

Supplementary data

Lead-free perovskite Cs₃Bi₂Br₉/TiO₂ composites for atmospheric photocatalytic oxidation of sulfides

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1. General

All commercial reagents were used directly without further purification, unless otherwise stated. Acetonitrile (ACN) was purchased from J & K chemical. DMSO- d_6 and $CDCl_3$ were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. All Schlenk tubes and sealed vessels (50 mL) were purchased from Beijing Synthware Glass. The following abbreviations were used to describe NMR signals: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets, q = quartet.

2. Experimental sections

2.1 Preparation of catalyst.

2.1.1 Preparation of $Cs_3Bi_2Br_9$ nanocrystals

The synthesis procedures were carried out following a published method in literature with some modifications [1]. Lead free perovskite $Cs_3Bi_2Br_9$ was synthesized at room temperature using an anti-solvent precipitation method. In brief, 2 mmol $BiBr_3$ and 3 mmol $CsBr$ were dissolved in 5 mL DMSO and stirred with a magnetic stirrer until completely dissolved. Then 1 mL of the above solution was added dropwise into 20 mL of vigorously stirred isopropanol to obtain a light-yellow suspension. The mixture was continuously stirred for 2 hours. The precipitate was filtered, washed with ethanol several times, and dried under vacuum at 80 °C overnight.

2.1.2 Preparation of $Cs_3Bi_2Br_9/TiO_2$ heterojunction

A series of $Cs_3Bi_2Br_9/TiO_2$ composite materials with different weight ratios were obtained through the anti-solvent method. Firstly, 100 mg of TiO_2 was added to 20 mL of isopropanol, and the mixture was sonicated to form a uniformly mixed solution. Then a certain amount of precursor solution was dropwise added under stirring conditions. The mixture was stirred vigorously for 2 hours. Afterwards, the precipitate was obtained by centrifugation, washed several times, and finally dried by vacuum overnight at 80 °C. A series of $Cs_3Bi_2Br_9/TiO_2$ composite materials with different weight ratios were obtained by adding different amounts of precursor solutions dropwise.

2.2 Structural Characterization of the $\text{Cs}_3\text{Bi}_2\text{Br}_9/\text{TiO}_2$ heterostructures

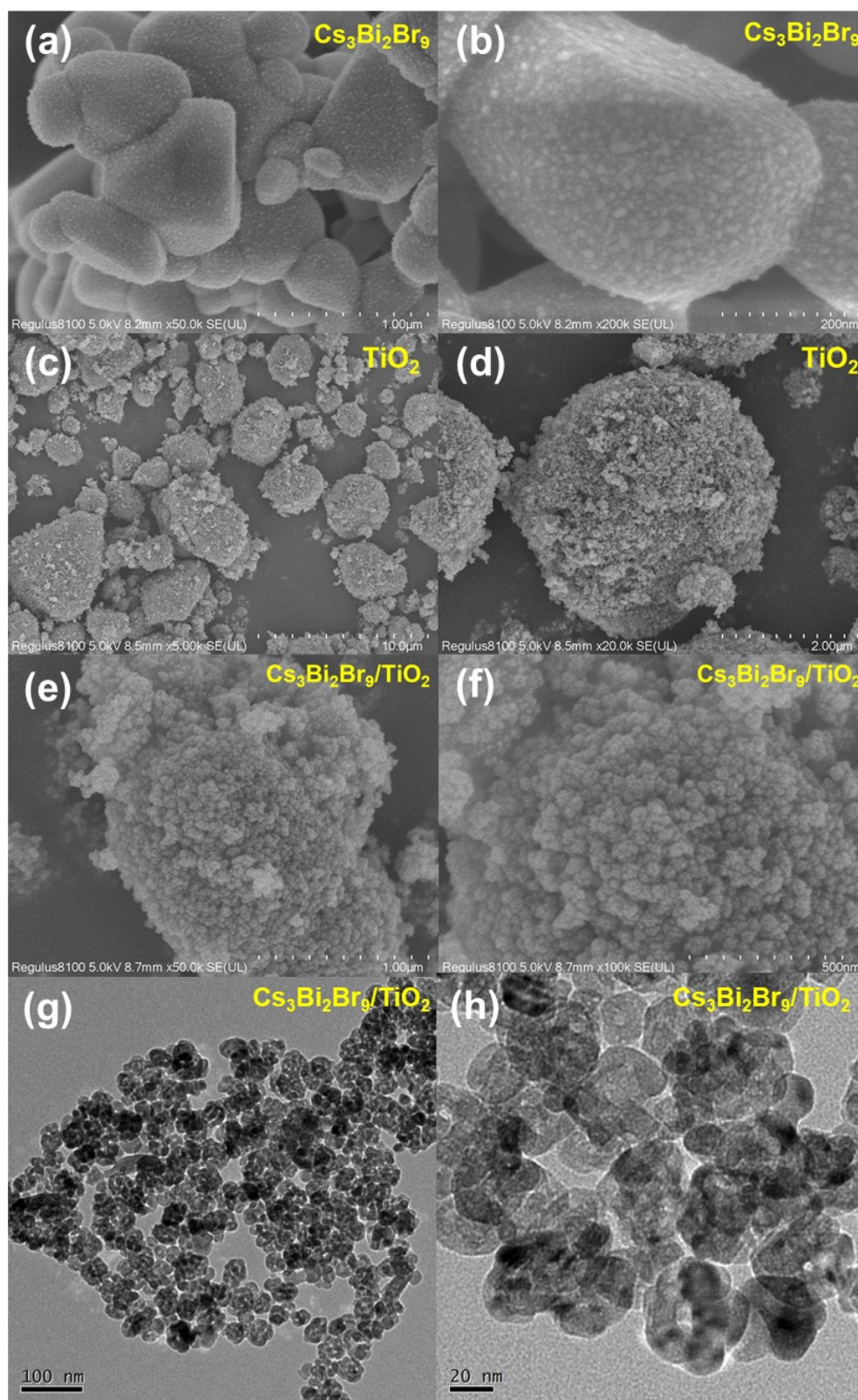


Figure S1. (a-b) SEM image of $\text{Cs}_3\text{Bi}_2\text{Br}_9$. (c-d) SEM image of TiO_2 . (e-f) SEM image of $\text{Cs}_3\text{Bi}_2\text{Br}_9/\text{TiO}_2$. (g-h) TEM images of $\text{Cs}_3\text{Bi}_2\text{Br}_9/\text{TiO}_2$.

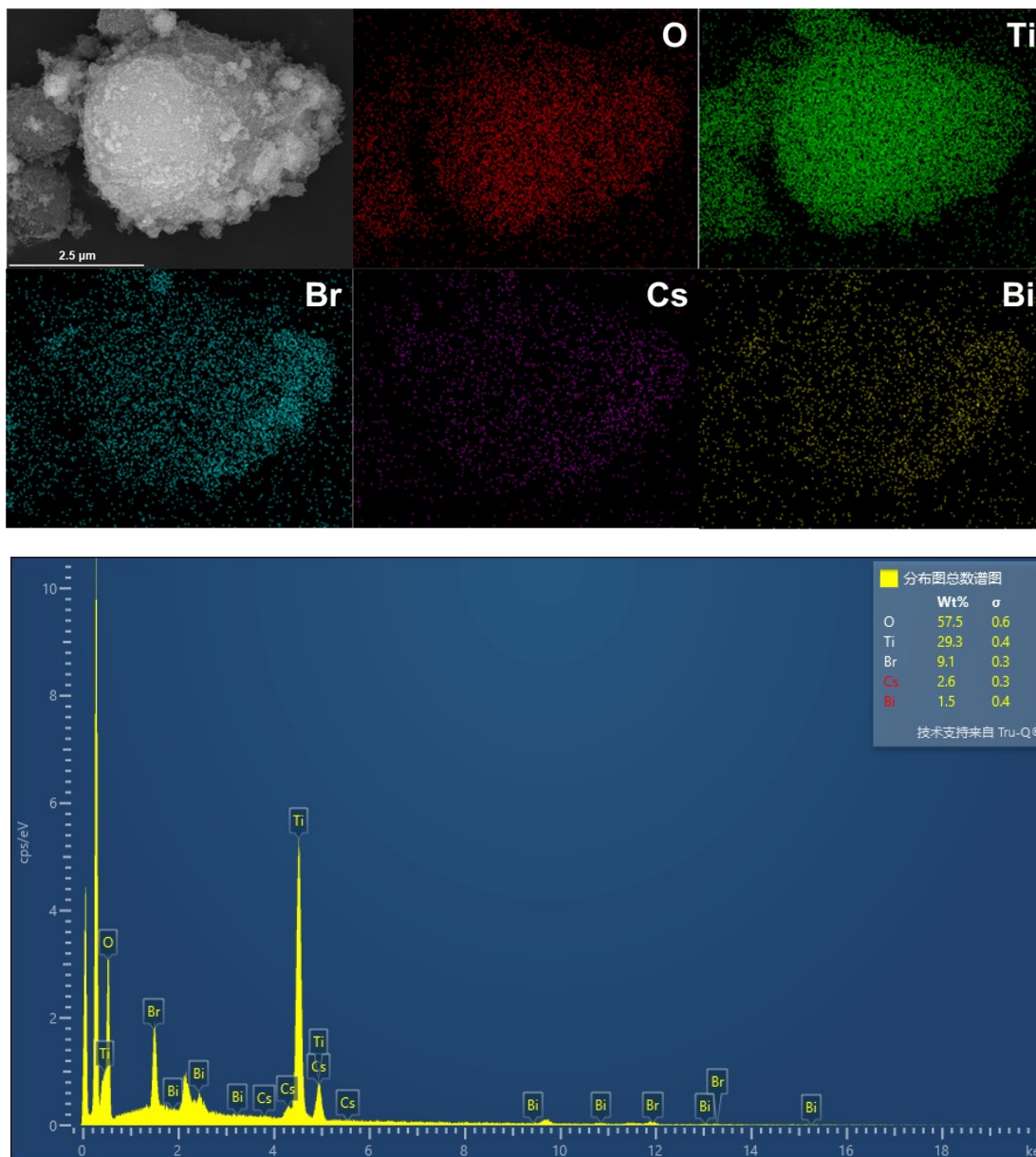
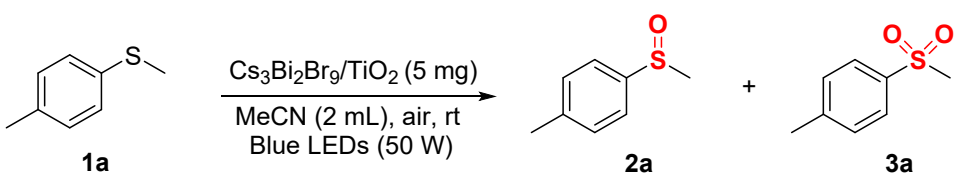


Figure S2. SEM image of $\text{Cs}_3\text{Bi}_2\text{Br}_9/\text{TiO}_2$ and EDS mapping.

2.3 Photocatalytic oxidation of sulfide.


In a 25 mL reaction pyrex tube, **1a** (27.6 mg, 0.2 mmol, 1 equiv.) and $\text{Cs}_3\text{Bi}_2\text{Br}_9/\text{TiO}_2$ (5 mg) were dispersed in CH_3CN (2 mL), the resulting mixture was stirred under irradiation of blue LEDs ($\lambda = 457$ nm, 50 W) at room temperature. After totally conversion of the starting materials, product was extracted by using ethyl acetate, and was separated by column chromatography.

2.4 Optimization of reaction conditions.

Table S1. Optimization of Reaction Conditions^a


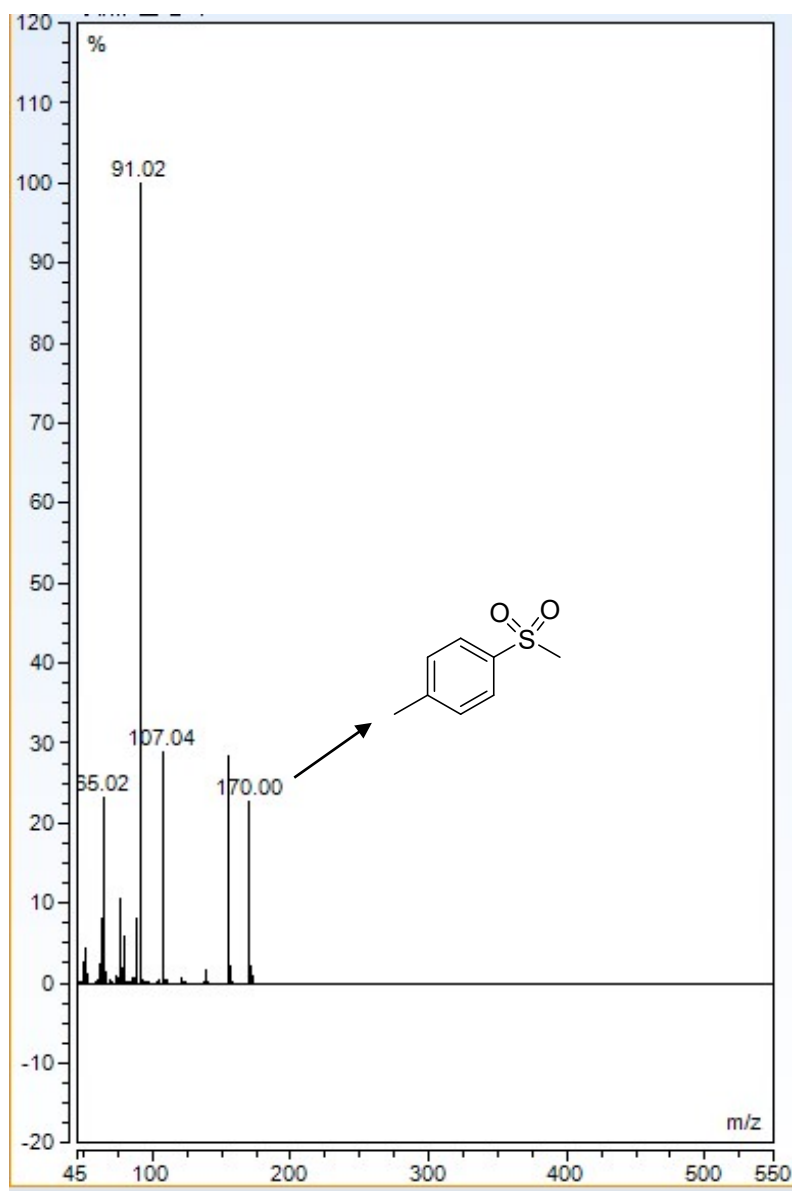
Entry	Variation from the “standard conditions”	Yield ^b (%)	
		2a	3a
1	none	86	0
2	without Cs ₃ Bi ₂ Br ₉ /TiO ₂	NR	0
3	without light	NR	0
4	Cs ₃ Bi ₂ Br ₉ was used	64	0
5	TiO ₂ was used	NR	2
6	N ₂ instead of air	NR	0
7	DCM instead of MeCN	13	9
8	DCE instead of MeCN	19	0
9	EtOH instead of MeCN	38	0
10	1,4-Dioxane instead of MeCN	45	5
11	THF instead of MeCN	17	0
12	white LEDs (18 W)	19	1
13	green LEDs (30 W)	12	0
14	CsBr	1	0
15	BiBr ₃	42	0

^aStandard conditions: **1a** (0.2 mmol), Cs₃Bi₂Br₉/TiO₂ (5 mg), MeCN (2.0 mL) under air at room temperature, blue LEDs (50 W) for 24 h. ^bIsolated yield. NR, no reaction.

