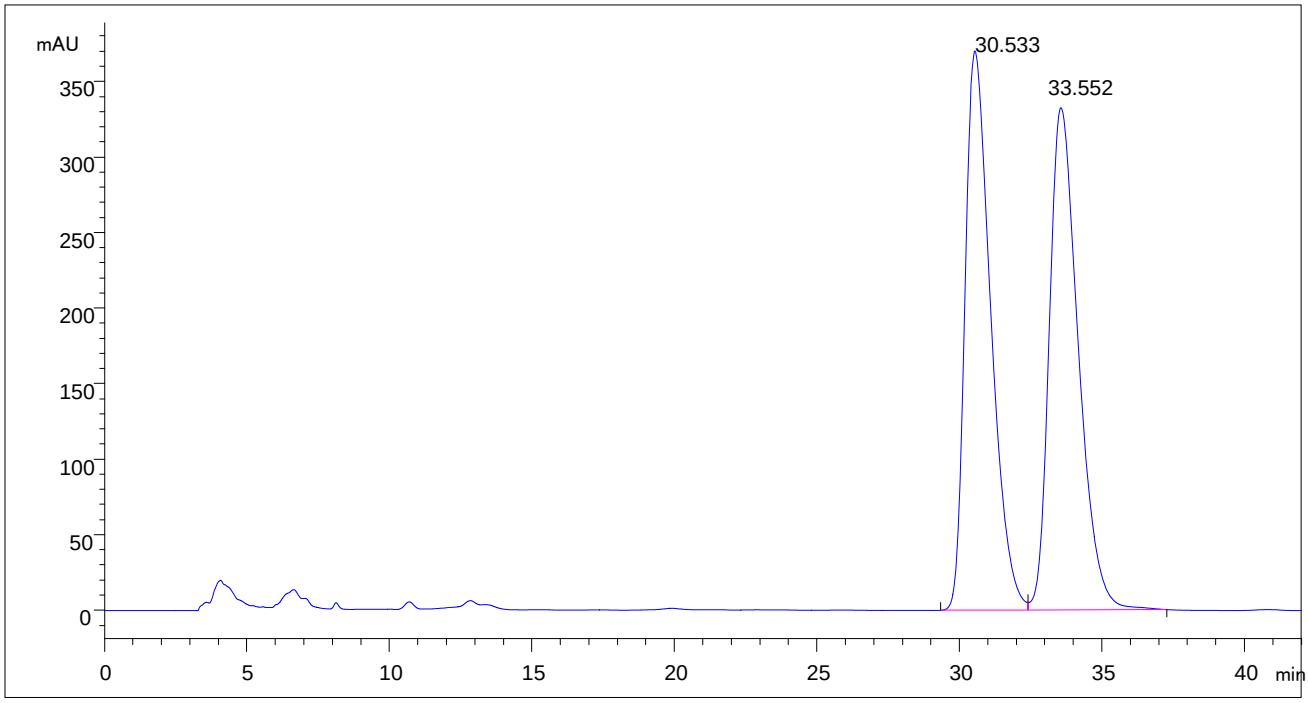
^{1}H NMR (400 MHz, DMSO-*d6*)

1n*

^{13}C NMR (100 MHz, DMSO-*d6*)

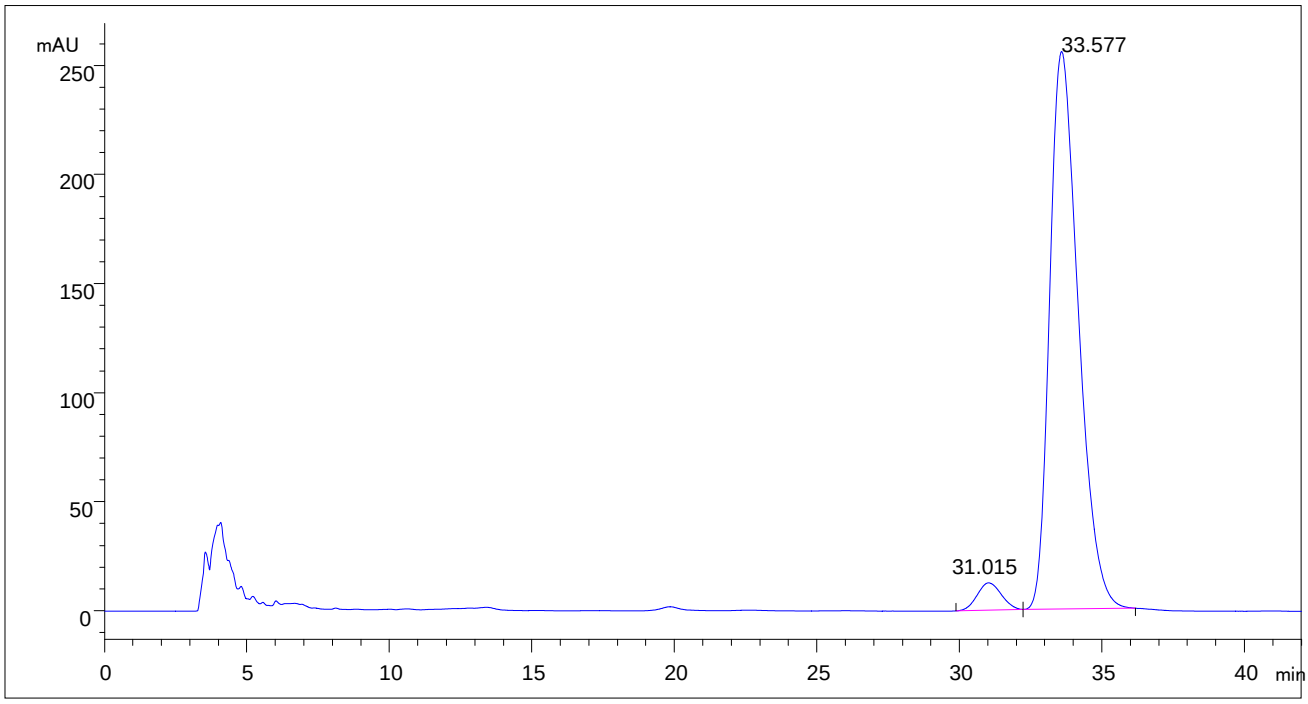


Racemic **1n**

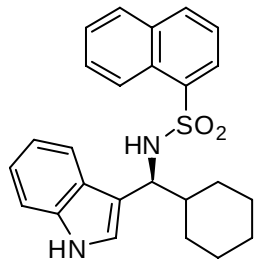


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	30.533	23327.4	370.2	0.9943	0.575	49.772
2	33.552	23541	332.4	1.065	0.63	50.228

Chiral **1n***

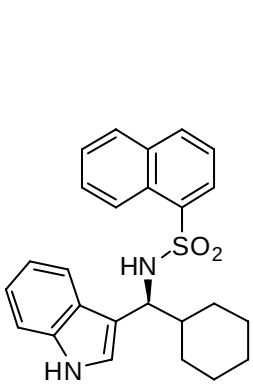


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	31.015	759.6	12.7	0.9263	0.868	4.071
2	33.577	17898.3	255.8	1.0871	0.665	95.929



1o*

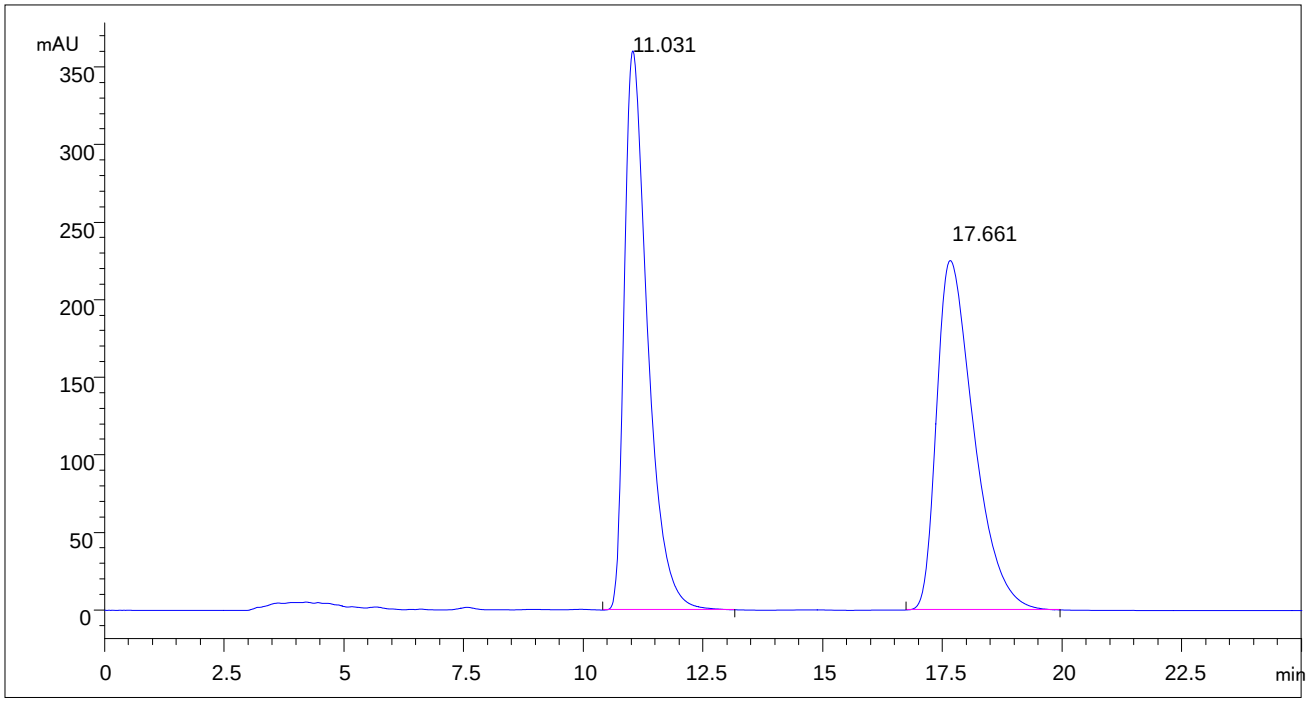
^{1}H NMR (400 MHz, DMSO-*d6*)



