Electronic Supplementary Information for

Construction of supramolecular dimers photosensitizers based on triphenylamine derivatives and cucurbit[8]uril for photocatalysis

Xin-Long Li, Dong-Liang Cheng, Kai-Kai Niu,* Hui Liu, Sheng-Sheng Yu, Yue-Bo Wang, and Ling-Bao Xing*

School of Chemistry and Chemical Engineering, Shandong University of Technology, Zibo 255000, P. R. China

*Corresponding author: Tel. /fax: +86 533 2781664. E-mail: kkai007@163.com; lbxing@sdut.edu.cn.

1. Detection of $^1O_2$ production in solution.

Compound 9,10-anthracenediyl-bis(methylene)-dimalonic acid (ABDA) was used as an indicator for detection of $^1O_2$ in the aqueous solution (Fig. S13). 50 μM of photocatalyst was dissolved in 3.0 mL solution containing 0.5 mM of ABDA. The mixture was then placed in a cuvette and irradiated with a blue light (450-455 nm). The absorption change of the sample at 378 nm was recorded by the UV-vis absorption spectrophotometer.

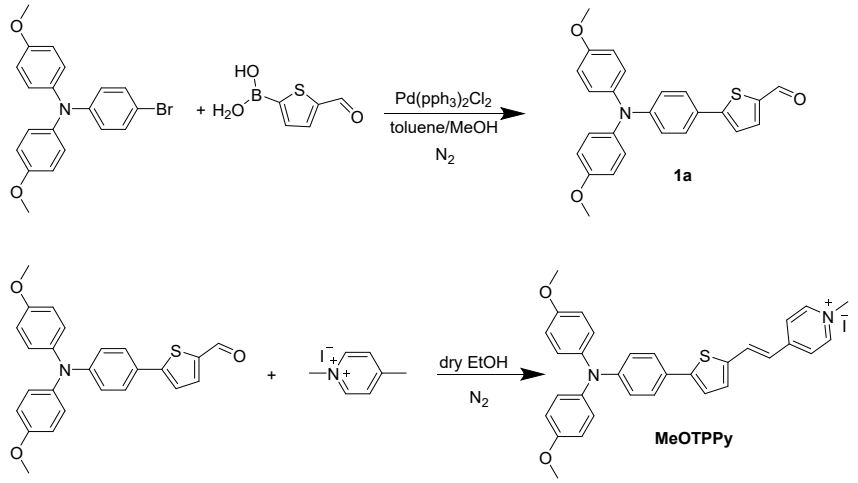
2. General procedure for the reaction of oxidation of thioanisole

Thioanisole (0.10 mmol) was dissolved in the freshly prepared 2MeOTPPy-CB[8] and 2MATM-CB[8] assembly solution (0.8 mol%, 2.0 mL). The mixture was subsequently irradiated by blue light (450-455 nm) at room temperature for 8 h. After that, it was extracted with dichloromethane, and the combined organic layer was dried with anhydrous Na_2SO_4. Then the organic solvent was concentrated in a vacuum. The crude product was separated by flash column chromatography with petroleum ether/ethyl acetate to obtain the product.

3. Experimental

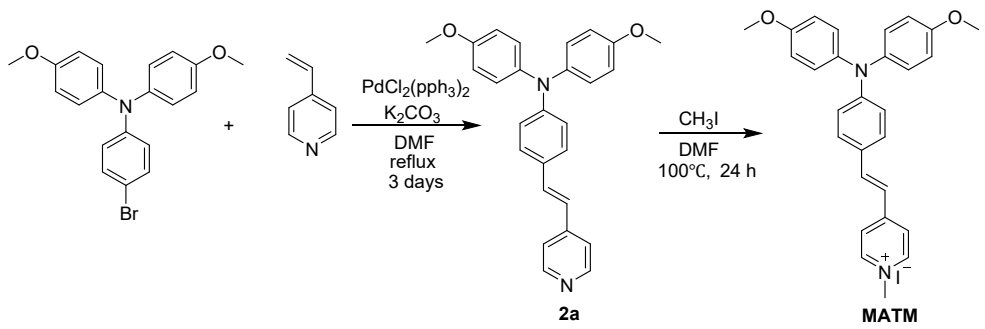
3.1 Materials

Unless specifically mentioned, the chemicals used are commercially available.



Scheme S1. Synthetic route of MeOTPPy

Synthesis of 1a: 4-broMo-N,N-bis(4-Methoxyphenyl)aniline (384 mg, 1.0 mmol) and 5-Formyl-2-thiopheneboronic acid (234 mg, 1.5 mmol) were dissolved in 20 mL MeOH/toluene = 1:1 mixed solution and reacted for 16 hours at 75℃ under N_2. After cool to room temperature, extracted the organic phase with dichloromethane and concentrated it under vacuum. Then, the crude product was separated by flash column chromatography with petroleum ether/ethyl acetate = 5:1 to obtain orange solid (300 mg, 0.72 mmol, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (s, 1H), 7.69 (d, J = 4.0 Hz, 1H), 7.48 - 7.43 (m, 2H), 7.25 (d, J = 3.9 Hz, 1H), 7.12 - 7.07 (m, 4H), 6.93 - 6.88 (m, 2H), 6.88 - 6.84 (m, 4H), 3.81 (s, 6H).



Scheme S2. Synthetic route of MATM

Synthesis of 2a: 4-broMo-N,N-bis(4-Methoxyphenyl)aniline (384 mg, 1.0 mmol) and 4-Vinylpyridine (210 mg, 2.0 mmol) were dissolved in 10 mL DMF and refluxed overnight.. After cool to room temperature, DMF was removed by vacuum distillation and extracted the organic phase with dichloromethane and concentrated it under vacuum. Then, the crude product was separated by flash column chromatography with petroleum ether/ethyl acetate = 20:1 to obtain pale yellow solid (250 mg, 0.61 mmol, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 - 8.49 (m, 2H), 7.36 - 7.30 (m, 4H), 7.23 (d, J = 16.3 Hz, 1H), 7.11 - 7.05 (m, 4H), 6.91 - 6.88 (m, 2H), 6.87 - 6.80 (m, 5H), 3.81 (s, 6H).

4. Characterization

^{1}H NMR was characterized on Bruker Avance 400 NMR instrument. UV-vis absorption spectra were characterized by a Shimadzu UV-2450 spectrophotometer. Fluorescence emission spectra were obtained by fluorescence spectrophotometer F-380A. DLS and Zeta potential tests were constructed on Malvern Zeta sizer Nano ZS90.

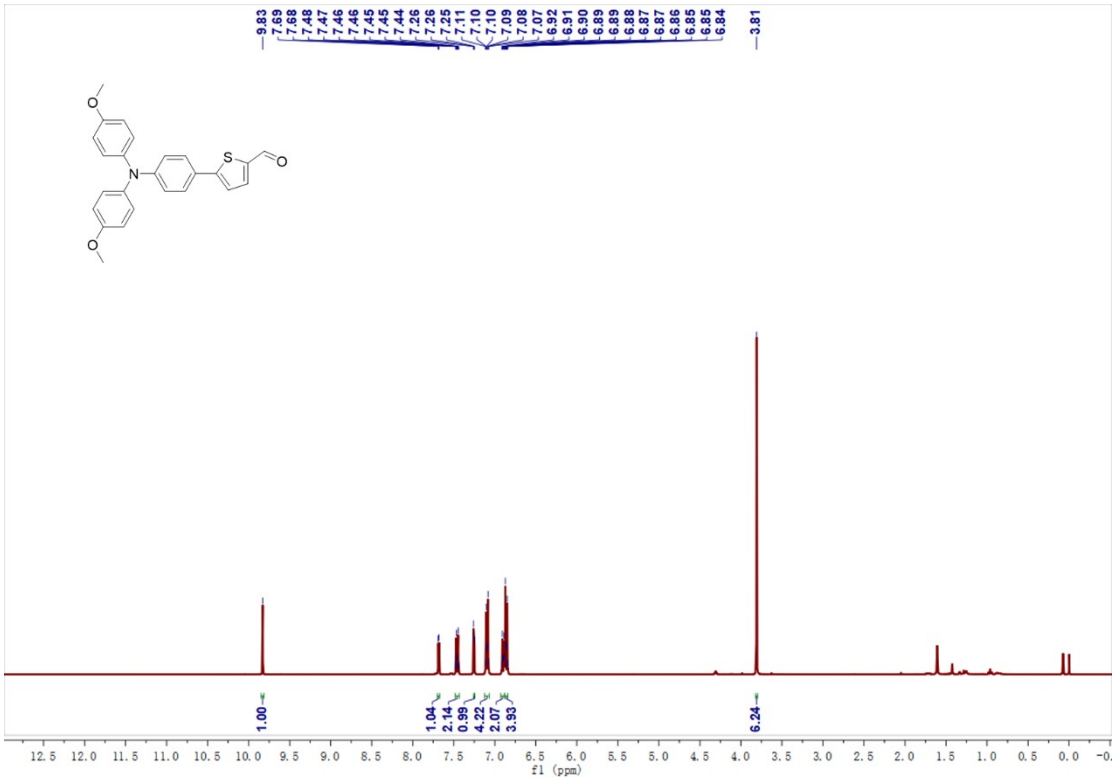


Fig. S1 ^{1}H NMR spectra of **1a** in $CDCl_3$.

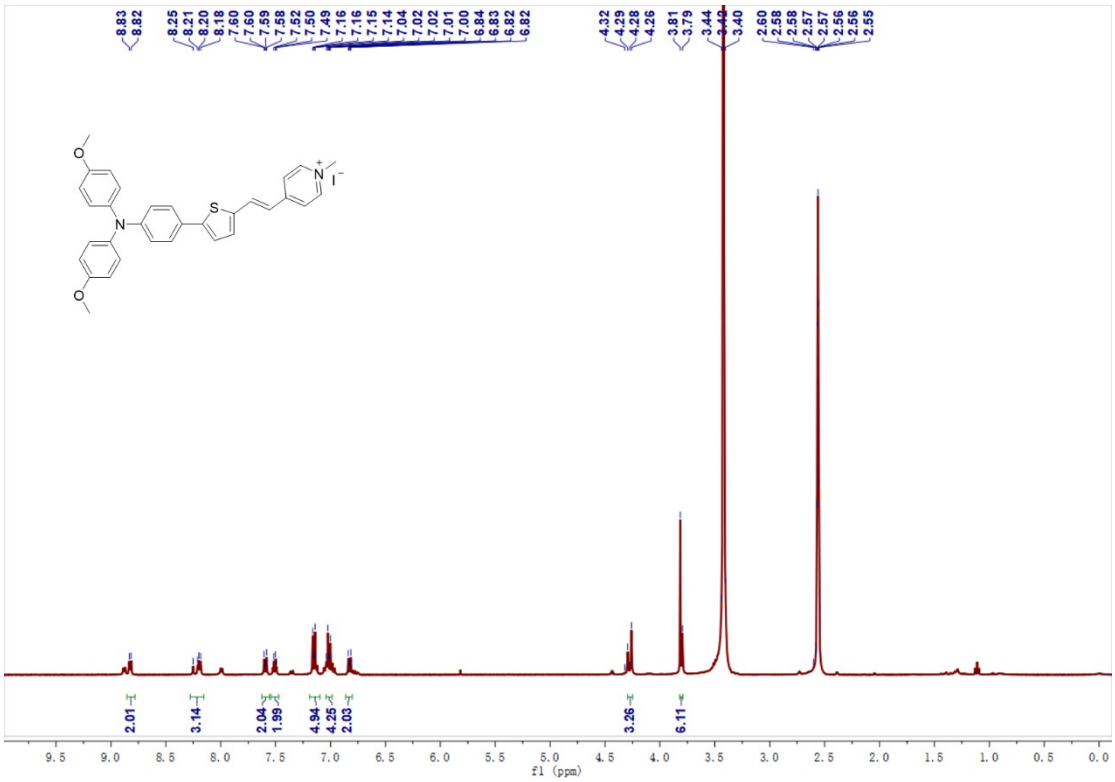


Fig. S2 ^{1}H NMR spectra of **MeOTPPy** in DMSO-d_6.

