Supporting Information for

A Bioinspired C–O/C–X σ-Bond Metathesis

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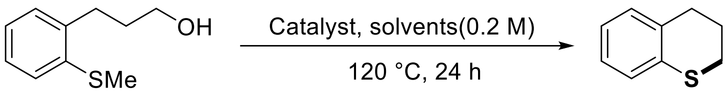
1 General information

All chemicals used in this manuscript were purchased from Energy chemical company, Bide Pharmatech Ltd, Inno-Chem Ltd, Adamas Company, Alfa Aesar Company and Cambridge Isotope Laboratories, Inc. Other commercially available compounds were used as provided without further purification. Unless otherwise noted, all reactions were performed under air. Reactions were monitored by thin layer chromatography (TLC) on silica gel pre-coated plastic sheets (0.2 mm). Visualization was accomplished by irradiation with UV light at 254 nm and $KMnO_4$. Flash column chromatography was performed over silica gel (200-300 mesh). ^{1}H-, ^{13}C- and ^{19}F-NMR spectra were recorded on Bruker AV400 or Bruker AscendTM 600MHz at room temperature. Chemical shifts were reported in ppm on the scale relative to $CDCl_3$ (δ = 7.26 for ^{1}H-NMR, δ = 77.00 for ^{13}C-NMR). Proton spectrum description analysis is as follows: chemical shift (ppm), multiplet analysis (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), unidentified coupling the methods are all analyzed by multiple peak processing, and the carbon spectrum is described in ppm. Coupling constants (*J*) were reported in Hertz (Hz). High resolution mass spectra (HR-MS) were determined on Bruker SolariX 7.0T FT-MS (ESI source). Mass spectra (GC-MS) were determined on Agilent 7890A/5975C (EI source).

2 Optimization of reaction conditions

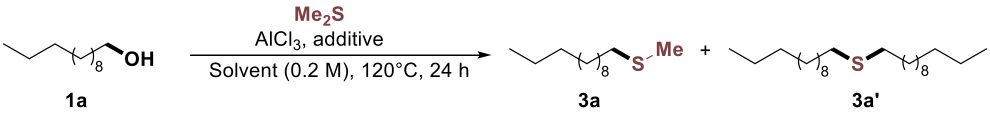
Table S1 Optimization conditions of substrate **5a**[a]



Entry	catalyst	loading	solvent	yield (%) [b]
1	Re_2O_7	2%	HFIP	7
2	$Fe(OTf)_3$	10%	HFIP	7
3	$Bi(OTf)_3$	10%	HFIP	7
4	**$Al(OTf)_3$**	**10%**	**THF**	**27**
5	$Al(OTf)_3$	30%	THF	48
6	**$Al(OTf)_3$**	**50%**	**THF**	**56**
7	$Al(OTf)_3$	70%	THF	50
8	$Al(OTf)_3$	100%	THF	38
9	$Al(OTf)_3$	50%	HFIP	29
10	**$Al(OTf)_3$**	**50%**	**toluene**	**74**
11	$Ga(OTf)_3$	50%	toluene	43
12	$GaCl_3$	50%	toluene	32
13	AlF_3	50%	toluene	NR
14	**$AlCl_3$**	**50%**	**toluene**	**92**
15	**$AlCl_3$**	**50%**	**cyclohexane**	**95**
16	$AlCl_3$	50%	DMSO	10
17	$AlCl_3$	50%	HFIP	67
18	TfOH	50%	cyclohexane	62

[a]**5a** (0.1 mmol, 18.23 mg), $AlCl_3$ (50 mol%, 6.67 mg), cyclohexane (0.2 M, 0.5mL), 120 ℃, 24 hours
[b]1,3,5-Trimethoxybenzene as the internal standard, measured by NMR

Table S2 Optimization conditions of substrate 1a[a]



Entry	Catalyst	Loading	Me_2S (equiv.)	additive	Solvent	yield[b]	ratio (A/B)[c]
1	$AlCl_3$	50%	2.0	none	Tol.	29%	
2	$AlCl_3$	50%	5.0	none	Tol.	41%	
3	$AlCl_3$	50%	10.0	none	Tol.	38%	
4	$AlCl_3$	50%	as solvent	none	Me_2S	18%	
5	$AlCl_3$	50%	5.0	NaCl 50%	Tol.	24%	
6	$AlCl_3$	50%	5.0	MgCl 50%	Tol.	33%	
7	$AlCl_3$	50%	5.0	$ZnCl_2$ 50%	Tol.	52%	
8	$AlCl_3$	50%	5.0	$ZnBr_2$ 50%	Tol.	56%	
9	$AlCl_3$	50%	5.0	ZnI_2 50%	Tol.	60%	
10	$AlCl_3$	50%	5.0	ZnI_2 100%	Tol.	82%	10/1
11	**$AlCl_3$**	**50%**	**5.0**	**$ZnI_2$100%**	**cyclohexane**	**77%**	**25/1**
12	$AlCl_3$	50%	5.0	$CoI_2$100%	cyclohexane	59%	
13	$AlCl_3$	50%	5.0	$BiI_2$100%	cyclohexane	23%	
14	$AlCl_3$	50%	5.0	AgI100%	cyclohexane	15%	
15	$AlCl_3$	50%	5.0	$InI_3$100%	cyclohexane	63%	
16	$AlCl_3$	50%	5.0	NH_4I100%	cyclohexane	10%	
17	$AlCl_3$	50%	5.0	TfOH 50%	cyclohexane	37%	
18	$AlCl_3$	50%	5.0	$ZnI_2$100%	DCE	26%	
19	$AlCl_3$	50%	5.0	$ZnI_2$100%	THF	NP	
20	$AlCl_3$	50%	5.0	$ZnI_2$100%	DMSO	NP	
21	$AlCl_3$	50%	5.0	$ZnI_2$100%	HFIP	44	
22	HCl	50%	5.0	none	cyclohexane	NP	
23	TfOH	50%	5.0	none	cyclohexane	59%	

[a]**1a** (0.2 mmol, 45 uL), Me_2S (1.0 mmol, 73 uL), $AlCl_3$ (50 mol%, 13.34 mg), ZnI_2 (100 mol%), cyclohexane (0.2 M, 1mL), 120 °C, 24 hours. [b]dodecane as the internal standard, measured by GC. [c]the ratio measured by NMR

3 Syntheses of starting materials and spectroscopic data

Method A

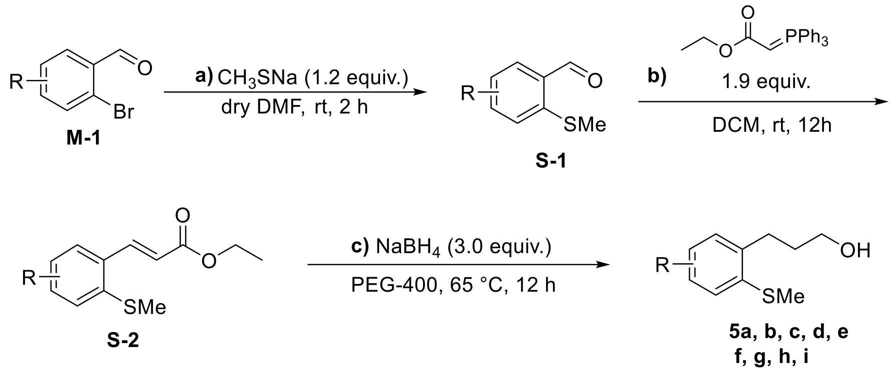


Figure S1. General synthetic method A

a) Following a reported procedure [1], a solution of **M-1** (10 mmol) in anhydrous DMF (17 mL) was treated with NaSMe (12 mmol, 1.2 equiv.), After the solution was stirred for 1 h. The organic phase was separated and the aqueous phase was extracted with ethyl acetate (3×10 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product **S-1** was used in the following step without further purification.

b) (Carbethoxmethylene)triphenylphosphorane (10 mmol, 1.9 equiv.) was added to a solution of aldehyde (**S-1**) in anhydrous DCM (10 mL) and the reaction mixture stirred at room temperature until TLC showed complete conversion of aldehyde. The reaction mixture was concentrated under reduced pressure and purified by column chromatography on silica gel (SiO_2, PE/EA = 50/1) to afford α, β-unsaturated ester **S-2** in 98% yield.

c) Following a reported procedure[2]: to the ester **S-2** (5 mmol) in PEG 400 (30 mL) was added sodium borohydride (0.6 g, 15 mmol) portion wise. Under stirring, the solution was slowly brought to 65 °C (evolution of hydrogen) and kept at this temperature for 10 hours. During this time the reaction was generally complete. Diluted HC1 (10%) was added to the reaction mixture dropwise, and the products were extracted (3 × 30 mL) with diethyl ether. Drying of the extracts with sodium sulfate and concentrated under reduced pressure, purified by column chromatography on silica gel (SiO_2, PE/EA = 3/1) to afford the product in 84% yield.

Method B

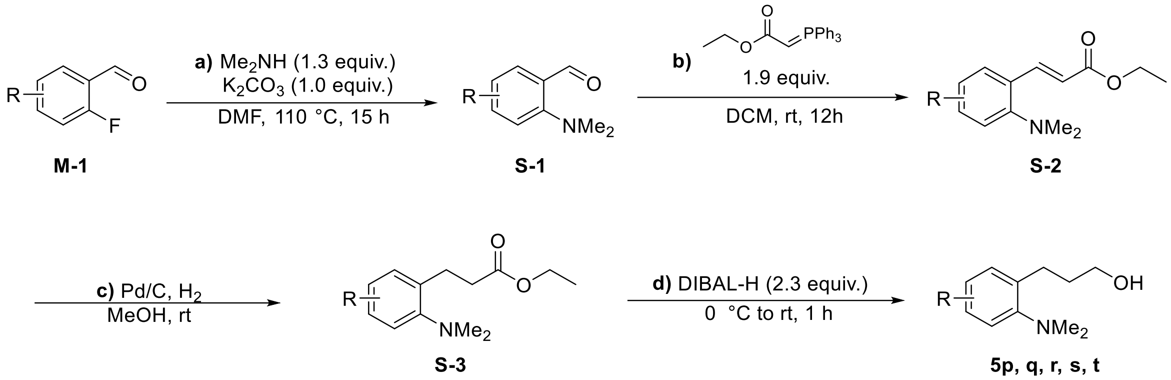


Figure S2. General synthetic method B

a) A solution of **M-1** (9 mmol) in anhydrous DMF (25 mL) was treated with K_2CO_3 (9 mmol, 1.0 equiv.) and Me_2NH (12 mmol, 1.3 equiv.). After the solution was stirred at 110 °C for 24 hours. The organic phase was separated and the aqueous phase was extracted with ethyl acetate (3×10 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product **S-1** was used in the following step without further purification.

c) Pd/C (10% on carbon, wetted with ca. 55% water) was added into the reaction flask, filled with nitrogen and purged with hydrogen three times. Methanol and **S-2** were added to the reaction flask. The mixture was stirred at 45 °C for 24 hours and filtered through a pad of silica gel. The filtrate was concentrated to give a crude product **S-3**, which was used in the following step without further purification.

d) To an ice cooled solution of **S-3** (5.0 mmol, 1.0 equiv.) in dichloromethane (10 mL) a solution of DIBAL-H (1.5 M in dichloromethane, 2.3 equiv.) was added slowly over 15 min. The reaction mixture was stirred at 0 °C for 30 min, and then at room temperature for 2 hours. After that, the reaction mixture was cooled to 0 °C (ice bath) again and the excess DBAL-H was quenched by sequential addition of water (2.0 mL), NaOH solution (1.5 mL, 10% aqueous) and water (2.0 mL). The ice bath was removed and the suspension was stirred for at room temperature for 1 hour. Afterwards, the suspension was filtered, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to give an oil. Purification by column chromatography on silica gel (SiO_2, PE/EA = 5/1) to give the product **5p**.

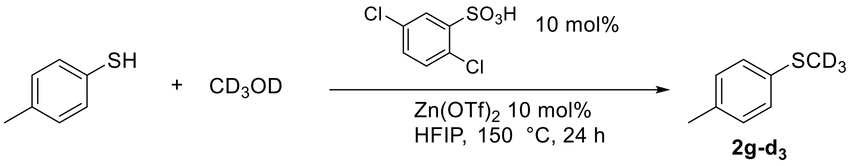
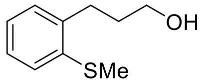


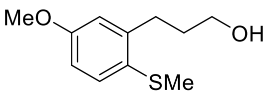
Figure S3. Synthesis of **2g-d3**

2,5-dichlorobenzenesulfonic acid (1mmol, 10 mol%), $Zn(OTf)_2$ (1mmol, 10 mol%) and HFIP (10 mL) were added into the reaction flask, to the solution 4-methylbenzenethiol (10 mmol, 1.0 equiv.) and CD_3OD were added (30 mmol, 3.0 equiv.). The mixture was stirred at 120 °C for 24 hours and then cooled to room temperature. The organic phase was separated and the aqueous phase was extracted with ethyl acetate (3×10 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by column chromatography on silica gel (PE) to give the product **2g-d3**. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.19 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 7.2 Hz, 2H), 2.32 (s, 3H).



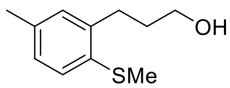
5a: 3-(2-(methylthio)phenyl)propan-1-ol. [25]

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.23 – 7.19 (m, 2H), 7.17 (d, *J* = 7.5 Hz, 1H), 7.13 – 7.08 (m, 1H), 3.67 (t, *J* = 6.2 Hz, 2H), 2.82 (dd, *J* = 8.4, 6.8 Hz, 2H), 2.47 (d, *J* = 0.8 Hz, 3H), 1.97 – 1.83 (m, 2H).



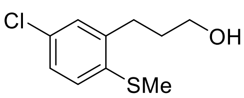
5b: 3-(5-methoxy-2-(methylthio)phenyl)propan-1-ol.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.25 (d, *J* = 8.4 Hz, 1H), 6.78 – 6.71 (m, 2H), 3.78 (s, 3H), 3.66 (t, *J* = 6.2 Hz, 2H), 2.88 – 2.78 (m, 2H), 2.40 (s, 3H), 1.91 – 1.85 (m, 2H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 158.34, 143.04, 130.53, 127.53, 115.26, 112.27, 61.88, 55.26, 33.44, 30.01, 18.07.



5c: 3-(5-methyl-2-(methylthio)phenyl)propan-1-ol.

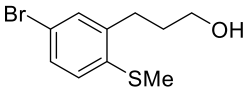
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.14 (d, *J* = 7.9 Hz, 1H), 7.01 (d, *J* = 13.2 Hz, 2H), 3.66 (t, *J* = 6.2 Hz, 2H), 2.80 (t, *J* = 7.6 Hz, 2H), 2.44 (s, 3H), 2.30 (s, 3H), 1.91 – 1.87 (m, 2H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 140.12, 135.19, 133.34, 130.10, 127.45, 126.67, 62.06, 33.23, 29.60, 20.82, 16.56.



5d: 3-(5-chloro-2-(methylthio)phenyl)propan-1-ol.

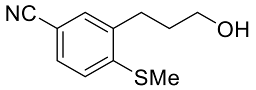
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.16 (d, *J* = 10.1 Hz, 2H), 7.11 (dd, *J* = 8.2, 1.8 Hz, 1H), 3.67 (td, *J* = 6.3, 1.9 Hz, 2H), 2.81 – 2.73 (m, 2H), 2.44 (s, 3H), 1.91 – 1.84 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 141.45, 135.65, 130.79, 128.91, 126.97, 126.66, 61.83, 32.47, 29.49, 15.94.



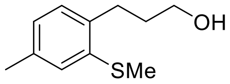
5e: 3-(5-bromo-2-(methylthio)phenyl)propan-1-ol.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.38 – 7.28 (m, 2H), 7.04 (d, *J* = 8.2 Hz, 1H), 3.67 (t, *J* = 6.2 Hz, 2H), 2.77 (dd, *J* = 8.5, 6.8 Hz, 2H), 2.44 (s, 3H), 1.91 – 1.84 (m, 2H).



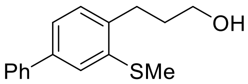
5f: 3-(3-hydroxypropyl)-4-(methylthio)benzonitrile.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 8.3 Hz, 1H), 7.40 (s, 1H), 7.18 (d, *J* = 8.3 Hz, 1H), 3.69 (t, *J* = 6.2 Hz, 2H), 2.79 (t, *J* = 7.9 Hz, 2H), 2.50 (s, 3H), 1.90 (t, *J* = 7.4 Hz, 2H).



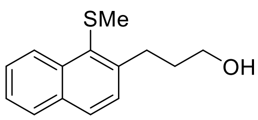
5g: 3-(4-methyl-2-(methylthio)phenyl)propan-1-ol.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.14 (d, *J* = 7.9 Hz, 1H), 7.01 (dd, *J* = 10.5, 2.7 Hz, 2H), 3.66 (t, *J* = 6.2 Hz, 2H), 2.85 – 2.76 (m, 2H), 2.44 (s, 3H), 2.30 (s, 3H), 1.92 – 1.85 (m, 2H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 140.12, 135.23, 133.36, 130.14, 127.57, 126.86, 62.06, 33.23, 29.60, 20.82, 16.56.



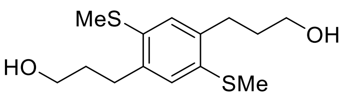
5h: 3-(3-(methylthio)-[1,1'-biphenyl]-4-yl)propan-1-ol.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 7.9 Hz, 2H), 7.45 (d, *J* = 7.5 Hz, 2H), 7.41 (d, *J* = 1.8 Hz, 1H), 7.37 – 7.30 (m, 2H), 7.24 (d, *J* = 7.8 Hz, 1H), 3.72 (t, *J* = 6.2 Hz, 2H), 2.86 (t, *J* = 7.6 Hz, 2H), 2.53 (s, 3H), 1.95 (t, *J* = 7.2 Hz, 2H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 140.83, 139.91, 138.72, 137.49, 129.52, 128.74, 127.28, 127.03, 124.46, 124.01, 62.11, 32.91, 29.30, 15.94.



5i: 3-(1-(methylthio)naphthalen-2-yl)propan-1-ol.

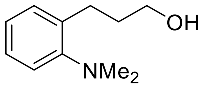
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.66 (d, *J* = 8.5 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.60 (ddd, *J* = 8.4, 6.8, 1.3 Hz, 1H), 7.51 – 7.46 (m, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 3.69 (t, *J* = 6.1 Hz, 2H), 3.25 (t, *J* = 7.6 Hz, 2H), 2.34 (s, 3H), 2.01 – 1.94 (m, 2H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 144.58, 134.76, 132.98, 131.66, 129.24, 128.48, 127.89, 126.96, 126.34, 125.36, 61.81, 34.57, 31.54, 20.02.



5j: 3,3'-(2,5-bis(methylthio)-1,4-phenylene)bis(propan-1-ol).

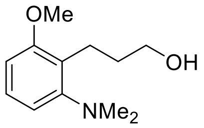
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.03 (s, 2H), 3.67 (t, *J* = 6.2 Hz, 4H), 2.84 – 2.73 (m, 4H), 2.44 (s, 6H), 1.93 – 1.84 (m, 4H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ

138.73, 133.95, 127.51, 62.06, 33.14, 29.46, 16.53.



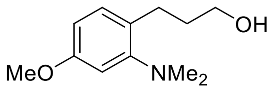
5p: 3-(2-(dimethylamino)phenyl)propan-1-ol.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.23 – 7.13 (m, 3H), 7.08 (td, *J* = 7.3, 1.5 Hz, 1H), 3.34 (t, *J* = 5.6 Hz, 2H), 2.86 – 2.78 (m, 2H), 2.71 (s, 6H), 1.83 – 1.73 (m, 2H).



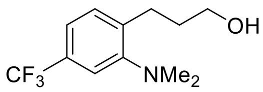
5q: 3-(2-(dimethylamino)-6-methoxyphenyl)propan-1-ol.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.17 (t, *J* = 8.1 Hz, 1H), 6.83 (d, *J* = 8.1 Hz, 1H), 6.70 (d, *J* = 8.2 Hz, 1H), 3.81 (s, 3H), 3.32 (d, *J* = 5.7 Hz, 2H), 2.87 (t, *J* = 6.5 Hz, 2H), 2.68 (d, *J* = 1.7 Hz, 6H), 1.77 (t, *J* = 6.2 Hz, 2H).



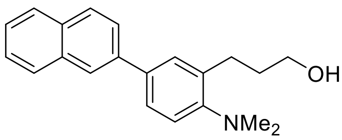
5r: 3-(2-(dimethylamino)-4-methoxyphenyl)propan-1-ol.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.08 (d, *J* = 8.4 Hz, 1H), 6.72 (s, 1H), 6.64 (d, *J* = 8.5 Hz, 1H), 3.79 (s, 3H), 3.34 (t, *J* = 5.7 Hz, 2H), 2.78 – 2.74 (m, 2H), 2.69 (d, *J* = 1.6 Hz, 6H), 1.76 (q, *J* = 6.3, 5.8 Hz, 2H).



5s: 3-(2-(dimethylamino)-4-(trifluoromethyl)phenyl)propan-1-ol.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.36 (s, 1H), 7.35 – 7.26 (m, 2H), 3.38 (t, *J* = 5.7 Hz, 2H), 2.88 (dt, *J* = 9.1, 4.3 Hz, 2H), 2.73 (s, 6H), 1.83 (q, *J* = 6.4 Hz, 2H).



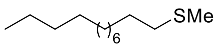
5t: 3-(2-(dimethylamino)-5-(naphthalen-2-yl)phenyl)propan-1-ol.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.01 (s, br, 1H), 7.90 (t, *J* = 7.9 Hz, 2H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.73 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.59 – 7.53 (m, 2H), 7.52 – 7.45 (m, 2H), 7.28 (d, *J* = 8.2 Hz, 1H), 3.42 (t, *J* = 5.6 Hz, 2H), 2.94 (t, *J* = 6.6 Hz, 2H), 2.78 (s, 6H), 1.92 – 1.86 (m, 2H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 151.74, 137.96, 137.51, 136.72, 133.65, 132.46, 129.67, 128.33, 128.06, 127.59, 126.23, 125.96, 125.77, 125.36, 125.31, 119.56, 59.43, 45.64, 33.83, 26.06.

4 C–O/C–X σ-bond metathesis of alcohols with thioethers

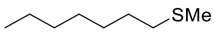
General procedure A for C–O/C–S(Se) σ-bond metathesis of alcohols with thioethers: to a 10 mL Schlenk tube was added $AlCl_3$ (50 mol%), ZnI_2 (100 mol%), alcohol (1.0 equiv.), thioether (5.0 equiv.) and cyclohexane (0.2 M). The reaction mixture was stirred at 120 °C for 24 hours, then the reaction was cooled to room temperature. The crude mixture was purified by flash column chromatography to afford the target product.

General procedure B for intramolecular ring-closing C–O/C–X σ-bond metathesis of alcohols with thioethers, ethers and amines: to a 10 mL Schlenk tube was added $AlCl_3$ (50 mol%), substrate (1.0 equiv.) and cyclohexane (0.2 M). The reaction mixture was stirred at 120 °C for 24 hours, then the reaction was cooled to room temperature. The crude mixture was purified by flash column chromatography to afford the target product.



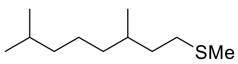
3a: Dodecyl(methyl)sulfane. [3]

Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.42 mg), ZnI_2 (0.2 mmol, 64.01 mg), **1a** (0.2 mmol, 45 uL), Me_2S (1 mmol, 73 uL) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **3a** (17.89 mg, 81% yield) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 2.48 (t, *J* = 7.4 Hz, 2H), 2.09 (s, 3H), 1.58 (q, *J* = 7.8 Hz, 3H), 1.26 (d, *J* = 6.6 Hz, 20H), 0.88 (t, *J* = 6.7 Hz, 3H).



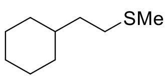
3b: Heptyl(methyl)sulfane. Mixture.

Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.19 mg), ZnI_2 (0.2 mmol, 63.82 mg), **1b** (0.2 mmol, 28 uL), Me_2S (1 mmol, 73 uL) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **3b** (19.87 mg, 68% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 2.49 (d, *J* = 7.5 Hz, 2.58H), 2.09 (s, 3H), 1.58 (d, *J* = 6.2 Hz, 3.34H), 1.42 – 1.22 (m, 11.28H), 0.88 (t, *J* = 6.7 Hz, 3.98H).



3c: (3,7-dimethyloctyl)(methyl)sulfane. Mixture,

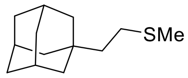
Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.36 mg), ZnI_2 (0.2 mmol, 63.87 mg), **1c** (0.2 mmol, 31.86 mg), Me_2S (1 mmol, 73 uL) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **3c** (29.36 mg, 78% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 2.58 – 2.43 (m, 2.67H), 2.10 (s, 3H), 1.68 – 1.46 (m, 5.68H), 1.45 – 1.35 (m, 1.76H), 1.12 (dd, *J* = 18.5, 9.8 Hz, 4.75H), 0.87 (t, *J* = 8.1 Hz, 13.50H).



3d: (2-cyclohexylethyl)(methyl)sulfane. Mixture.

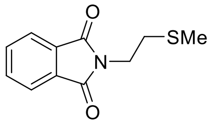
Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.57 mg), ZnI_2 (0.2 mmol, 63.75 mg), **1d** (0.2 mmol, 24.03 mg), Me_2S (1 mmol, 73 uL) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **3d** (24.05 mg, 76% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ

2.54 – 2.47 (m, 2.38H), 2.09 (s, 3H), 1.76 – 1.61 (m, 6.22H), 1.51 – 1.45 (m, 2.38H), 1.34 (tdq, *J* = 14.0, 6.8, 3.4 Hz, 1.11H), 1.27 – 1.08 (m, 4.05H), 0.94 – 0.84 (m, 2.55H).



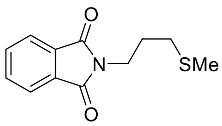
3e: (2-((3r,5r,7r)-adamantan-1-yl)ethyl)(methyl)sulfane. Mixture

Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.40 mg), ZnI_2 (0.2 mmol, 63.56 mg), **1e** (0.2 mmol, 36.28 mg), Me_2S (1 mmol, 73 uL) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **3e** (22.68 mg, 54% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 2.49 – 2.41 (m, 2.47H), 2.09 (s, 3H), 1.95 (s, 3.80H), 1.70 (dt, *J* = 12.3, 3.1 Hz, 4H), 1.62 (dq, *J* = 12.4, 2.1 Hz, 4H), 1.48 (d, *J* = 3.0 Hz, 7.63H), 1.39 – 1.33 (m, 2.47H).



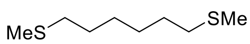
3f: 2-(2-(methylthio)ethyl)isoindoline-1,3-dione.

Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.48 mg), ZnI_2 (0.2 mmol, 63.76 mg), **1f** (0.2 mmol, 39.43 mg), Me_2S (1 mmol, 73 uL) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **3f** (22.05 mg, 50% yield) as white solid. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.88 – 7.82 (m, 2H), 7.74 – 7.67 (m, 2H), 3.91 (t, *J* = 7.0 Hz, 2H), 2.81 (t, *J* = 7.0 Hz, 2H), 2.17 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 168.16, 133.97, 132.01, 123.30, 36.39, 32.17, 15.10. **HRMS (APCI)** m/z: M calcd for $C_{11}H_{11}NO_2S$: 221.0510, found 221.0506.



3g: 2-(3-(methylthio)propyl)isoindoline-1,3-dione.

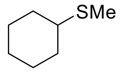
Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.48 mg), ZnI_2 (0.2 mmol, 63.76 mg), **1g** (0.2 mmol, 39.43 mg), Me_2S (1 mmol, 73 uL) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **3g** (69.11 mg, 59% yield) as white solid. **^{1}H NMR** (600 MHz, Chloroform-d) δ 7.85 (dt, J = 5.3, 2.3 Hz, 2H), 7.73 (dt, J = 5.2, 2.3 Hz, 2H), 3.80 (t, J = 7.3 Hz, 2H), 2.55 (t, J = 7.4 Hz, 2H), 2.11 (s, 3H), 1.99 (p, J = 7.4 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 168.31, 133.93, 132.12, 123.21, 37.08, 31.41, 27.90, 15.37. **HRMS (APCI)** m/z: M calcd for $C_{11}H_{13}NO_2S$: 235.0667, found 235.0669.



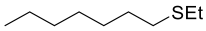
3h: 1,6-bis(methylthio)hexane.

Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.65 mg), ZnI_2 (0.2 mmol, 63.74 mg), **1h** (0.2 mmol, 29.62 mg), Me_2S (1 mmol, 73 uL) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **3h** (10.67 mg, 43% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 2.49 (t, *J* = 7.5 Hz, 4H), 2.10 (s, 6H), 1.60 (t, *J* = 7.0 Hz, 4H), 1.45 – 1.40 (m, 4H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 34.20, 29.03, 28.39, 15.53.

3i: cyclohexyl(methyl)sulfane.[5]

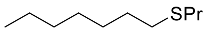


Following the general procedure A, $AlCl_3$ (0.25 mmol, 33.36 mg), ZnI_2 (0.5 mmol, 159.67 mg), **1i** (0.5 mmol, 53 uL), Me_2S (1 mmol, 184 uL) and cyclohexane (2 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **3i** (70% ^{1}H yield, the product is readily volatile.) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-d) δ 2.53 (d, J = 4.1 Hz, 1H), 2.08 (s, 3H), 2.02 – 1.91 (m, 2H), 1.76 (q, J = 6.6, 5.2 Hz, 2H), 1.37 – 1.17 (m, 6H).



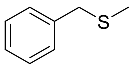
3j: Ethyl(heptyl)sulfane.

Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.46 mg), ZnI_2 (0.2 mmol, 63.88 mg), **1b** (0.2 mmol, 28 uL), Et_2S (1 mmol, 108 uL) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **3j** (21.23 mg, 66% yield) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-d) δ 2.57 – 2.48 (m, 4H), 1.58 (dd, J = 15.1, 7.2 Hz, 3H), 1.41 – 1.25 (m, 10H), 0.89 – 0.85 (m, 3H). **^{13}C NMR** (151 MHz, Chloroform-d) δ 34.21, 32.11, 31.73, 29.75, 28.91, 23.01, 22.59, 14.04, 13.51.



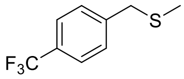
3k: Heptyl(propyl)sulfane.

Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.228 mg), ZnI_2 (0.2 mmol, 63.94 mg), **1b** (0.2 mmol, 28 uL), Pr_2S (1 mmol, 141 uL) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **3k** (21.98 mg, 663% yield) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 2.49 (td, *J* = 7.4, 4.6 Hz, 4H), 1.63 – 1.55 (m, 4H), 1.41 – 1.26 (m, 8H), 0.98 (t, *J* = 7.3 Hz, 3H), 0.87 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 32.18, 31.73, 31.67, 29.74, 29.67, 28.92, 25.91, 22.60, 14.81, 14.06.



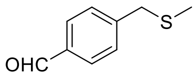
3l: Benzyl(methyl)sulfane. [6]

Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.41 mg), ZnI_2 (0.2 mmol, 63.98 mg), **1l** (0.2 mmol, 22.68 mg), Me_2S (1 mmol, 73 uL) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **3l** (15.14 mg, 52% yield, the product is readily volatile) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.36 – 7.28 (m, 5H), 3.71 (s, 2H), 2.03 (s, 3H).



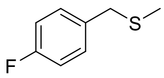
3m: Methyl(4-(trifluoromethyl)benzyl)sulfane. [7]

Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.99 mg), ZnI_2 (0.2 mmol, 64.13 mg), **1m** (0.2 mmol, 36.23 mg), Me_2S (1 mmol, 73 uL) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **3m** (25.96 mg, 61% yield, the product is readily volatile) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 3.71 (s, 2H), 2.00 (s, 3H).



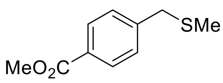
3n: 4-((methylthio)methyl)benzaldehyde. [8]

Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.46 mg), ZnI_2 (0.2 mmol, 64.56 mg), **1n** (0.2 mmol, 29.59 mg), Me_2S (1 mmol, 73 uL) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **3n** (17.21 mg, 55% yield, the product is readily volatile) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 9.99 (s, 1H), 7.84 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 7.9 Hz, 2H), 3.72 (s, 2H), 1.99 (s, 3H).



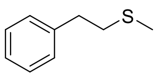
3o: (4-fluorobenzyl)(methyl)sulfane. [9]

Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.35 mg), ZnI_2 (0.2 mmol, 63.77 mg), **1o** (0.2 mmol, 26.48 mg), Me_2S (1 mmol, 73 uL) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **3o** (81% ^{1}H yield, the product is readily volatile) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.26 (d, *J* = 4.1 Hz, 2H), 7.00 (td, *J* = 8.7, 3.0 Hz, 2H), 3.64 (s, 2H), 1.98 (s, 3H).



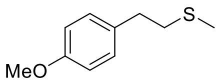
3p: methyl 4-((methylthio)methyl)benzoate. [10]

Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.35 mg), ZnI_2 (0.2 mmol, 63.77 mg), **1p** (0.2 mmol, 33.63 mg), Me_2S (1 mmol, 73 uL) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **3p** (81% ^{1}H yield, the product is readily volatile) as a colorless oil. colorless oil (18.02 mg, 46% yield). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.99 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 3.91 (s, 3H), 3.70 (s, 2H), 1.98 (s, 3H).



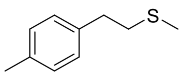
3q: Methyl(phenethyl)sulfane. [5]

Following the general procedure A, $AlCl_3$ (0.25 mmol, 33.00 mg), ZnI_2 (0.55 mmol, 161.04 mg), **1q** (0.5 mmol, 62.07 mg), Me_2S (1 mmol, 184 uL) and cyclohexane (2 mL). The reaction was stirred at 120 ℃ for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **3q** (54.12 mg, 70% yield, the product is readily volatile) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-d) δ 7.31 (m, 2H), 7.26 – 7.19 (m, 3H), 2.93 – 2.88 (m, 2H), 2.82 – 2.71 (m, 2H), 2.13 (s, 3H).



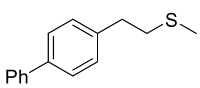
3r: (4-methoxyphenethyl)(methyl)sulfane.

Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.36 mg), ZnI_2 (0.2mmol, 63.84 mg), **1r** (0.2 mmol, 32.19 mg), Me_2S (1 mmol, 73 uL) and cyclohexane (1 mL). The reaction was stirred at 120 ℃ for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **3r** (16.95 mg, 44% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.13 (d, J = 8.6 Hz, 2H), 6.85 (d, J = 8.6 Hz, 2H), 3.79 (s, 3H), 2.87 – 2.82 (m, 2H), 2.76 – 2.69 (m, 2H), 2.12 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 158.09, 132.64, 129.40, 113.83, 55.22, 36.08, 34.95, 15.67. **HRMS (APCI)** m/z: M calcd for $C_{10}H_{14}OS$: 182.0765, found 182.0761.



3s: Methyl(4-methylphenethyl)sulfane. [11]

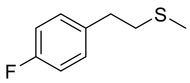
Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.46 mg), ZnI_2 (0.2mmol, 64.57 mg), **1s** (0.2 mmol, 26.43 mg), Me_2S (1 mmol, 73 uL) and cyclohexane (1 mL). The reaction was stirred at 120 ℃ for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **3s** (18.22 mg, 54% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.11 (m, 4H), 2.90 – 2.84 (m, 2H), 2.75 (d, J = 7.9 Hz, 2H), 2.33 (s, 3H), 2.13 (s, 3H).



3t: (2-([1,1'-biphenyl]-4-yl)ethyl)(methyl)sulfane.

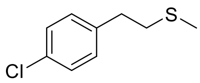
Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.62 mg), ZnI_2 (0.2mmol, 64.82 mg), **1t** (0.2 mmol, 42.36 mg), Me_2S (1 mmol, 73 uL) and cyclohexane (1 mL). The reaction was stirred at 120 ℃ for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **3t** (28.34, 61% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.59 (d, J = 6.8 Hz, 2H), 7.54 (d, J = 6.0 Hz, 2H), 7.44 (t, J = 6.7 Hz, 2H), 7.34 (t, J = 7.5 Hz, 1H), 7.30 (d, J = 6.1 Hz, 2H), 2.95 (t, J = 7.5 Hz, 2H), 2.85 – 2.75 (m, 2H), 2.16 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 140.91, 139.61, 139.27, 128.89, 128.70, 127.17, 127.09, 126.98, 35.75, 35.46, 15.72.

HRMS (APCI) m/z: M calcd for $C_{15}H_{16}S$: 228.0973, found 228.0968.



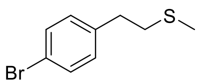
3u: (4-fluorophenethyl)(methyl)sulfane. [11]

Following the general procedure A, $AlCl_3$ (0.25 mmol, 33.76 mg), ZnI_2 (0.5mmol, 160.40 mg), **1s** (0.5 mmol, 71.84 mg), Me_2S (1 mmol, 184 uL) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **3s** (62.20 mg, 71% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.17 (dd, *J* = 8.5, 5.5 Hz, 2H), 6.98 (t, *J* = 8.7 Hz, 2H), 2.89 – 2.85 (m, 2H), 2.75 – 2.71 (m, 2H), 2.12 (s, 3H).



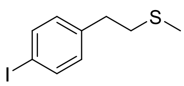
3v: (4-chlorophenethyl)(methyl)sulfane. [5]

Following the general procedure A, $AlCl_3$ (0.25 mmol, 33.69 mg), ZnI_2 (0.5mmol, 162.20 mg), **1v** (0.5 mmol, 78.65 mg), Me_2S (1 mmol, 184 uL) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **3v** (69.31 mg, 74% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.26 (d, *J* = 8.3 Hz, 2H), 7.14 (d, *J* = 8.3 Hz, 2H), 2.90 – 2.83 (m, 2H), 2.76 – 2.70 (m, 2H), 2.11 (s, 3H).



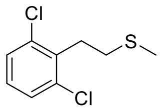
3w: **(4-bromophenethyl)(methyl)sulfane.** [11]

Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.32 mg), ZnI_2 (0.2mmol, 64.62 mg), **1w** (0.2 mmol, 40.17 mg), Me_2S (1 mmol, 73 uL) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **3w** (36.63, 75% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 8.3 Hz, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 2.87 – 2.83 (m, 2H), 2.73 (t, *J* = 7.6 Hz, 2H), 2.11 (s, 3H).



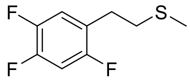
3x: (4-iodophenethyl)(methyl)sulfane.

Following the general procedure A, $AlCl_3$ (0.25 mmol, 33.17 mg), ZnI_2 (0.5mmol, 159.40 mg), **1x** (0.5 mmol, 124.21 mg), Me_2S (1 mmol, 184 uL) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **3x** (93.12 mg, 67% yield) as a white solid. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 8.3 Hz, 2H), 6.96 (d, *J* = 8.2 Hz, 2H), 2.86 – 2.80 (m, 2H), 2.72 (t, *J* = 7.9 Hz, 2H), 2.11 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 140.06, 137.43, 130.56, 91.47, 35.50, 35.22, 15.70. **HRMS (APCI)** m/z: M calcd for $C_9H_{11}IS$: 277.9626, found 277.9622.



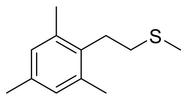
3y: (2,6-dichlorophenethyl)(methyl)sulfane. [12]

Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.19 mg), ZnI_2 (0.2mmol, 64.51 mg), **1y** (0.2 mmol, 38.87 mg), Me_2S (1 mmol, 73 uL) and cyclohexane (1 mL). The reaction was stirred at 120 ℃ for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **3y** (13.65 mg, 31% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.32 – 7.23 (m, 2H), 7.18 – 7.06 (m, 2H), 2.90 – 2.83 (m, 2H), 2.76 – 2.70 (m, 2H), 2.11 (s, 3H).



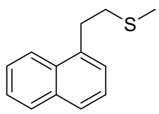
3z: Methyl(2,4,6-trifluorophenethyl)sulfane.

Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.39 mg), ZnI_2 (0.2mmol, 63.68 mg), **1z** (0.2 mmol, 37.02 mg), Me_2S (1 mmol, 73 uL) and cyclohexane (1 mL). The reaction was stirred at 120 ℃ for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **3z** (17.29 mg, 42% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.03 (dd, J = 17.3, 8.7 Hz, 1H), 6.94 – 6.81 (m, 1H), 2.91 – 2.84 (m, 2H), 2.76 – 2.66 (m, 2H), 2.13 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 123.62, 123.50, 118.32, 118.28, 118.20, 118.16, 105.51, 105.38, 105.32, 105.19, 34.05, 28.47, 15.54. **^{19}F NMR** (565 MHz, Chloroform-*d*) δ -120.21, -136.22 – -136.38 (m), -143.21.



3aa: Methyl(2,4,6-trimethylphenethyl)sulfane.

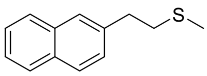
Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.33 mg), ZnI_2 (0.2mmol, 63.87 mg), **1aa** (0.2 mmol, 38.87 mg), Me_2S (1 mmol, 73 uL) and cyclohexane (1 mL). The reaction was stirred at 120 ℃ for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **3aa** (29.13 mg, 75% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 6.87 (s, 2H), 2.95 – 2.89 (m, 2H), 2.64 – 2.57 (m, 2H), 2.34 (s, 6H), 2.28 (s, 3H), 2.23 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 135.97, 135.58, 134.11, 128.98, 32.95, 29.60, 20.76, 19.67, 15.57. **HRMS (APCI)** m/z: M calcd for $C_{12}H_{18}S$: 194.1129, found 194.1124.



3bb: Methyl(2-(naphthalen-1-yl)ethyl)sulfane.

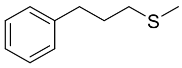
Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.37 mg), ZnI_2 (0.2mmol, 63.92 mg), **1bb** (0.2 mmol, 33.79 mg), Me_2S (1 mmol, 73 uL) and cyclohexane (1 mL). The reaction was stirred at 120 ℃ for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **3bb** (24.67 mg, 61% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.03 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 8.1 Hz, 1H), 7.75 (d, J = 8.1 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.52 – 7.46

(m, 1H), 7.45 – 7.40 (m, 1H), 7.38 (d, *J* = 6.9 Hz, 1H), 3.41 – 3.33 (m, 2H), 2.90 (t, *J* = 8.1 Hz, 2H), 2.20 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 136.54, 133.87, 131.60, 128.85, 127.13, 126.33, 125.99, 125.53, 125.50, 123.38, 35.05, 33.23, 15.77. **HRMS (APCI)** m/z: M calcd for $C_{13}H_{14}S$: 202.0816, found 202.0811.



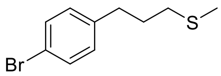
3cc: Methyl(2-(naphthalen-2-yl)ethyl)sulfane. [11]

Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.65 mg), ZnI_2 (0.2mmol, 64.36 mg), **1cc** (0.2 mmol, 34.49 mg), Me_2S (1 mmol, 73 uL) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **3cc** (18.18 mg, 45% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.80 (t, *J* = 9.7 Hz, 3H), 7.66 (s, 1H), 7.45 (p, *J* = 6.9 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 1H), 3.07 (t, *J* = 7.7 Hz, 2H), 2.88 – 2.82 (m, 2H), 2.16 (s, 3H).



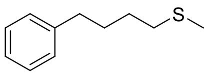
3dd: Methyl(3-phenylpropyl)sulfanemethyl(3-phenylpropyl)sulfane. [5]

Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.44 mg), ZnI_2 (0.2mmol, 63.81 mg), **1dd** (0.2 mmol, 27.24 mg), Me_2S (1 mmol, 73 uL) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **3dd** (19.27 mg, 58% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.29 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.12 (m, 3H), 2.73 (t, *J* = 7.6 Hz, 2H), 2.52 (t, *J* = 7.3 Hz, 2H), 2.10 (s, 3H), 2.00 – 1.88 (m, 2H).



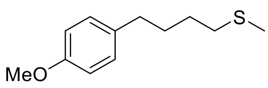
3ee: (3-(4-bromophenyl)propyl)(methyl)sulfane.

Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.55 mg), ZnI_2 (0.2mmol, 63.67 mg), **1ee** (0.2 mmol, 44.15 mg), Me_2S (1 mmol, 73 uL) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **3ee** (33.31 mg, 68% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.3 Hz, 2H), 2.72 – 2.63 (m, 2H), 2.49 (t, *J* = 7.2 Hz, 2H), 2.09 (s, 3H), 1.89 (t, *J* = 7.4 Hz, 2H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 140.49, 131.38, 130.20, 119.60, 34.01, 33.39, 30.37, 15.42. **HRMS (APCI)** m/z: M calcd for $C_{10}H_{13}BrS$: 243.9921, found 243.9918.



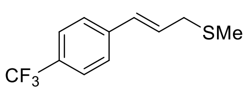
3ff: Methyl(4-phenylbutyl)sulfane. [4]

Following the general procedure A, $AlCl_3$ (0.25 mmol, 33.13 mg), ZnI_2 (0.5mmol, 160.71 mg), **1ff** (0.5 mmol, 73.46 mg), Me_2S (1 mmol, 184 uL) and cyclohexane (2 mL). The reaction was stirred at 120 ℃ for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **3ff** (63.03 mg, 70% yield) as colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.29 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.15 (m, 3H), 2.65 (t, *J* = 7.6 Hz, 2H), 2.53 (t, *J* = 7.3 Hz, 2H), 2.09 (s, 3H), 1.78 – 1.72 (m, 2H), 1.69 – 1.62 (m, 2H).



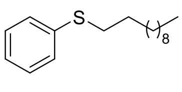
3gg: (4-(4-methoxyphenyl)butyl)(methyl)sulfane.

Following the general procedure A, $AlCl_3$ (0.25 mmol, 33.35 mg), ZnI_2 (0.5mmol, 160.65 mg), **1gg** (0.5 mmol, 90.12 mg), Me_2S (1 mmol, 184 uL) and cyclohexane (2 mL). The reaction was stirred at 120 ℃ for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **3gg** (43.08 mg, 41% yield) as colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.10 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 2.58 (t, *J* = 7.5 Hz, 2H), 2.51 (t, *J* = 7.2 Hz, 2H), 2.08 (s, 3H), 1.73 – 1.67 (m, 2H), 1.65 – 1.60 (m, 2H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 157.67, 134.27, 129.19, 113.66, 55.19, 34.50, 34.06, 30.66, 28.59, 15.48. **HRMS (APCI)** m/z: M calcd for $C_{12}H_{18}OS$: 210.1078, found 210.1074.



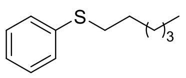
3hh: (E)-methyl(3-(4-(trifluoromethyl)phenyl)allyl)sulfane.

Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.48 mg), ZnI_2 (0.2mmol, 63.78 mg), **1hh** (0.2 mmol, 42.12 mg), Me_2S (1 mmol, 73 uL) and cyclohexane (1 mL). The reaction was stirred at 120 ℃ for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **3hh** (23.22 mg, 50% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 6.46 (d, *J* = 15.7 Hz, 1H), 6.28 (dt, *J* = 15.3, 7.4 Hz, 1H), 3.28 (d, *J* = 7.4 Hz, 2H), 2.07 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 140.19, 130.76, 128.45, 126.41, 125.56, 125.53, 125.51, 125.48, 36.20, 14.50.



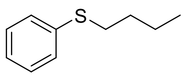
4a: phenyl(undecyl)sulfane. [13]

Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.33 mg), ZnI_2 (0.2mmol, 63.50 mg), **1a** (0.2 mmol, 34.66 mg), **2a** (1 mmol, 118 uL) and cyclohexane (1 mL). The reaction was stirred at 120 ℃ for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **4a** (38.04 mg, 72% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 7.8 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 2.95 (t, *J* = 7.5 Hz, 2H), 1.68 (p, *J* = 7.5 Hz, 2H), 1.45 (t, *J* = 7.4 Hz, 2H), 1.30 (d, *J* = 8.5 Hz, 14H), 0.92 (t, *J* = 7.0 Hz, 3H).



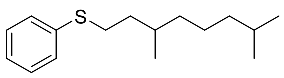
4b: Hexyl(phenyl)sulfane. [14]

Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.29 mg), ZnI_2 (0.2mmol, 63.86 mg), **1b-2** (0.2 mmol, 42.12 mg), **2a** (1 mmol, 118 uL) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **4b** (27.17 mg, 70% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.31 (d, J = 7.8 Hz, 2H), 7.26 (t, J = 7.9 Hz, 2H), 7.15 (t, J = 7.4 Hz, 1H), 2.90 (t, J = 7.5 Hz, 2H), 1.63 (p, J = 7.5 Hz, 2H), 1.41 (q, J = 7.2 Hz, 2H), 1.28 (s, 4H), 0.87 (t, J = 6.7 Hz, 3H).



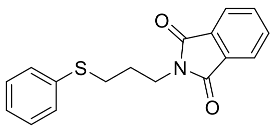
4c: Butyl(phenyl)sulfane. [14]

Following the general procedure A, $AlCl_3$ (0.2 mmol, 26.67 mg), ZnI_2 (0.4mmol, 127.15 mg), **1c-2** (0.4 mmol, 37 uL), **2c** (2.0 mmol, 235 uL) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **4c** (43.83, 66% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.32 (d, J = 7.8 Hz, 2H), 7.28 (d, J = 7.6 Hz, 2H), 7.16 (t, J = 7.4 Hz, 1H), 2.92 (t, J = 7.6 Hz, 2H), 1.64 (p, J = 7.6 Hz, 2H), 1.45 (h, J = 7.4 Hz, 2H), 0.92 (t, J = 7.4 Hz, 3H).



4d: (3,7-dimethyloctyl)(phenyl)sulfane.

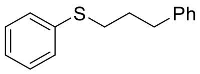
Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.68 mg), ZnI_2 (0.2mmol, 63.96 mg), **1c** (0.2 mmol, 39 uL mg), **2a** (1 mmol, 118 uL) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **4d** (36.02, 72% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.37 – 7.21 (m, 4H), 7.15 (t, J = 6.6 Hz, 1H), 3.00 – 2.83 (m, 2H), 1.65 (dd, J = 16.2, 7.1 Hz, 1H), 1.56 – 1.40 (m, 3H), 1.20 (d, J = 94.8 Hz, 6H), 0.87 (dd, J = 25.1, 4.5 Hz, 9H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 137.05, 128.77, 128.75, 125.57, 39.18, 36.87, 36.19, 32.21, 31.38, 27.93, 24.61, 22.67, 22.57, 19.34. **HRMS (APCI)** m/z: M calcd for $C_{16}H_{26}S$: 250.1755, found 250.1749.



4e: 2-(3-(phenylthio)propyl)isoindoline-1,3-dione. [15]

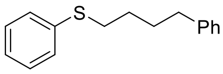
Following the general procedure A, $AlCl_3$ (0.25 mmol, 33.35 mg), ZnI_2 (0.5 mmol, 159.61 mg), **1g** (0.5 mmol, 102.61 mg), **2a** (2.5 mmol, 300 uL) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **4e** (123.26 mg, 83% yield) as a white solid. **^{1}H NMR** (600 MHz, Chloroform-d) δ 7.84 (dd, J = 5.6, 3.0 Hz, 2H), 7.72 (dd, J = 5.7, 3.1

Hz, 2H), 7.36 (d, $J = 7.3$ Hz, 2H), 7.28 (s, 2H), 7.19 (t, $J = 7.4$ Hz, 1H), 3.83 (t, $J = 6.8$ Hz, 2H), 2.96 (t, $J = 7.1$ Hz, 2H), 2.01 (q, $J = 7.2$ Hz, 2H).



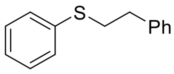
4f: Phenyl(3-phenylpropyl)sulfane. [16]

Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.55 mg), ZnI_2 (0.2mmol, 63.52 mg), **1dd**(0.2 mmol, 27.24 mg), **2a** (1 mmol, 118 uL) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **4f** (31.06, 68% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.29 (dt, $J = 16.5$, 8.5 Hz, 6H), 7.19 (p, $J = 7.6$ Hz, 4H), 2.93 (t, $J = 7.0$ Hz, 2H), 2.77 (t, $J = 7.2$ Hz, 2H), 1.99 (q, $J = 7.2$ Hz, 2H).



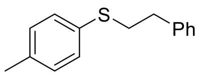
4g: Phenyl(4-phenylbutyl)sulfane. [16]

Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.39 mg), ZnI_2 (0.2mmol, 63.84 mg), **1ff** (0.2 mmol, 30.04 mg), **2a** (1 mmol, 118 uL) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **4g** (30.03 mg, 62% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.35 – 7.25 (m, 6H), 7.17 (d, $J = 7.5$ Hz, 4H), 2.95 (t, $J = 7.4$ Hz, 2H), 2.64 (t, $J = 7.7$ Hz, 2H), 1.74 (dd, $J = 39.2$, 7.7 Hz, 4H).



4h: Phenethyl(phenyl)sulfane. [17]

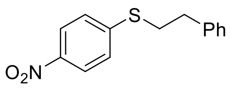
Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.35 mg), ZnI_2 (0.2mmol, 63.89 mg), **1q** (0.2 mmol, 24 uL), **2a** (1 mmol, 118 uL) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **4h** (36.11 mg, 82% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.37 (d, $J = 7.7$ Hz, 2H), 7.30 (d, $J = 3.9$ Hz, 4H), 7.21 (d, $J = 8.3$ Hz, 4H), 3.22 – 3.14 (m, 2H), 2.94 (t, $J = 8.1$ Hz, 2H).



4i: Phenethyl(p-tolyl)sulfane. [17]

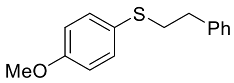
Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.34 mg), ZnI_2 (0.2mmol, 63.85 mg), **1q** (0.2 mmol, 24.90 mg), **2i** (1 mmol, 134 uL) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **4b** (30.08 mg, 66% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.34 – 7.26 (m, 4H), 7.25 – 7.17 (m, 3H), 7.13 (d, $J = 7.7$ Hz, 2H), 3.13 (t, $J = 7.8$ Hz, 2H), 2.91 (t, $J =$

7.6 Hz, 2H), 2.34 (s, 3H).



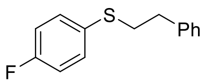
4j: (4-nitrophenyl)(phenethyl)sulfane. [18]

Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.53 mg), ZnI_2 (0.2mmol, 63.97 mg), **1q** (0.2 mmol, 24.43 mg), **2j** (1 mmol, 169.20 mg) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **4j** (23.09 mg, 44% yield) as white solid .**^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.16 (dd, *J* = 9.0, 4.3 Hz, 2H), 7.31 (dd, *J* = 60.4, 8.4 Hz, 7H), 3.33 – 3.30, (m, 2H), 3.06 – 3.03 (m, 2H).



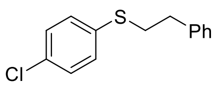
4k: (4-methoxyphenyl)(phenethyl)sulfane. [17]

Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.23 mg), ZnI_2 (0.2mmol, 64.09 mg), **1q** (0.2 mmol, 24.76 mg), **2k** (1 mmol, 139 uL) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **4k** (15.10 mg, 31% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.46 – 7.38 (m, 2H), 7.34 – 7.19 (m, 5H), 6.96 – 6.82 (m, 2H), 3.84 (s, 3H), 3.14 – 3.06 (m, 2H), 2.95 – 2.87 (m, 2H).



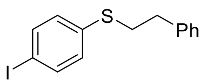
4l: (4-fluorophenyl)(phenethyl)sulfane. [19]

Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.88 mg), ZnI_2 (0.2mmol, 63.36 mg), **1q** (0.2 mmol, 23.66 mg), **2l** (1 mmol, 122 uL) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **4l** (34.01 mg, 73% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.36 (t, *J* = 4.5 Hz, 2H), 7.33 – 7.28 (m, 2H), 7.25 – 7.15 (m, 3H), 7.01 (t, *J* = 8.7 Hz, 2H), 3.12 (t, *J* = 8.0 Hz, 2H), 2.90 (t, *J* = 8.0 Hz, 2H).



