Supporting Information

Electrochemical Oxidative Cross Coupling of *NH*-Sulfoximines with Disulfides

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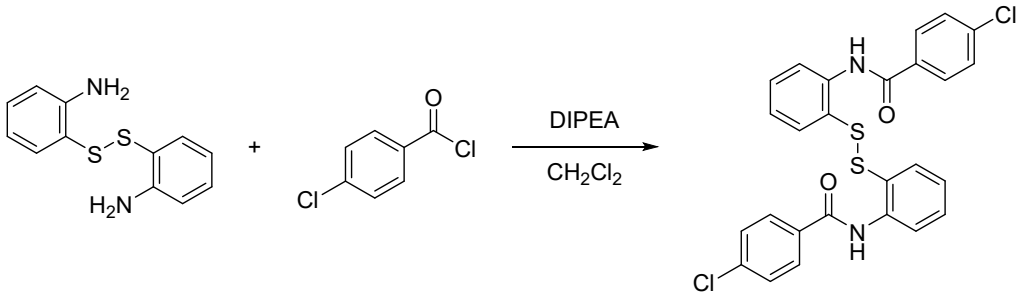
A. Instrumentation and Chemicals

All purchased reagents and solvents were used without further purification unless otherwise noted. All the electrochemical reactions were performed in an undivided cell unless otherwise noted. Cell lines of HeLa (Human cervical cancer cell line), MCF-7 (human breast cancer cells), HepG-2 (Hepatocellular carcinoma cells), and A549 (Human lung carcinoma cells) were purchased from the American Type Culture Collection. The electrolysis instrument used is an adjustable DC regulated power supply (PGD-2303S) (Taiwan Gwinstek Electronic Technology Co., Ltd.). Cyclic voltammograms were obtained on a CHI 760E potentiostat (CH Instruments, Inc.). All the thioether, electrolyte, and redox mediators were purchased from WuXi AppTec. TecAnalytical thin-layer chromatography was performed by using commercially prepared 100-400 mesh silica gel plates (GF_{254}) and visualization was effected at 254 nm. *NH*-sulfoximines, *NH*-sulfonimidamides and disulfides were prepared according to known procedures. The ES20B-H_2 detector is employed for the purpose of hydrogen producttion detection. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker DRX-400 spectrometer using $CDCl_3$ or DMSO-d_6 as solvent. The chemical shifts of $CDCl_3$ are referenced to signals at 7.26 and 77.0 ppm, respectively. The chemical shifts of DMSO-d_6 are referenced to signals at 2.50 and 39.5 ppm, respectively. Mass spectra were recorded on a Thermo Scientific ISQ gas chromatograph-mass spectrometer. The data of HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). Melting points were determined with a Büchi Melting Point B-545 instrument.

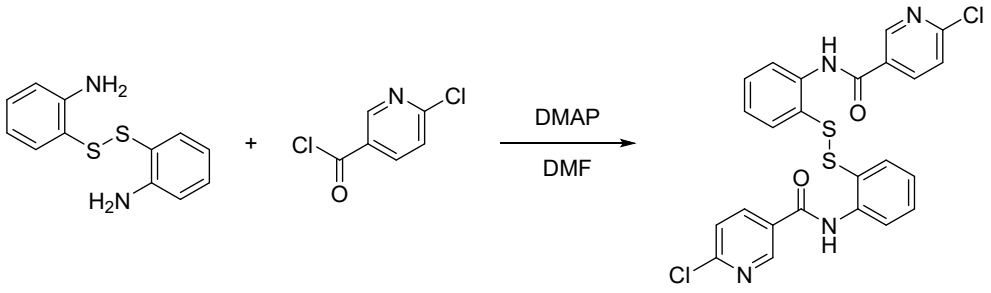
B. Experimental Procedure

B1.1 General Procedure for Synthesis of 2m[6], 2n[6] and 2o[10]



2-1 **6d** **2m**

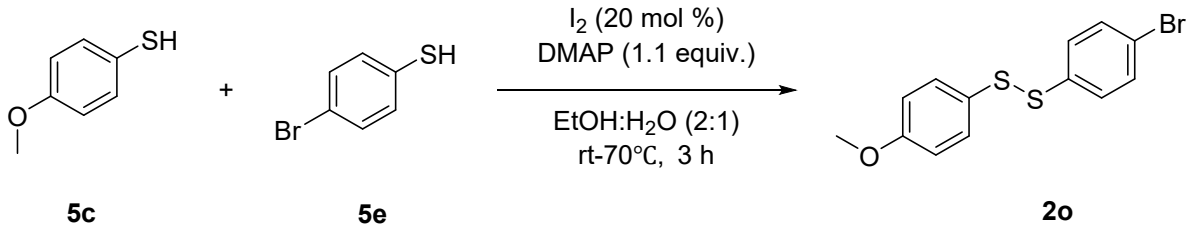
The compound was synthesized according to the reported procedures. 4-Chlorobenzoyl chloride **6d** (1.08 mL, 8.46 mmol) was added to a solution of 2,2'-Diaminodiphenyl disulphide **2-1** (1000 mg, 4.03 mmol) in *N,N*-diiso-propylethylamine (DIPEA) (1.75 mL, 10.1 mmol) and CH_2Cl_2 (13.4 mL). After stirring at rt for 2 h, the resulting white precipitate was collected and washed with water (20 mL). The resulting solid was dried at rt to afford **2m** as a white solid.



2-1 **6g** **2n**

The compound was synthesized according to the reported procedures. 4-dimethylaminopyridine (DMAP) (0.590 mL, 4.82 mmol) and 6-chloronicotinoyl chloride **6g** (850 mg, 4.82 mmol) were added to a solution of 2,2'-Diaminodiphenyl disulphide **2-1** (500 mg, 2.01 mmol) in *N,N*-dimethylformamide (DMF) (10 mL).

After stirring at rt for 9 h, DMF was removed and washed successively with water and EtOH. Recrystallization from $CHCl_3$ gave **2n** as colorless needles.



5c **5e** **2o**

To a round bottom flask was added thiol **5c** (3.6 mmol, 505 mg, 1.0 equiv.), thiol **5e** (3.6 mmol, 681 mg, 1.0 equiv.) in a mixed solvent system ($EtOH/H_2O$, 2:1, 10 mL) and stirred at room temperature. Base (DMAP, 4.2 mmol, 520 mg, 1.2 equiv.) was added to the above reaction mixture and stirred for five minutes at room temperature. Then added molecular iodine (0.72 mmol, 200 mg, 0.2 equiv.) into it and stirred at 70 °C for 3 h. Upon completion the reaction was quenched with saturated $Na_2S_2O_3$ solution. The organic layer was extracted with ethyl acetate (20 mL × 3), dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was chromatographed through silica gel eluting with petroleum ether/ethyl acetate to give the desired products **2o.**

B1.2 The Materials Used to Make the Electrolytic Cell

All the materials used to make the electrolytic cell were commercially available. The anode used graphite rod (φ= 0.6 cm, working height = 1.5 cm) and cathode used platinum plate electrodes (1.0 cm × 1.0 cm × 0.01 cm).

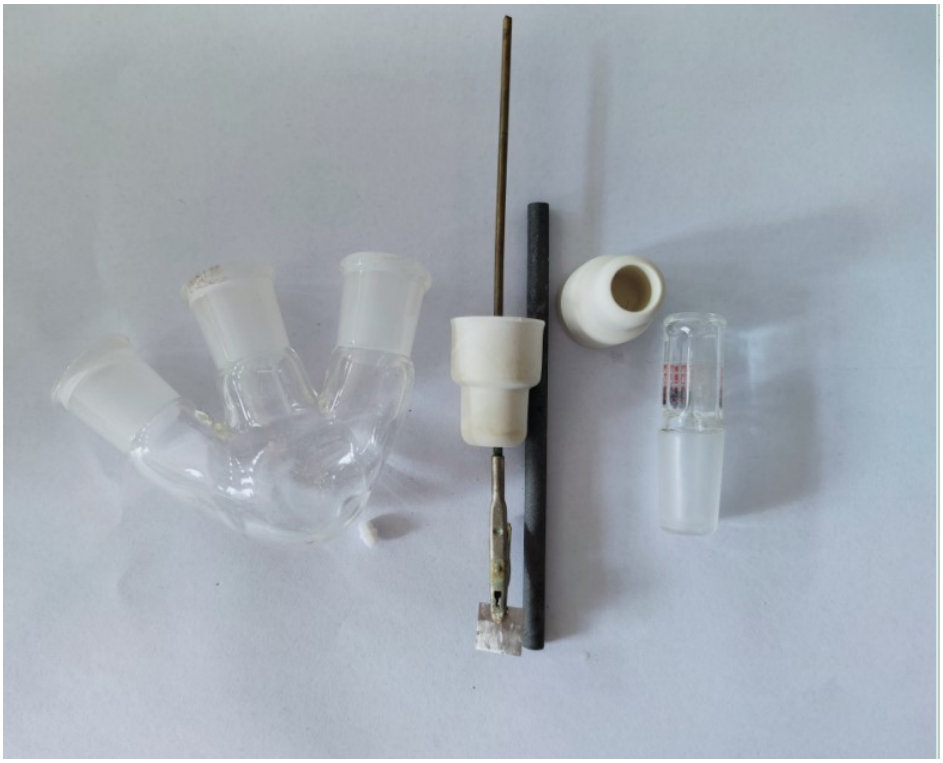
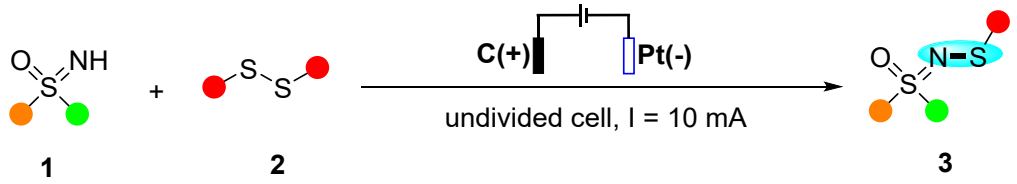


Figure S1. The materials

B1.3 General Procedure for the Synthesis of 3.



NH-sulfoximines **1** (0.1 mmol, 1 equiv.), disulfides **2** (0.1 mmol, 1 equiv.), and TBAI (0.2 mmol, 2 equiv.) were placed in a 10 mL round bottom flask with three necks. The flask was equipped with a carbon rod (φ= 0.6 cm, working height = 1.5 cm) as the anode, a platinum plate (1.0 cm × 1.0 cm × 0.01 cm) as the cathode. CH_3CN (3.0 mL) and *t*-BuOH (0.1 mmol, 1 equiv.) were added. The electrolysis was carried out under air atmosphere at rt using a constant current of 10 mA and stopped until complete consumption of *NH*-sulfoximines (monitored by TLC, about 1-3 h) (3.7-11.2 F/mol) (current efficiency (3.8-24.1%)). The mixture was cooled and diluted with brine, and the product was extracted with ethyl acetate (3 × 10 mL). The organic layer was dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with petroleum ether/ethyl acetate to give the desired products **3** (Figure S2).

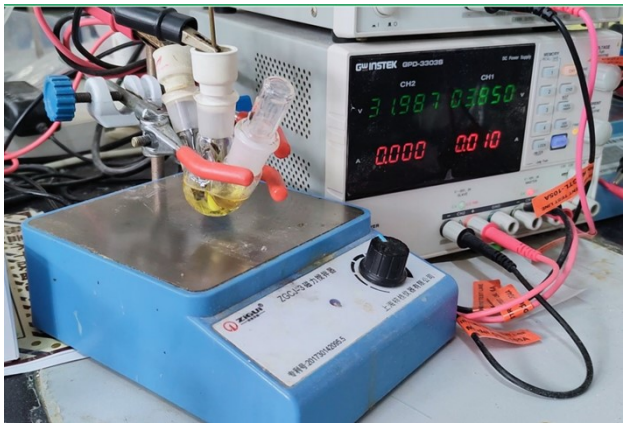
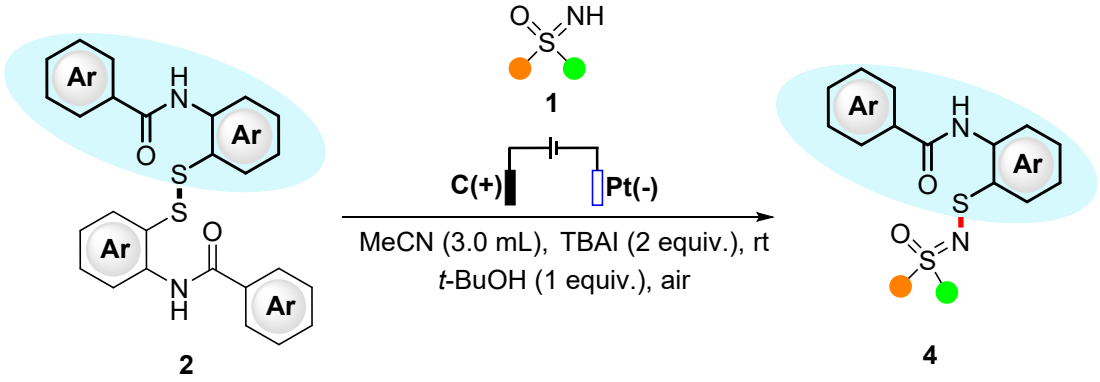


Figure S2. General procedure for the synthesis of 3

B1.4 General Procedure for the Synthesis of *N*-(2-Thiophenyl)benzamide Derivatives.



NH-sulfoximines **1** (0.1 mmol, 1 equiv.), disulfides **2** (0.1 mmol, 1 equiv.), and TBAI (0.2 mmol, 2 equiv.) were placed in a 10 mL round bottom flask with three necks. The flask was equipped with a carbon rod (φ= 0.6 cm, working height = 1.5 cm) as the anode, a platinum plate (1.0 cm × 1.0 cm × 0.01 cm) as the cathode. CH_3CN (3.0 mL) and *t*-BuOH (0.1 mmol, 1 equiv.) were added. The electrolysis was carried out under air atmosphere at rt using a constant current of 10 mA and stopped until complete consumption of *NH*-sulfoximines (monitored by TLC, about 1.5-2 h) (5.6-7.5 F/mol) (current efficiency (6.7-14.3%)). The mixture was cooled and diluted with brine, and the product was extracted with ethyl acetate (3 × 10 mL). The organic layer was dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with petroleum ether/ethyl acetate to give the desired products *N*-(2-Thiophenyl)benzamide derivatives **4.**

B2. Hydrogen Capture Experiment

To further verify whether the hydrogen generated, we use hydrogen detector. Sulfonimidoyldibenzene **1a** (0.1 mmol, 1 equiv.), 1,2-diphenyldisulfane **2a** (0.1 mmol, 1 equiv.), and TBAI (0.2 mmol) were placed in a 10 mL round bottom flask with three necks. The flask was equipped with a carbon rod (φ= 0.6 cm, working height = 1.5 cm) as the anode, a platinum plate (1.0 cm × 1.0 cm × 0.01 cm) as cathode. CH_3CN (3.0 mL) and *t*-BuOH (0.1 mmol, 1 equiv.) were added. The electrolysis was carried out under air atmosphere at rt using a constant current of 10 mA. After 10 minutes of reaction, install the ES20B-H_2 detector (Figure S3).

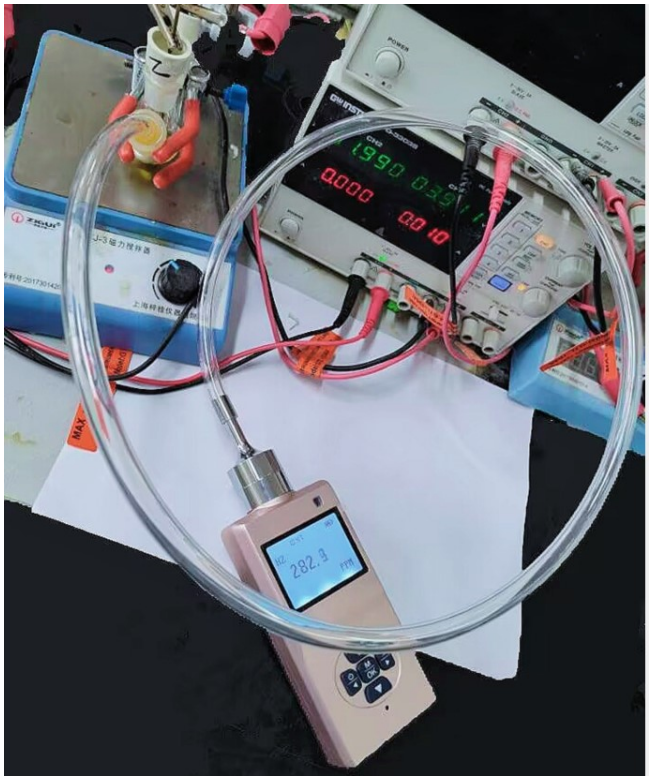


Figure S3. Hydrogen capture experiment

C. Optimization of the Reaction Conditions

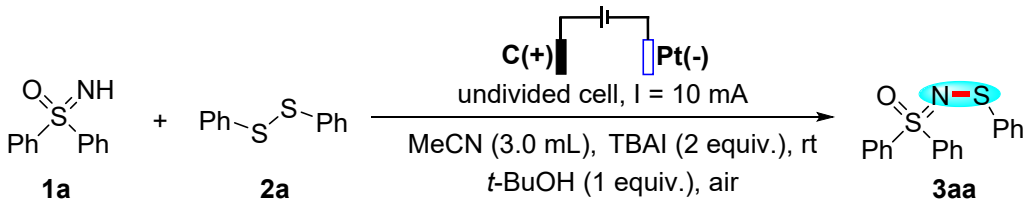
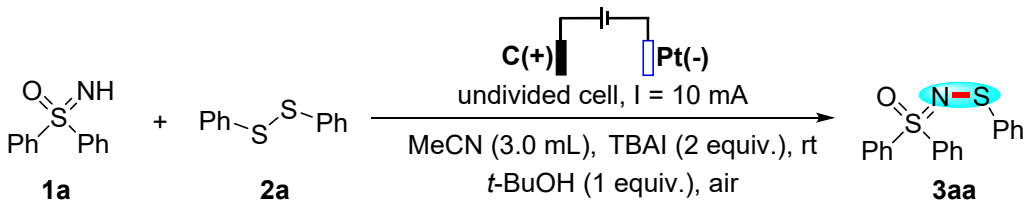


Table S1. Optimization of the Reaction Conditions[a]

Entry	Variation from the above conditions	Yield (%)[b]
1	**None**	**80**
2	MeOH as solvent	45
3	DCM as solvent	20
4	DMSO as solvent	23
5	DMF as solvent	14
6	HFIP as solvent	30
7	7 mA	70
8	13 mA	74
9	$LiClO_4$ instead of TBAI	trace
10	*n*-Bu_4NBF_4 instead of TBAI	trace
11	*n*-Bu_4NBr instead of TBAI	52
12	NH_4I instead of TBAI	61
13	Pt as the anode	62
14	Ni as the cathode	65
15	Without *t*-BuOH	55
16	Under N_2	80
17	0.5 eq./1.0 eq./3.0 eq. TBAI	42/60/68
18[c]	*S*-phenylester instead of **2a**	60
19[d]	4-Methoxybenzenethiol instead of **2a**	38
20[e]	4-Chlorothiophenol instead of **2a**	40
21	No electricity	n.r.

[a]Reaction conditions: C rod (Ø 0.6 cm) anode, Pt cathode (1.0 cm × 1.0 cm × 0.01 cm), **1a** (0.1 mmol), **2a** (0.1 mmol), TBAI (2 equiv.), *t*-BuOH (1 equiv.), CH_3CN (3.0 mL), 10 mA, rt, 1.5 h (5.6 F/mol) and under air; n.r. = not reaction. [b]Isolated yield. [c]Reaction time: 0.5 h (1.9 F/mol). [d]Product **3ac**. [e]Product **3ad.**

Table S2. Optimization of 3aa with different solvent



Entry[a]	Solvent	Yield (%)[b]
1	**None**	**80**
2	MeOH as solvent	45
3	DCM as solvent	20
4	DMSO as solvent	23
5	DMF as solvent	14
6	HFIP as solvent	30
7	DCE as solvent	26
8	EtOH as solvent	36

[a]Reaction conditions: C rod (Ø 0.6 cm) anode, Pt cathode (1.0 cm × 1.0 cm × 0.01 cm), **1a** (0.1 mmol), **2a** (0.1 mmol), TBAI (2 equiv.), *t*-BuOH (1 equiv.), solvent (3.0 mL), 10 mA, rt, 1.5 h (5.6 F/mol) and under air. [b]Isolated yield.

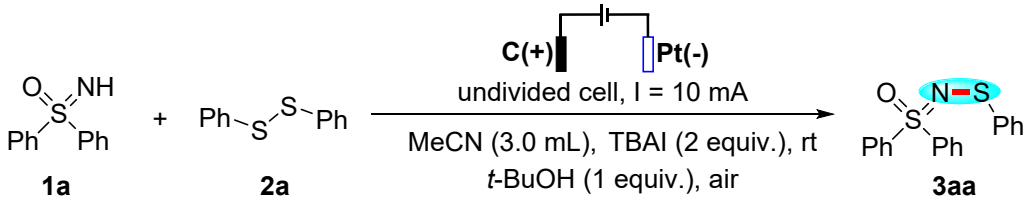


Table S3. Optimization of 3aa with different electolyte

Entry[a]	Electolyte	Yield (%)[b]
1	**None**	**80**
2	$LiClO_4$ instead of TBAI	trace
3	*n*-Bu_4NBF_4 instead of TBAI	trace
4	*n*-Bu_4NBr instead of TBAI	52
5	NH_4I instead of TBAI	61
6	KI instead of TBAI	59
7	NaI instead of TBAI	56
8	*n*-Bu_4NPF_6 instead of TBAI	trace

[a]Reaction conditions: C rod (Ø 0.6 cm) anode, Pt cathode (1.0 cm × 1.0 cm × 0.01 cm), **1a** (0.1 mmol), **2a** (0.1 mmol), electolyte (2 equiv.), *t*-BuOH (1 equiv.), CH_3CN (3.0 mL), 10 mA, rt, 1.5 h (5.6 F/mol) and under air. [b]Isolated yield.

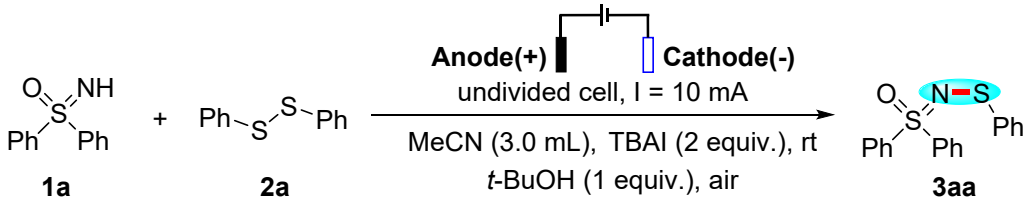


Table S4. Optimization of 3aa with different electrode

Entry[a]	Anode/Cathode	Yield (%)[b]
1	**C/Pt**	**80**

2	Pt/Pt	62
3	C/Ni	65
4	C/SS	63
5	C/GC	45
6	C/C	64
7	GC/Pt	42
8	Pt/C	55

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.1 mmol), TBAI (2 equiv.), *t*-BuOH (1 equiv.), CH_3CN (3.0 mL), 10 mA, rt, 1.5 h (5.6 F/mol) and under air. [b]Isolated yield.

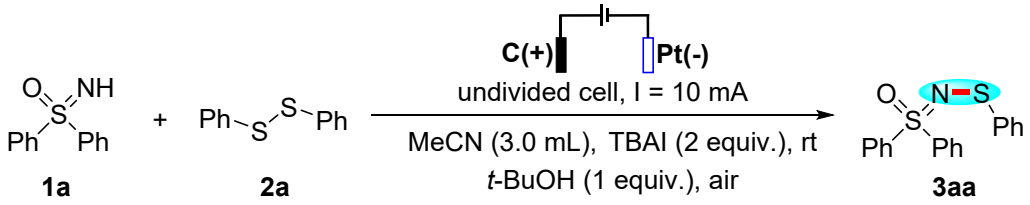
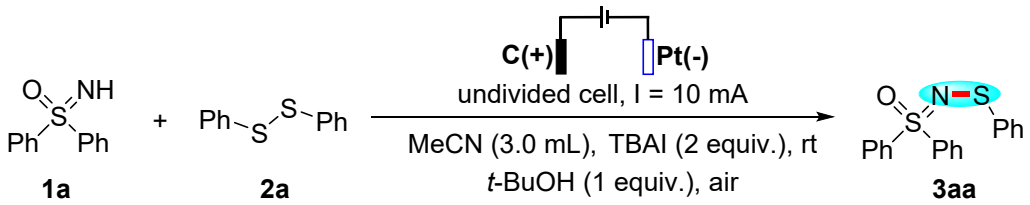


Table S5. Optimization of 3aa with different amounts of TBAI

Entry[a]	TBAI	Yield (%)[b]
1	**None**	**80**
2	10 mol %	15
3	20 mol %	20
4	0.5 eq.	42
5	1.0 eq.	60
6	3.0 eq.	68

[a]Reaction conditions: C rod (Ø 0.6 cm) anode, Pt cathode (1.0 cm × 1.0 cm × 0.01 cm), **1a** (0.1 mmol), **2a** (0.1 mmol), TBAI, *t*-BuOH (1 equiv.), CH_3CN (3.0 mL), 10 mA, rt, 1.5 h (5.6 F/mol) and under air. [b]Isolated yield.

Table S6. Optimization of 3aa with different additive

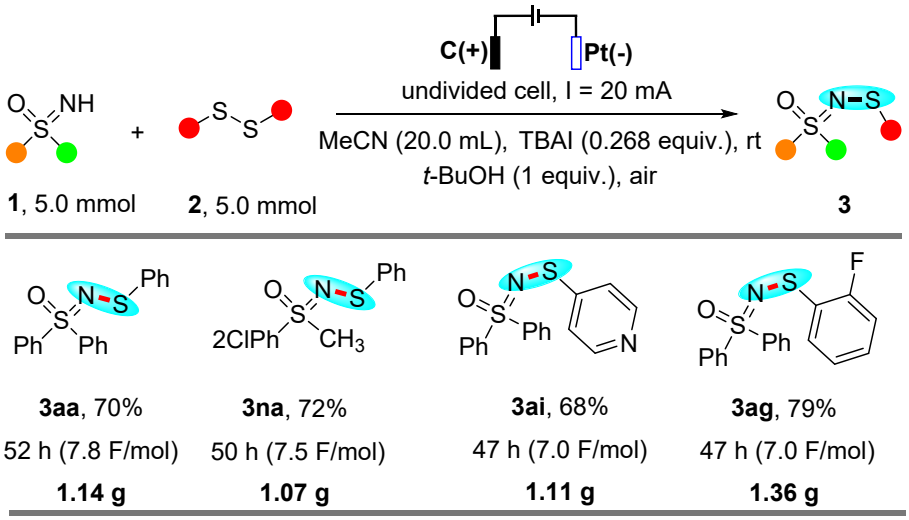


Entry[a]	Additive	Yield (%)[b]
1	**None**	**80**
2	$(C_2H_5)_3N$ instead of *t*-BuOH	56
3	CH_3COONa instead of *t*-BuOH	58
4	K_2CO_3 instead of *t*-BuOH	60
5	*t*-BuOK instead of *t*-BuOH	64
6	1.3 equiv. *t*-BuOH	80

[a]Reaction conditions: C rod (Ø 0.6 cm) anode, Pt cathode (1.0 cm × 1.0 cm × 0.01 cm), **1a** (0.1 mmol), **2a** (0.1 mmol), TBAI (2 equiv.), *t*-BuOH (1 equiv.), CH_3CN (3.0 mL), 10 mA, rt, 1.5 h (5.6 F/mol) and under air. [b]Isolated yield.

D. Gram-scale Experiment

NH-Sulfoximines **1** (5.0 mmol, 1 equiv.), disulfides **2** (5.0 mmol, 1 equiv.), and TBAI (1.34 mmol, 0.268 equiv.) were placed in a 100 mL round bottom flask with three necks. The flask was equipped with a carbon rod (φ= 0.6 cm, working height = 1.5 cm) as the anode, a platinum plate (1.0 cm × 1.0 cm × 0.01 cm) as cathode. CH_3CN (20.0 mL) and *t*-BuOH (5.0 mmol, 1 equiv.) were added. The electrolysis was carried out under air atmosphere at rt using a constant current of 20 mA and stopped until complete consumption of *NH*-sulfoximines (monitored by TLC, about 47-52 h) (7.0-7.8 F/mol) (current efficiency (9.0-11.3%)). The mixture was cooled and diluted with brine, and the product was extracted with ethyl acetate (3 × 30 mL). The organic layer was dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with petroleum ether/ethyl acetate to give the desired products **3**.



Scheme S1. Gram-Scale Experiments

E. Biological Applications

Standard 3-(4,5-dimethylthiazole)-2,5-diphenyltetraazolium bromide (MTT) assay procedures were used. Cells were placed in 96-well microassay culture plates (8×10^3 cells per well) and grown overnight at 37 °C in a 5% CO_2 incubator. The tested compounds were then added to the wells to achieve final concentrations ranging from 10^{-6} to 10^{-4} M. Control wells were prepared by the addition of a culture medium (100 μL). The plates were incubated at 37 °C in a 5% CO_2 incubator for 48 h. Upon completion of the incubation, stock MTT dye solution (20 μL, 5 $mg \cdot mL^{-1}$) was added to each well. After 4 h, DMSO (100 μL) was added to solubilize the MTT formazan. The optical density of each well was then measured with a microplate spectrophotometer at a wavelength of 490 nm. The IC_{50} values were calculated by plotting the percentage viability versus concentration on a logarithmic graph and reading of the concentration at which 50% of cells remained viable relative to the control. Each experiment was repeated at least three times to obtain the mean values. The results are summarized in Table S7.

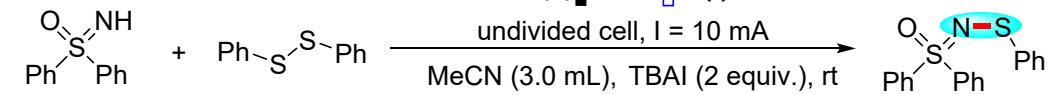
Table S7. Biological Applications[a]

Compounds	IC_{50} (μM)			
	A549	**HepG-2**	**MCF-7**	**Hela**
4a	76.4 ± 5.8	>100	85.3 ± 7.2	>100
4b	92.4 ± 7.1	>100	76.7 ± 7.4	79.9 ± 7.5
4c	32.8 ± 2.7	69.2 ± 6.7	>100	43.6 ± 3.7
4d	>100	>100	83.5 ± 5.9	>100
4e	97.5 ± 6.3	>100	>100	>100
4f	>100	>100	>100	>100
4g	29.7 ± 2.8	35.3 ± 2.5	41.6 ± 3.6	28.6 ± 2.7
4h	46.3 ± 4.3	51.4 ± 4.6	26.6 ± 2.3	35.4 ± 3.4
5-Fu	34.6 ± 3.1	40.7 ± 4.6	30.5 ± 3.9	32.9 ± 3.4

[a]IC_{50} (μM) values of compounds against the selected cancer cell lines; **5-Fu** = 5-fluorouracil.

F. Control Experiments

a)

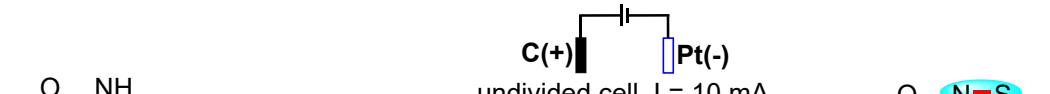


1a, 0.1 mmol + **2a**, 0.1 mmol → **3aa**

with addition of ***BHT*** (3 equiv.), **3aa**, 1.5 h, **15%**

with addition of ***p-BQ*** (3 equiv.), **3aa**, 1.5 h, **0%**

b)

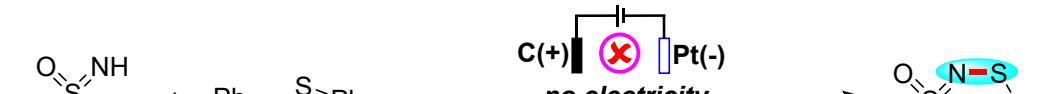


1a, 0.1 mmol + **2a**, 0.1 mmol → **3aa**

without addition of I_2 (1 equiv.), **3aa**, 1.5 h, **trace**

with addition of I_2 (1 equiv.), **3aa**, 10 min, **55%**

c)



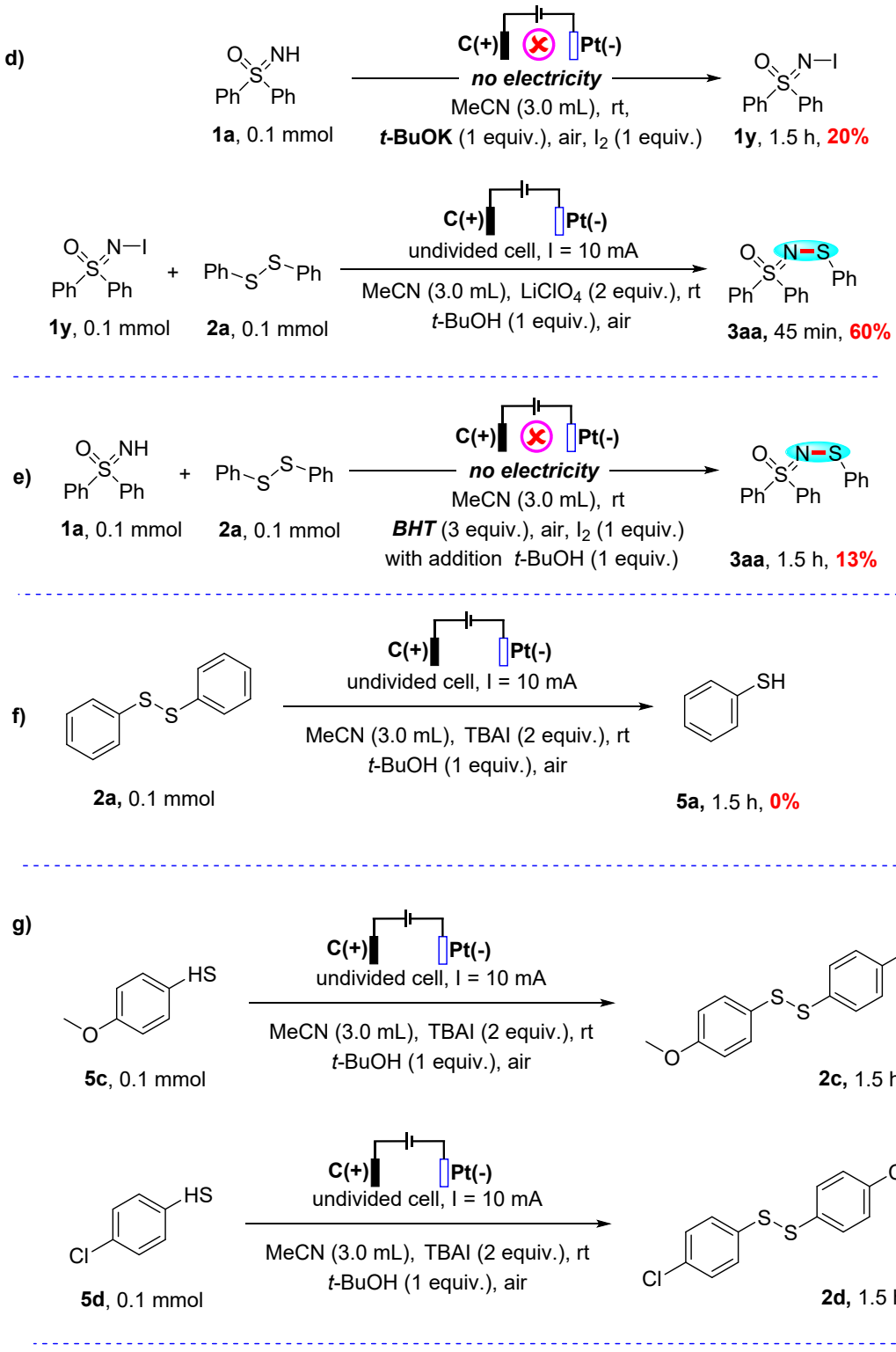
1a, 0.1 mmol + **2a**, 0.1 mmol → **3aa**, 10 min, **15%**

3aa, 1.5 h, **25%**

Change of the reaction conditions[a]

Entry	Additive	Catalyst (I_2)	Yield (%)[b]
1	*t*-BuOH	1 equiv.	25
2	$(C_2H_5)_3N$ instead of *t*-BuOH	1 equiv.	32
3	Na_2CO_3 instead of *t*-BuOH	1 equiv.	34
4	CH_3COONa instead of *t*-BuOH	1 equiv.	36
5	K_2CO_3 instead of *t*-BuOH	1 equiv.	51
6	*t*-BuOK instead of *t*-BuOH	1 equiv.	53

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.1 mmol), I_2 (1 equiv.), *t*-BuOH (1 equiv.), CH_3CN (3.0 mL), rt, 1.5 h, under air and no electricity. [b]Isolated yield.



Scheme S2. Control Experiments

G. Cyclic Voltammetry Experiments

The cyclic voltammetry experiments were carried out with a computer-controlled electrochemical analyzer for electrochemical measurements. The experiment was performed in a three-electrode cell with CH_3CN (3.0 mL) as the solvent, *t*-BuOH (10 mmol/L) as the additive, 0.1 M $LiClO_4$ as the supporting electrolyte, the tested compound (10 mmol/L). The working electrode is a diameter glassy carbon working electrode (GCE) ((φ=0.3⌀4.5 cm)) that was polished with 0.3 μm aluminum oxide and then washed in distilled water and ethanol before measurements. Pt wire (φ=0.05⌀3.7 cm) as the auxiliary electrode, and Ag/AgCl (saturated aqueous KCl, φ=0.4⌀4.5 cm) as the reference electrode that was washed with water and ethanol before measurements. The scan rate is 100 mV/s, ranging from 0 V to 2.0 V. CV plotting convention is IUPAC. The starting point was 0 V, and the direction of the initial scan was oxidative. Before the determination of the sample, ferrocene (Fc) (0.25 mmol) and 0.1 M $LiClO_4$ were weighed and dissolved in CH_3CN (3.0 mL) to test CV. The samples were tested after the data stabilized. Otherwise, polish the electrode until the data is stable.

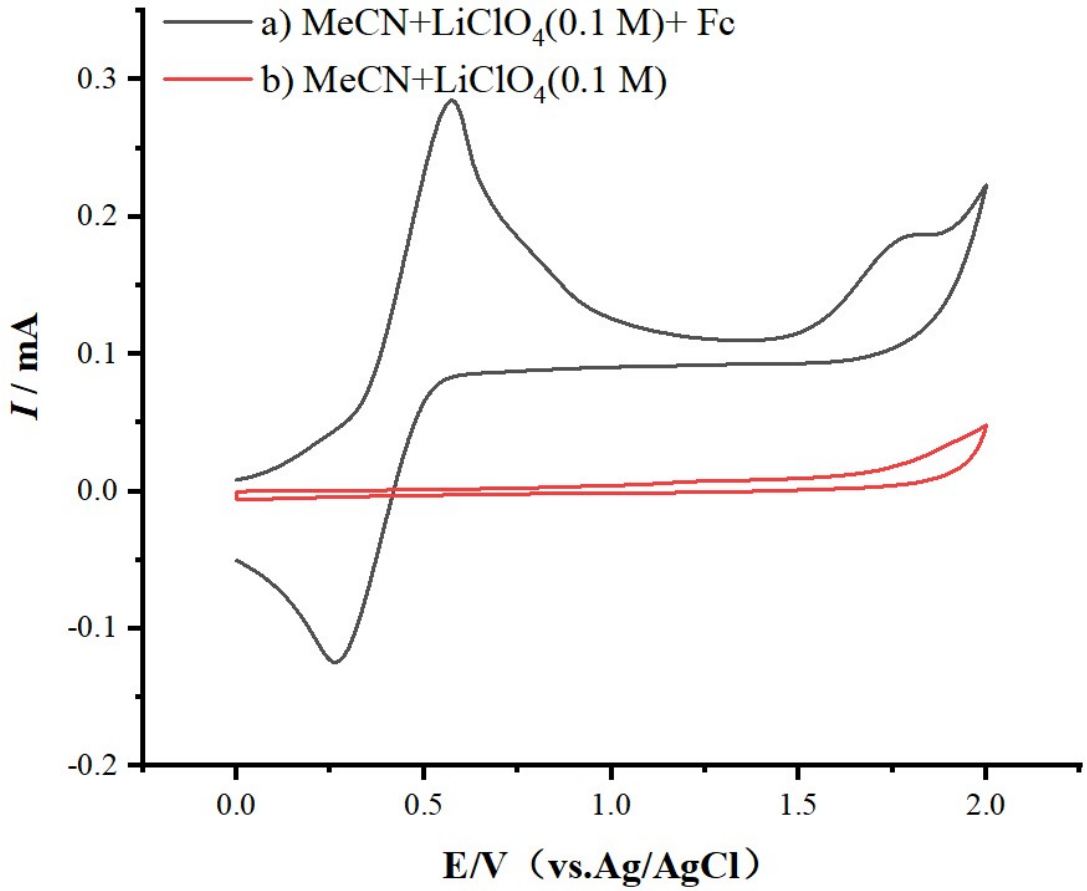


Figure S4 (a) Cyclic voltammograms of solution in a solvent of CH_3CN (3.0 mL), 0.1 M $LiClO_4$ and Fc (0.25 mmol). (b) Cyclic voltammograms of solution in a solvent of CH_3CN (3.0 mL) and 0.1 M $LiClO_4$. In the presence of Fc, the oxidative and reductive peaks were 0.57 V *vs* Ag/Ag^+ and 0.26 V *vs* Ag/Ag^+.

