

Supporting Information

Ring Opening of Thietanes and Other Cyclic Sulfides: An Electrophilic Aryne Activation Approach

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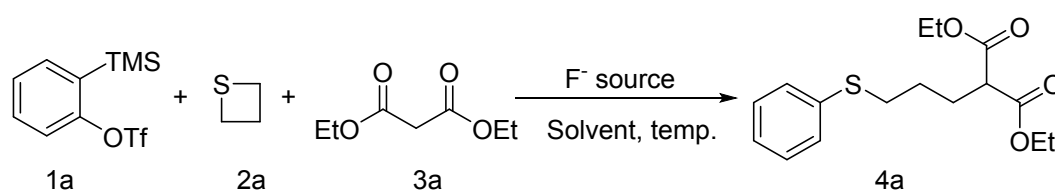
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I. General Methods.

All reactions were carried out in schlenk tubes. The reactions were monitored either by thin-layer chromatography on silica gel 60-F254 coated 0.2 mm plates (Yantai Chemical Industry Research Institute) or GC-MS (Thermo Fisher Trace 1300-ISQ). Visualization was accomplished by UV light (254 nm). The crude products were purified either using a preparative thin-layer chromatography (TLC) plate or flash column chromatography using silica gel (normal phase, 200-300 mesh, Branch of Qingdao Haiyang Chemical). ¹H NMR spectra was recorded on a 400 MHz spectrometer at ambient temperature. Data are reported as follows: (1) chemical shift in parts per million (δ , ppm) from CDCl₃ (7.26 ppm) (2) multiplicity (s = singlet, br = broad, d = doublet, t = triplet, q = quartet, quint = quintet and m = multiplet); (3) coupling constants (Hz). ¹³C NMR spectra were recorded on a 100 MHz spectrometer at ambient temperature. Chemical shifts are reported in ppm from CDCl₃ (77.16 ppm). HR-MS data were obtained on a QTOF mass spectrometer. All commercial materials were used as received unless otherwise noted. Aryne precursors are all prepared following the literature procedures.

II. Optimization of Substrate Ratio^[a]



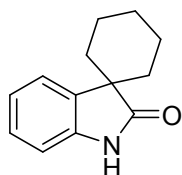
Entry	Ratio(1a: 2a:3a)	F ⁻ source	Solvent	Temp(°C)	Yield ^[b]	3a
						Addition time gap
1	1:0.75:1	CsF	CH ₃ CN	30°C	61%	0min
2	1:1.5:1	CsF	CH ₃ CN	30°C	62%	0min

3	1:2:1	CsF	CH ₃ CN	30°C	51%	0min
4	1:4:1	CsF	CH ₃ CN	30°C	58%	0min
5	0.8:1:1	CsF	CH ₃ CN	30°C	55%	0min
6	1:1:1	CsF	CH ₃ CN	30°C	48%	0min
7	2:1:1	CsF	CH ₃ CN	30°C	20%	0min
8	4:1:1	CsF	CH ₃ CN	30°C	32%	0min
9	1:1:0.67	CsF	CH ₃ CN	30°C	63%	0min
10	1:1:1.67	CsF	CH ₃ CN	30°C	63%	0min
11	1:1:2	CsF	CH ₃ CN	30°C	66%	0min
12	1:1:4	CsF	CH ₃ CN	30°C	78%	0min
13	1:1.5:2	CsF	CH ₃ CN	30°C	76%	0min
14	1:1.5:1.5	CsF	CH ₃ CN	30°C	66%	0min
15	1:1.5:2	CsF	CH ₃ CN	30°C	63%	0min
16	1:1.5:2.5	CsF	CH ₃ CN	30°C	78%	0min

[a]Reaction condition: Unless other noted, **1a**, **2a**, **3a**, CsF (0.5 mmol) and solvent (1 mL) were stirred under N₂ atmosphere for 12 h. [b]Yield was determined by ¹H NMR analysis.

III. Substrates Preparation

1) Synthesis of **3r**:

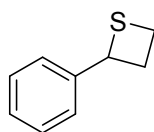


spiro[cyclohexane-1,3'-indolin]-2'-one (3r**)**

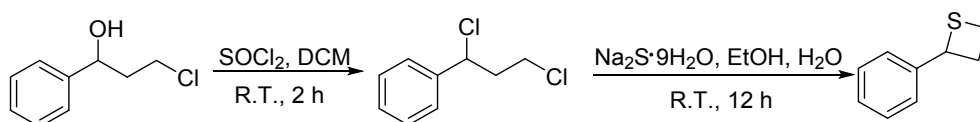
Following the literature procedure¹, the crude product was purified by silica gel

chromatography (PE: EA = 10:1 as the eluent) to give **3r** (81% yield) as a yellow solid. ^1H NMR (400 MHz, CDCl_3) δ 9.94 (br, 1H), 7.43 (d, $J = 7.5$ Hz, 1H), 7.18 (td, $J = 7.8$, 1.2 Hz, 1H), 6.99 (td, $J = 7.5$, 0.9 Hz, 1H), 6.90 (d, $J = 7.8$ Hz, 1H), 2.00-1.85 (m, 2H), 1.84-1.69 (m, 5H), 1.67-1.40 (m, 3H).

2) Synthesis of **2b**:



2-phenylthietane (**2b**)

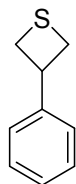


Synthesis of (1,3-dichloropropyl)benzene: to a solution of 3-chloro-1-phenylpropan-1-ol (5 mmol, 0.85 g, 1 equiv.) in 3 mL dichloromethane, thionyl chloride (SOCl_2 , 15 mmol, 1 mol/L in dichloromethane, 15 mL, 3 equiv.) was added dropwise at room temperature. The mixture was kept stirring for 2 h, then poured into 15% sodium hydroxide solution slowly, extracted with dichloromethane (DCM, 3×30 mL), dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was used directly without further purification.

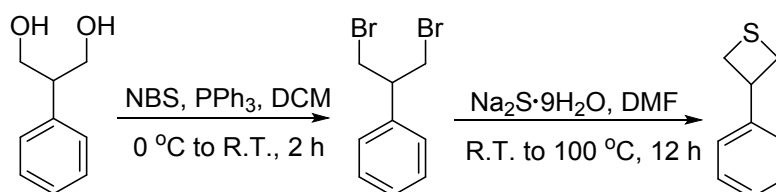
Synthesis of **2b**: to a mixture of the crude product in 40 mL ethanol and 10 mL water, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (5.5 mmol, 1.32 g, 1.1 equiv.) was added at room temperature, stirred at 70 °C for 12 h. The reaction was concentrated in vacuo, water (30 mL) was added, extracted with diethyl ether (3×20 mL), dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE: EA = 100:1 as the eluent) to give **2b** (15% yield) as a pale yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.48-7.44 (m, 2H), 7.34-7.28 (m, 2H), 7.24-7.20 (m, 1H), 4.91 (t, $J = 8.4$ Hz, 1H), 3.39-3.31 (m, 1H), 3.19-3.02 (m, 2H), 2.93 (td, $J =$

8.9, 3.7 Hz, 1H).

3) Synthesis of **2c**:



3-phenylthietane (**2c**)

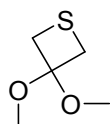


Synthesis of (1,3-dibromopropan-2-yl)benzene: to a mixture of 2-phenylpropane-1,3-diol (2.0 mmol, 0.30 g, 1.0 equiv.) and triphenylphosphine (2.2 mmol, 1.3 g, 2.2 equiv.) in dichloromethane (10 mL), N-Bromosuccinimide (NBS, 5.0 mmol, 0.89 g, 2.2 equiv.) was added in one portion at 0 °C. The cooling bath was removed and the reaction mixture was then stirred at room temperature for 2 h. After completion of the reaction, the solvent was evaporated and the product was purified by silica gel flash chromatography (PE: EA = 100:1 as the eluent) to give (1,3-dibromopropan-2-yl)benzene (79% yield) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.38-7.27 (m, 3H), 7.24-7.18 (m, 2H), 3.83 (dd, *J* = 10.3, 6.9 Hz, 2H), 3.76 (dd, *J* = 10.3, 6.3 Hz, 2H), 3.42 (quint, *J* = 6.5 Hz, 1H).

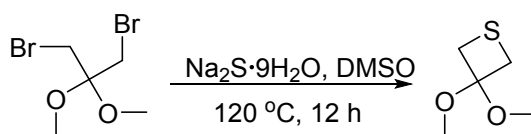
Synthesis of **2c**: to a mixture of (1,3-dibromopropan-2-yl)benzene (1.36 mmol, 0.37 g, 1.0 equiv.) in 10 mL anhydrous DMF was added Na₂S·9H₂O (1.63 mmol, 0.39 g, 1.2 equiv.) under nitrogen atmosphere in a flame-dried schlenk tube. The mixture was stirred at 100 °C for 12 h. The reaction was then quenched with water (30 mL) and extracted with ethyl acetate (3×20 mL), dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE as the eluent) to give **2c** (52% yield) as a colorless oil. ¹H NMR

(400 MHz, CDCl₃) δ 7.33-7.26 (m, 4H), 7.25-7.22 (m, 1H), 4.58 (quint, $J = 9.0$ Hz, 1H), 3.61 (dd, $J = 9.2$ Hz, 2H), 3.36 (dd, $J = 9.1$ Hz, 2H).

4) Synthesis of **2d**:



3,3-dimethoxythietane (**2d**)

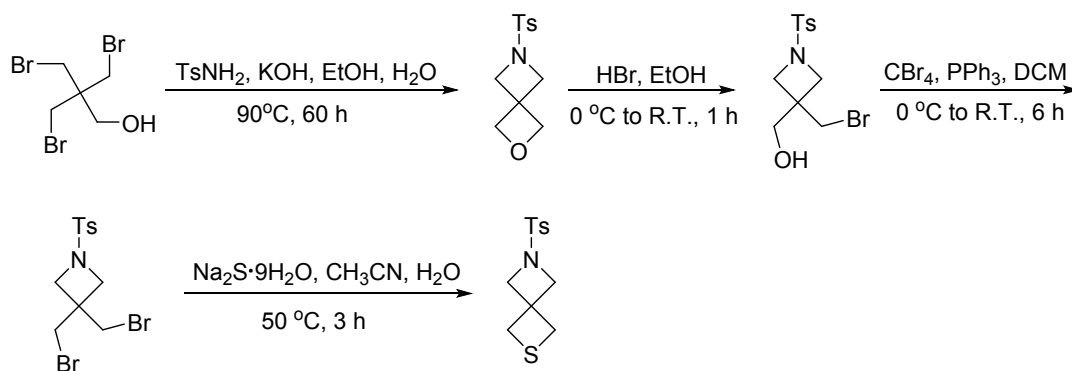


Synthesis of **2d**: a solution of 1,3-dibromo-2,2-dimethoxypropane (10 mmol, 2.62 g, 1 equiv.) and Na₂S·9H₂O (12 mmol, 2.88 g, 1.2 equiv.) in 50 mL dimethyl sulfoxide (DMSO) was stirred at 120 °C for 12 h. The reaction was then quenched with water (30 mL) and extracted with ethyl acetate (3×30 mL), dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE: EA = 20:1 as the eluent) to give **2d** (81% yield) as a yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 3.35 (s, 4H), 3.19 (s, 6H).

5) Synthesis of **2e**:



6-tosyl-2-thia-6-azaspiro[3.3]heptane (**2e**)



Synthesis of 6-tosyl-2-oxa-6-azaspiro[3.3]heptane: to a mixture of potassium hydroxide (KOH, 2.87 g, 51.2 mmol, 3.2 equiv.) and *p*-tosylamide (3.40 g, 19.2 mmol, 1.2 equiv.) in 260 mL ethanol, 3-bromo-2,2-bis(bromomethyl)propan-1-ol (5.23 g, 16 mmol, 1.0 equiv.) was added at room temperature and the reaction mixture was heated to 90 °C for 60 h. After completion of the reaction, the solvent was evaporated, then 50 mL 1M potassium hydroxide aqueous solution was added and the white suspension was stirred for additional 2 h at room temperature. The mixture was filtered and the white filter was rinsed with water until the washing water was neutral. The filter was dried under vacuum to give the crude product (53% yield) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.73-7.69 (m, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 4.59 (s, 4H), 3.91 (s, 4H), 2.46 (s, 3H).

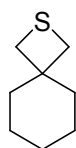
Synthesis of (3-(bromomethyl)-1-tosylazetidin-3-yl)methanol: to a mixture of crude 6-(*p*-toluenesulfonyl)-2-oxa-6-azaspiro[3.3] heptane (2.09 g, 8.4 mmol, 1 equiv.) in 80 mL Et₂O at 0 °C, a solution of hydrobromic acid (ca. 33% in AcOH, 3.7 mL, 12.6 mmol, 1.5 equiv.) in 10 mL Et₂O was added dropwise over a period of 30 minutes. The resulting mixture was warmed to room temperature and stirred for additional 30 minutes. Then the reaction mixture was poured into a saturated aqueous solution of NaHCO₃ (30 mL), extracted with Et₂O (3×30 mL), dried over sodium sulfate, filtered and concentrated in vacuo to give the product as a colorless solid. The crude product was pure enough for further transformations. ¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 3.68 (d, *J* = 2.5 Hz, 2H), 3.62 (d, *J* = 8.5 Hz, 2H), 3.55 (d, *J* = 8.5 Hz, 2H), 3.45 (s, 2H), 2.46 (s, 3H).

Synthesis of 3,3-bis(bromomethyl)-1-tosylazetidine: crude (3-(Bromomethyl)-1-

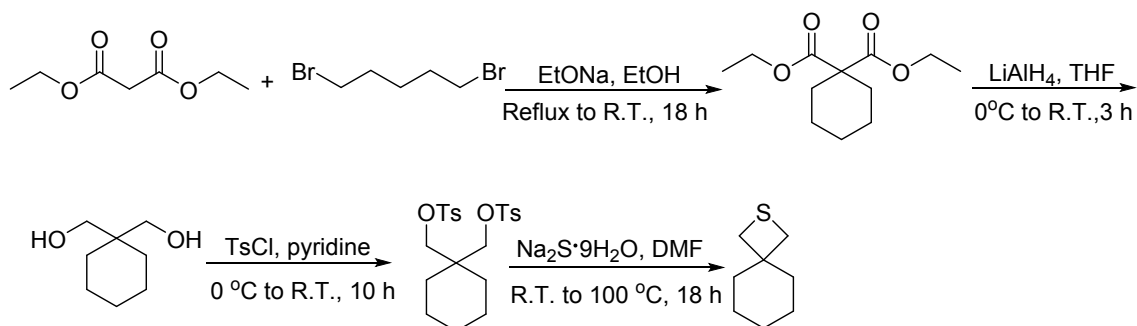
(*p*-toluenesulfonyl)azetidin-3-yl)methanol (calculated to be 2.3 g, 7 mmol, 1 equiv.) was dissolved in 20 mL DCM and carbon tetrabromide (CBr₄, 3.876 g, 11.7 mmol, 1.67 equiv.) was added in one portion. The resulting colorless solution was cooled to 0 °C and triphenylphosphine (PPh₃, 3.1 g, 11.7 mmol, 1.67 equiv.) was added in one portion. The reaction mixture turned to a dark orange solution, which was stirred at 0 °C for 2 h, then warmed to room temperature and stirred for additional 4 h. Then 20 mL Et₂O was added and the slightly yellow precipitate was filtered. The filtrate was concentrated under reduced pressure to afford a dark orange oil, which was purified by silica gel flash chromatography (PE: EA = 16:1 as the eluent) to give 3,3-Bis(bromomethyl)-1-(*p*-toluenesulfonyl)azetidine (74% yield) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 3.59 (s, 4H), 3.53 (s, 4H), 2.47 (s, 3H).

Synthesis of **2e**: 3,3-Bis(bromomethyl)-1-(*p*-toluenesulfonyl)azetidine (1.33 g, 3.3 mmol, 1 equiv.) was dissolved in a mixture of acetonitrile (ACN, 30 mL) and water (3 mL). To the resulting colorless solution was added Na₂S • 9H₂O (1.62 g, 6.6 mmol, 2 equiv.) and the reaction mixture was stirred at 50 °C for 3 h, then cooled to room temperature, EA (30 mL) and water (30 mL) were added. The organic phase was washed with brine (3 × 20 mL), dried over sodium sulfate, filtered, and concentrated in vacuo. The residue was purified by silica gel flash chromatography (PE: EA = 3:1 as the eluent) to give **2e** as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 3.78 (s, 4H), 3.13 (s, 4H), 2.45 (s, 3H).

6) Synthesis of 2f:



2-thiaspiro[3.5]nonane (2f)



Synthesis of diethyl cyclohexane-1,1-dicarboxylate: to a mixture of EtONa (41 mmol, 20% in EtOH, 14 g, 2.05 equiv.) in a round bottom bottle, dimethylmalonate (20 mmol, 3.2 g, 1 equiv.) was added and refluxed for 30 minutes. Then 1,5-dibromopentane (20 mmol, 4.6 g, 1 equiv.) in 20 mL anhydrous EtOH was added dropwise. After addition, the mixture was kept boiling for 3 h and then stirred at room temperature for 18 h. The reaction was then quenched with water (30 mL) and extracted with Et₂O (3×30 mL), dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE: EA = 10:1 as the eluent) to give diethylcyclohexane-1,1-dicarboxylate (51% yield) as a colorless oil.

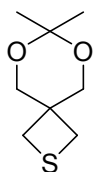
Synthesis of cyclohexane-1,1-diylbis(methylene)bis(4-methylbenzenesulfonate): a mixture of diethylcyclohexane-1,1-dicarboxylate (6.66 mmol, 1.55 g, 1 equiv.) and anhydrous tetrahydrofuran (THF, 14 mL) was added lithium aluminum hydride (LiAlH₄, 20 mmol, 8 mL, 2.5 mol/L in THF, 3 equiv.) dropwise under nitrogen atmosphere at 0 °C in a flame-dried schlenk tube. The mixture was kept stirring for 3 h at room temperature. The reaction was then carefully quenched with water (0.8 mL), 15 % aqueous sodium hydroxide (1.2 mL), water (1.2 mL) dropwise at 0 °C. After being stirred for 30 minutes, the mixture was diluted with ethyl acetate (50 mL), filtered through celite and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE: EA = 3:1 as the eluent) to give cyclohexane-1,1-diylbis(methylene)bis(4-methylbenzenesulfonate) (48% yield) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 3.60 (s, 4H), 3.20 (s, 2H), 1.50-1.31 (m, 10H).

Synthesis of cyclohexane-1,1-diylbis(methylene)bis(4-methylbenzenesulfonate): to a solution of cyclohexane-1,1-diylbis(methylene)bis(4-methylbenzenesulfonate) (2.85 mmol, 0.41 g, 1 equiv.) in

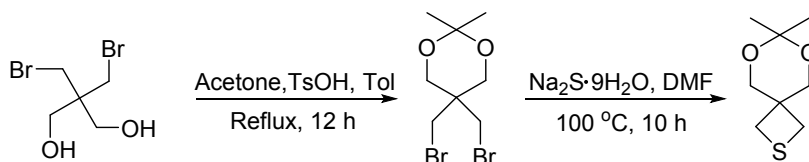
pyridine (1 mL), p-toluene sulfonyl chloride (6.3 mmol, 1.2 g, 2.2 equiv.) in 14 mL pyridine was added at 0 °C for 30 minutes, the reaction was kept stirring for 8h. The reaction was then diluted with ethyl acetate (50 mL) and washed with saturated cupric sulfate until the organic phase became colorless, dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE: EA = 10:1 as the eluent) to give product cyclohexane-1,1-diylbis(methylene)bis(4-methylbenzenesulfonate) (25% yield) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 8.2 Hz, 4H), 7.35 (d, *J* = 8.1 Hz, 4H), 3.83 (s, 4H), 2.46 (s, 6H), 1.32 (s, 10H).

Synthesis of **2f**: a solution of cyclohexane-1,1-diylbis(methylene)bis(4-methylbenzenesulfonate) (0.6 mmol, 0.36 g, 1 equiv.) and Na₂S·9H₂O (1.2 mmol, 0.288 g, 2 equiv.) in N,N-dimethylformamide (DMF, 5 mL) was stirred at 100 °C for 15 h. The reaction was then quenched with water (30 mL) and extracted with ethyl acetate (3×30 mL), dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE: EA = 10:1 as the eluent) to give product **2f** (48% yield) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 2.92 (s, 4H), 1.57-1.25 (m, 10H).

7) Synthesis of **2g**:



7,7-dimethyl-6,8-dioxa-2-thiaspiro[3.5]nonane (**2g**)

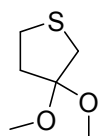


Synthesis of 5,5-bis(bromomethyl)-2,2-dimethyl-[1.3]dioxane : to a solution of 2,2-bis(bromomethyl)-1,3-propanediol (10 mmol, 2.6 g, 1 equiv.) and acetone (10 mL) in

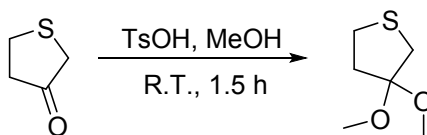
30 mL toluene was added p-toluenesulfonic acid (p-TsOH, 0.52 mmol, 0.1 g, 0.052 equiv.). The mixture was refluxed for 12 h, then quenched with saturated NaHCO₃ (30 mL), extracted with diethyl ether (3×30 mL), dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE: EA = 100:1 as the eluent) to give 5,5-bis(bromomethyl)-2,2-dimethyl-[1.3]dioxane (54% yield) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 3.80 (s, 4H), 3.58 (s, 4H), 1.48 (s, 6H).

Synthesis of **2g**: a solution of 5,5-bis(bromomethyl)-2,2-dimethyl-[1.3]dioxane (5 mmol, 1.36 g, 1 equiv.) and Na₂S·9H₂O (5.5 mmol, 1.32 g, 1.1 equiv.) in N,N-dimethylformamide (20 mL) was stirred at 100 °C for 10 h. The reaction was then quenched with water (30 mL) and extracted with diethyl ether (3×30 mL), dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE: EA = 50:1 as the eluent) to give **2g** (81% yield) as a yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 3.83 (s, 4H), 2.92 (s, 4H), 1.34 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 97.92, 68.35, 41.09, 30.81, 23.56.

8) Synthesis of 2h:



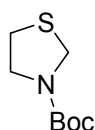
3,3-dimethoxytetrahydrothiophene (2h)



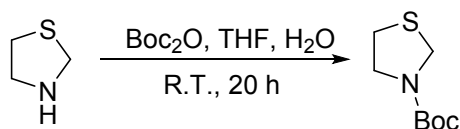
A solution of tetrahydrothiophen-3-one (0.51 g, 5 mmol, 1 equiv.) and p-toluenesulfonic acid (0.043 g, 0.25 mmol, 0.05 equiv.) in 50 mL MeOH was stirred at room temperature for 1.5 h. The reaction was then quenched with saturated NaHCO₃ (30 mL) and extracted with DCM (3×30 mL), dried over sodium sulfate, filtered and

concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE: EA = 20:1 as the eluent) to give **2h** (80% yield) as a colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 3.21 (s, 6H), 2.85 (s, 2H), 2.75 (t, *J* = 6.9 Hz, 2H), 2.09 (t, *J* = 6.9 Hz, 2H).

9) Synthesis of 2i:

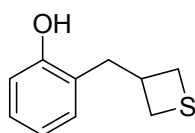


tert-butyl thiazolidine-3-carboxylate (2i)

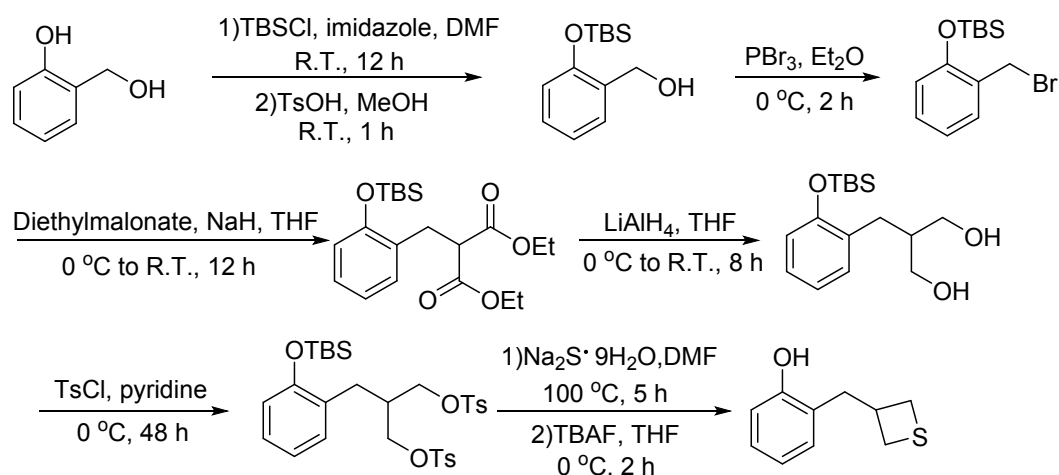


A mixture of thiazolidine (1.13 g, 10 mmol, 1 equiv.) and di-tert-butyl dicarbonate (Boc₂O, 2.13 g, 10 mmol, 1 equiv.) in 20 mL THF and 20 mL water was stirred for 20 h at room temperature. The reaction mixture was extracted with ethyl acetate (3×20 mL), dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was purified by silica gel flash chromatography (PE: EA = 20:1 as the eluent) to give **2i** (99% yield) as a colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 4.39 (s, 2H), 3.64 (s, 2H), 2.93 (t, *J* = 6.2 Hz, 2H), 1.43 (d, *J* = 1.7 Hz, 9H).

10) Synthesis of 2j:



2-(thietan-3-ylmethyl)phenol (2j)



Synthesis of (2-((tert-butyldimethylsilyl)oxy)phenyl)methanol : to a solution of 2-hydroxybenzyl alcohol (10 mmol, 1.24 g, 1 equiv.) and imidazole (50 mmol, 3.40 g, 5 equiv.) in 30 mL DMF, a solution of tert-butyldimethylsilyl chloride (TBSCl, 30 mmol, 4.53 g, 3 equiv.) in 10 mL DMF was added, the reaction was stirred at room temperature for 12 h. The reaction was then quenched with saturated NH_4Cl (50 mL) and extracted with ethyl acetate (3×30 mL), dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was used directly without further purification.

A solution of the crude product and p-TsOH (0.5 mmol, 85 mg) in MeOH (50 mL) was stirred at room temperature for 1 h. The reaction was concentrated in vacuo, saturated NH_4Cl (30 mL) was added, extracted with ethyl acetate (3×20 mL), dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was used directly without further purification.

Synthesis of (2-(bromomethyl)phenoxy)(tert-butyl)dimethylsilane: a solution of (2-((tert-butyldimethylsilyl)oxy)phenyl)methanol and anhydrous diethyl ether (20 mL) was added phosphorus tribromide (PBr_3 , 12 mmol, 1.2 mL, 1.2 equiv.) dropwise under nitrogen atmosphere at 0 °C in a flame-dried schlenk tube. The reaction was kept stirring for 2 h. The reaction was then quenched with saturated NaHCO_3 (30 mL) and extracted with ethyl acetate (3×30 mL), dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was used directly without further purification.

Synthesis of diethyl 2-(2-((tert-butyldimethylsilyl)oxy)benzyl)malonate : a mixture of sodium hydride (NaH, 11 mmol, 60% in mineral, 0.44 g, 1.1 equiv.) and anhydrous THF (15 mL) was added diethyl malonate (10 mmol, 1.6 g, 1 equiv.) under nitrogen atmosphere at 0 °C in a flame-dried schlenk tube. The mixture was kept stirring for 40 minutes until (2-(bromomethyl)phenoxy)(tert-butyl)dimethylsilane was added to the solution dropwise. The reaction was kept stirring at 0 °C for 12 h. The reaction was then quenched with saturated NH₄Cl (30 mL) and extracted with ethyl acetate (3×30 mL), dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE: EA = 20:1 as the eluent) to give diethyl-2-(2-((tert-butyldimethylsilyl)oxy)benzyl)malonate (4 steps 81% yield) as a pale yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.15-7.02 (m, 2H), 6.92-6.70 (m, 2H), 4.11 (q, *J* = 7.1 Hz, 4H), 3.78 (t, *J* = 7.8 Hz, 1H), 3.16 (d, *J* = 7.8 Hz, 2H), 1.17 (t, *J* = 7.1 Hz, 6H), 1.00 (s, 9H), 0.24 (s, 6H).

Synthesis of 2-(2-((tert-butyldimethylsilyl)oxy)benzyl)propane-1,3-diol : a mixture of diethyl-2-(2-((tert-butyldimethylsilyl)oxy)benzyl)malonate (8 mmol, 3.04 g, 1 equiv.) in 10 mL anhydrous THF was added lithium aluminum hydride (LiAlH₄, 32 mmol, 2.5 mol/L in THF, 12.8 mL, 4 equiv.) dropwise under nitrogen atmosphere at 0 °C in a flame-dried schlenk tube. The mixture was kept stirring for 8 h at room temperature. The reaction was then carefully quenched with 0.8 mL water, 1.2 mL 15 % aqueous sodium hydroxide, 1.2 mL water dropwise at 0 °C. After being stirred at 30 minutes, the mixture was diluted with 50 mL ethyl acetate, filtered through Celite and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE: EA = 10:1 as the eluent) to give 2-(2-((tert-butyldimethylsilyl)oxy)benzyl)propane-1,3-diol (31% yield) as a pale yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.16-7.03 (m, 2H), 6.95-6.77 (m, 2H), 3.77 (dd, *J* = 10.9, 3.2 Hz, 2H), 3.62 (dd, *J* = 10.9, 6.4 Hz, 2H), 2.77 (s, 2H), 2.64 (d, *J* = 7.7 Hz, 2H), 2.03-1.97 (m, 1H), 1.01 (s, 9H), 0.24 (s, 6H).

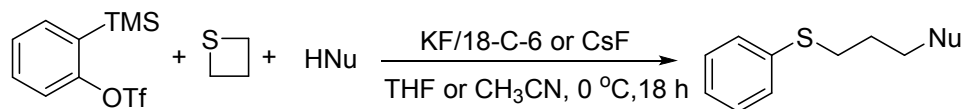
Synthesis of 2-(2-((tert-butyldimethylsilyl)oxy)benzyl)propane-1,3-diylbis(4-methylbenzenesulfonate): to a solution of diol 2-(2-((tert-

butyldimethylsilyl)oxy)benzyl)propane-1,3-diol (2.5 mmol, 0.76 g, 1 equiv.) in 2 mL anhydrous pyridine, a solution of p-toluene sulfonyl chloride (7.5 mmol, 1.43 g, 3 equiv.) in 15 mL anhydrous pyridine was added at 0 °C for 30 minutes, the reaction was kept stirring for 2 d. The reaction was then diluted with 50 mL ethyl acetate and washed with saturated CuSO₄(10×20 mL), dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE: EA = 8:1 as the eluent) to give 2-(2-((tert-butyl dimethylsilyl)oxy)benzyl)propane-1,3-diylbis(4-methylbenzenesulfonate) (50% yield) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, *J* = 8.1 Hz, 4H), 7.35 (d, *J* = 8.0 Hz, 4H), 6.92-6.67 (m, 4H), 3.99 (dd, *J* = 9.7, 4.3 Hz, 2H), 3.91 (dd, *J* = 9.7, 6.3 Hz, 2H), 2.55 (d, *J* = 7.5 Hz, 2H), 2.48 (s, 6H), 2.40-2.33 (m, 1H), 0.95 (s, 9H), 0.21 (s, 6H).

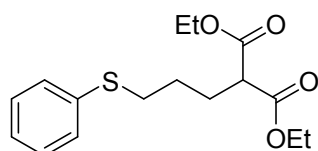
Synthesis of **2j**: a solution of 2-(2-((tert-butyl dimethylsilyl)oxy)benzyl)propane-1,3-diyl bis(4-methylbenzenesulfonate) (0.6 mmol, 0.36 g, 1 equiv.) and Na₂S·9H₂O (0.9 mmol, 0.22 g, 1.5 equiv.) in 5 mL N,N-dimethylformamide (DMF) was stirred at 100 °C for 10 h. The reaction was then quenched with 30 mL water and extracted with ethyl acetate (3×30 mL), dried over sodium sulfate, filtered and concentrated in vacuo and used for next step without purification. From the ¹H NMR, the target product and the deprotection product was discovered, and the ratio is 5:1. To a solution of the mixture in 1 mL THF, tetrabutylammonium fluoride (TBAF, 0.15mmol, 1 mol/L in THF, 0.15 mL, 1.5 equiv.) was added dropwise at 0 °C. The reaction was kept stirring for 2 h. The reaction was then quenched with saturated NH₄Cl (10 mL) and extracted with ethyl acetate (3×10 mL), dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE: EA = 10:1 as the eluent) to give **2j** (54% yield) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.17-6.99 (m, 2H), 6.85 (t, *J* = 7.3 Hz, 1H), 6.73 (d, *J* = 7.9 Hz, 1H), 5.16 (s, 1H), 3.68-3.58 (m, 1H), 3.23-3.05 (m, 4H), 2.89 (d, *J* = 7.7 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 153.69, 130.65, 127.61, 125.09, 120.77, 115.27, 40.24, 37.05, 31.34.