Table S2 Catalyst screening^a


Entry	[Cat.]	Yield (%) ^b
1	TiO ₂	NR
2	Cs ₃ Bi ₂ Br ₉	69
3	20 wt.%Cs ₃ Bi ₂ Br ₉ /TiO ₂	78
4	40 wt.%Cs₃Bi₂Br₉/TiO₂	86
5	60 wt.%Cs ₃ Bi ₂ Br ₉ /TiO ₂	80
6	80 wt.%Cs ₃ Bi ₂ Br ₉ /TiO ₂	63

^a Reaction condition: **1a** (0.2 mmol), Catalyst (5 mg) in CH₃CN (2 mL) at r.t. under 50 W blue LEDs for 24 h. ^b Isolated yield.



The GCMS spectrum of **3a**.

2.5 The recycle experiments.

In a 25 mL reaction pyrex tube, **1a** (27.6 mg, 0.2 mmol, 1 equiv.) and $\text{Cs}_3\text{Bi}_2\text{Br}_9/\text{TiO}_2$ (5 mg) were dispersed in CH_3CN (2 mL), the resulting mixture was stirred under irradiation of blue LEDs ($\lambda = 457$ nm, 50 W) at room temperature. After totally conversion of the starting materials, product was extracted by using ethyl acetate, and the composites could be reused up to 3 consecutive cycles with only a slightly decrease in the yields.

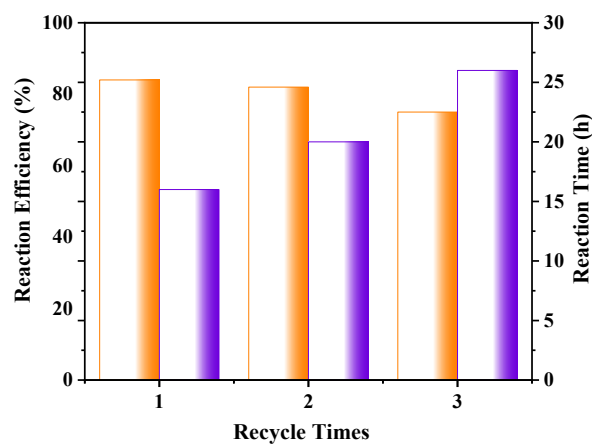


Figure S3. Stability and reusability experiments

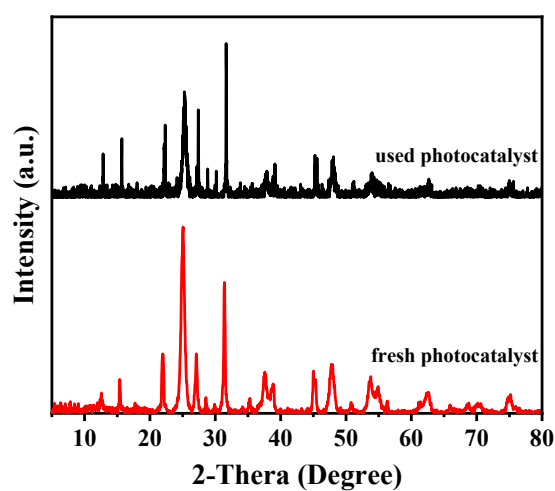


Figure S4. XRD of the $\text{Cs}_3\text{Bi}_2\text{Br}_9/\text{TiO}_2$ photocatalyst before and after stability test.

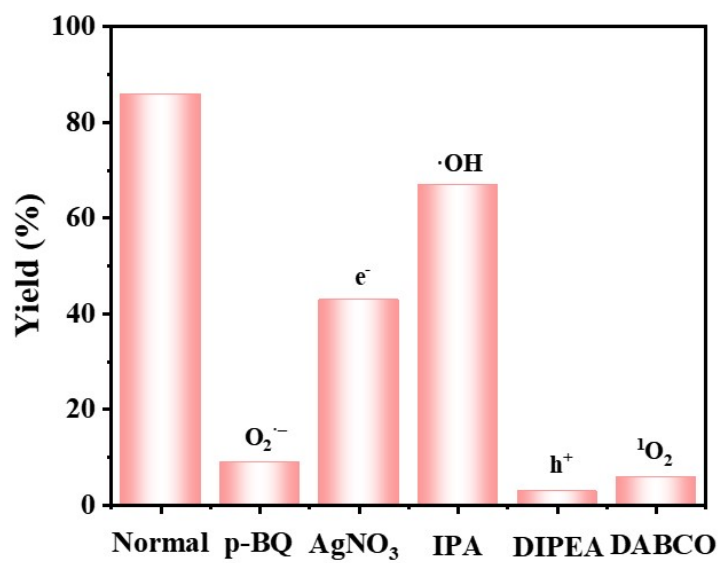
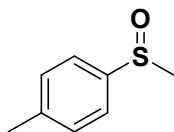


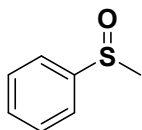
Figure S5. Trapping experiments of active species.

3. Data for the sulfoxide products.



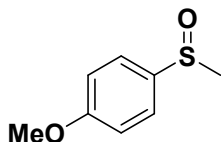
1-methyl-4-(methylsulfinyl)benzene

Thin-layer chromatography (petroleum ether/ethyl acetate 1:2) afforded the titled sulfoxide as a Colorless oil; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.53 (d, $J = 8.2$ Hz, 2H), 7.32 (d, $J = 8.0$ Hz, 2H), 2.70 (s, 3H), 2.40 (s, 3H).



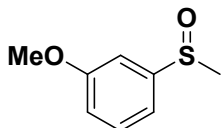
(methylsulfinyl)benzene

Thin-layer chromatography (petroleum ether/ethyl acetate 1:2) afforded the titled sulfoxide as a Colorless oil; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.69 – 7.60 (m, 2H), 7.56 – 7.47 (m, 3H), 2.72 (s, 3H).



1-methoxy-4-(methylsulfinyl)benzene

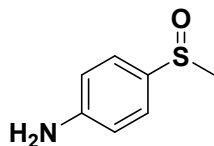
Thin-layer chromatography (petroleum ether/ethyl acetate 1:2) afforded the titled sulfoxide as a; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.55 (d, $J = 8.8$ Hz, 2H), 6.99 (d, $J = 8.8$ Hz, 2H), 3.81 (s, 3H), 2.66 (s, 3H).



1-methoxy-3-(methylsulfinyl)benzene

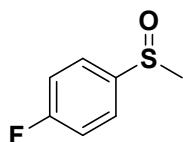
Thin-layer chromatography (petroleum ether/ethyl acetate 1:2) afforded the titled

sulfoxide as a; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.42 (t, $J = 7.9$ Hz, 1H), 7.29 – 7.24 (m, 1H), 7.13 (d, $J = 7.6$ Hz, 1H), 7.02 (d, $J = 8.1$ Hz, 1H), 3.87 (s, 3H), 2.73 (s, 3H).



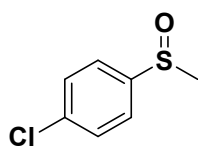
4-(methylsulfinyl)aniline

Thin-layer chromatography (petroleum ether/ethyl acetate 1:2) afforded the titled sulfoxide as a brown oil; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.45 – 7.38 (m, 2H), 6.75 – 6.69 (m, 2H), 4.41 (s, 2H), 2.68 (s, 3H).



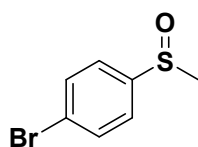
1-fluoro-4-(methylsulfinyl)benzene

Thin-layer chromatography (petroleum ether/ethyl acetate 1:2) afforded the titled sulfoxide as a white solid; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.67 (dd, $J = 8.6, 5.1$ Hz, 2H), 7.28 – 7.22 (m, 2H), 2.73 (s, 3H). ^{19}F NMR (471 MHz, Chloroform-*d*) δ -108.56.



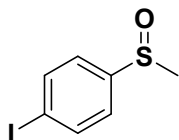
1-chloro-4-(methylsulfinyl)benzene

Thin-layer chromatography (petroleum ether/ethyl acetate 1:2) afforded the titled sulfoxide as a colorless oil; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.58 (d, $J = 8.2$ Hz, 2H), 7.49 (d, $J = 8.3$ Hz, 2H), 2.70 (s, 3H).



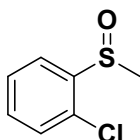
1-bromo-4-(methylsulfinyl)benzene

Thin-layer chromatography (petroleum ether/ethyl acetate 1:2) afforded the titled sulfoxide as a white solid; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.66 (d, $J = 8.4$ Hz, 2H), 7.51 (d, $J = 8.4$ Hz, 2H), 2.71 (s, 3H).



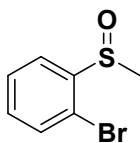
1-iodo-4-(methylsulfinyl)benzene

Thin-layer chromatography (petroleum ether/ethyl acetate 1:2) afforded the titled sulfoxide as a white solid; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.87 (d, $J = 8.3$ Hz, 2H), 7.38 (d, $J = 8.2$ Hz, 2H), 2.71 (s, 3H).



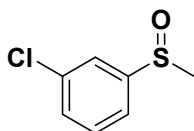
1-chloro-2-(methylsulfinyl)benzene

Thin-layer chromatography (petroleum ether/ethyl acetate 1:2) afforded the titled sulfoxide as a colorless oil; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.92 (dd, $J = 7.8, 1.7$ Hz, 1H), 7.51 (td, $J = 7.5, 1.3$ Hz, 1H), 7.42 (td, $J = 7.6, 1.7$ Hz, 1H), 7.37 (dd, $J = 7.9, 1.2$ Hz, 1H), 2.79 (s, 3H).



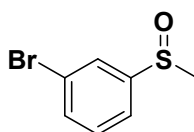
1-bromo-2-(methylsulfinyl)benzene

Thin-layer chromatography (petroleum ether/ethyl acetate 1:2) afforded the titled sulfoxide as a colorless oil; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.91 (dd, $J = 7.8, 1.7$ Hz, 1H), 7.59 – 7.51 (m, 2H), 7.37 – 7.32 (m, 1H), 2.79 (s, 3H).



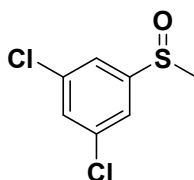
1-chloro-3-(methylsulfinyl)benzene

Thin-layer chromatography (petroleum ether/ethyl acetate 1:2) afforded the titled sulfoxide as a colorless oil; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.66 – 7.61 (m, 1H), 7.49 – 7.42 (m, 3H), 2.72 (s, 3H).



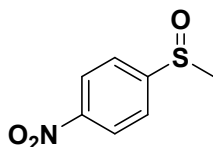
1-bromo-3-(methylsulfinyl)benzene

Thin-layer chromatography (petroleum ether/ethyl acetate 1:2) afforded the titled sulfoxide as a colorless oil; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.76 (t, $J = 1.8$ Hz, 1H), 7.57 (ddd, $J = 7.9, 2.0, 1.0$ Hz, 1H), 7.50 (dt, $J = 7.8, 1.3$ Hz, 1H), 7.36 (t, $J = 7.9$ Hz, 1H), 2.70 (s, 3H).



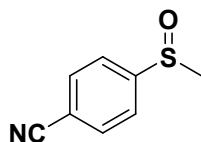
1,3-dichloro-5-(methylsulfinyl)benzene

Thin-layer chromatography (petroleum ether/ethyl acetate 1:2) afforded the titled sulfoxide as a colorless oil; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.51 (s, 2H), 7.47 (s, 1H), 2.76 (s, 3H).



