Synthesis of Chiral N-Free Sulfinamides by Asymmetric Condensation of Stable Sulfinates and Ammonium Salts

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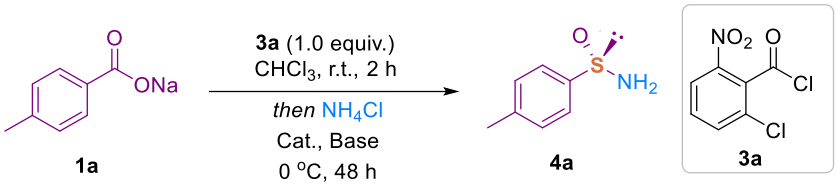
1. General information

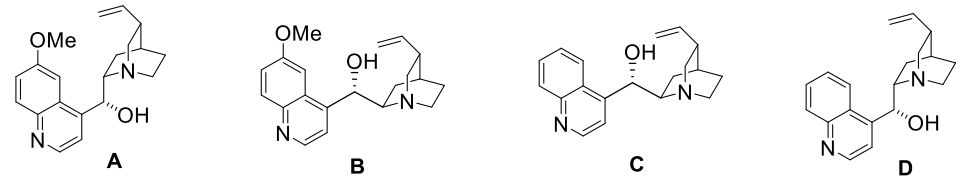
Commercially available materials purchased from J&K or Aladdin were used as received. THF was distilled over sodium. Unless otherwise specified, all reactions were carried out under an atmosphere of nitrogen in 10.0 mL dry Schlenk tube. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker (400 MHz) spectrometer or on a JEOL-ECX-500 (500 MHz) spectrometer. Chemical shifts were recorded in parts per million (ppm, δ) relative to tetramethyllsilane (δ = 0.00) or chloroform (δ = 7.26, singlet). ^{1}H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), dd (doublet of doublets); m (multiplets), and etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker (400 MHz) spectrometer. Fluorine (^{19}F) nuclear magnetic resonance (^{19}F NMR) spectra were recorded on a Bruker (AVANCE III HD 376 MHz) spectrometer. The melting points (m.p.) of the title compounds were determined when left untouched on an XT-4-MP apparatus from Beijing Tech. Instrument Co. (Beijing, China). High resolution mass spectral analysis (HRMS) was performed on a quadrupole/electrostatic field orbitrap mass spectrometer. Absolute configuration of the products was determined by X-ray crystallography. HPLC analyses were measured on Waters systems with Empower 3 system controller, Alliance 2695, and 2998 Diode Array Waters 2489 UV/Vis detector. Chiralcel brand chiral columns from Daicel Chemical Industries were used with models IA, IB, IC, ID, IG, OD-H or OJ-H in 4.6 x 250 mm size. The racemic products used to determine the er values were synthesized using racemic catalyst. Optical rotations were measured on a Insmark IP-digi Polarimeter in a 1 dm cuvette at 25 °C. The concentration (c) is given in g/100 mL. Analytical thin-layer chromatography (TLC) was carried out pre-coated silica gel plate (0.2 mm thickness). Visualization was performed using a UV lamp.

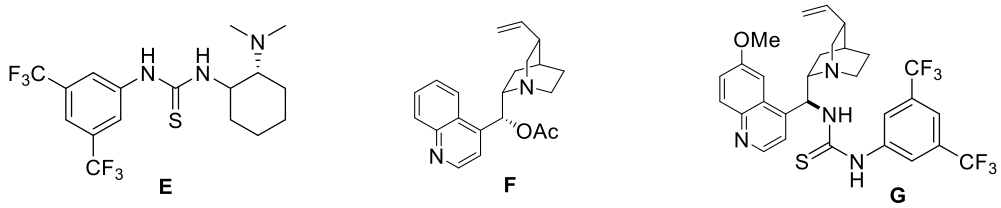
2. Experimental section

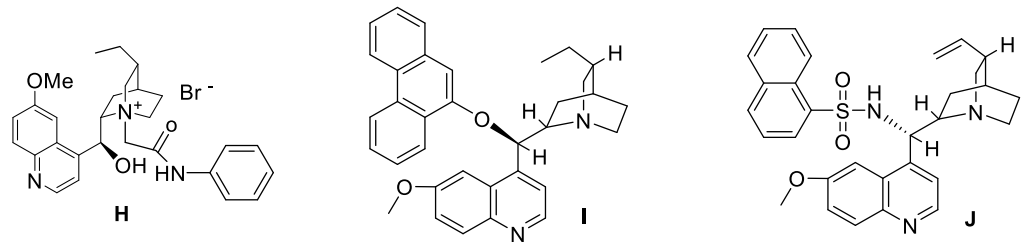
2.1 Supplemental results for asymmetric sulfinylation of amine nucleophiles reaction condition optimizations

Table S1. Screening of catalysts[a,b,c]



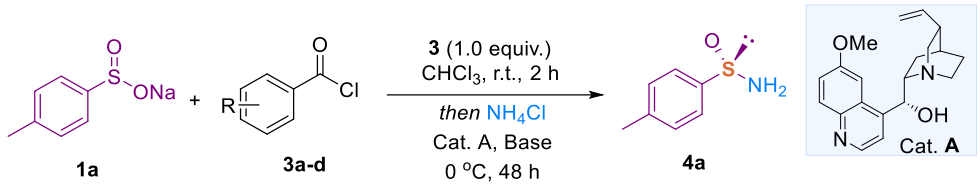






[a] Reaction conditions: sodium sulfinate **1a** (0.11 mmol, 1.1 equiv.), **3a** (0.1 mmol, 1.0 equiv.) in $CHCl_3$ (2.0 mL) at r.t. for 2 h, before reaction with Cat. (20 mol%), DIPEA (4.0 equiv.), NH_4Cl (4.0 equiv.) at 0 °C for 48 h; [b] Isolated yields were reported based on **3a**; [c] er values were determined by chiral HPLC analysis.

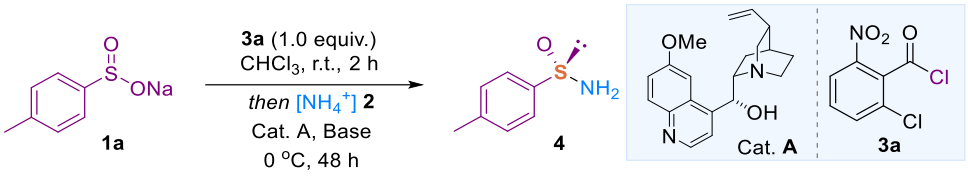
Table S2. Screening of acid chloride **3**[a,b,c]



3a	3b	3c	3d	3e
74%, 97:3 e.r.	49%, 93:7 e.r.	61%, 91:9 e.r.	31%, 82:18 e.r.	63%, 42:58 e.r.

[a] Reaction conditions: sodium sulfinate **1a** (0.11 mmol, 1.1 equiv.), **3** (0.1 mmol, 1.0 equiv.) in $CHCl_3$ (2.0 mL) at r.t. for 2 h, before reaction with Cat. **A** (20 mol%), DIPEA (4.0 equiv.), NH_4Cl (4.0 equiv.) at 0 °C for 48 h; [b] Isolated yields were reported based on **3**; [c] er values were determined by chiral HPLC analysis.

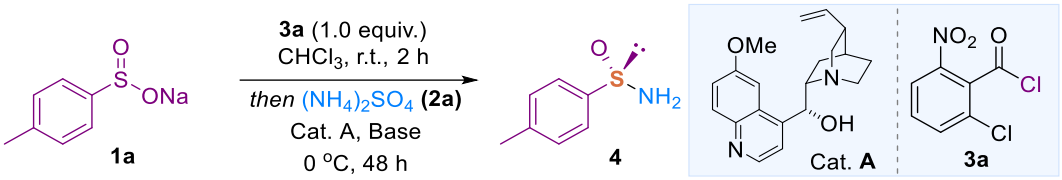
Table S3. Screening of solvents[a,b,c]



Entry	[NH_4^+]	Base	Solvent	Temp. (°C)	Yield of **4a** (%)	E.r.
1	NH_4Cl	Rb_2CO_3	$CHCl_3$	0	42	96:4
2	NH_4Cl	K_3PO_3	$CHCl_3$	0	30	40:60
3	NH_4Cl	DIPEA	$CHCl_3$	0	68	97:3
4	NH_4Cl	DIPEA	EA	0	39	49:51
5	NH_4Cl	DIPEA	toluene	0	33	47:53
6	NH_4Cl	DIPEA	DCM	0	45	96:4
7	NH_4Cl	DIPEA	DCE	0	48	96:4
8	NH_4Cl	DIPEA	THF	0	56	53:47
9	**$(NH_4)_2SO_4$**	**DIPEA**	**$CHCl_3$**	**0**	**74**	**97:3**
10	$(NH_4)_2SO_4$	DIPEA	$CHCl_3$	-20	63	96:4
11	$(NH_4)_2SO_4$	DIPEA	$CHCl_3$	-10	64	97:3
12	$(NH_4)_2SO_4$	DIPEA	$CHCl_3$	25	74	90:10

[a] Reaction conditions: sodium sulfinate **1a** (0.11 mmol, 1.1 equiv.), **3a** (0.1 mmol, 1.0 equiv.) in solvent (2.0 mL) at r.t. for 2 h, before reaction with Cat. **A** (20 mol%), base (4.0 equiv.), salt (4.0 equiv.) at 0 °C for 48 h; [b] Isolated yields were reported based on **3a**; [c] er values were determined by chiral HPLC analysis.

Table S4. Screening of the amount of used ammonium and base[a,b,c]

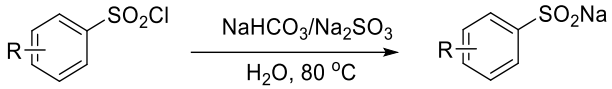


Entry	equiv. [NH_4^+]	equiv. (base)	Yield of **4a** (%)	E.r.
1	1.0	1.0	50	93:7
2	2.0	2.0	63	96:4
3	4.0	4.0	74	97:3
4	6.0	6.0	67	97:3
5	8.0	8.0	64	95:5
6	10.0	10.0	61	94:6

[a] Reaction conditions: sodium sulfinate **1a** (0.11 mmol, 1.1 equiv.), **3a** (0.1 mmol, 1.0 equiv.) in $CHCl_3$ (2.0 mL) at r.t. for 2 h, before reaction with Cat. **A** (20 mol%), DIPEA, salt at 0 °C for 48 h; [b] Isolated yields were reported based on **3a**; [c] er values were determined by chiral HPLC analysis.

2.2 Typical procedure for preparation of sulfinate salts and racemic sulfinate amide products

Scheme S1. Preparation of sulfinates from sulfonyl chlorides **1**[1]

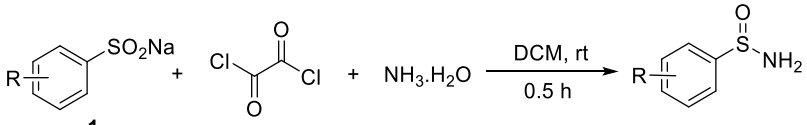


S1 **1**

A mixture of sulfonyl chloride **S1** (2.0 mmol, 1.0 equiv.), sodium sulfite (4.0 mmol, 2.0 equiv.) and sodium bicarbonate (4.0 mmol, 2.0 equiv.) dissolved in water (10.0 mL) was heated at 80 °C for 4-6 h under N_2 atmosphere. After cooing to room temperature, water was removed under vacuum to give the solid residue. After extraction with ethanol and filtration, the resulted filtrate was concentrated to give the resulting sodium sulfinate, which was washed with Et_2O (20.0 mL), collected by filtration, and dried under vacuum for 4 h to afford the starting material **1**.

Synthesis of racemic sulfinamides 4-5

Scheme S2. General procedure for synthesis of racemic sulfinamide **4a-5c**[2]



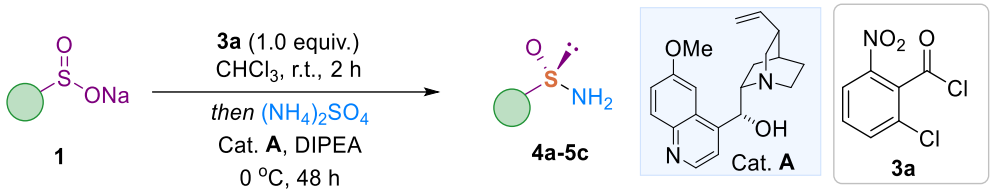
1 (±)-**4a-5c**

To a solution of sulfinate salt **1** (0.1 mmol), oxalyl chloride (0.11 mmol, 1.1 equiv.) in DCM (1.0 mL) was added ammonium hydroxide (0.15 mmol, 1.5 equiv.). The mixture was stirred at 0 °C for 30 min and then purified by flash chromatography (Petroleum ether / Ethyl acetate = 1:1) to afford the racemic sulfinamide **4a-5c**.

2.3 General procedure for catalytic enantioselective sulfinamide synthesis

Typical procedure for asymmetric synthesis of sulfinamide **4a-5c**

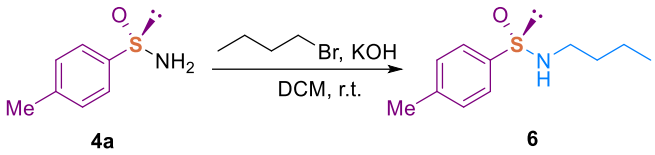
Asymmetric synthesis of sulfinamides (General Procedure A)



Under N_2 atmosphere, to an oven-dried 10.0 mL screw cap vial charged with a magnetic stirring bar was added **1** (0.11 mmol, 1.1 equiv.), **3a** (22.0 mg, 1.0 equiv.) in $CHCl_3$ (2.0 mL) at r.t. for 2 h, before reaction with Cat. **A** (6.49 mg, 0.02 mmol), DIPEA (69.67 mL, 4.0 equiv.), $(NH_4)_2SO_4$ (52.85 mg, 4.0 equiv.) at 0 °C for 48 h. After concentration *in vacuo*, the crude residue was purified by column chromatography on silica gel (Petroleum ether / Ethyl acetate = 5/1~1/1) to afford the desired sulfinamide product **4a-5c**.

2.4 Synthetic transformations of sulfinamide products

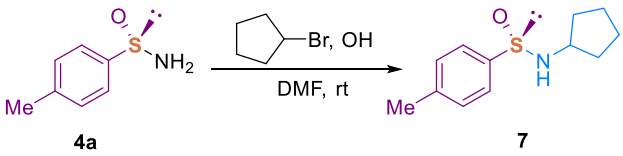
Scheme S3. Preparation of **6** from **4a**[3]



4a **6**

To a solution of **4a** (18.6 mg, 0.12 mmol, 1.2 equiv.) in THF (1.0 mL) was added *n*-butyl bromide (17.1 mg, 0.1 mmol, 1.0 equiv.) and potassium hydroxide (8.4 mg, 0.15 mmol, 1.5 equiv.). After stirring for 4 h, the reaction was quenched with saturated NH_4Cl aqueous solution and extracted with EtOAc. The combined organic layers were washed with brine and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to afford **6** (yellow oil, 13.7 mg, 78%, 96:4 e.r.).

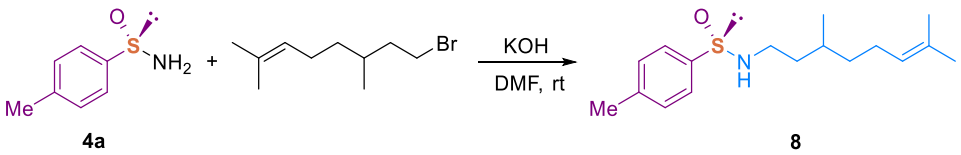
Scheme S4. Preparation of **7** from **4a**[3]



4a **7**

To a solution of **4a** (18.6 mg, 0.12 mmol, 1.2 equiv.) in THF (1.0 mL) was added cyclopentyl bromide (17.1 mg, 0.1 mmol, 1.0 equiv.) and potassium hydroxide (8.4 mg, 0.15 mmol, 1.5 equiv.). After stirring for 4 h, the reaction was quenched with saturated NH_4Cl aqueous solution and extracted with EtOAc. The combined organic layers were washed with brine and concentrated in *vacuo*. The residue was purified by column chromatography on silica gel to afford **7** (colorless oil, 13.9 mg, 75%, 96:4 e.r.).

Scheme S5. Preparation of **8** from **4a**[3]

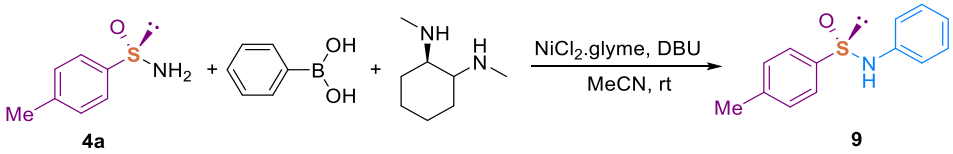


4a **8**

To a solution of **4a** (18.6 mg, 0.12 mmol, 1.2 equiv.) in THF (1.0 mL) was added 8-bromo-2,6-dimethyloct-2-ene (17.1 mg, 0.1 mmol, 1.0 equiv.) and potassium hydroxide (8.4 mg, 0.15 mmol, 1.5 equiv.). After stirring for 4 h, the reaction was quenched with saturated NH_4Cl aqueous solution and extracted with EtOAc. The

combined organic layers were washed with brine and concentrated in *vacuo*. The residue was purified by column chromatography on silica gel to afford **8** (yellow oil, 16.1 mg, 66%, 97:3 e.r.).

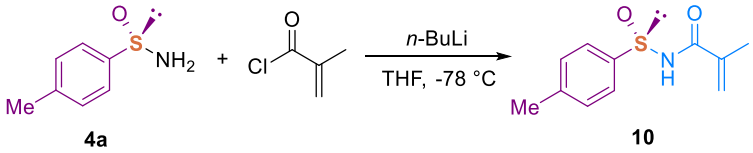
Scheme S6. Preparation of **9** from **4a**[4]



4a **9**

To a solution of $NiCl_2$.glyme (0.2 mmol, 0.2 equiv.) and *N*-2-dimethyicyclohexane-1,2-diamine (0.2 mmol. 0.2 equiv.) in MeCN (1.0 mL) was added DBU (2 mmol 2.0 equiv.). Stir the mixture open to air at room temperature until the color of system has changed. Then sulfinamide **4a** (1.0 mmol, 1.0 equiv.) and aryl boronic acid (1.3 mmol, 1.3 equiv.) were successively added into the system. After stirring for several hours, the reaction was quenched with water and extracted with ethyl acetate for 3 times. Dry the combined organic phase over Na_2SO_4 and concentrate *in vacuo*, then the resultant was purified by chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) to afford **9** (white solid, 16.9 mg, 73%, 96:4 e.r.).

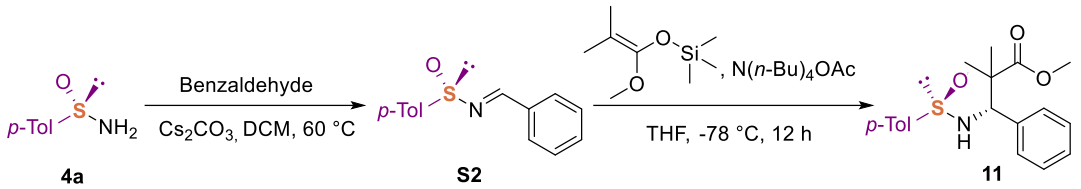
Scheme S7. Preparation of **10** from **4a**



4a **10**

Under nitrogen, sulfinamide **4a** (1.0 mmol, 1.0 equiv.) was dissolved in THF (2.0 mL) and cooled to -78 °C, before an *n*-butyllithium (1.2 mmol, 1.2 equiv.) solution was added dropwise. After stirring for 20 minutes, the reaction was quenched with HCl (aq.) and extracted with ethyl acetate for 3 times. Dry the combined organic phase over Na_2SO_4 and concentrate *in vacuo*, then the residue was purified by column chromatography on silica gel to afford **10** (colorless oil, 15.6 mg, 70%, 93:7 e.r.).

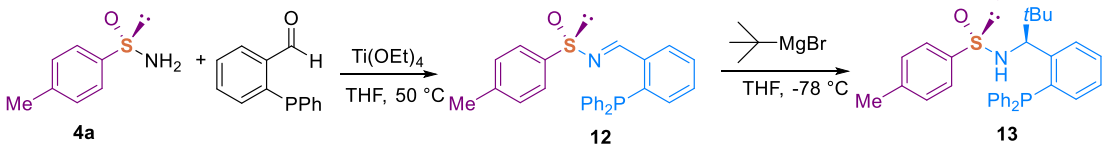
Scheme S8. Preparation of **11** from **4a**[5-6]



To a solution of **4a** (46.6 mg, 0.3 mmol, 1.0 equiv.) and benzaldehyde (31.7 mg, 0.3 mmol, 1.0 equiv.) in DCM (10.0 mL), was added pyrrolidine (2.1 mg, 0.03 mmol, 0.1 equiv.). The mixture was stirred in a sealed vial at 60 °C for 1 h. After concentration *in vacuo*, a residue was afforded and could be spin dried without further purification for the next step.

((1-methoxy-2-methylprop-1-en-1-yl) oxy) trimethylsilane (1.4 equiv.), **S2** (20.0 mg, 1.0 equiv.) and N(*n*-Bu)$_4$OAc (10 mol%) in THF (2.0 mL) was stirred at -78 °C for 12 h. The residue was purified by column chromatography on silica gel to afford **11** (colorless oil, 37.6 mg, 80%, 93:7 e.r.), >5.6:1 dr (determined by HPLC).

Scheme S9. Preparation of **12-13** from **4a**[7]

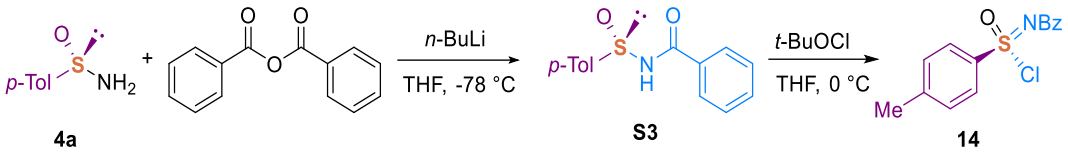


A solution of sulfinamide **4a** (0.32 mmol), 2-(diphenylphosphino)-benzaldehyde (0.32 mmol) and Ti(OEt)$_4$ (0.15 ml, 0.64 mmol) in THF (1.3 ml) was stirred at 50 °C for 12 h. Purification of the product by chromatography (80/20 hexane/EtOAc) afforded the intermediate **12** (yellow solid, 53.0 mg, 53%, 94:6 e.r.).

Cool the solution of *N*-sulfinylimine **12** (0.12 mmol, 1.0 equiv.) in anhydrous THF (0.4 mL) to -78 °C, add *tert*-butyl magnesium chloride solution (1.5 equiv., 0.5 M in THF) dropwise to the mixture, allow the mixture to stir until complete by TLC (approximately 5 hours), quench the reaction with saturated aqueous ammonium chloride. Extract the reaction mixture three times with EtOAc, wash the combined organics with brine. Dry the combined organics with sodium sulfate. Concentrate the combined organics in vacuo. Purification of the product by column chromatography (petroleum ether: ethyl acetate = 5:1) afforded **13** as a white solid (37.1 mg, 70%, >20:1

dr (determined by ^{1}H NMR)).

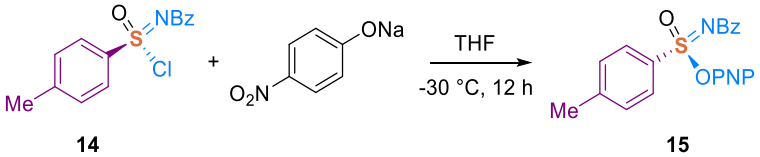
Scheme S10. Preparation of **14** from **4a**[8]



According to a published procedure,[8] **4a** (1.0 mmol, 1.0 equiv.) was dissolved in THF (14.0 mL) and cooled to -78 °C. At this temperature, *n*-BuLi (1.6 M in *n*-hexane, 2.1 equiv.) was added slowly over a period of 5 min, followed by benzoic anhydride (1.2 equiv.) as a solid in one portion. The reaction was allowed to warm up to room temperature overnight. To the mixture was added a saturated aqueous solution of NH_4Cl (5.0 mL), extracted with EtOAc (3 x 30 mL), dried with brine and Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (CH_2Cl_2/ MeOH = 100:1).

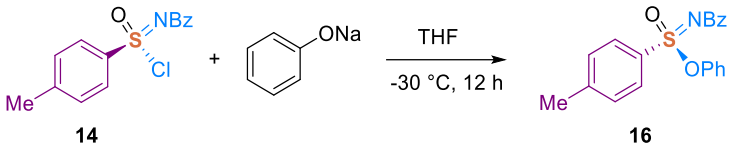
tert-Butyl hypochlorite (0.16 mL, 1.2 equiv.) was added dropwise to a solution of compound **S3** (0.3 g, 1.0 equiv.) in anhydrous THF (10.0 mL) at 0 ℃ under argon atmosphere. The mixture was stirred for 2 hours at 0 ℃. After work-up, the residue was purified quickly through a flash column chromatography (5% ethyl acetate in hexane) to afford **14** (white solid, 0.18 g, 60%, 96:4 e.r.).

Scheme S11. Preparation of **15** from **4a**[8]



In a 25 mL vial containing a magnetic stir bar, was added sulfonimidoyl chloride **14** (0.1 mmol) and THF (2.0 mL). The mixture was cooled to -30 °C. Then sodium phenoxide (0.15 mmol, 1.5 equiv.) was added quickly at this temperature. After stirring at -30 °C for 12 h, the reaction mixture was concentrated. The desired product was isolated by column chromatography on silica gel (petroleum ether: ethyl acetate = 12/1 - 3/1) to afford **15** (white solid, 45.0 mg, 90%, 93:7 e.r.)

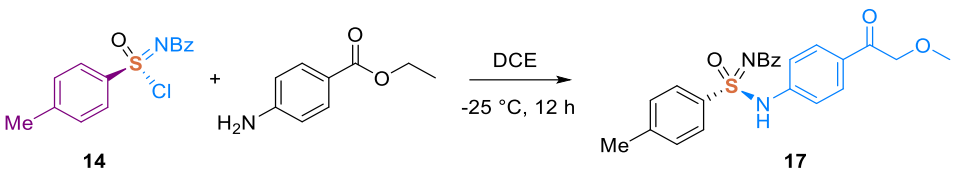
Scheme S12. Preparation of **16** from **4a**[8]



14 **16**

In a 25 mL vial containing a magnetic stir bar, was added sulfonimidoyl chloride **14** (0.1 mmol) and THF (2.0 mL). The mixture was cooled to -30 °C. Then the sodium phenoxide (0.15 mmol, 1.5 equiv.) was added quickly at this temperature. After stirring at -30 °C for 12 h, the reaction mixture was concentrated. The desired product was isolated by column chromatography on silica gel (petroleum ether: ethyl acetate = 12/1 - 3/1) to afford **16** (white solid, 19.5 mg, 65%, 96:4 e.r.).

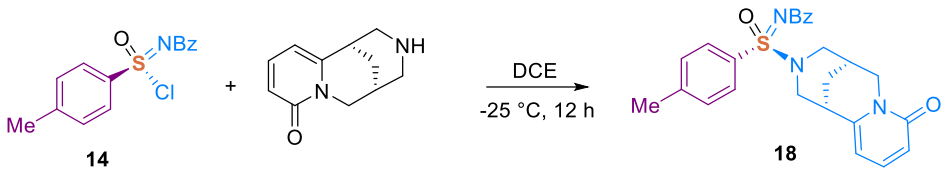
Scheme S13. Preparation of **17** from **4a**[8]



14 **17**

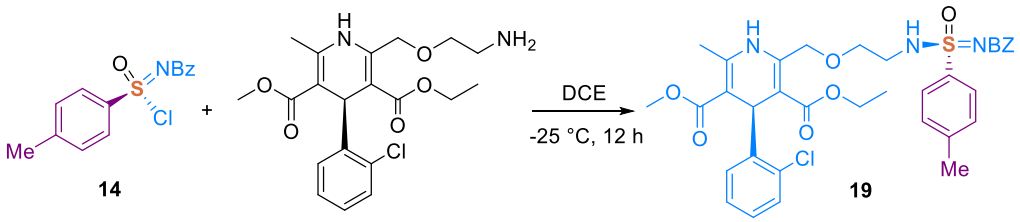
In a 10 mL vial containing a magnetic stir bar, was added sulfonimidoyl chlorides **14** (0.1 mmol) and 1,2-dichloroethane (2.0 mL). The mixture was cooled to -25 °C. Then the secondary amine (0.3 mmol, 3.0 equiv.) was added quickly at this temperature. After stirring at -25 °C for 12 h, the reaction mixture **17** was concentrated. The desired product was isolated by column chromatography on silica gel (petroleum ether: ethyl acetate = 9/1 - 1/1) to afford **17** (white solid, 16.5 mg, 55%, 95:5 e.r.).

Scheme S14. Preparation of **18** from **4a**[8]



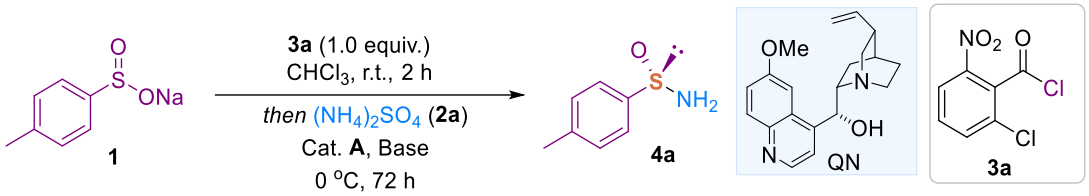
In a 10 mL vial containing a magnetic stir bar, was added sulfonimidoyl chlorides **14** (0.1 mmol) and 1,2-dichloroethane (2.0 mL). The mixture was cooled to -25 °C. Then the secondary amine (0.3 mmol, 3.0 equiv.) was added quickly at this temperature. After stirring at -25 °C for 12 h, the reaction mixture **18** was concentrated. The desired product was isolated by column chromatography on silica gel (petroleum ether: ethyl acetate = 5/1 - 0/1) to afford **18** (white solid, 21.3 mg, 71%, 95:5 e.r.).

Scheme S15. Preparation of **19** from **4a**[8]



In a 10 mL vial containing a magnetic stir bar, was added sulfonimidoyl chlorides **14** (0.1 mmol) and 1,2-dichloroethane (2.0 mL). The mixture was cooled to -25 °C. Then the secondary amine (0.3 mmol, 3.0 equiv.) was added quickly at this temperature. After stirring at -25 °C for 12 h, the reaction mixture was concentrated. The desired product was isolated by column chromatography on silica gel (petroleum ether: ethyl acetate = 9/1 - 1/1) to afford **19** (white solid, 20.9 mg, 70%, 96:4 e.r.).

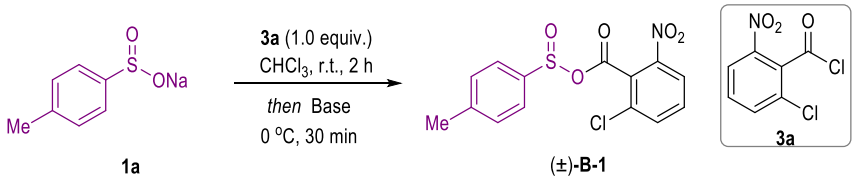
Scheme S16. Amplification of reaction **4a**



Under N_2 atmosphere, to an oven-dried 10.0 mL screw cap vial charged with a magnetic stirring bar was added **1** (1.7 g, 1.1 equiv.), **3a** (2.15 g, 1.0 equiv.) in $CHCl_3$ (100 mL) at r.t. for 2 h, before reaction with Cat. **A** (0.63 g, 0.02 mmol), DIPEA (6.8 mL, 4.0 equiv.), $(NH_4)_2SO_4$ (5.2 g, 4.0 equiv.) at 0 °C for 72 h. After concentration *in vacuo*, the crude residue was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5/1~1/1) to afford the desired sulfinamide product **4a** (white solid, 0.97 g, 74%, 97:3 e.r.).

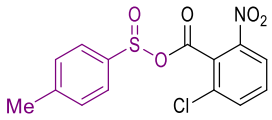
2.5 Preliminary mechanistic studies

Scheme S17. Isolation of mixed anhydride intermediate **I** under the catalytic conditions



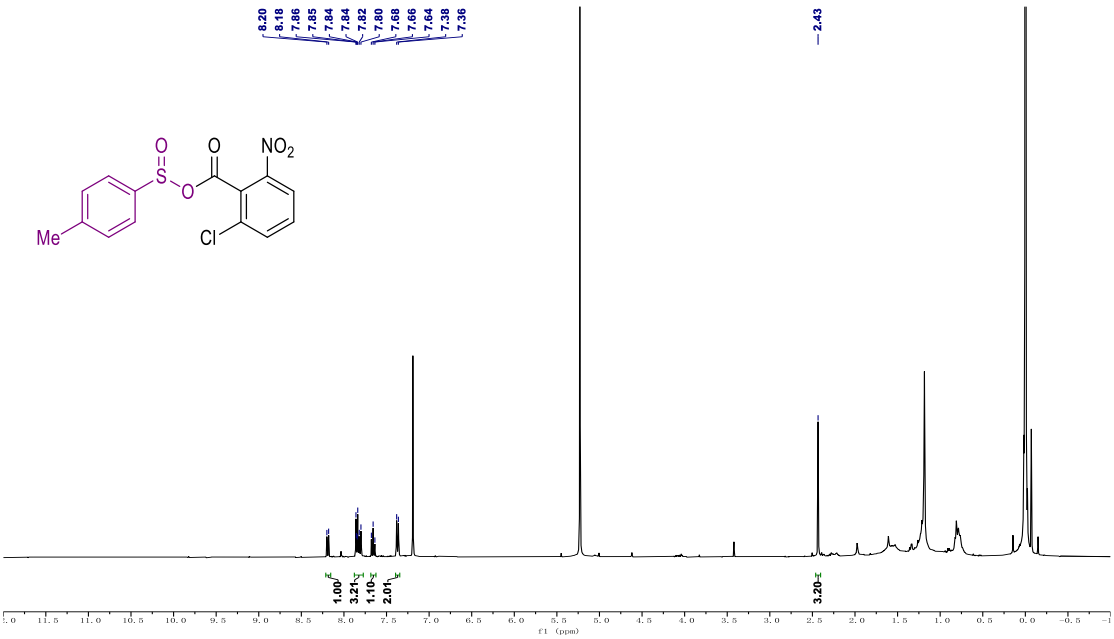
General procedure: Under nitrogen atmosphere, to a 10.0 mL dry Schlenk tube was added sodium *p*-toluenesulfinate (**1a**, 13.9 mg, 1.1 equiv.), 2-chloro-6-nitrobenzoyl chloride (**3a**, 20.0 mg, 1.0 equiv.) and $CHCl_3$ (2.0 mL). The mixture was kept stirring at r.t. for 2 h, then the base DIPEA (63.3 μL, 4 equiv.) was added and stirred at 0 °C for 30 min. A quick separation with preparative TLC (20 × 20 cm, Pentane: EA = 5:1, R_f = 0.2) could readily afford a white solid, which was confirmed to be the mixed anhydride (±)-**IA**.

2-Chloro-6-nitrobenzoic 4-methylbenzenesulfinic anhydride (±)-IA

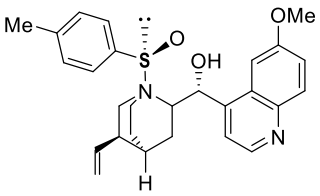


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.3 Hz, 1H), 7.83 (dd, J = 15.2, 8.2 Hz, 3H), 7.66 (t, J = 8.2 Hz, 1H), 7.37 (d, J = 8.1 Hz, 2H), 2.43 (s, 3H).

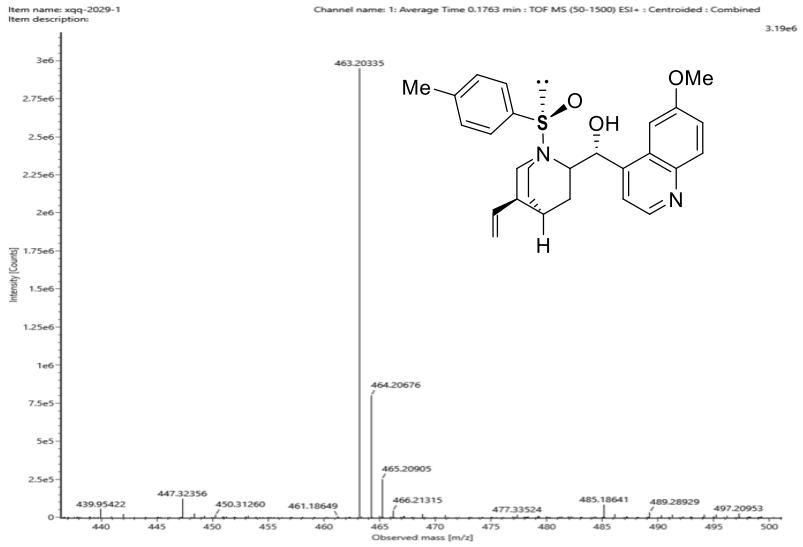
HRMS (ESI, m/z): calculated for $C_{14}H_{10}O_5NSClNa^+$ $[M+Na]^+$: 361.9860, found: 361.9850, 363.9824.



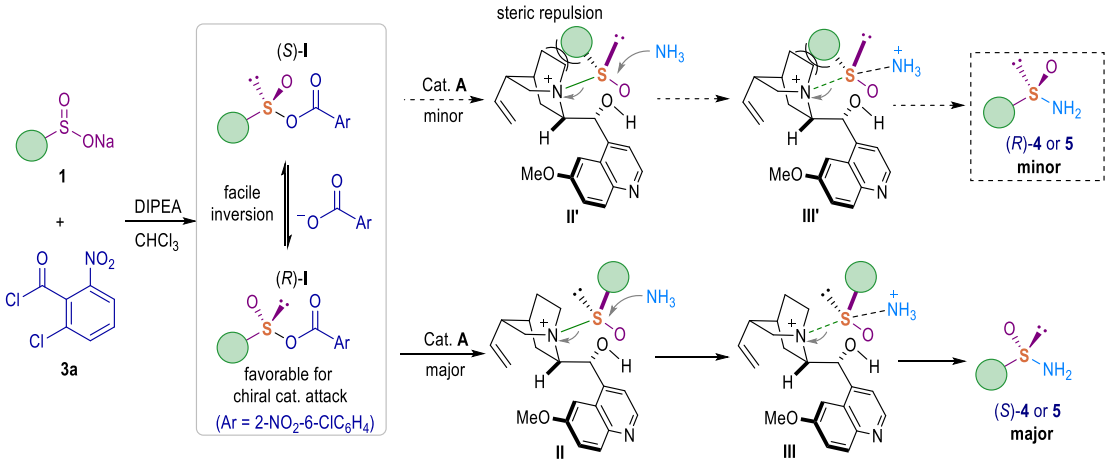
HRMS of sulfinylammonium salt intermediate **IIA**



HRMS of *p*-tolyl derived-sulfinylammonium salt intermediate (ESI, m/z): calculated for $C_{27}H_{31}N_2O_3S^+$ $[M]^+$: 463.2050, found:463.2034.



Scheme S18. Plausible mechanism

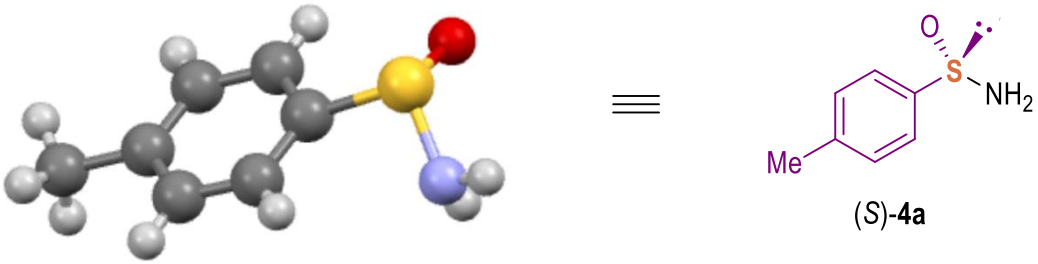


Built upon the preliminary mechanistic studies (Scheme S17), previous reports by us (*Chem.,* 2024, **10**, 1541 and *J. Am. Chem. Soc*. 2024, **146**, 25350.) and others by Tan, Shibata/Toru, Miller/Ellman, Senanayake,[9-17] a dynamic kinetic resolution process was rationally proposed to explain the stereochemical outcome obtained in our developed reaction, as illustrated in Scheme S18. First, the mixed anhydride (±)-**I** in racemic version was readily obtained from the sulfinate **1** and acyl chloride **3a**. Facile epimerization on the stereogenic sulfur center of anhydride (±)-**I** could be occurred under the assistance of benzoate anion. Chiral quinine catalyst Cat. **A** then underwent a stereoselective nucleophilic attack on the sulfur-center of the mixed anhydride **I** to form the key sulfinyl ammonium intermediate **II**. Subsequent S-N bond formation involving the approach of amine nucleophile from the back of S-N bond of intermediate **II** (via **III**) would afford the desired chiral product **4**-**5** and release the chiral catalyst **A** for the next catalytic cycle. An intermediate of **II** from catalyst addition of (*R*)-**I** was assumed to give rise to the product (*S*)-**4**-**5** in high enantioselectivity, considering the notable steric repulsion between the aryl/alkyl moiety of the sulfinyl and the catalyst backbone in intermediate **II'**.

2.6 Determination of the absolute configuration

(a) Stereochemistry determination of 4a via X-ray crystallographic analysis

Experimental. Single white plate-shaped crystals of sulfinamide (*S*)-**4a** were recrystallized from slow diffusion of a dichloromethane solution. A suitable crystal with dimensions 0.48 × 0.35 × 0.1 mm^3 was selected and the crystal was mounted on a mylar loop in perfluoroether oil on a STOE STADIVARI Cu diffractometer. The crystal was kept at a steady T = 150 K during data collection. **CCDC 2288291** for (*S*)-**4a** contains the supplementary crystallographic data that can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data request/cif.



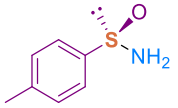
(*S*)-**4a**

Compound	(*S*)-**4a**
Empirical formula	C_7H_9NOS
Formula weight	155.21
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	4.9512(6)
b/Å	6.4395(8)
c/Å	24.625(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	785.11(16)

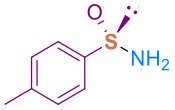
Z	4
ρ_{calc}g/cm^3	1.313
μ/mm^{-1}	0.341
F(000)	328.0
Crystal size/mm^3	0.48 × 0.35 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.54 to 50.012
Index ranges	$-5 \leq h \leq 5$, $-7 \leq k \leq 5$, $-29 \leq l \leq 26$
Reflections collected	3718
Independent reflections	1374 [R_{int} = 0.1247, R_{sigma} = 0.0993]
Data/restraints/parameters	1374/0/93
Goodness-of-fit on F^2	1.144
Final R indexes [I>=2σ (I)]	R_1 = 0.0676, wR_2 = 0.1703
Final R indexes [all data]	R_1 = 0.0729, wR_2 = 0.1735
Largest diff. peak/hole / e Å^{-3}	0.32/-0.37
Flack parameter	0.1(3)

(b) Further determination of the absolute configuration by literature comparison

4-Methylbenzenesulfinamide (4a) (*R* and *S* configurations are purchased through purchase)



(*R*), 99:1 e.r.



(*S*), 99:1 e.r.

lit: $[a]^{25}D$ = -102.523 (c = 0.3 in $CHCl_3$) for (*R*)

lit: $[a]^{25}D$ = +87.054 (c = 0.3 in $CHCl_3$) for (*S*)

(*R*)-4-Methylbenzenesulfinamide (commercially available):

$[\alpha]^{25}_D$ = -102.523 (*c* = 0.3 in $CHCl_3$);

Chiralcel IA (*i*-PrOH/*n*-Hexane = 10/90, 1.0 mL/min, 254 nm, 25 °C), 9.1 min, 10.7 min (major), 99:1 e.r.

(*S*)-4-Methylbenzenesulfinamide (commercially available):

$[\alpha]^{25}_D$ = +87.054 (*c* = 0.3 in $CHCl_3$);

Chiralcel IA (*i*-PrOH/*n*-Hexane = 10/90, 1.0 mL/min, 254 nm, 25 °C), 9.0 min (major), 10.9 min, 99:1 e.r.

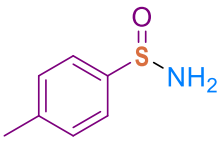
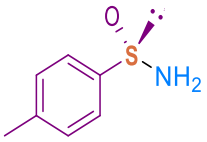
Optically enriched **4a** prepared by our catalytic method:

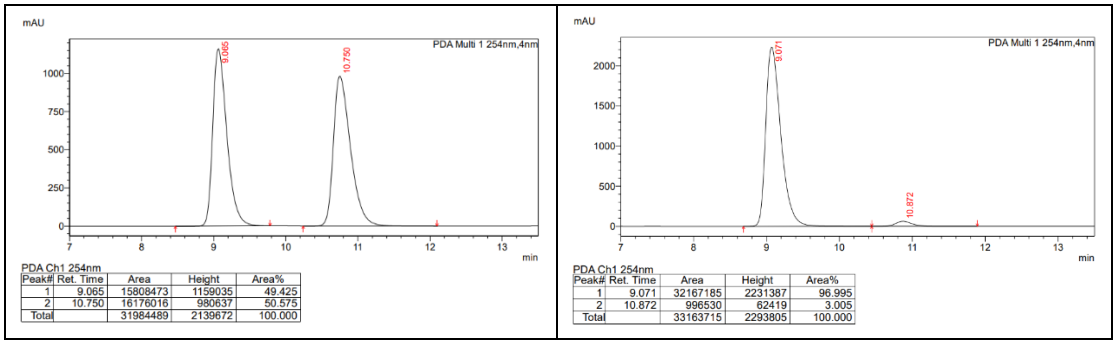
(*S*)-4-Methylbenzenesulfinamide:

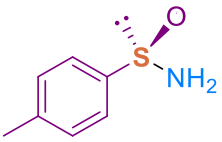
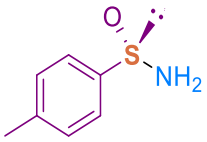
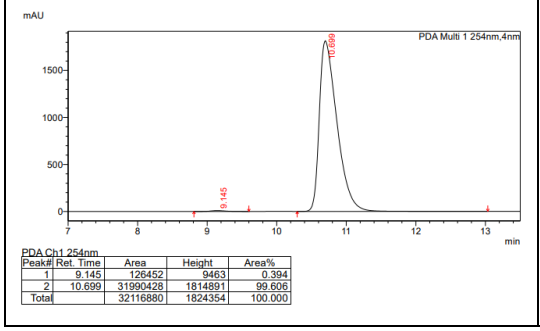
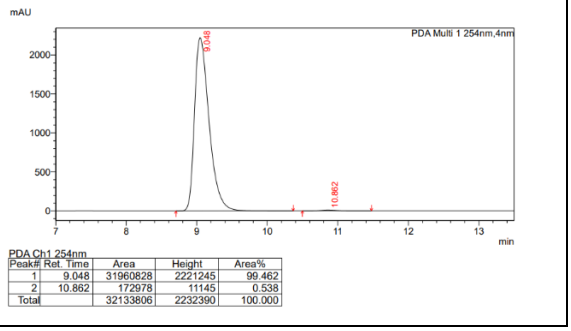
$[\alpha]^{25}_D$ = +62.717 (*c* = 0.2 in $CHCl_3$);

Chiralcel IA (*i*-PrOH/*n*-Hexane = 10/90, 1.0 mL/min, 254 nm, 25 °C), 9.1 min (major), 10.9 min, 97:3 e.r.

Comparison of HPLC traces

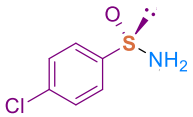
4-Methylbenzenesulfinamide	4-Methylbenzenesulfinamide (prepared by our catalytic method)
	



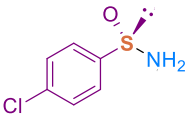
(*R*)-4-Methylbenzenesulfinamide	(*S*)-4-Methylbenzenesulfinamide
	
	

By comparing the optical rotation and HPLC trace, it can be inferred that the absolute configuration of **4a** was (*S*).

4-Chlorobenzenesulfinamide (4h)



(*S*), 95:5 e.r.
characterized by previous literature



4h, (*S*), 92:8 e.r.
by our catalytic method

(*S*)-4-Chlorobenzenesulfinamide characterized by previous literature [9]

Chiralcel IB (*i*-PrOH/*n*-Hexane = 20/80, 1.0 mL/min, 254 nm, 25 °C), 6.4 min, 7.7 min (major), 95:5 e.r.

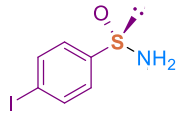
Optically enriched **4h** prepared by our catalytic method:

Chiralcel IB (*i*-PrOH/*n*-Hexane = 20/80, 1.0 mL/min, 254 nm, 25 °C), 8.0 min, 10.6 min (major), 92:8 e.r.

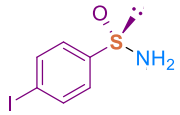
By comparing the optical rotation and HPLC trace, it can be inferred that the absolute

configuration of **4h** was (*S*).

4-Iodobenzenesulfinamide (4h)



(*S*), 95:5 e.r.
characterized by previous literature



4j, (*S*), 95:5 e.r.
by our catalytic method

(*S*)-4-Iodobenzenesulfinamide characterized by previous literature [9]

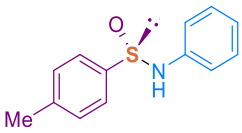
Chiralcel IB (*i*-PrOH/*n*-Hexane = 10/90, 1.0 mL/min, 254 nm, 25 °C), 7.8 min, 10.5 min (major), 95:5 e.r.

Optically enriched **4j** prepared by our catalytic method:

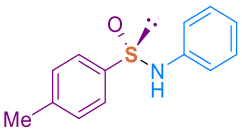
Chiralcel IB (*i*-PrOH/*n*-Hexane = 10/90, 1.0 mL/min, 254 nm, 25 °C), 6.6 min, 8.8 min (major), 95:5 e.r.

By comparing the optical rotation and HPLC trace, it can be inferred that the absolute configuration of **4j** was (*S*).

(*S*)-4-Methyl-*N*-phenylbenzenesulfinamide (9)



(*S*), 92:8 e.r.
characterized by previous literature



9, (*S*), 96:4 e.r.
by our catalytic method

(*S*)-4-Methyl-N-phenylbenzenesulfinamide characterized by previous literature:[11]

Chiralcel ID (*i*-PrOH/*n*-Hexane = 20/80, 1.0 mL/min, 254 nm, 25 °C), 11.4 min, 14.0 min (major), 92:8 e.r.

$[\alpha]^{25}D$ = +217.7 (c = 0.5 in EtOAc).

Optically enriched **9** prepared by our catalytic method:

Chiralcel ID (*i*-PrOH/*n*-Hexane = 20/80, 1.0 mL/min, 254 nm, 25 °C), 13.1 min (major), 15.9 min, 96:4 e.r.

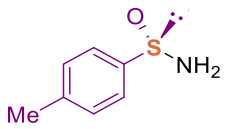
$[\alpha]^{25}D$ = +97.253 (c = 0.2 in $CHCl_3$).

By comparing the optical rotation and HPLC trace, it can be inferred that the absolute configuration of **9** was (*S*).

3. Characterizations of chiral sulfinyl amide products

3.1 Characterization of chiral sulfinamides 4-5

(*S*)-4-Methylbenzenesulfinamide (4a)



Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 3:1) yielded the title compound **4a**, faint yellow solid (11.64 mg, 75% yield); R_f 0.25 (Petroleum ether / Ethyl acetate = 1:1); m.p. 114.4 – 115.7 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.20 Hz, 2H), 7.19 (d, J = 7.80 Hz, 2H), 4.60 (s, 2H), 2.32 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 140.3, 128.5, 124.4, 20.3 ppm.

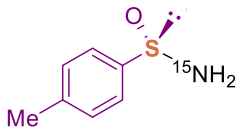
HRMS (ESI, m/z): Calculated for $C_7H_{10}NOS^+$ $[M + H]^+$: 156.0478, found: 156.0480.

$[\alpha]^{25}_D$ = +37.717 (c = 0.2, in $CHCl_3$).

HPLC analysis: 97:3 e.r. (Chiralcel IA, 15:85 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (major) = 11.4 min, Rt (minor) = 12.8 min.

** Reaction with quinidine catalyst, HPLC analysis: 5:95 e.r. (Chiralcel IA, 20:80 i-PrOH/n Hexane, 1.0 mL/min), Rt (major) = 9.3 min, Rt (minor) = 11.2 min.

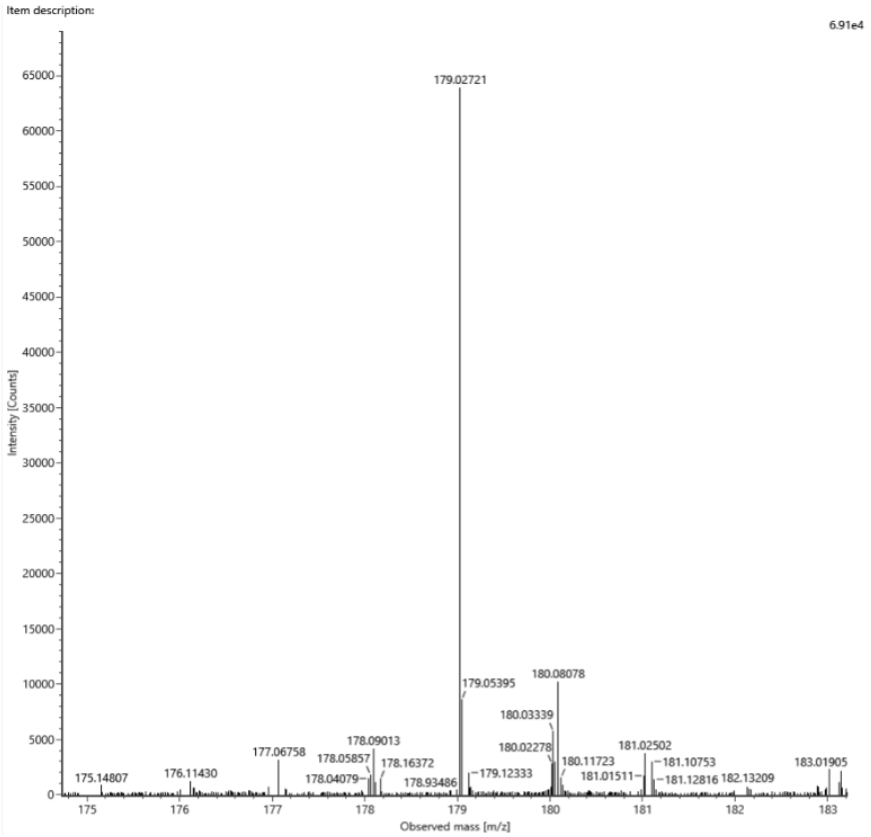
^{15}N-4a



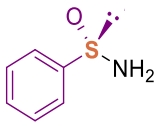
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.2 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 4.26 (s, 1H), 4.07 (s, 1H), 2.35 (s, 3H).

HRMS (ESI, m/z): Calculated for $C_7H_9{}^{15}NOS\ Na^+$ $[M + Na]^+$:179.0267, found: 179.0272.

HPLC analysis: 97:3 e.r. (Chiralcel IA, 20:80 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (major) = 6.7 min, Rt (minor) = 7.6 min.



(*S*)-Benzenesulfinamide (4b):



Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 3:1) yielded the title compound **4b**, faint yellow solid (10.17 mg, 72% yield); R_f 0.25 (Petroleum ether / Ethyl acetate = 1:1); m.p. 107.8 – 109.2 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.59 (m, 2H), 7.51 – 7.38 (m, 3H), 4.47 (s, 2H).

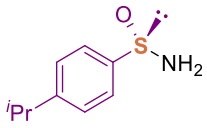
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.5, 131.1, 128.9, 125.5 ppm.

HRMS (ESI, m/z): Calculated for $C_6H_7NOSNa^+$ $[M + Na]^+$: 164.0141, found: 163.0155.

$[\alpha]^{25}_D$ = +18.689 (c = 0.2, in $CHCl_3$).

HPLC analysis: 95:5 e.r. (Chiralcel OJ-H , 10:90 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (minor) = 11.4 min, Rt (major) = 14.5 min.

(*S*)-4-Isopropylbenzenesulfonamide (4c)



Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 3:1) yielded the title compound **4c**, faint yellow solid (13.9 mg, 76% yield); R_f 0.25 (Petroleum ether / Ethyl acetate = 1:1); m.p. 128.5 – 129.1 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.54 (m, 2H), 7.32 – 7.26 (m, 2H), 4.32 (s, 2H), 2.90 (p, J = 6.9 Hz, 1H), 1.20 (d, J = 6.9 Hz, 6H).

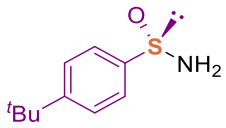
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.4, 143.7, 127.1, 125.5, 34.1, 23.8 ppm.

$[\alpha]^{25}_D$ = +3.002 (c = 0.5, in $CHCl_3$).

HRMS (ESI, m/z): Calculated for $C_9H_{13}NOSNa^+$ $[M + Na]^+$: 206.0610, found: 206.0607.

HPLC analysis: 92:8 e.r. (Chiralcel IB, 20:80 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (minor) = 6.0 min, Rt (major) = 6.8 min.

(*S*)-4-tert-Butylbenzenesulfonamide (4d)



Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 3:1) yielded the title compound **4d**, faint yellow solid (13.8 mg, 70% yield); R_f 0.25 (Petroleum ether / Ethyl acetate = 1:1); m.p. 114.5 – 116.0 ℃.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.54 – 6.96 (m, 4H), 6.18 (s, 2H), 1.30 (s, 9H).

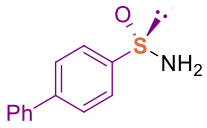
^{13}C NMR (101 MHz, DMSO-d_6) δ 153.5, 145.7, 126.0, 125.7, 35.0, 31.5 ppm.

HRMS (ESI, m/z): Calculated for $C_{10}H_{15}NOSNa^+$ $[M + Na]^+$: 220.0767, found: 220.0766.

$[\alpha]^{25}_D$ = +5.340 (c = 0.5, in $CHCl_3$).

HPLC analysis: 93:7 e.r. (Chiralcel IB, 20:80 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (minor) = 8.0 min, Rt (major) = 10.9 min.

(*S*)-[1,1'-Biphenyl]-4-sulfinamide (4e)



Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 3:1) yielded the title compound **4e**, faint yellow solid (15.4 mg, 71% yield); R_f 0.25 (Petroleum ether / Ethyl acetate = 1:1); m.p. 138.4 – 140.3 ℃.

^{1}H NMR (400 MHz, DMSO-d6) δ 7.78 (dd, J = 8.2, 1.6 Hz, 2H), 7.70 – 7.64 (m, 4H), 7.48 – 7.40 (m, 2H), 7.38 – 7.34 (m, 1H), 6.26 (s, 2H).

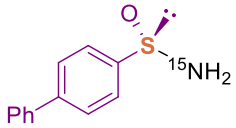
^{13}C NMR (101 MHz, DMSO-d_6) δ 147.6, 142.5, 139.7, 129.5, 128.5, 127.4, 127.4, 126.5 ppm.

HRMS (ESI, m/z): Calculated for $C_{12}H_{11}NOSNa^+$ $[M + Na]^+$: 240.0454, found: 240.0444.

$[\alpha]^{25}_D$ = +71.089 (c = 0.2, in $CHCl_3$).

HPLC analysis: 97:3 e.r. (Chiralcel IB, 20:80 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (minor) = 6.7 min, Rt (major) = 7.0 min.

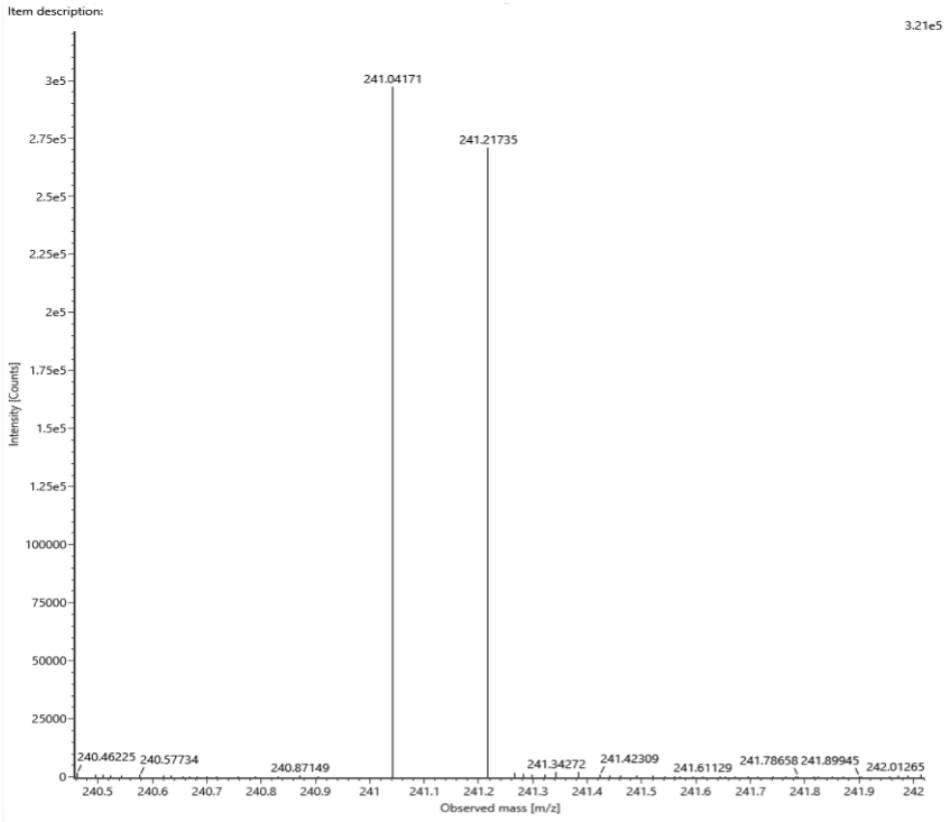
^{15}N-4e



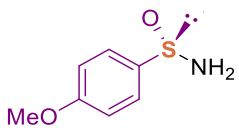
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 7.7 Hz, 2H), 7.41 (t, J = 7.5 Hz, 2H), 7.34 (d, J = 7.3 Hz, 1H), 4.34 (s, 1H), 4.15 (s, 1H).