IV. General Procedure for Aryne Reaction

1) Scope of Nucleophiles:



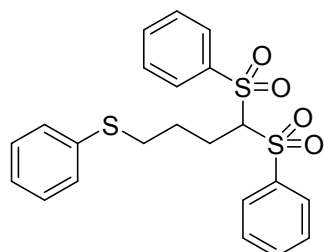
General procedure: a mixture of anhydrous cesium fluoride (CsF, 0.5 mmol, 0.076 g, 2.5 equiv.) or anhydrous potassium fluoride (KF, 0.5 mmol, 0.029 g, 2.5 equiv.) and 18-crown-6 (0.5 mmol, 0.132 g, 2.5 equiv.) in 1 mL anhydrous ACN or anhydrous THF was added 2-(trimethylsilyl)phenyltrifluoromethanesulfonate (0.2 mmol, 49 μ L, 1.0 equiv.) dropwise under nitrogen atmosphere at 0 °C in a flame-dried schlenk tube. Then thietane (0.3 mmol, 24 μ L, 1.5 equiv.) was added to the solution dropwise, which was then kept stirring at 0 °C. Once the solution became pale yellow (after 5 minutes), a solution of HNu (0.5 mmol, 2.5 equiv.) in 1 mL anhydrous ACN or anhydrous THF was added and kept stirring for 18 h at 0 °C. The reaction mixture was then treated with water (20 mL), extracted, dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography.



Diethyl 2-(3-(phenylthio)propyl)malonate (**4a**)

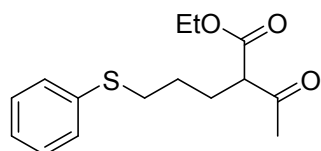
Following the general procedure with anhydrous potassium fluoride and 18-crown-6 in THF, extracted with ethyl acetate (3 \times 20 mL), the crude product was purified by silica gel chromatography (PE: EA = 20:1 as the eluent) to give **4a** (81% yield) as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.32 (dt, J = 8.1, 1.7 Hz, 2H), 7.29-7.25 (m, 2H), 7.21-7.14 (m, 1H), 4.21-4.14 (m, 4H), 3.32 (t, J = 7.5 Hz, 1H), 2.93 (t, J = 7.3 Hz, 2H), 2.07-1.95 (m, 2H), 1.72-1.63 (m, 2H), 1.25 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 169.20, 136.22, 129.34, 128.91, 126.02, 61.43, 51.58, 33.25, 27.79, 26.86,

14.07. HR-MS (ESI): Calcd for $C_{16}H_{23}O_4S^+$ $[M+H]^+$ requires 311.1312; found 311.1308.



(4,4-Bis(phenylsulfonyl)butyl)(phenyl)sulfane (4b)

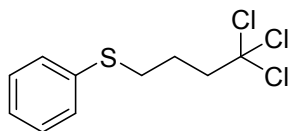
Following the general procedure with anhydrous potassium fluoride and 18-crown-6 in THF, extracted with chloroform (3×20 mL), the crude product was purified by silica gel chromatography (PE: EA = 20:1 as the eluent) to give **4b** (98% yield) as a white solid. 1H NMR (400 MHz, $CDCl_3$) δ 7.87-7.81 (m, 4H), 7.60 (t, J = 7.5 Hz, 2H), 7.47 (t, J = 7.8 Hz, 4H), 7.23-7.17 (m, 4H), 7.16-7.06(m, 1H), 4.35 (t, J = 5.7 Hz, 1H), 2.78 (t, J = 6.8 Hz, 2H), 2.28-2.18 (m, 2H), 1.90-1.77 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.72, 134.56, 133.60, 128.56, 128.12, 127.99, 125.31, 82.20, 32.14, 28.67, 26.12, 23.70. HR-MS (ESI): Calcd for $C_{22}H_{23}O_4S_3^+$ $[M+H]^+$ requires 447.0753; found 447.0752.



Ethyl 2-acetyl-5-(phenylthio)pentanoate (4c)

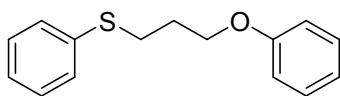
Following the general procedure with anhydrous cesium fluoride in ACN, the crude product was purified by silica gel chromatography (PE: EA = 20:1 as the eluent) to give **4c** (37% yield) as a colorless oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.34-7.29 (m, 2H), 7.30-7.26 (m, 2H), 7.20-7.15 (m, 1H), 4.21-4.13 (m, 2H), 3.40 (t, J = 7.4 Hz, 1H), 2.94-2.90

(m, 2H), 2.21 (s, 3H), 1.20-1.95 (m, 2H), 1.67-1.58 (m, 2H), 1.25 (t, $J = 5.9$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 202.74, 169.55, 136.17, 129.33, 128.93, 126.06, 61.47, 59.34, 33.32, 28.79, 27.07, 26.85, 14.09. HR-MS (ESI): Calcd for $\text{C}_{15}\text{H}_{21}\text{O}_3\text{S}^+ [\text{M}+\text{H}]^+$ requires 281.1206; found 281.1205.



Phenyl(4,4,4-trichlorobutyl)sulfane (4d)

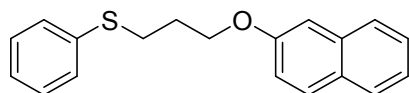
Following the general procedure with anhydrous potassium fluoride and 18-crown-6 in THF, extracted with ethyl acetate (3×20 mL), the crude product was purified by silica gel chromatography (PE: EA = 50:1 as the eluent) to give **4d** (40% yield) as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.39-7.36 (m, 1H), 7.33-7.27 (m, 1H), 7.24-7.19 (m, 1H), 3.01 (t, $J = 6.9$ Hz, 1H), 2.88-2.83 (m, 1H), 2.11 (dtd, $J = 11.5, 7.0, 4.7$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 134.38, 129.01, 128.01, 125.52, 98.38, 52.75, 31.82, 24.89. HR-MS (ESI): Calcd for $\text{C}_{10}\text{H}_{12}\text{Cl}_3\text{S}^+ [\text{M}+\text{H}]^+$ requires 268.9720; found 268.9723.



(3-Phenoxypropyl)(phenyl)sulfane (4e)

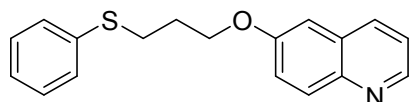
Following the general procedure with anhydrous potassium fluoride and 18-crown-6 in THF, extracted with ethyl acetate (3×20 mL), the crude product was purified by silica gel chromatography (PE: EA = 10:1 as the eluent) to give **4e** (83% yield) as a yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.38-7.32 (m, 2H), 7.30-7.25 (m, 4H), 7.20-7.14 m, 1H), 6.94 (dd, $J = 10.6, 4.1$ Hz, 1H), 6.88 (dt, $J = 3.5, 1.8$ Hz, 2H), 4.07 (t, $J = 6.0$ Hz, 2H), 3.12 (t, $J = 7.1$ Hz, 2H), 2.15-2.06 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 158.80,

136.21, 129.47, 129.22, 128.94, 126.00, 120.78, 114.52, 65.93, 30.21, 28.93. HR-MS (ESI): Calcd for $C_{15}H_{17}OS^+ [M+H]^+$ requires 245.0995; found 245.0989.



(3-(Naphthalen-2-yloxy)propyl)(phenyl)sulfane (4f)

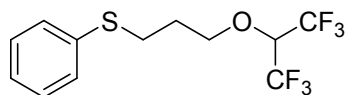
Following the general procedure with anhydrous potassium fluoride and 18-crown-6 in THF, extracted with ethyl acetate (3×20 mL), the crude product was purified by silica gel chromatography (PE: EA = 20:1 as the eluent) to give **4f** (86% yield) as a yellow oil. 1H NMR (400 MHz, $CDCl_3$) δ 8.20-8.14 (m, 1H), 7.74-7.66 (m, 1H), 7.41-7.35 (m, 2H), 7.34-7.28 (m, 2H), 7.28-7.22 (m, 2H), 7.19-7.13 (m, 2H), 7.10-7.04 (m, 1H), 6.68 (d, J = 7.4 Hz, 1H), 4.14 (t, J = 5.9 Hz, 2H), 3.13 (t, J = 7.2 Hz, 2H), 2.21-2.11 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.54, 136.28, 134.56, 129.27, 129.00, 127.54, 126.44, 126.05, 125.91, 125.68, 125.23, 121.98, 120.35, 104.72, 66.27, 30.49, 29.12. HR-MS (ESI): Calcd for $C_{19}H_{19}OS^+ [M+H]^+$ requires 295.1151; found 295.1156.



6-(3-(Phenylthio)propoxy)quinoline (4g)

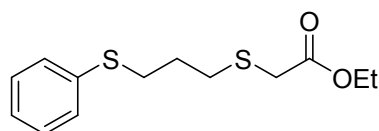
Following the general procedure with anhydrous potassium fluoride and 18-crown-6 in THF, extracted with ethyl acetate (3×20 mL), the crude product was purified by silica gel chromatography (PE: EA = 20:1 as the eluent) to give **4g** (80% yield) as a yellow oil. 1H NMR (400 MHz, $CDCl_3$) δ 8.76 (dd, J = 4.2, 1.6 Hz, 1H), 8.01 (dd, J = 11.7, 5.1 Hz, 2H), 7.36 (ddd, J = 8.3, 5.0, 1.8 Hz, 3H), 7.31-7.23 (m, 3H), 7.18 (d, J = 7.3 Hz, 1H), 7.04 (d, J = 2.7 Hz, 1H), 4.20 (t, J = 6.0 Hz, 2H), 3.17 (t, J = 7.0 Hz, 2H), 2.23-2.15 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.92, 147.99, 144.45, 136.07, 134.79,

130.88, 129.33, 128.98, 126.11, 122.43, 121.38, 106.01, 66.30, 30.27, 28.80. HR-MS (ESI): Calcd for $C_{18}H_{18}NOS^+ [M+H]^+$ requires 296.1104; found 296.1110.



(3-((1,1,1,3,3,3-Hexafluoropropan-2-yl)oxy)propyl)(phenyl)sulfane (4h)

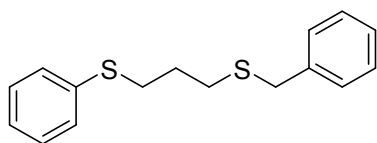
Following the general procedure with anhydrous potassium fluoride and 18-crown-6 in THF, extracted with ethyl acetate (3×20 mL), the crude product was purified by silica gel chromatography (PE: EA = 100:1 as the eluent) to give **4h** (35% yield) as a yellow oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.39-7.32 (m, 1H), 7.32-7.26 (m, 1H), 7.24-7.15 (m, 1H), 4.02 (dt, J = 12.0, 6.0 Hz, 1H), 3.96 (t, J = 5.9 Hz, 1H), 3.03 (t, J = 7.0 Hz, 1H), 1.97 (dq, J = 12.9, 6.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.67, 129.53, 129.02, 126.27, 121.49 (d, J = 286.9 Hz), 76.60 (quint, J = 32.19 Hz), 73.45, 29.66, 29.03. HR-MS (ESI): Calcd for $C_{12}H_{13}F_6OS^+ [M+H]^+$ requires 319.0586; found 319.0590.



ethyl 2-((3-(phenylthio)propyl)thio)acetate(4i)

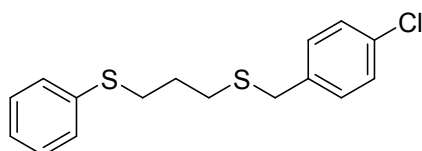
Following the general procedure with anhydrous potassium fluoride and 18-crown-6 in THF, extracted with ethyl acetate (3×20 mL), the crude product was purified by silica gel chromatography (PE: EA = 20:1 as the eluent) to give **4i** (85% yield) as a yellow oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 7.3 Hz, 2H), 7.31 (t, J = 7.4 Hz, 2H), 7.20 (t, J = 7.2 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.21 (s, 2H), 3.04 (t, J = 7.1 Hz, 2H), 2.80 (t, J = 7.1 Hz, 2H), 1.95 (quint, J = 7.1 Hz, 2H), 1.30 (t, J = 7.1 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.39, 136.04, 129.45, 128.95, 126.13, 61.38, 33.64, 32.39,

31.37, 28.23, 14.19. HR-MS (ESI): Calcd for $C_{13}H_{19}O_2S_2^+ [M+H]^+$ requires 271.0821; found 271.0820.



Benzyl(3-(phenylthio)propyl)sulfane (4j)

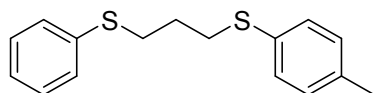
Following the general procedure with anhydrous potassium fluoride and 18-crown-6 in THF, extracted with ethyl acetate (3×20 mL), the crude product was purified by silica gel chromatography (PE: EA = 20:1 as the eluent) to give **4j** (72% yield) as a yellow oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.34-7.22 (m, 9H), 7.20-7.14 (m, 1H), 3.67 (s, 2H), 2.97 (t, $J = 7.1$ Hz, 2H), 2.52 (t, $J = 7.1$ Hz, 2H), 1.86 (quint, $J = 7.1$ Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.30, 136.20, 129.33, 128.93, 128.85, 128.53, 127.02, 126.04, 36.20, 32.47, 30.05, 28.50. HR-MS (ESI): Calcd for $C_{16}H_{19}S_2^+ [M+H]^+$ requires 275.0923; found 275.0935.



(4-chlorobenzyl)(3-(phenylthio)propyl)sulfane(4k)

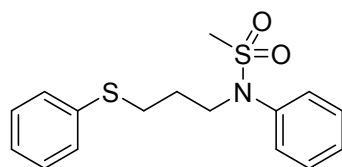
Following the general procedure with anhydrous potassium fluoride and 18-crown-6 in THF, extracted with ethyl acetate (3×20 mL), the crude product was purified by silica gel chromatography (PE: DCM = 100:1 as the eluent) to give **4k** (73% yield) as a yellow oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.40-7.28 (m, 6H), 7.26-7.20 (m, 3H), 3.67 (s, 2H), 3.01 (t, $J = 7.1$ Hz, 2H), 2.55 (t, $J = 7.1$ Hz, 2H), 1.89 (quint, $J = 7.1$ Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.81, 137.05, 133.72, 131.10, 130.31, 129.90, 129.61, 127.04,

36.48, 33.40, 30.97, 29.41. HR-MS (ESI): Calcd for $C_{16}H_{18}ClS_2^+$ $[M+H]^+$ requires 309.0533; found 309.0534.



Phenyl(3-(p-tolylthio)propyl)sulfane (**4l**)

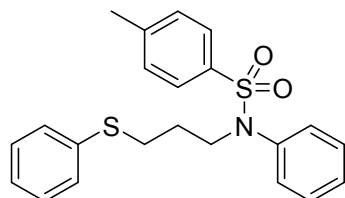
Following the general procedure with anhydrous potassium fluoride and 18-crown-6 in THF, extracted with ethyl acetate (3×20 mL), the crude product was purified by silica gel chromatography (PE: EA = 100:1 as the eluent) to give **4l** (30% yield) as a colorless oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.33-7.27 (m, 2H), 7.25-7.22 (m, 4H), 7.19-7.14 (m, 1H), 7.08 (d, J = 8.0 Hz, 2H), 3.01 (dt, J = 14.0, 7.0 Hz, 4H), 2.31 (s, 3H), 1.92 (quint, J = 7.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.34, 136.11, 132.13, 130.34, 129.73, 129.37, 128.92, 126.04, 33.23, 32.40, 28.40, 21.03. HR-MS (ESI): Calcd for $C_{16}H_{19}S_2^+$ $[M+H]^+$ requires 275.0923; found 275.2925.



N-phenyl-N-(3-(phenylthio)propyl)methanesulfonamide (**4m**)

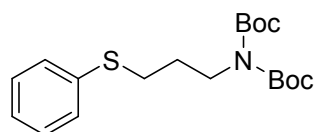
Following the general procedure with anhydrous potassium fluoride and 18-crown-6 in THF, 0.2mmol N-phenylmethanesulfonamide instead of 0.5 mmol, extracted with ethyl acetate (3×20 mL), the crude product was purified by silica gel chromatography (PE: DCM = 1:1 as the eluent) to give **4m** (73% yield) as a white solid. 1H NMR (400 MHz, $CDCl_3$) δ 7.32 (tt, J = 8.5, 2.0 Hz, 2H), 7.28-7.21 (m, 3H), 7.20-7.13 (m, 4H), 7.11-7.06 (m, 1H), 3.74 (t, J = 6.7 Hz, 2H), 2.90-2.83 (m, 2H), 2.78 (s, 3H), 1.76-1.66 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.87, 134.73, 128.60, 128.54, 127.88, 127.34, 127.16,

125.16, 48.39, 35.82, 29.71, 26.95. HR-MS (ESI): Calcd for $C_{16}H_{20}NO_2S_2^+$ $[M+H]^+$ requires 322.0930; found 322.0935.



4-Methyl-N-phenyl-N-(3-(phenylthio)propyl)benzenesulfonamide (**4n**)

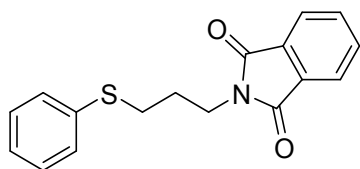
Following the general procedure with anhydrous potassium fluoride and 18-crown-6 in THF, extracted with ethyl acetate (3×20 mL), the crude product was purified by silica gel chromatography (PE: EA = 10:1 as the eluent) to give **4n** (73% yield) as a white solid. 1H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.3 Hz, 2H), 7.29-7.26 (m, 3H), 7.26-7.20 (m, 5H), 7.18-7.11 (m, 2H), 7.04-6.98 (m, 1H), 3.66 (t, J = 6.7 Hz, 2H), 2.94 (t, J = 7.2 Hz, 2H), 2.40 (s, 3H), 1.78-1.68 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.47, 138.96, 135.97, 135.09, 129.51, 129.43, 129.09, 128.90, 128.69, 127.97, 127.74, 126.10, 49.39, 30.82, 27.80, 21.57. HR-MS (ESI): Calcd for $C_{22}H_{24}NO_2S_2^+$ $[M+H]^+$ requires 398.1243; found 398.1245.



3-(phenylthio)propyl ditert-butylcarbamate (**4o**)

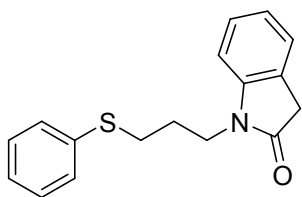
Following the general procedure with anhydrous potassium fluoride and 18-crown-6 in THF, extracted with ethyl acetate (3×20 mL), the crude product was purified by silica gel chromatography (PE: EA = 10:1 as the eluent) to give **4o** (70% yield) as a colorless oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.29-7.22 (m, 2H), 7.22-7.16 (m, 2H), 7.12-7.06 (m, 1H), 3.65-3.57 (m, 2H), 2.87-2.79 (m, 2H), 1.89-1.80 (m, 2H), 1.41 (s, 18H). ^{13}C NMR

(100 MHz, CDCl₃) δ 151.48, 135.38, 128.10, 127.87, 124.90, 81.32, 44.43, 29.98, 27.73, 27.04. HR-MS (ESI): Calcd for C₁₉H₃₀NO₄S⁺ [M+H]⁺ requires 368.1890; found 368.1889.



2-(3-(Phenylthio)propyl)isoindoline-1,3-dione (**4p**)

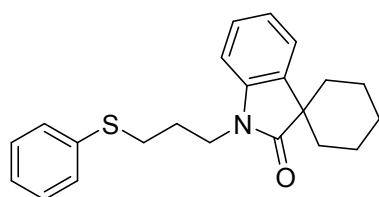
Following the general procedure with anhydrous potassium fluoride and 18-crown-6 in THF, extracted with ethyl acetate (3×20 mL), the crude product was purified by silica gel chromatography (PE: EA = 20:1 as the eluent) to give **4p** (75% yield) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.83 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.71 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.34 (dt, *J* = 3.1, 1.8 Hz, 2H), 7.29-7.24 (m, 2H), 7.20-7.14 (m, 1H), 3.82 (t, *J* = 7.0 Hz, 2H), 2.99-2.89 (m, 2H), 2.05-1.95 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 168.32, 135.84, 133.99, 132.08, 129.88, 128.95, 126.31, 123.27, 37.03, 31.46, 28.18. HR-MS (ESI): Calcd for C₁₇H₁₆NO₂S⁺ [M+H]⁺ requires 298.0896; found 298.0893.



1-(3-(Phenylthio)propyl)indolin-2-one (**4q**)

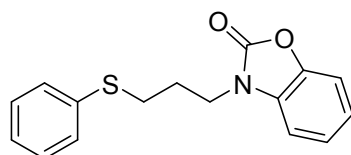
Following the general procedure with anhydrous potassium fluoride and 18-crown-6 in THF, extracted with ethyl acetate (3×20 mL), the crude product was purified by silica gel chromatography (PE: EA = 20:1 as the eluent) to give **4q** (49% yield) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.36 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.33-7.27 (m, 3H),

7.25-7.17 (m, 2H), 7.05 (t, $J = 7.5$ Hz, 1H), 6.82 (d, $J = 7.8$ Hz, 1H), 3.87 (t, $J = 7.1$ Hz, 2H), 3.55 (s, 2H), 3.01 (t, $J = 7.1$ Hz, 2H), 2.07-1.98 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 175.12, 144.38, 135.76, 129.62, 129.00, 127.90, 126.29, 124.57, 124.51, 122.29, 38.83, 35.77, 31.22, 26.88. HR-MS (ESI): Calcd for $\text{C}_{17}\text{H}_{18}\text{NOS}^+$ $[\text{M}+\text{H}]^+$ requires 284.1104; found 284.1106.



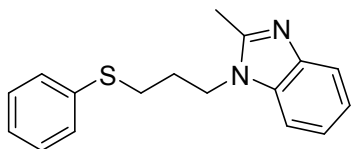
1'-(3-(phenylthio)propyl)spiro[cyclohexane-1,3'-indolin]-2'-one (4r)

Following the general procedure with anhydrous potassium fluoride and 18-crown-6 in THF, extracted with ethyl acetate (3×20 mL), the crude product was purified by silica gel chromatography (PE: EA = 5:1 as the eluent) to give **4r** (51% yield) as a yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.45 (d, $J = 7.2$ Hz, 1H), 7.33-7.27 (m, 2H), 7.26-7.23 (m, 2H), 7.23-7.14 (m, 2H), 7.06-6.99 (m, 1H), 6.82 (d, $J = 7.8$ Hz, 1H), 3.83 (t, $J = 7.0$ Hz, 2H), 2.94 (t, $J = 7.2$ Hz, 2H), 2.04-1.96 (m, 2H), 1.96-1.88 (m, 2H), 1.88-1.80 (m, 2H), 1.78-1.69 (m, 2H), 1.68-1.59 (m, 2H), 1.55 (ddd, $J = 10.0, 6.6, 3.0$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 180.76, 141.88, 135.90, 135.48, 129.42, 128.98, 127.45, 126.17, 124.05, 121.87, 108.12, 47.33, 38.59, 33.15, 31.04, 26.99, 25.20, 21.18. HR-MS (ESI): Calcd for $\text{C}_{22}\text{H}_{26}\text{NOS}^+$ $[\text{M}+\text{H}]^+$ requires 352.1730; found 352.1734.



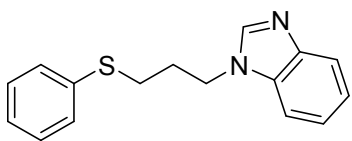
3-(3-(Phenylthio)propyl)benzo[d]oxazol-2(3H)-one (4s)

Following the general procedure with anhydrous potassium fluoride and 18-crown-6 in THF, extracted with ethyl acetate (3×20 mL), the crude product was purified by silica gel chromatography (PE: EA = 10:1 as the eluent) to give **4s** (96% yield) as an orange oil. ¹H NMR (400 MHz, CDCl₃) δ 7.37-7.31 (m, 2H), 7.31-7.24 (m, 2H), 7.20 (tt, *J* = 6.2, 1.9 Hz, 2H), 7.14 (td, *J* = 7.7, 1.5 Hz, 1H), 7.09 (td, *J* = 7.7, 1.5 Hz, 1H), 6.94 (dd, *J* = 7.6, 1.2 Hz, 1H), 3.96 (t, *J* = 7.0 Hz, 2H), 2.98 (t, *J* = 6.9 Hz, 2H), 2.09 (quint, *J* = 6.9 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 154.55, 142.68, 135.28, 131.10, 129.88, 129.10, 126.55, 123.89, 122.48, 110.11, 108.28, 40.90, 30.94, 27.04. HR-MS (ESI): Calcd for C₁₆H₁₆NO₂S⁺ [M+H]⁺ requires 286.0896; found 286.0892.



2-methyl-1-(3-(phenylthio)propyl)-1H-benzo[d]imidazole (4t)

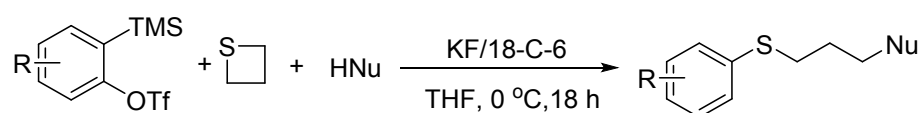
Following the general procedure with anhydrous potassium fluoride and 18-crown-6 in THF, extracted with ethyl acetate (3×20 mL), the crude product was purified by silica gel chromatography (DCM: EA = 10:1 as the eluent) to give **4t** (71% yield) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.62-7.57 (m, 1H), 7.27-7.17 (m, 5H), 7.16-7.08 (m, 3H), 4.16 (t, *J* = 7.1 Hz, 2H), 2.84 (t, *J* = 6.7 Hz, 2H), 2.49 (s, 3H), 2.08-1.98 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 150.38, 141.60, 134.05, 134.01, 128.73, 128.10, 125.57, 121.06, 120.87, 118.08, 108.06, 41.03, 29.70, 27.52, 12.88. HR-MS (ESI): Calcd for C₁₇H₁₉N₂S⁺ [M+H]⁺ requires 283.1263; found 283.1269.



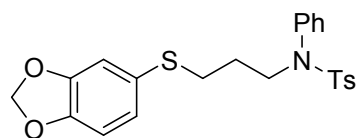
1-(3-(phenylthio)propyl)-1H-benzo[d]imidazole (4u)

Following the general procedure with anhydrous potassium fluoride and 18-crown-6 in THF, extracted with ethyl acetate (3×20 mL), the crude product was purified by silica gel chromatography (PE: EA =1:3 as the eluent) to give **4u** (48% yield) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.88 (s, 1H), 7.84-7.78 (m, 1H), 7.40-7.35 (m, 1H), 7.35-7.26 (m, 6H), 7.24-7.19 (m, 1H), 4.35 (t, *J* = 6.8 Hz, 2H), 2.88 (t, *J* = 6.7 Hz, 2H), 2.19 (p, *J* = 6.7 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 143.94, 143.05, 135.02, 133.67, 129.98, 129.16, 126.69, 123.01, 122.22, 120.53, 109.59, 43.07, 30.71, 28.65.

2) Scope of Aryne:

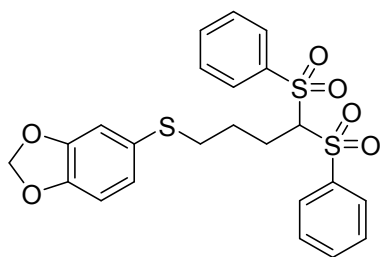


General procedure: a mixture of anhydrous potassium fluoride (KF, 0.5 mmol, 0.029 g, 2.5 equiv.) and 18-crown-6 (0.5 mmol, 0.132 g, 2.5 equiv.) in 1 mL anhydrous THF was added aryne (0.2 mmol, 1.0 equiv.) dropwise under nitrogen atmosphere at 0 °C in a flame-dried schlenk tube. Then thietane (0.3 mmol, 24 μL, 1.5 equiv.) was added to the solution dropwise, which was then kept stirring at 0 °C. Once the solution became pale yellow (after 5 minutes), a solution of HNu (0.5 mmol, 2.5 equiv.) in 1 mL anhydrous THF was added and kept stirring for 18 h at 0 °C. The reaction mixture was then treated with water (20 mL), extracted, dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography.



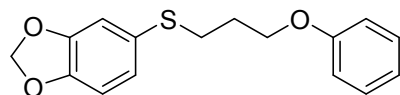
N-(3-(benzo[d][1,3]dioxol-5-ylthio)propyl)-4-methyl-N-phenylbenzenesulfonamide (5a)

Following the general, extracted with ethyl acetate (3×20 mL), the crude product was purified by silica gel chromatography (PE: EA = 20:1 as the eluent) to give **5a** (65% yield) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.45 (d, *J* = 8.3 Hz, 2H), 7.30-7.26 (m, 3H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.06-6.92 (m, 2H), 6.79 (dd, *J* = 5.8, 1.8 Hz, 2H), 6.67 (d, *J* = 8.5 Hz, 1H), 5.94 (s, 2H), 3.63 (t, *J* = 6.7 Hz, 2H), 2.83 (t, *J* = 7.2 Hz, 2H), 2.41 (s, 3H), 1.68 (quint, *J* = 6.8 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 147.94, 147.17, 143.45, 138.96, 135.11, 129.42, 129.06, 128.72, 127.96, 127.73, 127.43, 125.79, 112.35, 108.67, 101.28, 49.31, 32.98, 27.82, 21.57. HR-MS (ESI): Calcd for C₂₃H₂₄O₄NS₂⁺ [M+H]⁺ requires 442.1141; found 442.1142.



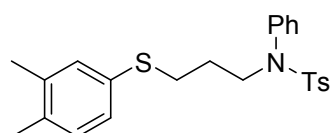
5-((4,4-bis(phenylsulfonyl)butyl)thio)benzo[d][1,3]dioxole (5b**)**

Following the general, extracted with chloroform (3×20 mL), the crude product was purified by silica gel chromatography (PE: EA = 5:1 as the eluent) to give **5b** (65% yield) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, *J* = 7.7 Hz, 4H), 7.69 (t, *J* = 7.4 Hz, 2H), 7.57 (t, *J* = 7.7 Hz, 4H), 6.82 (d, *J* = 9.4 Hz, 2H), 6.73 (d, *J* = 7.8 Hz, 1H), 5.96 (s, 2H), 4.40 (t, *J* = 5.7 Hz, 1H), 2.74 (t, *J* = 6.8 Hz, 2H), 2.32-2.25 (m, 2H), 1.90-1.80 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 148.06, 147.34, 137.79, 134.66, 129.63, 129.17, 127.08, 125.88, 112.36, 108.79, 101.37, 83.32, 35.31, 29.71, 27.26, 24.61. HR-MS (ESI): Calcd for C₂₃H₂₃O₆S₃⁺ [M+H]⁺ requires 491.0651; found 491.0648.



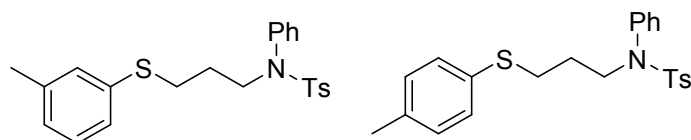
5-((3-phenoxypropyl)thio)benzo[d][1,3]dioxole (5c)

Following the general, extracted with ethyl acetate (3×20 mL), the crude product was purified by silica gel chromatography (PE: DCM = 10:1 as the eluent) to give **5c** (82% yield) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.22-7.16 (m, 2H), 6.88-6.78 (m, 5H), 6.68-6.63 (m, 1H), 5.86 (s, 2H), 3.97 (t, *J* = 6.0 Hz, 2H), 2.93 (t, *J* = 7.1 Hz, 2H), 2.02-1.93 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 157.77, 147.00, 146.02, 128.40, 124.29, 119.69, 113.46, 110.94, 107.68, 100.23, 64.81, 31.29, 28.00. HR-MS (ESI): Calcd for C₁₆H₁₇O₃S⁺ [M+H]⁺ requires 289.0893; found 289.0895.