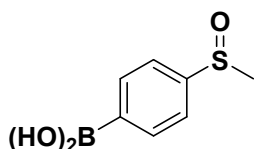
1-(methylsulfinyl)-4-nitrobenzene

Thin-layer chromatography (petroleum ether/ethyl acetate 1:2) afforded the titled sulfoxide as a yellow solid; ^1H NMR (500 MHz, Chloroform-*d*) δ 8.42 – 8.37 (m, 2H), 7.86 – 7.81 (m, 2H), 2.79 (s, 3H).



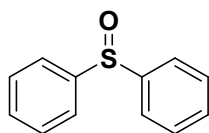
4-(methylsulfinyl)benzonitrile

Thin-layer chromatography (petroleum ether/ethyl acetate 1:2) afforded the titled sulfoxide as a white solid; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.83 (d, J = 8.3 Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H), 2.76 (s, 3H).



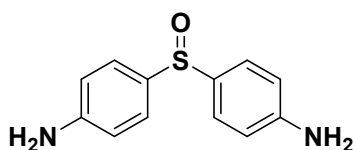
(4-(methylsulfinyl)phenyl)boronic acid

Thin-layer chromatography (petroleum ether/ethyl acetate 1:2) afforded the titled sulfoxide as a white solid; ^1H NMR (500 MHz, DMSO-*d*₆) δ 8.30 (s, 2H), 7.98 – 7.93 (m, 2H), 7.66 – 7.60 (m, 2H), 2.73 (s, 3H).



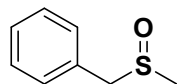
sulfinyldibenzene

Thin-layer chromatography (petroleum ether/ethyl acetate 1:2) afforded the titled sulfoxide as a white solid; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.69 – 7.61 (m, 4H), 7.49 – 7.42 (m, 6H).



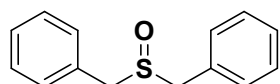
4,4'-sulfinyldianiline

Thin-layer chromatography (petroleum ether/ethyl acetate 1:2) afforded the titled sulfoxide as a yellow solid; ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 7.19 (d, $J = 8.2$ Hz, 4H), 6.59 (d, $J = 8.3$ Hz, 4H), 5.66 (s, 4H).



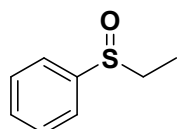
((methylsulfinyl)methyl)benzene

Thin-layer chromatography (petroleum ether/ethyl acetate 1:2) afforded the titled sulfoxide as a colorless oil; ^1H NMR (500 MHz, Chloroform- d) δ 7.39 – 7.30 (m, 3H), 7.32 – 7.24 (m, 2H), 4.01 (d, $J = 12.8$ Hz, 1H), 3.91 (d, $J = 12.8$ Hz, 1H), 2.42 (s, 3H).



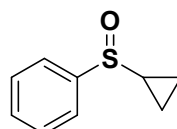
(sulfinylbis(methylene))dibenzene

Thin-layer chromatography (petroleum ether/ethyl acetate 1:2) afforded the titled sulfoxide as a white solid; ^1H NMR (500 MHz, Chloroform- d) δ 7.41 – 7.35 (m, 6H), 7.31 – 7.28 (m, 4H), 3.96 – 3.86 (m, 4H).



(ethylsulfinyl)benzene

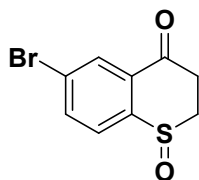
Thin-layer chromatography (petroleum ether/ethyl acetate 1:2) afforded the titled sulfoxide as a Colorless oil; ^1H NMR (500 MHz, Chloroform- d) δ 7.62 – 7.52 (m, 2H), 7.50 – 7.40 (m, 3H), 2.89 – 2.67 (m, 2H), 1.14 (t, $J = 7.4$ Hz, 3H).



(cyclopropylsulfinyl)benzene

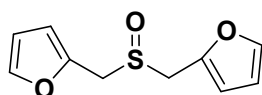
Thin-layer chromatography (petroleum ether/ethyl acetate 1:2) afforded the titled

sulfoxide as a Colorless oil; $^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 7.70 – 7.63 (m, 2H), 7.54 – 7.47 (m, 3H), 2.27 (td, $J = 8.0, 4.0$ Hz, 1H), 1.26 – 1.22 (m, 1H), 1.06 – 0.92 (m, 3H).



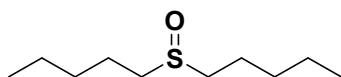
6-bromothiochroman-4-one 1-oxide

Thin-layer chromatography (petroleum ether/ethyl acetate 1:2) afforded the titled sulfoxide as a light yellow solid; $^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 8.29 (s, 1H), 7.90 (d, $J = 8.2$ Hz, 1H), 7.76 (d, $J = 8.2$ Hz, 1H), 3.48 (d, $J = 8.1$ Hz, 3H), 2.97 – 2.89 (m, 1H).



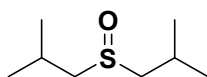
2,2'-(sulfinylbis(methylene))difuran

Thin-layer chromatography (petroleum ether/ethyl acetate 1:2) afforded the titled sulfoxide as a brown solid; $^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 7.48 – 7.34 (m, 2H), 6.51 – 6.30 (m, 4H), 4.14 – 3.85 (m, 4H).



1-(pentylsulfinyl)pentane

Thin-layer chromatography (petroleum ether/ethyl acetate 1:2) afforded the titled sulfoxide as a white solid; $^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 2.73 – 2.56 (m, 4H), 1.85 – 1.69 (m, 4H), 1.53 – 1.29 (m, 8H), 0.90 (t, $J = 7.1$ Hz, 6H).

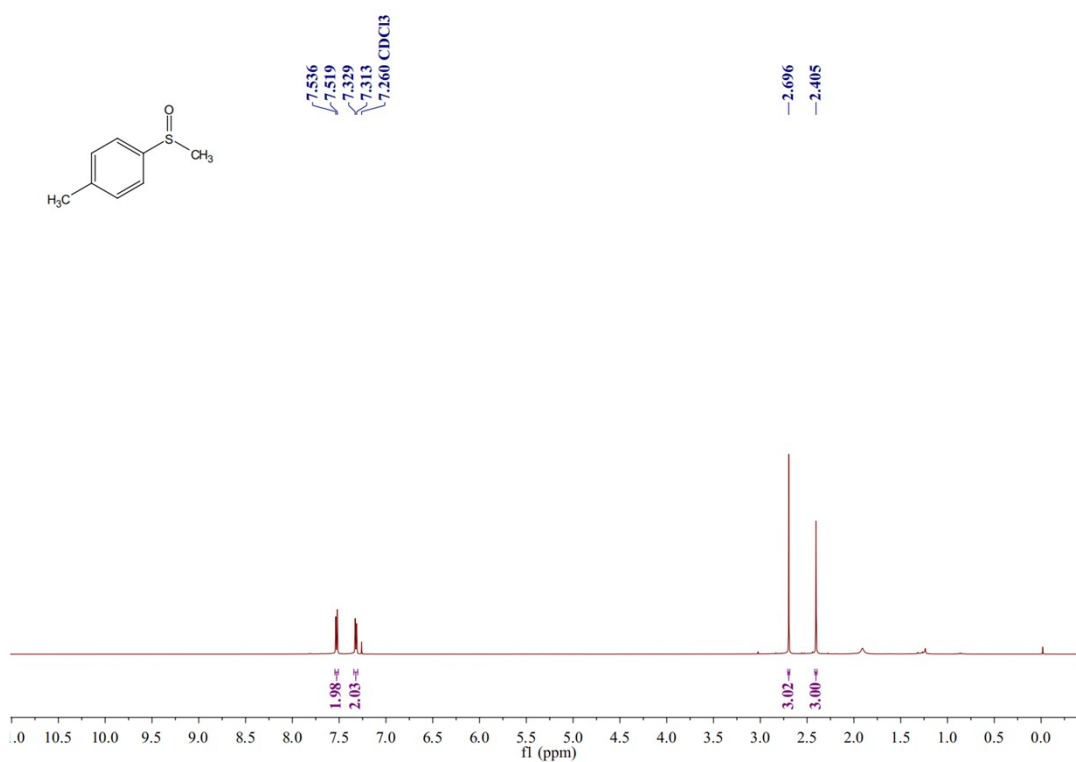


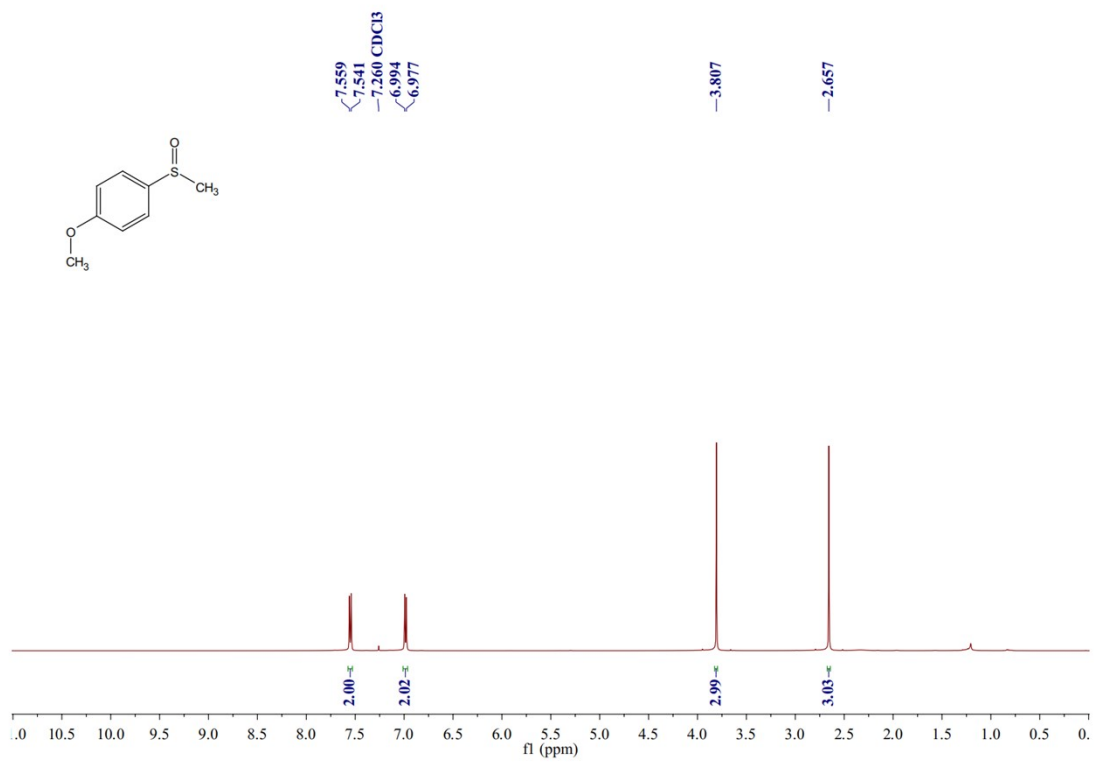
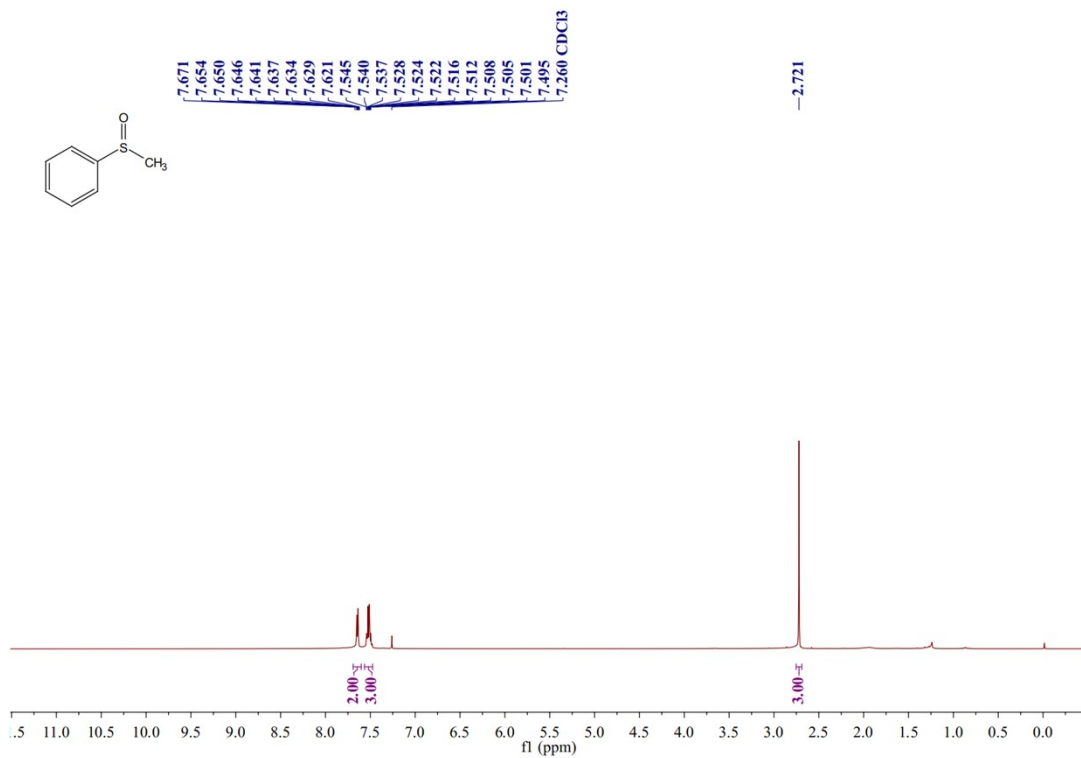
1-(isobutylsulfinyl)-2-methylpropane