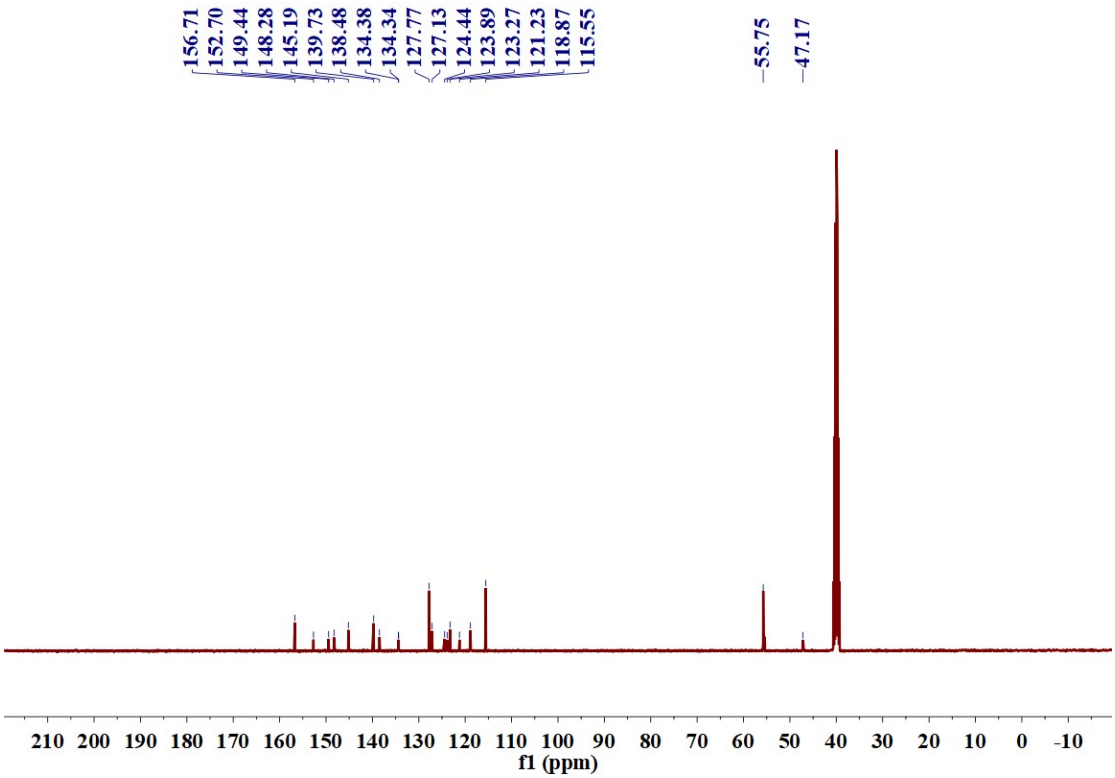


Fig. S3 ^{13}C NMR spectra of **MeOTPPy** in DMSO-d_6.

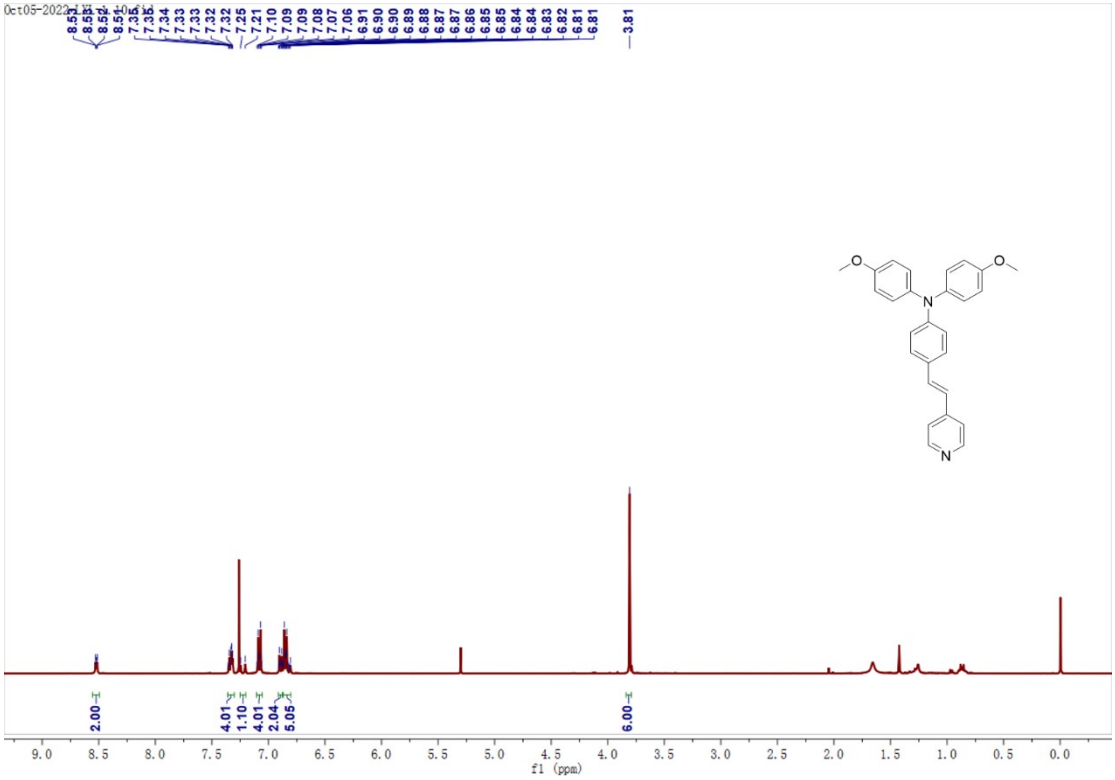


Fig. S4 ^{1}H NMR spectra of **2a** in $CDCl_3$.

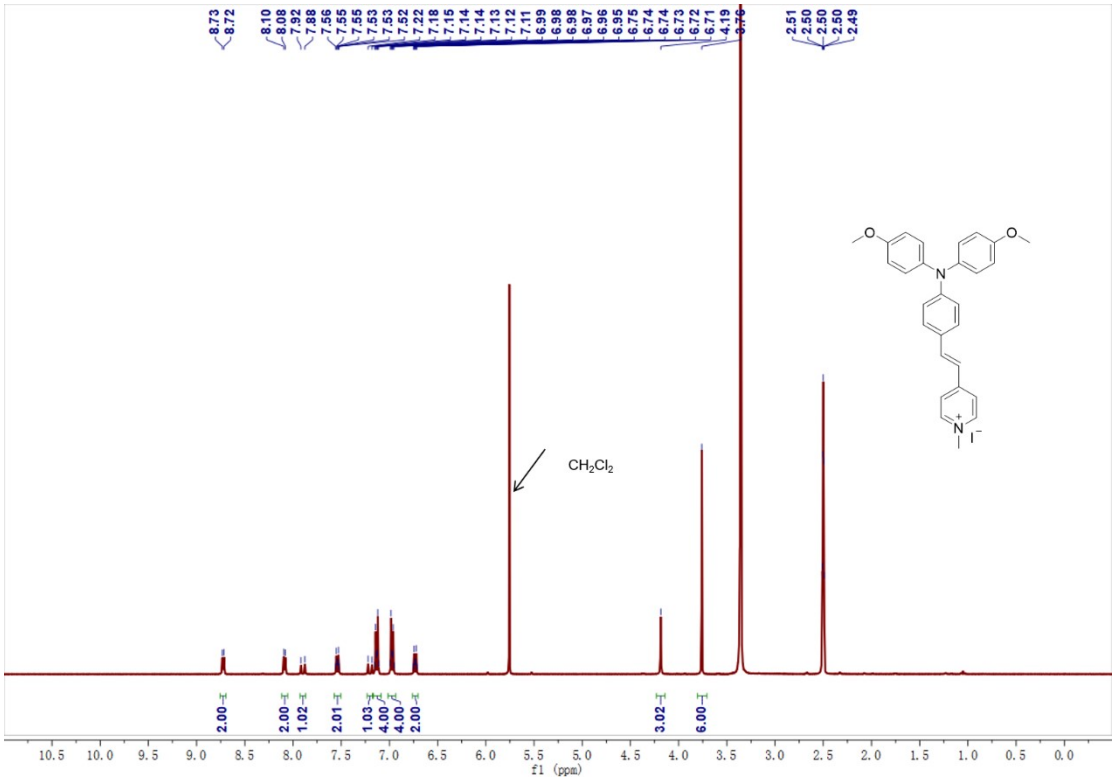


Fig. S5 ^{1}H NMR spectra of **MATM** in DMSO-d_6.