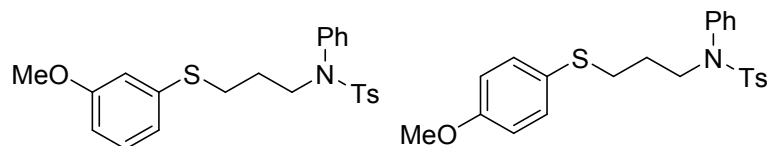
N-(3-((3,4-dimethylphenyl)thio)propyl)-4-methyl-N-phenylbenzenesulfonamide (5d)

Following the general, extracted with ethyl acetate (3×20 mL), the crude product was purified by silica gel chromatography (PE: EA = 10:1 as the eluent) to give **5d** (44% yield) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.45 (d, *J* = 8.3 Hz, 2H), 7.31-7.26 (m, 3H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.06 (s, 1H), 7.03-6.96 (m, 4H), 3.67-3.61 (m, 2H), 2.88 (t, *J* = 7.2 Hz, 2H), 2.41 (s, 3H), 2.21 (s, 3H), 2.20 (s, 3H), 1.76-1.67 (m, 2H). HR-MS (ESI): Calcd for C₂₄H₂₈NO₂S₂⁺ [M+H]⁺ requires 426.1556; found 426.1560.



4-methyl-N-phenyl-N-(3-(m-tolylthio)propyl)benzenesulfonamide (5e) and 4-methyl-N-phenyl-N-(3-(p-tolylthio)propyl)benzenesulfonamide (5e')

Following the general, extracted with ethyl acetate (3×20 mL), the crude product was purified by silica gel chromatography (PE: EA = 10:1 as the eluent) to give **5e** and **5e'** (1:1, 64% yield) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, *J* = 8.1 Hz, 4H), 7.33-7.23 (m, 12H), 7.17 (t, *J* = 8.2 Hz, 1H), 7.03 (ddd, *J* = 9.7, 7.0, 4.0 Hz, 4H), 6.88-6.77 (m, 4H), 6.73 (dd, *J* = 8.2, 1.6 Hz, 1H), 3.80 (d, *J* = 4.9 Hz, 6H), 3.67 (dt, *J* = 9.9, 6.5 Hz, 4H), 2.98 (t, *J* = 7.2 Hz, 2H), 2.85 (t, *J* = 7.2 Hz, 2H), 2.44 (s, 6H), 1.82-1.73 (m, 2H), 1.71-1.65 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 159.83, 159.04, 143.47, 143.42, 138.99, 137.31, 135.15, 135.06, 133.63, 129.72, 129.43, 129.42, 129.09, 129.05, 128.75, 128.68, 127.98, 127.93, 127.73, 125.87, 121.48, 114.77, 114.57, 111.89, 55.34, 55.28, 49.40, 49.38, 33.00, 30.68, 27.88, 27.83, 21.56. HR-MS (ESI): Calcd for C₂₃H₂₆NO₂S₂⁺ [M+H]⁺ requires 412.1399; found 412.1400.

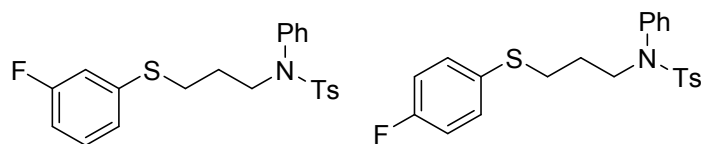


N-(3-((3-methoxyphenyl)thio)propyl)-4-methyl-N-phenylbenzenesulfonamide (5f)

N-(3-((4-methoxyphenyl)thio)propyl)-4-methyl-N-phenylbenzenesulfonamide (5f')

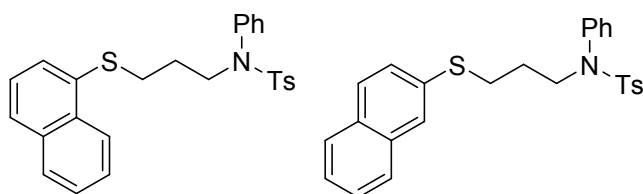
Following the general, extracted with ethyl acetate (3×20 mL), the crude product was purified by silica gel chromatography (PE: EA = 10:1 as the eluent) to give **5f** and **5f'** (1:1, 77% yield) as a pale yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, *J* = 8.1 Hz, 4H), 7.33-7.24 (m, 12H), 7.17 (t, *J* = 8.2 Hz, 1H), 7.03 (ddd, *J* = 9.7, 7.0, 3.7 Hz, 4H), 6.88-6.78 (m, 4H), 6.73 (dd, *J* = 8.2, 1.8 Hz, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 3.71-3.64 (m, 4H), 2.98 (t, *J* = 7.2 Hz, 2H), 2.85 (t, *J* = 7.2 Hz, 2H), 2.44 (s, 6H), 1.82-1.73 (m, 2H), 1.72-1.65 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 159.83, 159.04, 143.48, 143.43, 138.99, 138.96, 137.32, 135.15, 135.06, 133.63, 129.73, 129.43, 129.42, 129.09, 129.05, 128.75, 128.68, 127.98, 127.94, 127.73, 125.87, 121.48, 114.81, 114.57,

111.89, 55.34, 55.28, 49.40, 49.38, 33.00, 30.68, 27.89, 27.83, 21.56. HR-MS (ESI): Calcd for $C_{23}H_{26}NO_3S_2^+ [M+H]^+$ requires 428.1349; found 428.1349.



N-(3-((3-fluorophenyl)thio)propyl)-4-methyl-N-phenylbenzenesulfonamide (5g) and N-(3-((4-fluorophenyl)thio)propyl)-4-methyl-N-phenylbenzenesulfonamide (5g')

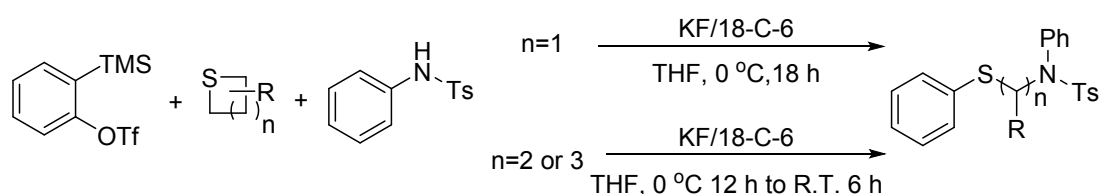
Following the general, extracted with ethyl acetate (3×20 mL), the crude product was purified by silica gel chromatography (PE: EA = 20:1 as the eluent) to give **5g** and **5g'** (1:2, 78% yield) as a pale yellow oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.47 (dd, J = 8.2, 2.6 Hz, 2H), 7.35-7.23 (m, 6.6H), 7.23-7.17 (m, 0.4H), 7.07-7.01 (m, 2H), 6.96 (t, J = 8.7 Hz, 1.66H), 6.85 (td, J = 8.4, 2.0 Hz, 0.33H), 3.73-3.69 (m, 0.66H), 3.67 (t, J = 6.8 Hz, 1.33H), 2.99 (t, J = 7.2 Hz, 0.66H), 2.92 (t, J = 7.2 Hz, 1.33H), 2.44 (s, 3H), 1.82-1.75 (m, 0.66H), 1.74-1.69 (m, 1.33H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.05, 163.09, 161.59, 160.64, 143.54, 143.51, 138.92, 138.88, 138.67, 138.59, 135.04, 134.99, 132.79, 132.71, 130.70, 130.66, 130.20, 130.11, 129.44, 129.14, 129.09, 128.68, 128.64, 128.06, 128.00, 127.73, 127.72, 124.35, 124.32, 116.11, 115.89, 115.61, 115.38, 112.92, 112.71, 49.28, 32.17, 27.76, 27.63, 21.56. HR-MS (ESI): Calcd for $C_{22}H_{23}FNO_2S_2^+ [M+H]^+$ requires 416.1149; found 416.1143.



4-methyl-N-(3-(naphthalen-1-ylthio)propyl)-N-phenylbenzenesulfonamide (5h)
and 4-methyl-N-(3-(naphthalen-2-ylthio)propyl)-N-phenylbenzenesulfonamide (5h')

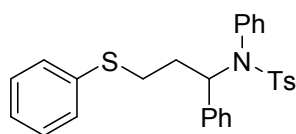
Following the general, extracted with ethyl acetate (3×20 mL), the crude product was purified by silica gel chromatography (PE: EA = 20:1 as the eluent) to give **5h** and **5h'** (1:1.22, 93% yield) as a pale yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 8.39 (d, *J* = 8.0 Hz, 0.45H), 7.89-7.84 (m, 0.55H), 7.81 (d, *J* = 7.8 Hz, 0.45H), 7.78-7.68 (m, 1.9H), 7.55 (td, *J* = 12.8, 6.1 Hz, 1.55H), 7.48 (d, *J* = 7.9 Hz, 3H), 7.40-7.34 (m, 1.1H), 7.28 (d, *J* = 3.5 Hz, 3H), 7.26-7.19 (m, 2H), 7.05 (dd, *J* = 6.6, 2.8 Hz, 0.9H), 7.03-6.96 (m, 1.1H), 3.71 (dd, *J* = 15.0, 6.8 Hz, 2H), 3.09 (t, *J* = 7.2 Hz, 0.9H), 3.04 (t, *J* = 7.2 Hz, 1.1H), 2.43 (s, 1.65H), 2.42 (s, 1.35H), 1.87-1.80 (m, 0.9H), 1.80-1.73 (m, 1.1H). ¹³C NMR (100 MHz, CDCl₃) δ 143.48, 143.47, 138.97, 138.90, 135.07, 133.98, 133.75, 133.48, 133.09, 132.94, 131.84, 129.44, 129.09, 129.07, 128.79, 128.69, 128.60, 128.46, 127.99, 127.97, 127.74, 127.62, 127.47, 127.14, 126.56, 126.47, 126.24, 125.75, 125.55, 125.10, 49.44, 31.32, 30.77, 27.86, 27.82, 21.57. HR-MS (ESI): Calcd for C₂₆H₂₆NO₂S₂⁺ [M+H]⁺ requires 448.1399; found 448.1392.

3) Scope of Cyclic thioether:



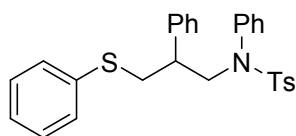
General procedure: a mixture of anhydrous potassium fluoride (KF, 0.5 mmol, 0.029 g, 2.5 equiv.) and 18-crown-6 (0.5 mmol, 0.132 g, 2.5 equiv.) in 1 mL anhydrous THF was added 2-(trimethylsilyl)phenyltrifluoromethanesulfonate (0.2 mmol, 49 μL, 1.0 equiv.) dropwise under nitrogen atmosphere at 0 °C in a flame-dried schlenk tube. Then cyclic thioether (0.3 mmol, 1.5 equiv.) was added to the solution dropwise, which was then kept stirring at 0 °C. Once the solution became pale yellow (after 5minutes), a

solution of 4-methyl-N-phenylbenzenesulfonamide (0.5 mmol, 0.125 g, 2.5 equiv.) in 1 mL anhydrous THF was added and kept stirring for 18 h at 0 °C or 0 °C to room temperature. The reaction mixture was then treated with water (20 mL), extracted, dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography.



4-methyl-N-phenyl-N-(1-phenyl-3-(phenylthio)propyl)benzenesulfonamide (**6a**)

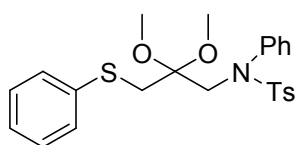
Following the general procedure at 0 °C for 18 h, extracted with ethyl acetate (3×20 mL), the crude product was purified by silica gel chromatography (PE: EA = 20:1 as the eluent) to give **6a** (60% yield) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, *J* = 8.2 Hz, 2H), 7.37-7.29 (m, 4H), 7.28-7.12 (m, 9H), 7.01 (d, *J* = 7.0 Hz, 2H), 6.55 (d, *J* = 7.4 Hz, 2H), 5.74 (t, *J* = 7.7 Hz, 1H), 2.97-2.88 (m, 2H), 2.42 (s, 3H), 2.24-2.07 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 143.11, 138.12, 138.08, 135.98, 134.86, 132.89, 129.64, 129.36, 129.00, 128.76, 128.70, 128.50, 128.23, 128.16, 127.55, 126.22, 61.55, 32.02, 30.86, 21.55. HR-MS (ESI): Calcd for C₂₈H₂₈NO₂S₂⁺ [M+H]⁺ requires 474.1556; found 474.1552.



4-methyl-N-phenyl-N-(2-phenyl-3-(phenylthio)propyl)benzenesulfonamide(**6b**)

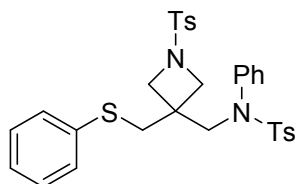
Following the general procedure at 0 °C to room temperature for 18 h, extracted with ethyl acetate (3×20 mL), the crude product was purified by silica gel chromatography (PE: EA = 10:1 as the eluent) to give **6b** (77% yield) as a colorless oil. ¹H NMR (400

MHz, CDCl₃) δ 7.36 (d, J = 8.1 Hz, 2H), 7.28-7.12 (m, 13H), 7.05 (d, J = 6.9 Hz, 2H), 6.86 (d, J = 7.7 Hz, 2H), 4.00 (dd, J = 13.3, 8.3 Hz, 1H), 3.69 (dd, J = 13.3, 6.9 Hz, 1H), 3.43 (dd, J = 13.2, 5.9 Hz, 1H), 3.14 (dd, J = 13.2, 8.8 Hz, 1H), 2.94-2.83 (m, 1H), 2.38 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 143.50, 140.37, 138.88, 136.19, 134.88, 129.80, 129.41, 129.02, 128.88, 128.66, 128.64, 127.99, 127.94, 127.77, 127.32, 126.19, 54.91, 43.93, 37.86, 21.57. HR-MS (ESI): Calcd for C₂₈H₂₈NO₂S₂⁺ [M+H]⁺ requires 474.1556; found 474.1559.



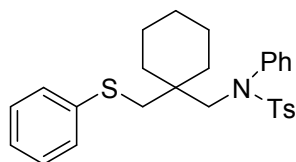
N-(2,2-dimethoxy-3-(phenylthio)propyl)-4-methyl-N-phenylbenzenesulfonamide (6c)

Following the general procedure at 0 °C for 18 h, extracted with ethyl acetate (3×20 mL), the crude product was purified by silica gel chromatography (PE: EA = 20:1 as the eluent) to give **6c** (55% yield) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.43 (d, J = 8.2 Hz, 2H), 7.24-7.08 (m, 10H), 7.05-7.01 (m, 2H), 3.89 (s, 2H), 3.09 (s, 6H), 3.01 (s, 2H), 2.41 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 143.62, 139.74, 136.35, 134.81, 129.38, 129.35, 129.26, 128.67, 128.65, 128.03, 127.99, 125.89, 101.29, 50.08, 48.83, 37.30, 21.58. HR-MS (ESI): Calcd for C₂₄H₂₈NNaO₄S₂⁺ [M+Na]⁺ requires 480.1274; found 480.1267.



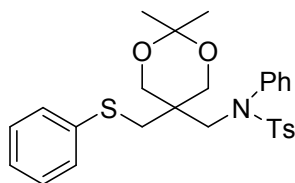
4-methyl-N-phenyl-N-((3-((phenylthio)methyl)-1-tosylazetidin-3-yl)methyl)benzenesulfonamide(6d)

Following the general procedure at 0 °C to room temperature for 18 h, extracted with ethyl acetate (3×20 mL), the crude product was purified by silica gel chromatography (PE: EA = 10:1 as the eluent) to give **6d** (85% yield) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.37-7.30 (m, 4H), 7.26-7.17 (m, 8H), 7.13 (d, *J* = 7.1 Hz, 2H), 6.87 (d, *J* = 6.9 Hz, 2H), 3.71 (s, 2H), 3.44 (dd, *J* = 28.1, 8.5 Hz, 4H), 3.04 (s, 2H), 2.46 (s, 3H), 2.41 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 144.03, 143.91, 140.10, 135.93, 134.45, 131.39, 129.85, 129.82, 129.48, 129.23, 129.05, 128.84, 128.48, 128.43, 127.86, 126.62, 56.94, 54.58, 39.92, 39.33, 31.95, 29.68, 29.39, 22.72, 21.65, 21.58, 14.14. HR-MS (ESI): Calcd for C₃₁H₃₃N₂O₄S₃⁺ [M+H]⁺ requires 593.1597; found 593.1586.



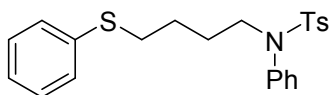
4-methyl-N-phenyl-N-((1-((phenylthio)methyl)cyclohexyl)methyl)benzenesulfonamide (6e)

Following the general procedure at 0 °C for 18 h, extracted with ethyl acetate (3×20 mL), the crude product was purified by silica gel chromatography (PE: EA = 20:1 as the eluent) to give **6e** (45% yield) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.35 (d, *J* = 8.1 Hz, 2H), 7.23-7.12 (m, 7H), 7.11-7.02 (m, 5H), 3.66 (s, 2H), 2.84 (s, 2H), 2.40 (s, 3H), 1.51-1.40 (m, 6H), 1.39-1.28 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 143.31, 141.08, 137.62, 134.99, 129.26, 129.22, 129.09, 128.64, 128.59, 127.85, 127.59, 125.56, 56.38, 41.07, 39.85, 33.22, 25.74, 21.55, 21.35. HR-MS (ESI): Calcd for C₂₇H₃₂NO₂S₂⁺ [M+H]⁺ requires 466.1869; found 466.1854.



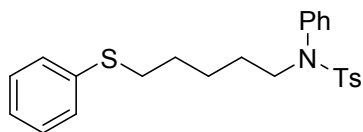
N-((2,2-dimethyl-5-((phenylthio)methyl)-1,3-dioxan-5-yl)methyl)-4-methyl-N-phenylbenzenesulfonamide (6f)

Following the general procedure at 0 °C for 18 h, extracted with ethyl acetate (3×20 mL), the crude product was purified by silica gel chromatography (PE: EA = 8:1 as the eluent) to give **6f** (43% yield) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.35 (d, *J* = 8.2 Hz, 2H), 7.28-7.25 (m, 5H), 7.24-7.19(m, 4H), 7.14 (t, *J* = 7.0 Hz, 1H), 7.12-7.05 (m, 2H), 3.79-3.65 (m, 6H), 3.12 (s, 2H), 2.41 (s, 3H), 1.33 (d, *J* = 3.2 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 143.65, 140.96, 137.08, 134.50, 129.38, 129.24, 128.96, 128.85, 128.63, 127.96, 127.89, 126.02, 98.31, 64.79, 52.43, 39.73, 37.29, 24.37, 23.08, 21.57. HR-MS (ESI): Calcd for C₂₇H₃₂NO₄S₂⁺ [M+H]⁺ requires 498.1767; found 498.1769.



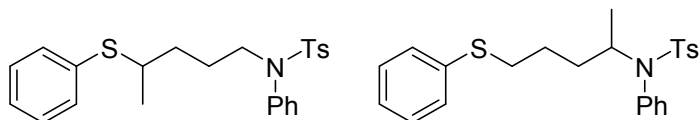
4-methyl-N-phenyl-N-(4-(phenylthio)butyl)benzenesulfonamide (6g)

Following the general procedure at 0 °C to room temperature for 18 h, extracted with ethyl acetate (3×20 mL), the crude product was purified by silica gel chromatography (PE: EA = 10:1 as the eluent) to give **6g** (98% yield) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.43 (d, *J* = 8.2 Hz, 2H), 7.30-7.23 (m, 7H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.16 (ddd, *J* = 8.4, 5.7, 2.3 Hz, 1H), 6.99 (dd, *J* = 6.6, 3.0 Hz, 2H), 3.53 (t, *J* = 6.8 Hz, 2H), 2.87 (t, *J* = 7.2 Hz, 2H), 2.40 (s, 3H), 1.73-1.64 (m, 2H), 1.58-1.49 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 143.40, 138.91, 136.40, 135.14, 129.41, 129.19, 129.03, 128.90, 128.75, 127.92, 127.73, 125.90, 49.69, 32.98, 27.01, 25.83, 21.57. HR-MS (ESI): Calcd for C₂₃H₂₆NO₂S₂⁺ [M+H]⁺ requires 412.1399; found 412.1401.



4-methyl-N-phenyl-N-(5-(phenylthio)pentyl)benzenesulfonamide (**6h**)

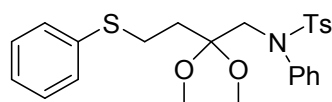
Following the general procedure at 0 °C to room temperature for 18 h, extracted with ethyl acetate (3×20 mL), the crude product was purified by silica gel chromatography (PE: EA = 10:1 as the eluent) to give **6h** (55% yield) as a pale yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.37 (d, *J* = 8.2 Hz, 2H), 7.24-7.19 (m, 5H), 7.19-7.13 (m, 4H), 7.10-7.03 (m, 1H), 6.98-6.92 (m, 2H), 3.43 (t, *J* = 6.6 Hz, 2H), 2.77 (t, *J* = 7.2 Hz, 2H), 2.33 (s, 3H), 1.55-1.47 (m, 2H), 1.40-1.30 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 143.32, 139.11, 136.72, 135.30, 129.38, 129.00, 128.86, 128.81, 128.34, 127.87, 127.72, 125.77, 50.27, 33.40, 28.59, 27.75, 25.54, 21.56. HR-MS (ESI): Calcd for C₂₄H₂₈NO₂S₂⁺ [M+H]⁺ requires 426.1556; found 426.1553.



4-methyl-N-phenyl-N-(4-(phenylthio)pentyl)benzenesulfonamide (**6i**) and 4-methyl-N-phenyl-N-(5-(phenylthio)pentan-2-yl)benzenesulfonamide (**6i'**)

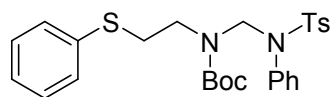
Following the general procedure at 0 °C to room temperature for 18 h, extracted with ethyl acetate (3×20 mL), the crude product was purified by silica gel chromatography (PE: EA = 20:1 as the eluent) to give **6i** and **6i'** (3:1, 57% yield) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.61 (d, *J* = 8.2 Hz, 0.5H), 7.47 (d, *J* = 8.1 Hz, 1.5H), 7.39-7.22 (m, 10H), 7.02 (dd, *J* = 9.8, 5.7 Hz, 2H), 4.47-4.31 (m, 0.3H), 3.61-3.49 (m, 1.5H), 3.25-3.14 (m, 0.7H), 2.94 (dt, *J* = 10.9, 7.0 Hz, 0.5H), 2.44 (s, 3H), 1.65 (ddd, *J* = 17.6, 9.4, 4.3 Hz, 4H), 1.24 (d, *J* = 6.7 Hz, 2.4H), 1.04 (d, *J* = 6.8 Hz, 0.8H). ¹³C NMR (100

MHz, CDCl₃) δ 143.35, 143.06, 138.95, 138.40, 136.56, 135.18, 135.04, 135.01, 132.32, 132.11, 129.43, 129.38, 129.05, 129.00, 128.92, 128.83, 128.76, 128.66, 127.89, 127.73, 127.45, 126.80, 125.88, 55.11, 50.01, 42.75, 34.51, 33.28, 33.20, 33.07, 26.18, 25.42, 21.55, 21.16, 20.32. HR-MS (ESI): Calcd for C₂₄H₂₈NO₂S₂⁺ [M+H]⁺ requires 426.1556; found 426.1552.



N-(2,2-dimethoxy-4-(phenylthio)butyl)-4-methyl-N-phenylbenzenesulfonamide (6j)

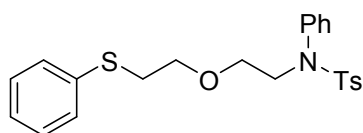
Following the general procedure at 0 °C to room temperature for 18 h, extracted with ethyl acetate (3×20 mL), the crude product was purified by silica gel chromatography (PE: EA = 20:1 as the eluent) to give **6j** (45% yield) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.37 (d, *J* = 8.3 Hz, 2H), 7.24-7.17 (m, 6H), 7.17-7.12 (m, 3H), 7.12-7.07 (m, 1H), 6.95-6.89 (m, 2H), 3.50-3.40 (m, 2H), 3.05 (s, 6H), 3.00 (s, 2H), 3.00 (s, 3H), 2.34 (s, 2H), 1.99-1.89 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 143.34, 139.08, 136.18, 135.23, 129.84, 129.40, 129.01, 128.95, 128.76, 127.92, 127.74, 101.43, 48.36, 45.97, 37.66, 32.09, 21.55. HR-MS (ESI): Calcd for C₂₅H₃₀NO₄S₂⁺ [M+H]⁺ requires 472.1611; found 472.1612.



tert-butyl(((4-methyl-N-phenylphenyl)sulfonamido)methyl)(2-(phenylthio)ethyl)carbamate (6k)

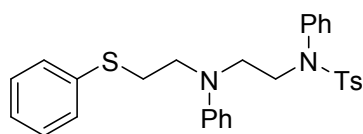
Following the general procedure at 0 °C to room temperature for 18 h, extracted with ethyl acetate (3×20 mL), the crude product was purified by silica gel chromatography (PE: EA = 20:1 as the eluent) to give **6k** (60% yield) as a colorless oil. ¹H NMR (400

MHz, CDCl₃) δ 7.42 (dt, J = 12.7, 8.2 Hz, 4H), 7.34-7.26 (m, 4H), 7.22 (d, J = 8.2 Hz, 3H), 7.17 (t, J = 6.7 Hz, 1H), 7.04-6.91 (m, 2H), 5.16 (s, 0.9H), 5.13 (s, 1.1H), 3.68 (t, J = 7.0 Hz, 1.1H), 3.61-3.50 (m, 0.9H), 3.23 (t, J = 7.0 Hz, 1.1H), 3.17-3.09 (m, 0.9H), 2.41 (s, 3H), 1.19 (s, 4H), 1.03 (s, 5H). ¹³C NMR (100 MHz, CDCl₃) δ 154.76, 154.14, 143.62, 137.98, 137.30, 136.48, 136.13, 135.82, 130.19, 129.56, 129.39, 129.21, 129.13, 129.01, 128.83, 128.54, 128.22, 127.45, 126.14, 125.85, 80.72, 80.40, 63.34, 61.67, 44.59, 44.41, 31.46, 31.24, 27.99, 27.70, 21.57. HR-MS (ESI): Calcd for C₂₇H₃₃N₂O₄S₂⁺ [M+H]⁺ requires 513.1876; found 513.1888.



4-methyl-N-phenyl-N-(2-(2-(phenylthio)ethoxy)ethyl)benzenesulfonamide (**6I**)

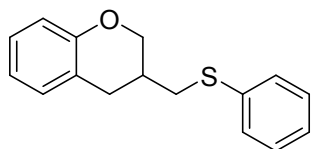
Following the general procedure at 0 °C to room temperature for 18 h, extracted with ethyl acetate (3×20 mL), the crude product was purified by silica gel chromatography (PE: EA = 60:1 as the eluent) to give **6I** (56% yield) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, J = 8.2 Hz, 2H), 7.35-7.25 (m, 9H), 7.21 (t, J = 7.1 Hz, 1H), 7.08 (dd, J = 6.6, 2.9 Hz, 2H), 3.74 (t, J = 6.3 Hz, 2H), 3.55 (dd, J = 14.7, 6.7 Hz, 4H), 3.01 (t, J = 6.9 Hz, 2H), 2.44 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 143.43, 139.58, 135.89, 135.55, 129.39, 129.38, 129.05, 129.01, 128.96, 128.01, 127.76, 126.19, 69.58, 68.70, 50.33, 33.08, 21.56. HR-MS (ESI): Calcd for C₂₃H₂₆NO₃S₂⁺ [M+H]⁺ requires 428.1349; found 428.1351.



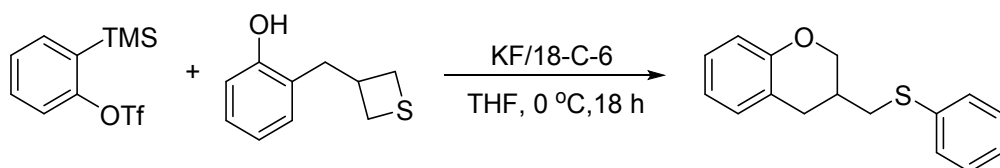
4-methyl-N-phenyl-N-(2-(phenyl(2-(phenylthio)ethyl)amino)ethyl)benzenesulfonamide (6m)

Following the general procedure with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.4 mmol, 98 μ L, 2.0 equiv.) and thiomorpholine (0.2 mmol, 0.021 g, 1.0 equiv.) at 0 °C to room temperature for 18 h, extracted with ethyl acetate (3 \times 20 mL), the crude product was purified by silica gel chromatography (PE: EA = 20:1 as the eluent) to give **6m** (68% yield) as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.43 (d, J = 8.1 Hz, 2H), 7.36-7.27 (m, 5H), 7.25 (t, J = 3.7 Hz, 1H), 7.20 (d, J = 8.1 Hz, 3H), 7.17-7.08 (m, 3H), 7.04 (dd, J = 6.4, 2.6 Hz, 2H), 6.67 (t, J = 7.2 Hz, 1H), 6.48 (d, J = 8.2 Hz, 2H), 3.68-3.60 (m, 2H), 3.52-3.45 (m, 2H), 3.44-3.35 (m, 2H), 3.03-2.93 (m, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 146.58, 143.55, 139.63, 135.33, 135.12, 129.94, 129.50, 129.46, 129.19, 129.05, 128.66, 128.10, 127.69, 126.52, 116.80, 111.84, 50.80, 50.28, 47.99, 31.02, 21.54. HR-MS (ESI): Calcd for $\text{C}_{29}\text{H}_{31}\text{N}_2\text{O}_2\text{S}_2^+$ $[\text{M}+\text{H}]^+$ requires 503.1821; found 503.1817.

4) Synthesis of 6n:



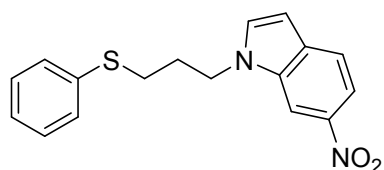
3-((phenylthio)methyl)chromane(6n)



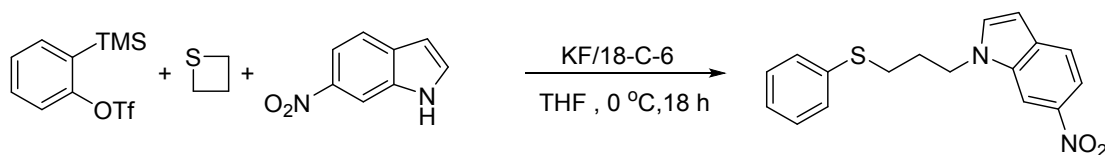
A mixture of anhydrous potassium fluoride (KF, 0.5 mmol, 0.029 g, 5 equiv.) and 18-crown-6 (0.5 mmol, 0.132 g, 5 equiv.) in 1 mL anhydrous THF was added 2-(trimethylsilyl)phenyltrifluoromethanesulfonate (0.2 mmol, 49 μ L, 2 equiv.) dropwise under nitrogen atmosphere at 0 °C in a flame-dried schlenk tube. Then a solution of 2-(thietan-3-ylmethyl)phenol (0.1 mmol, 0.018 g, 1 equiv.) in 1 mL anhydrous THF was

added and kept stirring for 18 h at 0 °C. The reaction mixture was then treated with water (20 mL), extracted with ethyl acetate (3×20 mL), dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE as the eluent) to give **6n** (66% yield) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.29 (dt, *J* = 3.0, 1.8 Hz, 2H), 7.24-7.19 (m, 2H), 7.15-7.09 (m, 1H), 7.01 (dd, *J* = 11.0, 4.4 Hz, 1H), 6.96 (d, *J* = 7.5 Hz, 1H), 6.82-6.76 (m, 1H), 6.74 (dd, *J* = 10.1, 5.3 Hz, 1H), 4.22 (ddd, *J* = 10.7, 3.0, 1.5 Hz, 1H), 3.91 (dd, *J* = 10.7, 7.6 Hz, 1H), 2.97-2.92 (m, 1H), 2.90 (dd, *J* = 7.2, 3.6 Hz, 2H), 2.60 (dd, *J* = 16.3, 7.7 Hz, 1H), 2.26-2.15 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 153.32, 134.93, 129.00, 128.64, 128.01, 126.40, 125.32, 119.67, 119.53, 115.53, 68.09, 34.74, 30.93, 29.59. HR-MS (ESI): Calcd for C₁₆H₁₇OS⁺ [M+H]⁺ requires 257.0995; found 257.0998.