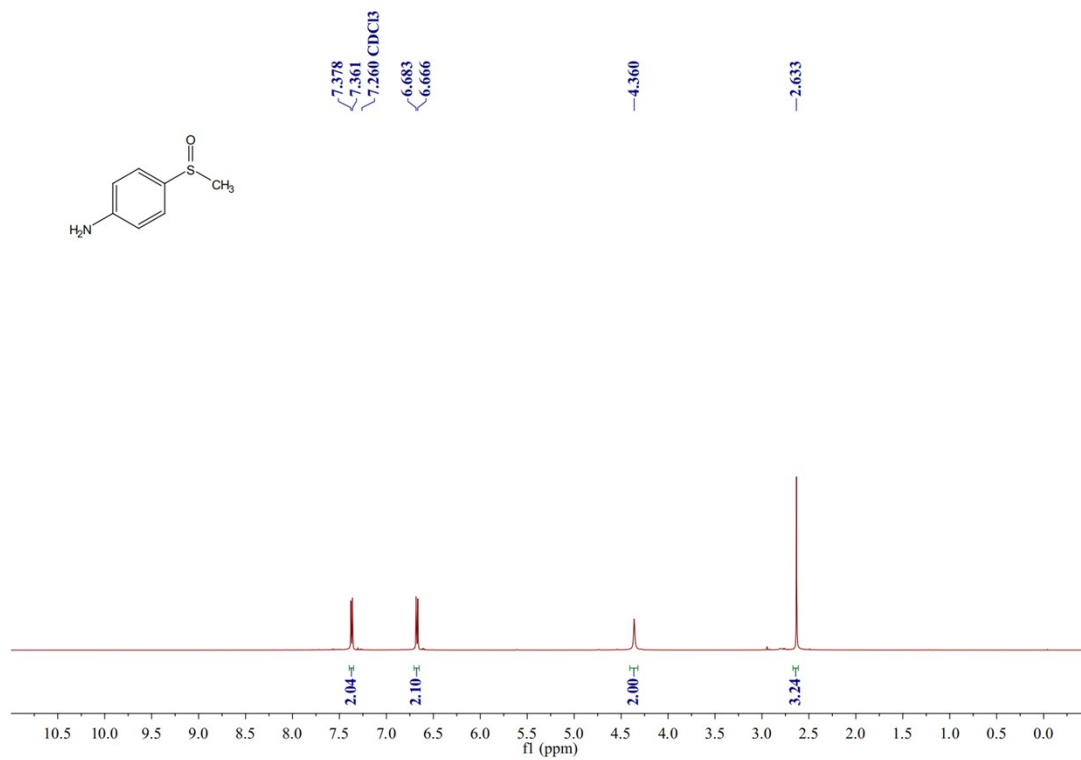
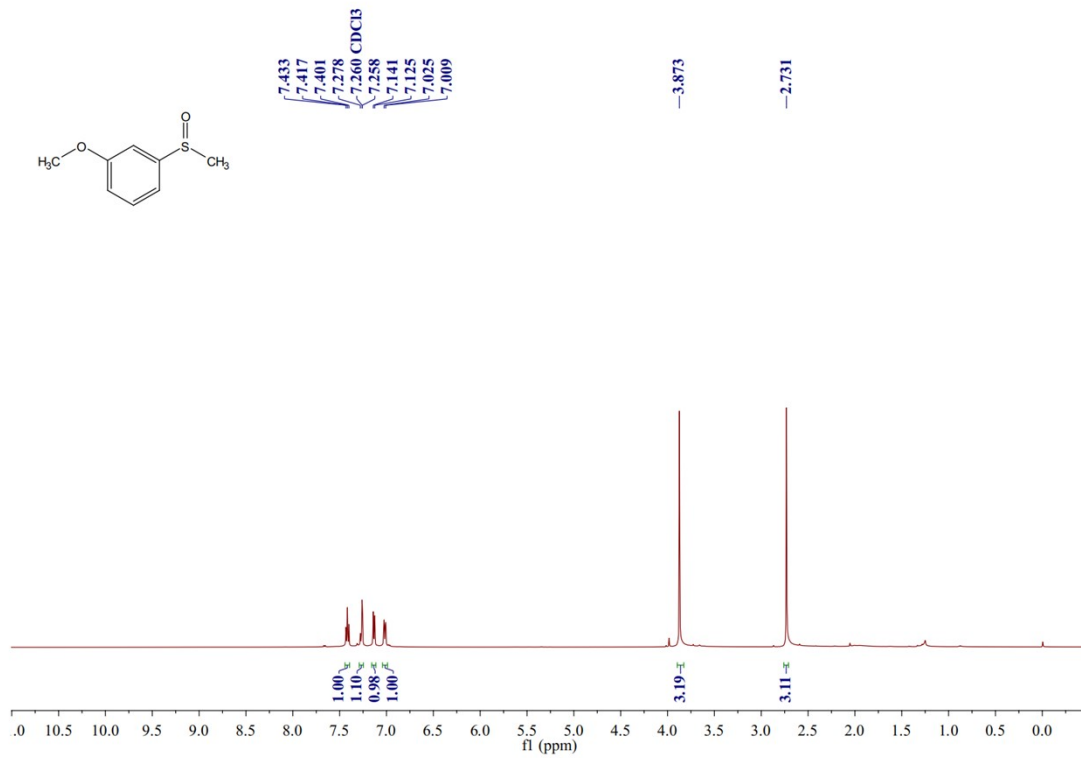
Thin-layer chromatography (petroleum ether/ethyl acetate 1:2) afforded the titled sulfoxide as a white solid; $^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 2.67 (dd, $J = 12.6, 4.7$

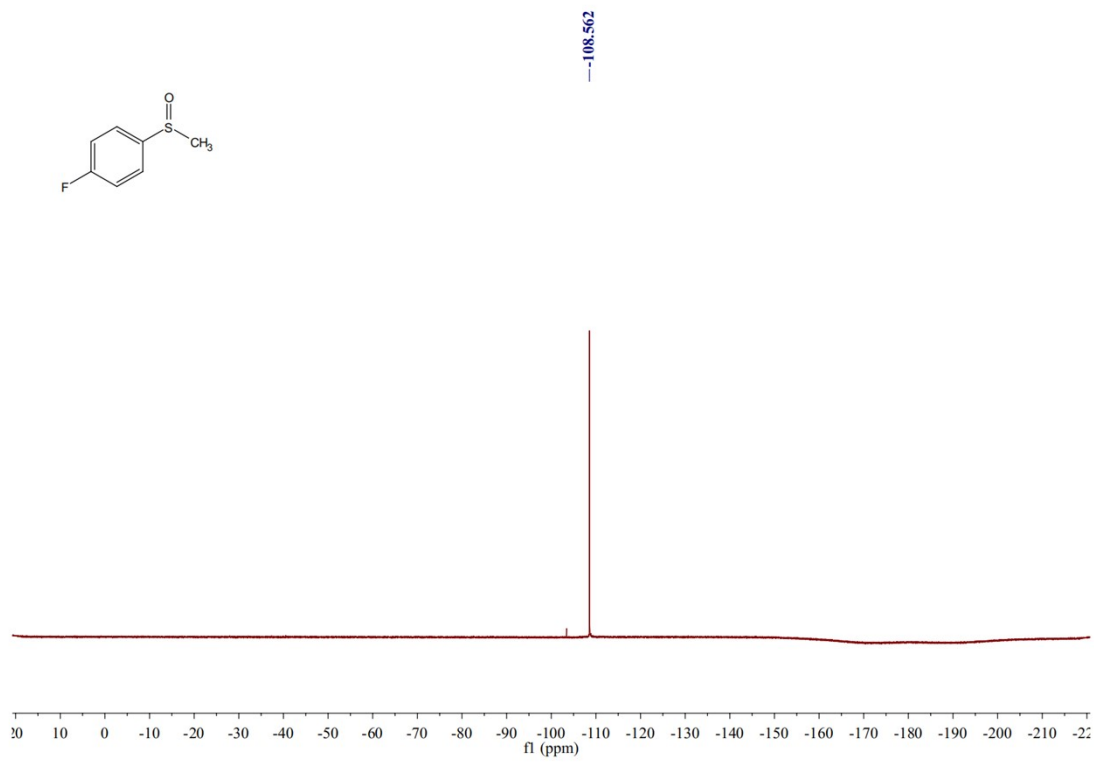
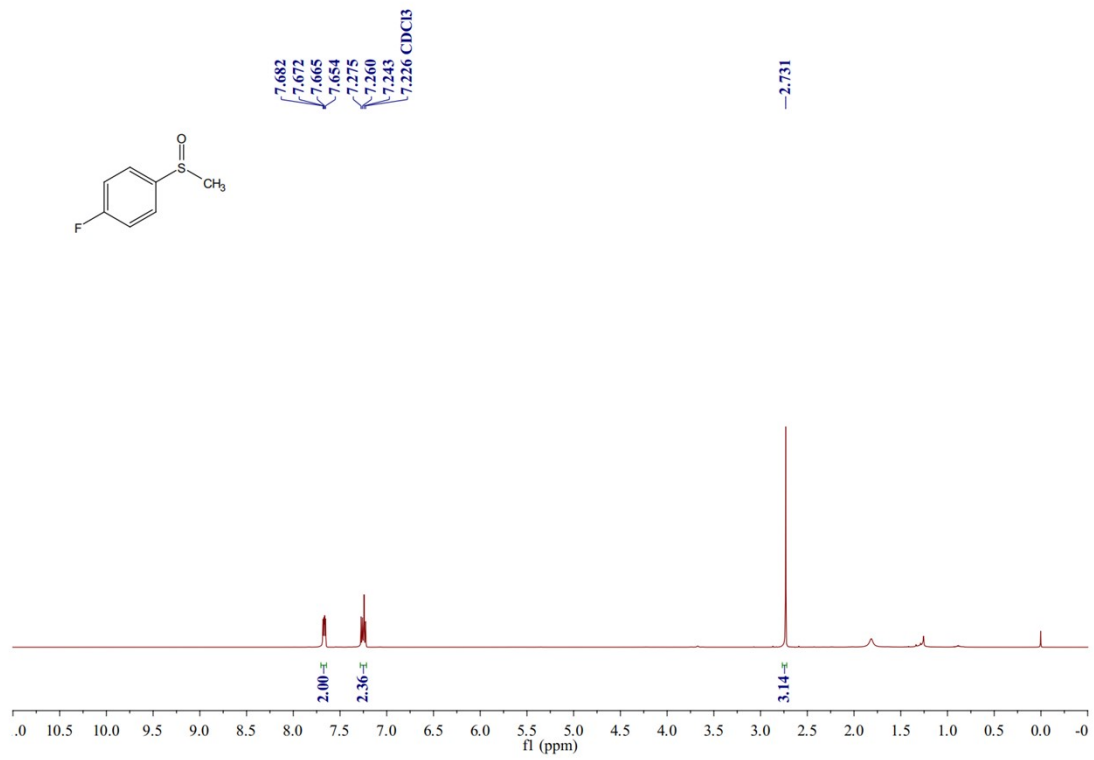
Hz, 2H), 2.38 – 2.32 (m, 2H), 2.22 (tdd, $J = 13.5, 11.4, 6.6$ Hz, 2H), 1.08 (dd, $J = 9.3, 6.5$ Hz, 12H).