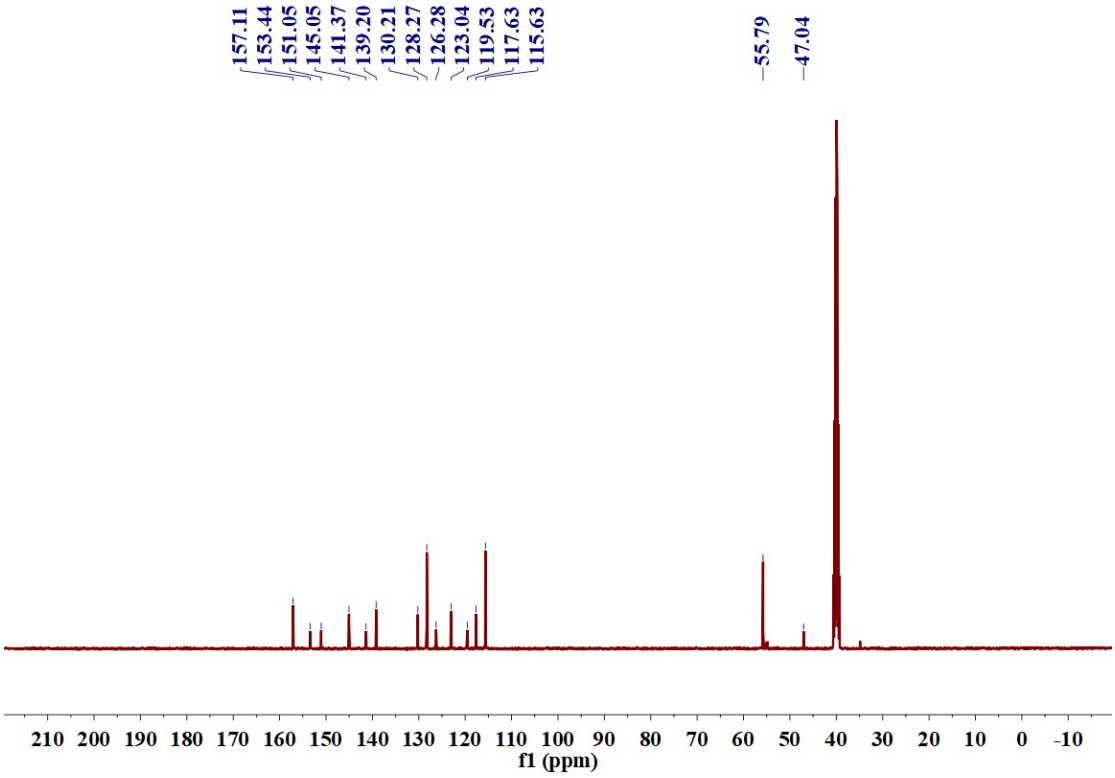


Fig. S6 ^{13}C NMR spectra of **MATM** in DMSO-d_6.

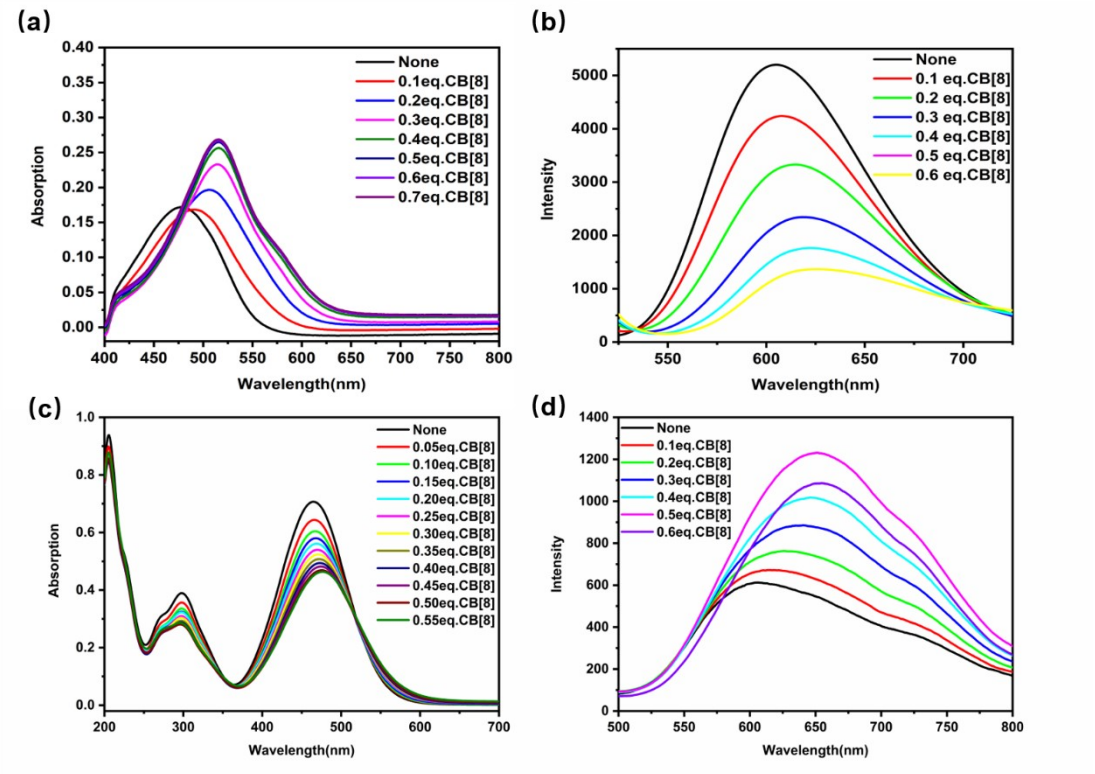


Fig. S7 (a) UV-vis absorption spectra of MeOTPPy in aqueous solution with different concentrations of CB[8]; (b) Fluorescence emission spectra of MeOTPPy in aqueous solution with different concentrations of CB[8]; (c) UV-vis absorption spectra of MATM in aqueous solution with different concentrations of CB[8]; (d) Fluorescence emission spectra of MATM in aqueous solution with different concentrations of CB[8].

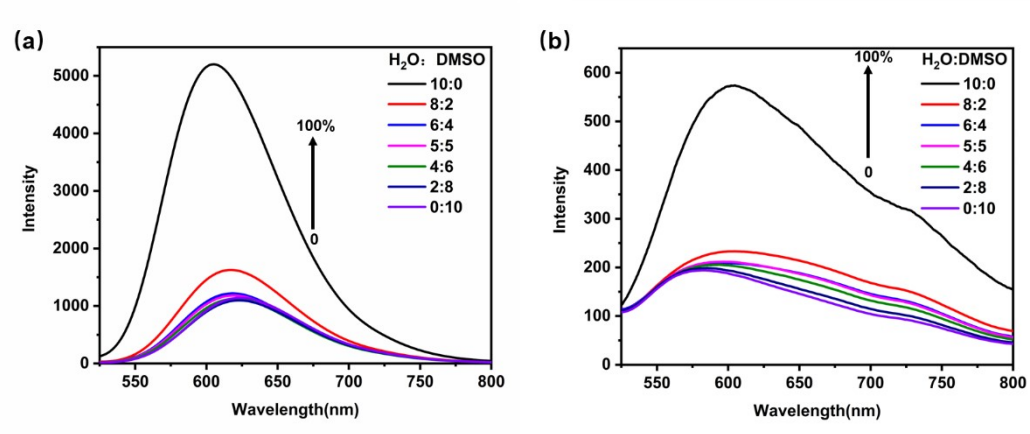


Fig. S8 (a) The fluorescence emission spectra of MeOTPPy in mixed solvents of DMSO and water with different ratios; (b) The fluorescence emission spectra of MATM in mixed solvents of DMSO and water with different ratios. [MeOTPPy] = 5.0×10^{-5} M, [MATM] = 5.0×10^{-5} M.

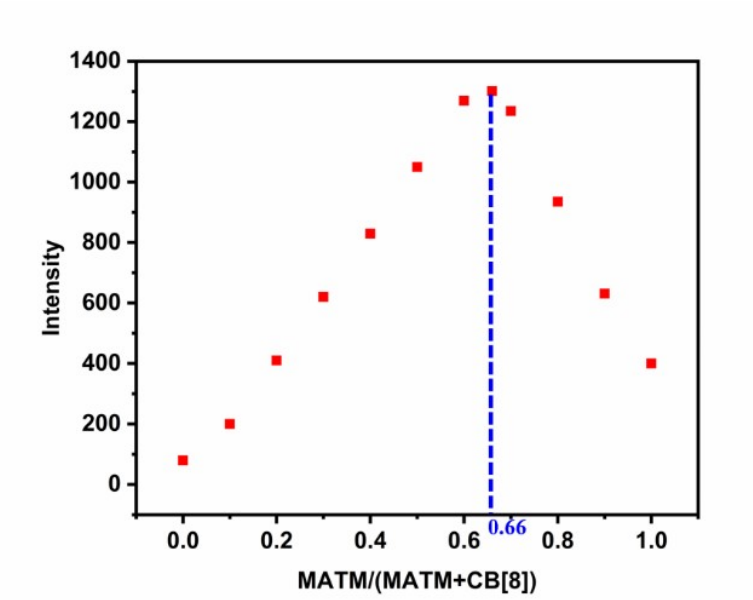


Fig. S9 Job's plot of the change in emission spectra at 600 nm for MATM and CB[8]; the excitation wavelength was 465 nm; the total concentration of MATM and CB [8] was fixed at 1.0×10^{-4}M.

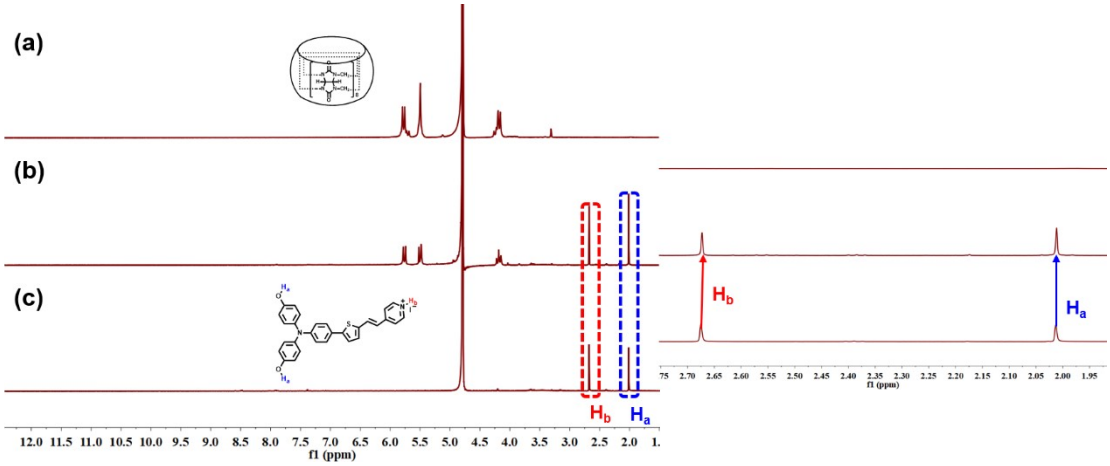


Fig. S10 ^{1}H NMR spectra of (a) CB[8], (b) 2MeOTPPy-CB[8], and (c) MeOTPPy in D_2O.

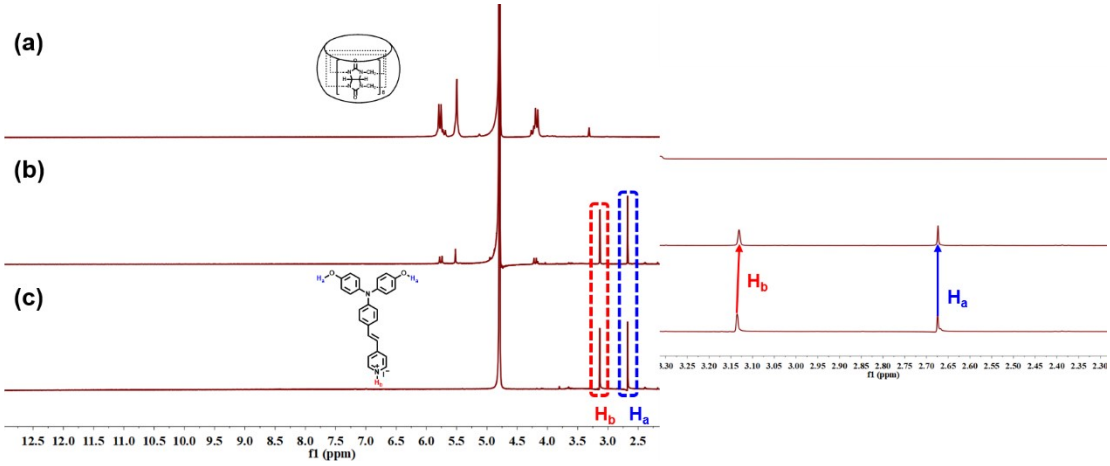


Fig. S11 ^{1}H NMR spectra of (a) CB[8], (b) 2MATM-CB[8], and (c) MATM in D_2O.