5) Synthesis of 7:



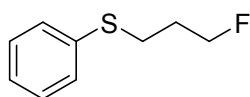
6-nitro-1-(3-(phenylthio)propyl)-1H-indole (7)



A mixture of anhydrous potassium fluoride (KF, 0.5 mmol, 0.029 g, 2.5 equiv.) and 18-crown-6 (0.5 mmol, 0.132 g, 2.5 equiv.) in 1 mL anhydrous THF was added 2-(trimethylsilyl)phenyltrifluoromethanesulfonate (0.2 mmol, 49 μL, 1.0 equiv.) dropwise under nitrogen atmosphere at 0 °C in a flame-dried schlenk tube. Then thietane (0.3 mmol, 24 μL, 1.5 equiv.) was added to the solution dropwise, which was then kept stirring at 0 °C. Once the solution became pale yellow (after 5 minutes), a solution of 6-nitro-1H-indole (0.5 mmol, 0.081 g, 2.5 equiv.) in 1 mL anhydrous THF

was added and kept stirring for 18 h at 0 °C. The reaction mixture was then treated with water (20 mL), extracted with ethyl acetate (3×20 mL), dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE: EA = 10:1 as the eluent) to give **7** (60% yield) as a red oil. ¹H NMR (400 MHz, CDCl₃) δ 8.31 (d, *J* = 1.8 Hz, 1H), 7.99 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.64 (d, *J* = 8.8 Hz, 1H), 7.37 (d, *J* = 3.1 Hz, 1H), 7.32 (dt, *J* = 3.0, 1.8 Hz, 2H), 7.29-7.25 (m, 2H), 7.22-7.16 (m, 1H), 6.58 (dd, *J* = 3.0, 0.5 Hz, 1H), 4.36 (t, *J* = 6.8 Hz, 2H), 2.84 (t, *J* = 6.7 Hz, 2H), 2.16 (quint, *J* = 6.8 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 143.02, 135.06, 134.51, 133.64, 133.40, 129.95, 129.14, 126.66, 120.90, 115.00, 106.45, 102.54, 44.92, 30.78, 29.17. HR-MS (ESI): Calcd for C₁₇H₁₇N₂O₂S⁺ [M+H]⁺ requires 313.1005; found 313.1002.

6) Synthesis of **8**:

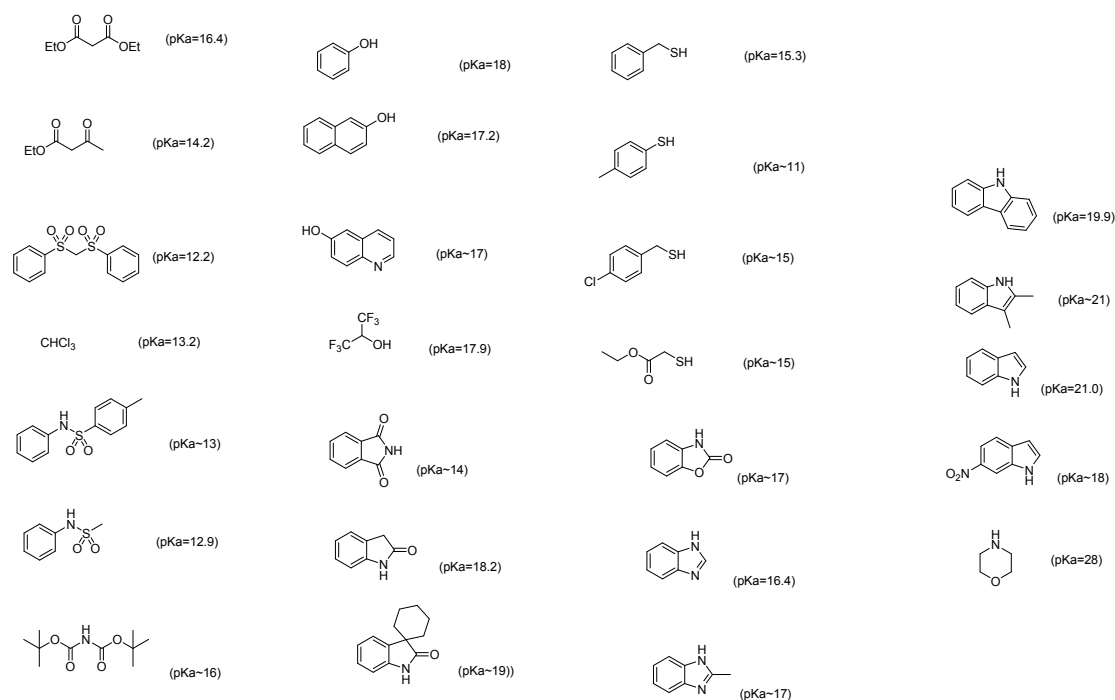


(3-fluoropropyl)(phenyl)sulfane (**8**)

A mixture of anhydrous potassium fluoride (KF, 0.5 mmol, 0.029 g, 2.5 equiv.) and 18-crown-6 (0.5 mmol, 0.132 g, 2.5 equiv.) in 1 mL anhydrous THF was added 2-(trimethylsilyl)phenyltrifluoromethanesulfonate (0.2 mmol, 49 μL, 1.0 equiv.) dropwise under nitrogen atmosphere at 0 °C in a flame-dried schlenk tube. Then thietane (0.3 mmol, 24 μL, 1.5 equiv.) was added to the solution dropwise, which was then kept stirring at 0 °C. Once the solution became pale yellow (after 5 minutes), a solution of carbazole (0.5 mmol, 0.083 g, 2.5 equiv.) in 1 mL anhydrous THF was added and kept stirring for 18 h at 0 °C. The reaction mixture was then treated with water (20 mL), extracted with ethyl acetate (3×20 mL), dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE:EA = 50:1 as the eluent) to give **8** (70% yield) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.39-7.32 (m, 2H), 7.32-7.26 (m, 2H), 7.22-7.16 (m,

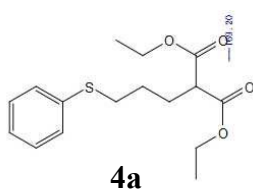
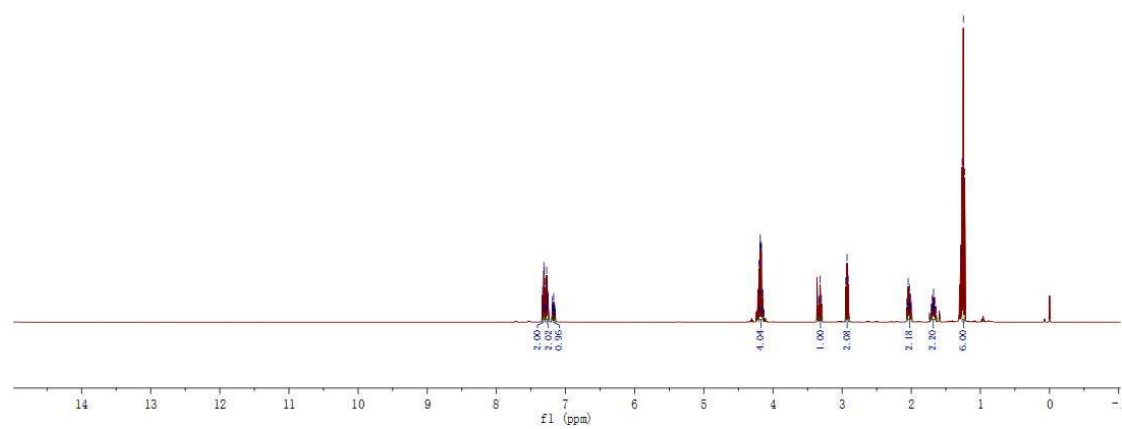
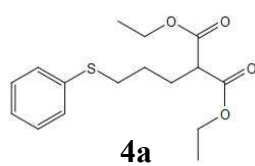
1H), 4.56 (dt, $J = 47.1, 5.7$ Hz, 2H), 3.05 (t, $J = 7.2$ Hz, 2H), 2.08-1.93 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 135.86, 129.42, 129.00, 126.20, 82.24 (d, $J = 165.6$ Hz), 30.06 (d, $J = 20.2$ Hz), 29.44 (d, $J = 4.5$ Hz). ^{19}F NMR (377 MHz, CDCl_3) δ -221.04. HR-MS (ESI): Calcd for $\text{C}_9\text{H}_{12}\text{FS}^+ [\text{M}+\text{H}]^+$ requires 171.0638; found 171.0623.

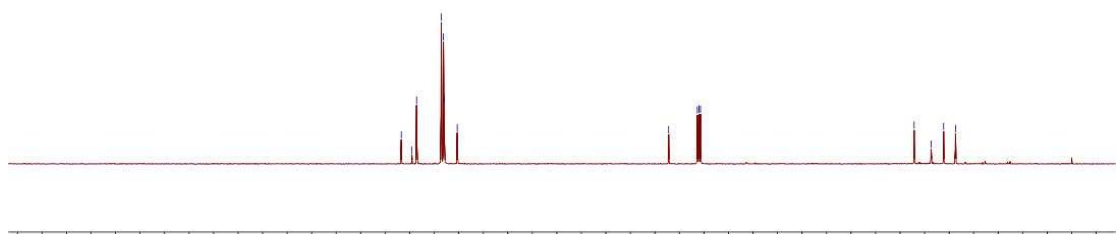
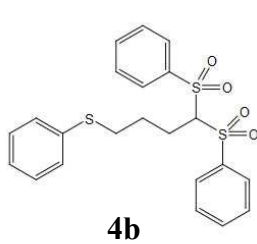
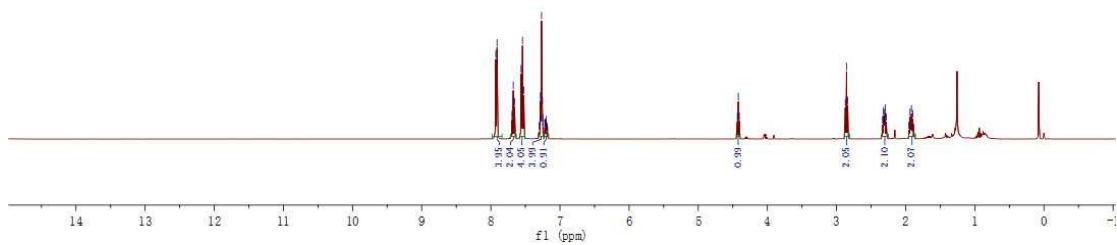
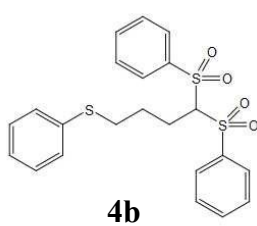
V. pKa Data for Substrates

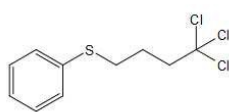


All the pKa data are from: <http://www.chem.wisc.edu/areas/reich/pkatable/index.htm>, which is measured in DMSO. Indeed, we found that substrates with pKa approximately from 13 to 19 are usually viable for this transformation. If the pKa of substrate is higher than 19, reduced reactivities were often observed and the competing fluorinated products as well as direct coupling products could be observed. If the pKa of the pronucleophile is lower, the deprotonated species are often not nucleophilic enough to open the ring. The acidic proton might also cause the decomposition of reaction intermediates. This is an experiential summary of our transformation, which we believe would be helpful for people who intend to apply our protocols.

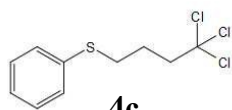
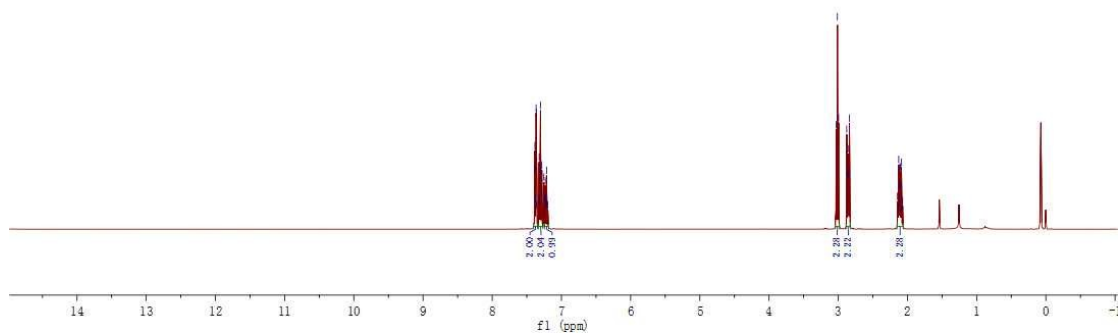
VI. Spectrum





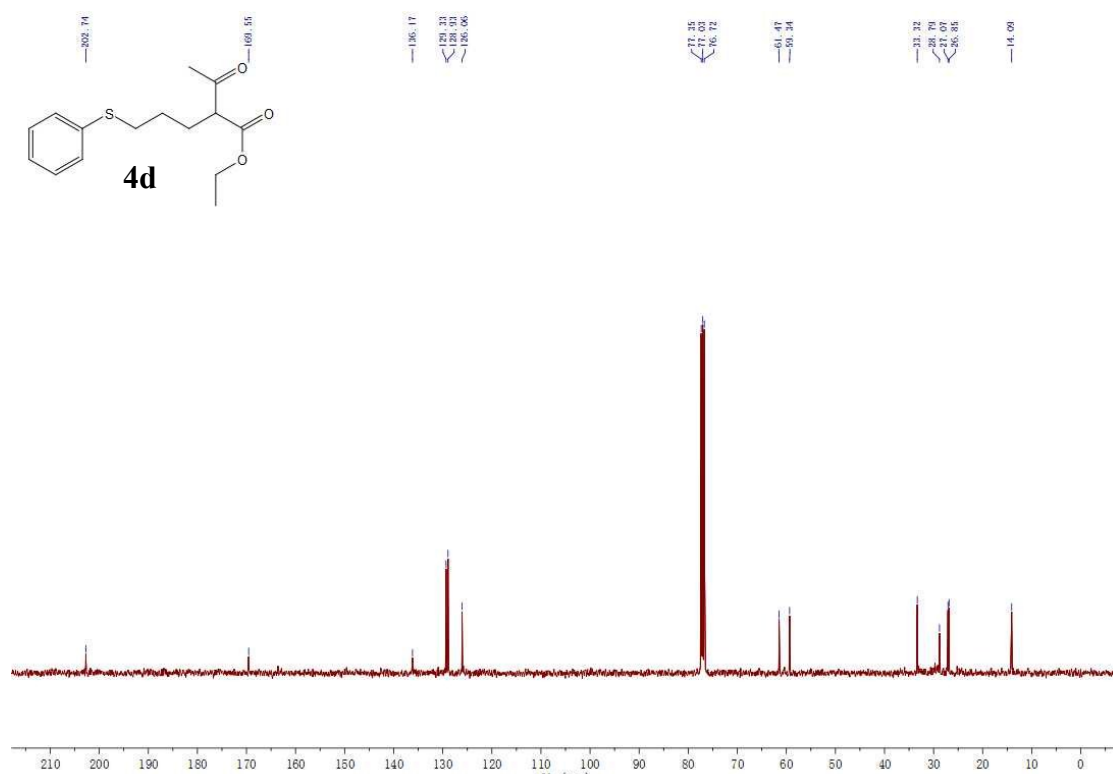
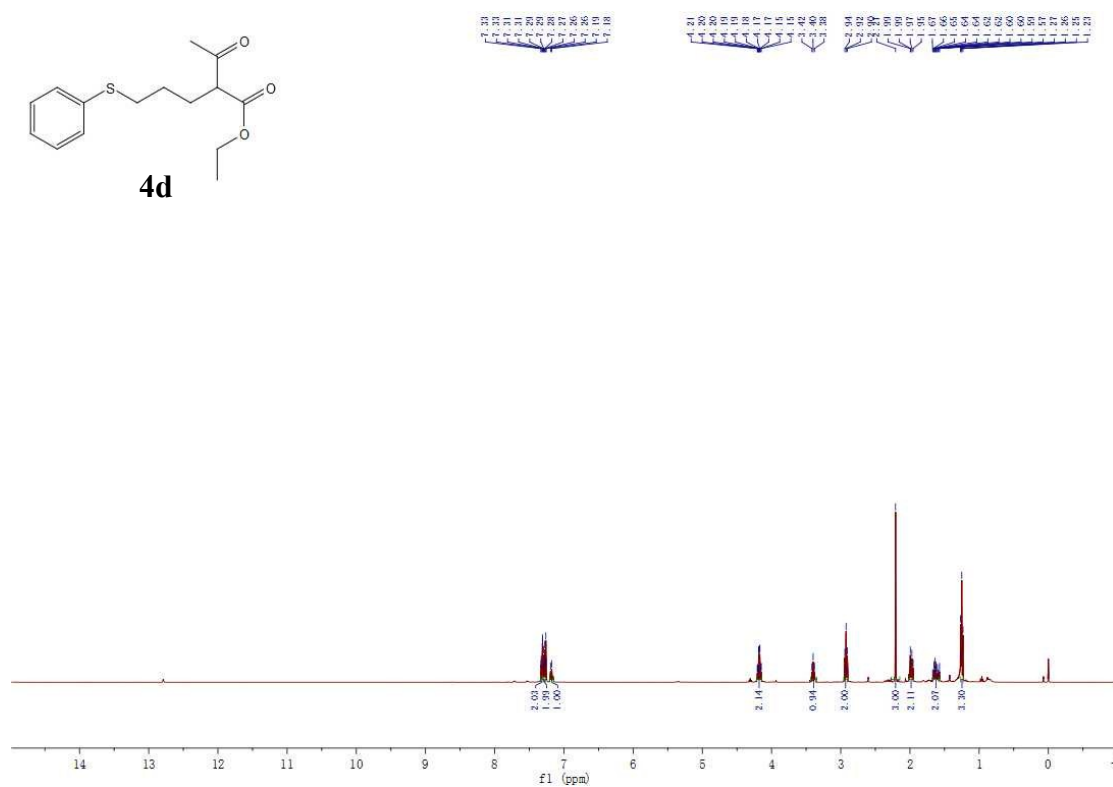
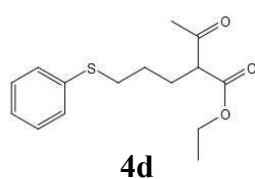


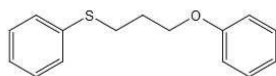
4c



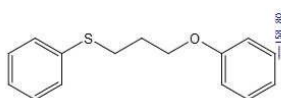
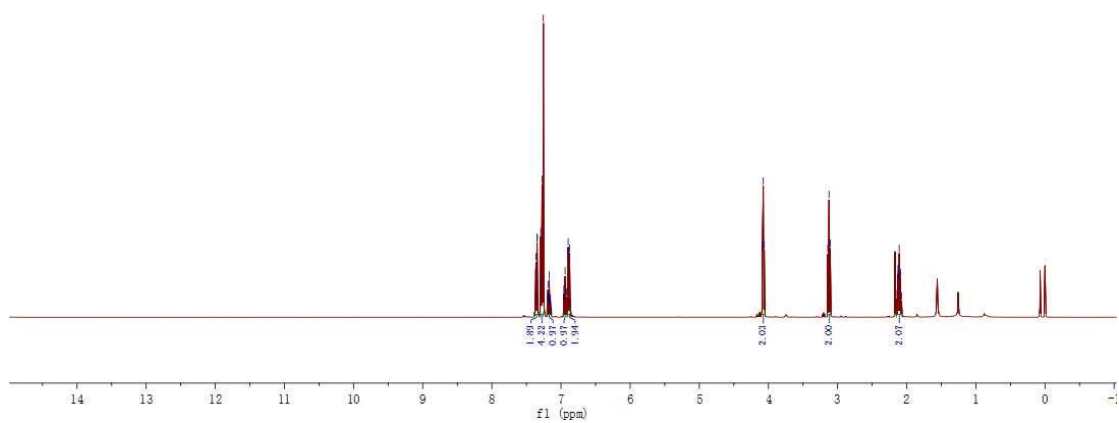
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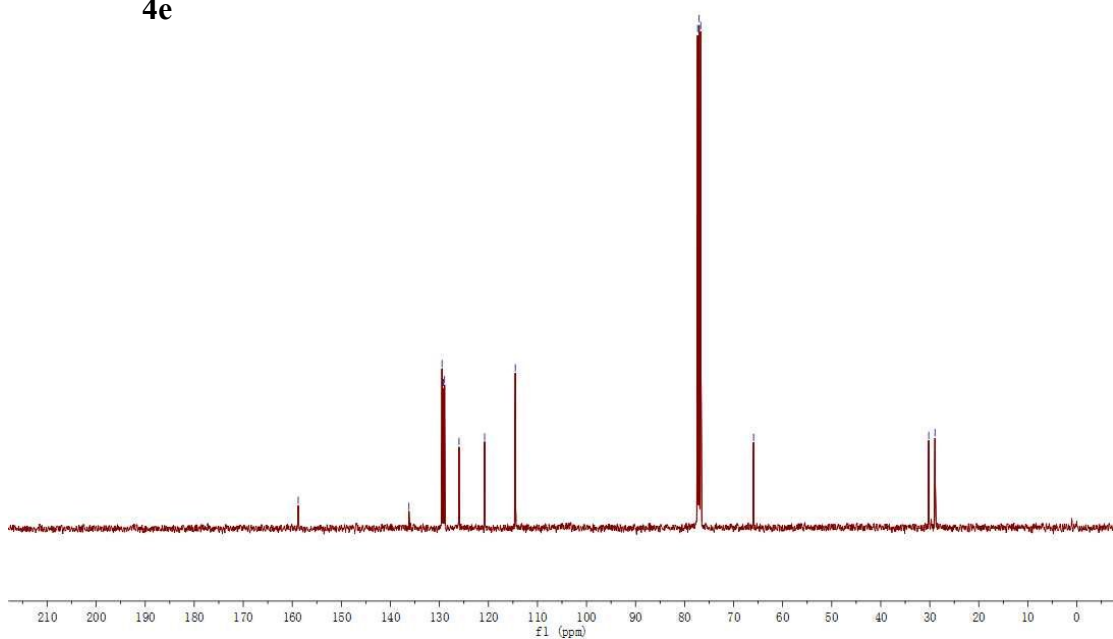


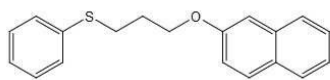


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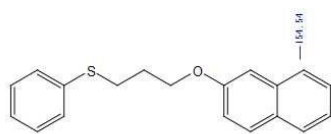
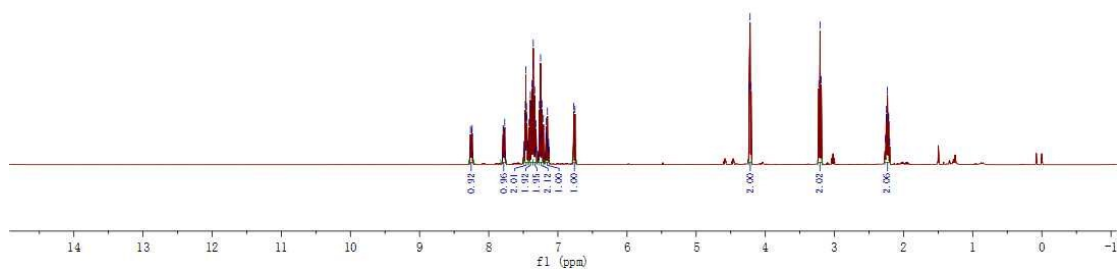


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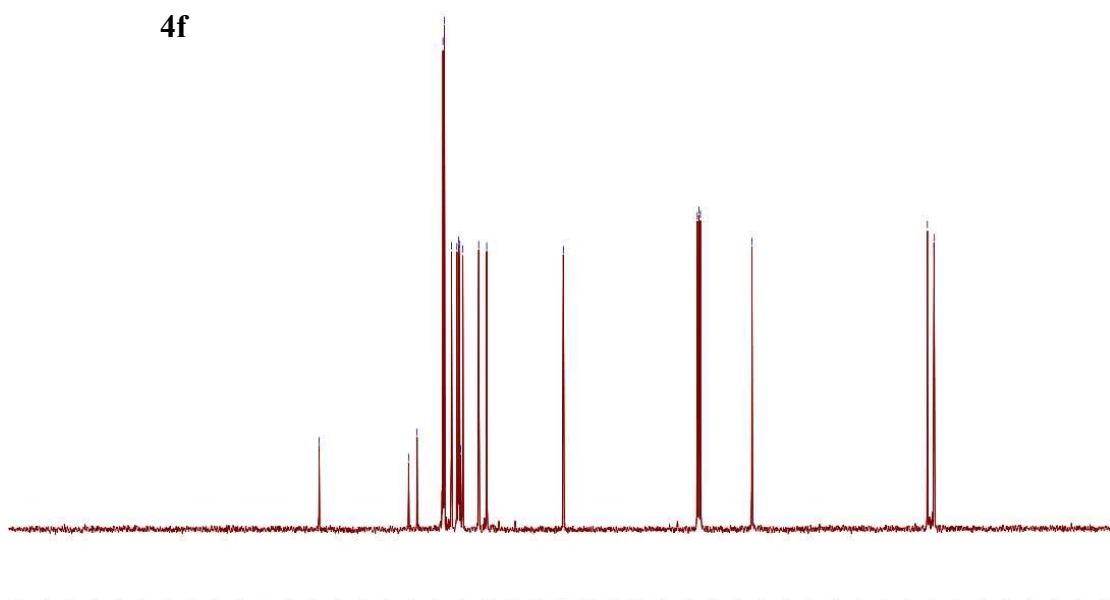


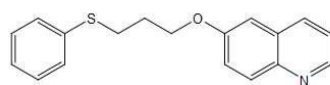


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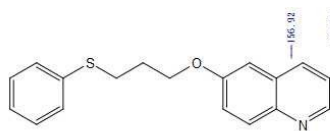
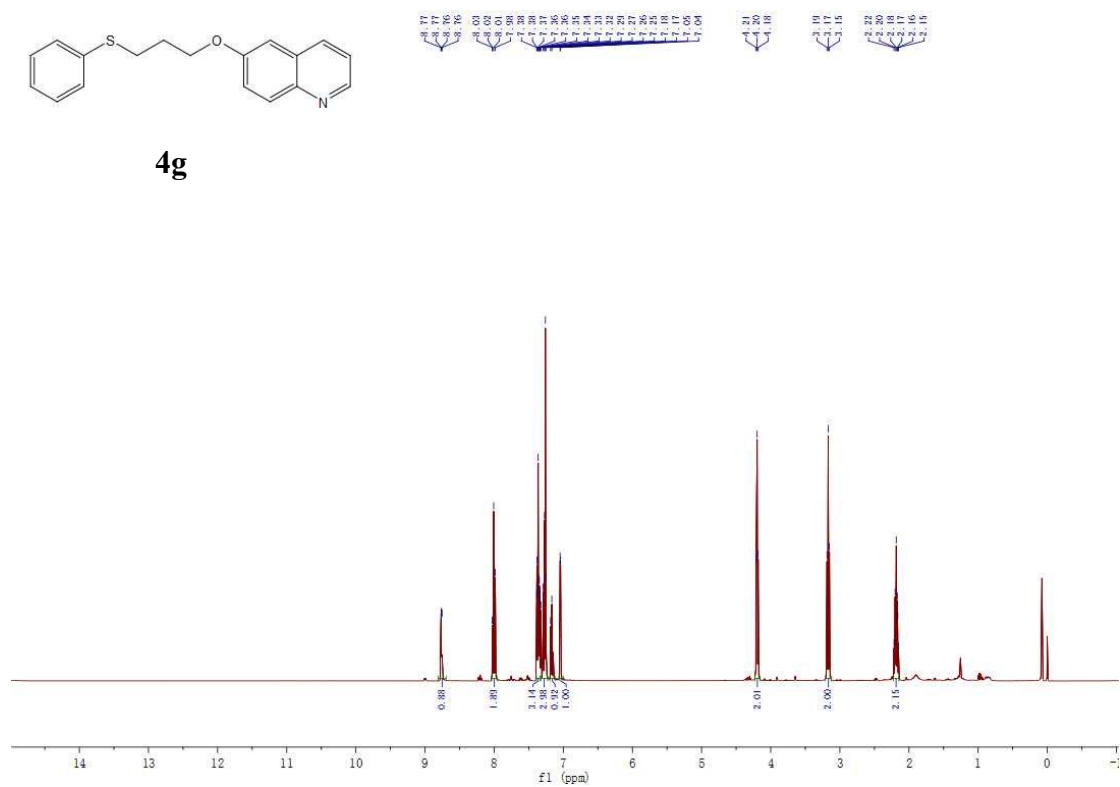


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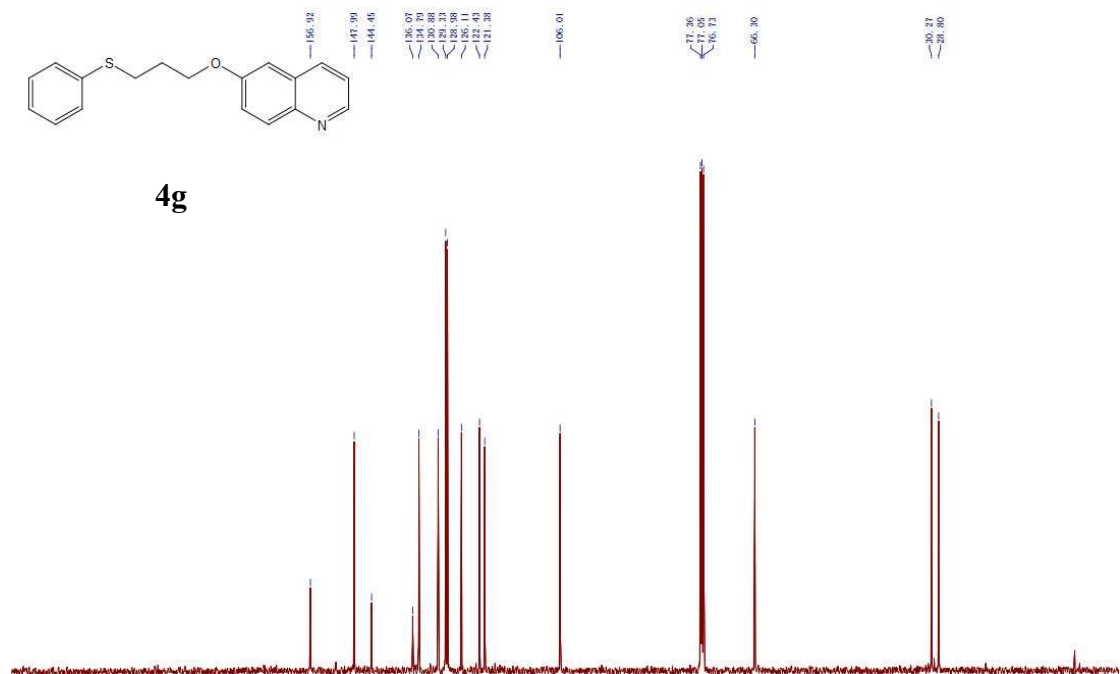


