

Supporting Information For:

Redox Transformation of β -Sulfinyl Esters for Asymmetric Synthesis of Sulfone-Based Axially Chiral Styrenes

Shiyu Xiang, Taotao Lu, Junjun Liu, Qingyang Zhao*^a

School of Pharmaceutical Sciences (Shenzhen), Shenzhen Campus of Sun Yat-sen University, Shenzhen, 518107, China

zhaoqy26@mail.sysu.edu.cn

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1. General information.

Unless otherwise stated, all reagents and solvents were purchased from commercial suppliers (Energy-chemical, TCI, Bidepharm, Adamas, innochem *et al.*), and used without further purification. All reactions were carried out under an atmosphere of nitrogen using a glovebox.

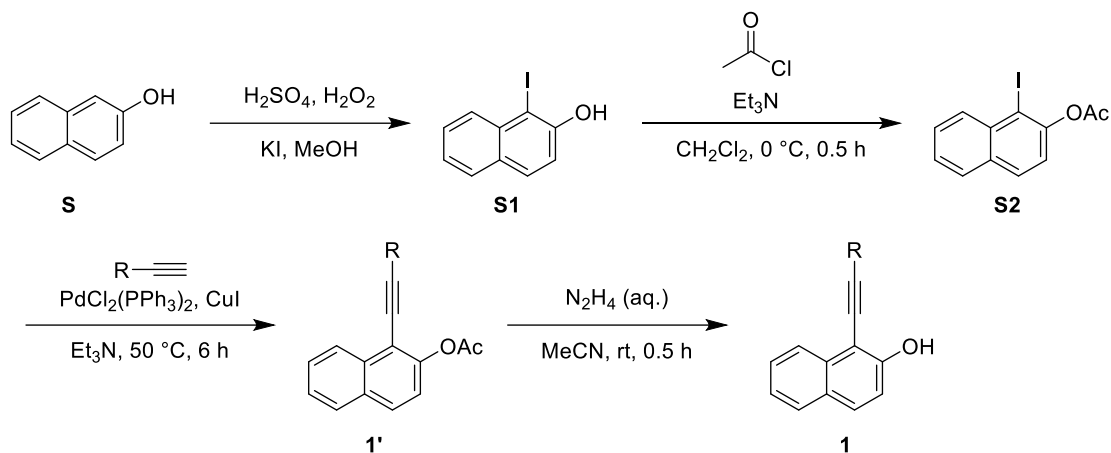
Reaction progresses were monitored by analytical thin layer chromatography (TLC) (TLC-Silica gel GF254 from Xinnuo). The TLC was visualized with a UV lamp (254 or 365 nm). Flash Column chromatography was carried out on silica gel (60 Å, 200-300 mesh) with technical grade solvents as the eluent. ¹H and ¹³C NMR spectra were recorded on Bruker instrument Advance 400 or 600 and referenced internally to the residual proton resonance in CDCl₃ (δ 7.26 ppm), or with tetramethylsilane (TMS, δ 0.00 ppm) as the internal standard. Chemical shifts (δ) were reported as part per million (ppm) in δ scale downfield from TMS. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad. Coupling constants *J* were reported in Hertz unit (Hz). Optical rotations were measured with a IP-digi300/1 automatic polarimeter purchased from Shanghai InsMark Instrument Technology Co., Ltd. using LED (λ = 589 nm) in the indicated solvent at the indicated temperature. The measurements were carried out in a 0.8 mL cell (50 mm length) with concentrations (10 mg/mL) reported in the corresponding solvent. The optical rotation values were reported as follows: [α]_D²⁰ (c = 10 mg/mL in CHCl₃).

HRMS were recorded on a Liquid chromatography quadrupole orbital trap mass spectrometer (Quadrupole-Orbitrap LC-MS, ThermoFisher) using Electron Spray Ionization (ESI). HPLC analysis was performed on an Waters e2695 Series and Shimadzu LC-2030C Plus using Chiralpak columns AD-H (Daicel Chiral Reagent Company). The solvents (n-hexane and iso-propanol, HPLC-grade) used as the eluent were purchased from Energy-chemical. The column type and the eluent (a mixture of n-hexane and iso-propanol) are indicated for each experiment. X-ray crystallography was performed on a Supernova diffractometer.

2. Substrate synthesis.

Compounds **1a-1q** were synthesized according to the reference.¹⁻⁴

Method A: (1a-1e, 1g-1q)



Sulfuric acid (75.0 mmol) was added to a solution of 2-naphthol (7.2 g, 50.0 mmol) and potassium iodide (8.3 g, 50 mmol) in methanol (150 mL) at 0 °C. A precipitate formed, and hydrogen peroxide (30% aqueous solution, 100 mmol) was added. After 1.5 h of warming slowly to room temperature, the mixture was filtered, and the filtrate was concentrated. The residue was dissolved in CH₂Cl₂, washed with 25% sat.aq. Na₂S₂O₃ and water, dried over Na₂SO₄. Then, the mixture was filtrated and the filtrate was concentrated. The material was purified by flash chromatography (PE:EA = 50:1) to provide a white solid **S1** (12.1 g, 90% yield).

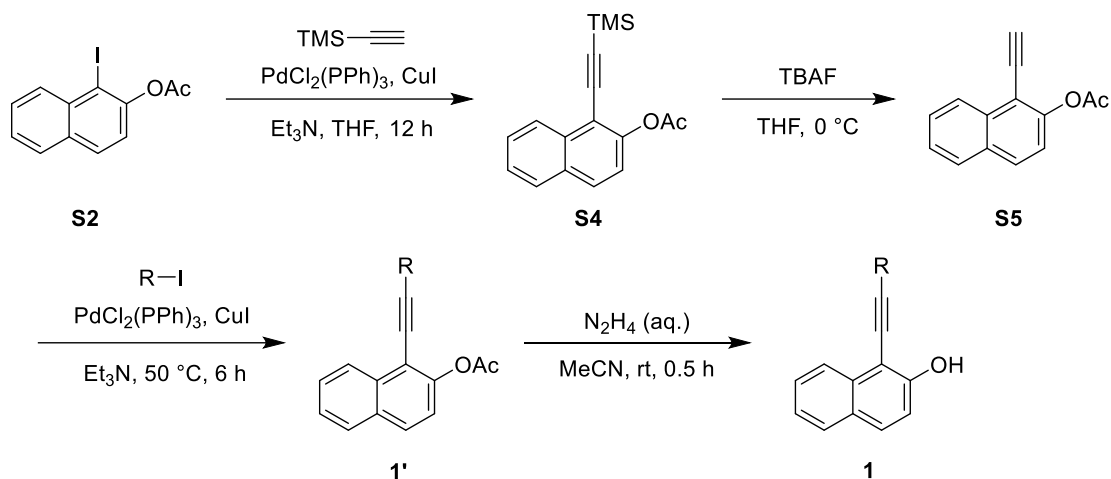
Acetyl chloride (1.5 equiv.) was dropwise added to a solution of **S1** (9.8 g, 36.3 mmol) and Et₃N (10.1 mL, 72.6 mmol) in CH₂Cl₂ (90 mL) at 0 °C under N₂. The reaction mixture was stirred at 0 °C for 30 min and then quenched with sat. aq. NH₄Cl followed by extraction with CH₂Cl₂. The organic phase was washed with brine and dried over Na₂SO₄, and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel (PE:EA = 20:1) to afford **S2** (11.3 g, 99% yield).

To a dry flask under N₂ containing **S2** (2.0 mmol) was sequentially added Et₃N (4 mL), appropriate alkynes (2.2 mmol), PdCl₂(PPh₃)₂ (28.0 mg, 0.04 mmol), CuI (19.0 mg, 0.1 mmol). The mixture was stirred for 6 h at 50 °C. Then the mixture was filtered through a pad of celite. Removal of solvent under reduced pressure afforded a residue which is purified by column chromatography on silica gel (PE:EA = 30:1 to 10:1) to afford **1'**.

Hydrazine monohydrate (5.0 mmol) was dropwise added to a solution of **1'** (1.0 mmol) in CH₃CN (5 mL). The mixture was stirred at room temperature for 0.5 h and then treated with sat. aq. NH₄Cl and extracted with CH₂Cl₂. The organic phase was dried over Na₂SO₄. Removal of solvent under reduced pressure afforded a residue

which is purified by column chromatography on silica gel (PE:EA = 30:1 to 10:1) to afford the compound **1**.

Method B: (1f)



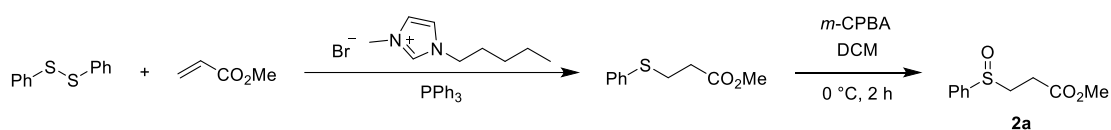
Trimethylsilylacetylene (2.7 mL, 19.5 mmol) was dropwise added to a solution of **S2** (4.7 g, 15.0 mmol), PdCl₂(PPh₃)₂ (210 mg, 0.3 mmol), CuI (142 mg, 0.75 mmol) and Et₃N (6.2 mL, 45.0 mmol) in THF (40 mL) at room temperature under N₂. Then, the mixture was stirred for 12 h. The reaction mixture was treated with sat. aq. NH₄Cl followed by extraction with CH₂Cl₂. The combined organic layer was washed with brine, dried over Na₂SO₄. Removal of solvent under reduced pressure afforded a residue which is purified by column chromatography on silica gel (PE:EA = 30:1) to afford **S4** (2.5 g, 80% yield).

To a solution of **S4** (2.5 g, 12.0 mmol) in THF (50 mL) was added TBAF in THF (1 M, 10.2 mL, 10.2 mmol) dropwise at 0 °C under N₂. Then the mixture was stirred for 1 h. The reaction mixture was treated with sat. aq. NH₄Cl followed by extraction with CH₂Cl₂. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (PE:EA = 100:1) to afford **S5** (1.9 g, 75% yield).

To a dry flask under N₂ containing the appropriate iodebenzenes (2.0 mmol) was sequentially added Et₃N (5.0 mL), **S5** (462 mg, 2.2 mmol), PdCl₂(PPh₃)₂ (28.0 mg, 0.04 mmol) and CuI (19.0 mg, 0.1 mmol). The mixture was stirred for 6 h at 50 °C. Then the mixture was filtered through a pad of celite. Removal of solvent under reduced pressure afforded a residue which is purified by column chromatography on silica gel (PE:EA = 20:1) to afford **1'**.

Hydrazine monohydrate (5.0 mmol) was dropwise added to a solution of **1'** (1.0 mmol) in CH₃CN (5 mL). The mixture was stirred at room temperature for 0.5 h and then treated with sat. aq. NH₄Cl and extracted with CH₂Cl₂. The organic phase was dried over Na₂SO₄. Removal of solvent under reduced pressure afforded a residue which is purified by column chromatography on silica gel (PE:EA = 10:1) to afford the compound **1**.

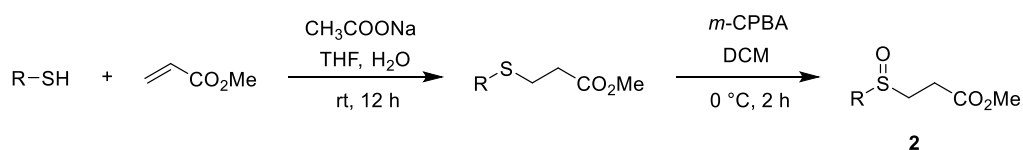
Compounds **2a** was synthesized according to the reference.^{5, 6}



A mixture of methyl acrylate (16.7 mmol), diphenyl disulfide (10.0 mmol), PPh₃ (11.7 mmol), and 1-methyl-3-pentyl-1H-imidazol-3-ium Bromide (6.7 mmol) was stirred at 75 °C for 5 h (monitored by TLC). The reaction mixture was extracted with Et₂O, and the organic layer was washed with brine and dried (Na₂SO₄). Evaporation of solvent left the crude product which was purified by column chromatography over silica gel (PE:EA = 30:1) to afford the sulfide (1.57 g, 80% yield) as a colorless liquid.

The sulfide (8 mmol) was dissolved in DCM (20 mL) and treated with *m*-CPBA (1.0 equiv., dissolved in 20 mL DCM) under 0 °C. Upon completion, the reaction mixture was quenched with sat. aq. NaHCO₃ and the aqueous mixture was extracted with DCM. The combined the organic layer was dried over Na₂SO₄, filtered and the solvent was removed under vacuum. Purified by flash chromatography on silica gel (PE:EA = 3:1) to afforded products **2a** (1.63 g, 96% yield).

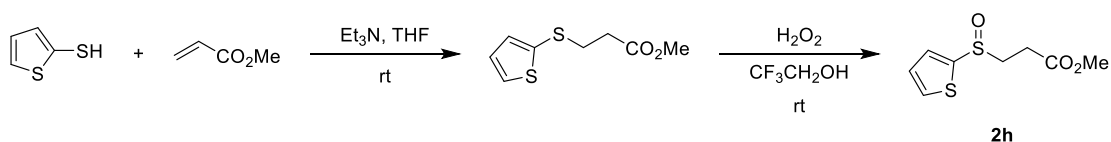
Compounds **2b-2g** were synthesized according to the reference.⁶



A 100 mL round bottom flask was charged with thiol (20.0 mmol, 1.0 equiv.), methyl acrylate (2.0 mL, 1.1 equiv.), THF (20 mL), H₂O (30 mL) and sodium acetate (246 mg, 15 mol%). The mixture was stirred at room temperature for 24 h. Upon completion, the reaction mixture was poured into saturated aq. NaHCO₃ and the aqueous mixture was extracted with ethyl acetate. The combined organic layer was dried over Na₂SO₄, filtered and the solvent was removed under vacuum. Purified by chromatography on silica gel (PE:EA = 30:1 to 10:1) to give product sulfide.

The sulfide (20 mmol) was dissolved in DCM (50 mL) and treated with *m*-CPBA (1.0 equiv., dissolved in 50 mL DCM) under 0 °C. Upon completion, the reaction mixture was quenched with sat. aq. NaHCO₃ and the aqueous mixture was extracted with DCM. The combined the organic layer was dried over Na₂SO₄, filtered and the solvent was removed under vacuum. Purified by flash chromatography on silica gel (PE:EA = 3:1 to 1:1) to afforded products **2b-2g**.

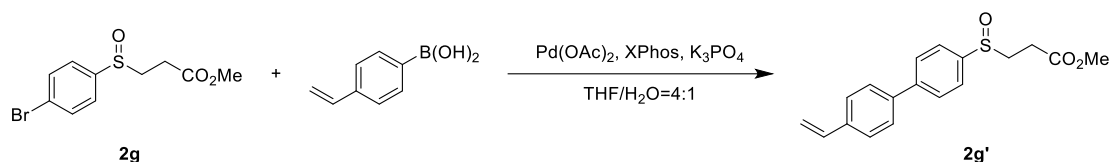
Compounds **2h** were synthesized according to the reference.⁷



Et₃N (5 mol%) was added to a solution of thiol (10.0 mmol) and methyl acrylate (10.0 mmol) in THF (2 mL) at 0 °C. The resulting reaction mixture was stirred for appropriate time at room temperature (monitored by TLC). After removing solvent under reduced pressure, the crude residue was used in next step without further purification.

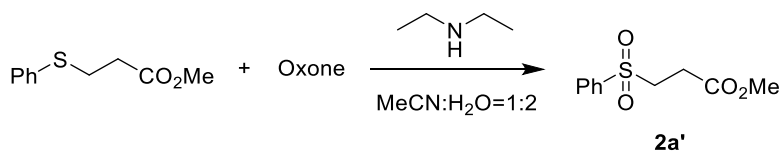
To a 2 M solution of sulfide (5.0 mmol) in 2,2,2-trifluoroethanol (TFE) (5.0 mL) at 0 °C, H₂O₂ (30% aqueous solution, 1.8 equiv.) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for appropriate time (monitored by TLC). Solid sodium sulfite (1.8 equiv.) was added then the reaction mixture was stirred for 30 min. The resulting mixture was filtered on celite, dried over Na₂SO₄, filtered and evaporated under reduced pressure. The crude product was then purified by column chromatography on silica gel (PE:EA = 2:1) to afford the product **2h** (1.64 g, 75% yield).

Compounds **2g'** were synthesized according to the reference.⁸



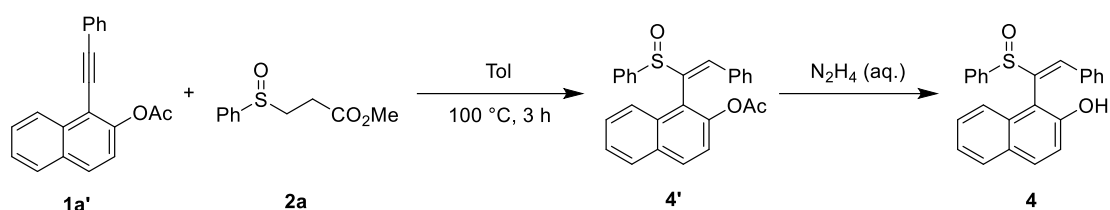
In an N₂-filled glove box, to a 50 mL Schlenk tube was charged sequentially Pd(OAc)₂ (0.12 mmol), XPhos (0.12 mmol), **2g** (1.0 mmol), 4-vinylphenylboronic acid (1.2 mmol), and 18 mL of THF. The mixture was stirred at 25 °C for 15 min, and then a solution of K₃PO₄ (2.0 mmol) in 4.5 mL of degassed H₂O was added to initiate the Suzuki reaction. The Schlenk tube was capped tightly and the reaction mixture was stirred vigorously at 25 °C for 12 h. The reaction mixture was extracted with ethyl acetate. The combined organic layer was dried over Na₂SO₄, filtered concentrated on a rotary evaporator. The resulting residue was purified by silica gel (PE:EA = 2:1) to provide the product **2g'** (166.0 mg, 53% yield).

Compounds **2a'** were synthesized according to the reference.⁹



To a well-stirred solution of sulfide (1.0 mmol) and diethylamine (0.2 mmol) in acetonitrile (2 mL) was added the solution of Oxone (1.5 mmol) in water (4 mL). Upon completion of the reaction, the mixture was diluted with chilled water. The product was extracted with ethyl acetate. The organic extract was washed with water, dried over Na₂SO₄, and the solvent was removed. The resultant residue on filtration through a short column of silica gel (PE:EA = 3:1) afforded the compound **2a'** (160.1 mg, 70% yield).

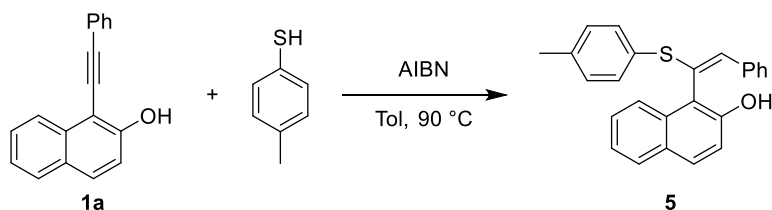
Compounds **4** were synthesized according to the reference.¹⁰



A flame-dried reaction tube equipped with a magnetic stirring bar was charged with β -sulfinyl ester derivative **2a** (3 mmol, 1 equiv.) and alkyne **1a'** (9 mmol, 3 equiv.) in toluene (15 mL). The mixture was stirred at 100 °C for 3 h. The solvent was evaporated under reduced pressure, and the crude reaction mixture was purified by silica gel column chromatography using PE/EA (4:1) as eluent and afforded the **4'** (210.4 mg, 17% yield).

Hydrazine monohydrate (2.5 mmol) was dropwise added to a solution of **4'** (0.51 mmol) in CH_3CN (2.5 mL). The mixture was stirred at room temperature for 0.5 h and then treated with sat. aq. NH_4Cl and extracted with CH_2Cl_2 . The organic phase was dried over Na_2SO_4 . Removal of solvent under reduced pressure afforded a residue which is purified by column chromatography on silica gel (PE:EA = 1:1) to afford the compound **4** (107.9 mg, 57% yield).

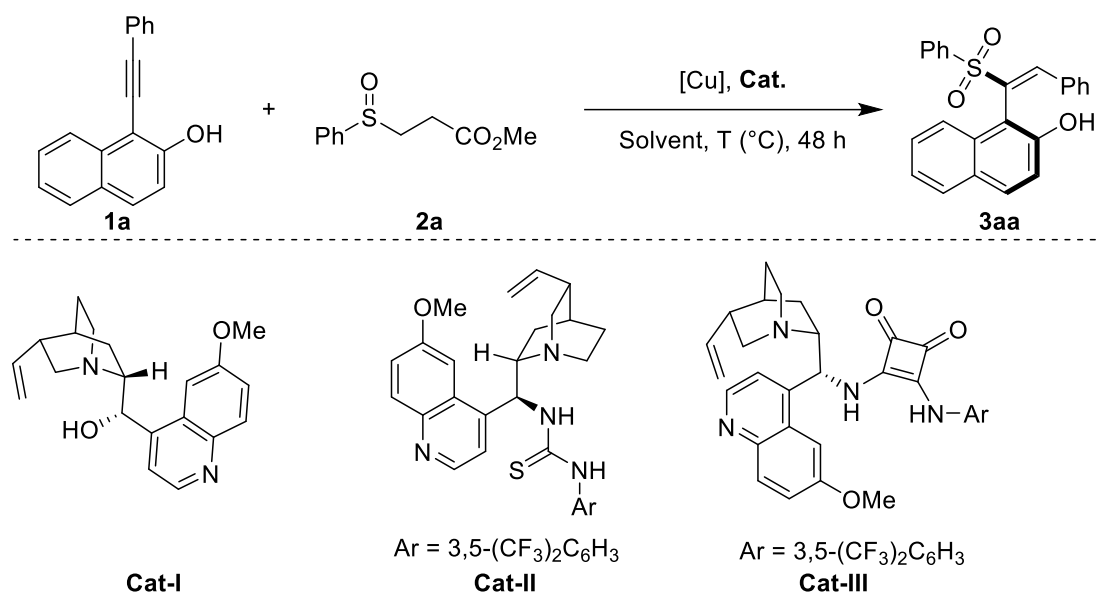
Compounds **5** were synthesized according to the reference.¹¹



A flame-dried reaction tube equipped with a magnetic stirring bar was charged with the substrate **1a** (1.0 mmol), 4-methylthiophenol (1.0 mmol) and AIBN (0.35 mmol). Then toluene (1 mL) was injected into the tube. The mixture was stirred at 90 °C for 2 h. Removal of solvent under reduced pressure afforded a residue which is purified by chromatography on silica gel (PE:EA = 15:1) to afford **5** (203.0 mg, 55% yield).

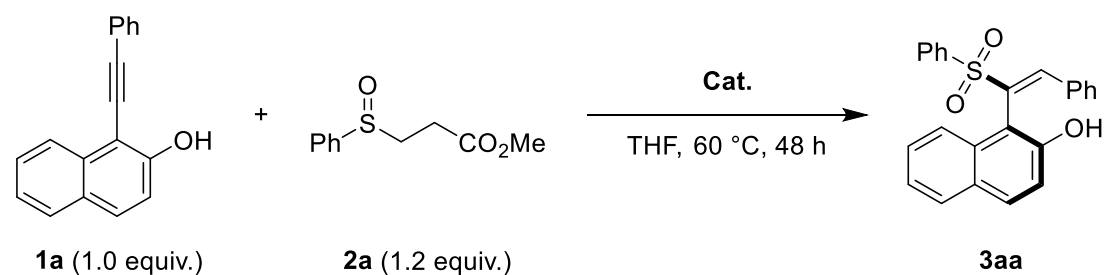
3. Experimental procedures.

3.1 General Procedure for conditions optimization (3aa).



The substrate **1a** (0.1 mmol), CuI (10 mol%) and **Cat-III** (10 mol%) was added to a 10 mL Schlenk tube with a magnetic stirring bar. Charging with N_2 , 2-Me-THF (1 mL) was injected into the tube followed by **2a** (0.5 mmol). The mixture was stirred at $60^{\circ}C$ (oil bath) for 48 h. Removal of solvent under reduced pressure afforded a residue which is purified by chromatography on silica gel (PE:EA = 5:1) to afford **3aa**.

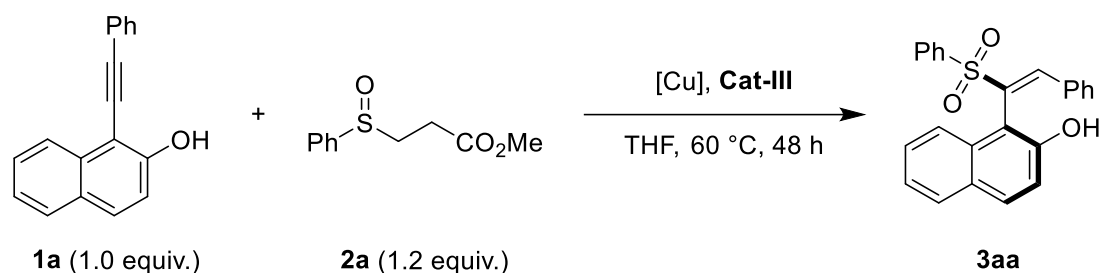
Supplementary Table 1. Screening of chiral ligands.



entry ^a	T($^{\circ}C$)	Cat.	solvent	yield (%) ^b	ee (%) ^c
1	60	I	THF	ND	/
2	60	II	THF	40	-76
3	60	III	THF	29	92

^a Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), and **Cat.** (10 mol%) in 1 mL THF at $60^{\circ}C$ for 48 h under nitrogen. ^b isolated yield. ^c Determined by chiral HPLC analysis Chiralpak columns. ND: No Detected.

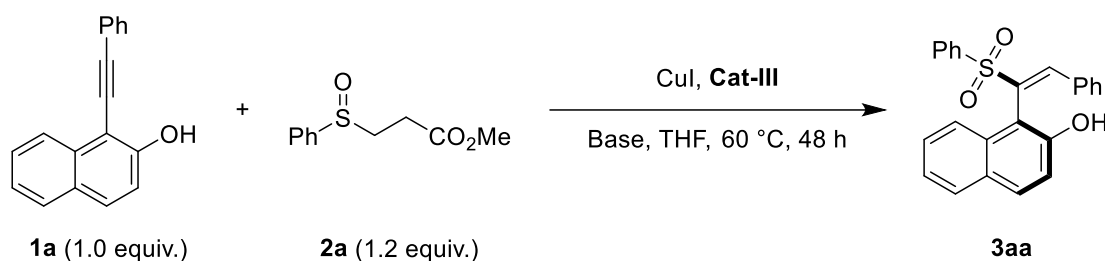
Supplementary Table 2. Screening of metals.



entry ^a	T(°C)	Cat.	M	solvent	yield (%) ^b	ee (%) ^c
1	60	III	Cu(acac) ₂	THF	27	96
2	60	III	CuSCN	THF	25	92
3	60	III	CuO	THF	38	93
4	60	III	CuTc	THF	17	89
5	60	III	CuOAc	THF	11	93
6	60	III	CuOTf	THF	23	96
7	60	III	Cu ₂ O	THF	42	94
8	60	III	CuCl	THF	27	94
9	60	III	CuBr	THF	36	94
10	60	III	CuI	THF	44	94

^a Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), [M] (10 mol%) and **Cat-III** (10 mol%) in 1 mL THF at 60 °C for 48 h under nitrogen. ^b isolated yield. ^c Determined by chiral HPLC analysis Chiralpak columns.

Supplementary Table 3. Screening of bases.

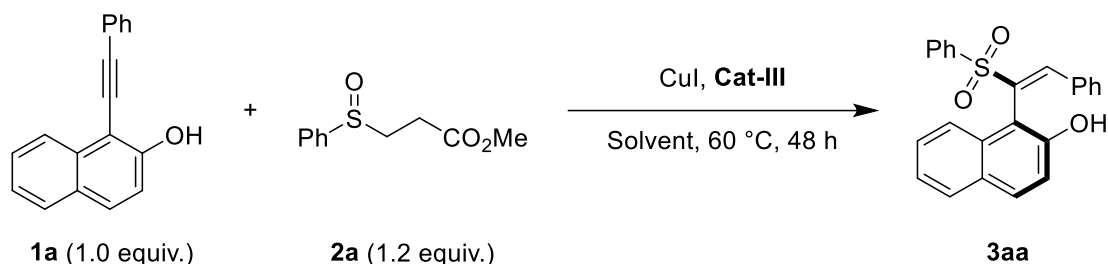


entry ^a	T(°C)	Cat.	M	base	solvent	yield (%) ^b	ee (%) ^c
1 ^d	25	III	CuI	KOH	THF	33	race
2	60	III	CuI	---	THF	44	94
3	60	III	CuI	Cs ₂ CO ₃	THF	Trace	/
4	60	III	CuI	CsF	THF	Trace	/
5	60	III	CuI	K ₂ CO ₃	THF	Trace	/
6	60	III	CuI	K ₃ PO ₄	THF	Trace	/
7	60	III	CuI	KOH	THF	ND	/
8	60	III	CuI	KF	THF	29	68
9	60	III	CuI	NaOAc	THF	40	91
10	60	III	CuI	t-BuOK	THF	ND	/
11	60	III	CuI	Et ₃ N	THF	31	89

^a Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), CuI (10 mol%), **Cat-III** (10 mol%) and base (0.1 mmol) in 1 mL THF at 60 °C for 48 h under nitrogen. ^b isolated

yield. ^c Determined by chiral HPLC analysis Chiralpak columns. ^d Reaction temperature is 25 °C. ND: No Detected.

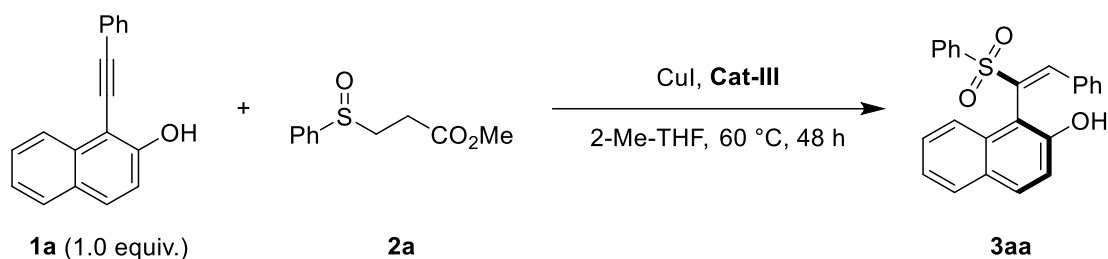
Supplementary Table 4. Screening of solvents.



entry ^a	T(°C)	Cat.	M	solvent	yield (%) ^b	ee (%) ^c
1	60	III	---	THF	29	92
2	60	III	---	Tol	15	90
3	60	III	---	MeCN	19	89
4	60	III	---	1,4-Dioxane	18	91
5	60	III	CuI	DIPE	46	93
6	60	III	CuI	DME	46	93
7	60	III	CuI	MTBE	49	92
8	60	III	CuI	2-Me-THF	57	93
9 ^d	60	III	CuI	THF	75	98
10 ^d	60	III	CuI	2-Me-THF	88	97

^a Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), CuI (10 mol%), and **Cat-III** (10 mol%) in 1 mL solvent at 60 °C for 48 h under nitrogen. ^b isolated yield. ^c Determined by chiral HPLC analysis Chiralpak columns. ^d **1a:2a** = 1:5. DIPE = Diisopropyl Ether; DME = 1,2-Dimethoxyethane; MTBE = *tert*-Butyl Methyl Ether.

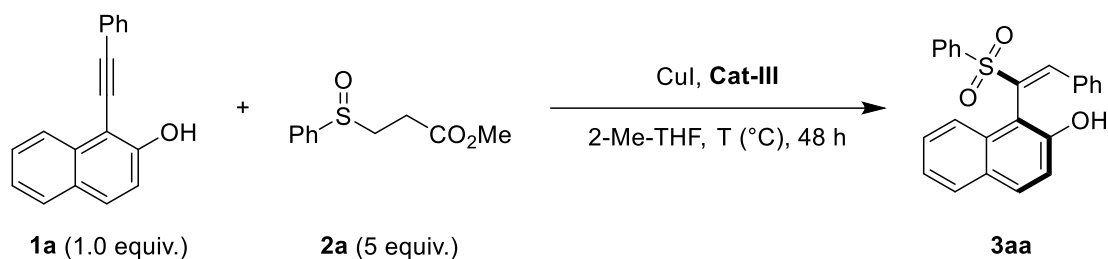
Supplementary Table 5. Screening of substrate ratios.



entry ^a	T(°C)	Cat.	M	2a:1a	solvent	yield (%) ^b	ee (%) ^c
1	60	III	CuI	1.2	2-Me-THF	57	93
2	60	III	CuI	3	2-Me-THF	74	96
3	60	III	CuI	4	2-Me-THF	81	96
4	60	III	CuI	5	2-Me-THF	88	97
5 ^d	60	III	CuI	5	2-Me-THF	83	97

^a Reaction conditions: **1a** (0.1 mmol), **2a**, CuI (10 mol%), and **Cat-III** (10 mol%) in 1 mL solvent at 60 °C for 48 h under nitrogen. ^b isolated yield. ^c Determined by chiral HPLC analysis Chiralpak columns. ^d 0.2 mmol **1a** was used.

Supplementary Table 6. Screening of temperature.

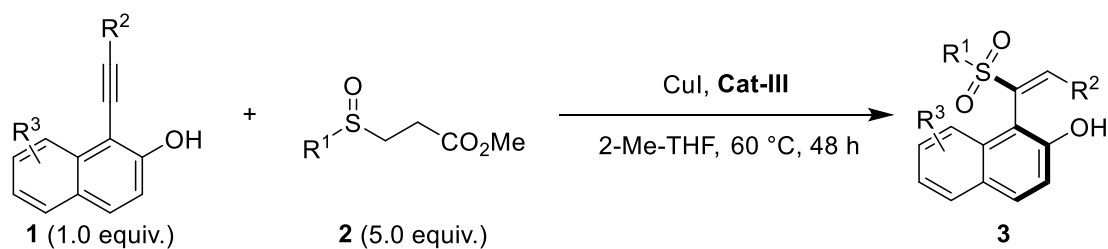


entry ^a	T(°C)	Cat.	M	solvent	yield (%) ^b	ee (%) ^c
1	50	III	CuI	2-Me-THF	80	97
2	60	III	CuI	2-Me-THF	88	97
3	70	III	CuI	2-Me-THF	73	97
4	80	III	CuI	2-Me-THF	66	92

^a Reaction conditions: **1a** (0.1 mmol), **2a** (0.5 mmol), CuI (10 mol%), and **Cat-III** (10 mol%) in 1 mL 2-Me-THF at reaction temperature for 48 h under nitrogen. ^b isolated yield. ^c Determined by chiral HPLC analysis Chiralpak columns.

3.2 General procedure for asymmetric reaction.

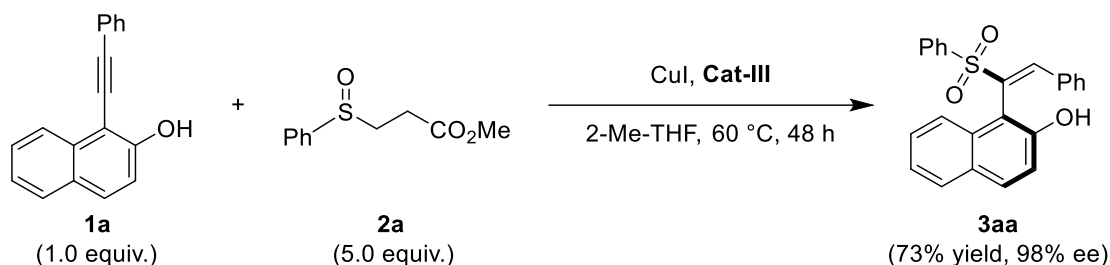
General procedure



The substrate **1** (0.2 mmol), CuI (10 mol%) and **Cat-III** (10 mol%) was added to a 10 mL Schlenk tube with a magnetic stirring bar. Charging with N₂, 2-Me-THF (2 mL) was injected into the tube followed by **2** (1.0 mmol). The mixture was stirred at 60 °C for 48 h. Removal of solvent under reduced pressure afforded a residue which is purified by chromatography on silica gel (PE:EA = 5:1) to afford **3**.

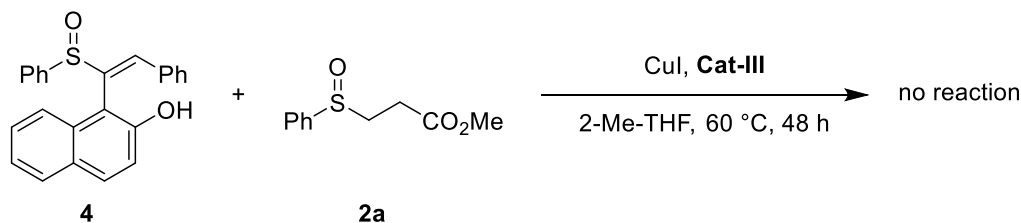
4. General procedure for scale-up reaction and control experiments.

4.1 General procedure for scale-up reaction.

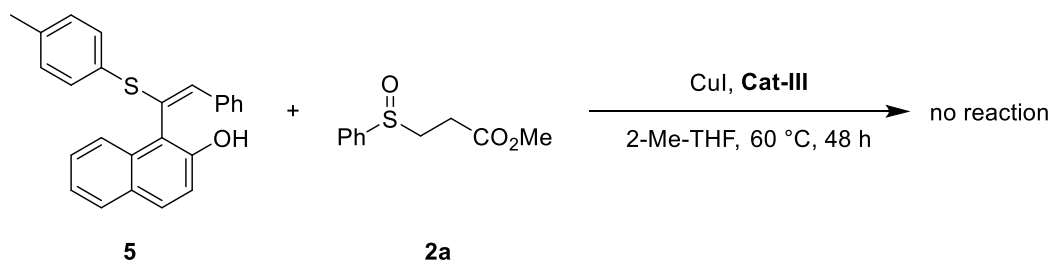


The substrate **1a** (1.0 mmol), CuI (10 mol%) and **Cat-III** (10 mol%) was added to a 50 mL Schlenk tube with a magnetic stirring bar. Charging with N₂, 2-Me-THF (10 mL) was injected into the tube followed by **2a** (5.0 mmol). The mixture was stirred at 60 °C for 48 h. Removal of solvent under reduced pressure afforded a residue which is purified by chromatography on silica gel (PE:EA = 5:1) to afford **3aa** (283.0 mg, 73% yield). At the same time, **2a** (230.6 mg) was recovered and **6** (138.2 mg) was separated.

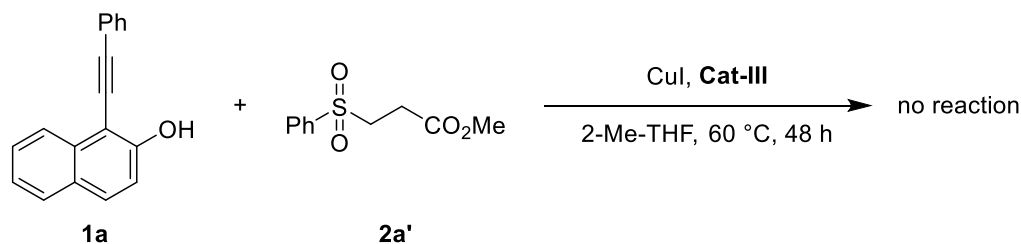
4.2 Control experiments.



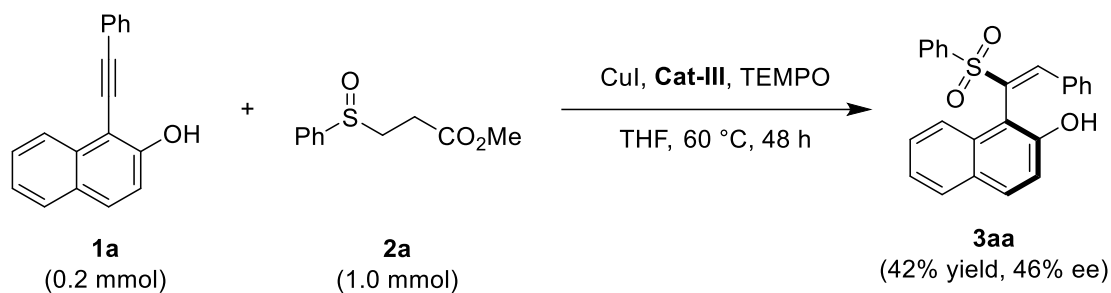
Refer to general procedure for the specific operation procedure.



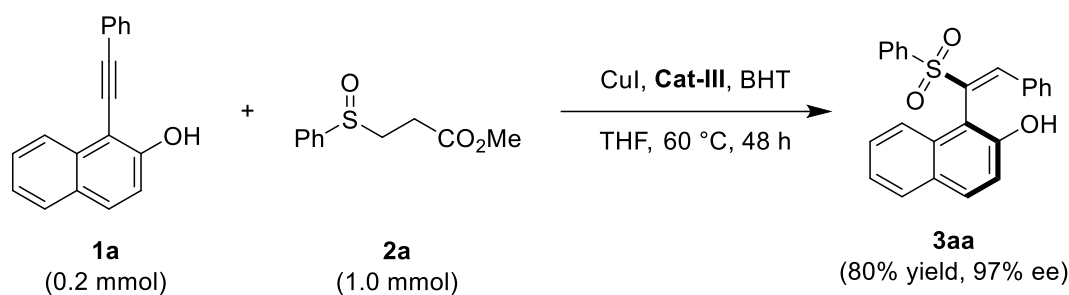
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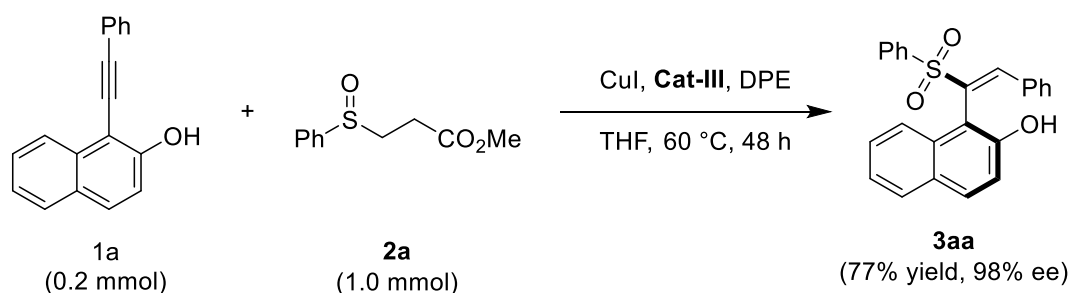
Refer to general procedure for the specific operation procedure.



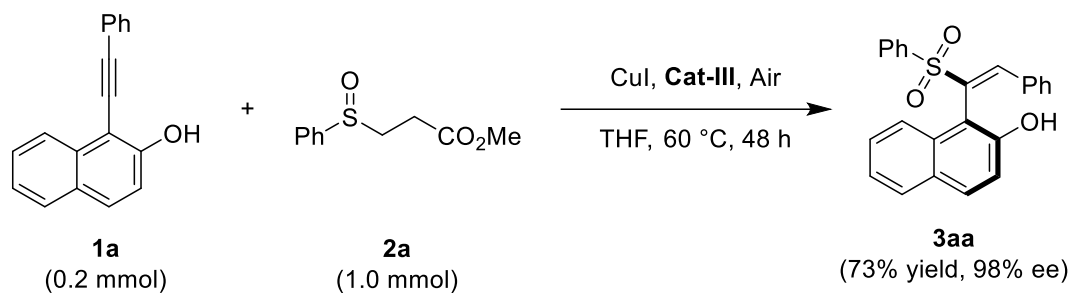
The substrate **1a** (0.2 mmol), CuI (10 mol%), **Cat-III** (10 mol%) and TEMPO (0.3 mmol) was added to a 10 mL Schlenk tube with a magnetic stirring bar. Charging with N₂, THF (2 mL) was injected into the tube followed by **2a** (1.0 mmol). The mixture was stirred at 60 °C for 48 h. Removal of solvent under reduced pressure afforded a residue which is purified by chromatography on silica gel (PE:EA = 5:1) to afford **3aa** (32.2 mg, 42% yield).



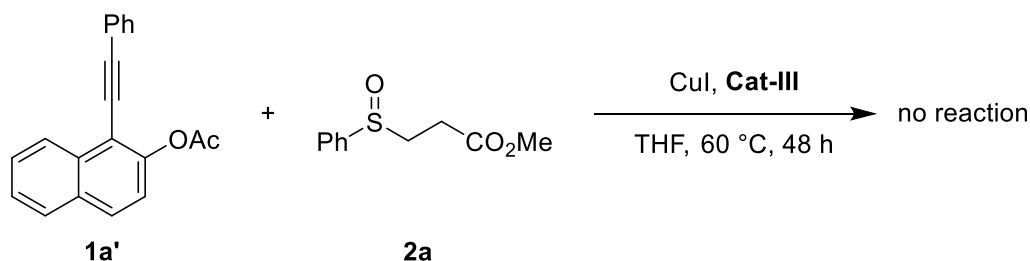
The substrate **1a** (0.2 mmol), CuI (10 mol%), **Cat-III** (10 mol%) and BHT (0.3 mmol) was added to a 10 mL Schlenk tube with a magnetic stirring bar. Charging with N₂, THF (2 mL) was injected into the tube followed by **2a** (1.0 mmol). The mixture was stirred at 60 °C for 48 h. Removal of solvent under reduced pressure afforded a residue which is purified by chromatography on silica gel (PE:EA = 5:1) to afford **3aa** (61.7 mg, 80% yield).



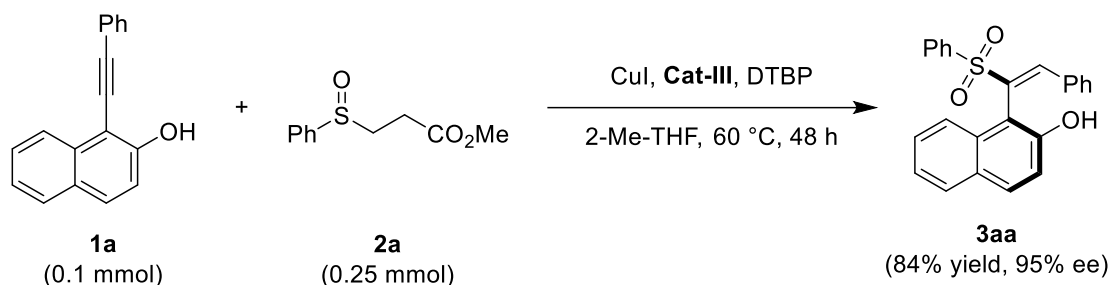
The substrate **1a** (0.2 mmol), CuI (10 mol%), **Cat-III** (10 mol%) and DPE (0.3 mmol) was added to a 10 mL Schlenk tube with a magnetic stirring bar. Charging with N₂, THF (2 mL) was injected into the tube followed by **2a** (1.0 mmol). The mixture was stirred at 60 °C for 48 h. Removal of solvent under reduced pressure afforded a residue which is purified by chromatography on silica gel (PE:EA = 5:1) to afford **3aa** (59.6 mg, 77% yield).