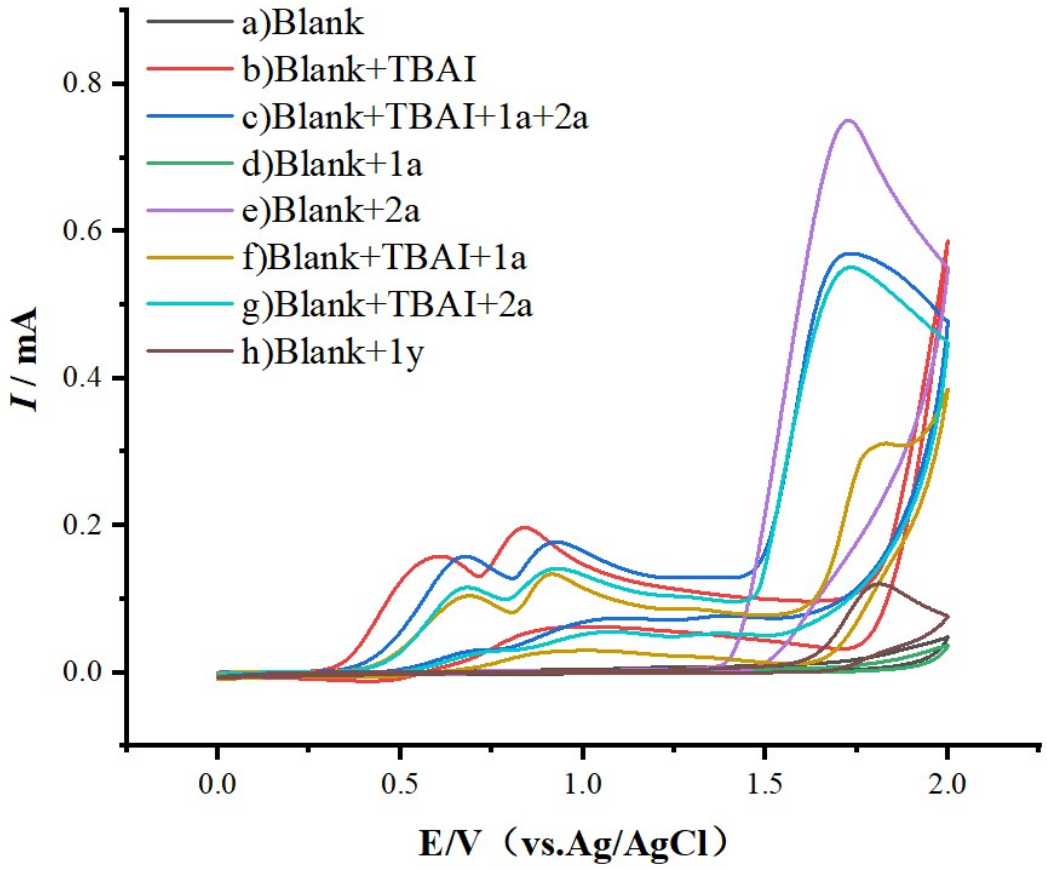


Figure S5 Cyclic voltammograms of solution in a solvent of CH_3CN (3.0 mL) containing *t*-BuOH (10 mmol/L) and 0.1 M $LiClO_4$. (a) Blank; (b) Blank + TBAI (10 mmol/L)(two oxidative peaks of TBAI were observed at 0.59 V *vs* Ag/Ag^+ and 0.84 V *vs* Ag/Ag^+); (c) Blank + **1a** (10 mmol/L) + **2a** (10 mmol/L) + TBAI (10 mmol/L) (In addition to two oxidative peaks in TBAI, an oxidative peak was 1.72 V *vs* Ag/Ag^+); (d) Blank + **1a** (10 mmol/L); (e) Blank + **2a** (10 mmol/L) (an oxidative peak of **2a** was 1.72 V *vs* Ag/Ag^+); (f) Blank + **1a** (10 mmol/L) + TBAI (10 mmol/L) (In addition to two oxidative peaks in TBAI, an oxidative peak was 1.80 V *vs* Ag/Ag^+); (g) Blank + **2a** (10 mmol/L) + TBAI (10 mmol/L) (In addition to two oxidative peaks in TBAI, an oxidative peak was 1.74 V *vs* Ag/Ag^+); (h) Blank + **1y** (10 mmol/L) (an oxidative peak of **1y** was 1.80 V *vs* Ag/Ag^+).

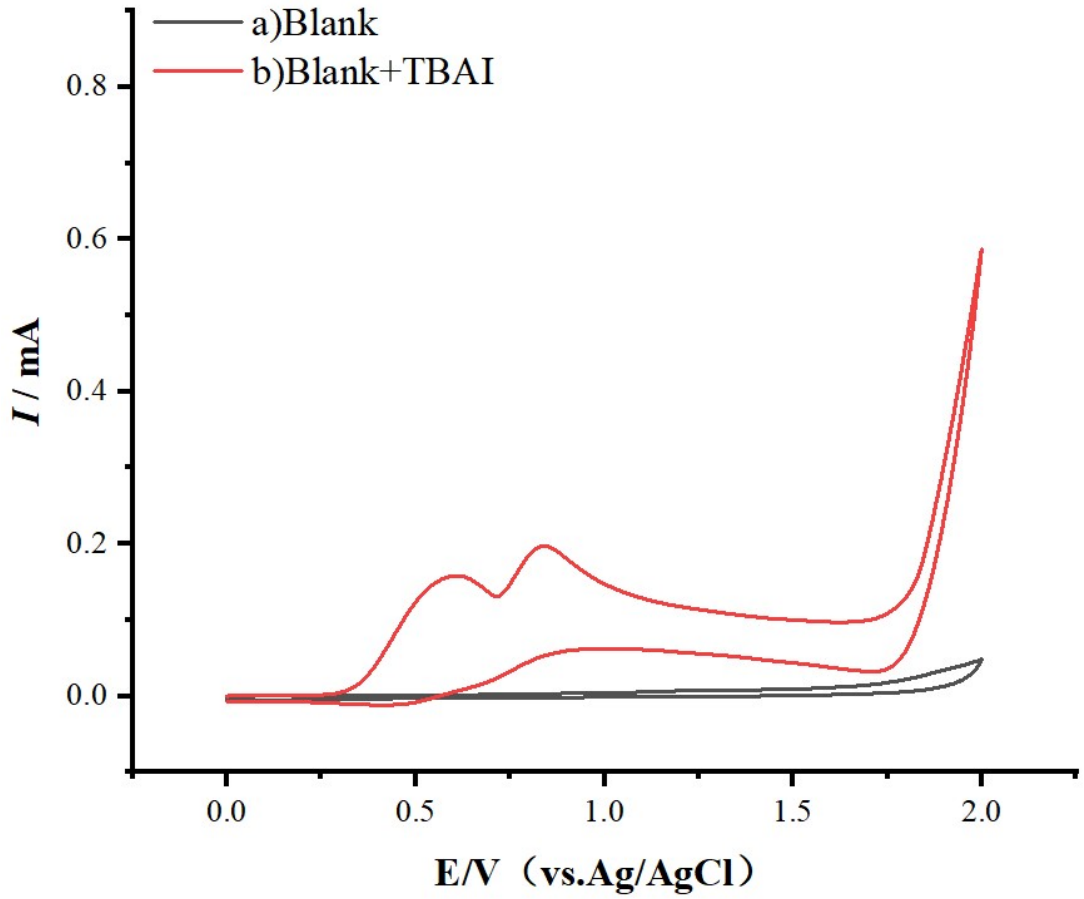


Figure S6 Cyclic voltammograms of solution in a solvent of CH_3CN (3.0 mL) containing *t*-BuOH (10 mmol/L) and 0.1 M $LiClO_4$. (a) Blank; (b) Blank + TBAI (10 mmol/L),

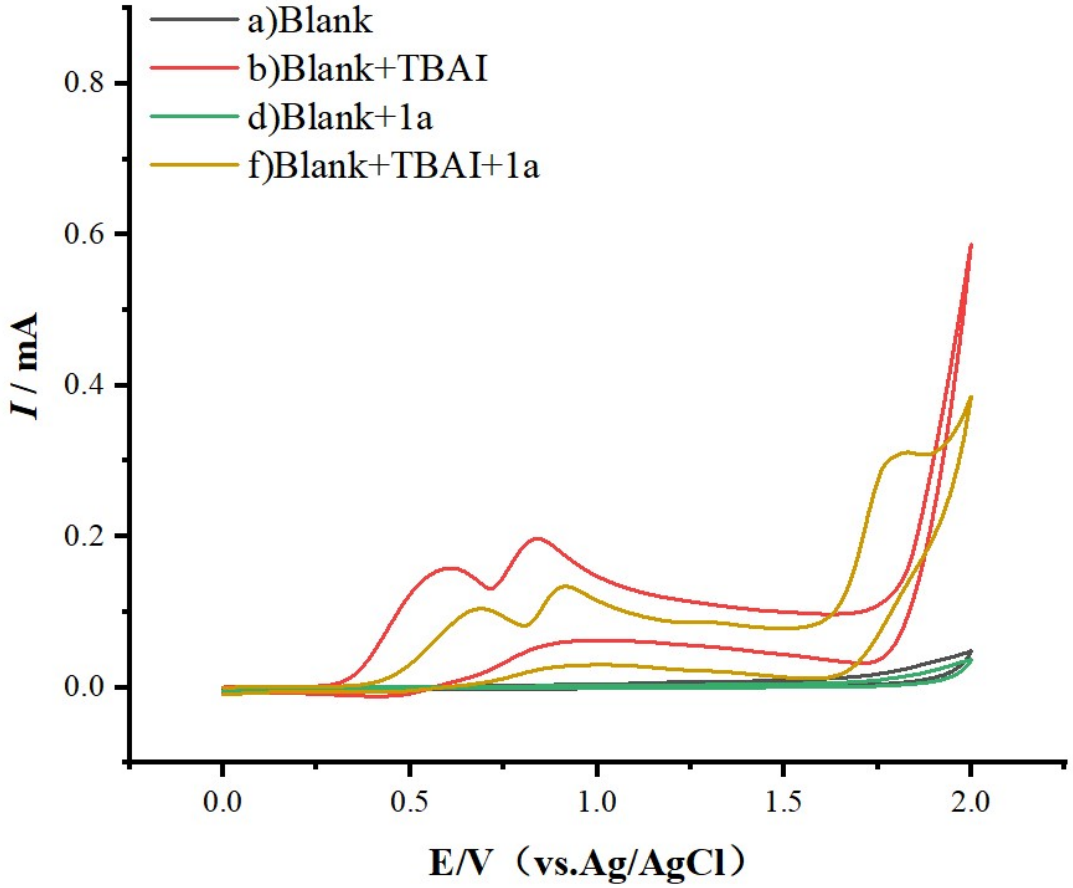


Figure S7 Cyclic voltammograms of solution in a solvent of CH_3CN (3.0 mL) containing *t*-BuOH (10 mmol/L) and 0.1 M $LiClO_4$. (a) Blank; (b) Blank + TBAI (10 mmol/L); (d) Blank + **1a** (10 mmol/L); (f) Blank + TBAI (10 mmol/L) + **1a** (10 mmol/L).

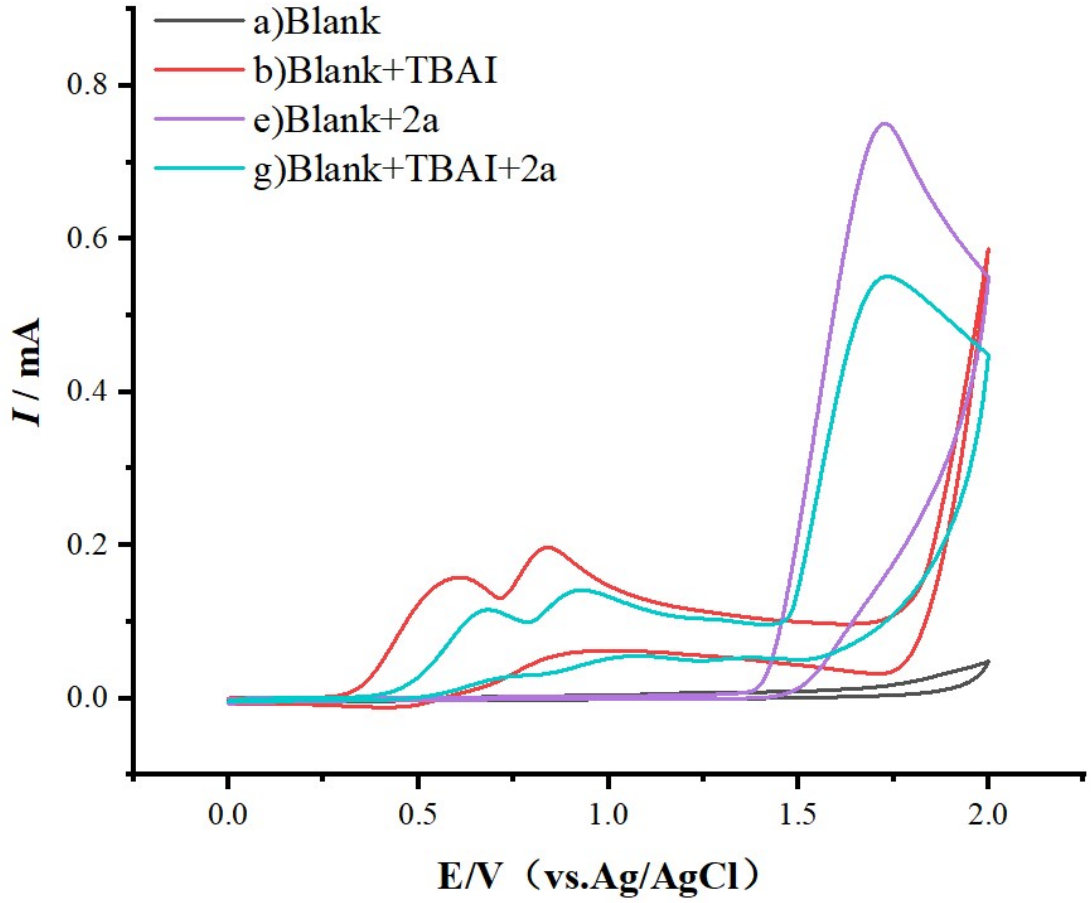


Figure S8 Cyclic voltammograms of solution in a solvent of CH_3CN (3.0 mL) containing *t*-BuOH (10 mmol/L) and 0.1 M $LiClO_4$. (a) Blank; (b) Blank + TBAI (10 mmol/L); (e) Blank + **2a** (10 mmol/L); (g) Blank + TBAI (10 mmol/L) + **2a** (10 mmol/L).

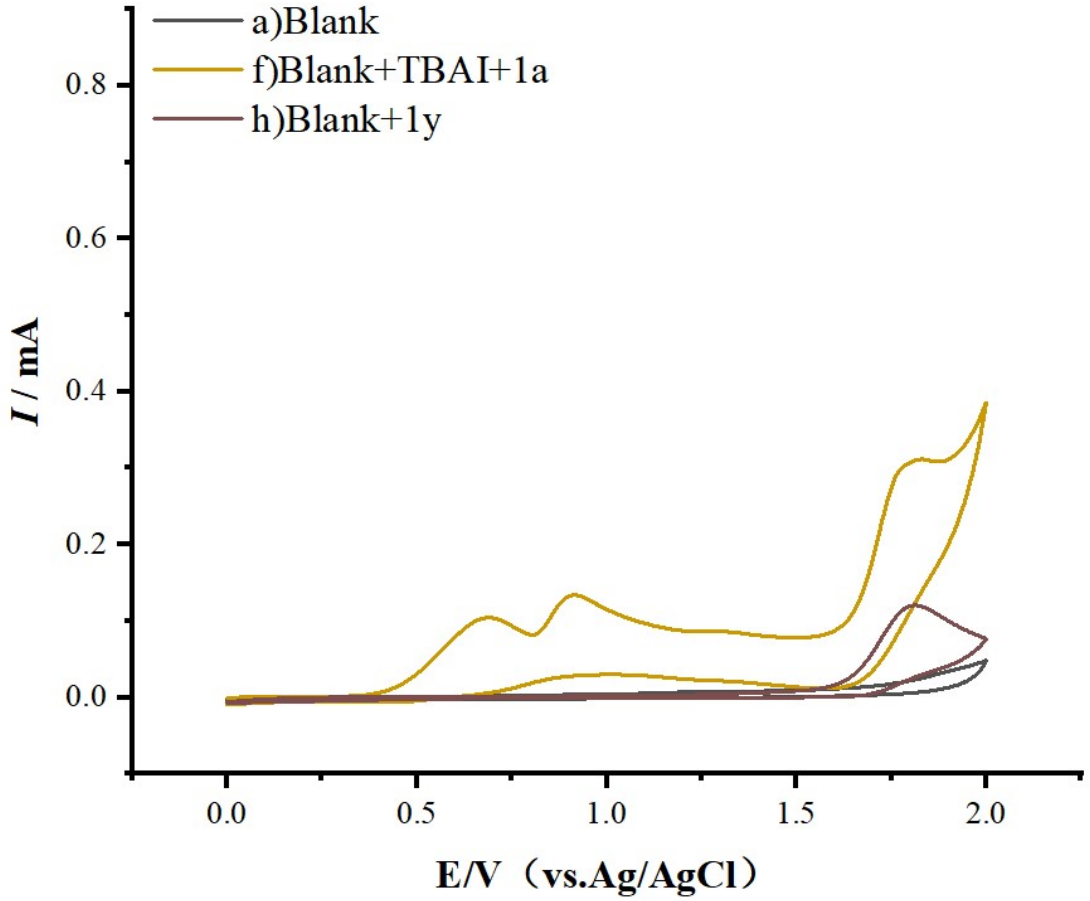


Figure S9 Cyclic voltammograms of solution in a solvent of CH_3CN (3.0 mL) containing *t*-BuOH (10 mmol/L) and 0.1 M $LiClO_4$. (a) Blank; (f) Blank + **1a** (10 mmol/L) + TBAI (10 mmol/L); (h) Blank + **1y** (10 mmol/L). These experiments indicate that **1y** intermediates may be formed in the reaction.

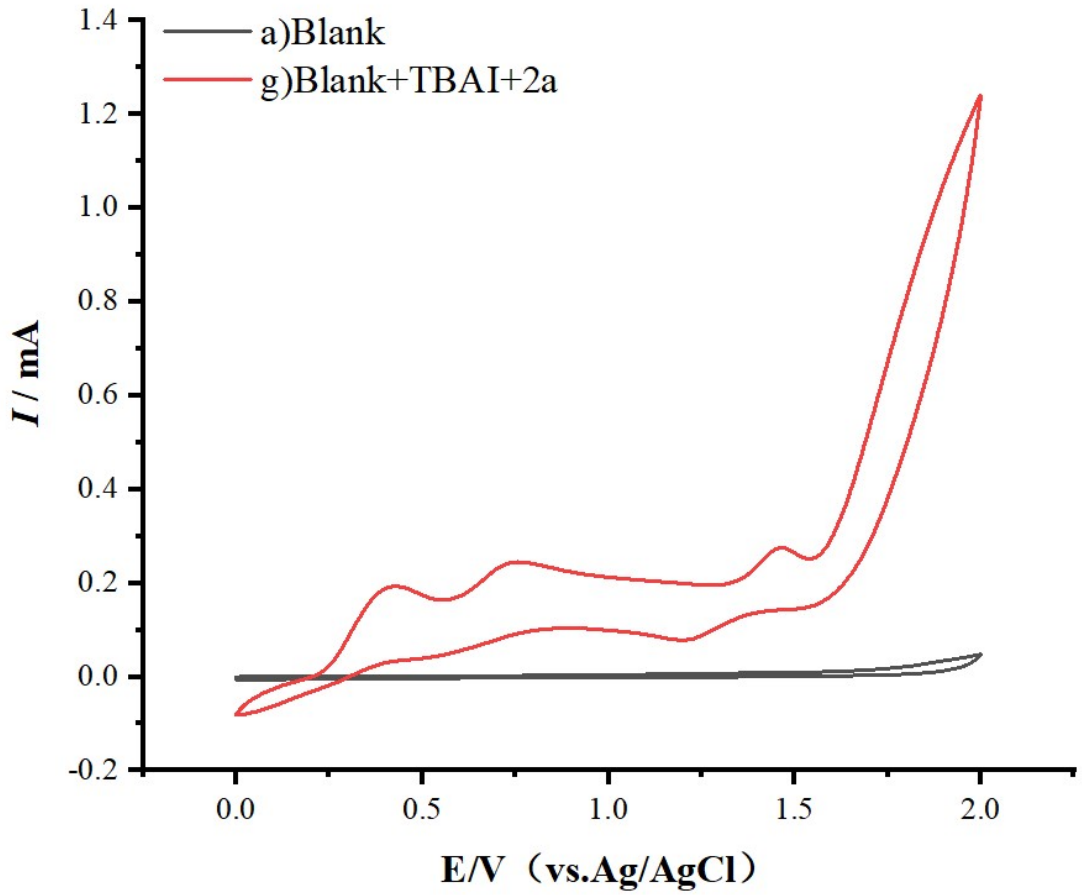


Figure S10 Cyclic voltammograms of solution in a solvent of CH_3CN (3.0 mL) containing *t*-BuOH (10 mmol/L) and 0.1 M $LiClO_4$. (a) Blank; (g) Blank + TBAI (10 mmol/L) + **2a** (10 mmol/L). The scan rate is 100 mV/s. Pt wire (φ=0.05⌀3.7 cm) as the working electrode and auxiliary electrode, and Ag/AgCl (saturated aqueous KCl, φ=0.4⌀4.5 cm) as the reference electrode that were washed with water and ethanol before measurements. CV plotting convention is IUPAC. The starting point was 0 V, and the direction of the initial scan was oxidative. In the presence of TBAI, the oxidative and reductive peaks of **2a** were 1.47 V *vs* Ag/Ag^+ and 1.20 V *vs* Ag/Ag^+, which demonstrated that disulfide **2a** may be circulated on the electrode.

H. Validation Experiment of I_2

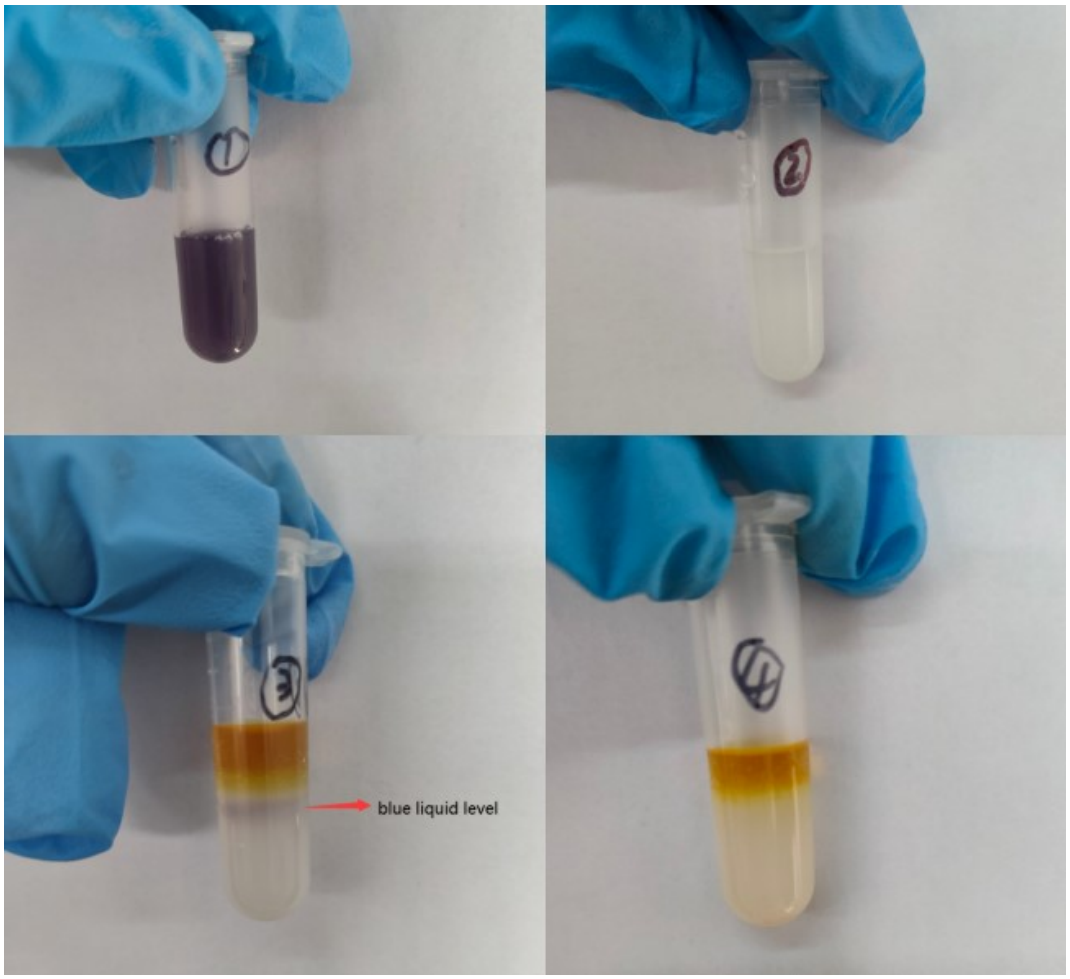
1. Prepare four 5 mL bottles by adding 2 mL of water and 15 mg of starch to each bottle and number them ①, ②, ③, ④.

2. Sulfonimidoyldibenzene **1a** (0.1 mmol, 1 equiv.), 1,2-diphenyldisulfane **2a** (0.1 mmol, 1 equiv.), and TBAI (0.2 mmol, 2 equiv.) were placed in a 10 mL round bottom flask with three necks. The flask was equipped with a carbon rod (φ= 0.6 cm, working height = 1.5 cm) as the anode, a platinum plate (1.0 cm × 1.0 cm × 0.01 cm) as cathode. CH_3CN (3.0 mL) and *t*-BuOH (0.1 mmol, 1 equiv.) were added.

3. TBAI (0.2 mmol, 2 equiv.) were placed in a 10 mL round bottom flask with three necks. The flask was equipped with a carbon rod (φ= 0.6 cm, working height = 1.5 cm) as the anode, a platinum plate (1.0 cm × 1.0 cm × 0.01 cm) as cathode. CH_3CN (3.0 mL) and *t*-BuOH (0.1 mmol, 1 equiv.) were added.

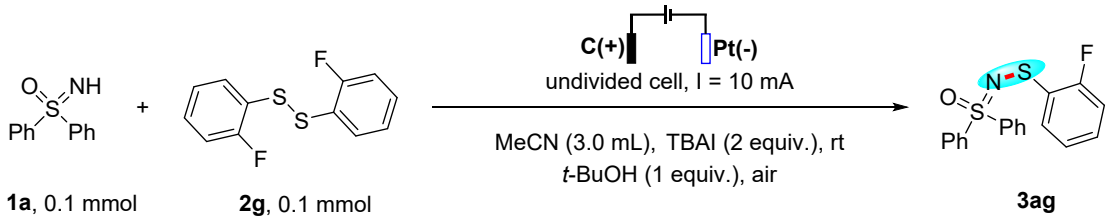
The experimental effect was shown in Scheme S3. First, add 0.05 mmol of iodine to bottle number ① and shake well. The solvent of bottle number ① was observed to turn blue. Then, procedure **2** is stirred for 0.5 h at room temperature and air conditions without electricity. Take 0.5 mL of this reaction system with a straw and add it to bottle number ②. It was observed that the color of solvent with bottle number ② did not change. Procedure **3** is stirred at room temperature and air conditions under 10 mA current electrolysis for 0.5 h. Take 0.5 mL of this reaction system with a straw and add it to bottle number ③. The solvent in bottle number ③ was observed to have a blue liquid level. Procedure **2** is stirred at room temperature and air conditions under 10 mA current electrolysis for 0.5 h. Take 0.5 mL of this

reaction system with a straw and add it to bottle number ④. The solvent in bottle number ④ did not turn blue. These results indicated that under energized conditions, TBAI may be oxidized to intermediate I_2 at the anode, and then undergo subsequent reactions.



Scheme S3. Validation Experiment of I_2

I. Electrode Stability and Reusability Experiments



Sulfonimidoyldibenzene **1a** (0.1 mmol, 1 equiv.), 2,2'-difluorodiphenyldisulfide **2g** (0.1 mmol, 1 equiv.), and TBAI (0.2 mmol, 2 equiv.) were placed in a 10 mL round bottom flask with three necks. The flask was equipped with a carbon rod (φ= 0.6 cm, working height = 1.5 cm) as the anode, and a platinum plate (1.0 cm × 1.0 cm × 0.01 cm) as the cathode. CH_3CN (3.0 mL) and *t*-BuOH (0.1 mmol, 1 equiv.) were added. The electrolysis was carried out under air atmosphere at rt using a constant current of 10 mA and stopped until complete consumption of sulfonimidoyldibenzene (monitored by TLC, about 1 h) (3.7 F/mol). This reaction was carried out six times in succession and after each reaction the electrode surface was cleaned with methylene chloride and water and wiped clean. After each reaction, the mixture was cooled and diluted with brine, and the product was extracted with ethyl acetate (3 × 10 mL). The organic layer was dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with petroleum ether/ethyl acetate to give the desired products **3ag** (Figure S11).

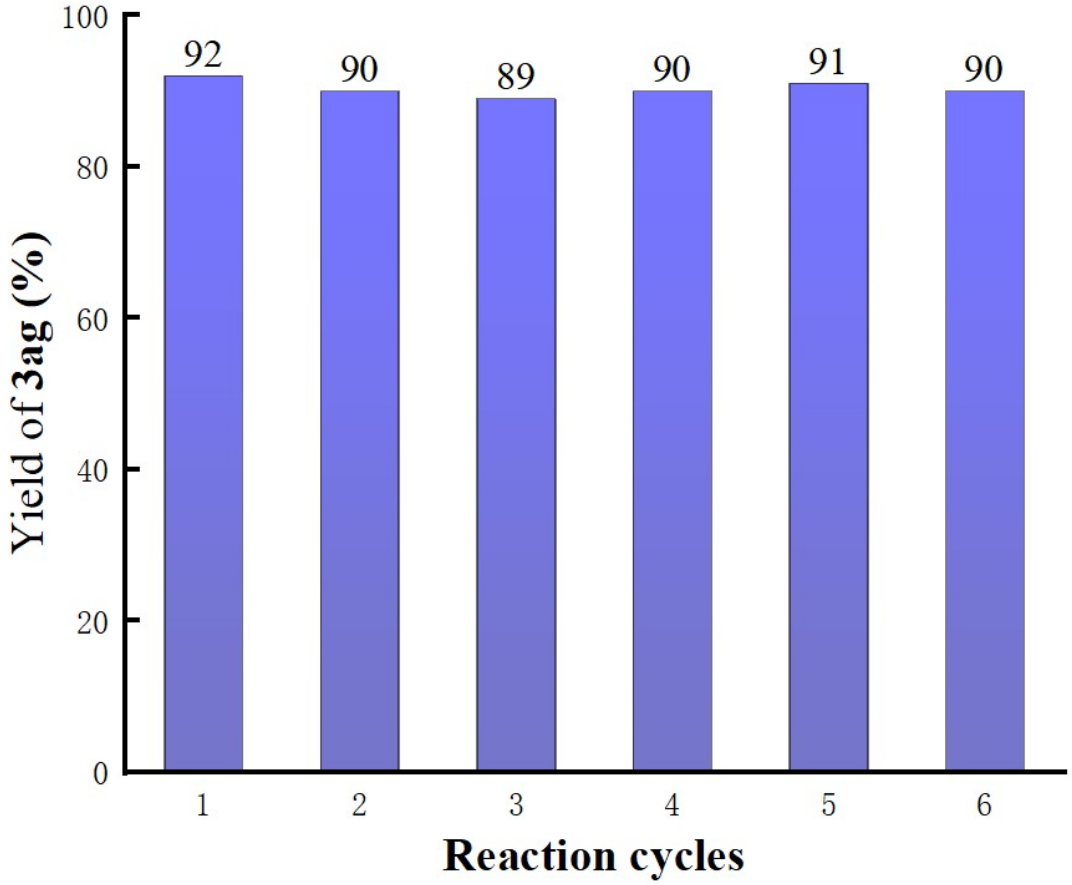
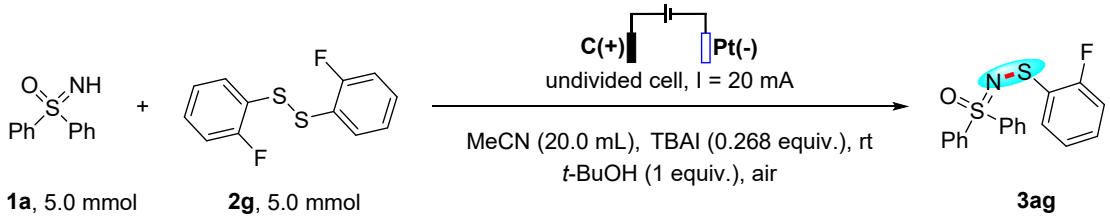


Figure S11 10 mA Electrode Stability and Reusability Experiments



The electrodes used above at 10 mA were tested at 20 mA. Sulfonimidoyldibenzene **1a** (5.0 mmol, 1 equiv.), 2,2'-difluorodiphenyldisulfide **2g** (5.0 mmol, 1 equiv.), and TBAI (1.34 mmol, 0.268 equiv.) were placed in a 100 mL round bottom flask with three necks. The flask was equipped with a carbon rod (φ= 0.6 cm, working height = 1.5 cm) as the anode, and a platinum plate (1.0 cm × 1.0 cm × 0.01 cm) as a cathode. CH_3CN (20.0 mL) and *t*-BuOH (5.0 mmol, 1 equiv.) were added. The electrolysis was carried out under air atmosphere at rt using a constant

current of 20 mA and stopped until complete consumption of sulfonimidoyldibenzene (monitored by TLC, about 47 h) (7.0 F/mol). This reaction was carried out three times in succession and after each reaction the electrode surface was cleaned with methylene chloride and water and wiped clean. After each reaction, the mixture was cooled and diluted with brine, and the product was extracted with ethyl acetate (3 × 30 mL). The organic layer was dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with petroleum ether/ethyl acetate to give the desired products **3ag**.

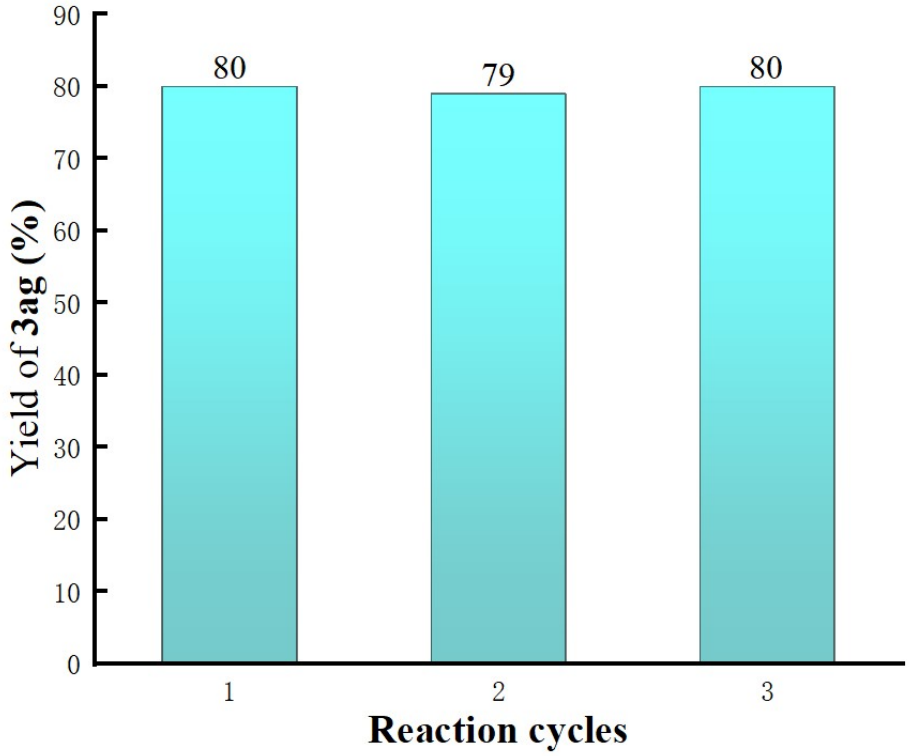
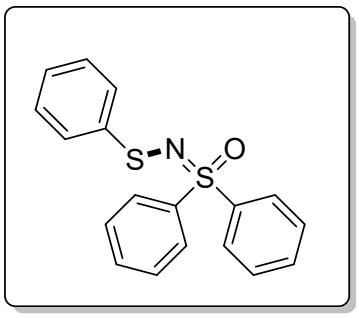
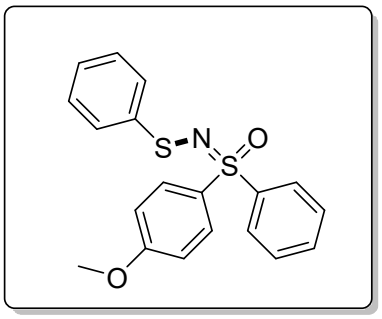


Figure S12 20 mA Electrode Stability and Reusability Experiment

J. Characterizing Data

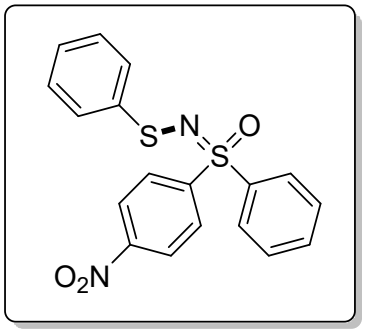


Diphenyl[(phenylthio)imino]-λ^6-sulfanone (3aa)[1]: Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (10:1) as eluent afforded the product as a white solid (26.0 mg, 80% yield). Mp: 105-107℃. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.5 Hz, 4H), 7.59 (t, *J* = 7.3 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 4H), 7.45 (d, *J* = 7.5 Hz, 2H), 7.28 (t, *J* = 7.7 Hz, 2H), 7.10 (t, *J* = 7.3 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.06, 139.88, 133.19, 129.31, 128.45, 128.42, 125.00, 123.91.

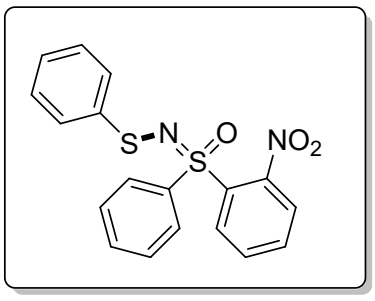


(4-Methoxyphenyl)(phenyl)((phenylthio)imino)-λ^6-sulfanone (3ba)[2]: Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (10:1) as eluent afforded the product as a yellow solid (27.7mg, 78% yield). Mp: 92-95 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 20.4, 7.9 Hz, 4H), 7.56 (d, *J* = 7.3 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 2H), 7.45 (d, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 5.9 Hz, 2H), 7.09 (t, *J* = 7.3 Hz, 1H), 7.00 (d, *J* = 8.9 Hz, 2H), 3.86 (s, 3H). **^{13}C NMR**

(126 MHz, $CDCl_3$) δ 163.47, 142.31, 140.65, 132.85, 130.94, 130.68, 129.21, 128.39, 128.14, 124.88, 123.86, 114.61, 55.64.

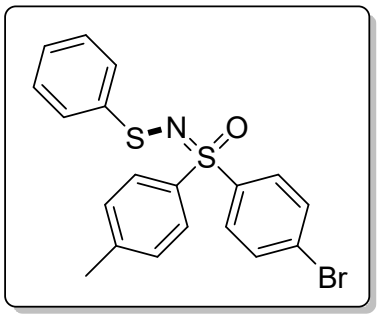


(4-Nitrophenyl)(phenyl)((phenylthio)imino)-λ⁶-sulfanone (3ca): Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (10:1) as eluent afforded the product as a yellow oil (25.9 mg, 70% yield**). ^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.7 Hz, 2H), 8.17 (d, *J* = 8.7 Hz, 2H), 8.08 (d, *J* = 7.7 Hz, 2H), 7.66 (t, *J* = 7.1 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.13 (t, *J* = 7.3 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.27, 146.18, 141.14, 138.43, 134.02, 129.77, 129.67, 128.73, 128.56, 125.53, 124.31. **HRMS (ESI)** *m/z* calcd for $C_{18}H_{14}N_2O_3NaS_2$ $[M+Na]^+$ 393.0344, found 393.0345.

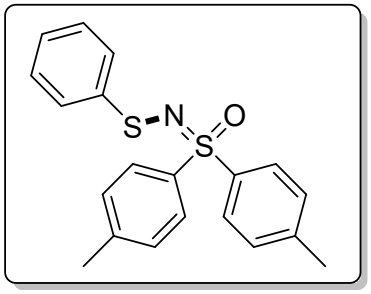


(2-Nitrophenyl)(phenyl)((phenylthio)imino)-λ⁶-sulfanone (3da): Following the general procedure and purification by column chromatography using petroleum

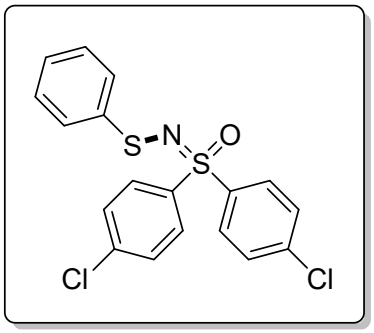
ether/ethyl acetate (10:1) as eluent afforded the product as a yellow oil (25.1 mg, 68% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.30 – 8.26 (m, 1H), 8.08 (d, *J* = 7.4 Hz, 2H), 7.73 (dd, *J* = 5.5, 2.8 Hz, 2H), 7.67 – 7.64 (m, 2H), 7.58 (t, *J* = 7.7 Hz, 2H), 7.41 (d, *J* = 7.5 Hz, 2H), 7.30 – 7.26 (m, 2H), 7.12 (t, *J* = 7.3 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.55, 140.97, 138.78, 134.50, 133.77, 132.56, 132.02, 131.90, 129.14, 128.64, 128.52, 125.50, 124.50. **HRMS (ESI)** *m/z* calcd for $C_{18}H_{15}N_2O_3S_2$ $[M+H]^+$ 371.0524, found 371.0527.



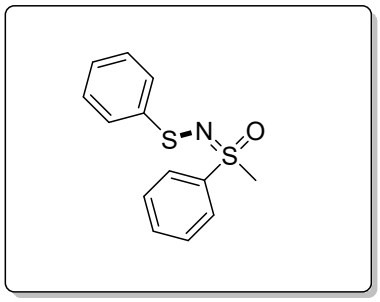
(4-Bromophenyl)((phenylthio)imino)(p-tolyl)-λ^6-sulfanone (3ea)[1]: Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (10:1) as eluent afforded the product as a yellow solid (25.0 mg, 60% yield). Mp: 124-125 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.3 Hz, 2H), 7.83 (d, *J* = 8.7 Hz, 2H), 7.61 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 7.7 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.25 (t, *J* = 7.8 Hz, 2H), 7.08 (t, *J* = 7.3 Hz, 1H), 2.41 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.55, 141.90, 139.41, 136.38, 132.48, 130.11, 129.84, 128.46, 128.44, 128.29, 125.07, 123.95, 21.52.



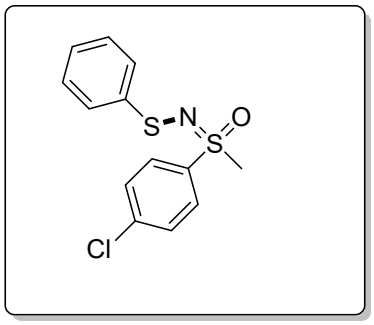
((Phenylthio)imino)di-p-tolyl-λ^6-sulfanone (3fa)[1]: Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (10:1) as eluent afforded the product as a white solid (25.4 mg, 72% yield). Mp: 108-110 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.1 Hz, 4H), 7.46 (d, *J* = 7.8 Hz, 2H), 7.30 (dd, *J* = 18.9, 7.8 Hz, 6H), 7.09 (t, *J* = 7.4 Hz, 1H), 2.42 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.01, 137.20, 129.93, 129.70, 128.36, 127.79, 124.80, 123.77, 21.48.



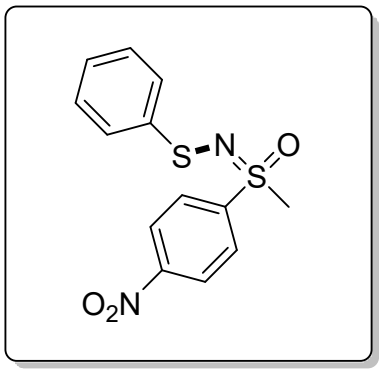
Bis(4-chlorophenyl)((phenylthio)imino)-λ^6-sulfanone(3ga)[1]: Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (10:1) as eluent afforded the product as a yellow solid (29.9 mg; 76% yield). Mp: 120-122 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.7 Hz, 4H), 7.48 (d, *J* = 8.7 Hz, 4H), 7.40 (d, *J* = 7.5 Hz, 2H), 7.27 (t, *J* = 7.8 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.43, 140.22, 138.08, 129.87, 129.71, 128.53, 125.36, 124.18.



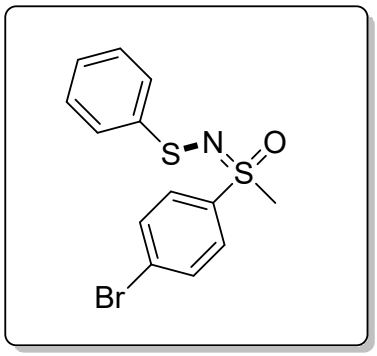
Methyl(phenyl)[(phenylthio)imino]-λ^6-sulfanone (3ha)[4]: Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (6:1) as eluent afforded the product as a yellow oil (16.6 mg, 63% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.3 Hz, 2H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 7.4 Hz, 2H), 7.29 (t, *J* = 7.8 Hz, 2H), 7.11 (t, *J* = 7.3 Hz, 1H), 3.31 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.06, 138.62, 133.70, 129.47, 128.47, 128.38, 125.05, 123.76, 43.71.