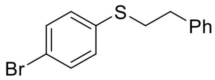
4m: (4-chlorophenyl)(phenethyl)sulfane. [19]

Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.45 mg), ZnI_2 (0.2mmol, 63.95 mg), **1q** (0.2 mmol, 25.03 mg), **2m** (1 mmol, 130 uL) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **4m** (37.20 mg, 75% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.33 – 7.21 (m, 7H), 7.19 (d, *J* = 7.4 Hz, 2H), 3.18 – 3.11 (m, 2H), 2.92 (t, *J* = 8.0 Hz, 2H).



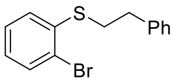
4n: (4-iodophenyl)(phenethyl)sulfane.

Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.36 mg), ZnI_2 (0.2mmol, 63.76 mg), **1q** (0.2 mmol, 24.67 mg), **2n** (1 mmol, 250.92mg) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **4n** (38.75 mg, 57% yield) as a white solid. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.60 (dd, *J* = 8.5, 2.7 Hz, 2H), 7.35 – 7.15 (m, 6H), 7.08 (dd, *J* = 8.5, 2.7 Hz, 2H), 3.17 – 3.13 (m, 2H), 2.94 – 2.90 (m, 2H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 139.85, 137.80, 136.57, 130.65, 128.53, 128.46, 126.53, 90.54, 35.41, 34.86.



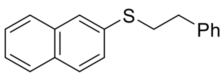
4o: (4-bromophenyl)(phenethyl)sulfane. [19]

Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.95 mg), ZnI_2 (0.2mmol, 64.08 mg), **1q** (0.2 mmol, 25.14 mg), **2o** (1 mmol,204.13 mg) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **4o** (37.98 mg, 65% yield) as a white solid. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 7.7 Hz, 2H), 7.22 (dt, *J* = 19.4, 8.2 Hz, 5H), 3.16 (t, *J* = 7.6 Hz, 2H), 2.93 (d, *J* = 8.3 Hz, 2H).



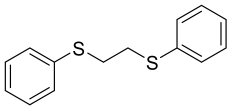
4p: (2-bromophenyl)(phenethyl)sulfane.

Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.46 mg), ZnI_2 (0.2mmol, 64.53 mg), **1q** (0.2 mmol, 24.43 mg), **2p** (1 mmol, 203.13 mg) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **4p** (35.09 mg, 60% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 8.1 Hz, 1H), 7.36 – 7.19 (m, 7H), 7.04 (q, *J* = 4.2, 3.7 Hz, 1H), 3.20 (t, *J* = 8.1 Hz, 2H), 2.99 (t, *J* = 8.1 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 139.93, 137.88, 133.01, 128.57, 128.44, 127.93, 127.70, 126.56, 126.52, 123.54, 34.99, 34.30.



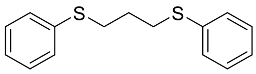
4q: naphthalen-2-yl(phenethyl)sulfane. [17]

Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.36 mg), ZnI_2 (0.2mmol, 63.89 mg), **1q** (0.2 mmol, 25.16 mg), **2q** (1 mmol, 174.26 mg) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **4q** (33.28 mg, 63% yield) as a white solid. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 8.0 Hz, 1H), 7.82 – 7.75 (m, 3H), 7.55 – 7.45 (m, 3H), 7.35 (d, *J* = 7.5 Hz, 2H), 7.27 (t, *J* = 8.4 Hz, 3H), 3.32 (t, *J* = 7.9 Hz, 2H), 3.02 (t, *J* = 8.0 Hz, 2H).



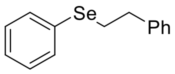
4r: 1,2-bis(phenylthio)ethane. [20]

Following the general procedure A, $AlCl_3$ (0.25 mmol, 34.07 mg), ZnI_2 (0.5 mmol, 159.60 mg), **1r** (0.5 mmol, 35.67 mg), **2a** (2.5 mmol, 300 uL) and cyclohexane (1 mL). The reaction was stirred at 120 ℃ for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **4r** (56.59 mg, 46% yield) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.34 – 7.26 (m, 8H), 7.24 – 7.17 (m, 2H), 3.09 (s, 4H).



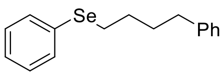
4s: 1,3-bis(phenylthio)propane. [21]

Following the general procedure A, $AlCl_3$ (0.25 mmol, 33.73 mg), ZnI_2 (0.5 mmol, 161.20 mg), **1s** (0.5 mmol, 39.07mg), **2a** (2.5 mmol, 293 uL) and cyclohexane (1 mL). The reaction was stirred at 120 ℃ for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **4s** (45.51 mg, 35% yield) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.38 – 7.32 (m, 4H), 7.32 – 7.26 (m, 4H), 7.23 – 7.15 (m, 2H), 3.08 (t, *J* = 7.0 Hz, 4H), 1.98 (p, *J* = 7.0 Hz, 2H).



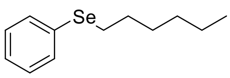
4t: Phenethyl(phenyl)selane. [22]

Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.78 mg), ZnI_2 (0.2mmol, 63.89 mg), **1q** (0.2 mmol, 24.43 mg), **2t** (1 mmol, 124 uL) and cyclohexane (1 mL). The reaction was stirred at 120 ℃ for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **4t** (38.90 mg, 74% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 7.2 Hz, 2H), 7.33 – 7.20 (m, 8H), 3.18 (t, *J* = 8.0 Hz, 2H), 3.03 (t, *J* = 8.0 Hz, 2H).



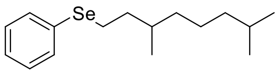
4u: phenyl(4-phenylbutyl)selane. [23]

Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.12 mg), ZnI_2 (0.2mmol, 63.99 mg), **1ff** (0.2 mmol, 29.92 mg), **2t** (1 mmol, 171.11 mg) and cyclohexane (1 mL). The reaction was stirred at 120 ℃ for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **4u** (38.84 mg, 67% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-d) δ 7.51 (d, J = 7.1 Hz, 2H), 7.29 (dd, J = 11.5, 7.6 Hz, 5H), 7.20 (t, J = 9.7 Hz, 3H), 2.97 (d, J = 6.3 Hz, 2H), 2.66 (d, J = 6.7 Hz, 2H), 1.78 (q, J = 3.9, 3.3 Hz, 4H).



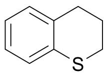
4v: hexyl(phenyl)selane. [24]

Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.13 mg), ZnI_2 (0.2mmol, 64.11 mg), **1b-2** (0.2 mmol, 25 uL), **2t** (1 mmol, 171.15 mg) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **4v** (36.05 mg, 70% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 7.4 Hz, 2H), 7.26 (dd, *J* = 12.9, 7.1 Hz, 3H), 2.94 (t, *J* = 7.4 Hz, 2H), 1.73 (p, *J* = 7.6 Hz, 2H), 1.43 (t, *J* = 7.4 Hz, 2H), 1.31 (dd, *J* = 7.0, 3.5 Hz, 4H), 0.91 (t, *J* = 6.6 Hz, 3H).



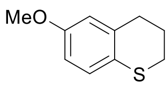
4w: (3,7-dimethyloctyl)(phenyl)selane.

Following the general procedure A, $AlCl_3$ (0.1 mmol, 13.85 mg), ZnI_2 (0.2mmol, 64.24 mg), **1c** (0.2 mmol, 38 uL), **2t** (1 mmol, 171.06 mg) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **4v** (52.95 mg, 89% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 7.4 Hz, 2H), 7.27 (dq, *J* = 13.3, 6.9, 5.5 Hz, 3H), 3.03 – 2.88 (m, 2H), 1.74 (q, *J* = 9.4, 8.6 Hz, 1H), 1.58 – 1.49 (m, 3H), 1.28 (ddd, *J* = 27.3, 13.7, 6.9 Hz, 3H), 1.14 (dq, *J* = 16.6, 7.9, 7.2 Hz, 3H), 0.90 (dd, *J* = 14.1, 6.1 Hz, 9H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 132.30, 130.70, 128.95, 126.55, 39.21, 37.26, 36.79, 33.13, 27.95, 25.71, 24.62, 22.69, 22.59, 19.27.



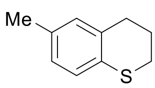
6a: Thiochromane. [26]

Following the general procedure B, $AlCl_3$ (0.1 mmol, 13.38mg), **5a** (0.2 mmol, 36.46 mg), and cyclohexane (1mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **6a** (24.64 mg, 82% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.15 – 6.92 (m, 4H), 3.07 – 3.00 (m, 2H), 2.82 (t, *J* = 6.2 Hz, 2H), 2.13 (q, *J* = 6.0 Hz, 2H).



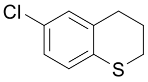
6b: 6-methoxythiochromane. [26]

Following the general procedure B, $AlCl_3$ (0.1 mmol, 13.23 mg), **5b** (0.2 mmol, 44.78 mg) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **6b** (27.03 mg, 75% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.00 (d, *J* = 8.6 Hz, 1H), 6.67 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.62 (d, *J* = 2.9 Hz, 1H), 3.76 (s, 3H), 3.04 – 2.96 (m, 2H), 2.79 (t, *J* = 6.2 Hz, 2H), 2.09 (p, *J* = 6.1 Hz, 2H).



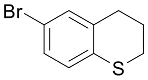
6c: 6-methylthiochromane. [26]

Following the general procedure B, $AlCl_3$ (0.1 mmol, 13.36 mg), **5c** (0.2 mmol, 42.71 mg) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **6c** (26.11 mg, 80% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-d) δ 6.98 (d, J = 7.9 Hz, 1H), 6.88 (d, *J* = 8.1 Hz, 1H), 6.85 (s, 1H), 3.05 – 2.98 (m, 2H), 2.77 (t, *J* = 6.2 Hz, 2H), 2.25 (s, 3H), 2.10 (t, *J* = 6.0 Hz, 2H).



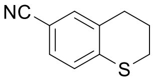
6d: 6-chlorothiochromane. [27]

Following the general procedure B, $AlCl_3$ (0.1 mmol, 13.57 mg), **5d** (0.2 mmol, 44.73 mg) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **6d** (33.11 mg, 90% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.01 (d, *J* = 4.0 Hz, 3H), 3.05 – 2.98 (m, 2H), 2.78 (t, *J* = 6.2 Hz, 2H), 2.09 (p, *J* = 6.1 Hz, 2H).



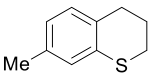
6e: 6-bromothiochromane.

Following the general procedure B, $AlCl_3$ (0.05 mmol, 6.76 mg), **5e** (0.1 mmol, 26.33 mg) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **6e** (16.18 mg, 71% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.16 (s, 2H), 6.95 (d, *J* = 8.3 Hz, 1H), 3.01 (dd, *J* = 7.3, 4.4 Hz, 2H), 2.78 (t, *J* = 6.2 Hz, 2H), 2.09 (t, *J* = 5.9 Hz, 2H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 135.84, 132.48, 132.15, 129.29, 127.97, 116.92, 29.48, 27.40, 22.41. **HRMS (APCI)** m/z: M calcd for C_9H_9BrS: 227.9608, found 227.9604.



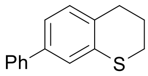
6f: thiochromane-6-carbonitrile.

Following the general procedure B, $AlCl_3$ (0.05 mmol, 6.79 mg), **5f** (0.1 mmol, 20.68 mg) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **6f** (6.21 mg, 34% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-d) δ 7.30 – 7.26 (m, 2H), 7.14 (d, J = 8.1 Hz, 1H), 3.08 – 3.04 (m, 2H), 2.83 – 2.80 (m, 2H), 2.14 – 2.09 (m, 2H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 135.44, 131.42, 129.61, 129.18, 127.64, 126.44, 29.53, 27.40, 22.44. **HRMS (APCI)** m/z: M calcd for $C_{10}H_9NS$: 175.0456, found 175.0451.



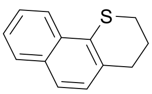
6g: 7-methylthiochromane.

Following the general procedure B, $AlCl_3$ (0.1 mmol, 13.68 mg), **5g** (0.2 mmol, 41.78 mg) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **6g** (26.12 mg, 80% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 6.98 (d, *J* = 7.9 Hz, 1H), 6.88 (d, *J* = 8.1 Hz, 1H), 6.85 (s, 1H), 3.01 (t, *J* = 6.0 Hz, 2H), 2.77 (t, *J* = 6.2 Hz, 2H), 2.25 (s, 3H), 2.10 (q, *J* = 6.0 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 133.68, 133.46, 130.65, 129.17, 127.24, 126.44, 29.59, 27.51, 23.04, 20.72. **HRMS (APCI)** m/z: M calcd for $C_{10}H_{12}S$: 164.0660, found 164.0655.



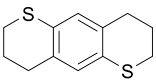
6h: 7-phenylthiochromane.

Following the general procedure B, $AlCl_3$ (0.1 mmol, 13.82 mg), **5h** (0.2 mmol, 51.77 mg) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **6h** (31.20 mg, 69% yield) as a white solid. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.37 – 7.27 (m, 2H), 7.22 (d, *J* = 7.9 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 3.14 – 3.03 (m, 2H), 2.86 (t, *J* = 6.4 Hz, 2H), 2.24 – 2.11 (m, 2H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 140.55, 139.48, 133.29, 132.81, 130.32, 128.66, 127.18, 126.88, 125.03, 122.80, 29.35, 27.62, 22.92. **HRMS (APCI)** m/z: M calcd for $C_{15}H_{14}S$: 226.0816, found 226.0811.



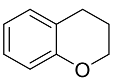
6i: 3,4-dihydro-2H-benzo[h]thiochromene. [26]

Following the general procedure B, $AlCl_3$ (0.05 mmol, 6.66 mg), **5i** (0.1 mmol, 23.69 mg) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **6i** (13.01 mg, 65% yield) as a white solid. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.49 (dd, *J* = 8.4, 5.3 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 3.15 (t, *J* = 5.9 Hz, 2H), 3.00 (t, *J* = 6.3 Hz, 2H), 2.29 – 2.18 (m, 2H).



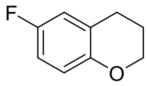
6j: 2,3,4,7,8,9-hexahydrothiopyrano[2,3-g]thiochromene.

Following the general procedure B, $AlCl_3$ (0.1 mmol, 13.45 mg), **5j** (0.1 mmol, 28.99 mg) and cyclohexane (0.5 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **6j** (8.20 mg, 37% yield) as a white solid. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 6.77 (s, 2H), 3.01 – 2.96 (m, 4H), 2.71 (t, *J* = 6.1 Hz, 4H), 2.07 (p, *J* = 6.1 Hz, 4H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 132.36, 127.93, 127.62, 29.14, 27.54, 23.04. **HRMS (APCI)** m/z: M calcd for $C_{12}H_{14}S_2$: 222.0537, found 222.0532.



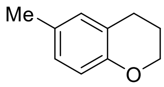
6k: Chromane. [29]

Following the general procedure B, $AlCl_3$ (0.1 mmol, 13.40 mg), **5k** (0.2 mmol, 35.47 mg) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **6k** (13.63mg, 62% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16 – 6.97 (m, 2H), 6.90 – 6.69 (m, 2H), 4.24 – 4.13 (m, 2H), 2.79 (t, J = 6.5 Hz, 2H), 2.06 – 1.96 (m, 2H).



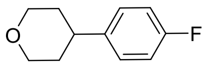
6l: 6-fluorochromane. [29]

Following the general procedure B, $AlCl_3$ (0.05 mmol, 6.65 mg), **5l** (0.1 mmol, 19.40 mg) and cyclohexane (0.5 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **6l** (9.12mg, 60% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.87 – 6.60 (m, 3H), 4.18 – 4.12 (m, 2H), 2.77 (t, J = 6.5 Hz, 2H), 2.02 – 1.95 (m, 2H).



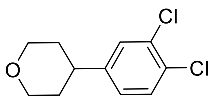
6m: 6-methylchromane. [29]

Following the general procedure B, $AlCl_3$ (0.1 mmol, 13.28 mg), **5m** (0.2 mmol, 37.11 mg) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **6m** (21.32 mg, 72% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.91 – 4.86(m, 2H), 6.71 (d, J = 8.2 Hz, 1H), 4.18 – 4.16 (m, 2H), 2.76 (t, J = 6.5 Hz, 2H), 2.26 (s, 3H), 2.03 – 1.97 (m, 2H).



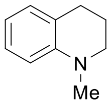
6n: 4-(4-fluorophenyl) tetrahydro-2H-pyran. [29]

Following the general procedure B, $AlCl_3$ (0.1 mmol, 13.57 mg), **5n** (0.2 mmol, 40.89 mg) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **6n** (19.82 mg, 66% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 – 7.16 (m, 2H), 7.02 – 6.98 (m, 2H), 4.11 – 4.04 (m, 2H), 3.52 (td, J = 11.3, 3.5 Hz, 2H), 2.80 – 2.68 (m, 1H), 1.84 – 1.72 (m, 4H).



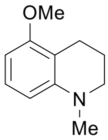
6o: 4-(3,4-dichlorophenyl) tetrahydro-2H-pyran. [29]

Following the general procedure B, $AlCl_3$ (0.05 mmol, 6.68 mg), **5o** (0.1 mmol, 26.91 mg) and cyclohexane (0.5 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **6o** (13.80 mg, 60% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.3 Hz, 1H), 7.30 (s, 1H), 7.05 (dd, J = 8.3, 2.1 Hz, 1H), 4.10 – 4.05 (m, 2H), 3.55 – 3.46 (m, 2H), 2.76 – 2.68 (m, 1H), 1.79 – 1.72 (m, 4H).



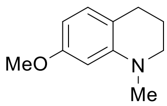
6p: 1-methyl-1,2,3,4-tetrahydroquinoline. [28]

Following the general procedure B, $AlCl_3$ (0.1 mmol, 13.30 mg), **5p** (0.2 mmol, 37.17 mg) and cyclohexane (1 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **6p** (24.78 mg, 84% yield) as a colorless oil. colorless oil (25.11 mg, 85% yield). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.11 (t, *J* = 7.8 Hz, 1H), 6.99 (d, *J* = 7.2 Hz, 1H), 6.69 – 6.51 (m, 2H), 3.26 (t, *J* = 5.6 Hz, 2H), 2.92 (s, 3H), 2.81 (t, *J* = 6.4 Hz, 2H), 2.06 – 2.00 (m, 2H).



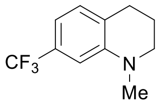
6q: 5-methoxy-1-methyl-1,2,3,4-tetrahydroquinoline. [28]

Following the general procedure B, $AlCl_3$ (0.05 mmol, 6.77 mg), **5q** (0.1 mmol, 21.56 mg) and cyclohexane (0.5 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **6q** (10.63 mg, 60% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-d) δ 7.11 – 6.96 (m, 1H), 6.30 (dd, J = 33.1, 8.2 Hz, 2H), 3.79 (d, J = 3.0 Hz, 3H), 3.16 (dd, J = 6.9, 3.6 Hz, 2H), 2.88 (d, J = 3.1 Hz, 3H), 2.70 – 2.65 (m, 2H), 1.97 (t, J = 5.3 Hz, 2H).



6r: 7-methoxy-1-methyl-1,2,3,4-tetrahydroquinoline. [28]

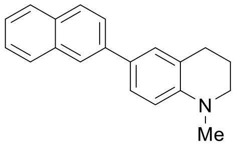
Following the general procedure B, $AlCl_3$ (0.05 mmol, 6.85 mg), **5r** (0.1 mmol, 20.91 mg) and cyclohexane (0.5 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **6r** (12.57 mg, 71% yield) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-d) δ 6.88 (d, J = 8.0 Hz, 1H), 6.25 – 6.15 (m, 2H), 3.80 (d, J = 2.2 Hz, 3H), 3.24 (d, J = 6.4 Hz, 2H), 2.90 (d, J = 2.2 Hz, 3H), 2.73 (t, J = 6.7 Hz, 2H), 2.01 – 1.95 (m, 2H).



6s: 1-methyl-7-(trifluoromethyl)-1,2,3,4-tetrahydroquinoline.

Following the general procedure B, $AlCl_3$ (0.05 mmol, 6.69 mg), **5s** (0.1 mmol, 25.72 mg) and cyclohexane (0.5 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **6s** (14.09 mg, 66% yield) as a colorless oil. colorless oil (14 mg, 66% yield). **^{1}H NMR** (600 MHz, Chloroform-d) δ 7.00 (d, J = 7.7 Hz, 1H), 6.82 (d, J = 7.7 Hz, 1H), 6.73 (s, 1H), 3.27 (t, J = 5.8 Hz, 2H), 2.92 (d, J = 1.7 Hz, 3H), 2.78 (t, J = 6.6 Hz, 2H), 1.98 (t, J = 6.2 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 146.65, 129.53, 129.22, 128.73, 126.28, 126.27, 126.04, 123.33, 112.37, 112.33, 112.29, 112.25, 106.81, 106.77, 106.73, 106.69,

50.95, 38.82, 27.76, 21.93. **HRMS (APCI)** m/z: M+H$^+$ calcd for $C_{11}H_{13}F_3N^+$: 216.0995, found 216.0995.



6t: 1-methyl-6-(naphthalen-2-yl)-1,2,3,4-tetrahydroquinoline.

Following the general procedure B, $AlCl_3$ (0.05 mmol, 6.85 mg), **5t** (0.1 mmol, 32.09 mg) and cyclohexane (0.5 mL). The reaction was stirred at 120 °C for 24 hours and purified through flash chromatography (100% petroleum ether) to give the desired product **6t** (25.12 mg, 88% yield) as a white solid. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.96 (s, 1H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.44 – 7.40 (m, 1H), 7.37 (s, 1H), 6.71 (d, J = 8.5 Hz, 1H), 3.29 (t, J = 5.6 Hz, 2H), 2.96 (s, 3H), 2.88 (t, *J* = 6.6 Hz, 2H), 2.08 – 2.01 (m, 2H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 146.27, 138.71, 133.90, 131.97, 128.61, 128.08, 127.89, 127.66, 127.55, 125.98, 125.93, 125.31, 125.10, 123.97, 123.10, 111.24, 51.26, 39.09, 27.97, 22.44. **HRMS (APCI)** m/z: M+H$^+$ calcd for $C_{20}H_{20}N^+$: 274.1590, found 274.1587.

5 Synthetic applications of C–O/C–S σ-bond metathesis

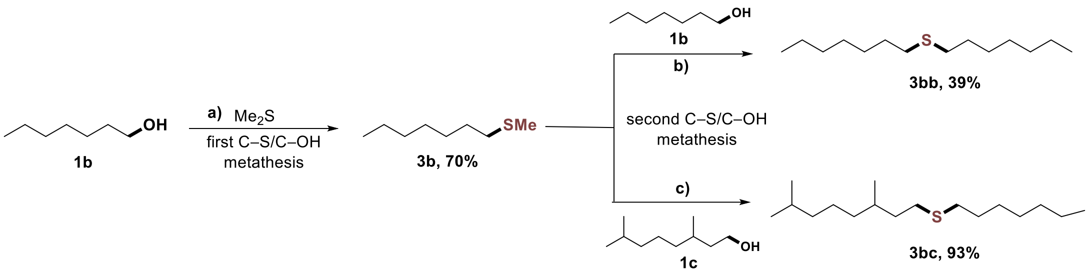


Figure S4: successive C–O/C–S σ-bond metathesis for Me_2S upgrading

a) To a 10 mL Schlenk tube was added $AlCl_3$ (0.1 mmol, 13.19 mg), ZnI_2 (0.2 mmol, 63.82 mg), **1b** (0.2 mmol, 28 uL), thioether (1.0 mmol, 73 uL) and cyclohexane (1 mL). The reaction mixture was stirred at 120 °C for 24 hours, then the reaction was cooled to room temperature. The crude mixture was purified by flash column chromatography to afford the target product **3b** (20.45 mg, 70% yield).

b) To a 10 mL Schlenk tube was added $AlCl_3$ (0.1 mmol, 13.36 mg), ZnI_2 (0.2 mmol, 63.90 mg), **3b** (0.2 mmol, 36 uL), **1b** (0.4 mmol, 56 uL) and cyclohexane (1 mL). The reaction mixture was stirred at 120 °C for 24 hours, then the reaction was cooled to room temperature. The crude mixture was purified by flash column chromatography to afford the target product **3bb** (18.0 mg, 39% yield).

c) To a 10 mL Schlenk tube was added $AlCl_3$ (0.1 mmol, 13.32 mg), ZnI_2 (0.2 mmol, 63.25 mg), **3b** (0.2 mmol, 36 uL), **1c** (0.4 mmol, 78 uL) and cyclohexane (1 mL). The reaction mixture was stirred at 120 °C for 24 hours, then the reaction was cooled to room temperature. The crude mixture was purified by flash column chromatography to afford the target product **3bc** (50.67 mg, 93% yield).

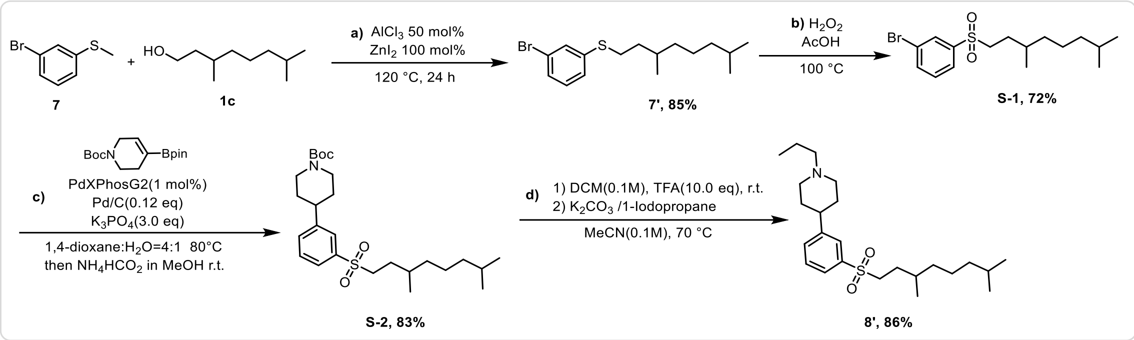


Figure S5: Pridopidine derivatization of **8'**

a) To a 10 mL Schlenk tube was added $AlCl_3$ (0.1 mmol, 50 mol%), ZnI_2 (0.2 mmol, 1.0 equiv.), **7** (1.0 mmol, 5.0 equiv.), **1c** (0.2 mmol, 1.0 equiv.) and cyclohexane (1 mL). The reaction mixture was stirred at 120 °C for 24 hours, then the reaction was cooled to room temperature. The crude mixture was purified by flash column chromatography to afford the target product **7'** (20.45 mg, 85% yield).

b) To a 10 mL Schlenk tube was added **7'** (5 mmol), AcOH (1.0 mL), H_2O_2 (2.2 mL), the reaction mixture was stirred at 100 °C for 12 hours, then the reaction was cooled to room temperature. Quenched with saturated $NaHCO_3$ solution, the organic phase was separated and the aqueous phase was extracted with ethyl acetate (3×10 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by column chromatography on silica get to give the product **S-1** (80% yield).

c) To an oven dried 2-5 mL microwave vial was added boronic ester/acid (0.25 mmol, 1 equiv.), PdXPhosG2 (0.0025 mmol, 0.01 equiv.), 10% Pd/C (0.04 mmol, 0.12 equiv.), K_3PO_4 (0.75 mmol, 3 equiv.) and **S-1** (0.25 mmol, 1 equiv.). The vial was capped and purged, then 1,4-dioxane (800 μL) and water (200 μL) were added. The reaction mixture was stirred at 80 °C for 4 h, followed by the addition of NH_4HCO_2 in MeOH (1.25 M) (158 mg NH_4HCO_2 in 2 mL MeOH, 10 eq. 2.5 mmol). After this, the reaction was stirred for 16 h at room temperature. The vial was de-capped, and the reaction mixture was diluted with ethyl acetate, filtered through Celite and rinsed through with further ethyl acetate. The solvent was removed in vacuo and purification by column chromatography on silica get to give the product **S-2** (83% yield).

d) To the solution of **S-2** (1.0 equiv.) in DCM TFA (10 equiv.) was added, the mixture stirred at room temperature until S-2 completely conversion. The solvent was removed under reduced pressure and dried with PhF for two times. The crude product was resolved in CH_3CN (0.1 M), K_2CO_3 (3.0 equiv.), 1-Iodoproane (1.2 equiv.) were added. The reaction mixture was stirred at 70 °C overnight and then cooled to room temperature. H_2O was added and the organic phase was separated and the aqueous phase was extracted with ethyl acetate (3×10 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by column chromatography on silica get to give the product **8'** in 86% yield.

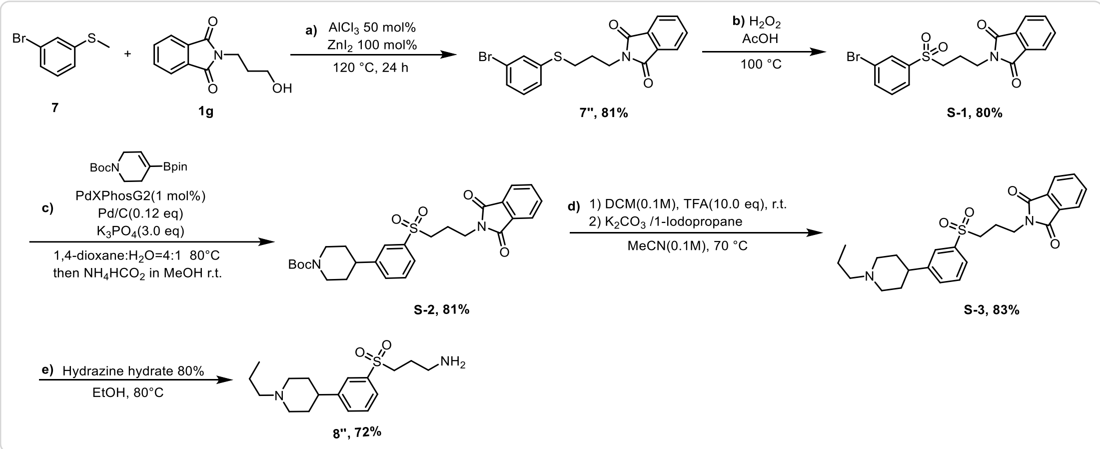
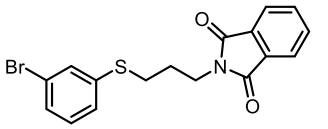


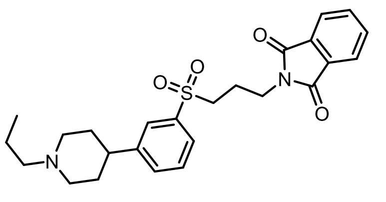
Figure S6: Pridopidine derivatization of 8''

e) S-3 (0.3 mmol) was dissolved in EtOH (2 mL), hydrazine hydrate (1 mL) was added. The reaction mixture was stirred at 80 °C for 3 hours and then cooled to room temperature. H_2O was added and the organic phase was separated and the aqueous phase was extracted with ethyl acetate (3×10 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by column chromatography on silica (DCM/MeOH = 5–10, Et_3N 1%) to give the product **8''** in 72% yield.



7'': 2-(3-((3-bromophenyl)thio)propyl)isoindoline-1,3-dione.

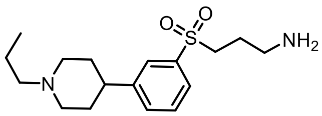
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.03 (s, 1H), 7.89 – 7.77 (m, 3H), 7.78 – 7.67 (m, 3H), 7.44 (td, *J* = 7.8, 2.2 Hz, 1H), 3.78 (t, *J* = 6.9 Hz, 2H), 3.18 (dd, *J* = 9.4, 6.6 Hz, 2H), 2.11 (p, *J* = 7.1 Hz, 2H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 168.10, 140.58, 136.95, 134.20, 131.79, 131.03, 130.87, 126.74, 123.43, 123.41, 53.96, 36.19, 22.31.



S-3: **2-(3-((3-(1-propylpiperidin-4-yl)phenyl)sulfonyl)propyl)isoindoline-1,3-dione**

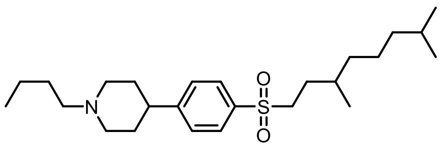
^{1}H NMR (400 MHz, Chloroform-d) δ 7.82 – 7.73 (m, 3H), 7.70 (dd, J = 5.5, 3.1 Hz, 3H), 7.60 (d, J = 7.8 Hz, 1H), 7.47 (t, J = 7.8 Hz, 1H), 3.73 (t, J = 6.8 Hz, 2H), 3.60 (d, J = 12.0 Hz, 2H), 3.21 – 3.12 (m, 2H), 2.98 (td, J = 12.1, 5.6 Hz, 5H), 2.55 (qd, J = 13.1, 3.8 Hz, 2H), 2.13 – 1.99 (m, 4H), 1.97

– 1.87 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H).



8'': 3-((3-(1-propylpiperidin-4-yl)phenyl)sulfonyl)propan-1-amine

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.77 (s, 1H), 7.73 (d, *J* = 7.7 Hz, 1H), 7.54 – 7.43 (m, 2H), 3.20 (t, *J* = 7.9 Hz, 2H), 3.14 (d, *J* = 11.3 Hz, 2H), 2.93 (br, 2H), 2.83 (d, *J* = 7.2 Hz, 2H), 2.67 – 2.60 (m, 1H), 2.42 (t, *J* = 8.0 Hz, 2H), 2.15 (d, *J* = 11.6 Hz, 2H), 1.93 – 1.87 (m, 6H), 1.62 – 1.55 (m, 2H), 0.92 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 147.71, 139.18, 132.14, 129.45, 126.47, 125.83, 60.64, 53.84, 53.78, 42.14, 40.13, 32.72, 25.54, 19.74, 11.90. **HRMS (APCI)** m/z: M+H$^+$ calcd for $C_{17}H_{29}O_2N_2S^+$: 325.1944, found 325.1937.



8': **4-(3-((3,7-dimethyloctyl)sulfonyl)phenyl)-1-propylpiperidine**

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.67 (s, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 3.24 (d, *J* = 11.7 Hz, 2H), 3.05 – 2.89 (m, 2H), 2.77 – 2.81 (m, 1H), 2.61– 2.52 (m, 4H), 2.08 (q, *J* = 12.9 Hz, 2H), 1.85 (d, *J* = 13.5 Hz, 2H), 1.65 – 1.59 (m, 3H), 1.46 – 1.33 (m, 3H), 1.14 – 1.05 (m, 3H), 0.99 – 0.95 (m, 3H), 0.83 (t, *J* = 7.5 Hz, 3H), 0.72 – 0.71 (m, 9H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 146.36, 139.02, 131.82, 129.30, 126.00, 125.75, 77.21, 59.55, 54.02, 52.98, 40.55, 38.65, 36.18, 31.46, 31.11, 28.73, 27.47, 24.56, 24.10, 22.29, 22.19, 18.83, 18.55, 11.31. **RMS (APCI)** m/z: M+H$^+$ calcd for $C_{24}H_{42}O_2NS^+$: 408.2931, found 408.2927.

6 Mechanistic experiments

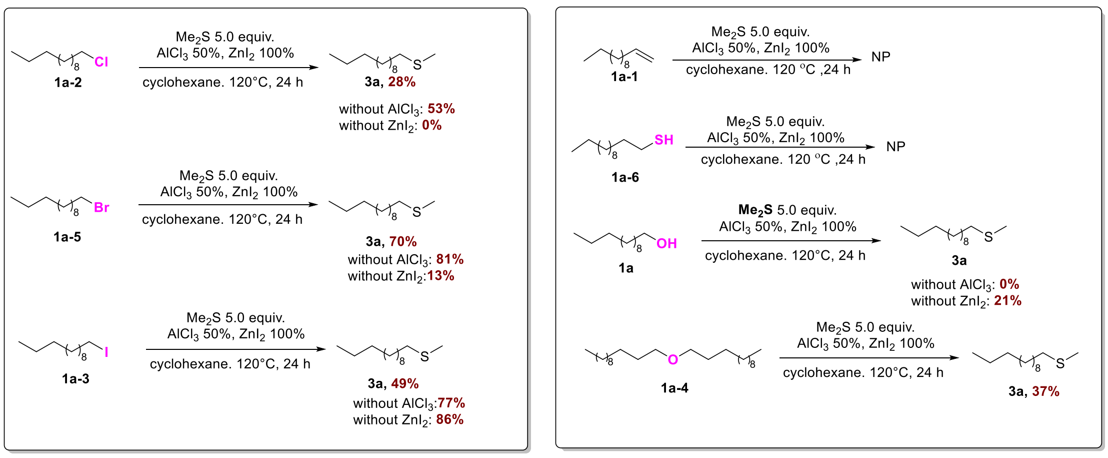


Figure S7: Control experiments I

1a-2, **1a-5**, **1a-3** were reacted without $AlCl_3$ respectively, without ZnI_2 respectively and reacted under standard conditions respectively, the corresponding yield was measured by gas chromatography. **1a-1**, **1a-6**, **1a**, **1a-4** were reacted under standard conditions respectively and the corresponding yield was measured by gas chromatography.

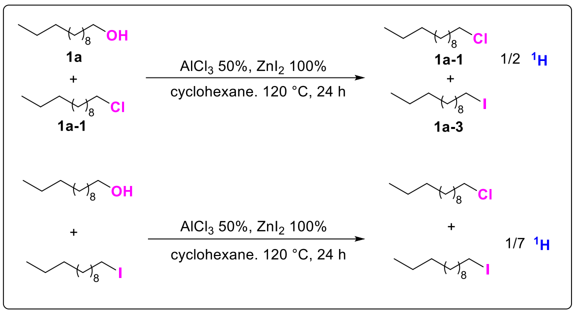


Figure S8: Control experiments II

1a and **1a-1** were added in equal proportion to react under standard conditions and the proportion of products was detected by NMR. **1a** and **1a-3** were added in equal proportion to react under standard conditions and the proportion of products was detected by NMR.

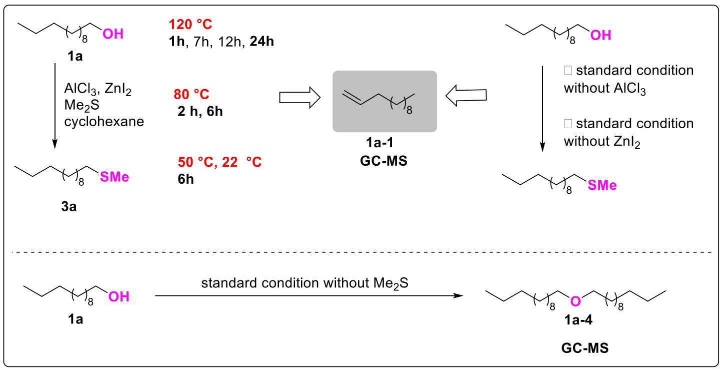


Figure S9: analysis of the reaction mixture with GC-MS

Under standard conditions, only olefins **1a-1** were detected by GC-MS at different reaction temperatures and reaction times. Under standard conditions, GC-MS detection of 1a without $AlCl_3$ or ZnI_2 also only found **1a-1**. 1a reacted without Me_2S, trace **1a-4** was detected.

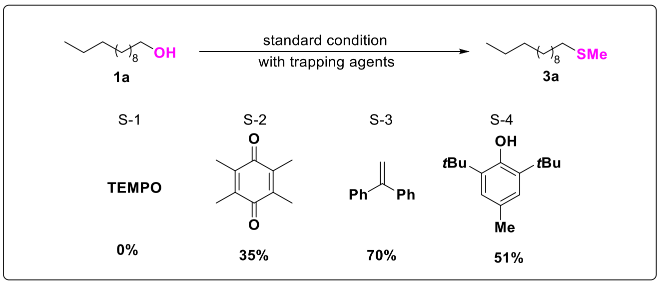


Figure S10: radical trap experiments

To a 10 mL Schlenk tube was added $AlCl_3$ (0.1 mmol, 13.35 mg), ZnI_2 (0.2 mmol, 63.89 mg), substrate **1a** (0.2 mmol, 45 uL), TEMPO (0.2 mmol, 31.69 mg) and cyclohexane (1.0 ml). The reaction mixture was stirred at 120 °C for 24 hours. Then the reaction was cooled to room temperature, and the solvent was removed under reduced pressure. There is no reaction measured by NMR.

To a 10 mL Schlenk tube was added $AlCl_3$ (0.1 mmol, 13.46 mg), ZnI_2 (0.2 mmol, 63.76 mg), substrate **1a** (0.2 mmol, 45 uL), **S-2** (0.2 mmol, 32.84 mg) and cyclohexane (1.0 ml). The reaction mixture was stirred at 120 °C for 24 hours. Then the reaction was cooled to room temperature, and the solvent was removed under reduced pressure. The yield of **3a** is 35% measured by NMR.

To a 10 mL Schlenk tube was added $AlCl_3$ (0.1 mmol, 13.51 mg), ZnI_2 (0.2 mmol, 63.52 mg), substrate **1a** (0.2 mmol, 45 uL), **S-3** (0.2 mmol, 35 uL) and cyclohexane (1.0 ml). The reaction mixture was stirred at 120 °C for 24 hours. Then the reaction was cooled to room temperature, and the solvent was removed under reduced pressure. The yield of **3a** is 70% measured by NMR.

To a 10 mL Schlenk tube was added $AlCl_3$ (0.1 mmol, 13.35 mg), ZnI_2 (0.2 mmol, 63.84 mg), substrate **1a** (0.2 mmol, 45 uL), **S-4** (0.2 mmol, 44.15 mg) and cyclohexane (1.0 ml). The reaction mixture was stirred at 120 °C for 24 hours. Then the reaction was cooled to room temperature, and the solvent was removed under reduced pressure. The yield of **3a** is 51% measured by NMR.

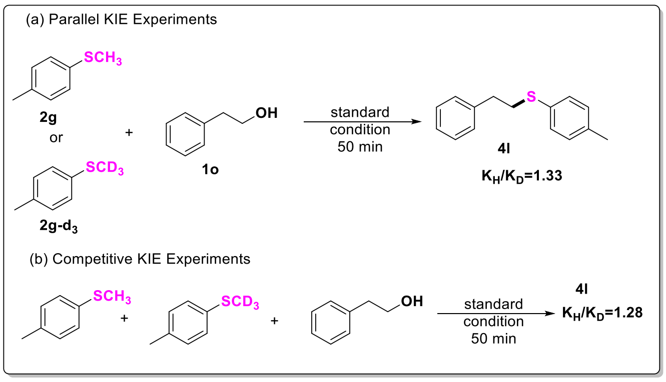


Figure S11：Kinetic isotope effect (KIE) experiments

Parallel Kinetic isotope effect (KIE) experiments: **2g** and **2g-d3** reacted with1o under standard conditions respectively, and then cooled to room temperature after reaction for 50 minutes. Isotrimethoxybenzene as the internal standard, the yield of **4l** was measured by NMR and calculated the KIE.

Competitive Kinetic isotope effect (KIE) experiments: **2g, 2g-d3** and **1o** were added in equal proportion to react for 50 minutes and then cooled to room temperature. Isotrimethoxybenzene as the internal standard, the residual amounts of **2g** and **2g-d3** were detected by NMR, and the conversion amounts of **2g** and **2g-d3** were calculated, then calculated the KIE.

7 DFT calculations

Density functional calculations were performed using the B3LYP hybrid functional with D3 dispersion corrections (BJ damping)[30,31] as implemented in the Gaussian 16 program.[32] Geometries were optimized using the def2-SVP basis sets, and analytic frequency calculations were carried out at the same level of theory as the geometry optimizations. The final energies in the toluene solvent were obtained by single-point calculations employing the SMD[33] continuum solvation model and the larger def2-TZVPP basis sets. The energies reported are Gibbs free energies, which include zero-point vibrational corrections, thermal and entropy corrections at 298.15 K and solvation energies.

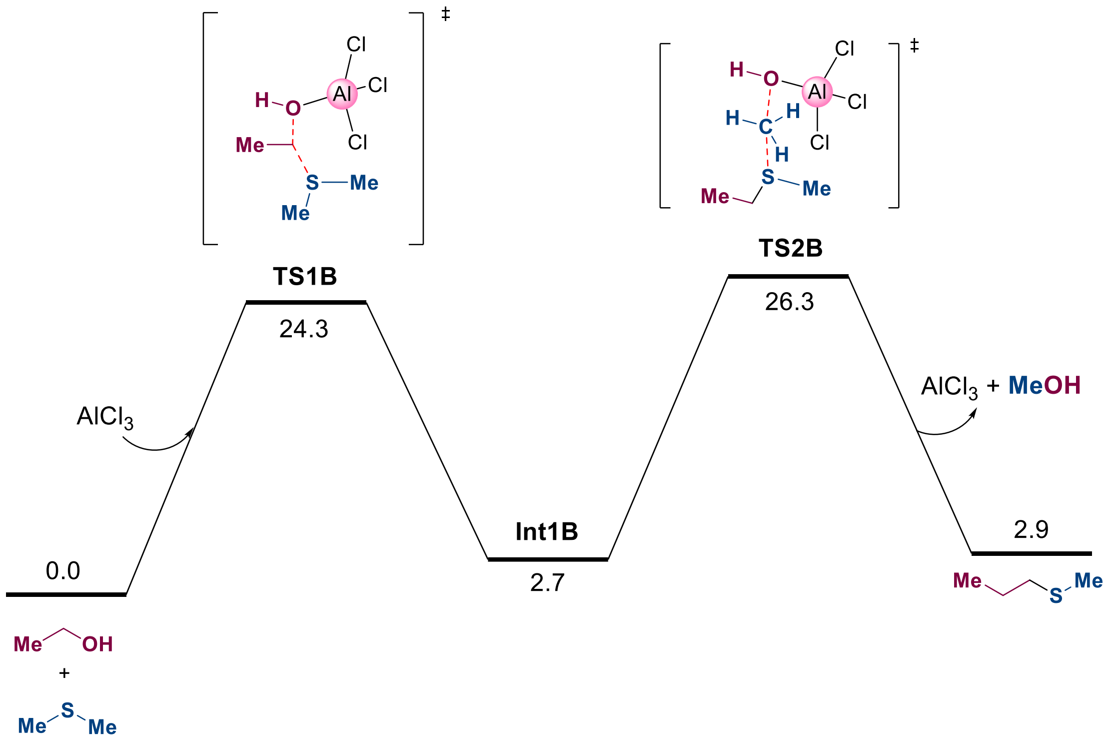


Figure S12: Gibbs free energy profile (in kcal/mol) for the C-O/C-S σ-bond metathesis of ethyl alcohol with dimethyl sulfide catalyzed by AlCl3 at the SMD-B3LYP-D3BJ/def2-TZVPP//B3LYP-D3BJ/def2-SVP level.

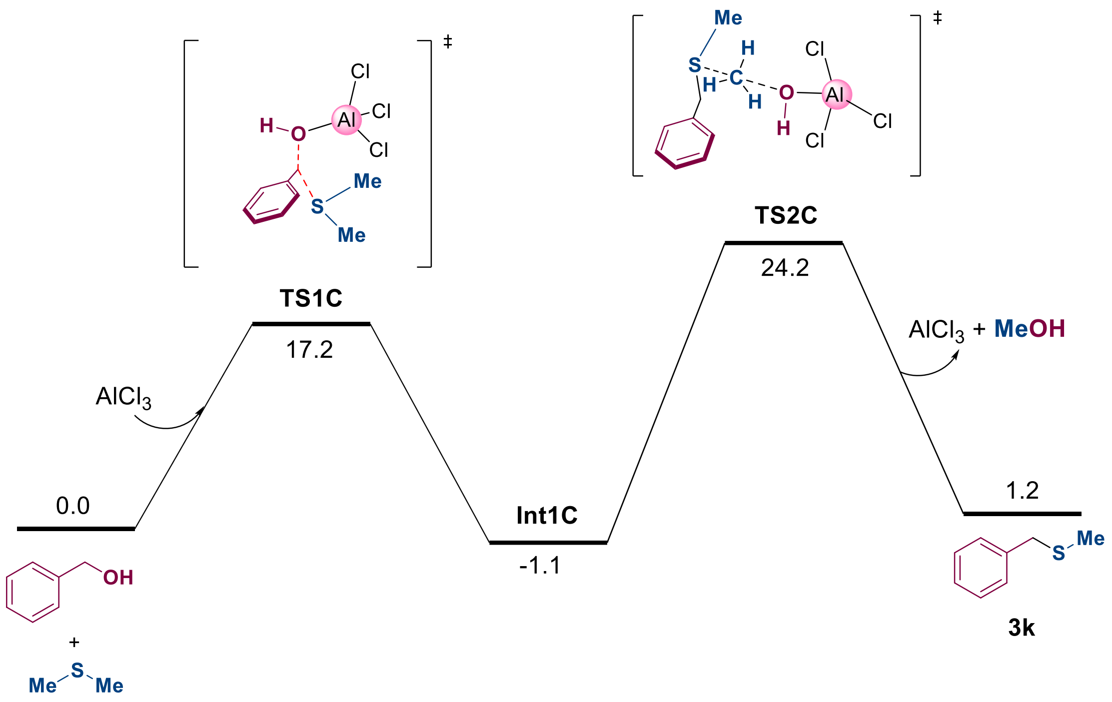


Figure S13: Gibbs free energy profile (in kcal/mol) for the C-O/C-S σ-bond metathesis of benzyl alcohol with dimethyl sulfide catalyzed by AlCl3 at the SMD-B3LYP-D3BJ/def2-TZVPP//B3LYP-D3BJ/def2-SVP level.

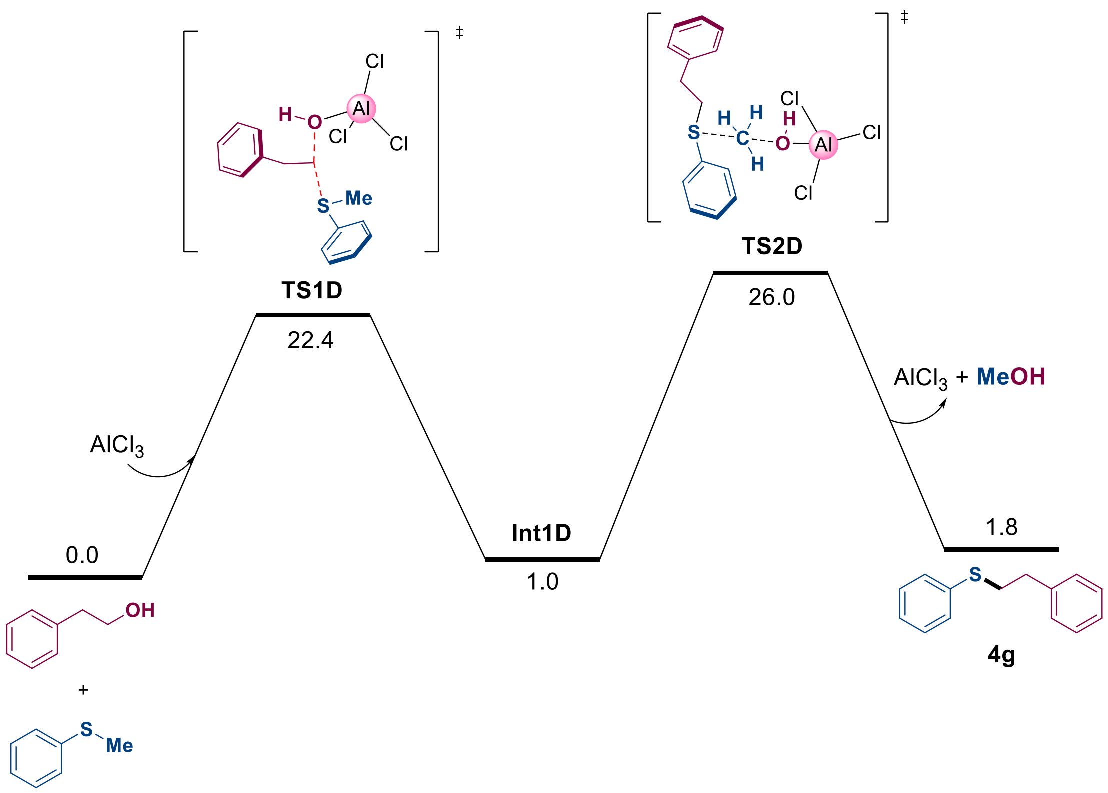


Figure S14: Gibbs free energy profile (in kcal/mol) for the C-O/C-S σ-bond metathesis of phenethyl alcohol with thioanisole catalyzed by AlCl3 at the SMD-B3LYP-D3BJ/def2-TZVPP//B3LYP-D3BJ/def2-SVP level.

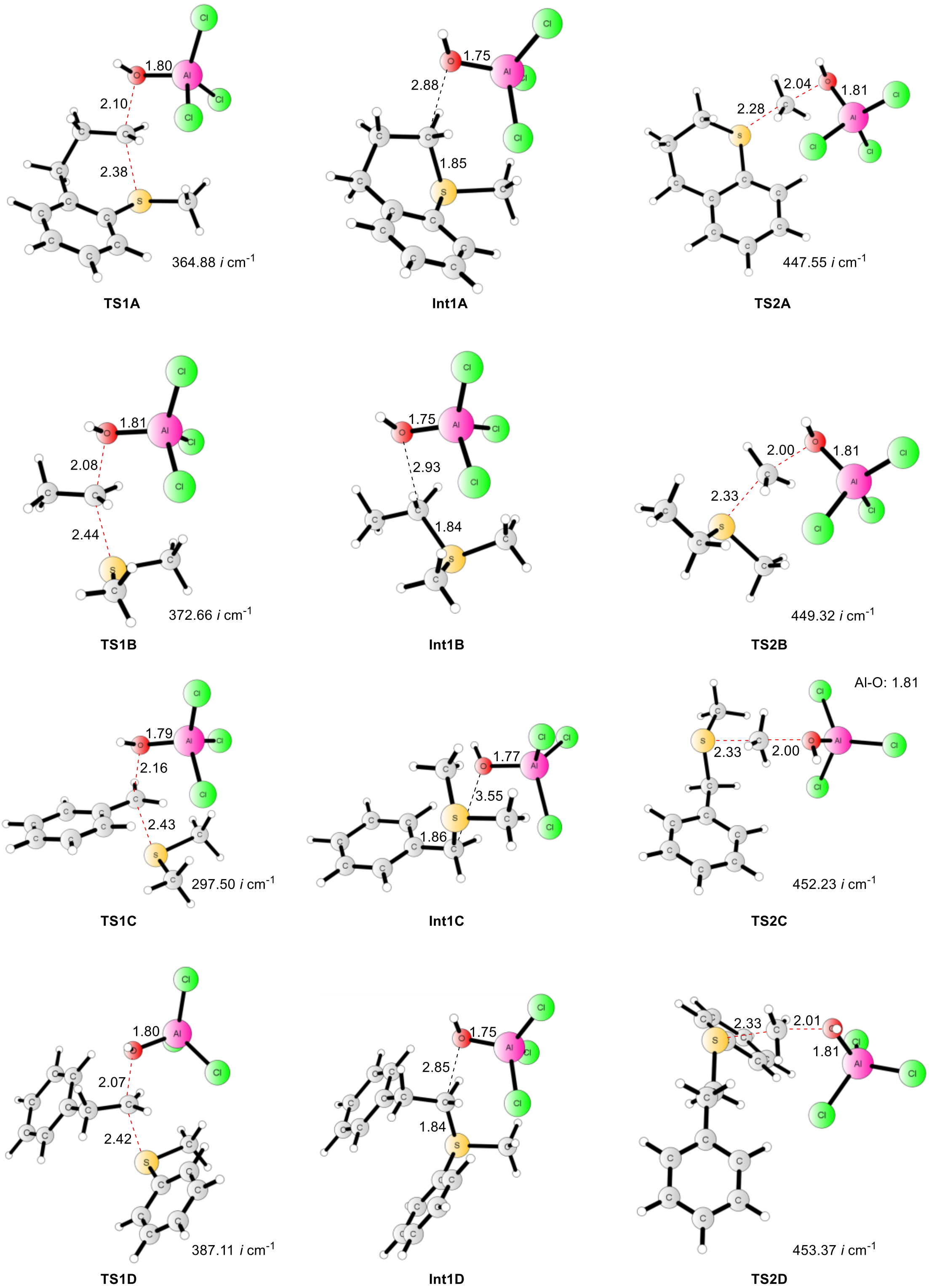


Figure S15: Optimized geometries of the critical intermediates and transition states. All distances are given in Å.

