Supporting Information

Electrochemically Driven Metal-Free Synthesis of Benzylic Thioethers via C-S Cross-Coupling

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Contents

1. General methods

The instruments for electrolysis used were ElectraSyn 2.0 Pro Package (IKA) and MAISHENG DC Power. Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. Reactions were monitored by thin-layer chromatography (TLC) with Haiyang GF 254 silica gel plates (Qingdao Haiyang chemical industry Co Ltd, Qingdao, China) using UV light and vanillic aldehyde or phosphomolybdic acid as visualizing agents. Flash column chromatography was performed using 200-300 mesh silica gel at increased pressure. ^{1}H NMR spectra, ^{19}F NMR spectra and ^{13}C NMR spectra were respectively recorded on 600 MHz, 565 MHz, and 151 MHz NMR spectrometers. Chemical shifts (δ) were expressed in ppm with TMS as the internal standard, and coupling constants (*J*) were reported in Hz. High-resolution mass spectra were obtained by using ESI ionization sources (quadrupole time-of-flight mass spectrometer, Bruker Impact II, Bremen, Germany). Cyclic voltammograms were obtained on a CHI 700E potentiostat (CH Instruments, Inc.).

Abbreviations: HFIP = 1,1,1,3,3,3-hexafluoropropan-2-ol, MeOH = methanol, DMA = *N*,*N*-dimethylaniline, DMF = *N*,*N*-dimethylformamide, DMSO = dimethyl sulfoxide, EA = ethyl acetate, DCE = dichloroethane, DCM = dichloromethane, MeCN = acetonitrile, TEMPO = 2,2,6,6-tetramethylpiperidinooxy, *m*CPBA = 3-chloroperoxybenzoic acid

2. Electrochemical reaction setup

0.5 mmol scale reaction:

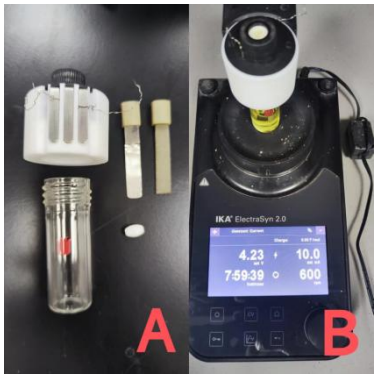


Figure S1. Electrochemical setup used for 0.5 mmol scale reaction.

(A): IKA ElectraSyn Electrode Starter Kit, platinum plates (52 mm x 8 mm x 0.2 mm), nickel foam (52 mm x 8 mm x 2 mm), 10 mL reaction vessel. (B): Standard IKA ElectraSyn 2.0. Parameter settings: Experiment Type (Constant Current), Value (10 mA), Reference Electrode (No), Experiment Duration (08:00:00 h:min:sec), Alternate Polarity (No).

Gram-scale reaction:

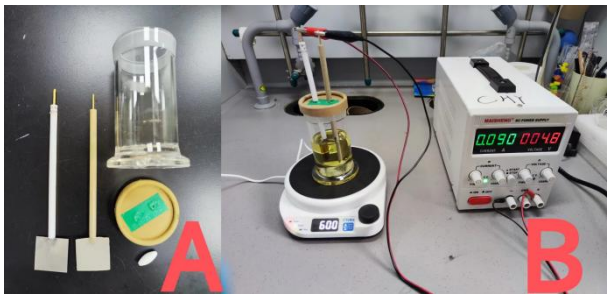


Figure S2. Electrochemical setup used for gram-scale reaction.

(A): A cylindrical bottle with a diameter of 5 cm and a height of 10 cm as reaction vessel, anode: Pt sheet (30 mm x 30 mm x 0.2 mm), cathode: Ni foam (30 mm x 30 mm x 2 mm). (B): The stirring rate: 600 rpm, and the current: 90 mA.

Divided cell experiment:

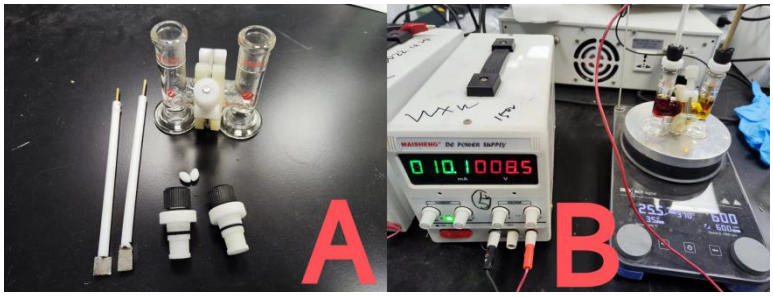
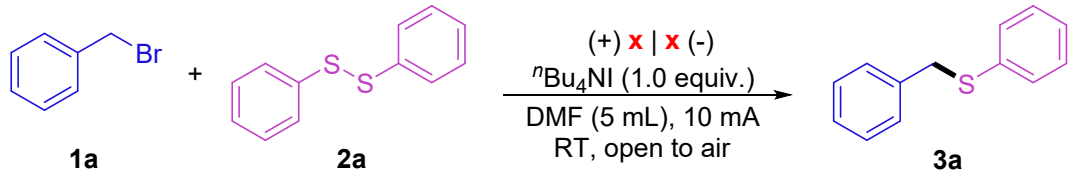


Figure S3. Electrochemical setup used for divided cell experiment.

(A): Pt sheet (10 mm x 10 mm x 0.1 mm) as anode, Ni foam (10 mm x 10 mm x 20 mm) as cathode. The reaction vessel: an H-type divided electrolytic cell (10 mL + 10 mL) separated by a hydrogen ion-permeable membrane (Dupont N-117). (B): The stirring rate: 600 rpm, and the current: 10 mA.

3. Reaction optimization

Table S1. Electrode screening [a]

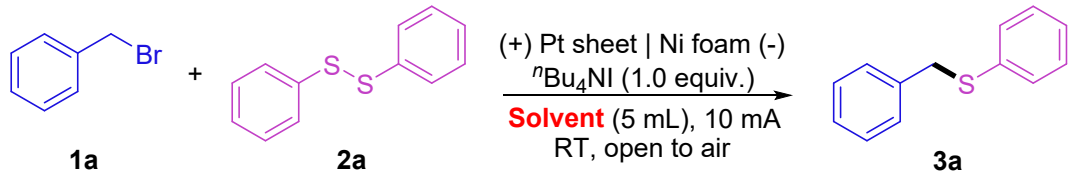


1a **2a** **3a**

Entry	Electrode material	Yield (%) [b]
1	C plate(+) | Pt sheet(-)	25
2	C plate(+) | C plate(-)	N.D.
3	Pt sheet(+) | Pt sheet(-)	34
4	Pt sheet(+) | C plate(-)	N.D.
5	**Pt** sheet**(+) | Ni foam(-)**	**57**
6	C plate(+) | Ni foam(-)	49
7	Pt sheet(+) | Cu foam(-)	50
8	C plate(+) | Cu foam(-)	40

[a] Reaction conditions: **1a** (0.5 mmol, 1 equiv.), **2a** (0.5 mmol, 1 equiv.), ^{n}Bu$_4$I (0.5 mmol, 1 equiv.), DMF (5 mL), constant current = 10 mA, 12 h, room temperature (RT), open air, undivided cell, reactions performed using Standard ElectraSyn 2.0 vessel (10 mL). [b] Isolated yield.

Table S2. Solvent screening [a]



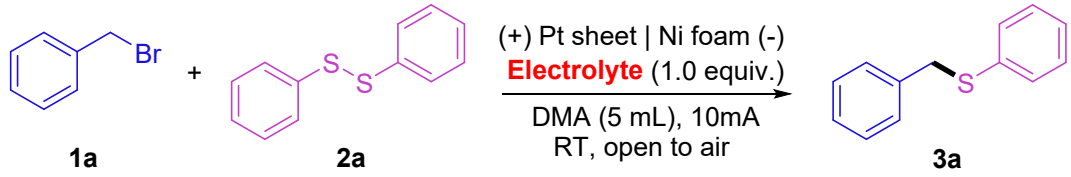
1a **2a** **3a**

Entry	Solvent	Yield (%) [b]
1	**DMA**	**78**
2	DCM	N.D.
3	DCE	N.D.

4	EA	N.D.
5	MeCN	29
6	DMF	57
7	DMSO	33
8	HFIP	N.D.
9	acetone	N.D.

[a] Reaction conditions: **1a** (0.5 mmol, 1 equiv.), **2a** (0.5 mmol, 1 equiv.), $^{n}Bu_4I$ (0.5 mmol, 1 equiv.), Solvent (5 mL), constant current = 10 mA, 10 h, room temperature (RT), open air, undivided cell, reactions performed using Standard ElectraSyn 2.0 vessel (10 mL). [b] Isolated yield.

Table S3. Electrolyte screening [a]

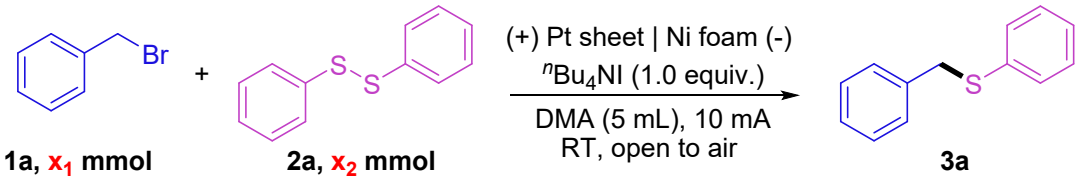


1a **2a** **3a**

Entry	Electrolyte	Yield (%) [b]
1	--	Voltage oveload
2	KI	18
3	NH_4I	25
4	$^{n}Et_4NI$	61
5	**$^{n}Bu_4NI$**	**85**
6	$^{n}Bu_4NBr$	N.D.
7	$^{n}Bu_4NOAc$	10
8	$^{n}Bu_4NPF_6$	Trace
10	$^{n}Bu_4NBF_4$	Trace
11	$NaBF_4$	Trace
12	$^{n}Bu_4NCF_3SO_3$	Trace
13	$LiClO_4$	N.D.
14	LiOAc	N.D.

[a] Reaction conditions: **1a** (0.5 mmol, 1 equiv.), **2a** (0.5 mmol, 1 equiv.), electrolyte (0.5 mmol, 1 equiv.), DMA (5 mL), constant current = 10 mA, 8 h, room temperature (RT), open air, undivided cell, reactions performed using Standard ElectraSyn 2.0 vessel (10 mL). [b] Isolated yield.

Table S4. Substrate ratio screening [a]

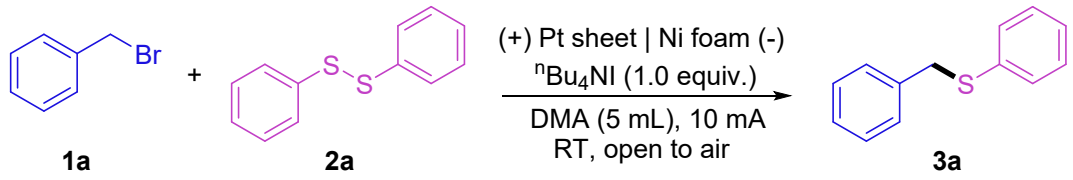


1a, x_1 mmol **2a, x_2 mmol** **3a**

Entry	x_1 (mmol)	x_2 (mmol)	Yield (%) [b]
1	0.3	0.3	26
2	0.5	0.25	39
3	0.5	0.5	85
4	**0.5**	**0.75**	**95**
5	0.5	1.0	95
6	0.5	1.25	92

[a] Reaction conditions: **1a** (x_1 mmol), **2a** (x_2 mmol), ^{n}Bu$_4$I (0.5 mmol), DMA (5 mL), constant current = 10 mA, 8 h, room temperature (RT), open air, undivided cell, reactions performed using Standard ElectraSyn 2.0 vessel (10 mL). [b] Isolated yield.

Table S5. Current screening [a]



1a **2a** **3a**

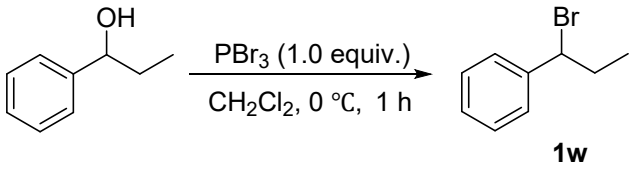
Entry	Current (mA)	Time (h)	Yield (%) [b]
1	5	16	69
2	8	10	88
3	**10**	**8**	**95**

4	12	6.5	91
5	15	5	78

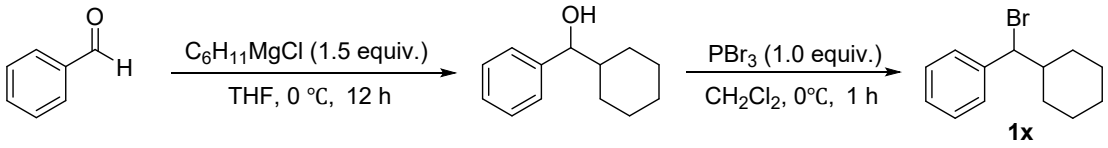
[a] Reaction conditions: **1a** (0.5 mmol, 1 equiv.), **2a** (0.75 mmol, 1.5 equiv.), $^{n}Bu_4I$ (0.5 mmol, 1 equiv.), DMA (5 mL), constant current, room temperature (RT), open air, undivided cell, reactions performed using Standard ElectraSyn 2.0 vessel (10 mL). [b] Isolated yield.

4. Experimental procedures for the synthesis of substrates

4.1. Synthesis of bromides.

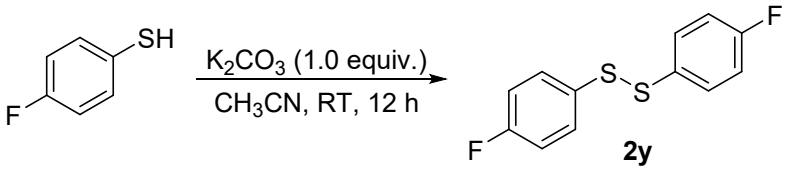


(1-Bromopropyl)benzene (1w). To a 25 mL vial equipped with a stirring bar were added alcohol (680 mg, 5.0 mmol) and CH_2Cl_2 (12 mL), and the solution was cooled to 0 °C. PBr_3 (185 uL, 5.0 mmol, 1.0 equiv.) was added to the solution dropwise, and reaction mixture was further stirred for 1 h at 0 °C. The reaction was quenched with water (10mL) and extracted with 30 mL CH_2Cl_2 three times. The combined organic layers were washed with 30 mL brine and dried over anhydrous Na_2SO_4. Then, the solvent was removed under reduced pressure. The resulting mixture was purified by column chromatography on silica gel (eluted with petroleum ether) to afford the desired product **1w** as a colorless oil (870.1 mg, 88% yield). ^{1}H NMR (600 MHz, $CDCl_3$). δ = 7.41–7.37 (m, 2H), 7.36–7.31(m, 2H), 7.30–7.27 (m, 1H), 4.88 (t, *J* = 7.3 Hz, 1H), 2.36–2.32 (m, 1H), 2.22–2.10 (m, 1H), 1.00 (t, *J* = 7.3 Hz, 3H). The spectral data is identical to those reported previously.[1]



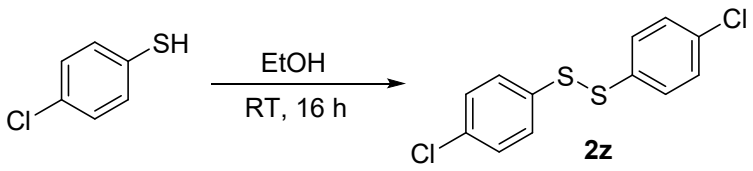
(Bromo(cyclohexyl)methyl)benzene (1x). To a 50 mL round-bottomed flask equipped with a stirring bar were added benzaldehyde (532.0 mg, 5.0 mmol, 1.0 equiv.) and THF (12 mL). The mixture was cooled to 0 ℃ under a positive pressure of N_2 and $C_6H_{11}MgCl$ (1.0 M in THF, 7.51 mL, 7.51 mmol, 1.5 equiv.) was then added dropwise over 30 min. The mixture was then warmed to room temperature and stirred for an additional 12 h. Upon completion, the reaction mixture was poured into 30 mL H_2O and extracted with 30 mL EtOAc three times. The combined organic layers were washed with 30 mL brine and dried over anhydrous Na_2SO_4. Then, the solvent was removed under reduced pressure. The resulting mixture was purified by column chromatography on silica gel (eluted with ethyl acetate/petroleum ether) to afford the desired product cyclohexyl(phenyl)methanol as a yellow oil and used directly in the next step. In a 25 mL vial equipped with a stirring bar, CH_2Cl_2 (12.0 mL) and the resultant alcohol **4** were charged, and the solution was cooled to 0 °C. PBr_3 (185 uL, 5.0 mmol, 1.0 equiv.) was added to the solution dropwise, and reaction mixture was further stirred for 1 h at 0 ℃. The reaction was quenched with water (10 mL) and extracted with 30 mL CH_2Cl_2 three times. The combined organic layers were washed with 30 mL brine and dried over anhydrous Na_2SO_4. Then, the solvent was removed under reduced pressure. The resulting mixture was purified by column chromatography on silica gel (eluted with ethyl acetate/petroleum ether) to afford the desired product **1x** as a colorless oil (382.6 mg, 30% yield, 2 steps). ^{1}H NMR (600 MHz, $CDCl_3$). δ = 7.44–7.27 (m, 5H), 4.71 (d, *J* = 9.2 Hz, 1H), 2.35–2.25 (m, 1H), 2.02–1.90 (m, 1H), 1.84–1.76 (m, 1H), 1.70–1.57 (m, 2H), 1.51–1.43 (m, 1H), 1.32–0.97 (m, 4H), 0.93–0.78 (m, 1H). The spectral data is identical to those reported previously.[1]

4.2. Synthesis of disulfides.

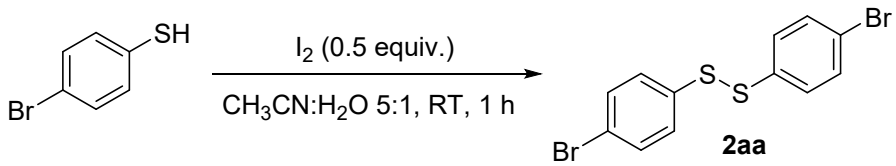


1,2-bis(4-fluorophenyl)disulfane (2y). To a 25 mL vial equipped with a stirring bar were added 4-fluorobenzenethiol (256.0 mg, 2.0 mmol, 1.0 equiv.) and MeCN (10 mL). K_2CO_3 (276.4 mg, 2 mmol, 2 equiv.) was then added in one portion and the mixture was stirred at room

temperature, open to air for 12 h. Upon completion, the reaction mixture was poured into 30 mL H_2O and extracted with 30 mL EtOAc three times. The combined organic layers were washed with 30 mL brine and dried over anhydrous Na_2SO_4. Then, the solvent was removed under reduced pressure. The resulting mixture was purified by column chromatography on silica gel (eluted with petroleum ether) to afford the desired product **2y** as a colorless oil (228.6 mg, 90% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.54–7.36 (m, 4H), 7.00 (dd, J = 8.5, 8.5 Hz, 4H). The spectral data is identical to those reported previously.[2]

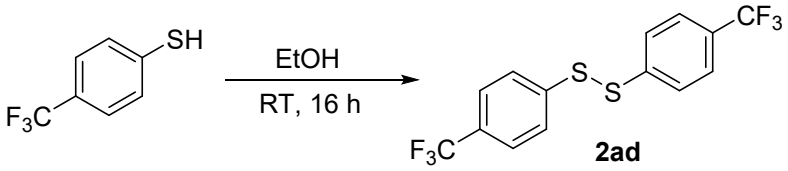


1,2-bis(4-chlorophenyl)disulfane (2z). To a 25 mL vial equipped with a stirring bar was added 4-chlorobenzenethiol (431.9 mg, 3.0 mmol, 1.0 equiv.) and EtOH (10 mL). The mixture was stirred at room temperature, open to air, for 16 h. Upon completion, the reaction mixture was poured into 30 mL H_2O and extracted with 30 mL EtOAc three times. The combined organic layers were washed with 30 mL brine and dried over anhydrous Na_2SO_4. Then, the solvent was removed under reduced pressure. The resulting mixture was purified by column chromatography on silica gel (eluted with petroleum ether) to afford the desired product **2z** as a white solid (386.0 mg, 90% yield). ^{1}H NMR (600 MHz, $CDCl_3$). δ = 7.42–7.36 (m, 4H), 7.30–7.23 (m, 4H). The spectral data is identical to those reported previously.[3]



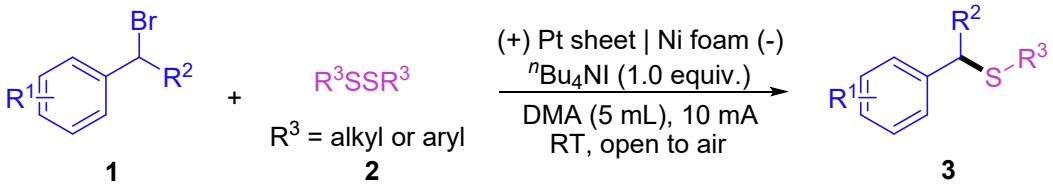
1,2-bis(4-bromophenyl)disulfane (2aa). To a 25 mL vial equipped with a stir bar were added 4-bromobenzenethiol (567.2 mg, 3.0 mmol, 1.0 equiv.), MeCN (10 mL), and deionized water (2 mL). I_2 (380.7 mg, 1.5 mmol, 0.5 equiv.) was added in one portion and the mixture was stirred at room temperature for 1 h. Upon completion, the reaction mixture was poured into 30 mL H_2O and extracted with 30 mL EtOAc three times. The combined organic layers were

washed with 30 mL brine and dried over anhydrous Na_2SO_4. Then, the solvent was removed under reduced pressure. The resulting mixture was purified by column chromatography on silica gel (eluted with petroleum ether) to afford the desired product **2aa** as a white solid (510.2 mg, 91% yield). ^{1}H NMR (600 MHz, $CDCl_3$). δ = 7.43 (dd, *J* = 8.4, 1.8 Hz, 4H), 7.33 (dd, *J* = 8.6, 1.7 Hz, 4H). The spectral data is identical to those reported previously.[2]



1,2-bis(4-(trifluoromethyl)phenyl)disulfane (2ad). To a 25 mL vial equipped with a stirring bar were added 4-(trifluoromethyl)benzenethiol (534.0 mg, 3.0 mmol, 1.0 equiv.) and EtOH (10 mL). The mixture was stirred at room temperature, open to air, for 16 h. Upon completion, the reaction mixture was poured into 30 mL H_2O and extracted with 30 mL EtOAc three times. The combined organic layers were washed with 30 mL brine and dried over anhydrous Na_2SO_4. Then, the solvent was removed under reduced pressure. The resulting mixture was purified by column chromatography on silica gel (eluted with ethyl acetate/petroleum ether) to afford the desired product **2ad** as a colorless oil (398.3 mg, 75% yield). ^{1}H NMR (600 MHz, $CDCl_3$). δ = 7.61–7.55 (m, 8H). The spectral data is identical to those reported previously.[4]

5. General procedure for the electrochemical synthesis of product 3



To a 10 mL standard IKA vessel were added bromide (**1**) (0.5 mmol, 1.0 equiv.), disulfide (**2**) (0.75 mmol, 1.5 equiv.), electrolyte ^{n}Bu$_4$NI (0.5 mmol, 1.0 equiv.), DMA (5 mL) and a magnetic stirring bar. A platinum plate (52 mm x 8 mm x 0.2 mm) was used as the anode, and a nickel foam (52 mm x 8 mm x 2 mm) was used as the cathode (the electrodes were immersed

1 cm in the reaction solution). The constant current (10 mA) electrolysis was then performed at room temperature under air atmosphere with vigorous stirring (600 rpm). Upon completion, the reaction mixture was poured into 30 mL H_2O and extracted with 30 mL EtOAc for three times. The combined organic layers were washed with 30 mL brine and dried over anhydrous Na_2SO_4. Then, the solvent was removed under reduced pressure. The resulting mixture was purified by column chromatography on silica gel (eluted with ethyl acetate/petroleum ether) to afford the desired product **3**.

6. Mechanistic investigation

6.1. Cyclic voltammetry experiments

The cyclic voltammetry experiments were carried out with a computer-controlled electrochemical analyzer for electrochemical measurements. The solution of interest was sparged with argon for 5 minutes before data collection with the CHI 700E potentiostat (CH Instruments, Inc.). The experiment was performed in a three-electrode cell with DMA (10 mL) as the solvent, $^{n}Bu_4NBF_4$ (0.05 M) as the supporting electrolyte, and the concentration of the tested compounds (**1a**, **2a**, $^{n}Bu_4NI$) was 2.0 mM. The scan speed was 100 mV/s. The oxidation potential ranges investigated were 0 V to +2.0 V *vs.* Ag/AgCl (saturated aqueous KCl) and reduction potential ranges investigated were -3.0 V to 0 V *vs.* Ag/AgCl (saturated aqueous KCl). CV plotting convention is IUPAC.

Working electrode: The working electrode is a 3 mm diameter glassy carbon working electrode. Polished with 0.05 μm aluminum oxide and then sonicated in distilled water and ethanol before measurements.

Reference electrode: The reference electrode is Ag/AgCl (saturated aqueous KCl) that was washed with water and ethanol before measurements.

Counter electrode: The counter electrode is a platinum wire that was polished with 0.05 μm aluminum oxide and then sonicated in distilled water and ethanol before measurements.

The onset potential for the oxidation of $^{n}Bu_4NI$ is around +0.75 V and the E_{ox} is approximately

+1.17 V. No oxidation peak of **1a** was detected. The onset potential for the oxidation of **2a** is around +1.10 V and the E_{ox} is approximately +1.23 V (Figure S4). The onset potential for the oxidation of **3a** is around +1.76 V and the E_{ox} is approximately +2.09 V (Figure S5). The onset potential for the reduction of **1a** is around -1.01 V and the E_{red} is approximately -2.09 V, the onset potential for the reduction of **2a** is around -1.50 V and the E_{red} is approximately -2.08 V, the onset potential for the reduction of Benzyl iodide (**7**) is around -1.11 V and the E_{red} is approximately -1.68 V. No reduction peak of $^{n}Bu_4NI$ was detected. $^{n}Bu_4NI$ was added to **1a**, and the reduction potential of **1a** remained basically unchanged after stirring for 10 min, 20 min and 30 min respectively.

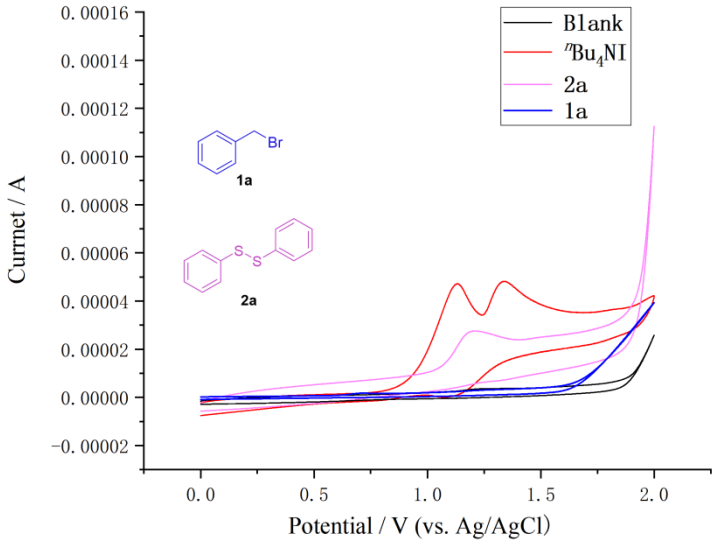


Figure S4. Cyclic voltammogram of **1a**, **2a** and $^{n}Bu_4NI$ in an electrolyte of $^{n}Bu_4NBF_4$ (0.05 M) in DMA from 0 to +2.0 V.

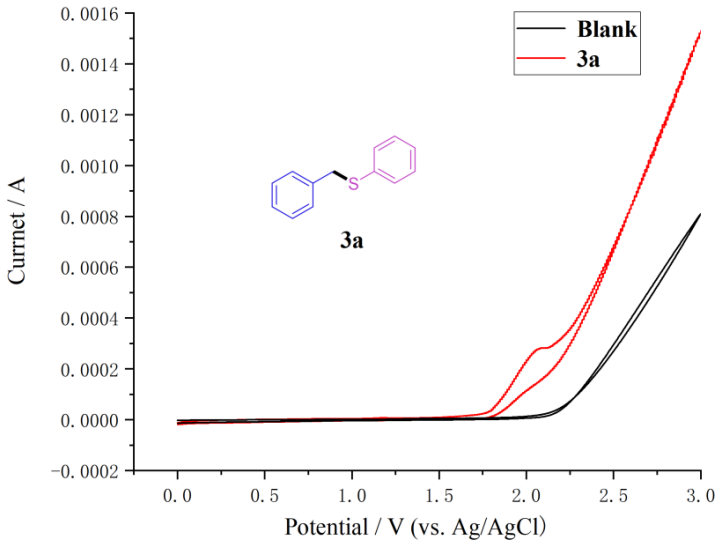


Figure S5. Cyclic voltammogram of **3a** in an electrolyte of $^{n}Bu_4NBF_4$ (0.05 M) in DMA from 0 to +3.0 V.

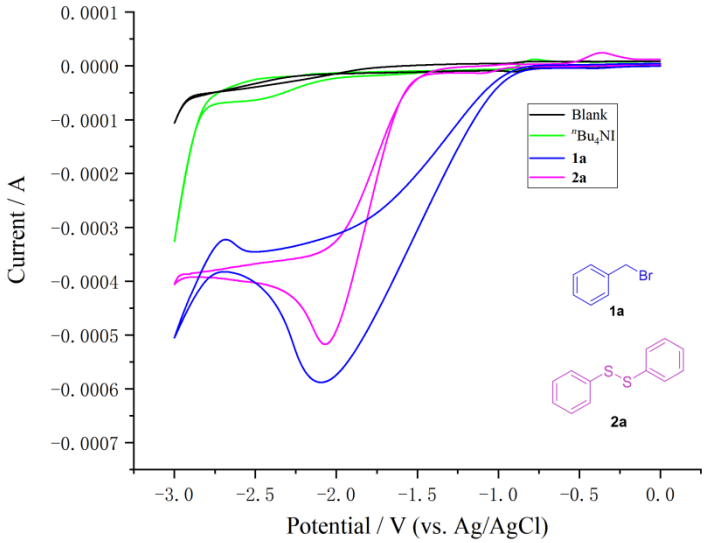


Figure S6. Cyclic voltammogram of $^{n}Bu_4NI$, **1a** and **2a** in an electrolyte of $^{n}Bu_4NBF_4$ (0.05 M) in DMA from 0 to -3.0 V.

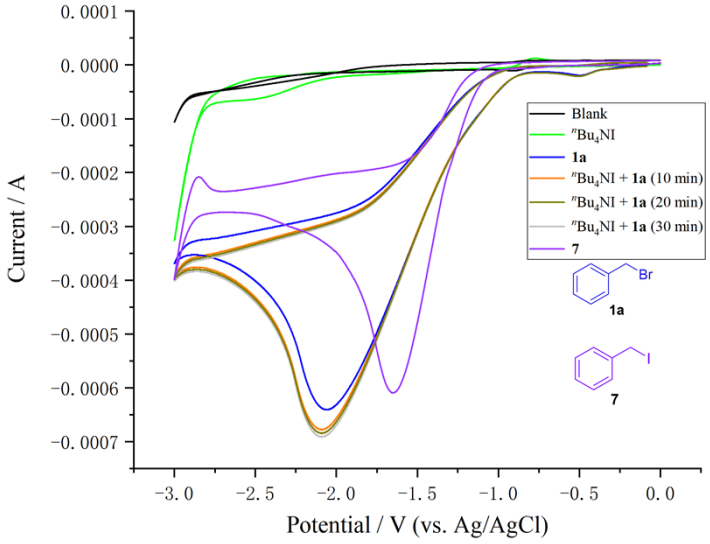


Figure S7. Cyclic voltammogram of $^{n}Bu_4NI$, **1a**, benzyl iodide and **1a** + $^{n}Bu_4NI$ in an electrolyte of $^{n}Bu_4NBF_4$ (0.05 M) in DMA from 0 to -3.0 V.

6.2. Radical trapping experiments

Under standard conditions, TEMPO (4.0 equiv. to **1a**) or 1,1-diphenylethylene (4.0 equiv. to **1a**) was added to the model reaction system at the beginning of the reaction. After 4 h, a small amount of reaction mixture was taken out for high-resolution mass spectrometry (HRMS) measurement.

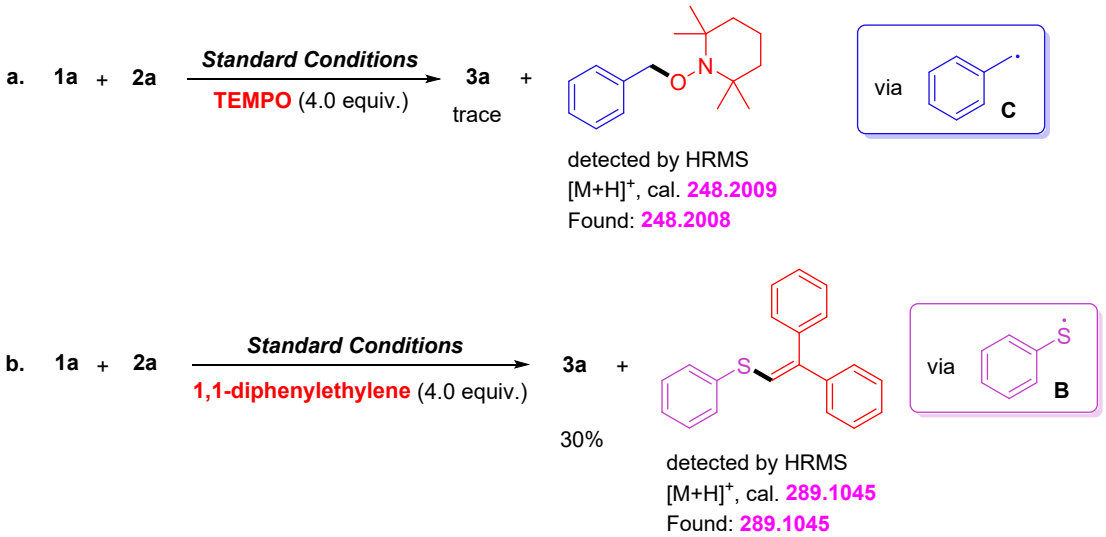


Figure S8. Radical trapping experiments.

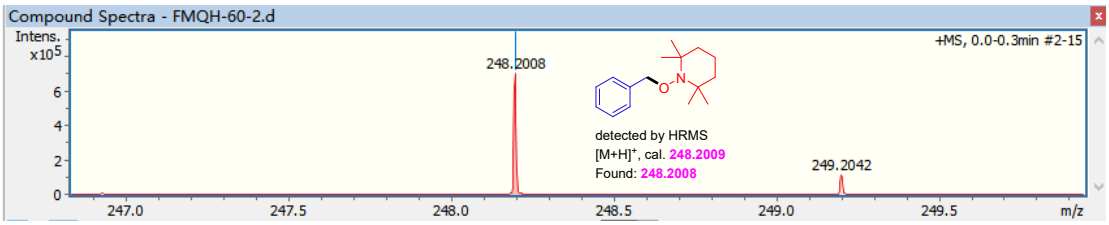


Figure S9. HRMS data of the radical trapping experiment (with TEMPO).

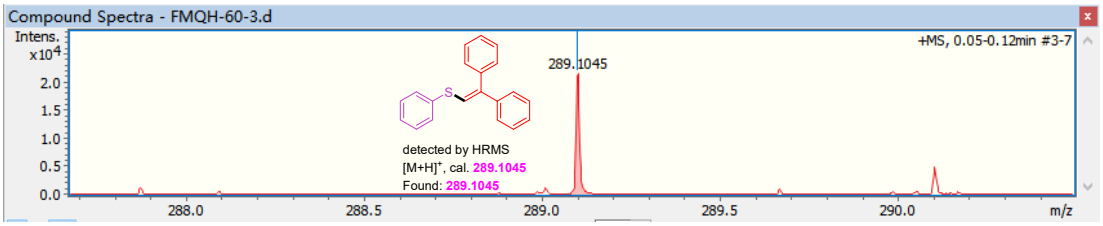
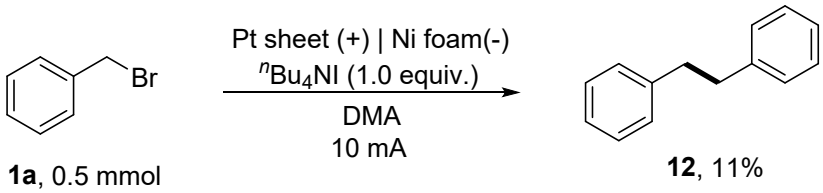


Figure S10. HRMS data of the radical trapping experiment (with 1,1-diphenylethylene).

6.3. Radical validation experiments



1a, 0.5 mmol

12, 11%

To a 10 mL standard IKA vessel were added bromide (**1a**) (0.5 mmol, 1.0 equiv.), electrolyte $^{n}Bu_4NI$ (0.5 mmol, 1.0 equiv.), DMA (5 mL) and a magnetic stirring bar. A platinum plate (52 mm x 8 mm x 0.2 mm) was used as the anode, and a nickel foam (52 mm x 8 mm x 2 mm) was used as the cathode (the electrodes were immersed 1 cm in the reaction solution). The constant current (10 mA) electrolysis was then performed at room temperature under air atmosphere with vigorous stirring (600 rpm). Upon completion, the reaction mixture was poured into 30 mL H_2O and extracted with 30 mL EtOAc for three times. The combined organic layers were washed with 30 mL brine and dried over anhydrous Na_2SO_4. Then, the solvent was removed under reduced pressure. The resulting mixture was purified by column chromatography on silica gel (eluted with petroleum ether) to afford product **12**. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.27 (m, *J* = 7.5 Hz, 4H), 7.18 (m, *J* = 7.7 Hz, 6H), 2.92 (s, 4H). ^{13}C NMR

(151 MHz, Chloroform-*d*) δ 141.8, 128.5, 128.4, 126.0, 38.0. The spectral data is identical to those reported previously[18].