(4-Chlorophenyl)(methyl)[(phenylthio)imino]-λ^6-sulfanone (3ia)[4]: Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (6:1) as eluent afforded the product as a yellow solid (15.5 mg, 52% yield). Mp: 102 – 104 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.9 Hz, 2H), 7.56 (d, *J* = 7.9 Hz, 2H), 7.40 (d, *J* = 7.8 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.12 (t, *J* = 7.2 Hz, 1H), 3.30 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.69, 140.50, 137.12, 129.89, 129.76, 128.51, 123.95, 43.81.

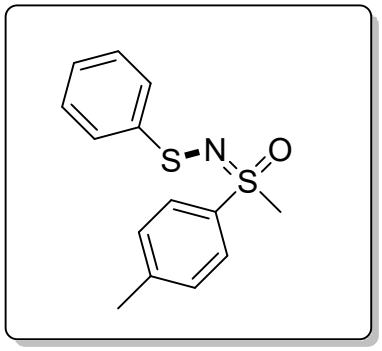


Methyl(4-nitrophenyl)[(phenylthio)imino]-λ^6 -sulfanone (3ja)[4]: Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (10:1) as eluent afforded the product as a yellow solid (12.3 mg, 40% yield). Mp: 128 – 130 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.6 Hz, 2H), 8.12 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 7.5 Hz, 2H), 7.27 (t, *J* = 7.5 Hz, 2H), 7.12 (t, *J* = 7.2 Hz, 1H), 3.35 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.77, 144.80, 140.97, 129.93, 128.62, 125.65, 124.49, 124.29, 43.61.

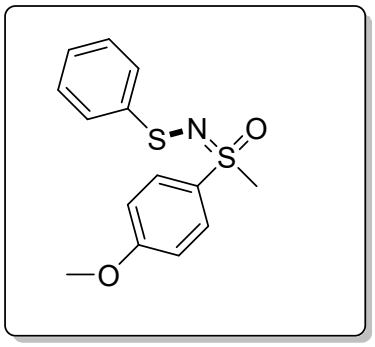


(4-Bromophenyl)(methyl)[(phenylthio)imino]-λ^6-sulfanone (3ka)[4]: Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (10:1) as eluent afforded the product as a yellow solid (19.2 mg, 56% yield). Mp: 109 – 111 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 7.5 Hz, 2H), 7.23 (t, *J* = 7.6 Hz, 2H), 7.06 (t, *J* =

7.3 Hz, 1H), 3.23 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.66, 137.69, 132.74, 129.96, 129.08, 128.51, 125.25, 123.97, 43.77.

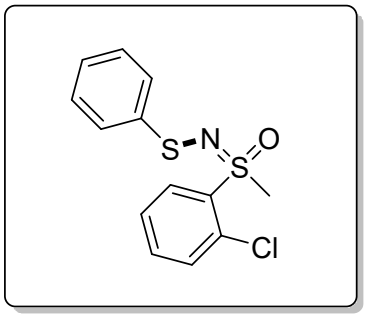


Methyl[(phenylthio)imino](*p*-tolyl)-λ^6-sulfanone (3la)[4]: Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (6:1) as eluent afforded the product as a yellow solid (11.7 mg, 42% yield). Mp: 121-126℃. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.40 (t, *J* = 9.2 Hz, 4H), 7.30 – 7.25 (m, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 3.28 (s, 3H), 2.48 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.75, 142.24, 135.55, 130.11, 128.41, 128.38, 124.92, 123.66, 43.83, 21.55.

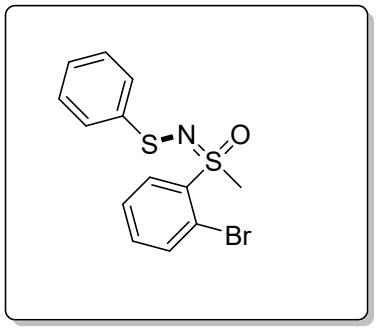


(4-Methoxyphenyl)(methyl)[(phenylthio)imino]-λ^6-sulfanone (3ma)[4]: Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (6:1) as eluent afforded the product as a white solid (17.6 mg, 60% yield). Mp: 70 – 72 ℃. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.6 Hz, 2H), 7.41

(d, *J* = 8.1 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.10 (t, *J* = 7.0 Hz, 1H), 7.05 (d, *J* = 8.6 Hz, 2H), 3.90 (s, 3H), 3.28 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.82, 142.32, 130.56, 129.67, 128.44, 124.92, 123.67, 114.71, 55.71, 44.07.

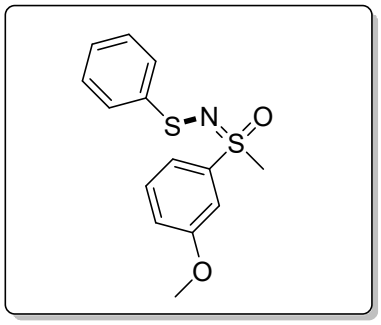


(2-Chlorophenyl)(methyl)((phenylthio)imino)-λ^6-sulfanone (3na)[4]: Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (6:1) as eluent afforded the product as a yellow oil (25.6 mg, 86% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.7 Hz, 1H), 7.46 (dt, *J* = 12.3, 6.8 Hz, 2H), 7.39 (t, *J* = 7.9 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 2H), 7.14 (t, *J* = 7.8 Hz, 2H), 6.98 (t, *J* = 7.3 Hz, 1H), 3.40 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.44, 135.75, 134.74, 132.85, 132.14, 132.07, 128.38, 127.48, 125.26, 124.48, 42.00.

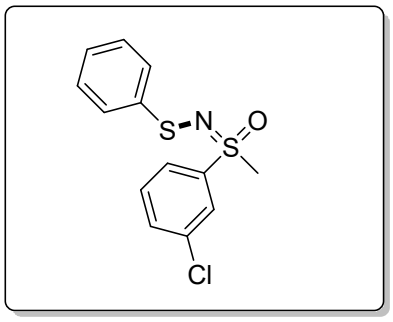


(2-Bromophenyl)(methyl)((phenylthio)imino)-λ^6-sulfanone (3oa): Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (6:1) as eluent afforded the product as a yellow oil (19.1 mg, 56%

yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.27 (d, *J* = 6.3 Hz, 1H), 7.80 (d, *J* = 4.7 Hz, 1H), 7.58 – 7.55 (m, 1H), 7.52 – 7.49 (m, 1H), 7.44 – 7.39 (m, 2H), 7.30 – 7.25 (m, 2H), 7.15 – 7.08 (m, 1H), 3.54 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.45, 137.54, 135.71, 134.67, 133.16, 128.40, 128.13, 125.29, 124.57, 120.62, 41.77. **HRMS (ESI)** m/z calcd for $C_{13}H_{12}NOS_2BrNa$ $[M+Na]^+$: 363.9441; found: 363.9445.

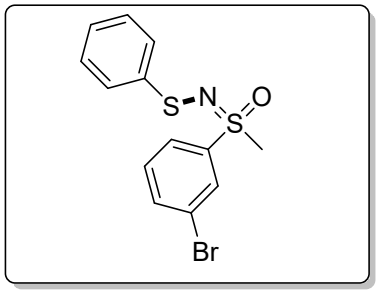


(3-Methoxyphenyl)(methyl)((phenylthio)imino)-λ^6-sulfanone (3pa)[5]: Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (6:1) as eluent afforded the product as a yellow oil (17.3 mg, 59% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51 (dt, *J* = 15.8, 7.6 Hz, 2H), 7.46 – 7.39 (m, 3H), 7.29 (t, *J* = 6.9 Hz, 2H), 7.19 (d, *J* = 7.4 Hz, 1H), 7.11 (t, *J* = 6.9 Hz, 1H), 3.85 (s, 3H), 3.30 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.23, 142.10, 139.86, 130.50, 128.48, 125.07, 123.85, 120.51, 120.39, 112.72, 55.70, 43.86.

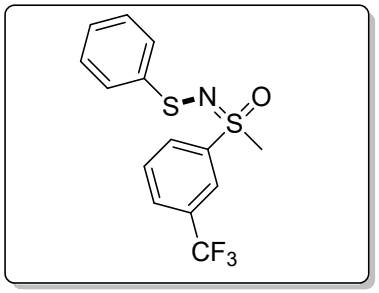


(3-Chlorophenyl)(methyl)[(phenylthio)imino]-λ^6-sulfanone (3qa)[4]: Following the general procedure and purification by column chromatography using petroleum

ether/ethyl acetate (6:1) as eluent afforded the product as a yellow oil (14.0 mg, 47% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.80 (d, *J* = 7.7 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.49 (t, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.26 (t, *J* = 7.5 Hz, 2H), 7.09 (t, *J* = 6.9 Hz, 1H), 3.27 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.53, 140.51, 135.74, 133.82, 130.66, 128.55, 128.52, 126.47, 125.35, 124.11, 43.73.

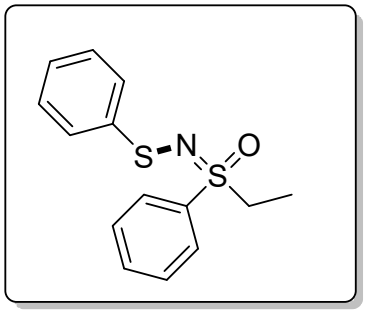


(3-Bromophenyl)(methyl)((phenylthio)imino)-λ^6-sulfanone (3ra)[5]: Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (6:1) as eluent afforded the product as a yellow oil (27.7 mg, 81% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.44 (t, *J* = 7.9 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 7.4 Hz, 2H), 7.10 (t, *J* = 6.9 Hz, 1H), 3.29 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.51, 140.61, 136.75, 131.39, 130.88, 128.54, 126.93, 125.37, 124.12, 123.49, 43.80.

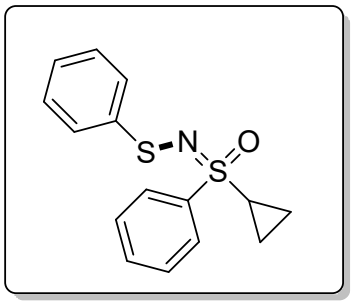


Methyl((phenylthio)imino)(3-(trifluoromethyl)phenyl)-λ^6-sulfanone (3sa): Following the general procedure and purification by column chromatography using

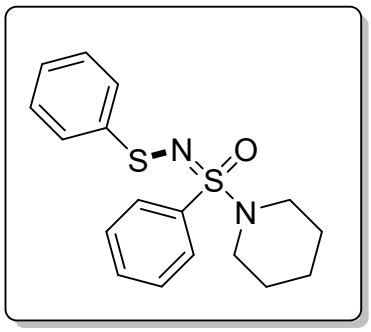
petroleum ether/ethyl acetate (6:1) as eluent afforded the product as a yellow oil (21.2 mg, 64% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.22 (s, 1H), 8.15 (d, *J* = 7.7 Hz, 1H), 7.93 (d, *J* = 7.6 Hz, 1H), 7.74 (t, *J* = 7.7 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.13 (t, *J* = 7.2 Hz, 1H), 3.34 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.8 (d, *J* = 153.8 Hz), 132.23 (q, *J* = 33.8 Hz), 131.8, 130.46 (q, *J* = 2.5 Hz), 130.3, 128.63, 125.69 (q, *J* = 3.8 Hz), 125.53, 124.23, 123.06 (q, *J* = 272.5 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.75. **HRMS (ESI)** *m/z* calcd for $C_{14}H_{12}NOF_3NaS_2$ $[M+Na]^+$ 354.0207, found 354.0210.



Ethyl(phenyl)((phenylthio)imino)-λ^6-sulfanone (3ta)[3]: Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (10:1) as eluent afforded the product as a yellow oil (18.2 mg, 66% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.6 Hz, 2H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 7.7 Hz, 2H), 7.28 (t, *J* = 7.7 Hz, 2H), 7.10 (t, *J* = 7.3 Hz, 1H), 3.46 (ddq, *J* = 65.1, 14.6, 7.4 Hz, 2H), 1.33 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.37, 136.54, 133.62, 129.35, 129.15, 128.38, 124.86, 123.63, 50.20, 7.74.

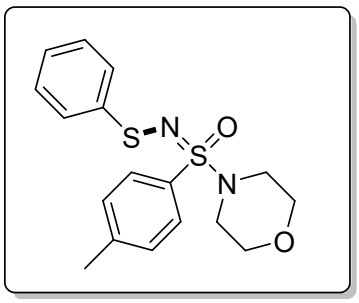


Cyclopropyl(phenyl)((phenylthio)imino)-λ^6-sulfanone (3ua)[3]: Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (6:1) as eluent afforded the product as a colorless oil **(**14.7 mg, 51% yield**). ^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.7 Hz, 2H), 7.65 (t, *J* = 7.3 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 7.8 Hz, 2H), 7.29 – 7.25 (m, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 2.70 (tt, *J* = 8.0, 4.7 Hz, 1H), 1.73 – 1.67 (m, 1H), 1.28 – 1.15 (m, 2H), 0.95 (p, *J* = 7.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.53, 139.03, 133.28, 129.29, 128.35, 124.81, 123.60, 32.91, 6.62, 5.56.

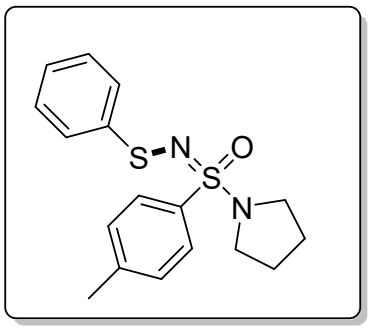


***N*-[Oxo(phenyl)(piperidin-1-yl)-λ^6-sulfaneylidene]-*S*-phenylthiohydroxylamine (3va)[4]:** Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (10:1) as eluent afforded the product as a yellow solid (22.5 mg, 68% yield). Mp: 138 – 140 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.7 Hz, 2H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 7.8 Hz,

2H), 7.18 (t, *J* = 7.7 Hz, 2H), 6.99 (t, *J* = 7.4 Hz, 1H), 2.97 (hept, *J* = 5.8, 5.2 Hz, 4H), 1.55 (p, *J* = 5.6 Hz, 4H), 1.36 (q, *J* = 6.3 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.03, 135.94, 132.61, 128.89, 128.42, 127.90, 124.79, 123.79, 47.48, 25.17, 23.56.

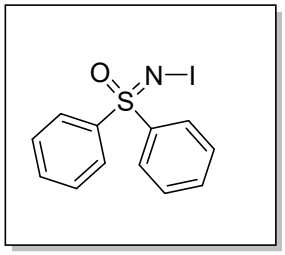


***N*-(Morpholino(oxo)(p-tolyl)-λ^6-sulfaneylidene)-*S*-phenylthiohydroxylamine (3wa)[4]:** Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (10:1) as eluent afforded the product as a white solid (21.0 mg, 60% yield). Mp: 115-117 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.5 Hz, 2H), 7.44 (d, *J* = 7.9 Hz, 2H), 7.37 (d, *J* = 7.7 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.09 (t, *J* = 6.9 Hz, 1H), 3.72 (t, *J* = 4.9 Hz, 4H), 3.02 (ddd, *J* = 23.6, 12.1, 6.8 Hz, 4H), 2.46 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.07, 141.61, 131.44, 129.73, 128.51, 128.15, 125.07, 124.02, 66.09, 46.64, 21.51.

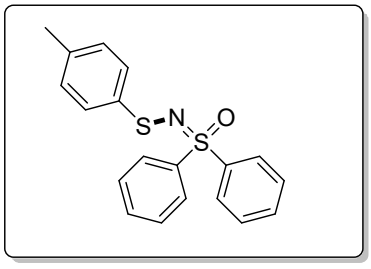


***N*-(Oxo(pyrrolidin-1-yl)(p-tolyl)-λ^6-sulfaneylidene)-*S*-phenylthiohydroxylamine (3xa):** Following the general procedure and purification by column chromatography

using petroleum ether/ethyl acetate (10:1) as eluent afforded the product as a white solid (19.6 mg, 59% yield). Mp: 87-90 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 7.7 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.29 – 7.24 (m, 2H), 7.08 (t, *J* = 7.3 Hz, 1H), 3.28 (dtt, *J* = 13.7, 9.5, 4.8 Hz, 4H), 2.46 (s, 3H), 1.82 – 1.77 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.53, 142.25, 133.30, 129.63, 128.39, 128.03, 124.66, 123.57, 25.32, 21.49. **HRMS (ESI)** *m/z* calcd for $C_{17}H_{21}N_2OS_2$ $[M+H]^+$ 333.1095, found 333.1100.

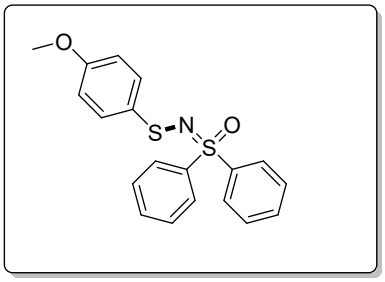


(iodoimino)diphenyl-λ^6-sulfanone (1y)[7]: Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (6:1) as eluent afforded the product as a yellow solid (6.9 mg, 20% yield). Mp: 114.2−114.9 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.4 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 2H).

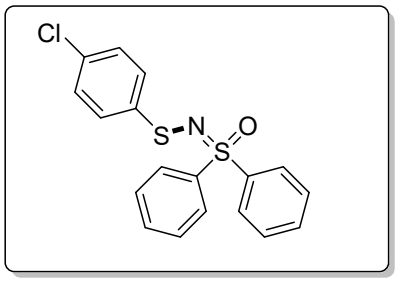


Diphenyl((p-tolylthio)imino)-λ^6-sulfanone (3ab)[1]: Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (10:1) as eluent afforded the product as a yellow solid (23.1 mg, 68% yield). Mp: 110-112

°C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.4 Hz, 4H), 7.56 (t, *J* = 7.4 Hz, 2H), 7.50 (t, *J* = 7.7 Hz, 4H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.07 (d, *J* = 7.9 Hz, 2H), 2.29 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.04, 138.25, 133.08, 129.26, 129.23, 128.49, 125.18, 20.99.

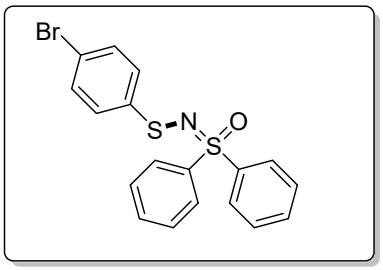


(((4-Methoxyphenyl)thio)imino)diphenyl-λ^{6}-sulfanone (3ac)[1]: Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (10:1) as eluent afforded the product as a yellow oil (26.2 mg 74% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.1 Hz, 4H), 7.52 – 7.43 (m, 8H), 6.82 (d, *J* = 8.7 Hz, 2H), 3.77 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.68, 140.14, 133.08, 131.96, 129.49, 129.28, 128.53, 114.28, 55.37.

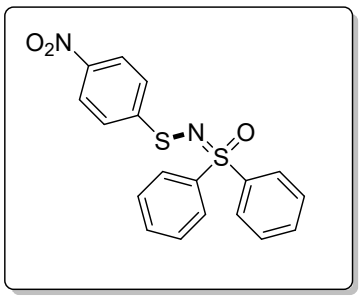


(((4-Chlorophenyl)thio)imino)diphenyl-λ^{6}-sulfanone (3ad)[1]: Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (10:1) as eluent afforded the product as a white solid (20.3 mg, 56% yield). Mp: 121-123°C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.8 Hz, 4H), 7.62

– 7.58 (m, 2H), 7.54 (t, *J* = 7.4 Hz, 4H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.89, 139.68, 133.30, 130.51, 129.37, 128.46, 128.37, 125.15.

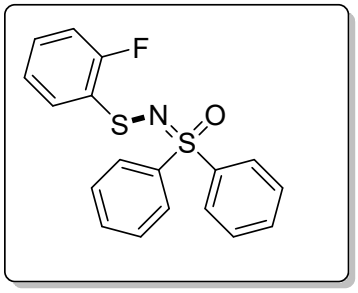


(((4-Bromophenyl)thio)imino)diphenyl-λ^6-sulfanone (3ae)[1]: Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (10:1) as eluent afforded the product as a white solid (26.3 mg, 65% yield). Mp: 122-124℃. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.1 Hz, 4H), 7.57 (t, *J* = 7.3 Hz, 2H), 7.51 (t, *J* = 7.7 Hz, 4H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.67, 139.68, 133.29, 131.30, 129.35, 128.36, 125.33.

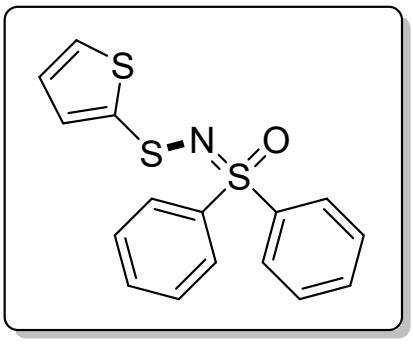


(((4-Nitrophenyl)thio)imino)diphenyl-λ^6-sulfanone (3af)[3]: Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (10:1) as eluent afforded the product as a yellow solid (15.1 mg, 41% yield). Mp: 164-165℃. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.6 Hz, 2H), 8.02 (d, *J* =

7.8 Hz, 4H), 7.62 (t, *J* = 7.0 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 4H), 7.48 (d, *J* = 8.6 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.44, 144.67, 139.33, 133.64, 129.57, 128.32, 123.64.

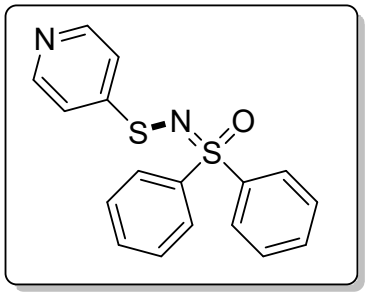


(((2-Fluorophenyl)thio)imino)diphenyl-λ^6-sulfanone (3ag)[1]: Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (10:1) as eluent afforded the product as a white solid (30.9 mg, 90% yield). Mp: 107-109 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.4 Hz, 4H), 7.77 – 7.72 (m, 1H), 7.57 (t, *J* = 7.3 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 4H), 7.12 (t, *J* = 7.1 Hz, 1H), 7.08 – 7.03 (m, 1H), 6.90 (t, *J* = 8.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.11 (d, *J* = 240.0 Hz), 139.80, 133.38, 129.76 (d, *J* = 16.2 Hz), 129.45, 128.46, 126.27 (d, *J* = 2.5 Hz), 126.11 (d, *J* = 6.25 Hz), 124.46 (d, *J* = 2.5 Hz), 144.50 (d, *J* = 20.0 Hz).

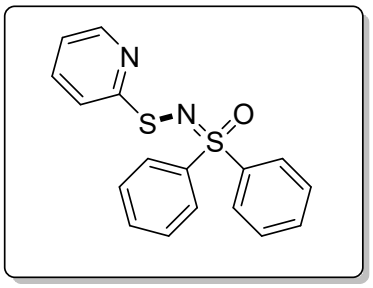


Diphenyl((thiophen-2-ylthio)imino)-λ^6-sulfanone (3ah)[1]: Following the general procedure and purification by column chromatography using petroleum ether/ethyl

acetate (10:1) as eluent afforded the product as a yellow oil (14.5 mg, 44% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.9 Hz, 4H), 7.56 – 7.52 (m, 2H), 7.48 (t, *J* = 7.5 Hz, 4H), 7.38 (d, *J* = 5.2 Hz, 1H), 7.13 (d, *J* = 3.3 Hz, 1H), 6.91 – 6.87 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.83, 133.76, 133.05, 130.92, 129.20, 128.47, 127.15.

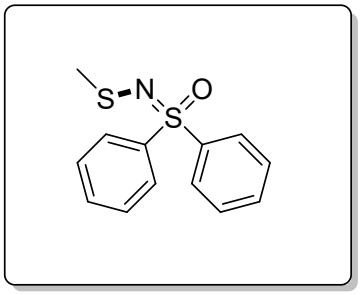


Diphenyl((pyridin-4-ylthio)imino)-λ^6-sulfanone (3ai)[3]: Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (6:1) as eluent afforded the product as a white solid (27.1 mg, 83% yield). Mp: 102-104 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.36 (s, 2H), 8.02 (d, *J* = 7.4 Hz, 4H), 7.61 (t, *J* = 7.4 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 4H), 7.31 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.18, 148.28, 139.37, 133.55, 129.51, 128.32, 117.01.

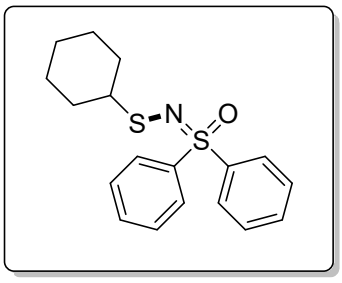


Diphenyl((pyridin-2-ylthio)imino)-λ^6-sulfanone (3aj)[3]: Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (6:1) as eluent afforded the product as a white solid (25.5 mg, 78% yield). Mp:

105-106°C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 3.7 Hz, 1H), 8.03 (d, *J* = 7.7 Hz, 4H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.59 – 7.49 (m, 7H), 6.94 – 6.88 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.05, 148.35, 139.58, 136.57, 133.33, 129.39, 128.42, 118.92, 117.89.

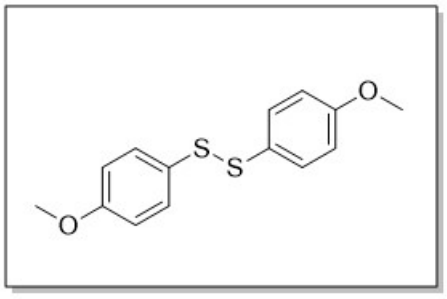


((Methylthio)imino)diphenyl-λ^6-sulfanone (3ak): Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (6:1) as eluent afforded the product as a Colorless oil (11.9 mg, 45% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (ddd, *J* = 37.1, 19.3, 7.7 Hz, 4H), 7.63 – 7.45 (m, 6H), 2.58 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 133.04, 129.28, 128.48, 25.93. **HRMS (ESI)** *m/z* calcd for $C_{13}H_{13}NONaS_2$ $[M+Na]^+$ 286.0336, found 286.0333.

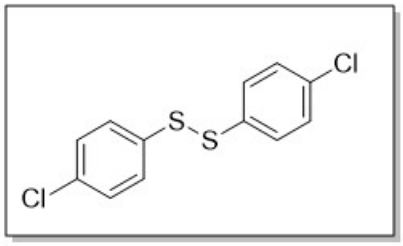


((Cyclohexylthio)imino)diphenyl-λ^6-sulfanone (3al): Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (10:1) as eluent afforded the product as a Colorless oil (13.9 mg, 42% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.7 Hz, 4H), 7.49 (dt, *J* = 14.9, 7.2 Hz,

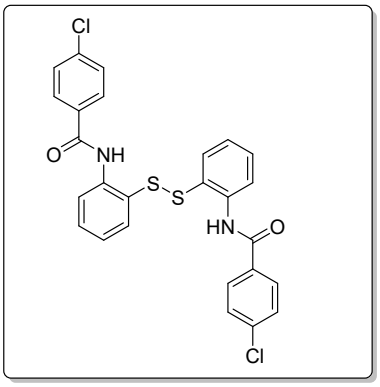
6H), 3.02 (t, *J* = 8.3 Hz, 1H), 2.08 (d, *J* = 11.2 Hz, 2H), 1.78 – 1.72 (m, 2H), 1.59 (d, *J* = 12.0 Hz, 1H), 1.29 (dt, *J* = 23.5, 11.6 Hz, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.55, 132.78, 129.16, 128.42, 50.39, 31.25, 25.95, 25.91. **HRMS (ESI)** *m/z* calcd for $C_{18}H_{21}NONaS_2$ $[M+Na]^+$ 354.0962, found 354.0964.



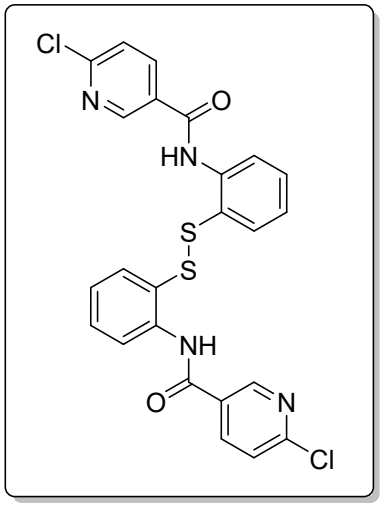
1,2-Bis(4-methoxyphenyl) disulfane (2c)[8]: Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (100:1) as eluent afforded the product as a white solid (4.5 mg, 16% yield). Mp: 42–44 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 6.8 Hz, 4H), 6.84 (d, *J* = 6.8 Hz, 4H), 3.80 (s, 6H).



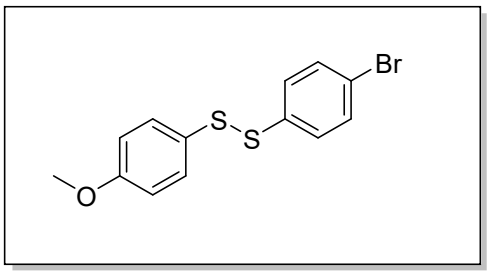
Bis(4-chlorophenyl) disulfide (2d)[9]: Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (100:1) as eluent afforded the product as a White solid (5.7 mg, 20% yield). Mp: 71–72 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 4H), 7.31 (d, *J* = 8.3 Hz, 4H).



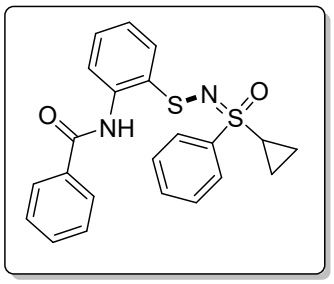
***N,N'*-(Disulfanediylbis(2,1-phenylene))bis(4-chlorobenzamide) (2m)[6]:** The resulting solid was dried at rt to afford a white solid (1576.4 mg, 74% yield). Mp: 178.0–178.8°C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.83 (s, 2H), 8.44 (d, *J* = 8.3 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 4H), 7.48 (d, *J* = 7.8 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 4H), 7.31 (t, *J* = 7.8 Hz, 2H), 6.99 (t, *J* = 7.5 Hz, 2H).



***N,N'*-(Disulfanediylbis(2,1-phenylene))bis(6-chloronicotinamide) (2n)[6]:** Recrystallization from $CHCl_3$ gave **2n** as colorless needles (474.7 mg, 44.8% yield). Mp: 216.1–218.0°C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 10.57 (s, 2H), 8.95 (s, 2H), 8.34 (d, *J* = 8.4 Hz, 2H), 7.69 (dd, *J* = 26.0, 8.1 Hz, 4H), 7.39 – 7.29 (m, 6H).

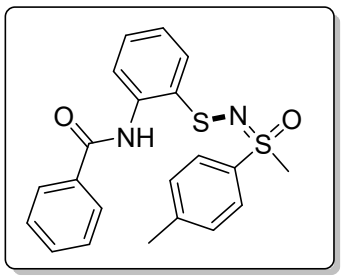


1-(4-bromophenyl)-2-(4-methoxyphenyl)disulfane (2o)[10]: Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (100:1) as eluent afforded the product as yellow liquid (589 mg, 50% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46 – 7.38 (m, 6H), 6.86 (d, *J* = 8.7 Hz, 2H), 3.81 (s, 3H).

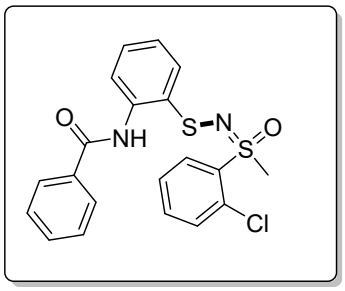


***N*-(2-(((Cyclopropyl(oxo)(phenyl)-λ^6-sulfaneylidene)amino)thio)phenyl)benzamide (4a):** Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (6:1) as eluent afforded the product as a yellow oil (29.8 mg, 73% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.14 (s, 1H), 8.49 (d, *J* = 8.1 Hz, 1H), 8.10 (d, *J* = 7.6 Hz, 2H), 7.70 (d, *J* = 7.9 Hz, 2H), 7.57 – 7.51 (m, 2H), 7.43 (dt, *J* = 23.5, 7.7 Hz, 4H), 7.30 (dd, *J* = 14.8, 7.0 Hz, 2H), 6.91 (t, *J* = 7.5 Hz, 1H), 2.54 (tt, *J* = 8.2, 4.8 Hz, 1H), 1.55 (ddt, *J* = 10.2, 7.4, 4.9 Hz, 1H), 1.13 – 1.01 (m, 2H), 0.85 (ddd, *J* = 13.1, 10.3, 6.6 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.97, 139.25, 137.96, 134.78, 133.31, 131.60, 130.56, 129.36, 129.06, 128.45, 128.06,

127.33, 123.40, 120.91, 32.43, 6.39, 5.43. **HRMS (ESI)** *m/z* calcd for $C_{22}H_{20}N_2O_2NaS_2$ $[M+Na]^+$ 431.0864, found 431.0863.

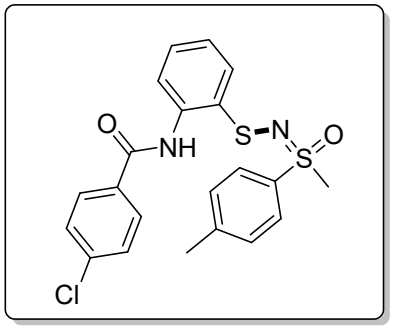


***N*-(2-(((Methyl(oxo)(p-tolyl)-λ^6-sulfaneylidene)amino)thio)phenyl)benzamide (4b):** Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (6:1) as eluent afforded the product as a yellow oil (27.8 mg, 70% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.99 (s, 1H), 8.46 (d, *J* = 8.0 Hz, 1H), 8.06 (d, *J* = 6.9 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.31 (d, *J* = 7.7 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 6.92 (t, *J* = 7.7 Hz, 1H), 3.14 (s, 3H), 2.39 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.12, 144.96, 139.36, 134.96, 134.75, 131.76, 131.28, 130.00, 129.69, 128.63, 128.29, 128.10, 127.46, 123.64, 121.14, 43.54, 21.59. **HRMS (ESI)** *m/z* calcd for $C_{21}H_{20}N_2O_2NaS_2$ $[M+Na]^+$ 419.0864, found 419.0864.



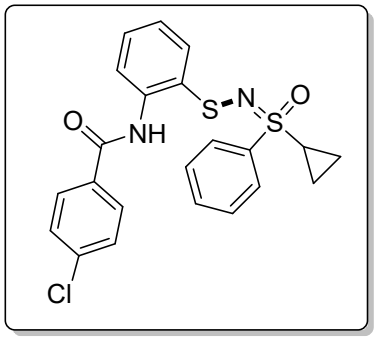
***N*-(2-((((2-Chlorophenyl)(methyl)(oxo)-λ^6-sulfaneylidene)amino)thio)phenyl)benzamide (4c):** Following the general procedure and purification by column

chromatography using petroleum ether/ethyl acetate (6:1) as eluent afforded the product as a yellow oil (33.4 mg, 80% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.89 (s, 1H), 8.45 (d, *J* = 8.2 Hz, 1H), 8.15 (dd, *J* = 7.6, 2.1 Hz, 1H), 8.11 – 8.08 (m, 2H), 7.56 – 7.53 (m, 1H), 7.50 – 7.46 (m, 3H), 7.44 – 7.41 (m, 1H), 7.33 – 7.26 (m, 2H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.80 (t, *J* = 7.3 Hz, 1H), 3.42 (d, *J* = 2.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.86, 139.75, 135.00, 134.82, 134.72, 132.51, 132.02, 131.71, 131.64, 131.23, 129.89, 128.54, 127.30, 126.36, 123.20, 120.84, 42.01. **HRMS (ESI)** *m/z* calcd for $C_{20}H_{17}N_2O_2NaS_2Cl$ $[M+Na]^+$ 439.0318, found 439.0323.

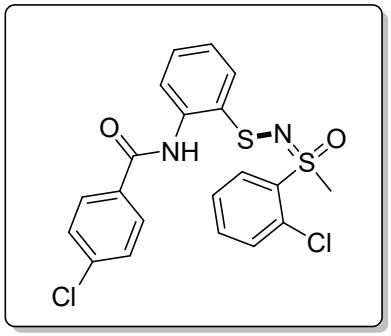


4-Chloro-N-(2-(((methyl(oxo)(p-tolyl)-λ^6-sulfaneylidene)amino)thio)phenyl)benz-amide (4d): Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (6:1) as eluent afforded the product as a white solid (21.5 mg, 50% yield). Mp: 118-120℃. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.02 (s, 1H), 8.44 (d, *J* = 8.3 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.35 – 7.31 (m, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.94 (t, *J* = 7.5 Hz, 1H), 3.16 (s, 3H), 2.42 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.99, 145.05, 139.21, 137.91, 134.69, 133.37, 131.21, 130.00, 129.75, 128.88,

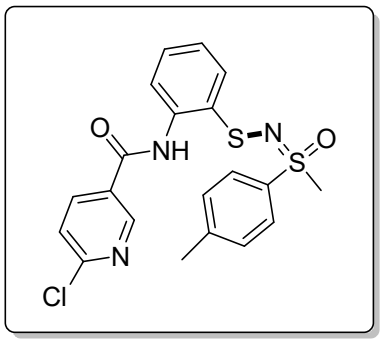
128.80, 128.20, 128.00, 123.77, 121.10, 43.40, 21.55. **HRMS (ESI)** *m/z* calcd for $C_{21}H_{19}N_2O_2NaS_2Cl$ $[M+Na]^+$ 453.0474, found 453.0474.



4-Chloro-N-(2-(((cyclopropyl(oxo)(phenyl)-λ⁶-sulfaneylidene)amino)thio)phenyl)-benzamide (4e): Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (6:1) as eluent afforded the product as a yellow oil (28.8 mg, 65% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.17 (s, 1H), 8.47 (d, *J* = 8.3 Hz, 1H), 8.06 (d, *J* = 8.2 Hz, 2H), 7.72 (d, *J* = 7.9 Hz, 2H), 7.60 (t, *J* = 7.8 Hz, 1H), 7.45 (dd, *J* = 14.3, 7.7 Hz, 4H), 7.35 – 7.27 (m, 2H), 6.94 (t, *J* = 7.6 Hz, 1H), 2.56 (tt, *J* = 8.3, 4.7 Hz, 1H), 1.58 (dq, *J* = 11.1, 5.4 Hz, 1H), 1.19 – 1.03 (m, 2H), 0.90 (p, *J* = 7.7 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.97, 139.24, 138.07, 137.91, 133.47, 133.35, 130.71, 129.60, 129.20, 128.93, 128.77, 128.20, 128.16, 123.67, 121.03, 32.48, 6.48, 5.54. **HRMS (ESI)** *m/z* calcd for $C_{22}H_{19}N_2O_2NaS_2Cl$ $[M+Na]^+$ 465.0474, found 465.0477.

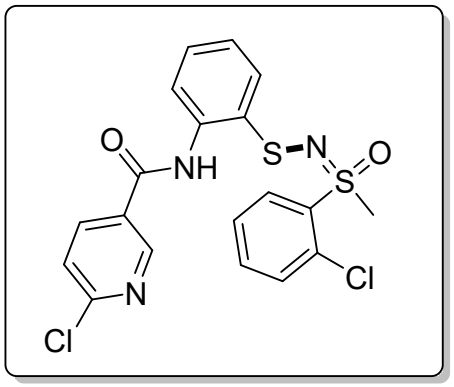


4-Chloro-N-(2-((((2-chlorophenyl)(methyl)(oxo)-λ^6-sulfaneylidene)amino)thio)-phenyl)benzamide (4f): Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (6:1) as eluent afforded the product as a white solid (29.3 mg, 65% yield). Mp: 146-148℃. **^{1}H NMR** (500 MHz,) δ 9.88 (s, 1H), 8.41 (d, *J* = 7.8 Hz, 1H), 8.14 (d, *J* = 7.6 Hz, 1H), 8.03 (d, *J* = 6.8 Hz, 2H), 7.46 (dd, *J* = 21.7, 7.1 Hz, 4H), 7.29 (t, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 7.4 Hz, 1H), 6.81 (t, *J* = 7.6 Hz, 1H), 3.42 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.95, 139.78, 138.02, 135.18, 134.89, 133.43, 132.64, 132.17, 131.88, 131.28, 130.12, 128.94, 128.91, 127.47, 126.52, 123.51, 121.00, 42.10. **HRMS (ESI)** *m/z* calcd for $C_{20}H_{16}N_2O_2NaS_2Cl_2$ $[M+Na]^+$ 472.9928, found 472.9926.



6-Chloro-N-(2-(((methyl(oxo)(p-tolyl)-λ^6-sulfaneylidene)amino)thio)phenyl)nicot-inamide (4g): Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (6:1) as eluent afforded the product as a white solid (24.2 mg, 56% yield). Mp: 149-151℃. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.22 (s, 1H), 9.12 (s, 1H), 8.36 (d, *J* = 41.2 Hz, 2H), 7.72 – 7.58 (m, 2H), 7.45 – 7.41 (m, 1H), 7.33 (dd, *J* = 23.7, 5.1 Hz, 4H), 7.00 (d, *J* = 5.1 Hz, 1H), 3.20 (s, 3H), 2.46 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.13, 154.34, 148.82, 145.20,

138.88, 138.17, 134.60, 131.08, 130.15, 129.78, 129.62, 128.38, 128.24, 124.24, 121.42, 43.58, 21.58. **HRMS (ESI)** *m/z* calcd for $C_{20}H_{18}N_3O_2NaS_2Cl$ $[M+ Na]^+$ 454.0427, found 454.0428.



6-Chloro-N-(2-((((2-chlorophenyl)(methyl)(oxo)-λ^6-sulfaneylidene)amino)thio)-phenyl)nicotinamide (4h): Following the general procedure and purification by column chromatography using petroleum ether/ethyl acetate (6:1) as eluent afforded the product as a white solid (30.4 mg, 67% yield). Mp: 134-136°C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.03 (s, 1H), 9.13 (s, 1H), 8.36 (t, *J* = 7.9 Hz, 2H), 8.16 (d, *J* = 7.5 Hz, 1H), 7.53 – 7.48 (m, 2H), 7.46 (d, *J* = 8.3 Hz, 1H), 7.32 (t, *J* = 6.5 Hz, 2H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.84 (t, *J* = 7.4 Hz, 1H), 3.45 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.95, 154.32, 148.77, 139.25, 138.09, 134.91, 132.64, 131.94, 131.80, 130.77, 129.92, 129.52, 127.46, 126.88, 124.26, 123.87, 121.19, 42.04. **HRMS (ESI)** *m/z* calcd for $C_{19}H_{15}N_3O_2NaS_2Cl_2$ $[M+Na]^+$ 473.9880, found 473.9878.