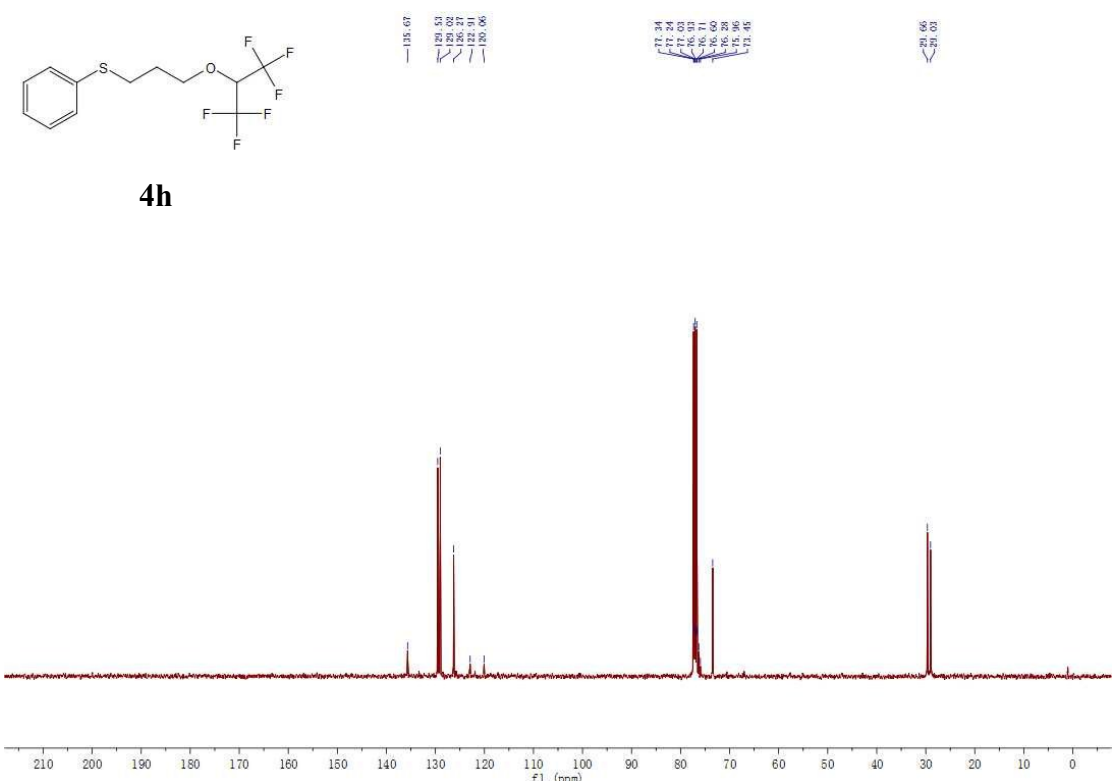


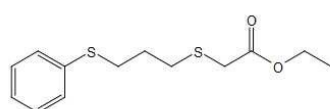
4g



4g





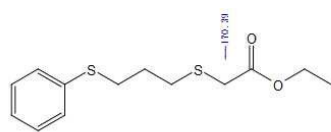
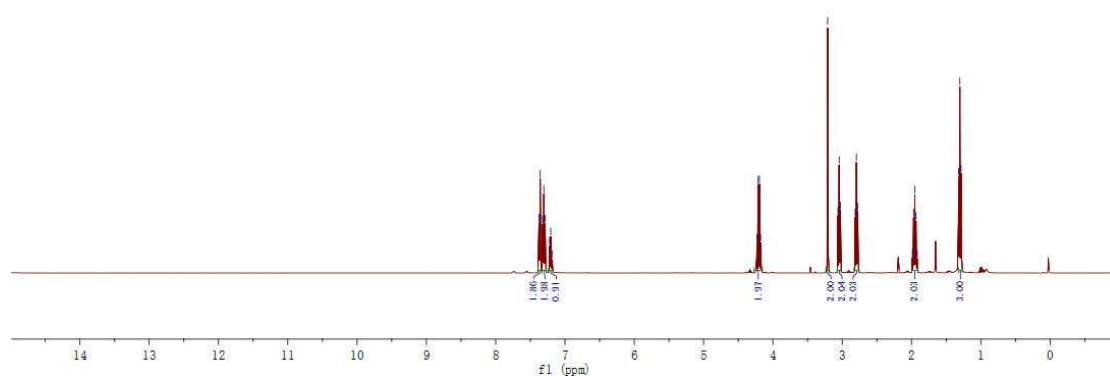


4i

7.38
7.32
7.31
7.22
7.21
7.19

4.31
4.21
4.19

3.21
3.04
3.03
2.80
2.78
1.99
1.97
1.93
1.92
1.85



4i

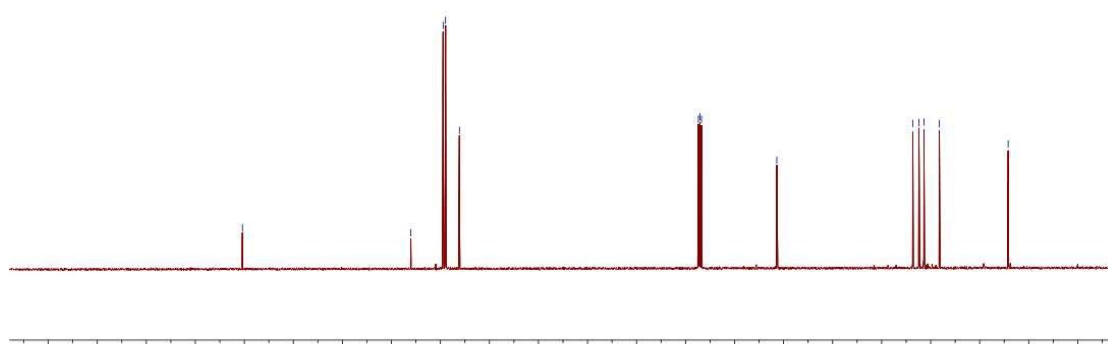
136.04
129.45
128.95
126.13

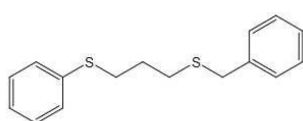
77.00
76.75

61.38

31.64
31.31
28.23

14.19

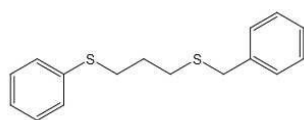
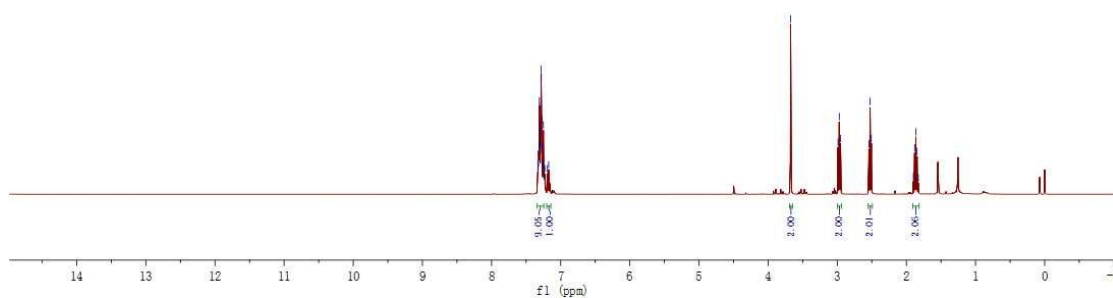




4j

7.33, 7.33, 7.32, 7.31, 7.31, 7.31, 7.30, 7.29, 7.29, 7.28, 7.27, 7.27, 7.26, 7.25, 7.24, 7.19, 7.17

2.67, 2.99, 2.97, 2.94, 2.92, 1.90, 1.88, 1.85, 1.83



4j

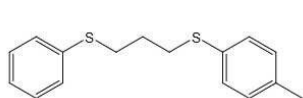
138.20, 136.20, 129.33, 128.94, 128.53, 127.02, 126.04

77.85, 77.80, 76.73

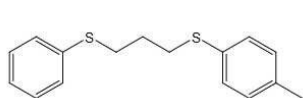
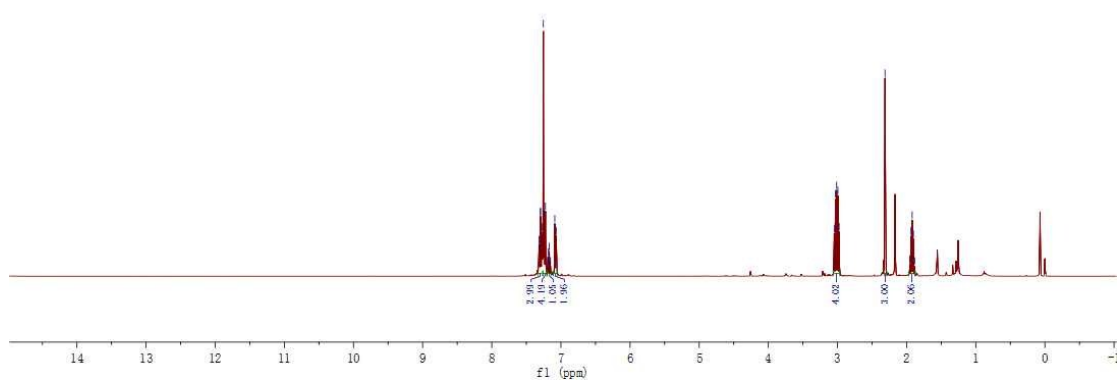
36.20, 32.47, 31.65, 28.90



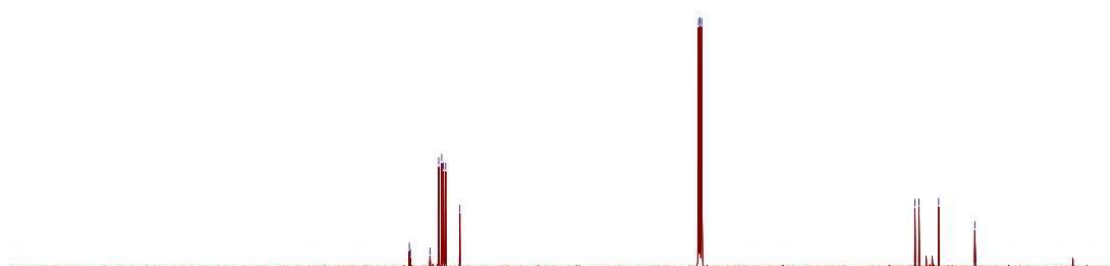


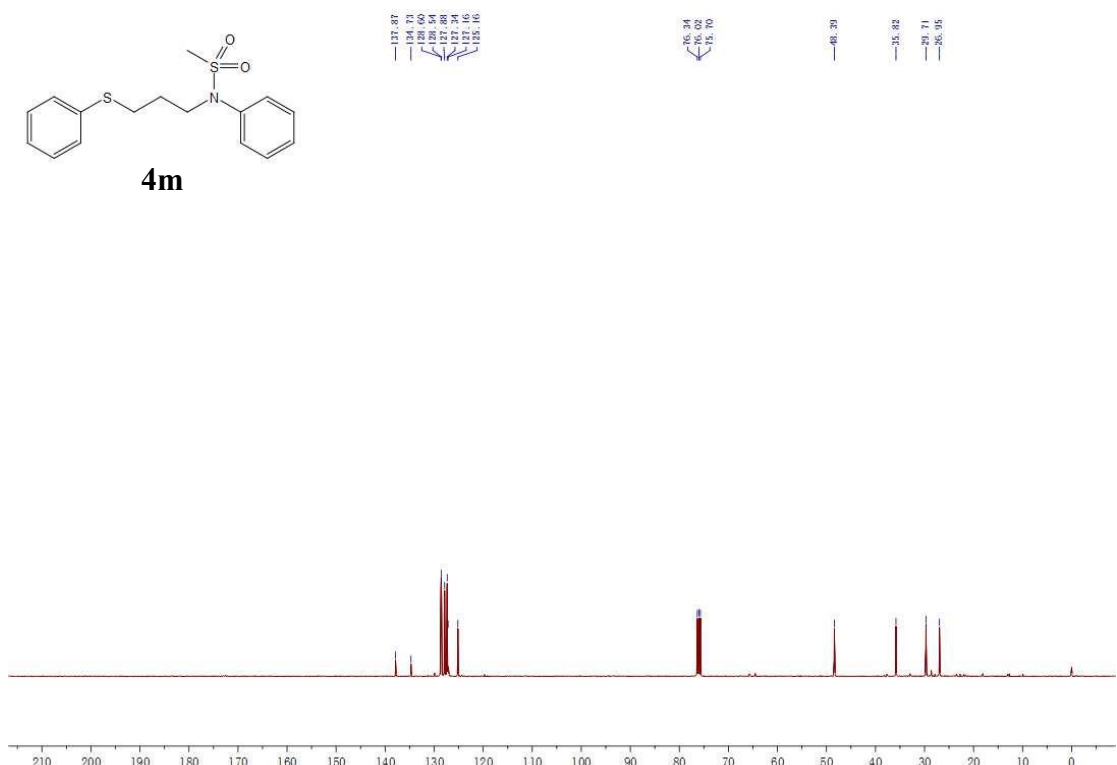
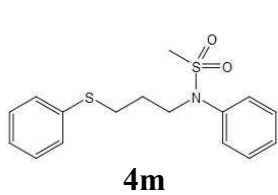
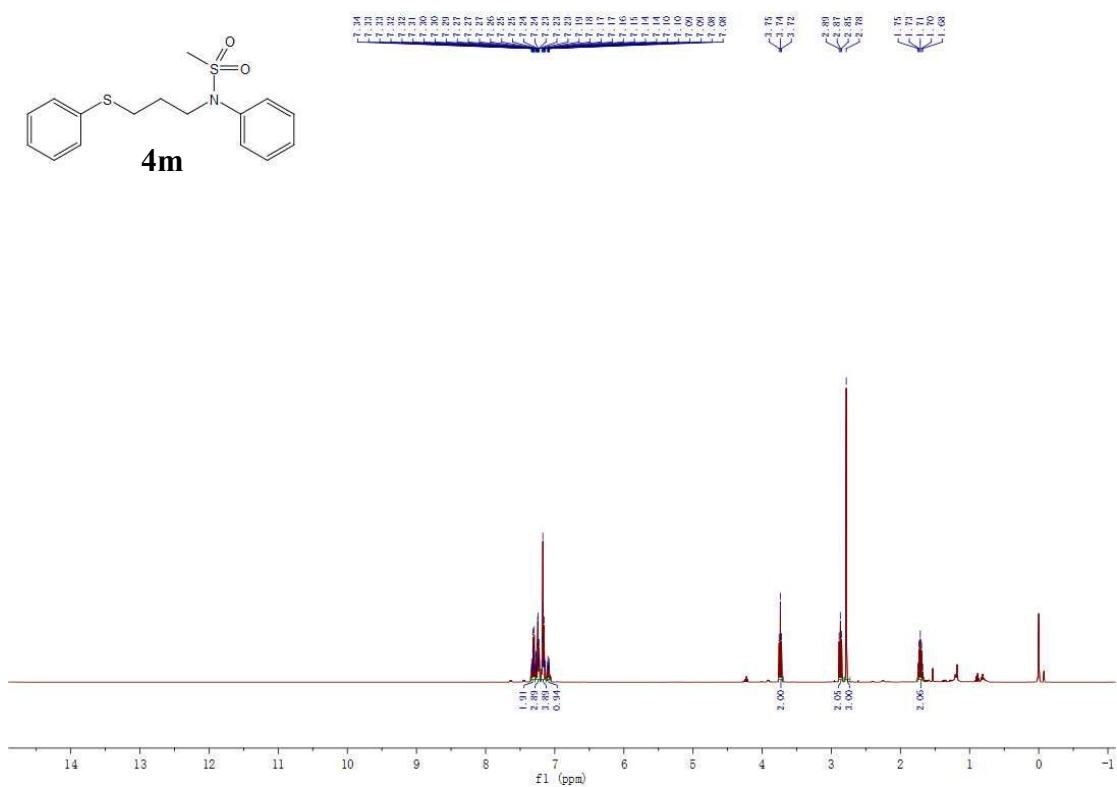
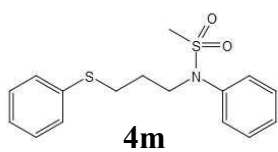


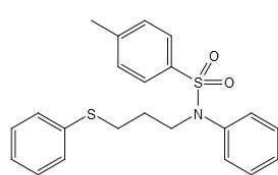
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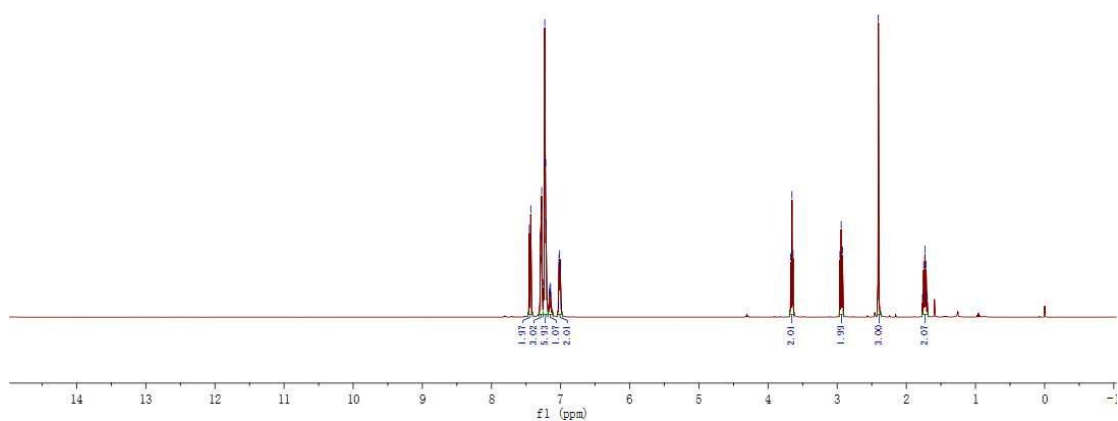
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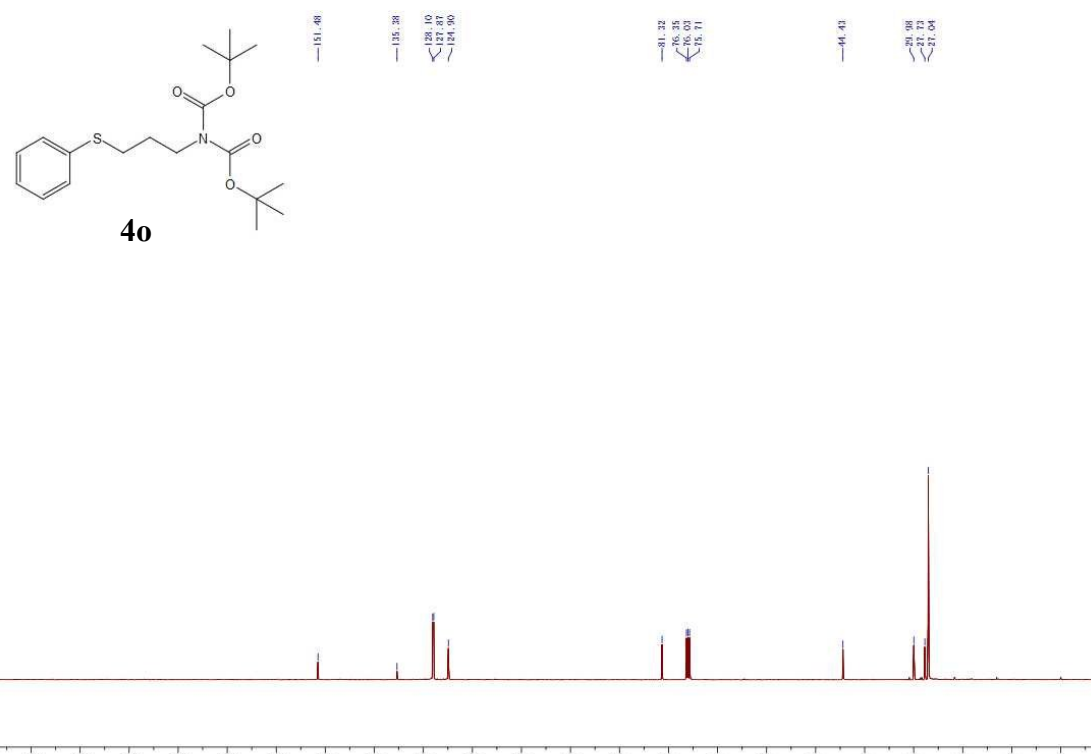
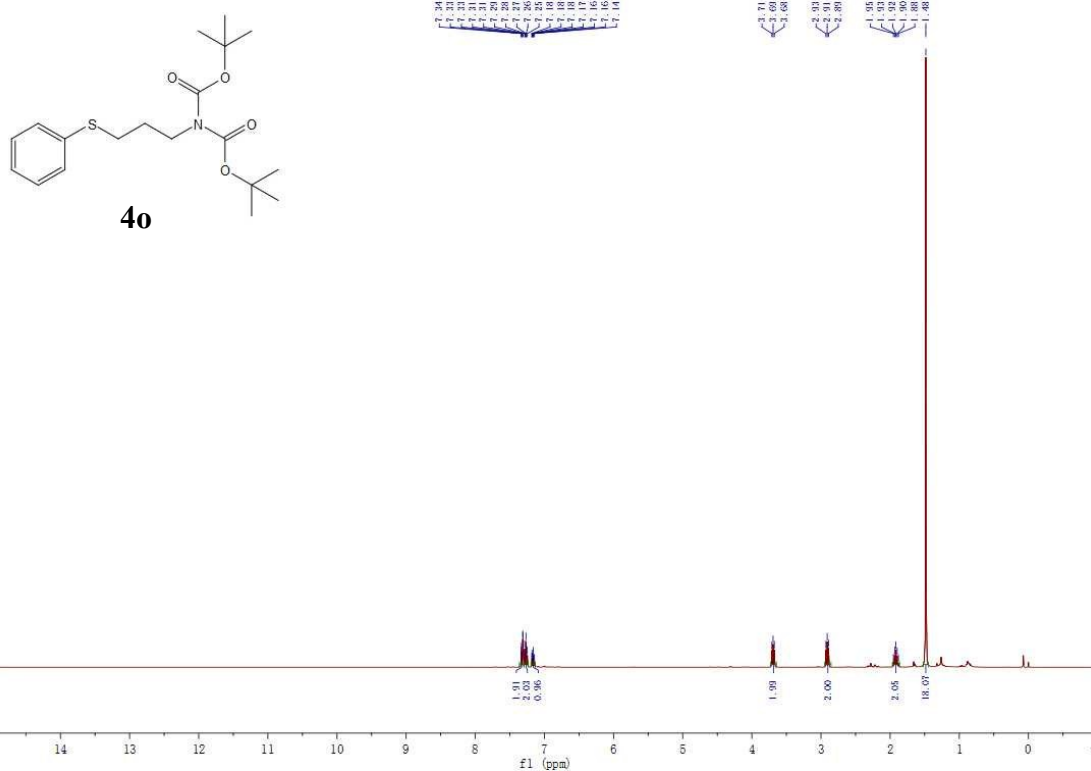


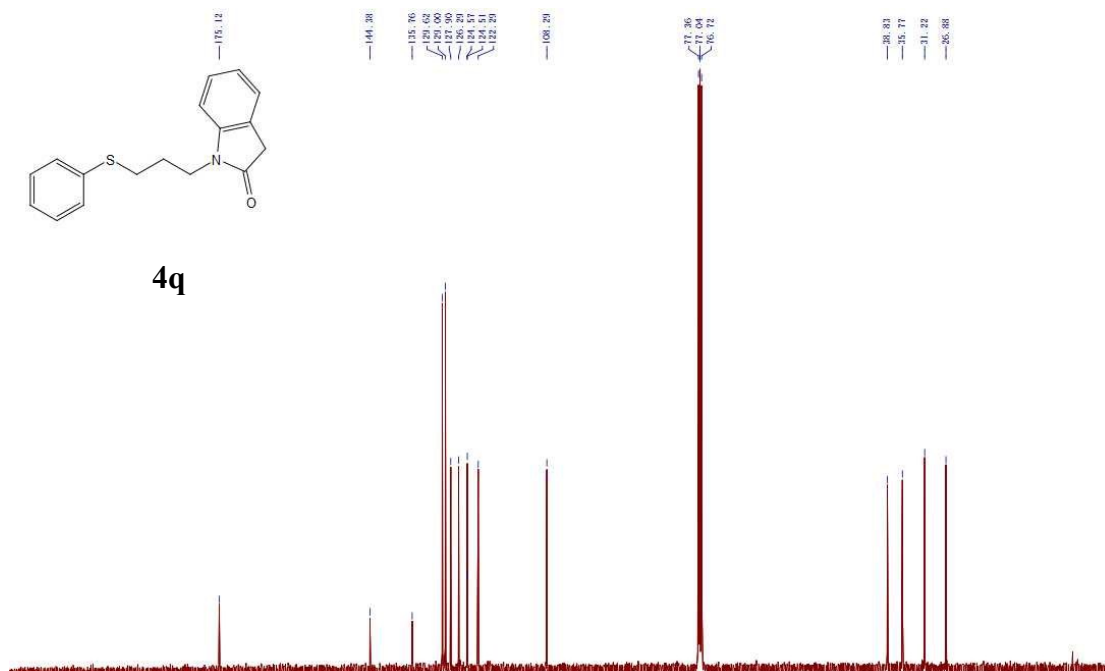
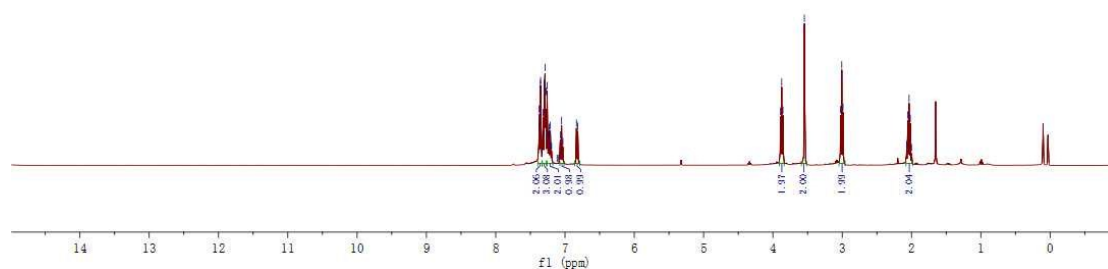


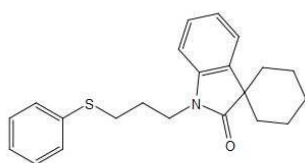


4n

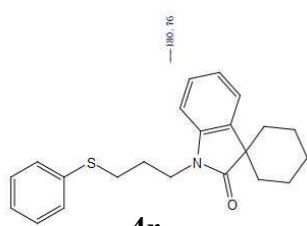
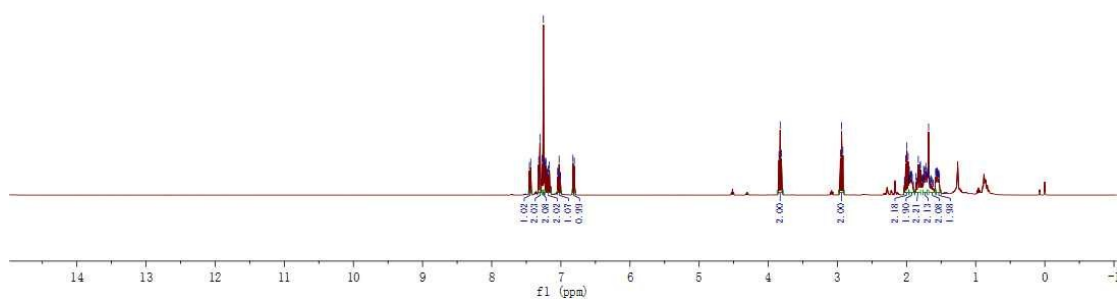








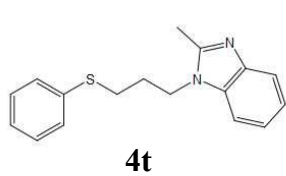
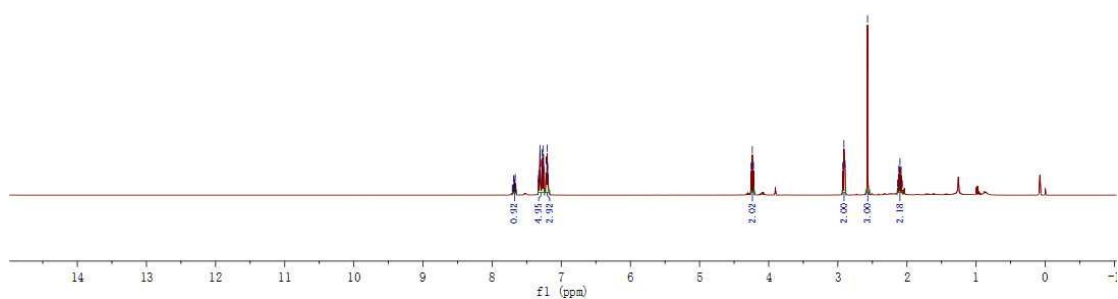
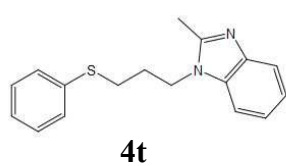
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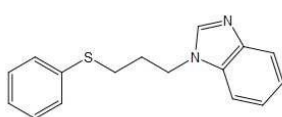


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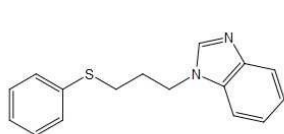
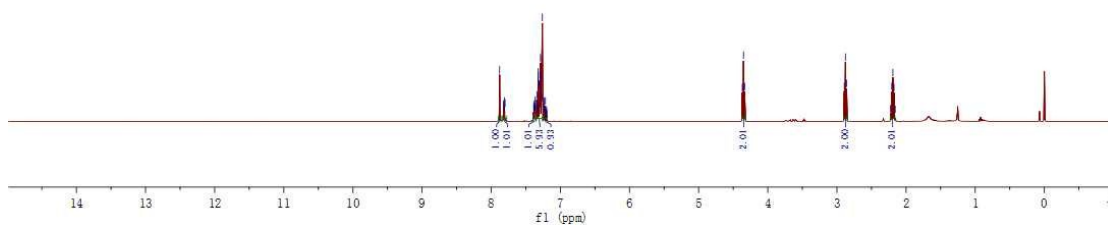




