Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Iron-Catalyzed C−S Bond-Forming Reaction via Photo-Induced Ligand to Metal Charge Transfer

Ao-Men Hu,[a,#] Jia-Lin Tu,[a,#] Chao Yang,[a] Lin Guo[a,*] and Wujiong Xia[a,b,*]

[a] State Key Lab of Urban Water Resource and Environment, Harbin Institute of Technology (Shenzhen), Shenzhen 518055, China

[b] School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007, China

[#] A.-M. H. and J.-L.T. contributed equally to this work.

Email: guolin@hit.edu.cn; xiawj@hit.edu.cn

Table of Contents

1. General information

^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) and ^{19}F NMR (376 MHz) spectra were recorded on a Quantum-I Plus 400 NMR spectrometer with $CDCl_3$ as solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts were reported in parts per million (ppm, δ scale) downfield from TMS at 0.00 ppm and referenced to $CDCl_3$ at 7.26 ppm (for ^{1}H NMR) and 77.16 ppm (for ^{13}C NMR). HR-MS spectra were recorded on a Waters Xevo G2QTOF/UPLC mass spectrometer using electrospray ionization. EPR experiments were conducted using Bruker Elexsys E580 Spectrometer. All commercially available reagents and solvents were purchased from Energy Chemical and Adamas-beta® and used as received unless otherwise specified.

2. Photochemical reaction setup

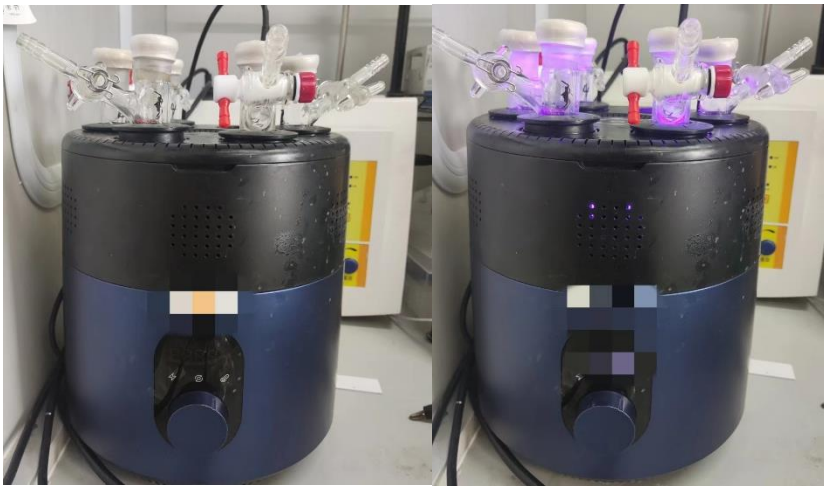


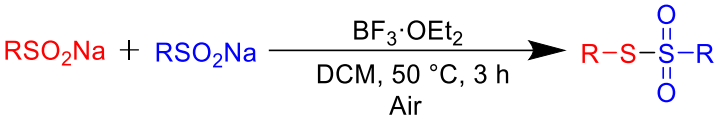
Figure S1: Reaction setup

Light source: Purple LEDs was purchased from Shanghai 3S Technology Co., Ltd (390-395 nm), China (Figure S1).

3. General procedures for synthesis of substrates

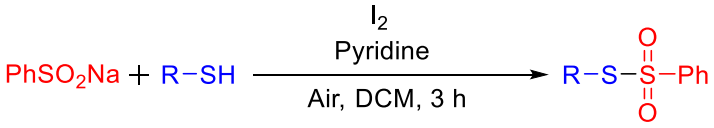
3.1 Synthesis of substrates

Method A[1]:



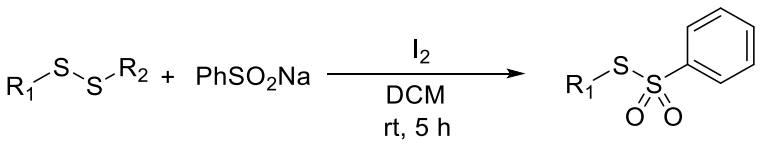
The mixture of sodium sulfinate (5 mmol), sodium sulfinate (5 mmol) and BF_3 OEt_2 (3 equiv) in CH_2Cl_2 (50 mL) was stirred at 50 ℃ under air for 3 h at ambient temperature, the reaction mixture was diluted with H_2O (15 mL) and extracted with CH_2Cl_2 (3 × 15 mL). The organic extracts were dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvents under reduced pressure, the crude product was purified by column chromatography on silica gel to afford the desired product.

Method B[2]:



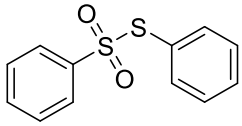
In a single-necked flask was added thiol (1.00 equiv), pyridine (1.05 equiv), iodine (2.00 equiv) and dichloromethane as solvent. After reaction and stirring for five minutes, added sodium benzenesulfite (1.7 equiv). The mixture was stirred for 3 h in air. The product was purified by silica-gel chromatography (petroleum ether/EtOAc= 10：1 as eluent).

Method C[3]:

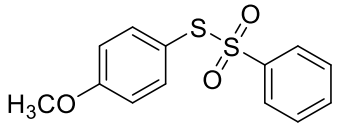


To a mixture of Disulfide ether (1.0 equiv), sodium benzenesulfinate (3.2 equiv) in DCM (50 mL, 0.2 M) was added I_2 (2.0 equiv) portionwise with stirring. Then the mixture was stirred at room temperature until the disulfide was totally consumed (about

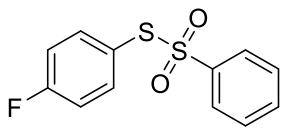
5 h, monitored by TLC). After completion, the mixture was diluted by DCM (50 mL) and saturated aqueous solution of $Na_2S_2O_3$ (about 10 mL) was added with stirring until the color of I_2 disappeared. The organic layer was seperated, washed with H_2O (20 mL × 2) and dried over anhydrous Na_2SO_4. After the removal of volatiles *in vacuo*, purification by flash column chromatography (eluting with EA/PE=1:10) afforded production as a yellow solid.



***S*-phenyl benzenesulfonothioate** (**S1**): Prepared using general procedure A from sodium benzenesulfinate. Yellow oil; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.64 – 7.57 (m, 3H), 7.54 – 7.49 (m, 1H), 7.48 – 7.43 (m, 2H), 7.41 – 7.33 (m, 4H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.9, 136.6, 133.6, 131.4, 129.4, 128.8, 127.8, 127.6.

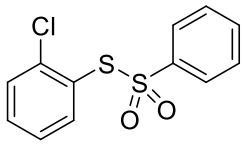


***S*-(4-methoxyphenyl) benzenesulfonothioate (S2):** Prepared using general procedure B from sodium benzenesulfinate and 4-methoxybenzenethiol. Colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.64 – 7.57 (m, 3H), 7.49 – 7.43 (m, 2H), 7.28 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 3.86 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.3, 142.9, 138.3, 133.5, 128.8, 127.6, 118.5, 115.0, 77.4, 77.0, 76.7, 55.5.

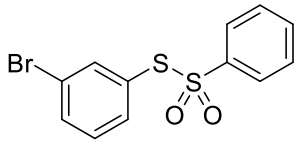


***S*-(4-fluorophenyl) benzenesulfonothioate (S5):** Prepared using general procedure B from sodium benzenesulfinate and 4-fluorobenzenethiol. Yellow oil.**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.63 – 7.53 (m, 3H), 7.48 – 7.41 (m, 2H), 7.35 – 7.28 (m, 2H), 7.05 – 6.98 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.0, 163.5, 142.6, 138.8 (d, *J* = 9.1

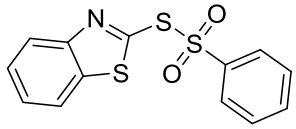
Hz), 134.0, 129.0, 127.5, 123.3 (d, *J* = 3.0 Hz), 77.5, 77.2, 76; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -106.98 (s, 1F).



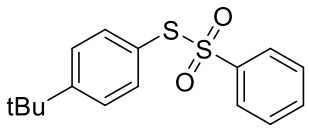
***S*-(2-chlorophenyl) benzenesulfonothioate (S6):** Prepared using general procedure B from 2-chlorobenzenethiol and sodium benzenesulfinate. Colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.72 (d, *J* = 7.7, 1.3 Hz, 1H), 7.68 – 7.59 (m, 3H), 7.51 – 7.41 (m, 4H), 7.39 – 7.33 (m, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.4, 140.3, 139.6, 134.0, 133.0, 130.3, 129.0, 127.7, 127.5, 127.0.



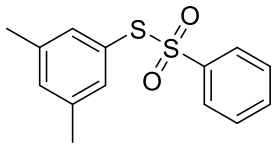
***S*-(3-bromophenyl) benzenesulfonothioate (S7):** Prepared using general procedure B from 3-bromobenzenethiol and sodium benzenesulfinate. Colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.69 – 7.58 (m, 4H), 7.54 – 7.47 (m, 2H), 7.46 – 7.41 (m, 1H), 7.37 (d, *J* = 7.9 Hz, 1H), 7.31 – 7.27 (m, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.6, 138.9, 135.1, 134.5, 134.0, 130.8, 129.7, 129.0, 127.6, 122.7.



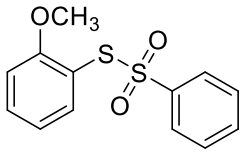
***S*-(benzo[d]thiazol-2-yl) benzenesulfonothioate (S8):** Prepared using general procedure C from 1, 2-bis(benzo[d]thiazol-2-yl)disulfane and sodium benzenesulfinate. Colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.11 – 8.06 (m, 1H), 7.97 – 7.93 (m, 1H), 7.85 – 7.81 (m, 2H), 7.71 – 7.66 (m, 1H), 7.60 – 7.56 (m, 1H), 7.55 – 7.50 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 154.3, 153.2, 143.4, 138.8, 134.6, 129.3, 127.8, 127.0, 126.9, 124.4, 121.5.



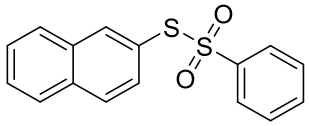
***S*-(4-(tert-butyl) phenyl) benzenesulfonothioate (S10):** Prepared using general procedure B from sodium benzenesulfinate and 4-(tert-butyl) benzenethiol. Colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.58 (d, *J* = 8.1 Hz, 3H), 7.47 – 7.39 (m, 2H), 7.37 (d, *J* = 5.6 Hz, 2H), 7.29 (d, *J* = 5.7 Hz, 2H), 1.33 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.2, 143.0, 136.3), 133.6, 128.8, 127.5, 126.6, 124.3, 34.9, 31.1.



***S*-(3,5-dimethylphenyl) benzenesulfonothioate (S35):** Prepared using general procedure A from 3,5-dimethylbenzenethiol. Colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.71 – 7.60 (m, 3H), 7.55 – 7.47 (m, 2H), 7.16 (s, 1H), 6.98 (s, 2H), 2.30 (s, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.8, 139.2, 134.2, 133.7, 133.3, 128.7, 127.8, 127.0, 21.1.

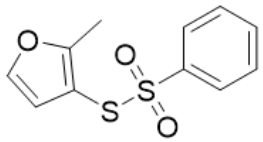


***S*-(2-methoxyphenyl) benzenesulfonothioate (S42):** Prepared using general procedure A from 2-methoxybenzenethiol and sodium benzenesulfinate. Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.63 – 7.49 (m, 4H), 7.48 – 7.32 (m, 4H), 6.99 – 6.89 (m, 1H), 6.76 (d, *J* = 8.3 Hz, 1H), 3.40 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.9, 144.2, 139.5, 133.97, 133.3, 128.5, 127.5, 121.3, 115.2, 111.3, 55.4.

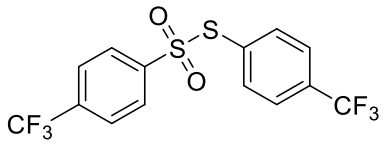


***S*-(naphthalen-2-yl) benzenesulfonothioate (S46):** Prepared using general procedure B from sodium benzenesulfinate and naphthalene-2-thiol. Colorless oil.

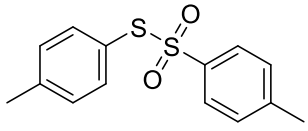
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.8 Hz, 2H), 7.82 (d, *J* = 8.6 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.66 – 7.52 (m, 5H), 7.45 – 7.37 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.9, 137.6, 134.1, 133.7, 133.3, 131.8, 129.2, 128.9, 128.4, 128.3, 127.8, 127.6, 127.0, 124.9.



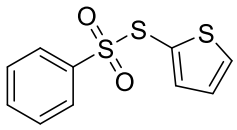
***S*-(2-methylfuran-3-yl) benzenesulfonothioate (S47):** Prepared using general procedure A from s 2-methylfuran-3-thiol and sodium benzenesulfinate. Brown oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.54 – 7.43 (m, 2H), 6.26 (s, 1H), 1.93 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.4, 142.7, 141.6, 133.8, 129.1, 127.4, 115.2, 105.3, 11.3.



***S*-(4-(trifluoromethyl)phenyl)-4-(trifluoromethyl)benzenesulfonothioate (S60):** P repared using general procedure A from sodium 4-(trifluoromethyl)benzenesulfin ate. Colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.81 – 7.73 (m, 4H), 7.68 (d, *J* = 8.1 Hz, 2H), 7.61 – 7.54 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 14 6.1, 136.7 (s), 135.3 (q, *J* = 33.9, 8.9 Hz)，133.7 (q, *J* = 32.7, 11.7 Hz), 131. 6, 127.9, 126.5 (q, *J* = 3.6 Hz), 126.3 (q, *J* = 6.8, 3.2 Hz), 124.4 (q, *J* = 36. 5, 18.1 Hz), 121.7 (q, *J* = 39.2, 20.0 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -6 3.08 (s, 3F), -63.19 (s, 3F).



***S*-(p-tolyl) 4-methylbenzenesulfonothioate (S61):** Prepared using general procedure A from sodium 4-methylbenzenesulfinate. Colorless oil; **^{1}H NMR (400 MHz, CDCl3)** δ 7.49 (d, J = 7.8 Hz, 2H), 7.31 – 7.26 (m, 2H), 7.25 (d, J = 8.3 Hz, 2H), 7.17 (d, J = 7.8 Hz, 2H), 2.45 (s, 3H), 2.41 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 144.6, 142.0, 140.4, 136.5, 130.2, 129.4, 127.6, 124.6, 26.9, 21.6.

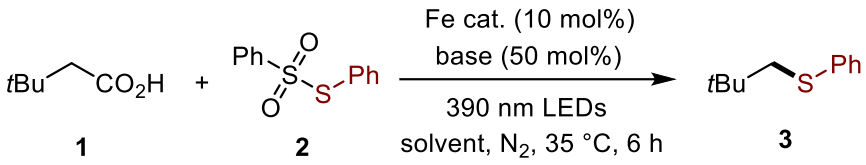


***S*-(thiophen-2-yl) benzenesulfonothioate (S67):** Prepared using general procedure B from sodium benzenesulfinate and thiophene-2-thiol. Brown oil.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.75 – 7.62 (m, 4H), 7.54 – 7.47 (m, 2H), 7.16 (d, *J* = 3.7 Hz, 1H), 7.12 – 7.07 (m, 1H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 142.0, 139.5, 135.4, 134.0, 129.05, 128.4, 127.8, 124.9.

4. Optimization of the reaction conditions

Table S1. Optimization of Alkyl decarboxylation thioetherification

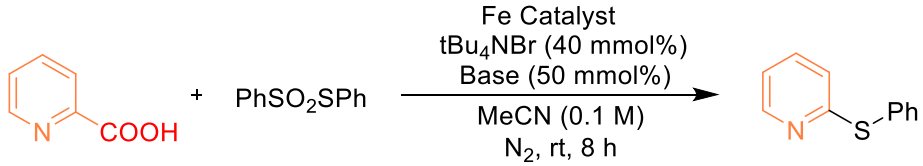


1 2 3

Entry	Fe catal	Solvent	Base	Time	Yield[c]
1[b]	$Fe(NO_3)_3$ $9H_2O$	MeCN	Na_2CO_3 (10 %)	6 h	51%
2	$Fe(NO_3)_3$ $9H_2O$	MeCN	Na_2CO_3 (10 %)	6 h	68%
3	$Fe(acac)_3$	MeCN	Na_2CO_3 (10 %)	6 h	61%
4	$Fe_2(SO_4)_3$	MeCN	Na_2CO_3 (10 %)	6 h	21%
5	$Fe(OTf)_3$	MeCN	Na_2CO_3 (10 %)	6 h	14%
6	$Fe(NO_3)_3$ $9H_2O$	toluene	Na_2CO_3 (10 %)	6 h	86%
7	$Fe(NO_3)_3$ $9H_2O$	DCE	Na_2CO_3 (10 %)	6 h	11%
8	$Fe(NO_3)_3$ $9H_2O$	DCM	Na_2CO_3 (10 %)	6 h	N.R.
9	$Fe(NO_3)_3$ $9H_2O$	THF	Na_2CO_3 (10 %)	6 h	28%
10	$Fe(NO_3)_3$ $9H_2O$	MeCN	Na_2CO_3 (50 %)	6 h	89%
11	$Fe(NO_3)_3$ $9H_2O$	MeCN	Na_2CO_3 (80 %)	6 h	86%
12	$Fe(NO_3)_3$ $9H_2O$	MeCN	Na_2CO_3 (100 %)	6 h	84%
13	$Fe(NO_3)_3$ $9H_2O$	MeCN	CH_3COONa (50 %)	6 h	44%
14	$Fe(NO_3)_3$ $9H_2O$	MeCN	NaOH (50 %)	6 h	78%
15	$Fe(NO_3)_3$ $9H_2O$	MeCN	$NaHCO_3$ (50 %)	6 h	41%
16	$Fe(NO_3)_3$ $9H_2O$	MeCN	K_2CO_3 (50 %)	6 h	91%
17	$Fe(NO_3)_3$ $9H_2O$	MeCN	KOH (50 %)	6 h	34%
18	$Fe(NO_3)_3$ $9H_2O$	MeCN	CH_3COOK (50 %)	6 h	51%
19	$Fe(NO_3)_3$ $9H_2O$	MeCN	KF (50 %)	6 h	N.R.
20	$Fe(NO_3)_3$ $9H_2O$	MeCN	$CsCO_3$ (50 %)	6 h	54%
22[d]	$Fe(NO_3)_3$ $9H_2O$	MeCN	Na_2CO_3 (50 %)	6 h	N.R.

[a] Reaction conditions: **1** (0.40 mmol, 2 equiv), **2** (0.20 mmol, 1.0 equiv.), Metal catalyst (10 mol%) in CH_3CN (2 mL, 0.1 M), 35 ℃, 390 nm purple LEDs, N_2 asmopheras as internal standard.[b] The 1.0 equiv. **1** was used. [c] Isolated yield. [d] The reaction proceeds in dark.

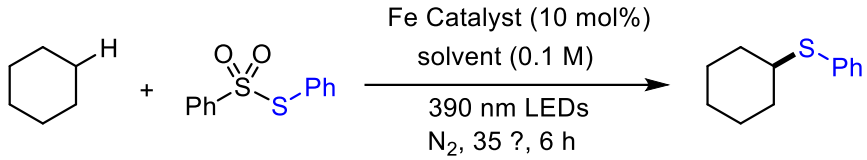
Table S2. Optimization of Alkyl decarboxylation thioetherification



Entry	Catalyst	Base	Addition	Solvent	Yield [b]
1	$Fe(NO_3)_3$ $9H_2O$	K_2CO_3 (50%)	nBu_4NBr (40%)	MeCN	70%
2	$Fe(acac)_3$	K_2CO_3 (50%)	nBu_4NBr (40%)	MeCN	65%
3	$FeCl_3$	K_2CO_3 (50%)	nBu_4NBr (40%)	MeCN	73.4%
4	$Fe_2(SO_4)_3$	K_2CO_3 (50%)	nBu_4NBr (40%)	MeCN	N.D.
5	$Fe(OTf)_3$	K_2CO_3 (50%)	nBu_4NBr (40%)	MeCN	69%
6	$FeBr_3$ (10 mol%)	K_2CO_3 (50%)	nBu_4NBr (40%)	MeCN	94%
7	$FeBr_3$ (5 mol%)	K_2CO_3 (50%)	nBu_4NBr (40%)	MeCN	80%
8	$FeBr_3$ (15 mol%)	K_2CO_3 (50%)	nBu_4NBr (40%)	MeCN	84%
9	$FeBr_3$ (20 mol%)	K_2CO_3 (50%)	nBu_4NBr (40%)	MeCN	79%
10	$FeBr_3$ (10 mol%)	Na_2CO_3 (50%)	nBu_4NBr (40%)	MeCN	80%
11	$FeBr_3$ (10 mol%)	K_2CO_3 (50%)	nBu_4NBr (40%)	MeCN	94%
12	$FeBr_3$ (10 mol%)	Na_3PO4	nBu_4NBr (40%)	MeCN	23%
13	$FeBr_3$ (10 mol%)	NaF	nBu_4NBr (40%)	MeCN	82%
14	$FeBr_3$ (10 mol%)	tBuONa	nBu_4NBr (40%)	MeCN	64%
15 [c]	$FeBr_3$ (10 mol%)	K_2CO_3 (50%)	nBu_4NBr (40%)	MeCN	N.D.

[a] Reaction conditions: **1** (0.40 mmol, 2 equiv), **2** (0.20 mmol, 1.0 equiv.), Metal catalyst (10 mol%), K_2CO_3 (50 mol%) and tBuNBr (40 mol%) in CH_3CN (2 mL, 0.1 M), 35 ℃, 390 nm purple LEDs, N_2 asmopheras as internal standard.. [b] Isolated yield. [c] The reaction proceeds in dark.

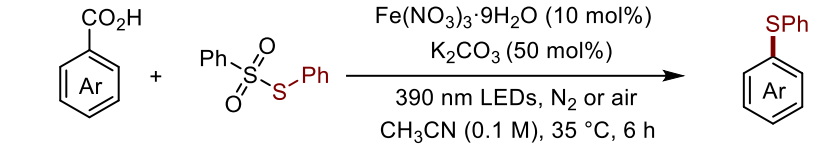
Table S3. Optimization of C-H thioetherification reactions

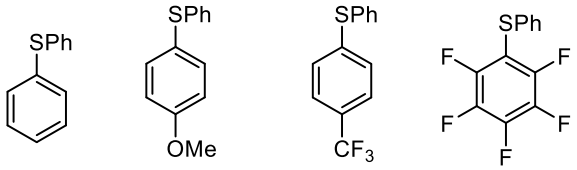


Entry	Metal catalyst	Solvent	Addition	Yield[b]
1	$Fe(Cl)_3$ (10 mol%)	DCM	\	5%
2	$Fe(Cl)_3$ (10 mol%)	DCE	\	8%
3	$Fe(Cl)_3$ (10 mol%)	MeCN	\	74%
4	$Fe(Cl)_3$ (10 mol%)	THF	\	22%
5	$Fe(Cl)_3$ (10 mol%)	Acetone	\	33%
6	$Fe(Cl)_3$ (10 mol%)	H_2O	\	N.R
7	$Fe(Cl)_3$ (10 mol%)	MeCN:Acetone=1:1	\	51
8	$Fe(Br)_3$ (10 mol%)	MeCN	\	N.R
9	$Fe(Cl)_3$ (5 mol%)	MeCN	\	70%
10	$Fe(Cl)_3$ (15 mol%)	MeCN	\	72%
11	$Fe(Cl)_3$ (20 mol%)	MeCN	\	68%
12	$Fe(Cl)_3$ (10 mol%)	MeCN	LiCl (10 %)	91%
13	$Fe(Cl)_3$ (10 mol%)	MeCN	TBAC (10 %)	84%
14	$Fe(Cl)_3$ (10 mol%)	MeCN	HCl (10 %)	70%
15[c]	$Fe(Cl)_3$ (10 mol%)	MeCN	\	N.R

[a] Reaction conditions: alkane substrate (2.0 mmol, 10.0 equiv.), thiosulfonate (0.2 mmol, 1.0 equiv.), Fe catalyst (10 mol%) in solevnt (2 mL, 0.1 M), 390 nm purple LEDs, N_2 asmophere. [b]Isolated yield. [c]The reaction proceeds in dark.

Table S4. Decarboxylative thiolation on aromatic carboxylic acid

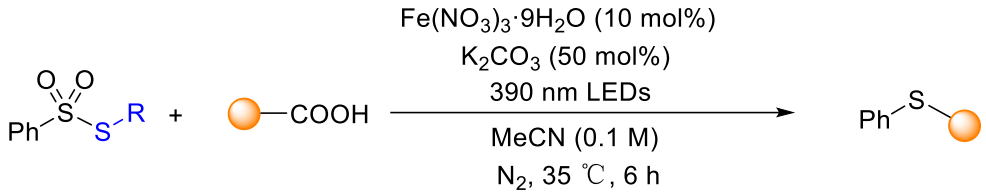




0% 0% trace < 5%

We initially attempted the decarboxylative thiolation reaction using benzoic acid and its derivatives. However, for substrates without substitution or containing electron-donating groups, the reaction did not proceed at all. Traces of product were obtained when using trifluoromethyl benzoic acid as the substrate, while the use of pentafluorobenzoic acid gave less than 5% yield of the desired product. Following these unsuccessful attempts, we then considered utilizing 2-quinolinecarboxylic acid as the substrate for further investigations.

5. General procedures for iron catalyzed LMCT reaction



General procedure 1: To a 25 mL quartz tube equipped with a magnetic stir bar, Carboxylic acid (0.4 mmol, 2.0 equiv.), **2** (0.2 mmol, 1.0 equiv.), $Fe(NO_3)_3$ $9H_2O$ (8.0 mg, 10 mol%) and CH_3CN (2 mL) were added. The resulting mixture was stirred in nitrogen astmoshpere under a purple LEDs and irradiated for 6 hours. After the reaction was finished (monitored by TLC), the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel.

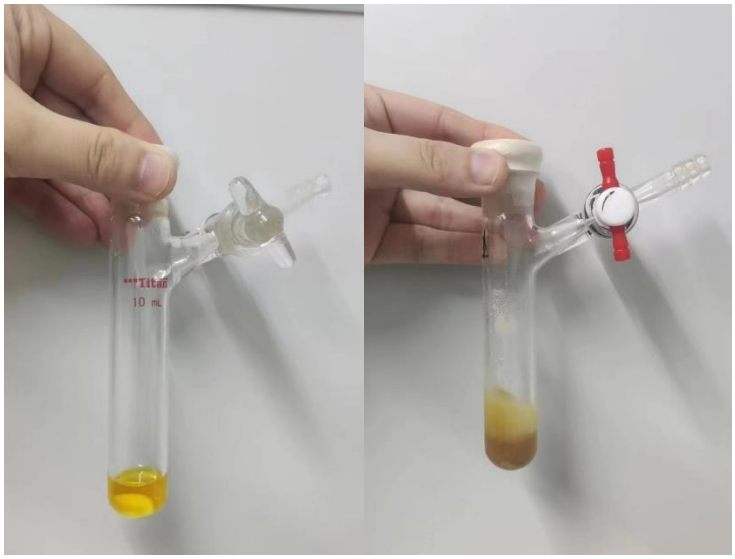
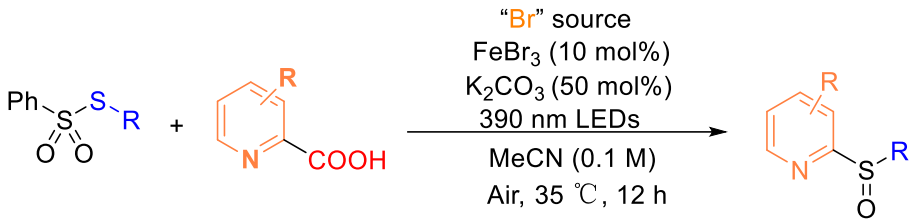


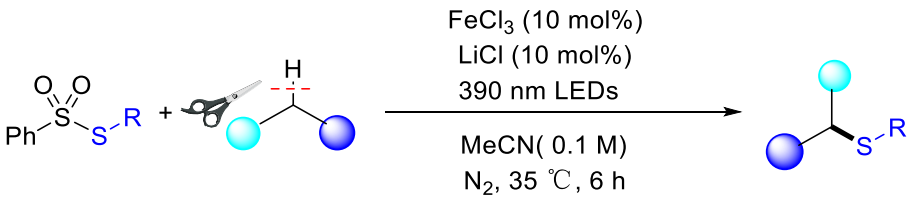
Figure S2. Before and after the photochemical reaction



General procedure 2: To a 25 mL quartz tube equipped with a magnetic stir bar, The **2** (0.2 mmol, 1.0 equiv.), Pyridine carboxylic acid (0.2 mmol, 1.0 equiv.), FeBr (7.0 mg,

10 mol%), Tetrabutylammonium bromide (25.7 mg, 40 %), K_2CO_3 (13.8 mg, 50 mol%,) and CH_3CN (2 mL) were added. The resulting mixture was stirred in Air under a purple LEDs and irradiated for 12 hours. After the reaction was finished (monitored by TLC), the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel.

Figure S3. Before and after photochemical reaction



General procedure 3: To a 25 mL quartz tube equipped with a magnetic stir bar, The alkane substrate (2.0 mmol, 10.0 equiv.), thiosulfonate (0.2 mmol, 1.0 equiv.), $FeCl_3$ (3.2 mg, 10 mol%), LiCl (0.85 mg, 10 mol%) and CH_3CN (2 mL) were added. The resulting mixture was stirred in nitrogen astmoshpere under a purple LEDs and irradiated for 6 hours. After the reaction was finished (monitored by TLC), the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel.

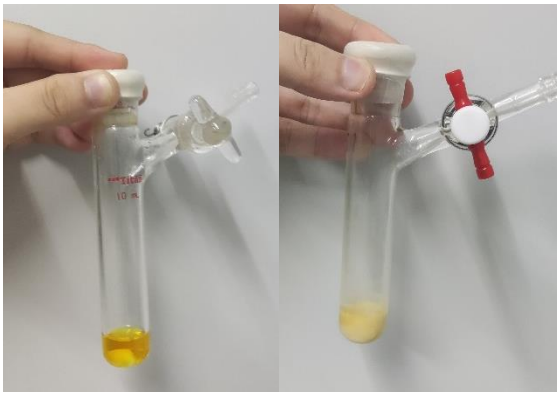
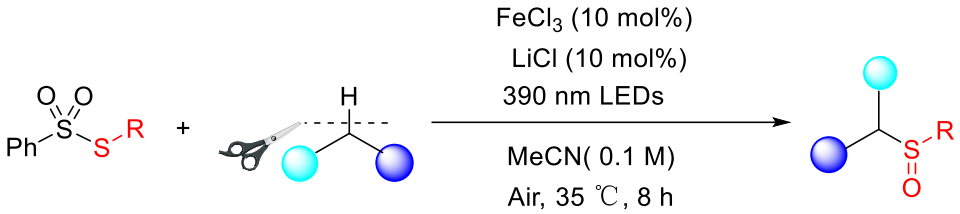


Figure S4. Before and after photochemical reaction



General procedure 4: To a 25 mL quartz tube equipped with a magnetic stir bar, The alkane substrate (2.0 mmol, 10.0 equiv.), thiosulfonate (0.2 mmol, 1.0 equiv.), $FeCl_3$ (3.2 mg, 10 mol%), LiCl (0.85 mg, 10 mol%) and CH_3CN (2 mL) were added. The resulting mixture was stirred in air under a purple LEDs and irradiated for 8 hours. After the reaction was finished (monitored by TLC), the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel.

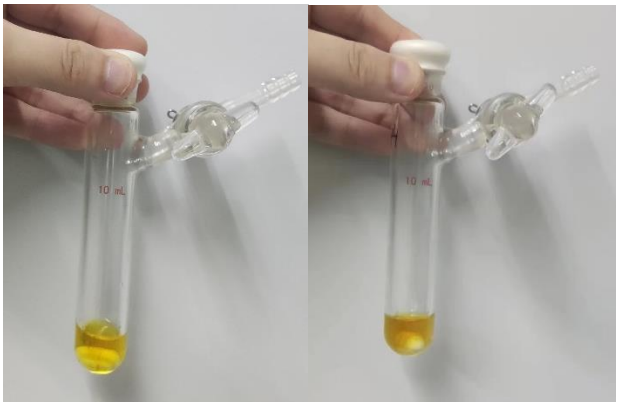
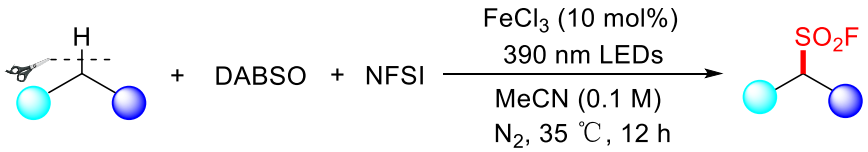


Figure S5. Before and after phtotchemical reaction



General procedure 5: To a 25 mL quartz tube equipped with a magnetic stir bar, The Corresponding alkane (2 mmol, 10.0 equiv.), DABSO (1, 4-Diazabicyclo[2.2.2]octane-1,4-diium-1,4-disulfinate, 0.2 mmol, 1.0 equiv.), NFSI (*N*-Fluorobenzenesulfonimide, 0.4 mmol, 2.0 equiv) $FeCl_3$ (3.2 mg, 10 mol%) and CH_3CN (2 mL) were added. The resulting mixture was stirred in N_2 under a purple LEDs and irradiated for 12 hours. After the reaction was finished (monitored by TLC), the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel.

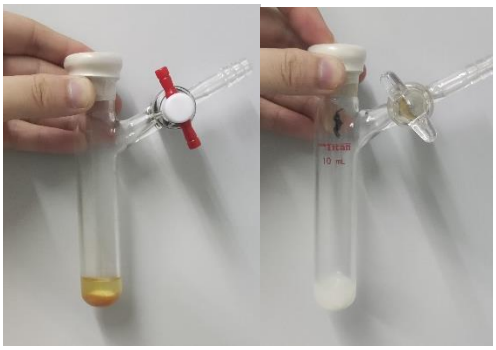
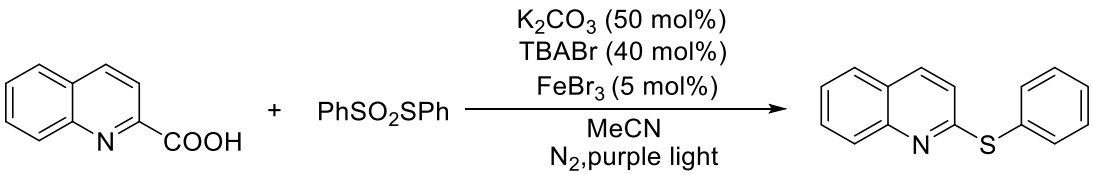


Figure S6. Before and after photochemical reaction

Scale-up synthesis of compound 39



To a 100 mL Two-necked flask equipped with a magnetic stir bar, Quinaldic acid (1.0 g, 6 mmol, 1.0 equiv.), *S*-phenyl benzenesulfonothioate (1.50 g, 6 mmol, 1.0 equiv.), $FeBr_3$ (88.5 mg, 5 mol%), tetrabutylammonium bromide (772.8 mg, 40 mol%) and CH_3CN (50 mL) were added. The resulting mixture was stirred in N_2 under a 390 nm

LEDs and irradiated for 36 hours. After the reaction was finished (monitored by TLC), the solvent was removed under reduced pressure and the residue was purified by flash column chromatography to give **40** (881.6 mg, 62% yield) as a yellow oil.

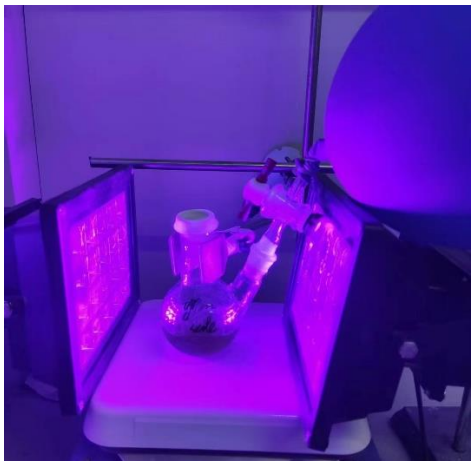
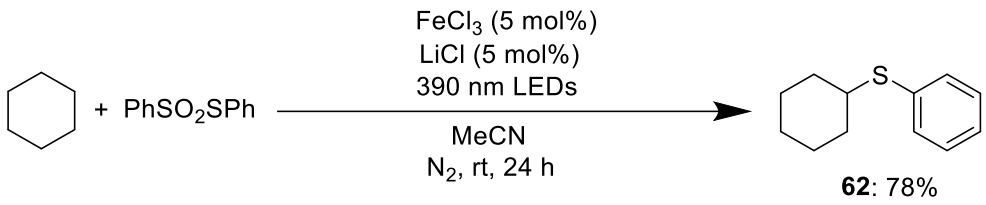


Figure S7. Gram-scale pyridine thioetherification photoreaction

Scale-up synthesis of compound 62



To a 100 mL Two-necked flask equipped with a magnetic stir bar, cyclohexane (50 mmol, 10.0 equiv.), *S*-phenylbenzenesulfonate (2.5 g, 10 mmol, 1.0 equiv.), $FeCl_3$ (82.1 mg, 5 mol%), LiCl (21.2 mg, 5 mol%) and CH_3CN (50 mL) were added. The resulting mixture was stirred in N_2 under a 390 nm LEDs and irradiated for 24 hours. After the reaction was finished (monitored by TLC), the solvent was removed under reduced pressure and the residue was purified by flash column chromatography to give **62** (1.49 g, 78% yield) as a yellow oil.

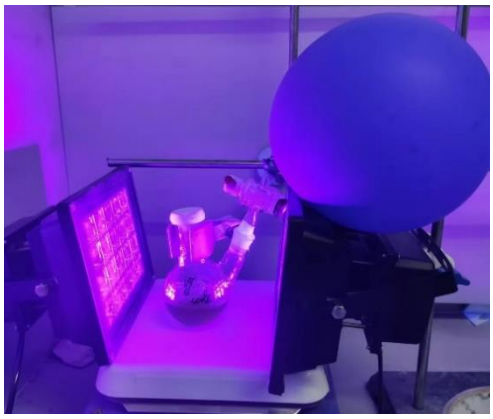
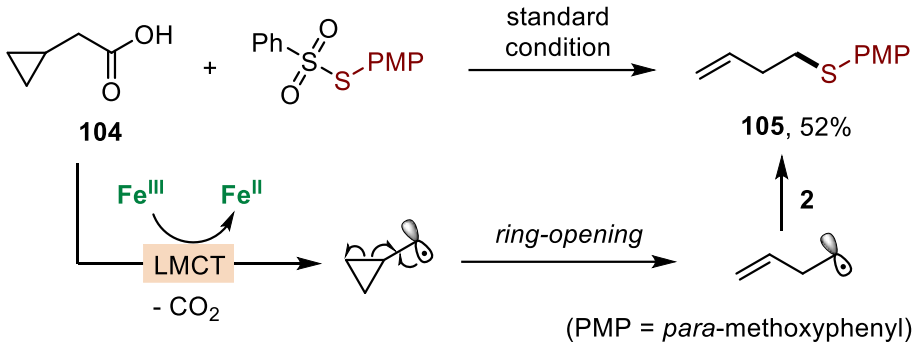


Figure S8. Gram-scale alkane thioetherification photoreaction

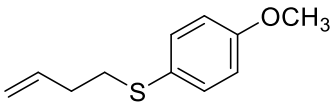
6. Mechanistic studies

6.1 Ring-opening experiments



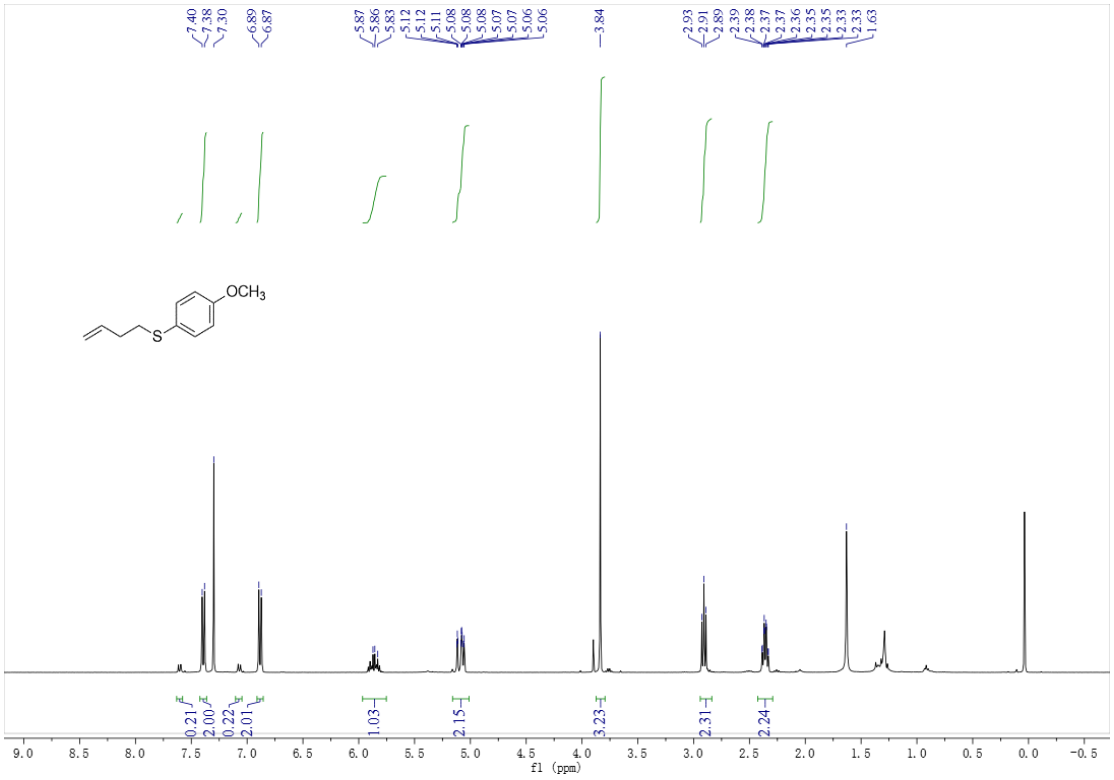
General procedure: To a 25 mL quartz tube equipped with a magnetic stir bar, **104** (0.2 mmol, 1.0 equiv.), thiosulfonate (0.2 mmol, 1.0 equiv.), $Fe(NO_3)_3$ $9H_2O$ (8.0 mg, 10 mol%), K_2CO_3 (50 mol%) and CH_3CN (2 mL) were added. The resulting mixture was stirred in N_2 under a 390 nm LEDs and irradiated for 5 hours. After the reaction was finished (monitored by TLC), the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel.

To probe the mechanism of the reaction, cyclopropylacetic acid (**104**) was employed as the substrate, which afforded the ring-opening product (**105**) in 52% yield. The result demonstrated that (**104**) underwent decarboxylation, releasing one molecule of carbon dioxide and generating the corresponding carbon radical intermediate. This then triggered a ring-opening process.

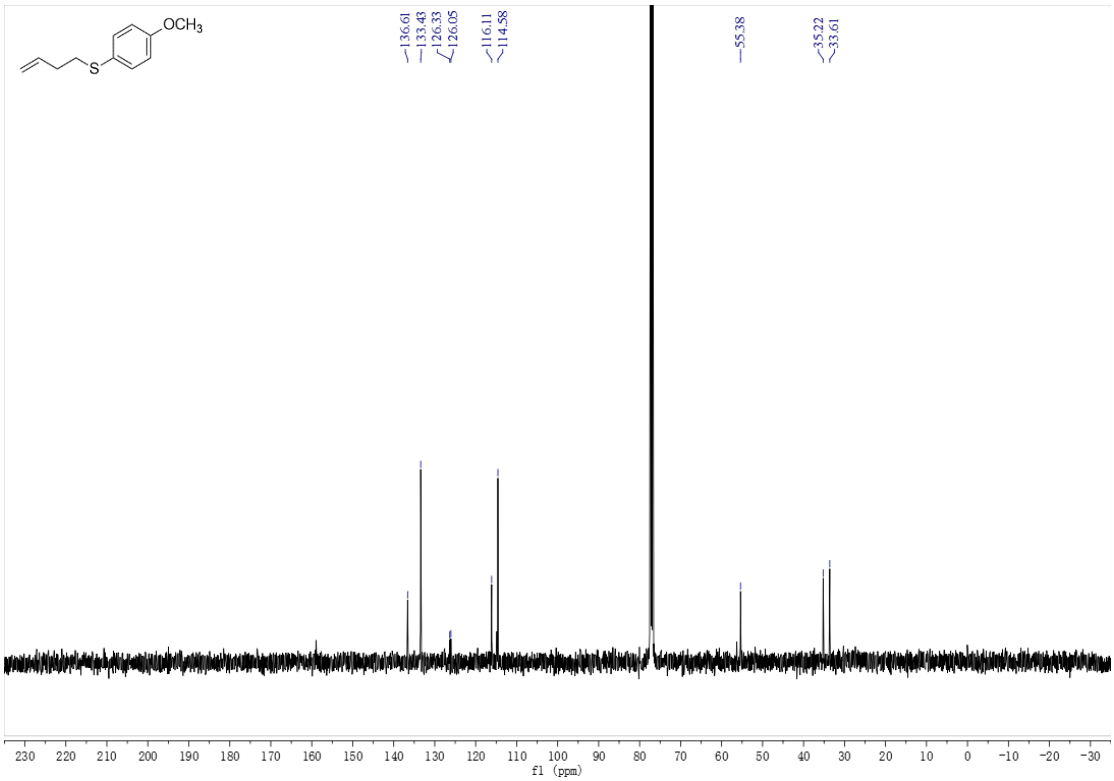


but-3-en-1-yl(4-methoxyphenyl)sulfane (105): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 5.91 – 5.81 (m, 1H), 5.15 – 5.05 (m, 2H), 3.84 (s, 3H), 2.91 (t, *J* = 7.1 Hz, 2H), 2.40 – 2.32 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 136.6, 133.4, 126.3, 126.0, 116.1, 114.5, 55.3, 35.2, 33.6.

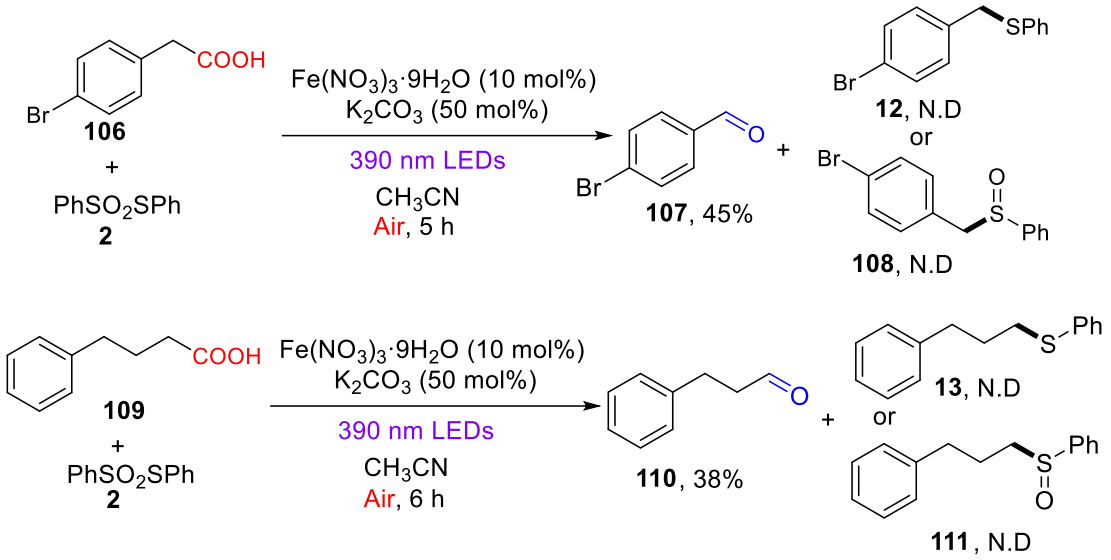
^{1}H NMR spectrum (400 MHz, CDCl3, 23 ℃) of **105**



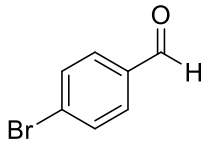
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **105**



6.2 The decarboxylation-oxidation experiment



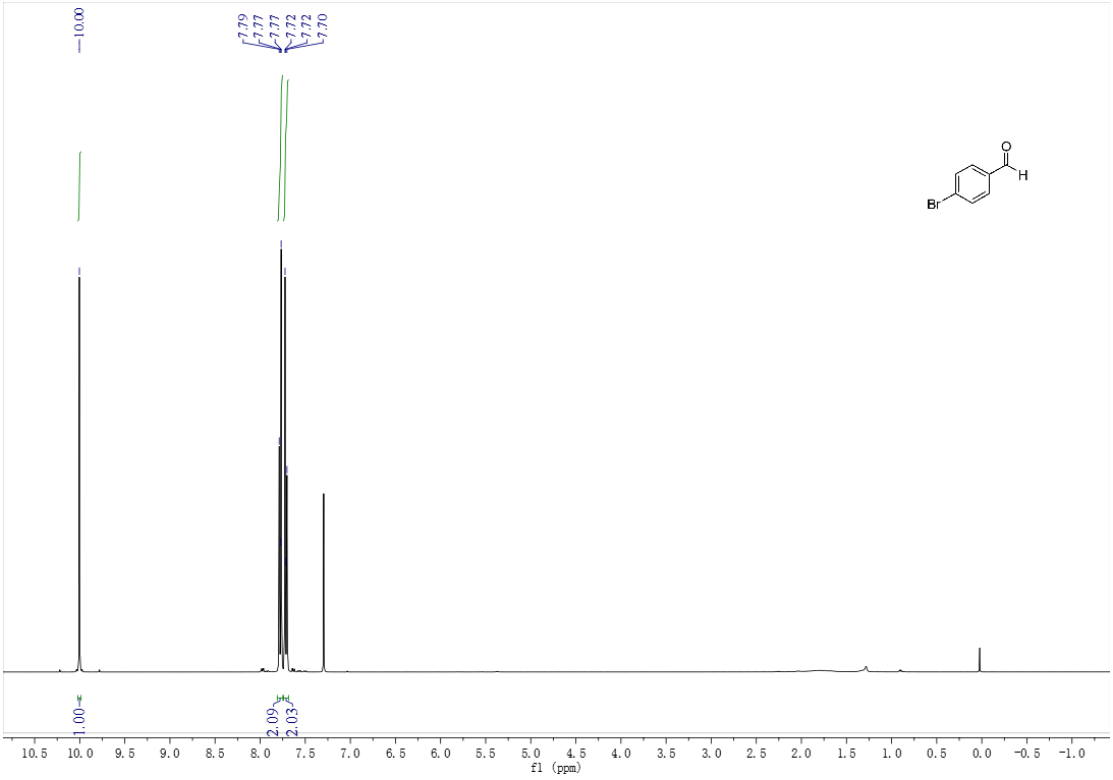
General procedure: To a 25 mL quartz tube equipped with a magnetic stir bar, The **107/110** (0.2 mmol, 1.0 equiv.), **2** (0.2 mmol, 1.0 equiv.), $Fe(NO_3)_3$ $9H_2O$ (8.0 mg, 10 mol%), K_2CO_3 (50 mol%) and CH_3CN (2 mL) were added. The resulting mixture was stirred in air under LEDs and irradiated for 5 hours. After the reaction was finished (monitored by TLC), the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel. Attempts at oxidizing the thioether to the corresponding sulfoxide utilizing atmospheric oxygen were unsuccessful, with the anticipated product undetected. As anticipated, experimentation revealed the generation of a highly reactive carbon-centered radical species via acid-mediated decarboxylation. Owing to the inherent instability of the radical intermediate, rapid oxidation and subsequent transformations yielded aldehyde products. This rationalized the non-generation of the decarboxylated thioether product.



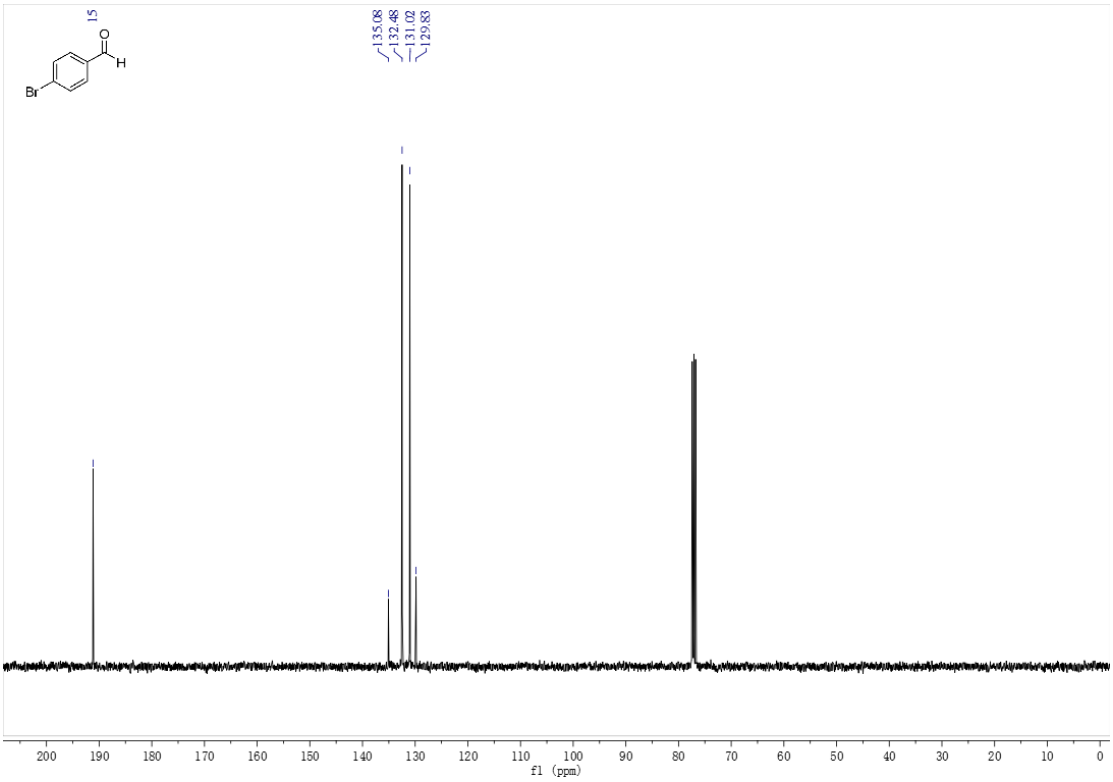
4-bromobenzaldehyde (107): ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 7.80 – 7.75 (m, 2H), 7.74 – 7.69 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 191.1, 135.0, 132.4,

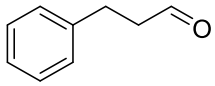
131.0, 129.8.

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **107**



^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **107**

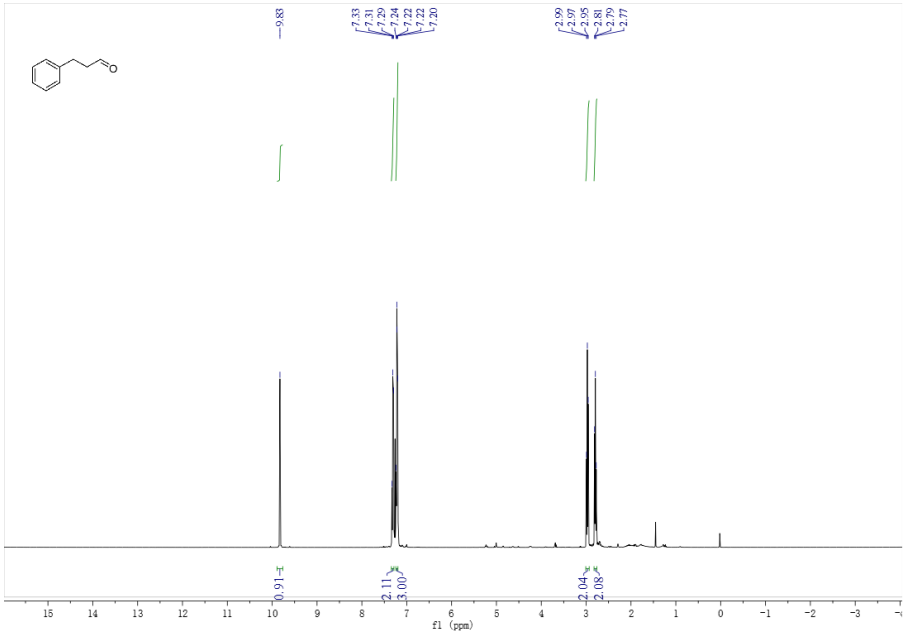




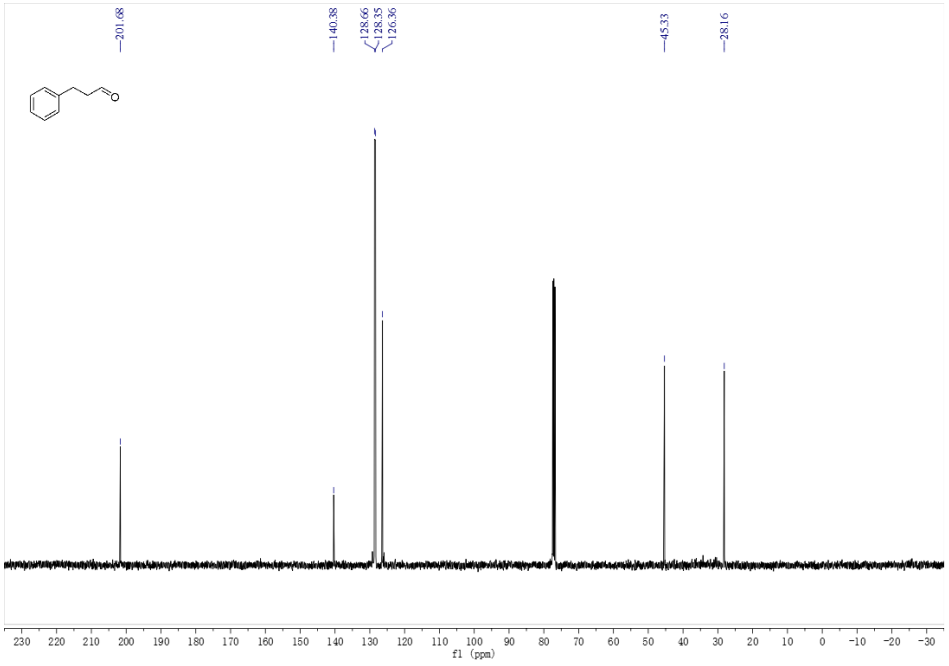
2-phenylacetaldehyde (110): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (s, 1H), 7.34 – 7.29 (m, 2H), 7.24 – 7.20 (m, 3H), 2.97 (t, *J* = 7.5 Hz, 2H), 2.82 – 2.76 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 201.6, 140.3, 128.6, 128.3, 126.3, 45.3, 28.1.

Spectral data is in agreement with the literature[4].

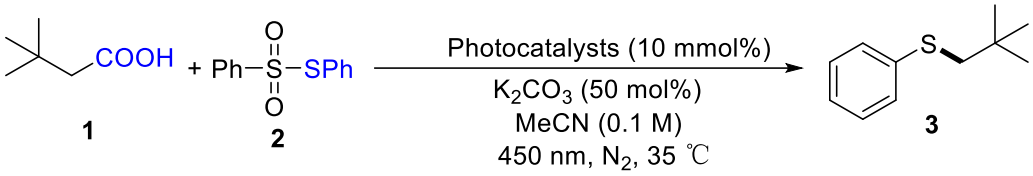
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **111**



^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **110**



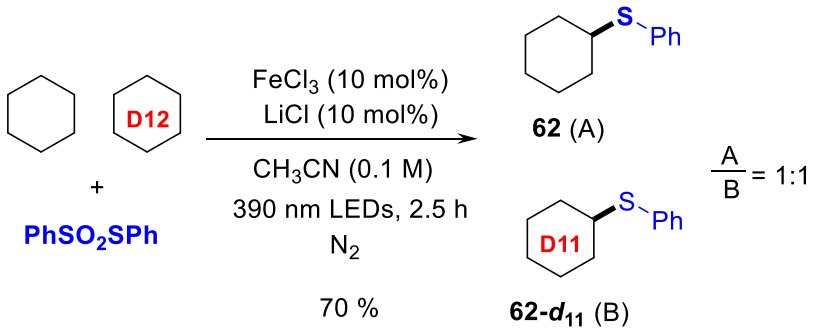
6.3 Traditional photocatalyst catalyzed reactions



entry	Fe cat.	$E_{1/2}(*P/^{-}P$, V vs. SCE)	yield (%)
1	$Ir[dF(CF_3)ppy]_2(dtbpy)]PF_6$	+1.21	trace
2	$[Ru(bpy)_3](PF_6)_2$	+0.77	trace
3	Eosin Y	+0.83	trace
4	4-CzIPN	+1.35	trace

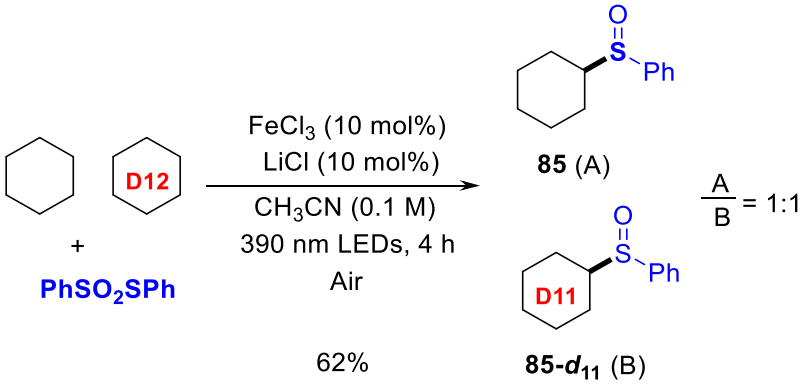
To underscore the distinctness of the visible light-induced iron-catalyzed decarboxylation transformation, a selection of prevalent photoredox catalysts including $Ir[dF(CF_3)ppy]_2(dtbpy)]PF_6$, $Ru(bpy)_3](PF_6)_2$, Eosin Y, and 4-CzIPN were employed to perform the reaction. The outcomes of these experiments revealed that in the presence of these catalytic systems, the anticipated products could only be furnished in measly amounts.

6.4 Kinetic isotopic effect (KIE) experiment



Thioether KIE experiment: To a 10 mL oven-dried round-bottom Schlenk bottle equipped with a magnetic stir bar, *S*-phenyl benzenesulfonothioate (0.2 mmol, 1.0 equiv.), $FeCl_3$ (3.2mg, 10 mol %), LiCl (0.85mg, 10 mol%), were added. CH_3CN (2 mL) and cyclohexane (1.0 mmol, 5.0 equiv.), and cyclohexane-d_{12} (1.0 mmol, 5.0 equiv.) were then added under argon atmosphere. The resulting mixture was sealed and then

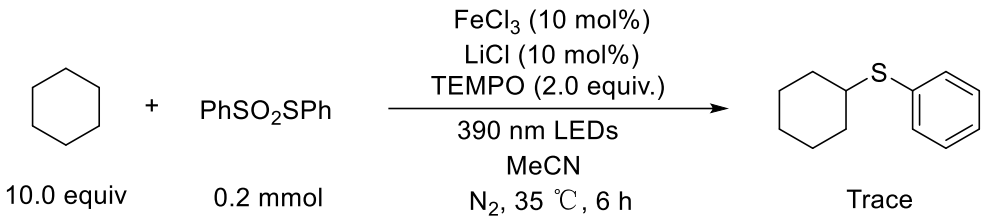
subjected to freeze-pump-thaw for three times. After that, the resulting mixture was stirred in N_2 under LEDs and irradiated for 2.5 hours. The temperature was maintained at 35 ℃ when the 390 nm LED light was on. After the reaction was finished (monitored by TLC), the mixture were removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to afford the mixture of products **62** and **62-*d*$_{11}$** in combined 70% yield. Comparing the ^{1}H NMR spectra, we found the ratio of **62**:**62-*d*$_{11}$** was 1:1, so the intermolecular KIE value was 1.0.



Sulfoxide KIE experiment: To a 25ml over-dired quartz tube equipped with a magnetic stir bar was added *S*-phenyl benzenesulfonothioate (50.0 mg ,1 equiv), $FeCl_3$ (3.2 mg, 10 mol%), LiCl (0.85 mg, 10 mol%), cyclohexane (84 mg, 5.0 equiv) ,cyclohexane-d_{12} (96 mg, 5.0 equiv) and CH_3CN (2 mL). The resulting mixture was stirred in nitrogen under a purple 390 nm LEDs and irradiated for 4 hours. The mixture were removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to afford the mixture of products **85** and **85-*d*$_{11}$** in combined 62% yield. Comparing the ^{1}H NMR spectra, we found the ratio of **85**:**85-*d*$_{11}$** was 1:1, so the intermolecular KIE value was 1.0.

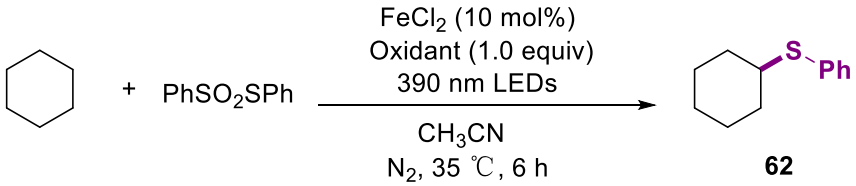
6.5 Control experiment for thioether

a) Radical trapping experiment



To a 25 mL quartz tube equipped with a magnetic stir bar, cyclohexane (168 mg, 10.0 equiv), **2** (0.2 mmol, 1.0 equiv.), $FeCl_3$ (3.2 mg, 10 mol%), LiCl (0.85 mg, 10 mol%), TEMPO (2,2,6,6-Tetramethylpiperidinooxy, 0.4 mmol, 2.0 equiv.) and CH_3CN (2 mL) were added. The mixture was strictly deaerated and irradiated for 5 hours by purple LEDs (λ=390 nm). The addition of TEMPO greatly inhibited the reaction. This result indicates that TEMPO suppressed the reaction progress, demonstrating that the reaction proceeded via a radical process.

b) The effect of oxidation state of the iron catalyst on the reaction

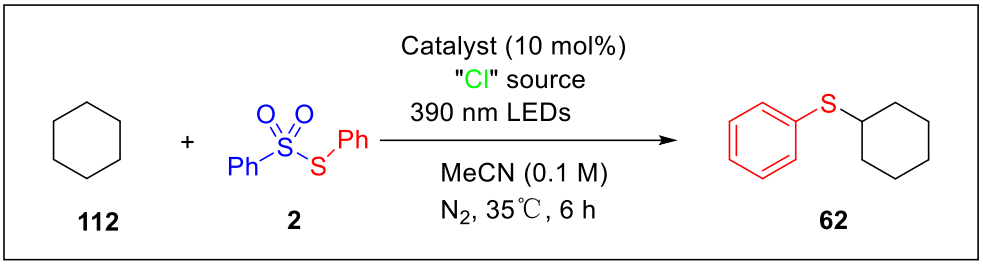


entry	Oxidant	yield (%)[a]
1	NFSI	65%
2	-	N.D

[a] Isolated yield.

Standard conditions. cyclohexane (168 mg, 10.0 equiv), **2** (0.2 mmol, 1.0 equiv.), and $FeCl_3$ (10 mol%) were added into MeCN (2 mL). The mixture was strictly deaerated and irradiated for 5 hours by purple LEDs (λ=390 nm). The product was separated by column chromatography. When ferrous chloride was used as catalyst to participate in the reaction, the target product was not detected, but the corresponding target product was detected when adding NFSI (126 mg, 1.0 equiv). The above results suggested that the coordination of high valent iron species with chloride is the key to generating free chlorine radicals, which would undergo the following HAT process.

c) The effect of chlorine source on the reaction



Standard conditions. cyclohexane (168 mg, 10.0 equiv), **2** (0.2 mmol, 1.0 equiv.) and $FeCl_3$ (10 mol%) were added into MeCN (2 mL). The mixture was strictly deaerated and irradiated for 6 hours by purple LEDs (λ=390 nm). The product was separated by column chromatography.

Table S5. Different iron catalysts and chlorine sources

Entry	Fe Catalyst	"Cl" source	Yield[a]
1	$Fe(NO_3)_3$ $9H_2O$	LiCl	41%
2	$Fe(OTf)_3$	LiCl	68
3	$Fe(acac)_3$	LiCl	73
4	$Fe(NO_3)_3$ $9H_2O$	/	N.D

[a] Isolated yield.

This indicates that under visible light irradiation, the synergistic effect of ferrous ions and chloride ions led to an electron transfer process from metal to chloride ligands (a ligand-to-metal charge transfer), which resulted in the cleavage of the Fe-Cl bond to generate chlorine radicals. The chlorine radicals then proceeded to abstract hydrogen atoms from the substrate via hydrogen atom transfer.

Proposed mechanism

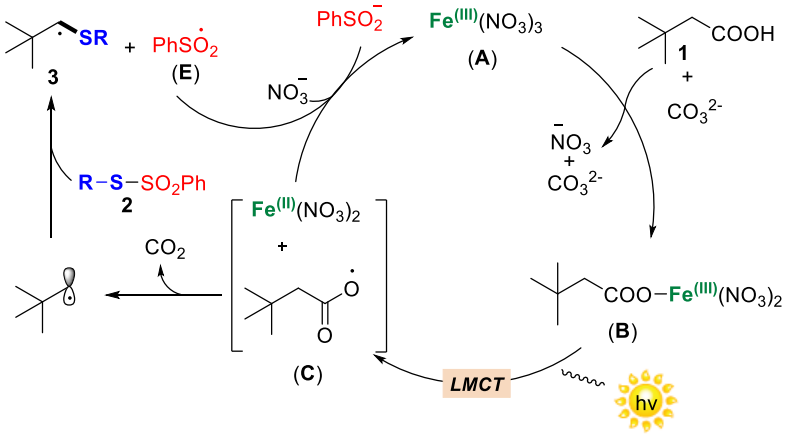


Figure S9. Possible mechanism of decarboxylative thiolation

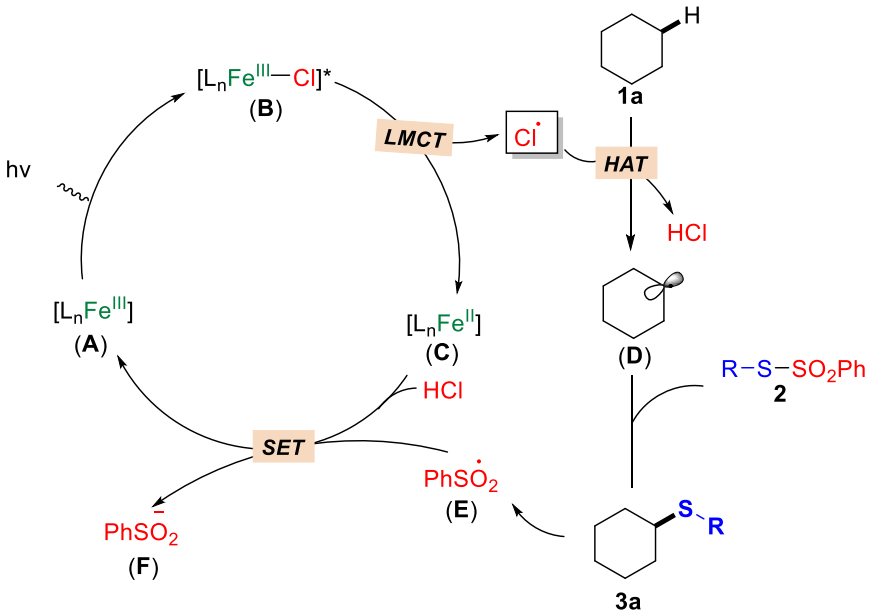


Figure S10. Possible mechanism of C(sp^3)-H thiolation

6.6 UV-vis absorbtion study

UV-visible absorption spectra were collected on a SPECORD 200 PLUS. $Fe(NO_3)_3 \cdot 9H_2O$, Quinolinecarboxylic acid were prepared 1.0×10^{-5} mol/L in CH_3CN (Figure S11). In the spectrum of $Fe(NO_3)_3 \cdot 9H_2O$ with Quinolinecarboxylic acid, a

broad absorption peak was observed around 350 nm, indicative of photochemical activity under purple LED light irradiation.

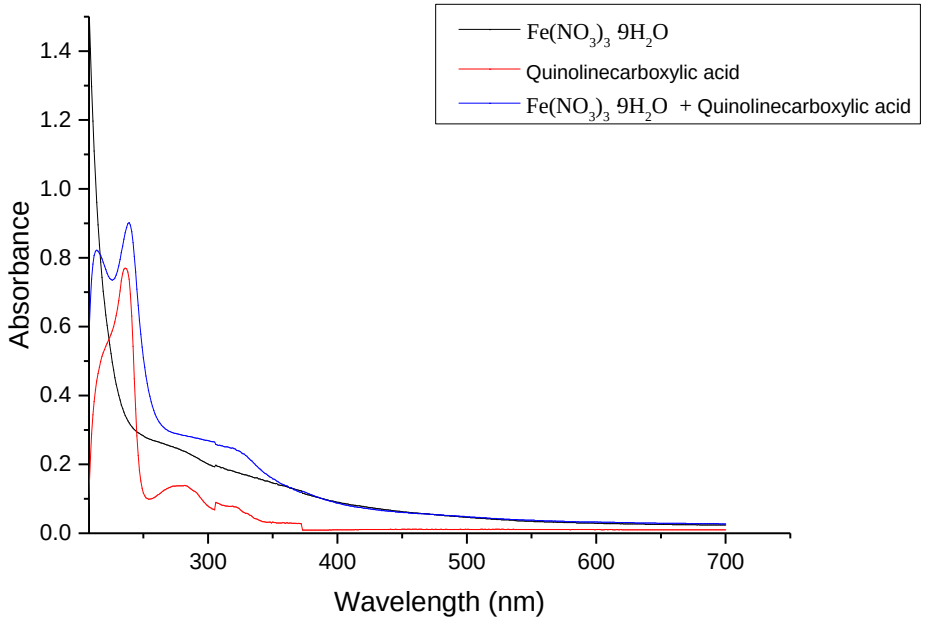
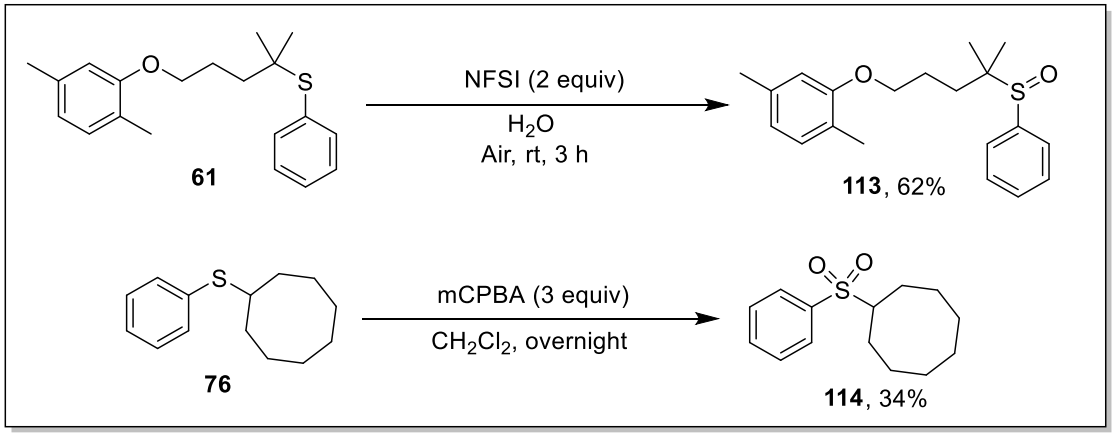


Figure S11. UV-vis absorbtion study

6.7 Derivatization study



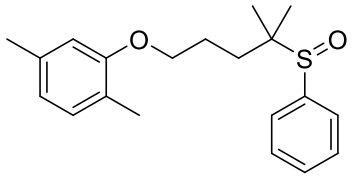
6.7.1 Preparation of Sulfoxide

To a 25 mL round bottom flask equipped with a magnetic stir bar, sulfide (0.1 mmol,

1.0 equiv.), NFSI (0.2 mmol, 2.0 equiv.), and water (1 mL) were added. The resulting mixture was stirred in air and react for 6 hours. After the reaction was finished (monitored by TLC), the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel.

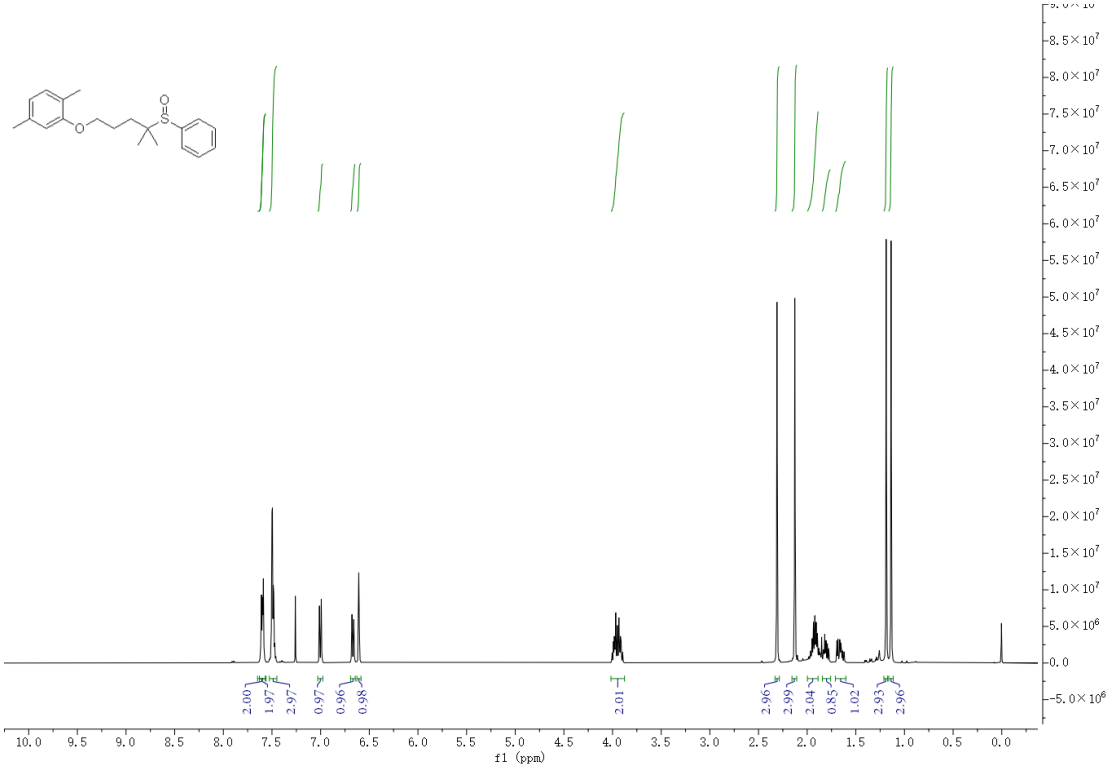
6.7.2 Sulfone preparation

To a 25 mL round bottom flask equipped with a magnetic stir bar, sulfide (0.1 mmol, 1.0 equiv.), mCPBA (0.3 mmol, 3.0 equiv.), and CH_2Cl_2 were added. The resulting mixture was stirred in air and react for overnight. After the reaction was finished (monitored by TLC), the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel.

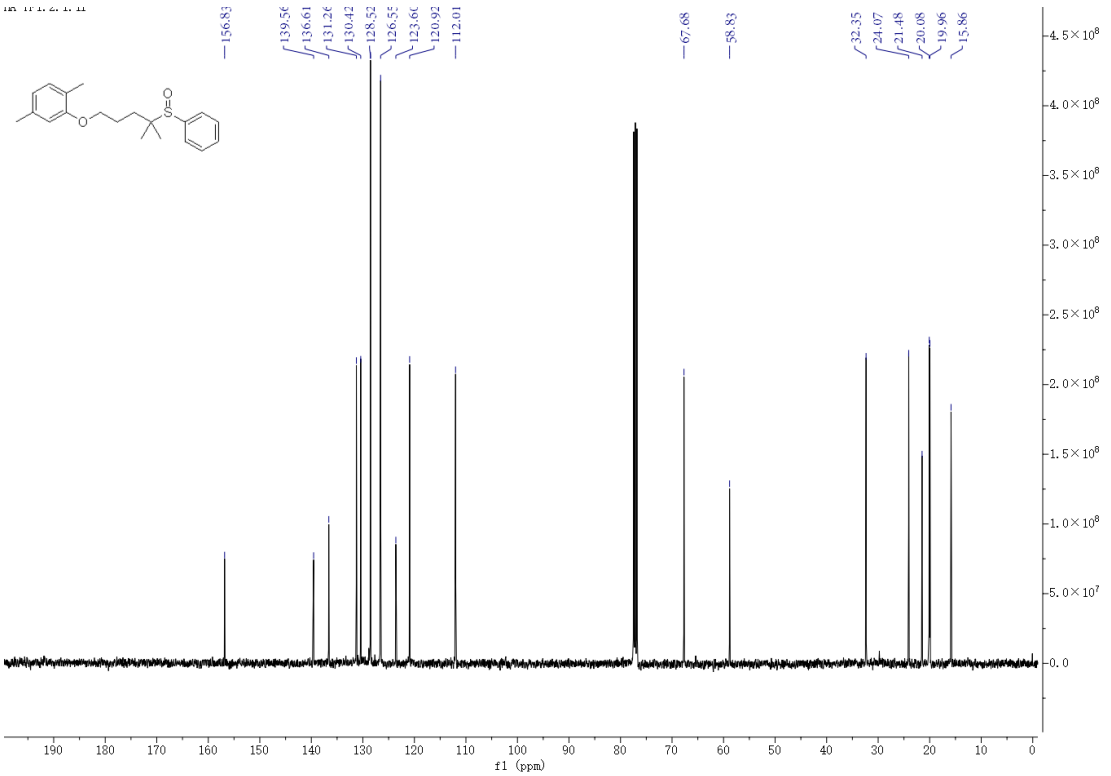


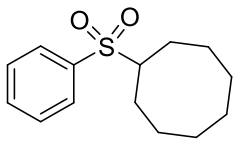
1,4-dimethyl-2-((4-methyl-4-(phenylsulfinyl)pentyl)oxy)benzene (113): **1H NMR (400 MHz, Chloroform-d)** δ 7.65 – 7.56 (m, 2H), 7.53 – 7.45 (m, 3H), 7.00 (d, J = 7.5 Hz, 1H), 6.67 (d, J = 7.4 Hz, 1H), 6.61 (s, 1H), 4.03 – 3.87 (m, 2H), 2.31 (s, 3H), 2.13 (s, 3H), 2.00 – 1.87 (m, 2H), 1.86 – 1.76 (m, 1H), 1.72 – 1.60 (m, 1H), 1.19 (s, 3H), 1.14 (s, 3H); **13C NMR (101 MHz, CDCl3)** δ 156.8, 139. 6, 136.6, 131.3, 130.4, 128.5, 126.6, 123.6, 120.9, 112.0, 67.7, 58.8, 32.4, 24.1, 21.5, 20.1, 20.0, 15.9.

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **113**



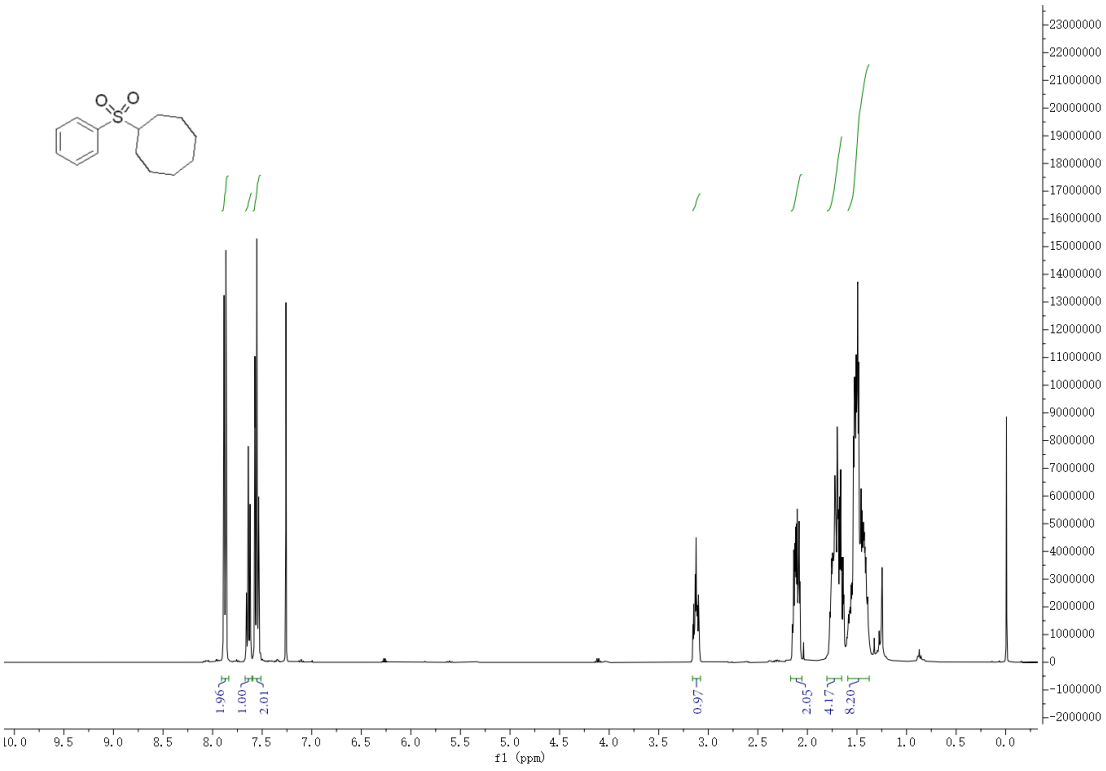
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **113**



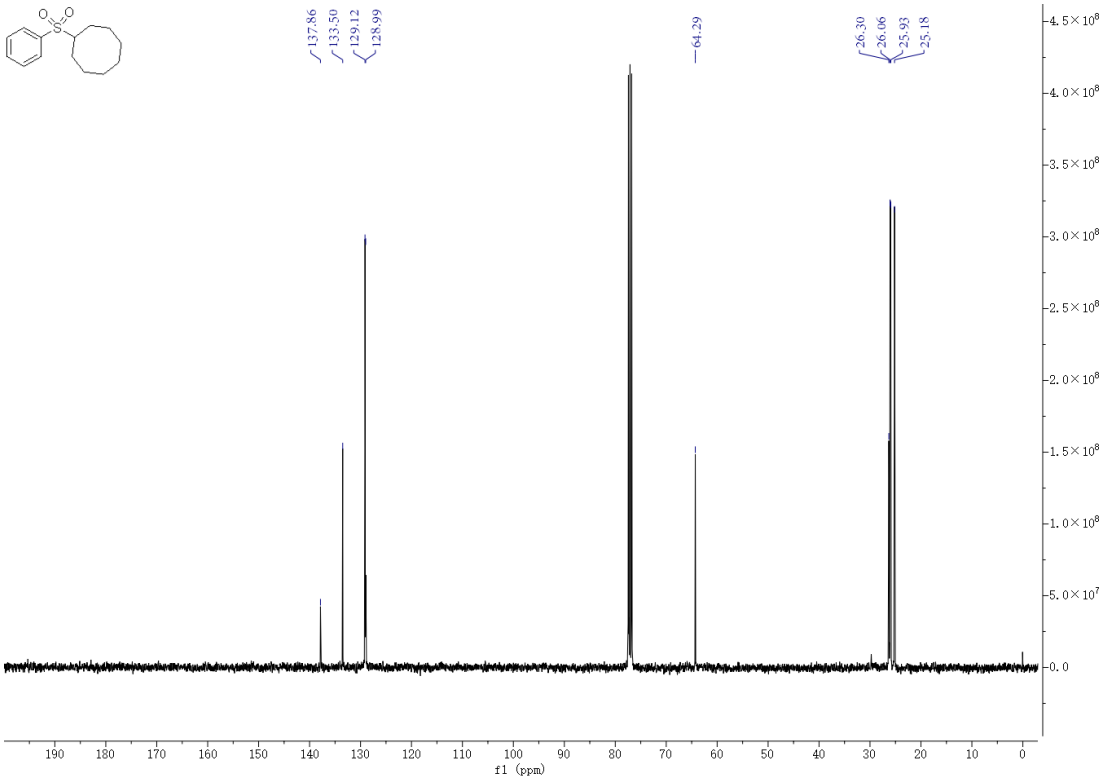


(phenylsulfonyl)cyclooctane (114): ^{1}H NMR (400 MHz, CDCl3) δ 7.91 – 7.84 (m, 2H), 7.69 – 7.60 (m, 1H), 7.60 – 7.51 (m, 2H), 3.16 – 3.07 (m, 1H), 2.17 – 2.05 (m, 2H), 1.81 – 1.61 (m, 4H), 1.60 – 1.37 (m, 8H); **^{13}C NMR (101 MHz, CDCl3)** δ 137.9, 133.5, 129.1, 129.0, 64.3, 26.3, 26.1, 25.9, 25.2.

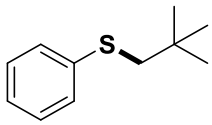
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **114**



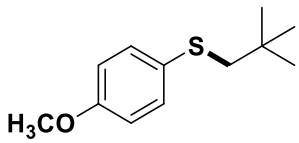
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **114**



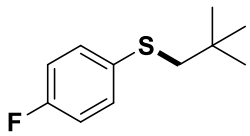
7. Characterization of the products



neopentyl(phenyl)sulfane (3): Followed the general procedure 1 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and 3,3-dimethylbutanoic acid (46.4 mg, 0.4 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 32.7 mg of the title compound (Colorless oil); 91% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.41 – 7.31 (m, 2H), 7.31 – 7.25 (m, 2H), 7.20 – 7.12 (m, 1H), 2.92 (s, 2H), 1.06 (s, 9H): **^{13}C NMR (101 MHz, $CDCl_3$)** δ 138.4, 128.8, 128.7, 125.4, 48.5, 32.4, 29.0. **HRMS (ESI)** calcd $C_{11}H_{16}S$ $[M + H]^+$: 181.1045, found: 181.1044.

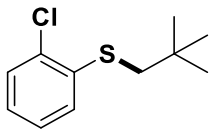


(4-methoxyphenyl)(neopentyl)sulfane (**4**): Followed the general procedure 1 with *S*-(4-methoxyphenyl) benzenesulfonothioate (56.0 mg, 0.2 mmol) and 3,3-dimethylbutanoic acid (46.4 mg, 0.4 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 22.2 mg of the title compound (Colorless oil); 91% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 – 7.33 (m, 2H), 6.92 – 6.77 (m, 2H), 3.83 (d, *J* = 4.4 Hz, 3H), 2.86 (s, 2H), 1.05 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.4, 132.5, 128.8, 114.5, 55.3, 51.1, 32.6, 29.0; **HRMS (ESI)** calcd $C_{11}H_{13}O_2$ $[M + H]^+$: 210.1078, found: 210.1079.

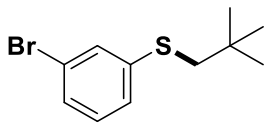


(4-fluorophenyl)(neopentyl)sulfane (5): Followed the general procedure 1 with *S*-(4-fluorophenyl) benzenesulfonothioate (54.0 mg, 0.2 mmol) and 3,3-dimethylbutanoic acid (46.4 mg, 0.4 mmol) and purified using flash chromatography (petroleum ether as

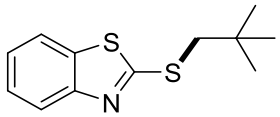
eluent) to give 22.1 mg of the title compound (Colorless oil); 56% yield; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.43 – 7.33 (m, 2H), 7.06 – 6.91 (m, 2H), 2.91 (s, 2H), 1.06 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 161.4 (d, *J* = 245.3 Hz), 133.3, 131.71 (d, *J* = 7.8 Hz), 115.8 (d, *J* = 21.8 Hz), 50.1, 32.6, 29.0; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -116.56 (s, 1F); **HRMS (ESI)** calcd $C_{11}H_{15}FS$ $[M + H]^+$: 199.0951, found: 199.0955.



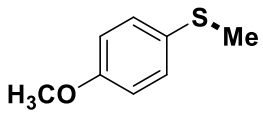
(2-chlorophenyl)(neopentyl)sulfane (6): Followed the general procedure 1 with *S*-(2-chlorophenyl) benzenesulfonothioate (56.6 mg, 0.2 mmol) and 3,3-dimethylbutanoic acid (46.4 mg, 0.4 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 27.4 mg of the title compound (Colorless oil); 64% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.38 (d, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.23 (t, *J* = 7.3 Hz, 1H), 7.14 – 7.08 (m, 1H), 2.90 (s, 2H), 1.12 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 137.4, 133.4, 129.5, 128.2, 127.0, 126.0, 47.2, 32.2, 29.2; **HRMS (ESI)** calcd $C_{11}H_{15}{}^{35}ClS$ $[M + H]^+$: 215.0656, found: 215.0654.



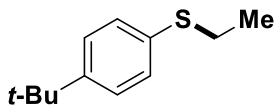
(3-bromophenyl)(neopentyl)sulfane (7): Followed the general procedure 1 with *S*-(2-chlorophenyl) benzenesulfonothioate (65.4 mg, 0.2 mmol) and 3,3-dimethylbutanoic acid (46.4 mg, 0.4 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 34.8 mg of the title compound (Colorless oil); 53% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.50 – 7.48 (m, 1H), 7.31 – 7.28 (m, 2H), 7.17 – 7.12 (m, 1H), 2.91 (s, 2H), 1.08 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.0, 130.8, 130.0, 128.3, 127.0, 122.7, 48.1, 32.5, 29.1; **HRMS (ESI)** calcd $C_{11}H_{15}{}^{79}BrS$ $[M + H]^+$: 259.0151, found: 259.0148.



2-(neopentylthio)benzo[d]thiazole (8): Followed the general procedure 1 with *S*-(benzo[d]thiazol-2-yl) benzenesulfonothioate (61.2 mg, 0.2 mmol) and 3,3-dimethylbutanoic acid (46.4 mg, 0.4 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 21.8 mg of the title compound (Colorless oil); 46% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.90 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.44 (t, *J* = 11.3, 4.0 Hz, 1H), 7.35 – 7.30 (m, 1H), 3.43 (s, 2H), 1.13 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.3, 153.0, 135.1, 126.0, 124.1, 121.3, 120.9, 47.3, 32.4, 28.8; **HRMS (ESI)** calcd $C_{12}H_{15}NS_2$ $[M + H]^+$: 239.0719, found: 239.0722.

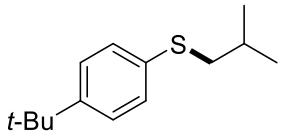


(4-methoxyphenyl)(methyl)sulfane (9): Followed the general procedure 1 with *S*-(4-methoxyphenyl) benzenesulfonothioate (56.0 mg, 0.2 mmol) and acetic acid (24 mg, 0.4 mmol) and purified using flash chromatography (petroleum ether : EA= 30: 1) to give 21.8 mg of the title compound (Colorless oil); 84% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.31 (d, *J* = 8.8 Hz, 2H), 6.93 – 6.85 (m, 2H), 3.83 (s, 3H), 2.48 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.2, 130.2, 128.78, 114.6, 55.4, 18.1; **HRMS (ESI)** calcd $C_8H_{10}OS$ $[M + H]^+$: 155.0525, found: 155.0524.

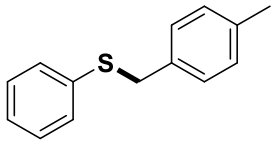


(4-(tert-butyl)phenyl)(ethyl)sulfane (10): Followed the general procedure 1 with *S*-(4-(tert-butyl)phenyl) benzenesulfonothioate (61.2 mg, 0.2 mmol) and propionic acid (29.6 mg, 0.4 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 36.5 mg of the title compound (Colorless oil); 94% yield **; ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.38 – 7.31 (m, 4H), 2.97 (q, *J* = 7.3, 1.4 Hz, 2H), 1.35 (M, 3H), 1.34 (S, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.1, 132.9, 129.3, 125.9, 34.4, 31.3, 28.1,

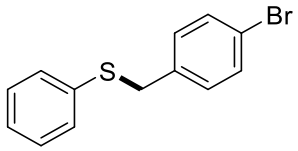
14.5; **HRMS (ESI)** calcd $C_{12}H_{18}S$ $[M + H]^+$: 195.1202, found: 195.1199.



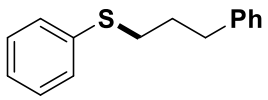
(4-(tert-butyl)phenyl)(isobutyl)sulfane (11): Followed the general procedure 1 with *S*-(4-(tert-butyl)phenyl) benzenesulfonothioate (61.2 mg, 0.2 mmol) and 3-methylbutanoic acid (40.8 mg, 0.4 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 21.3 mg of the title compound (Colorless oil); 48% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.37 – 7.29 (m, 4H), 2.83 (d, *J* = 6.9 Hz, 2H), 1.97 – 1.85 (m, 1H), 1.36 (s, 10H), 1.07 (d, *J* = 6.6 Hz, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 148.9, 133.7, 129.0, 125.9, 43.0, 34.4, 31.3, 28.3, 22.1; **HRMS (ESI)** calcd $C_{14}H_{22}S$ $[M + H]^+$: 223.1515, found: 223.1515.



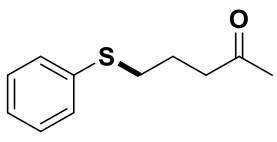
(4-methylbenzyl)(phenyl)sulfane (12): Followed the general procedure 1 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and 2-(p-tolyl)acetic acid (30.0 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 36.5 mg of the title compound (Colorless oil); 79% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.35 (d, *J* = 7.9 Hz, 2H), 7.30 (t, *J* = 6.4 Hz, 2H), 7.25 – 7.18 (m, 3H), 7.14 (d, *J* = 7.7 Hz, 2H), 4.14 (s, 2H), 2.36 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 136.8, 136.6, 134.3, 129.6, 129.2, 128.8, 128.7, 126.2, 38.7, 21.1; **HRMS (ESI)** calcd $C_{14}H_{14}S$ $[M + H]^+$: 215.0889, found: 215.0889.



(4-bromobenzyl)(phenyl)sulfane (13): Followed the general procedure 1 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and 2-(4-bromophenyl)acetic acid (30.0 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 29.5 mg of the title compound (Colorless oil); 53% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42 – 7.37 (m, 2H), 7.31 – 7.26 (m, 3H), 7.26 – 7.18 (m, 2H), 7.14 (d, *J* = 8.3 Hz, 2H), 4.04 (s, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 136.7, 135.6, 131.6, 130.5, 130.3, 128.9, 126.7, 121.0, 38.6; **HRMS (ESI)** calcd $C_{13}H_{11}{}^{79}BrS$ $[M + H]^+$: 278.9838, found: 278.9837.

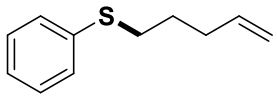


phenyl(3-phenylpropyl)sulfane (14): Followed the general procedure 1 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and 4-phenylbutanoic acid (32.8mg, 0.2 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 21.8 mg of the title compound (Colorless oil); 48% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.34 – 7.27 (m, 6H), 7.24 – 7.16 (m, 4H), 2.93 (t, *J* = 7.3 Hz, 2H), 2.77 (t, *J* = 7.5 Hz, 2H), 2.03 – 1.93 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.3, 136.5, 129.1, 128.9, 128.5, 128.4, 126.0, 125.8, 34.7, 32.9, 30.6; **HRMS (ESI)** calcd $C_{15}H_{16}S$ $[M + H]^+$: 229.1045, found: 229.1049.

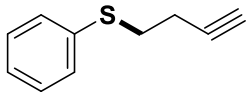


5-(phenylthio)pentan-2-one (15): Followed the general procedure 1 with *S*-phenyl

benzenesulfonothioate (50.0 mg, 0.2 mmol) and 5-oxohexanoic acid (26.0 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether : EA= 20: 1) to give 26.0 mg of the title compound (Colorless oil); 67% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.37 (d, *J* = 7.4 Hz, 2H), 7.32 (d, *J* = 7.4 Hz, 2H), 7.24 – 7.17 (m, 1H), 2.97 (t, *J* = 7.0 Hz, 2H), 2.64 (t, *J* = 7.1 Hz, 2H), 2.16 (s, 3H), 1.94 (p, *J* = 7.0 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 208.1, 129.2, 128.9, 126.0, 41.9, 32.9, 30.0, 22.9; **HRMS (ESI)** calcd $C_{11}H_{14}OS$ $[M + H]^+$: 195.0838, found: 195.0842.

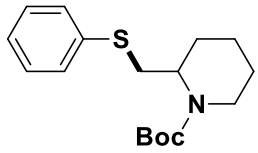


pent-4-en-1-yl(phenyl)sulfane (16): Followed the general procedure 1 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and hex-5-enoic acid (22.8 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 18.1 mg of the title compound (Colorless oil); 51% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.37 (d, *J* = 7.5 Hz, 2H), 7.34 – 7.30 (m, 2H), 7.24 – 7.18 (m, 1H), 5.89 – 5.75 (m, 1H), 5.12 – 4.99 (m, 2H), 2.96 (t, *J* = 7.4 Hz, 2H), 2.23 (q, *J* = 7.0 Hz, 2H), 1.78 (p, *J* = 7.3 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 137.6, 136.7, 129.0, 128.9, 125.8, 115.4, 32.9, 32.7, 28.3; **HRMS (ESI)** calcd $C_{11}H_{14}S$ $[M + H]^+$: 178.0889, found: 178.0889.

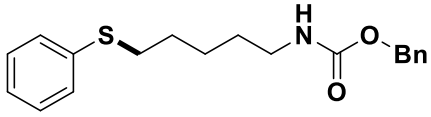


but-3-yn-1-yl(phenyl)sulfane (17): Followed the general procedure 1 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and pent-4-ynoic acid (19.6 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 17.1 mg of the title compound (Colorless oil); 53% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44 – 7.38 (m, 2H), 7.36 – 7.31 (m, 2H), 7.30 – 7.26 (m, 1H), 3.17 – 3.06 (m, 2H), 2.57 – 2.47 (m, 2H), 2.11 – 2.03 (m, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 135.1, 130.1, 129.8,

126.6, 82.3, 69.7, 32.8, 19.3; **HRMS (ESI)** calcd $C_{10}H_{10}S$ $[M + H]^+$: 163.0576, found: 163.0579.

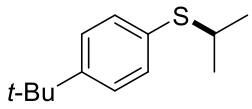


tert-butyl 2-((phenylthio)methyl)piperidine-1-carboxylate (18): Followed the general procedure 1 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and 2-(1-(tert-butoxycarbonyl)piperidin-2-yl)acetic acid (48.6 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether : EA= 10: 1) to give 30.1 mg of the title compound (Colorless oil); 49% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.40 (d, *J* = 7.8 Hz, 2H), 7.34 – 7.30 (m, 2H), 7.23 – 7.17 (m, 1H), 4.42 (s, 1H), 4.05 (d, *J* = 12.0 Hz, 1H), 3.24 – 3.02 (m, 2H), 2.78 (t, *J* = 12.5 Hz, 1H), 1.98 (d, *J* = 13.3 Hz, 1H), 1.75 – 1.55 (m, 4H), 1.43 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 154.9, 136.3, 129.1, 128.9, 126.0, 79.6, 49.5, 33.3, 28.4, 26.4, 25.2, 18.7; **HRMS (ESI)** calcd $C_{17}H_{25}NO_2S$ $[M + H]^+$: 308.1679, found: 308.1675.

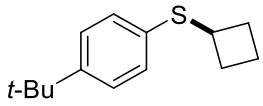


benzyl (5-(phenylthio)pentyl)carbamate (19): Followed the general procedure 1 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and 6-(((benzyloxy)carbonyl)amino)hexanoic acid (53.1 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether : EA= 10: 1) to give 38.1 mg of the title compound (Yellow oil); 49% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.40 – 7.38 (m, 4H), 7.38 – 7.30 (m, 5H), 7.24 – 7.18 (m, 1H), 5.13 (s, 2H), 4.78 (s, 1H), 3.26 – 3.16 (m, 2H), 2.94 (t, *J* = 7.2 Hz, 2H), 1.74 – 1.60 (m, 5H), 1.59 – 1.45 (m, 5H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.4, 136.6, 129.0, 128.9, 128.5, 128.1, 125.8, 124.0, 66.6, 40.9, 33.5, 29.6, 28.7, 25.9;

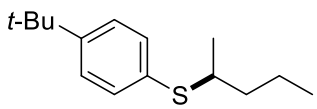
HRMS (ESI) calcd $C_{19}H_{23}NO_2S$ [M + H]$^+$: 330.1522, found: 330.1518.



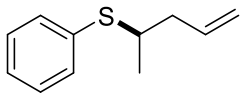
(4-(tert-butyl)phenyl)(isopropyl)sulfane (20): Followed the general procedure 1 with *S*-(4-(tert-butyl)phenyl) benzenesulfonothioate (61.2 mg, 0.2 mmol) and isobutyric acid (35.2 mg, 0.4 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 18.7 mg of the title compound (Colorless oil); 45% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.41 – 7.32 (m, 4H), 3.41 – 3.31 (m, 1H), 1.35 (s, 9H), 1.32 (d, *J* = 6.7 Hz, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 150.08, 132.18, 131.76, 125.84, 38.52, 34.54, 31.32, 23.25; **HRMS (ESI)** calcd $C_{13}H_{20}S$ [M + H]$^+$: 209.1358, found: 209.1355.



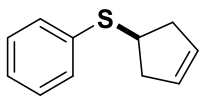
(4-(tert-butyl)phenyl)(cyclobutyl)sulfane (21): Followed the general procedure 1 with *S*-(4-(tert-butyl)phenyl) benzenesulfonothioate (61.2 mg, 0.2 mmol) and cyclobutanecarboxylic acid (40.0 mg, 0.4 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 33.8 mg of the title compound (Colorless oil); 77% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.34 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 3.89 (p, *J* = 7.8 Hz, 1H), 2.52 – 2.43 (m, 2H), 2.16 – 1.95 (m, 4H), 1.34 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.0, 133.2, 129.2, 125.8, 40.5, 34.4, 31.3, 30.7, 18.7; **HRMS (ESI)** calcd $C_{14}H_{20}S$ [M + H]$^+$: 211.1358, found: 211.1357.



(*S*)-pentan-2-yl(phenyl)sulfane (22): Followed the general procedure 1 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and 3-methylbutanoic acid (40.8 mg, 0.4 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 17.2 mg of the title compound (Colorless oil); 48% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.39 – 7.33 (m, 4H), 3.29 – 3.07 (m, 1H), 1.72 – 1.55 (m, 2H), 1.54 – 1.49 (m, 2H), 1.34 (s, 9H), 1.32 – 1.29 (m, 3H), 0.96 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.9, 132.1, 131.7, 125.8, 43.2, 38.8, 34.5, 31.3, 21.2, 20.3, 13.9; **HRMS (ESI)** calcd $C_{15}H_{24}S$ $[M + H]^+$: 237.1671, found: 237.1667.

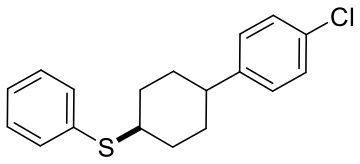


pent-4-en-2-yl(phenyl)sulfane (23): Followed the general procedure 1 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and 2-methylpent-4-enoic acid (22.8 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 20.5 mg of the title compound (Colorless oil); 53% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.55 – 7.48 (m, 2H), 7.43 – 7.37 (m, 2H), 7.37 – 7.33 (m, 1H), 6.01 – 5.88 (m, 1H), 5.21 – 5.13 (m, 2H), 3.38 (dd, *J* = 12.2, 5.4 Hz, 1H), 2.56 – 2.46 (m, 1H), 2.39 – 2.28 (m, 1H), 1.38 (d, *J* = 4.2 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 135.4, 135.1, 132.1, 128.9, 126.9, 117.3, 42.7, 40.9, 20.5; **HRMS (ESI)** calcd $C_{11}H$ S $[M + H]^+$: 179.0889, found: 179.0839.