1o*

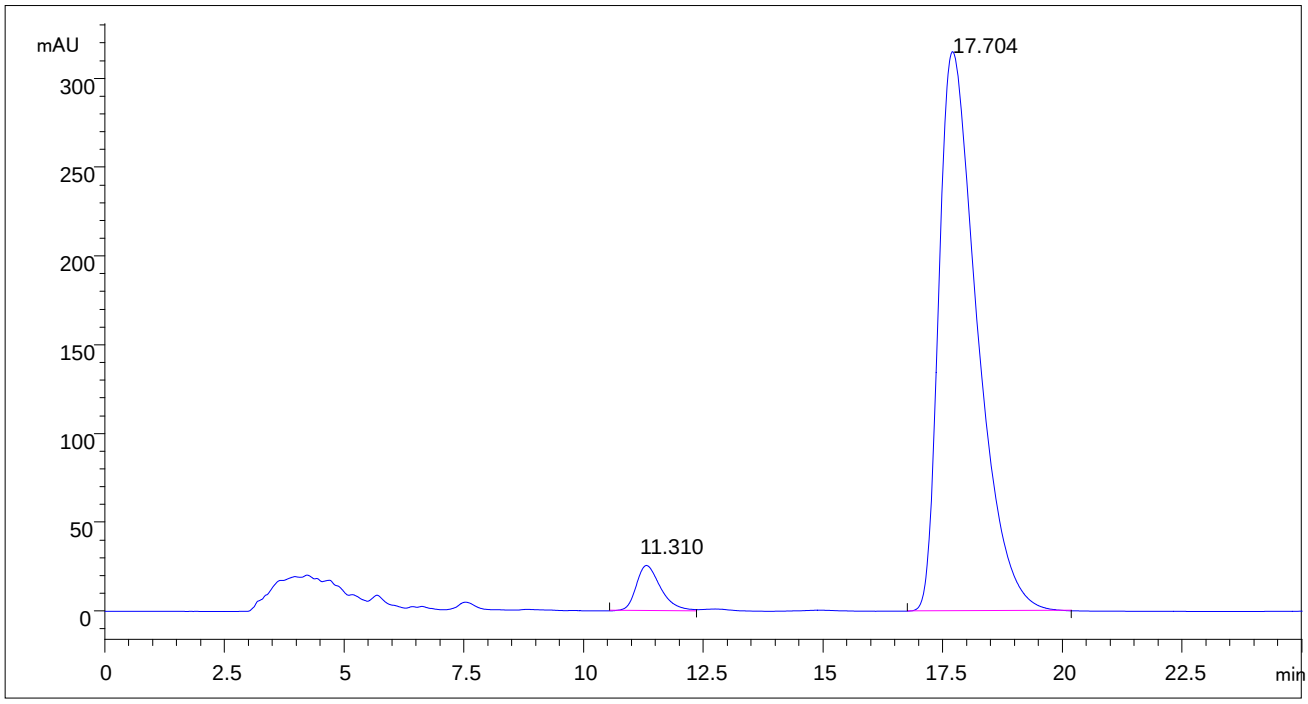
^{13}C NMR (100 MHz, DMSO-*d6*)

Racemic **1o**

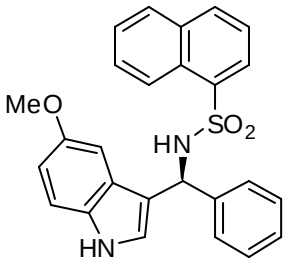


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	11.031	12220.8	360.5	0.512	0.53	50.062
2	17.661	12190.3	225.3	0.8132	0.544	49.938

Chiral **1o***

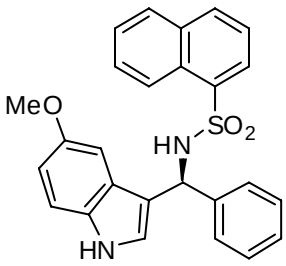


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	11.31	921.9	25.6	0.5449	0.675	4.982
2	17.704	17581	315.2	0.8401	0.517	95.018



1p*

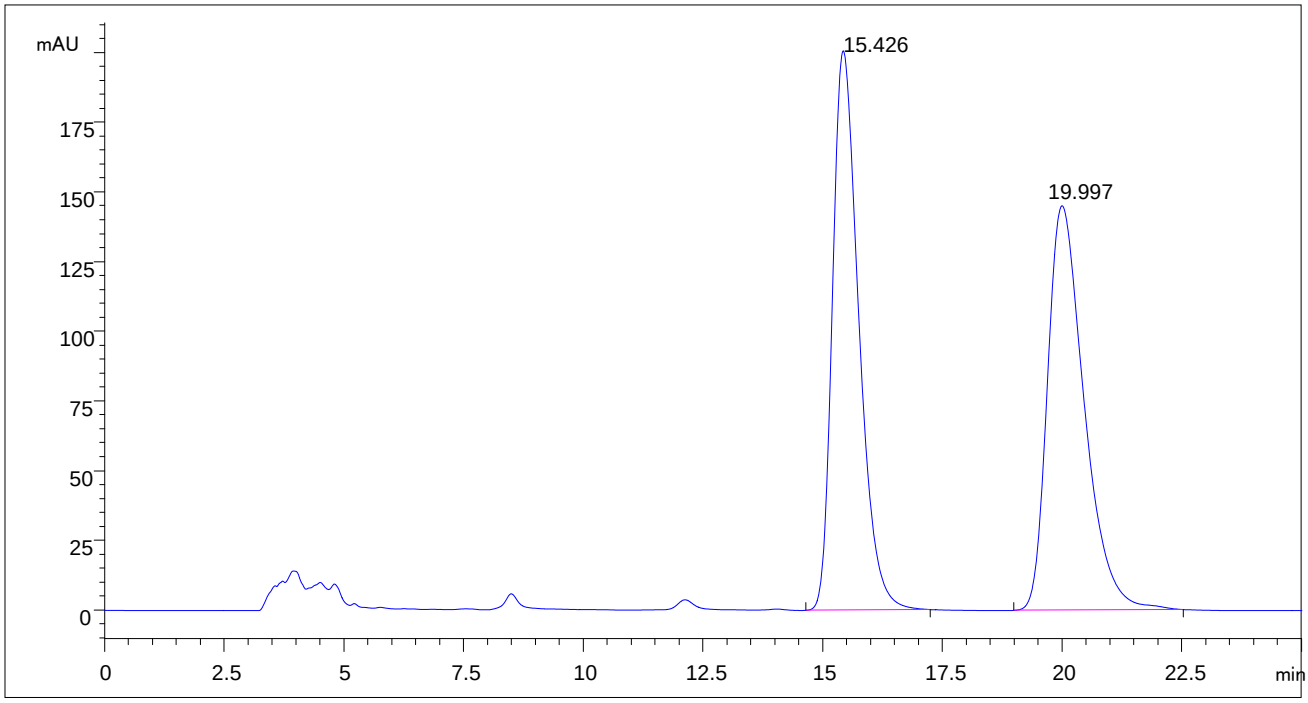
^{1}H NMR (400 MHz, DMSO-*d6*)



1p*

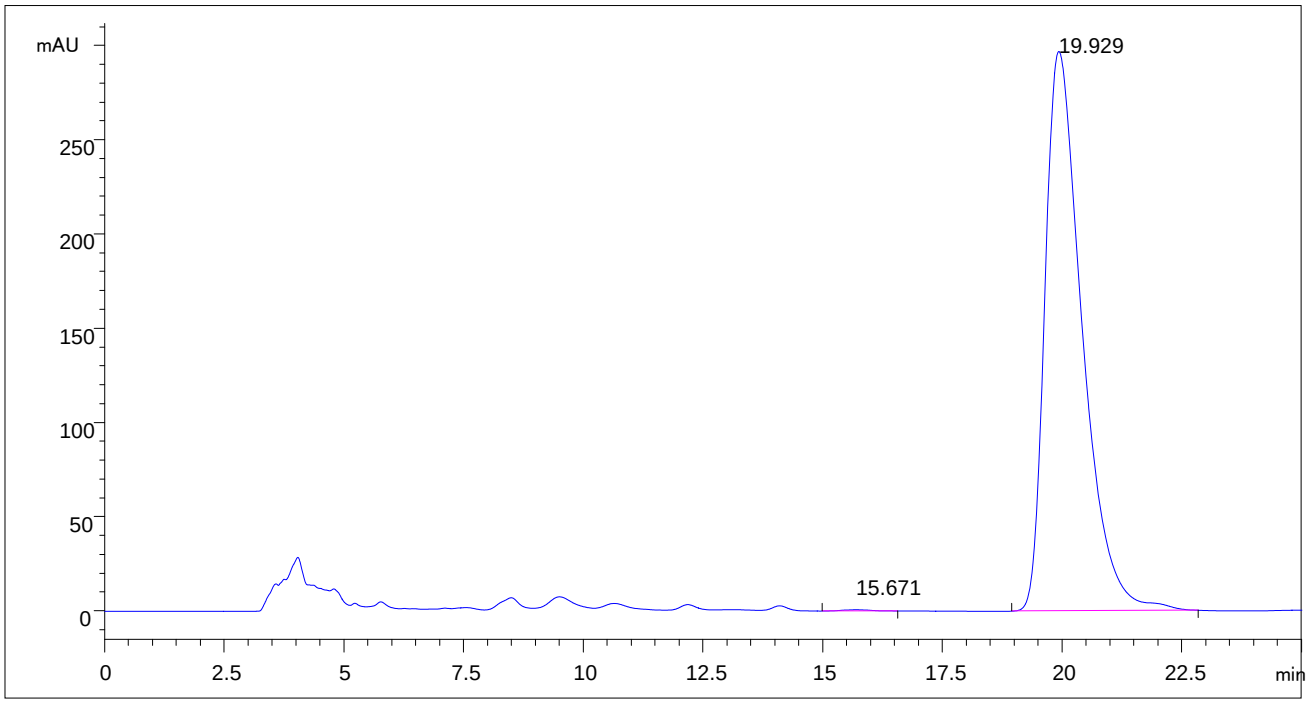
^{13}C NMR (100 MHz, DMSO-*d6*)