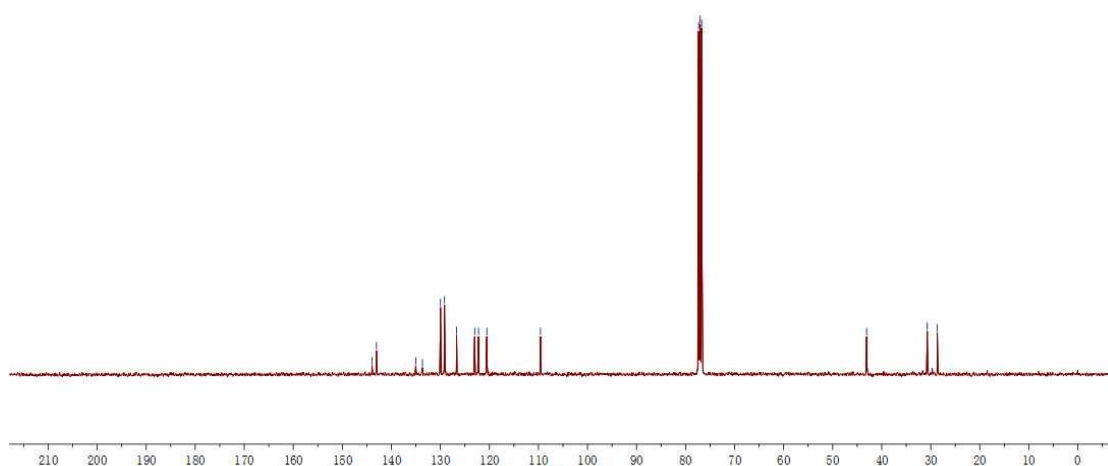


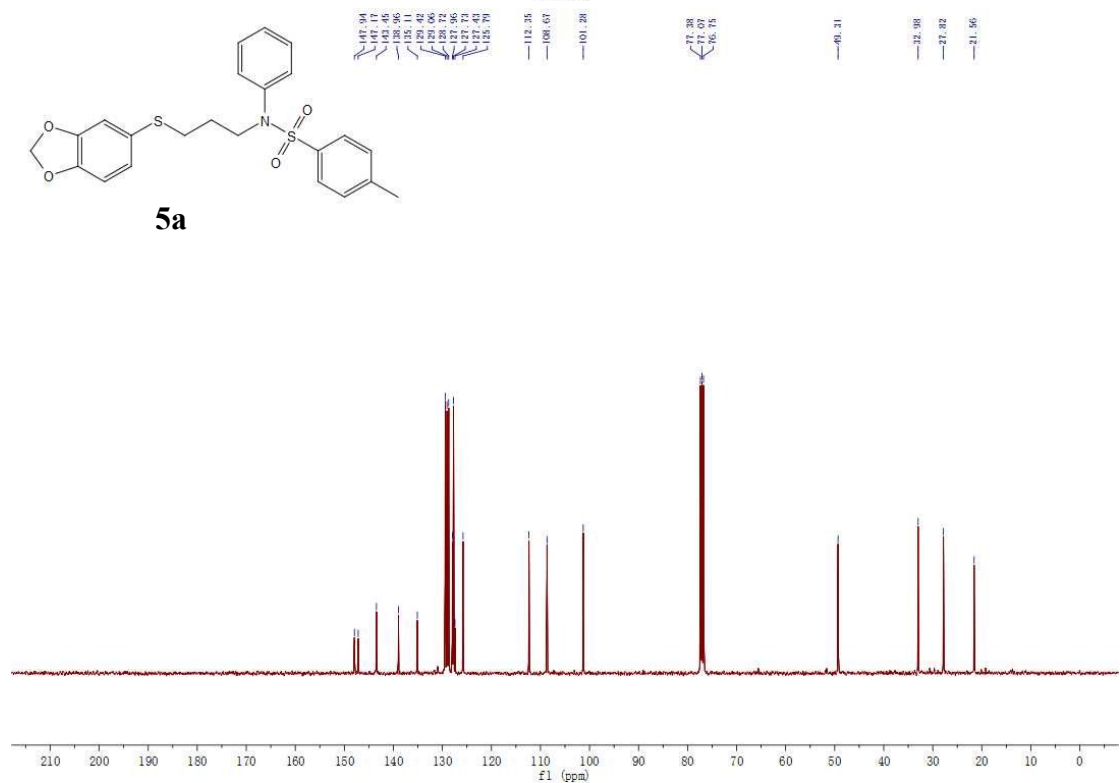
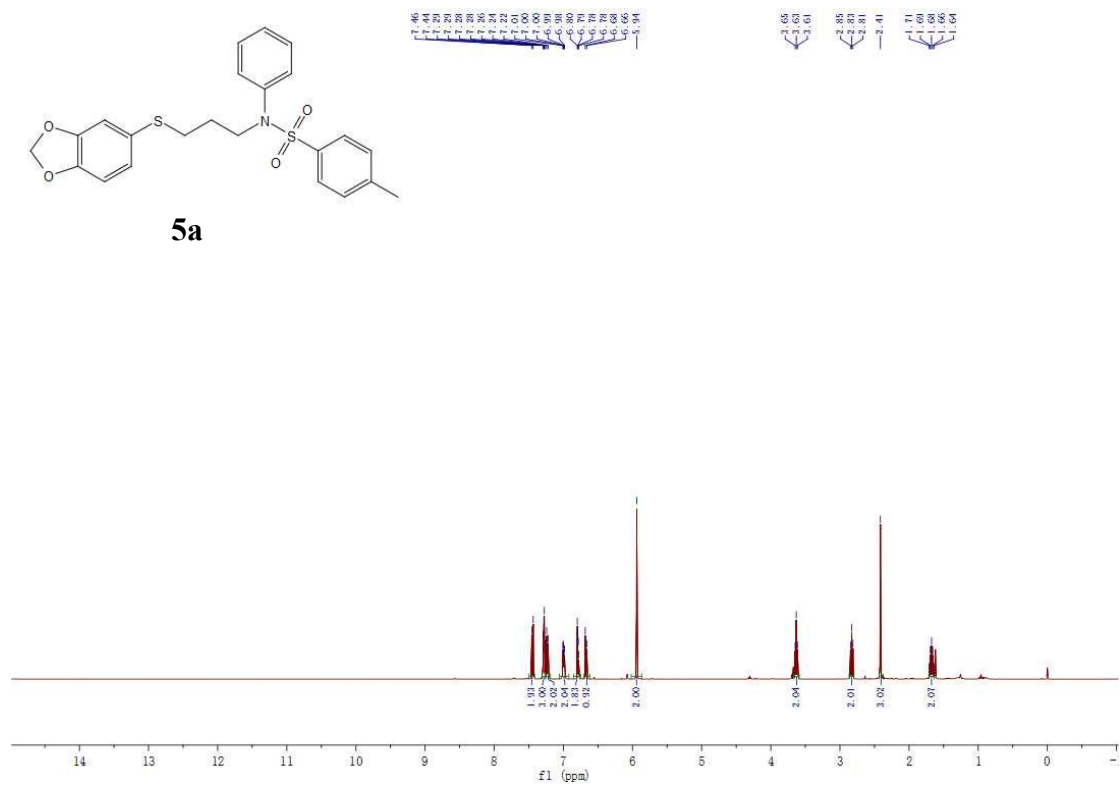
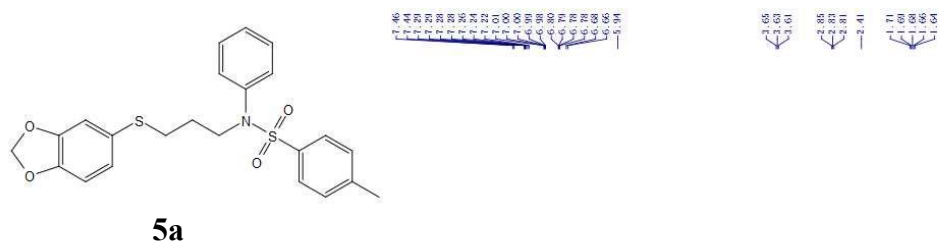


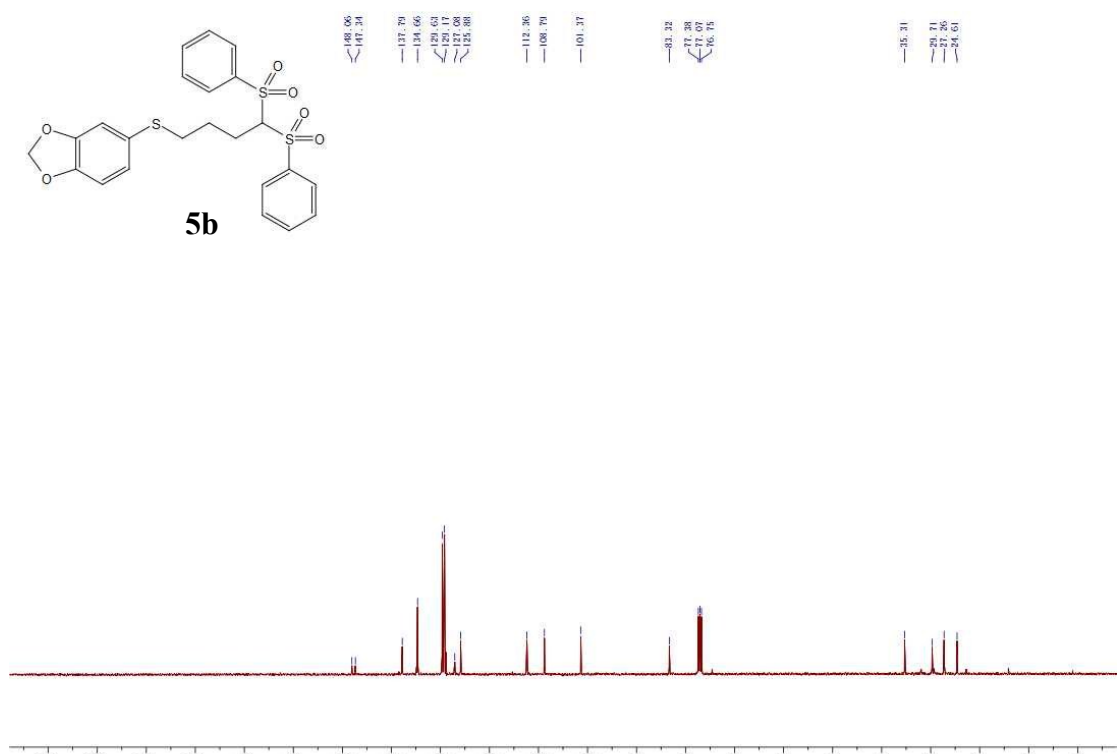
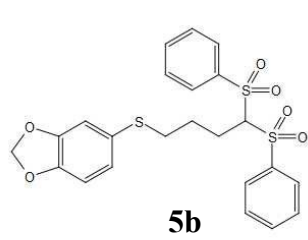
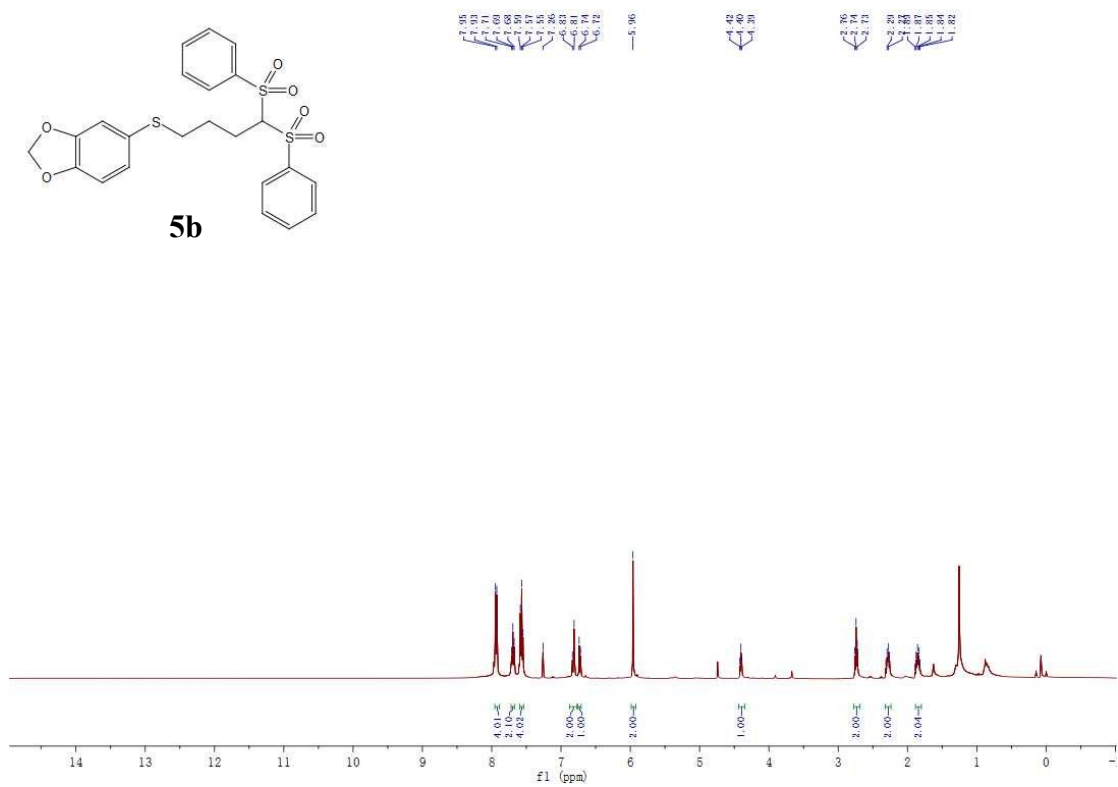
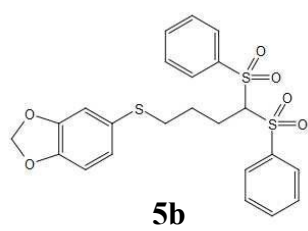
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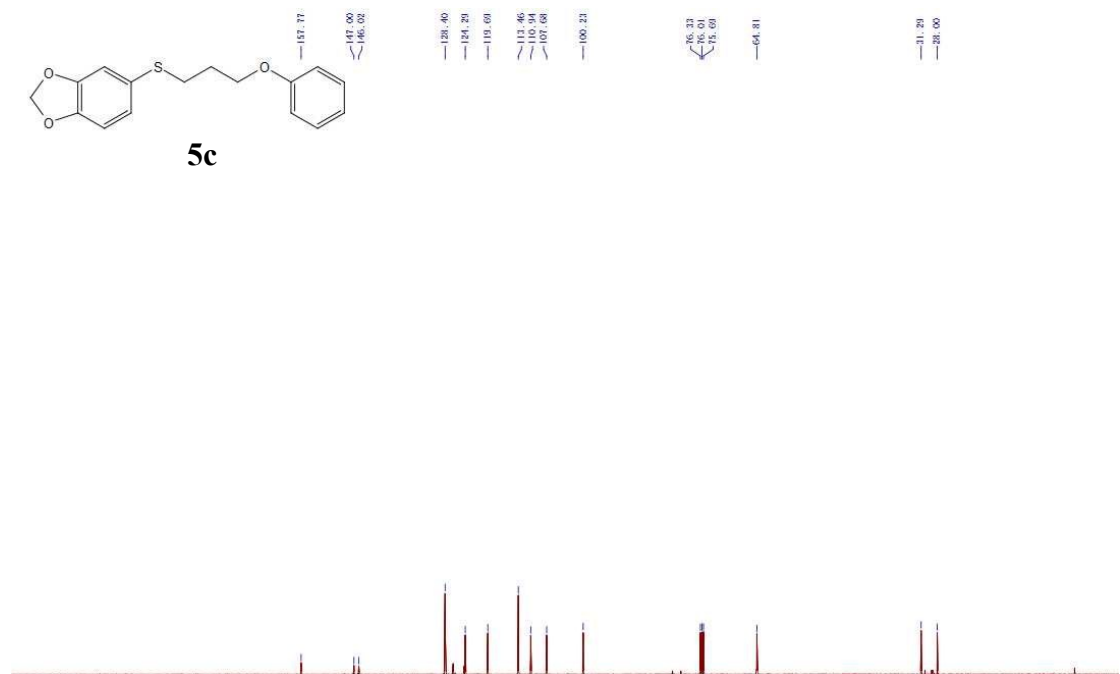
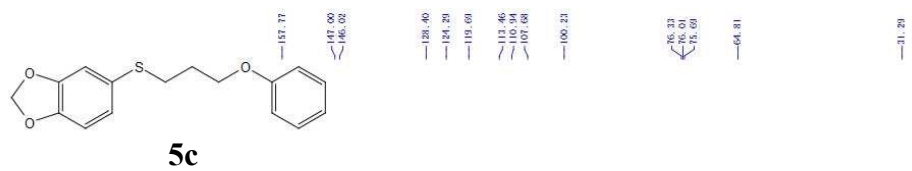
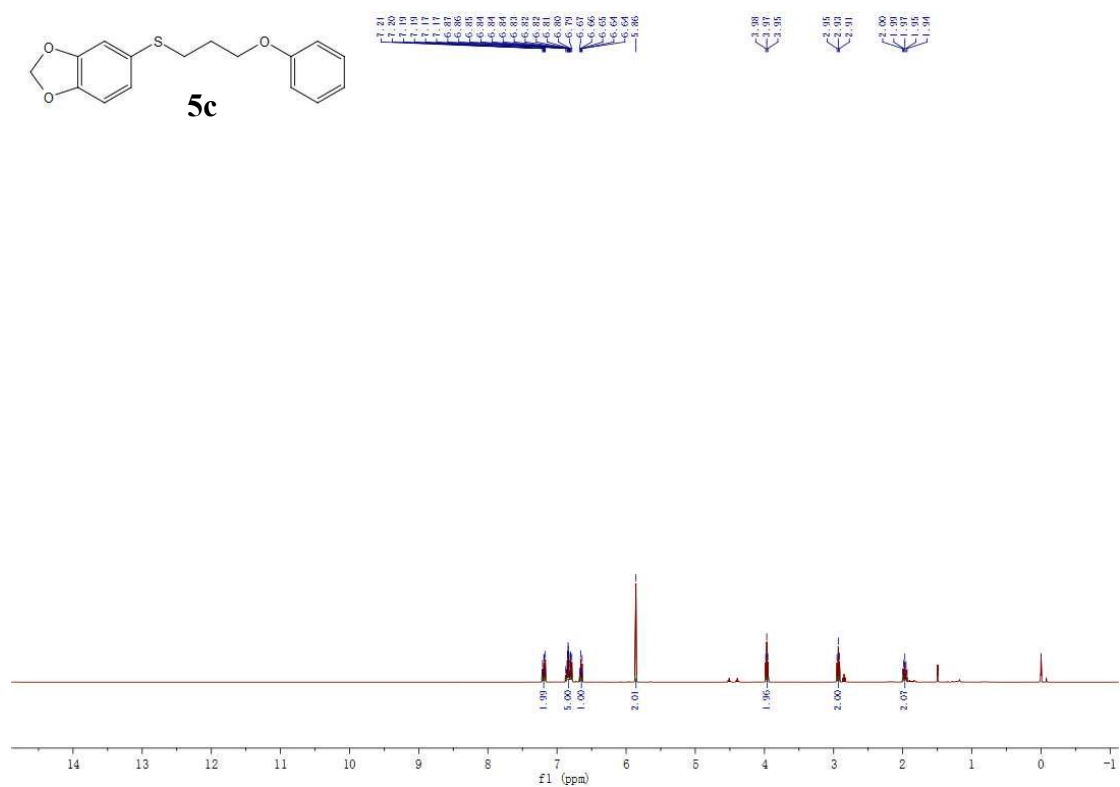
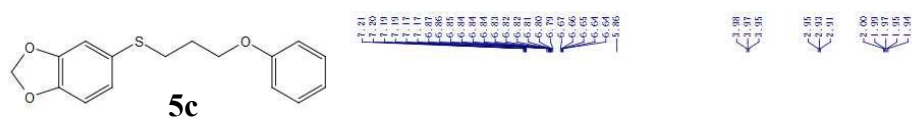


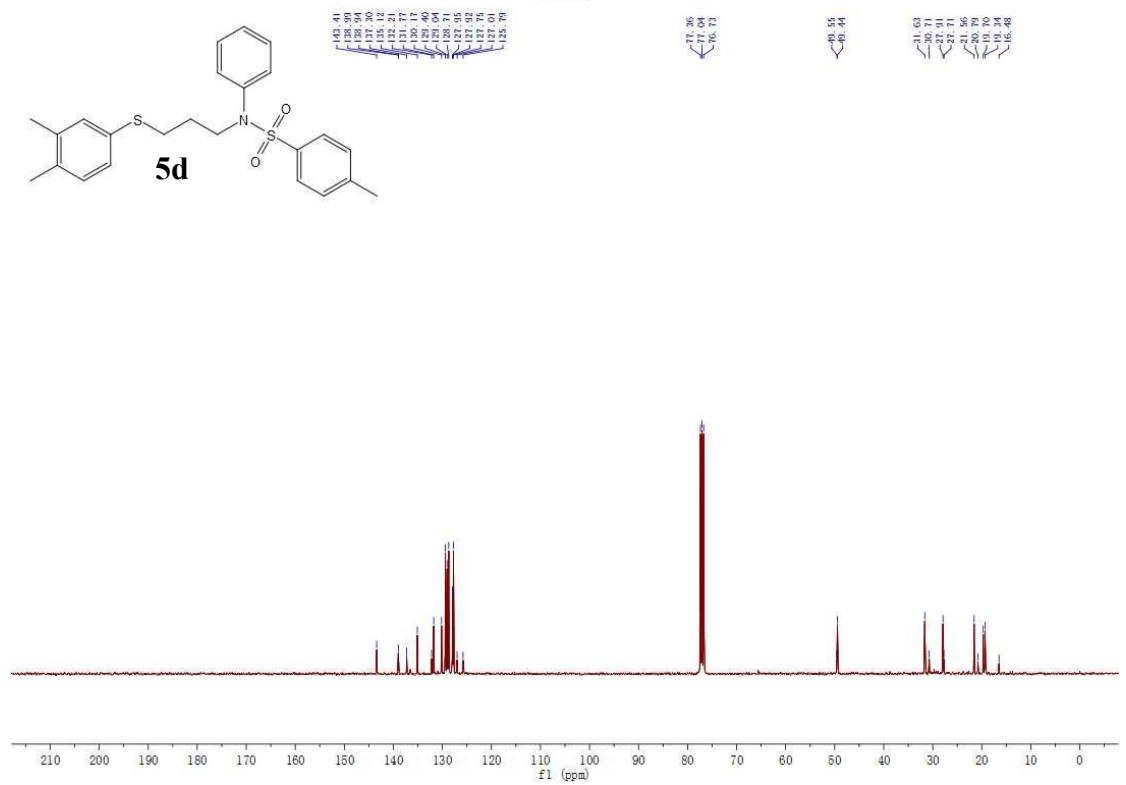
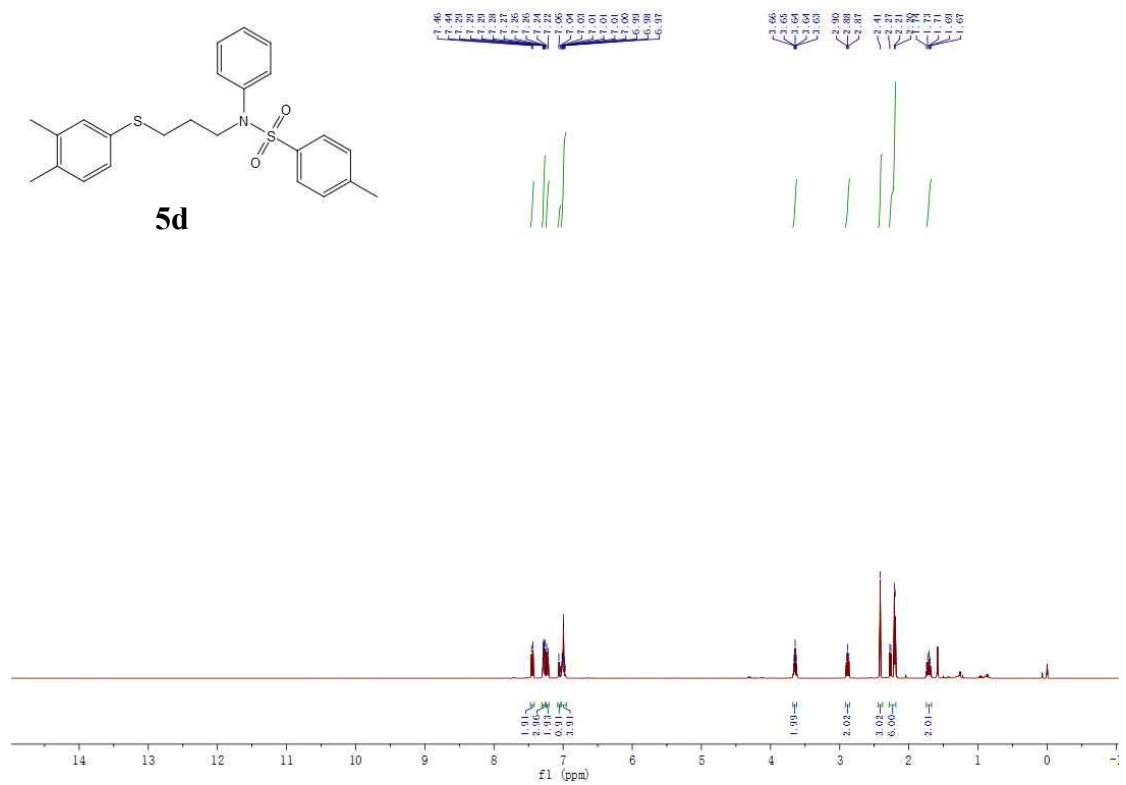
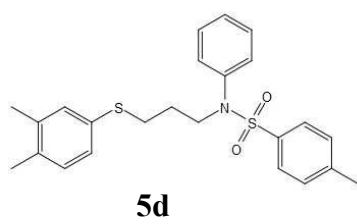
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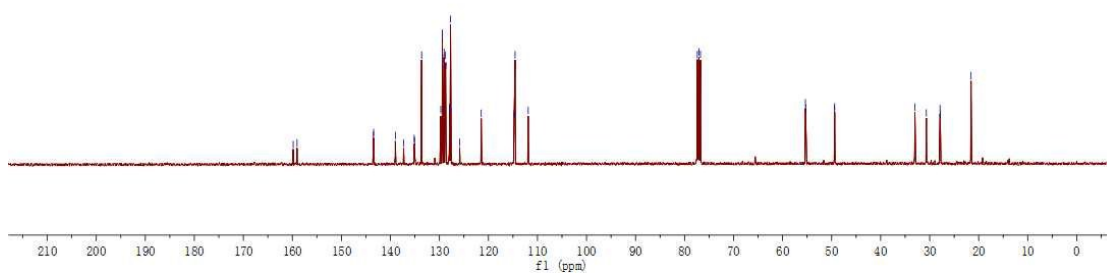
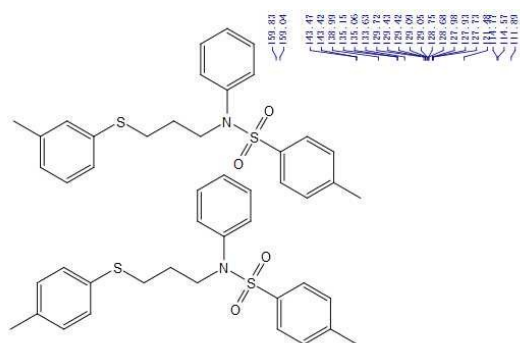
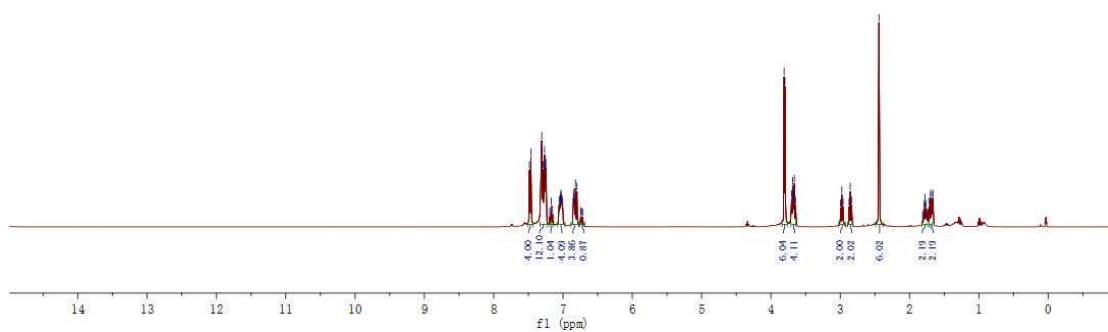
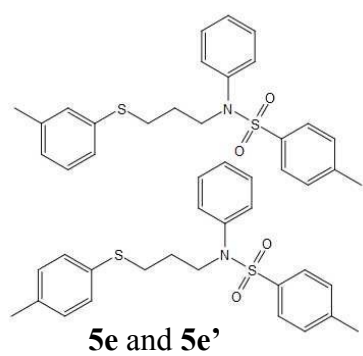


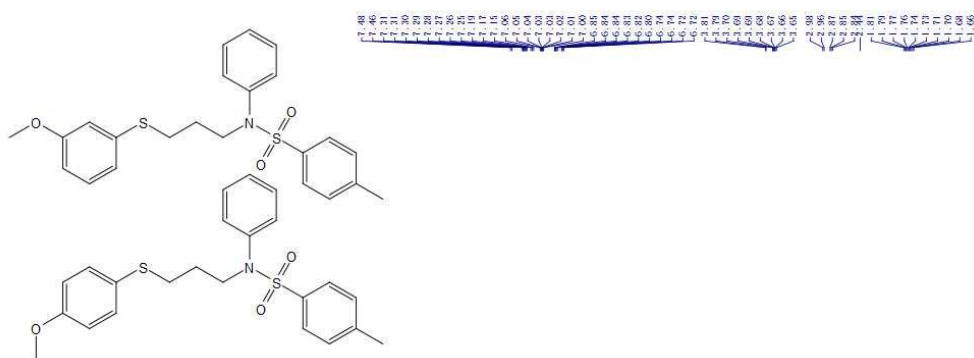




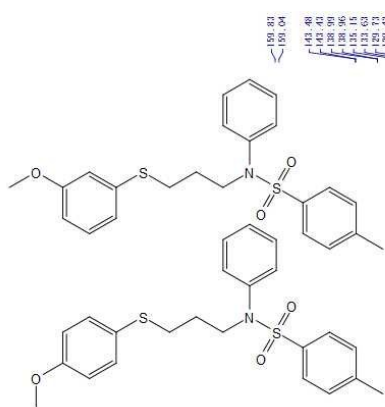
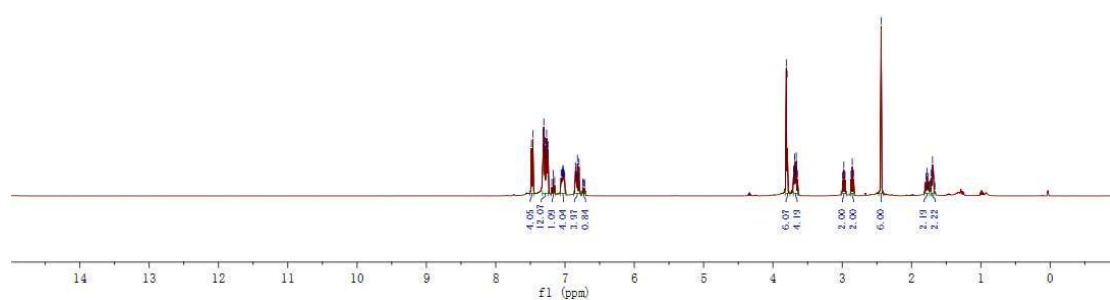




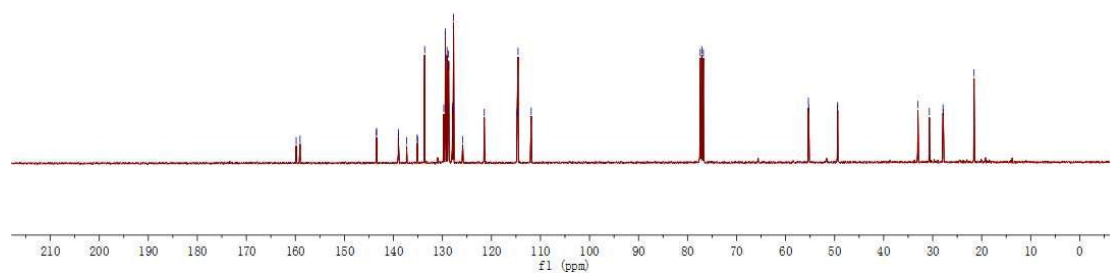


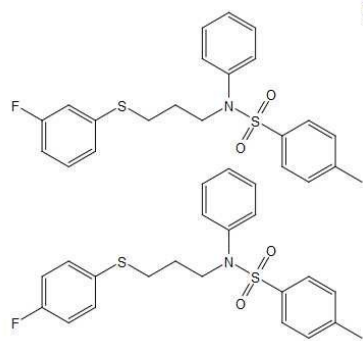


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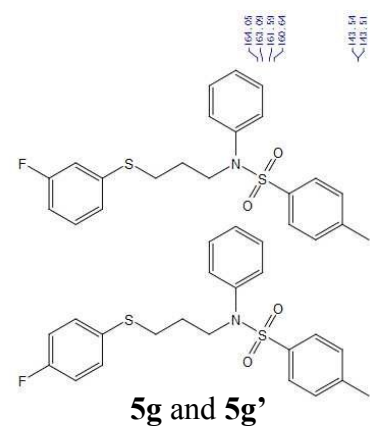
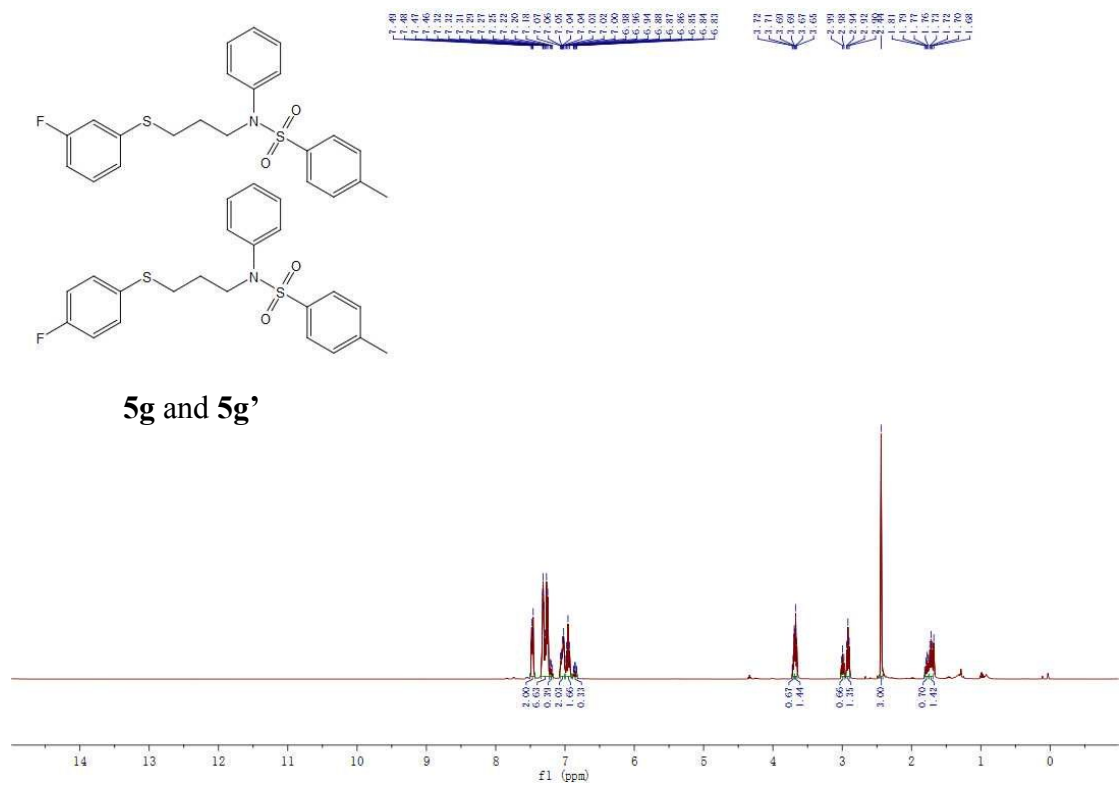