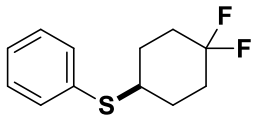


cyclopent-3-en-1-yl(phenyl)sulfane (24): Followed the general procedure 1 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and cyclopent-3-ene-1-carboxylic acid (22.4 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 20.5 mg of the title compound (Colorless oil); 56% yield; **^{1}H NMR (400**

MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.36 – 7.30 (m, 2H), 7.26 – 7.19 (m, 1H), 5.83 – 5.71 (m, 2H), 4.09 – 3.91 (m, 1H), 3.02 – 2.82 (m, 2H), 2.58 – 2.38 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 136.8, 129.6, 129.2, 128.8, 125.9, 42.8, 40.4; **HRMS (ESI)** calcd $C_{11}H_{12}S$ $[M + H]^+$: 177.0732, found: 177.0734.

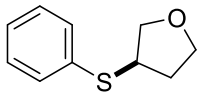


(4-(4-chlorophenyl)cyclohexyl)(phenyl)sulfane (25): Followed the general procedure 1 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and 4-(4-chlorophenyl)cyclohexane-1-carboxylic acid (47.6 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 19.3 mg of the title compound (Colorless oil); 32% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47 (d, *J* = 7.9 Hz, 2H), 7.37 – 7.32 (m, 2H), 7.30 – 7.26 (m, 3H), 7.15 (d, *J* = 8.4 Hz, 2H), 3.19 – 3.08 (m, 1H), 2.60 – 2.49 (m, 1H), 2.27 – 2.15 (m, 2H), 1.98 – 1.92 (m, 2H), 1.56 – 1.49 (m, 4H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 145.1, 134.6, 132.3, 131.7, 128.8, 128.5, 128.1, 126.9, 46.0, 43.0, 34.2, 33.6; **HRMS (ESI)** calcd $C_{18}H_{19}{}^{35}ClS$ $[M + H]^+$: 303.0969, found: 303.0966.

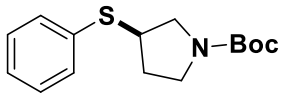


(4,4-difluorocyclohexyl)(phenyl)sulfane (26): Followed the general procedure 1 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and 4,4-difluorocyclo-hexane-1-carboxylic acid (32.8 mg, 0.2 mmol) and purified using flash chromato-graphy (petroleum ether as eluent) to give 22.8 mg of the title compound (Colorless oil); 50% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.49 – 7.44 (m, 2H), 7.39 – 7.33 (m, 2H), 7.33 – 7.30 (m, 1H), 3.33 – 3.24 (m, 1H), 2.29 – 2.14 (m, 2H), 2.11 – 2.02 (m, 2H), 1.95 – 1.72 (m, 5H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 134.1, 132.5, 129.0, 122.8 (t, *J* = 241.3

Hz), 32.2 (t, *J* = 24.4 Hz), 28.6 (t, *J* = 4.8 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -95.8 (d, *J* = 233.2 Hz), -97.9 (d, *J* = 216.3 Hz); **HRMS (ESI)** calcd $C_{12}H_{14}F_2S$ $[M + H]^+$: 229.0857, found: 229.0860.

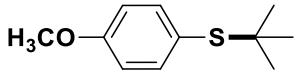


(3-(phenylthio)tetrahydrofuran (27): Followed the general procedure 1 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and tetrahydrofuran-3-carboxylic acid (46.4 mg, 0.4 mmol) and purified using flash chromatography (petroleum ether : EA= 20: 1) to give 24.1 mg of the title compound (Colorless oil); 67% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.45 – 7.38 (m, 2H), 7.38 – 7.32 (m, 2H), 7.29 – 7.24 (m, 1H), 4.18 – 4.10 (m, 1H), 4.03 – 3.95 (m, 1H), 3.94 – 3.81 (m, 2H), 3.77 – 3.70 (m, 1H), 2.43 – 2.32 (m, 1H), 2.02 – 1.91 (m, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 135.6, 130.6, 129.0, 126.7, 73.6, 67.6, 44.8, 33.1; **HRMS (ESI)** calcd $C_{10}H_{12}OS$ $[M + H]^+$: 181.0682, found: 181.0679.

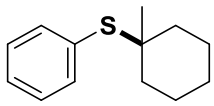


tert-butyl-3-(phenylthio)pyrrolidine-1-carboxylate (28): Followed the general procedure 1 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and 1-(tert-butoxycarbonyl)pyrrolidine-3-carboxylic acid (43 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether : EA= 20: 1) to give 22.8 mg of the title compound (Colorless oil); 67% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47 – 7.42 (m, 2H), 7.38 – 7.30 (m, 3H), 3.82 – 3.68 (m, 2H), 3.65 – 3.34 (m, 3H), 2.31 – 2.20 (m, 1H), 1.99 – 1.89 (m, 1H), 1.71 (s, 1H), 1.49 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 154.4, 131.7, 131.6, 129.1, 127.24, 79.5, 51.9, 51.7, 45.2, 44.9, 44.6, 32.0, 31.5, 28.5;

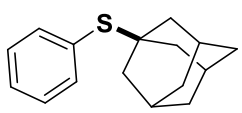
HRMS (ESI) calcd $C_{15}H_{21}NO_2S$ $[M + H]^+$: 280.1366, found: 280.1362.



tert-butyl(4-methoxyphenyl)sulfane (29): Followed the general procedure 1 with *S*-phenyl *S*-(4-methoxyphenyl) benzenesulfonothioate (56.0 mg, 0.2 mmol) and pivalic acid (20.4 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 22.0 mg of the title compound (Colorless oil); 56% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.51 – 7.44 (m, 2H), 6.92 – 6.84 (m, 2H), 3.85 (s, 3H), 1.28 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.2, 138.9, 123.6, 113.9, 55.3, 45.5, 30.7; **HRMS (ESI)** calcd $C_{11}H_{16}OS$ $[M + H]^+$: 197.0995, found: 197.0990.

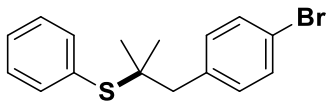


(1-methylcyclohexyl)(phenyl)sulfane (30): Followed the general procedure 1 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and 1-methylcyclohexane-1-carboxylic acid (28.4 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 21.4 mg of the title compound (Colorless oil); 52% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.55 (d, *J* = 6.5 Hz, 2H), 7.41 – 7.31 (m, 3H), 1.85 – 1.75 (m, 2H), 1.71 – 1.65 (m, 2H), 1.56 – 1.45 (m, 5H), 1.25 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 137.7, 132.0, 128.5, 128.4, 50.2, 38.3, 28.7, 25.9, 22.6; **HRMS (ESI)** calcd $C_{13}H_{18}S$ $[M + H]^+$: 207.1202, found: 207.1202.

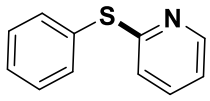


(3r, 5r, 7r)-adamantan-1-yl)(phenyl)sulfane (31): Followed the general procedure 1

with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and (3r,5r,7r)-adamantane-1-carboxylic acid (28.4 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 23.0 mg of the title compound (Colorless oil); 47% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.54 (d, *J* = 6.8 Hz, 2H), 7.43 – 7.31 (m, 3H), 2.04 (s, 3H), 1.85 (s, 6H), 1.65 (q, *J* = 12.1 Hz, 7H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 137.7, 130.5, 128.6, 128.3, 47.8, 43.6, 36.2, 30.0; **HRMS (ESI)** calcd $C_{16}H_{20}S$ $[M + H]^+$: 245.1358, found: 245.1358.

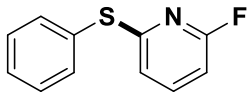


(1-(4-bromophenyl)-2-methylpropan-2-yl)(phenyl)sulfane (32): Followed the general procedure 1 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and 3-(4-bromophenyl)-2,2-dimethylpropanoic acid (51.2 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 23.0 mg of the title compound (Yellow oil); 42% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.60 (d, *J* = 7.6 Hz, 2H), 7.46 – 7.36 (m, 5H), 7.09 (d, *J* = 8.1 Hz, 2H), 2.88 (s, 2H), 1.23 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 137.7, 136.7, 132.4, 131.8, 131.0, 128.9, 128.6, 120.5, 49.0, 48.3, 28.0; **HRMS (ESI)** calcd $C_{16}H_{17}{}^{79}BrS$ $[M + H]^+$: 321.0307, found: 321.0302.

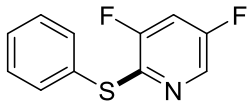


2-(phenylthio)pyridine (33): Followed the general procedure 1 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and picolinic acid (24.6 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether : EA= 20: 1) to give 30.4 mg of the title compound (Colorless oil); 81% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.46 (d, *J* = 4.7 Hz, 1H), 7.67 – 7.59 (m, 2H), 7.53 – 7.38 (m, 4H), 7.03 (M, 1H), 6.92 (d, *J* = 8.1 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 161.6, 149.6, 136.8, 135.0, 129.7, 129.1,

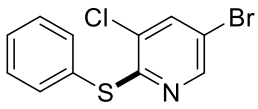
121.3, 119.9; **HRMS (ESI)** calcd $C_{11}H_9NS$ $[M + H]^+$: 188.0528 found: 188.0529.



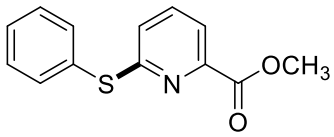
2-fluoro-6-(phenylthio)pyridine (34): Followed the general procedure 1 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and 6-fluoropicolinic acid (24.6 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether : EA= 20: 1) to give 25.5 mg of the title compound (Colorless oil); 62% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.68 – 7.61 (m, 2H), 7.59 – 7.52 (m, 1H), 7.51 – 7.45 (m, 3H), 6.72 (d, *J* = 7.7 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.0, 161.6, 160.78 (d, *J* = 14.1 Hz), 141.23 (d, *J* = 7.8 Hz), 135.4, 129.8, 129.6, 117.9 (d, *J* = 4.1 Hz), 105.0, 104.6; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -66.83 (s, 1F); **HRMS (ESI)** calcd $C_{11}H_8FNS$ $[M + H]^+$: 206.0434 found: 206.0433.



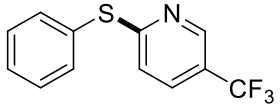
2,4-difluoro-6-(phenylthio)pyridine (35): Followed the general procedure 1 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and 4,6-difluoropicolinic acid (31.8 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether : EA= 20: 1) to give 24.2 mg of the title compound (Colorless oil); 54% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.21 (d, *J* = 2.3 Hz, 1H), 7.58 – 7.52 (m, 2H), 7.44 – 7.40 (m, 3H), 7.24 – 7.18 (m, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.1 (d, *J* = 4.2 Hz), 155.6 (d, *J* = 190.8 Hz), 155.5 (d, *J* = 192.3 Hz), 134.1, 133.72 (dd, *J* = 23.2, 3.7 Hz), 129.8, 129.2, 128.8, 111.4 (t, *J* = 22.0 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -113.56 (s, 1F), -127.38 (s, 1F); **HRMS (ESI)** calcd $C_{11}H_7F_2NS$ $[M + H]^+$: 224.0340 found: 224.0340.



5-bromo-3-chloro-2-(phenylthio)pyridine (36): Followed the general procedure 1 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and 5-bromo-3-chloropicolinic acid (46.8 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether : EA= 20: 1) to give 34.2 mg of the title compound (Colorless oil); 57% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.29 (s, 1H), 7.79 – 7.76 (m, 1H), 7.62 – 7.54 (m, 2H), 7.51 – 7.43 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.5, 148.3, 138.3, 135.5, 129.4, 129.1, 128.9, 128.8, 115.8; **HRMS (ESI)** calcd $C_{11}H_7{}^{79}Br^{35}ClNS$ $[M + H]^+$: 299.9244 found: 299.9242.

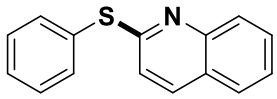


methyl 6-(phenylthio)picolinate (37): Followed the general procedure 1 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and 6-(methoxycarbonyl)picolinic acid (36.2 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether : EA= 20: 1) to give 37.4 mg of the title compound (Colorless oil); 76% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.85 (d, *J* = 7.6 Hz, 1H), 7.70 – 7.63 (m, 2H), 7.59 (t, *J* = 7.9 Hz, 1H), 7.51 – 7.46 (m, 3H), 6.98 (d, *J* = 8.1 Hz, 1H), 4.02 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.4, 163.3, 147.7, 137.5, 135.4, 129.9, 129.6, 124.1, 121.2, 53.0; **HRMS (ESI)** calcd $C_{13}H_{11}NO_2S$ $[M + H]^+$: 246.0583 found: 246.0585.

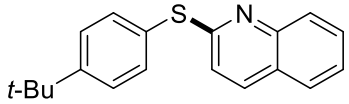


2-(phenylthio)-5-(trifluoromethyl)pyridine (38): Followed the general procedure 1 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and 5-(trifluoromethyl)pi-

colinic acid (38.2 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether : EA= 20: 1) to give 29.4 mg of the title compound (Colorless oil); 58% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.71 – 8.65 (m, 1H), 7.69 – 7.62 (m, 3H), 7.54 – 7.48 (m, 3H), 6.95 (d, *J* = 8.5 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.9, 146.38 (q, *J* = 7.7, 3.7 Hz), 135.6, 133.5 (q, *J* = 3.2 Hz), 130.0, 129.2, 123.6 (q, *J* = 271.8 Hz), 122.7, 122.4, 120.0. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.18 (s, 3F); **HRMS (ESI)** calcd $C_{12}H_8F_3NS$ $[M + H]^+$: 254.0402 found: 254.0403.

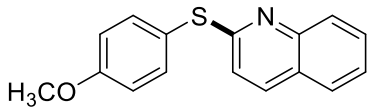


2-(phenylthio)quinoline (39): Followed the general procedure 1 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and quinoline-2-carboxylic acid (34.6 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether : EA= 20: 1) to give 47.7 mg of the title compound (Colorless oil); 94% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.99 (d, *J* = 8.5 Hz, 1H), 7.92 (d, *J* = 8.7 Hz, 1H), 7.76 – 7.67 (m, 4H), 7.52 – 7.45 (m, 4H), 7.02 (d, *J* = 8.7 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 161.7, 148.0, 136.5, 135.2, 130.9, 130.1, 129.7, 129.3, 128.3, 127.6, 125.8, 119.5; **HRMS (ESI)** calcd $C_{15}H_{11}NS$ $[M + H]^+$: 254.0998 found: 254.0998.

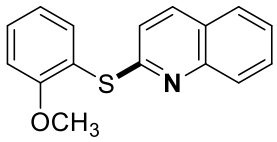


2-((4-(tert-butyl)phenyl)thio)quinoline (40): Followed the general procedure 1 with *S*-(4-(tert-butyl)phenyl) benzenesulfonothioate (61.2 mg, 0.2 mmol) and quinoline-2-carboxylic acid (34.6 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether : EA= 20: 1) to give 41.1 mg of the title compound (Colorless oil); 63% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.00 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.7 Hz, 1H), 7.76 – 7.66 (m, 2H), 7.65 – 7.60 (m, 2H), 7.53 – 7.44 (m, 3H), 7.01 (d, *J* = 8.7 Hz,

1H), 1.40 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.3, 152.7, 148.0, 136.5, 135.0, 130.0, 128.2, 127.6, 127.1, 126.8, 125.7, 119.3, 34.87, 31.3; **HRMS (ESI)** calcd$C_{19}H_{19}NS$ $[M + H]^+$: 294.1311 found: 294.1309.

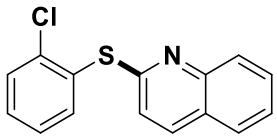


2-((4-methoxyphenyl)thio)quinoline (41): Followed the general procedure 1 with *S*-phenyl *S*-(4-methoxyphenyl) benzenesulfonothioate (56.0 mg, 0.2 mmol) and quinoline-2-carboxylic acid (34.6 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether : EA= 20: 1) to give 35.9 mg of the title compound (Colorless oil); 67% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.7 Hz, 1H), 7.75 – 7.66 (m, 2H), 7.63 (d, *J* = 6.7 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 6.8 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 1H), 3.90 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.9, 160.8, 147.9, 137.4, 136.5, 130.1, 128.1, 127.6, 125.7, 125.6, 120.9, 118.8, 115.3, 55.4; **HRMS (ESI)** calcd $C_{16}H_{13}NOS$ $[M + H]^+$: 268.0791 found: 268.0795.

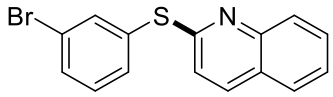


2-((2-methoxyphenyl)thio)quinoline (42): Followed the general procedure 1 with *S*-(2-methoxyphenyl) benzenesulfonothioate (56.0 mg, 0.2 mmol) and quinoline-2-carboxylic acid (34.6 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether : EA= 20: 1) to give 27.3 mg of the title compound (Colorless oil); 51% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.00 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.7 Hz, 1H), 7.75 – 7.65 (m, 3H), 7.53 – 7.44 (m, 2H), 7.10 – 7.03 (m, 2H), 6.96 (d, *J* = 8.7, 2.1 Hz, 1H), 3.83 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 161.3, 159.9, 147.9, 137.2, 136.2, 131.5, 129.9, 128.2, 127.5, 125.8, 125.6, 121.4, 119.1, 111.7, 56.0; **HRMS (ESI)**

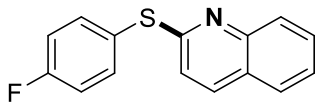
calcd $C_{16}H_{13}NOS$ $[M + H]^+$: 268.0791 found: 268.0791.



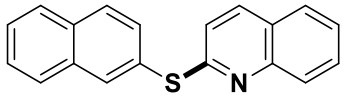
2-((2-chlorophenyl)thio)quinoline (43): Followed the general procedure 1 with *S*-(3-bromophenyl) benzenesulfonothioate (56.6 mg, 0.2 mmol) and quinoline-2-carboxylic acid (34.6 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether : EA= 20: 1) to give 34.8 mg of the title compound (Colorless oil); 64% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.04 – 7.93 (m, 2H), 7.82 – 7.74 (m, 2H), 7.74 – 7.68 (m, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.46 – 7.40 (m, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 8.7 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.6, 148.0, 139.1, 137.1, 136.8, 130.8, 130.5, 130.1, 128.3, 127.7, 127.6, 126.0, 119.5; **HRMS (ESI)** calcd $C_{15}H_{10}{}^{35}ClNS$ $[M + H]^+$: 272.0295 found: 272.0296.



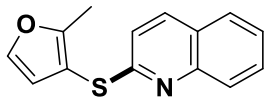
2-((3-bromophenyl)thio)quinoline (44): Followed the general procedure 1 with *S*-(2-chlorophenyl) benzenesulfonothioate (65.4 mg, 0.2 mmol) and quinoline-2-carboxylic acid (34.6 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether : EA= 20: 1) to give 44.2 mg of the title compound (Colorless oil); 70% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.02 – 7.97 (m, 2H), 7.87 – 7.85 (m, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.72 (t, *J* = 7.7 Hz, 1H), 7.64 – 7.58 (m, 2H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.09 (d, *J* = 8.7 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.0, 147.9, 137.21, 136.92, 133.3, 132.2, 130.8, 130.3, 128.3, 127.6, 126.2, 126.0, 123.1, 119.9; **HRMS (ESI)** calcd $C_{15}H_{10}{}^{79}BrNS$ $[M + H]^+$: 315.9790 found: 315.9791.



2-((4-fluorophenyl)thio)quinoline (45): Followed the general procedure 1 with *S*-(4-fluorophenyl) benzenesulfonothioate (54.0 mg, 0.2 mmol) and quinoline-2-carboxylic acid (34.6 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether : EA= 20: 1) to give 31.2 mg of the title compound (Colorless oil); 61% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.98 – 7.91 (m, 2H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.72 – 7.66 (m, 3H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.23 – 7.16 (m, 2H), 7.00 (d, *J* = 8.7 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.7, 162.2, 161.2, 148.0, 137.51 (d, *J* = 8.5 Hz), 136.6, 130.1, 128.3, 127.6, 125.8, 119.2, 116.8 (d, *J* = 22.0 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -111.1 (s, 1F); **HRMS (ESI)** calcd $C_{15}H_{10}FNS$ $[M + H]^+$: 256.0591 found: 256.0591.

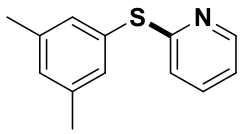


2-(naphthalen-2-ylthio)quinoline (46): Followed the general procedure 1 with *S*-phenyl *S*-(naphthalen-2-yl) benzenesulfonothioate (60.3 mg, 0.2 mmol) and quinoline-2-carboxylic acid (34.6 mg, 0.2 mmol) and purified using flash chroma-tography (petroleum ether : EA= 20: 1) to give 29.9 mg of the title compound (Colorless oil); 52% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.25 (s, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.97 – 7.88 (m, 4H), 7.77 – 7.67 (m, 3H), 7.63 – 7.56 (m, 2H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 8.7 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 161.6, 147.9, 136.7, 134.8, 133.9, 133.3, 131.6, 130.2, 129.3, 128.2, 128.0, 127.8, 127.6, 127.2, 126.8, 125.9, 119.7; **HRMS (ESI)** calcd $C_{19}H_{13}NS$ $[M + H]^+$: 288.0841 found: 288.0839.

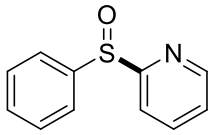


2-((2-methylfuran-3-yl)thio)quinoline (47): Followed the general procedure 1 with *S*-

(2-methylfuran-3-yl) benzenesulfonothioate (50.8 mg, 0.2 mmol) and quinoline-2-carboxylic acid (34.6 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether : EA= 20: 1) to give 28.0 mg of the title compound (Colorless oil); 58% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.99 – 7.89 (m, 2H), 7.73 – 7.64 (m, 2H), 7.48 – 7.42 (m, 2H), 7.02 (d, *J* = 8.7 Hz, 1H), 6.53 – 6.47 (m, 1H), 2.39 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 161.6, 157.7, 148.0, 141.5, 136.6, 130.1, 128.1, 127.6, 125.7, 118.0, 115.7, 106.3, 12.0; **HRMS (ESI)** calcd $C_{14}H_{11}NOS$ $[M + H]^+$: 242.0634 found: 242.0630.

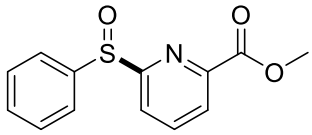


2-((3,5-dimethylphenyl)thio)pyridine (48): Followed the general procedure 1 with *S*-(3,5-dimethylphenyl) benzenesulfonothioate (56.0 mg, 0.2 mmol) and picolinic acid (24.6 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether : EA= 20: 1) to give 27.2 mg of the title compound (Yellow oil); 63% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.48 – 8.44 (m, 1H), 7.51 – 7.45 (m, 1H), 7.26 (s, 2H), 7.08 (s, 1H), 7.04 – 6.99 (m, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 2.37 (s, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.1, 149.5, 139.3, 136.7, 132.6, 131.0, 130.2, 121.2, 119.7, 21.2; **HRMS (ESI)** calcd $C_{13}H_{13}NS$ $[M + H]^+$: 216.0841 found: 216.0840

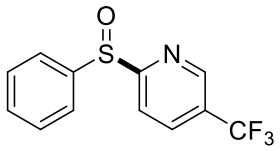


2-(phenylsulfinyl)pyridine (49): Followed the general procedure 2 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and quinoline-2-carboxylic acid (24.6 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether：EA= 4：1 as eluent) to give 9.7 mg of the title compound (Yellow oil); 24% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.62 – 8.56 (m, 1H), 8.09 (d, *J* = 7.9 Hz, 1H), 7.94 – 7.88 (m, 1H),

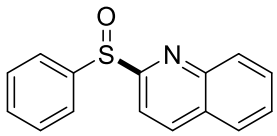
7.87 – 7.81 (m, 2H), 7.51 – 7.46 (m, 3H), 7.37 – 7.32 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.8, 149.8, 144.1, 138.1, 131.1, 129.2, 124.9, 124.7, 118.5; **HRMS (ESI)** calcd $C_{11}H_9NOS$ $[M + H]^+$: 204.0478 found: 204.0476.



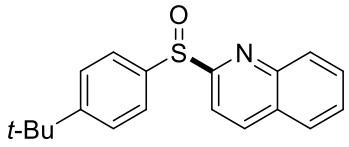
methyl 6-(phenylsulfinyl)picolinate (50): Followed the general procedure 2 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and 6-(methoxycarbonyl)picolinic acid (36.2 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether：EA= 4：1 as eluent) to give 14.6 mg of the title compound (Yellow oil); 28% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.28 (d, *J* = 7.8 Hz, 1H), 8.15 (d, *J* = 7.6 Hz, 1H), 8.09 – 8.04 (m, 1H), 7.89 (d, *J* = 7.8 Hz, 2H), 7.54 – 7.44 (m, 3H), 4.04 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.8, 164.6, 148.0, 143.6, 139.2, 131.2, 129.3, 126.0, 124.6, 121.4, 53.1; **HRMS (ESI)** calcd $C_{13}H_{11}NO_3S$ $[M + H]^+$: 262.0532 found: 262.0531.



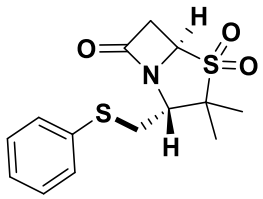
2-(phenylsulfinyl)-5-(trifluoromethyl)pyridine (51): Followed the general procedure 2 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and 6-(methoxycarbonyl)-picolinic acid (36.2 mg, 0.2 mmol) and purified using flash chromatogra-phy (petroleum ether：EA= 4：1 as eluent) to give 10.8 mg of the title compound (Yellow oil); 20% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.84 (s, 1H), 8.26 (d, *J* = 8.2 Hz, 1H), 8.20 – 8.12 (m, 1H), 7.88 – 7.80 (m, 2H), 7.56 – 7.47 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.1, 146.7 (q, *J* = 3.2 Hz), 143.1, 135.44 (q, *J* = 3.3 Hz), 131.6, 129.4, 127.54 (q, *J* = 33.1 Hz), 124.9, 122.9 (d, *J* = 272.3 Hz), 118.3; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.36 (s, 3F); **HRMS (ESI)** calcd $C_{12}H_8F_3NOS$ $[M + H]^+$: 272.0351 found: 272.0350.



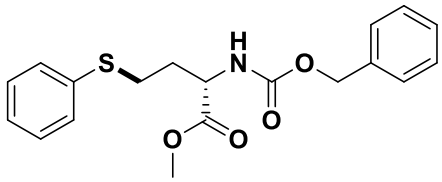
2-(phenylsulfinyl)quinoline (52): Followed the general procedure 2 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and quinoline-2-carboxylic acid (34.6 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether：EA= 4：1 as eluent) to give 16.2 mg of the title compound (Yellow oil); 32% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.37 (d, *J* = 8.5 Hz, 1H), 8.14 (M, 2H), 7.95 – 7.87 (m, 3H), 7.84 – 7.78 (m, 1H), 7.64 (t, *J* = 7.3 Hz, 1H), 7.51 – 7.40 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.8, 147.5, 144.1, 138.7, 131.0, 130.7, 129.5, 129.2, 128.3, 128.0, 127.9, 124.6, 114.5; **HRMS (ESI)** calcd $C_{15}H_{11}NOS$ $[M + H]^+$: 254.0634 found: 254.0630.



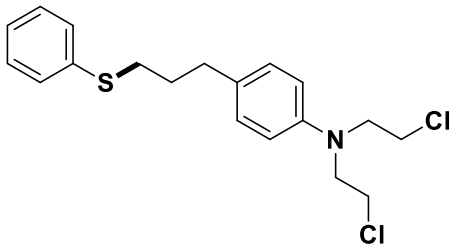
2-((4-(tert-butyl)phenyl)sulfinyl)quinoline (53): Followed the general procedure 2 with *S*-(4-(tert-butyl)phenyl) benzenesulfonothioate (61.2 mg, 0.2 mmol) and quinoline-2-carboxylic acid (34.6 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether：EA= 4：1 as eluent) to give 16.0 mg of the title compound (Yell-ow oil); 26% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.36 (d, *J* = 8.6 Hz, 1H), 8.15 (t, *J* = 8.2 Hz, 2H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.84 – 7.75 (m, 3H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 2H), 1.30 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 154.5, 147.5, 140.8, 138.6, 130.6, 129.5, 128.3, 128.0, 127.8, 126.3, 124.5, 114.6, 34.9, 31.1; **HRMS (ESI)** calcd $C_{19}H_{19}NOS$ $[M + H]^+$: 310.1260 found: 310.1259.



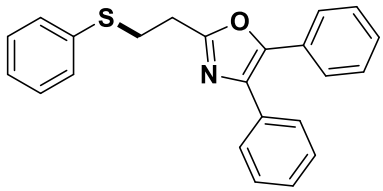
(2S,5R)-3,3-dimethyl-2-((phenylthio)methyl)-4-thia-1-azabicyclo[3.2.0]heptan-7-one 4,4-dioxide (54): Followed the general procedure 1 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and Sulbactam (49.4 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether : EA=10:1 as eluent) to give 22.6 mg of the title compound (Colorless oil); 47% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.52 – 7.44 (m, 2H), 7.42 – 7.34 (m, 3H), 5.75 (s, 1H), 5.13 – 4.96 (m, 1H), 3.33 (dt, *J* = 15.3, 4.3 Hz, 1H), 2.82 (d, *J* = 15.3 Hz, 1H), 1.90 – 1.74 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.2, 135.1, 129.9, 129.5, 129.3, 129.1, 115.8, 60.0, 43.6, 22.8, 19.2; **HRMS (ESI)** calcd $C_{14}H_{17}NO_3S_2$ $[M + H]^+$: 312.0723 found: 321.0724.



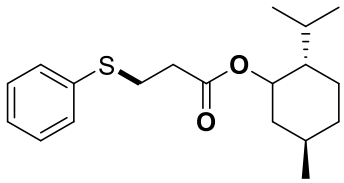
methyl N-((benzyloxy)carbonyl)-S-phenyl-L-homocysteinate (55): Followed the general procedure 1 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and Z-GLU-OME (59.0 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether：EA= 4：1 as eluent) to give 34.4 mg of the title compound (Colorless oil); 48% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44 – 7.31 (m, 9H), 7.27 – 7.21 (m, 1H), 5.44 (d, *J* = 7.7 Hz, 1H), 5.17 – 5.12 (m, 2H), 4.60 – 4.51 (m, 1H), 3.77 (s, 3H), 3.04 – 2.91 (m, 2H), 2.29 – 2.16 (m, 1H), 2.05 – 1.95 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.3, 155.9, 136.1, 135.5, 129.7, 129.0, 128.6, 128.3, 128.2, 126.4, 67.2, 53.1, 52.6, 32.3, 29.7; **HRMS (ESI)** calcd $C_{19}H_{21}NO_4S$ $[M + H]^+$: 360.1264 found: 360.1260.



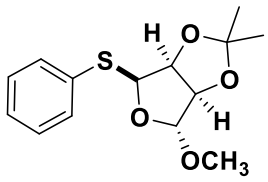
N,N-bis(2-chloroethyl)-4-(3-(phenylthio)propyl)aniline (56): Followed the general procedure 1 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and Chlorambucil (60.6 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 36.7 mg of the title compound (Colorless oil); 50% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.39 – 7.29 (m, 4H), 7.24 – 7.17 (m, 1H), 7.10 (d, *J* = 7.4 Hz, 2H), 6.66 (d, *J* = 7.3 Hz, 2H), 3.81 – 3.70 (m, 4H), 3.69 – 3.60 (m, 4H), 2.96 (t, *J* = 7.2 Hz, 2H), 2.70 (t, *J* = 7.4 Hz, 2H), 2.02 – 1.89 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 144.3, 136.6, 130.4, 129.7, 129.1, 128.9, 125.8, 112.1, 53.6, 40.5, 33.5, 32.8, 30.8; **HRMS (ESI)** calcd $C_{19}H_{23}{}^{35}Cl_2NS$ $[M + H]^+$: 368.1001 found: 368.1002.



4,5-diphenyl-2-(2-(phenylthio)ethyl)oxazole (57): Followed the general procedure 1 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and Oxaprozin (58.6 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether : EA= 20: 1) to give 27.8 mg of the title compound (Colorless oil); 39% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65 (d, *J* = 6.9 Hz, 2H), 7.58 (d, *J* = 6.8 Hz, 2H), 7.49 – 7.43 (m, 2H), 7.42 – 7.30 (m, 9H), 3.55 – 3.38 (m, 2H), 3.32 – 3.14 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 145.4, 132.4, 130.4, 129.1, 128.6, 128.6, 128.5, 128.1, 127.9, 126.7, 126.5, 31.33, 28.8; **HRMS (ESI)** calcd $C_{23}H_{19}NOS$ $[M + H]^+$: 358.1260 found: 358.1258.

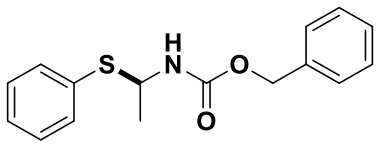


(2S,5R)-2-isopropyl-5-methylcyclohexyl 3-(phenylthio)propanoate (58): Followed the general procedure 1 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and Monomethyl succinate (45.6 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether：EA= 10：1 as eluent) to give 33.9 mg of the title compound (Colorless oil); 53% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.43 – 7.38 (m, 2H), 7.36 – 7.31 (m, 2H), 7.28 – 7.20 (m, 1H), 4.74 (td, *J* = 10.9, 4.4 Hz, 1H), 3.20 (t, *J* = 7.4 Hz, 2H), 2.64 (t, *J* = 7.4 Hz, 2H), 2.05 – 1.97 (m, 1H), 1.96 – 1.84 (m, 1H), 1.76 – 1.68 (m, 2H), 1.64 (s, 1H), 1.56 – 1.46 (m, 1H), 1.42 – 1.35 (m, 1H), 1.12 – 1.04 (m, 1H), 0.99 (d, *J* = 11.3 Hz, 1H), 0.93 (t, *J* = 6.8 Hz, 6H), 0.79 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.3, 135.4, 130.0, 129.0, 126.5, 74.7, 47.0, 40.9, 34.7, 34.2, 31.4, 29.2, 26.2, 23.4, 22.0, 20.8, 16.3; **HRMS (ESI)** calcd $C_{19}H_{28}O_2S$ $[M + H]^+$: 321.1883 found: 321.1882.

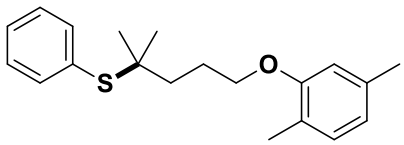


(3aR,4R,6S,6aS)-4-methoxy-2,2-dimethyl-6-(phenylthio)tetrahydrofuro[3,4-d][1,3]dioxole (59): Followed the general procedure 1 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and Ribosic acide (43.6 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether：EA= 20：1 as eluent) to give 35.5 mg of the title compound (Colorless oil); 63% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.53 (d, *J* = 7.2 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.30 – 7.26 (m, 1H), 5.65 (s, 1H), 5.15 (s, 1H), 4.97 (d, *J* = 5.8 Hz, 1H), 4.76 (d, *J* = 5.8 Hz, 1H), 3.44 (s, 3H), 1.51 (s, 3H), 1.36 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 135.3, 130.8, 129.1, 127.1, 113.0, 110.4, 93.3, 85.9, 84.7, 55.2, 26.4, 25.1; **HRMS (ESI)** calcd $C_{14}H_{18}O_4S$ $[M + H]^+$: 283.0999 found:

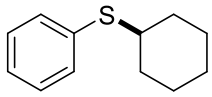
283.1002.



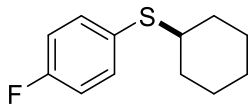
benzyl (R)-(1-(phenylthio)ethyl)carbamate (60): Followed the general procedure 1 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and *N*-Cbz-D-Alanine (44.6 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether：EA= 10：1 as eluent) to give 32.7 mg of the title compound (Colorless oil); 57% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.53 – 7.47 (m, 2H), 7.42 – 7.30 (m, 8H), 5.40 – 5.24 (m, 1H), 5.15 – 4.96 (m, 3H), 1.53 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 154.89, 136.23, 133.86, 132.28, 128.97, 128.56, 128.22, 128.11, 66.87, 55.17, 22.53; **HRMS (ESI)** calcd $C_{16}H_{17}NO_2S$ $[M + H]^+$: 288.1053 found: 288.1053.



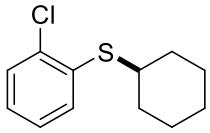
(5-(2,5-dimethylphenoxy)-2-methylpentan-2-yl)(phenyl)sulfane (61): Followed the general procedure 1 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and N-Cbz-D-Alanine (44.6 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether：EA= 20：1 as eluent) to give 32.7 mg of the title compound (Colorless oil); 57% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.60 – 7.53 (m, 2H), 7.44 – 7.32 (m, 3H), 7.05 (d, *J* = 5.5 Hz, 1H), 6.75 – 6.64 (m, 2H), 4.04 – 3.95 (m, 2H), 2.40 – 2.33 (m, 3H), 2.24 – 2.18 (m, 3H), 2.09 – 1.98 (m, 2H), 1.74 – 1.66 (m, 2H), 1.32 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.0, 137.5, 136.5, 132.2, 130.3, 128.7, 128.5, 123.6, 120.7, 111.9, 68.0, 49.0, 38.7, 28.8, 25.1, 21.4, 15.9; **HRMS (ESI)** calcd $C_{20}H_{26}OS$ $[M + H]^+$: 315.1777 found: 315.1773.



cyclohexyl(phenyl)sulfane (62): Followed the general procedure 3 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and cyclohexane (84.1 mg, 1mmol) and purified using flash chromatography (petroleum ether as eluent) to give 35.0 mg of the title compound (Colorless oil); 91% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 – 7.41 (m, 2H), 7.35 – 7.27 (m, 3H), 3.21 – 3.08 (m, 1H), 2.08 – 1.99 (m, 2H), 1.85 – 1.77 (m, 2H), 1.70 – 1.62 (m, 1H), 1.39 – 1.29 (m, 5H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 135.1, 131.8, 128.7, 127.5, 126.6, 77.3, 77.0, 76.7, 46.5, 33.3, 29.76, 26.1, 25.8; **HRMS (ESI)** calcd $C_{12}H_{16}S$ $[M + H]^+$: 193.1045 found: 193.1046.

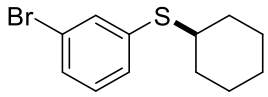


cyclohexyl(4-fluorophenyl)sulfane (**63**): Followed the general procedure 3 with *S*-(4-fluorophenyl) benzenesulfonothioate (54.0 mg, 0.2 mmol) and cyclohexane (84.1 mg, 1 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 26.0 mg of the title compound (yellow oil); 62% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.43 (dd, *J* = 8.5, 5.4 Hz, 2H), 7.10 – 6.95 (m, 2H), 3.15 – 2.92 (m, 1H), 2.06 – 1.92 (m, 2H), 1.87 – 1.73 (m, 2H), 1.67 – 1.56 (m, 2H), 1.40 – 1.28 (m, 5H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.26 (d, *J* = 246.8 Hz), 135.03 (d, *J* = 8.0 Hz), 129.7, 115.83 (d, *J* = 21.7 Hz), 47.6, 33.3, 26.0, 25.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.87(s, 1F); **HRMS (ESI)** calcd $C_{12}H_{15}FS$ $[M + H]^+$: 211.0951 found: 211.0947.

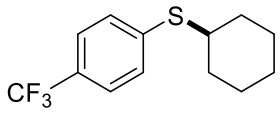


(2-chlorophenyl)(cyclohexyl)sulfane (**64**): Followed the general procedure 3 with *S*-(2-chlorophenyl) benzenesulfonothioate (55.6 mg, 0.2 mmol) and cyclohexane (84.1

mg, 2 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 25.7 mg of the title compound (Colorless oil); 57% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42 (d, *J* = 7.9 Hz, 2H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 3.35 – 3.22 (m, 1H), 2.09 – 1.98 (m, 2H), 1.92 – 1.77 (m, 2H), 1.73 – 1.63 (m, 1H), 1.52 – 1.30 (m, 5H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 135.2, 134.8, 131.3, 129.8, 127.1, 126.9, 45.2, 33.0, 26.0, 25.8; **HRMS (ESI)** calcd $C_{12}H_{15}{}^{35}ClS$ $[M + H]^+$: 227.0656 found: 227.0656.

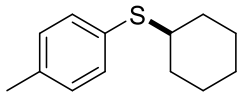


(3-bromophenyl)(cyclohexyl)sulfane (**65**): Followed the general procedure 3 with *S*-(3-bromophenyl) benzenesulfonothioate (65.4 mg, 0.2 mmol) and cyclohexane (84.1 mg, 1 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 39.96 mg of the title compound (Colorless oil); 57% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.54 – 7.50 (m, 1H), 7.35 – 7.27 (m, 2H), 7.16 – 7.11 (m, 1H), 3.17 – 3.07 (m, 1H), 2.04 – 1.95 (m, 2H), 1.81 – 1.74 (m, 2H), 1.65 – 1.58 (m, 1H), 1.41 – 1.27 (m, 5H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 137.8, 133.7, 130.1, 129.8, 129.4, 122.6, 46.5, 33.2, 26.0, 25.7; **HRMS (ESI)** calcd $C_{12}H_{15}{}^{79}BrS$ $[M + H]^+$: 271.0151 found: 271.0153.

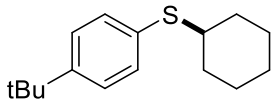


cyclohexyl(4-(trifluoromethyl)phenyl)sulfane (66): Followed the general procedure 3 with *S*-(4-(trifluoromethyl)phenyl) 4-(trifluoromethyl)benzenesulfonothioate (77.1 mg, 0.2 mmol) and cyclohexane (84.1 mg, 1 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 22.8 mg of the title compound (yellow oil); 54% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.55 (d, *J* = 7.0 Hz, 2H), 7.45 (d, *J* = 7.1 Hz, 2H), 3.34 – 3.18 (m, 1H), 2.12 – 1.94 (m, 2H), 1.92 – 1.76 (m, 2H), 1.78 – 1.64 (m, 1H), 1.46 – 1.30 (m, 5H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.2, 129.7, 127.8 (q, *J* = 32.6 Hz), 125.6 (q, *J* = 3.6 Hz), 121.5 (q, *J* = 273.9 Hz), 45.6, 33.1, 26.0,

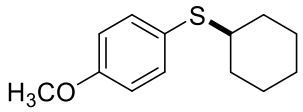
25.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.40 (s, 3F); **HRMS (ESI)** calcd $C_{13}H_{15}F_3S$ [M + H]$^+$: 261.0919 found: 261.0920.



cyclohexyl(p-tolyl)sulfane (67): Followed the general procedure 3 with *S*-(p-tolyl) 4-methylbenzenesulfonothioate (56.2 mg, 0.2 mmol) and cycloheptane (84.1 mg, 1 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 28.8 mg of the title compound (yellow oil); 70 % yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.35 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 3.10 – 2.99 (m, 1H), 2.36 (s, 3H), 2.03 – 1.93 (m, 2H), 1.82 – 1.74 (m, 2H), 1.67 – 1.59 (m, 3H), 1.41 – 1.25 (m, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 136.9, 132.8, 131.1, 129.5, 47.1, 33.4, 26.1, 25.8, 21.1; **HRMS (ESI)** calcd $C_{13}H_{18}S$ [M + H]$^+$: 207.1202 found: 207.1199.

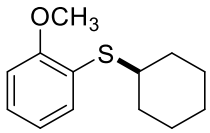


(4-(tert-butyl)phenyl)(cyclohexyl)sulfane (**68**): Followed the general procedure 3 with *S*-(4-(tert-butyl)phenyl) benzenesulfonothioate (61.2 mg, 0.2 mmol) and cyclohexane (84.1mg, 1 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 33.7 mg of the title compound (yellow oil); 68% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.40 – 7.32 (m, 4H), 3.14 – 3.04 (m, 1H), 2.06 – 1.98 (m, 2H), 1.84 – 1.76 (m, 2H), 1.69 – 1.60 (m, 1H), 1.42 – 1.37 (m, 2H), 1.35 (s, 9H), 1.34 – 1.29 (m, 4H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.9, 132.1, 131.4, 125.8, 46.8, 34.5, 33.4, 31.3, 26.1, 25.8; **HRMS (ESI)** calcd $C_{16}H_{24}S$ [M + H]$^+$: 249.1671 found: 249.1675.

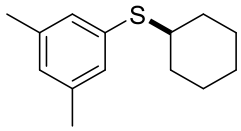


cyclohexyl(4-methoxyphenyl)sulfane (**69**): Followed the general procedure 3 wi th *S*-phenyl *S*-(4-methoxyphenyl) benzenesulfonothioate (56.0 mg, 0.2 mmol) an d cyclohexane (84.1mg, 1 mmol) and purified using flash chromatography (petr

oleum ether as eluent) to give 37.7 mg of the title compound (yellow oil); 85 % yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42 (d, *J* = 6.0 Hz, 2H), 6.87 (d, *J* = 6.0 Hz, 2H), 3.83 (s, 3H), 3.01 – 2.88 (m, 1H), 2.01 – 1.94 (m, 2H), 1.82 – 1.75 (m, 2H), 1.68 – 1.61 (m, 1H), 1.38 – 1.25 (m, 5H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.3, 135.6, 125.0, 114.3, 55.3, 47.9, 33.4, 26.1, 25.8; **HR MS (ESI)** calcd $C_{13}H_{18}OS$ $[M + H]^+$: 223.1151 found: 223.1146.

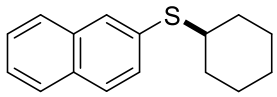


cyclohexyl(2-methoxyphenyl)sulfane (**70**): Followed the general procedure 3 with *S*-(2-methoxyphenyl) benzenesulfonothioate (56.0 mg, 0.2 mmol) and cyclohexane (84.1 mg, 1 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 30.2 mg of the title compound (yellow oil); 63% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.37 (d, *J* = 7.6 Hz, 1H), 7.28 – 7.21 (m, 1H), 6.97 – 6.92 (m, 1H), 6.90 (d, *J* = 8.2 Hz, 1H), 3.92 (s, 3H), 3.35 – 3.11 (m, 1H), 2.05 – 1.96 (m, 2H), 1.86 – 1.76 (m, 2H), 1.71 – 1.59 (m, 1H), 1.48 – 1.27 (m, 5H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.1, 144.2, 139.5, 133.9, 133.3, 128.5, 127.5, 121.3, 115.2, 111.3, 55.4; **HRMS (ESI)** calcd $C_{13}H_{18}OS$ $[M + H]^+$: 223.1151 found: 223.1153.

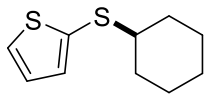


cyclohexyl(3,5-dimethylphenyl)sulfane (**71**): Followed the general procedure 3 with *S*-(3,5-dimethylphenyl) benzenesulfonothioate (56.0 mg, 0.2 mmol) and cyclohexane (84.1 mg, 1 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 24.6 mg of the title compound (yellow oil); 56% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.07 (s, 2H), 6.89 (s, 1H), 3.18 – 3.06 (m, 1H), 2.33 (s, 6H), 2.07 – 1.96 (m, 2H), 1.86 – 1.76 (m, 2H), 1.68 – 1.59 (m, 1H), 1.42 – 1.29 (m, 5H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 138.3, 134.6, 129.5, 128.5, 46.5, 33.4, 26.1, 25.8, 21.2; **HRMS (ESI)**

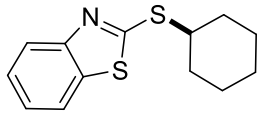
calcd $C_{14}H_{20}S$ $[M + H]^+$: 221.1358 found: 221.1358.



cyclohexyl(naphthalen-2-yl)sulfane (**72**): Followed the general procedure 3 with *S*-phenyl *S*-(naphthalen-2-yl) benzenesulfonothioate (60.3 mg, 0.2 mmol) and cyclohexane (84.1mg, 1 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 32 mg of the title compound (yellow oil); 65% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.90 (s, 1H), 7.86 – 7.78 (m, 3H), 7.57 – 7.45 (m, 3H), 3.40 – 3.14 (m, 1H), 2.13 – 2.05 (m, 2H), 1.87 – 1.80 (m, 2H), 1.72 – 1.63 (m, 1H), 1.50 – 1.32 (m, 5H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 133.7, 132.7, 132.1, 130.2, 129.6, 128.2, 127.7, 127.3, 126.4, 125.9, 46.6, 33.4, 26.1, 25.8; **HRMS (ESI)** calcd $C_{16}H_{18}S$ $[M + H]^+$: 243.1202 found: 243.1199.

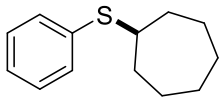


2-(cyclohexylthio)thiophene (**73**): Followed the general procedure 3 with *S*-(thiophen-2-yl) benzenesulfonothioate (51.1 mg, 0.2 mmol) and cyclohexane (84.1 mg, 1 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 22.9 mg of the title compound (yellow oil); 58% yield. **1H NMR (400 MHz, CDCl3)** δ 7.39 (d, J = 5.3 Hz, 1H), 7.14 (d, J = 3.5 Hz, 1H), 7.04 – 7.00 (m, 1H), 2.96 – 2.83 (m, 1H), 2.03 – 1.97 (m, 2H), 1.83 – 1.78 (m, 2H), 1.65 – 1.60 (m, 1H), 1.39 – 1.25 (m, 5H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 134.9, 132.8, 129.7, 127.4, 49.9, 33.2, 26.1, 25.6; **HRMS (ESI)** calcd $C_{10}H_{14}S_2$ $[M + H]^+$: 199.0610 found: 199.0607.

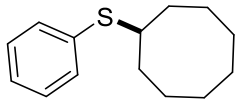


2-(cyclohexylthio)benzo[d]thiazole (74): Followed the general procedure 3 with *S*-(benzo[d]thiazol-2-yl) benzenesulfonothioate (48.6 mg, 0.2 mmol) and cyclohexane (84.1 mg, 1 mmol) and purified using flash chromatography (petroleum ether as eluent)

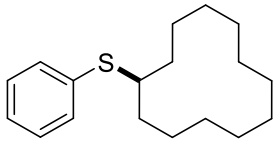
to give 22.9 mg of the title compound (yellow oil); 46% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.95 – 7.88 (m, 1H), 7.82 – 7.76 (m, 1H), 7.48 – 7.40 (m, 1H), 7.37 – 7.30 (m, 1H), 4.01 – 3.88 (m, 1H), 2.25 (d, *J* = 12.4 Hz, 2H), 1.90 – 1.80 (m, 2H), 1.69 – 1.64 (m, 1H), 1.64 – 1.26 (m, 5H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.5, 153.4, 135.3, 126.0, 124.2, 121.6, 120.9, 47.4, 33.3, 25.9, 25.6; **HRMS (ESI)** calcd $C_{13}H_{15}NS_2$ $[M + H]^+$: 250.0719 found: 250.0724.



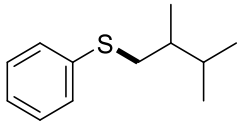
cycloheptyl(phenyl)sulfane (**75**): Followed the general procedure 3 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and cycloheptane (98.1 mg, 1 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 23.9 mg of the title compound (yellow oil); 58% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.41 (d, *J* = 7.1 Hz, 2H), 7.35 – 7.30 (m, 2H), 7.27 – 7.21 (m, 1H), 3.45 – 3.27 (m, 1H), 2.12 – 2.01 (m, 2H), 1.83 – 1.71 (m, 2H), 1.67 – 1.48 (m, 8H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 136.2, 131.2 128.8, 126.3, 47.9, 34.6, 28.3, 26.0; **HRMS (ESI)** calcd $C_{13}H_{18}S$ $[M + H]^+$: 207.1202 found: 207.1200.



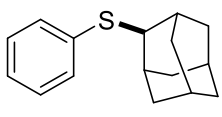
cyclooctyl(phenyl)sulfane (**76**): Followed the general procedure 3 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and cyclooctane (112.2 mg, 1 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 26.9 mg of the title compound (yellow oil); 61% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.41 (d, *J* = 7.6 Hz, 2H), 7.35 – 7.29 (m, 2H), 7.26 – 7.21 (m, 1H), 3.51 – 3.38 (m, 1H), 2.08 – 1.91 (m, 2H), 1.83 – 1.50 (m, 12H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 136.1, 131.4, 128.8, 126.4, 47.6, 32.0, 27.1, 25.8, 25.2; **HRMS (ESI)** calcd $C_{14}H_{20}S$ $[M + H]^+$: 221.1358 found: 221.1358.



cyclododecyl(phenyl)sulfane (**77**): Followed the general procedure 3 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and cyclododecane (168.3 mg, 1 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 33.7 mg of the title compound (yellow oil); 61% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.41 (d, *J* = 7.8 Hz, 2H), 7.34 – 7.28 (m, 2H), 7.26 – 7.20 (m, 1H), 3.40 – 3.19 (m, 1H), 1.80 – 1.68 (m, 2H), 1.65 – 1.55 (m, 4H), 1.49 – 1.28 (m, 16H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 136.0, 131.2, 128.8, 126.3, 44.7, 29.9, 24.2, 23.8, 23.4, 22.1; **HRMS (ESI)** calcd $C_{18}H_{28}S$ $[M + H]^+$: 277.1984 found: 277.1987.

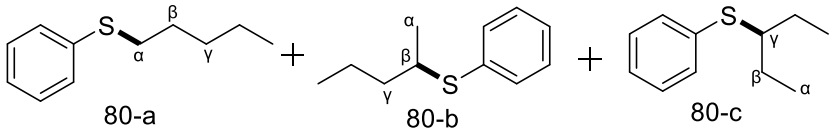


(2,3-dimethylbutyl)(phenyl)sulfane (**78**): Followed the general procedure 3 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and 2,3-dimethylbutane (85.1 mg, 1 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 15.1 mg of the title compound (yellow oil); 39% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.36 (d, *J* = 8.2 Hz, 2H), 7.31 – 7.27 (m, 2H), 7.22 – 7.15 (m, 1H), 3.10 – 3.00 (m, 1H), 2.81 – 2.68 (m, 1H), 1.87 – 1.74 (m, 1H), 1.71 – 1.60 (m, 1H), 1.03 – 0.97 (m, 3H), 0.97 – 0.91 (m, 3H), 0.92 – 0.83 (m, 4H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 137.5, 128.8, 128.7, 125.5, 38.9, 38.4, 31.4, 20.33, 17.7, 15.1; **HRMS (ESI)** calcd $C_{12}H_{18}S$ $[M + H]^+$: 195.1202 found: 195.1204.

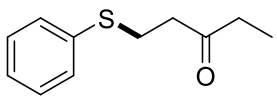


((1r, 5R, 7S)-adamantan-2-yl)(phenyl)sulfane (**79**): Followed the general procedure 3 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and cyclododecane (168.3 mg, 1 mmol) and purified using flash chromatography (petroleum ether as eluent) to

give 25.8 mg of the title compound (yellow oil); 53% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42 (d, *J* = 7.9 Hz, 2H), 7.34 – 7.30 (m, 2H), 7.25 – 7.19 (m, 1H), 3.62 – 3.58 (m, 1H), 2.31 – 2.24 (m, 2H), 2.11 – 2.05 (m, 2H), 1.98 – 1.90 (m, 4H), 1.87 – 1.77 (m, 4H), 1.64 – 1.58 (m, 3H); **^{13}C NMR (101 MHz, CfDCl$_3$)** δ 136.7, 130.8, 128.8, 126.1, 55.5, 38.7, 37.7, 32.9, 32.0, 27.7, 27.4; **HRMS (ESI)** calcd $C_{16}H_{20}S$ $[M + H]^+$: 245.1358 found: 245.1361.

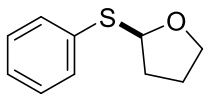


5-(phenylthio)pentan-1-ylium (80-a), pentan-2-yl(phenyl)sulfane (80-b), pentan-3-yl(phenyl)sulfane (80-c): Followed the general procedure 3 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and pentane (72.0 mg, 1 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 11.1 mg of the title compound (yellow oil); 31% yield (α:β:γ=31:46:23); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.56 – 7.51 (m, 1H), 7.46 – 7.40 (m, 1H), 7.38 – 7.30 (m, 2H), 7.29 – 7.17 (m, 1H), 3.32 – 3.21 (m, 0.33 H, **80-a**), 3.08 – 3.00 (m, 0.17H, **80-c**), 2.98 – 2.93 (m, 0.45 H, **80-b**), 1.74 – 1.58 (m, 2H), 1.57 – 1.35 (m, 2H), 1.32 – 1.28 (m, 1H), 1.08 – 1.02 (m, 1H), 0.99 – 0.87 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 137.0, 135.5, 131.8, 131.7, 129.1, 128.8, 128.8, 127.5, 127.2, 126.6, 126.4, 125.6, 52.2, 43.0, 38.8, 33.5, 31.0, 29.7, 28.8, 26.7, 22.3, 21.1, 20.3, 14.0, 13.9, 11.2; **HRMS (ESI)** calcd $C_{11}H_{16}S$ $[M + H]^+$: 181.1045 found: 181.1042.

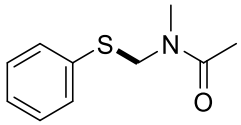


1-(phenylthio)pentan-3-one (**81**): Followed the general procedure 3 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and pentan-3-one (86.1 mg, 1 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 13.1 mg of the title compound (yellow oil); 34% yield (α:β>20:1); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.39 – 7.35 (m, 2H), 7.32 (dd, *J* = 13.3, 5.2 Hz, 2H), 7.25 – 7.20 (m, 1H), 3.18 (t, *J* = 7.3 Hz,

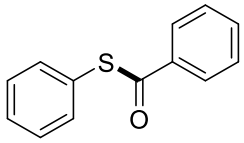
2H), 2.76 (t, *J* = 7.3 Hz, 2H), 1.08 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 209.4, 135.7, 129.0, 129.0, 126.3, 41.7, 36.3, 27.6, 7.7; **HRMS (ESI)** calcd $C_{11}H_{14}OS$ $[M + H]^+$: 195.0838 found: 195.0842.



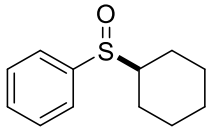
2-(phenylthio)tetrahydrofuran (**82**): Followed the general procedure 3 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and tetrahydrofuran (72.1 mg, 1 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 19.4 mg of the title compound (yellow oil); 54% yield(α:β>20:1); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.55 (d, *J* = 7.3 Hz, 2H), 7.36 – 7.30 (m, 2H), 7.29 – 7.23 (m, 1H), 5.75 – 5.63 (m, 1H), 4.13 – 3.95 (m, 2H), 2.47 – 2.34 (m, 1H), 2.12 – 1.96 (m, 2H), 1.96 – 1.86 (m, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 135.7, 131.1, 128.8, 126.8, 87.1, 67.3, 32.6, 24.9; **HRMS (ESI)** calcd $C_{10}H_{12}OS$ $[M + H]^+$: 181.0682 found: 181.0687.



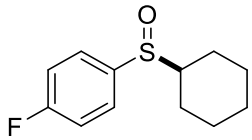
***N*-methyl-N-((phenylthio)methyl)acetamide** (**83**): Followed the general procedure 3 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and *N*,*N*-dimethylacetamide (87.0 mg, 1 mmol) and purified using flash chromatography (petroleum ether as eluent) to give 19.9 mg of the title compound (yellow oil); 51% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.54 – 7.47 (m, 3H), 7.40 – 7.23 (m, 6H), 4.97 – 4.84 (m, 2H), 4.76 – 4.64 (m, 2H), 3.05 – 3.01 (m, 3H), 3.00 (s, 2H), 2.08 – 2.00 (m, 2H), 1.67 (s, 2H), 1.21 (s, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.6, 135.0, 134.0, 132.4, 131.5, 129.4, 129.0, 127.3, 57.8, 51.7, 35.2, 32.8, 21.9, 20.7; **HRMS (ESI)** calcd $C_{10}H_{13}NOS$ $[M + H]^+$: 196.0791 found: 196.0789.



S-phenyl benzothioate (84): Followed the general procedure 3 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and Benzaldehyde (106.1 mg, 1 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 10:1) to give 20.6 mg of the title compound (yellow oil); 48% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.08 (d, *J* = 7.5 Hz, 2H), 7.71 – 7.62 (m, 1H), 7.59 – 7.48 (m, 7H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 190.2, 136.6, 135.1, 133.7, 129.6, 129.3, 128.8, 127.5; **HRMS (ESI)** calcd $C_{13}H_{10}OS$ $[M + H]^+$: 215.0525 found: 215.0527.

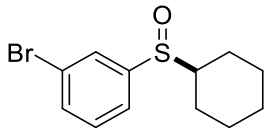


(cyclohexylsulfinyl)benzene (85): Followed the general procedure 4 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and cyclohexane (84.1 mg, 1 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 4:1) to give 36.6 mg of the title compound (yellow oil); 88% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 – 7.58 (m, 2H), 7.58 – 7.48 (m, 3H), 2.69 – 2.51 (m, 1H), 1.90 – 1.83 (m, 4H), 1.72 – 1.64 (m, 1H), 1.52 – 1.35 (m, 2H), 1.34 – 1.23 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.8, 130.9, 128.9, 125.0, 63.2, 26.3, 25.6, 25.4, 25.3, 24.0; **HRMS (ESI)** calcd $C_{12}H_{16}OS$ $[M + H]^+$: 209.0995 found: 209.0992.

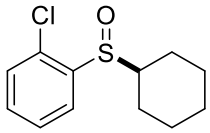


1-(cyclohexylsulfinyl)-4-fluorobenzene (86): Followed the general procedure 4 with *S*-(4-fluorophenyl) benzenesulfonothioate (53.2 mg, 0.2 mmol) and cyclohe xane (84.1 mg, 1 mmol) and purified using flash chromatography (petroleum et her/EtOAc = 4:1) to give 25.3 mg of the title compound (yellow oil); 56% yi eld. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65 – 7.56 (m, 2H), 7.27 – 7.20 (m, 2 H), 2.64 – 2.51 (m, 1H), 1.91 – 1.83 (m, 4H), 1.72 – 1.63 (m, 1H), 1.50 – 1.

20 (m, 5H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.3 (d, *J* = 251.2 Hz), 137.2 (d), 127.2 (d, *J* = 8.8 Hz), 116.3 (d, *J* = 22.4 Hz), 63.3, 26.1, 25.5, 25.4, 25. 3, 24.1; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -108.76(s, 1F); **HRMS (ESI)** calcd $C_{12}H_{15}FOS$ $[M + H]^+$: 227.0900 found: 227.0903.

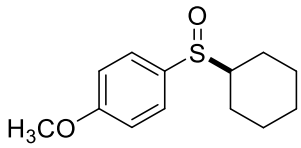


(*S*)-1-bromo-3-(cyclohexylsulfinyl)benzene (87): Followed the general procedure 4 with *S*-(3-bromophenyl) benzenesulfonothioate (65.4 mg, 0.2 mmol) and cycl ohexane (84.1 mg, 1 mmol) and purified using flash chromatography (petroleu m ether/EtOAc = 4:1) to give 32.0 mg of the title compound (yellow oil); 56% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 1.6 Hz, 1H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.44 – 7.36 (m, 1H), 2.58 (tt, *J* = 1 1.9, 3.5 Hz, 1H), 1.95 – 1.83 (m, 4H), 1.81 – 1.74 (m, 1H), 1.71 – 1.65 (m, 1H), 1.47 – 1.42 (m, 1H), 1.31 – 1.21 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 144.2, 134.0, 130.3, 127.7, 123.6, 123.3, 63.2, 26.3, 25.6, 25.3, 25.3, 23.7; **HRMS (ESI)** calcd $C_{12}H_{15}{}^{79}BrOS$ $[M + H]^+$: 287.0100 found: 287.0104.

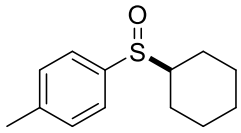


(*S*)-1-chloro-2-(cyclohexylsulfinyl)benzene (88): Followed the general procedure 4 with *S*-(2-chlorophenyl) benzenesulfonothioate (55.6 mg, 0.2 mmol)) and cyclohexane (84.1 mg, 1 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 4:1) to give 25.6 mg of the title compound (yellow oil); 53% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.67 (d, *J* = 7.6 Hz, 1H), 7.40 – 7.33 (m, 1H), 7.32 – 7.27 (m, 1H), 7.26 – 7.11 (m, 1H), 2.82 – 2.67 (m, 1H), 1.94 (d, *J* = 11.8 Hz, 1H), 1.82 – 1.64 (m, 2H), 1.59 – 1.47 (m, 2H), 1.47 – 1.35 (m, 1H), 1.34 – 1.03 (m, 4H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 139.88, 131.62, 130.61, 129.64, 127.28, 127.15, 59.78, 27.32, 25.89, 25.16, 21.93;

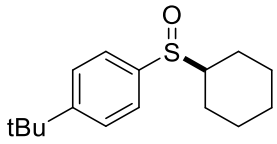
HRMS (ESI) calcd $C_{12}H_{15}{}^{35}ClOS$ $[M + H]^+$: 243.0605 found: 243.0605.



1-(cyclohexylsulfinyl)-4-methoxybenzene (89): Followed the general procedure 4 with *S*-(4-methoxyphenyl) benzenesulfonothioate (56.0 mg, 0.2 mmol) and cyclohexane (84.1 mg, 1 mmol)) and purified using flash chromatography (petroleum ether/EtOAc = 10:1) to give 27.6 mg of the title compound (yellow oil); 58% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.56 (d, *J* = 7.5 Hz, 2H), 7.05 (d, *J* = 8.6 Hz, 2H), 3.89 (s, 3H), 2.63 – 2.51 (m, 1H), 2.00 – 1.80 (m, 4H), 1.51 – 1.32 (m, 2H), 1.32 – 1.15 (m, 4H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 161.9, 132.7, 126.9, 114.5, 63.3, 55.5, 26.0, 25.5, 25.3, 24.7; **HRMS (ESI)** calcd $C_{13}H_{18}O_2S$ $[M + H]^+$: 239.1100 found: 239.1098.

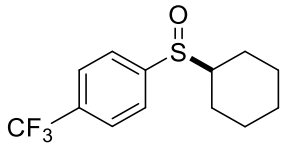


1-(cyclohexylsulfinyl)-4-methylbenzene (90): Followed the general procedure 4 with *S*-(p-tolyl) 4-methylbenzenesulfonothioate (56.2 mg, 0.2 mmol) and cycloh exane (84.1 mg, 1 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 10:1) to give 25.8 mg of the title compound (Colorless oil); 53 % yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.50 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 2.61 – 2.51 (m, 1H), 2.44 (s, 3H), 1.92 – 1.77 (m, 4H), 1.71 – 1.62 (m, 1H), 1.48 – 1.31 (m, 2H), 1.30 – 1.16 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.4, 138.5, 129.6, 125.1, 63.2, 26.2, 25.6, 25.5, 25.3, 24.2, 21.4; **HRMS (ESI)** calcd $C_{13}H_{18}OS$ $[M + H]^+$: 223.1151 found: 223.1149.

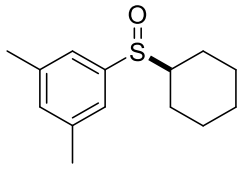


1-(tert-butyl)-4-(cyclohexylsulfinyl)benzene (91): Followed the general procedur

e 4 with *S*-(4-(tert-butyl)phenyl) benzenesulfonothioate (61.2 mg, 0.2 mmol) an d cyclohexane (84.1 mg, 1 mmol)) and purified using flash chromatography (p etroleum ether/EtOAc = 10:1) to give 35.9 mg of the title compound (yellow oil); 68% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.60 – 7.47 (m, 4H), 2.65 – 2.52 (m, 1H), 1.96 – 1.79 (m, 4H), 1.72 – 1.63 (m, 1H), 1.55 – 1.39 (m, 2 H), 1.37 (s, 9H), 1.33 – 1.21 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 154.5, 138.6, 126.0, 124.9, 63.1, 35.0, 31.2, 26.2, 25.6, 25.5, 25.3, 24.3; **HRMS (ES I)** calcd $C_{16}H_{24}OS$ $[M + H]^+$: 265.1621 found: 265.1622.

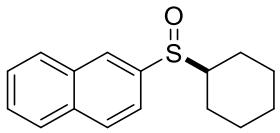


1-(cyclohexylsulfinyl)-4-(trifluoromethyl)benzene (92):Followed the general pro cedure 4 with *S*-(4-(trifluoromethyl)phenyl)4-(trifluoromethyl)benzenesulfonothioat e (77.1 mg, 0.2 mmol) and cyclohexane (84.1 mg, 1 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 10:1) to give 22.6 mg of the title compound (yellow oil); 41% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.78 (d, *J* = 7.3 Hz, 2H), 7.71 (d, *J* = 7.4 Hz, 2H), 2.65 – 2.52 (m, 1H), 1.95 – 1 .79 (m, 3H), 1.73 – 1.60 (m, 2H), 1.54 – 1.39 (m, 2H), 1.32 – 1.13 (m, 4H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.3, 132.9 (q, *J* = 32.8 Hz), 125.9 (q, *J* = 3.6 Hz), 125.4, 77.4, 77.06, 76.74, 63.3, 26.4, 25.6, 25.3 (q, *J* = 2.4 Hz), 2 3.5; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.75 (s, 3F); **HRMS (ESI)** calcd $C_{13}H_{15}F_3OS$ $[M + H]^+$: 277.0868 found: 277.0869.

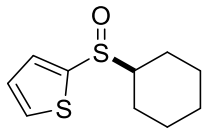


1-(cyclohexylsulfinyl)-3,5-dimethylbenzene (93): Followed the general procedur e 4 with *S*-(3,5-dimethylphenyl) benzenesulfonothioate (56.0 mg, 0.2 mmol) and cyclohexane (84.1 mg, 1 mmol)) and purified using flash chromatography (pet

roleum ether/EtOAc = 10:1) to give 27.4 mg of the title compound (yellow oi l); 58% yield. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.21 (s, 2H), 7.13 (s, 1H), 2.63 – 2.52 (m, 1H), 2.41 (s, 6H), 1.95 – 1.81 (m, 4H), 1.72 – 1.63 (m, 1H), 1.52 – 1.36 (m, 2H), 1.32 – 1.17 (m, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 141.6, 138.8, 132.7, 122.5, 63.0, 26.4, 25.6, 25.5, 25.3, 24.1, 21.3; **HRMS (ESI)** calcd $C_{14}H_{20}OS$ $[M + H]^+$: 237.1308 found: 237.1305.

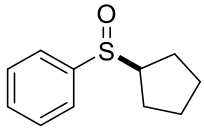


2-(cyclohexylsulfinyl)naphthalene (94): Followed the general procedure 4 with *S*-(naphthalen-2-yl) benzenesulfonothioate (60.6 mg, 0.2 mmol) and cyclohexane (84.1 mg, 1 mmol)) and purified using flash chromatography (petroleum ether/EtOAc = 10:1) to give 26.3 mg of the title compound (yellow oil); 51% yield. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.17 (s, 1H), 8.03 – 7.91 (m, 3H), 7.67 – 7.58 (m, 3H), 2.76 – 2.61 (m, 1H), 1.96 – 1.81 (m, 4H), 1.70 – 1.68 (m, 1H), 1.57 – 1.44 (m, 2H), 1.31 – 1.24 (m, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 139.0, 134.5, 132.7, 129.0, 128.5, 128.0, 127.7, 127.2, 125.7, 120.8, 63.0, 30.9, 26.4, 25.6, 25.4, 25.3, 24.0; **HRMS (ESI)** calcd $C_{16}H_{18}OS$ $[M + H]^+$: 258.1151 found: 258.1151.

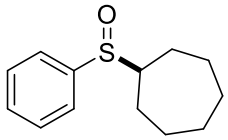


2-(cyclohexylsulfinyl)thiophene (95): Followed the general procedure 4 with *S*-(thiophen-2-yl) benzenesulfonothioate (51.3 mg, 0.2 mmol) and cyclohexane (84.1 mg, 1 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 10:1) to give 20.1 mg of the title compound (yellow oil); 47% yield. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.76 – 7.65 (m, 1H), 7.54 – 7.38 (m, 1H), 7.22 – 7.13 (m, 1H), 3.02 – 2.76 (m, 1H), 2.30 – 2.19 (m, 1H), 2.03 – 1.83 (m, 2H), 1.72 – 1.67 (m, 2H), 1.39 – 1.24 (m,

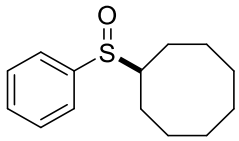
5H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 144.2, 131.0, 130.3, 127.2, 64.8, 25.8, 25.5, 25.3, 25.1; **HRMS (ESI)** calcd $C_{10}H_{14}OS_2$ $[M + H]^+$: 215.0559 found: 215.0558.



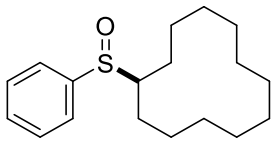
(cyclopentylsulfinyl)benzene (96): Followed the general procedure 4 with *S*-(p-t olyl) *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and cyclopentane (70 .1 mg, 1 mmol) and purified using flash chromatography (petroleum ether/EtO Ac = 10:1) to give 20.9 mg of the title compound (Colorless oil); 54% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.64 (d, *J* = 6.0 Hz, 2H), 7.56 – 7.42 (m, 3 H), 3.19 – 3.04 (m, 1H), 2.17 – 2.02 (m, 1H), 1.84 – 1.59 (m, 7H); **^{13}C NM R (101 MHz, $CDCl_3$)** δ 143.7, 130.9, 129.0, 124.6, 77.3, 77.0, 76.7, 64.4, 27. 6, 26.1 25.6, 24.9; **HRMS (ESI)** calcd $C_{11}H_{14}OS$ $[M + H]^+$: 195.0838 found: 195.0839.



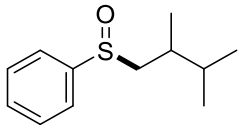
(phenylsulfinyl)cycloheptane (97): Followed the general procedure 4 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and cycloheptane (98.1 mg, 1 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 10:1) to give 21.7 mg of the title compound (yellow oil); 49% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.69 – 7.58 (m, 2H), 7.56 – 7.49 (m, 3H), 2.91 – 2.60 (m, 1H), 2.02 – 1.90 (m, 2H), 1.80 – 1.71 (m, 2H), 1.61 – 1.41 (m, 8H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.0, 131.0, 128.8, 125.3, 64.3, 28.4, 28.3, 27.4, 26.3, 26.0, 25.8; **HRMS (ESI)** calcd $C_{13}H_{18}OS$ $[M + H]^+$: 223.1151 found: 223.1153.



(phenylsulfinyl)cyclododecane (98): Followed the general procedure 4 with *S*-p henyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and cyclooctane (112.2 mg, 1 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 10: 1) to give 24.0 mg of the title compound (yellow oil); 51% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.69 – 7.61 (m, 2H), 7.59 – 7.48 (m, 3H), 2.89 – 2.79 (m, 1H), 2.03 – 1.93 (m, 2H), 1.80 – 1.67 (m, 2H), 1.63 – 1.38 (m, 10H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.9 (s), 131.0, 128.8, 125.4, 63.6, 26.3, 26.3, 26.2, 25.6, 25.6, 24.9; **HRMS (ESI)** calcd $C_{14}H_{20}OS$ $[M + H]^+$: 237.1308 fou nd: 237.1310.

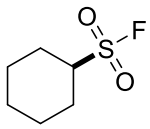


(phenylsulfinyl)cyclododecane (99): Followed the general procedure 4 with *S*-phenyl benzenesulfonothioate (50.0 mg, 0.2 mmol) and cyclododecane (168.3 mg, 1 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 10:1) to give 25.6 mg of the title compound (yellow oil); 44% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.68 – 7.60 (m, 2H), 7.58 – 7.48 (m, 3H), 2.85 – 2.65 (m, 1H), 1.84 – 1.76 (m, 2H), 1.72 – 1.63 (m, 2H), 1.61 – 1.56 (m, 2H), 1.43 – 1.31 (m, 16H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.2, 130.8, 128.9, 125.0, 61.3, 32.5, 24.1, 23.9, 23.9, 23.8, 23.8 23.4, 23.4, 23.2, 22.5, 22.3, 22.1; **HRMS (ESI)** calcd $C_{18}H_{2}8OS$ $[M + H]^+$: 293.1934 found: 293.1935.

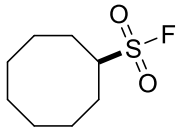


((2,3-dimethylbutyl)sulfinyl)benzene (100): Followed the general procedure 4 with *S*-phenyl benzenesulfonothioate e (50.0 mg, 0.2 mmol) and 2,3-dimethylbutane (86.2 mg, 1 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 10:1)

to give 15.5 mg of the title compound (yellow oil); 37% yiel (d:r = 3:2). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.67 (d, *J* = 6.3 Hz, 2H), 7.55 (d, *J* = 6.7 Hz, 3H), 2.90 – 2.83 (m, 0.57 H), 2.79 – 2.73 (m, 0.77 H), 2.43 (t, *J* = 11.9 Hz, 1H), 2.16 – 2.06 (m, 1H), 1.95 – 1.82 (m, 1H), 1.75 – 1.64 (m, 1H), 1.14 (d, *J* = 6.8 Hz, 2H), 1.03 – 0.98 (m, 1H), 0.95 – 0.80 (m, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 144.8, 144.6, 131.1 130.9, 129.3, 124.1, 123.9, 64.4, 63.6, 34.1, 33.7, 32.5, 31.1, 19.8, 19.6, 18.1, 17.2, 15.6, 15.0; **HRMS (ESI)** calcd $C_{12}H_{18}OS$ $[M + H]^+$: 211.1151 found: 211.1151.

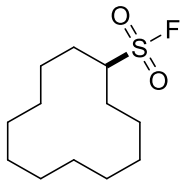


cyclohexanesulfonyl fluoride (101): Followed the general procedure 5 with cyclohexane (84.1 mg, 1 mmol), NFSI (63.1 mg, 0.2 mmol) and DABSO (84.0 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 15:1) to give 23.9 mg of the title compound (Colorless oil); 72% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 3.34 (t, *J* = 12.1 Hz, 1H), 2.33 (d, *J* = 12.0 Hz, 2H), 1.99 (d, *J* = 13.3 Hz, 2H), 1.82 – 1.67 (m, 3H), 1.49 – 1.21 (m, 4H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 61.0 (d, *J* = 12.5 Hz), 26.5, 24.74, 24.69; **^{19}F NMR (376 MHz, $CDCl_3$)** δ 40.83 (s, 1F); **HRMS (ESI)** calcd $C_6H_{11}FO_2S$ $[M + H]^+$: 167.0537 found: 167.0533.



cycloheptanesulfonyl fluoride (102): Followed the general procedure 5 with cycloheptane (98.1 mg, 1 mmol), NFSI (63.1 mg, 0.2 mmol) and DABSO (84.0 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 15:1) to give 19.8 mg of the title compound (Colorless oil); 55% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 3.60 – 3.46 (m, 1H), 2.38 – 2.28 (m, 2H), 2.06 – 1.95 (m, 2H), 1.92 – 1.84 (m, 2H), 1.66 – 1.59 (m, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 62.2 (d, *J* = 10.3 Hz), 26.6, 26.0, 24.8; **^{19}F NMR (376 MHz, $CDCl_3$)** δ 41.06 (s, 1F); **HRMS (ESI)** calcd

$C_8H_{15}FO_2S$ [M + H]$^+$: 195.0850 found: 195.0847.



cyclododecanesulfonyl fluoride (103): Followed the general procedure 5 with cyclododecane (168.3 mg, 1 mmol), NFSI (63.1 mg, 0.2 mmol) and DABSO (84.0 mg, 0.2 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 15:1) to give 24.5 mg of the title compound (Colorless oil); 49% yield; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 3.48 (s, 1H), 2.02 – 1.95 (m, 2H), 1.65 – 1.54 (m, 4H), 1.46 – 1.34 (m, 16H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 59.4 (d, *J* = 10.3 Hz), 25.1, 23.7, 23.4, 23.3, 21.9. **^{19}F NMR (376 MHz, $CDCl_3$)** δ 45.9 (s, 1F); **HRMS (ESI)** calcd $C_{12}H_{23}FO_2S$ [M + H]$^+$: 251.1476 found: 251.1478.

Reference:

(1) Cao, L.; Luo, S.-H.; Jiang, K.; Hao, Z.-F.; Wang, B.-W.; Pang, C.-M.; Wang, Z.-Y. Disproportionate Coupling Reaction of Sodium Sulfinates Mediated by BF_3 OEt_2: An Approach to Symmetrical/Unsymmetrical Thiosulfonates. *Organic Letters* **2018**, *20* (16), 4754-4758.

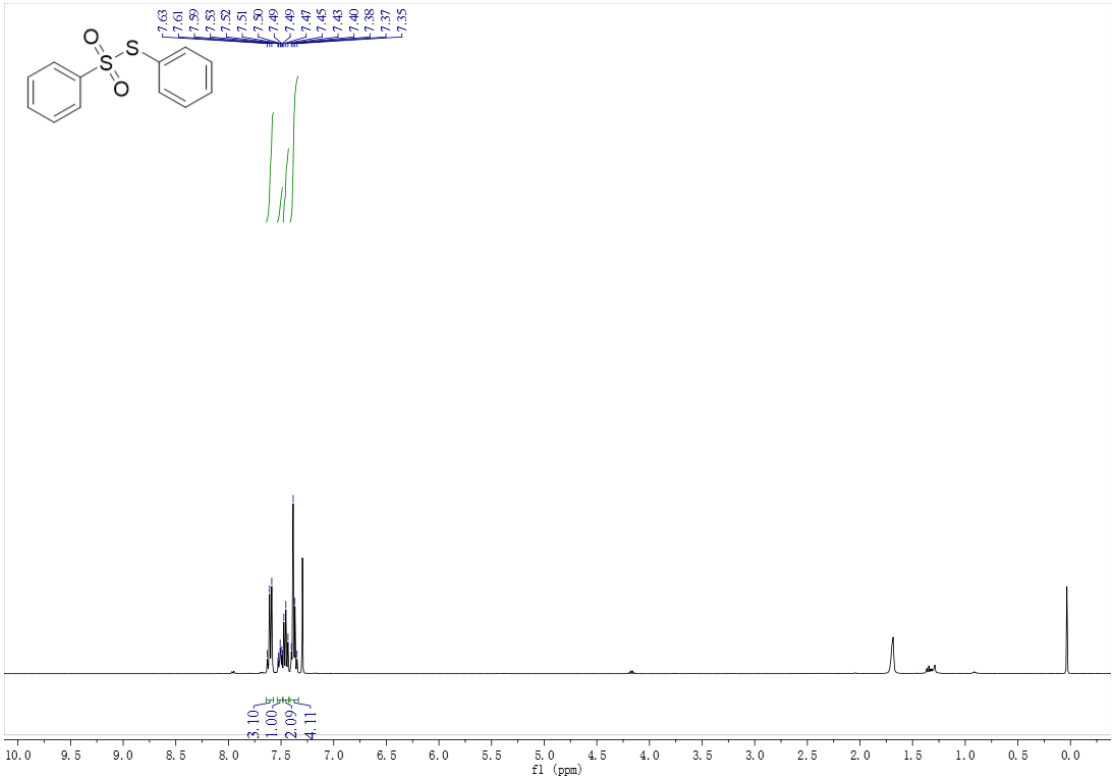
(2) Delarue Bizzini, L.; Zwick, P.; Mayor, M. Preparation of Unsymmetrical Disulfides from Thioacetates and Thiosulfonates. *European Journal of Organic Chemistry* **2019**, *2019* (41), 6956-6960..

(3) Ren, H.; Zhang, P.; Xu, J.; Ma, W.; Tu, D.; Lu, C.-S.; Yan, H. Direct B–H Functionalization of Icosahedral Carboranes via Hydrogen Atom Transfer. *Journal of the American Chemical Society* **2023**, *145* (13), 7638-7647.

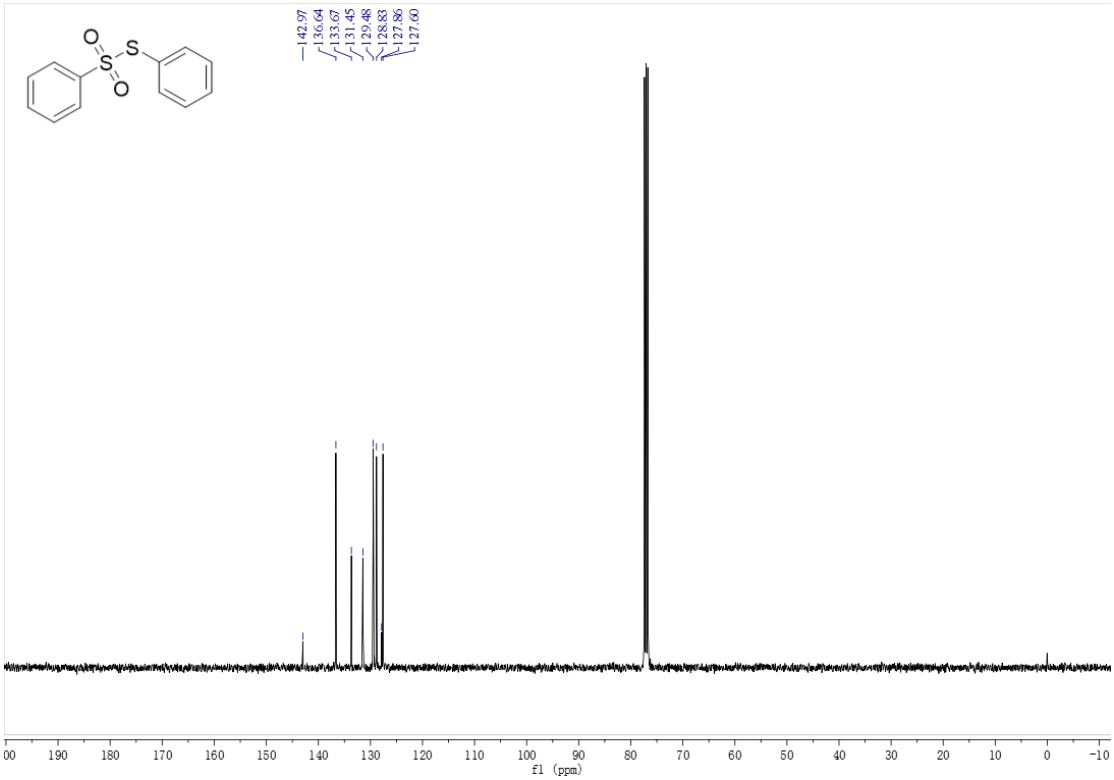
(4) Tu, J.-L.; Gao, H.; Luo, M.; Zhao, L.; Yang, C.; Guo, L.; Xia, W. Iron-catalyzed ring-opening of cyclic carboxylic acids enabled by photoinduced ligand-to-metal charge transfer. *Green Chemistry* **2022**, *24* (14), 5553-5558.

8. NMR Spectra for the substrates and products

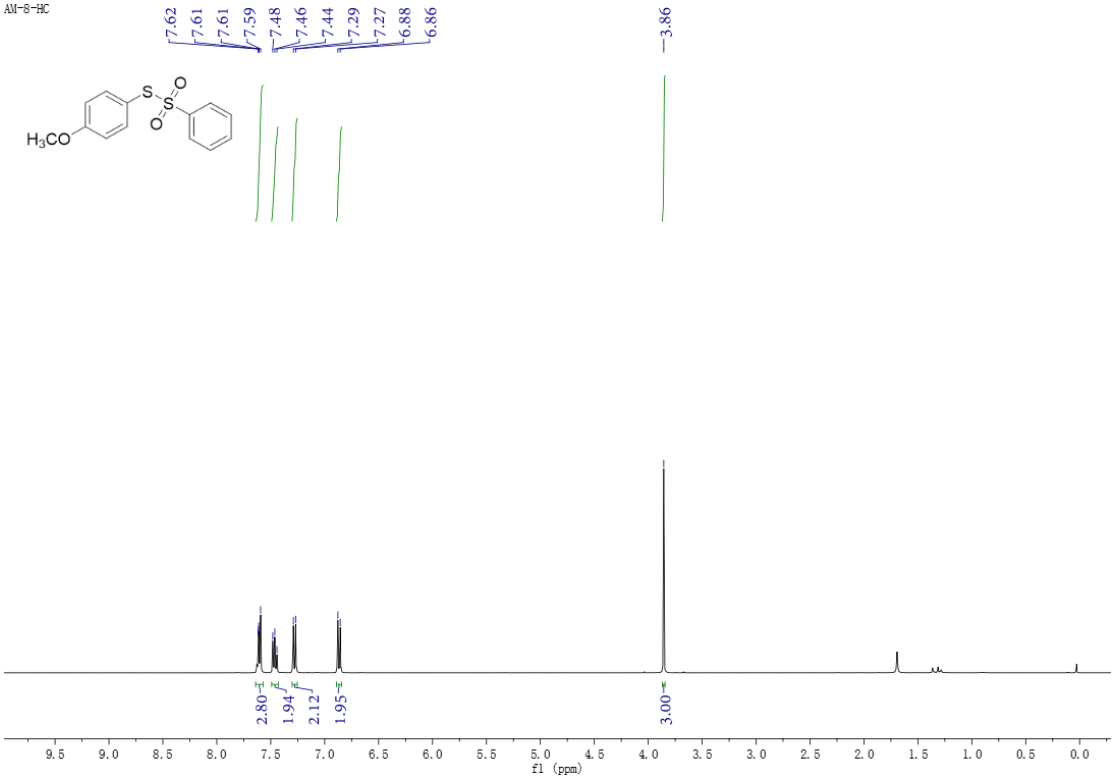
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S1**



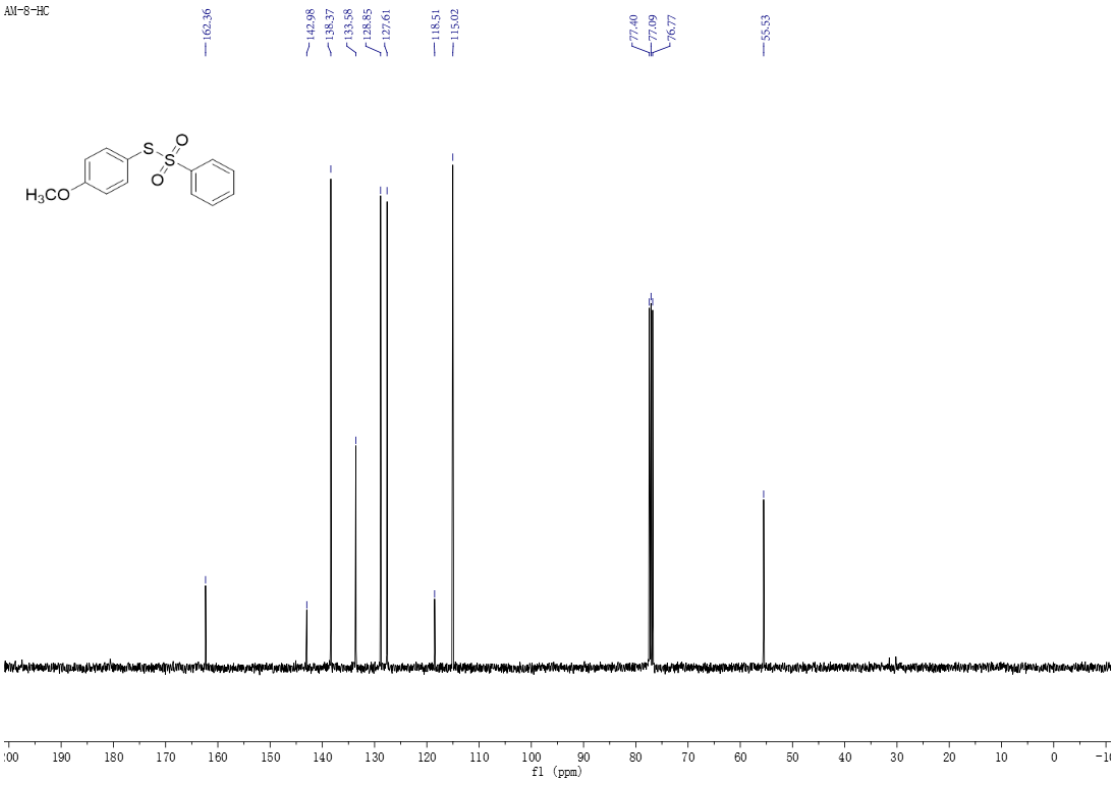
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **S1**



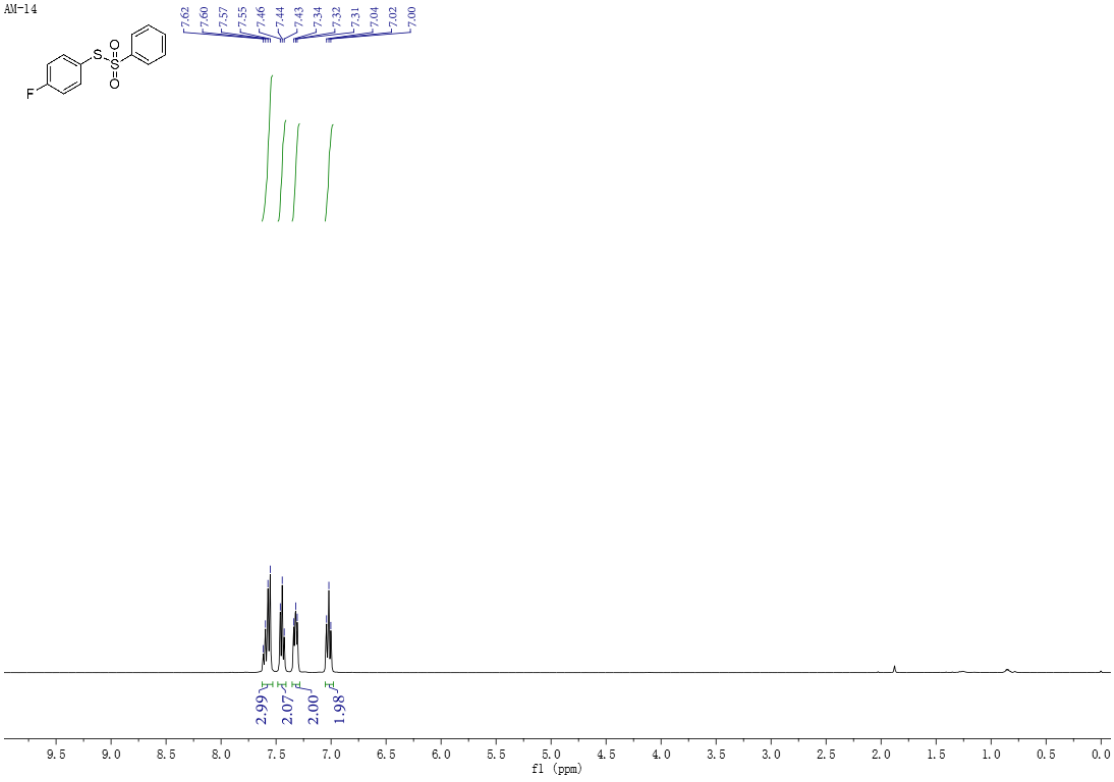
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S2**



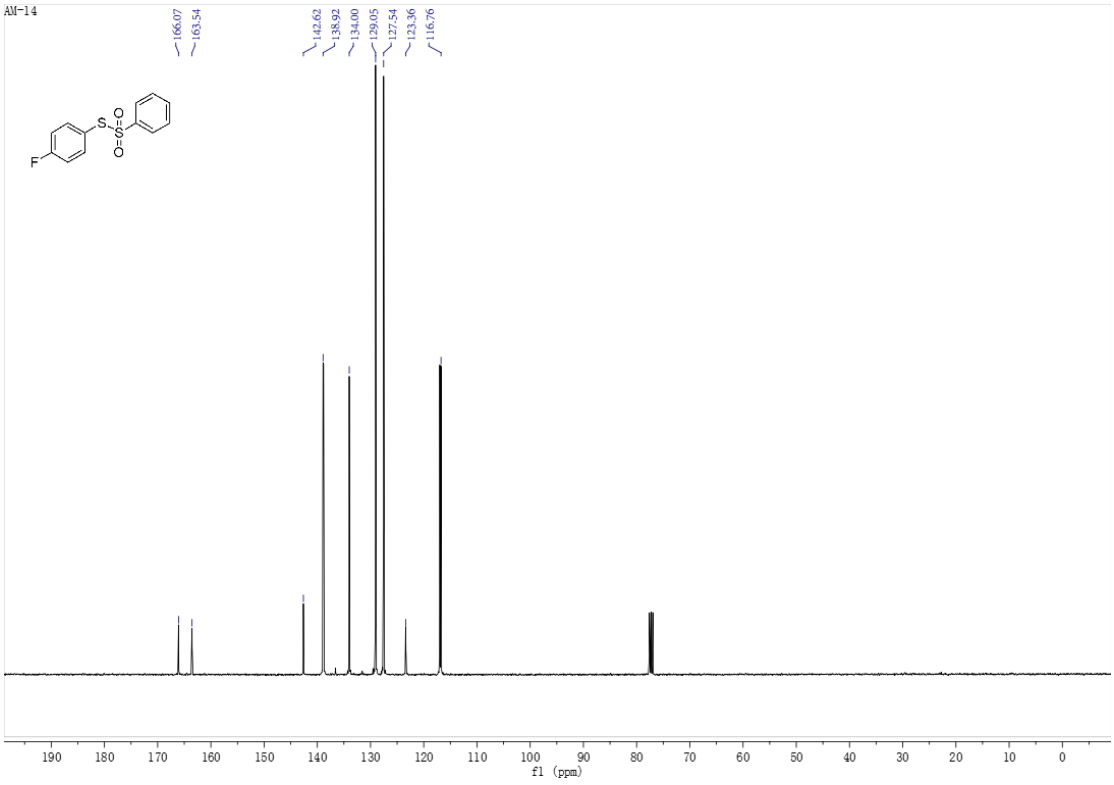
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **S2**



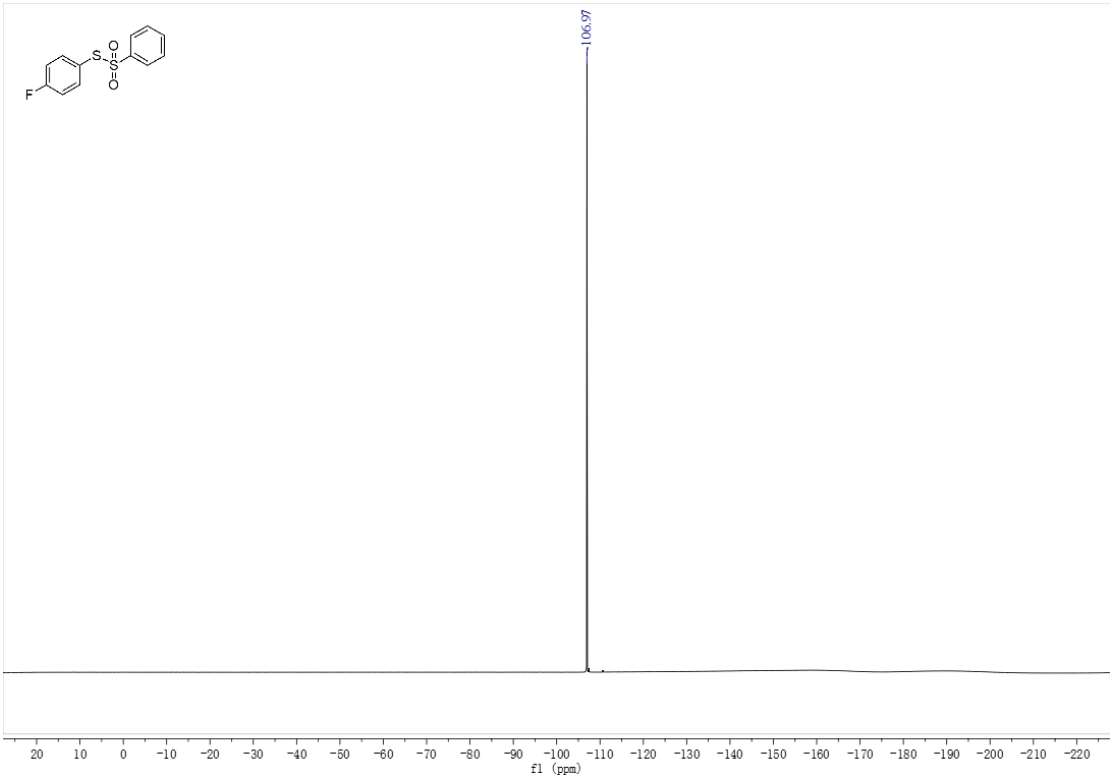
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S5**



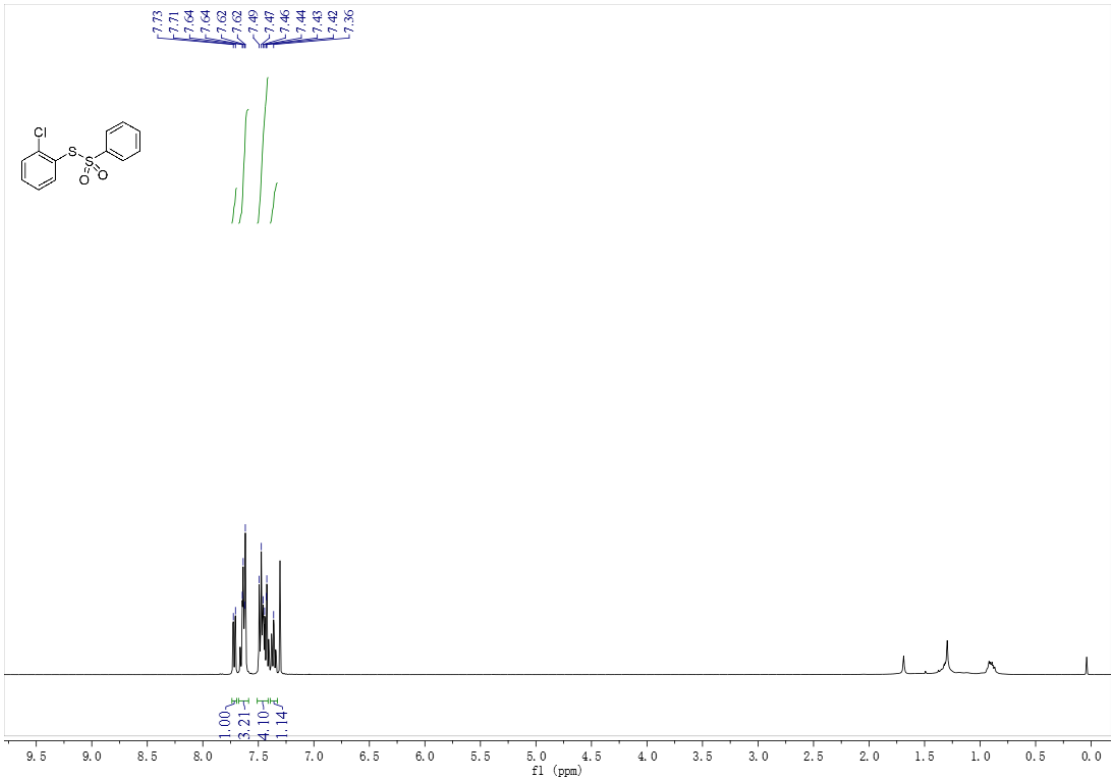
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **S5**



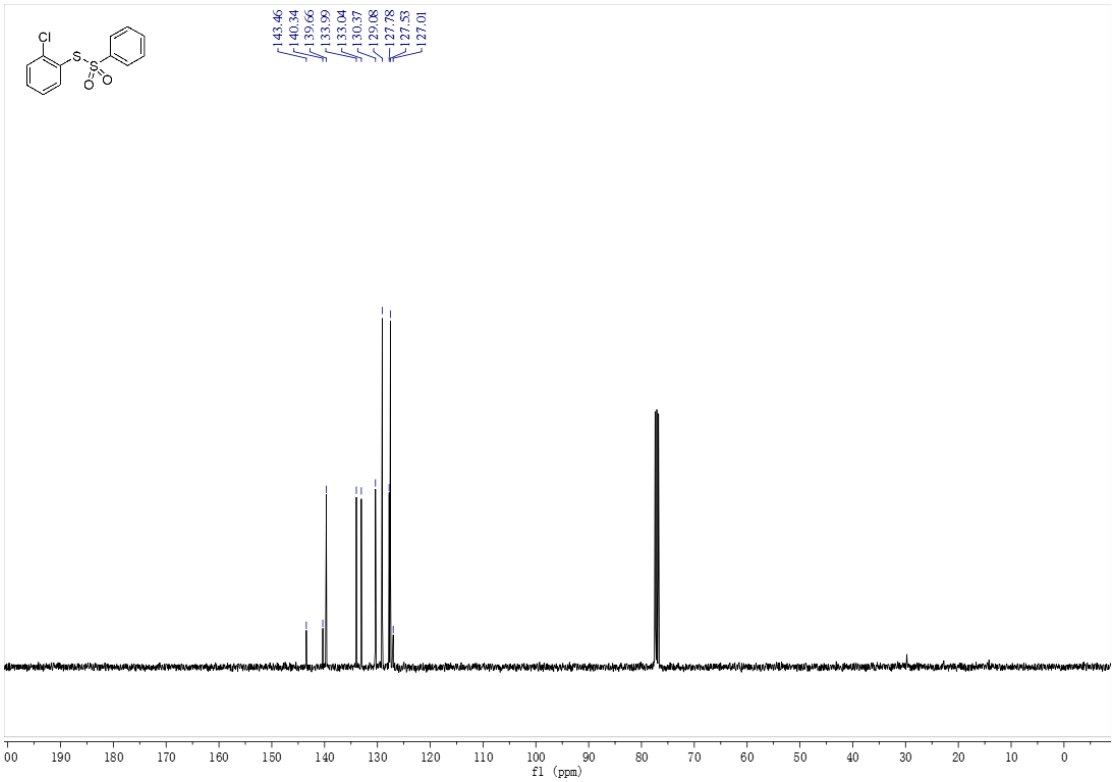
^{19}F NMR spectrum (376 MHz, $CDCl_3$，23 ℃) of **S5**



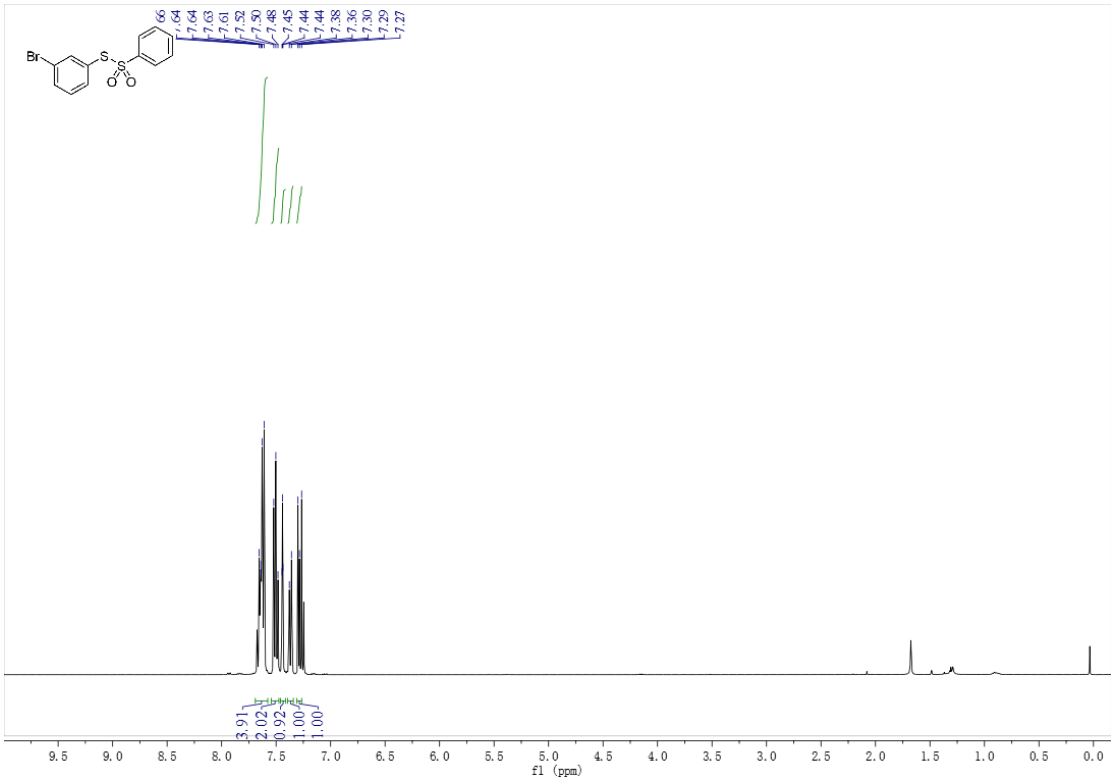
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S6**