HRMS (ESI, m/z): Calculated for $C_{12}H_{11}{}^{15}NOS\ Na^+$ $[M + Na]^+$: 241.0424, found: 241.0417.

HPLC analysis: 97:3 e.r. (Chiralcel IB, 20:80 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (minor) = 5.3 min, Rt (major) = 5.9 min.



(*S*)-4-Methoxybenzenesulfinamide (4f)



Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 3:1) yielded the title compound **4f**, faint yellow solid (12.7 mg, 74% yield); R_f 0.25 (Petroleum ether / Ethyl acetate = 1:1); m.p. 136.7 – 137.2 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.08 – 7.44 (m, 2H), 7.30 – 6.78 (m, 2H), 6.13 (s, 2H), 3.80 (s, 3H).

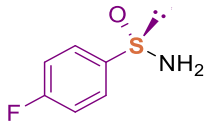
^{13}C NMR (101 MHz, DMSO-d_6) δ 161.3, 140.1, 127.5, 114.5, 55.9 ppm.

HRMS (ESI, m/z): Calculated for $C_7H_9NOSNa^+$ $[M + Na]^+$: 194.0246, found: 194.02036.

$[\alpha]^{25}_D$ = +20.692 (c = 0.5, in $CHCl_3$).

HPLC analysis: 93:7 e.r. (Chiralcel IA, 10:90 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (major) = 12.6 min, Rt (minor) = 14.6 min.

(*S*)-4-Fluorobenzenesulfinamide (4g)



Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 3:1) yielded the title compound **4g**, faint yellow solid (12.9 mg, 81% yield); R_f 0.25 (Petroleum ether / Ethyl acetate = 1:1); m.p. 120.1 – 122.4 ℃.

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.84 – 7.55 (m, 2H), 7.41 – 7.27 (m, 2H), 6.31 (s, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 163.7 (d, J = 247.2 Hz), 144.6 (d, J = 2.9 Hz), 128.4 (d, J = 9.0 Hz), 116.1 (d, J = 22.3 Hz) ppm.

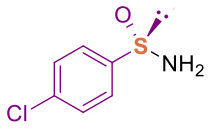
^{19}F NMR (377 MHz, DMSO-d_6) δ -111.4 ppm.

HRMS (ESI, m/z): Calculated for $C_6H_7FNOS^+$ $[M + H]^+$: 160.0227, found: 160.0223.

$[\alpha]^{25}_D$ = +14.352 (c = 0.5, in $CHCl_3$).

HPLC analysis: 95:5 e.r. (Chiralcel IB, 20:80 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (minor) = 7.8 min, Rt (major) = 9.2 min.

(*S*)-4-Chlorobenzenesulfinamide (4h)



Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 3:1) yielded the title compound **4h**, faint yellow solid (13.7 mg, 78% yield); R_f 0.25 (Petroleum ether / Ethyl acetate = 1:1); m.p. 122.4 – 123.7 ℃.

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.68 – 7.63 (m, 2H), 7.62 – 7.55 (m, 2H), 6.36 (s, 2H).

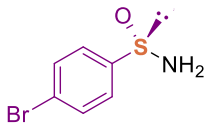
^{13}C NMR (101 MHz, DMSO-d_6) δ 147.6, 135.6, 129.1, 127.9 ppm.

HRMS (ESI, m/z): Calculated for $C_6H_6ClNOSNa^+$ $[M + Na]^+$: 197.9751, found: 197.9744.

$[\alpha]^{25}_D$ = +27.744 (c = 0.5, in $CHCl_3$).

HPLC analysis: 92:8 e.r. (Chiralcel IB, 20:80 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (minor) = 8.0 min, Rt (major) = 10.6 min.

(*S*)-4-Bromobenzenesulfinamide (4i)



Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 3:1) yielded the title compound **4i**, faint yellow solid (16.1 mg, 73% yield); R_f 0.25 (Petroleum ether / Ethyl acetate = 1:1); m.p. 130.5 – 132.4 ℃.

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.78 – 7.68 (m, 2H), 7.64 – 7.54 (m, 2H), 6.36 (s, 2H).

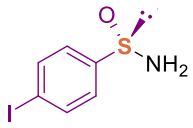
^{13}C NMR (101 MHz, DMSO-d_6) δ 148.1, 132.1, 128.1, 124.4 ppm.

HRMS (ESI, m/z): Calculated for $C_6H_6BrNOSNa^+$ $[M + Na]^+$: 241.9246, found: 241.9257.

$[\alpha]^{25}_D$ = +28.034 (c = 0.5, in $CHCl_3$).

HPLC analysis: 94:6 e.r. (Chiralcel IA, 20:80 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (major) = 6.4 min, Rt (minor) = 7.6 min.

(*S*)-4-Iodobenzenesulfinamide (4j)



Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 3:1) yielded the title compound **4j**, faint yellow solid (21.9 mg, 82% yield); R_f 0.25 (Petroleum ether / Ethyl acetate = 1:1); m.p. 140.1 – 141.7 ℃.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.10 – 7.72 (m, 2H), 7.59 – 7.22 (m, 2H), 6.32 (s, 2H).

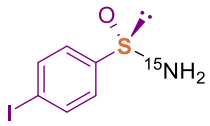
^{13}C NMR (101 MHz, DMSO-d_6) δ 148.6, 137.9, 128.0, 98.0 ppm.

HRMS (ESI, m/z): Calculated for $C_6H_7INOS^+$ $[M + H]^+$: 267.9288, found: 267.9287.

$[\alpha]^{25}_D$ = +17.343 (c = 0.2, in $CHCl_3$).

HPLC analysis: 95:5 e.r. (Chiralcel IB, 20:80 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (minor) = 7.0 min, Rt (major) = 8.8 min.

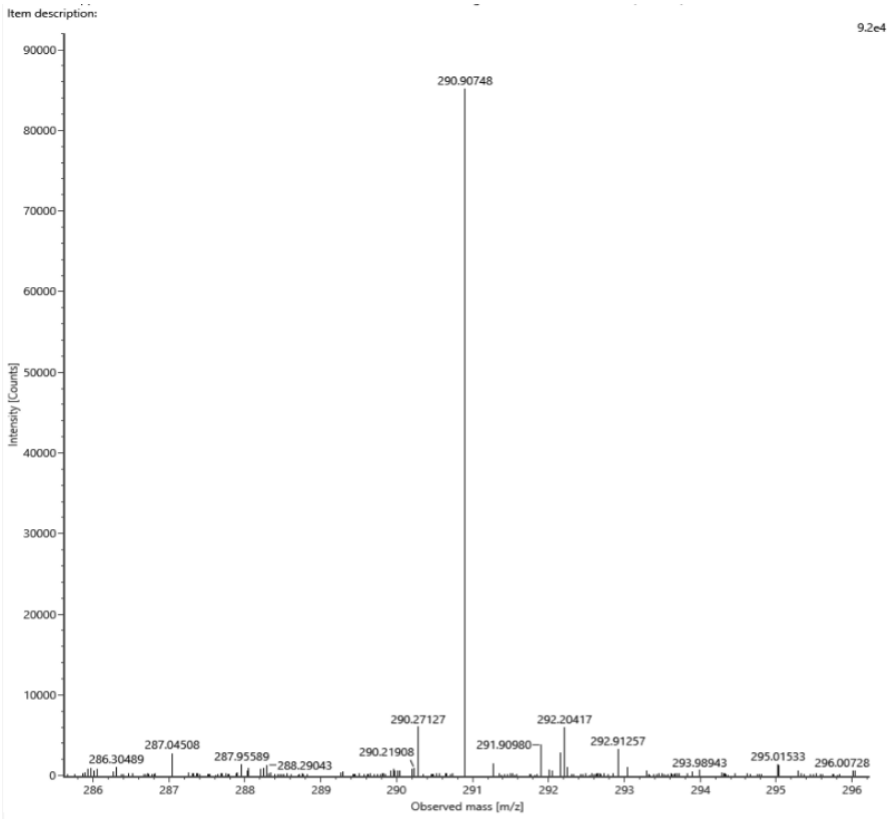
^{15}N-4j



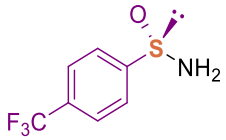
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 8.00 (m, 2H), 7.71 – 7.62 (m, 2H), 4.31 (s, 1H), 4.13 (s, 1H).

HRMS (ESI, m/z): Calculated for $C_6H_6I^{15}NOS\ Na^+$ $[M + Na]^+$: 290.9077, found: 290.9075.

HPLC analysis: 95:5 e.r. (Chiralcel IA, 20:80 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (major) = 11.8 min, Rt (minor) = 13.7 min.



(*S*)-4-Trifluoromethylbenzenesulfonamide (4k)



Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 3:1) yielded the title compound **4k**, faint yellow solid (13.6 mg, 65% yield); R_f 0.25 (Petroleum ether / Ethyl acetate = 1:1); m.p. 125.4 – 126.7 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.2 Hz, 2H), 7.71 (d, J = 8.2 Hz, 2H), 4.42 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 133.2 (d, J = 32.6 Hz), 126.3, 126.0 (q, J = 3.7 Hz), 124.9, 122.2 ppm.

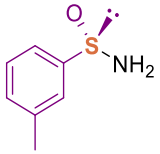
^{19}F NMR (377 MHz, DMSO-d_6) δ -61.2 ppm.

HRMS (ESI, m/z): Calculated for $C_7H_7F_3NOS^+$ $[M + H]^+$: 208.0049, found: 208.0047.

$[\alpha]^{25}_D$ = +5.006 (c = 0.5, in $CHCl_3$).

HPLC analysis: 89:11 e.r. (Chiralcel IB, 20:80 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (minor) = 7.0 min, Rt (major) = 10.3 min.

(*S*)-4-Methylbenzenesulfonamide (4l)



Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 3:1) yielded the title compound **4l**, faint yellow solid (9.6 mg, 62% yield); R_f 0.25 (Petroleum ether / Ethyl acetate = 1:1); m.p. 115.4 – 116.3 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.40 (m, 1H), 7.30 (t, J = 7.6 Hz, 1H), 7.24 – 7.16 (m, 1H), 4.42 (s, 2H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 139.0, 131.8, 128.8, 125.7, 122.5, 21.4 ppm.

$[\alpha]^{25}_D$ = +8.502 (c = 0.5, in $CHCl_3$).

HRMS (ESI, m/z): Calculated for $C_7H_9NOSNa^+$ $[M + Na]^+$: 178.0297, found: 178.0295.

HPLC analysis: 96:4 e.r. (Chiralcel OJ-H, 20:80 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt

(minor) = 5.6 min, Rt (major) = 6.6 min.

(*S*)-3-Chlorobenzenesulfonamide (4m)

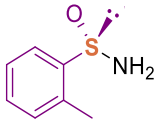
Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 3:1) yielded the title compound **4m**, faint yellow solid (10.5 mg, 60% yield); R_f 0.25 (Petroleum ether / Ethyl acetate = 1:1); m.p. 127.5 – 128.1 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.64 (q, J = 1.5 Hz, 1H), 7.62 – 7.52 (m, 3H), 6.42 (s, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 151.0, 133.9, 131.1, 130.7, 125.5, 124.8 ppm.
HRMS (ESI, m/z): Calculated for $C_6H_7ClNOS^+$ $[M + H]^+$: 175.9931, found: 175.9931.
$[\alpha]^{25}_D$ = +3.002 (c = 0.5, in $CHCl_3$).

HPLC analysis: 88:12 e.r. (Chiralcel OJ-H , 10:90 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (minor) = 10.7 min, Rt (major) = 12.1 min.

(*S*)-2-Methylbenzenesulfonamide (4n)



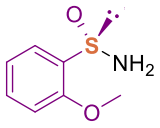
Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 3:1) yielded the title compound **4n**, faint yellow solid (8.8 mg, 57% yield); R_f 0.25 (Petroleum ether / Ethyl acetate = 1:1); m.p. 117.4 – 118.6 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.86 (m, 1H), 7.32 (dd, J = 5.7, 3.4 Hz, 2H), 7.14 (dd, J = 5.45, 3.4 Hz, 1H), 4.20 (s, 2H), 2.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 135.9, 131.1, 130.9, 126.6, 122.8, 18.6 ppm.
HRMS (ESI, m/z): Calculated for $C_7H_9NOSNa^+$ $[M + Na]^+$: 178.0297, found: 178.0285.
$[\alpha]^{25}_D$ = +34.042 (c = 0.2, in $CHCl_3$).

HPLC analysis: 94:6 e.r. (Chiralcel IB, 20:80 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (minor) = 5.1 min, Rt (major) = 5.6 min.

(*S*)-2-Methoxybenzenesulfinamide (4o)



Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 3:1) yielded the title compound **4o**, faint yellow solid (10.8 mg, 63% yield); R_f 0.25 (Petroleum ether / Ethyl acetate = 1:1); m.p. 127.0 – 128.2 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, J = 7.6, 1.6 Hz, 1H), 7.40 (ddd, J = 8.8, 7.4, 1.8 Hz, 1H), 7.10 – 6.98 (m, 1H), 6.90 (d, J = 8.2 Hz, 1H), 4.28 (s, 2H), 3.86 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 134.3, 132.9, 125.0, 121.1, 111.6, 56.0 ppm.

HRMS (ESI, m/z): Calculated for $C_7H_9NOSNa^+$ $[M + Na]^+$: 194.0246, found: 194.0242.

$[\alpha]^{25}_D$ = +5.673 (c = 0.5, in $CHCl_3$).

HPLC analysis: 90:10 e.r. (Chiralcel IB, 20:80 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (minor) = 7.7 min, Rt (major) = 8.3 min.

(*S*)-2-Fluorobenzenesulfonamide(4p)

Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 3:1) yielded the title compound **4p**, faint yellow solid (8.1 mg, 51% yield); R_f 0.25 (Petroleum ether / Ethyl acetate = 1:1); m.p. 124.1 – 125.4 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (td, J = 7.4, 1.8 Hz, 1H), 7.42 (tdd, J = 7.2, 5.0, 1.8 Hz, 1H), 7.24 (td, J = 7.6, 1.1 Hz, 1H), 7.05 (ddd, J = 9.4, 8.2, 1.1 Hz, 1H), 4.56 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 157.5, 133.7 (d, J = 15.3 Hz), 133.4 (d, J = 7.8 Hz), 126.1 – 123.1 (m), 116.3 (d, J = 20.5 Hz) ppm.

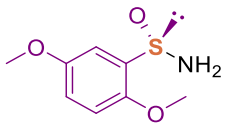
^{19}F NMR (377 MHz, $CDCl_3$) δ -113.4 ppm.

HRMS (ESI, m/z): Calculated for $C_6H_6FNOSNa^+$ $[M + Na]^+$: 182.0046, found: 182.0050.

$[\alpha]^{25}_D$ = +10.678 (c = 0.5, in $CHCl_3$).

HPLC analysis: 98:2 e.r. (Chiralcel OJ-H, 10:90 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (minor) = 14.3 min, Rt (major) = 18.0 min.

(*S*)-2,5-Dimethoxybenzenesulfonamide (4q)



Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 3:1) yielded the title compound **4q**, faint yellow solid (10.1 mg, 50% yield); R_f 0.25 (Petroleum ether / Ethyl acetate = 1:1); m.p. 131.0 – 131.8 ℃..

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 3.1 Hz, 1H), 6.92 (dd, J = 8.8, 3.0 Hz, 1H), 6.84 (d, J = 8.9 Hz, 1H), 4.30 (s, 2H), 3.80 (s, 3H), 3.74 (s, 3H).

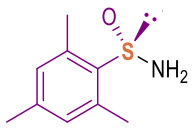
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.1, 150.2, 135.0, 118.9, 113.2, 109.1, 56.6, 56.0 ppm.

HRMS (ESI, m/z): Calculated for $C_8H_{11}NO_3SNa^+$ [M + Na]$^+$: 224.0352, found: 224.0352.

$[\alpha]^{25}_D$ = +13.669 (c = 0.5, in $CHCl_3$).

HPLC analysis: 86:14 e.r. (Chiralcel IB, 10:90 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (minor) = 22.1 min, Rt (major) = 25.4 min.

(*S*)-2,4,6-Trimethylbenzenesulfinamide (4r)



Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 3:1) yielded the title compound **4r**, faint yellow solid (9.5 mg, 52% yield); R_f 0.25 (Petroleum ether / Ethyl acetate = 1:1); m.p. 110.2 – 112.1 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78 (s, 2H), 2.52 (s, 6H), 2.20 (s, 3H).

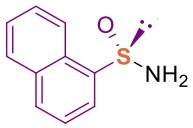
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.8, 138.9, 136.3, 130.9, 21.0, 19.2 ppm.

HRMS (ESI, m/z): Calculated for $C_9H_{13}NOSNa^+$ [M + Na]$^+$: 206.0610, found: 206.0611.

$[\alpha]^{25}_{D}$ = +10.013 (c = 0.5, in $CHCl_3$).

HPLC analysis: 93:7 e.r. (Chiralcel OJ-H, 30:70 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (minor) = 8.8 min, Rt (major) = 14.0 min.

(*S*)-Naphthalene-1-sulfinamide (4s)



Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 3:1) yielded the title compound **4s**, faint yellow solid (14.3 mg, 75% yield); R_f 0.25 (Petroleum ether / Ethyl acetate = 1:1); m.p. 125.5 – 127.1 ℃.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.23 (dd, J = 7.4, 2.0 Hz, 1H), 8.14 – 8.02 (m, 3H), 7.68 (t, J = 7.7 Hz, 1H), 7.62 (tt, J = 7.0, 5.3 Hz, 2H), 6.28 (s, 2H).

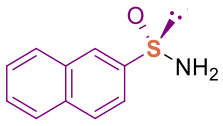
^{13}C NMR (101 MHz, DMSO-d_6) δ 143.6, 133.8, 131.4, 129.1 (d, J = 4.7 Hz), 127.2, 126.9, 125.6, 123.6, 122.7 ppm.

HRMS (ESI, m/z): Calculated for $C_{10}H_9NOSNa^+$ $[M + Na]^+$: 214.0297, found: 214.0290.

$[\alpha]^{25}_{D}$ = +8.342 (c = 0.5, in $CHCl_3$).

HPLC analysis: 99:1 e.r. (Chiralcel IB, 90:10 *i*-PrOH/*n*-Hexane, 1 mL/min), Rt (major) = 11.4 min, Rt (minor) = 12.0 min.

(*S*)-Naphthalene-2-sulfinamide(4t)



Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 3:1) yielded the title compound **4t**, faint yellow solid (14.9 mg, 78% yield); R_f 0.25 (Petroleum ether / Ethyl acetate = 1:1); m.p. 120.8 – 121.4 ℃.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.28 (d, J = 1.7 Hz, 1H), 8.15 – 7.98 (m, 3H), 7.73 (dd, J = 8.5, 1.8 Hz, 1H), 7.69 – 7.58 (m, 2H), 6.38 (s, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 146.0, 134.1, 132.7, 129.0 (d, J = 9.6 Hz), 128.2,

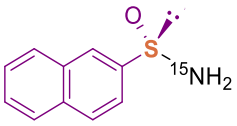
128.0, 127.5, 125.5, 122.9 ppm.

$[\alpha]^{25}_{D}$ = +10.011 (c = 0.5, in $CHCl_3$).

HRMS (ESI, m/z): Calculated for $C_{10}H_9NOSNa^+$ $[M + Na]^+$: 214.0297, found: 214.0288.

HPLC analysis: 98:2 e.r. (Chiralcel IB, 10:90 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (major) = 10.9 min, Rt (minor) = 12.8 min.

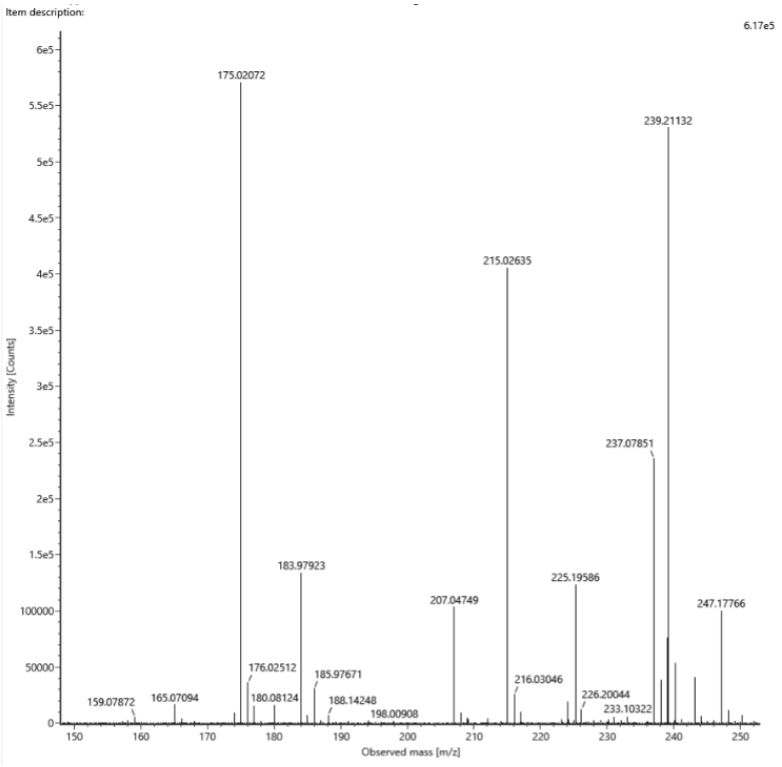
^{15}N-4t



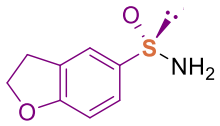
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.90 (dd, *J* = 8.8, 5.8 Hz, 2H), 7.84 (d, *J* = 6.5 Hz, 1H), 7.64 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.55 – 7.50 (m, 2H), 4.36 (s, 1H), 4.17 (s, 1H).

HRMS (ESI, m/z): Calculated for $C_{10}H_9{}^{15}NOS\ Na^+$ $[M + Na]^+$: 215.0267, found: 215.0264.

HPLC analysis: 97:3 e.r. (Chiralcel IA, 10:90 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (major) = 12.6 min, Rt (minor) = 17.4 min.



(*S*)-2,3-Dihydrobenzofuran-5-sulfonamide (4u)



Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 3:1) yielded the title compound **4u**, faint yellow solid (12.3 mg, 67% yield); R_f 0.25 (Petroleum ether / Ethyl acetate = 1:1); m.p. 110.4 – 112.5 ℃.

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.49 (t, J = 1.6 Hz, 1H), 7.36 (dd, J = 8.2, 2.0 Hz, 1H), 6.86 (d, J = 8.2 Hz, 1H), 6.08 (s, 2H), 4.58 (t, J = 8.8 Hz, 2H), 3.22 (t, J = 8.8 Hz, 2H).

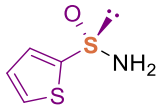
^{13}C NMR (101 MHz, DMSO-d_6) δ 162.0, 140.1, 128.6, 126.2, 122.8, 109.2, 72.2, 29.2 ppm.

HRMS (ESI, m/z): Calculated for $C_8H_9NO_2SNa^+$ [M + Na]$^+$: 206.0246, found: 206.0246.

$[\alpha]^{25}_D$ = +16.021 (c = 0.2, in $CHCl_3$).

HPLC analysis: 99:1 e.r. (Chiralcel IA, 10:90 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (major) = 14.2 min, Rt (minor) = 16.3 min.

(*S*)-2-Thienesulfonamide (4v)



Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 3:1) yielded the title compound **4v**, faint yellow solid (9.9 mg, 67% yield); R_f 0.25 (Petroleum ether / Ethyl acetate = 1:1); m.p. 92.5 – 93.7 ℃.

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.83 (dd, J = 5.0, 1.4 Hz, 1H), 7.32 (dd, J = 3.6, 1.4 Hz, 1H), 7.25 – 7.13 (m, 1H), 6.60 (s, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 151.7, 131.6, 129.3, 128.4 ppm.

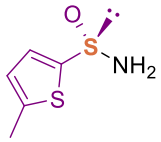
HRMS (ESI, m/z): Calculated for $C_4H_5NOSNa^+$ [M + Na]$^+$: 169.9722, found: 169.9722.

$[\alpha]^{25}_D$ = +9.010 (c = 0.5, in $CHCl_3$).

HPLC analysis: 97:3 e.r. (Chiralcel IB, 10:90 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt

(minor) = 14.6 min, Rt (major) = 15.9 min.

(*S*)-5-Methylthiophene sulfonamide (4w)



Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 3:1) yielded the title compound **4w**, faint yellow solid (10.5 mg, 65% yield); R_f 0.25 (Petroleum ether / Ethyl acetate = 1:1); m.p. 105.6 – 106.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.17 (m, 1H), 6.79 (dq, J = 3.4, 1.1 Hz, 1H), 4.52 (s, 2H), 2.53 (d, J = 1.1 Hz, 3H).

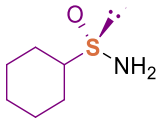
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.7, 145.4, 129.9, 126.3, 15.7 ppm.

HRMS (ESI, m/z): Calculated for $C_5H_7NOSNa^+$ $[M + Na]^+$: 183.9952, found: 183.9959.

$[\alpha]^{25}_D$ = +7.669 (c = 0.5, in $CHCl_3$).

HPLC analysis: 98:2 e.r. (Chiralcel IA, 10:90 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (major) = 9.9 min, Rt (minor) = 11.8 min.

(*S*)-Cyclohexylsulfonamide (4x)



Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 3:1) yielded the title compound **3x**, colorless oil (9.0 mg, 61% yield); R_f 0.25 (Petroleum ether / Ethyl acetate = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.04 (s, 2H), 2.48 (tt, J = 11.3, 3.7 Hz, 1H), 2.10 – 1.99 (m, 2H), 1.88 (tt, J = 11.5, 3.0 Hz, 2H), 1.70 (dt, J = 10.7, 3.9 Hz, 1H), 1.50 – 1.26 (m, 5H).

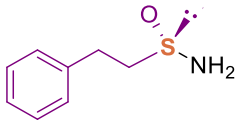
^{13}C NMR (101 MHz, $CDCl_3$) δ 63.5, 25.7 (d, J = 17.4 Hz), 25.3, 25.1 (d, J = 3.0 Hz) ppm.

HRMS (ESI, m/z): Calculated for $C_6H_{13}NOSNa^+$ $[M + Na]^+$: 170.0610, found: 170.0612.

$[\alpha]^{25}_D$ = +17.424 (c = 0.5, in $CHCl_3$).

HPLC analysis: 94:6 e.r. (Chiralcel IA, 5:95 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (major) = 14.2 min, Rt (minor) = 16.5 min.

(*S*)-2-Phenyl-ethanesulfonamide (4y)



Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 3:1) yielded the title compound **4y**, colorless oil (10.5 mg, 62% yield); R_f 0.25 (Petroleum ether / Ethyl acetate = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.21 (m, 2H), 7.20 – 7.12 (m, 3H), 4.17 (s, 2H), 3.11 – 2.47 (m, 4H).

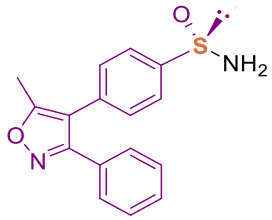
^{13}C NMR (101 MHz, DMSO-*d*6) δ 141.5, 128.8, 128.7, 126.3, 53.5, 32.0 ppm.

HRMS (ESI, m/z): Calculated for $C_8H_{11}NOSNa^+$ $[M + Na]^+$: 192.0454, found: 192.0455.

$[\alpha]^{25}_D$ = +6.924 (c = 0.5, in $CHCl_3$).

HPLC analysis: 92:8 e.r. (Chiralcel IB, 20:80 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (minor) = 6.9 min, Rt (major) = 8.8 min.

(*S*)-4-(5-Methyl-3-phenylisoxazol-4-yl) benzenesulfinamide (5a)



Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 3:1) yielded the title compound **5a**, colorless oil (21.3 mg, 57% yield); R_f 0.3 (Petroleum ether / Ethyl acetate = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.62 (m, 2H), 7.38 – 7.29 (m, 3H), 7.29 – 7.22 (m, 4H), 4.39 (s, 2H), 2.40 (d, *J* = 1.5 Hz, 3H).

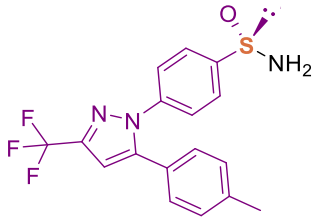
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 167.1, 161.2, 145.7, 133.6, 130.2, 129.6, 128.7, 128.5, 126.0, 114.8, 11.7 ppm.

HRMS (ESI, m/z): Calculated for $C_{16}H_{14}N_2O_2SNa^+$ $[M + Na]^+$: 321.0703, found: 321.0701.

$[\alpha]^{25}_D$ = +7.175 (c = 0.5, in $CHCl_3$).

HPLC analysis: 99:1 e.r. (Chiralcel IA, 10:90 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (major) = 16.8 min, Rt (minor) = 18.9 min.

(*S*)-4-(5-(p-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)benzenesulfinamide (5b)



Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 3:1) yielded the title compound **5b**, colorless oil (22.5 mg, 51% yield); R_f 0.3 (Petroleum ether / Ethyl acetate = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.58 (m, 2H), 7.50 – 7.32 (m, 2H), 7.14 – 6.95 (m, 4H), 6.66 (s, 1H), 4.33 (s, 2H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.2, 145.1, 144.0, 141.6, 139.6, 129.7, 128.7, 126.6, 125.9, 125.6, 106.0, 21.3 ppm.

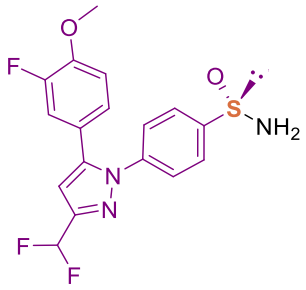
^{19}F NMR (377 MHz, $CDCl_3$) *δ* -62.4 ppm.

HRMS (ESI, m/z): Calculated for $C_{17}H_{13}F_3N_3OSNa^+$ $[M + Na]^+$: 387.0646, found: 387.0631.

$[\alpha]^{25}_D$ = +15.373 (c = 0.5, in $CHCl_3$).

HPLC analysis: 96:4 e.r. (Chiralcel IA, 90:10 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (major) =13.9 min, Rt (minor) = 16.3 min.

(*S*)-(4-(3-(Difluoromethyl)-5-(3-fluoro-4-methoxyphenyl)-1*H*-pyrazol-1-yl) phenyl) (methylidyne) (λ^1-oxidaneyl)- λ^6-sulfanamine (5c)



Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 3:1) yielded the title compound **5c**, colorless oil (29.2 mg, 64% yield); R_f 0.25 (Petroleum ether / Ethyl acetate = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.64 (m, 2H), 7.46 – 7.30 (m, 2H), 6.92 – 6.80 (m, 3H), 6.74 – 6.50 (m, 2H), 4.38 (s, 2H), 3.84 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.7, 149.3, 147.2 – 146.2 (m), 144.5, 142.1, 140.0, 125.2, 124.3 – 123.1 (m), 120.4 (d, J = 7.2 Hz), 115.1 (d, J = 20.1 Hz), 113.1 – 111.4 (m), 109.5, 107.2, 103.9, 54.7 ppm.

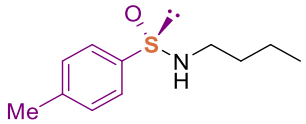
^{19}F NMR (377 MHz, $CDCl_3$) δ -112.2, -133.5 ppm.

HRMS (ESI, m/z): Calculated for $C_{17}H_{15}F_3N_3O_2S^+$ $[M + H]^+$: 382.0832, found: 382.0829.

$[\alpha]^{25}_D$ = +9.223 (c = 0.5, in $CHCl_3$).

HPLC analysis: 97:3 e.r. (Chiralcel IA, 15:85 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (major) = 8.4 min, Rt (minor) = 9.8 min.

(*S*)-*N*-Butyl-4-methyl Benzenesulfinamide (6)



Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 1:1) yielded the title compound **6**, brown oil (13.7 mg, 78% yield); R_f 0.5 (Petroleum ether / Ethyl acetate = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.40 (m, 2H), 7.38 – 7.10 (m, 2H), 3.92 (t, J = 6.2 Hz, 1H), 3.04 (dtd, J = 12.4, 7.1, 5.4 Hz, 1H), 2.75 (dq, J = 12.4, 7.0 Hz, 1H), 2.34 (s, 3H), 1.42 (p, J = 7.0 Hz, 2H), 1.30 – 1.20 (m, 2H), 0.80 (t, J = 7.3 Hz, 3H).

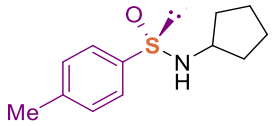
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 141.2, 129.5, 125.9, 40.9, 32.6, 21.3, 19.1, 13.7 ppm.

HRMS (ESI, m/z): Calculated for $C_{11}H_{17}NOSNa^+$ $[M + Na]^+$: 234.0923, found: 234.0919.

$[\alpha]^{25}_D$ = +8.928 (c = 0.4 in $CHCl_3$).

HPLC analysis: 96:4 e.r. (Chiralcel OD-H, 5:95 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (minor) = 13.2 min, Rt (major) = 15.9 min.

(*S*)-*N*-Cyclopentyl-4-methylbenzenylsulfinamide (7)



Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 1:1) yielded the title compound **7**, colorless oil (13.9 mg, 75% yield); R_f 0.5 (Petroleum ether / Ethyl acetate = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.32 (m, 2H), 7.34 – 7.10 (m, 2H), 3.88 (d, J = 6.2 Hz, 1H), 3.66 (h, J = 6.4 Hz, 1H), 2.34 (s, 3H), 2.02 – 1.84 (m, 1H), 1.82 – 1.68 (m, 1H), 1.66 – 1.54 (m, 3H), 1.54 – 1.38 (m, 2H), 1.38 – 1.28 (m, 1H).

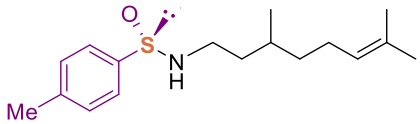
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.2, 141.1, 129.5, 125.8, 55.0, 34.7, 34.2, 23.41, 23.36, 21.3 ppm.

HRMS (ESI, m/z): Calculated for $C_{12}H_{17}NOSNa^+$ $[M + Na]^+$: 246.0923, found: 246.0922.

$[\alpha]^{25}_D$ = +43.557 (c = 0.2 in $CHCl_3$).

HPLC analysis: 96:4 e.r. (Chiralcel OD-H, 10:90 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (minor) = 6.0 min, Rt (major) = 6.9 min.

(*S*)-*N*-(3,7-Dimethyloct-6-en-1-yl)-4-methylbenzenesulfinamide (8)



Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 1:1) yielded the title compound **8**, brown oily (16.1 mg, 66% yield); R_f 0.5 (Petroleum ether / Ethyl acetate = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 7.9 Hz, 2H), 7.30 (d, J = 7.9 Hz, 2H), 5.05 (t, J = 7.2 Hz, 1H), 3.91 (t, J = 6.2 Hz, 1H), 3.16 (ddt, J = 11.6, 8.7, 5.4 Hz, 1H), 2.81 (ddt, J = 12.9, 8.6, 6.5 Hz, 1H), 2.41 (s, 3H), 1.93 (hept, J = 7.5 Hz, 2H), 1.67 (s, 3H), 1.58 (s, 3H), 1.55 – 1.40 (m, 2H), 1.34 (dtd, J = 14.2, 7.6, 6.8, 2.6 Hz, 2H), 1.12 (ddt, J = 13.5, 9.2, 7.0 Hz, 1H), 0.94 – 0.84 (m, 1H), 0.81 (d, J = 6.4 Hz, 3H).

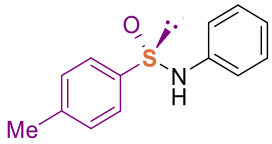
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 141.2, 131.4, 129.5, 125.9, 124.6, 39.1, 37.6, 36.9, 30.1, 25.7, 25.3, 21.3, 19.3, 17.7 ppm.

HRMS (ESI, m/z): Calculated for $C_{17}H_{27}NOSNa^+$ $[M + Na]^+$: 316.1706, found: 316.1693.

$[\alpha]^{25}_D$ = +3.338 (c = 0.4 in $CHCl_3$).

HPLC analysis: 97:3 e.r. (Chiralcel OD-H, 10:90 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (minor) = 8.1 min, Rt (major) = 11.6 min.

(*S*)-4-Methyl-*N*-phenylbenzenesulfinamide (9)



Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 5:1) yielded the title compound **9**, faint white solid (16.9 mg, 73% yield); R_f 0.4 (Petroleum ether / Ethyl acetate = 5:1); m.p. 100.4 – 103.2 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.57 (m, 2H), 7.35 – 7.19 (m, 4H), 7.12 – 6.97 (m, 3H), 6.42 (s, 1H), 2.41 (s, 3H).

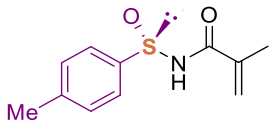
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9, 141.5 (d, J = 2.6 Hz), 140.8, 129.8, 129.5, 125.54, 123.5, 118.8, 21.4 ppm.

HRMS (ESI, m/z): Calculated for $C_{13}H_{14}NOS^+$ $[M + H]^+$: 232.0791, found: 232.0793.

$[\alpha]^{25}_D$ = +97.253 (c = 0.2 in $CHCl_3$).

HPLC analysis: 96:4 e.r. (Chiralcel ID, 20:80 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (minor) = 13.2 min, Rt (major) = 15.9 min.

(*S*)-*N*-(*p*-Tolylsulfinyl) methacrylamide (10)



Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 1:1) yielded the title compound **10**, colorless oil (15.6 mg, 70% yield); R_f 0.4 (Petroleum ether / Ethyl acetate = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.65 – 7.58 (m, 2H), 7.35 (d, J = 8.0 Hz, 2H), 5.76 (d, J = 1.1 Hz, 1H), 5.56 (q, J = 1.6 Hz, 1H), 2.44 (s, 3H), 1.97 (t, J = 1.3 Hz, 3H).

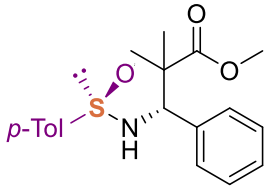
^{13}C NMR (101 MHz, $CDCl_3$) δ 136.5, 130.2, 129.4, 128.3, 127.6, 124.59, 21.7, 21.5.

HRMS (ESI, m/z): Calculated for $C_{11}H_{13}NO_2SNa^+$ $[M + Na]^+$: 246.0559, found: 246.0556.

$[\alpha]^{25}_D$ = +11.680 (c = 0.5 in $CHCl_3$).

HPLC analysis: 93:7 e.r. (Chiralcel ID, 10:90 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (minor) = 13.9 min, Rt (major) = 23.8 min.

(*R*)-*N*-[(*S*)-2,2-Dimethyl-1-phenylpropionate methyl ester]-4-methylbenzene-sulfin-amide (11)



Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 1:1) yielded the title compound **11**, colorless oil (34.6 mg, 80% yield, 6:1 d.r. (determined by HPLC)); R_f 0.5 (Petroleum ether / Ethyl acetate = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 2H), 7.11 – 7.01 (m, 3H), 6.96 (d, J = 7.9 Hz, 2H), 6.86 – 6.80 (m, 2H), 5.45 (d, J = 7.7 Hz, 1H), 4.29 (d, J = 7.7 Hz, 1H), 3.62 (s, 3H), 2.22 (s, 3H), 1.21 (s, 3H), 1.08 (d, J = 17.3 Hz, 1H), 1.00 (s, 3H).

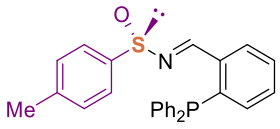
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.9, 141.0, 140.9, 139.7, 129.0, 127.9, 127.70, 127.2, 125.9, 62.8, 52.1, 47.2, 24.8, 21.4, 21.2 ppm.

HRMS (ESI, m/z): Calculated for $C_{19}H_{23}NO_3SNa^+$ [M + Na]$^+$: 368.1291, found: 368.1280.

$[\alpha]^{25}_D$ = 20.511 (c = 0.2, in $CHCl_3$).

HPLC analysis: 93:7 e.r. (Chiralcel IA, 10:90 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (major) = 8.5 min, Rt (minor) = 10.8 min.

(*S*)-*N*-(2-(Diphenylphosphaneyl) benzyl)-4-methylbenzenesulfinamide (12)



Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 5:1) yielded the title compound **12**, yellow solid (53.0 mg, 53% yield); R_f 0.7 (Petroleum ether / Ethyl acetate = 5:1); m.p. 115.3 – 117.5 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38 (d, *J* = 5.2 Hz, 1H), 7.94 (ddd, *J* = 7.6, 3.8, 1.4 Hz, 1H), 7.30 (tddd, *J* = 14.1, 8.2, 7.0, 3.0 Hz, 14H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.94 (ddd, *J* = 7.6, 4.2, 1.4 Hz, 1H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 159.5, 141.7, 141.4, 140.2, 140.0, 137.3, 137.2, 136.8 – 136.4 (m), 136.1 (d, *J* = 9.8 Hz), 134.4, 134.2 (d, *J* = 3.6 Hz), 133.9 (d, *J* = 4.8 Hz), 131.8, 129.9 (d, *J* = 4.0 Hz), 129.7, 129.0 – 128.9 (m), 128.7 (dd, *J* = 7.2, 1.7 Hz), 124.8, 21.5 ppm.

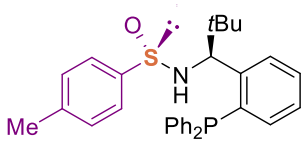
^{31}P NMR (162 MHz, $CDCl_3$) δ -13.3 ppm.

HRMS (ESI, m/z): Calculated for $C_{26}H_{22}NOPSNa^+$ [M + Na]$^+$: 450.1052, found: 450.1048.

$[\alpha]^{25}_D$ = +81.511 (c = 0.5 in $CHCl_3$).

HPLC analysis: 94:6 e.r. (Chiralcel IA, 10:90 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (minor) = 7.0 min, Rt (major) = 9.0 min.

(*S*)-*N*-((*S*)-1-(2-(diphenylphosphaneyl) phenyl) *tert*-butyl)-4-methylbenzenesulfin Amide (13)



Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 5:1) yielded the title compound **13**, a white solid. (37.1 mg, 70% yield, >20:1 d.r. (determinedby ^{1}H NMR)); R_f 0.5 (Petroleum ether / Ethyl acetate = 5:1); m.p. 88.3 – 90.5 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.30 (m, 8H), 7.25 – 7.09 (m, 10H), 5.64 (dd, *J* = 11.1, 4.7 Hz, 1H), 4.28 (d, *J* = 4.9 Hz, 1H), 2.32 (s, 3H), 0.86 (s, 9H).

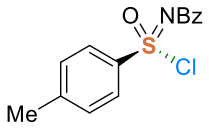
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.6, 146.4, 143.2, 141.1, 138.4, 138.3, 137.56 (d, *J* = 14.0 Hz), 136.7 (d, *J* = 11.7 Hz), 135.8, 133.8, 133.6 (d, *J* = 6.5 Hz), 133.4, 129.4, 128.8, 128.6 (d, *J* = 4.9 Hz), 128.5 – 128.3 (m), 127.4, 125.5, 63.0, 62.7, 36.1, 29.7, 27.2 (d, *J* = 2.8 Hz), 21.4 ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ -19.0 ppm.

HRMS (ESI, m/z): Calculated for $C_{30}H_{32}NOPSNa^+$ $[M + Na]^+$: 508.1834, found: 508.1844.

$[\alpha]^{25}_D$ = +41.389 (c = 0.2 in $CHCl_3$).

(*S*)-*N*-Benzoyl-1-methyl-(p-tolyl)-oxidanesulfinimidic chloride (14)



Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 10:1) yielded the title compound **14**, white solid (0.18 g, 60% yield).; R_f 0.7 (Petroleum ether / Ethyl acetate = 10:1); m.p. 97.3 – 100.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (ddd, J = 11.6, 7.4, 1.6 Hz, 4H), 7.62 '– 7.52 (m, 1H), 7.52 – 7.40 (m, 4H), 2.50 (s, 3H).

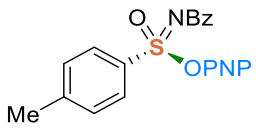
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 147.0, 140.1, 134.2, 133.4, 130.4, 129.78, 128.4, 127.2, 21.9 ppm.

HRMS (ESI, m/z): Calculated for $C_{14}H_{12}ClNO_2SNa^+$ $[M + Na]^+$: 316.0169, found: 316.0170.

$[\alpha]^{25}_{D}$ = -44.356 (c = 0.2 in $CHCl_3$).

HPLC analysis: 96:4 e.r. (Chiralcel IA, 10:90 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (major) = 13.6 min, Rt (minor) = 16.9 min.

(*S*)-4-Nitrophenyl *N*-benzoyl-4-methylbenzenesulfonimidate (15)



Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 10:1) yielded the title compound **15**, faint yellow solid (45 mg, 90% yield); R_f 0.5 (Petroleum ether / Ethyl acetate = 10:1); m.p. 131.5 – 133.3 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.16 (m, 2H), 8.15 – 8.10 (m, 2H), 8.03 – 7.91 (m, 2H), 7.63 – 7.50 (m, 1H), 7.42 (dt, *J* = 7.8, 3.6 Hz, 4H), 7.36 – 7.28 (m, 2H), 2.49 (s, 3H).

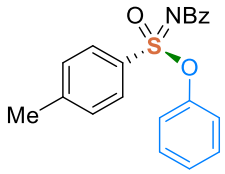
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 153.9, 146.6, 146.3, 134.7, 132.9, 130.3, 129.8, 128.3, 128.2, 125.4, 123.8, 21.8 ppm.

HRMS (ESI, m/z): Calculated for $C_{20}H_{16}N_2O_5SNa^+$ $[M + Na]^+$: 419.0672, found: 419.0672.

$[\alpha]^{25}_{D}$ = +7.288 (c = 0.2 in $CHCl_3$).

HPLC analysis: 93:7 e.r. (Chiralcel IB, 10:90 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (major) = 16.8 min, Rt (minor) = 18.9 min.

(*S*)-Phenyl N-benzoyl-4-methylbenzenesulfonimidate (16)



Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 10:1) yielded the title compound **16**, colorless oil (19.5 mg, 65% yield); R_f 0.5 (Petroleum ether / Ethyl acetate = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 7.99 (m, 2H), 7.89 – 7.82 (m, 2H), 7.50 – 7.39 (m, 1H), 7.38 – 7.25 (m, 4H), 7.25 – 7.14 (m, 3H), 7.09 – 6.99 (m, 2H), 2.37 (s, 3H).

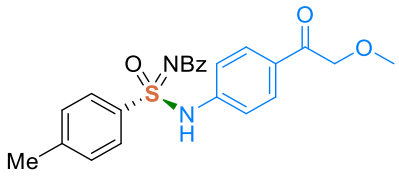
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 149.3, 145.8, 135.3, 133.2, 132.5, 129.94, 129.7, 128.3, 128.1, 127.4, 122.9, 21.8 ppm.

HRMS (ESI, m/z): Calculated for $C_{20}H_{17}NO_3SNa^+$ [M + Na]$^+$: 374.0821, found: 374.0828.

$[\alpha]^{25}_D$ = +6.557 (c = 0.2 in $CHCl_3$).

HPLC analysis: 96:4 e.r. (Chiralcel IA, 20:80 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (minor) = 9.1 min, Rt (major) = 11.2 min.

(*S*)-4-Nitrophenyl *N*-benzoyl-4-methylbenzenesulfonimidate (17)



Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 5:1) yielded the title compound **17**, colorless oil (16.5 mg, 55% yield); R_f 0.3 (Petroleum ether / Ethyl acetate = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.13 (m, 2H), 7.96 – 7.89 (m, 2H), 7.88 – 7.80 (m, 2H), 7.58 – 7.49 (m, 1H), 7.42 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 7.23 – 7.15 (m, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H).

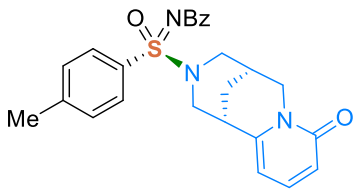
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 165.9, 145.0, 140.4, 136.0, 135.1, 132.8, 131.2, 130.1, 129.7, 128.2, 127.2, 126.8, 119.9, 61.0, 21.6, 14.3 ppm.

HRMS (ESI, m/z): Calculated for $C_{23}H_{22}N_2O_4SNa^+$ [M + Na]$^+$: 423.1373, found: 423.1369.

$[\alpha]^{25}_D$ = +15.938 (c = 0.4 in $CHCl_3$).

HPLC analysis: 95:5 e.r. (Chiralcel IC, 25:75 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (major) = 16.6 min, Rt (minor) = 21.9 min.

(*S*)-*N*-(Oxo((1R,5R)-8-oxo-1,5,6,8-tetrahydro-2*H*-1,5-methanopyrido[1,2-a] [1,5] diazocin-3(4*H*)-yl) (*p*-tolyl)-λ^6-sulfaneylidene) benzamide (18)



Prepared according to general procedure A. Flash column chromatography (Ethyl acetate) yielded the title compound **18**, colorless oil (21.3 mg, 71% yield); R_f 0.2 (Ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.01 (m, 2H), 7.60 – 7.40 (m, 3H), 7.36 (tt, *J* = 6.7, 1.4 Hz, 2H), 7.28 (dd, *J* = 9.1, 6.8 Hz, 1H), 7.16 (d, *J* = 8.2 Hz, 2H), 6.46 (dd, *J* = 9.1, 1.4 Hz, 1H), 6.04 (dd, *J* = 6.9, 1.4 Hz, 1H), 4.03 (ddd, *J* = 12.0, 3.4, 1.9 Hz, 1H), 3.70 – 3.57 (m, 1H), 3.47 (dd, *J* = 12.1, 2.0 Hz, 1H), 3.42 – 3.30 (m, 2H), 3.17 – 3.09 (m, 1H), 3.09 – 2.97 (m, 1H), 2.36 (s, 3H), 1.88 (t, *J* = 3.2 Hz, 5H).

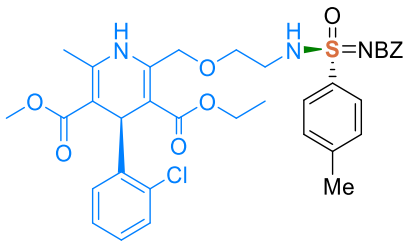
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 163.2, 149.1, 145.0, 139.1, 135.6, 134.4, 132.3, 130.1, 129.5, 128.1, 127.6, 117.3, 105.4, 53.5, 51.0, 48.9, 34.7, 27.1, 25.2, 21.7 ppm.

HRMS (ESI, m/z): Calculated for $C_{25}H_{25}N_3O_3SNa^+$ $[M + Na]^+$: 448.1689, found: 448.1689.

$[\alpha]^{25}_D$ = -13.585 (c = 0.2, in $CHCl_3$).

HPLC analysis: 95:5 e.r. (Chiralcel IA, 50:50 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (minor) = 8.1 min, Rt (major) = 10.2 min.

(*S*)-3-Ethyl-5-methyl (4*S*)-2-((2-((*N*′-benzoyl-4-methylphenyl) sulfonoamidimid amido) ethoxy) methyl)-4-(2-chlorophenyl)-6-methyl-1,4-dihydropyridine-3,5-dicarboxylate (20)



Prepared according to general procedure A. Flash column chromatography (Petroleum ether / Ethyl acetate = 5:1) yielded the title compound **20**, colorless oil (20.855 mg, 70% yield); R_f 0.6 (Petroleum ether / Ethyl acetate = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (t, *J* = 6.0 Hz, 1H), 8.08 – 8.00 (m, 2H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.50 – 7.39 (m, 1H), 7.31 (ddt, *J* = 21.4, 13.9, 7.4 Hz, 6H), 7.15 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.07 (td, *J* = 7.4, 1.4 Hz, 1H), 6.96 (td, *J* = 7.6, 1.6 Hz, 1H), 5.32 (s, 1H), 4.64 (q, *J* = 15.6 Hz, 2H), 3.96 (qd, *J* = 7.0, 4.1 Hz, 2H), 3.67 (ddd, *J* = 9.8, 6.6, 3.2 Hz, 1H), 3.54 (s, 3H), 3.32 (dtd, *J* = 13.4, 6.7, 3.4 Hz, 1H), 3.13 (ddd, *J* = 14.0, 6.8, 3.4 Hz, 1H), 2.36 (d, *J* = 5.4 Hz, 6H), 1.68 (s, 1H), 1.10 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 168.1, 167.3, 146.0, 144.9 (d, *J* = 4.2 Hz), 144.7, 136.0, 135.4, 132.5, 132.2, 131.5, 130.1, 129.5, 129.2, 128.1, 127.4, 127.3, 127.0, 103.8, 101.8, 69.2, 68.0, 59.9, 50.8, 41.7, 37.0, 25.6, 21.6, 19.2, 14.3 ppm.

HRMS (ESI, m/z): Calculated for $C_{34}H_{36}ClN_3O_7SNa^+$ $[M + Na]^+$: 666.2035, found: 666.2025.

$[\alpha]^{25}_D$ = -16.687 (c = 0.2, in $CHCl_3$).

HPLC analysis: 96:4 e.r. (Chiralcel IG, 90:10 *i*-PrOH/*n*-Hexane, 1.0 mL/min), Rt (major) = 14.5 min, Rt (minor) = 17.9 min.