Racemic **1p**

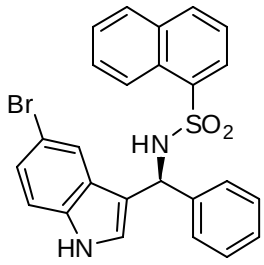


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	15.426	7683	200.7	0.5865	0.647	49.829
2	19.997	7735.7	145.1	0.8127	0.616	50.171

Chiral **1p***

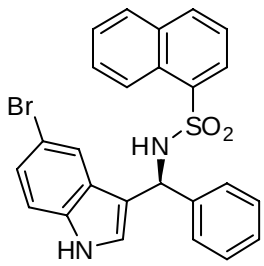


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	15.671	35.3	7.7E-1	0.7593	0.895	0.219
2	19.929	16068.6	296.8	0.8193	0.551	99.781



1q*

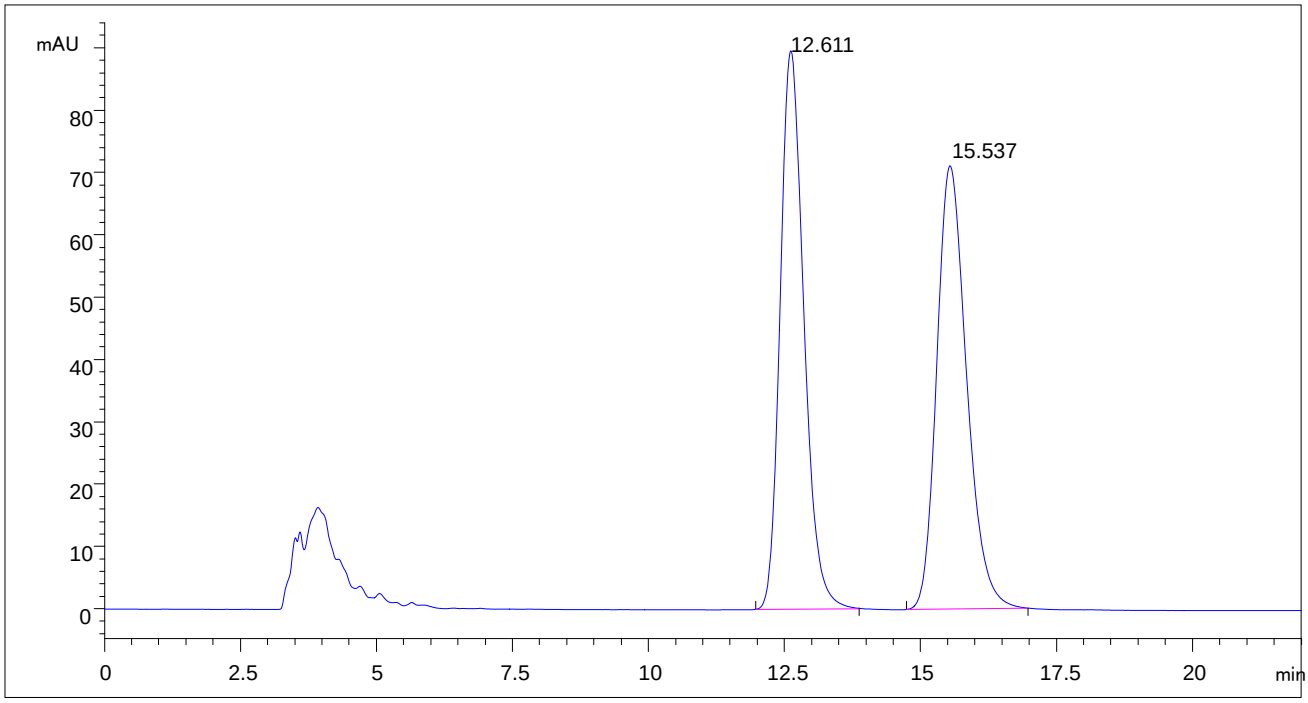
^{1}H NMR (400 MHz, DMSO-*d6*)



1q*

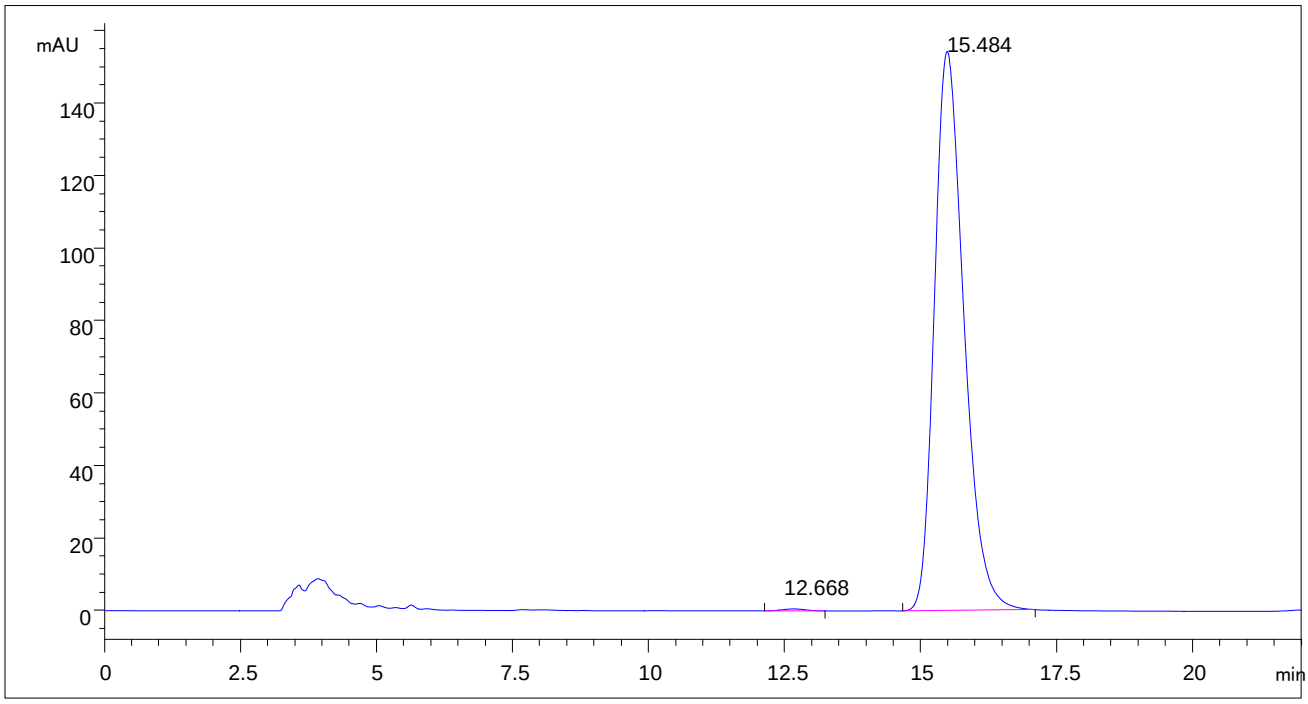
^{13}C NMR (100 MHz, DMSO-*d6*)

Racemic **1q**

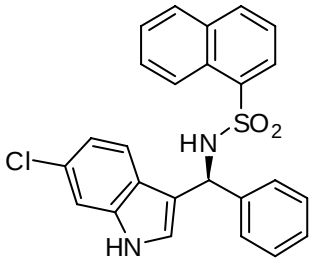


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	12.611	2716.8	89.6	0.4687	0.762	49.992
2	15.537	2717.7	71.2	0.5868	0.748	50.008

Chiral **1q***

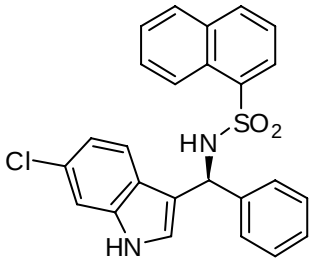


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	12.668	18.2	5.8E-1	0.5182	1.007	0.311
2	15.484	5823.9	154.3	0.5788	0.707	99.689