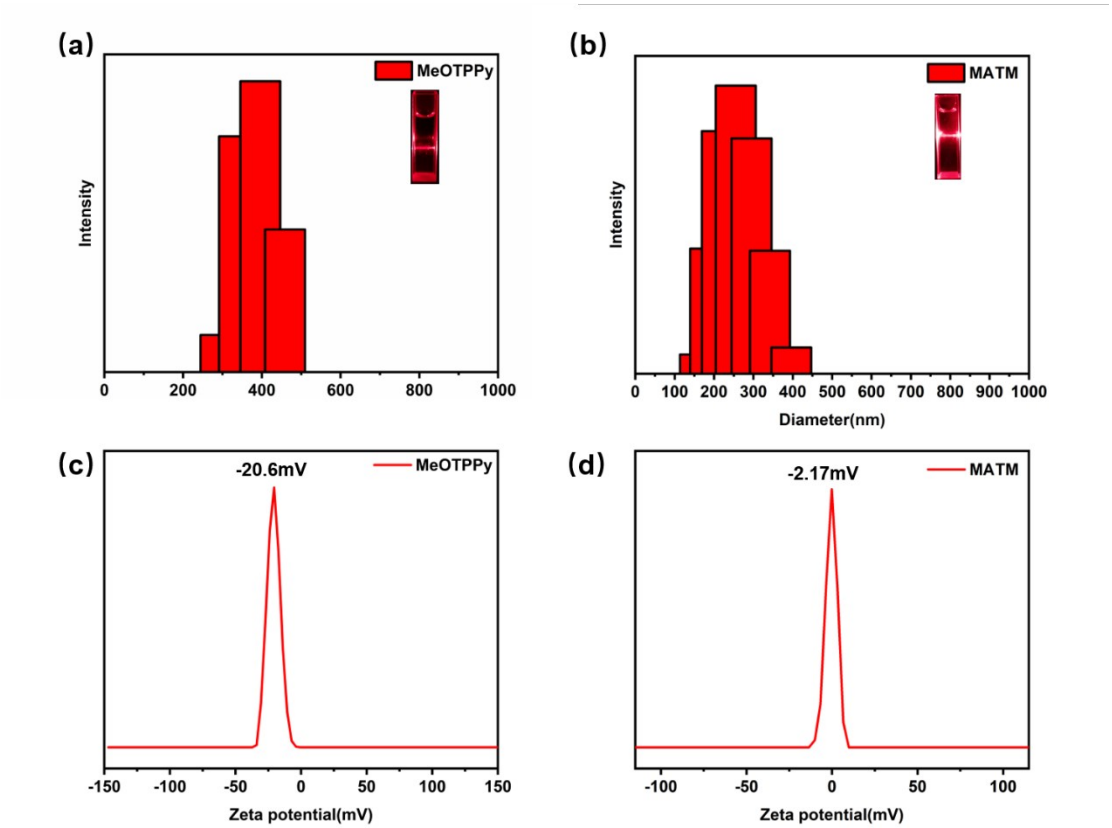


Fig. S12 Particle size distribution of (a) MeOTPPy aqueous solutions and (b) MATM aqueous solutions (Insets: Tyndall effect); Zeta potential of (c) MeOTPPy and (d) MATM in the aqueous solution.

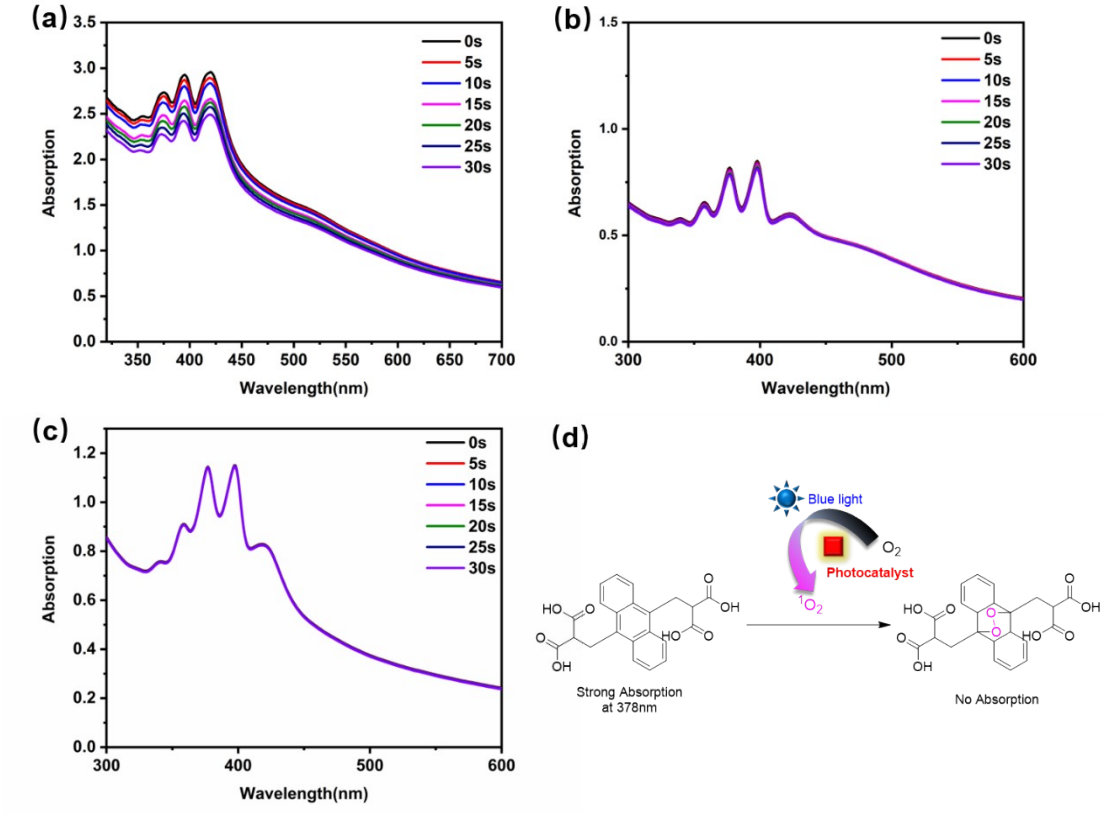


Fig. S13 The absorption spectra of ABDA after irradiation by blue light (450-455 nm) for a different time in the presence of (a) 2MeOTPPy-CB[8]+ABDA in H_2O, (b) 2MATM-CB[8]+ABDA in H_2O and (c) ABDA in H_2O; (d) The mechanism of 9,10-anthracenediyl-bis(methylene)-dimalonic acid (ABDA) as the $^1O_2$ scavenger monitors singlet oxygen generation in the solution.

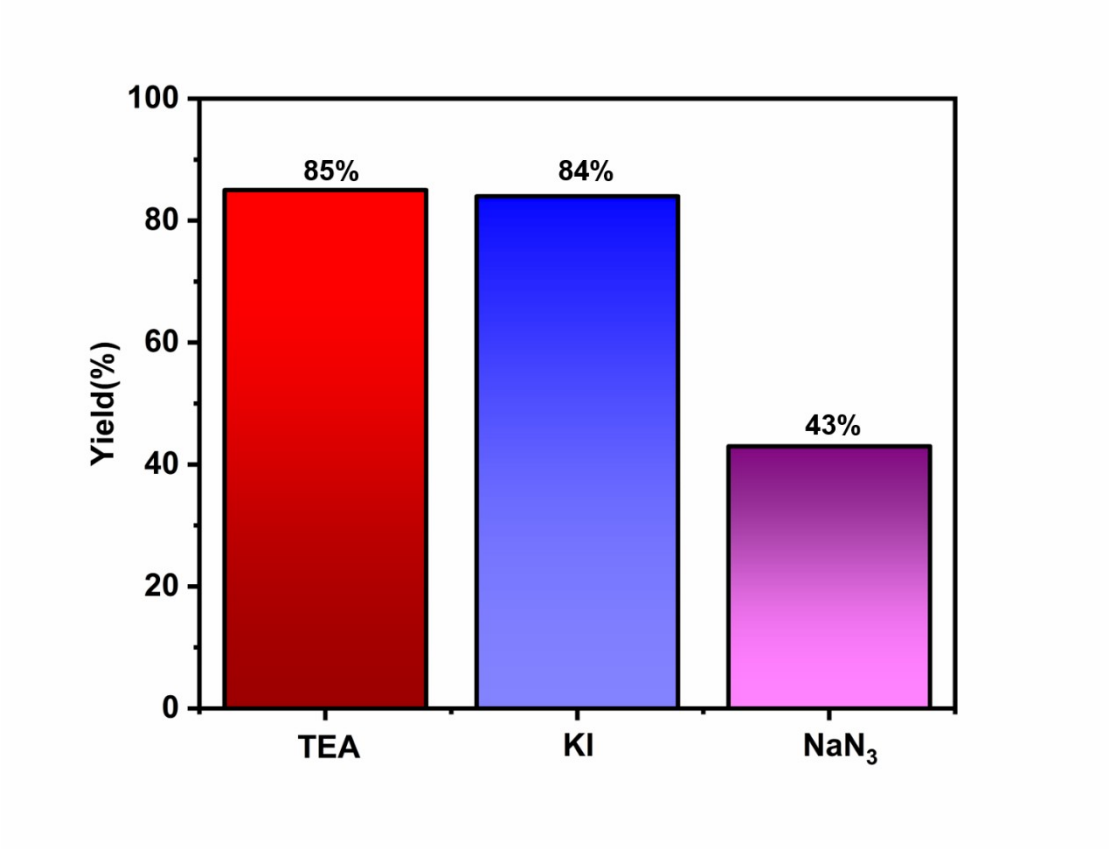
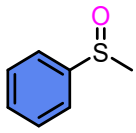


Fig. S14 The yields of the photooxidation reactions of thioanisole with different scavengers.

^{1}H NMR spectra and data of 2a-2n

2a. (Methylsulfinyl)benzene



87% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 - 7.64 (m, 2H), 7.58 - 7.48 (m, 3H), 2.74 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.65, 131.04, 129.36, 123.49, 43.97.