4. References

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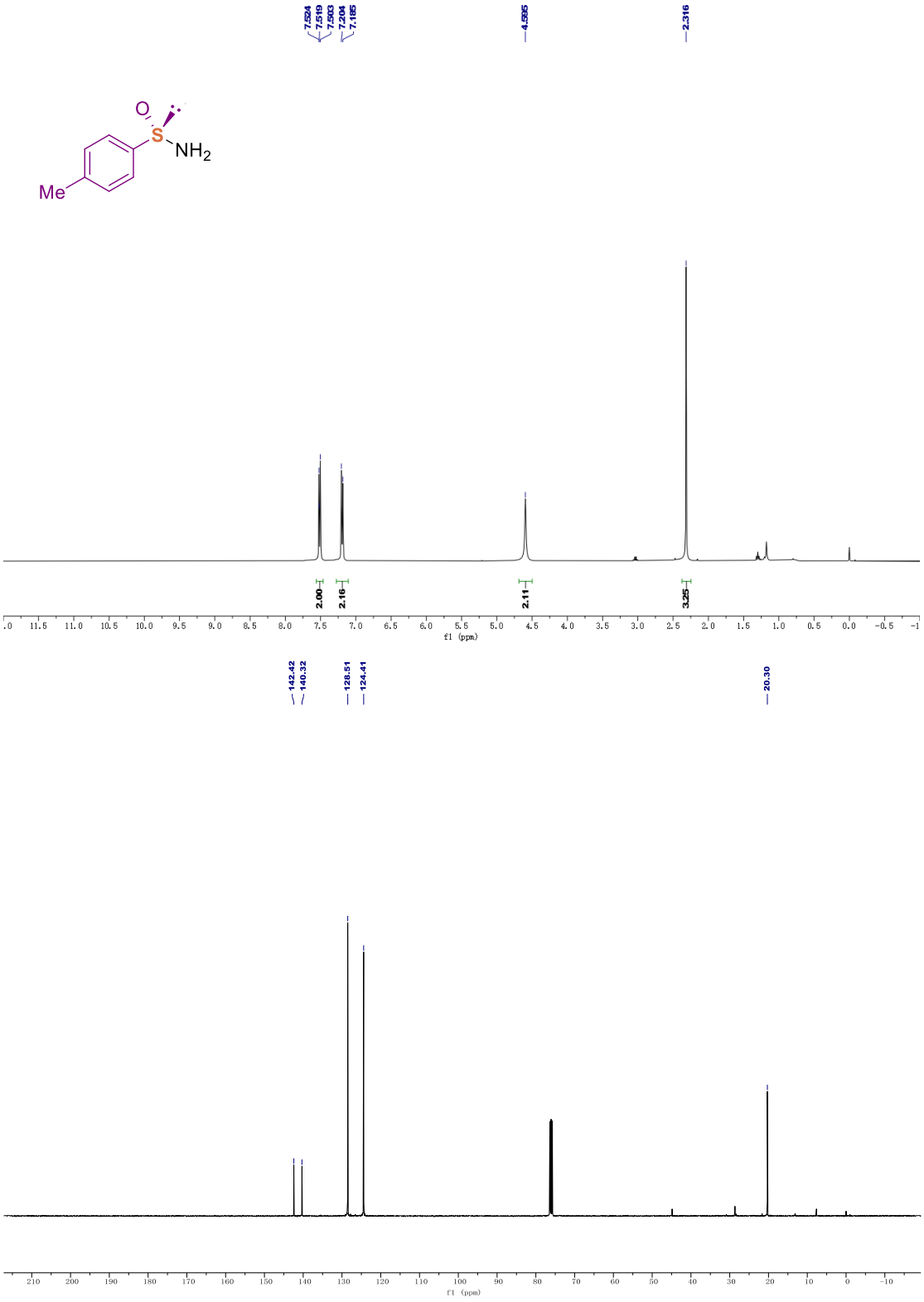
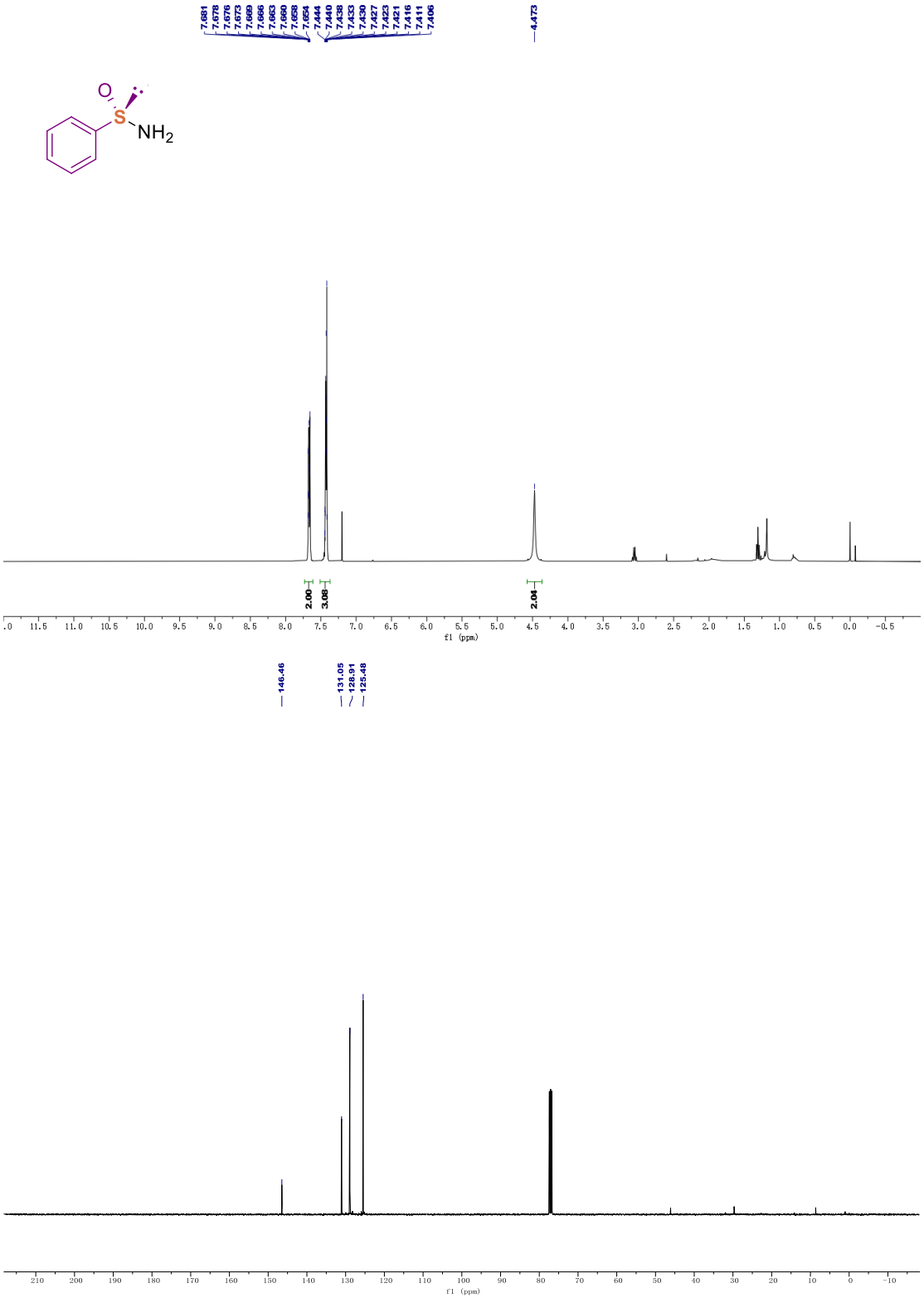
5. Copies of ^{1}H, ^{19}F and ^{13}C NMR

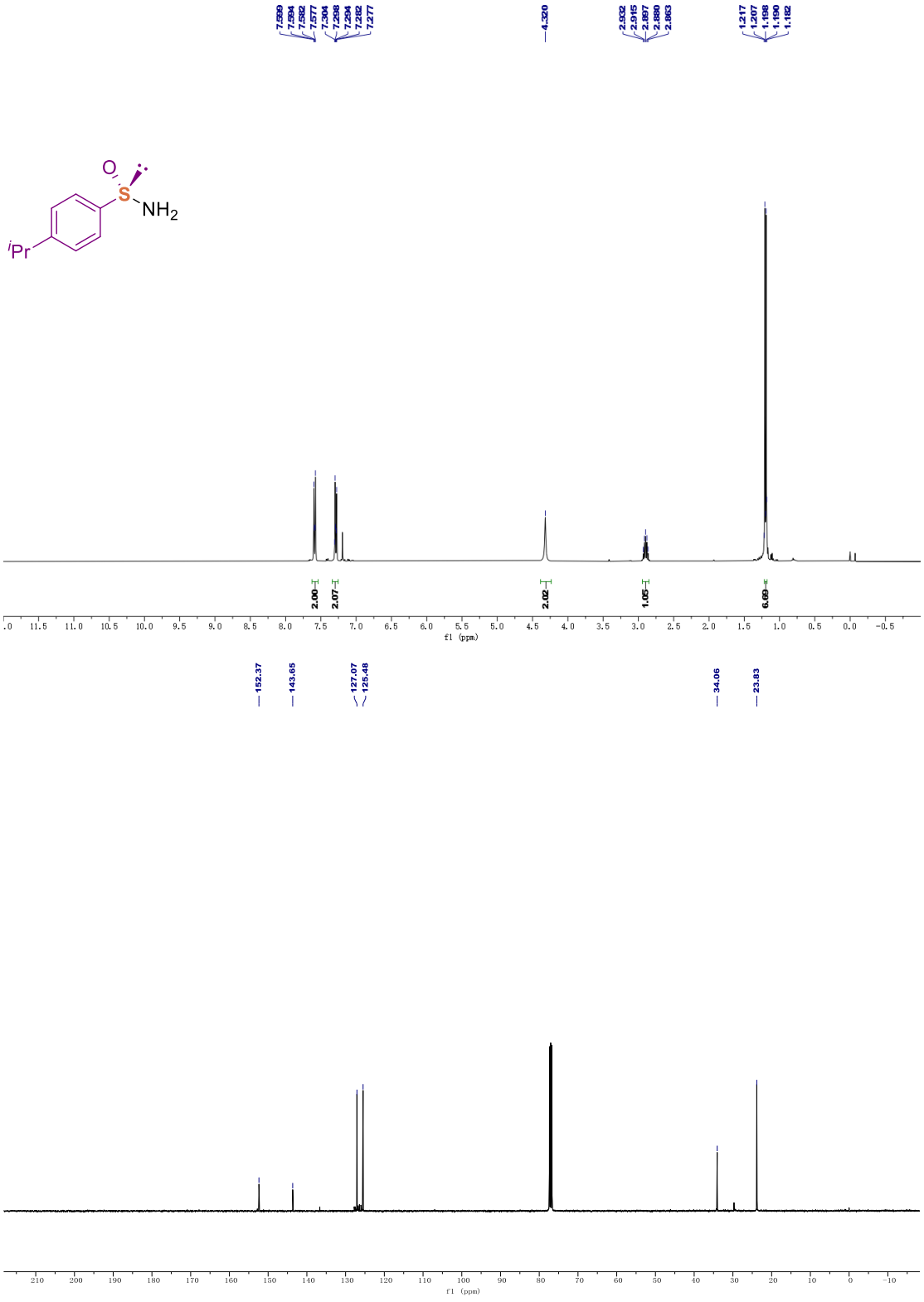
(*S*)-4-Methylbenzenesulfinamide (4a):



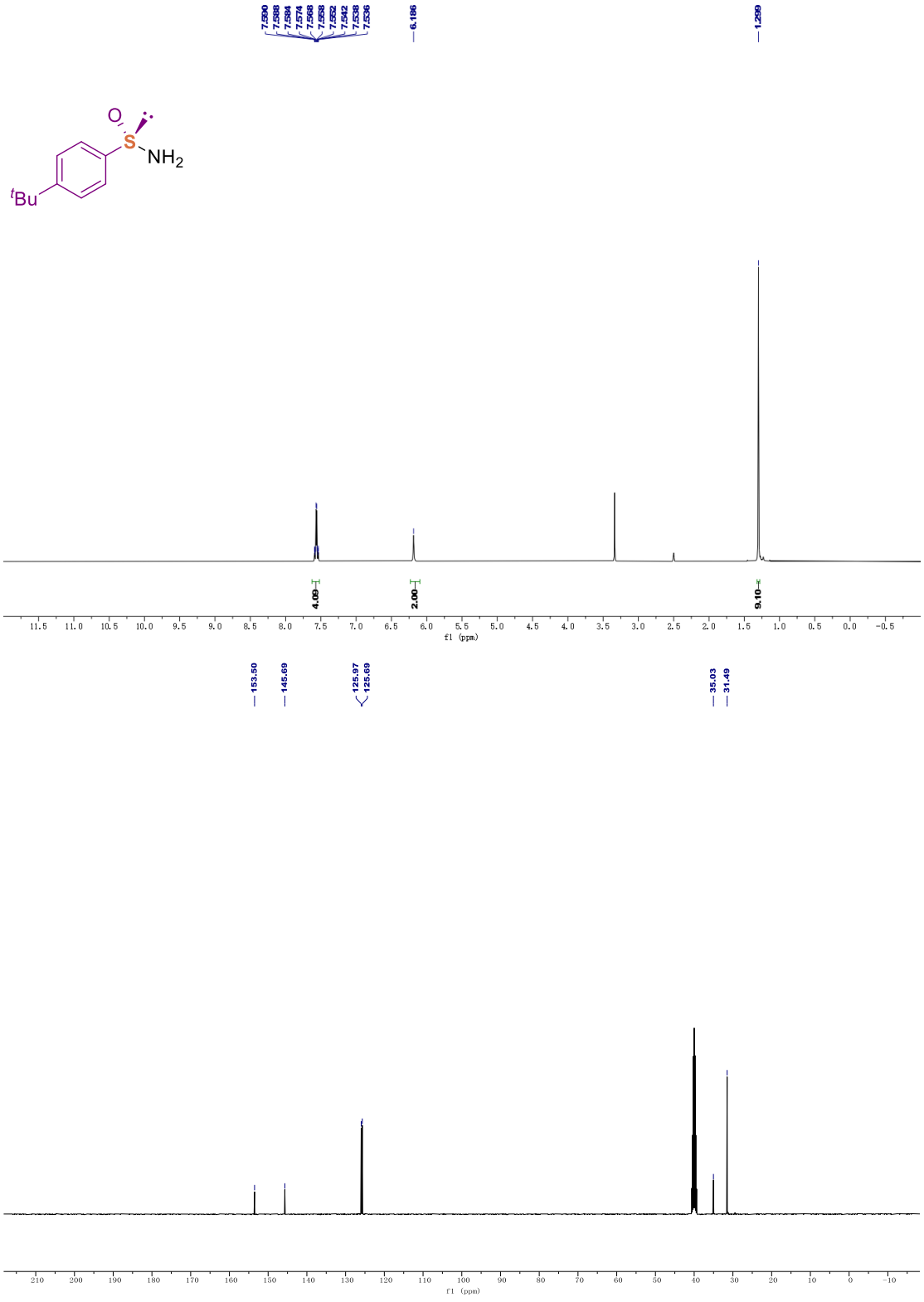
(*S*)-Benzenesulfinamide (4b):



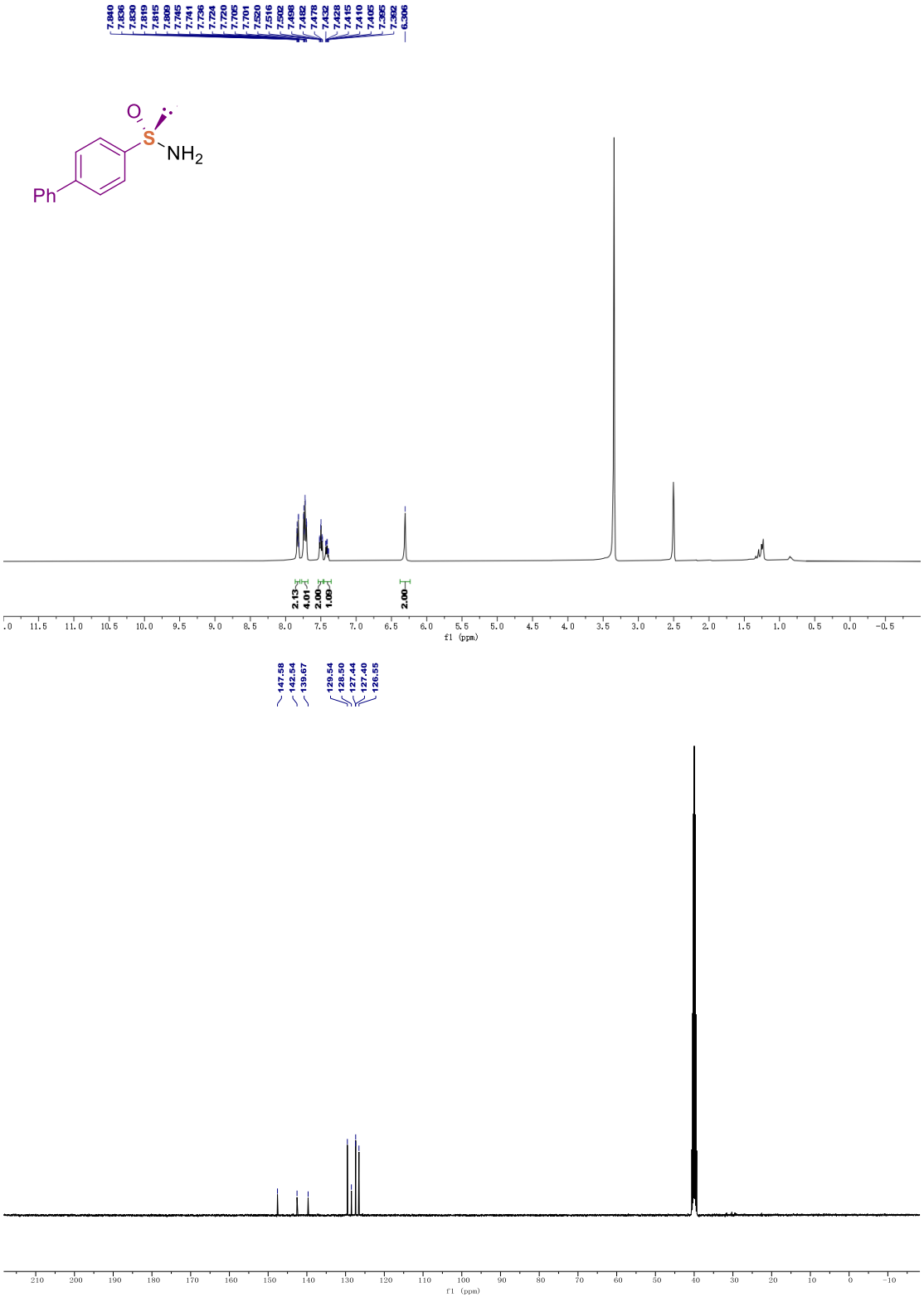
(*S*)-4-Isopropylbenzenesulfonamide (4c):



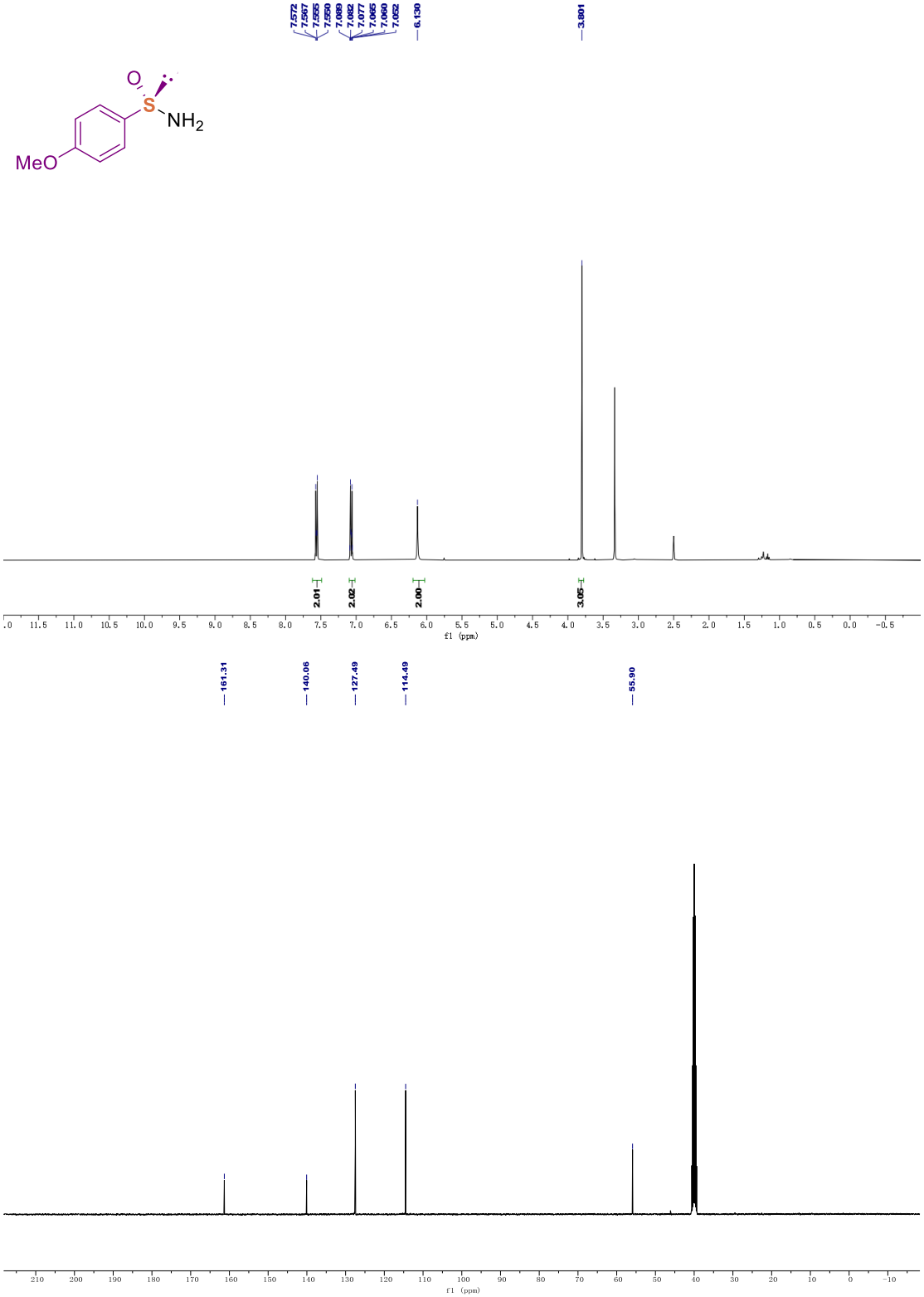
(*S*)-4-Tert-butylbenzenesulfonamide (4d):



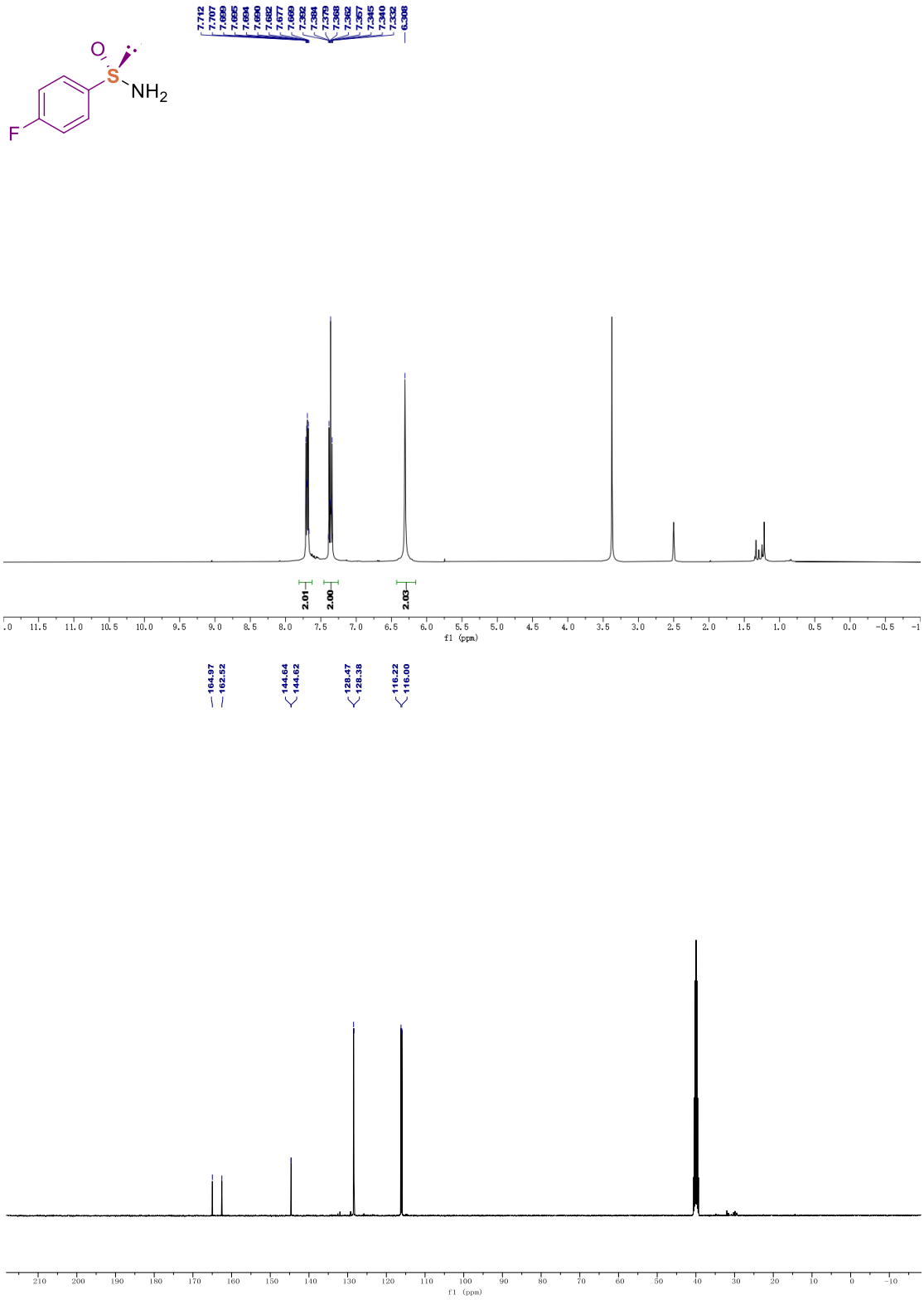
(*S*)-[1,1'-Biphenyl]-4-sulfinamide (4e):

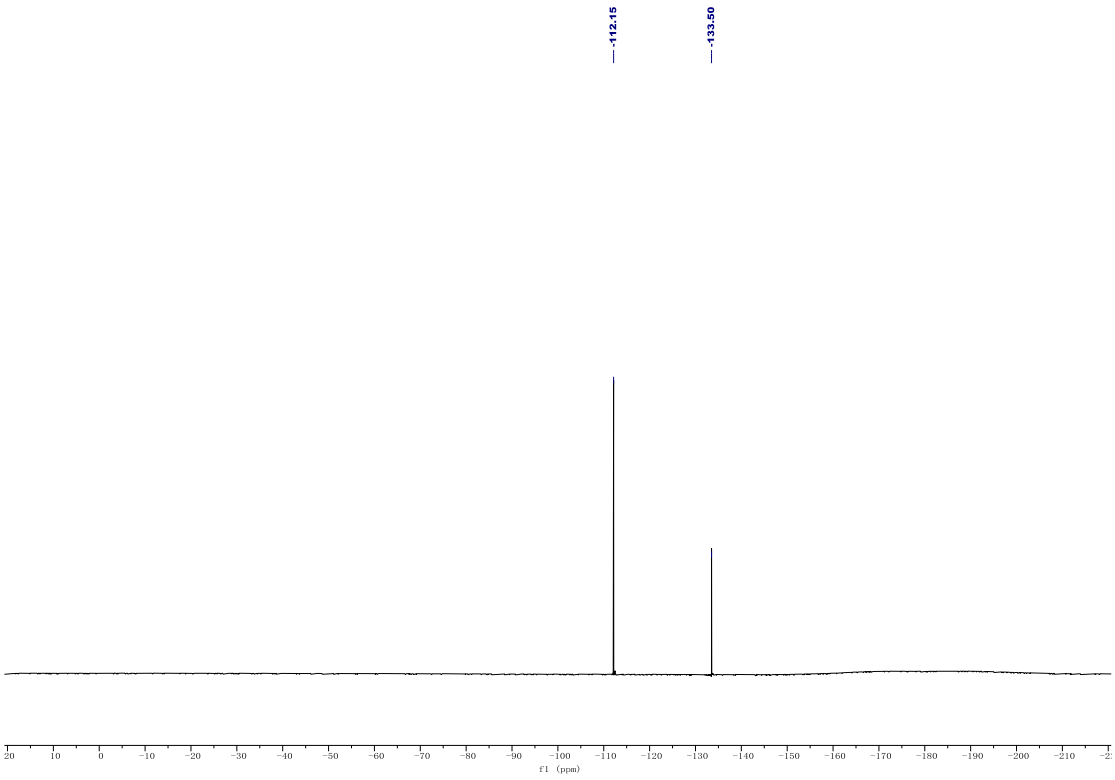


(*S*)-4-Methoxybenzenesulfinamide (4f):

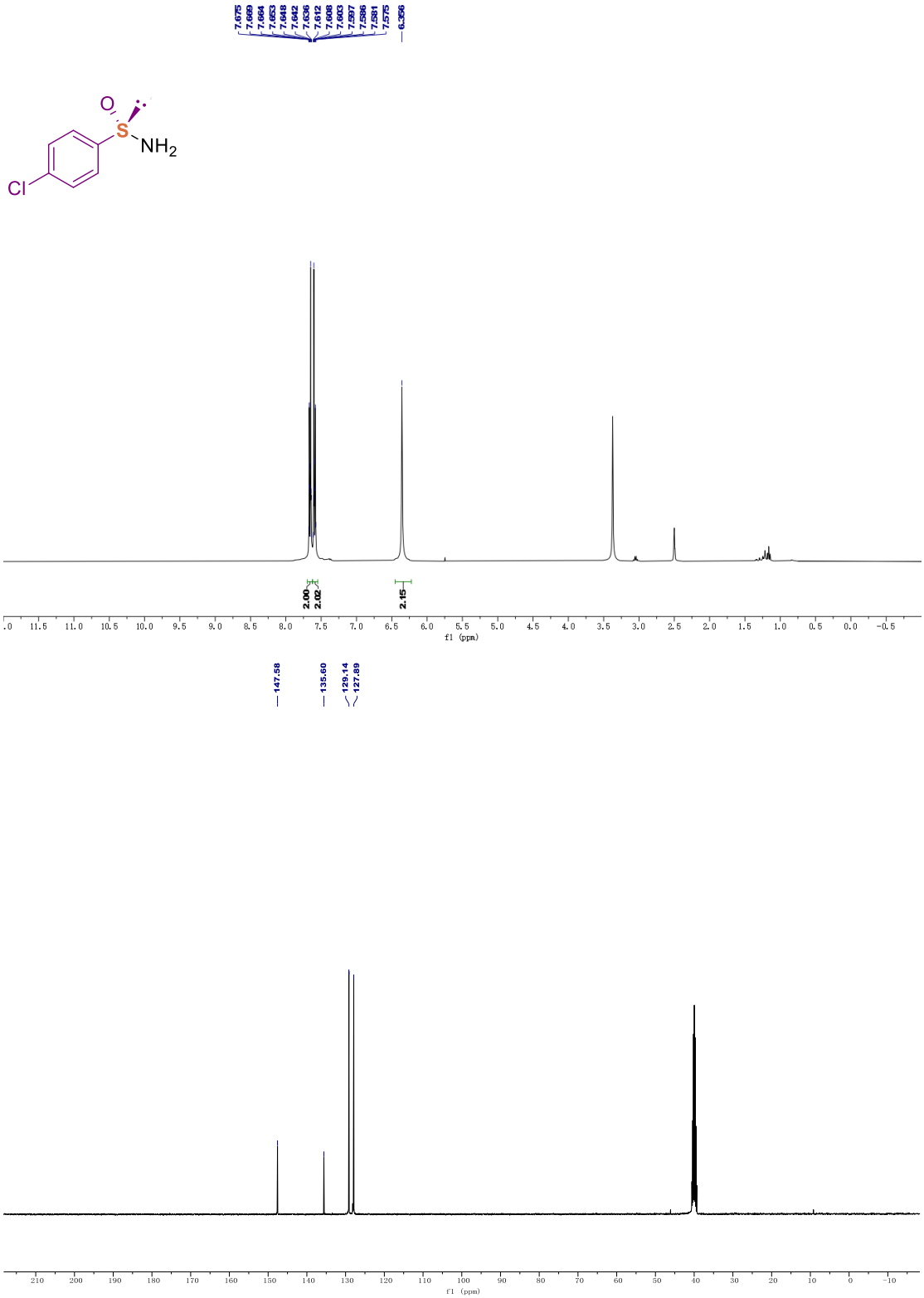


(*S*)-4-Fluorobenzenesulfinamide (4g):

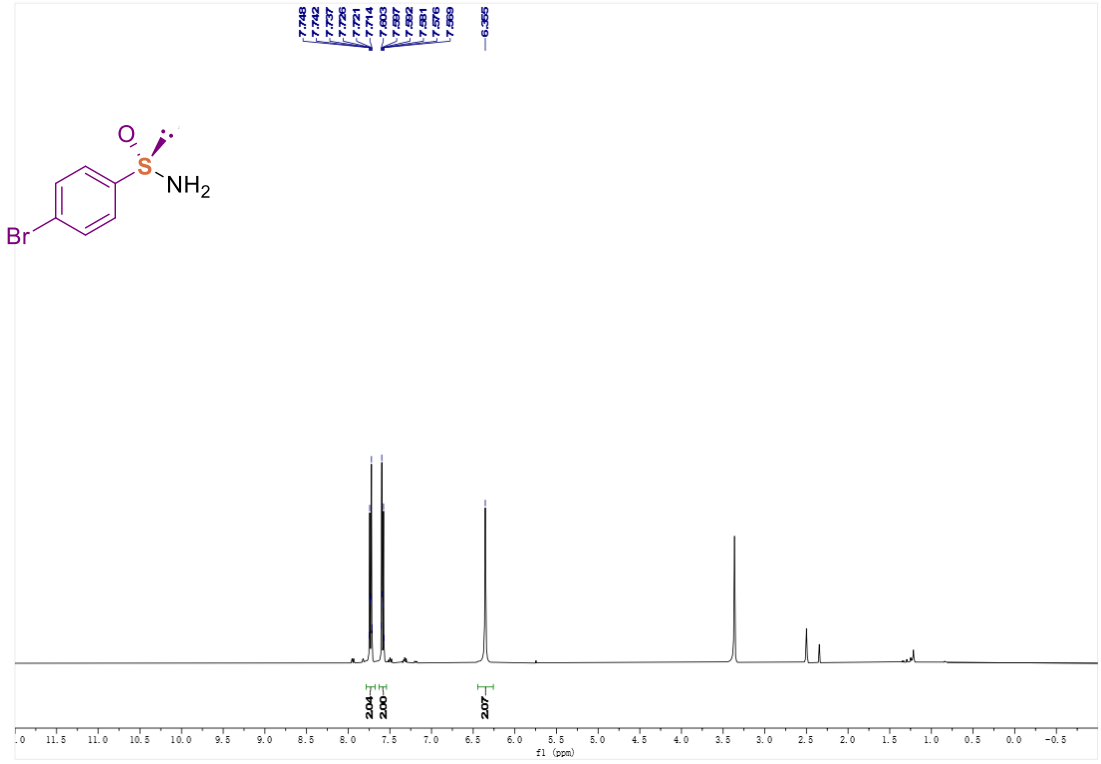


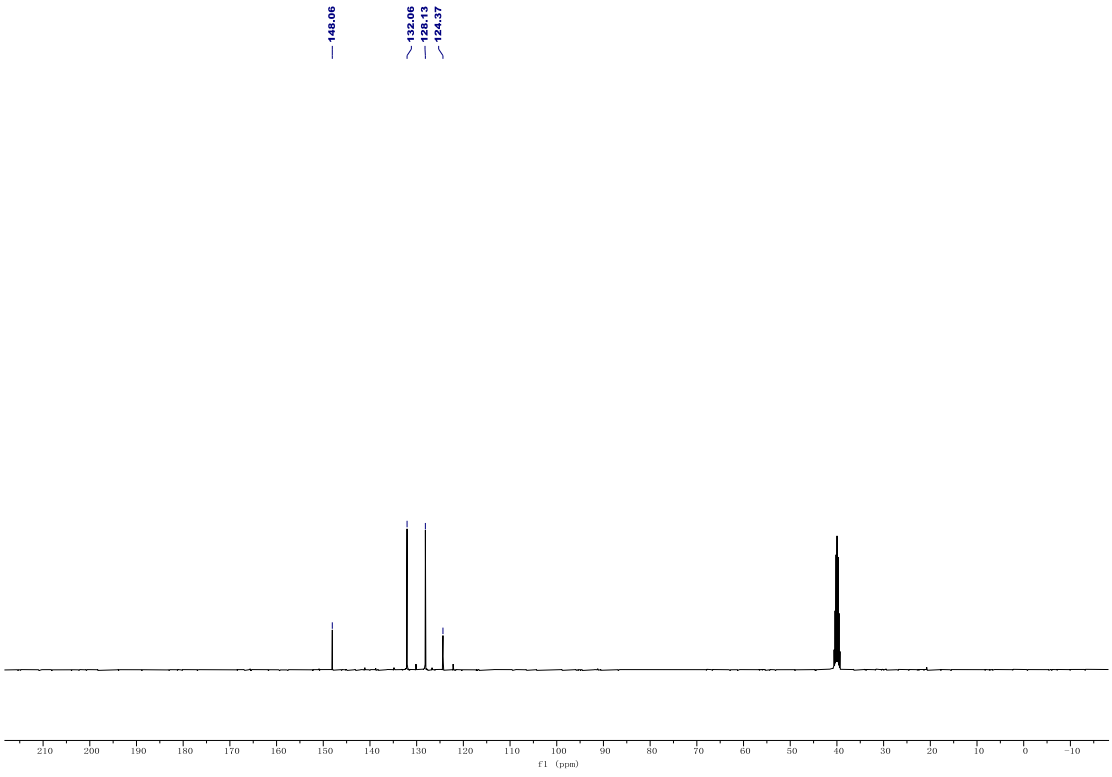

-112.15
-133.50
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

(*S*)-4-Chlorobenzenesulfinamide (4h):

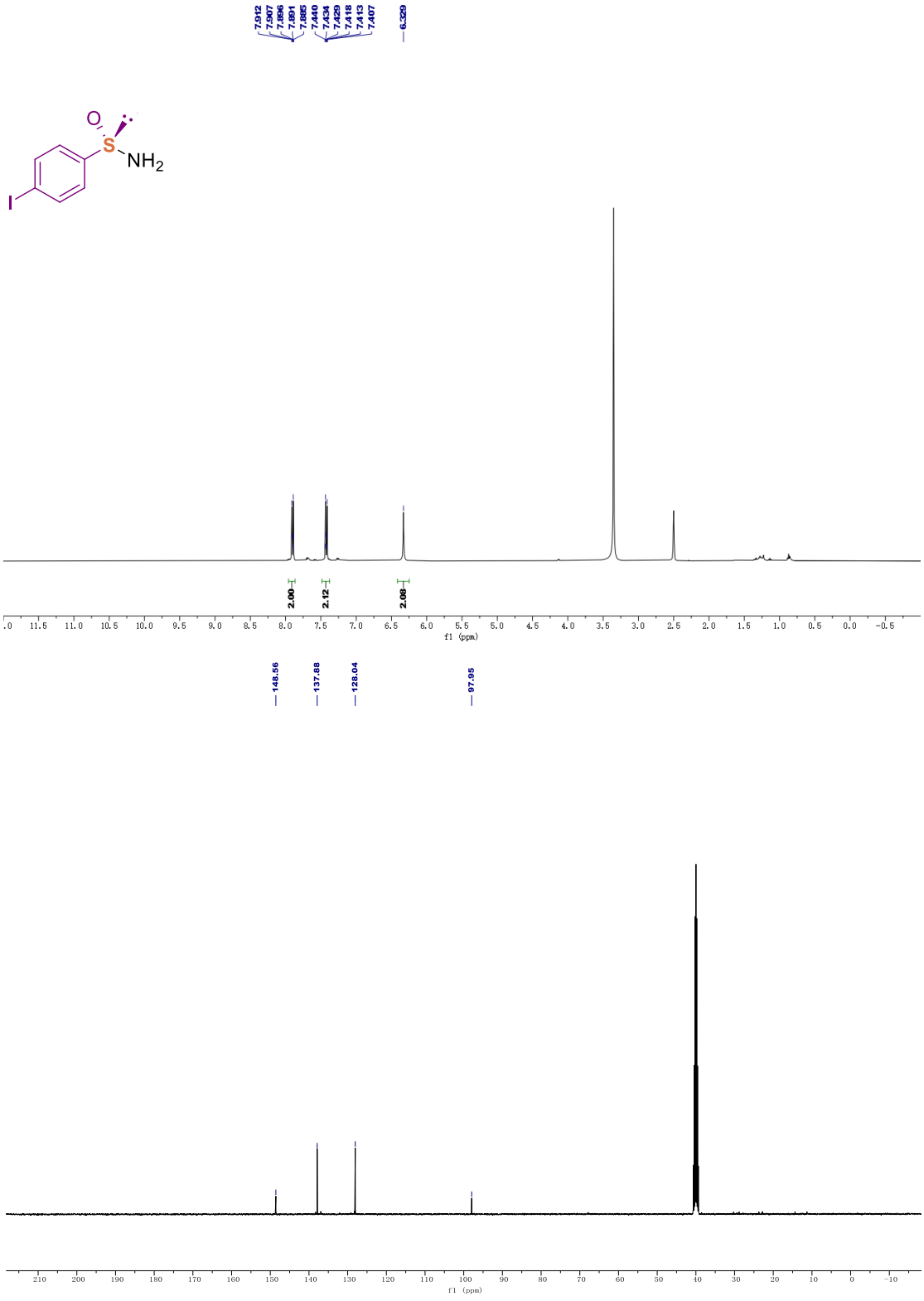


(*S*)-4-Bromobenzenesulfinamide (4i):

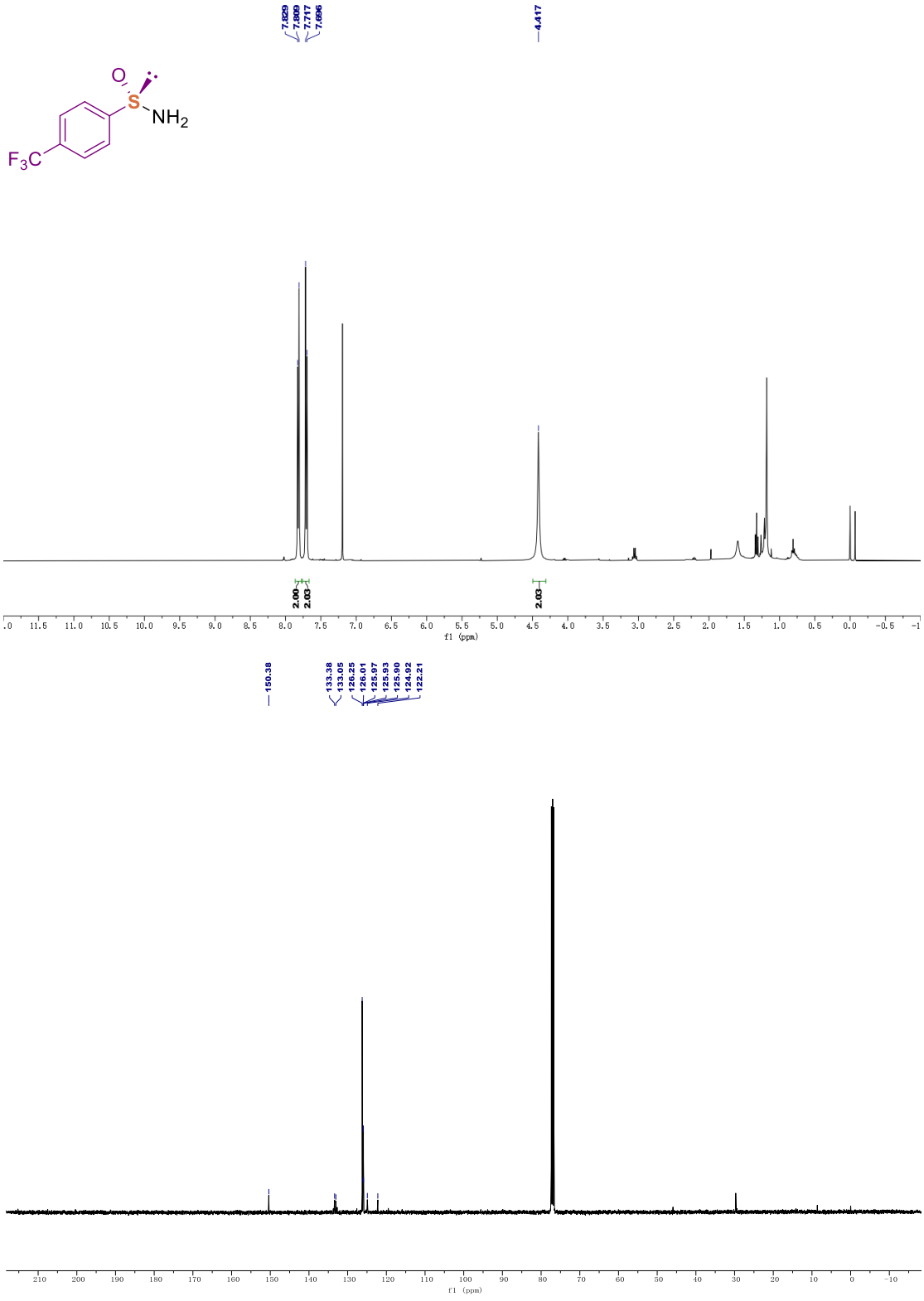


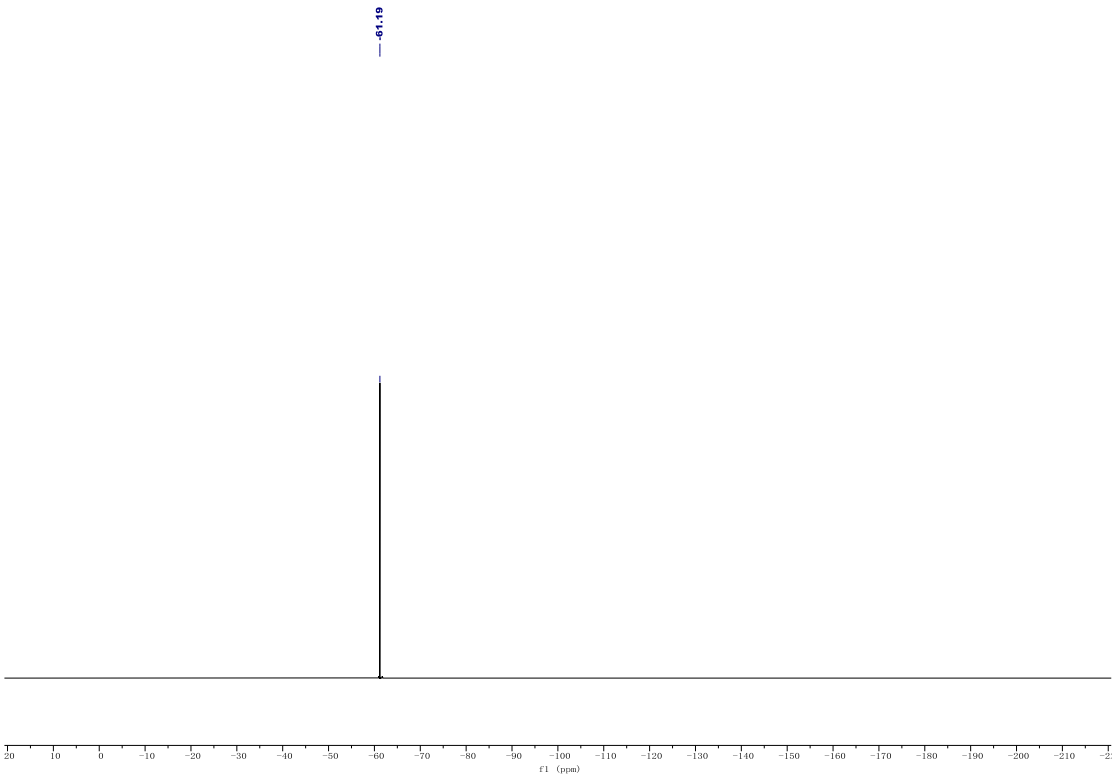


(*S*)-4-Iodobenzenesulfinamide (4j):

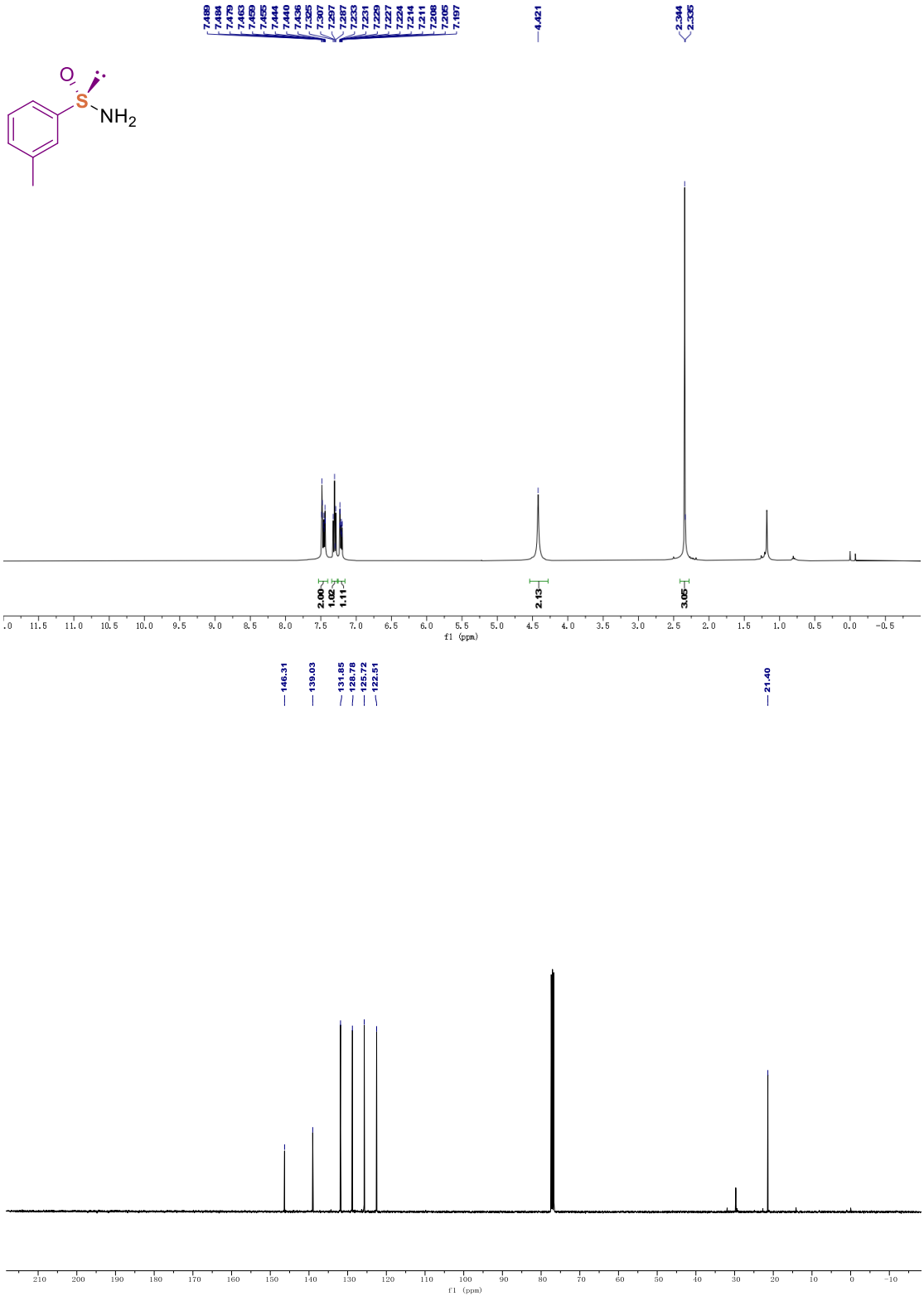


(*S*)-4-Trifluoromethylbenzenesulfonamide (4k):

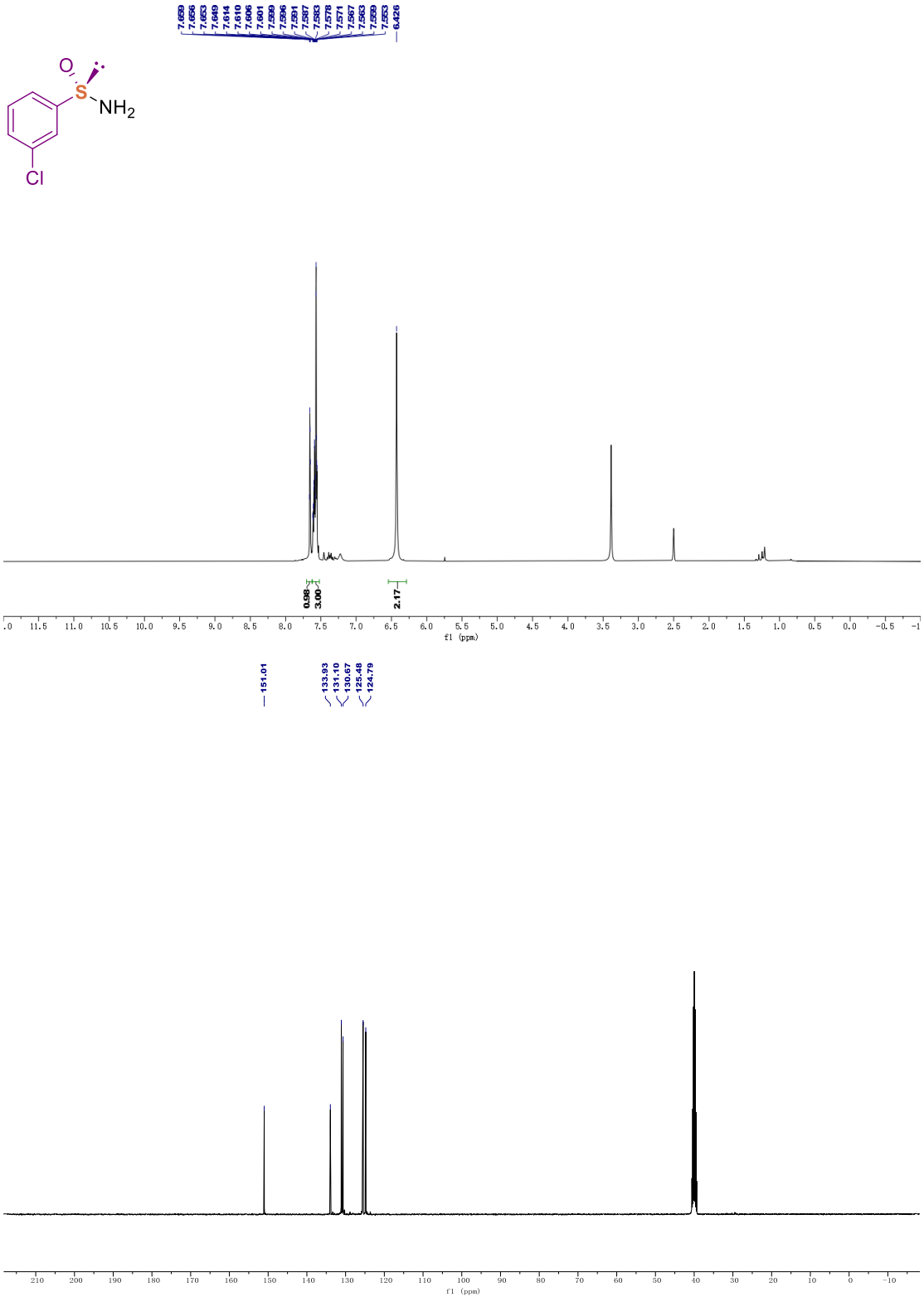



-61.19
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

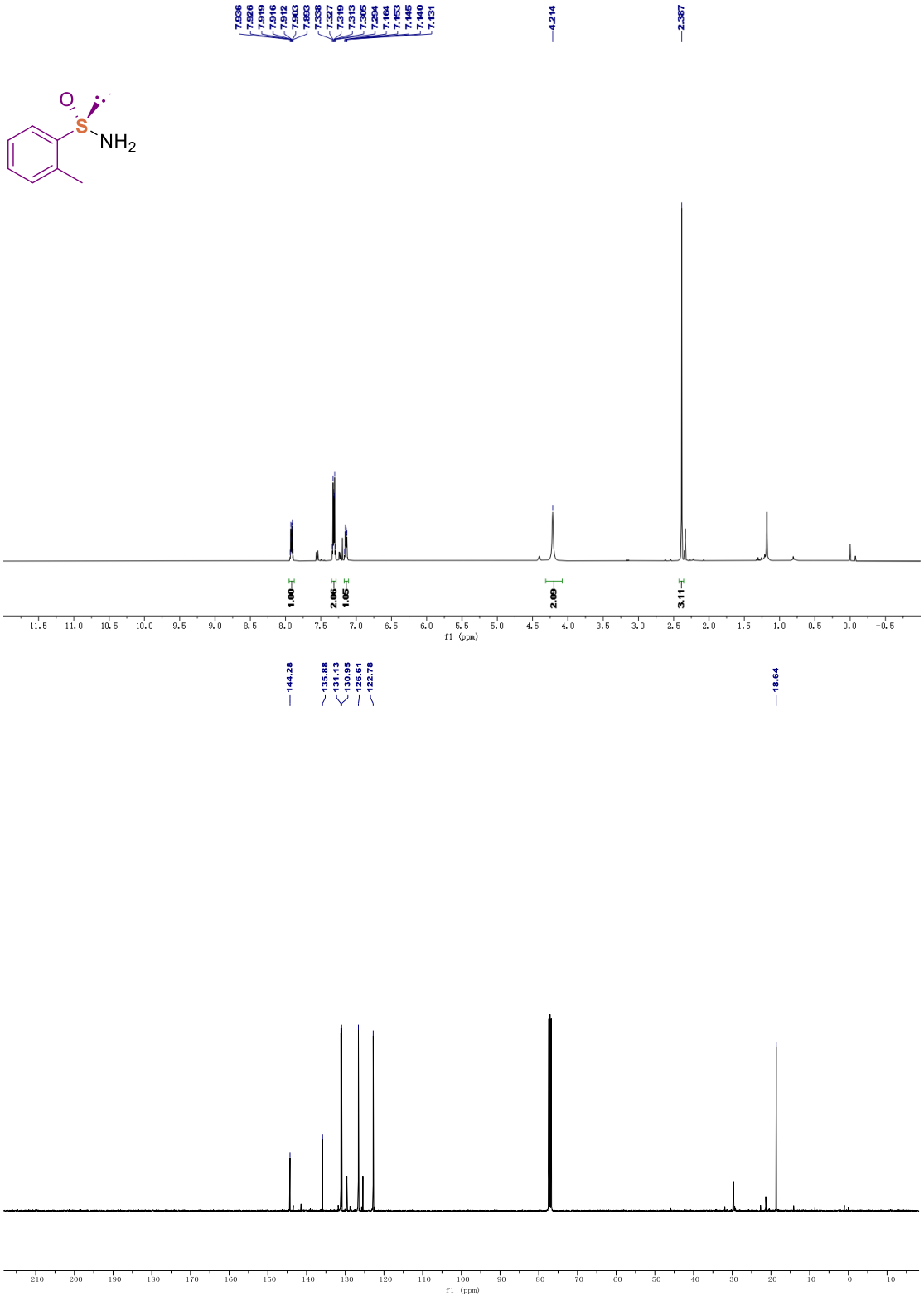
(*S*)-4-Methylbenzenesulfonamide (4l):



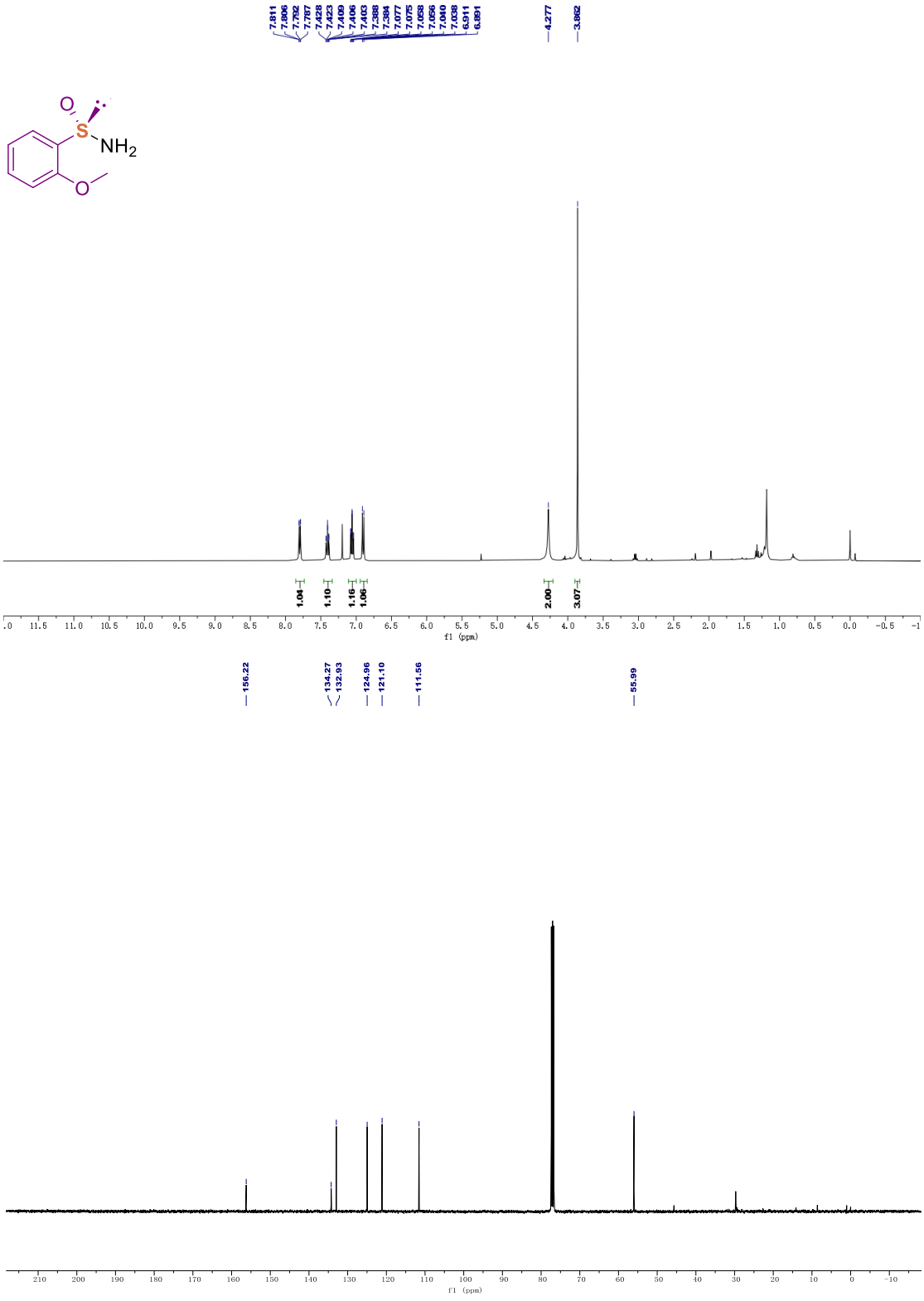
(*S*)-3-Chlorobenzenesulfonamide (4m):



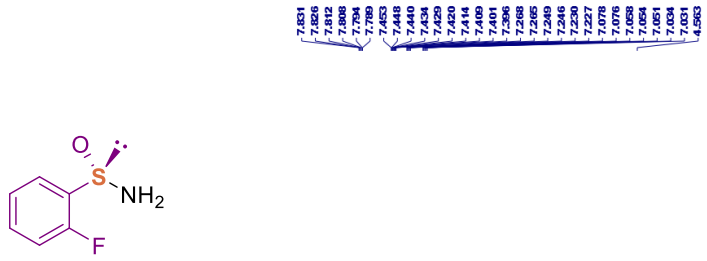
(*S*)-2-Methylbenzenesulfonamide (4n):

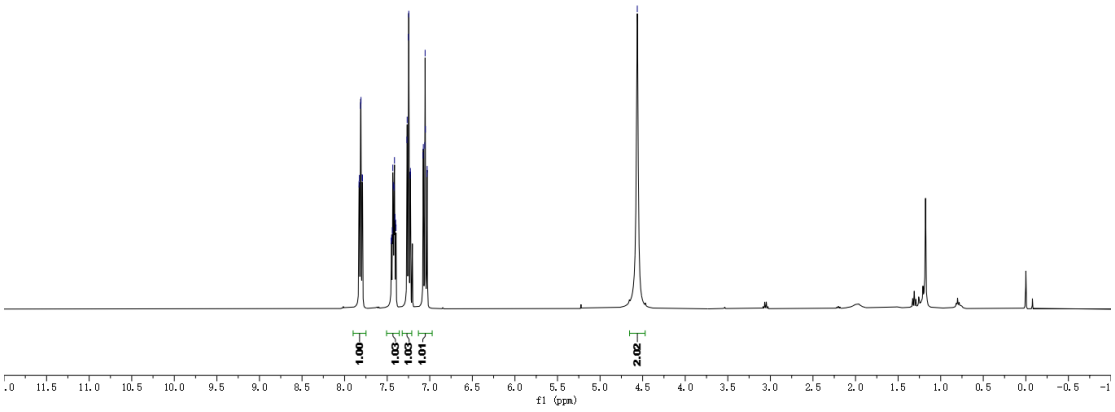


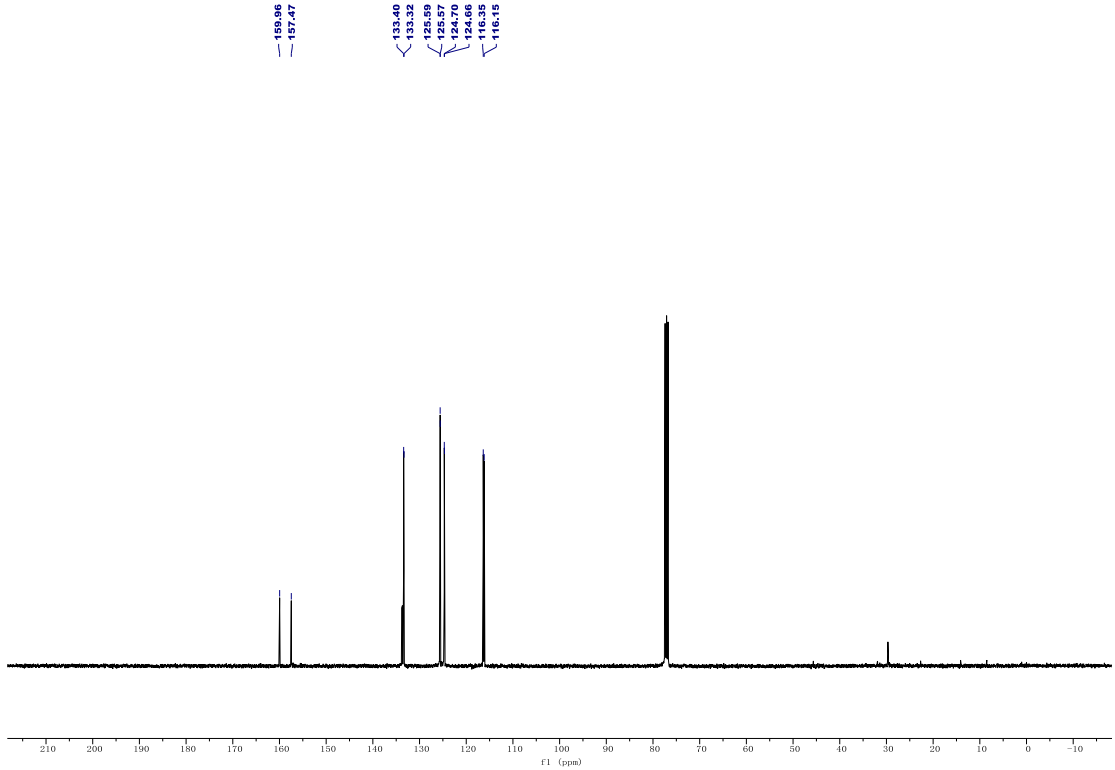
(*S*)-2-Methoxybenzenesulfinamide (4o):