Table S3 Calculated energies (in Hartree) for all stationary points

Stationary point	Thermal correction to Gibbs free energy	Single-point energy (SMD)-B3LYP-D3BJ/def2-TZVPP
5a	0.17975	-863.18468
6a	0.13281	-747.39035
CH_3OH	0.02831	-115.78387
$AlCl_3$-**5a**	0.17866	-2486.62475
TS1A	0.17566	-2486.58541
Int1A	0.17485	-2486.61482
TS2A	0.17505	-2486.58159
CH_3CH_2OH	0.05429	-155.12402
$AlCl_3$-CH_3CH_2OH	0.04837	-1778.55518
CH_3SCH_3	0.04810	-478.09456
$CH_3CH_2SCH_3$	0.07427	-517.43033
TS1B	0.11579	-2256.62624
Int1B	0.11858	-2256.66350
TS2B	0.11667	-2256.62397
$C_6H_5CH_2OH$	0.10041	-346.95118
$AlCl_3$-$C_6H_5CH_2OH$	0.09715	-1970.38364
3k (C6H5CH2SCH3)	0.12113	-709.26082
TS1C	0.16413	-2448.46658
Int1C	0.16646	-2448.49814
TS2C	0.16450	-2448.45582
$C_6H_5CH_2CH_2OH$	0.12810	-386.28789
$AlCl_3$-$C_6H_5CH_2CH_2OH$	0.12520	-2009.71955
$C_6H_5SCH_3$	0.09660	-669.92657
4g ($C_6H_5CH_2CH_2SC_6H_5$)	0.19592	-940.42733
TS1D	0.23838	-2679.62404
Int1D	0.24035	-2679.66011
TS2D	0.24045	-2679.62034

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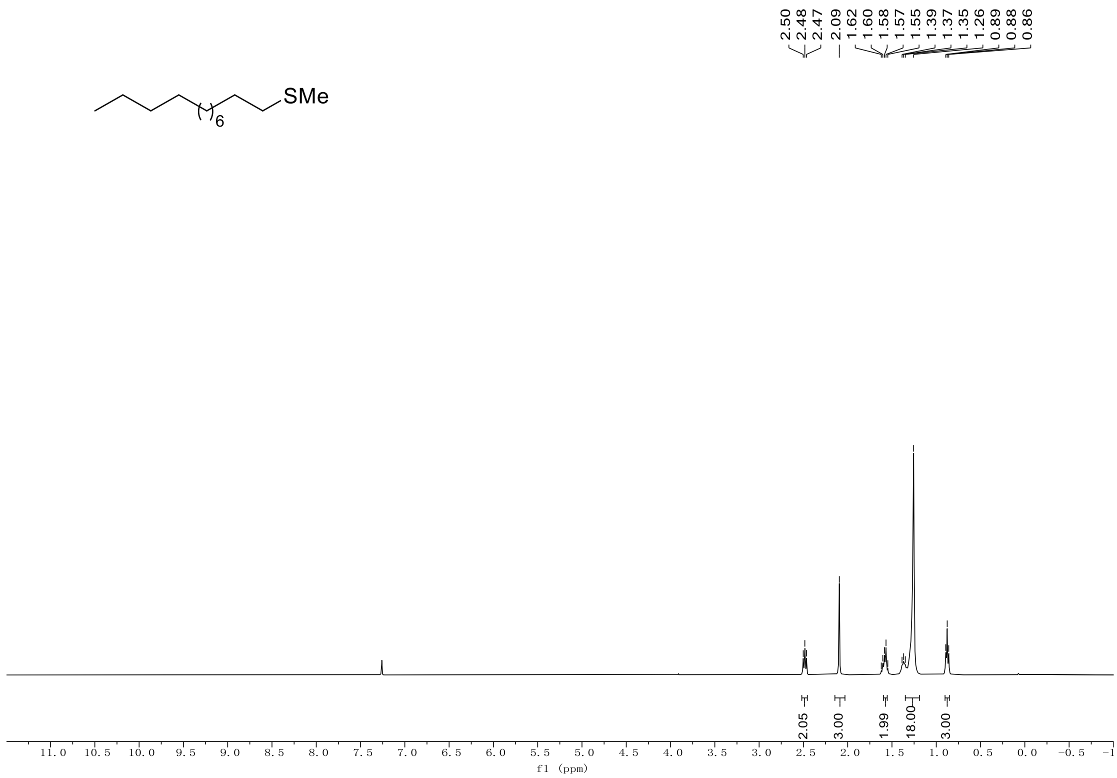
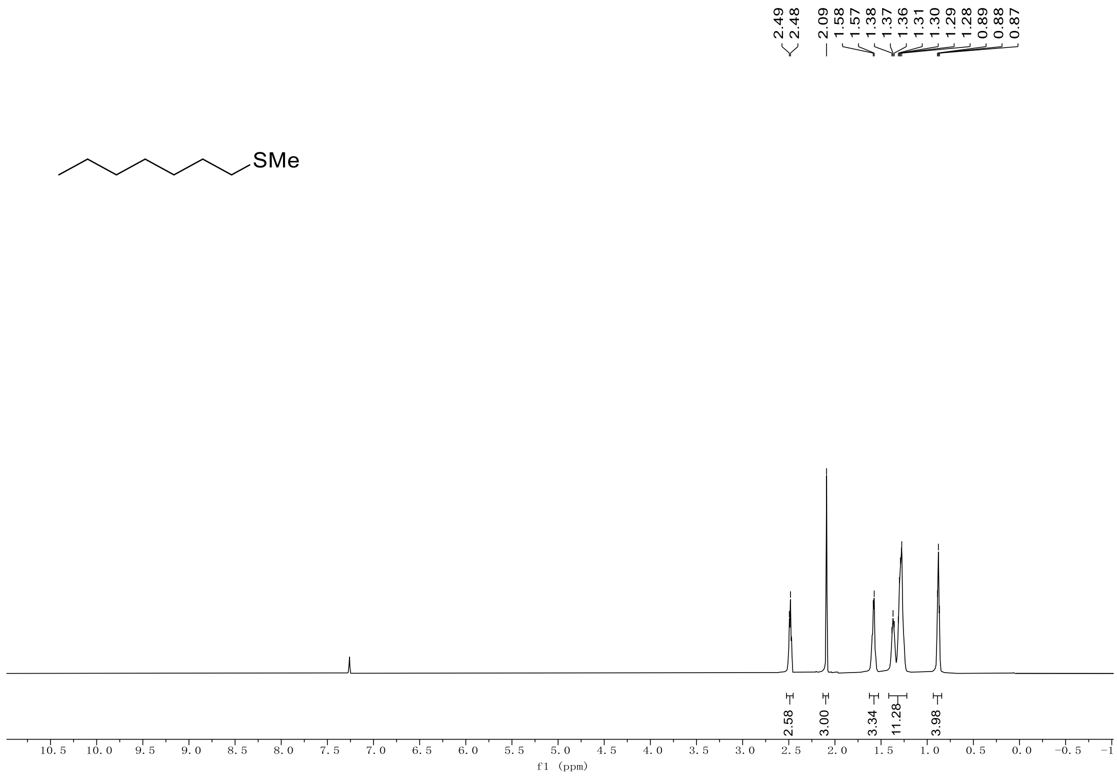
9 NMR spectroscopic data



[1]H NMR of compound **3a** (400 MHz, $CDCl_3$)



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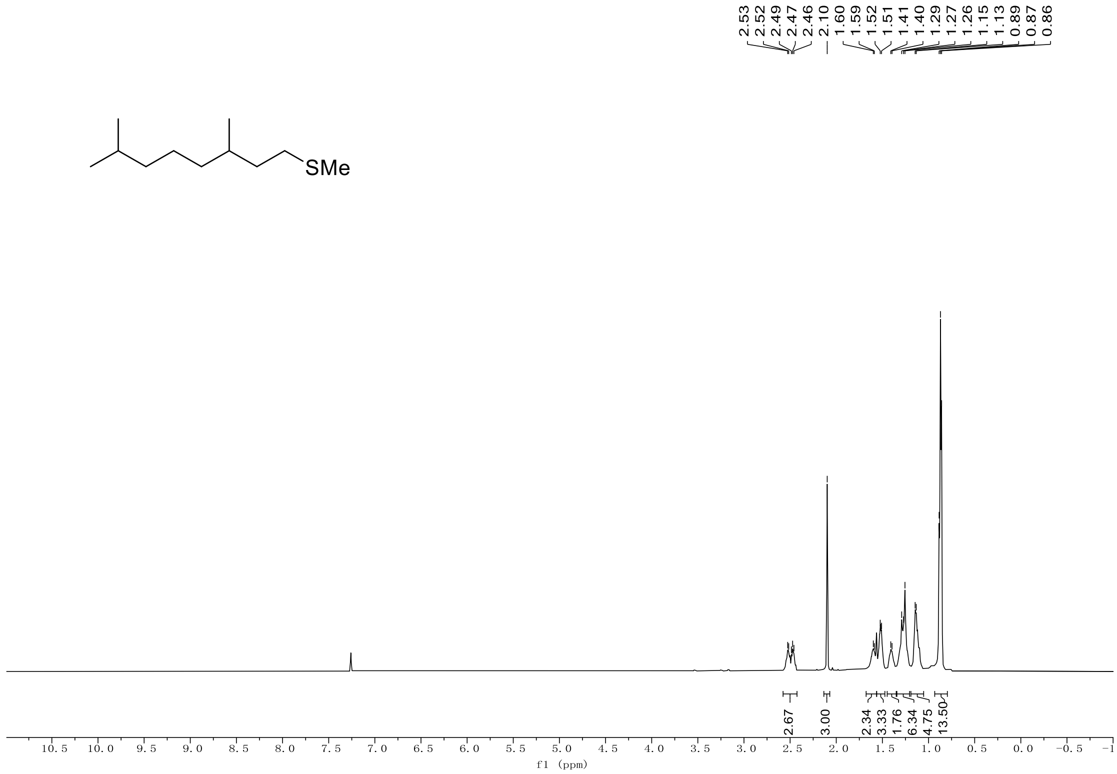
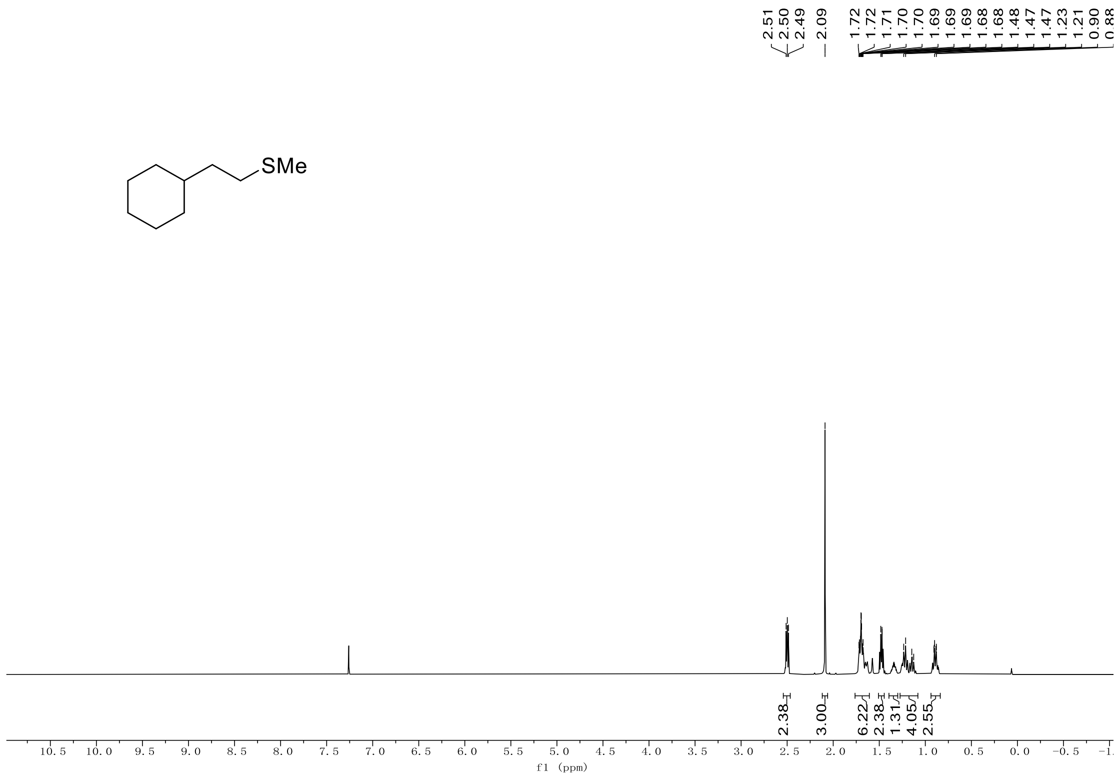
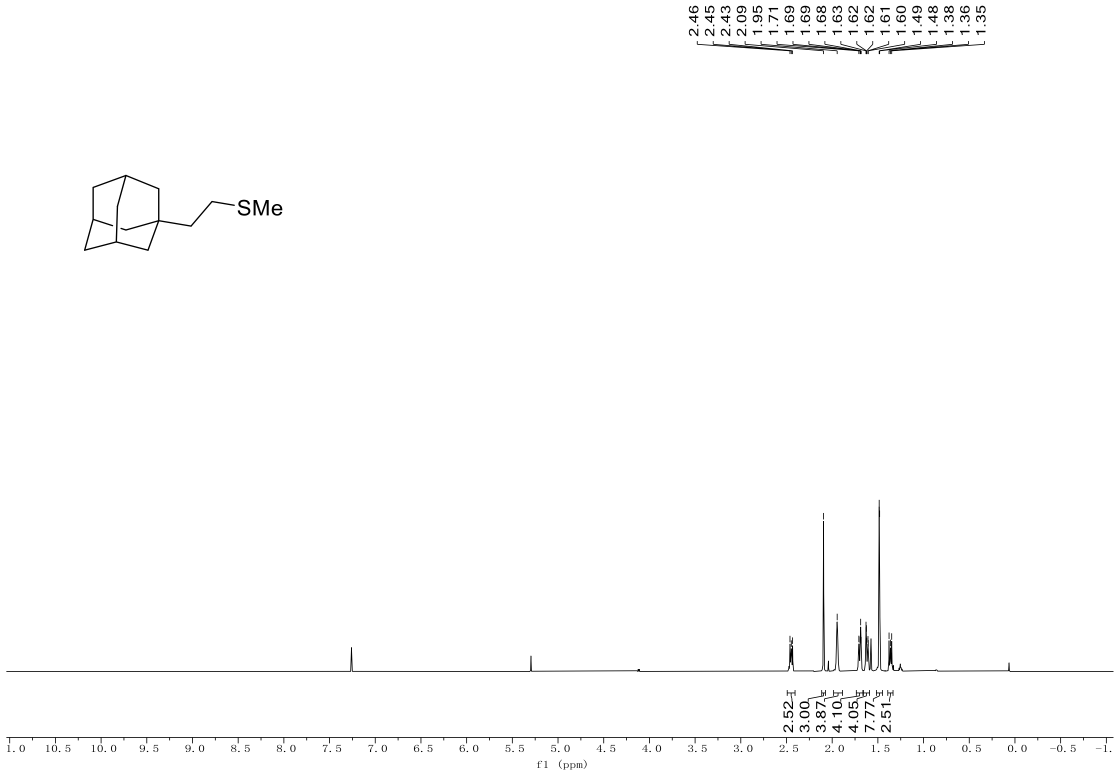


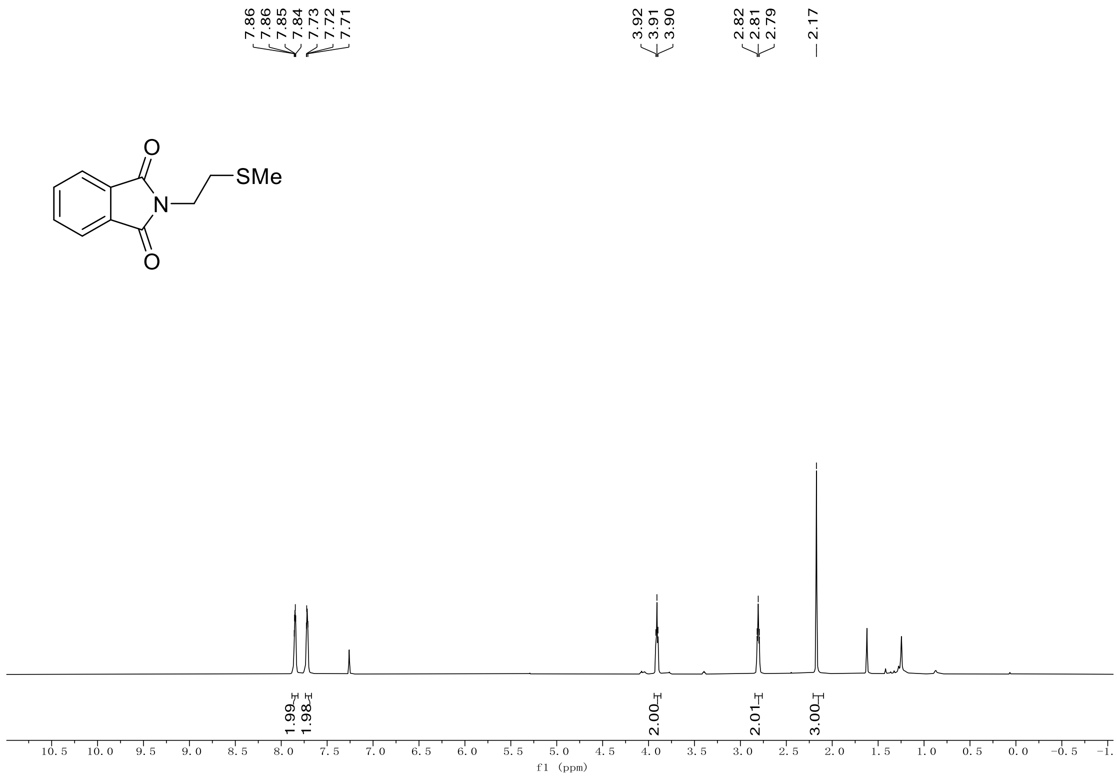
^{1}H NMR of compound **3c** (600 MHz, $CDCl_3$)



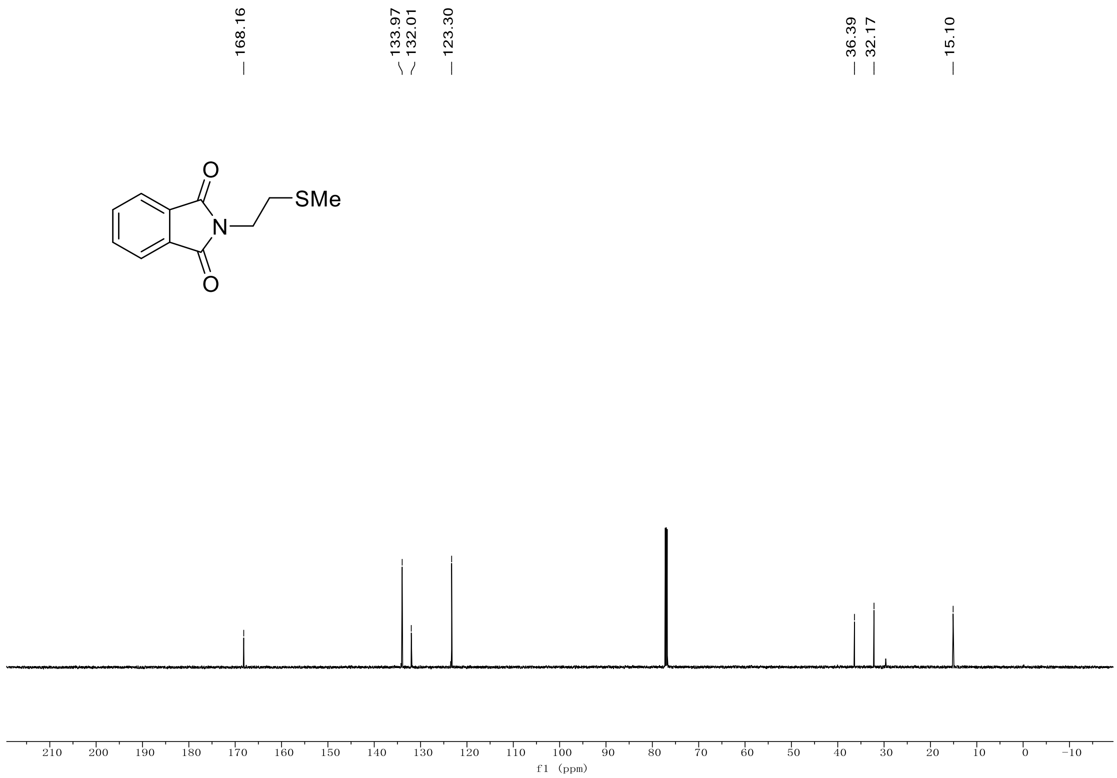
^{1}H NMR of compound **3d** (600 MHz, $CDCl_3$)



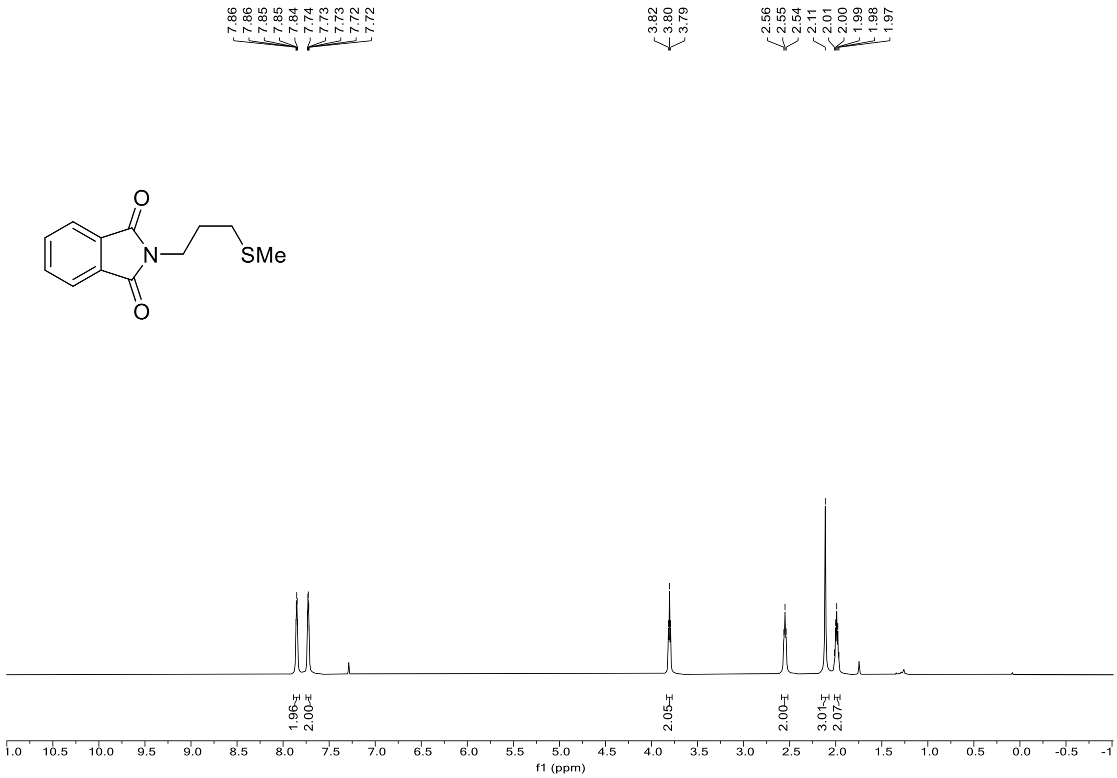
[1]H NMR of compound **3e** (600 MHz, $CDCl_3$)



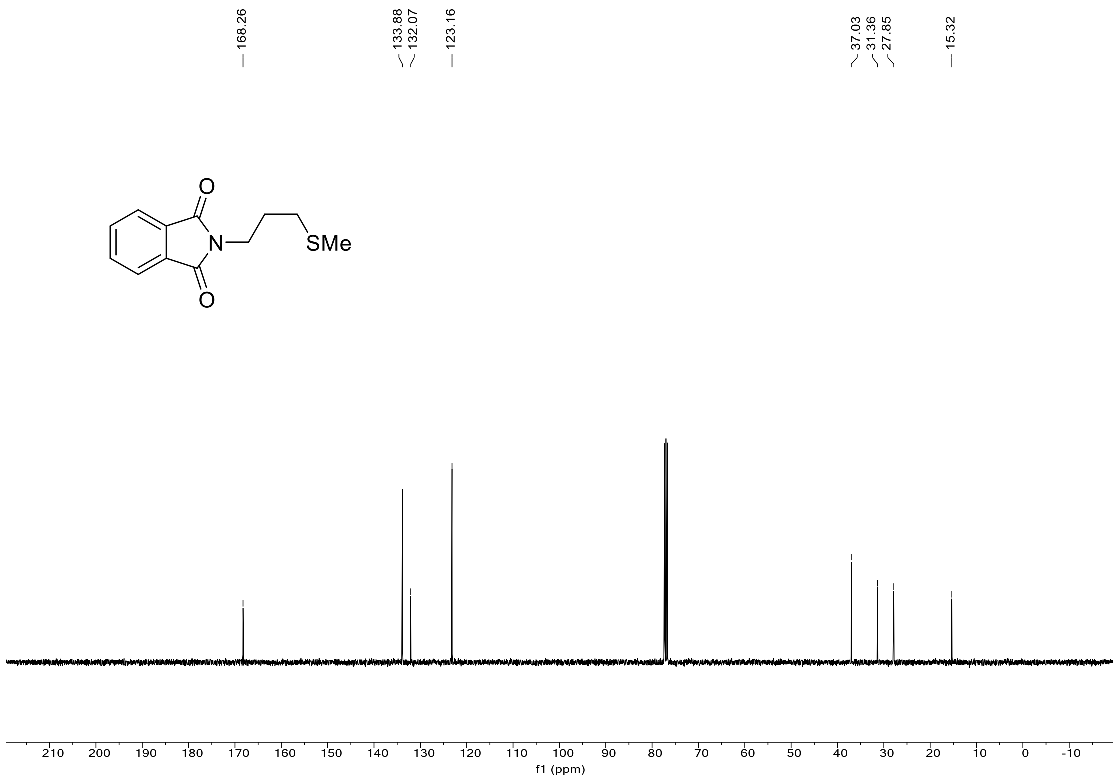
[1]H NMR of compound **3f** (600 MHz, $CDCl_3$)



^{13}C NMR of compound **3f** (151 MHz, $CDCl_3$)



^{1}H NMR of compound **3g** (600 MHz, $CDCl_3$)



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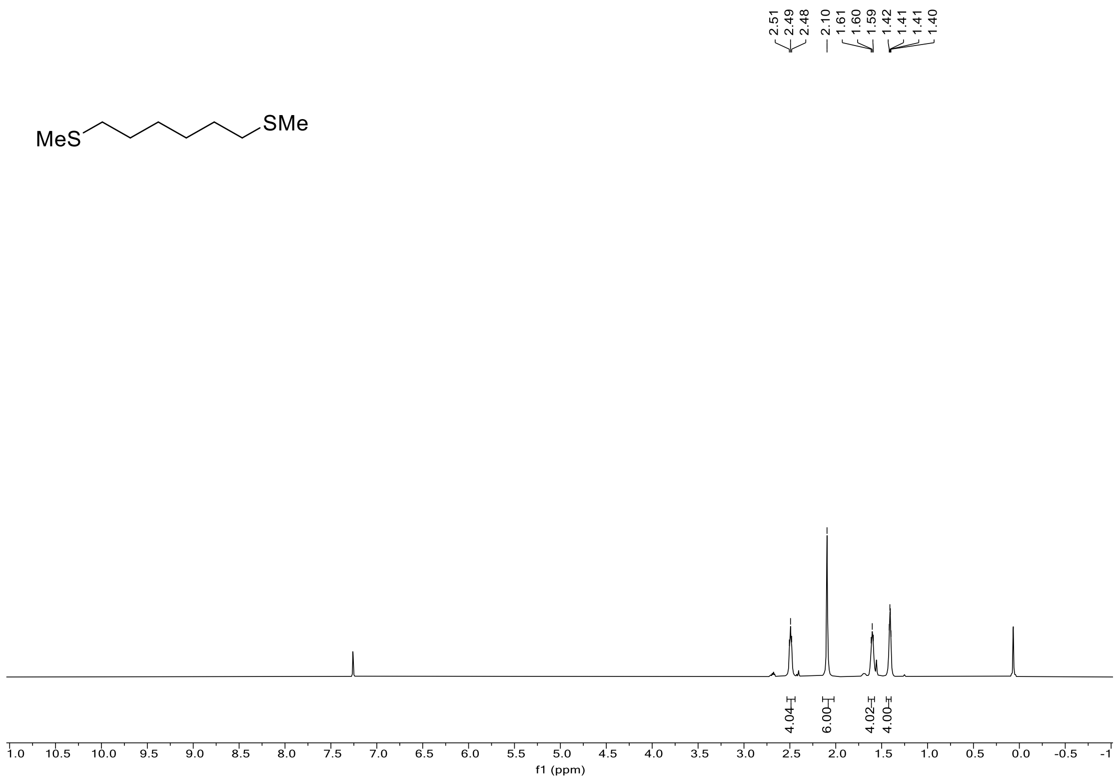
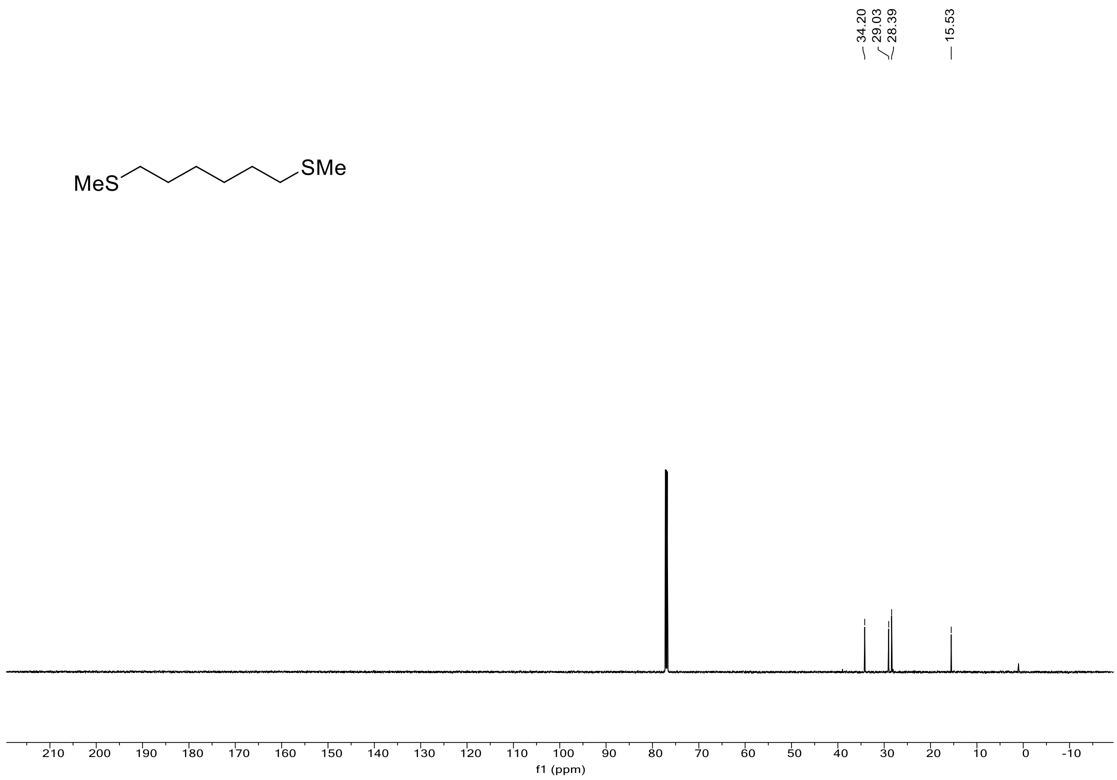
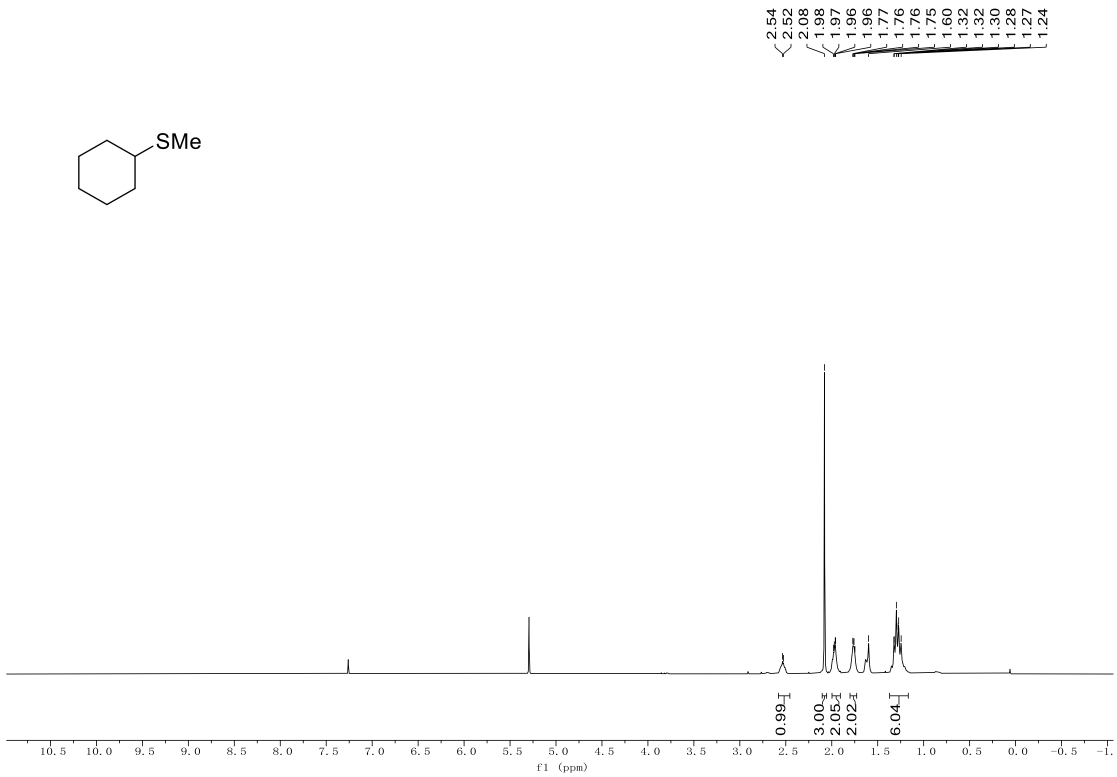


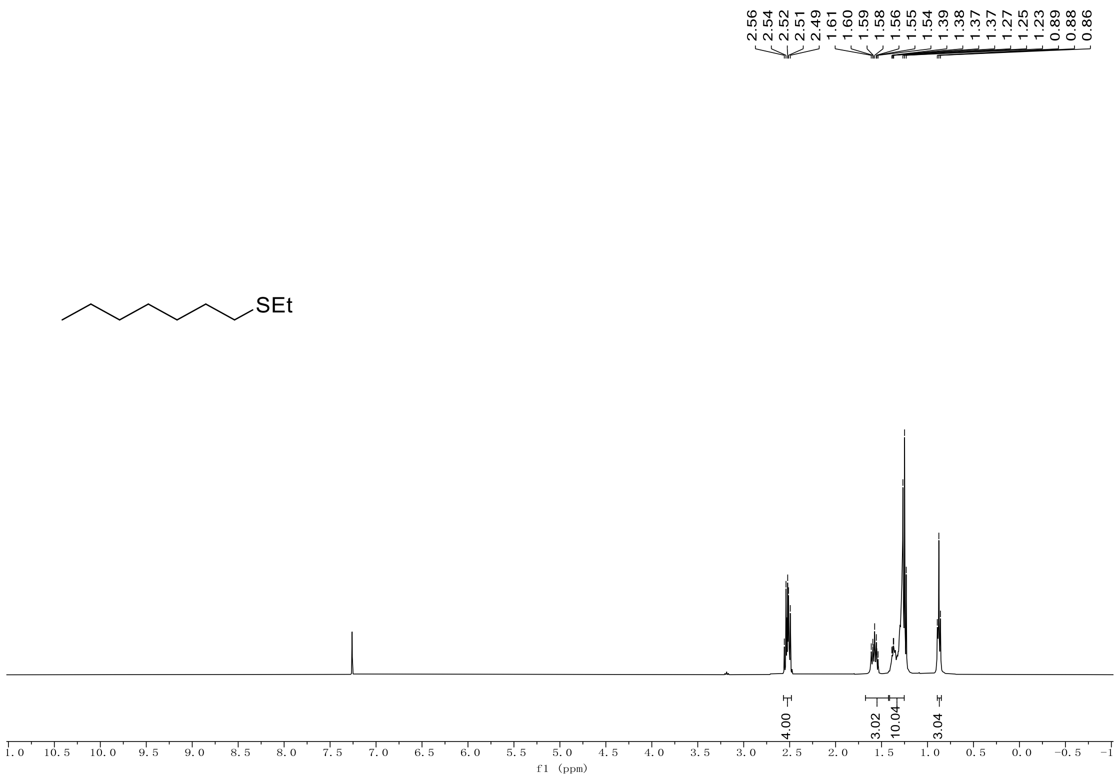
^{1}H NMR of compound **3h** (600 MHz, $CDCl_3$)



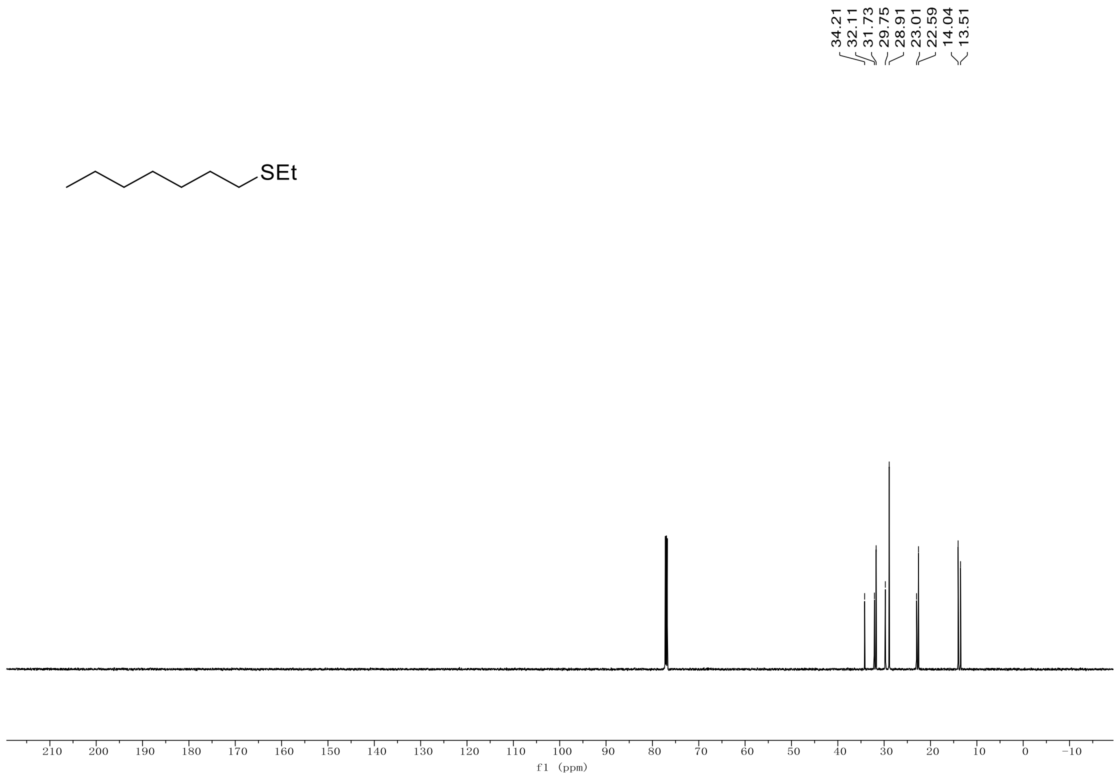
^{13}C NMR of compound **3h** (151 MHz, CDCl$_3$)



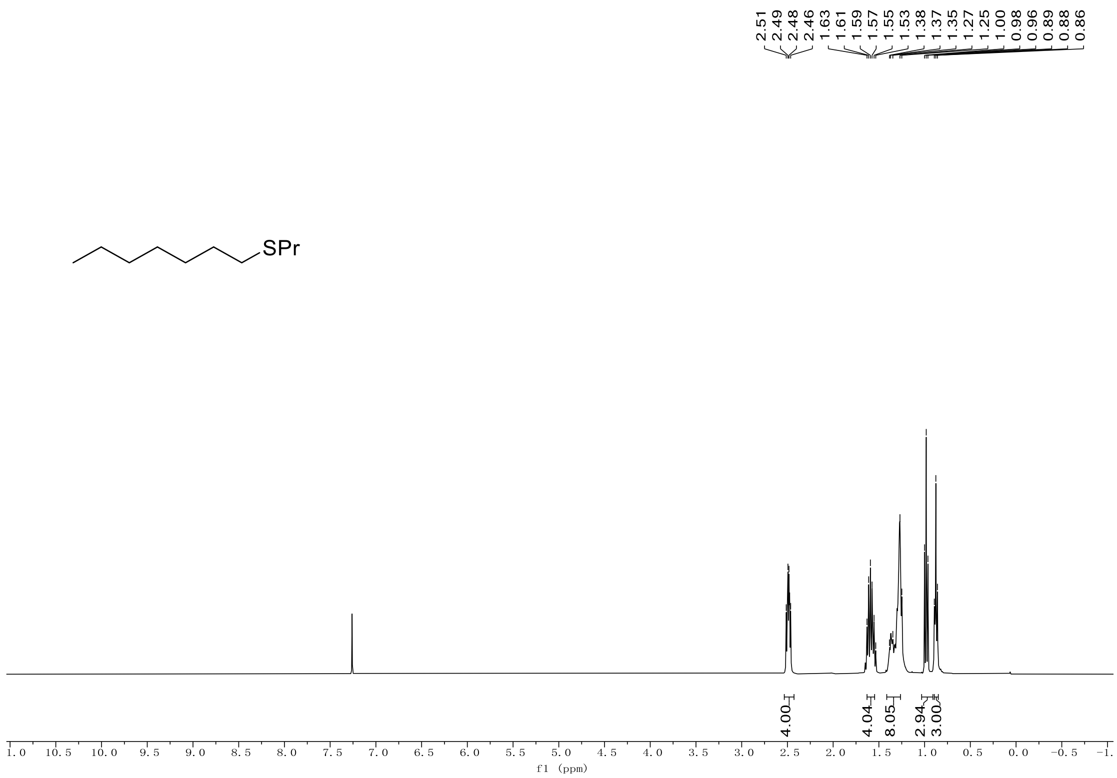
^{1}H NMR of compound **3i** (400 MHz, CDCl$_3$)



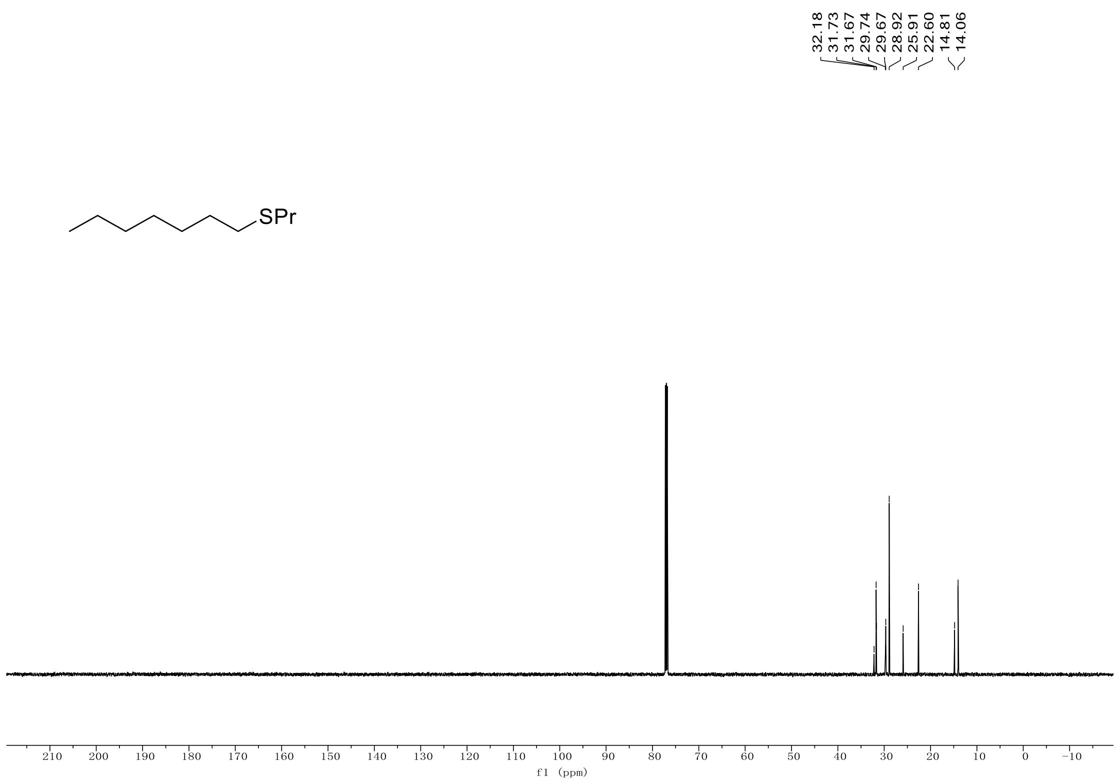
[1]H NMR of compound **3j** (400 MHz, $CDCl_3$)



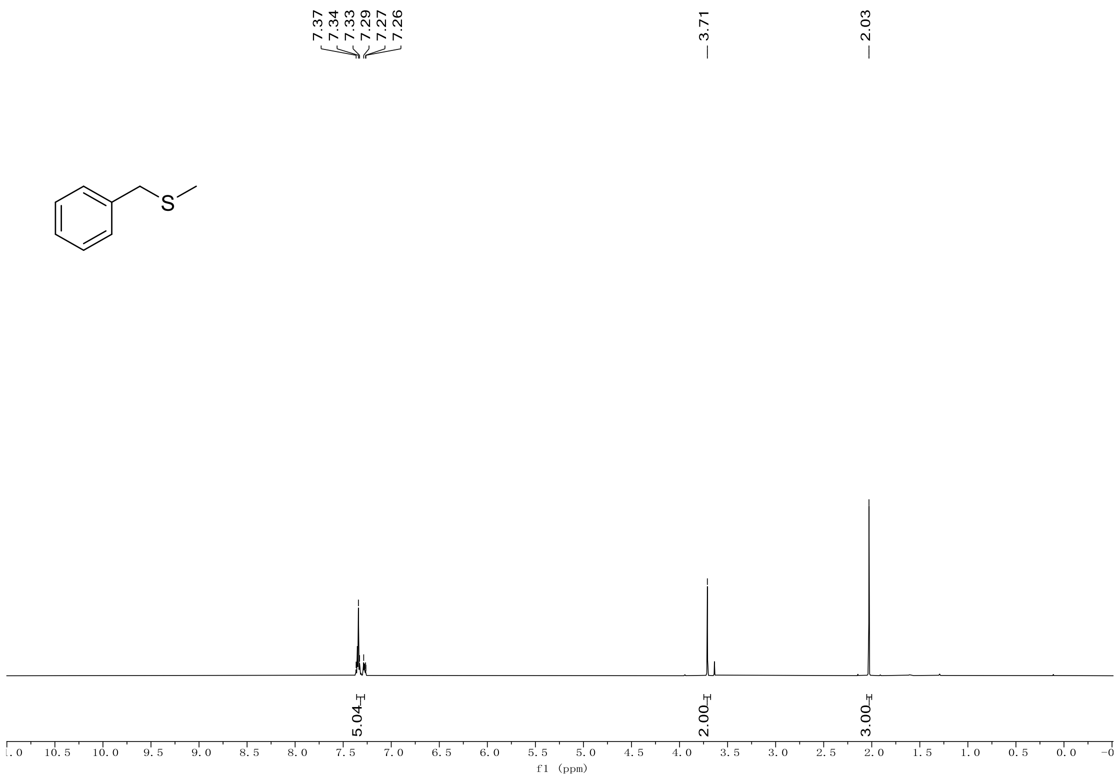
[13]C NMR of compound **3j** (151 MHz, $CDCl_3$)



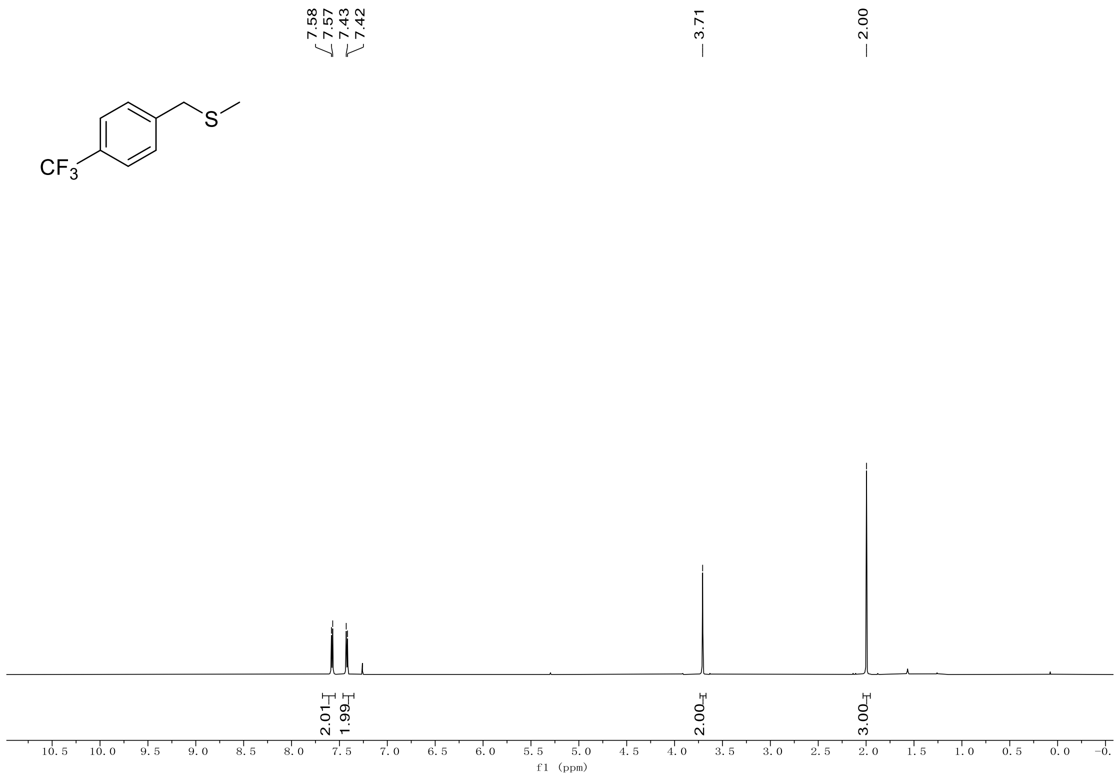
^{1}H NMR of compound **3k** (400 MHz, $CDCl_3$)



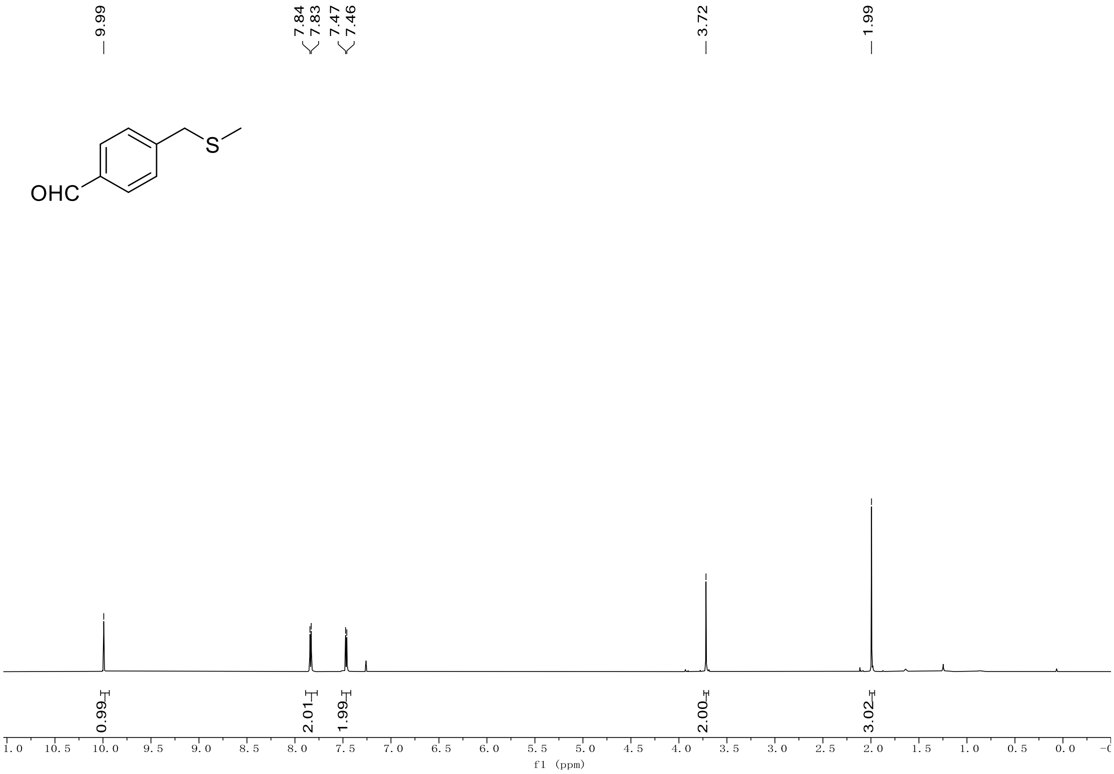
^{13}C NMR of compound **3k** (151 MHz, $CDCl_3$)