1r*

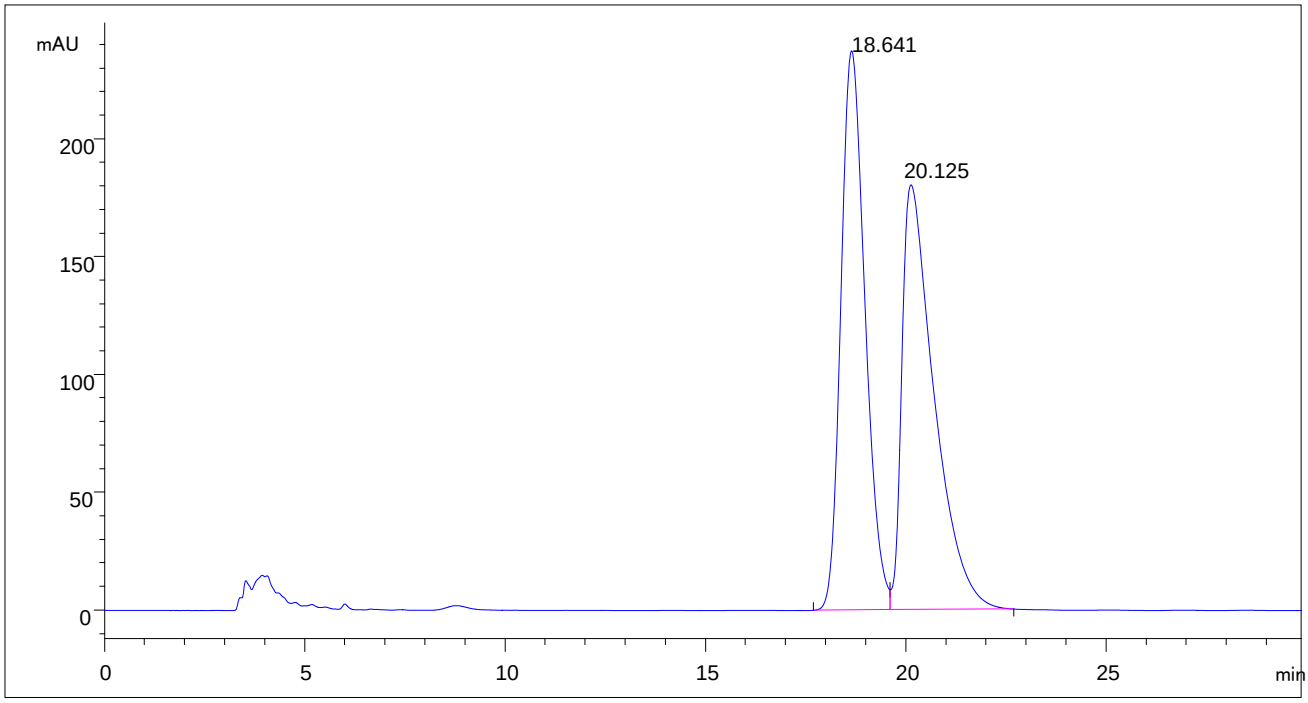
^{1}H NMR (400 MHz, DMSO-*d6*)



1r*

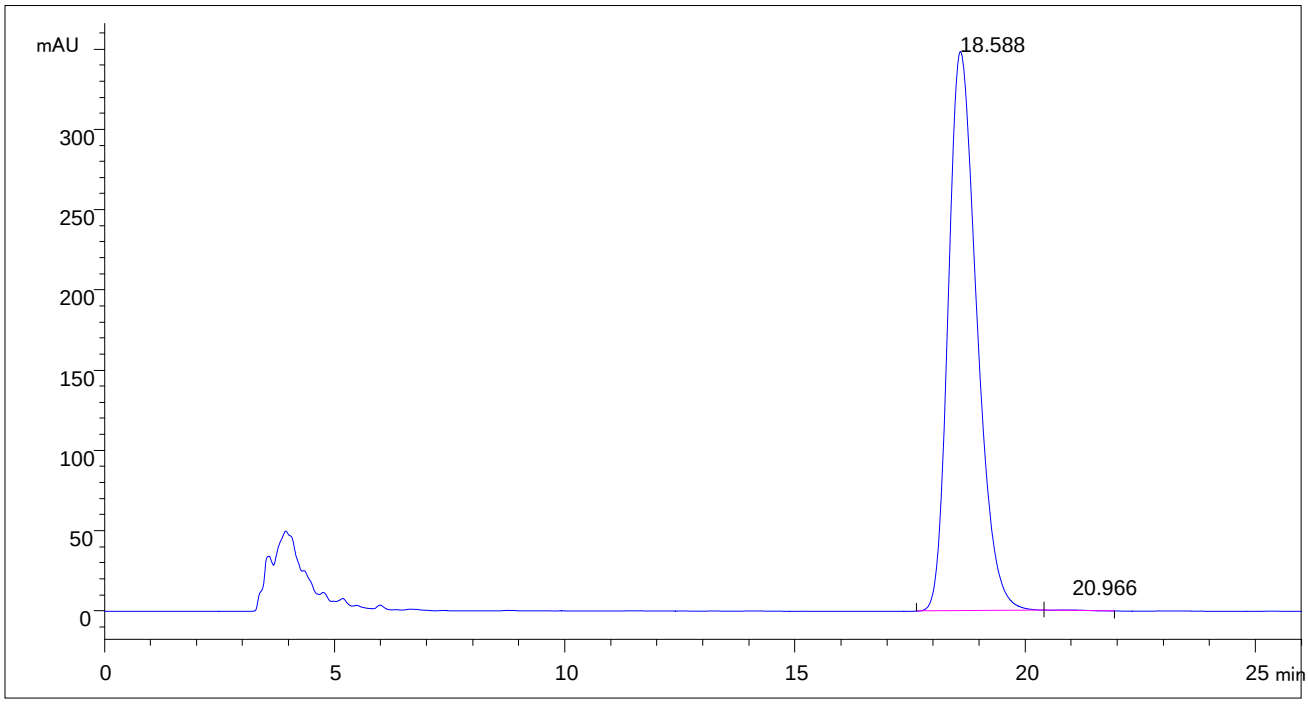
^{13}C NMR (100 MHz, DMSO-*d6*)

Racemic **1r**

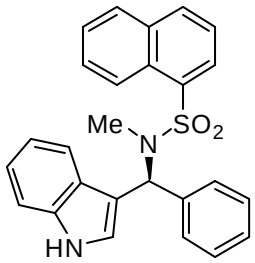


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	18.641	9973.1	237.4	0.6474	0.747	49.702
2	20.125	10092.5	180.4	0.8158	0.365	50.298

Chiral **1r***

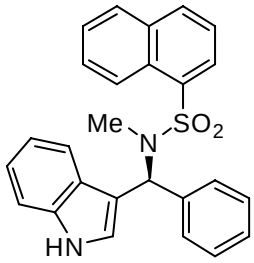


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	18.588	14998.5	348.4	0.6638	0.698	99.796
2	20.966	30.6	5.3E-1	0.9546	0.876	0.204



1s*

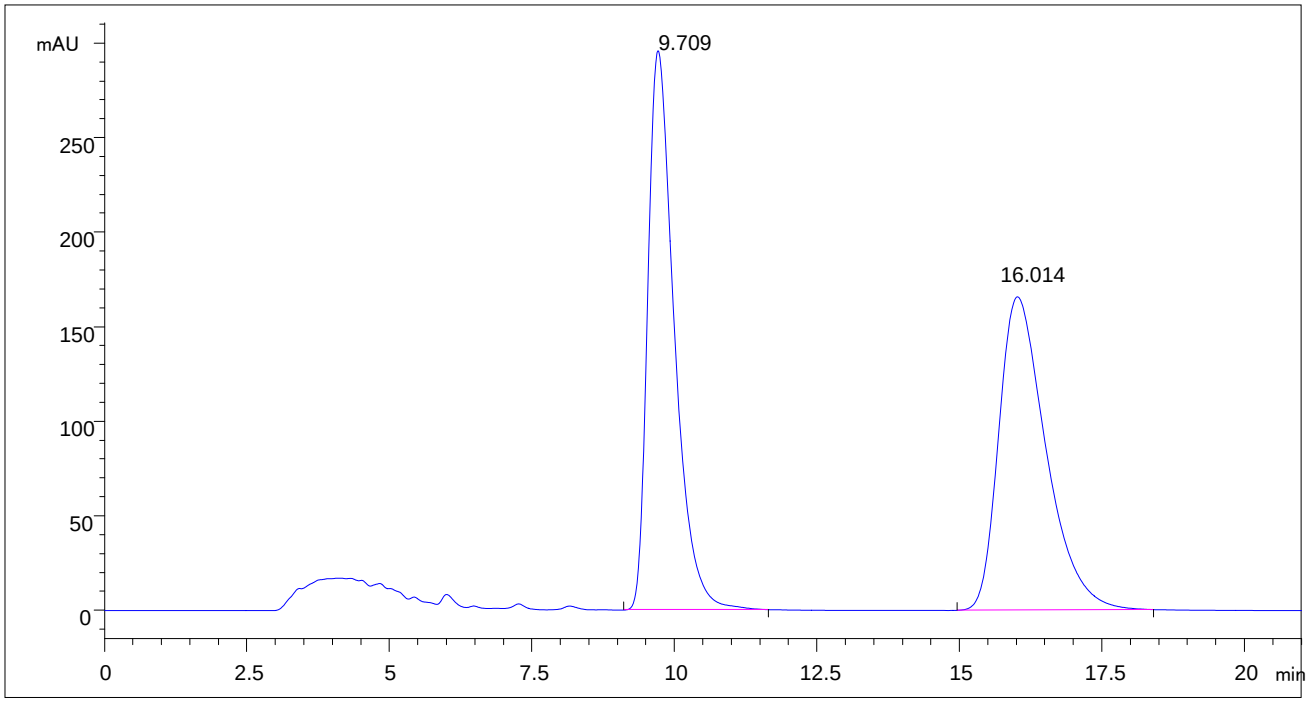
^{1}H NMR (400 MHz, DMSO-*d6*)