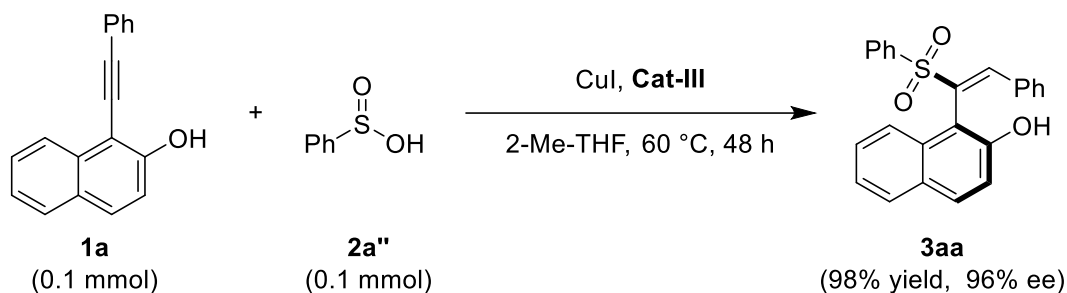
The substrate **1a** (0.2 mmol), CuI (10 mol%), **Cat-III** (10 mol%) was added to a 10 mL Schlenk tube with a magnetic stirring bar. THF (2 mL) was injected into the tube followed by **2a** (1.0 mmol). The mixture was stirred at 60 °C for 48 h. Removal of solvent under reduced pressure afforded a residue which is purified by chromatography on silica gel (PE:EA = 5:1) to afford **3aa** (56.3 mg, 73% yield).



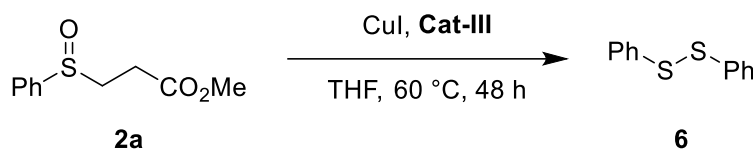
Refer to general procedure for the specific operation procedure.



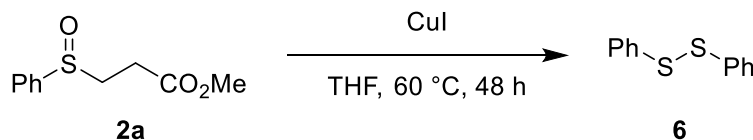
The substrate **1a** (0.1 mmol), CuI (10 mol%), and **Cat-III** (10 mol%) was added to a 10 mL schlenk tube with a magnetic stirring bar. Charging with N₂, 2-Me-THF (1 mL) was injected into the tube followed by **2a** (0.25 mmol) and DTBP (0.25 mmol). The mixture was stirred at 60 °C for 48 h. Removal of solvent under reduced pressure afforded a residue which is purified by chromatography on silica gel (PE:EA = 5:1) to afford **3aa** (32.5 mg, 84% yield).



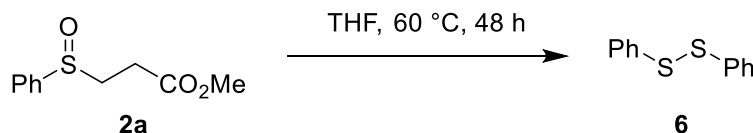
The substrate **2a''** (0.1 mmol), CuI (0.1 mmol), and **Cat-III** (0.1 mmol) was added to a 10 mL Schlenk tube with a magnetic stirring bar. Charging with N₂, 2-Me-THF (1 mL) was injected into the tube. Stir the mixture at room temperature for 30 min. Then the substrate **1a** (0.1 mmol) was added. The mixture was stirred at 60 °C for 48 h. Removal of solvent under reduced pressure afforded a residue which is purified by chromatography on silica gel (PE:EA = 5:1) to afford **3aa** (37.8 mg, 98% yield).



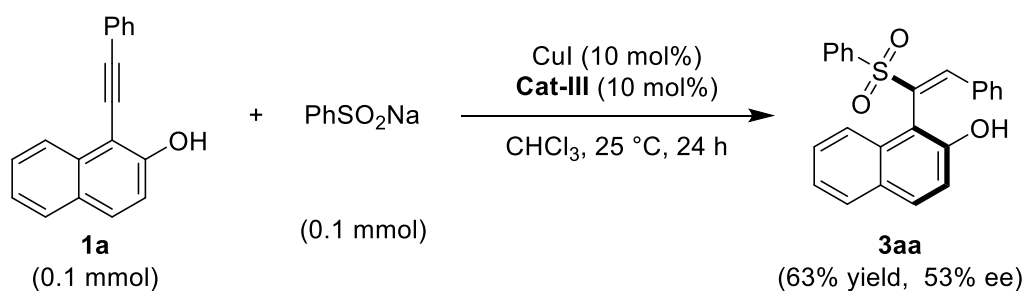
To a 10 mL Schlenk tube charging with CuI (10 mol%) and **Cat-III** (10 mol%) added THF (0.5 mL), then the substrate **2a** (0.05 mmol) was injected into the tube. The mixture was stirred at 60 °C for 48 h. Removal of solvent under reduced pressure afforded a residue which is purified by chromatography on silica gel to afford **6** (1.9 mg, 35% yield).



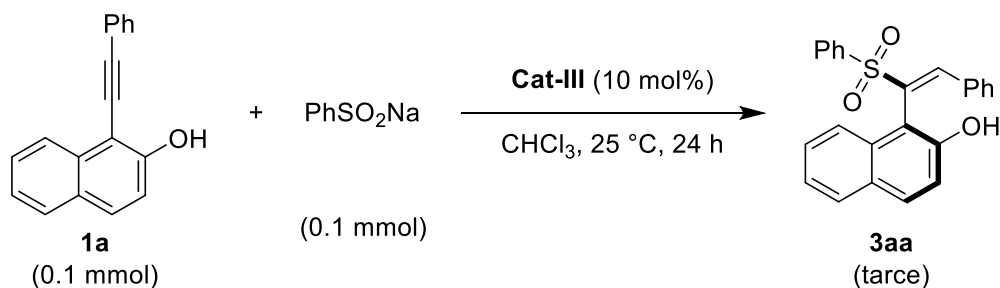
To a 10 mL Schlenk tube charging with CuI (10 mol%) added THF (0.5 mL), then the substrate **2a** (0.05 mmol) was injected into the tube. The mixture was stirred at 60 °C for 48 h. Removal of solvent under reduced pressure afforded a residue which is purified by chromatography on silica gel (PE) to afford **6** (1.8 mg, 33% yield).



To a 10 mL Schlenk tube charging with THF (1 mL) added substrate **2a** (0.05 mmol) The mixture was stirred at 60 °C for 48 h. Removal of solvent under reduced pressure afforded a residue which is purified by chromatography on silica gel (PE) to afford **6** (1.0 mg, 18% yield).

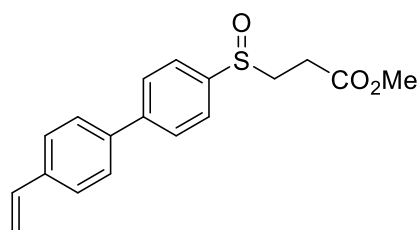


The substrate **1a** (0.1 mmol), sodium benzene sulfinate (0.1 mmol), CuI (10 mol%), and **Cat-III** (10 mol%) was added to a 10 mL Schlenk tube with a magnetic stirring bar. Charging with N₂, Chloroform (1 mL) was injected into the tube. Stir the mixture at room temperature for 24 h. Removal of solvent under reduced pressure afforded a residue which is purified by chromatography on silica gel (PE:EA = 5:1) to afford **3aa** (24.4 mg, 63% yield).



The substrate **1a** (0.1 mmol), sodium benzene sulfinate (0.1 mmol) and **Cat-III** (10 mol%) was added to a 10 mL Schlenk tube with a magnetic stirring bar. Charging with N₂, Chloroform (1 mL) was injected into the tube. Stir the mixture at room temperature for 24 h. Only trace **3aa** was detected.

5. ^1H , ^{13}C NMR and HRMS data of compound **2g'**.



2g'

White foam. 166.0 mg. Yield = 53%.

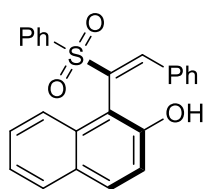
^1H NMR (400 MHz, CDCl₃) δ 7.78 – 7.64 (m, 4H), 7.61 – 7.48 (m, 4H), 6.76 (dd, J = 17.6, 10.9 Hz, 1H), 5.82 (d, J = 18.2 Hz, 1H), 5.31 (d, J = 10.9 Hz, 1H), 3.66 (s, 3H), 3.33 – 3.22 (m, 1H), 3.05 – 2.97 (m, 1H), 2.92 – 2.82 (m, 1H), 2.64 – 2.55 (m, 1H).

^{13}C NMR (101 MHz, CDCl₃) δ 171.7, 143.8, 141.7, 137.6, 136.2, 127.8, 127.4, 126.9, 124.7, 114.7, 52.2, 51.2, 26.1.

HRMS (ESI) calcd for C₁₈H₁₉O₃S⁺ m/z [M + H]⁺: 315.1049; found: 315.1041.

6. Spectroscopic Data and HPLC of products.

Compounds **3aa-3ab**, **3ae-3ag**, **3ba-3da**, **3ga-3ha**, **3la-3na**, **3pa** were known and the spectroscopic data match those reported.⁴



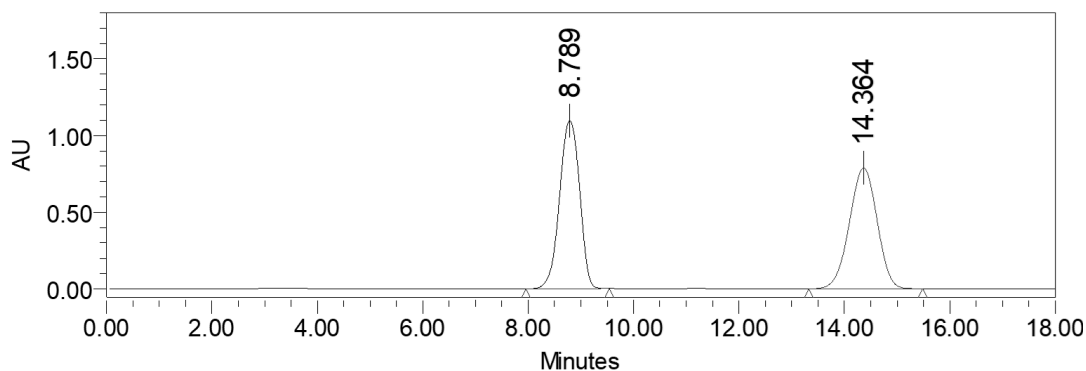
3aa

White foam. 68.2 mg. Yield = 88%. $[\alpha]_D^{20} = -131.416^\circ$ ($c = 1.0$, CHCl_3).

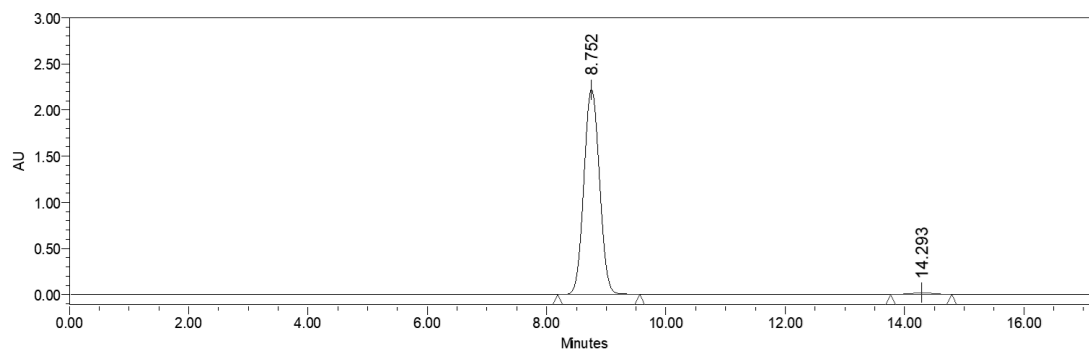
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.32 (s, 1H), 7.82 (d, $J = 8.9$ Hz, 1H), 7.62 (d, $J = 8.1$ Hz, 1H), 7.60 – 7.53 (m, 2H), 7.34 – 7.28 (m, 2H), 7.22 – 6.94 (m, 9H), 6.89 – 6.84 (m, 1H), 6.80 (d, $J = 8.3$ Hz, 1H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 153.9, 142.0, 136.7, 134.5, 133.7, 132.3, 132.2, 132.0, 130.9, 130.5, 129.0, 128.9, 128.8, 128.7, 128.1, 126.9, 123.7, 122.8, 119.8, 111.1.

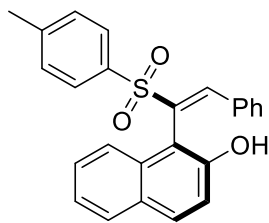
HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm): t_1 (major) = 8.752 min, t_2 (minor) = 14.293 min.



	Retention Time	Area	% Area	Height
1	8.789	28918301	50.06	1093960
2	14.364	28852209	49.94	788461



	Retention Time	Area	% Area	Height
1	8.752	40394399	98.68	2220504
2	14.293	541146	1.32	18472



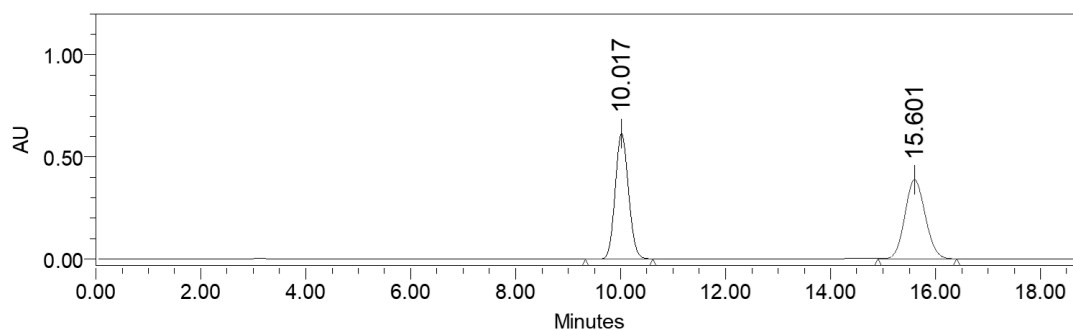
3ab

White foam. 66.3 mg. Yield = 83%. $[\alpha]_D^{20} = -61.196^\circ$ ($c = 1.0$, CHCl_3).

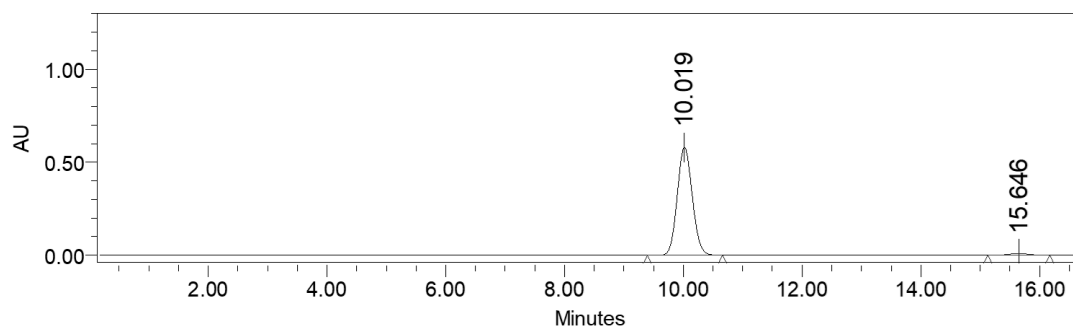
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.29 (s, 1H), 7.82 (d, $J = 8.9$ Hz, 1H), 7.62 (d, $J = 8.1$ Hz, 1H), 7.46 – 7.37 (m, 3H), 7.30 (d, $J = 8.9$ Hz, 1H), 7.15 (t, $J = 7.3$ Hz, 1H), 7.12 – 7.06 (m, 1H), 7.03 (t, $J = 7.7$ Hz, 2H), 6.99 – 6.91 (m, 4H), 6.91 – 6.85 (m, 1H), 6.82 (d, $J = 8.5$ Hz, 1H), 2.19 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 153.8, 144.8, 141.6, 134.8, 133.6, 132.3, 132.2, 132.1, 130.8, 130.4, 129.4, 129.0, 128.9, 128.7, 128.0, 126.8, 123.6, 122.9, 119.8, 111.2, 21.6.

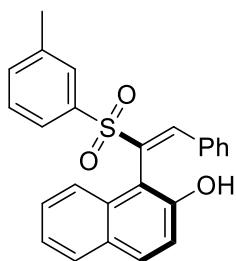
HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm): t_1 (major) = 10.019 min, t_2 (minor) = 15.646 min.



	Retention Time	Area	% Area	Height
1	10.017	13409474	50.95	764048
2	15.601	12907272	49.05	480625



	Retention Time	Area	% Area	Height
1	10.019	10229514	97.94	581881
2	15.646	215594	2.06	8325



3ac

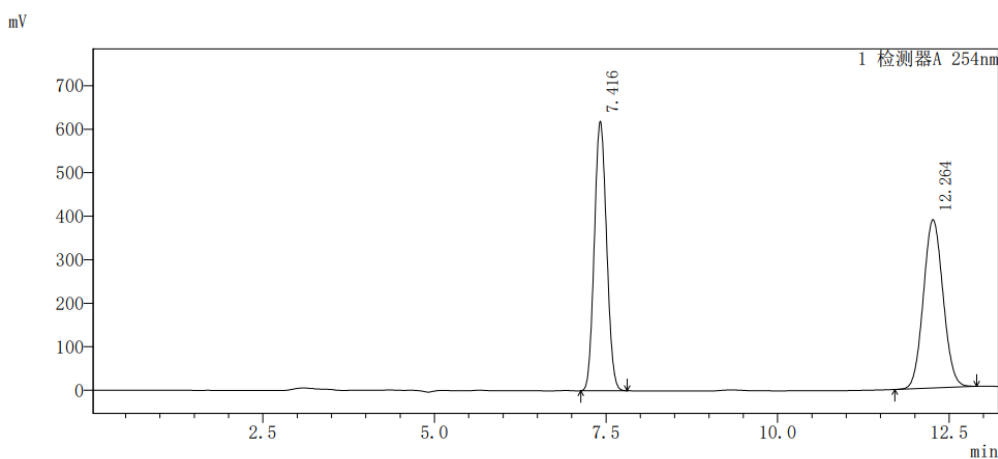
White foam. 62.4 mg. Yield = 78%. $[\alpha]_D^{20} = -99.358^\circ$ ($c = 1.0$, CHCl_3).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.30 (s, 1H), 7.82 (d, $J = 8.9$ Hz, 1H), 7.63 (d, $J = 8.2$ Hz, 1H), 7.41 – 7.27 (m, 4H), 7.19 – 7.14 (m, 1H), 7.13 – 6.97 (m, 7H), 6.91 – 6.85 (m, 1H), 6.81 (d, $J = 8.5$ Hz, 1H), 2.07 (s, 3H).

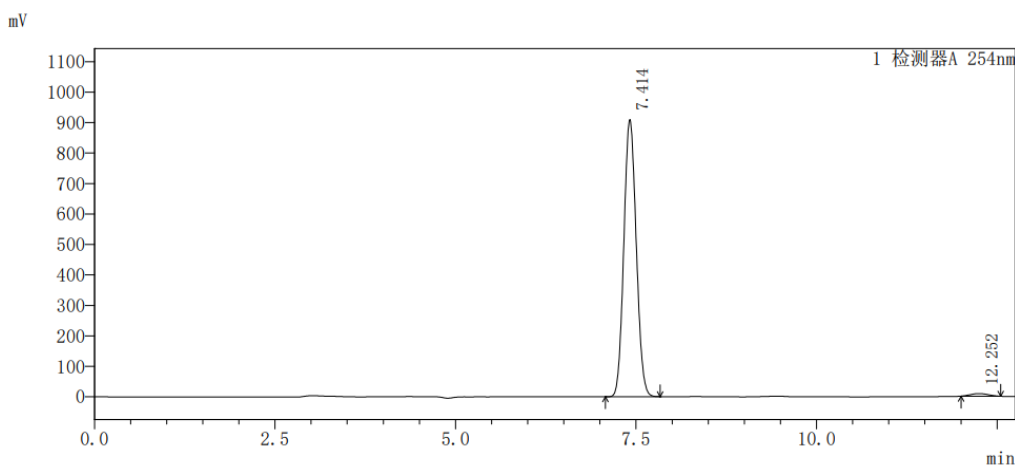
$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 153.8, 141.8, 139.0, 136.3, 134.6, 134.4, 132.3, 132.2, 132.1, 130.9, 130.5, 129.3, 129.0, 128.8, 128.6, 128.0, 126.8, 126.0, 123.7, 122.8, 119.9, 111.3, 20.9.

HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{21}\text{O}_3\text{S}^+$ m/z $[\text{M} + \text{H}]^+$: 401.1206; found: 401.1203.

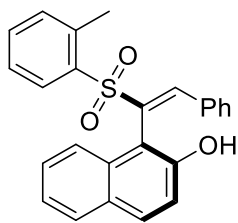
HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm): t_1 (major) = 7.414 min, t_2 (minor) = 12.252 min.



峰号	保留时间	面积	面积%	高度
1	7.416	7701108	49.982	619584
2	12.264	7706534	50.018	387132
总计		15407642	100.000	1006717



峰号	保留时间	面积	面积%	高度
1	7.414	10870128	98.664	910075
2	12.252	147153	1.336	8584
总计		11017281	100.000	918659



3ad

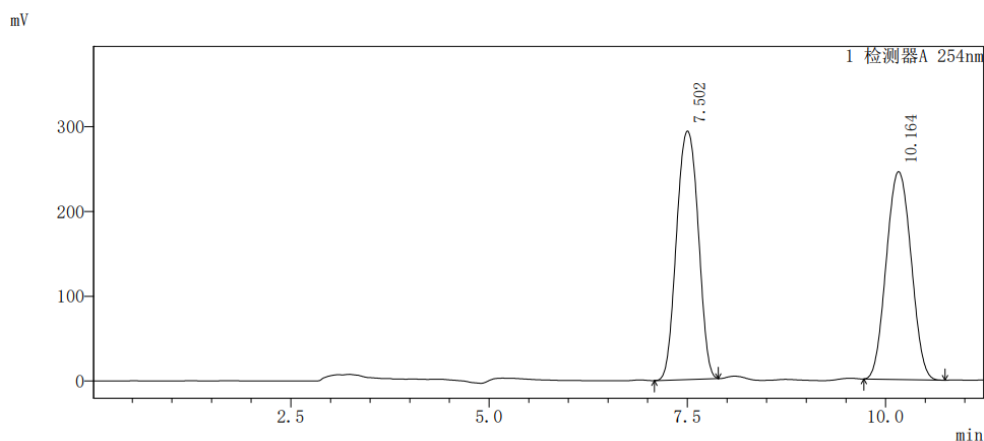
White foam. 70.8 mg. Yield = 88%. $[\alpha]_D^{20} = -100.699^\circ$ ($c = 1.0$, CHCl_3).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.32 (s, 1H), 7.79 (d, $J = 8.9$ Hz, 1H), 7.61 (d, $J = 8.2$ Hz, 1H), 7.54 (dd, $J = 8.0, 1.4$ Hz, 1H), 7.39 (s, 1H), 7.27 (d, $J = 8.9$ Hz, 1H), 7.22 – 7.14 (m, 2H), 7.12 – 6.97 (m, 6H), 6.95 – 6.85 (m, 3H), 2.54 (s, 3H).

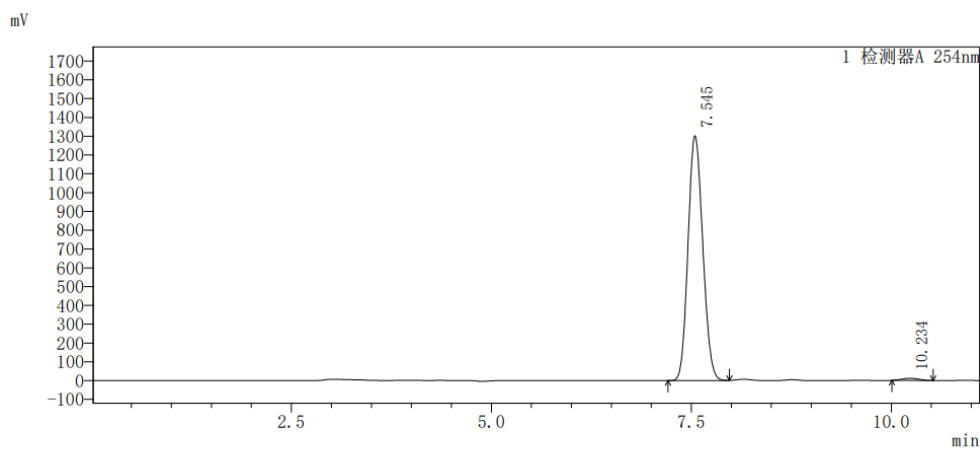
$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 153.9, 142.2, 139.2, 134.5, 134.5, 133.8, 132.6, 132.2, 132.2, 132.2, 131.3, 130.9, 130.5, 129.0, 128.8, 128.1, 126.8, 126.3, 123.7, 122.6, 119.8, 111.1, 20.8.

HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{21}\text{O}_3\text{S}^+$ m/z $[\text{M} + \text{H}]^+$: 401.1206; found: 401.1203.

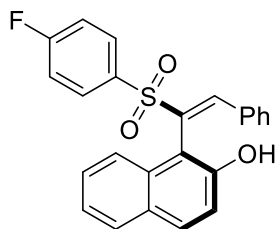
HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm): t_1 (major) = 7.545 min, t_2 (minor) = 10.234 min.



峰号	保留时间	面积	面积%	高度
1	7.502	5591931	51.153	293336
2	10.164	5339949	48.847	245319
总计		10931881	100.000	538655



峰号	保留时间	面积	面积%	高度
1	7.545	16725934	98.990	1302431
2	10.234	170663	1.010	11263
总计		16896598	100.000	1313694



3ae

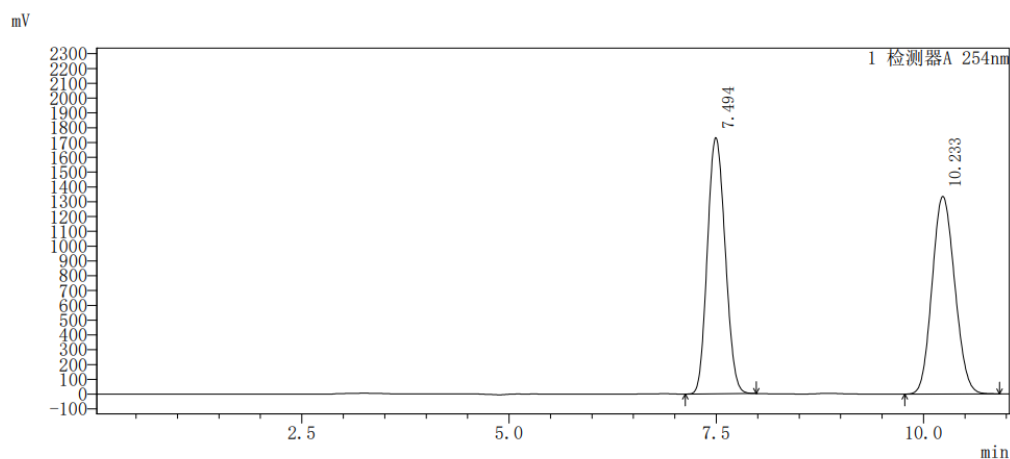
White foam. 66.6 mg. Yield = 82%. $[\alpha]_D^{20} = -84.219^\circ$ ($c = 1.0$, CHCl_3).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.32 (s, 1H), 7.84 (d, $J = 8.9$ Hz, 1H), 7.65 (d, $J = 8.2$ Hz, 1H), 7.58 – 7.52 (m, 2H), 7.31 (d, $J = 8.9$ Hz, 1H), 7.26 (s, 1H), 7.20 – 7.15 (m, 1H), 7.15 – 7.10 (m, 1H), 7.08 – 6.98 (m, 4H), 6.96 – 6.91 (m, 1H), 6.86 – 6.79 (m, 3H).

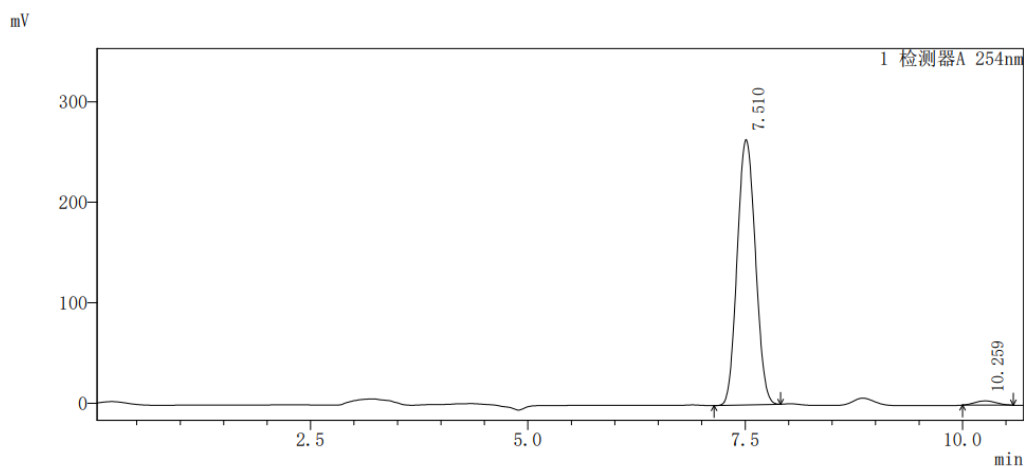
$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 165.9 (d, $J = 257.8$ Hz), 153.8, 142.2, 134.2, 132.8 (d, $J = 3.1$ Hz), 132.4, 132.1, 131.9, 131.8, 131.7, 131.0, 130.5, 129.0, 128.8, 128.2, 127.1, 123.9, 122.6, 119.8, 116.1, 115.9, 110.8.

$^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -103.30.

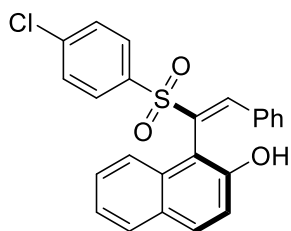
HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm): t_1 (major) = 7.510 min, t_2 (minor) = 10.259 min.



检测器A 254nm				
峰号	保留时间	面积	面积%	高度
1	7.494	25846097	50.456	1730687
2	10.233	25378708	49.544	1335548
总计		51224805	100.000	3066235



检测器A 254nm				
峰号	保留时间	面积	面积%	高度
1	7.510	3837313	98.145	264043
2	10.259	72530	1.855	4255
总计		3909844	100.000	268298



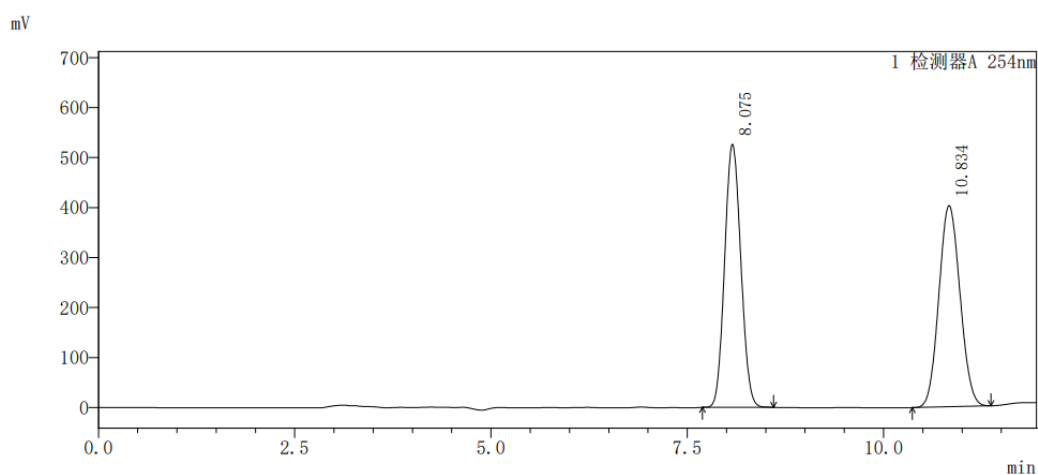
3af

White foam. 60.1 mg. Yield = 71%. $[\alpha]_D^{20} = -53.985^\circ$ ($c = 1.0$, CHCl_3).

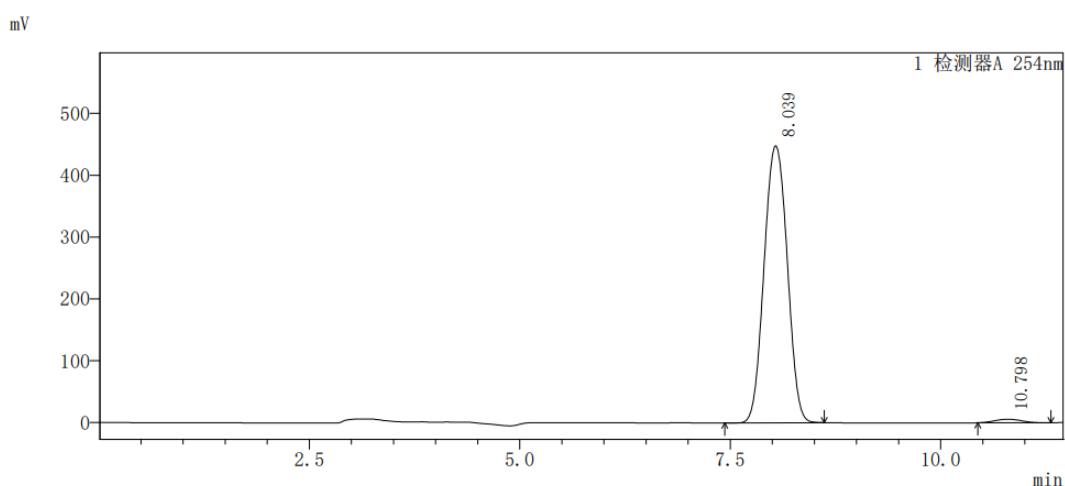
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.31 (s, 1H), 7.84 (d, $J = 8.9$ Hz, 1H), 7.66 (d, $J = 8.1$ Hz, 1H), 7.47 (d, $J = 8.6$ Hz, 2H), 7.30 (d, $J = 8.9$ Hz, 1H), 7.22 – 7.09 (m, 5H), 7.10 – 6.96 (m, 4H), 6.97 – 6.91 (m, 1H), 6.82 (d, $J = 8.4$ Hz, 1H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 153.8, 142.5, 140.6, 135.3, 134.1, 132.5, 132.1, 131.9, 131.1, 130.5, 130.4, 129.0, 128.9, 128.3, 127.2, 123.9, 122.6, 119.8, 110.8.

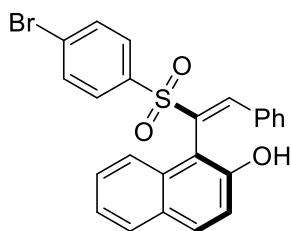
HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm): t_1 (major) = 8.039 min, t_2 (minor) = 10.798 min.



峰号	保留时间	面积	面积%	高度
1	8.075	7562912	50.070	526577
2	10.834	7541807	49.930	402695
总计		15104719	100.000	929272



峰号	保留时间	面积	面积%	高度
1	8.039	8567539	98.564	448182
2	10.798	124785	1.436	5709
总计		8692324	100.000	453890



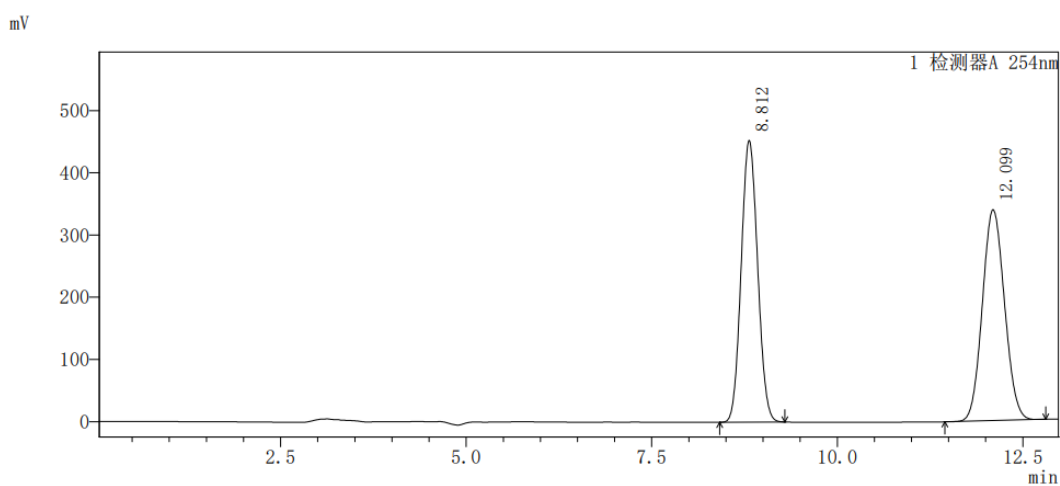
3ag

White foam. 78.8 mg. Yield = 85%. $[\alpha]_D^{20} = -82.211^\circ$ (c = 1.0, CHCl₃).

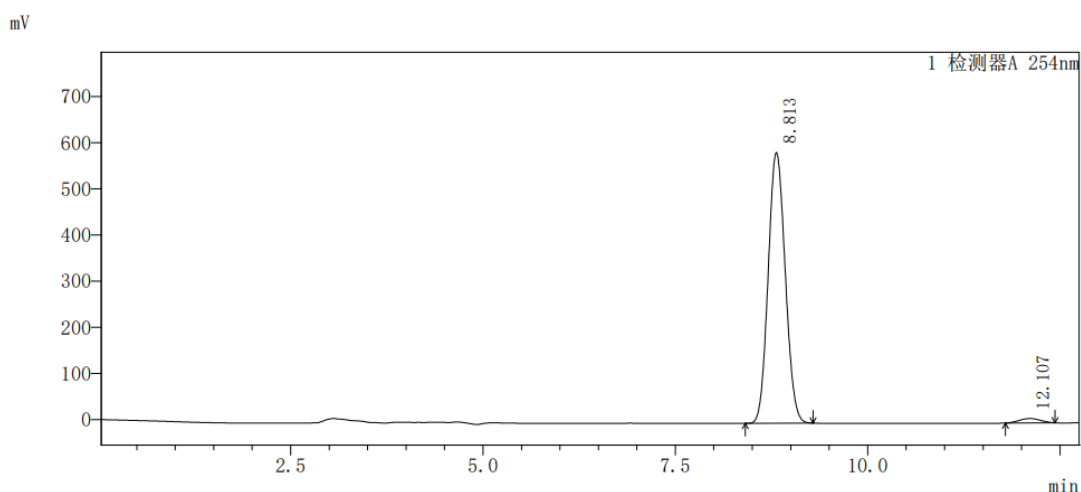
¹H NMR (400 MHz, CDCl₃) δ 8.31 (s, 1H), 7.85 (d, *J* = 8.9 Hz, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.39 (d, *J* = 8.6 Hz, 2H), 7.33 – 7.27 (m, 3H), 7.22 – 7.12 (m, 3H), 7.09 – 7.03 (m, 2H), 7.03 – 6.98 (m, 2H), 6.97 – 6.91 (m, 1H), 6.81 (d, *J* = 8.5 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 153.8, 142.5, 135.9, 134.0, 132.5, 132.1, 132.0, 131.9, 131.2, 130.5, 130.4, 129.2, 129.0, 128.9, 128.3, 127.2, 123.9, 122.6, 119.8, 110.8.

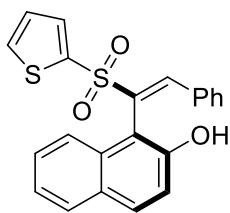
HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm): t₁ (major) = 8.813 min, t₂ (minor) = 12.107 min.



峰号	保留时间	面积	面积%	高度
1	8.812	6971751	49.772	452966
2	12.099	7035688	50.228	339184
总计		14007439	100.000	792150



峰号	保留时间	面积	面积%	高度
1	8.813	9061470	98.053	587143
2	12.107	179963	1.947	9516
总计		9241433	100.000	596660



3ah

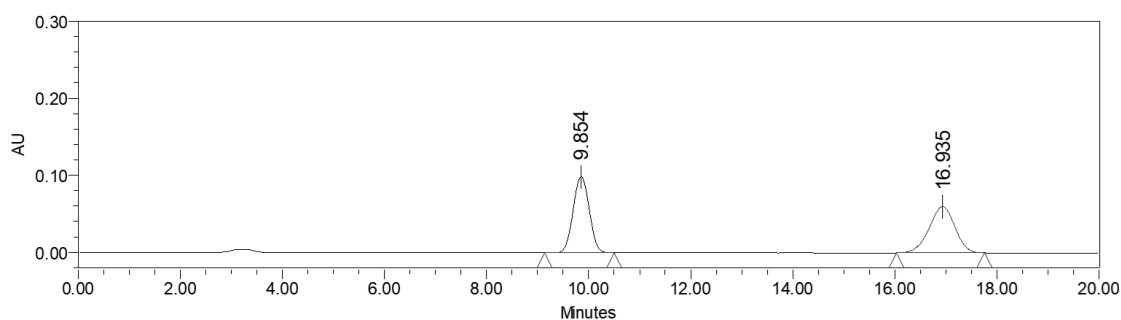
White foam. 58.0 mg. Yield = 74%. $[\alpha]_D^{20} = -92.158^\circ$ ($c = 1.0$, CHCl_3).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.32 (s, 1H), 7.85 (d, $J = 8.9$ Hz, 1H), 7.67 (d, $J = 8.1$ Hz, 1H), 7.39 (dd, $J = 5.0, 1.3$ Hz, 1H), 7.33 (d, $J = 8.9$ Hz, 1H), 7.23 (dd, $J = 3.9, 1.4$ Hz, 1H), 7.20 – 6.93 (m, 9H), 6.73 (dd, $J = 4.9, 3.8$ Hz, 1H).

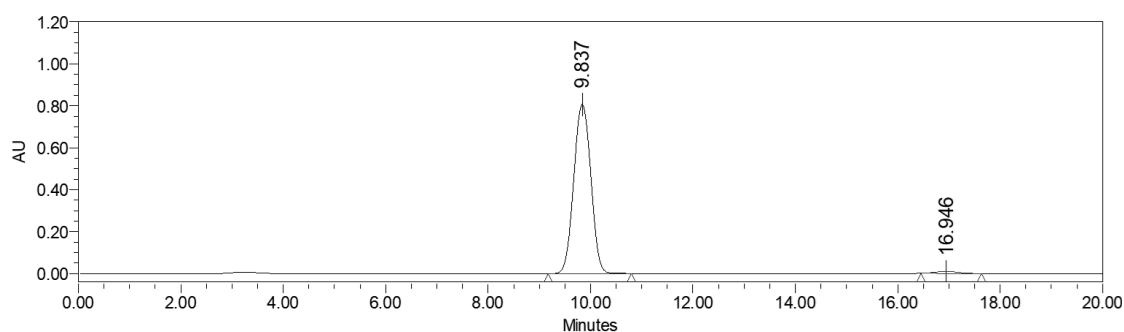
$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 153.9, 141.8, 137.1, 135.6, 135.1, 134.6, 132.5, 132.4, 132.1, 131.0, 130.5, 129.0, 128.8, 128.2, 127.8, 127.2, 123.8, 122.5, 119.9, 110.9.

HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{17}\text{O}_3\text{S}_2^+$ m/z $[\text{M} + \text{H}]^+$: 393.0614; found: 393.0609.

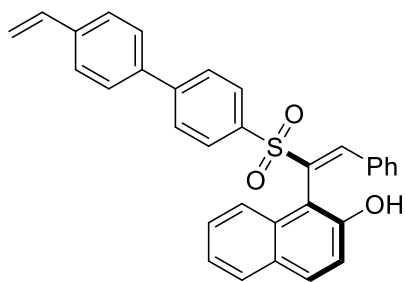
HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 244$ nm): t_1 (major) = 9.837 min, t_2 (minor) = 16.946 min.



	Retention Time	Area	% Area	Height
1	9.854	2165545	50.78	98760
2	16.935	2099006	49.22	59956



	Retention Time	Area	% Area	Height
1	9.837	18700324	98.43	806442
2	16.946	298392	1.57	9362



3ag'

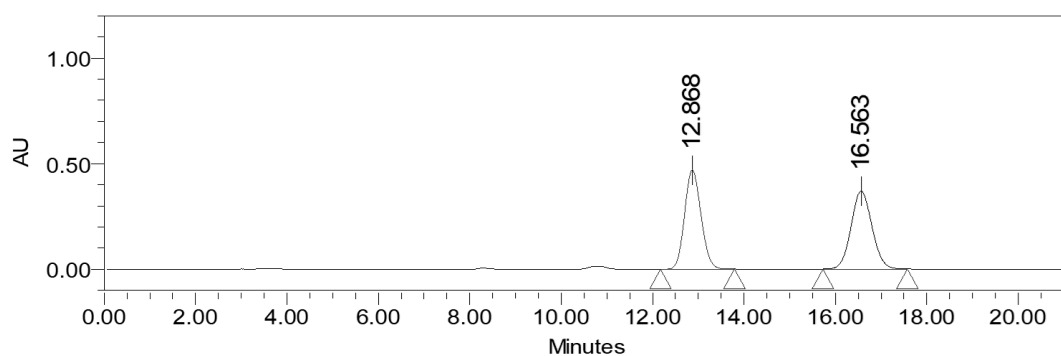
White foam. 81.1 mg. Yield = 83%. $[\alpha]_D^{20} = -102.153^\circ$
($c = 1.0$, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ 8.33 (s, 1H), 7.84 (d, $J = 8.9$ Hz, 1H), 7.62 (d, $J = 8.1$ Hz, 1H), 7.59 – 7.55 (m, 2H), 7.46 – 7.40 (m, 2H), 7.37 – 7.28 (m, 6H), 7.20 – 7.16 (m, 1H), 7.09 – 6.97 (m, 5H), 6.86 – 6.79 (m, 2H), 6.72 (dd, $J = 17.6, 10.9$ Hz, 1H), 5.79 (d, $J = 17.7$ Hz, 1H), 5.30 (d, $J = 10.8$ Hz, 1H).