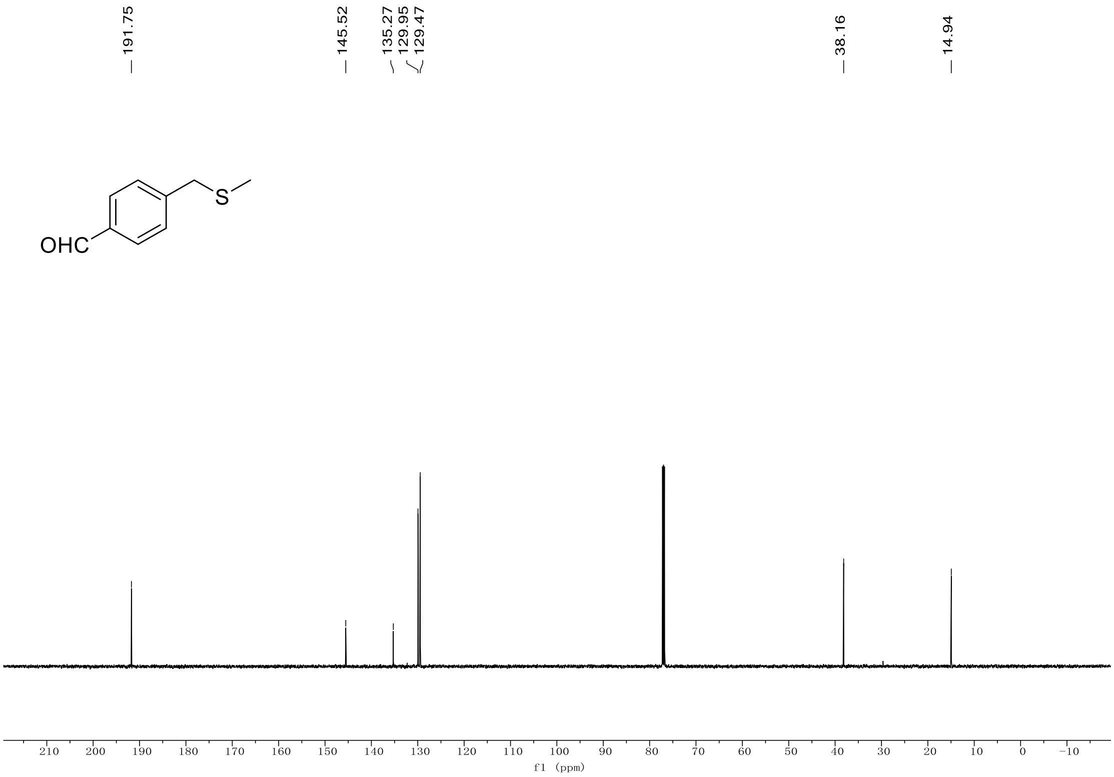
[1]H NMR of compound **3l** (600 MHz, $CDCl_3$)



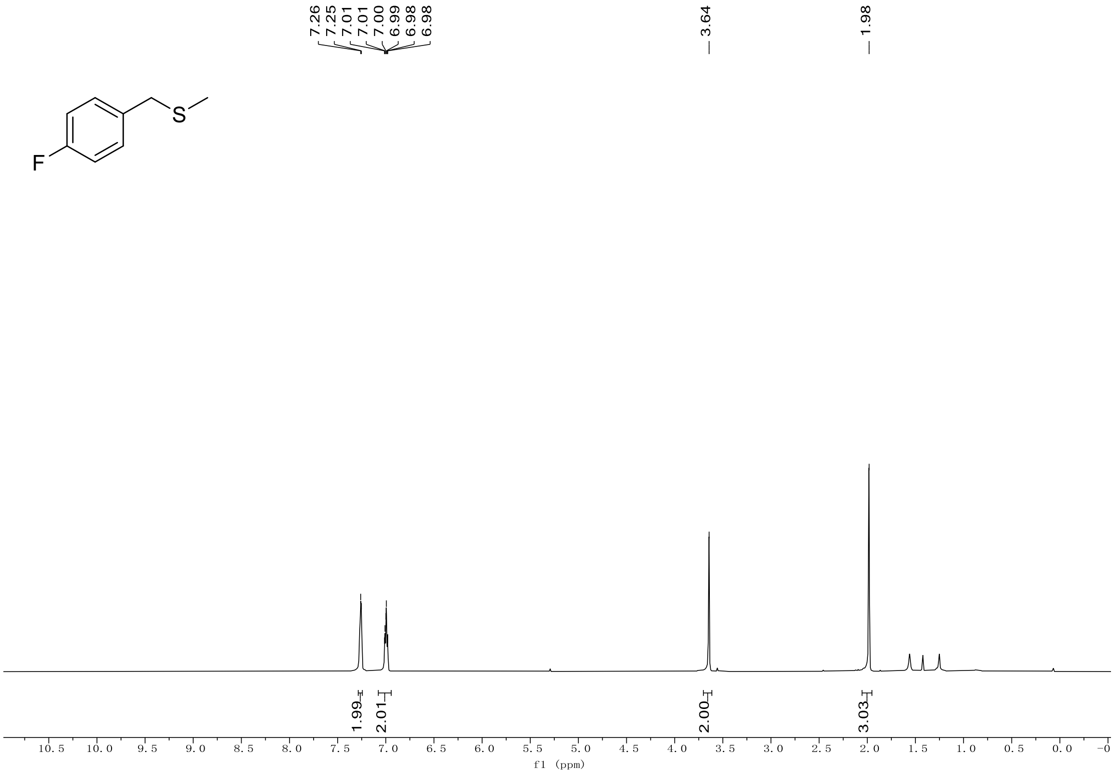
[1]H NMR of compound **3m** (600 MHz, $CDCl_3$)



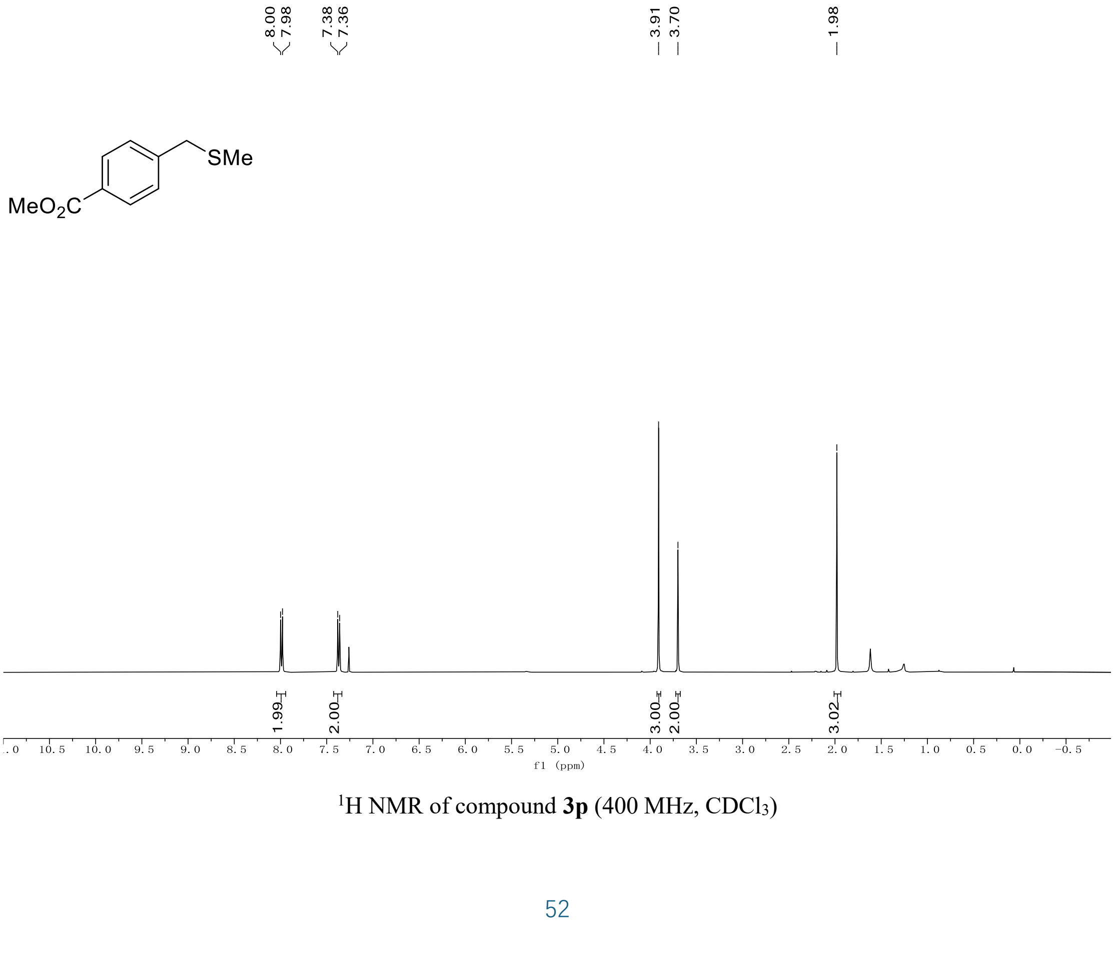
^{1}H NMR of compound **3n** (600 MHz, $CDCl_3$)



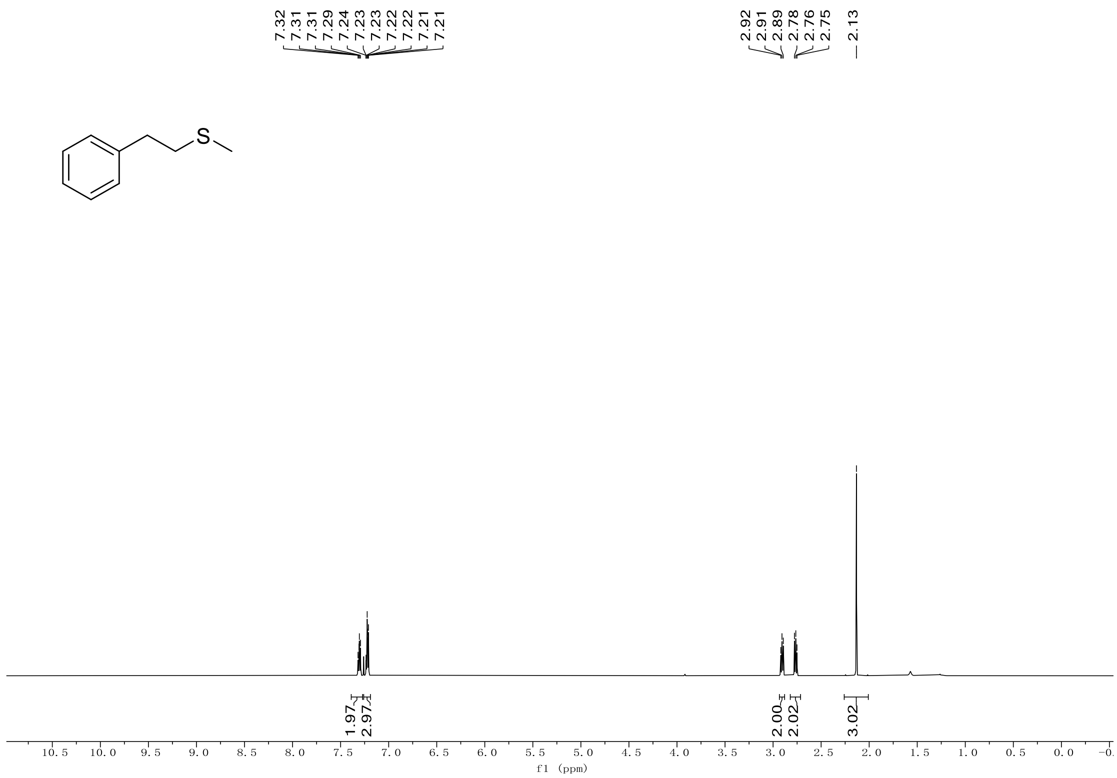
^{13}C NMR of compound **3n** (151 MHz, $CDCl_3$)



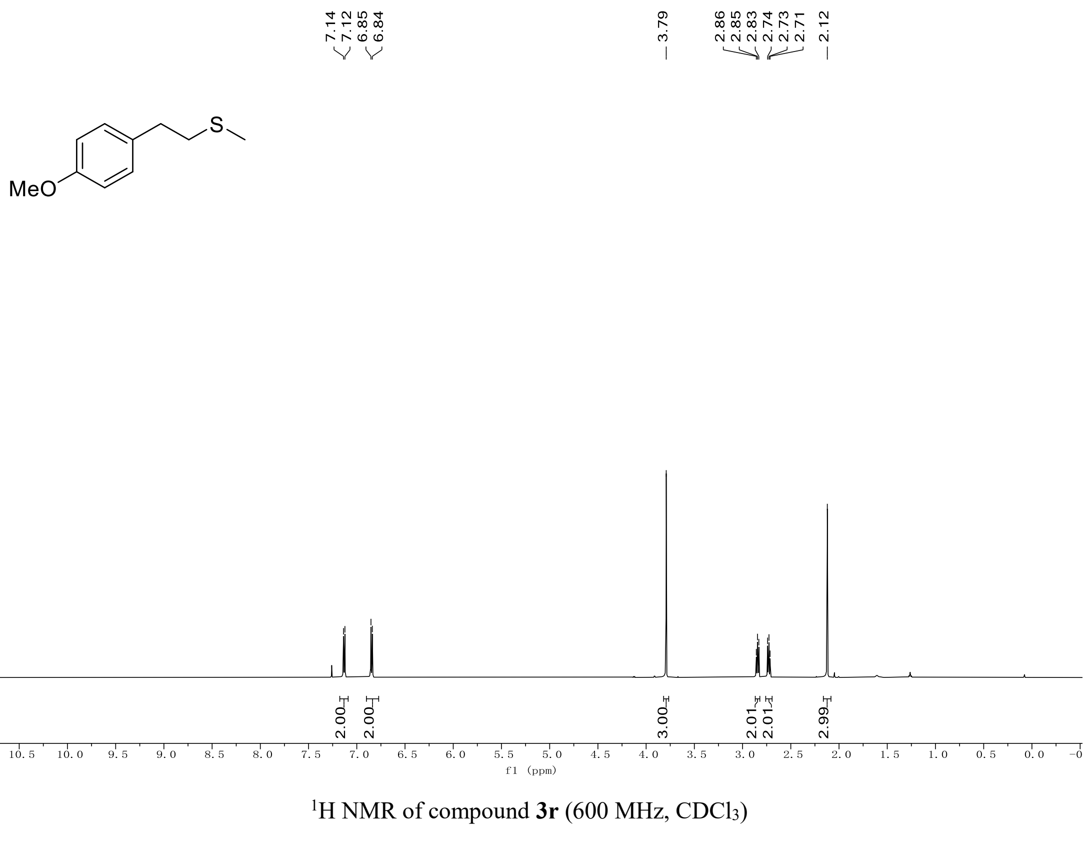
[1]H NMR of compound **3o** (600 MHz, $CDCl_3$)



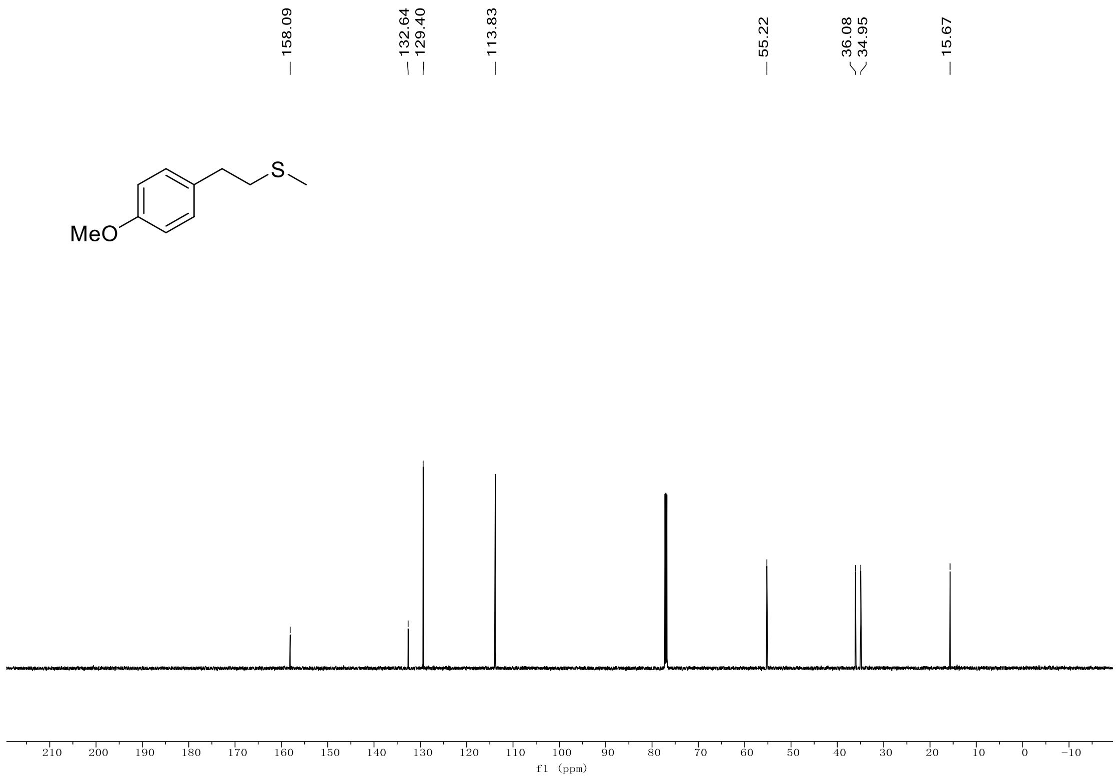
[1]H NMR of compound **3p** (400 MHz, $CDCl_3$)



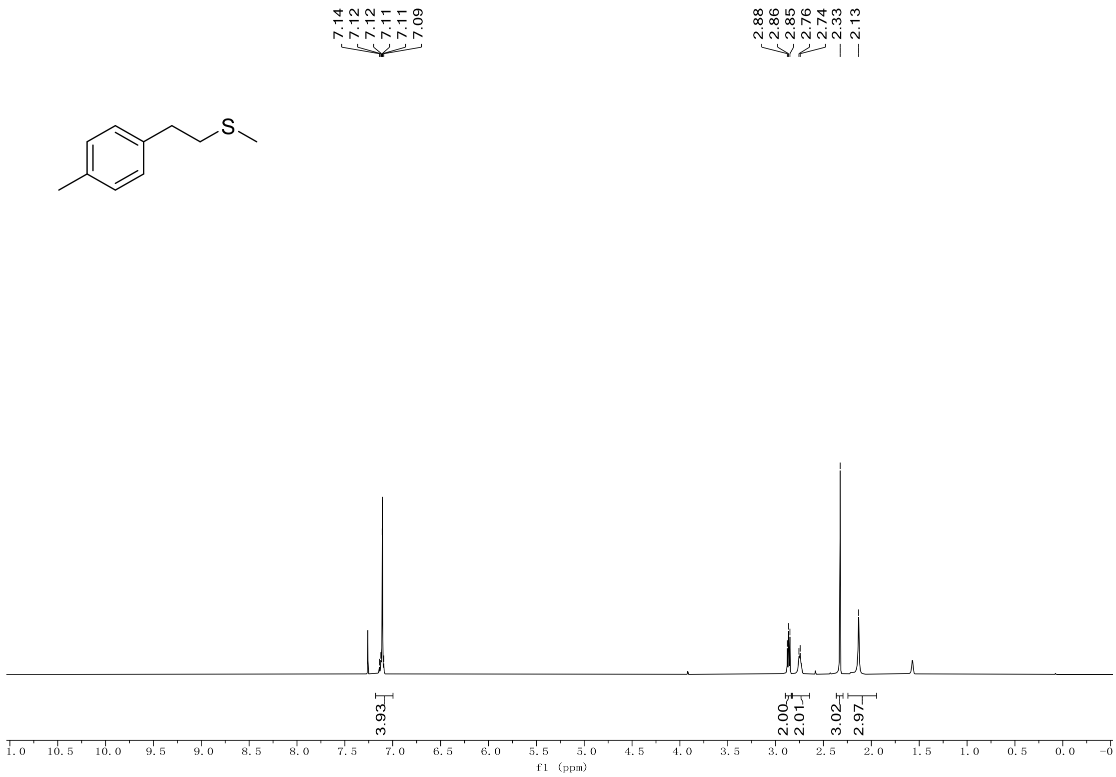
[1]H NMR of compound **3q** (600 MHz, $CDCl_3$)



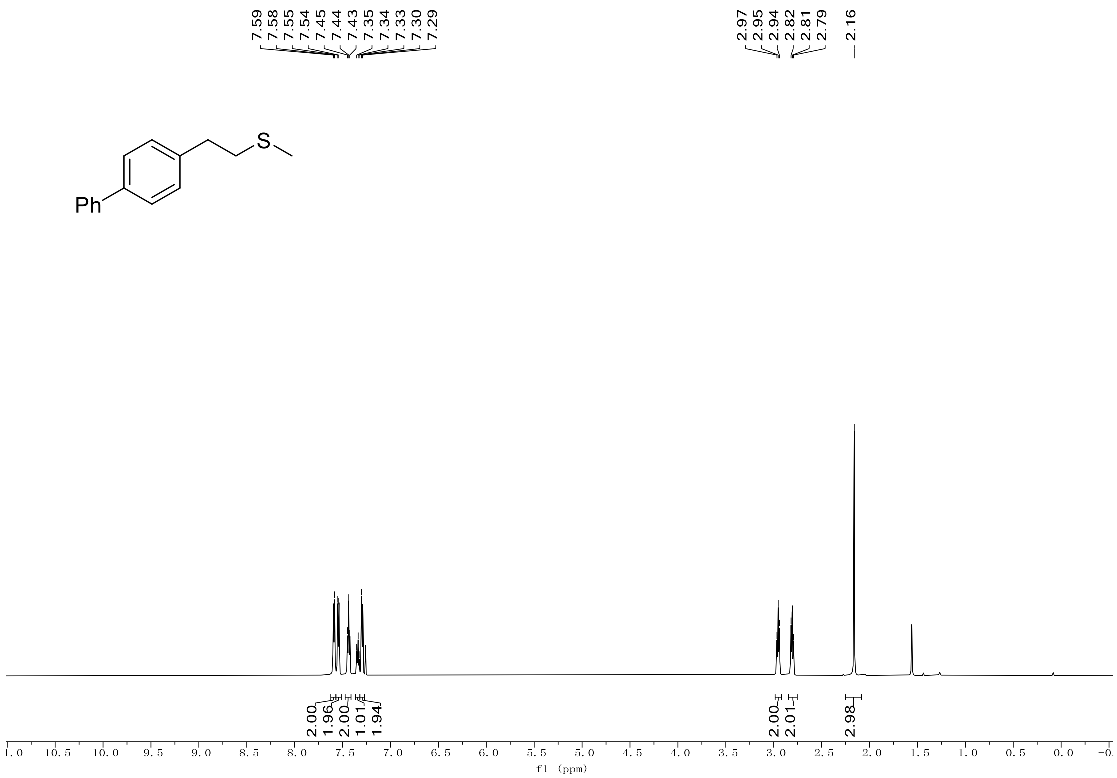
[1]H NMR of compound **3r** (600 MHz, $CDCl_3$)



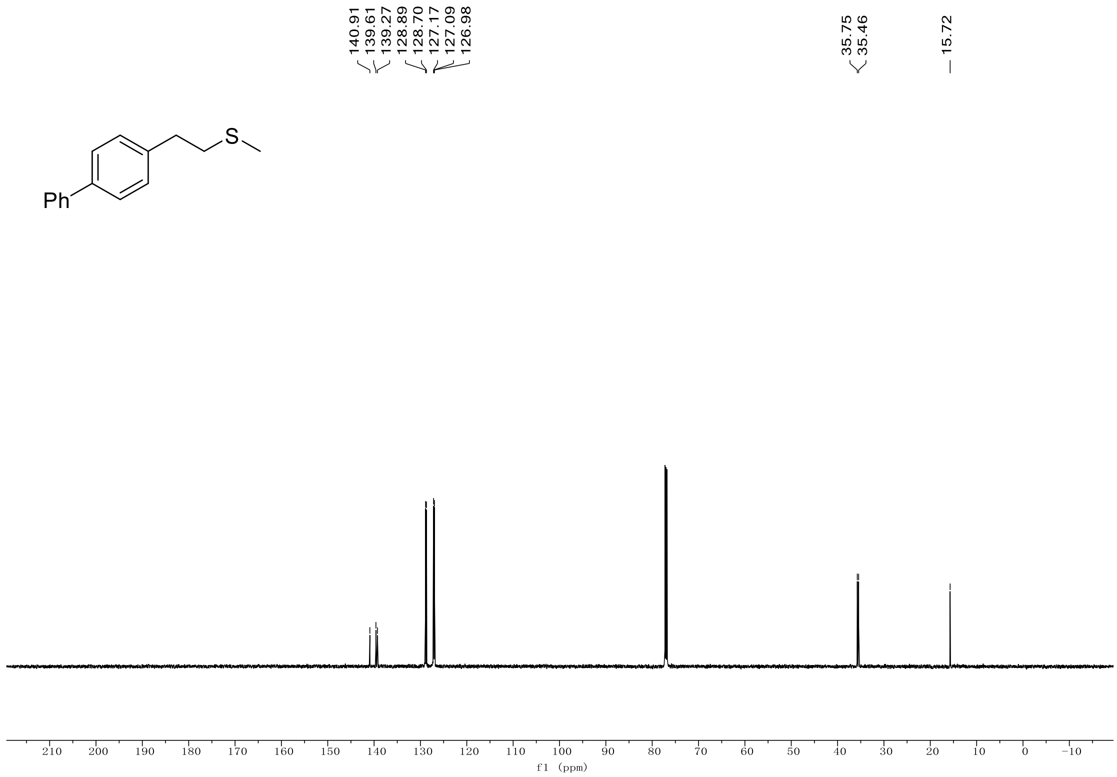
^{13}C NMR of compound **3r** (151 MHz, $CDCl_3$)



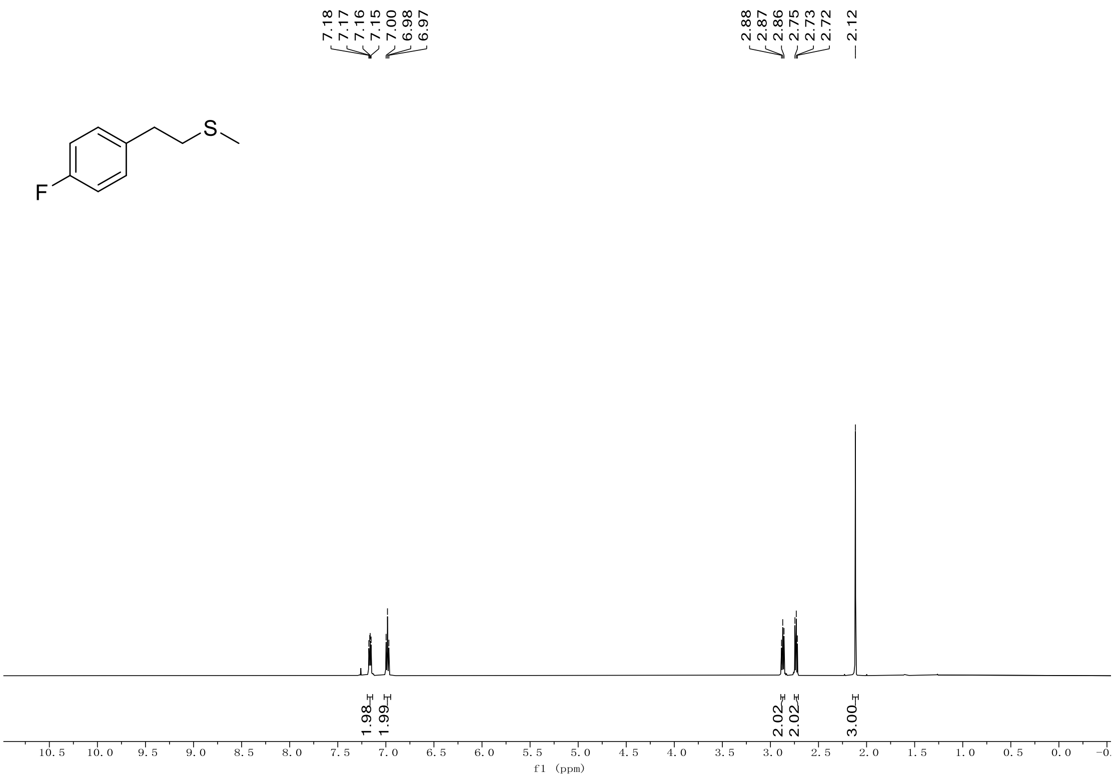
^{1}H NMR of compound **3s** (600 MHz, $CDCl_3$)



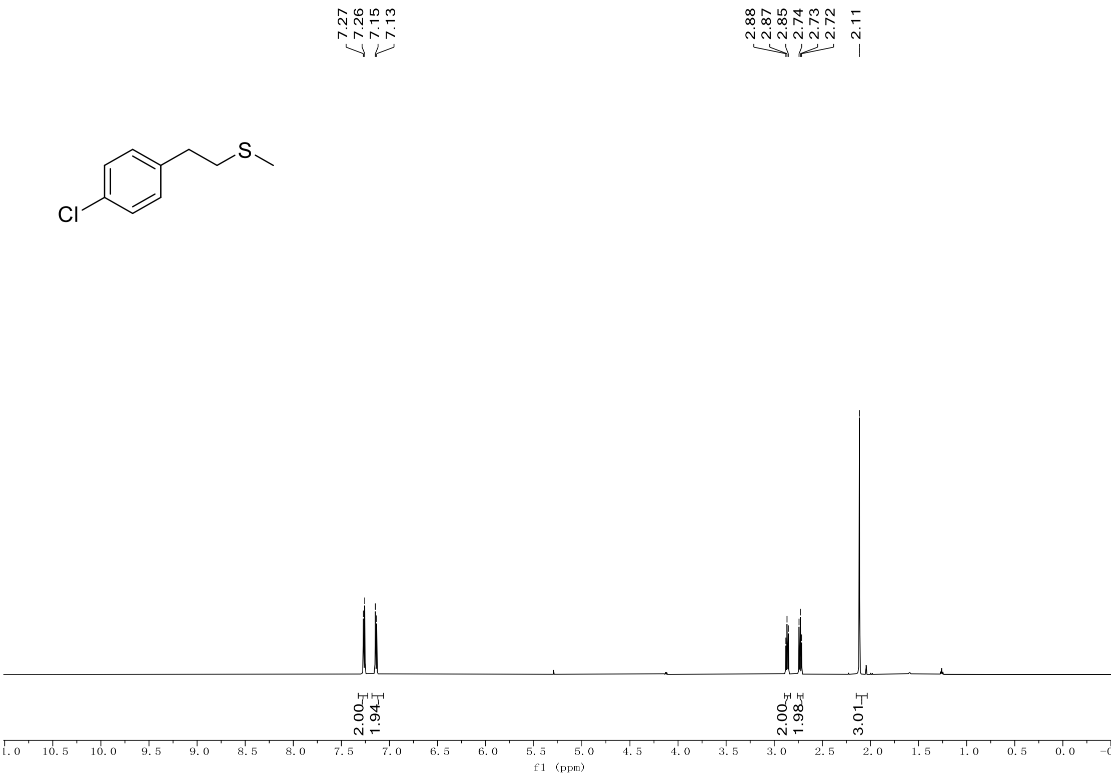
[1]H NMR of compound **3t** (600 MHz, $CDCl_3$)



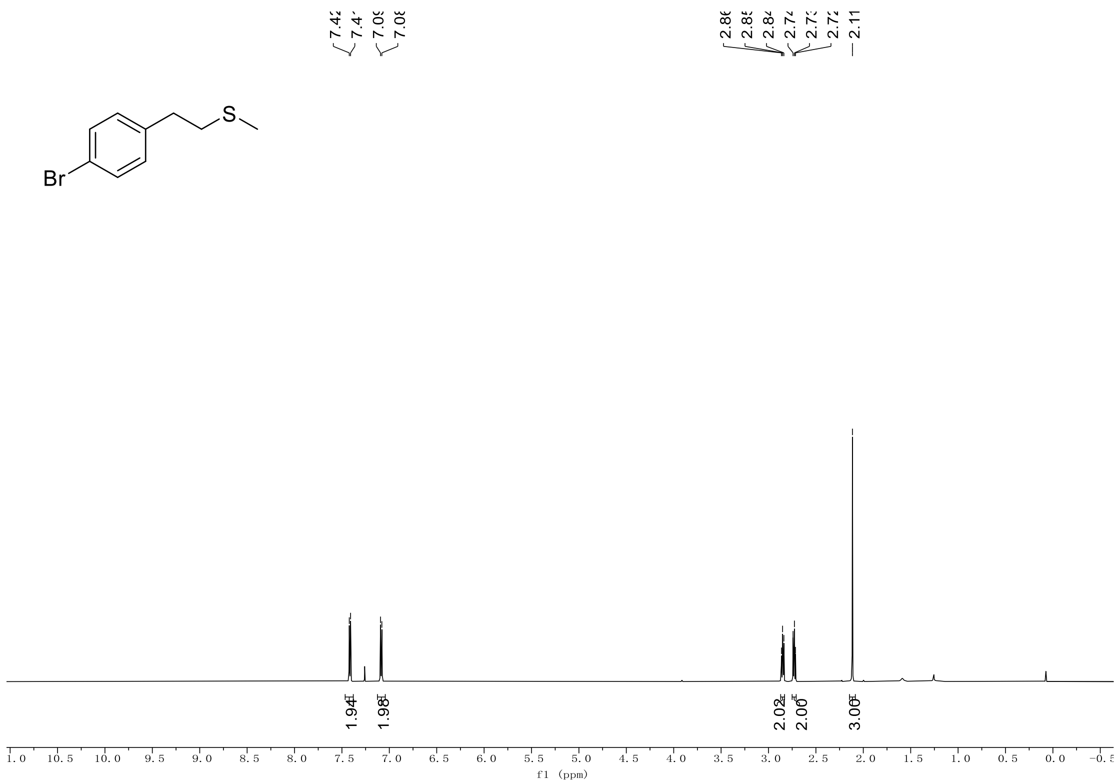
[13]C NMR of compound **3t** (151 MHz, $CDCl_3$)



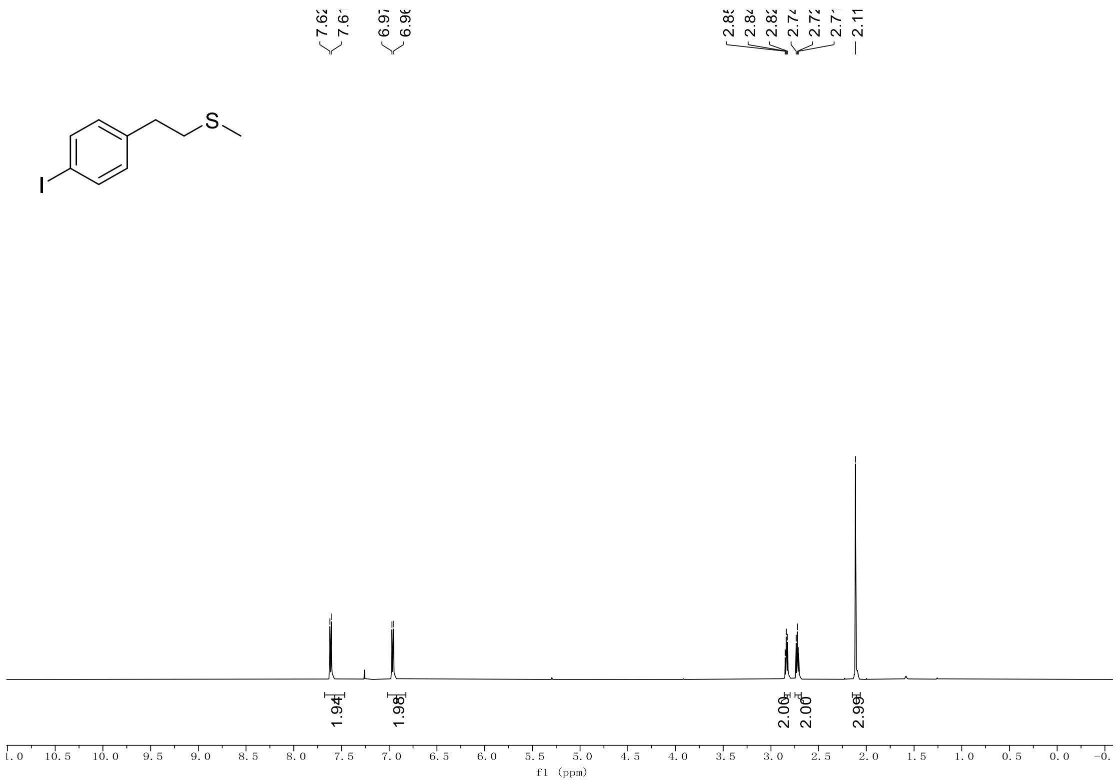
[1]H NMR of compound **3u** (600 MHz, $CDCl_3$)



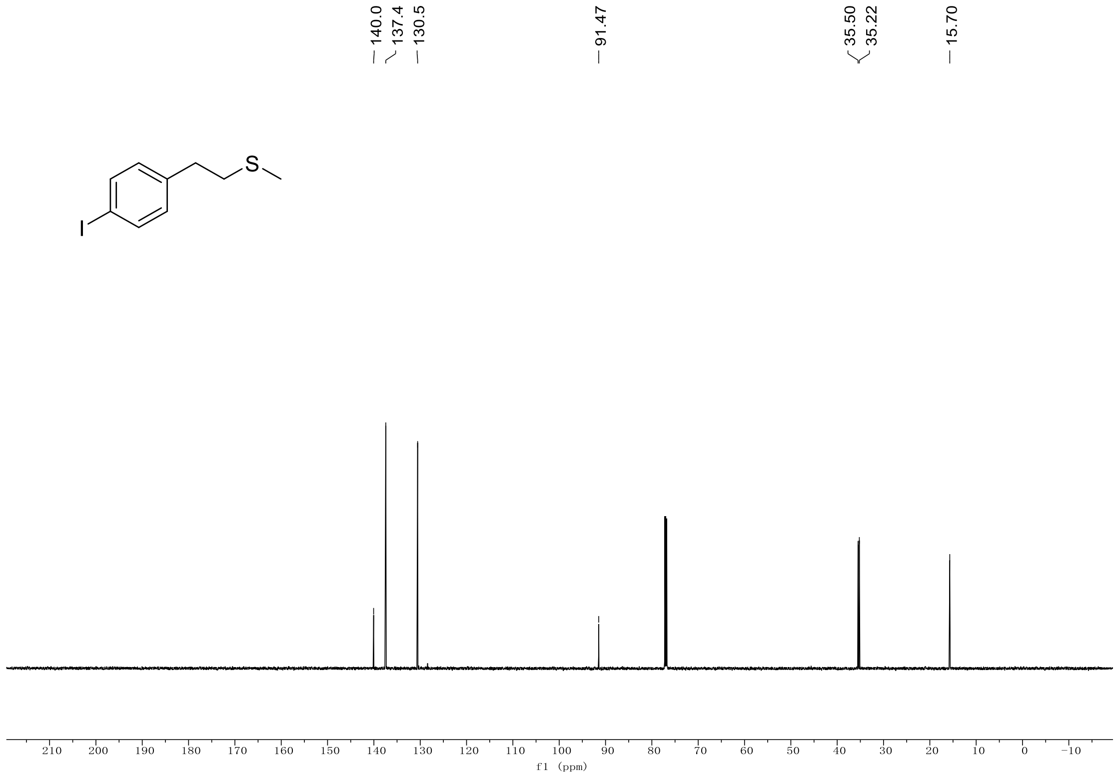
[1]H NMR of compound **3v** (600 MHz, $CDCl_3$)



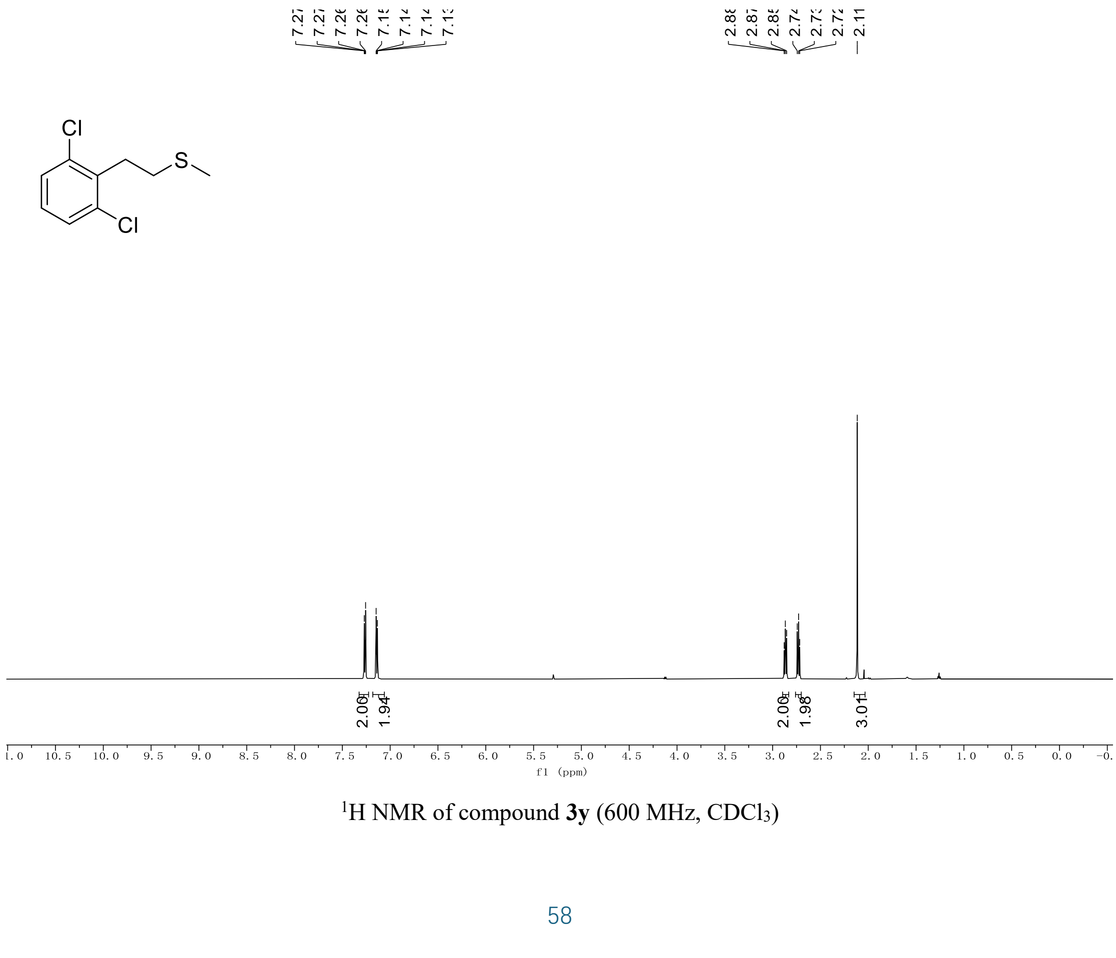
^{1}H NMR of compound **3w** (600 MHz, $CDCl_3$)



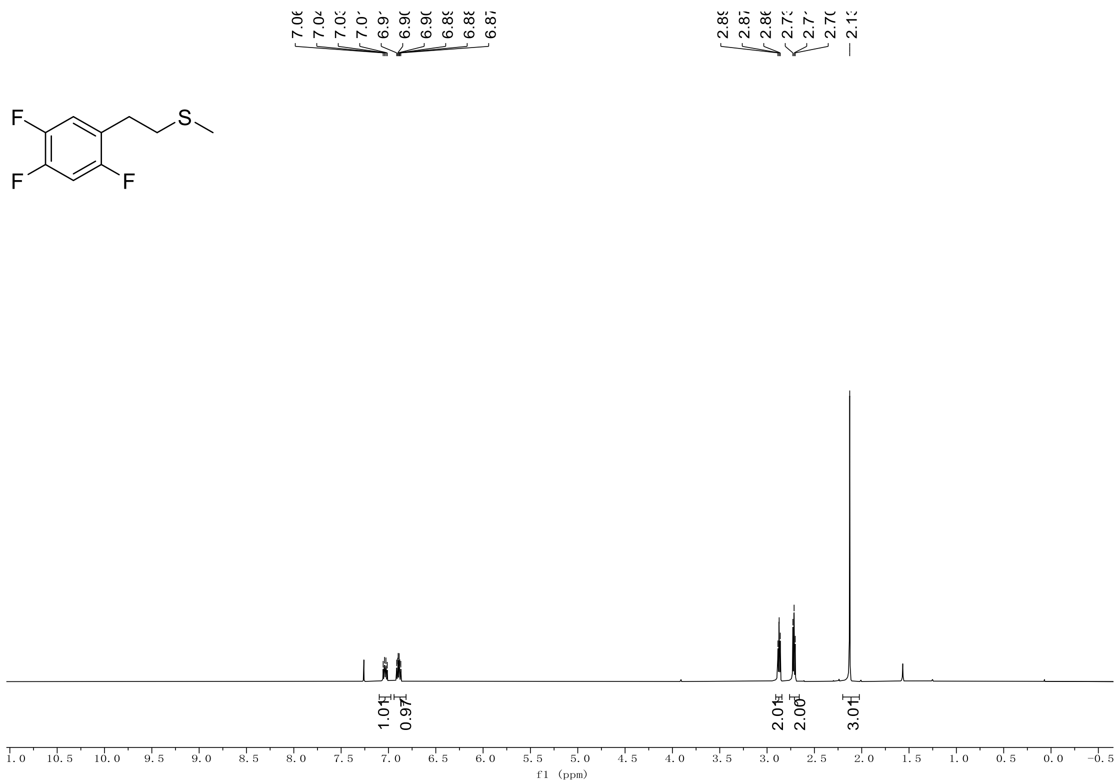
^{1}H NMR of compound **3x** (600 MHz, $CDCl_3$)



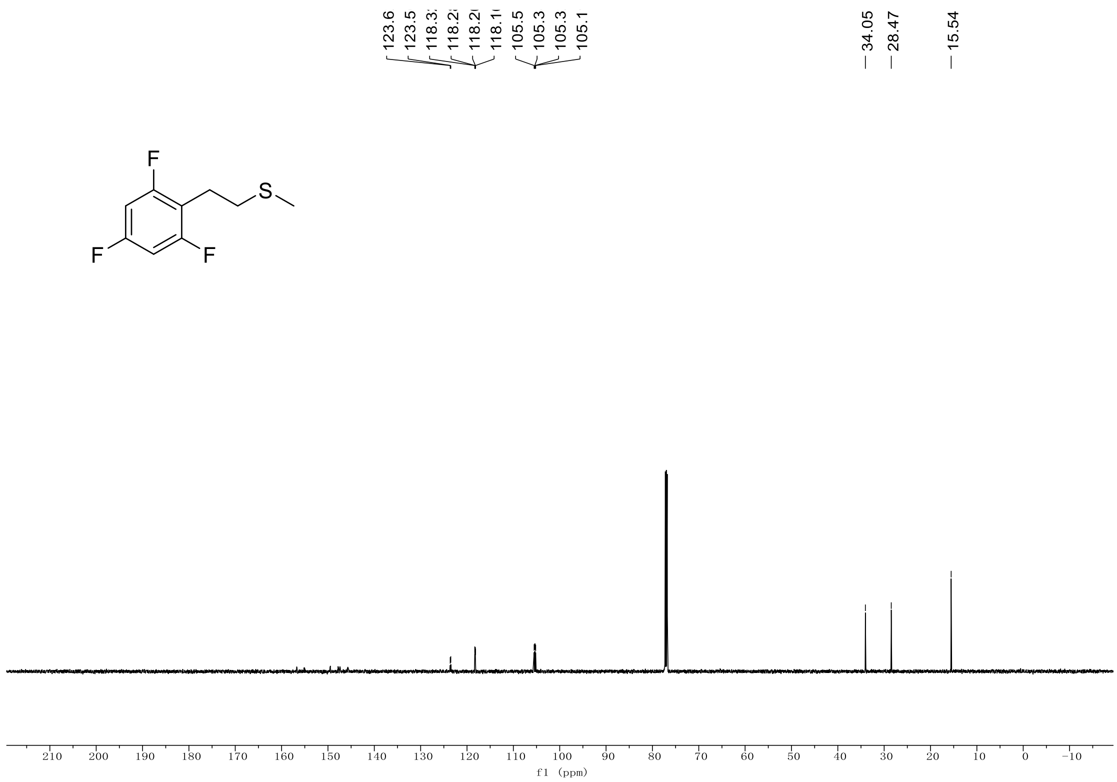
^{13}C NMR of compound **3x** (151 MHz, $CDCl_3$)



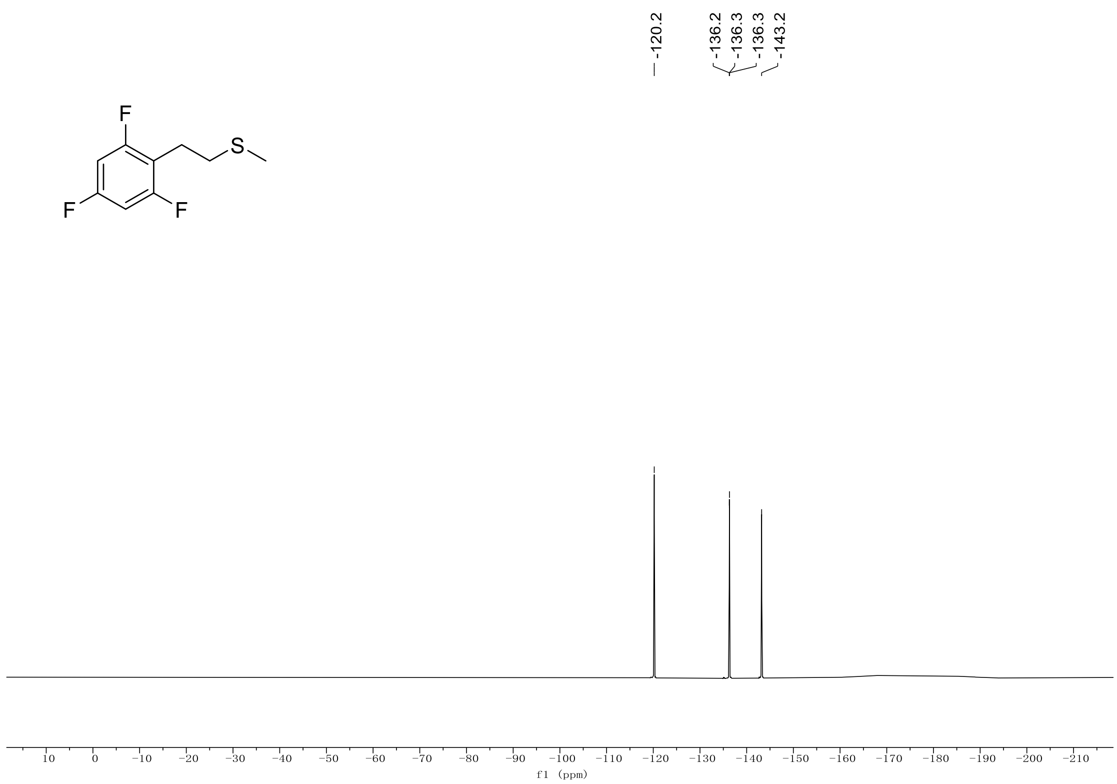
^{1}H NMR of compound **3y** (600 MHz, $CDCl_3$)



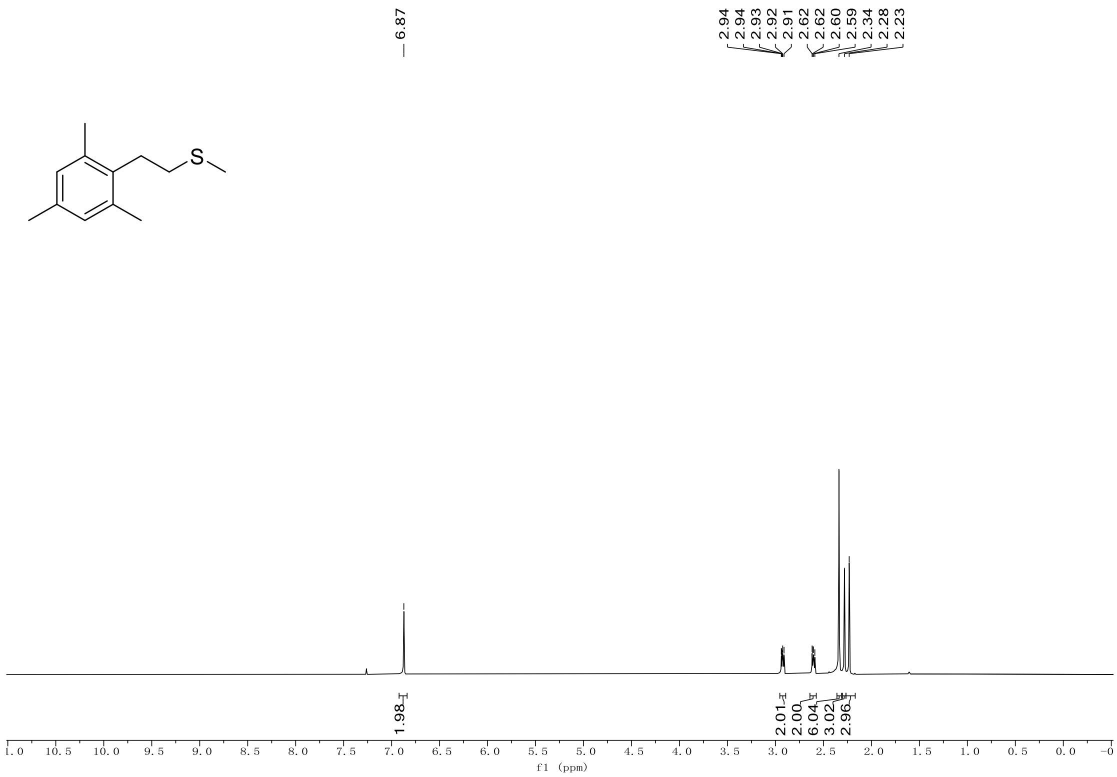
[1]H NMR of compound **3z** (600 MHz, $CDCl_3$)



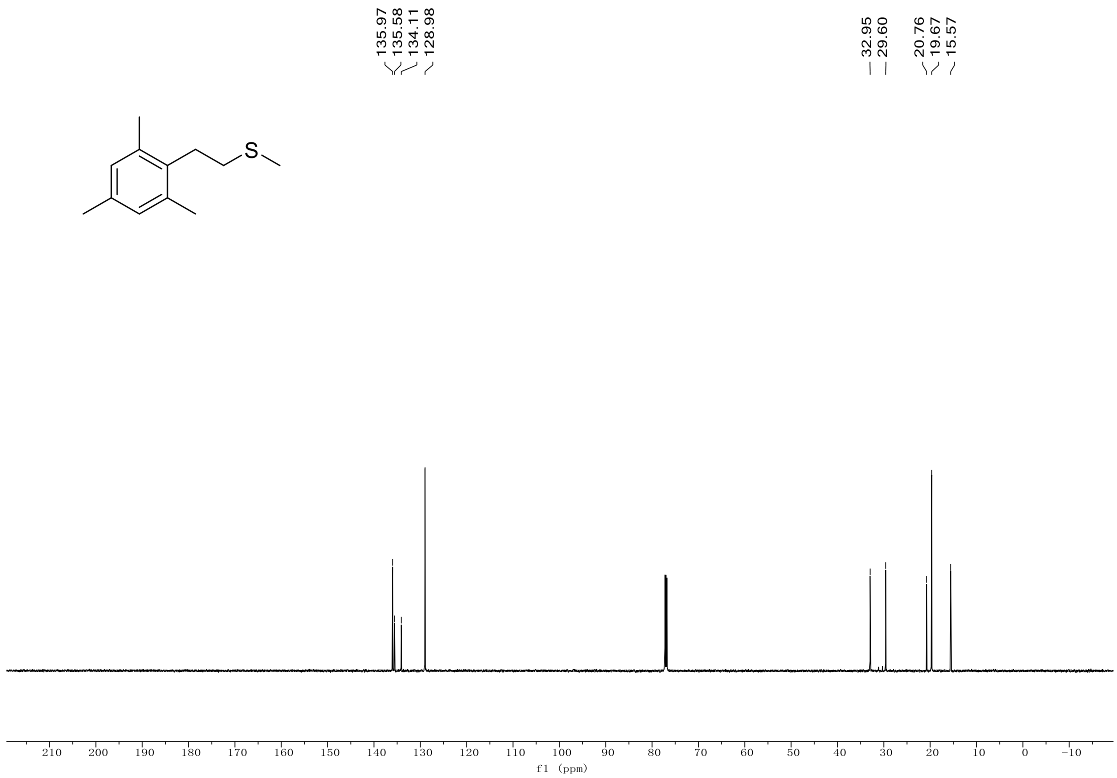
[13]C NMR of compound **3z** (151 MHz, $CDCl_3$)