6.4. Divided cell experiments

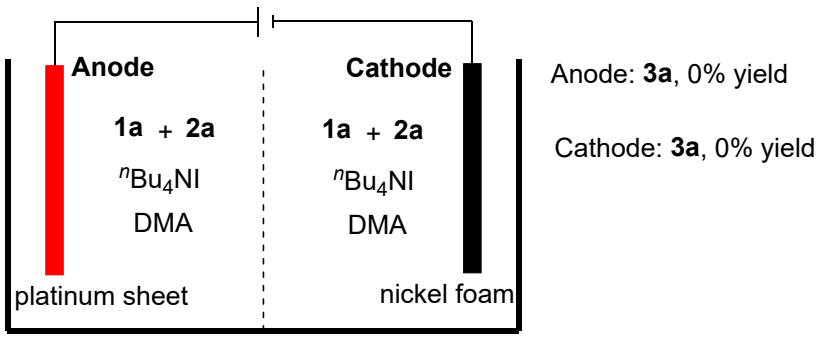


Figure S11. Divided cell experiments

To the left and right parts of the H-type divided electrolytic cell were added bromide (**1a**) (0.5 mmol, 1.0 equiv.), disulfide (**2a**) (0.75 mmol, 1.5 equiv.), electrolyte ^{n}Bu$_4$NI (0.5 mmol, 1.0 equiv.), 5 mL DMA and a magnetic stirrer bar. A platinum plate (10 mm x 8 mm x 0.2 mm) was used as the anode and a nickel foam (10 mm x 8 mm x 2 mm) was used as the cathode. The constant current (10 mA) electrolysis was then performed at room temperature under air atmosphere with vigorous stirring (600 rpm) for 6 h. Through TLC detection, no target product **3a** was detected at either the anode or the cathode.

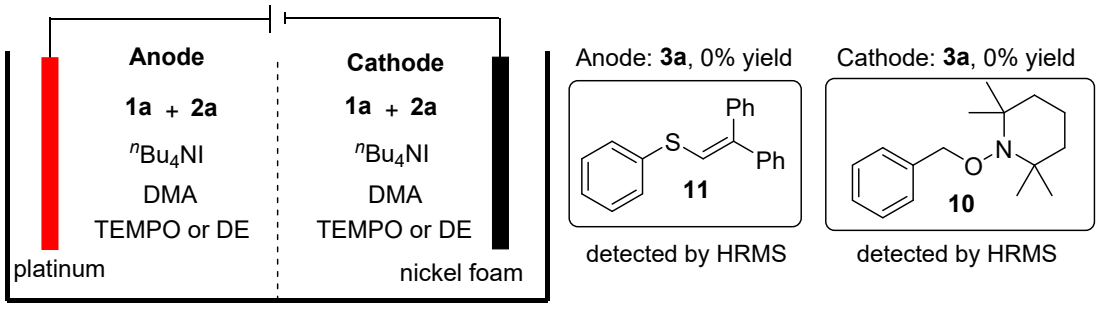
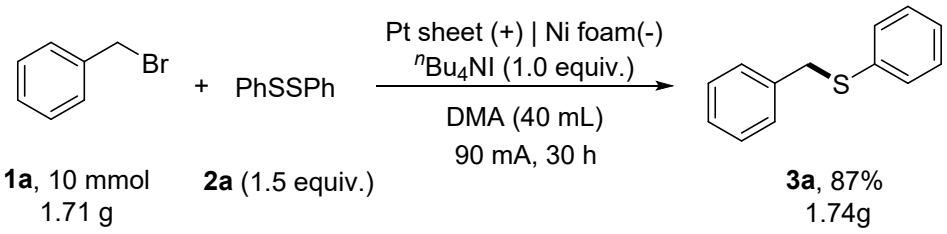


Figure S12. Radical trapping experiments in a divided cell

Under the conditions of the aforementioned divided cell experiment (Figure S11), DE (4.0 equiv.) or TEMPO (4.0 equiv.) was added to the anode pool and cathode pool, respectively. Adduct **11** was detected at the anode, and adduct **10** was detected at the cathode.

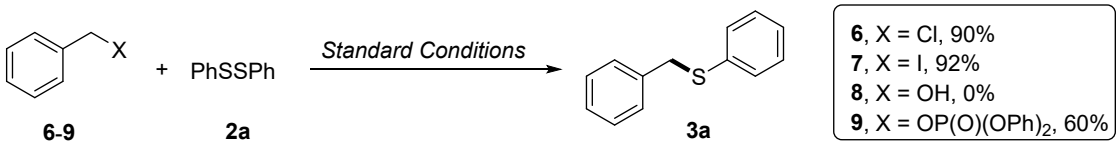
7. Synthetic application procedures

7.1. Gram-scale preparation of product 3a



To a cylindrical bottle (with a diameter of 5 cm and a height of 10 cm) were added bromide (**1a**) (10 mmol, 1.0 equiv.), disulfide (**2a**) (15 mmol, 1.5 equiv.), electrolyte ^{n}Bu$_4$NI (10 mmol, 1.0 equiv.), DMA (40 mL) and a magnetic stirring bar. A platinum plate (30 mm x 30 mm x 0.2 mm) was used as the anode and a nickel foam (30 mm x 30 mm x 2 mm) was used as the cathode. The constant current (90 mA) electrolysis was then performed at room temperature under air atmosphere with vigorous stirring (600 rpm). Upon completion, the reaction mixture was poured into 100 mL H_2O and extracted with 30 mL EtOAc three times. The combined organic layers were washed with 30 mL brine and dried over anhydrous Na_2SO_4. Then, the solvent was removed under reduced pressure. The resulting mixture was purified by column chromatography on silica gel (petroleum ether) to afford the desired product **3a** as a yellow oil (1.74 g, 87% yield).

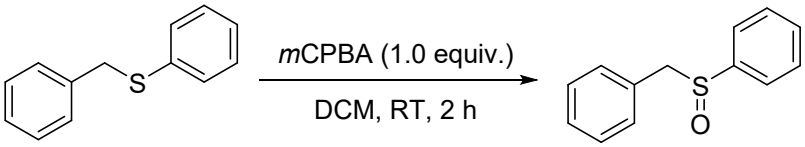
7.2. (Pseudo)halide evaluation



To a 10 mL standard IKA vessel were added benzyl halide or pseudohalide (**6-9**) (0.5 mmol, 1.0 equiv.), disulfide (**2a**) (0.75 mmol, 1.5 equiv.), ^{n}Bu$_4$NI (0.5 mmol, 1.0 equiv.), DMA (5 mL) and a magnetic stirring bar. A platinum plate (52 mm x 8 mm x 0.2 mm) was used as the anode and a nickel foam (52 mm x 8 mm x 2 mm) was used as cathode (the electrodes were immersed 1 cm in the reaction solution). The constant current (10 mA) electrolysis was then performed at room temperature under air atmosphere with vigorous stirring (600 rpm). Upon completion,

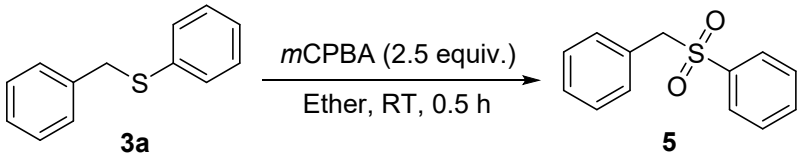
the reaction mixture was poured into 30 mL H_2O and extracted with 30 mL EtOAc three times. The combined organic layers were washed with 30 mL brine and dried over anhydrous Na_2SO_4. Then, the solvent was removed under reduced pressure. The resulting mixture was purified by column chromatography on silica gel (eluted with petroleum ether) to afford the desired product **3a**.

7.3. The procedure for the conversion of product 3a into sulfoxide 4 and sulfone 5



3a **4**

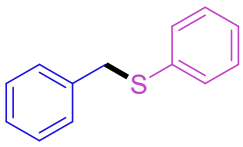
(benzylsulfinyl)benzene (4). To a 20 mL vial equipped with a stirring bar were added benzyl(phenyl)sulfane (**3a**) (100.0 mg, 0.5 mmol, 1.0 equiv.), *m*CPBA (86.3 mg, 1.0 equiv.) and DCM (5.0 mL). The mixture was stirred at room temperature, open to air, for 4 h. Upon completion, the reaction mixture was poured into 30 mL H_2O and extracted with 30 mL DCM three times. The combined organic layers were washed with 30 mL brine and dried over anhydrous Na_2SO_4. Then, the solvent was removed under reduced pressure. The resulting mixture was purified by column chromatography on silica gel (eluted with ethyl acetate/petroleum ether) to afford the desired product **4** as a white solid (86.5 mg, 80% yield). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.47 – 7.35 (m, 5H), 7.30 – 7.21 (m, 3H), 6.98 (d, J = 7.1 Hz, 2H), 4.10 (d, J = 12.6 Hz, 1H), 4.00 (d, J = 12.6 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-d) δ 131.2, 130.4, 129.2, 128.9, 128.5, 128.3, 124.5, 63.7. The spectral data is identical to those reported previously[16].



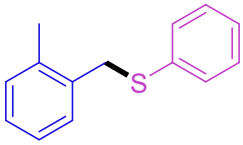
3a **5**

(benzylsulfonyl)benzene (5). To a 20 mL vial equipped with a stirring bar were added benzyl(phenyl)sulfane (**3a**) (100.0 mg, 0.5 mmol, 1.0 equiv.), *m*CPBA (215.8 mg, 2.5 equiv.) and diethyl ether (5.0 mL). The mixture was stirred at room temperature, open to air, for 0.5 h. Upon completion, the reaction mixture was poured into 30 mL H_2O and extracted with 30 mL EtOAc three times. The combined organic layers were washed with 30 mL brine and dried over anhydrous Na_2SO_4. Then, the solvent was removed under reduced pressure. The resulting mixture was purified by column chromatography on silica gel (eluted with ethyl acetate/petroleum ether) to afford the desired product **5** as a white solid (103.4 mg, 89% yield). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.65 – 7.57 (m, 3H), 7.46 – 7.42 (m, 2H), 7.33 – 7.28 (m, 1H), 7.25 (dd, J = 8.2, 6.7 Hz, 2H), 7.10 – 7.04 (m, 2H), 4.31 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 137.9, 133.7, 130.8, 128.9, 128.8, 128.6, 128.6, 128.1, 62.9. The spectral data is identical to those reported previously[17].

8. Characterization data of products

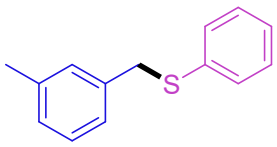


Benzyl(phenyl)sulfane (3a)[5]: R_f = 0.25 (100% Petroleum ether). 95.1 mg, 95% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 7.7 Hz, 2H), 7.29 – 7.25 (m, 4H), 7.25 – 7.21 (m, 3H), 7.18 (d, *J* = 7.4 Hz, 1H), 4.11 (s, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 137.5, 136.4, 129.9, 128.9, 128.9, 128.5, 127.2, 126.4, 39.2.

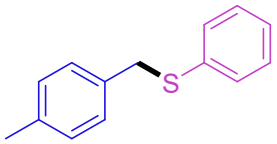


(2-Methylbenzyl)(phenyl)sulfane (3b)[5]: R_f = 0.25 (100% Petroleum ether). 91.3 mg, 80% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 7.7 Hz, 2H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.15 (t, *J* = 6.0 Hz, 3H), 7.11 – 7.06 (m, 1H), 4.10 (s, 2H), 2.39 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 136.8, 136.7, 135.1, 130.5, 130.3, 129.8,

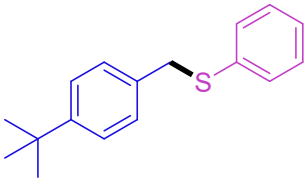
128.9, 127.5, 126.5, 126.0, 37.5, 19.2.



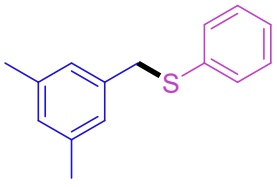
(3-Methylbenzyl)(phenyl)sulfane (3c)[5]: R_f = 0.25 (100% Petroleum ether). 94.4 mg, 88% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.33 – 7.28 (m, 2H), 7.26 – 7.21 (m, 2H), 7.17 (dp, *J* = 7.7, 2.9, 2.4 Hz, 2H), 7.12 – 7.06 (m, 2H), 7.04 (d, *J* = 7.6 Hz, 1H), 4.08 (s, 2H), 2.30 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 138.2, 137.3, 136.6, 129.8, 129.6, 128.9, 128.4, 128.0, 126.3, 125.9, 39.1, 21.4.



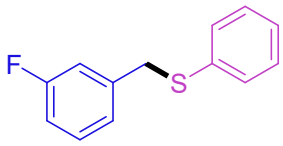
(4-Methylbenzyl)(phenyl)sulfane (3d)[5]: R_f = 0.25 (100% Petroleum ether). 98.5 mg, 92% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 6.8 Hz, 2H), 7.26 – 7.23 (m, 2H), 7.20 – 7.14 (m, 3H), 7.08 (d, *J* = 7.6 Hz, 2H), 4.09 (s, 2H), 2.31 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 136.9, 136.6, 134.3, 129.7, 129.2, 128.8, 128.7, 126.2, 38.8, 21.1.



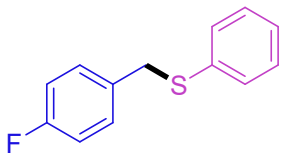
(4-(Tert-butyl)benzyl)(phenyl)sulfane (3e)[5]: R_f = 0.25 (100% Petroleum ether). 108.8 mg, 85% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.31 (dd, *J* = 8.0, 5.0 Hz, 4H), 7.27 – 7.22 (m, 4H), 7.17 (t, *J* = 7.5 Hz, 1H), 4.11 (s, 2H), 1.30 (s, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 150.2, 136.9, 134.3, 129.4, 128.8, 128.5, 126.1, 125.5, 38.5, 34.5, 31.4.



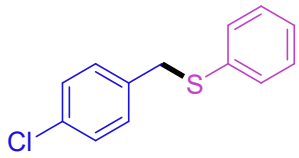
(3,5-Dimethylbenzyl)(phenyl)sulfane (3f)[5]: R_f = 0.25 (100% Petroleum ether). 92.1 mg, 80% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.33 – 7.29 (m, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.17 (td, *J* = 7.0, 3.3 Hz, 1H), 6.91 (s, 2H), 6.87 (s, 1H), 4.05 (s, 2H), 2.27 (s, 6H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 138.1, 137.1, 136.8, 129.6, 128.9, 128.8, 126.7, 126.2, 39.0, 21.2.



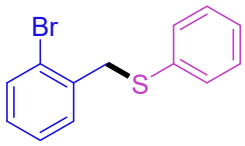
(3-Fluorobenzyl)(phenyl)sulfane (3g)[5]: R_f = 0.25 (100% Petroleum ether). 94.9 mg, 87% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.32 – 7.27 (m, 2H), 7.24 (dtd, *J* = 14.3, 7.7, 2.5 Hz, 3H), 7.20 – 7.17 (m, 1H), 7.03 (d, *J* = 7.5 Hz, 1H), 7.02 – 6.97 (m, 1H), 6.91 (td, *J* = 8.4, 2.9 Hz, 1H), 4.07 (s, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 162.8 (d, *J* = 246.1 Hz), 140.2 (d, *J* = 7.3 Hz), 135.7, 130.2, 129.9 (d, *J* = 8.3 Hz), 128.9, 126.7, 124.5 (d, *J* = 2.7 Hz), 115.7 (d, *J* = 21.9 Hz), 114.1 (d, *J* = 21.1 Hz), 38.8 (d, *J* = 1.4 Hz). ^{19}F NMR (565 MHz, Chloroform-*d*) δ -113.14.



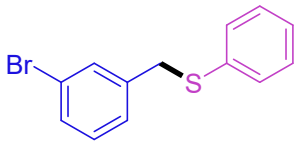
(4-Fluorobenzyl)(phenyl)sulfane (3h)[5]: R_f = 0.25 (100% Petroleum ether). 99.1 mg, 91% yield. Yellow solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 7.2 Hz, 2H), 7.23 (ddd, *J* = 14.3, 8.7, 6.3 Hz, 4H), 7.19 (d, *J* = 7.2 Hz, 1H), 6.95 (tt, *J* = 9.1, 3.1 Hz, 2H), 4.07 (s, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 162.0 (d, *J* = 245.6 Hz), 135.9, 133.3, 130.4 (d, *J* = 8.1 Hz), 130.3, 128.9, 126.6, 115.3 (d, *J* = 21.5 Hz), 38.5. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -115.39.



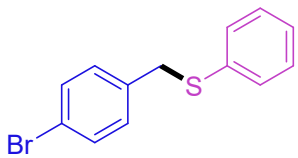
(4-Chlorobenzyl)(phenyl)sulfane (3i)[5]: R_f = 0.25 (100% Petroleum ether). 105.3 mg, 90% yield. White solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 7.1 Hz, 2H), 7.26 – 7.21 (m, 4H), 7.21 – 7.16 (m, 3H), 4.05 (d, *J* = 2.9 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 136.2, 135.7, 133.0, 130.3, 130.1, 128.9, 128.6, 126.7, 38.6.



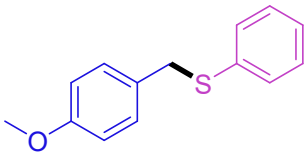
(2-Bromobenzyl)(phenyl)sulfane (3j)[6]: R_f = 0.25 (100% Petroleum ether). 112.7 mg, 81% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.56 (dd, *J* = 8.3, 4.6 Hz, 1H), 7.33 (d, *J* = 7.3 Hz, 2H), 7.27 – 7.22 (m, 3H), 7.19 (dt, *J* = 14.1, 7.8 Hz, 2H), 7.09 (t, *J* = 7.6 Hz, 1H), 4.21 (d, *J* = 3.8 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 136.9, 135.7, 133.0, 130.8, 130.7, 128.9, 128.8, 127.4, 126.8, 124.5, 39.8.



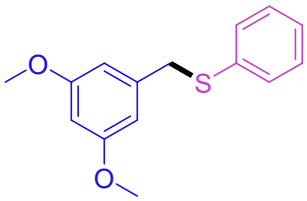
(3-Bromobenzyl)(phenyl)sulfane (3k)[6]: R_f = 0.25 (100% Petroleum ether). 120.1 mg, 86% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.45 – 7.39 (m, 1H), 7.37 – 7.32 (m, 1H), 7.31 – 7.27 (m, 2H), 7.27 – 7.23 (m, 2H), 7.22 – 7.16 (m, 2H), 7.13 (dq, *J* = 7.7, 3.7 Hz, 1H), 4.04 (s, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 130.0, 135.6, 131.9, 130.4, 130.3, 130.0, 129.0, 127.4, 126.8, 122.5, 38.8.



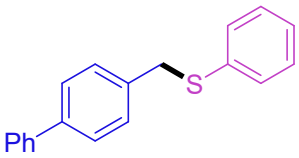
(4-Bromobenzyl)(phenyl)sulfane (3l)[5]: R_f = 0.25 (100% Petroleum ether). 127.7 mg, 92% yield. Yellow solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.38 (dt, *J* = 8.9, 2.8 Hz, 2H), 7.29 – 7.23 (m, 4H), 7.19 (td, *J* = 5.8, 2.5 Hz, 1H), 7.13 (dt, *J* = 8.8, 2.8 Hz, 2H), 4.03 (s, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 136.7, 135.7, 131.6, 130.5, 130.3, 129.0, 126.7, 121.1, 38.7.



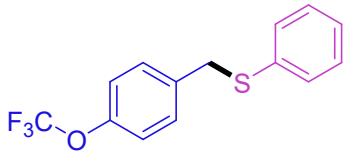
(4-Methoxybenzyl)(phenyl)sulfane (3m)[7]: R_f = 0.25 (Petroleum ether/EtOAc, 10:1). 113.8 mg, 99% yield. Yellow solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.32 – 7.27 (m, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.22 – 7.19 (m, 2H), 7.19 – 7.15 (m, 1H), 6.81 (dt, *J* = 9.0, 2.8 Hz, 2H), 4.07 (s, 2H), 3.78 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.8, 136.6, 129.9, 129.8, 129.4, 128.8, 126.3, 113.9, 55.3, 38.5.



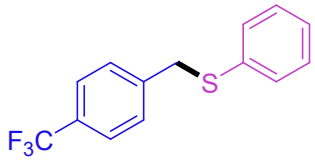
(3,5-Dimethoxybenzyl)(phenyl)sulfane (3n)[new]: R_f = 0.25 (Petroleum ether/EtOAc, 10:1). 104.3 mg, 80% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.35 – 7.29 (m, 2H), 7.27 – 7.24 (m, 2H), 7.21 – 7.15 (m, 1H), 6.45 (d, *J* = 2.5 Hz, 2H), 6.34 (s, 1H), 4.05 (s, 2H), 3.74 (s, 6H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 160.8, 139.8, 136.4, 129.9, 128.9, 126.4, 106.7, 99.5, 55.3, 39.4. HRMS (ESI): m/z: calcd for $C_{15}H_{17}O_2S$ ($M+H^+$) 261.0944; found 261.0943.



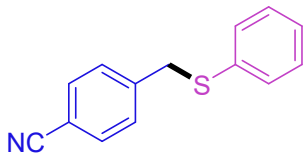
([1,1'-Biphenyl]-4-ylmethyl)(phenyl)sulfane (3o)[8]: R_f = 0.25 (100% Petroleum ether). 127.1 mg, 92% yield. Yellow solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.59 – 7.54 (m, 2H), 7.53 – 7.49 (m, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.34 (dd, *J* = 11.6, 7.8 Hz, 5H), 7.25 (dd, *J* = 14.6, 6.1 Hz, 3H), 7.18 (t, *J* = 7.4 Hz, 1H), 4.15 (s, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 140.8, 140.1, 136.6, 136.4, 129.9, 129.3, 128.9, 128.8, 127.3, 127.2, 127.0, 126.4, 38.9.



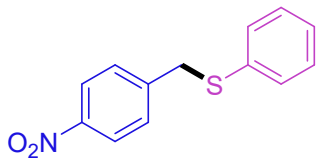
Phenyl(4-(trifluoromethoxy)benzyl)sulfane (3p)[9]: R_f = 0.25 (100% Petroleum ether). 122.3 mg, 86% yield. Yellow solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.31 – 7.23 (m, 6H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.11 (d, *J* = 8.1 Hz, 2H), 4.08 (s, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 148.3, 136.4, 135.6, 130.4, 130.1, 128.9, 126.8, 121.0, 120.5 (q, *J* = 257.1 Hz), 38.5. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -57.88.



Phenyl(4-(trifluoromethyl)benzyl)sulfane (3q)[8]: R_f = 0.25 (100% Petroleum ether). 127.1 mg, 95% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 7.9 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.25 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 4.12 (s, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 141.9, 135.4, 130.5, 129.4 (q, *J* = 32.4 Hz), 129.1, 129.0, 126.9, 125.4 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 273.0 Hz), 38.9. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -62.49.

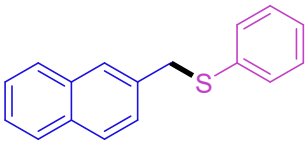


4-((Phenylthio)methyl)benzonitrile (3r)[6]: R_f = 0.25 (Petroleum ether/EtOAc, 10:1). 103.0 mg, 91% yield. Yellow solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.55 – 7.51 (m, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.28 – 7.23 (m, 4H), 7.21 (dd, *J* = 8.4, 4.4 Hz, 1H), 4.09 (s, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 143.4, 134.7, 132.3, 130.9, 129.5, 129.1, 127.2, 118.8, 111.0, 39.2.

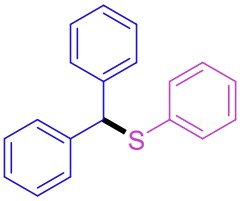


(4-Nitrobenzyl)(phenyl)sulfane (3s)[8]: R_f = 0.25 (Petroleum ether/EtOAc, 10:1). 110.8 mg,

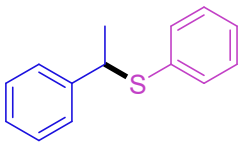
90% yield. Yellow solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.29 – 7.24 (m, 4H), 7.24 – 7.20 (m, 1H), 4.13 (s, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 147.1, 145.6, 134.5, 131.1, 129.6, 129.1, 127.3, 123.7, 39.0.



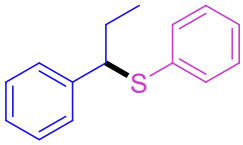
(Naphthalen-2-ylmethyl)(phenyl)sulfane (3t)[8]: R_f = 0.25 (100% Petroleum ether). 102.6 mg, 82% yield. Yellow solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.79 (dd, *J* = 12.0, 7.2 Hz, 2H), 7.76 – 7.72 (m, 1H), 7.67 (s, 1H), 7.48 – 7.42 (m, 3H), 7.32 (d, *J* = 7.4 Hz, 2H), 7.25 – 7.21 (m, 2H), 7.17 (t, *J* = 7.4 Hz, 1H), 4.27 (s, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 136.3, 135.0, 133.3, 132.6, 130.1, 128.9, 128.3, 127.7, 127.7, 127.4, 127.0, 126.5, 126.1, 125.8, 39.5.



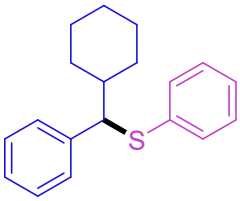
Penzhydryl(phenyl)sulfane (3u)[10]: R_f = 0.25 (100% Petroleum ether). 98.0 mg, 71% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 7.5 Hz, 4H), 7.28 (t, *J* = 7.6 Hz, 4H), 7.22 (t, *J* = 7.8 Hz, 4H), 7.16 (t, *J* = 7.4 Hz, 2H), 7.14 – 7.10 (m, 1H), 5.53 (s, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 141.1, 136.2, 130.6, 128.7, 128.6, 128.5, 127.3, 126.6, 57.5.



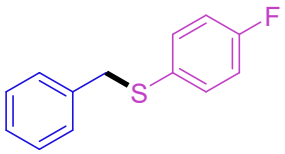
Phenyl(1-phenylethyl)sulfane (3v)[5]: R_f = 0.25 (100% Petroleum ether). 99.5 mg, 93% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.32 – 7.24 (m, 6H), 7.20 (d, *J* = 7.6 Hz, 4H), 4.33 (q, *J* = 6.9 Hz, 1H), 1.62 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 143.2, 135.2, 132.5, 128.7, 128.4, 127.3, 127.1, 48.1, 22.4.



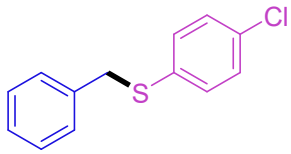
Phenyl(1-phenylpropyl)sulfane (3w)[10]: R_f = 0.25 (100% Petroleum ether). 97.1 mg, 85% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.24 (td, *J* = 9.1, 7.8, 4.4 Hz, 6H), 7.18 (dd, *J* = 10.8, 5.6 Hz, 4H), 4.04 (dd, *J* = 8.8, 5.8 Hz, 1H), 2.05 – 1.89 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 142.0, 135.2, 132.4, 128.6, 128.3, 127.9, 127.1, 127.0, 55.4, 29.4, 12.3.



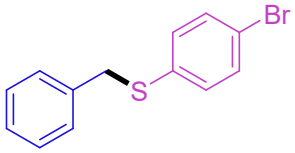
(Cyclohexyl(phenyl)methyl)(phenyl)sulfane (3x)[11]: R_f = 0.25 (100% Petroleum ether). 81.8 mg, 58% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.21 (d, *J* = 5.0 Hz, 4H), 7.18 – 7.16 (m, 2H), 7.16 – 7.06 (m, 4H), 3.96 (d, *J* = 7.9 Hz, 1H), 2.22 – 2.15 (m, 1H), 1.86 – 1.73 (m, 2H), 1.68 – 1.55 (m, 3H), 1.29 – 1.21 (m, 1H), 1.13 (dddd, *J* = 32.4, 20.5, 9.5, 6.0 Hz, 3H), 0.97 (qd, *J* = 12.3, 3.4 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 141.7, 135.9, 131.8, 128.6, 128.5, 128.0, 126.7, 126.5, 60.8, 43.5, 31.7, 31.1, 26.3, 26.3.



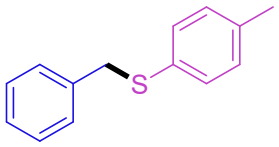
Benzyl(4-fluorophenyl)sulfane (3y)[5]: R_f = 0.25 (100% Petroleum ether). 98.2 mg, 90% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.26 (td, *J* = 6.9, 5.4, 2.2 Hz, 4H), 7.21 (t, *J* = 9.9 Hz, 3H), 6.93 (t, *J* = 8.4 Hz, 2H), 4.02 (s, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 162.1 (d, *J* = 246.8 Hz), 137.5, 133.5 (d, *J* = 8.1 Hz), 130.8 (d, *J* = 3.3 Hz), 128.9, 128.5, 127.2, 115.9 (d, *J* = 21.7 Hz), 40.5. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -114.84.



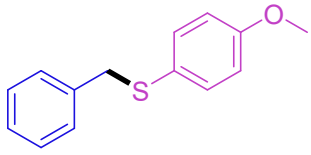
Benzyl(4-chlorophenyl)sulfane (3z)[5]: R_f = 0.25 (100% Petroleum ether). 112.2 mg, 96% yield. Yellow solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.30 – 7.28 (m, 1H), 7.28 – 7.23 (m, 4H), 7.20 (d, *J* = 1.2 Hz, 4H), 4.07 (s, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 137.1, 134.7, 132.5, 131.5, 129.0, 128.8, 128.6, 127.3, 39.4.



Benzyl(4-bromophenyl)sulfane (3aa)[5]: R_f = 0.25 (100% Petroleum ether). 131.0 mg, 94% yield. Yellow solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 8.1 Hz, 2H), 7.30 – 7.22 (m, 5H), 7.14 (d, *J* = 8.1 Hz, 2H), 4.08 (s, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 137.1, 135.4, 131.9, 131.5, 128.8, 128.6, 127.4, 120.4, 39.1.

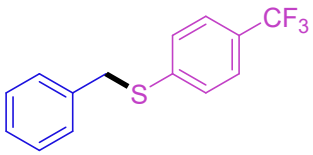


Benzyl(p-tolyl)sulfane (3ab)[5]: R_f = 0.25 (100% Petroleum ether). 101.7 mg, 95% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.26 (d, *J* = 5.9 Hz, 4H), 7.21 (d, *J* = 7.9 Hz, 3H), 7.06 (d, *J* = 7.8 Hz, 2H), 4.06 (s, 2H), 2.30 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 137.8, 136.6, 132.5, 130.8, 129.6, 128.9, 128.5, 127.1, 39.9, 21.1.

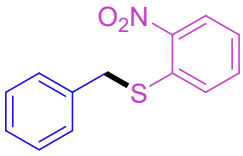


Benzyl(4-methoxyphenyl)sulfane (3ac)[5]: R_f = 0.25 (Petroleum ether/EtOAc, 10:1). 108.1 mg, 94% yield. Yellow solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.25 (dd, *J* = 8.8, 6.6 Hz, 4H), 7.21 (d, *J* = 7.0 Hz, 1H), 7.19 – 7.17 (m, 2H), 6.78 (d, *J* = 8.6 Hz, 2H), 3.98 (s, 2H), 3.77 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.2, 138.2, 134.2, 128.9, 128.4, 127.0,126.1,

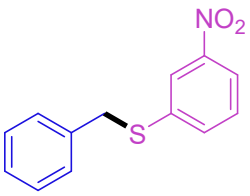
114.4, 55.3, 41.2.



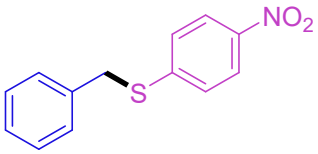
Benzyl(4-(trifluoromethyl)phenyl)sulfane (3ad)[12]: R_f = 0.25 (100% Petroleum ether). 120.8 mg, 90% yield. Yellow solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 8.1 Hz, 2H), 7.36 – 7.33 (m, 4H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.27 – 7.24 (m, 1H), 4.18 (s, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 142.1, 136.4, 128.8 (q, *J* = 32.5 Hz), 128.5, 128.0, 127.5, 125.66, 125.6 (q, *J* = 3.6 Hz), 124.2 (q, *J* = 272.1 Hz), 37.8. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -62.45.



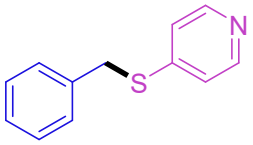
Benzyl(2-nitrophenyl)sulfane (3ae)[13]: R_f = 0.25 (Petroleum ether/EtOAc, 10:1). 74.5 mg, 61% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.23 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.54 (td, *J* = 7.6, 7.2, 1.5 Hz, 1H), 7.49 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.45 (d, *J* = 7.1 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.34 – 7.30 (m, 1H), 7.28 (dt, *J* = 6.0, 1.3 Hz, 1H), 4.23 (s, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 146.2, 137.6, 135.1, 133.4, 129.1, 128.8, 127.8, 127.2, 126.0, 124.8, 37.7.



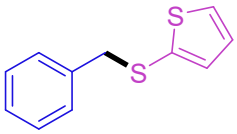
Benzyl(3-nitrophenyl)sulfane (3af)[14]: R_f = 0.25 (Petroleum ether/EtOAc, 10:1). 110.4 mg, 90% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.15 (t, *J* = 2.1 Hz, 1H), 8.05 – 7.99 (m, 1H), 7.60 – 7.54 (m, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.38 – 7.31 (m, 4H), 7.29 (d, *J* = 7.6 Hz, 1H), 4.23 (s, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 148.5, 139.4, 136.1, 134.7, 129.4, 128.8, 128.7, 127.7, 123.3, 120.8, 38.4.



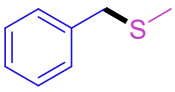
Benzyl(4-nitrophenyl)sulfane (3ag)[14]: R_f = 0.25 (Petroleum ether/EtOAc, 10:1). 114.1 mg, 93% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 8.9 Hz, 2H), 7.41 (d, *J* = 7.1 Hz, 2H), 7.37 (dd, *J* = 8.2, 5.8 Hz, 4H), 7.33 – 7.31 (m, 1H), 4.28 (s, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 147.2, 145.4, 135.5, 128.8, 128.7, 127.8, 126.8, 123.9, 37.2.



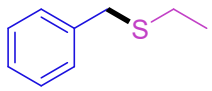
4-(Benzylthio)pyridine (3ah)[15]: R_f = 0.25 (Petroleum ether/EtOAc, 8:1). 74.6 mg, 74% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.39 – 8.36 (m, 2H), 7.39 (d, *J* = 7.1 Hz, 2H), 7.35 – 7.31 (m, 2H), 7.30 – 7.26 (m, 1H), 7.14 – 7.11 (m, 2H), 4.21 (s, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 149.2, 135.6, 135.6, 128.8, 128.7, 127.7, 120.7, 35.8.



2-(Benzylthio)thiophene (3ai)[12]: R_f = 0.25 (100% Petroleum ether). 92.7 mg, 90% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.30 (dd, *J* = 5.2, 1.5 Hz, 1H), 7.28 – 7.21 (m, 3H), 7.18 – 7.13 (m, 2H), 6.94 – 6.88 (m, 2H), 3.95 (s, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 137.7, 134.4, 133.6, 129.7, 129.0, 128.4, 127.4, 127.2, 43.9.



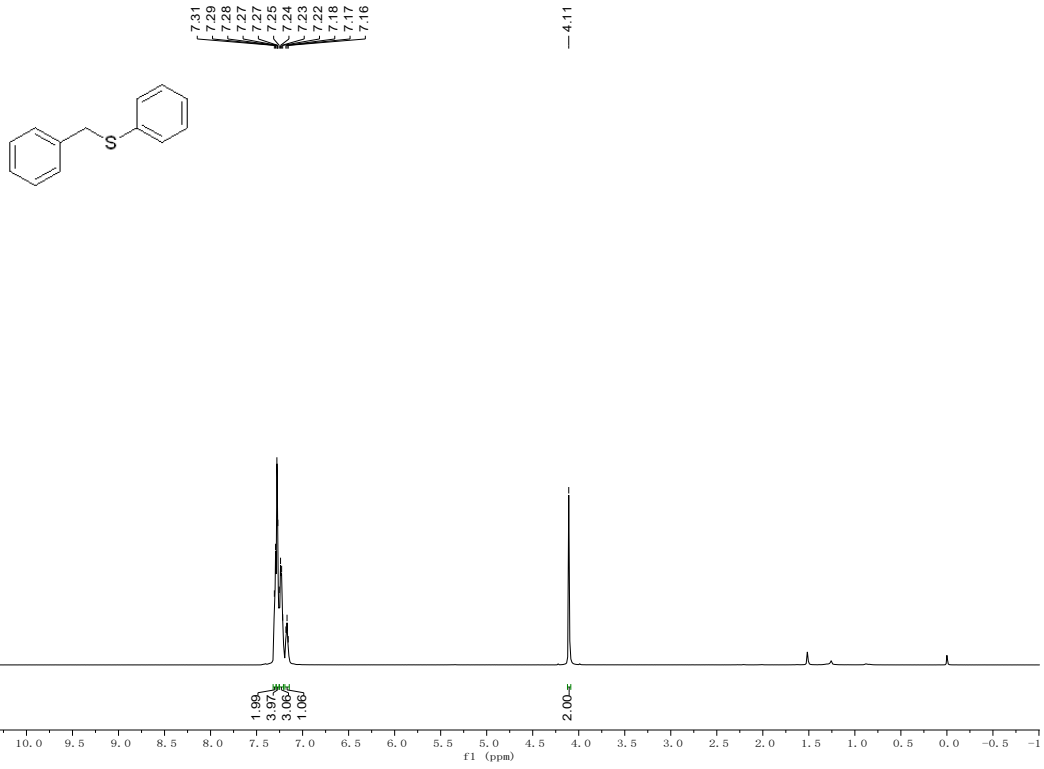
Benzyl(methyl)sulfane (3aj)[6]: R_f = 0.25 (100% Petroleum ether). 56.5 mg, 82% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.34 – 7.28 (m, 4H), 7.26 – 7.22 (m, 1H), 3.68 (s, 2H), 2.00 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 138.2, 128.9, 128.5, 127.0, 38.4, 15.0.