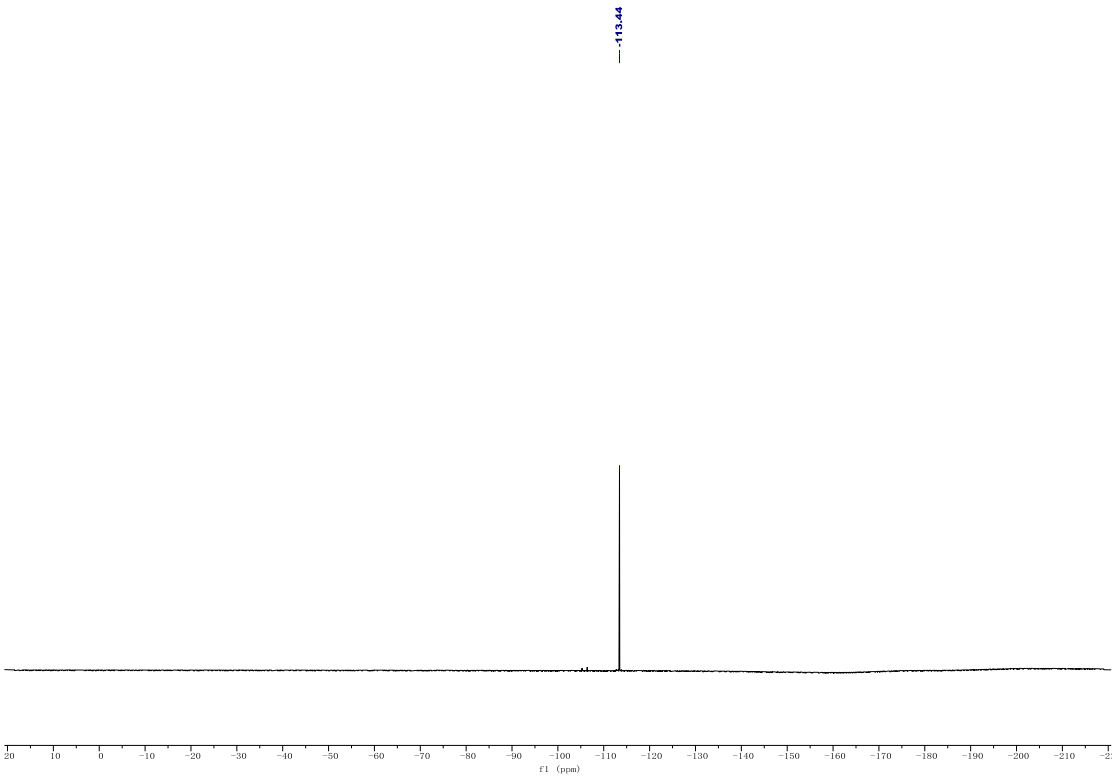


(*S*)-2-Fluorobenzenesulfonamide(4p):








-113.44
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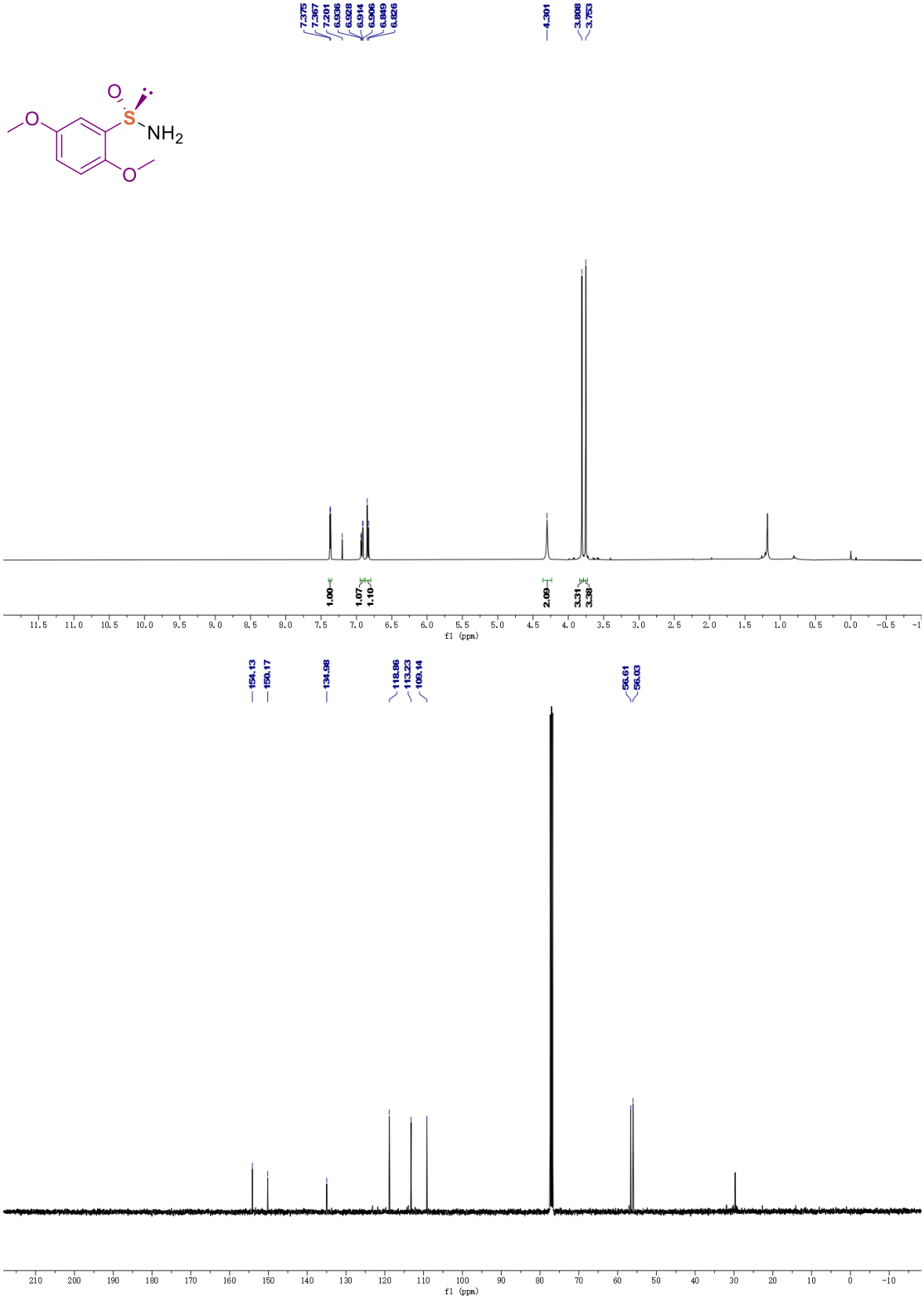
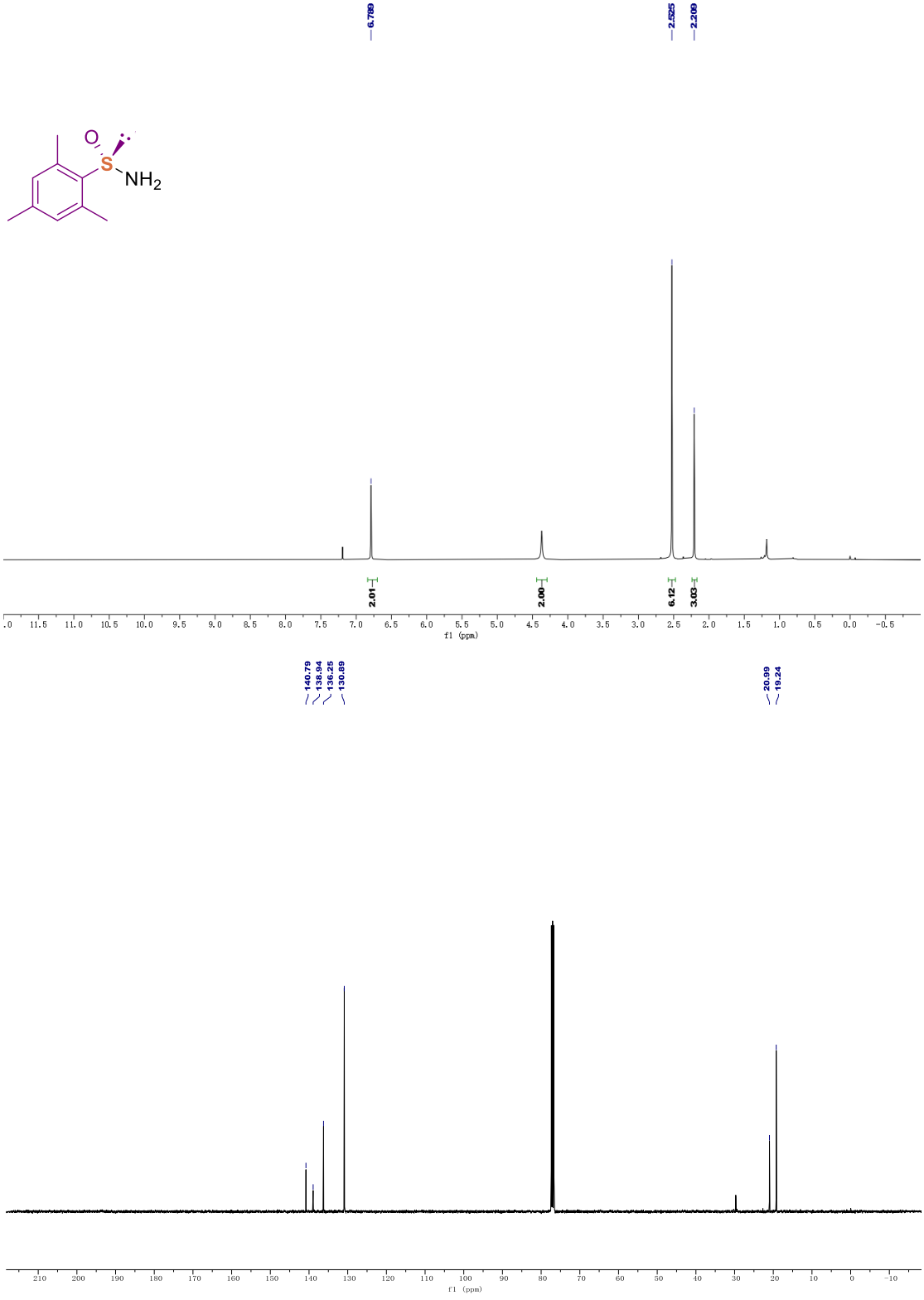
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

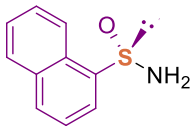
(*S*)-2,5-Dimethoxybenzenesulfonamide (4q):

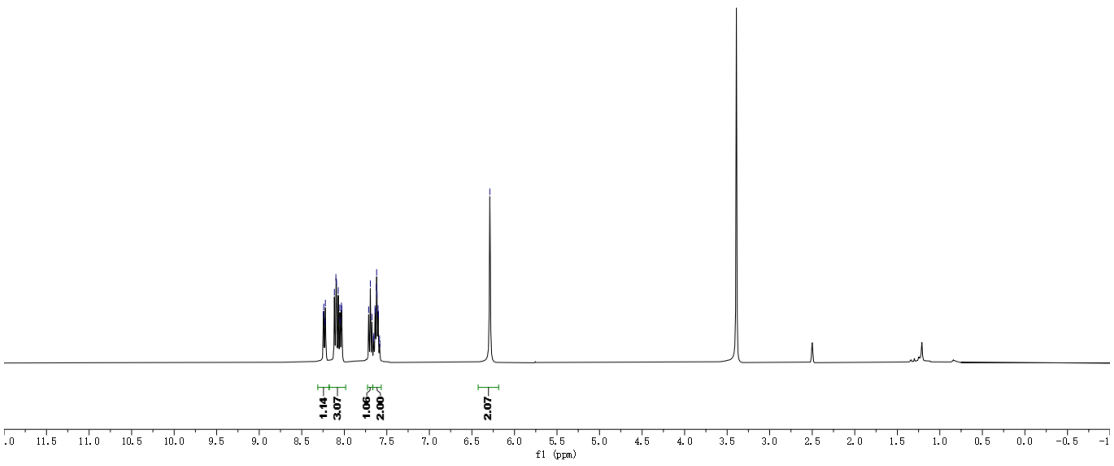


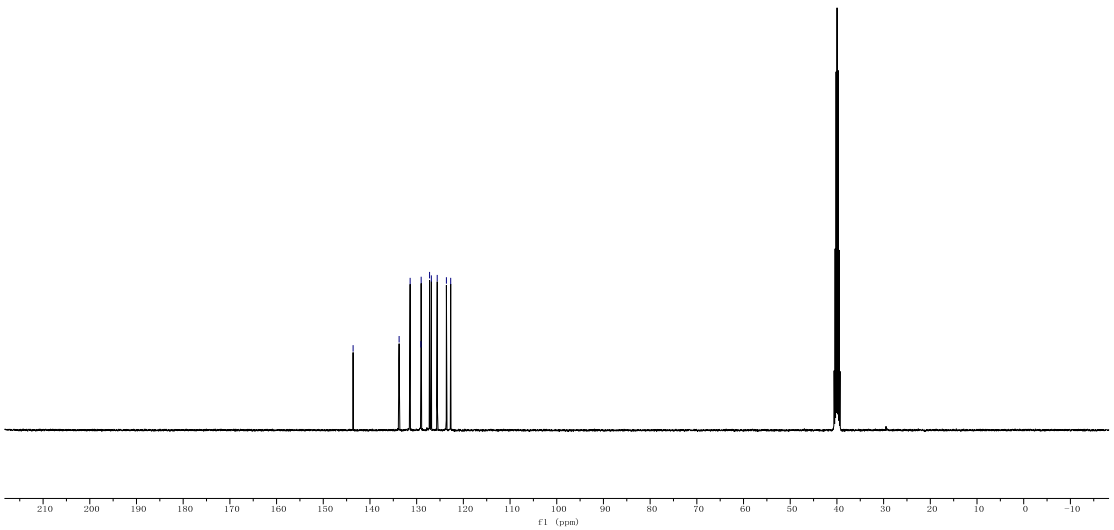
(*S*)-2,4,6-Trimethylbenzenesulfinamide (4r):



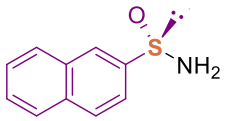
(*S*)-Naphthalene-1-sulfinamide (4s):

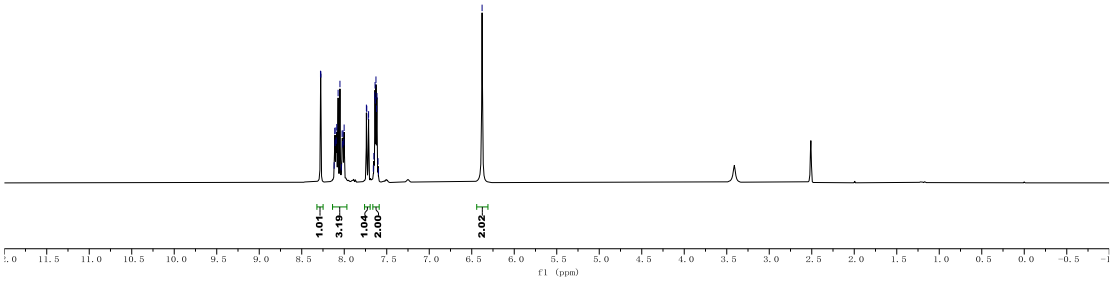


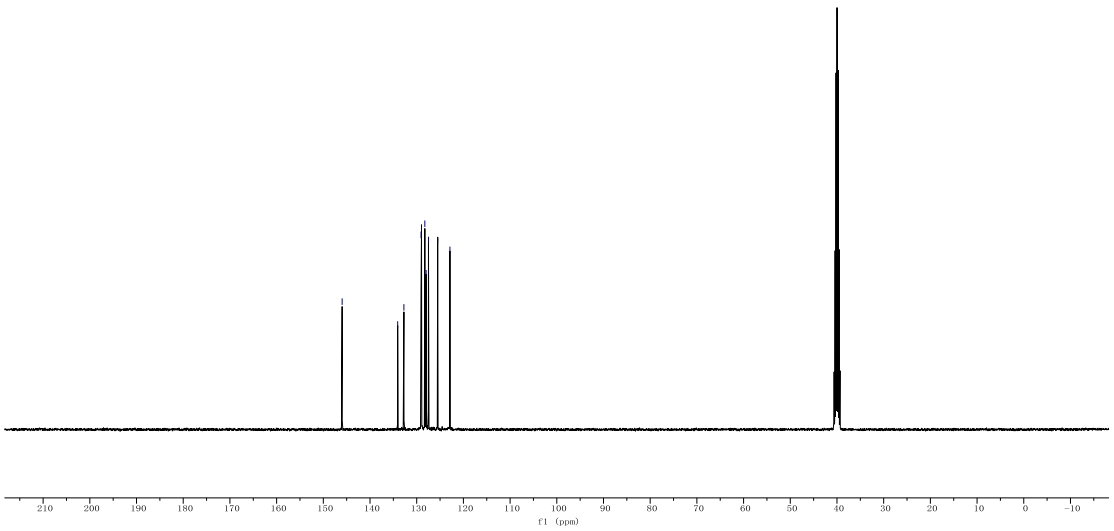




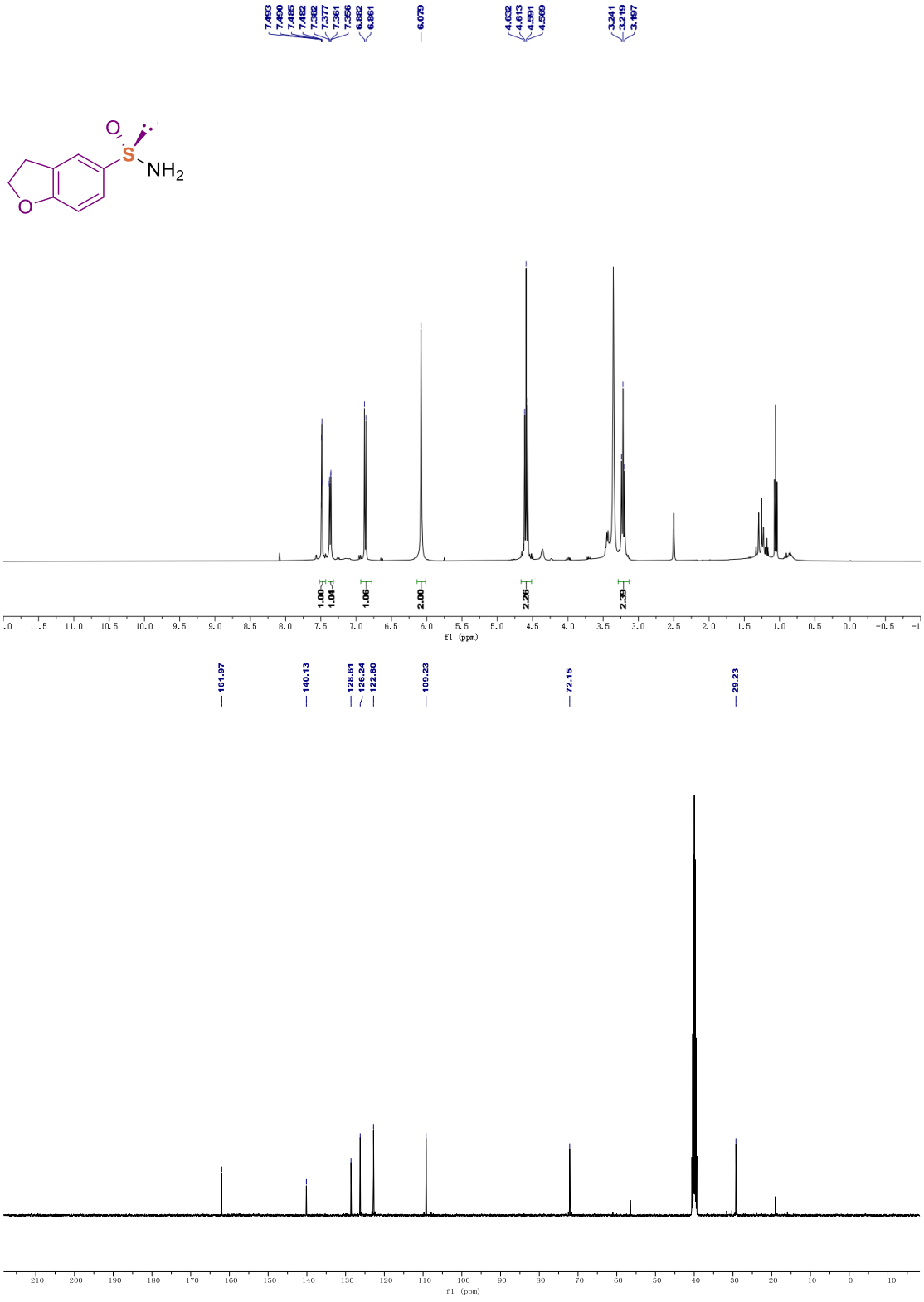
(*S*)-Naphthalene-2-sulfinamide(4t):



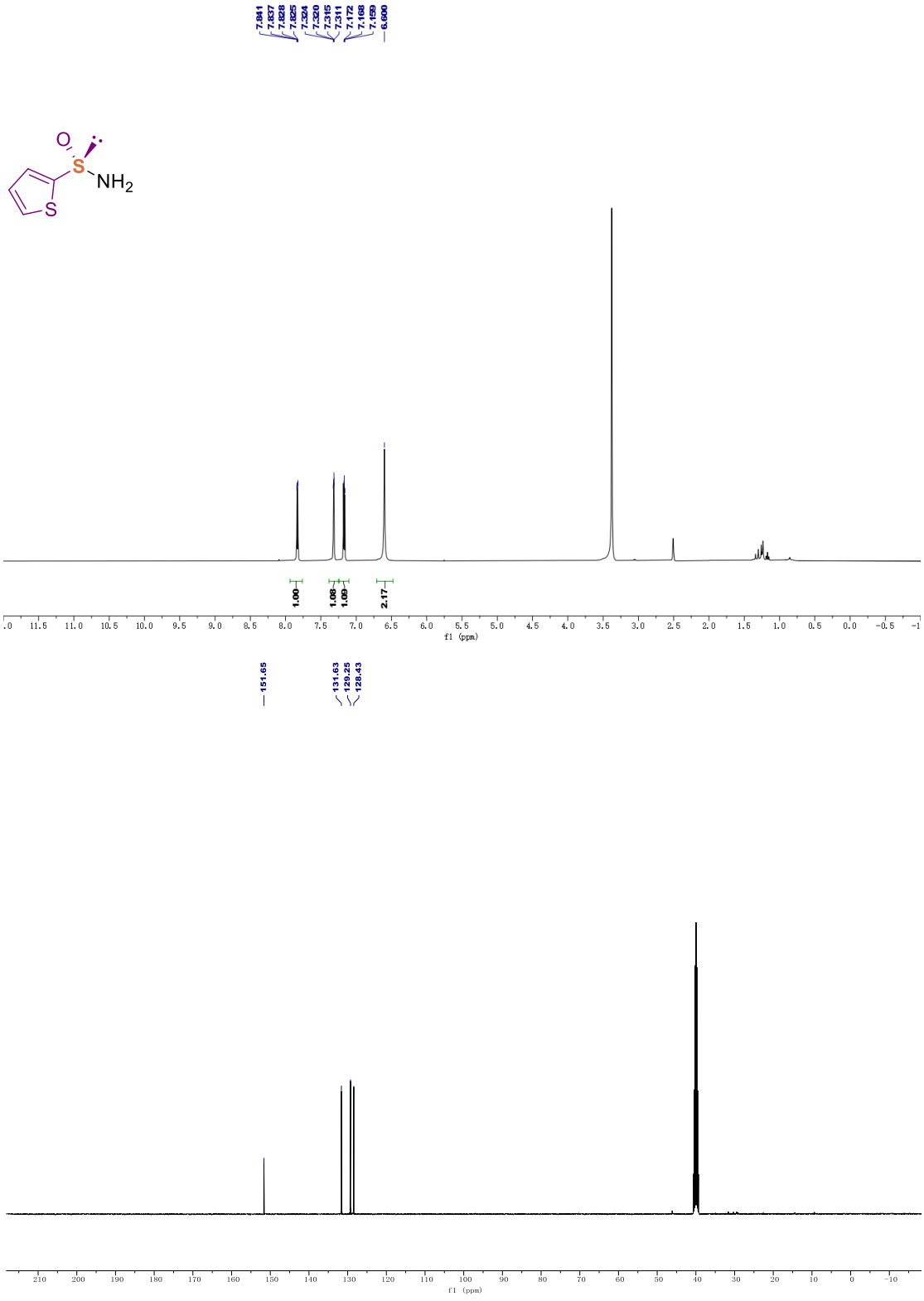




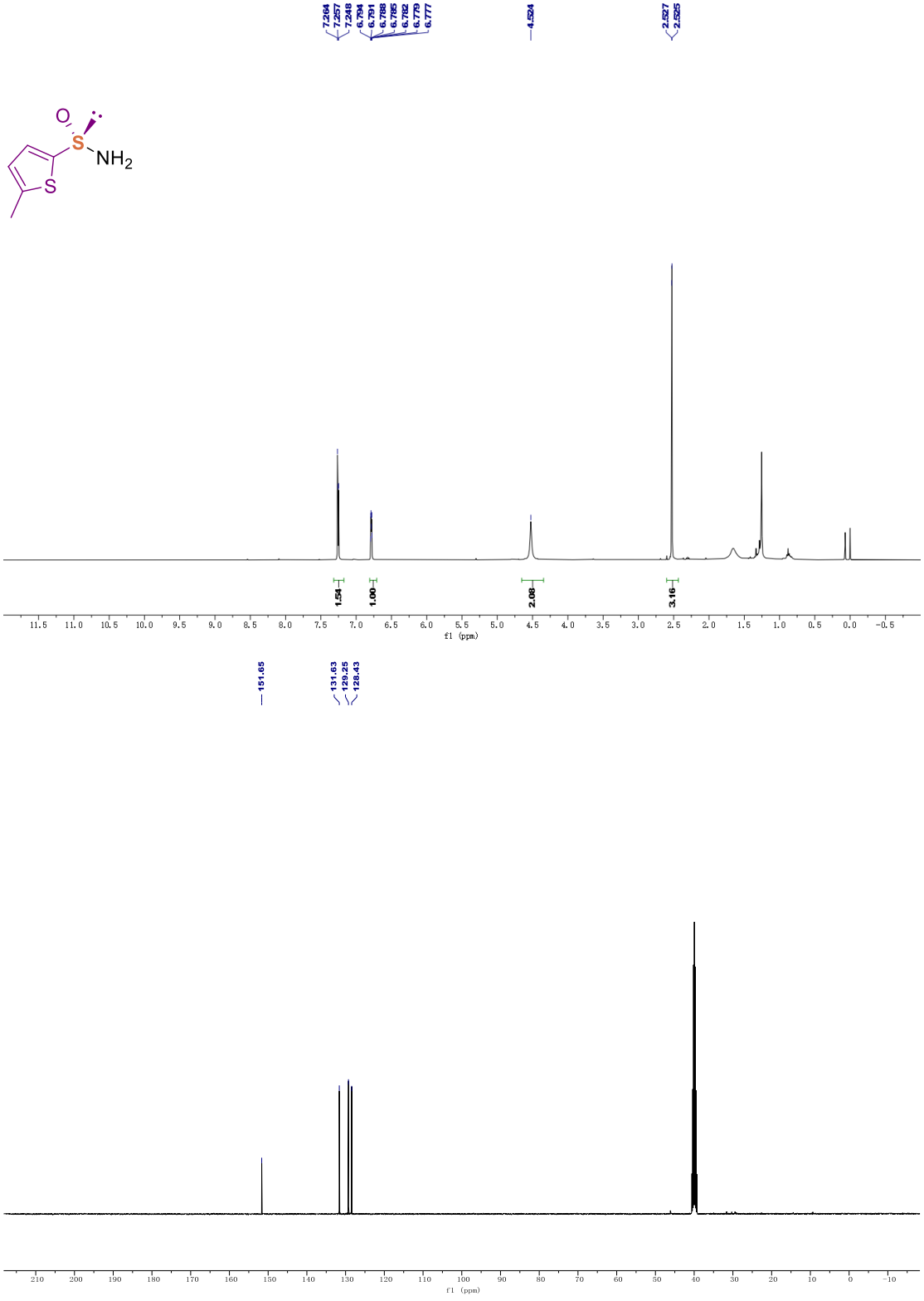
(*S*)-2,3-Dihydrobenzofuran-5-sulfonamide (4u):



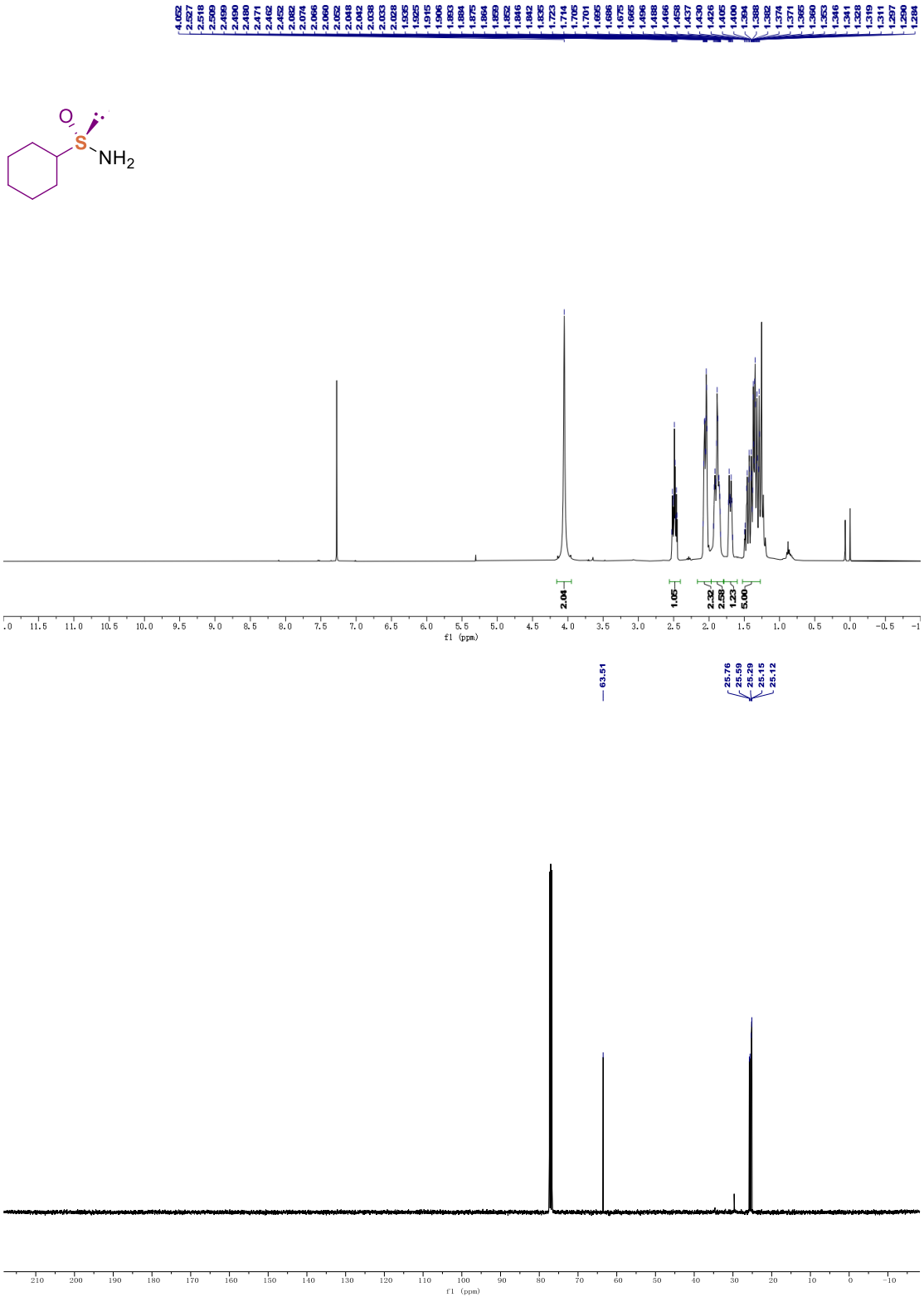
(*S*)-2-Thienesulfonamide (4v):



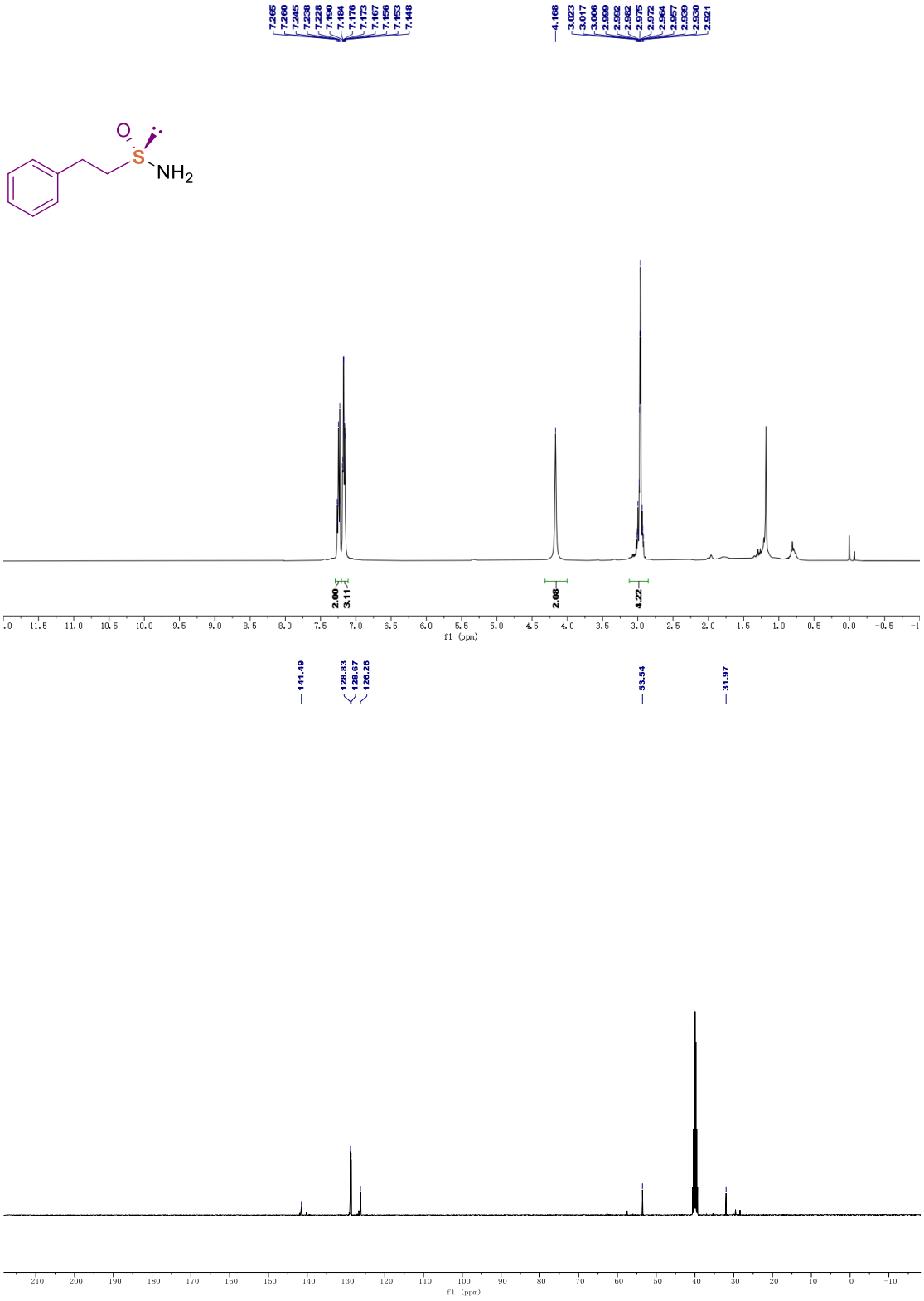
(*S*)-5-Methylthiophene sulfonamide (4w):



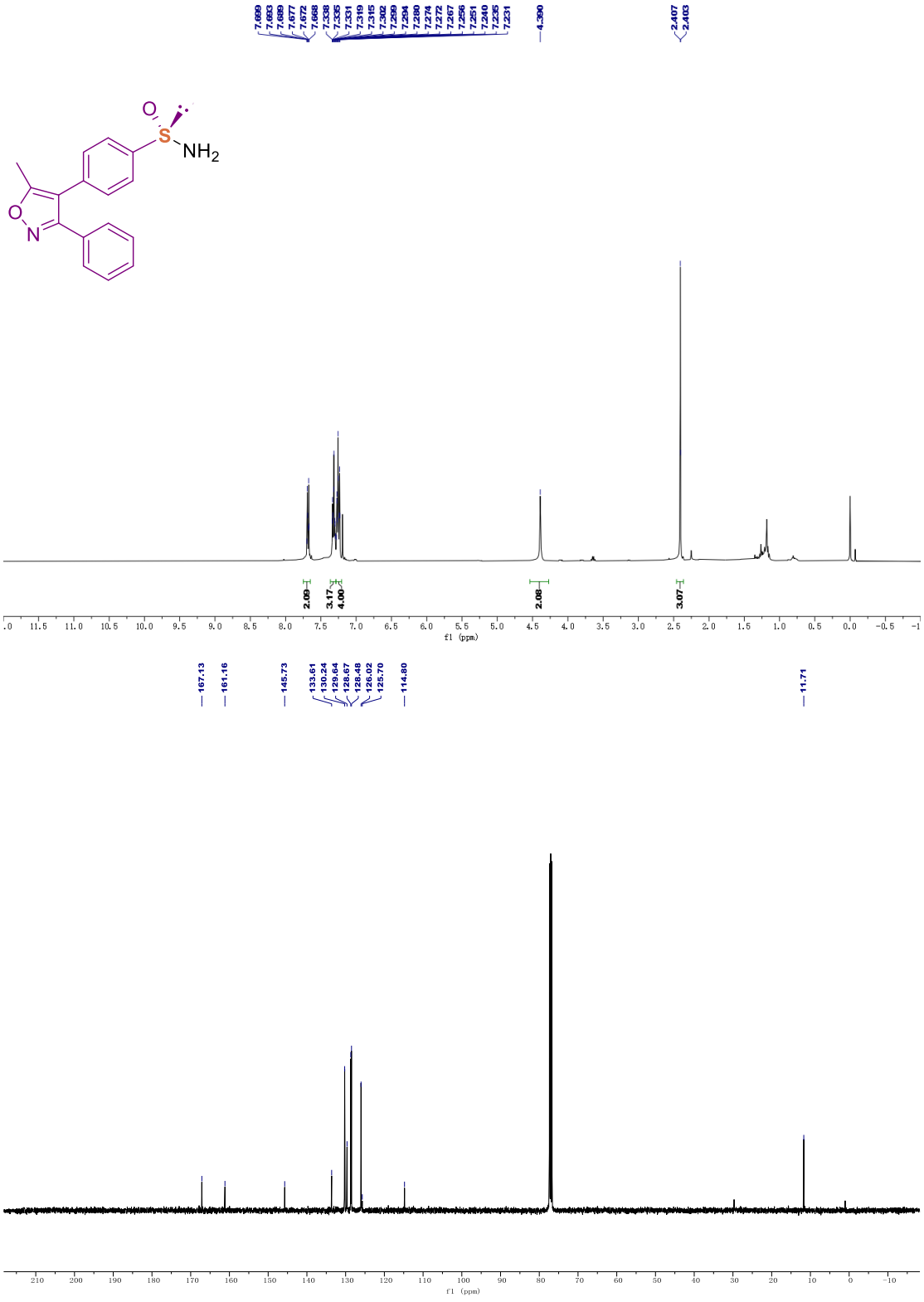
(*S*)-Cyclohexylsulfonamide (4x):



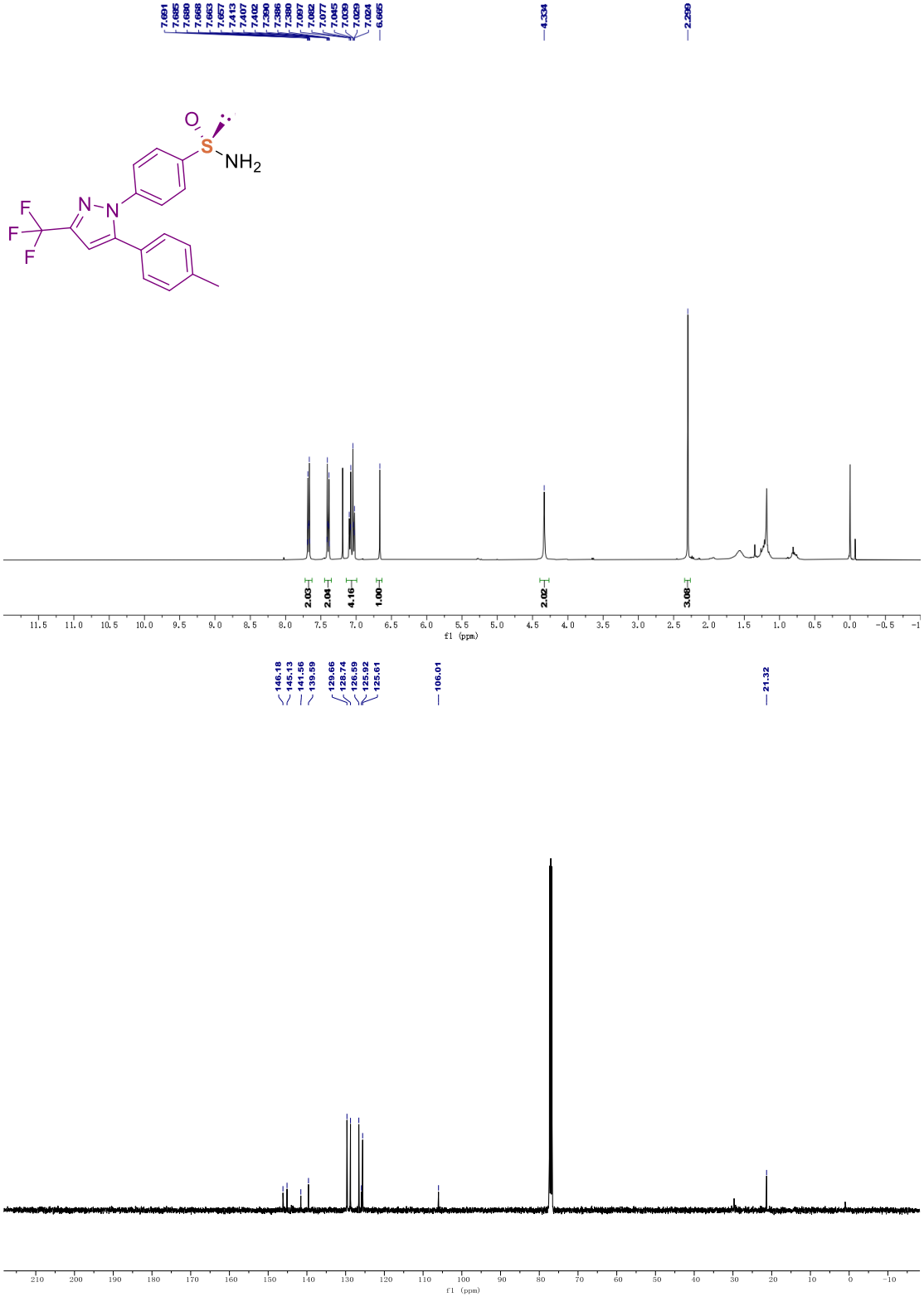
(*S*)-2-Phenyl-ethanesulfonamide (4y):

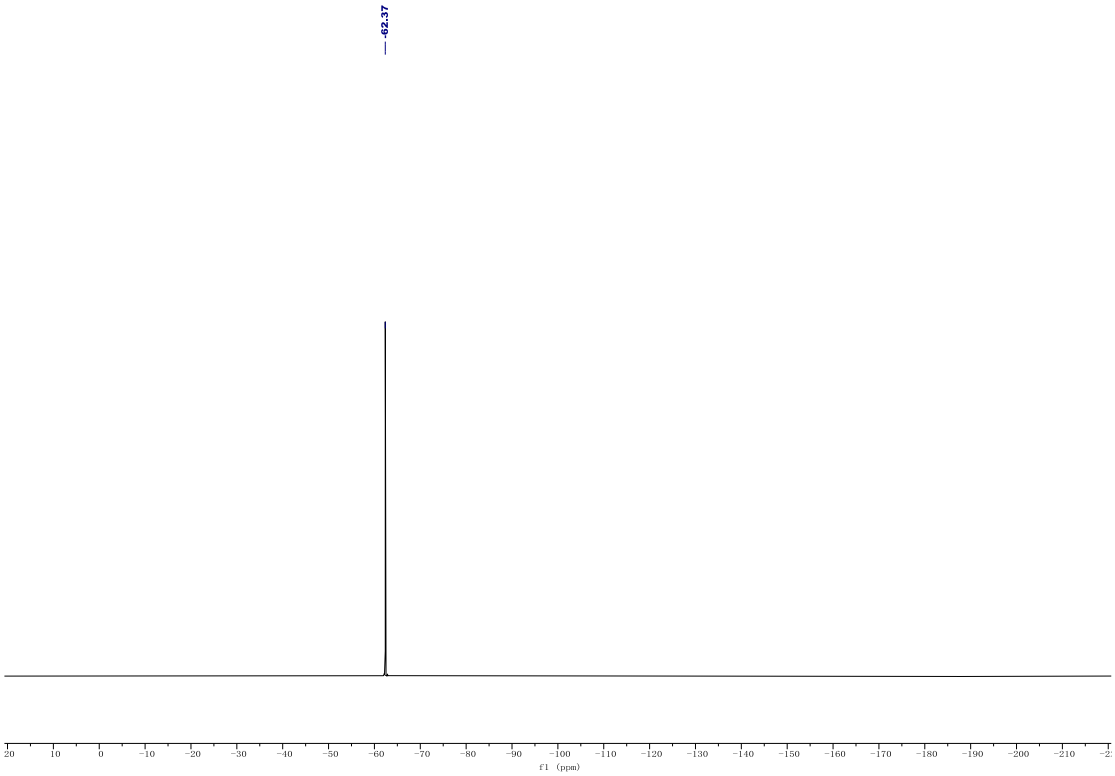


(*S*)-4-(5-Methyl-3-phenylisoxazol-4-yl) benzenesulfinamide (5a):

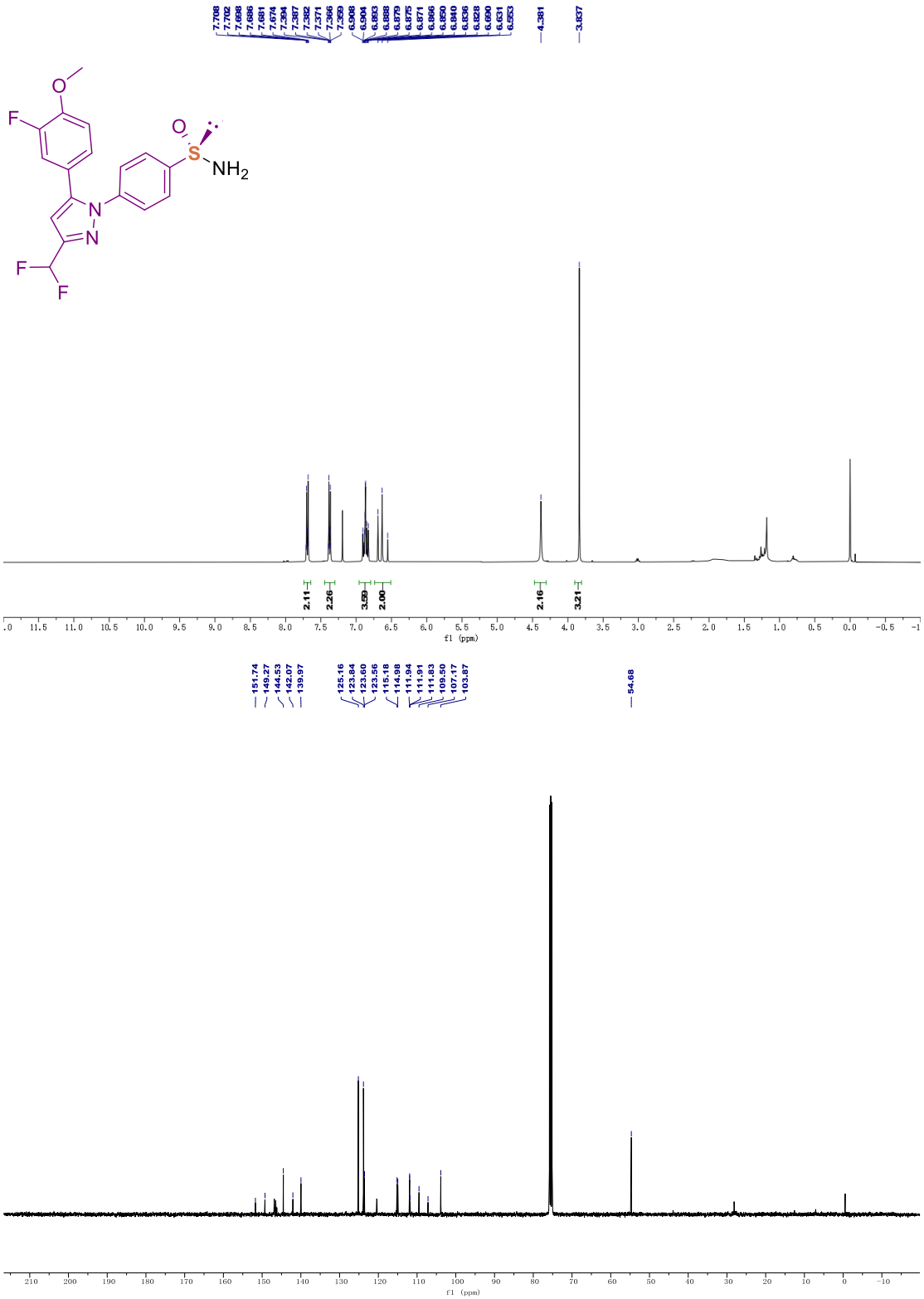


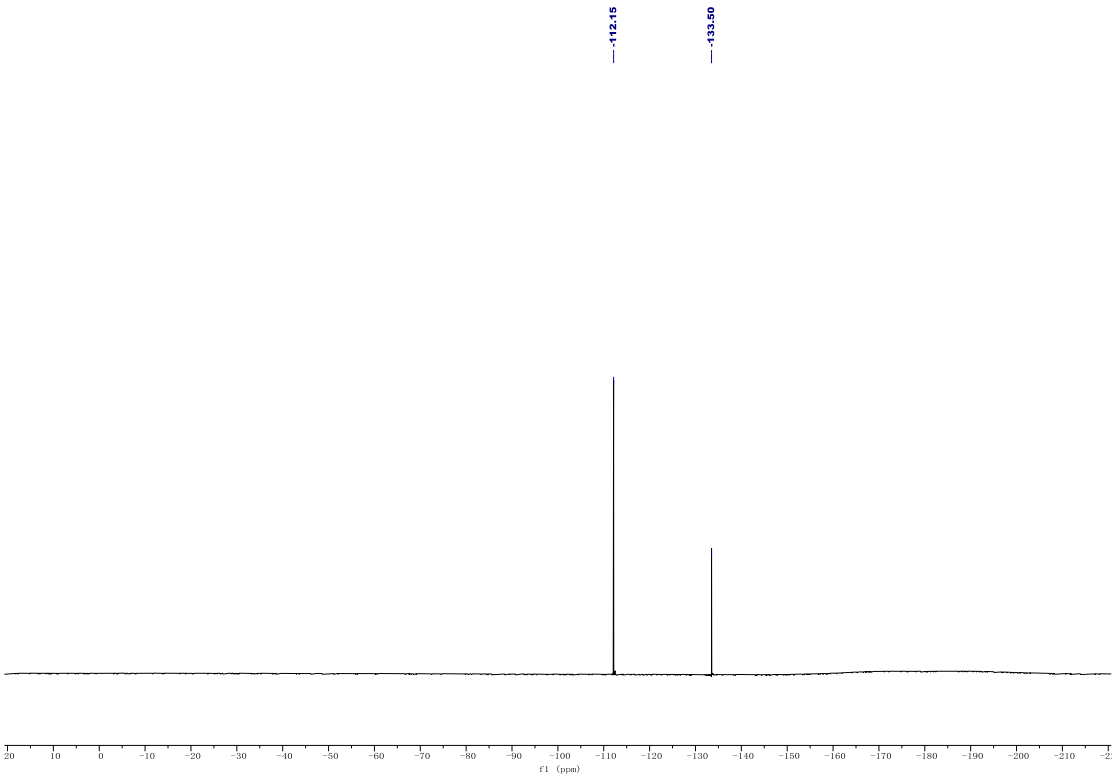
(*S*)- 4-(5-(p-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)benzenesulfinamide (5b):




-62.37
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

(*S*)-(4-(3-(Difluoromethyl)-5-(3-fluoro-4-methoxyphenyl)-1*H*-pyrazol-1-yl) phenyl) (methylidyne) (λ^1-oxidaneyl)- λ^6-sulfanamine (5c):




-112.15
-133.50
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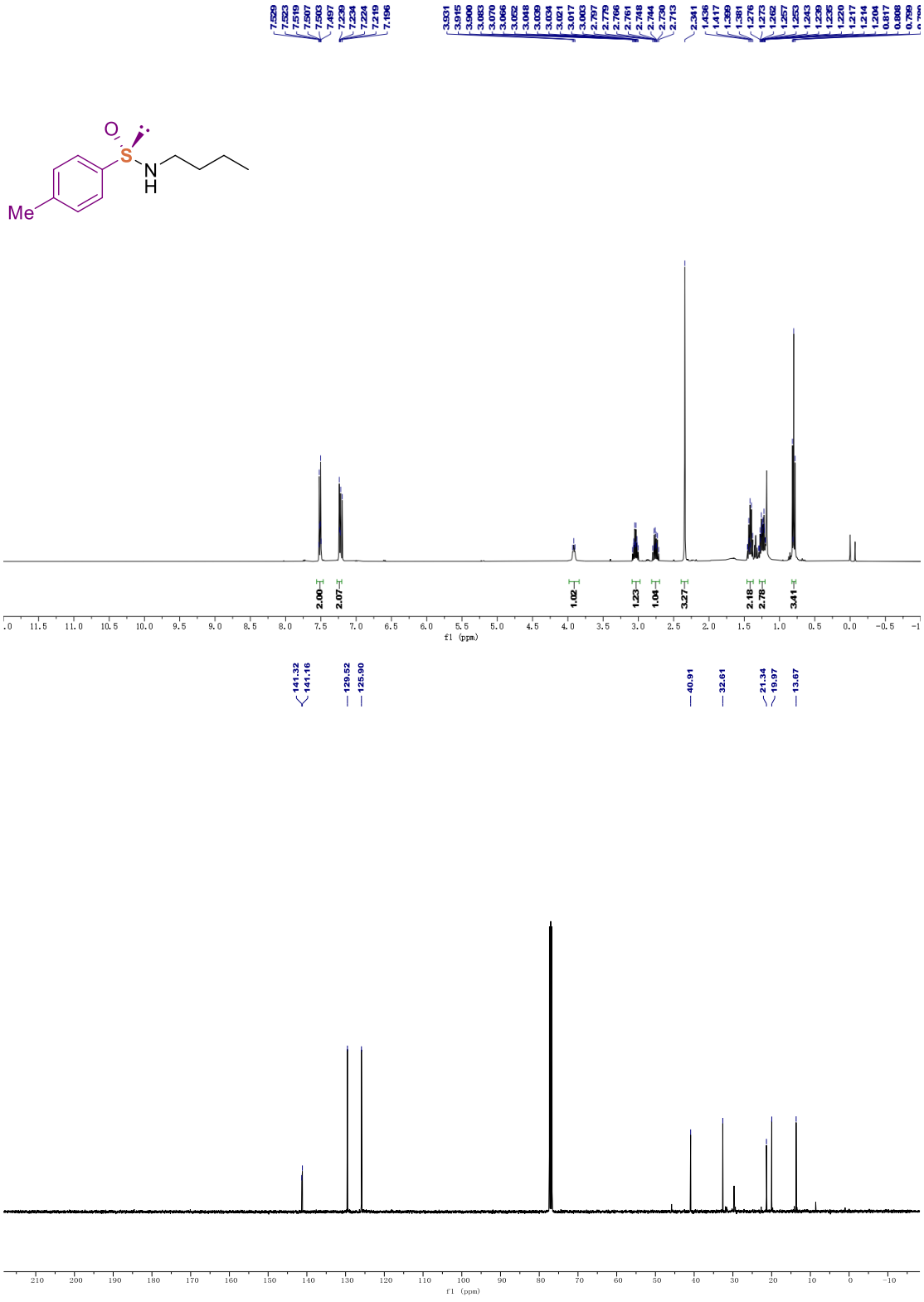
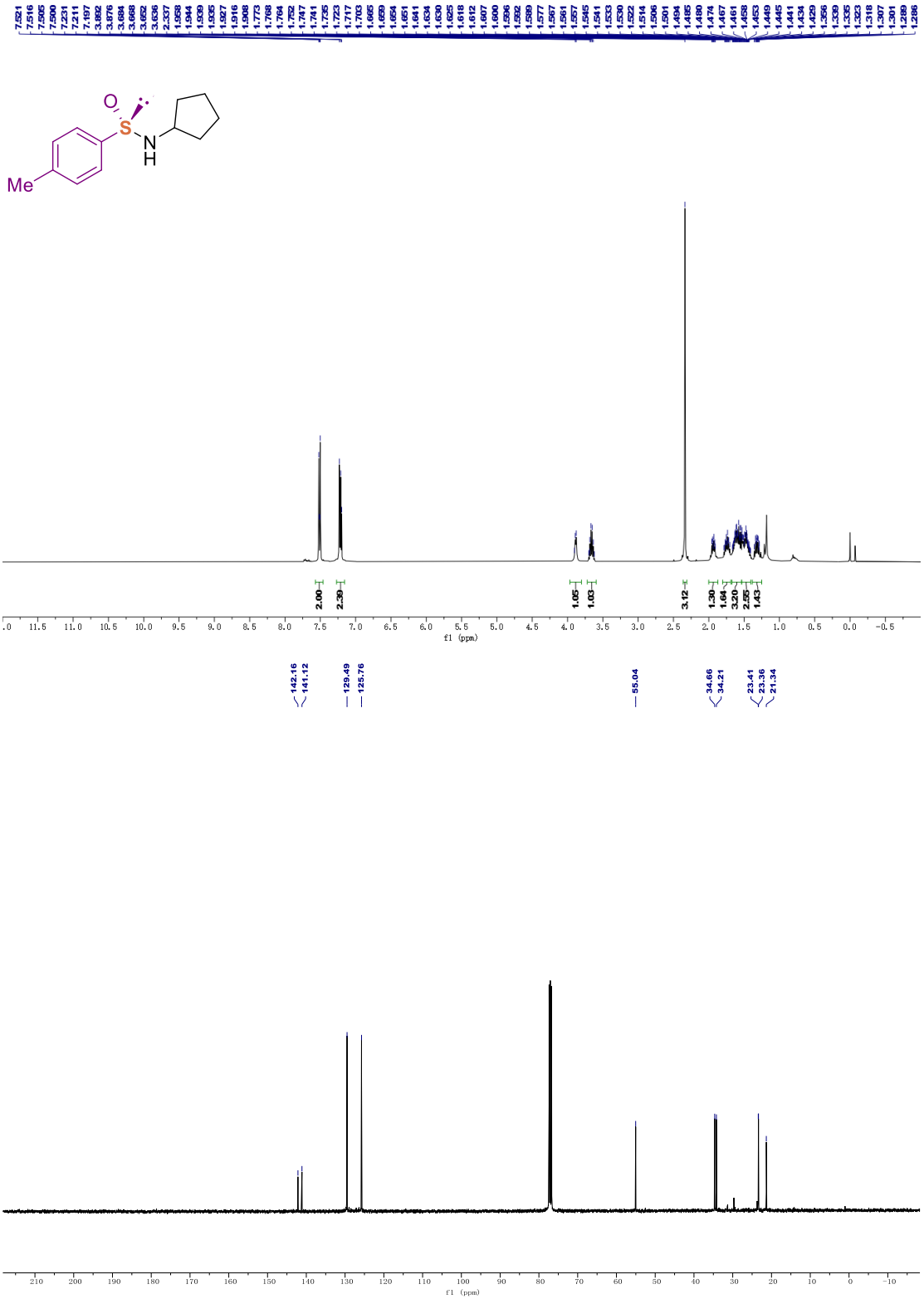
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

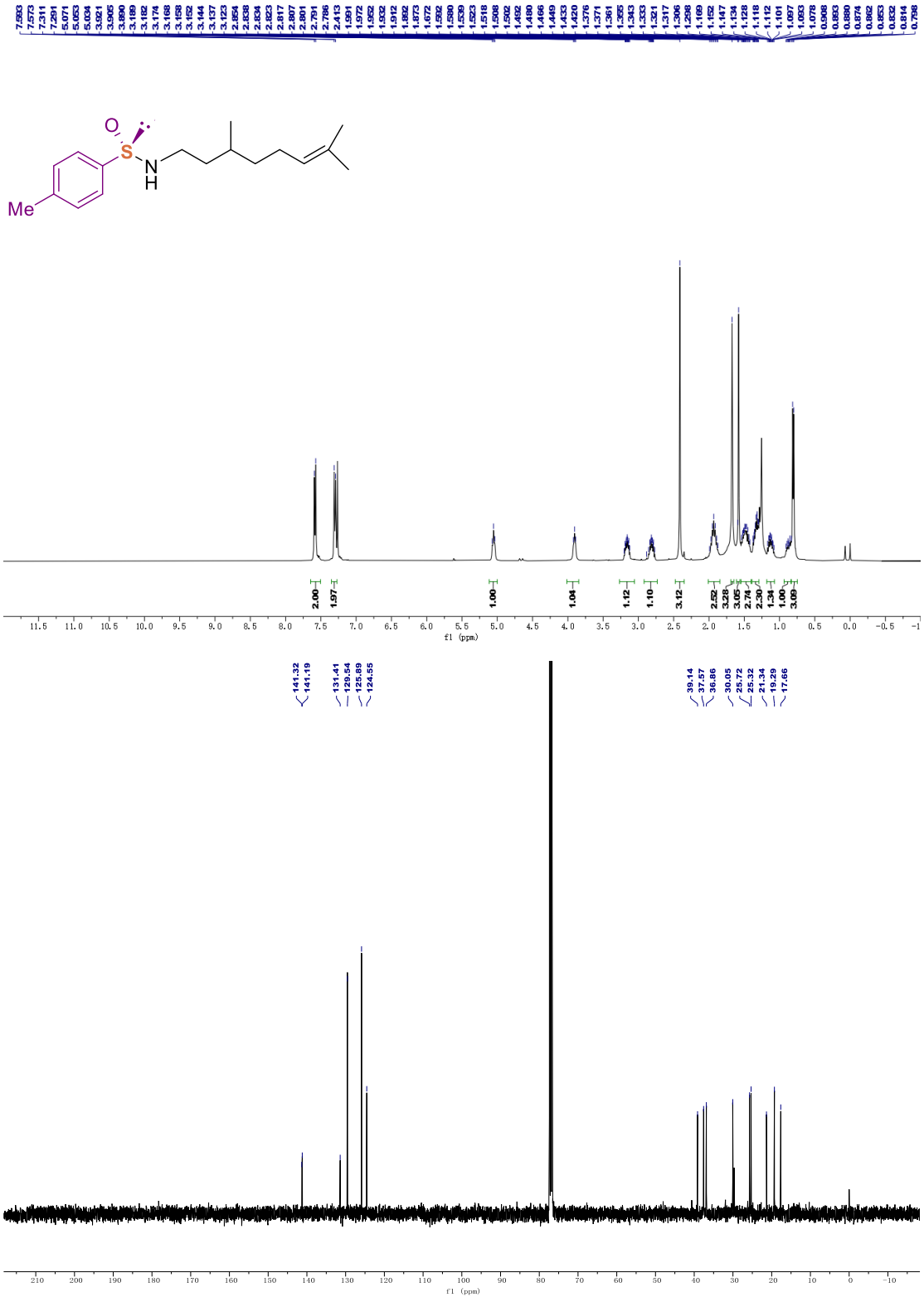
(*S*)-*N*-Butyl-4-methyl benzenesulfinamide (6):



