Synthesis of Anthraquinone-Containing Polymeric Photosensitizer And Its Application in Aerobic Photooxidation of Thioethers

Yang Chen[a], Jianhua Hu[a,*], Aishun Ding[b,*]

[a] State Key Laboratory of Molecular Engineering of Polymers and Department of Macromolecular Science, Fudan University, 2005 Songhu Road, Shanghai 200438, PR China. E-mail address: hujh@fudan.edu.cn (J. Hu), Fax: +86-21-31242888, Tel: +86-21-55665280

[b] Department of Chemistry, Fudan University, 2005 Songhu Road, Shanghai 200438, PR China. E-mail address: shunzi0522@126.com, Fax: +86-21-31249190, Tel: +86-21-31249190

Supporting Information

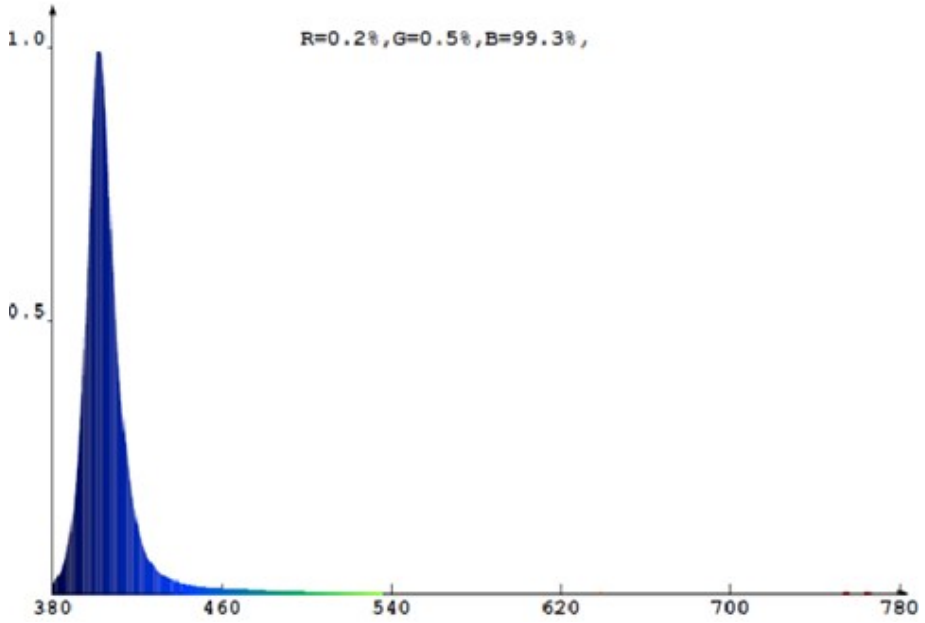


Figure S1. Emission spectra of purple LED

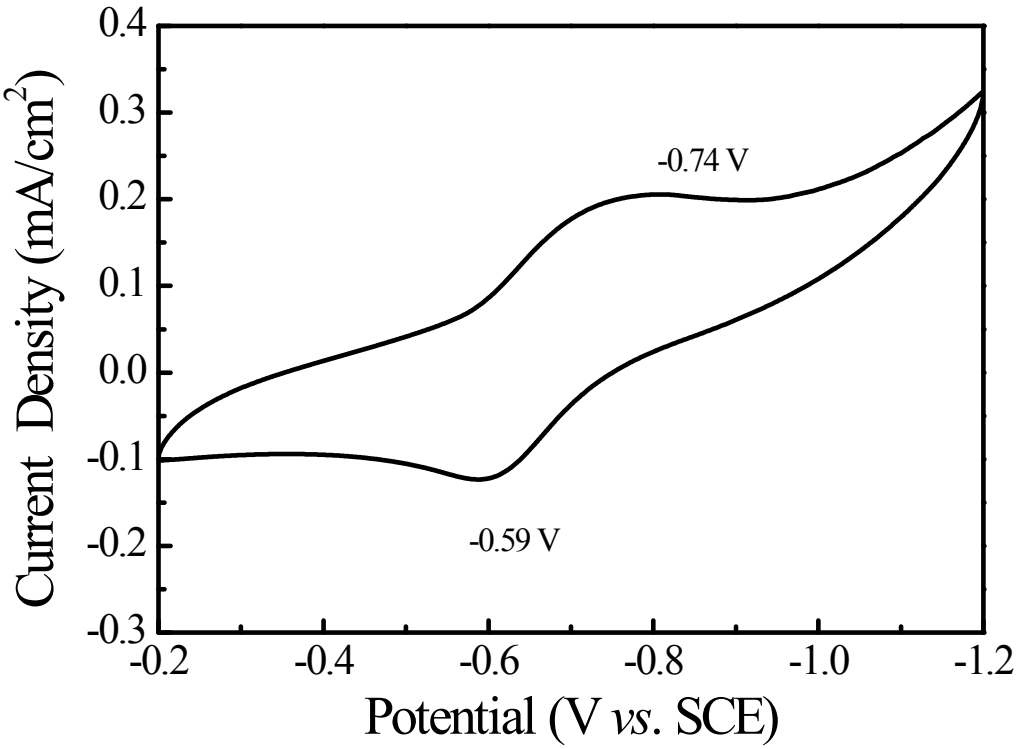


Figure S2. CV of AQ-PHEMA coated on GC electrode, 0.05 mol/L KCl electrolyte solutions at the scan rates at 100 mV/s.

Experimental Section

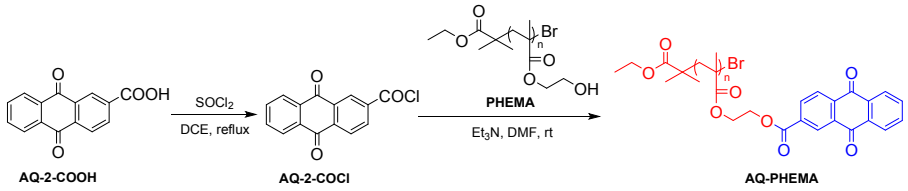
General experimental methods

All the photo reactions were carried out using purple LED (1 m strip × 2, Greethink 5050, 12 V/m) at a distance of 8-10 cm at rt under air atmosphere unless stated otherwise. ^{1}H (400 MHz), and ^{13}C (100 MHz) NMR spectra of samples in $CDCl_3$ or DMSO-d_6 at 298 K were recorded on an AVANCE III 400 spectrometer. IR spectra were recorded on an Avatar 360 FT-IR spectrometer. UV-Vis spectroscopies were recorded on an Evolution 220 UV-Visible spectrophotometer. Cyclic voltammogram (CV) was measured by using an electrochemical analyser (CHI 660E, Chenhua, Shanghai, China). A Pt wire and Hg/Hg_2Cl_2 (SCE) electrode were used as the auxiliary and reference electrodes, respectively. In the 0.05 mol/L KCl as the electrolyte. An initial potential of –0.2 V was applied for 2 s, and subsequently cyclic scans to a final potential of –1.2 V were done for 10 cycles. The CV curves and data reported in the present work were the 10th cycle. HRMS (ESI) determinations were carried out on a Bruker Daltonics micrOTOF II spectrometer. The apparent molecular weight (MW) and molecular weight distribution (Mw/Mn) of polymers were analyzed by size exclusion chromatography (SEC) measurement, which was performed in LiBr-added *N*,*N*-dimethylformamide (DMF) ([LiBr] = 14 mM) at 55 °C with an elution rate of 1.0 mL/min on an Agilent 1260 equipped with a G1310B pump, a G1362A refractive index detector, and a G1314F variable wavelength detector. Two 5 μm LP gel columns (500 Å, molecular range 500-1.2 × 10^5 Da and 200-1.0 × 10^6 Da) were calibrated using poly (methyl methacrylate) (PMMA) standards. Compounds **AQ-2-COOH**, **1a-1j**, **1m-1o**, **1q** and **1t-v** were commercial available. Compounds **1k**[1] and **1l**[2] were prepared according to literature procedures.

Synthesis and characterization of AQ-PHEMA

The AQ-PHEMA was prepared by reaction of PHEMA with AQ-2-COCl **(Scheme S1)**. At first, AQ-2-COCl was synthesized as the following procedure. In a dry 250 mL of Schlenk flask, under argon atmosphere, AQ-2-COOH (2.704 g, 10.7 mmol) was refluxed with $SOCl_2$ (2.5 mL) in anhydrous dichloroethane (20 mL). After 4 hours, the mixture was concentrated under vacuum and the residue was stripped twice with anhydrous dichloroethane (10 mL × 2). Subsequently, the residue was dissolved in anhydrous DMF (20 mL) and transferred into another dry 100 mL of Schlenk flask containing precursor PHEMA (2.792 g) which was previously dried by azeotropic distillation with toluene (100 mL). After that, anhydrous DMF (20 mL) was added. Anhydrous Et_3N (16 mL) as acid-binding agent was syringed

into the flask. The mixture was stirred for 62 hours at rt. The mixture was precipitated with water (500 mL) twice and methanol (500 mL) once. The obtained AQ-PHEMA was further dried under vacuum at 60 °C to a constant weight. ^{1}H NMR (400 MHz, d_6-DMSO, δ, ppm, TMS): 1.00-0.65 (m, -$CH_2C(CH_3)$-), 2.15-1.47 (m, -$CH_2C(CH_3)$-), 4.23-3.41 (m, AQCOOCH_2CH_2-), 8.75-7.93 (m, Ar-***H***). $M_{n,GPC}$ = 43,000, M_w/M_n = 1.53.



Scheme S1. The synthetic procedure for AQ-PHEMA.

The ^{1}H NMR spectra for AQ-2-COOH, PHEMA and AQ-PHEMA were shown in **Figure S3**. According to our previous work,[3] the structure of AQ could be confirmed by the characteristic resonance signal on phenyl at 8.73-7.92 ppm. The characteristic resonance signals for methylene protons (HOCH_2CH_2-) of PHEMA could be clearly discriminated at 4.05-3.42 ppm, and signal for methyl protons (-$CH_2CBr(CH_3)$-) could be observed at 1.00-0.65 ppm. The characteristic resonance signals for the alkyl and phenyl groups were substantially identical to that of PHEMA and AQ-2-COOH. We also performed IR spectrum characterization of AQ-PHEMA and found that hydroxyl groups were not all modified (**Figure S4**).

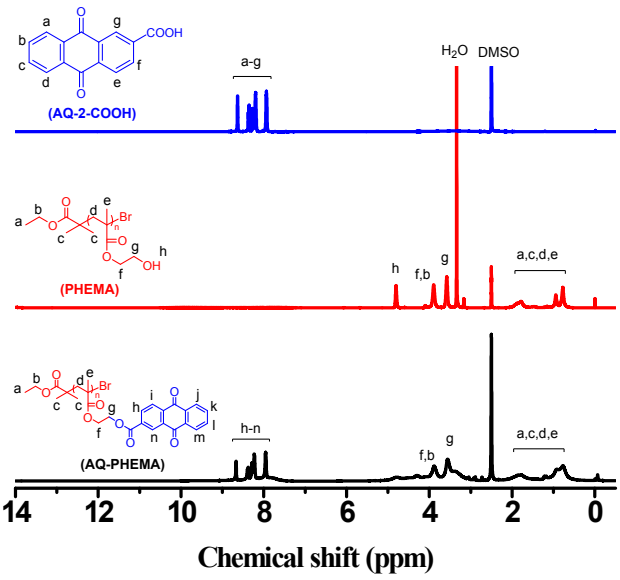


Figure S3. ^{1}H NMR spectra for AQ-2-COOH, PHEMA and AQ-PHEMA in d_6-DMSO.

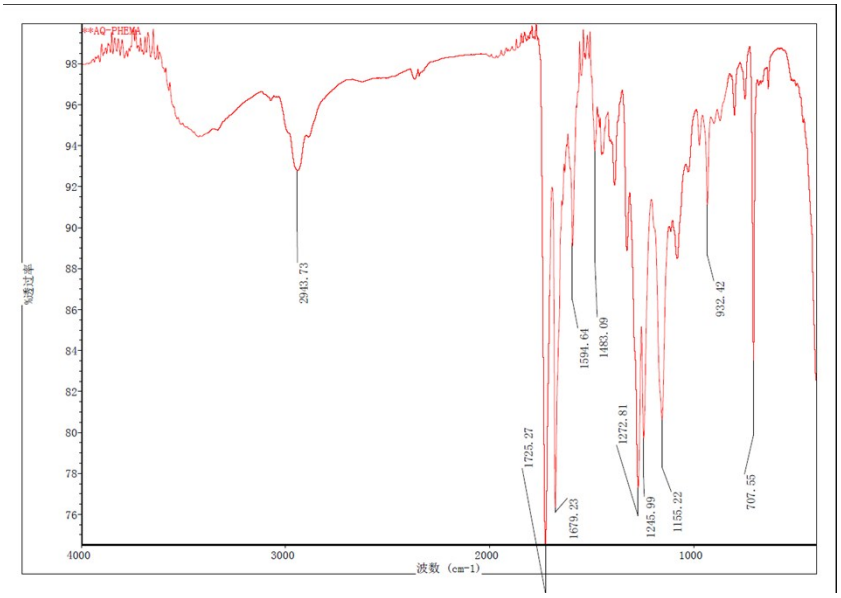


Figure S4. IR spectrum of AQ-PHEMA.