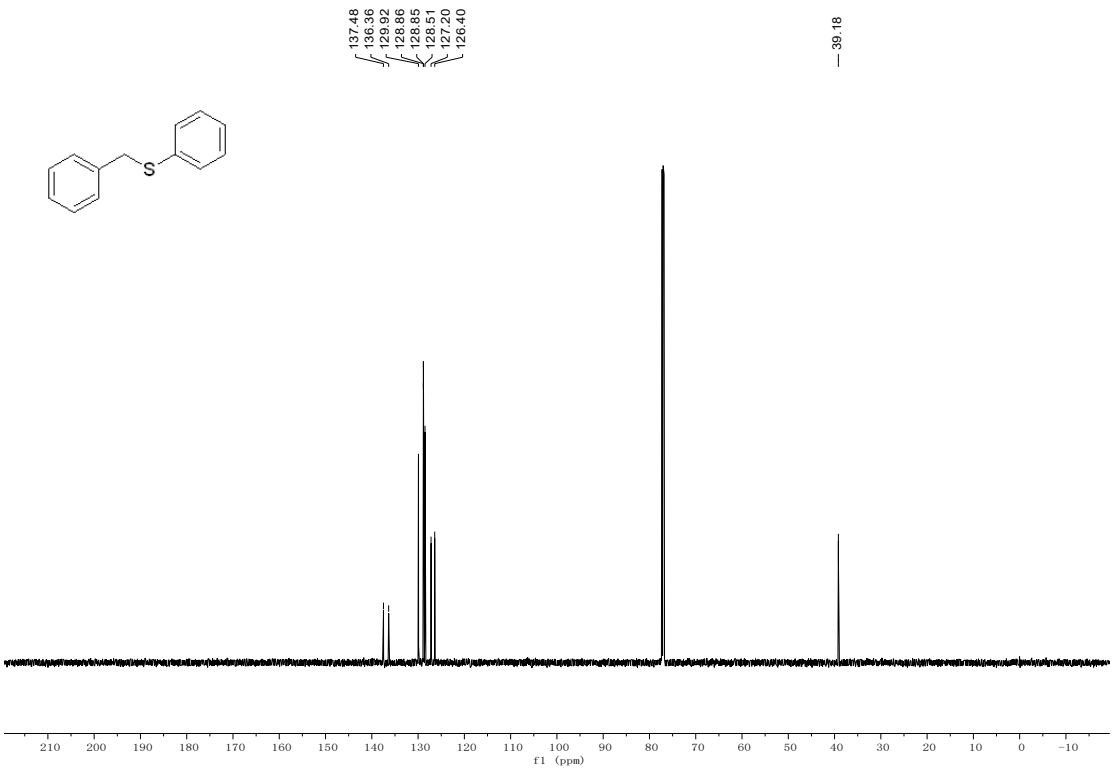
Benzyl(ethyl)sulfane (3ak)[6]: R_f = 0.25 (100% Petroleum ether). 67.2 mg, 88% yield. Yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.31 (dt, *J* = 3.1, 1.6 Hz, 4H), 7.25 – 7.21 (m, 1H), 3.72 (s, 2H), 2.44 (q, *J* = 7.3 Hz, 2H), 1.23 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 138.56, 128.8, 128.5, 126.9, 36.0, 25.3, 14.4.

9. NMR Spectra of Products

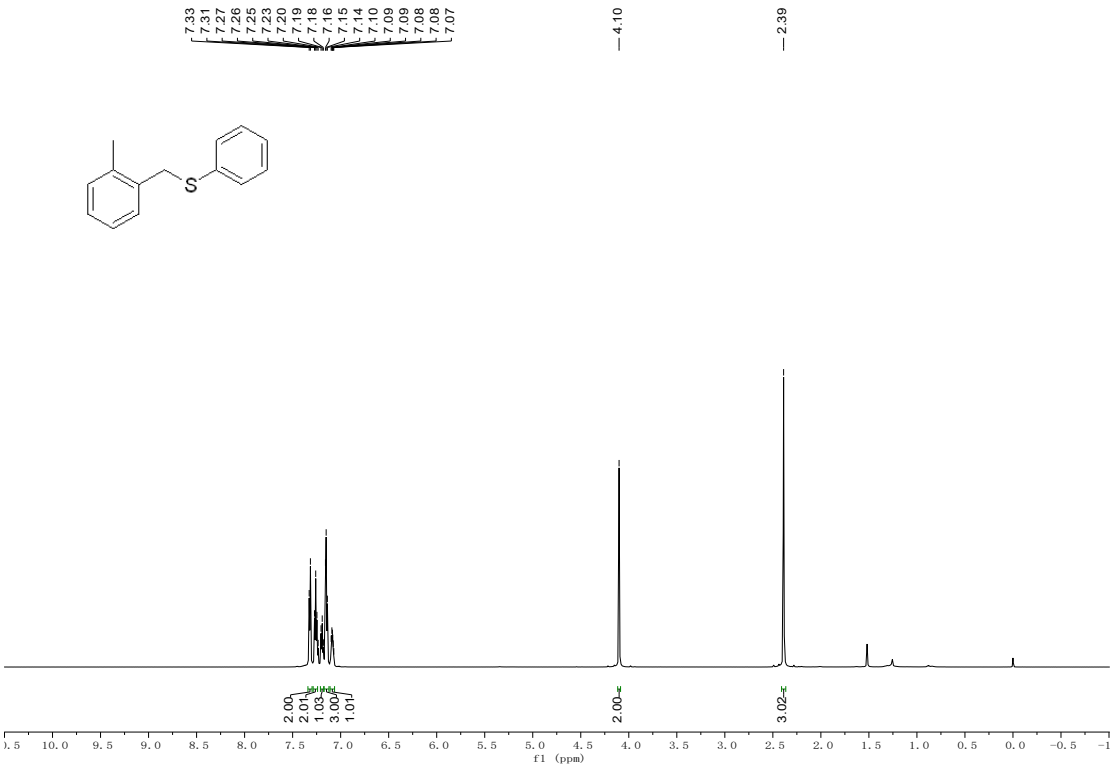
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3a



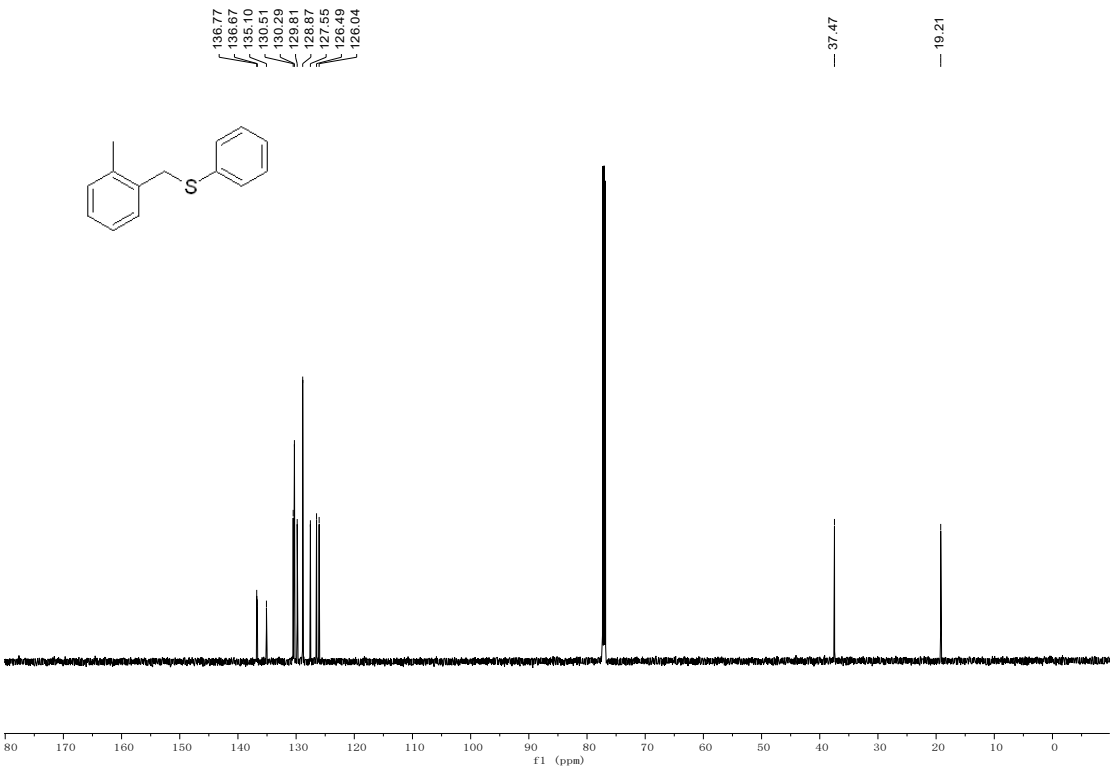
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3a



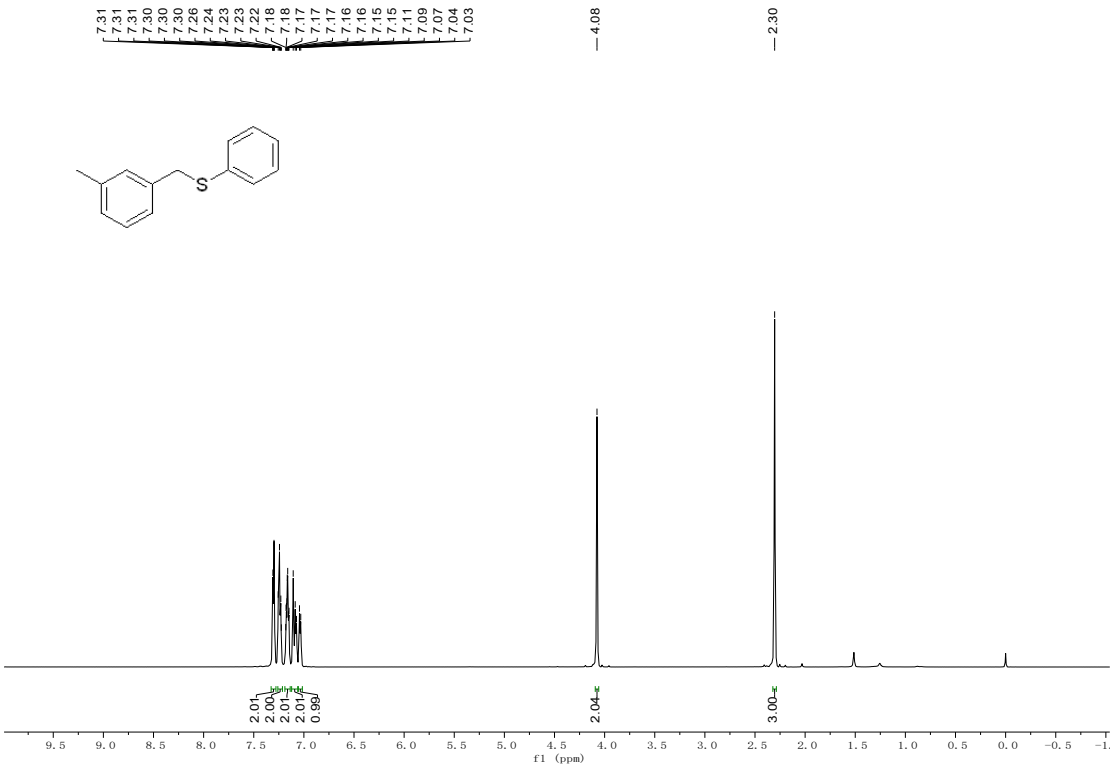
^{1}H-NMR Spectrum (400MHz, $CDCl_3$) of 3b



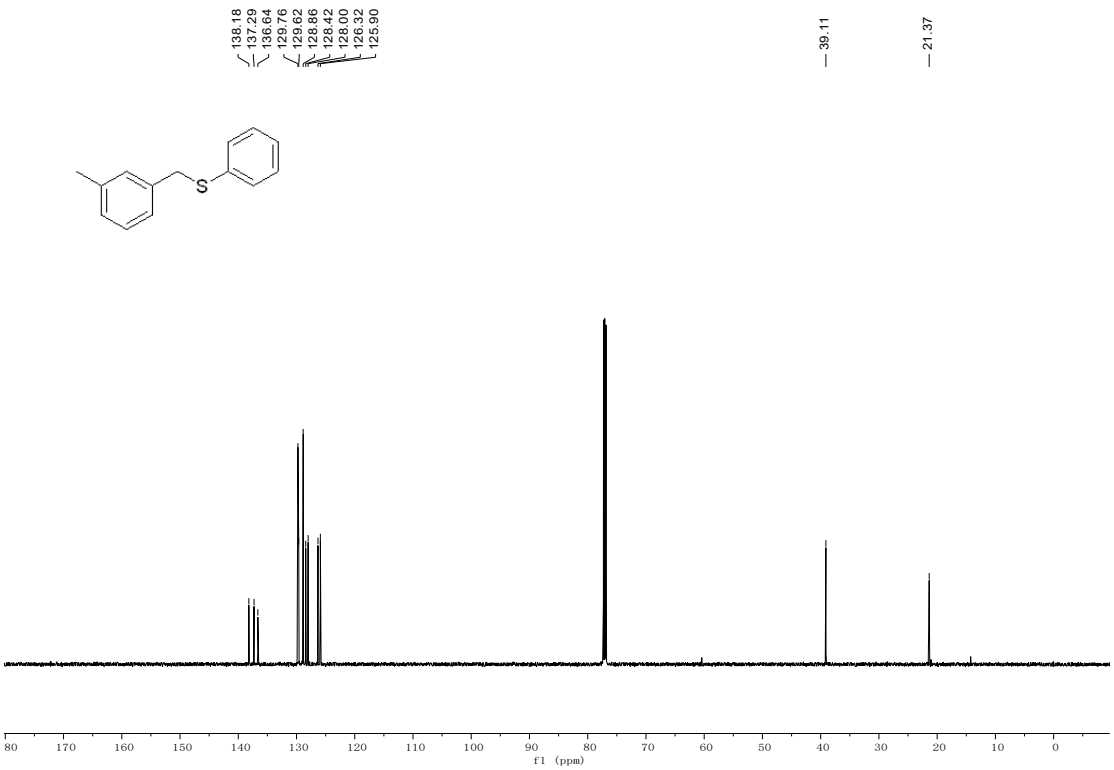
^{13}C-NMR Spectrum (101MHz, $CDCl_3$) of 3b



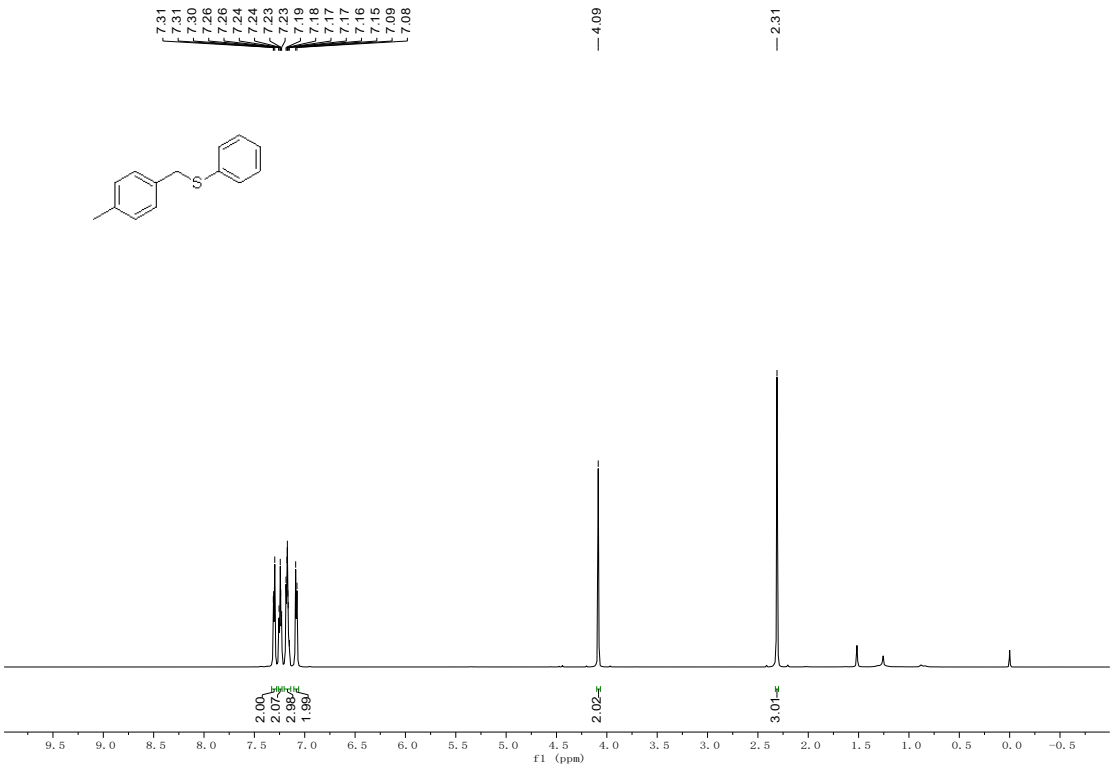
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3c



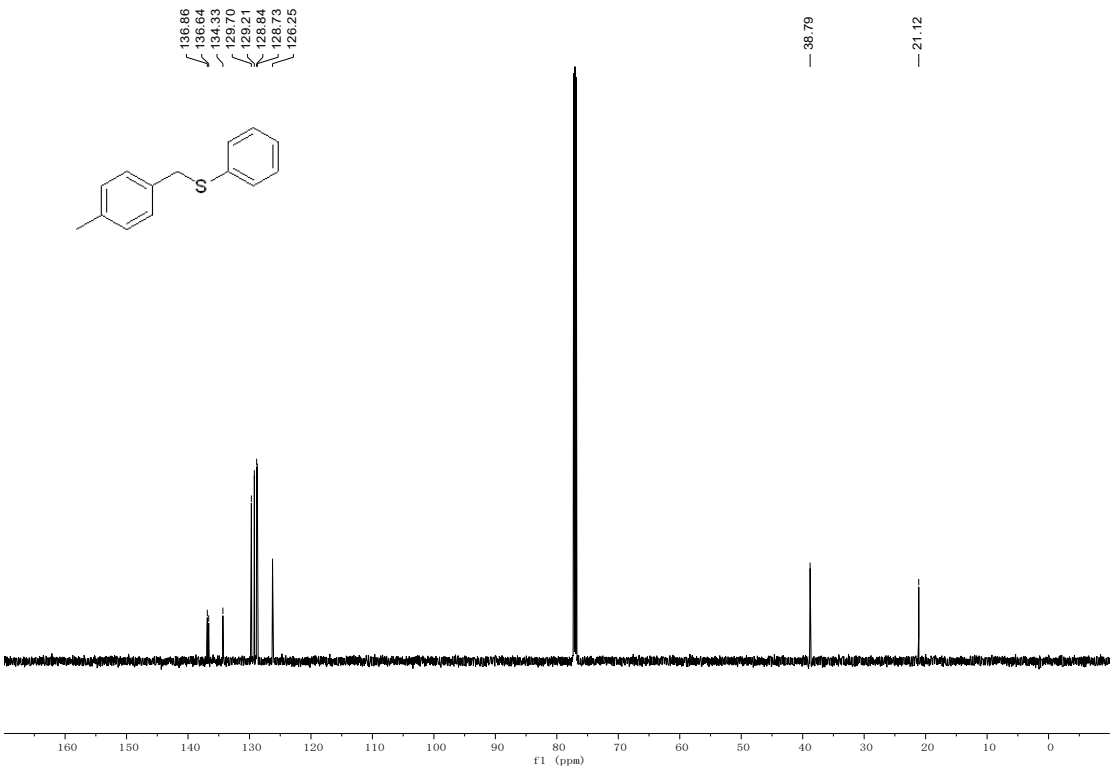
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3c



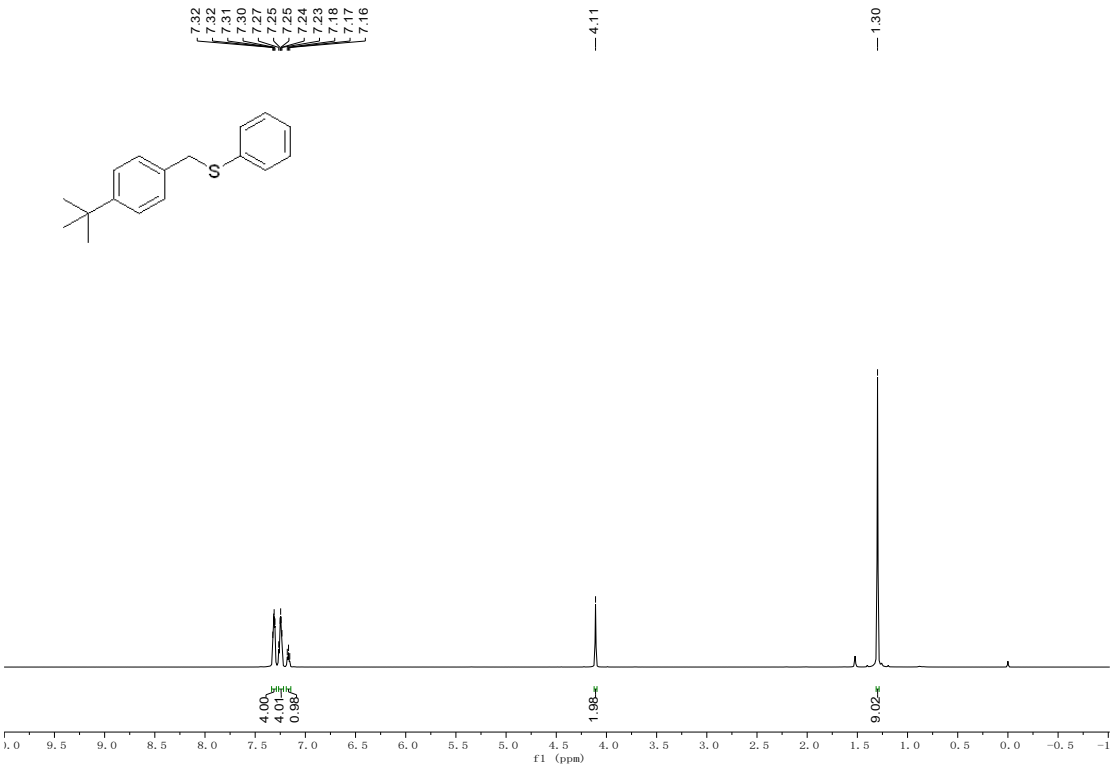
^{1}H-NMR Spectrum (400MHz, $CDCl_3$) of 3d



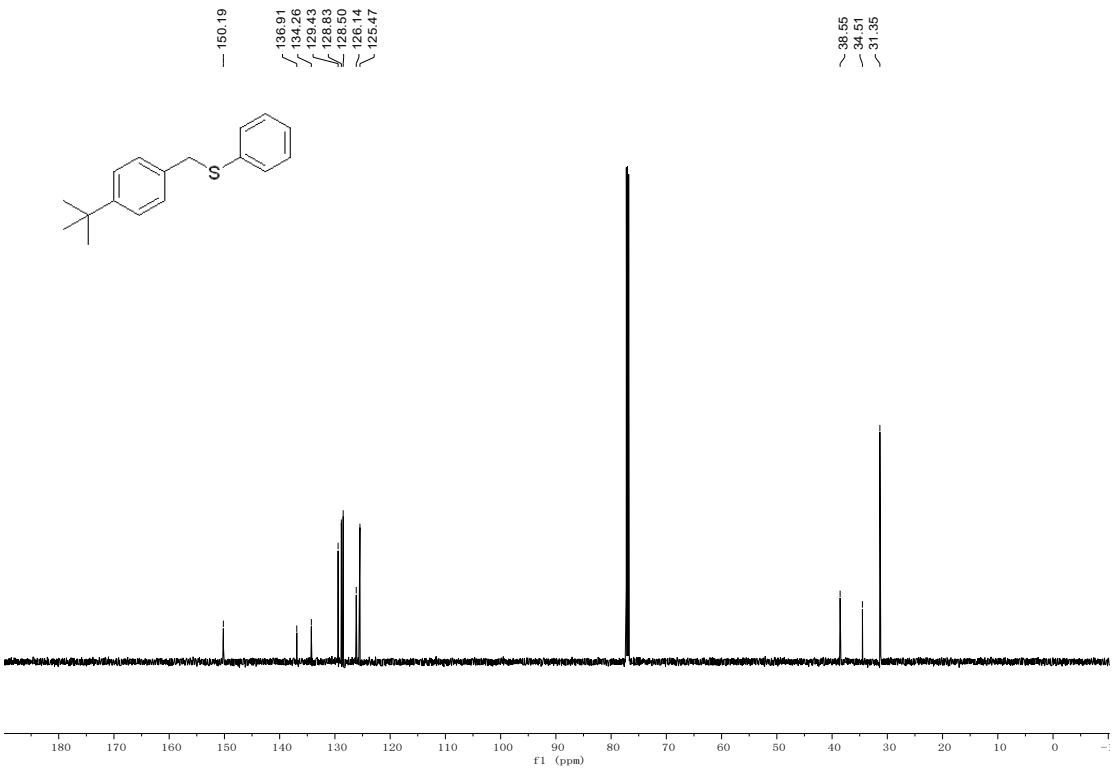
^{13}C-NMR Spectrum (151MHz, $CDCl_3$) of 3d



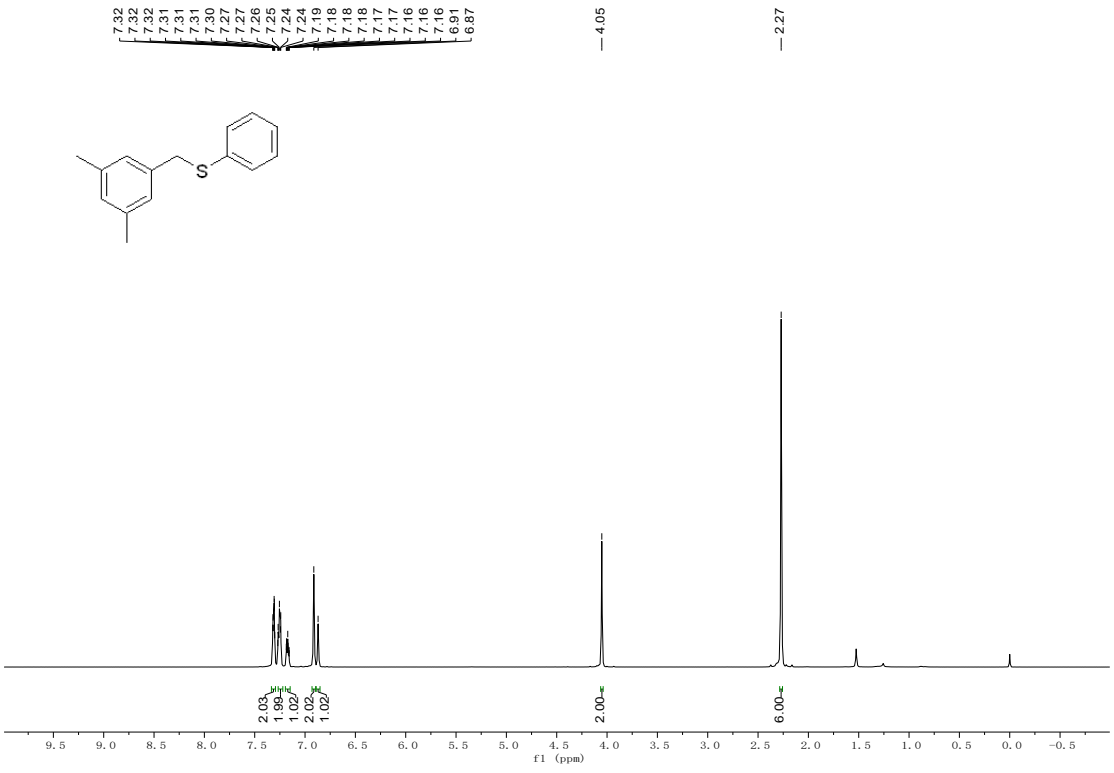
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3e



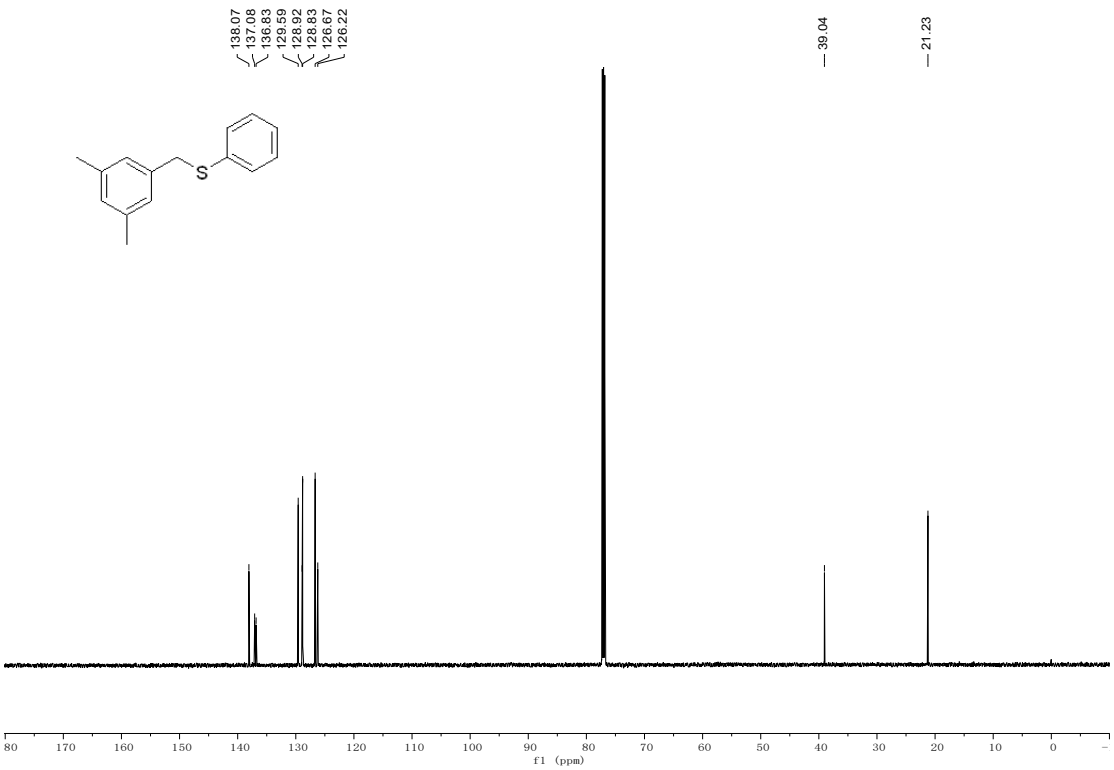
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3e



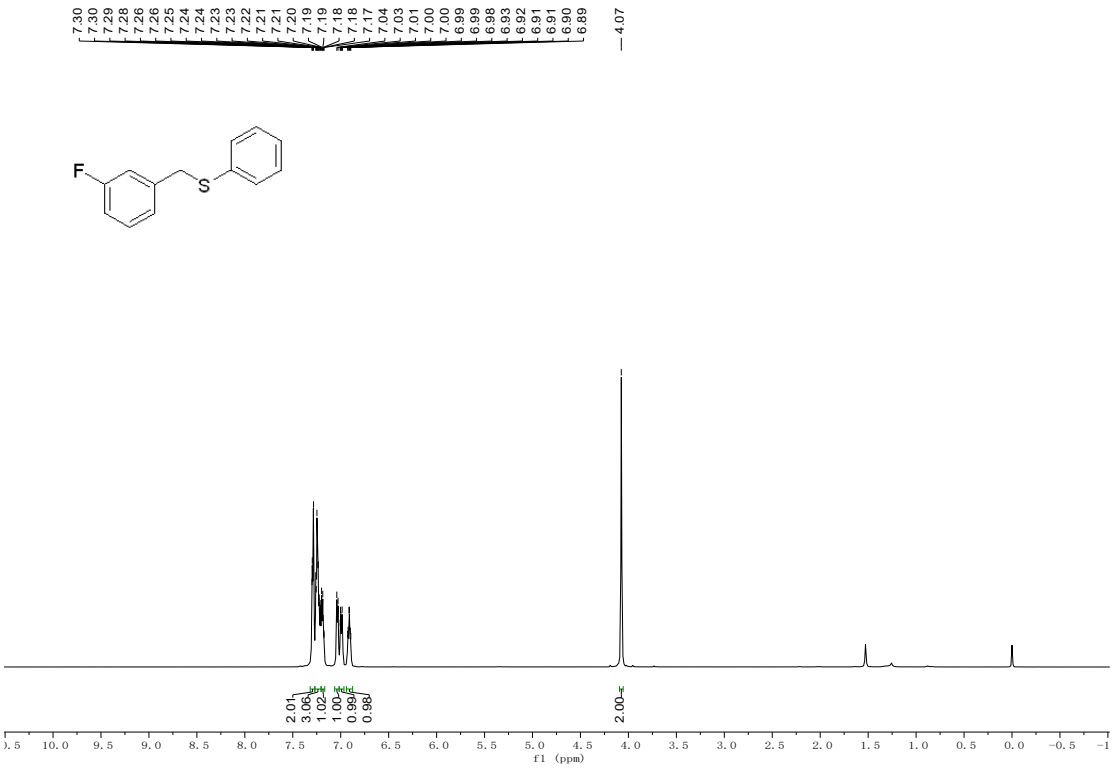
^{1}H-NMR Spectrum (400MHz, $CDCl_3$) of 3f



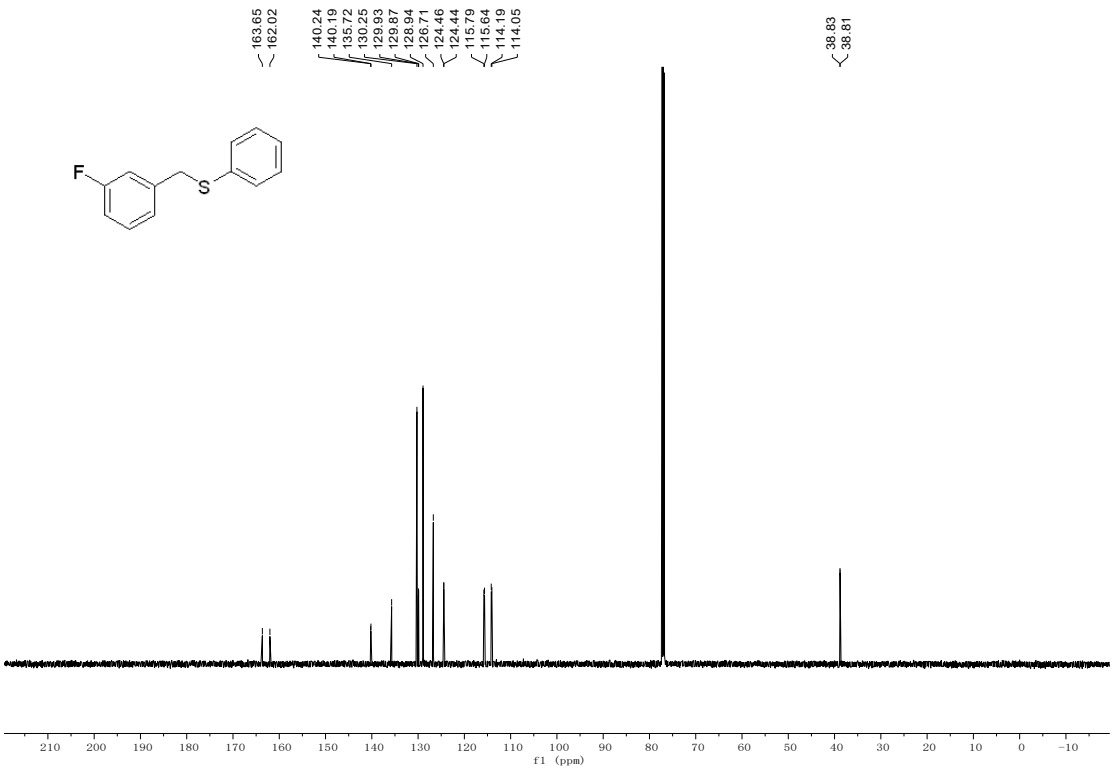
^{13}C-NMR Spectrum (101MHz, $CDCl_3$) of 3f



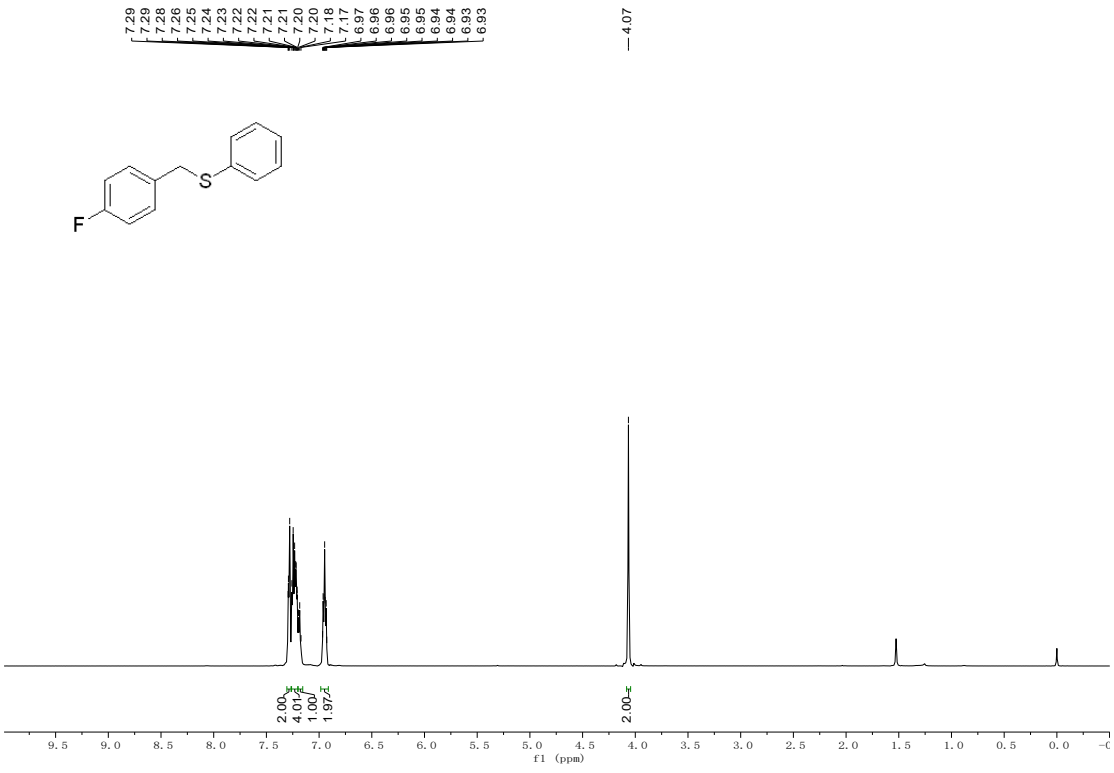
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3g