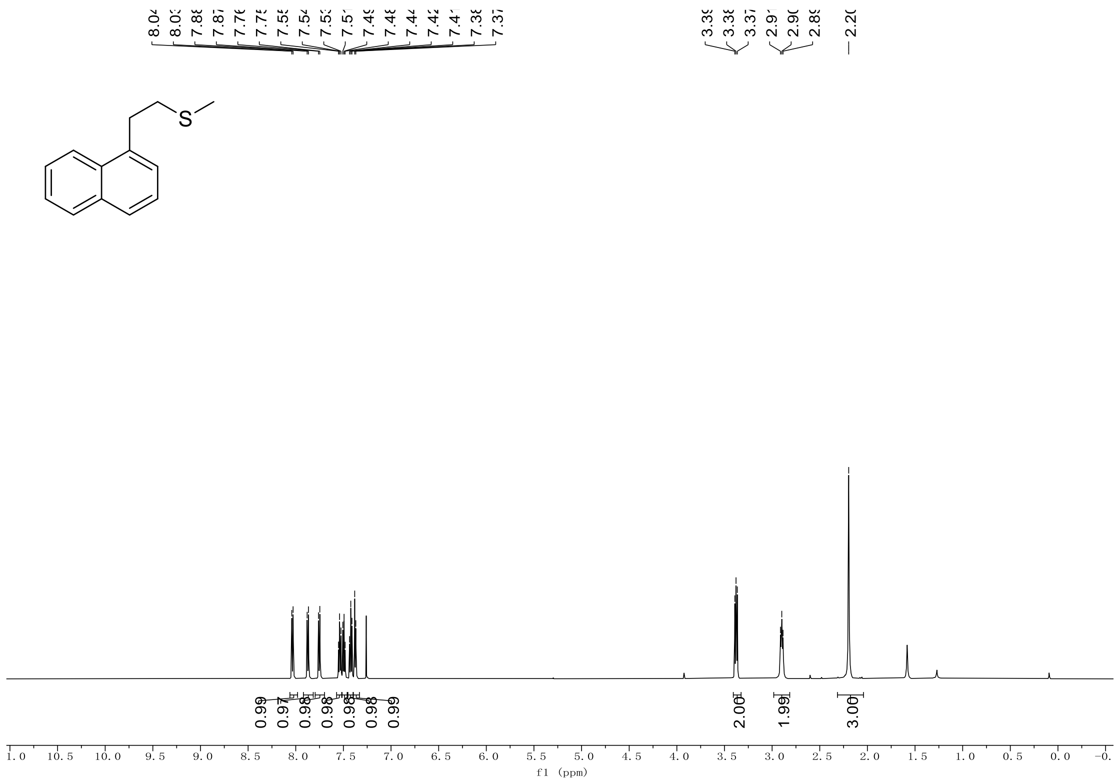
^{19}F NMR of compound **3z** (600 MHz, $CDCl_3$)



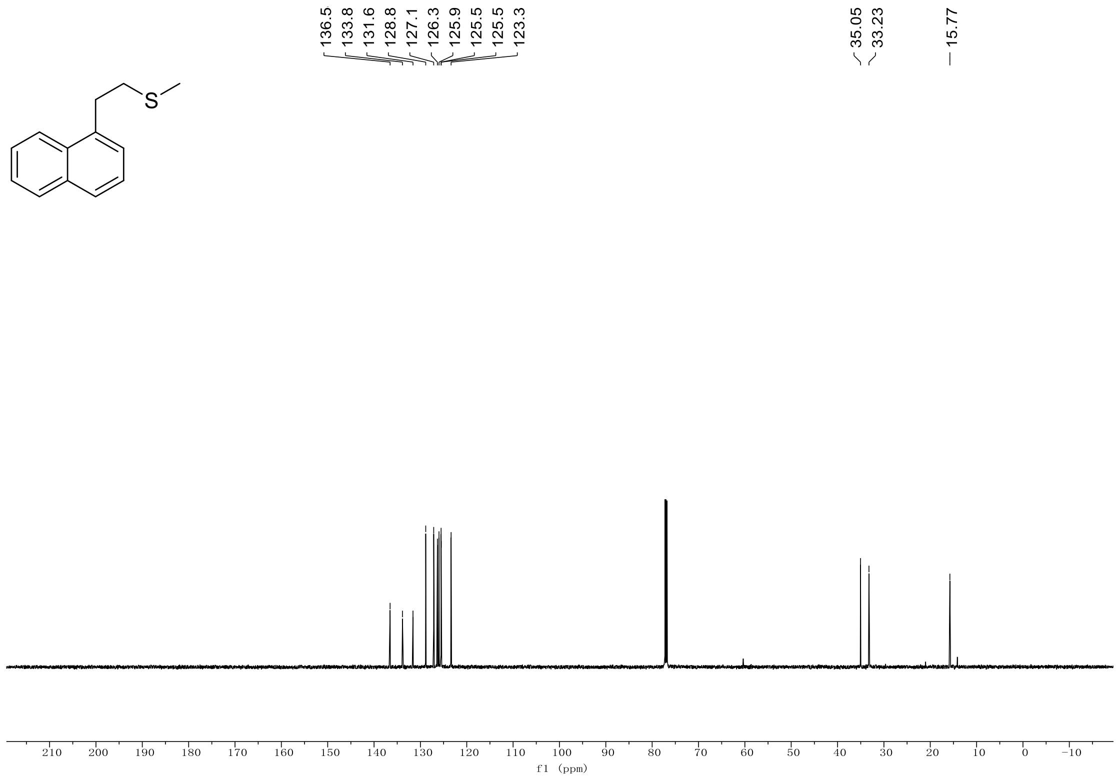
^{1}H NMR of compound **3aa** (600 MHz, $CDCl_3$)



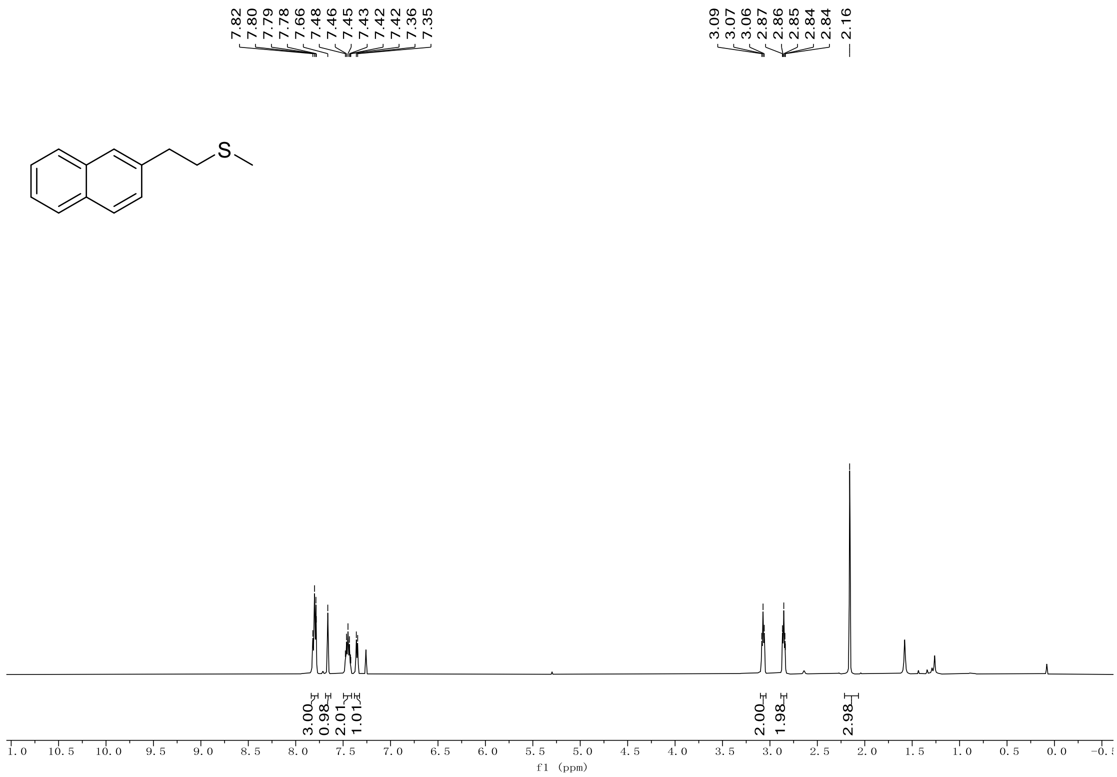
^{13}C NMR of compound **3aa** (151 MHz, $CDCl_3$)



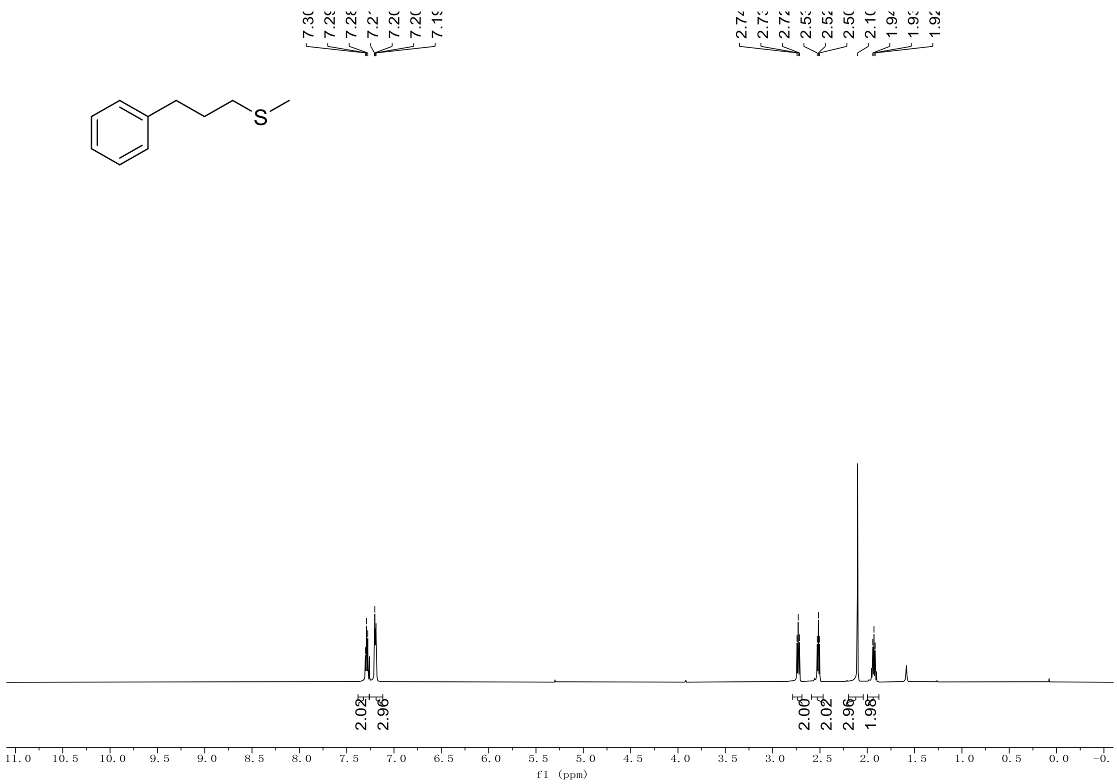
^{1}H NMR of compound **3bb** (600 MHz, $CDCl_3$)



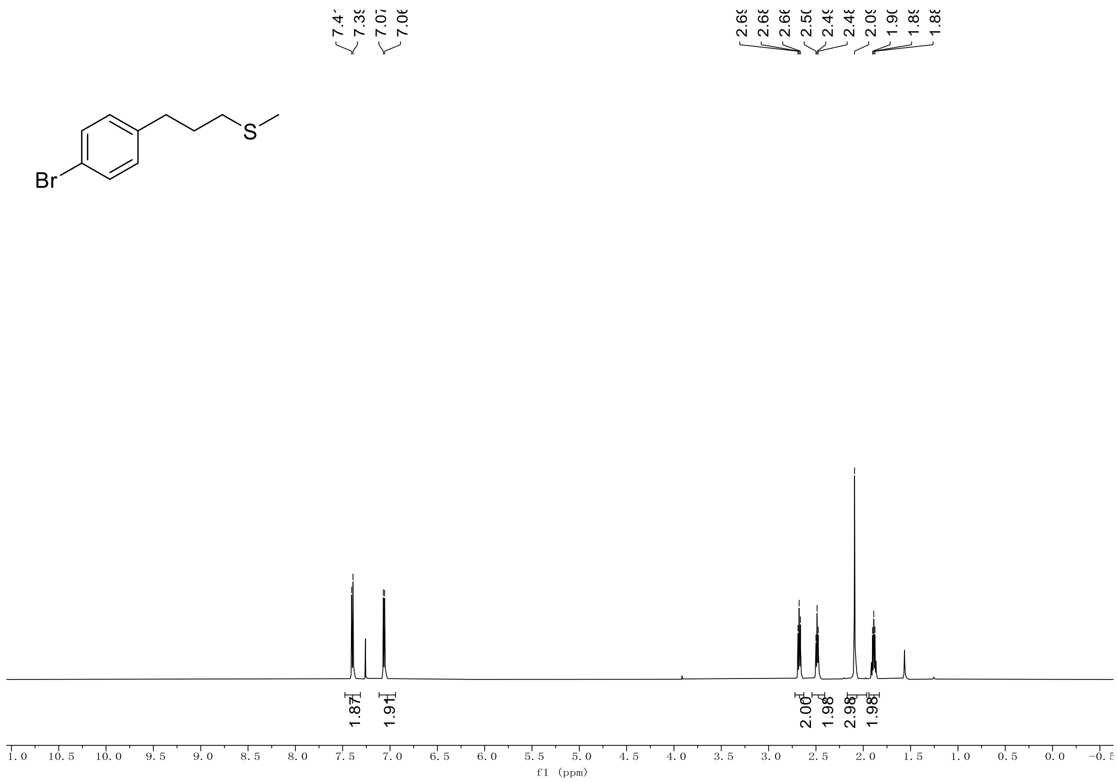
[13]C NMR of compound **3bb** (600 MHz, $CDCl_3$)



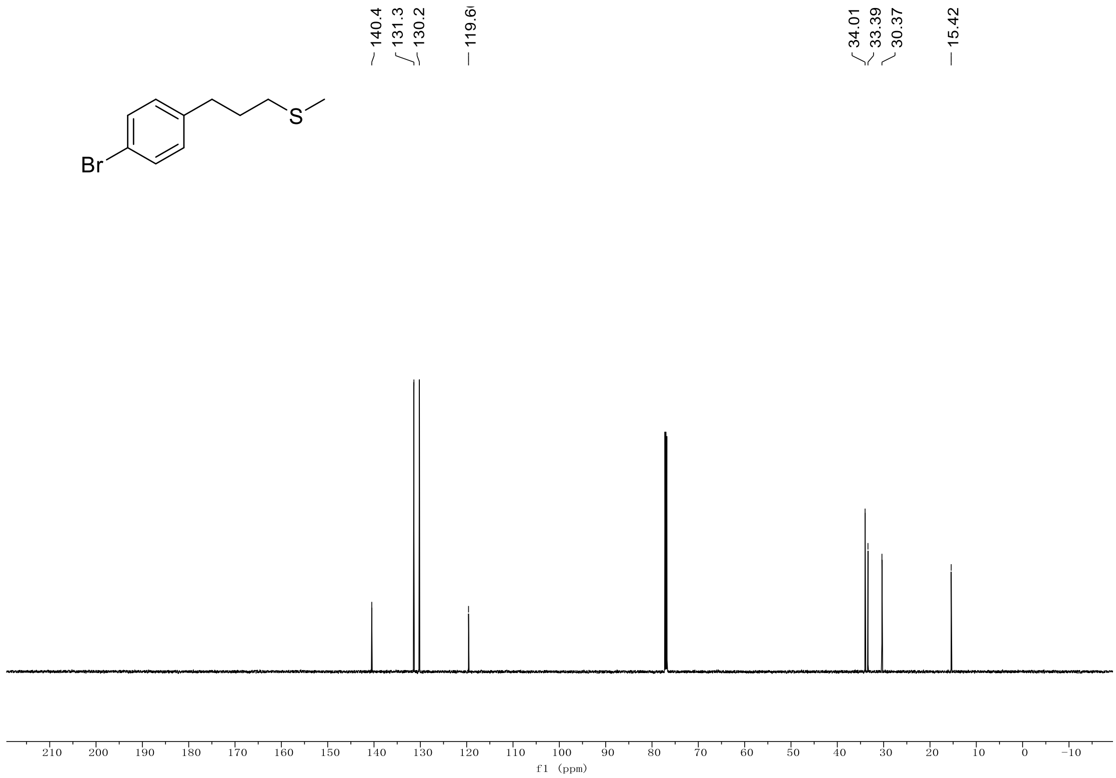
[1]H NMR of compound **3cc** (600 MHz, $CDCl_3$)



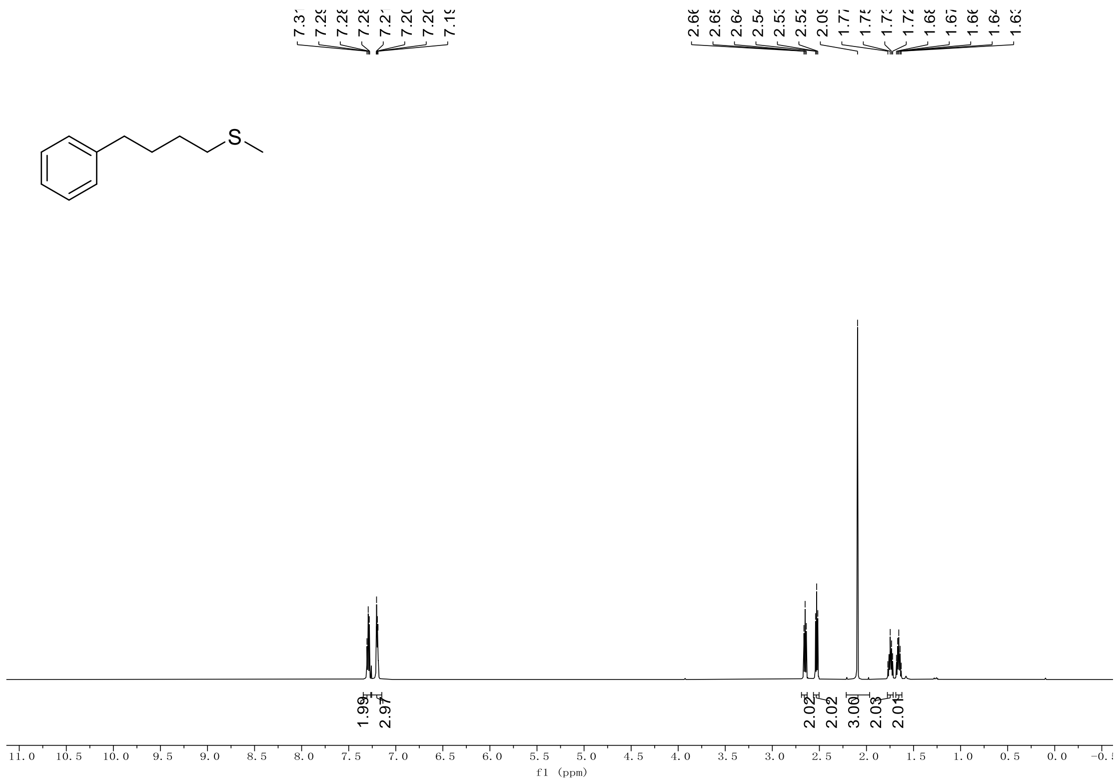
[1]H NMR of compound **3dd** (600 MHz, $CDCl_3$)



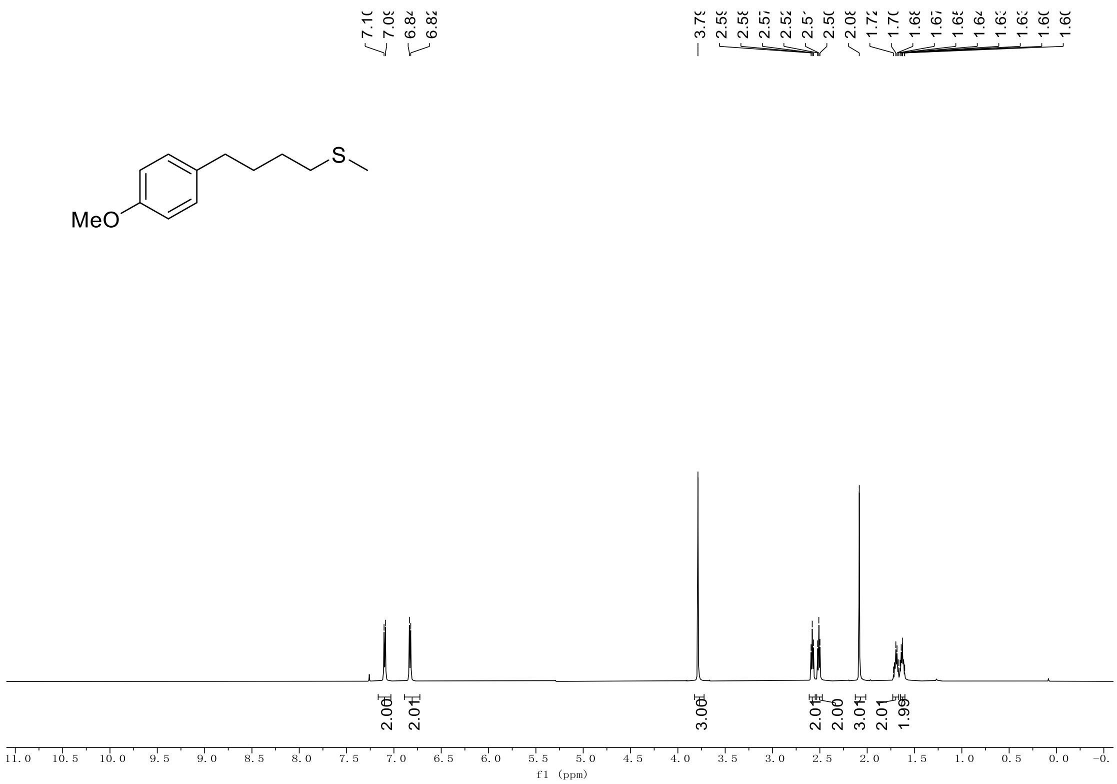
[1]H NMR of compound **3ee** (600 MHz, $CDCl_3$)



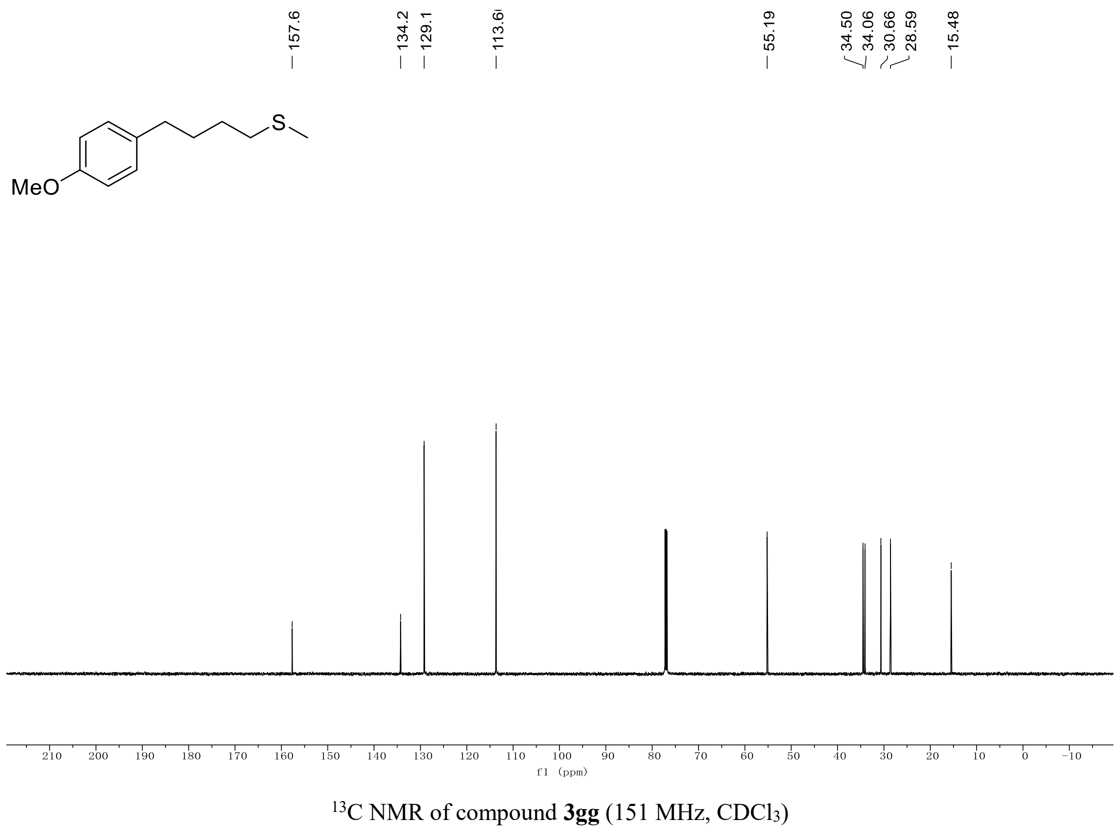
^{13}C NMR of compound **3ee** (151 MHz, $CDCl_3$)



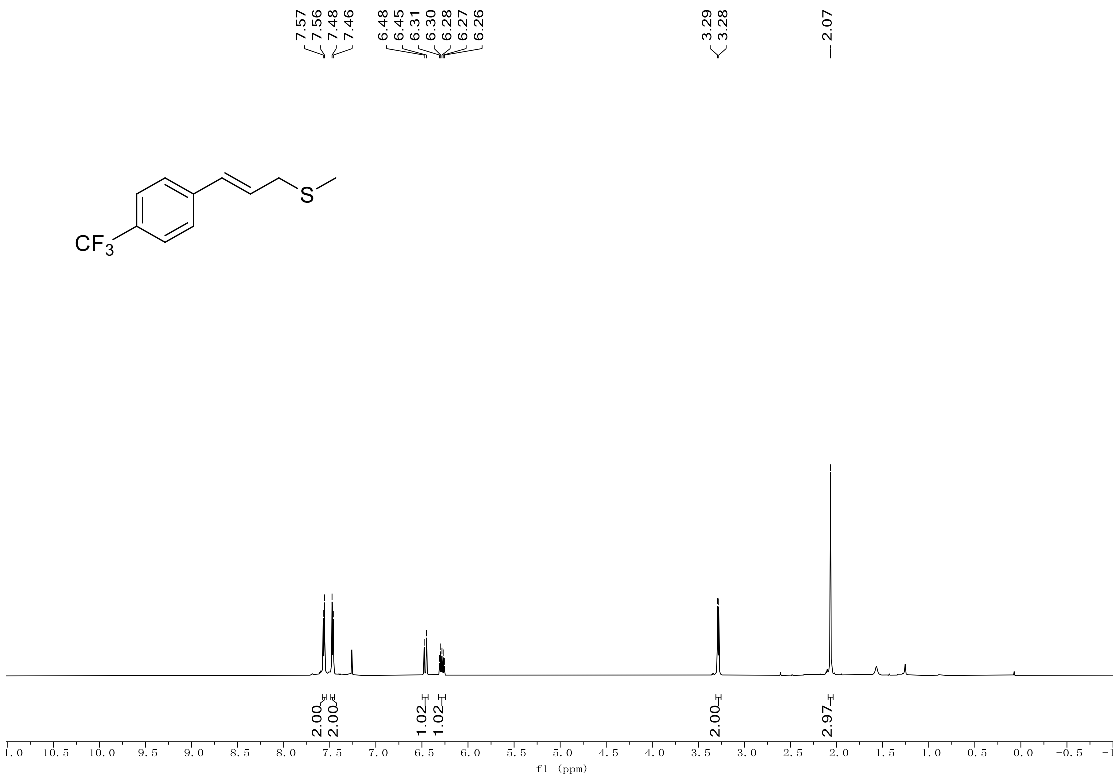
^{1}H NMR of compound **3ff** (600 MHz, $CDCl_3$)



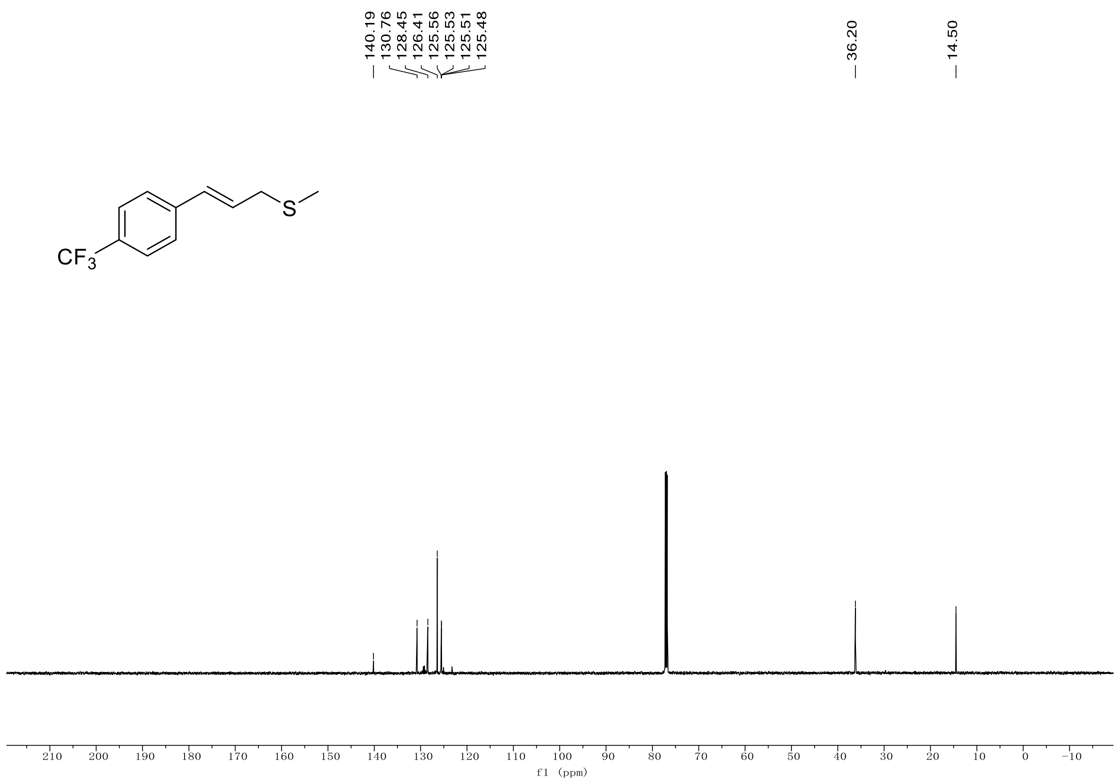
^{1}H NMR of compound **3gg** (600 MHz, $CDCl_3$)



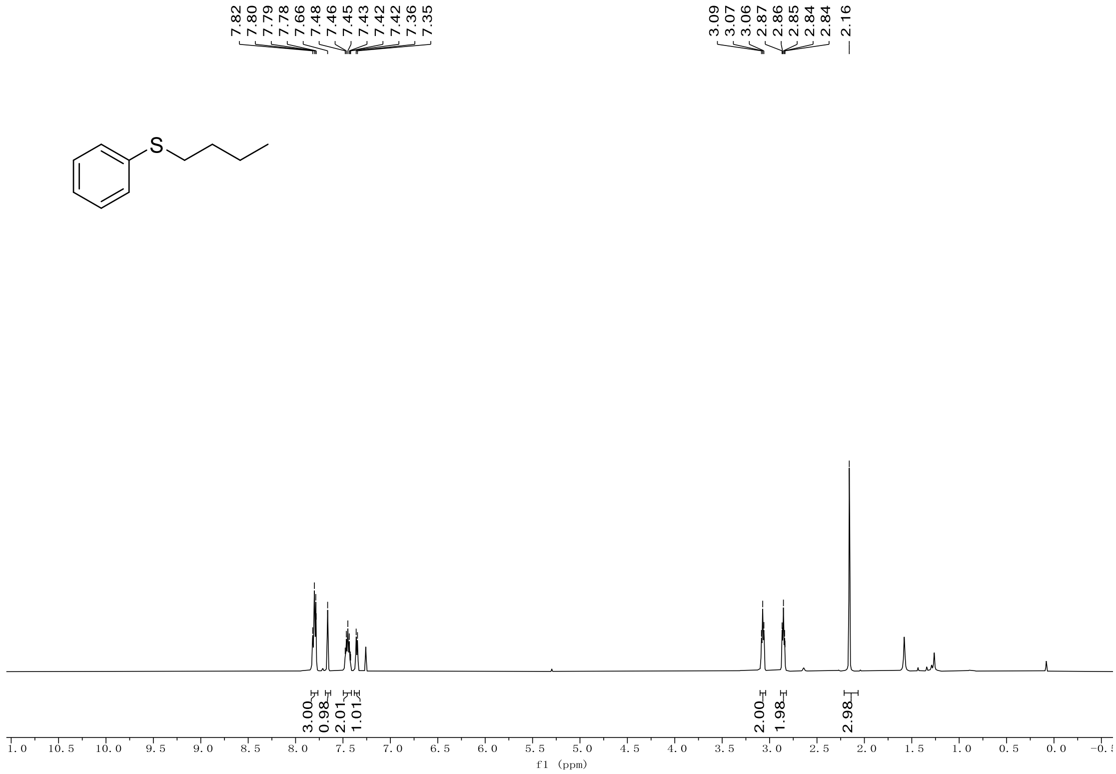
^{13}C NMR of compound **3gg** (151 MHz, $CDCl_3$)



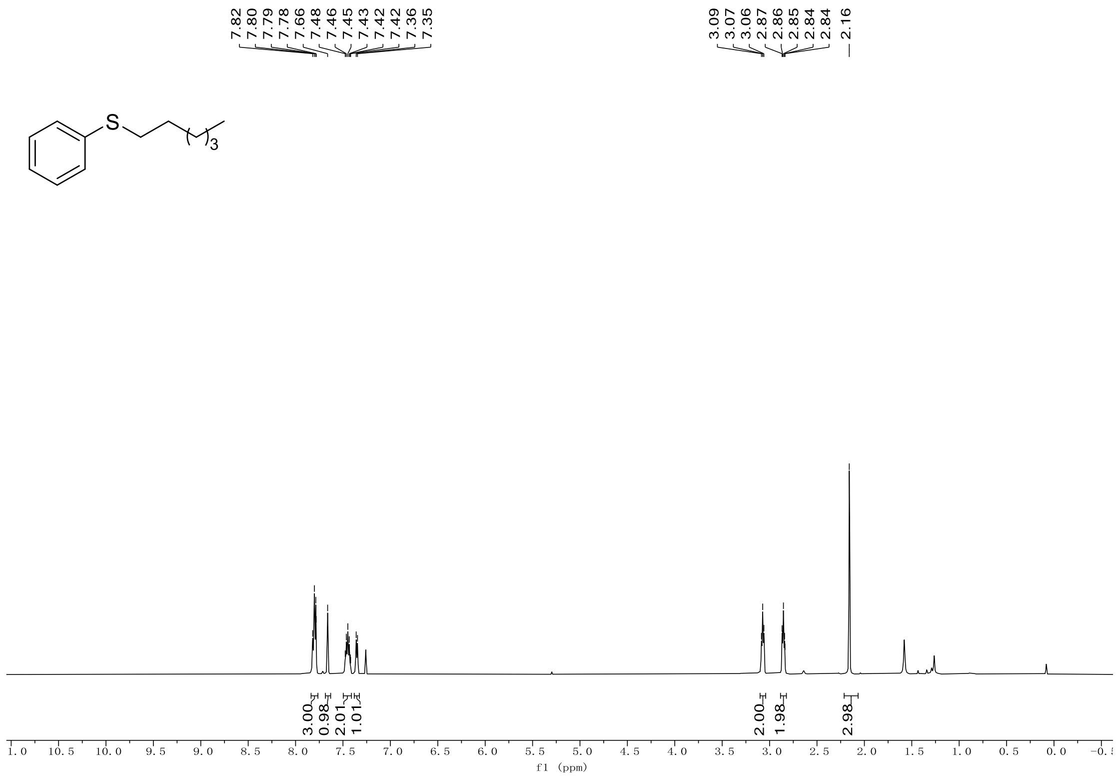
^{1}H NMR of compound **3hh** (600 MHz, $CDCl_3$)



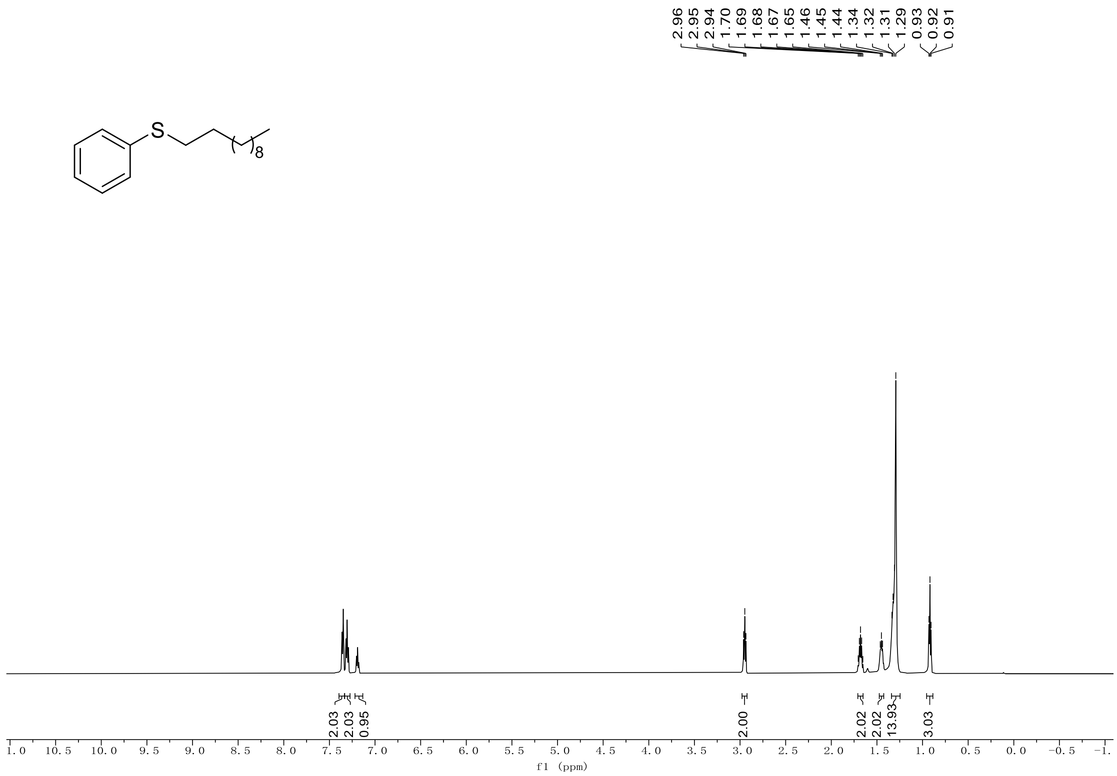
^{13}C NMR of compound **3hh** (151 MHz, $CDCl_3$)



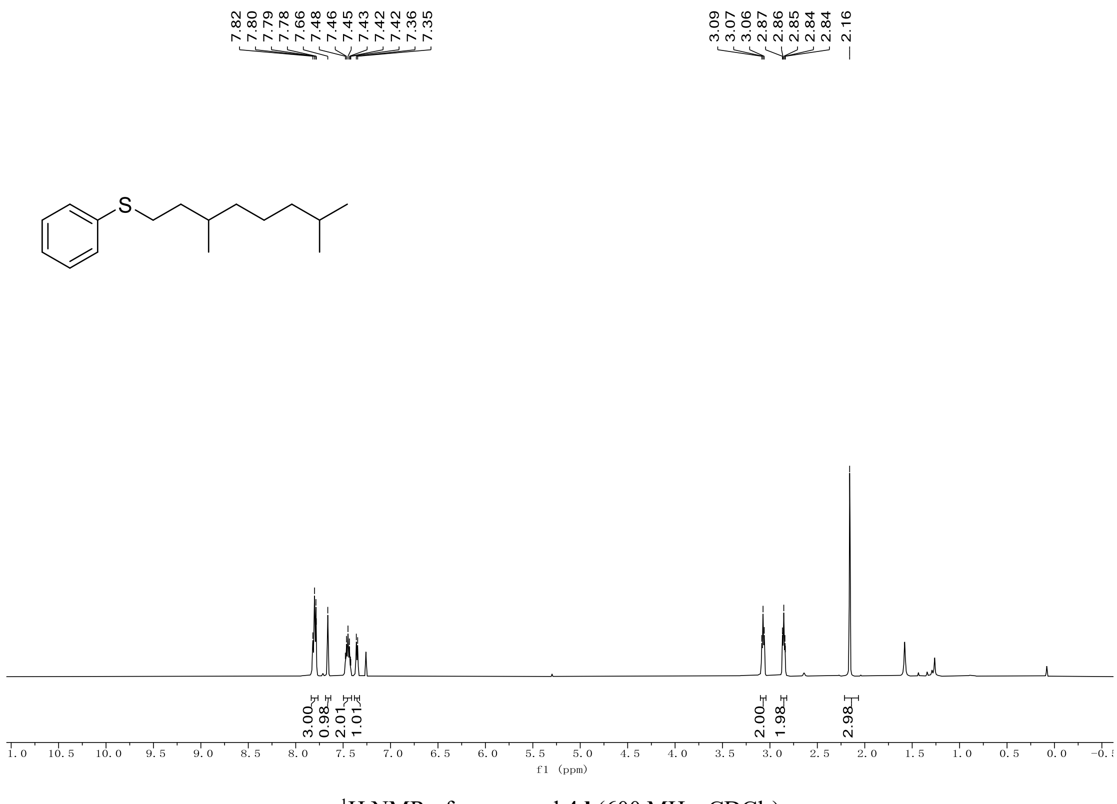
[1]H NMR of compound **4a** (600 MHz, $CDCl_3$)



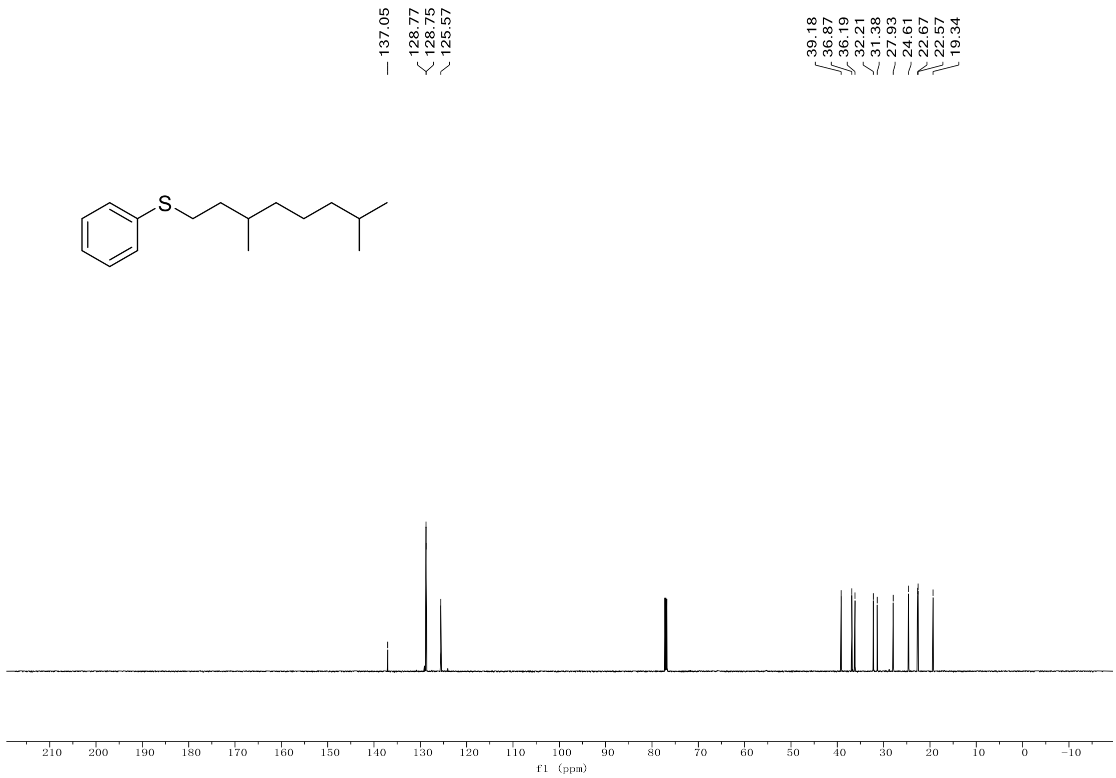
[1]H NMR of compound **4b** (600 MHz, $CDCl_3$)



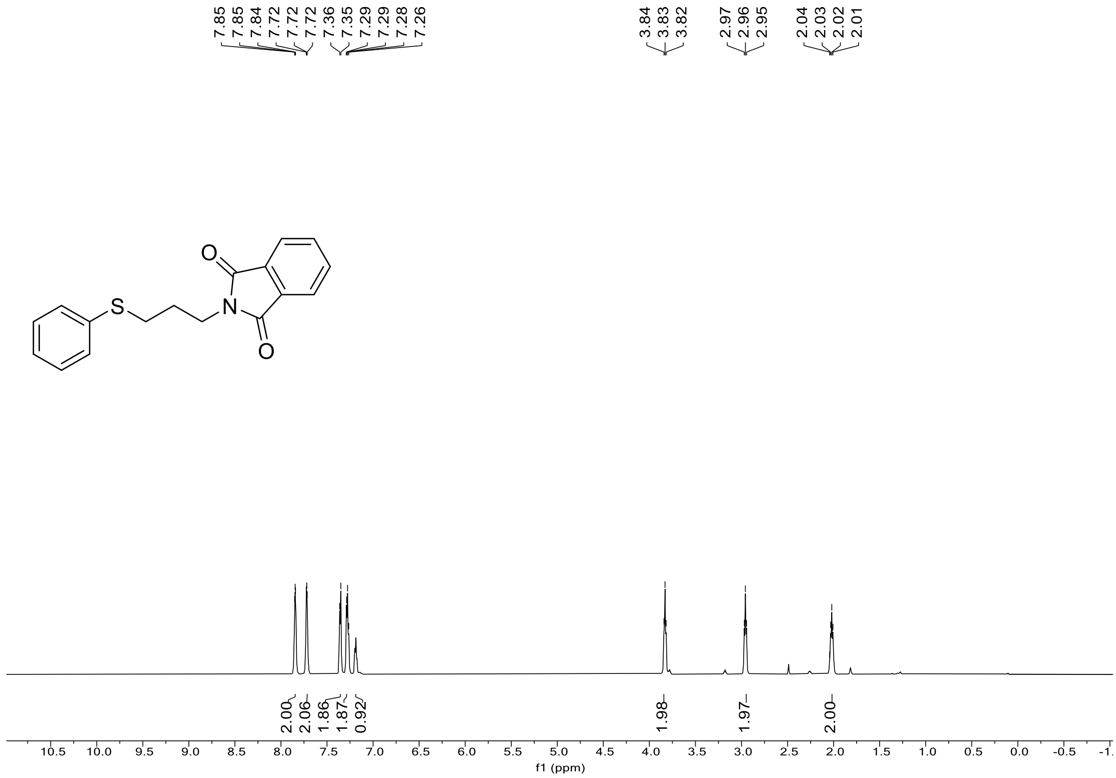
[1]H NMR of compound **4c** (600 MHz, $CDCl_3$)



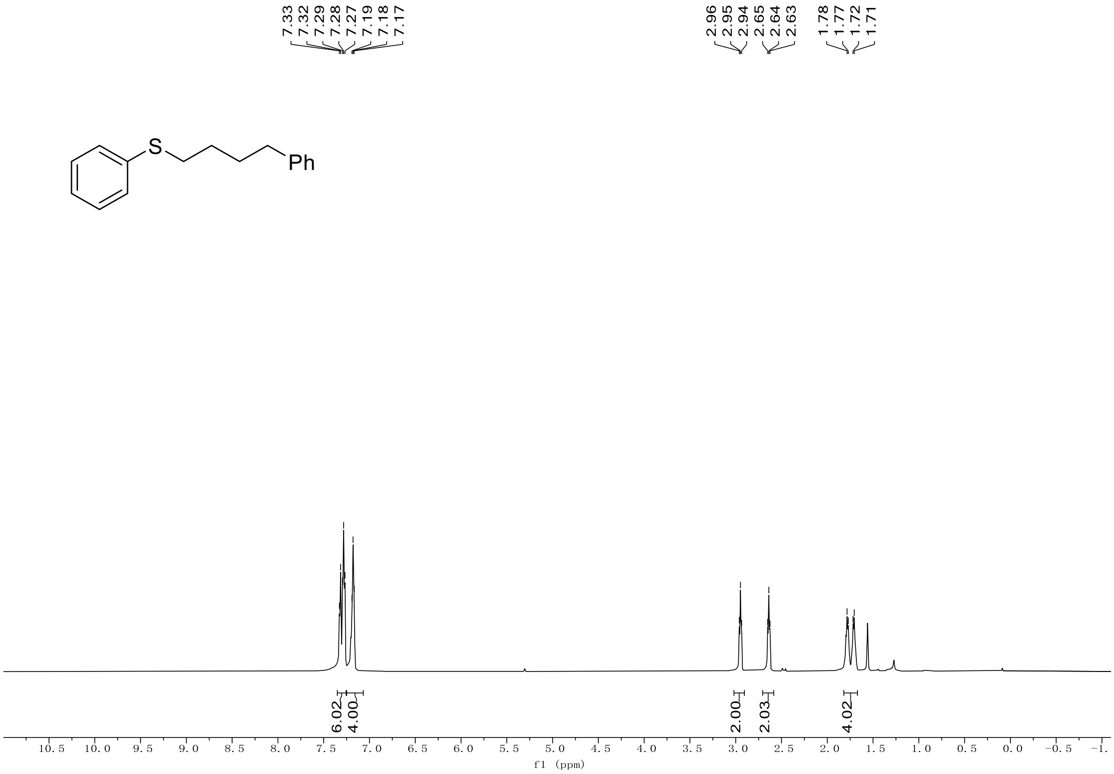
[1]H NMR of compound **4d** (600 MHz, $CDCl_3$)



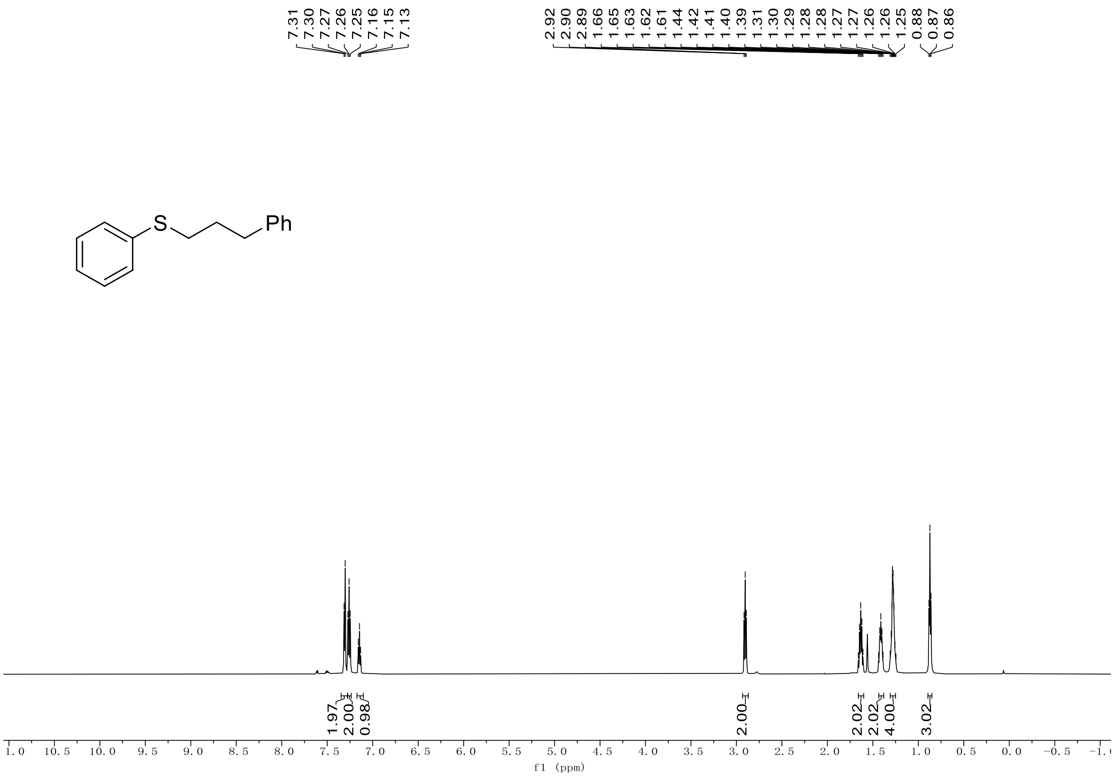
^{13}C NMR of compound **4d** (151 MHz, $CDCl_3$)



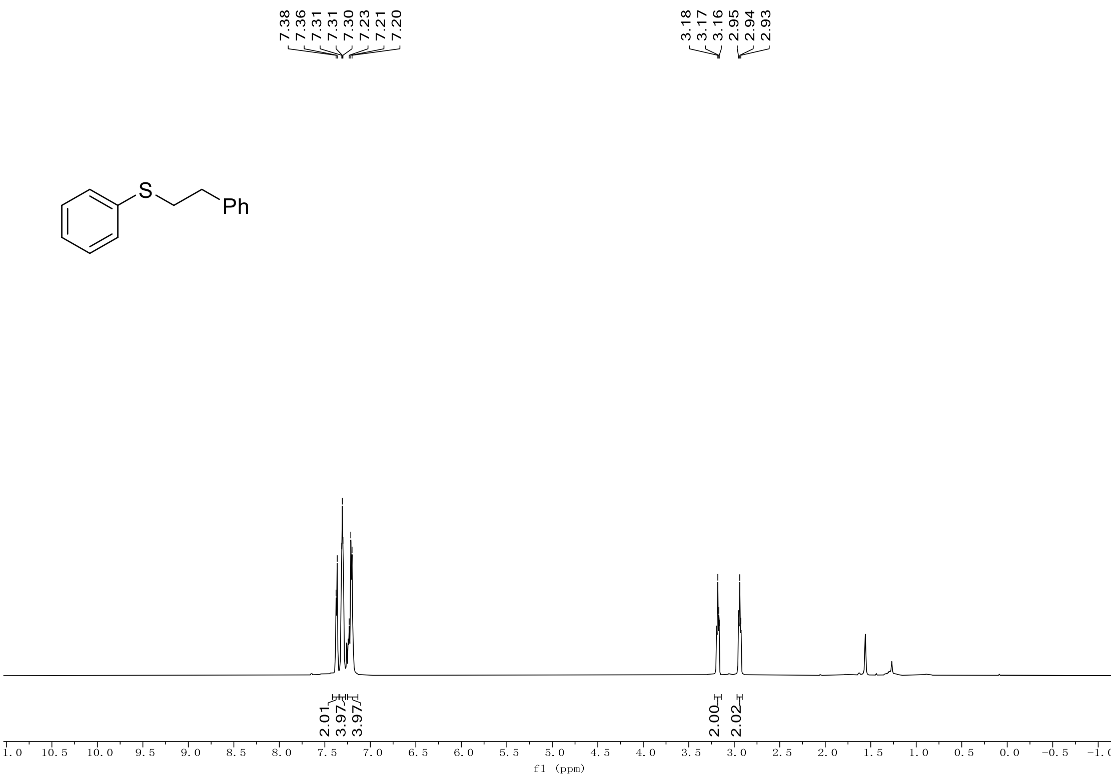
^{1}H NMR of compound **4e** (600 MHz, $CDCl_3$)