1s*

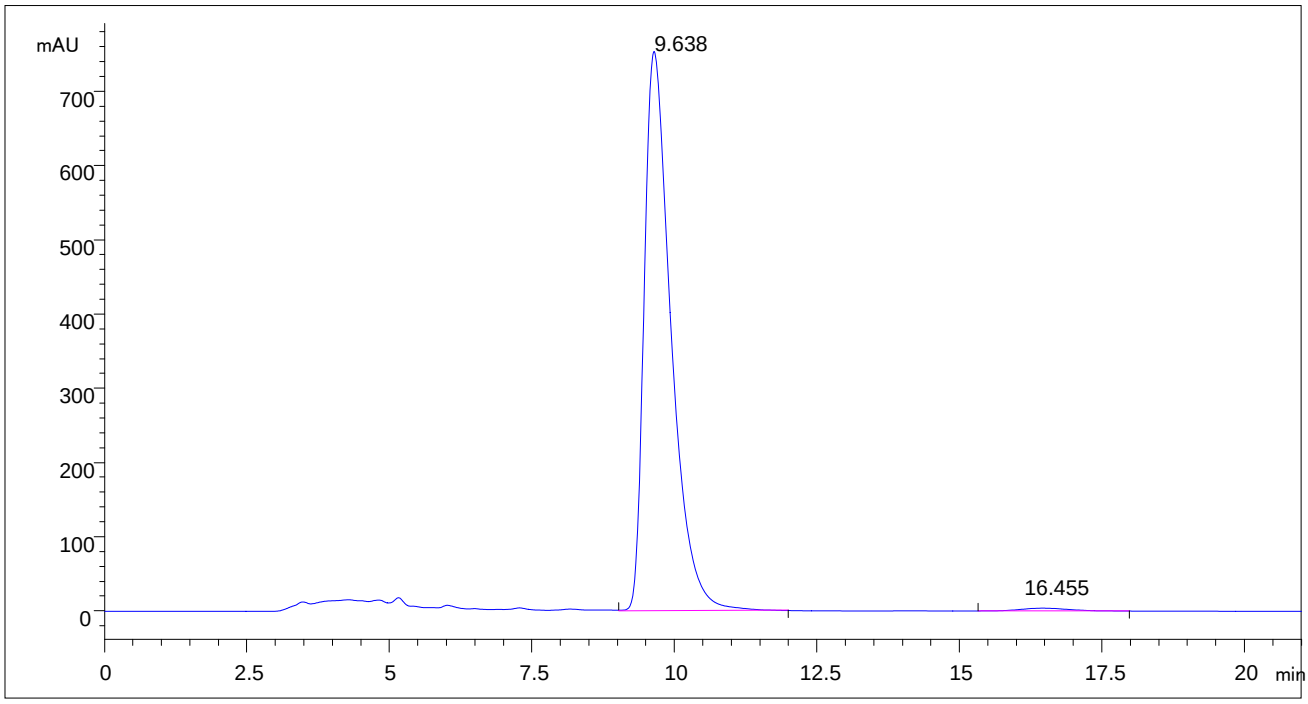
^{13}C NMR (100 MHz, DMSO-*d6*)

Racemic **1s**

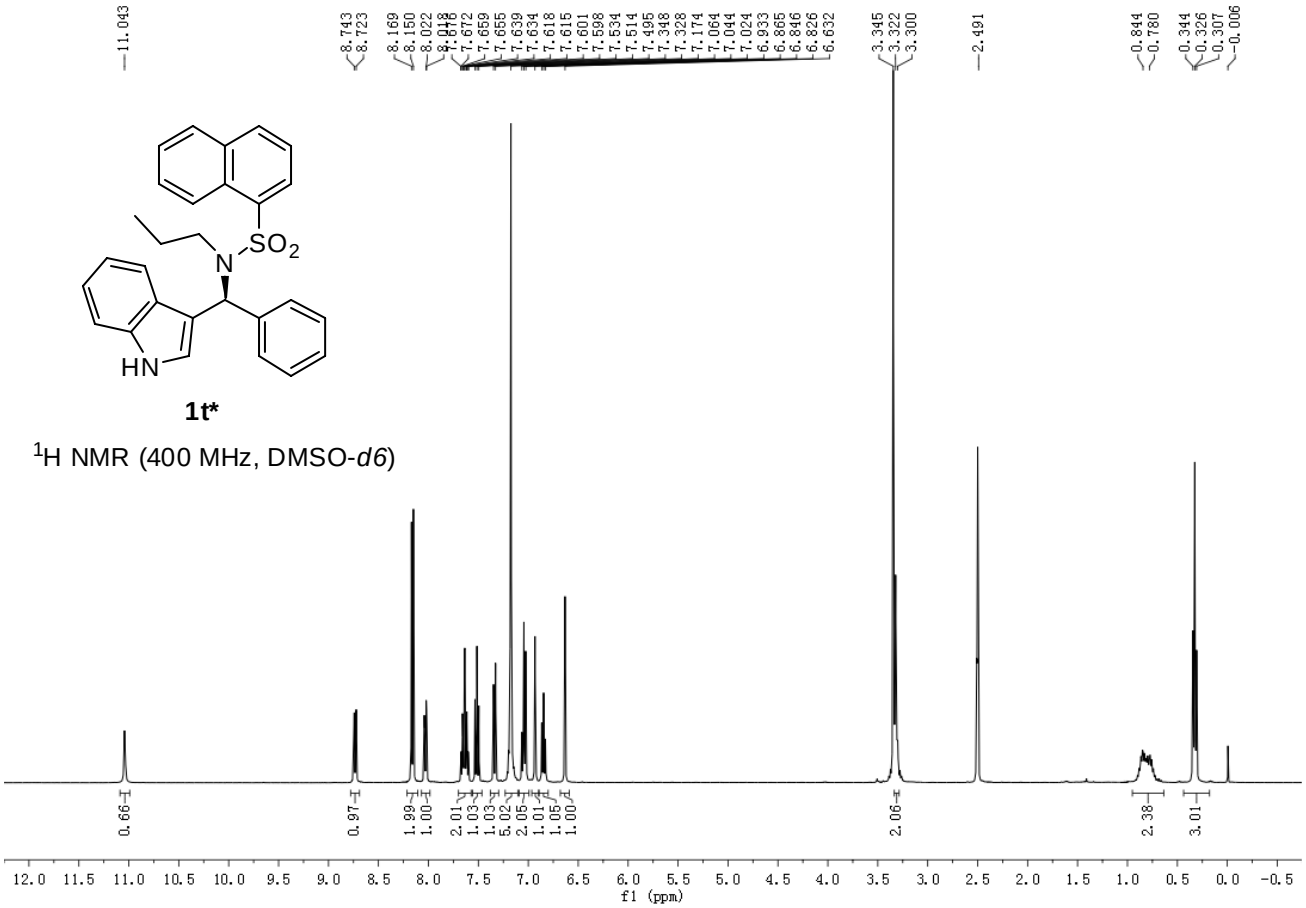


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	9.709	9588.3	295.8	0.4932	0.583	50.103
2	16.014	9548.7	165.7	0.879	0.614	49.897

Chiral **1s***

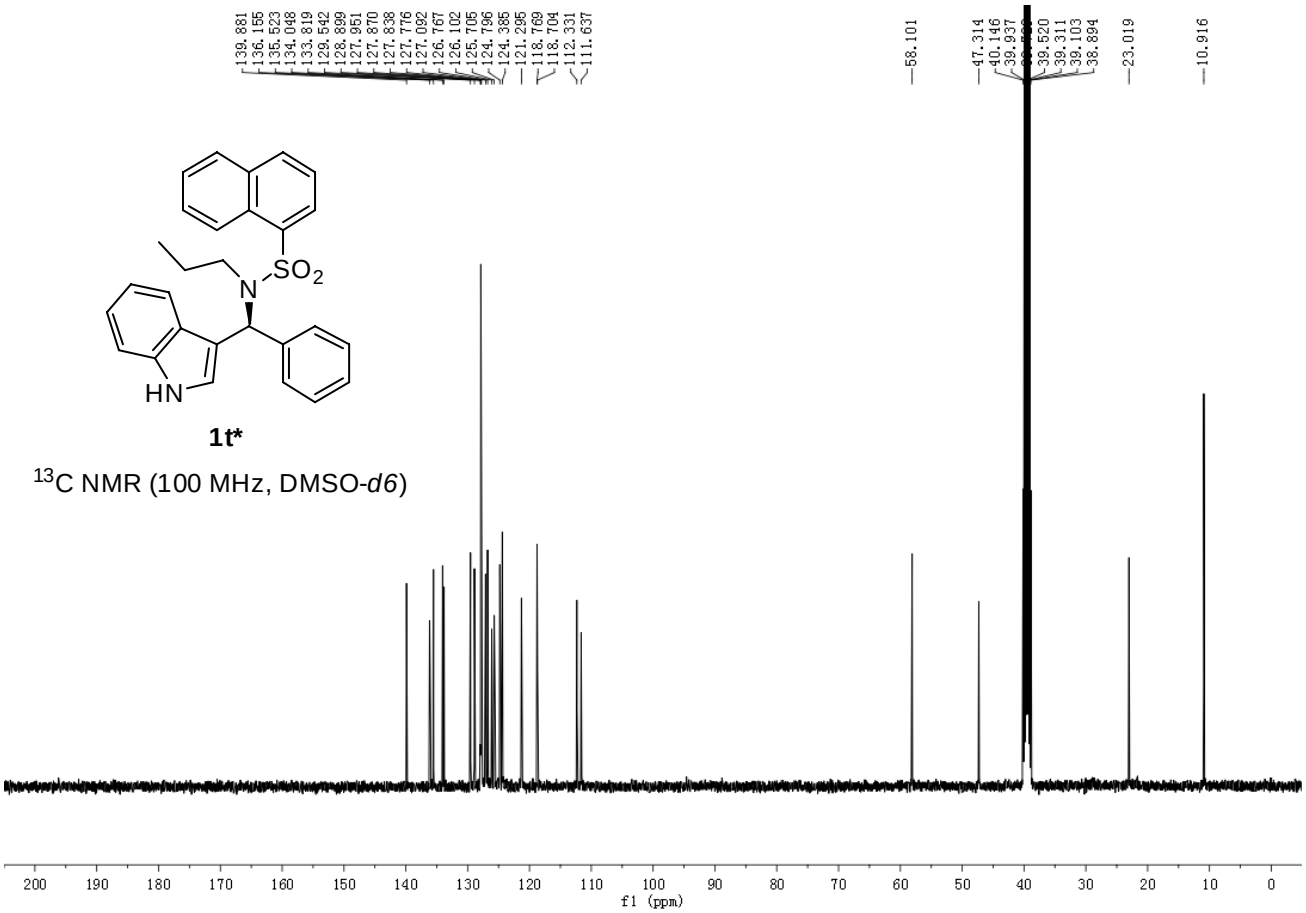


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	9.638	24730.2	753.4	0.4951	0.531	99.028
2	16.455	242.7	4	0.8704	0.827	0.972