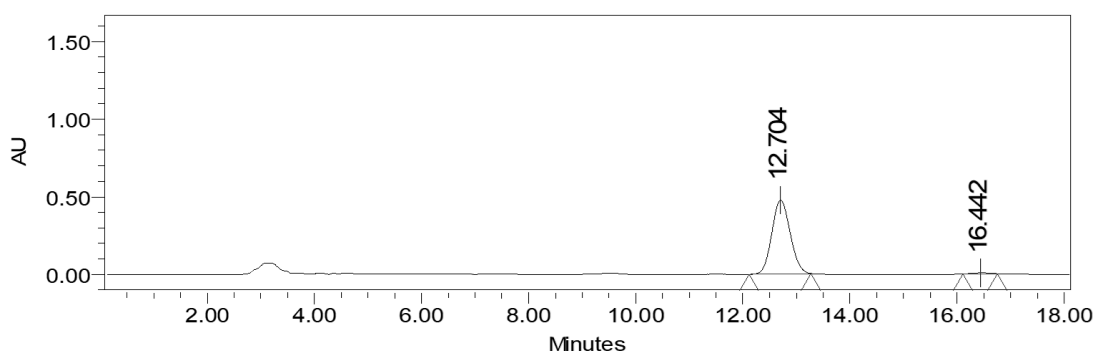
¹³C NMR (101 MHz, CDCl₃) δ 153.9, 146.3, 141.9, 138.5, 138.0, 136.1, 135.0, 134.6, 132.3, 132.3, 132.1, 130.9, 130.5, 129.5, 129.0, 128.8, 128.1, 127.5, 127.1, 126.9, 126.9, 123.7, 122.8, 119.9, 115.0, 111.2.

HRMS (ESI) calcd for C₃₂H₂₅O₃S⁺ m/z [M + H]⁺: 489.1519; found: 489.1505.

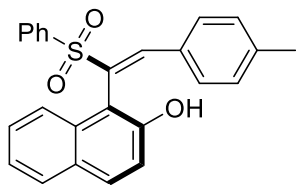
HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm): t_1 (major) = 12.704 min, t_2 (minor) = 16.442 min.



	Retention Time	Area	% Area	Height
1	12.868	11723631	49.92	470622
2	16.563	11759394	50.08	369632



	Retention Time	Area	% Area	Height
1	12.704	11298292	98.72	475290
2	16.442	146390	1.28	6627



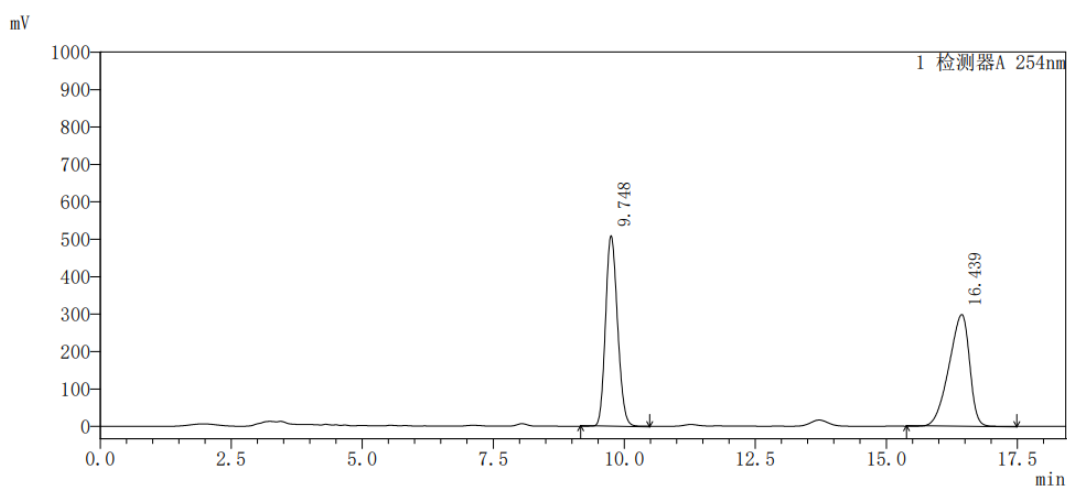
3ba

White foam. 72.1 mg. Yield = 90%. $[\alpha]_D^{20} = -184.739^\circ$ ($c = 0.7$, CHCl_3).

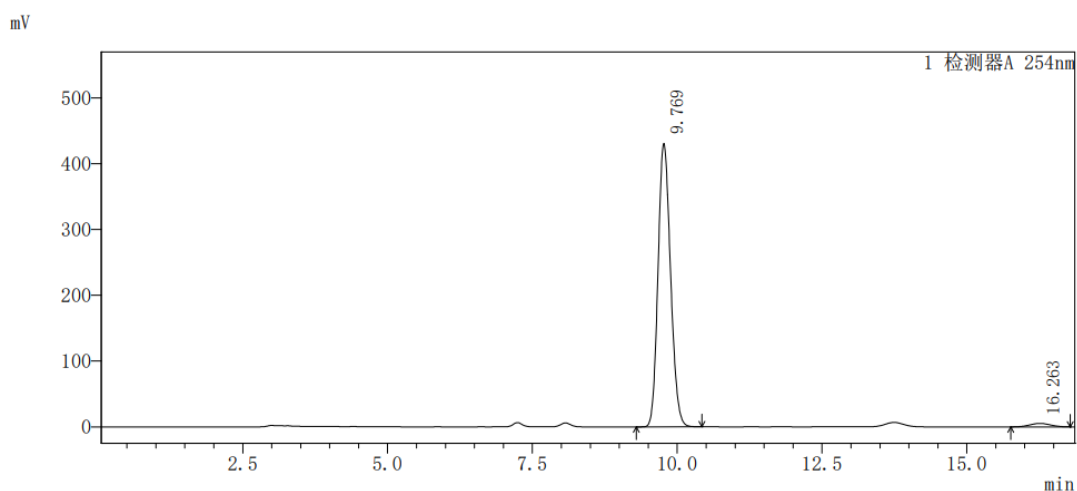
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.29 (s, 1H), 7.82 (d, $J = 8.9$ Hz, 1H), 7.62 (d, $J = 8.1$ Hz, 1H), 7.59 – 7.54 (m, 2H), 7.36 (s, 1H), 7.34 – 7.28 (m, 2H), 7.15 (t, $J = 7.9$ Hz, 2H), 7.11 – 7.06 (m, 1H), 6.90 – 6.78 (m, 6H), 2.16 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 153.9, 142.1, 141.6, 136.9, 133.6, 133.1, 132.2, 132.1, 130.6, 129.6, 129.5, 129.0, 128.9, 128.7, 128.0, 126.9, 123.7, 122.9, 119.8, 111.3, 21.5.

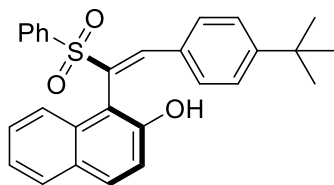
HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm): t_1 (major) = 9.769 min, t_2 (minor) = 16.263 min.



峰号	保留时间	面积	面积%	高度
1	9.748	8122141	49.889	509552
2	16.439	8158374	50.111	298704
总计		16280515	100.000	808256



峰号	保留时间	面积	面积%	高度
1	9.769	6467668	98.000	430626
2	16.263	131974	2.000	5289
总计		6599642	100.000	435916



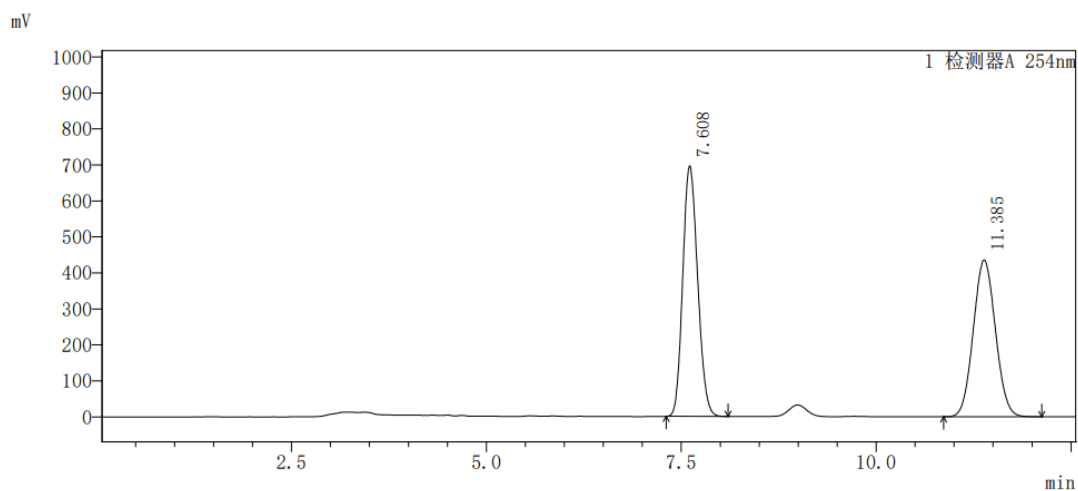
3ca

White foam. 57.7 mg. Yield = 65%. $[\alpha]_D^{20} = -155.153^\circ$ ($c = 1.0$, CHCl_3).

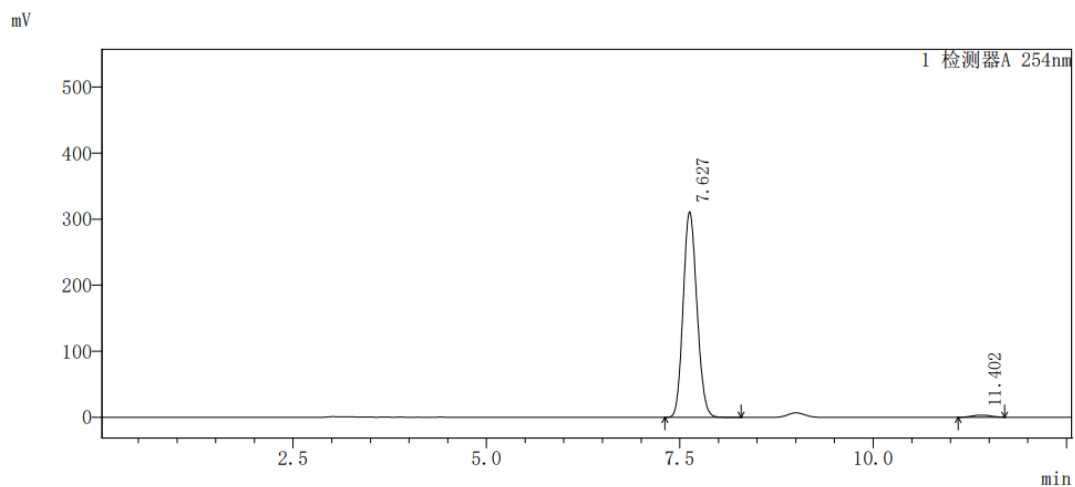
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.30 (s, 1H), 7.84 (d, $J = 8.9$ Hz, 1H), 7.65 (d, $J = 8.2$ Hz, 1H), 7.55 (d, $J = 7.0$ Hz, 2H), 7.35 – 7.29 (m, 2H), 7.22 (s, 1H), 7.19 – 7.05 (m, 5H), 6.93 – 6.82 (m, 4H), 1.15 (s, 9H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 154.7, 153.7, 141.9, 136.9, 133.6, 133.1, 132.3, 132.2, 130.6, 129.3, 129.0, 128.9, 128.7, 128.1, 126.9, 125.9, 123.7, 123.0, 119.8, 111.3, 34.9, 31.0.

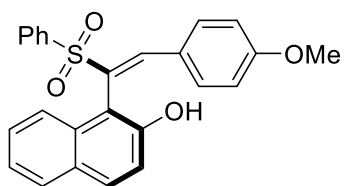
HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm): t_1 (major) = 7.627 min, t_2 (minor) = 11.402 min.



峰号	保留时间	面积	面积%	高度
1	7.608	9256827	51.827	696517
2	11.385	8604271	48.173	435424
总计		17861099	100.000	1131941



峰号	保留时间	面积	面积%	高度
1	7.627	3858458	98.502	311677
2	11.402	58688	1.498	3374
总计		3917146	100.000	315051



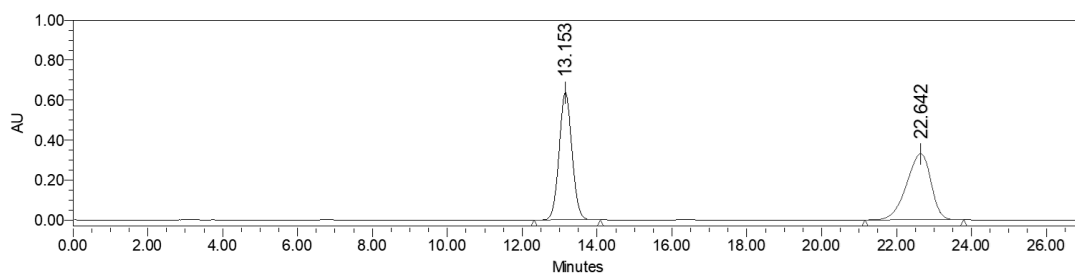
3da

White foam. 75.3 mg. Yield = 90%. $[\alpha]_D^{20} = -192.913^\circ$ ($c = 1.0$, CHCl_3).

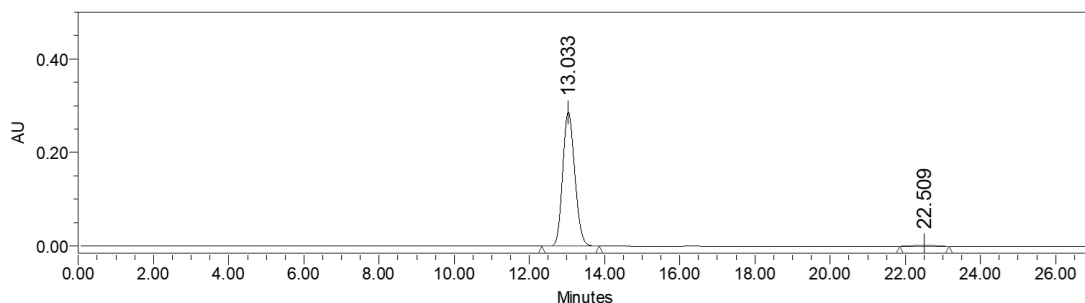
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.26 (s, 1H), 7.82 (d, $J = 8.9$ Hz, 1H), 7.63 (d, $J = 8.1$ Hz, 1H), 7.58 – 7.53 (m, 2H), 7.40 (s, 1H), 7.34 – 7.28 (m, 2H), 7.19 – 7.05 (m, 3H), 6.94 – 6.85 (m, 3H), 6.81 (d, $J = 8.5$ Hz, 1H), 6.55 (d, $J = 8.9$ Hz, 2H), 3.65 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 161.7, 153.9, 141.7, 137.0, 133.5, 132.5, 132.2, 132.1, 131.1, 129.0, 128.8, 128.7, 128.1, 126.9, 124.9, 123.7, 122.9, 119.9, 114.3, 111.3, 55.3.

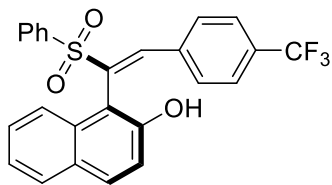
HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm): t_1 (major) = 13.033 min, t_2 (minor) = 22.509 min.



	Retention Time	Area	% Area	Height
1	13.153	15165410	50.29	638064
2	22.642	14992151	49.71	331128



	Retention Time	Area	% Area	Height
1	13.033	6402060	98.30	286639
2	22.509	110457	1.70	2997



3ea

White foam. 78.1 mg. Yield = 86%. $[\alpha]_D^{20} = -75.069^\circ$ (c = 1.0, CHCl₃).

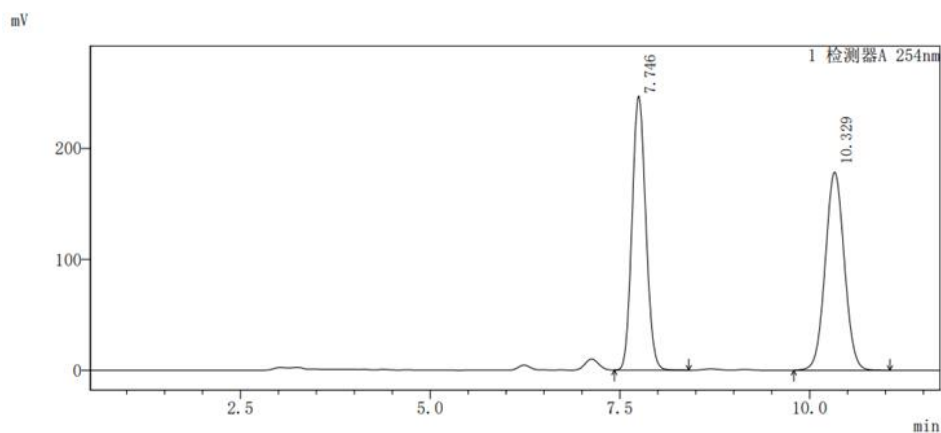
¹H NMR (400 MHz, CDCl₃) δ 8.33 (s, 1H), 7.84 (d, *J* = 8.9 Hz, 1H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.58 (d, *J* = 7.9 Hz, 2H), 7.39 – 7.28 (m, 5H), 7.17 (t, *J* = 7.8 Hz, 2H), 7.13 – 7.07 (m, 3H), 6.92 – 6.86 (m, 1H), 6.76 (d, *J* = 8.5 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 153.8, 140.0, 137.6, 136.2, 135.6, 134.0, 132.7, 132.2, 131.9, 131.8, 130.4, 129.1, 128.9, 128.9, 128.2, 127.2, 125.7, 125.7, 123.9, 122.4, 119.9, 110.6.

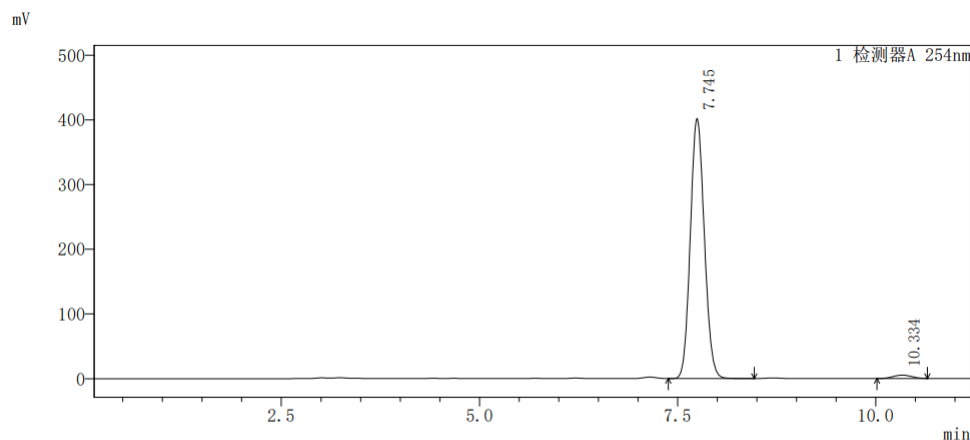
¹⁹F NMR (376 MHz, CDCl₃) δ -63.18.

HRMS (ESI) calcd for C₂₅H₁₈F₃O₃S⁺ m/z [M + H]⁺: 455.0923; found: 455.0919.

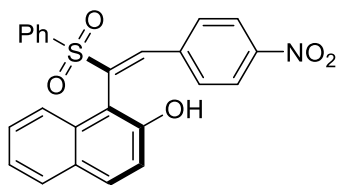
HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm): t₁ (major) = 7.745 min, t₂ (minor) = 10.334 min.



检测器A 254nm				
峰号	保留时间	面积	面积%	高度
1	7.746	3121787	49.903	247099
2	10.329	3133874	50.097	178541
总计		6255661	100.000	425640



检测器A 254nm				
峰号	保留时间	面积	面积%	高度
1	7.745	4955331	98.294	402187
2	10.334	85992	1.706	5261
总计		5041323	100.000	407448



3fa

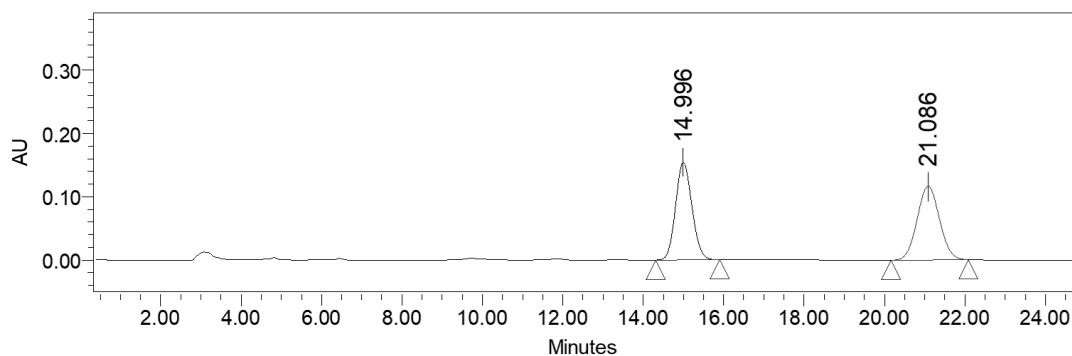
Yellow foam. 44.2 mg. Yield = 51%. $[\alpha]_D^{20} = -111.737^\circ$
($c = 0.6$, CHCl_3).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.34 (s, 1H), 7.93 – 7.83 (m, 3H), 7.64 (d, $J = 8.2$ Hz, 1H), 7.59 (d, $J = 8.0$ Hz, 2H), 7.45 (s, 1H), 7.40 – 7.31 (m, 2H), 7.23 – 7.07 (m, 5H), 6.92 – 6.86 (m, 1H), 6.71 (d, $J = 8.4$ Hz, 1H).

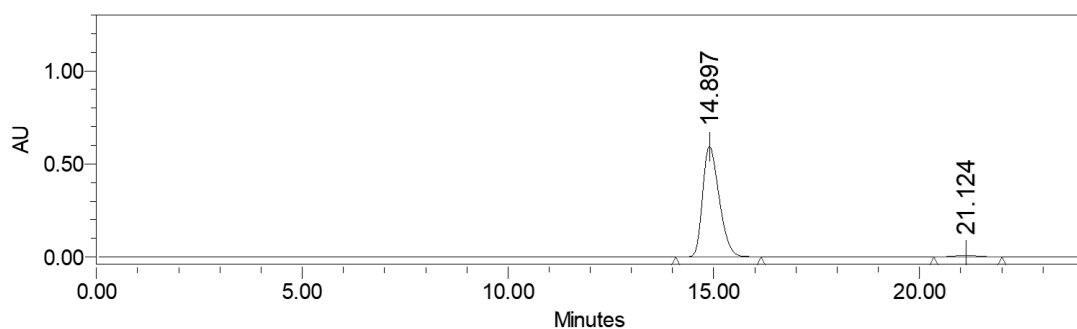
$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 154.0, 148.4, 139.5, 138.9, 138.4, 135.9, 134.2, 132.9, 131.6, 130.8, 129.1, 129.0, 128.3, 127.3, 124.1, 123.8, 122.1, 120.0.

HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{16}\text{NO}_5\text{S}^-$ m/z $[\text{M} - \text{H}]^-$: 430.0755; found: 430.0757.

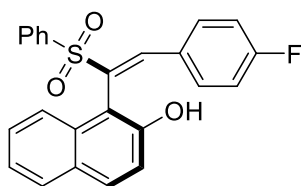
HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 300$ nm): t_1 (major) = 14.897 min, t_2 (minor) = 21.124 min.



	Retention Time	Area	% Area	Height
1	14.996	4355175	49.20	154199
2	21.086	4496913	50.80	116537



	Retention Time	Area	% Area	Height
1	14.897	16539980	97.91	592865
2	21.124	353471	2.09	9449



3ga

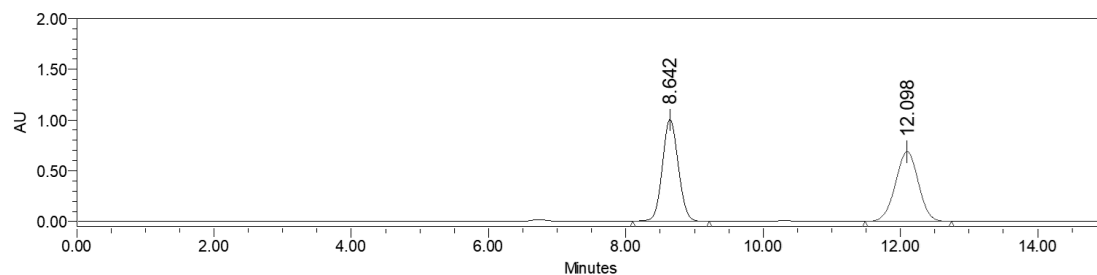
White foam. 49.7 mg. Yield = 61%. $[\alpha]_D^{20} = -127.529^\circ$ ($c = 1.0$, CHCl_3).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.28 (s, 1H), 7.83 (d, $J = 8.9$ Hz, 1H), 7.63 (d, $J = 8.1$ Hz, 1H), 7.59 – 7.54 (m, 2H), 7.43 (s, 1H), 7.35 – 7.29 (m, 2H), 7.15 (t, $J = 7.9$ Hz, 2H), 7.12 – 7.06 (m, 1H), 7.00 – 6.94 (m, 2H), 6.91 – 6.85 (m, 1H), 6.80 – 6.69 (m, 3H).

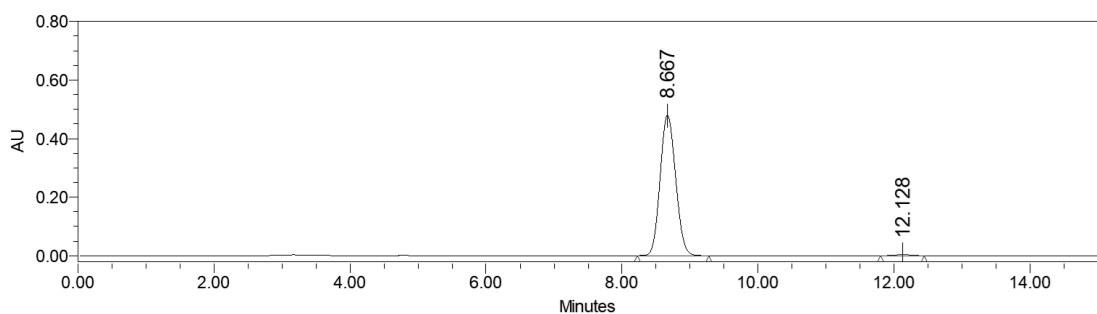
$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 163.9 (d, $J = 254.4$ Hz), 153.9, 140.6, 136.6, 134.2 (d, $J = 2.5$ Hz), 133.8, 132.6, 132.5, 132.4, 131.9, 129.0, 128.9, 128.8, 128.5 (d, $J = 3.3$ Hz), 128.1, 127.0, 123.8, 122.6, 119.9, 116.1, 115.9, 110.8.

$^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -107.68.

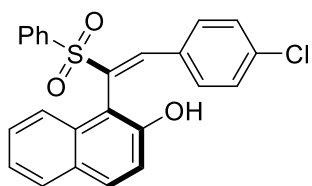
HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm): t_1 (major) = 8.667 min, t_2 (minor) = 12.128 min.



	Retention Time	Area	% Area	Height
1	8.642	16244855	50.51	1003618
2	12.098	15913848	49.49	686819



	Retention Time	Area	% Area	Height
1	8.667	7594783	98.92	479169
2	12.128	82631	1.08	4286



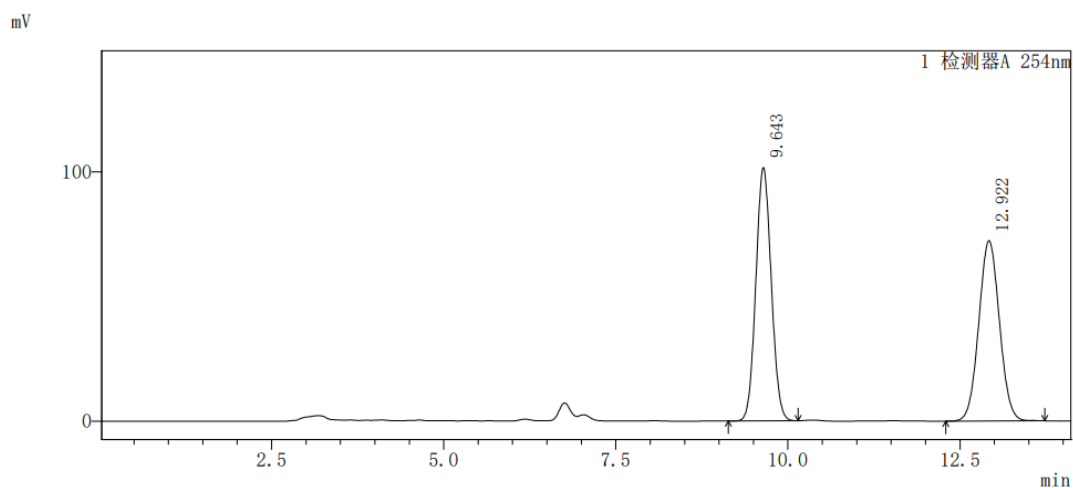
3ha

White foam. 59.8 mg. Yield = 71%. $[\alpha]_D^{20} = +165.966^\circ$ (c = 1.0, CHCl₃).

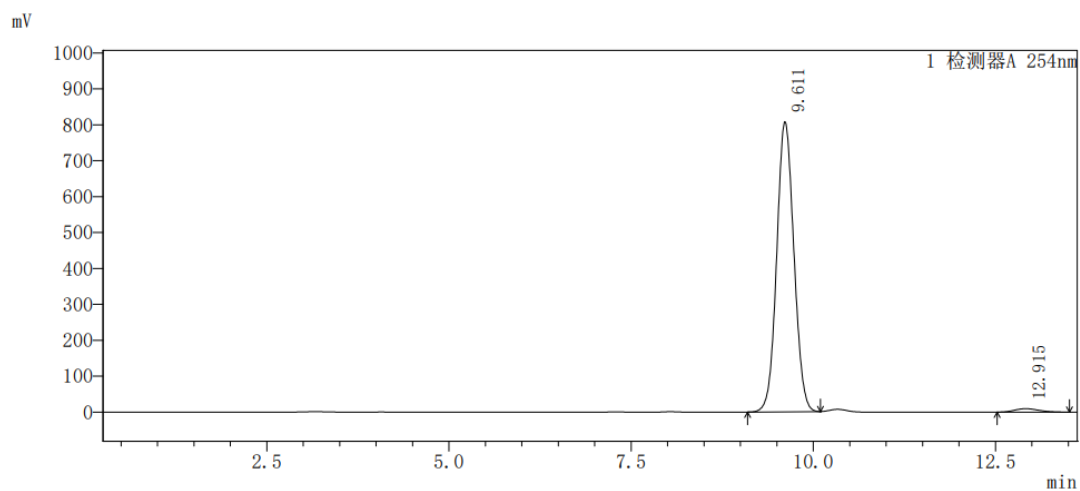
¹H NMR (400 MHz, CDCl₃) δ 8.26 (s, 1H), 7.82 (d, *J* = 8.9 Hz, 1H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.59 – 7.54 (m, 2H), 7.43 (s, 1H), 7.35 – 7.28 (m, 2H), 7.19 – 7.13 (m, 2H), 7.12 – 7.06 (m, 1H), 7.03 – 6.98 (m, 2H), 6.92 – 6.85 (m, 3H), 6.76 (d, *J* = 8.5 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 153.9, 140.5, 137.0, 136.5, 135.3, 133.8, 132.5, 131.8, 131.5, 130.7, 129.1, 128.9, 128.8, 128.1, 127.1, 123.8, 122.5, 119.8, 110.7.

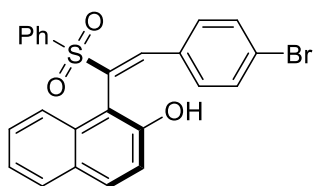
HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm): t₁ (major) = 9.611 min, t₂ (minor) = 12.915 min.



峰号	保留时间	面积	面积%	高度
1	9.643	1583561	51.187	101703
2	12.922	1510139	48.813	72397
总计		3093699	100.000	174100



峰号	保留时间	面积	面积%	高度
1	9.611	13241619	98.347	808155
2	12.915	222522	1.653	9691
总计		13464141	100.000	817847



3ia

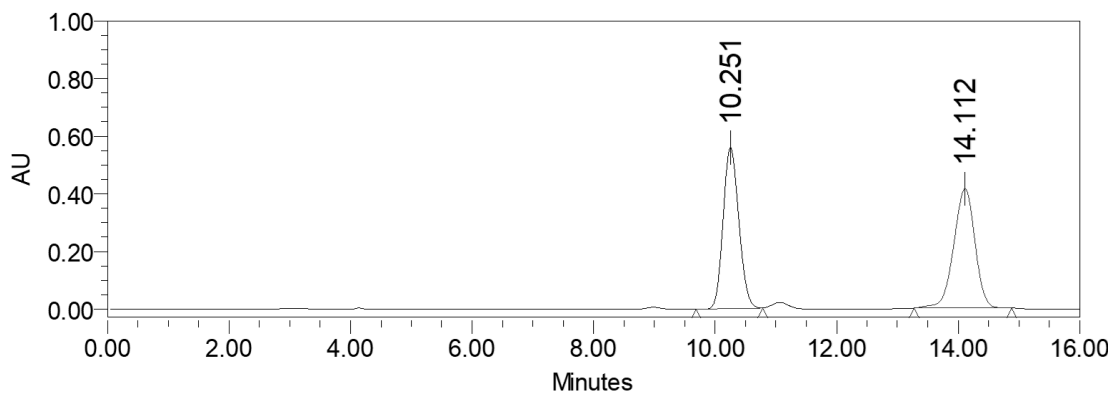
White foam. 60.3 mg. Yield = 65%. $[\alpha]_D^{20} = -149.706^\circ$ (c = 1.0, CHCl_3).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.24 (s, 1H), 7.83 (d, $J = 8.8$ Hz, 1H), 7.63 (d, $J = 8.1$ Hz, 1H), 7.59 – 7.54 (m, 2H), 7.41 (s, 1H), 7.36 – 7.29 (m, 2H), 7.22 – 7.13 (m, 4H), 7.13 – 7.07 (m, 1H), 6.91 – 6.80 (m, 3H), 6.75 (d, $J = 8.5$ Hz, 1H).

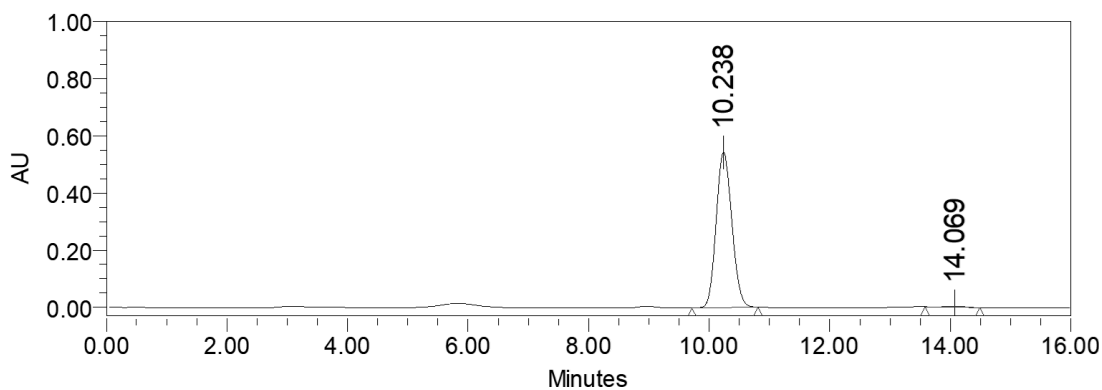
$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 153.8, 140.5, 136.4, 135.4, 133.9, 132.5, 132.1, 131.8, 131.7, 131.1, 129.0, 128.8, 128.2, 127.1, 125.6, 123.8, 122.5, 119.9, 110.8.

HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{18}\text{BrO}_3\text{S}^+$ m/z $[\text{M} + \text{H}]^+$: 465.0155; found: 465.0155.

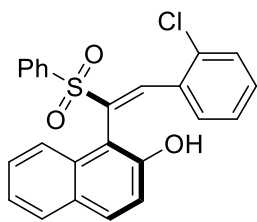
HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 270$ nm): t_1 (major) = 10.238 min, t_2 (minor) = 14.069 min.



	Retention Time	Area	% Area	Height
1	10.251	10010862	49.88	558510
2	14.112	10058385	50.12	414261



	Retention Time	Area	% Area	Height
1	10.238	9815522	99.12	543938
2	14.069	86738	0.88	4313



3ja

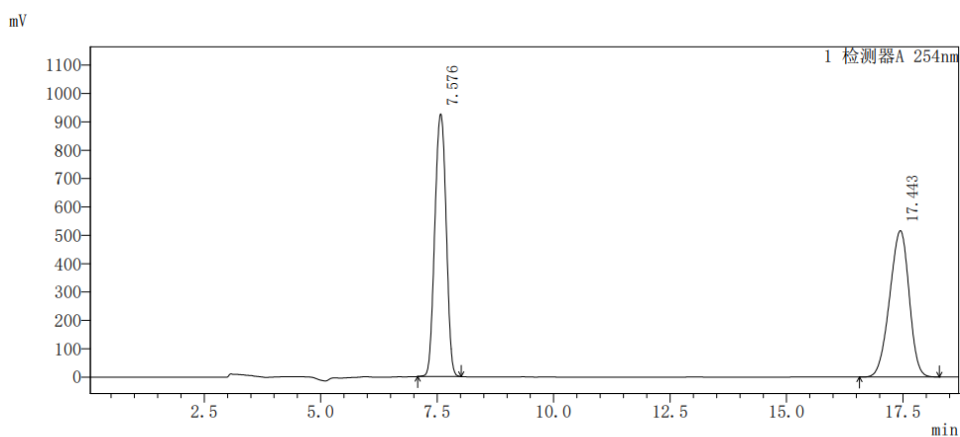
White foam. 70.0 mg. Yield = 83%. $[\alpha]_D^{20} = +108.438^\circ$ ($c = 1.0$, CHCl_3).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.66 (s, 1H), 7.74 (d, $J = 8.9$ Hz, 1H), 7.65 – 7.57 (m, 3H), 7.54 (d, $J = 8.1$ Hz, 1H), 7.36 – 7.30 (m, 1H), 7.30 – 7.22 (m, 2H), 7.21 – 7.15 (m, 2H), 7.06 – 6.98 (m, 2H), 6.93 – 6.87 (m, 1H), 6.80 (d, $J = 8.5$ Hz, 1H), 6.75 (dd, $J = 7.9, 1.8$ Hz, 1H), 6.71 – 6.66 (m, 1H).

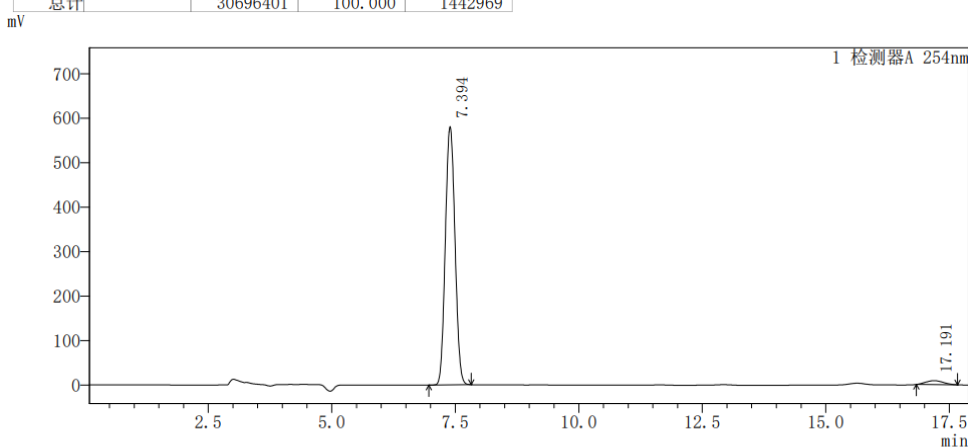
$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 154.5, 139.4, 137.6, 136.5, 135.1, 133.9, 132.3, 131.9, 131.2, 130.9, 129.5, 129.3, 129.0, 128.9, 128.9, 128.8, 128.0, 126.9, 126.8, 123.6, 122.5, 119.5, 110.7.

HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{18}\text{ClO}_3\text{S}^+$ m/z $[\text{M} + \text{H}]^+$: 421.0660; found: 421.0657.

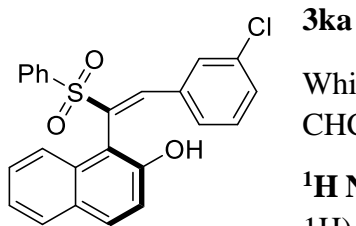
HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm): t_1 (major) = 7.394 min, t_2 (minor) = 17.191 min.



峰号	保留时间	面积	面积%	高度
1	7.576	15689849	51.113	926609
2	17.443	15006552	48.887	516360
总计		30696401	100.000	1442969



峰号	保留时间	面积	面积%	高度
1	7.394	7873254	97.308	581328
2	17.191	217793	2.692	8827
总计		8091047	100.000	590155



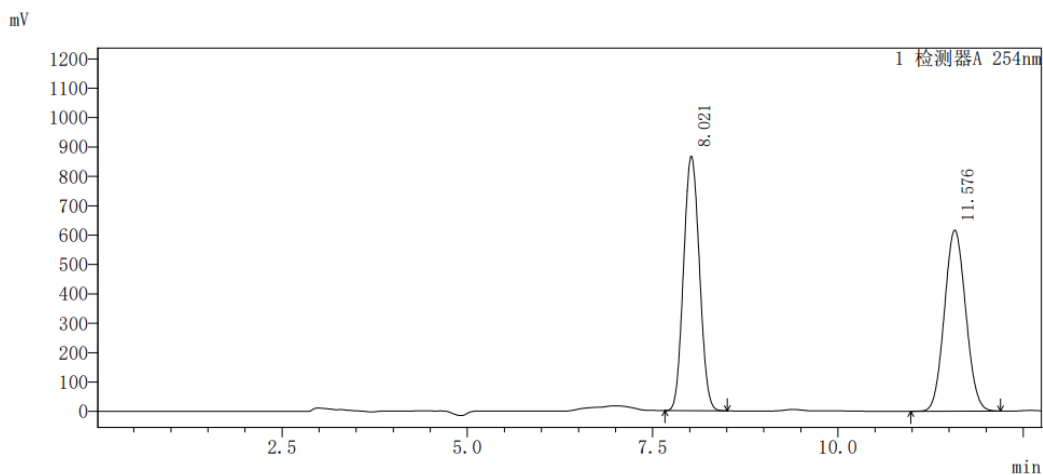
White foam. 55.4 mg. Yield = 66%. $[\alpha]_D^{20} = -106.576^\circ$ (c = 1.0, CHCl_3).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.23 (s, 1H), 7.83 (d, $J = 8.9$ Hz, 1H), 7.62 (d, $J = 8.0$ Hz, 1H), 7.60 – 7.55 (m, 2H), 7.43 (s, 1H), 7.36 – 7.29 (m, 2H), 7.20 – 7.14 (m, 2H), 7.14 – 7.06 (m, 2H), 7.00 (t, $J = 2.0$ Hz, 1H), 6.95 – 6.85 (m, 2H), 6.79 (d, $J = 8.0$ Hz, 1H), 6.75 (d, $J = 8.5$ Hz, 1H).

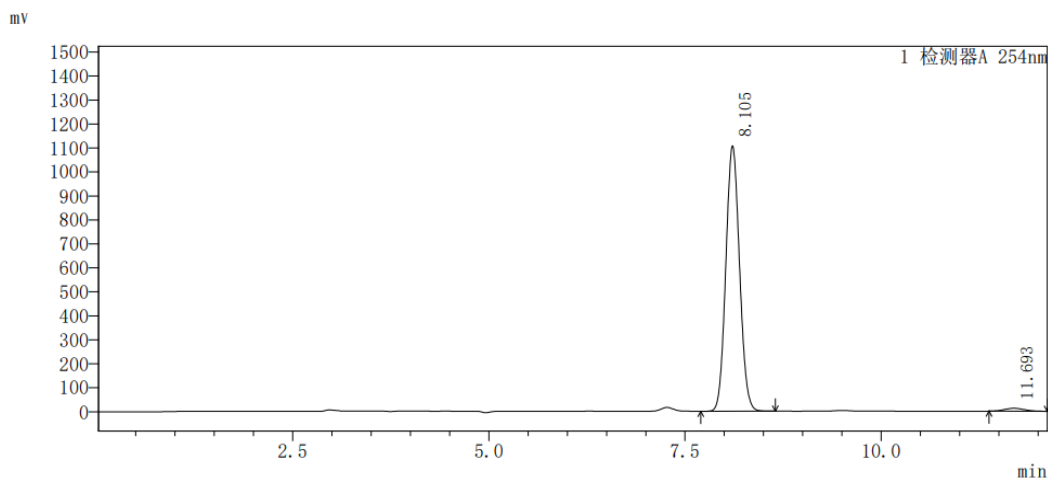
$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 153.9, 140.3, 136.5, 136.4, 134.6, 134.0, 133.9, 132.6, 131.8, 130.7, 130.5, 129.9, 129.0, 129.0, 128.8, 128.2, 127.9, 127.1, 123.8, 122.5, 119.9, 110.7.

HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{18}\text{ClO}_3\text{S}^+$ m/z $[\text{M} + \text{H}]^+$: 421.0660; found: 421.0656.

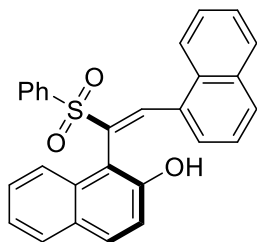
HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm): t_1 (major) = 8.105 min, t_2 (minor) = 11.693 min.



峰号	保留时间	面积	面积%	高度
1	8.021	12943341	51.209	866734
2	11.576	12331955	48.791	616673
总计		25275297	100.000	1483406



峰号	保留时间	面积	面积%	高度
1	8.105	13428255	98.426	1106844
2	11.693	214719	1.574	12299
总计		13642974	100.000	1119143



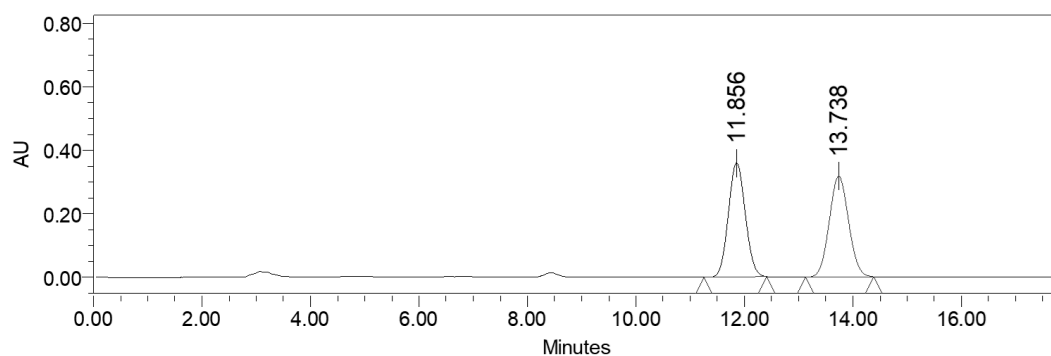
3la

White foam. 60.2 mg. Yield = 69%. $[\alpha]_D^{20} = +202.712^\circ$ (c = 1.0, CHCl_3).