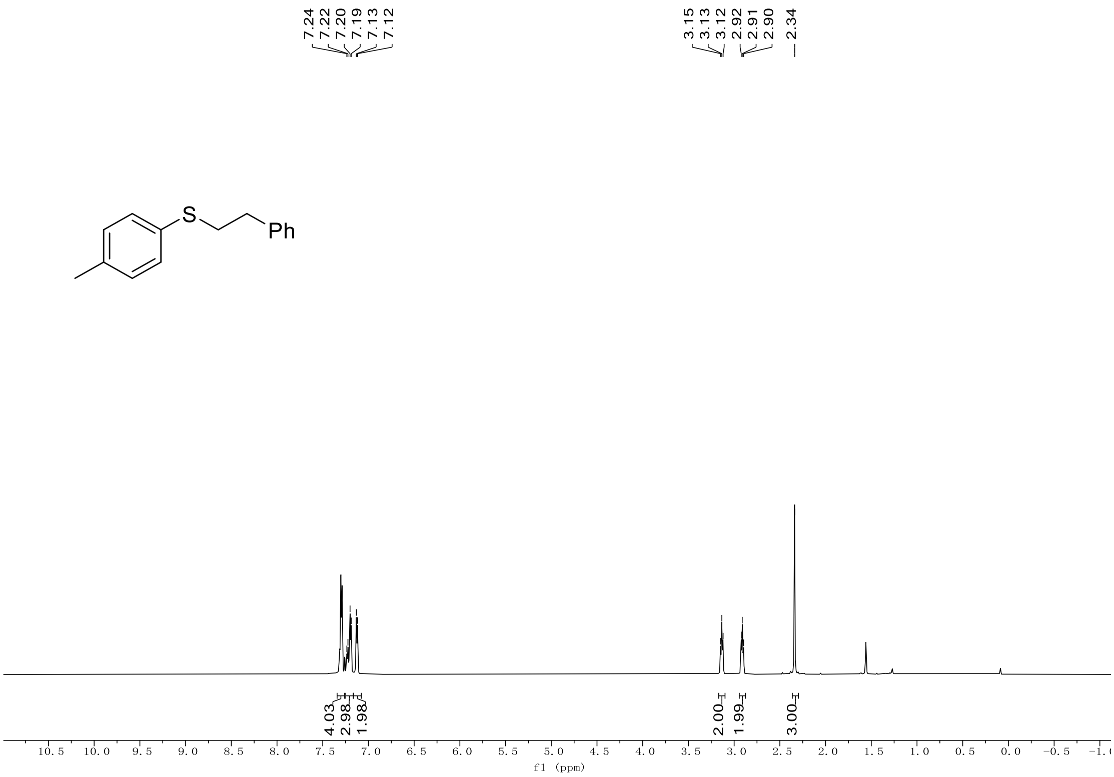
^{1}H NMR of compound **4f** (600 MHz, $CDCl_3$)



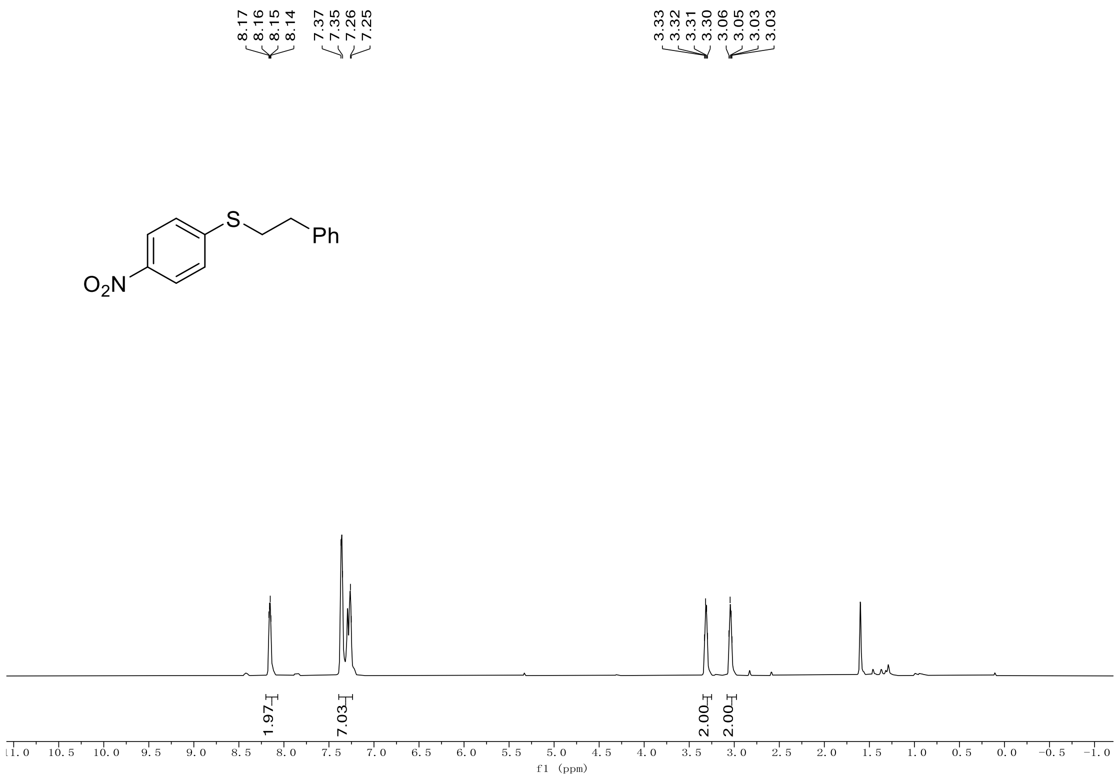
^{1}H NMR of compound **4g** (600 MHz, $CDCl_3$)



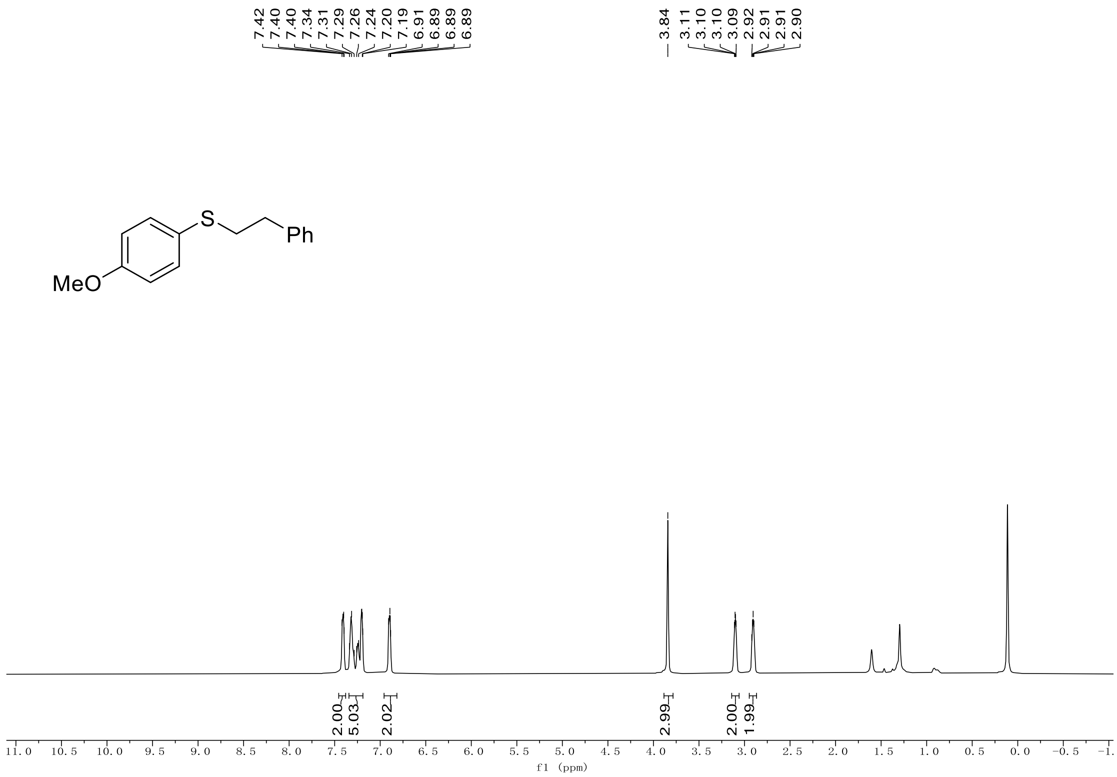
^{1}H NMR of compound **4h** (600 MHz, $CDCl_3$)



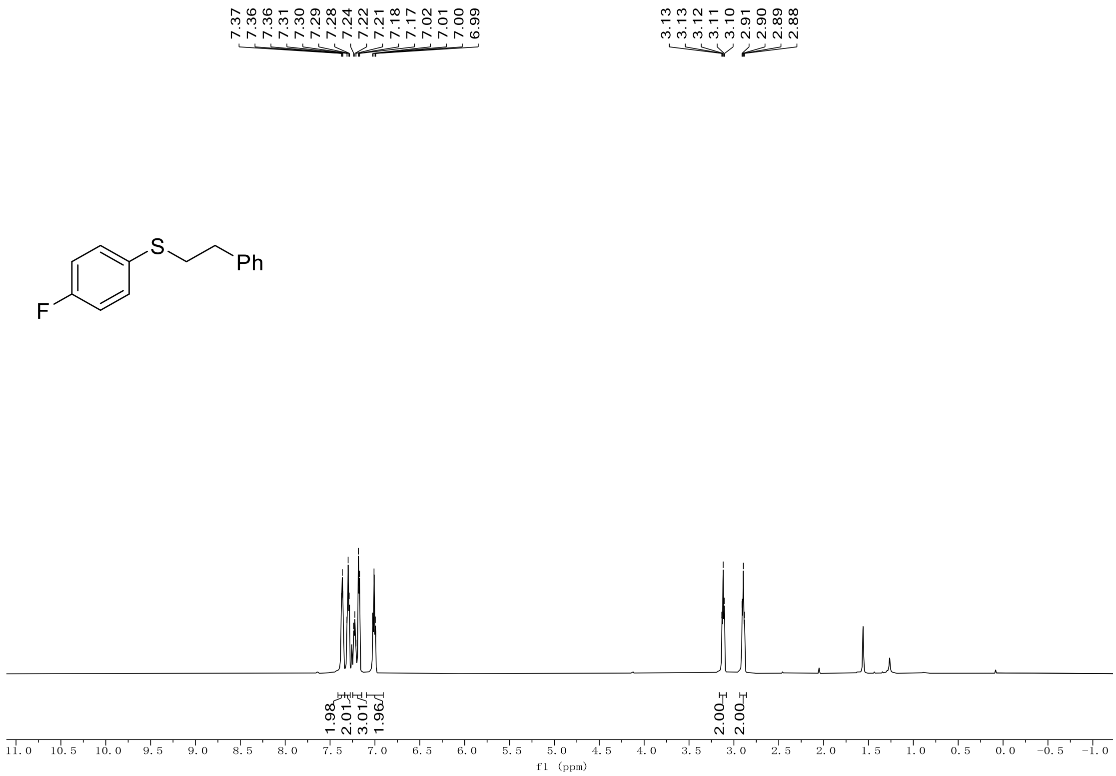
^{1}H NMR of compound **4i** (600 MHz, $CDCl_3$)



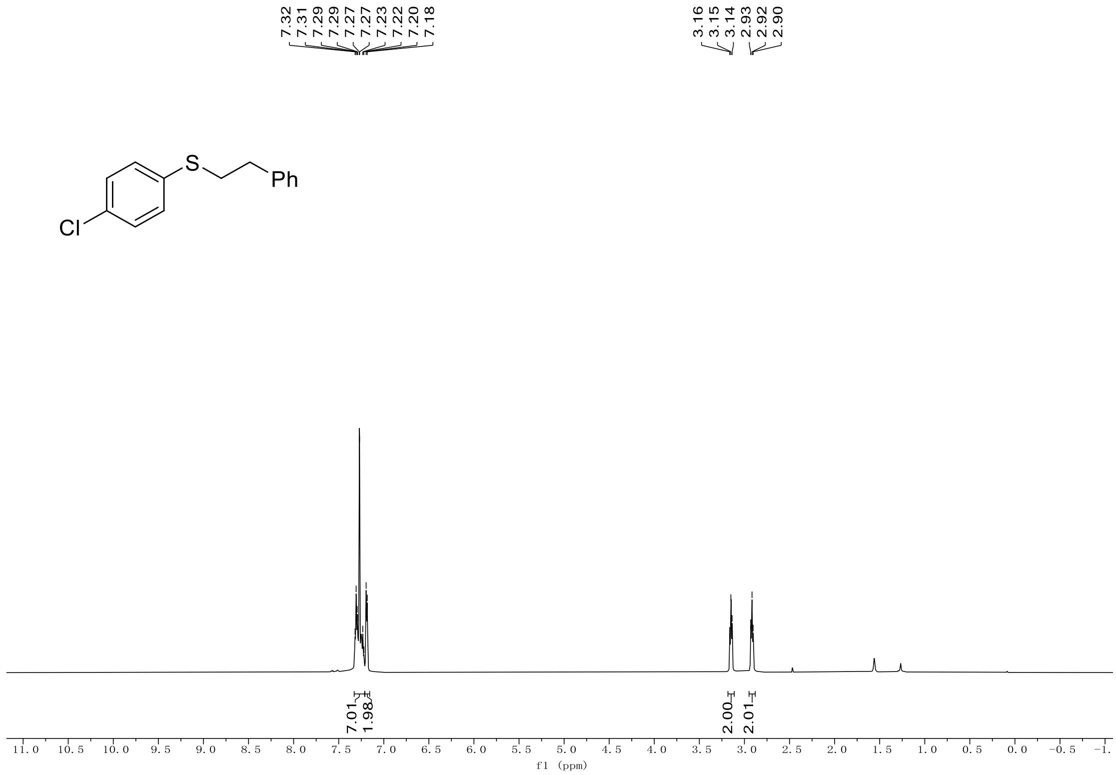
[1]H NMR of compound **4j** (600 MHz, $CDCl_3$)



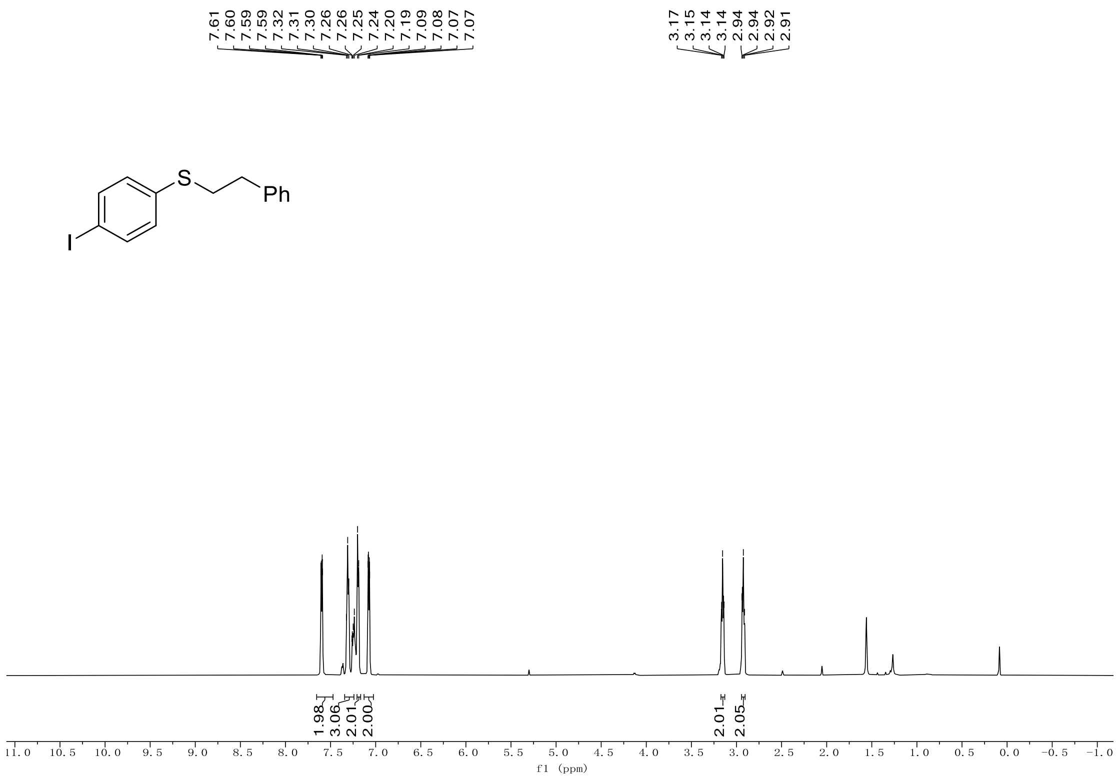
[1]H NMR of compound **4k** (600 MHz, $CDCl_3$)



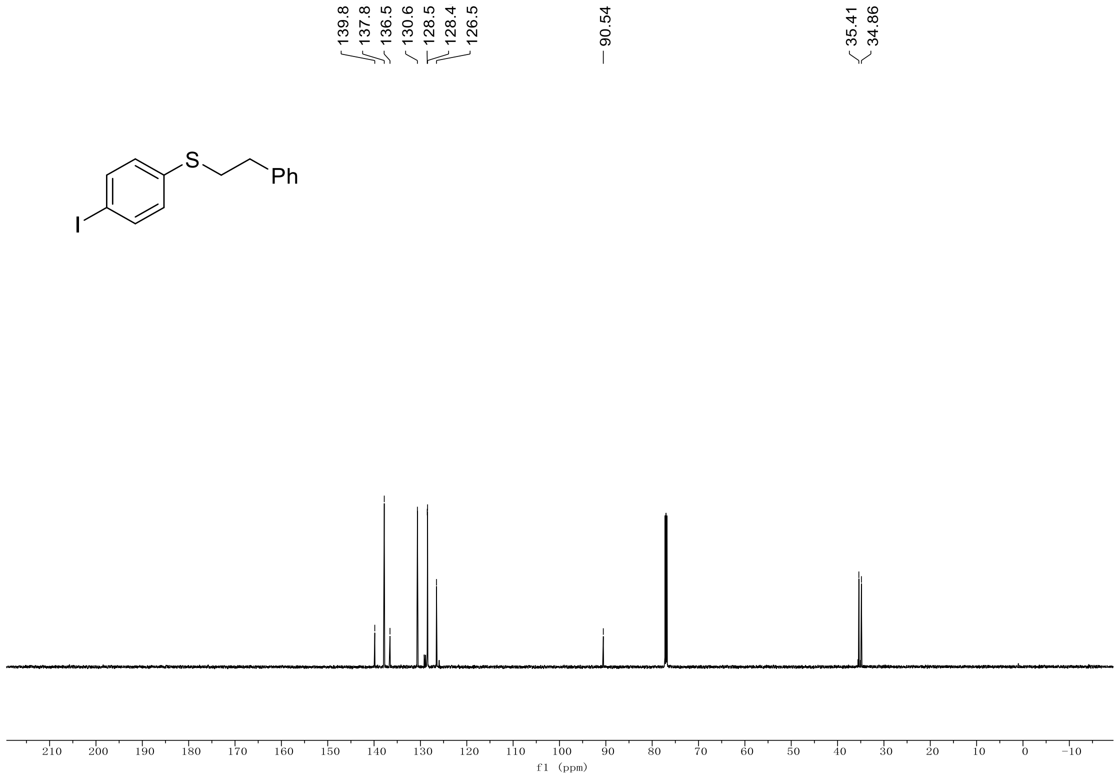
^{1}H NMR of compound **4l** (600 MHz, $CDCl_3$)



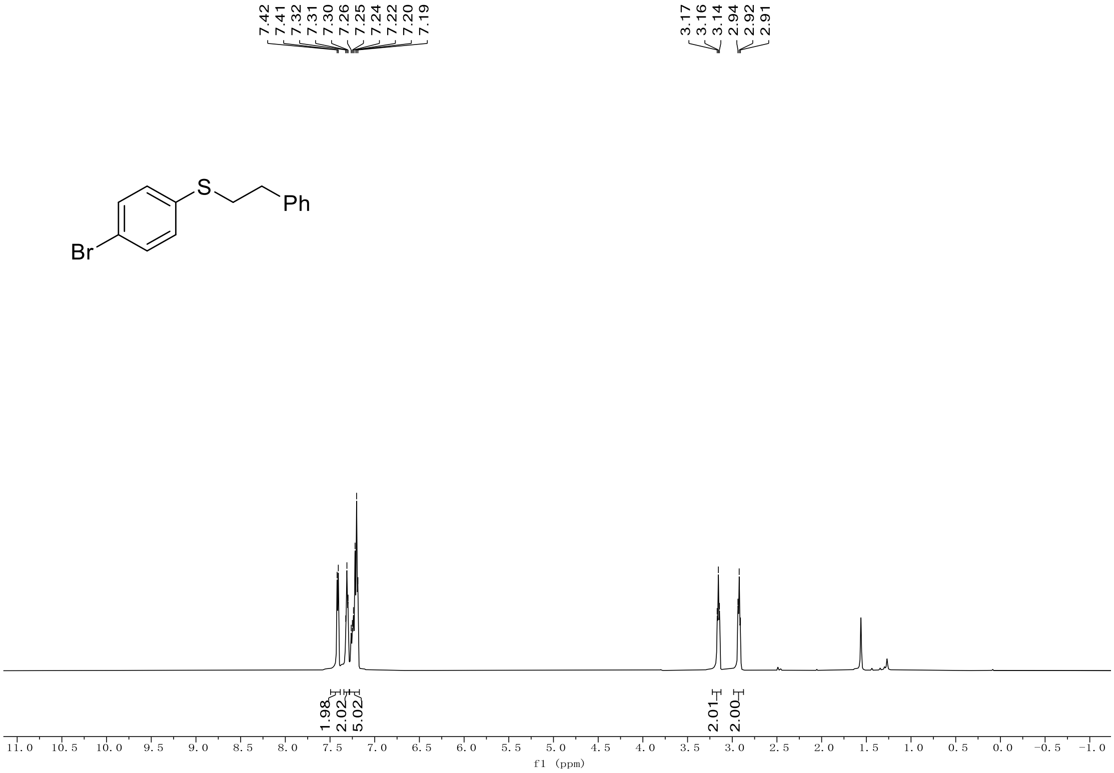
^{1}H NMR of compound **4m** (600 MHz, $CDCl_3$)



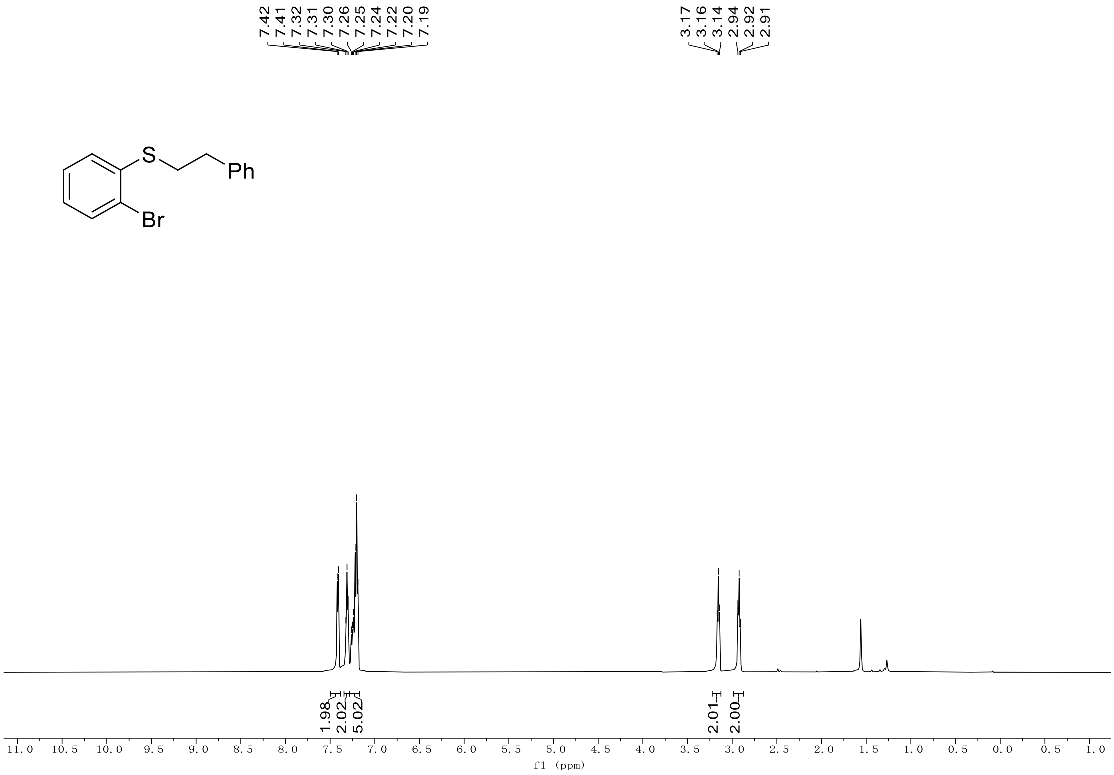
^{1}H NMR of compound **4n** (600 MHz, $CDCl_3$)



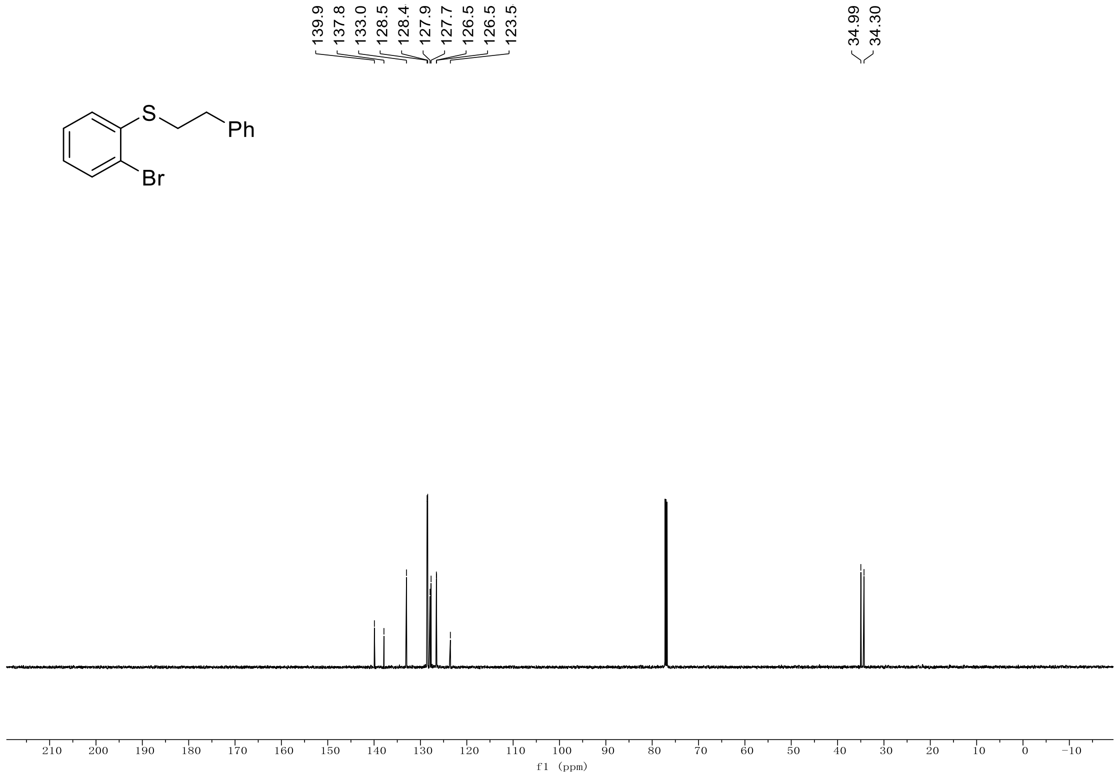
^{13}C NMR of compound **4n** (151 MHz, $CDCl_3$)



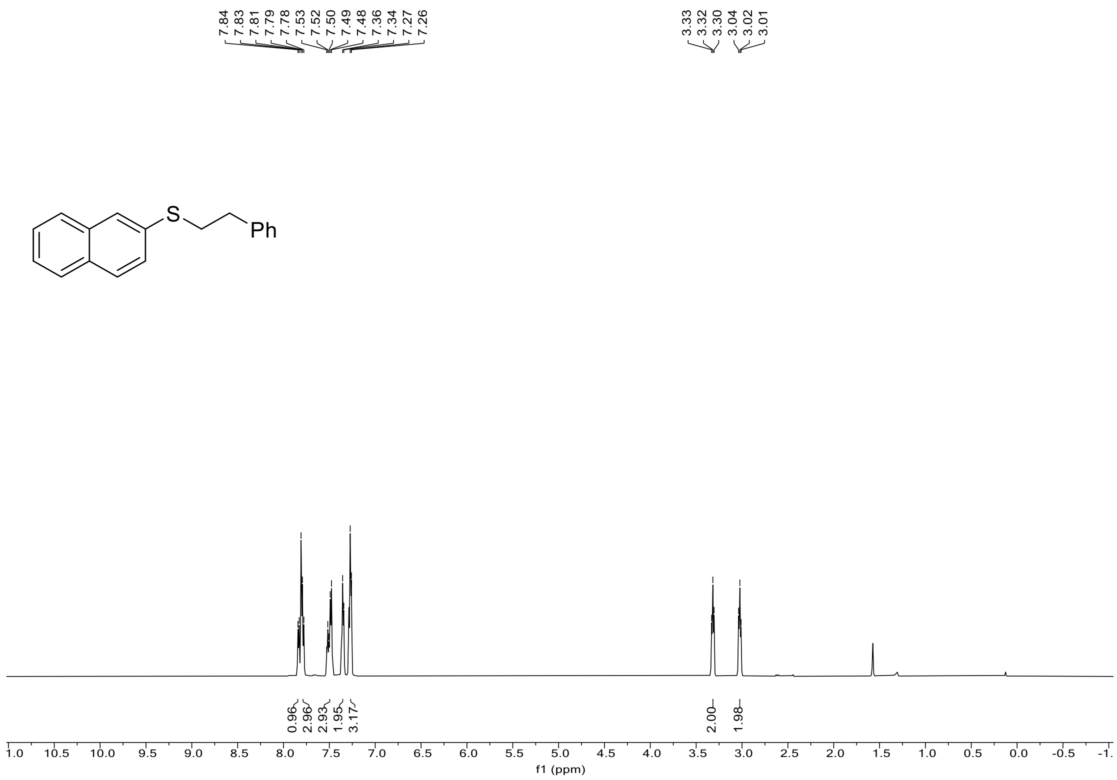
^{1}H NMR of compound **4o** (600 MHz, $CDCl_3$)



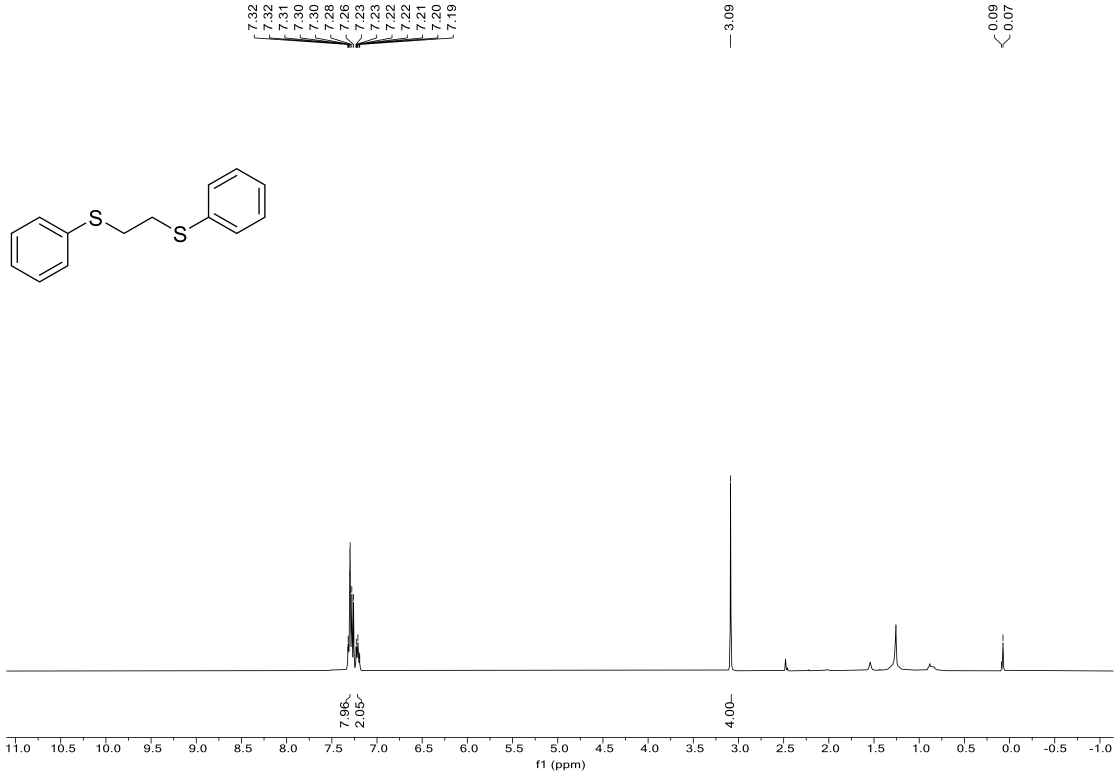
^{1}H NMR of compound **4P** (600 MHz, $CDCl_3$)



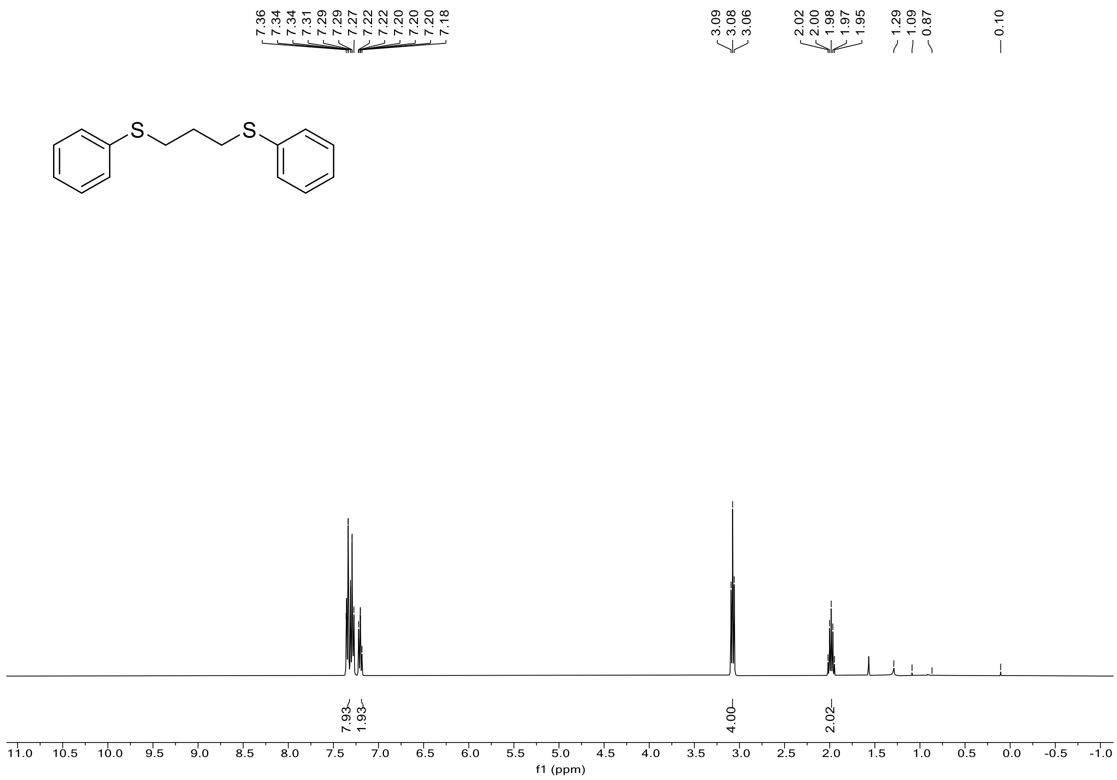
^{13}C NMR of compound **4P** (600 MHz, CDCl$_3$)



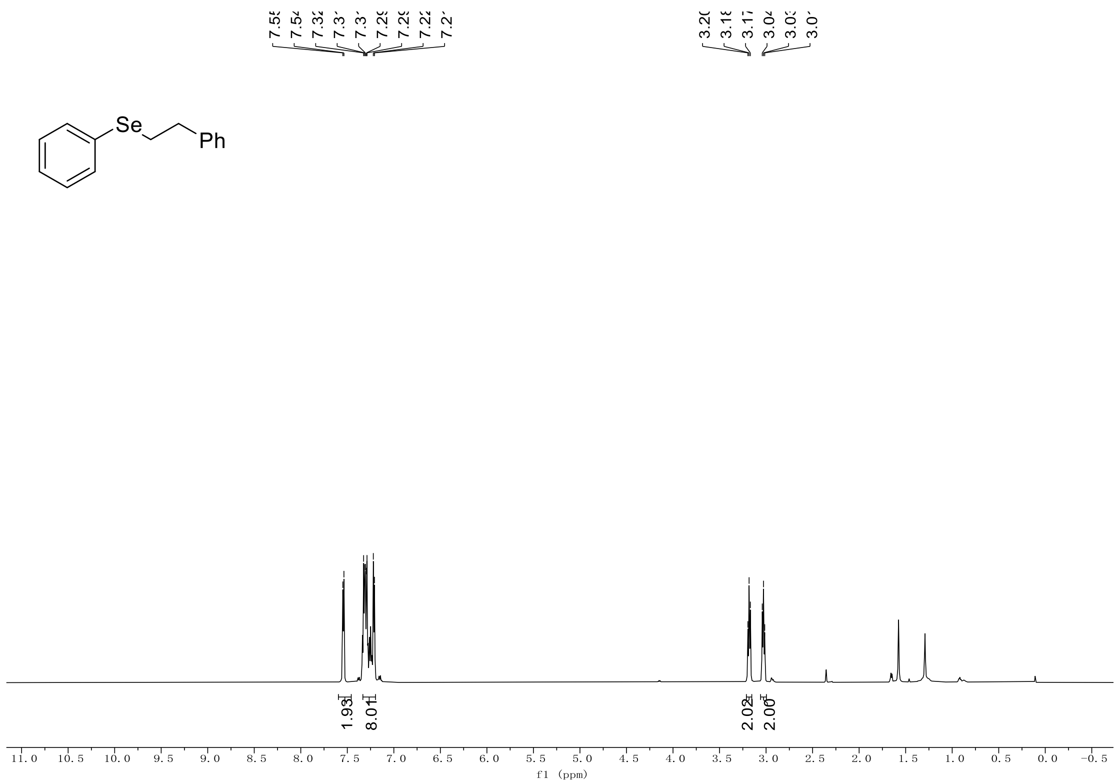
^{1}H NMR of compound **4q** (600 MHz, CDCl$_3$)



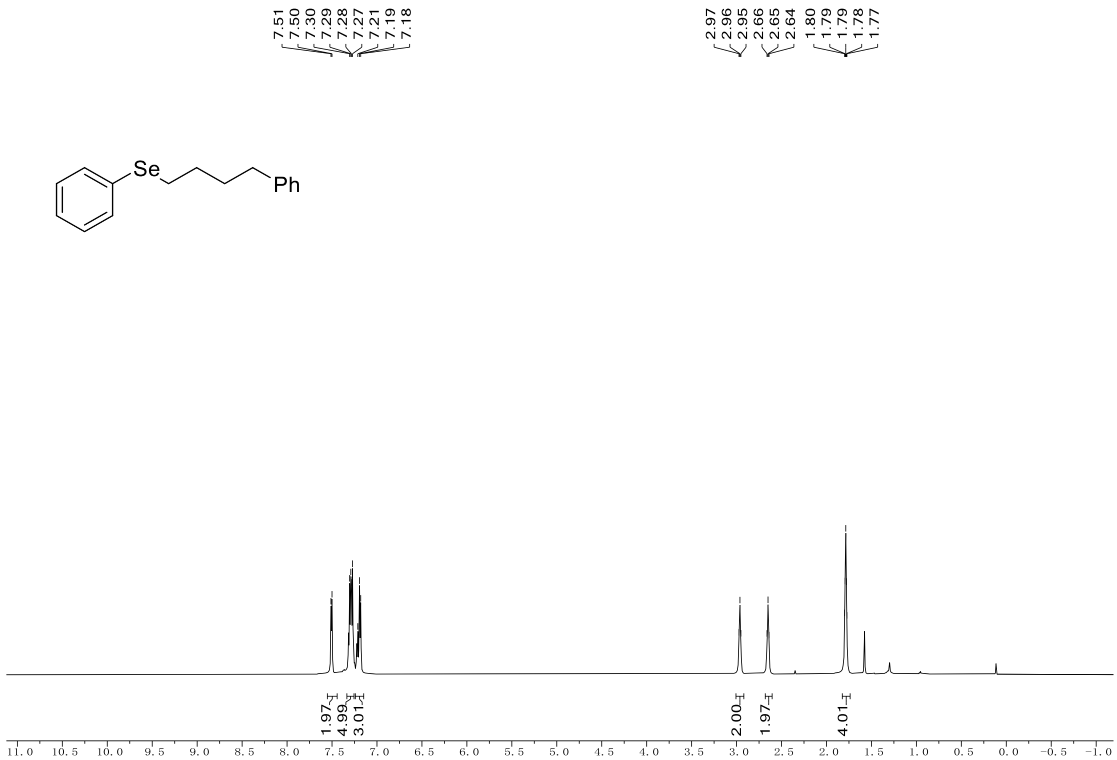
[1]H NMR of compound **4r** (400 MHz, $CDCl_3$)



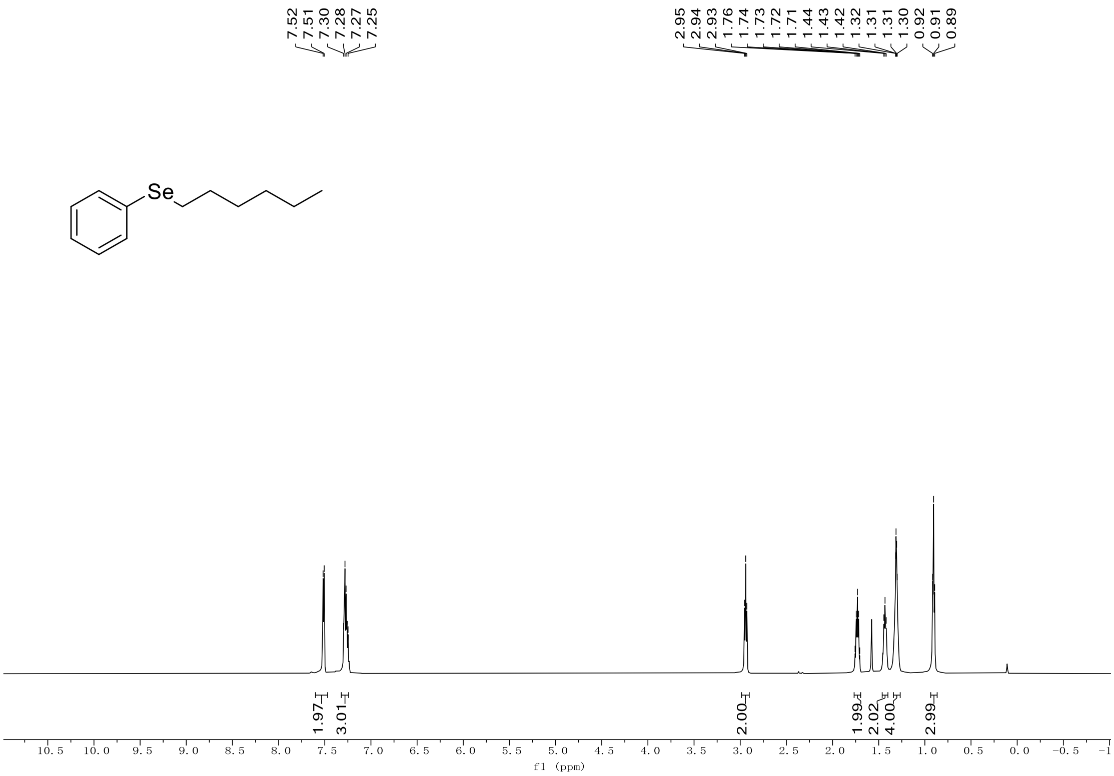
[1]H NMR of compound **4s** (400 MHz, $CDCl_3$)



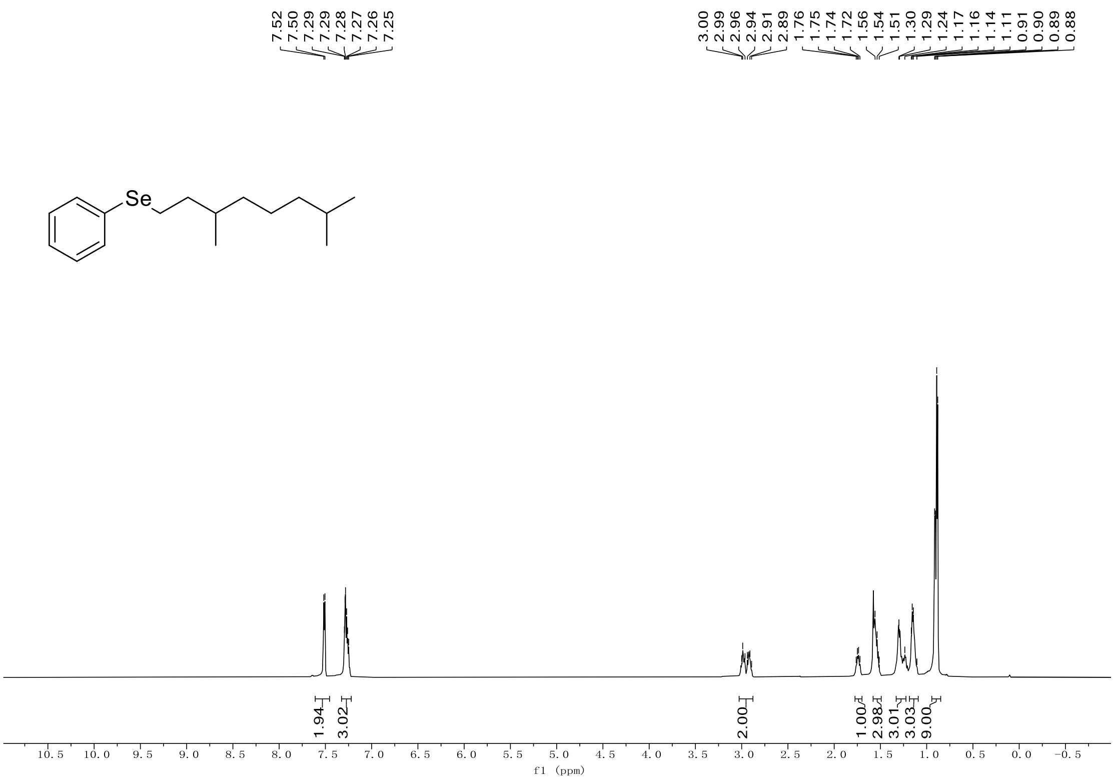
[1]H NMR of compound **4t** (600 MHz, $CDCl_3$)



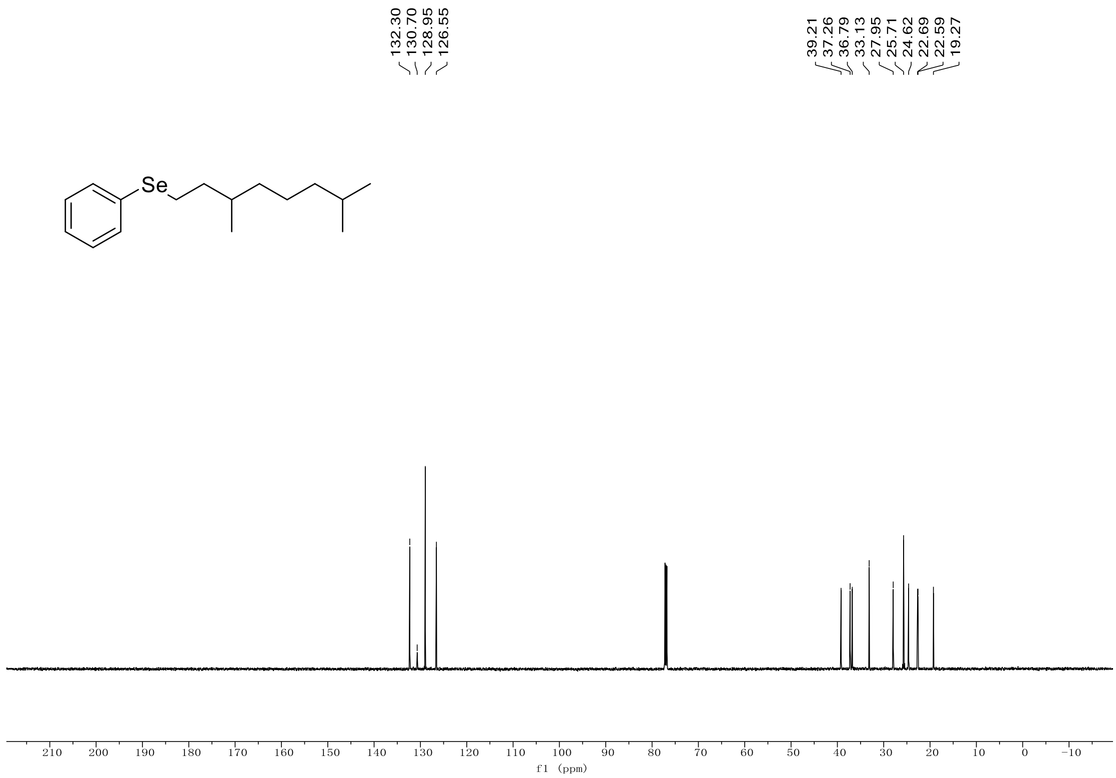
[1]H NMR of compound **4u** (600 MHz, $CDCl_3$)



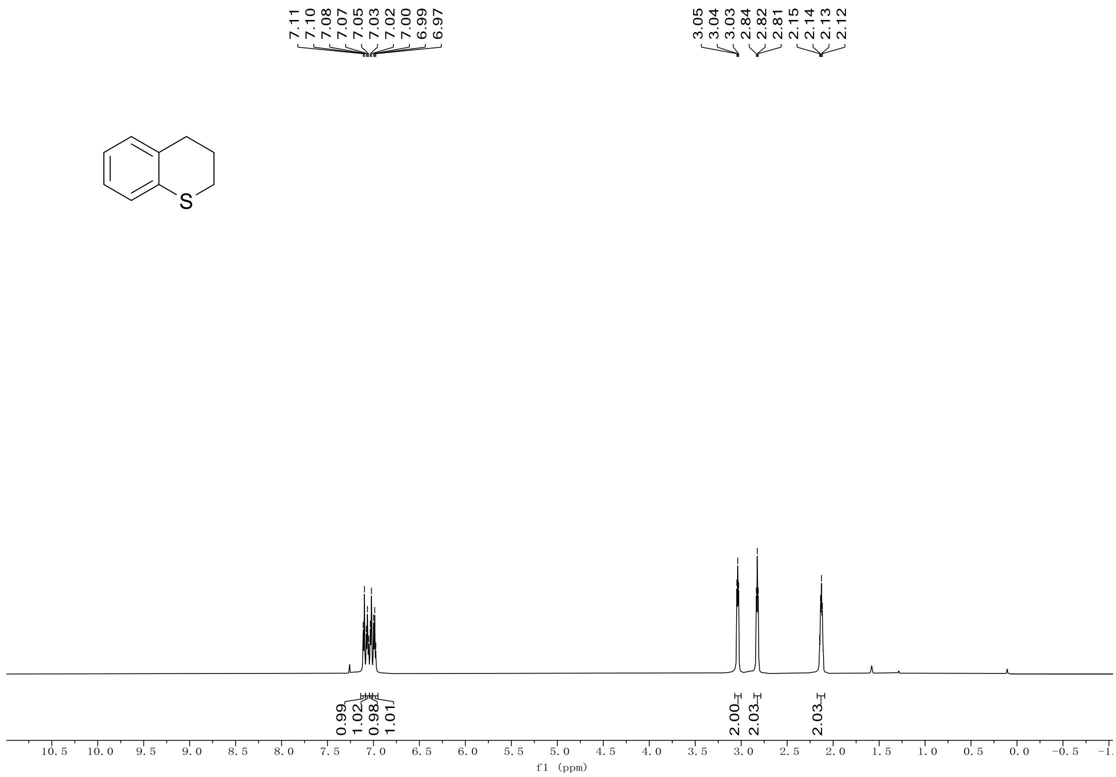
[1]H NMR of compound **4v** (600 MHz, $CDCl_3$)



[1]H NMR of compound **4w** (600 MHz, $CDCl_3$)

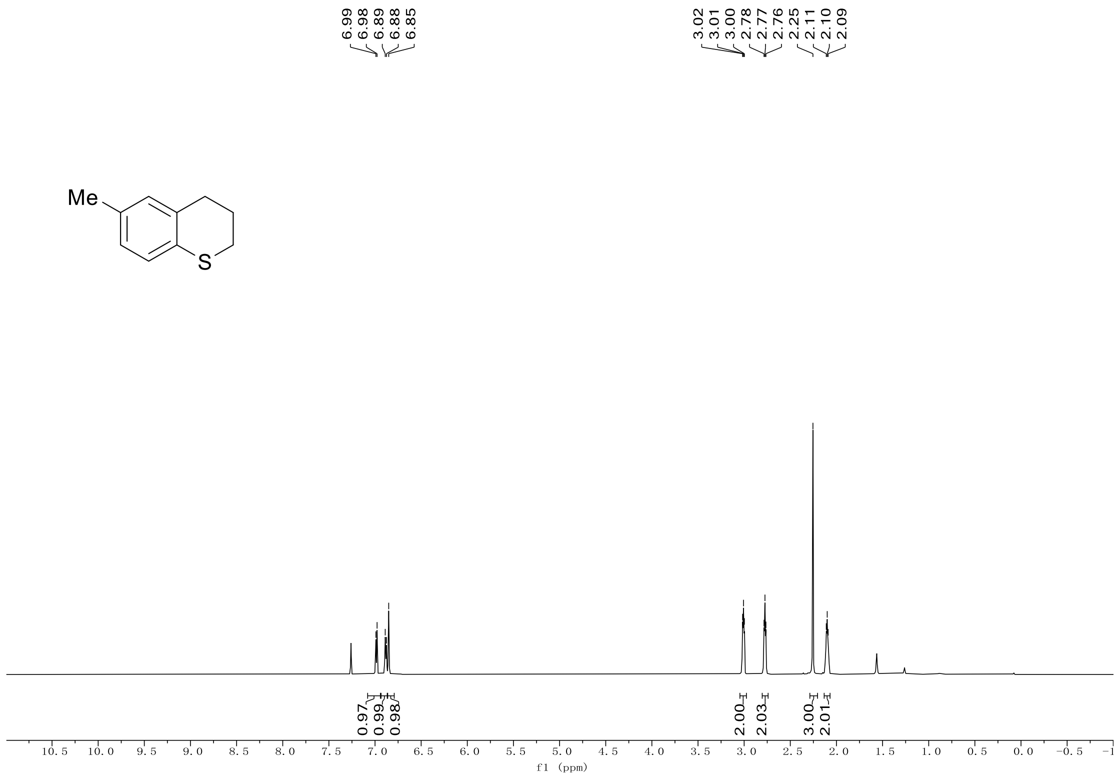


^{13}C NMR of compound **4w** (151 MHz, $CDCl_3$)