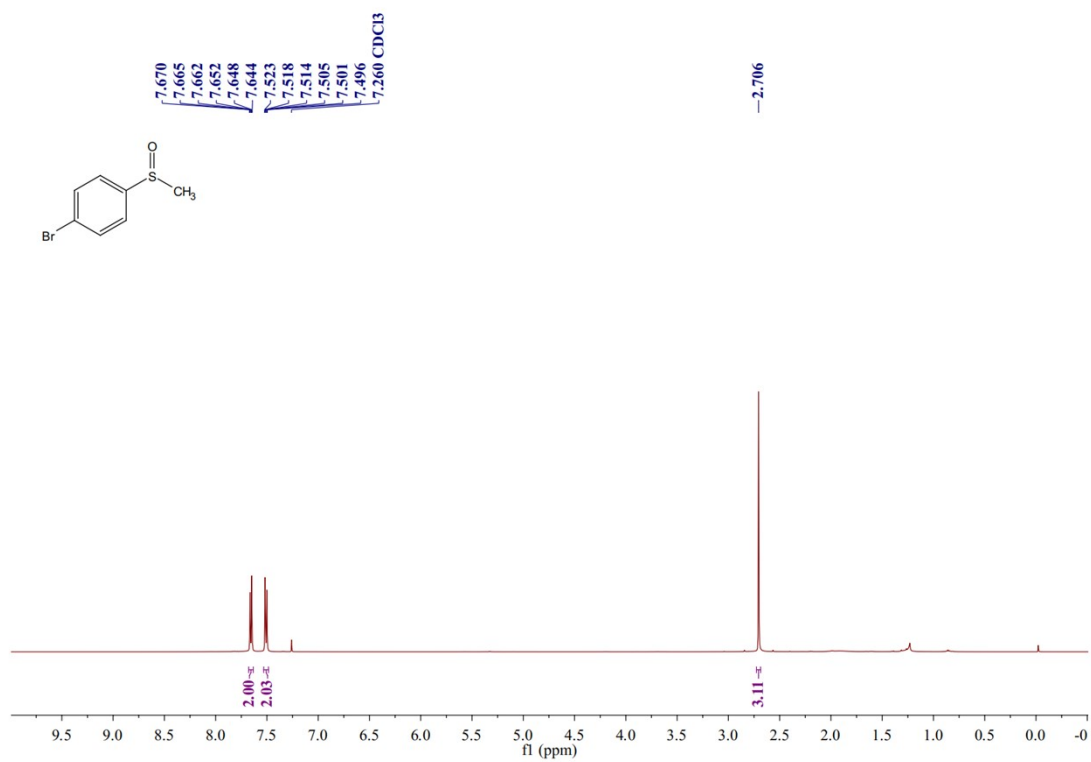
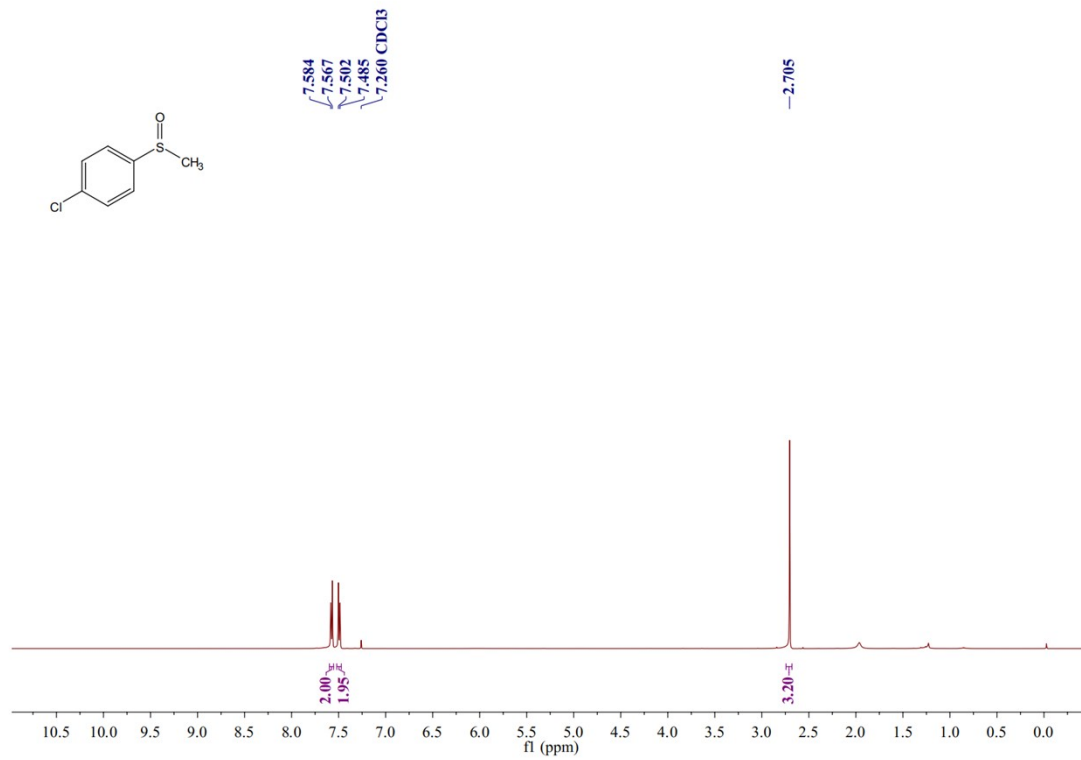
4. ^1H NMR and ^{19}F NMR for the sulfoxide products.

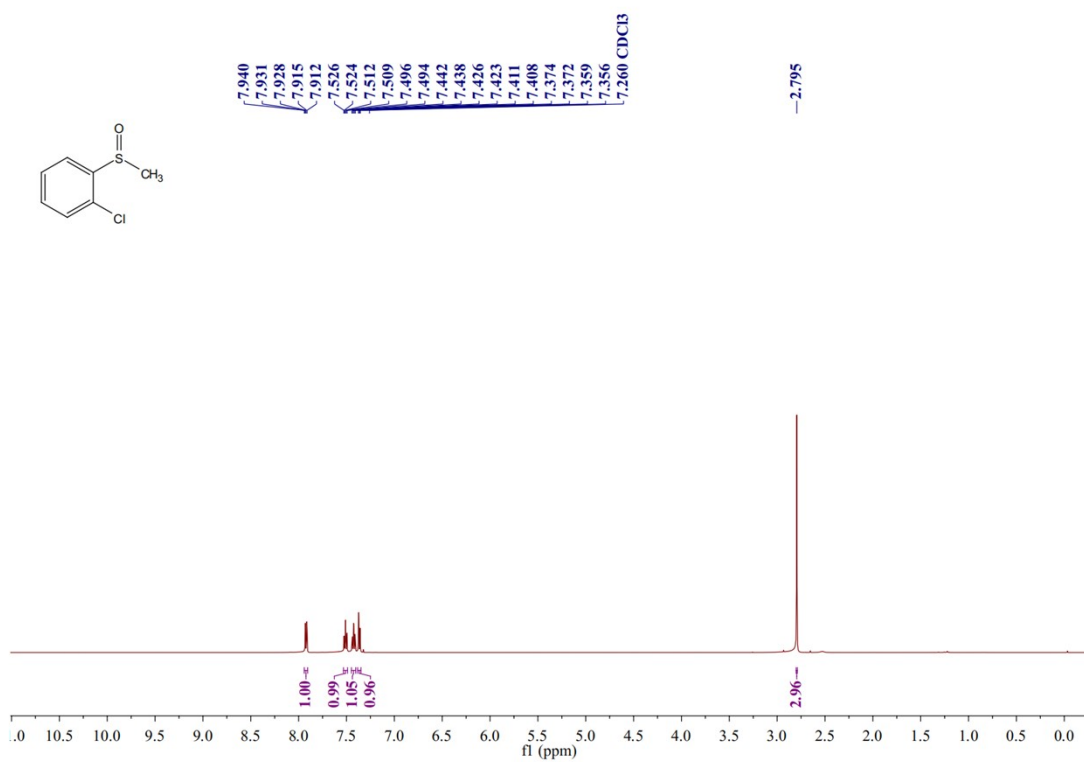
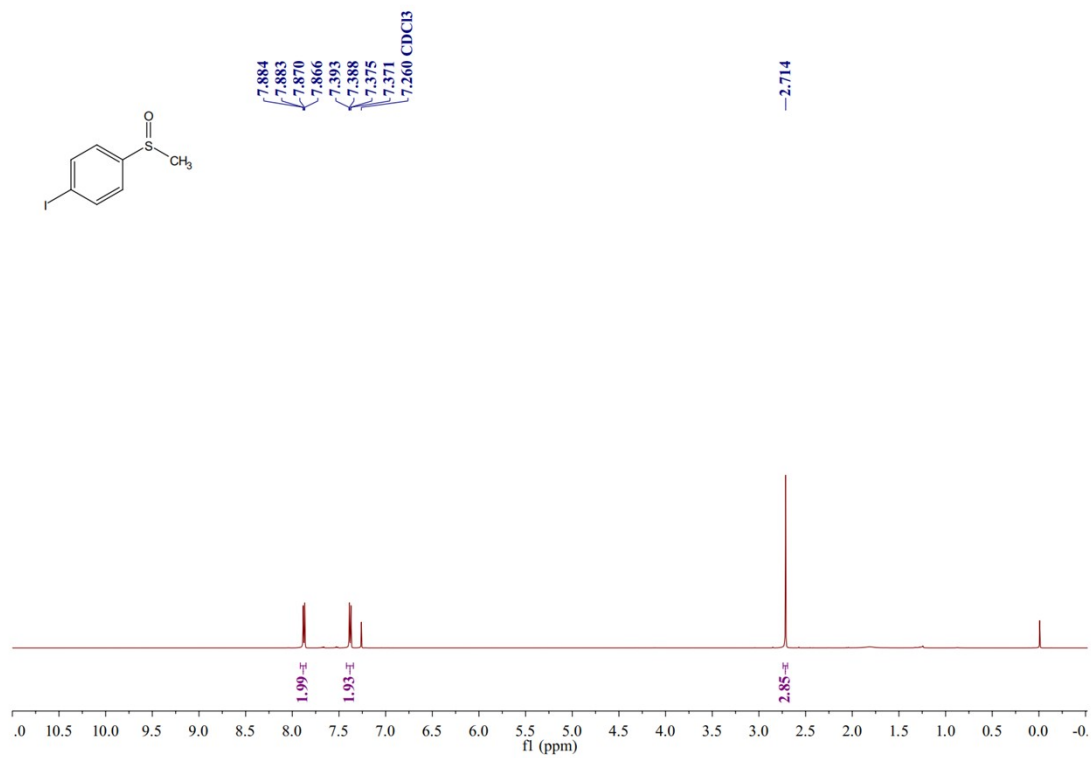


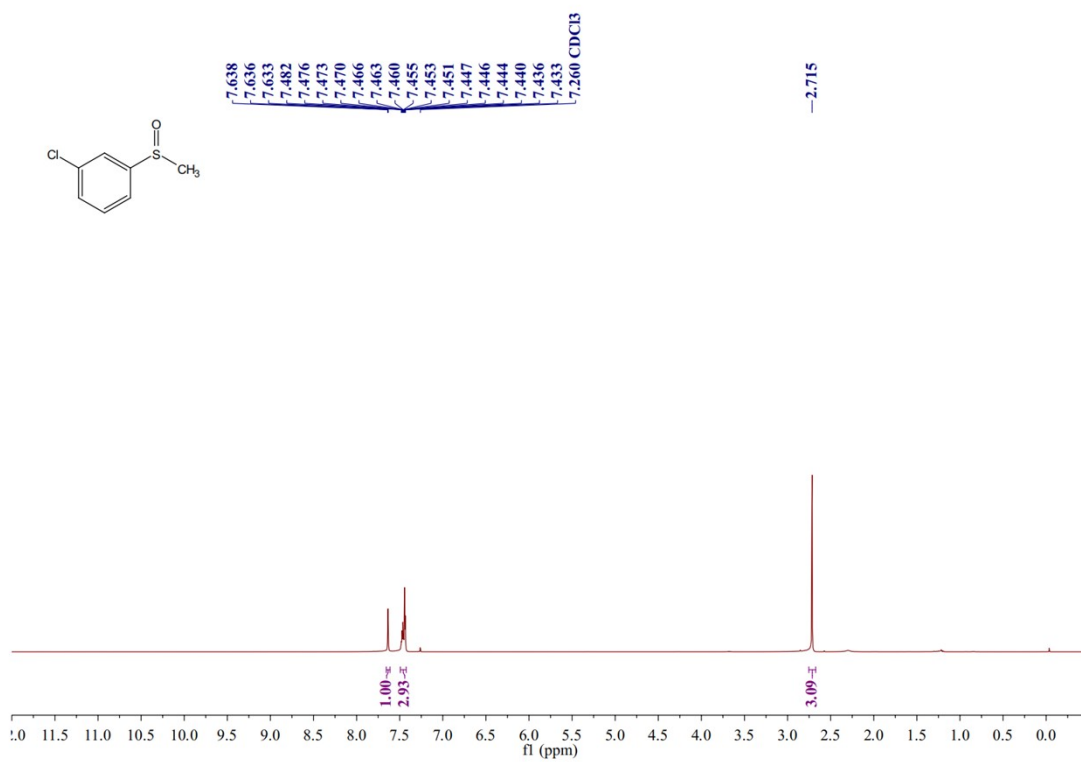
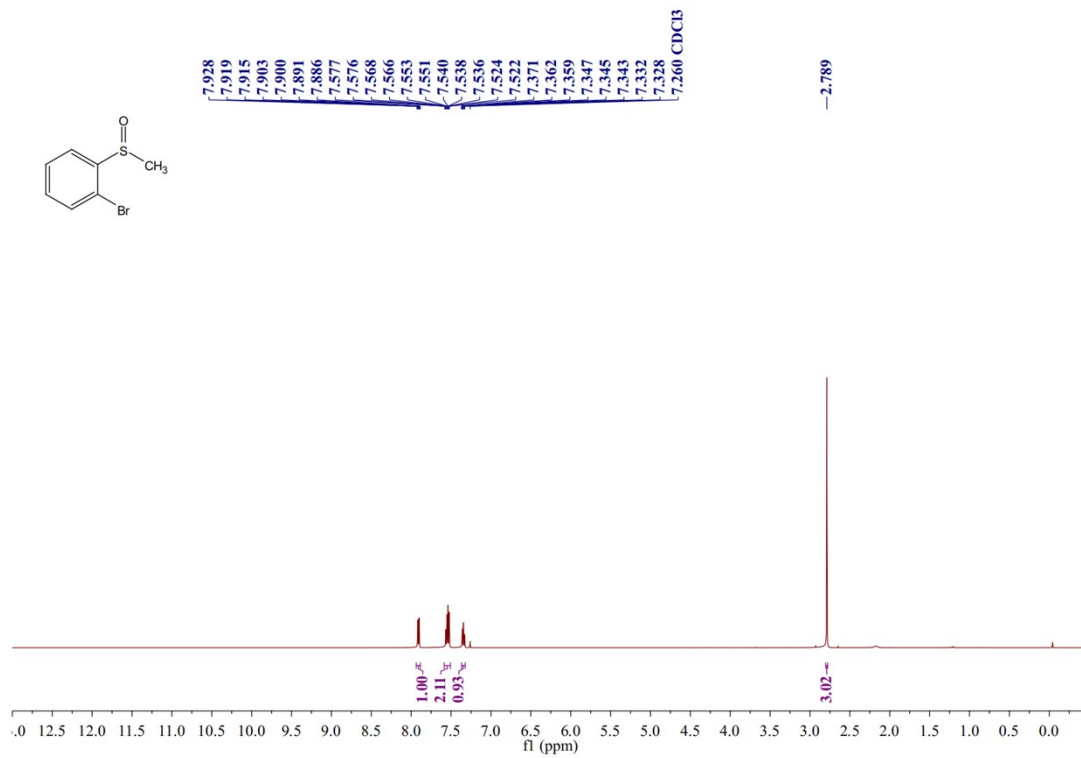