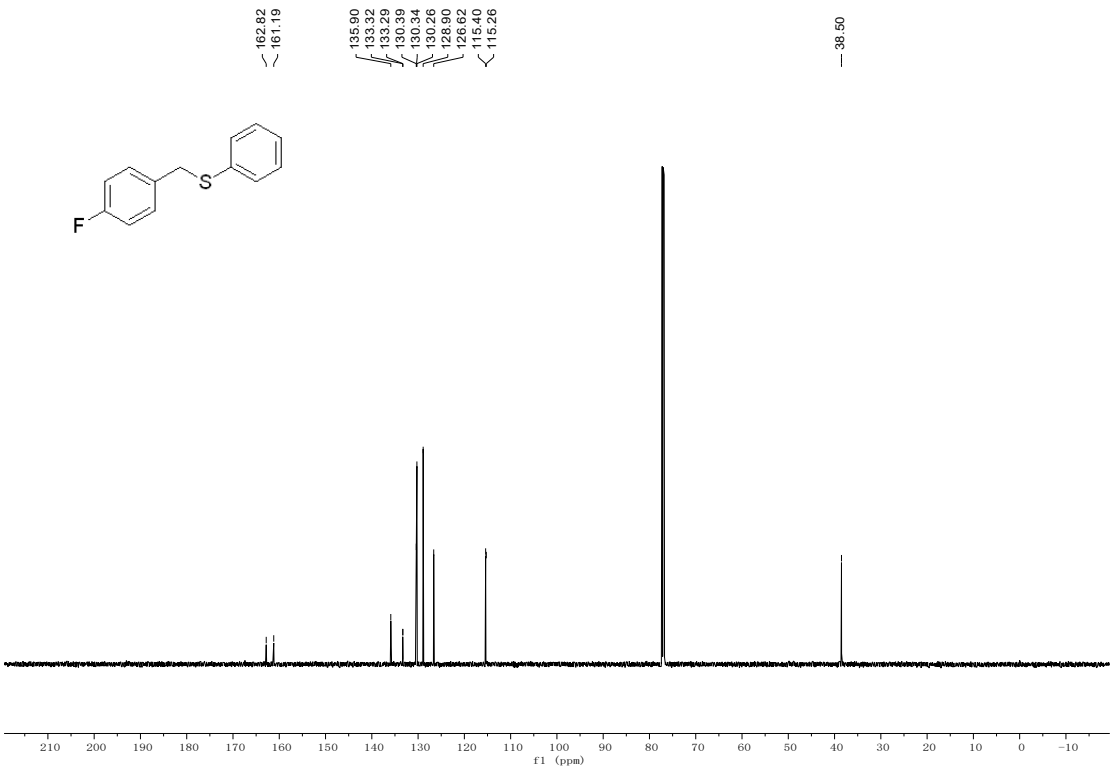
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3g



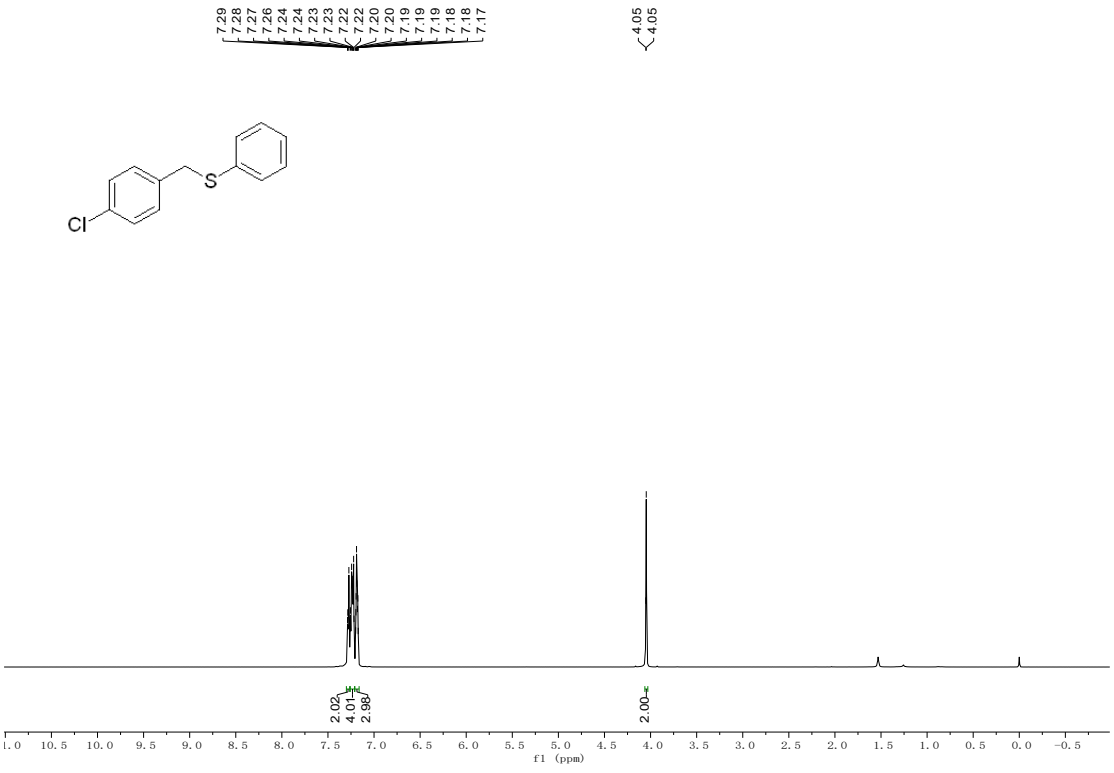
[1]H-NMR Spectrum (600MHz, DMSO) of 3h



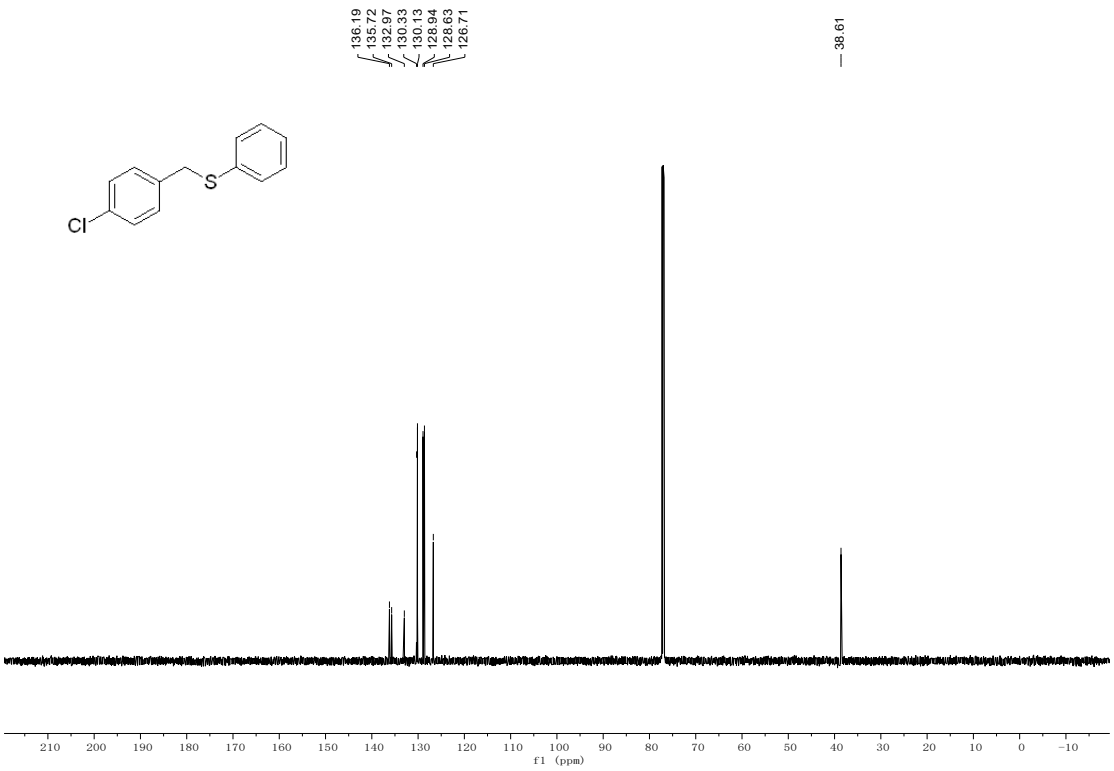
[13]C-NMR Spectrum (151MHz, DMSO) of 3h



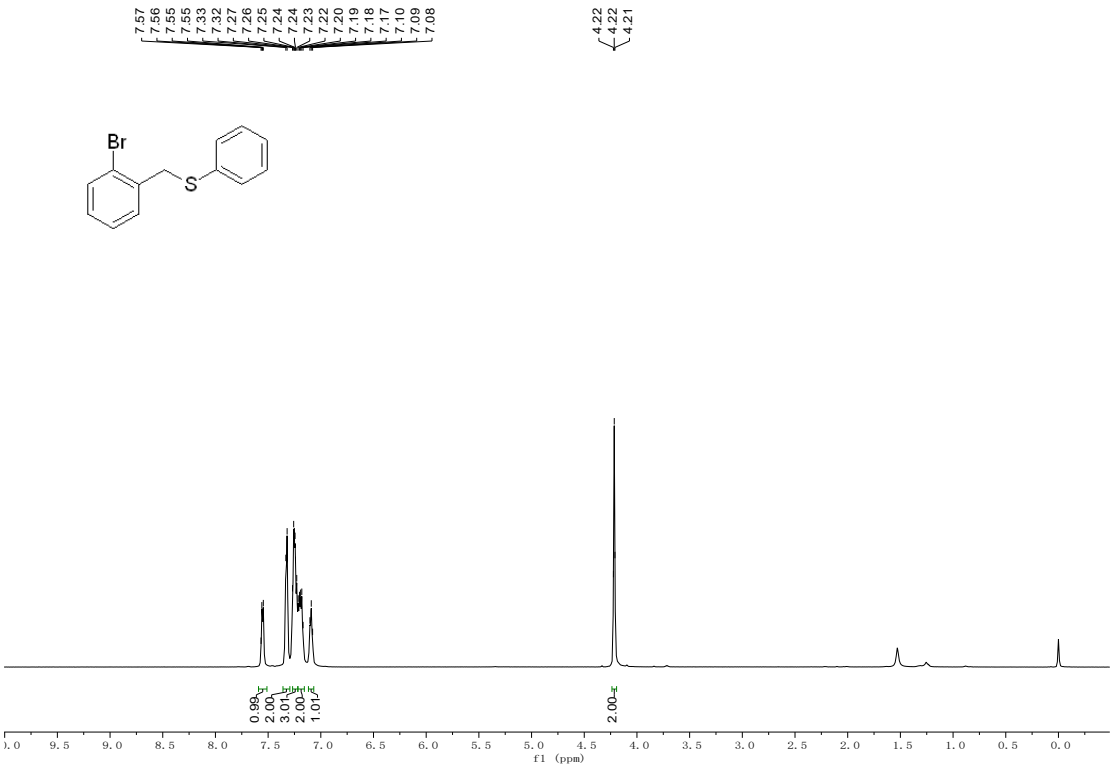
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3i



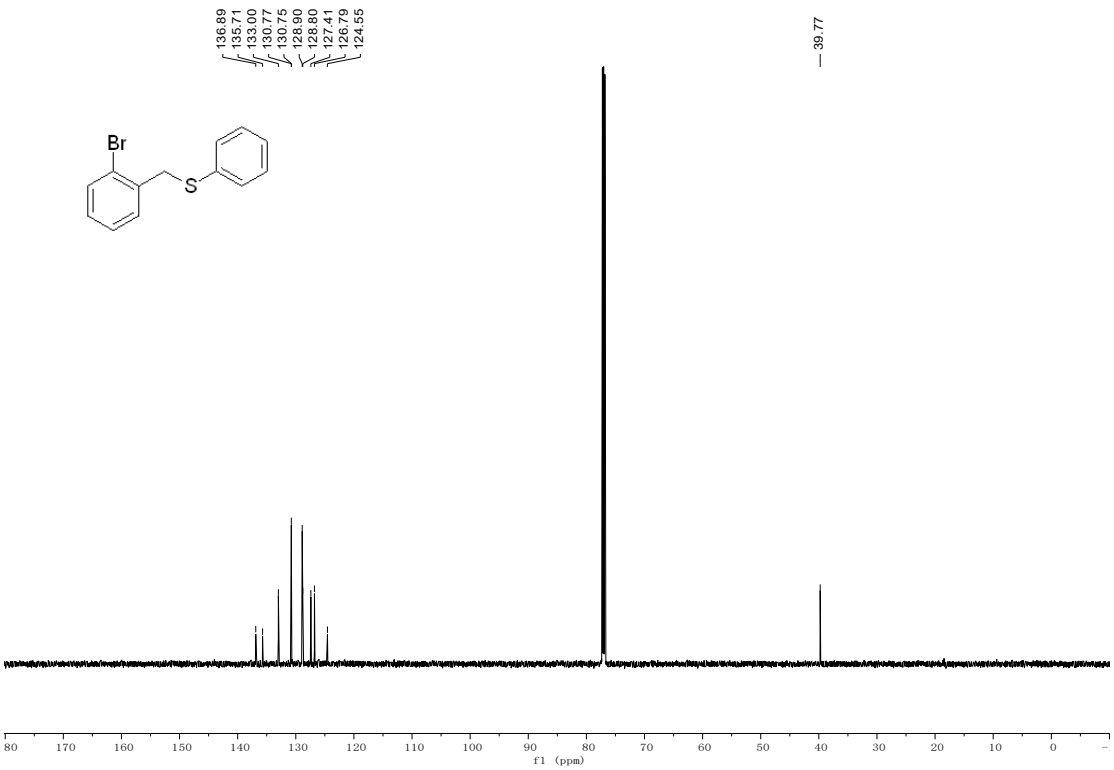
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3i



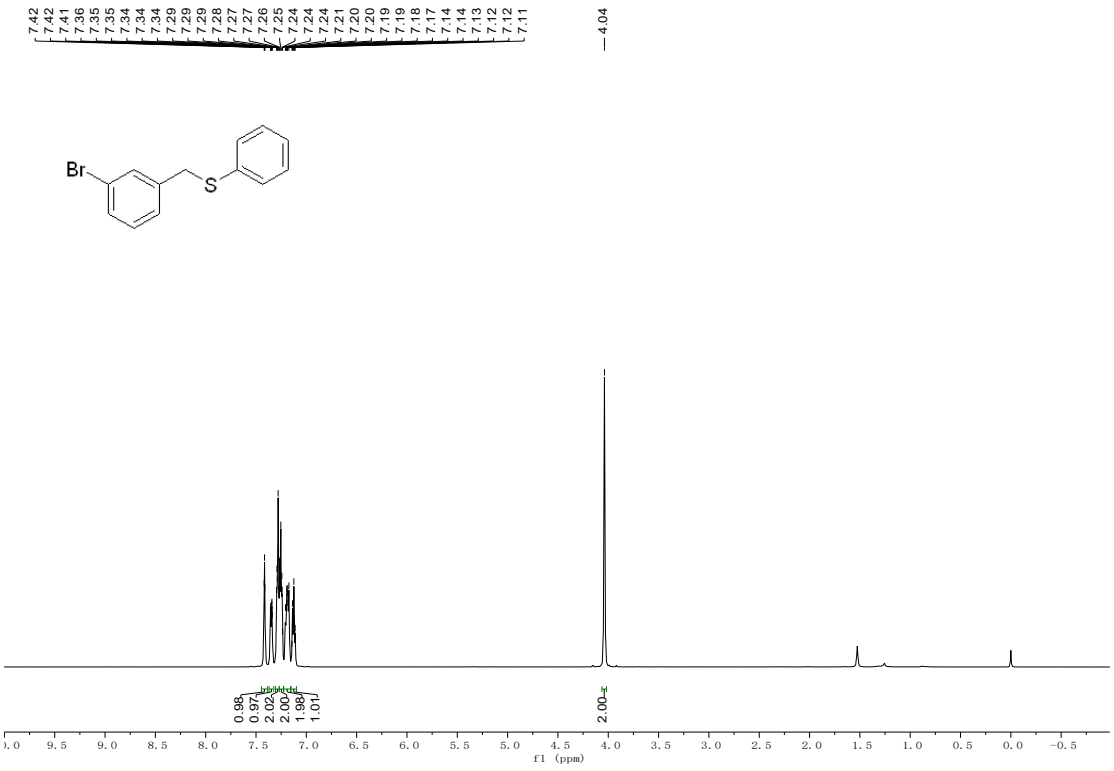
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3j



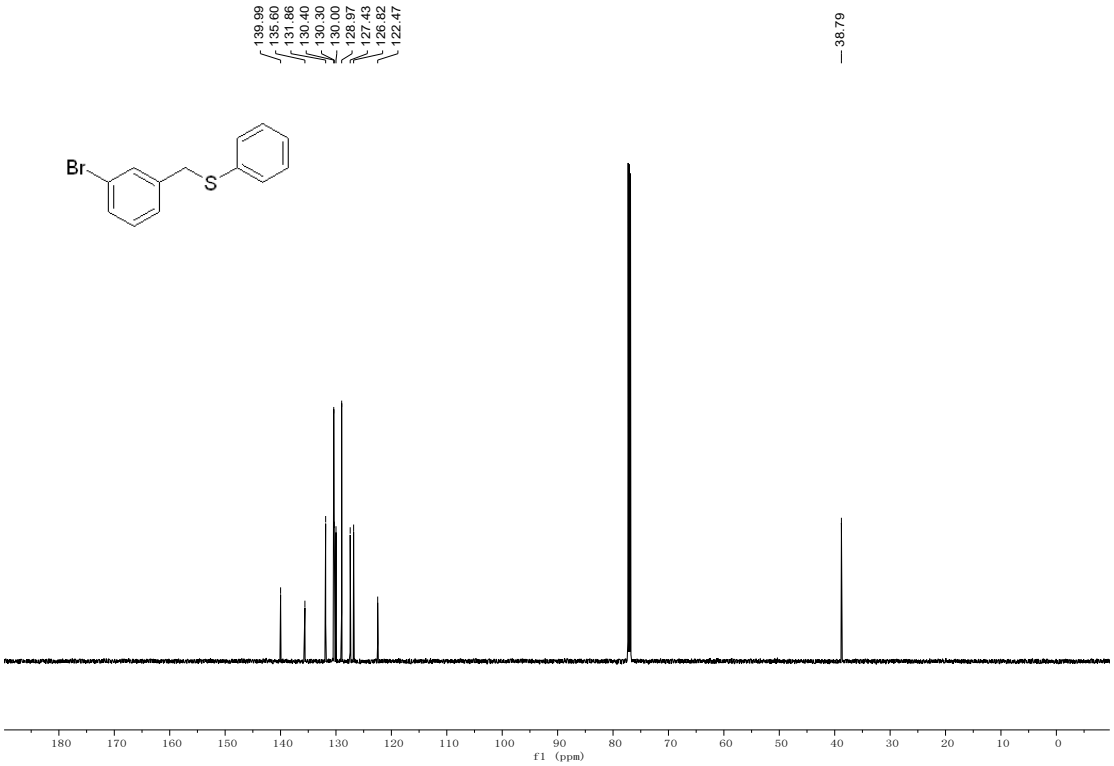
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3j



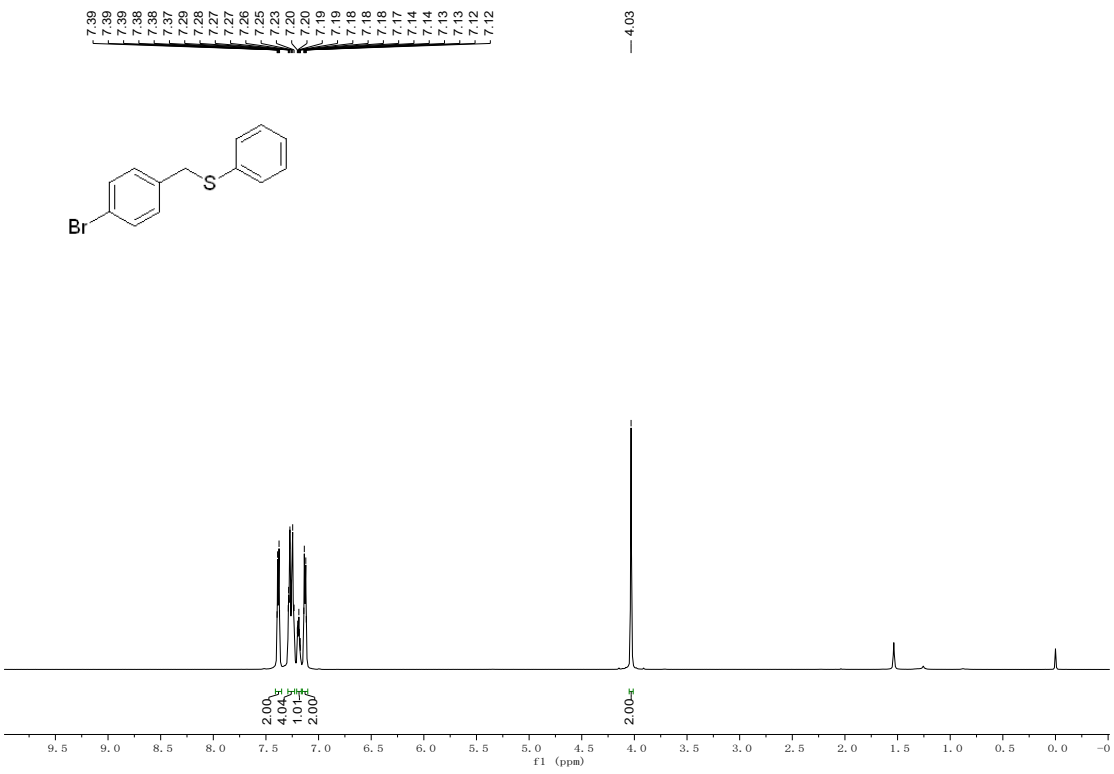
^{1}H-NMR Spectrum (400MHz, $CDCl_3$) of 3k



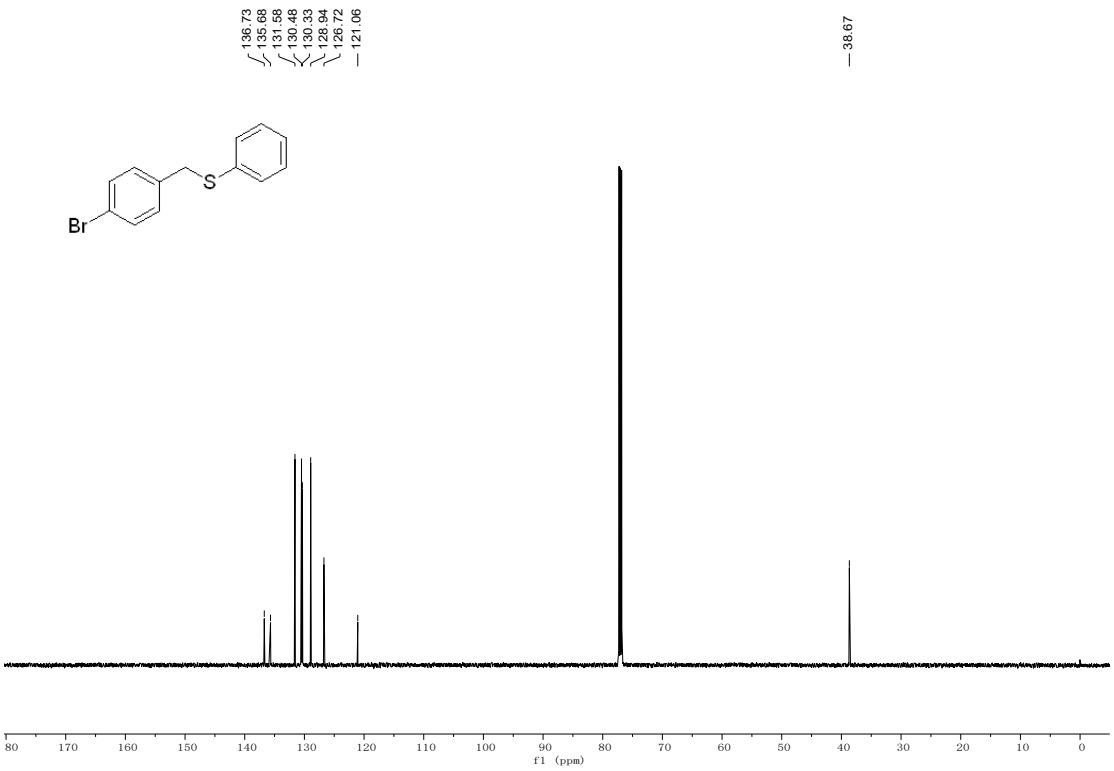
^{13}C-NMR Spectrum (151MHz, $CDCl_3$) of 3k



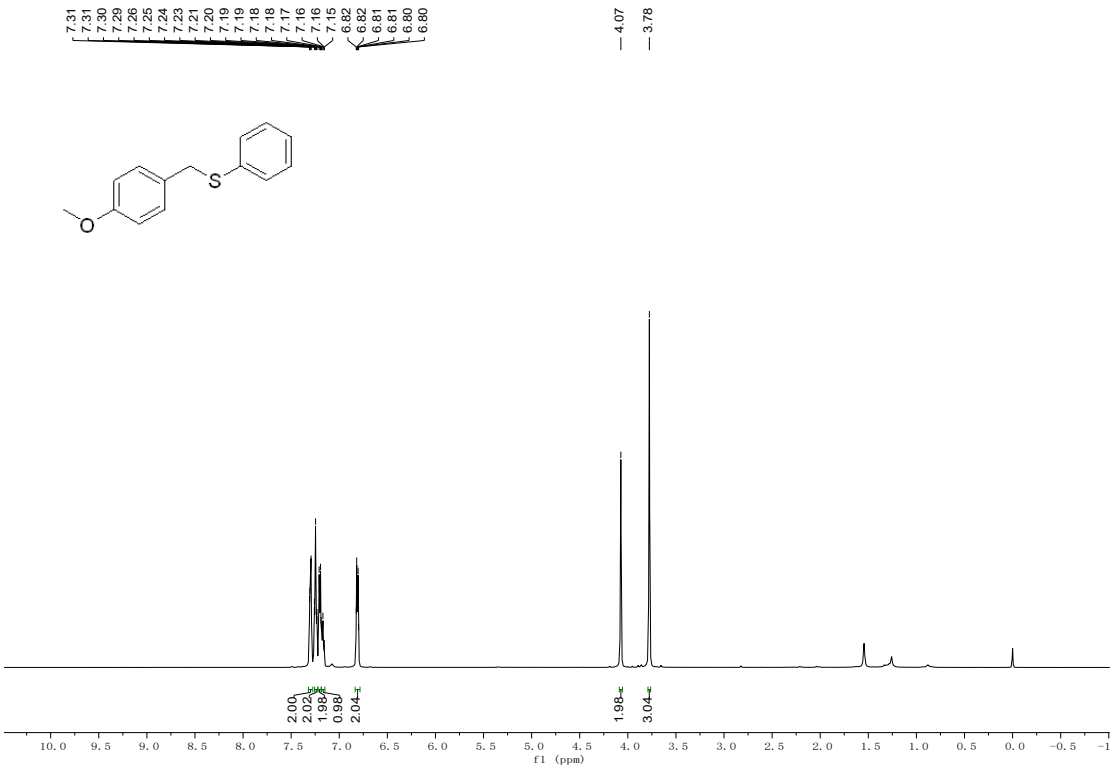
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3l



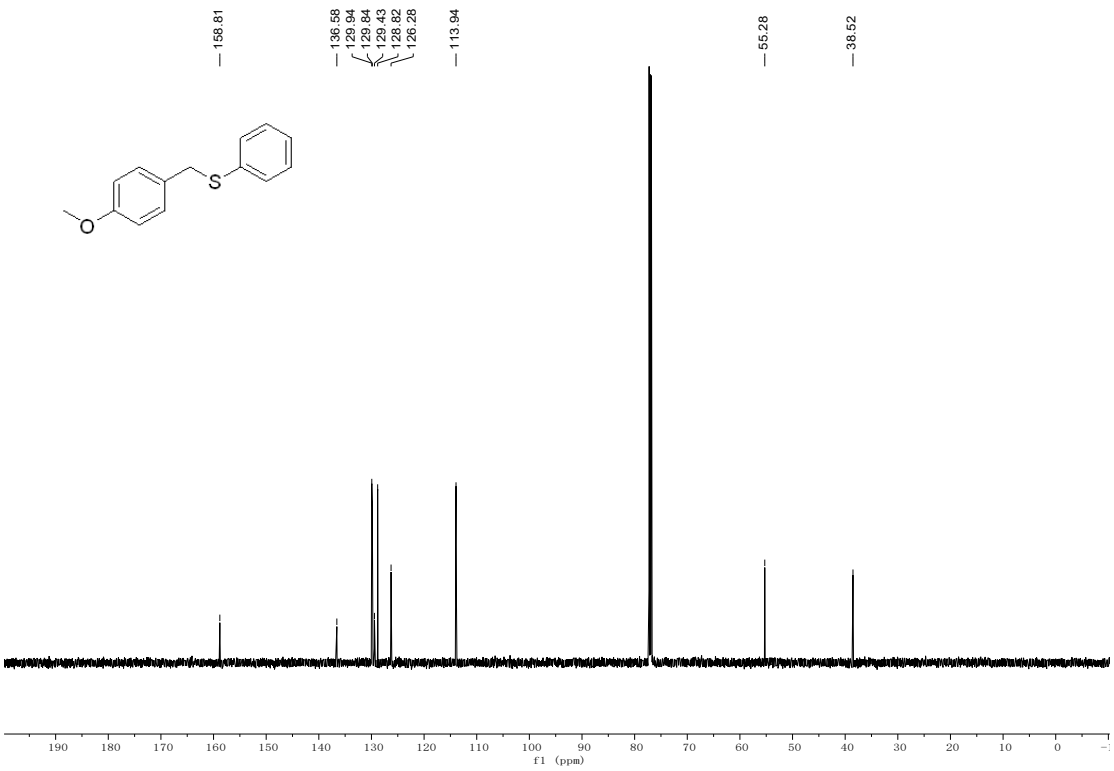
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3l



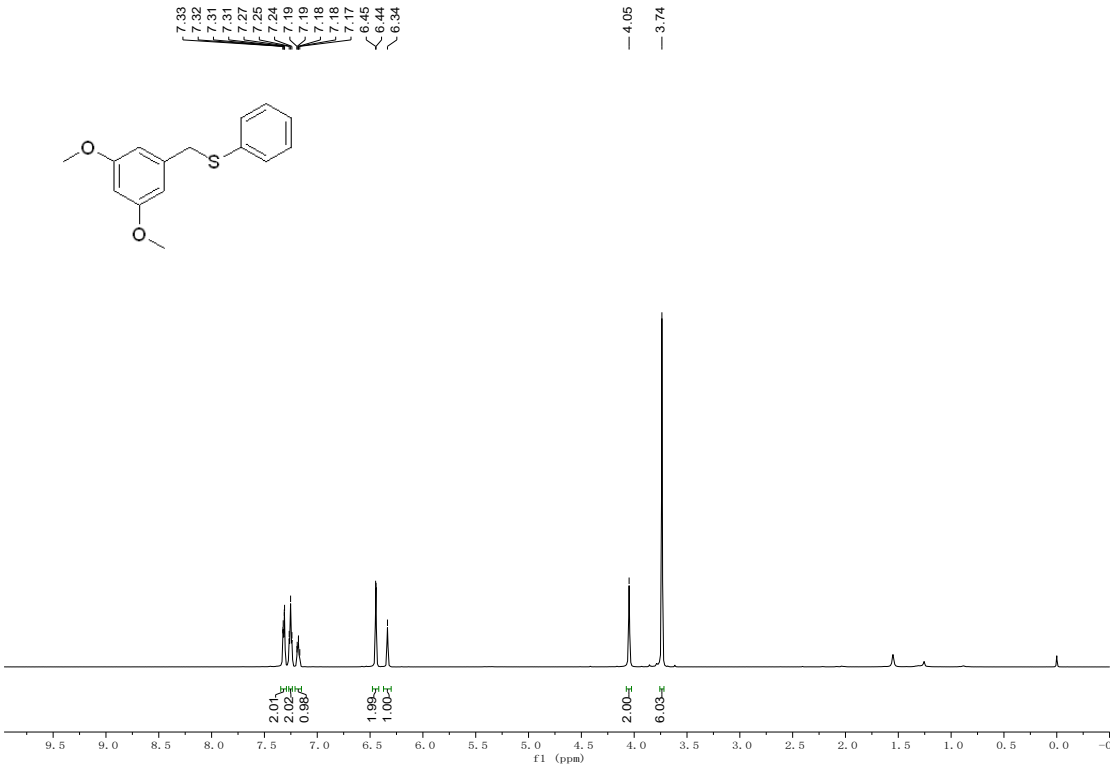
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3m



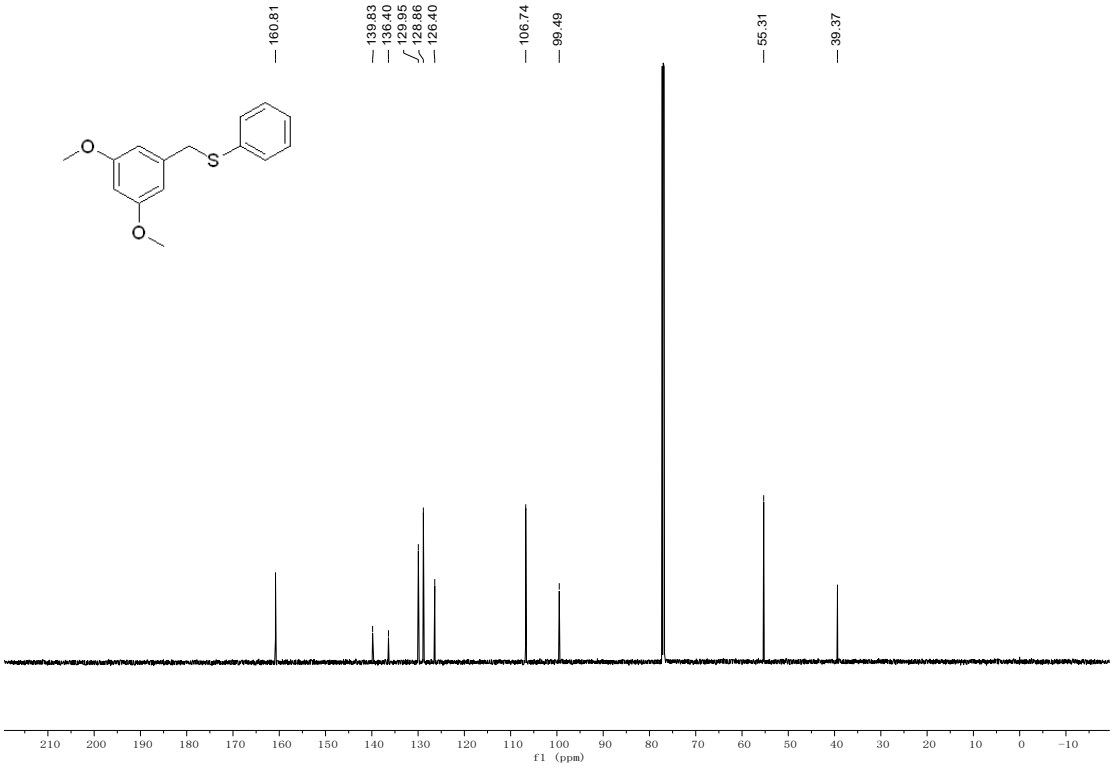
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3m



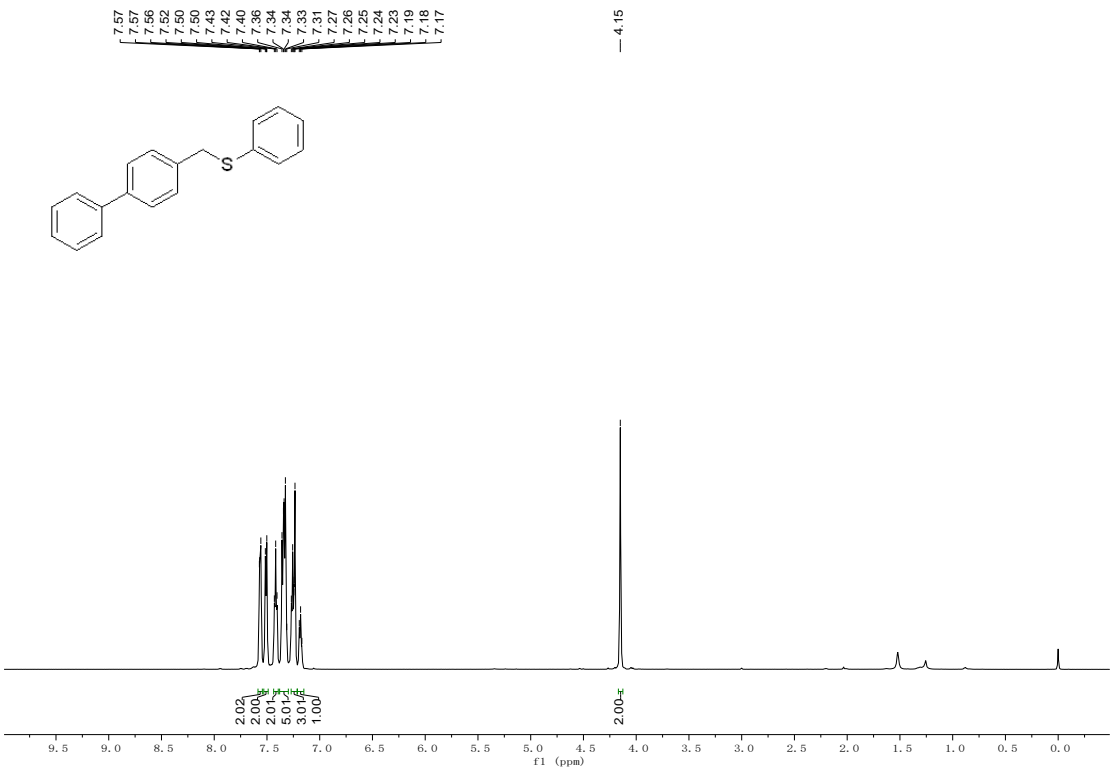
^{1}H-NMR Spectrum (600MHz, $CDCl_3$) of 3n