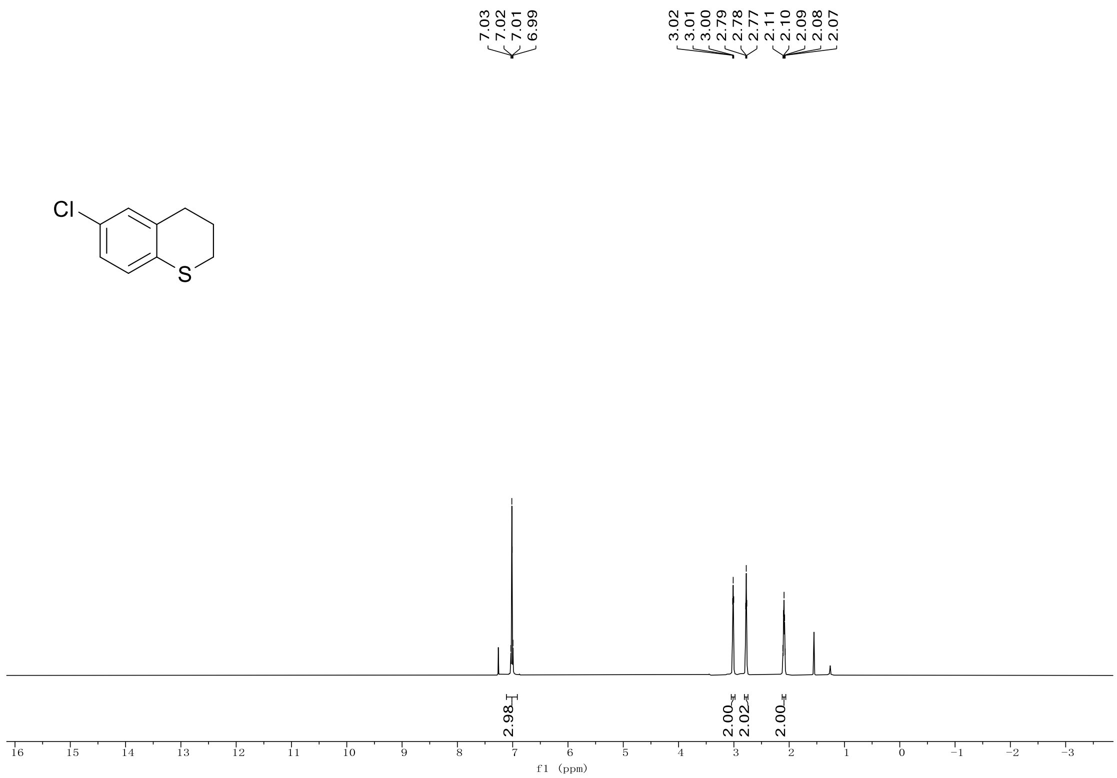


^{1}H NMR of compound **6a** (600 MHz, $CDCl_3$)

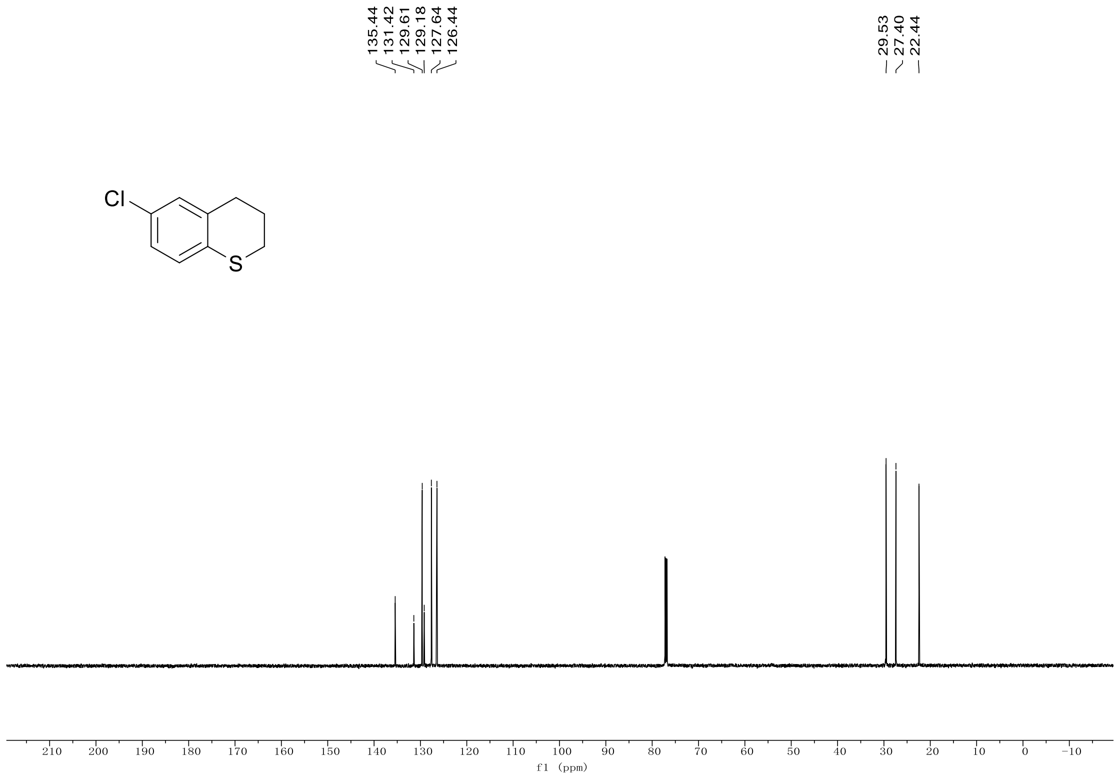
^{1}H NMR of compound **6b** (600 MHz, $CDCl_3$)



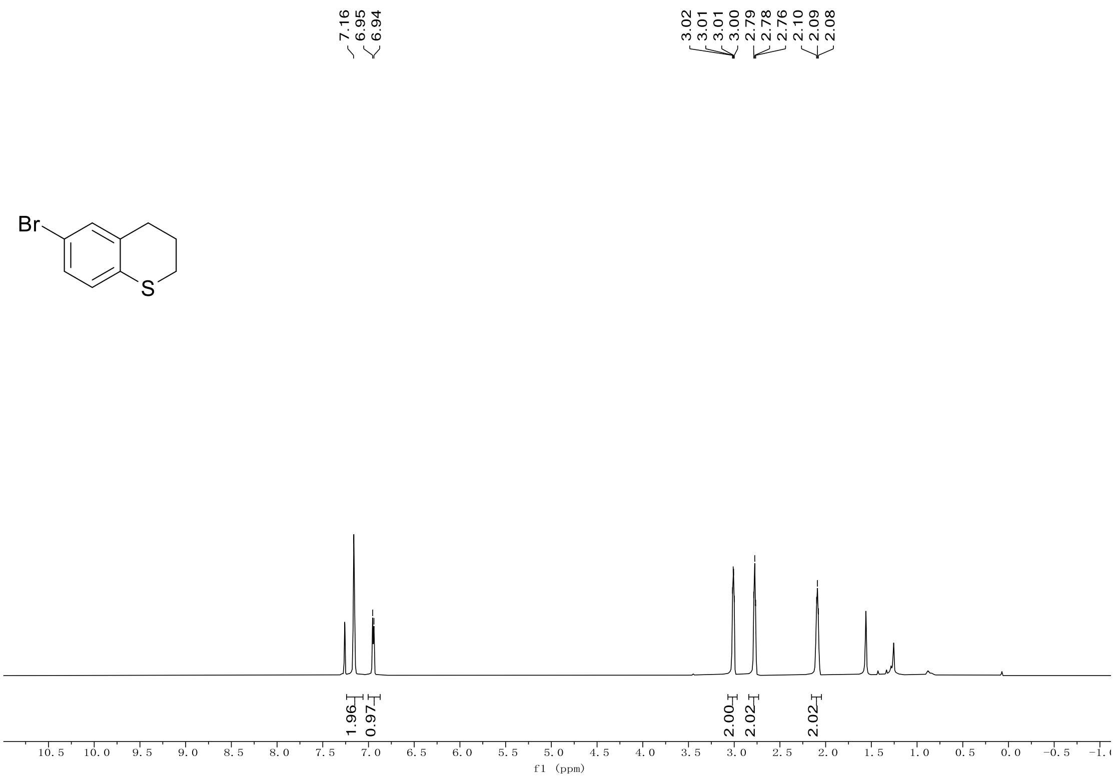
^{1}H NMR of compound **6c** (600 MHz, $CDCl_3$)



^{1}H NMR of compound **6d** (600 MHz, $CDCl_3$)

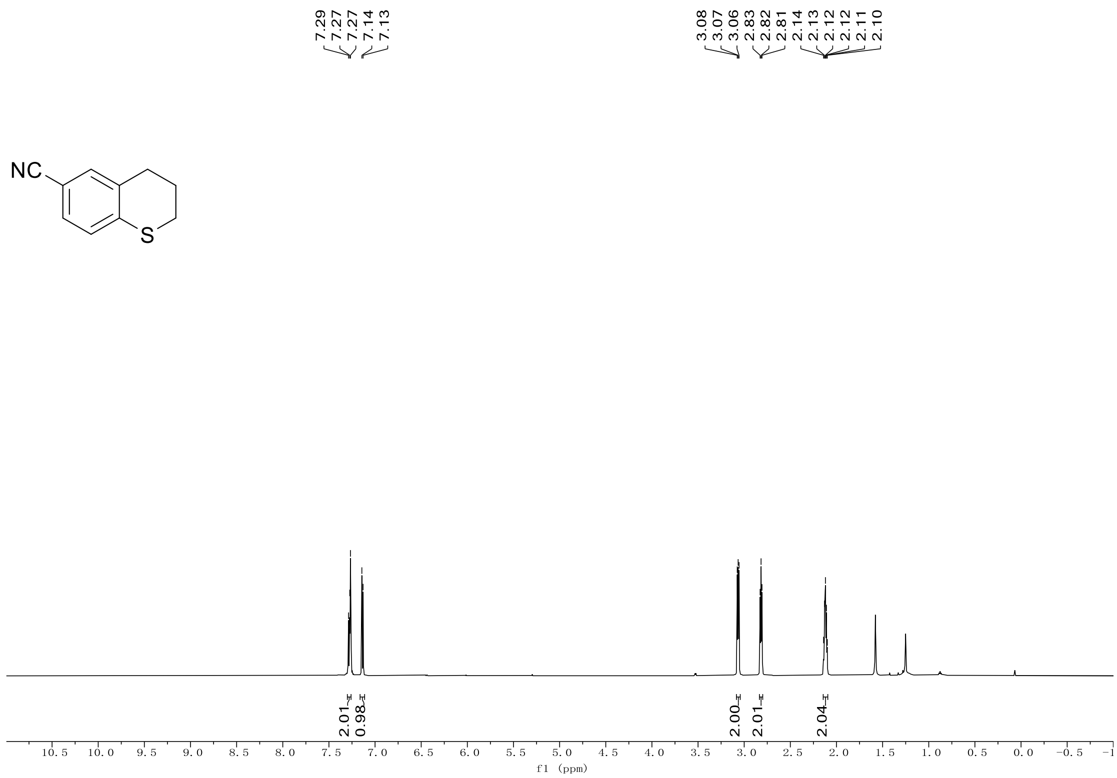


^{13}C NMR of compound **6d** (151 MHz, $CDCl_3$)



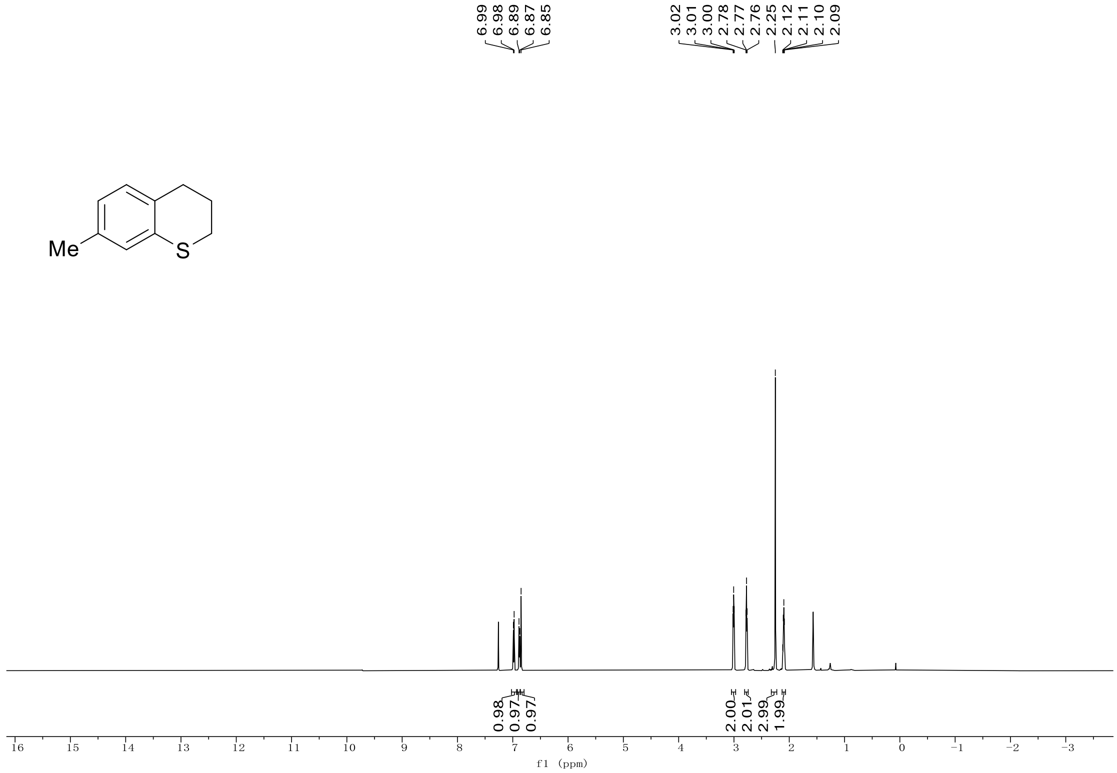
^{1}H NMR of compound **6e** (600 MHz, $CDCl_3$)

^{13}C NMR of compound **6e** (151 MHz, $CDCl_3$)

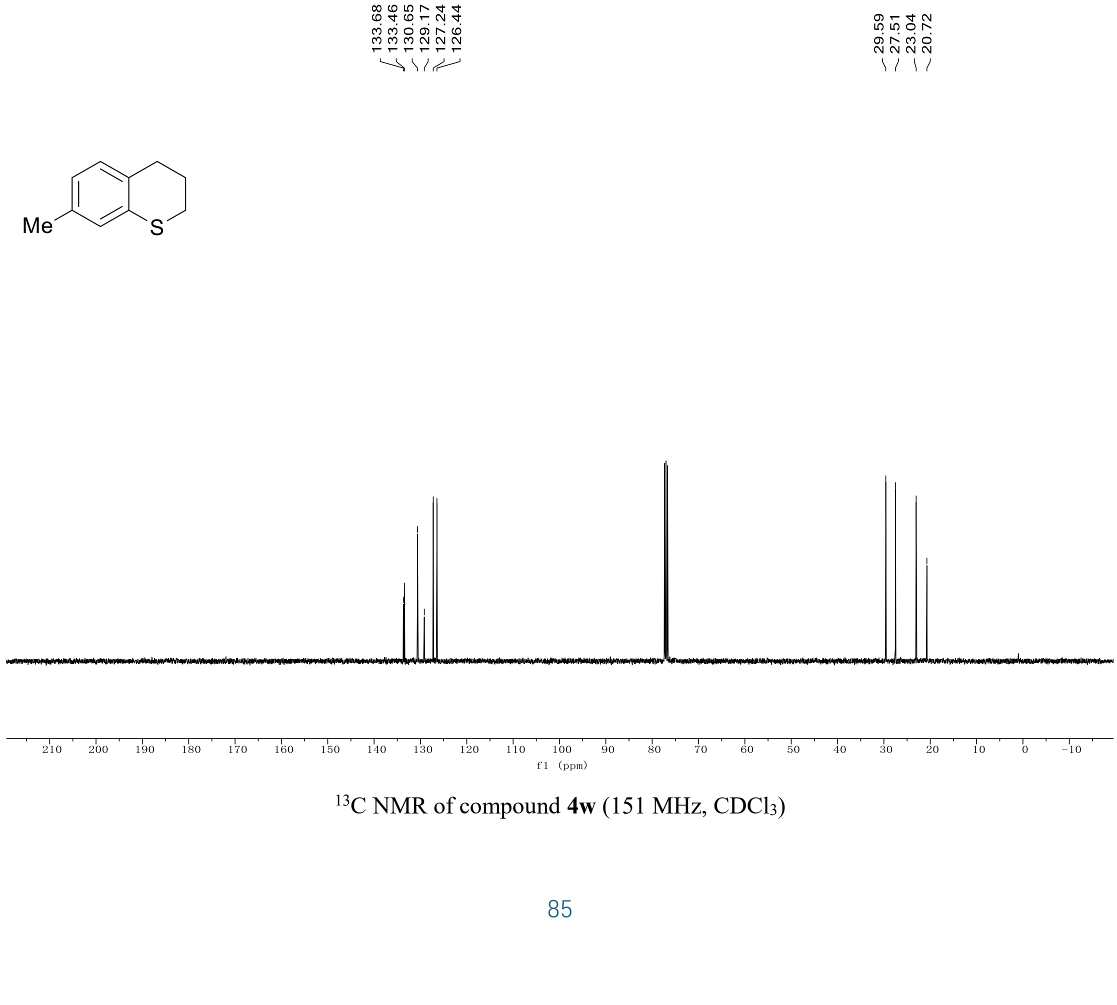


^{1}H NMR of compound **6e** (600 MHz, $CDCl_3$)

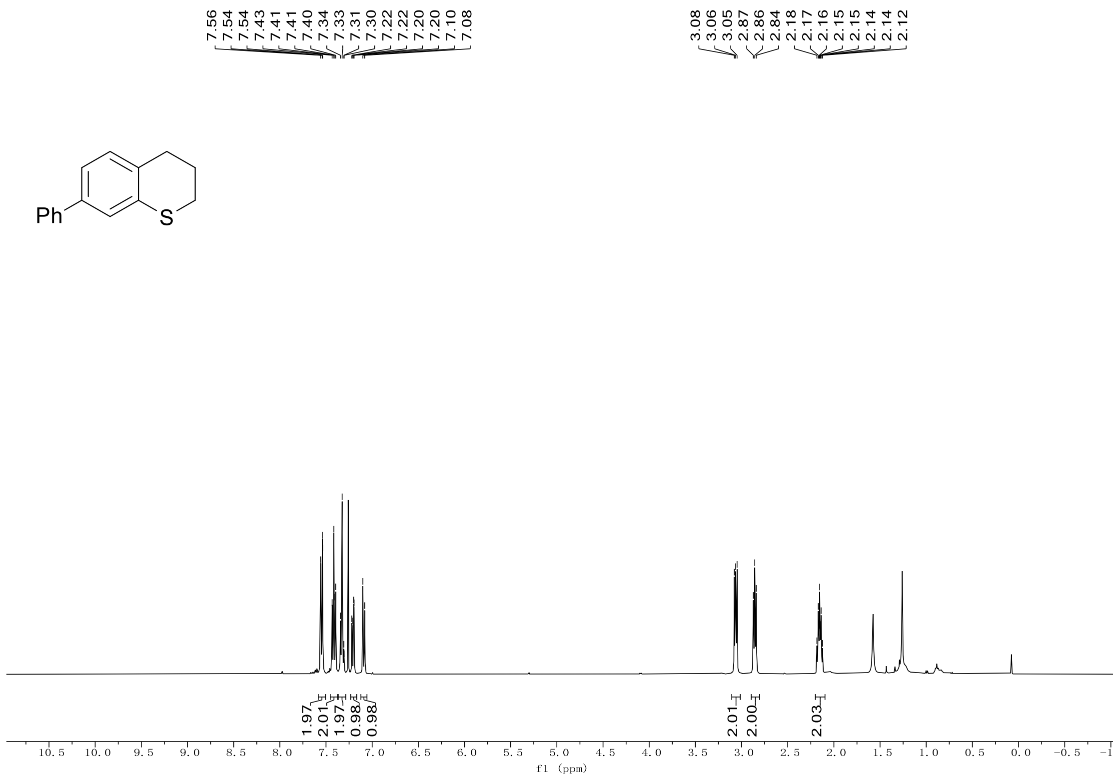
^{13}C NMR of compound **4w** (151 MHz, $CDCl_3$)



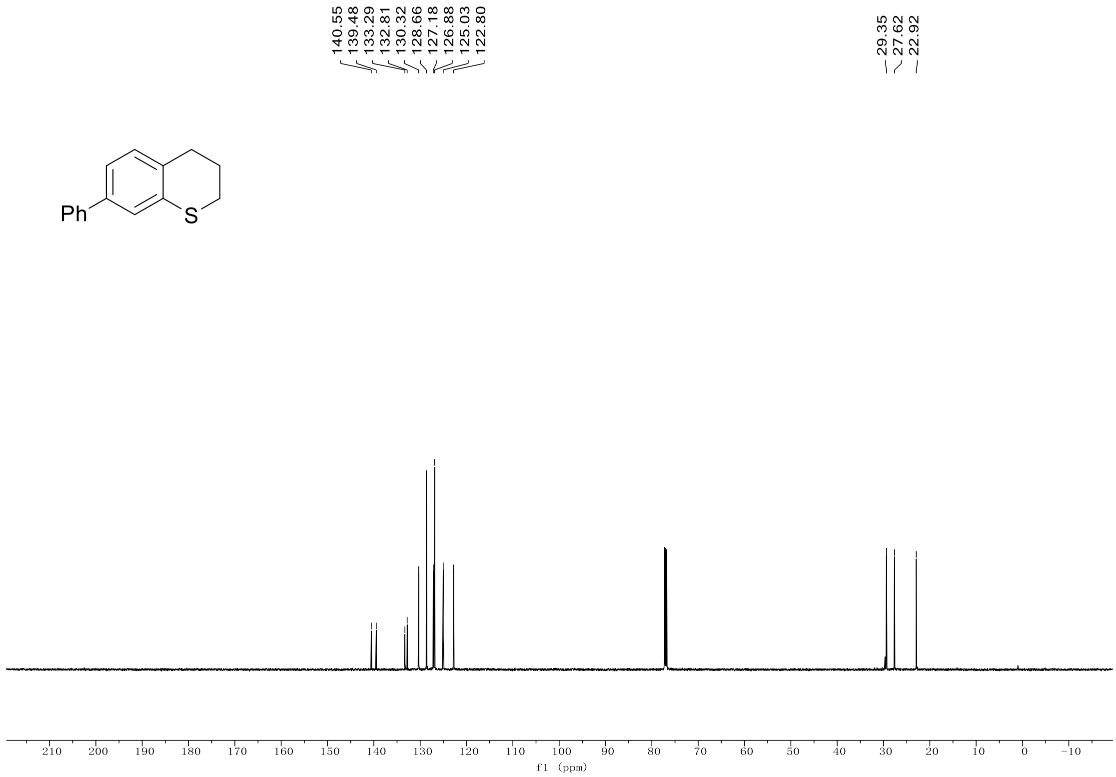
^{1}H NMR of compound **6e** (600 MHz, $CDCl_3$)



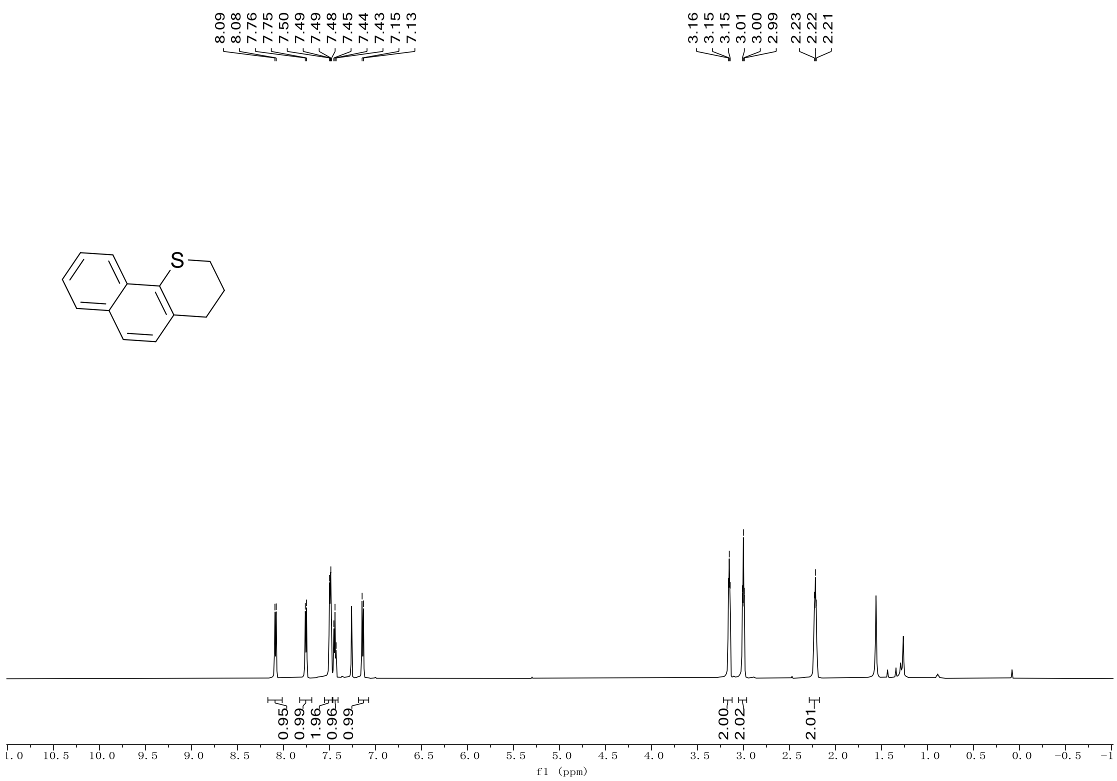
^{13}C NMR of compound **4w** (151 MHz, $CDCl_3$)



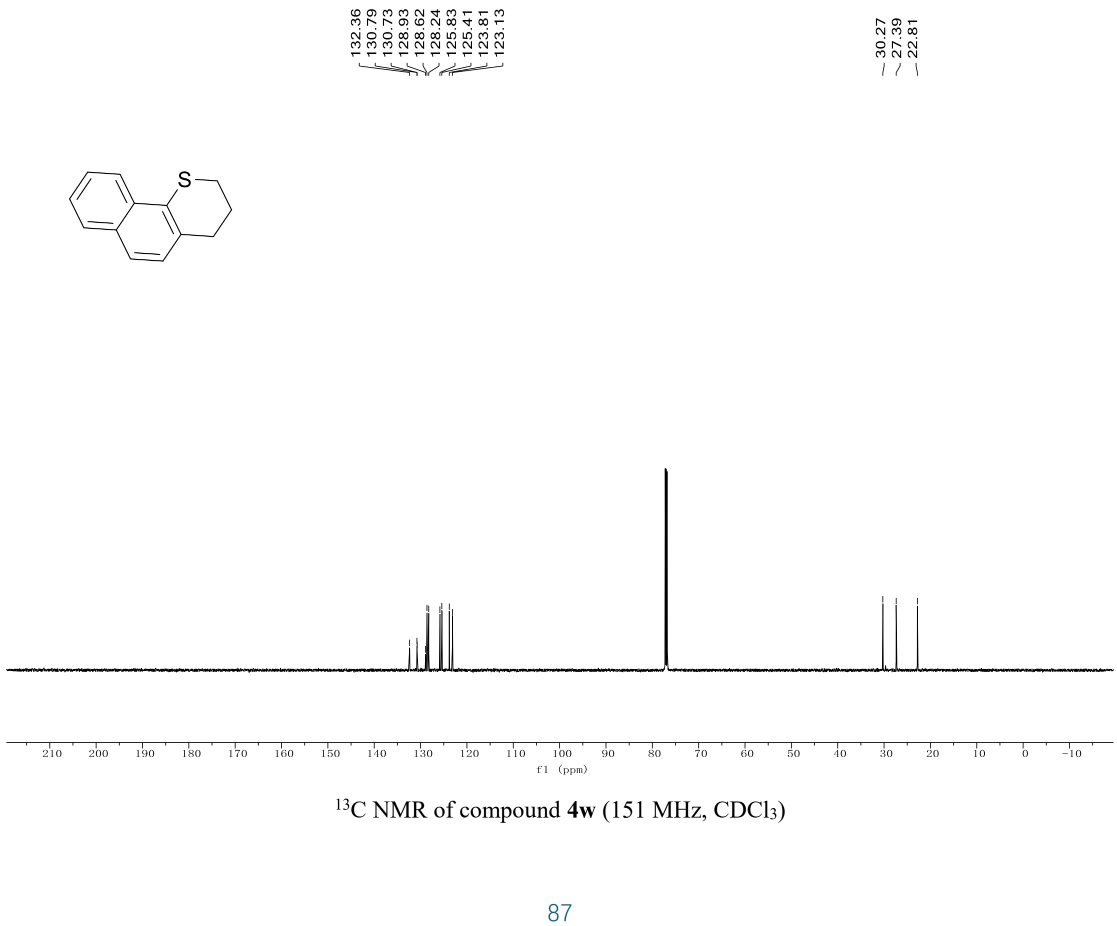
[1]H NMR of compound **6e** (600 MHz, $CDCl_3$)



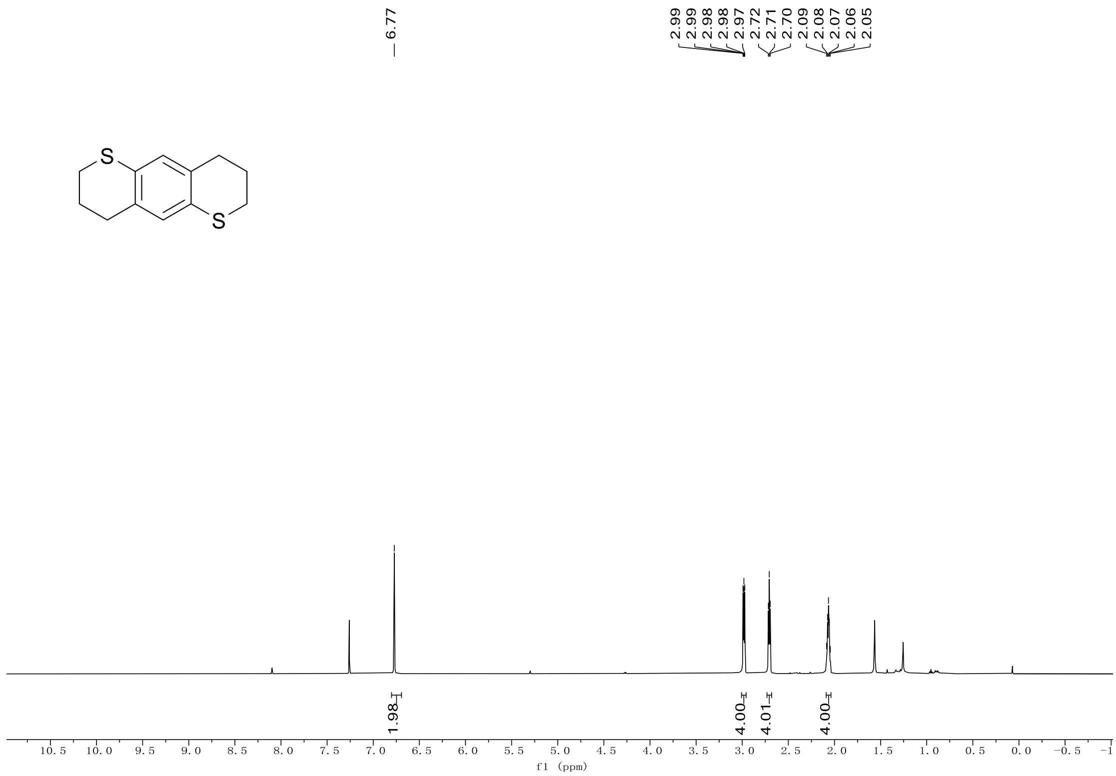
[13]C NMR of compound **4w** (151 MHz, $CDCl_3$)



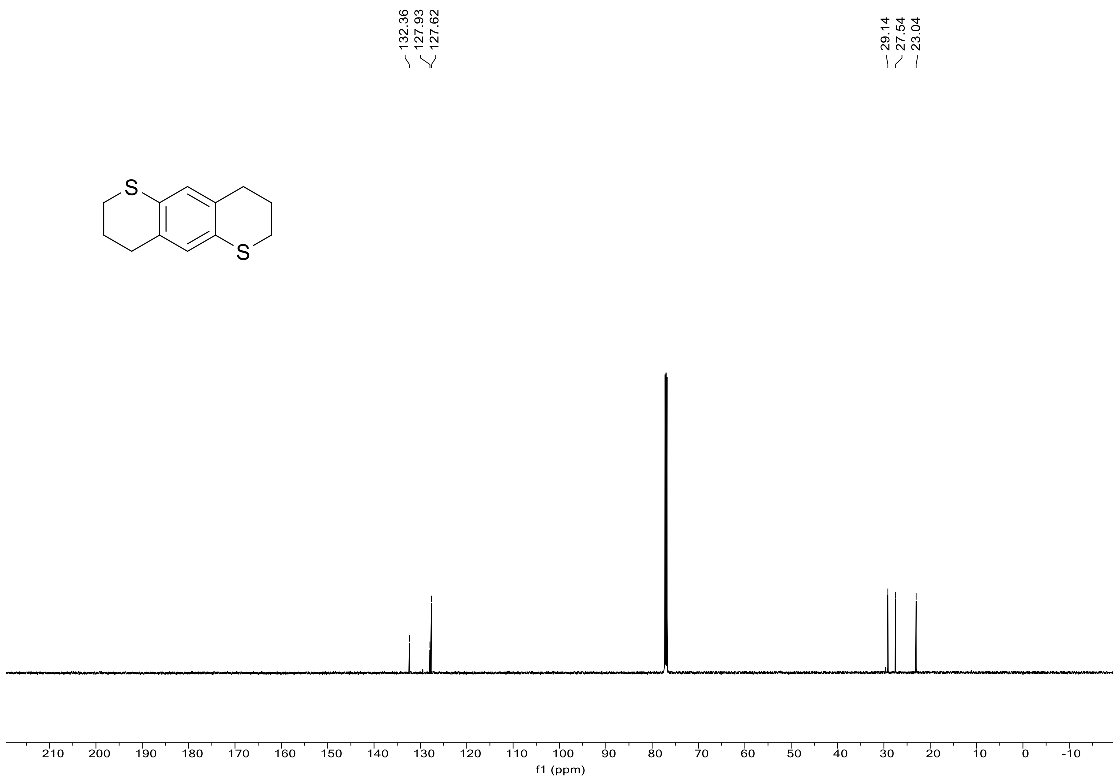
[1]H NMR of compound **6e** (600 MHz, $CDCl_3$)



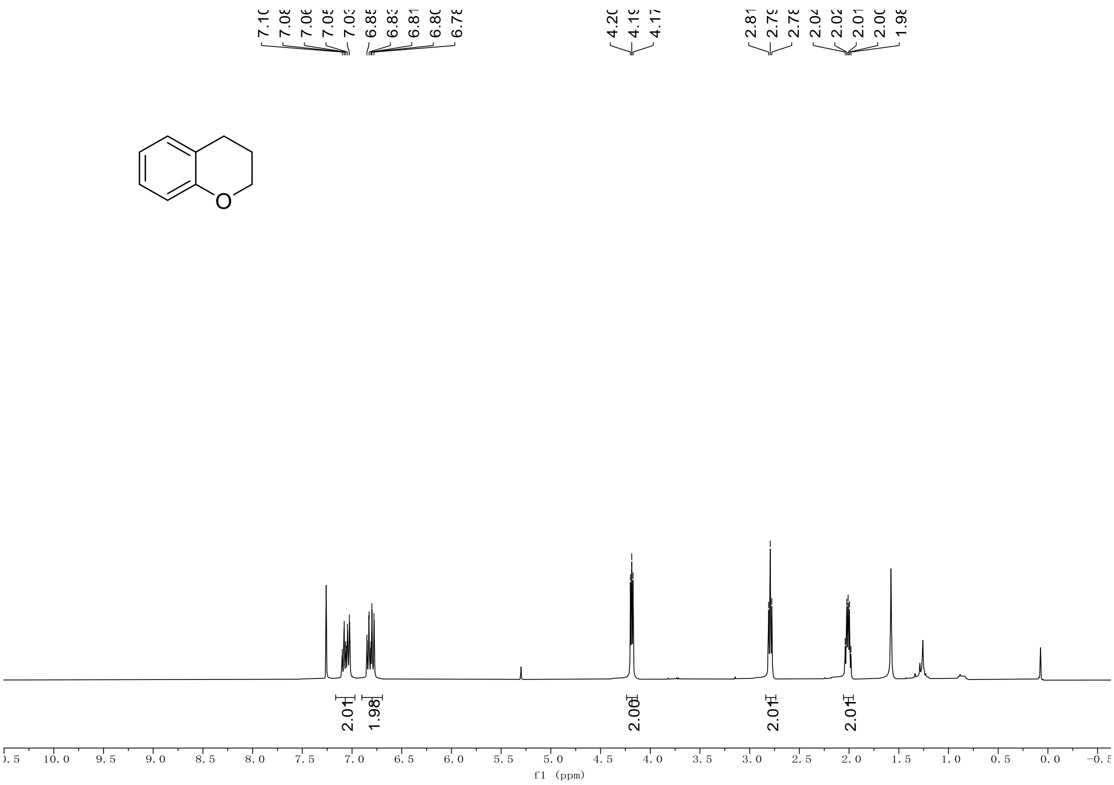
[13]C NMR of compound **4w** (151 MHz, $CDCl_3$)



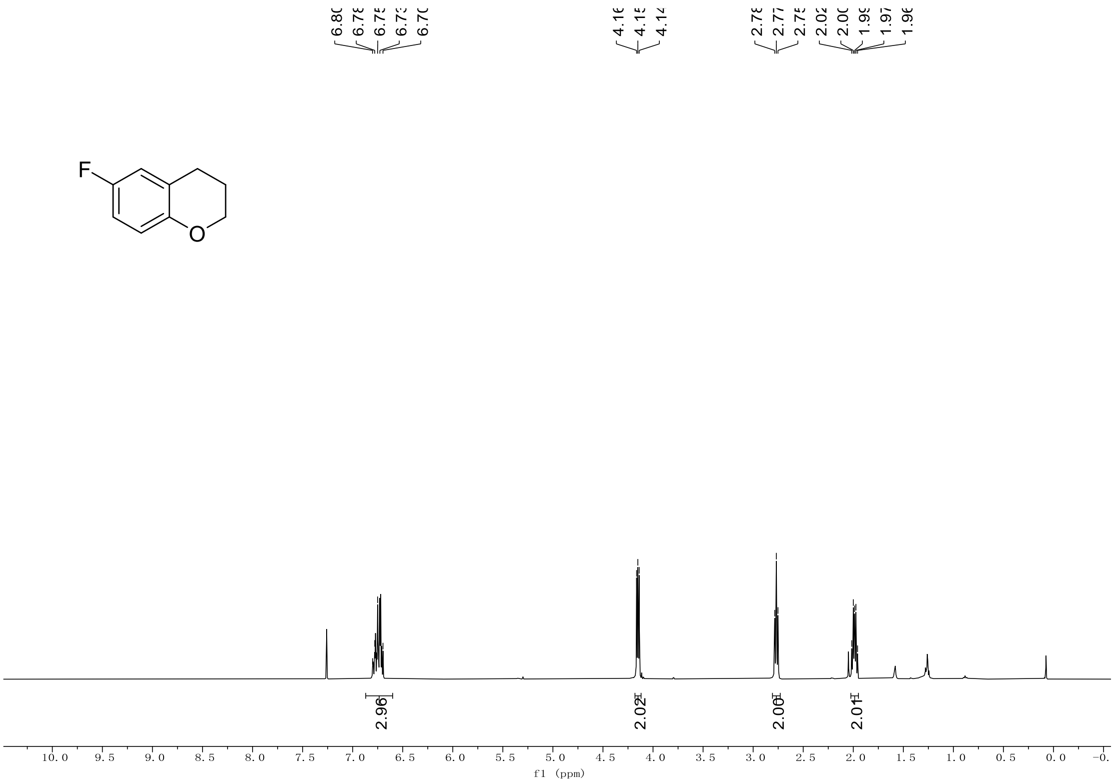
^{1}H NMR of compound **6e** (600 MHz, $CDCl_3$)



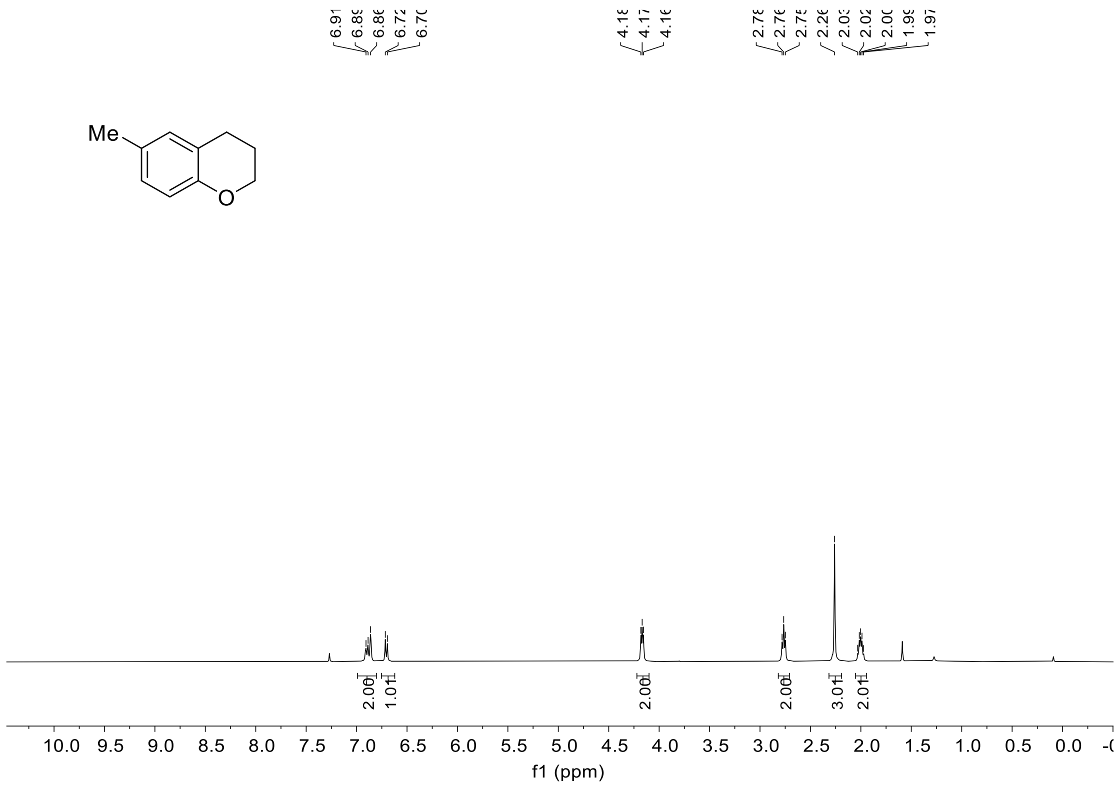
^{13}C NMR of compound **4w** (151 MHz, $CDCl_3$)



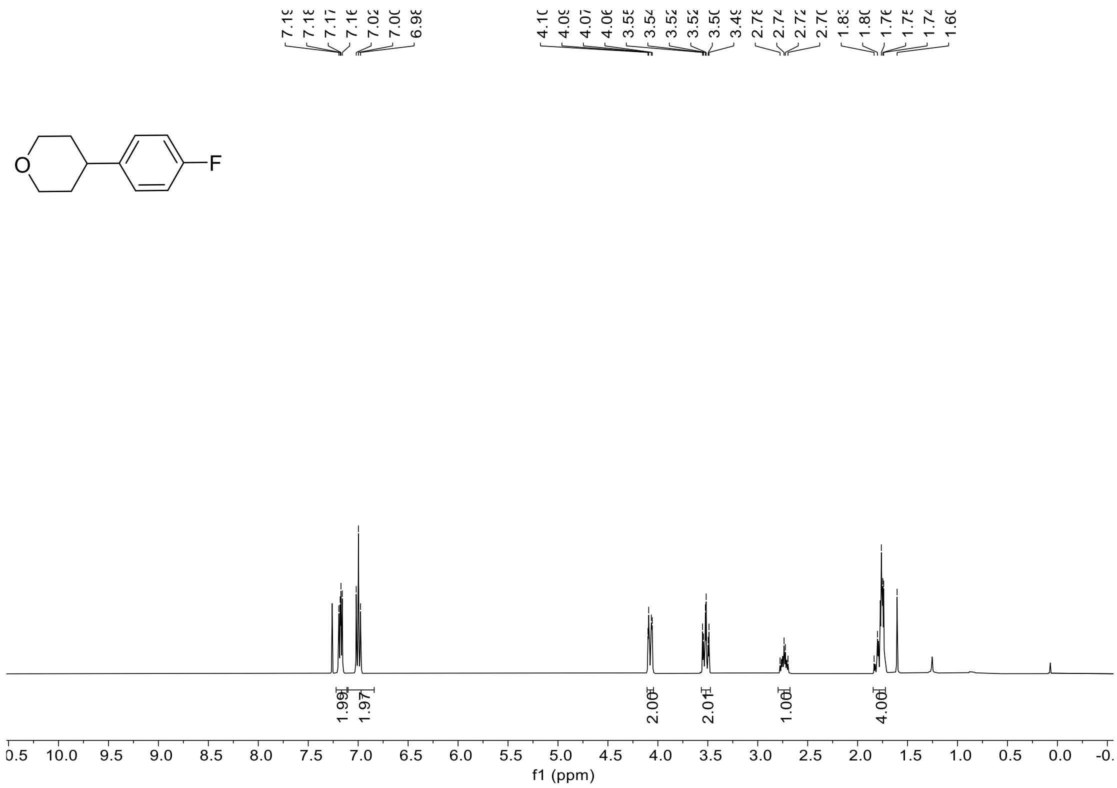
^{1}H NMR of compound **6k** (400 MHz, $CDCl_3$)



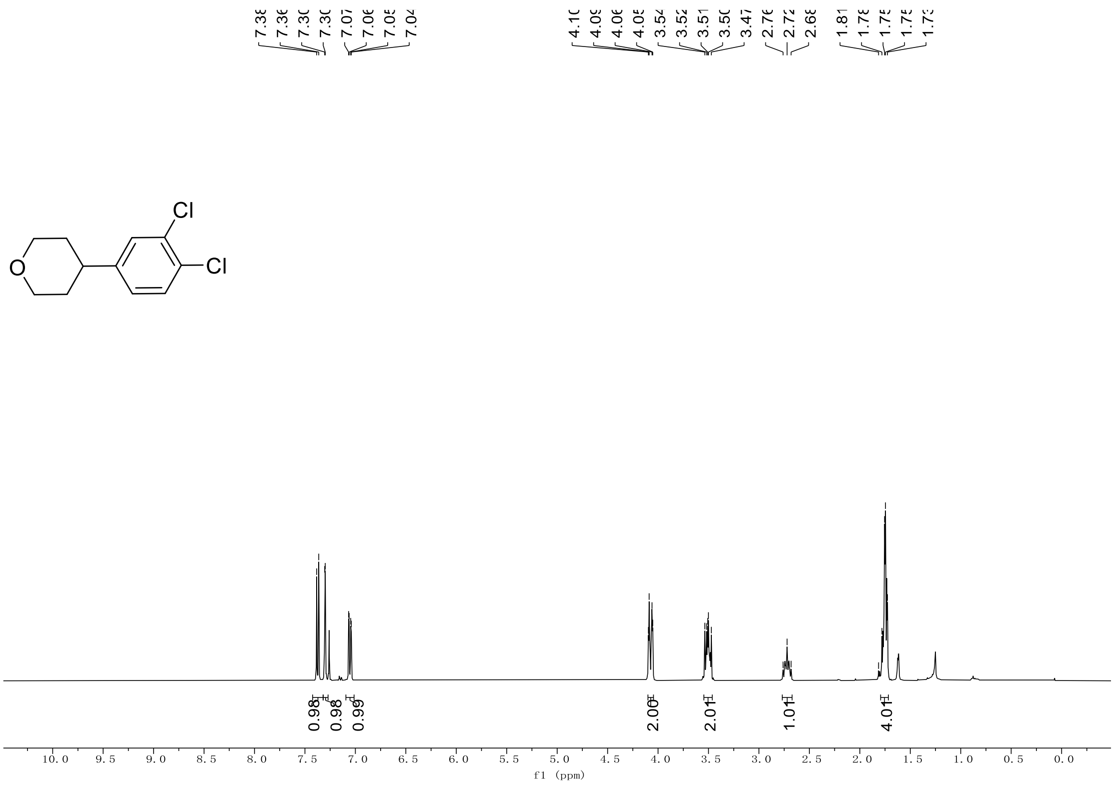
^{1}H NMR of compound **6l** (400 MHz, $CDCl_3$)



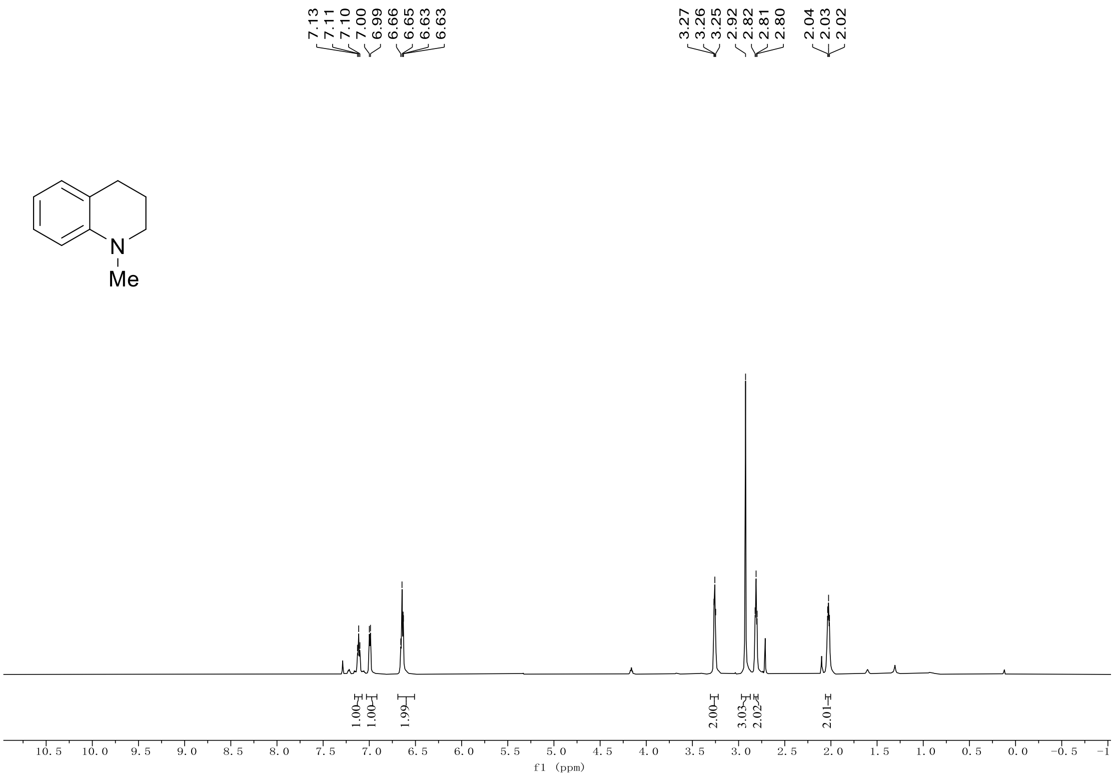
^{1}H NMR of compound **6m** (400 MHz, $CDCl_3$)



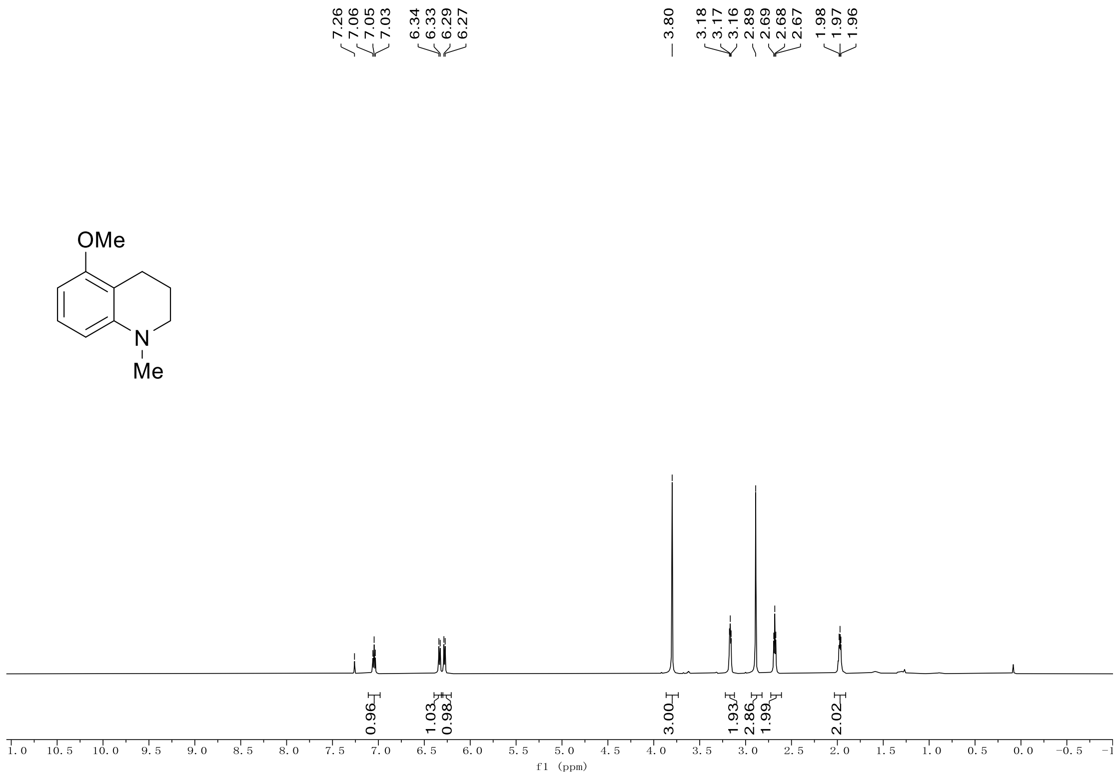
^{1}H NMR of compound **6n** (400 MHz, $CDCl_3$)