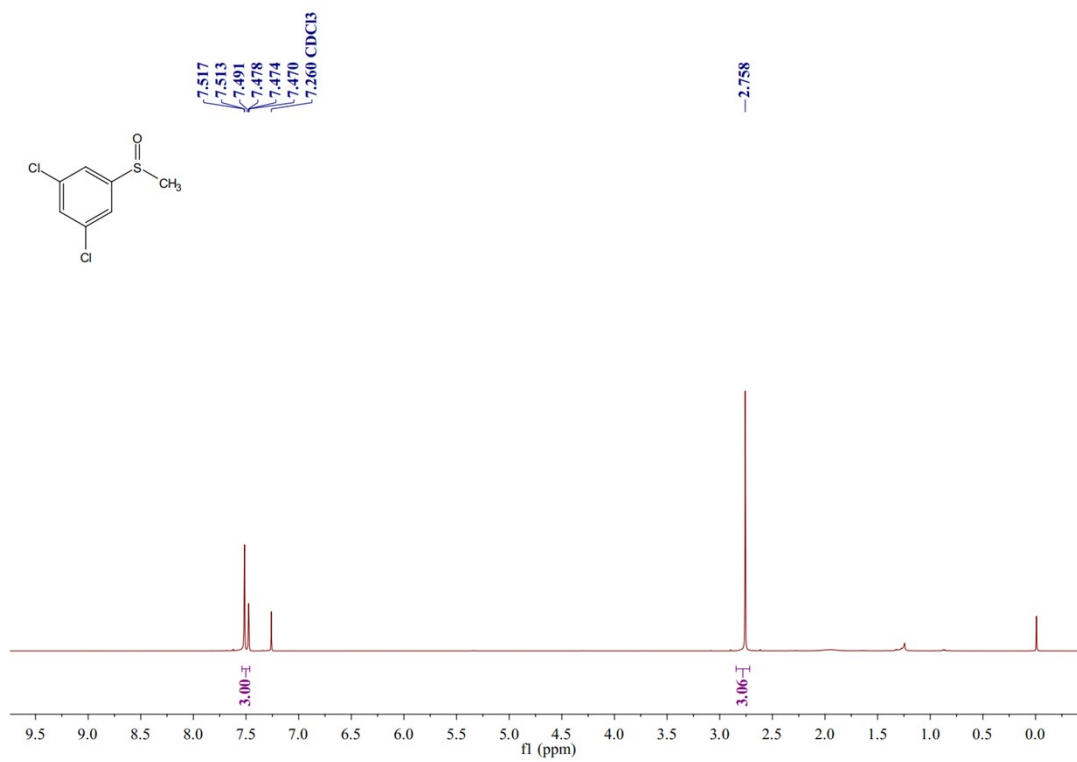
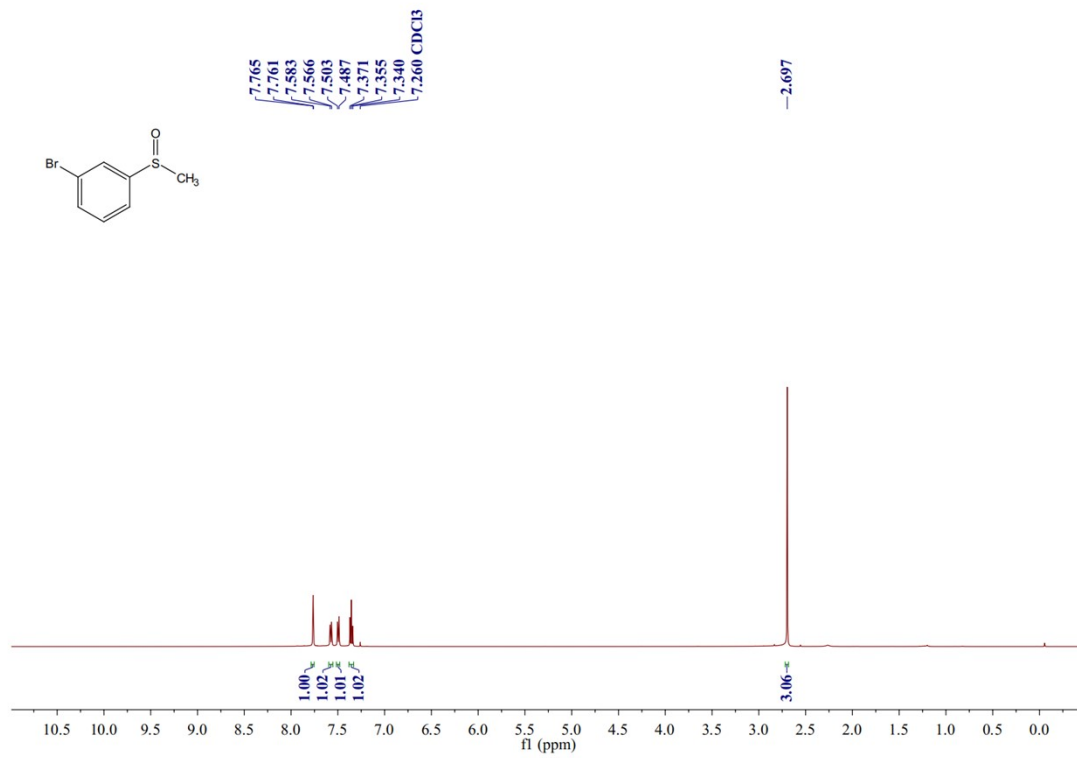


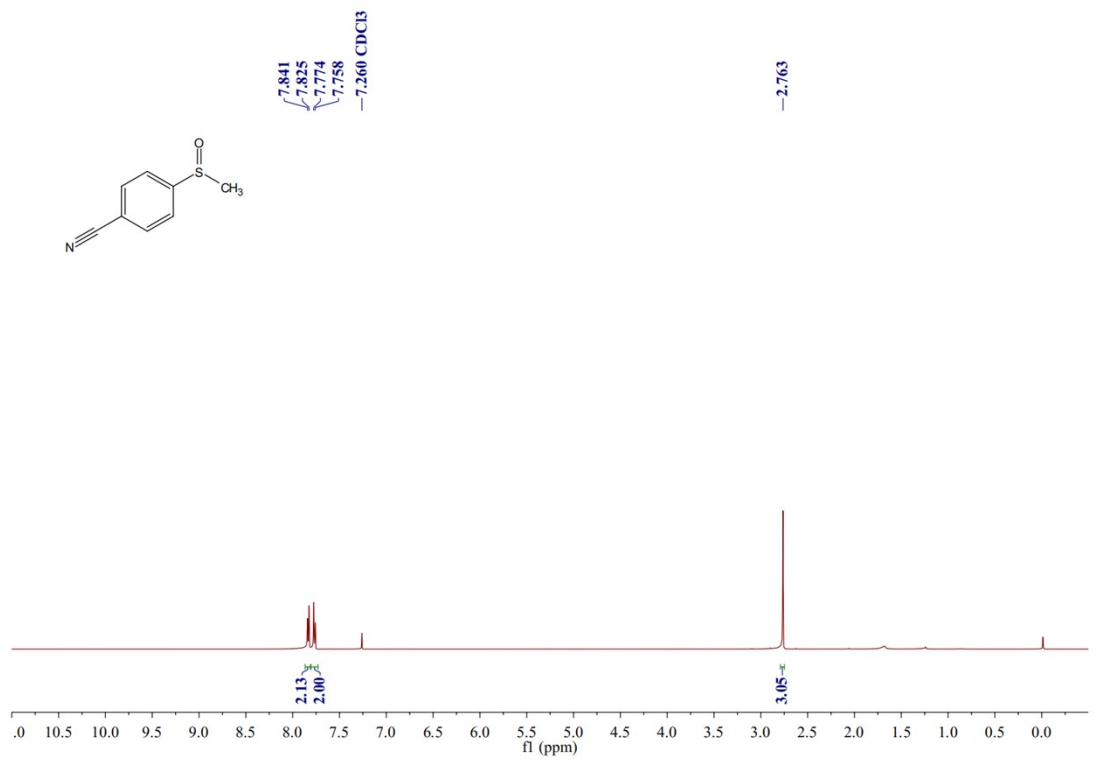
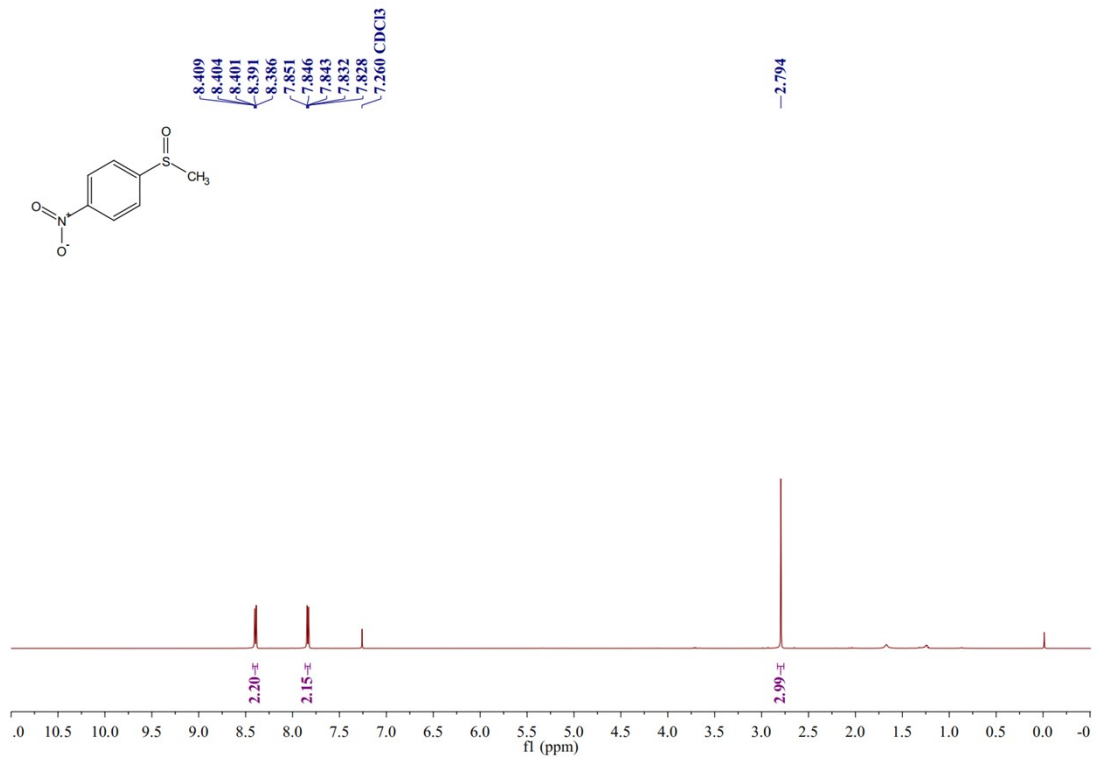