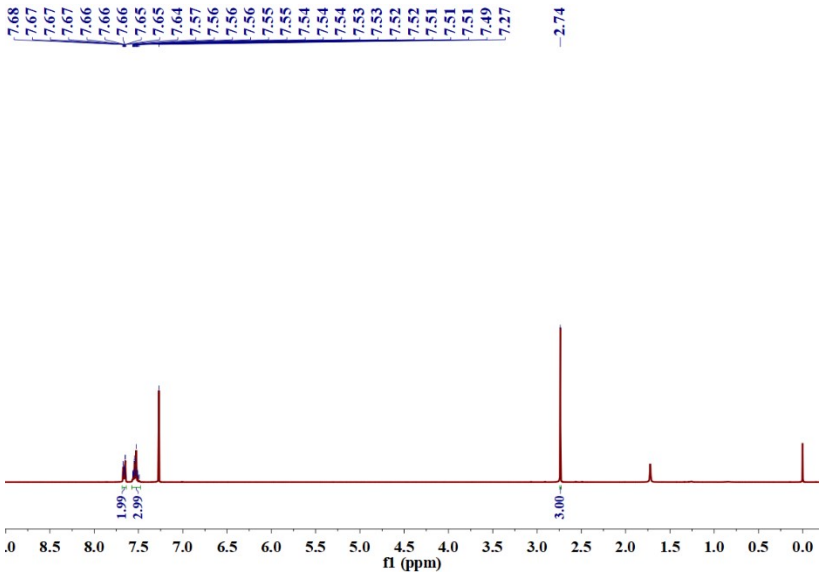


Fig. S15 ^{1}H NMR spectra of (methylsulfinyl)benzene in $CDCl_3$.

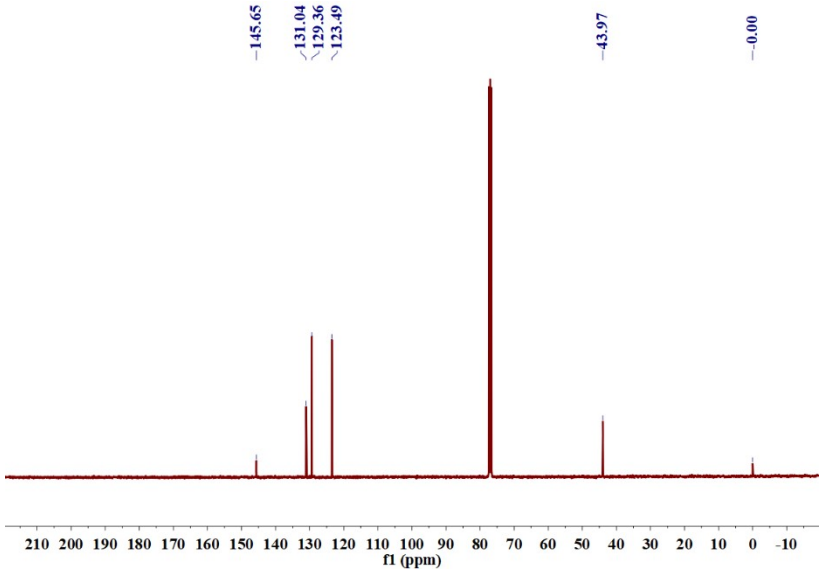
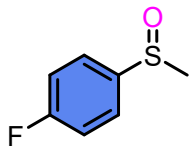


Fig. S16 ^{13}C NMR spectra of (methylsulfinyl)benzene in $CDCl_3$.

2b. 1-Fluoro-4-(methylsulfinyl) benzene



91% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 - 7.56 (m, 2H), 7.23 - 7.14 (m, 2H), 2.68 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 163.0, 141.1, 141.1, 125.9, 125.8, 116.8, 116.6, 44.1.

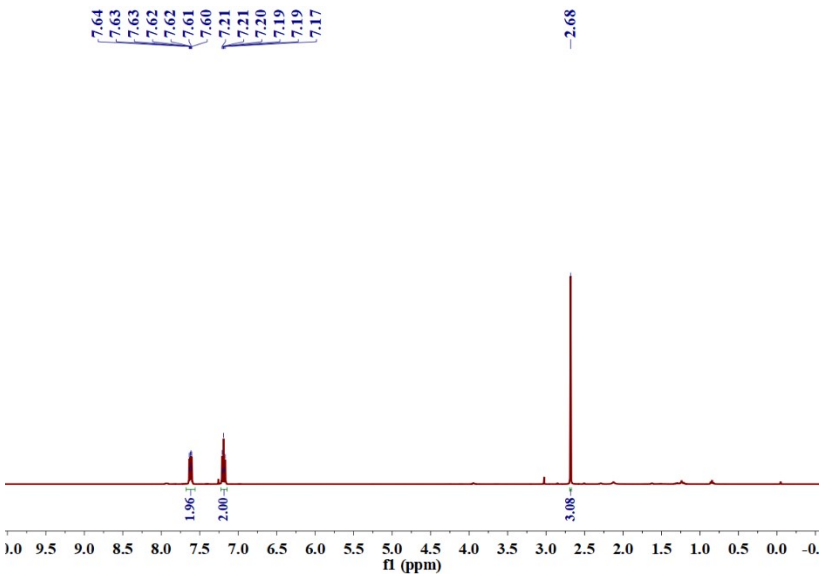


Fig. S17 ^{1}H NMR spectra of 1-Fluoro-4-(methylsulfinyl) benzene in $CDCl_3$.

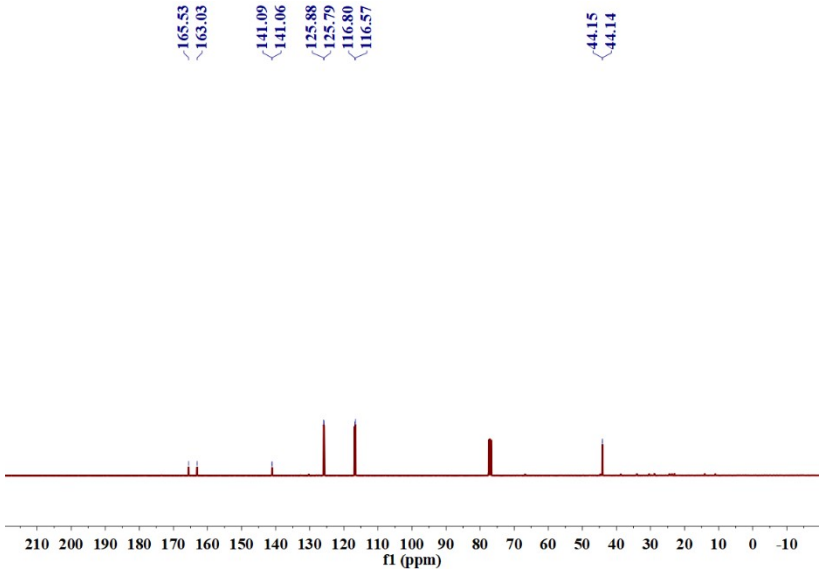
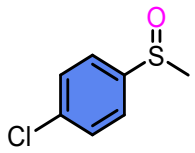


Fig. S18 ^{13}C NMR spectra of 1-Fluoro-4-(methylsulfinyl) benzene in $CDCl_3$.

2c. 1-Chloro-4-(methylsulfinyl)benzene



92% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 - 7.49 (m, 2H), 7.46 - 7.40 (m, 2H), 2.65 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 137.2, 129.6, 124.9, 43.9.

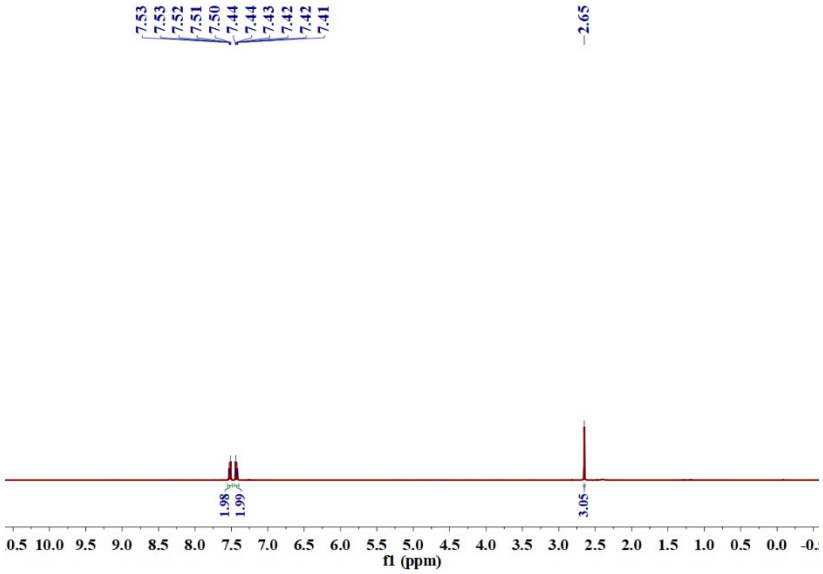


Fig. S19 ^{1}H NMR spectra of 1-Chloro-4-(methylsulfinyl)benzene in $CDCl_3$.

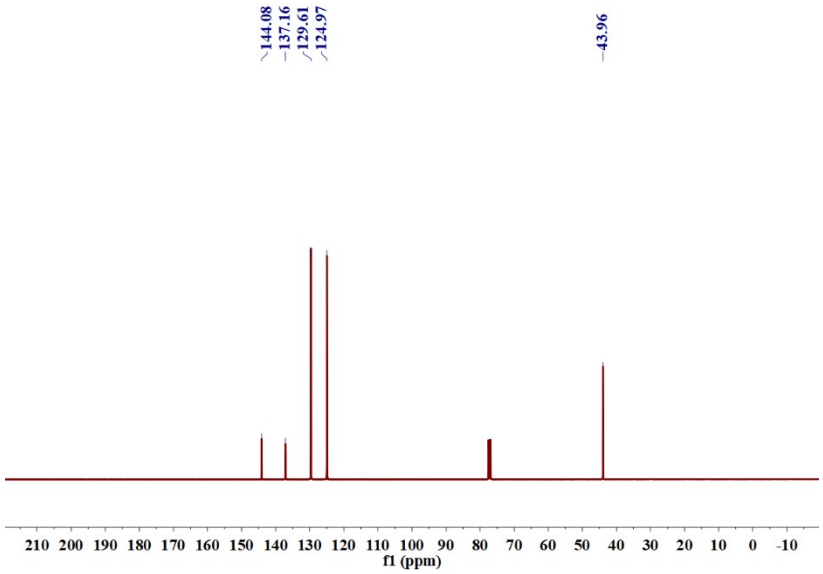
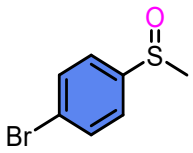


Fig. S20 ^{13}C NMR spectra of 1-Chloro-4-(methylsulfinyl)benzene in $CDCl_3$.

2d. 1-Bromo-4-(methylsulfinyl)benzene



88% yield;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 - 7.54 (m, 2H), 7.48 - 7.40 (m, 2H), 2.63 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.82, 132.51, 125.37, 125.14, 43.96.