K. References

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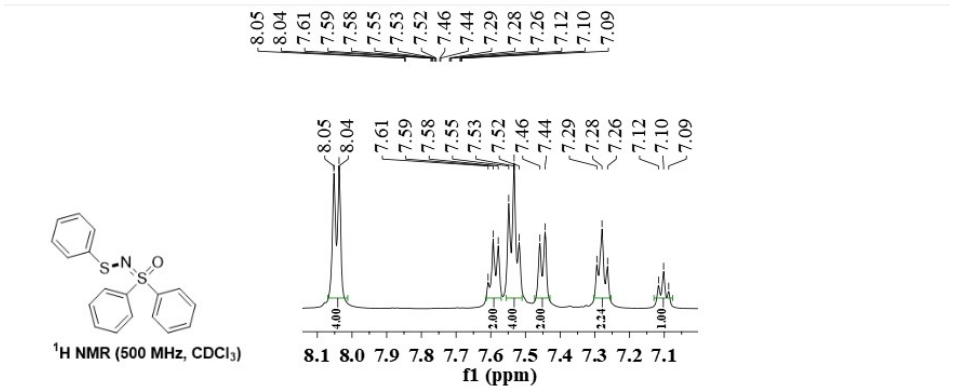
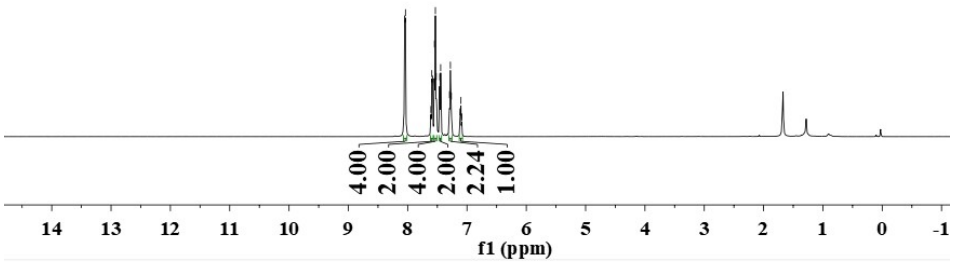
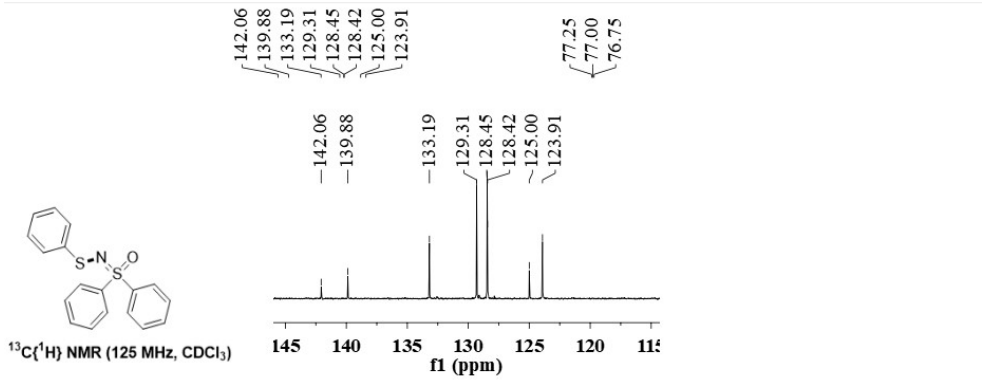
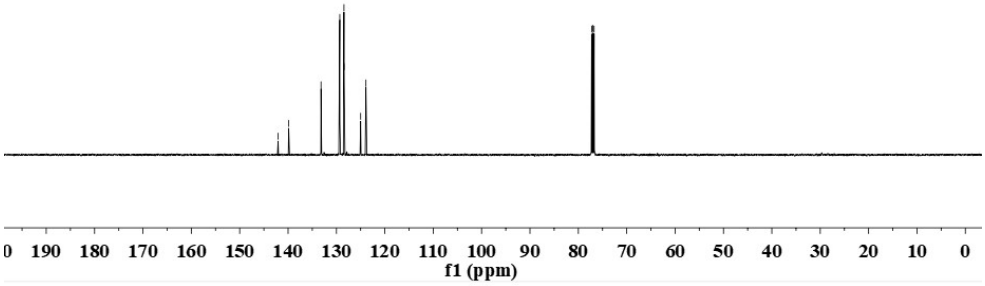
L. Copies of ^{1}H and ^{13}C NMR Spectra

Diphenyl[(phenylthio)imino]-λ^{6}-sulfanone (3aa)

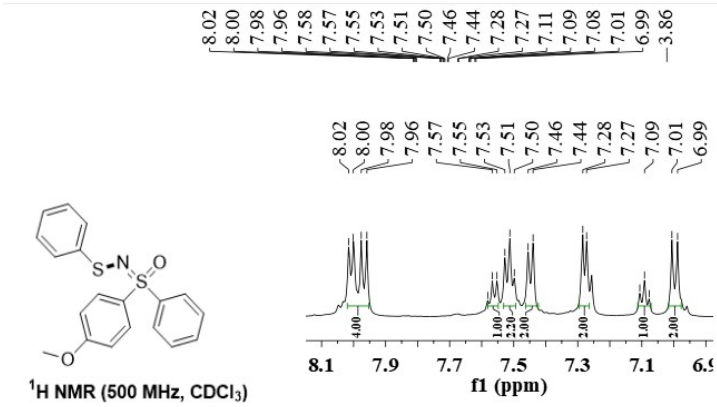


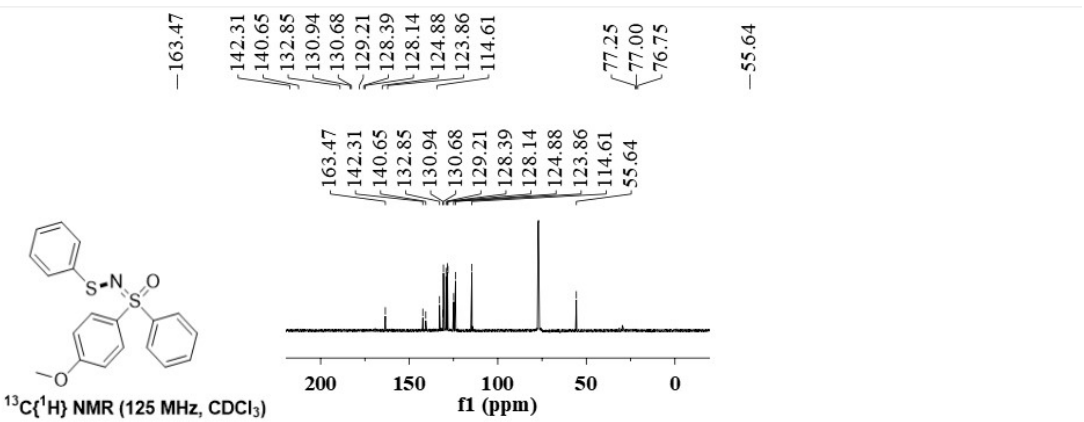


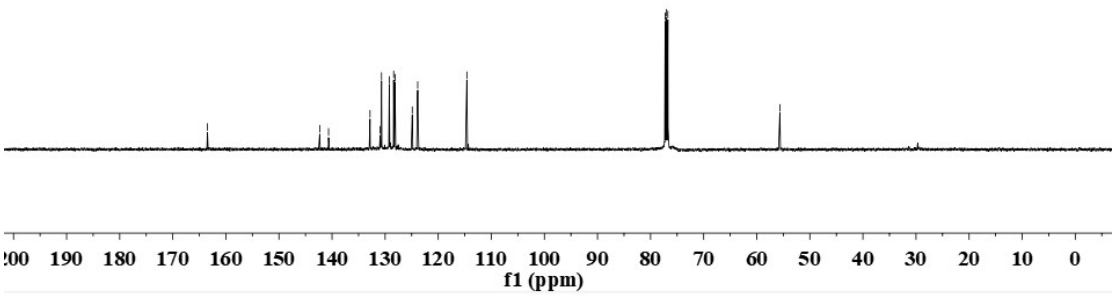




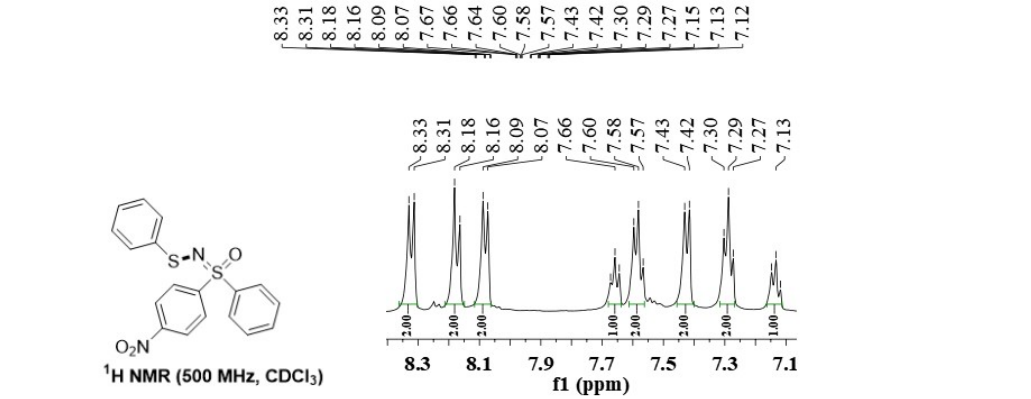
(4-Methoxyphenyl)(phenyl)((phenylthio)imino)-λ⁶-sulfanone (3ba)

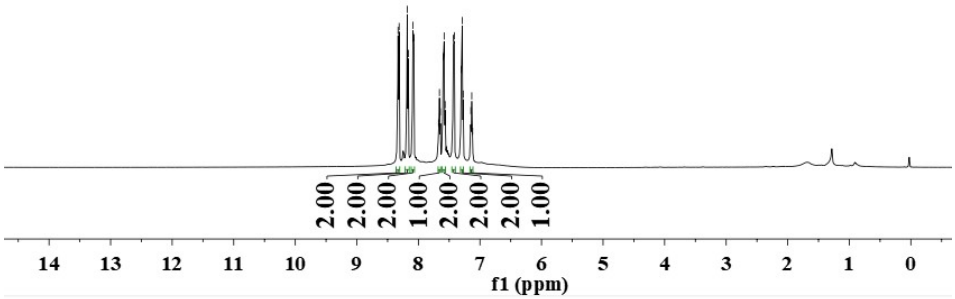


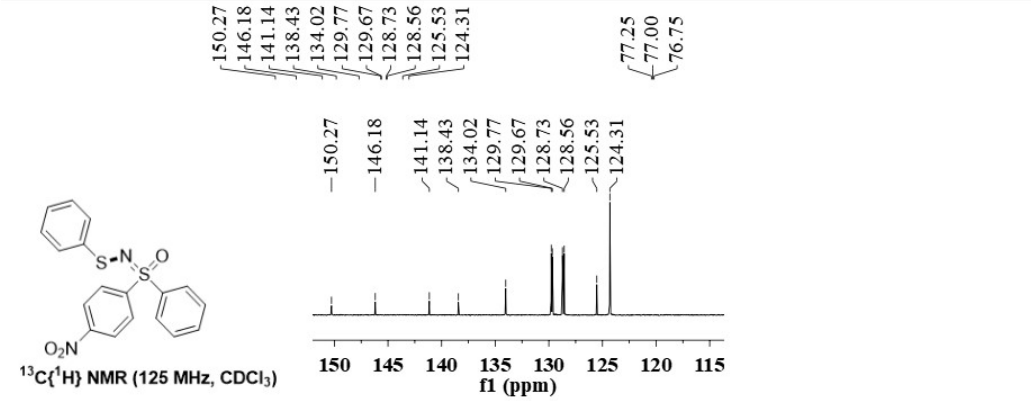


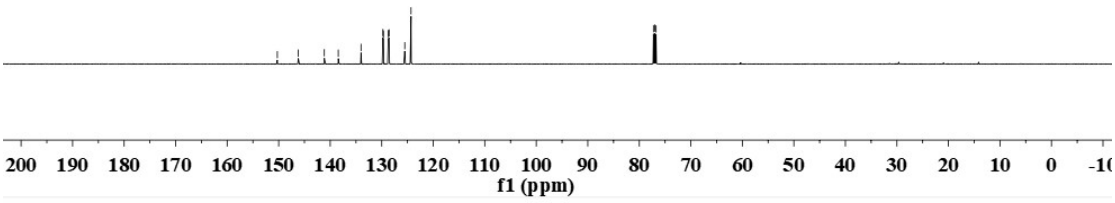


(4-Nitrophenyl)(phenyl)((phenylthio)imino)-λ⁶-sulfanone (3ca)

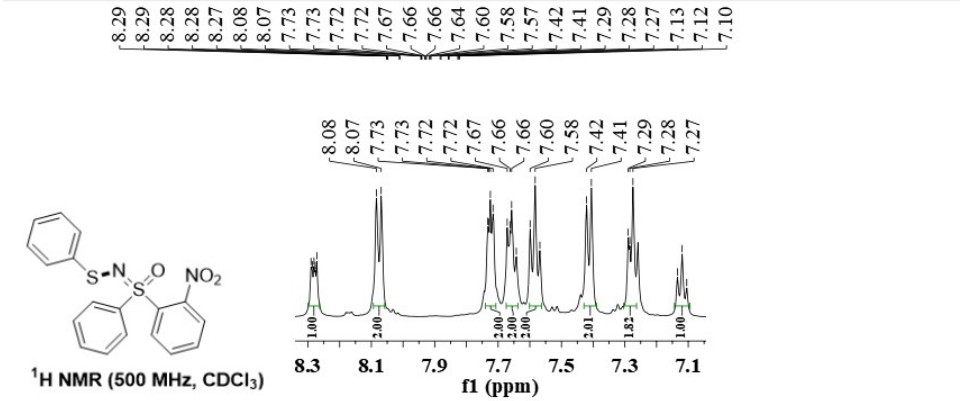


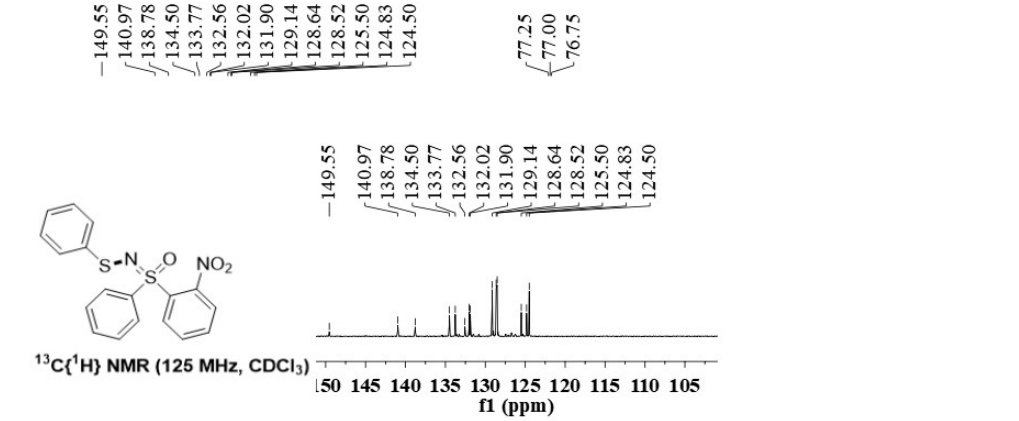


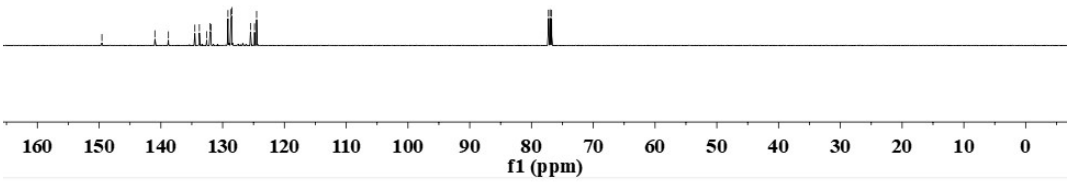




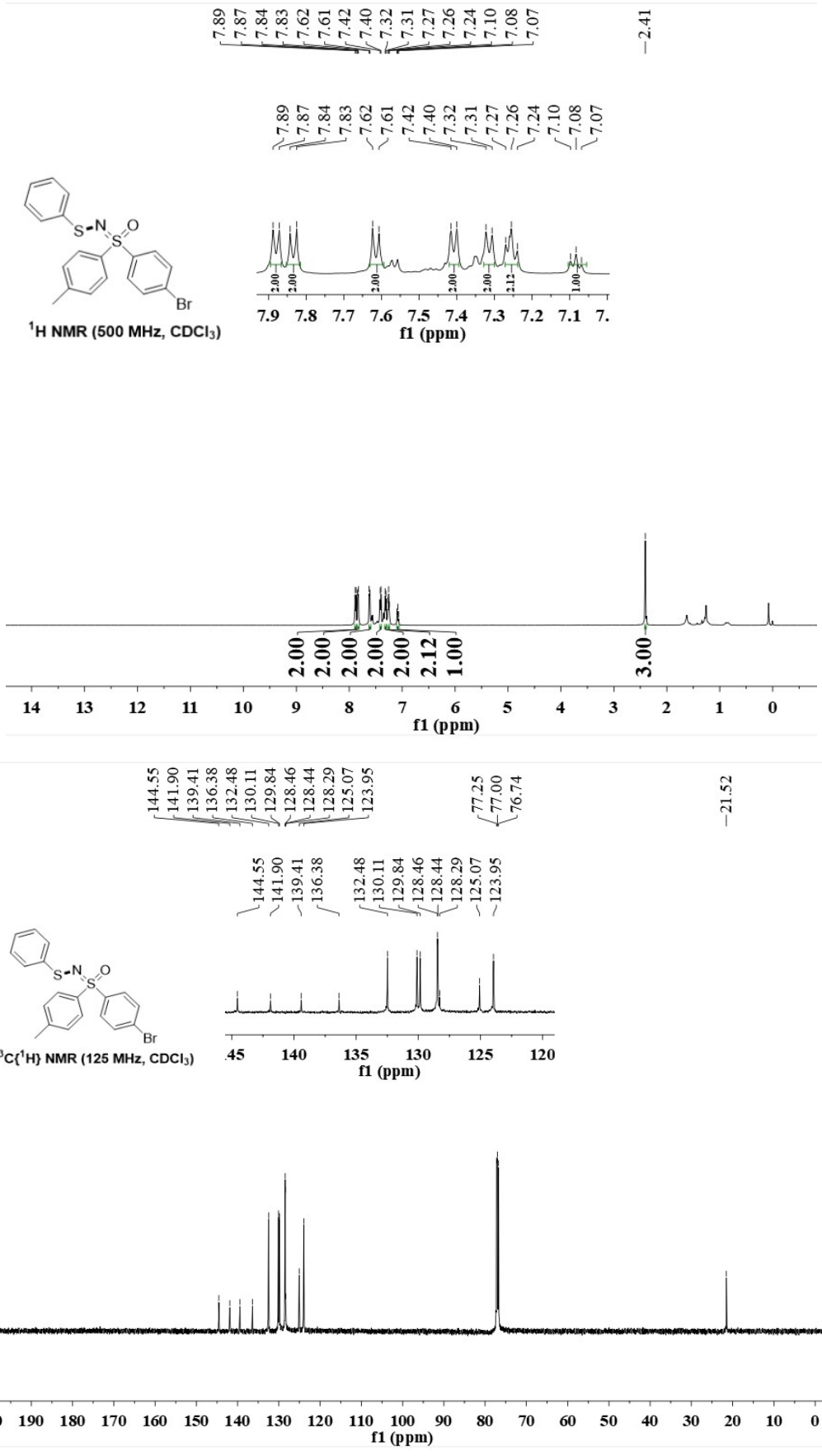
(2-Nitrophenyl)(phenyl)((phenylthio)imino)-λ⁶-sulfanone (3da)



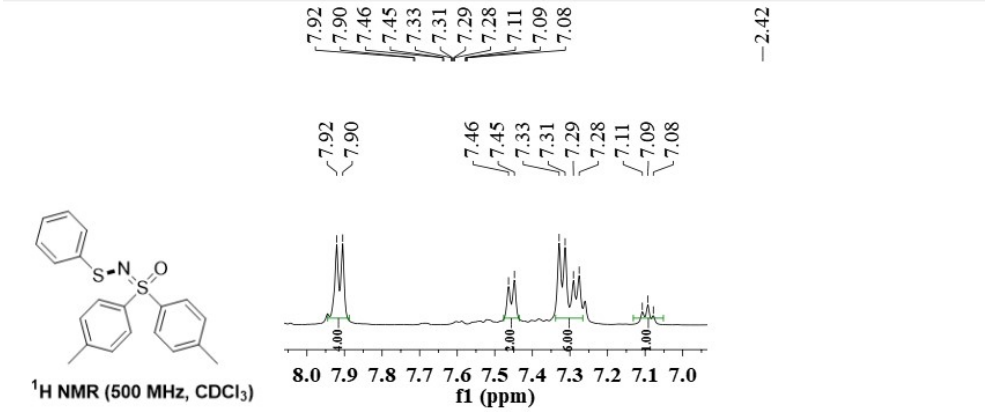




(4-Bromophenyl)((phenylthio)imino)(p-tolyl)-λ⁶-sulfanone (3ea)



((Phenylthio)imino)di-p-tolyl-λ^6-sulfanone (3fa)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7.45
7.33
7.31
7.29
7.28
7.11
7.09
7.08
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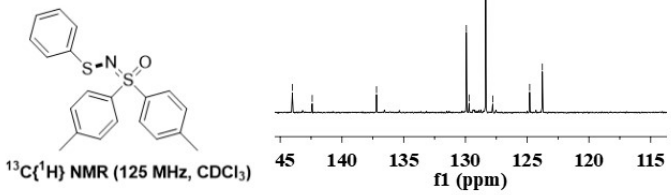
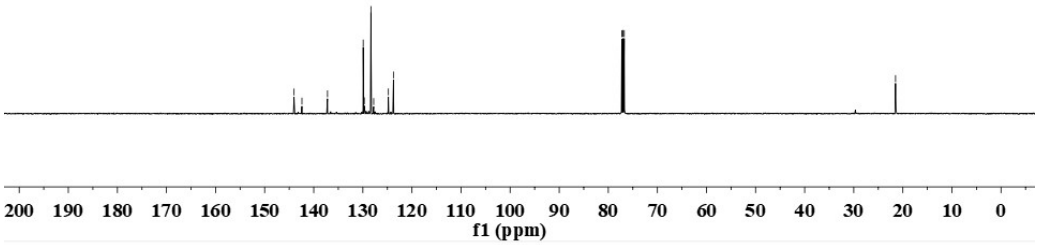
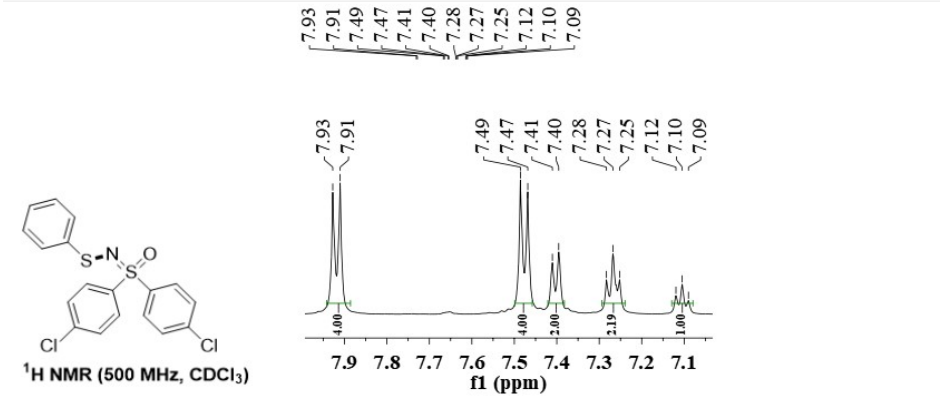
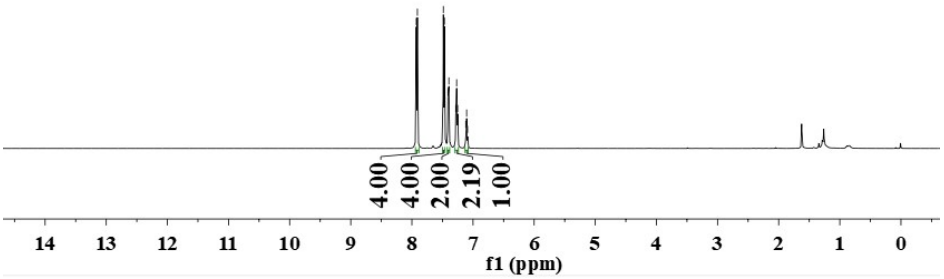
2.00
6.00
1.00
6.00
f1 (ppm)

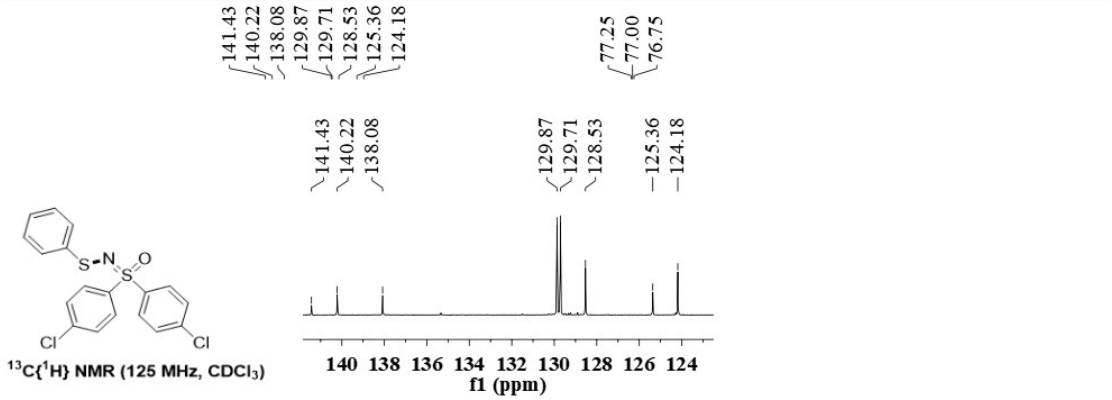

144.01
142.41
137.20
129.93
129.70
128.36
127.79
124.80
123.77
77.25
77.00
76.75
21.48
f1 (ppm)

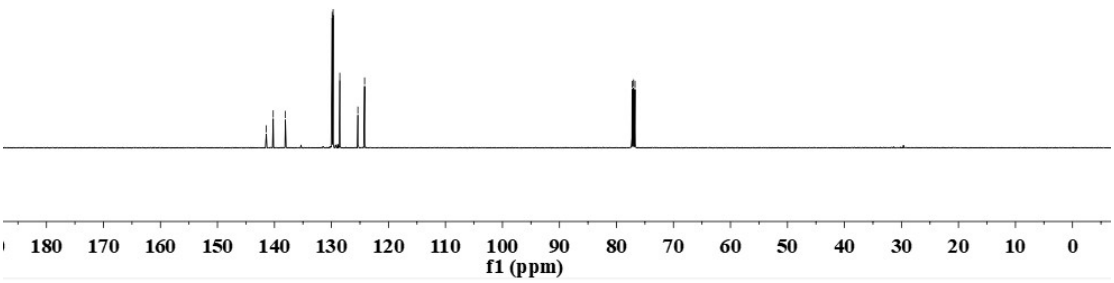

f1 (ppm)

Bis(4-chlorophenyl)((phenylthio)imino)-λ⁶-sulfanone(3ga)

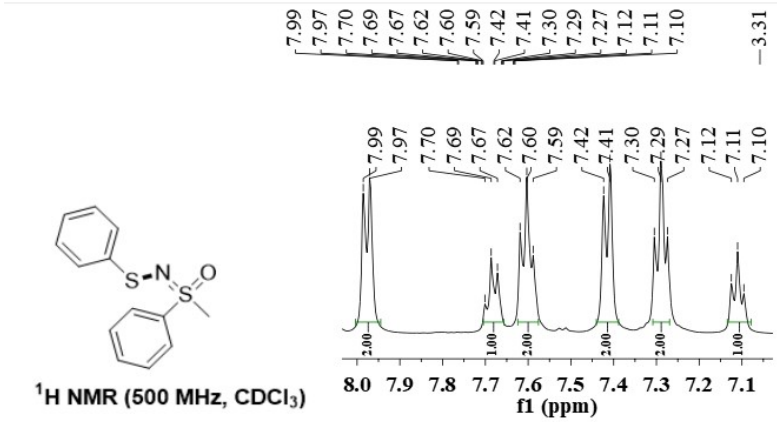




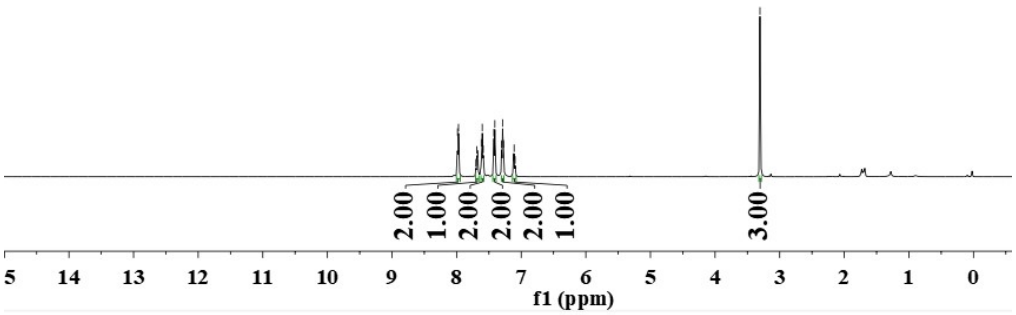


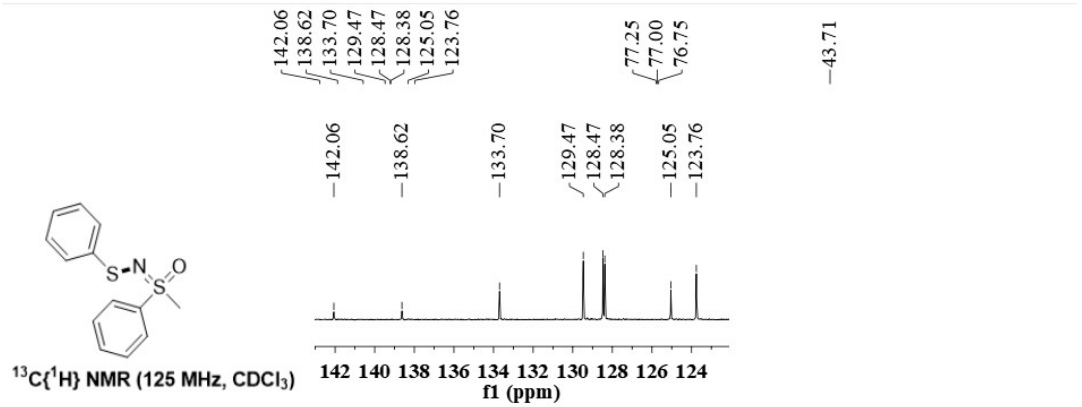


Methyl(phenyl)[(phenylthio)imino]-λ⁶ -sulfanone (3ha)

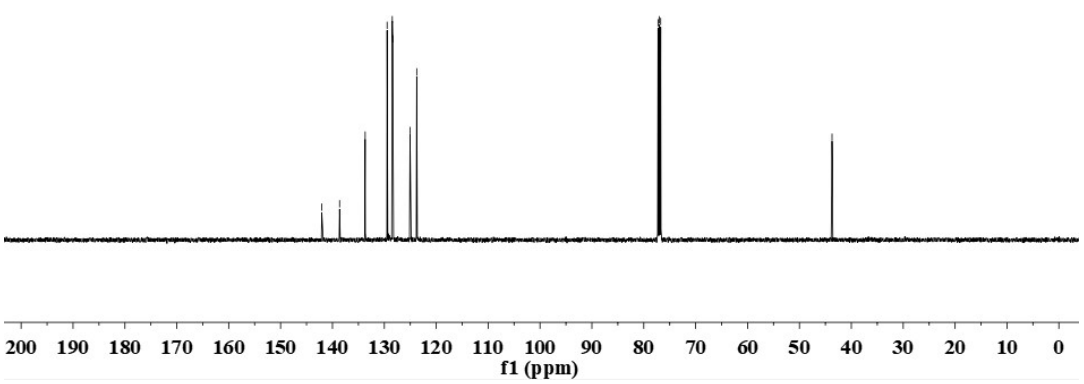


^{1}H NMR (500 MHz, $CDCl_3$)

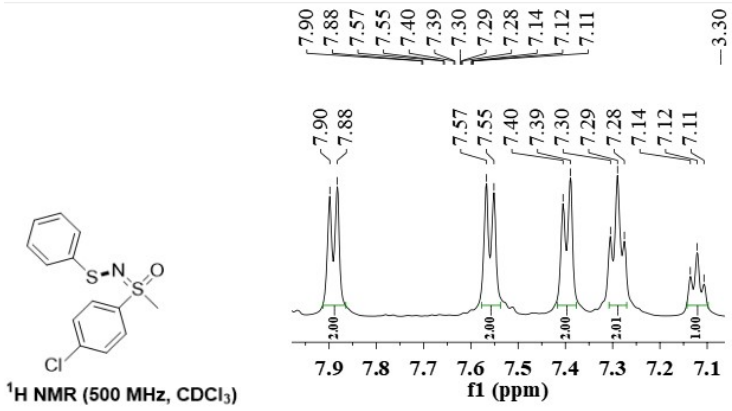


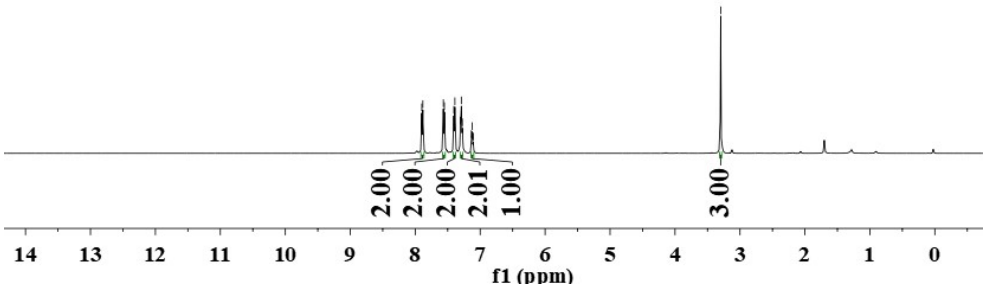


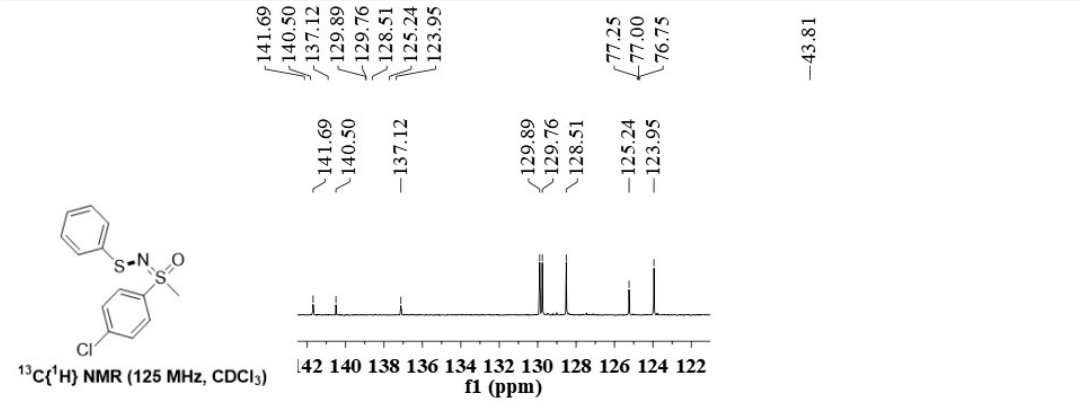
$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$)

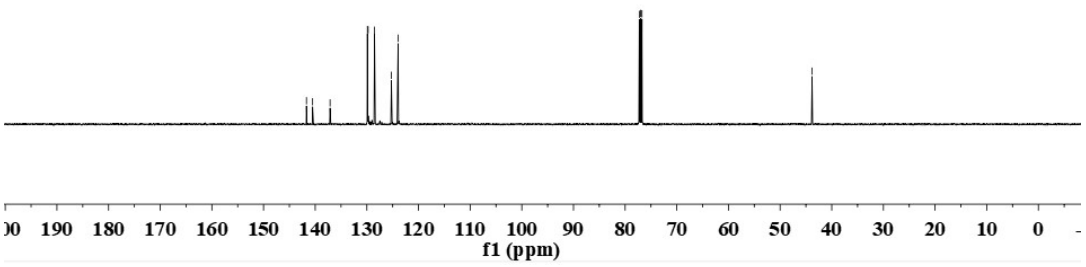


(4-Chlorophenyl)(methyl)[(phenylthio)imino]-λ⁶ -sulfanone (3ia)

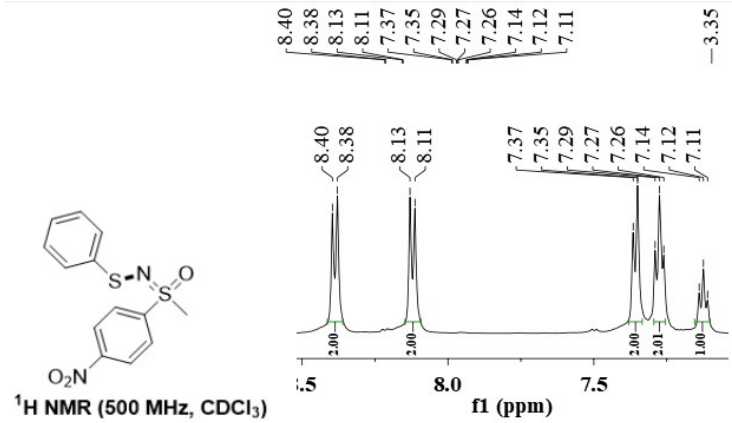


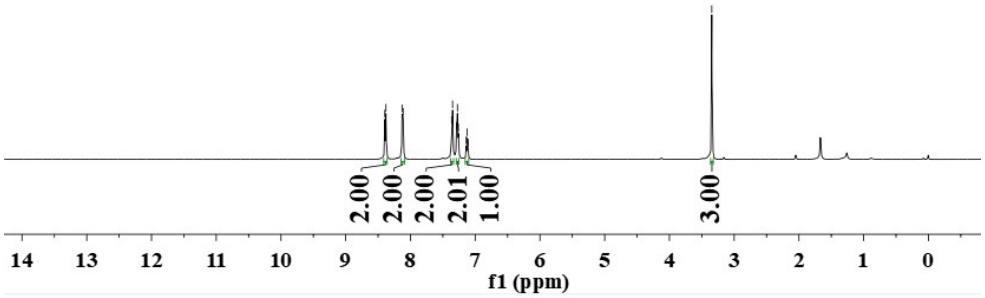


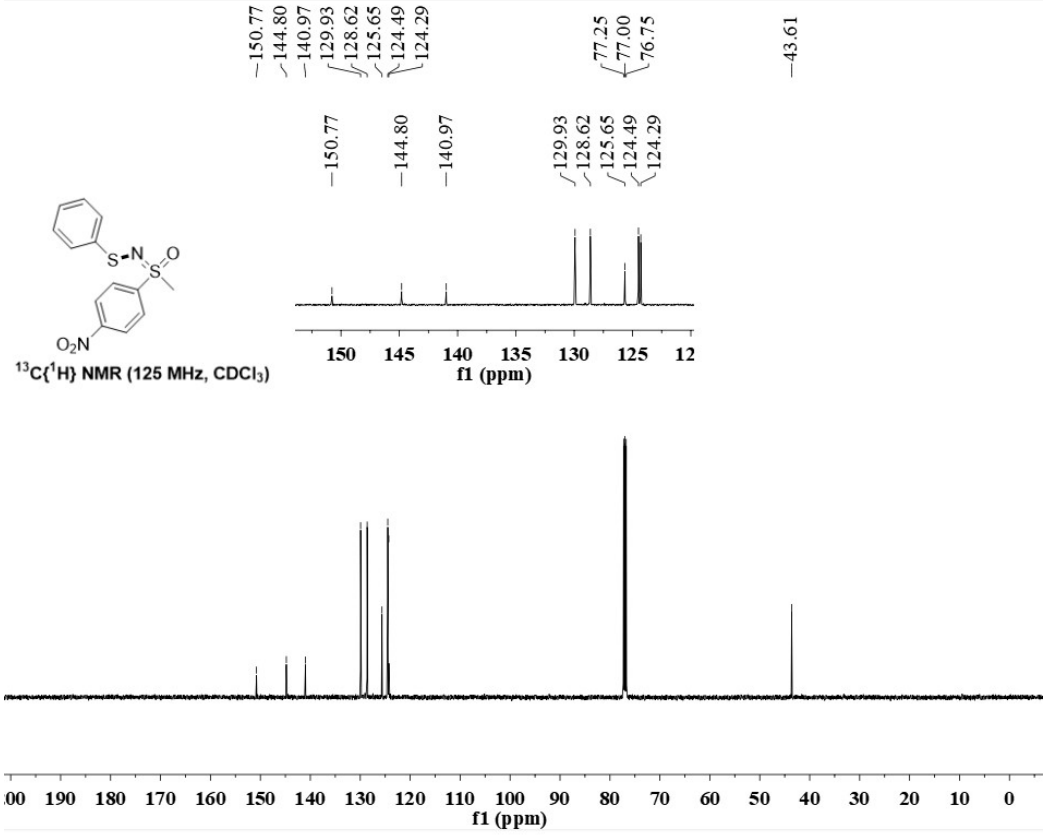




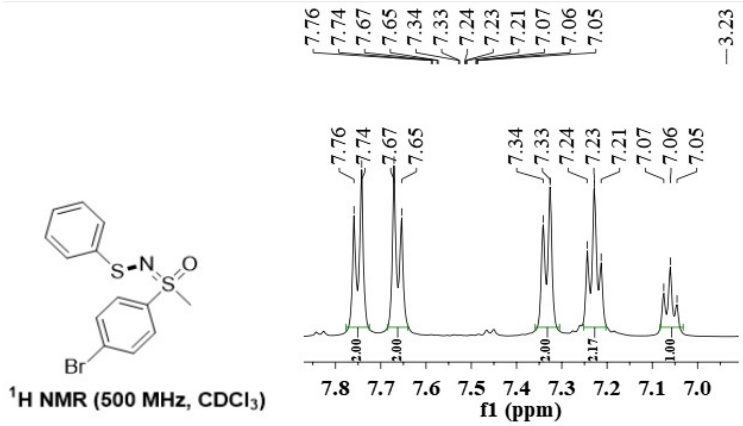
Methyl(4-nitrophenyl)[(phenylthio)imino]-λ⁶-sulfanone (3ja)



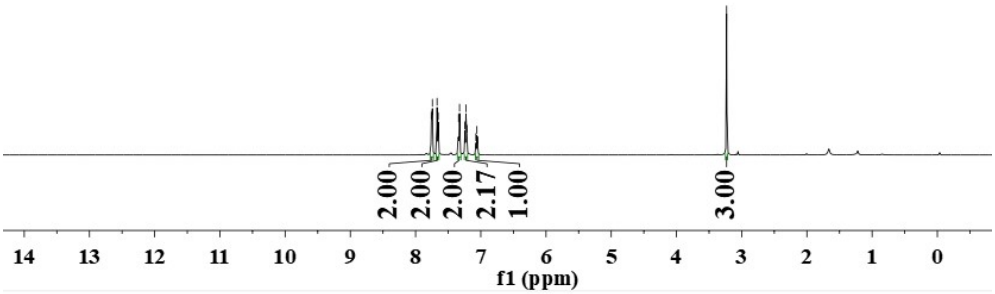


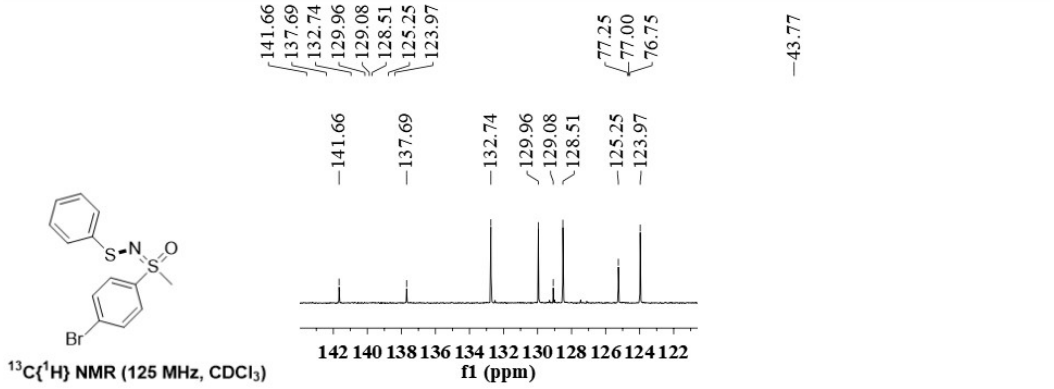


(4-Bromophenyl)(methyl)[(phenylthio)imino]-λ^6 -sulfanone (3ka)