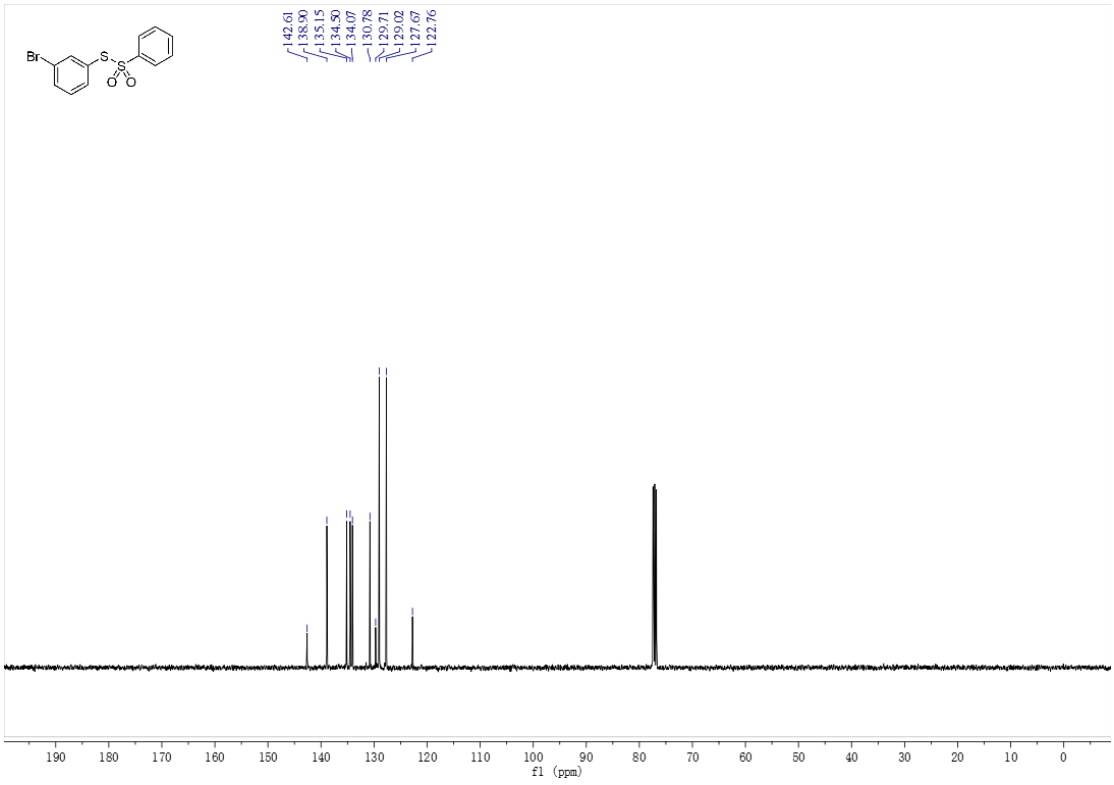
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **S6**



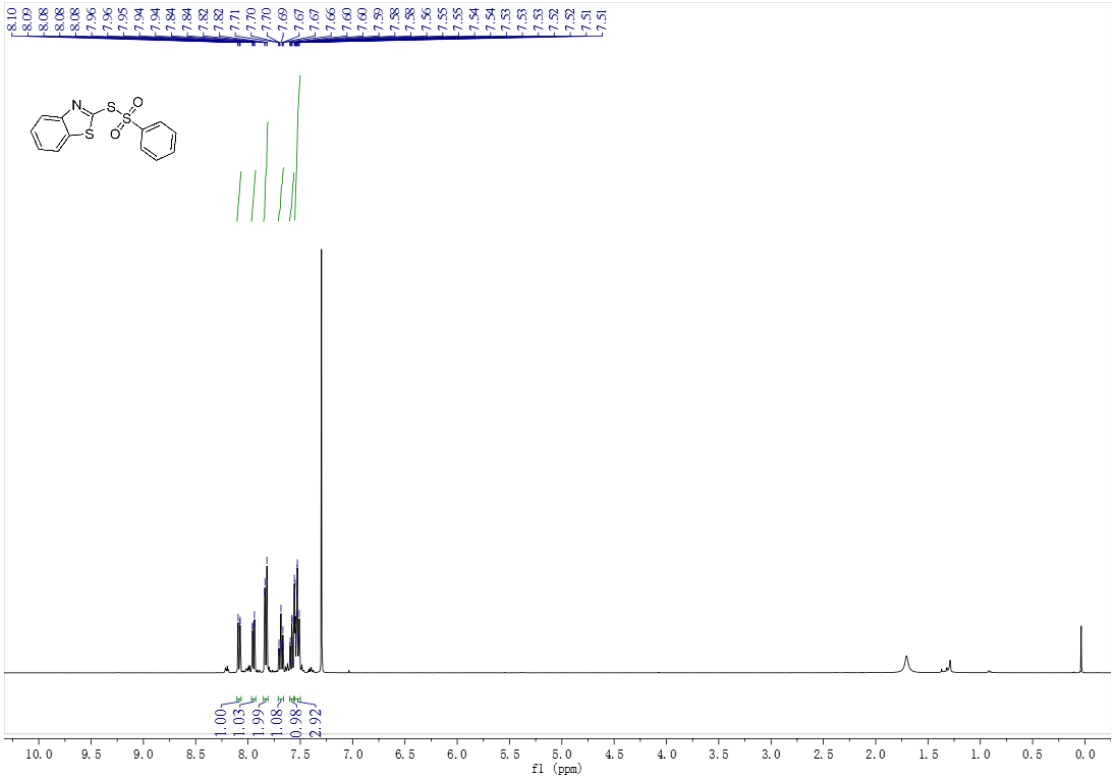
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S7**



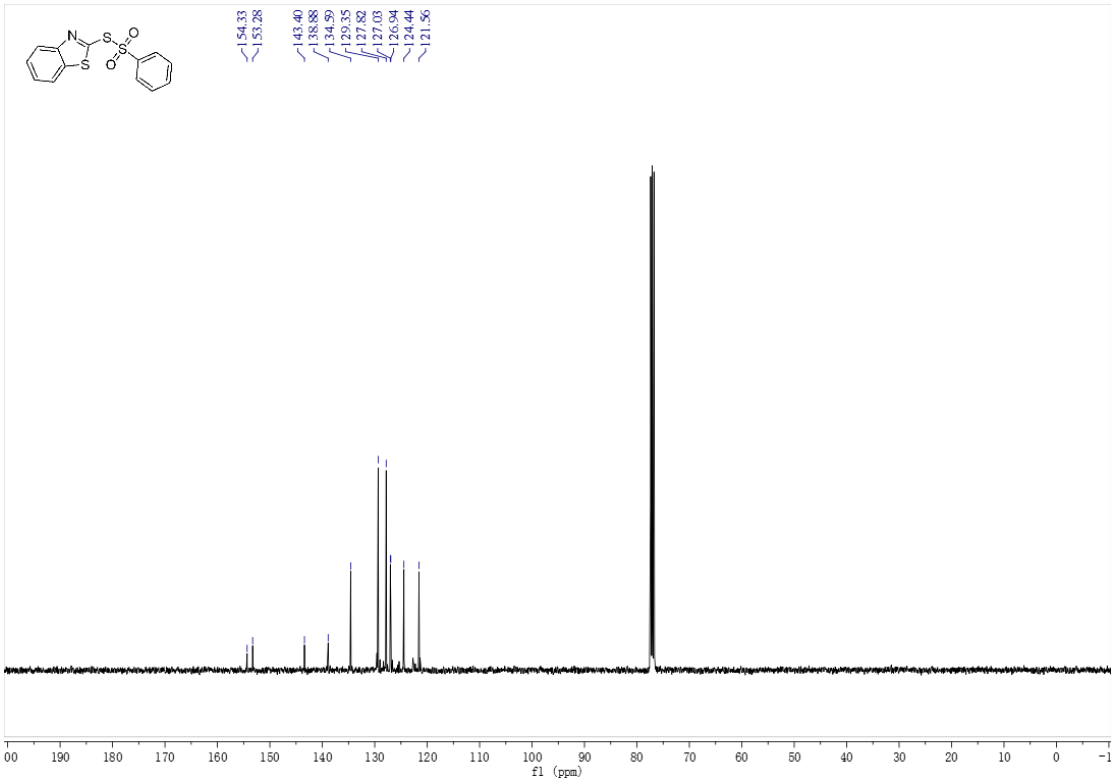
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **S7**



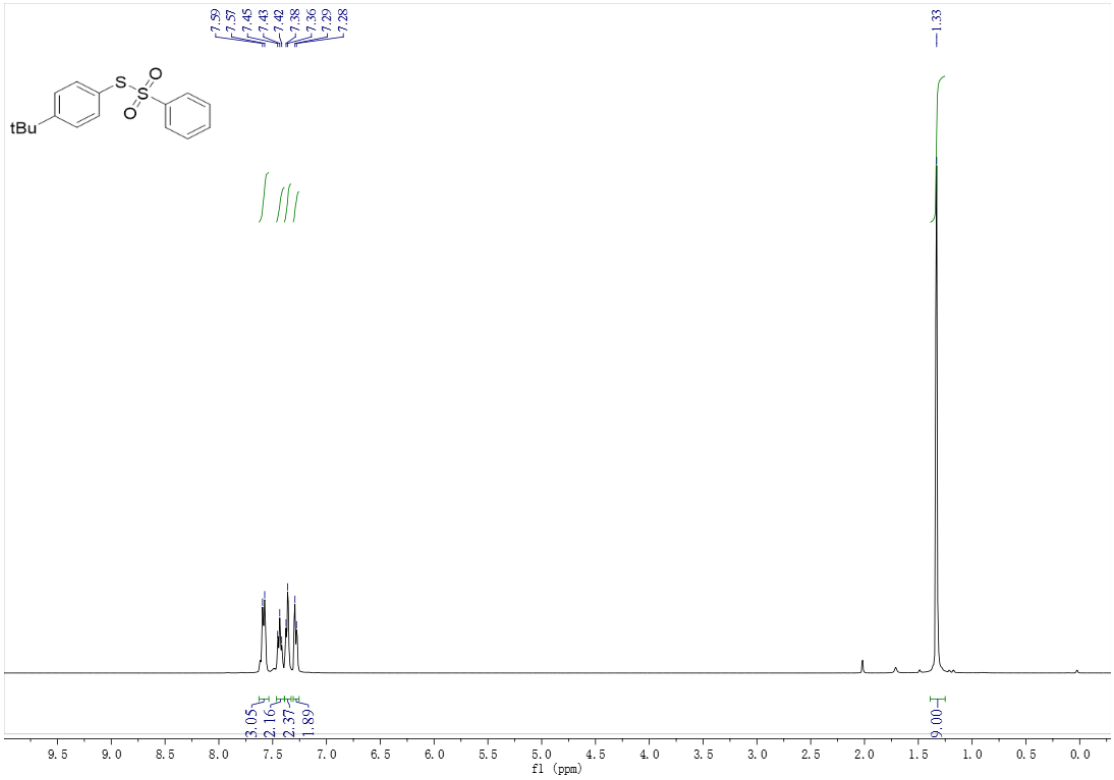
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S8**



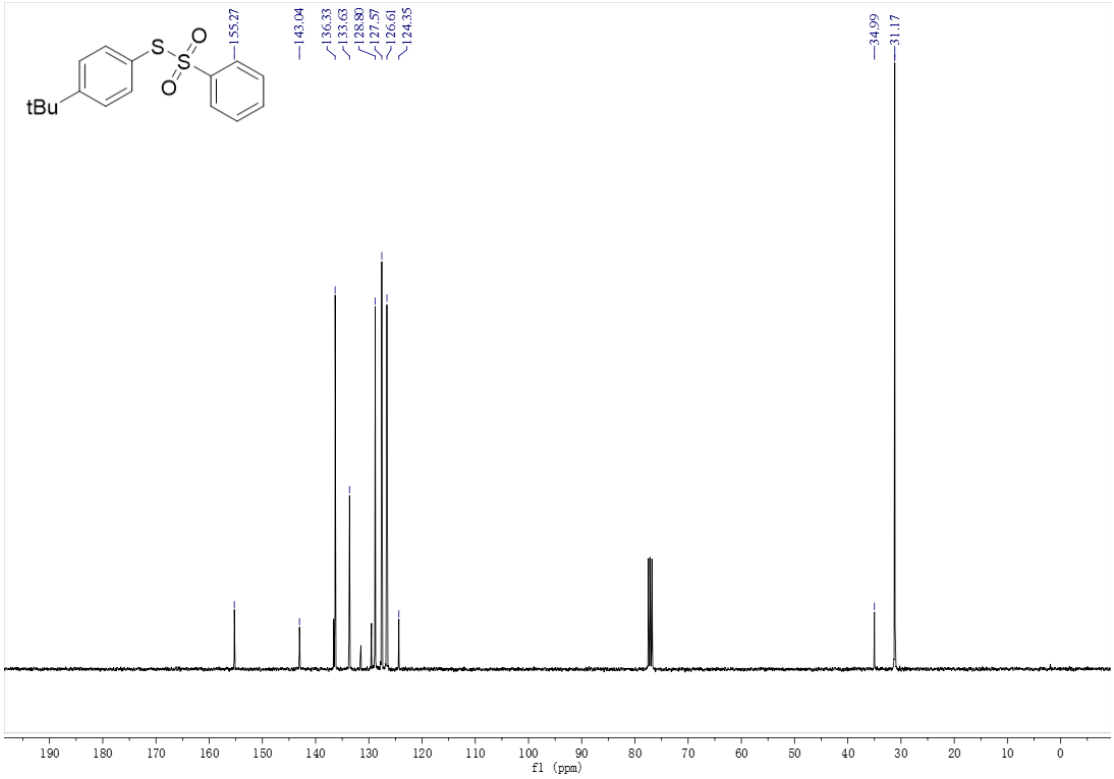
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **S8**



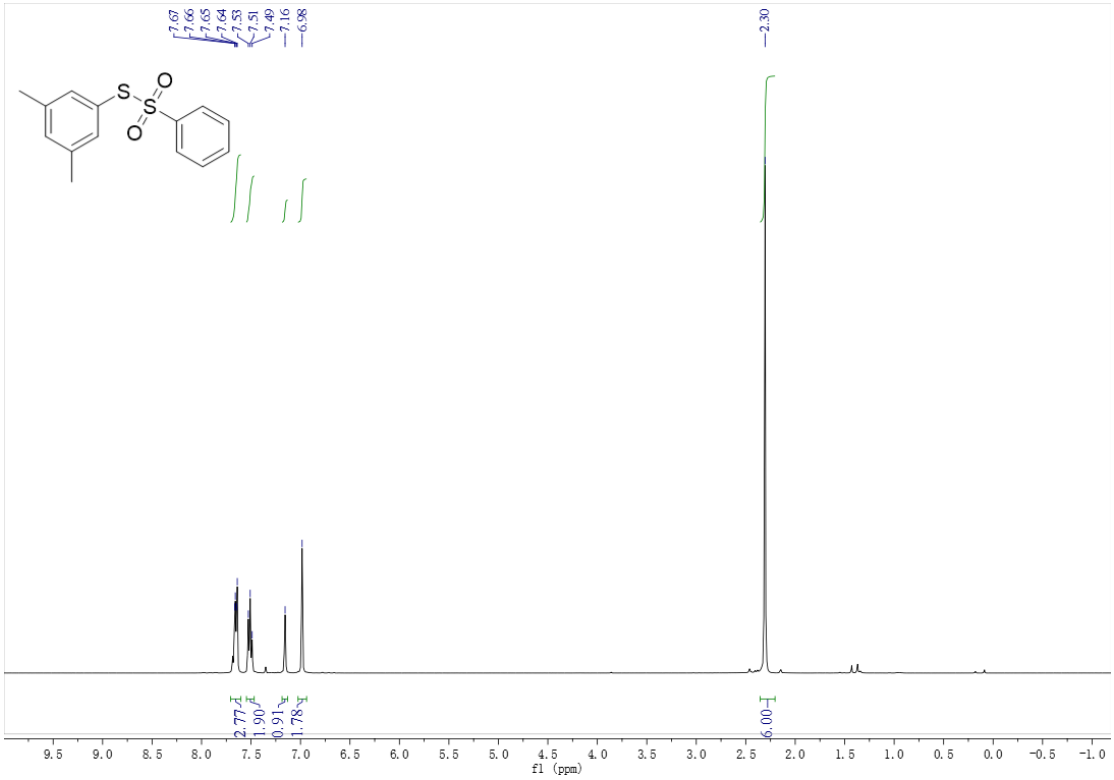
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S10**



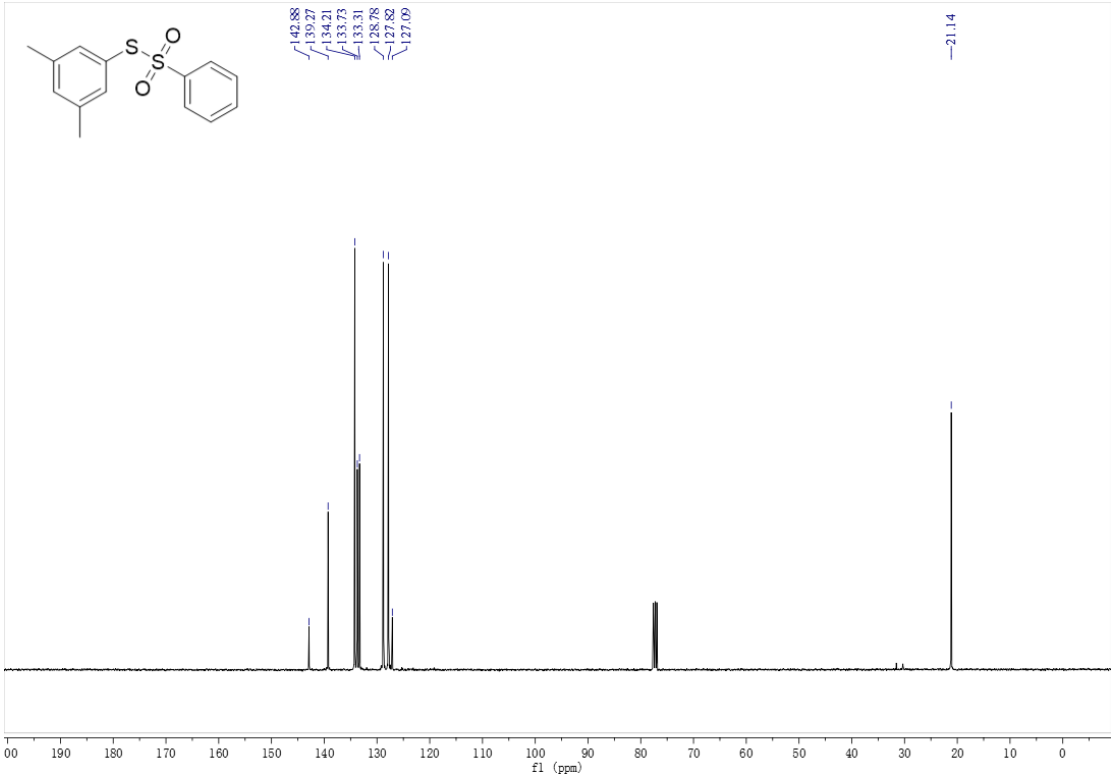
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **S10**



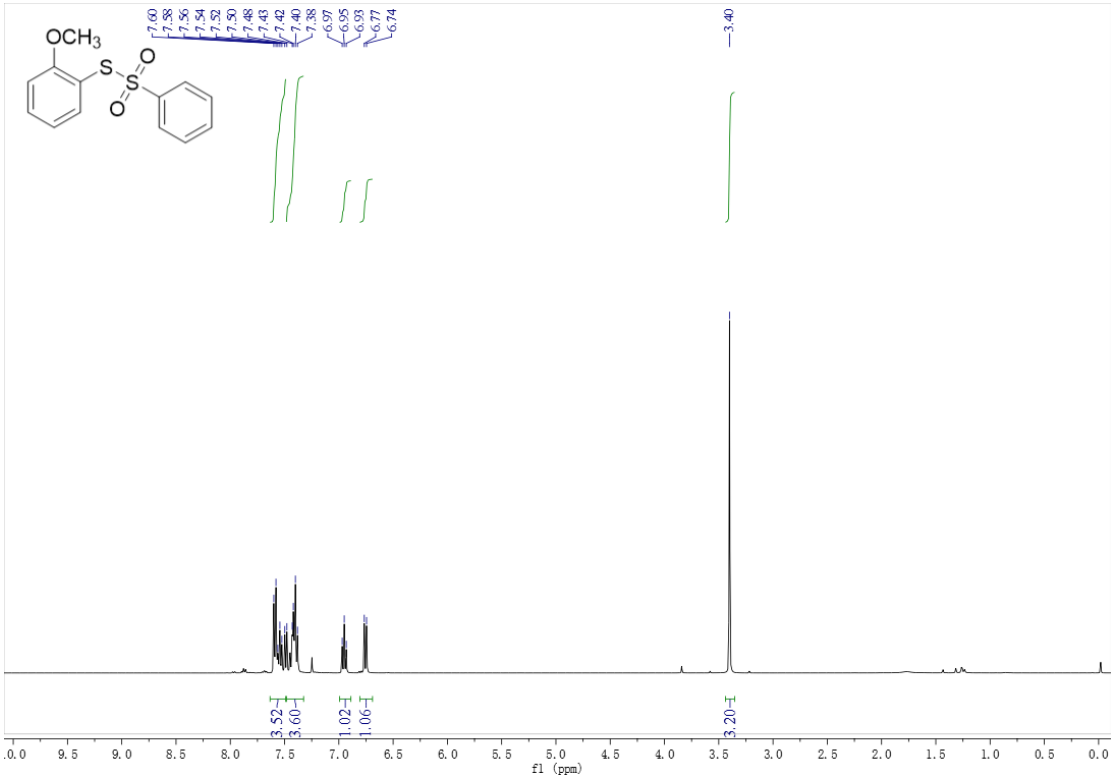
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S35**



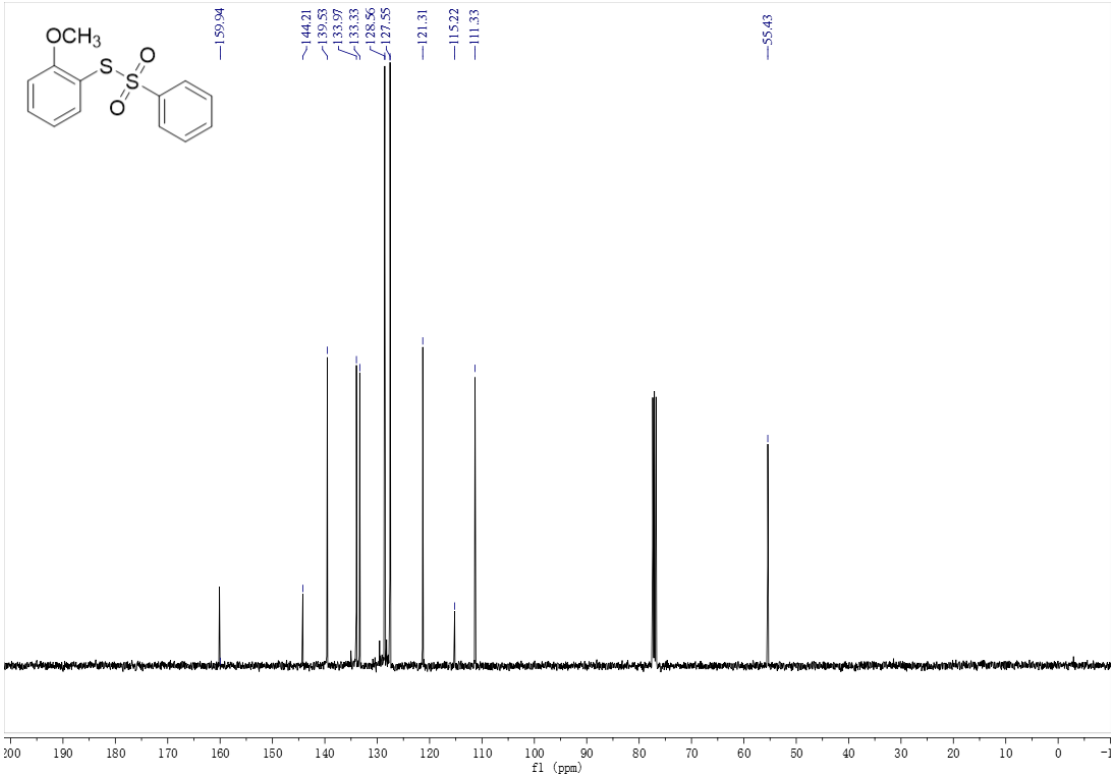
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of S**35**



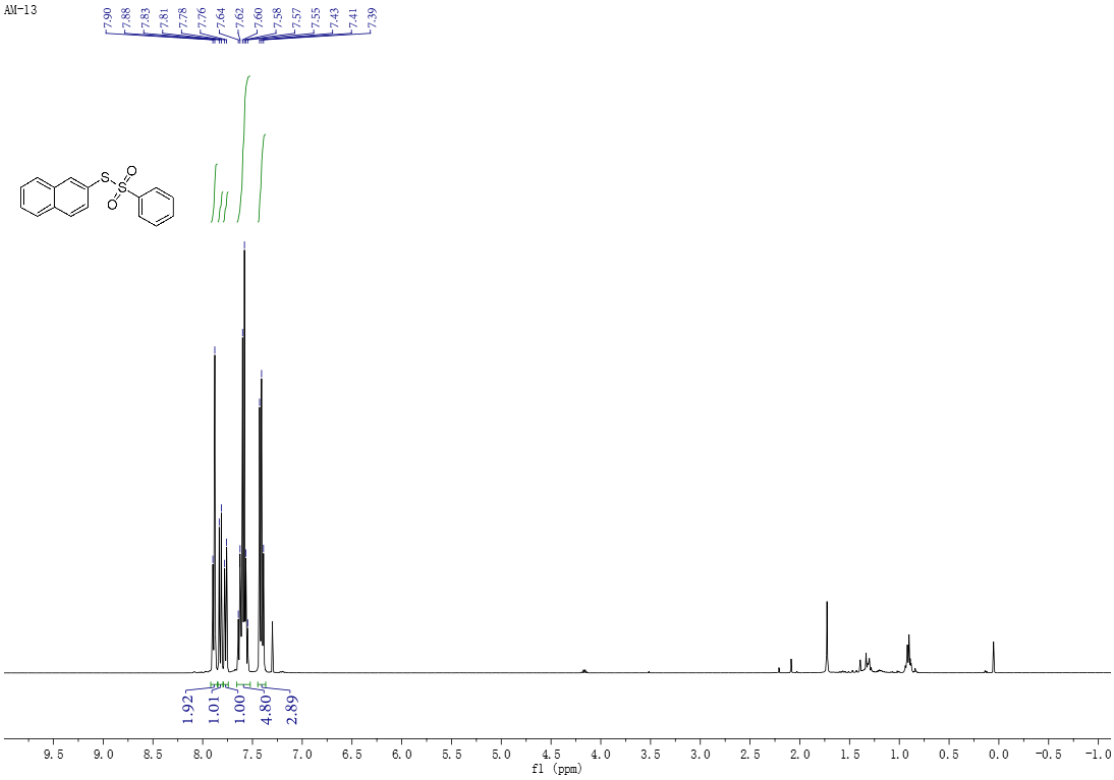
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S42**



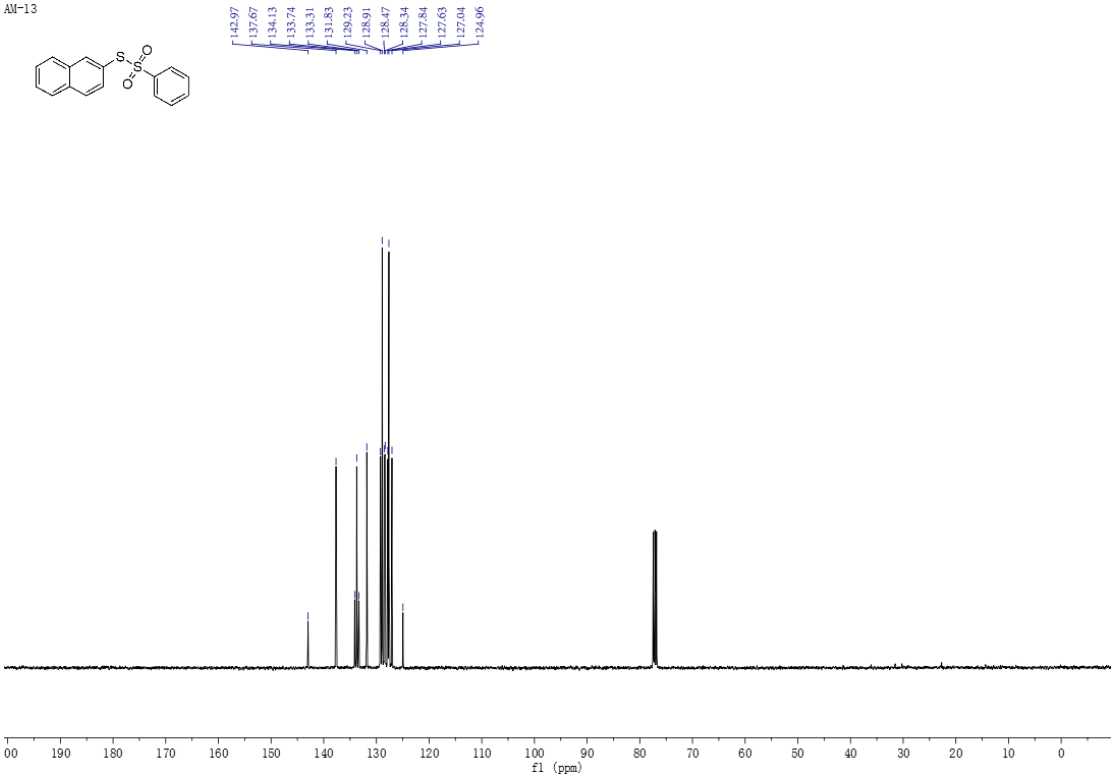
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **S42**



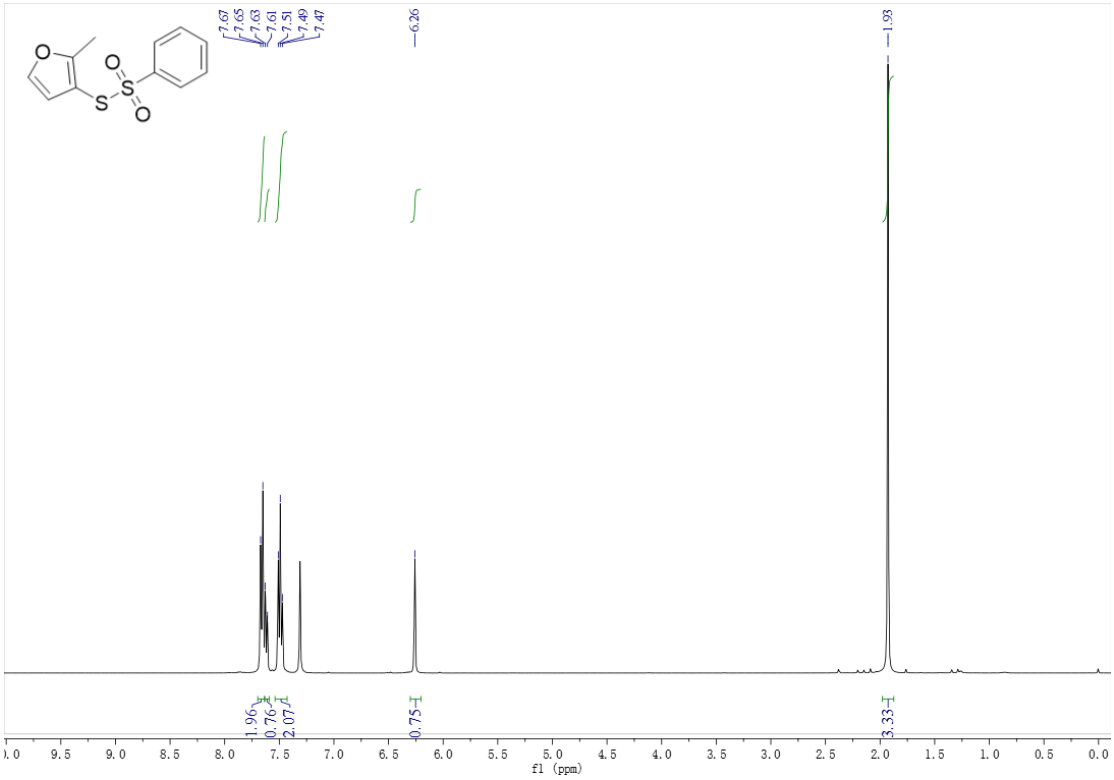
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S46**



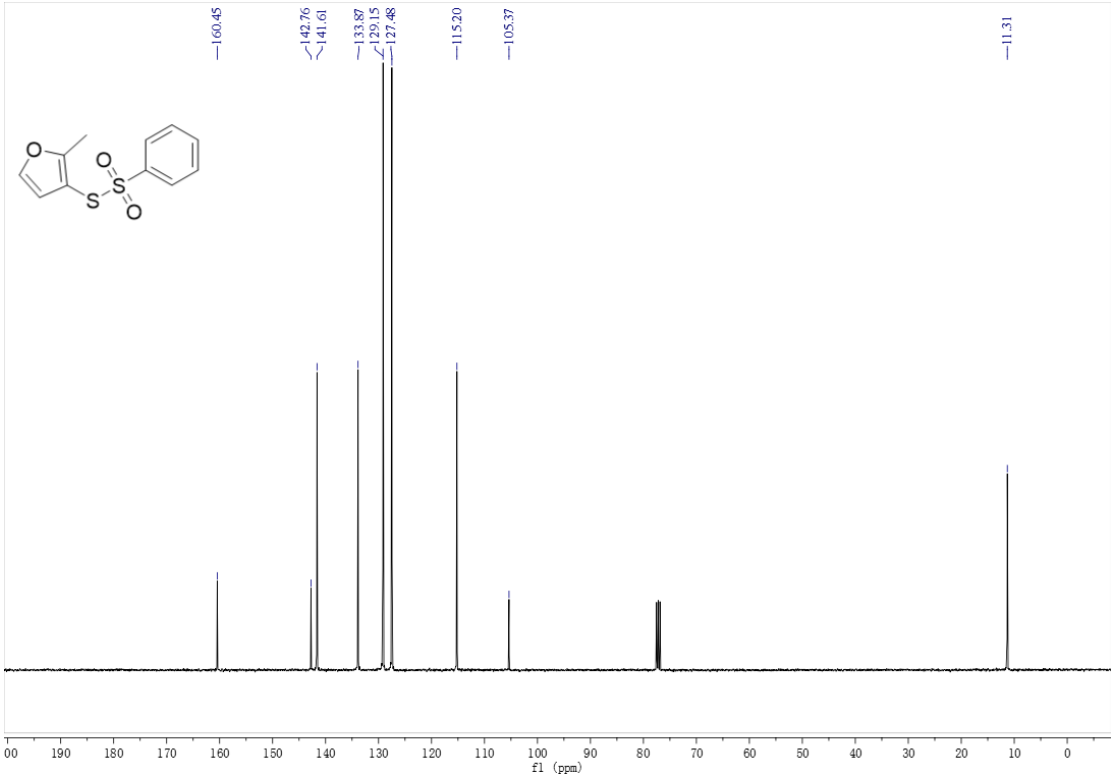
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **S46**



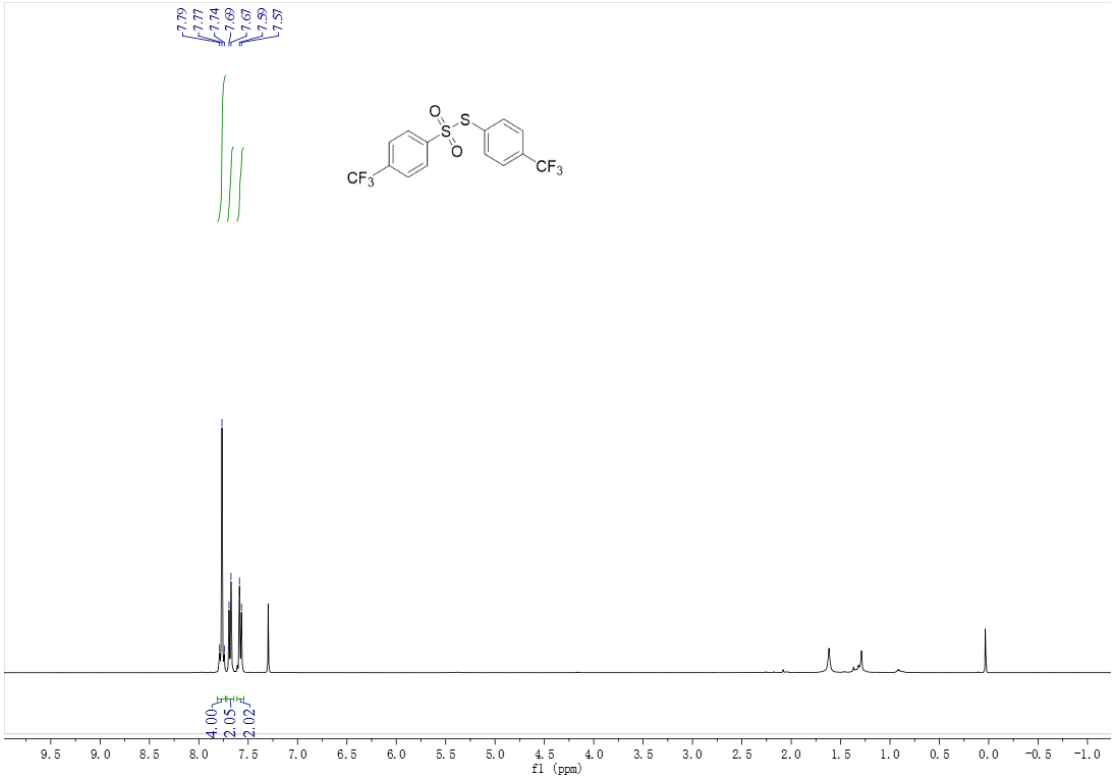
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S47**



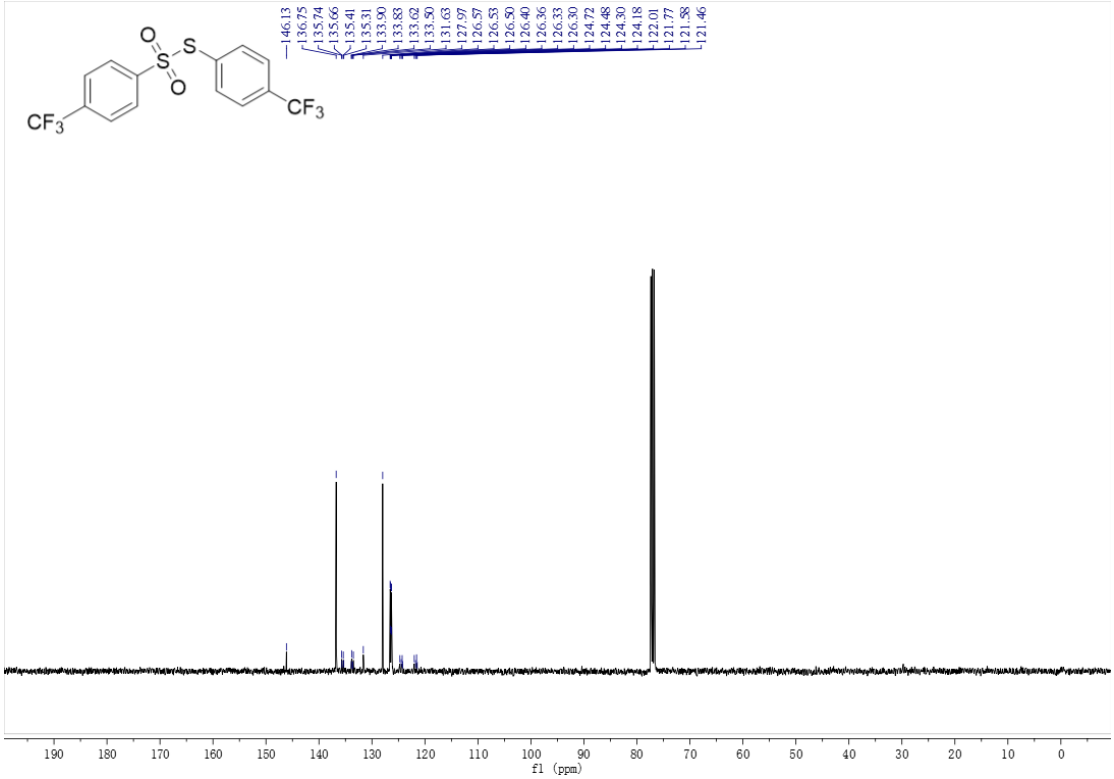
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **S47**



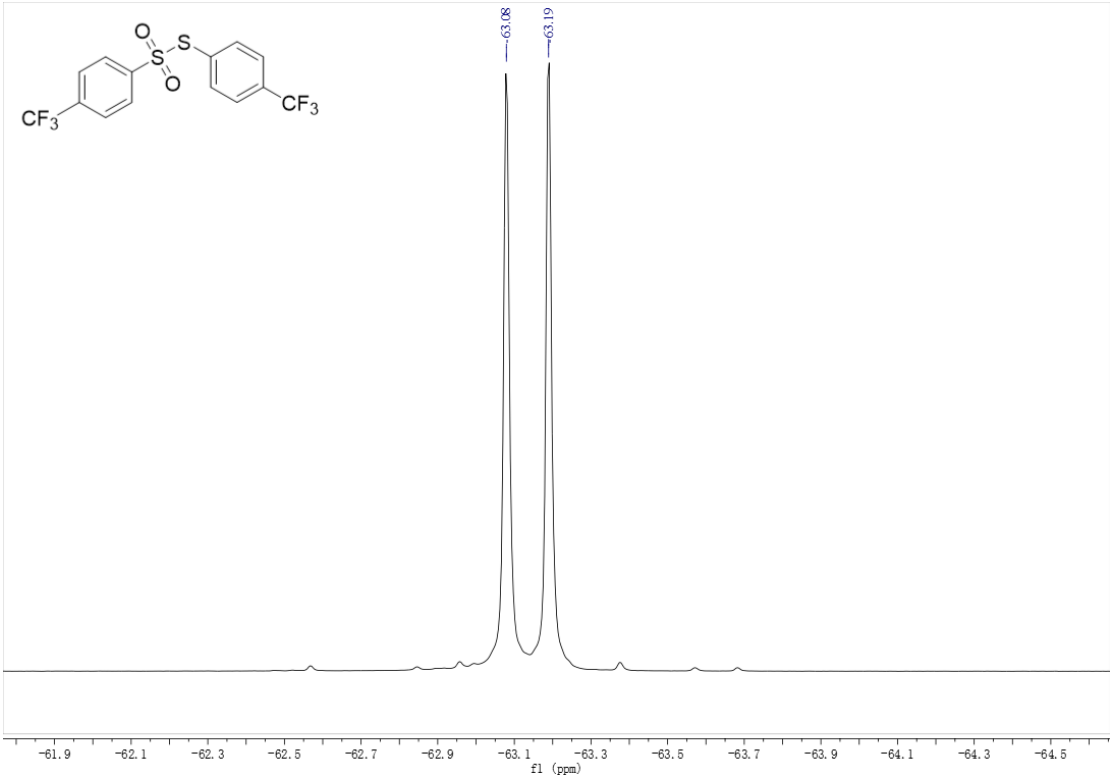
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S60**



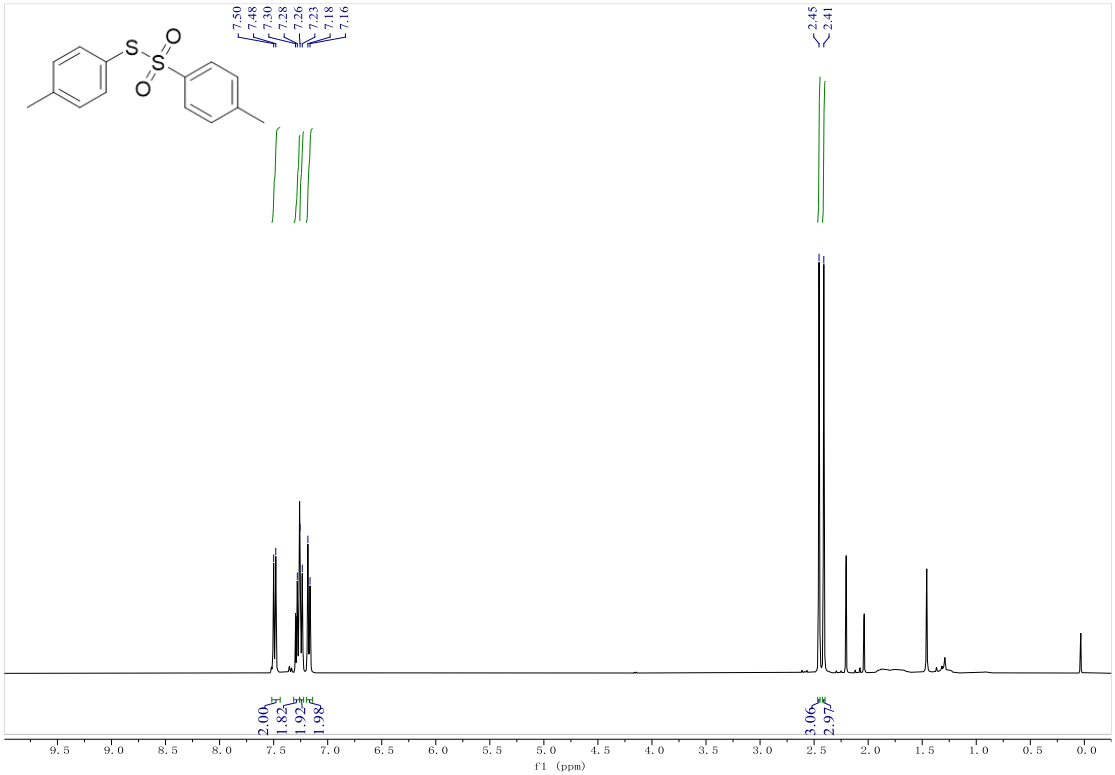
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **S60**



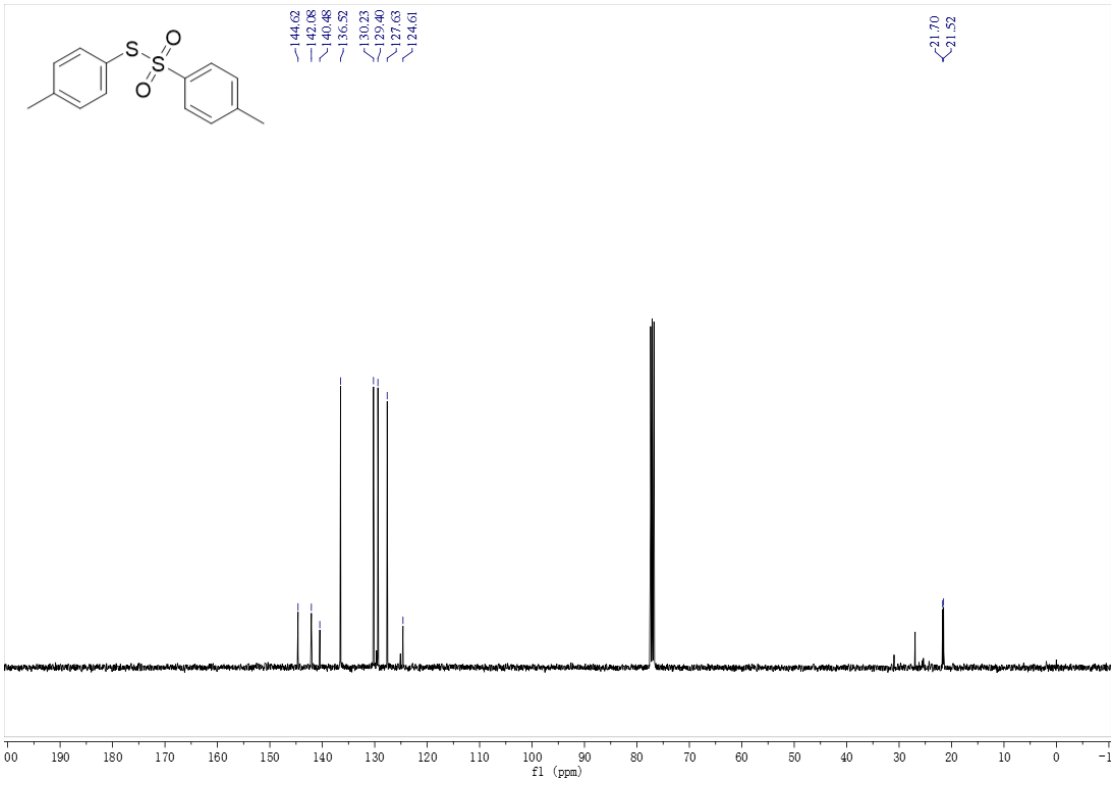
^{19}F NMR spectrum (376 MHz, $CDCl_3$，23 ℃) of **S60**



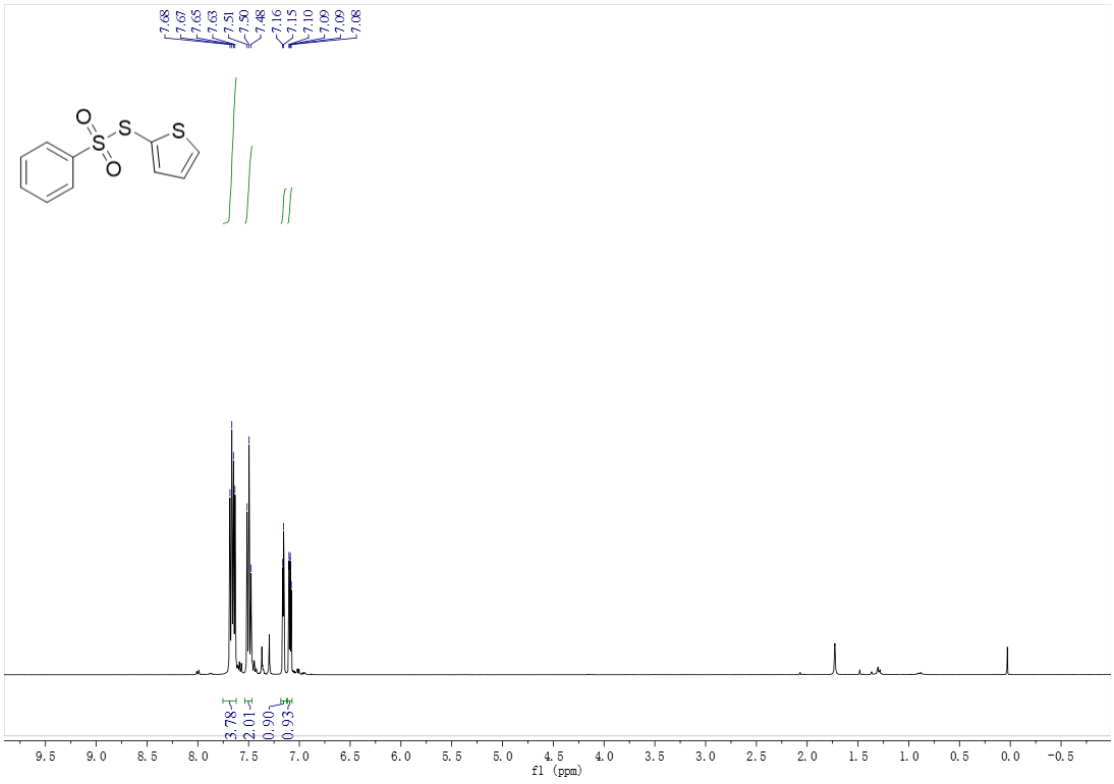
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S61**



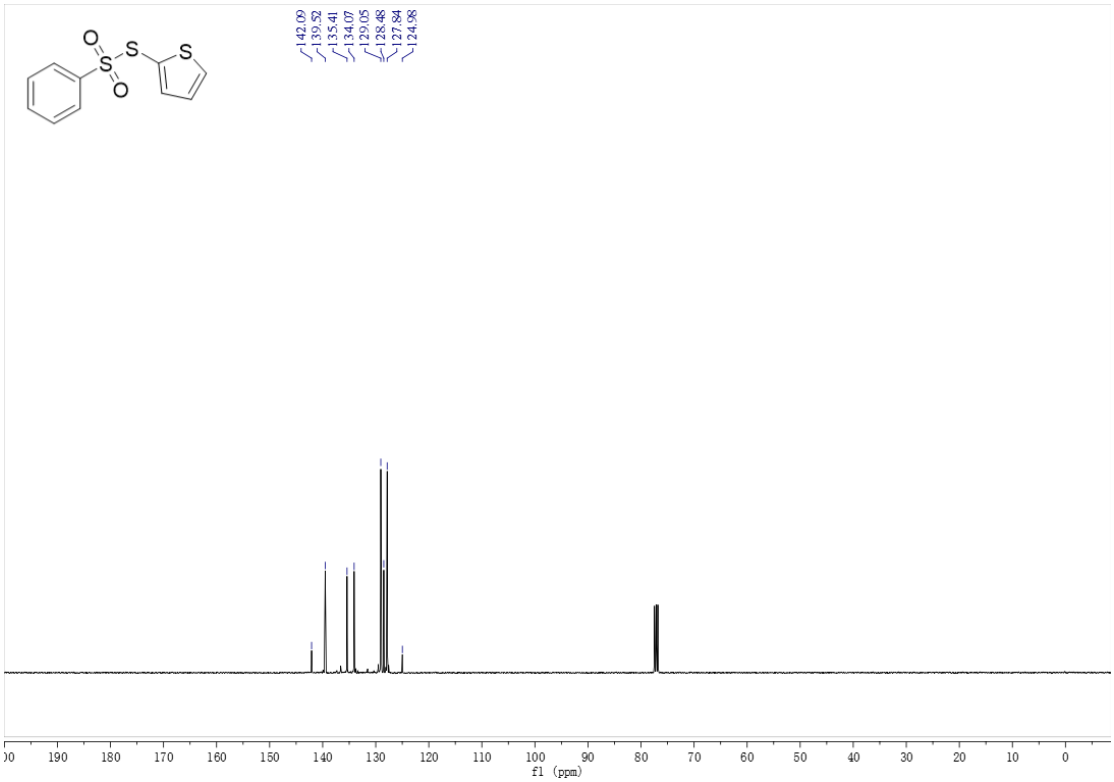
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **S61**



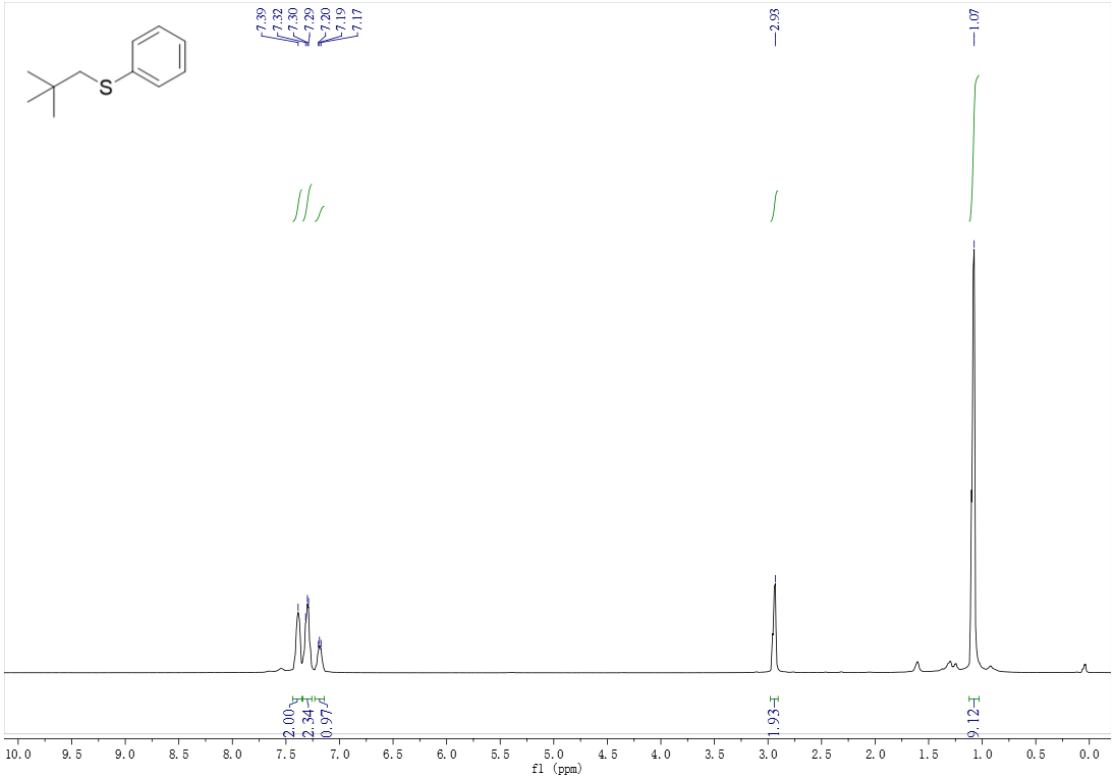
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S67**



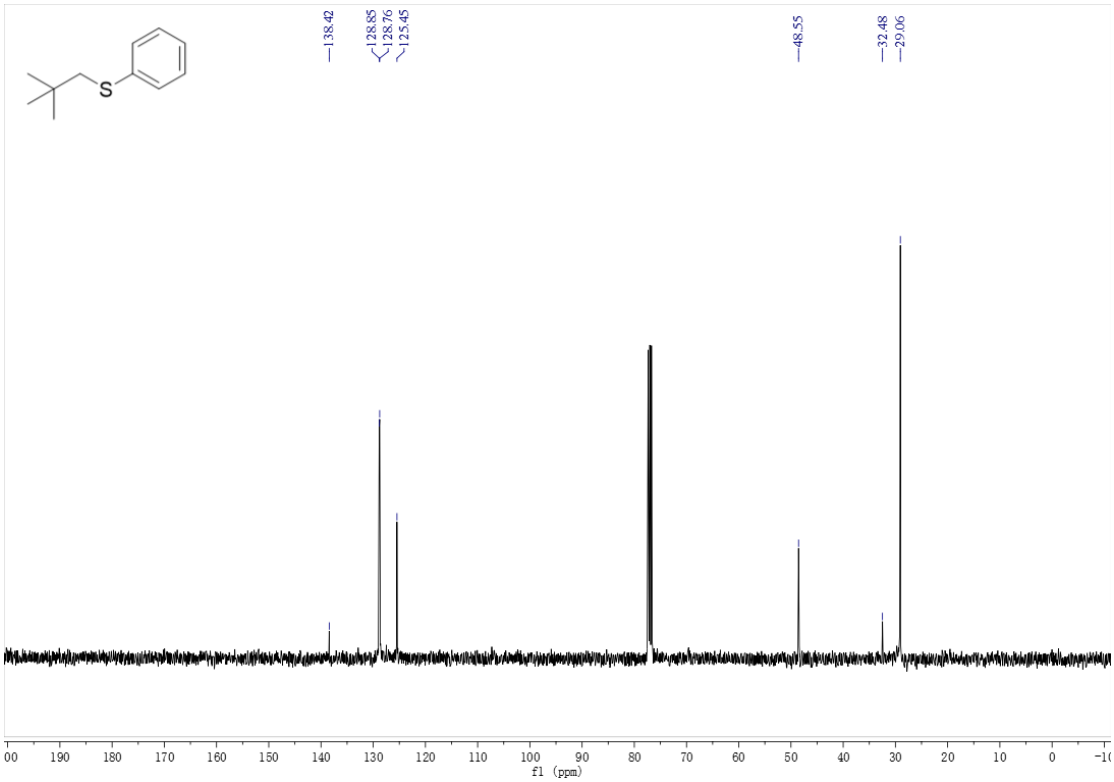
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **S67**



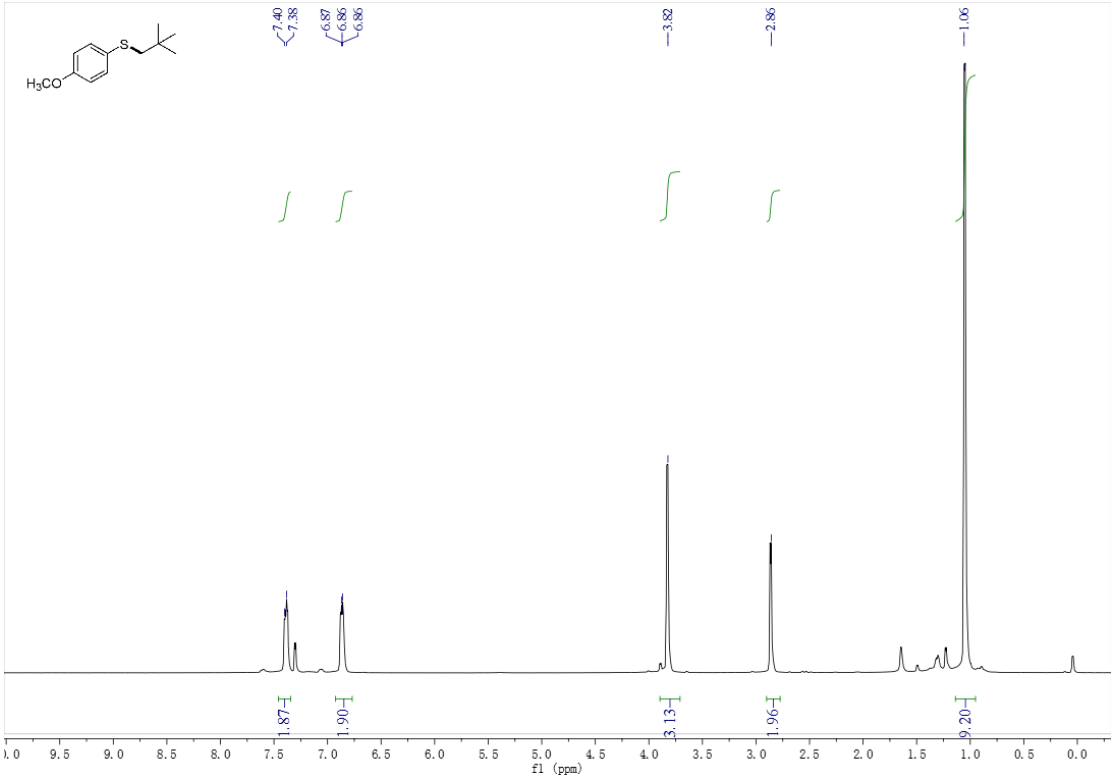
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **3**



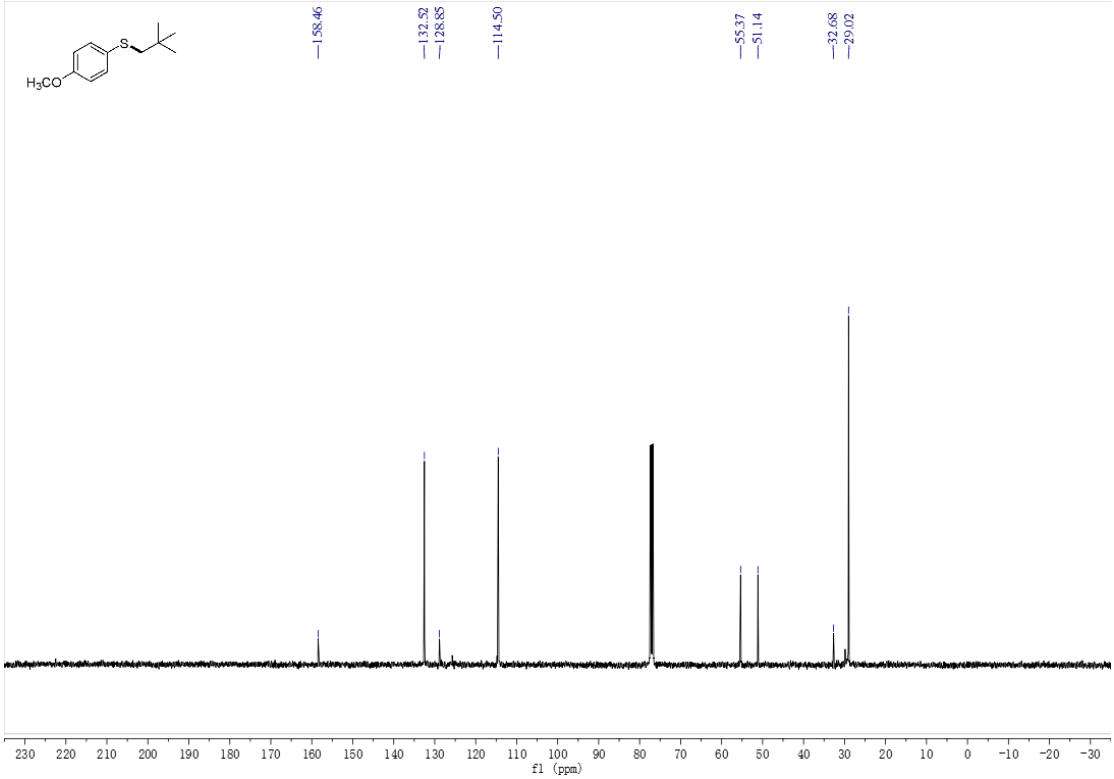
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **3**



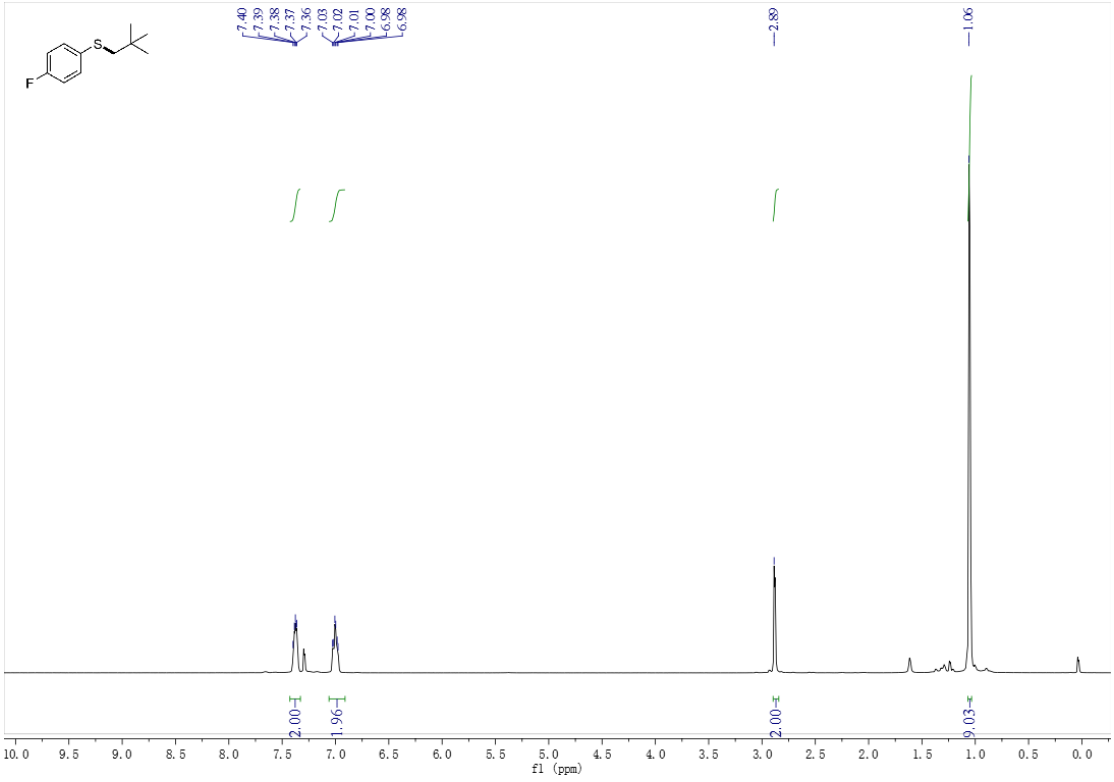
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **4**



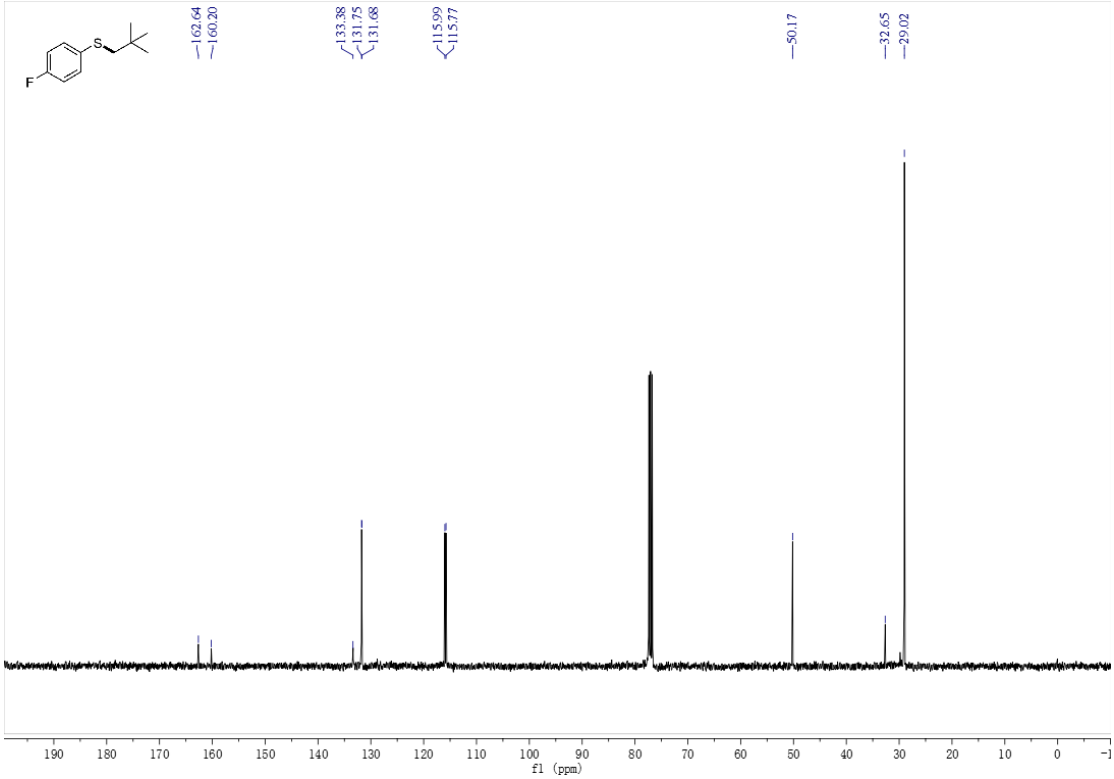
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **4**



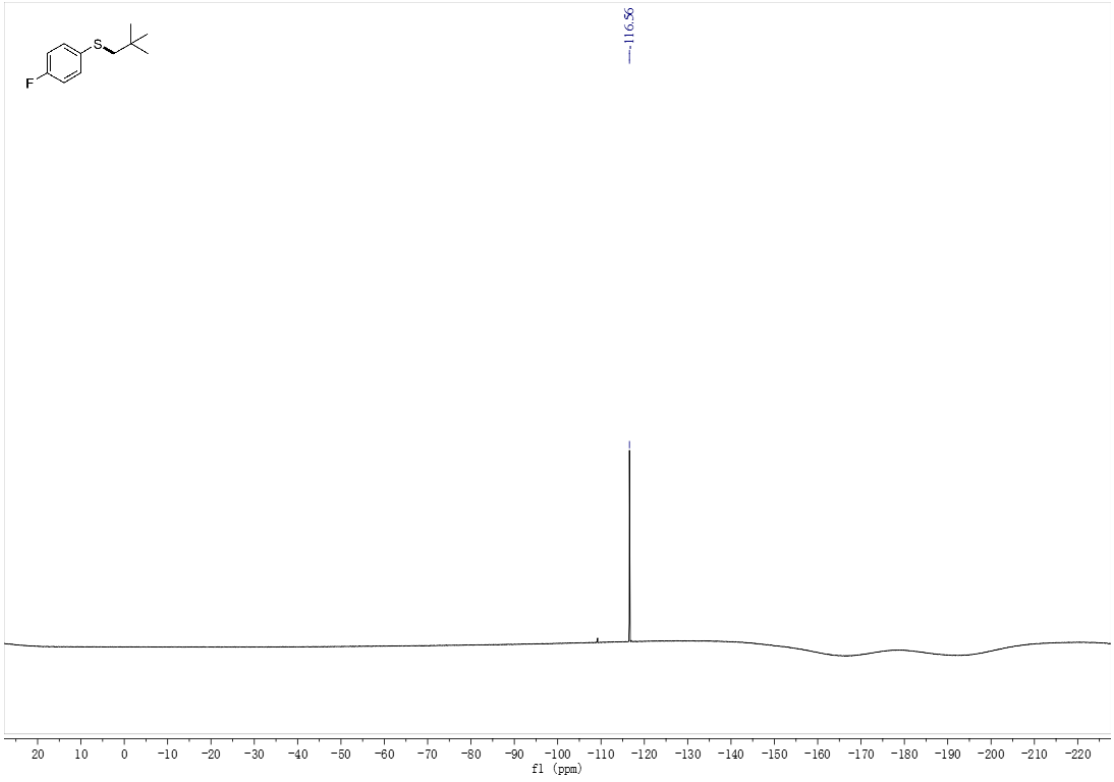
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **5**



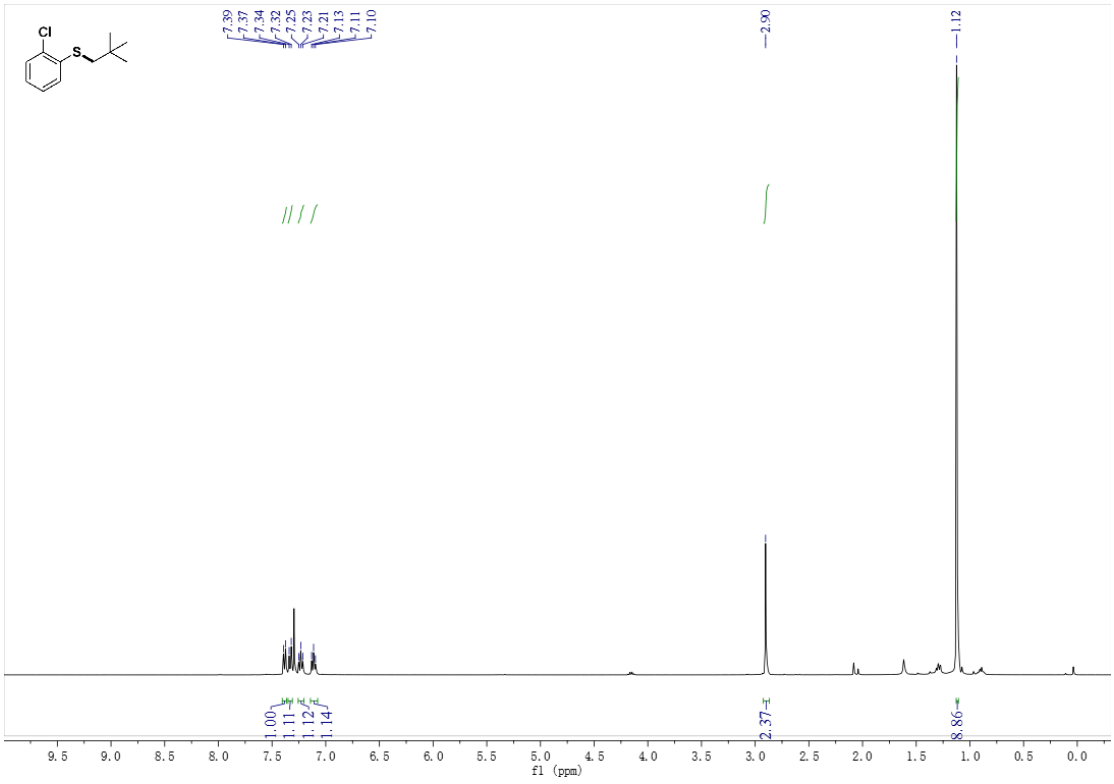
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **5**



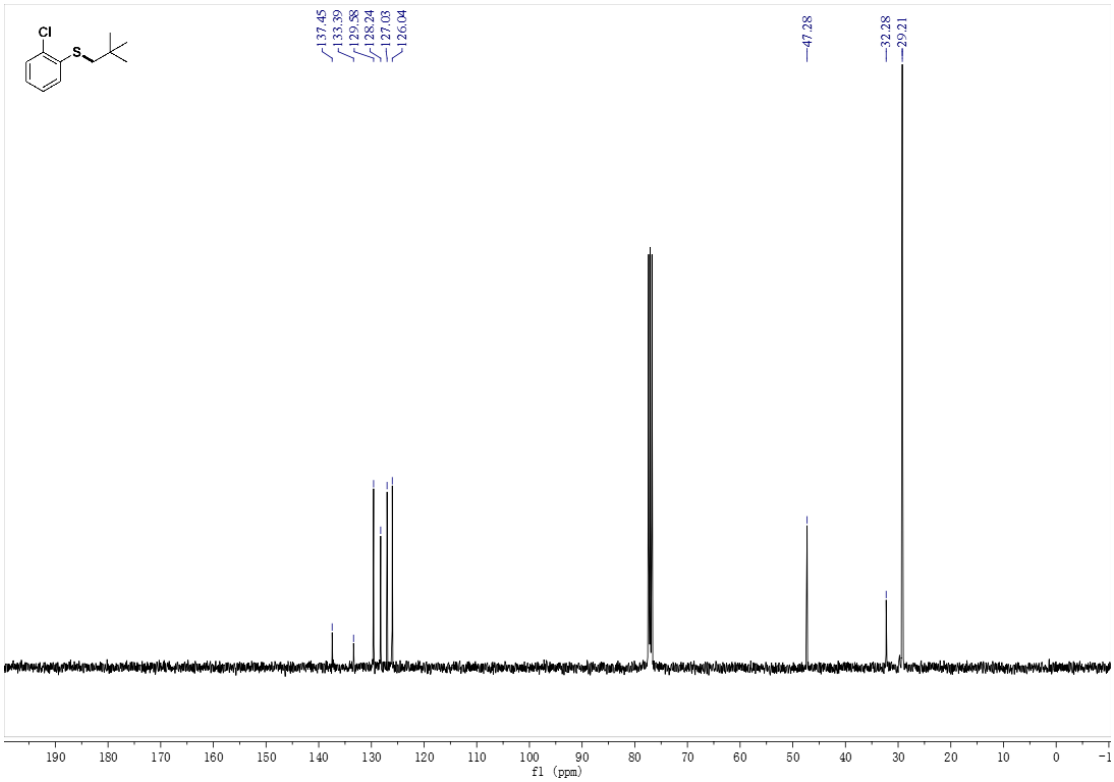
^{19}F NMR spectrum (376 MHz, $CDCl_3$，23 ℃) of **5**



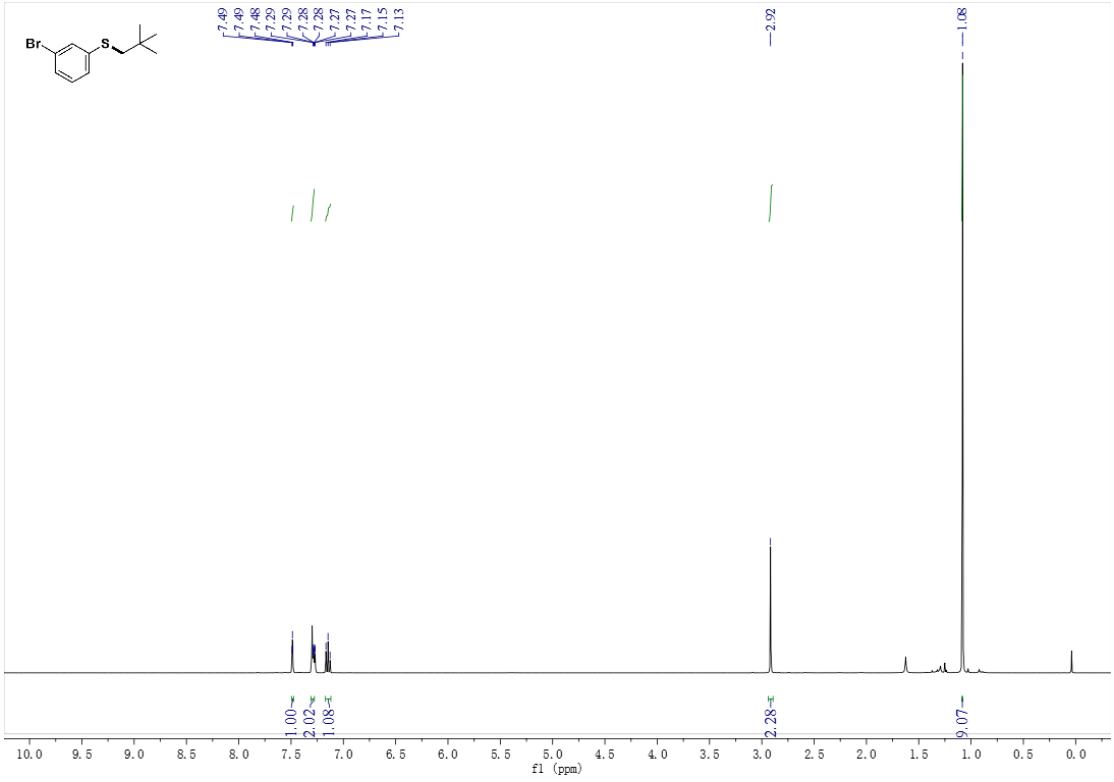
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **6**



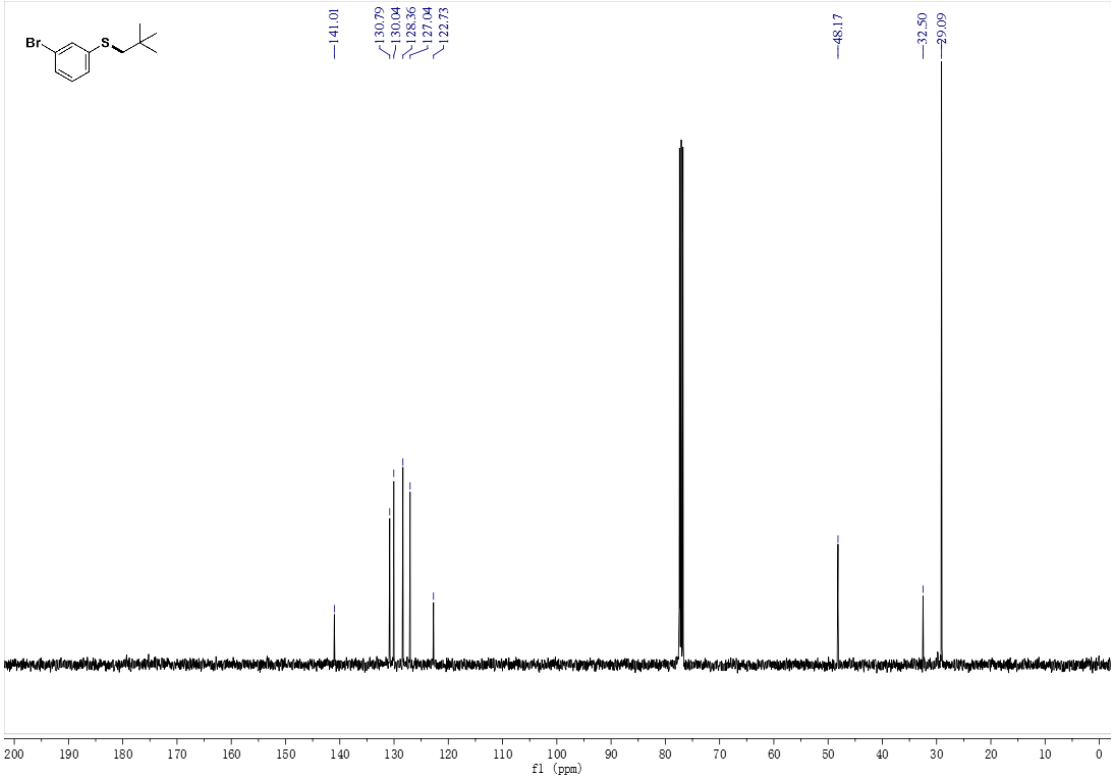
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **6**



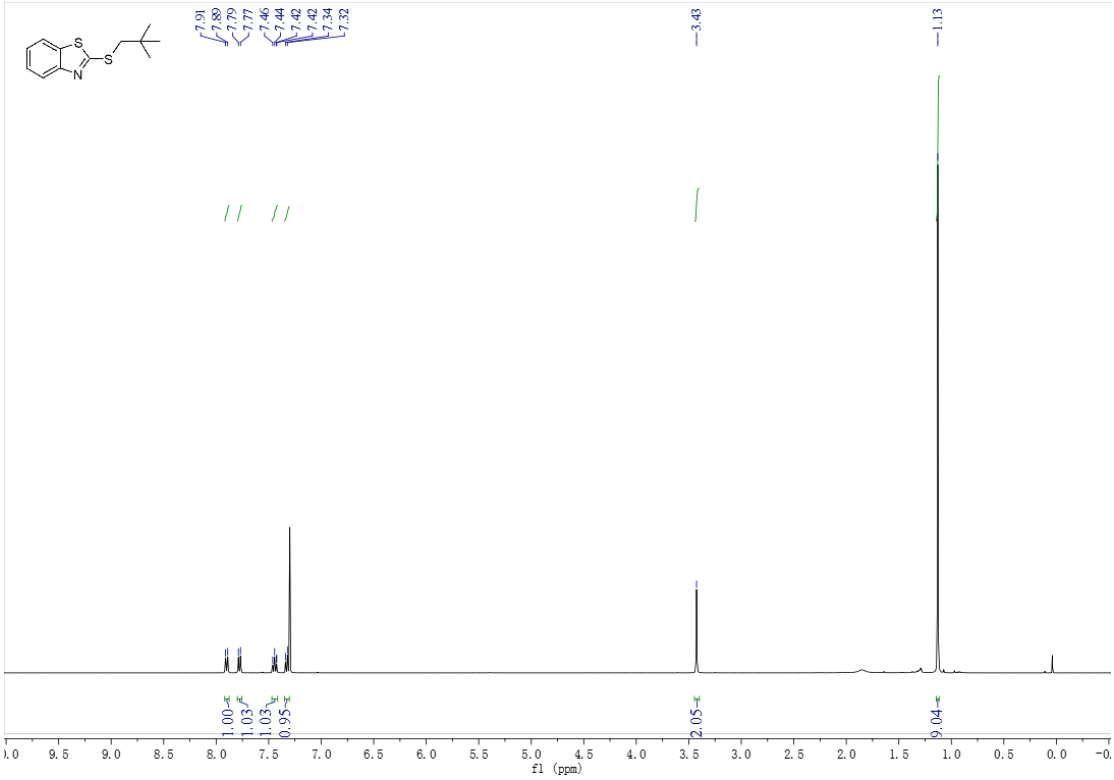
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **7**



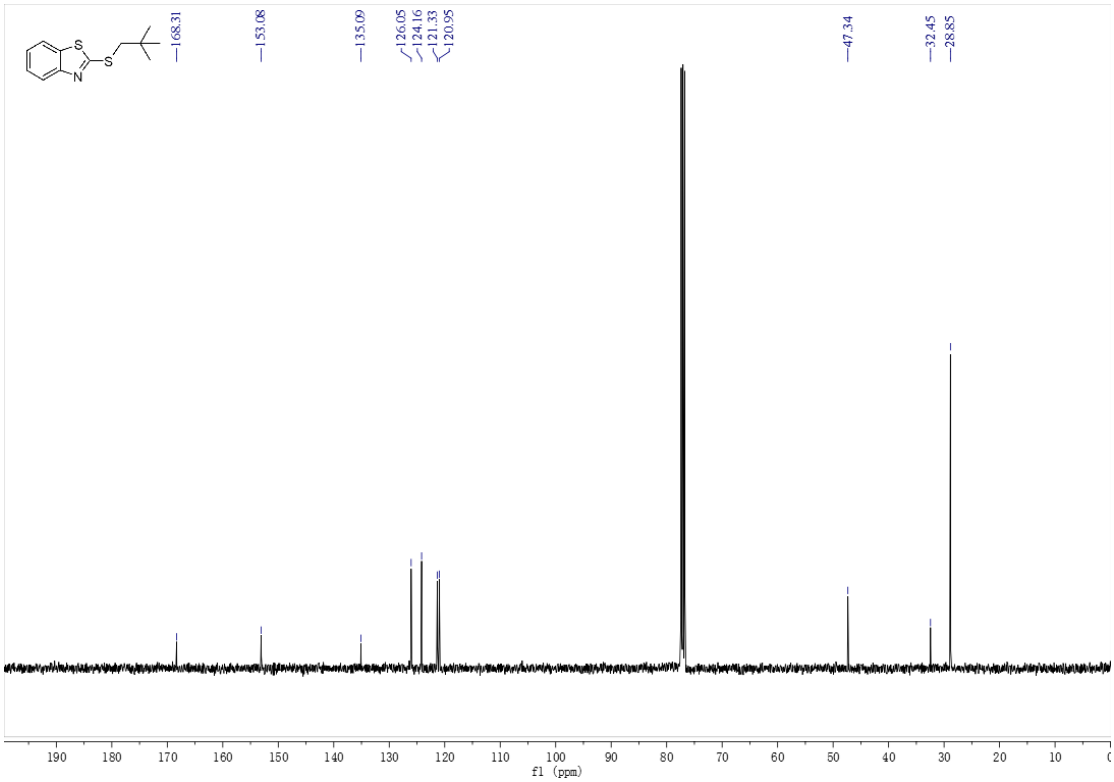
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **7**



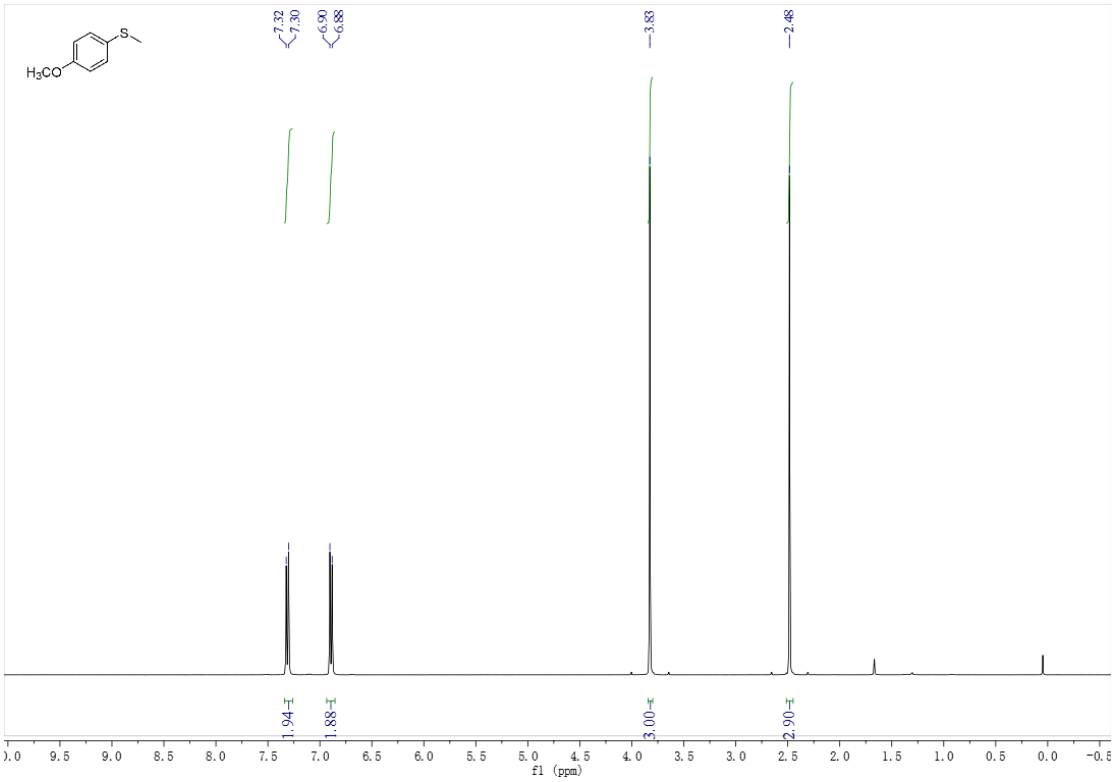
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **8**



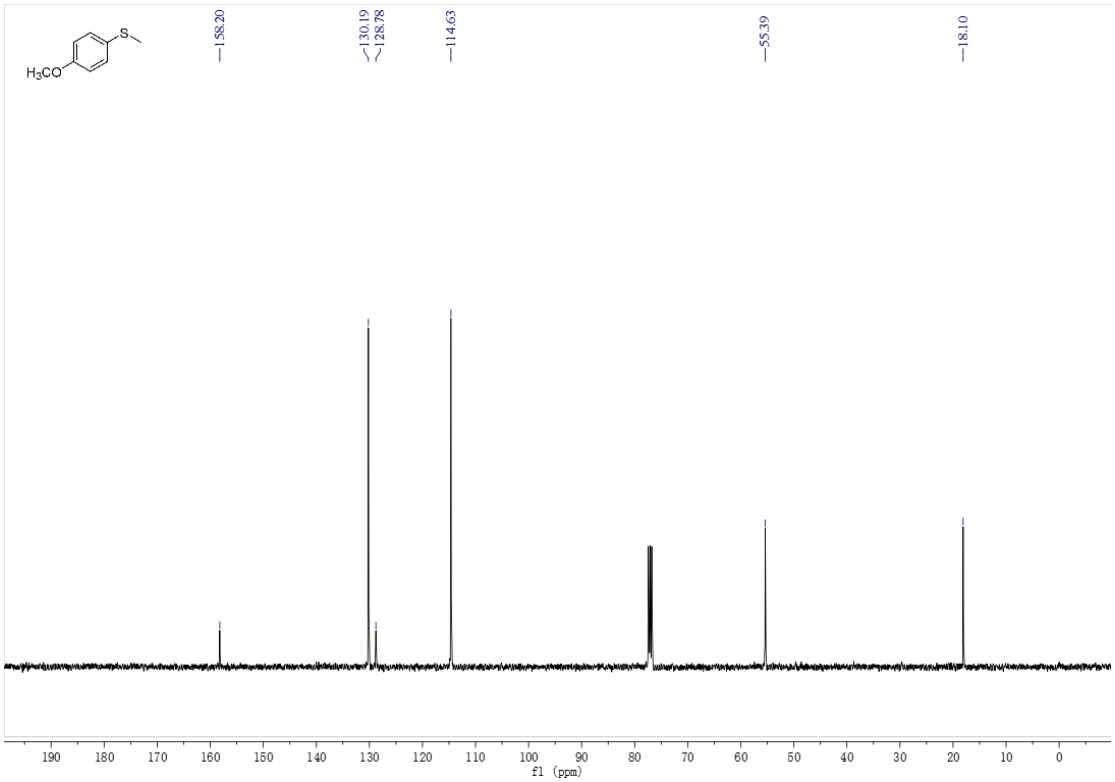
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **8**



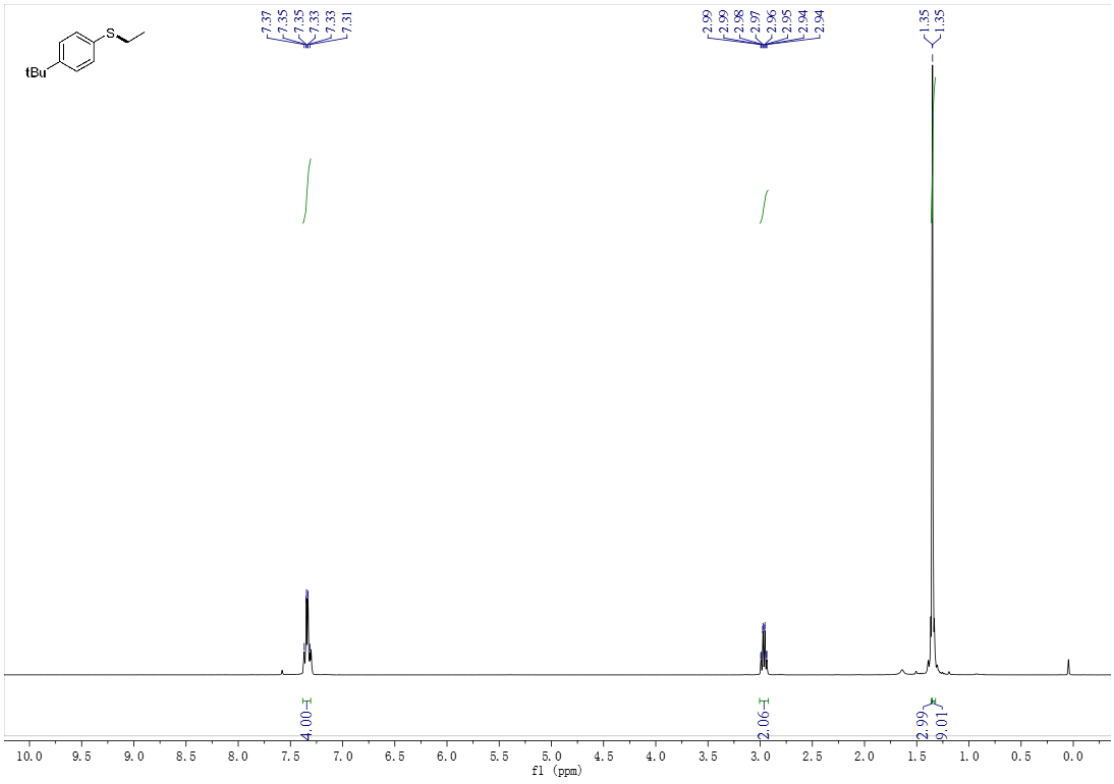
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **9**



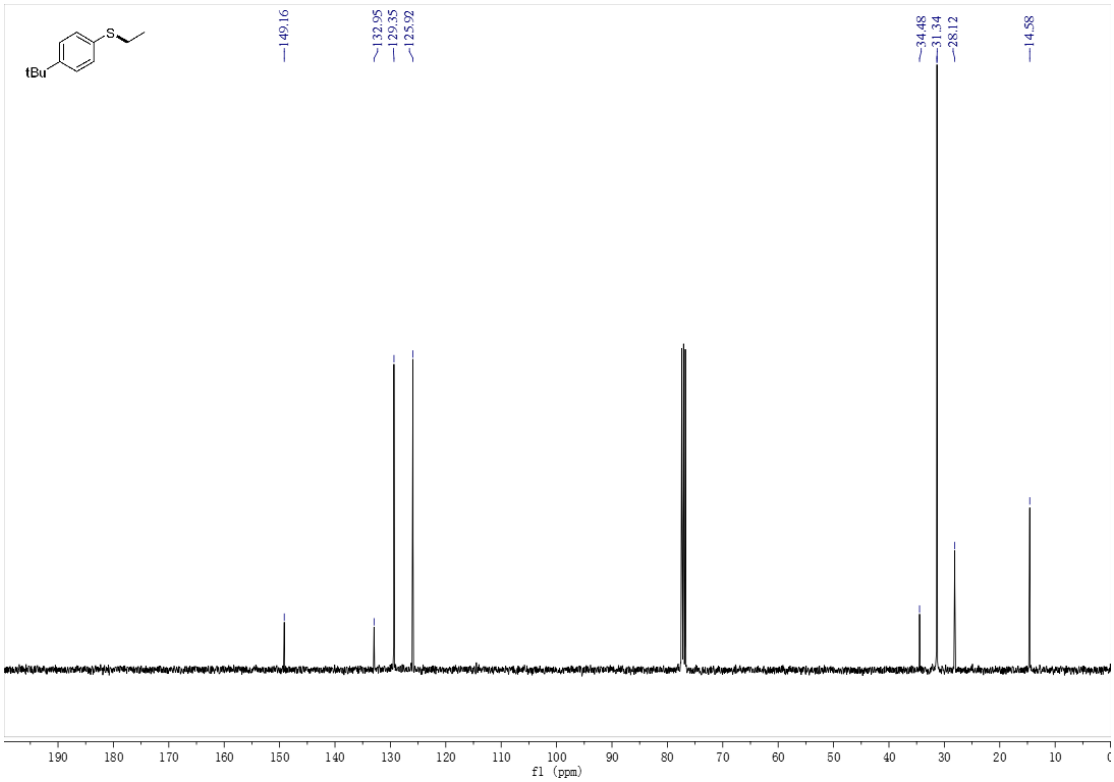
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **9**



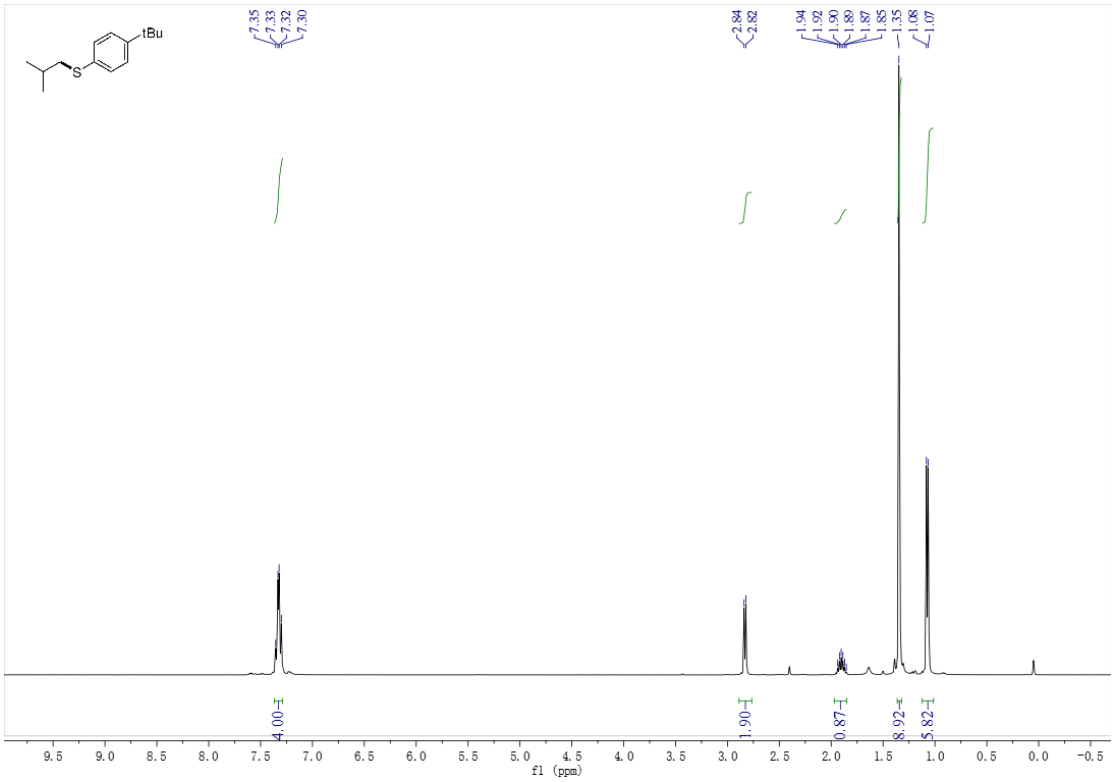
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **10**



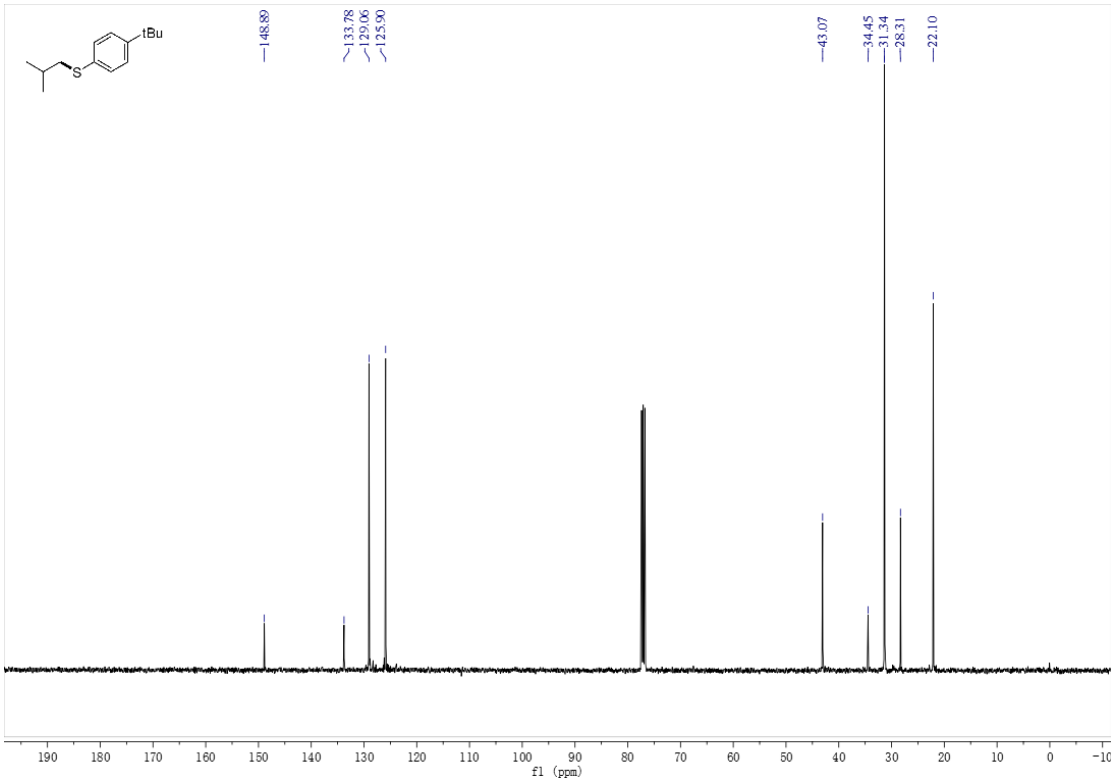
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **10**



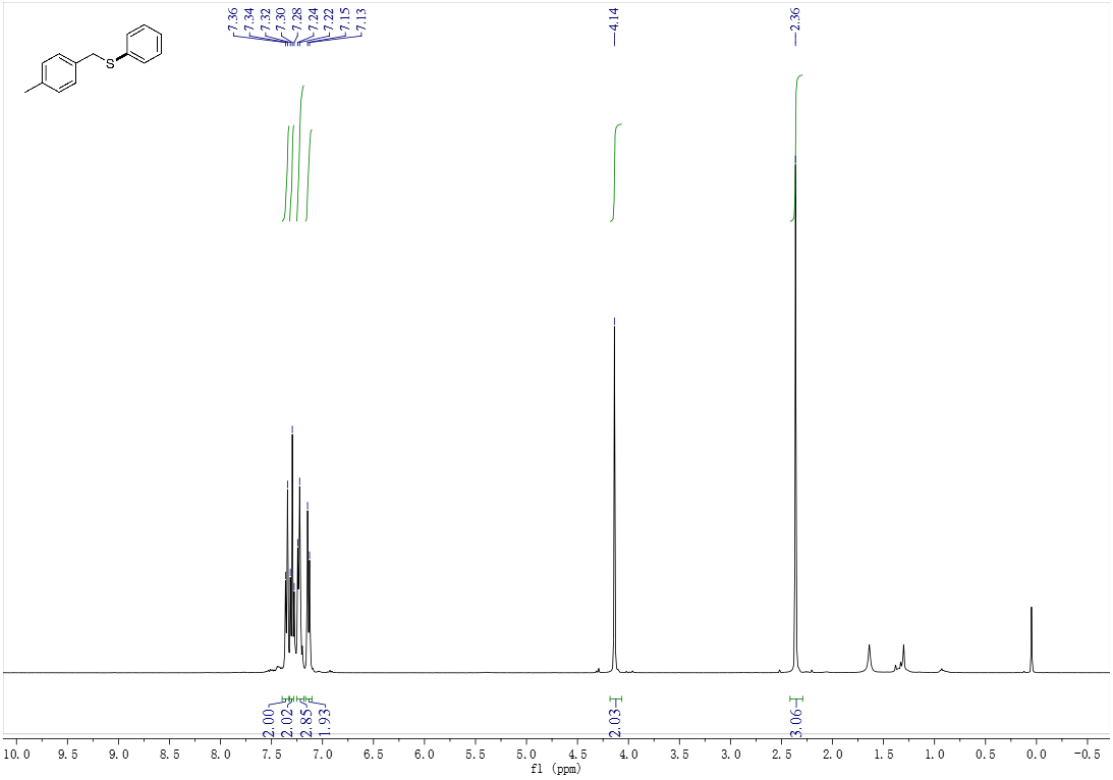
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **11**