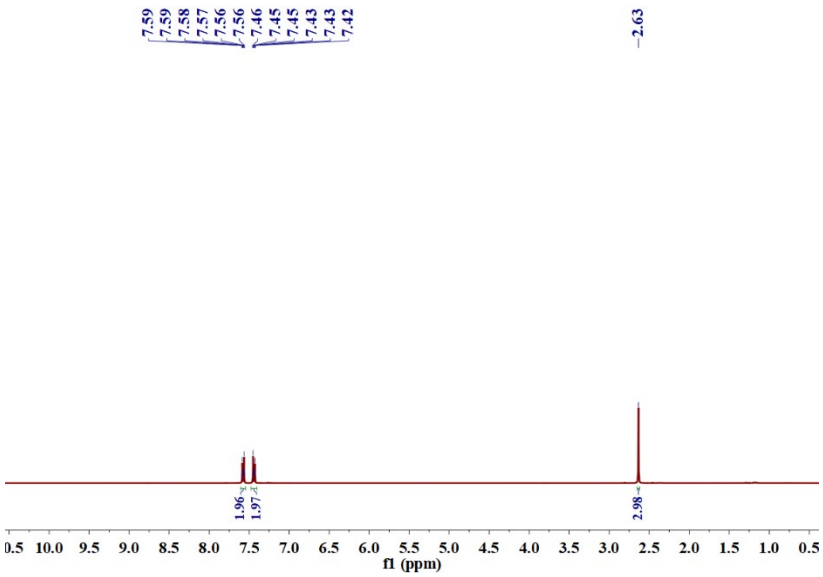


Fig. S21 ^{1}H NMR spectra of 1-Bromo-4-(methylsulfinyl)benzene in $CDCl_3$.

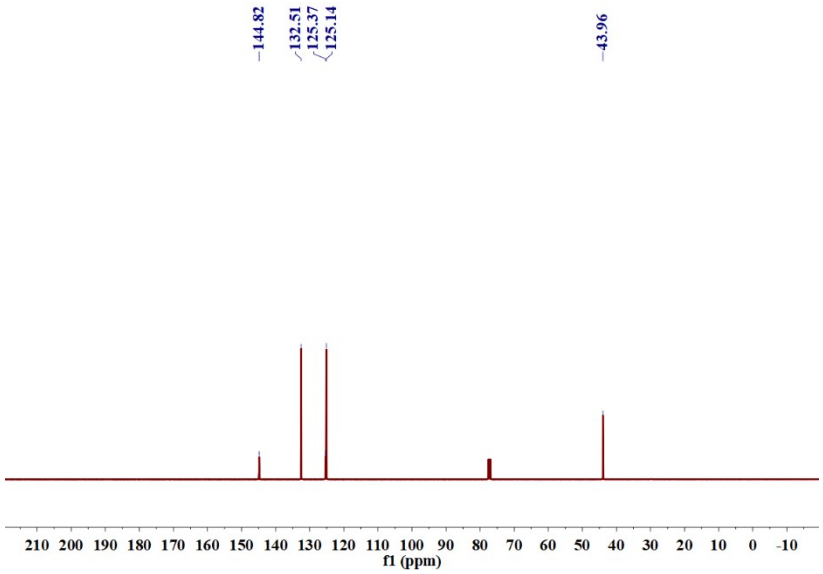
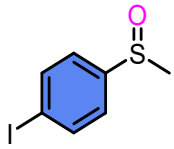


Fig. S22 ^{13}C NMR spectra of 1-Bromo-4-(methylsulfinyl)benzene in $CDCl_3$.

2e. 1-Iodine-4- (methylsulfinyl) benzene



90% yield;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 - 7.78 (m, 2H), 7.35 - 7.31 (m, 2H), 2.66 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.61, 138.43, 125.15, 97.45, 43.95.

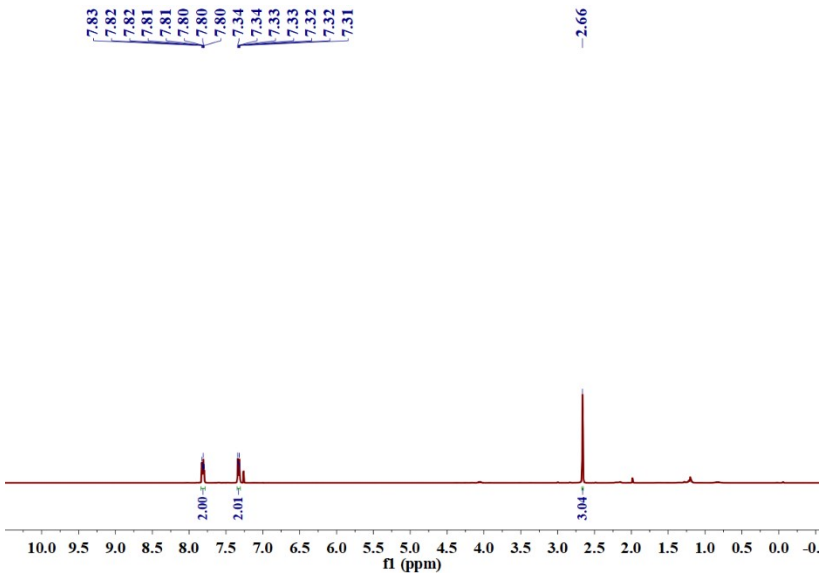


Fig. S23 ^{1}H NMR spectra of 1-Iodine-4- (methylsulfinyl) benzene in $CDCl_3$.

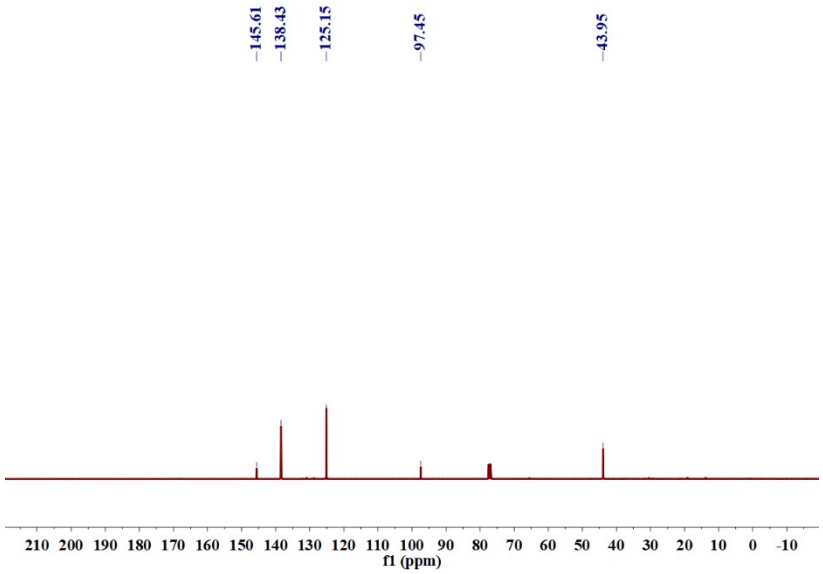
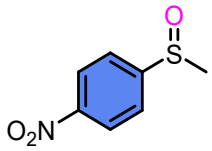


Fig. S24 ^{13}C NMR spectra of 1-Iodine-4- (methylsulfinyl) benzene in $CDCl_3$.

2f. 1-Methanesulfinyl-4-nitrobenzene



89% yield;^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 8.8 Hz, 2H), 7.82 (d, J = 8.8 Hz, 2H), 2.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.23, 149.46, 124.68, 124.50, 43.87.

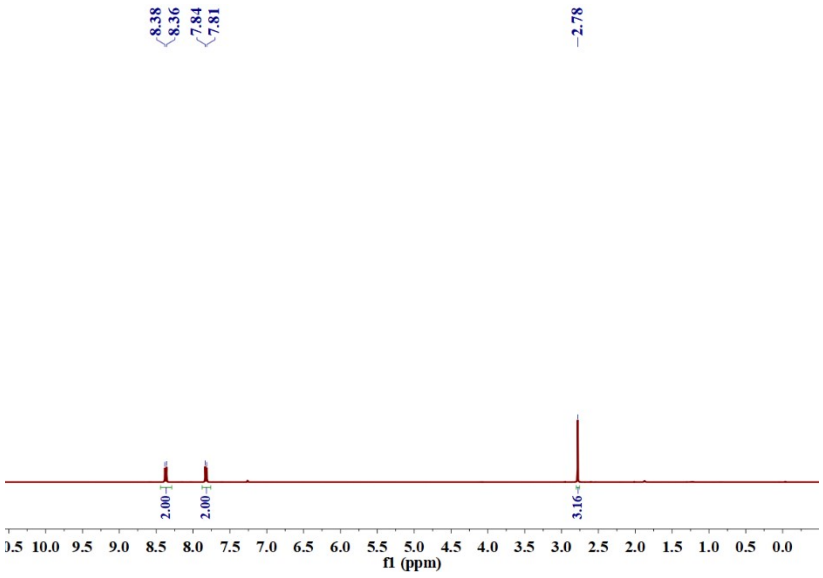


Fig. S25 ^{1}H NMR spectra of 1-Methanesulfinyl-4-nitrobenzene in $CDCl_3$.

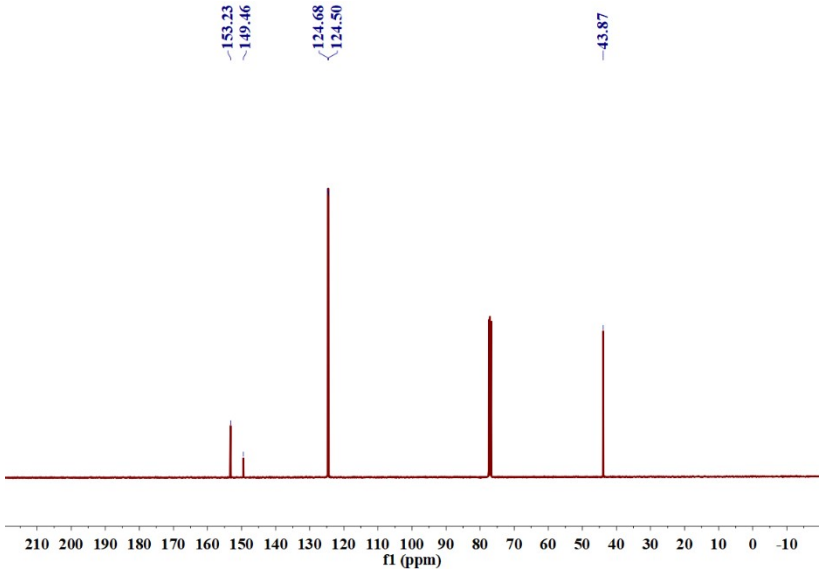
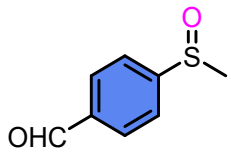


Fig. S26 ^{13}C NMR spectra of 1-Methanesulfinyl-4-nitrobenzene in $CDCl_3$.

2g. 4-(Methylsulfinyl)benzaldehyde



86% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 8.8 Hz, 2H), 7.82 (d, J = 8.8 Hz, 2H), 2.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.19, 152.34, 138.09, 130.42, 124.17, 43.74.