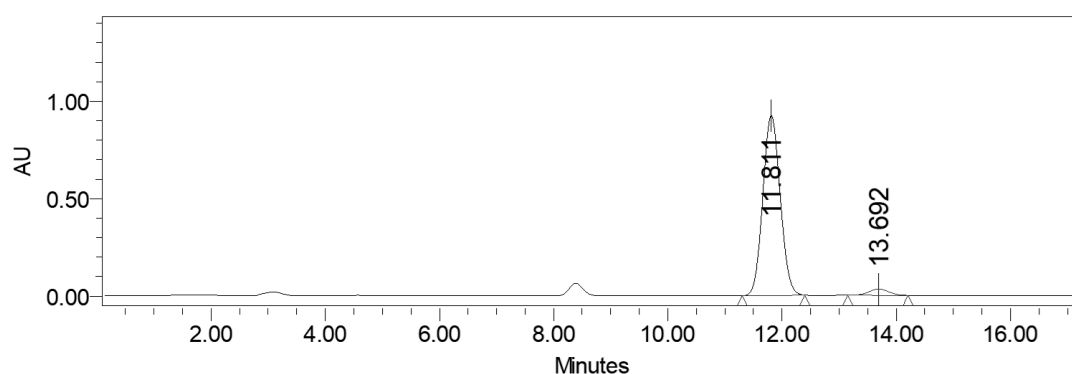
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.13 (s, 1H), 8.26 (d, J = 8.4 Hz, 1H), 7.77 – 7.70 (m, 2H), 7.67 – 7.55 (m, 5H), 7.54 – 7.46 (m, 2H), 7.36 – 7.27 (m, 2H), 7.22 – 7.14 (m, 2H), 7.06 (d, J = 7.3 Hz, 1H), 7.00 – 6.92 (m, 2H), 6.79 (d, J = 8.4 Hz, 1H), 6.75 – 6.70 (m, 1H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 154.5, 139.9, 136.7, 136.6, 133.8, 133.4, 132.1, 132.0, 131.8, 130.8, 129.0, 129.0, 128.8, 128.8, 127.9, 127.2, 126.9, 126.7, 126.3, 125.3, 123.5, 123.2, 122.6, 119.6, 111.3.

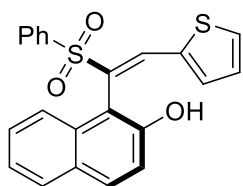
HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 220$ nm): t_1 (major) = 11.811 min, t_2 (minor) = 13.692 min.



	Retention Time	Area	% Area	Height
1	11.856	7783472	49.80	359280
2	13.738	7847164	50.20	317473



	Retention Time	Area	% Area	Height
1	11.811	19517773	96.19	923589
2	13.692	773498	3.81	31975



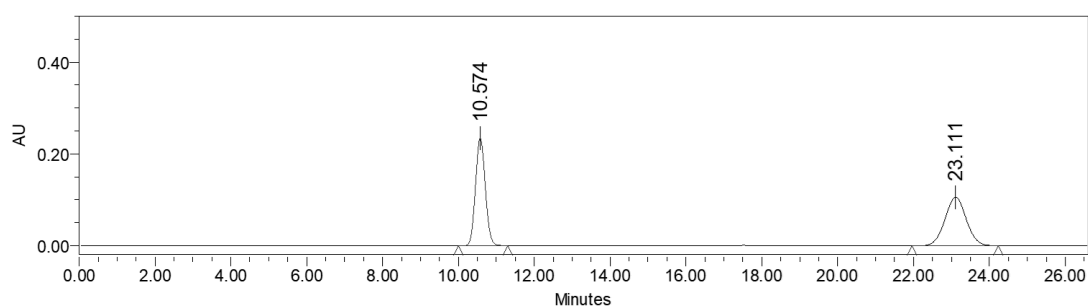
3ma

White foam. 62.8 mg. Yield = 80%. $[\alpha]_D^{20} = -235.772^\circ$ ($c = 0.3$, CHCl_3).

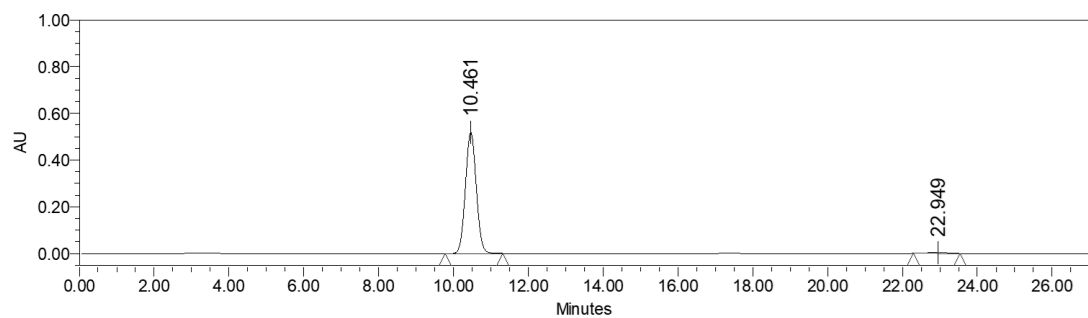
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.48 (s, 1H), 7.88 (d, $J = 8.9$ Hz, 1H), 7.67 (d, $J = 8.1$ Hz, 1H), 7.64 – 7.60 (m, 2H), 7.40 – 7.30 (m, 2H), 7.28 – 7.09 (m, 6H), 6.93 – 6.85 (m, 2H), 6.79 (d, $J = 8.5$ Hz, 1H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 154.3, 137.1, 135.7, 135.5, 135.2, 133.7, 133.1, 132.8, 132.7, 130.8, 129.4, 128.9, 128.9, 128.9, 128.2, 127.0, 126.9, 123.7, 122.4, 120.0, 110.1.

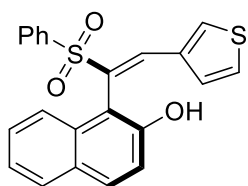
HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 220$ nm): t_1 (major) = 10.461 min, t_2 (minor) = 22.949 min.



	Retention Time	Area	% Area	Height
1	10.574	4199030	50.58	234221
2	23.111	4101960	49.42	105235



	Retention Time	Area	% Area	Height
1	10.461	10437362	98.44	519086
2	22.949	165903	1.56	4270



3na

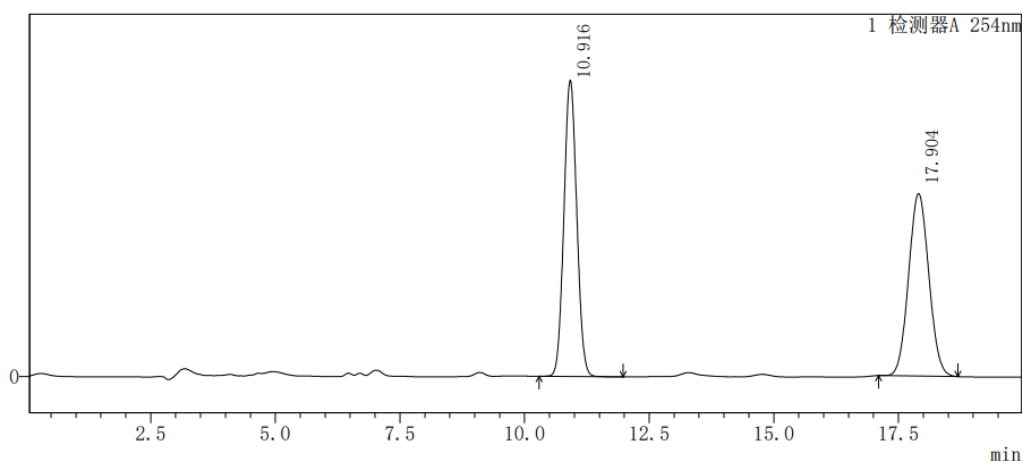
White foam. 60.1 mg. Yield = 76%. $[\alpha]_D^{20} = -162.932^\circ$ ($c = 1.0$, CHCl_3).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.32 (s, 1H), 7.84 (d, $J = 8.9$ Hz, 1H), 7.65 (d, $J = 8.1$ Hz, 1H), 7.61 – 7.55 (m, 2H), 7.39 – 7.29 (m, 3H), 7.21 – 7.08 (m, 4H), 6.94 – 6.86 (m, 2H), 6.79 (d, $J = 8.5$ Hz, 1H), 6.24 (dd, $J = 5.1, 1.3$ Hz, 1H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 153.7, 136.9, 135.8, 134.3, 133.7, 132.5, 132.3, 131.8, 128.9, 128.8, 128.8, 128.1, 127.5, 127.0, 126.5, 123.8, 122.8, 119.9, 111.2.

HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm): t_1 (major) = 10.901 min, t_2 (minor) = 17.889 min.

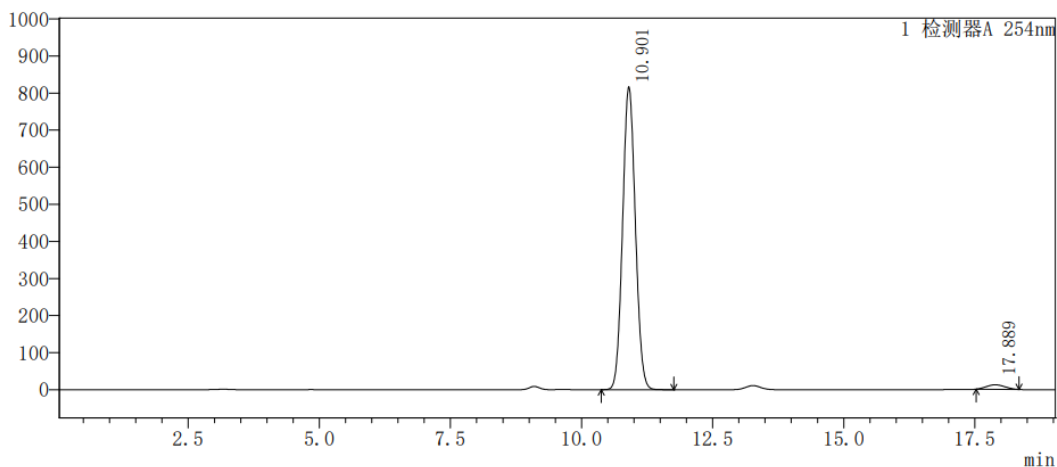
mV



检测器A 254nm

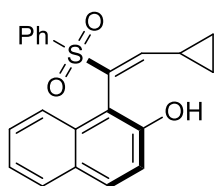
峰号	保留时间	面积	面积%	高度
1	10.916	822733	50.766	45928
2	17.904	797900	49.234	28265
总计		1620632	100.000	74193

mV



检测器A 254nm

峰号	保留时间	面积	面积%	高度
1	10.901	13827000	97.906	817180
2	17.889	295674	2.094	12062
总计		14122674	100.000	829242



30a

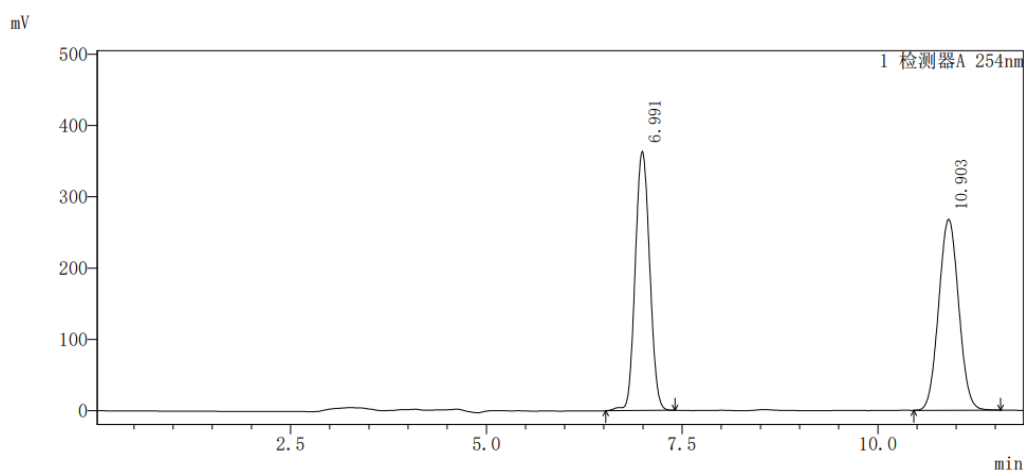
White foam. 37.0 mg. Yield = 53%. $[\alpha]_D^{20} = -37.021^\circ$ (c = 0.6, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, $J = 8.8$ Hz, 1H), 7.65 (d, $J = 8.3$ Hz, 1H), 7.60 (s, 1H), 7.58 – 7.52 (m, 2H), 7.36 – 7.31 (m, 1H), 7.28 (d, $J = 8.9$ Hz, 1H), 7.22 – 7.12 (m, 3H), 7.07 – 7.01 (m, 1H), 6.94 – 6.88 (m, 2H), 0.98 – 0.88 (m, 1H), 0.88 – 0.75 (m, 4H).

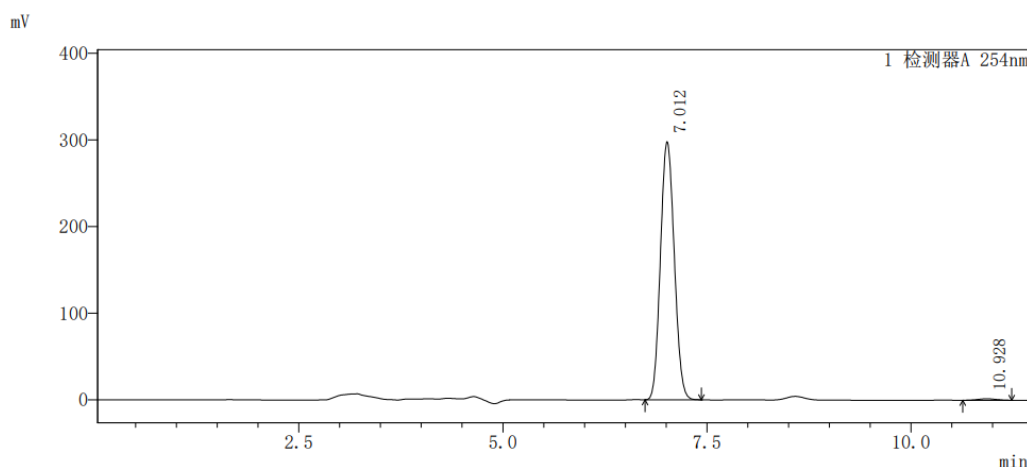
¹³C NMR (101 MHz, CDCl₃) δ 154.2, 153.2, 137.4, 133.5, 132.9, 132.8, 131.8, 128.8, 128.8, 128.5, 128.1, 126.7, 123.4, 123.1, 119.8, 110.5, 13.0, 9.4, 9.2.

HRMS (ESI) calcd for C₂₁H₁₉O₃S⁺ m/z [M + H]⁺: 351.1049; found: 351.1051.

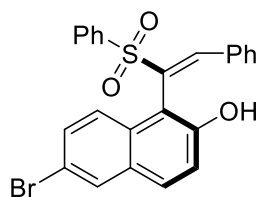
HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm): t_1 (major) = 7.012 min, t_2 (minor) = 10.928 min.



检测器A 254nm				
峰号	保留时间	面积	面积%	高度
1	6.991	4668497	49.547	363352
2	10.903	4753813	50.453	267803
总计		9422310	100.000	631155



检测器A 254nm				
峰号	保留时间	面积	面积%	高度
1	7.012	3511596	99.231	297675
2	10.928	27207	0.769	1687
总计		3538803	100.000	299363



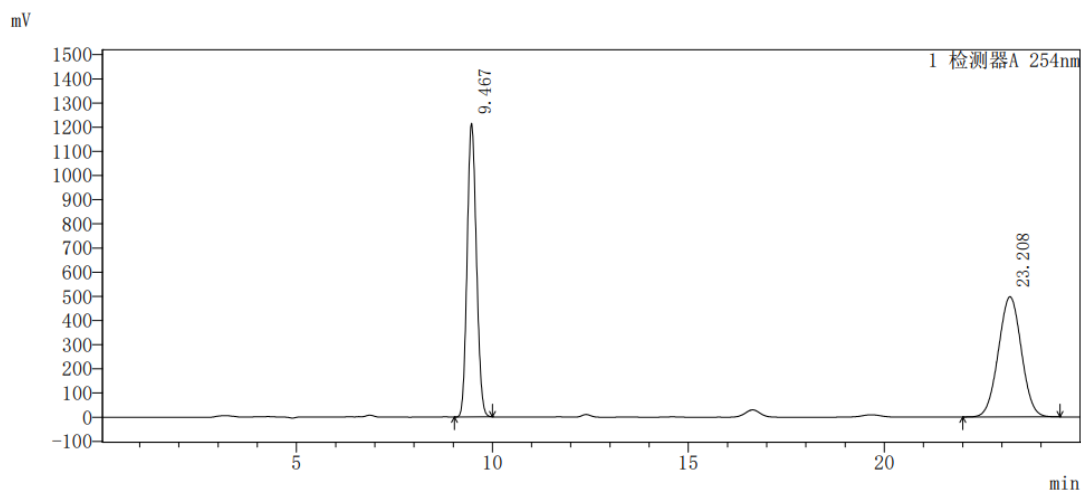
3pa

White foam. 72.4 mg. Yield = 78%. $[\alpha]_D^{20} = -118.708^\circ$ (c = 1.0, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ 8.31 (s, 1H), 7.78 (d, *J* = 2.1 Hz, 1H), 7.73 (d, *J* = 9.0 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.47 (s, 1H), 7.43 – 7.34 (m, 1H), 7.33 (d, *J* = 8.9 Hz, 1H), 7.24 – 7.16 (m, 3H), 7.10 – 7.02 (m, 2H), 6.98 – 6.90 (m, 3H), 6.67 (d, *J* = 9.0 Hz, 1H).

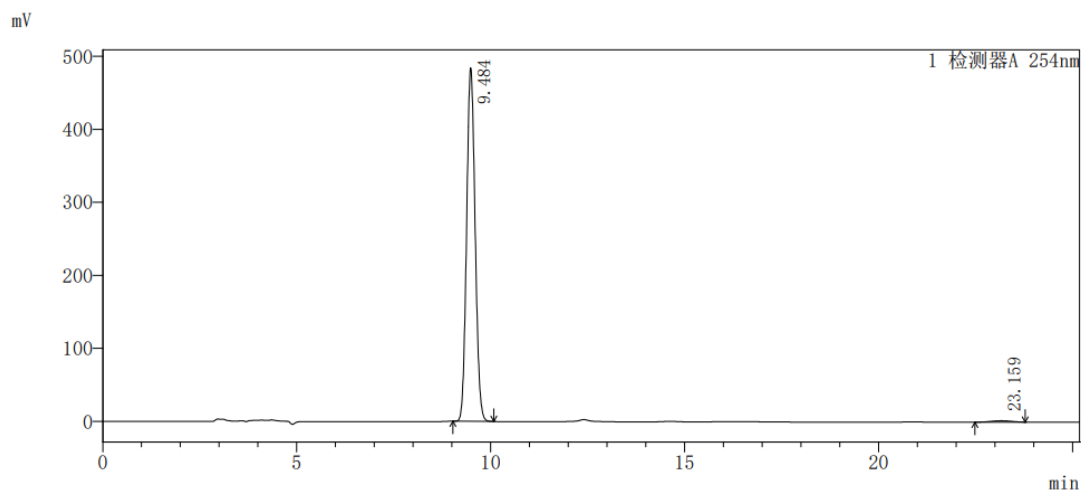
¹³C NMR (101 MHz, CDCl₃) δ 154.3, 142.4, 136.5, 134.0, 133.9, 132.0, 131.3, 131.1, 130.6, 130.4, 130.1, 128.9, 128.9, 128.9, 124.6, 121.1, 117.5, 111.4.

HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm): t₁ (major) = 9.484 min, t₂ (minor) = 23.159 min.



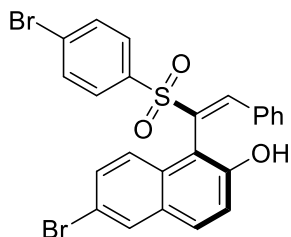
检测器A 254nm

峰号	保留时间	面积	面积%	高度
1	9.467	20018677	49.656	1215358
2	23.208	20296207	50.344	497456
总计		40314884	100.000	1712814



检测器A 254nm

峰号	保留时间	面积	面积%	高度
1	9.484	7388617	99.026	484183
2	23.159	72675	0.974	1979
总计		7461291	100.000	486162



3pg

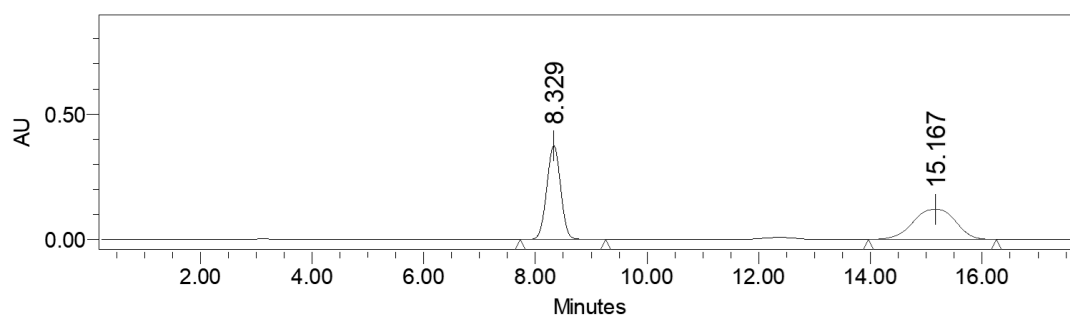
White foam. 101.5 mg. Yield = 93%. $[\alpha]_D^{20} = -71.002^\circ$ (c = 1.0, CHCl_3).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.30 (s, 1H), 7.83 (d, $J = 2.1$ Hz, 1H), 7.766 (d, $J = 9.0$ Hz, 1H), 7.44 – 7.38 (m, 2H), 7.37 – 7.32 (m, 3H), 7.25 – 7.19 (m, 2H), 7.11 – 7.05 (m, 2H), 7.02 (dd, $J = 9.0, 2.0$ Hz, 1H), 6.99 – 6.94 (m, 2H), 6.71 (d, $J = 9.0$ Hz, 1H).

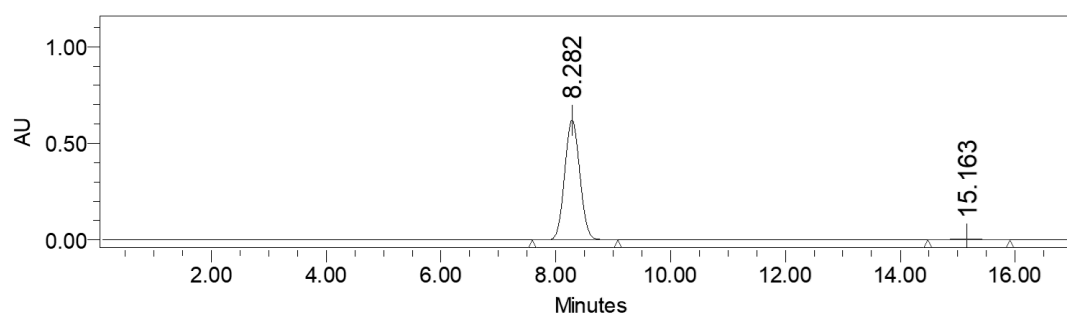
$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 154.1, 142.9, 135.8, 133.5, 132.1, 131.8, 131.5, 131.3, 130.6, 130.4, 130.4, 130.3, 130.3, 130.1, 129.4, 128.9, 124.5, 120.9, 117.7, 110.9.

HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{17}\text{Br}_2\text{O}_3\text{S}^+$ m/z $[\text{M} + \text{H}]^+$: 542.9260; found: 542.9257.

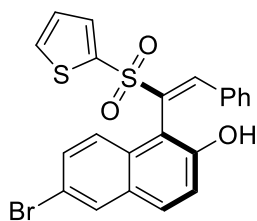
HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm): t_1 (major) = 8.282 min, t_2 (minor) = 15.163 min.



	Retention Time	Area	% Area	Height
1	8.329	6431975	50.50	373488
2	15.167	6305561	49.50	119864



	Retention Time	Area	% Area	Height
1	8.282	11357966	98.32	620948
2	15.163	194297	1.68	4230



3ph

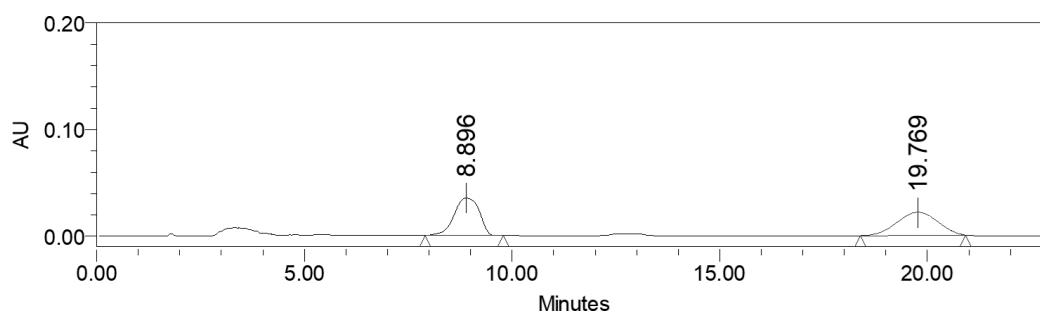
White foam. 87.5 mg. Yield = 93%. $[\alpha]_D^{20} = -75.740^\circ$ ($c = 1.0$, CHCl_3).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.31 (s, 1H), 7.83 (d, $J = 2.1$ Hz, 1H), 7.77 (d, $J = 8.9$ Hz, 1H), 7.46 (dd, $J = 5.0, 1.3$ Hz, 1H), 7.38 – 7.30 (m, 2H), 7.26 (dd, $J = 3.8, 1.4$ Hz, 1H), 7.23 – 7.16 (m, 1H), 7.10 – 7.01 (m, 3H), 7.00 – 6.94 (m, 2H), 6.83 (d, $J = 9.0$ Hz, 1H), 6.79 (dd, $J = 5.0, 3.8$ Hz, 1H)

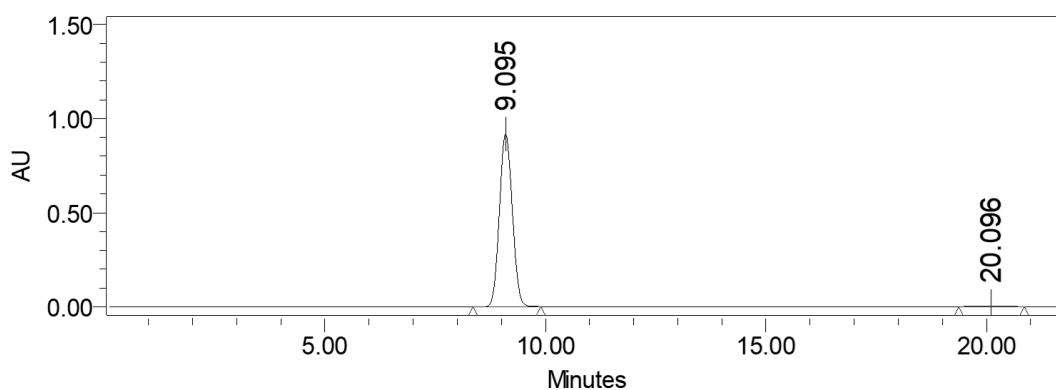
$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 154.4, 142.2, 137.0, 135.6, 135.4, 134.0, 131.9, 131.4, 131.2, 131.1, 130.4, 130.3, 130.2, 130.1, 128.9, 128.0, 124.4, 121.1, 117.6, 111.2.

HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{16}\text{BrO}_3\text{S}_2^+$ m/z $[\text{M} + \text{H}]^+$: 470.9719; found: 470.9714.

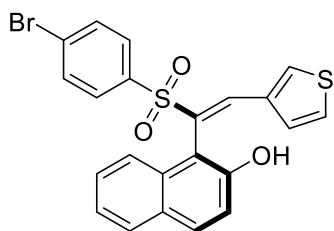
HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 280$ nm): t_1 (major) = 9.095 min, t_2 (minor) = 20.096 min.



	Retention Time	Area	% Area	Height
1	8.896	1482985	50.04	35216
2	19.769	1480687	49.96	21752



	Retention Time	Area	% Area	Height
1	9.095	18641788	99.08	917405
2	20.096	173007	0.92	3409



3ng

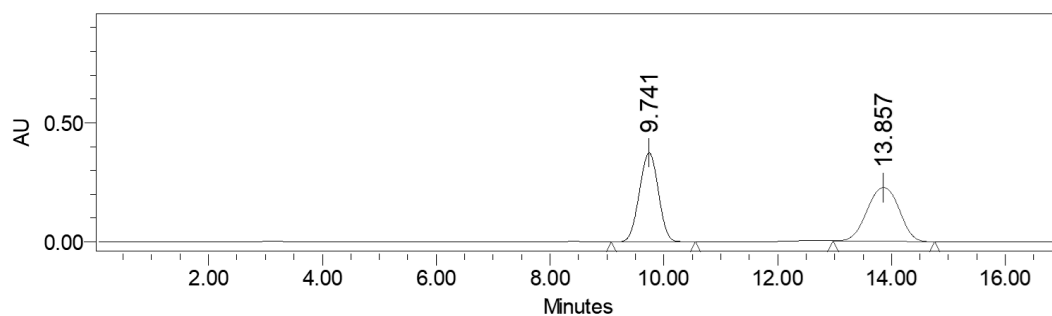
White foam. 67.3 mg. Yield = 71%. $[\alpha]_D^{20} = -35.498^\circ$ (c = 1.0, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ 8.32 (s, 1H), 7.86 (d, *J* = 9.0 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.44 – 7.39 (m, 2H), 7.35 – 7.29 (m, 3H), 7.23 – 7.13 (m, 3H), 7.01 – 6.92 (m, 2H), 6.81 (d, *J* = 8.5 Hz, 1H), 6.27 (dd, *J* = 5.2, 1.1 Hz, 1H).

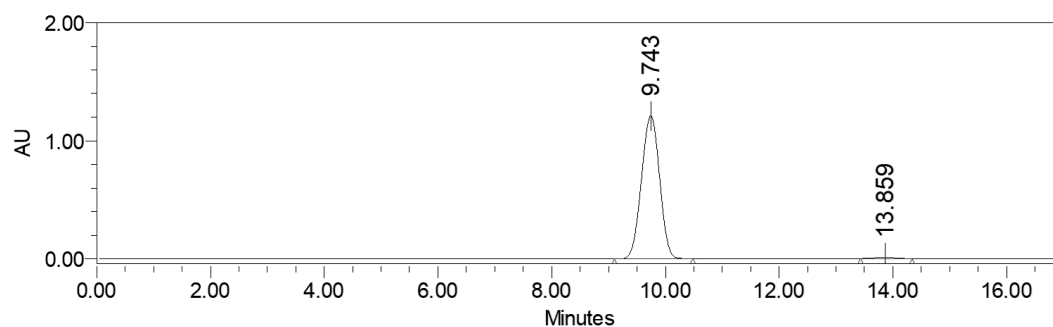
¹³C NMR (101 MHz, CDCl₃) δ 153.8, 136.2, 136.2, 134.2, 132.5, 132.2, 132.1, 132.1, 130.3, 129.1, 129.0, 128.3, 127.4, 127.3, 126.7, 124.0, 122.6, 119.8, 110.8.

HRMS (ESI) calcd for C₂₂H₁₆BrO₃S₂⁺ m/z [M + H]⁺: 470.9719; found: 470.9717.

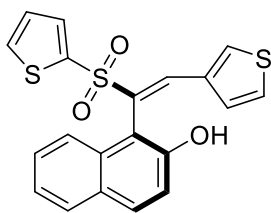
HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm): t₁ (major) = 9.743 min, t₂ (minor) = 13.859 min.



	Retention Time	Area	% Area	Height
1	9.741	8666025	49.58	374032
2	13.857	8811702	50.42	225525



	Retention Time	Area	% Area	Height
1	9.743	26827499	98.74	1210079
2	13.859	343038	1.26	11125



3nh

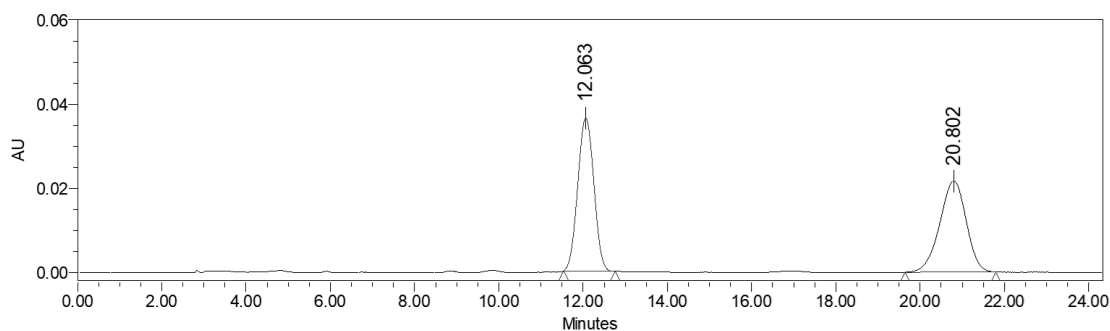
White foam. 58.1 mg. Yield = 73%. $[\alpha]_D^{20} = -109.573^\circ$ ($c = 1.0$, CHCl_3).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.31 (s, 1H), 7.87 (d, $J = 9.0$ Hz, 1H), 7.71 (d, $J = 8.4$ Hz, 1H), 7.43 (dt, $J = 4.9, 1.1$ Hz, 2H), 7.31 (dd, $J = 8.9, 1.5$ Hz, 1H), 7.27 – 7.24 (m, 1H), 7.21 – 7.14 (m, 2H), 7.05 – 6.97 (m, 2H), 6.95 – 6.91 (m, 1H), 6.81 – 6.74 (m, 1H), 6.28 (dd, $J = 5.2, 1.2$ Hz, 1H).

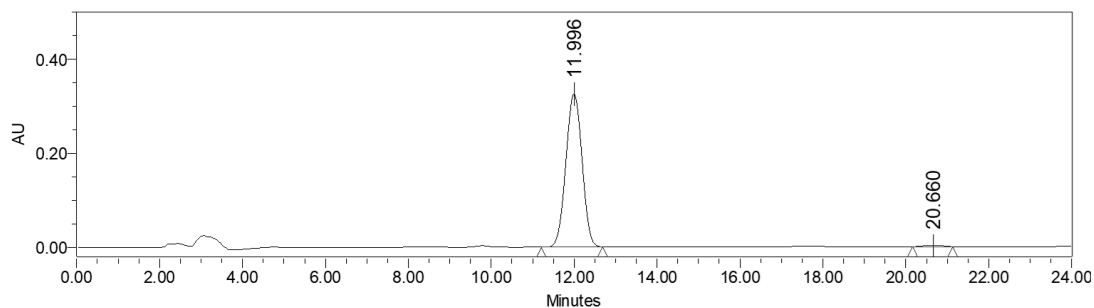
$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 153.9, 137.8, 135.4, 135.3, 134.8, 134.3, 132.9, 132.3, 131.7, 128.8, 128.2, 127.8, 127.4, 127.2, 126.5, 123.8, 122.6, 119.7, 119.7, 110.8.

HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{15}\text{O}_3\text{S}_3^+$ m/z $[\text{M} + \text{H}]^+$: 399.0178; found: 399.0176.

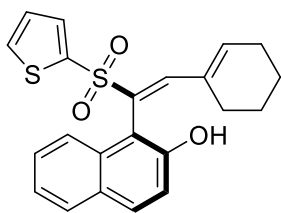
HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 230$ nm): t_1 (major) = 11.996 min, t_2 (minor) = 20.660 min.



	Retention Time	Area	% Area	Height
1	12.063	963767	50.54	36341
2	20.802	943041	49.46	21649



	Retention Time	Area	% Area	Height
1	11.996	8810487	98.91	325097
2	20.660	97160	1.09	2913



3qh

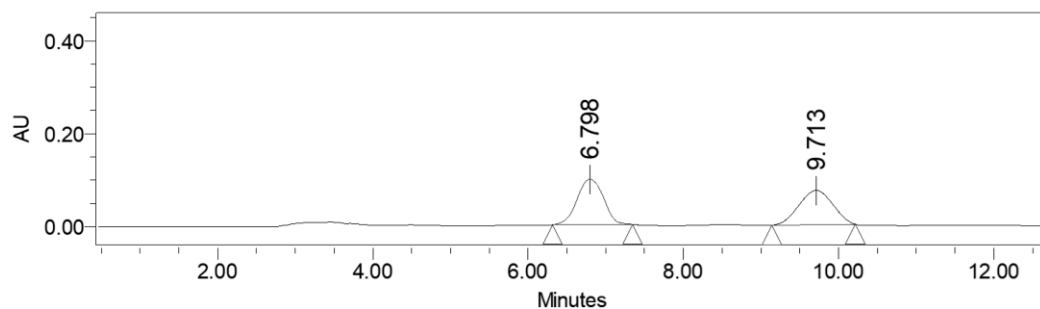
White foam. 49.5 mg. Yield = 62%. $[\alpha]_D^{20} = +14.146^\circ$ (c = 1.0, CHCl_3).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.86 (s, 1H), 7.78 (d, $J = 8.9$ Hz, 1H), 7.66 (d, $J = 8.1$ Hz, 1H), 7.37 (dd, $J = 5.0, 1.4$ Hz, 1H), 7.24 (d, $J = 8.9$ Hz, 1H), 7.21 – 7.15 (m, 1H), 7.15 – 7.06 (m, 3H), 7.00 (d, $J = 8.4$ Hz, 1H), 6.70 (dd, $J = 4.9, 3.8$ Hz, 1H), 6.40 (t, $J = 4.2$ Hz, 1H), 2.220 – 2.10 (m, 2H), 1.51 – 1.37 (m, 2H), 1.23 – 1.12 (m, 3H), 0.96 – 0.83 (m, 1H).

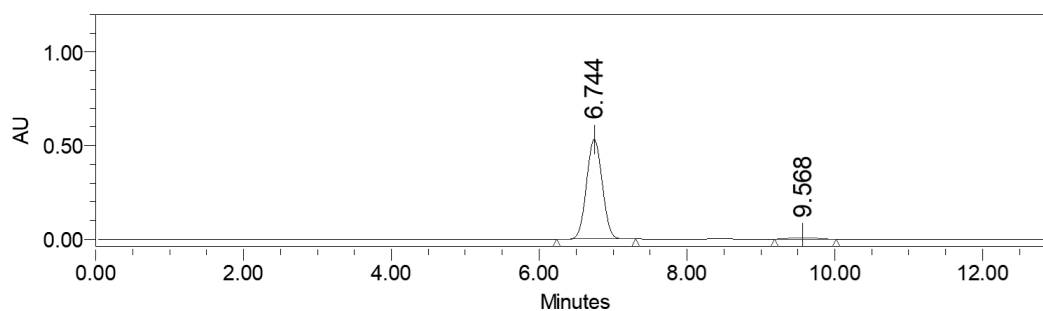
$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 154.0, 146.0, 144.8, 137.9, 135.1, 134.6, 134.5, 132.0, 130.0, 128.3, 128.0, 127.6, 126.9, 123.5, 123.0, 119.3, 111.8, 27.0, 24.5, 22.1, 21.1.

HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{21}\text{O}_3\text{S}_2^+$ m/z $[\text{M} + \text{H}]^+$: 397.0927; found: 397.0923.

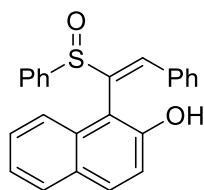
HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 300$ nm): t_1 (major) = 6.744 min, t_2 (minor) = 9.568 min.



	Retention Time	Area	% Area	Height
1	6.798	2311505	50.80	97655
2	9.713	2239130	49.20	73982



	Retention Time	Area	% Area	Height
1	6.744	7848550	97.70	532342
2	9.568	184521	2.30	7641



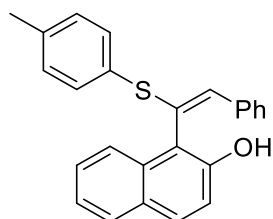
4

Yellow oil. 107.9 mg. Yield = 57%.

¹H NMR (400 MHz, DMSO) δ 10.37 (s, 1H), 7.86 (d, J = 8.9 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.61 (s, 1H), 7.32 (d, J = 8.9 Hz, 1H), 7.25 – 7.17 (m, 1H), 7.144 – 7.05 (m, 9H), 7.04 – 6.99 (m, 1H), 6.74 – 6.66 (m, 1H), 6.41 (d, J = 8.5 Hz, 1H).

¹³C NMR (101 MHz, DMSO) δ 153.9, 142.5, 142.1, 134.0, 131.7, 131.4, 130.9, 128.7, 128.6, 128.5, 128.2, 127.9, 127.5, 126.2, 124.6, 122.7, 122.6, 118.1, 110.3.

HRMS (ESI) calcd for C₂₄H₁₉O₂S⁺ m/z [M + H]⁺: 371.1100; found: 371.1093.



5

White foam. 203.0 mg. Yield = 55%. (*E/Z* mixture of ratio: 1/0.4).

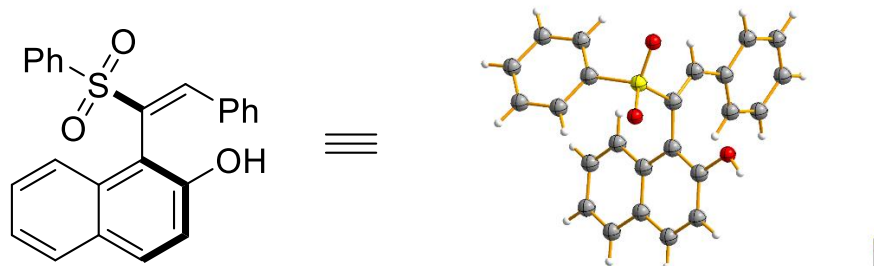
¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, J = 8.4 Hz, 0.49H), 7.77-7.66 (m, 5.48H), 7.59 (d, J = 8.8 Hz, 0.47H), 7.52 – 7.48 (m, 0.39H), 7.48 – 7.43 (m, 1.04H), 7.43 – 7.38 (m, 1.04H), 7.37 – 7.29 (m, 5.51H), 7.18 – 7.11 (m, 3.24H), 7.11 – 7.04 (m, 1.18H), 6.99 (d, J = 8.0 Hz, 2.00H), 6.91 (d, J = 8.8 Hz, 0.45H), 6.73 (d, J = 8.0 Hz, 1.99H), 6.69 (s, 0.42H), 5.95 (s, 0.94H), 5.27 (s, 0.39H), 2.29 (s, 1.27H), 2.07 (s, 3.00H).

¹³C NMR (101 MHz, CDCl₃) δ 149.9, 149.5, 143.9, 142.9, 139.5, 138.6, 136.9, 136.2, 133.5, 132.9, 130.9, 130.4, 130.0, 129.9, 129.9, 129.5, 129.5, 129.2, 129.1, 129.0, 129.0, 128.8, 128.7, 128.6, 128.5, 128.4, 128.4, 128.1, 126.9, 126.6, 126.0, 125.7, 125.3, 124.8, 124.1, 123.9, 123.6, 120.5, 118.4, 117.9, 116.4, 116.0, 112.4, 100.6, 21.3, 21.0.

HRMS (ESI) calcd for C₂₅H₂₀NaOS⁺ m/z [M + Na]⁺: 391.1127; found: 391.1128.

7. X-ray crystal structures.

The crystal of compound (**S**)-**3aa** was obtained by slow evaporation of petroleum ether and dichloromethane solution at room temperature.



CCDC 2251662

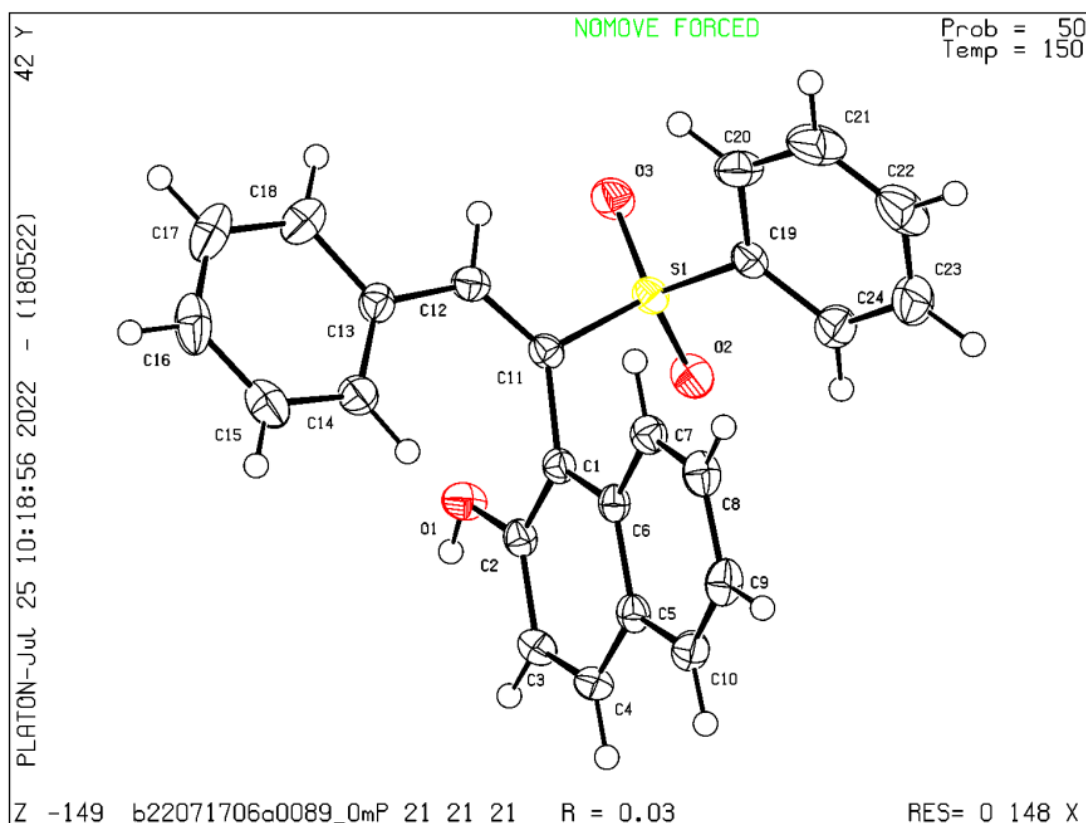
Atomic displacement parameters for non-H atoms are at 30% probability level.