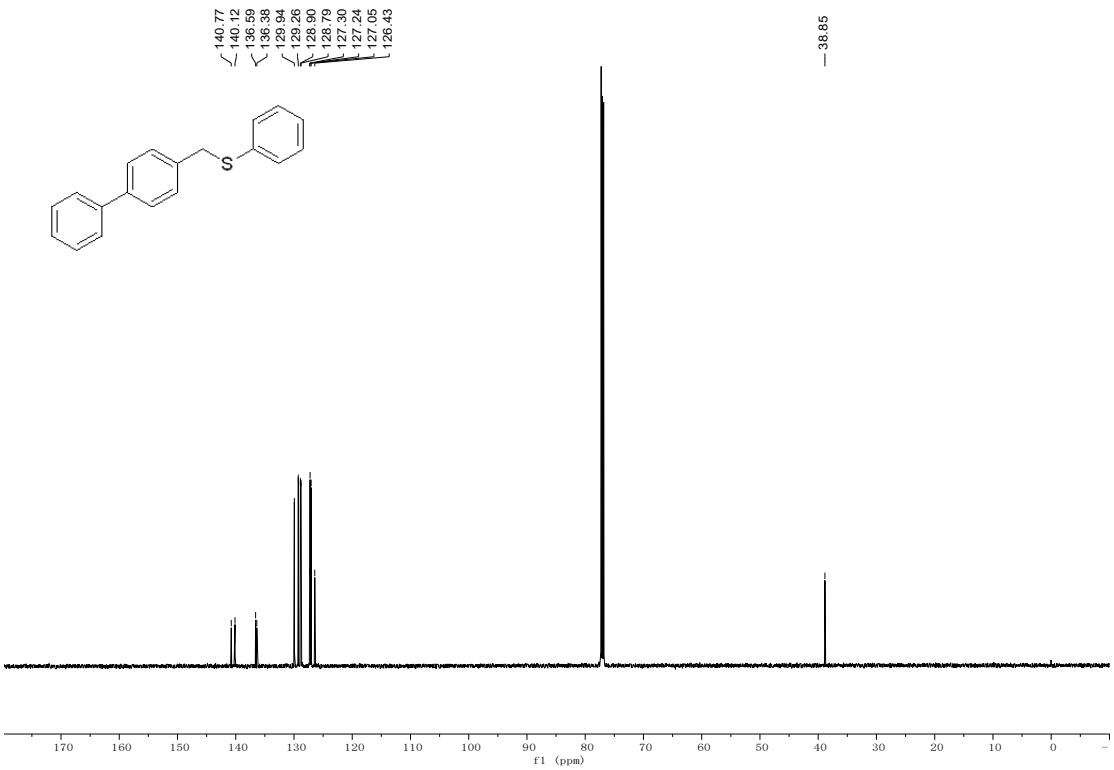
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3n



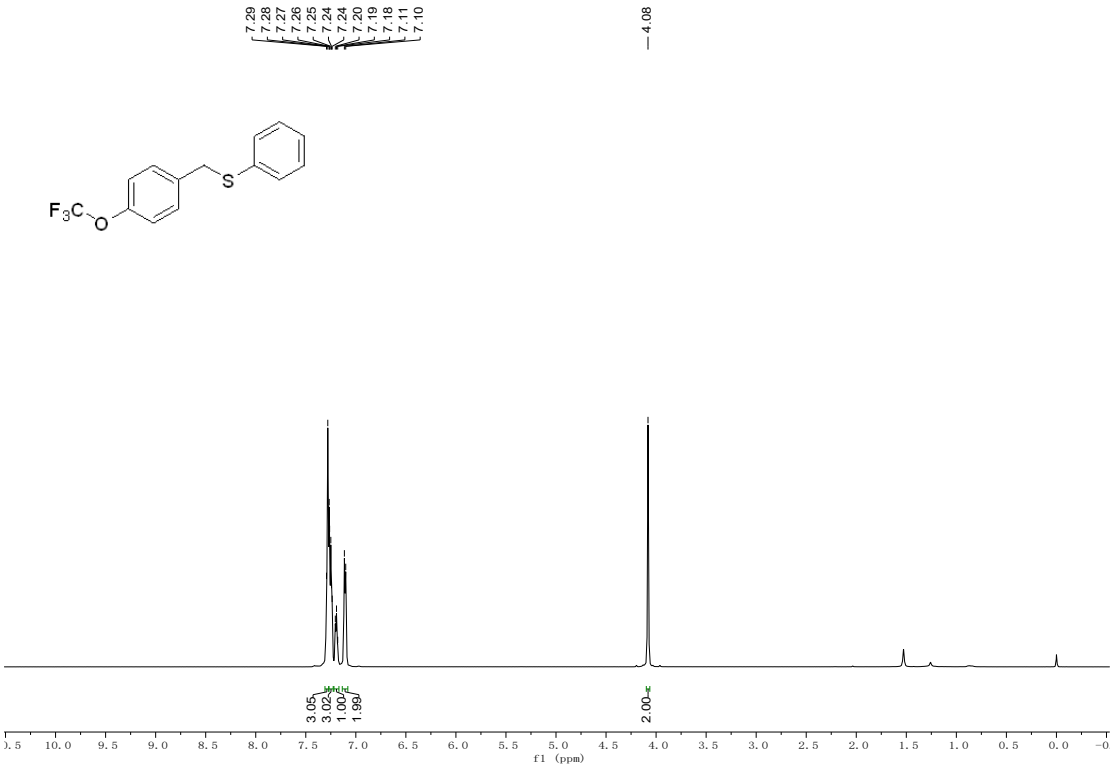
^{1}H-NMR Spectrum (400MHz, $CDCl_3$) of 3o



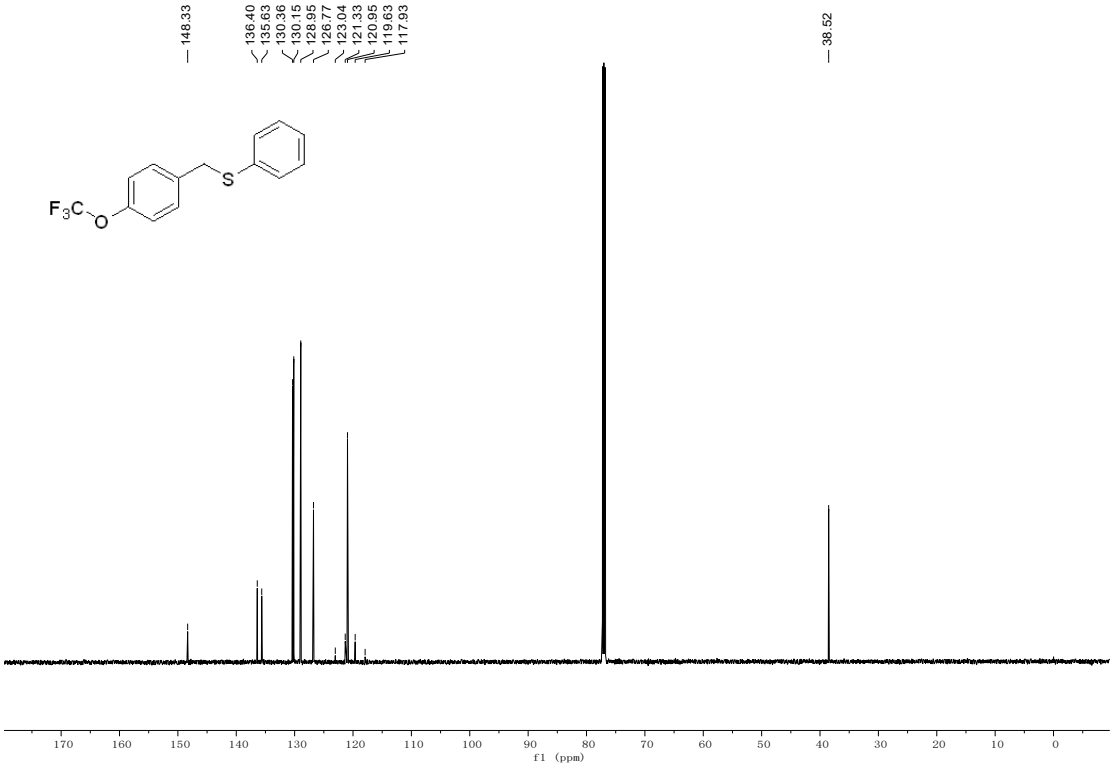
^{13}C-NMR Spectrum (101MHz, $CDCl_3$) of 3o



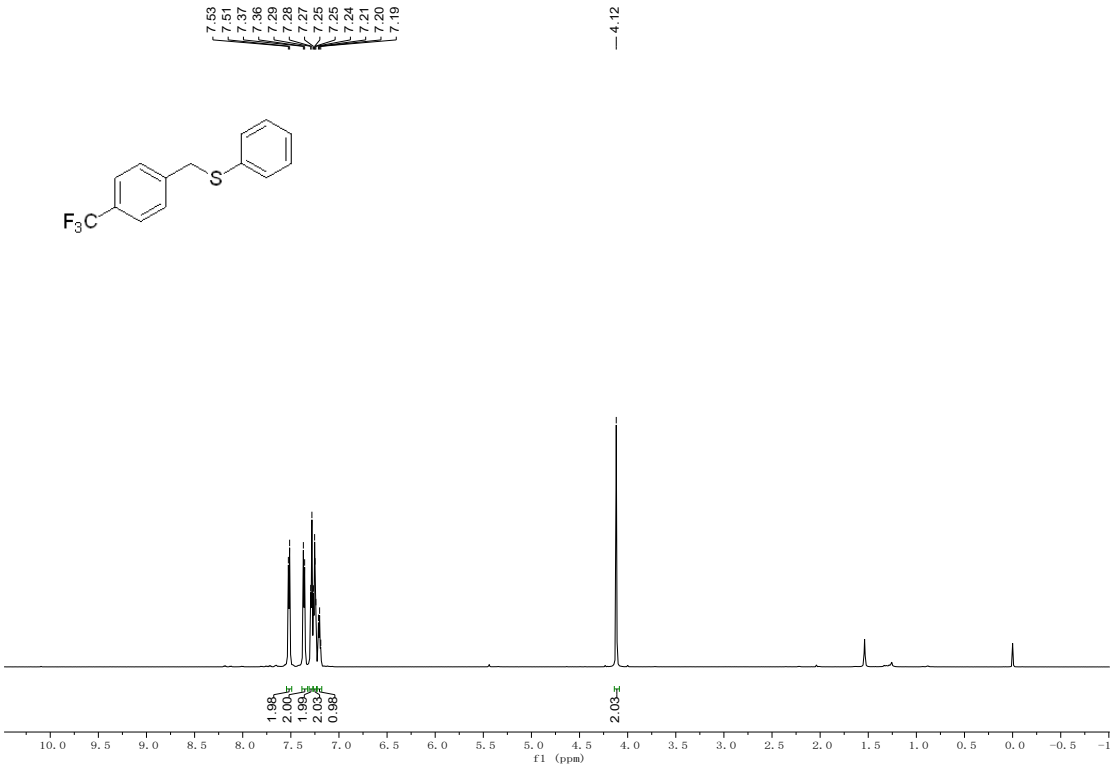
^{1}H-NMR Spectrum (400MHz, $CDCl_3$) of 3p



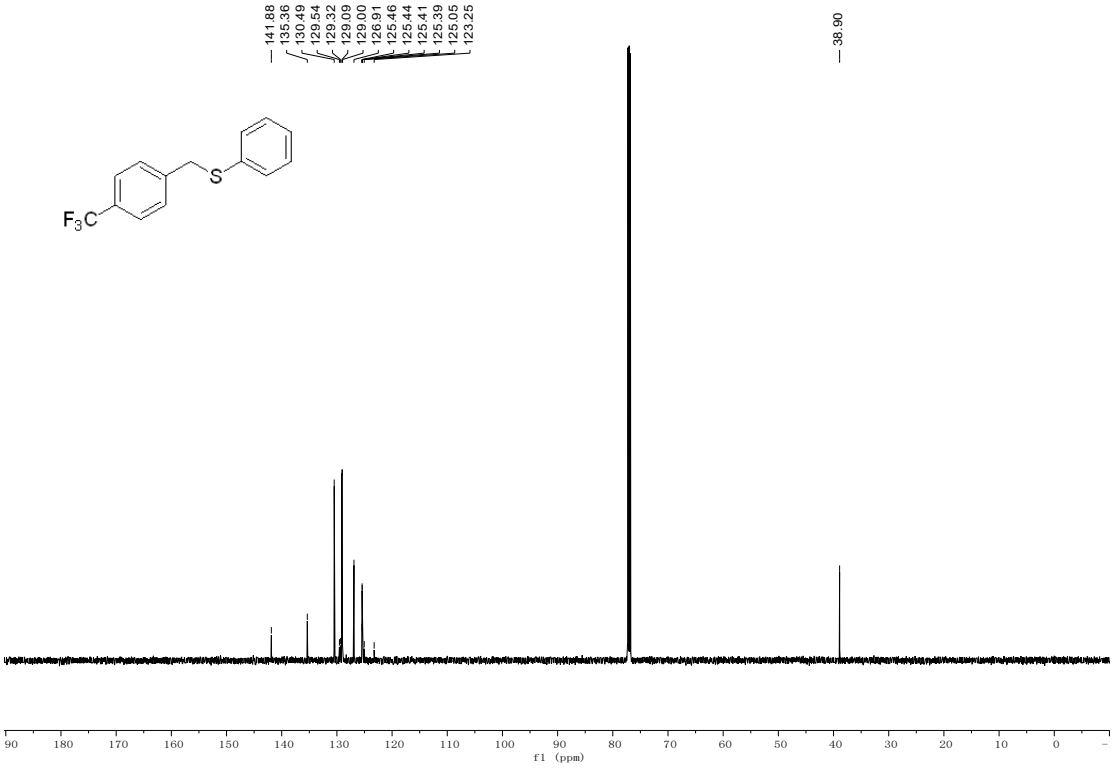
^{13}C-NMR Spectrum (101MHz, $CDCl_3$) of 3p



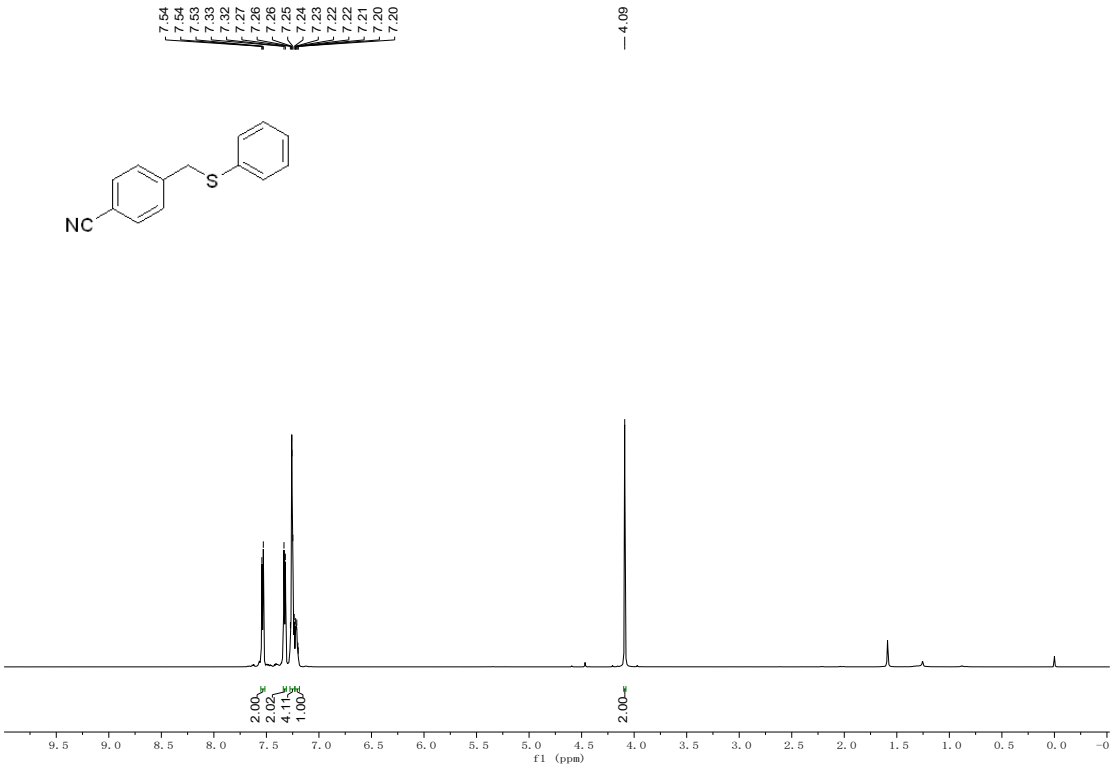
^{1}H-NMR Spectrum (600MHz, $CDCl_3$) of 3q



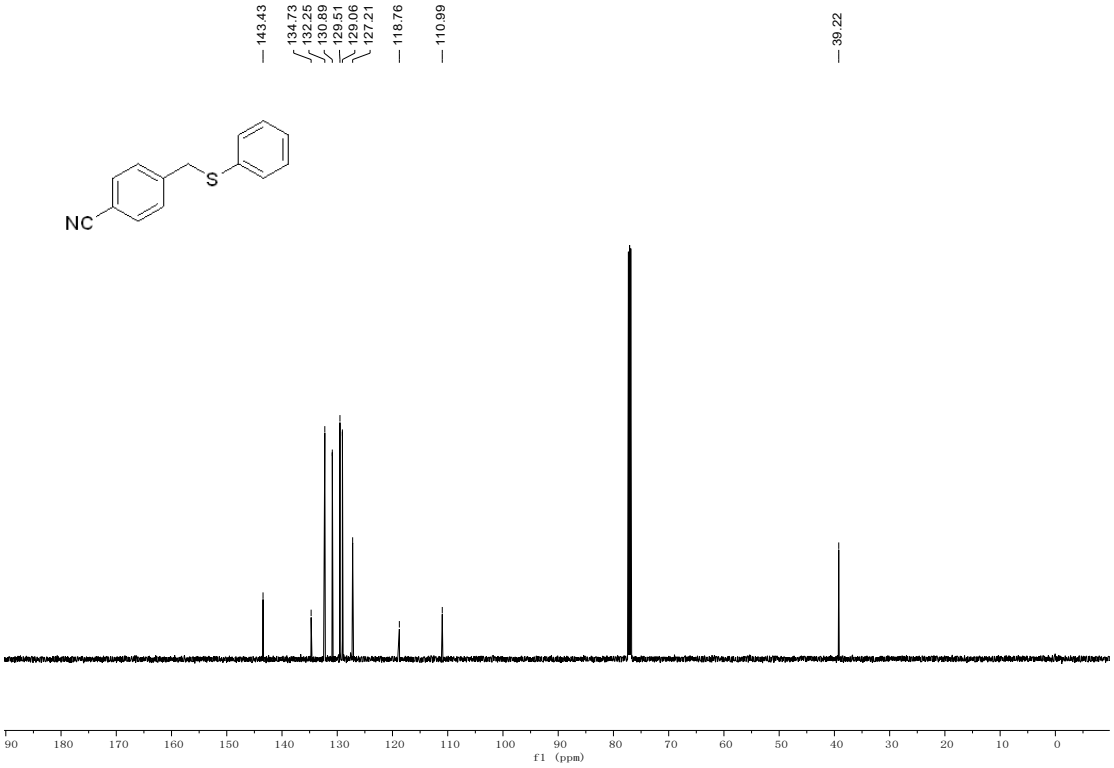
^{13}C-NMR Spectrum (151MHz, DMSO) of 3q



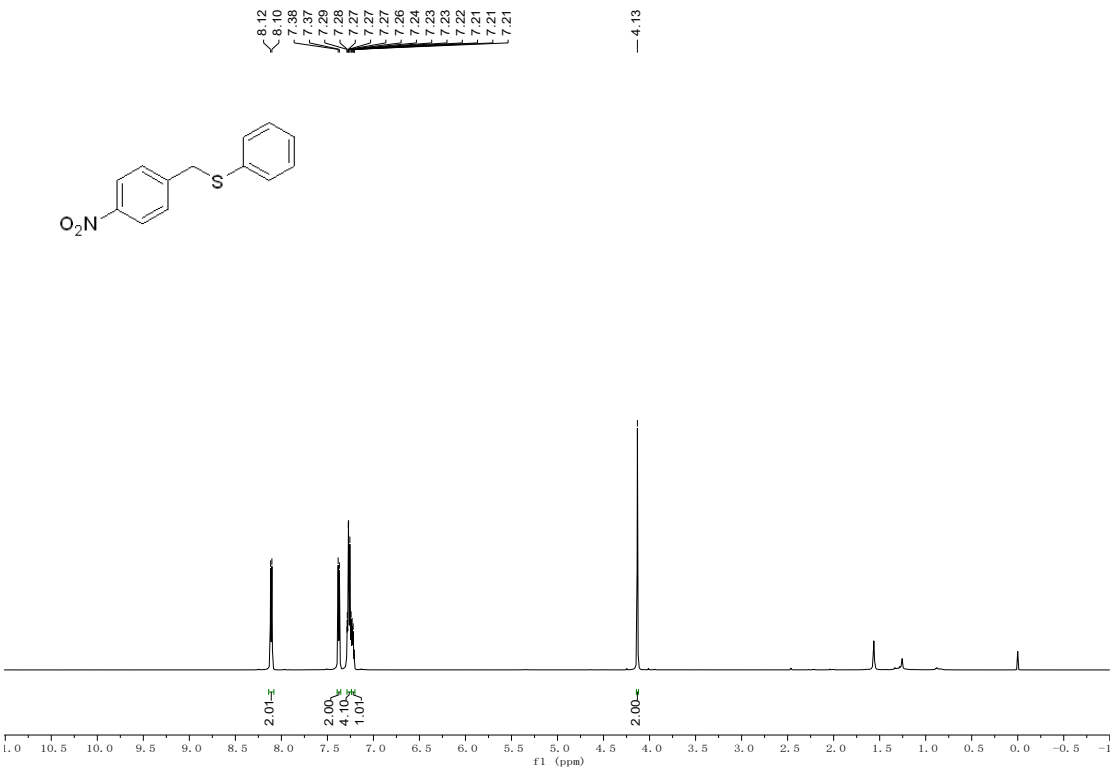
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3r



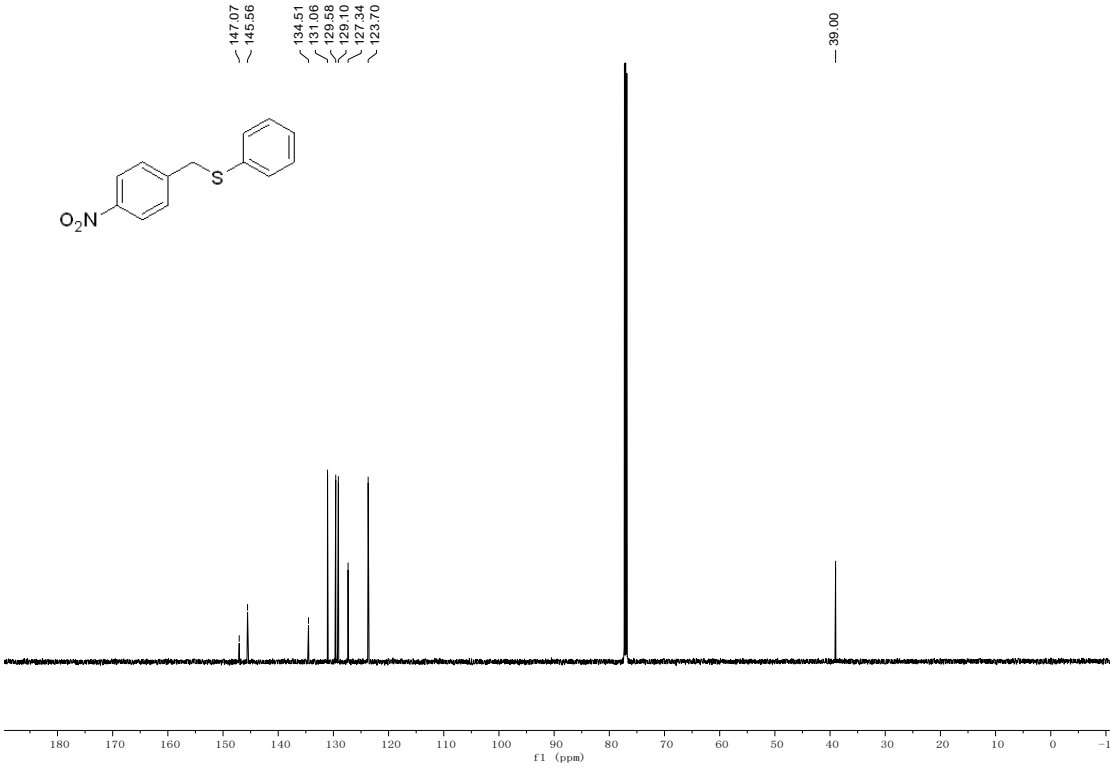
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3r



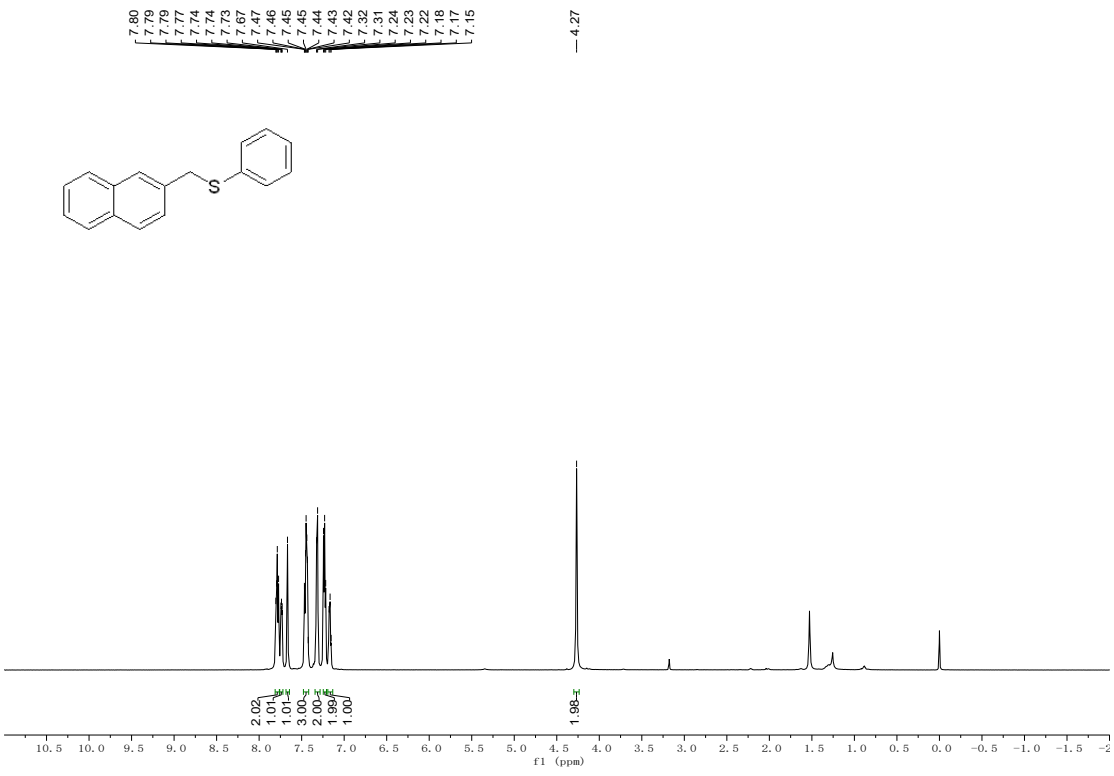
^{1}H-NMR Spectrum (600MHz, $CDCl_3$) of 3s



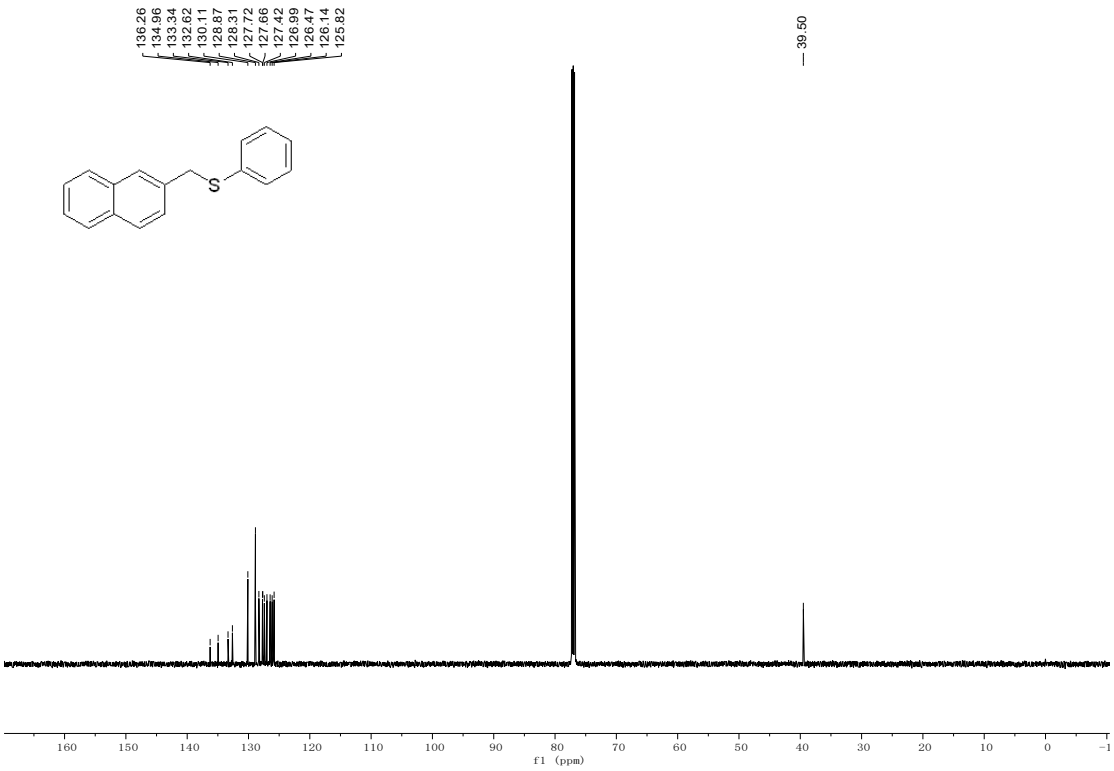
^{13}C-NMR Spectrum (151MHz, $CDCl_3$) of 3s



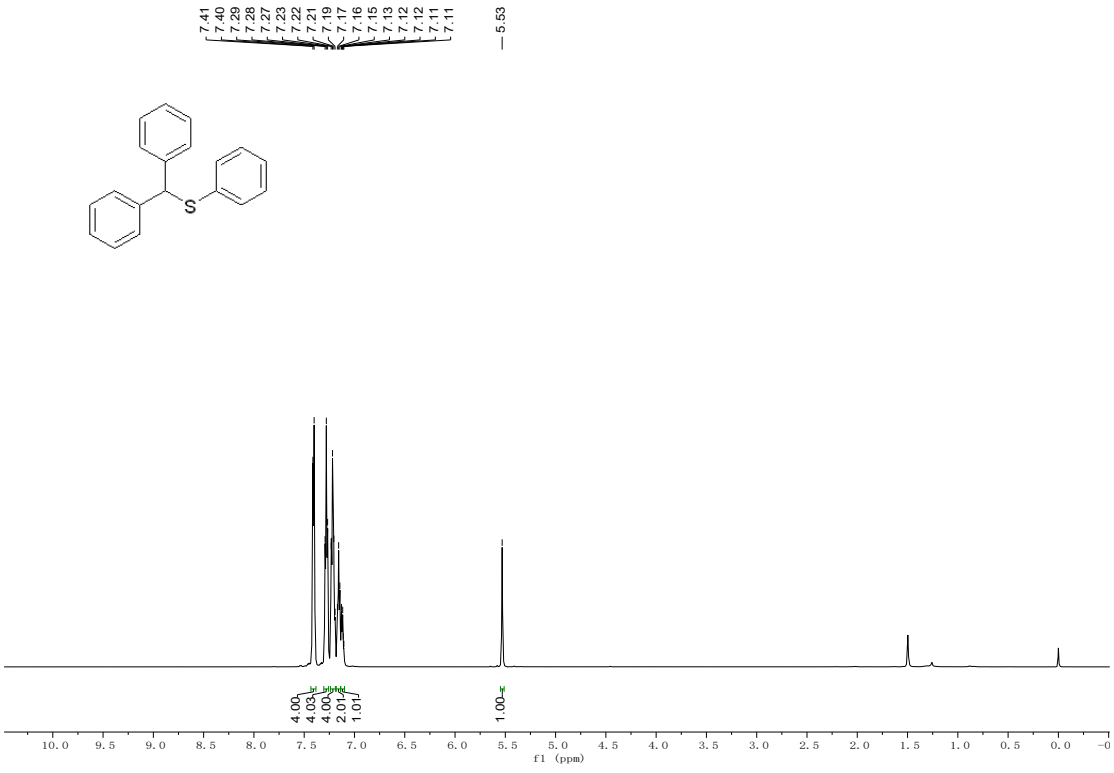
^{1}H-NMR Spectrum (400MHz, $CDCl_3$) of 3t



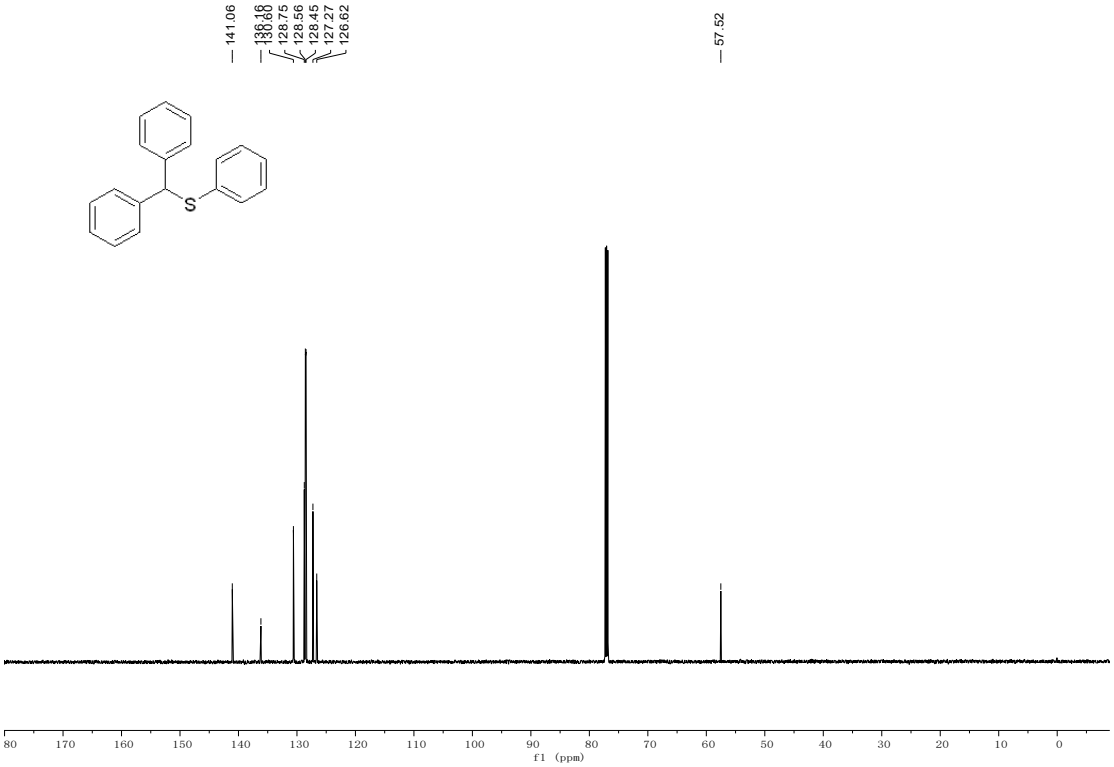
^{13}C-NMR Spectrum (101MHz, $CDCl_3$) of 3t



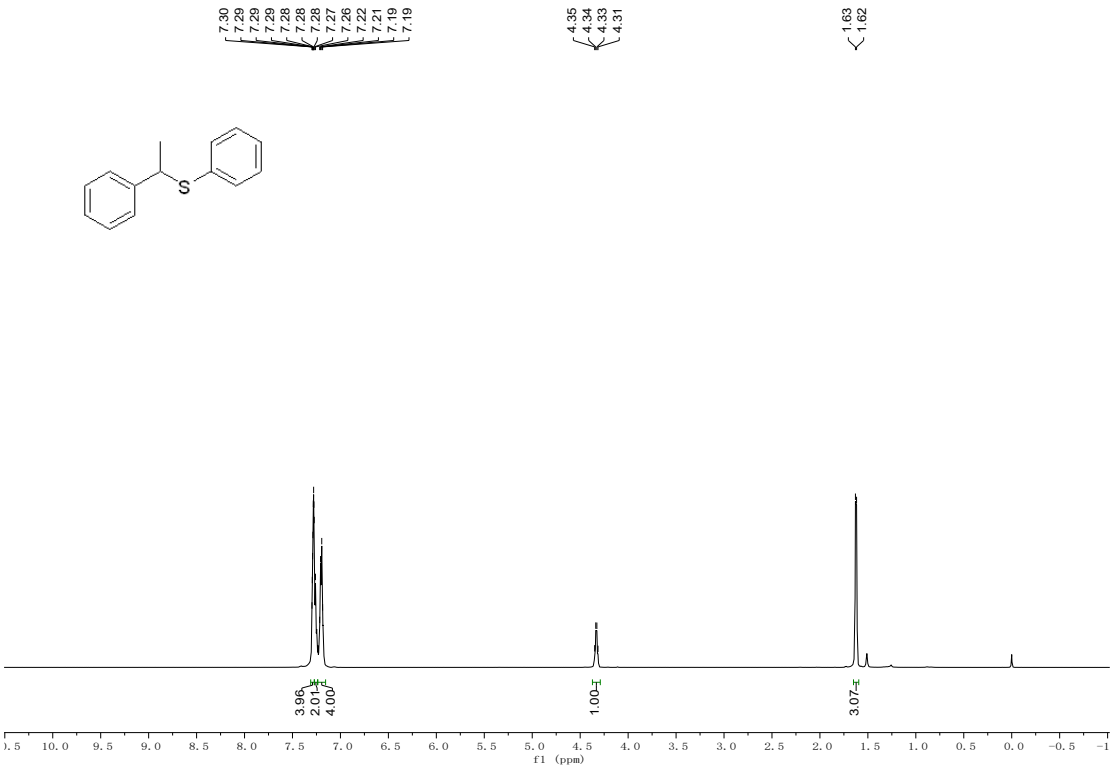
^{1}H-NMR Spectrum (400MHz, $CDCl_3$) of 3u