5f and 5f'

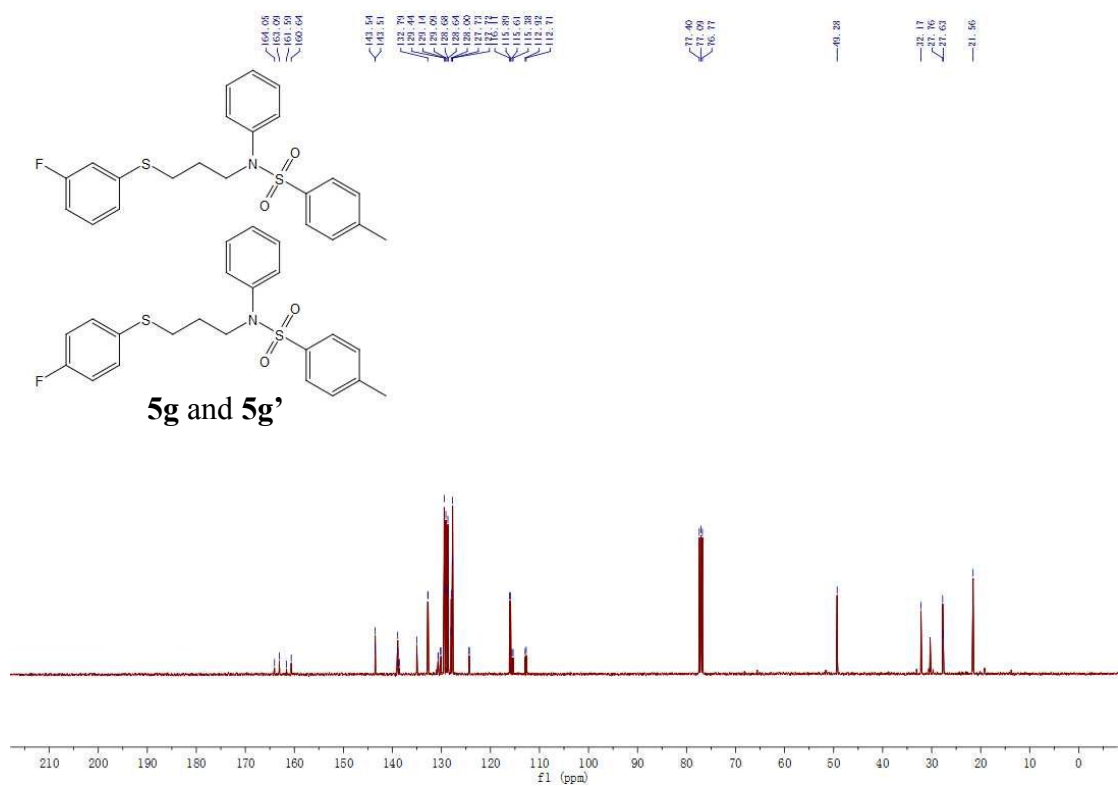


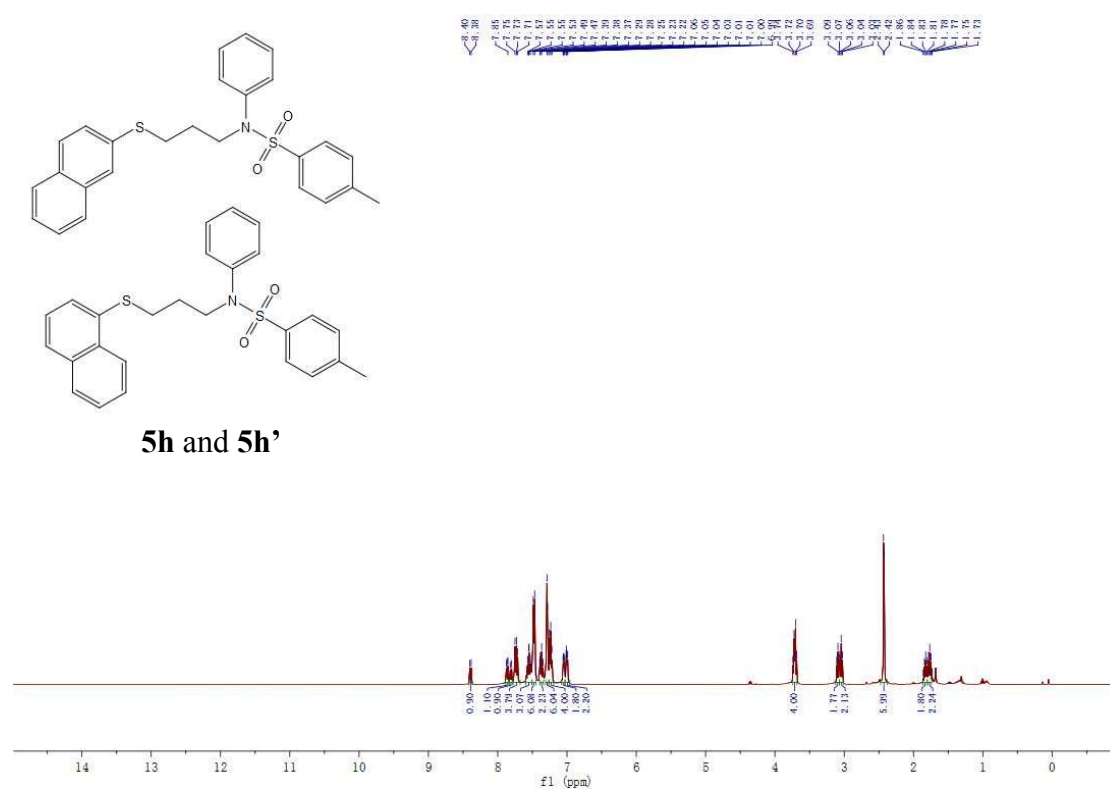
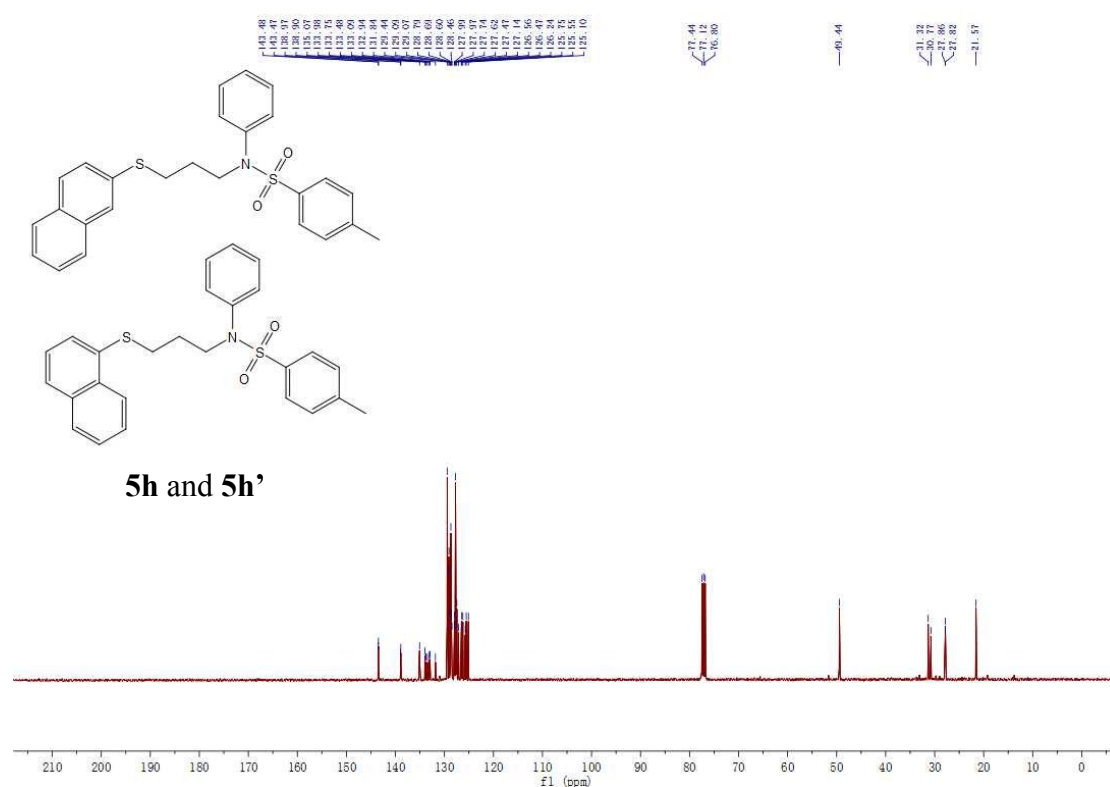


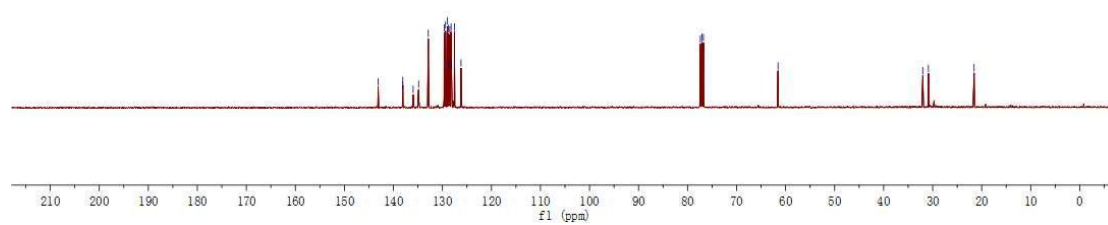
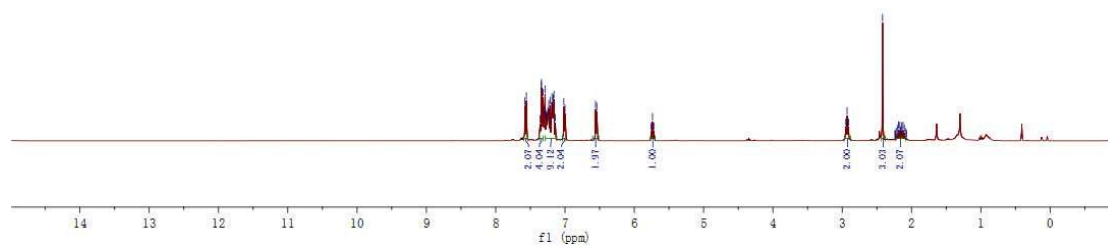
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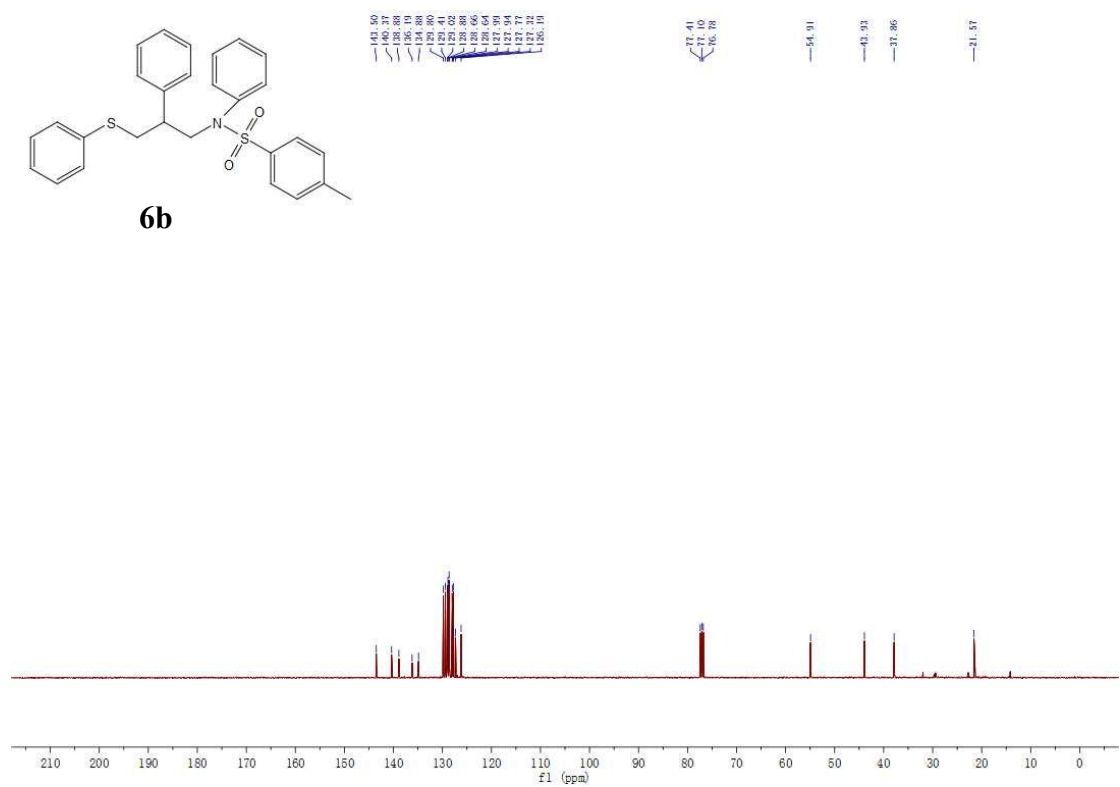
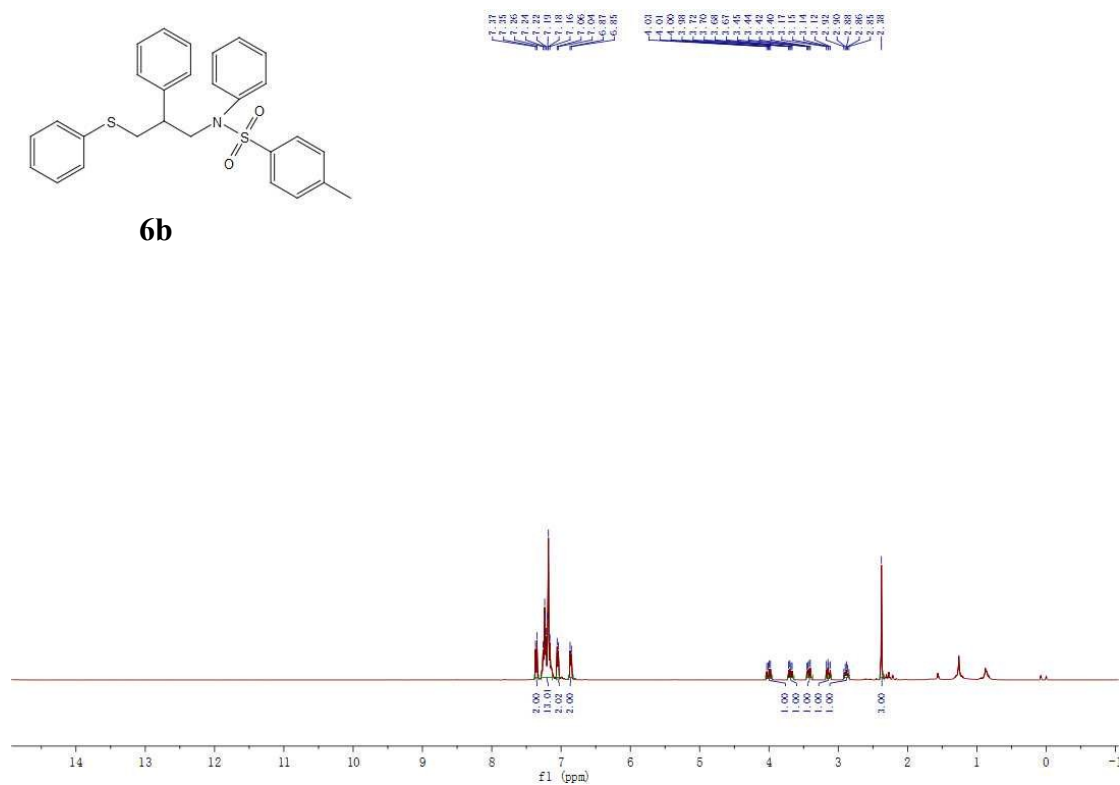
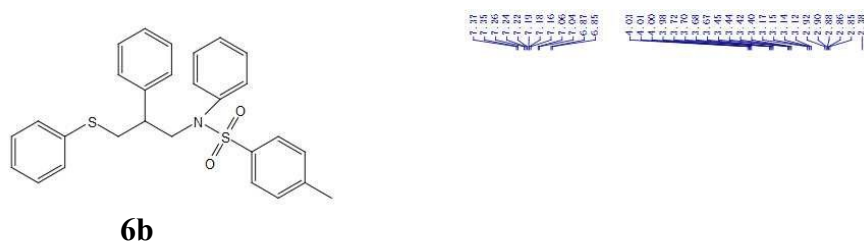


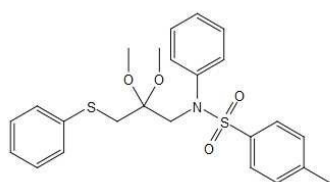
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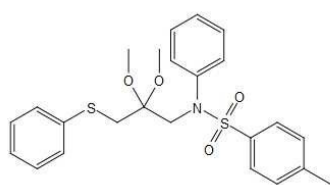
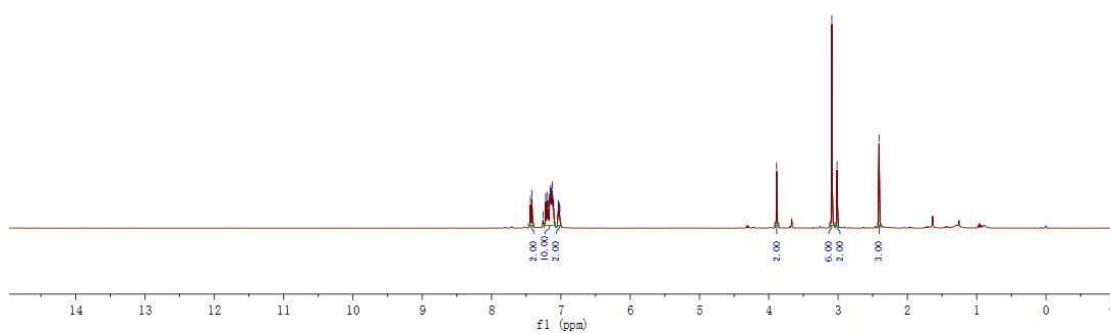




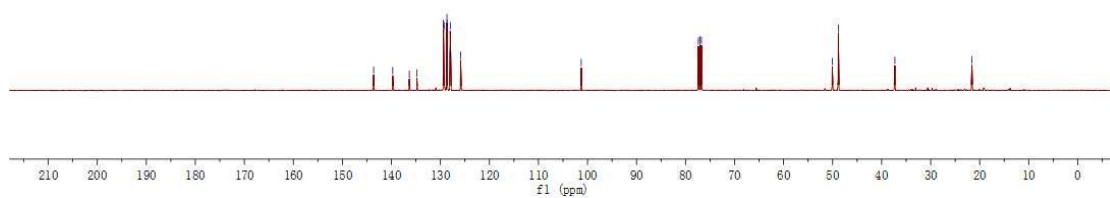




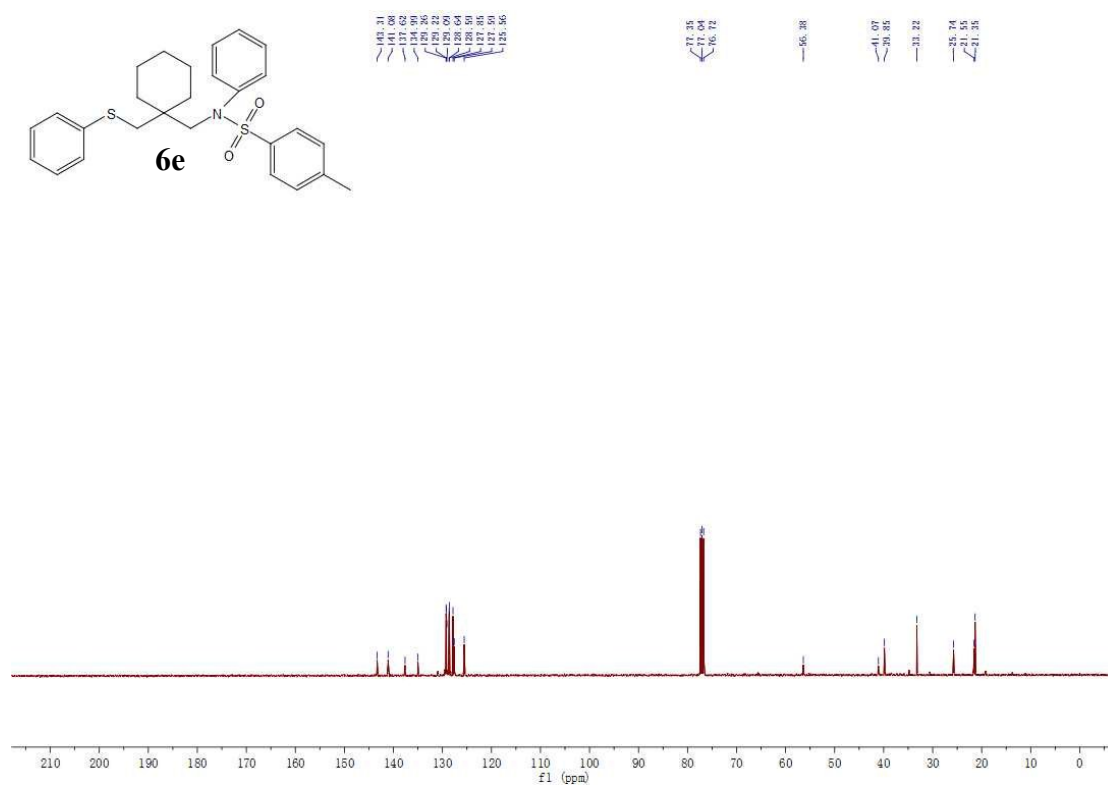
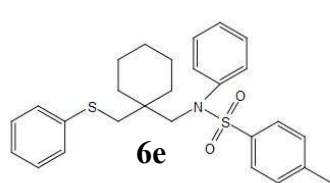
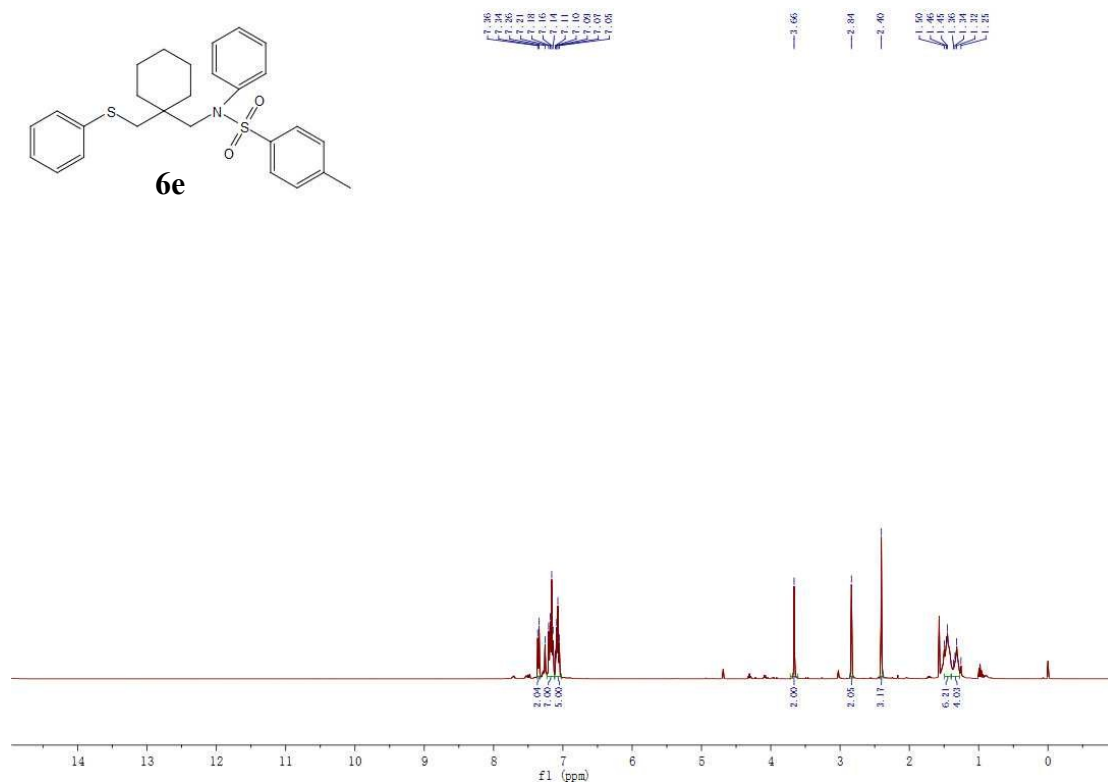
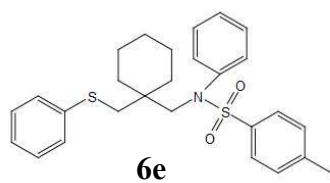
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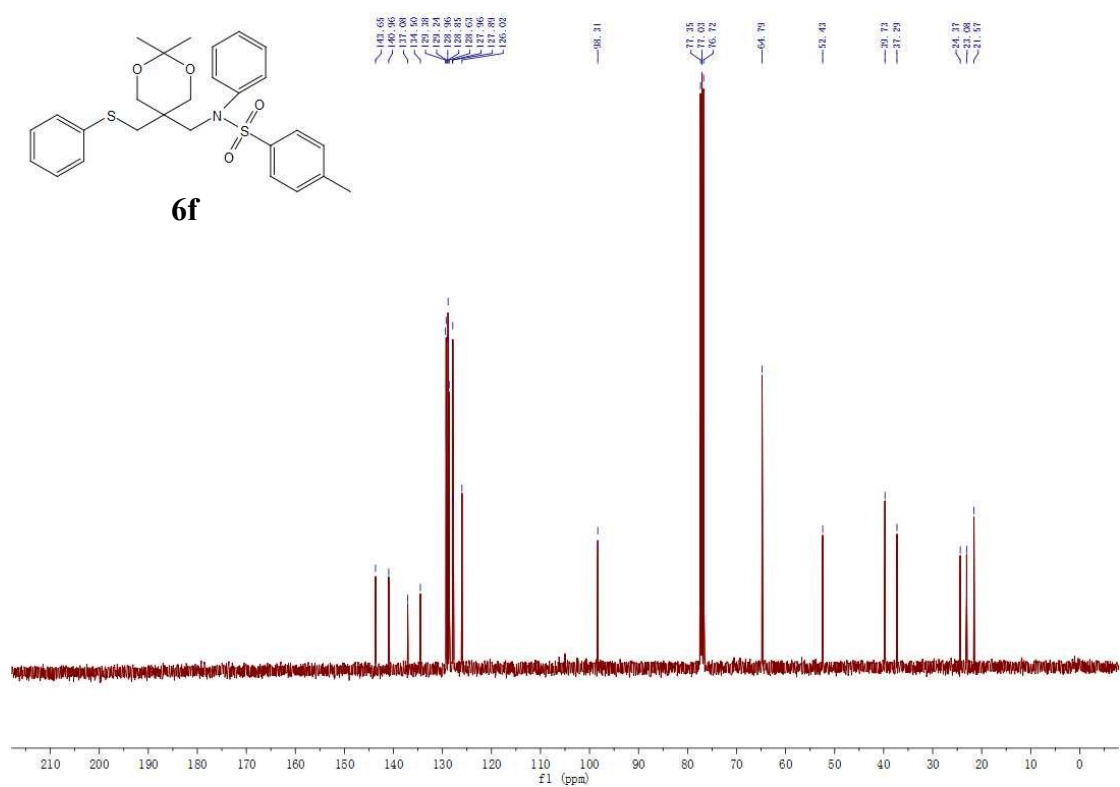


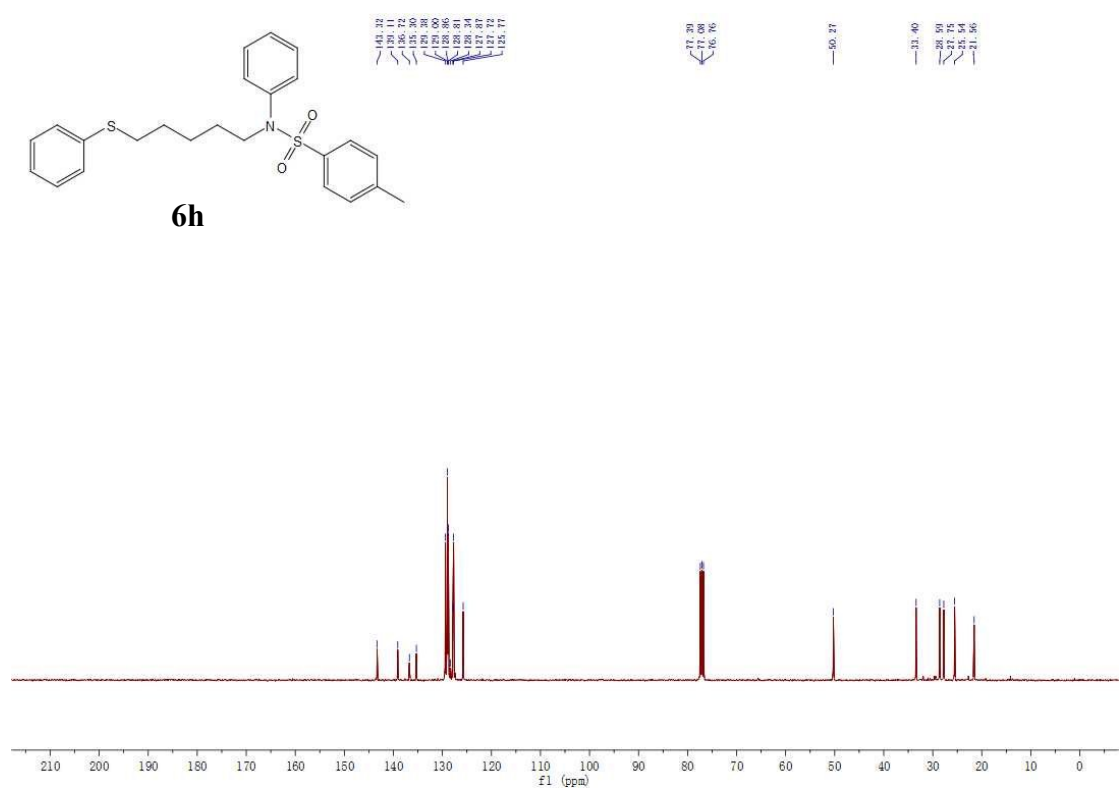
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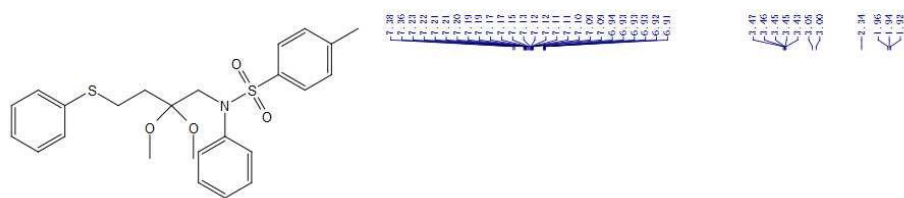




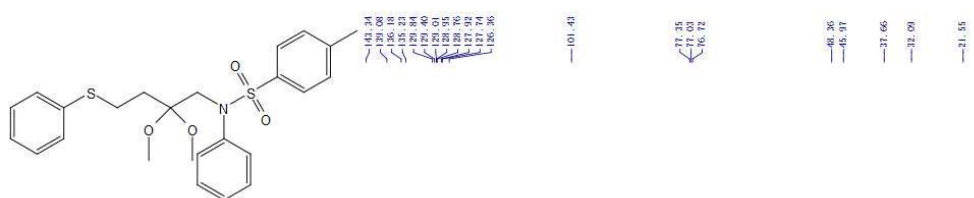
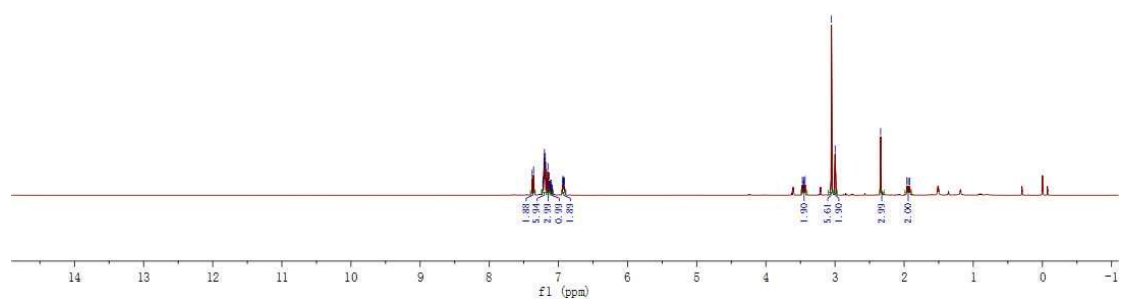