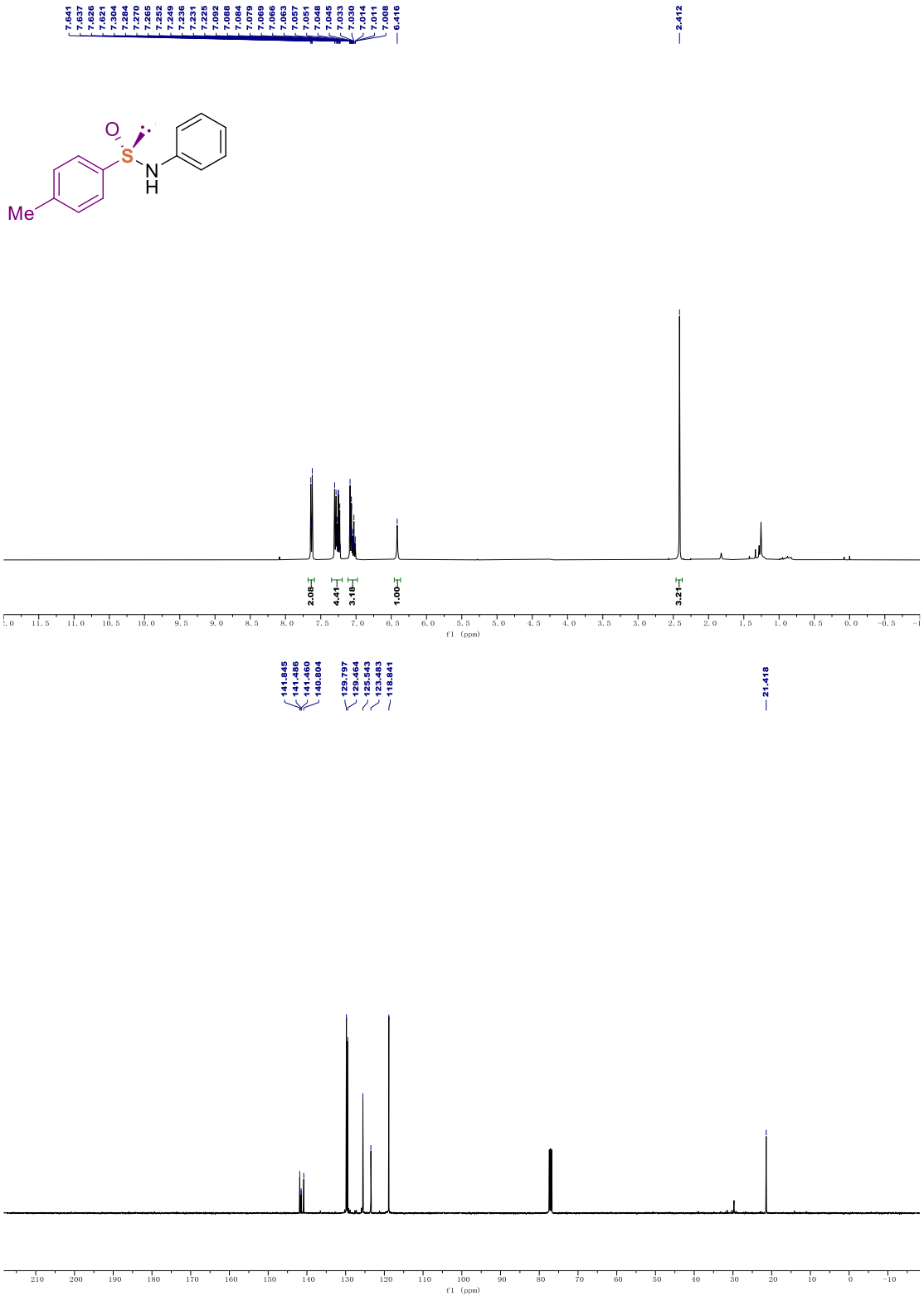
(*S*)-N-Cyclopentyl-4-methylbenzenylsulfinamide (7):



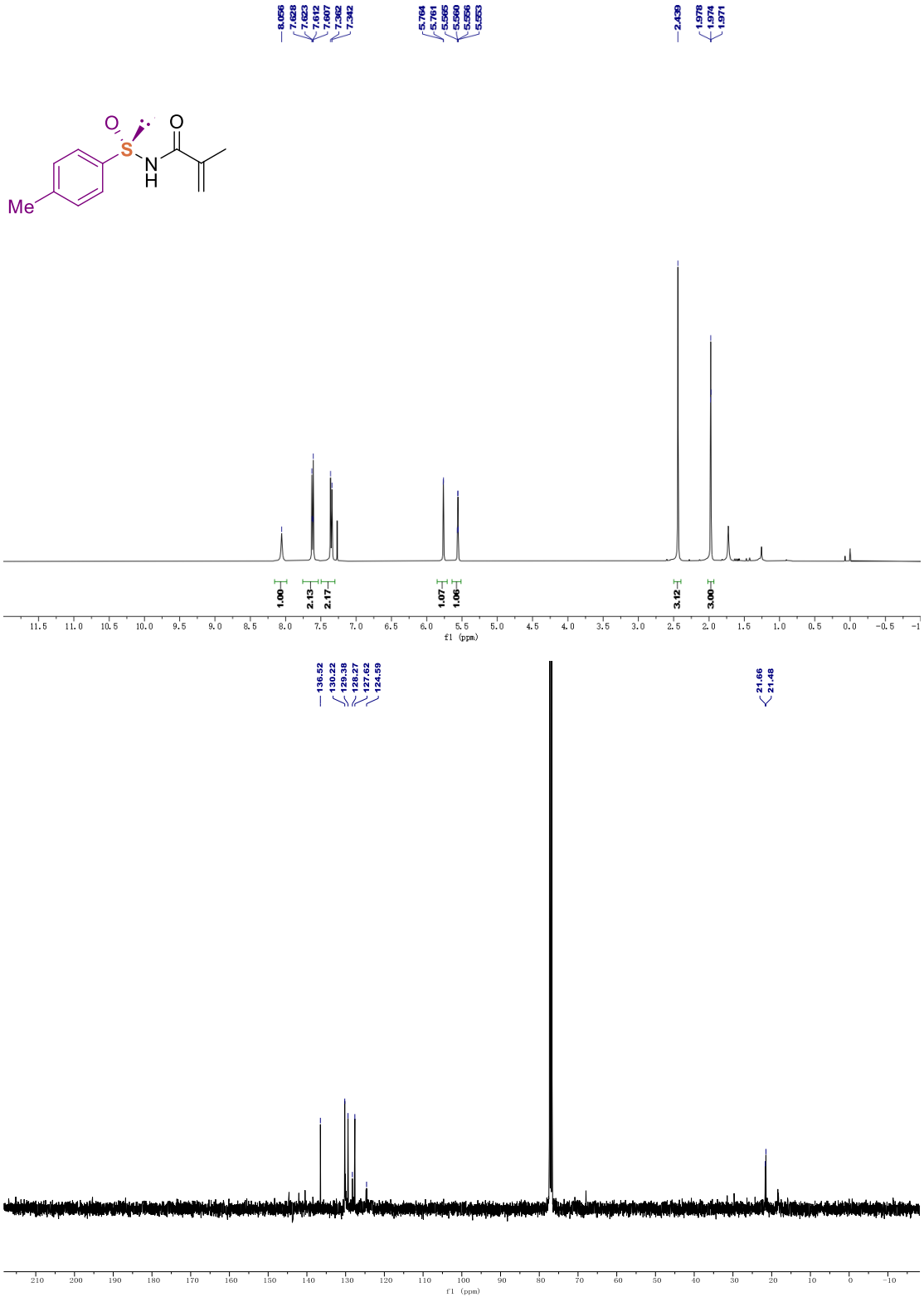
(*S*)-*N*-(3,7-Dimethyloct-6-en-1-yl)-4-methylbenzenesulfinamide (8):



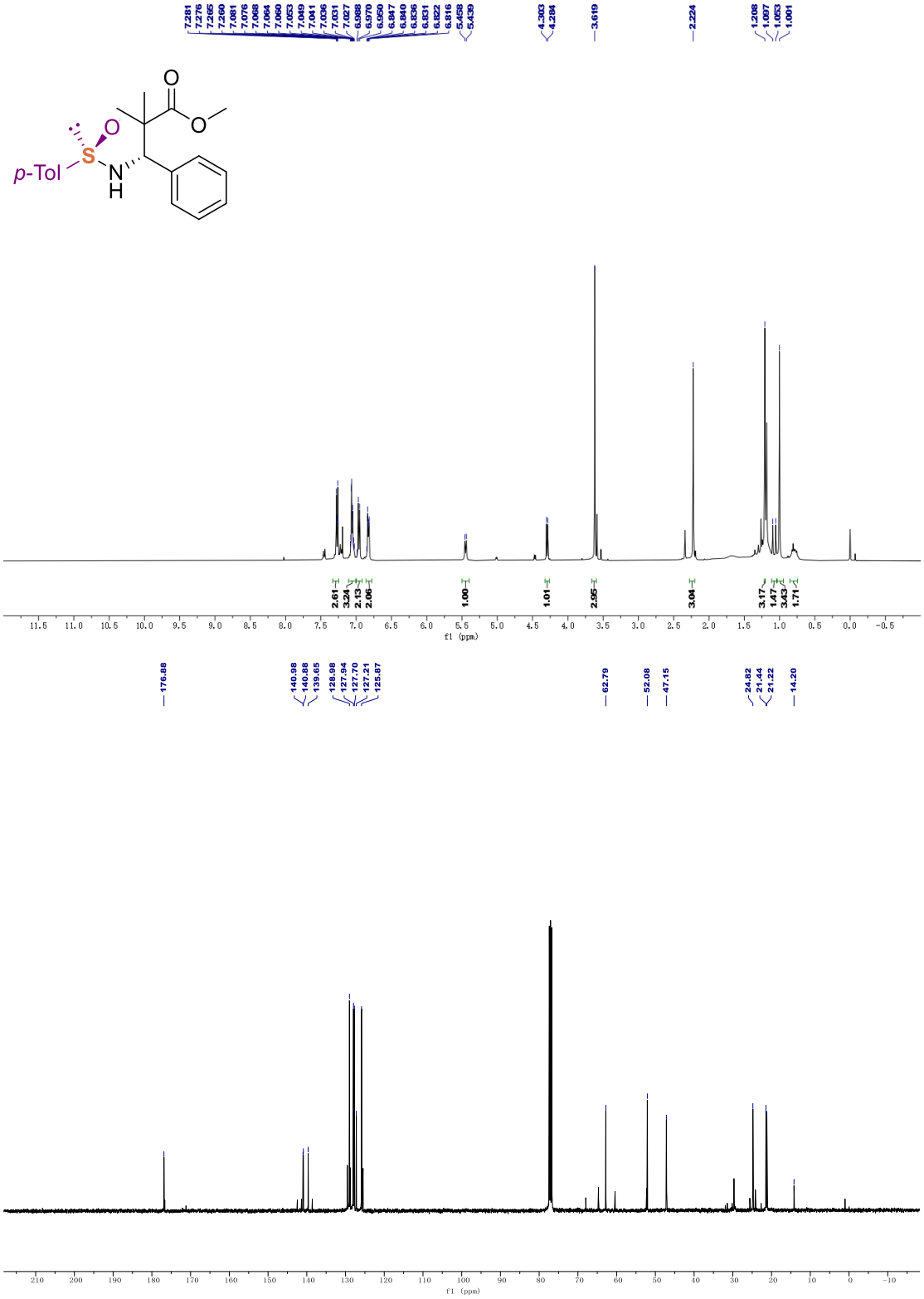
(*S*)-4-Methyl-*N*-phenylbenzenesulfinamide (9):



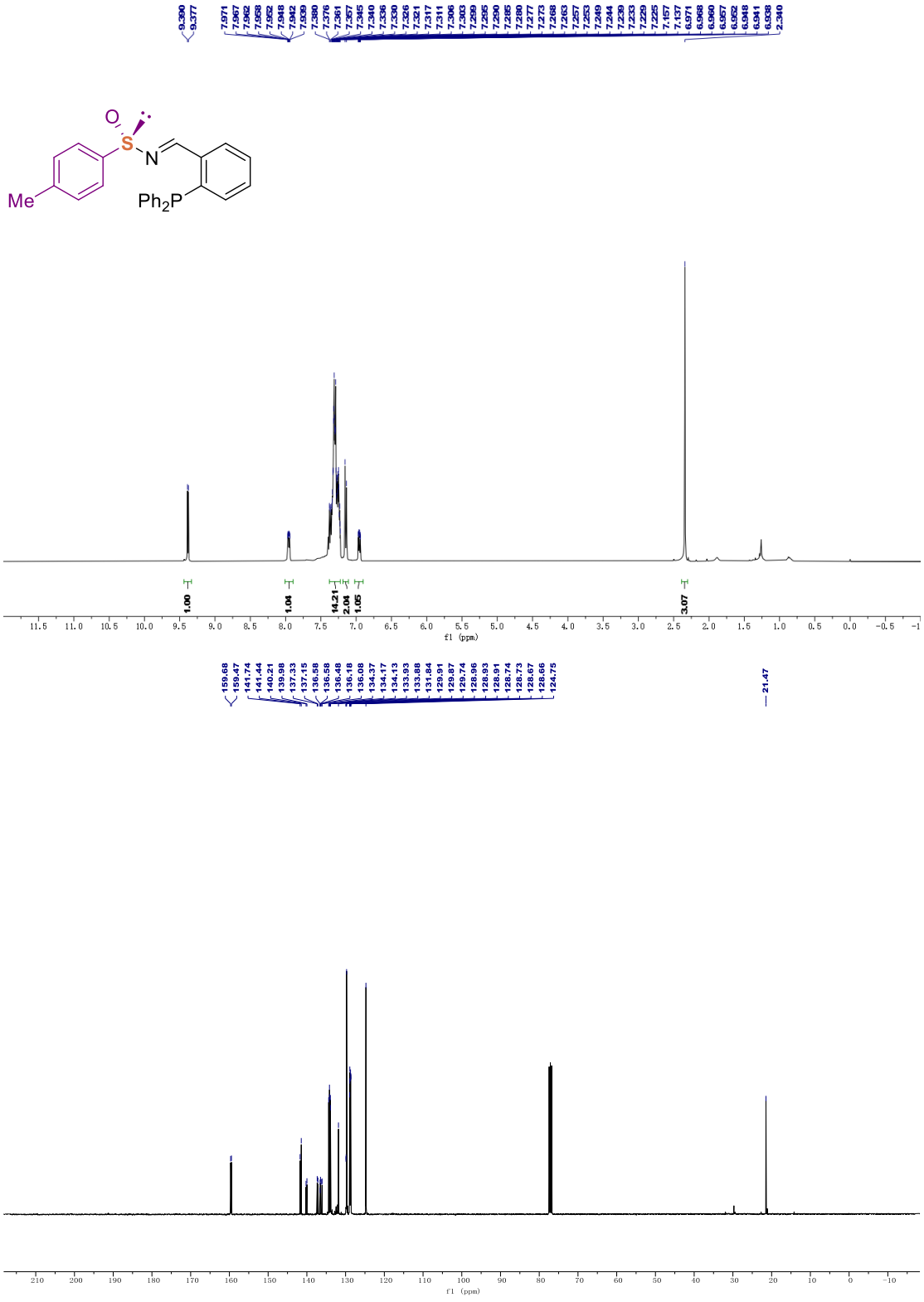
(*S*)-*N*-(*p*-Tolylsulfinyl) methacrylamide (10):

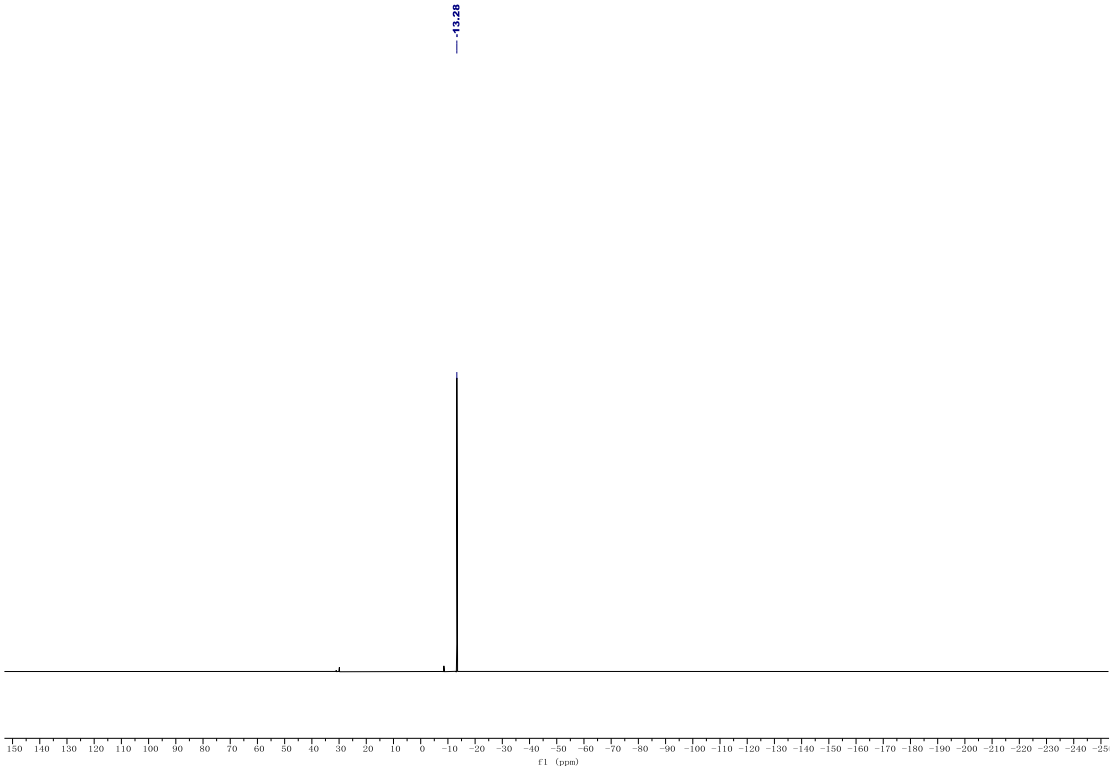


(*R*)-*N*-[(*S*)-2,2-Dimethyl-1-phenylpropionate methyl ester]-4-methylbenzene-sulfin-amide (11):

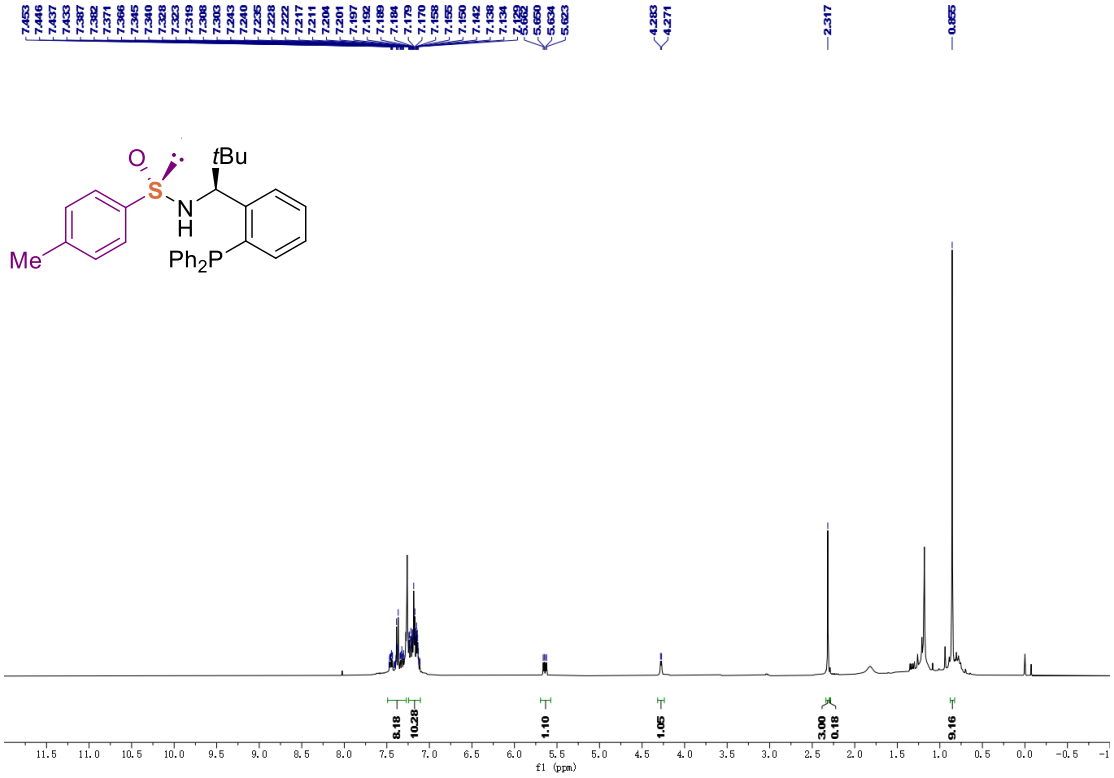


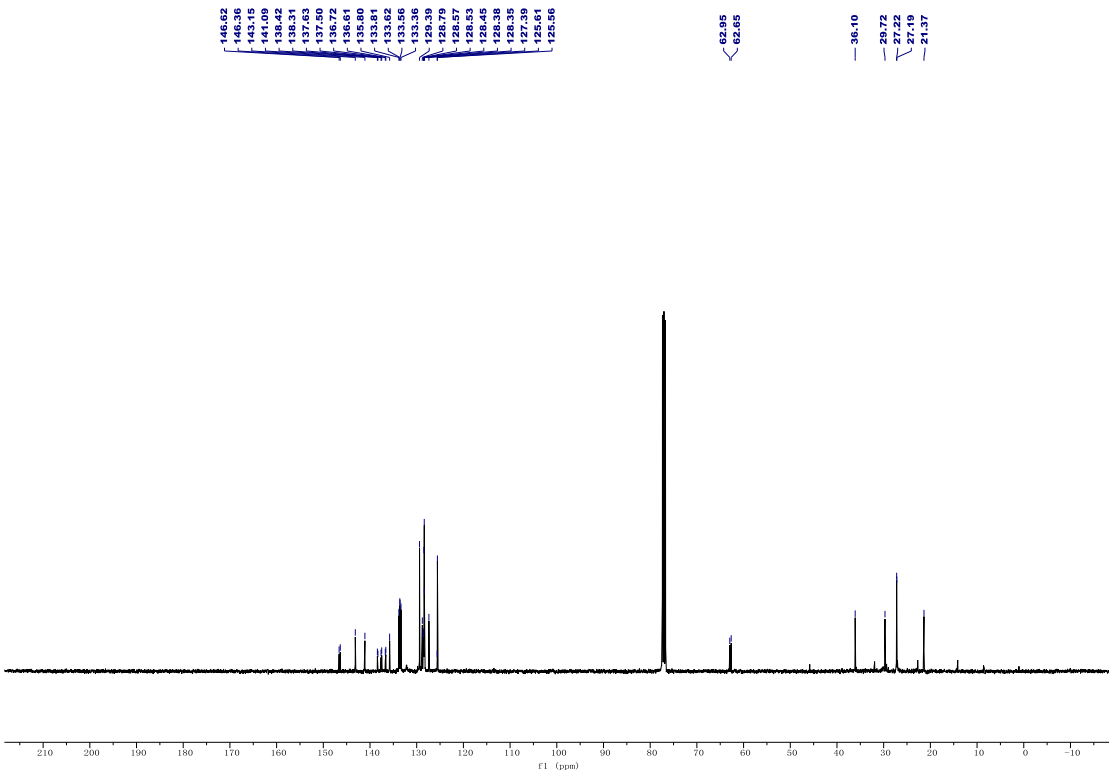
(*S*)-*N*-(2-(Diphenylphosphaneyl) benzyl)-4-methylbenzenesulfinamide (12):

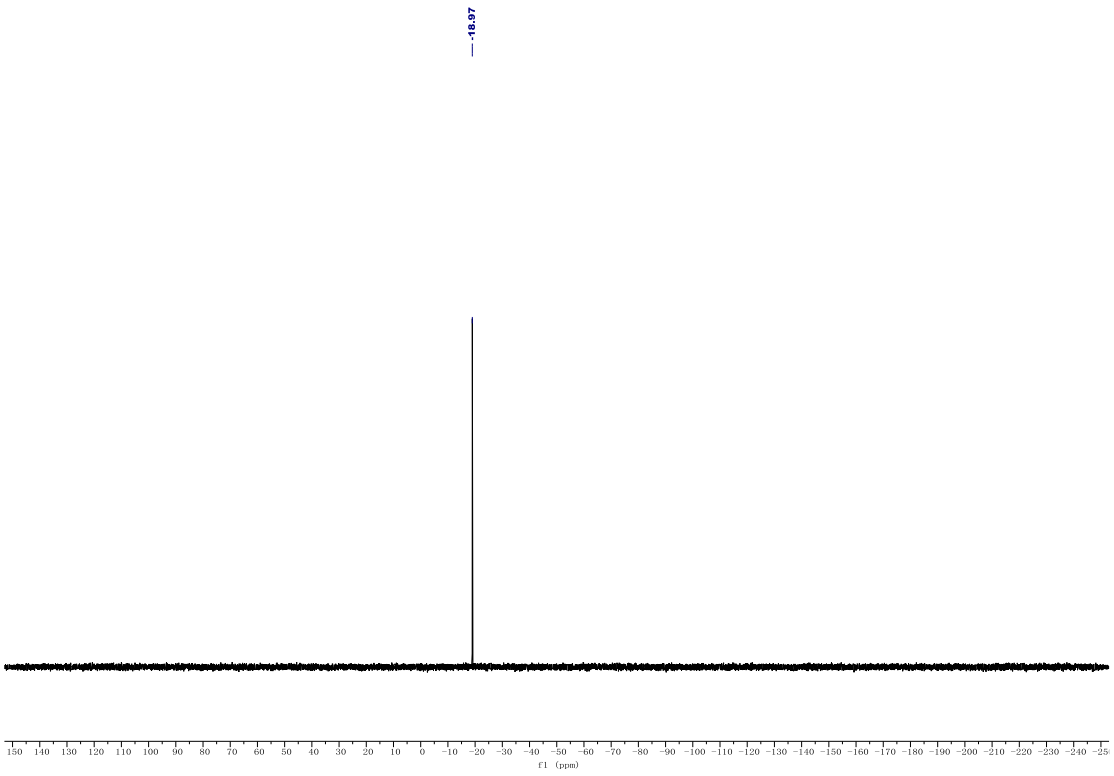



13.28
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

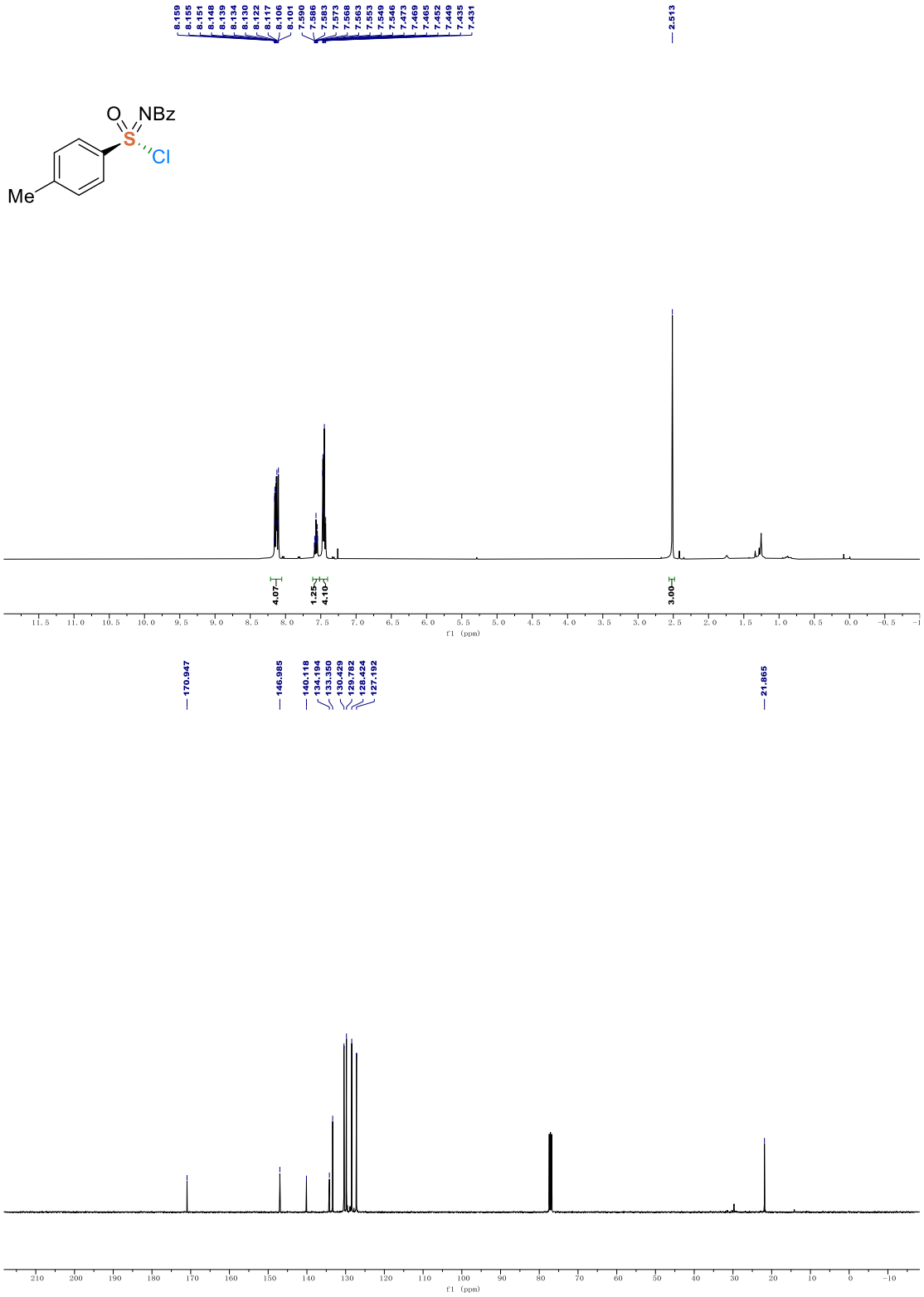
(*S*)-*N*-((*S*)-1-(2-(diphenylphosphaneyl) phenyl) *tert*-butyl)-4-methylbenzenesulfin Amide (13):



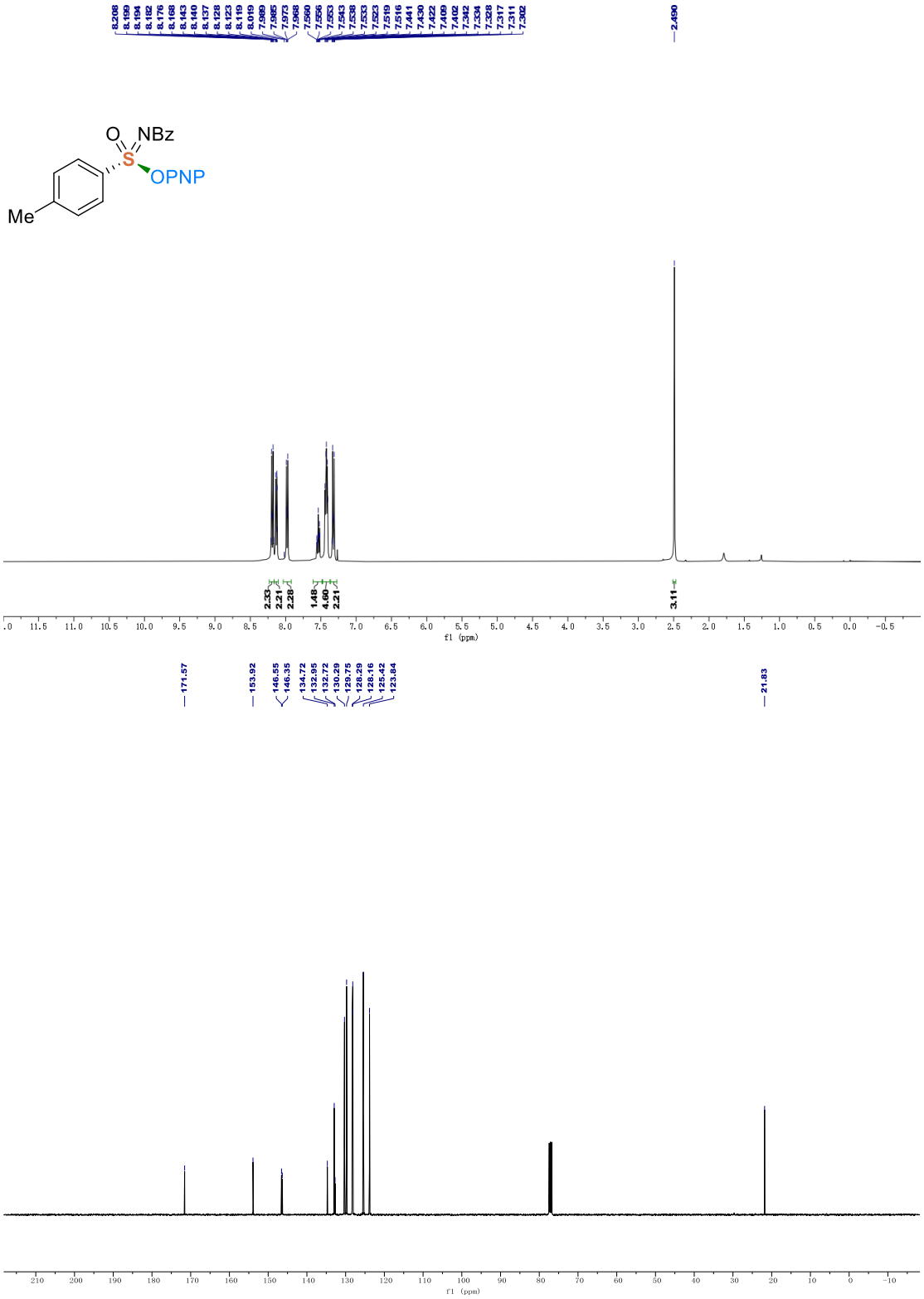



-18.97
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -25
f1 (ppm)

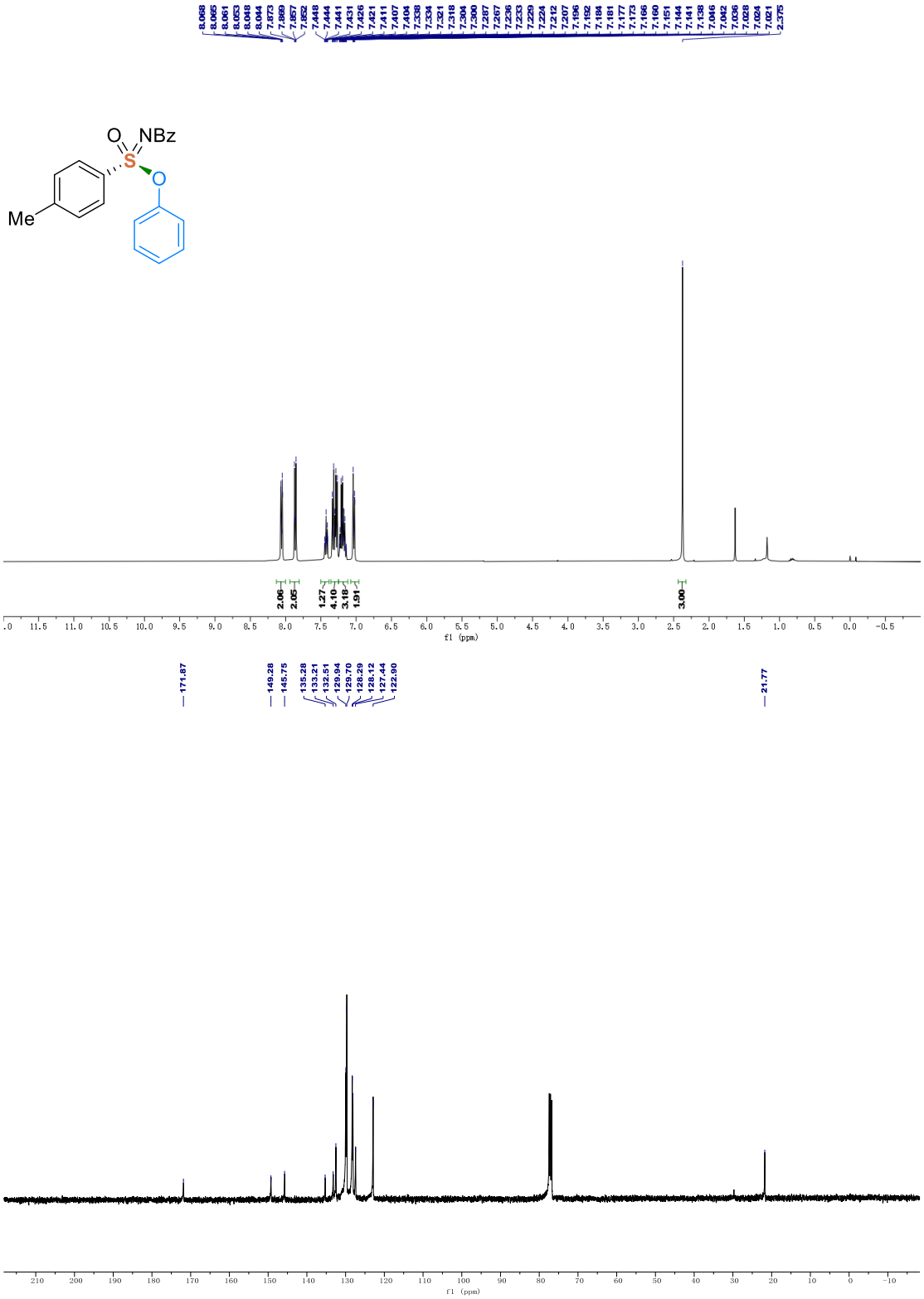
(*S*)-*N*-Benzoyl-1-methyl-(*p*-tolyl)-oxidanesulfinimidic chloride (14):



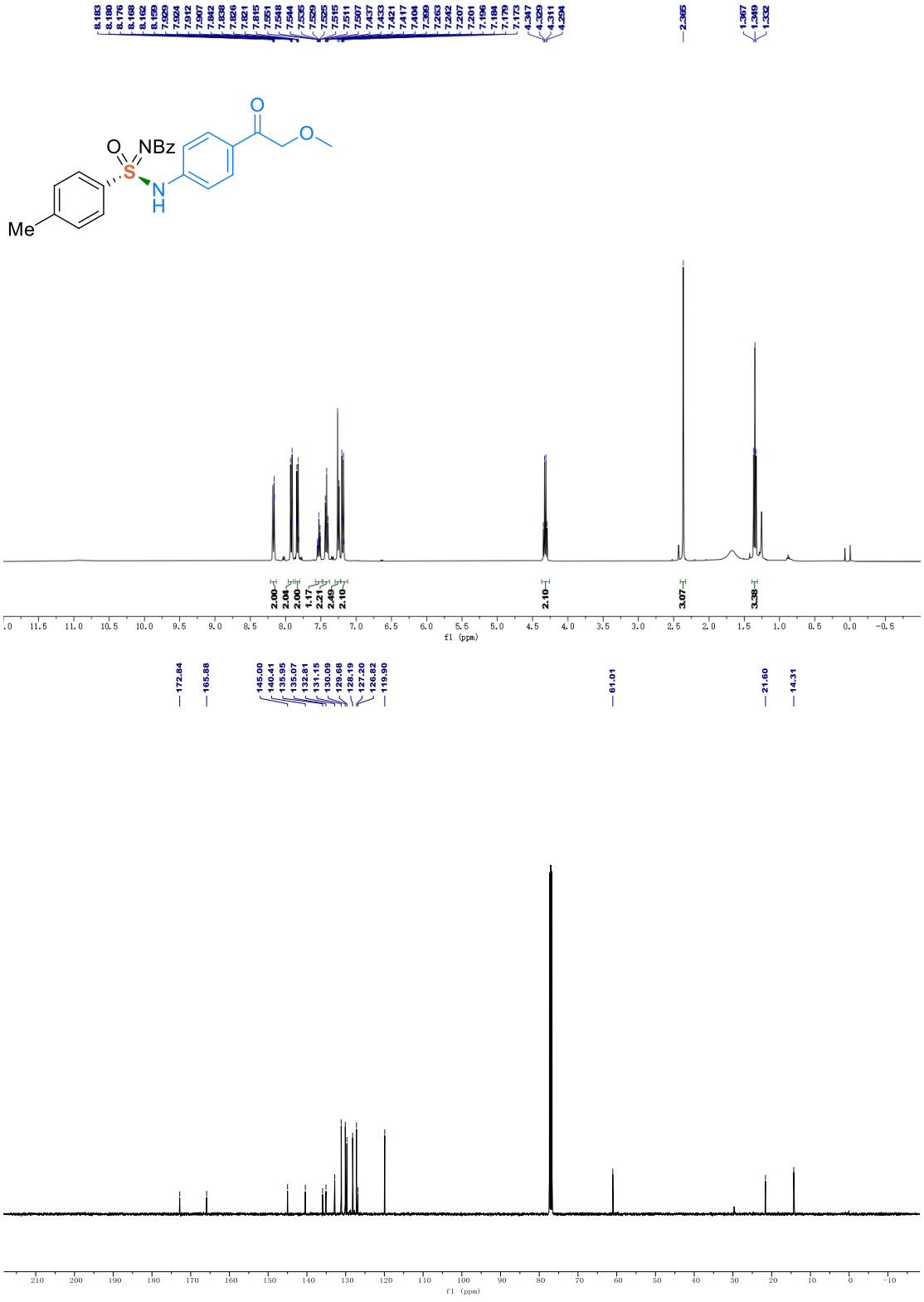
(*S*)-4-Nitrophenyl *N*-benzoyl-4-methylbenzenesulfonimidate (15):



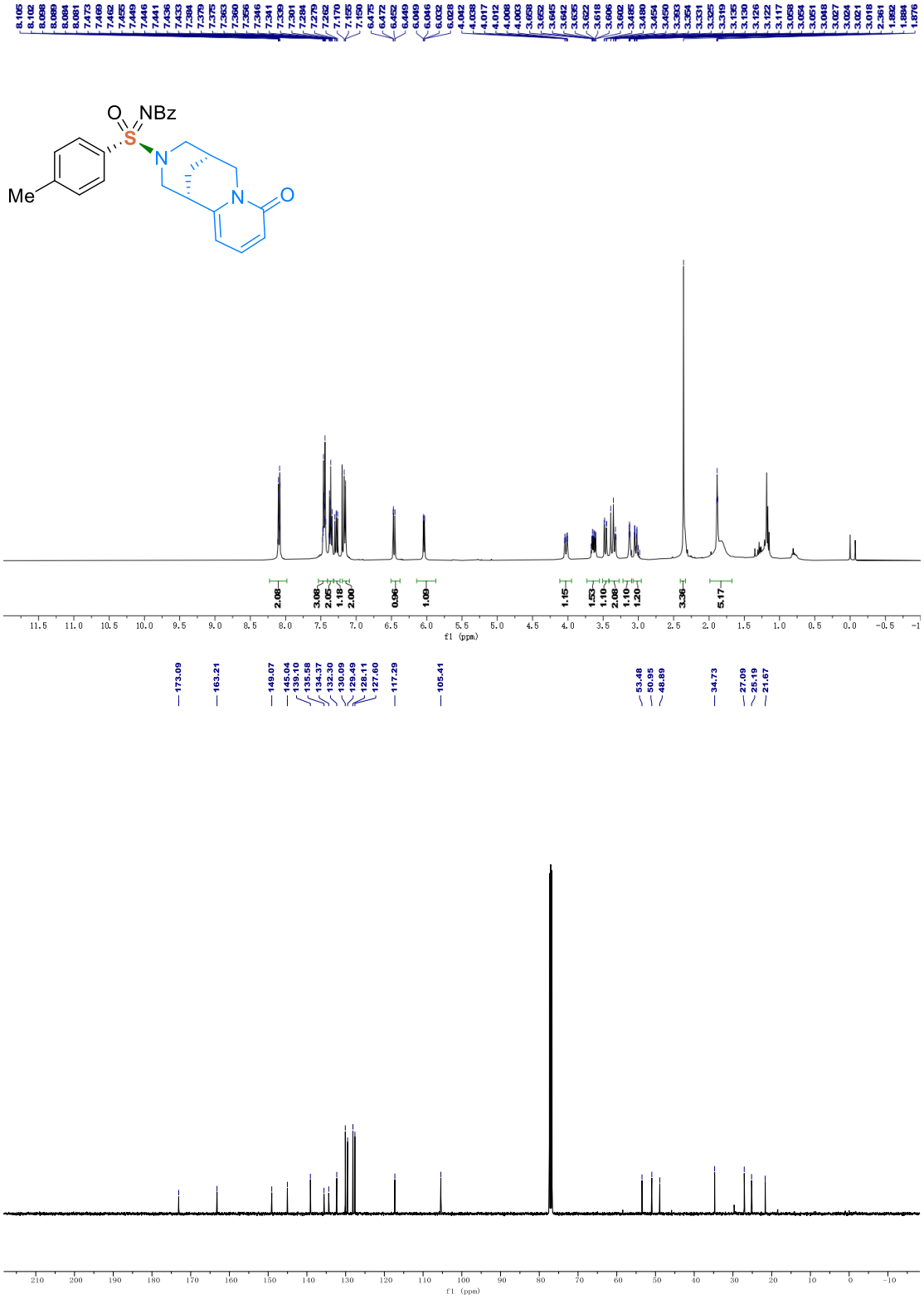
(*S*)-Phenyl *N*-benzoyl-4-methylbenzenesulfonimidate (16):



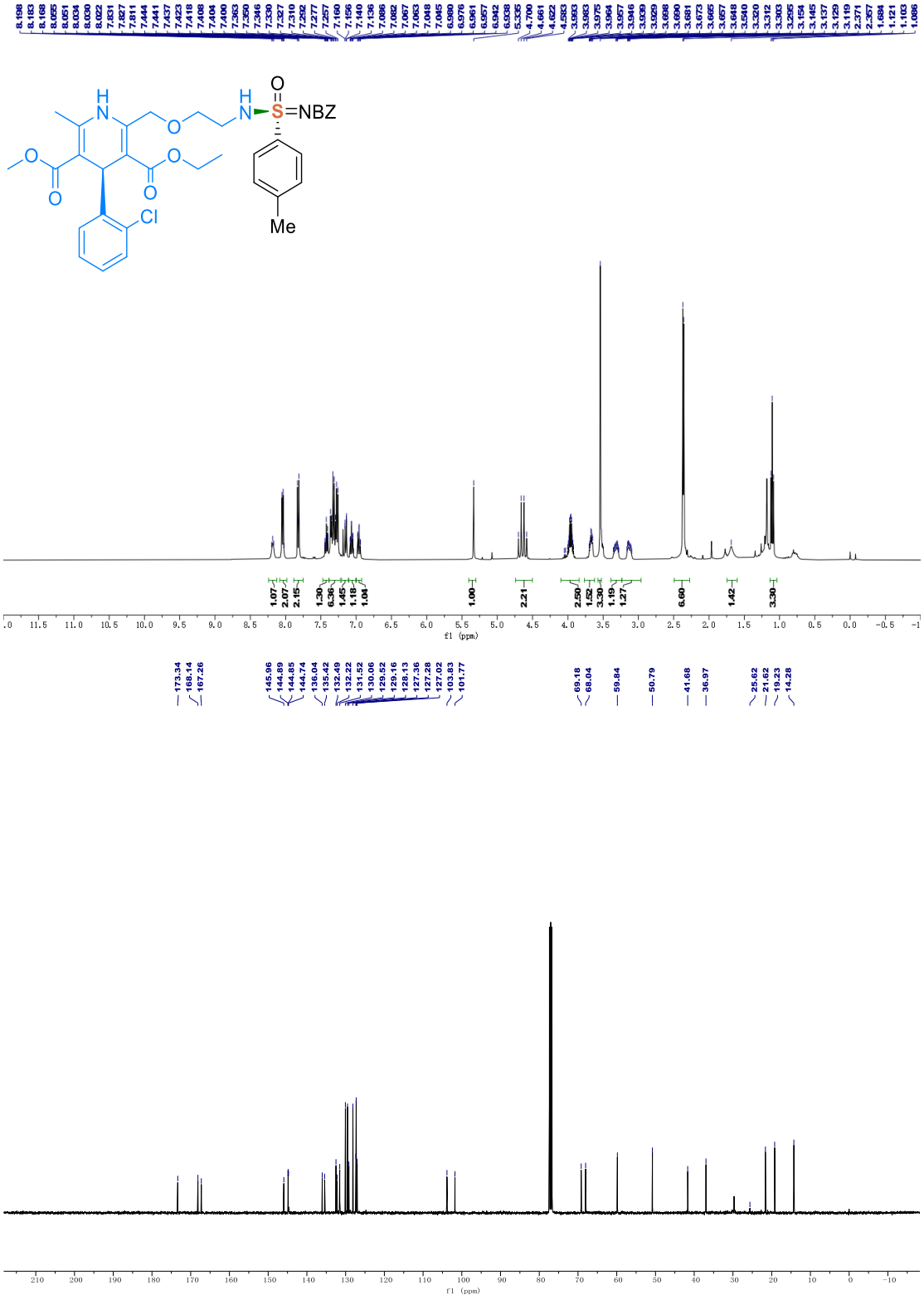
(*S*)-4-Nitrophenyl *N*-benzoyl-4-methylbenzenesulfonimidate (17):



((*S*)-*N*-(Oxo((1R,5R)-8-oxo-1,5,6,8-tetrahydro-2*H*-1,5-methanopyrido[1,2-a] [1,5] diazocin-3(4*H*)-yl) (*p*-tolyl)-λ^6-sulfaneylidene) benzamide (18):

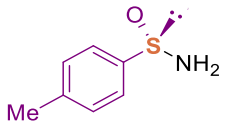


(*S*)-3-Ethyl-5-methyl (4*S*)-2-((2-((*N'*-benzoyl-4-methylphenyl) sulfonoamidimid amido) ethoxy) methyl)-4-(2-chlorophenyl)-6-methyl-1,4-dihydropyridine-3,5-dicarboxylate (20):

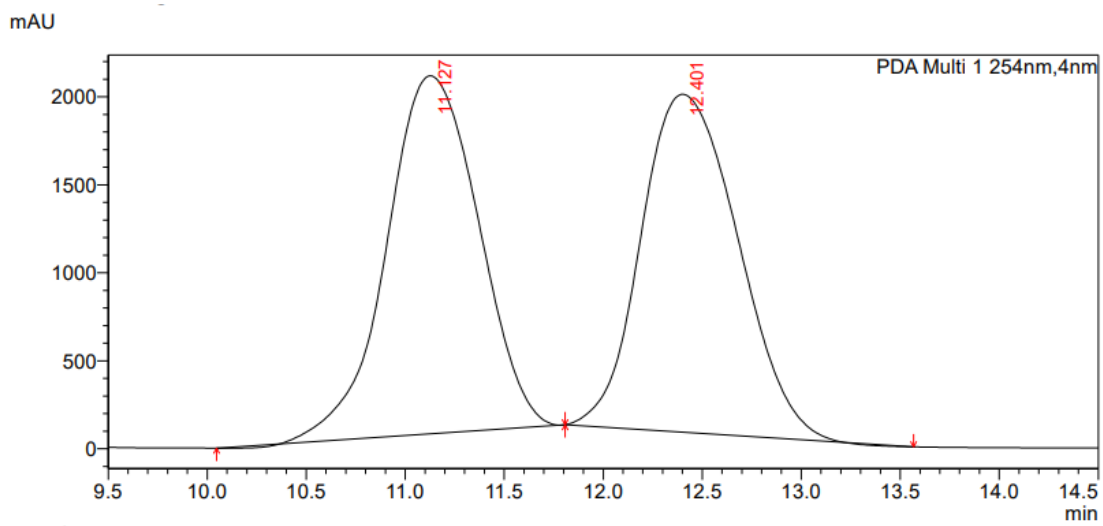


6. HPLC traces of the obtained chiral products

(*S*)-4-Methylbenzenesulfinamide (4a):

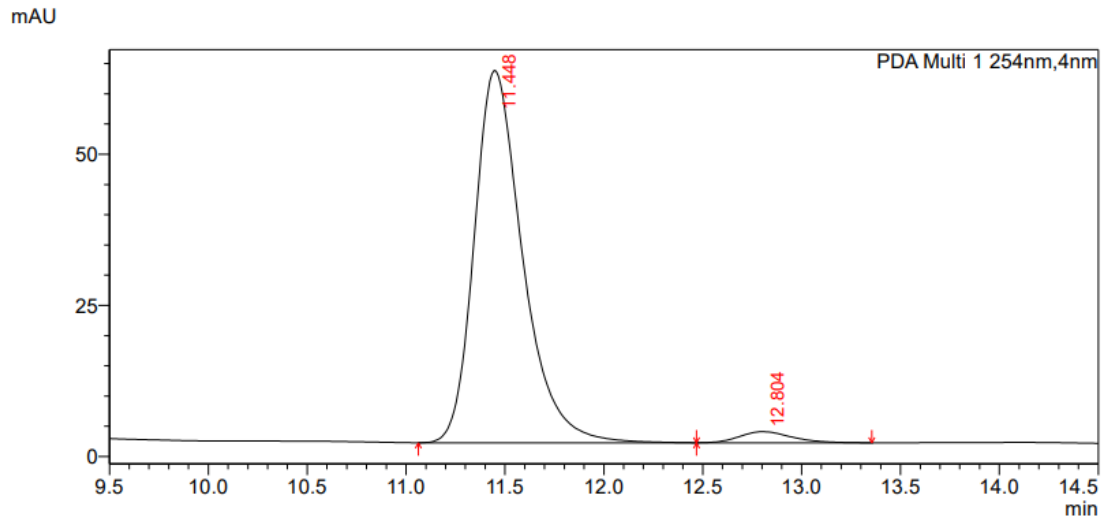


HPLC conditions: Chiralcel IA (*i*-PrOH/*n*-Hexane, 15：85), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

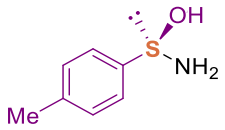
Peak#	Ret. Time	Area	Height	Area%
1	11.127	65745586	2034233	50.140
2	12.401	65379171	1920467	49.860
Total		131124756	3954700	100.000



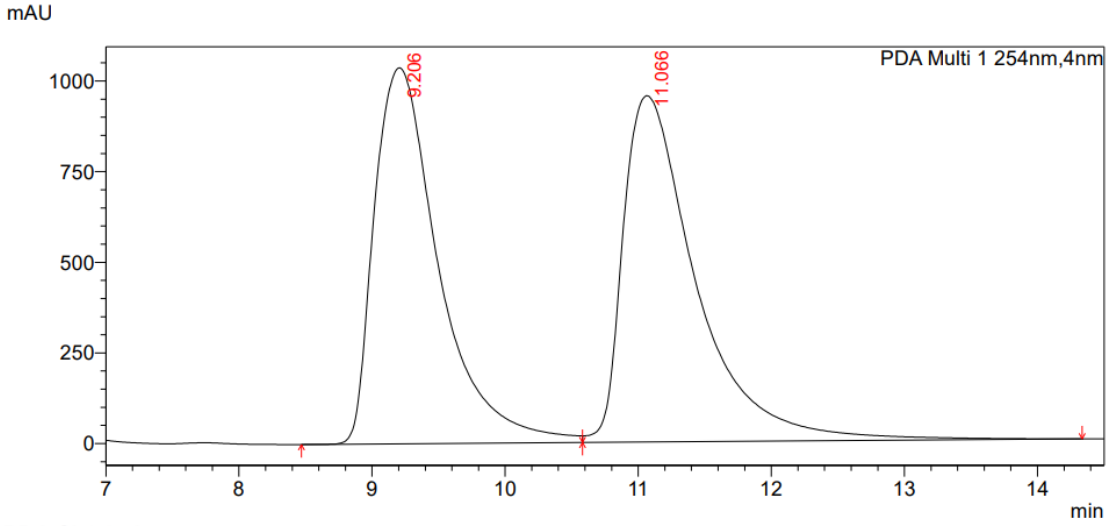
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	11.448	1050810	61595	96.890
2	12.804	33725	1836	3.110
Total		1084535	63431	100.000

(*R*)-4-Methylbenzenesulfinamide (4a):

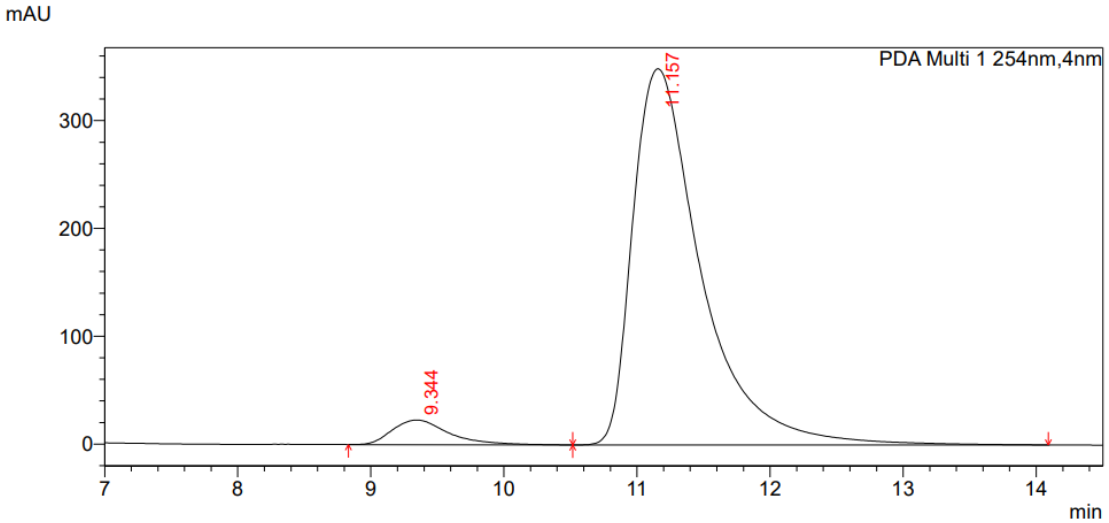


HPLC conditions: Chiralcel IA (*i*-PrOH/*n*-Hexane, 20：80), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

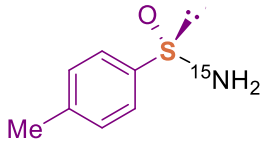
Peak#	Ret. Time	Area	Height	Area%
1	9.206	34910412	1037015	48.809
2	11.066	36614795	955024	51.191
Total		71525207	1992039	100.000



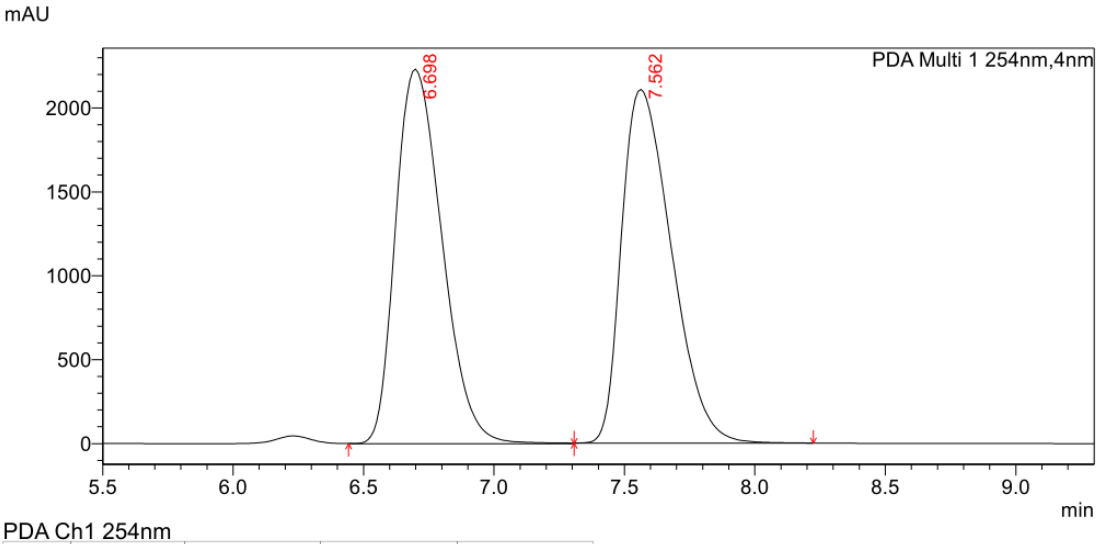
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	9.344	674147	22860	5.124
2	11.157	12482455	348931	94.876
Total		13156602	371791	100.000

