Supporting Information

Selective synthesis of sulfoxides and sulfones via controllable oxidation of sulfides with N-fluorobenzenesulfonimide

Xiaobo Xu,*a Leyu Yan,a Shengqiang Wang,a Panpan Wang,a A-Xiu Yang,a Xiaolong Li,a Hao Lu,a and Zhong-Yan Cao*nb

aCollege of Chemistry and Pharmaceutical Engineering, Huanghuai University, Zhumadian 463000, China
bCollege of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, China

Table of Contents

1. General Information ........................................................................................................2
2. General Procedures ........................................................................................................3
3. Characterization of Products ........................................................................................6
4. References .....................................................................................................................17
5. NMR Spectra ................................................................................................................19
1. General Information

Unless otherwise noted, reactions were carried out in oven-dried glassware or sealed tube under ambient atmosphere. N, N-Dimethylformamide (DMF) was distilled from calcium hydride. Tetrahydrofuran (THF) was dried and distilled from sodium. Reactions were monitored by analytical thin-layer chromatography (TLC) on Merck silica gel 60 F254 plates (0.25 mm), visualized by ultraviolet light (254 nm) or by staining with ceric ammonium molybdate. $^1$H NMR spectra were obtained on a Bruker AVANCE 400 MHz spectrometer at ambient temperature. Data were reported as follows: chemical shift on the $\delta$ scale using residual proton solvent as internal standard [$\delta$ 7.26 (CHCl$_3$); $\delta$ 2.50 (DMSO); $\delta$ 4.79 (H$_2$O); TMS: 0.00 ppm], multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets), integration, and coupling constant (J) in hertz (Hz). $^{13}$C NMR spectra were obtained with proton decoupling on a Bruker AVANCE (100 MHz) spectrometer and were reported in ppm with residual solvent for internal standard [$\delta$ 77.0 (CHCl$_3$); $\delta$ 39.52 (DMSO)]. High resolution mass spectra were obtained on a Bruker SolariX 7.0T spectrometer. NCS = N-Chlorosuccinimide, NFSI = N-Fluorobenzenesulfonimide, TEMPO = 2,2,6,6-Tetramethylpiperidinoxy.
2. Experimental procedures

General procedure for substrates: A flame-dried test tube containing a magnetic stirring bar was charged with CuI (0.2 mmol), K$_2$CO$_3$ (2 mmol), Na$_2$S·9H$_2$O (1.2 mmol), the 1-chloro-4-iodobenzene (2.0 mmol), and DMF (4 mL) under argon. The mixture was heated at 120 °C for 18 h and allowed to cool to room temperature. The resulting mixture was extracted with ethyl acetate (3×50 mL). The combined organic layers were dried with Na$_2$SO$_4$ and then concentrated under vacuum. The residue was purified by column chromatography on silica gel with an eluent consisting of petroleum ether and ethyl acetate.

General procedure for sulfoxides: To a solution of diphenyl sulfide 1a (186 mg, 1.0 mmol) and NFSI (315 mg, 1.0 equiv.) in H$_2$O (2.0 mL) at room temperature. The resulting reaction mixture was stirred for 6 h and EtOAc (10 mL) was then added to the mixture. The resulting mixture was extracted with EtOAc (3×20 mL), and the combined organic phase was dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The resultant residue was purified by flash chromatography on silica gel to afford the desired product 2a as a white solid (192 mg, 95% yield).
General procedure for sulfones: To a solution of diphenyl sulfide 1a (186 mg, 1.0 mmol) and NFSI (788 mg, 2.5 equiv.) in H$_2$O (4.0 mL) at room temperature. The resulting reaction mixture was stirred for 24 h and EtOAc (10 mL) was then added to the mixture. The resulting mixture was extracted with EtOAc (3×20 mL), and the combined organic phase was dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The resultant residue was purified by flash chromatography on silica gel to afford the desired product 3a as a white solid (200 mg, 92% yield).

Isotope labeling experiment with H$_2^{18}$O: To a solution of diphenyl sulfide 1a (93 mg, 0.5 mmol) and NFSI (158 mg, 1.0 equiv.) in H$_2^{18}$O (100 mg, 5.0 mmol) at room temperature. The resulting reaction mixture was stirred for 6 h and EtOAc (10 mL) was then added to the mixture. The resulting mixture was extracted with EtOAc (3×20 mL), and the combined organic phase was dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The resultant residue was purified by flash chromatography on silica gel to afford the desired product $^{18}$O-2a in 91% yield. HRMS of $^{18}$O-2a: calcd for C$_{12}$H$_{11}^{18}$OS$^+$ [M+H$^+$]: 205.0568; found: 205.0568.

Intermediate probe experiment: To a solution of diphenyl sulfoxide 2a (101 mg, 0.5 mmol) and NFSI (236 mg, 1.5 equiv.) in H$_2$O (2.0 mL) at room temperature. The resulting reaction mixture was stirred for 24 h and EtOAc (10 mL) was then added to the mixture. The resulting mixture was extracted with EtOAc (3×20 mL), and the combined organic phase was dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The resultant residue was purified by flash chromatography on silica gel to afford the desired product 3a in 98% yield.
Radical trapping experiments: To a solution of diphenyl sulfide 1a (93 mg, 0.5 mmol), radical scavenger TEMPO (390 mg, 5.0 equiv.) and NFSI (394 mg, 2.5 equiv.) in H₂O (2.0 mL) at room temperature. The resulting reaction mixture was stirred for 24 h and EtOAc (10 mL) was then added to the mixture. The resulting mixture was extracted with EtOAc (3×20 mL), and the combined organic phase was dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The resultant residue was purified by flash chromatography on silica gel to afford the desired product 3a in 87% yield.
3. Characterization of Products

Sulfinyldibenzene (2a): Known compound. Isolated yield 95% (192 mg). \(^1\)H NMR (d\(^6\)-DMSO, 400 MHz): \(\delta\) (ppm) 7.74-7.72 (m, 4H), 7.56-7.50 (m, 6H); \(^{13}\)C NMR (d\(^6\)-DMSO, 100 MHz): \(\delta\) (ppm) 145.92, 131.06, 129.4, 124.08.