1t*

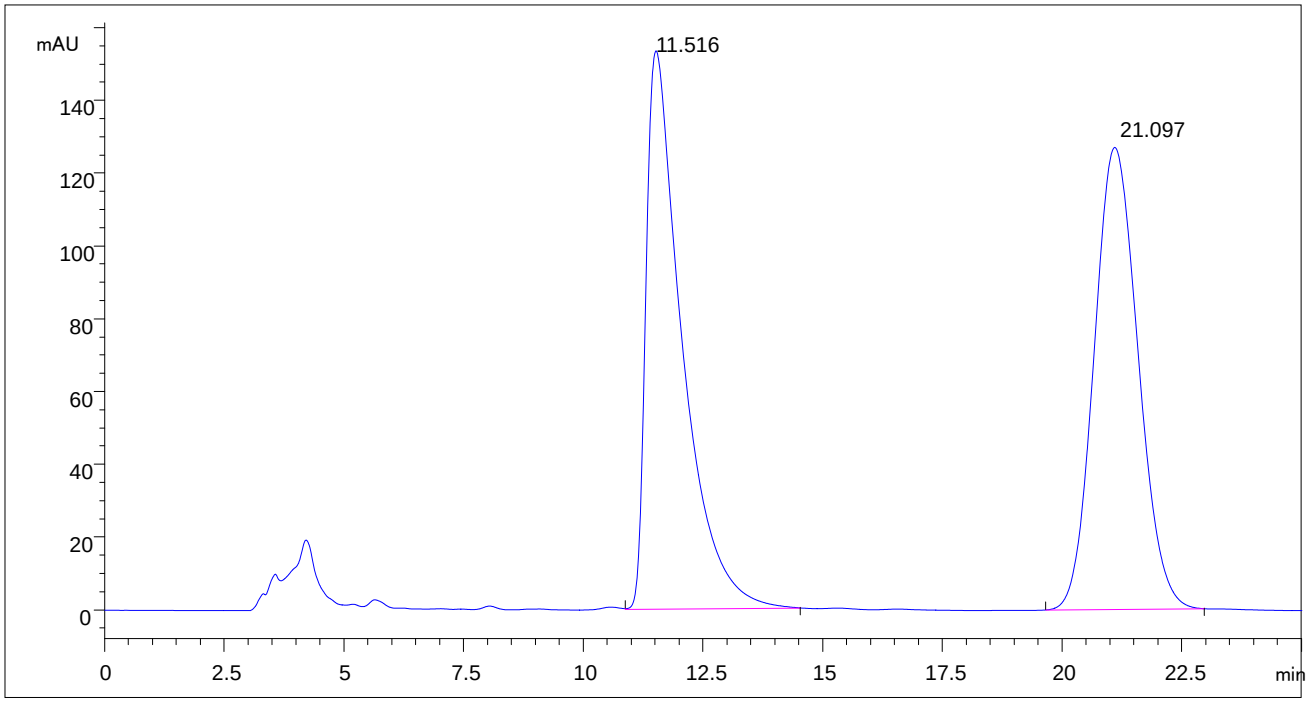
^{1}H NMR (400 MHz, DMSO-*d6*)



1t*

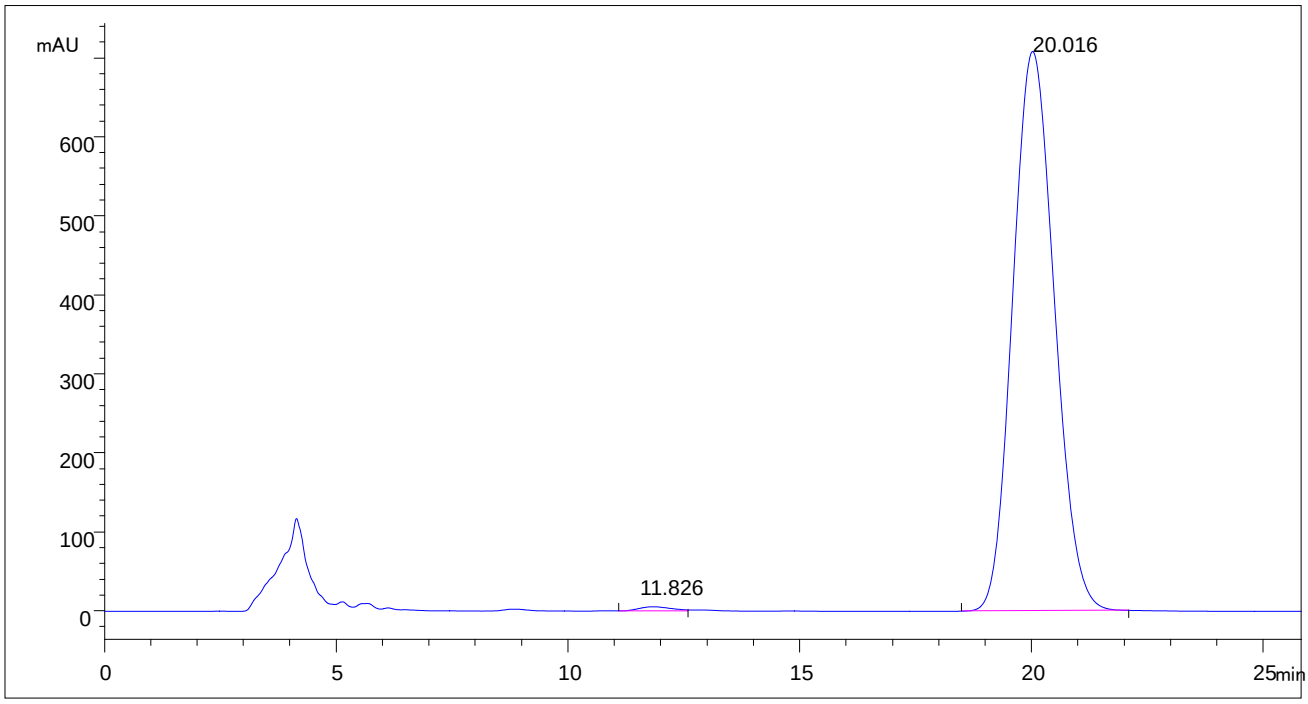
^{13}C NMR (100 MHz, DMSO-*d6*)