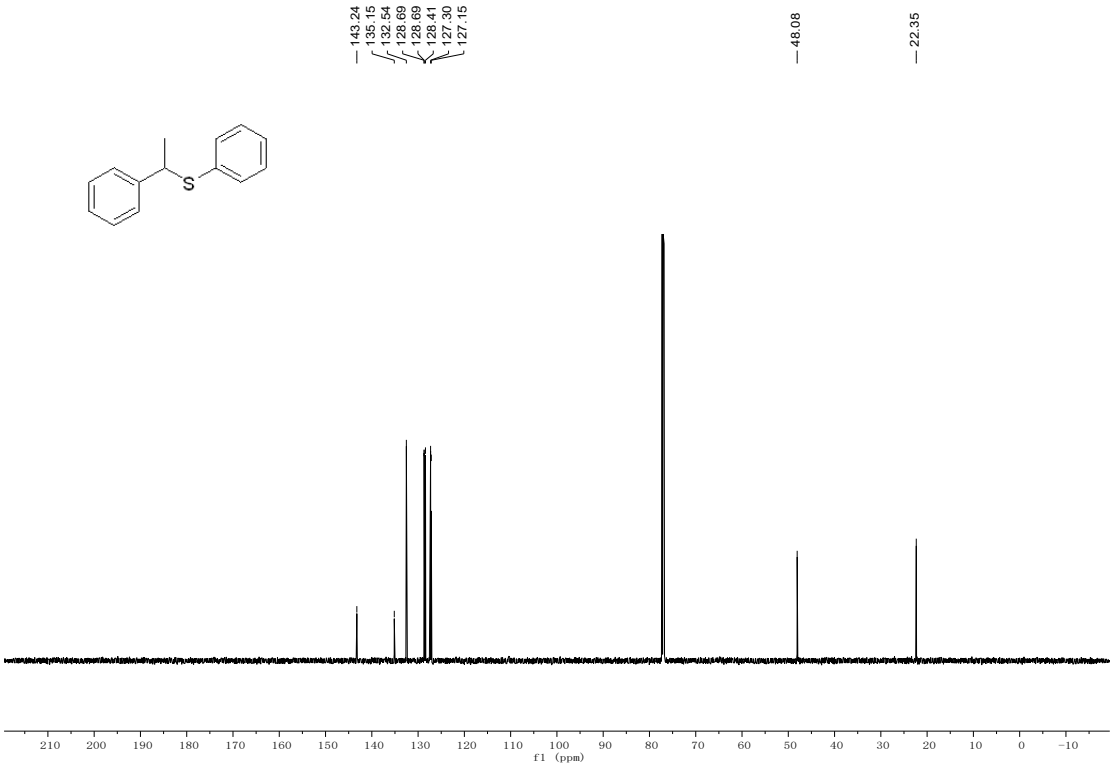
^{13}C-NMR Spectrum (101MHz, $CDCl_3$) of 3u



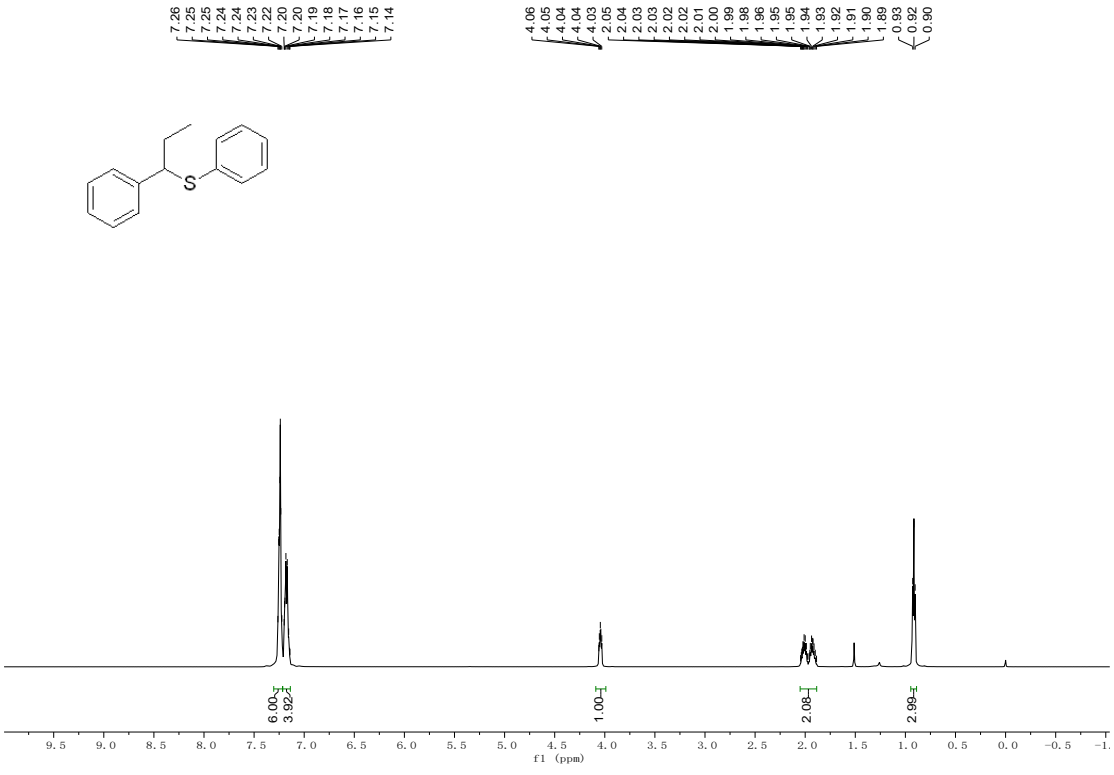
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3v



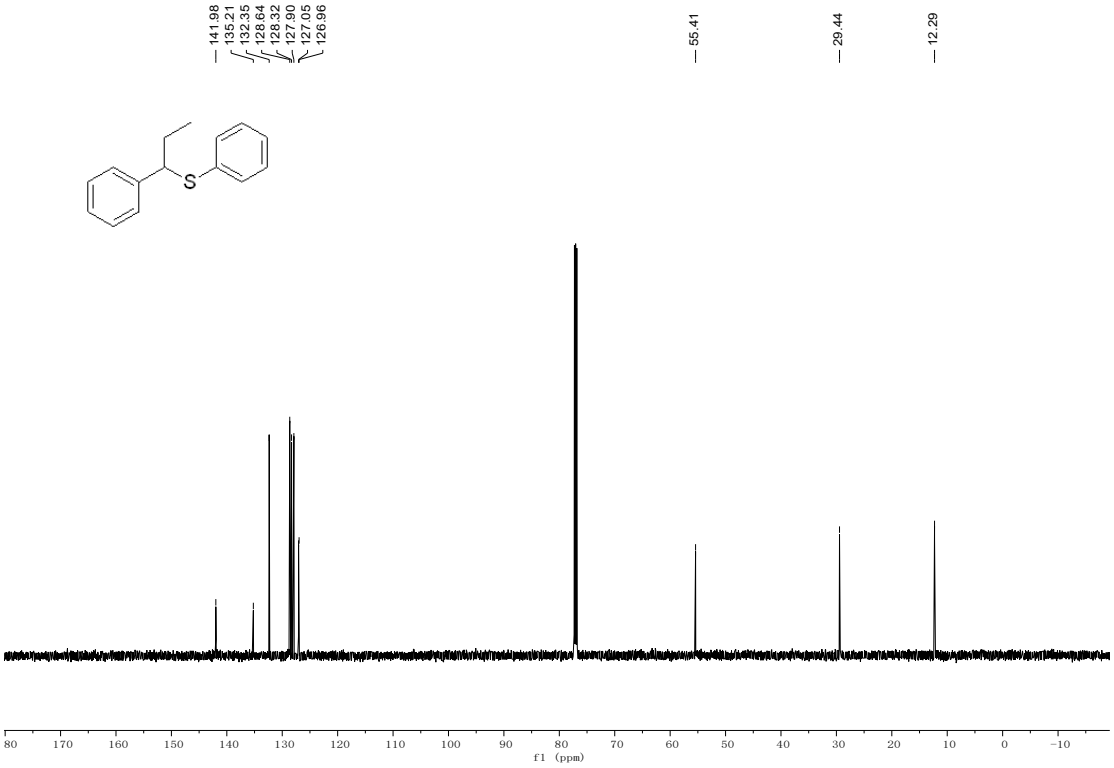
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3v



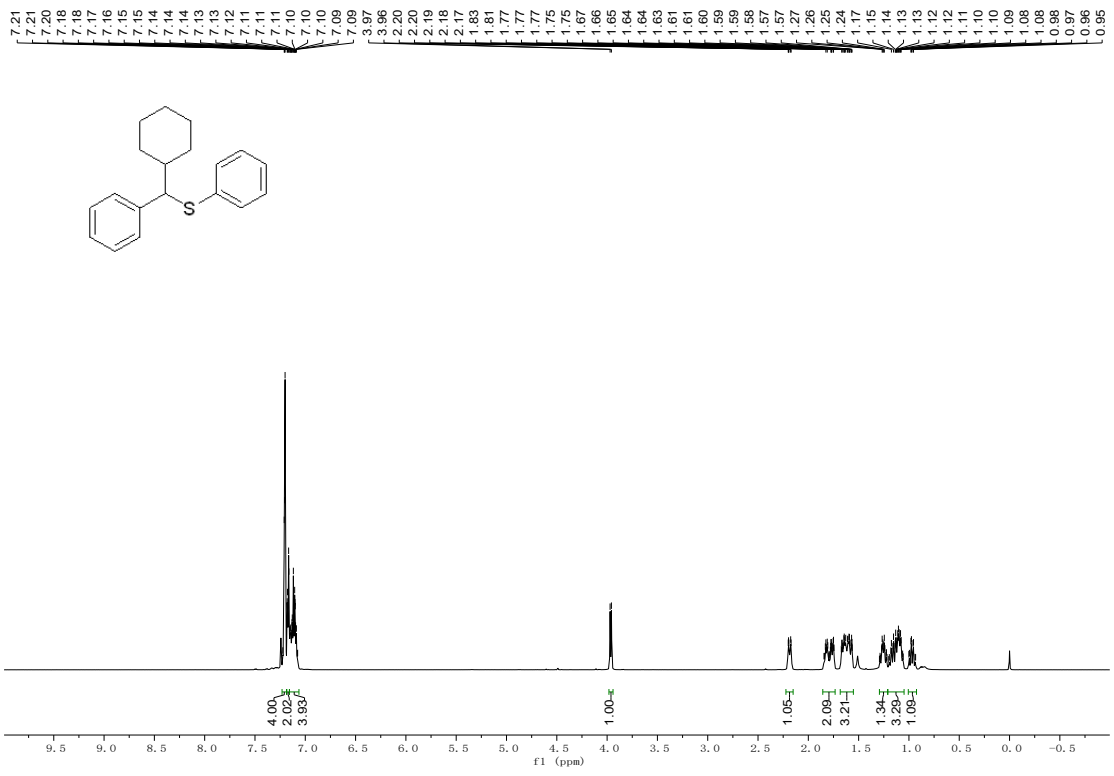
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3w



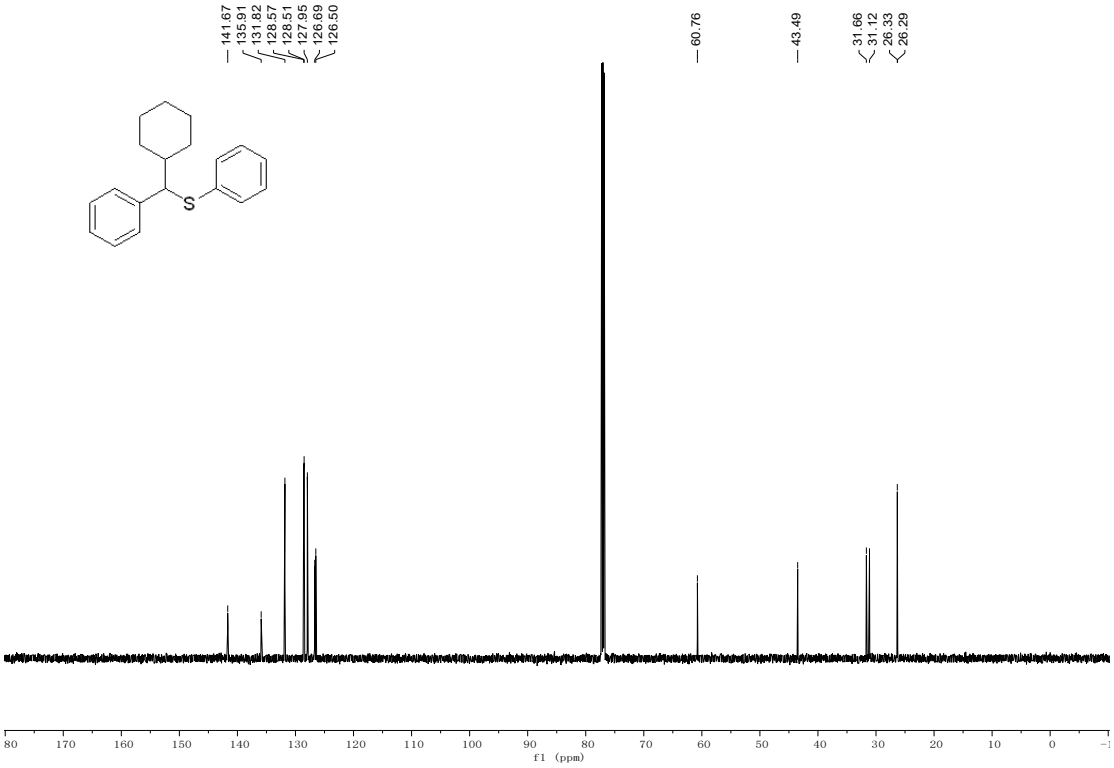
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3w



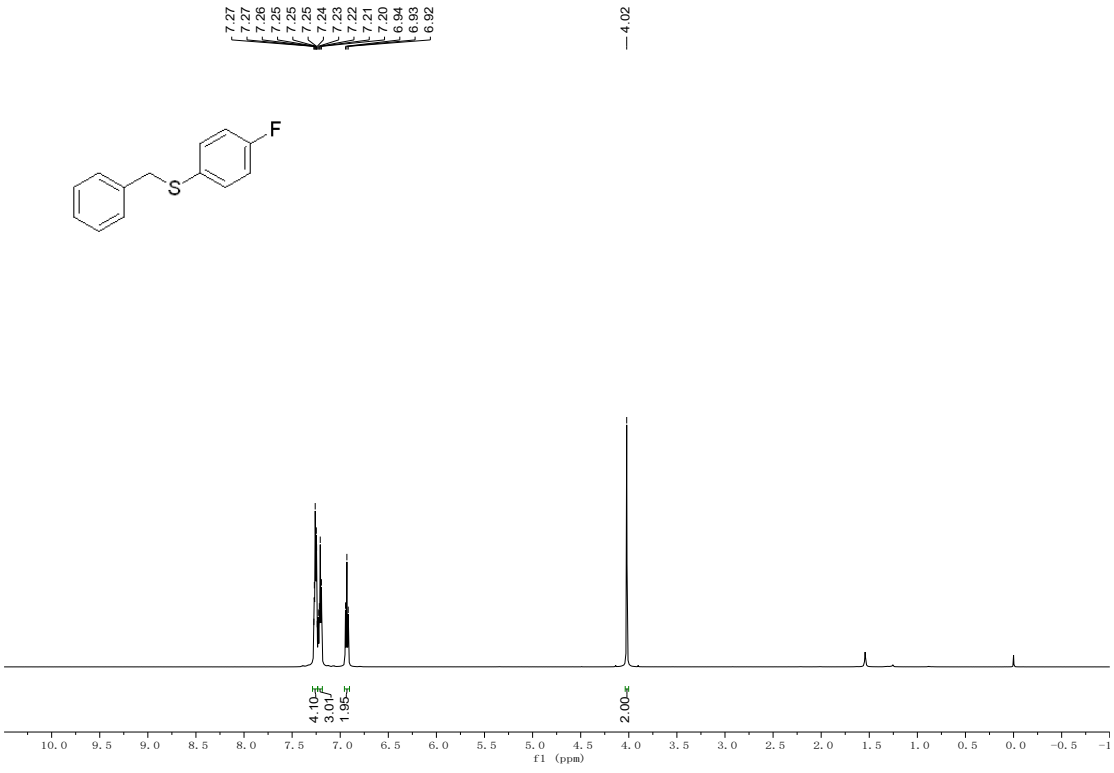
^{1}H-NMR Spectrum (400MHz, $CDCl_3$) of 3x



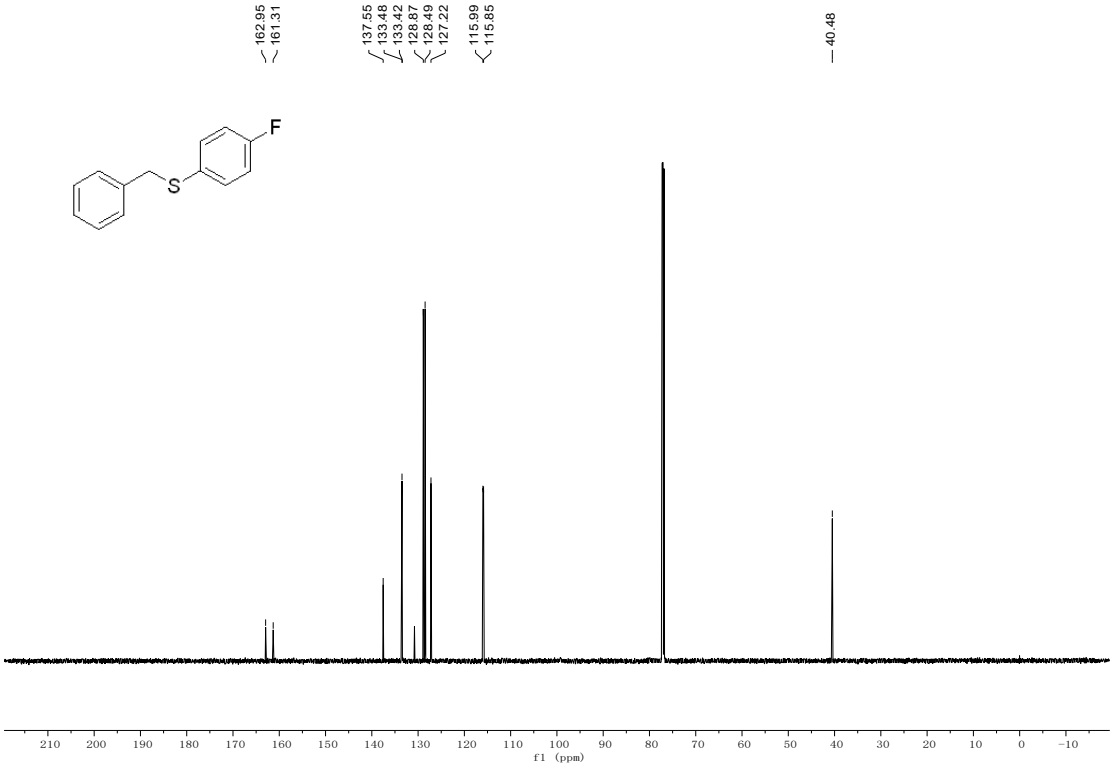
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3x



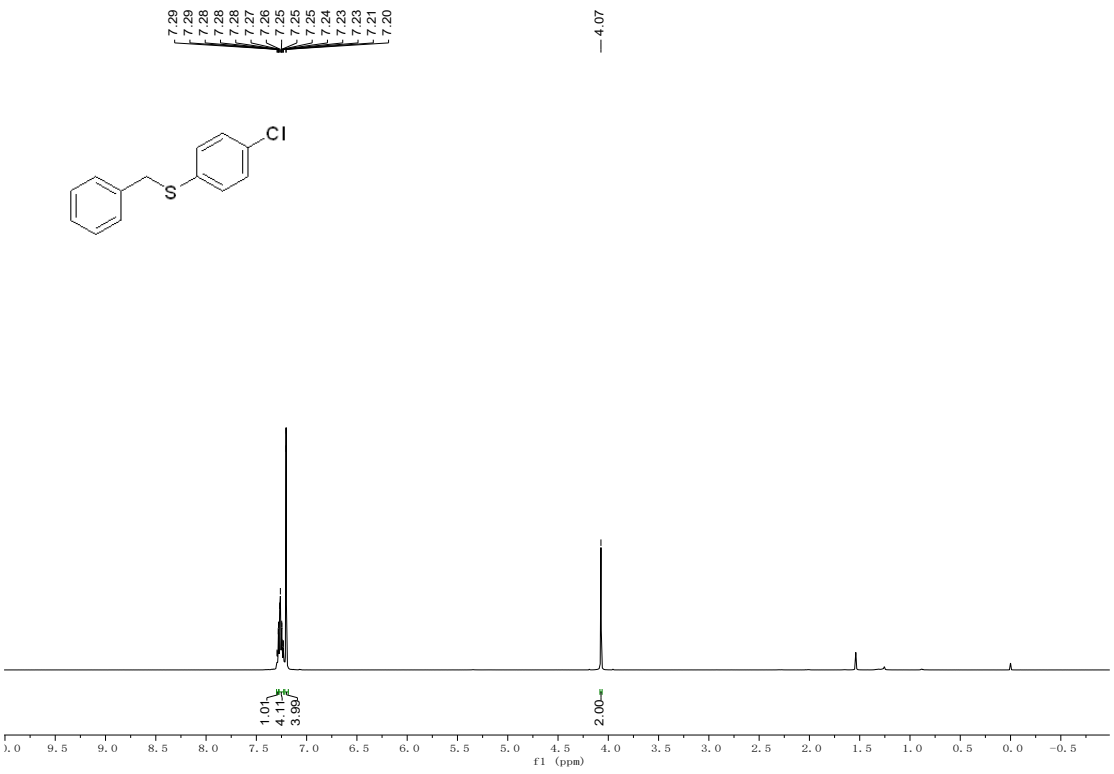
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3y



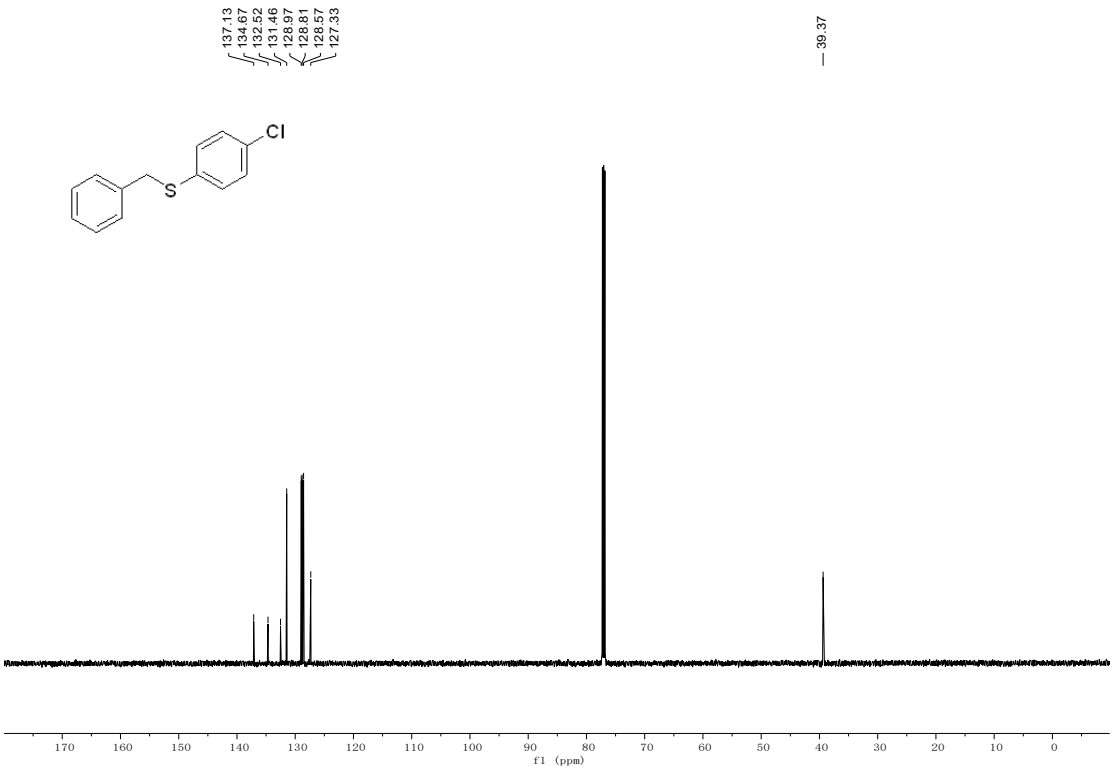
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3y



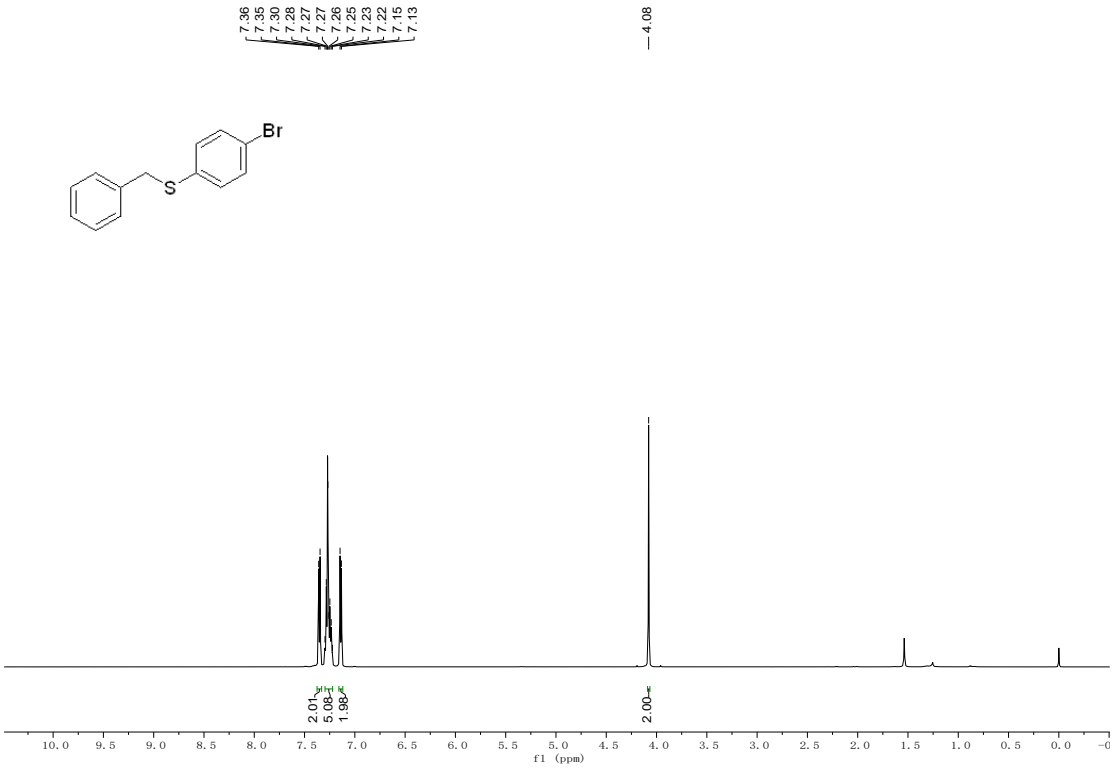
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3z



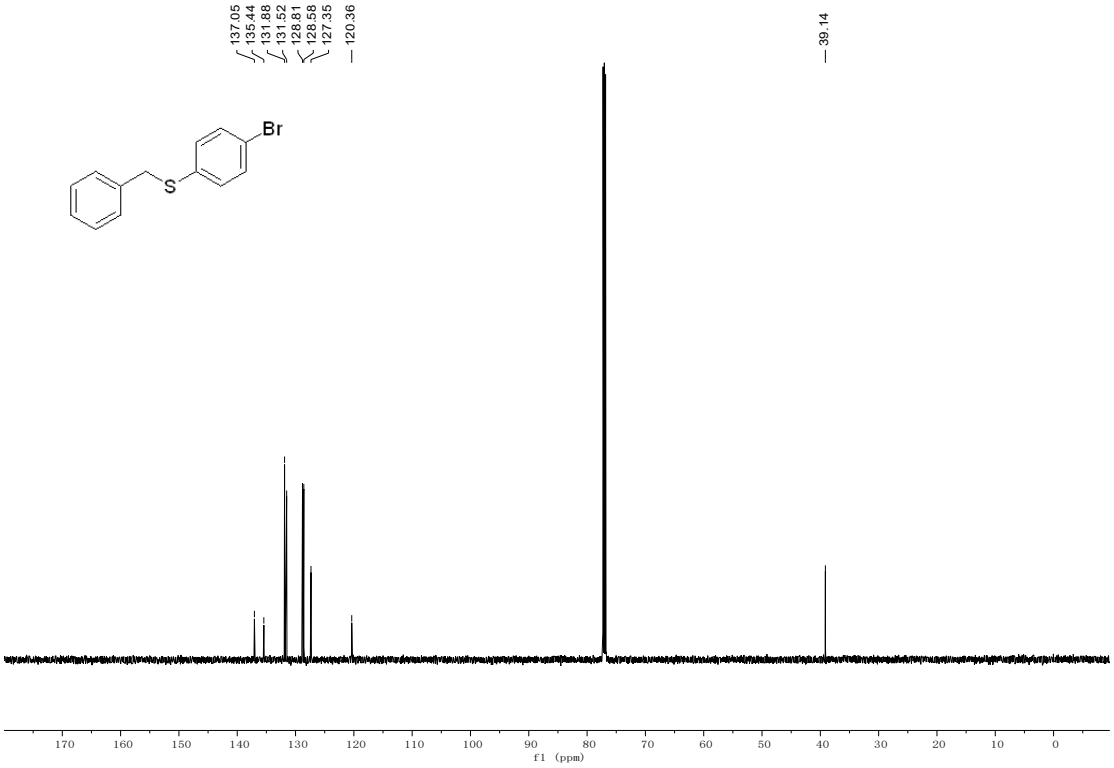
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3z



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



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



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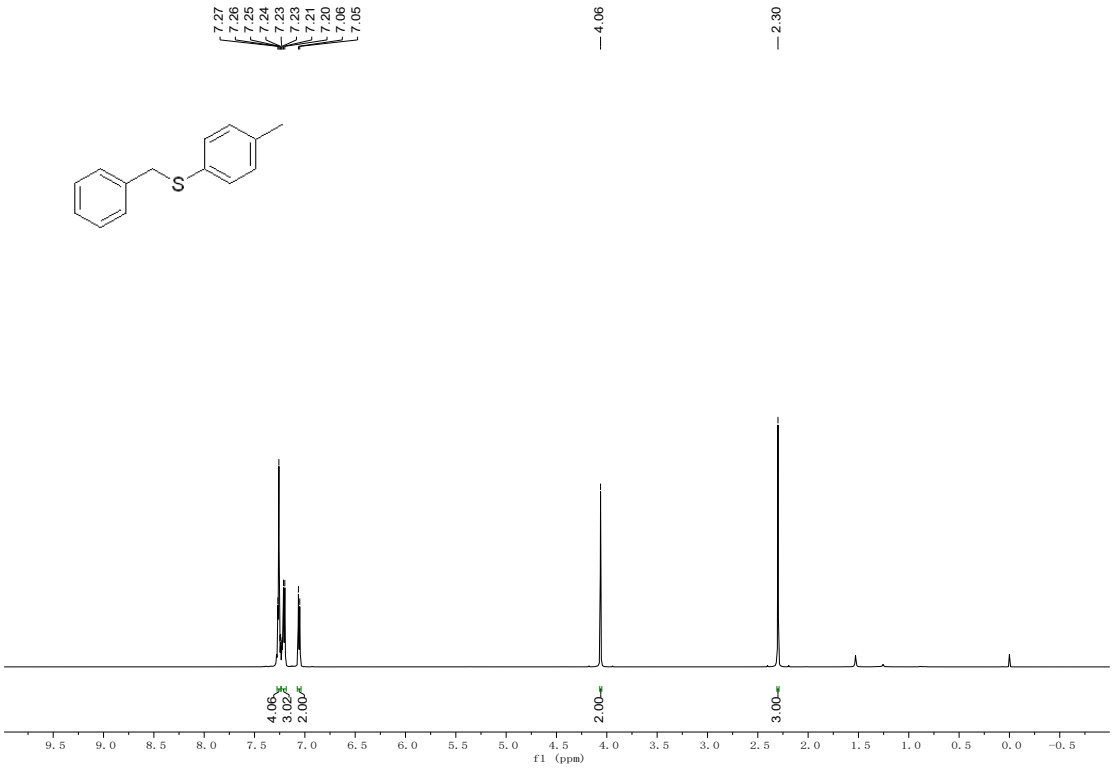
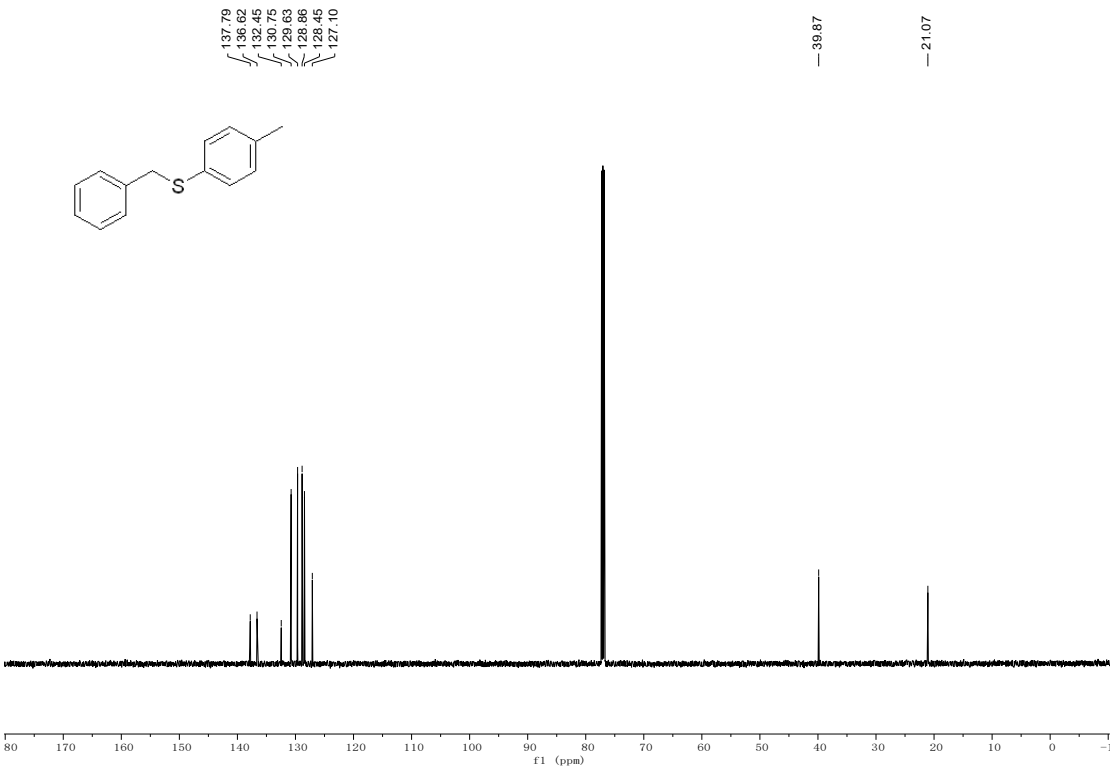