Crystal data and structure refinement for B22071706A0089_0m.

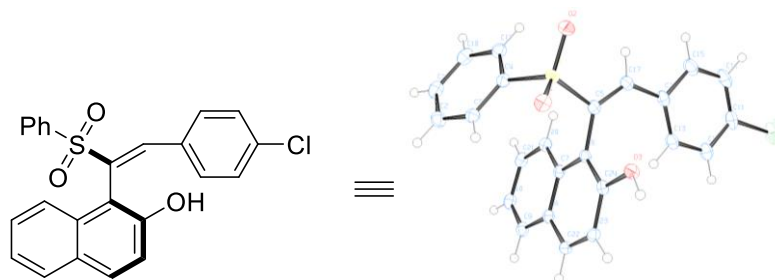
Identification code	B22071706A0089_0m
Empirical formula	C ₂₄ H ₁₈ O ₃ S
Formula weight	386.44
Temperature/K	150.0
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	9.6878(5)
b/Å	9.8802(5)
c/Å	19.6818(10)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	1883.89(17)
Z	4
ρ _{calc} /cm ³	1.363
μ/mm ⁻¹	1.108
F(000)	808.0
Crystal size/mm ³	0.06 × 0.05 × 0.03
Radiation	GaKα (λ = 1.34138)
2θ range for data collection/°	7.816 to 115.984
Index ranges	-12 ≤ h ≤ 12, -12 ≤ k ≤ 12, -24 ≤ l ≤ 24
Reflections collected	42198
Independent reflections	3893 [R _{int} = 0.0397, R _{sigma} = 0.0274]
Data/restraints/parameters	3893/0/254
Goodness-of-fit on F ²	1.090
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0336, wR ₂ = 0.0891
Final R indexes [all data]	R ₁ = 0.0337, wR ₂ = 0.0892
Largest diff. peak/hole / e Å ⁻³	0.70/-0.37

Flack parameter

0.079(4)



The crystal of compound **(S)-3ha** was obtained by slow evaporation of petroleum ether and dichloromethane solution at room temperature.



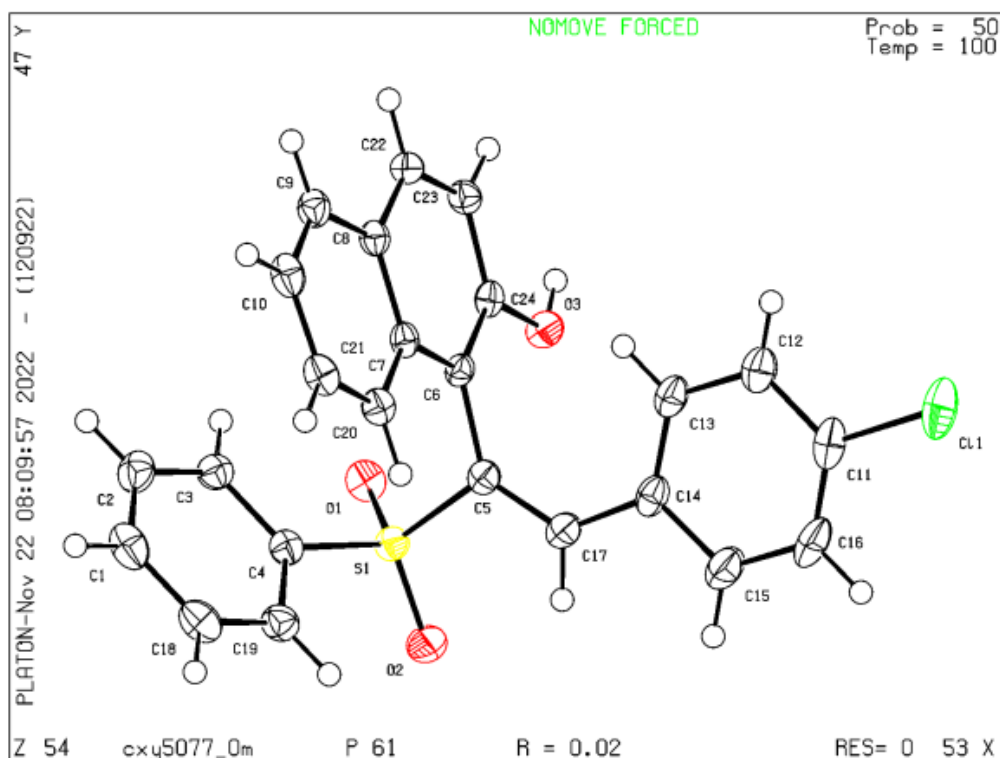
CCDC 2251663

Atomic displacement parameters for non-H atoms are at 30% probability level.

Crystal data and structure refinement for cxy5077_0m.

Identification code	cxy5077_0m
Empirical formula	C ₂₄ H ₁₇ ClO ₃ S
Formula weight	420.89
Temperature/K	100.0(2)
Crystal system	hexagonal

Space group	P6 ₁
a/Å	21.0471(5)
b/Å	21.0471(5)
c/Å	8.1060(3)
α/°	90
β/°	90
γ/°	120
Volume/Å ³	3109.72(19)
Z	6
ρ _{calc} /cm ³	1.348
μ/mm ⁻¹	1.817
F(000)	1308.0
Crystal size/mm ³	0.31 × 0.2 × 0.18
Radiation	GaKα (λ = 1.34138)
2θ range for data collection/°	7.308 to 114.068
Index ranges	-26 ≤ h ≤ 26, -26 ≤ k ≤ 26, -10 ≤ l ≤ 10
Reflections collected	74919
Independent reflections	4242 [R _{int} = 0.0456, R _{sigma} = 0.0153]
Data/restraints/parameters	4242/1/264
Goodness-of-fit on F ²	1.026
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0229, wR ₂ = 0.0609
Final R indexes [all data]	R ₁ = 0.0232, wR ₂ = 0.0611
Largest diff. peak/hole / e Å ⁻³	0.22/-0.28
Flack parameter	0.005(5)

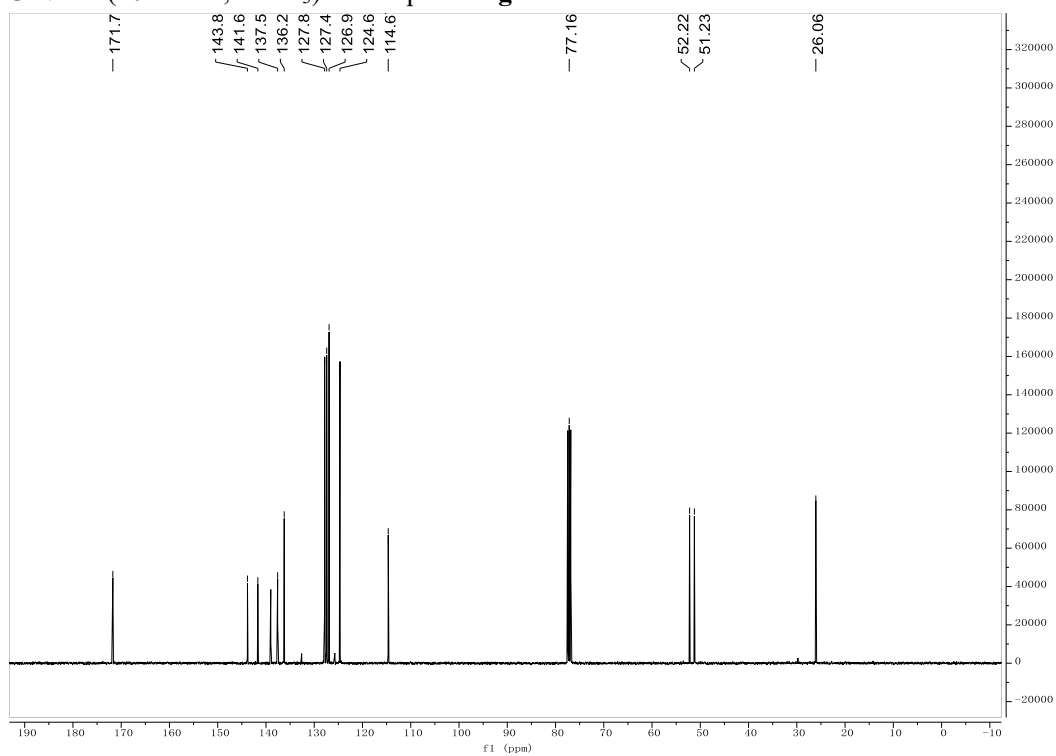


8. Copies of NMR Spectra.

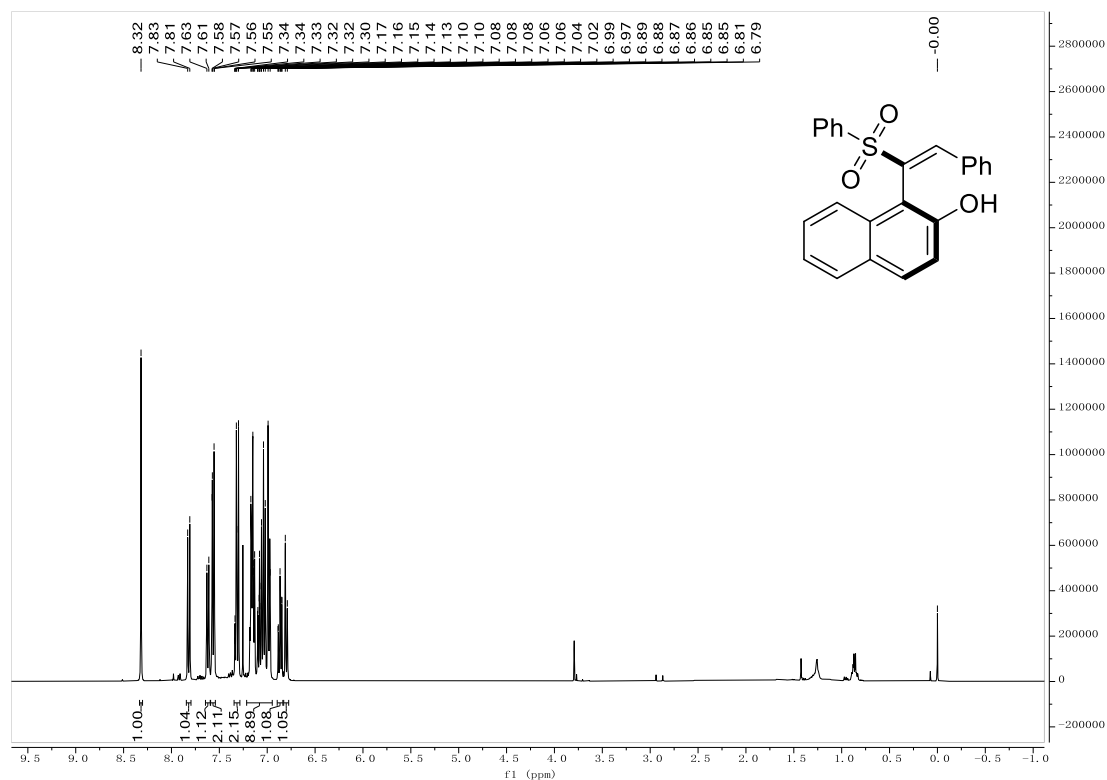
^1H NMR (400 MHz, CDCl_3) of compound **2g'**



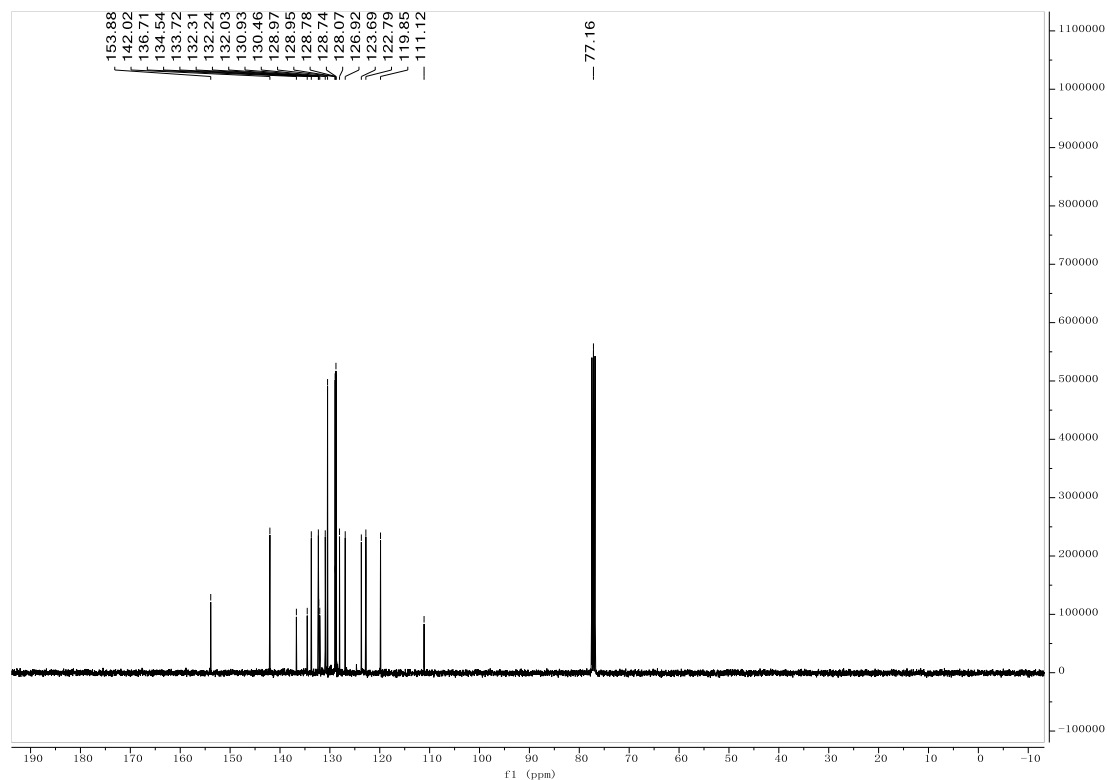
^{13}C NMR (101 MHz, CDCl_3) of compound **2g'**



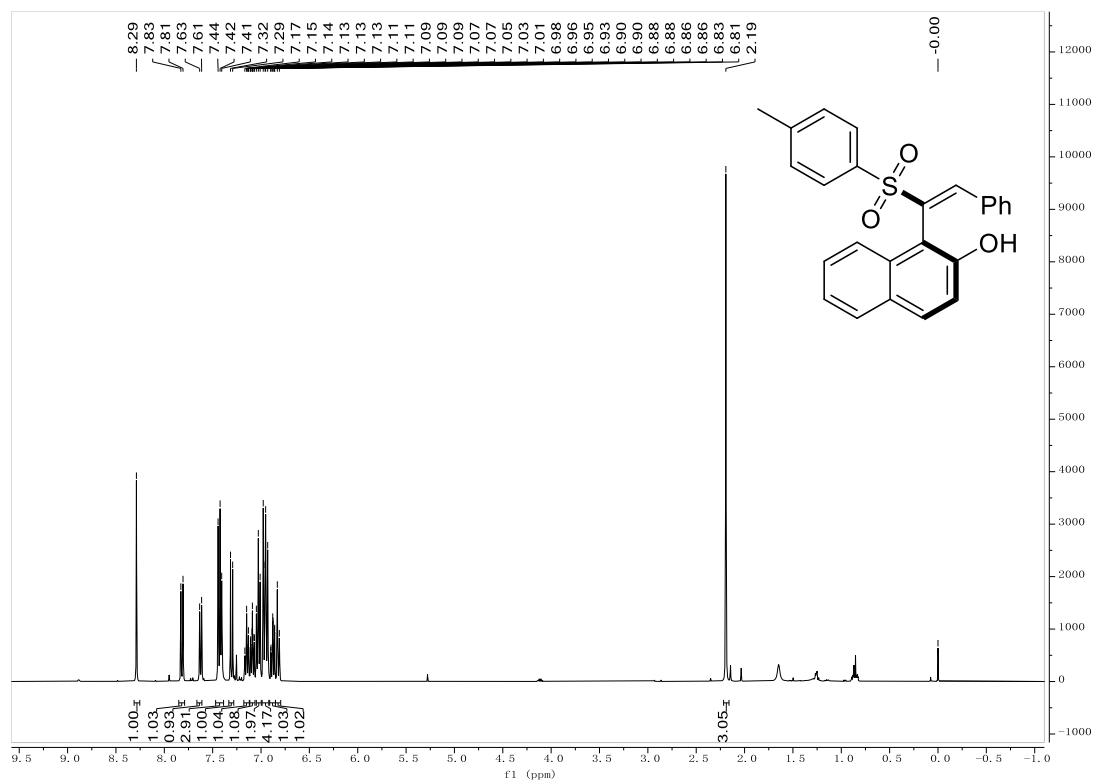
¹H NMR (400 MHz, CDCl₃) of compound **3aa**



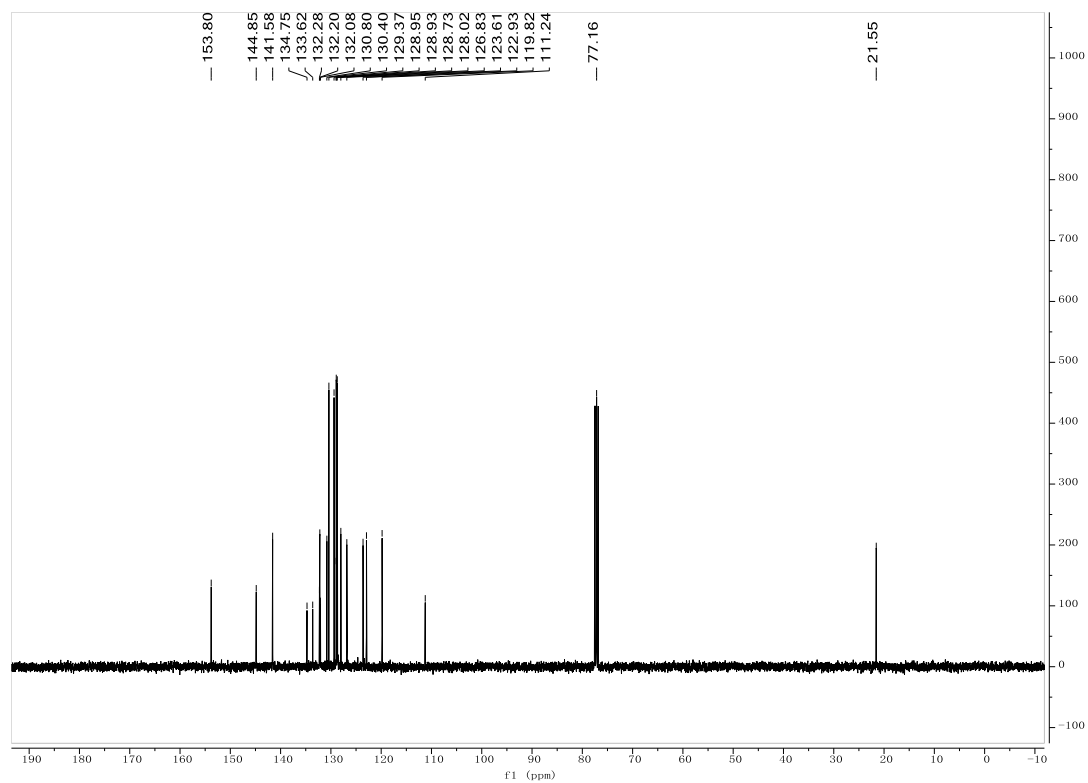
¹³C NMR (101 MHz, CDCl₃) of compound **3aa**



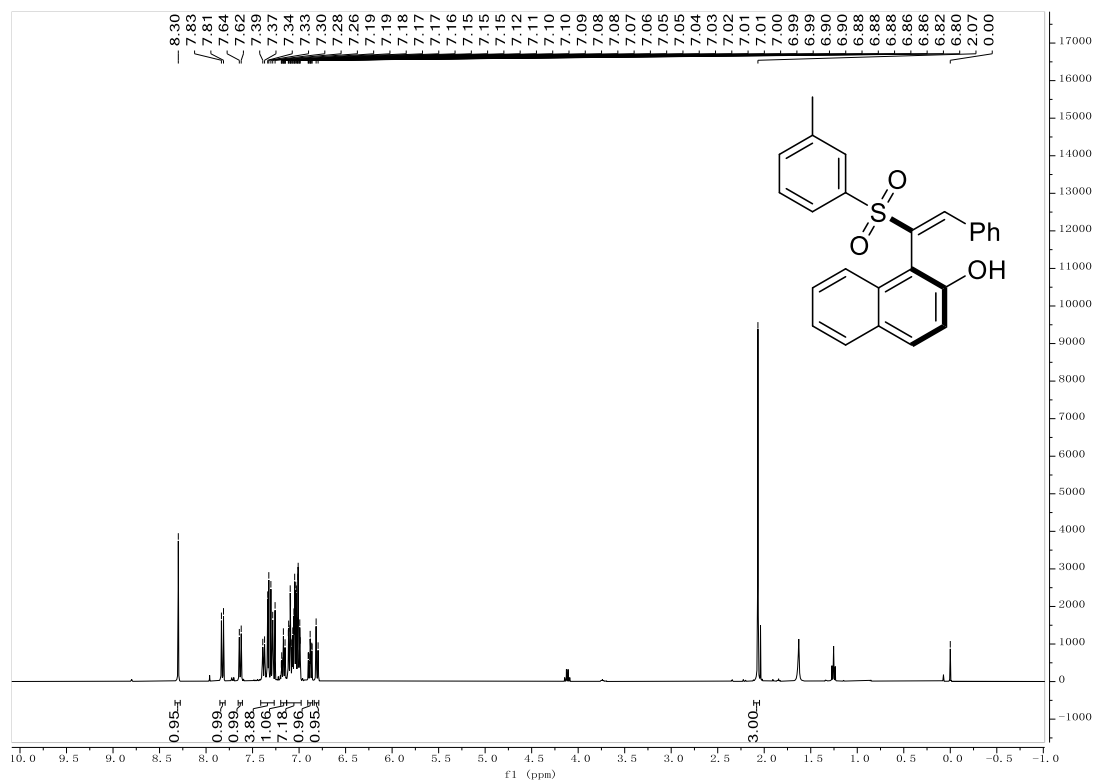
¹H NMR (400 MHz, CDCl₃) of compound 3ab



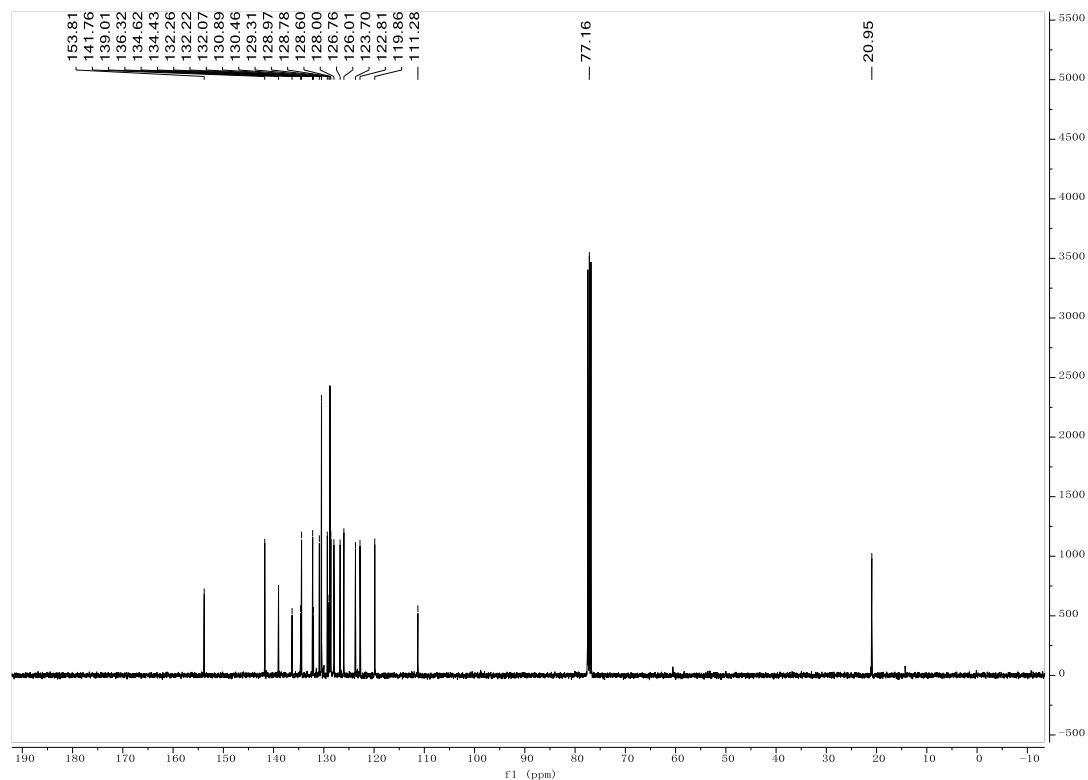
¹³C NMR (101 MHz, CDCl₃) of compound 3ab



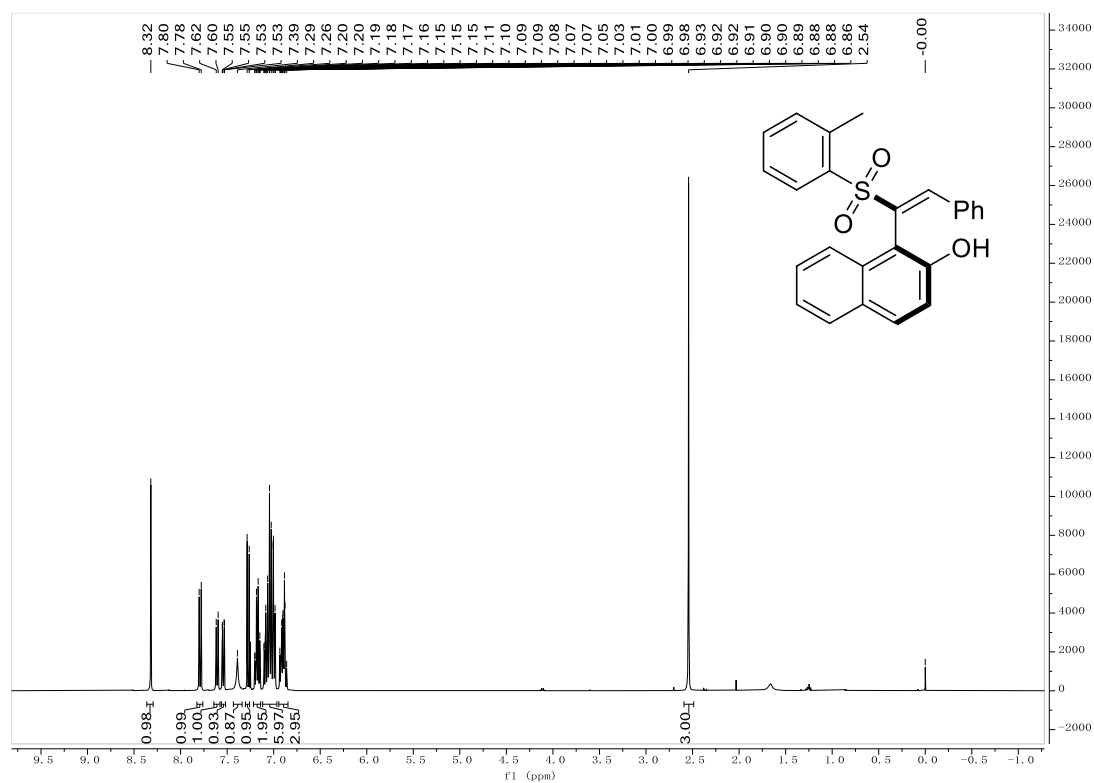
¹H NMR (400 MHz, CDCl₃) of compound **3ac**



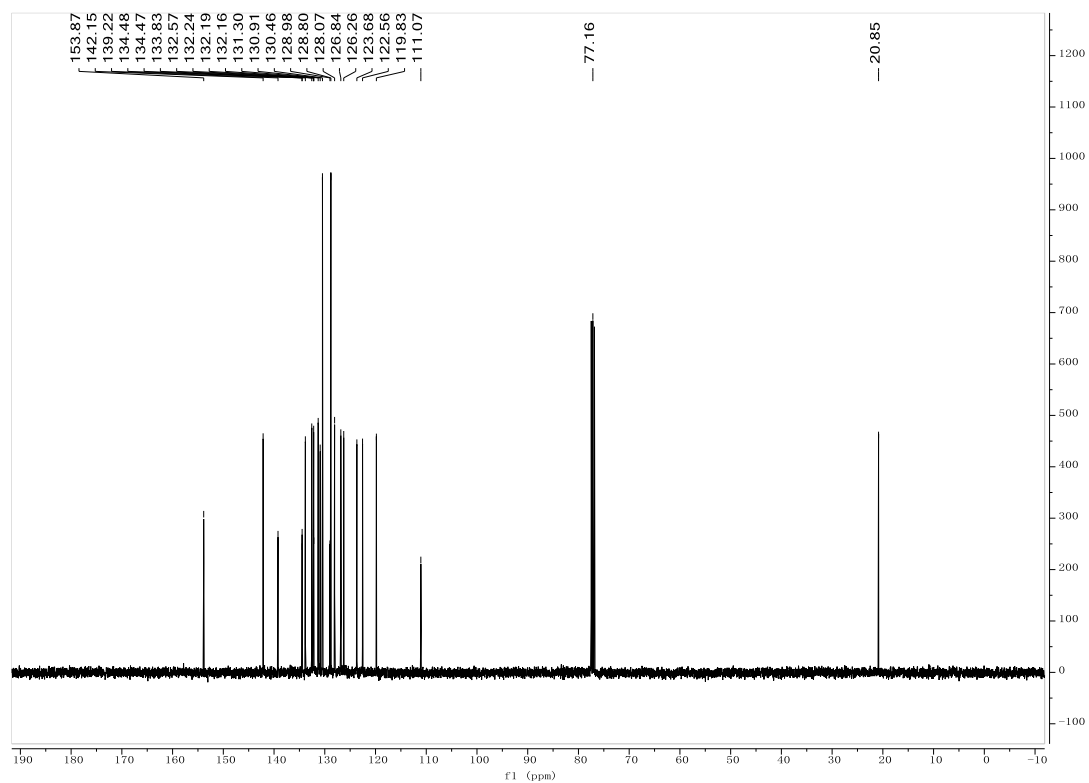
¹³C NMR (101 MHz, CDCl₃) of compound **3ac**



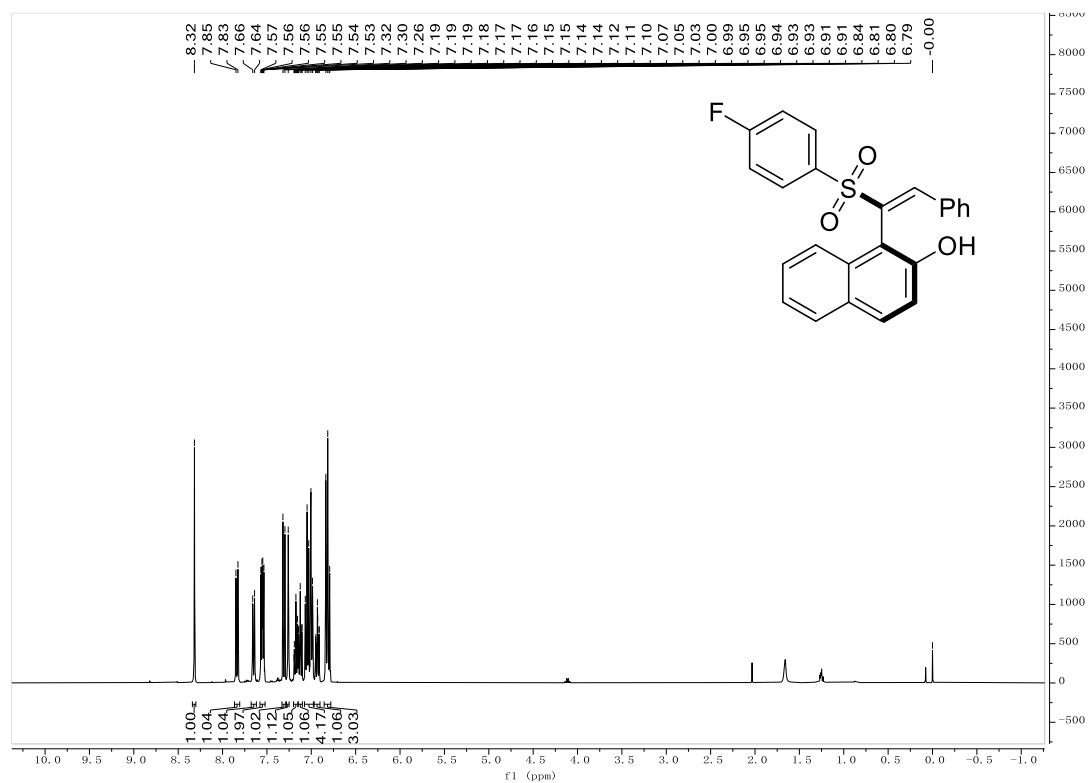
¹H NMR (400 MHz, CDCl₃) of compound 3ad



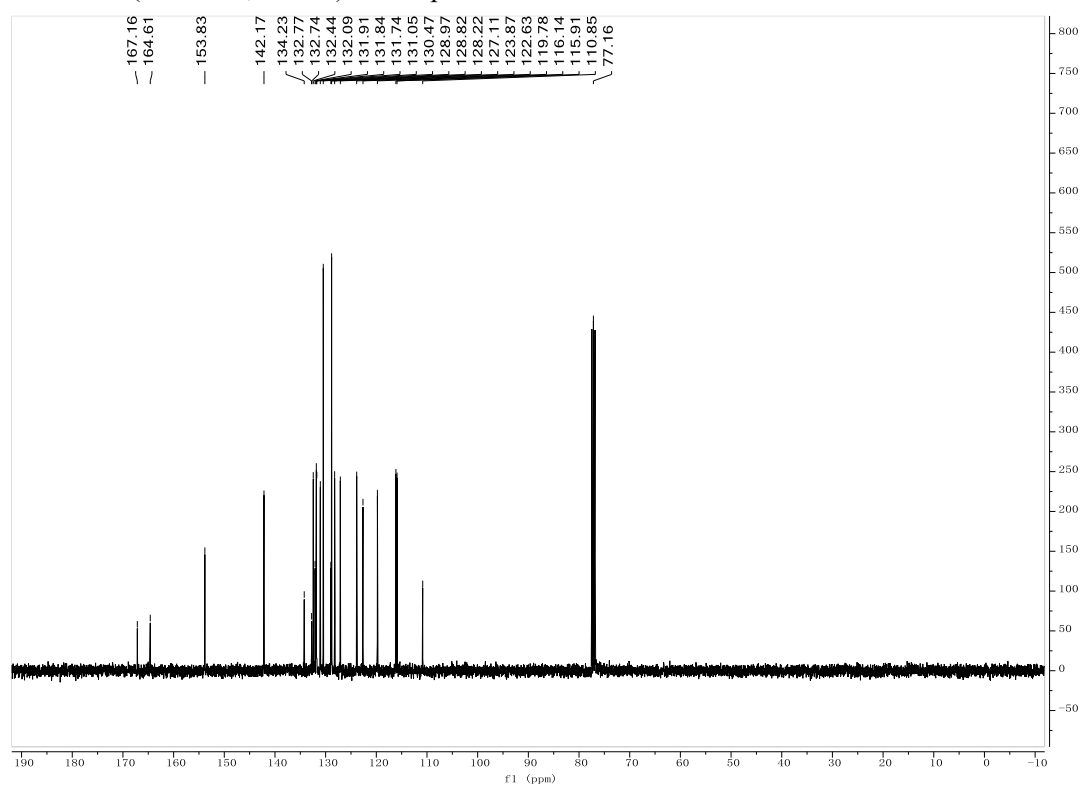
¹³C NMR (101 MHz, CDCl₃) of compound 3ad



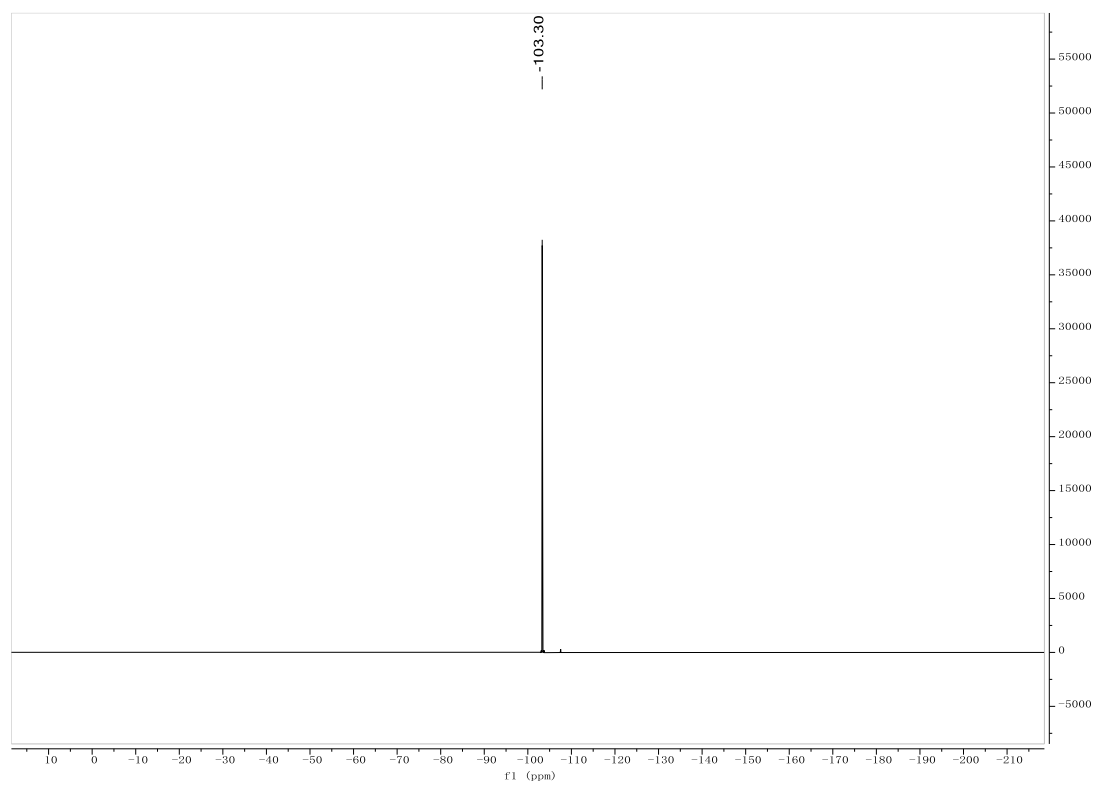
¹H NMR (400 MHz, CDCl₃) of compound 3ae



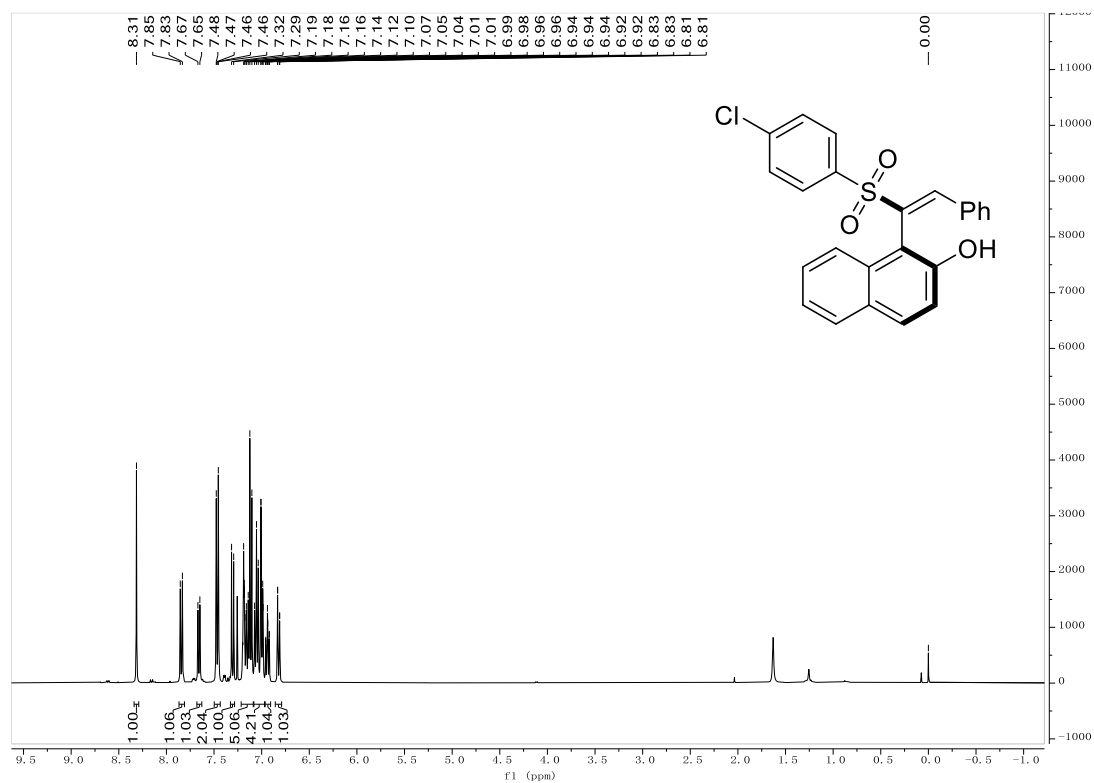
¹³C NMR (101 MHz, CDCl₃) of compound 3ae



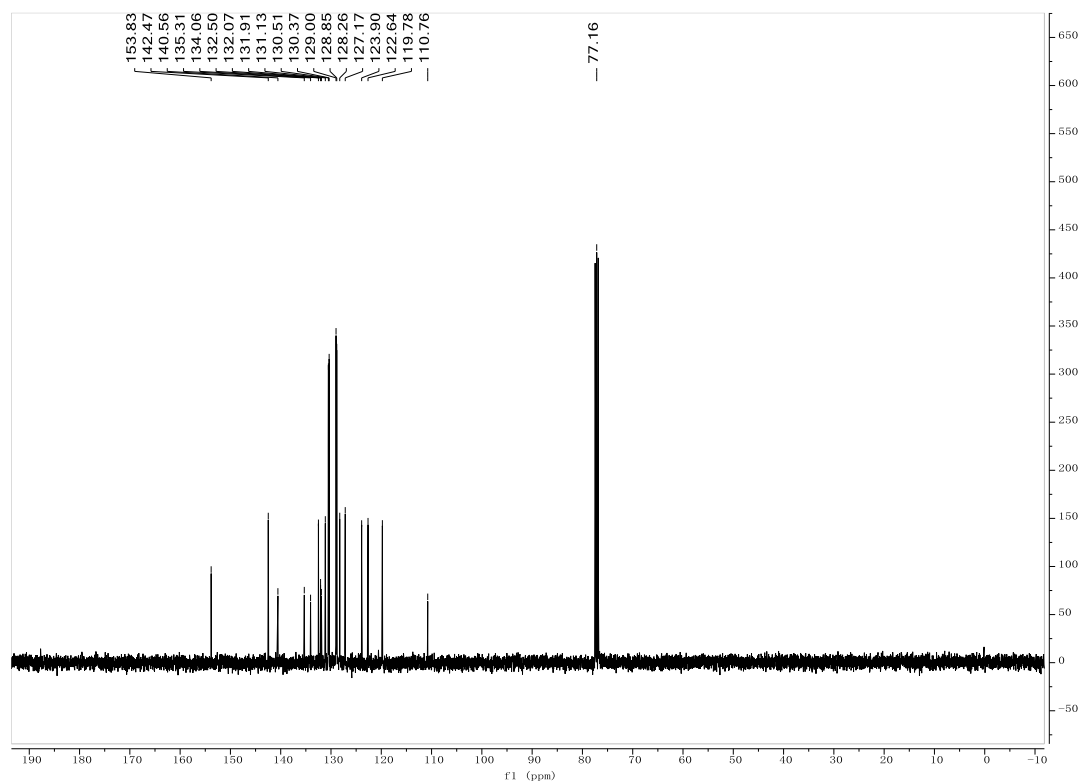
^{19}F NMR (376 MHz, CDCl_3) of compound **3ae**