Racemic **1t**

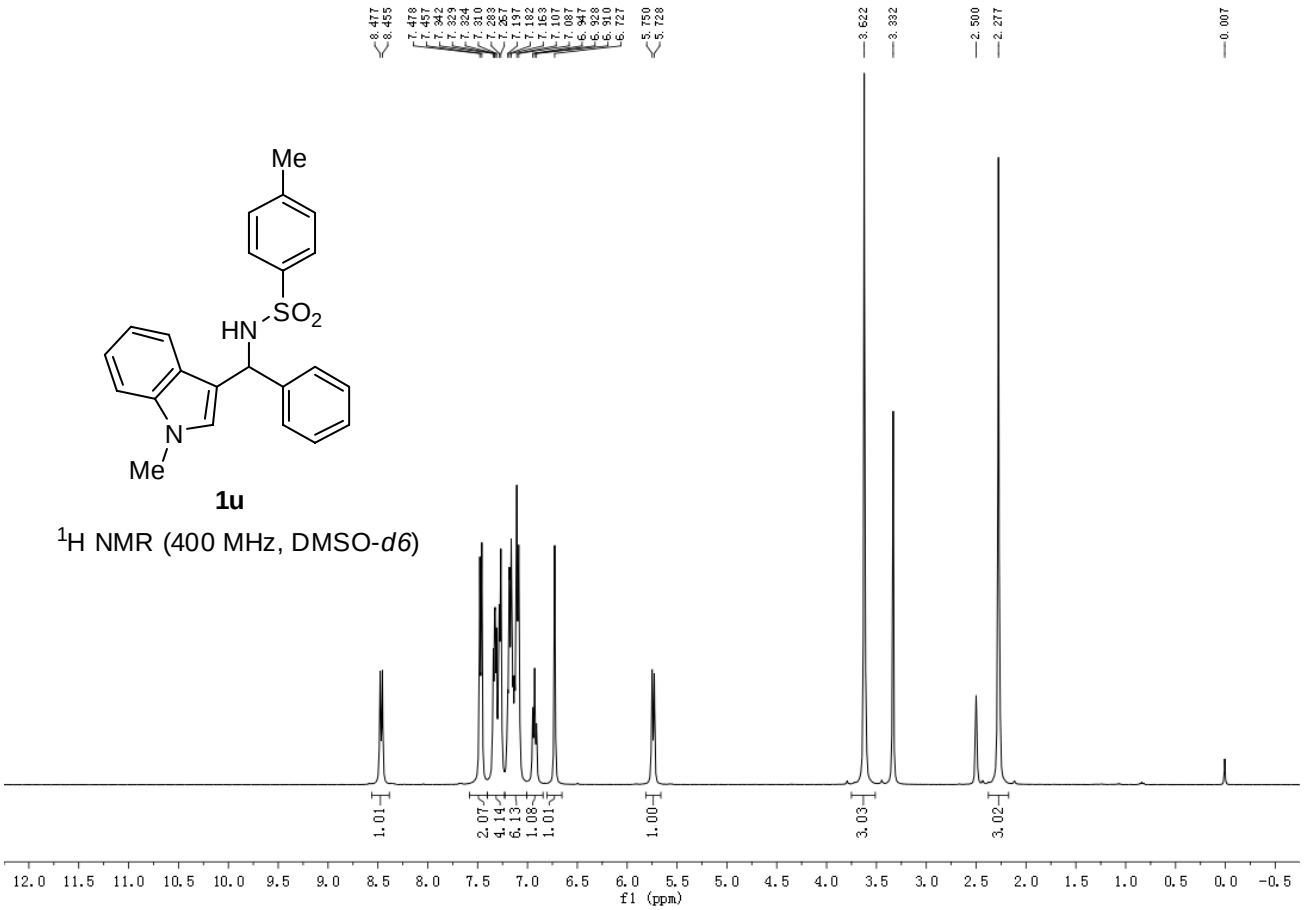


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	11.516	8044	153.5	0.7484	0.351	49.759
2	21.097	8121.8	127	1.0068	0.855	50.241

Chiral **1t***

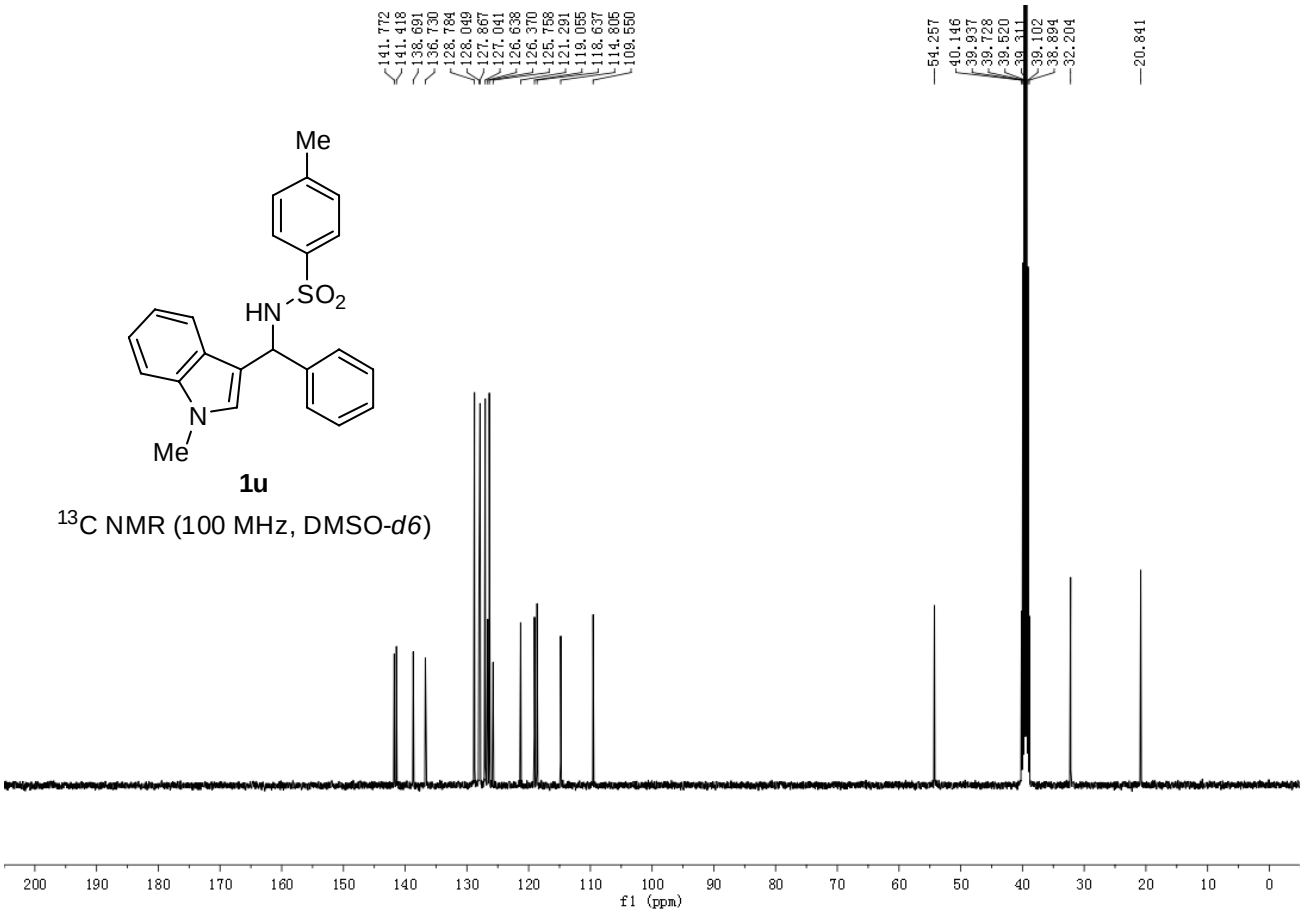


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	11.826	262.2	5.3	0.8237	0.73	0.589
2	20.016	44279.4	708	0.9903	0.868	99.411



1u

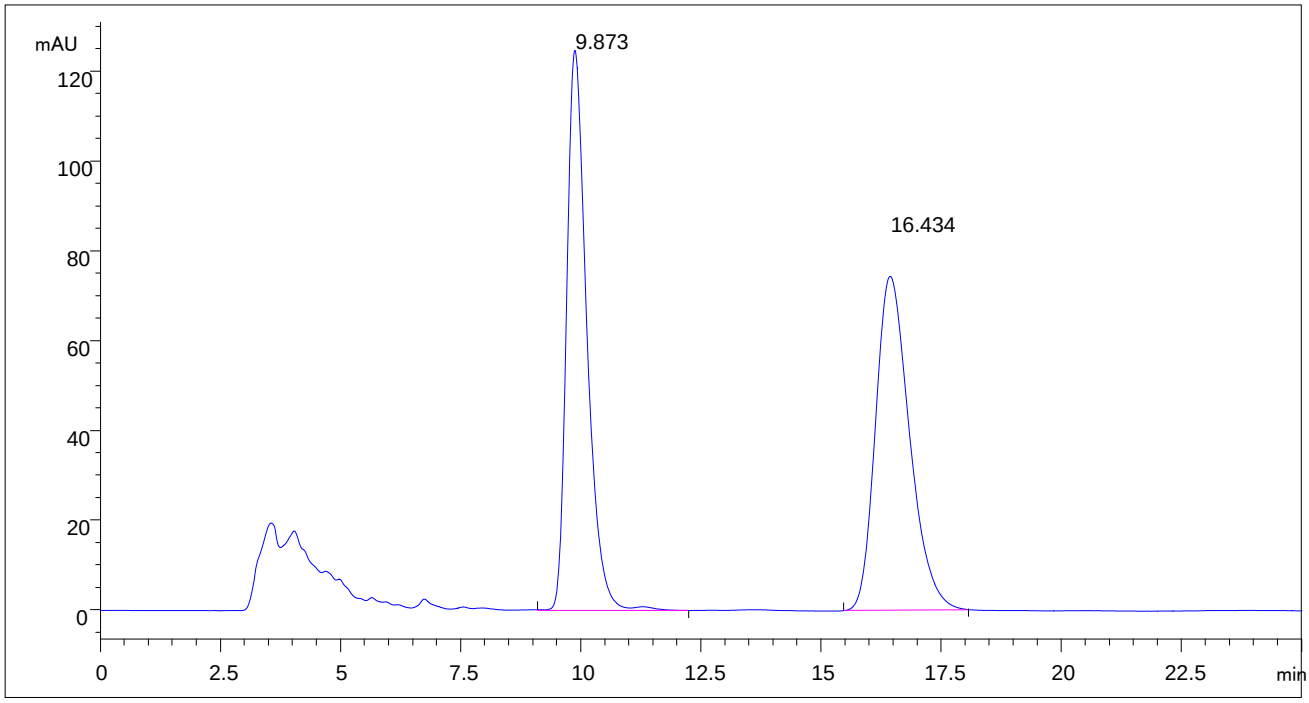
^{1}H NMR (400 MHz, DMSO-*d6*)