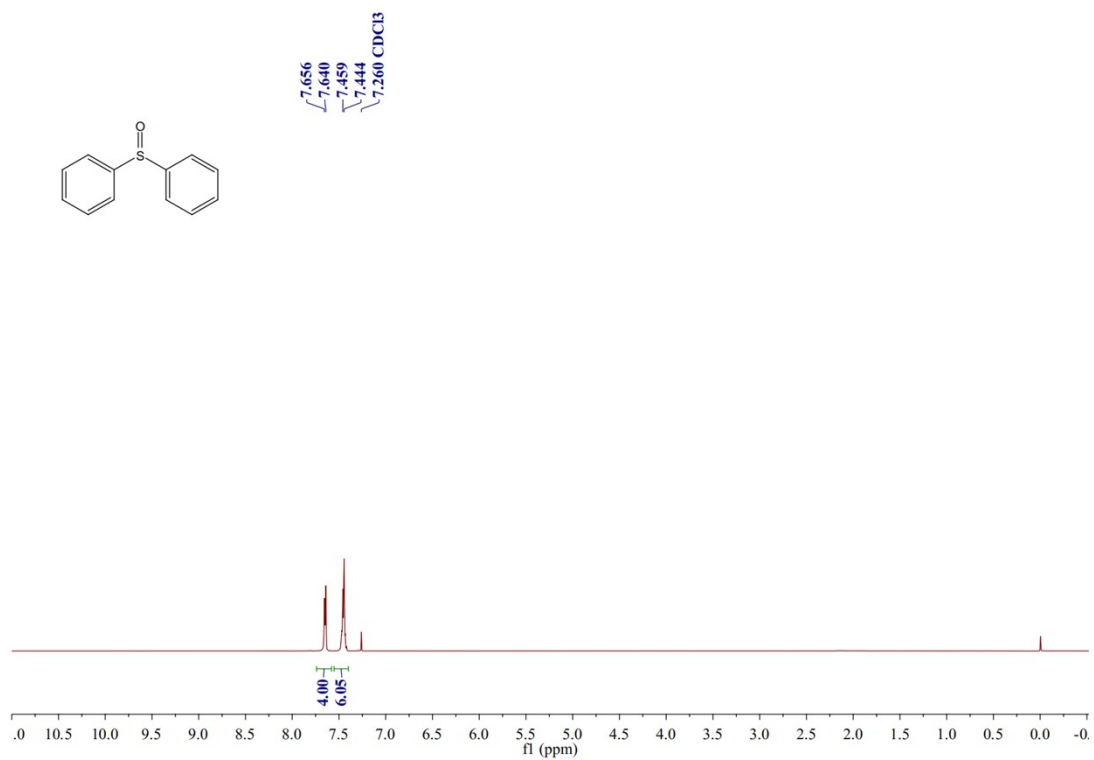
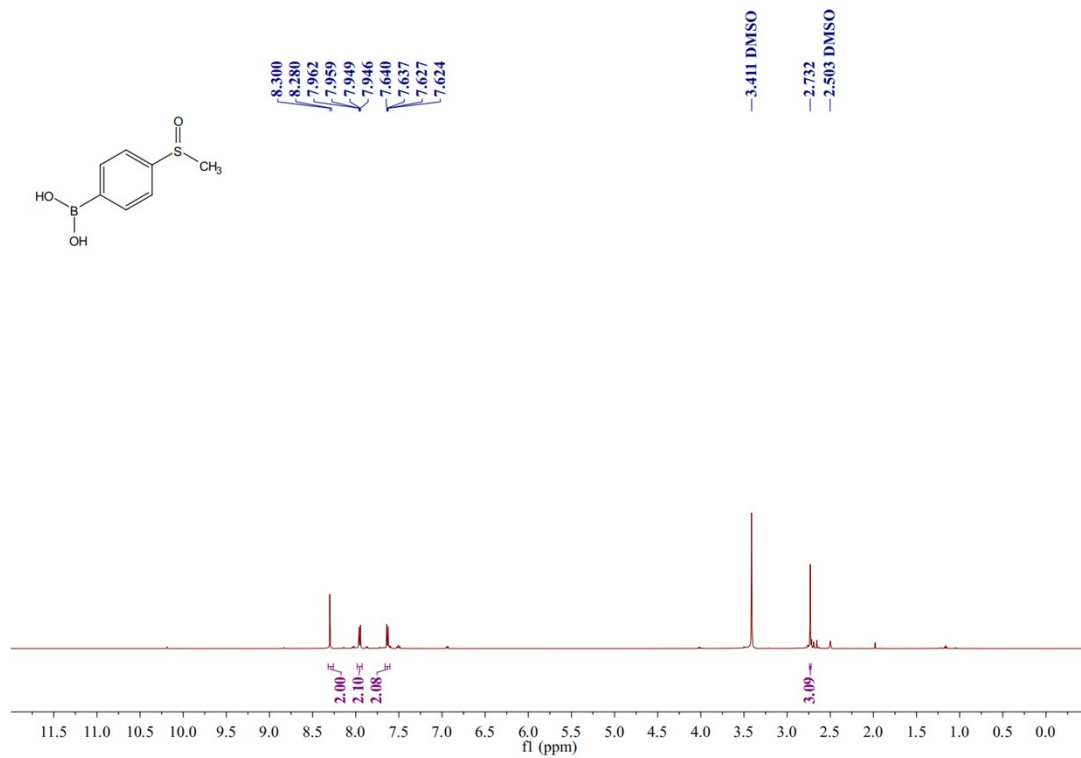


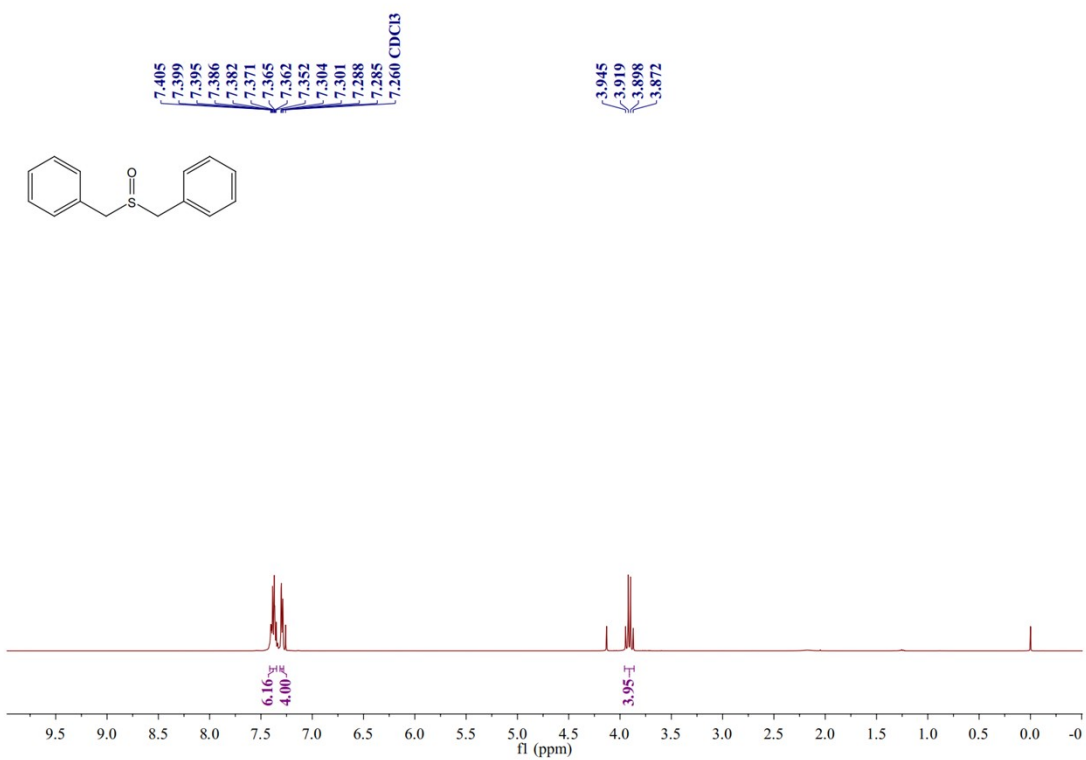
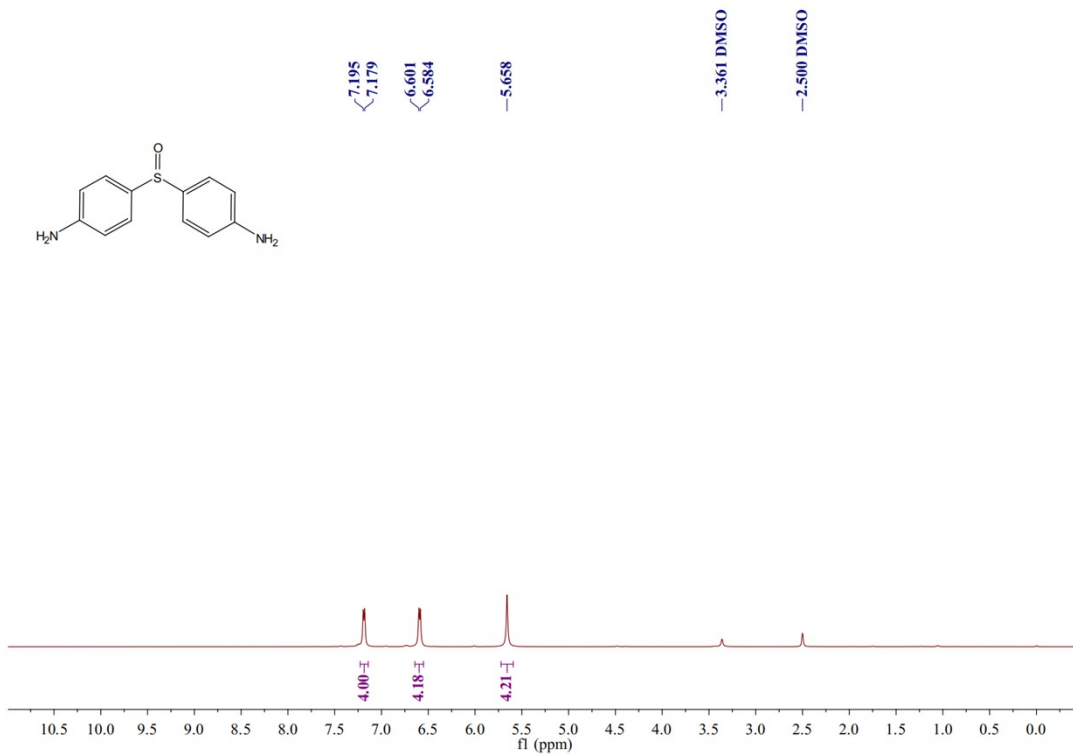


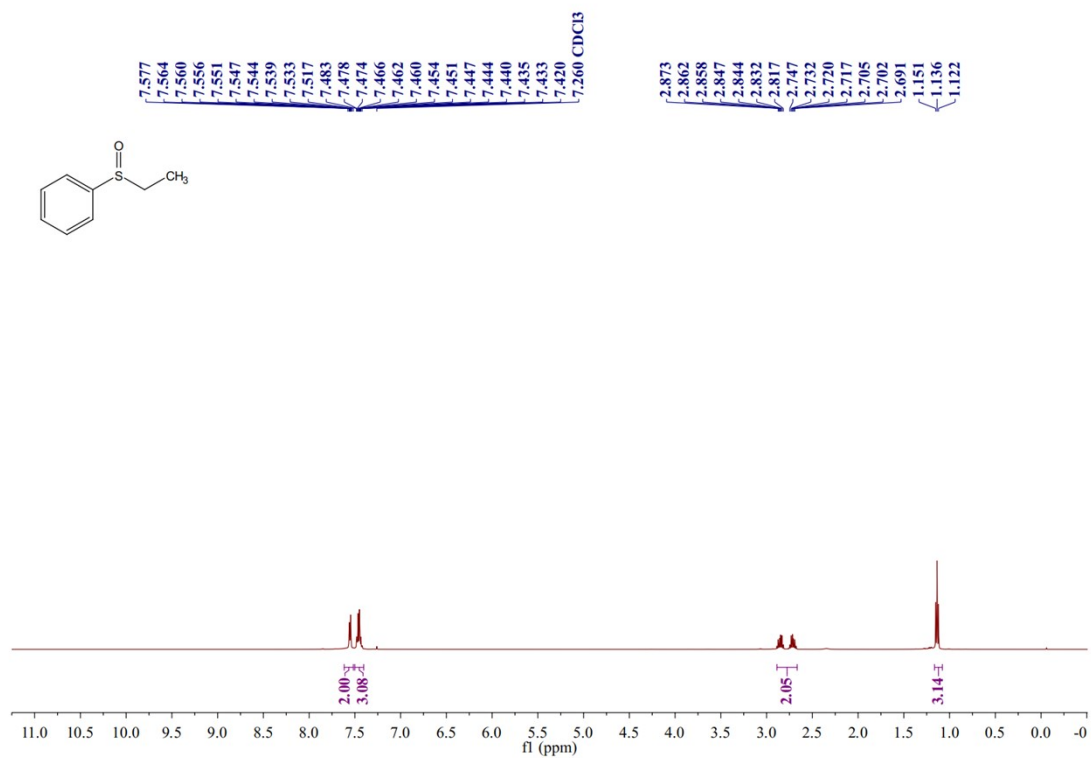
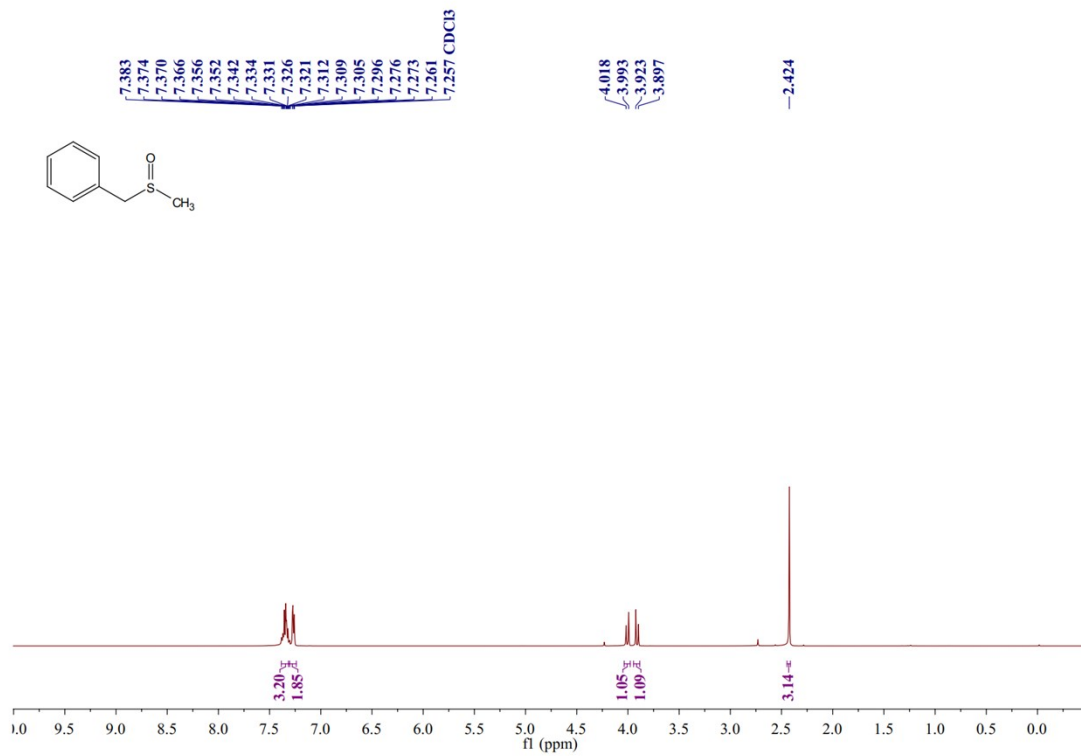