The apparent molecular weight of PHEMA was calibrated as 27,800 g/mol by SEC instrument using PMMA as calibration. Obviously, the GPC curve of AQ-PHEMA is significantly shift to the higher molecular weight region (43,000 g/mol) (**Figure S5**). The above results indicated that the AQ functional group was successfully attached to PHEMA.

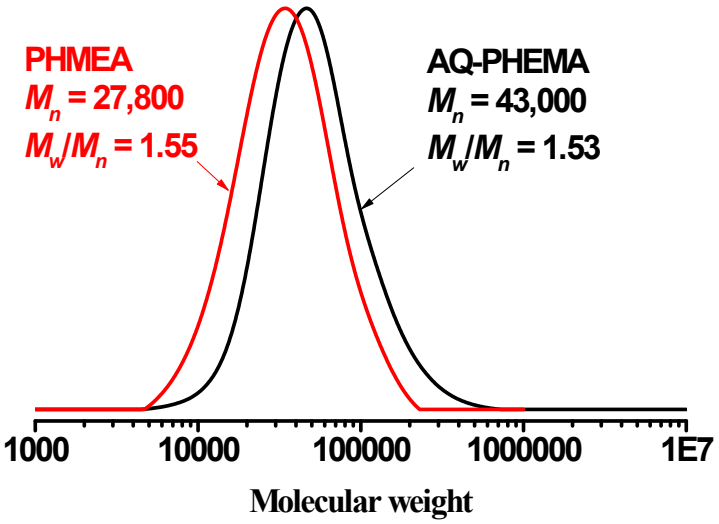


Figure S5. The GPC traces of PHEMA and AQ-PHEMA.

Calculate the ratio of AQ in AQ-PHEMA by UV-Vis spectrophotometer

Next, AQ-2-COOH, PHEMA and AQ-PHEMA DMF solutions were measured by UV-Vis spectrophotometer to determine the ratio of AQ in AQ-PHEMA. As shown in **Figure S6**, at the range of 250-700 nm wavelengths, PHEMA had no absorption, AQ-PHEMA had two absorption peaks at 268 nm and 330 nm, which was identical with AQ-2-COOH. However, the absorption at 268 nm was significantly interfered by solvent. Therefore, 330 nm was selected as the maximum absorption wavelength. Five different concentrations of AQ-2-COOH DMF standard solutions were prepared to obtain a calibration curve (**Figure S7**). Finally, a DMF solution of AQ-PHEMA (0.044 mg/mL) was measured at 330 nm with the absorbance as 0.772. Since PHEMA had no absorption at 330 nm, the absorption signal in the AQ-PHEMA solution was solely from its AQ functional group. According to the linear regression equation from the calibration curve of AQ-2-COOH, the concentration of AQ in AQ-PHEMA DMF solution (0.044 mg/mL) was calculated as 1.302×10^{-4} mmol/mL. Thus, the ratio of AQ in AQ-PHEMA was calculated as 2.959 mmol/g.

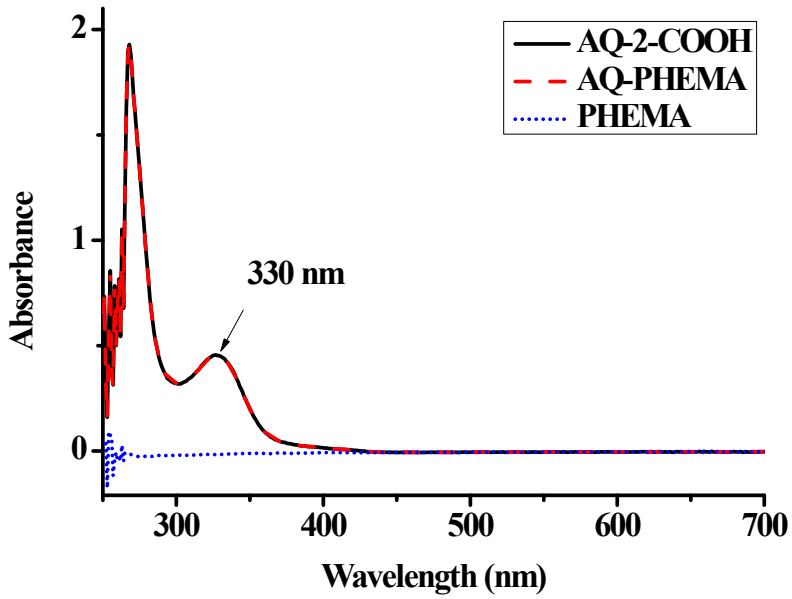


Figure S6. UV-Vis absorption spectra of AQ-2-COOH, PHEMA and AQ-PHEMA in DMF.

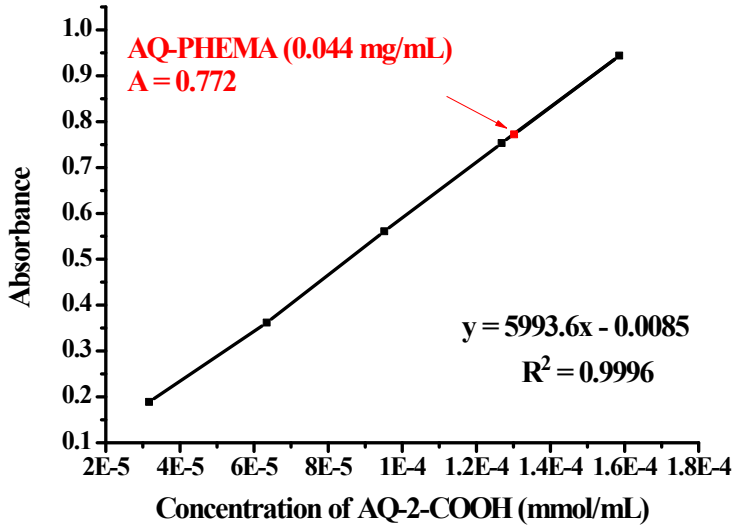
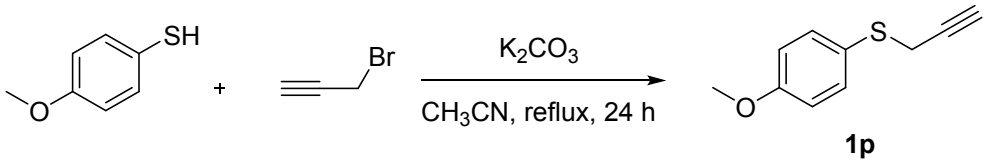


Figure S7. Calibration curve of AQ-2-COOH measured by UV-Vis spectrophotometry at 330 nm.

Synthesis of (4-methoxyphenyl)(prop-2-yn-1-yl)sulfane (1p)[4]

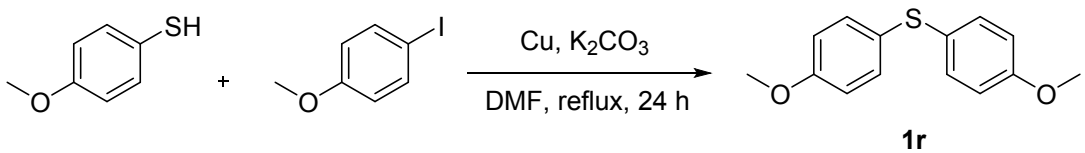


1p

To a solution of 4-methoxybenzenethiol (0.60 mL, 4.9 mmol) in CH_3CN (30 mL) was added K_2CO_3 (1.382 g, 10.0 mmol), the mixture was heated to reflux for 30 minutes. Then 3-bromoprop-1-yne (0.65 mL, 7.5 mmol) was syringed into the flask. After refluxed for 24 hours, the reaction mixture was cooled to room temperature and the solid was removed by filtration. The residue was concentrated in vacuum and purified by flash chromatography on silica gel (eluent: petroleum ether/ether acrtate = 50/1) to afford **1p** as a liquid (643 mg, 72%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.4 Hz, 2 H), 6.87 (d, J = 8.4 Hz, 2 H), 3.81 (s, 3 H), 3.49 (d, J = 2.4 Hz, 2 H), 2.22 (s, 1 H).

Typical Procedure I for the synthesis of thioethers.

Synthesis of bis(4-methoxyphenyl)sulfane (1r)[5]



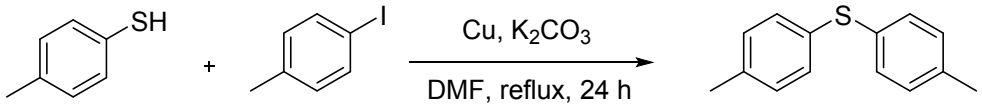
1r

To a solution of 4-methoxybenzenethiol (0.60 mL, 4.9 mmol) in DMF (20 mL) was added 1-iodo-4-methoxybenzene (1.170 g, 5.0 mmol), K_2CO_3 (144 mg, 1.04 mmol) and Cu powder (64 mg, 1.0 mmol). The mixture was heated to reflux. After 24 hours, the mixture was cooled to room temperature and

filtered. Then the residue was extracted three times with 100 mL of ethyl acetate and 100 mL of deionized water. The combined organic phases were washed with brine and dried over anhydrous $MgSO_4$, filtered and concentrated in vacuum. The residue was purified by flash chromatography on silica gel (eluent: petroleum ether→petroleum ether/ether acetate = 80/1→50/1) to afford **1r** as a solid (1.121 g, 91%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.4 Hz, 4 H), 6.83 (d, *J* = 8.4 Hz, 4 H), 3.79 (s, 6 H).

The following compound was prepared according to Typical Procedure I.

Synthesis of bis(4-methylphenyl)sulfane (1s)[5]

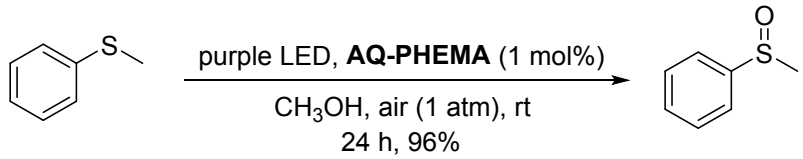


1s

A solution of 4-methylbenzenethiol (0.60 mL, 4.9 mmol), 1-iodo-4-methylbenzene (0.65 mL, 5.0 mmol), K_2CO_3 (142 mg, 1.03 mmol), Cu powder (64 mg, 1.0 mmol) and DMF (20 mL) afforded **1s** as a solid (1.007 g, 94%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 7.6 Hz, 4 H), 7.10 (d, *J* = 7.6 Hz, 4 H), 2.32 (s, 6 H).

Typical Procedure II for the photoreaction.

Synthesis of methyl phenyl sulfoxide (2a)[6]

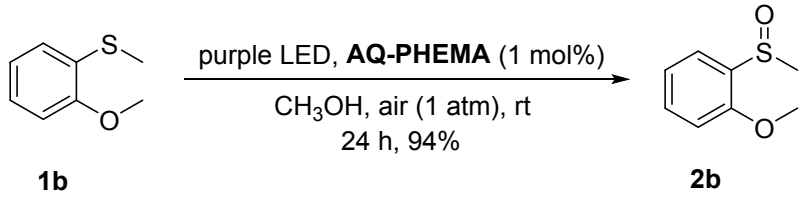


1a **2a**

A solution of **1a** (0.12 mL, 1.0 mmol), **AQ-PHEMA** (3 mg, 0.01 mmol), and CH_3OH (5 mL) were added to a 25 mL of Schleck bottle which was equipped with a magnetic stirrer. The mixture was irradiated by a purple LED at rt under air atmosphere. The photoreaction was completed after 24 hours as monitored by TLC (eluent: petroleum ether/ether acetate = 20/1). The solvent was removed and the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ether acetate = 20/1→10/1→5/1→1/1) to afford **2a** as a liquid (135 mg, 96%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.63 (m, 2 H), 7.57-7.48 (m, 3 H), 2.73 (s, 3 H).

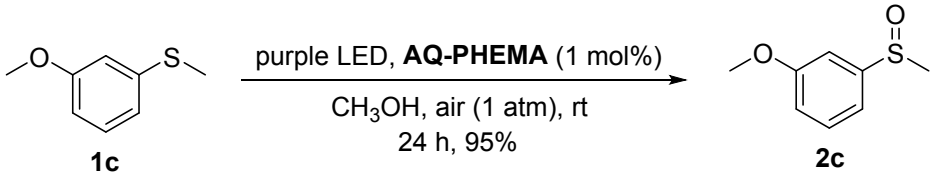
The following compounds were prepared according to Typical Procedure II.