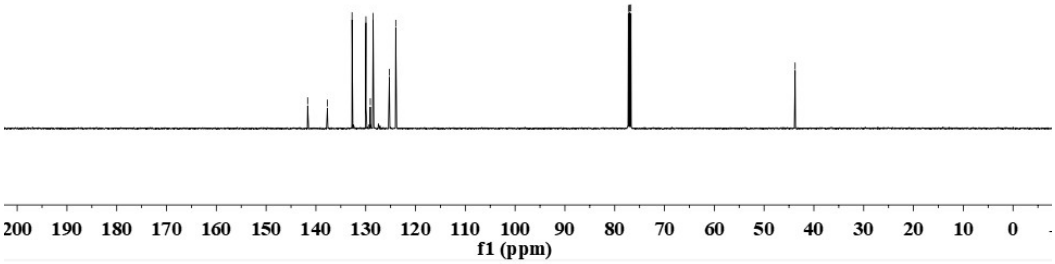


^{1}H NMR (500 MHz, $CDCl_3$)

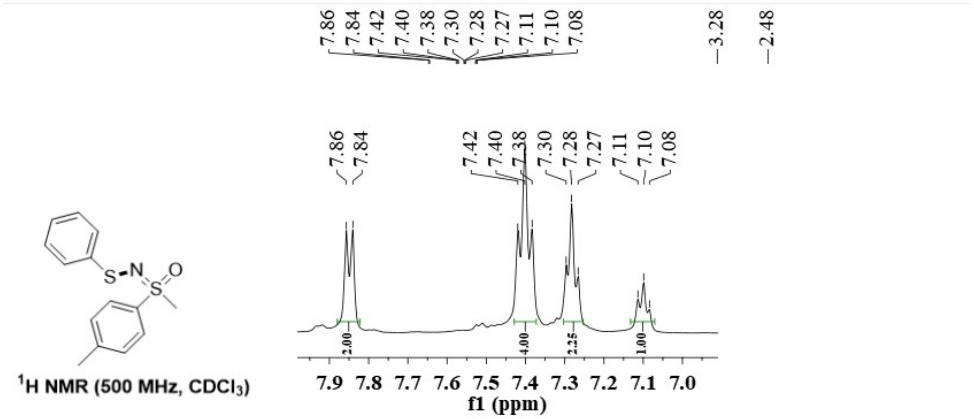




$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$)



Methyl[(phenylthio)imino](*p*-tolyl)-λ⁶-sulfanone (3la)



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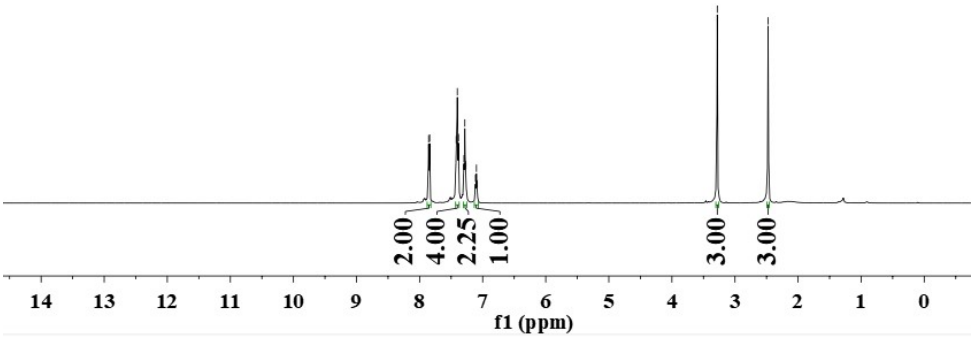
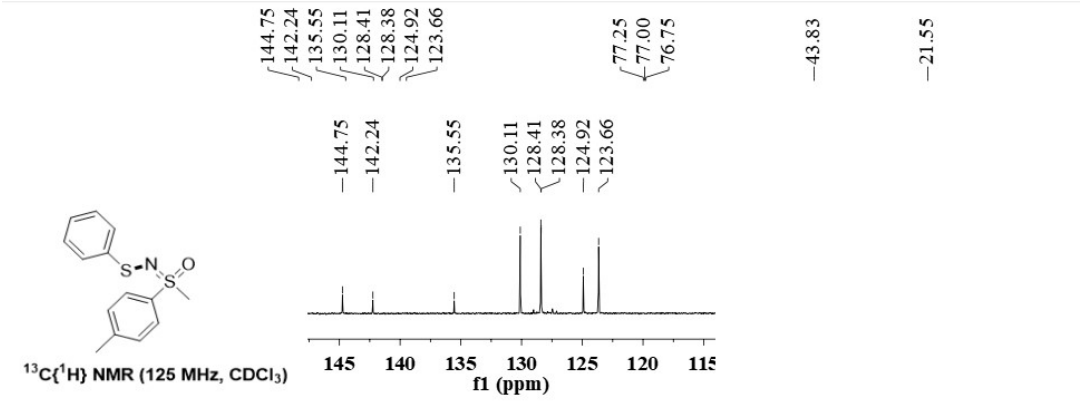
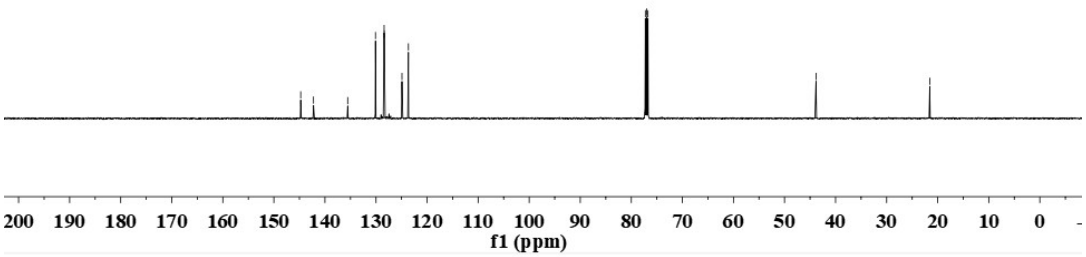
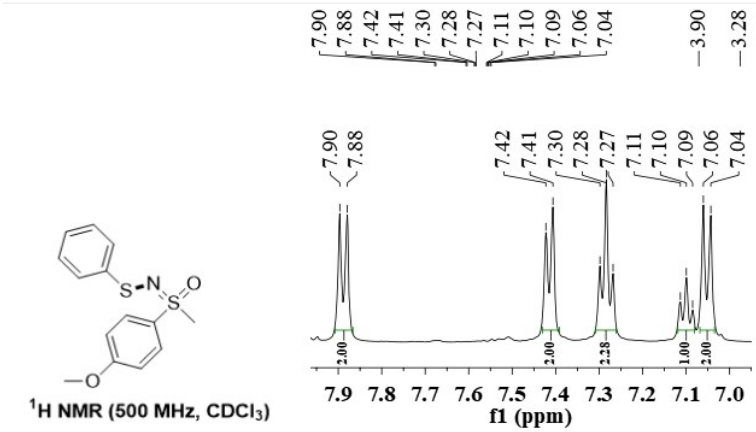


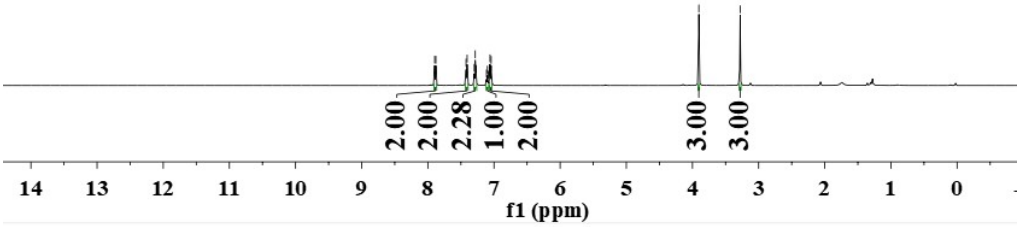


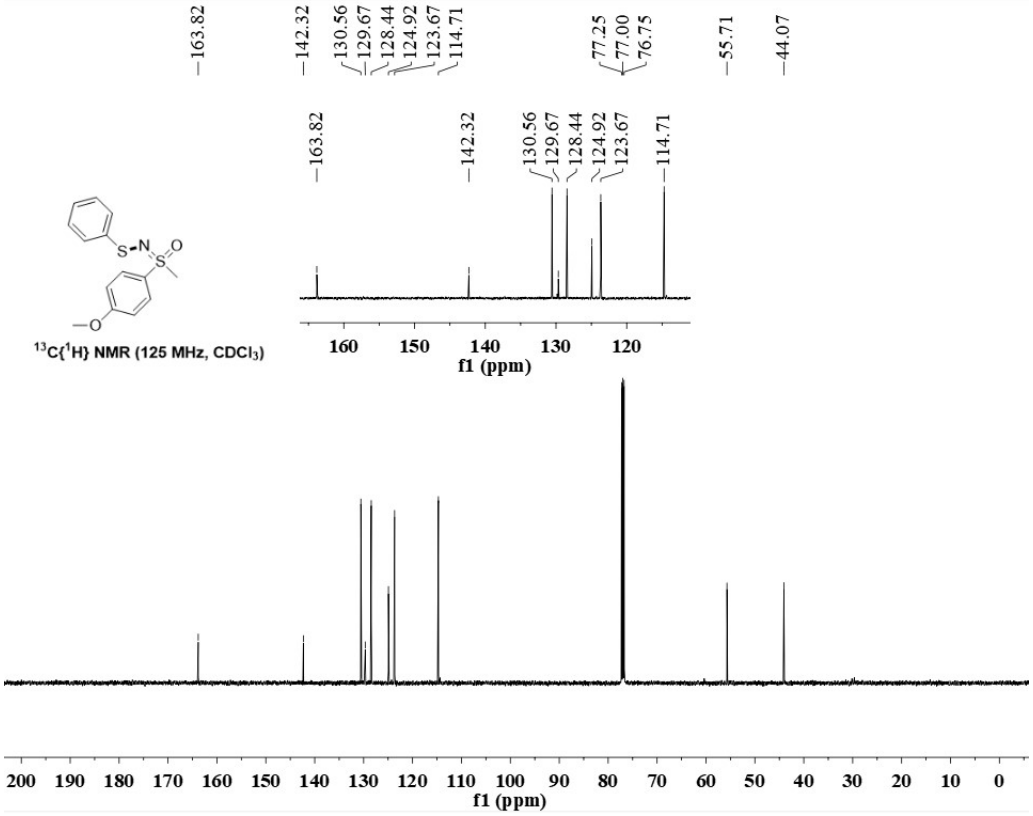
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



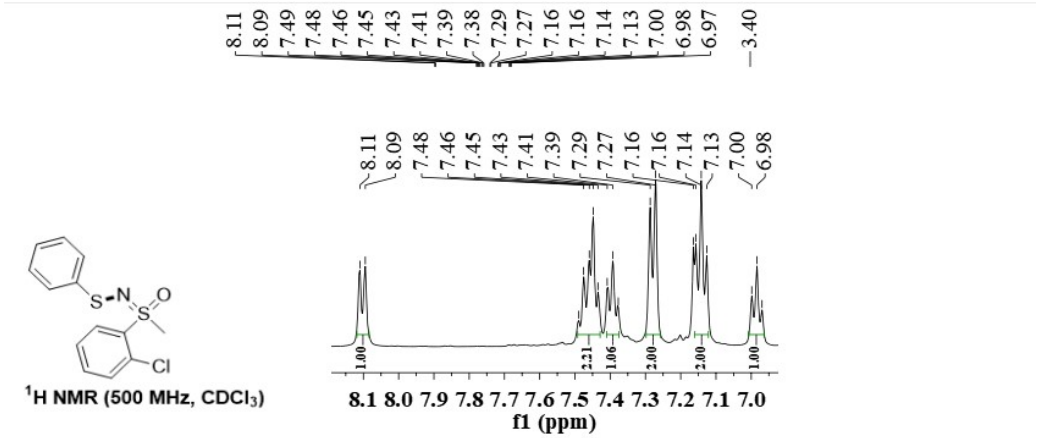
(4-Methoxyphenyl)(methyl)[(phenylthio)imino]-λ⁶-sulfanone (3ma)

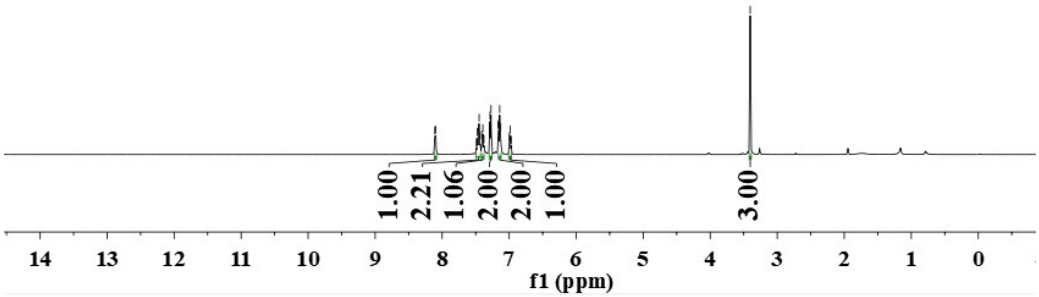


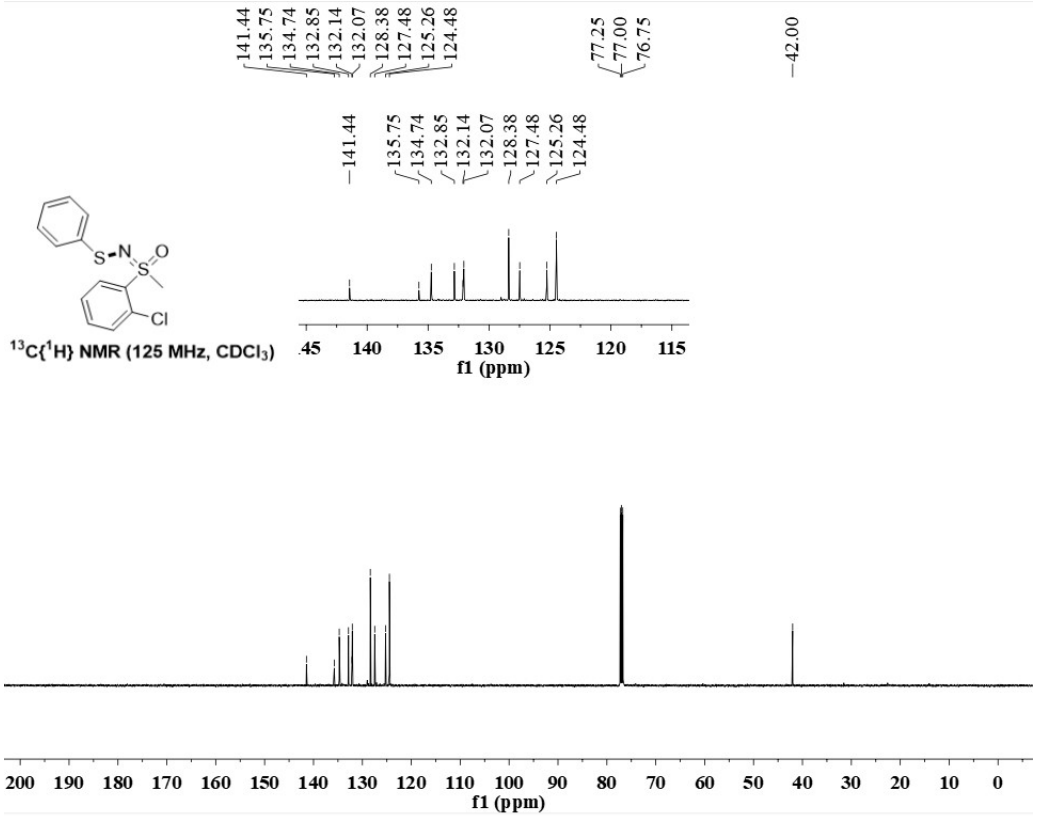




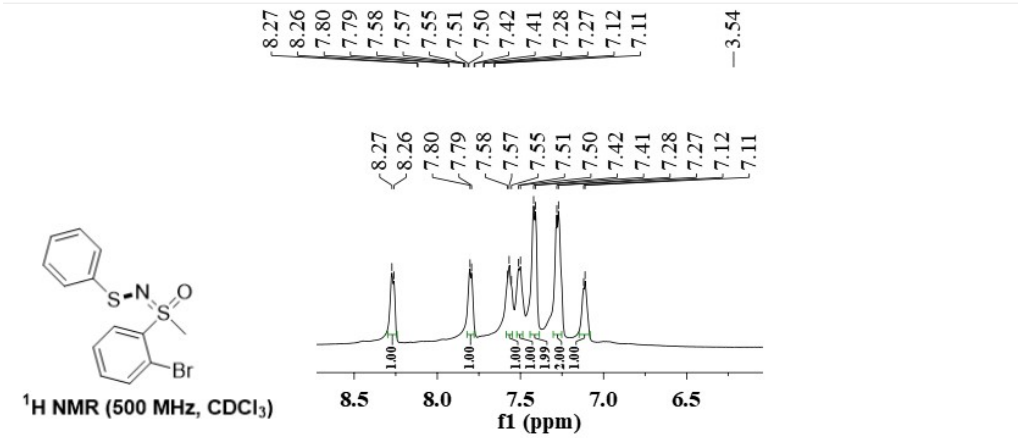
(2-Chlorophenyl)(methyl)((phenylthio)imino)-λ⁶-sulfanone (3na)

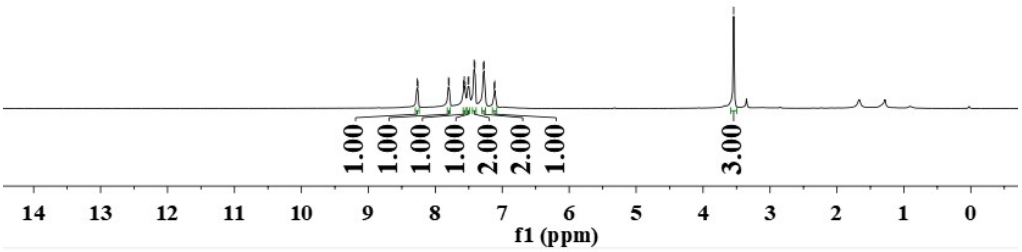


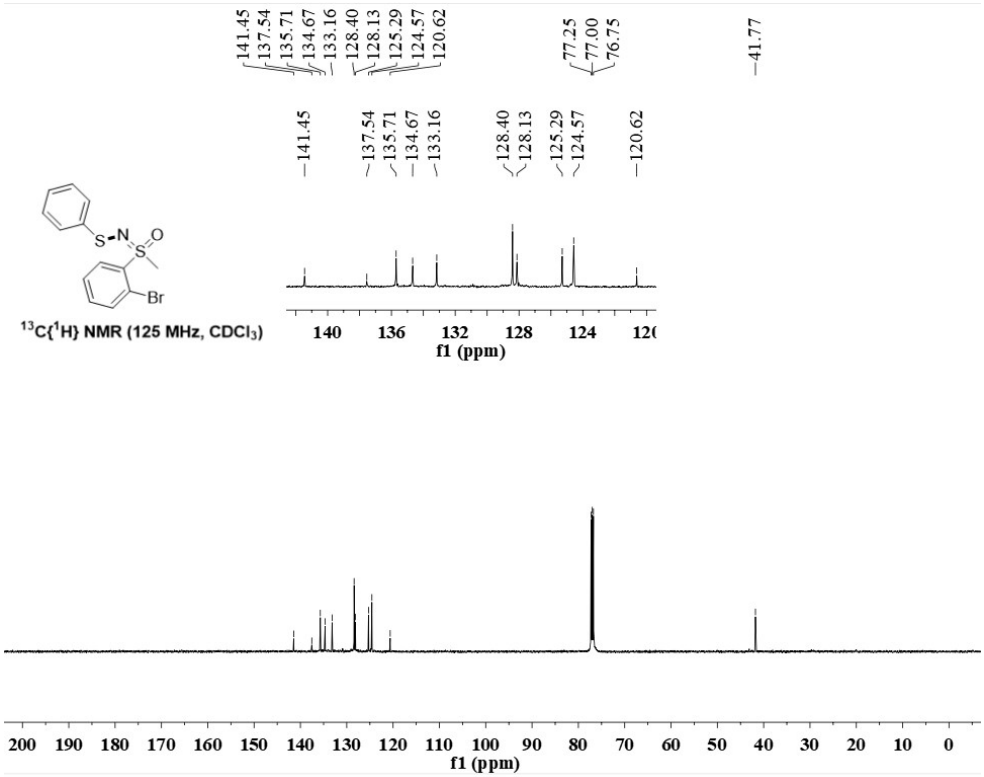




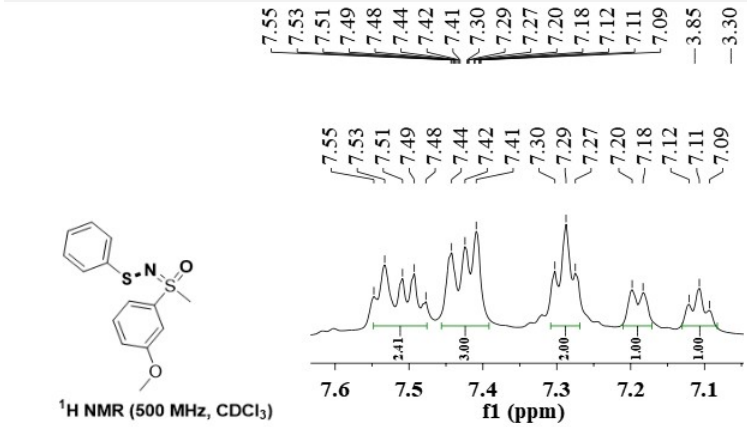
(2-Bromophenyl)(methyl)((phenylthio)imino)-λ⁶-sulfanone(3oa)

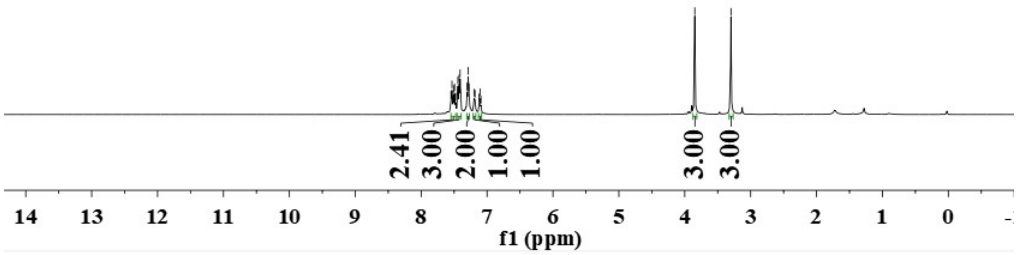


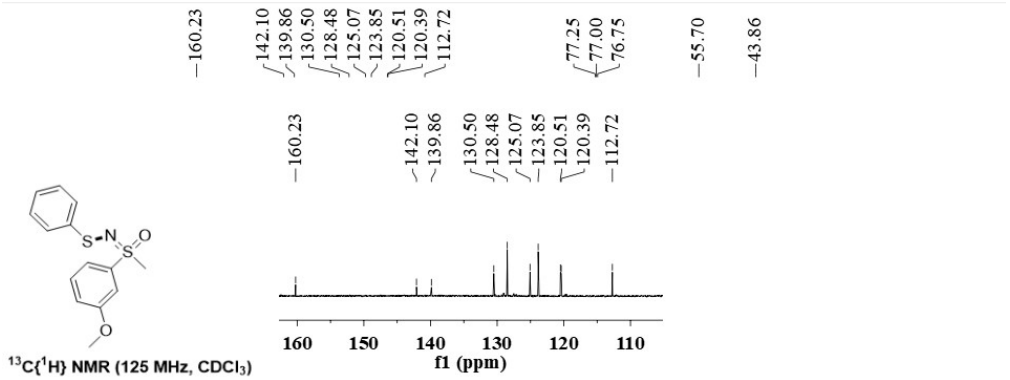


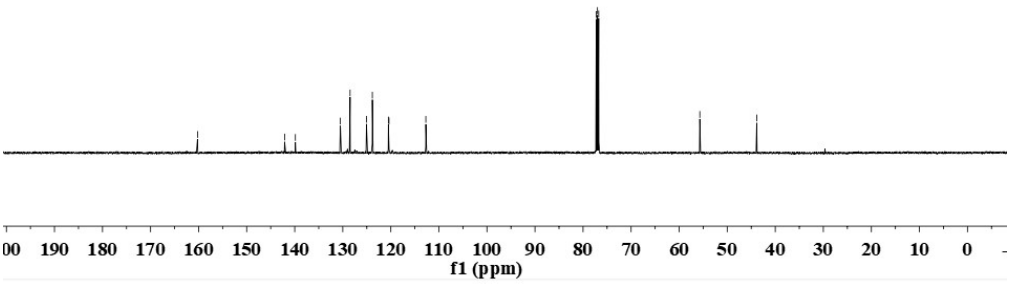


(3-Methoxyphenyl)(methyl)((phenylthio)imino)-λ⁶-sulfanone (3pa)

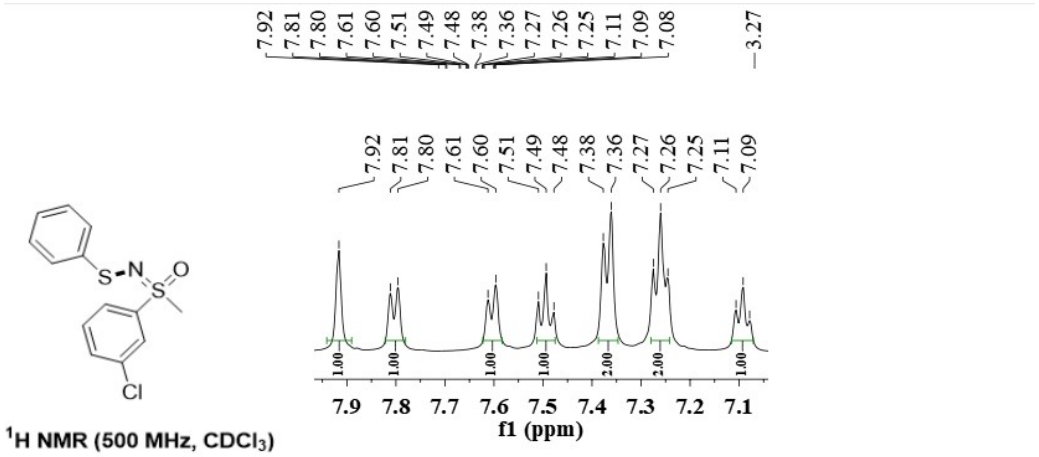




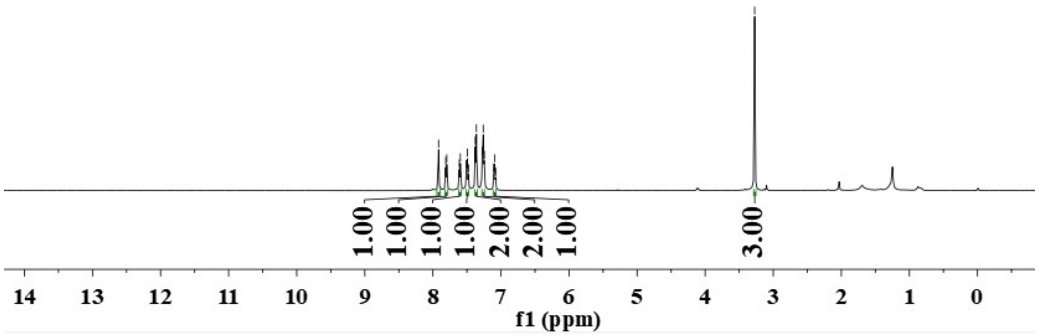


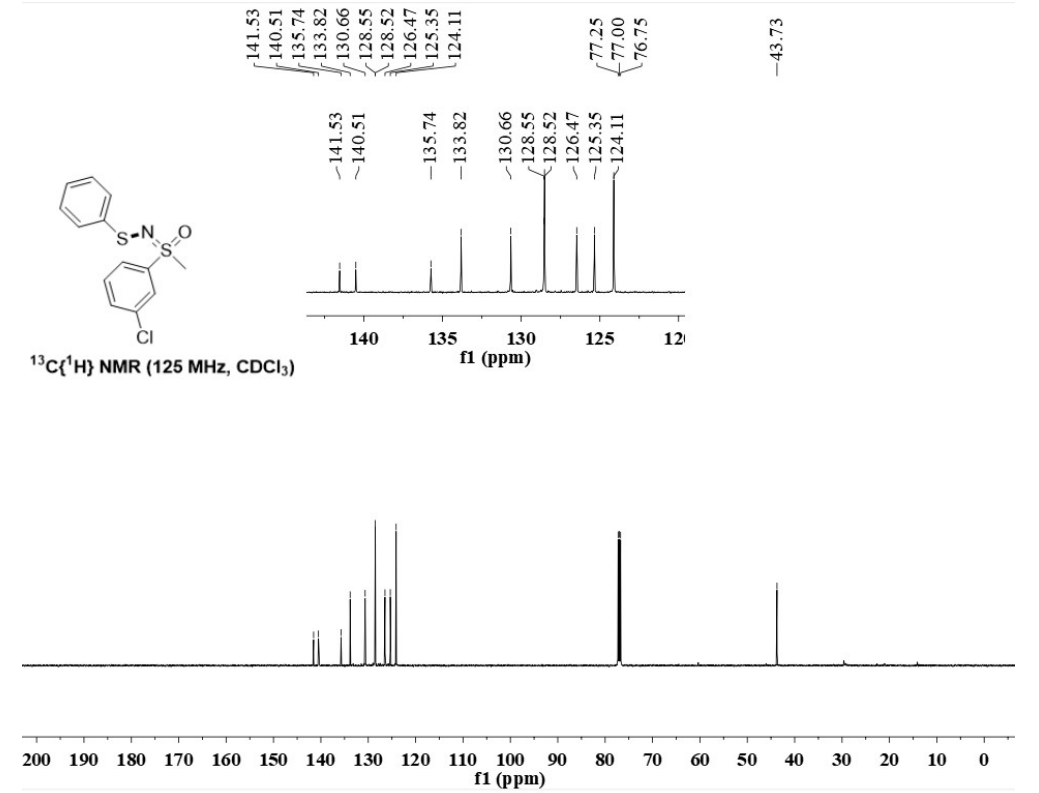


(3-Chlorophenyl)(methyl)[(phenylthio)imino]-λ⁶-sulfanone (3qa)



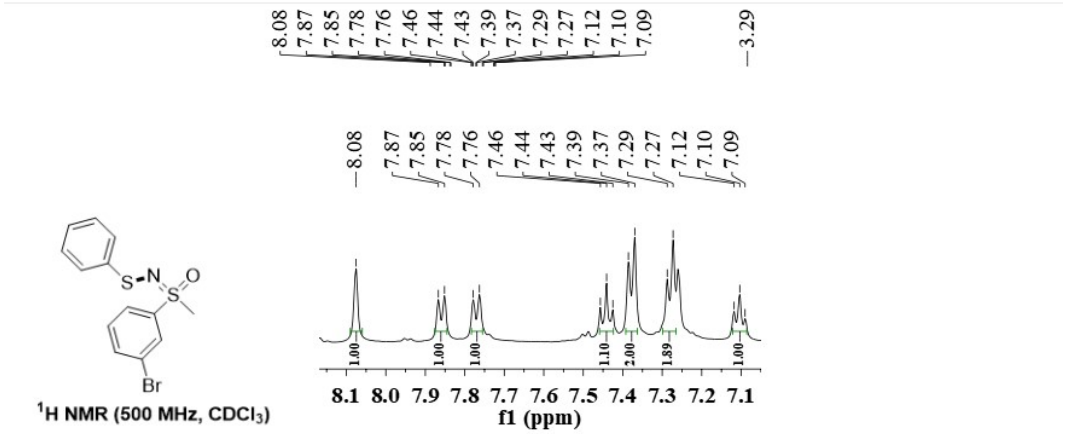
^{1}H NMR (500 MHz, $CDCl_3$)

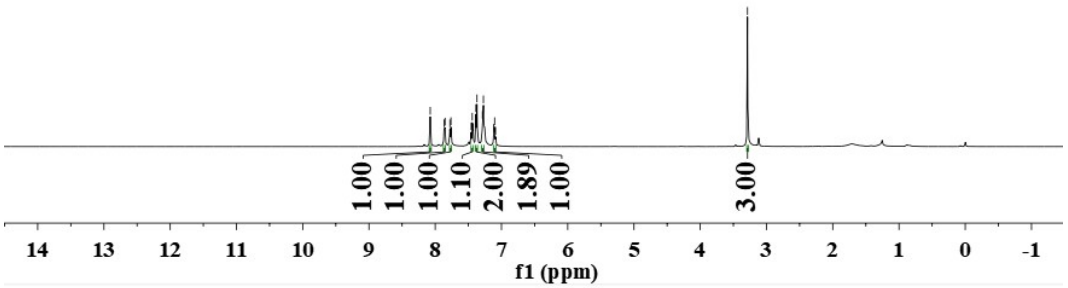


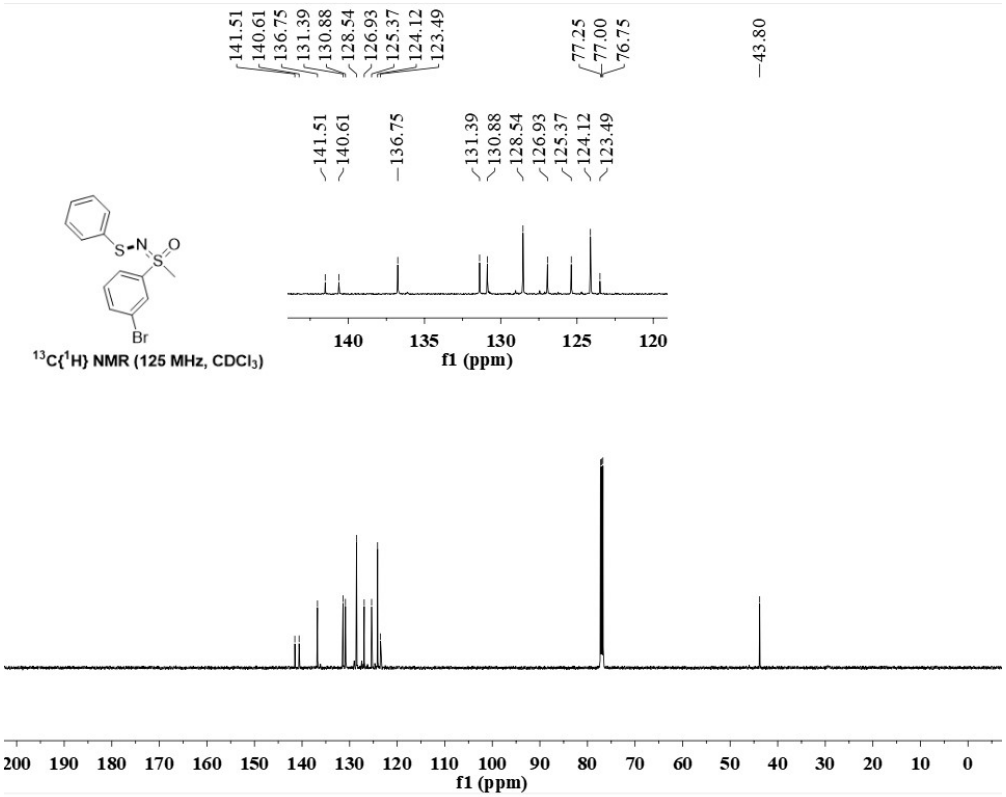


$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$)

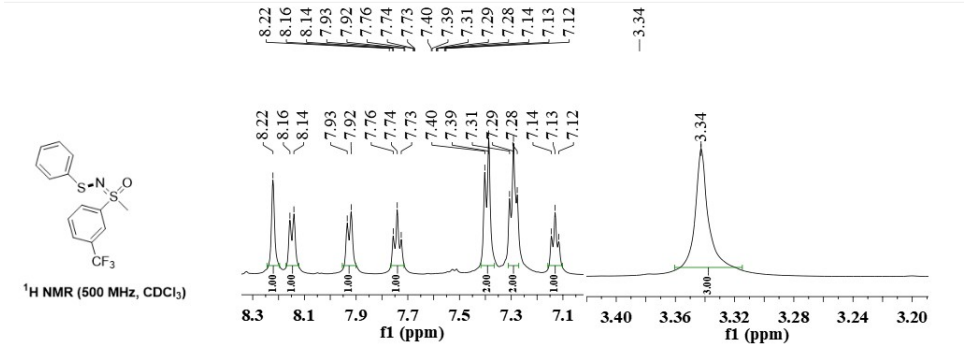
(3-Bromophenyl)(methyl)((phenylthio)imino)-λ⁶-sulfanone (3ra)

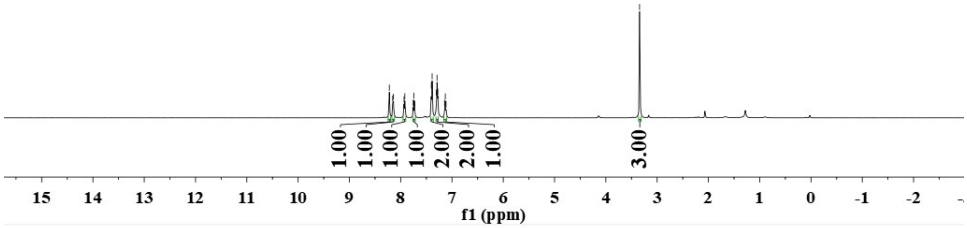


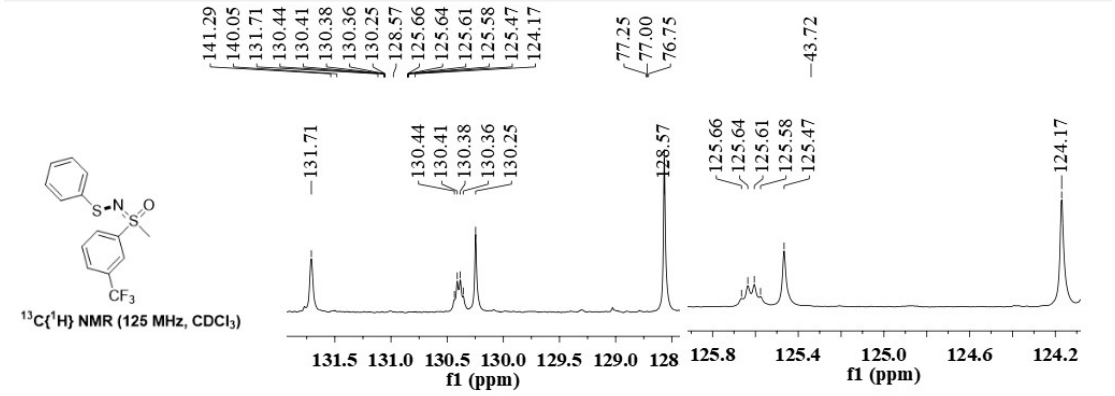


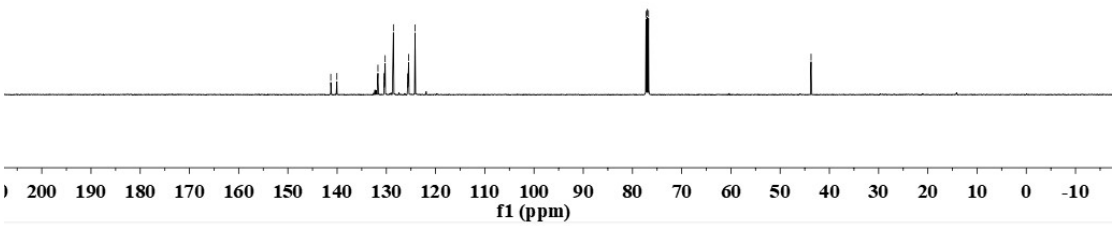


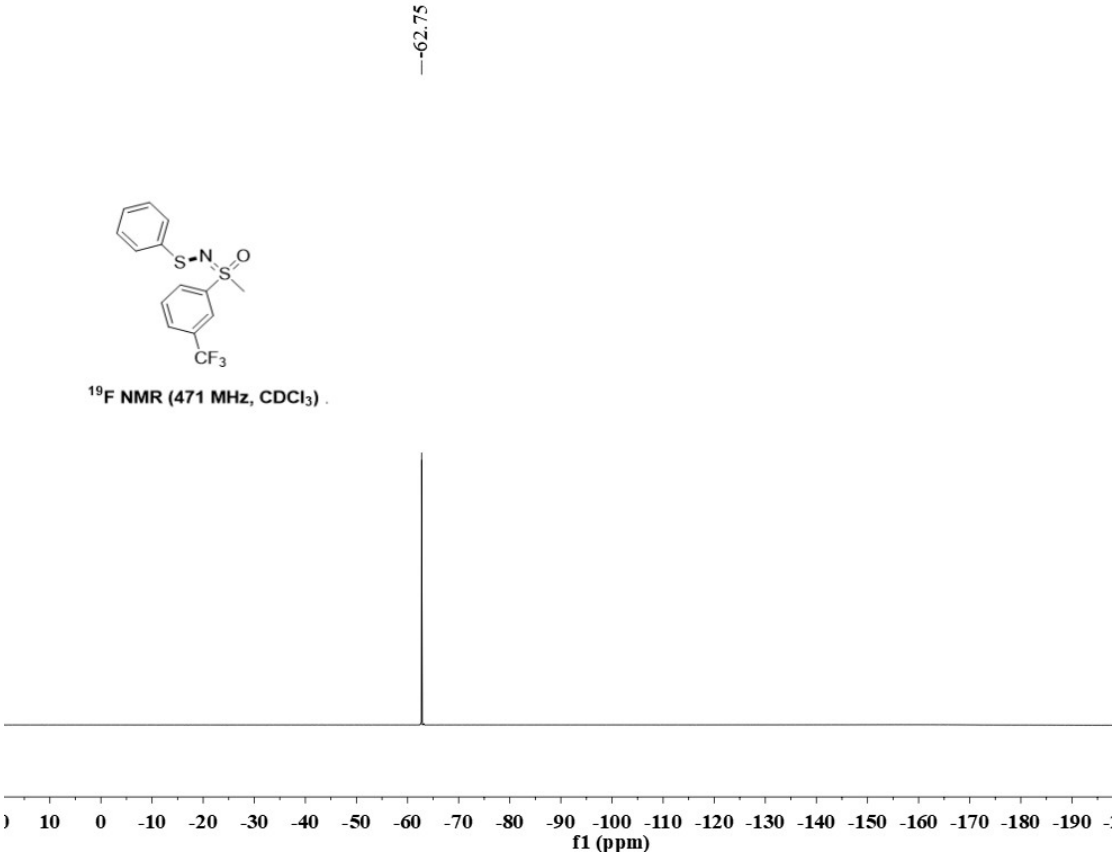
Methyl((phenylthio)imino)(3-(trifluoromethyl)phenyl)-λ⁶-sulfanone (3sa)





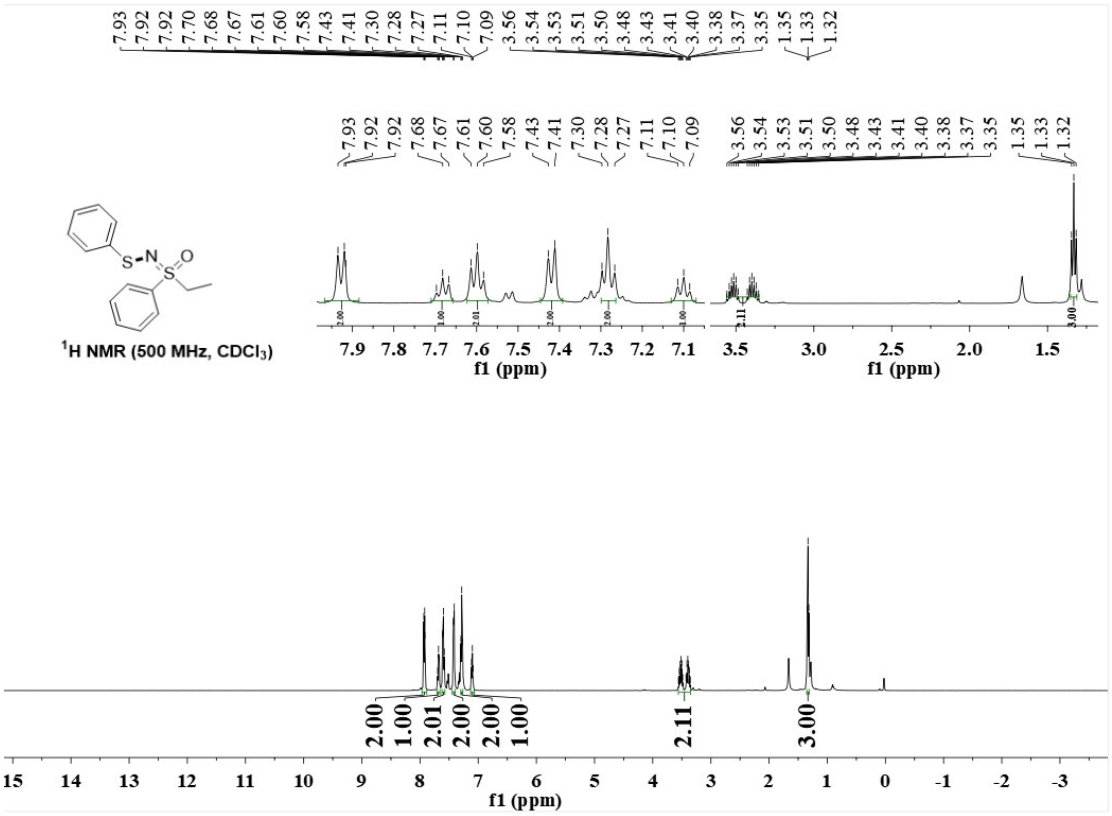


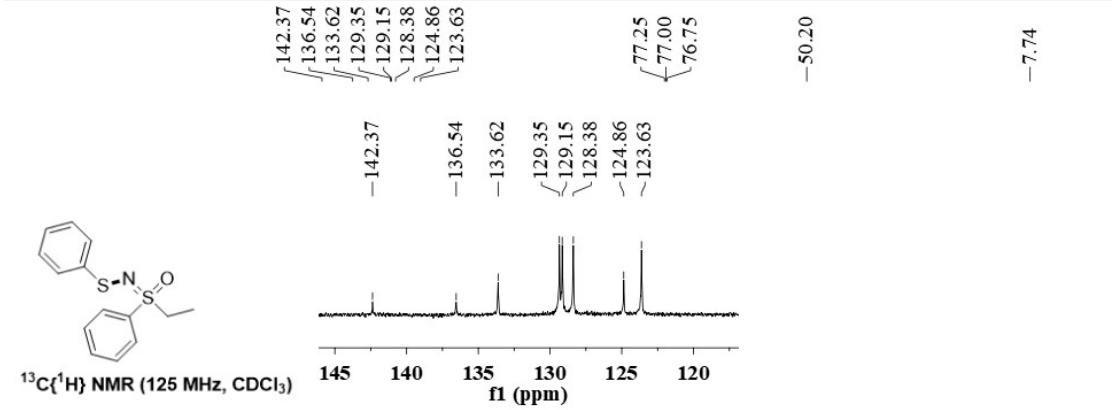


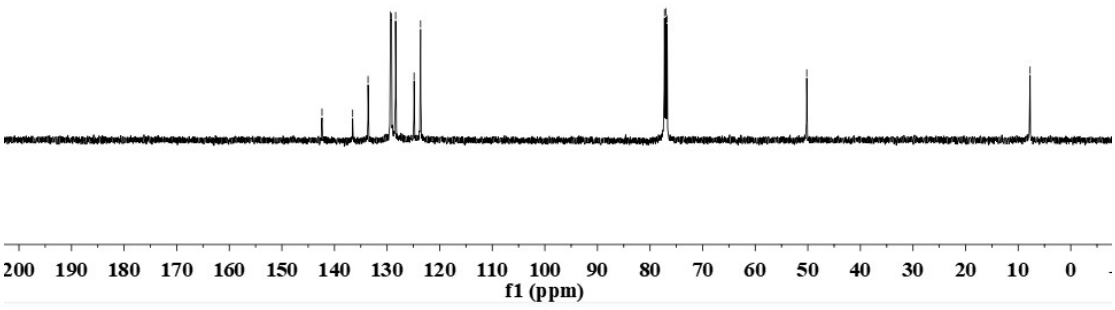


^{19}F NMR (471 MHz, $CDCl_3$) .