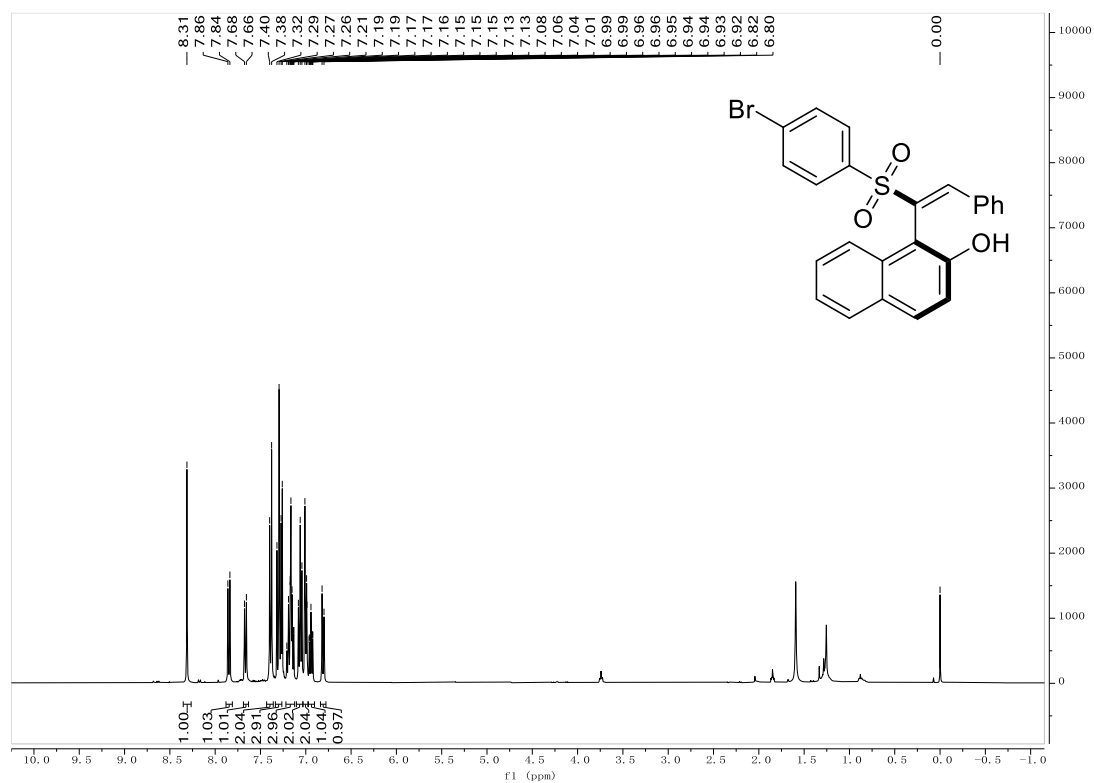
¹H NMR (400 MHz, CDCl₃) of compound 3af



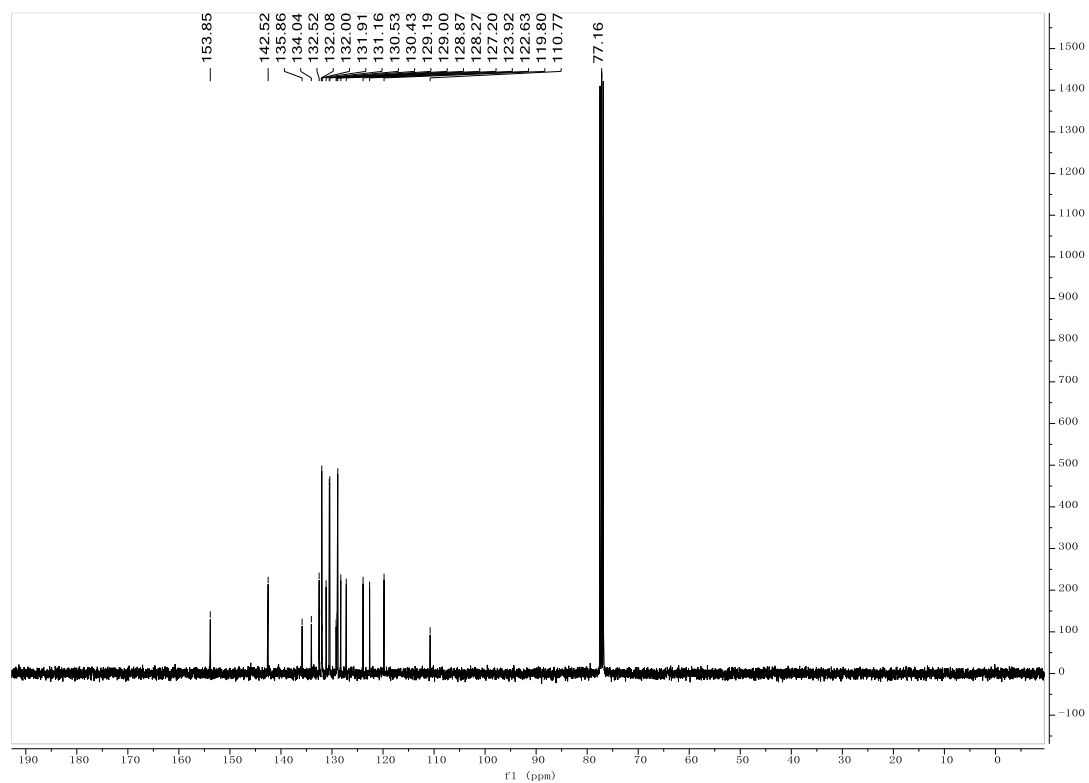
¹³C NMR (101 MHz, CDCl₃) of compound 3af



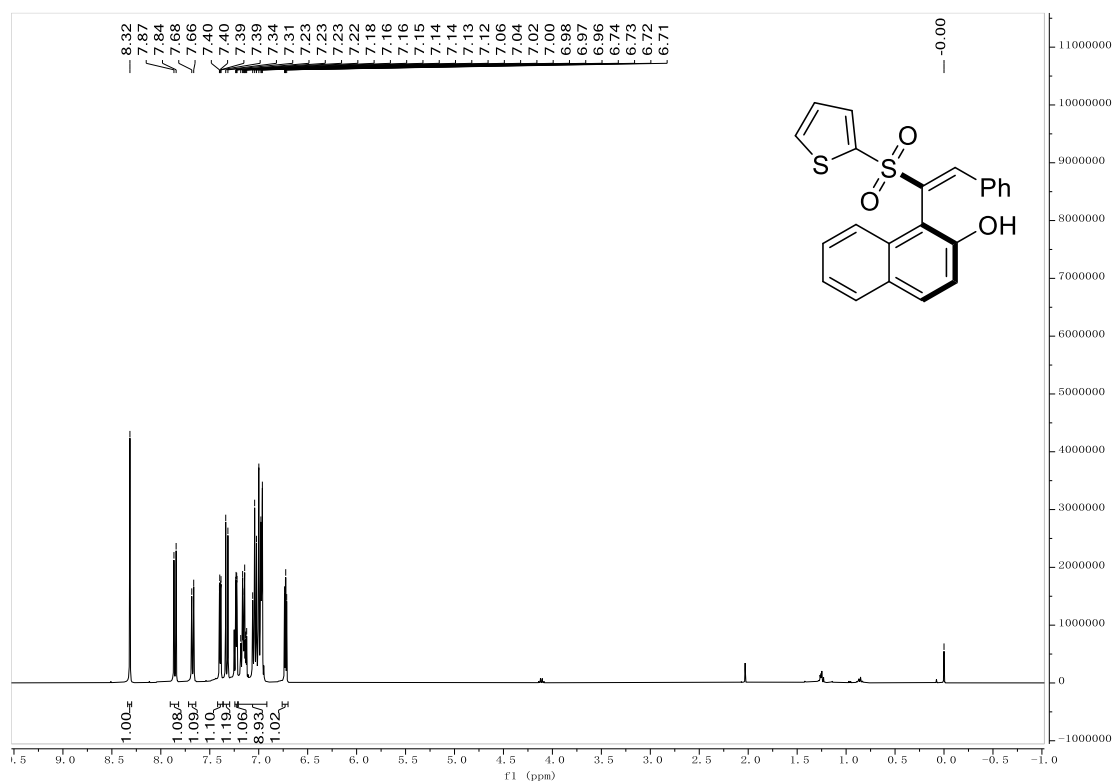
¹H NMR (400 MHz, CDCl₃) of compound **3ag**



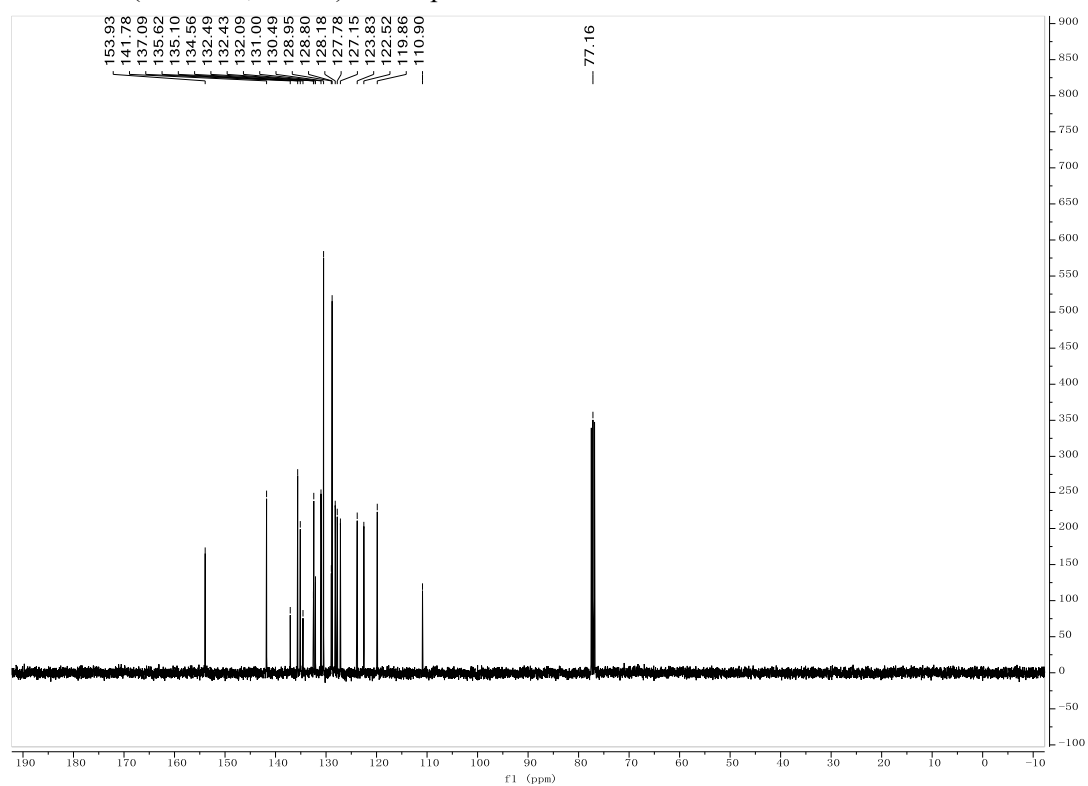
¹³C NMR (101 MHz, CDCl₃) of compound **3ag**



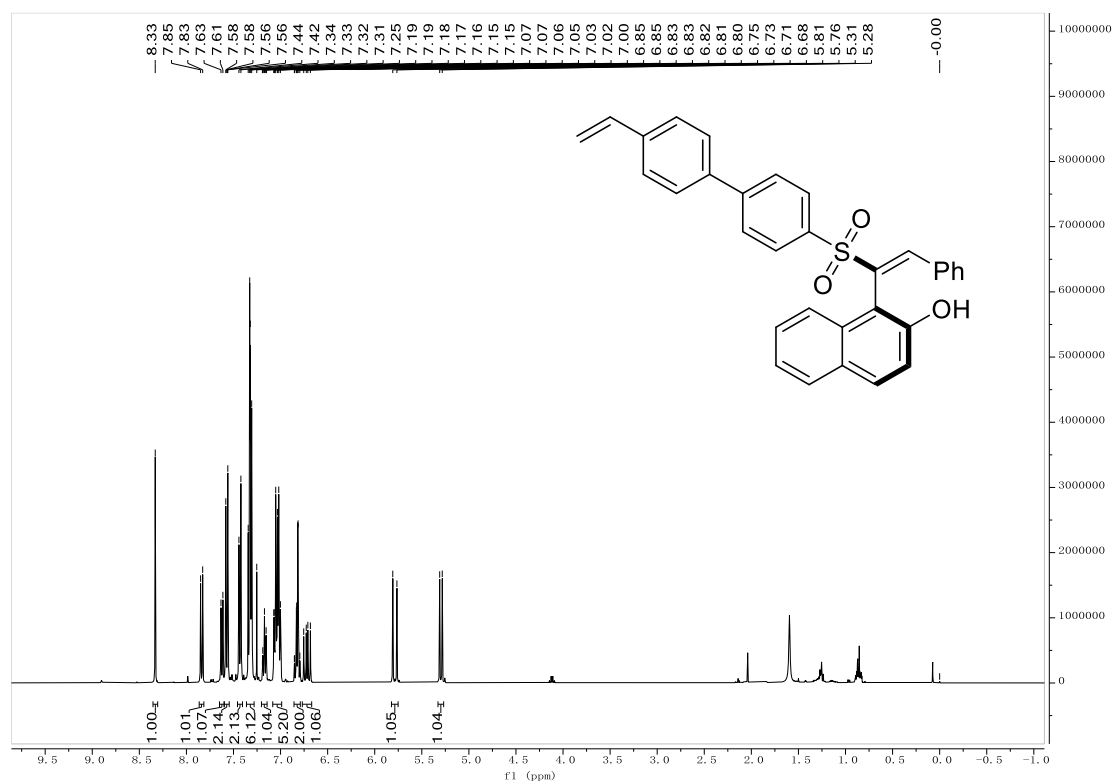
¹H NMR (400 MHz, CDCl₃) of compound 3ah



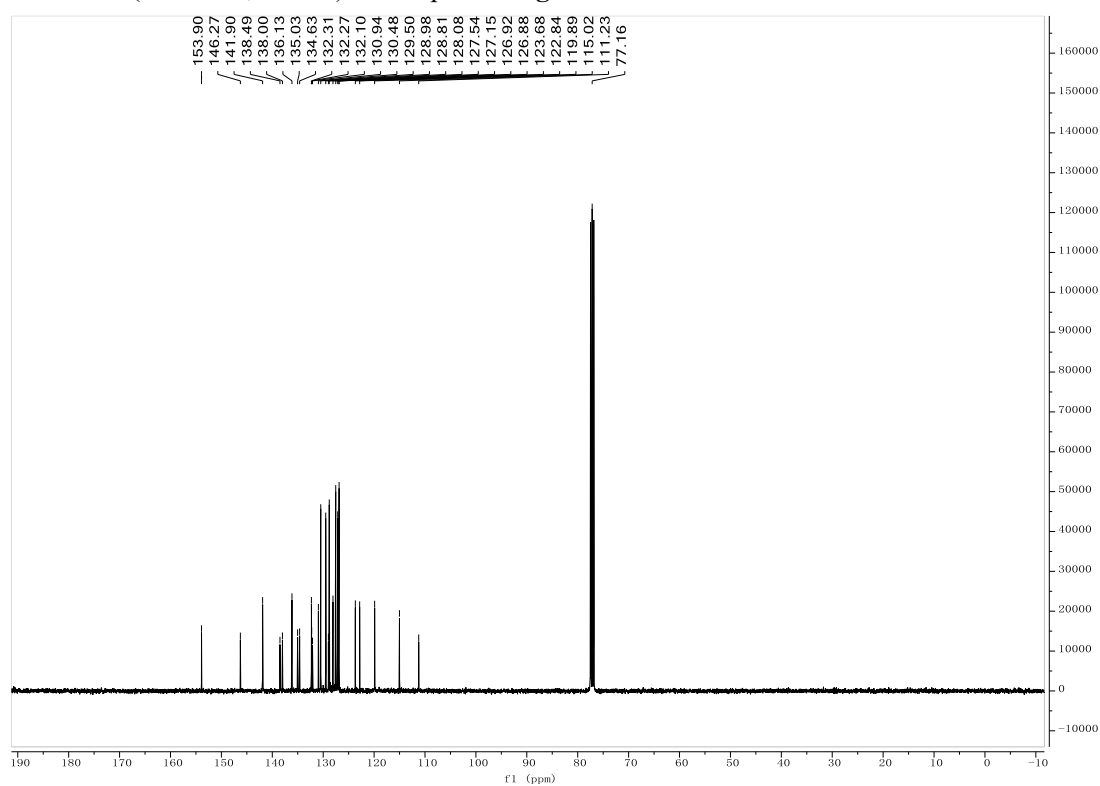
¹³C NMR (101 MHz, CDCl₃) of compound 3ah



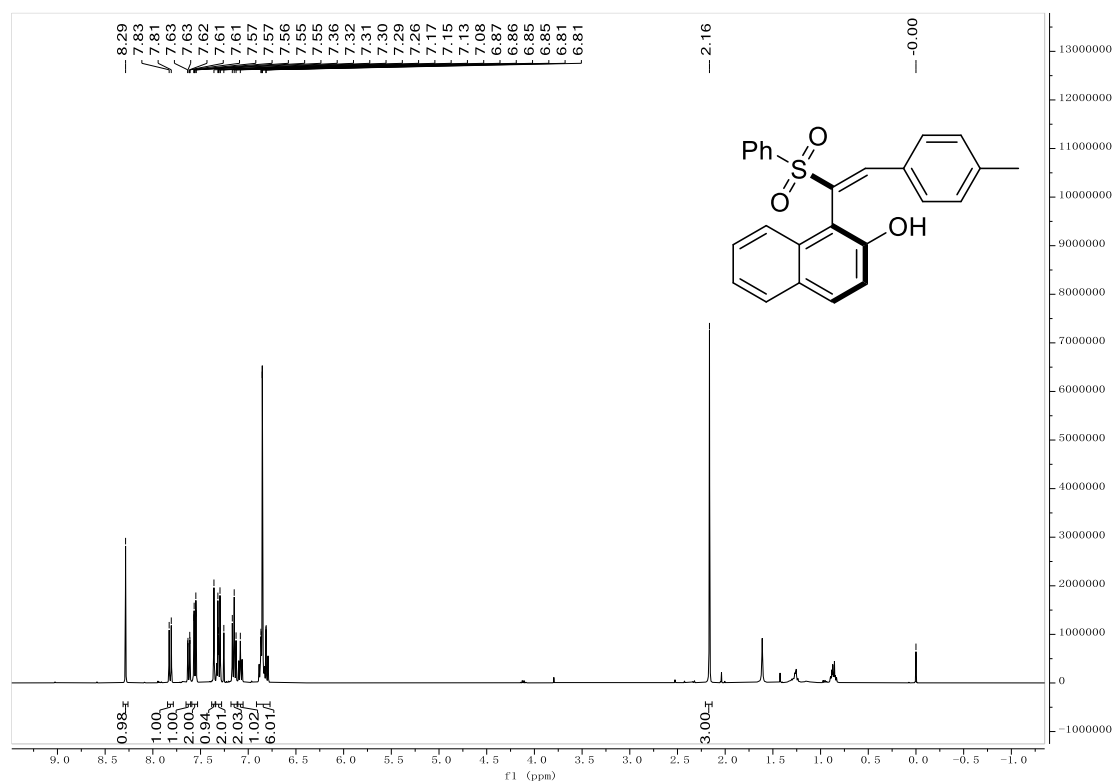
¹H NMR (400 MHz, CDCl₃) of compound 3ag'



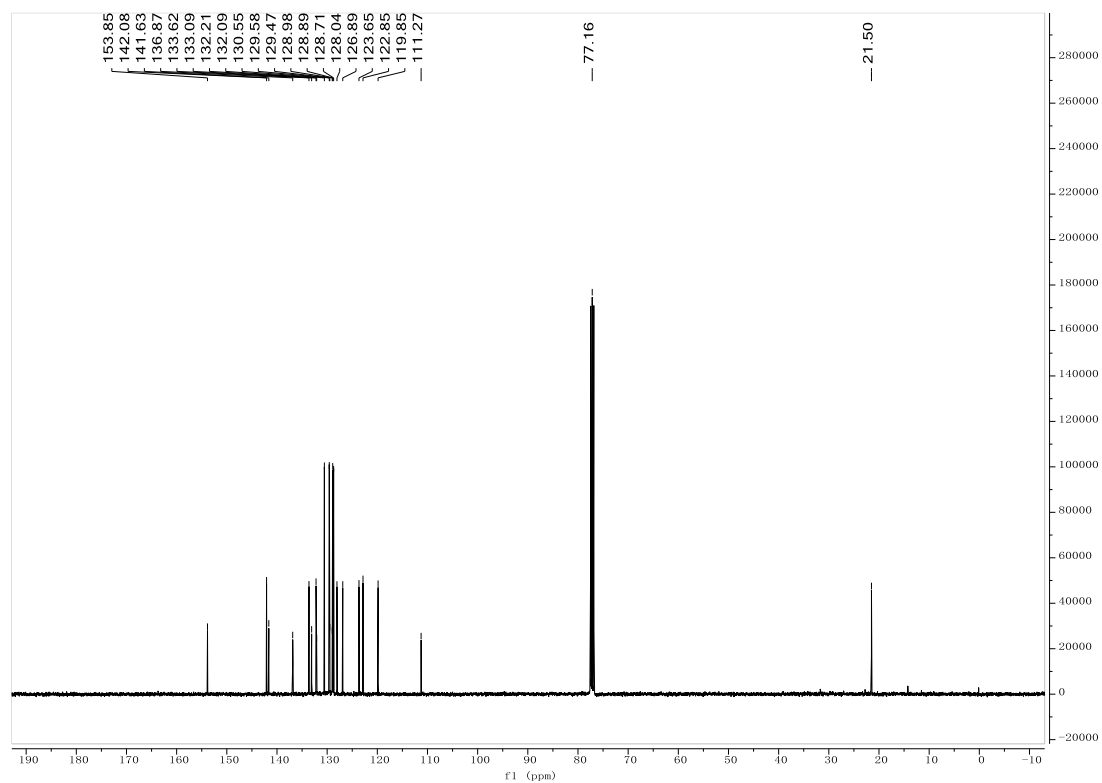
¹³C NMR (101 MHz, CDCl₃) of compound 3ag'



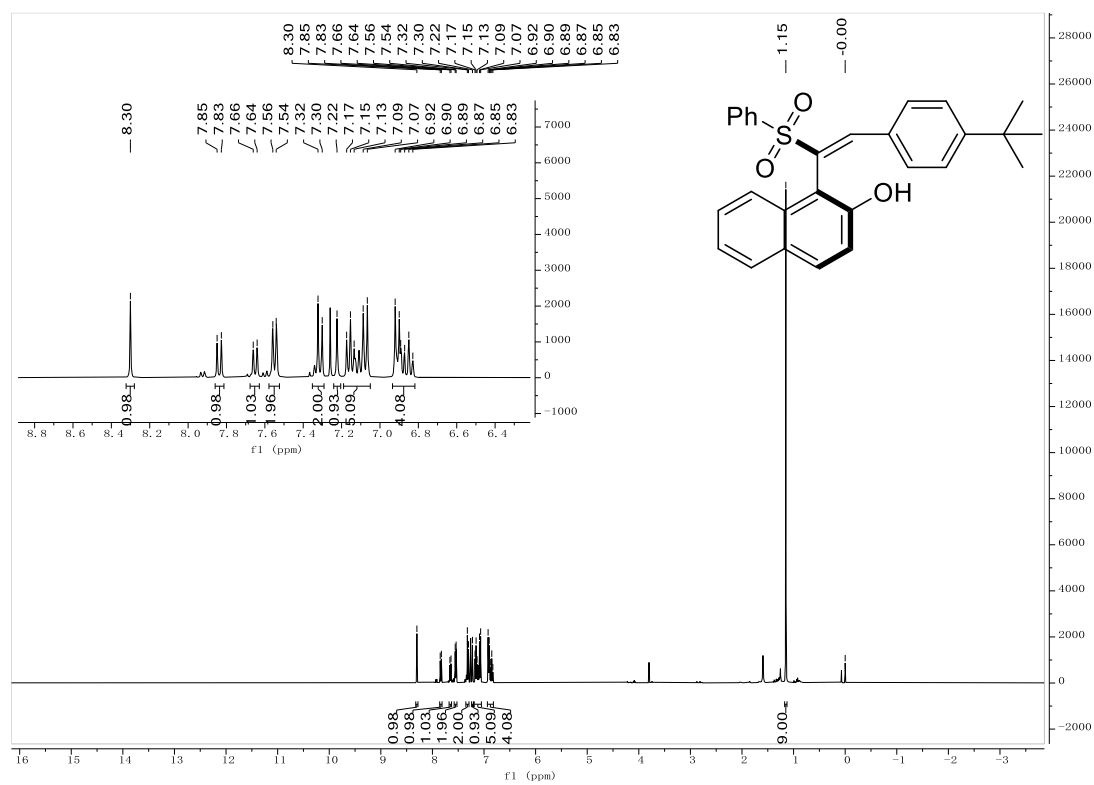
¹H NMR (400 MHz, CDCl₃) of compound 3ba



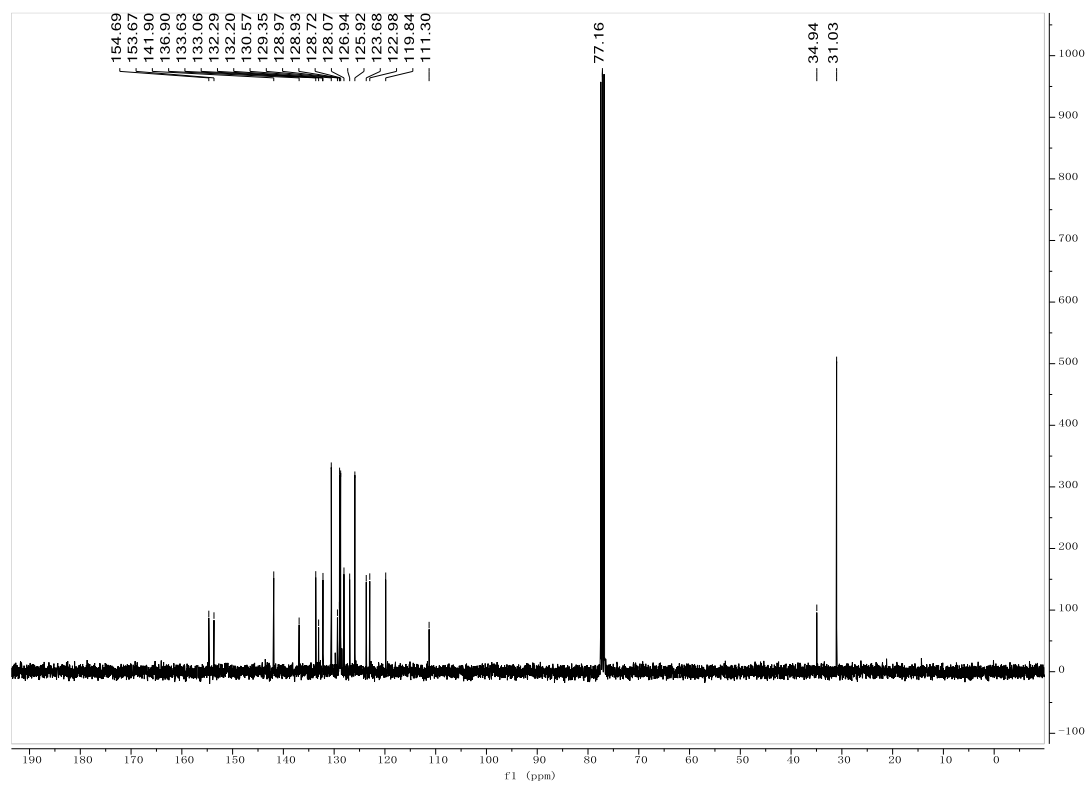
¹³C NMR (101 MHz, CDCl₃) of compound 3ba



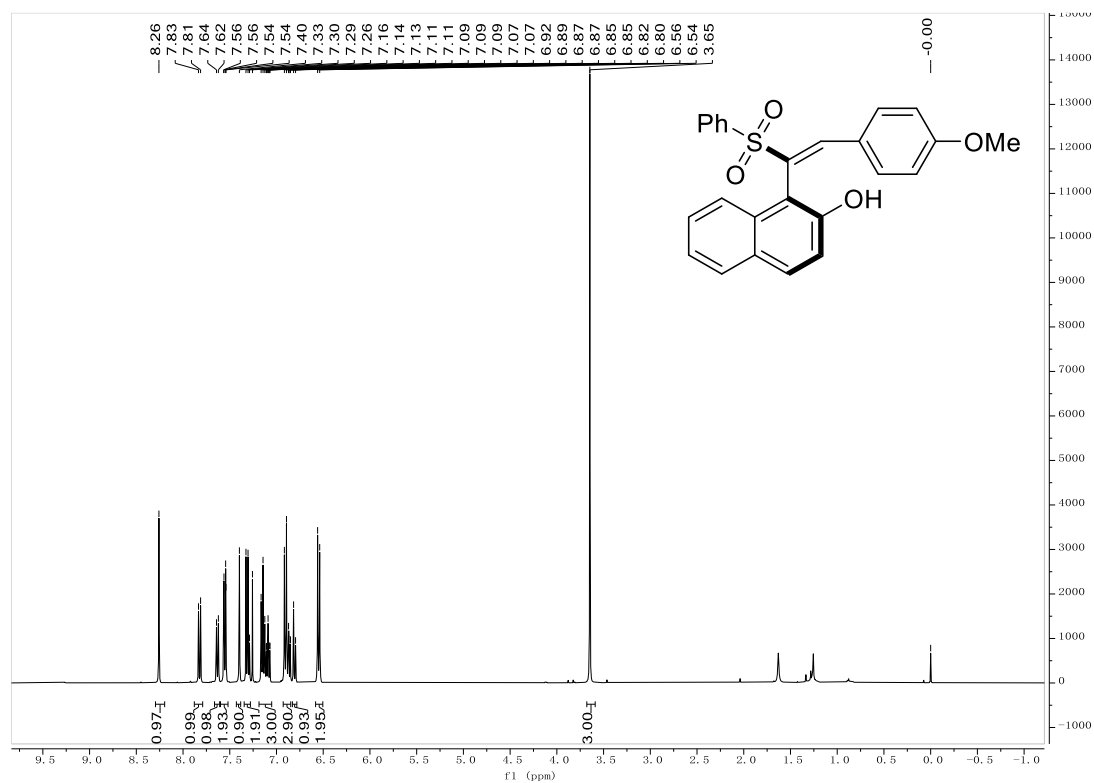
¹H NMR (400 MHz, CDCl₃) of compound 3ca



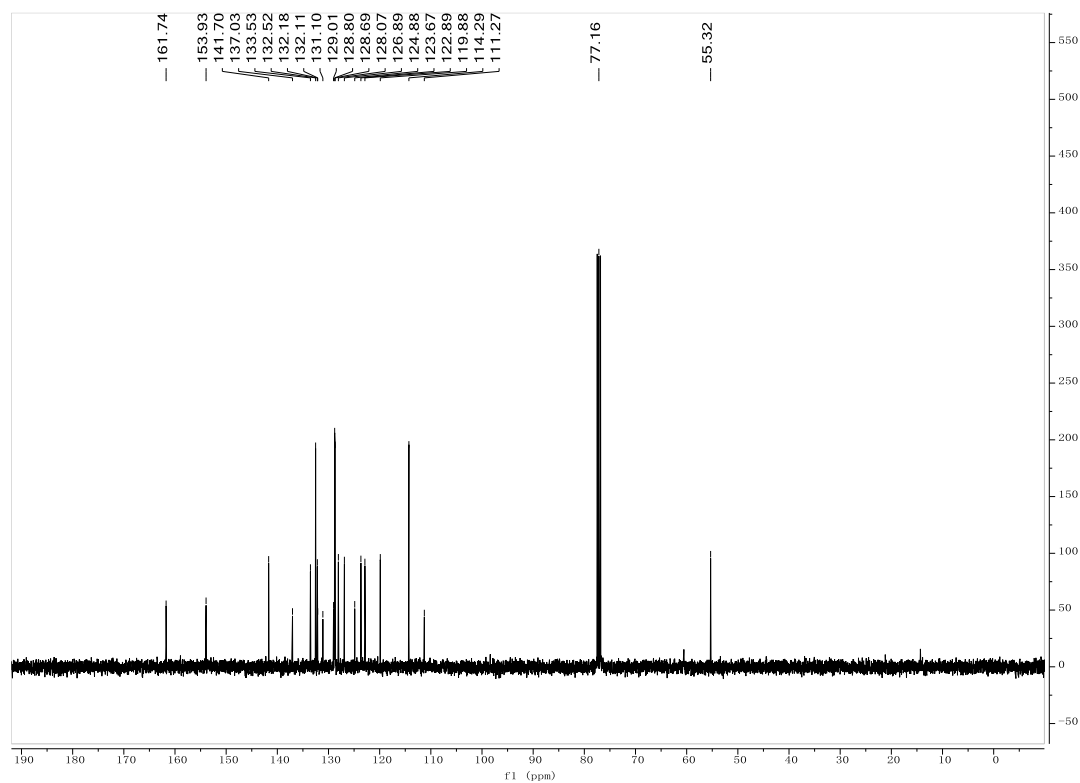
¹³C NMR (101 MHz, CDCl₃) of compound 3ca



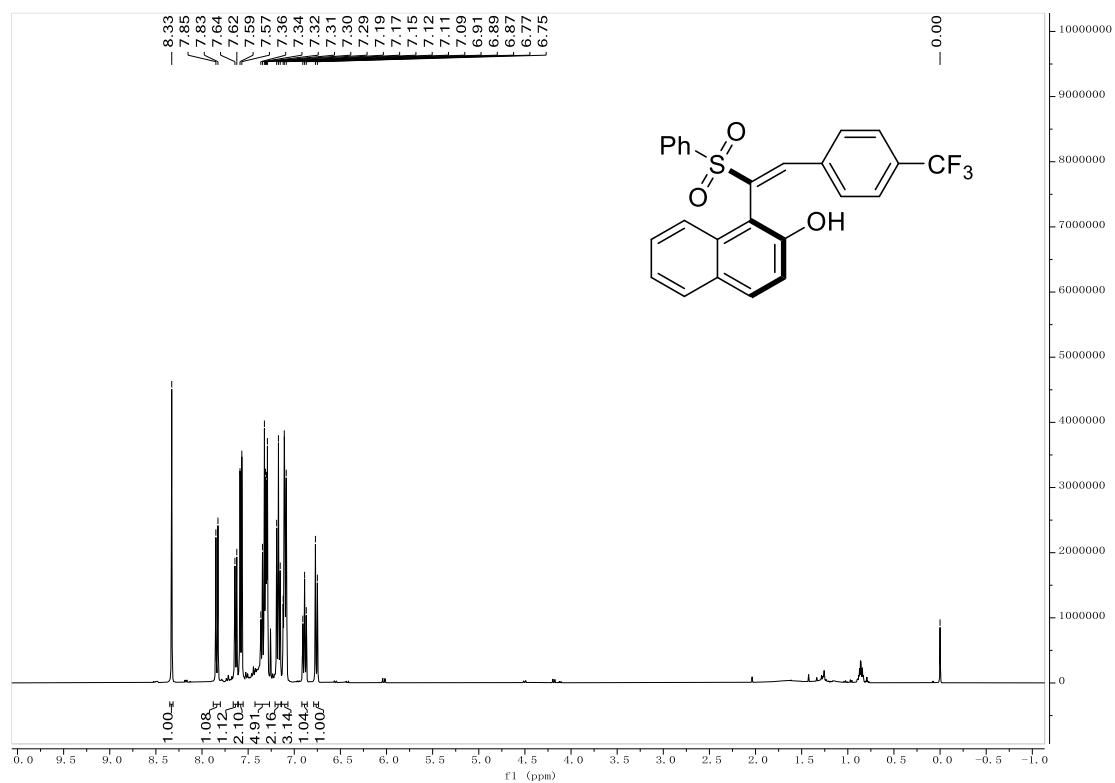
¹H NMR (400 MHz, CDCl₃) of compound 3da



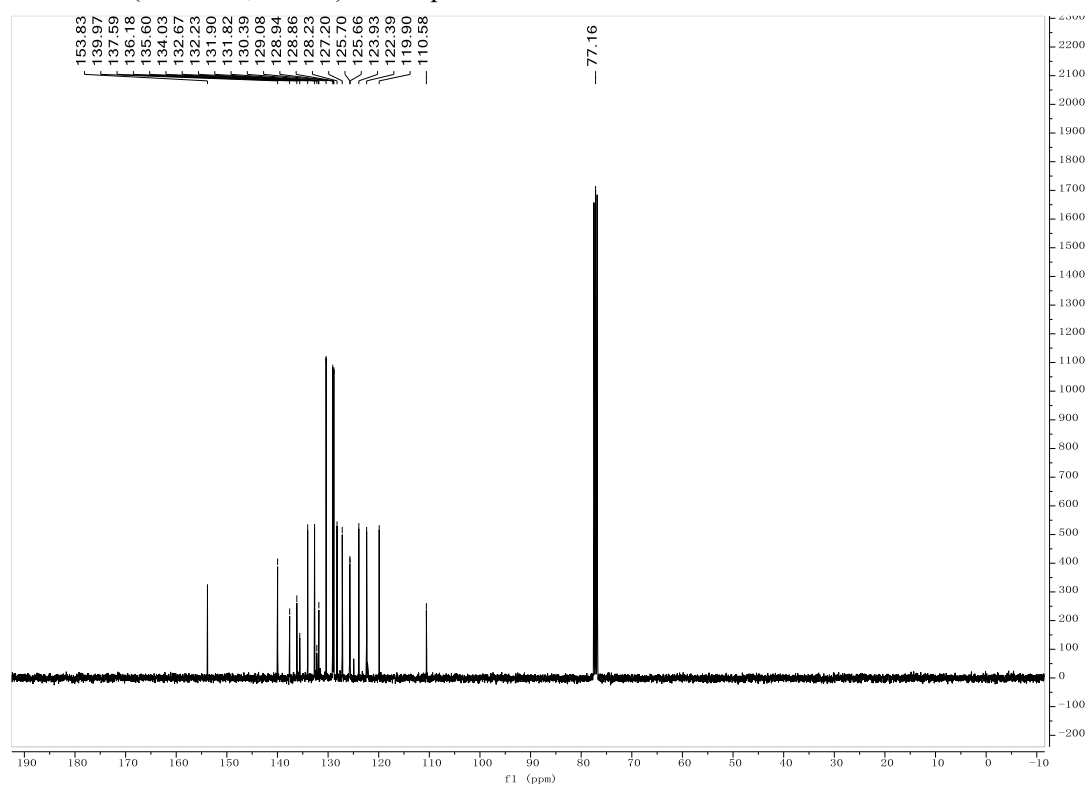
¹³C NMR (101 MHz, CDCl₃) of compound 3da



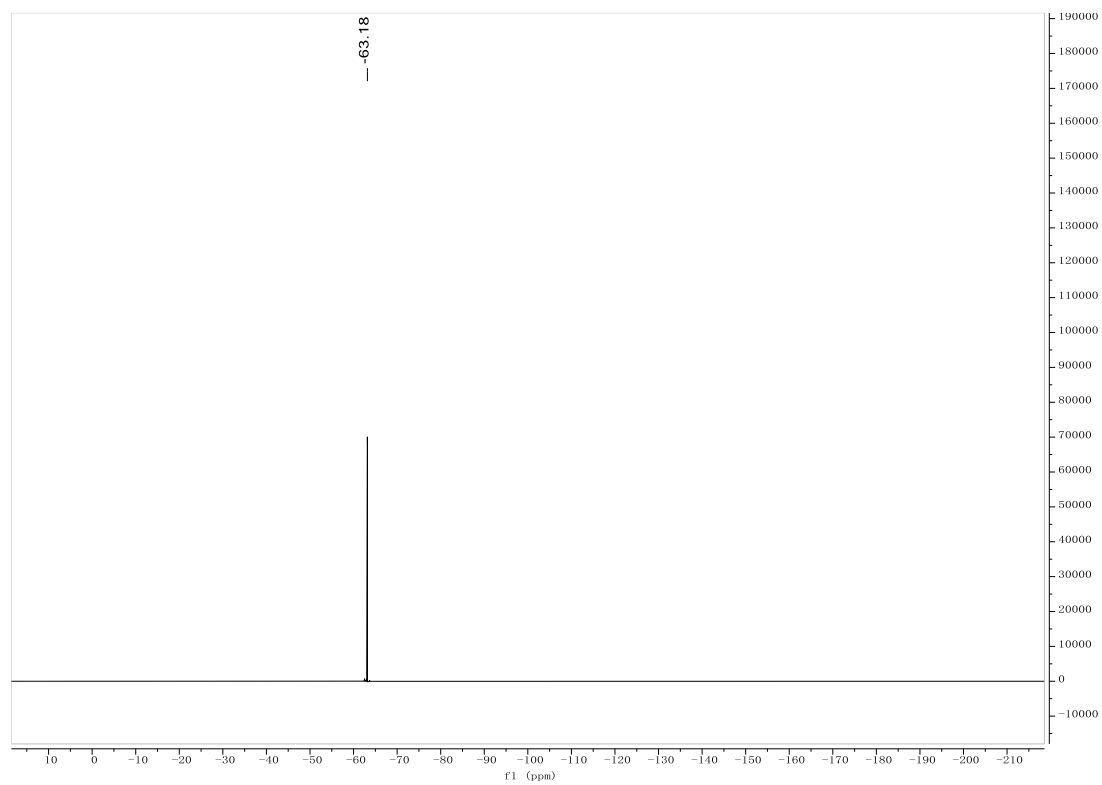
¹H NMR (400 MHz, CDCl₃) of compound **3ea**



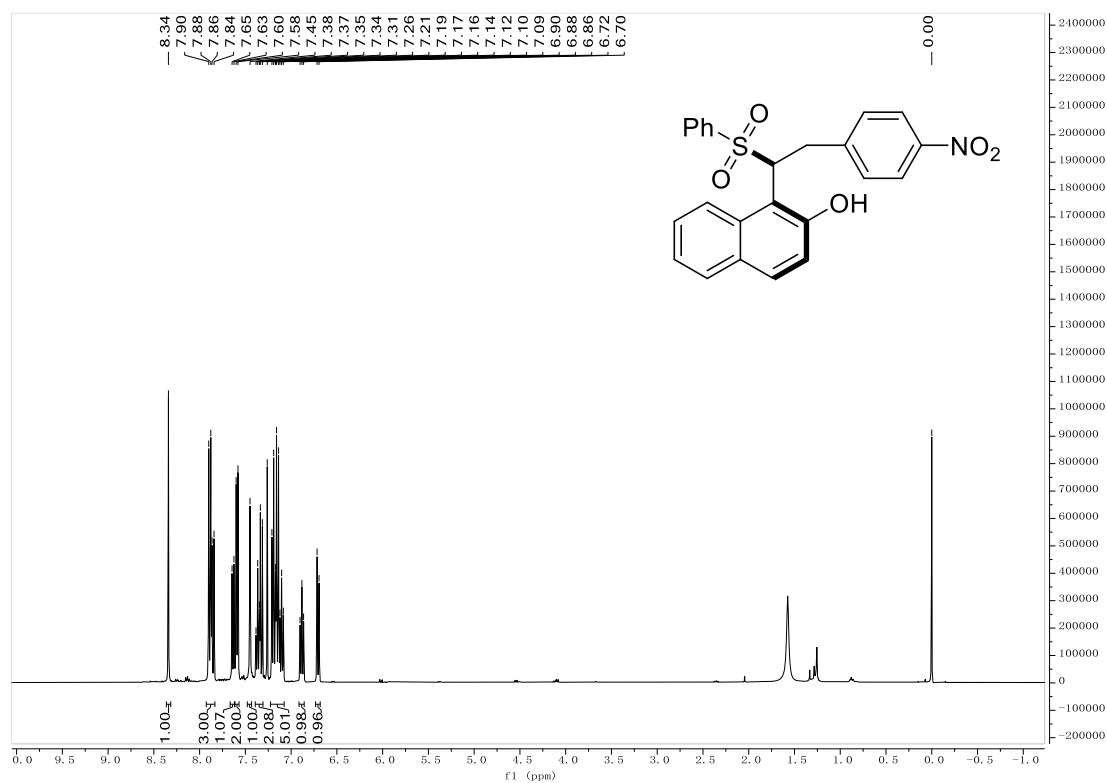
¹³C NMR (101 MHz, CDCl₃) of compound **3ea**



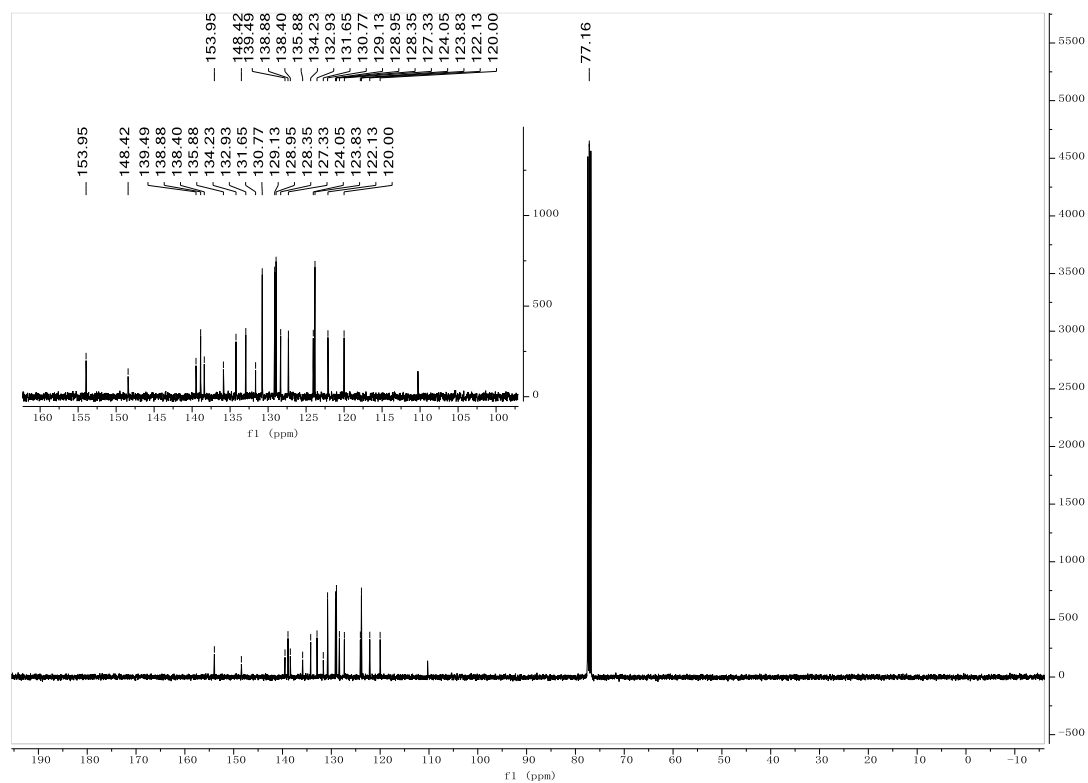
^{19}F NMR (376 MHz, CDCl_3) of compound **3ea**



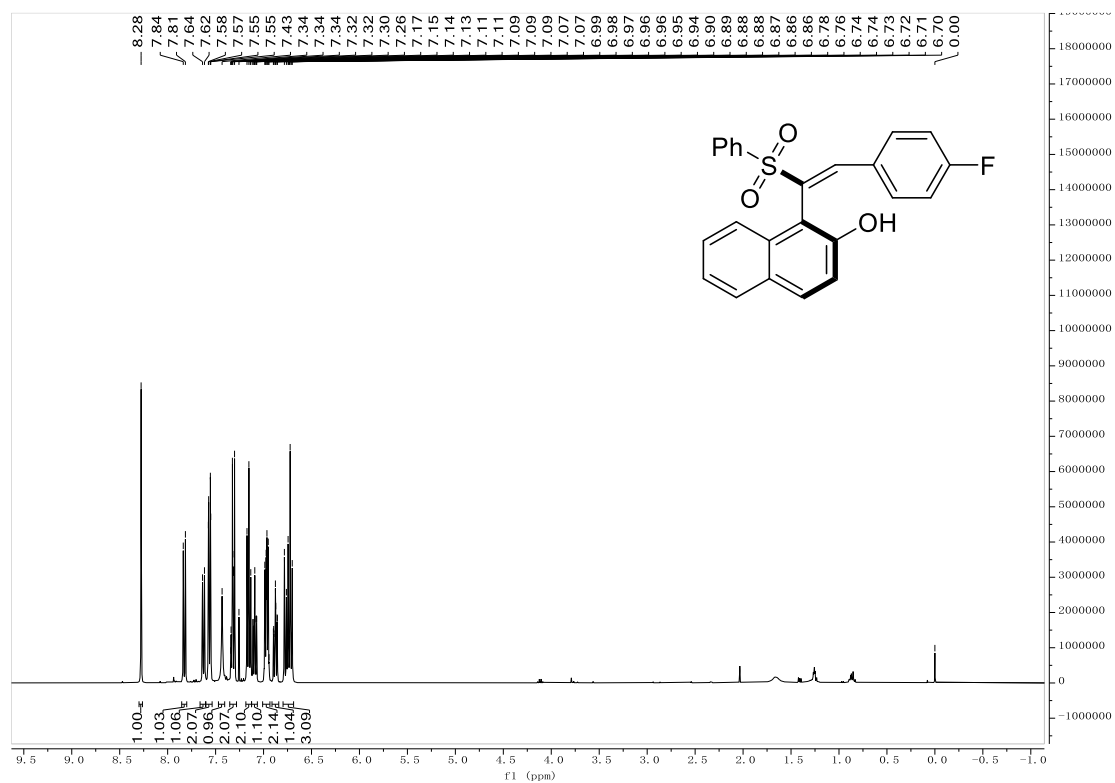
¹H NMR (400 MHz, CDCl₃) of compound **3fa**