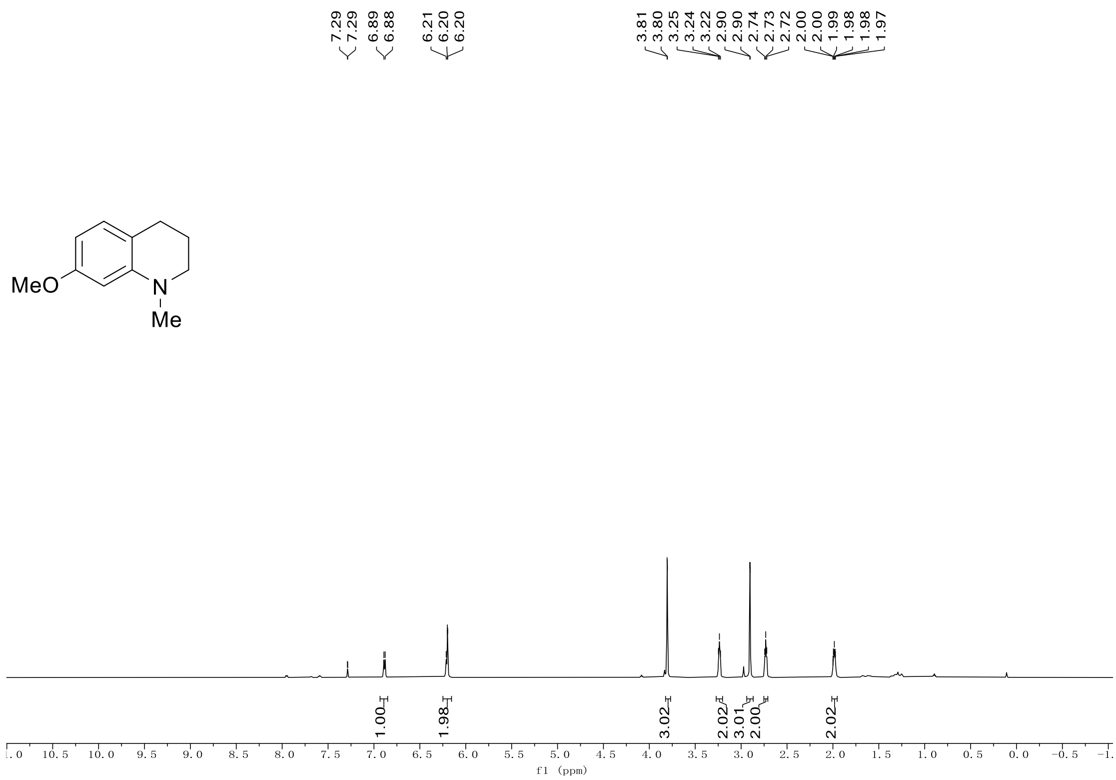
[1]H NMR of compound **6o** (400 MHz, $CDCl_3$)



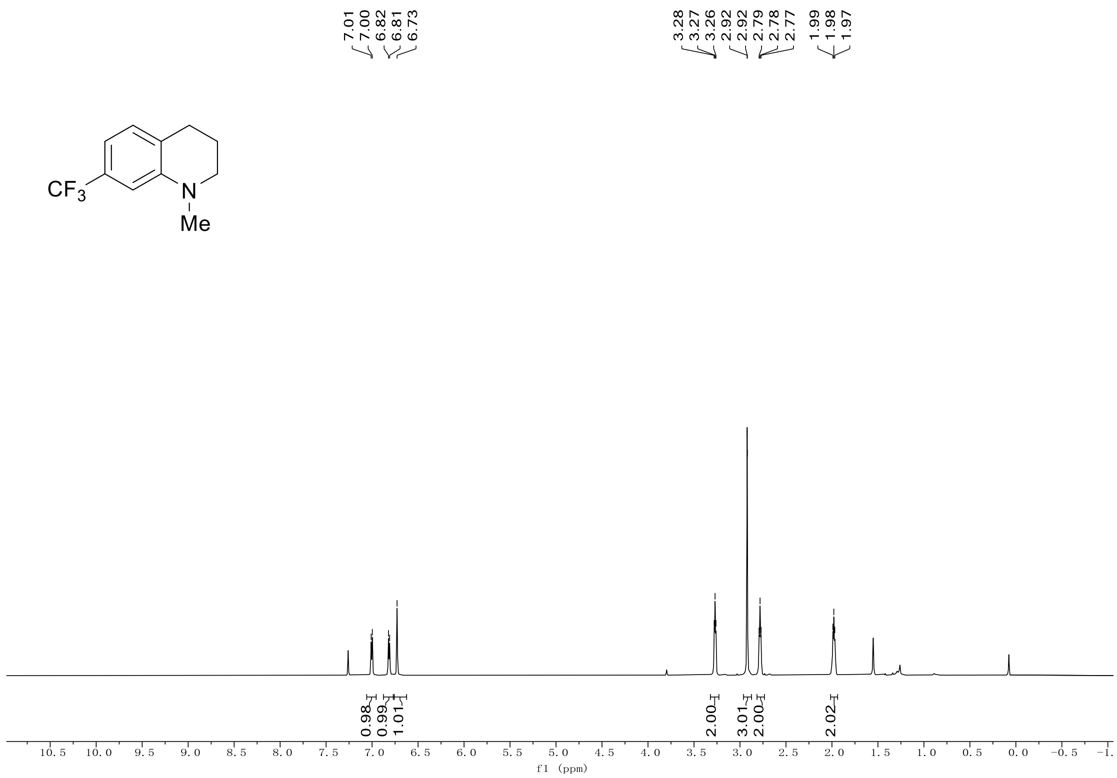
[1]H NMR of compound **6p** (600 MHz, $CDCl_3$)



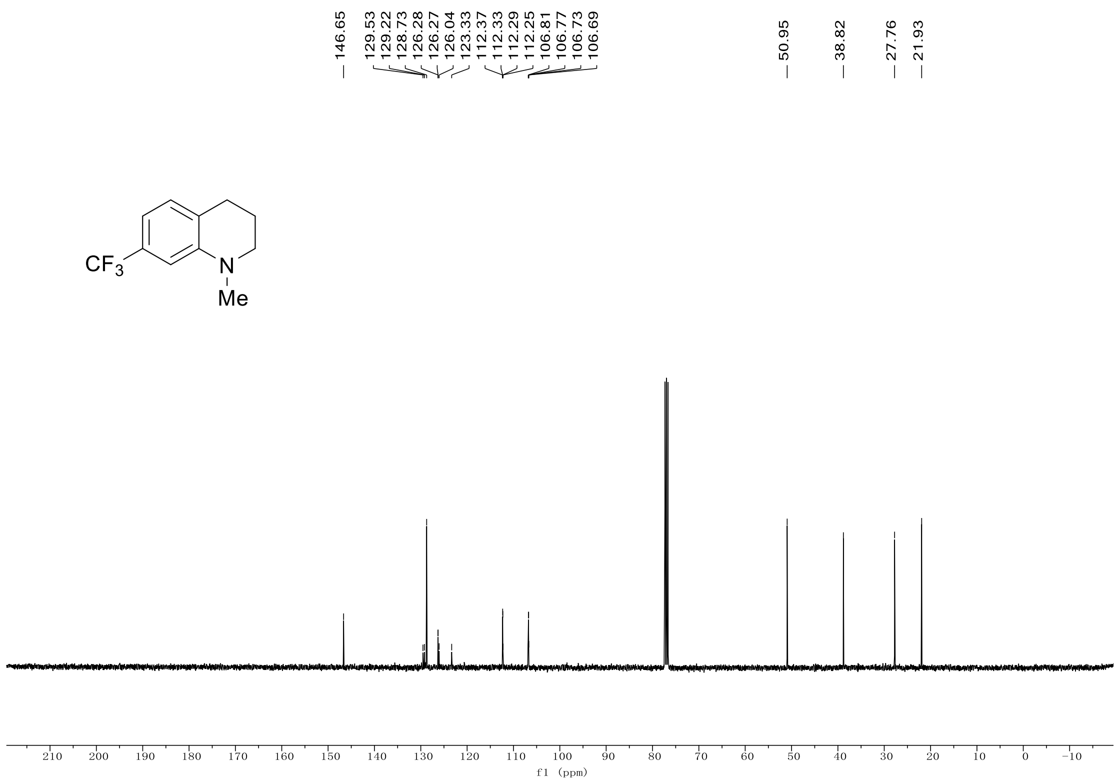
^{1}H NMR of compound **6q** (600 MHz, $CDCl_3$)



^{1}H NMR of compound **6r** (600 MHz, $CDCl_3$)

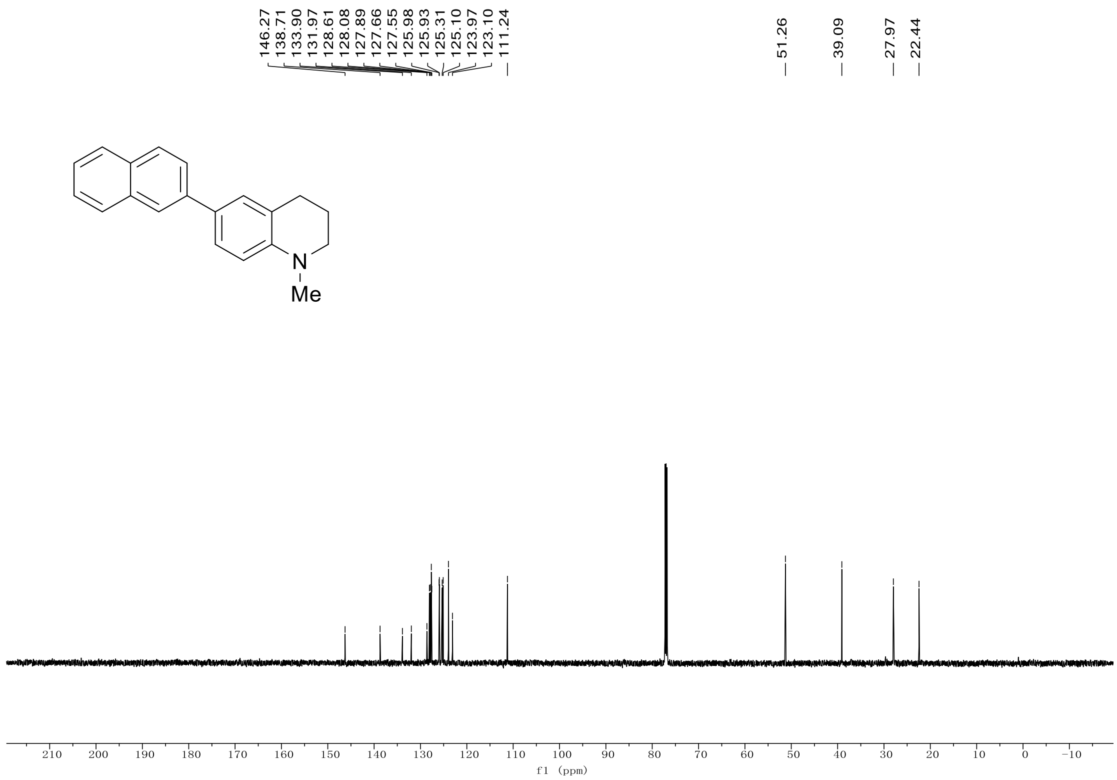


^{1}H NMR of compound **6s** (600 MHz, $CDCl_3$)

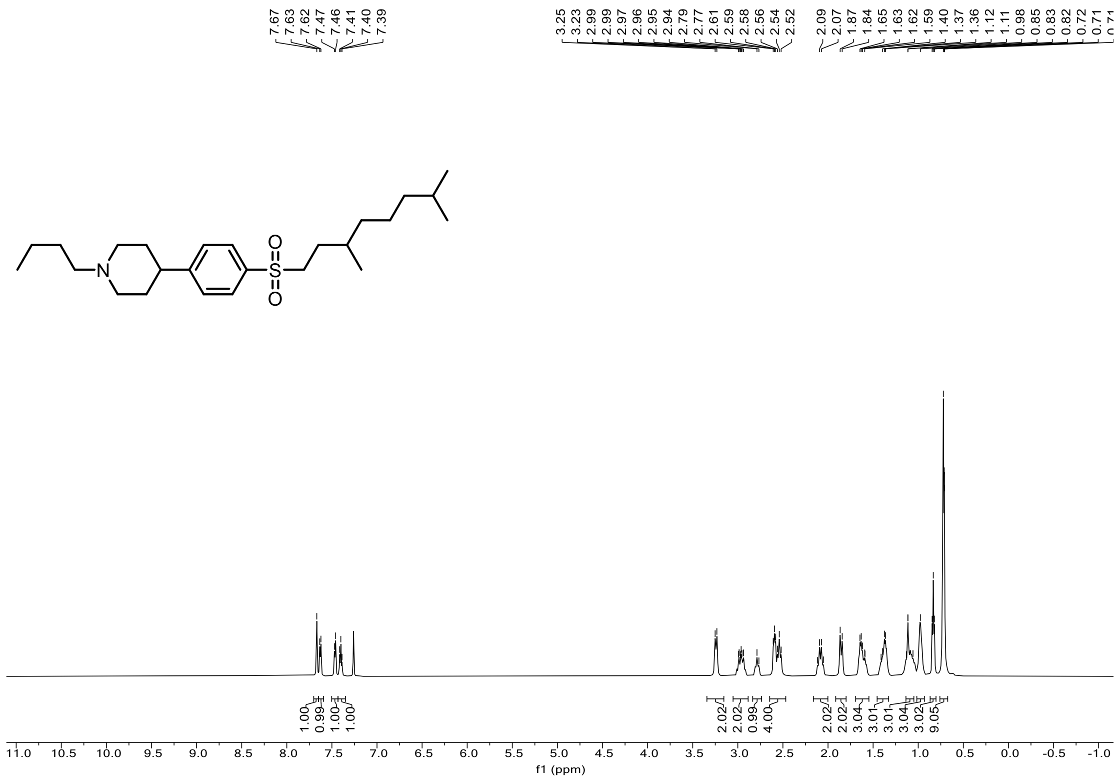


^{13}C NMR of compound **6s** (101 MHz, $CDCl_3$)

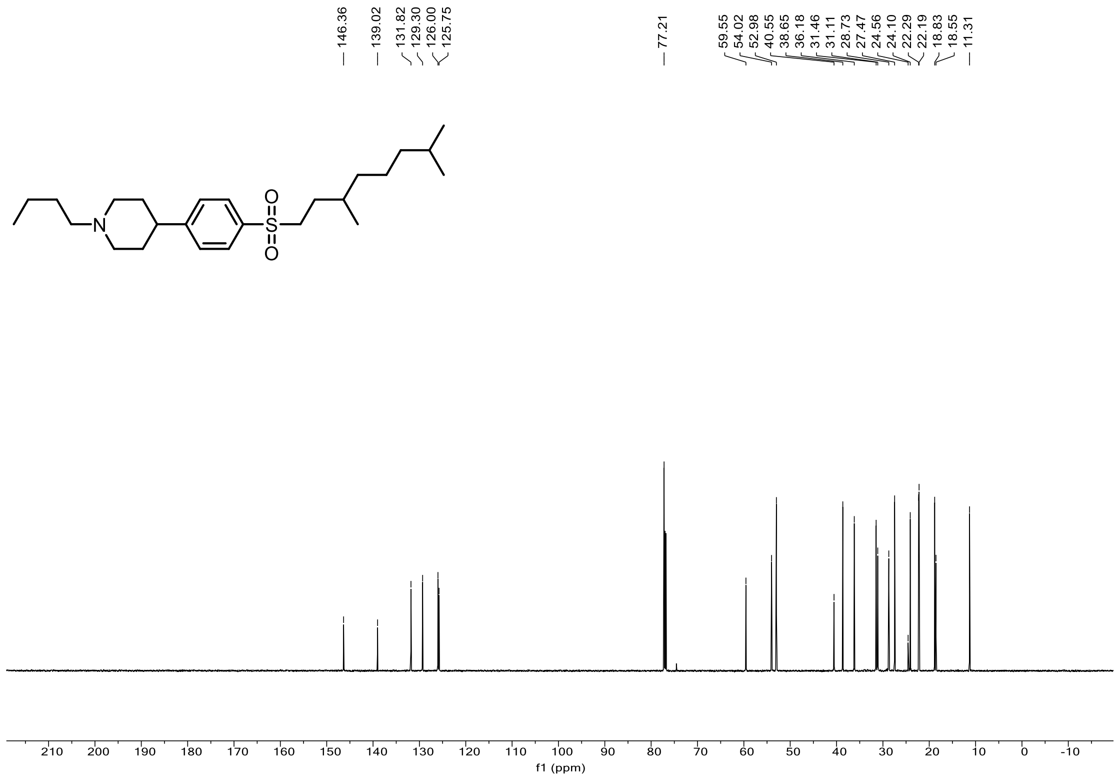
^{1}H NMR of compound **6t** (600 MHz, $CDCl_3$)



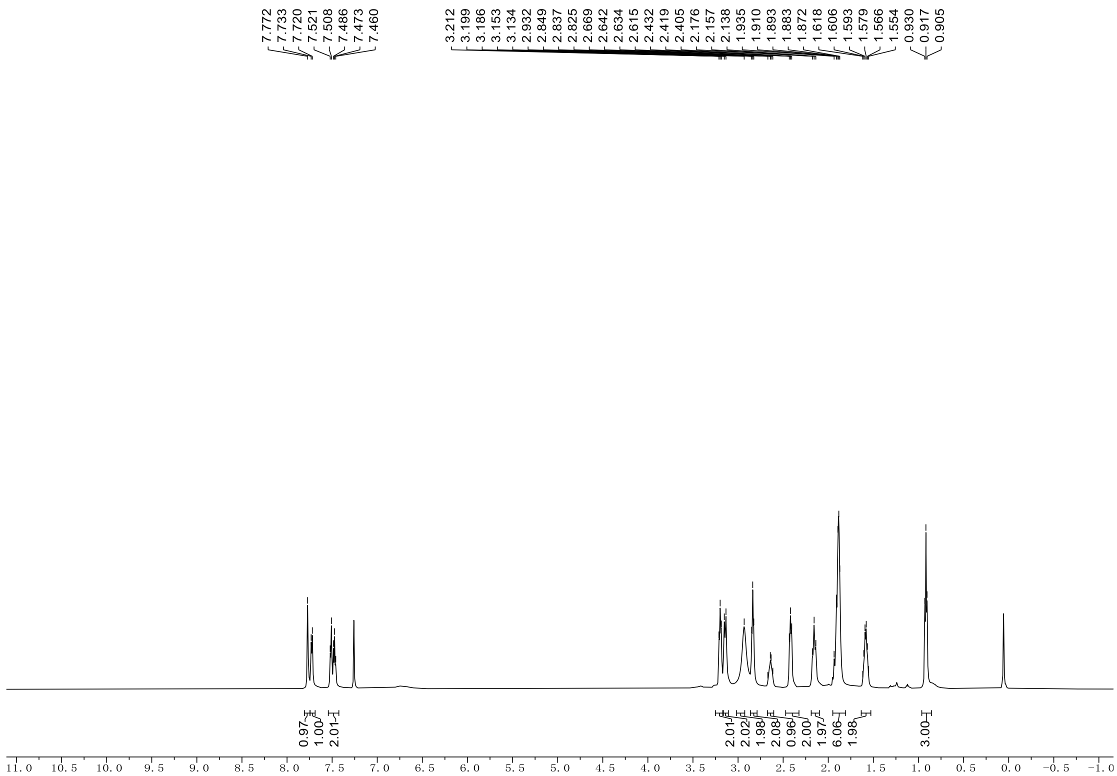
^{13}C NMR of compound **6t** (151 MHz, $CDCl_3$)



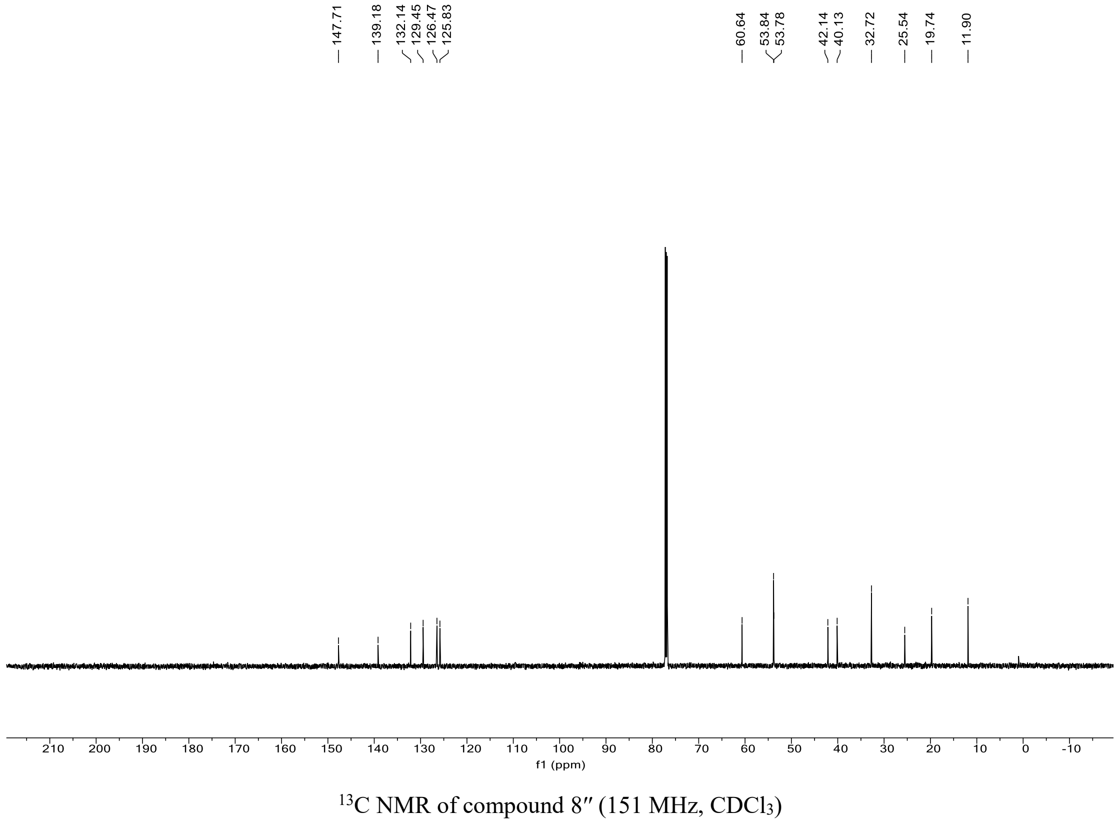
^{1}H NMR of compound 8′ (600 MHz, $CDCl_3$)



^{13}C NMR of compound 8′ (151 MHz, $CDCl_3$)



[1]H NMR of compound 8″ (600 MHz, $CDCl_3$)



[13]C NMR of compound 8″ (151 MHz, $CDCl_3$)

10 Cartesian coordinates of all optimized structures

5a

C	-1.63869500	-1.31748400	-0.40125900
C	-0.96023700	-0.20782400	0.12571800
C	0.34376200	-0.36685800	0.65804100
C	0.90259500	-1.65170600	0.65787700
C	0.22840100	-2.75779800	0.13348400
C	-1.04597700	-2.58238800	-0.40295000
H	-2.63906100	-1.20670100	-0.81788900
H	1.89046900	-1.78895600	1.10904000
H	0.69384700	-3.74553700	0.15159700
H	-1.59260100	-3.43109300	-0.82097200
C	1.14735900	0.80019800	1.18501600
H	0.53202700	1.39527600	1.88092900
H	1.99096300	0.40280500	1.76899500
C	1.71095200	1.73410100	0.09292500
H	0.90311700	2.34126600	-0.34718900
H	2.41481900	2.43434000	0.57308000
C	2.42296900	0.99664400	-1.03996000
H	2.89014500	1.73324200	-1.71473200
H	1.68079000	0.43916900	-1.64248300
S	-1.67238700	1.42271800	0.17983500
C	-3.36617000	1.16047900	-0.41029100
H	-3.85419600	2.14256100	-0.34102700
H	-3.38906300	0.82701100	-1.45810200
H	-3.90976800	0.44541700	0.22442000
O	3.45368600	0.13871200	-0.58477700
H	3.04747700	-0.70617100	-0.35640500

6a

C	-1.42756100	-1.38107200	0.05696100
C	-0.27622700	-0.61606900	-0.16391100
C	-0.34736000	0.79211700	-0.22332800
C	-1.58838700	1.40689700	-0.02115300
C	-2.74088800	0.64675500	0.19639100
C	-2.66140600	-0.74861300	0.22430000
H	-1.34743900	-2.46916400	0.10858200
H	-1.65320000	2.49809000	-0.05563600
H	-3.70236300	1.14450100	0.34287100
H	-3.55971500	-1.34726900	0.39347000

C	0.90369800	1.55822100	-0.56069100
H	1.18696100	1.27619400	-1.59026700
H	0.70519800	2.64040300	-0.56580800
C	2.11080800	1.24539500	0.35017200
H	3.02743400	1.56404200	-0.17056700
H	2.04393300	1.84499200	1.27270500
C	2.22141500	-0.23776400	0.75181600
H	3.26492900	-0.58373200	0.75397700
H	1.81327200	-0.40421500	1.75918200
S	1.31602800	-1.38494000	-0.36949100

CH_3OH

C	0.65445000	-0.01958700	0.00000000
H	1.09166200	0.99097500	-0.00000100
H	1.04098200	-0.54686400	-0.89598900
H	1.04098200	-0.54686300	0.89599000
O	-0.74535300	0.12246900	0.00000000
H	-1.13750200	-0.75948400	0.00000000

$AlCl_3$-**5a**

Al	2.06494800	0.03237200	-0.40125500
Cl	2.51275100	1.09402700	1.39070300
Cl	3.51214300	-1.40279300	-0.97662400
Cl	1.15293900	1.21437900	-1.92593400
C	-2.28985100	1.24836800	-0.96747100
C	-2.06872300	0.52314600	0.21696500
C	-2.38973300	-0.85887400	0.25934600
C	-2.92478300	-1.45659000	-0.89230900
C	-3.13687000	-0.73408000	-2.06536800
C	-2.81280700	0.62400100	-2.09759800
H	-2.03934300	2.30643500	-1.01584900
H	-3.17511900	-2.52070400	-0.85907600
H	-3.54770400	-1.22760400	-2.94828700
H	-2.96261100	1.20597800	-3.00948600
C	-2.12497100	-1.72084700	1.48086400
H	-2.10149100	-1.10397300	2.39184800
H	-2.96873000	-2.41765500	1.60356000
C	-0.83087900	-2.55494900	1.39341400
H	-0.76072500	-3.19784100	2.28658900
H	-0.87608800	-3.22984500	0.52200600
C	0.45715900	-1.75518600	1.32891400
H	1.33796000	-2.41073800	1.34947500

H	0.53156600	-1.01923500	2.14219700
S	-1.36813000	1.26687900	1.67710800
C	-0.70667100	2.84430600	1.06819600
H	-0.07945400	3.22313400	1.88580300
H	-0.07410200	2.68714600	0.18454000
H	-1.50930600	3.56447200	0.85589900
O	0.56425300	-1.03331000	0.06629100
H	-0.29750700	-0.63518500	-0.18514400

TS1A

Al	-2.76089700	-0.24501900	0.20805000
Cl	-1.57315100	0.20894500	1.98160600
Cl	-2.78808700	1.50685600	-1.06706000
Cl	-4.65976700	-1.07860900	0.67938300
C	3.31695600	1.06146600	1.04836100
C	2.75051100	0.50343000	-0.10126700
C	3.06539900	-0.80569700	-0.51778800
C	3.97420600	-1.53844900	0.25510300
C	4.54991600	-0.99034900	1.40339500
C	4.21802500	0.30711700	1.80173100
H	3.06044900	2.07523500	1.35846000
H	4.22742800	-2.55748200	-0.04851500
H	5.25536900	-1.58009100	1.99245400
H	4.66159700	0.73770600	2.70193900
C	2.37897800	-1.39255300	-1.72399700
H	2.51867400	-0.73941500	-2.60178500
H	2.83745700	-2.35911400	-1.97733100
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H	0.42529000	-2.02389800	-2.43784800
H	0.75045000	-2.39520000	-0.73139200
C	0.05271100	-0.43448100	-1.07243700
H	-0.57807900	0.11674800	-1.76208300
H	-0.01186600	-0.19403800	-0.01540700
S	1.59476700	1.37049100	-1.14225700
C	0.67043600	2.43777500	0.00308000
H	-0.25865300	2.70148100	-0.52201600
H	0.40690200	1.88462400	0.91481800
H	1.25392900	3.34004300	0.22680800
O	-1.76874400	-1.42598700	-0.72465200
H	-1.68836200	-2.31045100	-0.34297900

Int1A

Al	-2.53737000	0.30077400	0.33497000
Cl	-1.00566100	1.57002500	-0.63419000
Cl	-2.71480200	-1.46924600	-0.95076600
Cl	-4.39538400	1.34277300	0.52535100
C	2.66382900	0.90445700	-1.40911400
C	2.46091200	-0.12045800	-0.48742600
C	2.92326500	-0.05634200	0.84002000
C	3.60958400	1.10263400	1.21973300
C	3.83276300	2.13887100	0.31047400
C	3.36439200	2.04084400	-1.00151800
H	2.27149800	0.84090300	-2.42371900
H	3.96952600	1.18986000	2.24759000
H	4.36816200	3.03461000	0.63192900
H	3.52581100	2.85623500	-1.70899300
C	2.67813600	-1.21033400	1.78085300
H	3.27736400	-2.06798800	1.42444200
H	3.06306400	-0.96609300	2.78041100
C	1.19810300	-1.66079600	1.87788300
H	1.16751200	-2.71318800	2.19559100
H	0.65219400	-1.07211500	2.62977100
C	0.39923400	-1.46050100	0.59640700
H	-0.42543000	-2.16694200	0.44788100
H	0.01764400	-0.43844300	0.52282400
S	1.51102900	-1.59675800	-0.87401500
C	0.44505200	-1.11498400	-2.25616100
H	-0.37936600	-1.84028700	-2.26590700
H	0.03172200	-0.11375400	-2.06329700
H	1.04801500	-1.17873900	-3.17054600
O	-1.85805800	-0.20262200	1.86551200
H	-2.39612700	-0.02575700	2.64392300

TS2A

Al	2.86422800	-0.11976700	-0.11630400
Cl	1.57402100	0.76968100	-1.61847500
Cl	2.40548800	0.75064800	1.81213700
Cl	4.92001700	-0.13398300	-0.66464700
C	-1.09553100	1.20526000	0.73359000
C	-2.12674600	0.28685300	0.52900200
C	-3.35679900	0.65852900	-0.04984900
C	-3.51056300	1.98895500	-0.45275800
C	-2.48301800	2.91855900	-0.26570800
C	-1.28295100	2.52938700	0.33110900
H	-0.14455300	0.91984400	1.18331100

H	-4.45263900	2.29904900	-0.91227400
H	-2.62195200	3.95187700	-0.59115300
H	-0.46923400	3.24310500	0.47110400
C	-4.45101600	-0.36957000	-0.17628000
H	-4.76204300	-0.65868600	0.84322800
H	-5.33488100	0.07015600	-0.65965400
C	-4.03177800	-1.65471300	-0.92583300
H	-4.73266200	-2.45998900	-0.66000000
H	-4.12073200	-1.49679600	-2.01192200
C	-2.58888400	-2.10437700	-0.64313400
H	-2.49635300	-3.19796300	-0.58272700
H	-1.89297100	-1.73665800	-1.41068400
S	-1.94281200	-1.44680100	0.95269100
C	0.27361400	-1.73487900	0.48546000
H	0.20216900	-2.81910400	0.44206400
H	0.16489100	-1.12896000	-0.41053400
H	0.59513600	-1.27302700	1.41410700
O	2.26198400	-1.81434300	0.05664500
H	2.45008100	-2.40423100	-0.68598000

CH_3CH_2OH

C	0.09075100	0.54169500	0.00007700
H	0.13600000	1.20328100	0.89058200
H	0.13623800	1.20345300	-0.89027000
O	1.14839200	-0.39671200	0.00018700
H	1.98403500	0.08571200	-0.00138200
C	-1.22151300	-0.21933600	-0.00009300
H	-1.29087600	-0.86288400	-0.89097600
H	-1.29050000	-0.86361500	0.89028500
H	-2.07745900	0.47359200	0.00036200

$AlCl_3$-CH_3CH_2OH

Al	-0.67836100	0.05611600	-0.03495200
Cl	-0.76077800	1.14554100	1.78701100
Cl	-0.65084500	1.23293500	-1.79402700
Cl	-1.66676700	-1.82503400	-0.06208200
C	2.29852000	0.14048300	0.31258000
H	2.13636200	1.08537300	-0.22290800
H	2.30488000	0.34856800	1.39307000
O	1.11147900	-0.64706900	0.00970400
H	1.16521800	-1.56181600	0.33234200
C	3.54247100	-0.57210500	-0.16393900

H	3.68283900	-1.53338200	0.35809600
H	3.49801700	-0.75997900	-1.24692800
H	4.42623300	0.04951100	0.04590000

CH_3SCH_3

C	-1.38527400	0.51425000	-0.00000300
S	-0.00000200	-0.66379200	0.00000000
C	1.38527900	0.51423800	0.00000300
H	2.31267500	-0.07622100	0.00034500
H	1.37189000	1.15030100	-0.89928200
H	1.37155600	1.15081400	0.89892100
H	-1.37192400	1.15026700	0.89930900
H	-1.37151800	1.15080600	-0.89892800
H	-2.31266800	-0.07622200	-0.00036300

$CH_3CH_2SCH_3$

C	-0.80243700	0.63640100	-0.00004200
S	0.50896100	-0.64061500	-0.00001700
C	1.97103600	0.43967400	0.00002500
H	2.85628000	-0.21207000	0.00022400
H	2.00075800	1.07548100	-0.89890000
H	2.00050700	1.07567800	0.89883100
H	-0.67568300	1.27570500	0.88989900
H	-0.67577100	1.27560900	-0.89005900
C	-2.17718100	-0.02154000	0.00004000
H	-2.97073800	0.74235500	-0.00004000
H	-2.31361800	-0.65514000	-0.89043400
H	-2.31361100	-0.65498500	0.89062100

TS1B

Al	-1.68917200	0.01606000	-0.01263000
Cl	-0.62362500	-1.23242200	-1.46522800
Cl	-1.15424000	-0.64880700	1.96807500
Cl	-3.76241400	0.16530500	-0.45265500
C	3.27216100	-0.55805600	-1.44993800
C	1.13948300	1.28889400	0.08572500
H	0.81876300	0.84033600	1.02301500
H	1.00257800	0.70859800	-0.81923200
S	3.16411000	-0.06459200	0.29705200
C	2.30713500	-1.51794700	0.98017900
H	2.04623700	-1.28676400	2.02100800

H	1.38587500	-1.71252700	0.41307000
H	2.98151200	-2.38497900	0.94761800
O	-0.90092300	1.63612100	-0.13899000
H	-1.09538900	2.13186100	-0.94669600
H	3.96392400	-1.40594500	-1.55266800
H	2.27525700	-0.83525000	-1.82418800
H	3.66600300	0.30040500	-2.01118900
C	1.66847400	2.68560700	0.07591600
H	2.10921800	2.96092600	-0.89265900
H	0.83132800	3.36629800	0.29286000
H	2.41675900	2.83247300	0.86775600

Int1B

Al	-1.67141700	0.18467000	-0.14887500
Cl	-0.69133700	-1.71541700	-0.75303500
Cl	-0.99728900	0.55488800	1.89624300
Cl	-3.79053700	-0.01975700	-0.31618000
C	2.82850800	-1.24585300	-1.17013100
C	1.75683300	1.16563700	-0.15956700
H	1.25448100	1.45804500	0.77345000
H	0.98070100	0.76352700	-0.82500100
S	2.87824100	-0.20801700	0.31742100
C	1.91581100	-1.19927700	1.49267800
H	1.68586400	-0.55206200	2.34751200
H	0.98486600	-1.53417000	1.01255400
H	2.56257300	-2.03506900	1.79189400
O	-0.98108900	1.43754700	-1.15382000
H	-1.50762300	1.73386500	-1.90361000
H	3.44185300	-2.13605800	-0.97824600
H	1.77862900	-1.50628000	-1.37568400
H	3.26875300	-0.65733500	-1.98562500
C	2.52295800	2.30309100	-0.80888900
H	3.04966900	1.98720500	-1.72346600
H	1.77808200	3.05747400	-1.10351200
H	3.24851800	2.77134900	-0.12708500

TS2B

Al	1.84490200	-0.10124200	0.08226200
Cl	0.65654900	-1.03808800	-1.50110300
Cl	1.58581400	2.03300900	-0.06692100
Cl	3.83242400	-0.84679800	0.15746200
C	-3.33340100	-0.76662000	-0.55355400

C	-0.92867600	0.00020900	1.30365900
H	-0.53369300	1.00537500	1.19475300
H	-0.90083300	-0.69113900	0.47030400
S	-2.95573900	0.74214000	0.41841600
C	-2.14047900	1.74038000	-0.86716700
H	-1.74980600	2.64526000	-0.38365500
H	-1.30441900	1.17764500	-1.30733200
H	-2.87741400	2.01654400	-1.63354200
O	0.97847500	-0.51507000	1.61852600
H	1.07853200	-1.41958600	1.94572900
H	-4.06478700	-0.47415700	-1.32244800
H	-2.40431400	-1.07131500	-1.06174400
H	-1.28701300	-0.31766300	2.28034200
C	-3.87897500	-1.86624600	0.34615900
H	-4.12695000	-2.75100300	-0.25971400
H	-3.13871900	-2.17622300	1.09981100
H	-4.79246200	-1.54570200	0.87020100

$C_6H_5CH_2OH$

C	1.90775600	0.62661600	0.00001600
H	2.12012700	1.25761600	0.88855700
H	2.12013800	1.25769000	-0.88847000
O	2.68966000	-0.54506300	-0.00002600
H	3.61948200	-0.29097100	0.00007300
C	0.43744600	0.27744800	0.00000200
C	-0.52042700	1.30215500	-0.00001400
C	0.00922100	-1.05404700	0.00000200
C	-1.88272800	1.00144100	-0.00000200
H	-0.19571700	2.34744200	-0.00003100
C	-1.35661500	-1.35570900	-0.00000200
H	0.75812200	-1.84606000	0.00000800
C	-2.30620100	-0.33214900	0.00000700
H	-2.61812600	1.80992300	0.00000500
H	-1.67922200	-2.40008100	-0.00000600
H	-3.37279200	-0.56959400	0.00001400

$AlCl_3$-$C_6H_5CH_2OH$

Al	-1.90631600	0.12561000	-0.05828700
Cl	-3.37689100	-1.35727100	0.26847900
Cl	-1.34930700	1.22626900	1.68212000
Cl	-1.96743500	1.19388300	-1.89760700
C	0.70859200	-1.35521500	0.48918700

H	0.29622300	-1.13695300	1.48252200
H	0.76507600	-2.44253700	0.34408000
O	-0.29664100	-0.83935100	-0.44440000
H	0.08862900	-0.61675900	-1.30926200
C	2.02958100	-0.68443400	0.25855600
C	3.10076200	-1.39800800	-0.29634000
C	2.18822000	0.67875200	0.56200100
C	4.32131800	-0.76257700	-0.54000400
H	2.98063200	-2.45860000	-0.53406500
C	3.40533900	1.31176800	0.31145800
H	1.35298200	1.23456500	0.99483700
C	4.47295500	0.59260300	-0.23786100
H	5.15297400	-1.32652300	-0.96817700
H	3.52404800	2.37102400	0.54996700
H	5.42582500	1.09135200	-0.42981500

3k ($C_6H_5CH_2SCH_3$)

C	1.01827600	-0.00157300	0.84102100
S	2.04968500	0.00094900	-0.68272300
C	3.69778100	-0.00020500	0.08768800
H	4.43541700	0.00115400	-0.72753300
H	3.85308400	0.89774800	0.70633300
H	3.85325800	-0.90012200	0.70343100
H	1.26836000	-0.89498000	1.43491500
H	1.26861400	0.88988600	1.43773100
C	-0.43686700	-0.00081700	0.46016600
C	-1.12120900	-1.20730500	0.25276400
C	-1.12015300	1.20651100	0.25415500
C	-2.46248300	-1.20816100	-0.13563900
H	-0.59297200	-2.15360600	0.39630000
C	-2.46143600	1.20899000	-0.13424600
H	-0.59110500	2.15220300	0.39868800
C	-3.13687000	0.00082800	-0.32923200
H	-2.98353000	-2.15646900	-0.28841700
H	-2.98161100	2.15796200	-0.28587900
H	-4.18671700	0.00142800	-0.63206400

TS1C

Al	-2.22786400	-0.53670300	-0.11746800
Cl	-1.46433200	-0.13522900	1.90725800
Cl	-2.69737400	1.38075800	-0.99132000
Cl	-3.77274700	-1.99793500	-0.09657500

C	1.70950700	2.16905200	1.66255600
C	0.76188100	0.34387500	-0.71014500
H	0.54707400	0.70056300	-1.71317700
H	0.09071500	0.61031000	0.09469900
S	1.79709200	2.46775200	-0.12748700
C	0.30051500	3.47113500	-0.37257700
H	0.27499400	3.75310100	-1.43384300
H	-0.60533400	2.89399200	-0.13267800
H	0.36443500	4.37827900	0.24452200
O	-0.81733400	-1.08994100	-1.06817300
H	-0.49556400	-1.99247600	-0.94921900
H	1.89172500	3.10988500	2.20038200
H	0.72924400	1.74969200	1.93583700
H	2.50150600	1.44790300	1.90521400
C	1.84348200	-0.59489400	-0.45477200
C	1.90846300	-1.25354900	0.79008000
C	2.81588900	-0.86682200	-1.43450700
C	2.93606100	-2.15967200	1.04577800
H	1.12480700	-1.06882600	1.52872500
C	3.84419200	-1.76884600	-1.17061800
H	2.76151600	-0.35976200	-2.40089300
C	3.90659500	-2.41440400	0.07004400
H	2.97830200	-2.67554500	2.00755100
H	4.59865900	-1.97445100	-1.93304700
H	4.71155200	-3.12436800	0.27399300

Int1C

Al	-2.35309100	-0.60416200	0.00537400
Cl	-2.79088300	1.16964000	1.20059600
Cl	-1.83859700	0.10259700	-2.00007600
Cl	-3.95645300	-2.01380800	0.03203900
C	0.65868200	1.12903100	1.71170600
C	1.54364000	0.75691900	-0.99635000
H	1.82912600	1.33124500	-1.88992900
H	0.59032100	0.24189800	-1.18168300
S	1.20126800	2.07528600	0.26305700
C	-0.29122300	2.86828600	-0.39936800
H	-0.96378900	2.11961100	-0.83977300
H	-0.78660500	3.38554100	0.43088300
H	0.06230500	3.58709800	-1.15093600
O	-0.85292200	-1.30199100	0.63082200
H	-0.97264000	-2.02716300	1.25566300
H	0.04658900	1.80624900	2.32000400

H	0.07760700	0.23852100	1.40628100
H	1.58072700	0.85248200	2.23880400
C	2.63486000	-0.14807800	-0.51004800
C	2.30142900	-1.39435300	0.04253200
C	3.98070800	0.24433700	-0.58485100
C	3.31328300	-2.23897500	0.50653600
H	1.24637500	-1.67644900	0.11000800
C	4.98602000	-0.60180300	-0.11642200
H	4.24204900	1.21431300	-1.01762000
C	4.65220800	-1.84607600	0.42957800
H	3.05261100	-3.21197300	0.92939400
H	6.03209200	-0.29419300	-0.18233800
H	5.43973400	-2.51075700	0.79251500

TS2C

Al	-2.60546900	-0.46632100	-0.10953600
Cl	-1.27772400	-0.88172000	1.58182100
Cl	-3.12262100	1.62656100	-0.04182300
Cl	-4.20006200	-1.86161300	-0.25035500
C	2.08432700	1.12527300	0.99106900
C	-0.00833700	0.64872100	-1.25502900
H	-0.72883700	1.44988100	-1.38315100
H	0.09035700	0.14919300	-0.30075700
S	1.56318300	2.16885300	-0.44184700
C	0.34812300	3.25084500	0.37287400
H	-0.00487700	3.96683900	-0.38166500
H	-0.50588700	2.66571600	0.74522100
H	0.83790400	3.79616300	1.19132800
O	-1.55122300	-0.58369100	-1.57456300
H	-1.26297100	-1.46822300	-1.83824500
H	2.66950200	1.77884400	1.65538600
H	1.17237100	0.80269000	1.51453100
H	0.56982800	0.30445400	-2.10896700
C	2.88714400	-0.04711700	0.49691900
C	4.17624700	0.14542500	-0.02501900
C	2.34523500	-1.34124100	0.52321200
C	4.91153400	-0.93584100	-0.51171700
H	4.60463400	1.15117900	-0.05040400
C	3.08529000	-2.42330100	0.03813000
H	1.34446700	-1.50253900	0.93191500
C	4.36641800	-2.22375000	-0.48157700
H	5.91471500	-0.77450100	-0.91308600
H	2.65670500	-3.42767400	0.07089600

H	4.94307600	-3.07093400	-0.86008400

$C_6H_5CH_2CH_2OH$

C	2.44196100	-0.40901900	-0.40024900
H	2.08594900	-0.72661900	-1.40033300
H	3.39871200	-0.93655700	-0.20733500
O	2.61114800	0.99285700	-0.33033700
H	3.08802700	1.28736300	-1.11521800
C	1.42077000	-0.83622600	0.65250300
H	1.45053600	-1.93444900	0.73504300
H	1.75598800	-0.43180300	1.62283700
C	0.00944400	-0.38560700	0.35609700
C	-0.34820600	0.96995900	0.44636400
C	-0.96768700	-1.30787300	-0.04557900
C	-1.64593400	1.38600500	0.14349900
H	0.40871800	1.69762100	0.74228100
C	-2.26847700	-0.89447700	-0.34765900
H	-0.70651100	-2.36765900	-0.11902800
C	-2.61190900	0.45595100	-0.25387400
H	-1.90668600	2.44482200	0.21982600
H	-3.01549400	-1.63085300	-0.65483800
H	-3.62820400	0.78299300	-0.48715200

$AlCl_3$-$C_6H_5CH_2CH_2OH$

Al	1.62112000	-0.26571400	0.17755200
Cl	3.59721400	0.35666800	0.61488700
Cl	0.31912700	-0.37792500	1.84488600
Cl	1.43623000	-1.72592500	-1.37045900
C	0.02741100	2.28682900	-0.47598200
H	0.02193400	2.26392700	0.62103500
H	0.50902800	3.21372800	-0.82187400
O	0.88339300	1.17725700	-0.86217000
H	0.79026700	0.93292000	-1.79792200
C	-1.37834400	2.12600900	-1.04447600
H	-1.94099600	3.03186000	-0.76542900
H	-1.32154800	2.12635900	-2.14803500
C	-2.07806200	0.88380400	-0.54693800
C	-1.91154300	-0.34029100	-1.20705700
C	-2.82199200	0.91451800	0.64033800
C	-2.45262900	-1.51446100	-0.68052700
H	-1.33695800	-0.39105200	-2.13534200
C	-3.37585200	-0.25444700	1.16261800

H	-2.95622700	1.86213500	1.16969900
C	-3.18535600	-1.47377400	0.50688500
H	-2.28867000	-2.46286900	-1.19616900
H	-3.94843500	-0.21594100	2.09214400
H	-3.60558900	-2.39186800	0.92357500

$C_6H_5SCH_3$

S	1.82391200	-0.72004000	-0.00002300
C	2.71064600	0.86154100	-0.00002600
H	3.77856000	0.60270400	-0.00009400
H	2.48802700	1.45243700	-0.90081600
H	2.48798500	1.45239800	0.90076900
C	0.11809700	-0.23119000	0.00009600
C	-0.83122700	-1.27075800	0.00002200
C	-0.32846200	1.09904100	0.00008700
C	-2.19379000	-0.98129100	-0.00001600
H	-0.49253700	-2.31001500	0.00005500
C	-1.69906600	1.37790800	-0.00001800
H	0.38082000	1.92635700	0.00009000
C	-2.63820600	0.34601600	-0.00004900
H	-2.91624300	-1.80133000	-0.00004300
H	-2.03027100	2.41955700	-0.00006400
H	-3.70688800	0.57093700	-0.00010300

4g ($C_6H_5CH_2CH_2SC_6H_5$)

C	-0.22231600	-0.43936300	0.00015700
S	1.27497100	-1.48232500	0.00026400
H	-0.22279200	0.20773600	0.89106600
H	-0.22274600	0.20759900	-0.89085100
C	-1.46551600	-1.33762300	0.00020000
H	-1.43837300	-1.99279700	-0.88522200
H	-1.43844300	-1.99262000	0.88575700
C	2.60021900	-0.30238300	0.00006600
C	3.90615200	-0.82820600	-0.00016300
C	2.42679800	1.09051200	0.00013400
C	5.00929200	0.02249700	-0.00029700
H	4.05059200	-1.91160800	-0.00024900
C	3.54185500	1.93472100	-0.00002000
H	1.42989400	1.53004200	0.00030900
C	4.83527500	1.41124100	-0.00022900
H	6.01548300	-0.40410900	-0.00047300
H	3.38934100	3.01705000	0.00002800

H	5.70121100	2.07670800	-0.00034600
C	-2.73237600	-0.51497400	0.00006200
C	-3.31829700	-0.10132900	1.20553500
C	-3.31841800	-0.10191300	-1.20554900
C	-4.46092200	0.70217100	1.20779200
H	-2.87453700	-0.41800200	2.15379500
C	-4.46104800	0.70158500	-1.20807900
H	-2.87475000	-0.41903600	-2.15370000
C	-5.03575000	1.10685300	-0.00021300
H	-4.90640900	1.01074700	2.15676300
H	-4.90662700	1.00970000	-2.15715600
H	-5.93107400	1.73306400	-0.00031700

TS1D

Al	-2.44684400	-1.58335400	-0.16852900
Cl	-0.89300300	-3.01871600	0.36899400
Cl	-2.76276200	-0.25012000	1.50242100
Cl	-4.17818300	-2.51279300	-0.97745100
C	0.05124400	0.25063600	-0.56458100
H	-0.60689800	0.36210500	0.29113200
H	0.49554100	-0.72207300	-0.75659700
S	1.80900500	0.58563700	1.06941900
C	0.96844800	-0.37897600	2.36342500
H	0.21565100	0.29355100	2.79591100
H	0.45407600	-1.25280000	1.94161500
H	1.70035700	-0.67500000	3.12622500
O	-1.68724300	-0.50625600	-1.40106300
H	-1.54578600	-0.88895300	-2.27788800
C	0.30365200	1.41970200	-1.46736400
H	1.36727300	1.44553500	-1.75267500
H	-0.25125400	1.22708300	-2.40083200
C	2.99053000	-0.56068400	0.38032200
C	4.20097600	-0.01988500	-0.07683300
C	2.71907200	-1.92792800	0.22592000
C	5.14093600	-0.85006500	-0.69113100
H	4.40625000	1.04434800	0.05895700
C	3.67351800	-2.74845900	-0.37926100
H	1.77088400	-2.35689000	0.55398100
C	4.88121300	-2.21523800	-0.83960700
H	6.08411100	-0.42787500	-1.04525700
H	3.46201500	-3.81356800	-0.49703700
H	5.62035300	-2.86443500	-1.31403500
C	-0.13541800	2.73852700	-0.87243900

C	-1.44206700	2.88548400	-0.38036300
C	0.75105900	3.81839200	-0.78616700
C	-1.84820300	4.09469400	0.18612500
H	-2.13903400	2.04609300	-0.43187000
C	0.34252000	5.03085400	-0.22292500
H	1.77310900	3.70923100	-1.15979800
C	-0.95854700	5.17101300	0.26520700
H	-2.86630200	4.19439600	0.56957000
H	1.04502100	5.86551400	-0.16124700
H	-1.27900500	6.11648300	0.70917600

Int1D

Al	-3.28308900	0.37250300	-0.32141200
Cl	-2.70547300	-1.75843000	-0.08084100
Cl	-2.75089800	1.33864400	1.57155800
Cl	-5.37044200	0.51366000	-0.75780100
C	0.13579400	0.40849200	-0.17369000
H	-0.40980700	1.23026300	0.30918800
H	-0.59359900	-0.33518400	-0.50961800
S	1.08785900	-0.34950900	1.20100600
C	-0.23032000	-0.94404800	2.29836400
H	-0.75320300	-0.04884200	2.66178900
H	-0.94505000	-1.55851900	1.73460300
H	0.26198700	-1.49239400	3.11122100
O	-2.26187500	1.05574100	-1.56476200
H	-2.71157100	1.33325200	-2.36963300
C	1.04336700	0.87564000	-1.30029600
H	1.48008300	0.00799300	-1.81816200
H	0.34799400	1.35837700	-2.00573400
C	1.73023100	-1.84088800	0.44739800
C	3.11339200	-2.03483500	0.51686200
C	0.88767900	-2.74412200	-0.21182100
C	3.66696900	-3.16818300	-0.08399200
H	3.74550200	-1.30485200	1.02624400
C	1.45850700	-3.87115800	-0.80497500
H	-0.19130500	-2.57679700	-0.27194500
C	2.84049400	-4.08307100	-0.74181200
H	4.74534100	-3.33358000	-0.03796800
H	0.81525000	-4.58566100	-1.32263400
H	3.27579900	-4.96785900	-1.21159800
C	2.13065100	1.81827400	-0.84408400
C	1.80300900	3.07518400	-0.31171800
C	3.47844200	1.43607000	-0.88769000

C	2.79999300	3.92655900	0.16678900
H	0.75597200	3.38942800	-0.27676000
C	4.47955000	2.28718400	-0.40917000
H	3.74570900	0.46166000	-1.30599800
C	4.14204900	3.53386000	0.12192900
H	2.52932000	4.90359000	0.57412300
H	5.52611400	1.97593400	-0.45491200
H	4.92186800	4.20126600	0.49602300

TS2D

Al	2.21329300	-2.11020900	0.12774900
Cl	0.30208200	-1.81076600	-0.91725000
Cl	3.59277200	-0.63950300	-0.60548300
Cl	2.81552800	-4.14944600	0.08993600
C	-1.66501100	1.26762600	0.40741500
C	0.84328300	0.08878900	1.85029100
H	1.72963200	0.54521600	1.41949400
H	0.13870300	-0.43281300	1.21495000
S	-0.36435900	2.04440200	1.45204100
O	1.89475600	-1.62620600	1.83733300
H	1.52209400	-2.30365400	2.41775200
H	-2.16736700	2.08149200	-0.13427100
H	-1.17152600	0.60916400	-0.32144500
H	0.72277400	0.09041900	2.93069500
C	-2.65162800	0.48118900	1.27380600
H	-2.10856700	-0.29566800	1.83653800
H	-3.11408400	1.15242700	2.01448300
C	0.71522600	2.77277300	0.22478500
C	1.05835600	4.12237800	0.38158200
C	1.25032500	2.01249500	-0.82394400
C	1.94519500	4.71314500	-0.52073200
H	0.63256400	4.70138500	1.20357700
C	2.13740200	2.61524100	-1.71688800
H	1.00768800	0.95639000	-0.94775900
C	2.48437700	3.96091000	-1.56866900
H	2.21586800	5.76467600	-0.40203300
H	2.57230400	2.01237000	-2.51606200
H	3.18352500	4.42394800	-2.26856400
C	-3.71601600	-0.16386300	0.41441400
C	-4.98749700	0.41336600	0.29458800
C	-3.42745800	-1.32908200	-0.31304900
C	-5.95678300	-0.16316300	-0.53061700
H	-5.22323800	1.32085500	0.85788500

C	-4.39474300	-1.90456800	-1.13909700
H	-2.43674300	-1.78525500	-0.24012000
C	-5.66194700	-1.32399600	-1.24989400
H	-6.94548000	0.29527400	-0.60984400
H	-4.15563500	-2.81191600	-1.69866300
H	-6.41859600	-1.77665900	-1.89507600