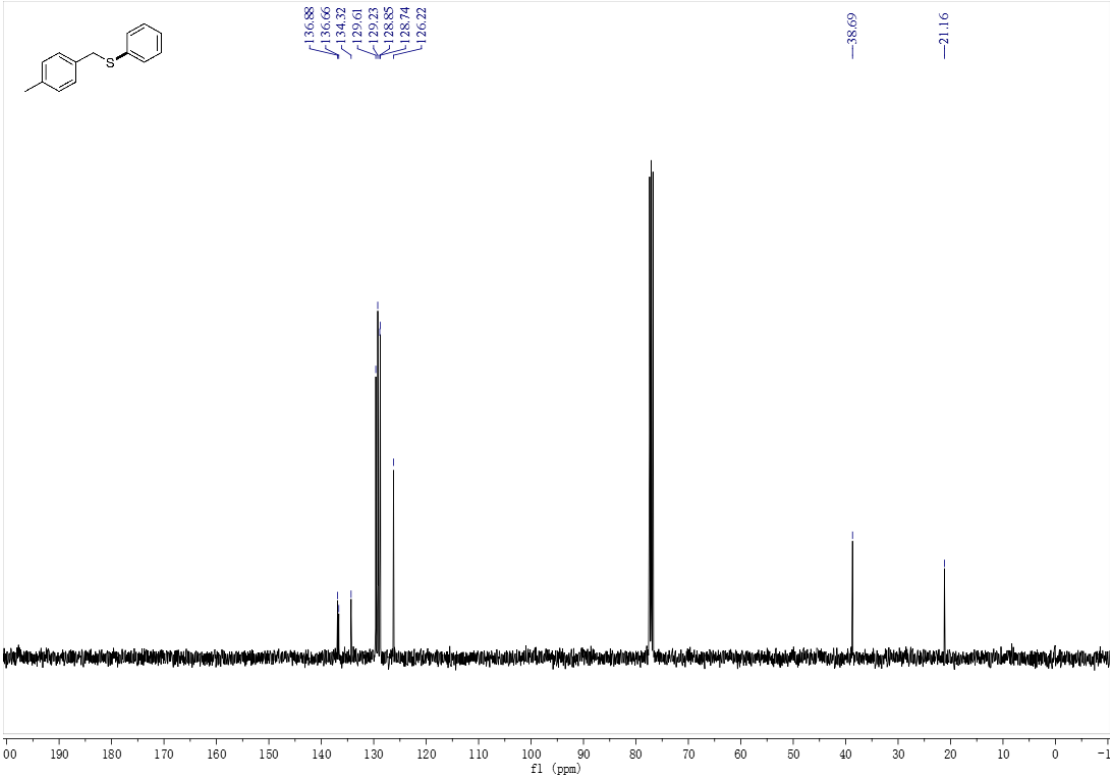
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **11**



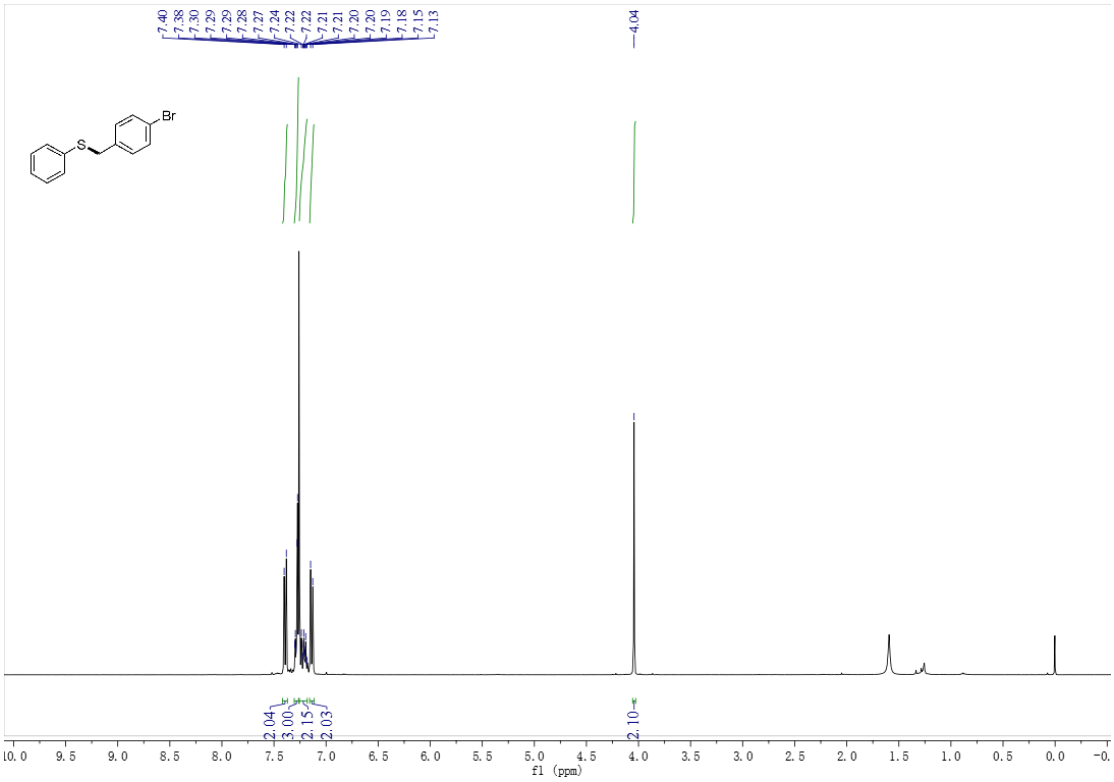
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **12**



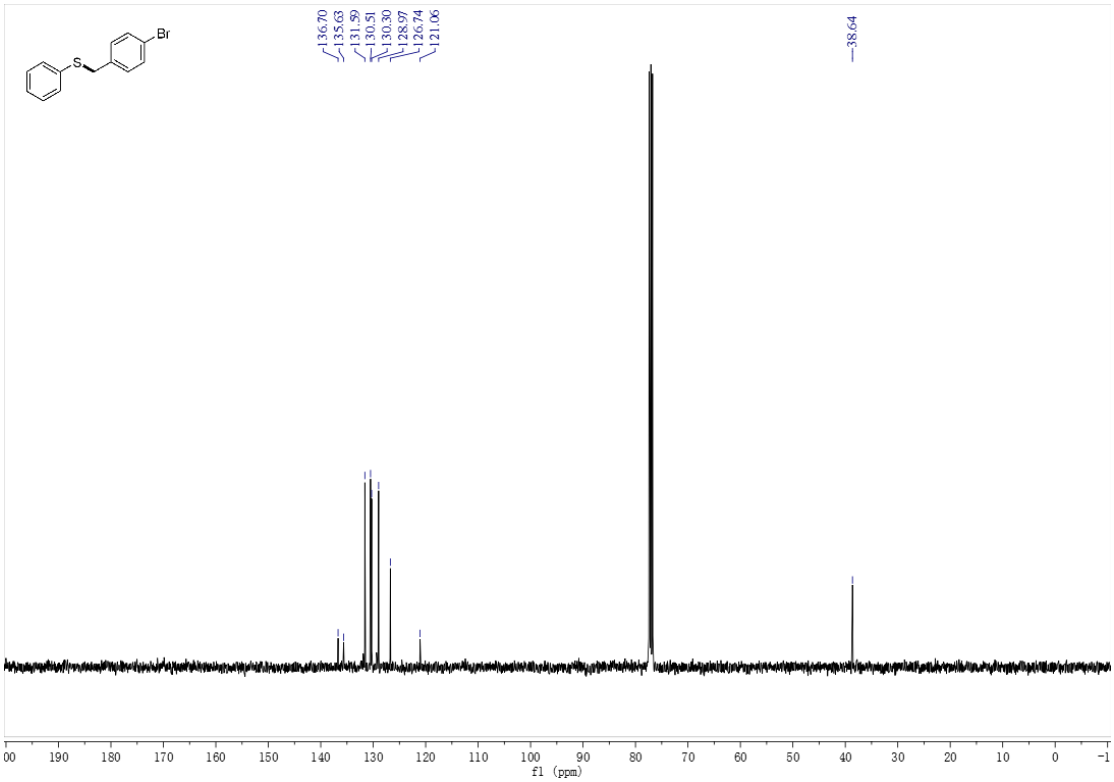
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **12**



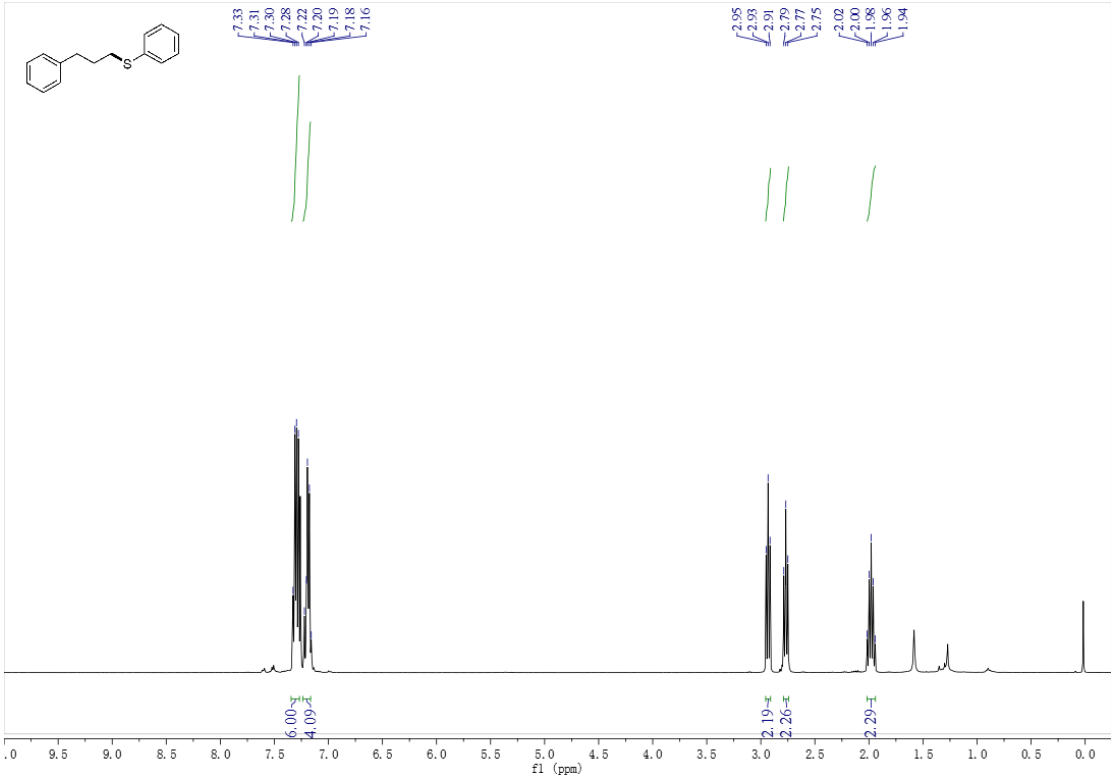
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **13**



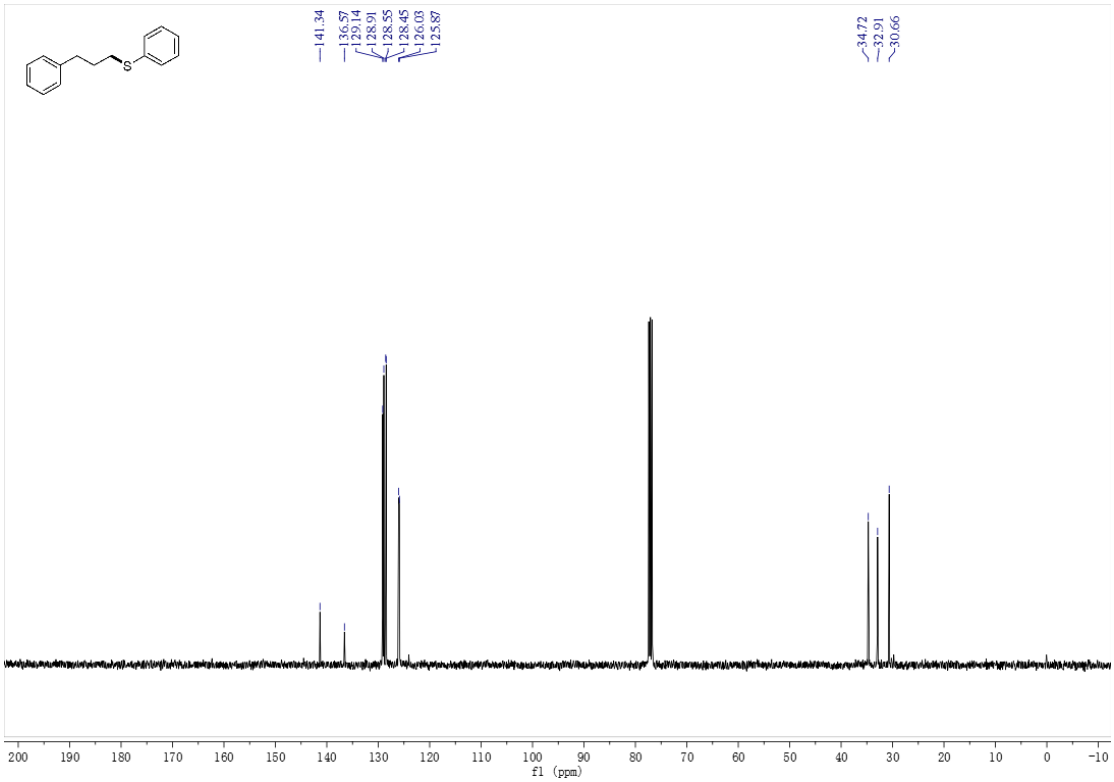
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **13**



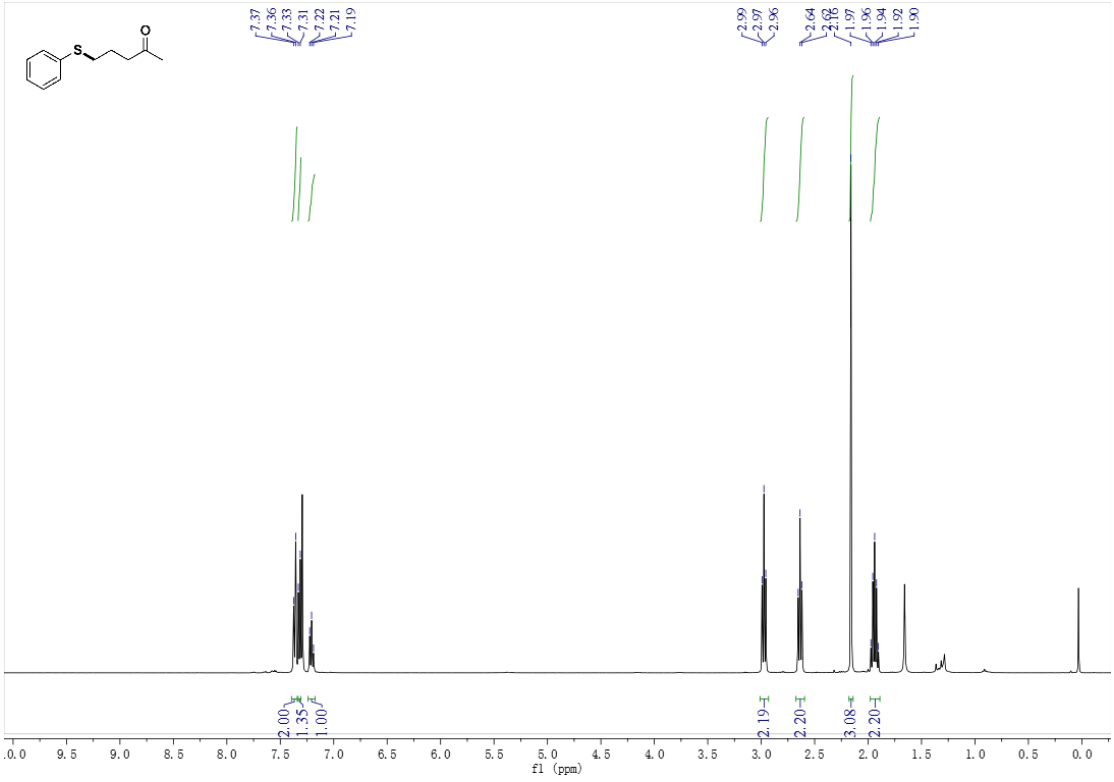
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **14**



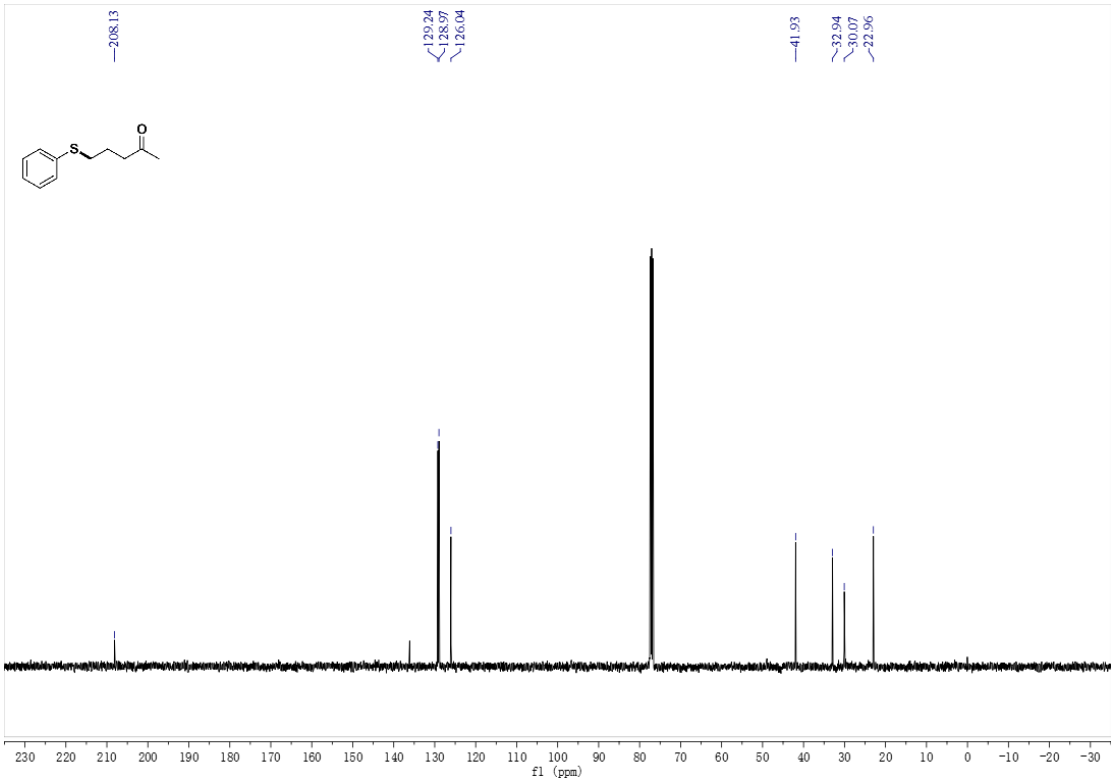
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **14**



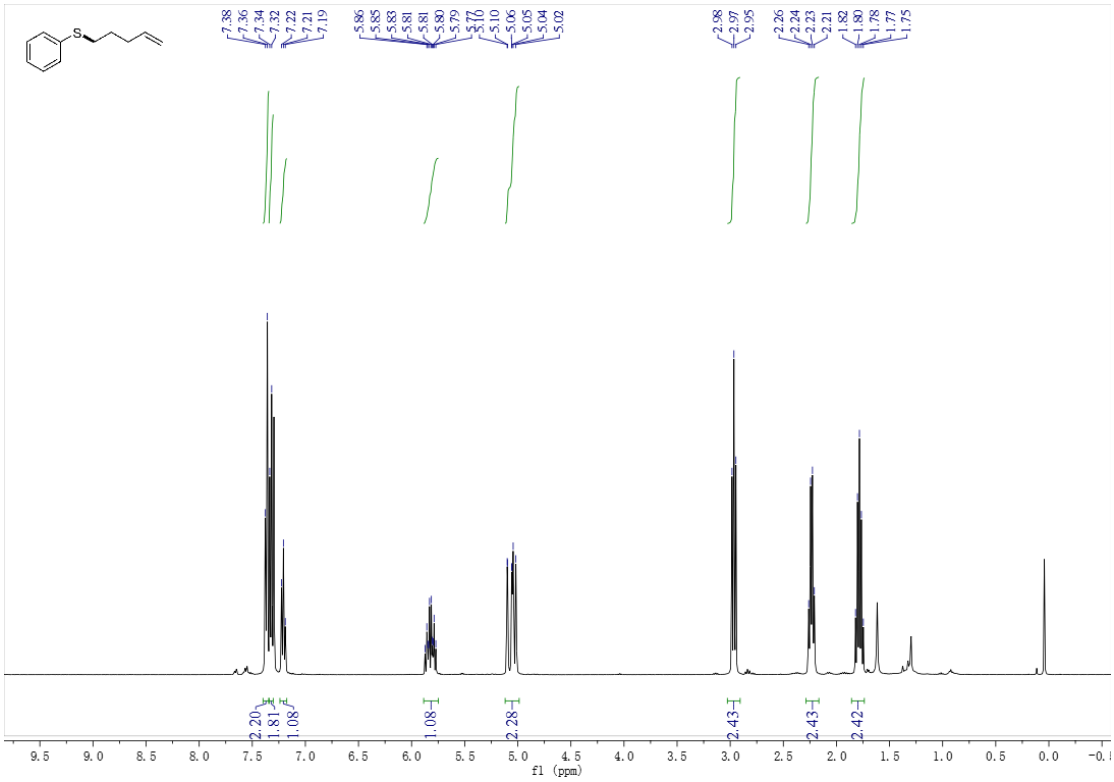
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **15**



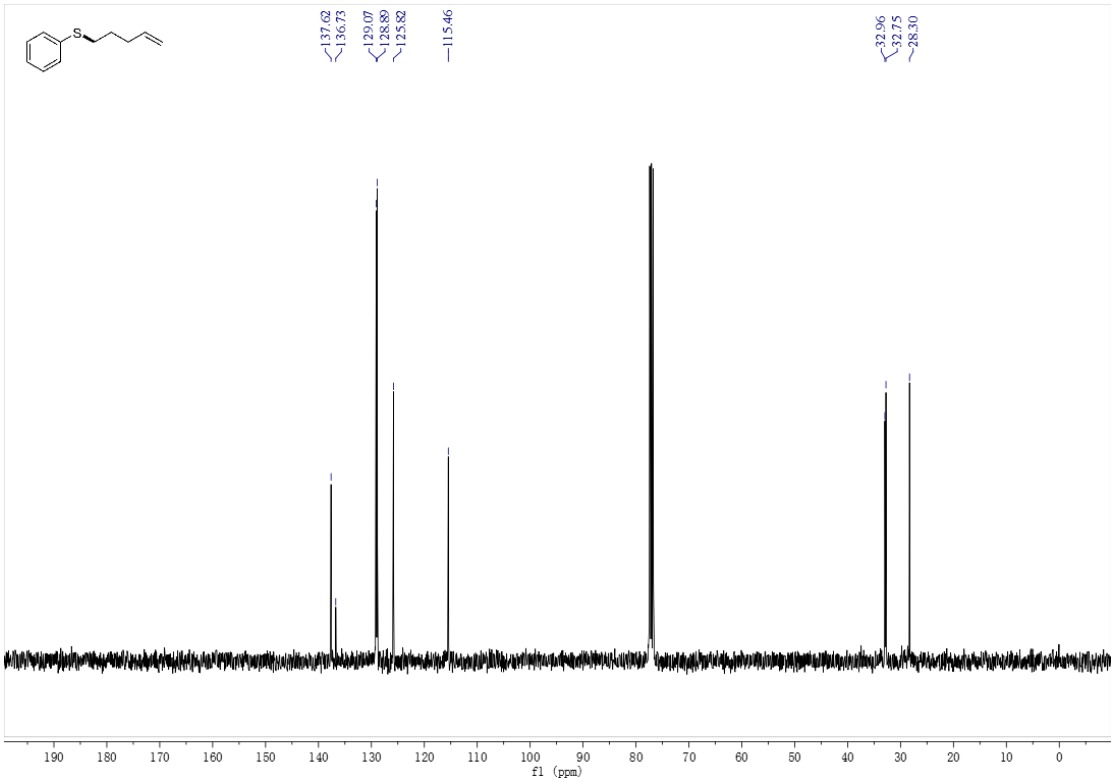
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **15**



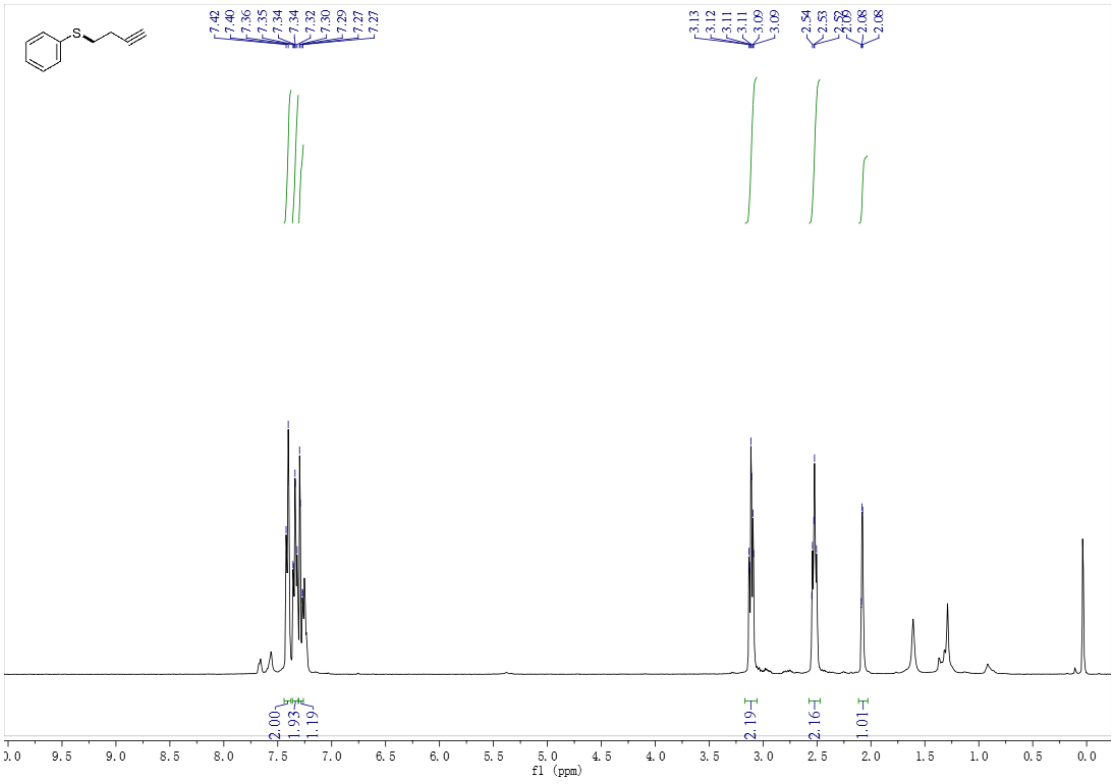
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **16**



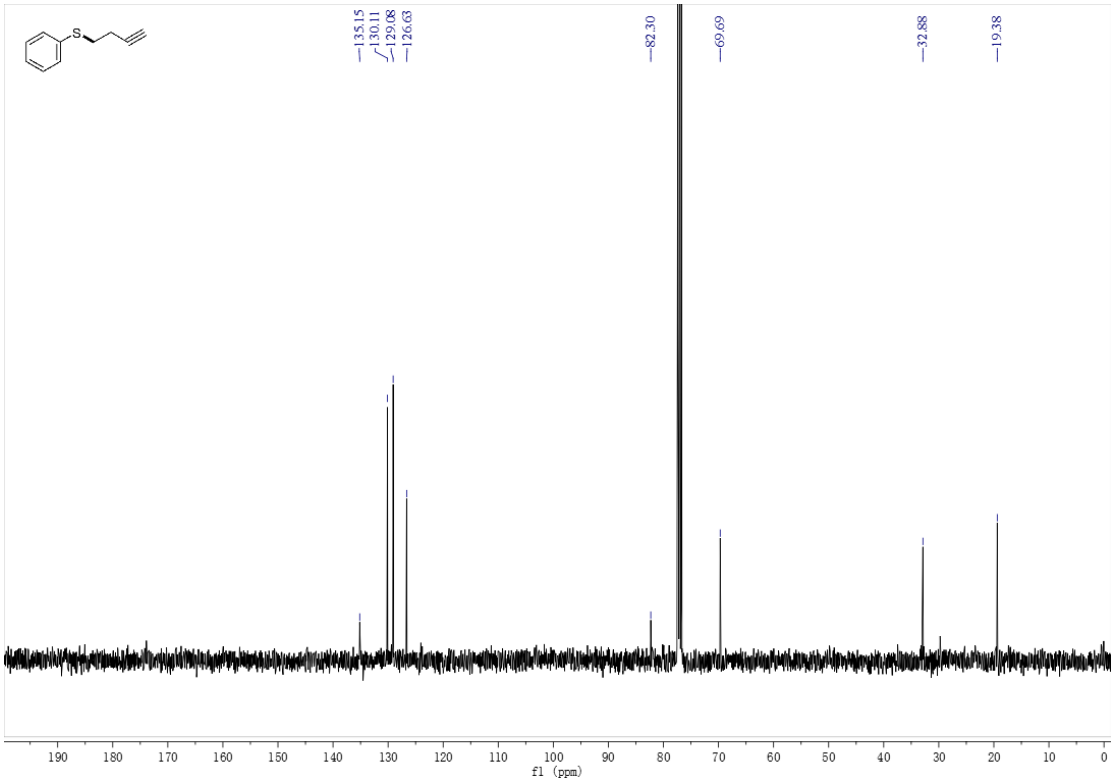
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **16**



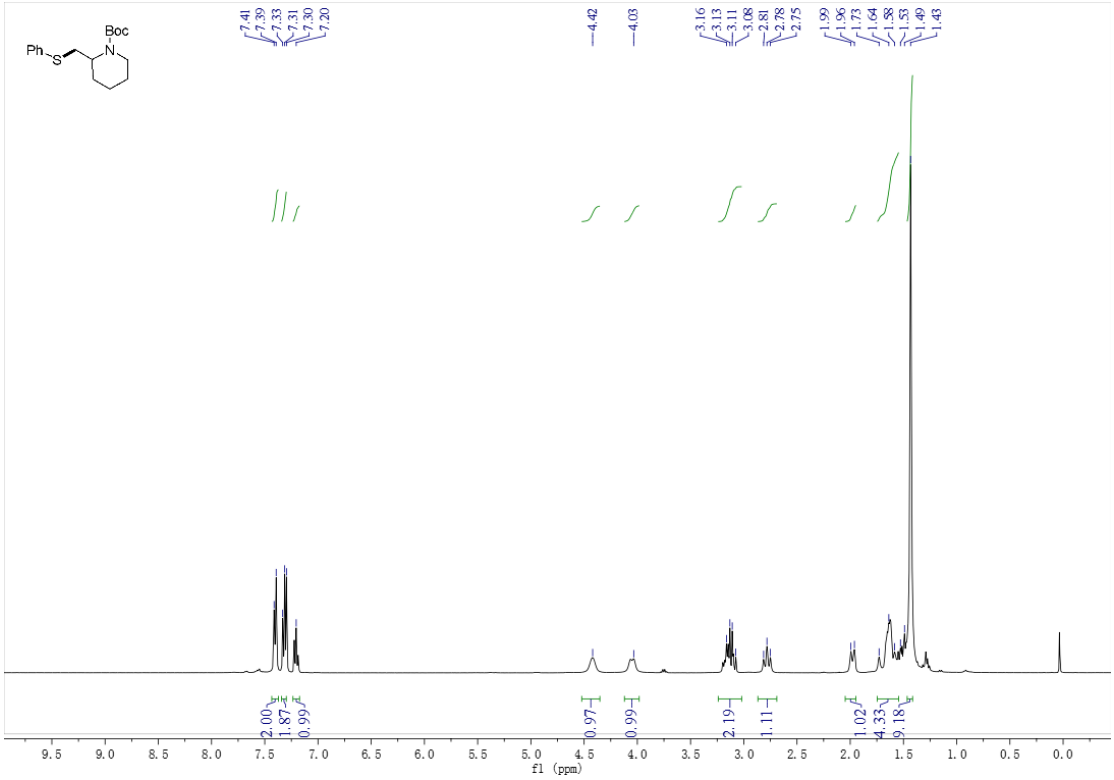
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **17**



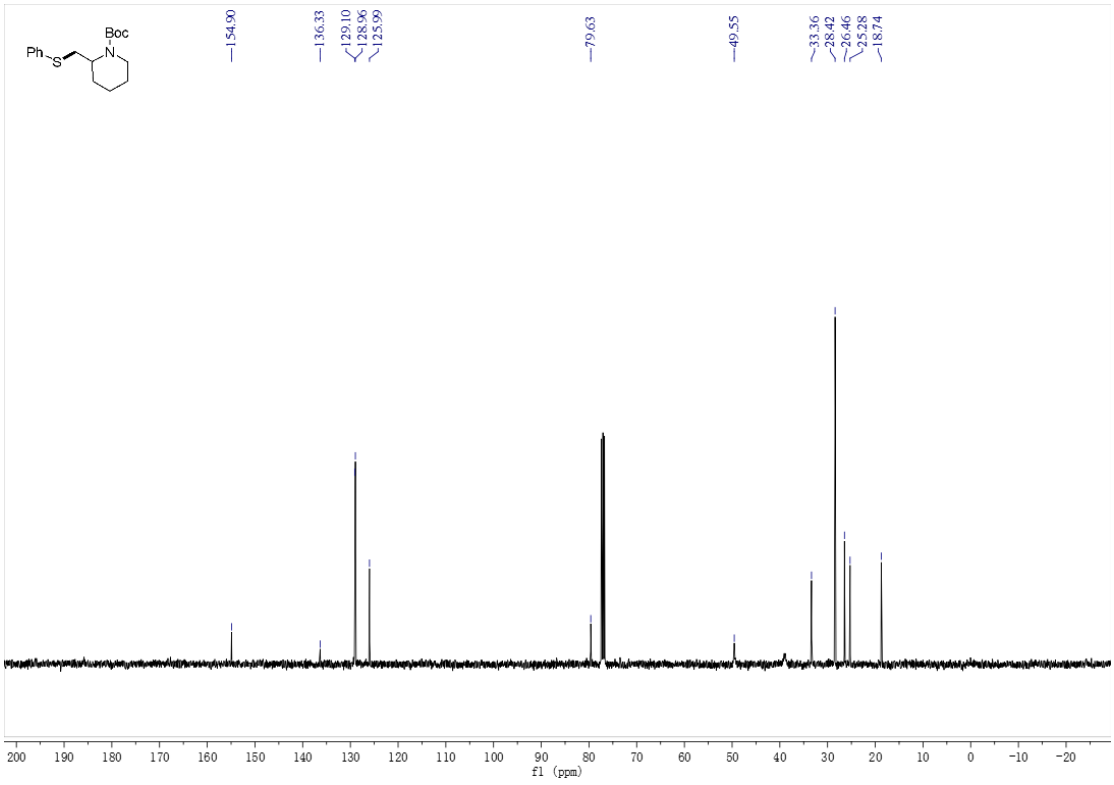
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **17**



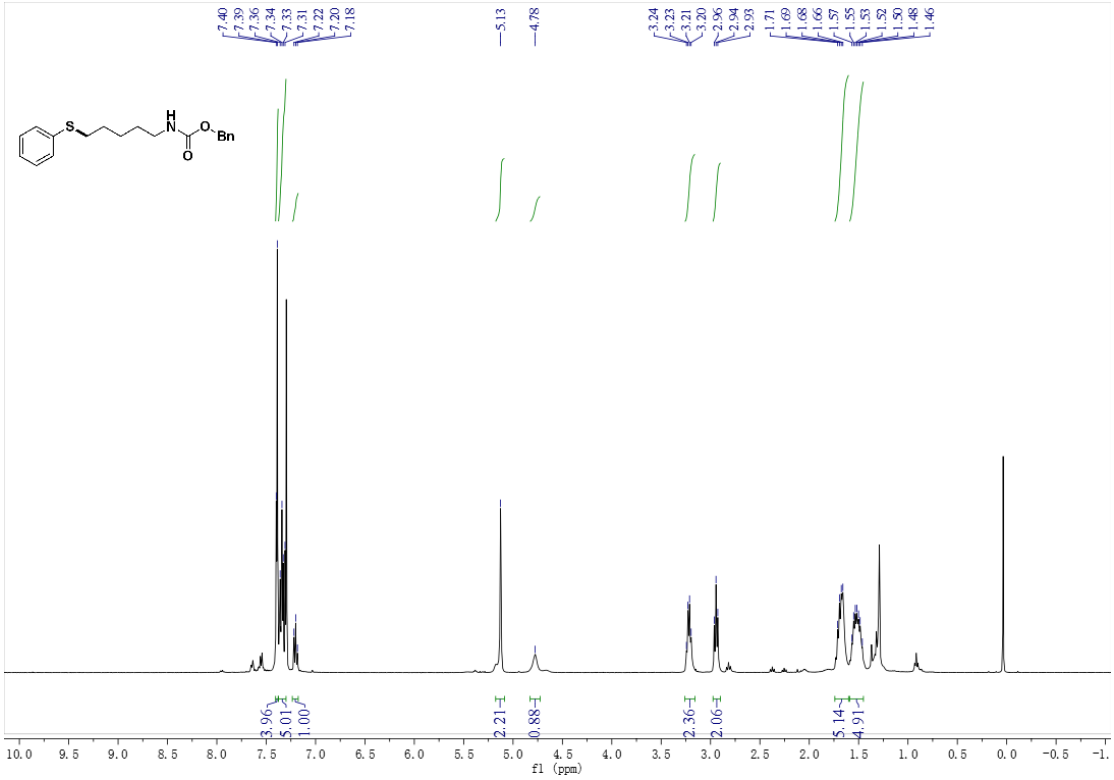
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **18**



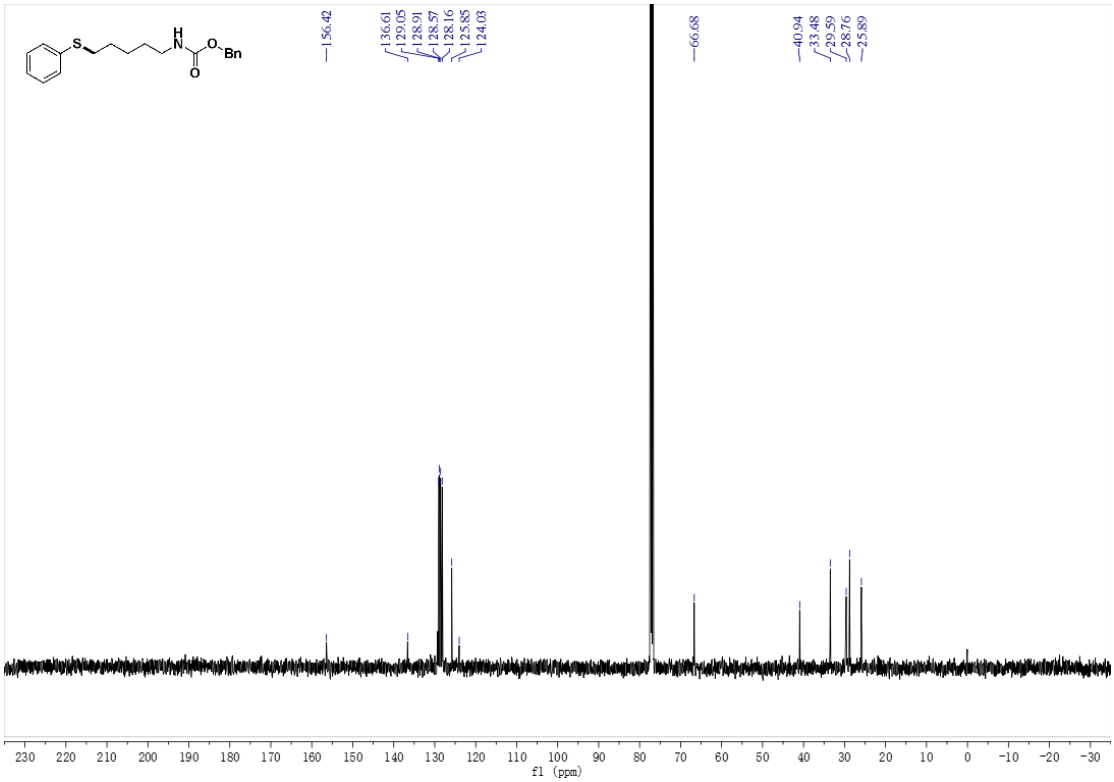
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **18**



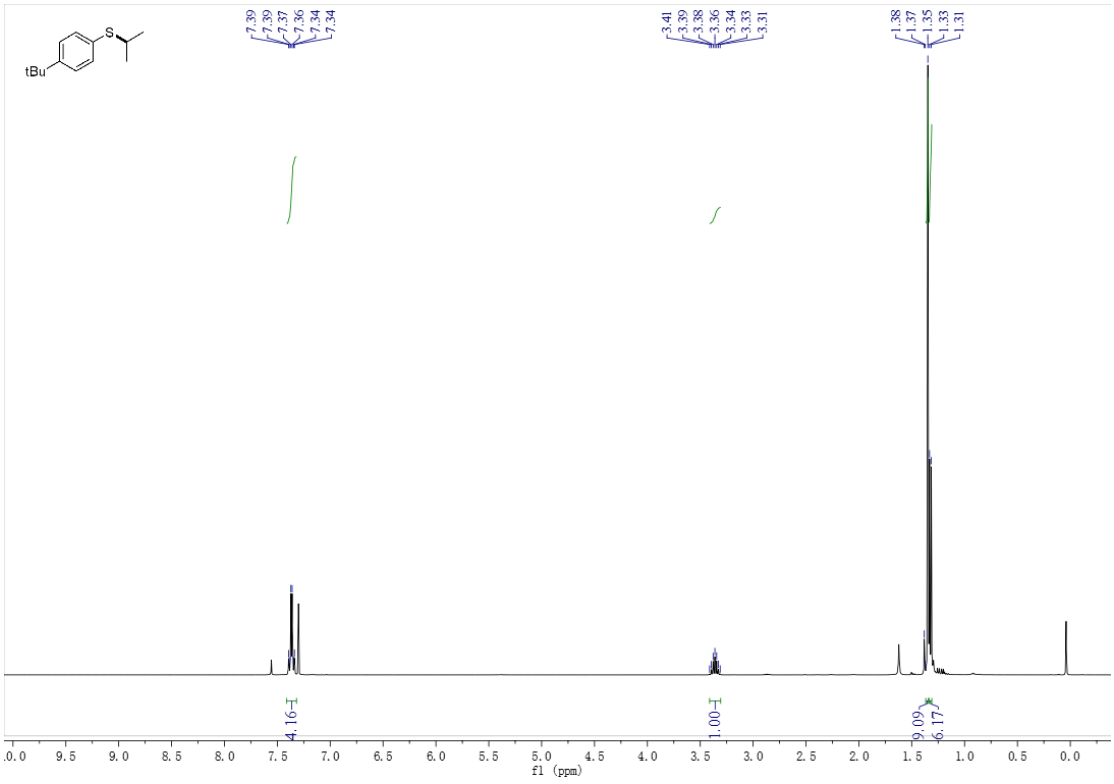
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **19**



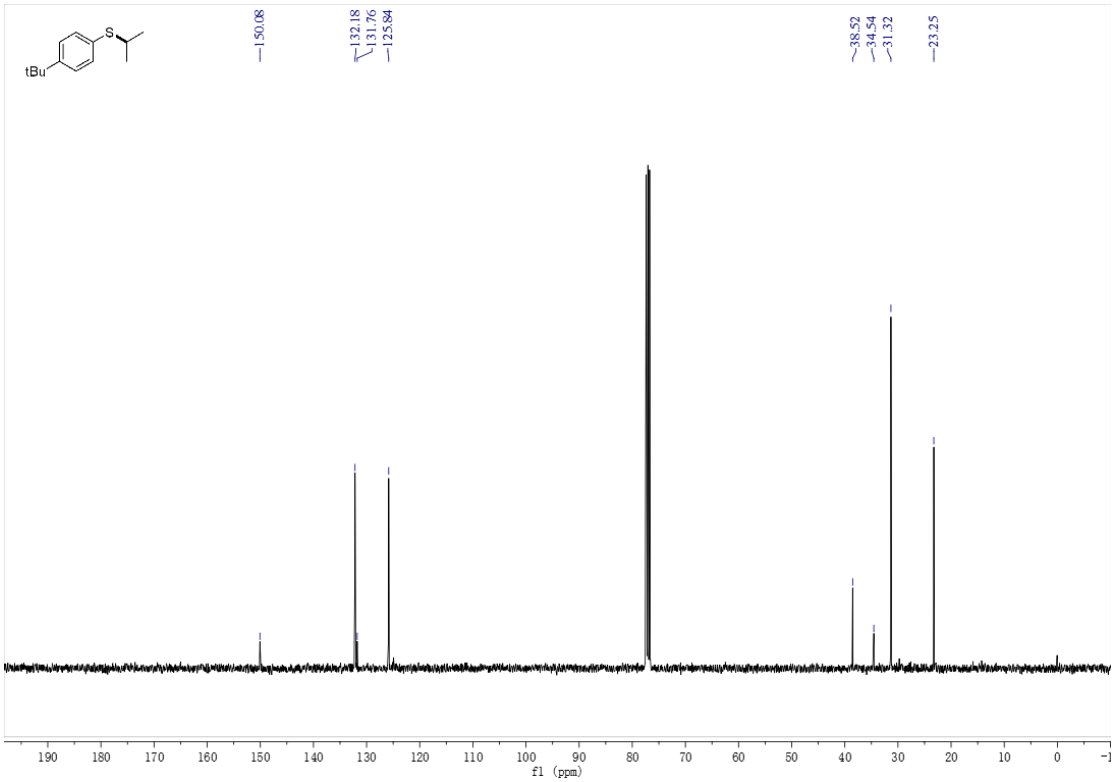
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **19**



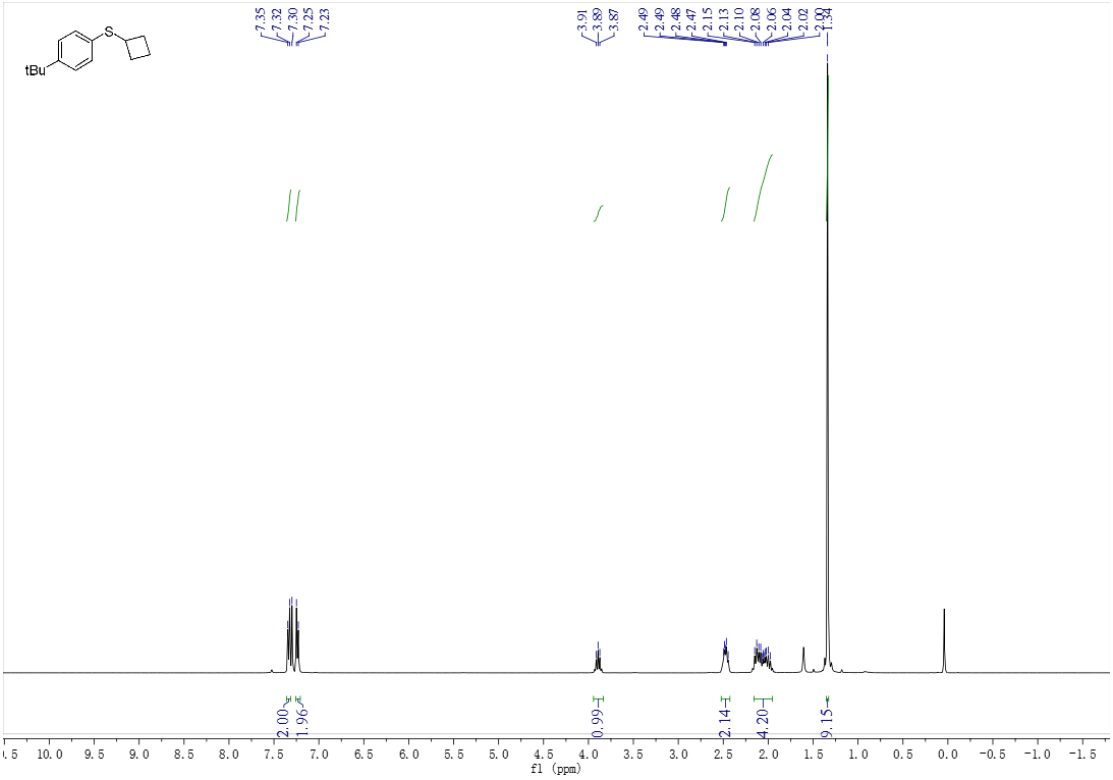
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **20**



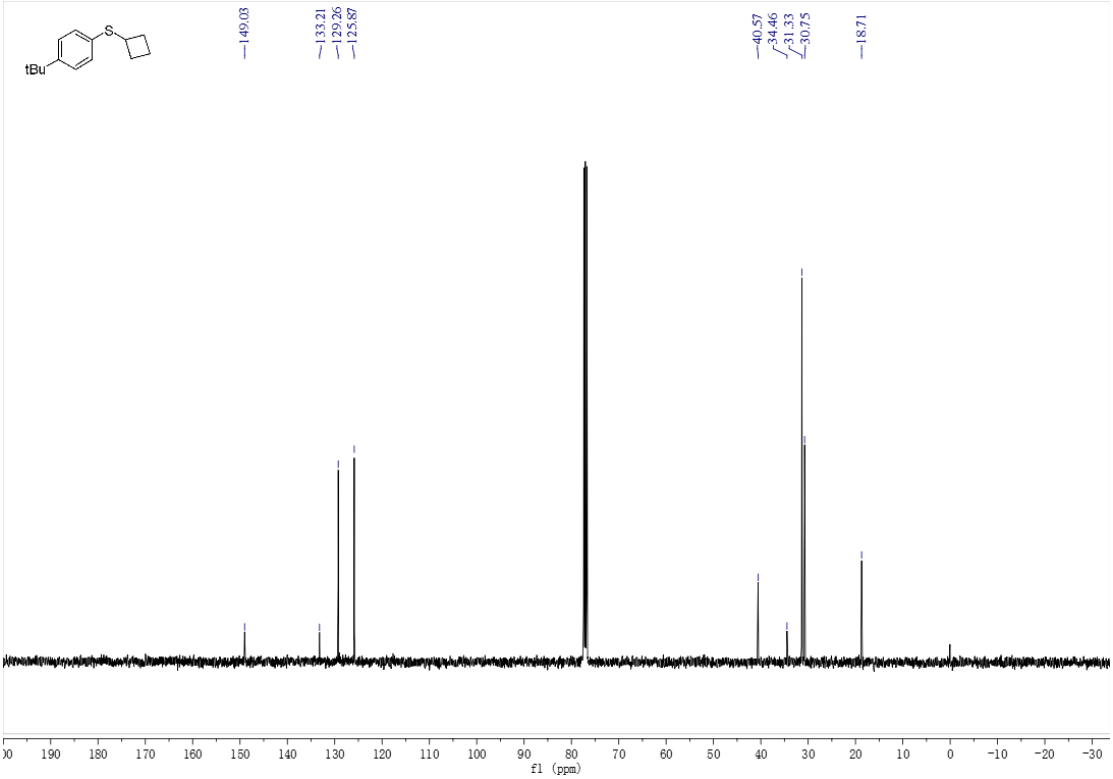
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **20**



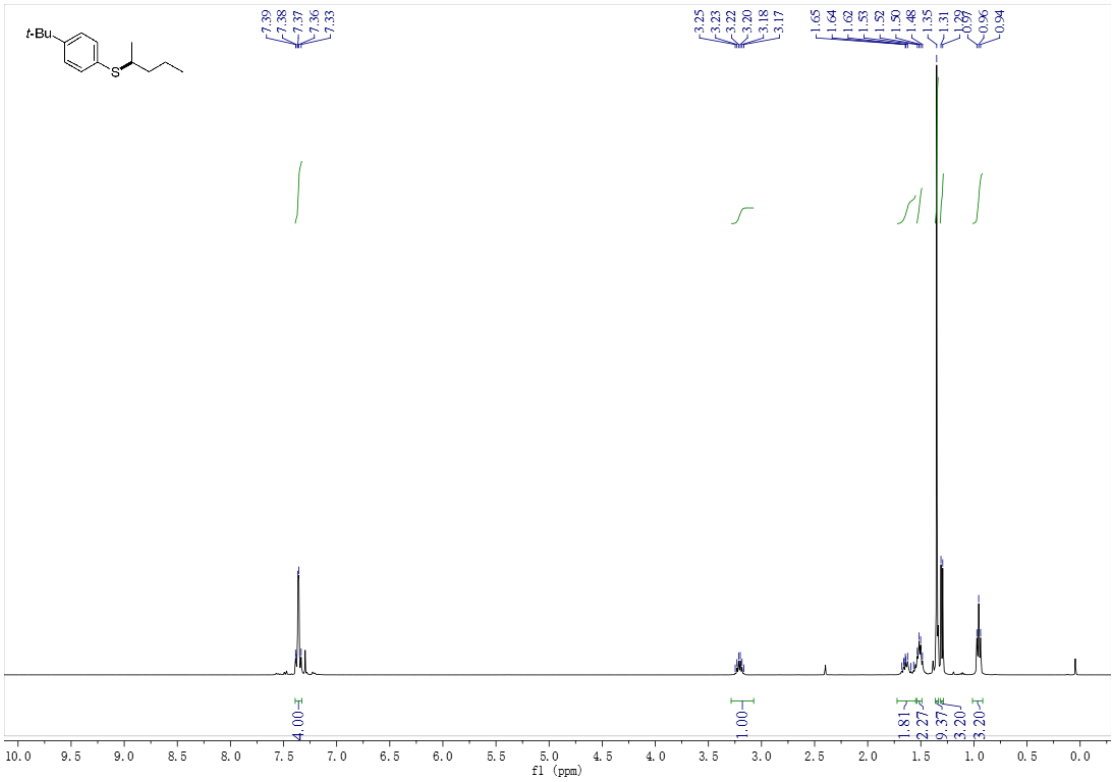
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **20**



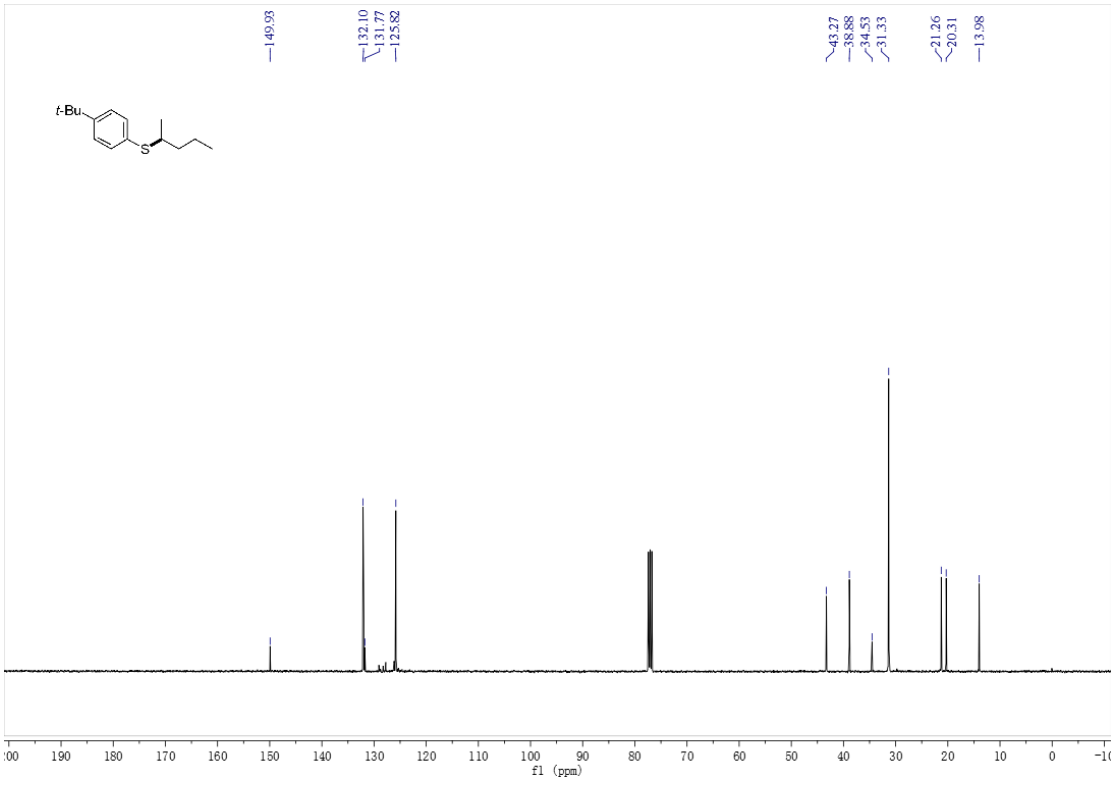
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **20**



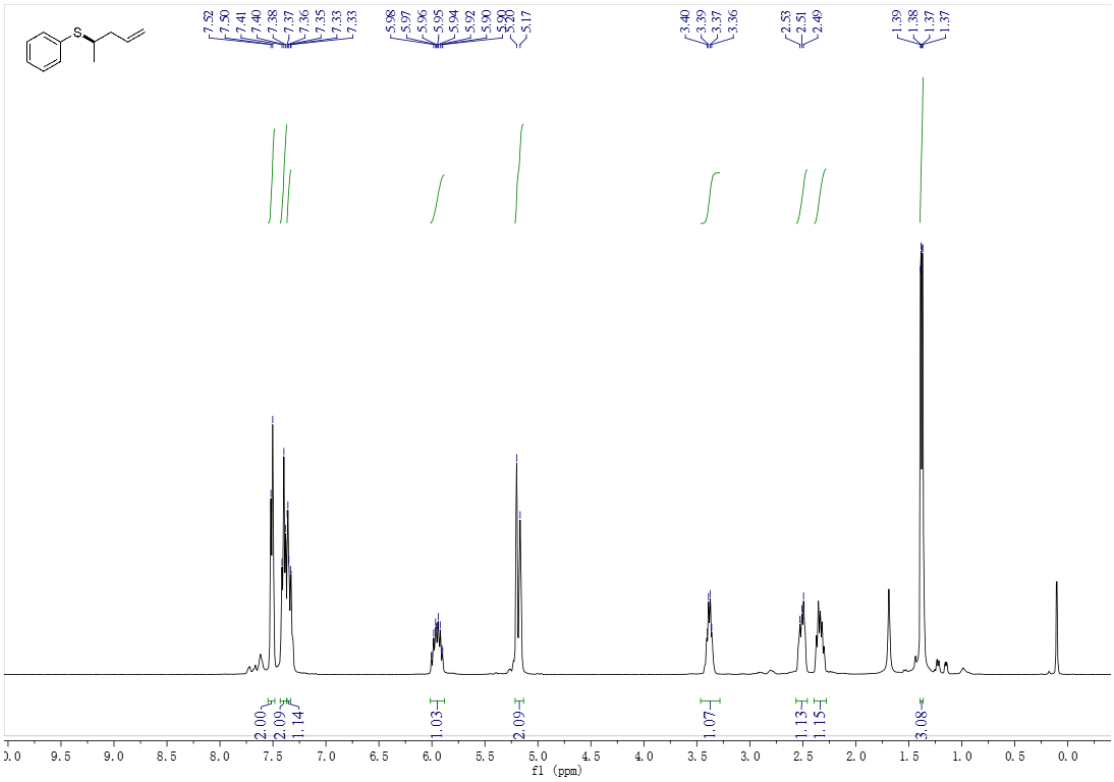
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **22**



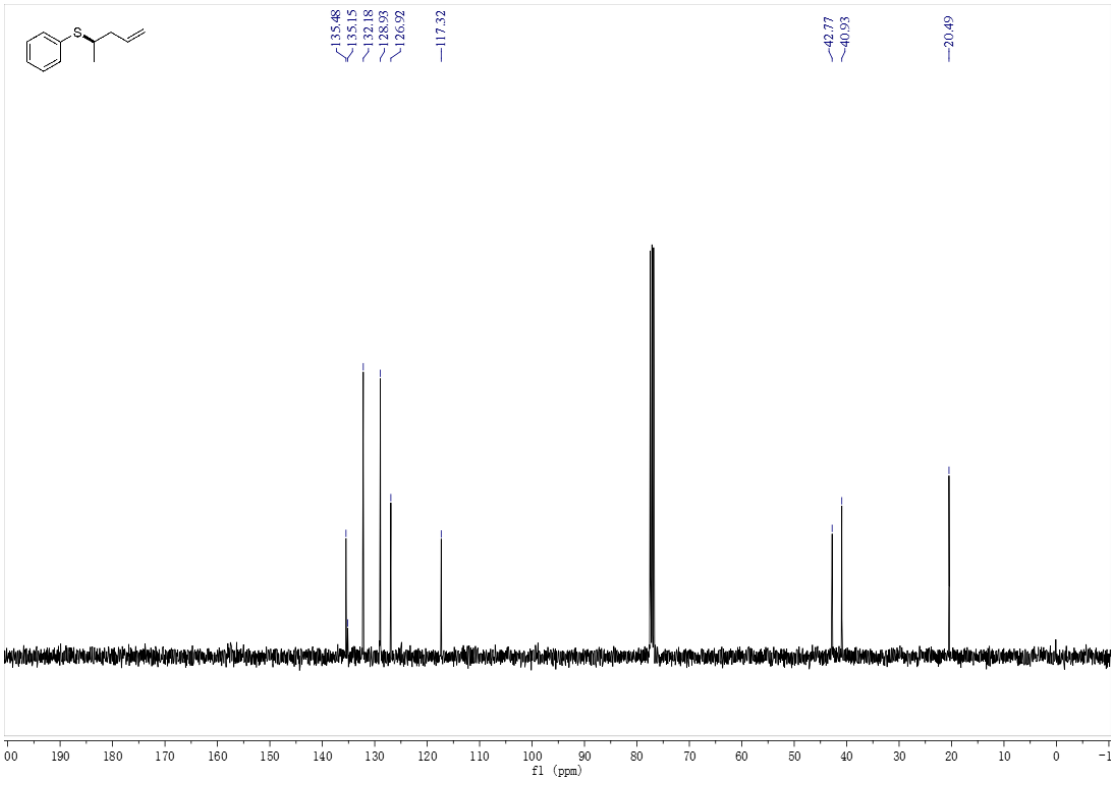
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **22**



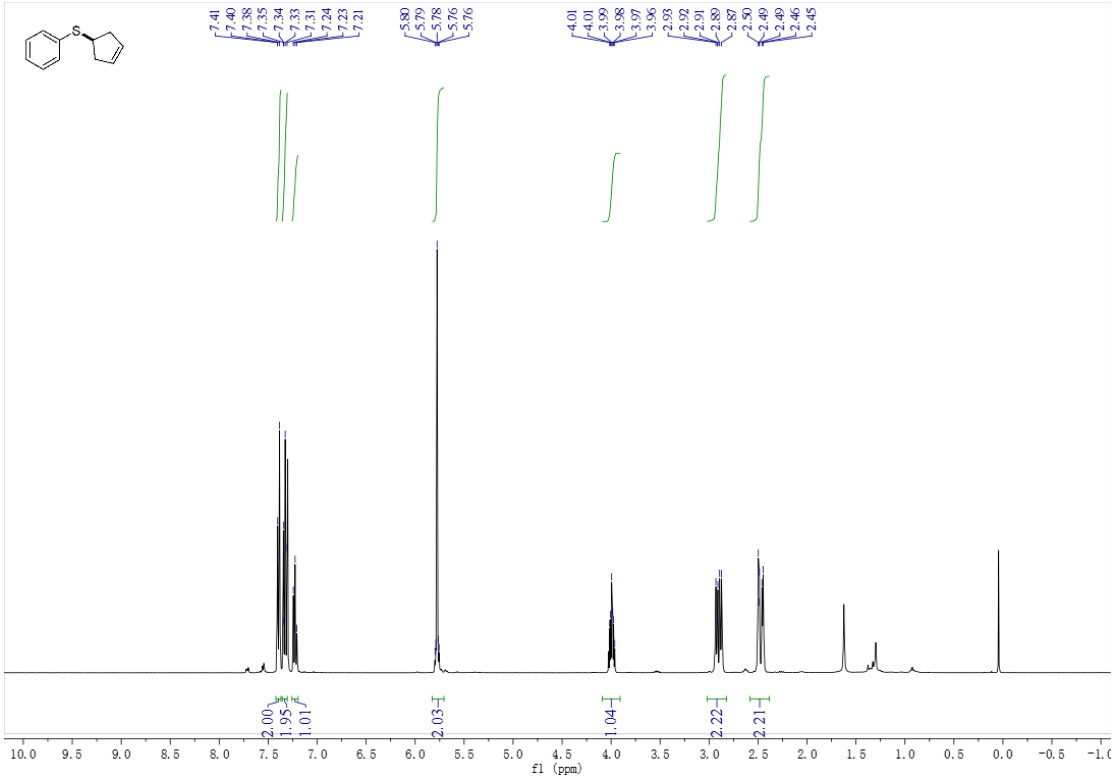
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **23**



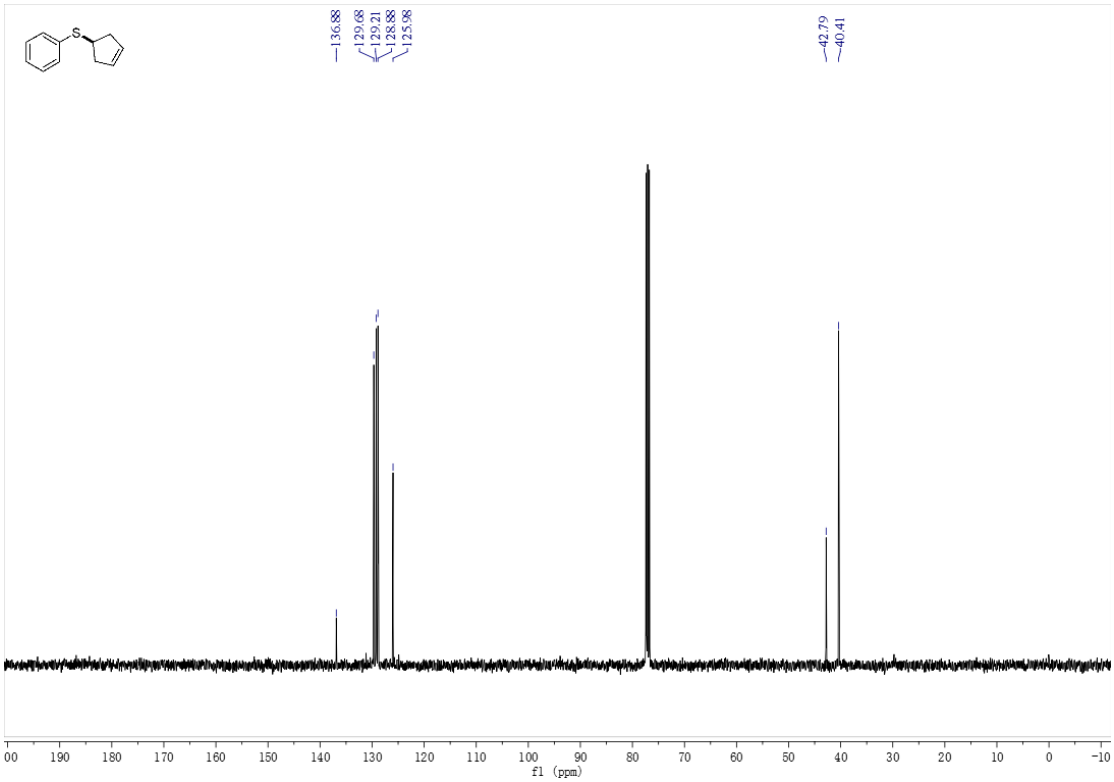
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **23**



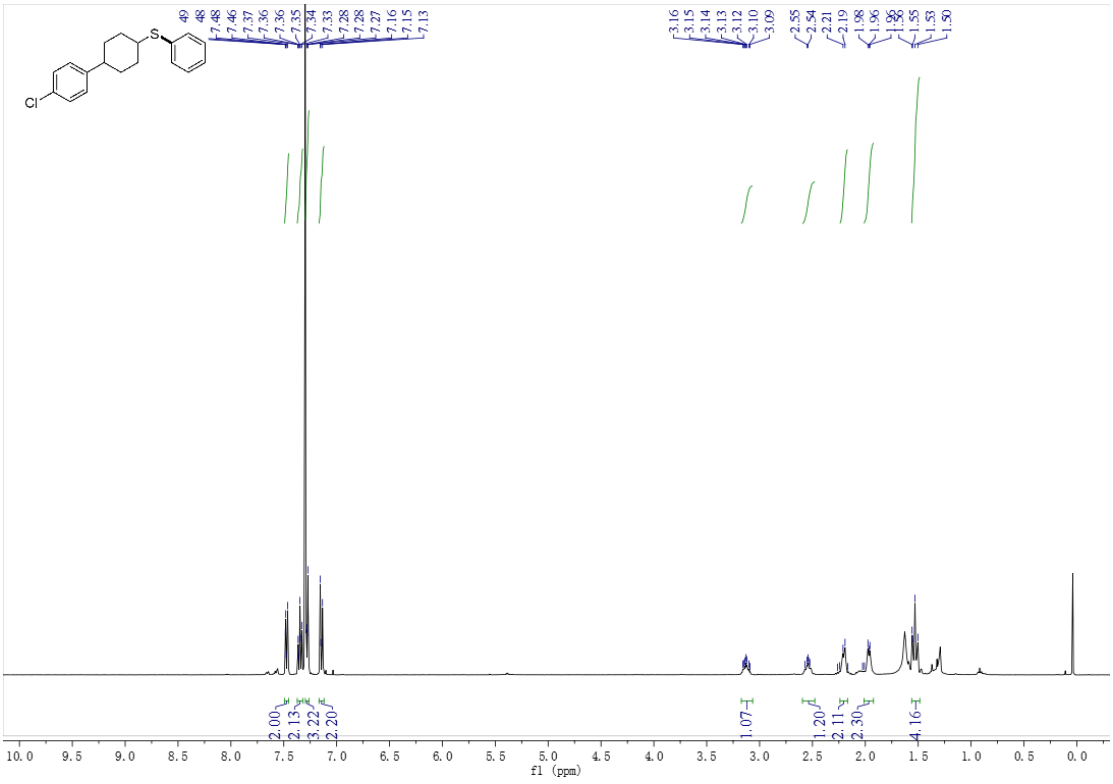
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **24**



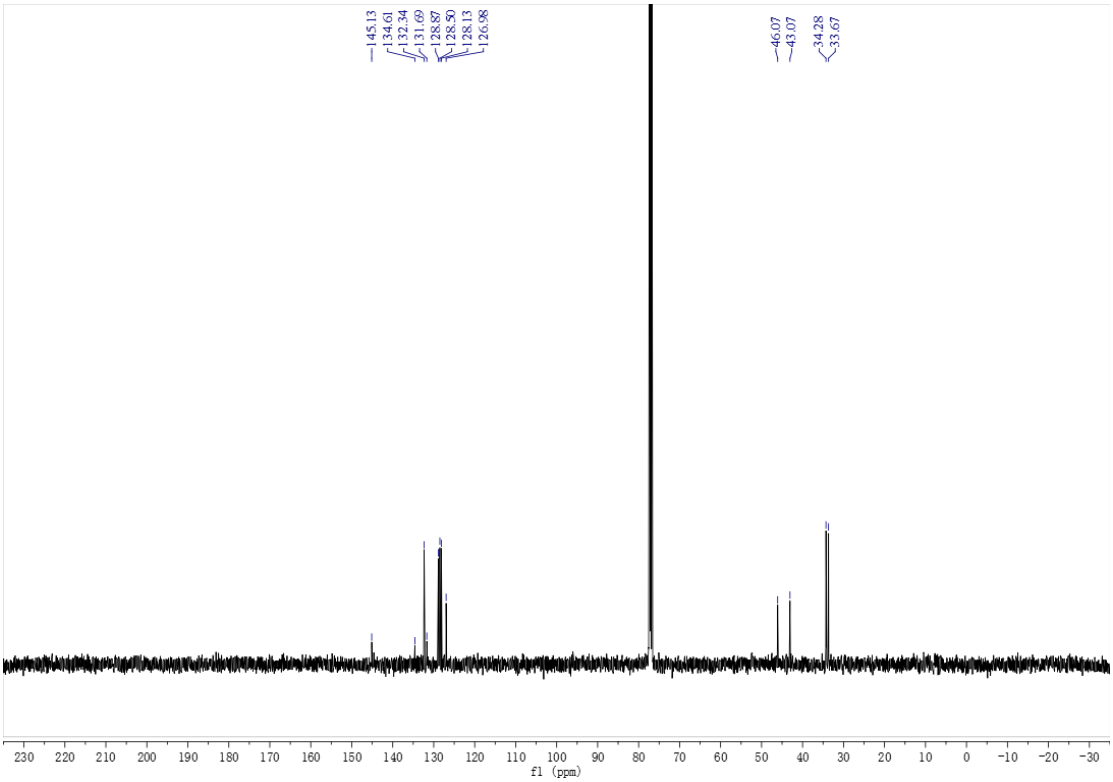
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **24**



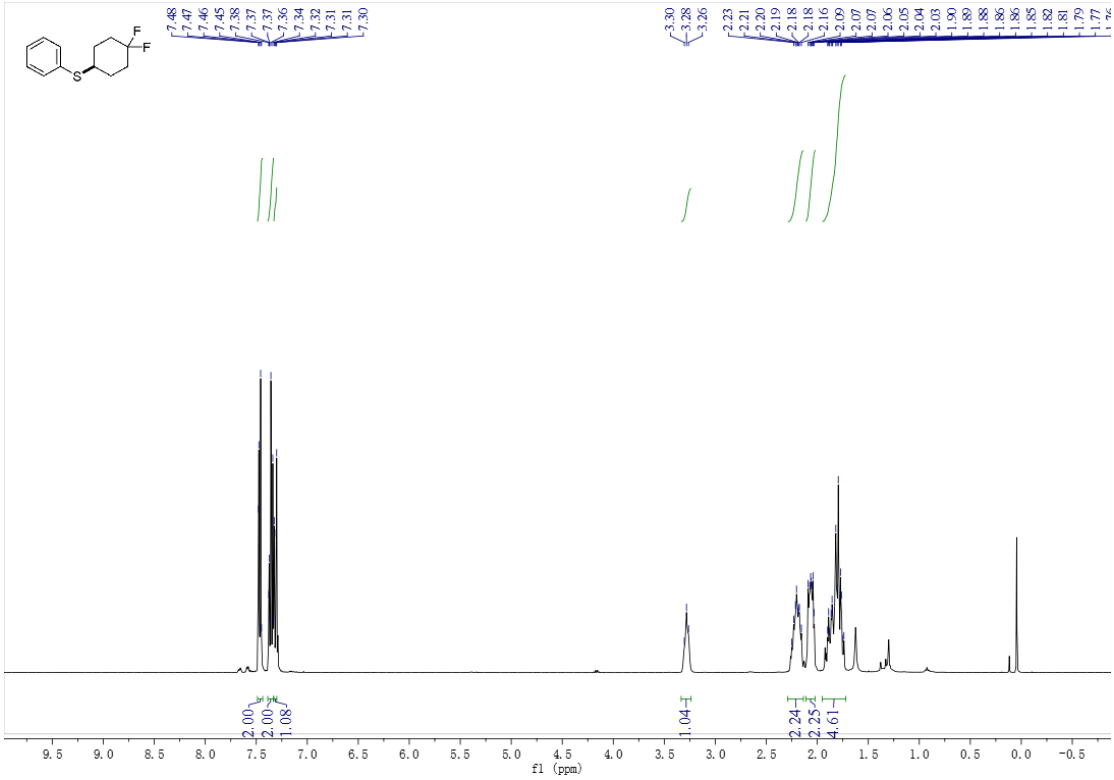
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **25**



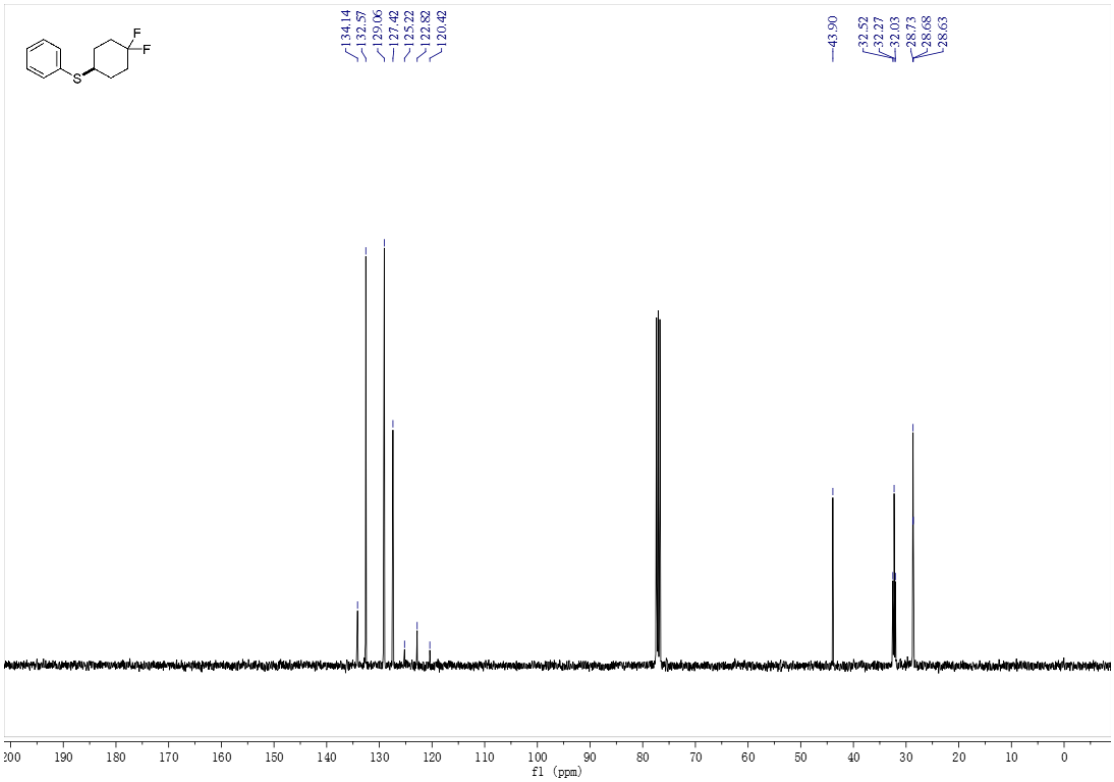
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **25**



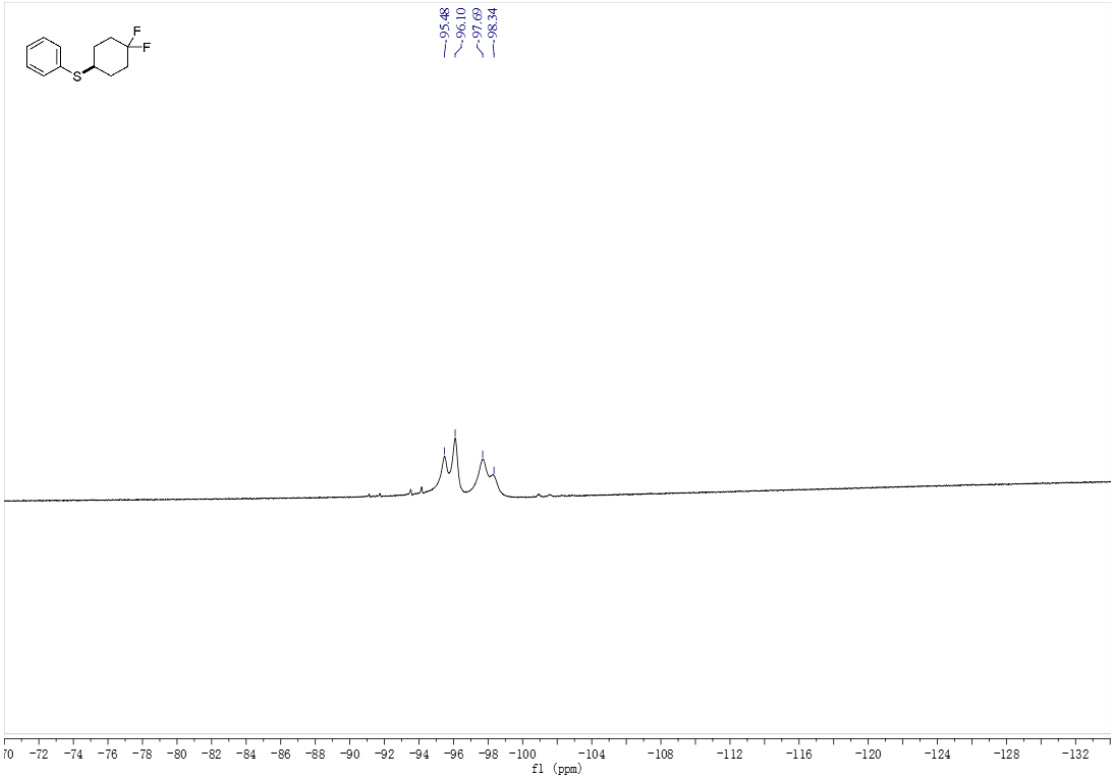
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **26**



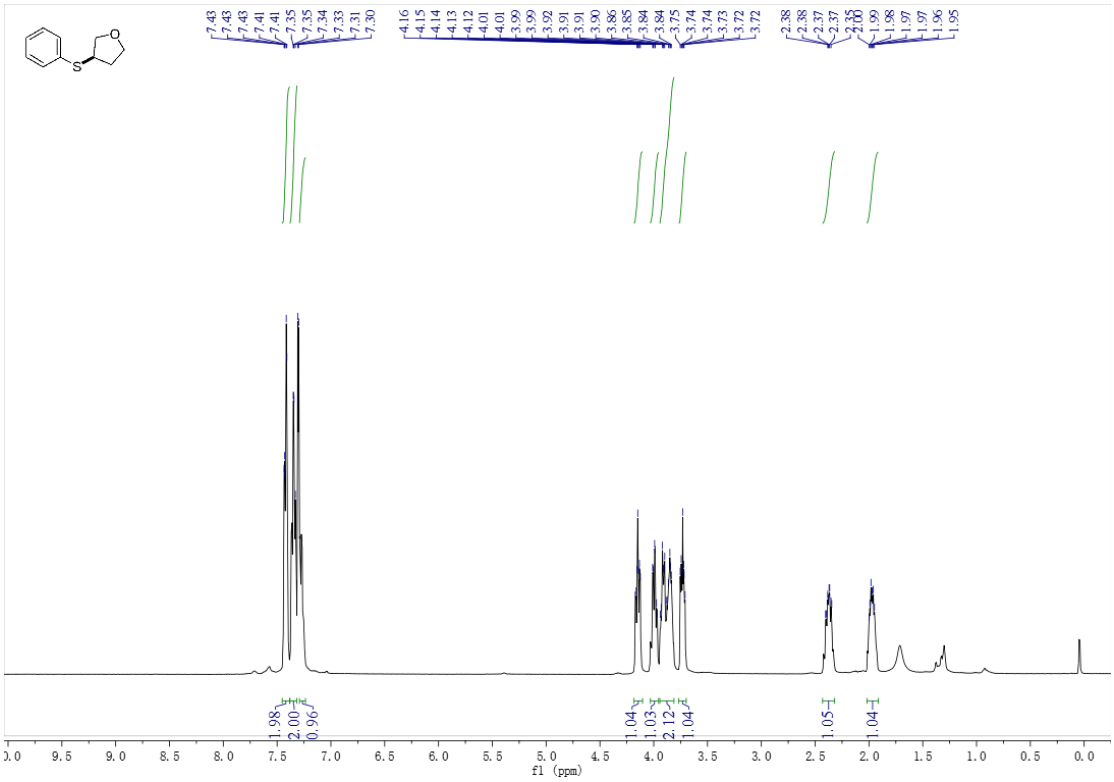
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **26**



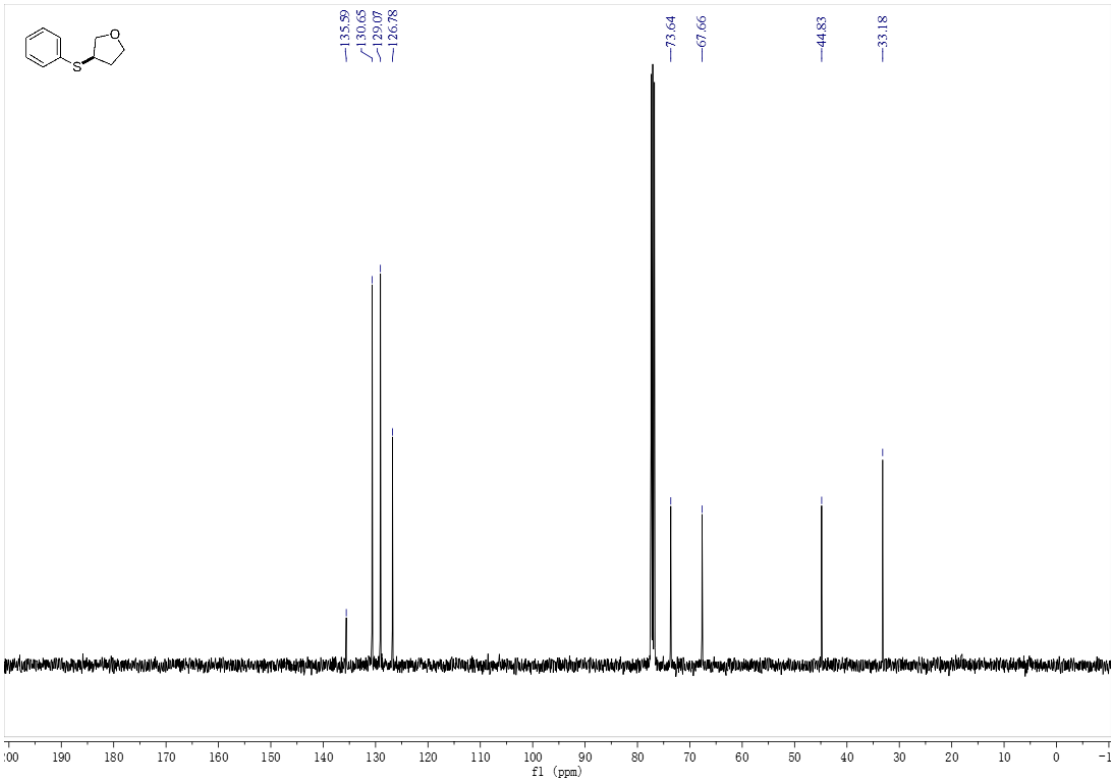
^{19}F NMR spectrum (376 MHz, $CDCl_3$，23 ℃) of **26**



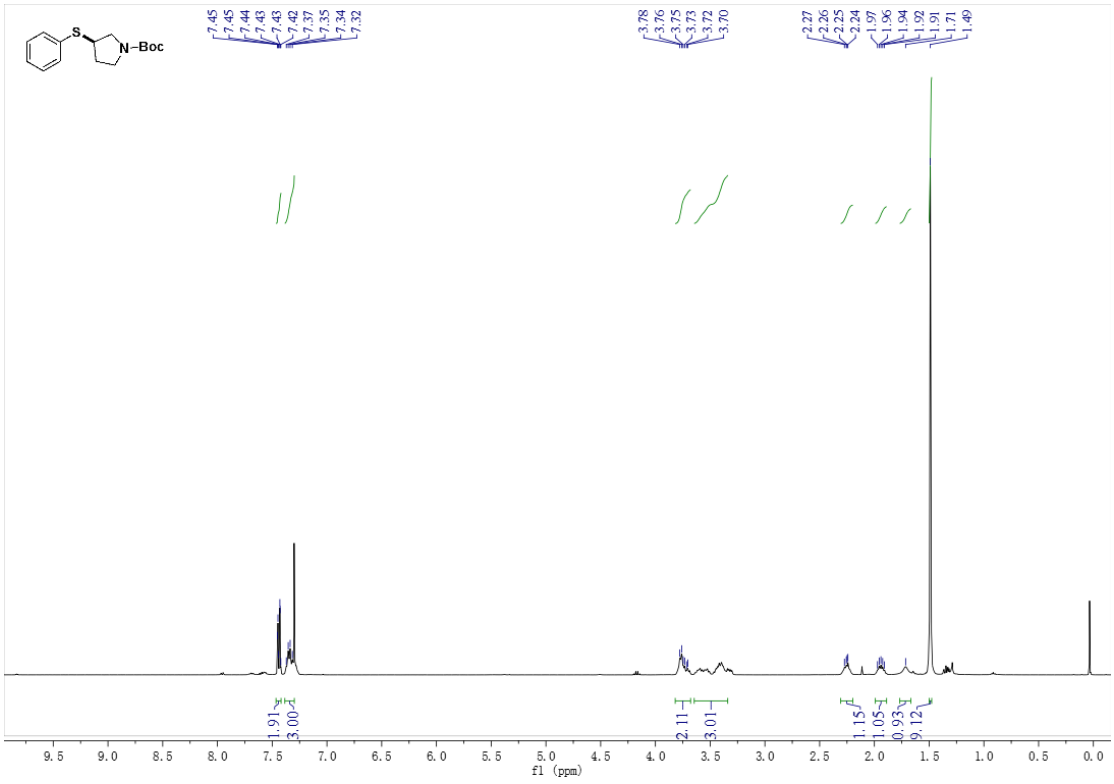
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **27**



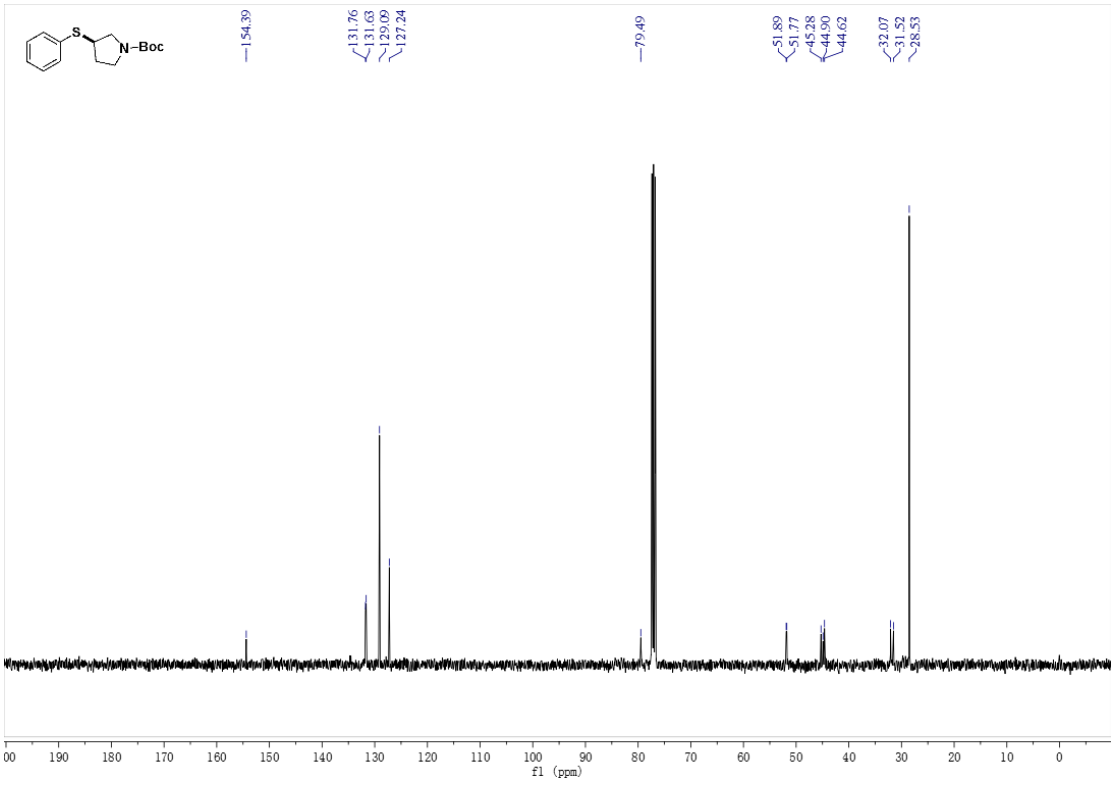
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **27**



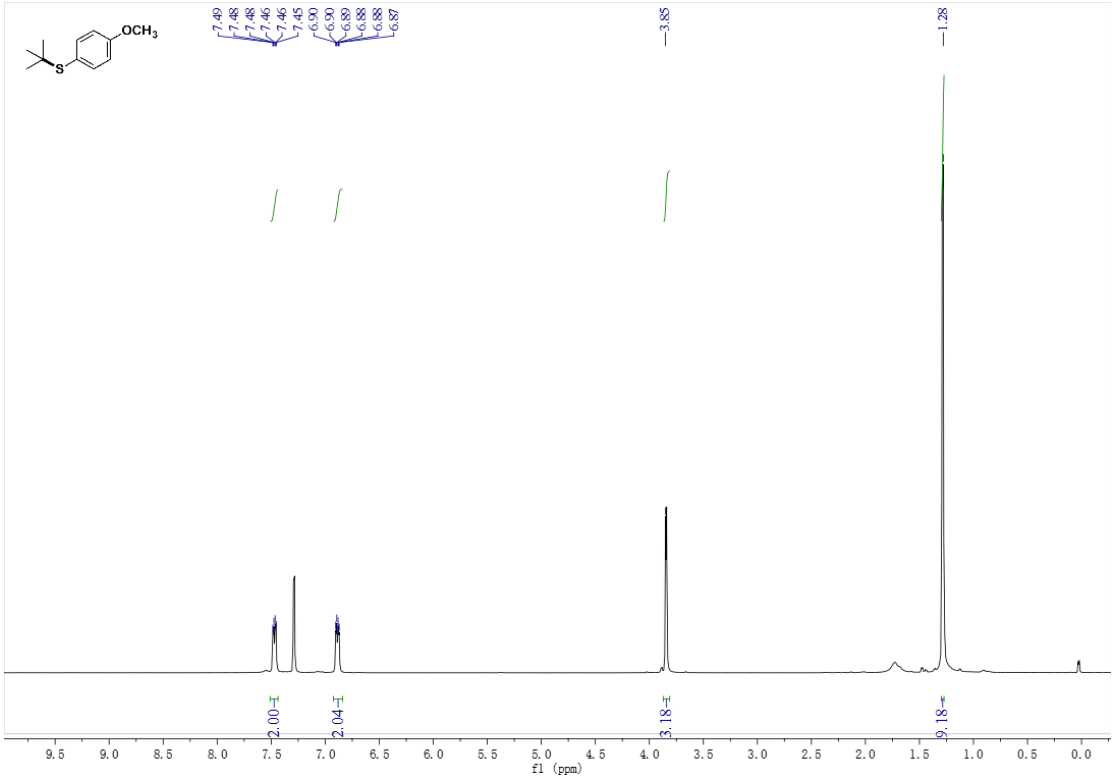
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **28**



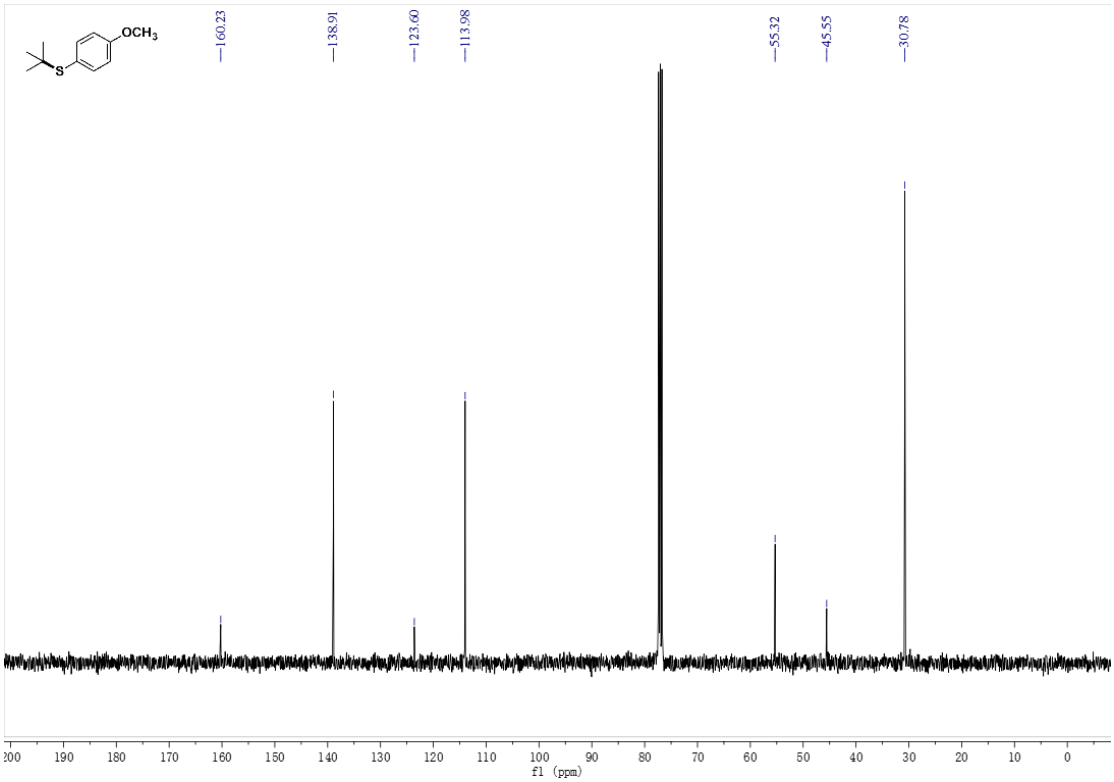
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **28**



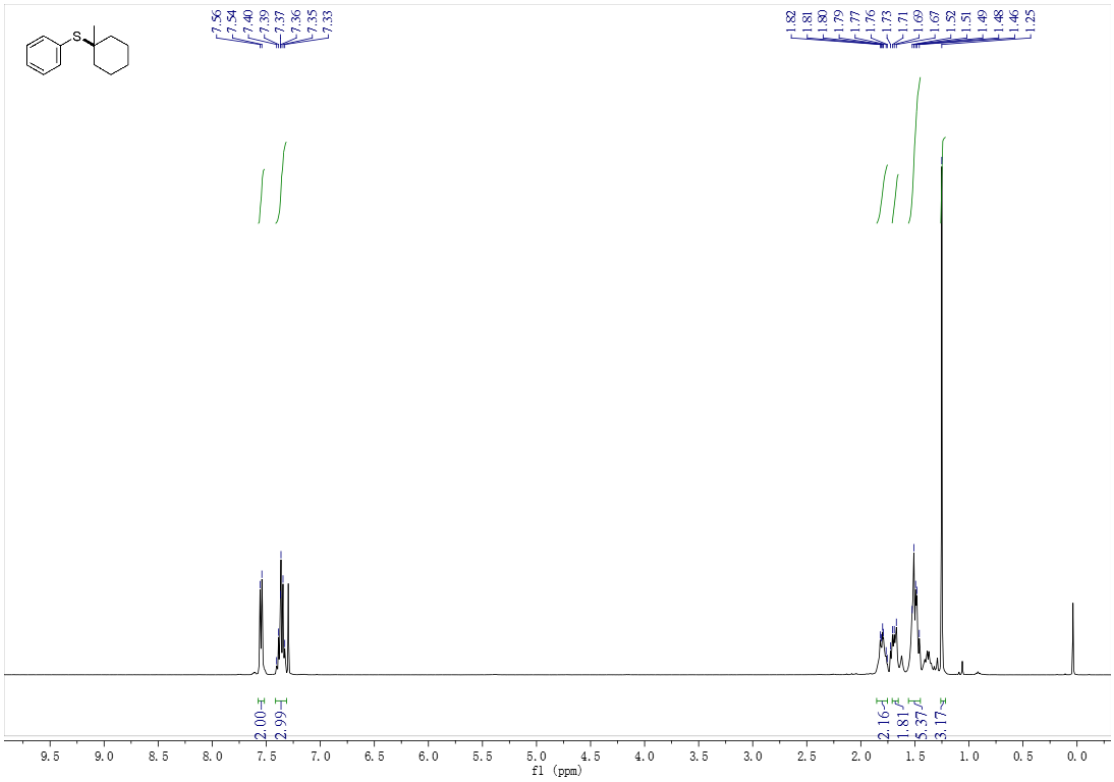
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **29**



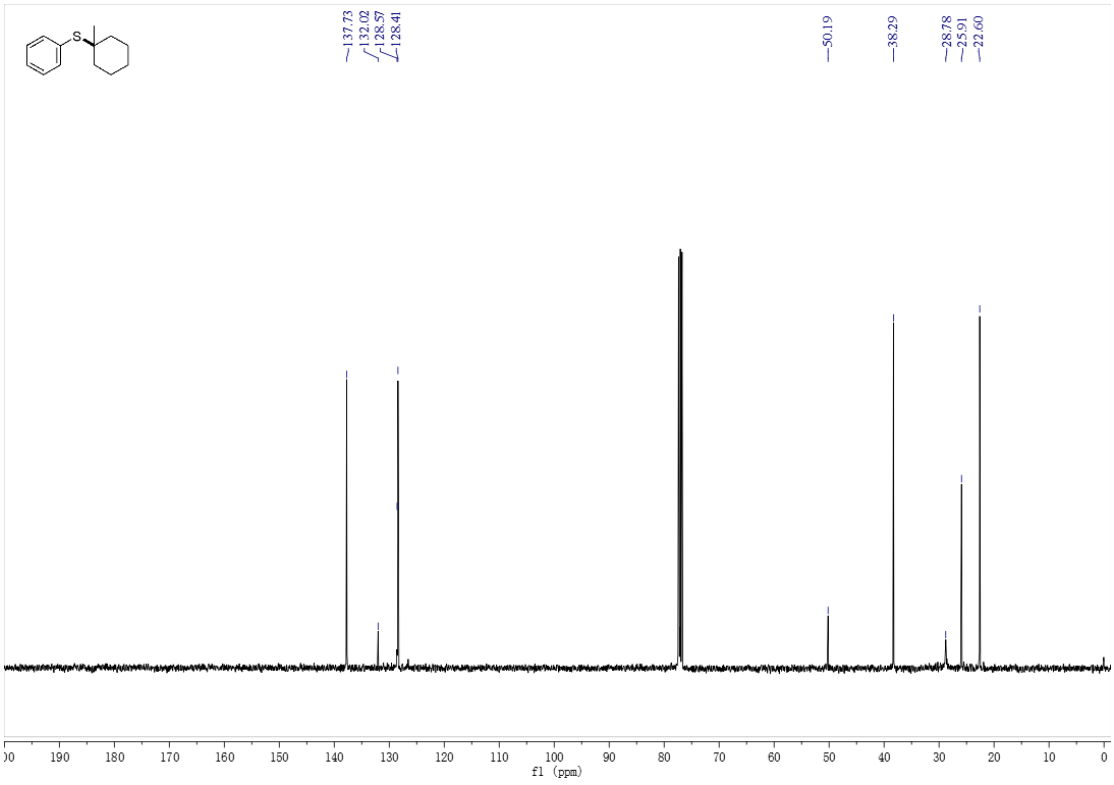
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **29**



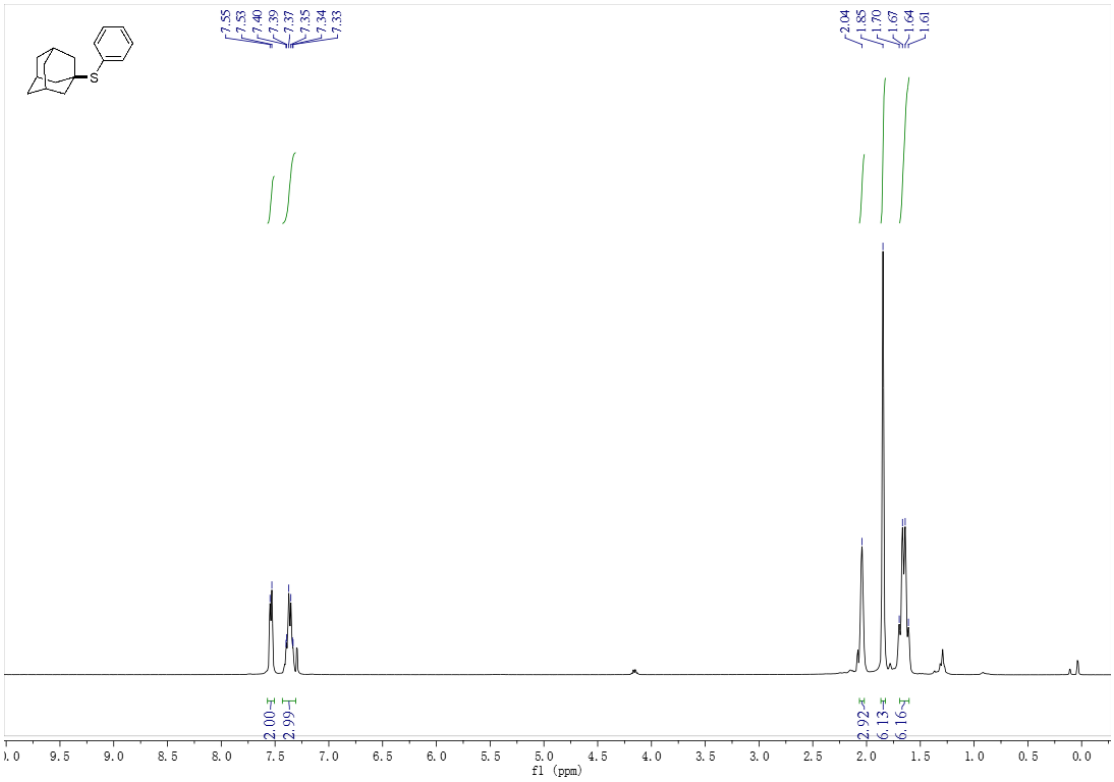
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **30**



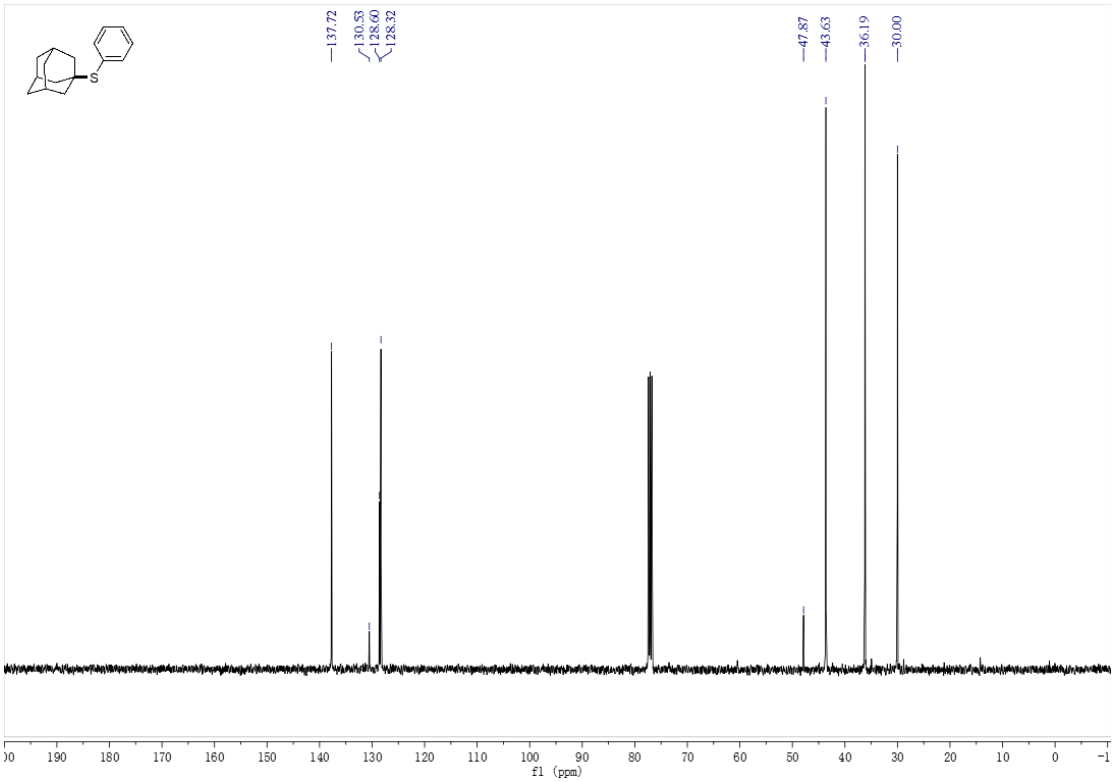
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **30**