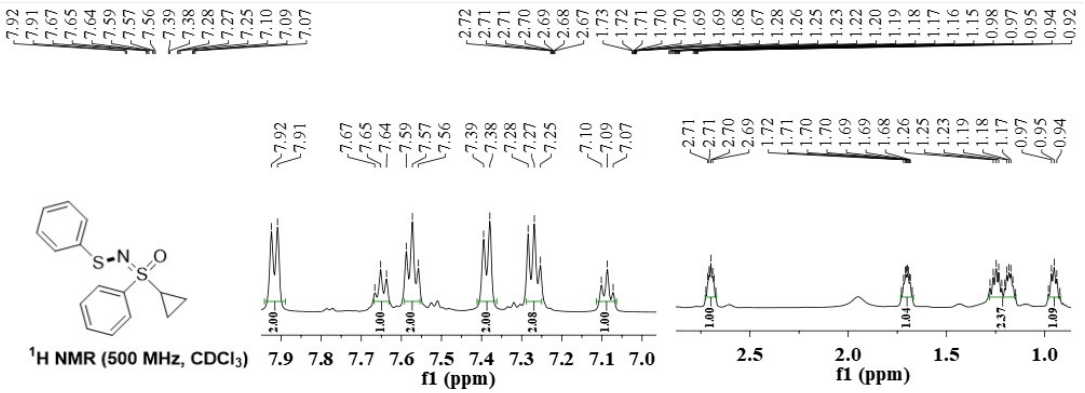
Ethyl(phenyl)((phenylthio)imino)-λ⁶-sulfanone (3ta)

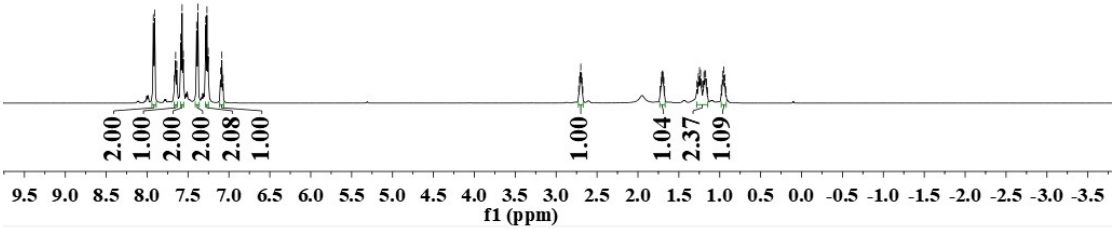


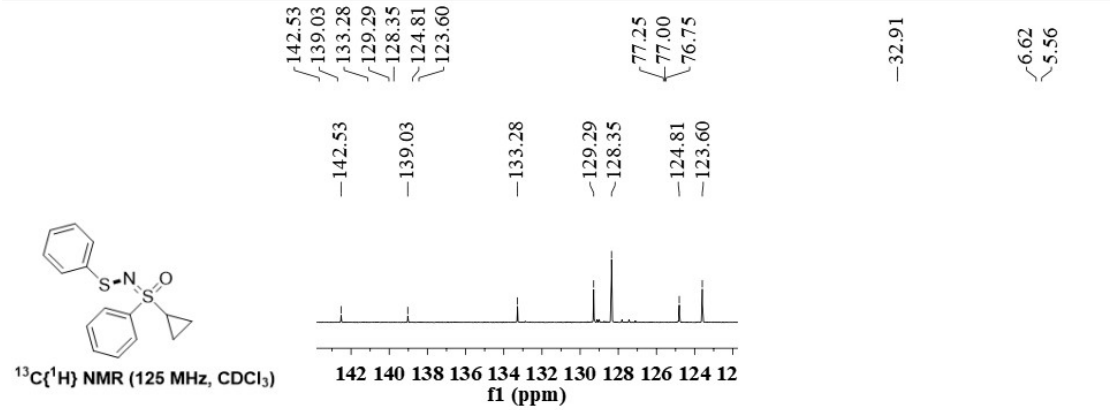


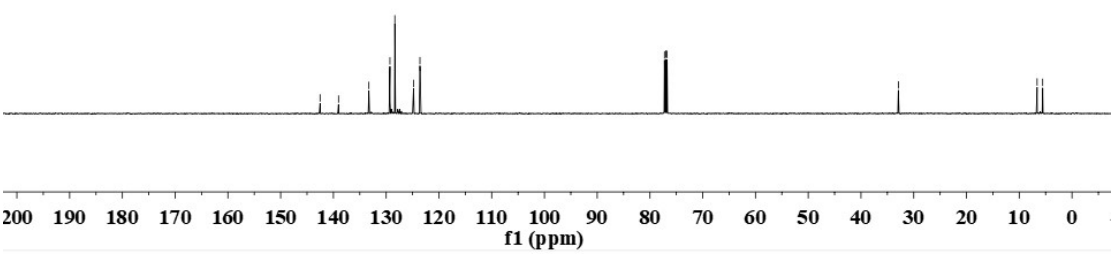


Cyclopropyl(phenyl)((phenylthio)imino)-λ⁶-sulfanone (3ua)



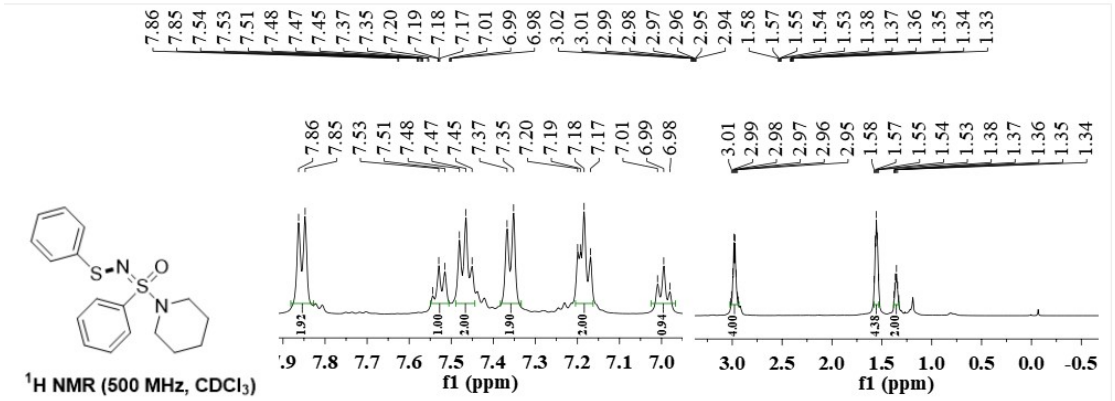




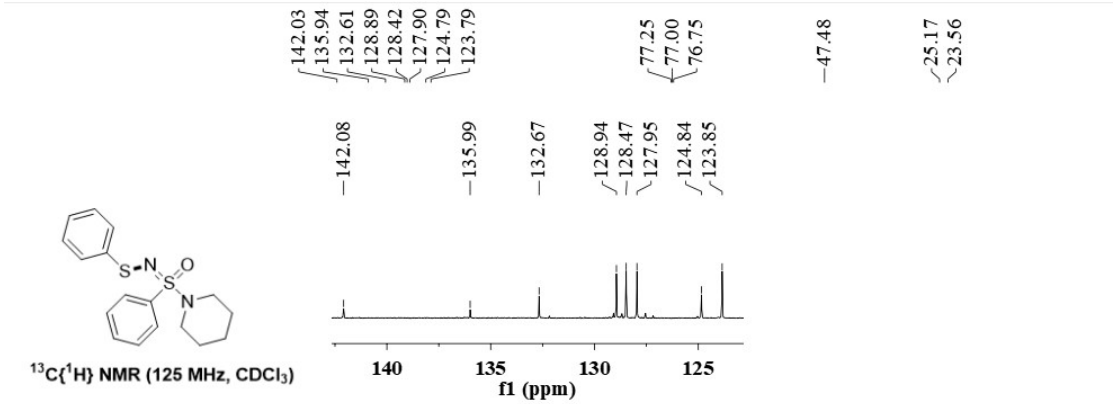


***N*-[Oxo(phenyl)(piperidin-1-yl)-λ⁶ -sulfaneylidene]-*S*-phenylthiohydroxylamine**

(3va)

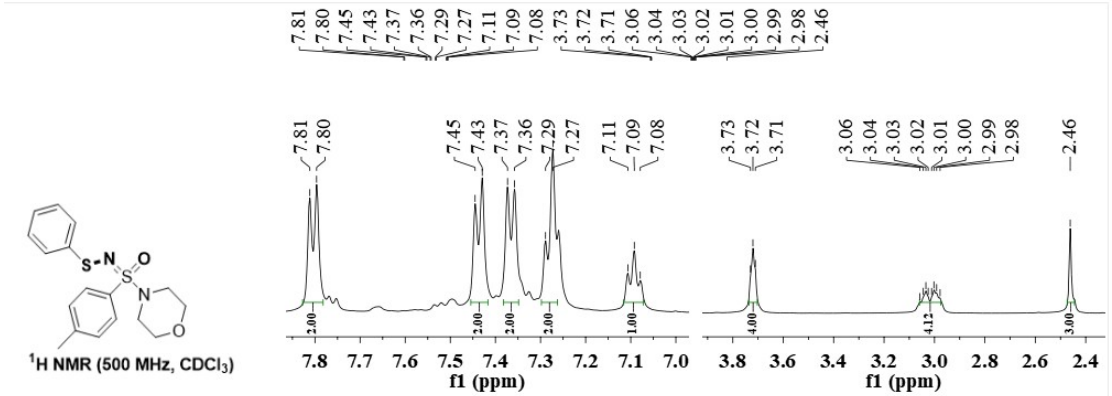


^{1}H NMR (500 MHz, $CDCl_3$)

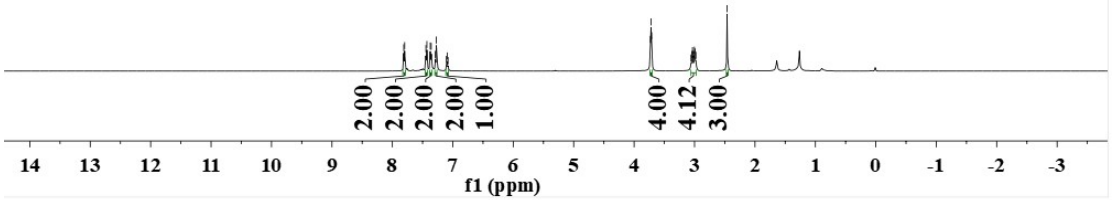


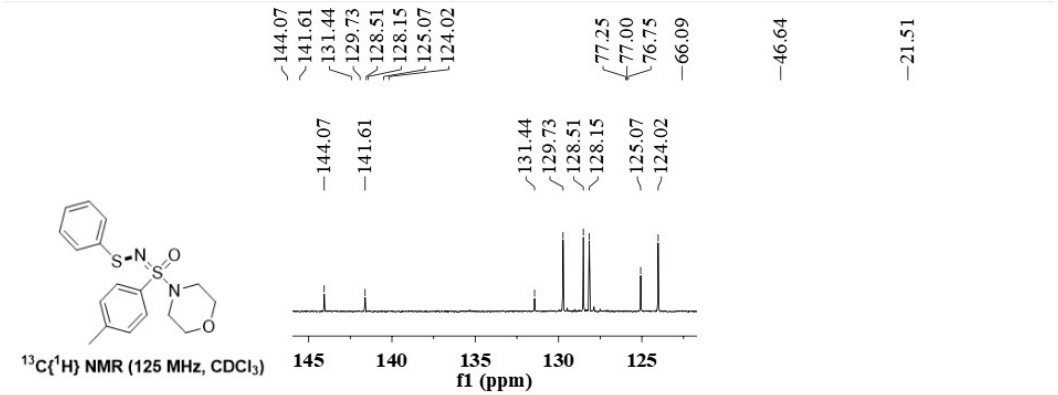
$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$)

N-(Morpholino(oxo)(p-tolyl)-λ⁶-sulfaneylidene)-*S*-phenylthiohydroxylamine (3wa)

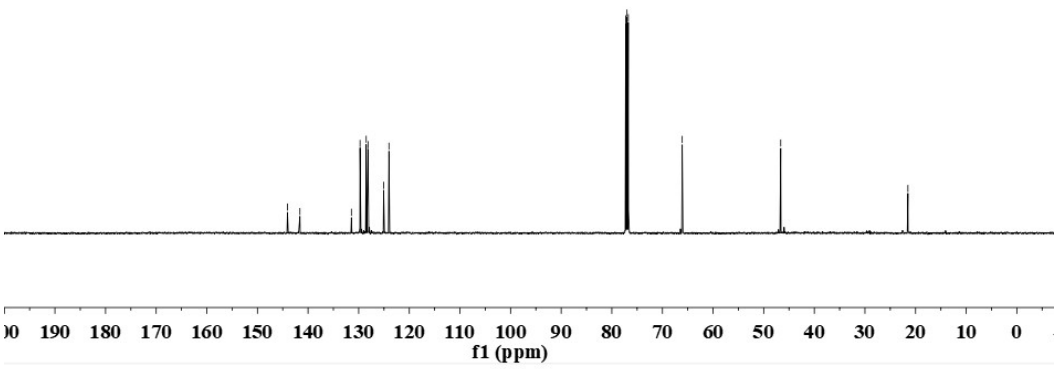


^{1}H NMR (500 MHz, $CDCl_3$)

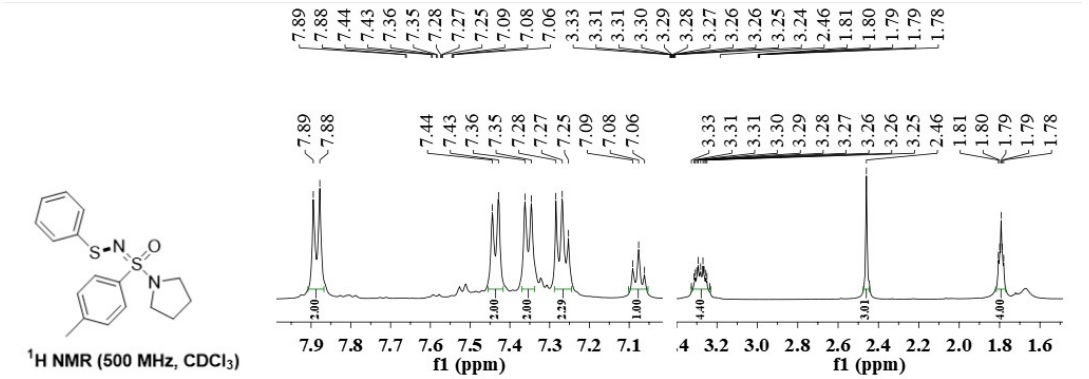




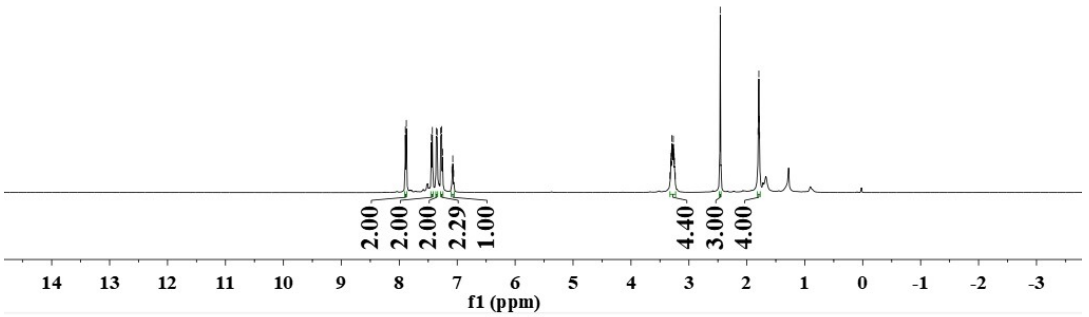
$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$)

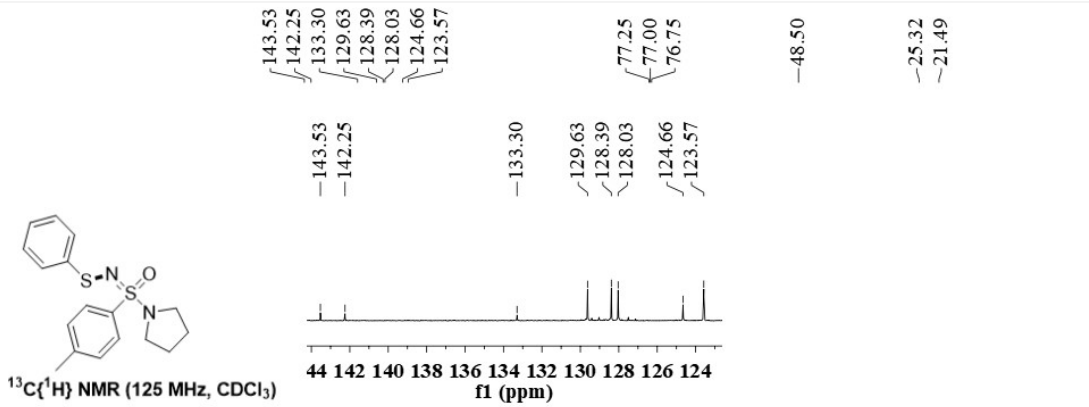


***N*-(Oxo(pyrrolidin-1-yl)(p-tolyl)-λ^6-sulfaneylidene)-*S*-phenylthiohydroxylamine (3xa)**

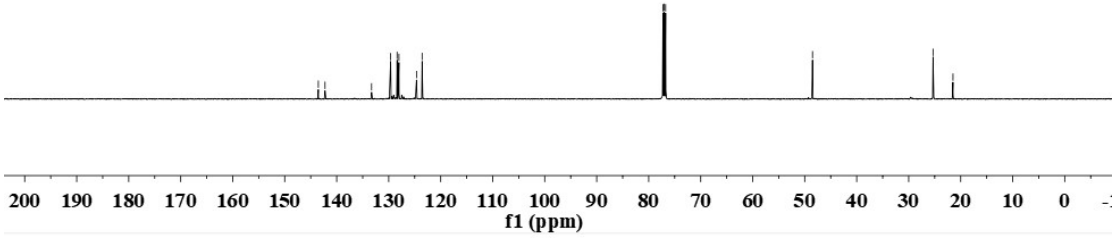


^{1}H NMR (500 MHz, $CDCl_3$)

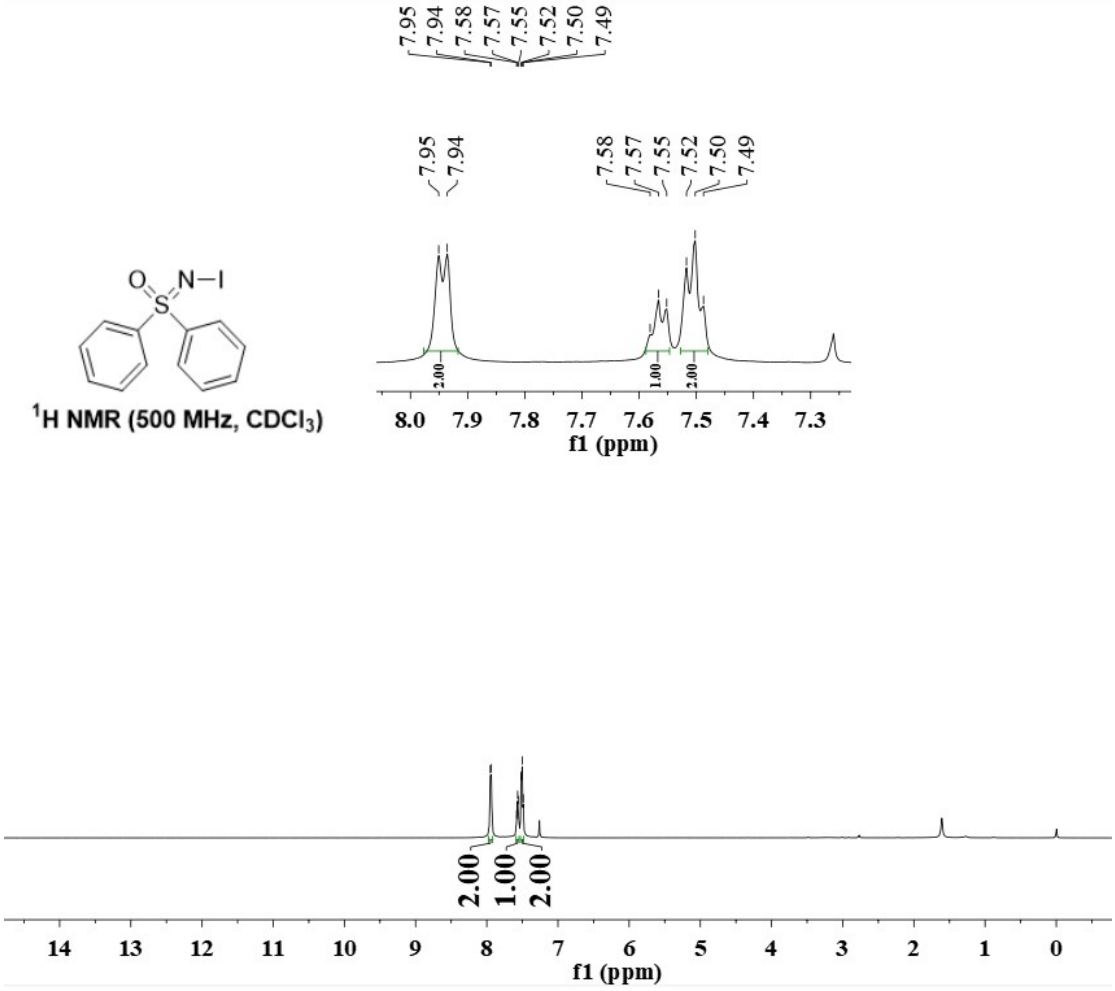




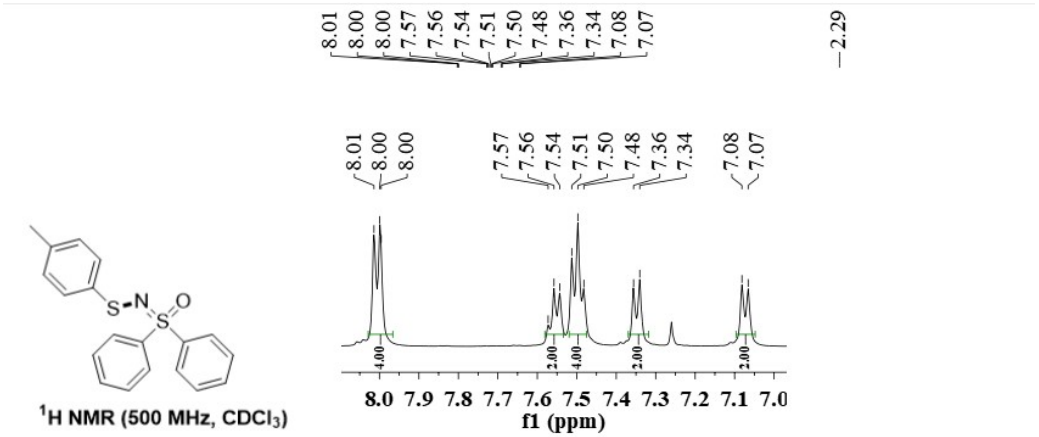
$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$)

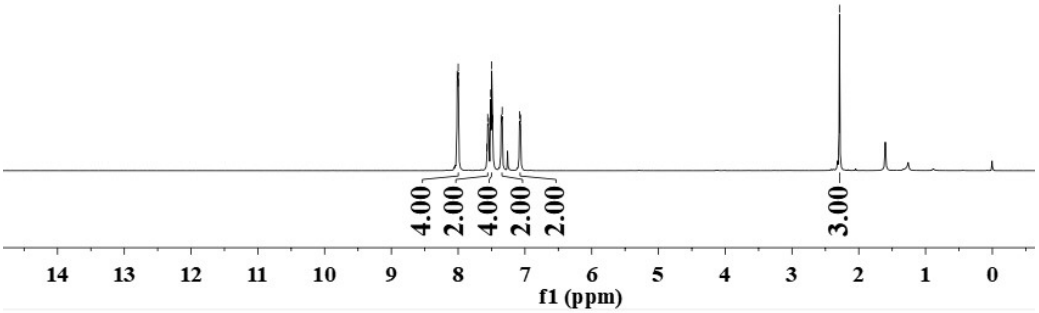


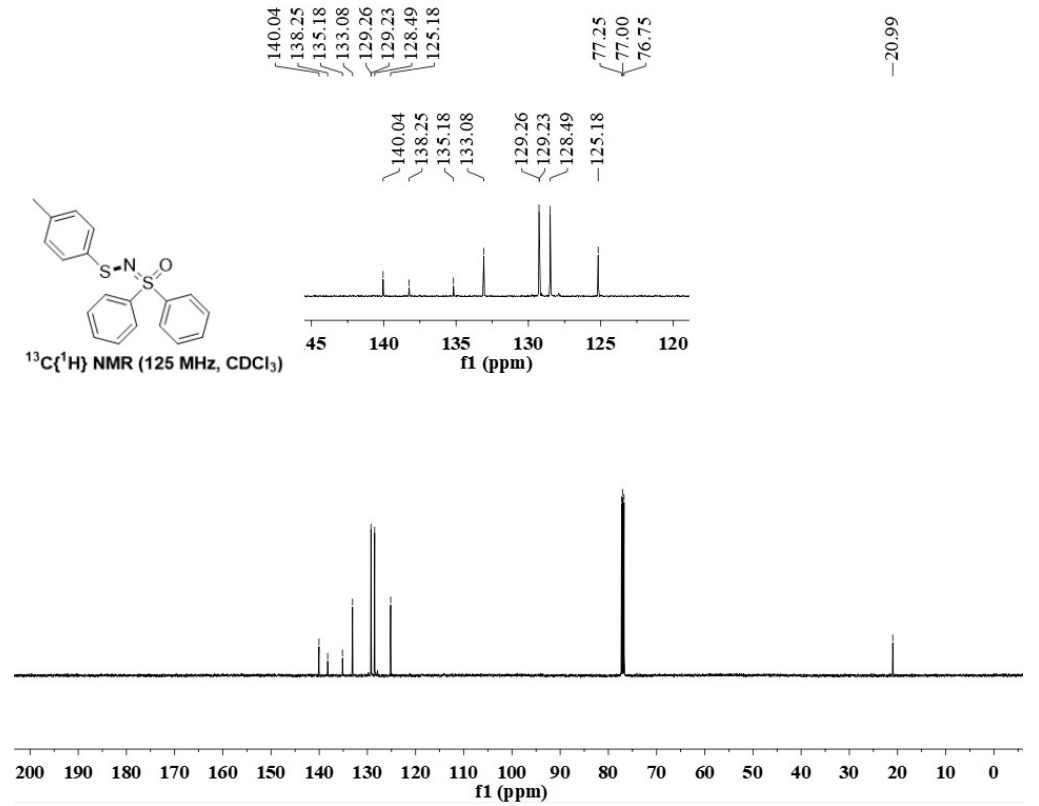
(iodoimino)diphenyl-λ6-sulfanone (1y)



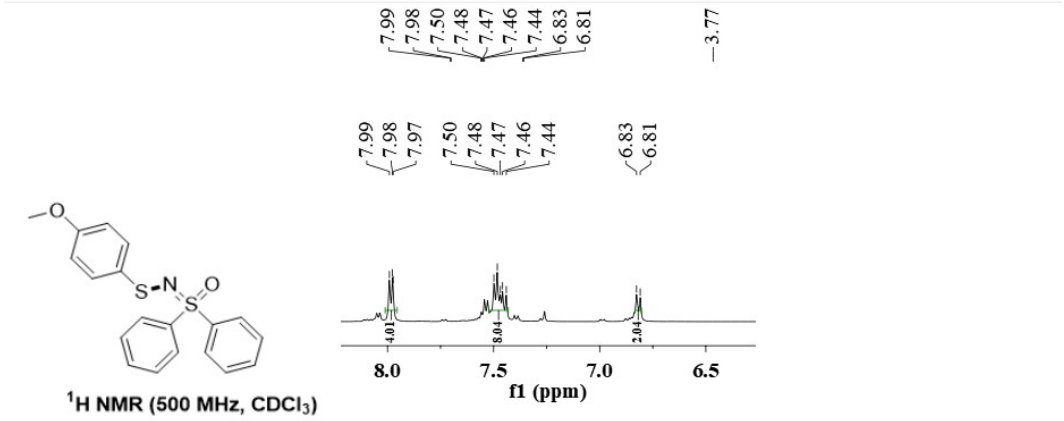
Diphenyl((p-tolylthio)imino)-λ⁶-sulfanone (3ab)



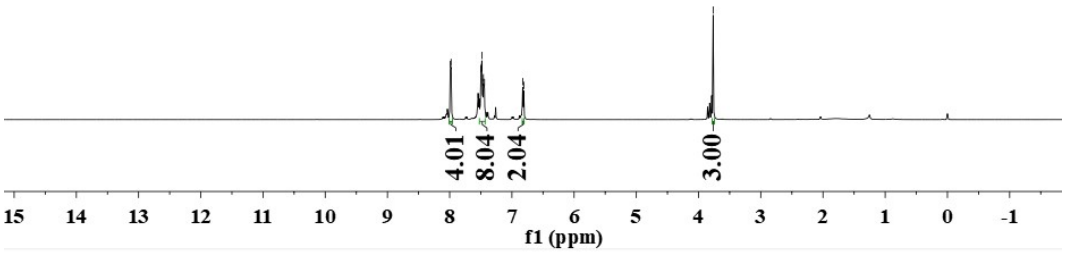


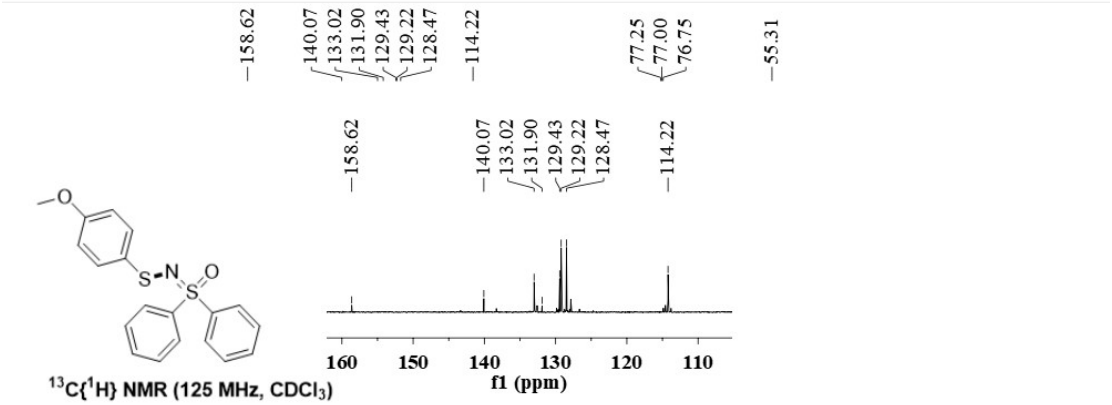


(((4-Methoxyphenyl)thio)imino)diphenyl-λ⁶-sulfanone (3ac)

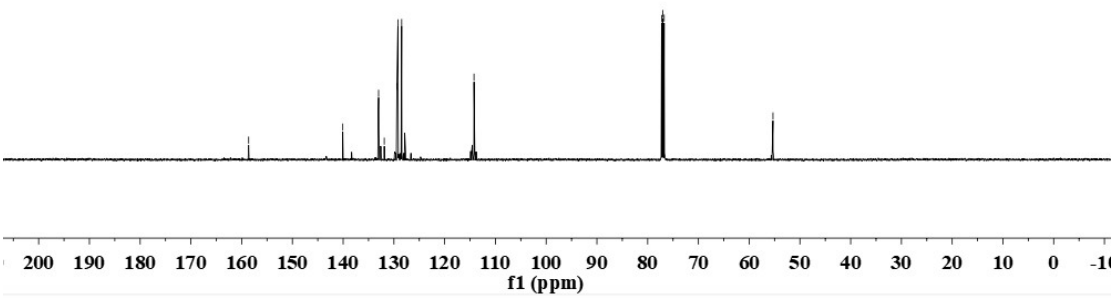


^{1}H NMR (500 MHz, $CDCl_3$)

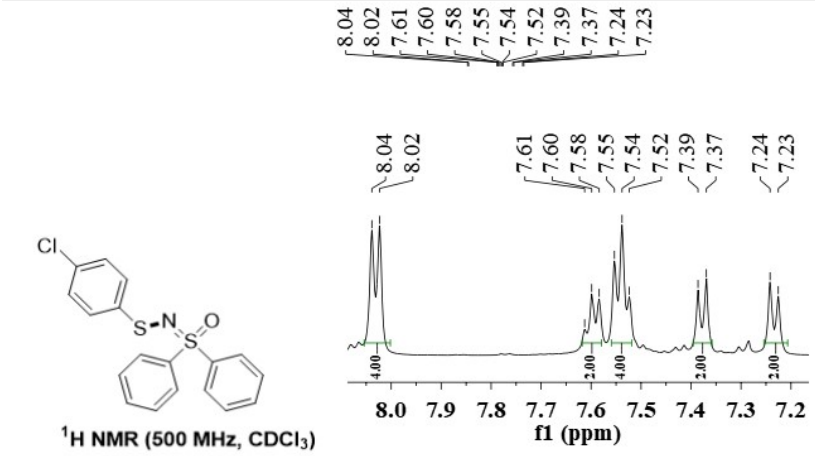


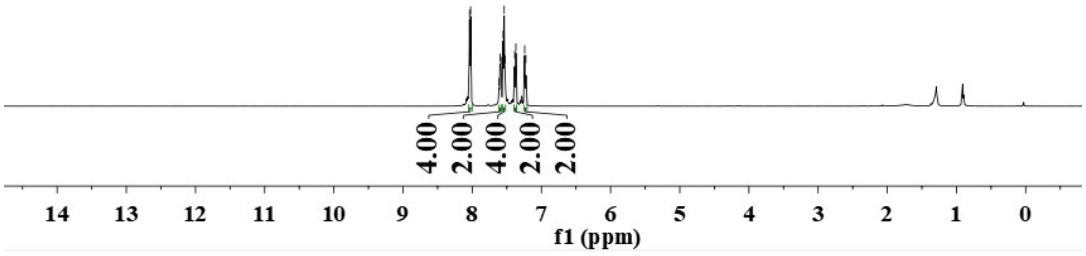


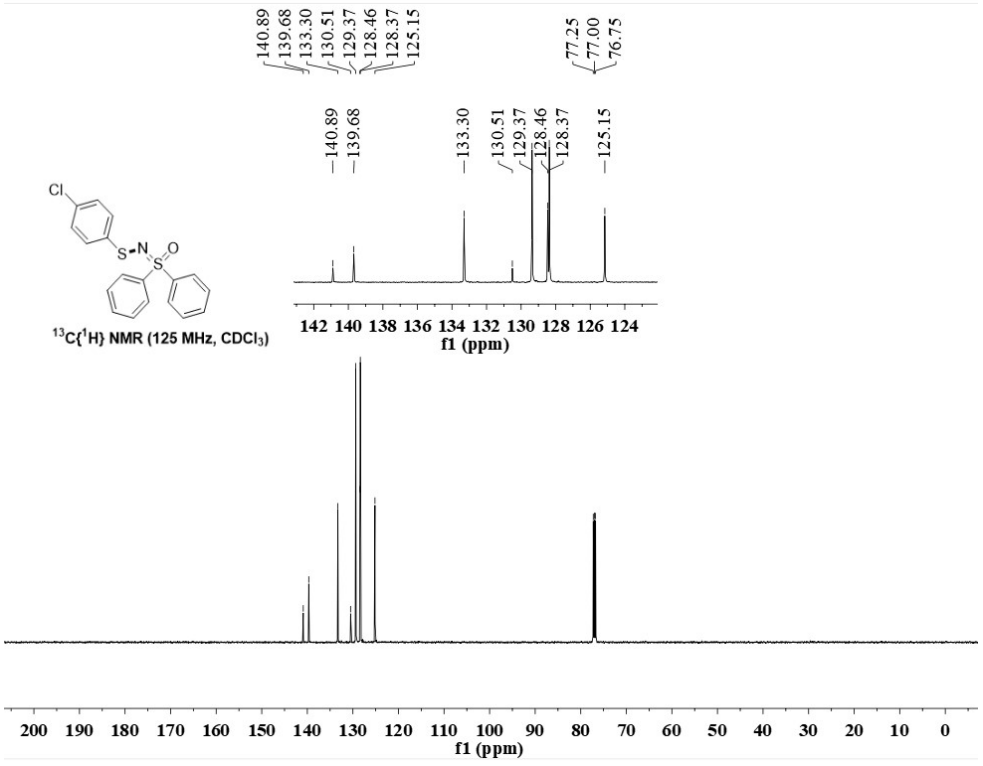
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



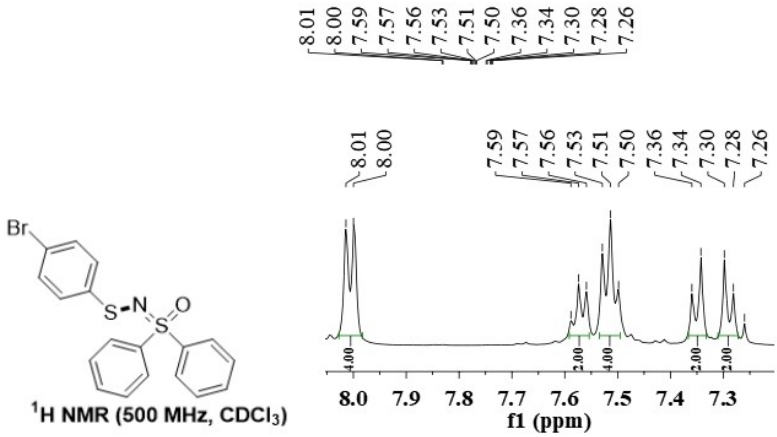
(((4-Chlorophenyl)thio)imino)diphenyl-λ⁶-sulfanone (3ad)