^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3ab



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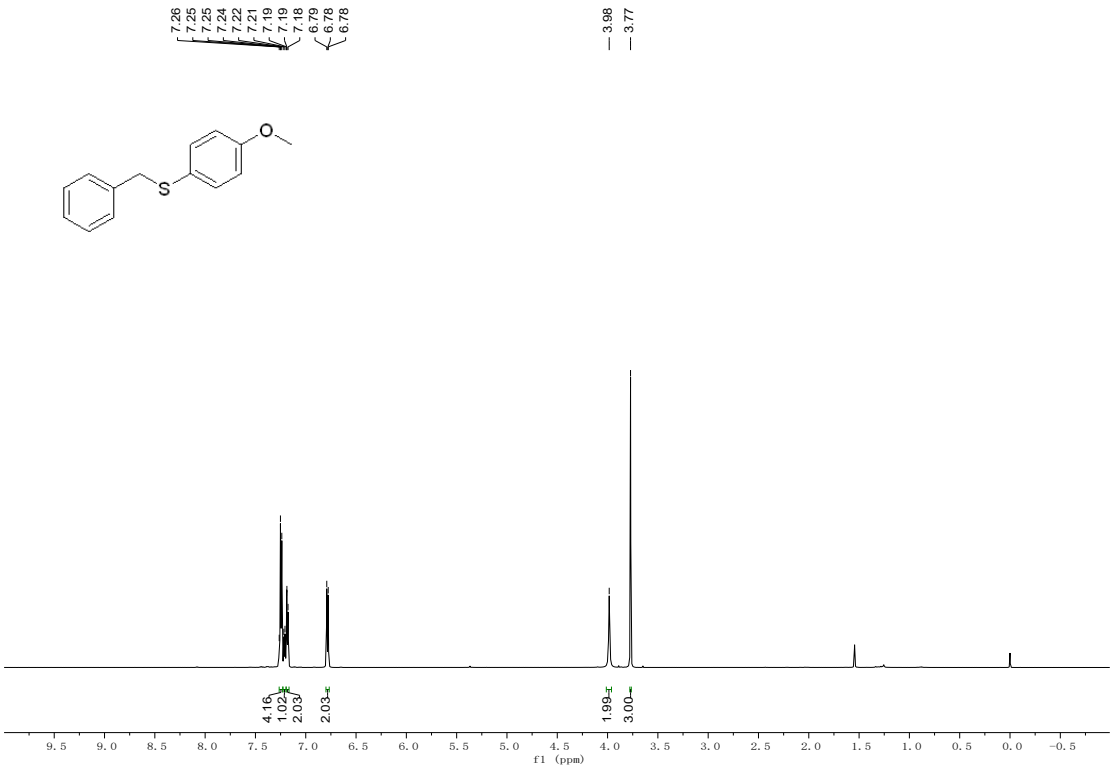
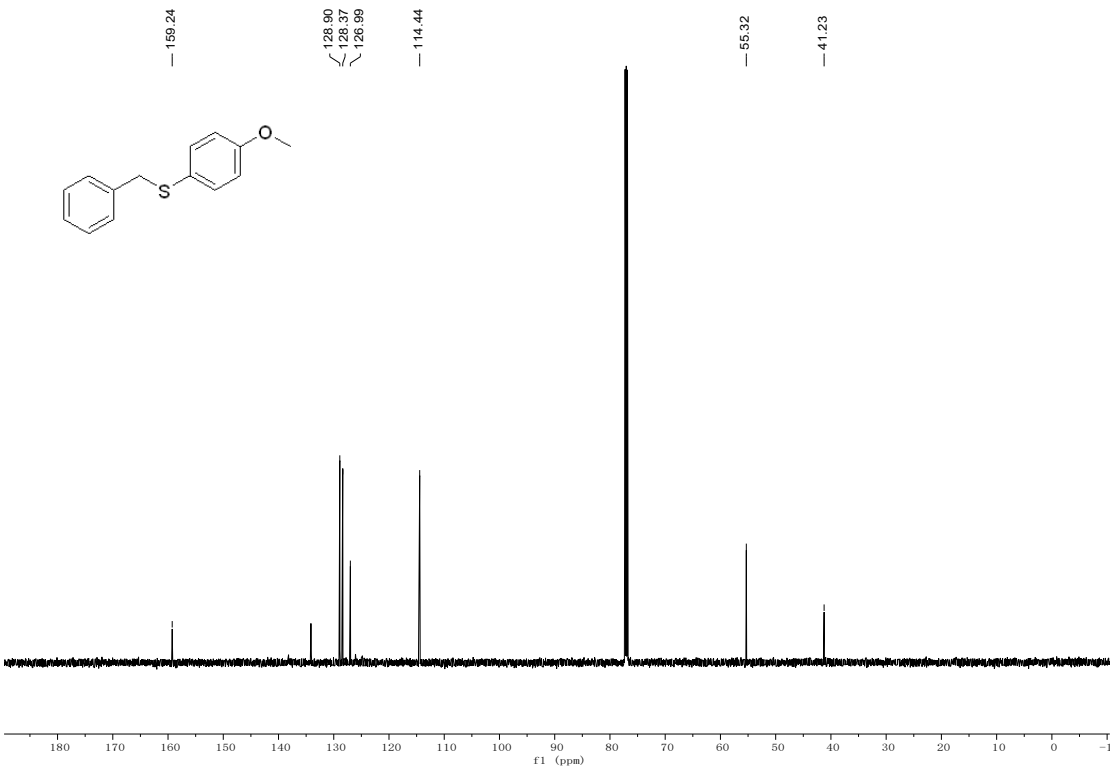
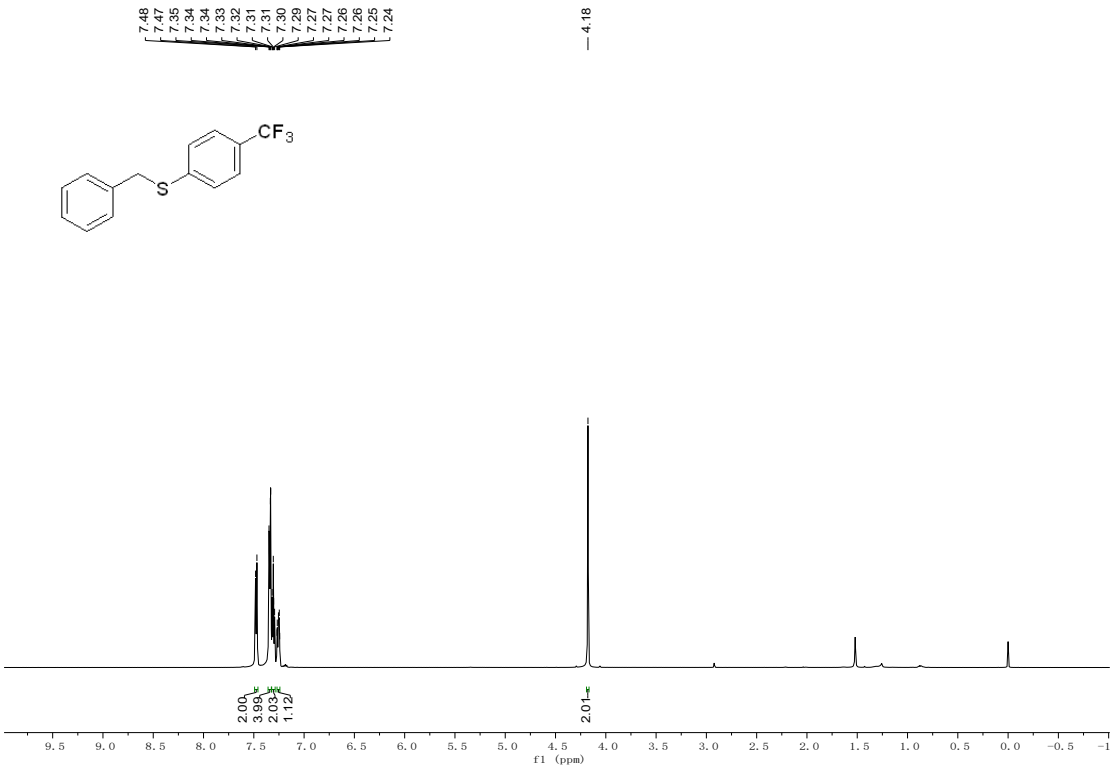


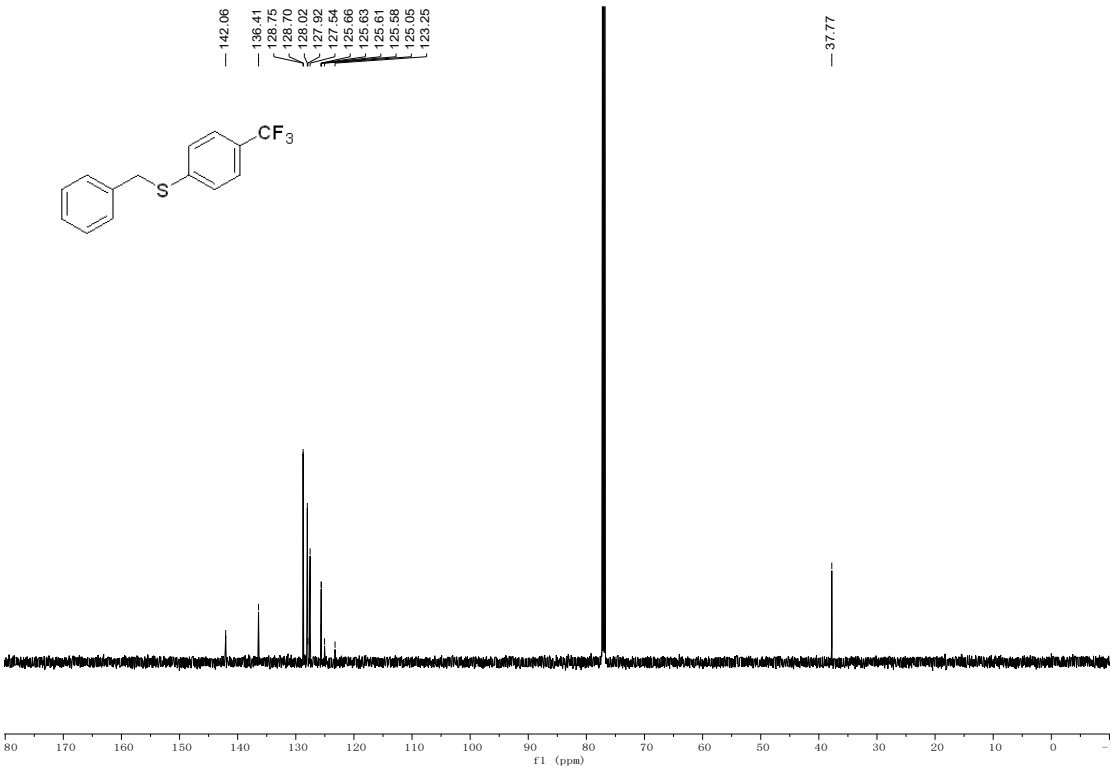
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3ac



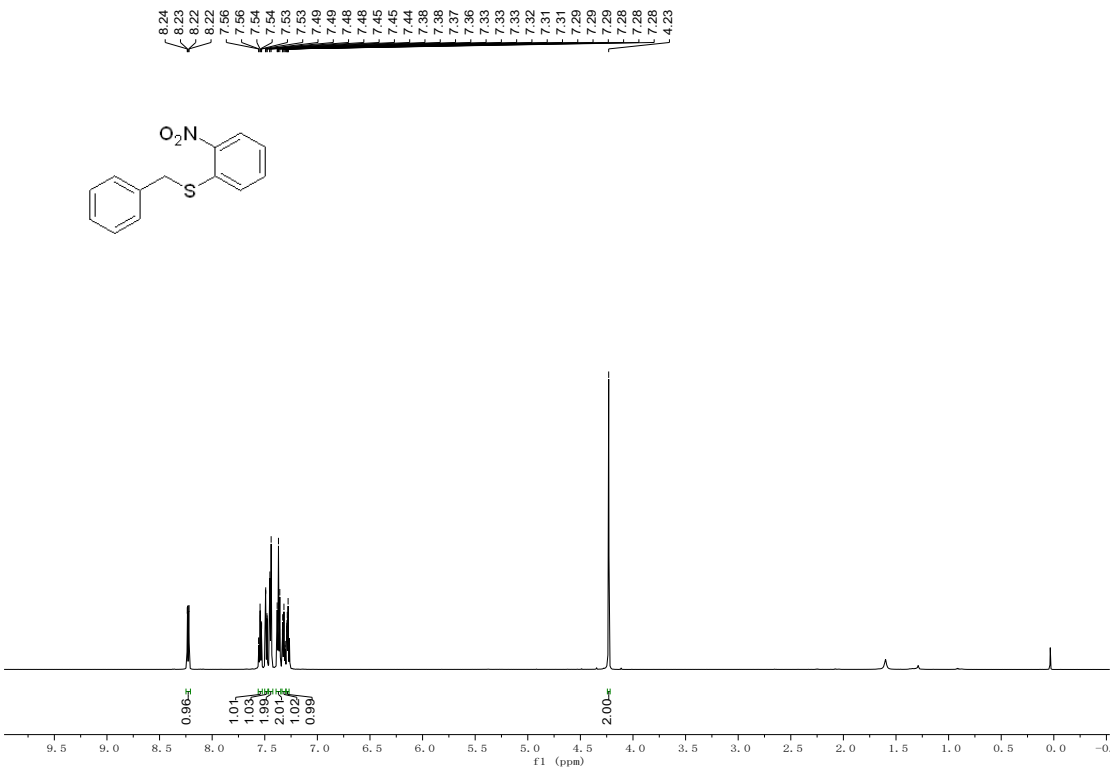
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3ad



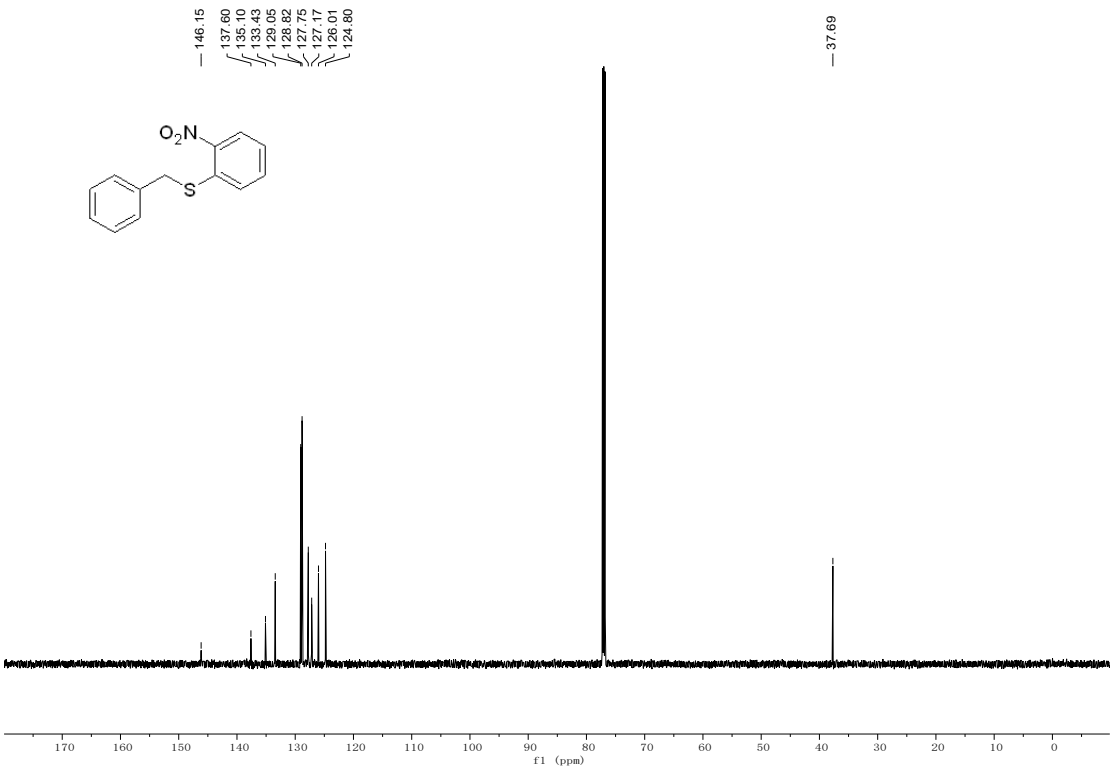
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3ad



^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3ae



^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3ae



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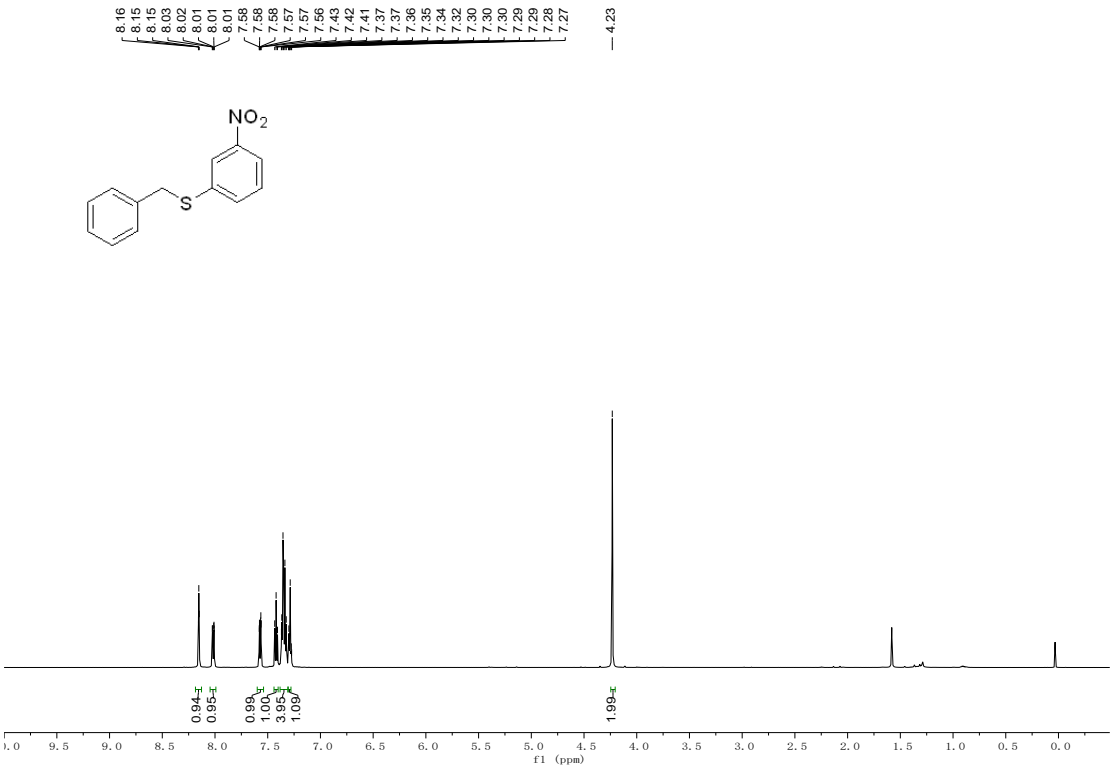

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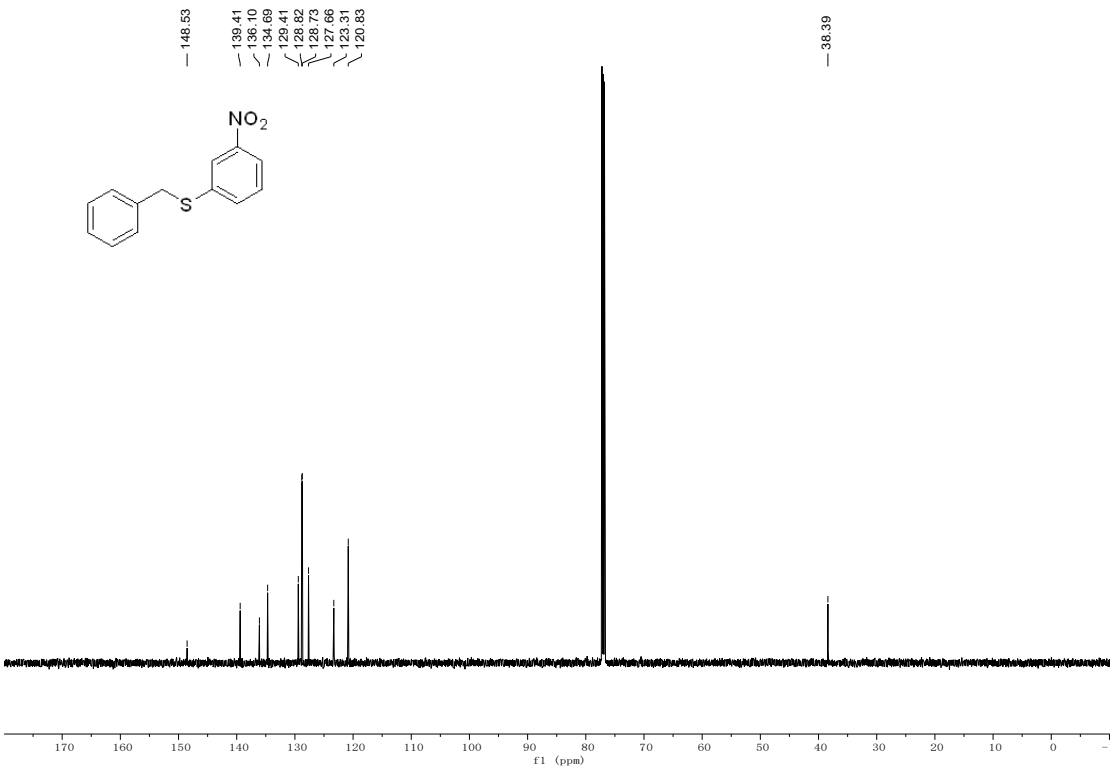
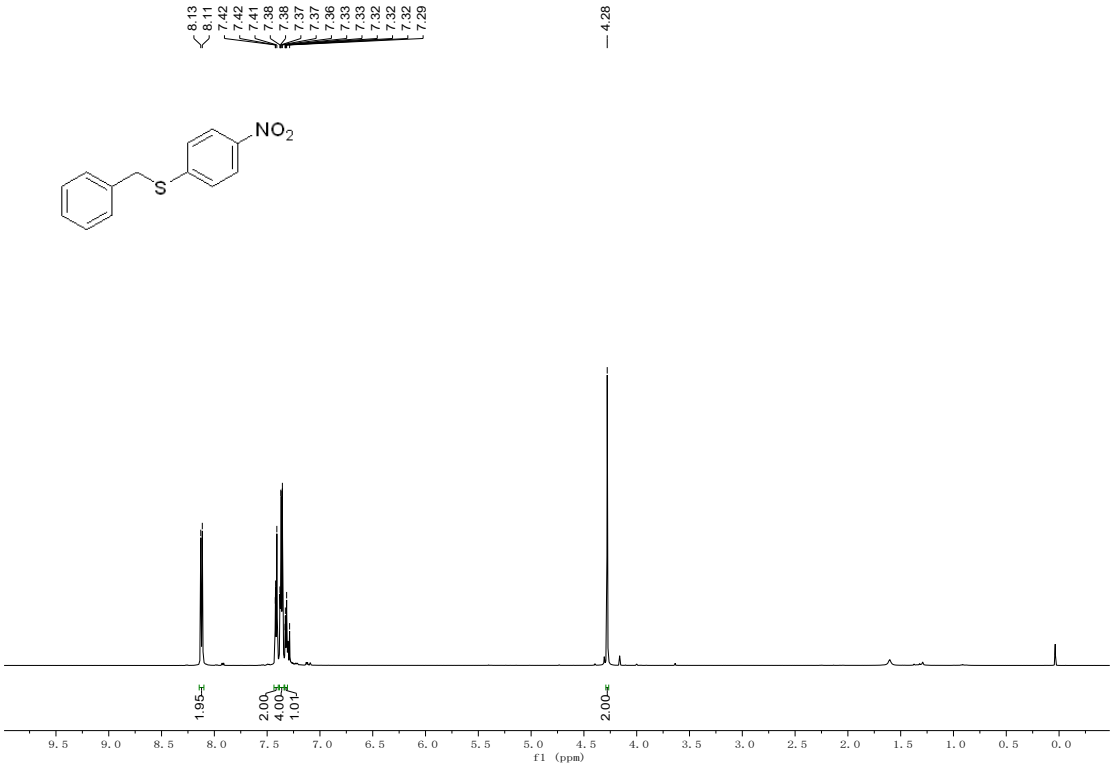
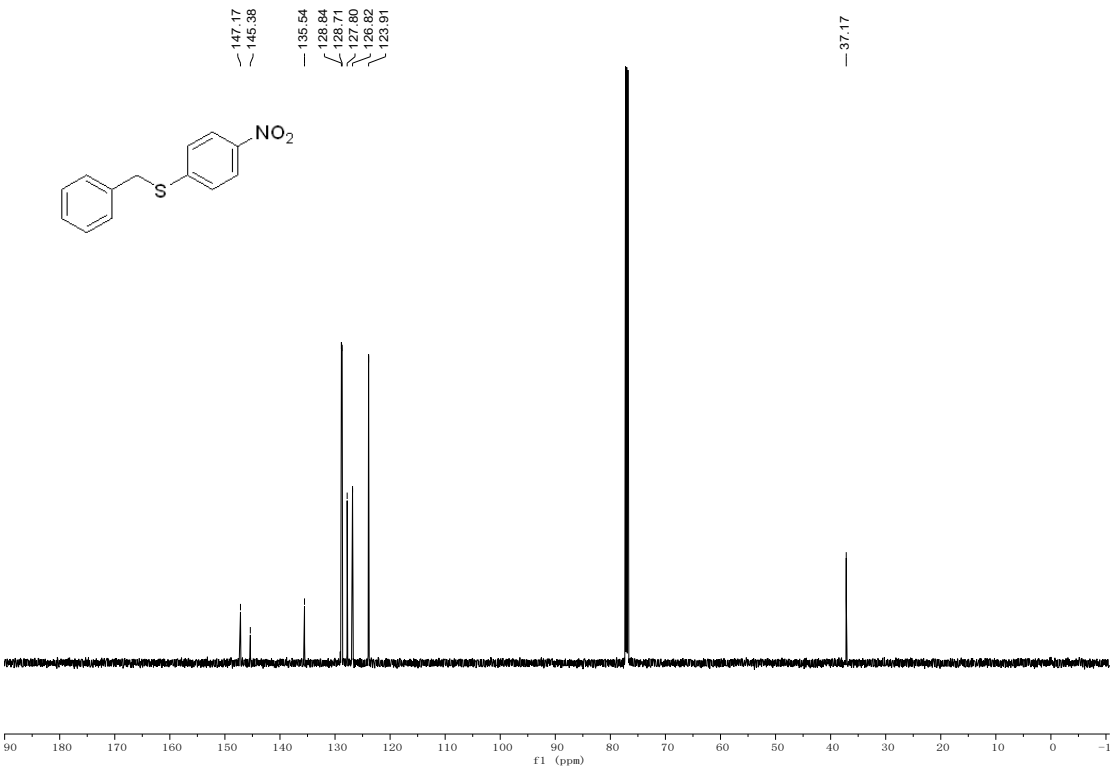


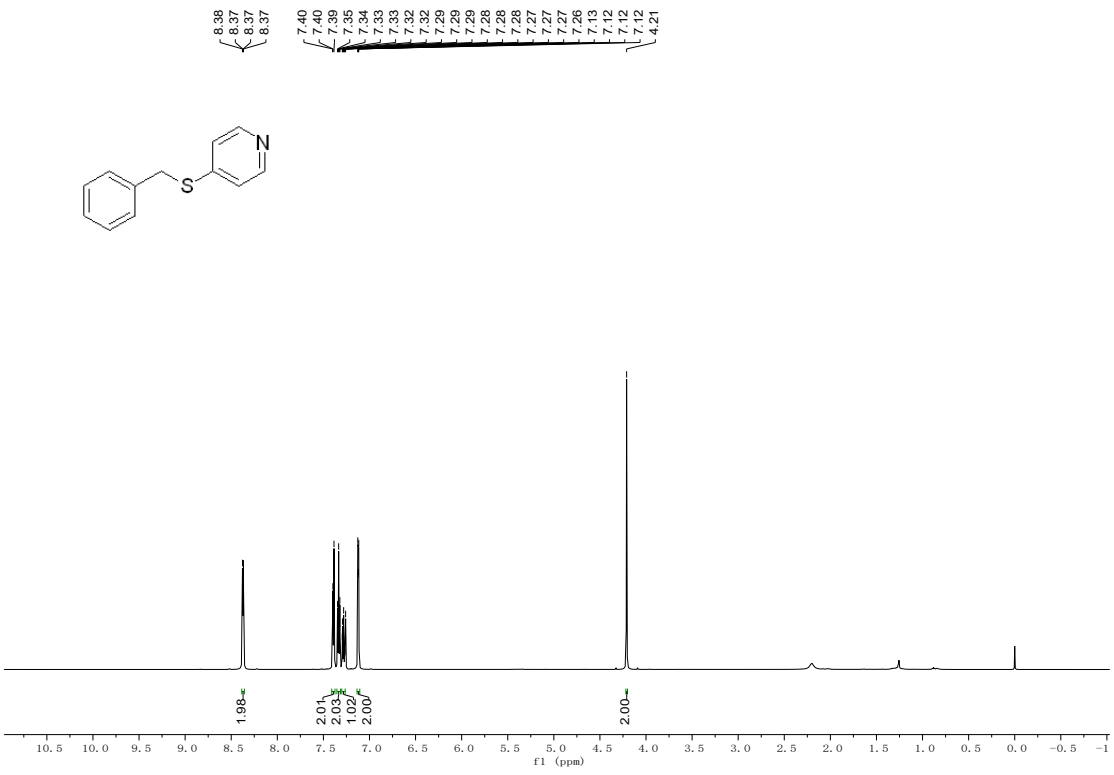
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3ag



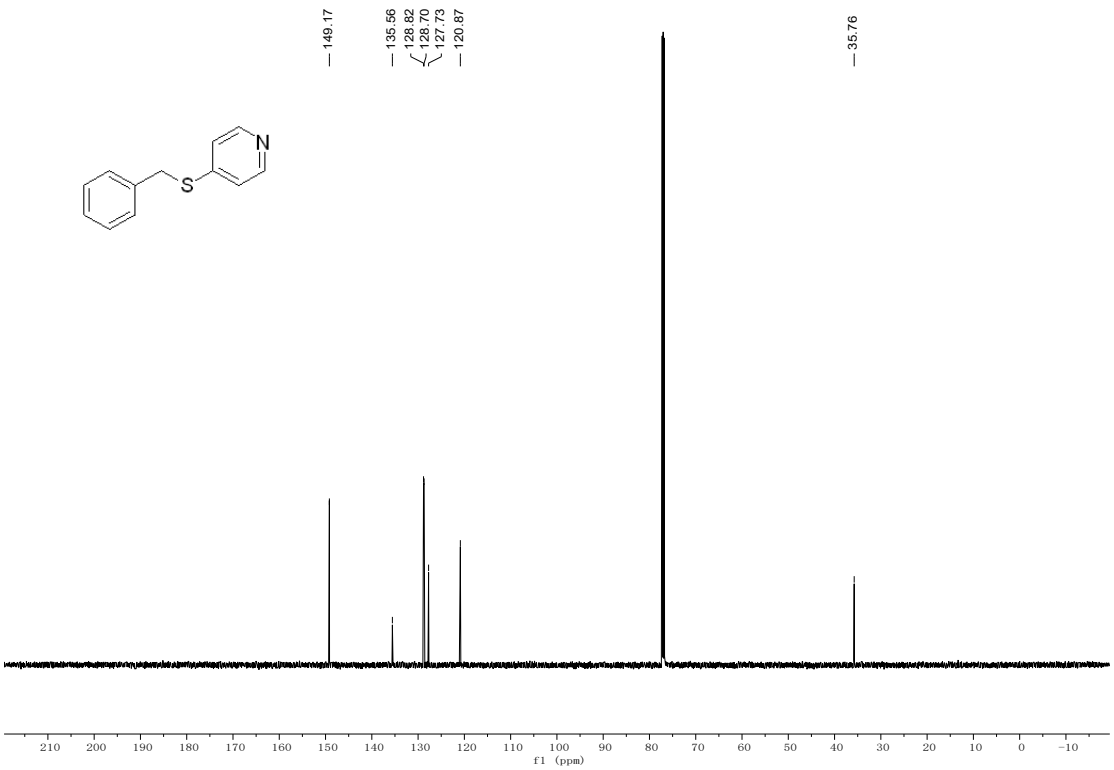
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3ag



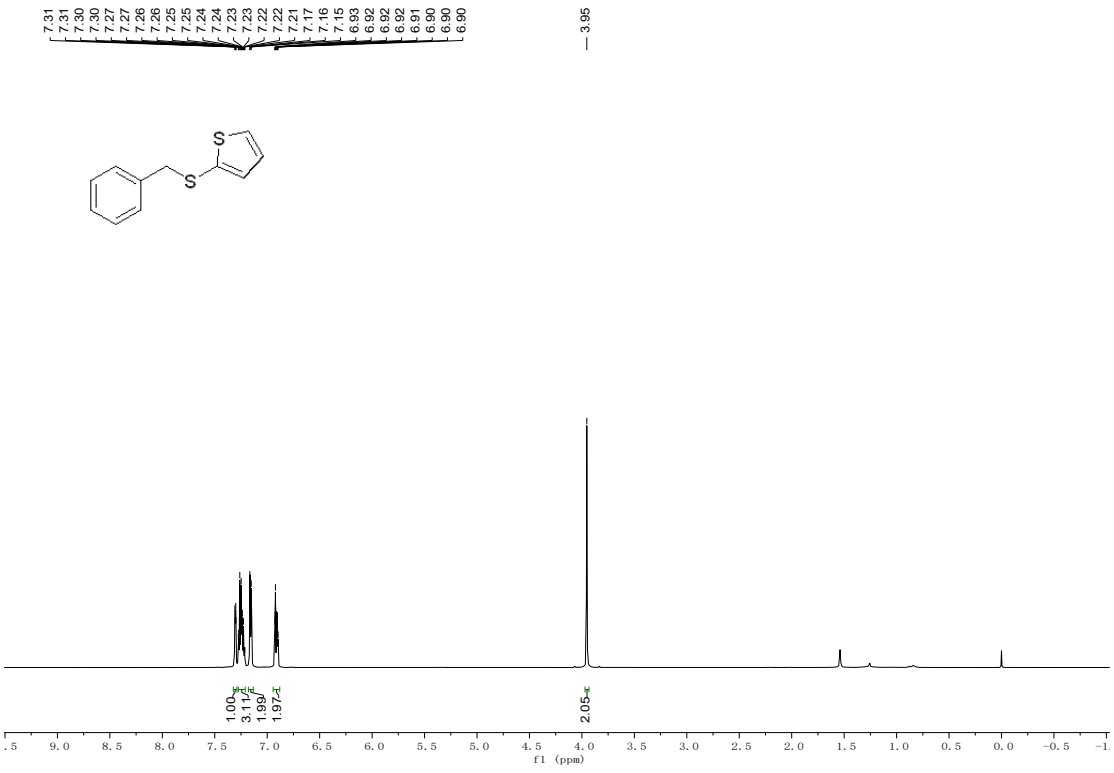
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3ah



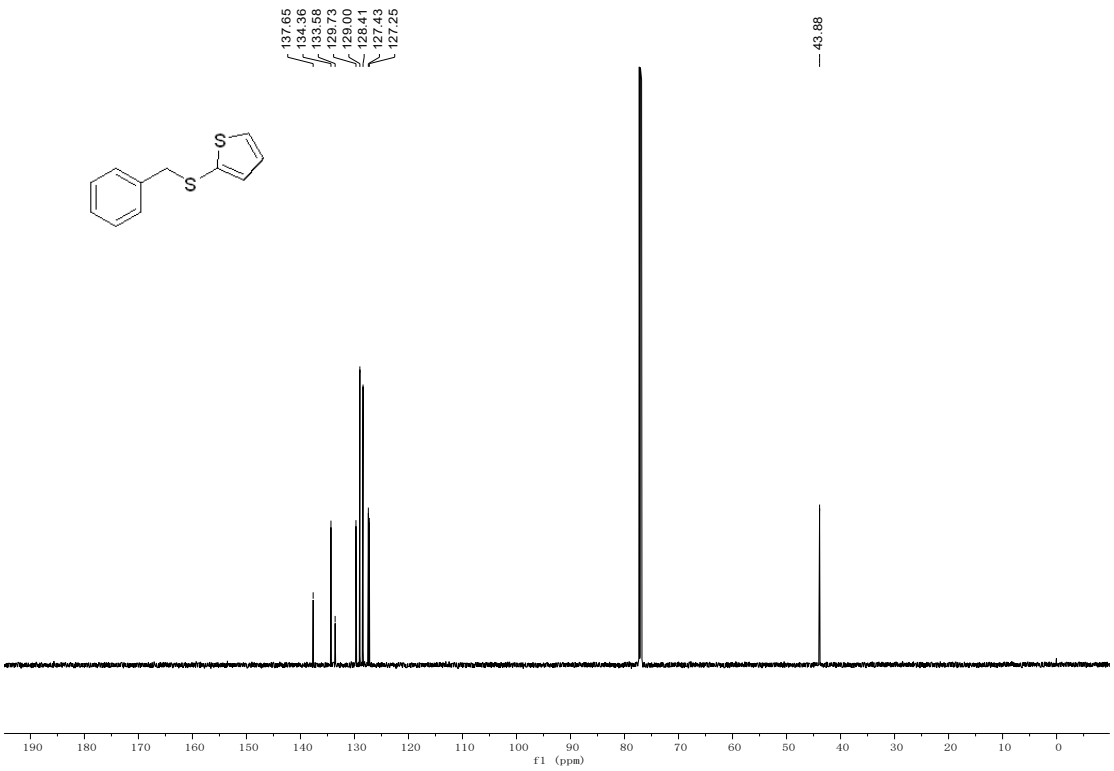
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3ah



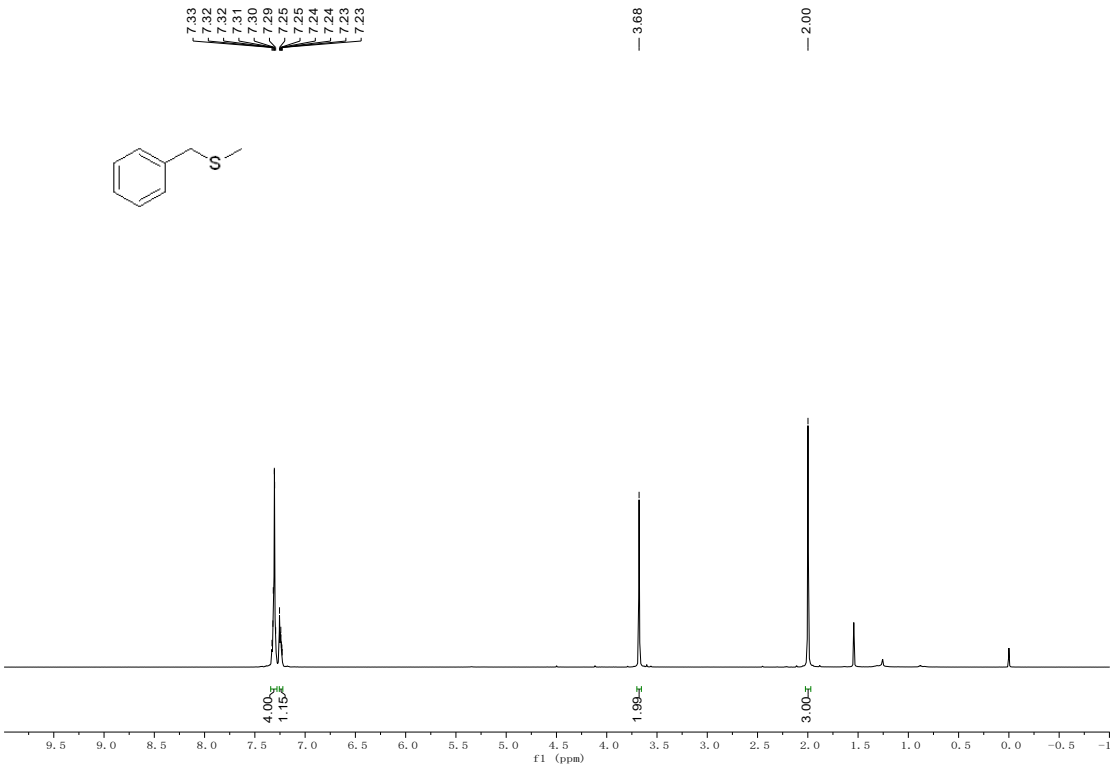
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3ai