^{15}N-4a

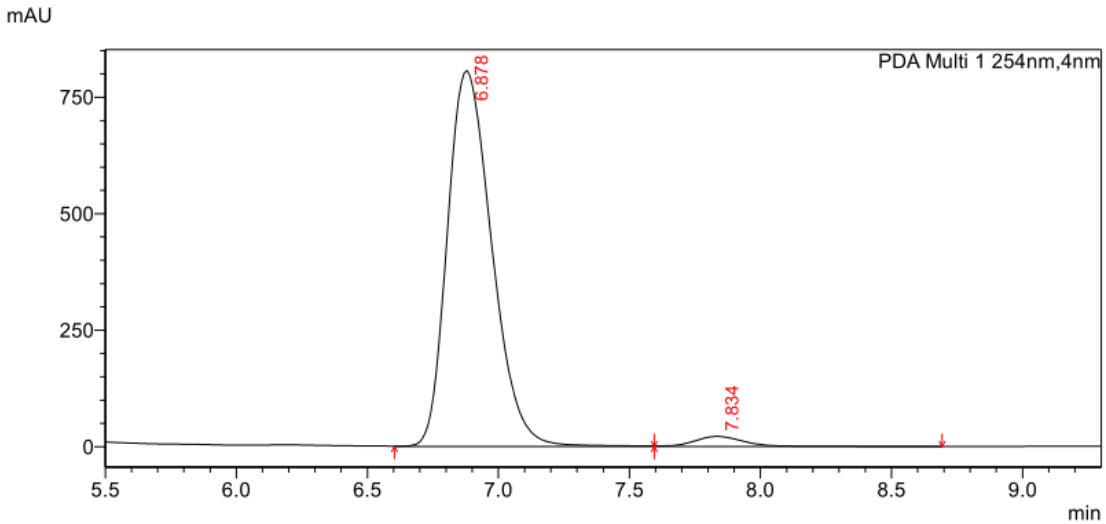


HPLC conditions: Chiralcel IA (*i*-PrOH/*n*-Hexane, 20：80), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

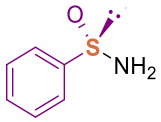
Peak#	Ret. Time	Area	Height	Area%
1	6.698	27674156	2232162	49.700
2	7.562	28008607	2107660	50.300
Total		55682763	4339822	100.000



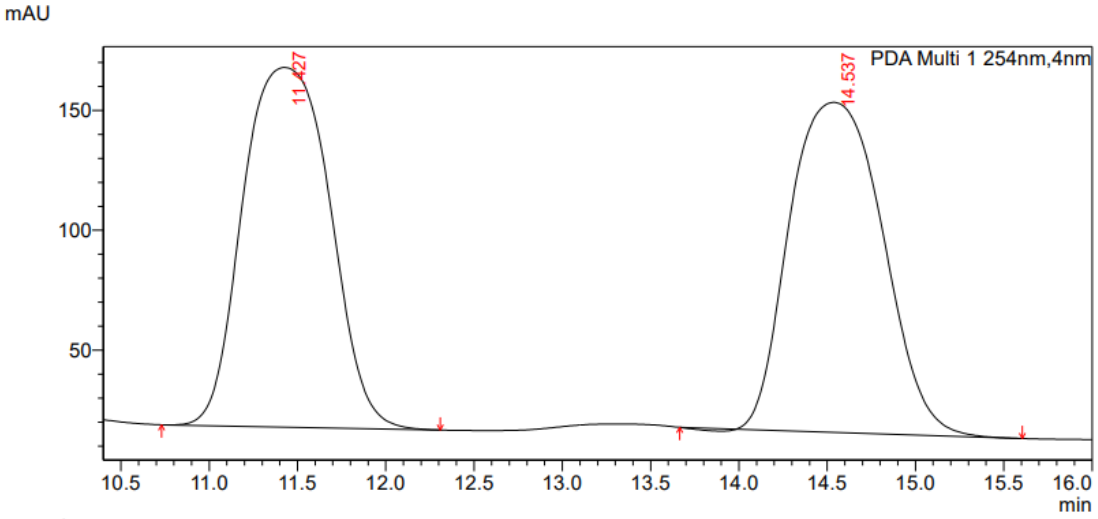
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	6.878	9517216	806872	97.083
2	7.834	285949	21746	2.917
Total		9803165	828618	100.000

(*S*)-Benzenesulfinamide (4b):

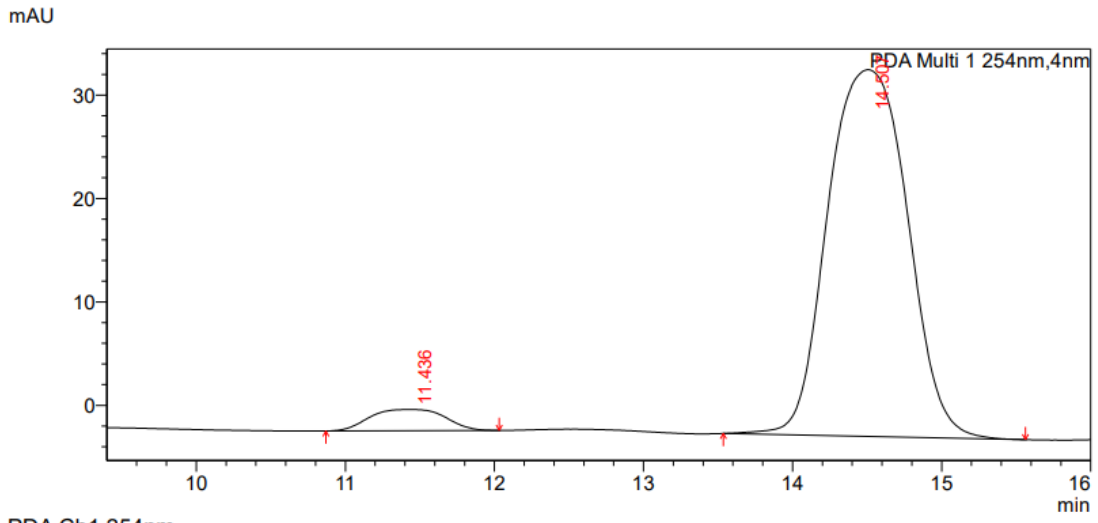


HPLC conditions: Chiralcel OJ-H (*i*-PrOH/*n*-Hexane, 10:90), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

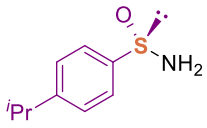
Peak#	Ret. Time	Area	Height	Area%
1	11.427	5159547	149891	50.452
2	14.537	5067011	137575	49.548
Total		10226558	287466	100.000



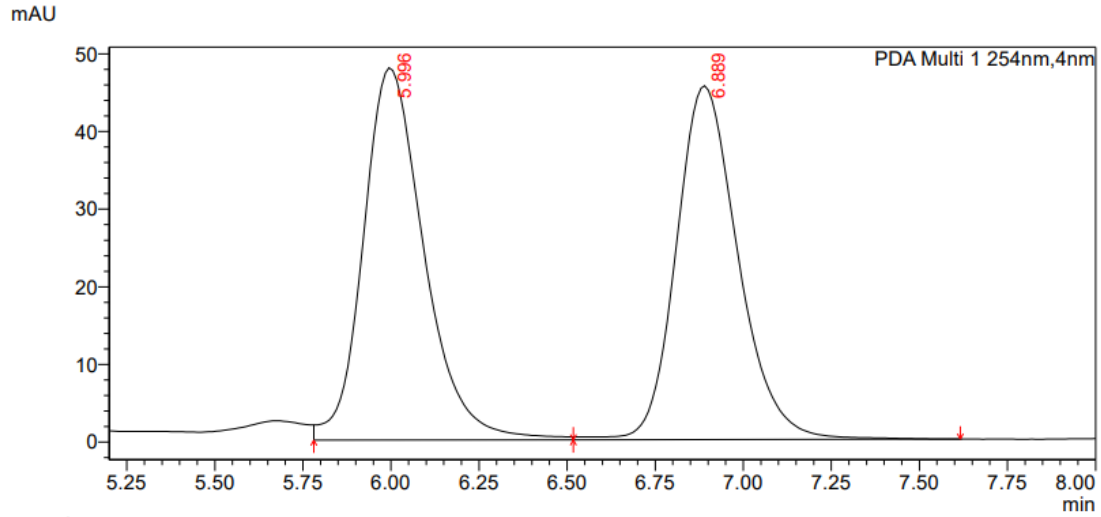
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	11.436	71638	2060	5.139
2	14.507	1322327	35459	94.861
Total		1393965	37519	100.000

(*S*)-4-Isopropylbenzenesulfonamide (4c):

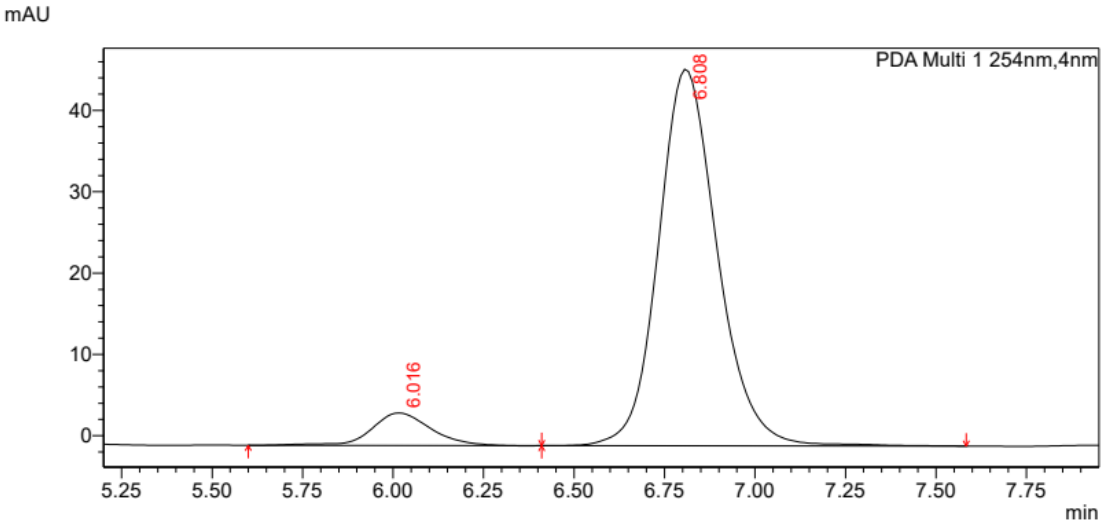


HPLC conditions: Chiralcel IB (*i*-PrOH/*n*-Hexane, 20:80), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

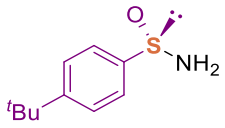
Peak#	Ret. Time	Area	Height	Area%
1	5.996	576198	47951	50.808
2	6.889	557866	45571	49.192
Total		1134064	93523	100.000



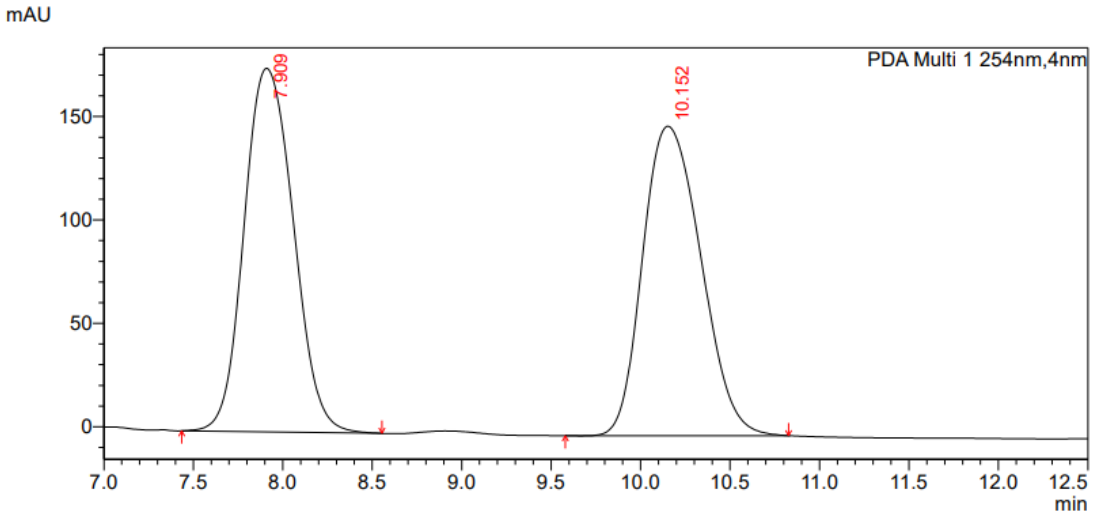
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	6.016	45795	4008	8.011
2	6.808	525888	46298	91.989
Total		571683	50306	100.000

(*S*)-4-Tert-Butylbenzenesulfonamide (4d):

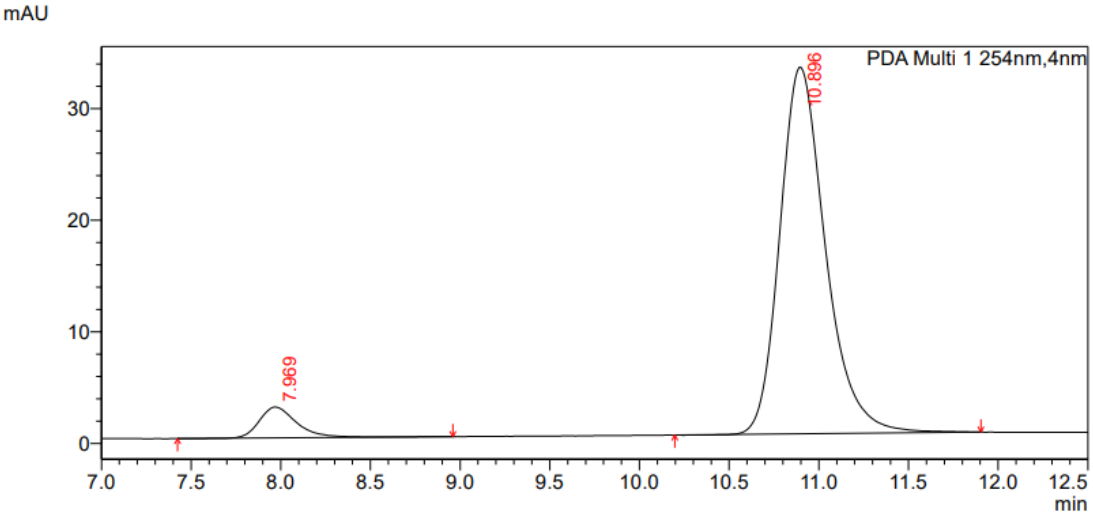


HPLC conditions: Chiralcel IB (*i*-PrOH/*n*-Hexane, 20:80), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

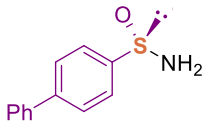
Peak#	Ret. Time	Area	Height	Area%
1	7.909	3383697	175755	49.912
2	10.152	3395633	149635	50.088
Total		6779330	325390	100.000



PDA Ch1 254nm

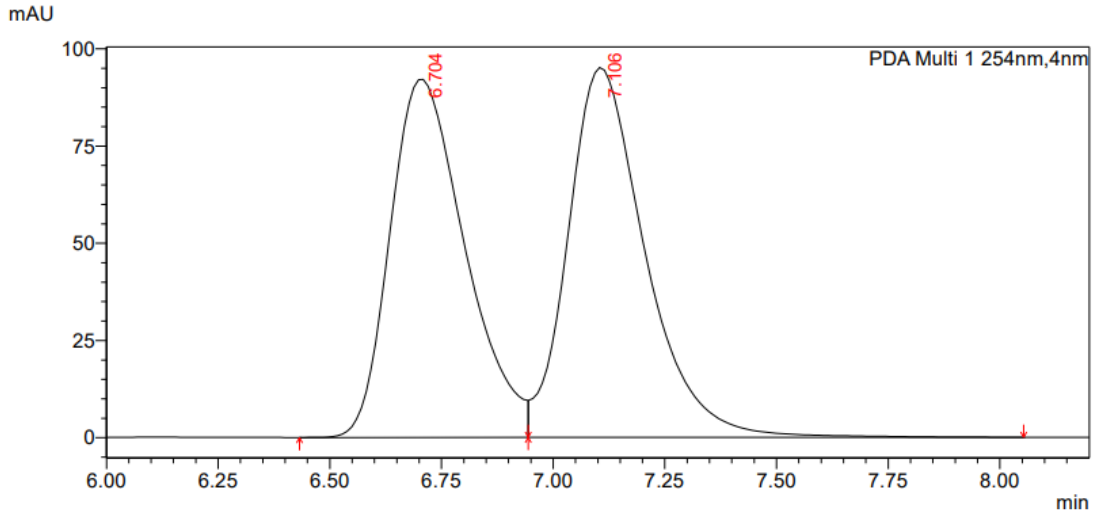
Peak#	Ret. Time	Area	Height	Area%
1	7.969	40492	2760	6.506
2	10.896	581866	32861	93.494
Total		622359	35621	100.000

(*S*)-[1,1'-Biphenyl]-4-sulfinamide (4e):



HPLC conditions: Chiralcel IB (*i*-PrOH/*n*-Hexane, 20:80), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.

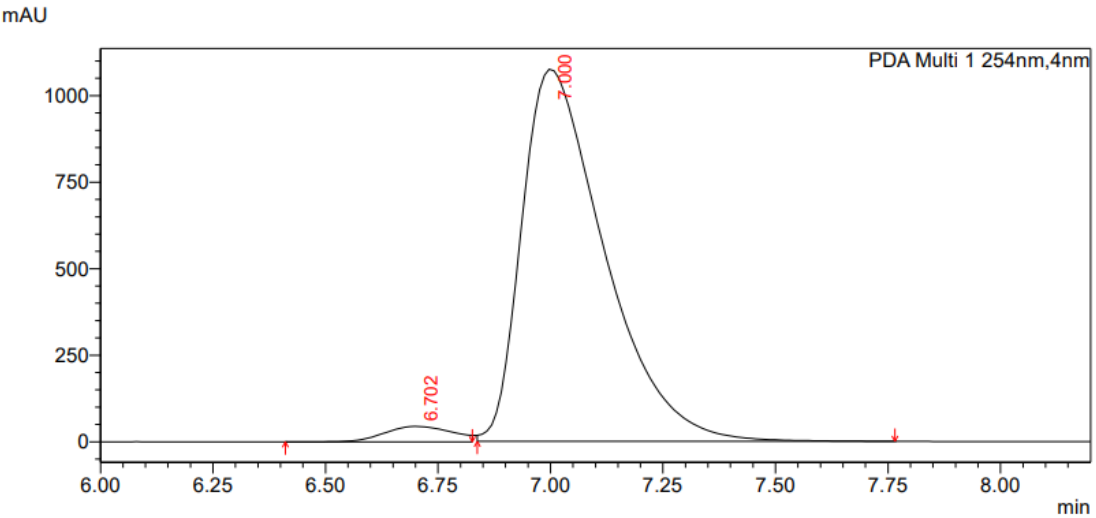
<Chromatogram>



PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	6.704	1078338	92050	48.585
2	7.106	1141164	95105	51.415
Total		2219502	187155	100.000

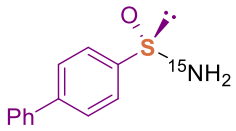
<Chromatogram>



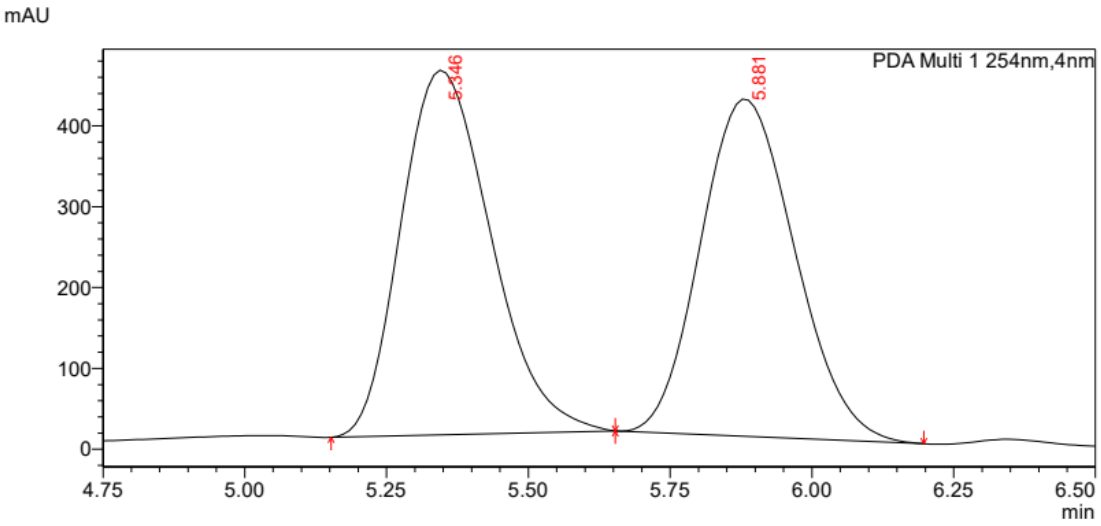
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	6.702	465835	44477	3.273
2	7.000	13766202	1075217	96.727
Total		14232037	1119694	100.000

^{15}N-4e

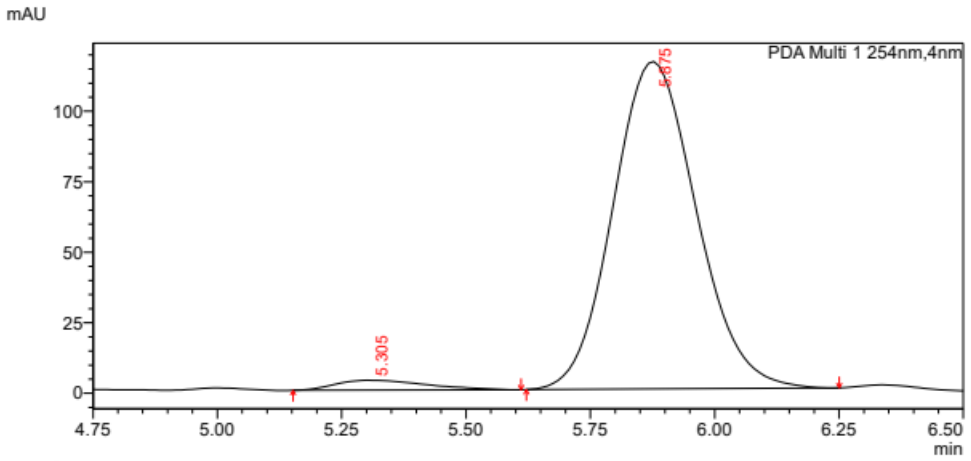


HPLC conditions: Chiralcel IB (*i*-PrOH/*n*-Hexane, 20:80), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

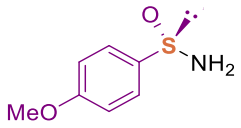
Peak#	Ret. Time	Area	Height	Area%
1	5.346	4976665	450900	50.780
2	5.881	4823849	416990	49.220
Total		9800515	867890	100.000



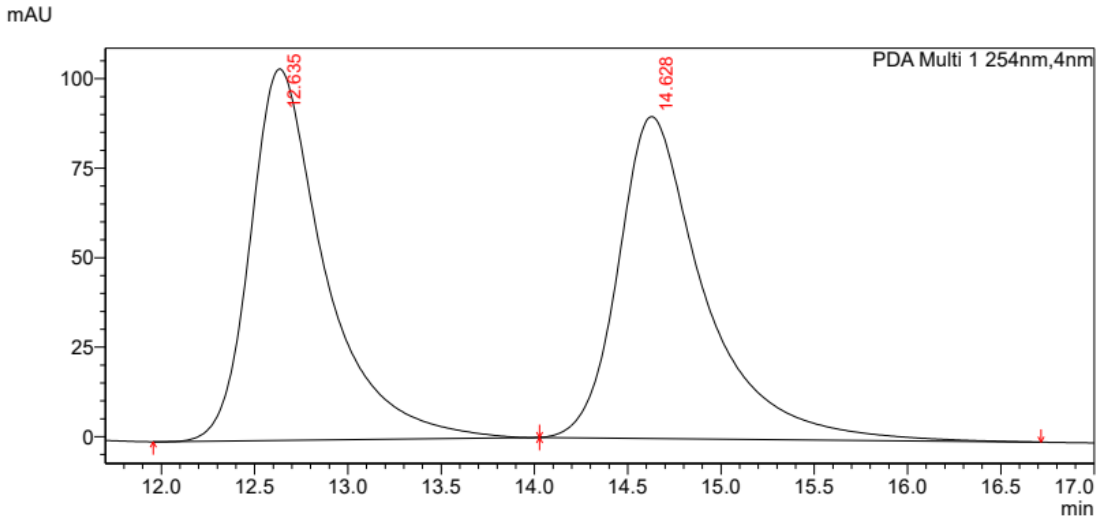
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	5.305	44346	3495	3.170
2	5.875	1354507	116083	96.830
Total		1398853	119578	100.000

(*S*)-4-Methoxybenzenesulfinamide (4f):

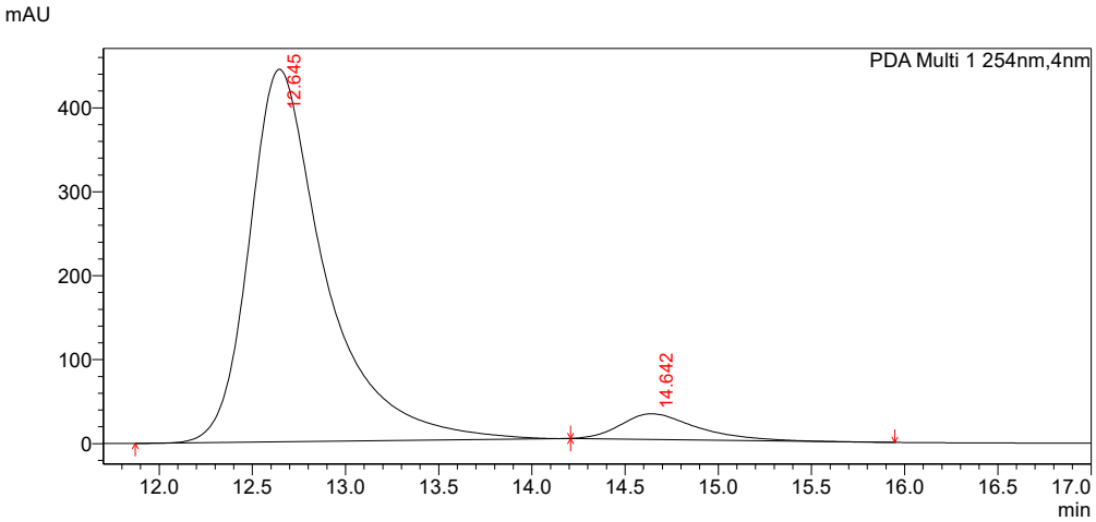


HPLC conditions: Chiralcel IA (*i*-PrOH/*n*-Hexane, 10:90), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

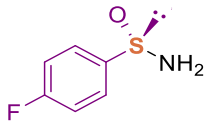
Peak#	Ret. Time	Area	Height	Area%
1	12.635	2899870	103718	49.951
2	14.628	2905517	89929	50.049
Total		5805387	193647	100.000



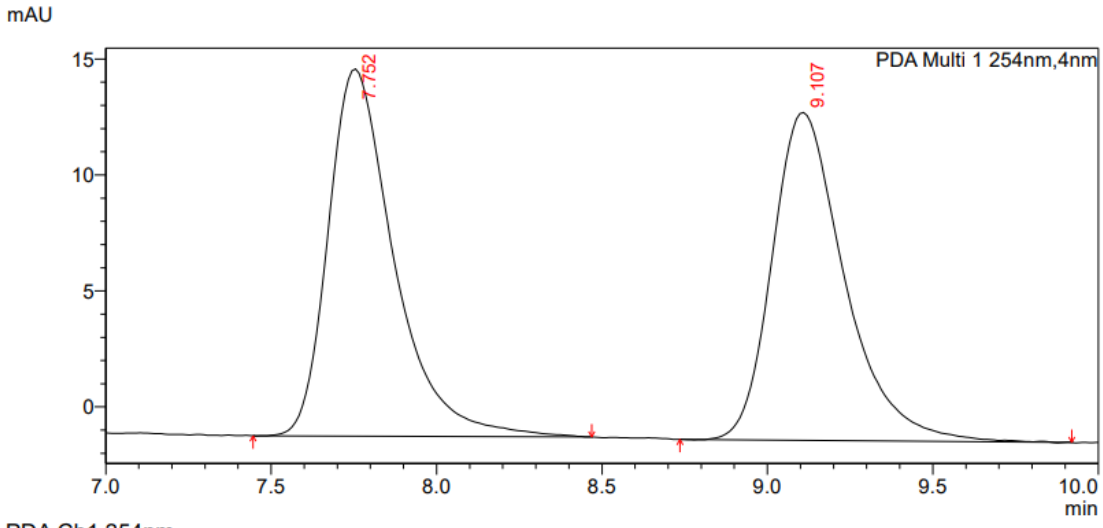
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	12.645	12595974	443596	93.518
2	14.642	873121	30612	6.482
Total		13469095	474208	100.000

(*S*)-4-Fluorobenzenesulfinamide (4g):

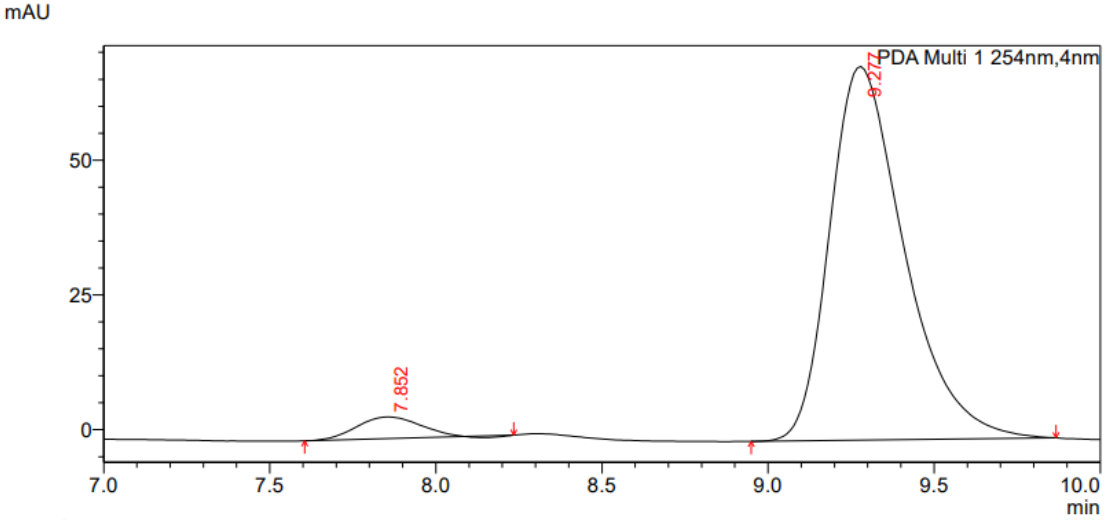


HPLC conditions: Chiralcel IB (*i*-PrOH/*n*-Hexane, 20:80), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

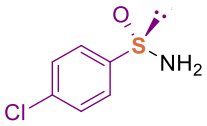
Peak#	Ret. Time	Area	Height	Area%
1	7.752	219079	15825	50.390
2	9.107	215687	14130	49.610
Total		434766	29955	100.000



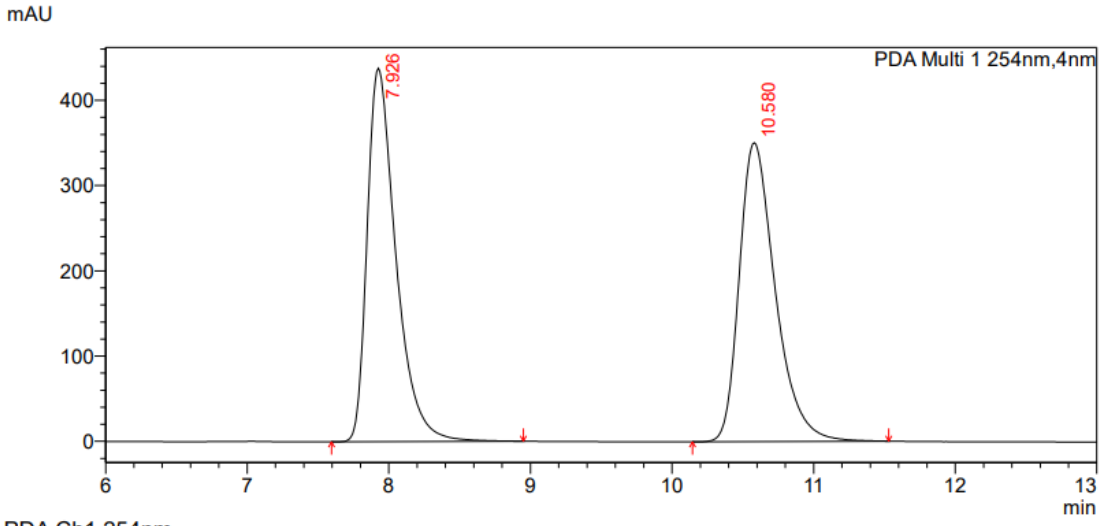
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	7.852	52169	4017	4.593
2	9.277	1083778	69290	95.407
Total		1135947	73308	100.000

(*S*)-4-Chlorobenzenesulfinamide (4h):

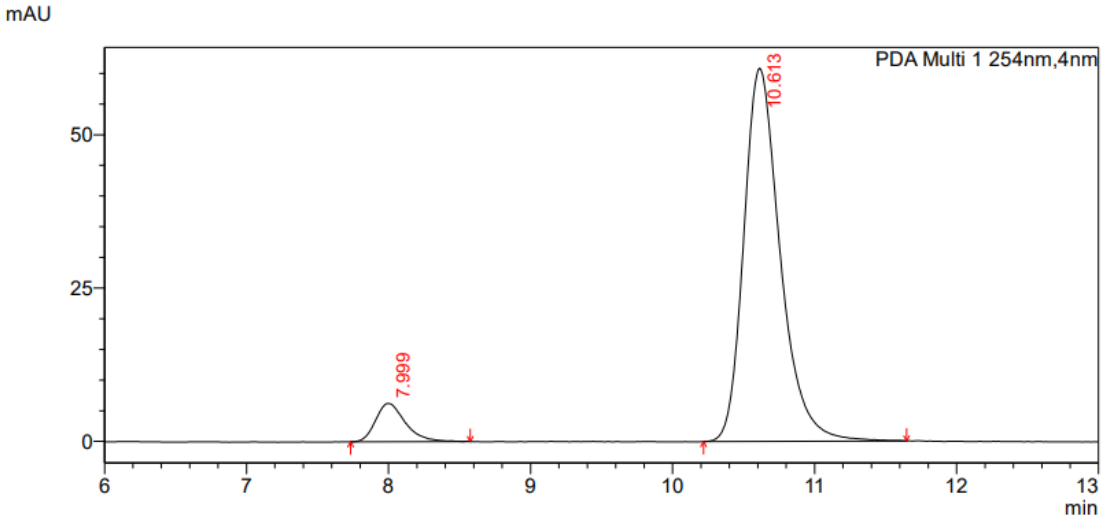


HPLC conditions: Chiralcel IB (*i*-PrOH/*n*-Hexane, 20:80), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

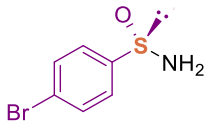
Peak#	Ret. Time	Area	Height	Area%
1	7.926	6197950	437893	49.998
2	10.580	6198503	350584	50.002
Total		12396454	788478	100.000



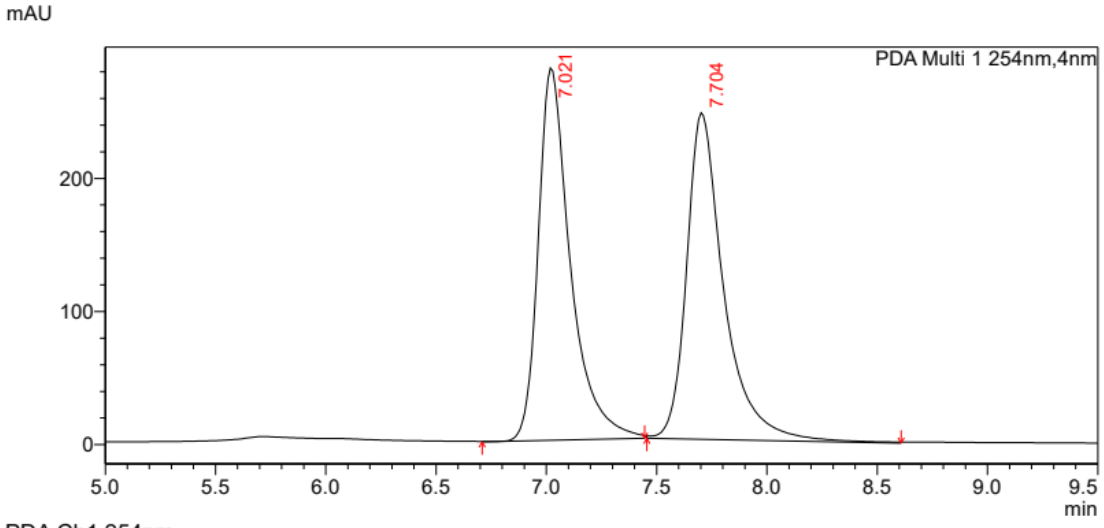
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	7.999	90707	6256	7.722
2	10.613	1083945	60819	92.278
Total		1174652	67075	100.000

(*S*)-4-Bromobenzenesulfinamide (4i):

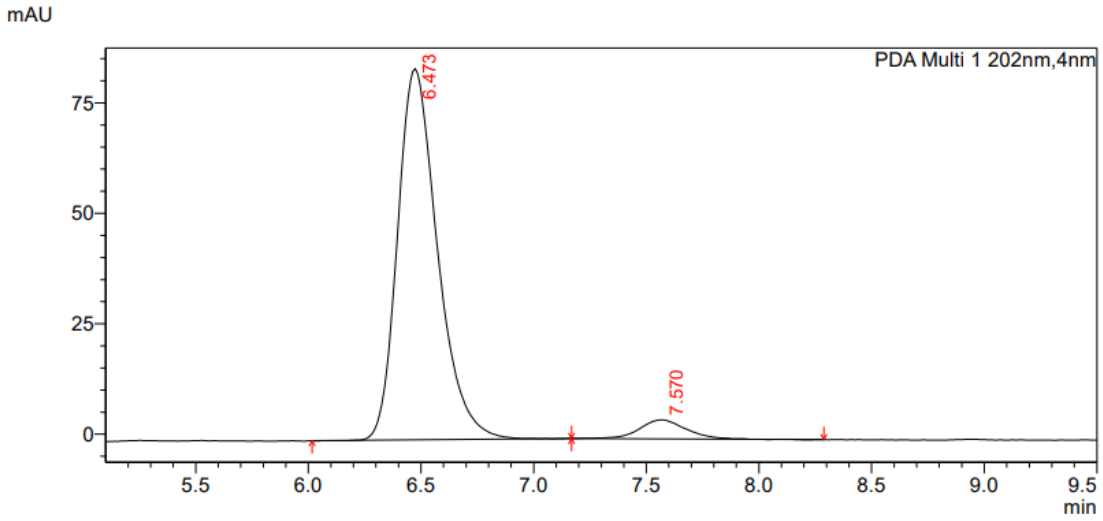


HPLC conditions: Chiralcel IA (*i*-PrOH/*n*-Hexane, 20:80), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

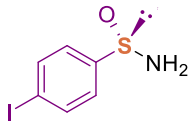
Peak#	Ret. Time	Area	Height	Area%
1	7.021	2841733	279624	49.619
2	7.704	2885326	245214	50.381
Total		5727059	524838	100.000



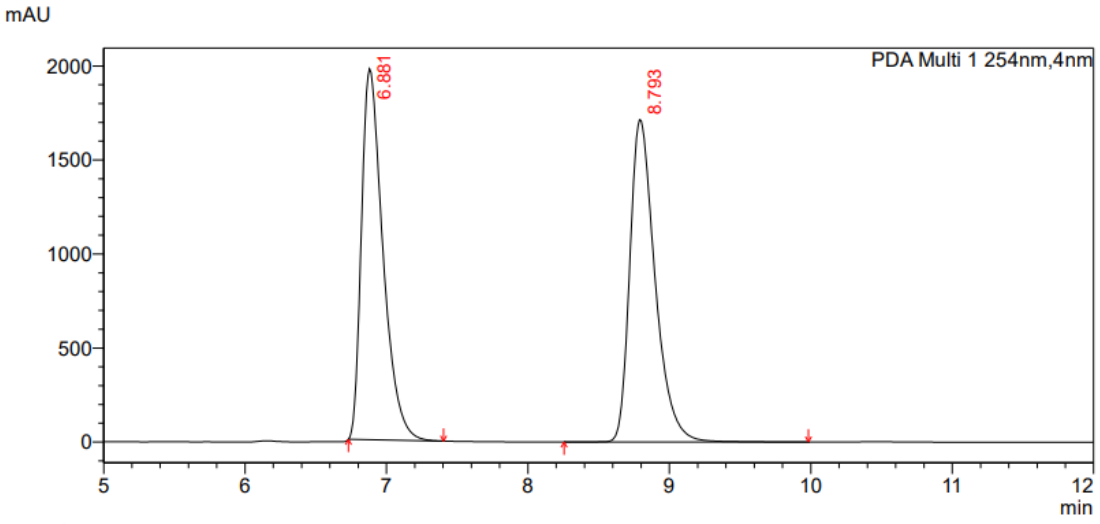
PDA Ch1 202nm

Peak#	Ret. Time	Area	Height	Area%
1	6.473	1036221	83990	94.404
2	7.570	61424	4280	5.596
Total		1097645	88270	100.000

(*S*)-4-Iodobenzenesulfinamide (4j):

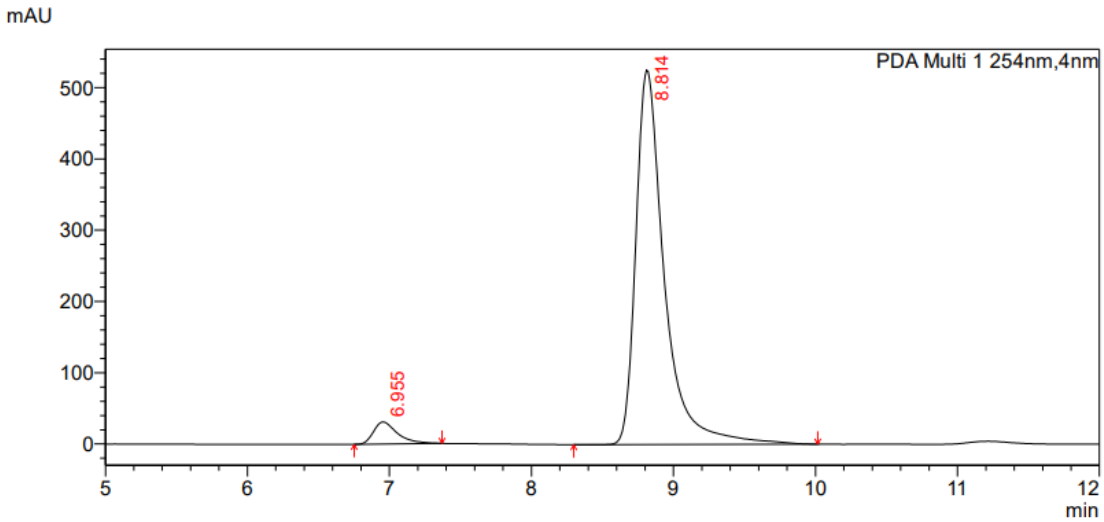


HPLC conditions: Chiralcel IB (*i*-PrOH/*n*-Hexane, 20:80), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

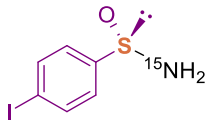
Peak#	Ret. Time	Area	Height	Area%
1	6.881	20839838	1972108	49.397
2	8.793	21348517	1714357	50.603
Total		42188355	3686466	100.000



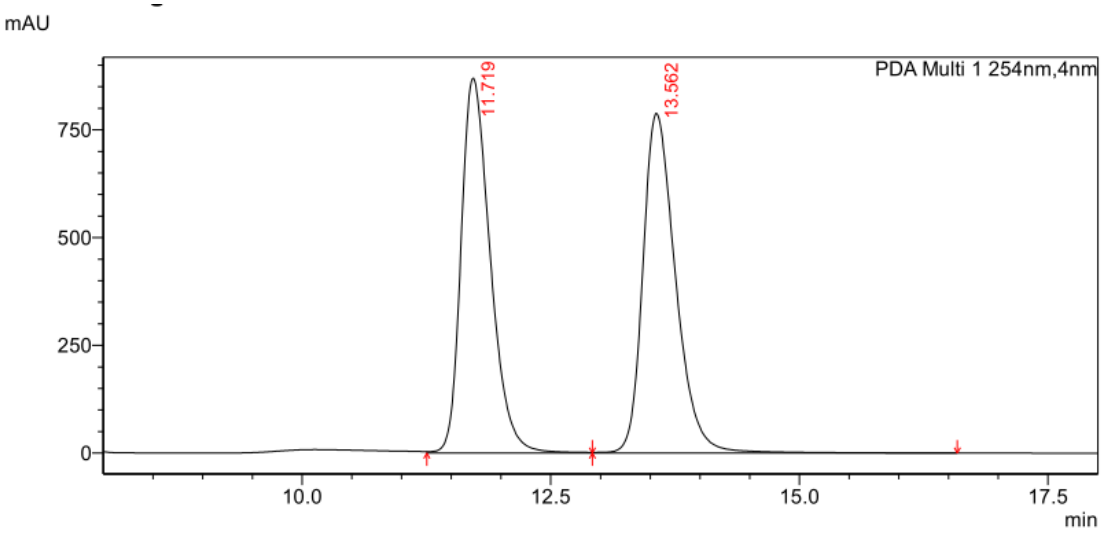
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	6.955	367243	31226	4.763
2	8.814	7343681	525255	95.237
Total		7710924	556481	100.000

^{15}N-4j

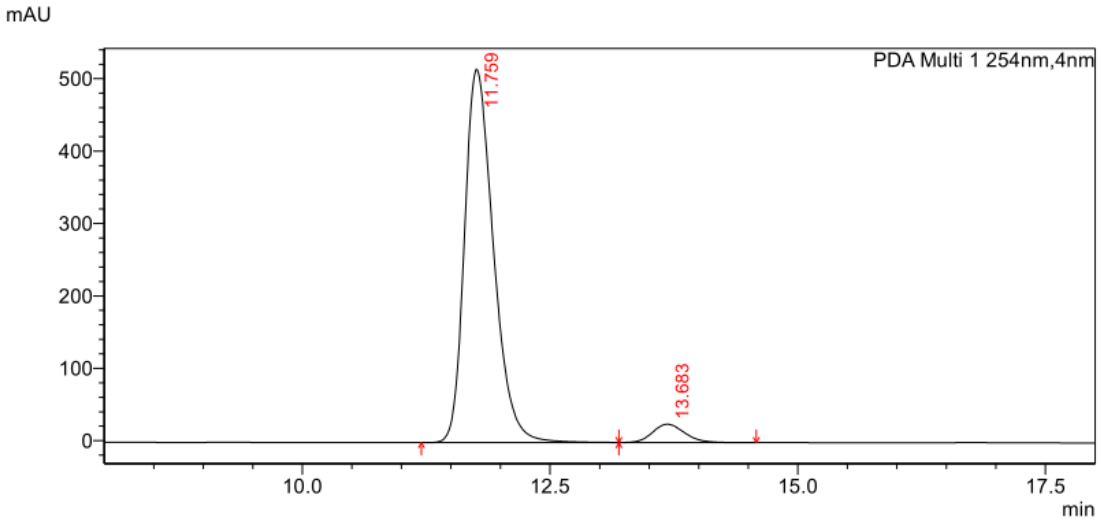


HPLC conditions: Chiralcel IA (*i*-PrOH/*n*-Hexane, 10:90), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

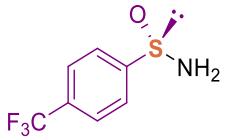
Peak#	Ret. Time	Area	Height	Area%
1	11.719	17781273	869507	49.589
2	13.562	18076321	787857	50.411
Total		35857593	1657364	100.000



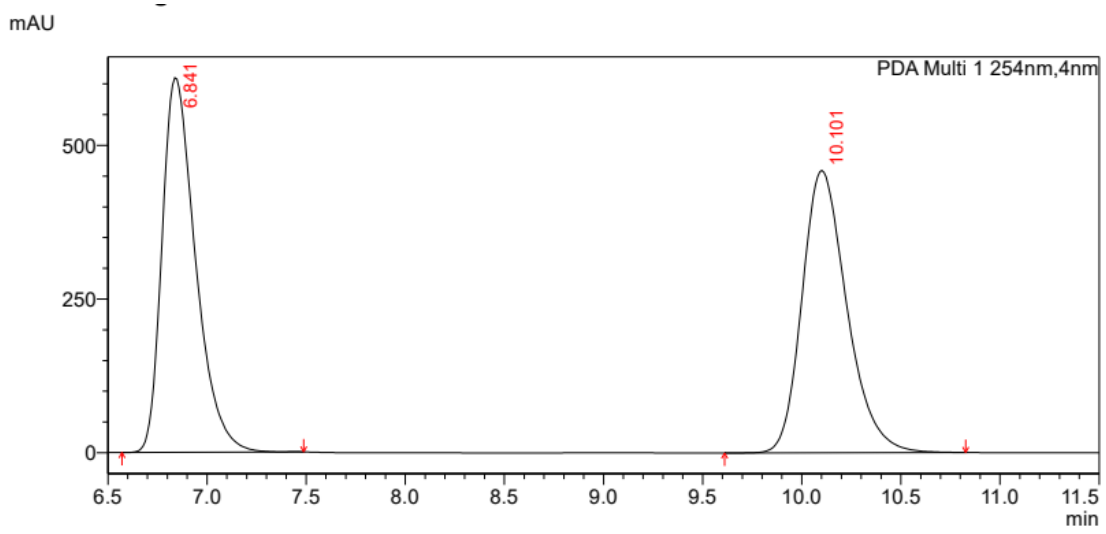
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	11.759	10495054	515554	94.767
2	13.683	579537	25515	5.233
Total		11074591	541068	100.000

(*S*)-4-Trifluoromethylbenzenesulfonamide (4k):

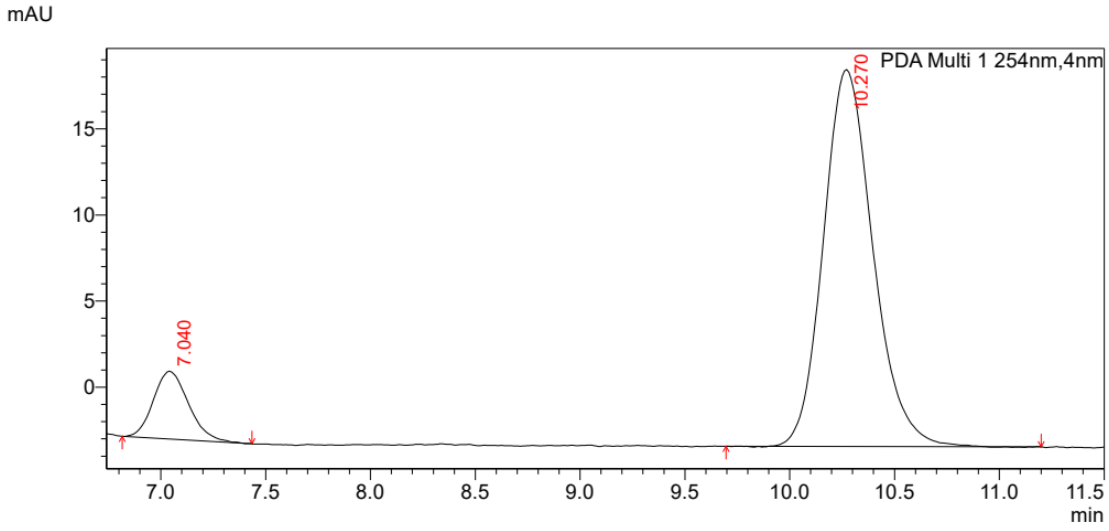


HPLC conditions: Chiralcel IB (*i*-PrOH/*n*-Hexane, 20:80), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

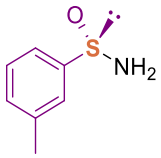
Peak#	Ret. Time	Area	Height	Area%
1	6.841	7170943	609036	49.836
2	10.101	7218248	459389	50.164
Total		14389191	1068425	100.000



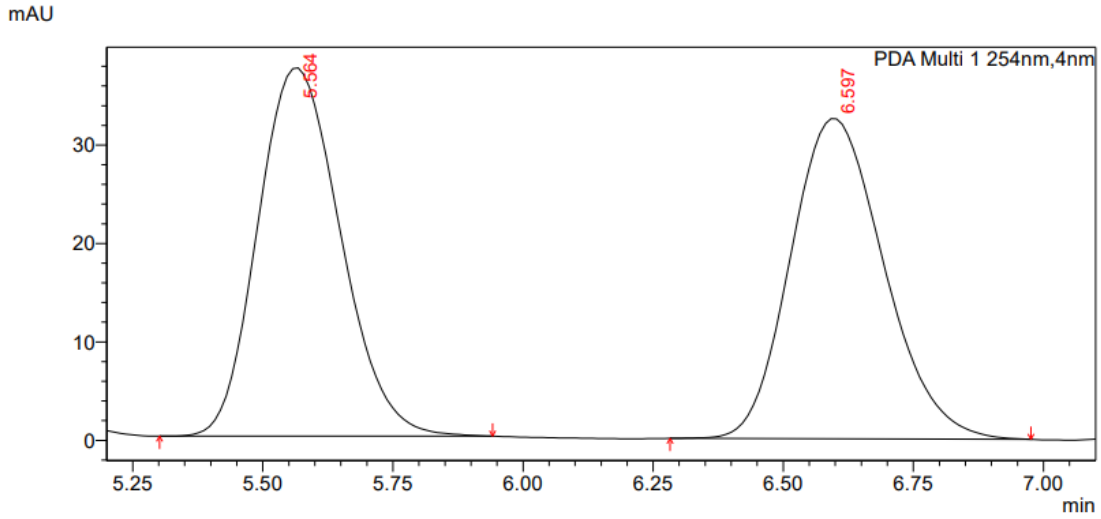
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	7.040	45987	3943	11.331
2	10.270	359879	21873	88.669
Total		405866	25815	100.000

(*S*)-4-Methylbenzenesulfonamide (4l):

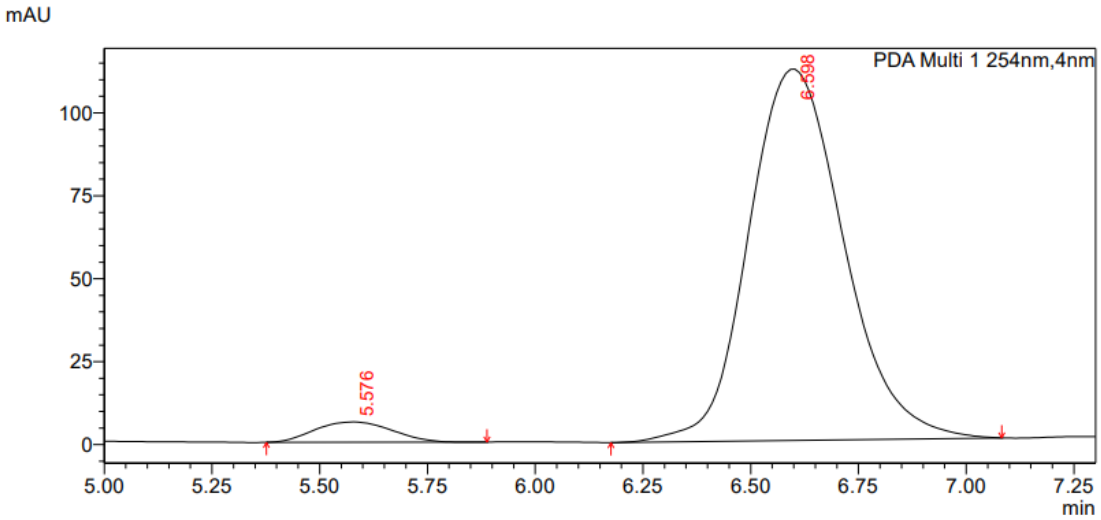


HPLC conditions: Chiralcel OJ-H (*i*-PrOH/*n*-Hexane, 20:80), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

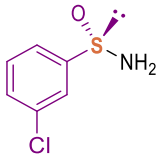
Peak#	Ret. Time	Area	Height	Area%
1	5.564	414626	37411	50.489
2	6.597	406602	32536	49.511
Total		821228	69946	100.000



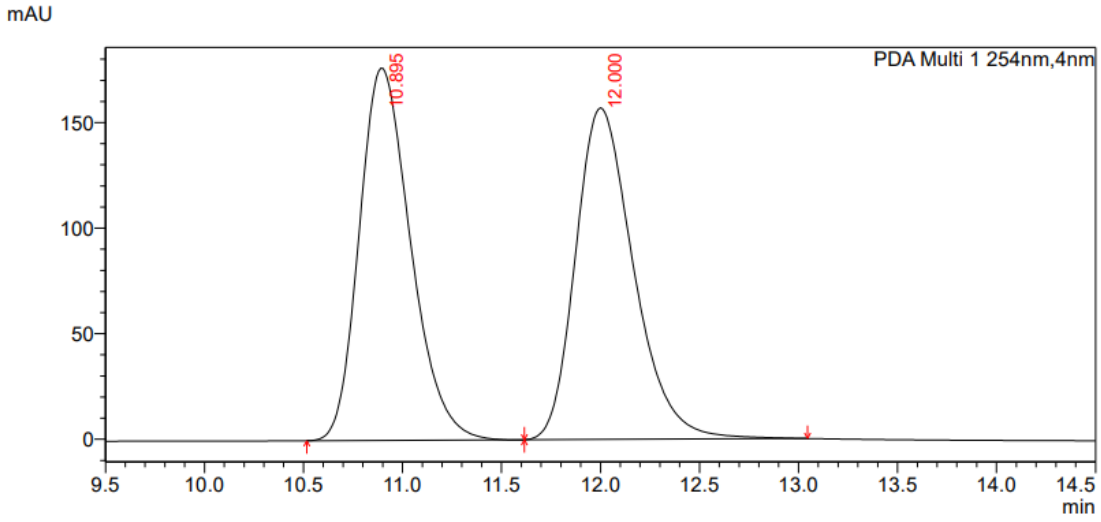
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	5.576	76161	6122	4.244
2	6.598	1718496	111889	95.756
Total		1794657	118011	100.000

(*S*)-3-Chlorobenzenesulfonamide (4m):

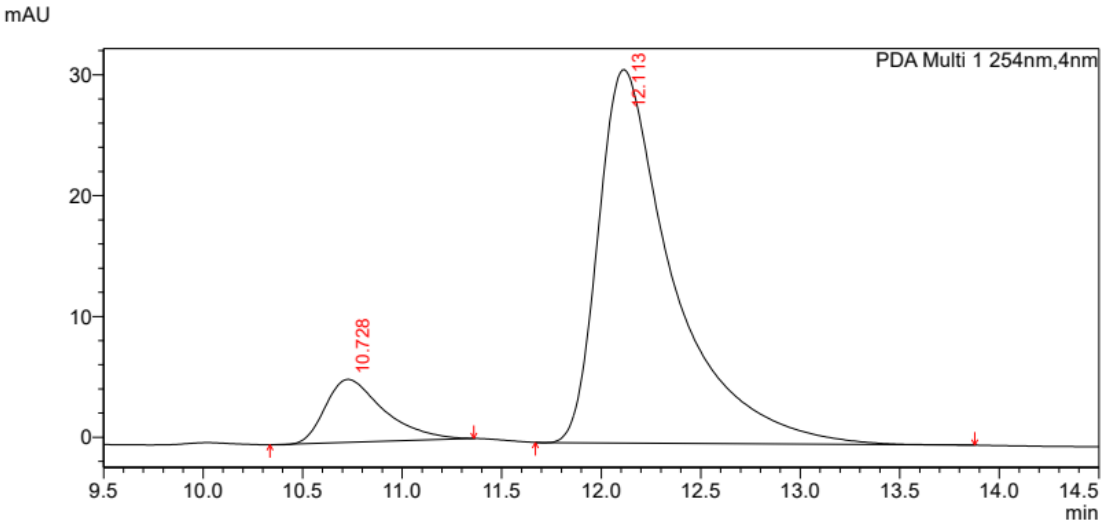


HPLC conditions: Chiralcel OJ-H (*i*-PrOH/*n*-Hexane, 10:90), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

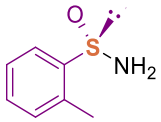
Peak#	Ret. Time	Area	Height	Area%
1	10.895	3182056	176268	49.836
2	12.000	3203063	157056	50.164
Total		6385119	333324	100.000