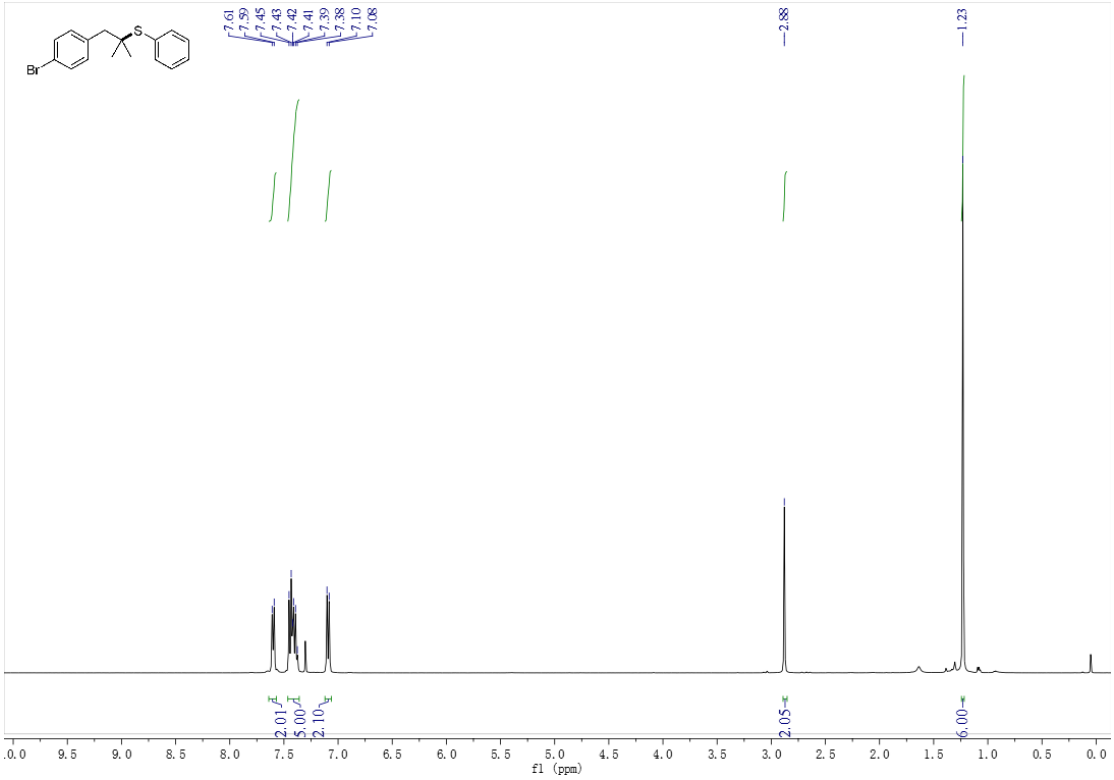
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **31**



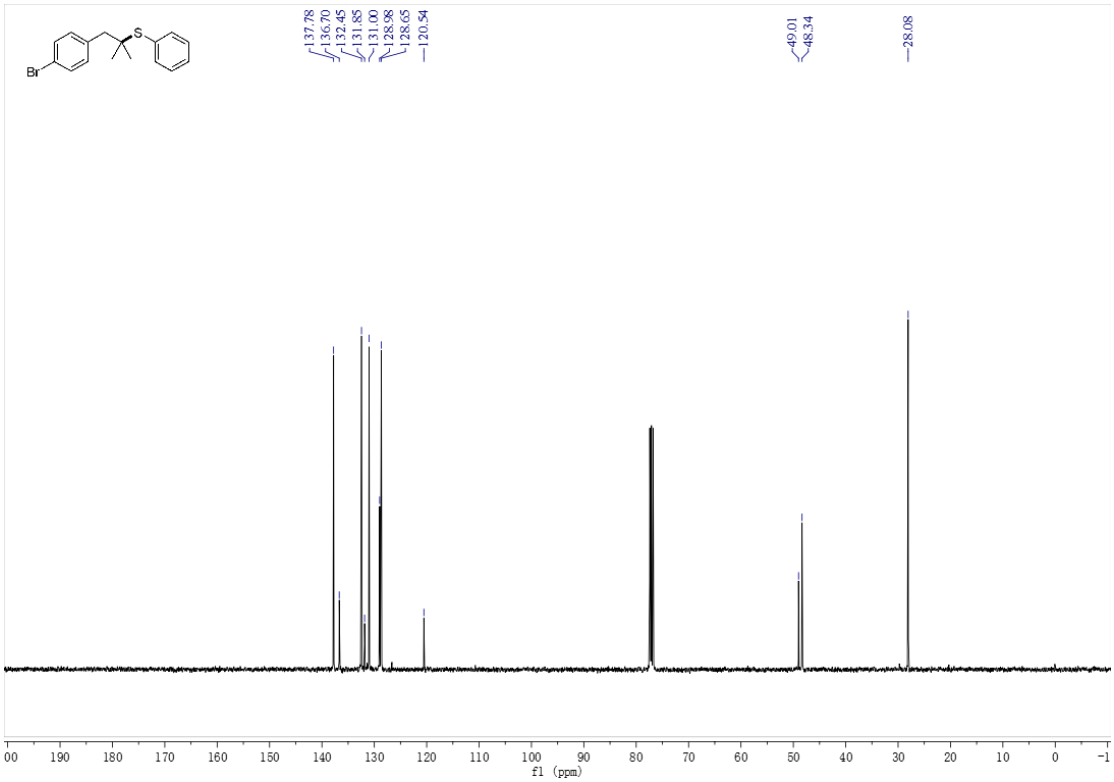
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **31**



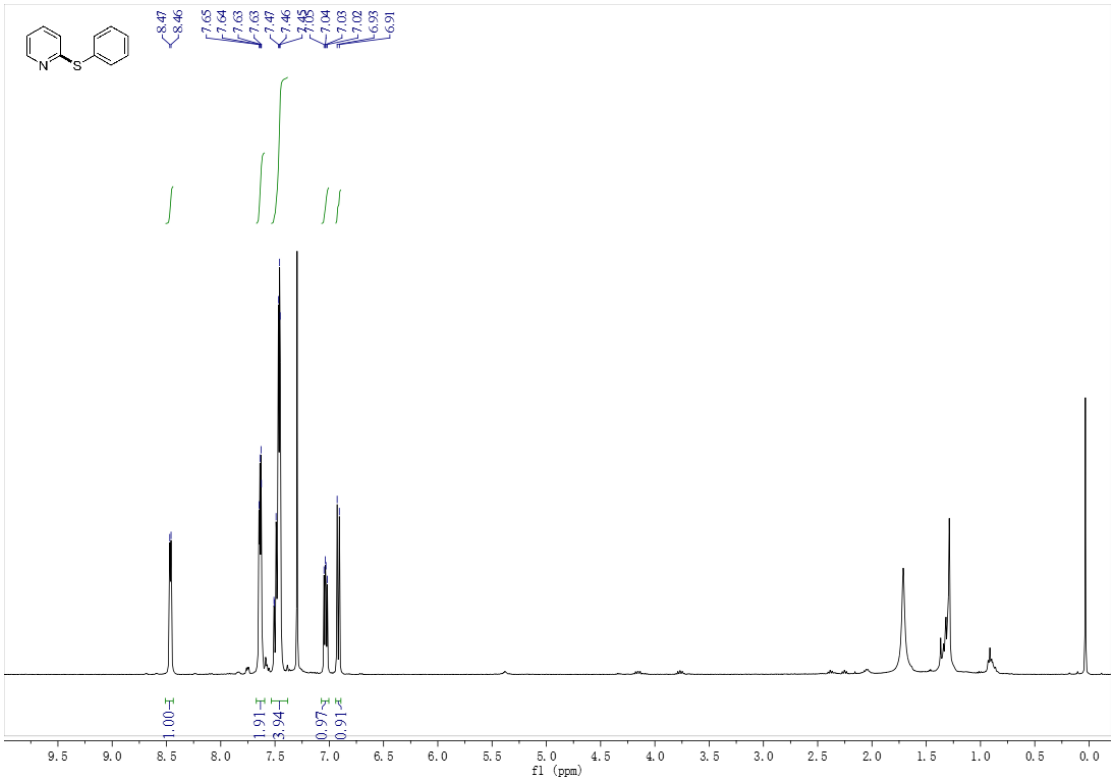
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **32**



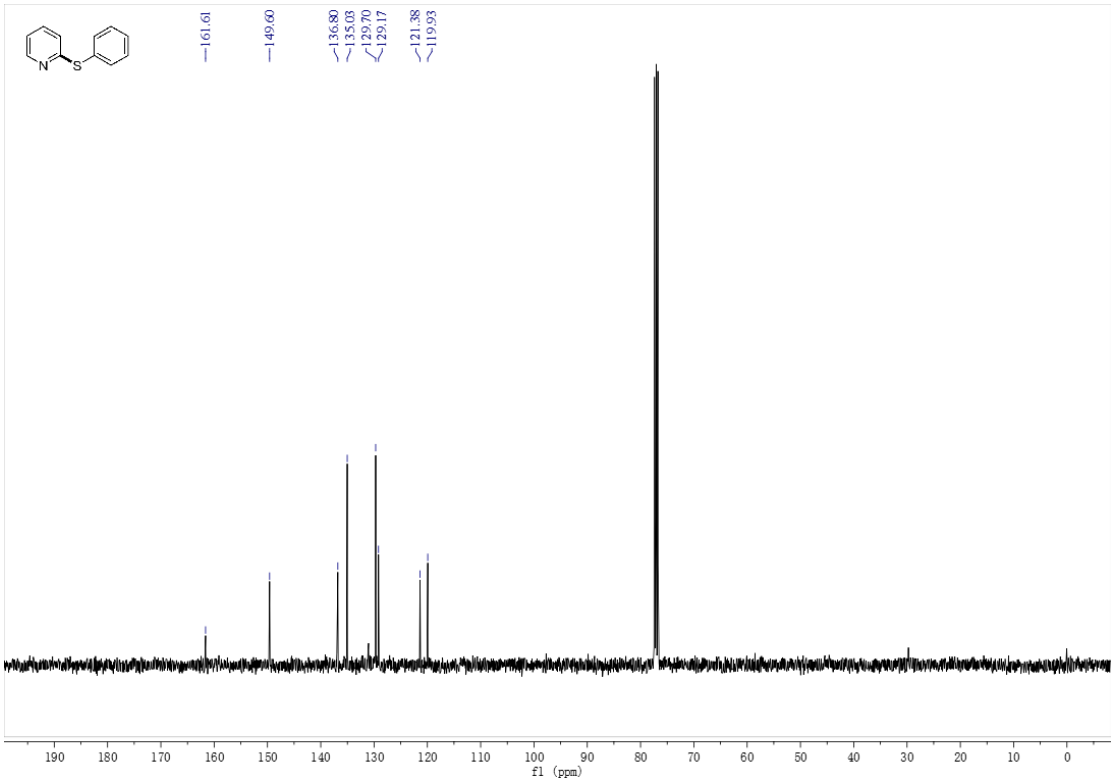
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **32**



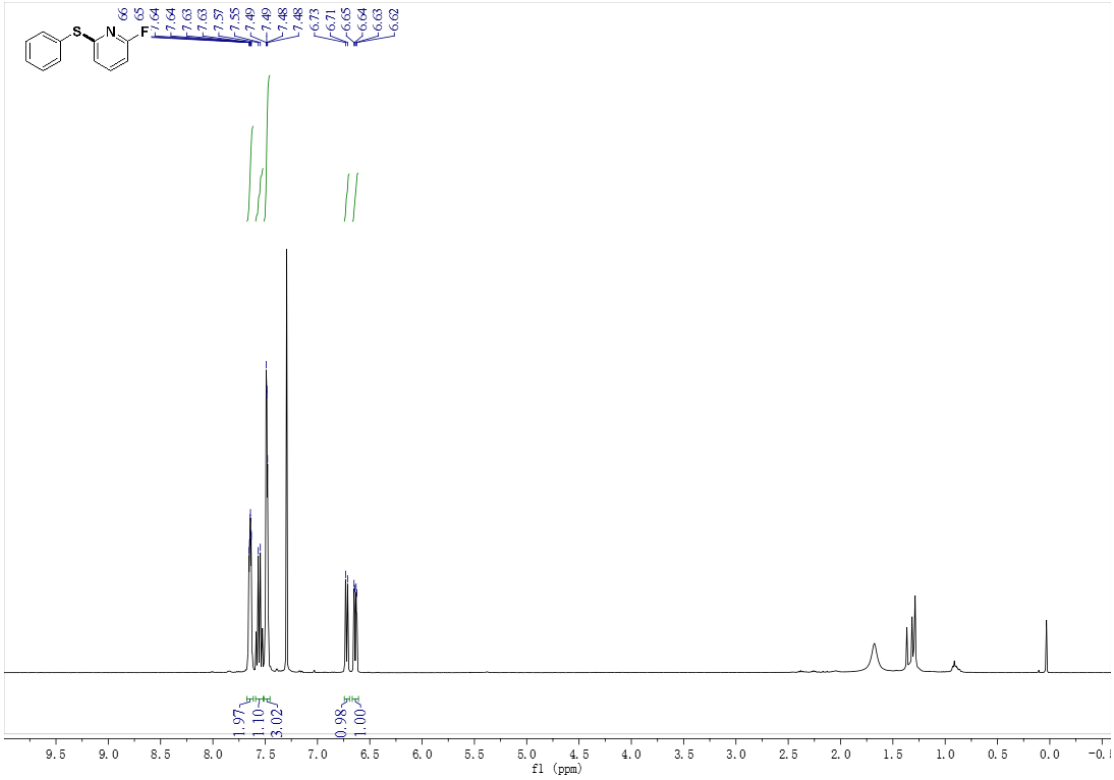
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **33**



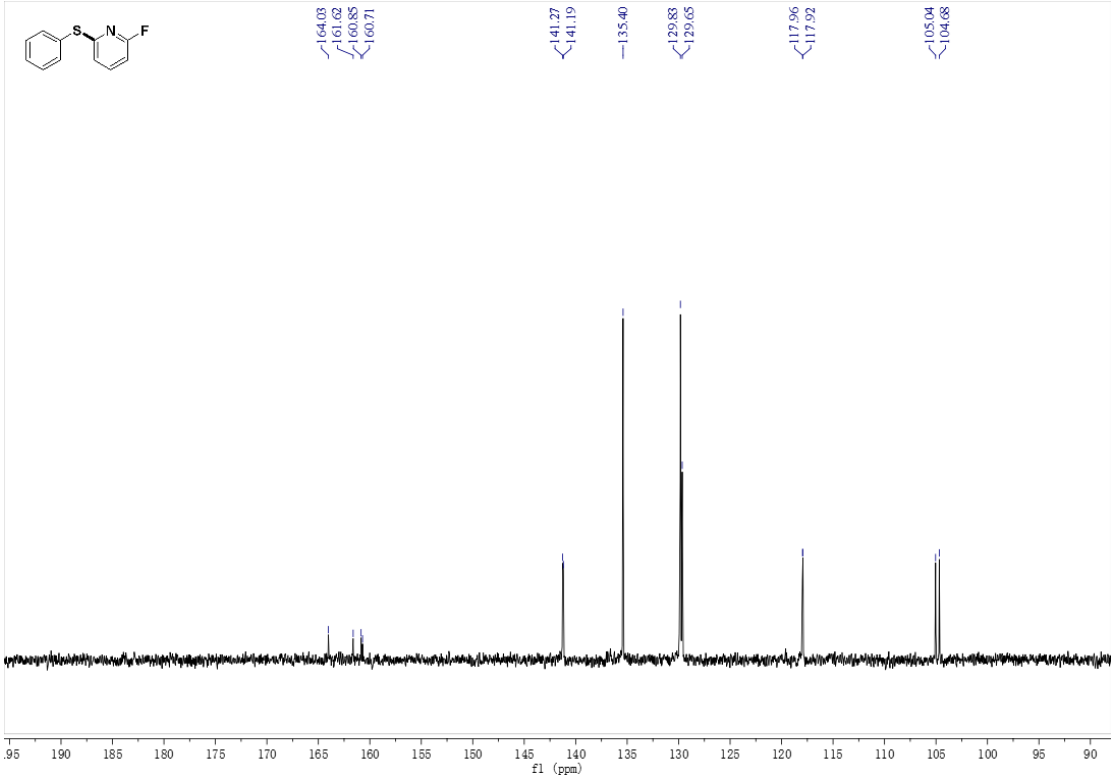
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **33**



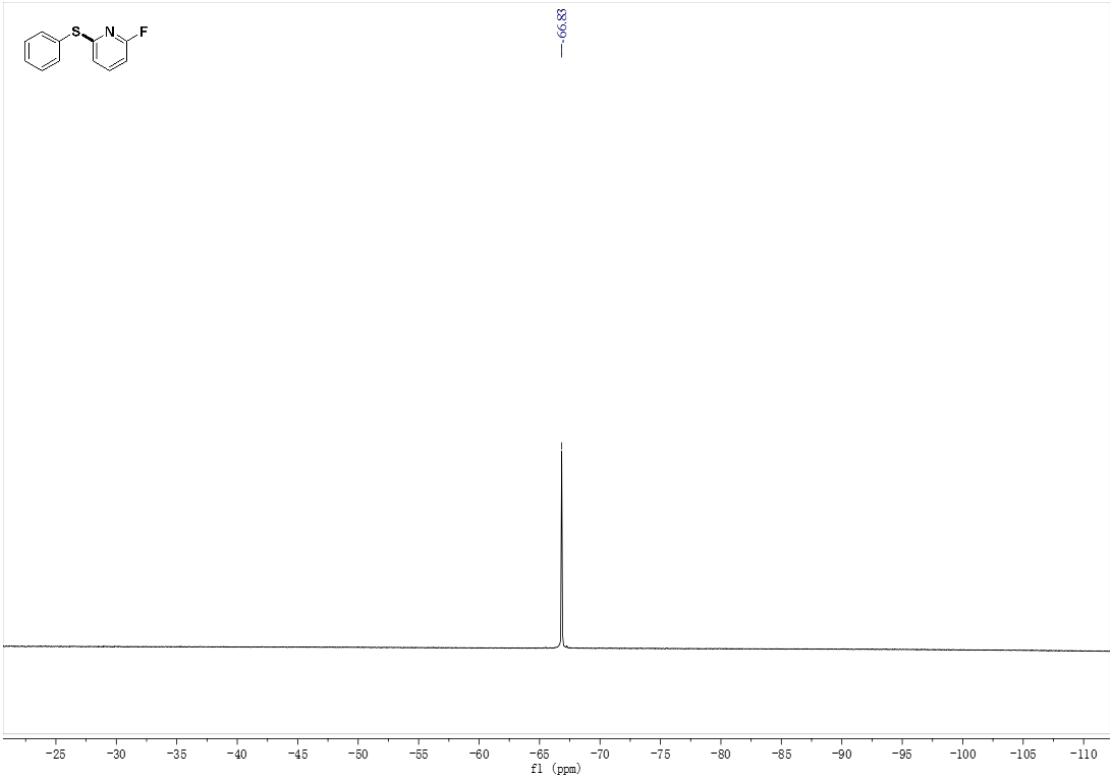
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **34**



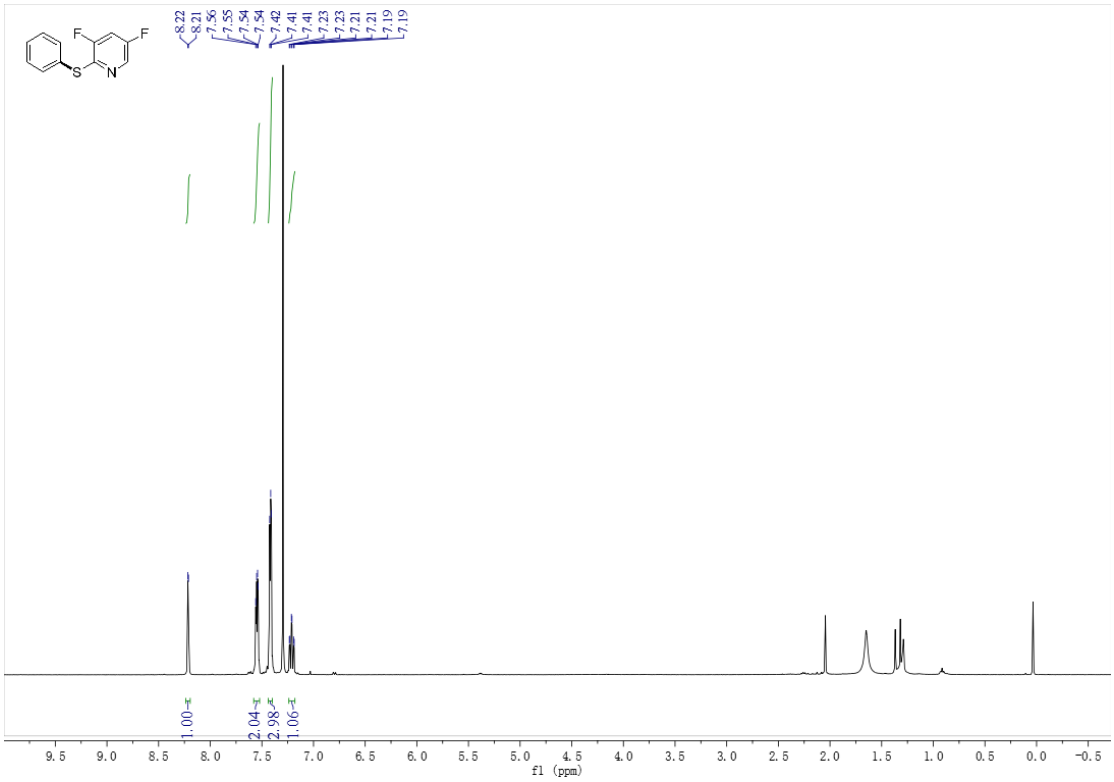
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **34**



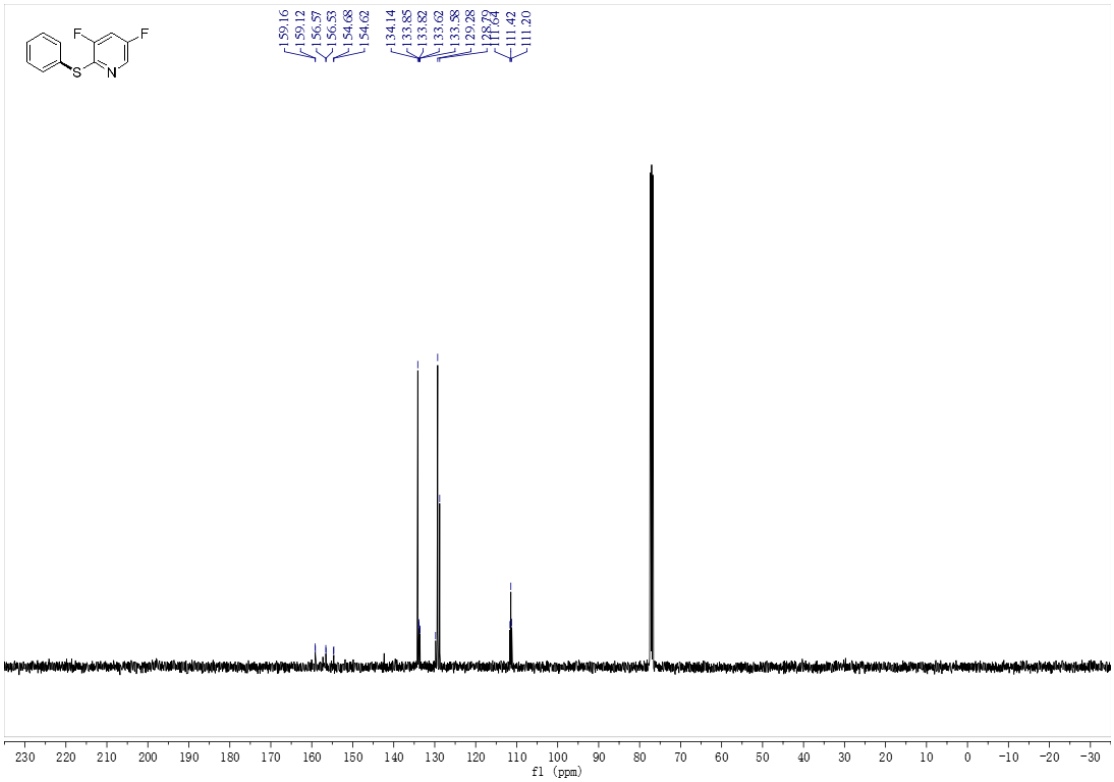
^{19}F NMR spectrum (376 MHz, $CDCl_3$，23 ℃) of **34**



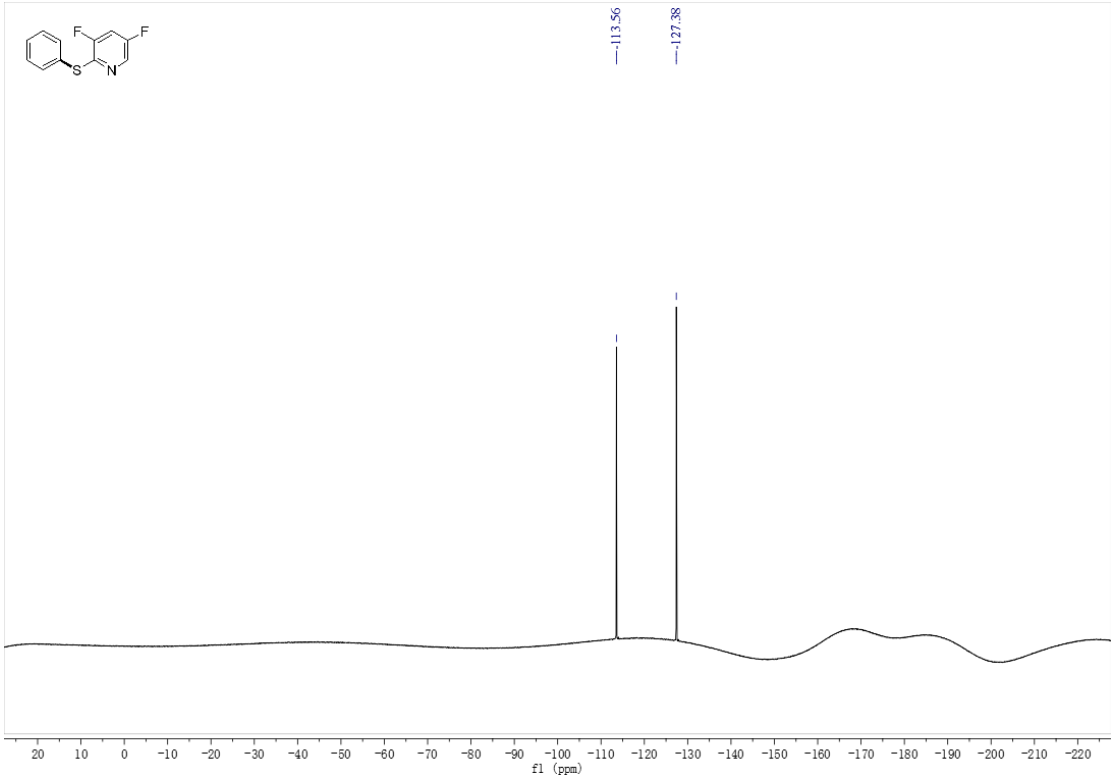
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **35**



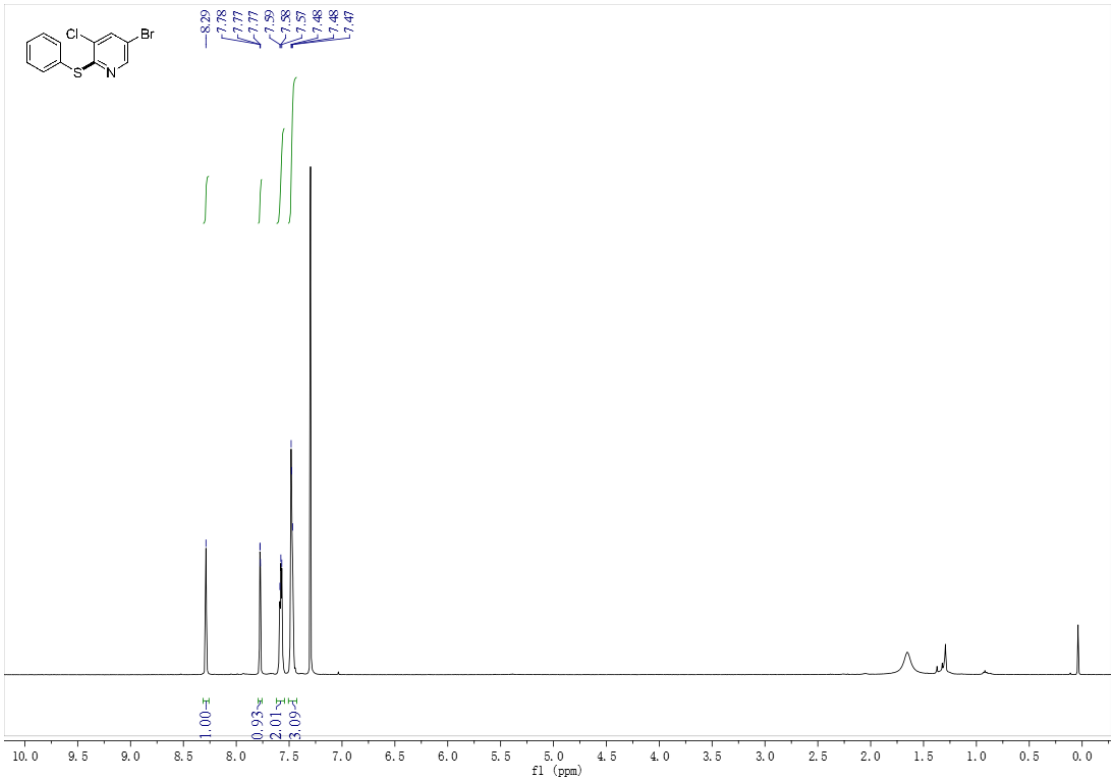
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **35**



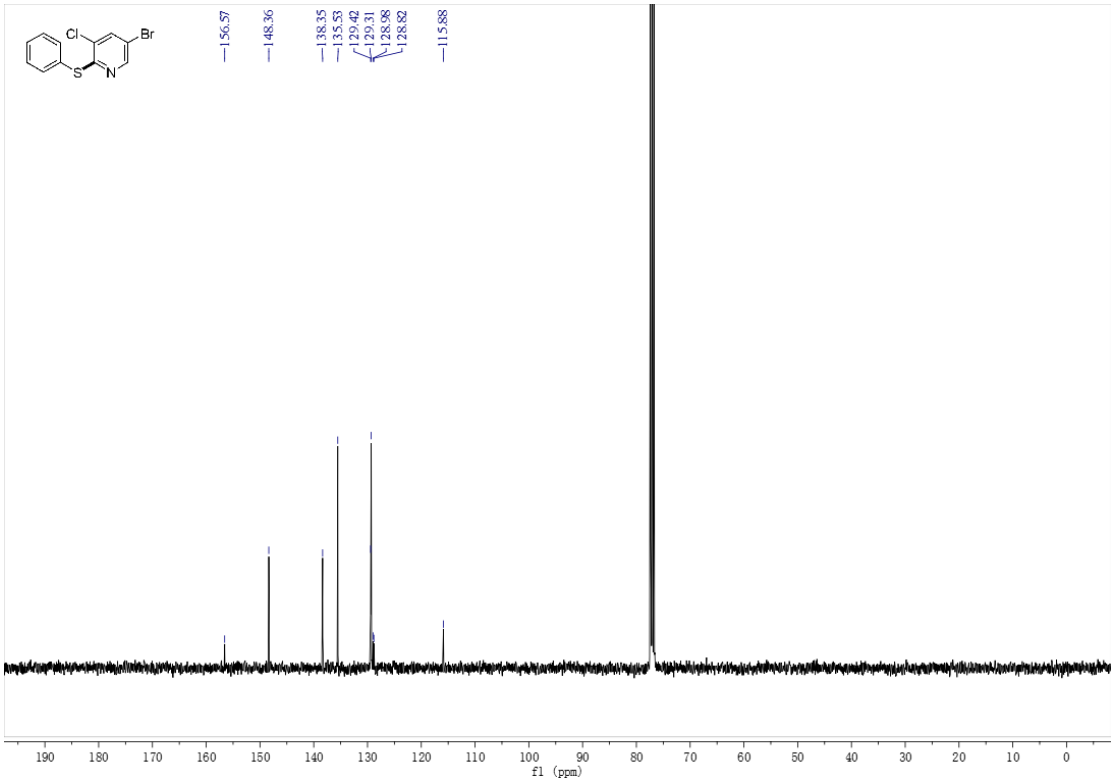
^{19}F NMR spectrum (376 MHz, $CDCl_3$，23 ℃) of **35**



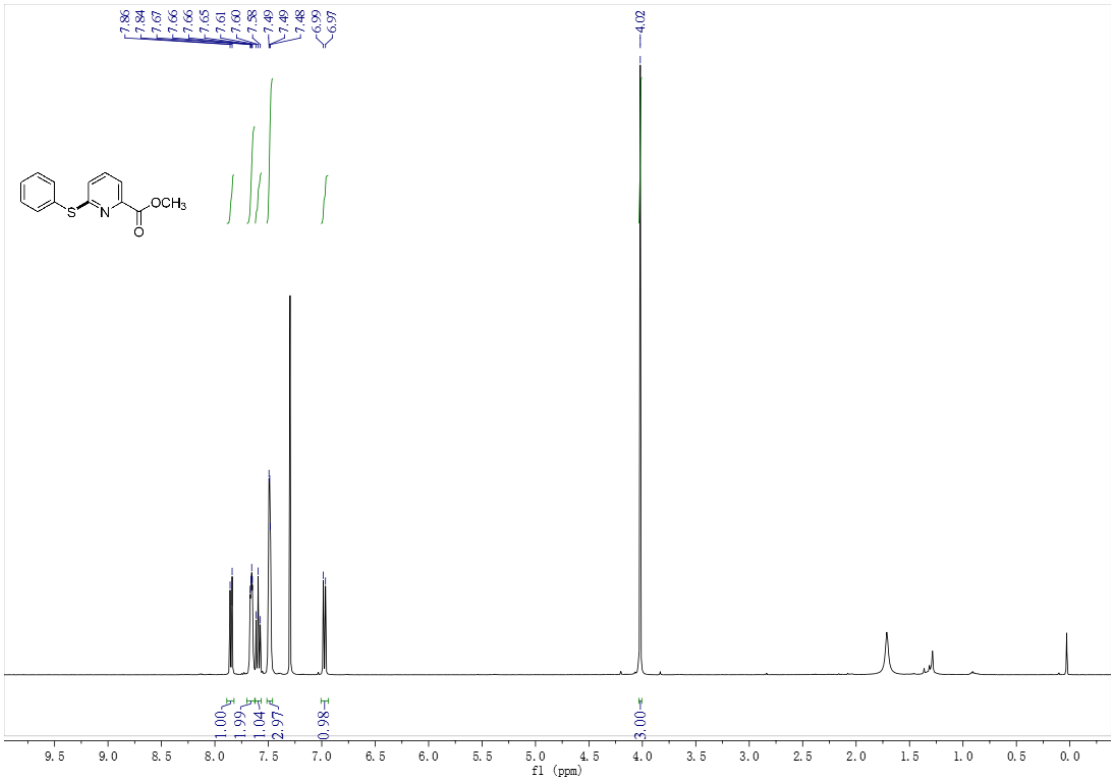
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **36**



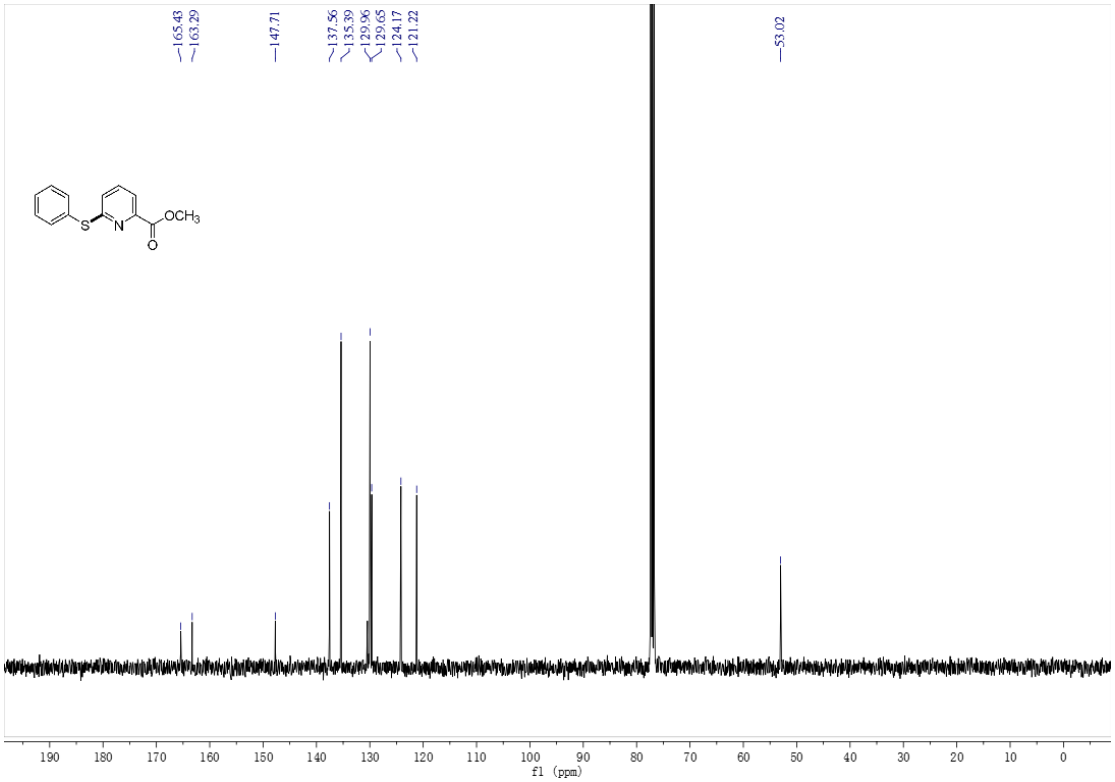
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **36**



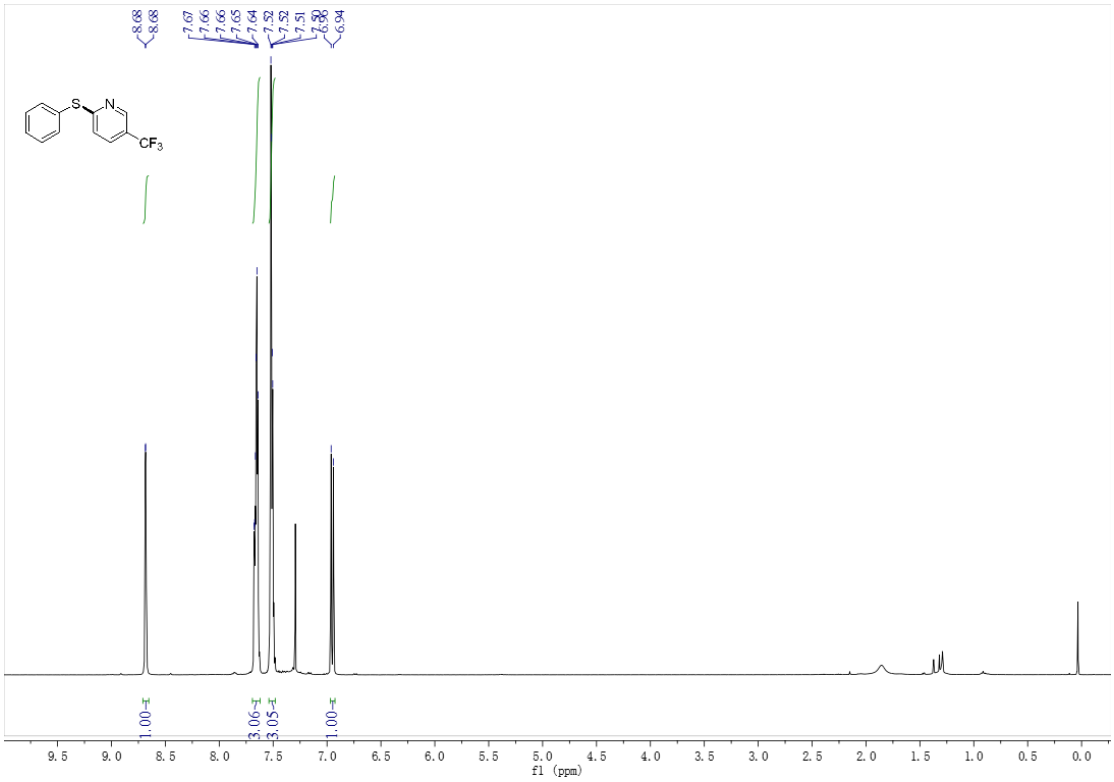
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **37**



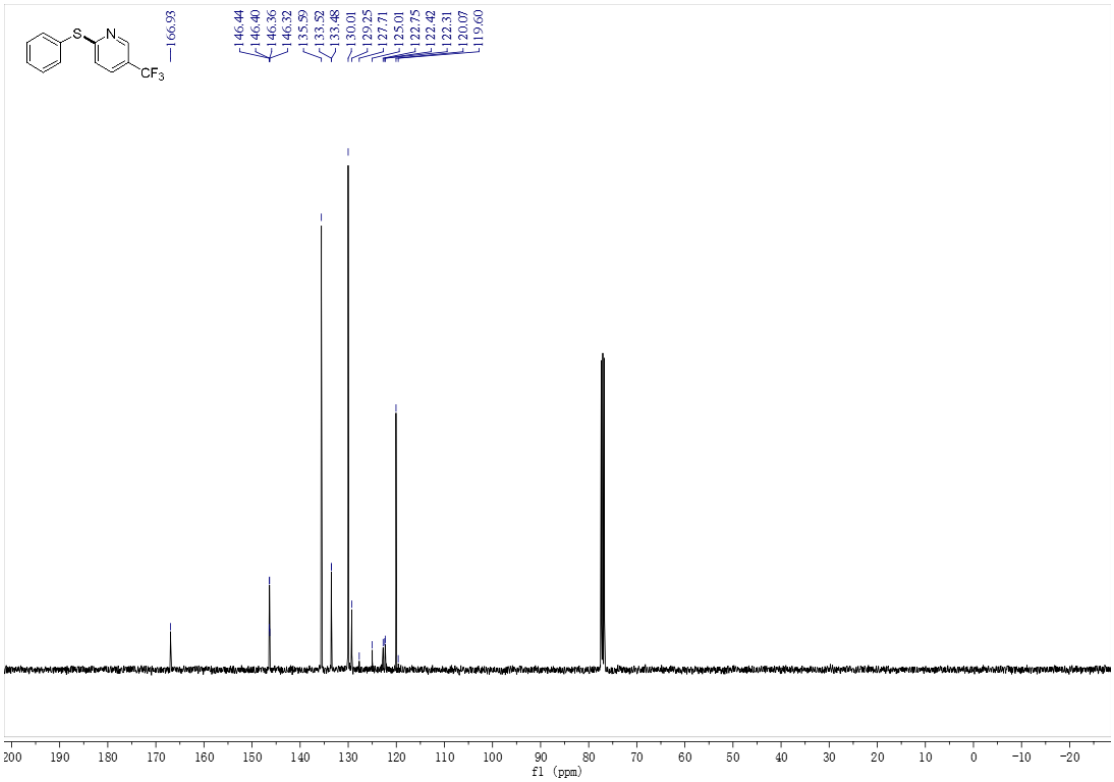
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **37**



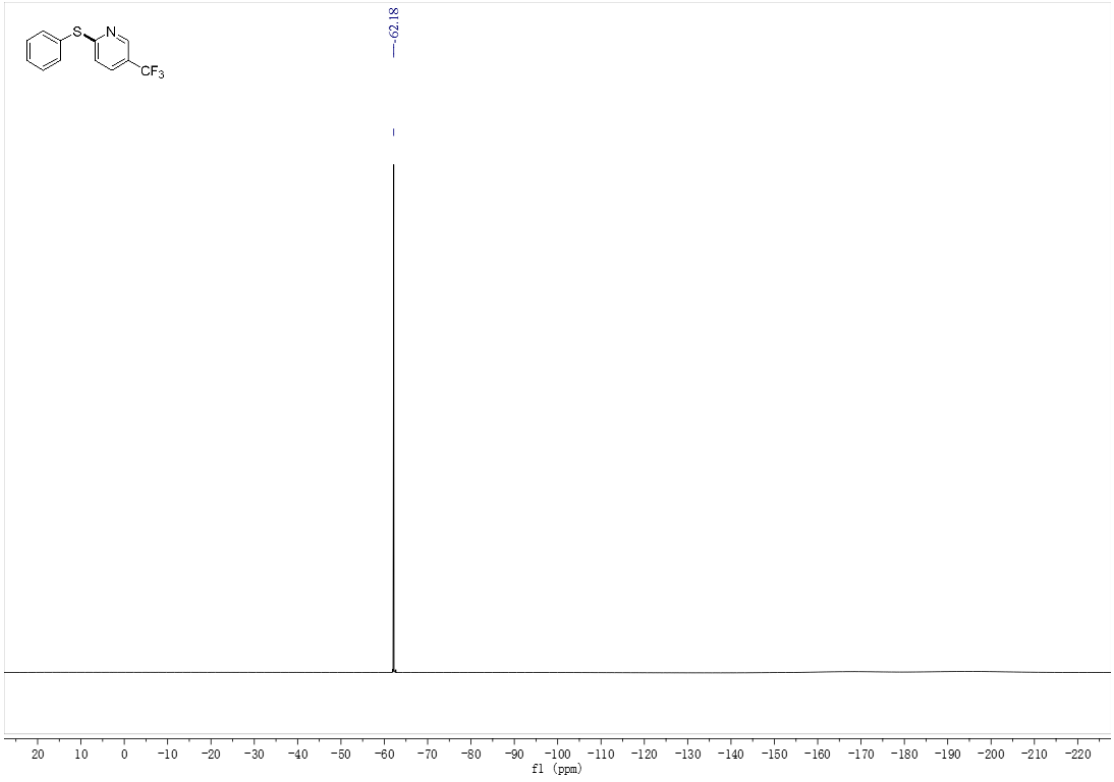
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **38**



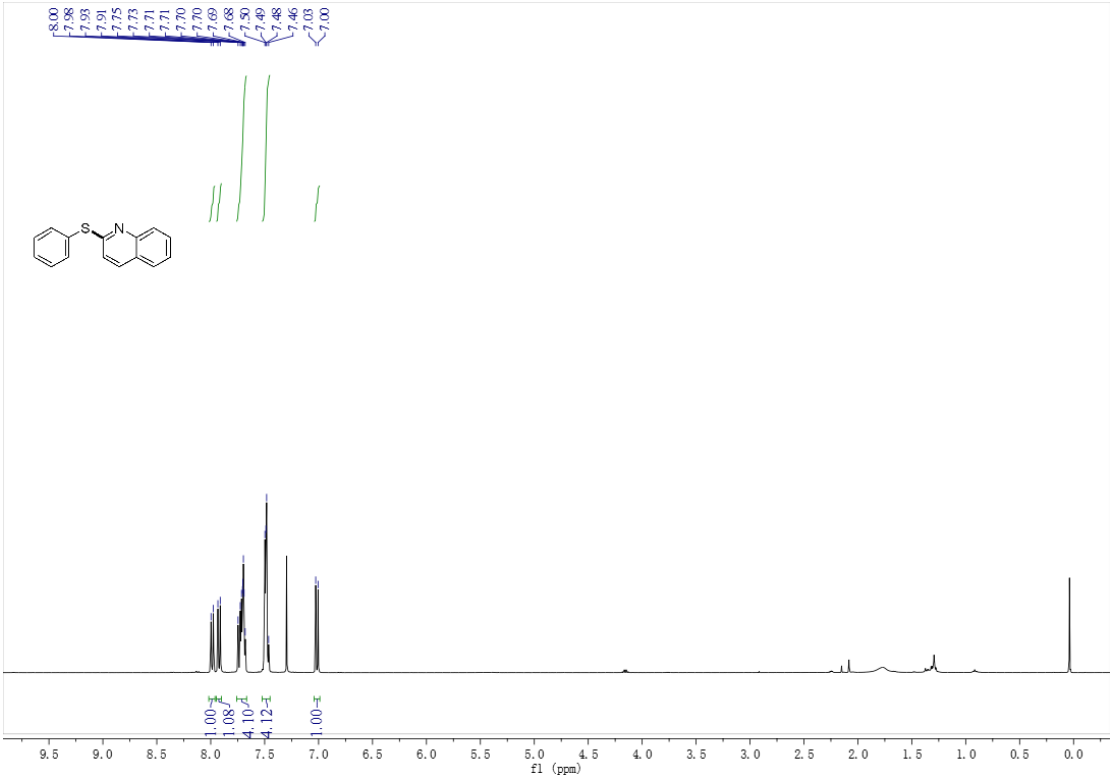
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **38**



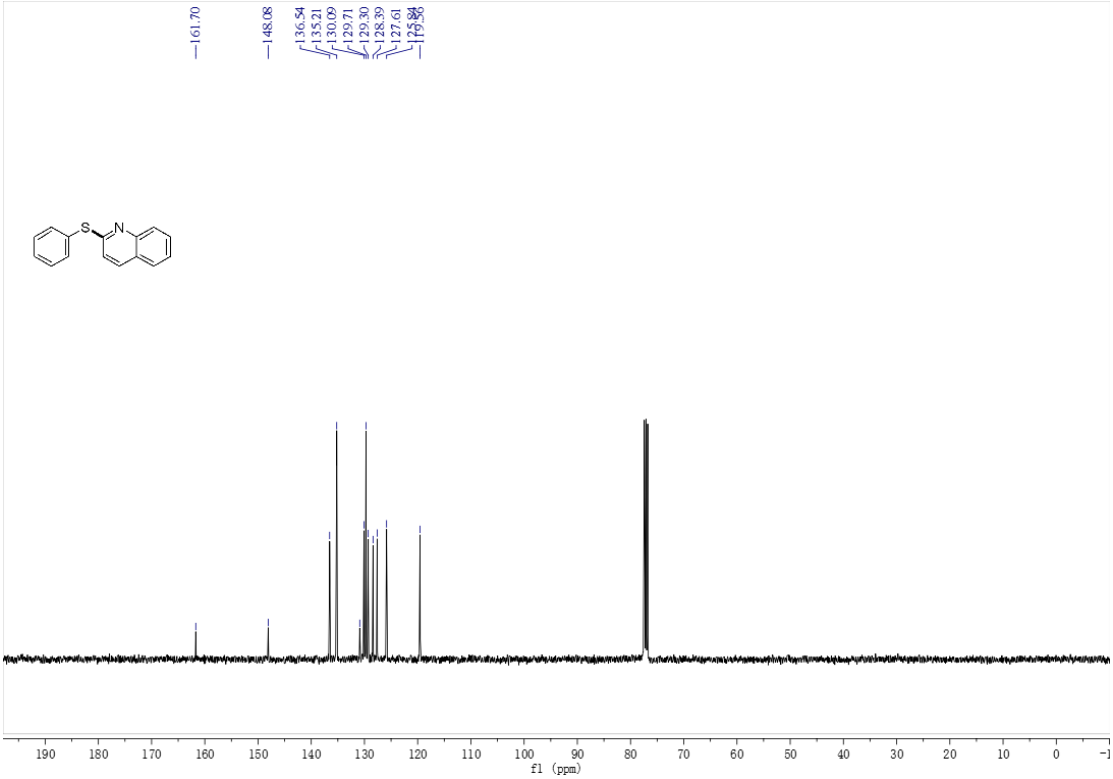
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **38**



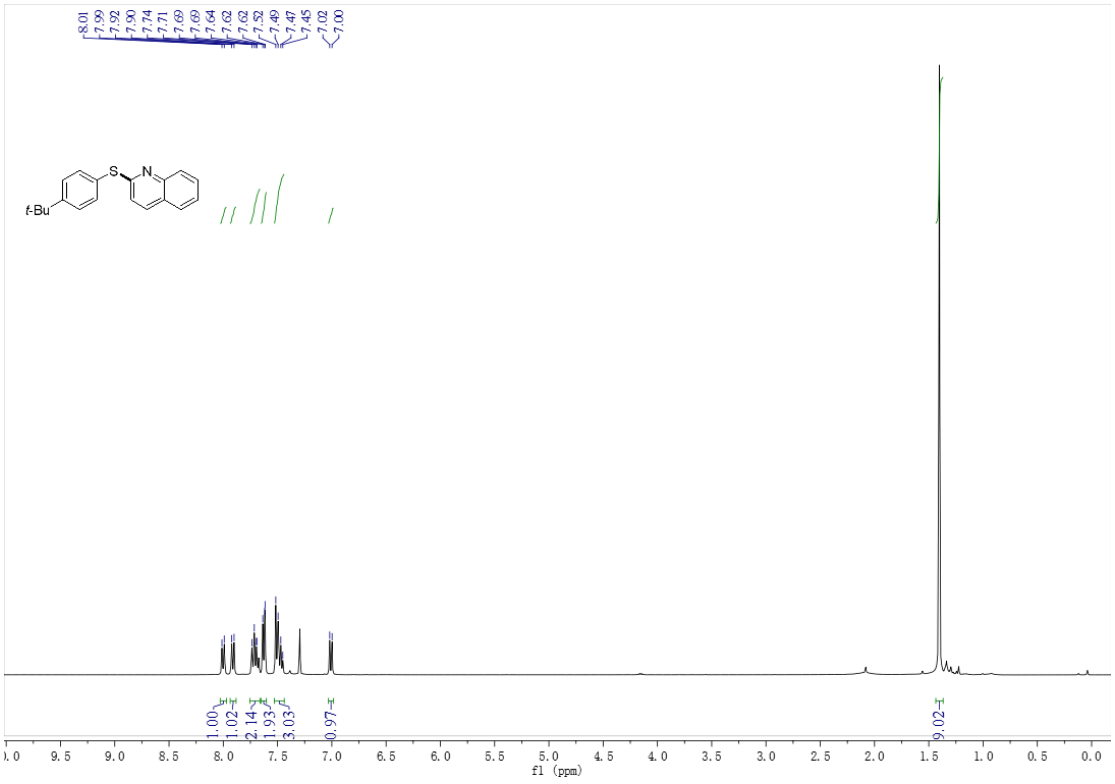
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **39**



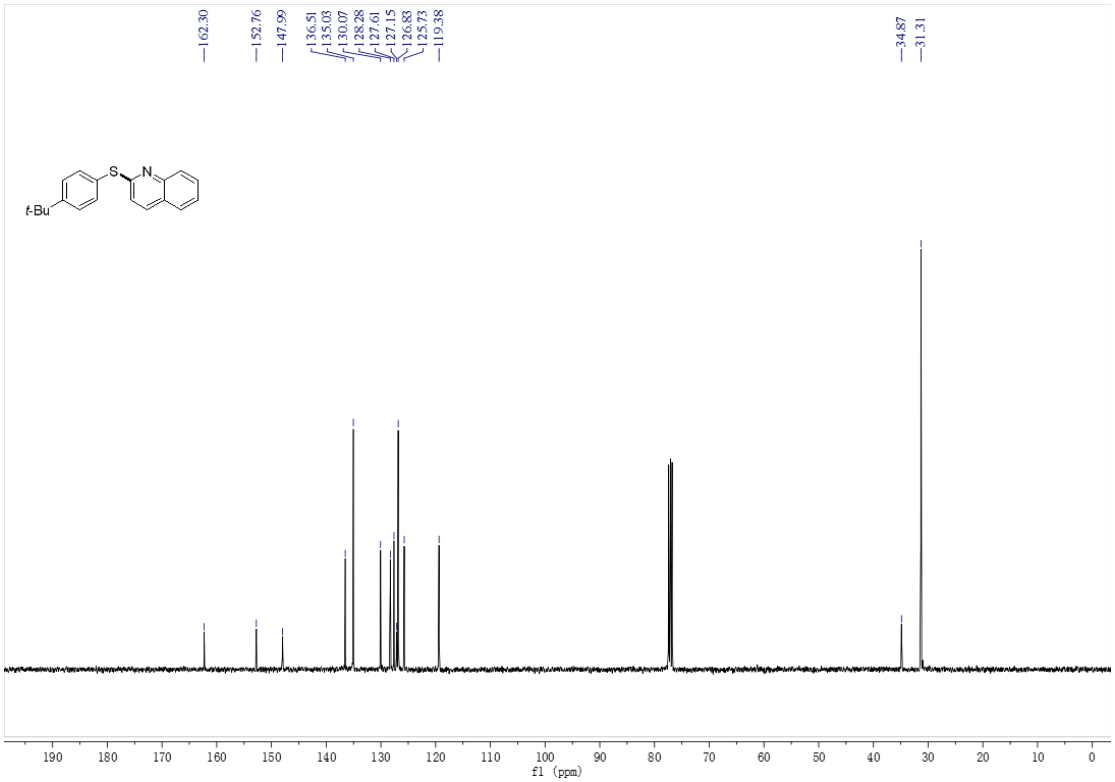
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **39**



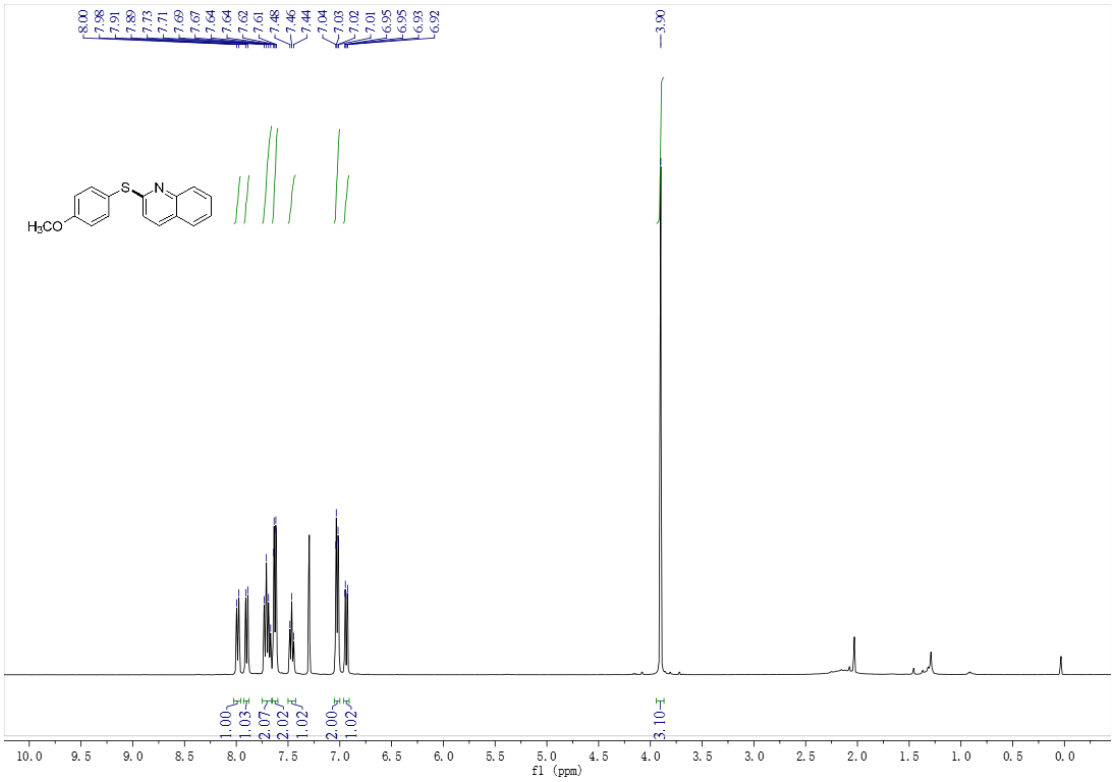
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **40**



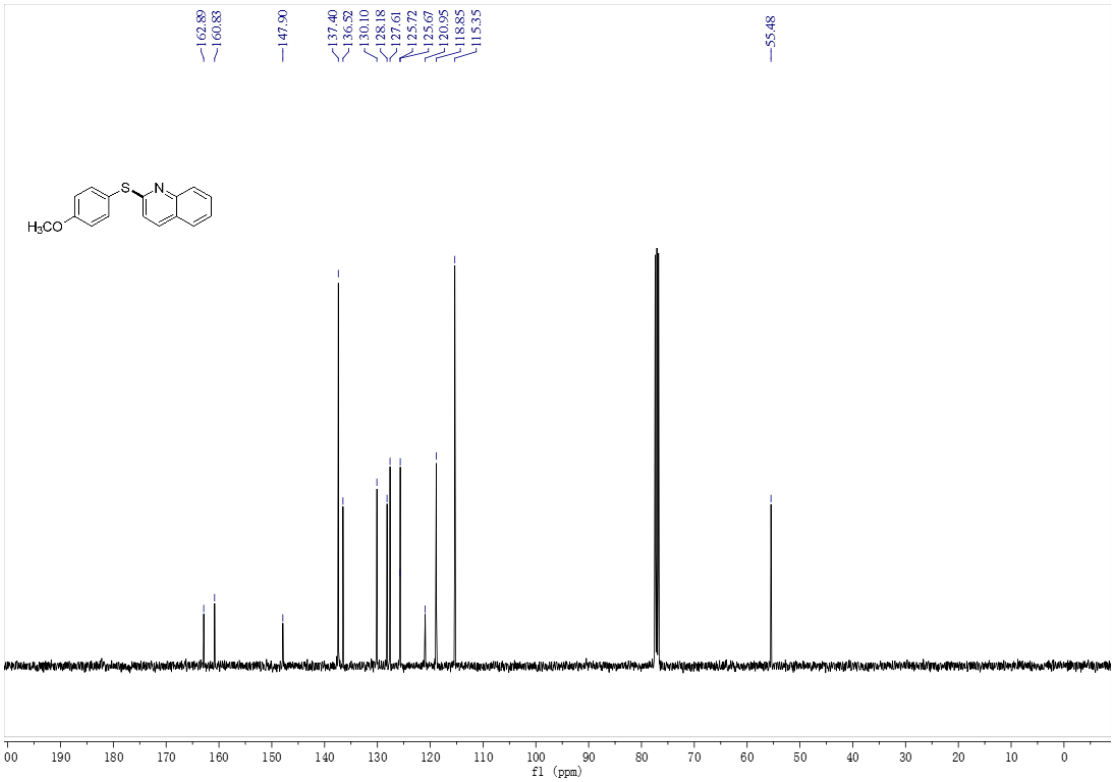
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **40**



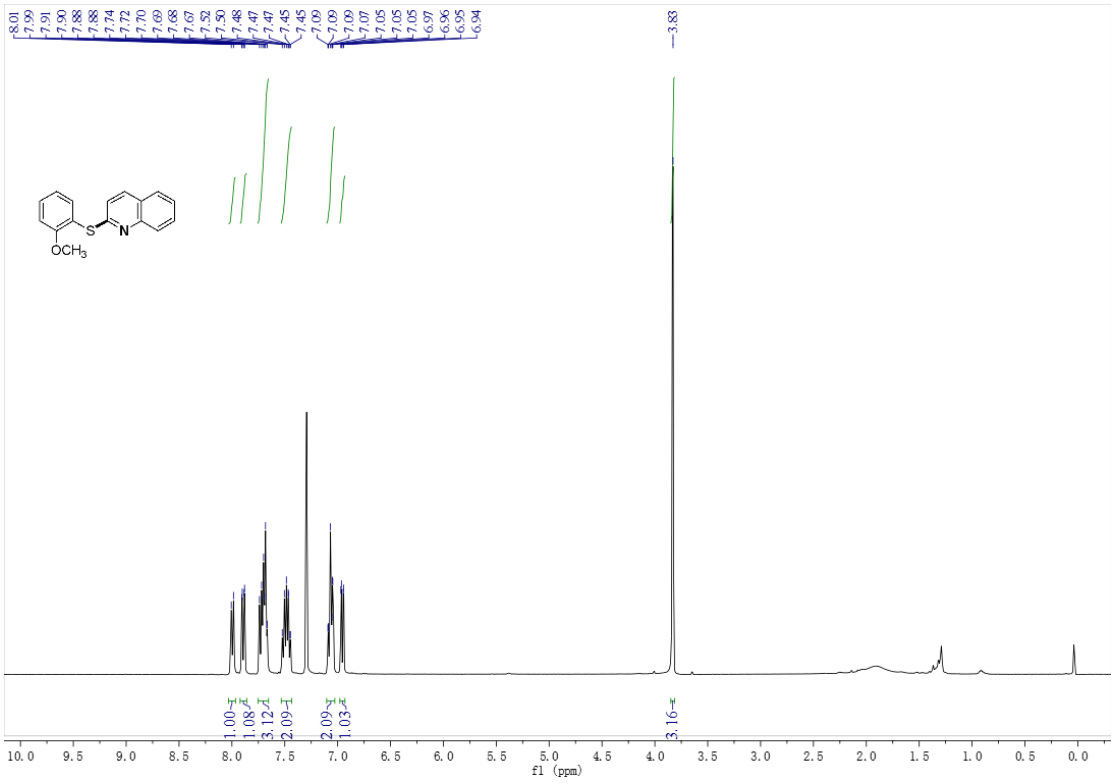
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **41**



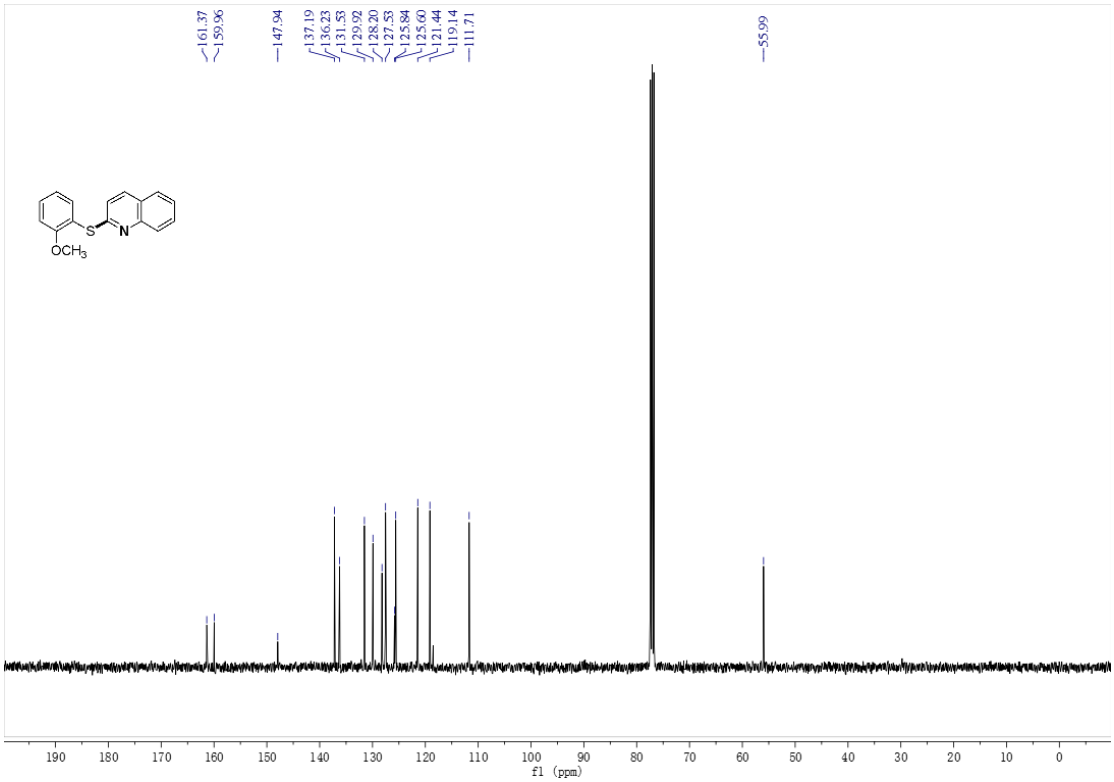
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **41**



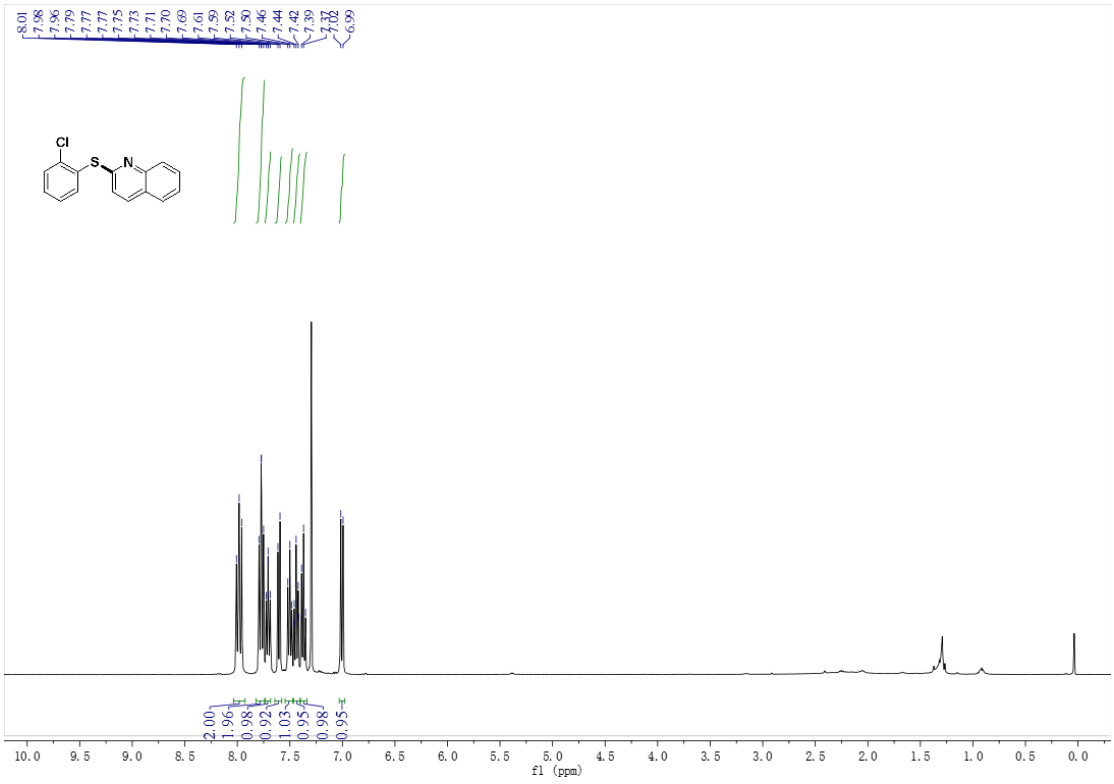
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **42**



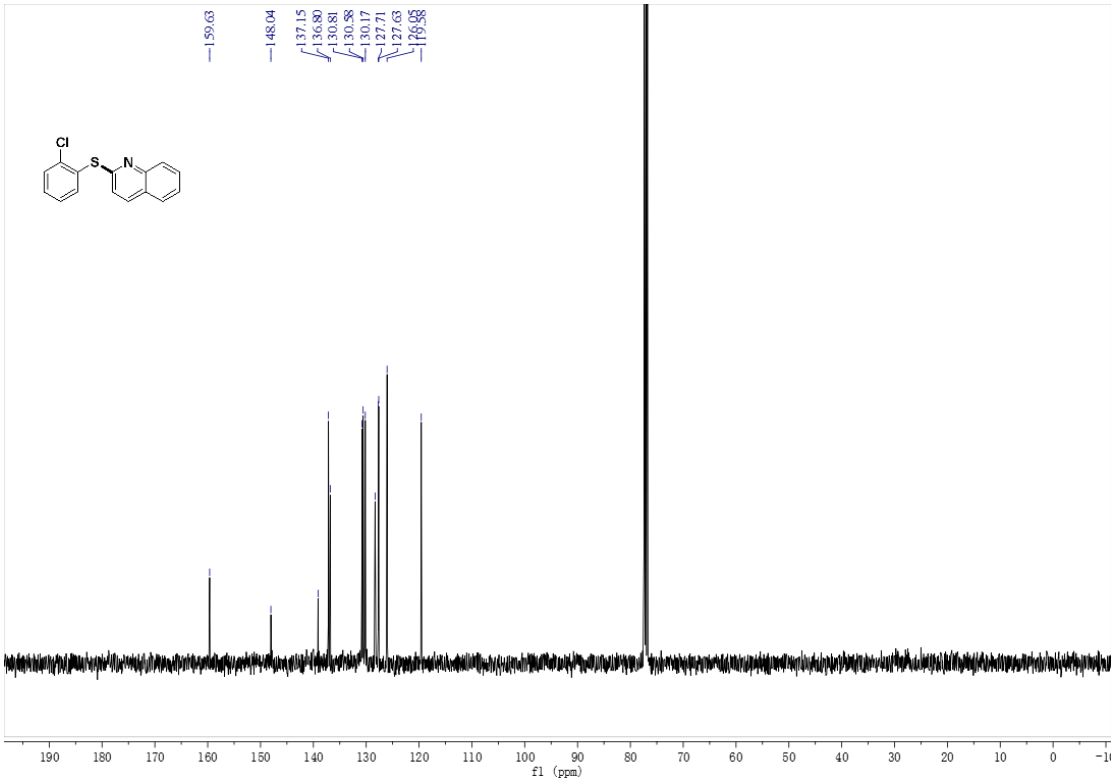
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **42**



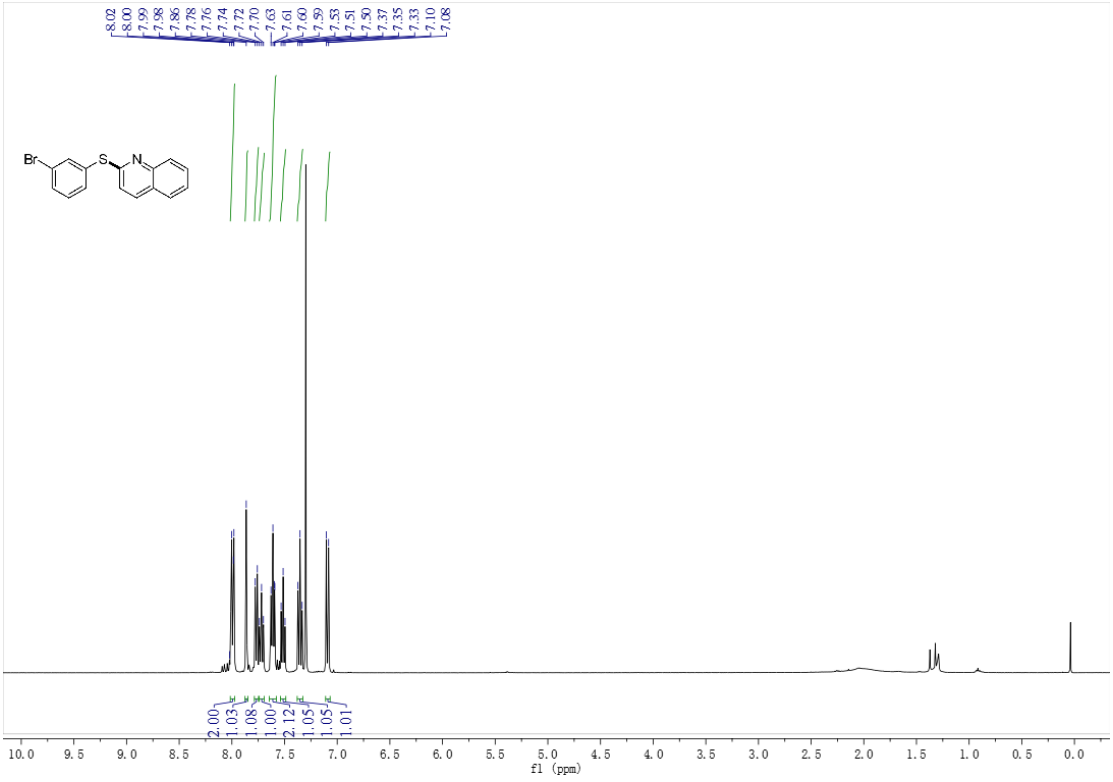
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **43**



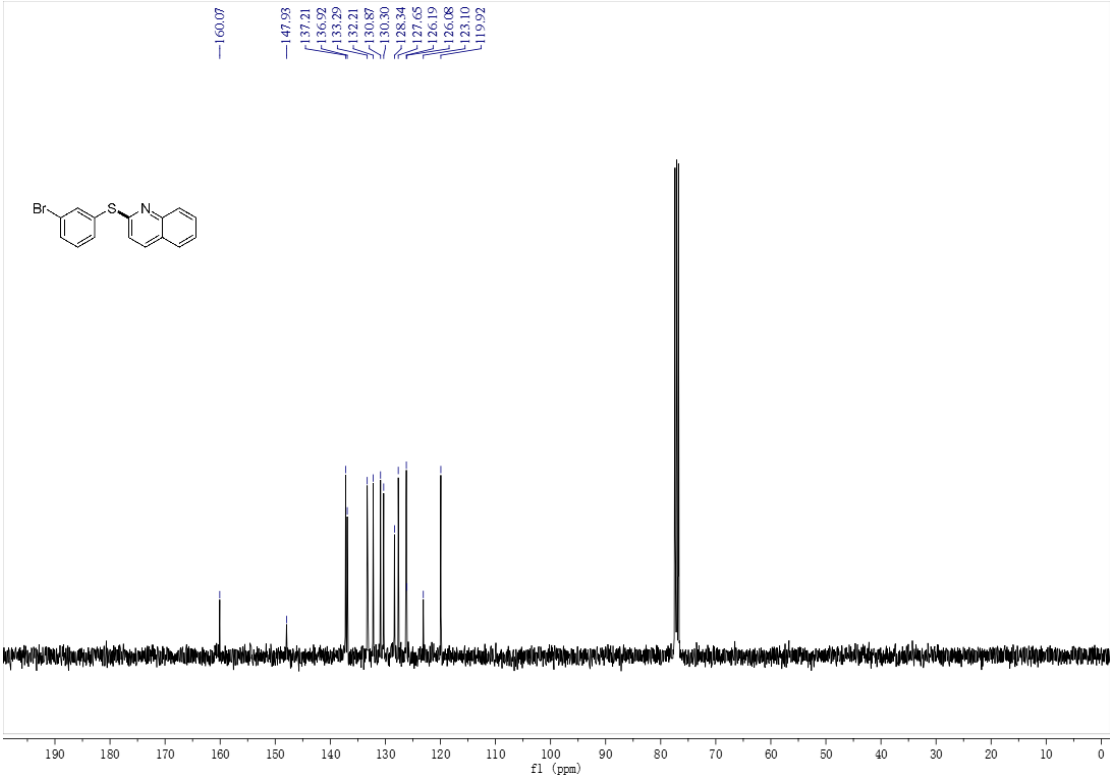
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **43**



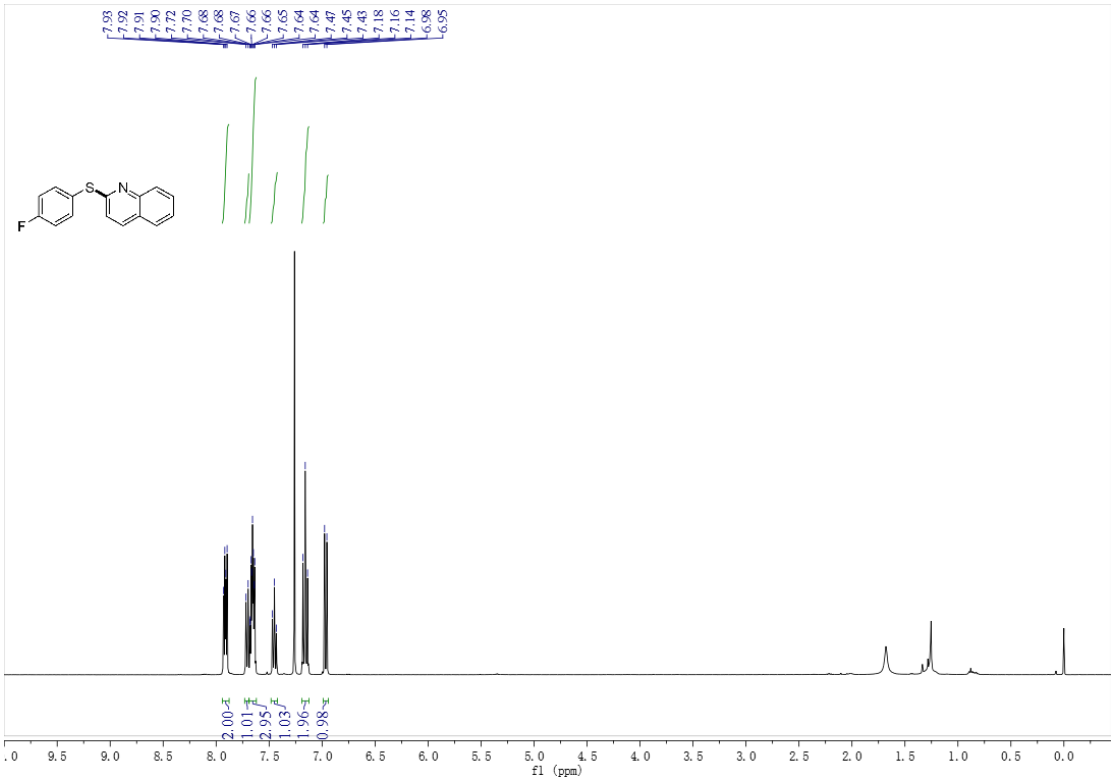
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **44**



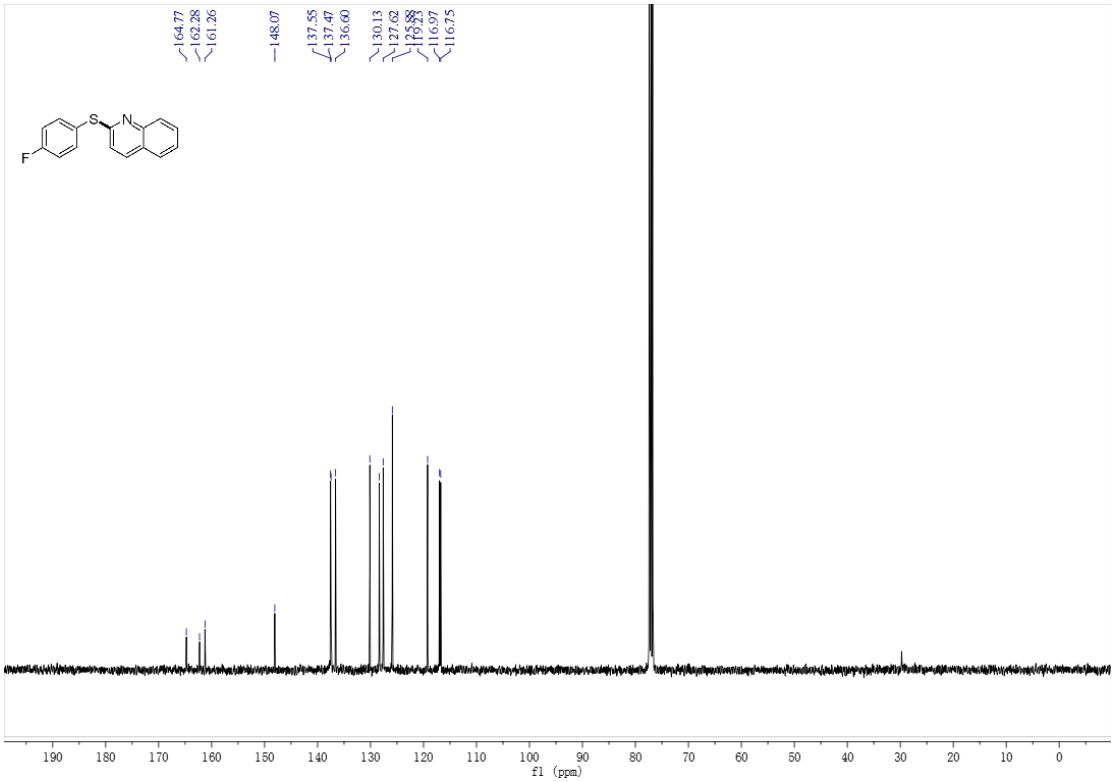
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **44**



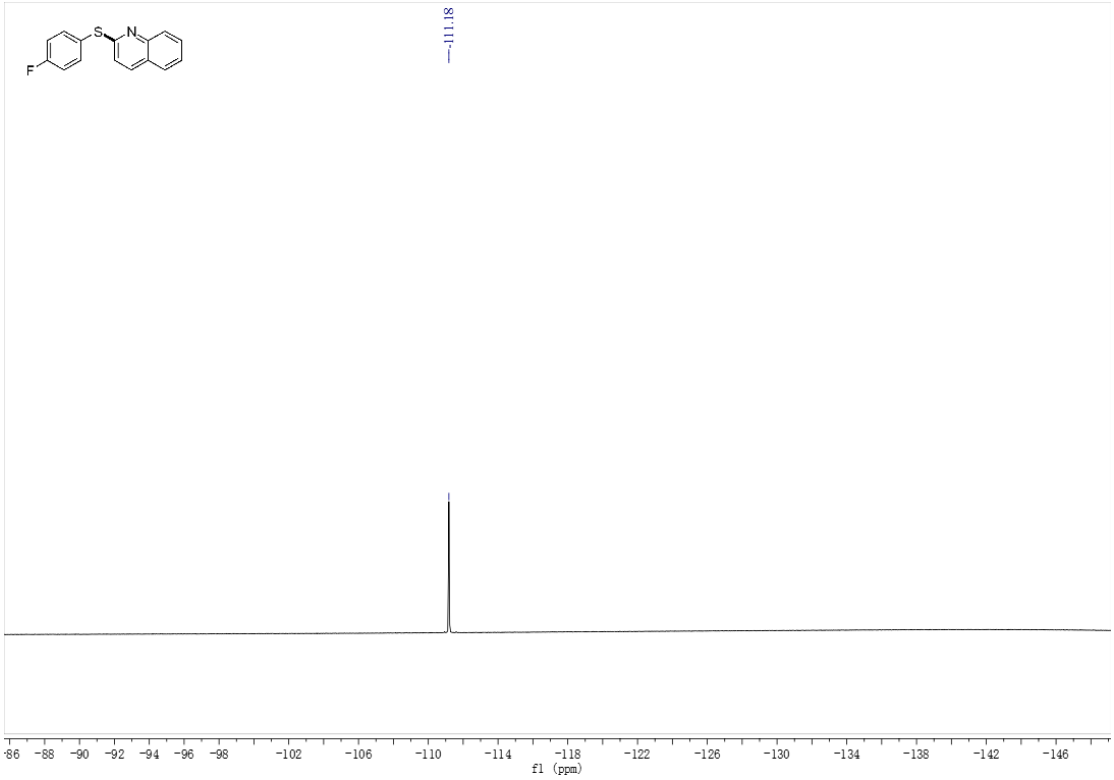
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **45**



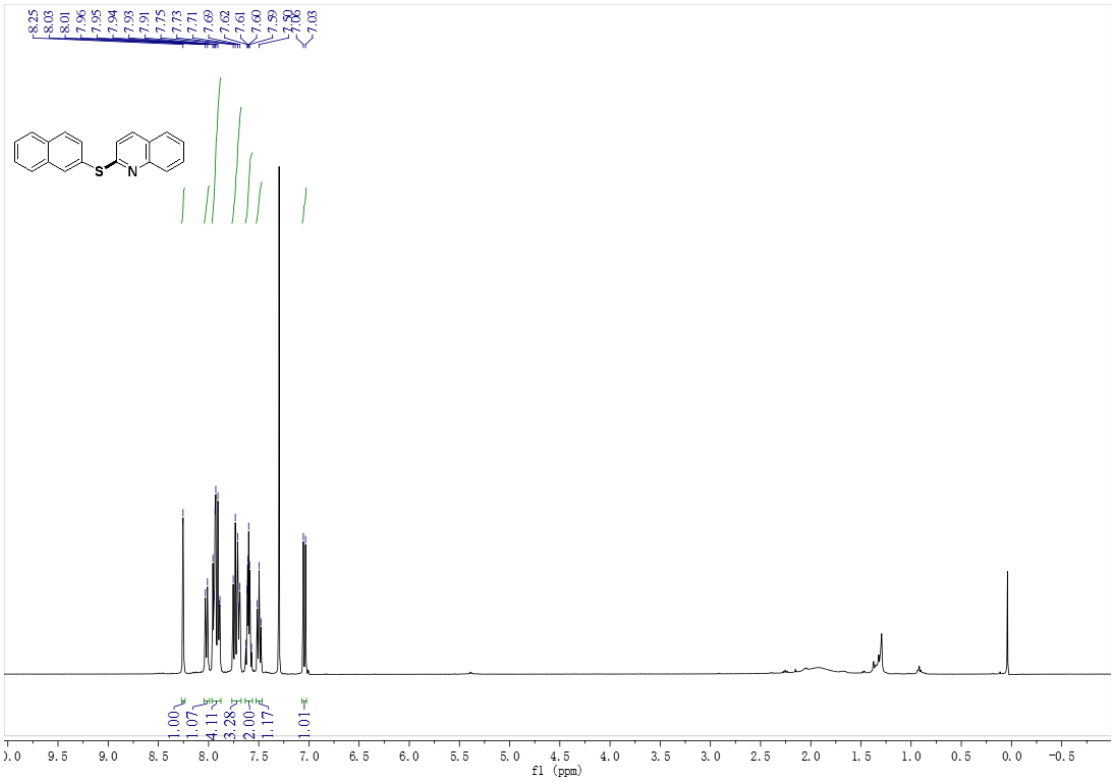
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **45**



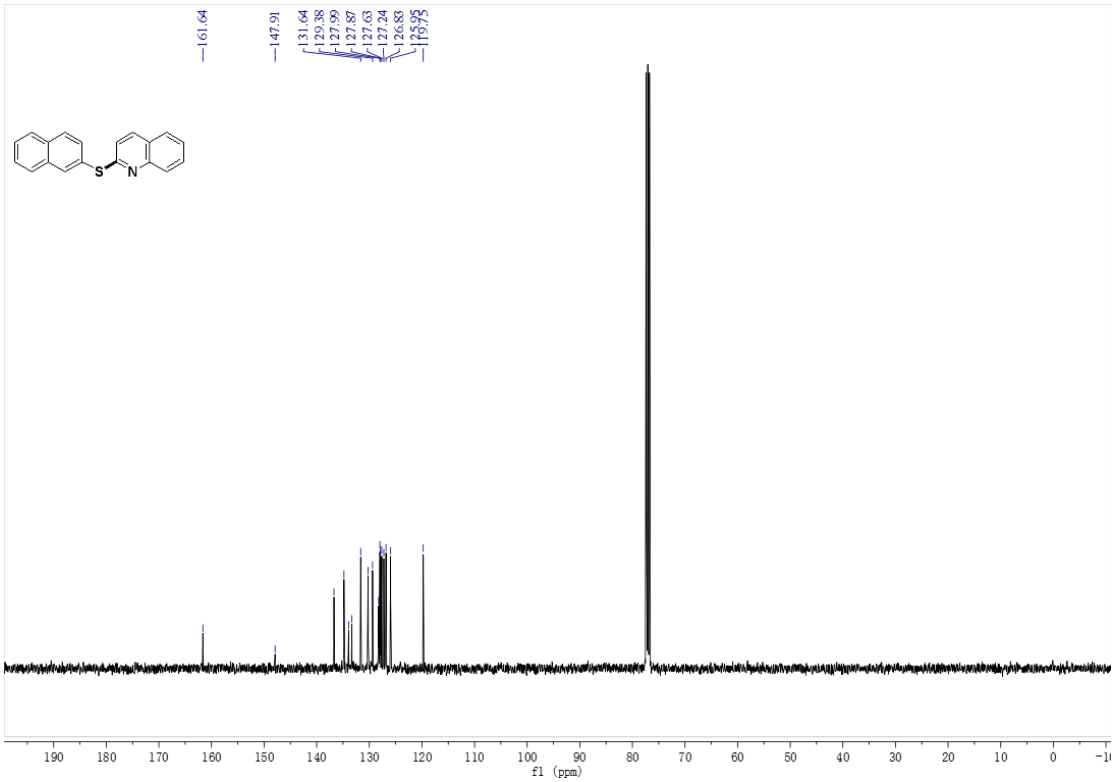
^{19}F NMR spectrum (376 MHz, $CDCl_3$，23 ℃) of **45**



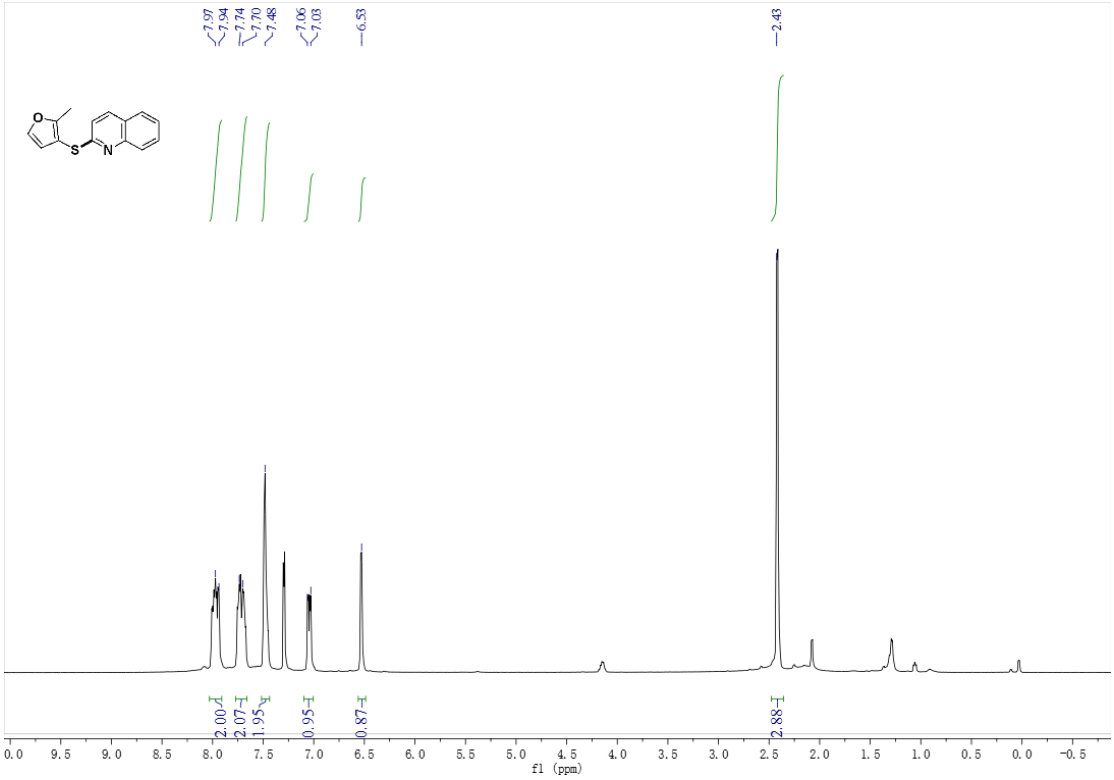
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **46**



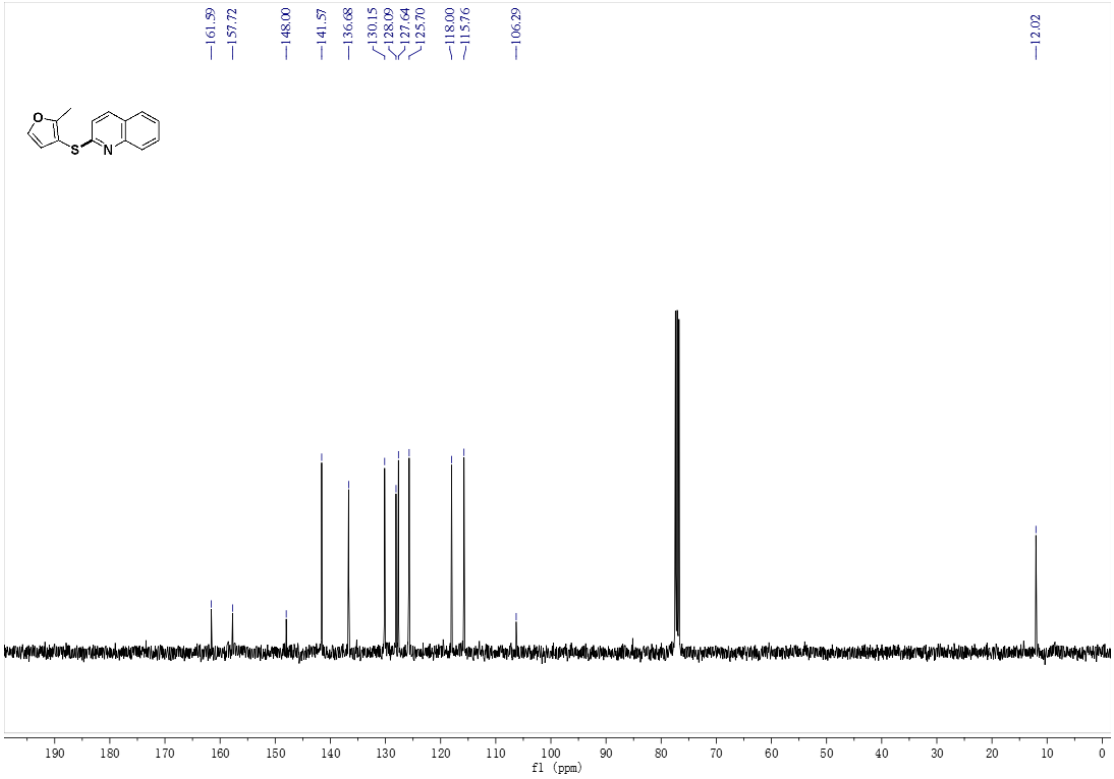
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **46**



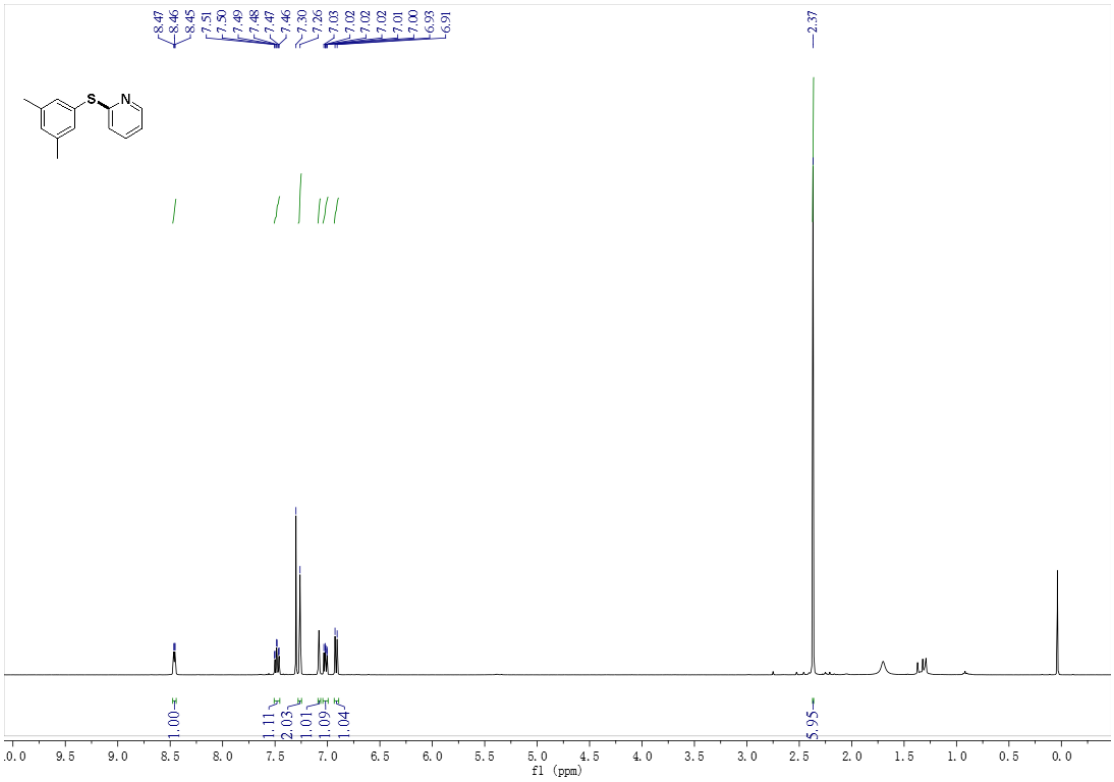
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **47**



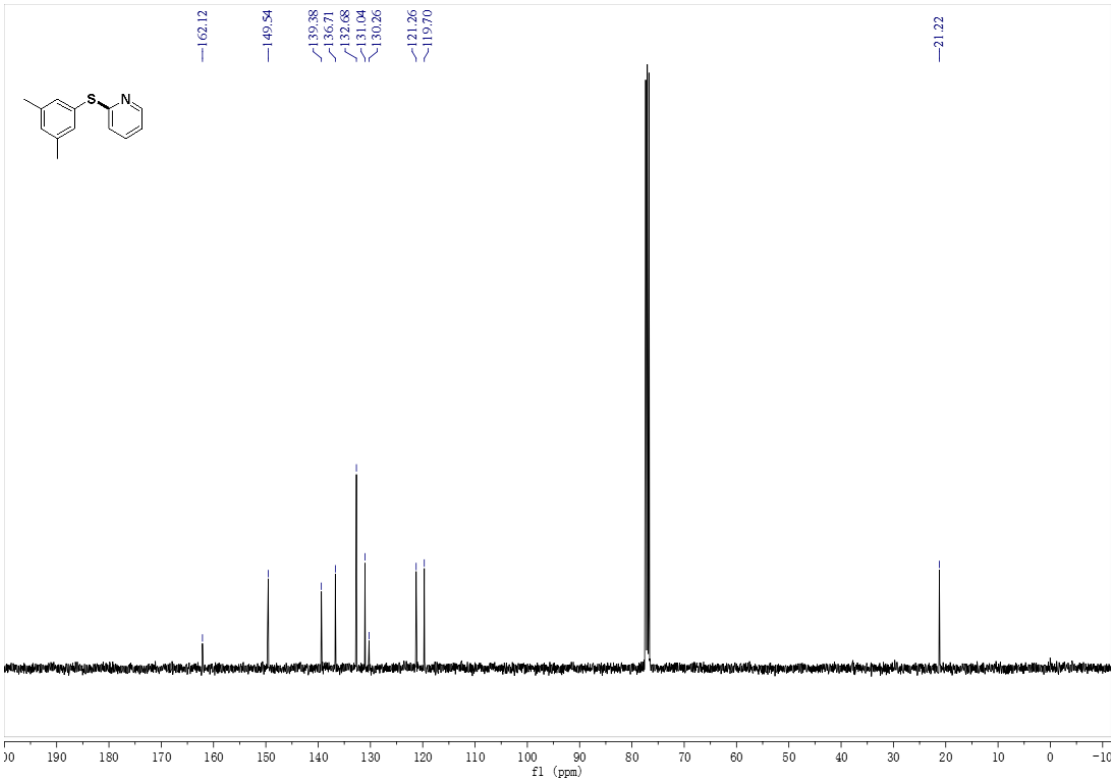
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **47**



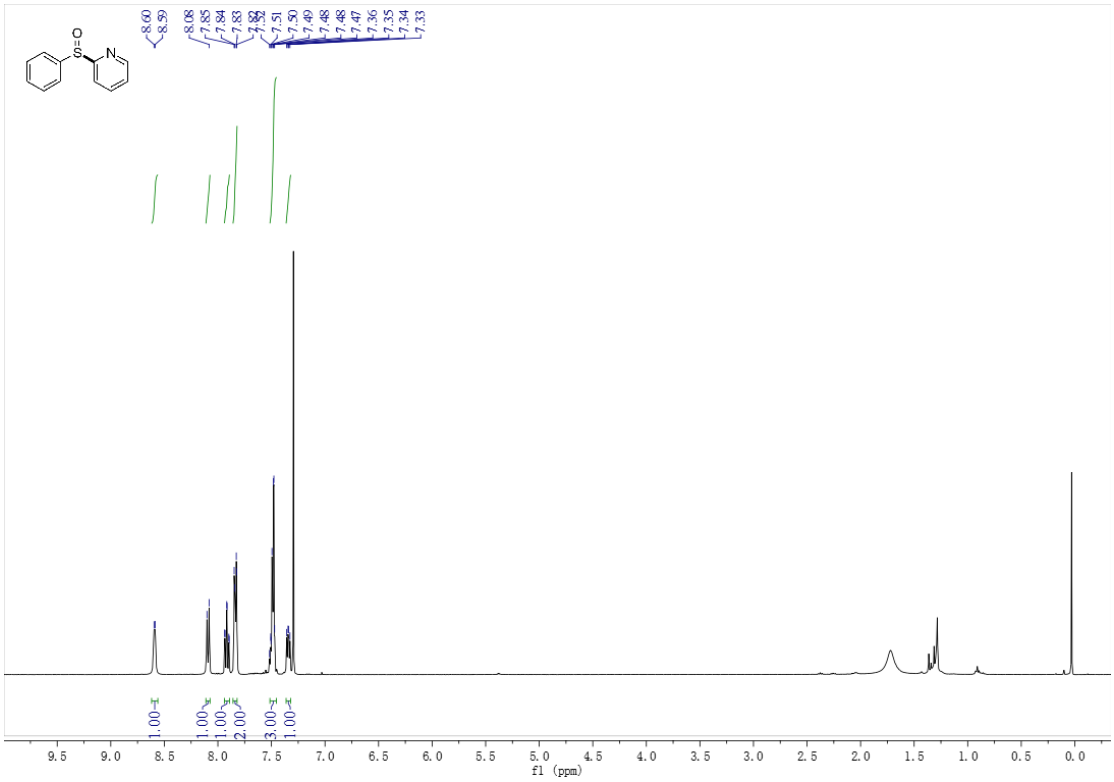
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **48**



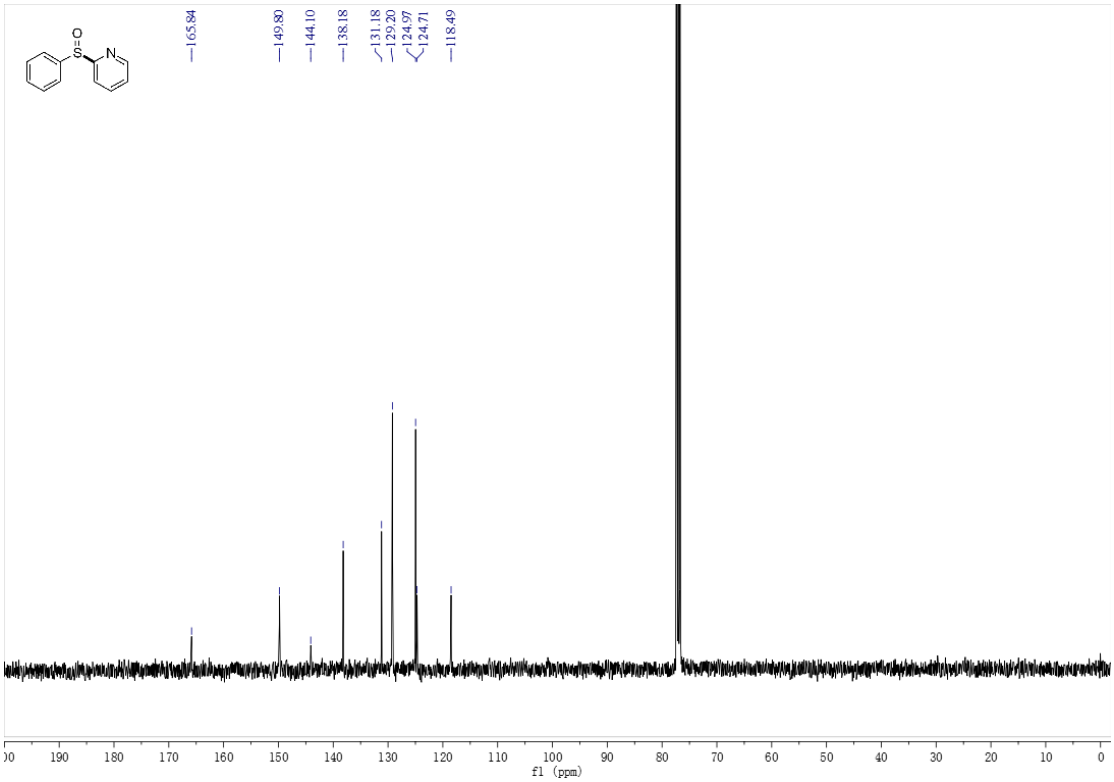
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **48**