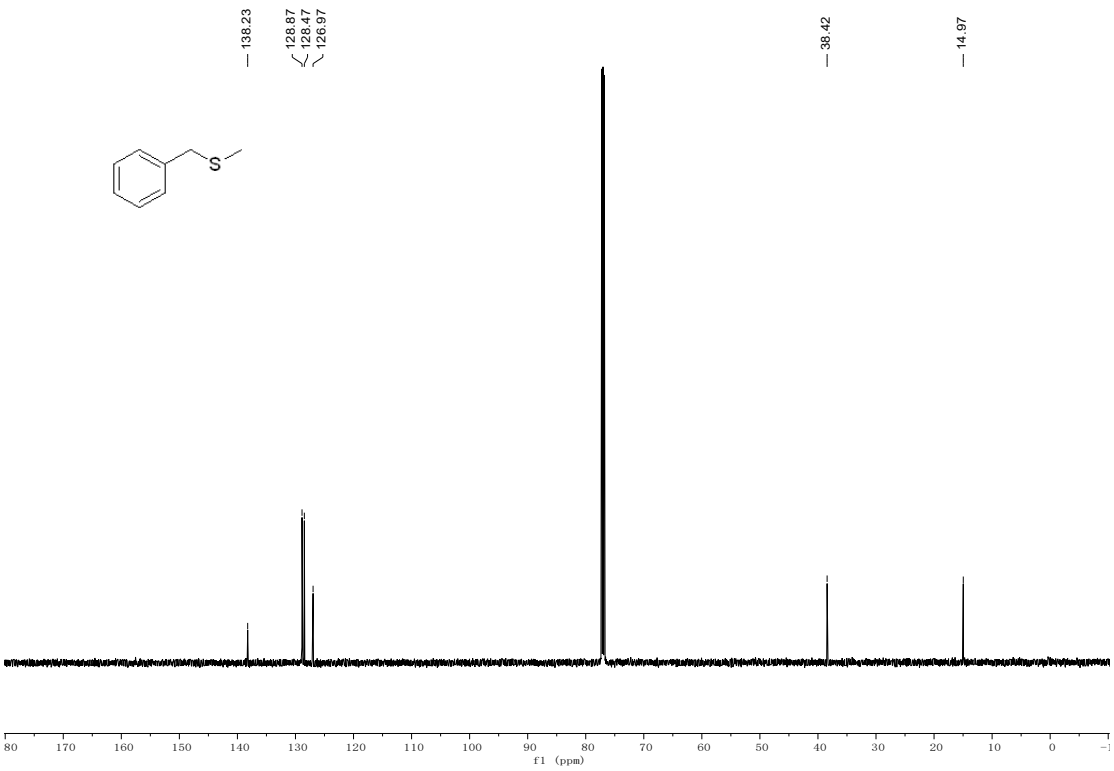
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3ai



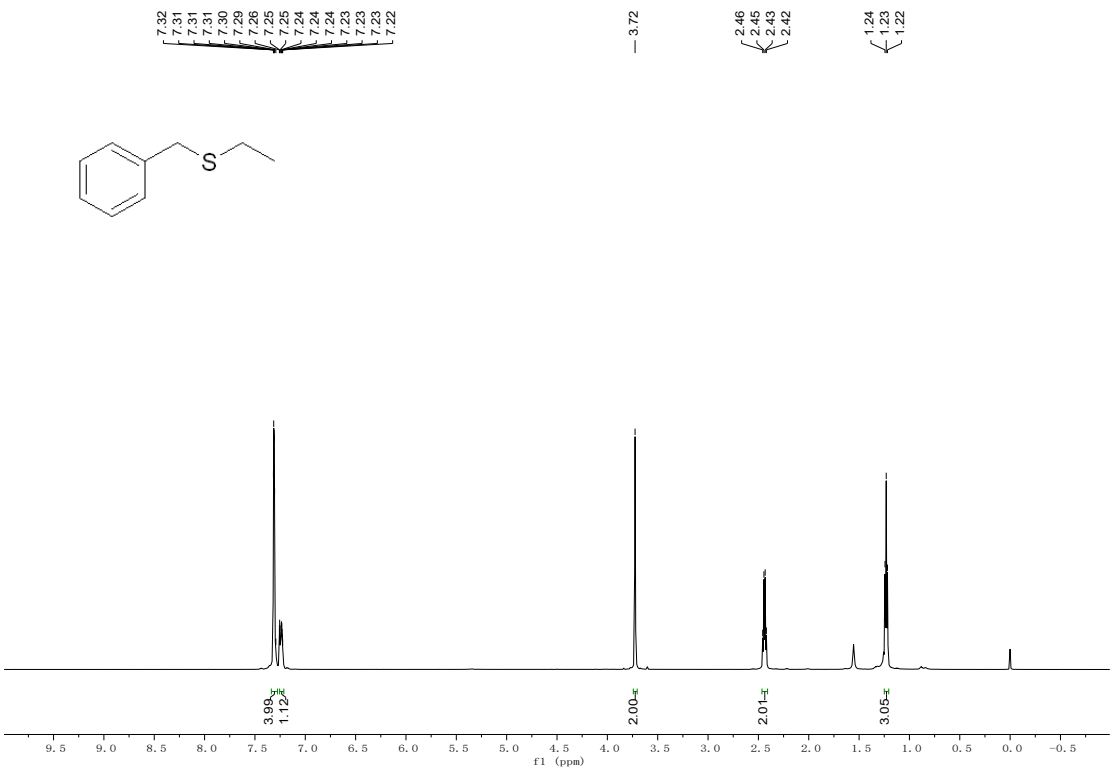
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3aj



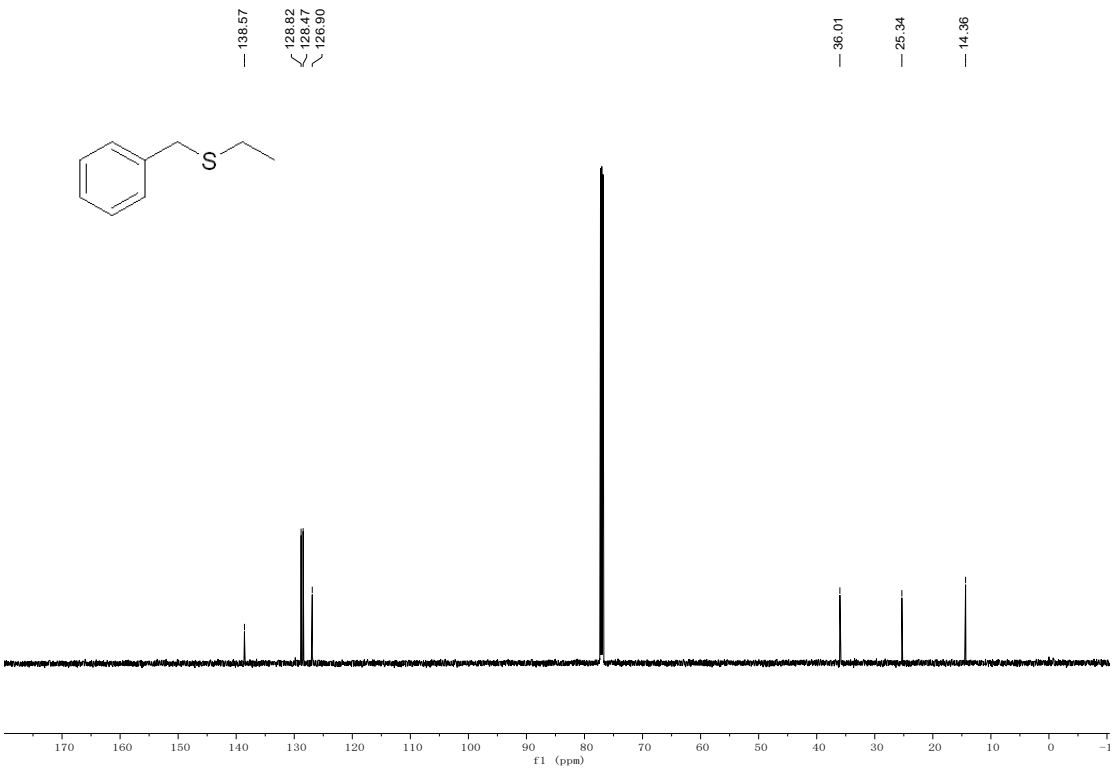
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3aj



^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3ak



^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3ak



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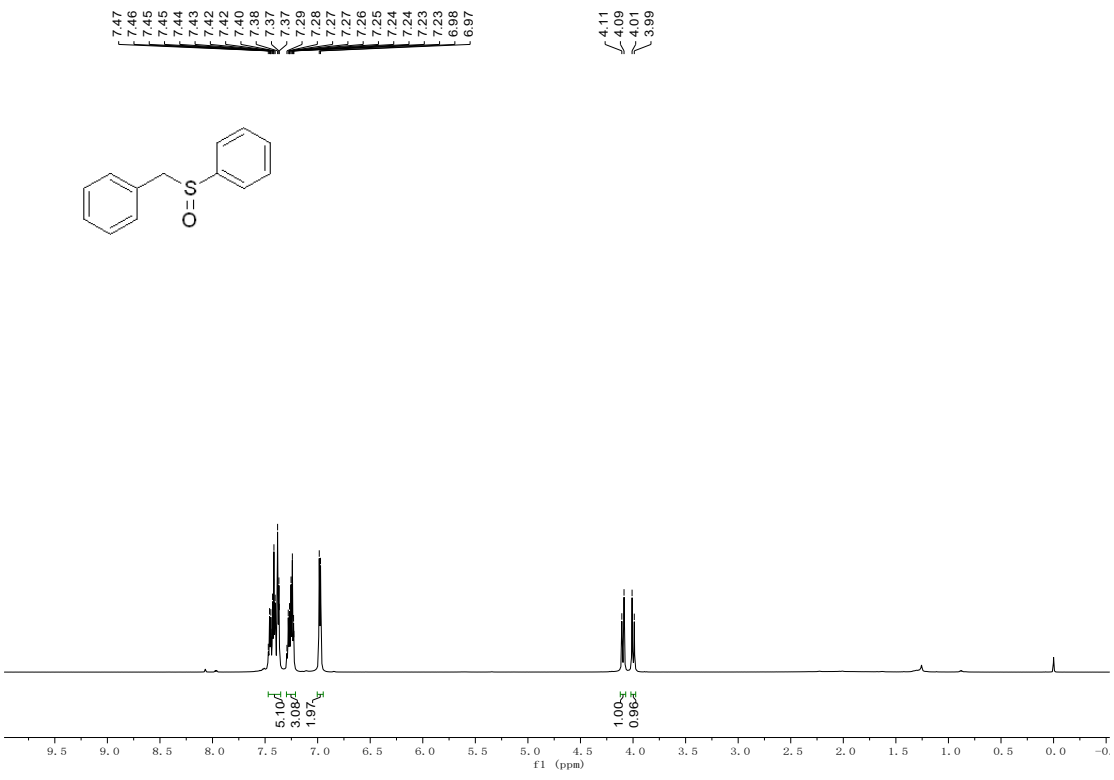
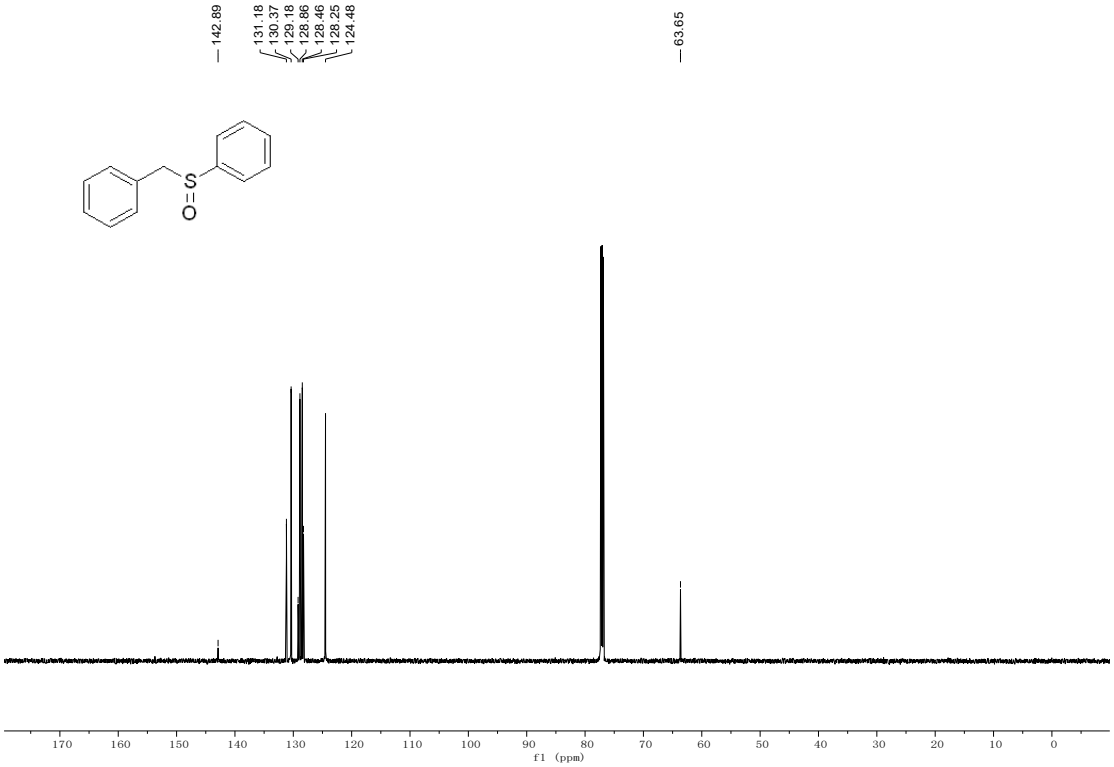


^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 4



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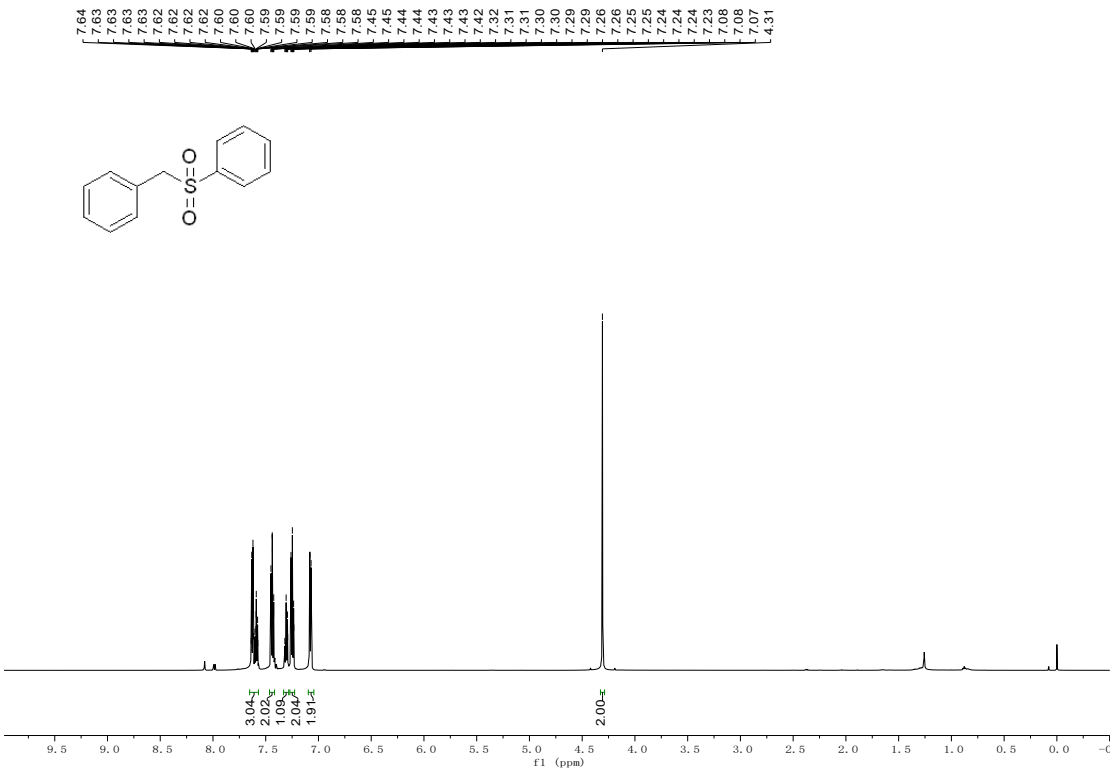
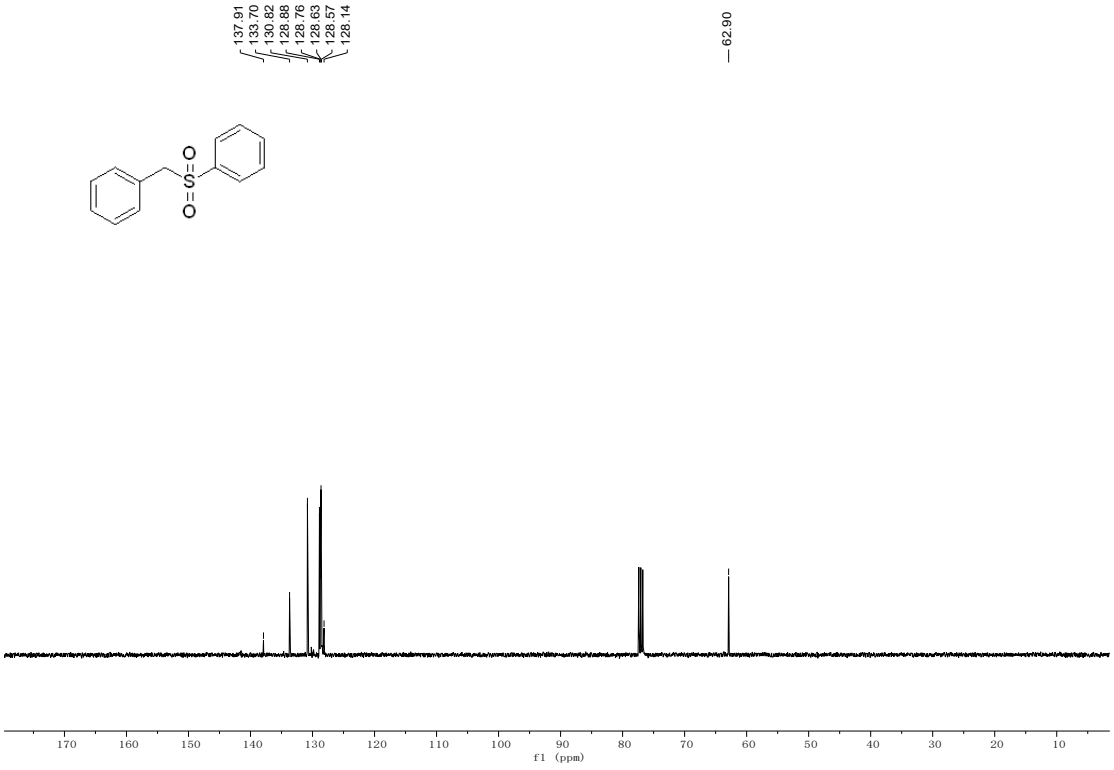


^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 5



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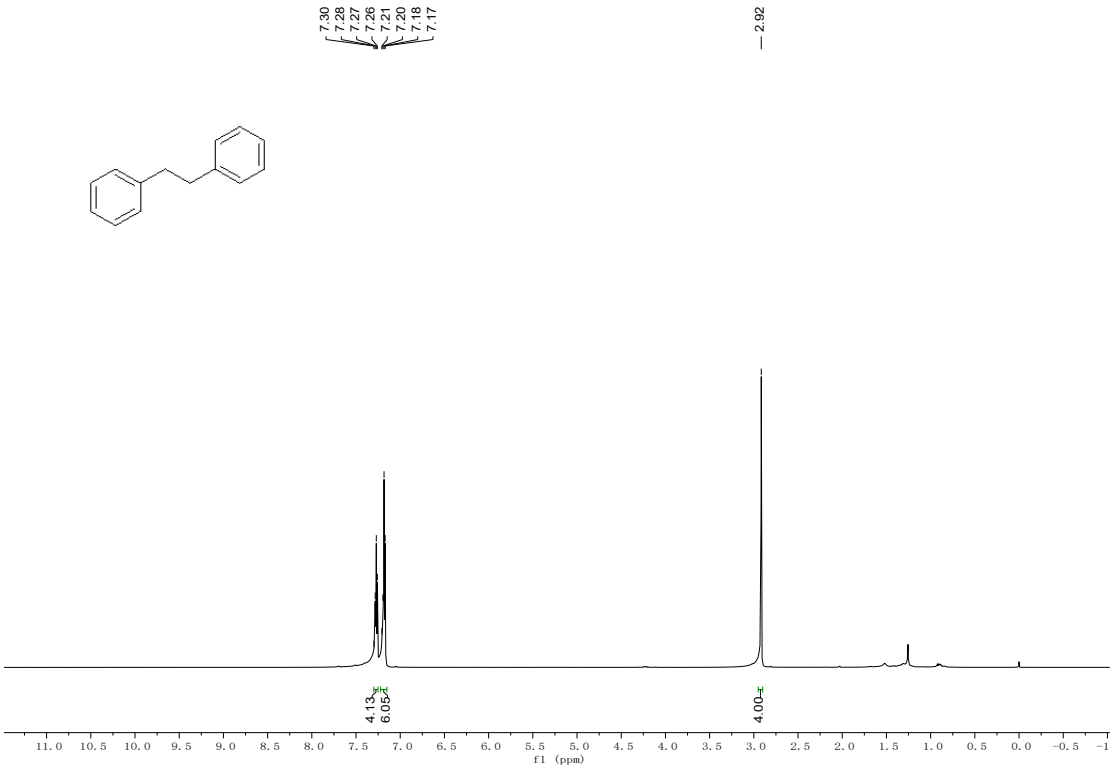
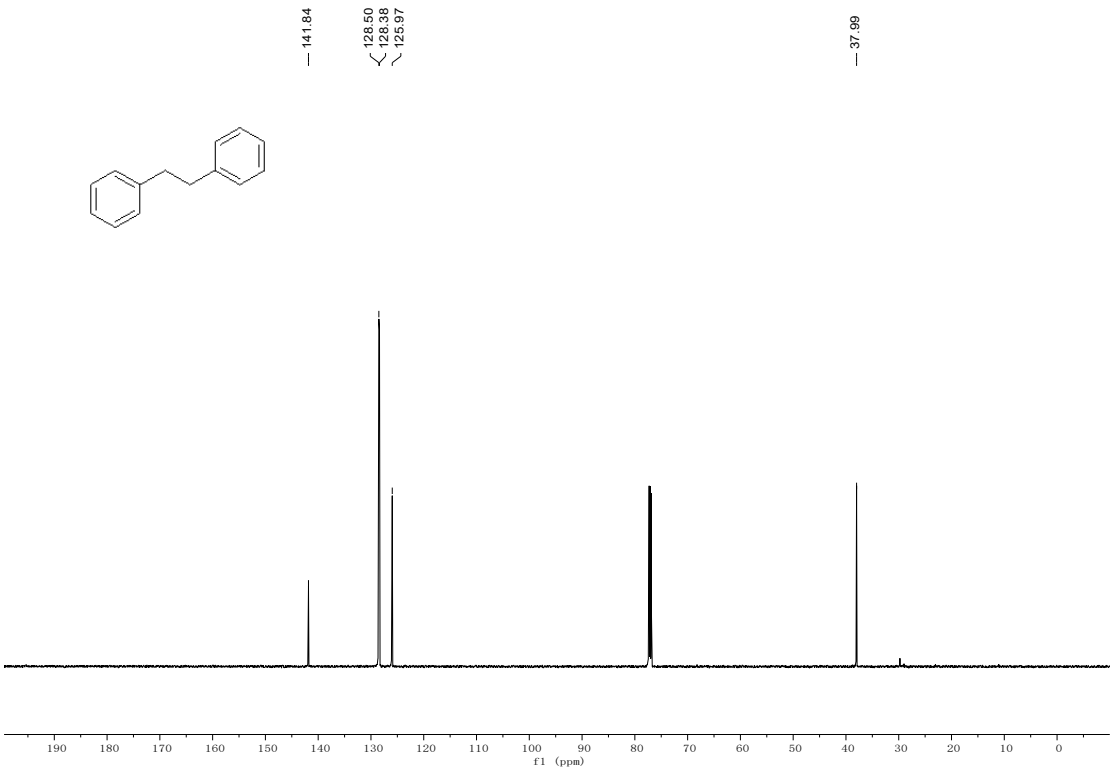
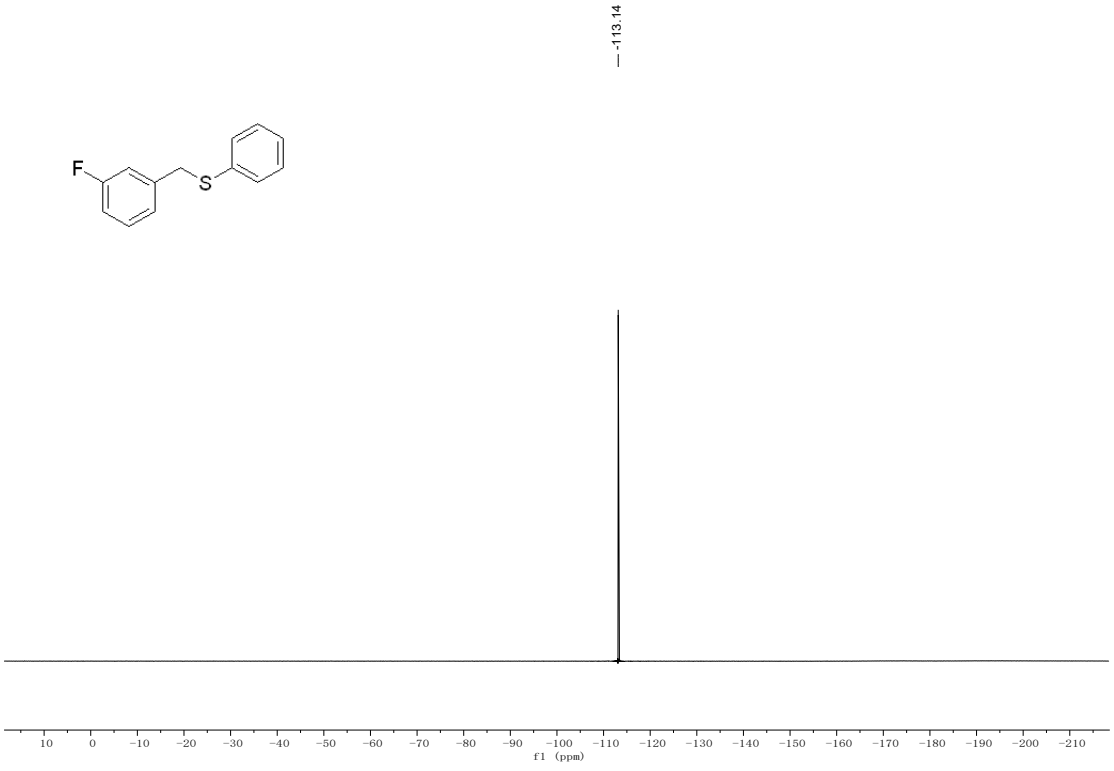


^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 12

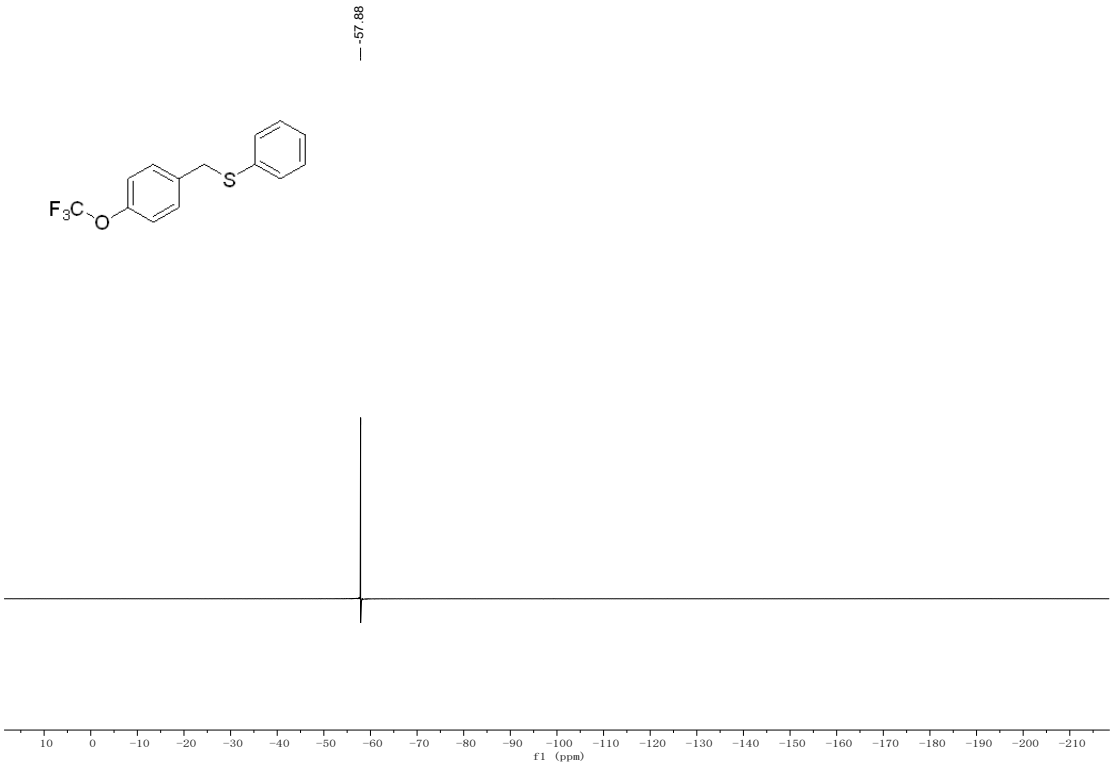


^{19}F-NMR Spectrum (565 MHz, $CDCl_3$) of 3g

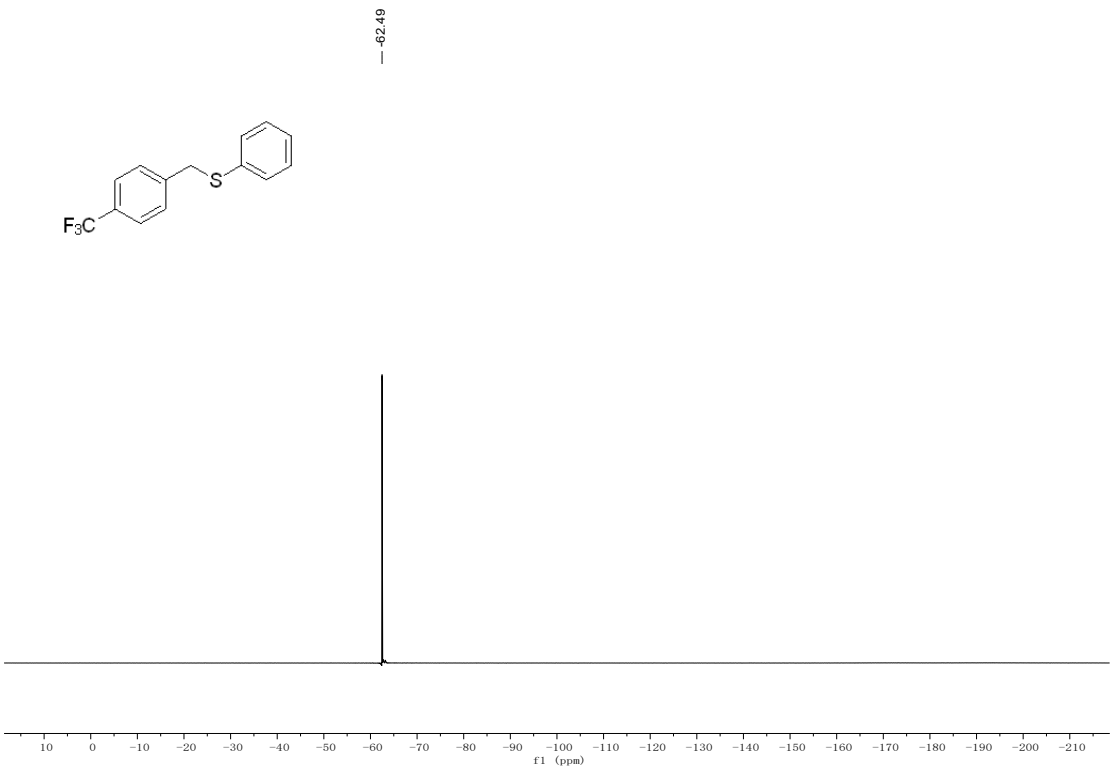


^{19}F-NMR Spectrum (565 MHz, $CDCl_3$) of 3h

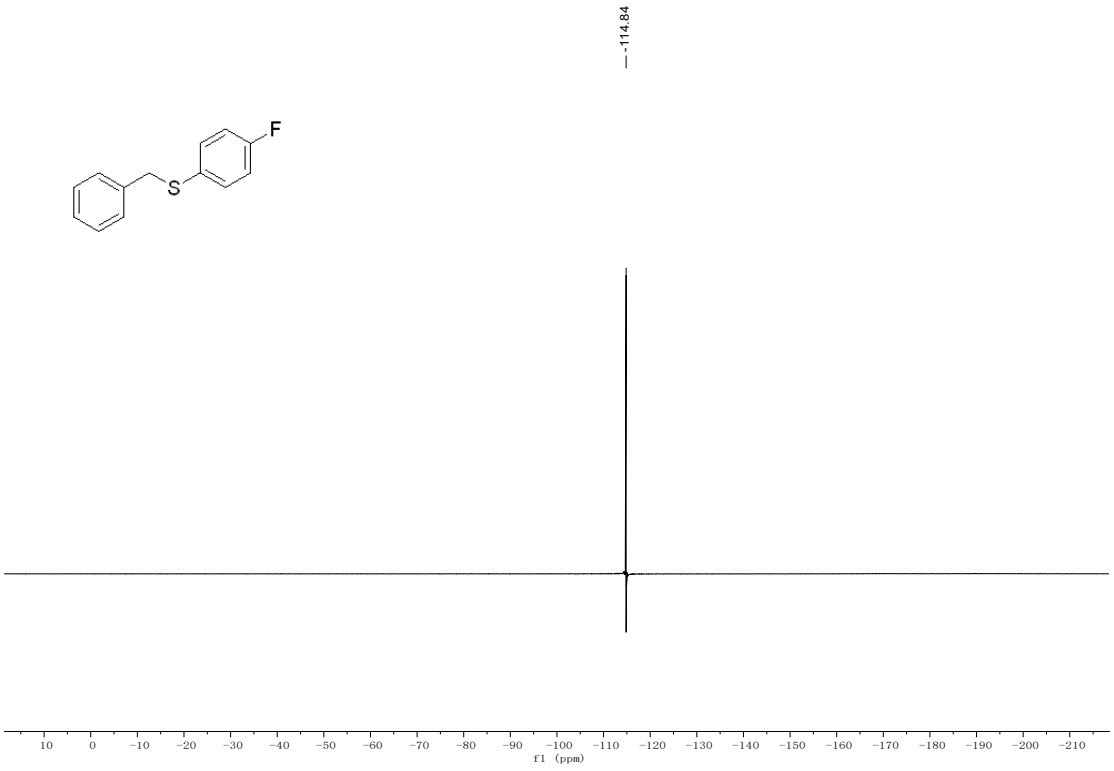
^{19}F-NMR Spectrum (565 MHz, $CDCl_3$) of 3p



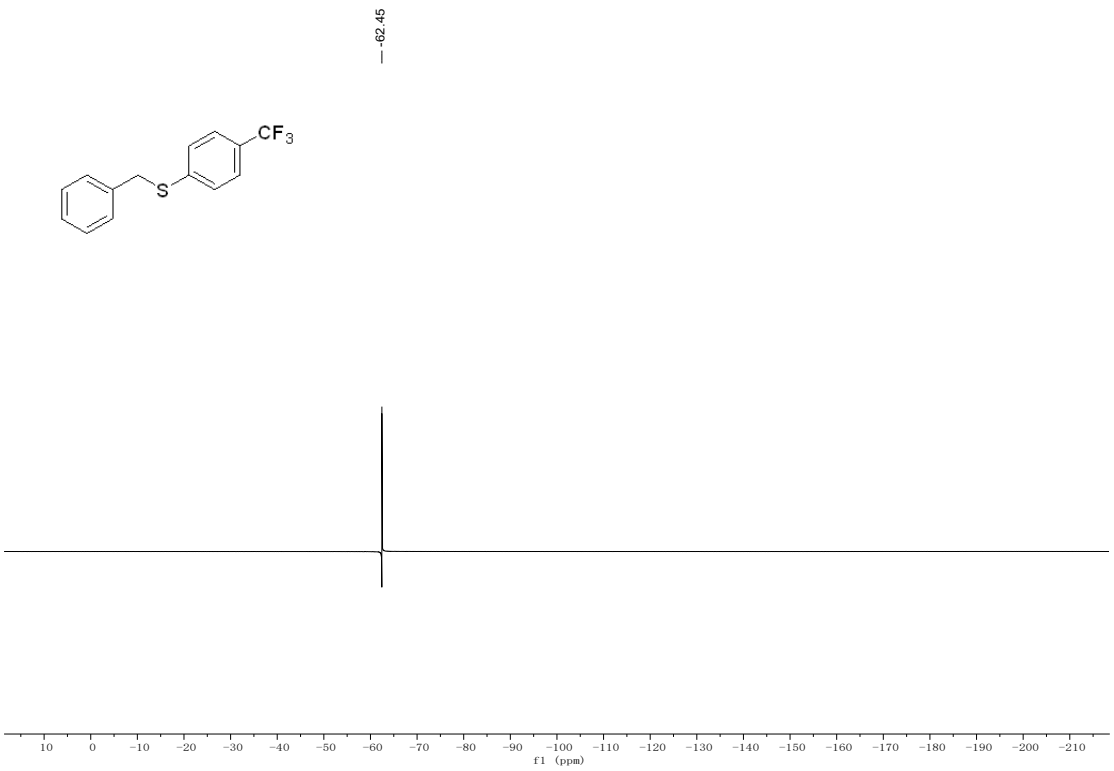
^{19}F-NMR Spectrum (565 MHz, $CDCl_3$) of 3q



^{19}F-NMR Spectrum (565 MHz, $CDCl_3$) of 3y



^{19}F-NMR Spectrum (565 MHz, $CDCl_3$) of 3ad



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