(1) 2-Methoxyphenyl methyl sulfoxide (2b)[6]



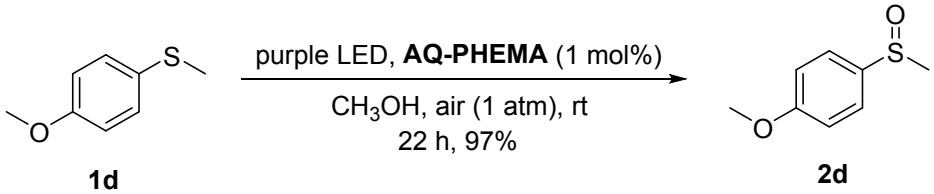
The reaction of **1b** (0.14 mL, 1.0 mmol), **AQ-PHEMA** (3 mg, 0.01 mmol), and CH_3OH (5 mL) afforded **2b** as a liquid (160 mg, 94%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 7.6, 1.6 Hz, 1 H), 7.49-7.42 (m, 1 H), 7.19 (t, *J* = 7.4 Hz, 1 H), 6.93 (d, *J* = 8.4 Hz, 1 H), 3.89 (s, 3 H), 2.78 (s, 3 H).

(2) 3-Methoxyphenyl methyl sulfoxide (2c)[6]



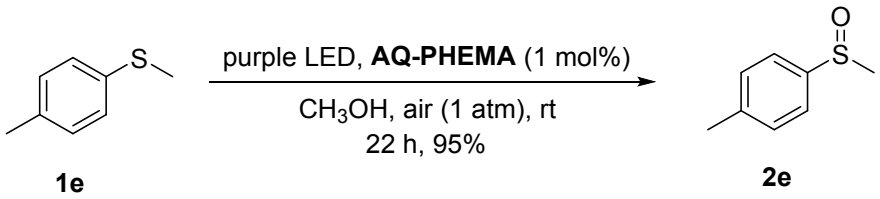
The reaction of **1c** (0.14 mL, 1.0 mmol), **AQ-PHEMA** (3 mg, 0.01 mmol), and CH_3OH (5 mL) afforded **2c** as a liquid (162 mg, 95%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (t, *J* = 7.8 Hz, 1 H), 7.28-7.22 (m, 1 H), 7.14 (d, *J* = 7.6 Hz, 1 H), 7.01 (dd, *J* = 8.4, 2.4 Hz, 1 H), 3.87 (s, 3 H), 2.73 (s, 3 H).

(3) 4-Methoxyphenyl methyl sulfoxide (2d)[6]



The reaction of **1d** (0.14 mL, 1.0 mmol), **AQ-PHEMA** (3 mg, 0.01 mmol), and CH_3OH (5 mL) afforded **2d** as a liquid (165 mg, 97%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.4 Hz, 2 H), 7.03 (d, *J* = 8.4 Hz, 2 H), 3.86 (s, 3 H), 2.70 (s, 3 H).

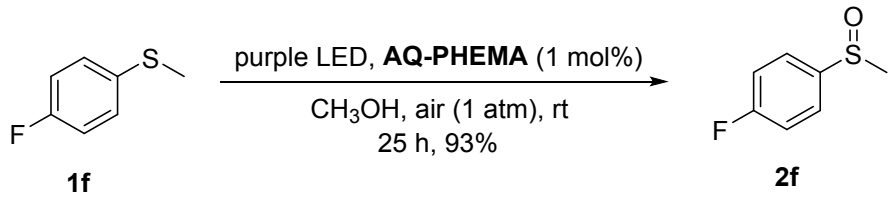
(4) 4-Methylphenyl methyl sulfoxide (2e)[6]



The reaction of **1e** (0.13 mL, 1.0 mmol), **AQ-PHEMA** (3 mg, 0.01 mmol), and CH_3OH (5 mL) afforded

2e as a liquid (147 mg, 95%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.0 Hz, 2 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 2.70 (s, 3 H), 2.41 (s, 3 H).

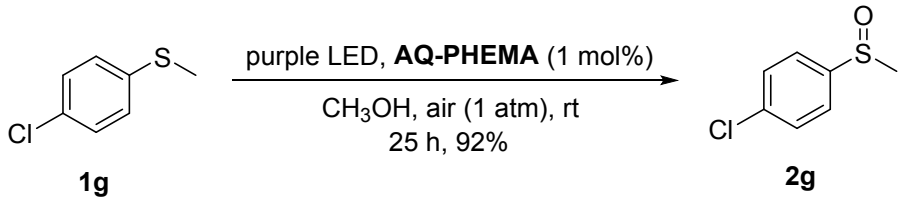
(5) 4-Fluorophenyl methyl sulfoxide (2f)[6]



1f **2f**

The reaction of **1f** (0.12 mL, 1.0 mmol), **AQ-PHEMA** (3 mg, 0.01 mmol), and CH_3OH (5 mL) afforded **2f** as a liquid (147 mg, 93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71-7.62 (m, 2 H), 7.28-7.19 (m, 2 H), 2.73 (s, 3 H).

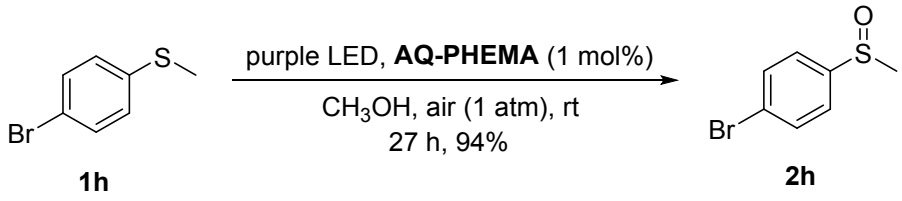
(6) 4-Chlorophenyl methyl sulfoxide (2g)[6]



1g **2g**

The reaction of **1g** (0.13 mL, 1.0 mmol), **AQ-PHEMA** (3 mg, 0.01 mmol), and CH_3OH (5 mL) afforded **2g** as a liquid (161 mg, 92%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.4 Hz, 2 H), 7.51 (d, *J* = 8.4 Hz, 2 H), 2.73 (s, 3 H).

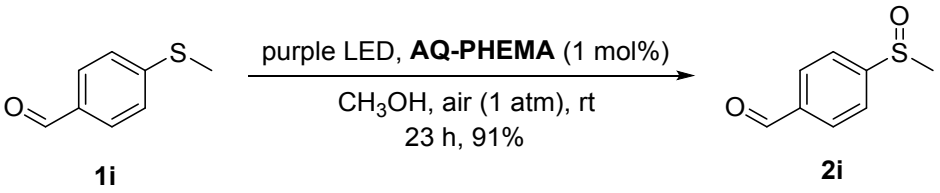
(7) 4-Bromophenyl methyl sulfoxide (2h)[6]



1h **2h**

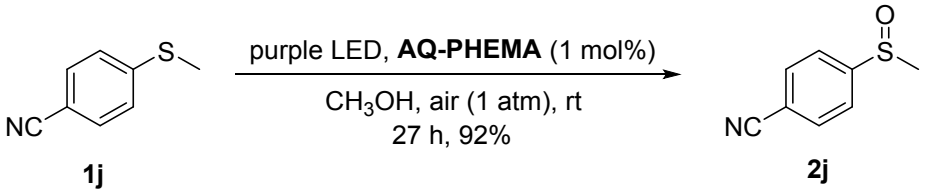
The reaction of **1h** (203 mg, 1.0 mmol), **AQ-PHEMA** (3 mg, 0.01 mmol), and CH_3OH (5 mL) afforded **2h** as a solid (206 mg, 94%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.0 Hz, 2 H), 7.54 (d, *J* = 8.0 Hz, 2 H), 2.73 (s, 3 H).

(8) 4-Formylphenyl methyl sulfoxide (2i)[6]



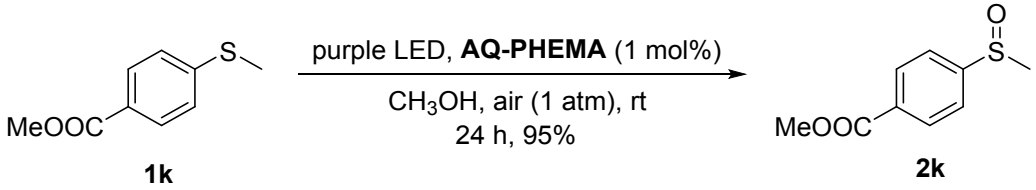
The reaction of **1i** (0.13 mL, 1.0 mmol), **AQ-PHEMA** (3 mg, 0.01 mmol), and CH_3OH (5 mL) afforded **2i** as a solid (153 mg, 91%); ^1H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 1 H), 8.06 (d, J = 8.4 Hz, 2 H), 7.84 (d, J = 8.4 Hz, 2 H), 2.80 (s, 3 H).

(9) 4-Cyanophenyl methyl sulfoxide (2j)[6]



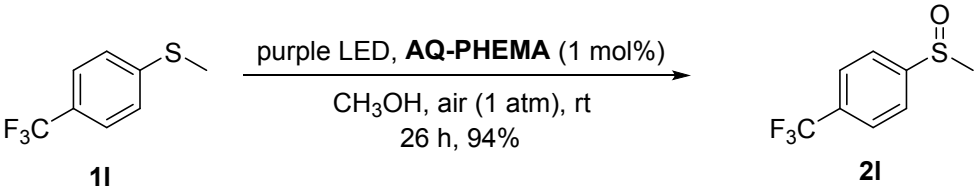
The reaction of **1j** (149 mg, 1.0 mmol), **AQ-PHEMA** (3 mg, 0.01 mmol), and CH_3OH (5 mL) afforded **2j** as a solid (152 mg, 92%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.4 Hz, 2 H), 7.79 (d, J = 8.4 Hz, 2 H), 2.78 (s, 3 H).

(10) 4-(Methoxycarbonyl)phenyl methyl sulfoxide (2k)[6]



The reaction of **1k** (182 mg, 1.0 mmol), **AQ-PHEMA** (3 mg, 0.01 mmol), and CH_3OH (5 mL) afforded **2k** as a solid (188 mg, 95%); ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.4 Hz, 2 H), 7.72 (d, J = 8.4 Hz, 2 H), 3.96 (s, 3 H), 2.76 (s, 3 H).

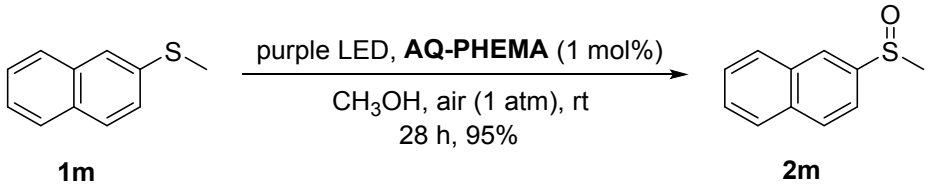
(11) 4-(Trifluoromethyl)phenyl methyl sulfoxide (2l)[7]



The reaction of **1l** (192 mg, 1.0 mmol), **AQ-PHEMA** (3 mg, 0.01 mmol), and CH_3OH (5 mL) afforded

2l as a solid (196 mg, 94%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.72 (m, 4 H), 2.77 (s, 3 H).

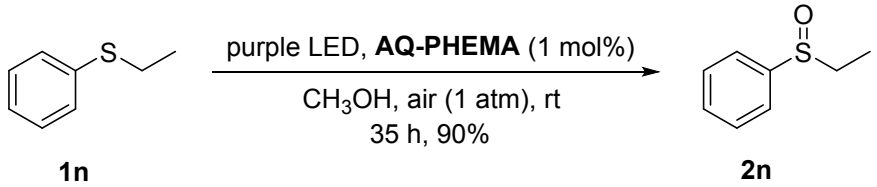
(12) Methyl 2-naphthyl sulfoxide (2m)[6]



1m **2m**

The reaction of **1m** (174 mg, 1.0 mmol), **AQ-PHEMA** (3 mg, 0.01 mmol), and CH_3OH (5 mL) afforded **2m** as a solid (181 mg, 95%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1 H), 8.02-7.86 (m, 3 H), 7.64-7.55 (m, 3 H), 2.79 (s, 3 H).

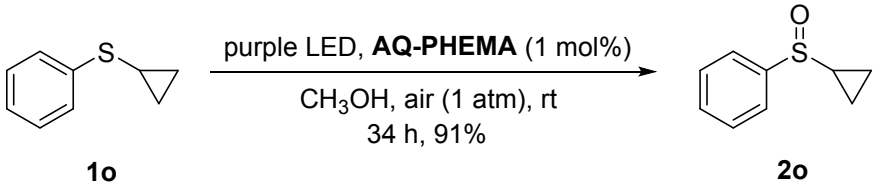
(13) Ethyl phenyl sulfoxide (2n)[6]



1n **2n**

The reaction of **1n** (0.14 mL, 1.0 mmol), **AQ-PHEMA** (3 mg, 0.01 mmol), and CH_3OH (5 mL) afforded **2n** as a liquid (139 mg, 90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.58 (m, 2 H), 7.56-7.45 (m, 3 H), 2.98-2.71 (dm, 2 H), 1.20 (t, J = 7.4 Hz, 3 H).