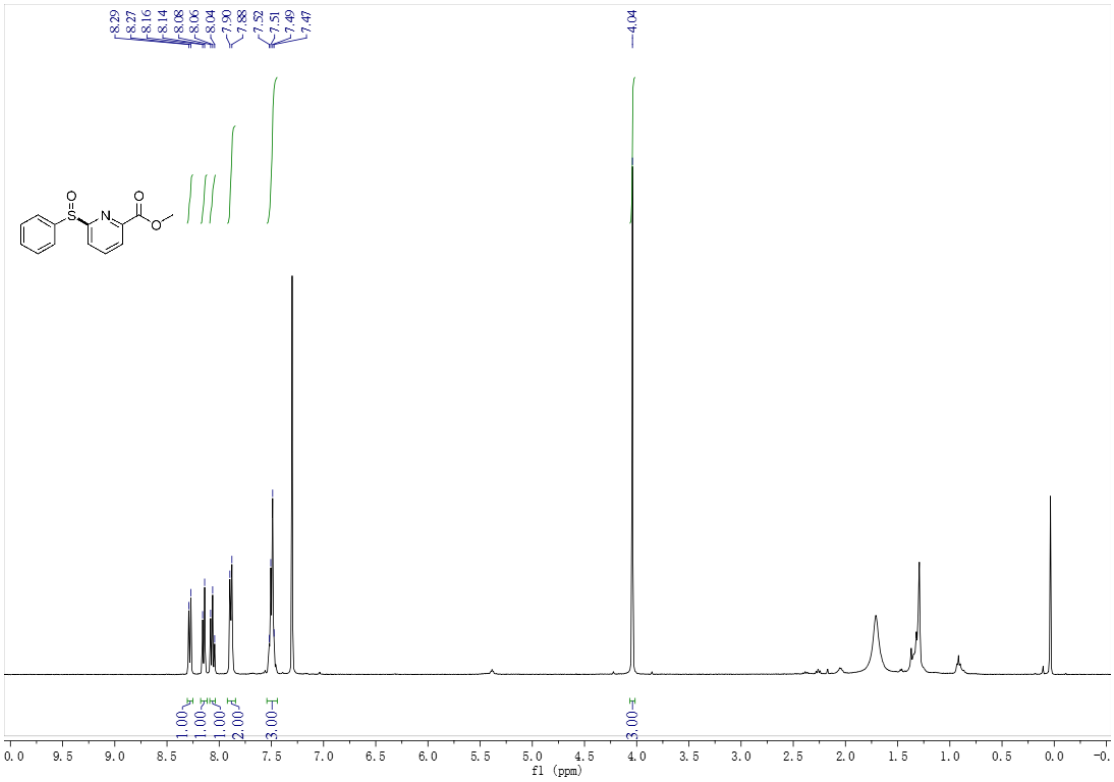
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **49**



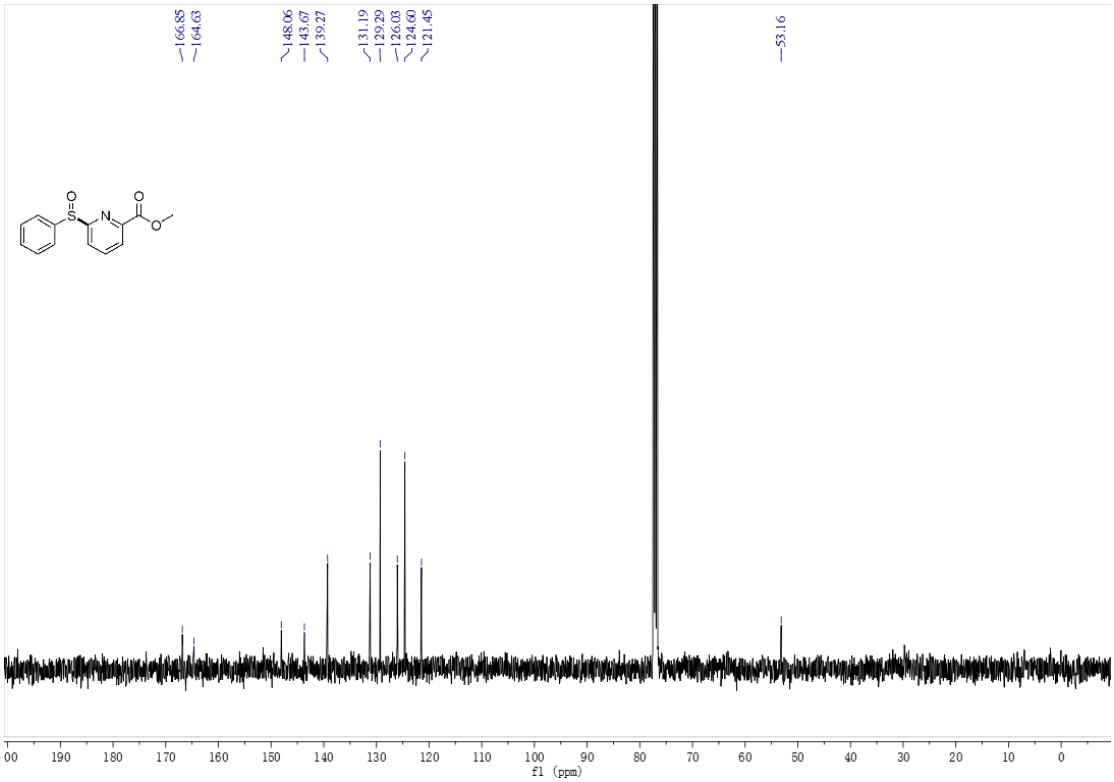
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **49**



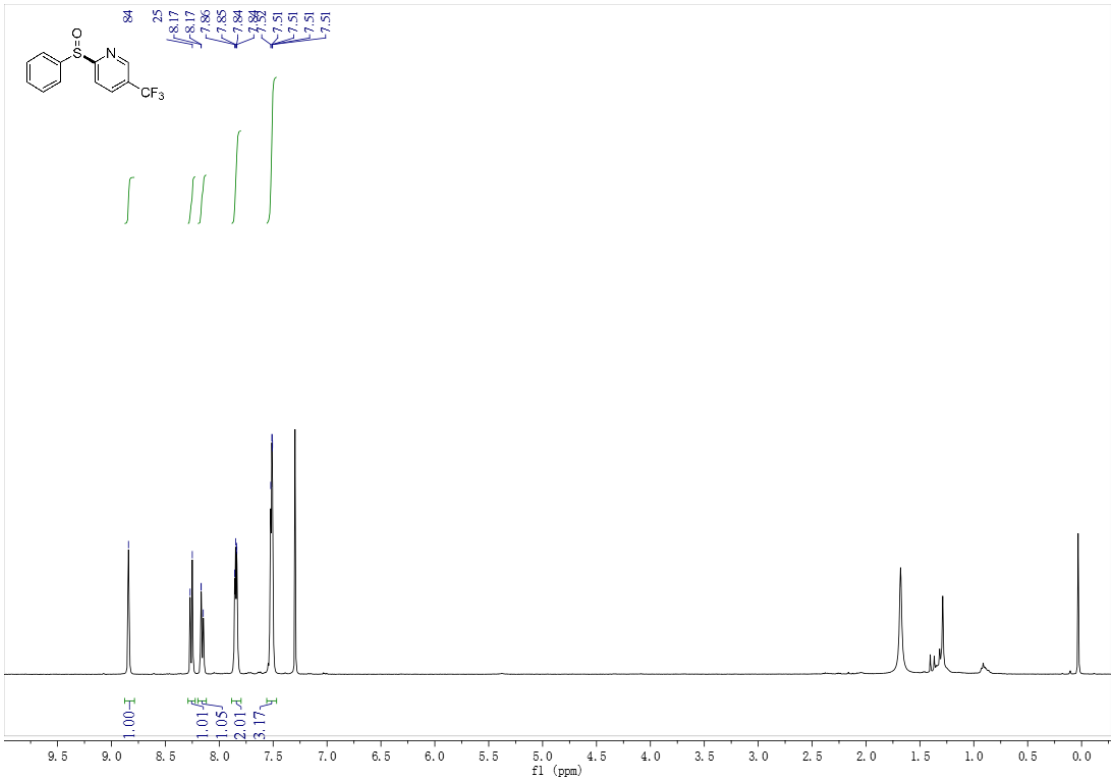
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **50**



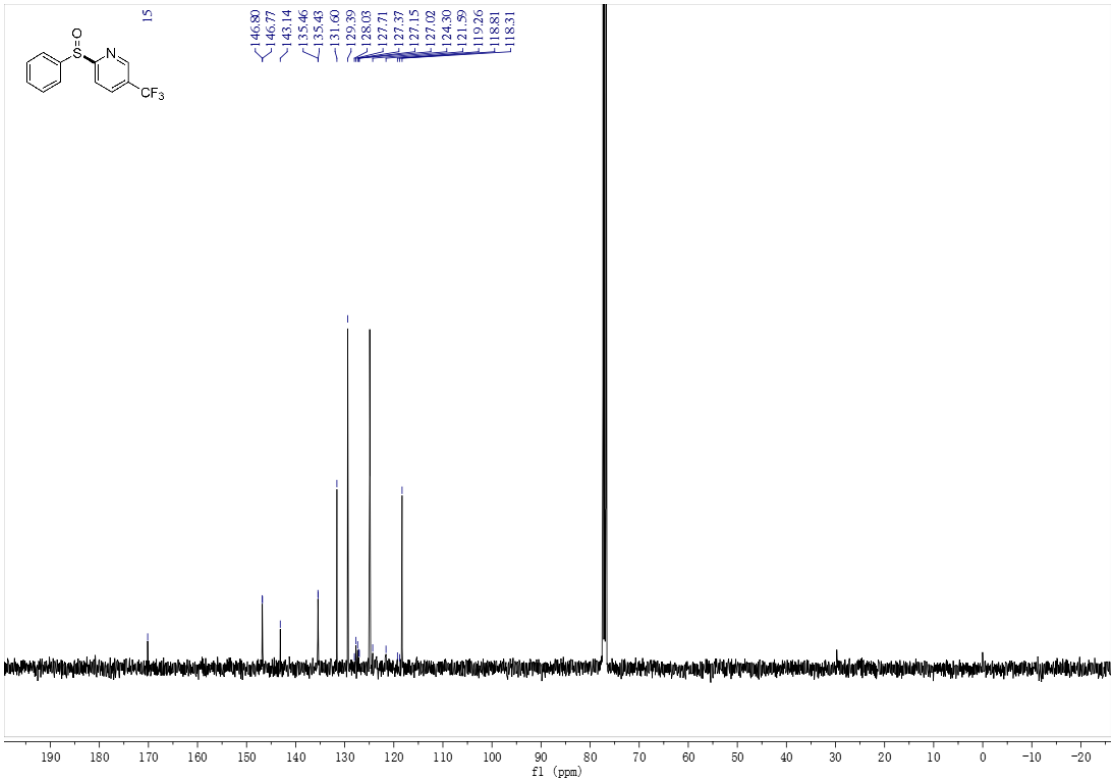
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **50**



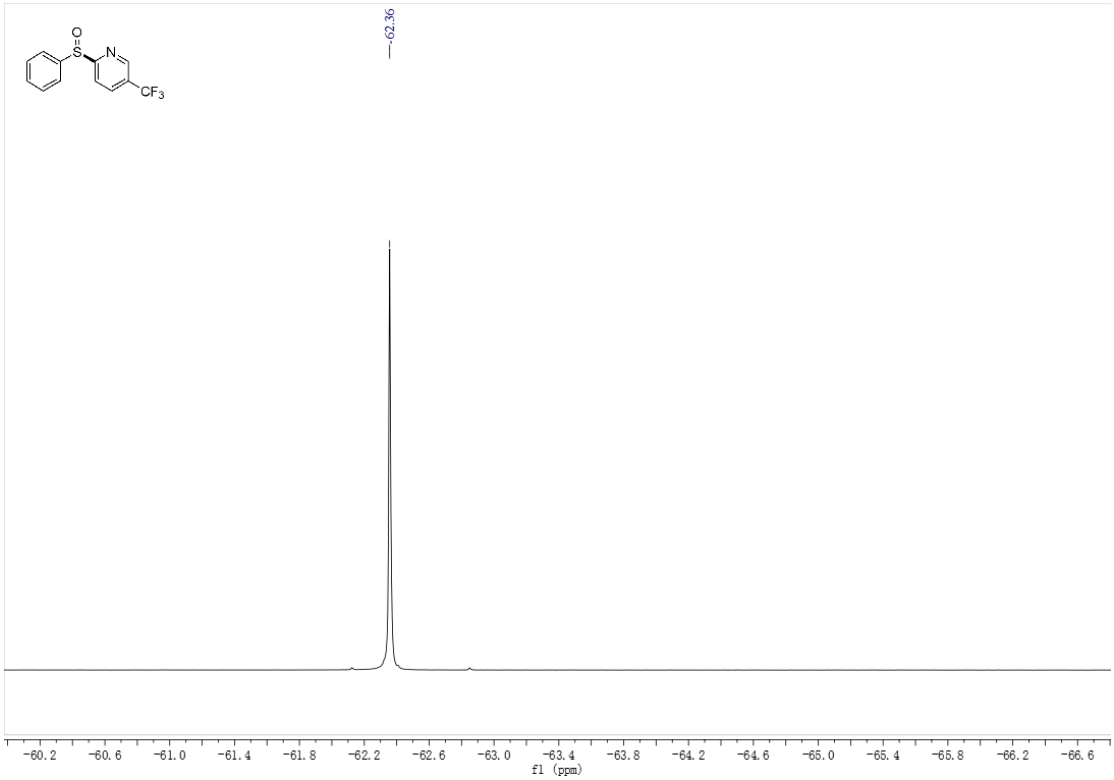
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **51**



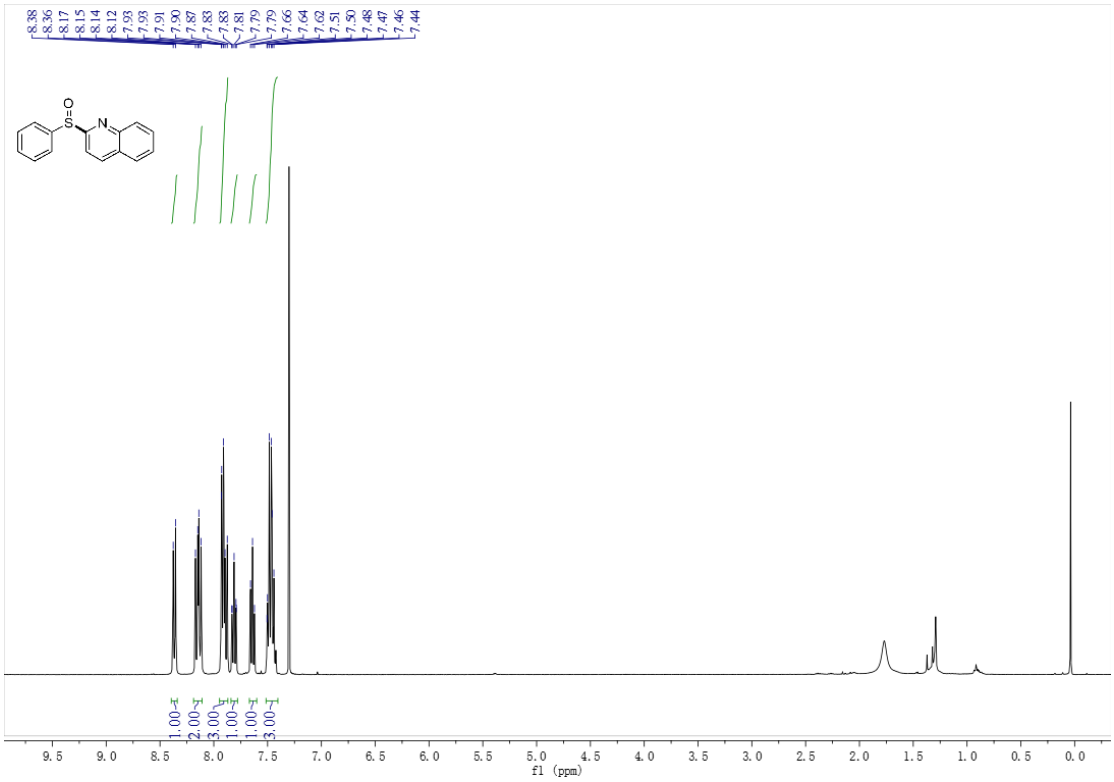
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **51**



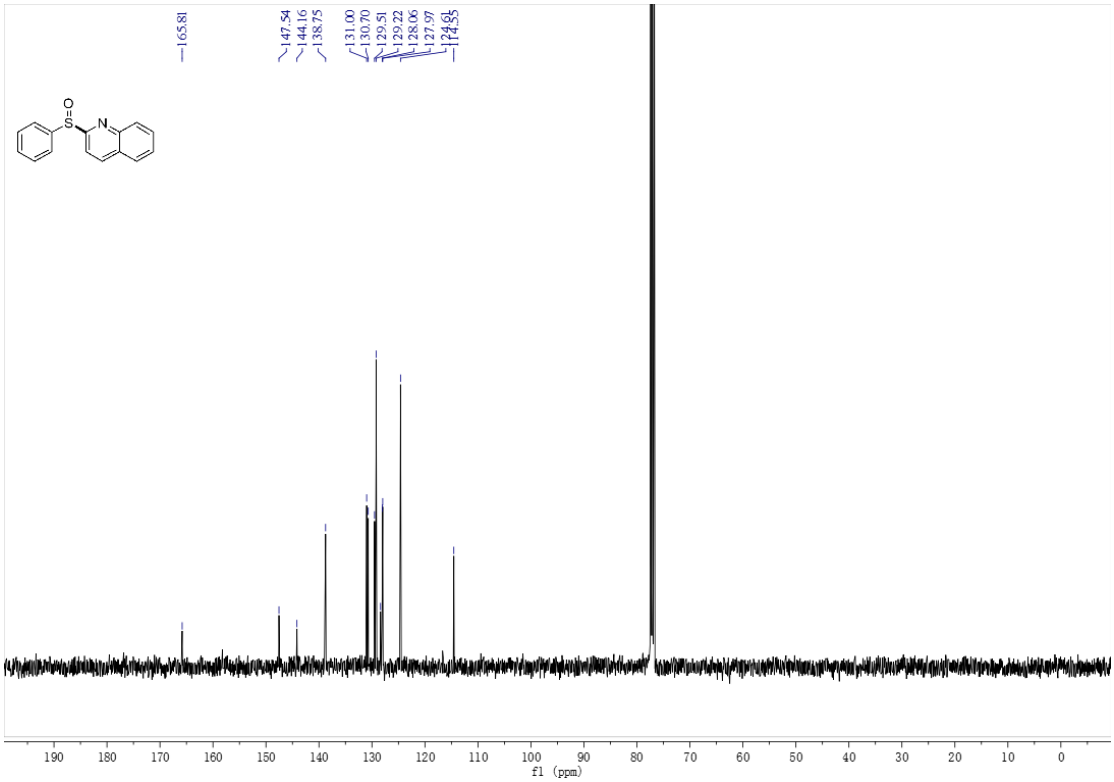
^{19}F NMR spectrum (376 MHz, $CDCl_3$，23 ℃) of **51**


-62.36
O
S
N
CF3
-60.2
-60.6
-61.0
-61.4
-61.8
-62.2
-62.6
-63.0
-63.4
-63.8
-64.2
-64.6
-65.0
-65.4
-65.8
-66.2
-66.6
f1 (ppm)

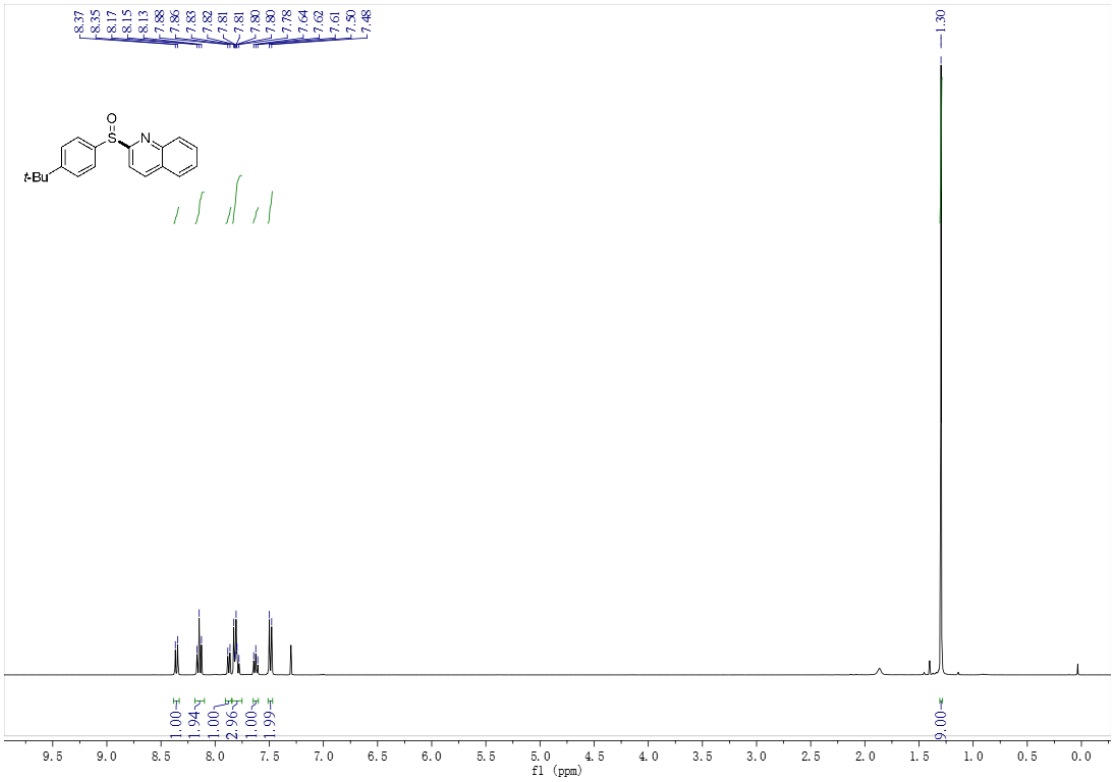
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **52**



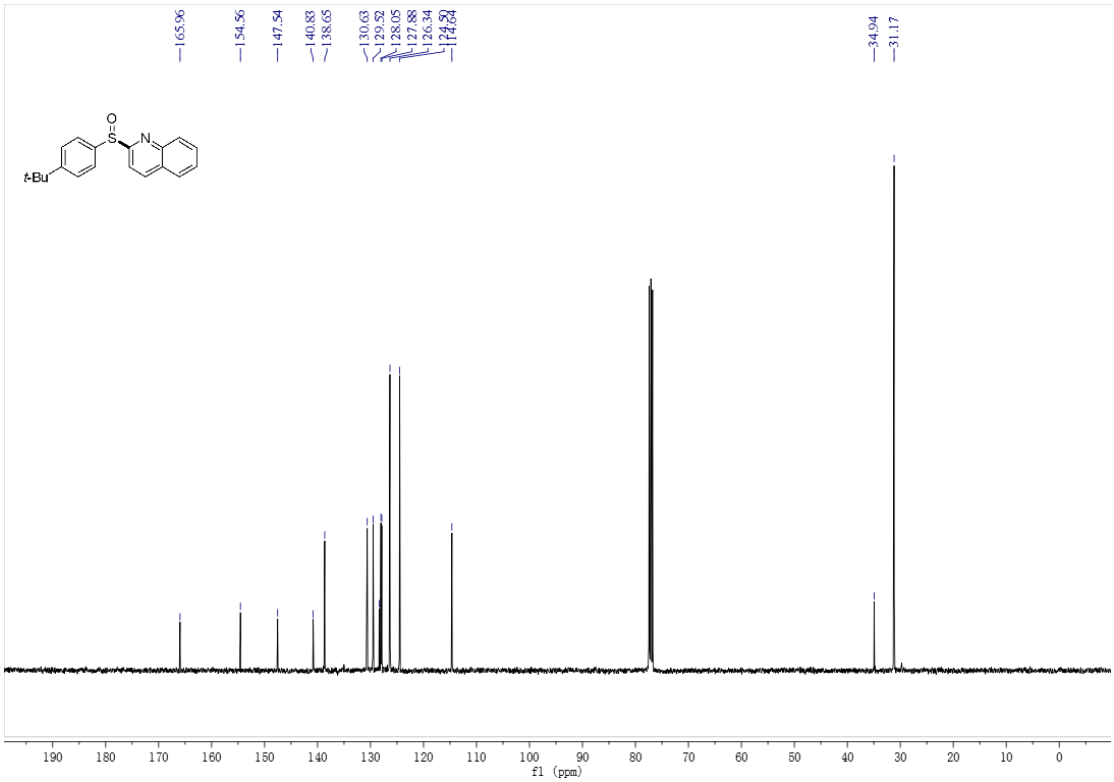
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **52**



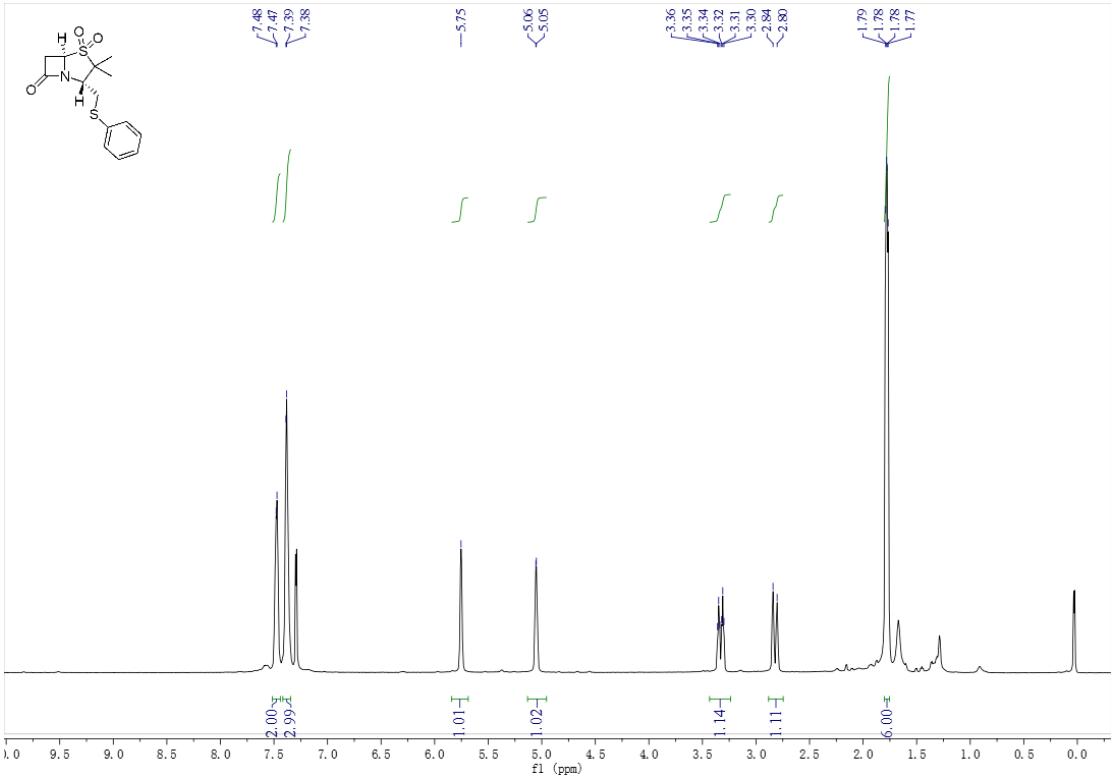
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **53**



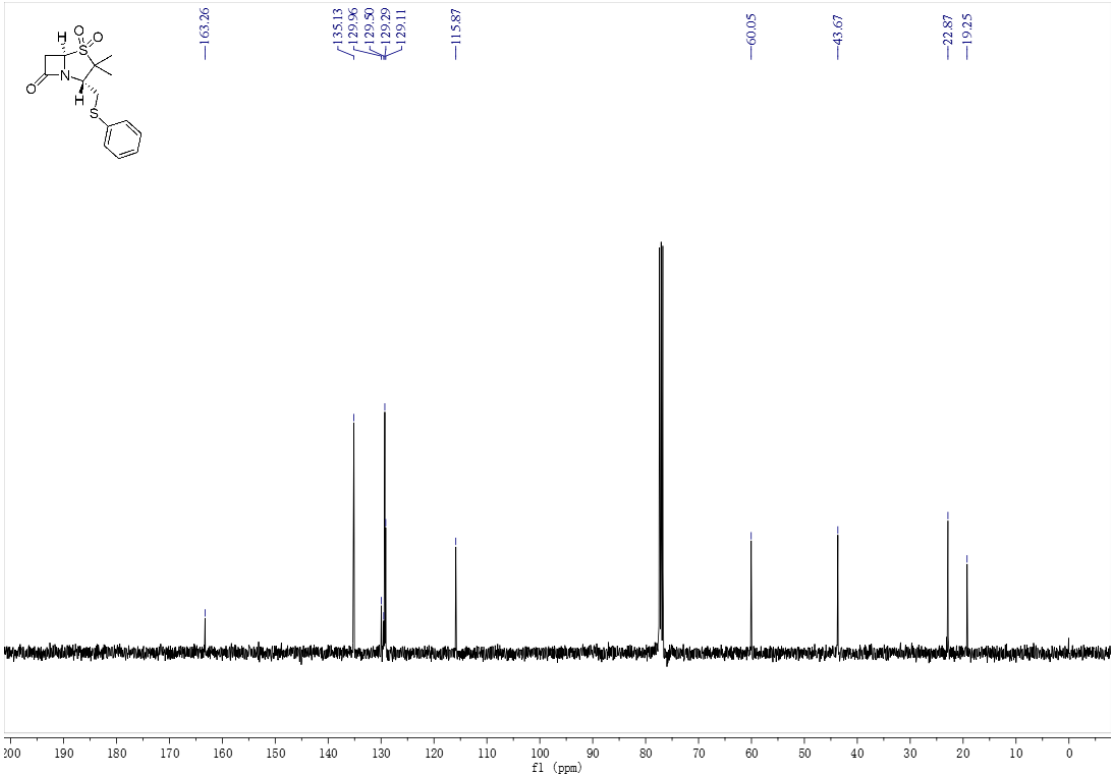
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **53**



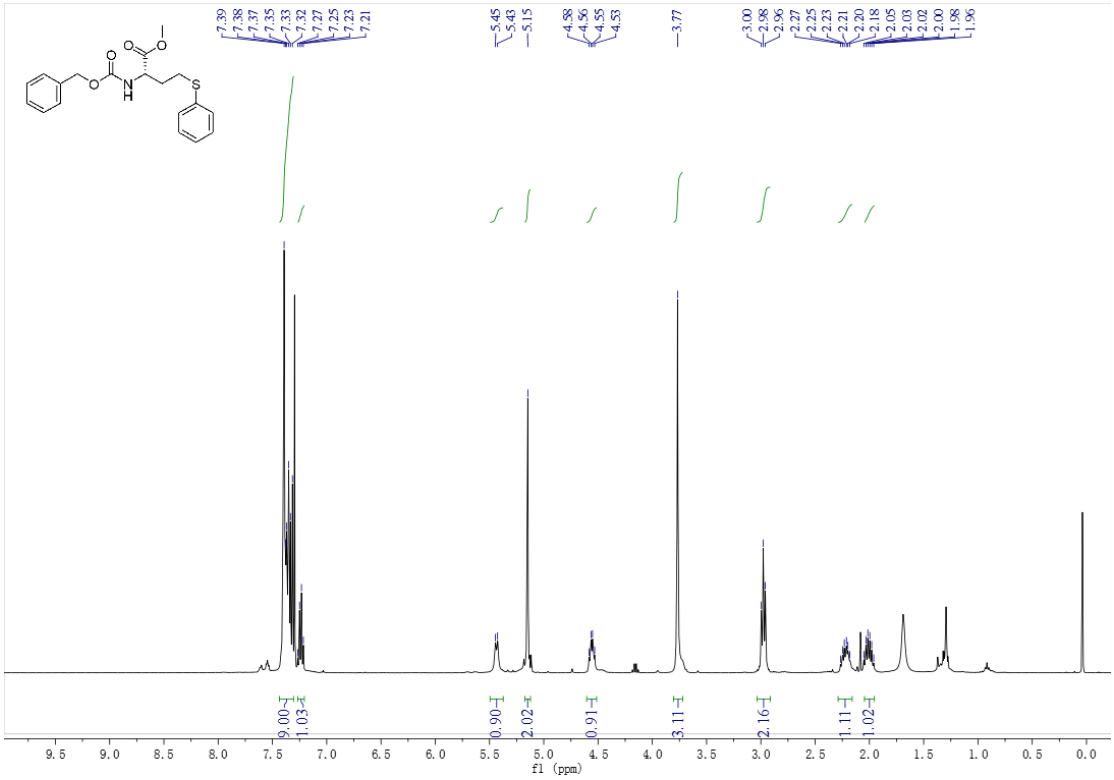
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **54**



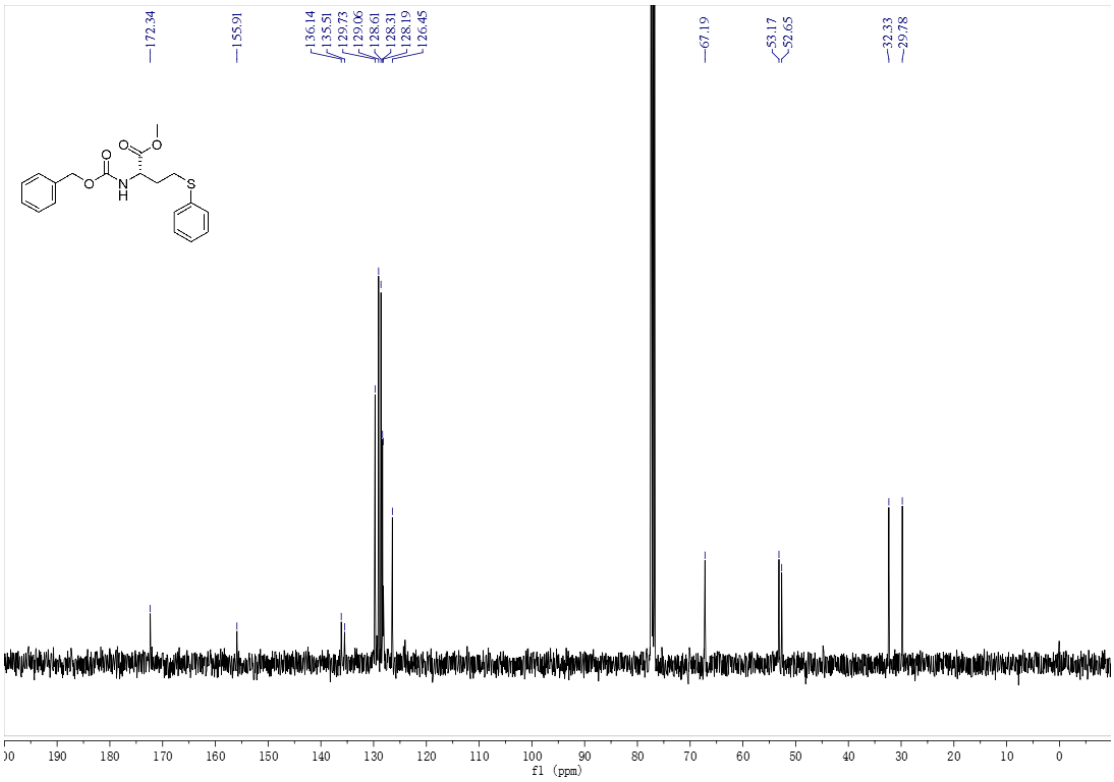
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **54**



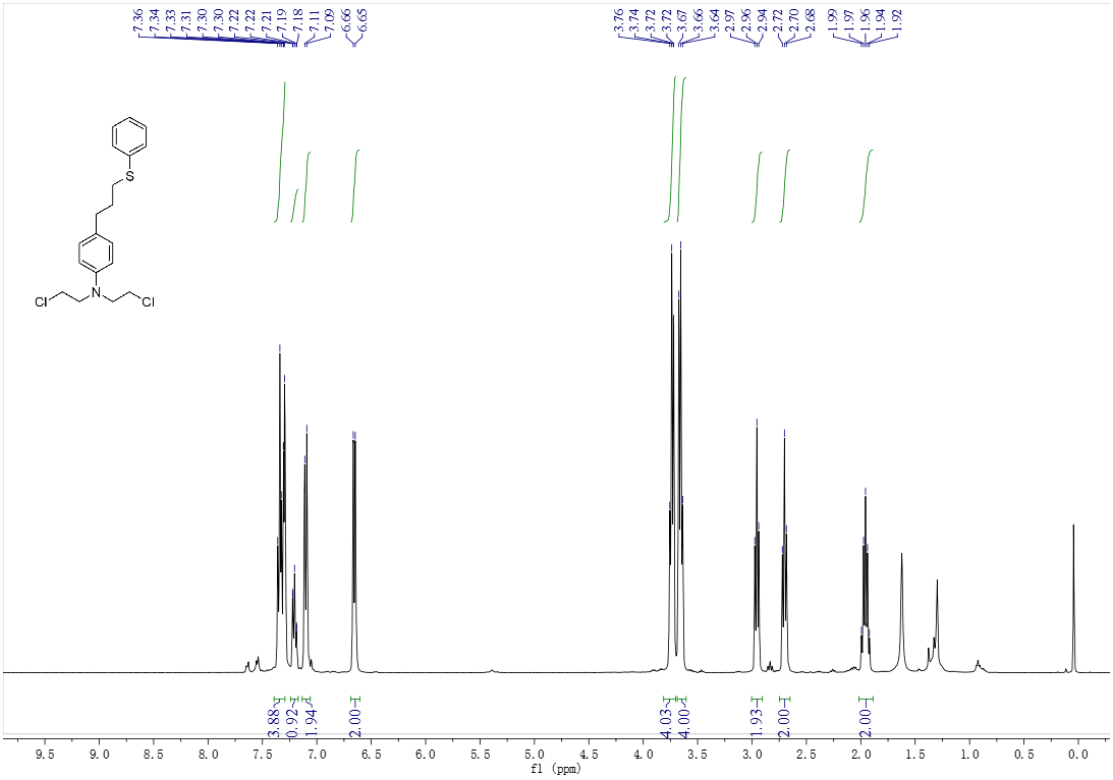
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **55**



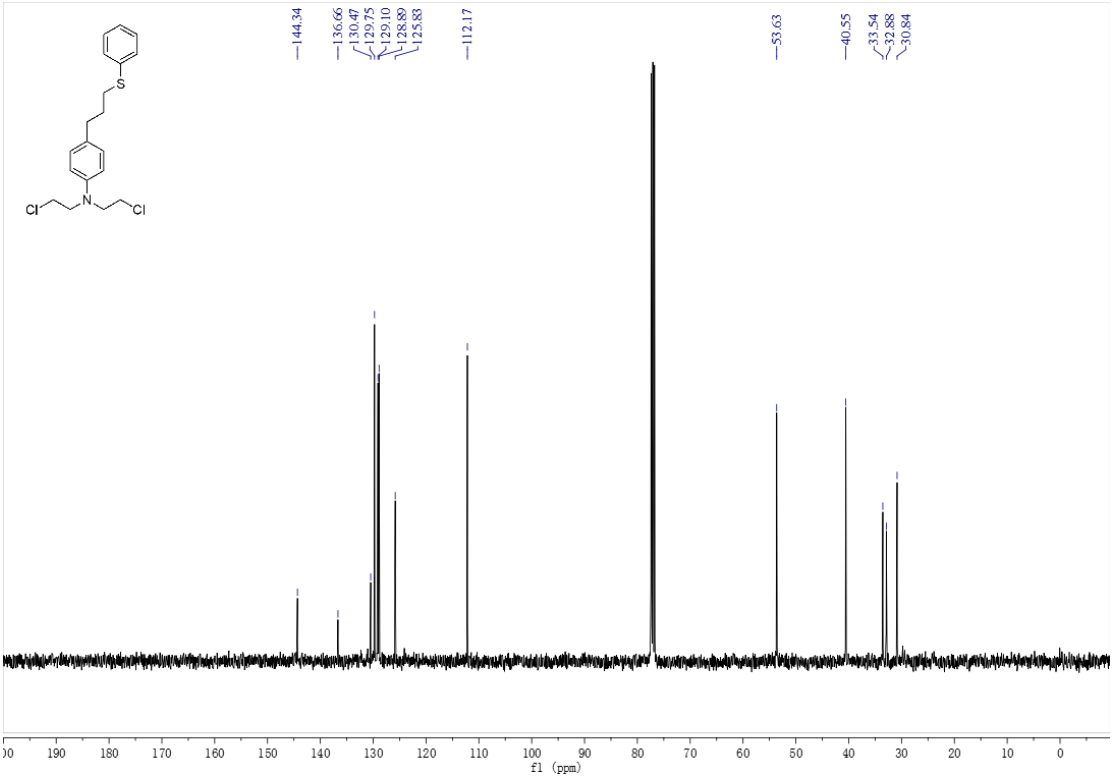
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **55**



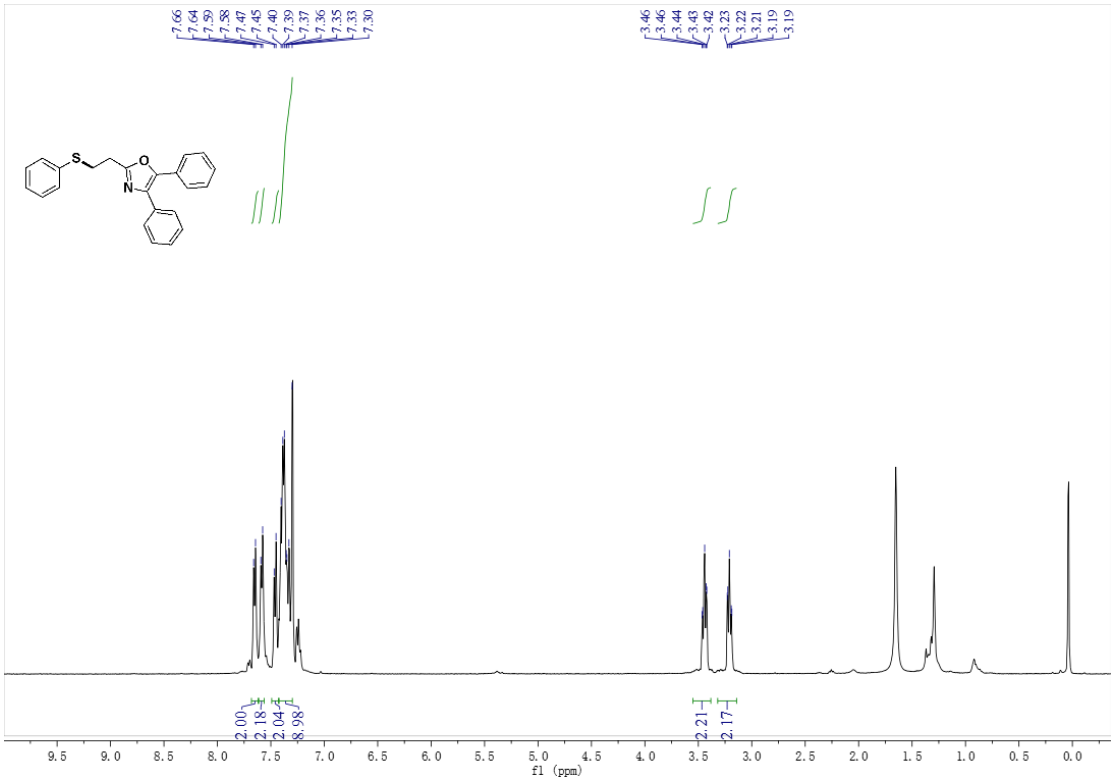
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **56**



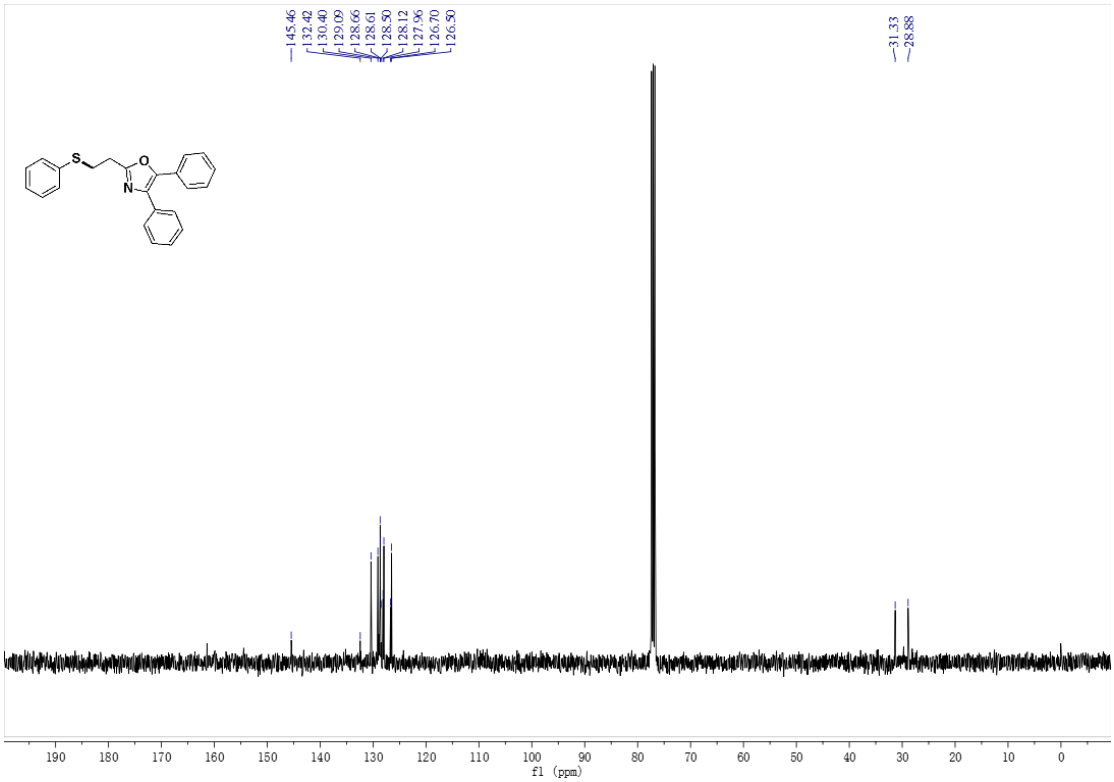
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **56**



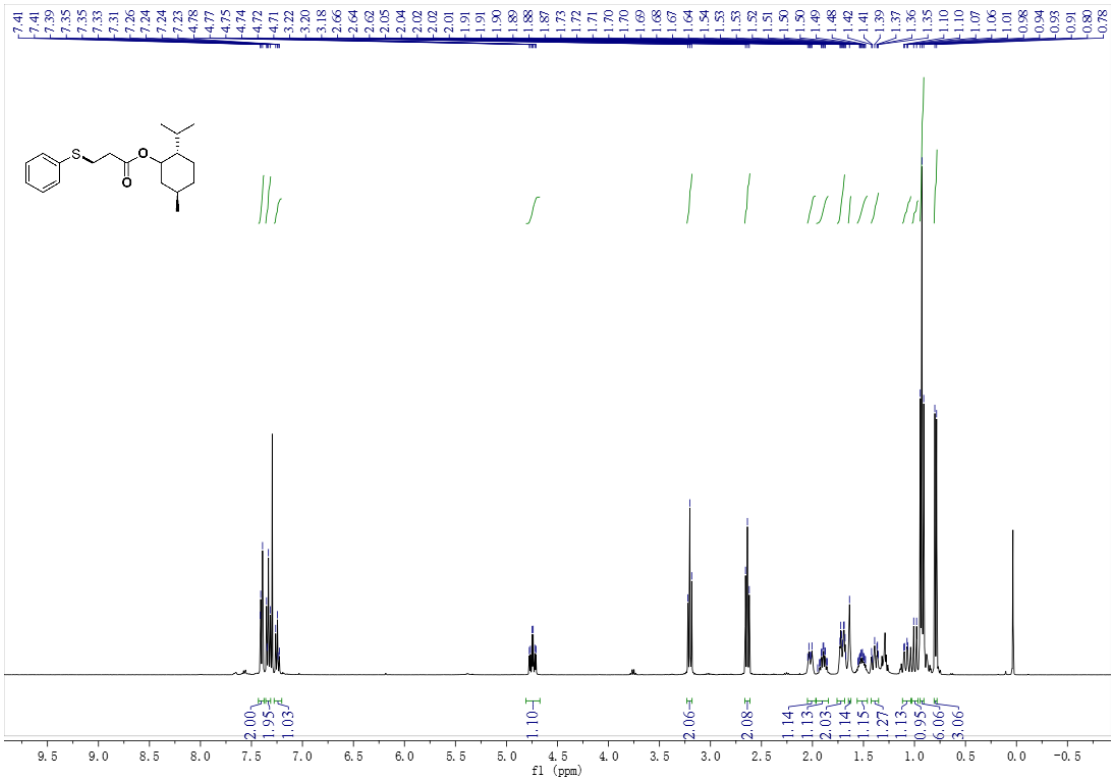
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **57**



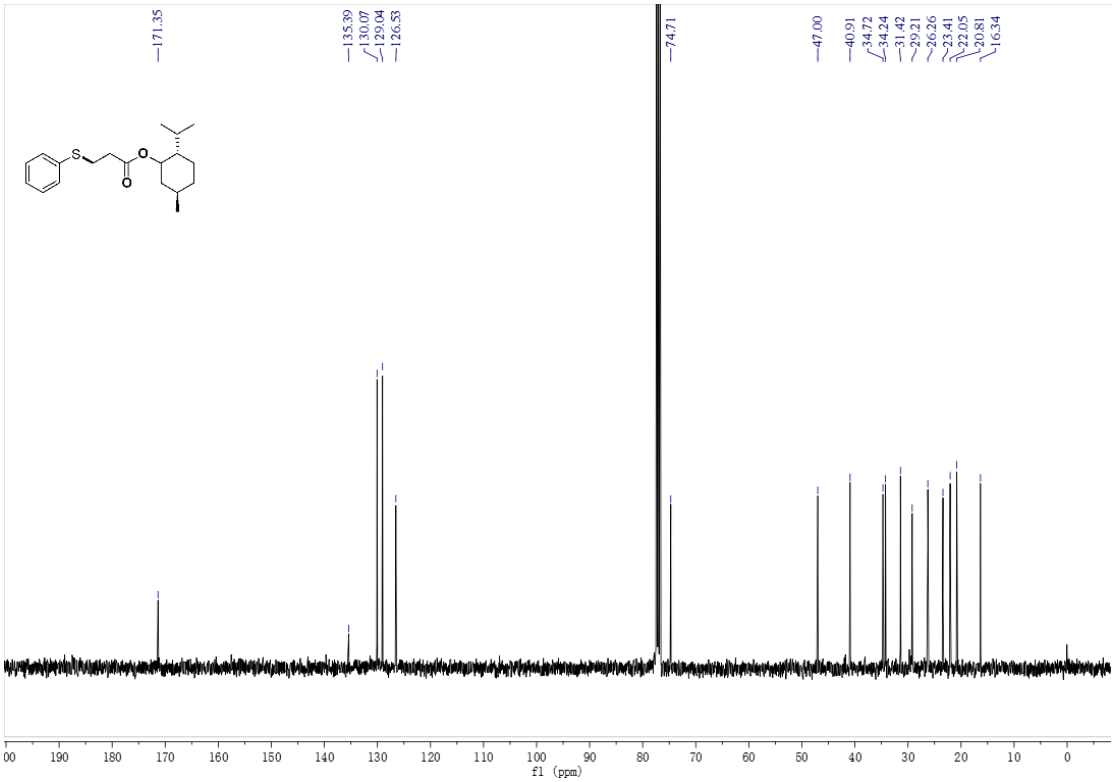
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **57**



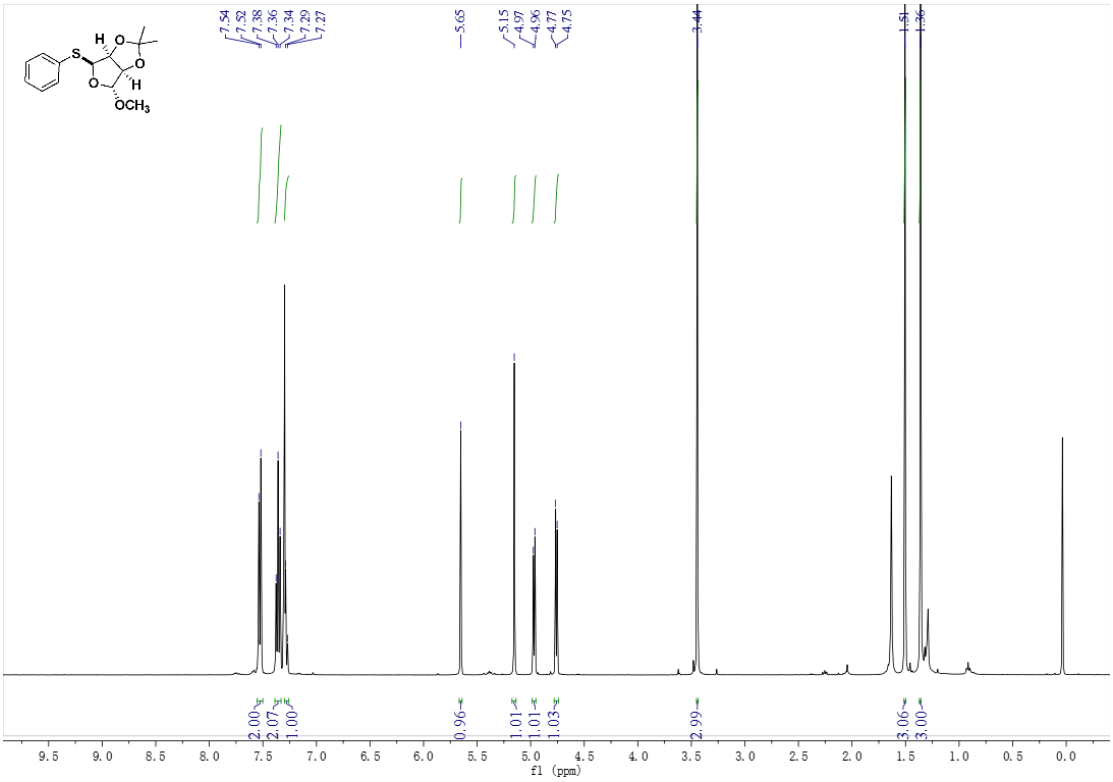
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **58**



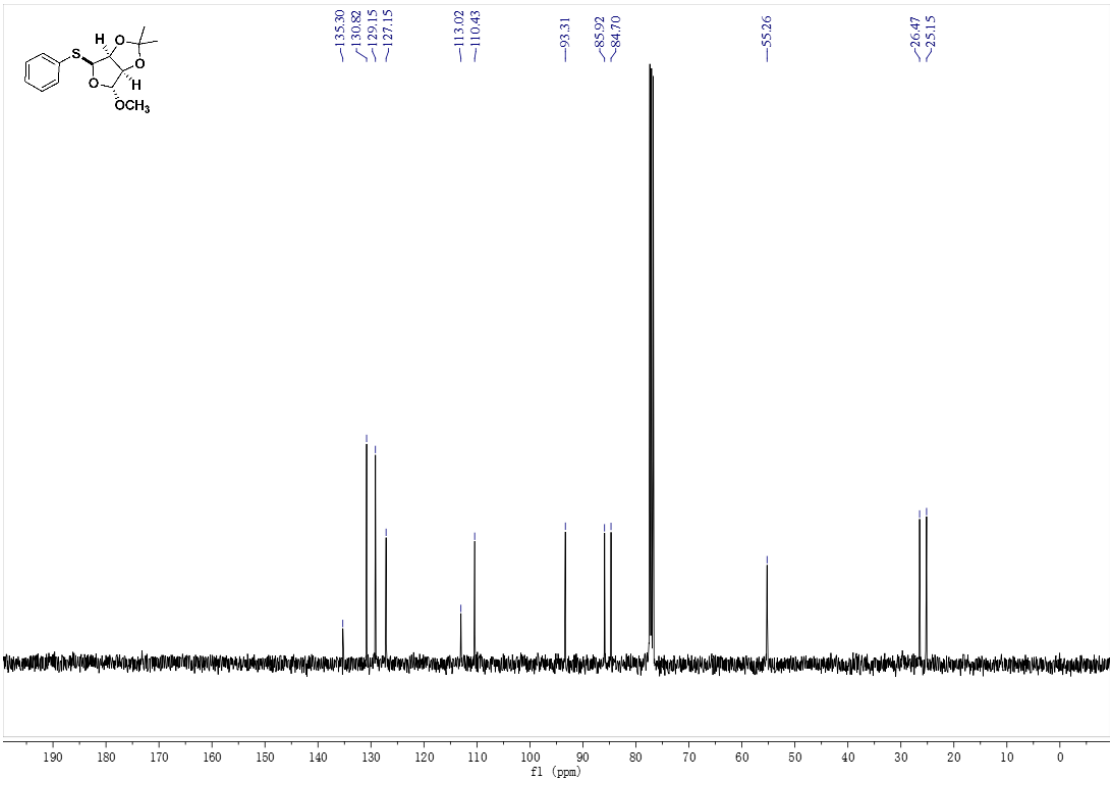
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **58**



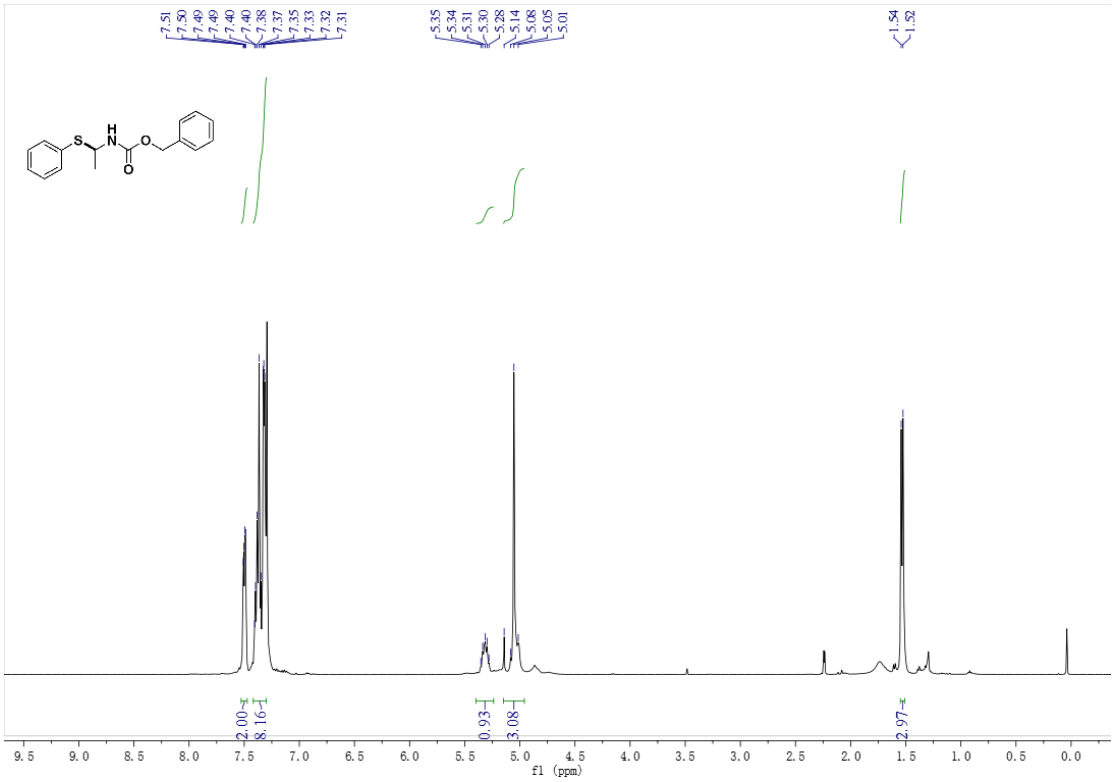
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **59**



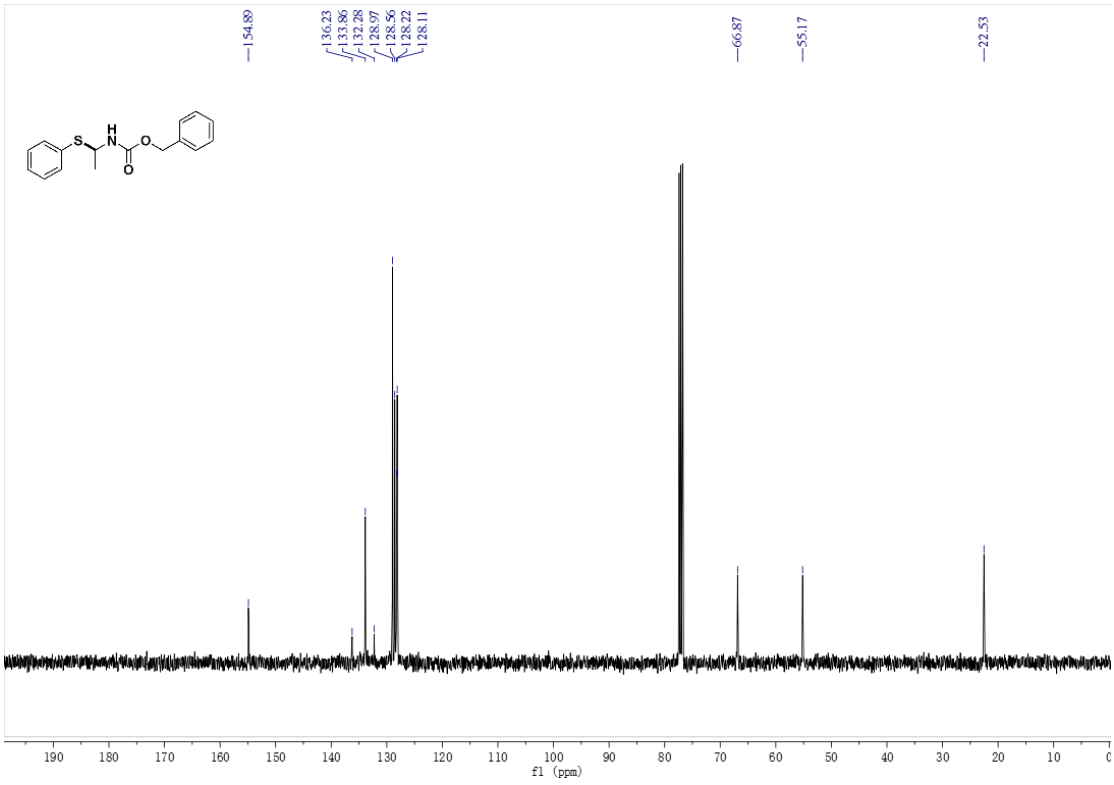
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **59**



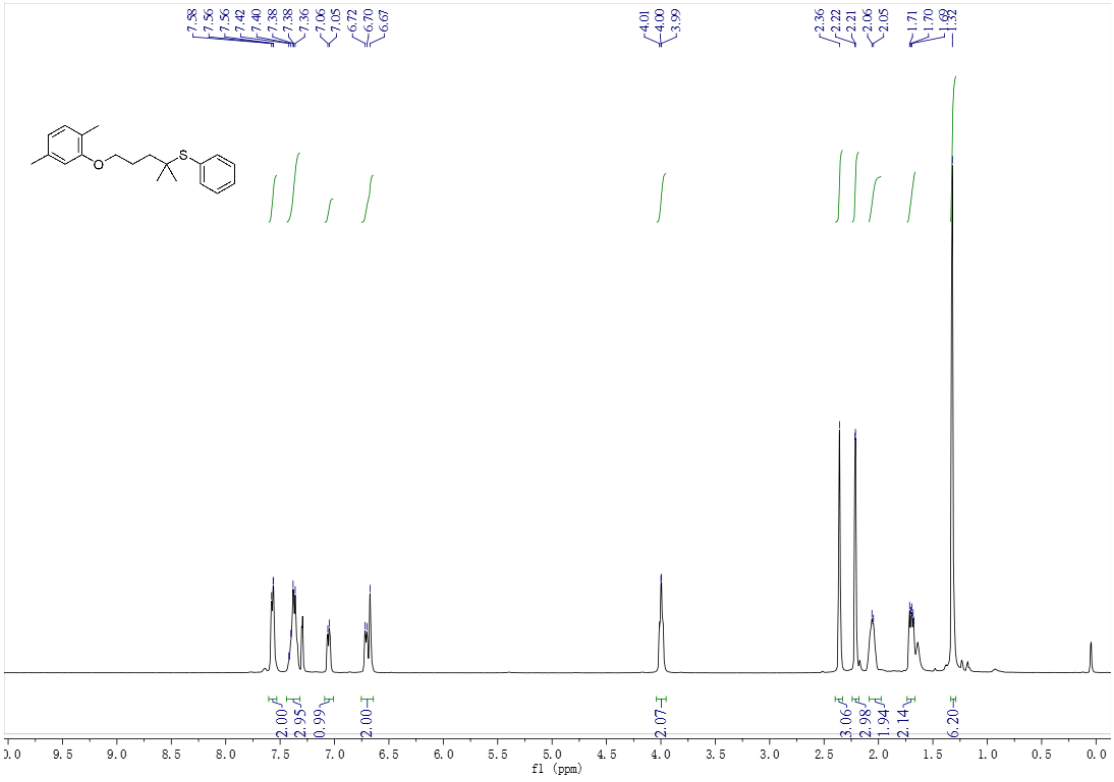
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **60**



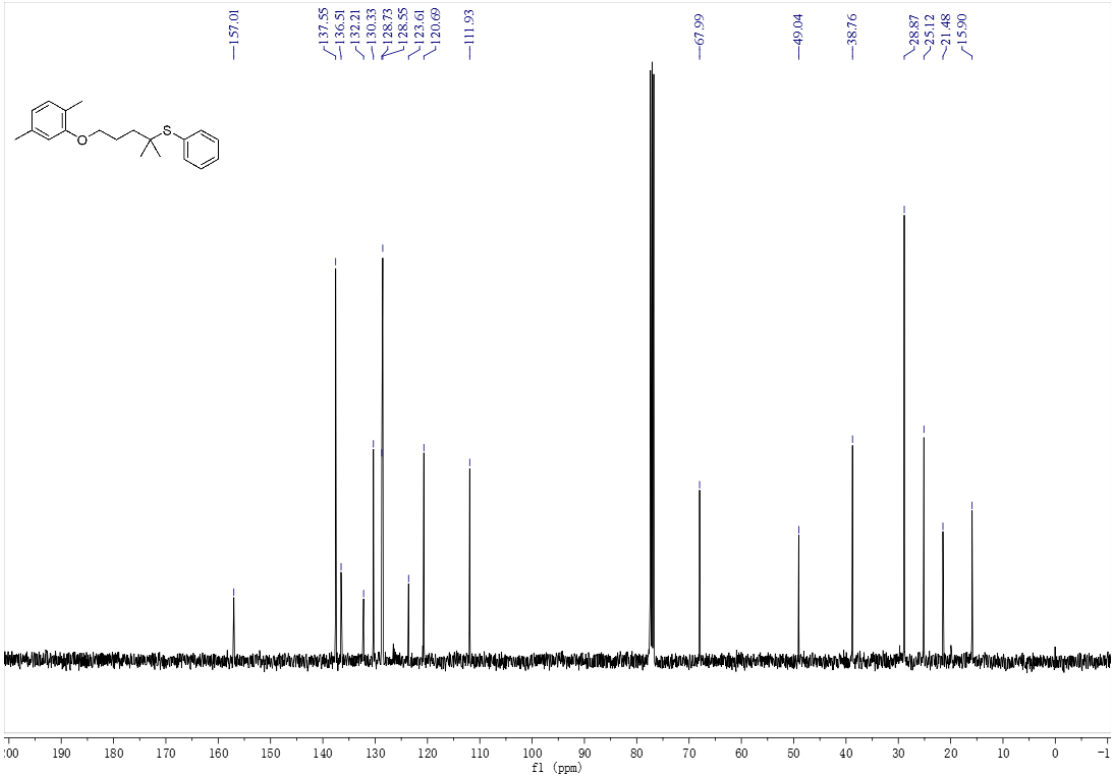
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **60**



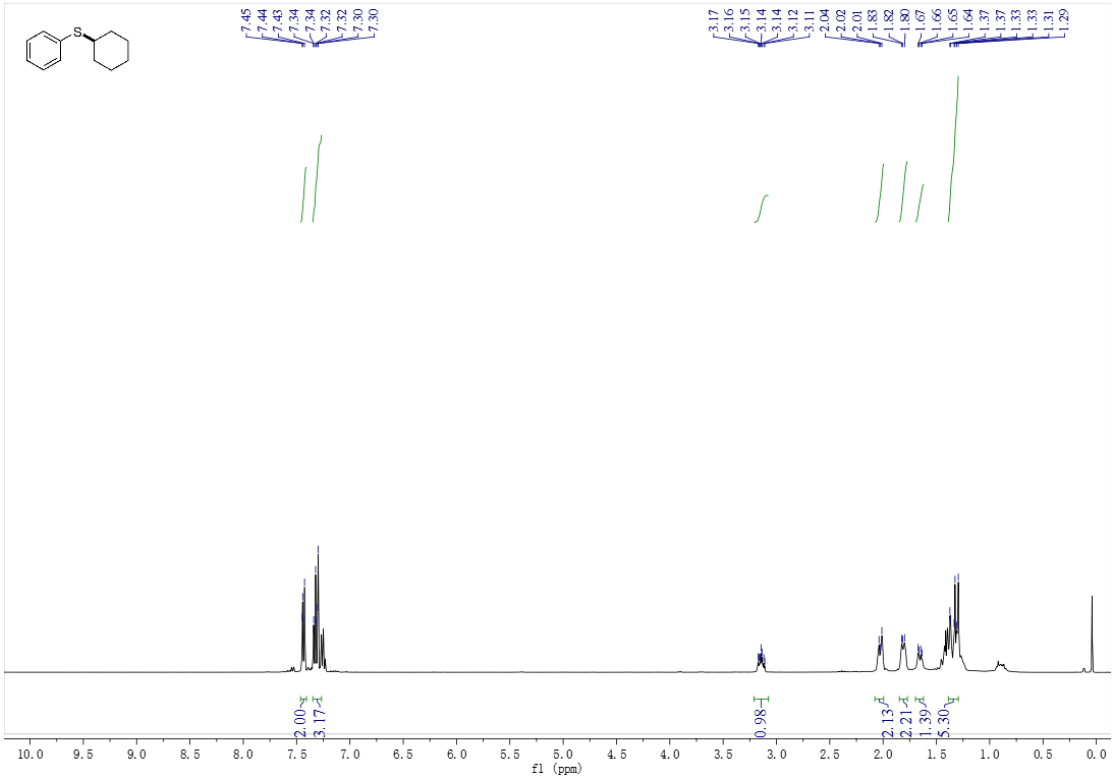
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **61**



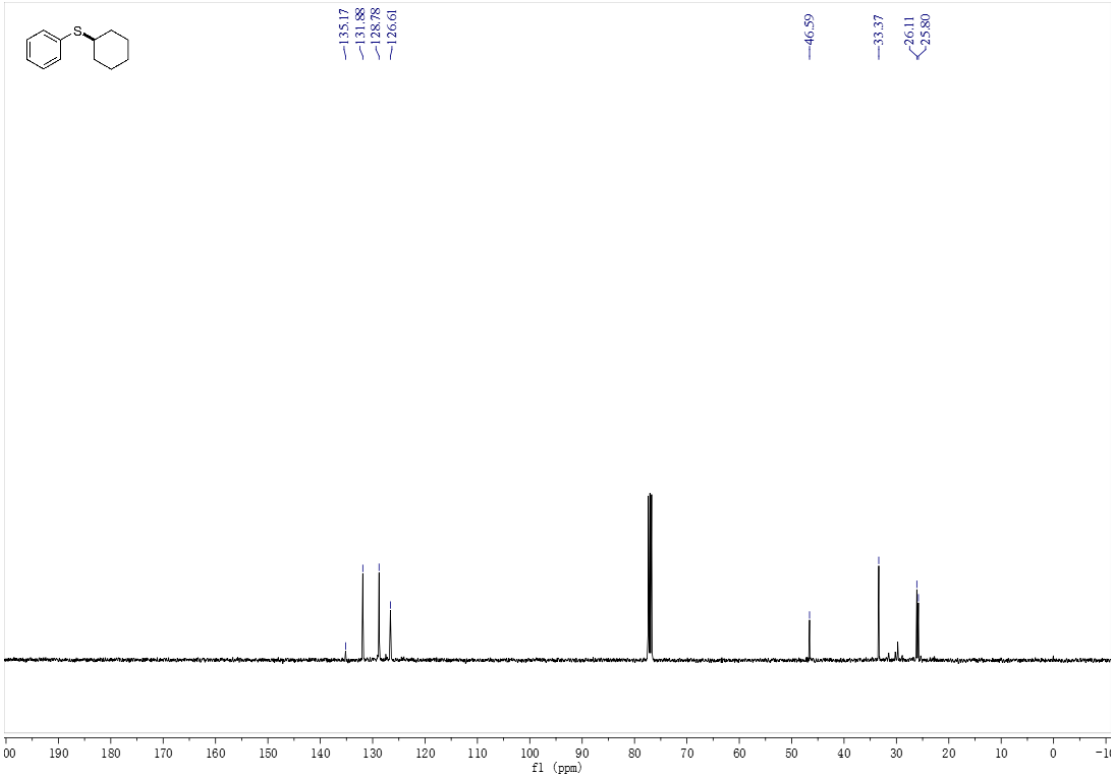
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **61**



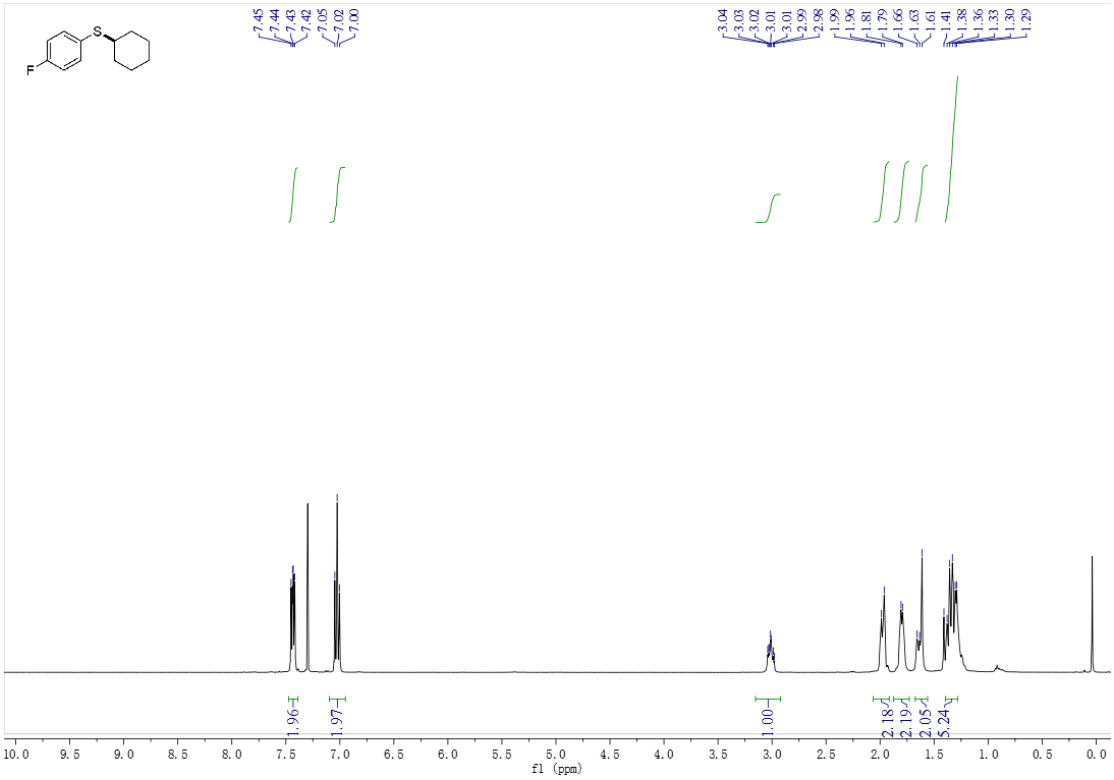
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **62**



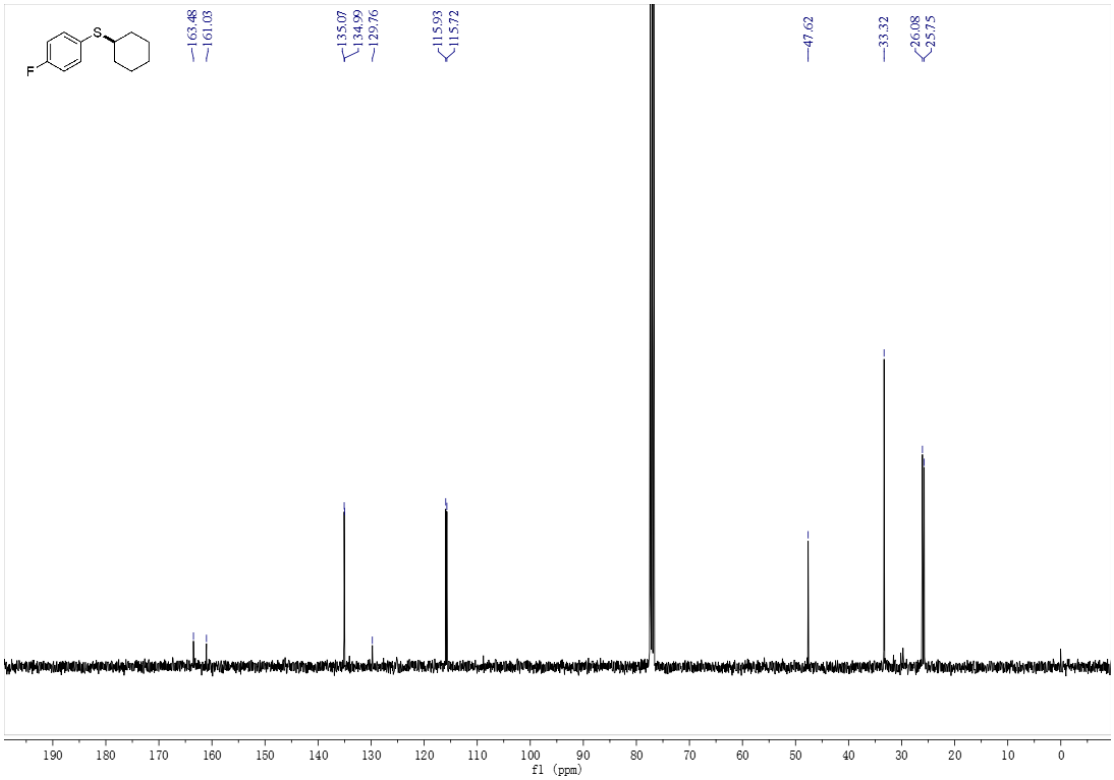
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **62**



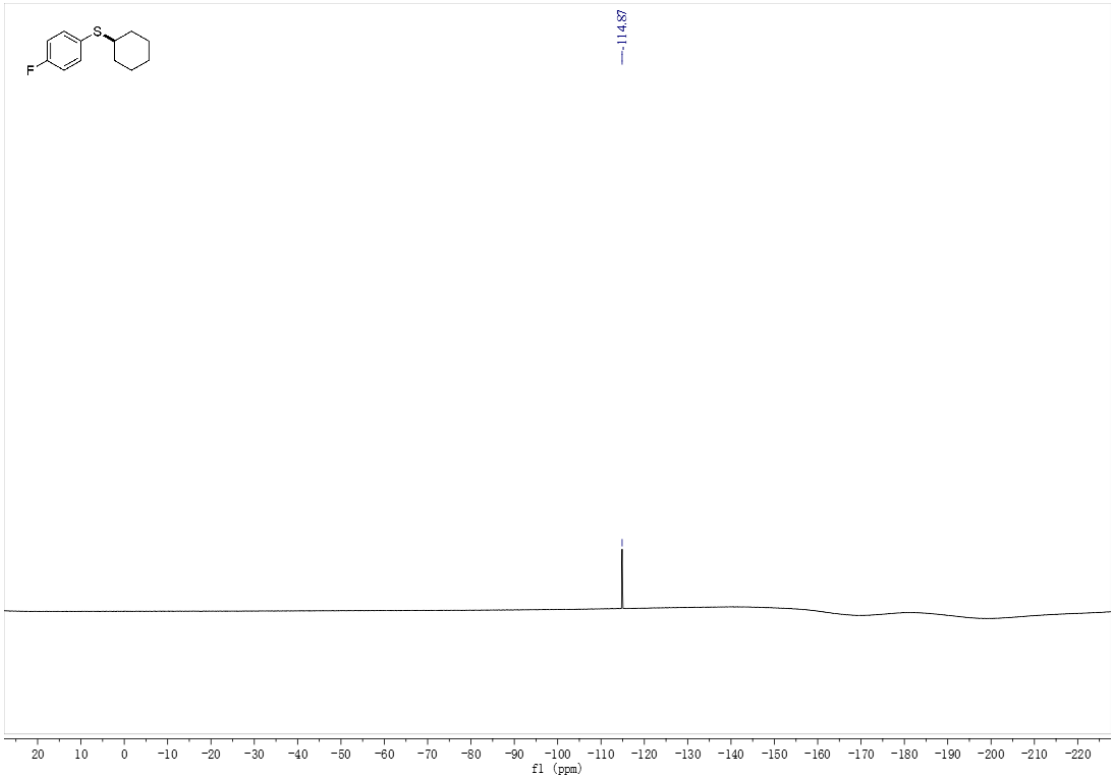
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **63**



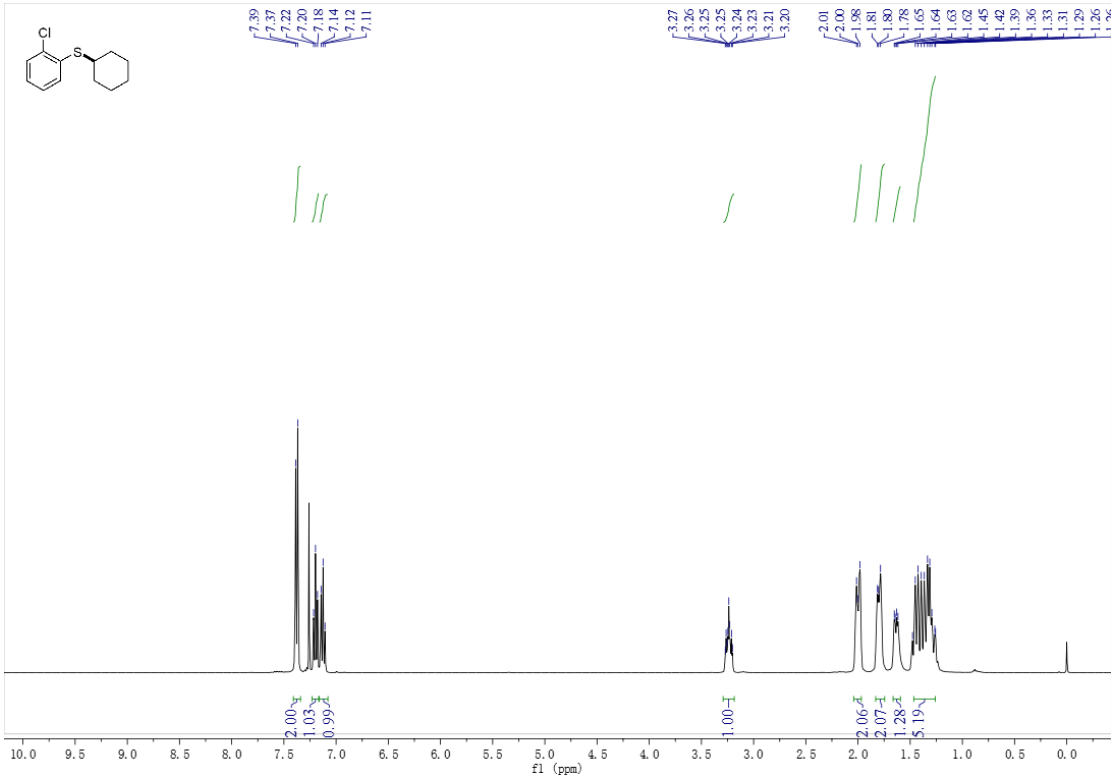
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **63**



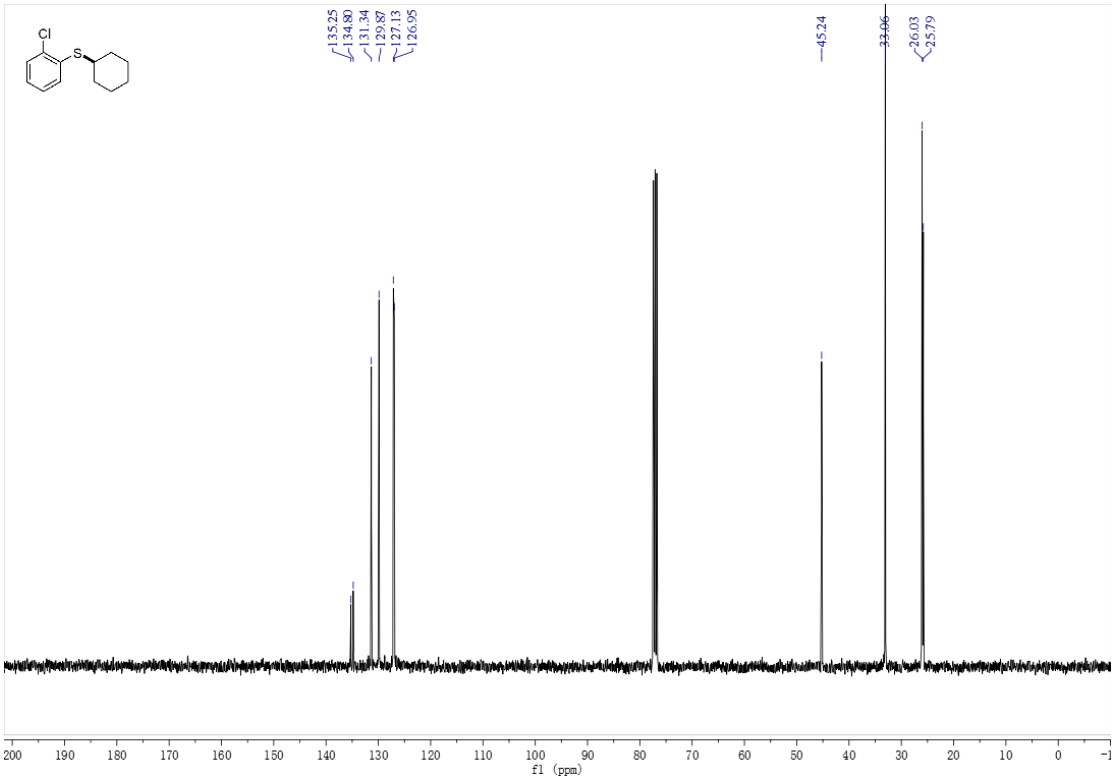
^{19}F NMR spectrum (376 MHz, $CDCl_3$，23 ℃) of **63**



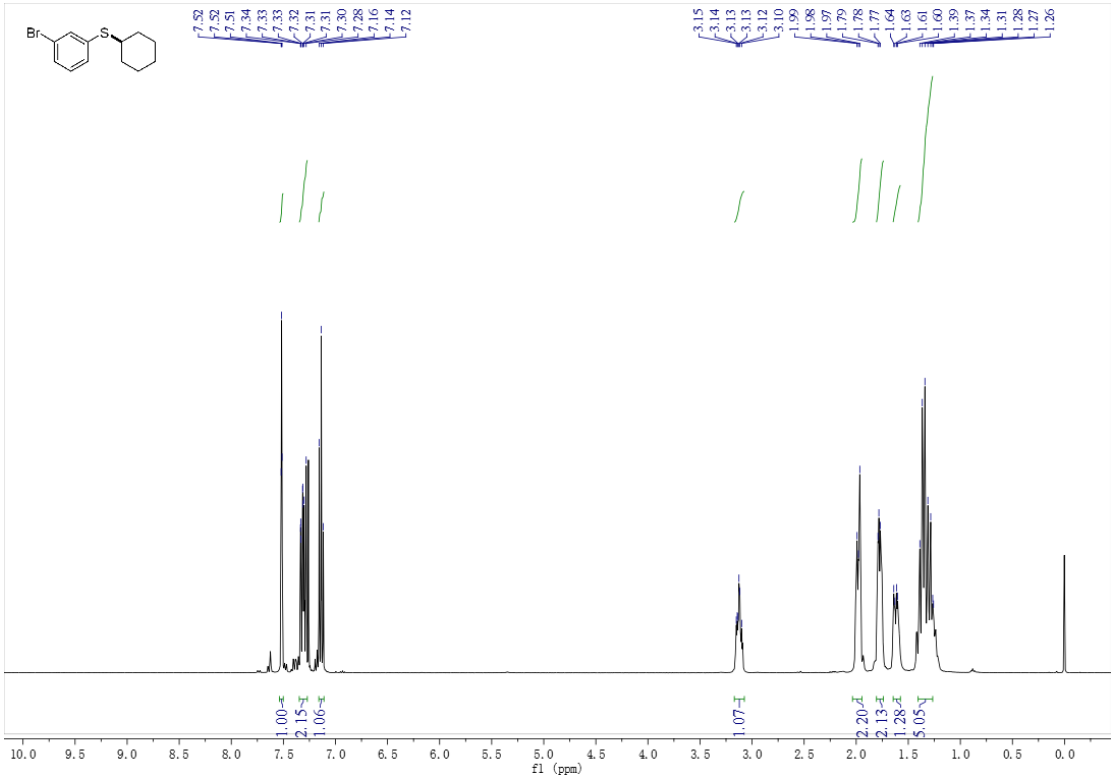
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **64**



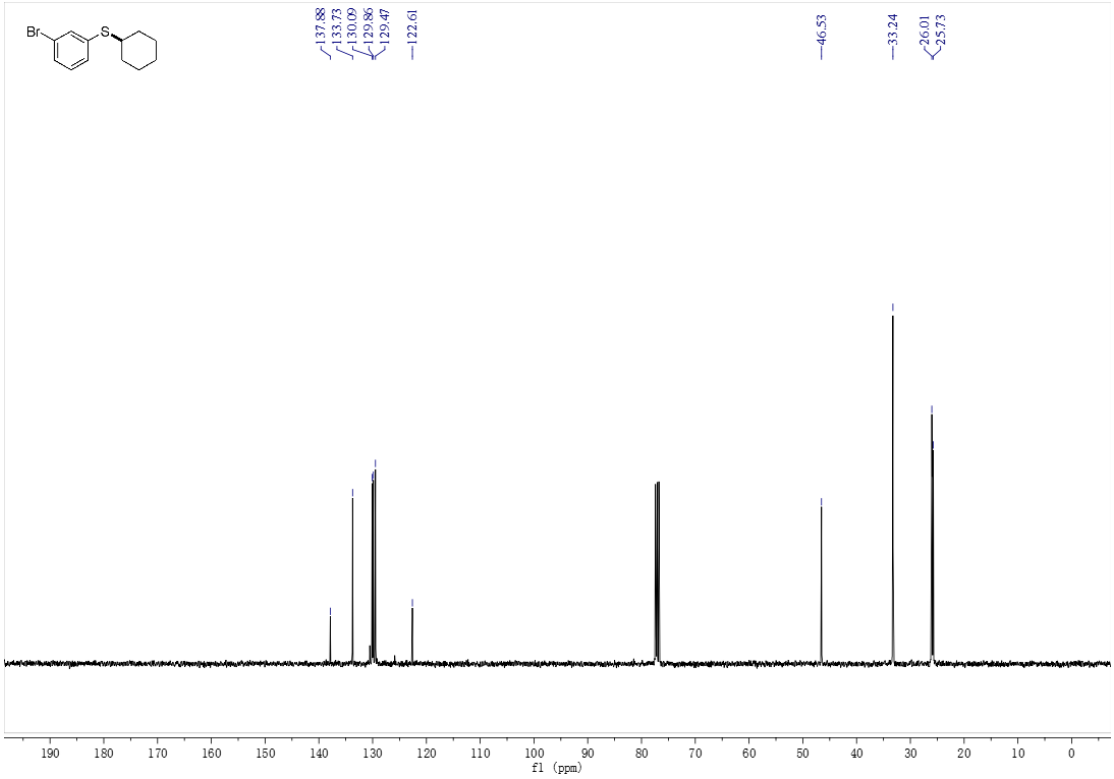
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **64**



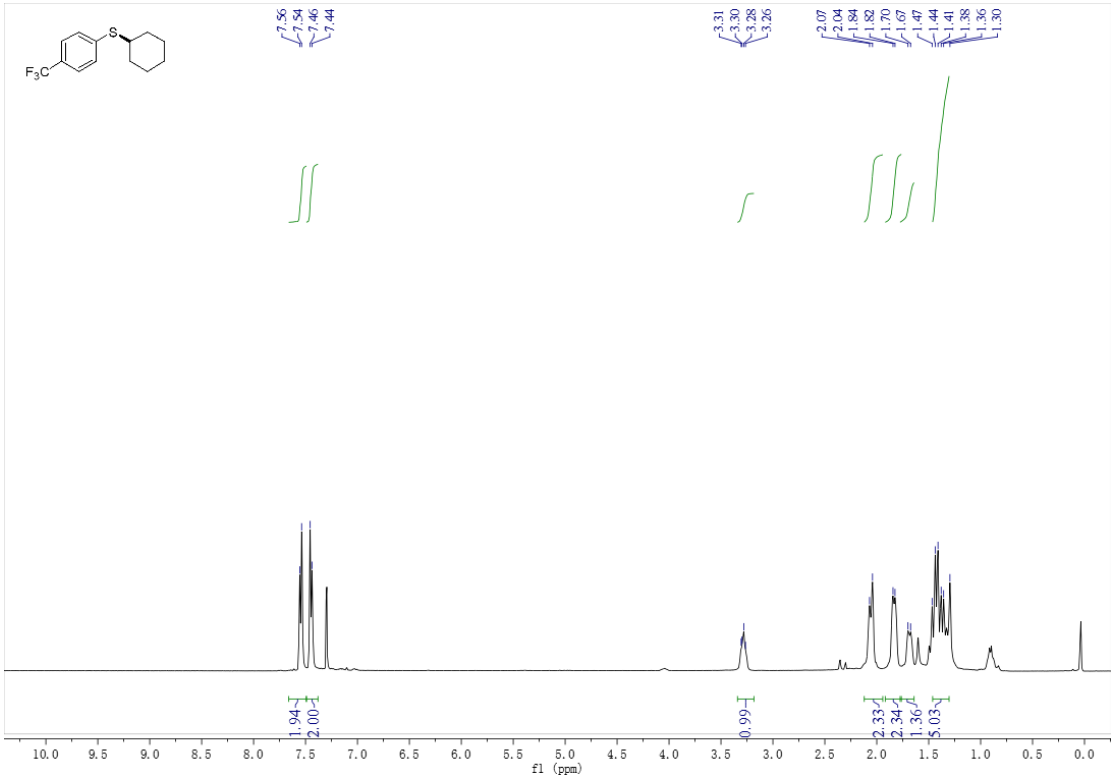
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **65**



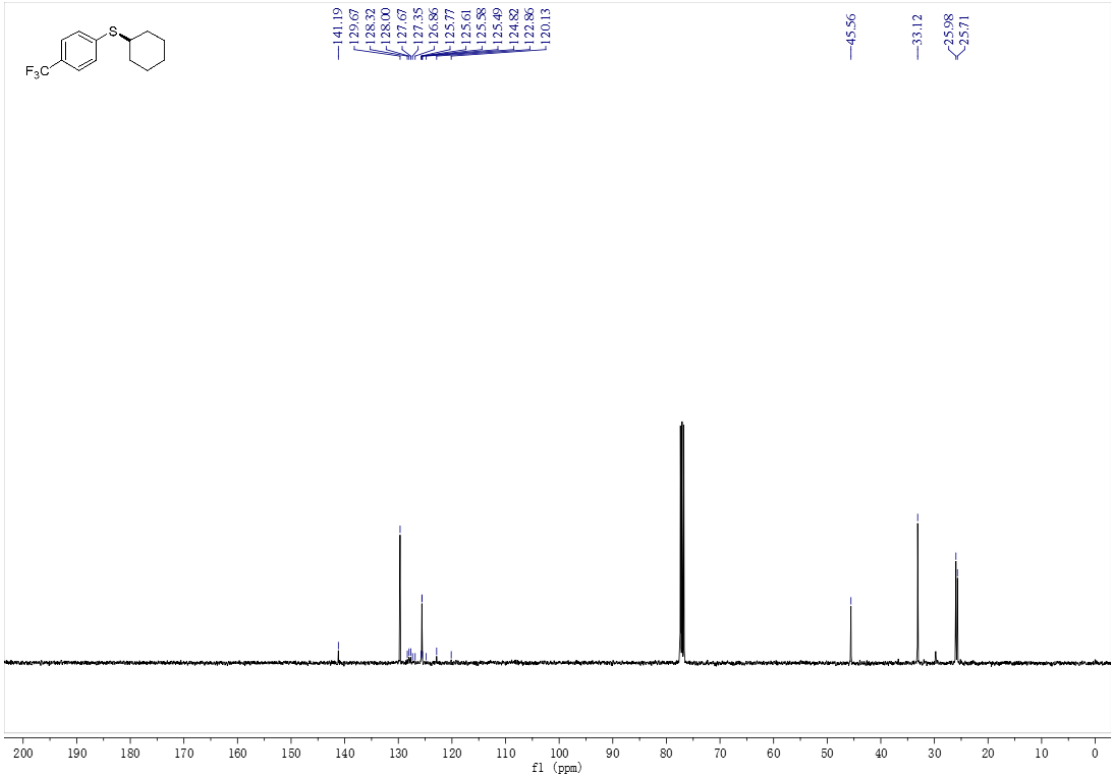
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **65**



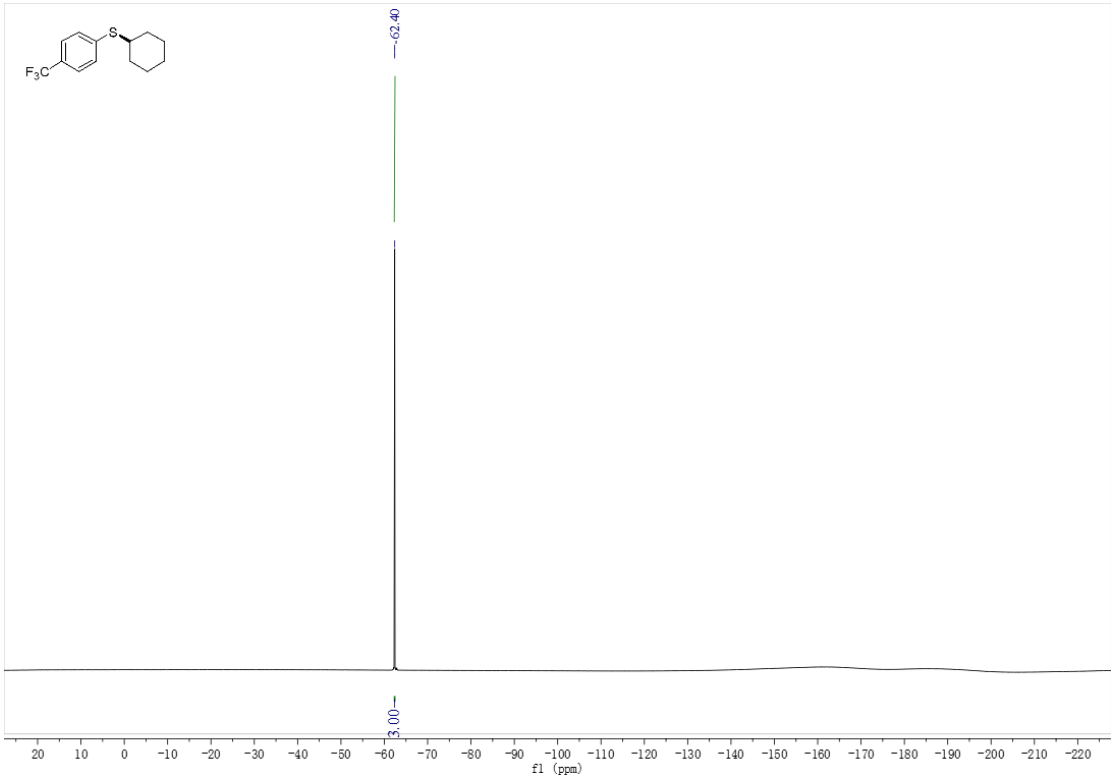
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **66**



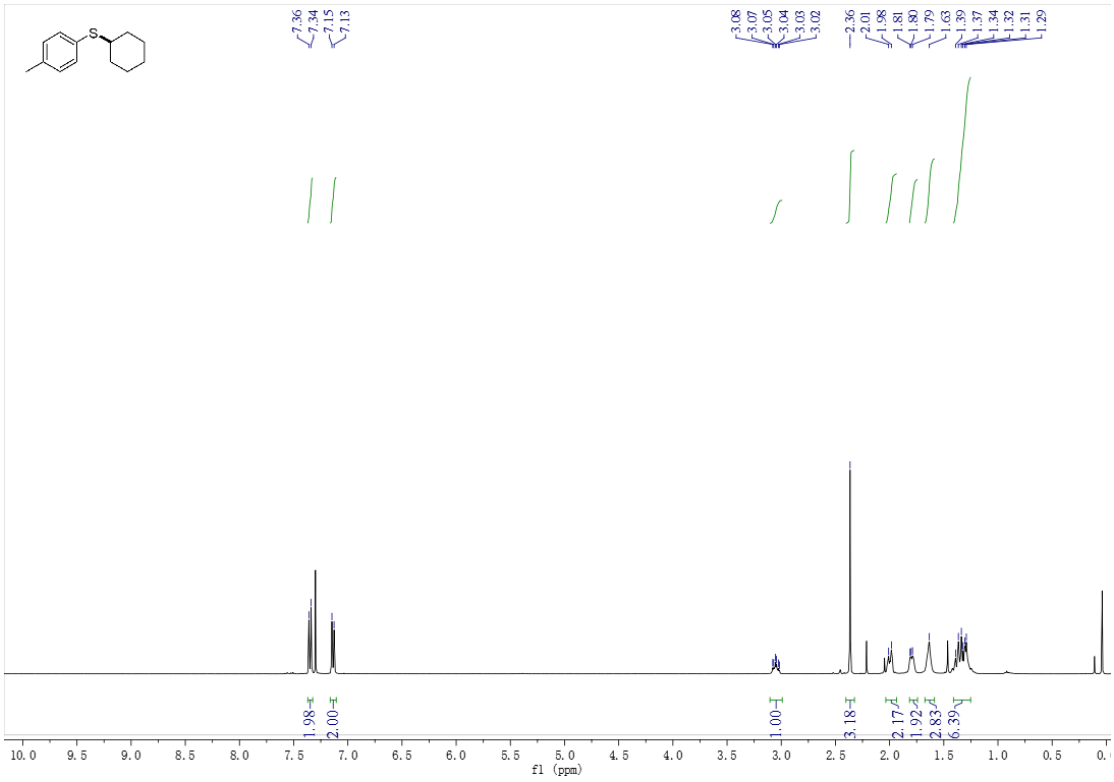
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **66**



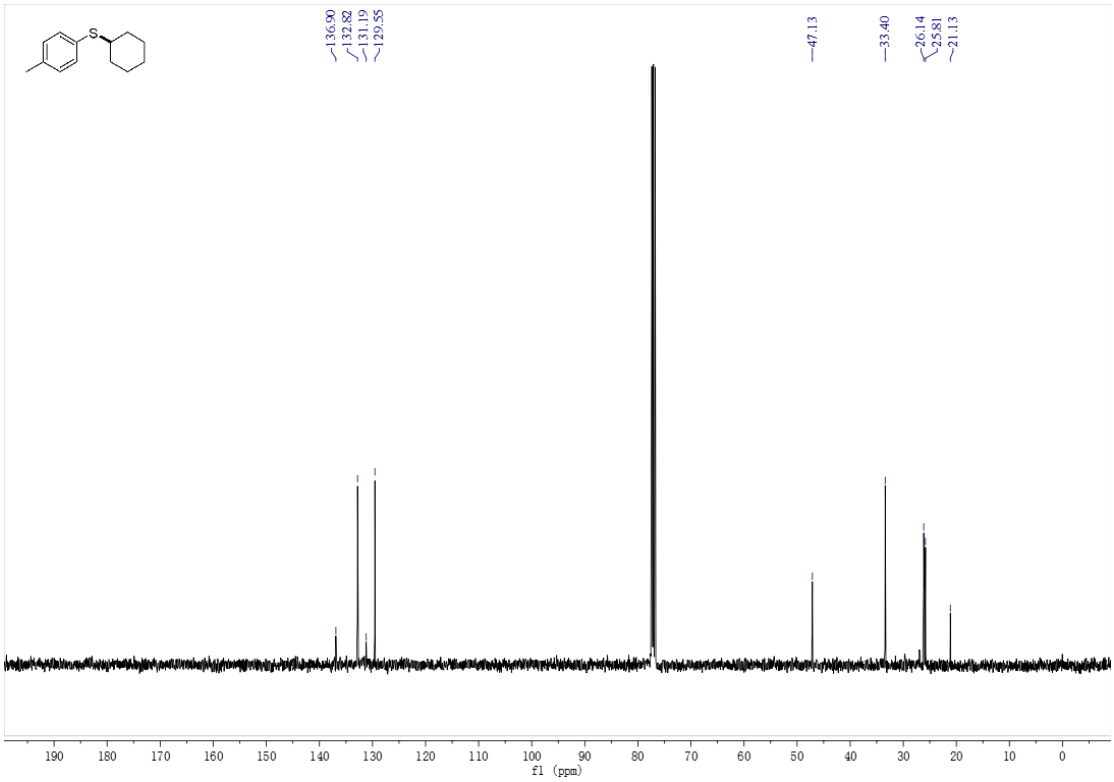
^{19}F NMR spectrum (376 MHz, $CDCl_3$，23 ℃) of **66**