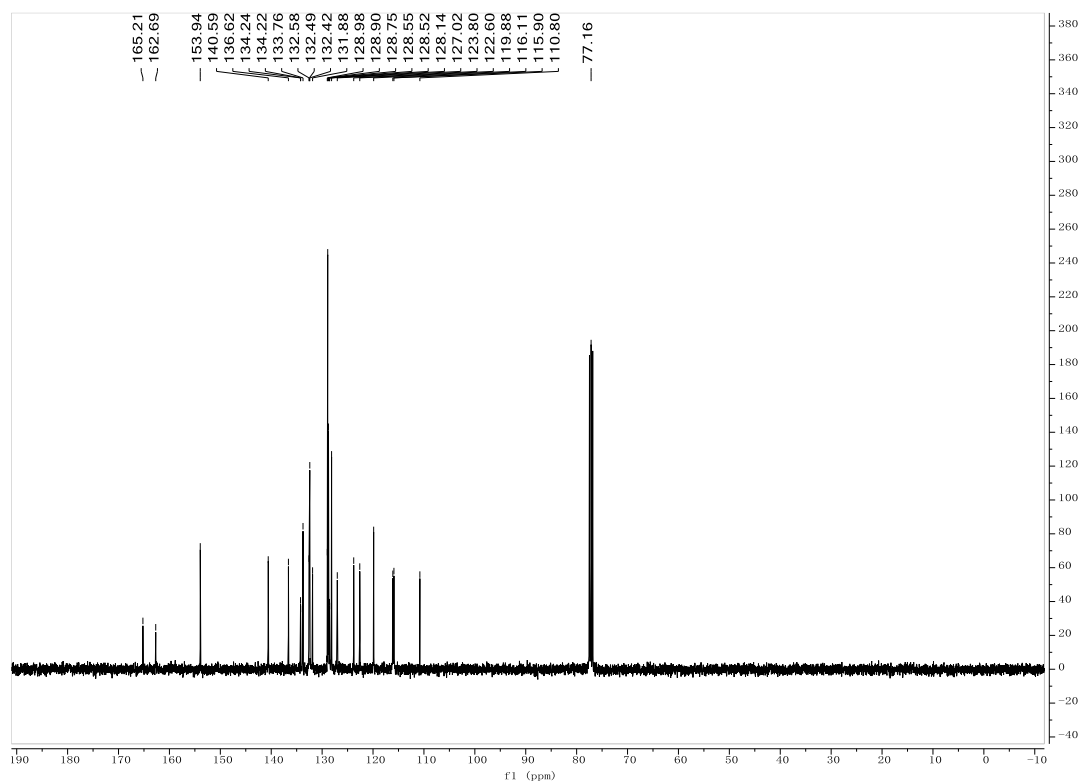
¹³C NMR (101 MHz, CDCl₃) of compound **3fa**



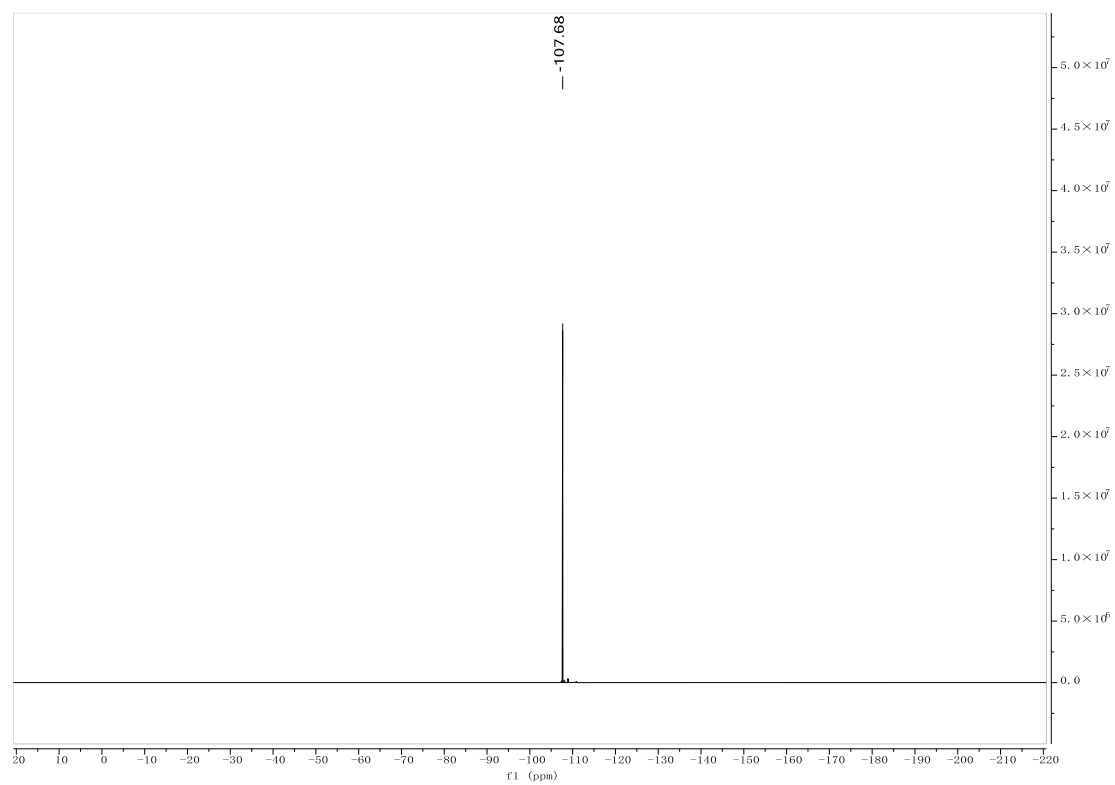
¹H NMR (400 MHz, CDCl₃) of compound **3ga**



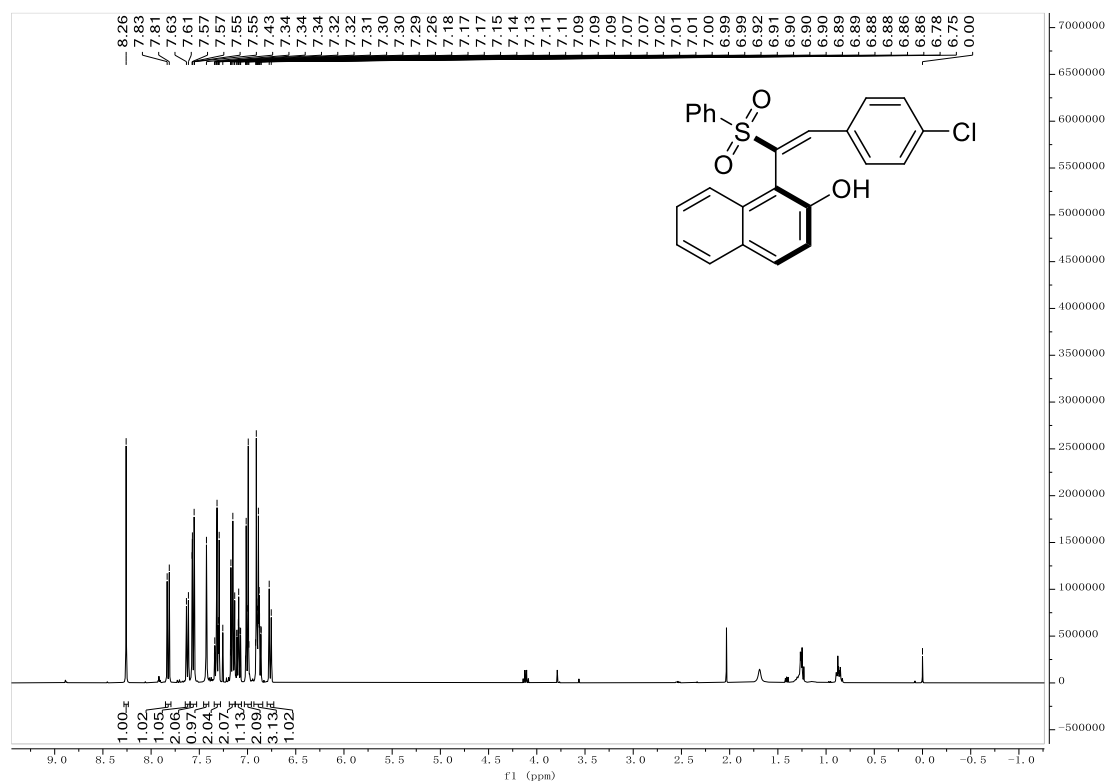
¹³C NMR (101 MHz, CDCl₃) of compound **3ga**



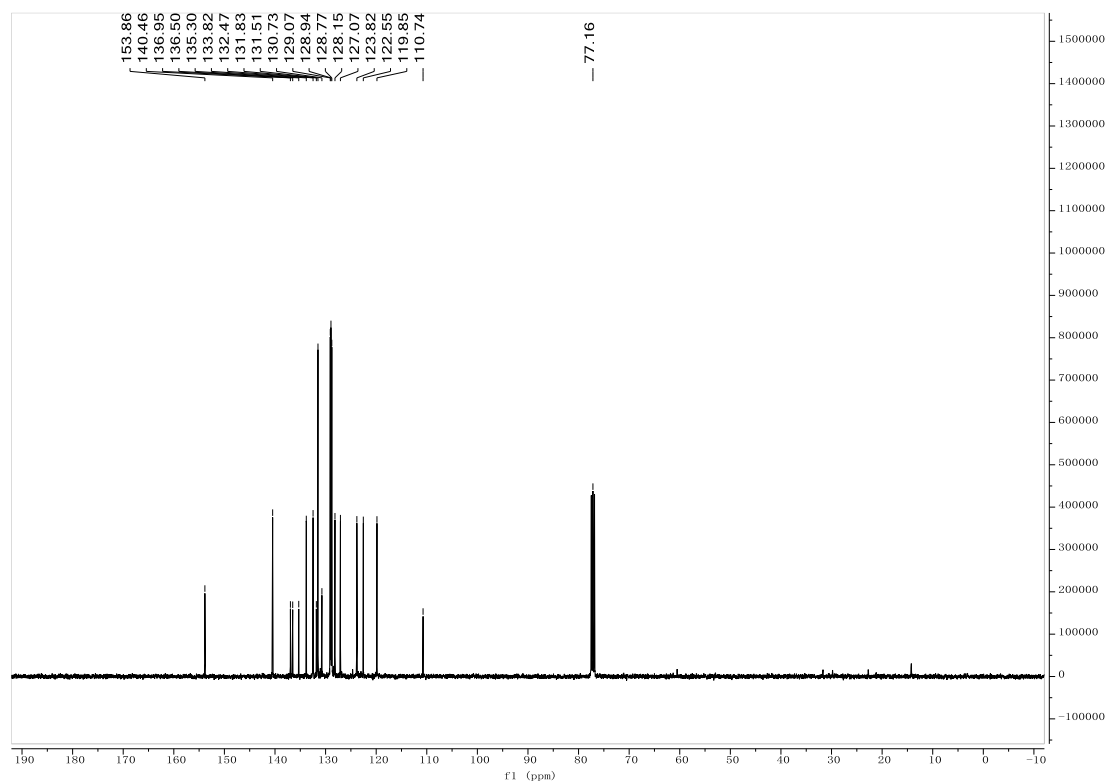
^{19}F NMR (376 MHz, CDCl_3) of compound **3ga**



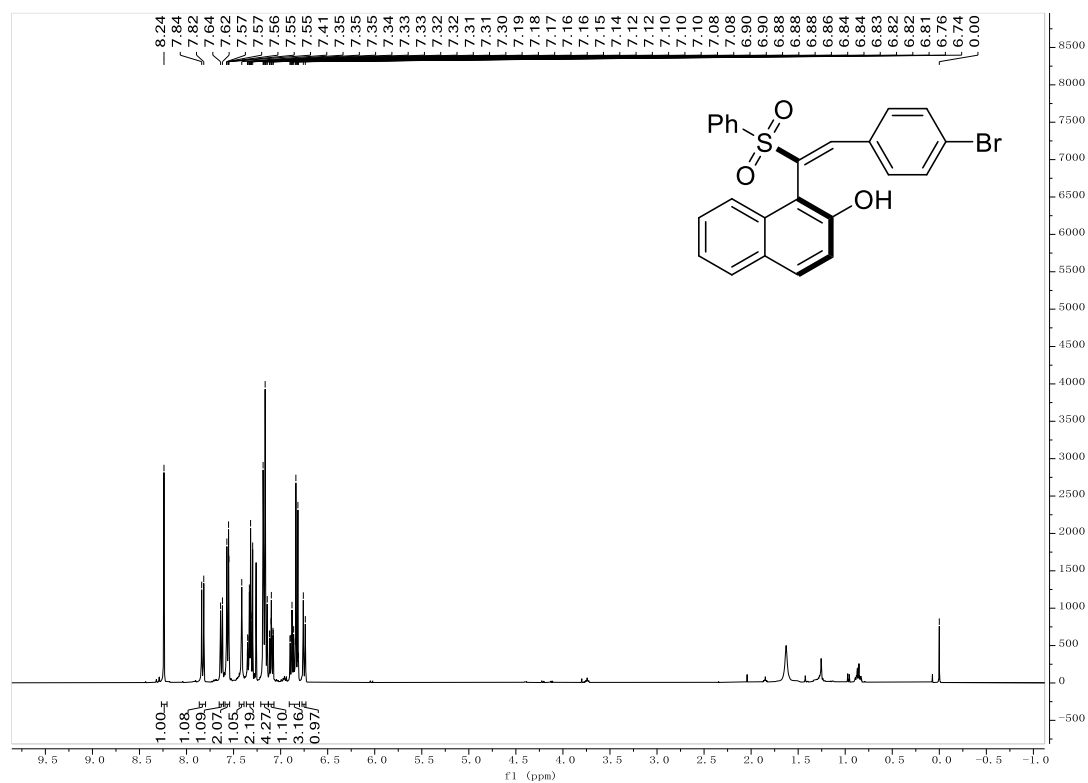
¹H NMR (400 MHz, CDCl₃) of compound 3ha



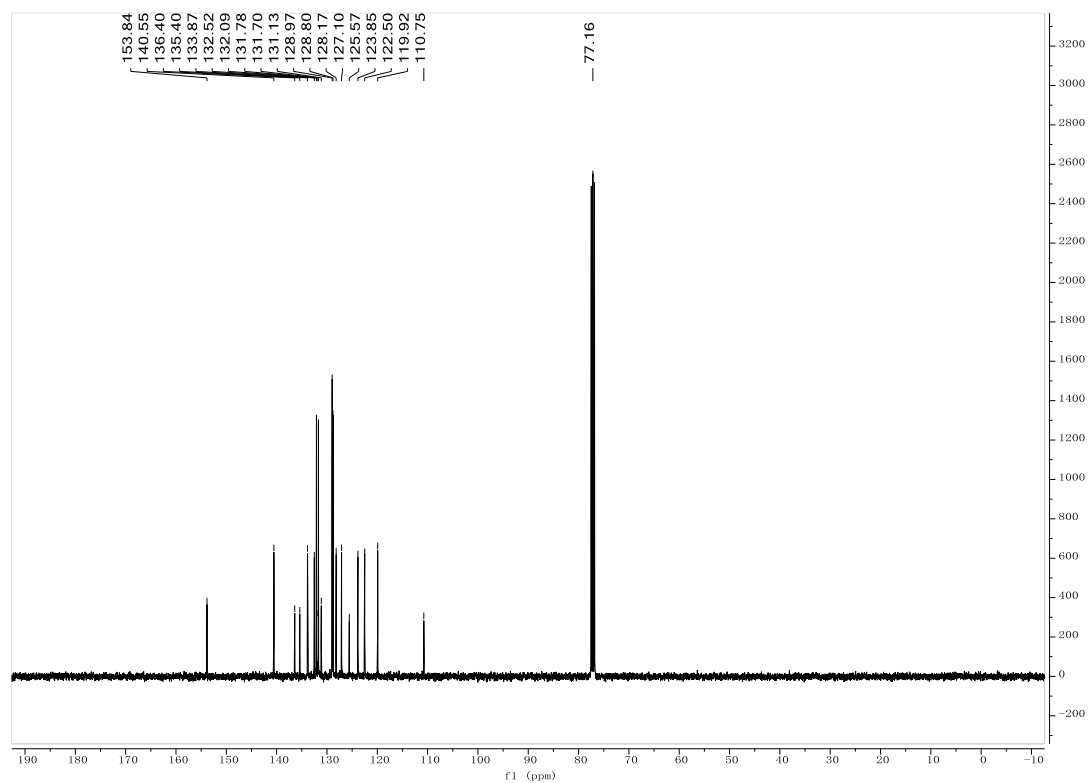
¹³C NMR (101 MHz, CDCl₃) of compound 3ha



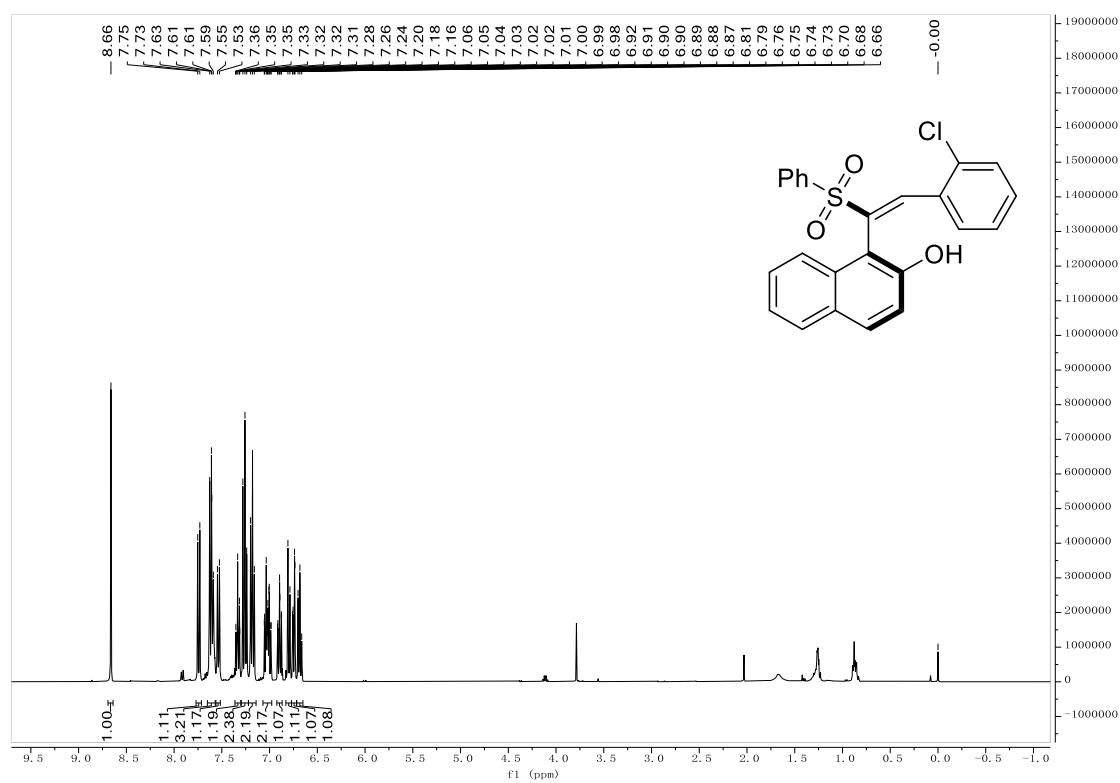
¹H NMR (400 MHz, CDCl₃) of compound **3ia**



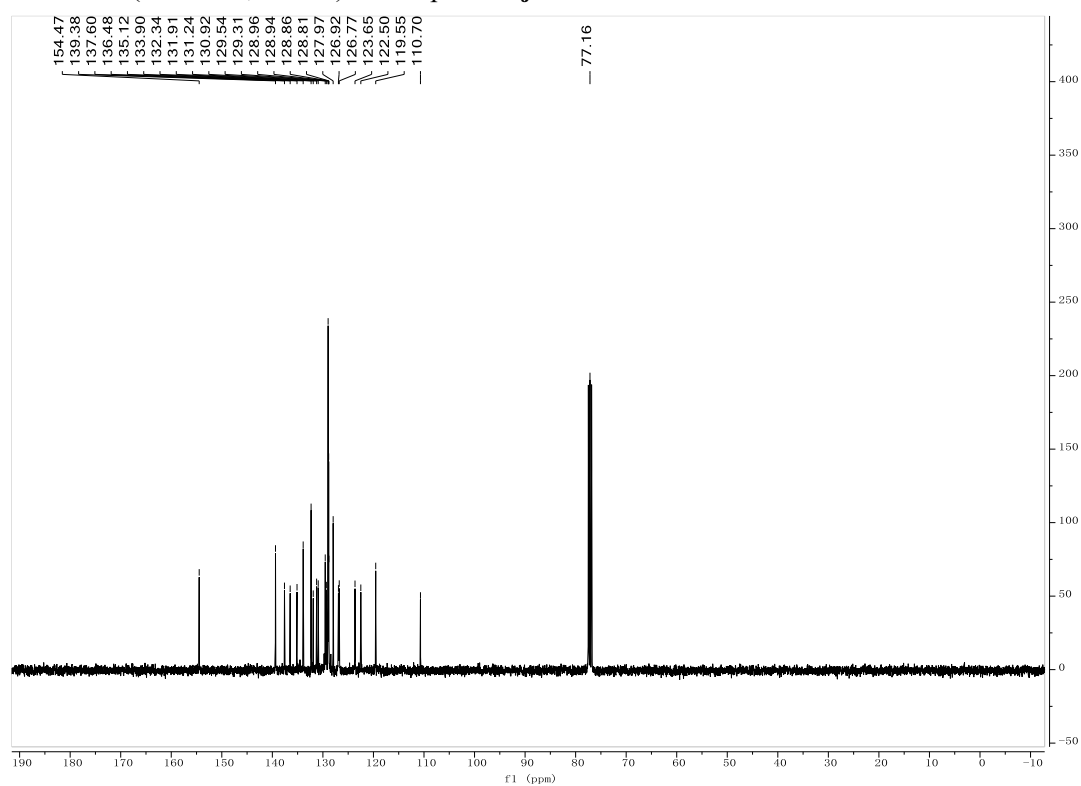
¹³C NMR (101 MHz, CDCl₃) of compound **3ia**



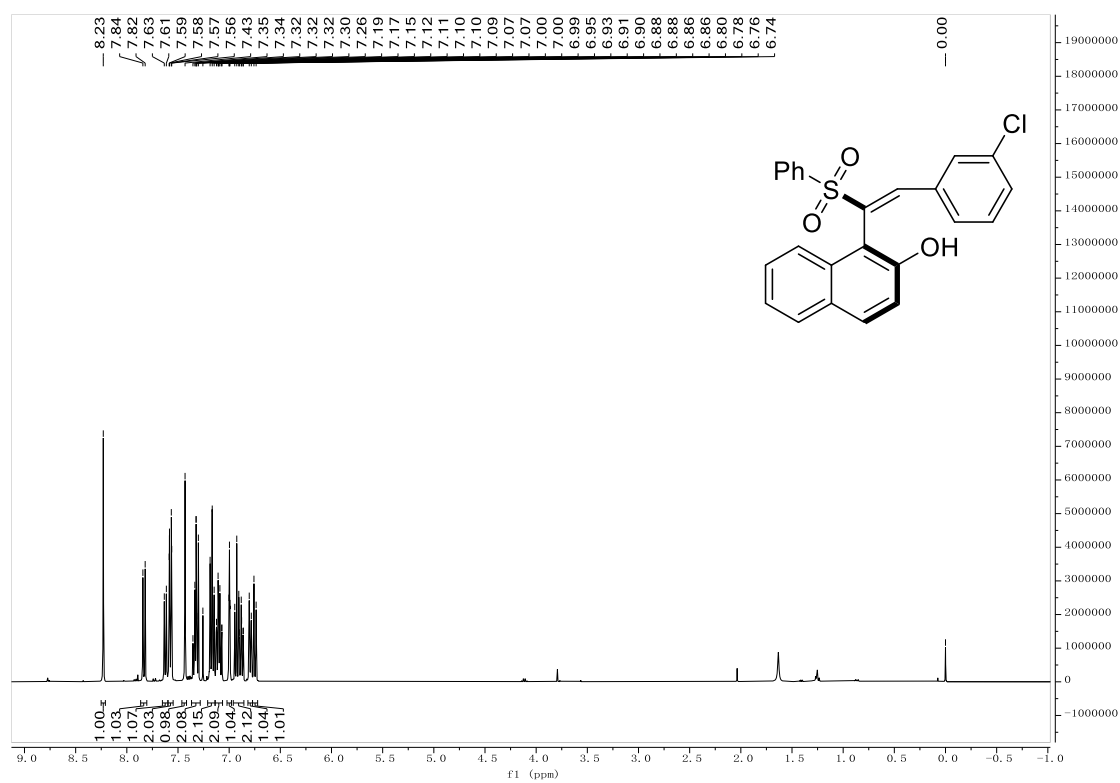
¹H NMR (400 MHz, CDCl₃) of compound 3ja



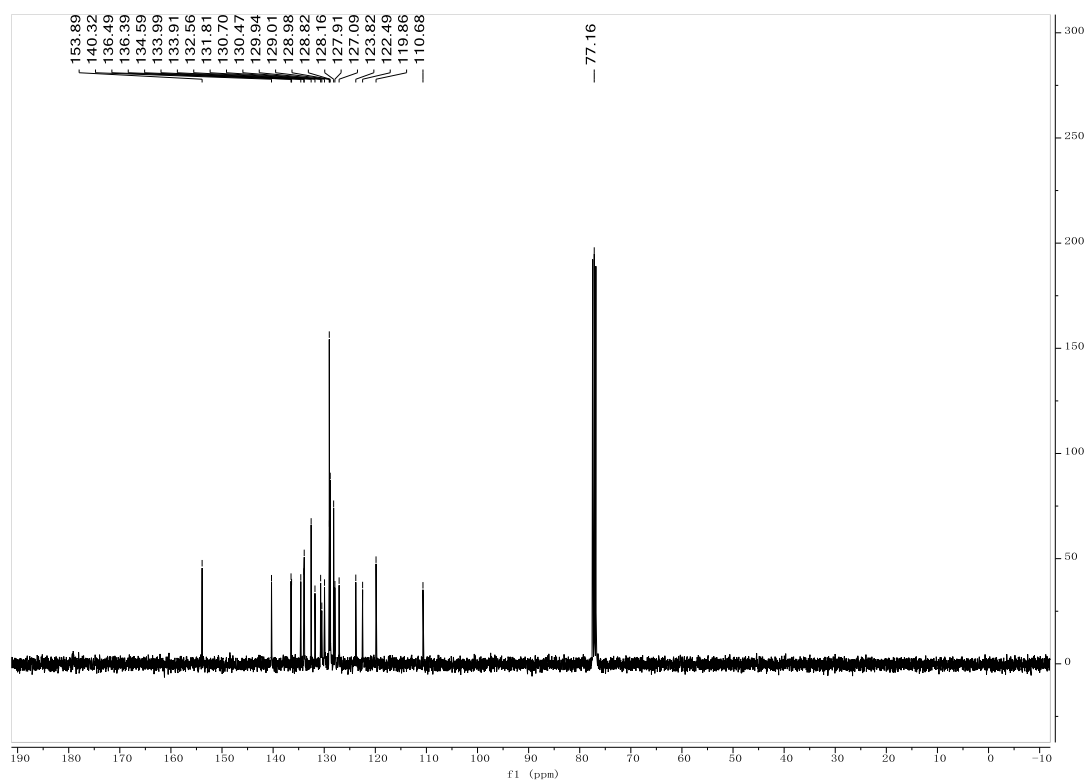
¹³C NMR (101 MHz, CDCl₃) of compound 3ja



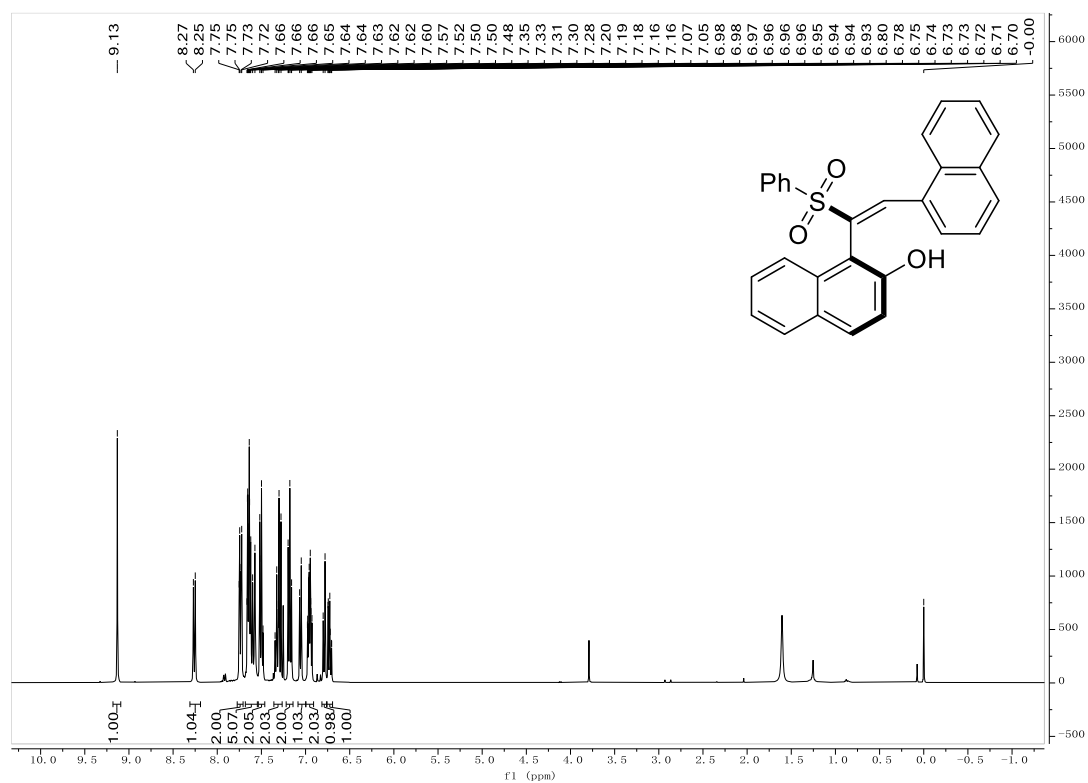
¹H NMR (400 MHz, CDCl₃) of compound 3ka



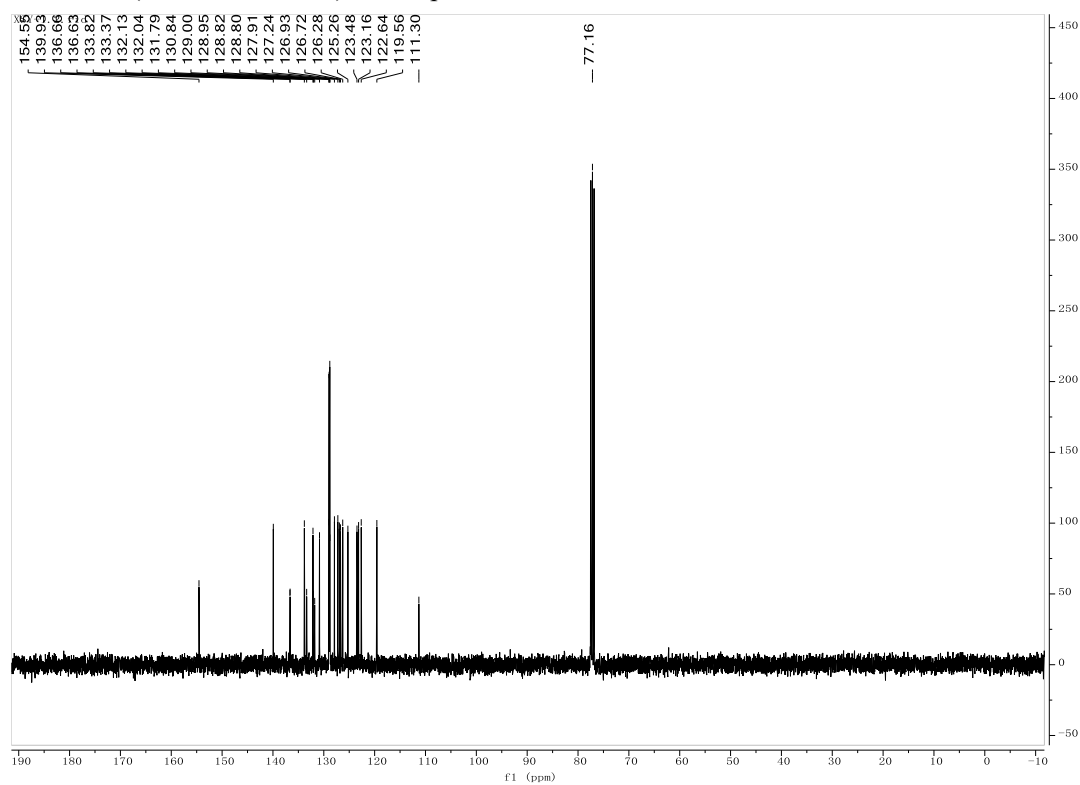
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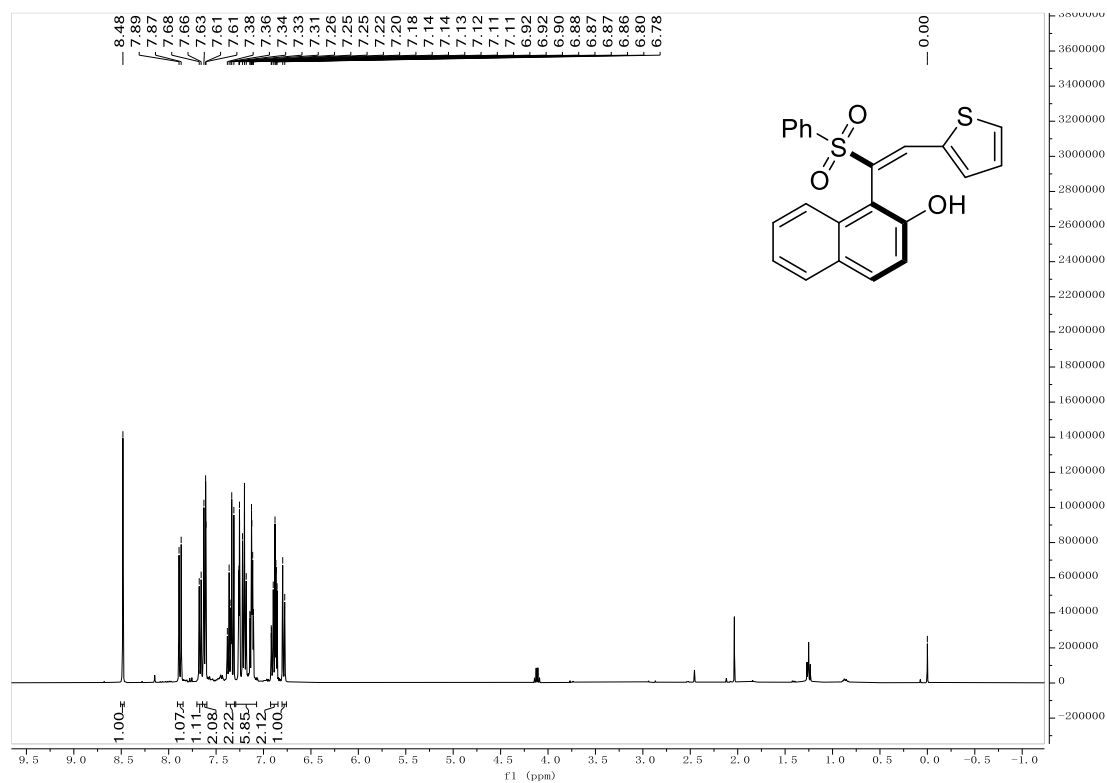
¹H NMR (400 MHz, CDCl₃) of compound 31a



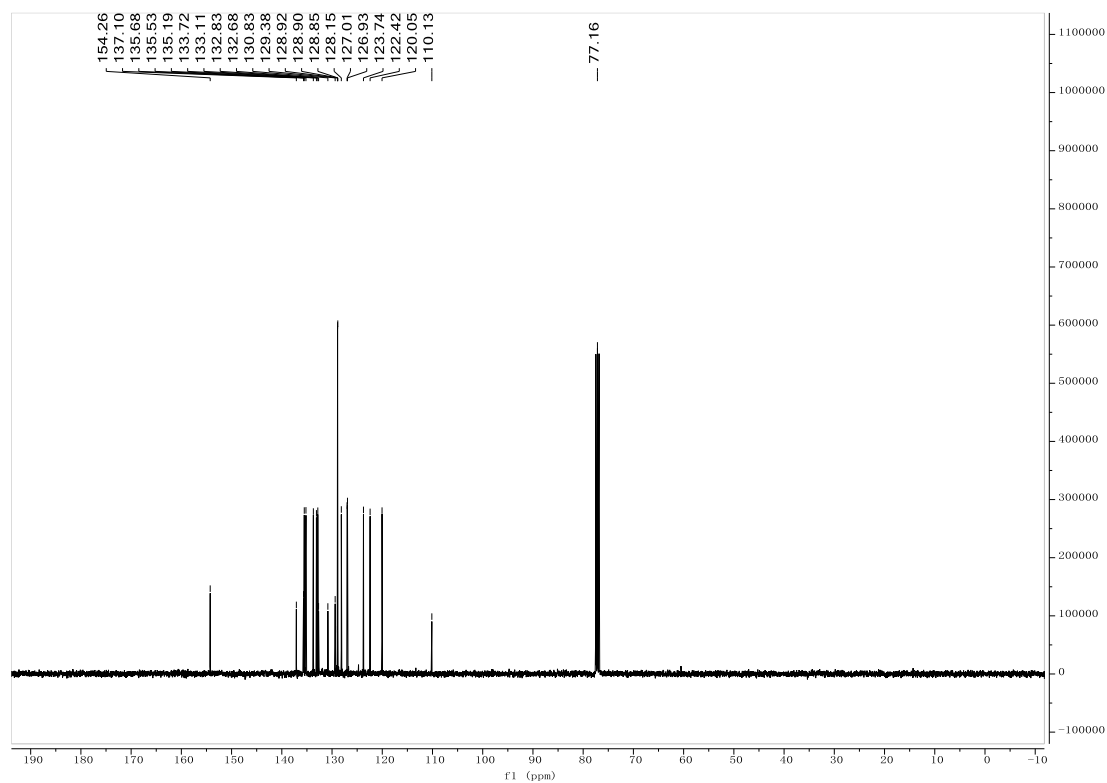
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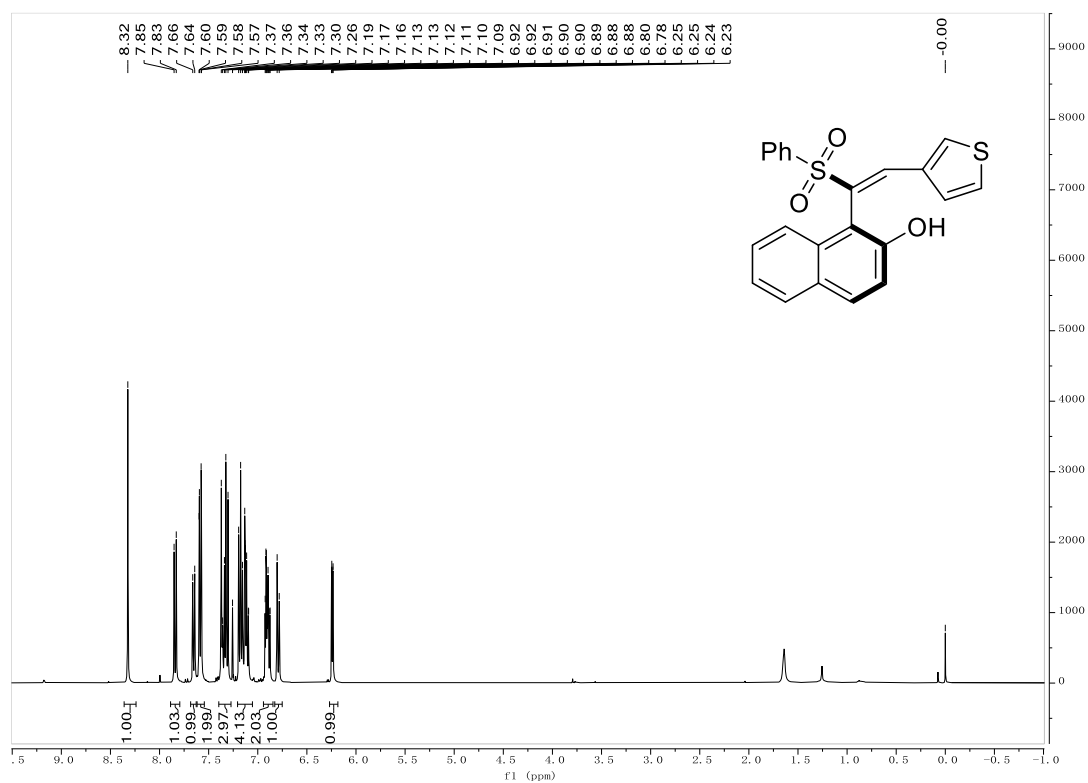
¹H NMR (400 MHz, CDCl₃) of compound **3ma**



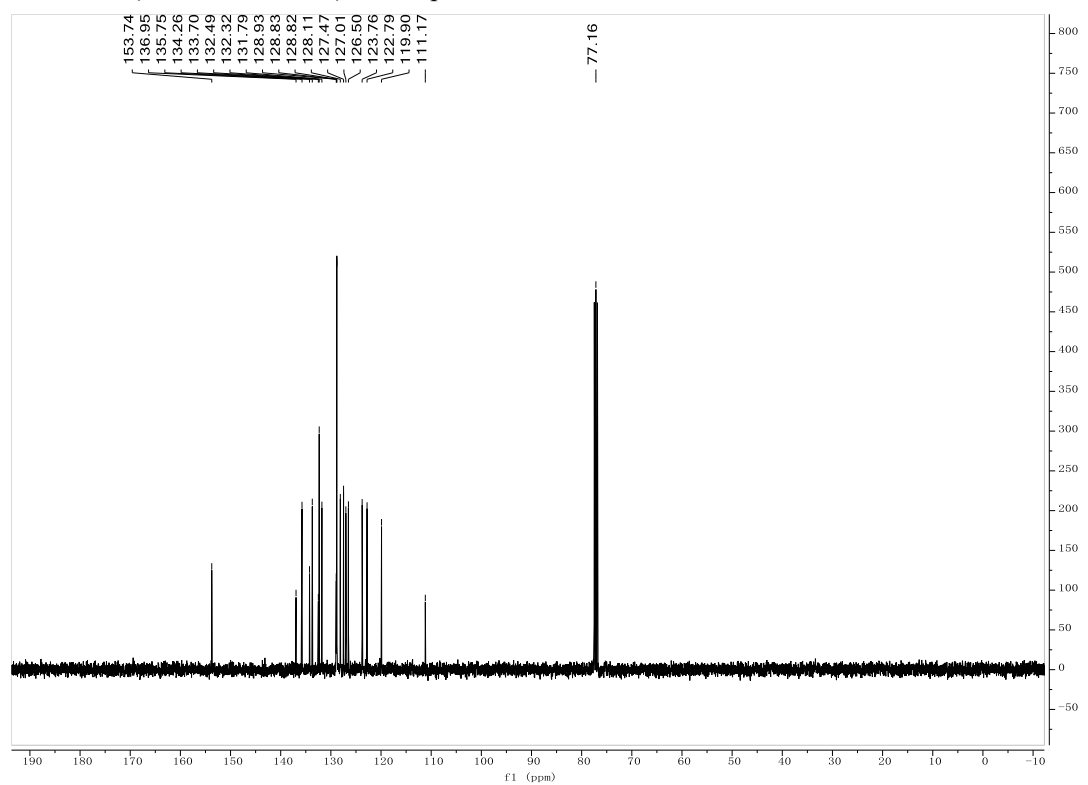
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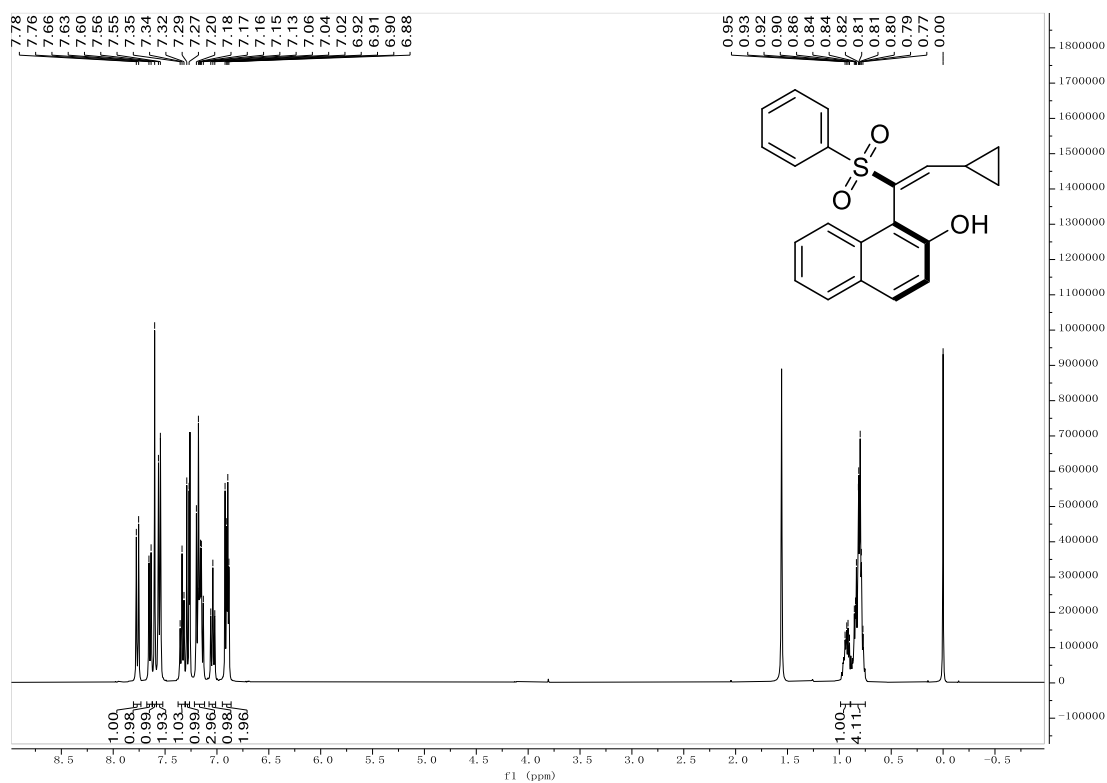
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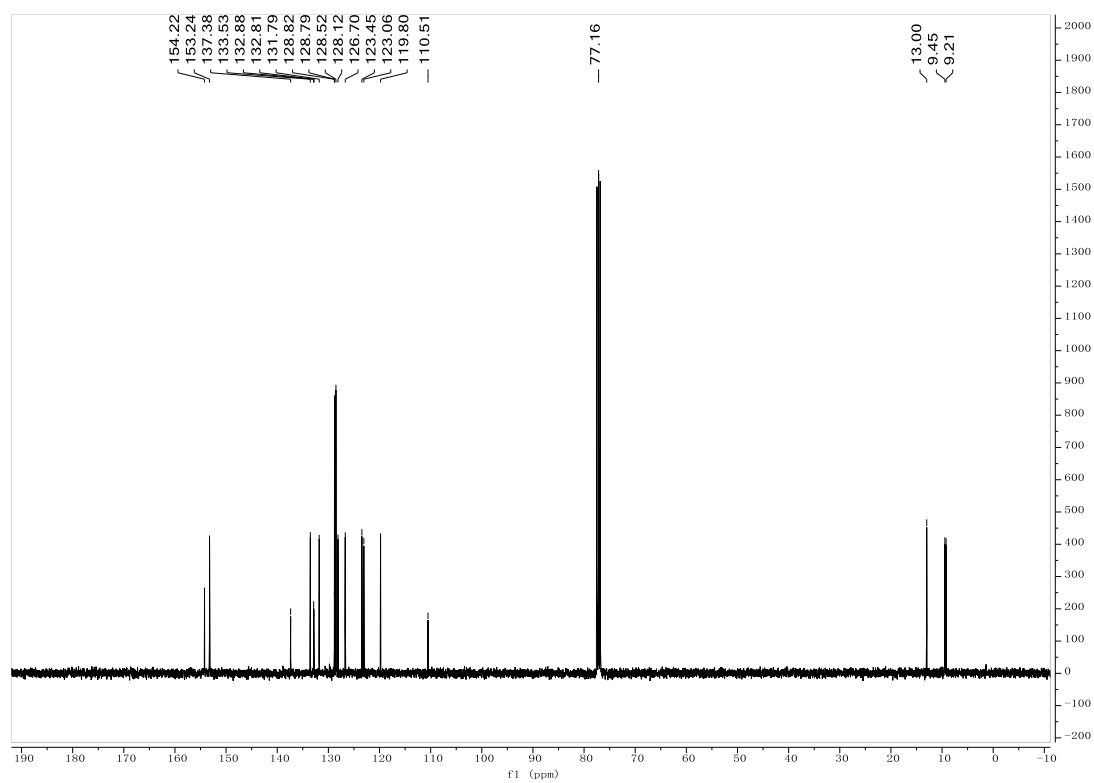
¹³C NMR (101 MHz, CDCl₃) of compound 3na