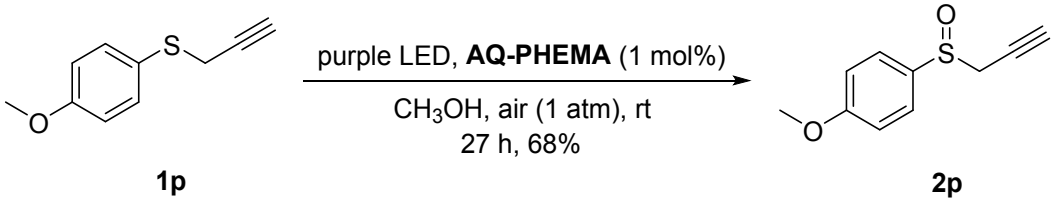
(14) Cyclopropyl phenyl sulfoxide (2o)[6]



1o **2o**

The reaction of **1o** (0.14 mL, 1.0 mmol), **AQ-PHEMA** (3 mg, 0.01 mmol), and CH_3OH (5 mL) afforded **2o** as a liquid (151 mg, 91%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.61 (m, 2 H), 7.55-7.43 (m, 3 H), 2.31-2.19 (m, 1 H), 1.25-1.14 (m, 1 H), 1.06-0.85 (m, 3 H).

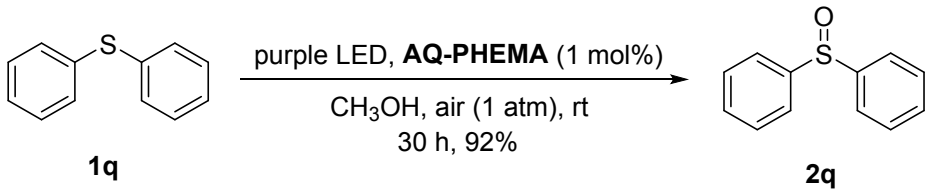
(15) 4-Methoxyphenyl prop-2-yn-1-yl sulfoxide (2p)



1p **2p**

The reaction of **1p** (179 mg, 1.0 mmol), **AQ-PHEMA** (3 mg, 0.01 mmol), and CH_3OH (5 mL) afforded **2p** as a liquid (132 mg, 68%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.4 Hz, 2 H), 7.04 (d, J = 8.4 Hz, 2 H), 3.87 (s, 3 H), 3.68 (d, J = 15.6 Hz, 1 H), 3.58 (d, J = 15.6 Hz, 1 H), 2.34 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 133.5, 126.4, 114.5, 76.2, 72.9, 55.4, 47.7; IR (neat) 1594, 1577, 1496, 1457 cm^{-1}; HRMS (ESI) calcd for $C_{10}H_{11}O_2S$ ($M+H^+$) 195.0474, found 195.0485.

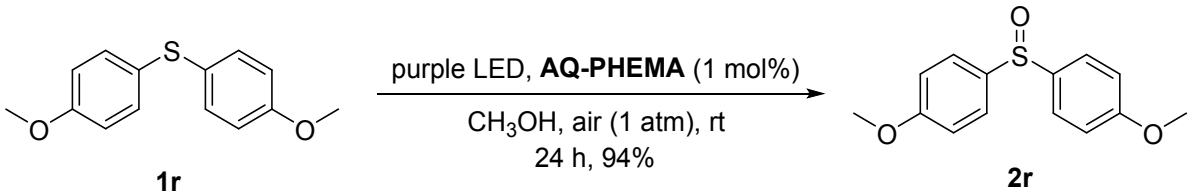
(16) Diphenyl sulfoxide (2q)[6]



1q **2q**

The reaction of **1q** (0.17 mL, 1.0 mmol), **AQ-PHEMA** (3 mg, 0.01 mmol), and CH_3OH (5 mL) afforded **2q** as a solid (186 mg, 92%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.61 (m, 4 H), 7.48-7.36 (m, 6 H).

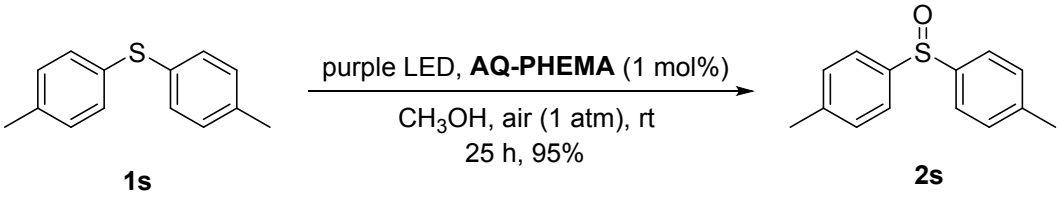
(17) Di-(4-methoxyphenyl) sulfoxide (2r)[5]



1r **2r**

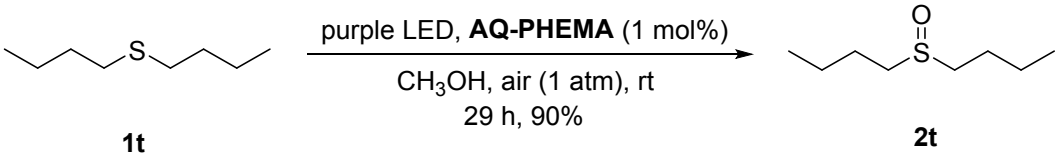
The reaction of **1r** (246 mg, 1.0 mmol), **AQ-PHEMA** (3 mg, 0.01 mmol), and CH_3OH (5 mL) afforded **2r** as a solid (246 mg, 94%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.4 Hz, 4 H), 6.96 (d, J = 8.4 Hz, 4 H), 3.82 (s, 6 H).

(18) Di-(4-methylphenyl) sulfoxide (2s)[5]



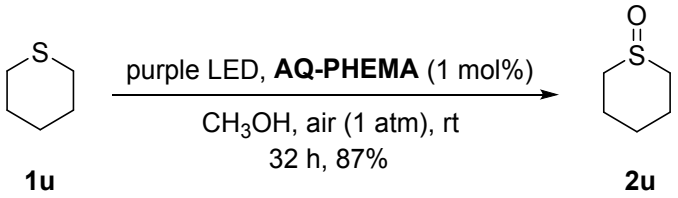
The reaction of **1s** (214 mg, 1.0 mmol), **AQ-PHEMA** (3 mg, 0.01 mmol), and CH_3OH (5 mL) afforded **2s** as a solid (219 mg, 95%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.0 Hz, 4 H), 7.25 (d, J = 8.0 Hz, 4 H), 2.36 (s, 6 H).

(19) Dibutyl sulfoxide (2t)[6]



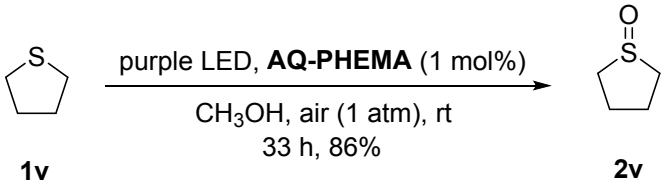
The reaction of **1t** (0.17 mL, 1.0 mmol), **AQ-PHEMA** (3 mg, 0.01 mmol), and CH_3OH (5 mL) afforded **2t** as a liquid (146 mg, 90%); ^1H NMR (400 MHz, $CDCl_3$) δ 2.78-2.58 (m, 4 H), 1.81-1.68 (m, 4 H), 1.55-1.42 (m, 4 H), 0.97 (t, J = 7.4 Hz, 6 H).

(20) Thiane 1-oxide (2u)[6]



The reaction of **1u** (0.10 mL, 1.0 mmol), **AQ-PHEMA** (3 mg, 0.01 mmol), and CH_3OH (5 mL) afforded **2u** as a liquid (103 mg, 87%); ^1H NMR (400 MHz, $CDCl_3$) δ 2.94-2.84 (m, 2 H), 2.81-2.70 (m, 2 H), 2.27-2.19 (m, 2 H), 1.73-1.52 (m, 4 H).

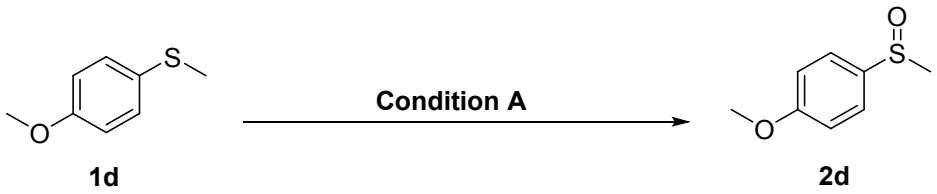
(21) Tetramethylene sulfoxide (2v)[6]



The reaction of **1v** (0.09 mL, 1.0 mmol), **AQ-PHEMA** (3 mg, 0.01 mmol), and CH_3OH (5 mL) afforded

2v as a liquid (90 mg, 86%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.96-2.77 (m, 4 H), 2.52-2.41 (m, 2 H), 2.12-1.96 (m, 2 H).

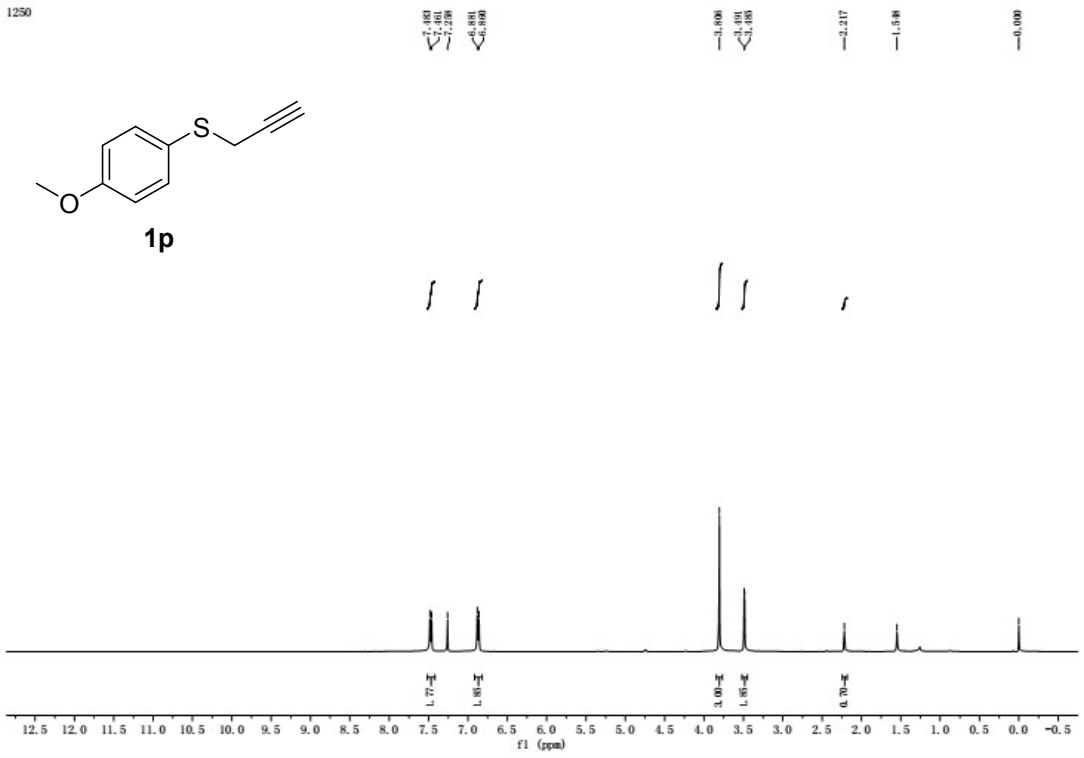
The specific plan for Recycling experiments



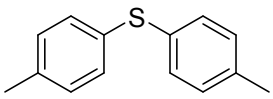
1d **2d**

A solution of **1d** (0.14 mL, 1.0 mmol), **AQ-PHEMA** (3 mg, 0.01 mmol), and CH_3OH (5 mL) were added to a 25 mL of Schleck bottle which was equipped with a magnetic stirrer. The mixture was irradiated by a purple LED at rt under air atmosphere. The photoreaction was completed after 24 hours as monitored by TLC (eluent: petroleum ether/ether acetate = 20/1). After the first cycle, the catalyst AQ-PHEMA was filtered and washed by CH_3OH (5 mL×5). The filtrate was collected in a 100 mL round bottom flask and for crude ^{1}H NMR analysis. The residue (AQ-PHEMA) was dried under air and carefully transferred to another 25 mL Schleck bottle, then **1d** (0.14 mL, 1.0 mmol) and 5 mL CH_3OH were added. The reaction was irradiated with purple LED light for the second cycle experiment. The following cycles of the reactions were performed under the same procedure. After the each cycle experiment, the residue was concentrated in vacuum and the yield was determined by ^{1}H NMR analysis of the crude reaction mixture using CH_2Br_2 (1 mmol) as internal standard.