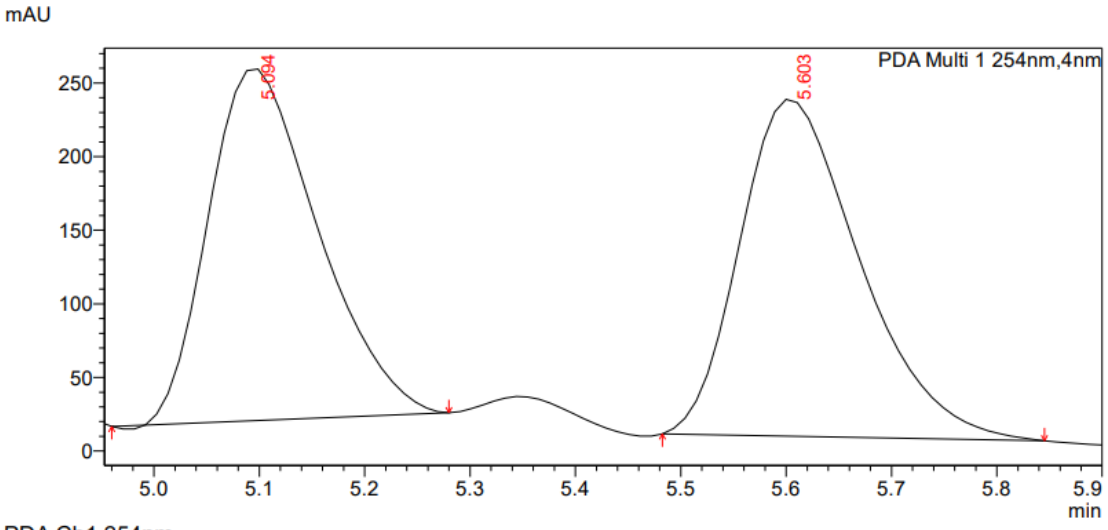
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	10.728	106105	5212	11.595
2	12.113	808991	30897	88.405
Total		915096	36109	100.000

(*S*)-2-Methylbenzenesulfonamide (4n):

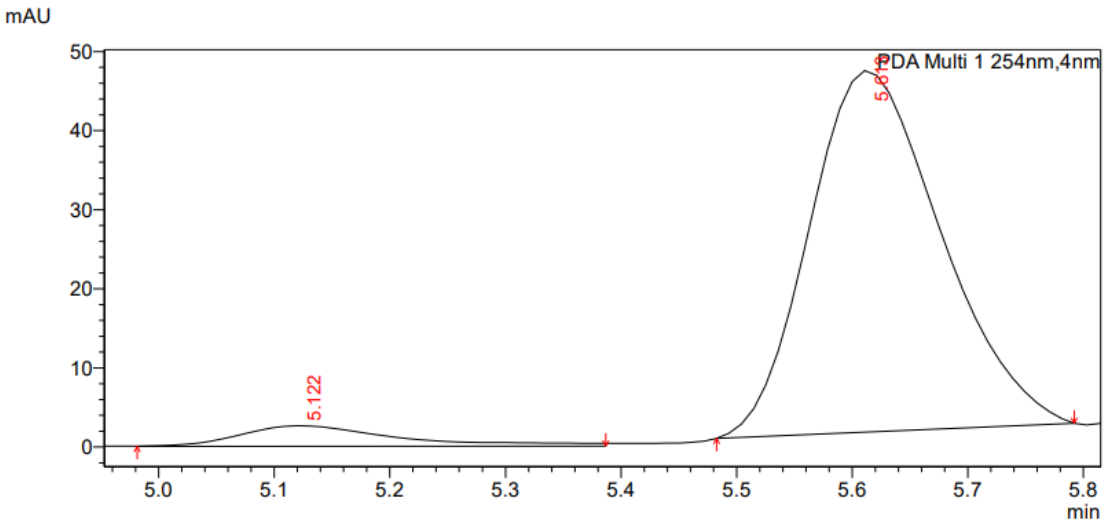


HPLC conditions: Chiralcel IB (*i*-PrOH/*n*-Hexane, 20:80), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

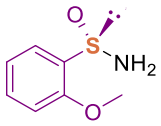
Peak#	Ret. Time	Area	Height	Area%
1	5.094	1727185	238773	48.869
2	5.603	1807100	228766	51.131
Total		3534285	467539	100.000



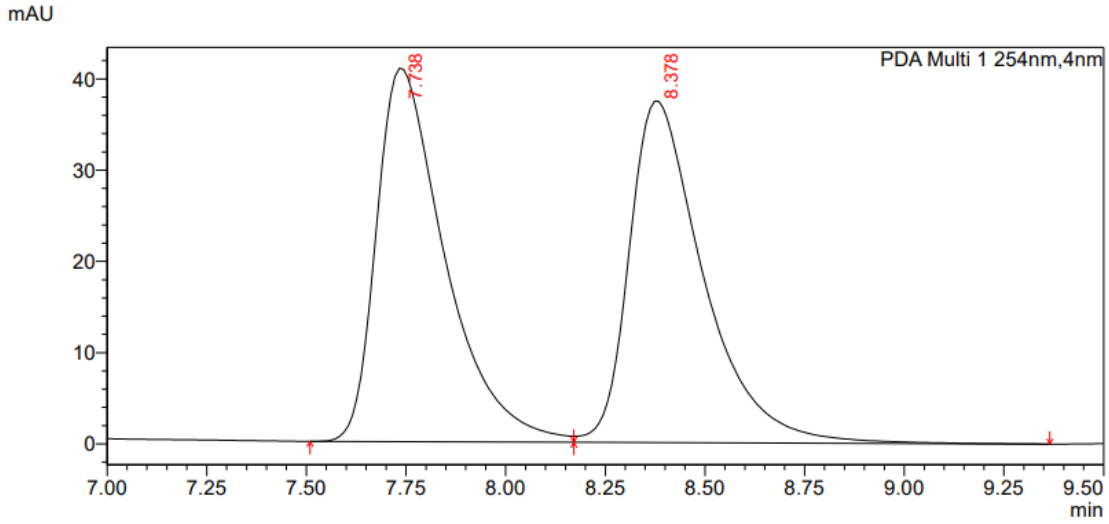
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	5.122	24782	2597	6.427
2	5.613	360832	45685	93.573
Total		385614	48282	100.000

(*S*)-2-Methoxybenzenesulfinamide (4o):

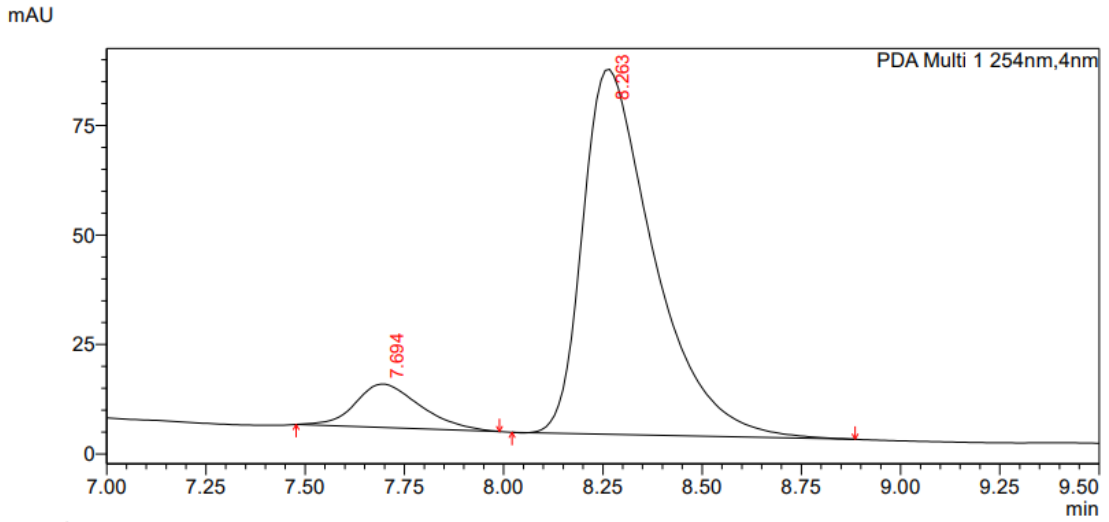


HPLC conditions: Chiralcel IB (*i*-PrOH/*n*-Hexane, 20:80), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	7.738	491418	40923	50.233
2	8.378	486858	37418	49.767
Total		978276	78341	100.000

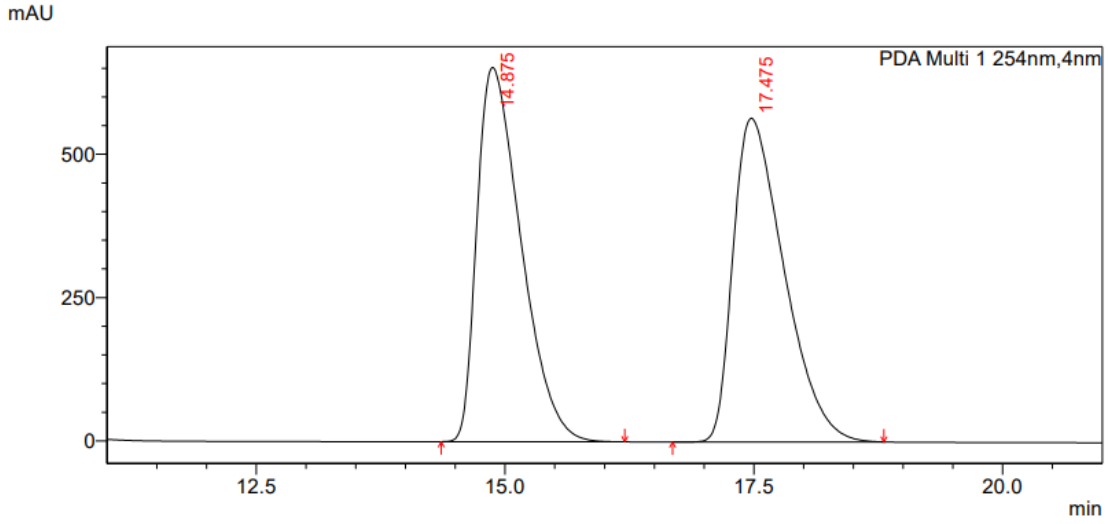


PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	7.694	112545	9896	9.768
2	8.263	1039614	83270	90.232
Total		1152159	93166	100.000

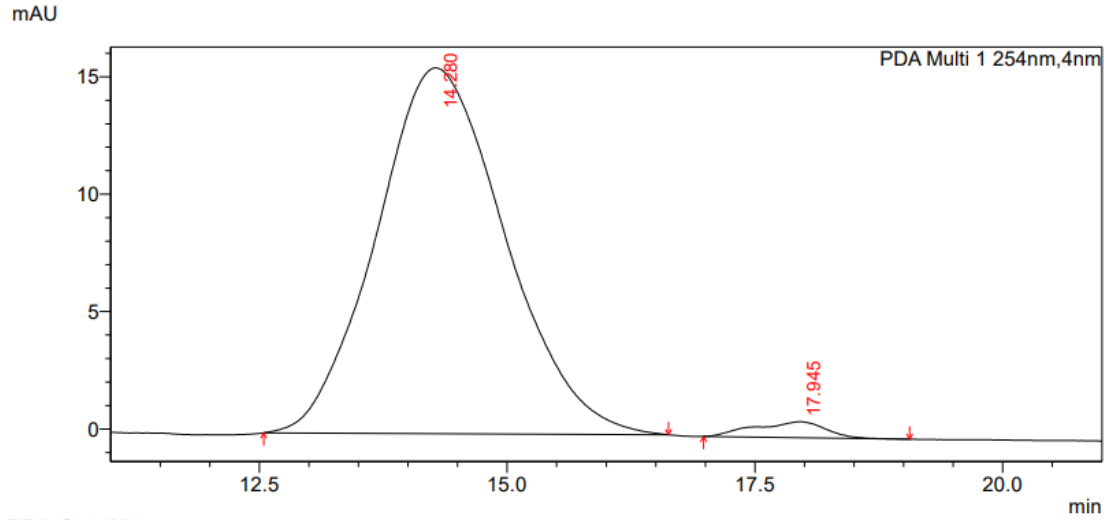
(*S*)-2-Fluorobenzenesulfonamide(4p):

HPLC conditions: Chiralcel OJ-H (*i*-PrOH/*n*-Hexane, 10:90), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

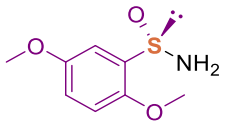
Peak#	Ret. Time	Area	Height	Area%
1	14.875	20102077	652522	49.976
2	17.475	20121058	564631	50.024
Total		40223136	1217152	100.000



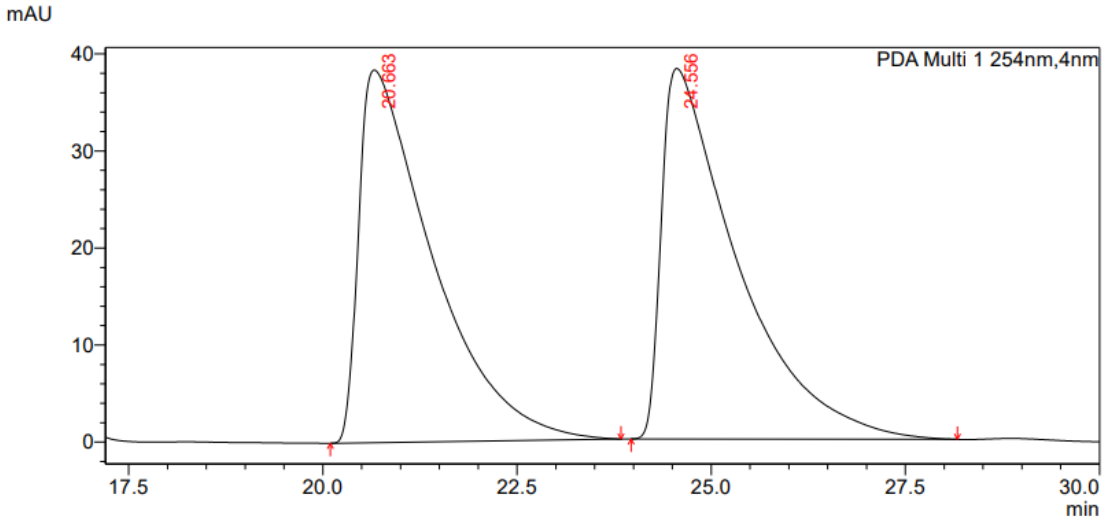
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	14.280	1404473	15577	97.623
2	17.945	34190	684	2.377
Total		1438663	16262	100.000

(*S*)-2,5-Dimethoxybenzenesulfonamide (4q):

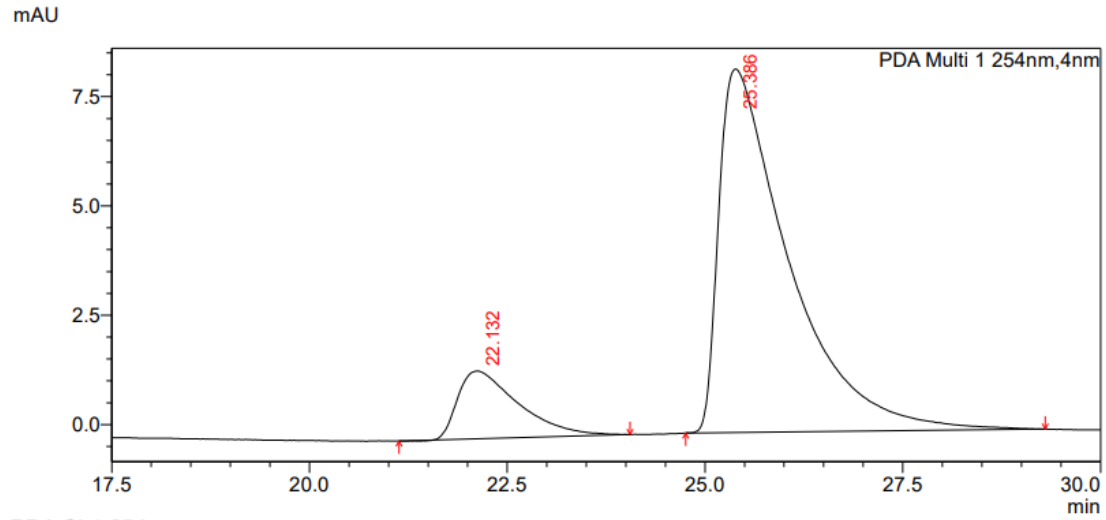


HPLC conditions: Chiralcel IB (*i*-PrOH/*n*-Hexane, 10:90), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

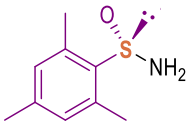
Peak#	Ret. Time	Area	Height	Area%
1	20.663	2533099	38379	49.394
2	24.556	2595281	38179	50.606
Total		5128380	76558	100.000



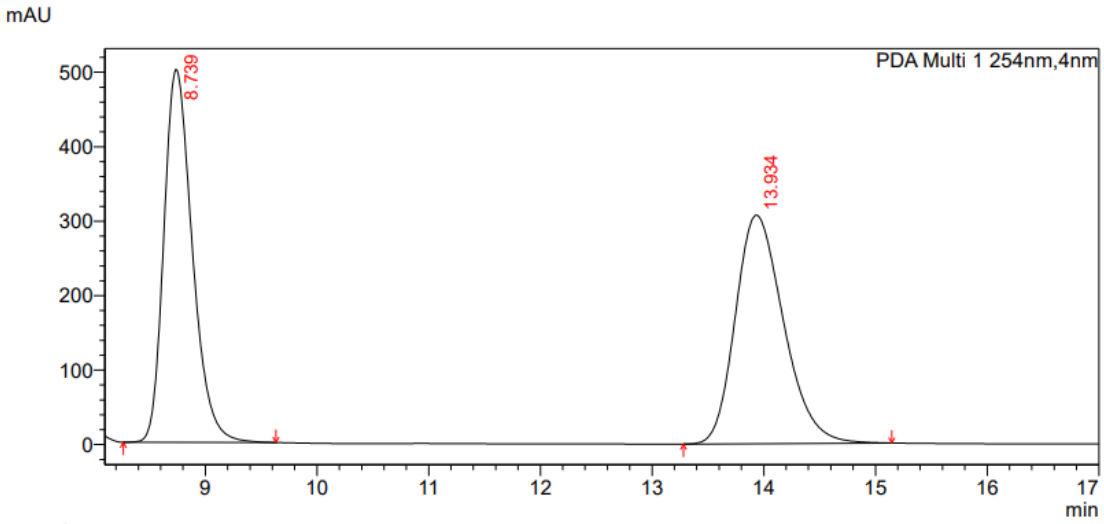
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	22.132	82172	1550	13.819
2	25.386	512451	8311	86.181
Total		594623	9862	100.000

(*S*)-2,4,6-Trimethylbenzenesulfinamide (4r):

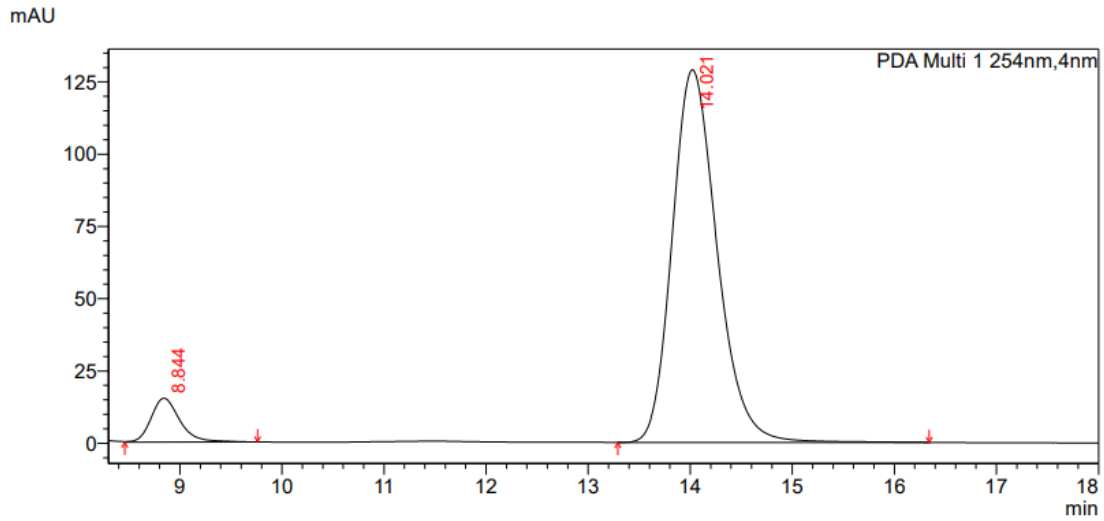


HPLC conditions: Chiralcel OJ-H (*i*-PrOH/*n*-Hexane, 30:70), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

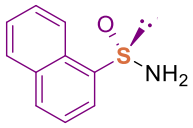
Peak#	Ret. Time	Area	Height	Area%
1	8.739	8897462	500780	49.104
2	13.934	9222000	306870	50.896
Total		18119462	807650	100.000



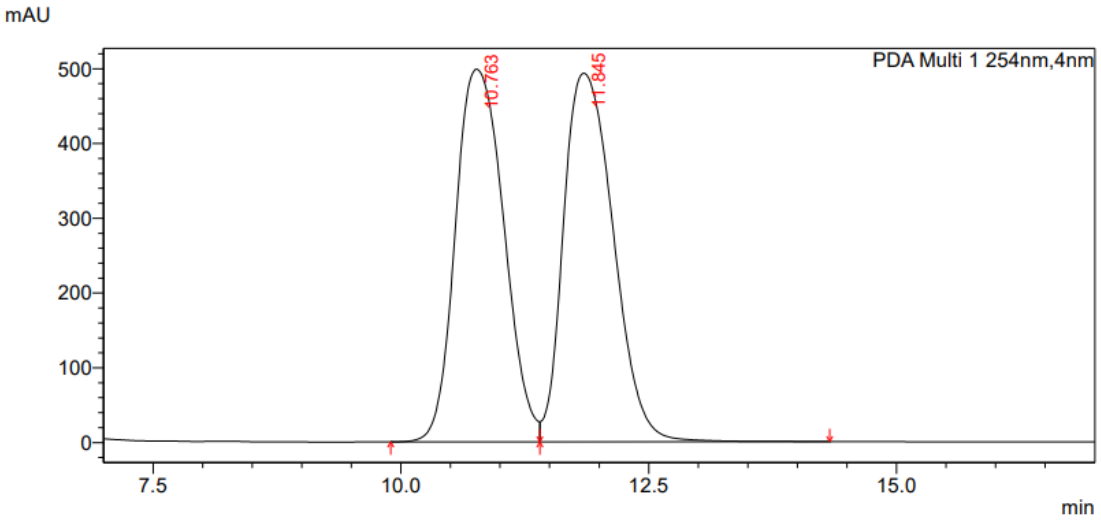
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.844	297047	15198	7.014
2	14.021	3938098	128900	92.986
Total		4235145	144098	100.000

(*S*)-Naphthalene-2-sulfinamide(4s):

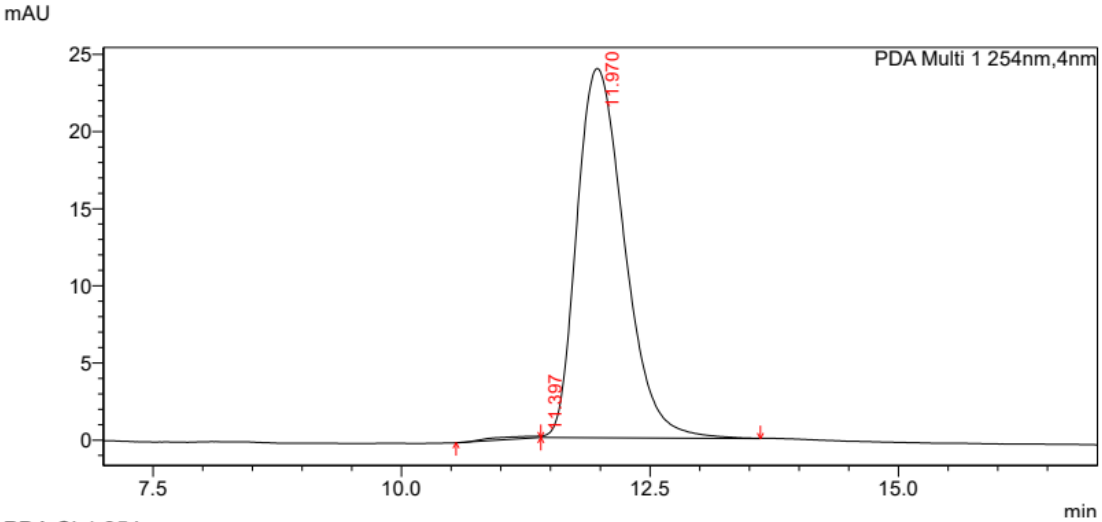


HPLC conditions: Chiralcel IB (*i*-PrOH/*n*-Hexane, 10:90), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

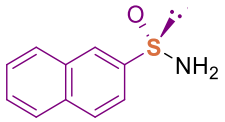
Peak#	Ret. Time	Area	Height	Area%
1	10.763	16940831	498490	49.553
2	11.845	17246618	493110	50.447
Total		34187449	991600	100.000



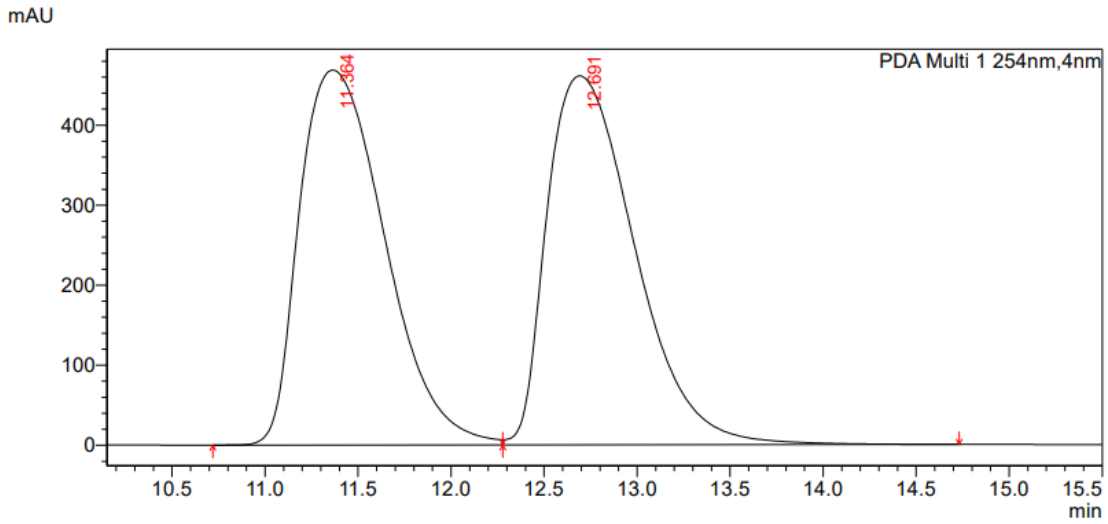
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	11.397	5619	99	0.699
2	11.970	798754	23940	99.301
Total		804373	24039	100.000

(*S*)-Naphthalene-2-sulfinamide(4t):

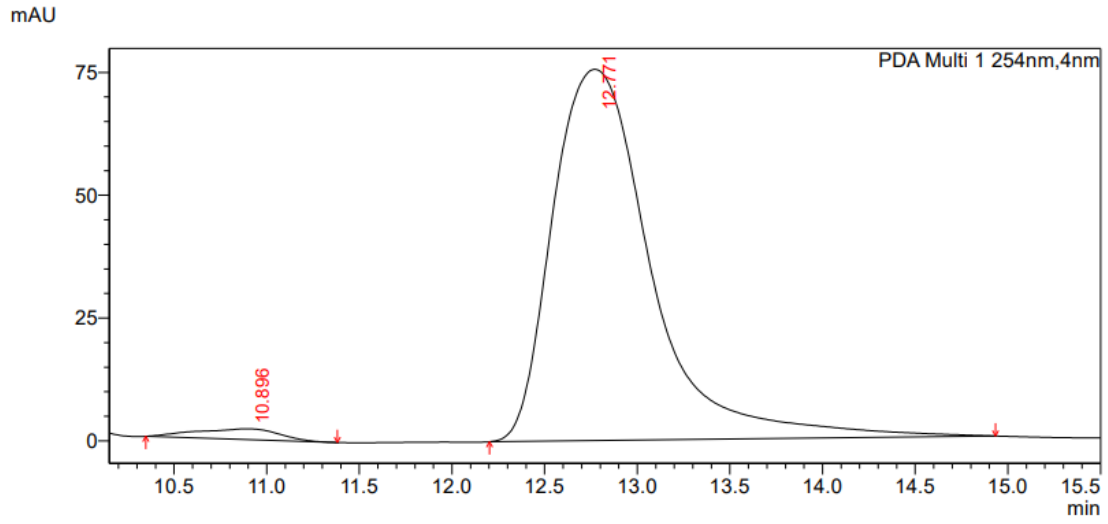


HPLC conditions: Chiralcel IB (*i*-PrOH/*n*-Hexane, 10:90), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

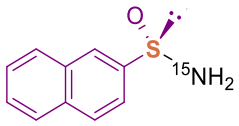
Peak#	Ret. Time	Area	Height	Area%
1	11.364	14975772	468412	49.682
2	12.691	15167673	460994	50.318
Total		30143446	929406	100.000



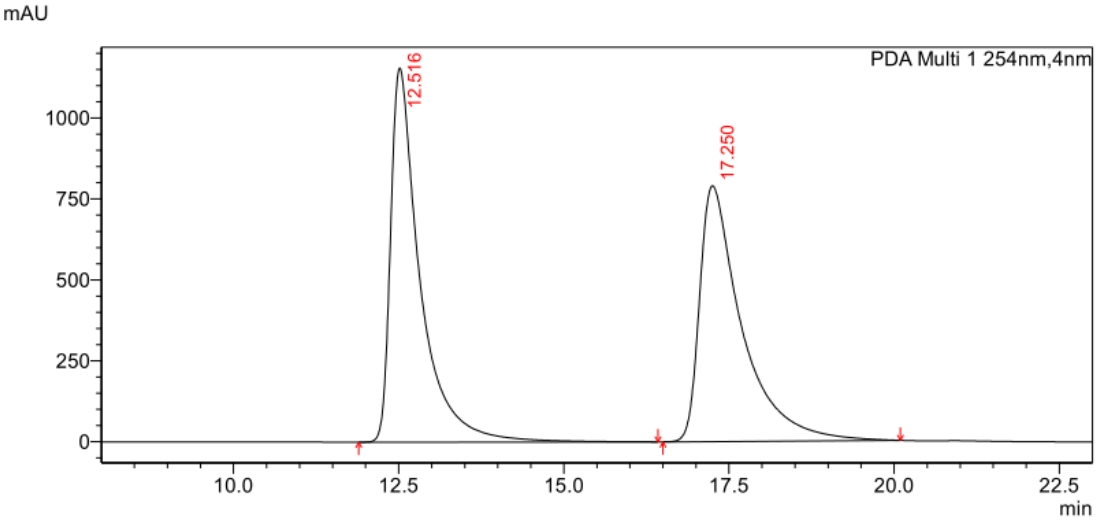
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	10.896	66687	2210	2.321
2	12.771	2806312	75561	97.679
Total		2872999	77771	100.000

^{15}N-4t

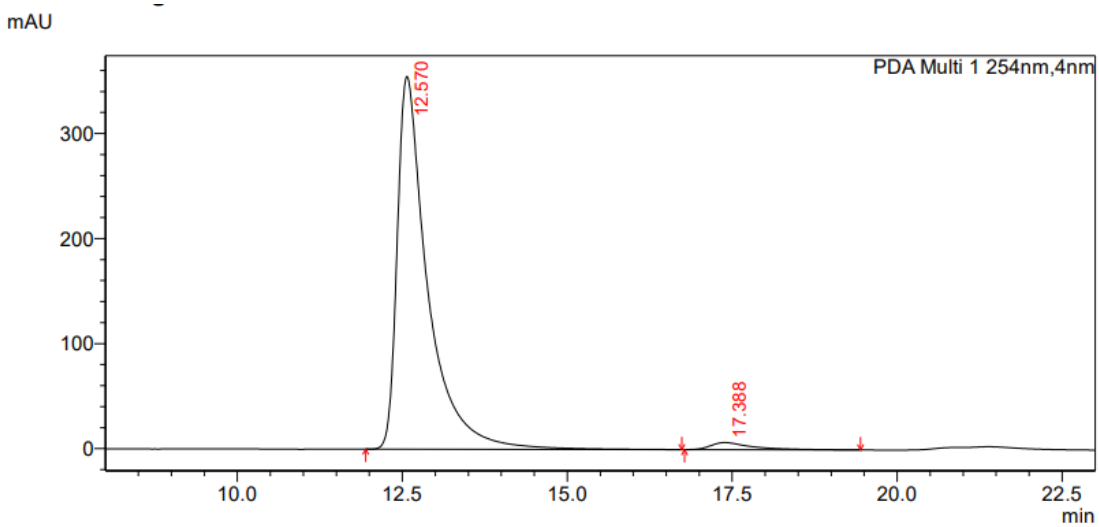


HPLC conditions: Chiralcel IA (*i*-PrOH/*n*-Hexane, 10:90), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

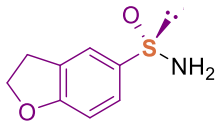
Peak#	Ret. Time	Area	Height	Area%
1	12.516	35981733	1155115	50.636
2	17.250	35077720	790021	49.364
Total		71059453	1945137	100.000



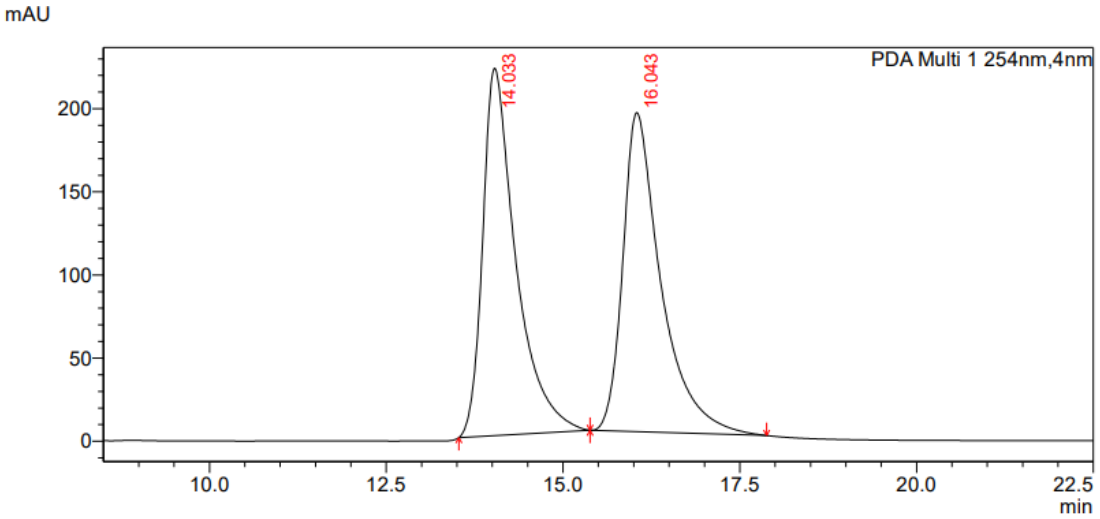
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	12.570	11414806	354696	97.483
2	17.388	294699	6764	2.517
Total		11709505	361460	100.000

(*S*)-2,3-Dihydrobenzofuran-5-sulfonamide (4u):

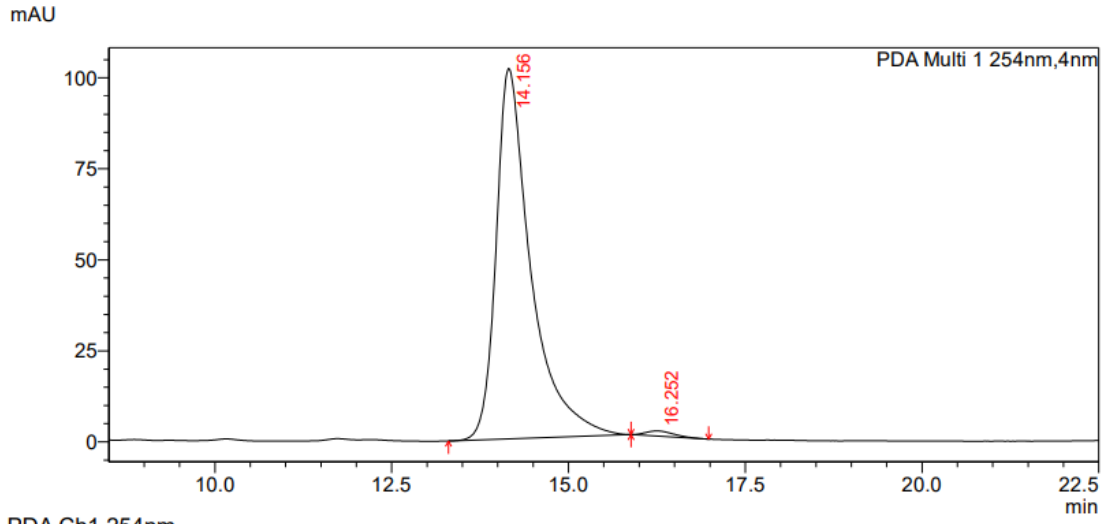


HPLC conditions: Chiralcel IA (*i*-PrOH/*n*-Hexane, 10:90), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

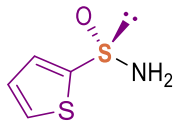
Peak#	Ret. Time	Area	Height	Area%
1	14.033	7215399	220920	50.019
2	16.043	7209878	191890	49.981
Total		14425278	412809	100.000



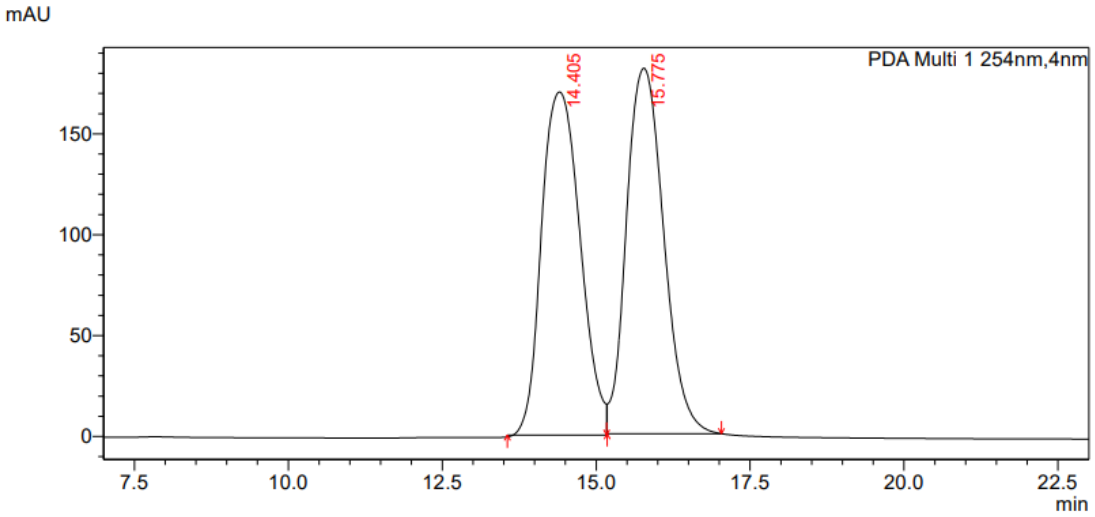
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	14.156	3486754	101712	98.880
2	16.252	39500	1432	1.120
Total		3526254	103145	100.000

(*S*)-2-Thienesulfonamide (4v):

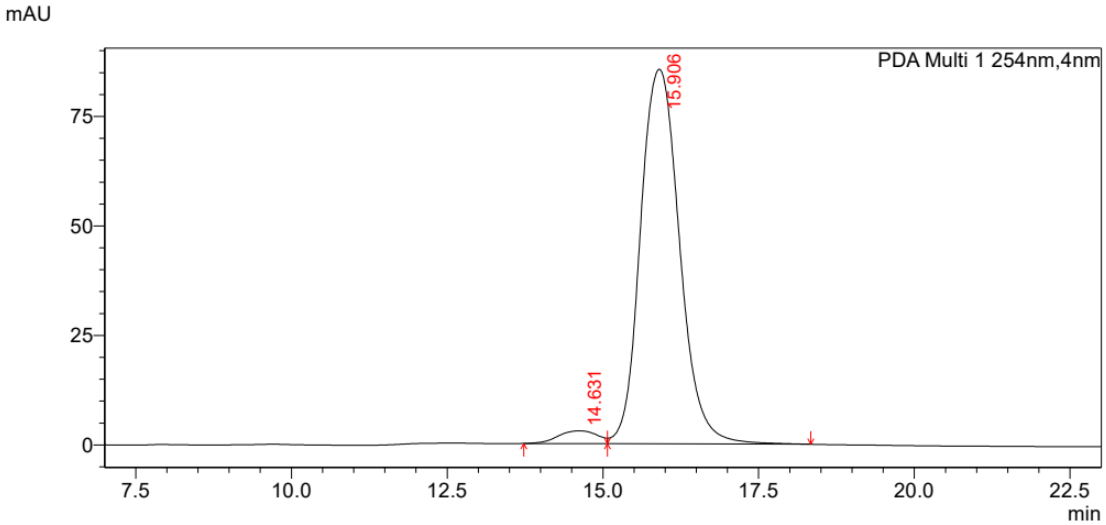


HPLC conditions: Chiralcel IB (*i*-PrOH/*n*-Hexane, 10:90), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

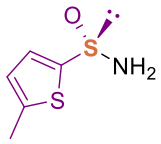
Peak#	Ret. Time	Area	Height	Area%
1	14.405	7435829	170106	49.354
2	15.775	7630412	181208	50.646
Total		15066241	351313	100.000



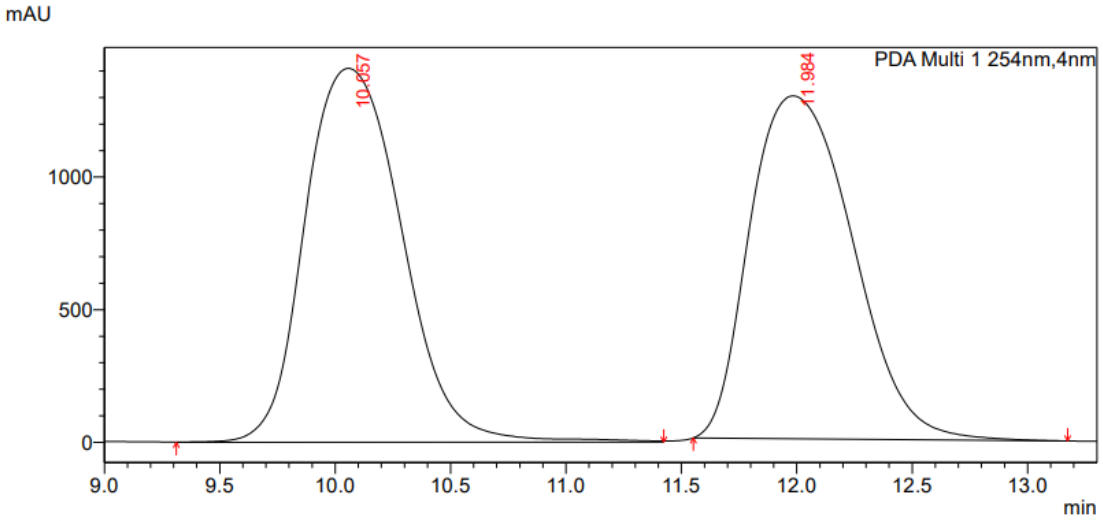
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	14.631	129840	2923	3.353
2	15.906	3743076	85499	96.647
Total		3872915	88422	100.000

(*S*)-5-Methylthiophene sulfonamide (4w):

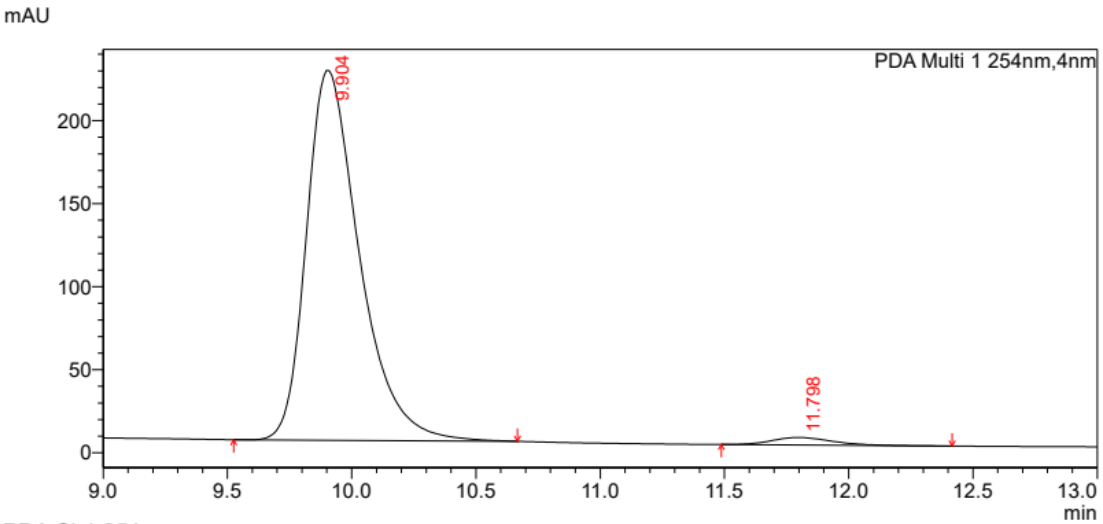


HPLC conditions: Chiralcel IA (*i*-PrOH/*n*-Hexane, 10:90), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

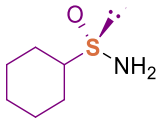
Peak#	Ret. Time	Area	Height	Area%
1	10.057	41374782	1409425	50.755
2	11.984	40143268	1292476	49.245
Total		81518050	2701901	100.000



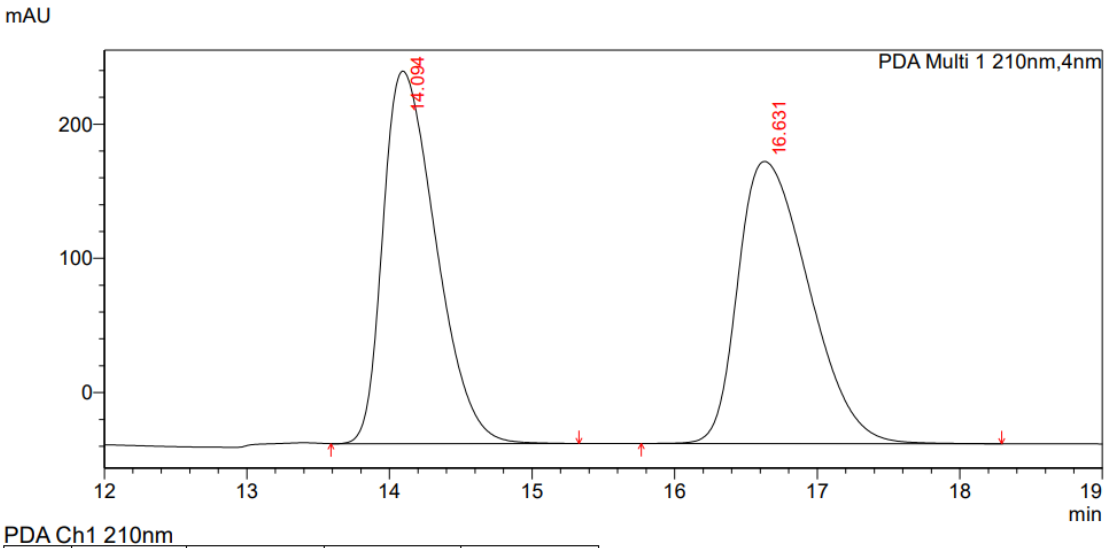
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	9.904	3311790	222678	97.703
2	11.798	77857	4577	2.297
Total		3389648	227254	100.000

(*S*)-Cyclohexylsulfonamide (4x):

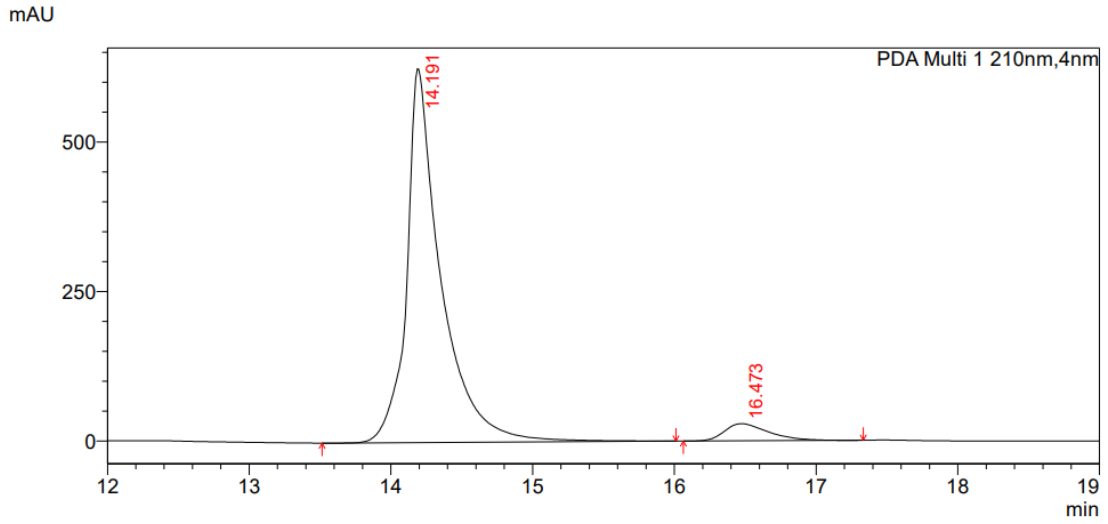


HPLC conditions: Chiralcel IA (*i*-PrOH/*n*-Hexane, 5:95), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 210nm

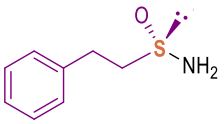
Peak#	Ret. Time	Area	Height	Area%
1	14.094	7170031	277608	49.664
2	16.631	7267116	210333	50.336
Total		14437147	487940	100.000



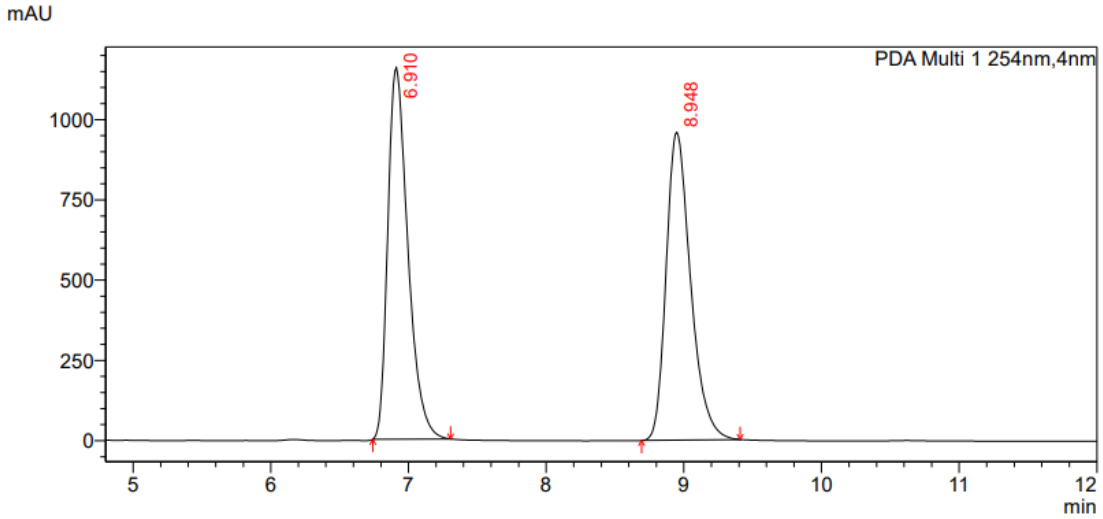
PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	14.191	10493212	624792	94.442
2	16.473	617533	28603	5.558
Total		11110744	653396	100.000

(*S*)-2-Phenyl-ethanesulfonamide (4y):

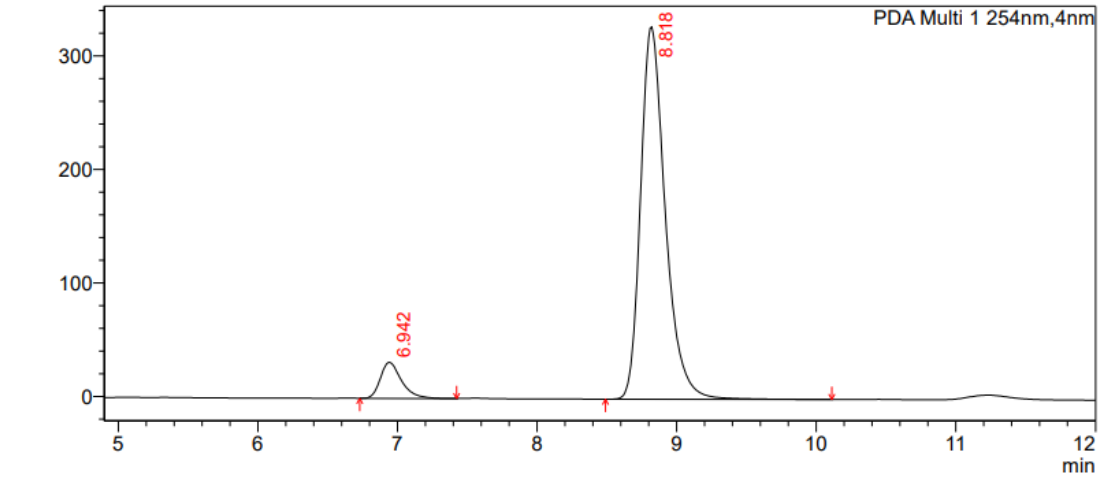


HPLC conditions: Chiralcel IB (*i*-PrOH/*n*-Hexane, 20:80), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

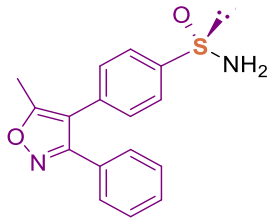
Peak#	Ret. Time	Area	Height	Area%
1	6.910	11744455	1156654	49.804
2	8.948	11837022	959246	50.196
Total		23581477	2115899	100.000



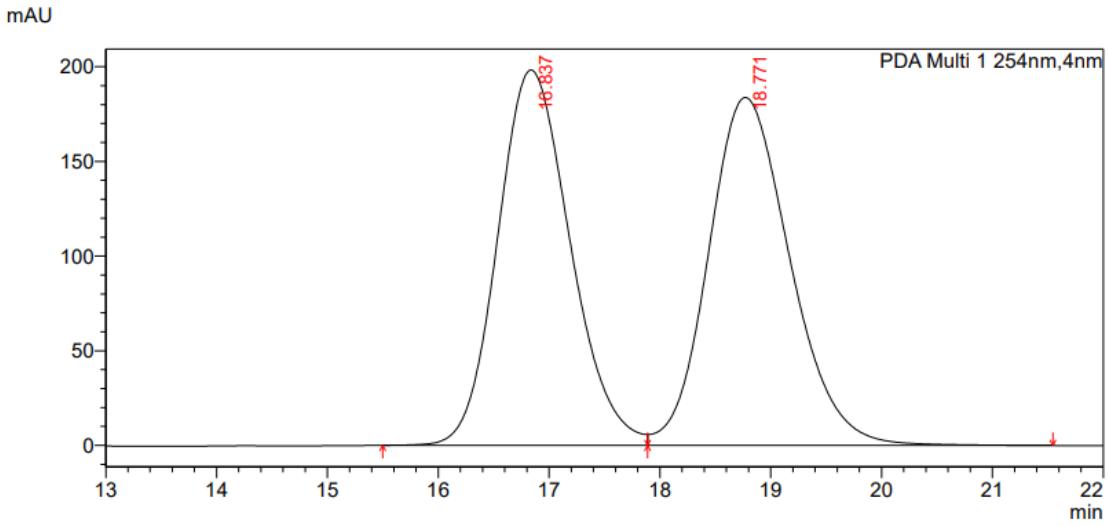
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	6.942	335390	31803	7.668
2	8.818	4038663	327986	92.332
Total		4374053	359789	100.000

(*S*)-4-(5-Methyl-3-phenylisoxazol-4-yl) benzenesulfinamide (5a):

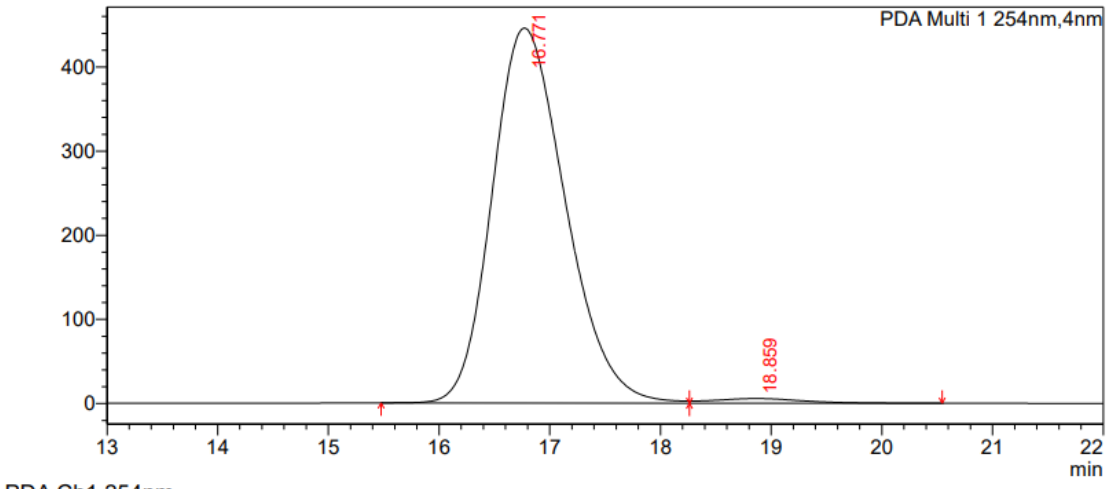


HPLC conditions: Chiralcel IA (*i*-PrOH/*n*-Hexane, 10:90), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

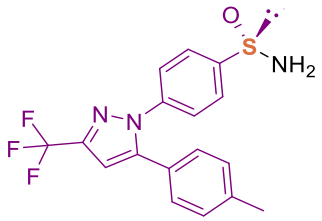
Peak#	Ret. Time	Area	Height	Area%
1	16.837	9021238	198232	48.984
2	18.771	9395613	183769	51.016
Total		18416850	382001	100.000



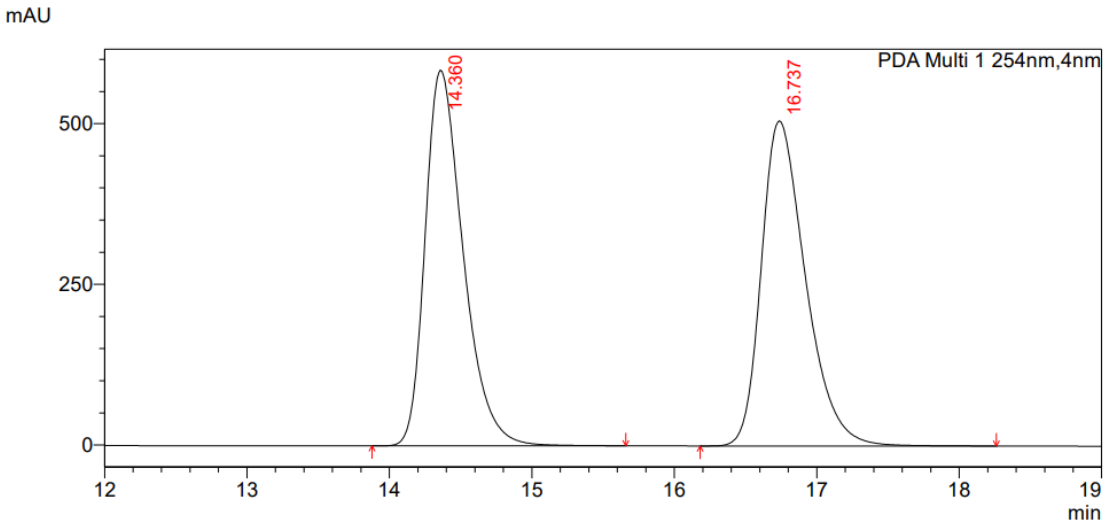
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	16.771	20490928	445556	98.567
2	18.859	297881	5402	1.433
Total		20788810	450958	100.000

(*S*)- 4-(5-(p-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)benzenesulfinamide (5b):

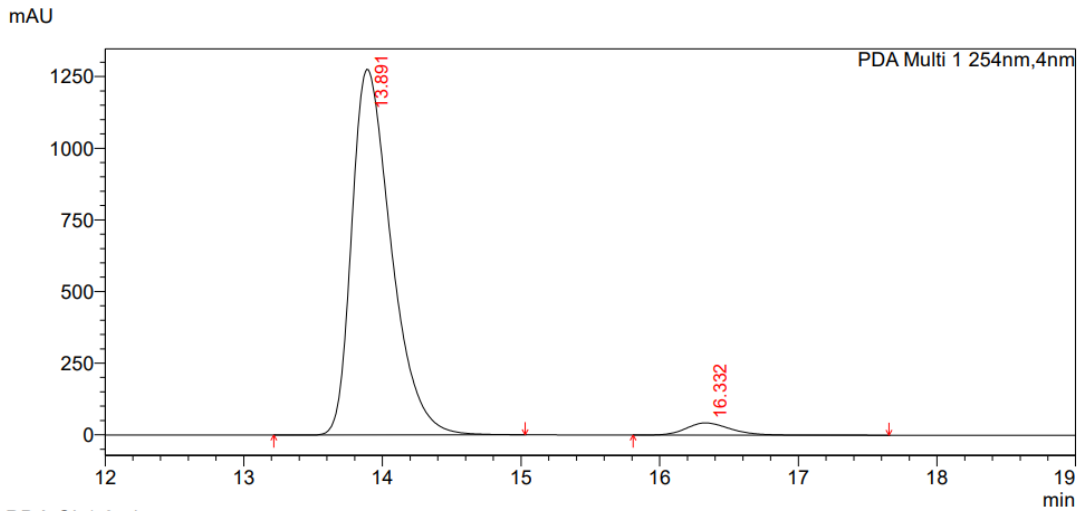


HPLC conditions: Chiralcel IA (*i*-PrOH/*n*-Hexane, 10:90), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