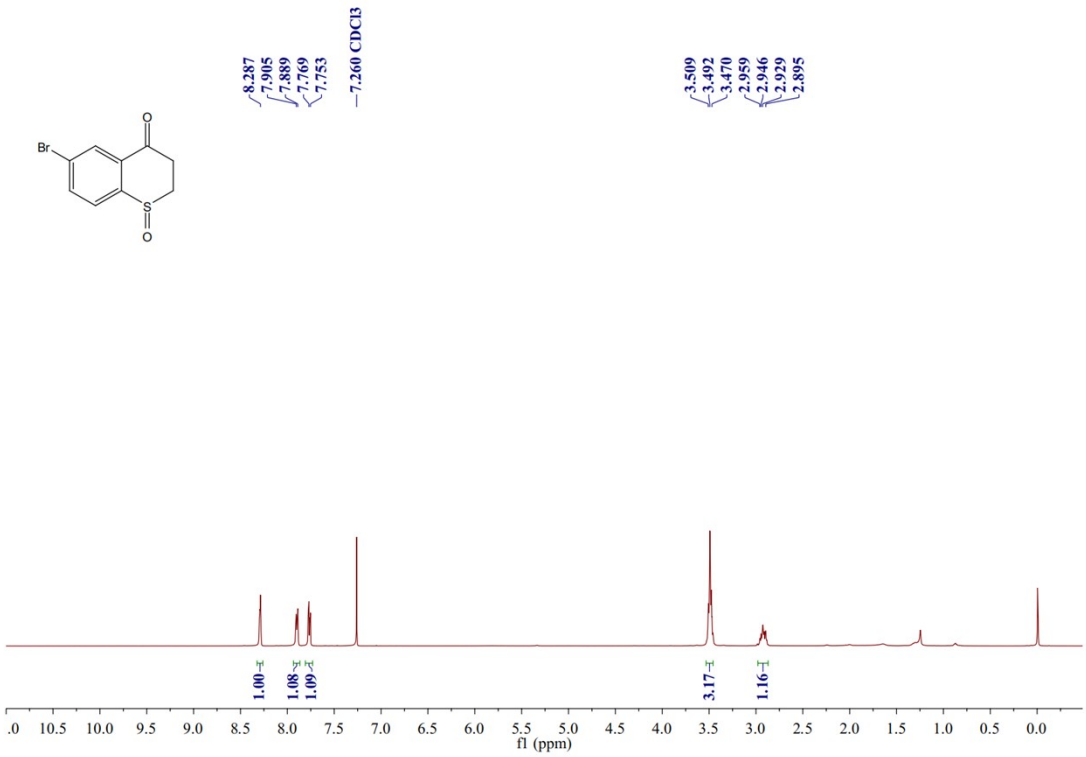
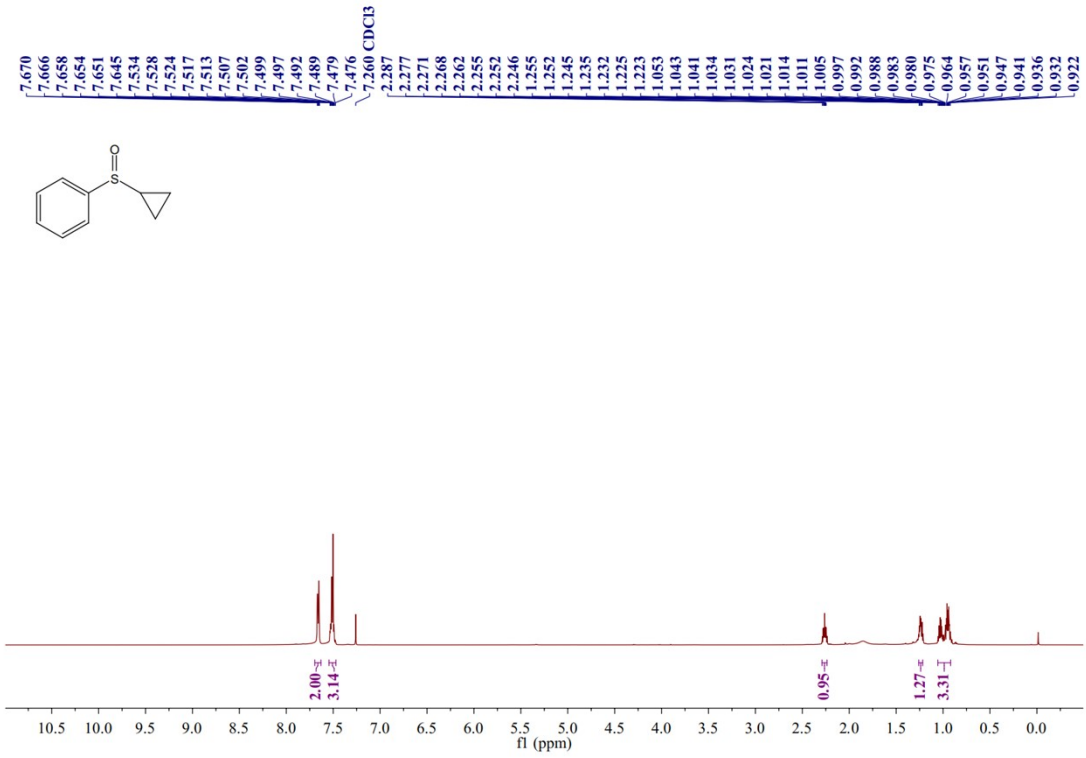


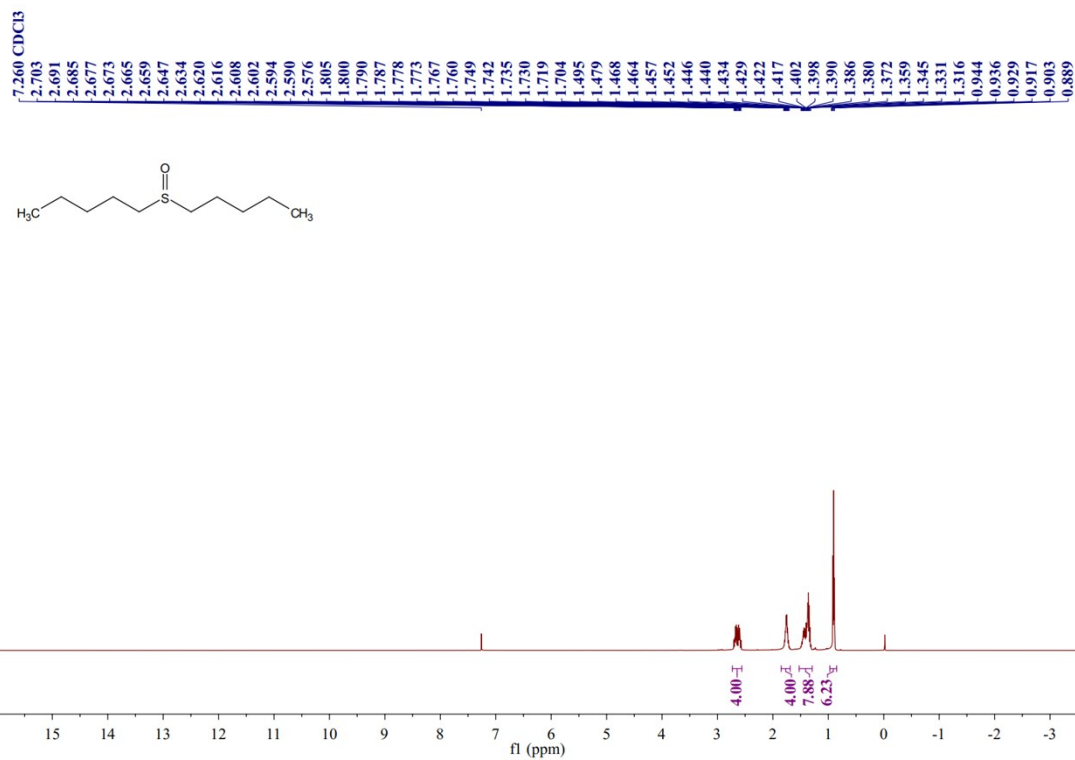
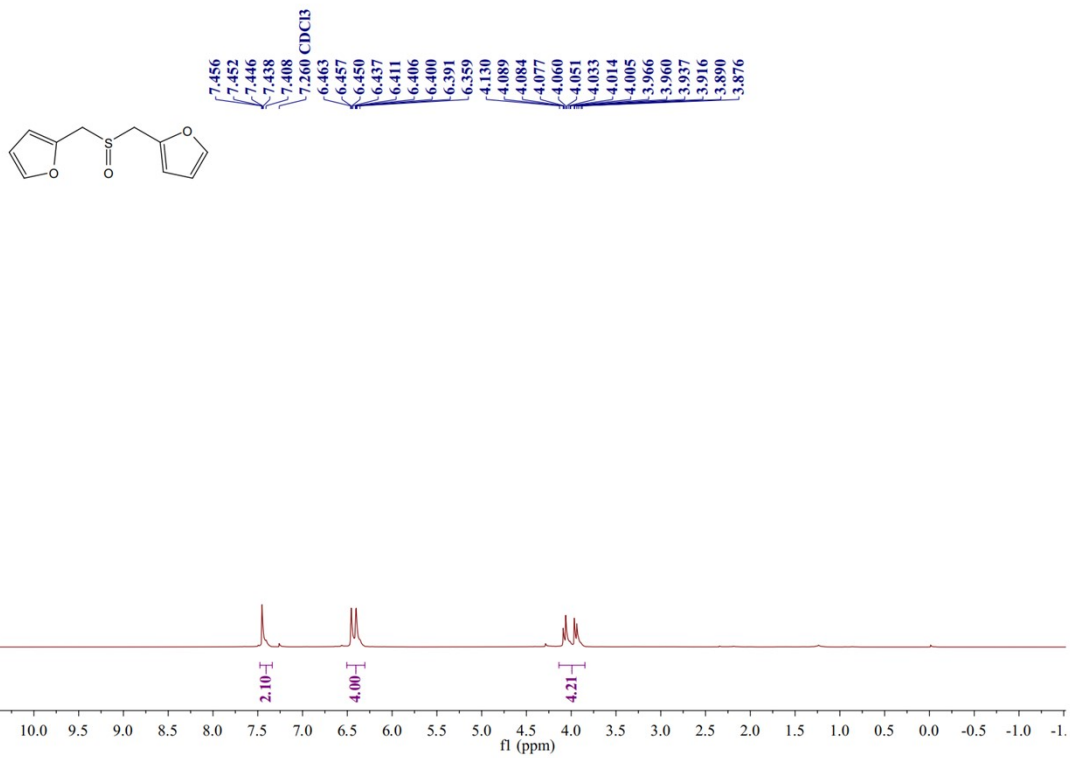


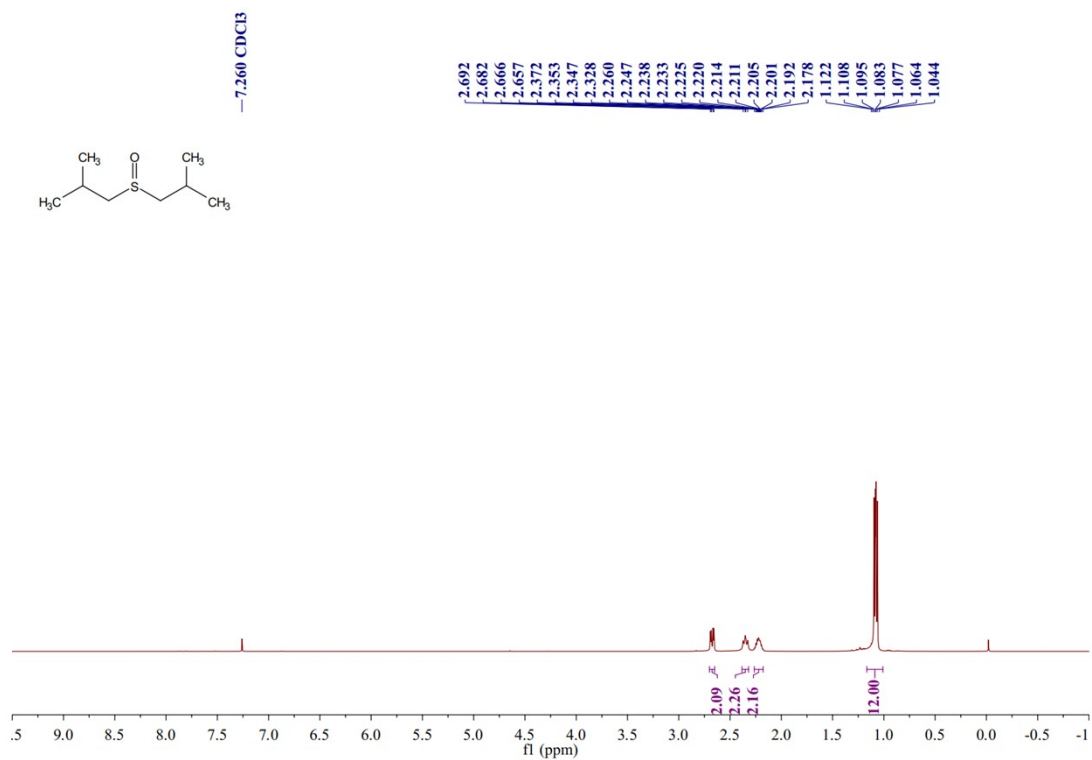












Reference

- [1] Z. Cui, Q. Zhang, H. Fu, Q. Liu, X. Liu, Y. Wu, P. Gao, Z. Wang, Z. Zheng, H. Cheng, Y. Liu, Y. Dai, B. Huang and P. Wang, *Appl. Catal. B Environ.*, 2023, **333**, 122812.