NMR Spectra

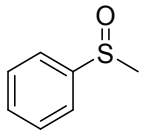


1173

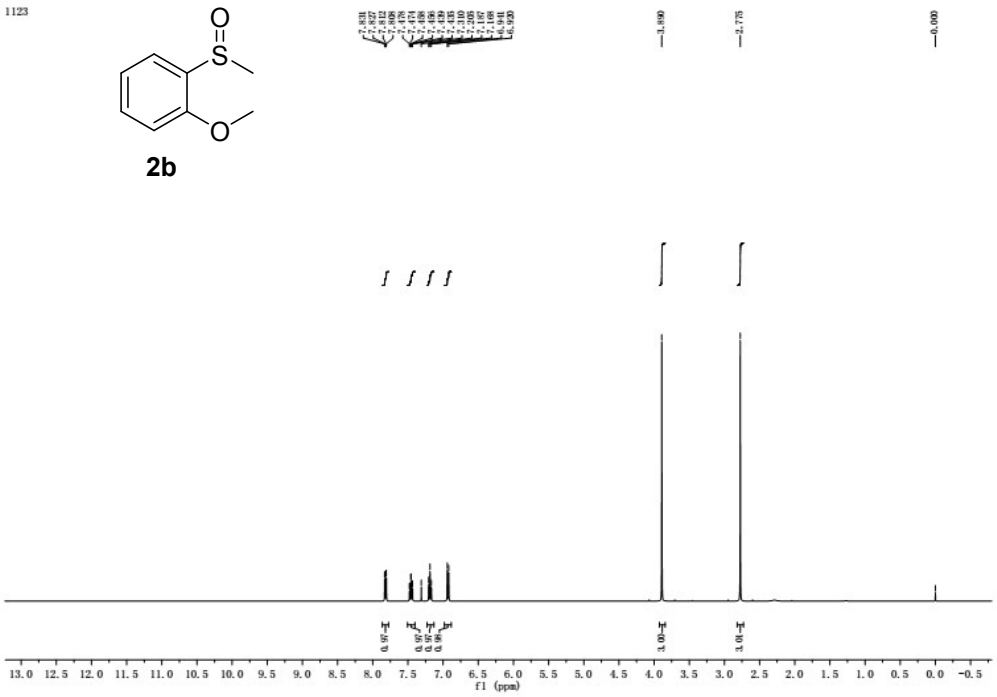


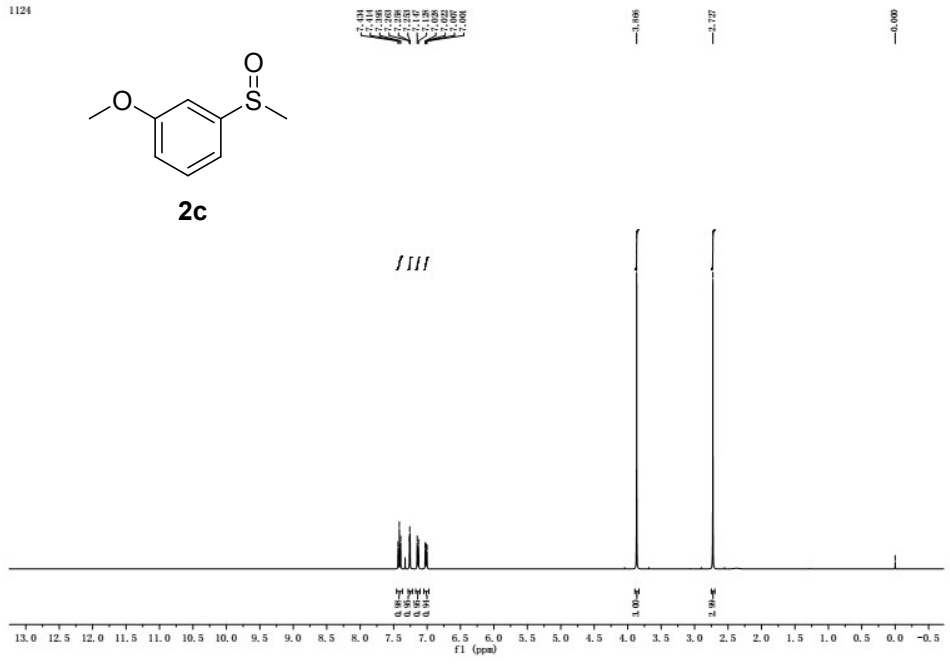
1s

1118



2a

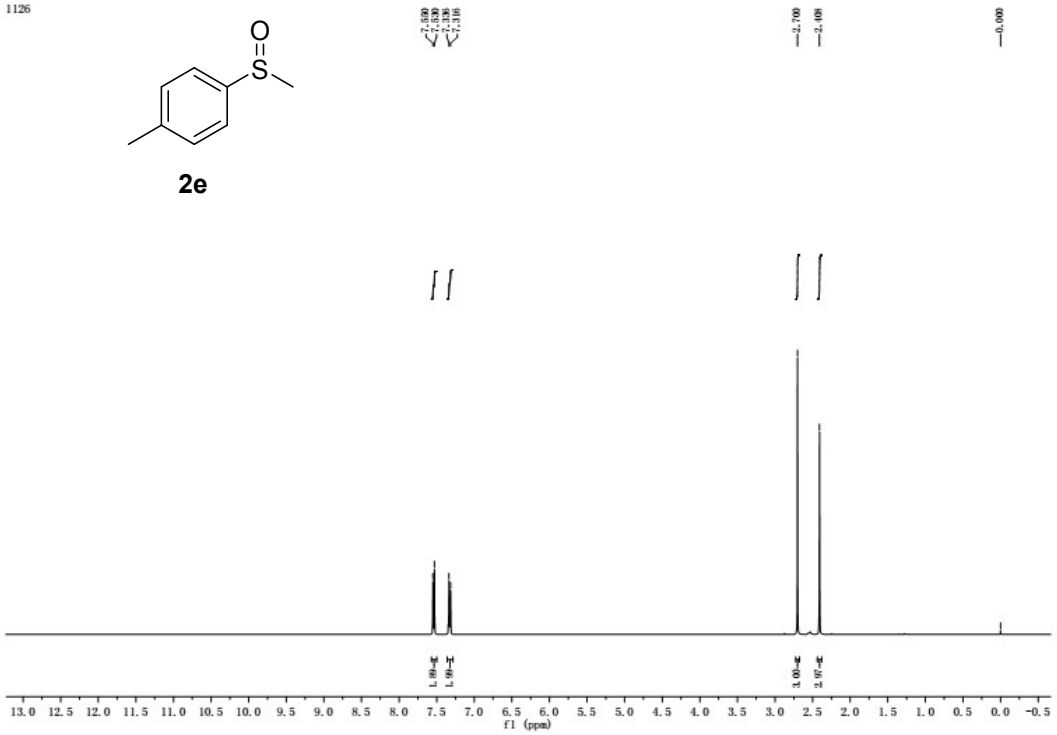

1123
2b
f1 (ppm)


1124
2c
f1 (ppm)