1u

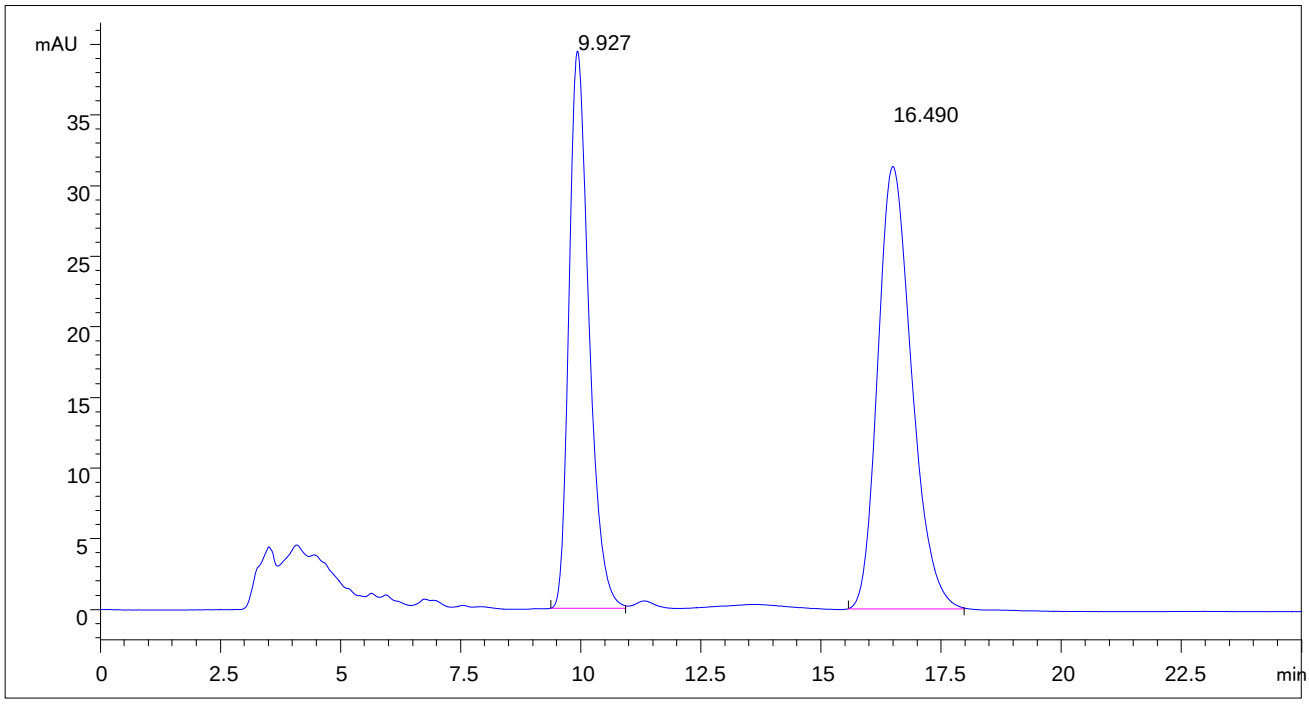
^{13}C NMR (100 MHz, DMSO-*d6*)

Racemic **1u**

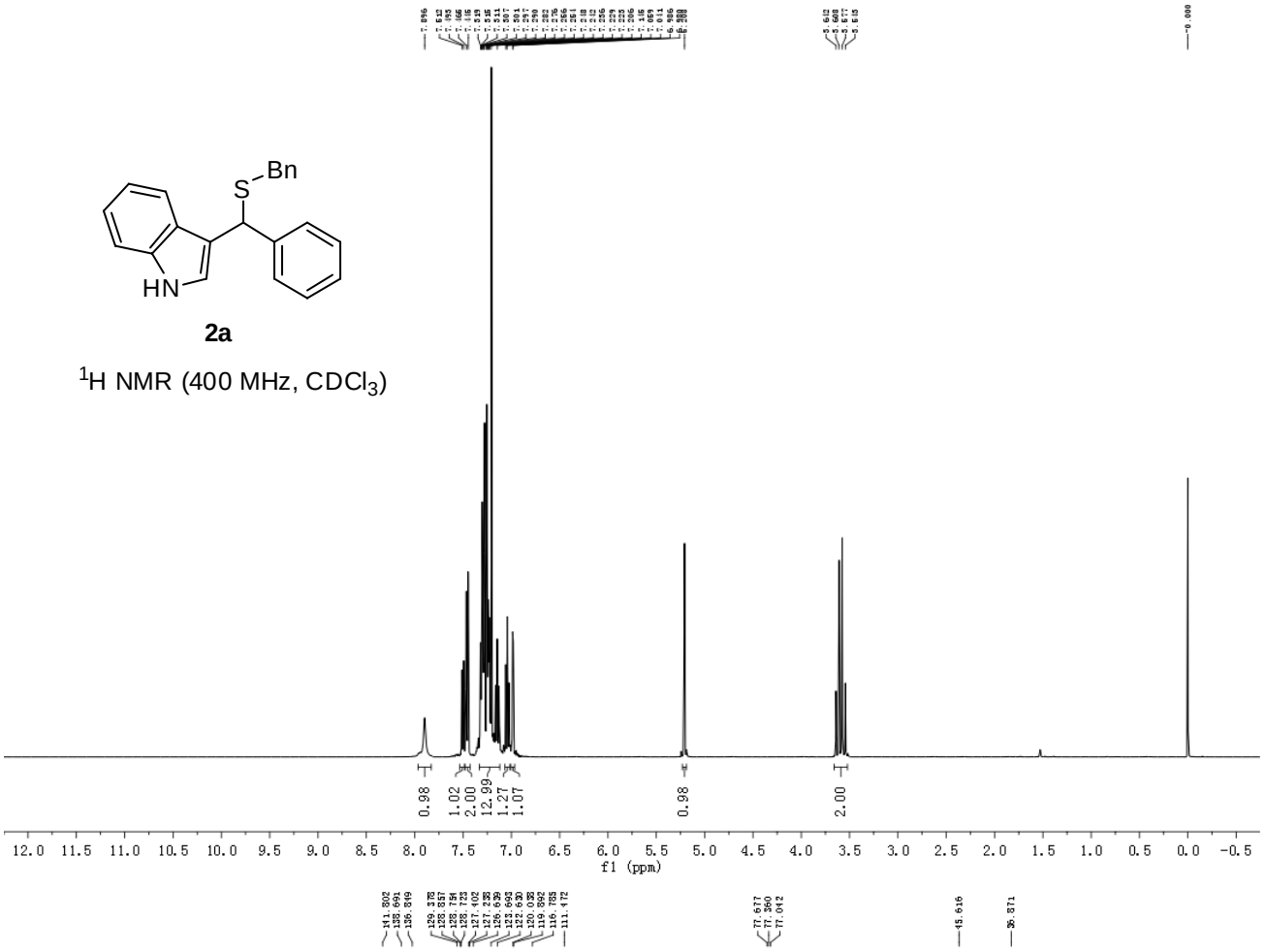


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	9.873	3651.3	124.7	0.4879	0.66	49.882
2	16.434	3668.6	74.4	0.7571	0.716	50.118

Chiral **1u***

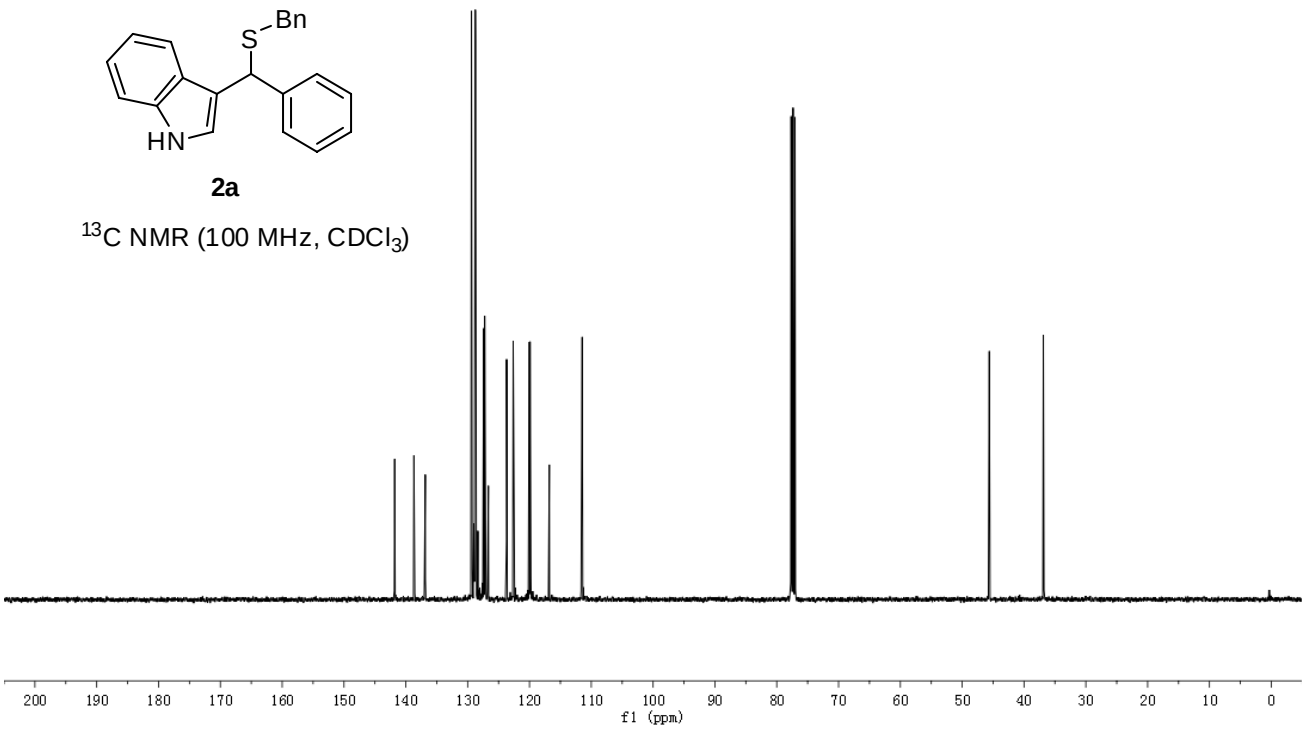


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	9.927	1145.1	39.5	0.4432	0.689	42.654
2	16.49	1539.5	31.4	0.7621	0.755	57.346



2a

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



2a

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