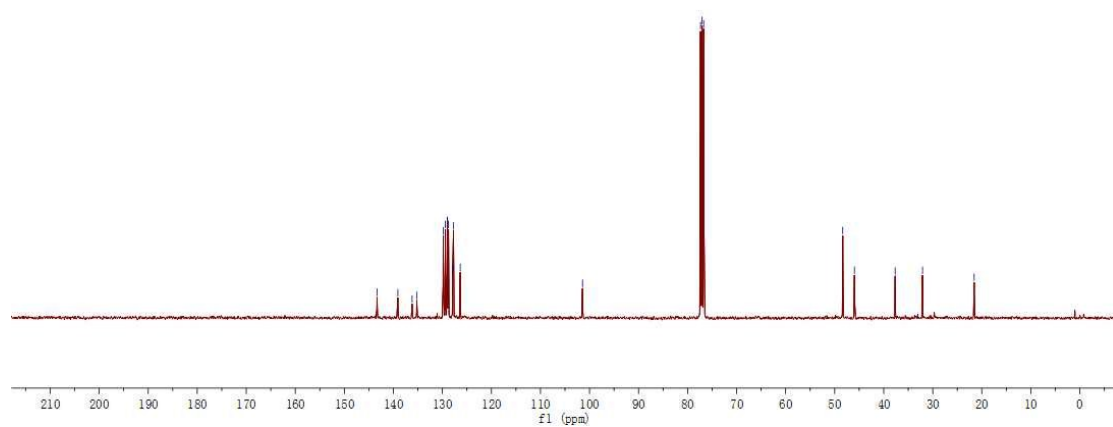


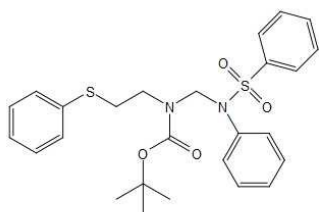


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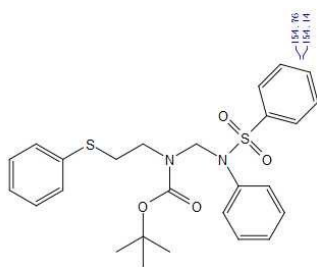
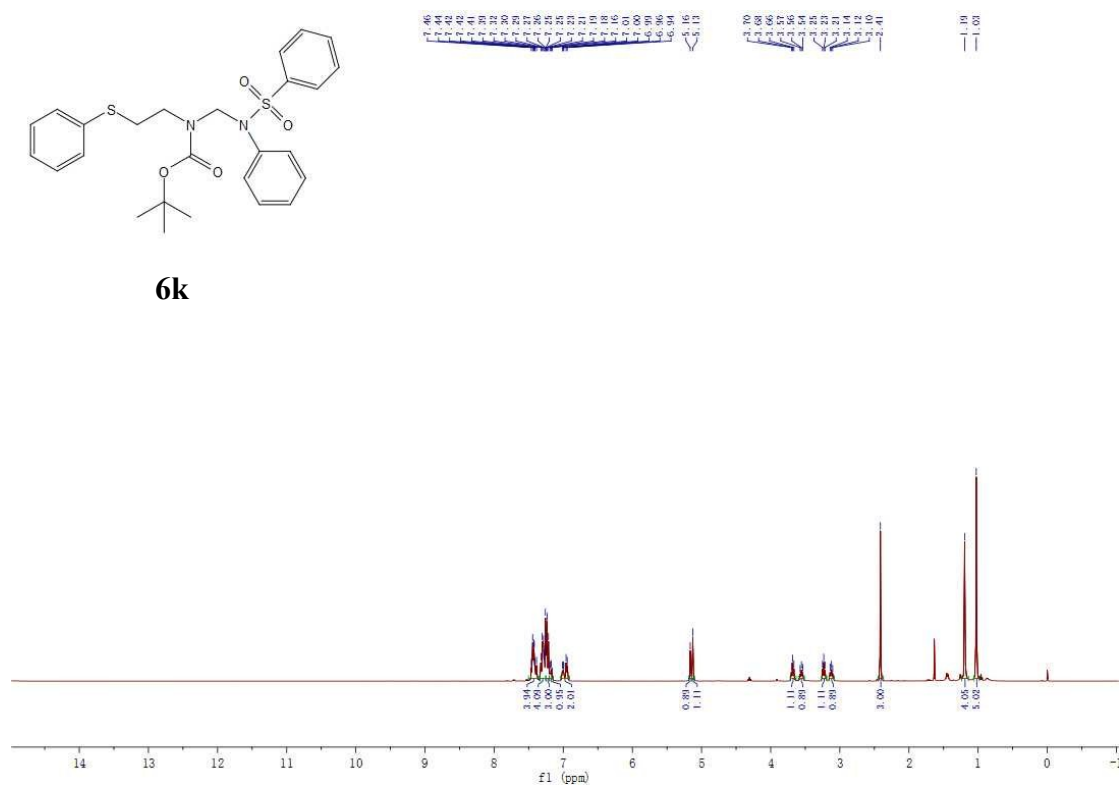


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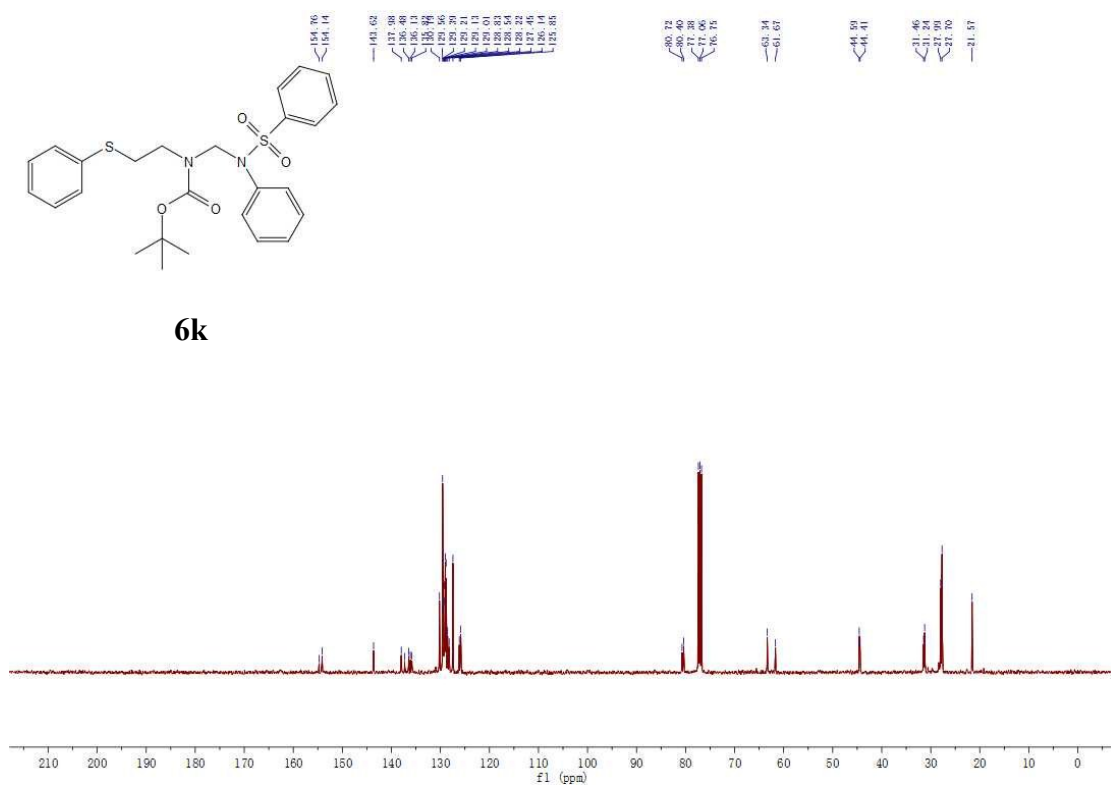


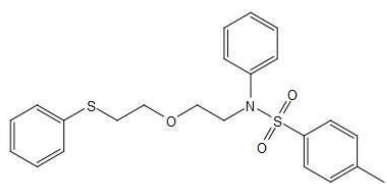


6k



6k

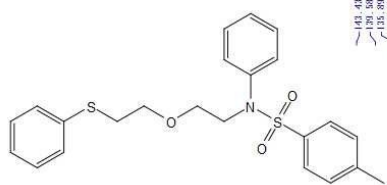
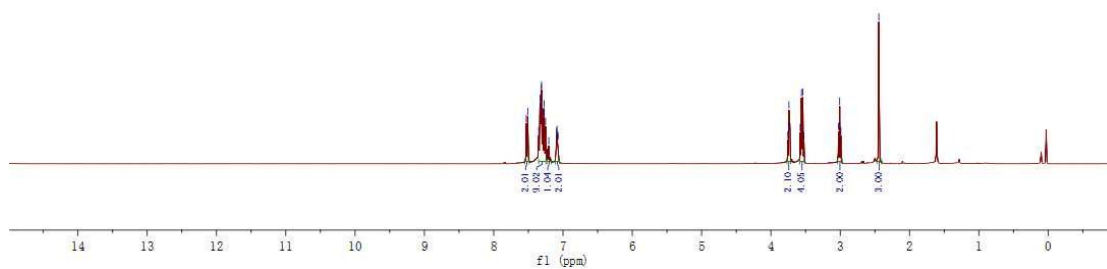




6l

7.53
7.51
7.35
7.33
7.31
7.29
7.27
7.25
7.23
7.10
7.09
7.08
7.07

3.76
3.74
3.53
3.52
3.54
3.51
3.02
3.01
2.44



6l

142.40
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132.55
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128.96
128.01
127.76
126.13

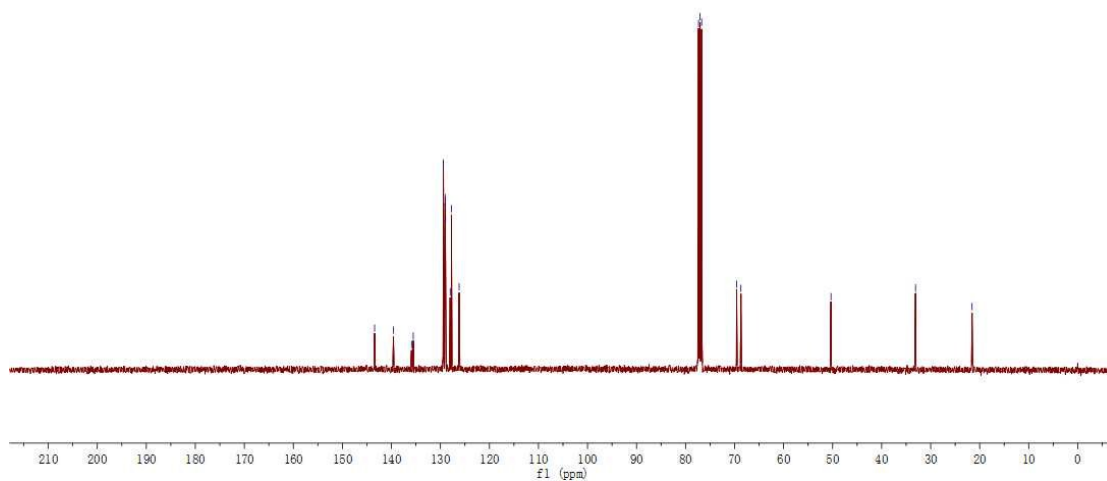
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76.71

69.58
68.70

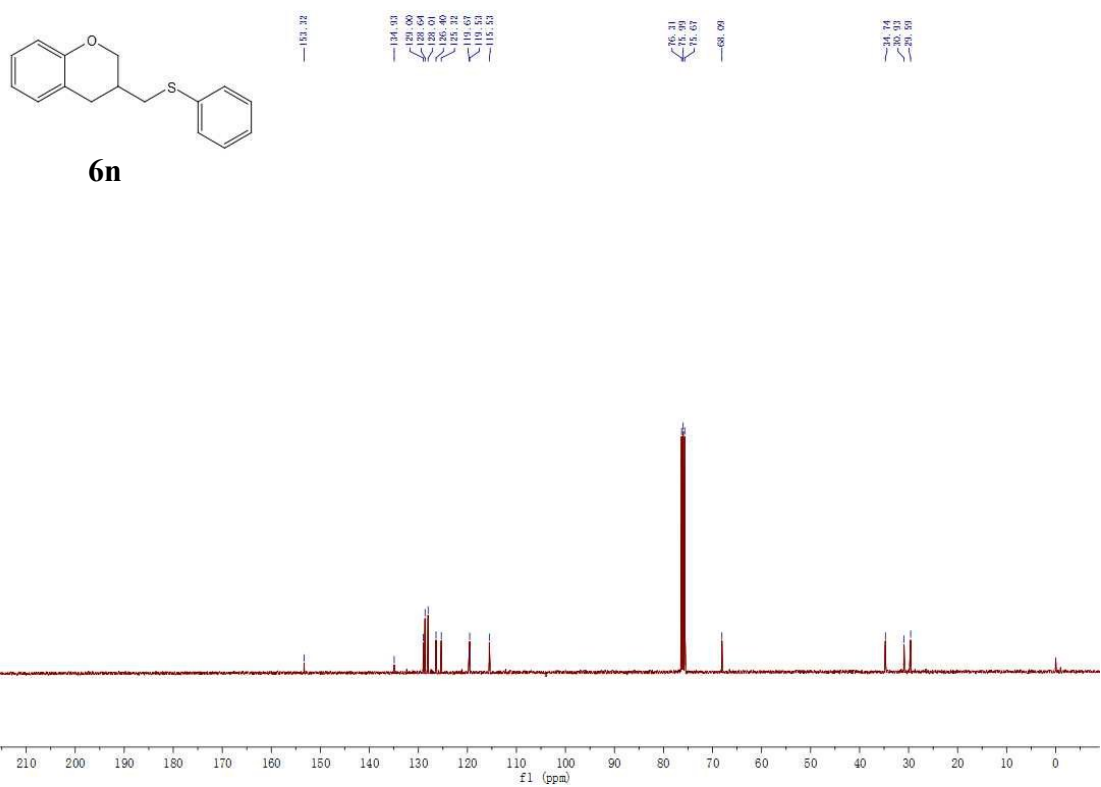
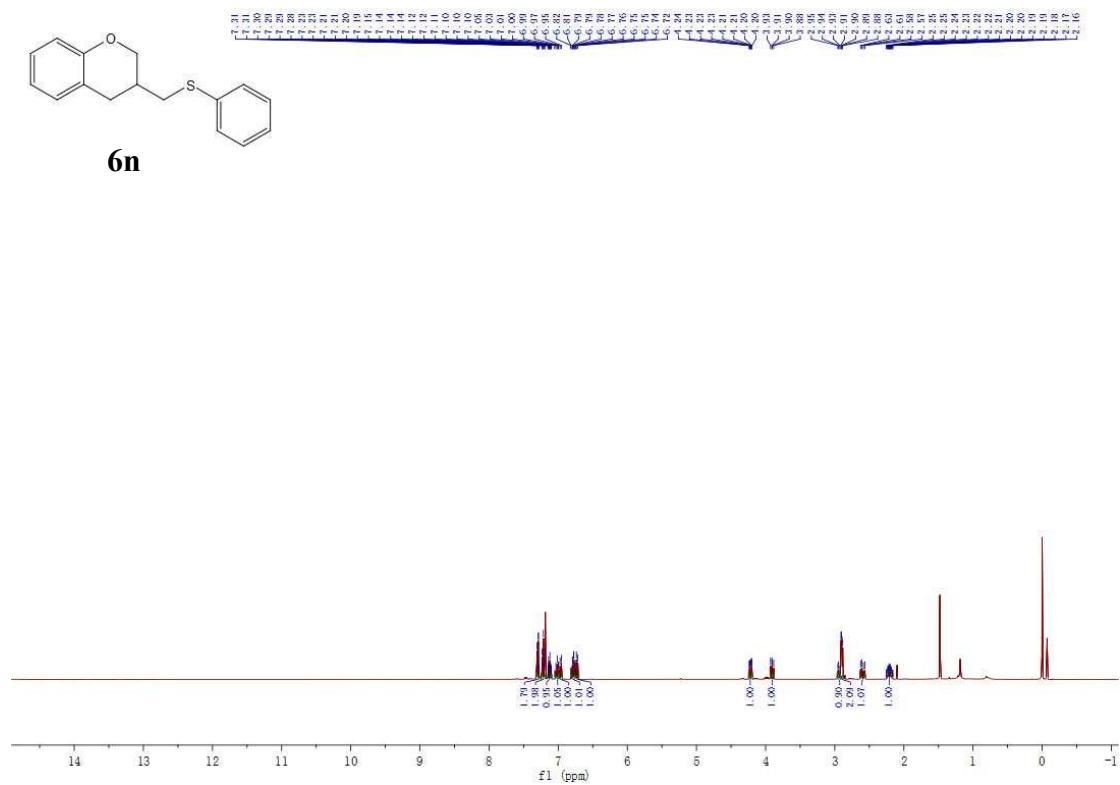
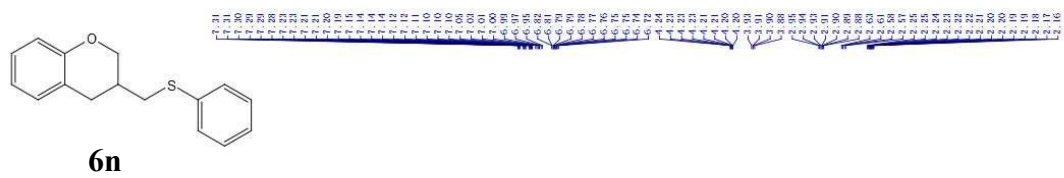
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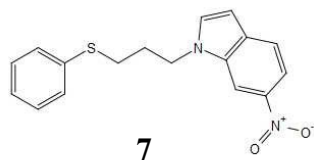
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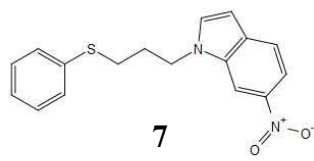
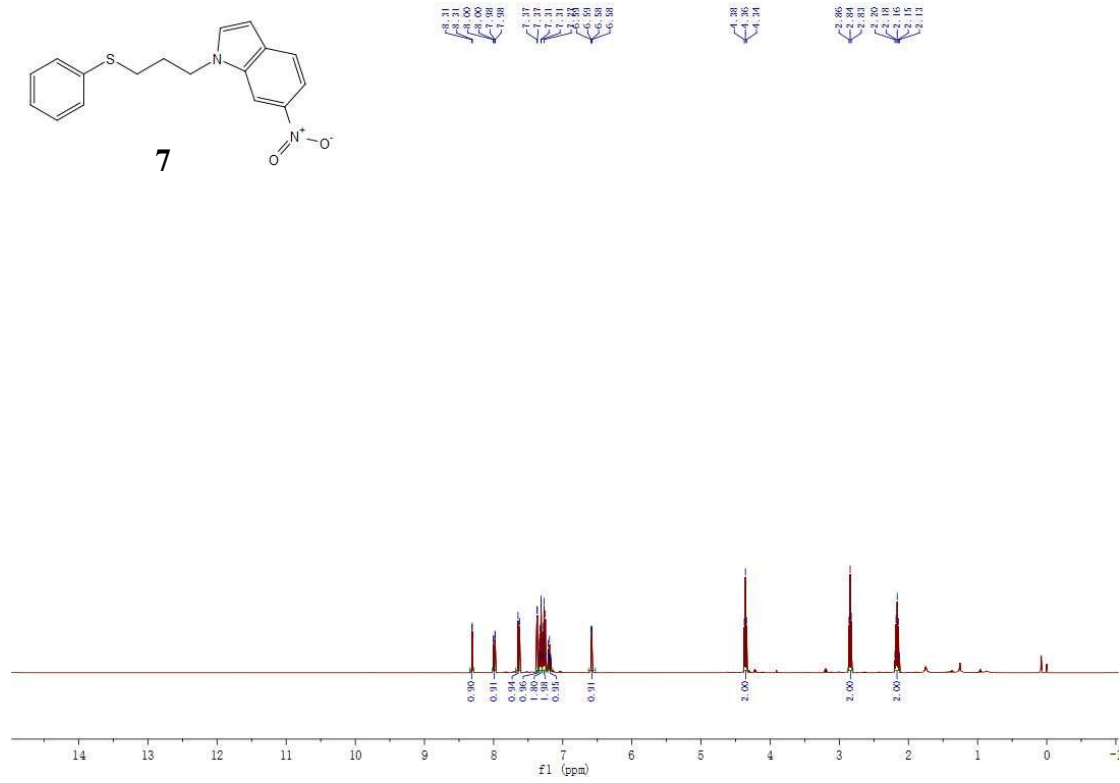




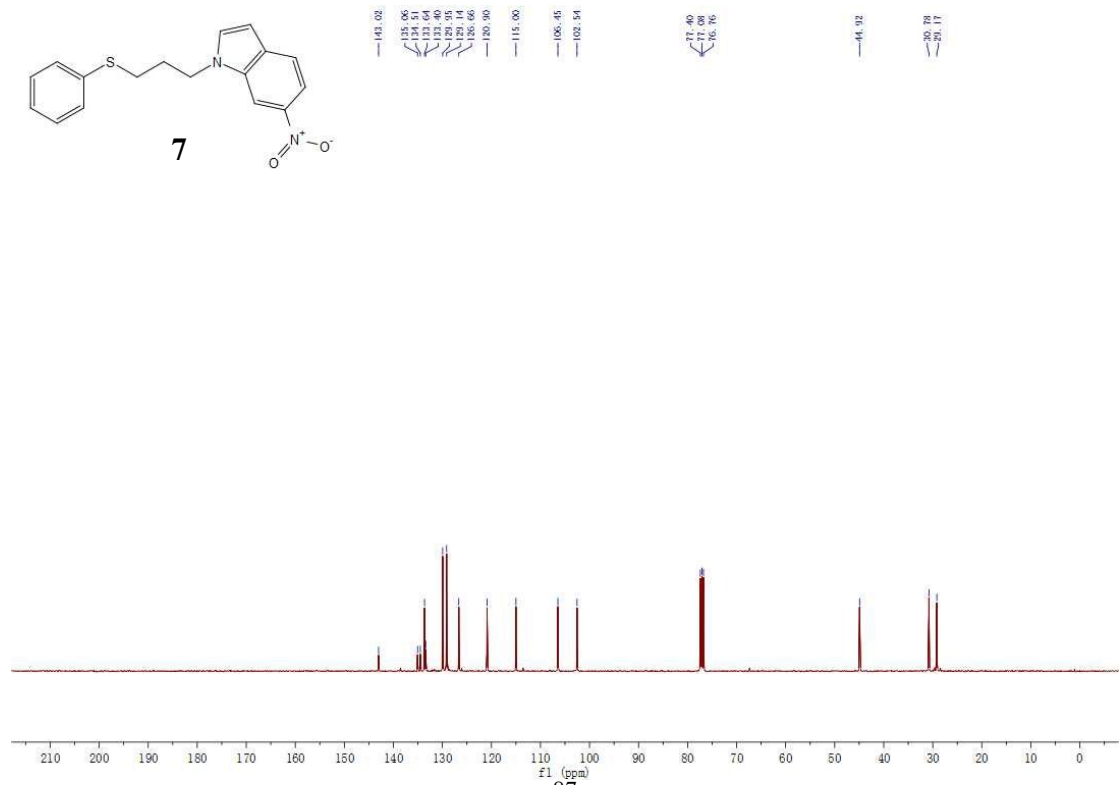


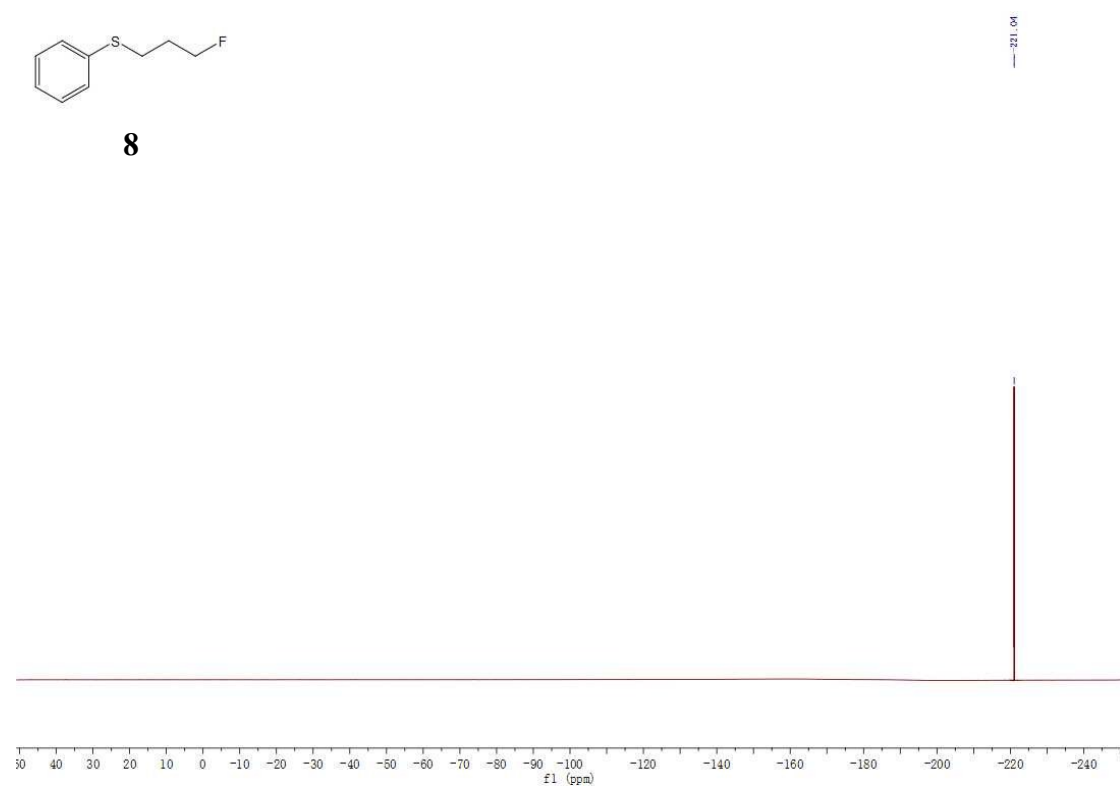
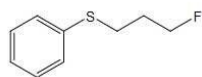
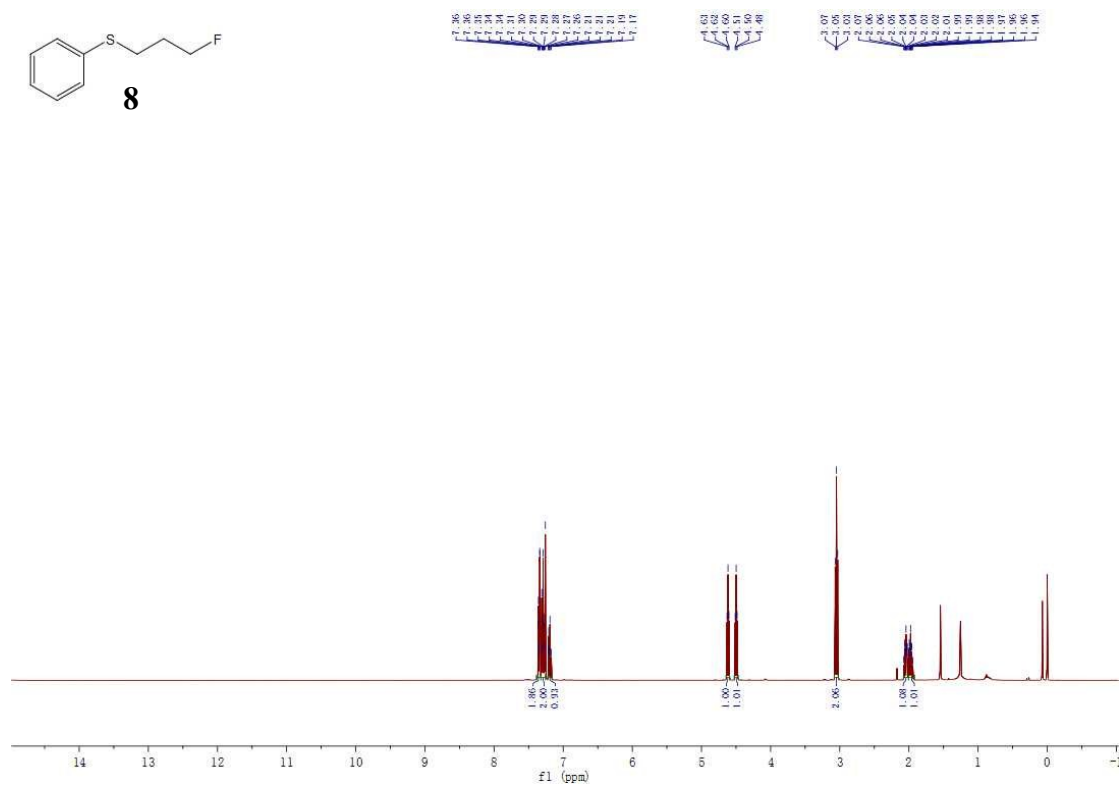
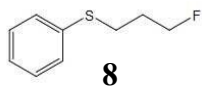


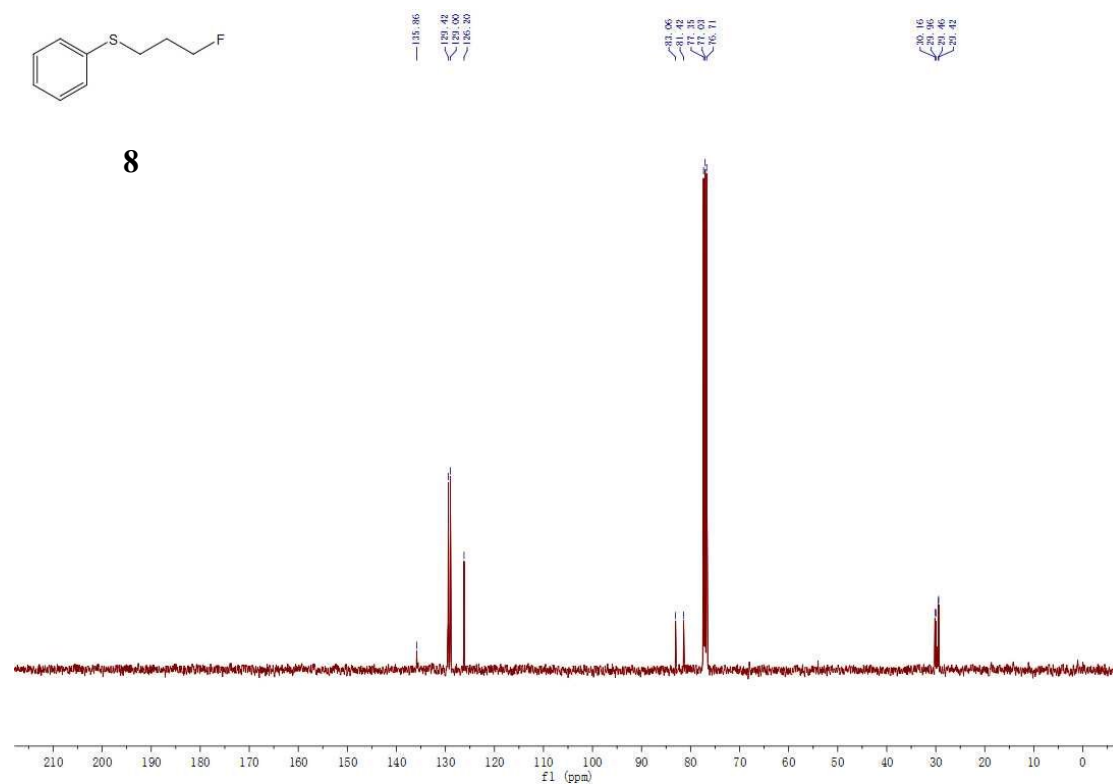
7



7







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