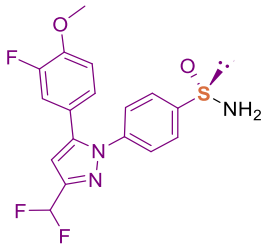
Peak#	Ret. Time	Area	Height	Area%
1	14.360	10858888	584499	49.862
2	16.737	10918958	505790	50.138
Total		21777846	1090288	100.000



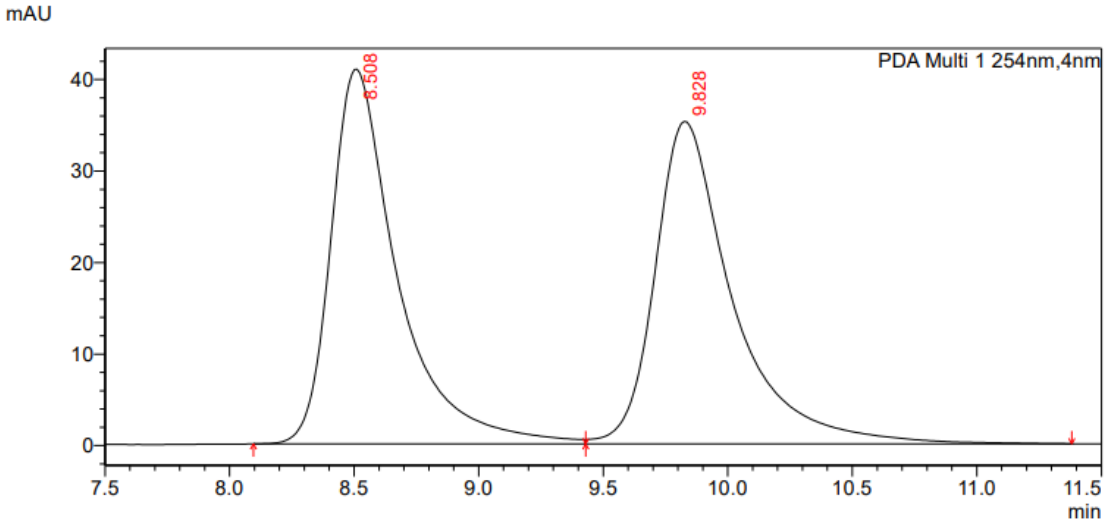
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	13.891	25263400	1276073	96.330
2	16.332	962527	42866	3.670
Total		26225927	1318939	100.000

(*S*)-(4-(3-(Difluoromethyl)-5-(3-fluoro-4-methoxyphenyl)-1*H*-pyrazol-1-yl) phenyl) (methylidyne) (λ^1-oxidaneyl)- λ^6-sulfanamine (5c):

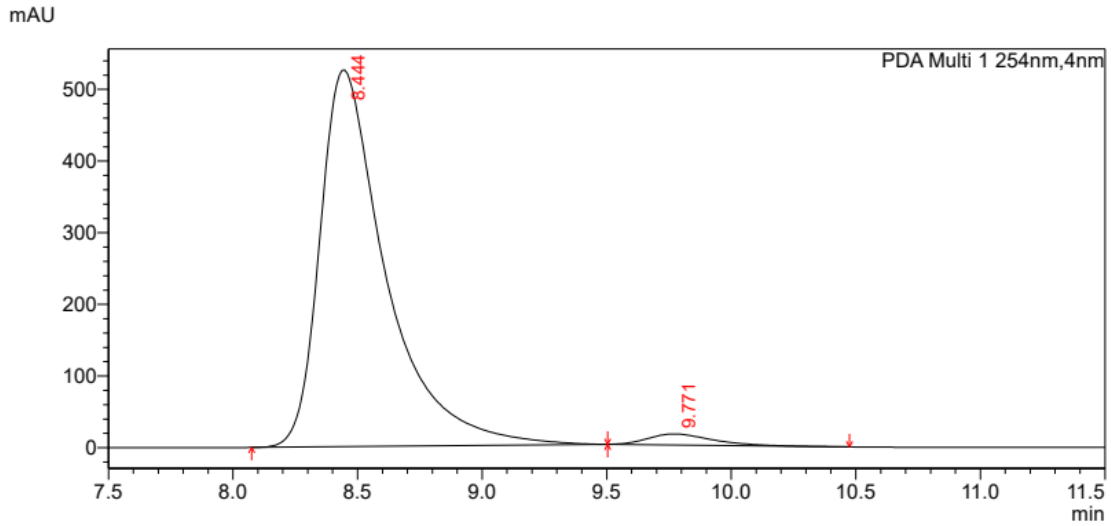


HPLC conditions: Chiralcel IA (*i*-PrOH/*n*-Hexane, 15:85), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

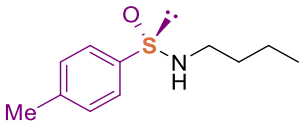
Peak#	Ret. Time	Area	Height	Area%
1	8.508	761223	40922	49.889
2	9.828	764614	35221	50.111
Total		1525837	76142	100.000



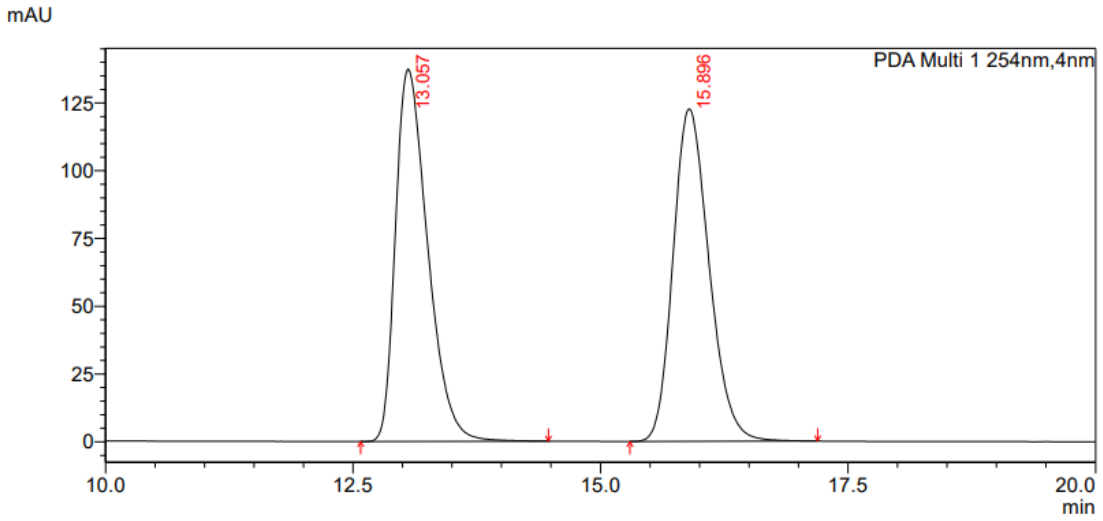
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.444	9704878	525650	97.219
2	9.771	277615	15422	2.781
Total		9982493	541072	100.000

(*S*)-*N*-Butyl-4-methyl Benzenesulfinamide (6):

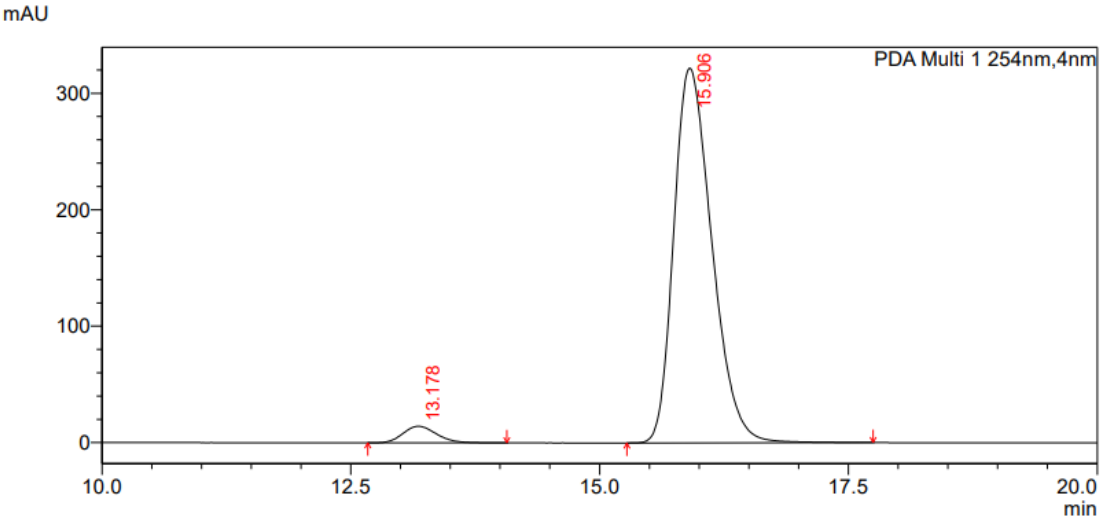


HPLC conditions: Chiralcel OD-H (*i*-PrOH/*n*-Hexane, 5:95), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

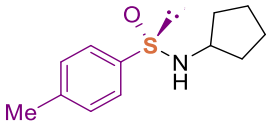
Peak#	Ret. Time	Area	Height	Area%
1	13.057	3103432	137343	49.998
2	15.896	3103695	122667	50.002
Total		6207127	260010	100.000



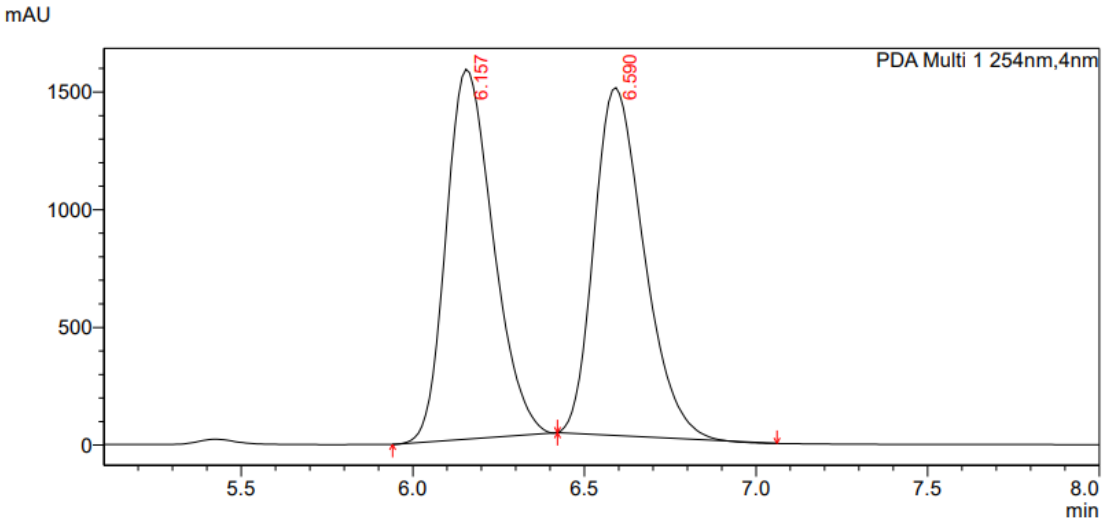
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	13.178	332785	14241	3.740
2	15.906	8566331	321768	96.260
Total		8899116	336009	100.000

(*S*)-*N*-Cyclopentyl-4-methylbenzenylsulfinamide (7):

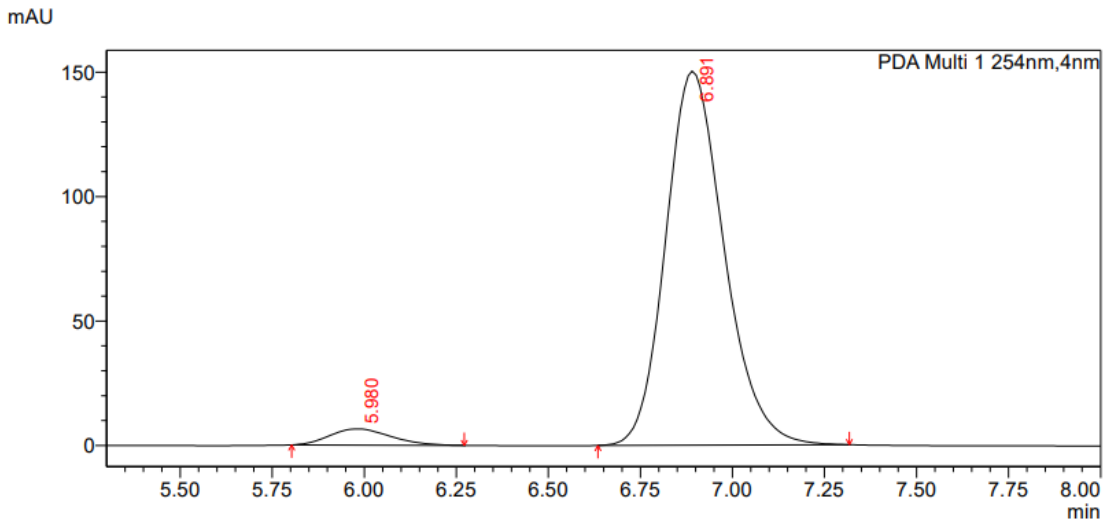


HPLC conditions: Chiralcel OD-H (*i*-PrOH/*n*-Hexane, 10:90), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

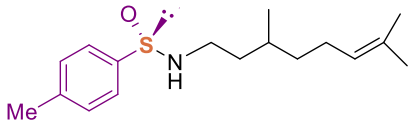
Peak#	Ret. Time	Area	Height	Area%
1	6.157	14985075	1571162	50.020
2	6.590	14973341	1478315	49.980
Total		29958416	3049477	100.000



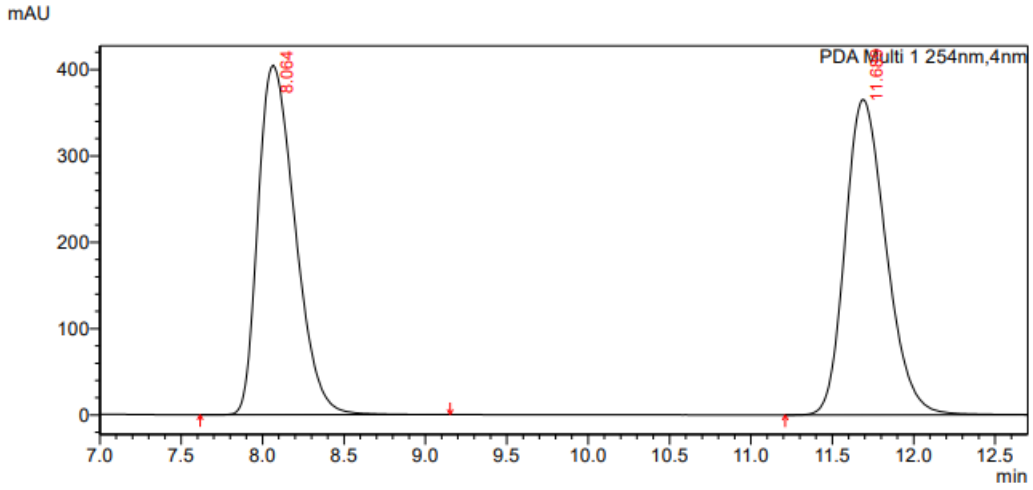
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	5.980	74222	6491	4.280
2	6.891	1660110	150240	95.720
Total		1734333	156731	100.000

(*S*)-*N*-(3,7-Dimethyloct-6-en-1-yl)-4-methylbenzenesulfinamide (8):

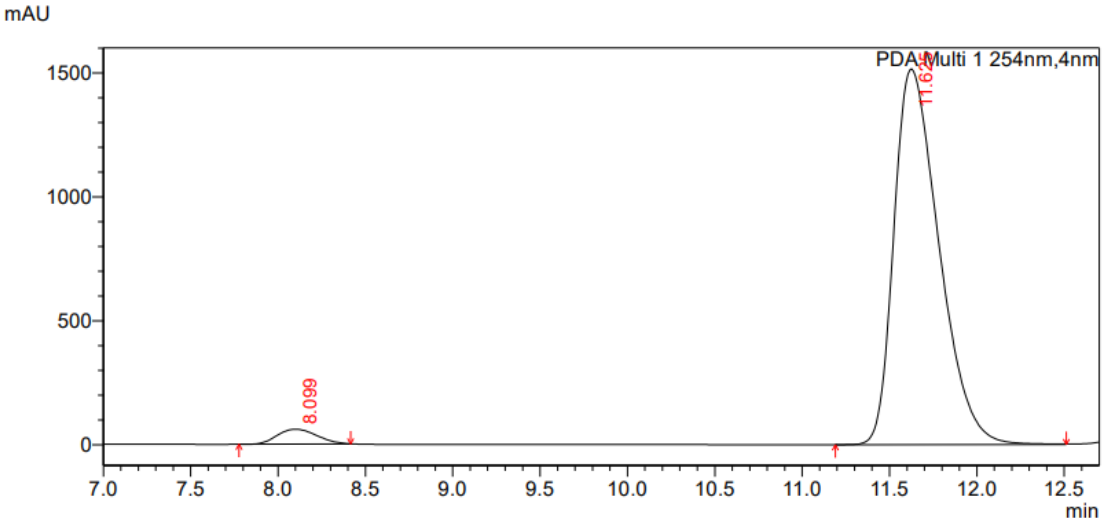


HPLC conditions: Chiralcel OD-H (*i*-PrOH/*n*-Hexane, 10:90), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

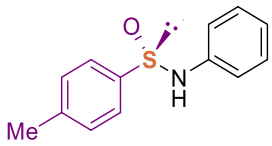
Peak#	Ret. Time	Area	Height	Area%
1	8.064	6399124	404590	50.008
2	11.689	6397045	365399	49.992
Total		12796169	769989	100.000



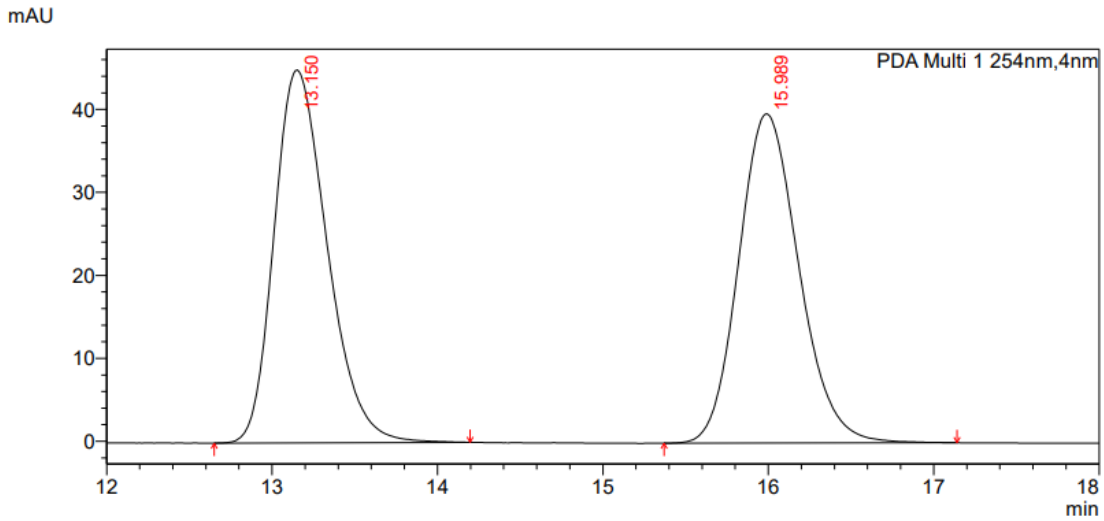
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.099	943228	59990	3.358
2	11.625	27142309	1515818	96.642
Total		28085537	1575808	100.000

(*S*)-4-Methyl-*N*-phenylbenzenesulfinamide (9):

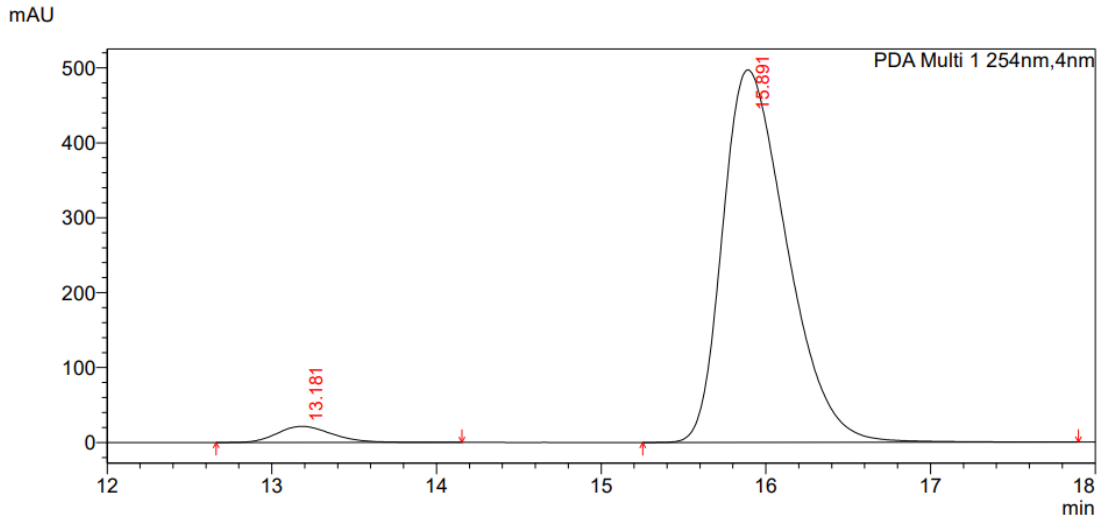


HPLC conditions: Chiralcel ID (*i*-PrOH/*n*-Hexane, 20:80), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

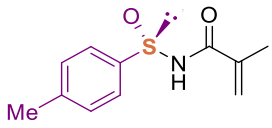
Peak#	Ret. Time	Area	Height	Area%
1	13.150	1003694	44934	49.954
2	15.989	1005543	39689	50.046
Total		2009237	84623	100.000



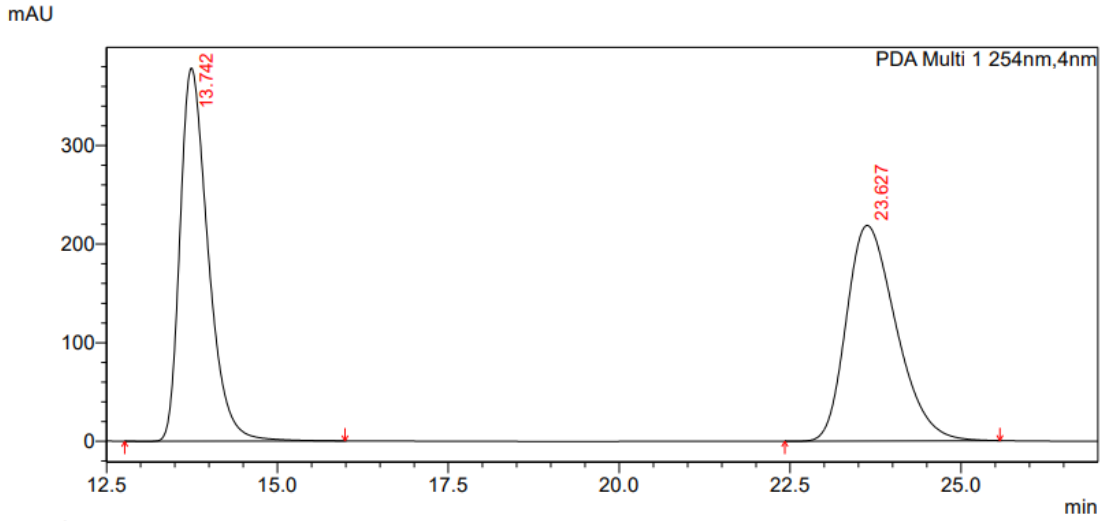
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	13.181	498027	21485	3.564
2	15.891	13474713	497311	96.436
Total		13972740	518796	100.000

(*S*)-*N*-(*p*-Tolylsulfinyl) methacrylamide (10):

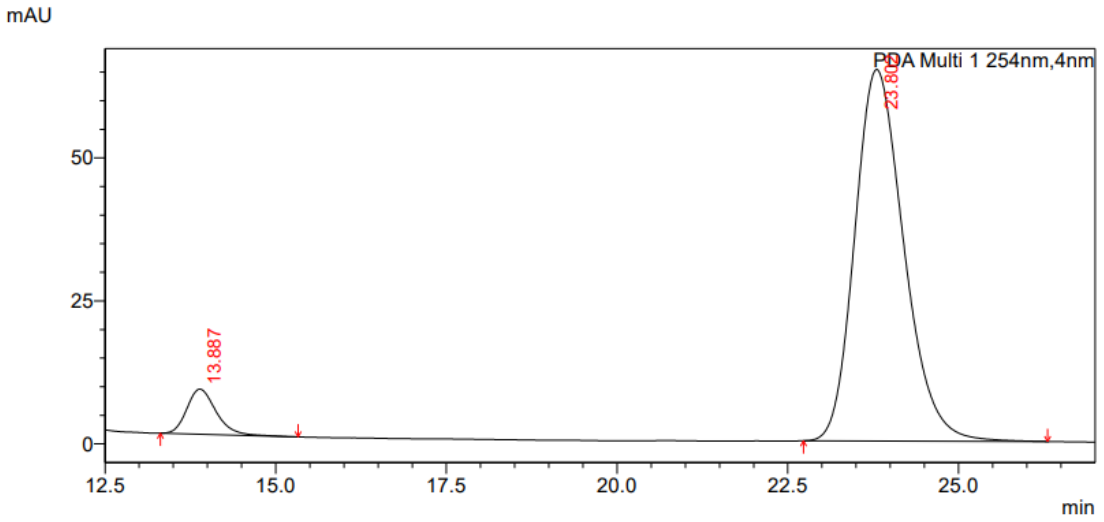


HPLC conditions: Chiralcel ID (*i*-PrOH/*n*-Hexane, 10:90), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

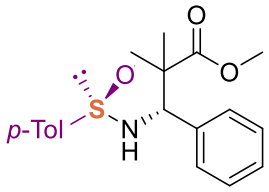
Peak#	Ret. Time	Area	Height	Area%
1	13.742	10808910	378313	49.411
2	23.627	11066739	218730	50.589
Total		21875649	597043	100.000



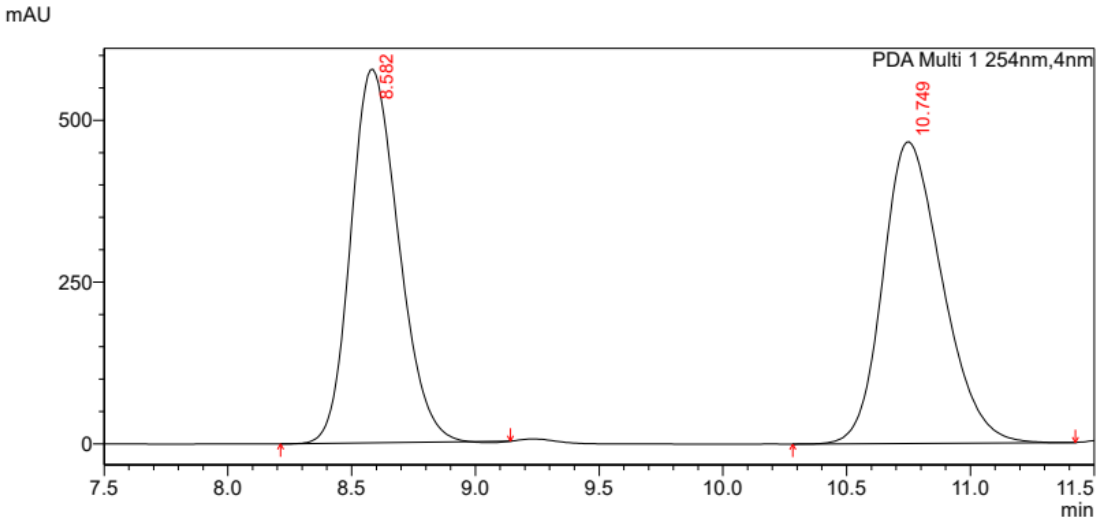
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	13.887	236850	7884	6.791
2	23.802	3250799	64957	93.209
Total		3487649	72842	100.000

(*R*)-*N*-[(*S*)-2,2-Dimethyl-1-phenylpropionate methyl ester]-4-methylbenzene-sulfinamide (11):

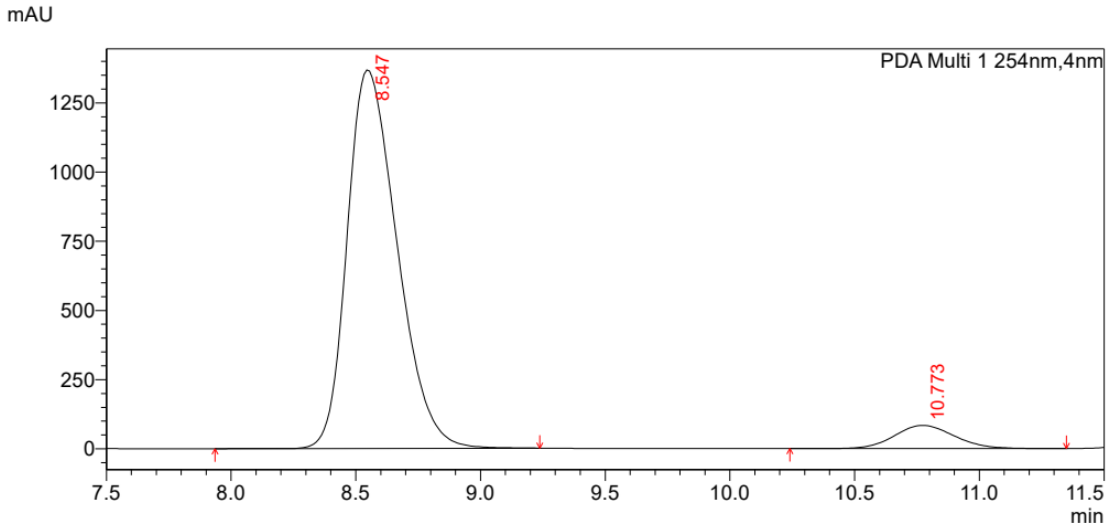


HPLC conditions: Chiralcel IA (*i*-PrOH/*n*-Hexane, 10:90), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

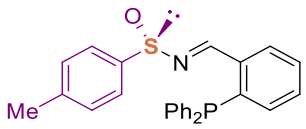
Peak#	Ret. Time	Area	Height	Area%
1	8.582	7752411	577281	49.815
2	10.749	7810144	466231	50.185
Total		15562556	1043512	100.000



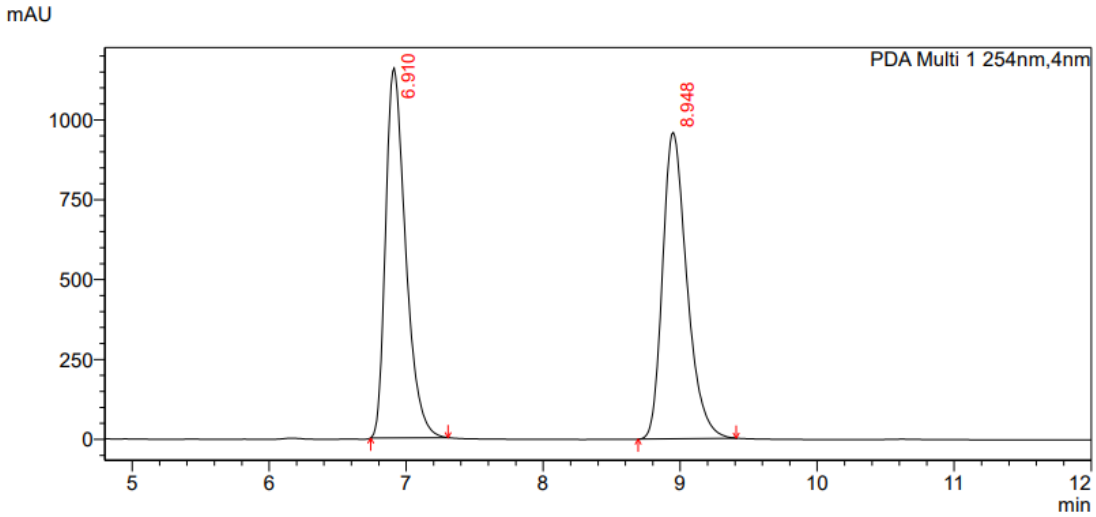
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.547	19024778	1367501	93.163
2	10.773	1396246	83645	6.837
Total		20421025	1451146	100.000

(*S*)-*N*-(2-(Diphenylphosphaneyl) benzyl)-4-methylbenzenesulfinamide (12):

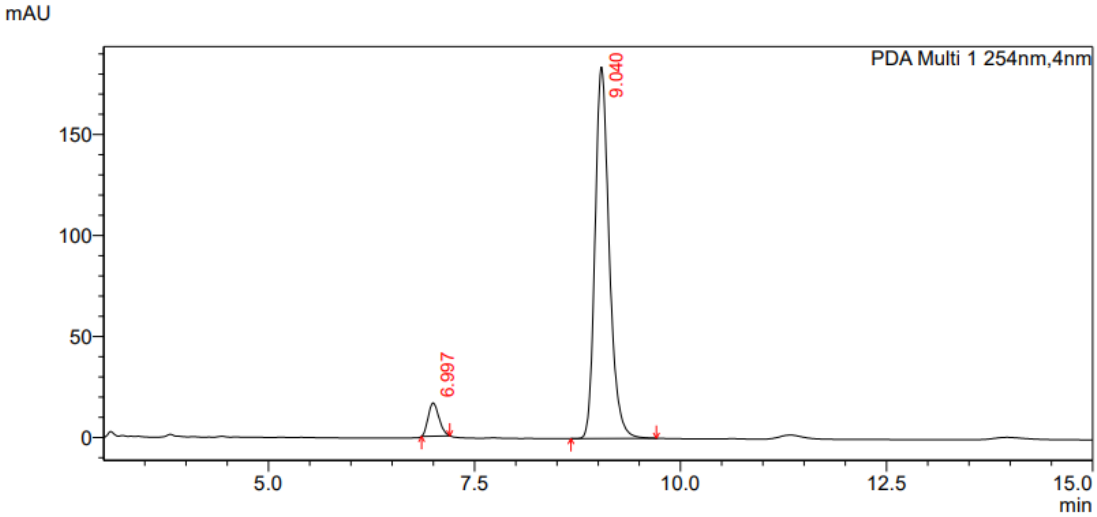


HPLC conditions: Chiralcel IA (*i*-PrOH/*n*-Hexane, 10:90), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

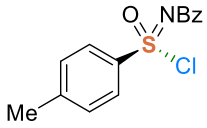
Peak#	Ret. Time	Area	Height	Area%
1	6.910	11744455	1156654	49.804
2	8.948	11837022	959246	50.196
Total		23581477	2115899	100.000



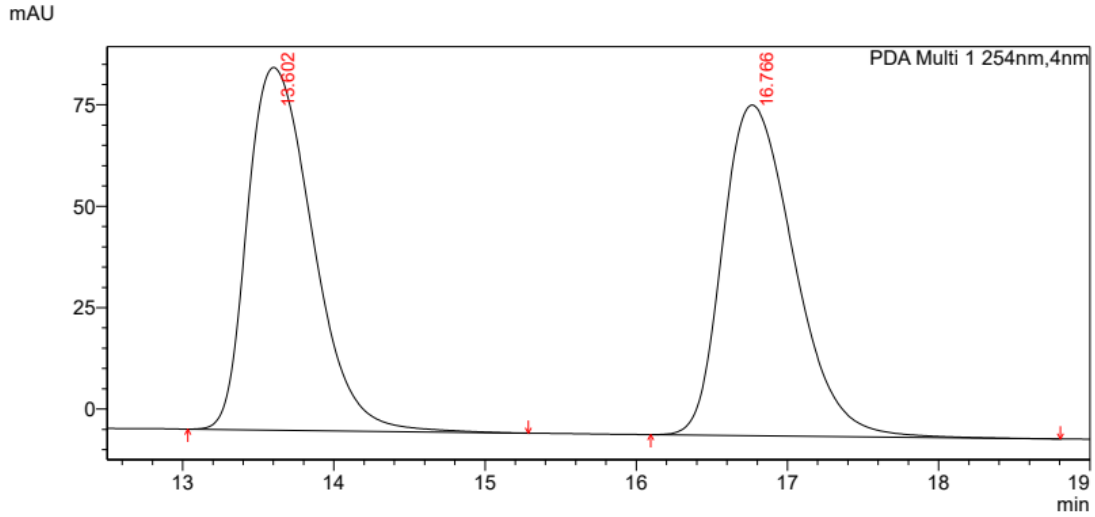
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	6.997	149551	16415	6.342
2	9.040	2208396	183789	93.658
Total		2357948	200204	100.000

(*S*)-*N*-Benzoyl-1-methyl-(*p*-tolyl)-oxidanesulfinimidic chloride (14):

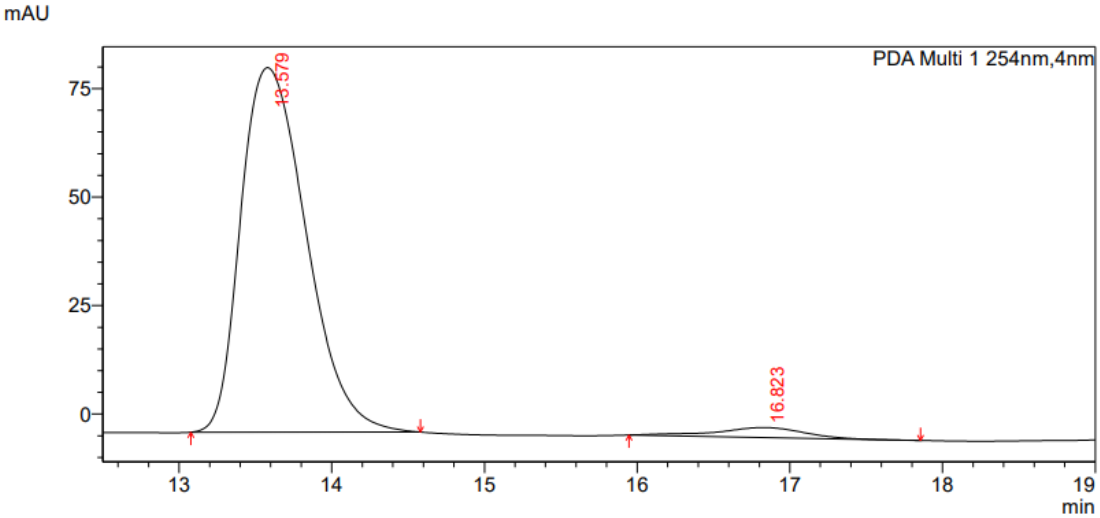


HPLC conditions: Chiralcel IA (*i*-PrOH/*n*-Hexane, 10:90), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

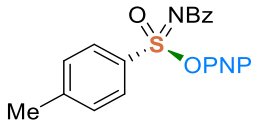
Peak#	Ret. Time	Area	Height	Area%
1	13.602	2678676	89394	50.006
2	16.766	2678030	81492	49.994
Total		5356707	170886	100.000



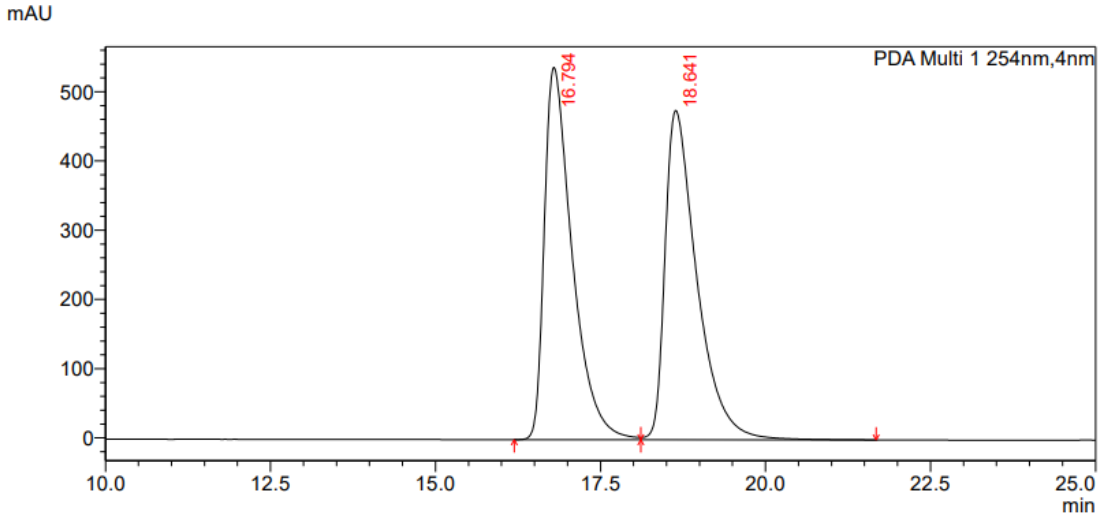
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	13.579	2504412	83999	96.464
2	16.823	91800	2295	3.536
Total		2596213	86293	100.000

(*S*)-4-Nitrophenyl *N*-benzoyl-4-methylbenzenesulfonimidate (15):

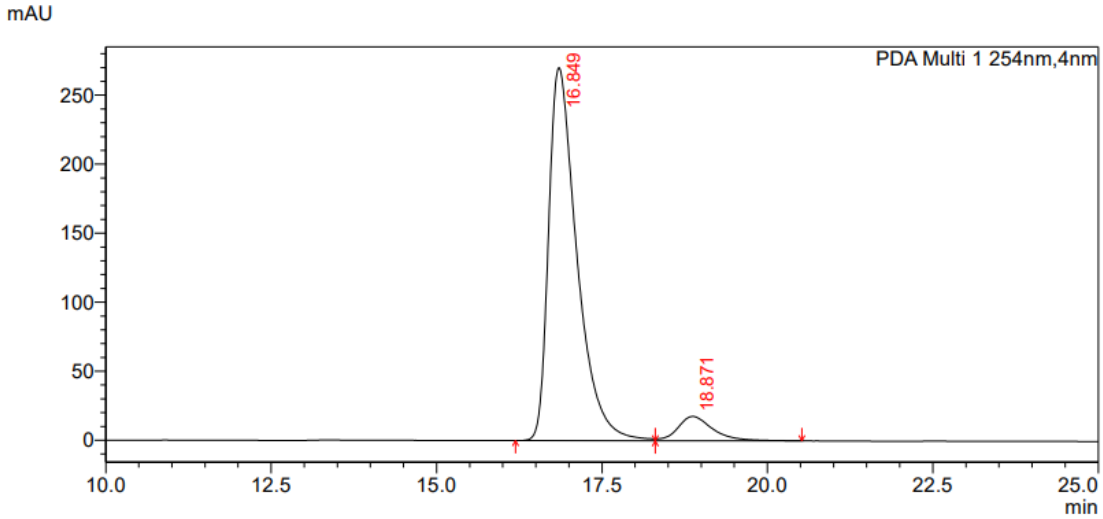


HPLC conditions: Chiralcel IB (*i*-PrOH/*n*-Hexane, 10:90), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

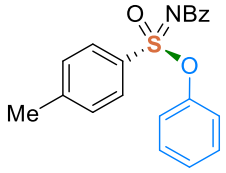
Peak#	Ret. Time	Area	Height	Area%
1	16.794	15804655	537488	49.751
2	18.641	15963047	475345	50.249
Total		31767702	1012833	100.000



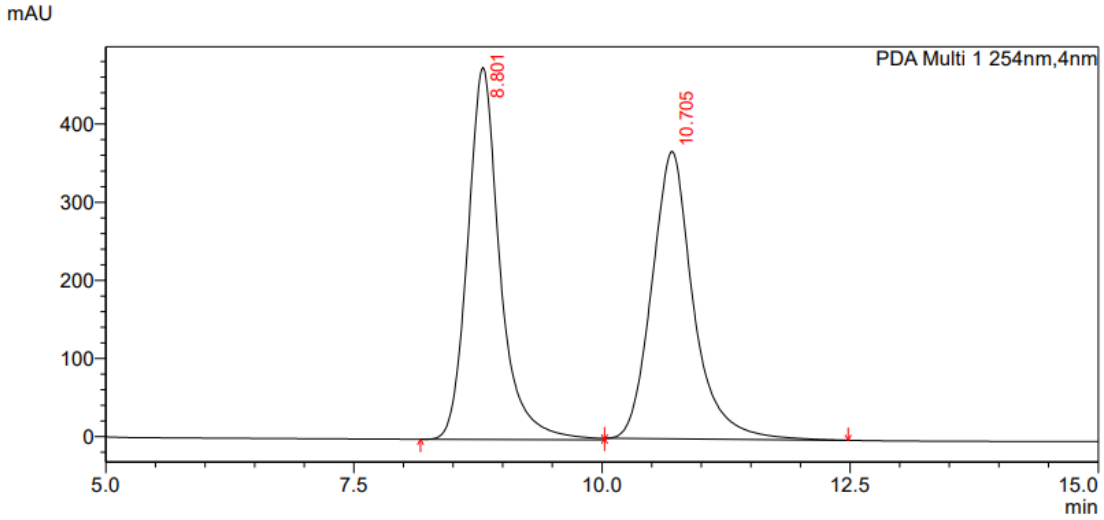
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	16.849	8060722	270158	92.590
2	18.871	645086	17619	7.410
Total		8705808	287778	100.000

(*S*)-Phenyl *N*-benzoyl-4-methylbenzenesulfonimidate (16):

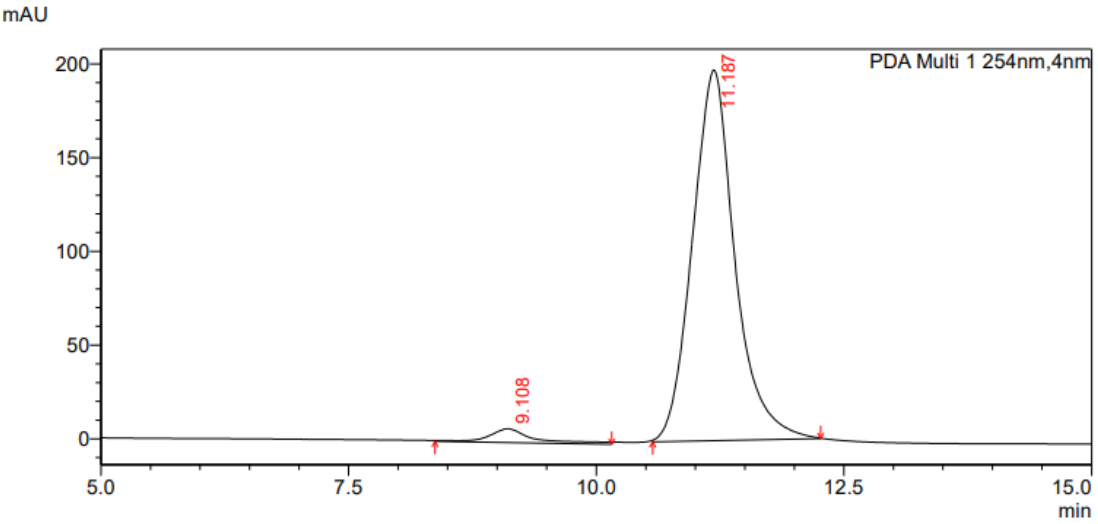


HPLC conditions: Chiralcel IA (*i*-PrOH/*n*-Hexane, 20:80), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

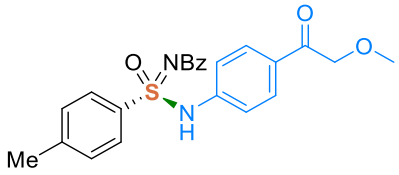
Peak#	Ret. Time	Area	Height	Area%
1	8.801	10786193	476111	50.212
2	10.705	10694950	368201	49.788
Total		21481143	844313	100.000



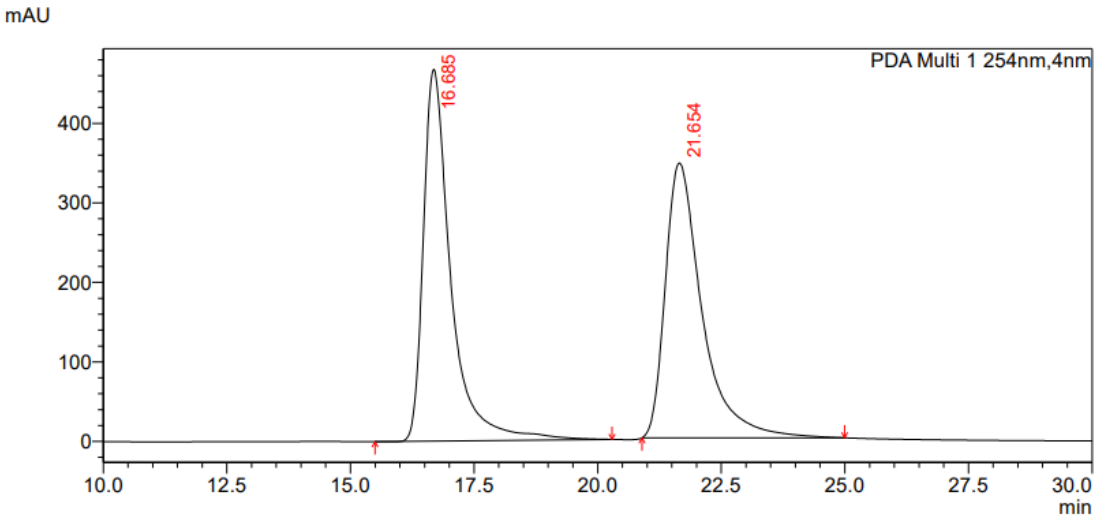
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	9.108	235629	7349	3.837
2	11.187	5904836	197668	96.163
Total		6140466	205017	100.000

(*S*)-4-Nitrophenyl *N*-benzoyl-4-methylbenzenesulfonimidate (17):

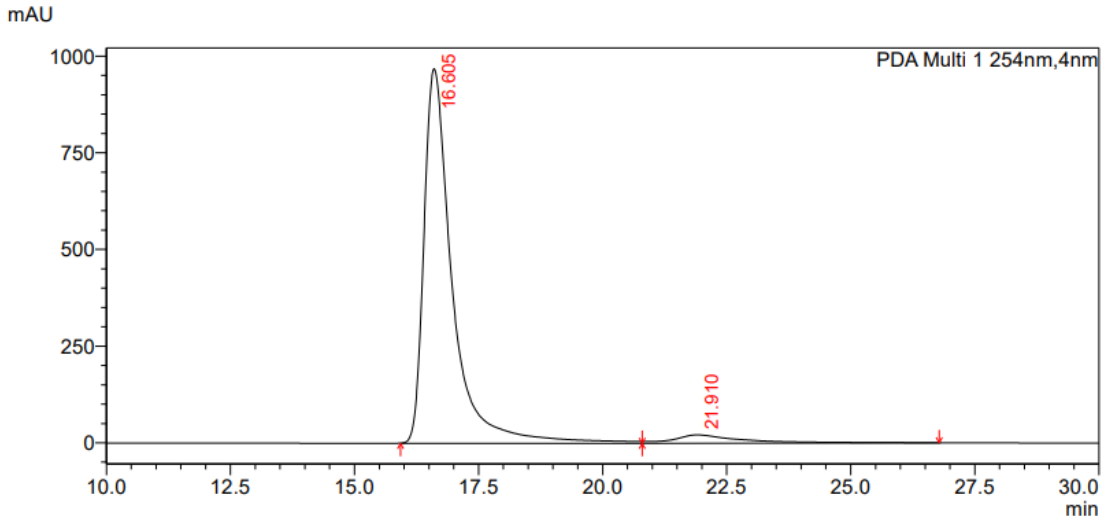


HPLC conditions: Chiralcel IC (*i*-PrOH/*n*-Hexane, 25:75), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

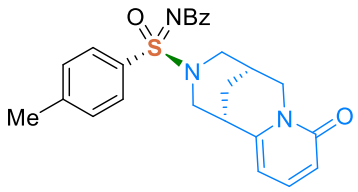
Peak#	Ret. Time	Area	Height	Area%
1	16.685	18081910	467409	50.305
2	21.654	17862467	345540	49.695
Total		35944377	812949	100.000



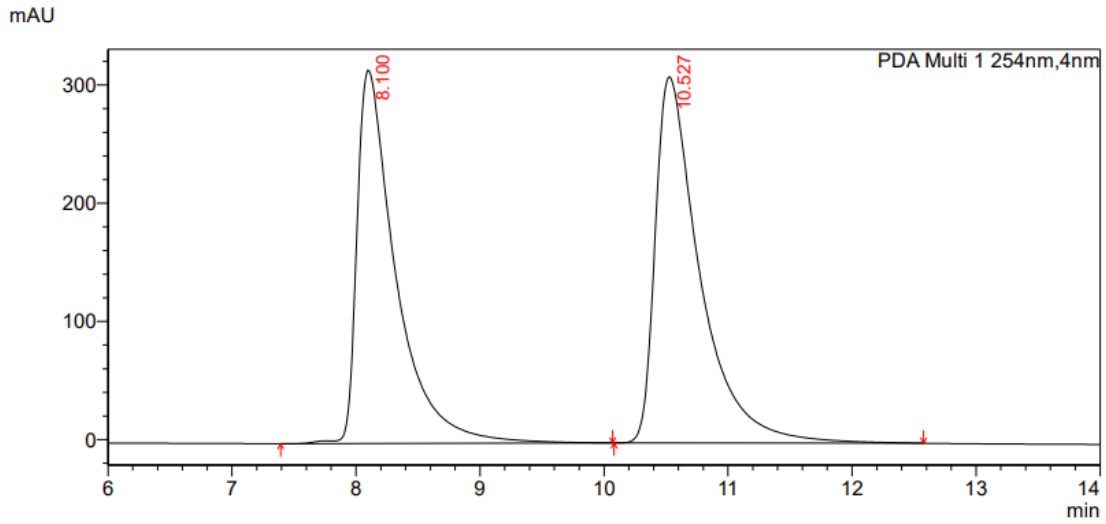
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	16.605	38521036	968262	94.756
2	21.910	2131736	21628	5.244
Total		40652772	989890	100.000

(*S*)-*N*-(Oxo((1R,5R)-8-oxo-1,5,6,8-tetrahydro-2*H*-1,5-methanopyrido[1,2-a] [1,5] diazocin-3(4*H*)-yl) (*p*-tolyl)-λ^6-sulfaneylidene) benzamide (18):

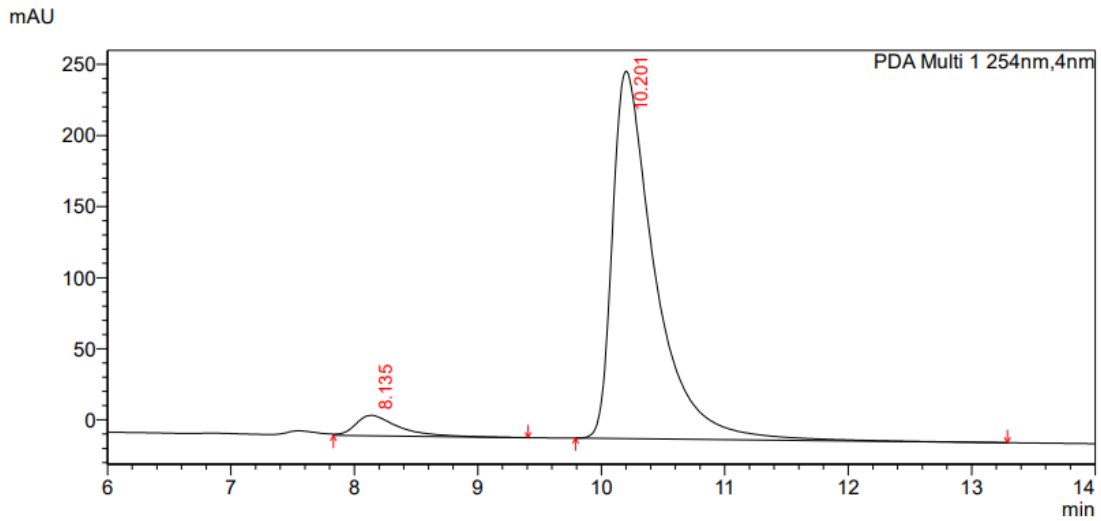


HPLC conditions: Chiralcel IA (*i*-PrOH/*n*-Hexane, 50:50), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

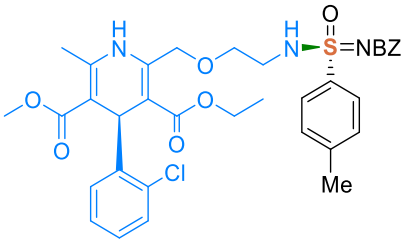
Peak#	Ret. Time	Area	Height	Area%
1	8.100	6876968	315771	46.933
2	10.527	7775820	309969	53.067
Total		14652789	625740	100.000



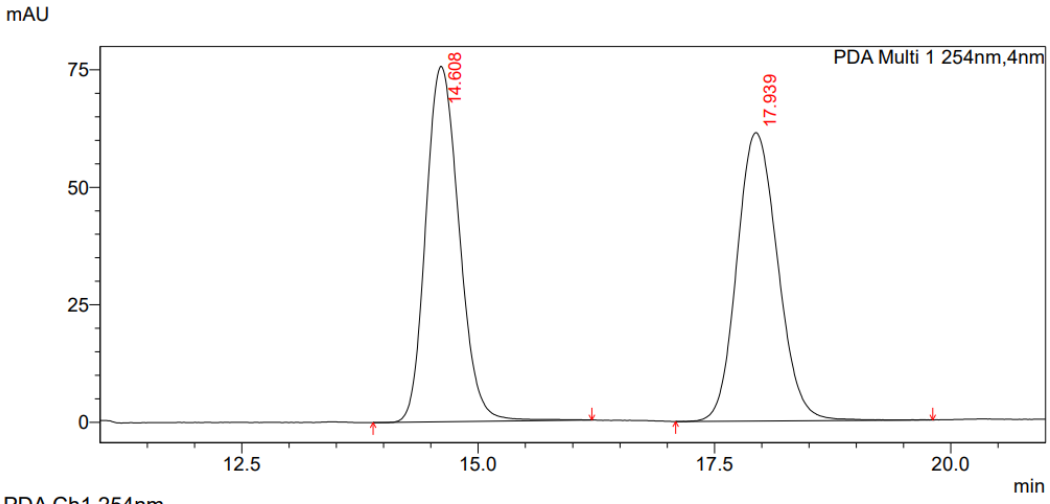
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.135	345118	14346	5.277
2	10.201	6195487	258424	94.723
Total		6540605	272770	100.000

(*S*)-3-Ethyl-5-methyl (4*S*)-2-((2-((*N*′-benzoyl-4-methylphenyl) sulfonoamidimid amido) ethoxy) methyl)-4-(2-chlorophenyl)-6-methyl-1,4-dihydropyridine-3,5-dicarboxylate (20):

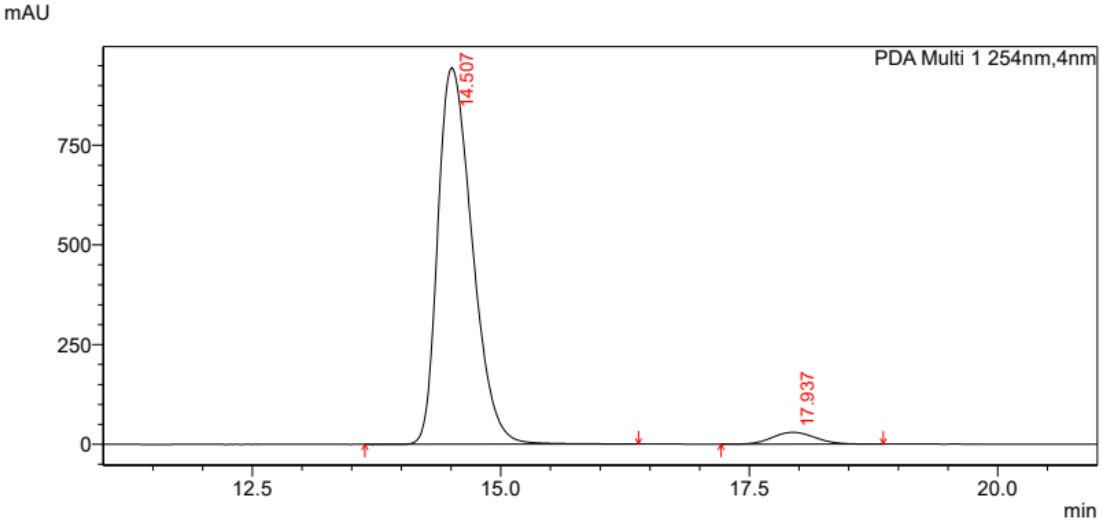


HPLC conditions: Chiralcel IG (*i*-PrOH/*n*-Hexane, 10:90), Flow: 1.0 mL.min^{-1}, Temp: 25 °C.



PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	14.608	1852607	75622	50.147
2	17.939	1841726	61381	49.853
Total		3694333	137003	100.000



PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	14.507	22699203	944476	96.227
2	17.937	890071	29520	3.773
Total		23589274	973996	100.000