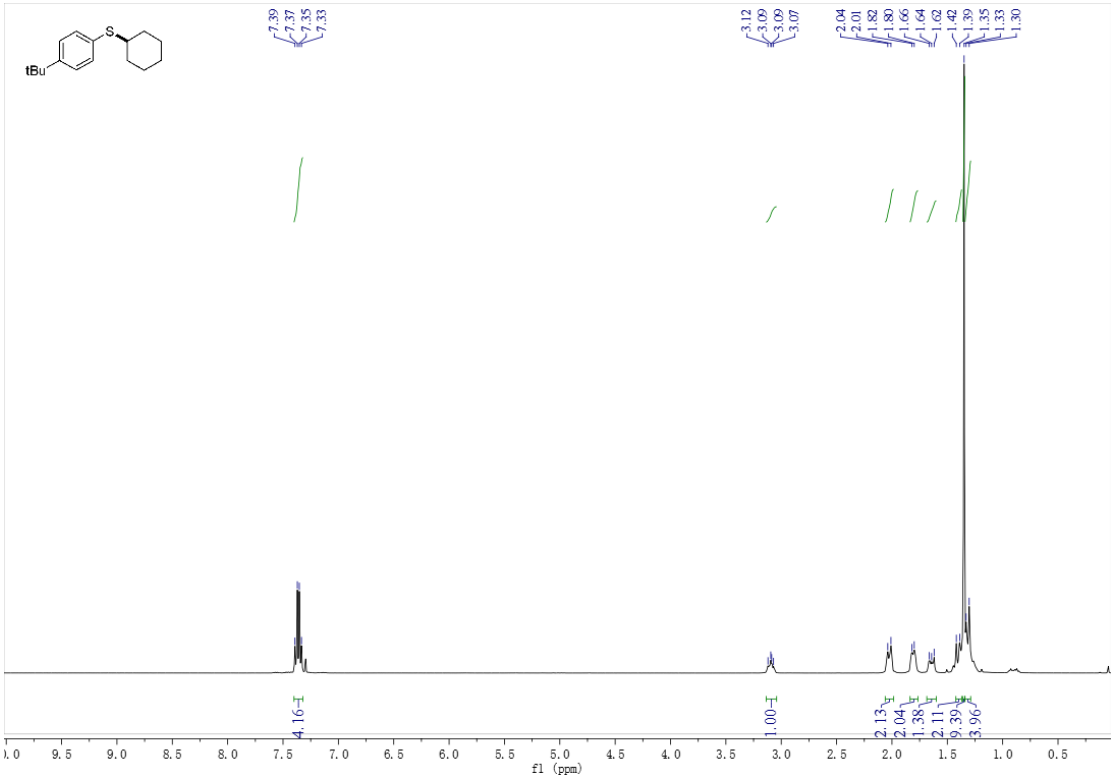
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **67**



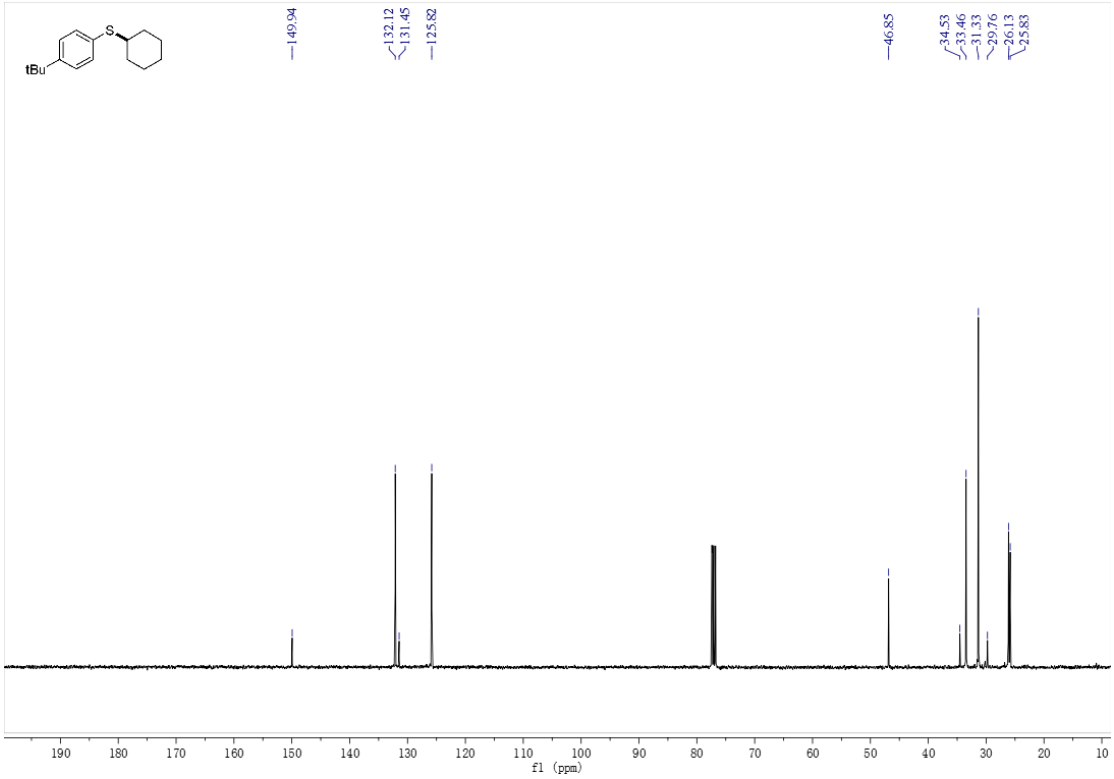
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **67**



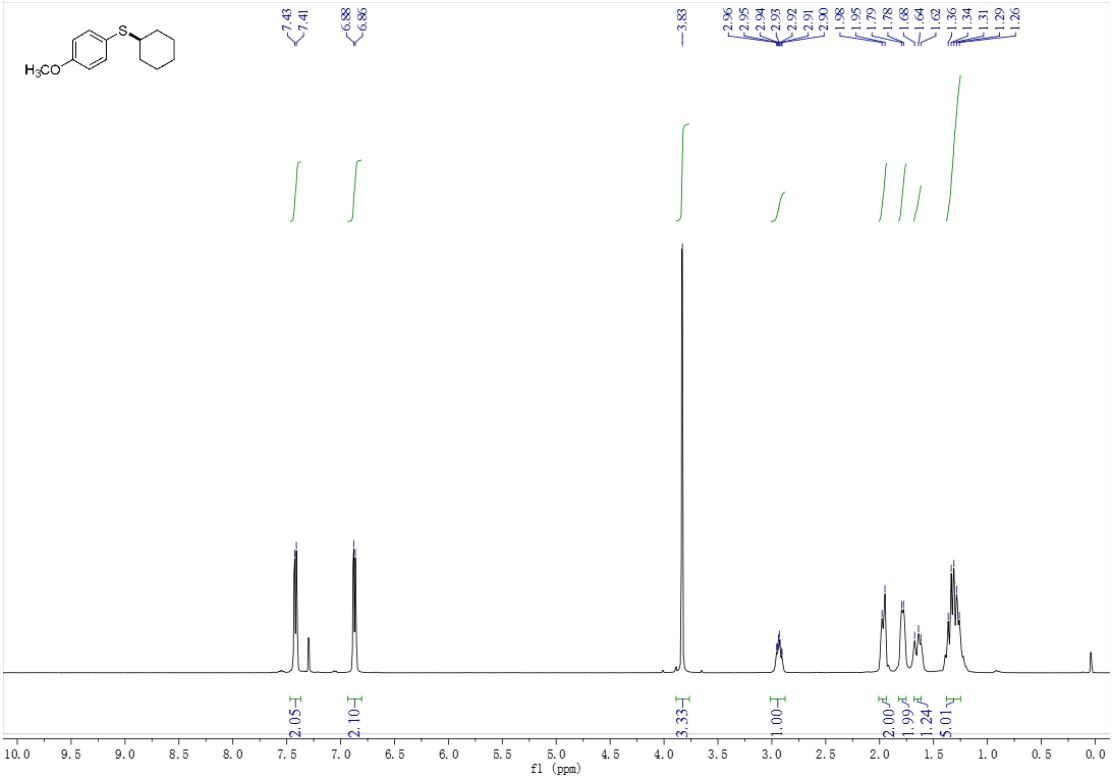
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **68**



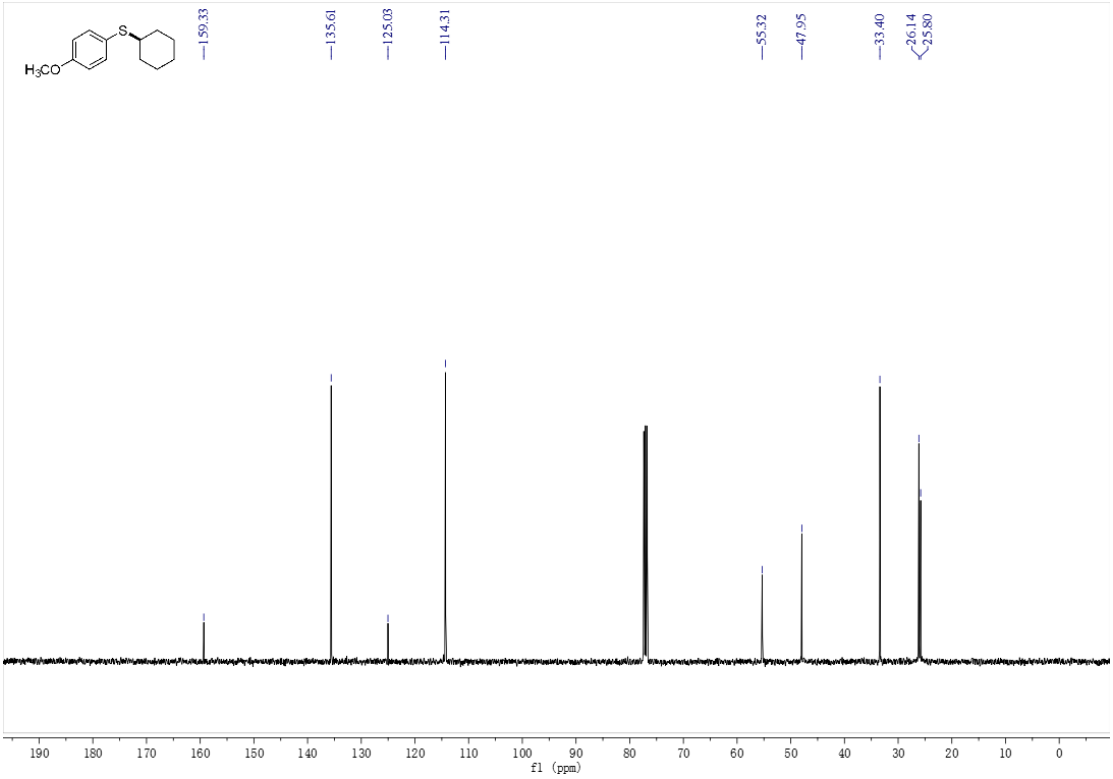
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **68**



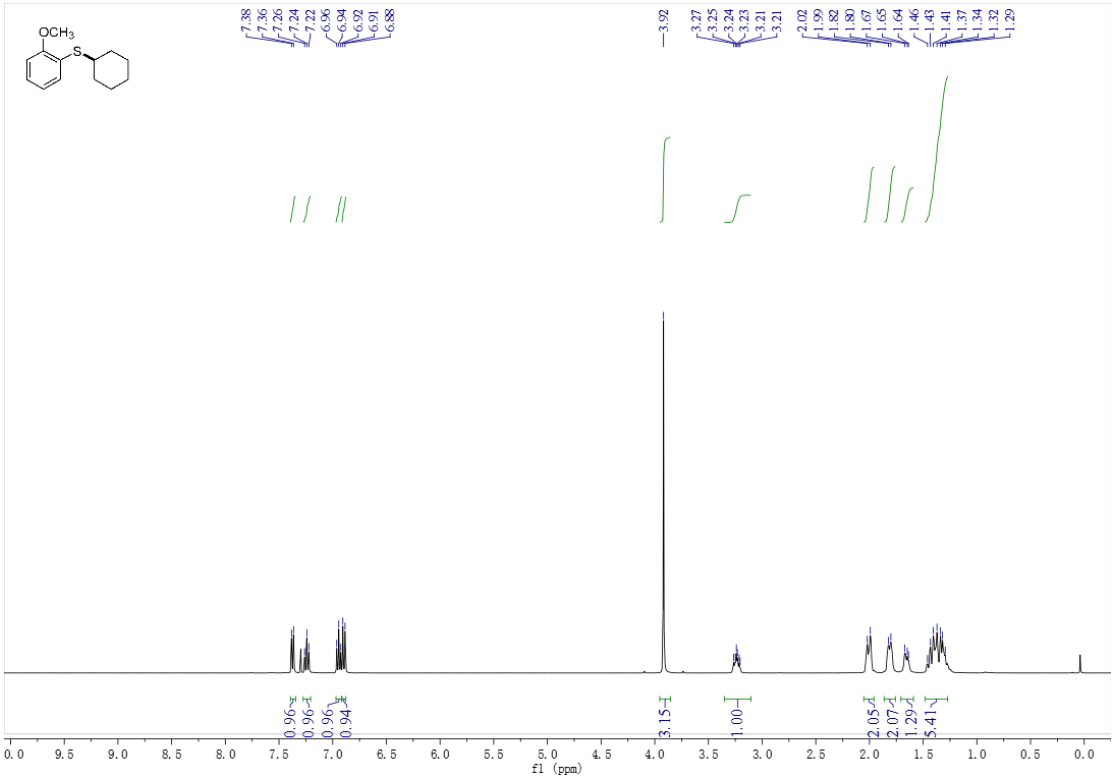
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **69**



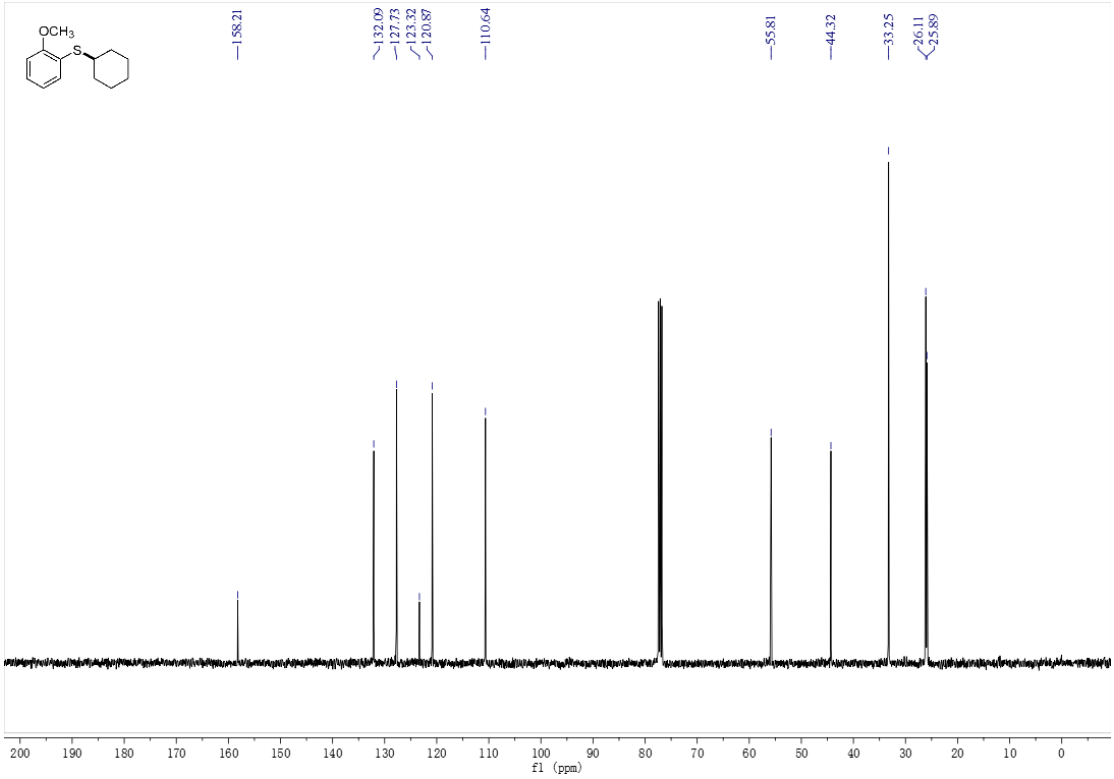
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **69**



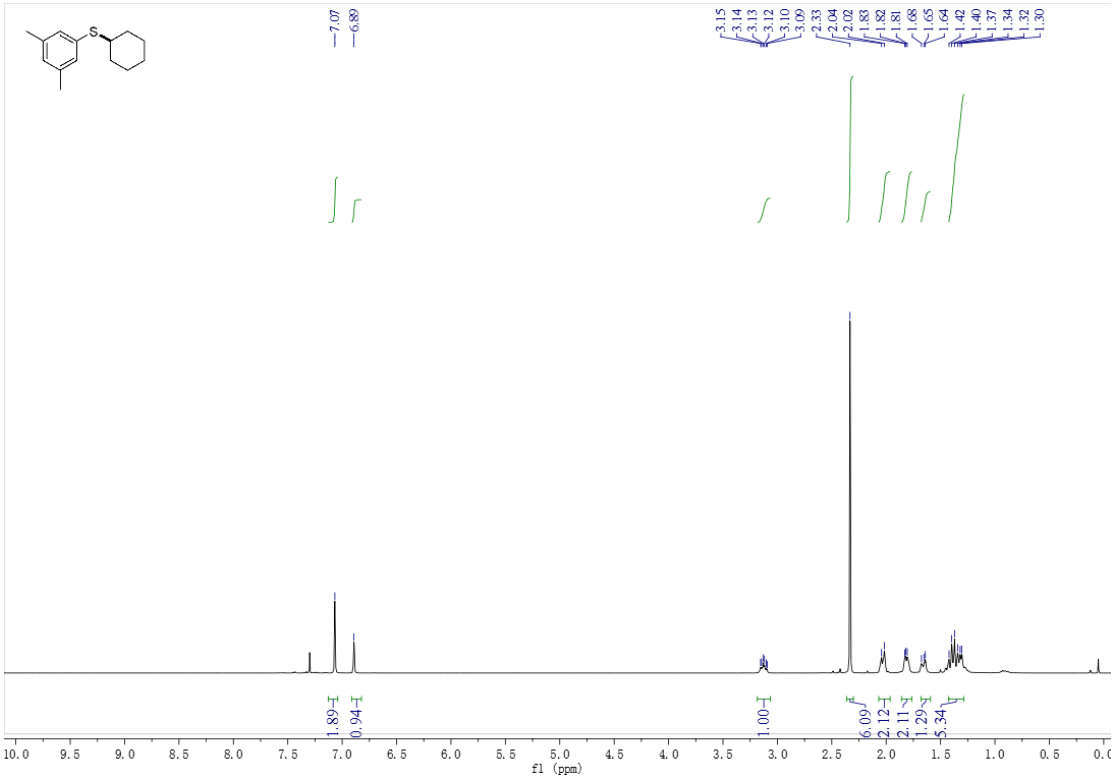
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **70**



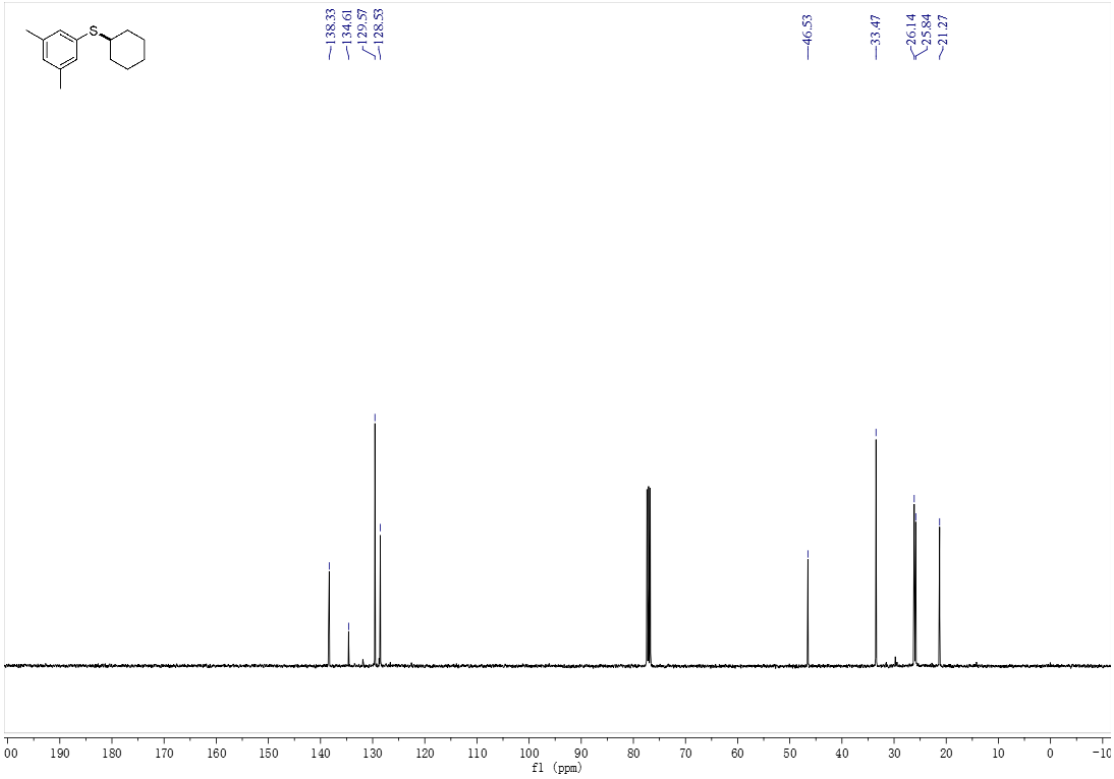
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **70**



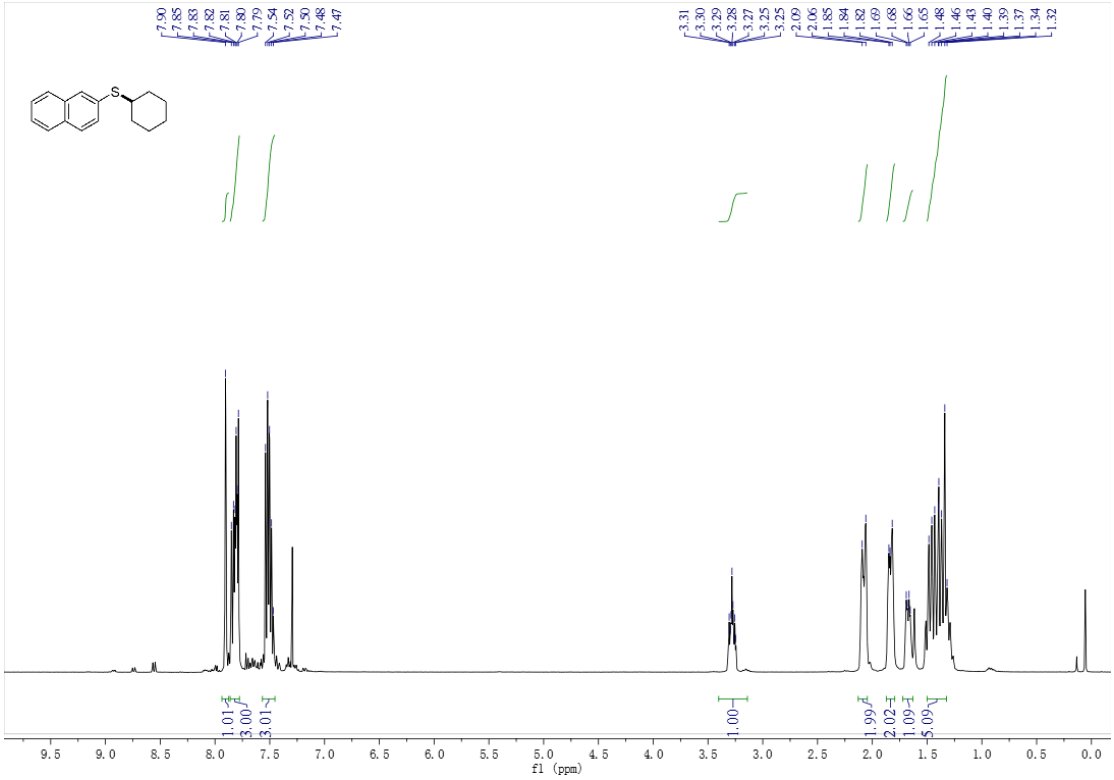
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **71**



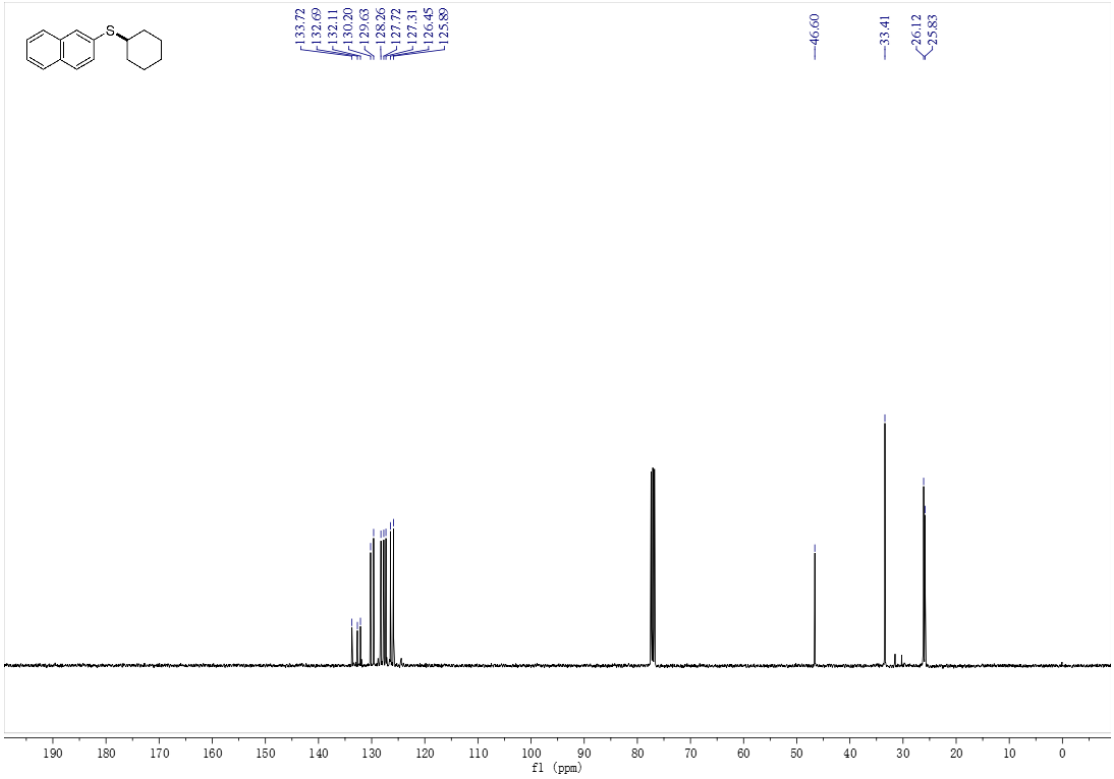
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **71**



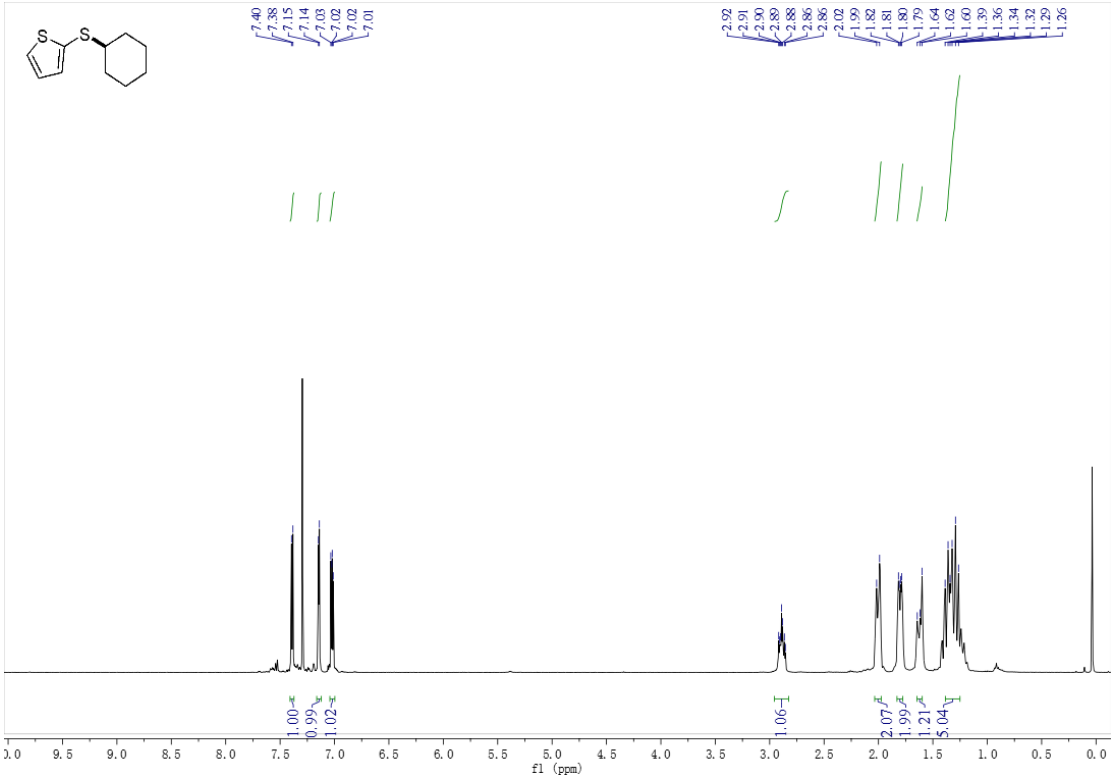
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **72**



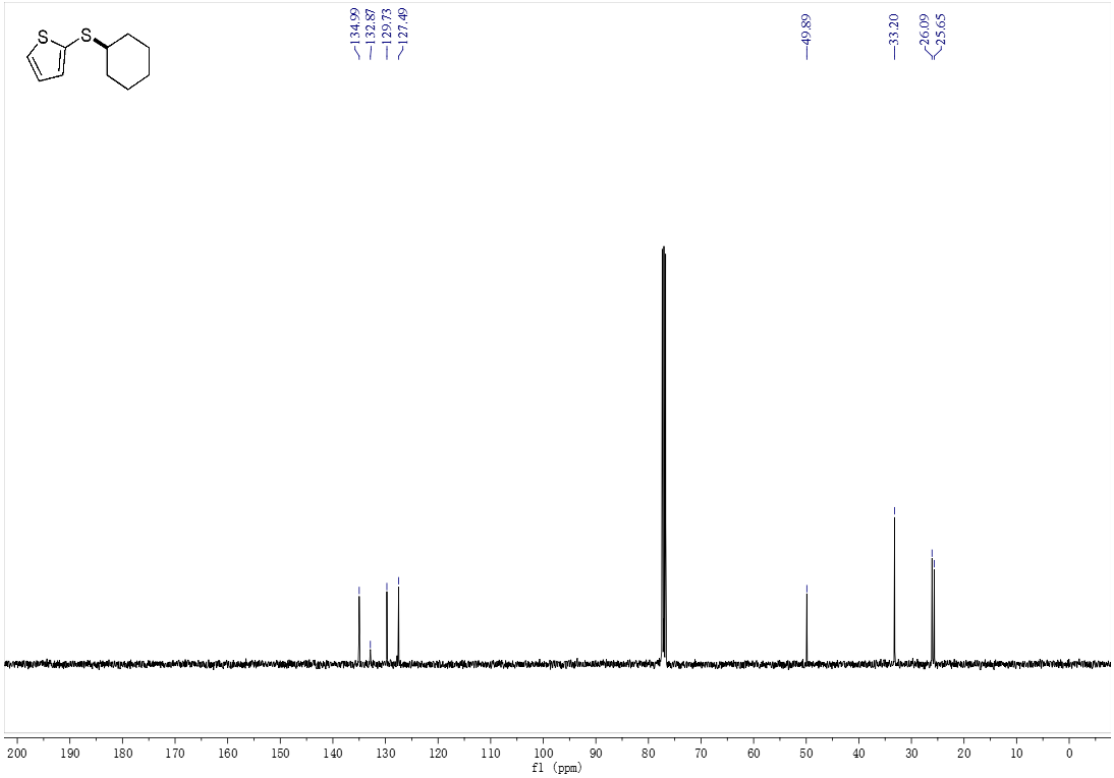
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **72**



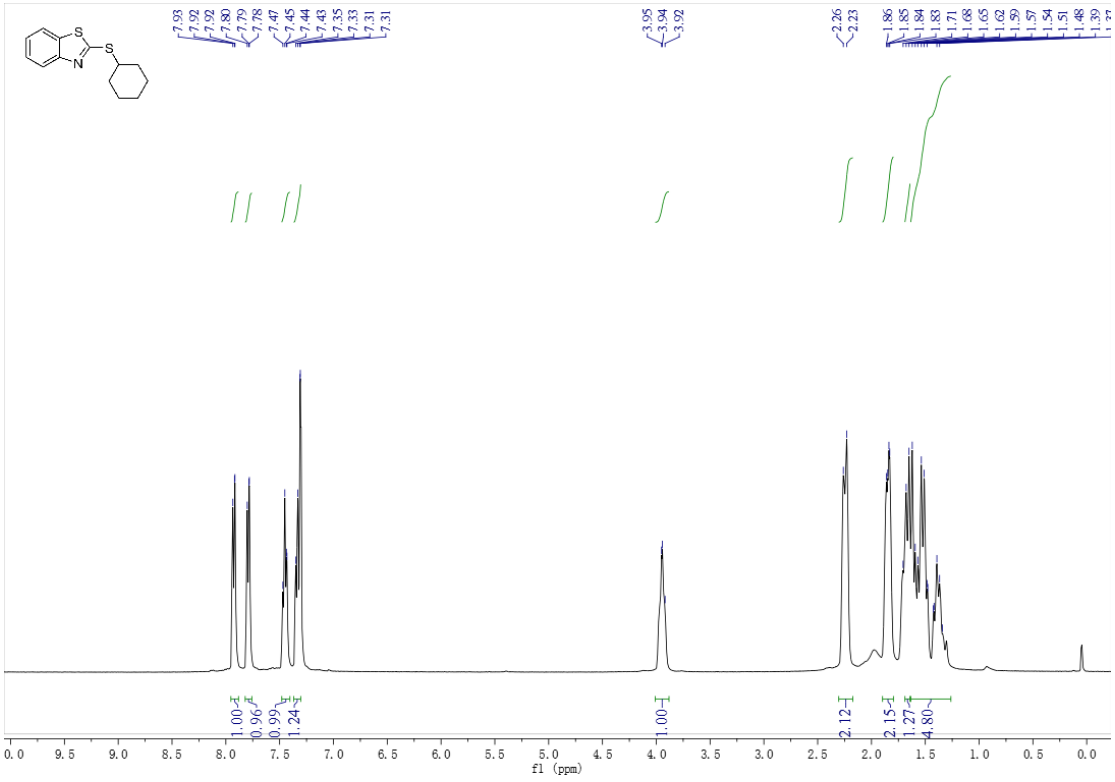
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **73**



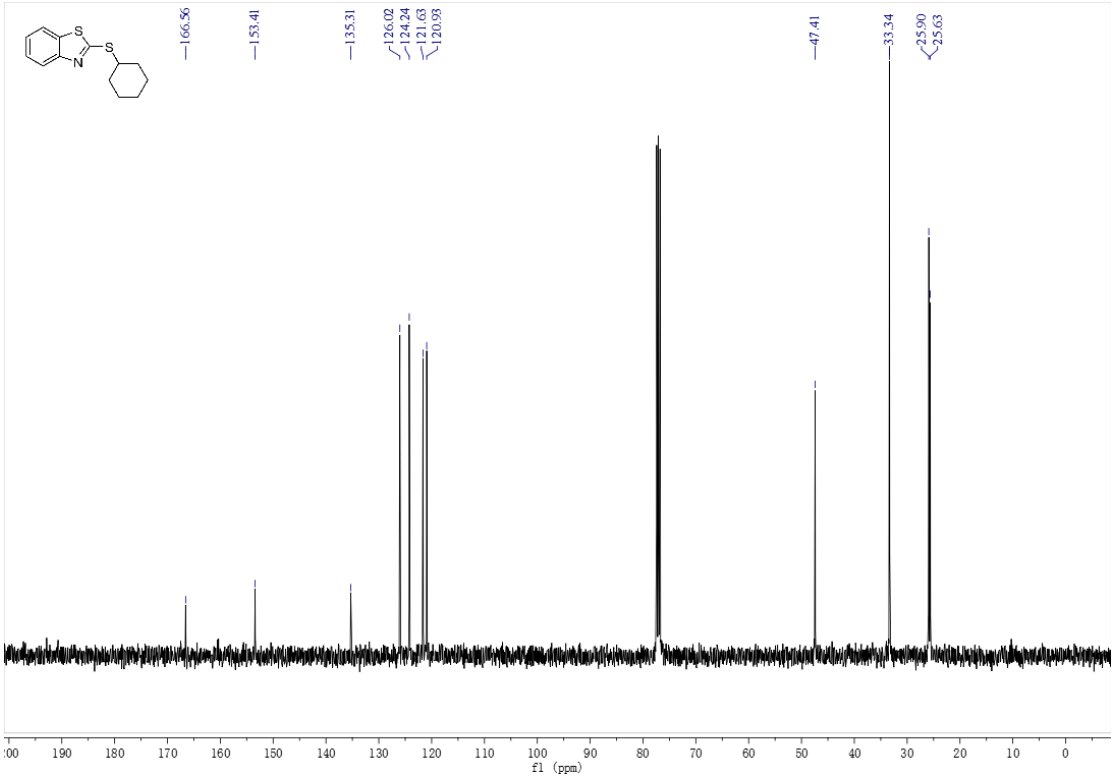
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **73**



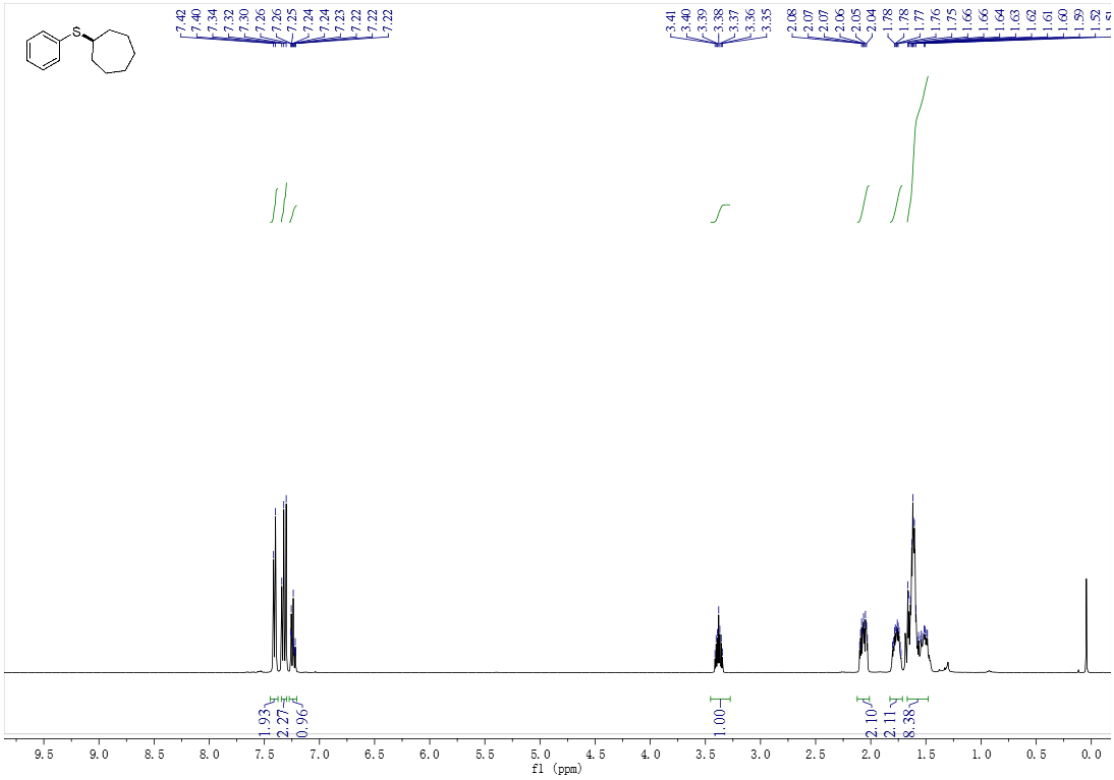
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **74**



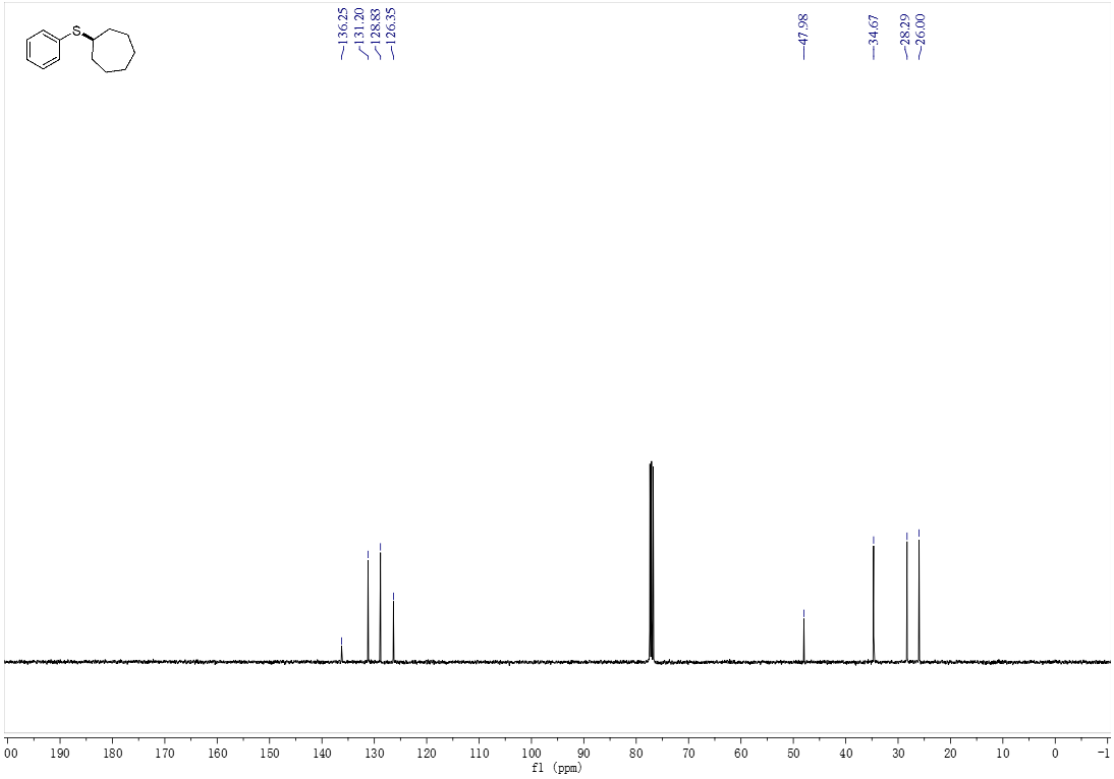
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **74**



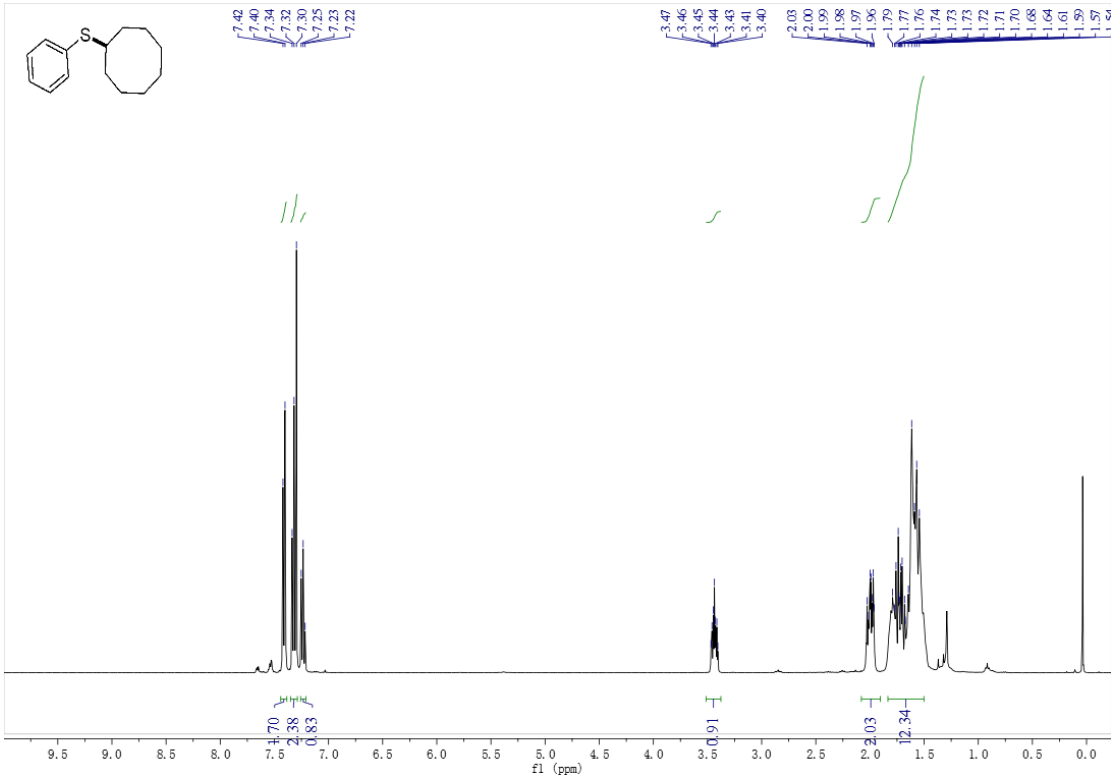
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **75**



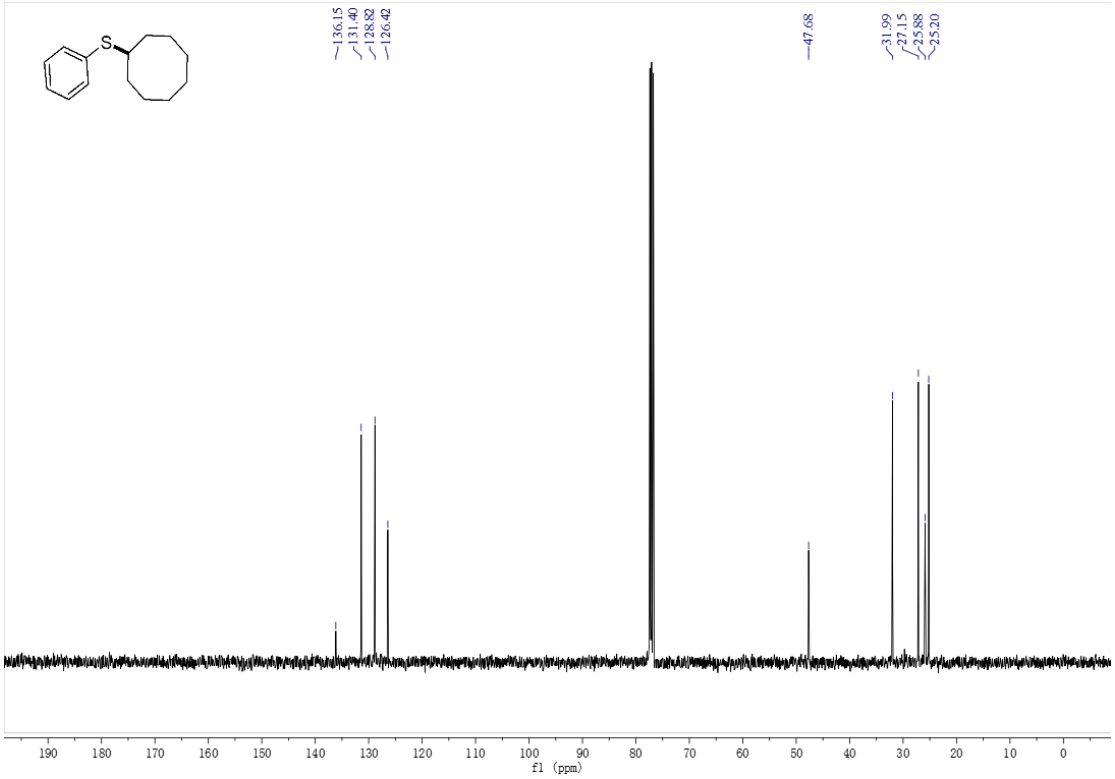
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **75**



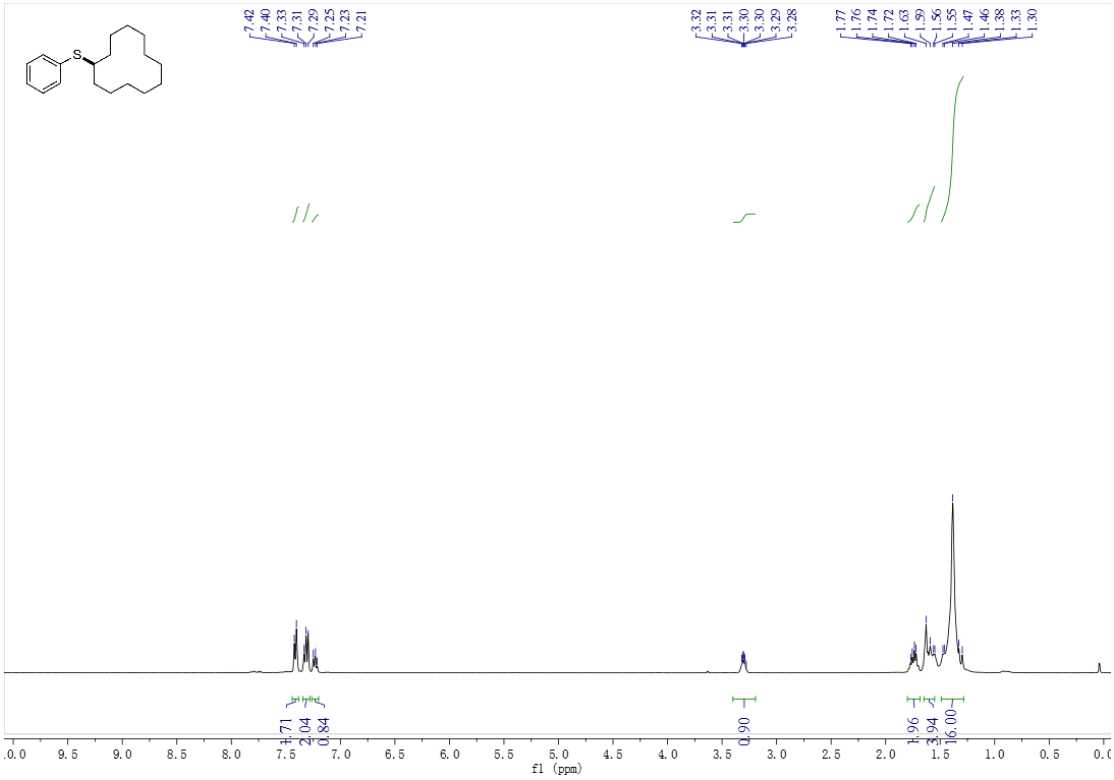
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **76**



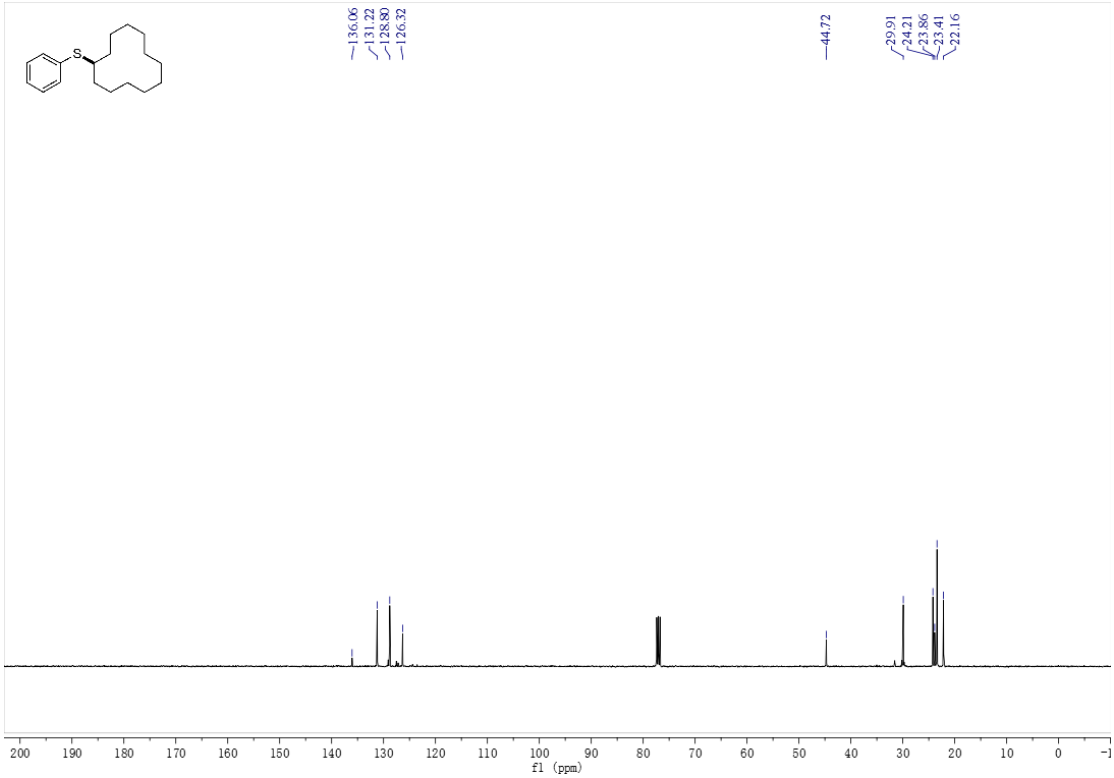
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **76**



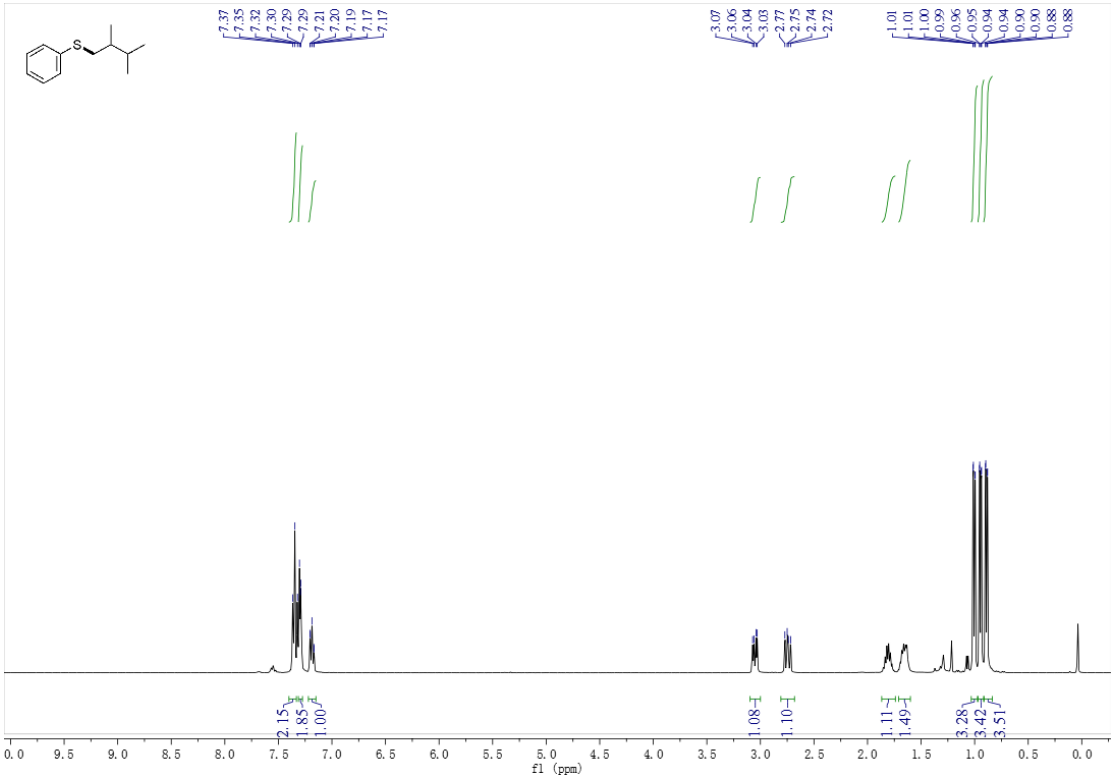
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **77**



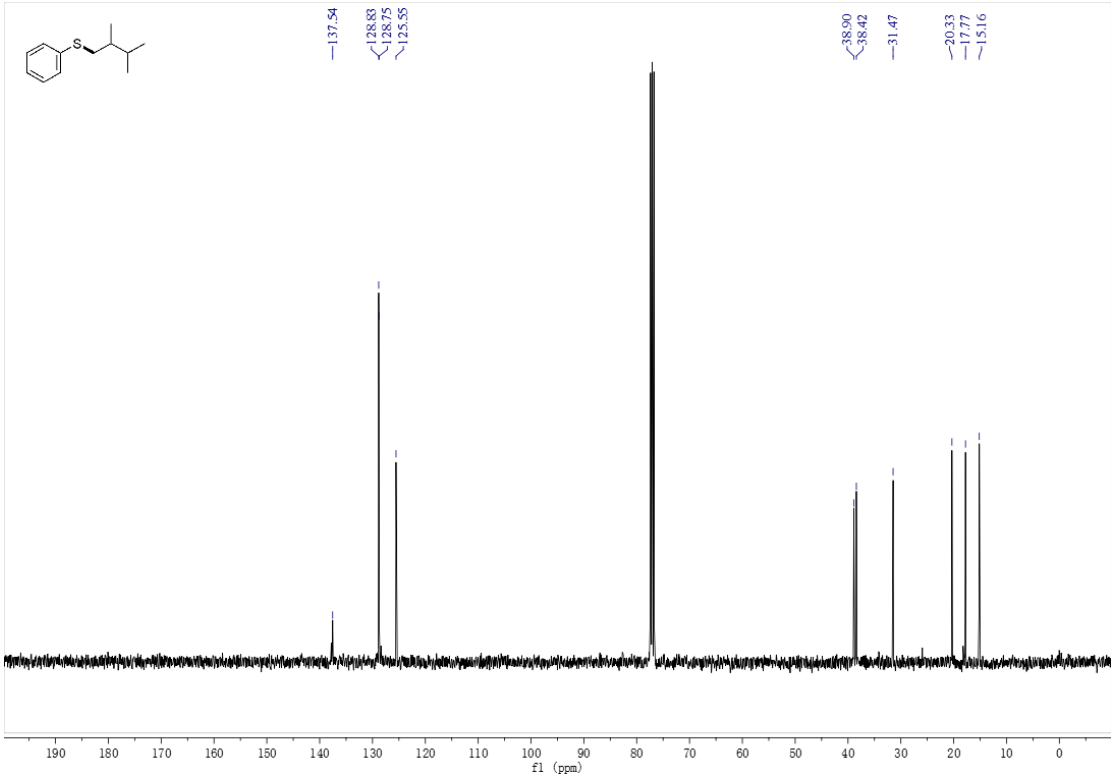
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **77**



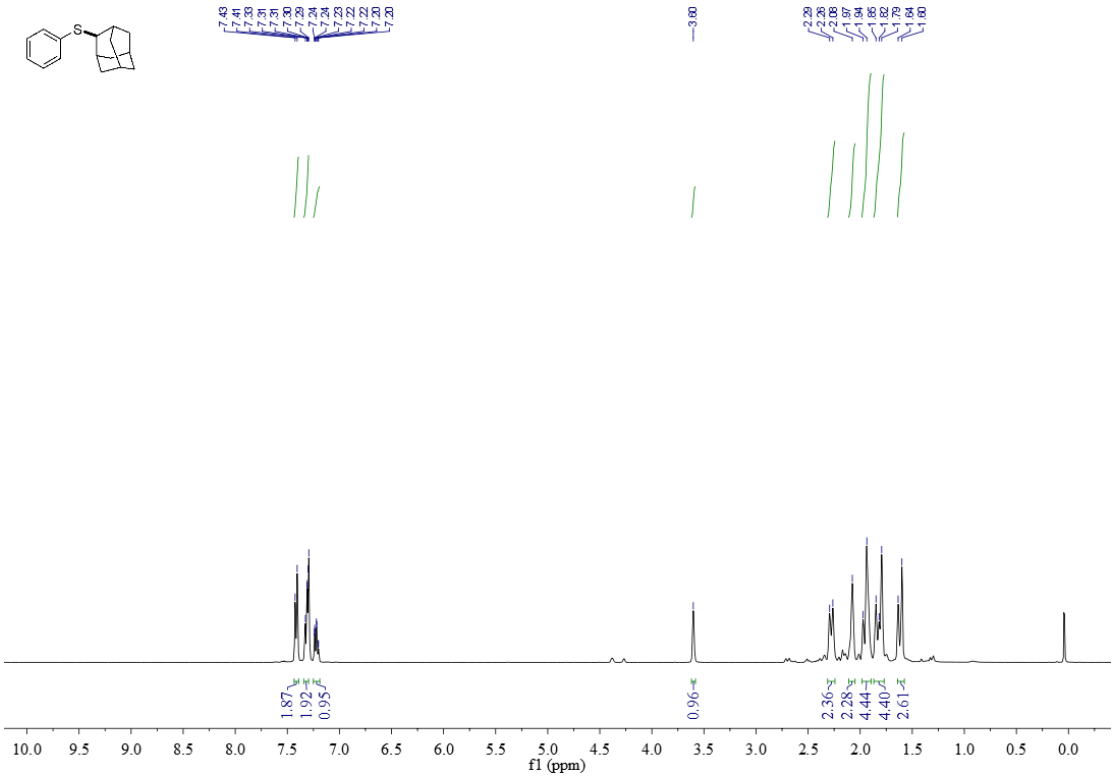
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **78**



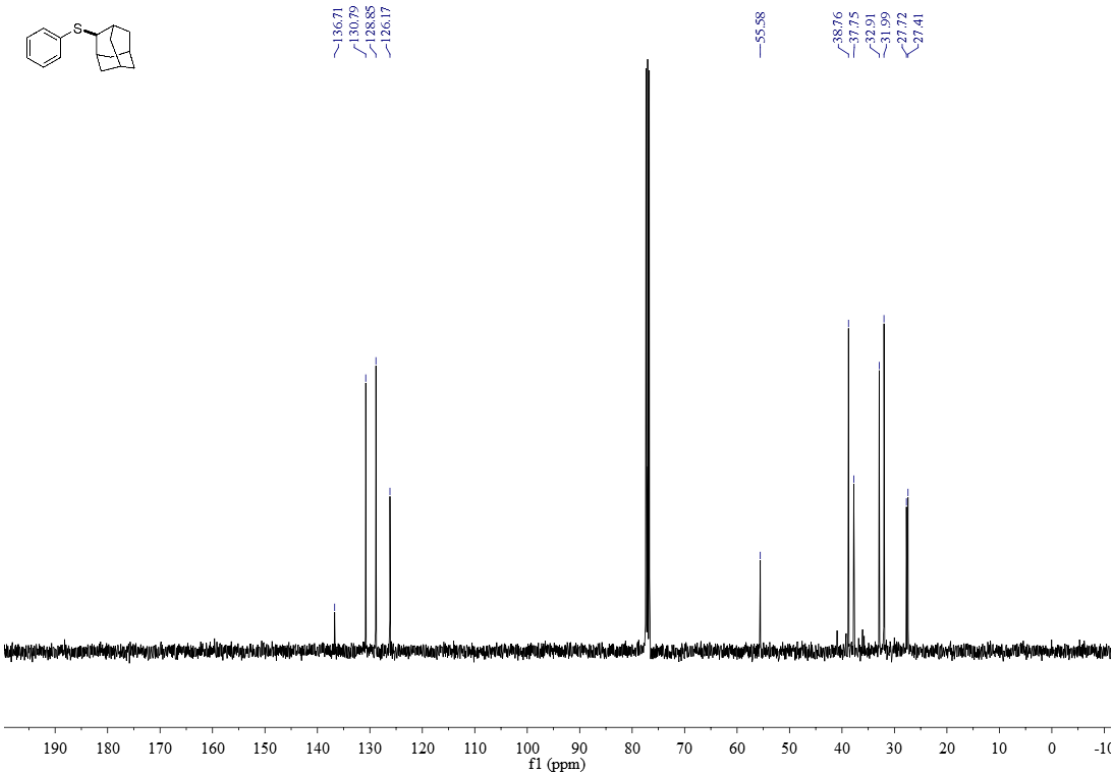
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **78**



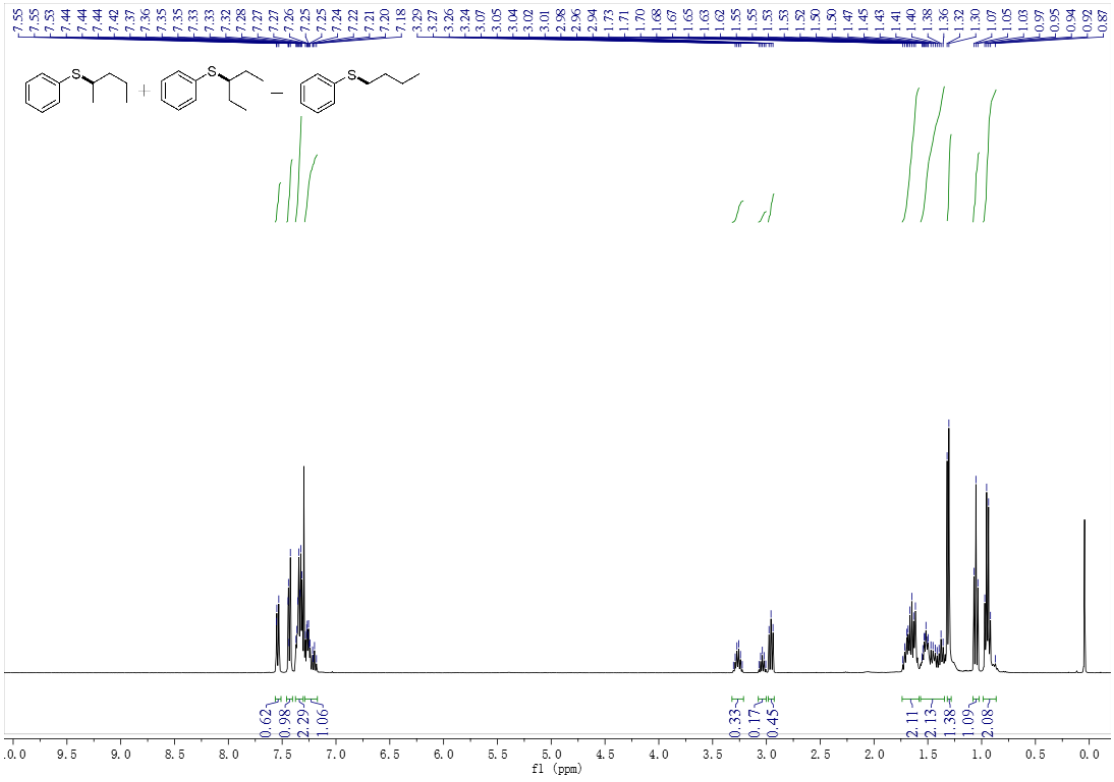
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **79**



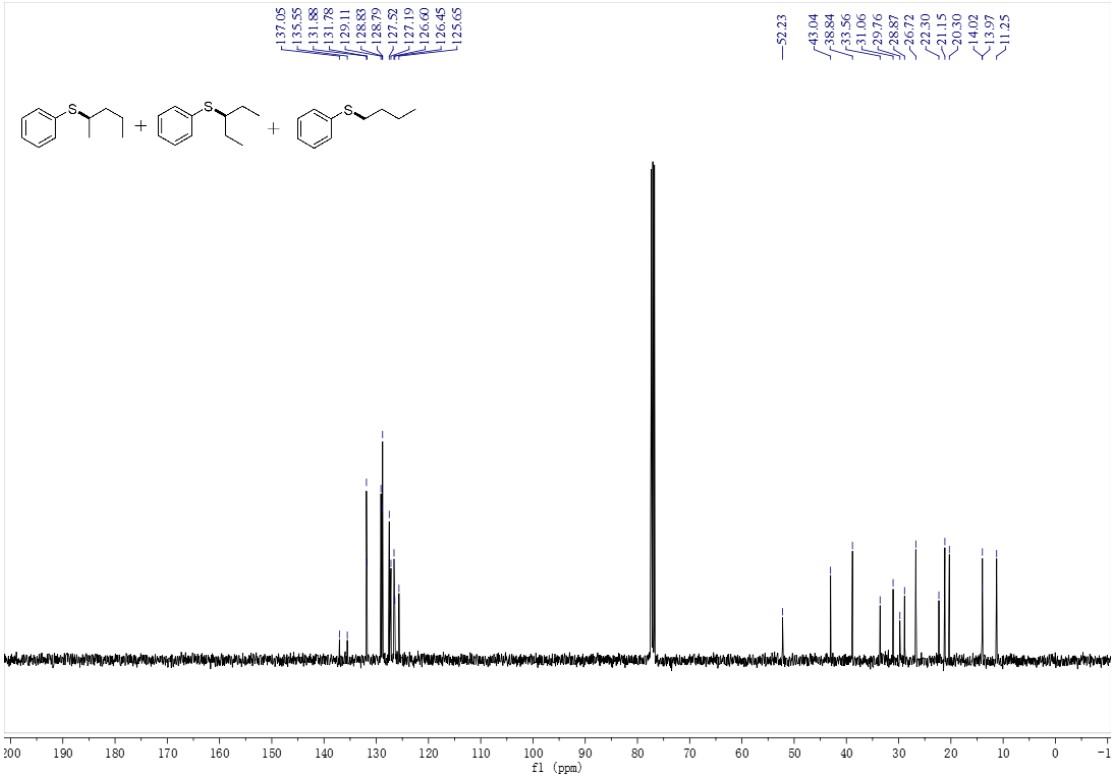
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **79**



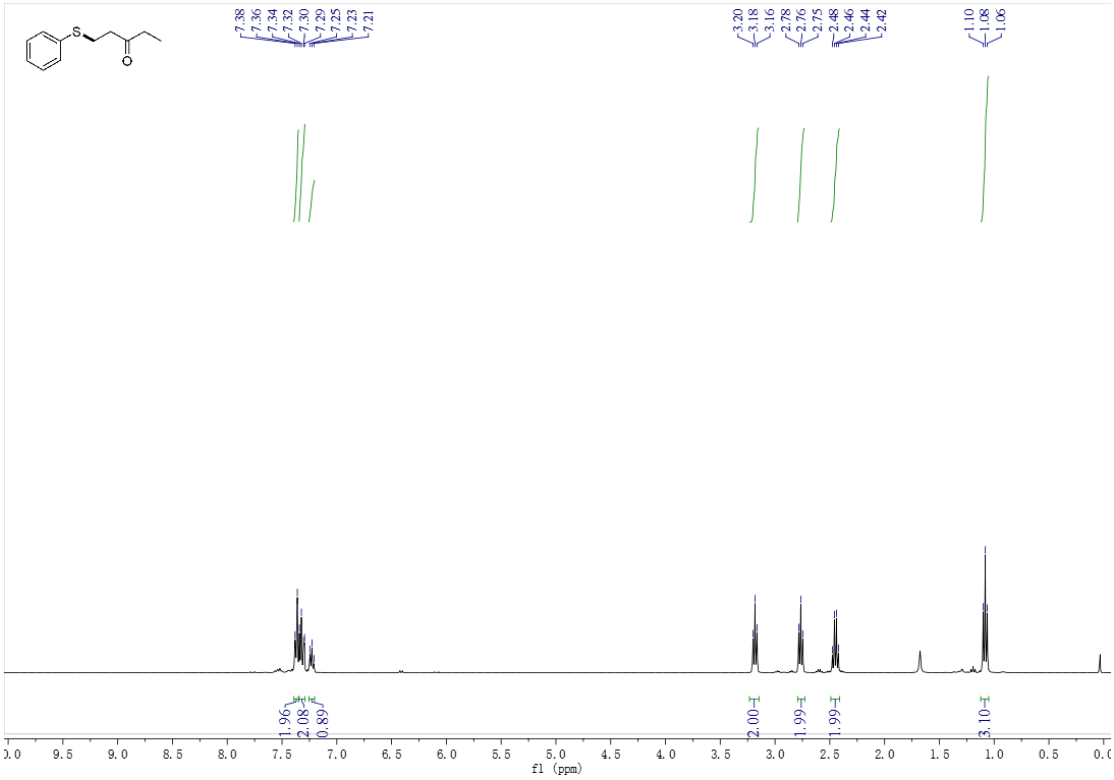
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **80**



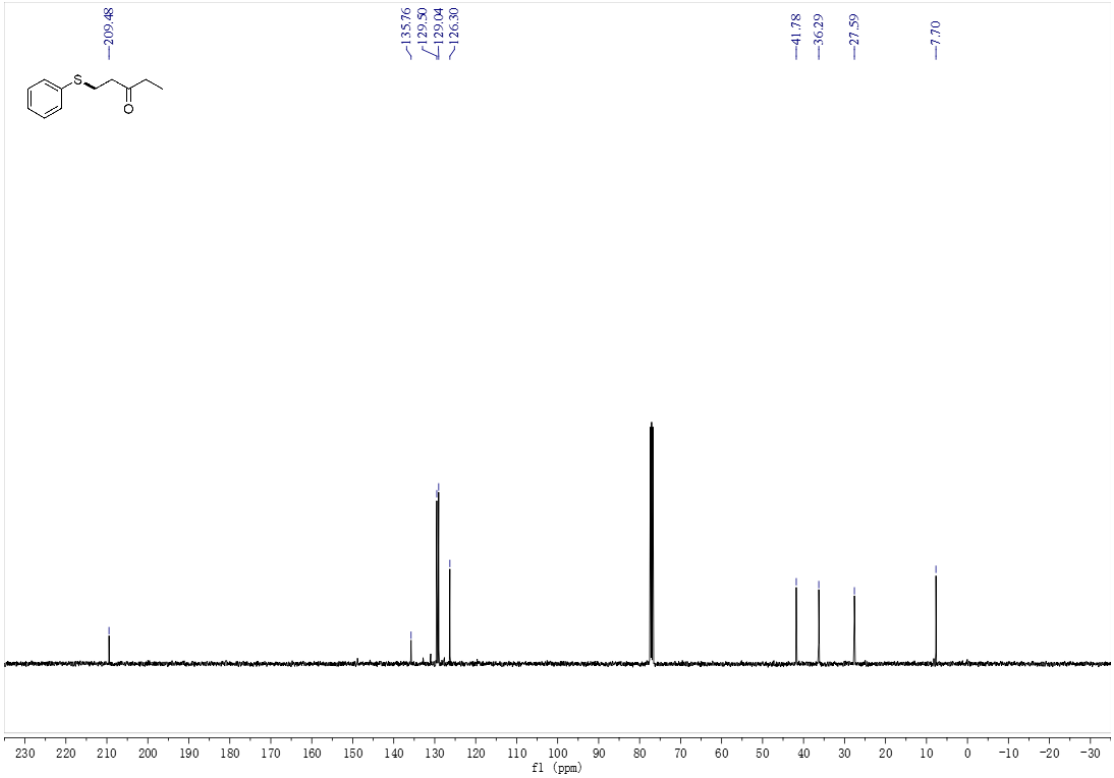
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **80**



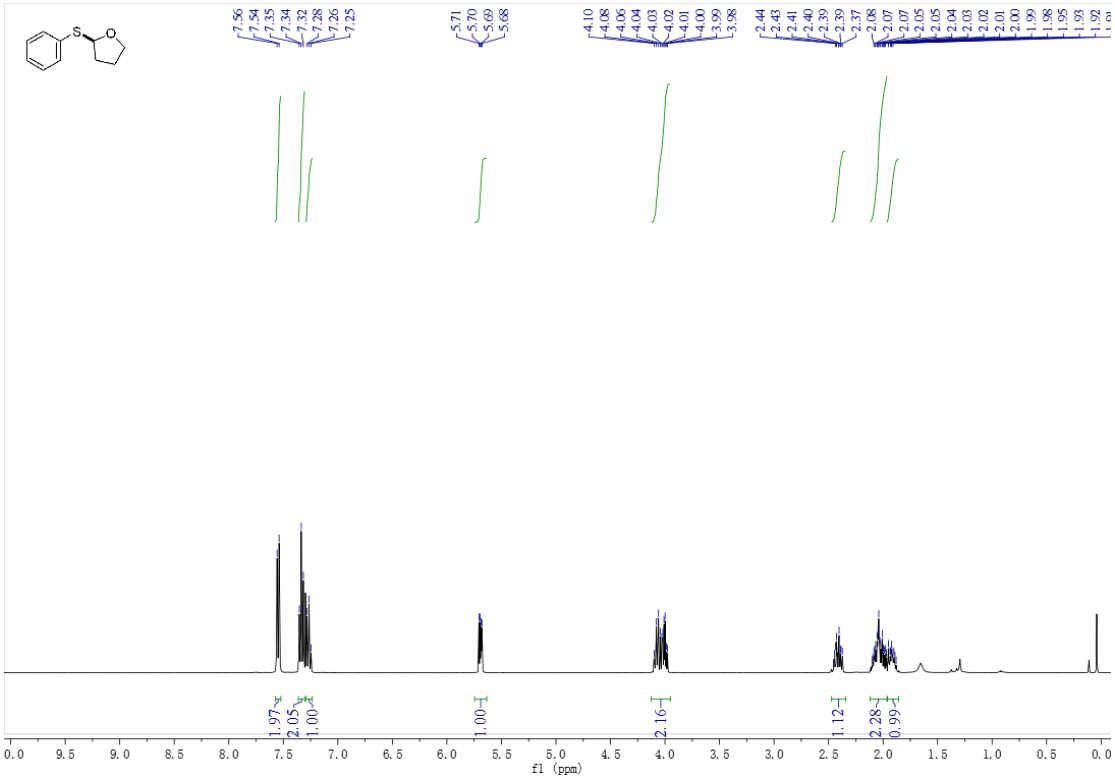
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **81**



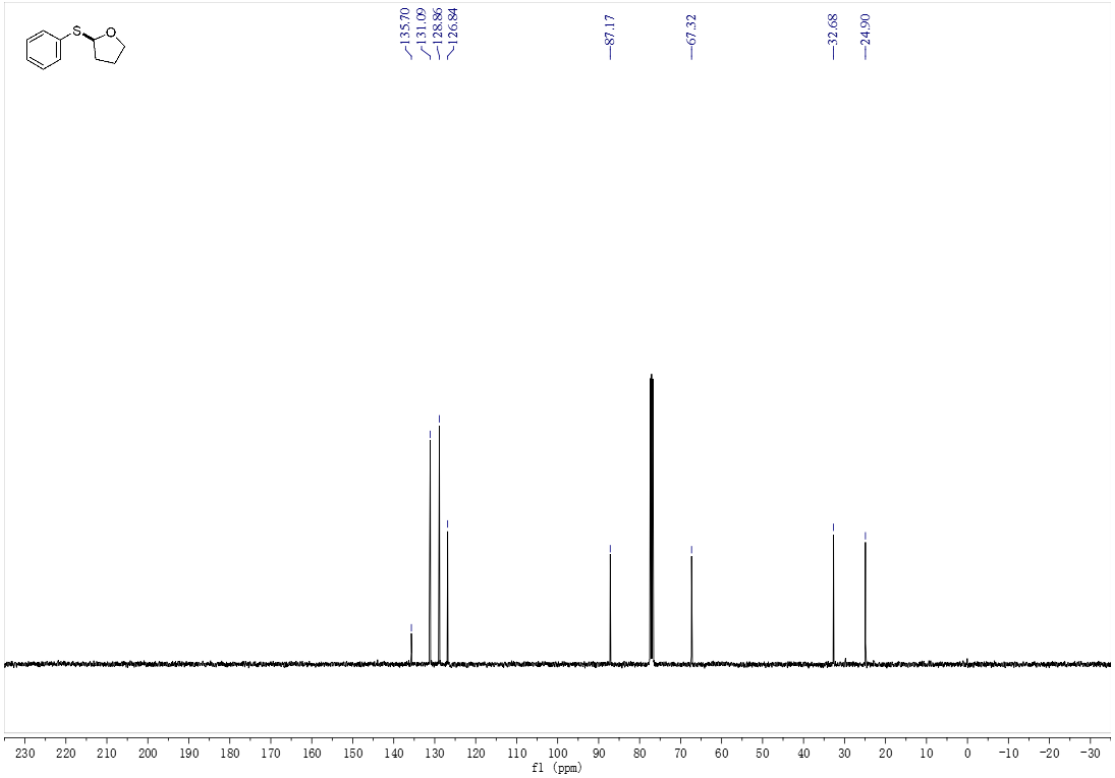
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **81**



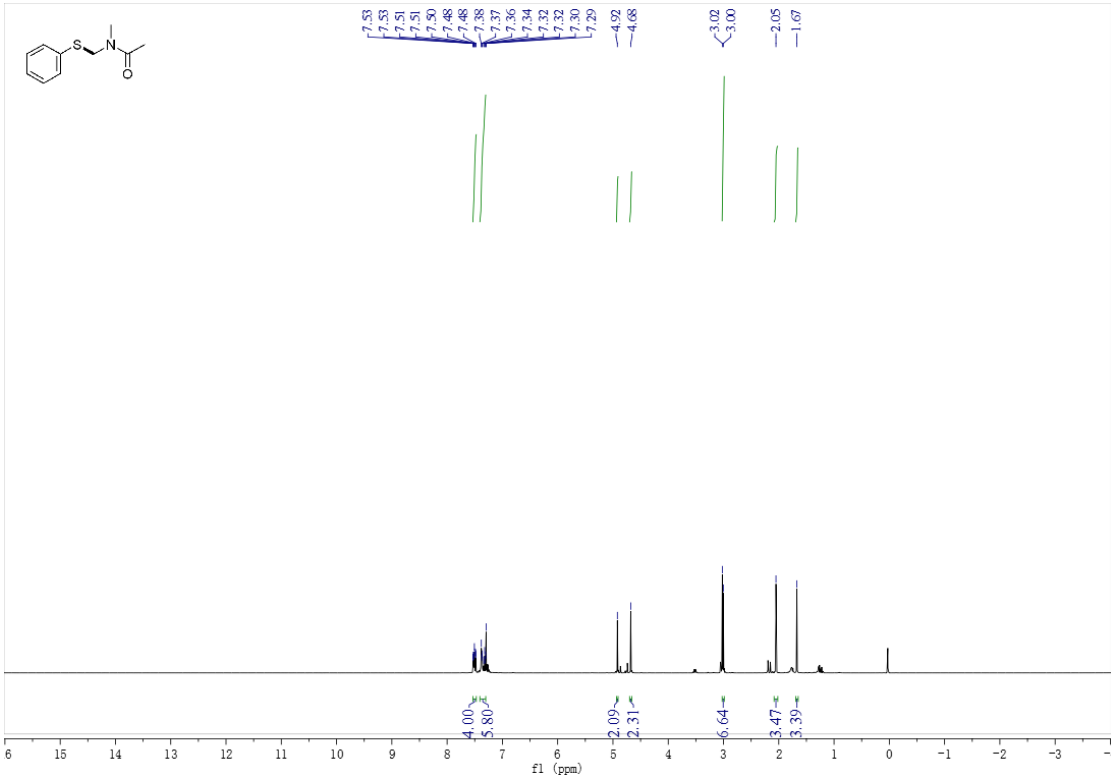
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **82**



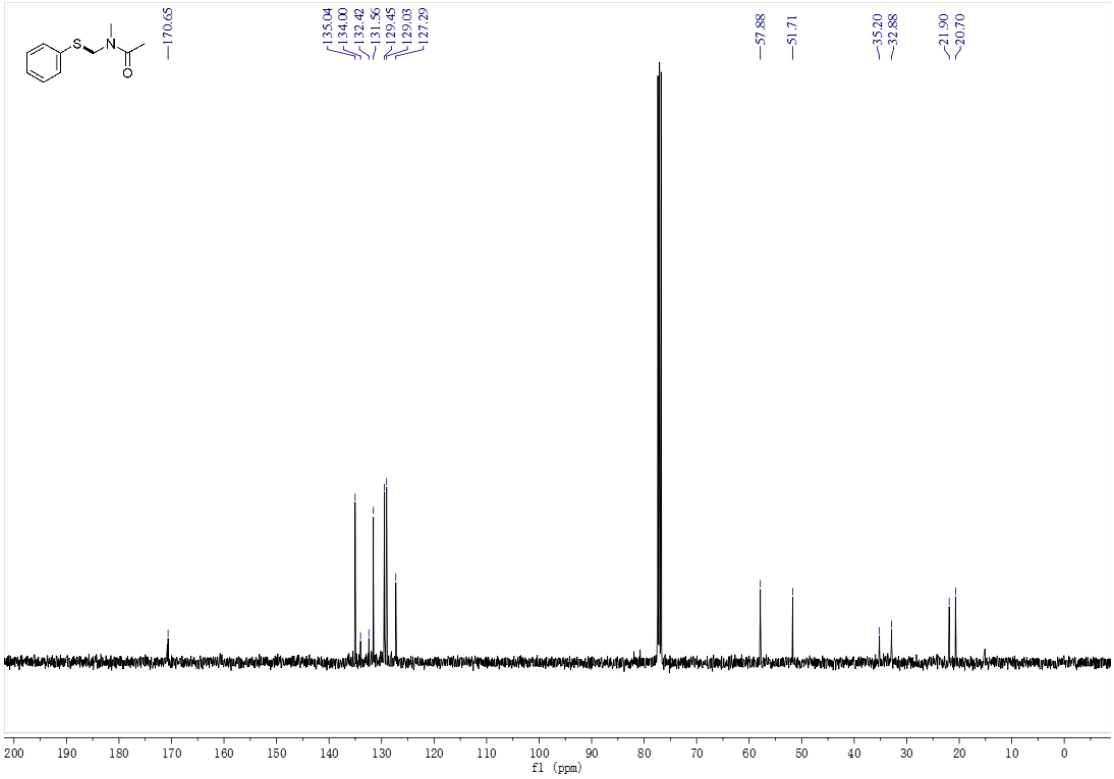
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **82**



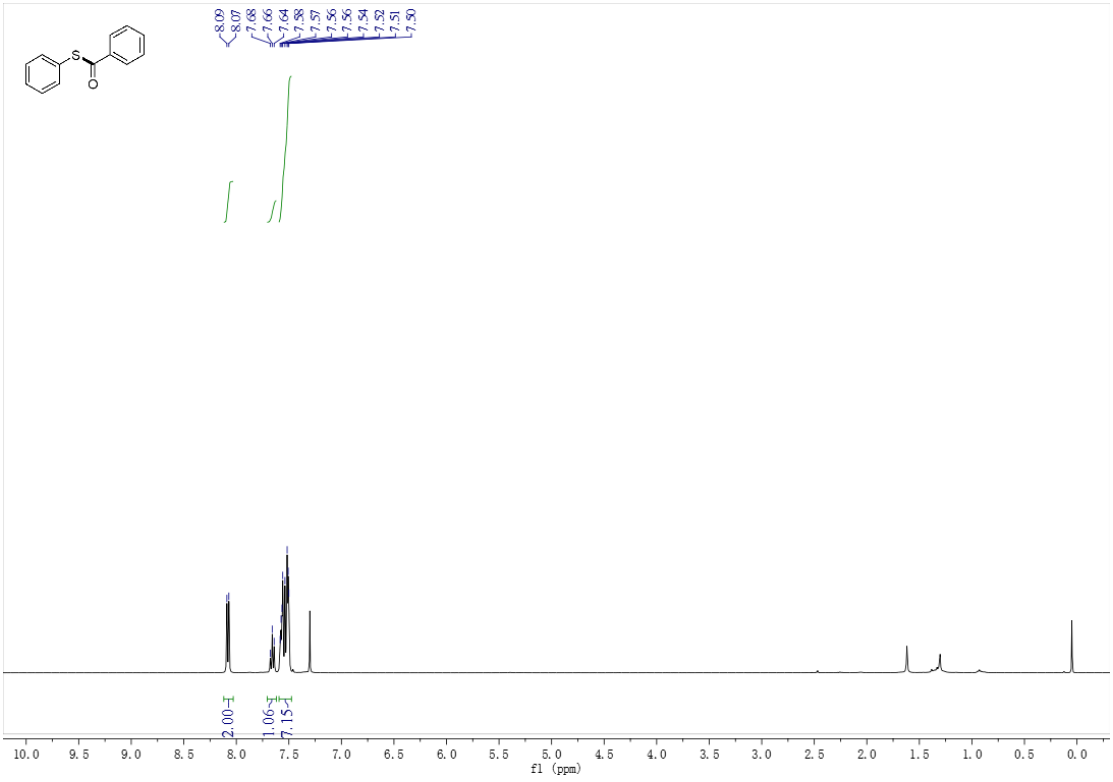
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **83**



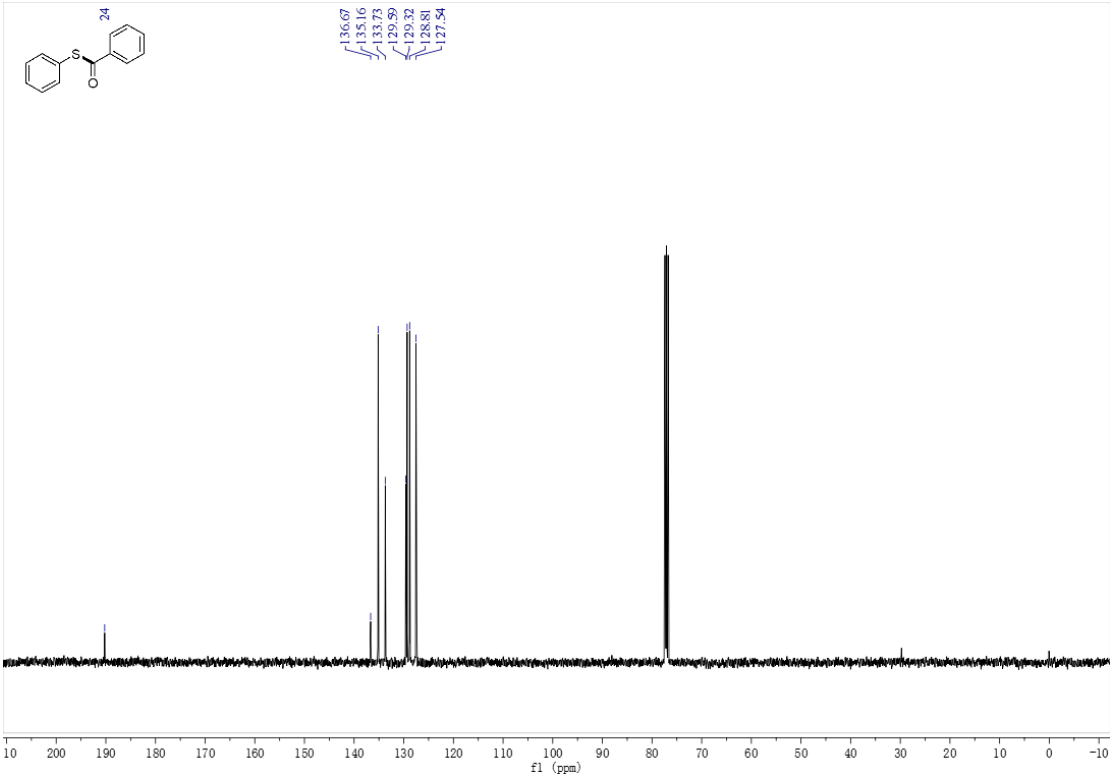
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **83**



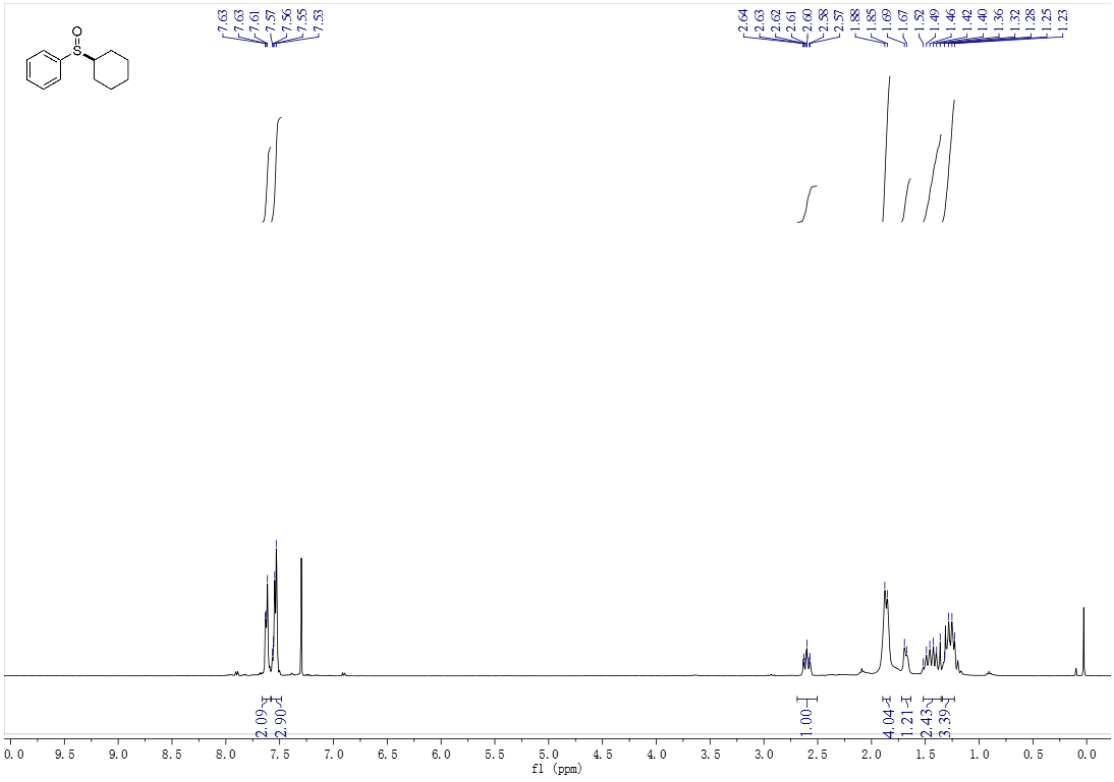
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **84**



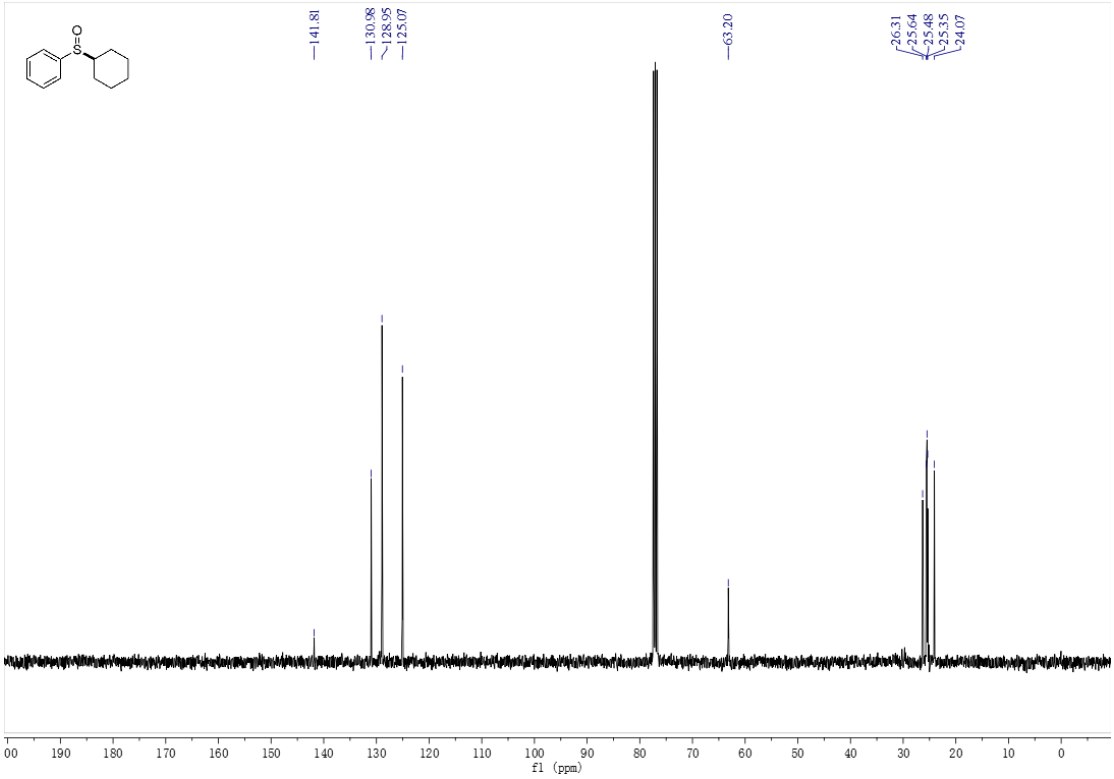
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **84**



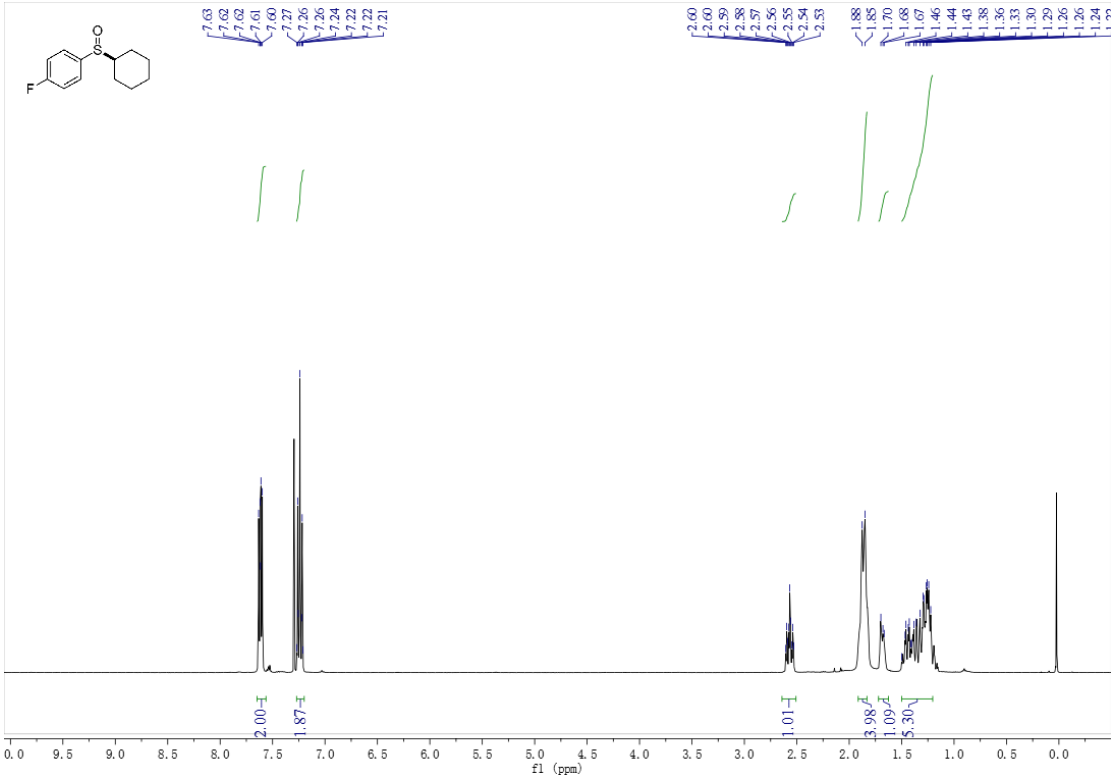
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **85**



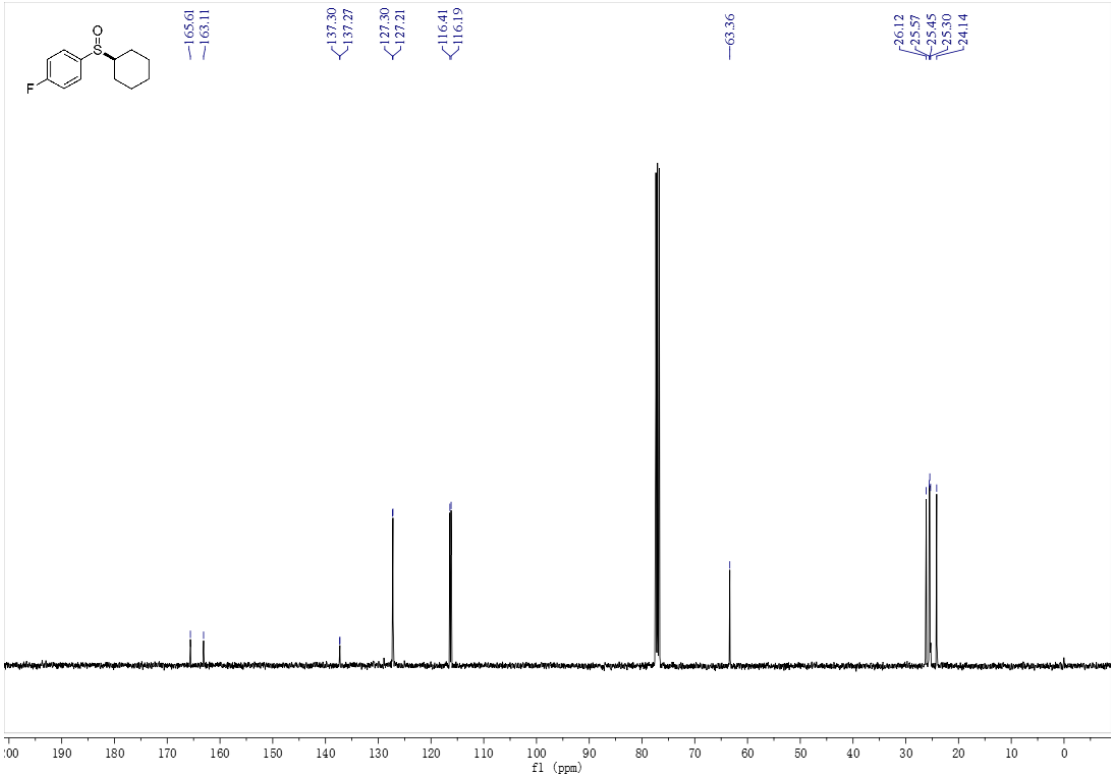
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **85**



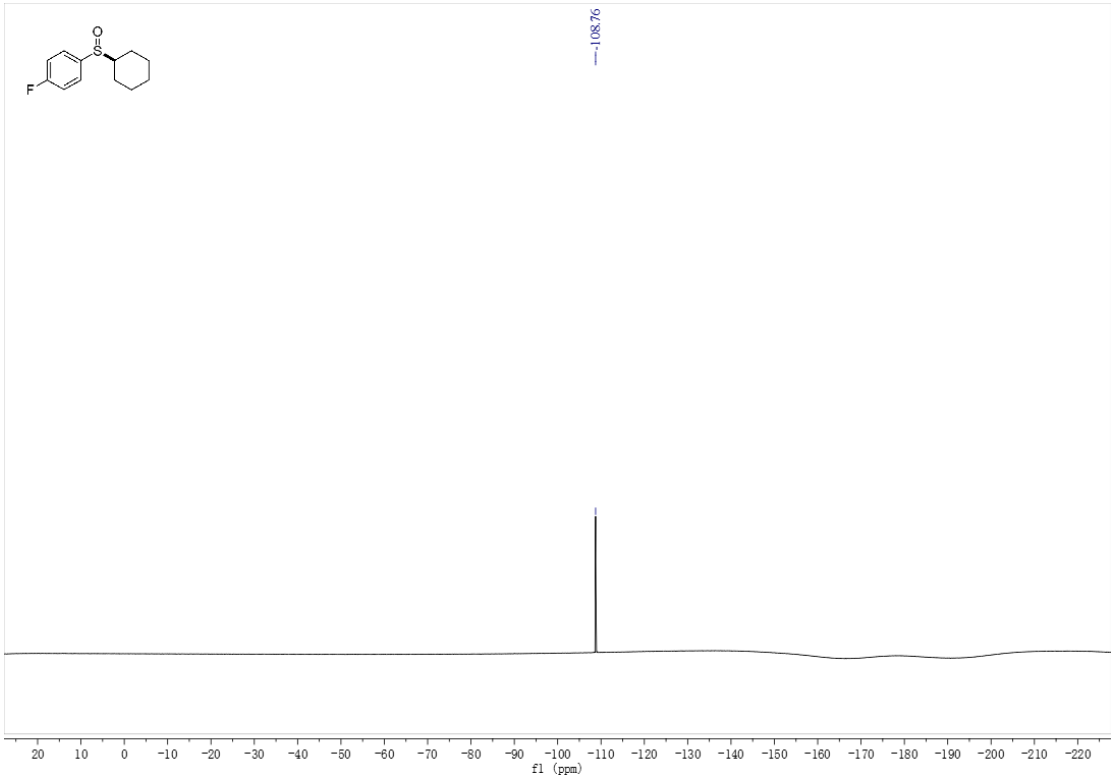
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **86**



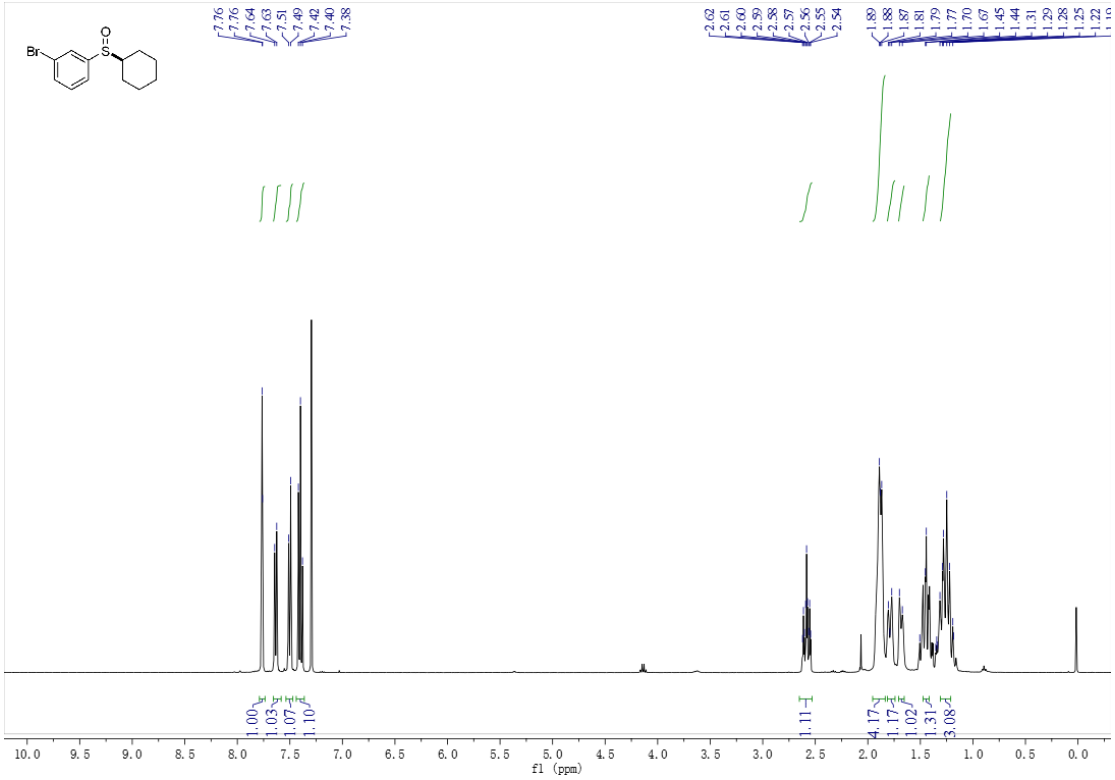
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **86**