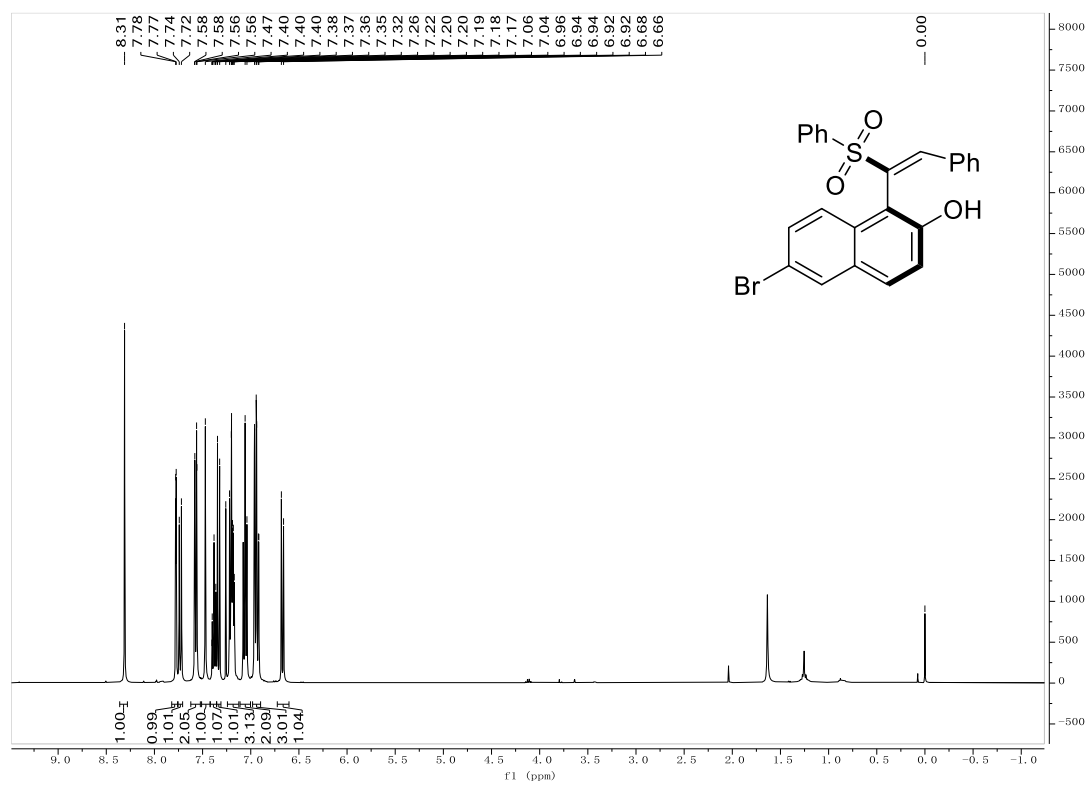
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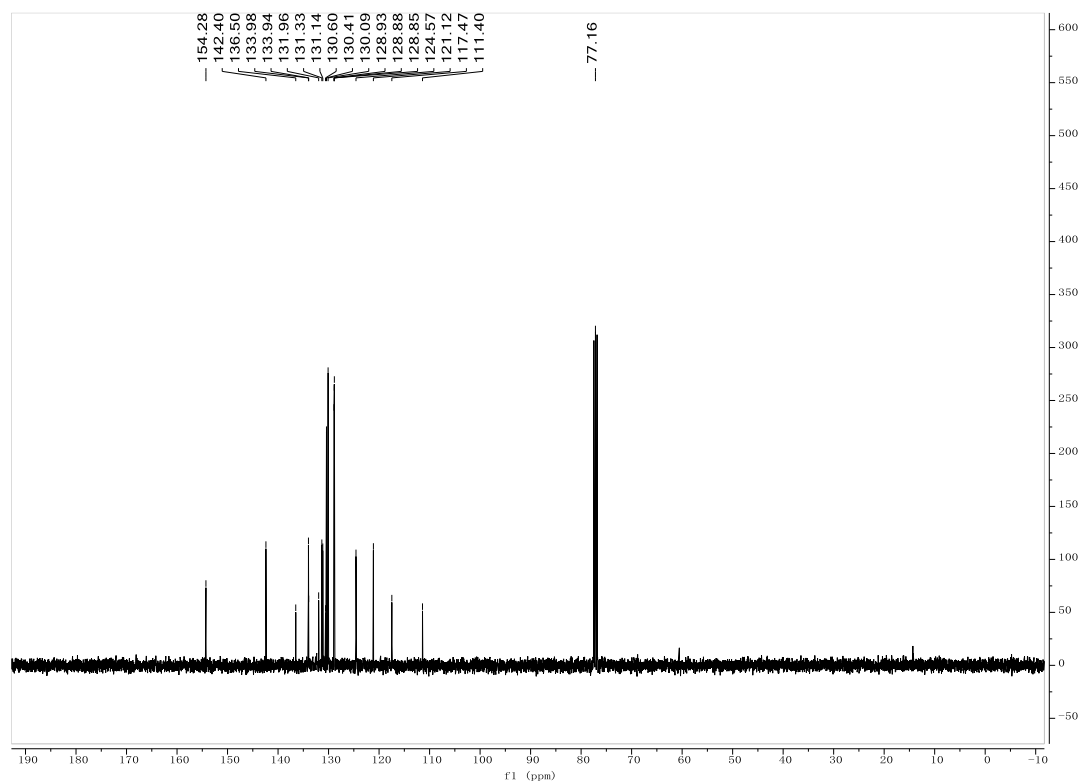
¹³C NMR (101 MHz, CDCl₃) of compound **3oa**



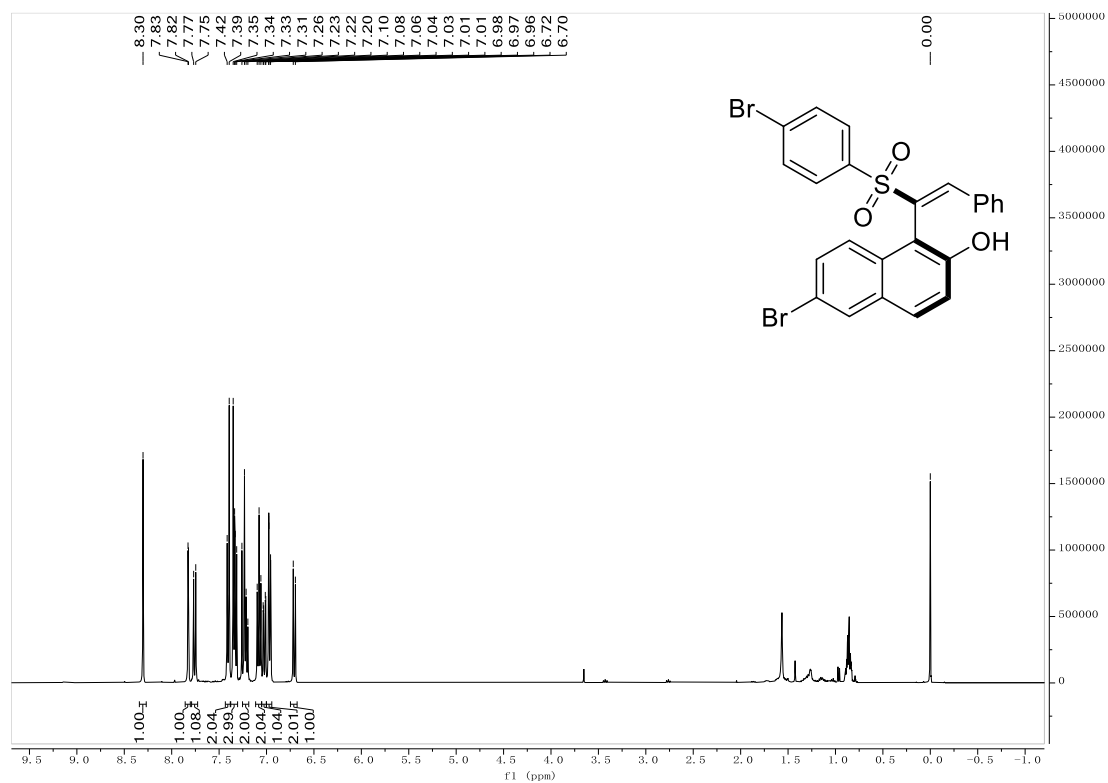
¹H NMR (400 MHz, CDCl₃) of compound 3pa



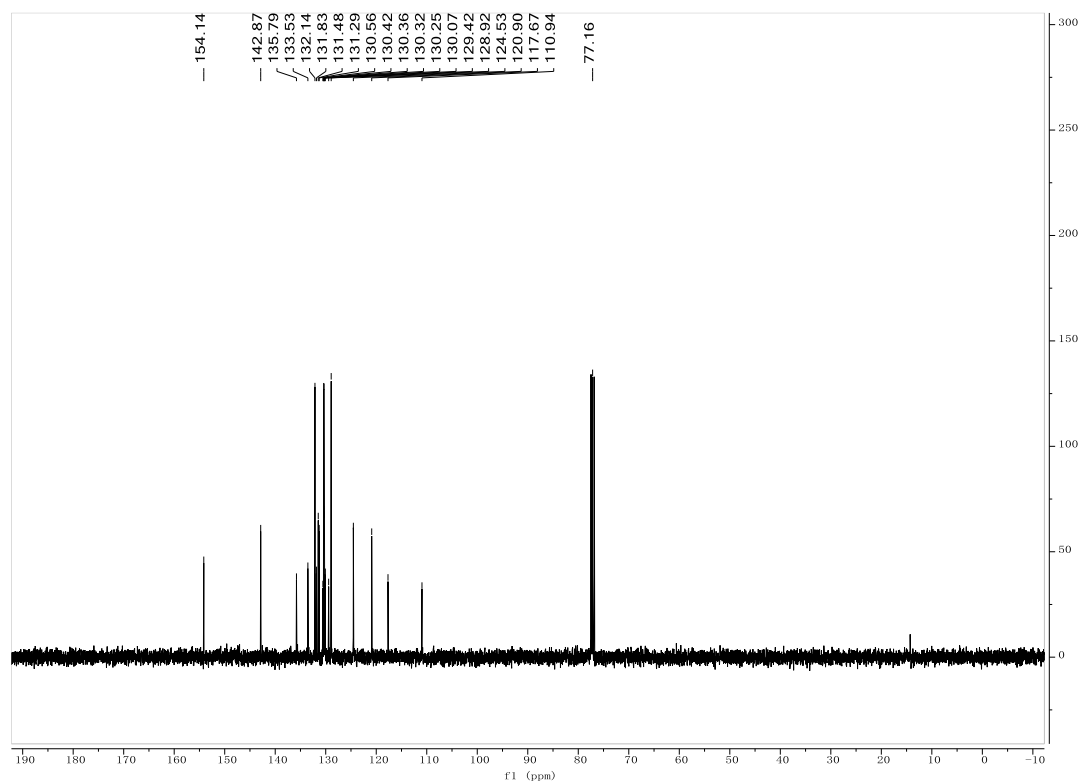
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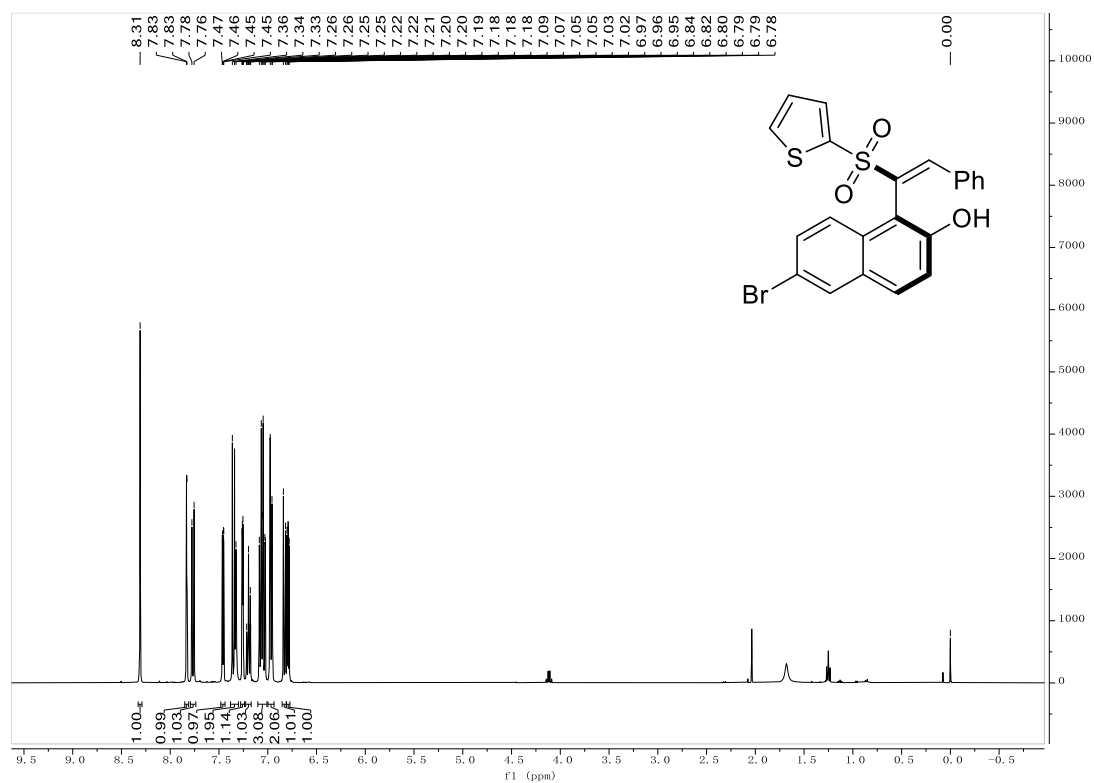
¹H NMR (400 MHz, CDCl₃) of compound 3pg



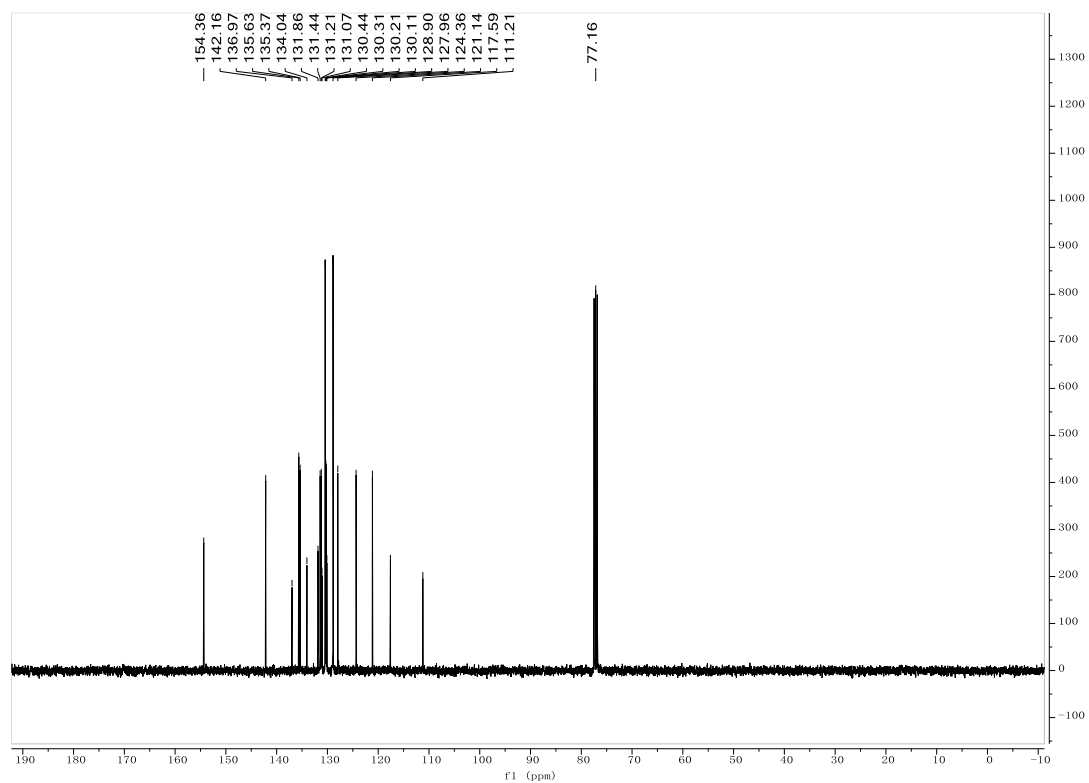
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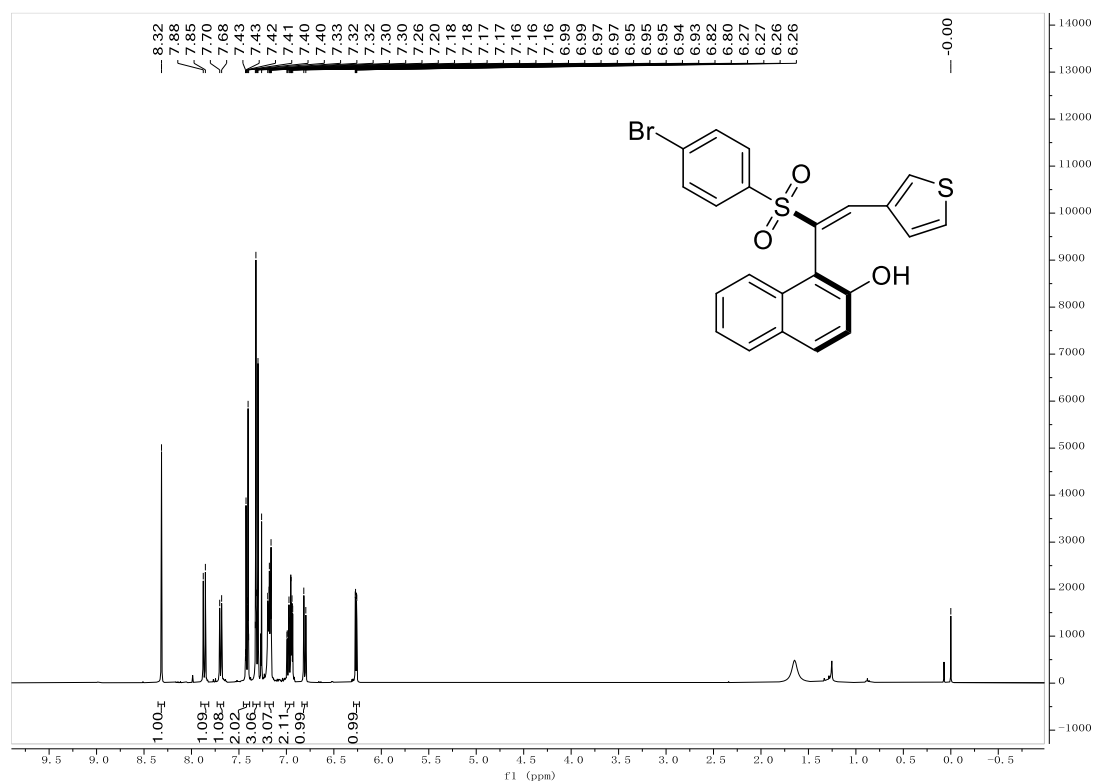
¹H NMR (400 MHz, CDCl₃) of compound 3ph



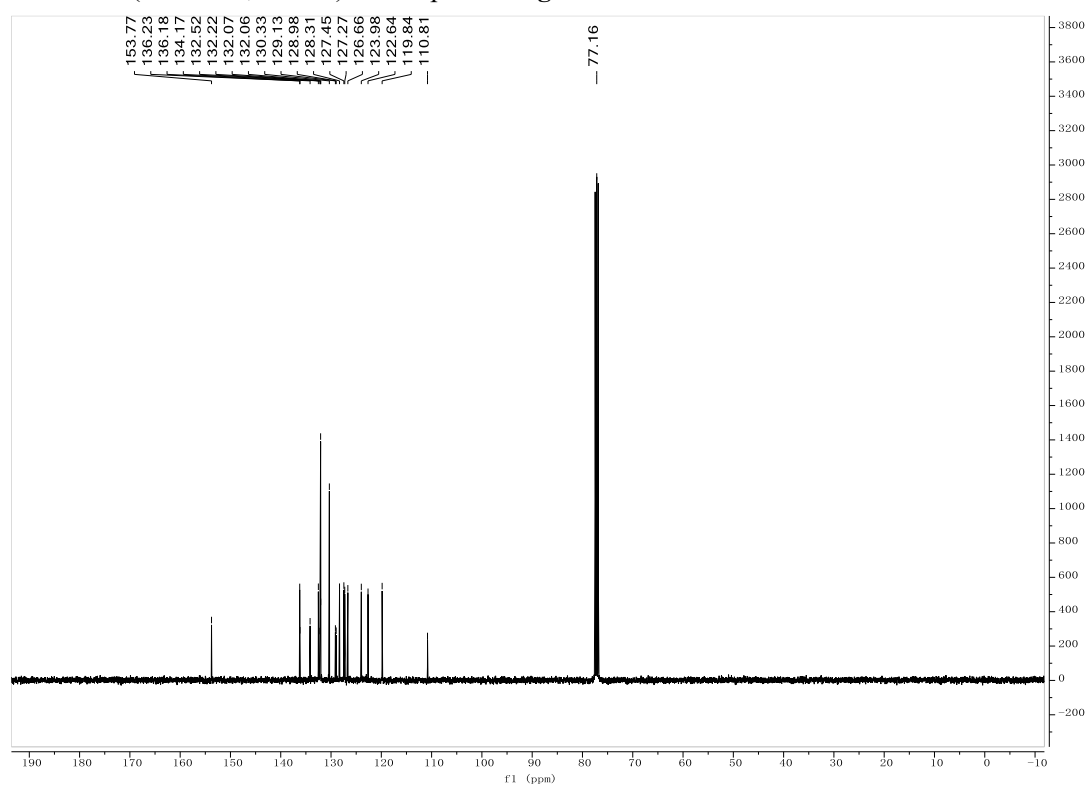
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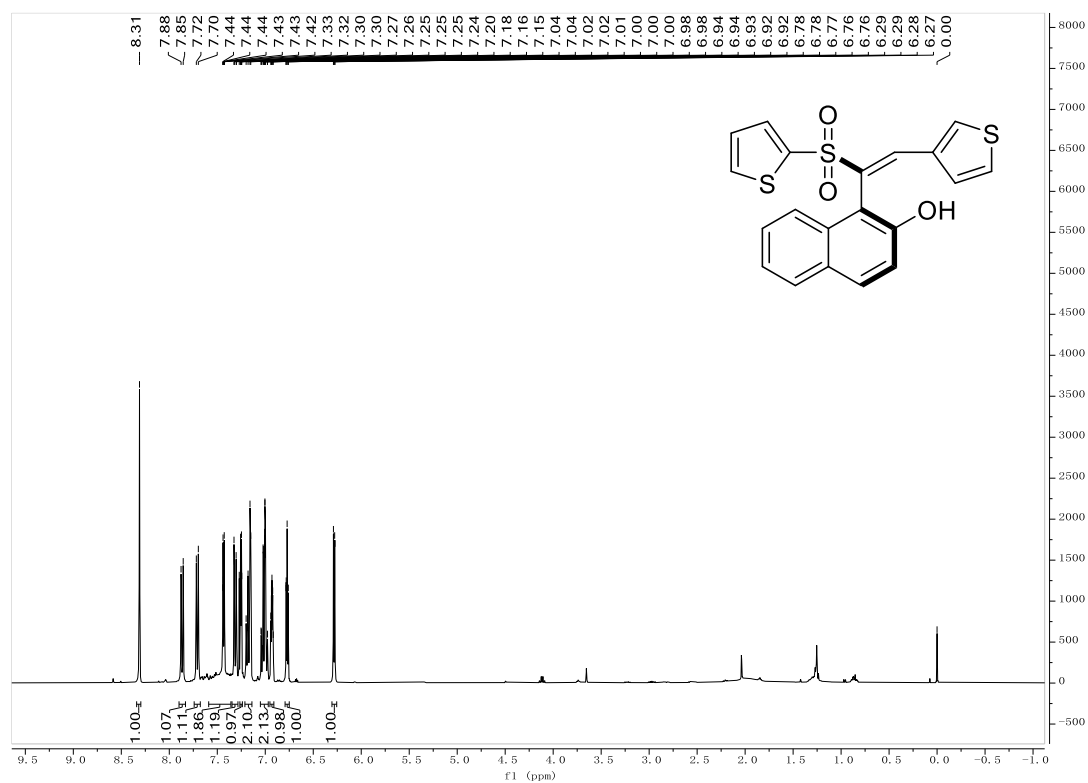
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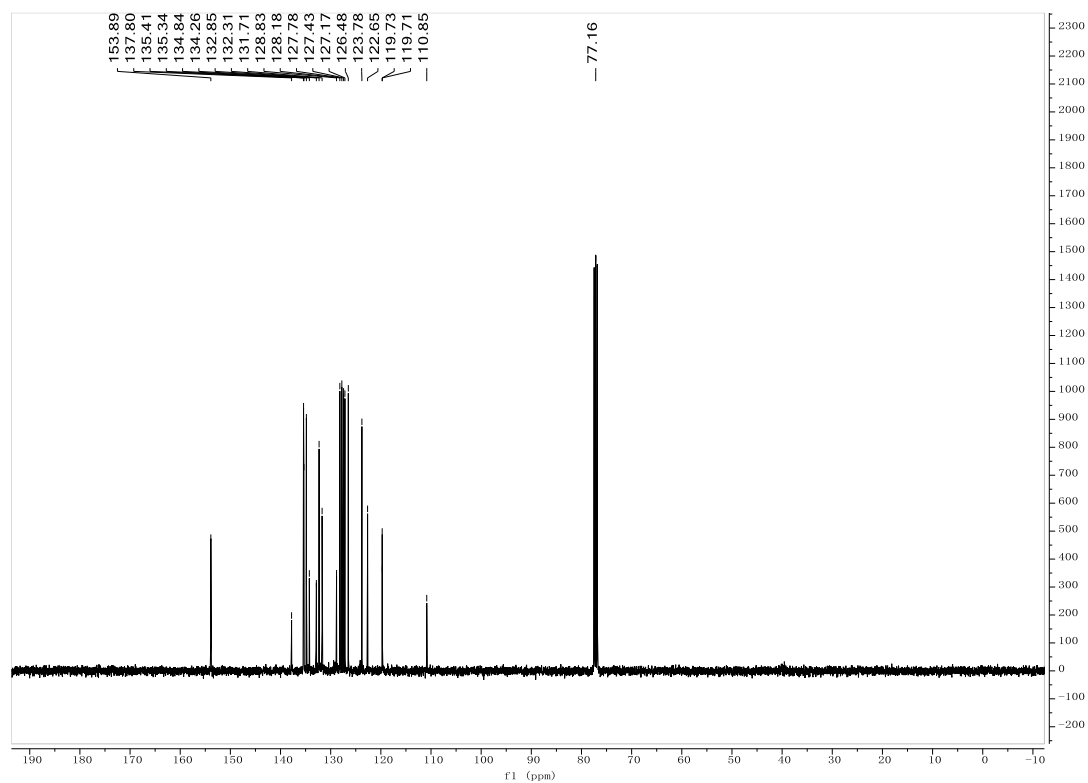
¹³C NMR (101 MHz, CDCl₃) of compound 3ng



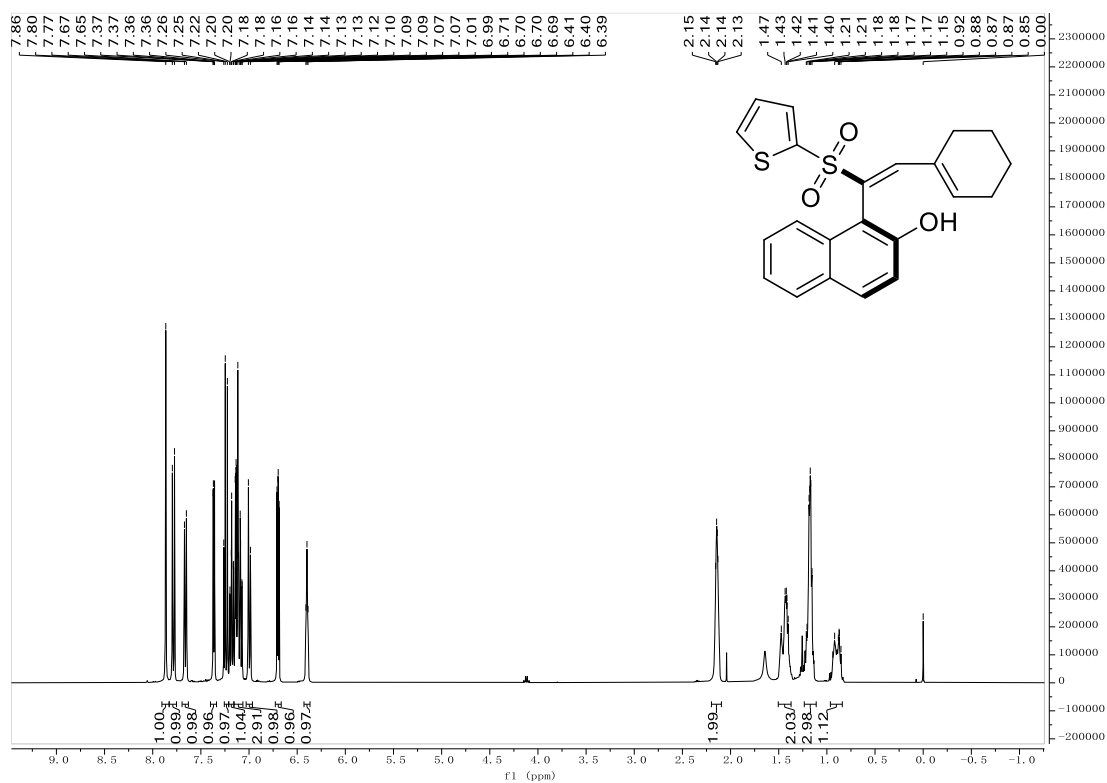
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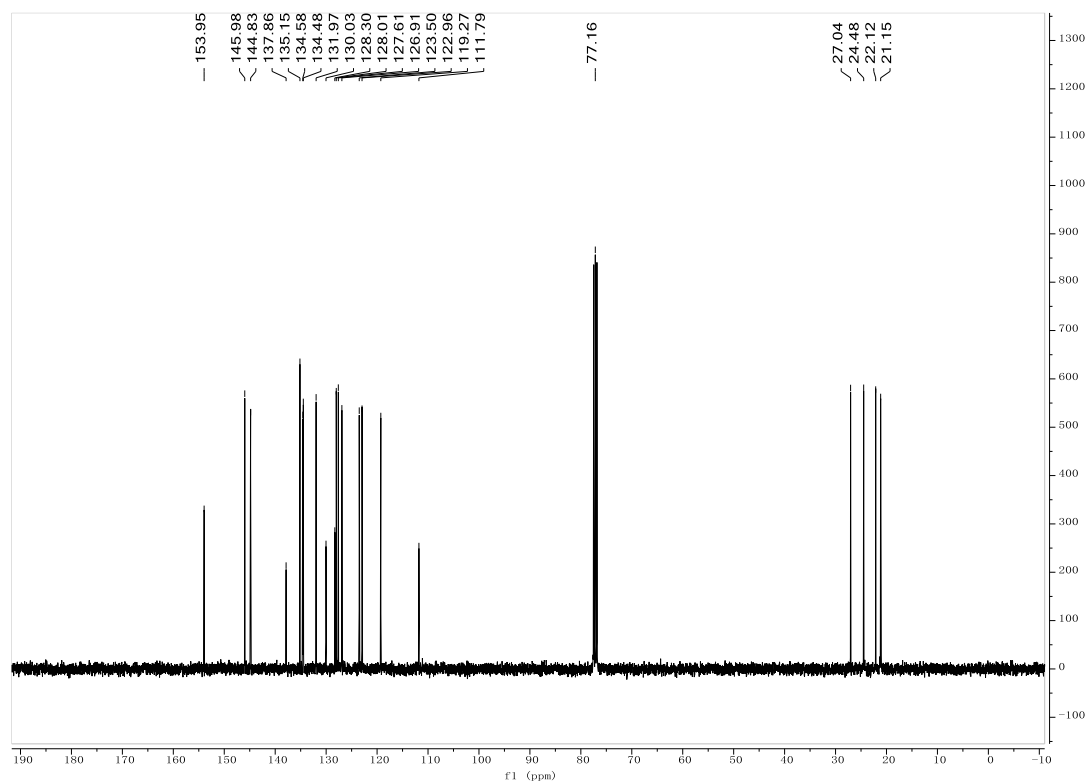
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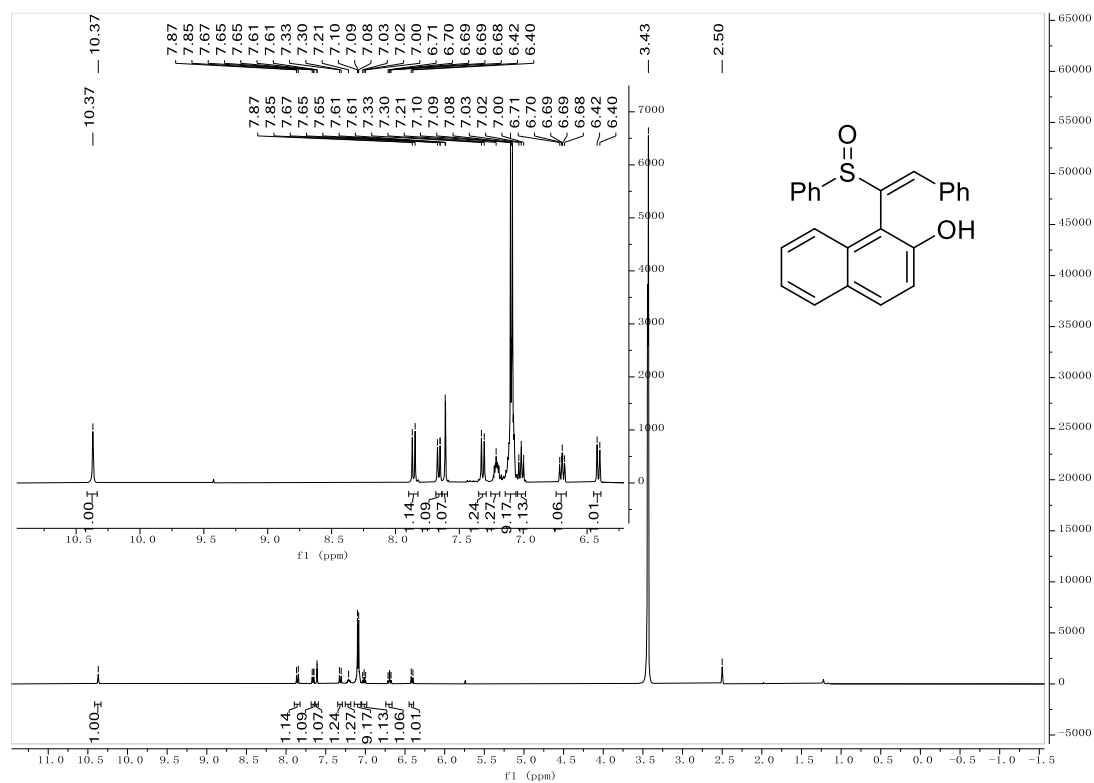
¹H NMR (400 MHz, CDCl₃) of compound 3qh



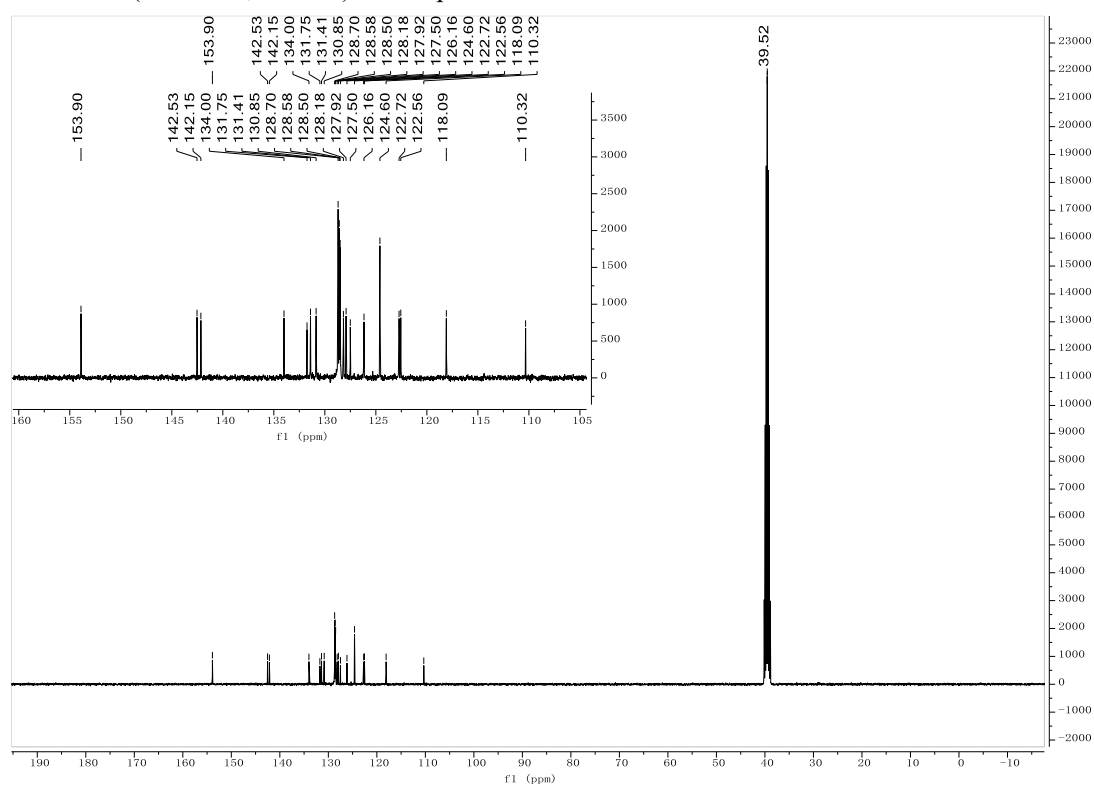
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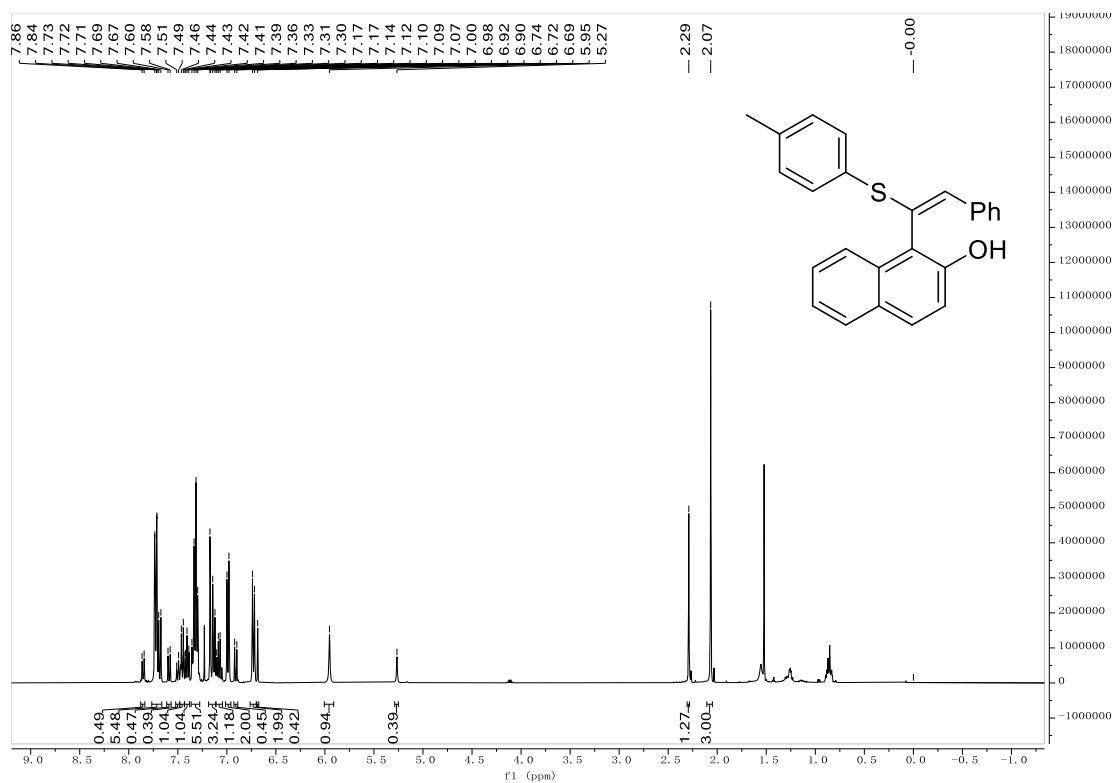
¹H NMR (400 MHz, DMSO) of compound 4



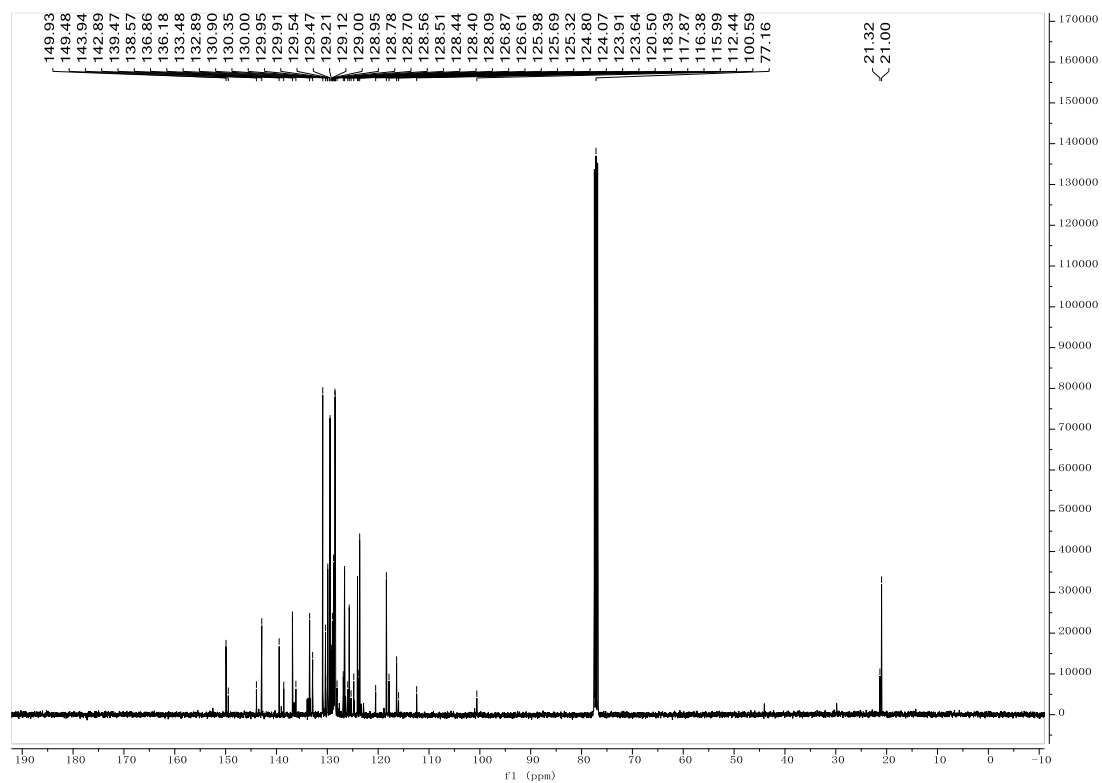
¹³C NMR (101 MHz, DMSO) of compound 4



¹H NMR (400 MHz, CDCl₃) of compound 5



¹³C NMR (101 MHz, CDCl₃) of compound 5



9. References.

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