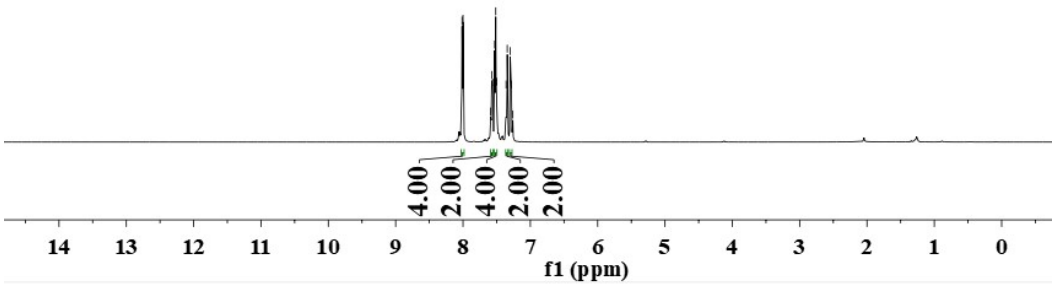


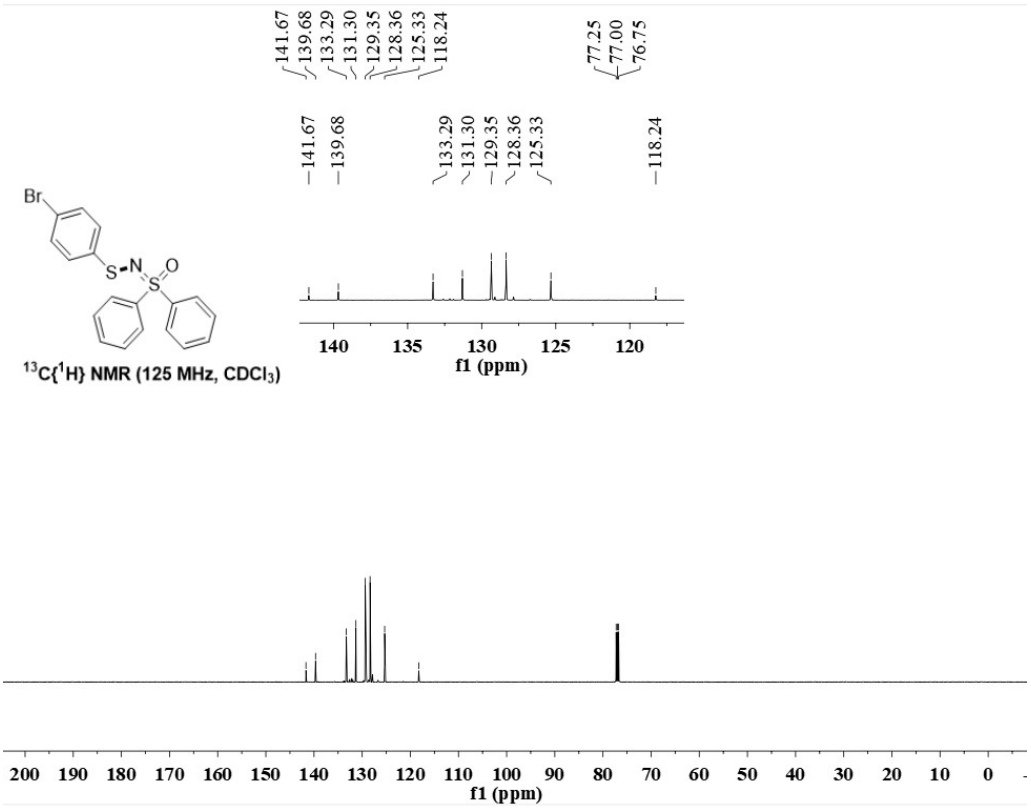


(((4-Bromophenyl)thio)imino)diphenyl-λ⁶-sulfanone (3ae)



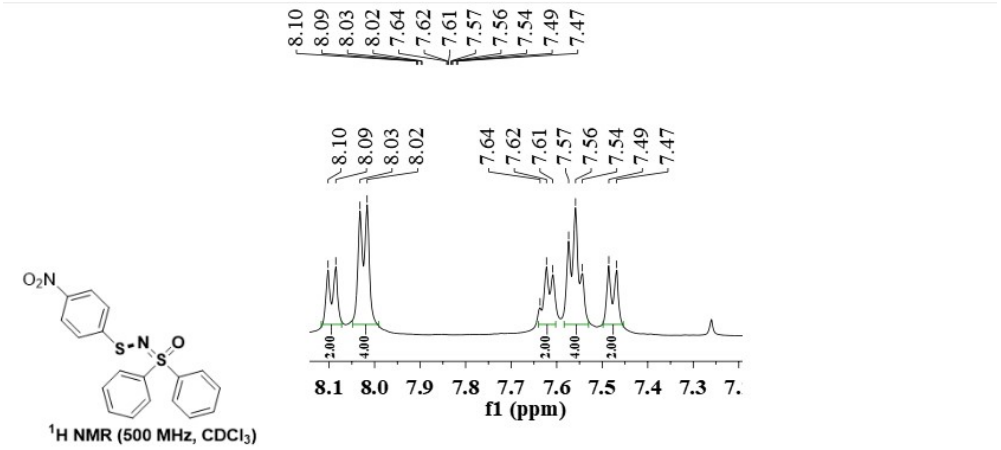
^{1}H NMR (500 MHz, $CDCl_3$)

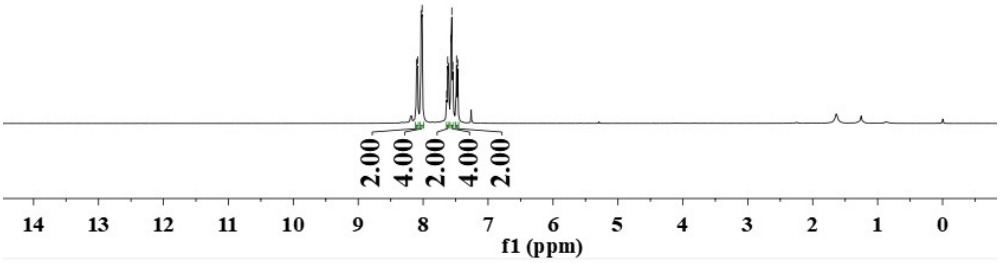


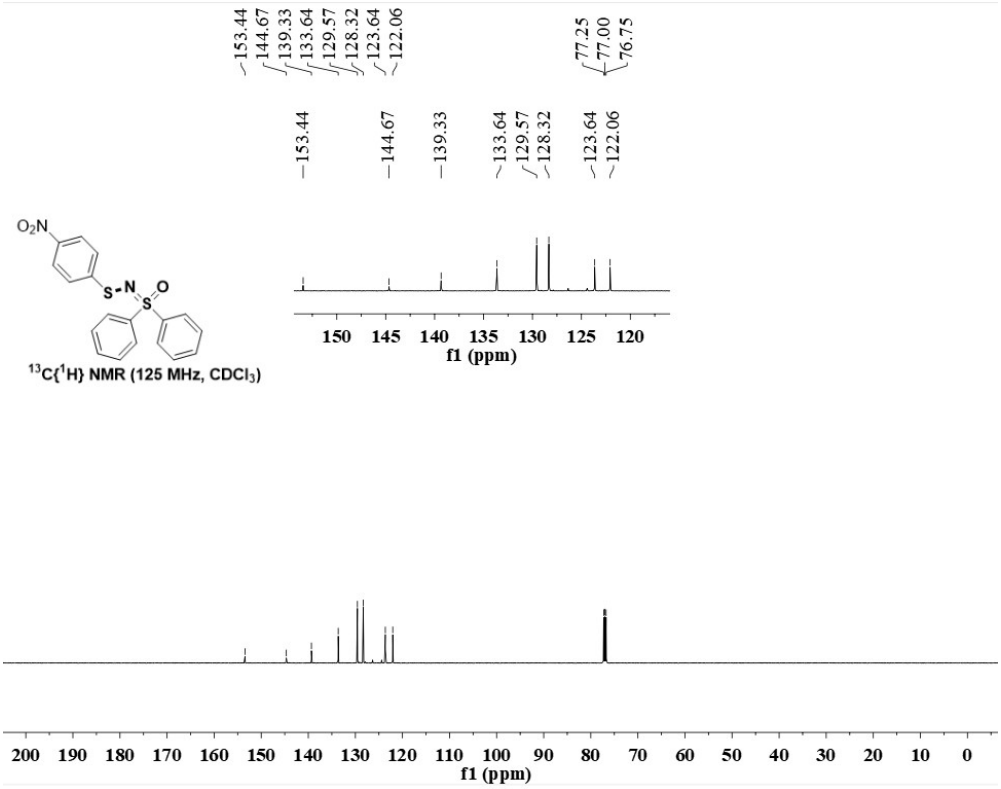


$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

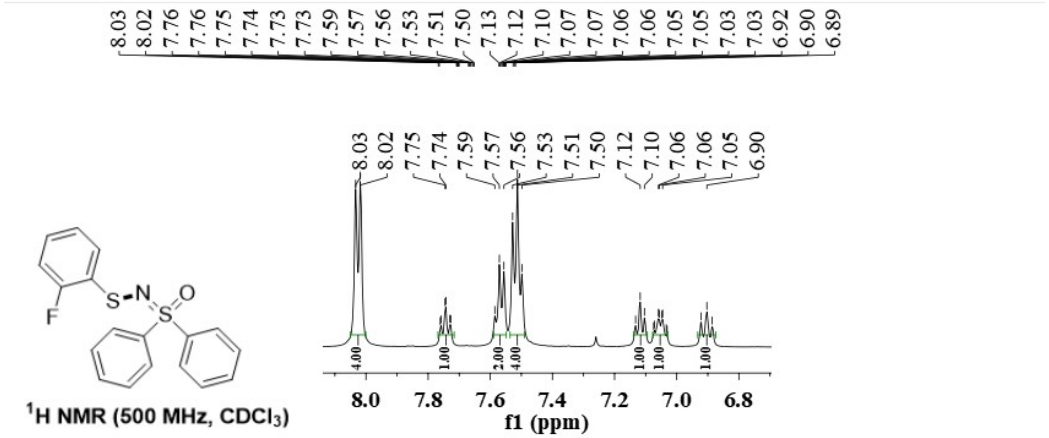
(((4-Nitrophenyl)thio)imino)diphenyl-λ^6-sulfanone (3af)



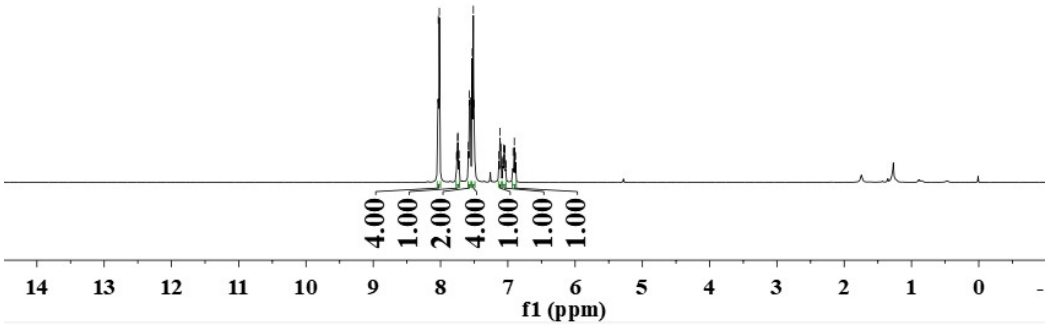


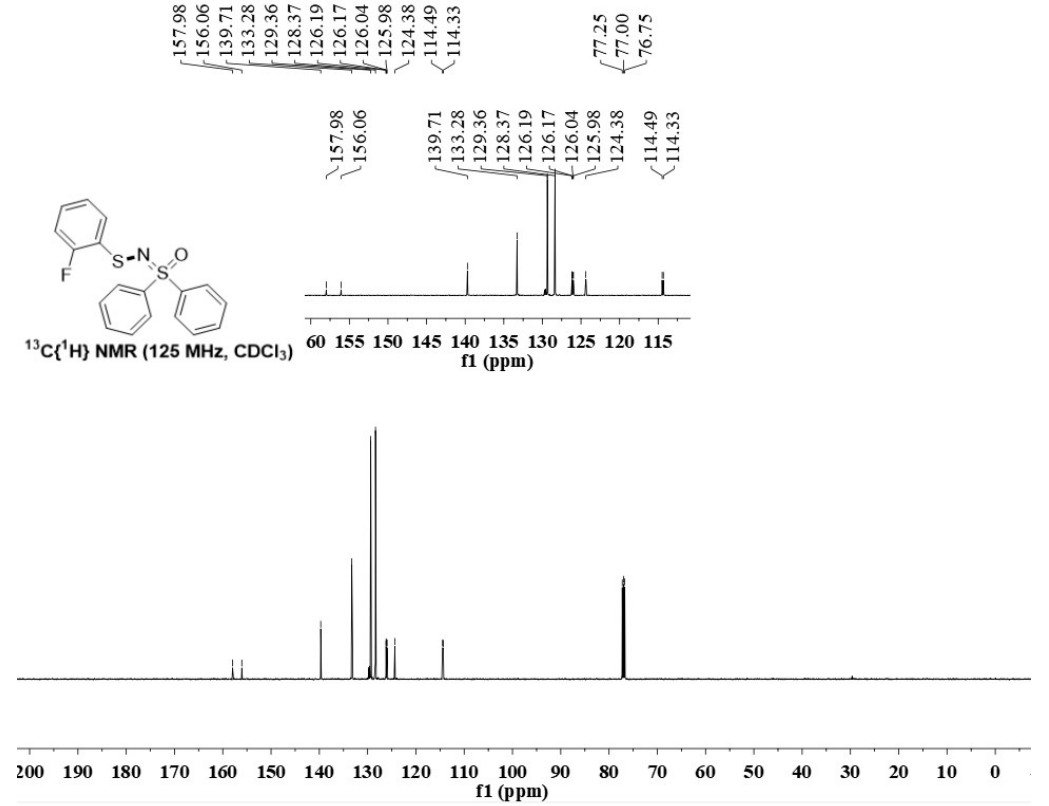


(((2-Fluorophenyl)thio)imino)diphenyl-λ⁶-sulfanone (3ag)



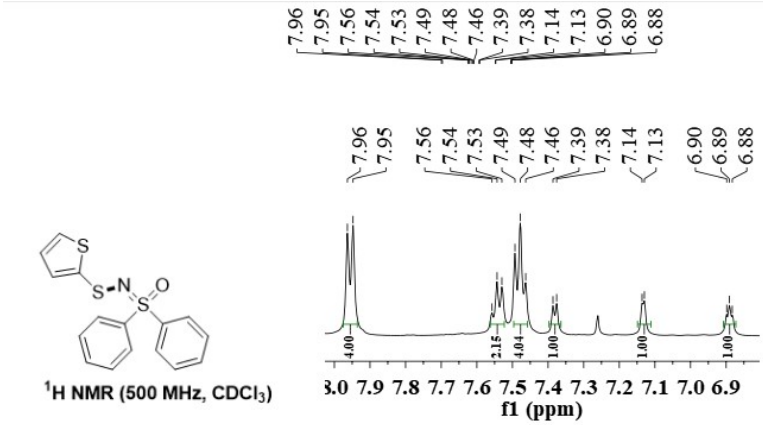
^{1}H NMR (500 MHz, $CDCl_3$)



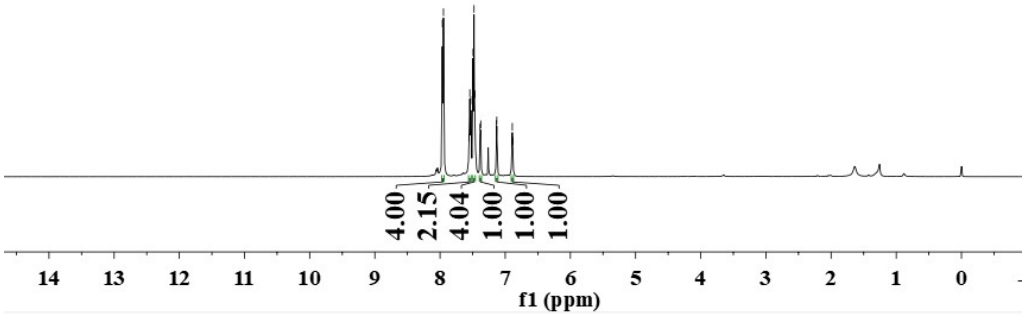


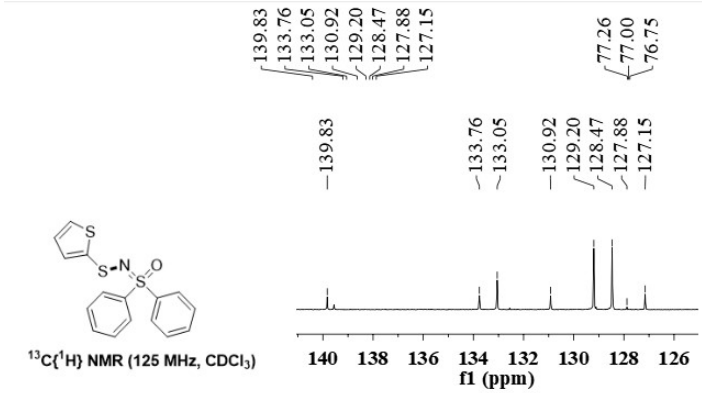
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

Diphenyl((thiophen-2-ylthio)imino)-λ⁶-sulfanone (3ah)

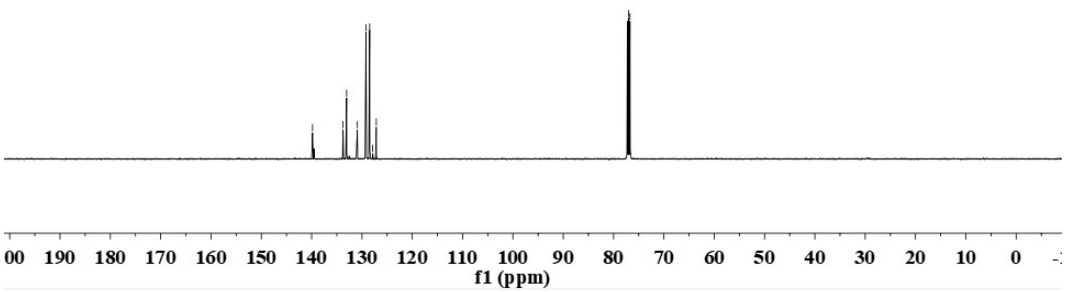


^{1}H NMR (500 MHz, $CDCl_3$)

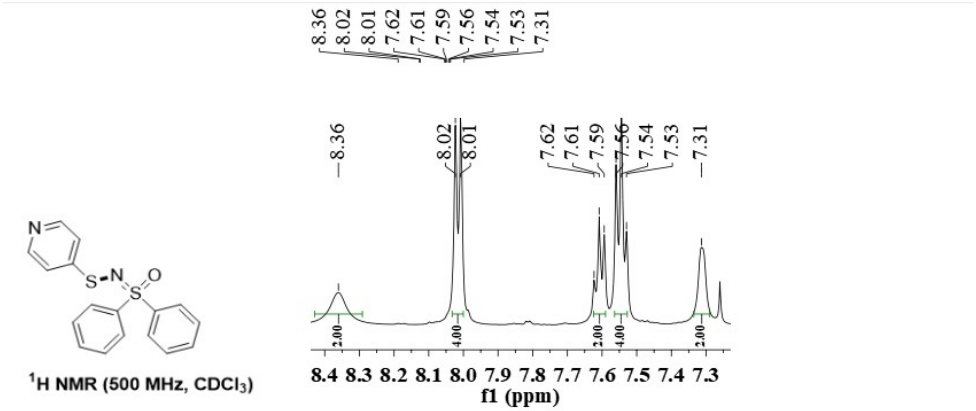




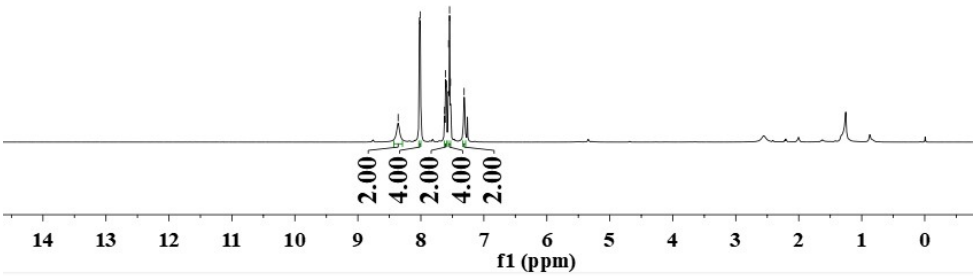
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)

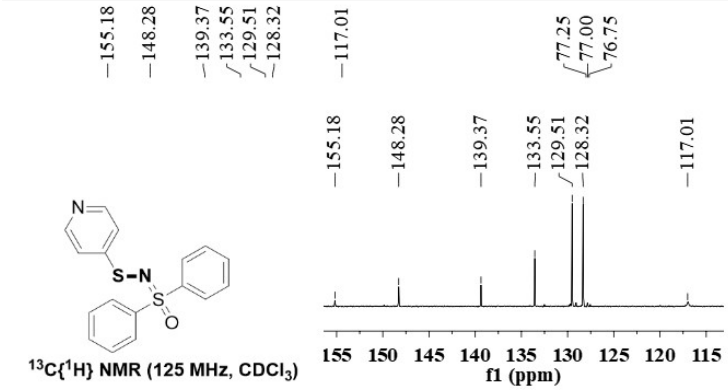


Diphenyl((pyridin-4-ylthio)imino)-λ⁶-sulfanone (3ai)

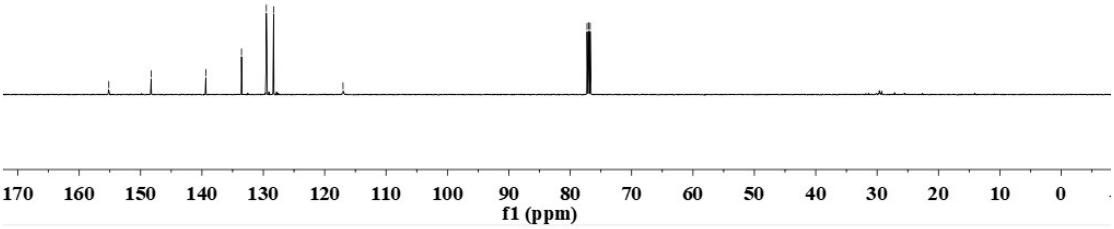


^{1}H NMR (500 MHz, $CDCl_3$)

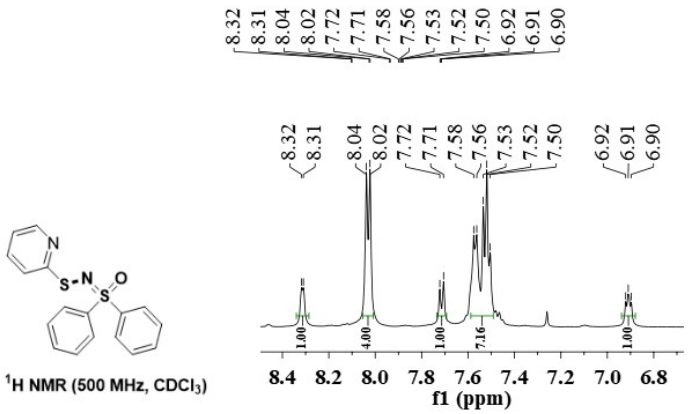




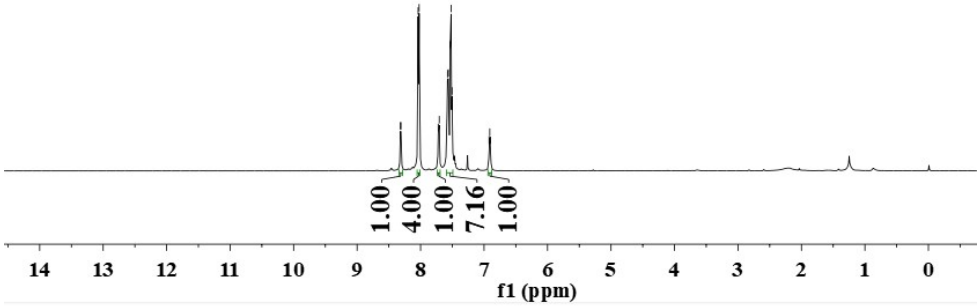
$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$)

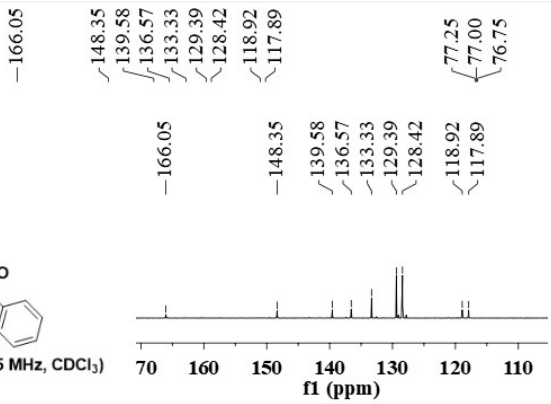


Diphenyl((pyridin-2-ylthio)imino)-λ⁶-sulfanone (3aj)

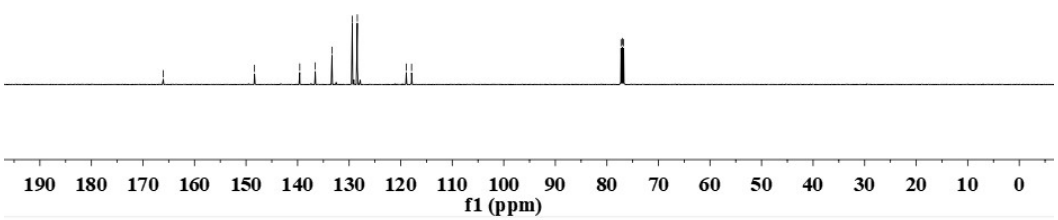


^{1}H NMR (500 MHz, $CDCl_3$)

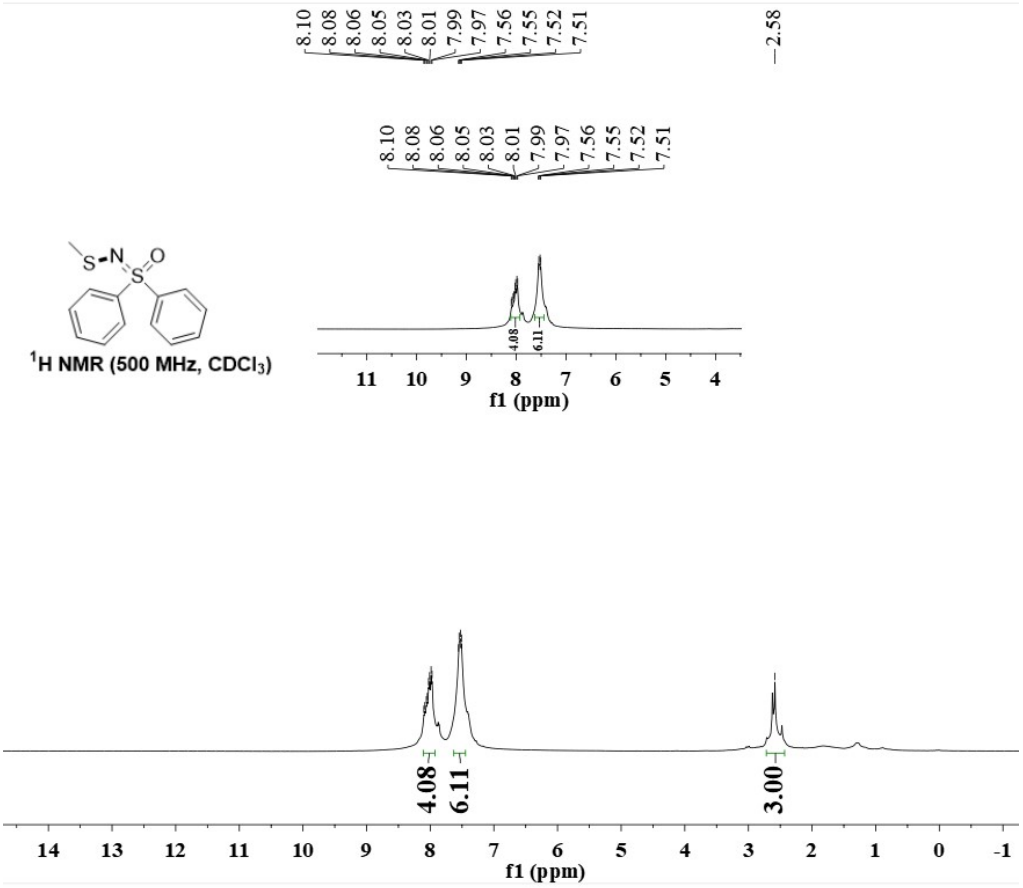




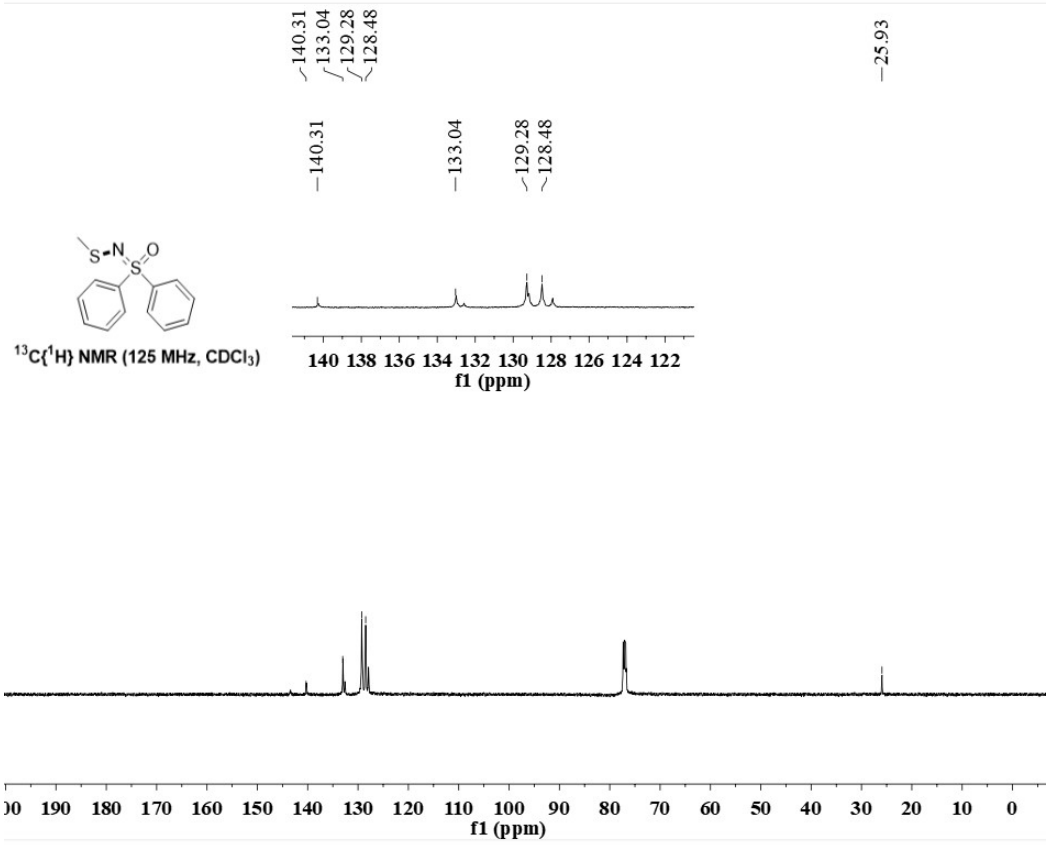
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



((Methylthio)imino)diphenyl-λ^6-sulfanone (3ak)

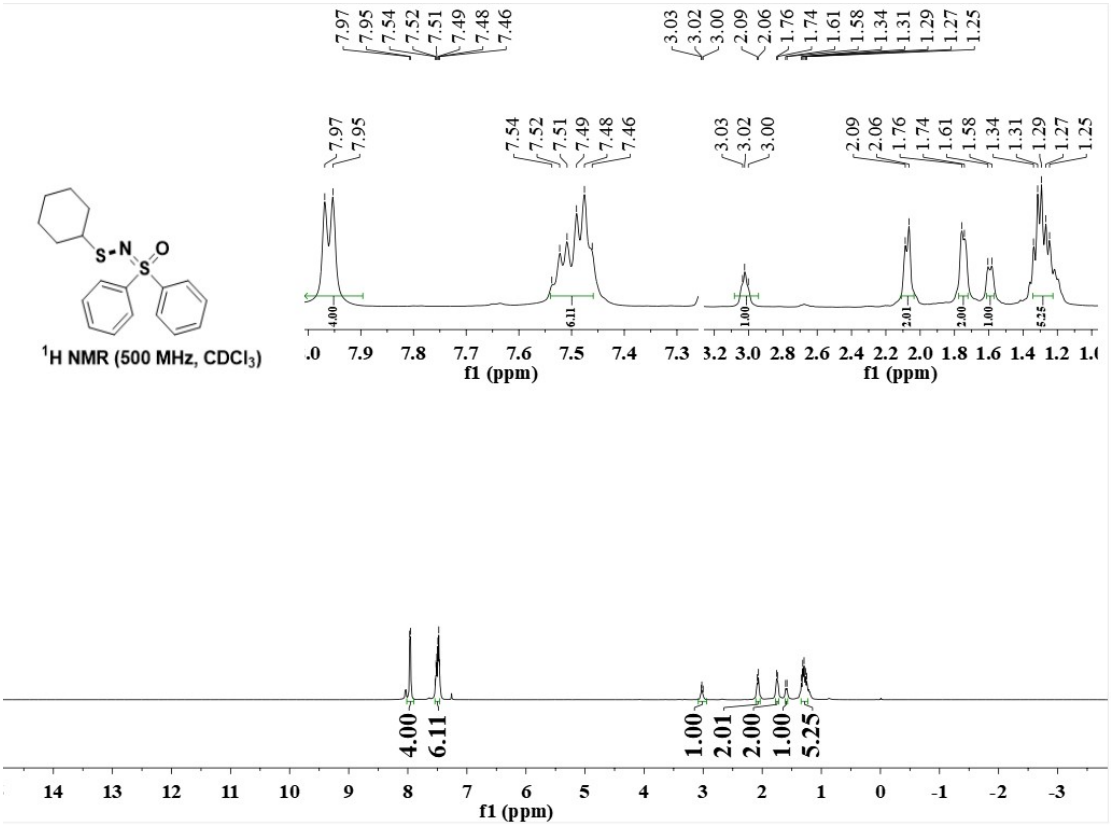


^{1}H NMR (500 MHz, $CDCl_3$)

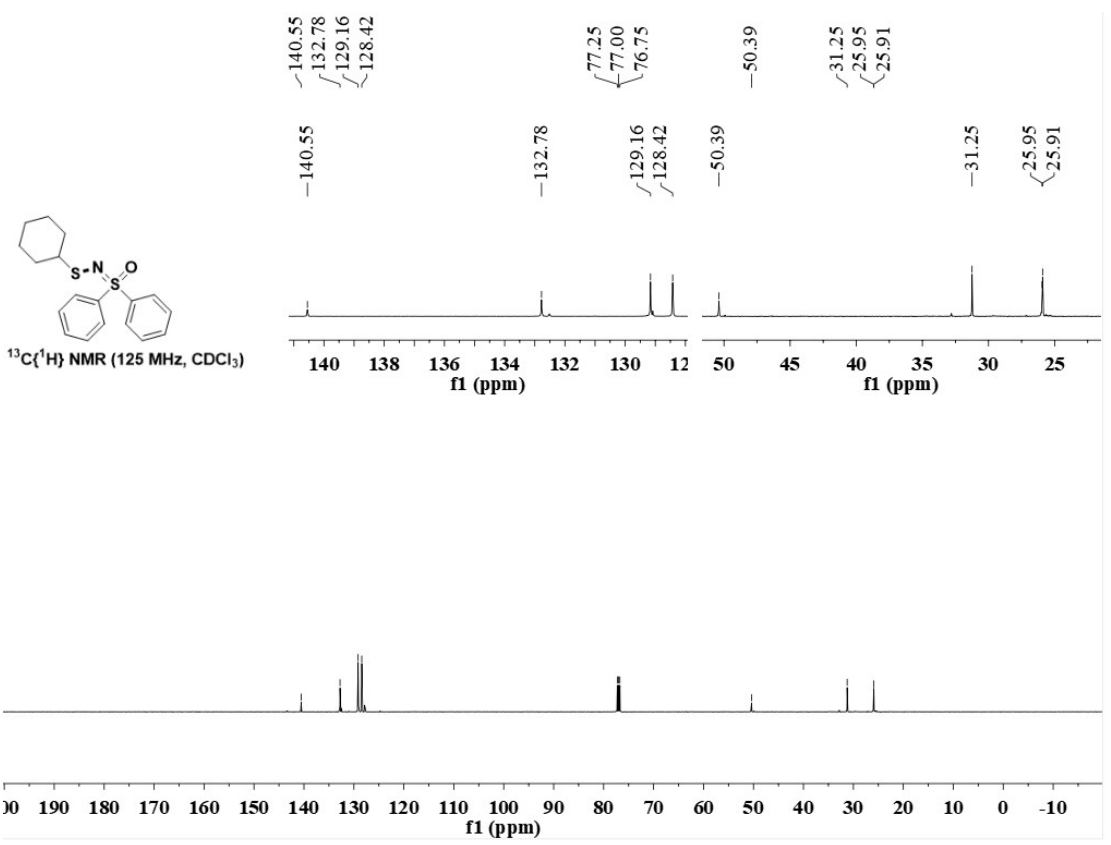


$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$)

((Cyclohexylthio)imino)diphenyl-λ⁶-sulfanone (3al)

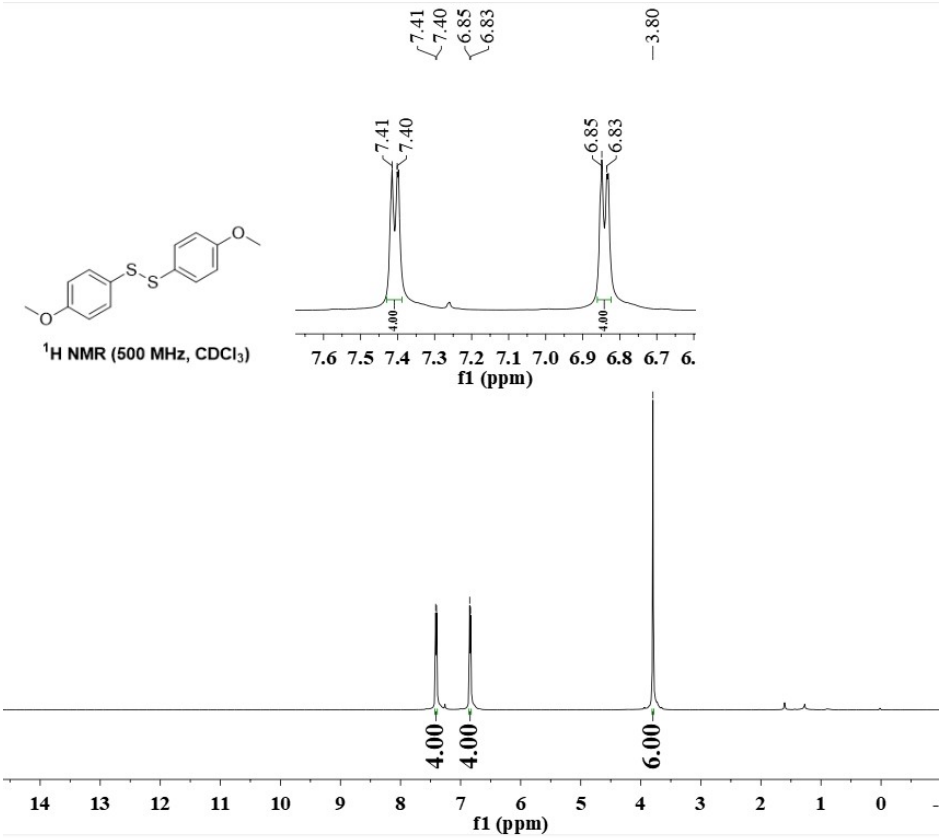


^{1}H NMR (500 MHz, $CDCl_3$)

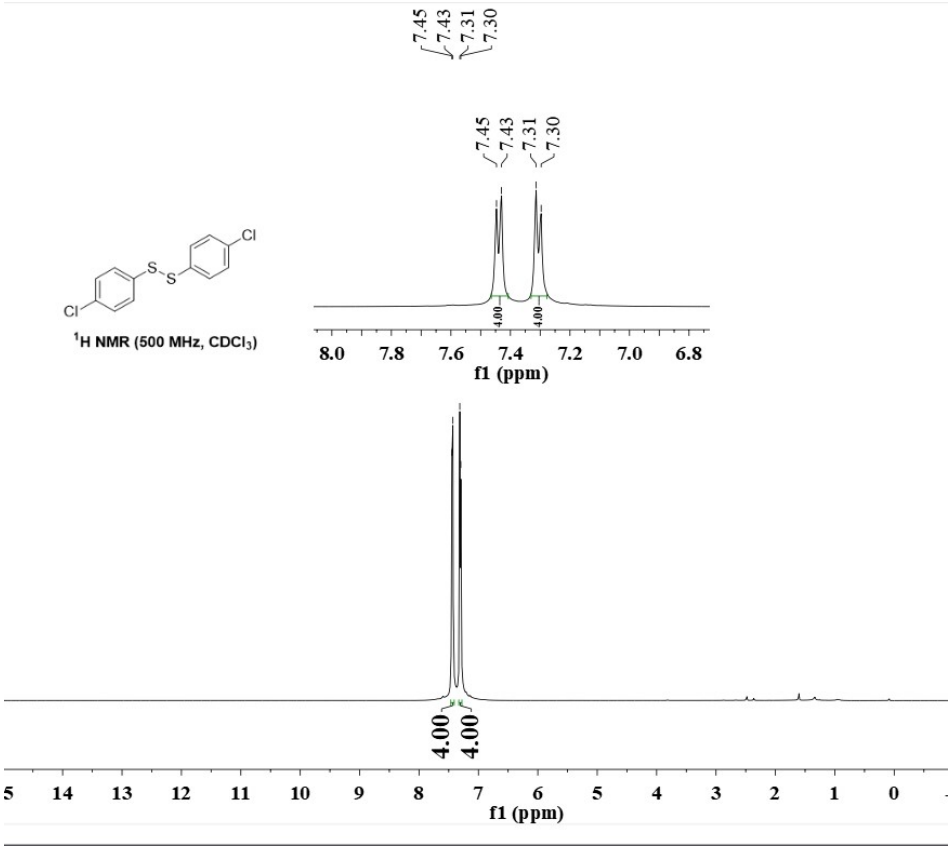


$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$)

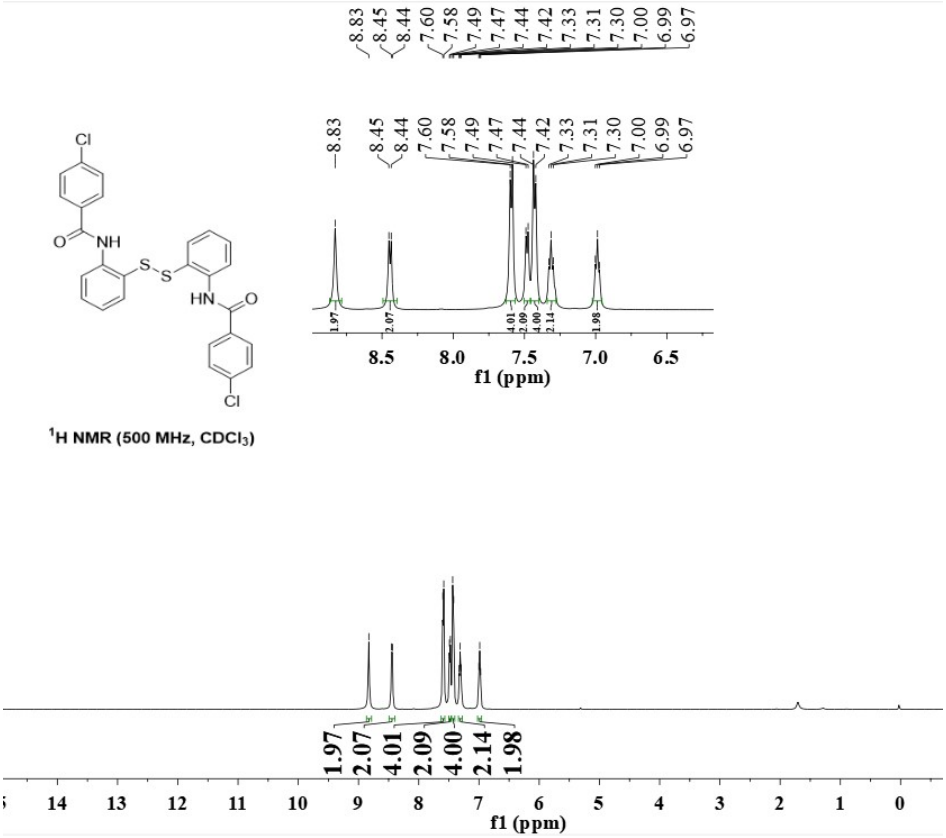
1,2-Bis(4-methoxyphenyl) disulfane (2c)