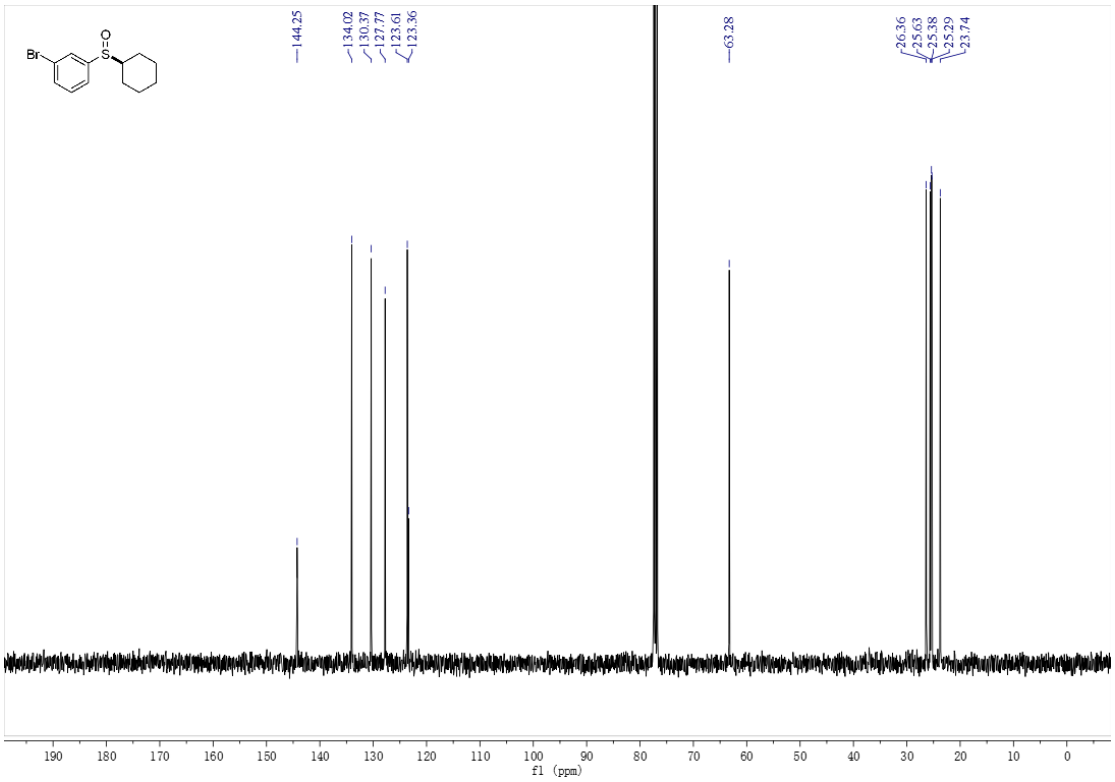
^{19}F NMR (376 MHz, $CDCl_3$, 23 ℃) of **86**



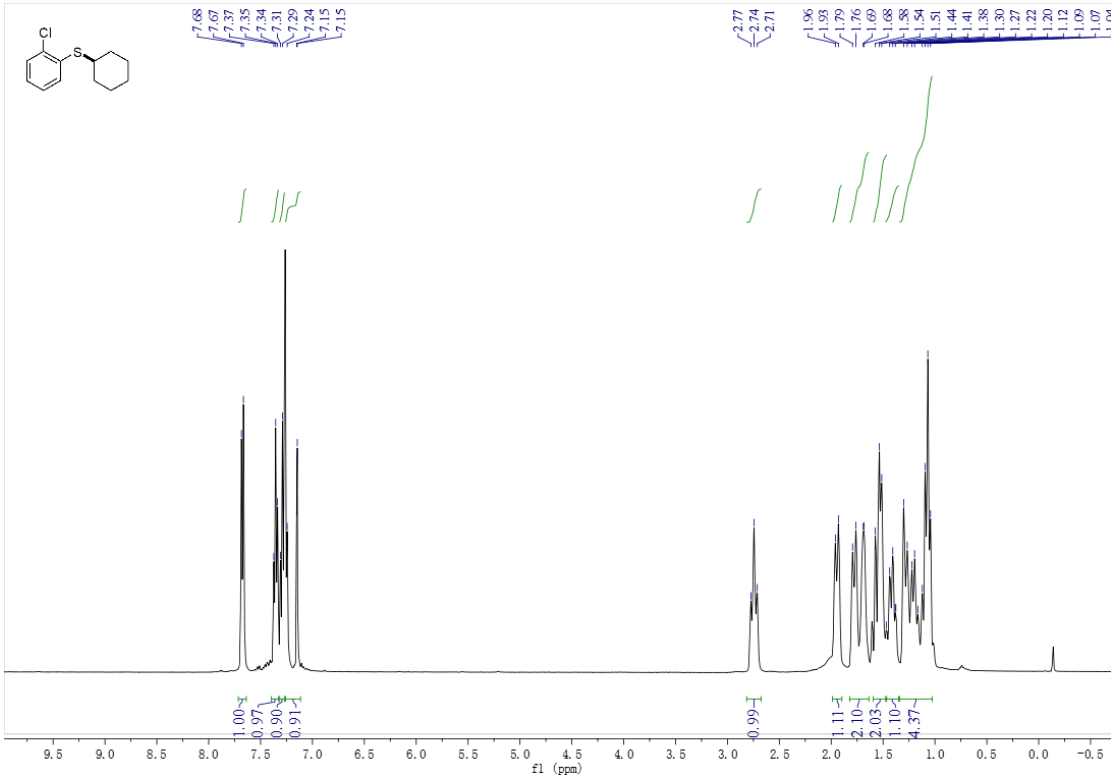
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **87**



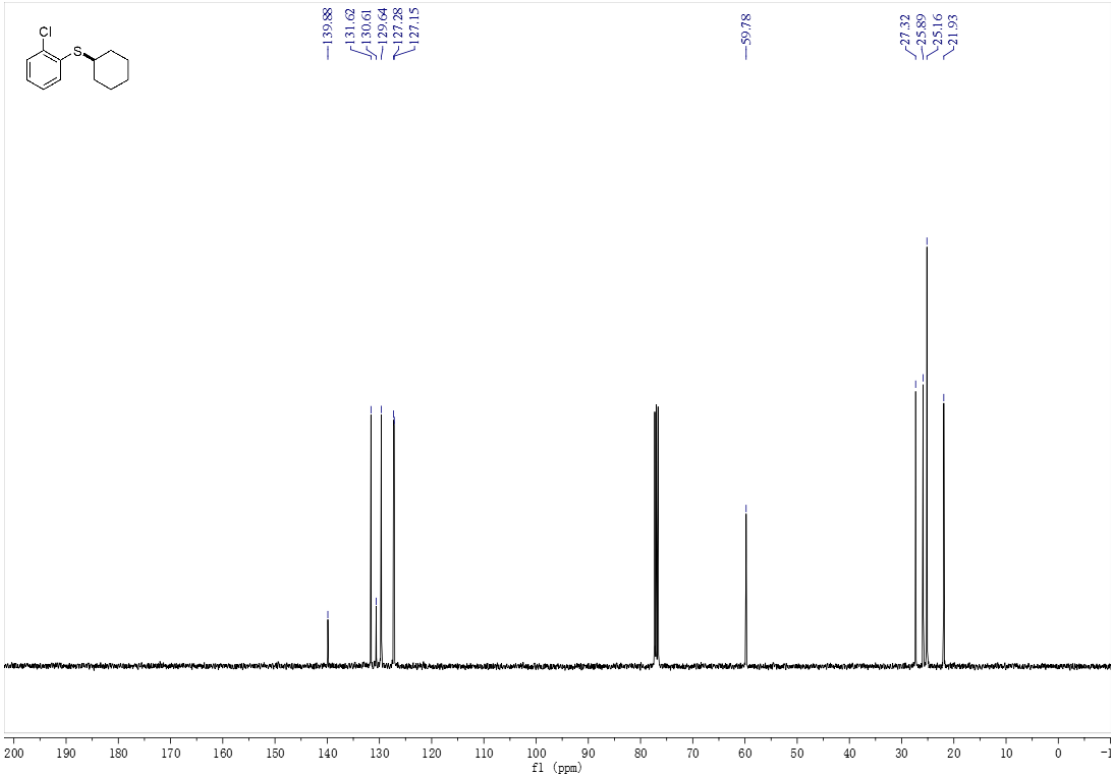
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **87**



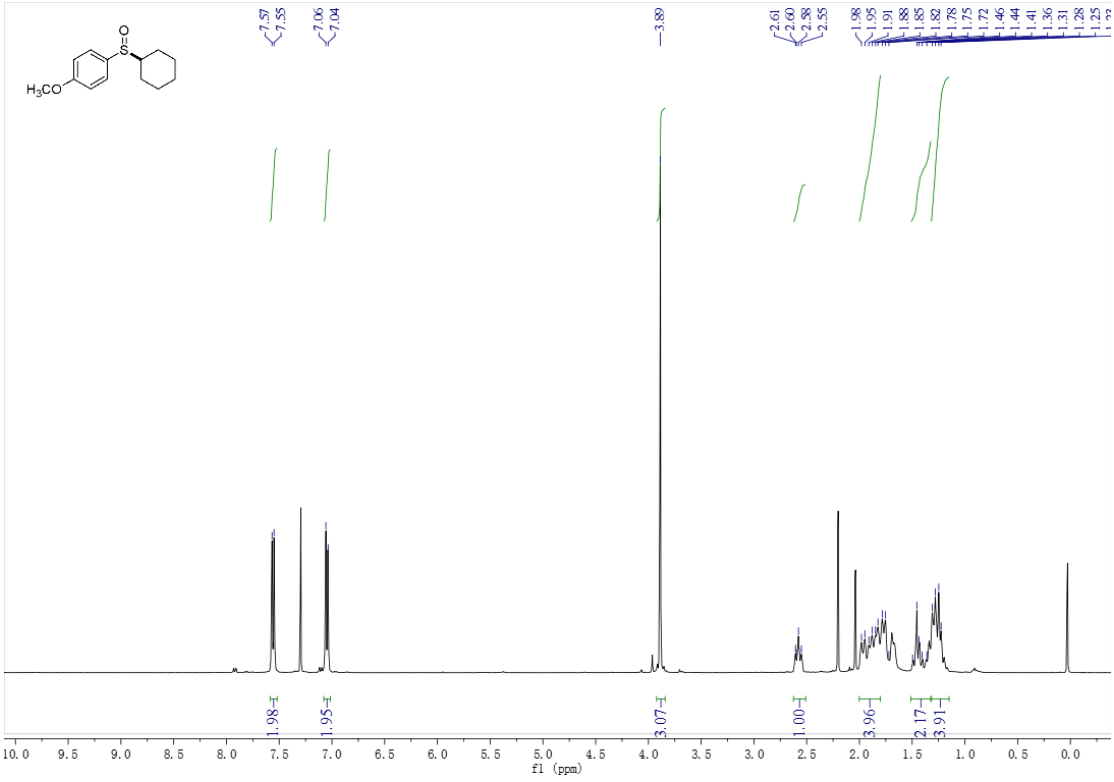
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **88**



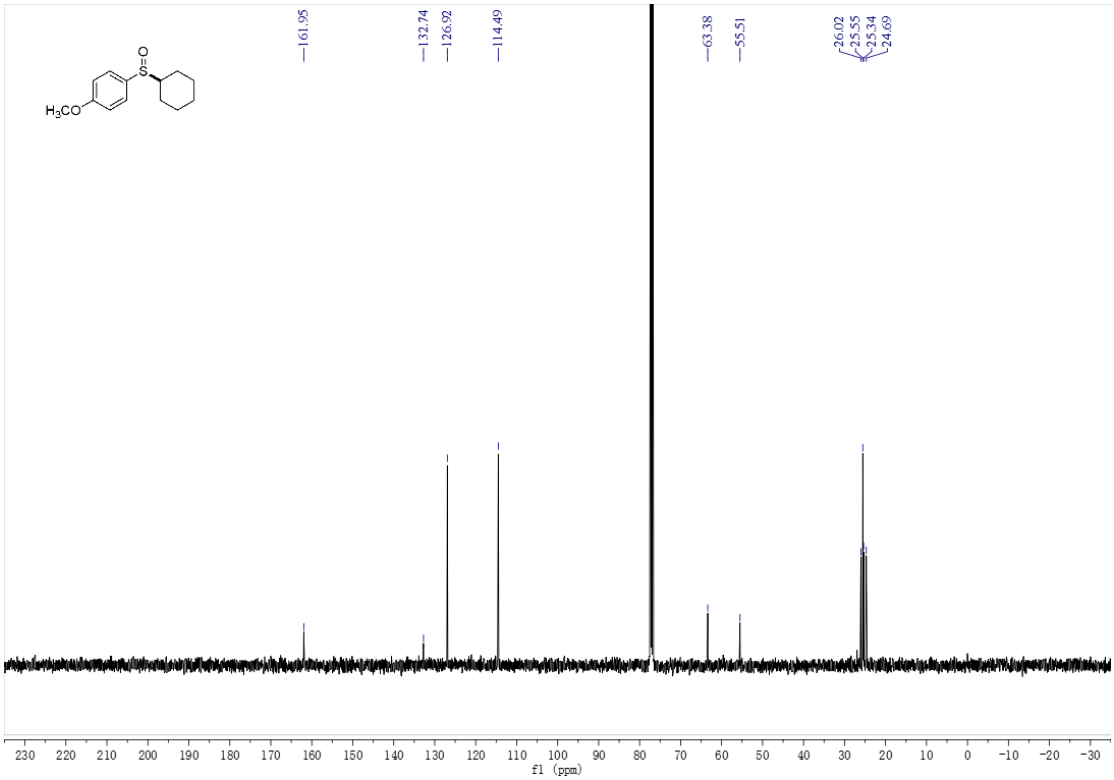
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **88**



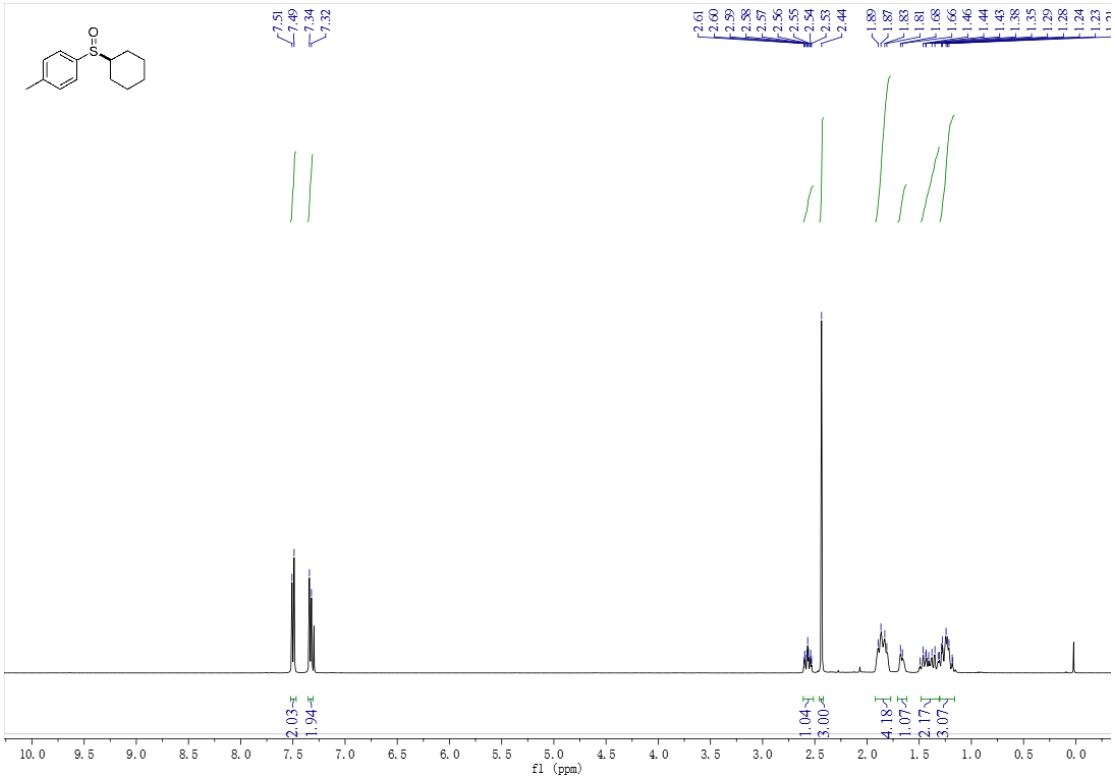
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **89**



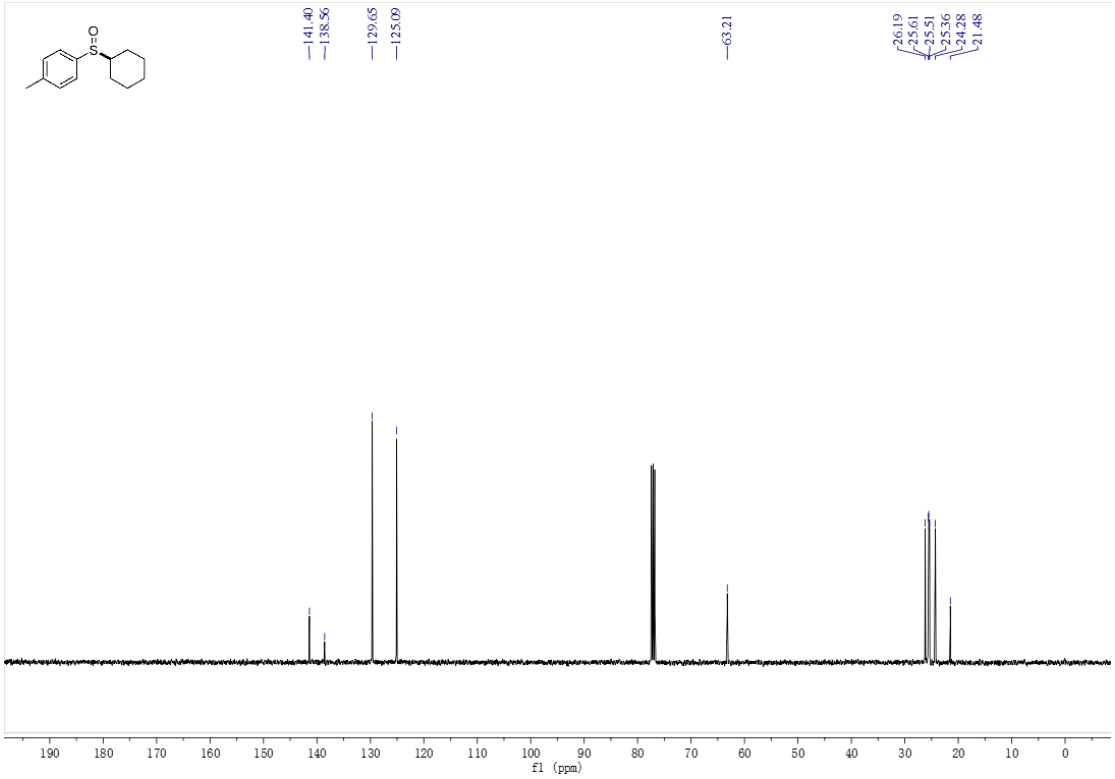
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **89**



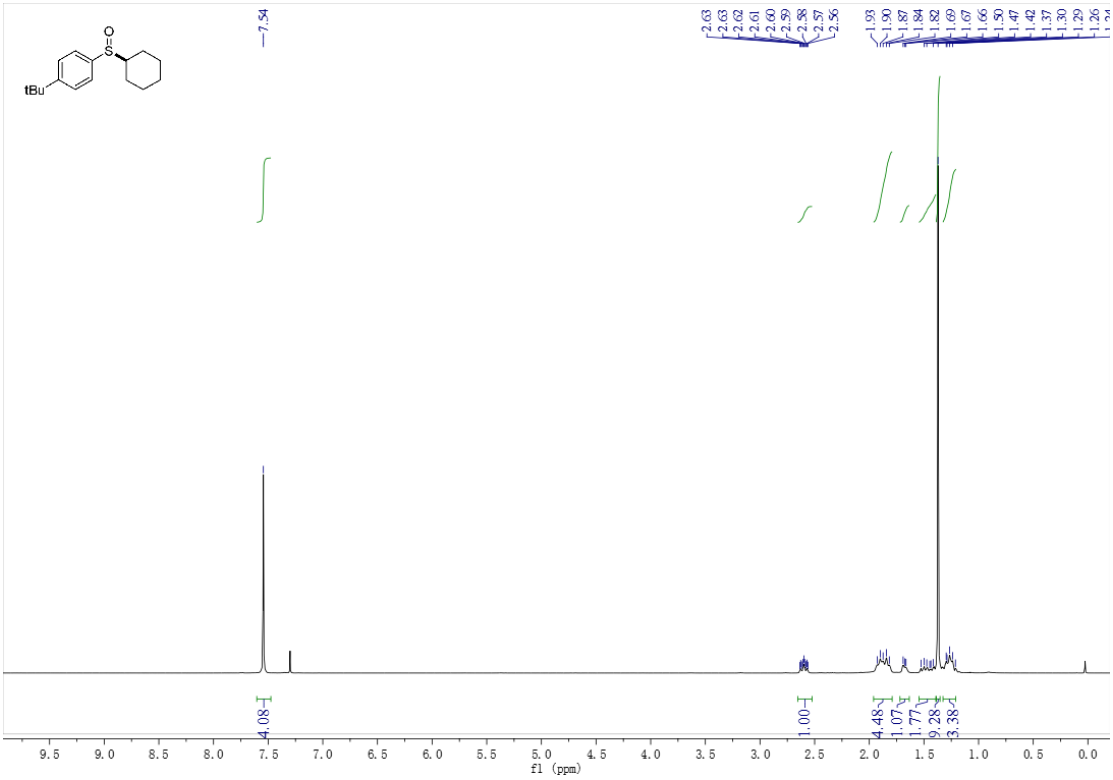
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **90**



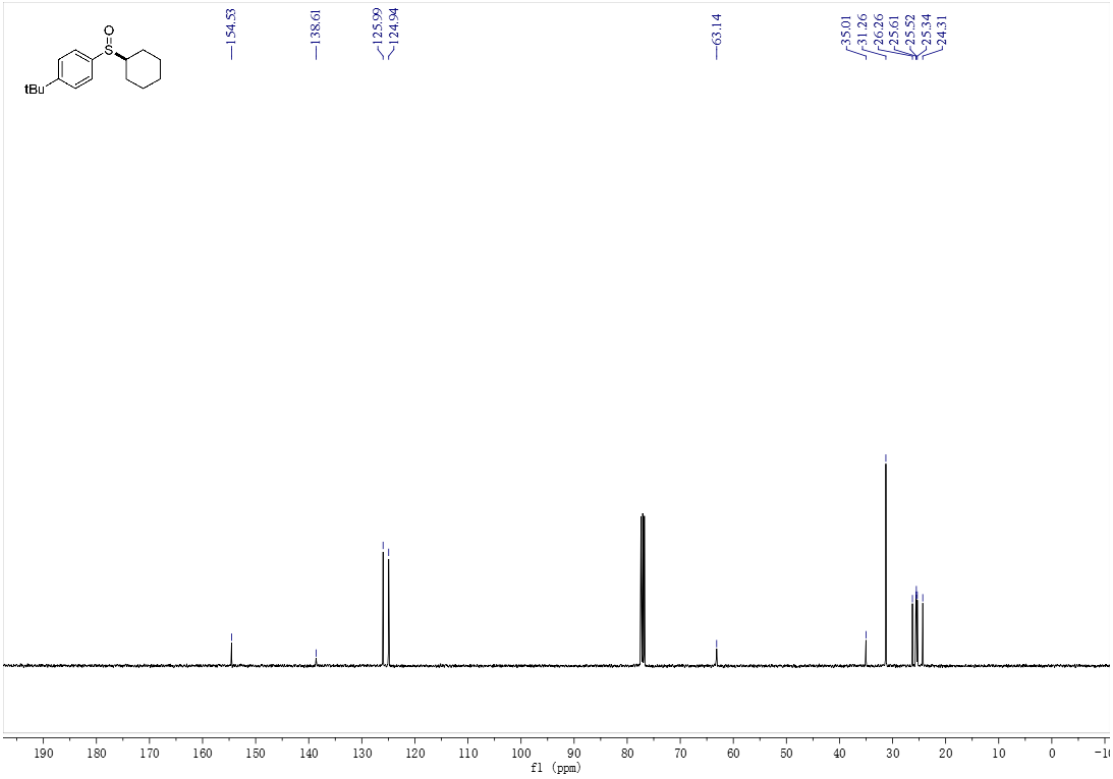
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **90**



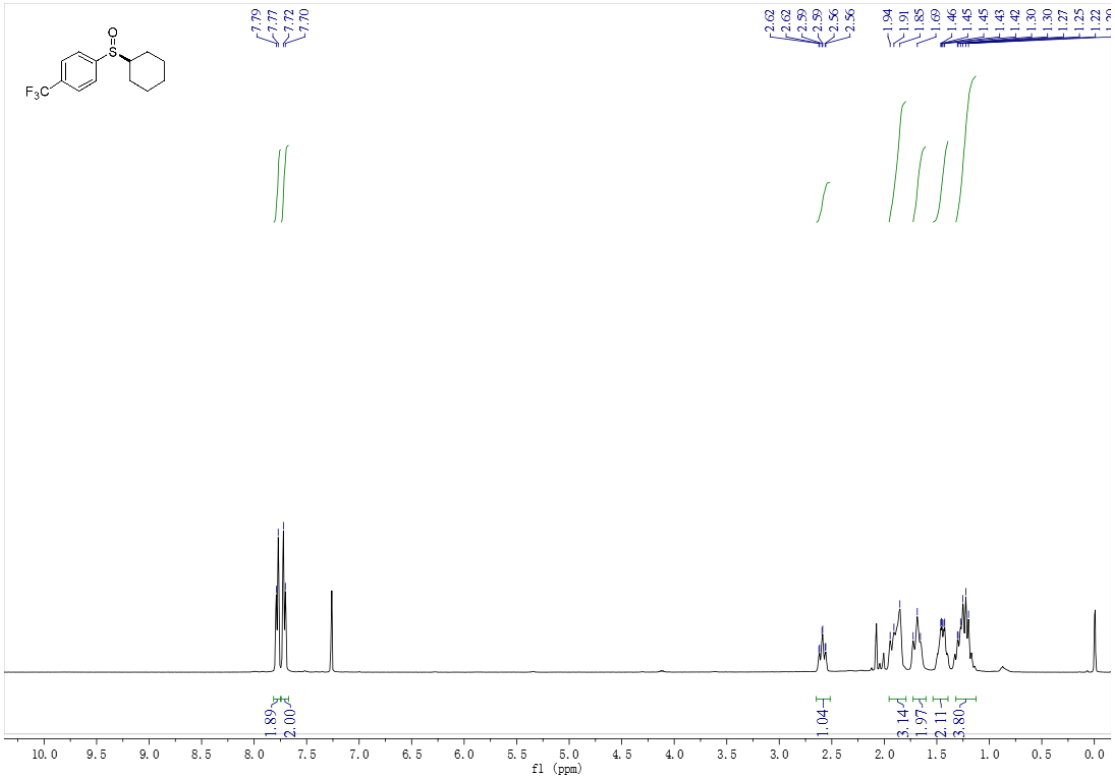
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **91**



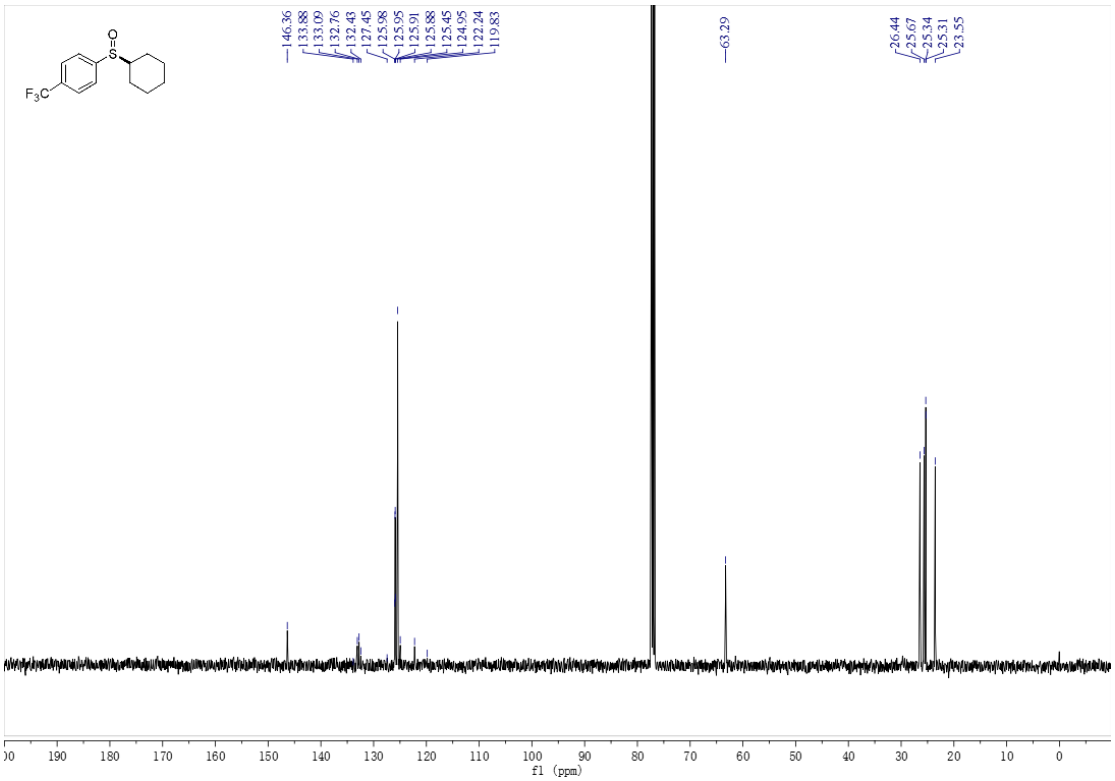
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **91**



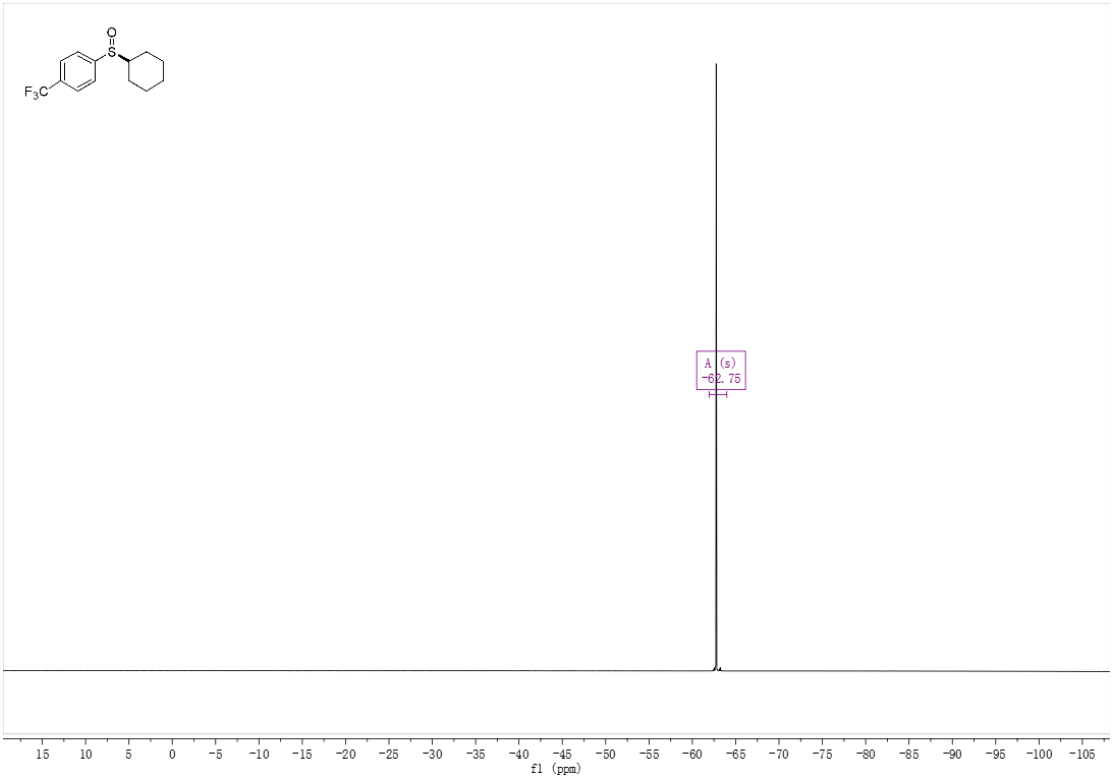
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **92**



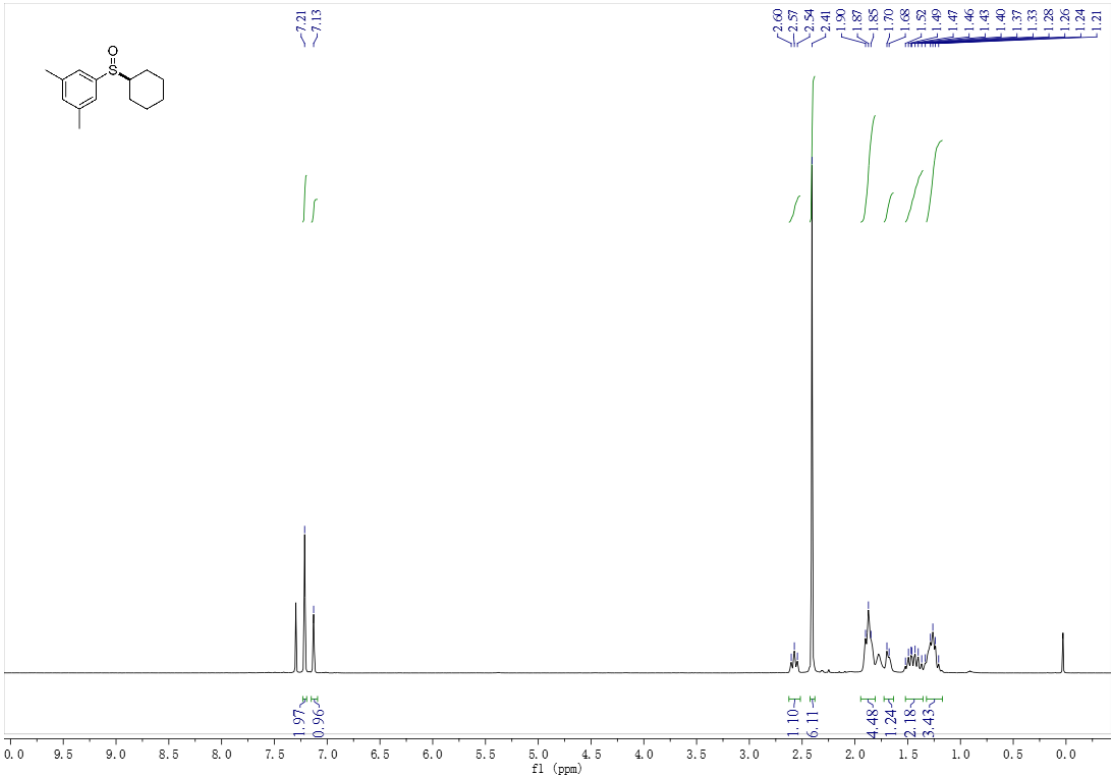
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **92**



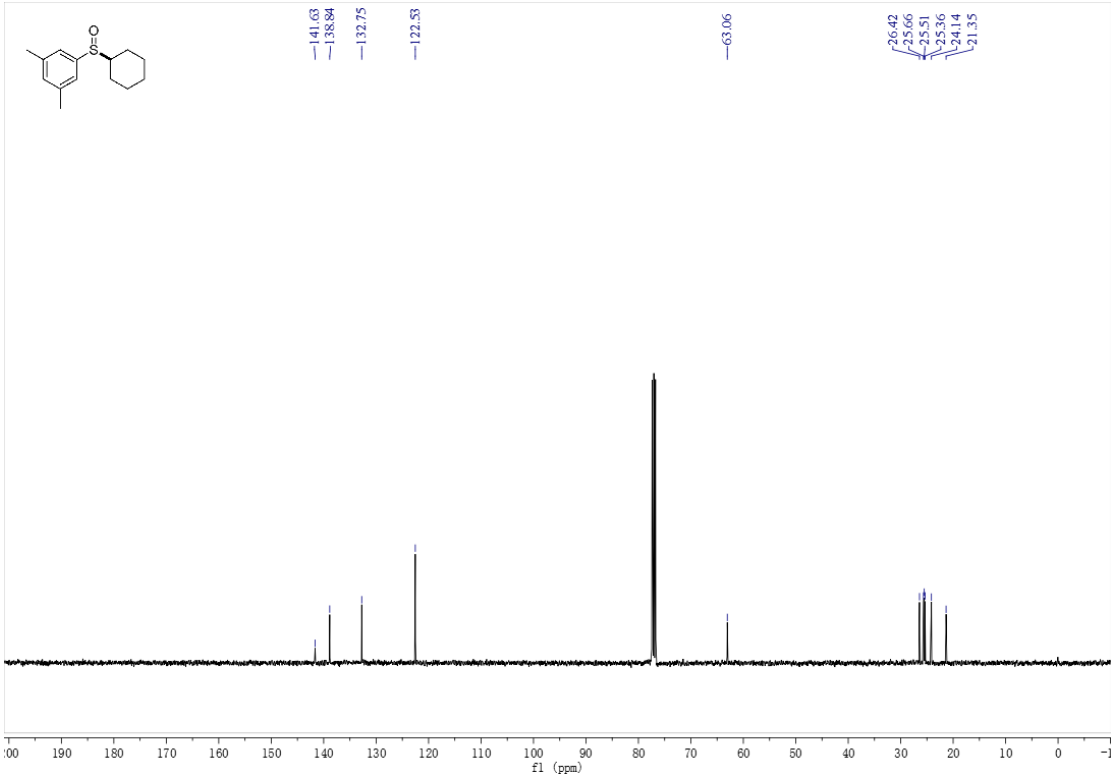
^{19}F NMR (376 MHz, $CDCl_3$, 23 ℃) of **92**



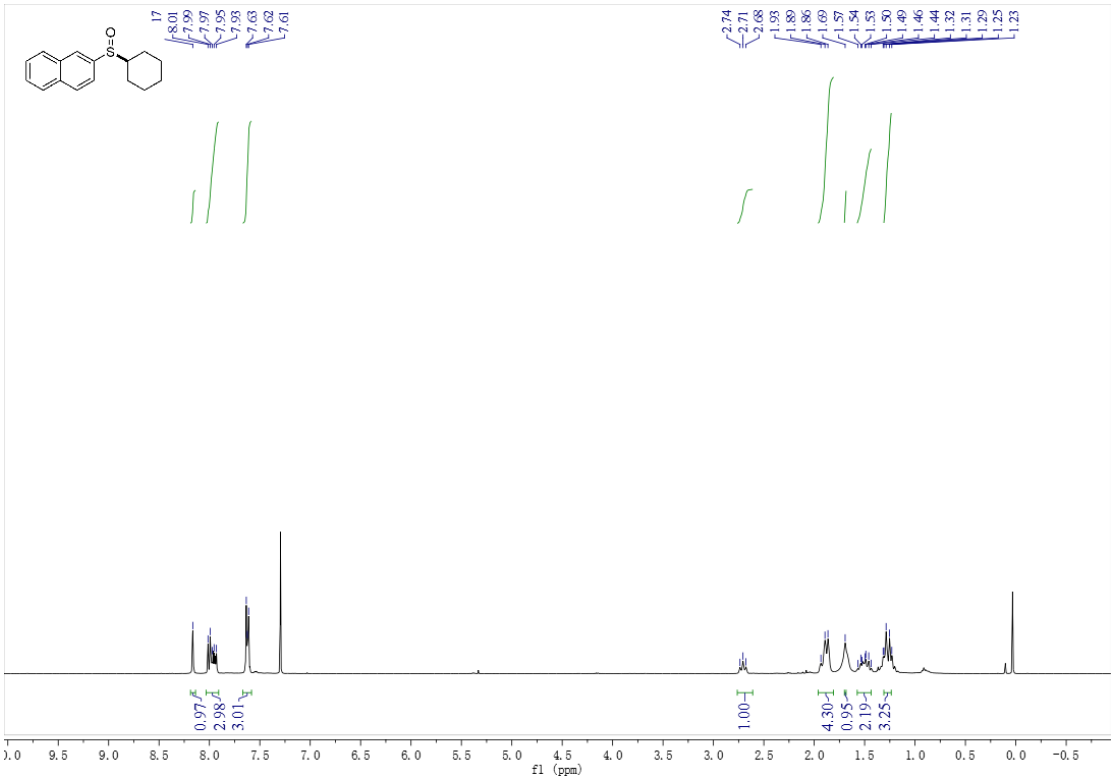
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **93**



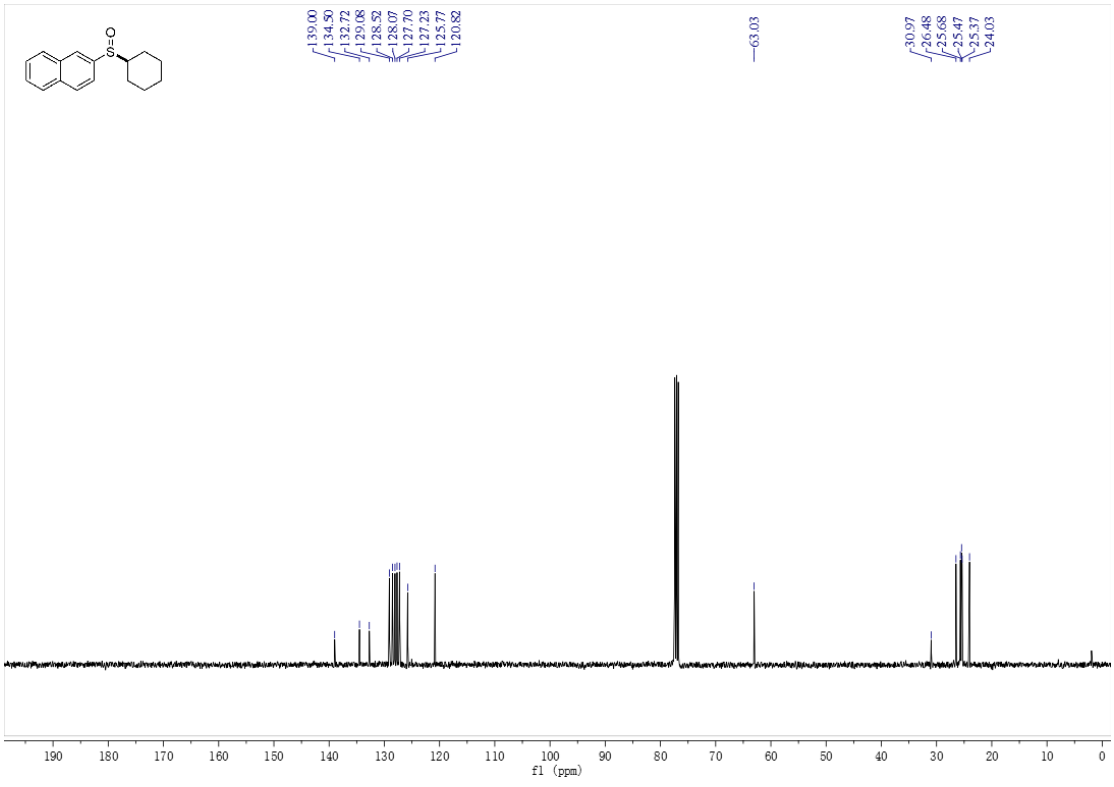
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **93**



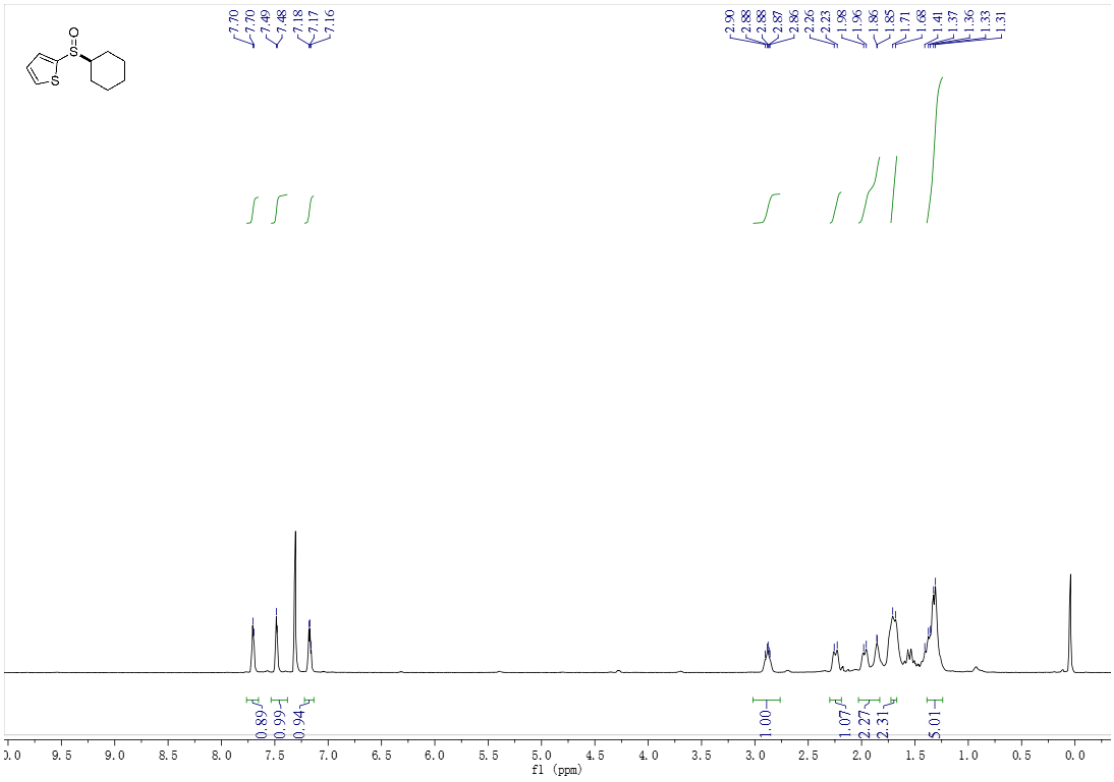
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **94**



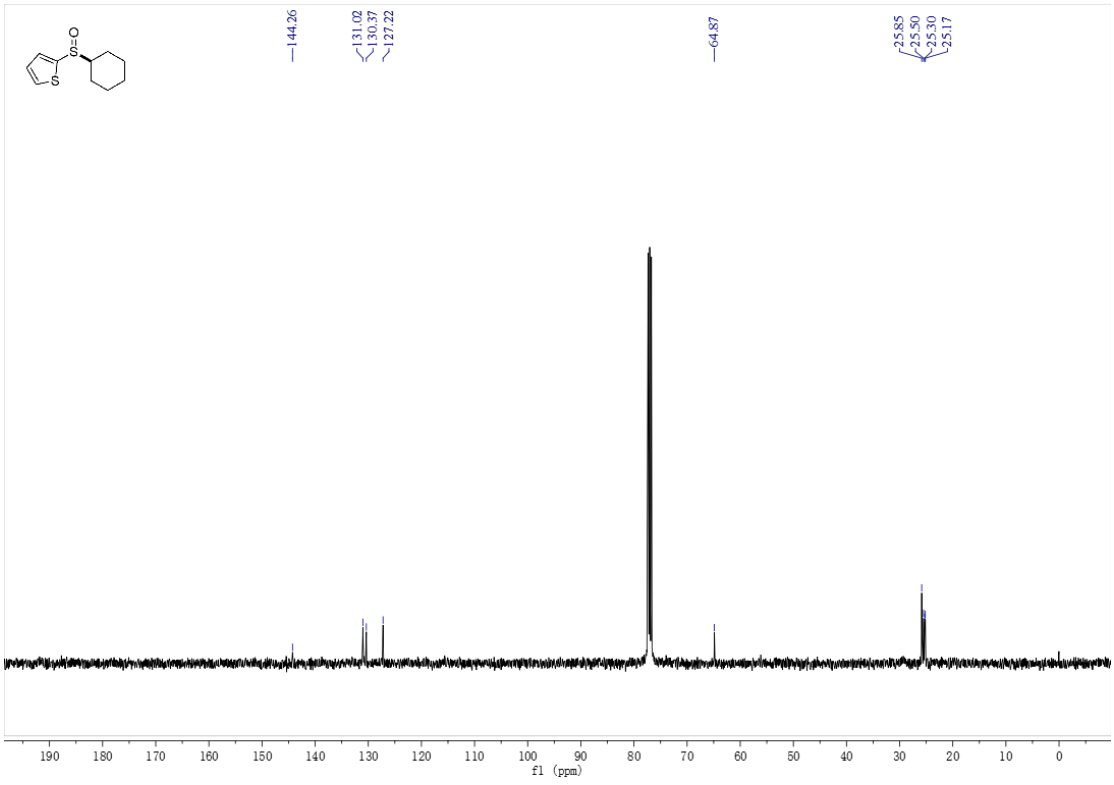
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **94**



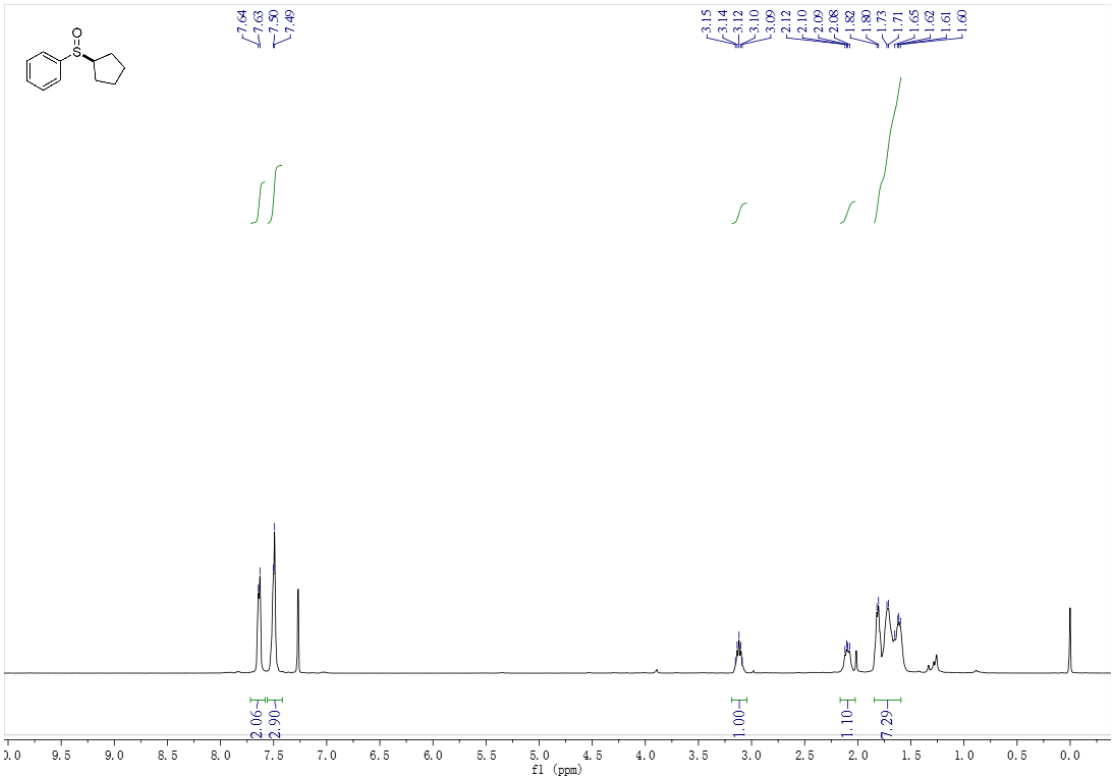
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **95**



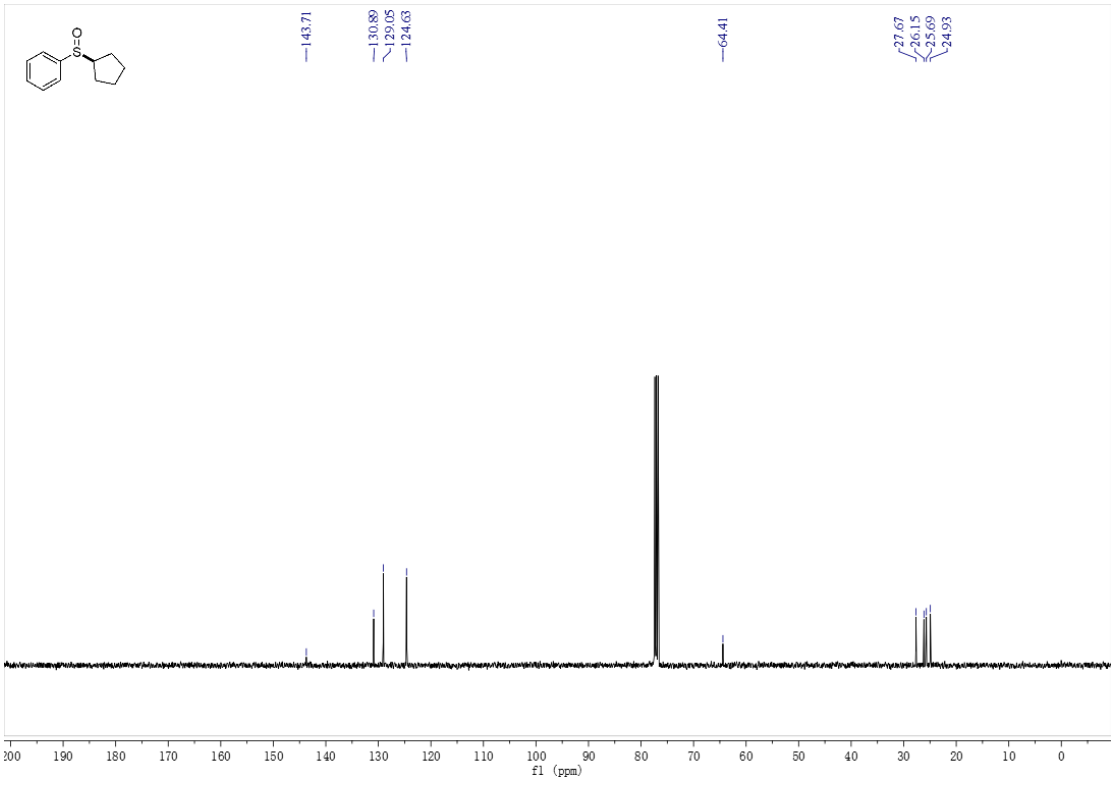
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **95**



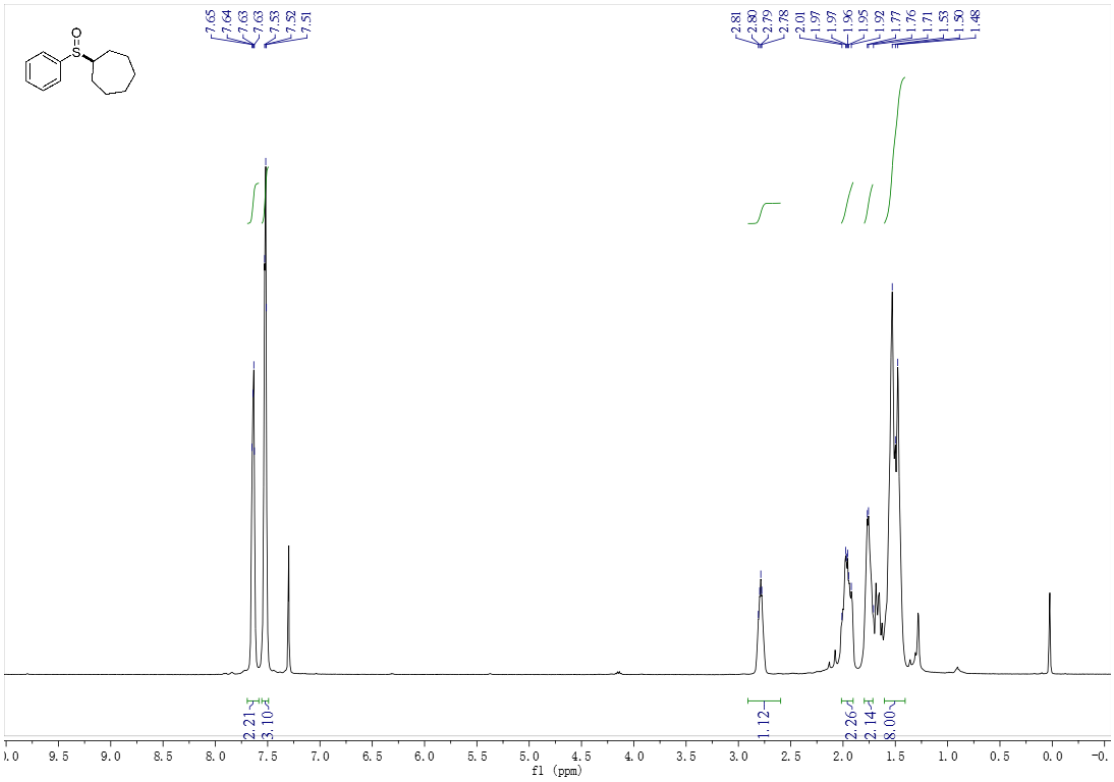
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **96**



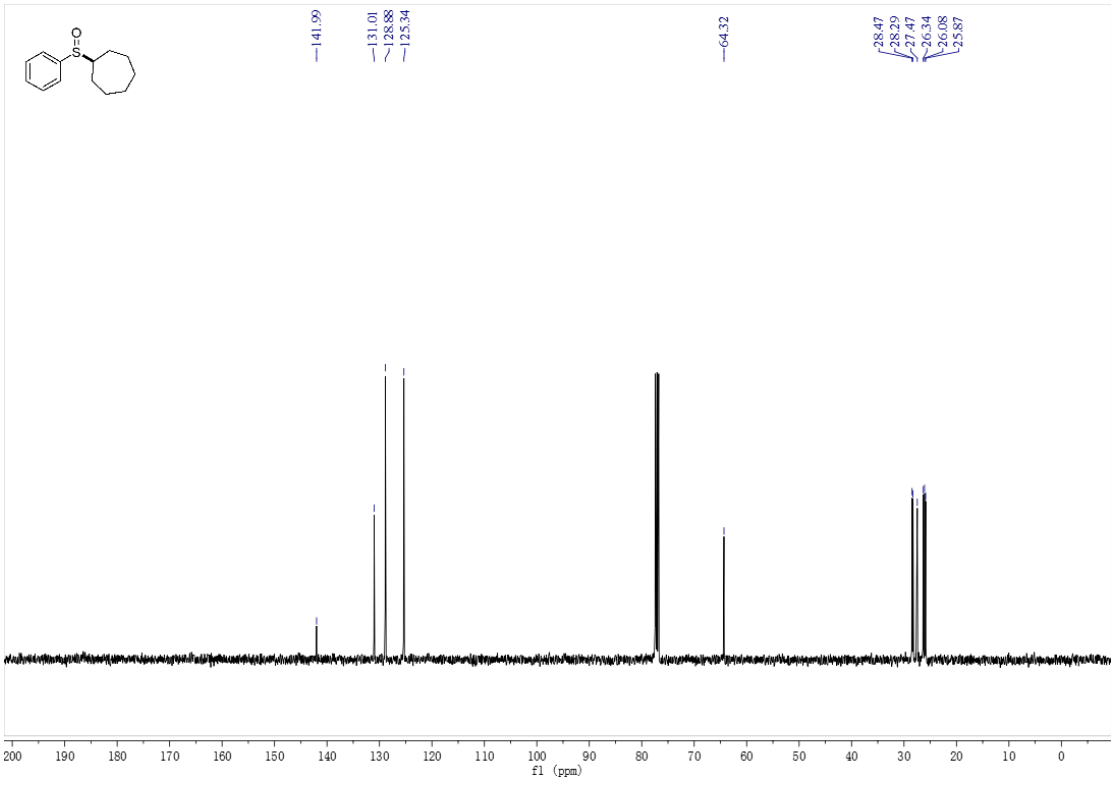
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **96**



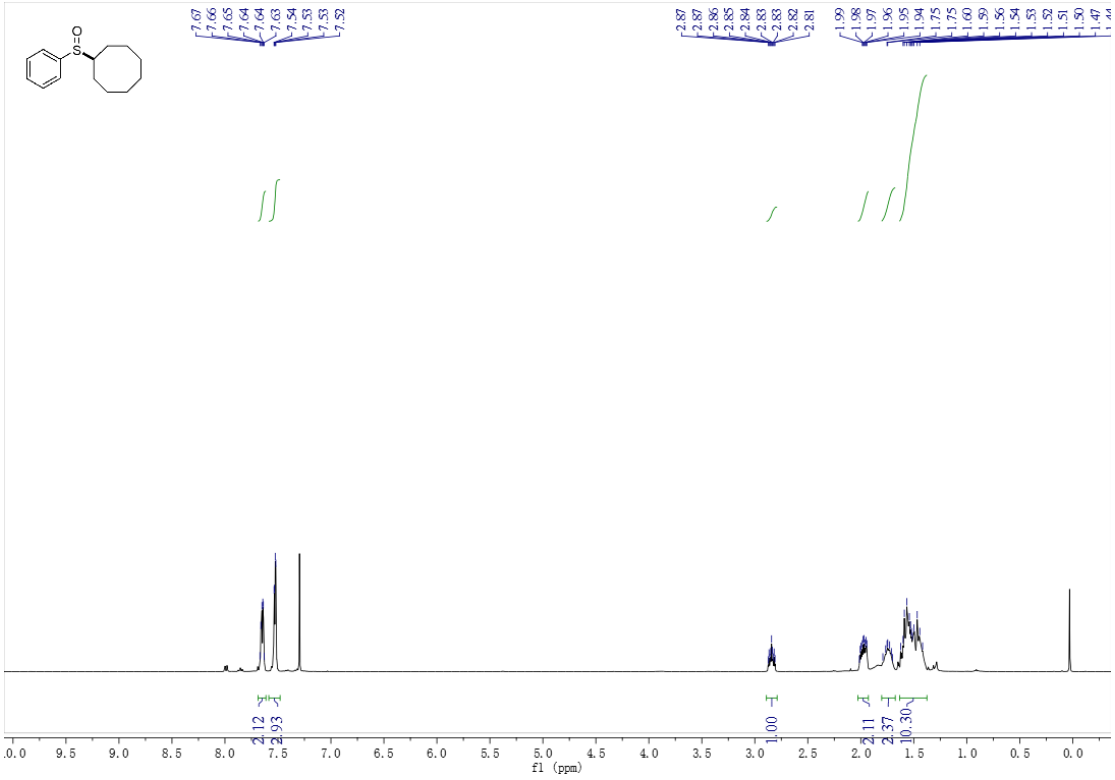
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **97**



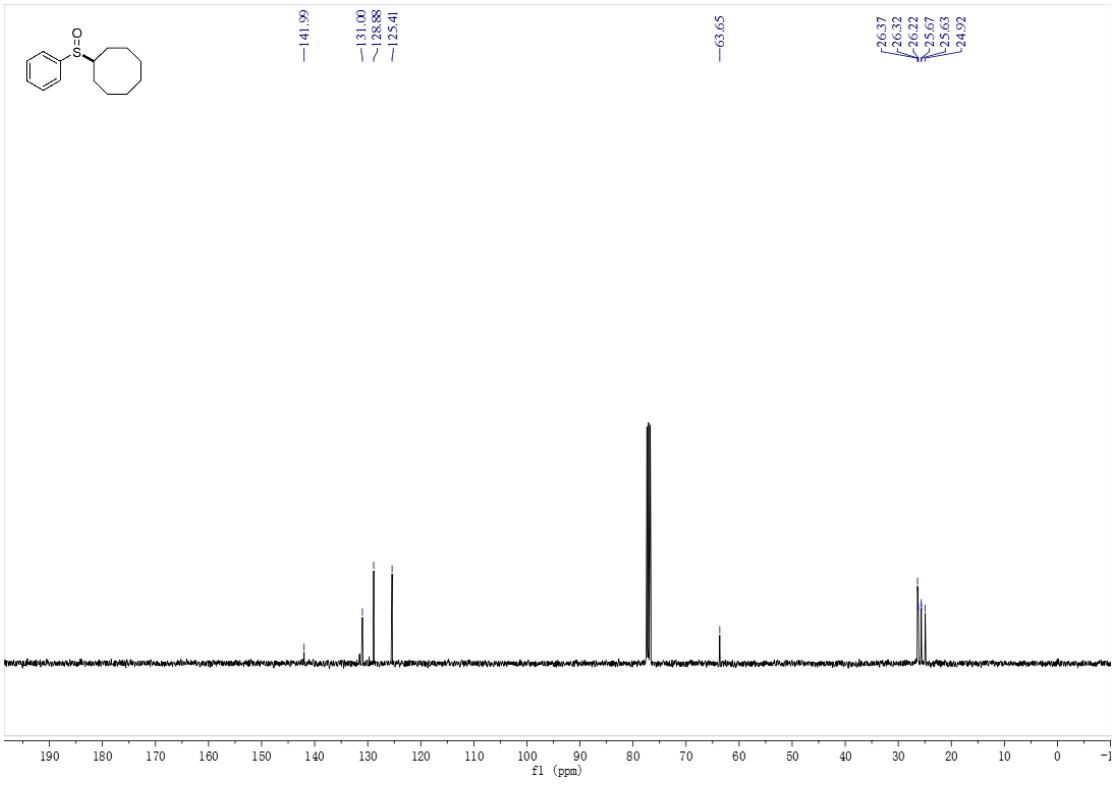
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **97**



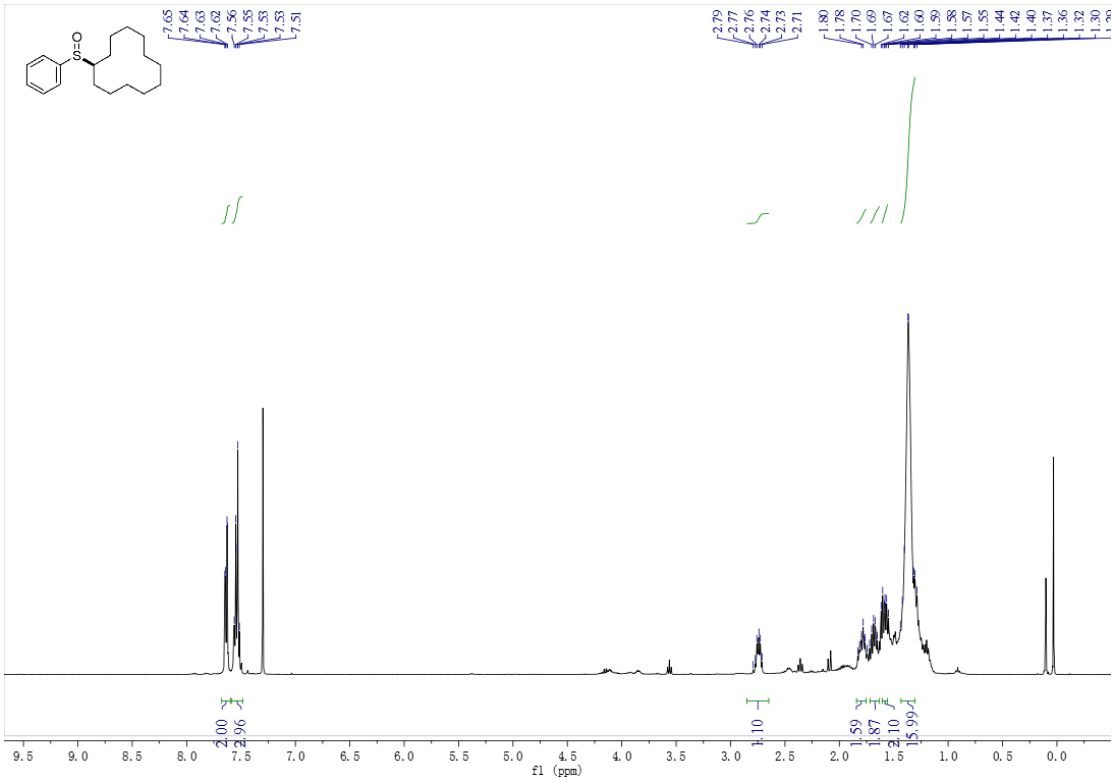
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **98**



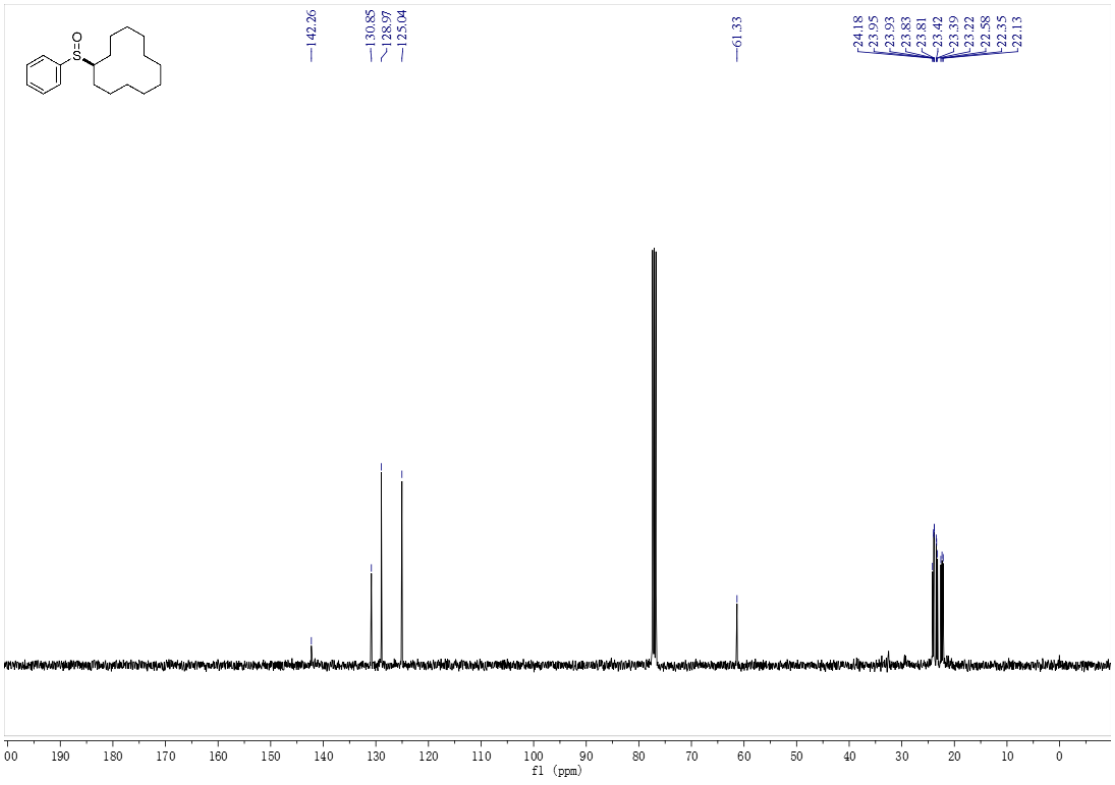
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **98**



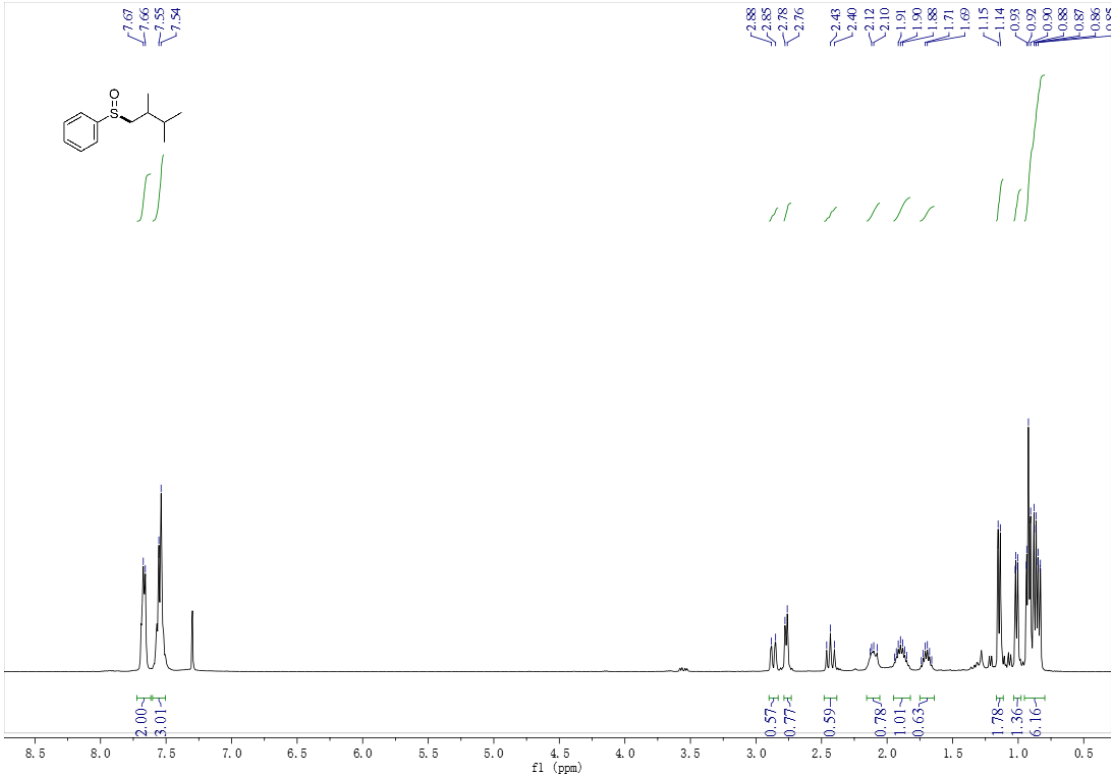
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **99**



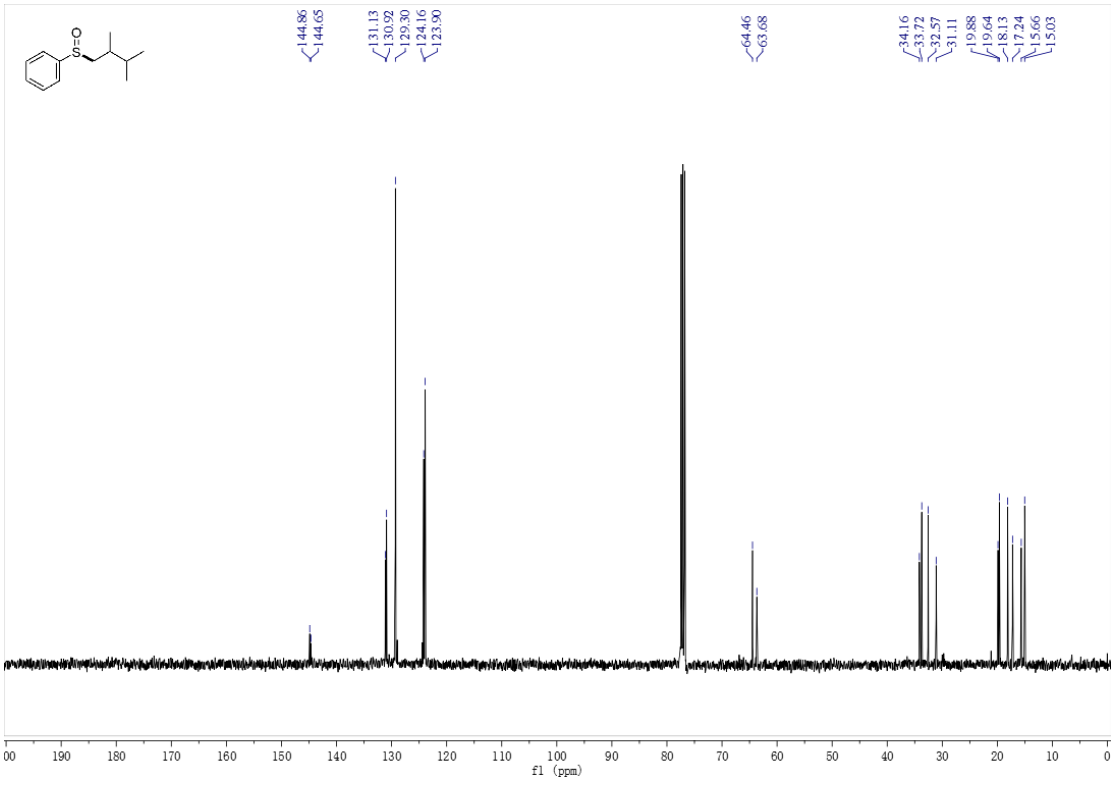
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **99**



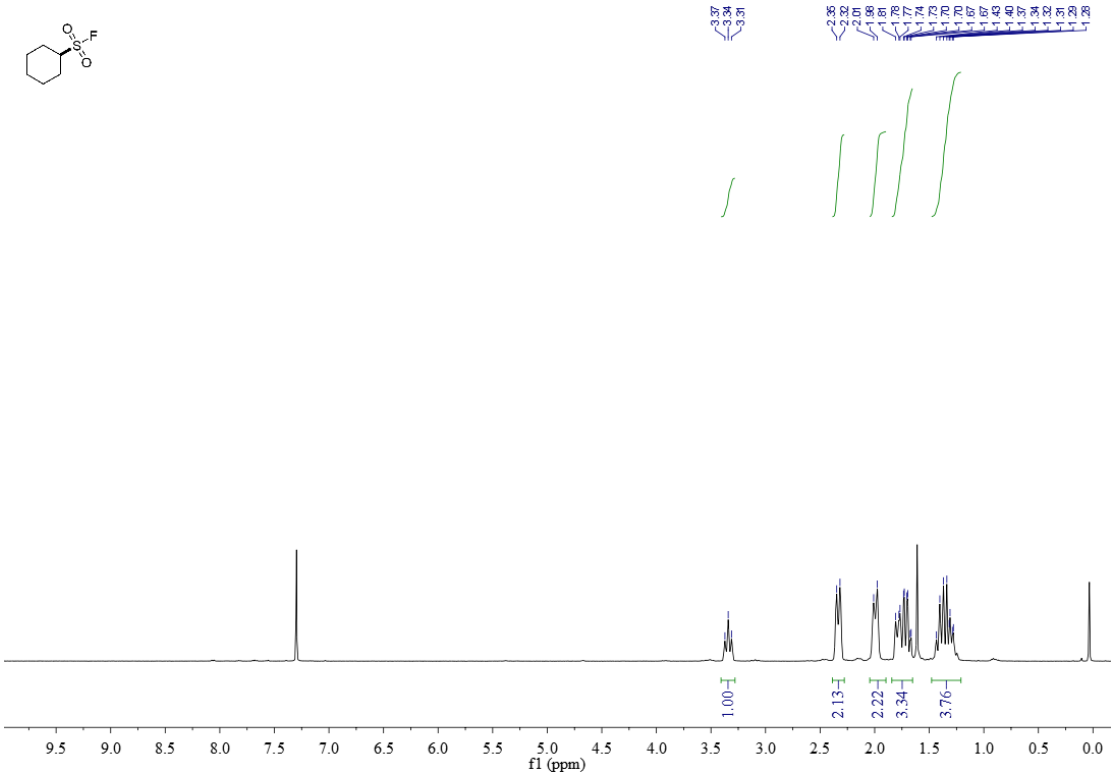
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **100**



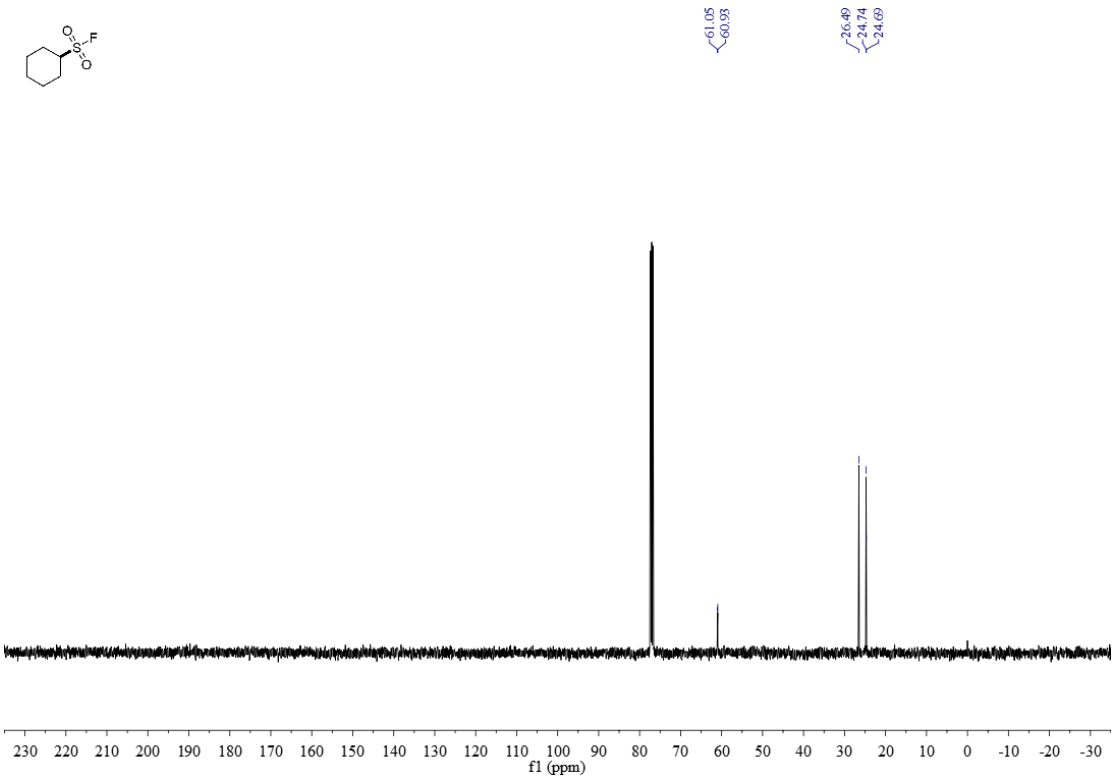
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **100**



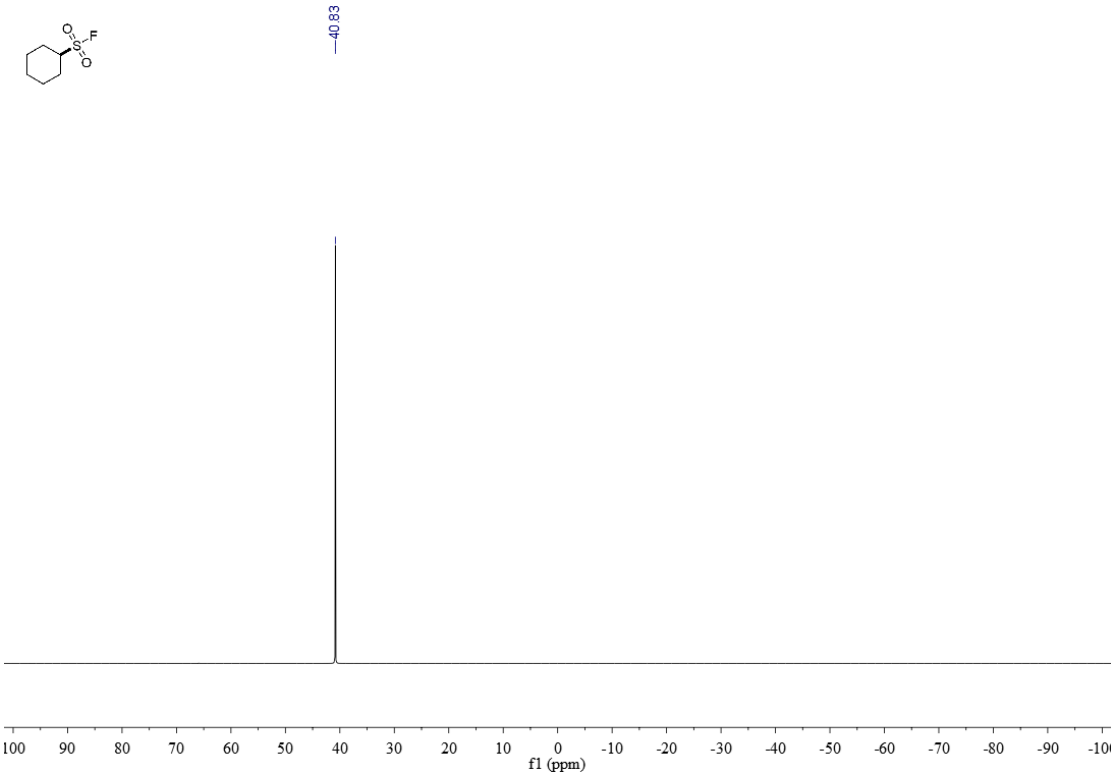
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **101**



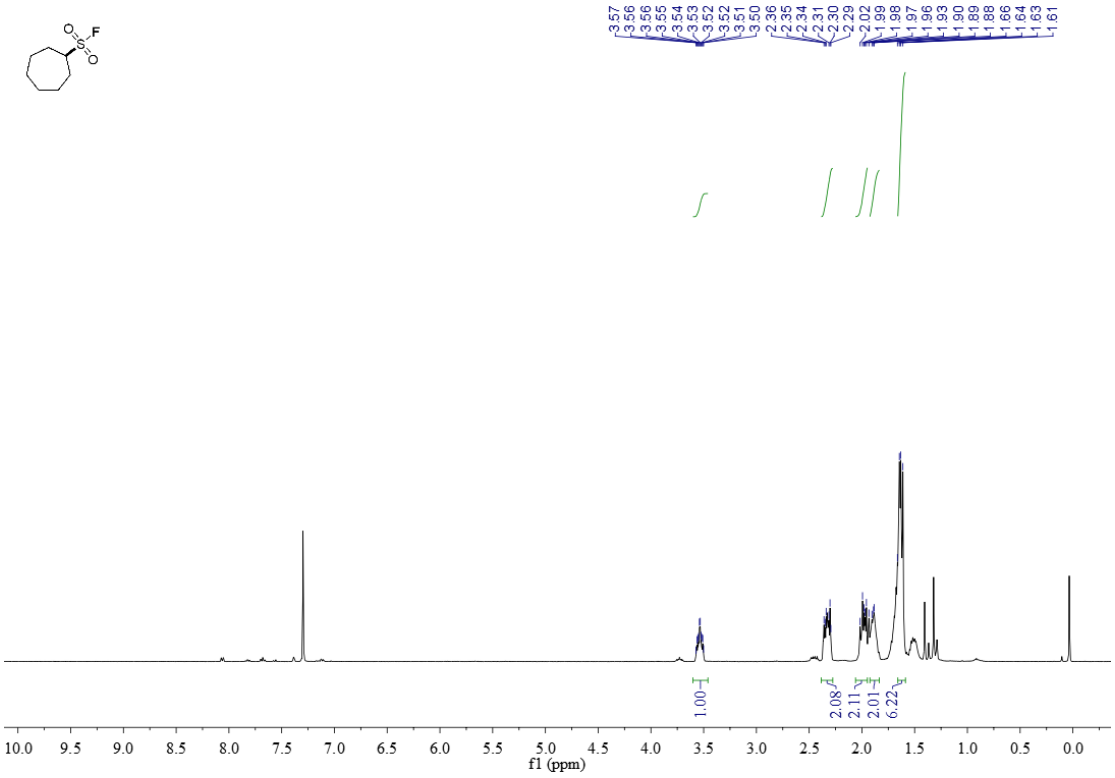
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **101**



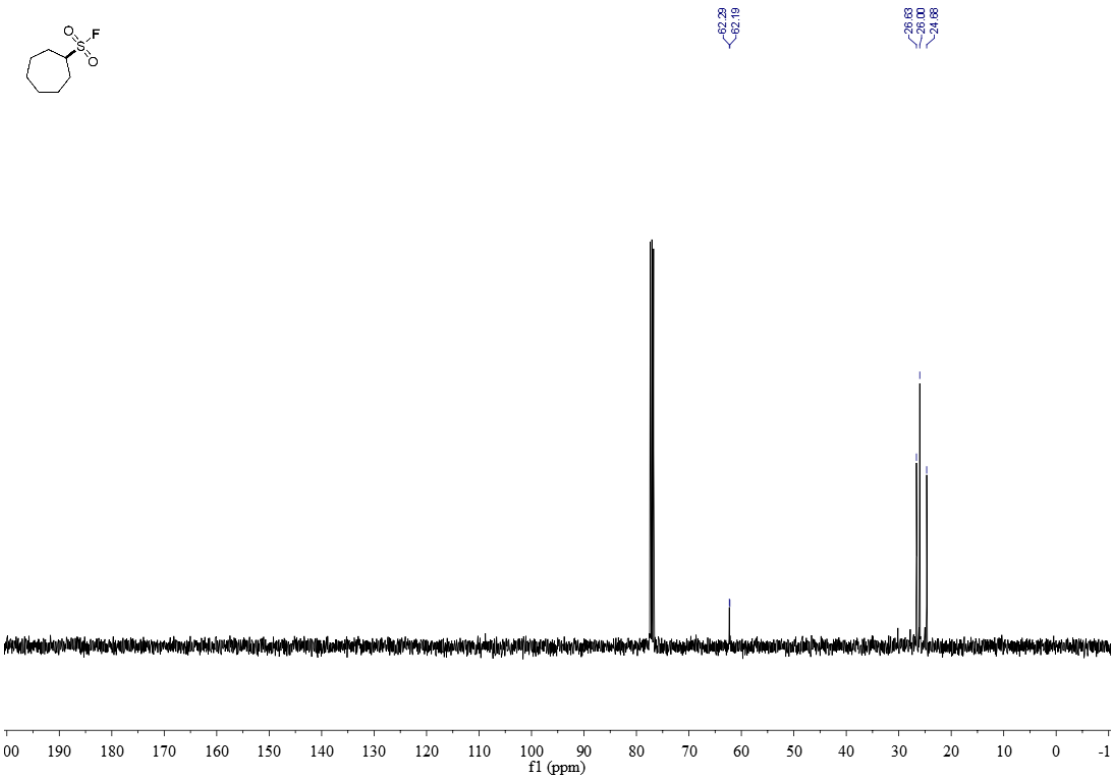
^{19}F NMR (376 MHz, $CDCl_3$, 23 ℃) of **101**



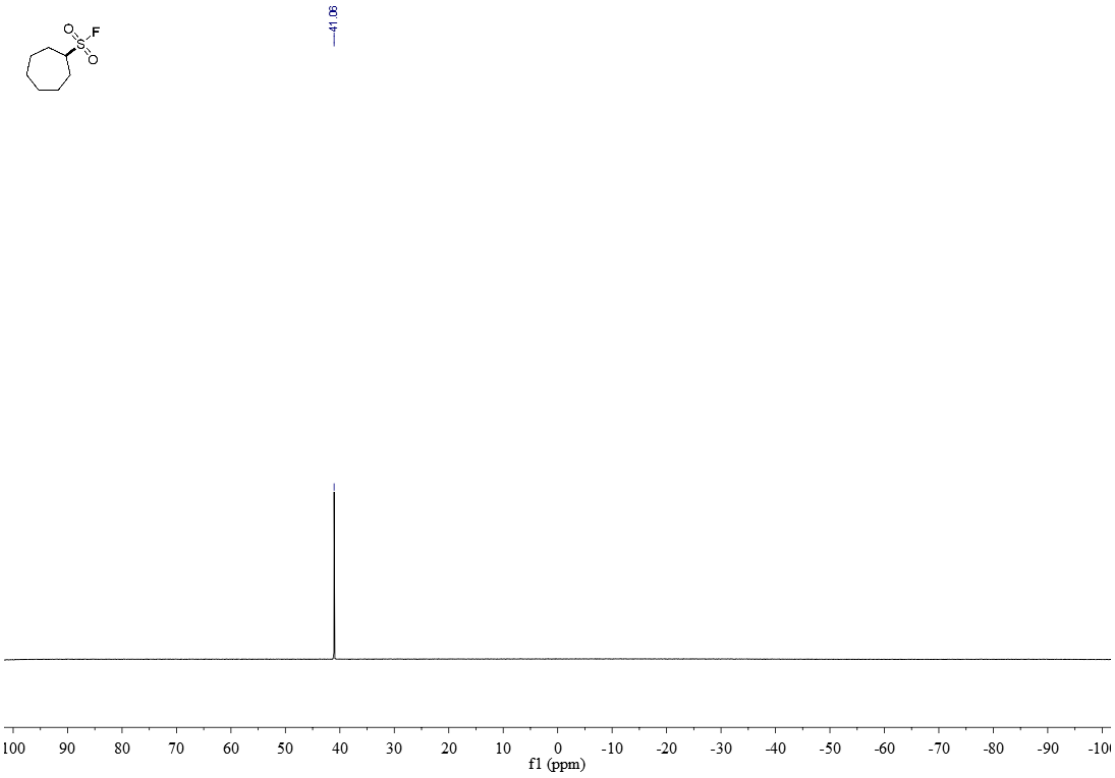
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **102**



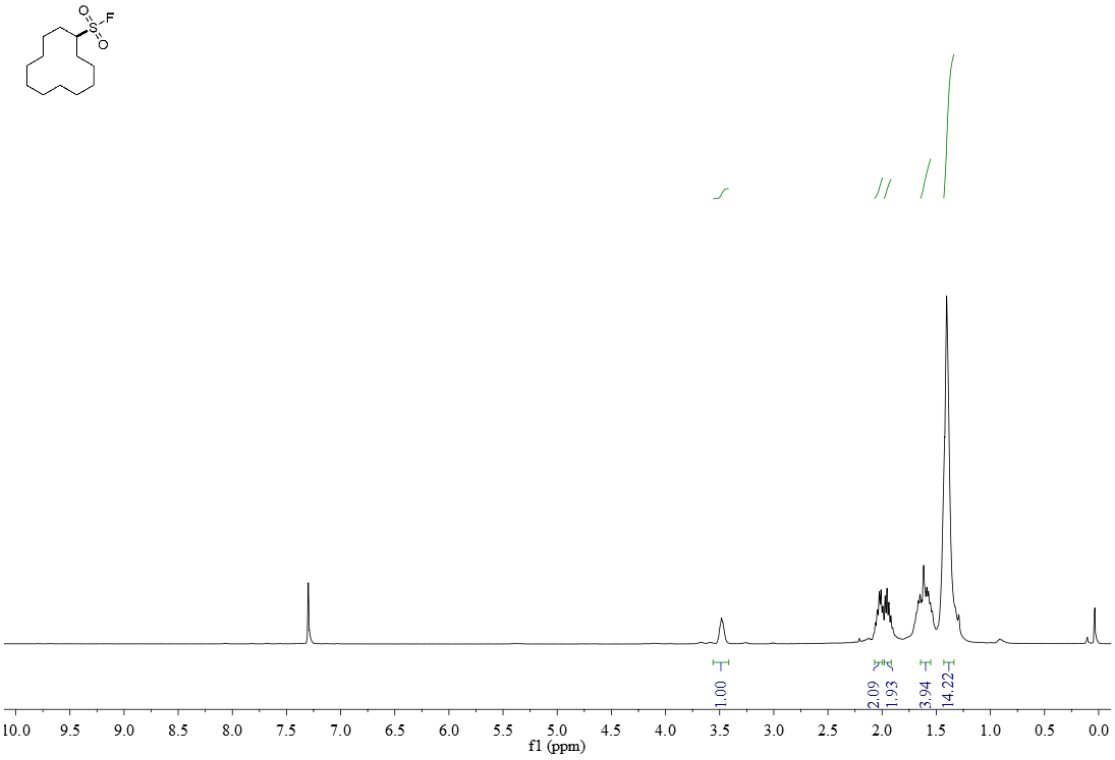
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **102**



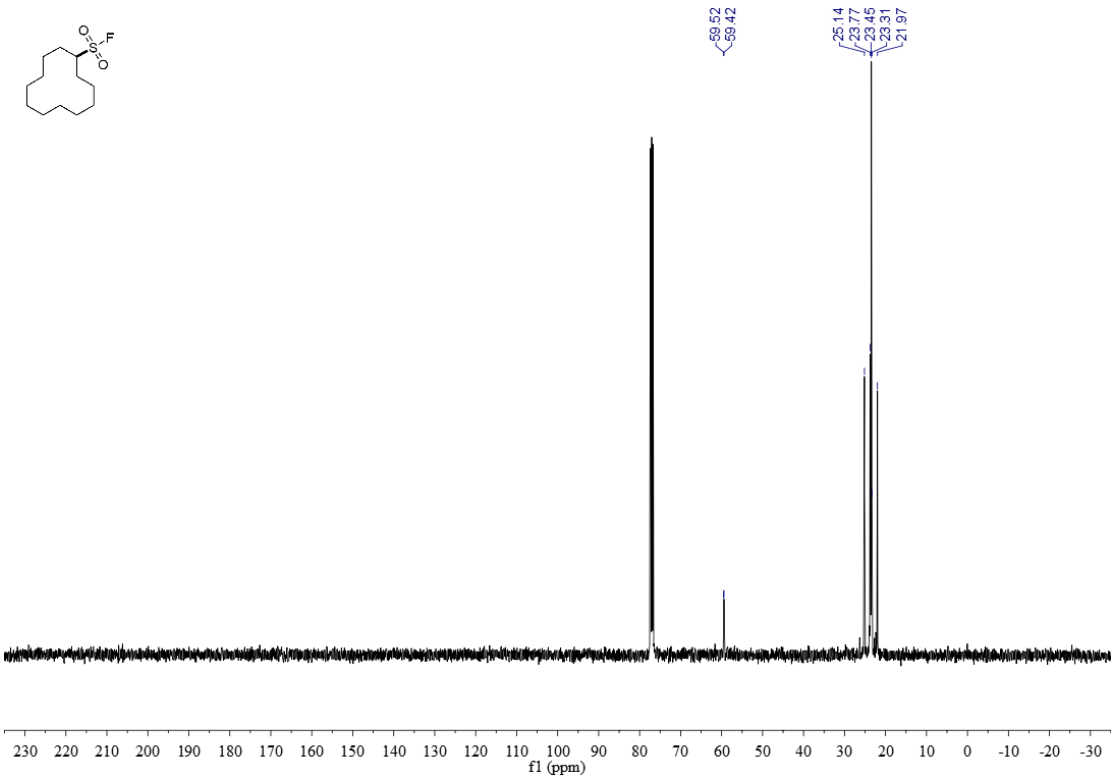
^{19}F NMR (376 MHz, $CDCl_3$, 23 ℃) of **102**



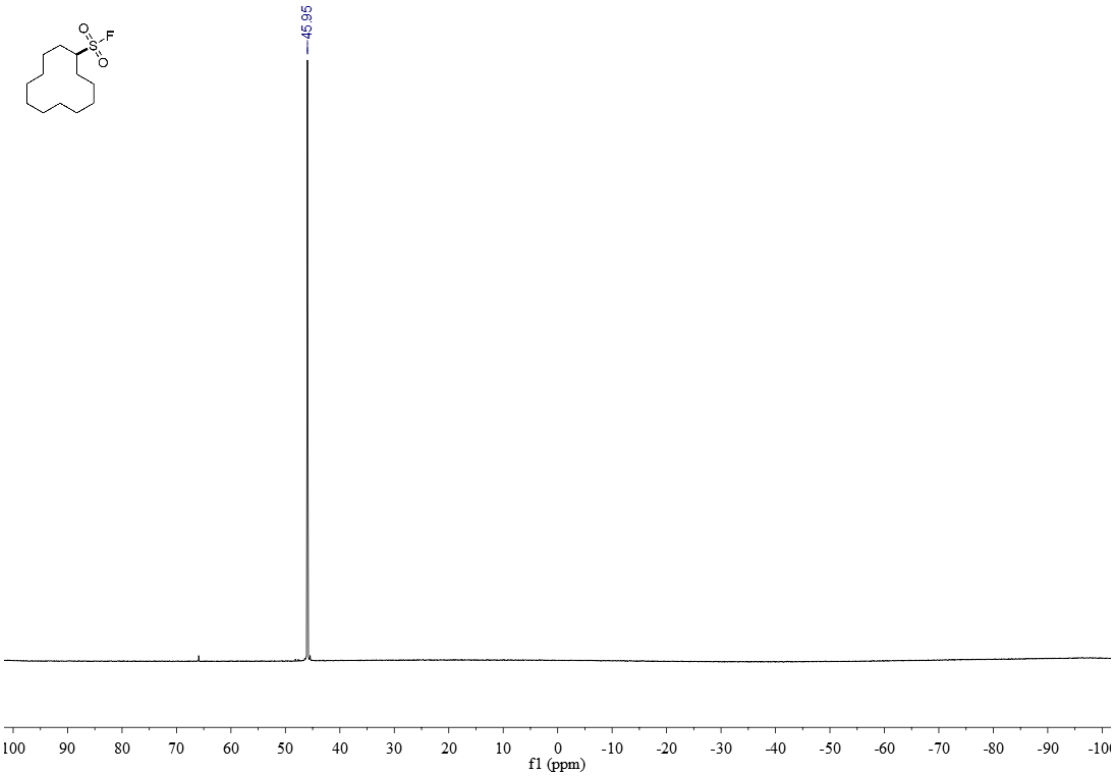
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **103**



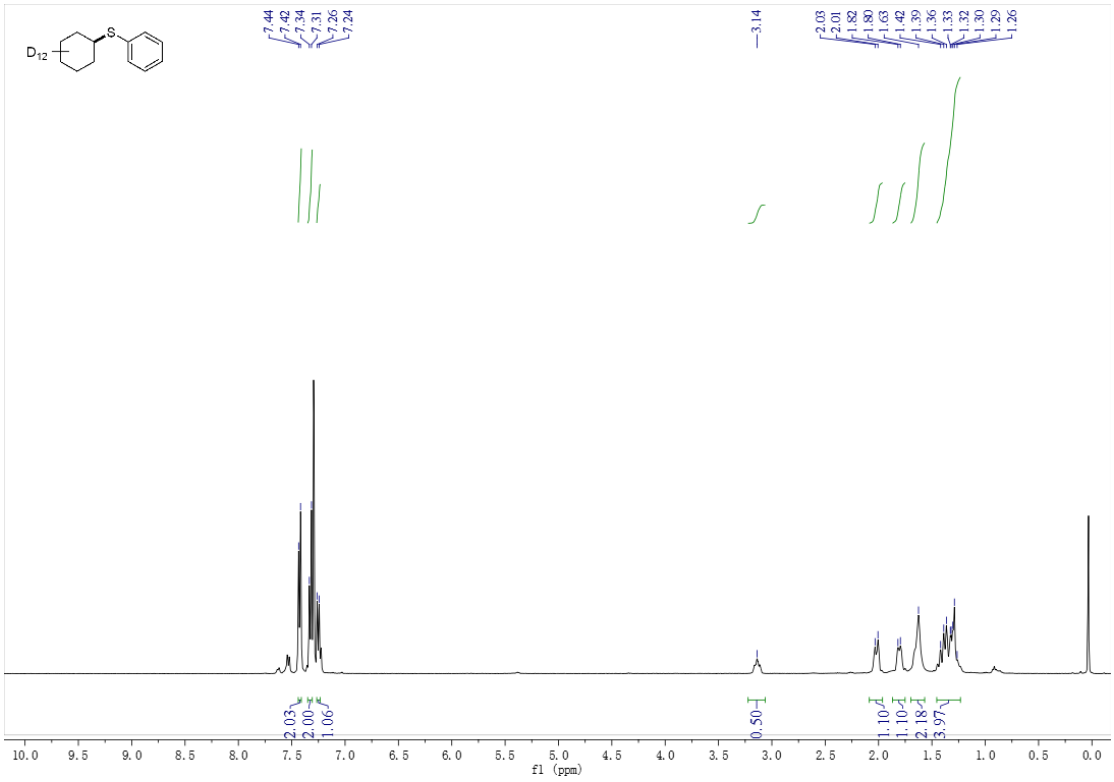
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **103**



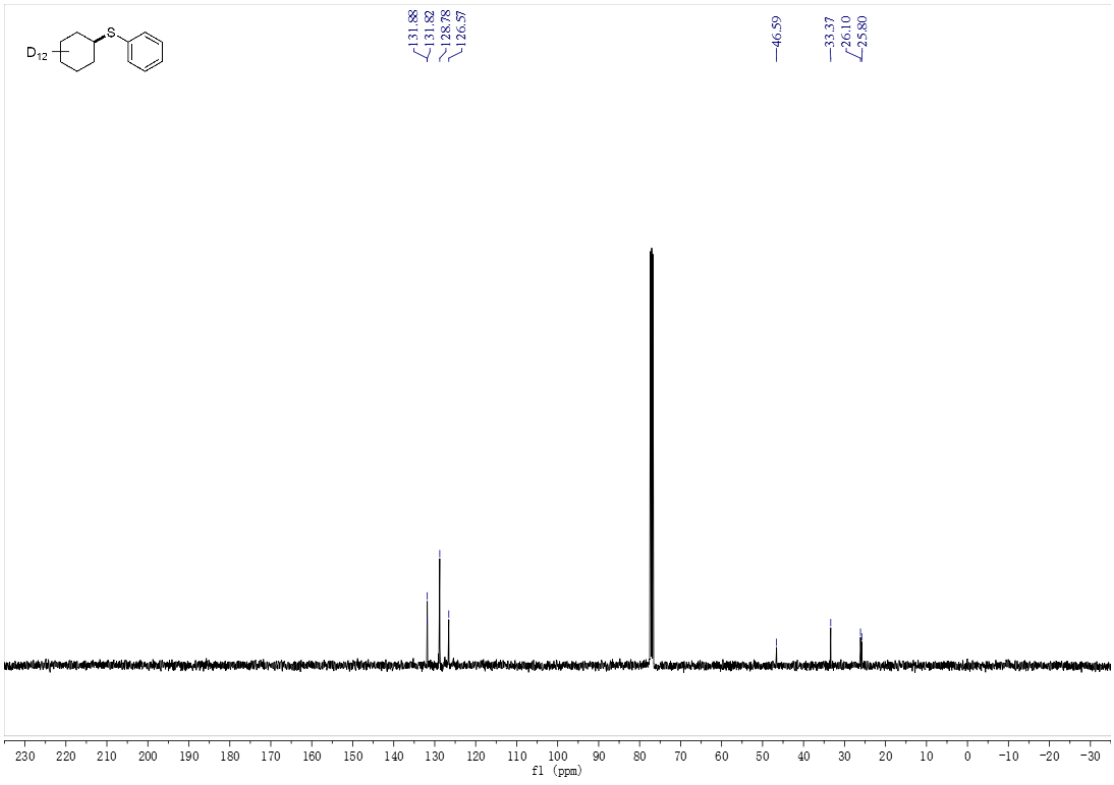
^{19}F NMR (376 MHz, $CDCl_3$, 23 ℃) of **103**



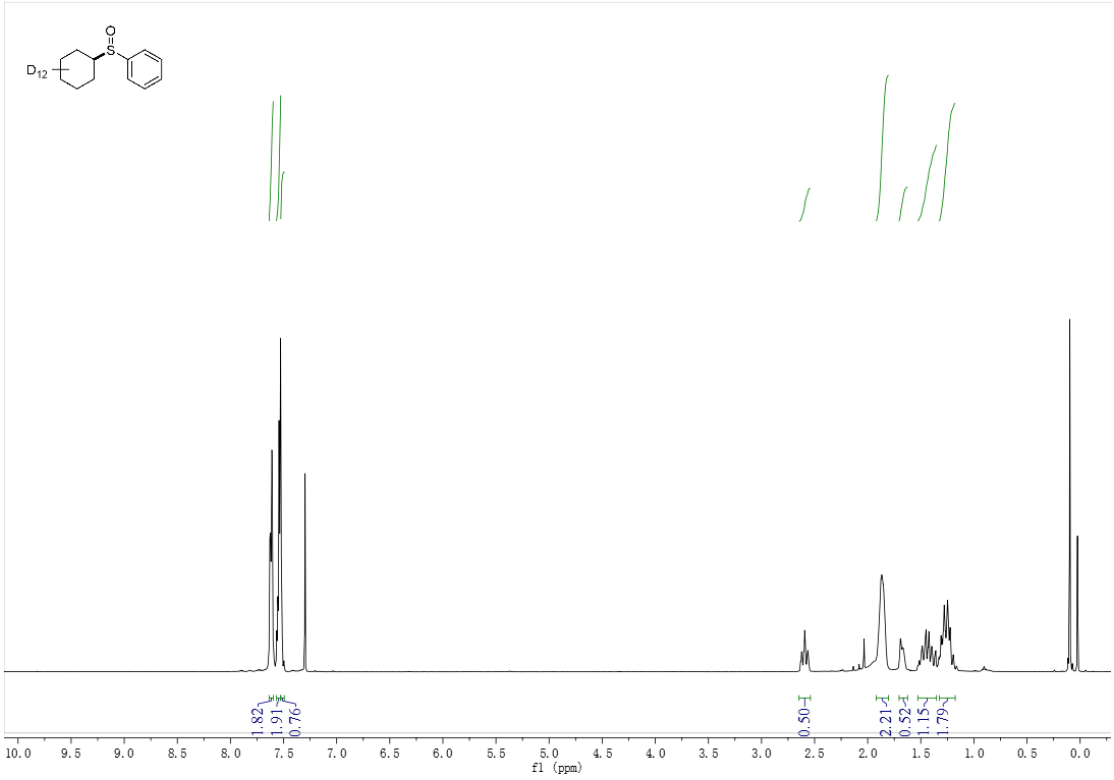
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **62**



^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **62**



^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **85**



^{13}C NMR spectrum (100 MHz, $CDCl_3$, 23 ℃) of **85**