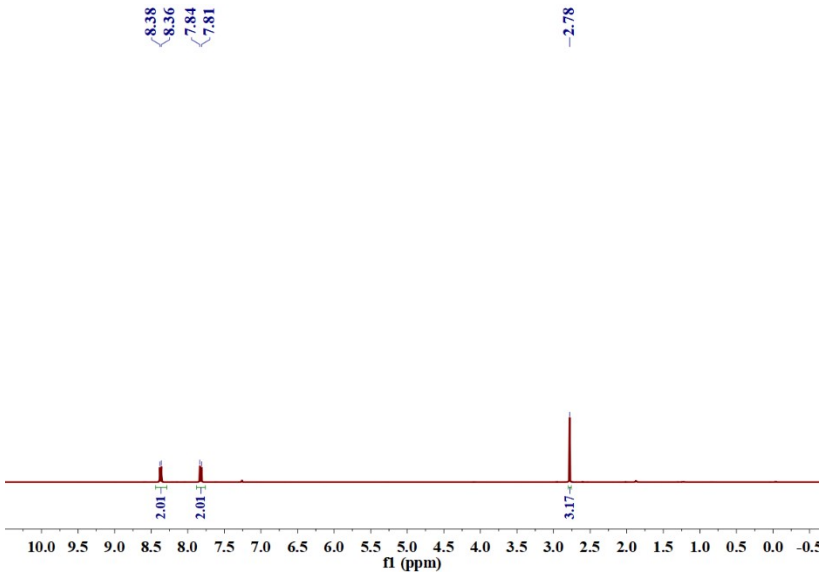


Fig. S27 ^{1}H NMR spectra of 4-(Methylsulfinyl)benzaldehyde in $CDCl_3$.

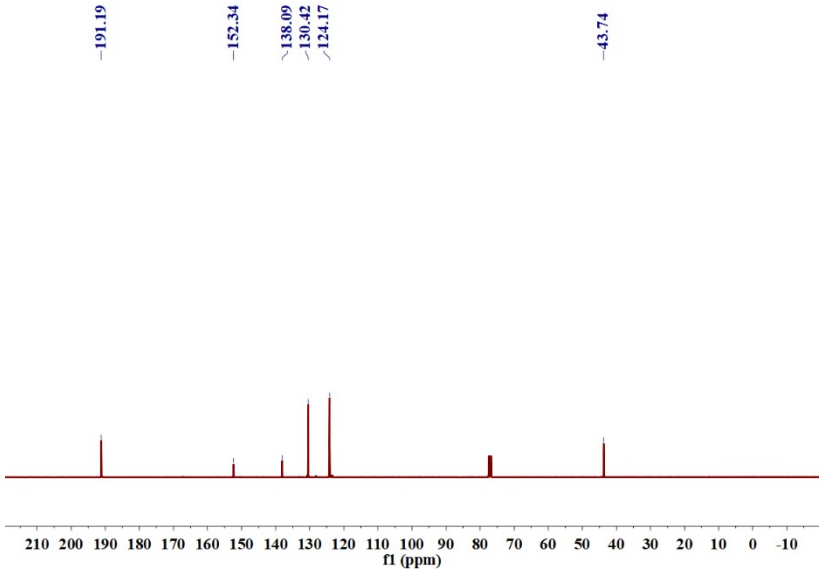
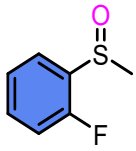


Fig. S28 ^{13}C NMR spectra of 4-(Methylsulfinyl)benzaldehyde in $CDCl_3$.

2h. 1- Fluoro -2-(methylsulphinyl)benzene



77% yield;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, J = 7.8, 1.6 Hz, 1H), 7.57 - 7.50 (m, 2H), 7.34 (ddd, J = 8.0, 7.3, 1.7 Hz, 1H), 2.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.64, 156.19, 132.75, 132.68, 125.45, 125.41, 125.33, 125.30, 115.79, 115.59, 42.07, 42.06.

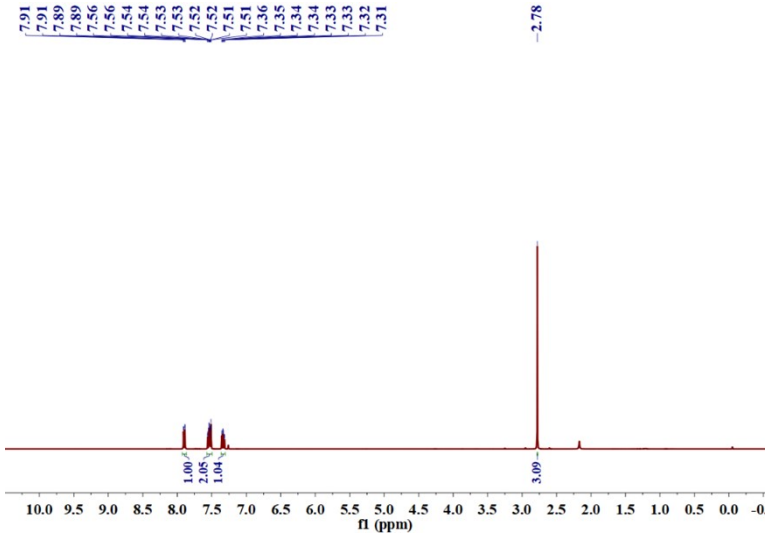


Fig. S29 ^{1}H NMR spectra of 1- Fluoro -2-(methylsulphinyl)benzene in $CDCl_3$.

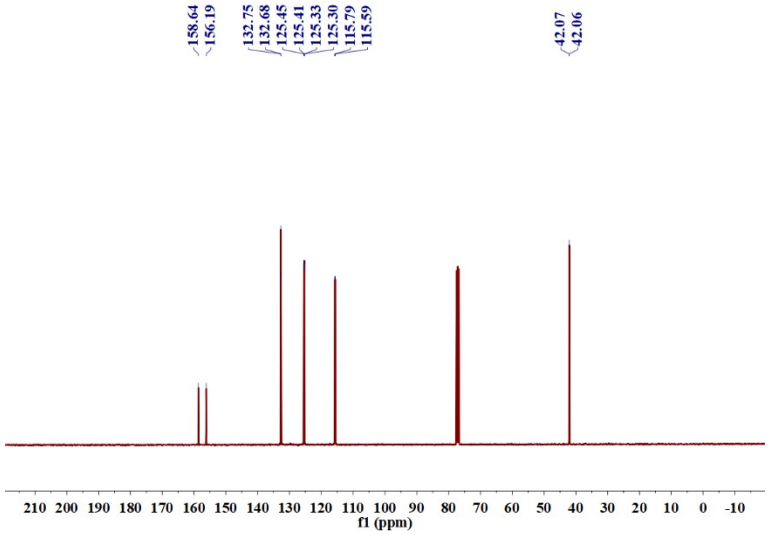
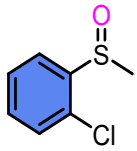


Fig. S30 ^{13}C NMR spectra of 1- Fluoro -2-(methylsulphinyl)benzene in $CDCl_3$.

2i. 1-Chloro-2-(methylsulphinyl)benzene



75% yield;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, J = 7.8, 1.7 Hz, 1H), 7.46 (td, J = 7.5, 1.3 Hz, 1H), 7.41 - 7.28 (m, 2H), 2.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.42, 132.00, 129.75, 129.70, 128.14, 125.22, 41.59.

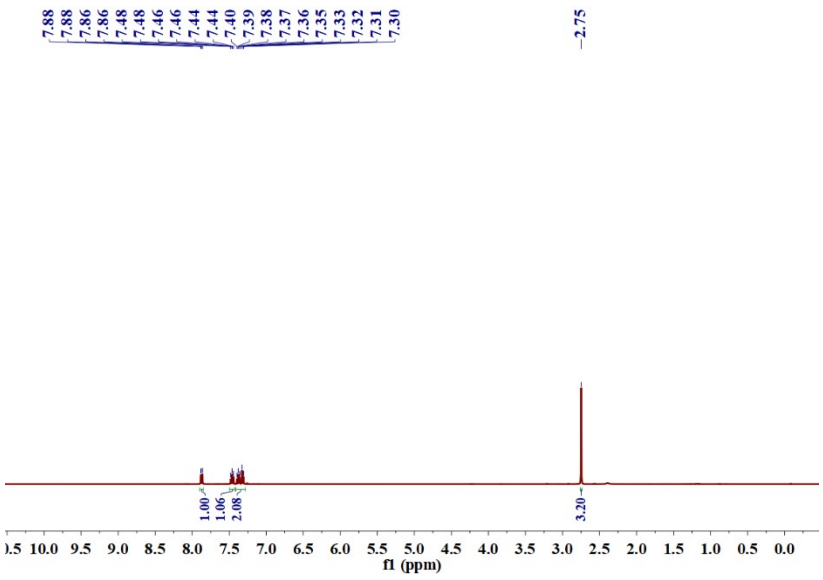


Fig. S31 ^{1}H NMR spectra of 1-Chloro-2-(methylsulphinyl)benzene in $CDCl_3$.

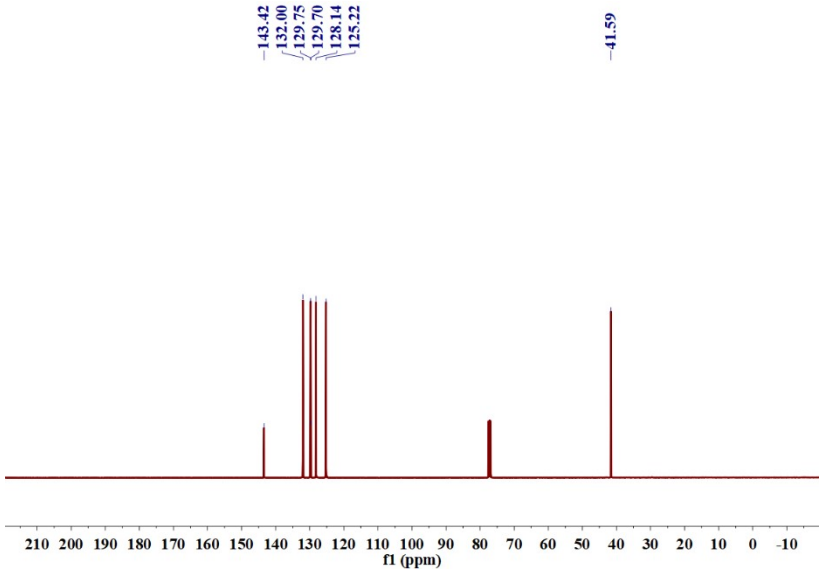
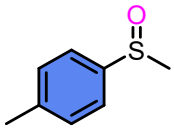


Fig. S32 ^{13}C NMR spectra of 1-Chloro-2-(methylsulphinyl)benzene in $CDCl_3$.

2j.1-Methyl-4-(methylsulfinyl)benzene



84% yield;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.2 Hz, 2H), 7.34 - 7.29 (m, 2H), 2.69 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.35, 141.57, 130.05, 123.55, 43.96, 21.42.