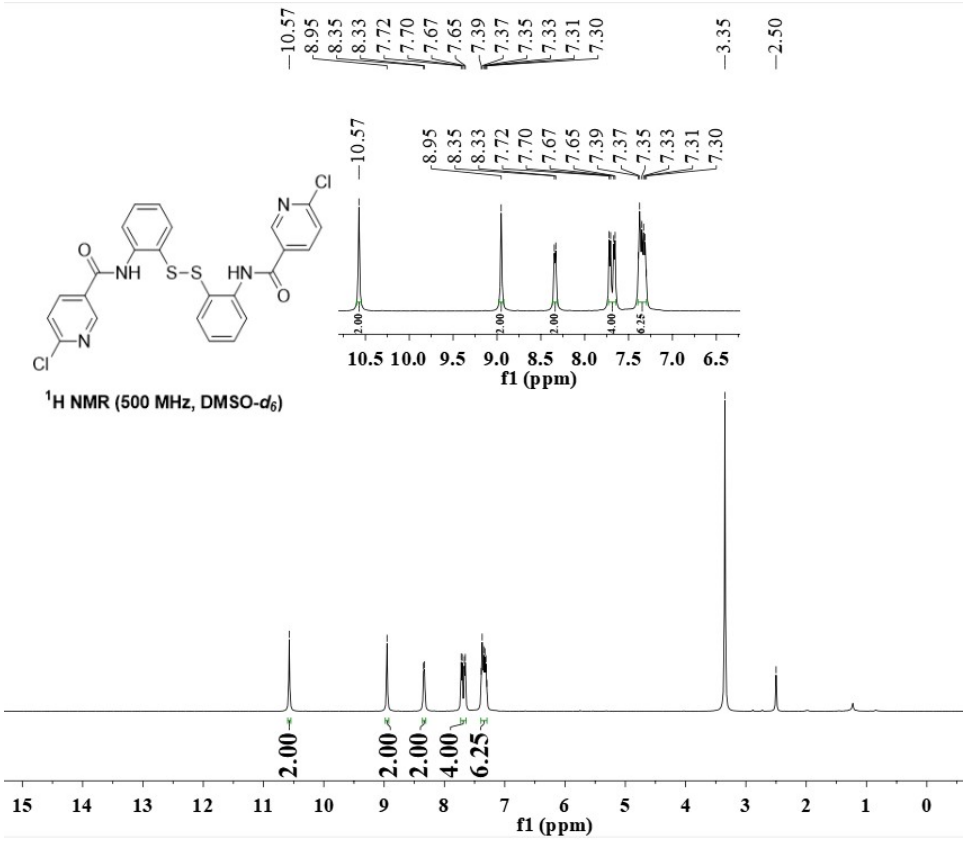
Bis(4-chlorophenyl) disulfide (2d)



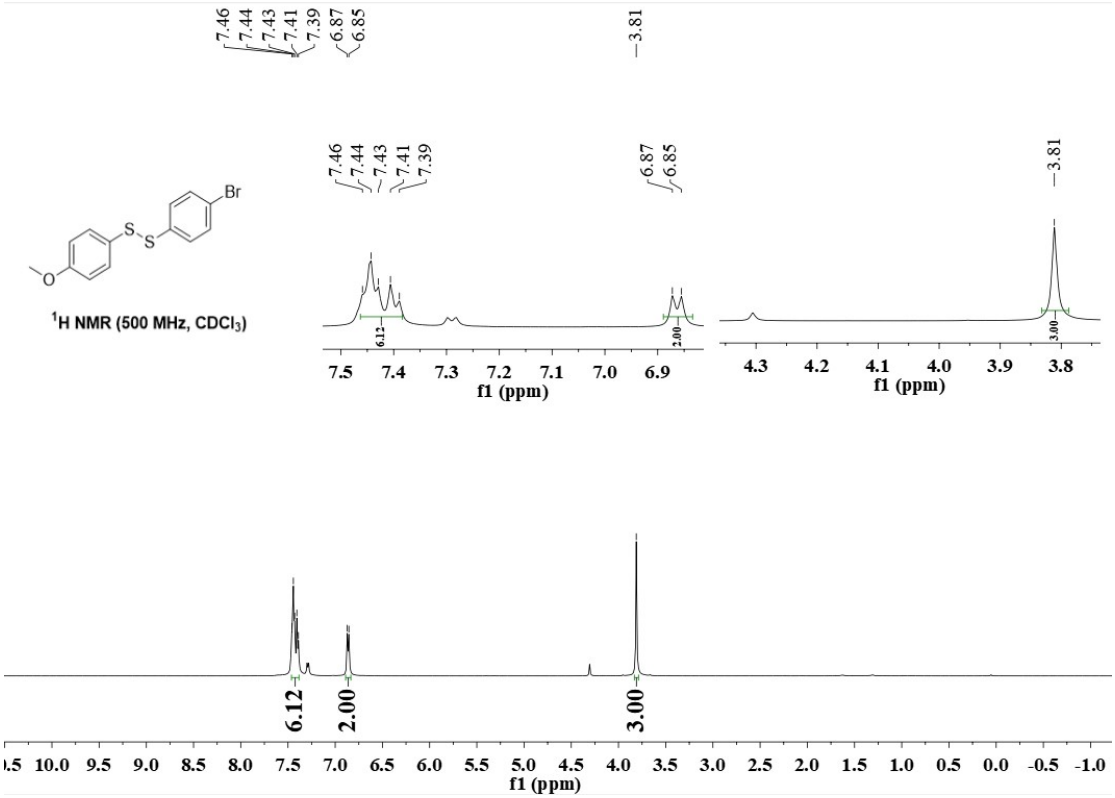
***N,N'*-(Disulfanediylbis(2,1-phenylene))bis(4-chlorobenzamide) (2m)**



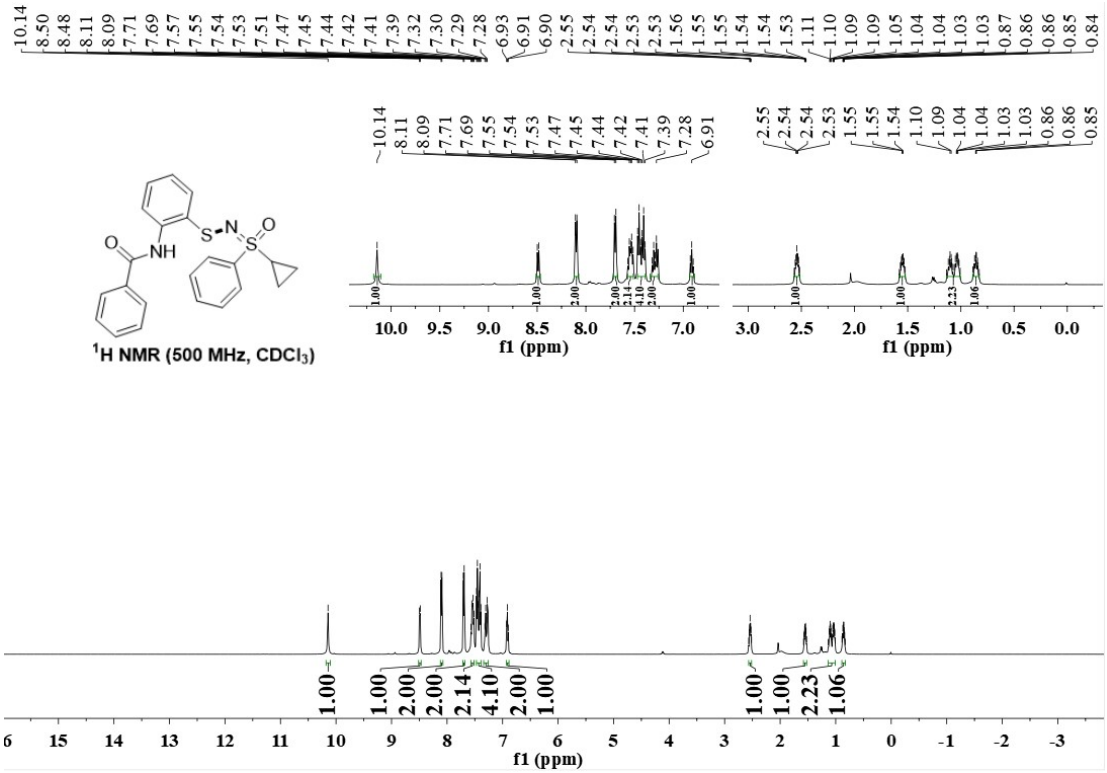
***N,N'*-(Disulfanediylbis(2,1-phenylene))bis(6-chloronicotinamide) (2n)**

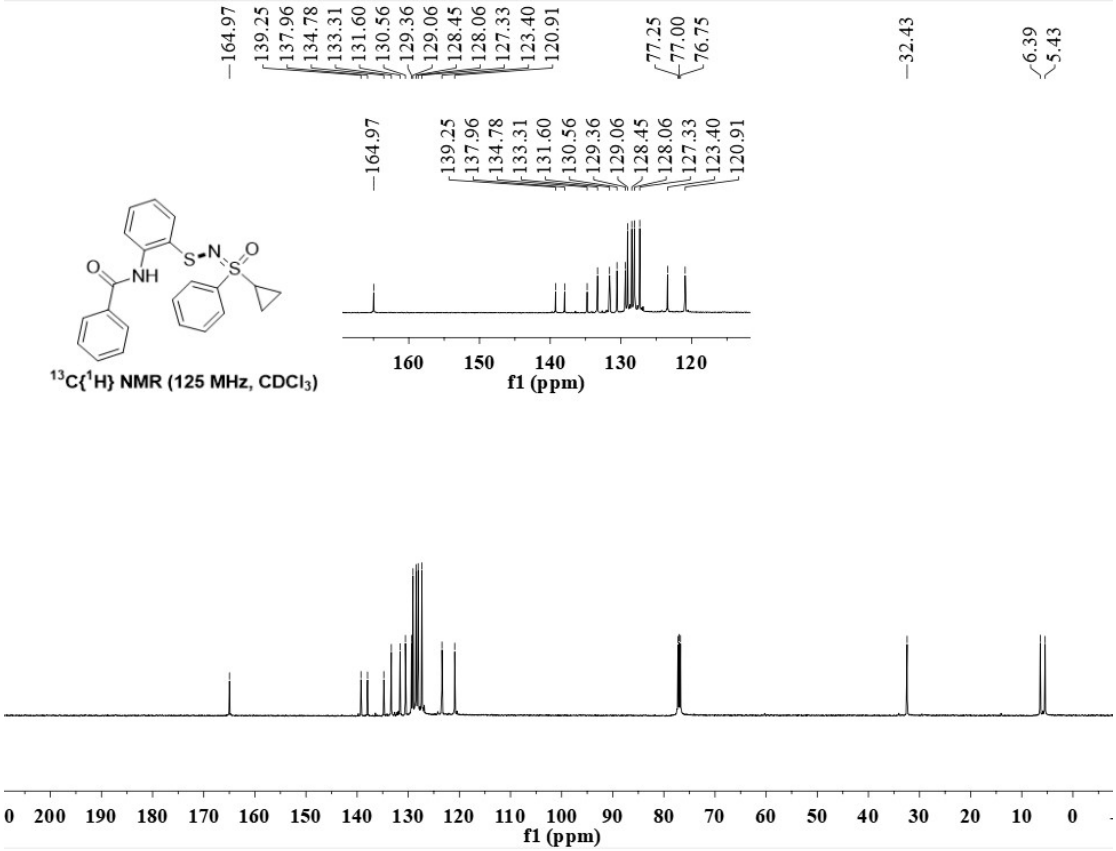


1-(4-Bromophenyl)-2-(4-methoxyphenyl)disulfane (2o)

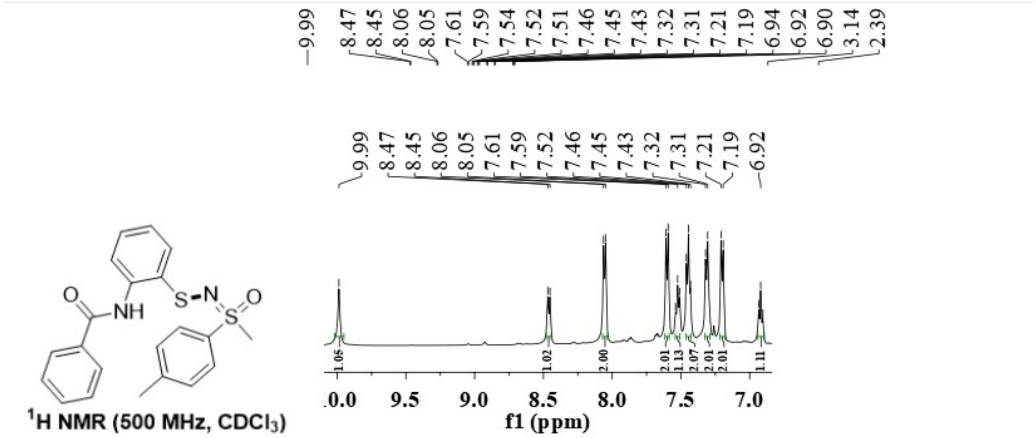


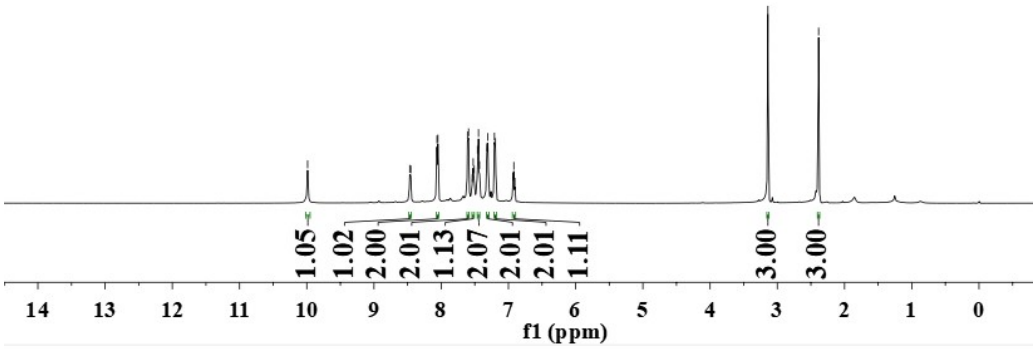
***N*-(2-(((Cyclopropyl(oxo)(phenyl)-λ⁶-sulfaneylidene)amino)thio)phenyl)-benzamide (4a)**

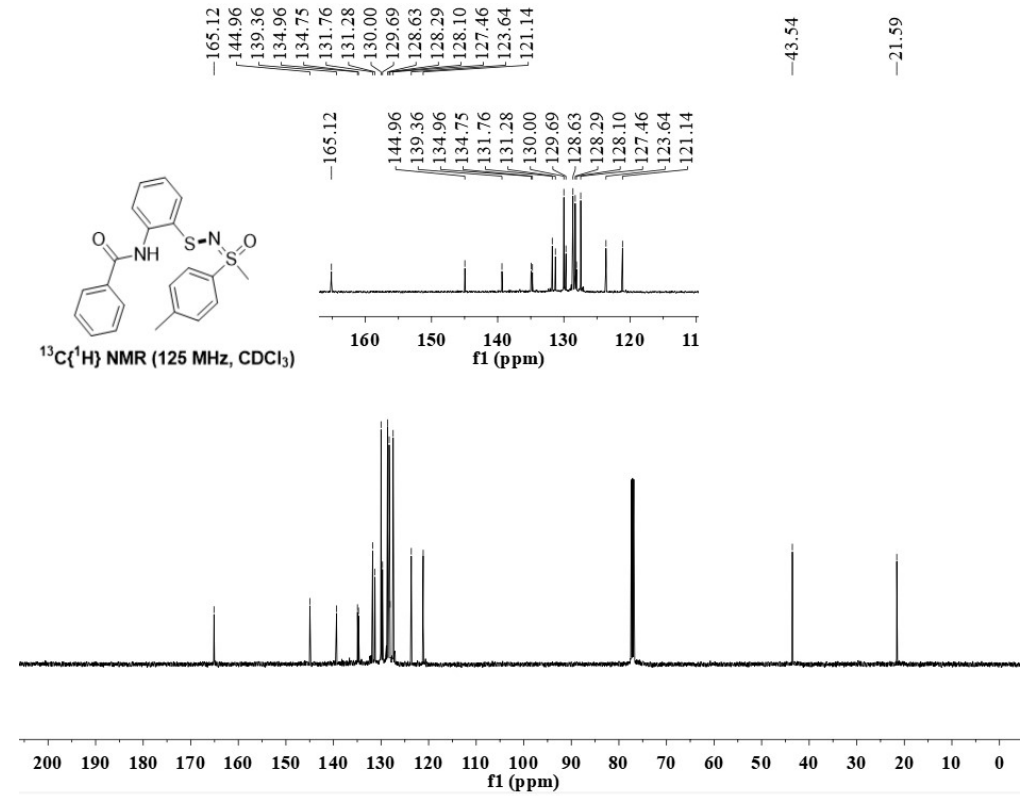




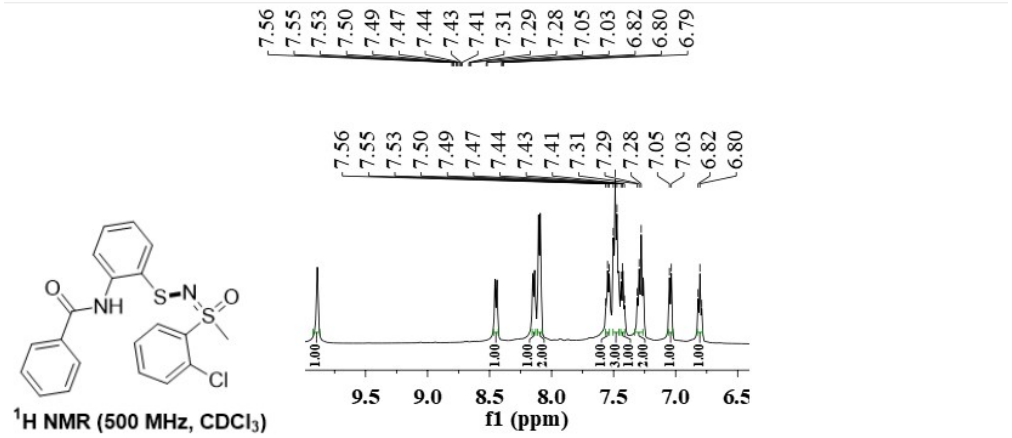
N-(2-(((Methyl(oxo)(p-tolyl)-λ^6-sulfaneylidene)amino)thio)phenyl)benzamide (4b)

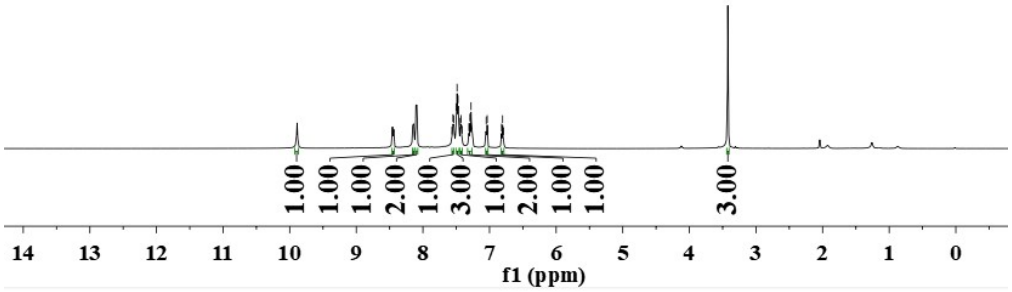


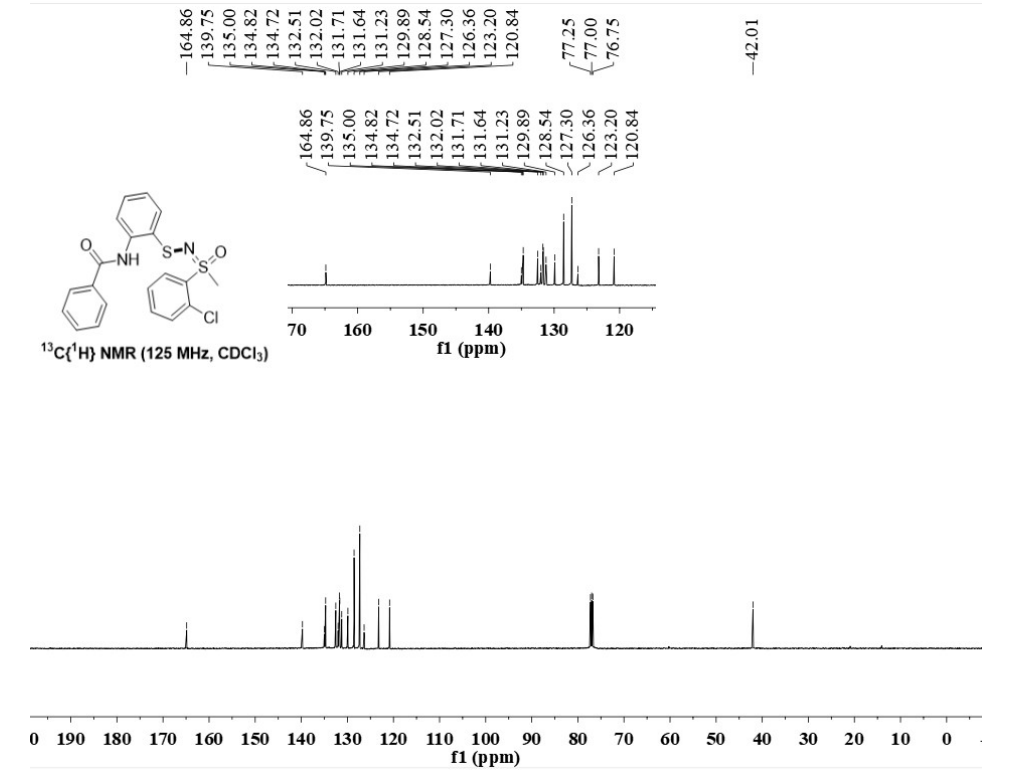




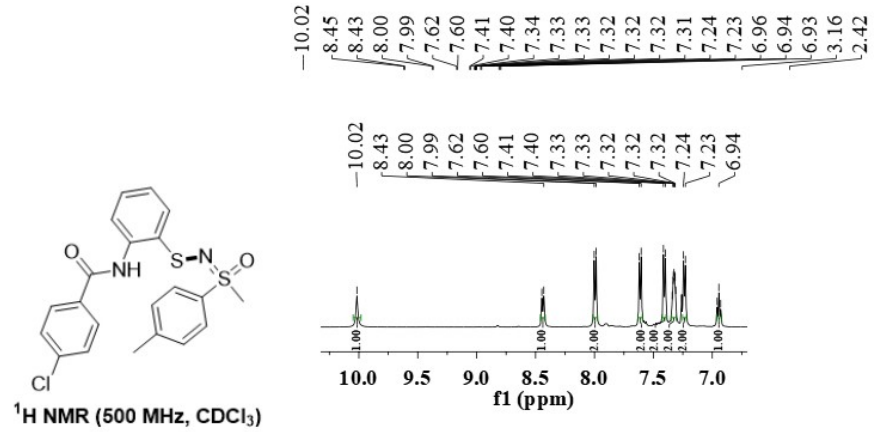
***N*-(2-((((2-Chlorophenyl)(methyl)(oxo)-λ⁶-sulfaneylidene)amino)thio)phenyl)-benzamide (4c)**

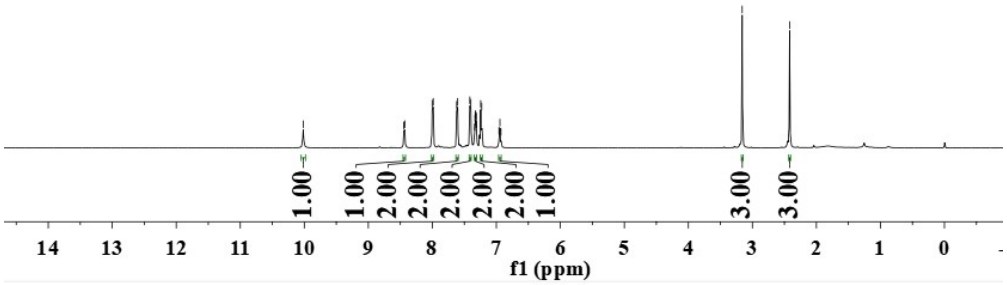


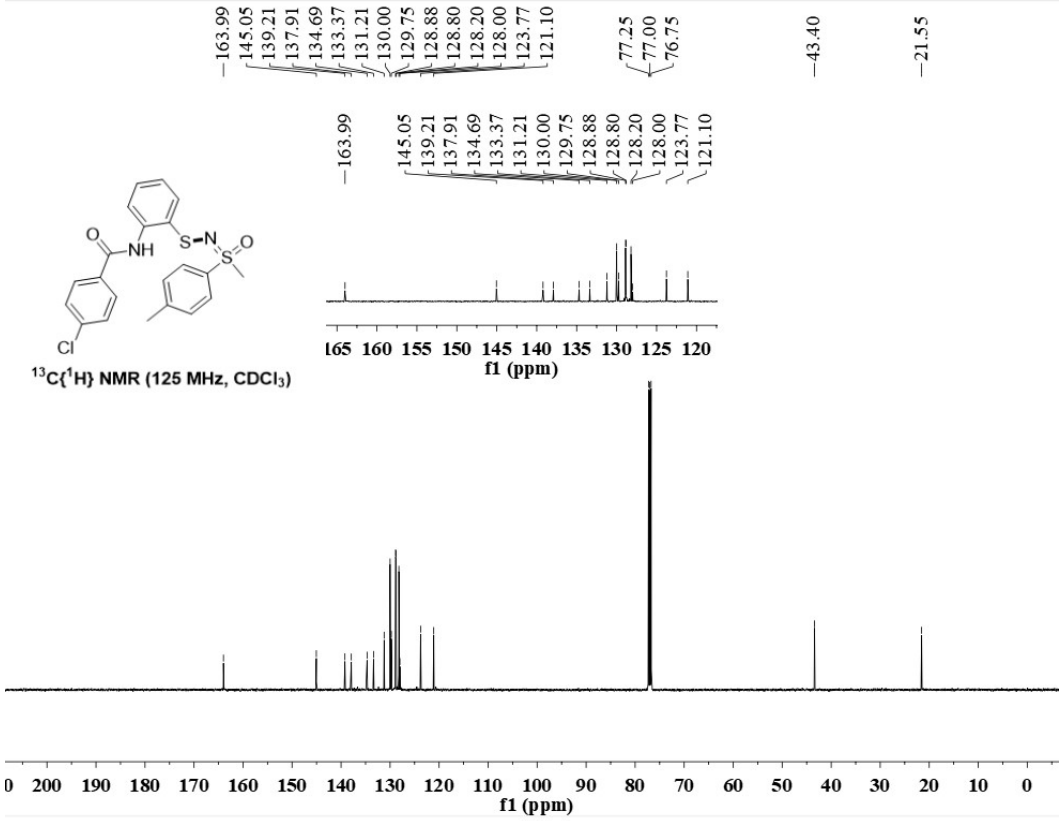




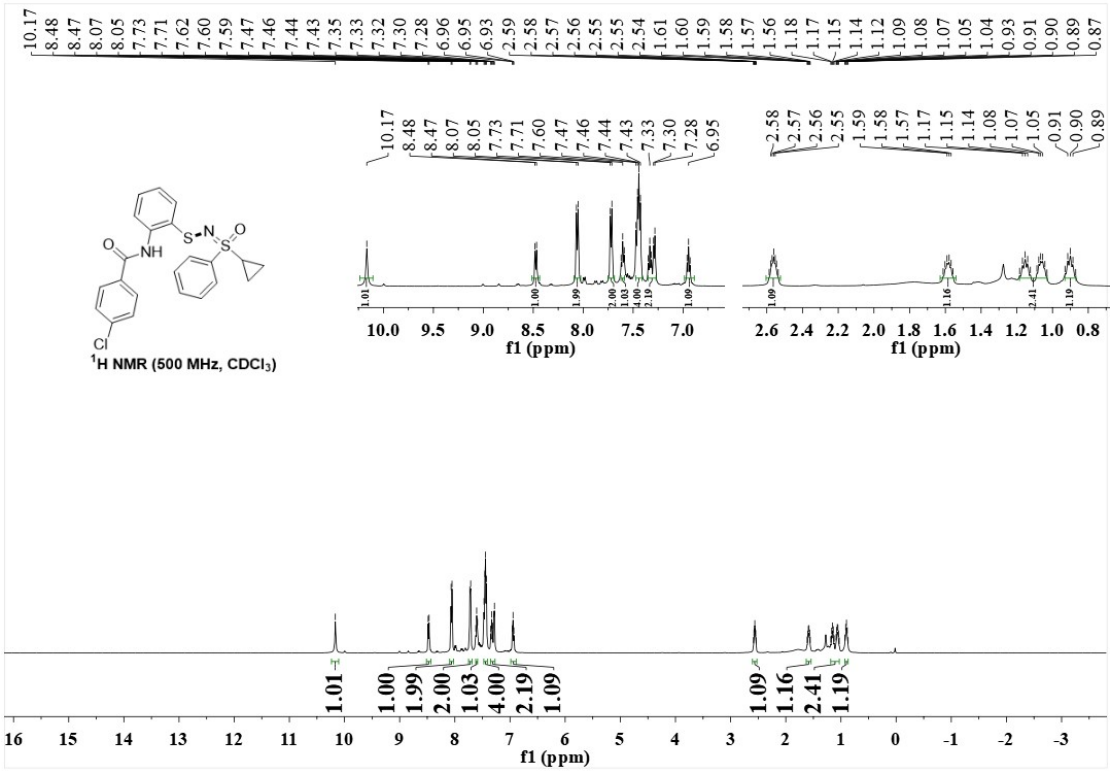
4-Chloro-N-(2-(((methyl(oxo)(p-tolyl)-λ⁶-sulfaneylidene)amino)thio)phenyl)-benzamide (4d)

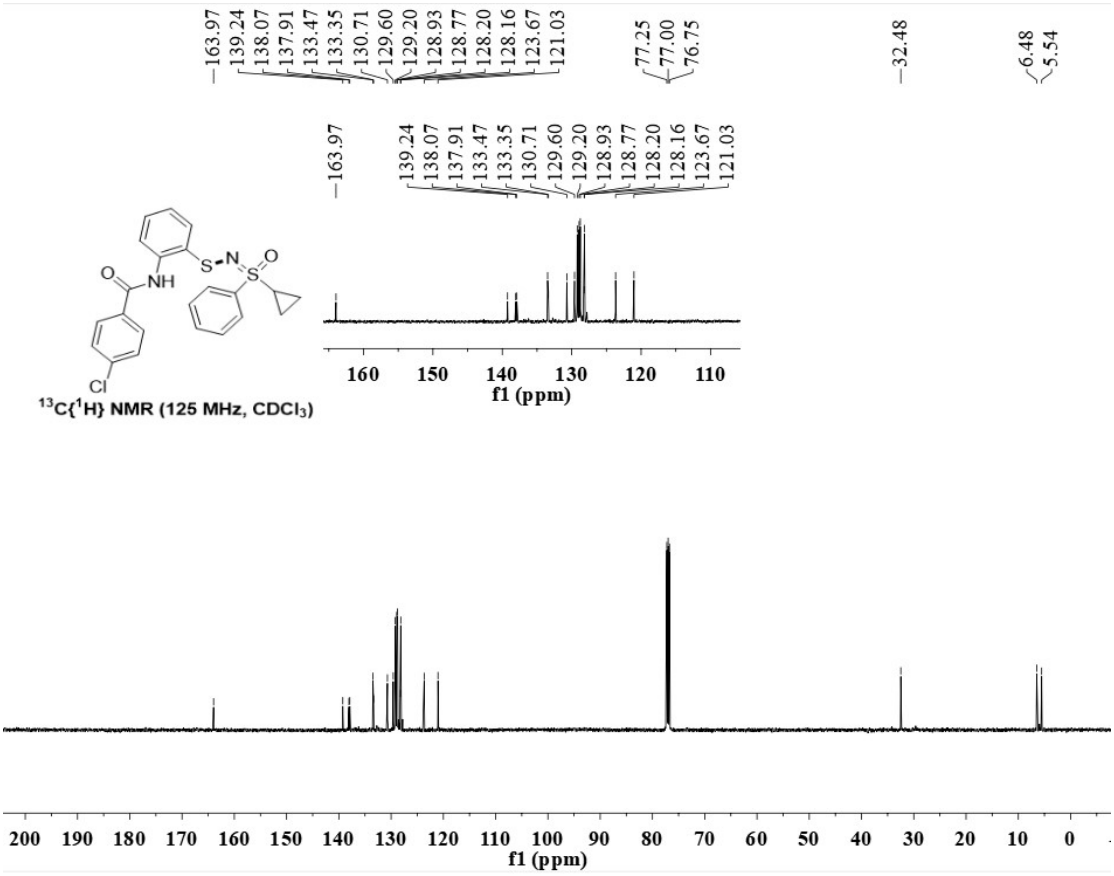




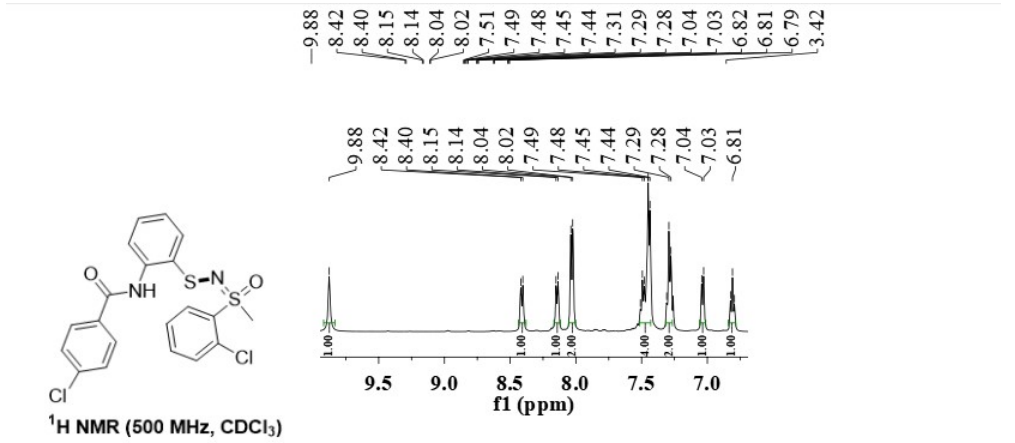


4-Chloro-N-(2-(((cyclopropyl(oxo)(phenyl)-λ⁶-sulfaneylidene)amino)thio)phenyl)-benzamide (4e)

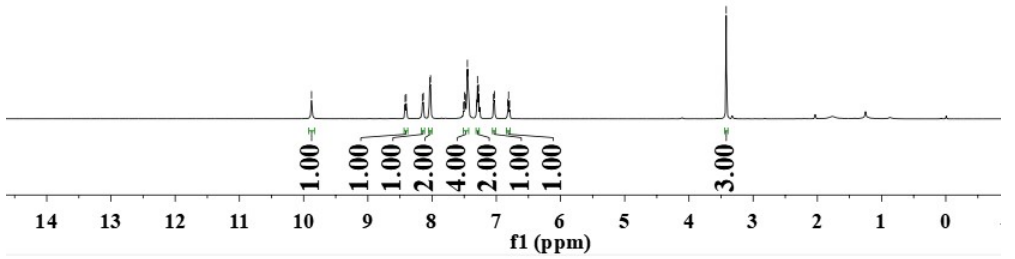


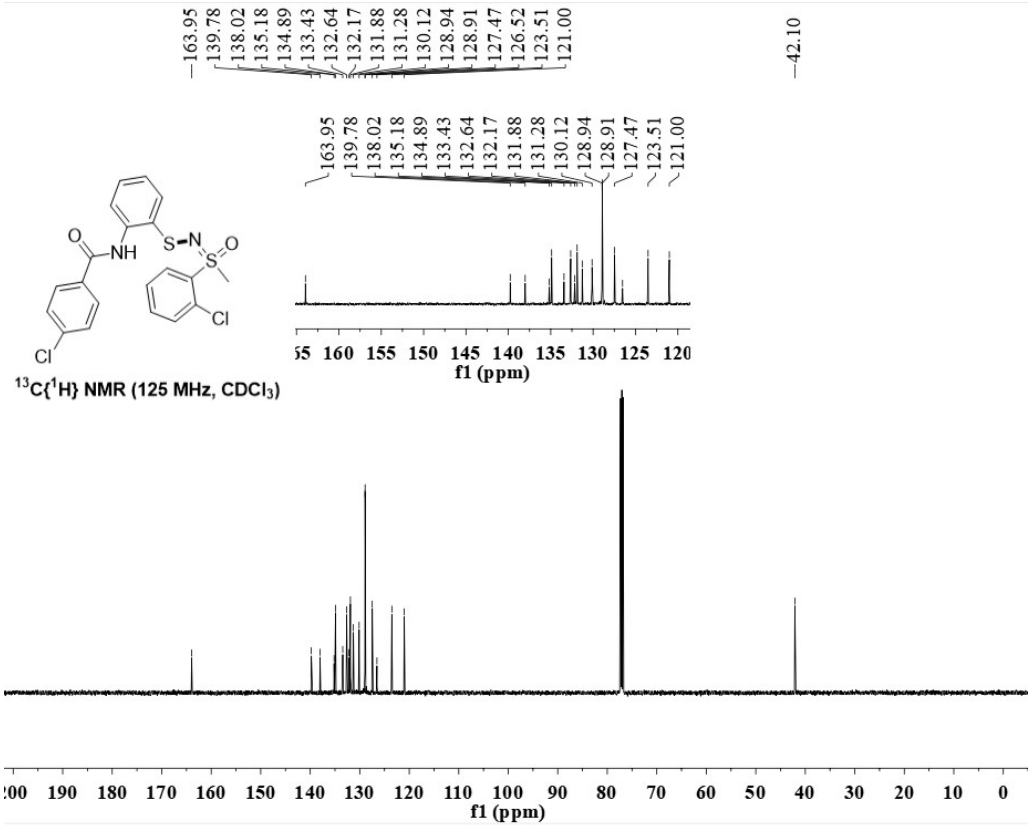


4-Chloro-N-(2-((((2-chlorophenyl)(methyl)(oxo)-λ^6-sulfaneylidene)amino)thio)-phenyl)benzamide (4f)



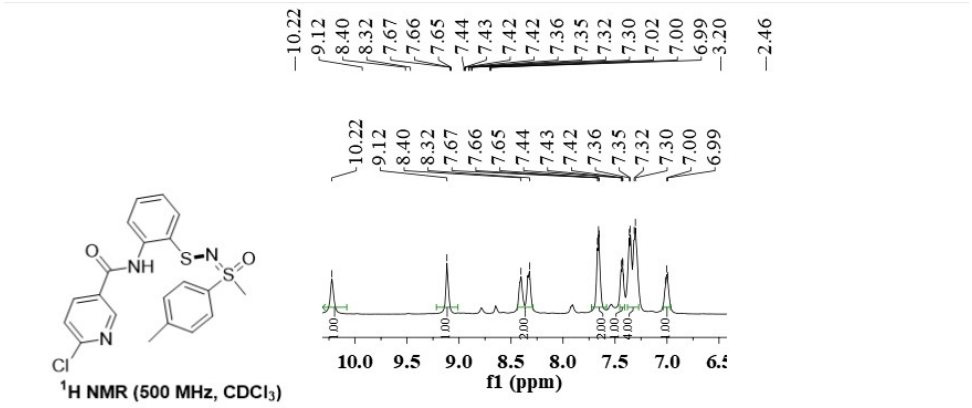
^{1}H NMR (500 MHz, $CDCl_3$)



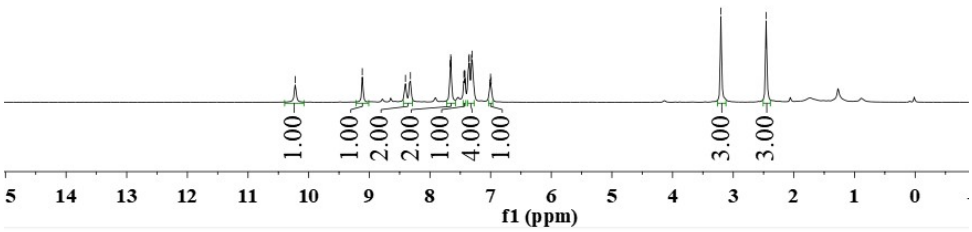


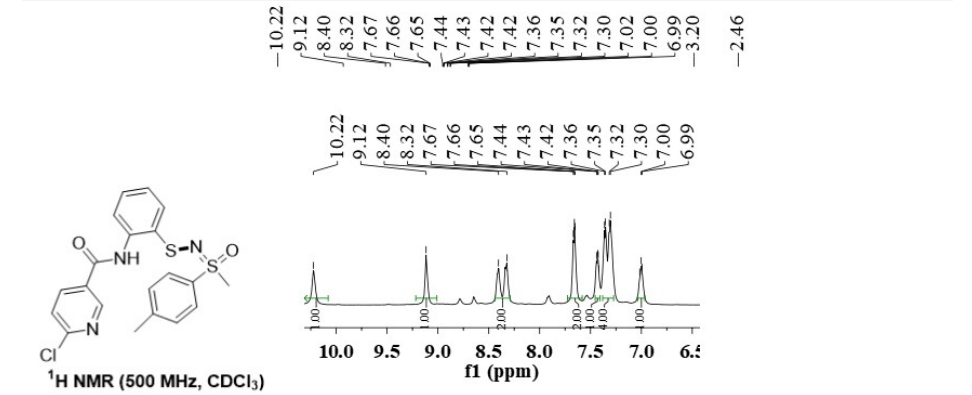
$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$)

6-Chloro-N-(2-(((methyl(oxo)(p-tolyl)-λ⁶-sulfaneylidene)amino)thio)phenyl)-nicotinamide （4g）

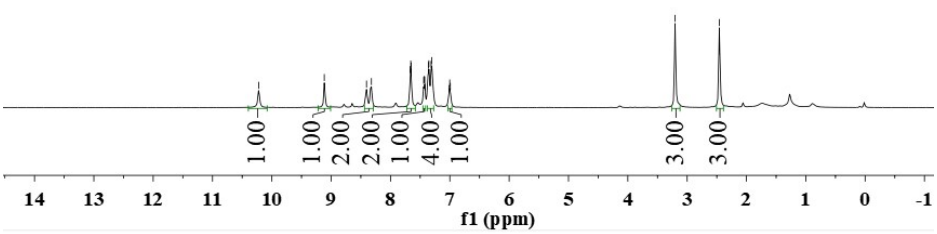


^{1}H NMR (500 MHz, $CDCl_3$)





^{1}H NMR (500 MHz, $CDCl_3$)



6-Chloro-N-(2-((((2-chlorophenyl)(methyl)(oxo)-λ^6-sulfaneylidene)amino)thio)-phenyl)nicotinamide (4h)