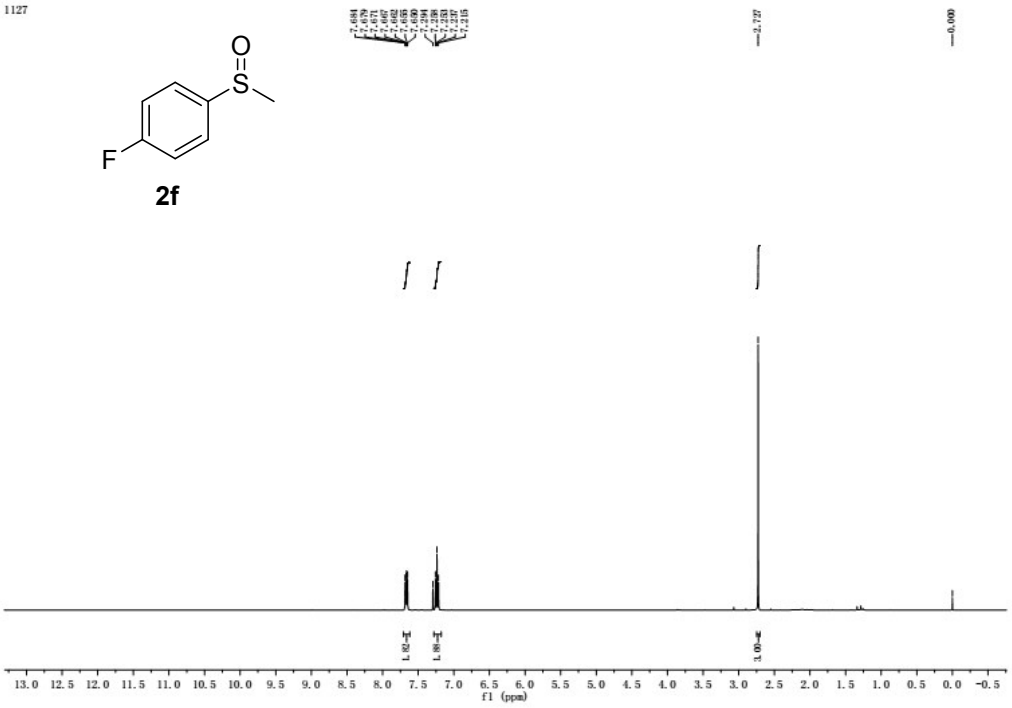
1125

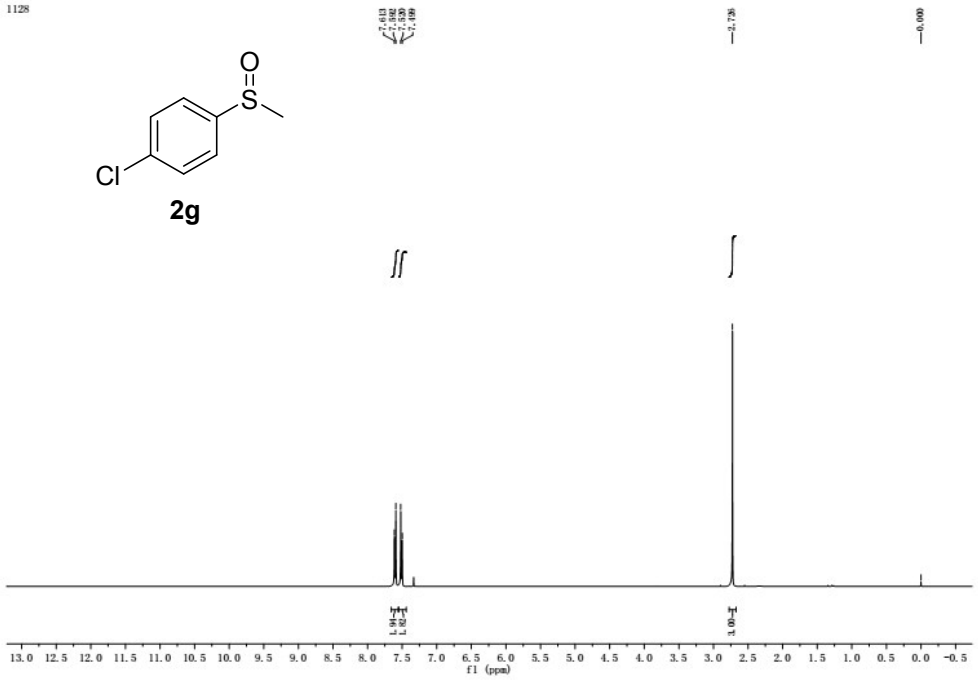
2d

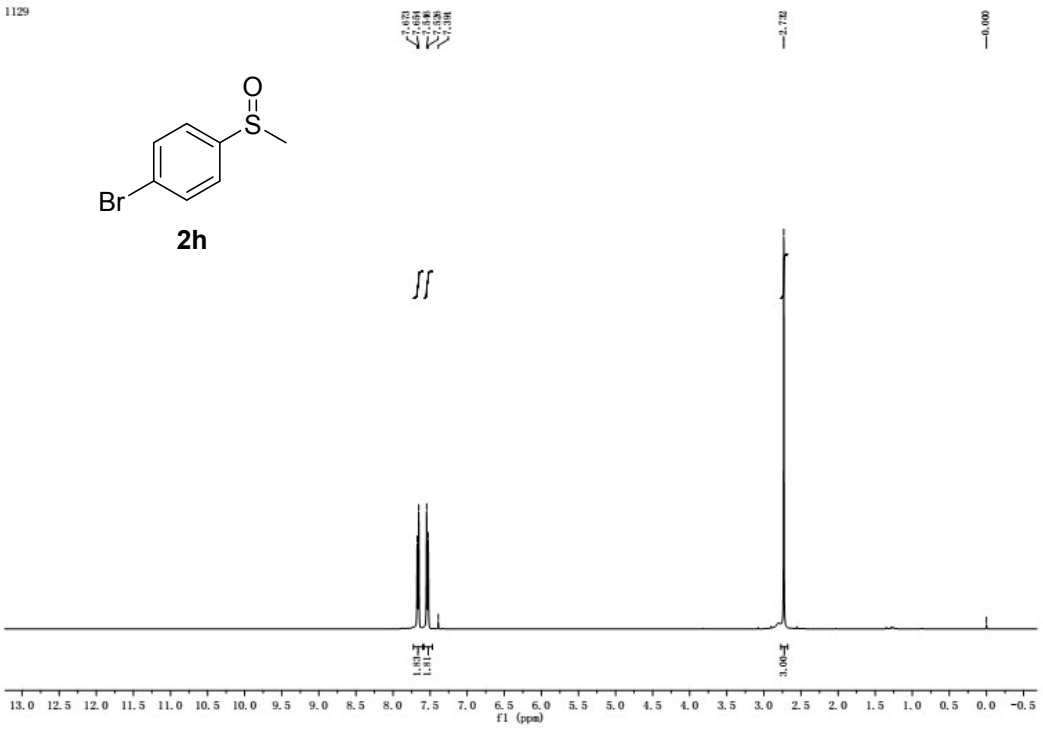
1126

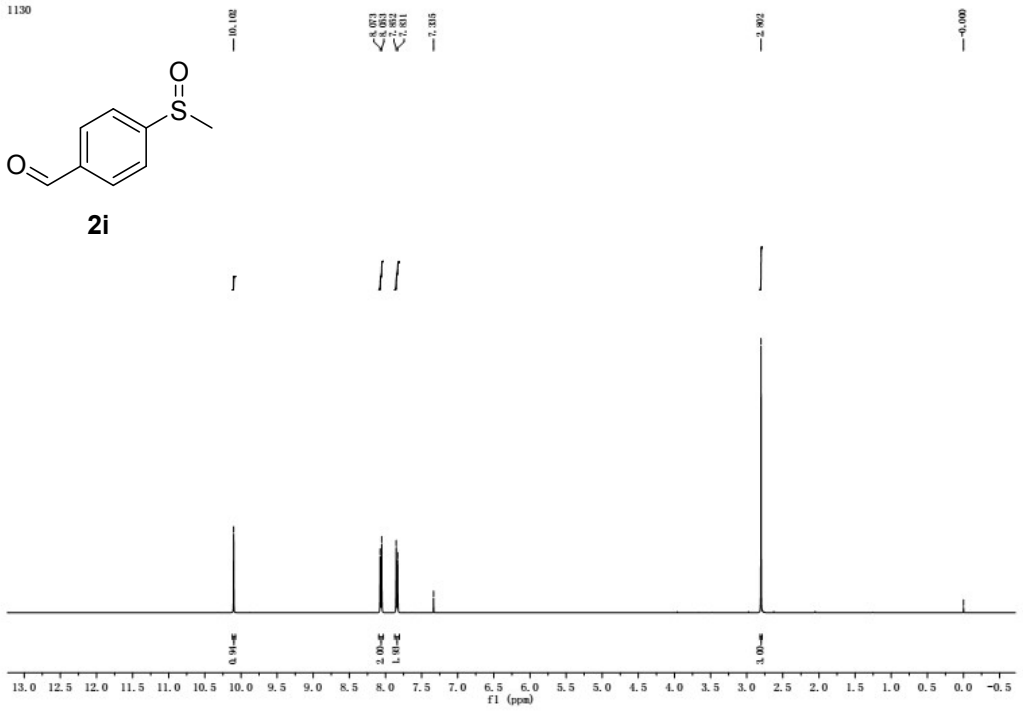


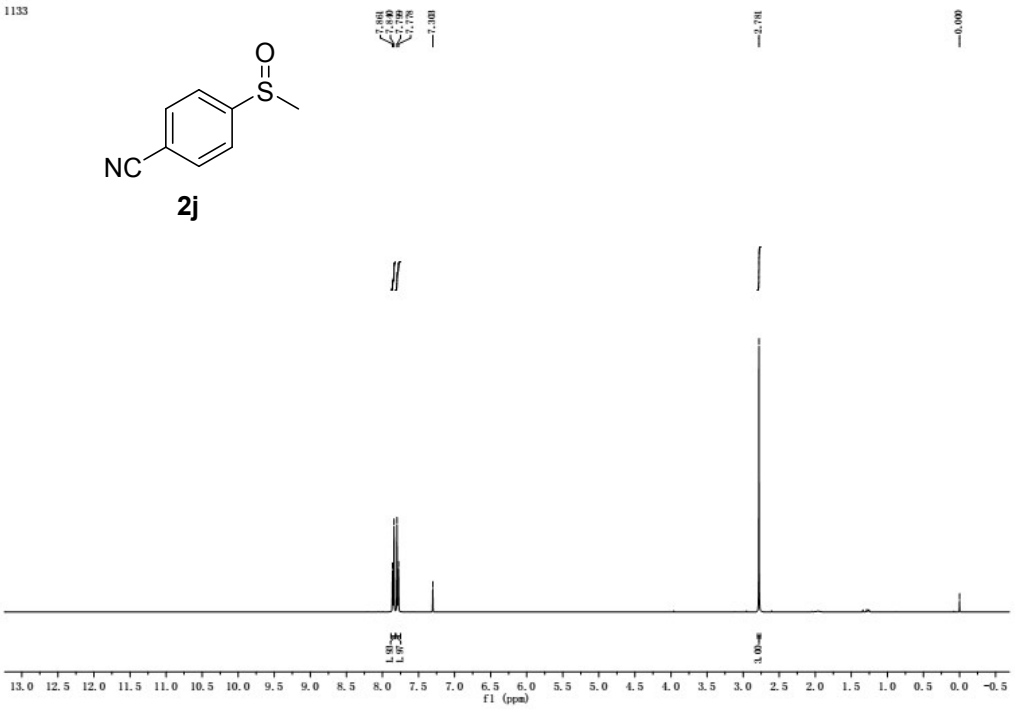
2e

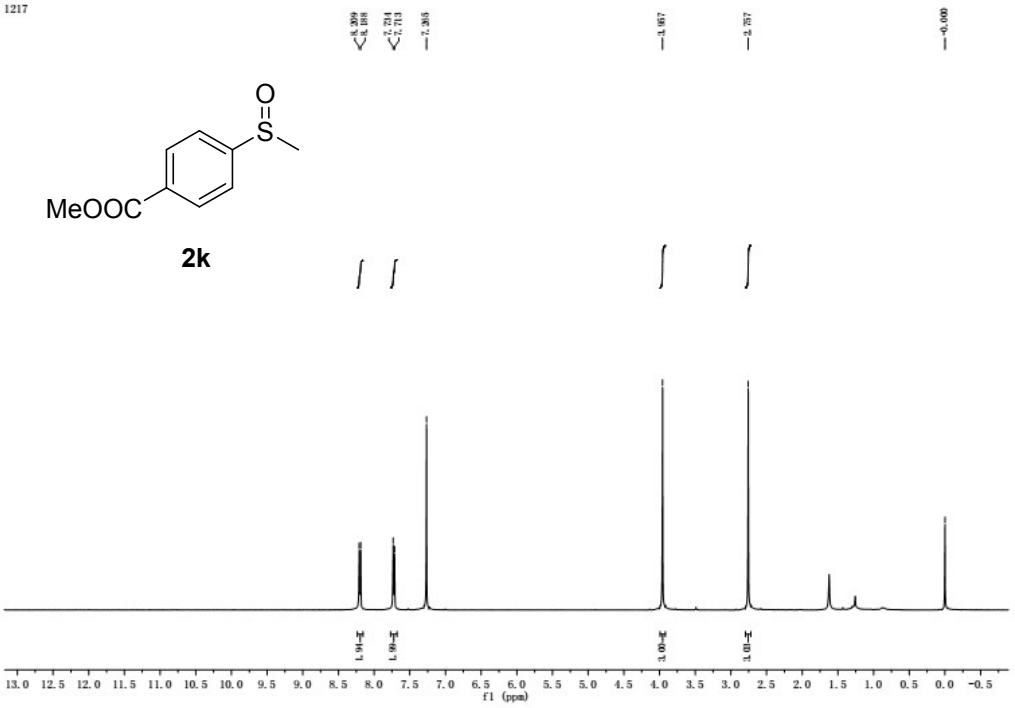

1127
F
2f
1.82
1.88
3.00
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

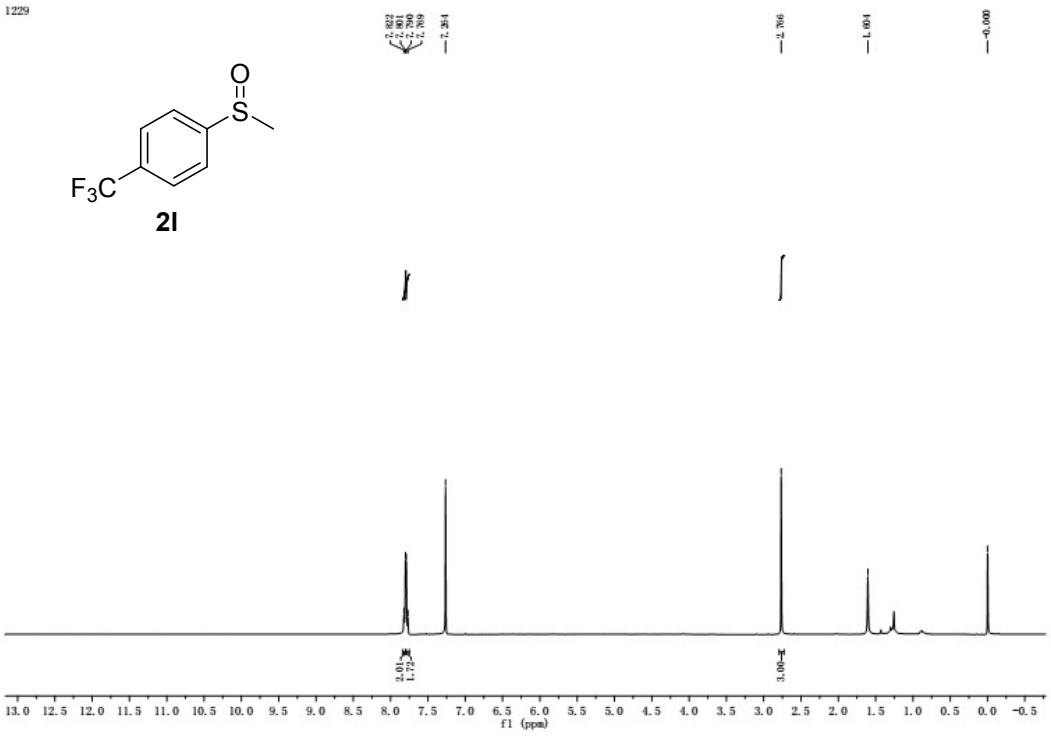

1128
Cl
2g
1.94
1.82
3.00
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

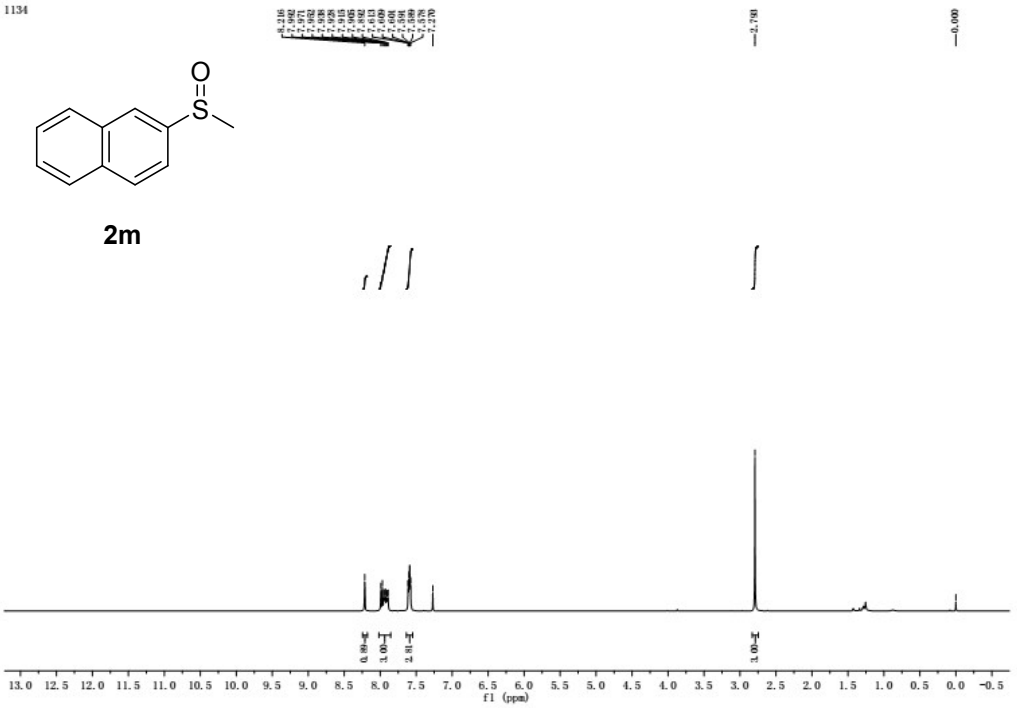

1129
Br
2h
f1 (ppm)


1130
O
2i
f1 (ppm)

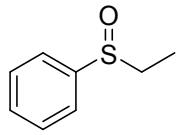

1133
NC
2j
f1 (ppm)


1217
MeOOC
2k
f1 (ppm)

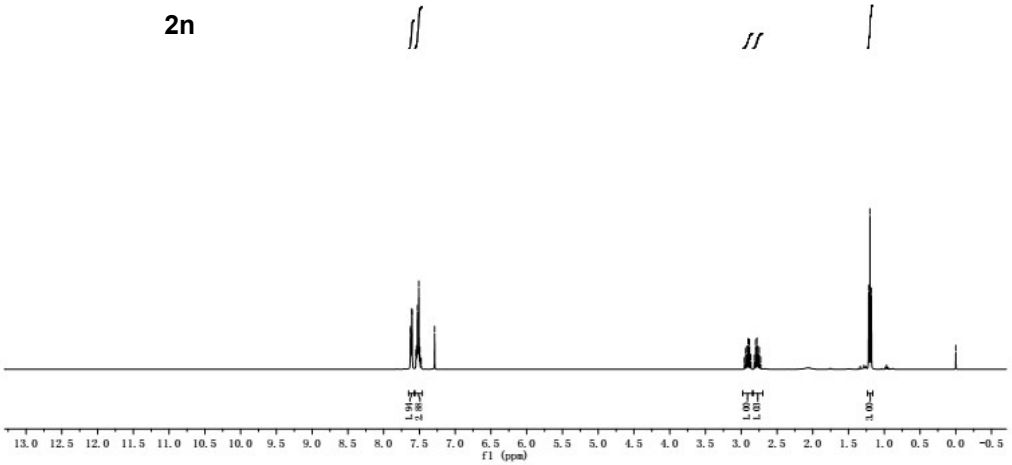

1229
O
S
F3C
2l
f1 (ppm)


1134
O
S
2m
f1 (ppm)