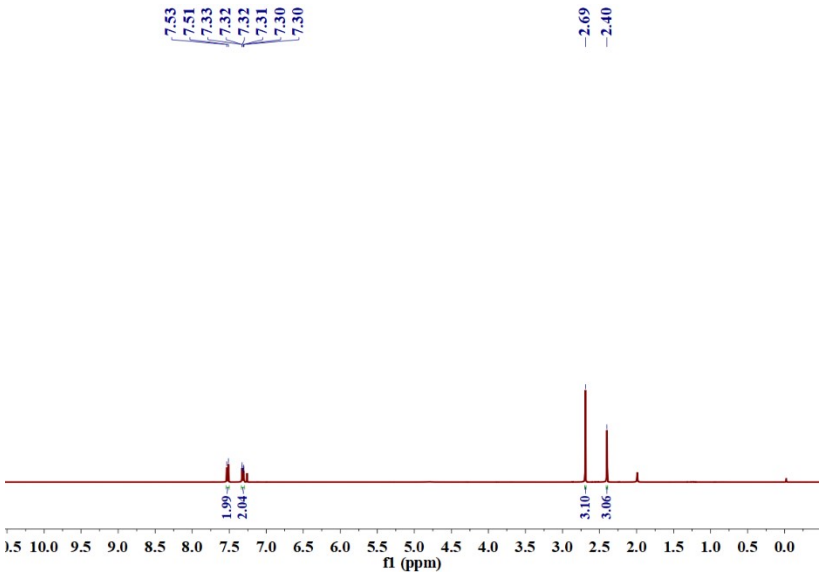


Fig. S33 ^{1}H NMR spectra of 1-Methyl-4-(methylsulfinyl)benzene in $CDCl_3$.

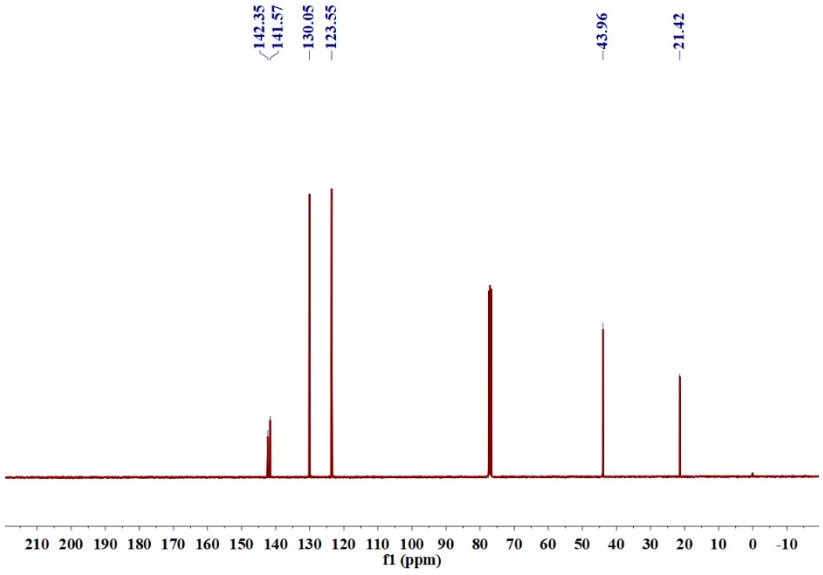
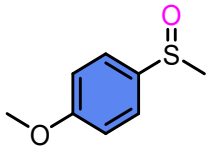


Fig. S34 ^{13}C NMR spectra of 1-Methyl-4-(methylsulfinyl)benzene in $CDCl_3$.

2k. 1-Methoxy-4-(methylsulfinyl)benzene



85% yield;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.8 Hz, 2H), 7.02 (d, J = 8.8 Hz, 2H), 3.84 (s, 3H), 2.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.06, 136.55, 125.58, 125.55, 125.49, 114.95, 114.92, 114.86, 55.64, 55.57, 44.06, 43.98.

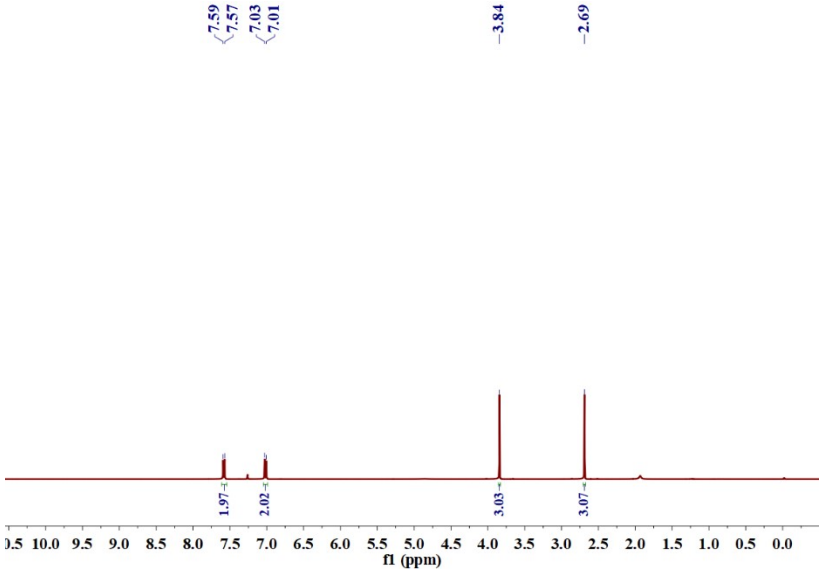


Fig. S35 ^{1}H NMR spectra of 1-Methoxy-4-(methylsulfinyl)benzene in $CDCl_3$.

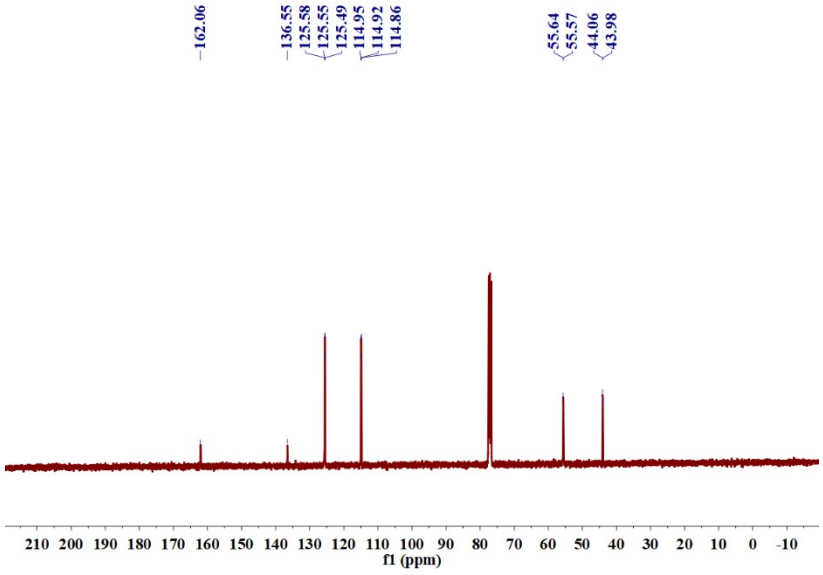
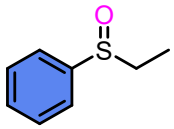


Fig. S36 ^{13}C NMR spectra of 1-Methoxy-4-(methylsulfinyl)benzene in $CDCl_3$.

2l. (Ethylsulfinyl)benzene



94% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 - 7.56 (m, 2H), 7.54 - 7.44 (m, 3H), 2.82 (ddq, J = 54.0, 13.3, 7.4 Hz, 2H), 1.18 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.16, 130.95, 129.14, 124.17, 50.27, 5.99.

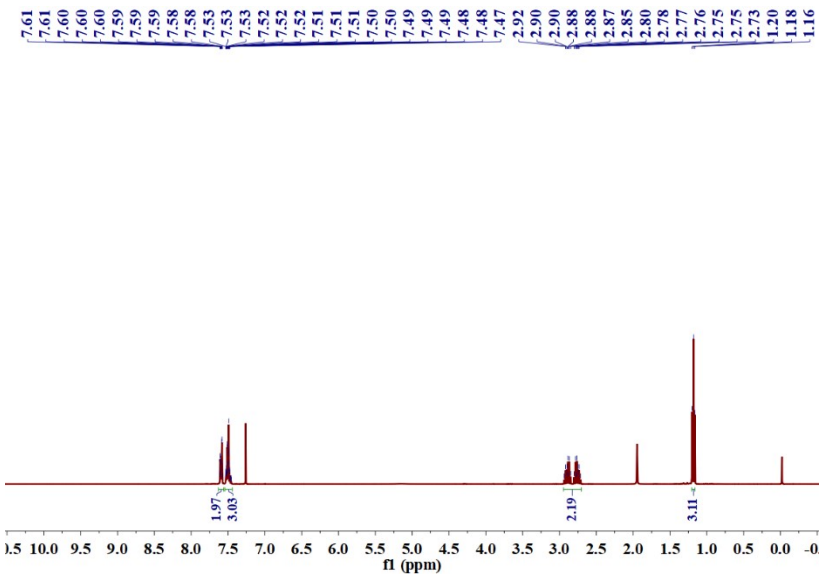


Fig. S37 ^{1}H NMR spectra of (Ethylsulfinyl)benzene in $CDCl_3$.

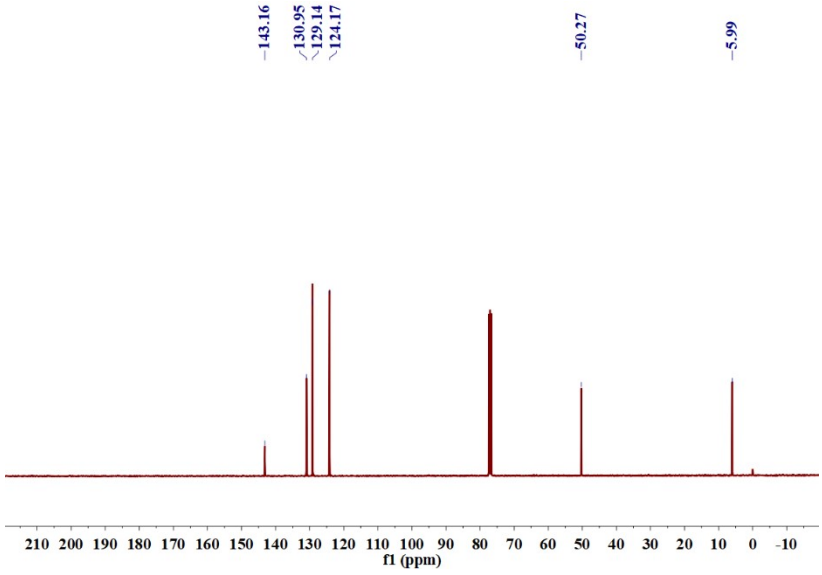


Fig. S38 ^{13}C NMR spectra of (Ethylsulfinyl)benzene in $CDCl_3$.