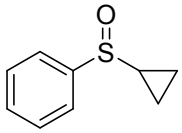
1135



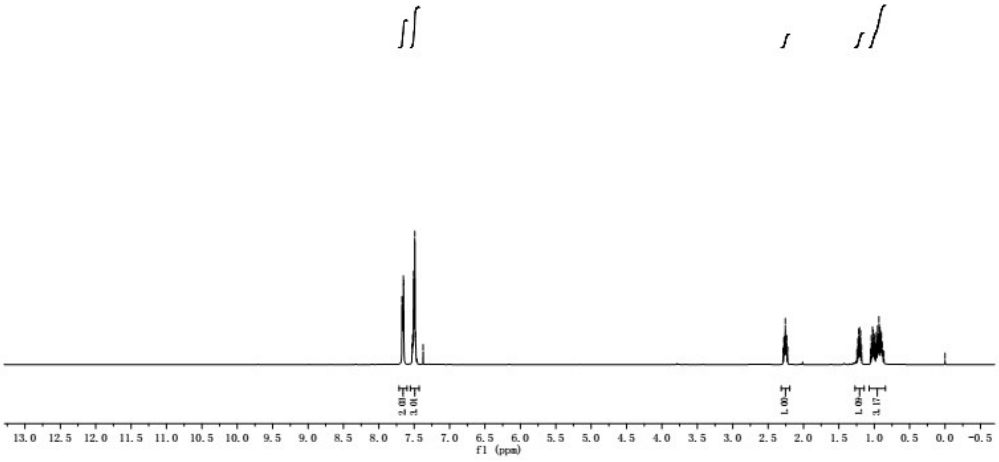
2n

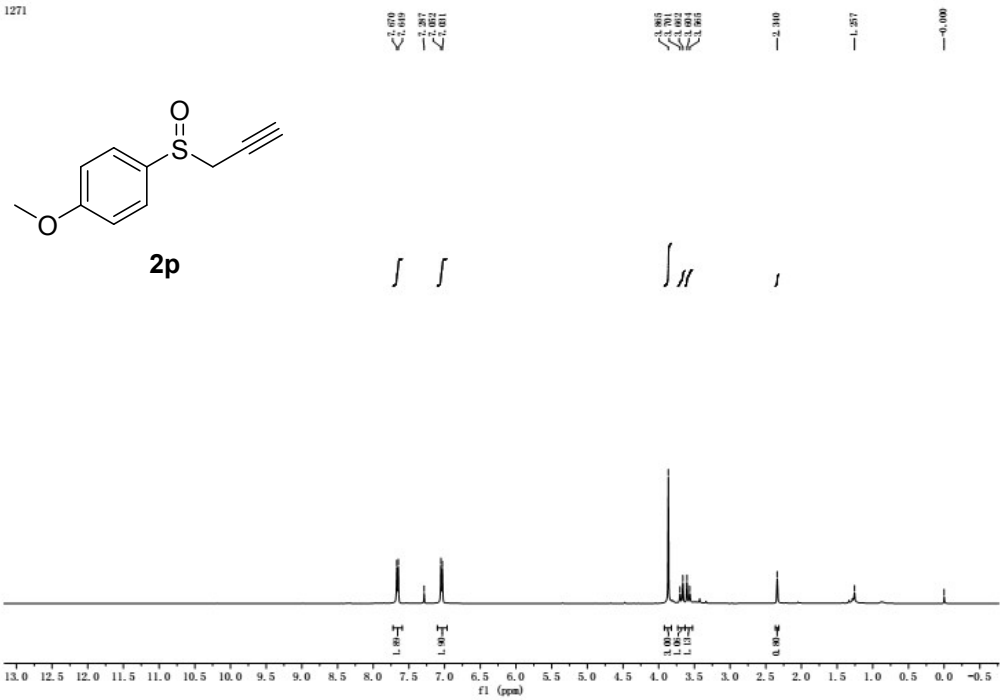


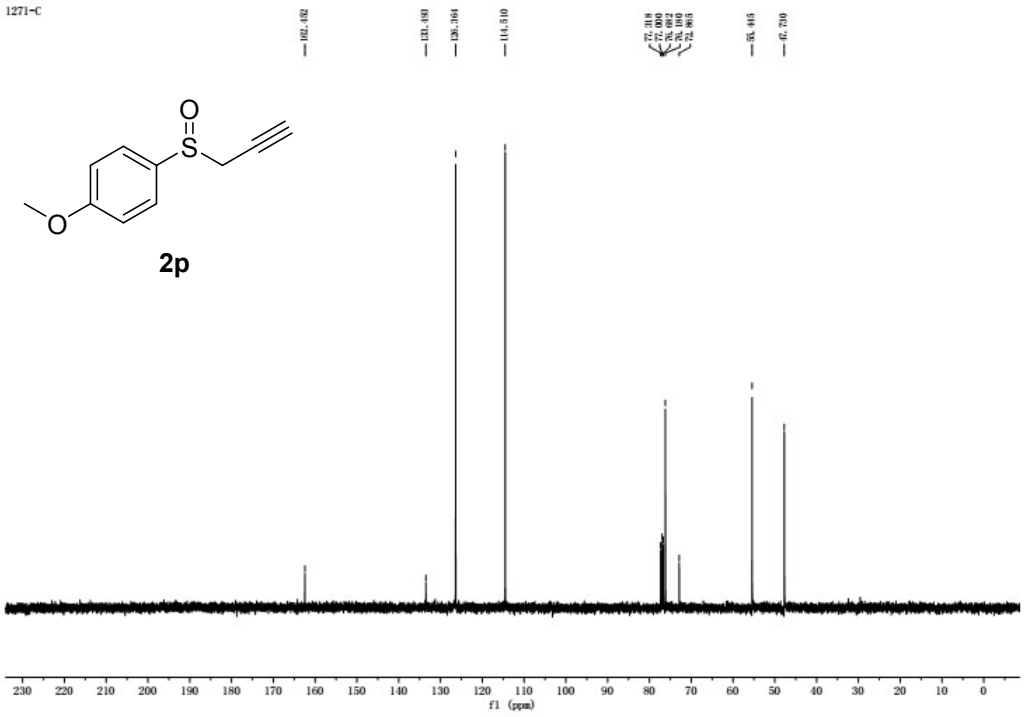
1136

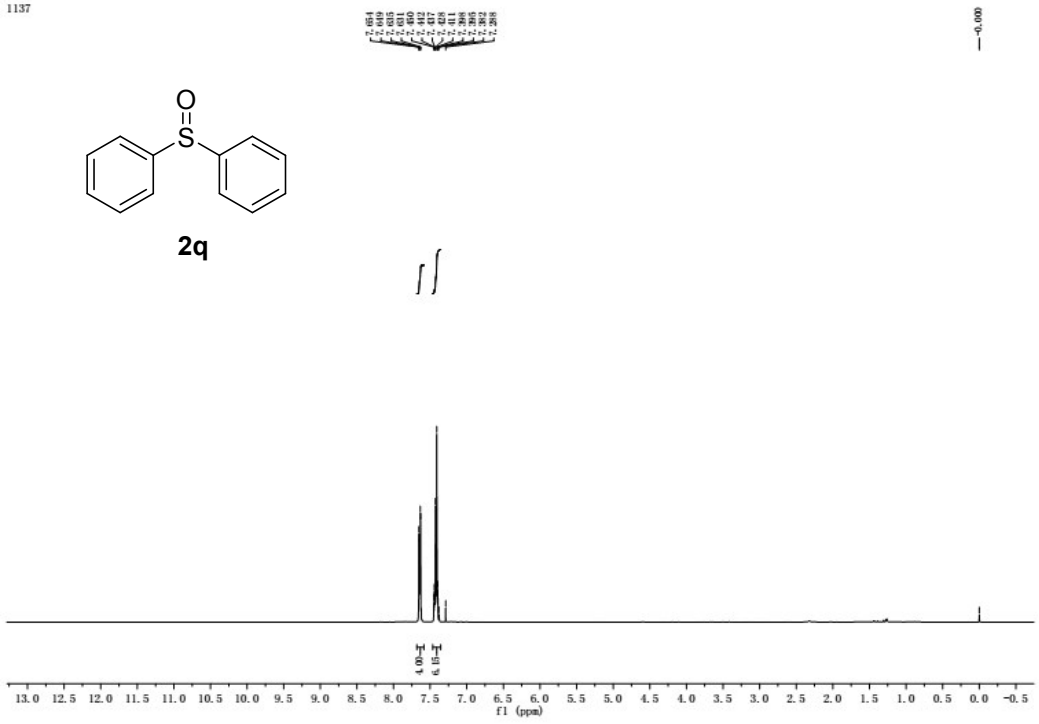


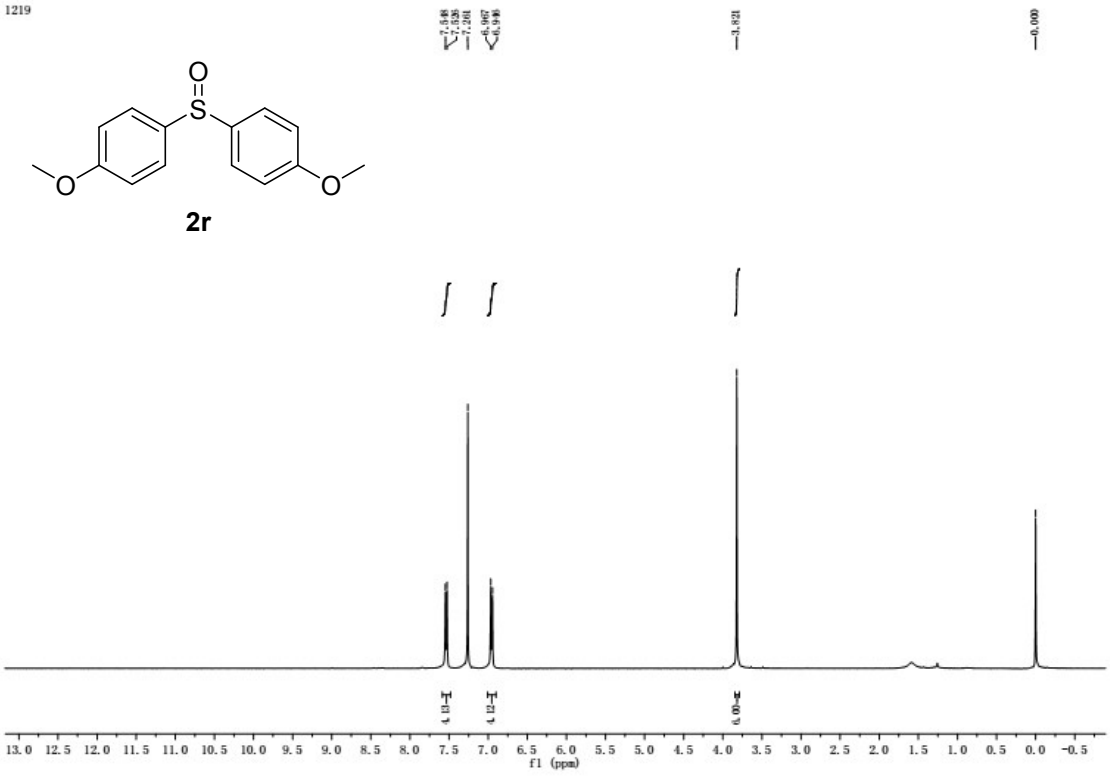
2o

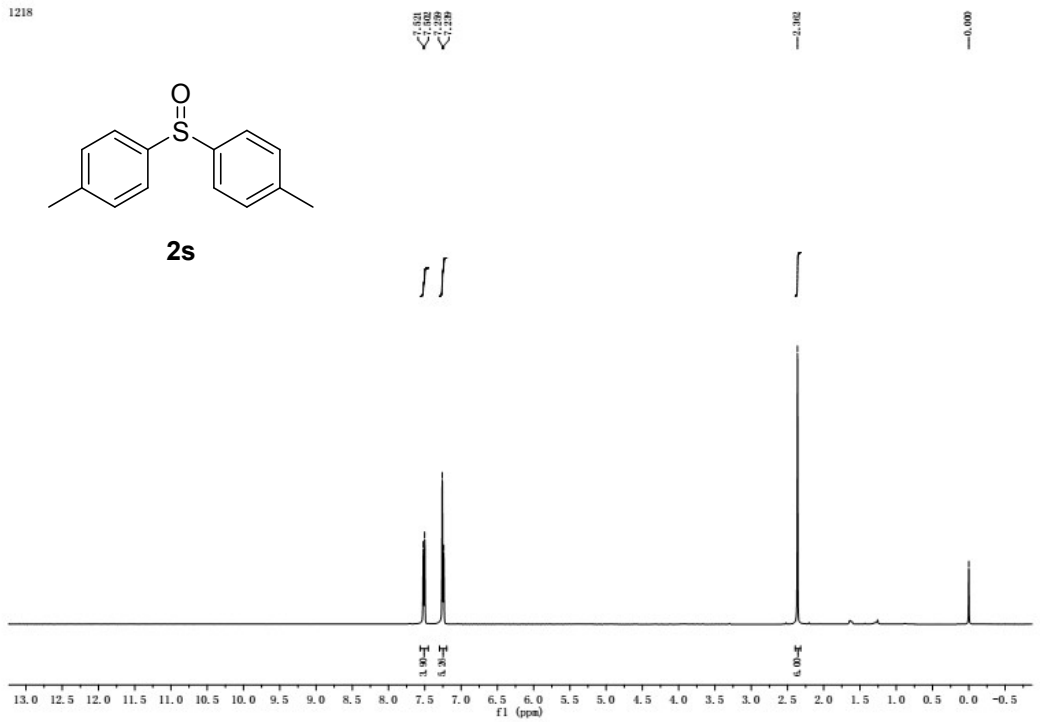



1271
2p
f1 (ppm)

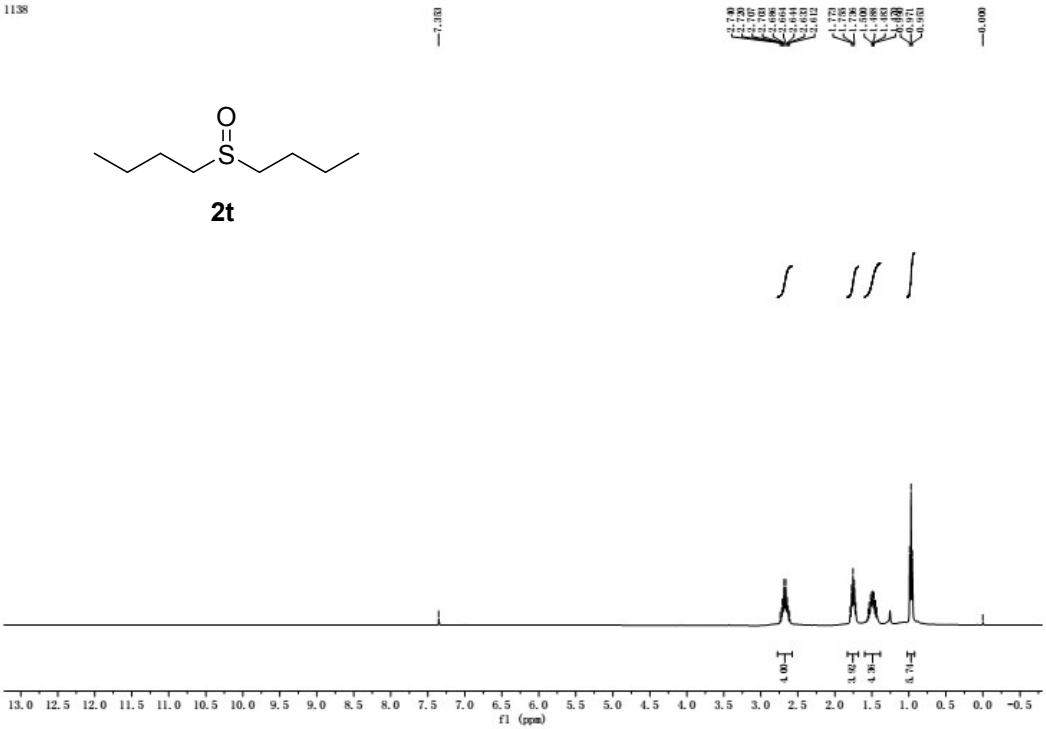

1271-C
2p
f1 (ppm)


1137
O
S
2q
f1 (ppm)

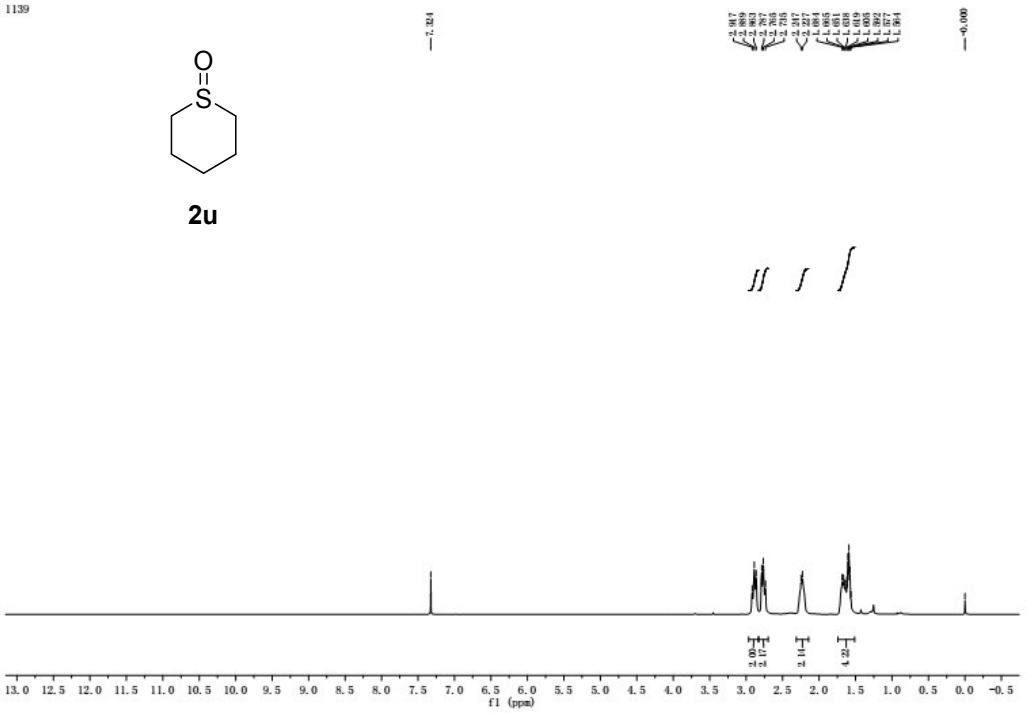

1219
O
S
O
O
2r
f1 (ppm)

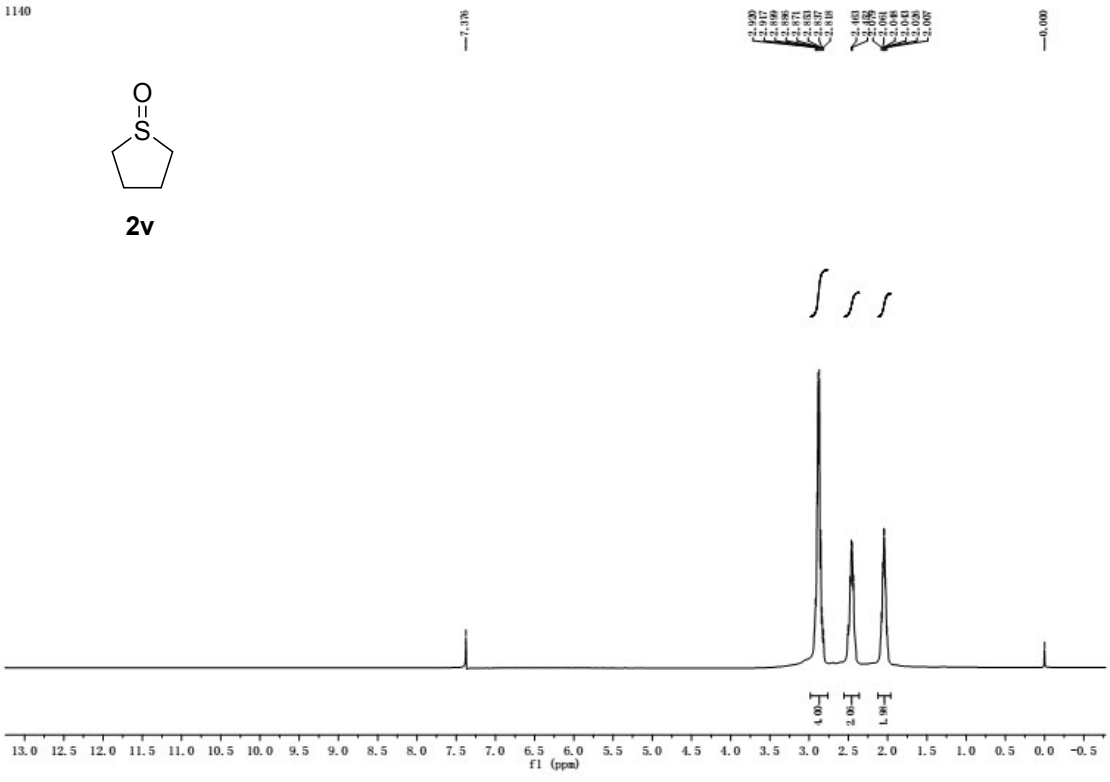

1218
7.321
7.302
7.299
7.239
2.392
0.000
O
S
1.90
1.36
6.00
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

2s


1138
7.353
0.000
O
S
1.00
3.92
1.36
6.74
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

2t


1139
O
S
2u
f1 (ppm)


1140
O
S
2v
f1 (ppm)

References

1. Y. Uetake, T. Niwa and T. Hosoya, *Org. Lett*, 2016, **18**, 2758-2761.
2. S. Kim, J. E. Kim, J. Lee and P. H. Lee, *Adv. Synth. Catal.,* 2015, **357**, 3707-3717.
3. A. Ding, Y. Chen, G. Wang, Y. Zhang, J. Hu and H. Guo, *Polymer*, 2019, **174**, 101-108.
4. K. N. Lehane, E. J. A. Moynihan, N. Brondel, S. E. Lawrence and A. R. Maguire, *CrystEngComm*, 2007, **9**, 1041-1050
5. X. Li, J. Du, Y. Zhang, H. Chang, W. Gao and W. Wei, *Org. Biomol. Chem*., 2019, **17**, 3048-3055.
6. C. Ye, Y. Zhang, A. Ding, Y. Hu and H. Guo, *Sci, Rep.*, 2018, **8**, 2205.
7. M. Frings, C. Bolm, A. Blum and C. Gnamm, *Eur. Med. Chem.*, 2017, **126**, 225-245.