4,4'-Dimethyldiphenylsulfoxide (2b): Known compound. Isolated yield 94% (216 mg). \(^1\)H NMR (d\(^6\)-DMSO, 400 MHz): \(\delta\) (ppm) 7.56 (d, \(J = 7.9\) Hz, 4H), 7.33 (d, \(J = 7.9\) Hz, 4H), 2.32 (s, 6H); \(^{13}\)C NMR (d\(^6\)-DMSO, 100 MHz): \(\delta\) (ppm) 143.05, 141.01, 129.93, 124.16, 20.80.

4,4'-Sulfinylbisphenol (2c): Known compound. Isolated yield 89% (208 mg). \(^1\)H NMR (d\(^6\)-DMSO, 400 MHz): \(\delta\) (ppm) 10.09 (s, 2H, OH), 7.44-7.42 (m, 4H), 6.89-6.87 (m, 4H); \(^{13}\)C NMR (d\(^6\)-DMSO, 100 MHz): \(\delta\) (ppm) 159.86, 135.5, 126.50, 116.10.

4,4'-Sulfinylbis(chlorobenzene) (2d): Known compound. Isolated yield 92% (248 mg). \(^1\)H NMR (d\(^6\)-DMSO, 400 MHz): \(\delta\) (ppm) 7.77-7.75 (m, 4H), 7.64-7.62 (m, 4H);
$^{13}$C NMR ($d^6$-DMSO, 100 MHz): $\delta$ (ppm) 144.52, 136.08, 129.67, 126.05.

![Nitrobenzene](image)

**1-Nitro-2-(phenylsulfinyl)benzene ($2e$)**: Known compound. Isolated yield 85% (210 mg). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ (ppm) 8.60 (d, $J = 7.9$ Hz, 1H), 8.28 (d, $J = 8.1$ Hz, 1H), 8.03 (t, $J = 7.6$ Hz, 1H), 7.71 (dt, $J = 8.6$, 4.0 Hz, 3H), 7.42 (dd, $J = 5.3$, 1.9 Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$(ppm) 145.08, 144.56, 143.84, 135.36, 131.54, 131.41, 129.25, 126.77, 126.28, 125.30.

![Methoxybenzene](image)

**1-Methoxy-4-(methylsulfinyl)benzene ($2f$)**: Known compound. Isolated yield 90% (153 mg). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ (ppm) 7.59 (d, $J = 8.6$ Hz, 2H), 7.02 (d, $J = 8.6$ Hz, 2H), 3.85 (s, 3H), 2.69 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$(ppm) 161.85, 136.46, 125.35, 114.74, 55.42, 43.88.

![Chlorobenzene](image)

**1-Chloro-4-(methylsulfinyl)benzene ($2g$)**: Known compound. Isolated yield 88% (153 mg). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ (ppm) 7.60 (d, $J = 8.4$ Hz, 2H), 7.51 (d, $J = 8.1$ Hz, 2H), 2.73 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$(ppm) 144.10, 137.22, 129.61, 124.95, 43.97.
1-(Methylsulfinyl)-4-nitrobenzene (2h): Known compound. Isolated yield 83% (154 mg). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ (ppm) 8.40 (d, $J = 8.5$ Hz, 2H), 7.85 (d, $J = 8.6$ Hz, 2H), 2.81 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ (ppm) 152.99, 149.56, 124.79, 124.56, 43.77.

![Dibenzothiophene-5-oxide](image)

Dibenzothiophene-5-oxide (2i): Known compound. Isolated yield 87% (174 mg). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ (ppm) 8.00 (d, $J = 7.6$ Hz, 2H), 7.82 (d, $J = 7.7$ Hz, 2H), 7.61 (t, $J = 7.5$ Hz, 2H), 7.51 (t, $J = 7.5$ Hz, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ (ppm) 145.04, 136.99, 132.46, 129.45, 127.42, 121.83.

(Sulfinylbis(methylene))dibenzene (2j): Known compound. Isolated yield 95% (218 mg). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ (ppm) 7.40-7.26 (m, 10H), 3.94-3.86 (m, 4H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ (ppm) 130.07 (2C), 128.89, 128.29, 57.20.

![Difurfuryl sulfoxide](image)

Difurfuryl sulfoxide (2k): Known compound. Isolated yield 92% (193 mg). $^1$H NMR ($d^6$-DMSO, 400 MHz): $\delta$ (ppm) 7.71 (s, 2H), 6.49-6.47 (m, 4H), 4.29 (d, $J = 14.1$ Hz, 2H), 4.07 (d, $J = 14.1$ Hz, 2H); $^{13}$C NMR ($d^6$-DMSO, 100 MHz): $\delta$ (ppm) 145.35, 143.83, 111.16, 111.06, 49.53.

![2-((Methylsulfinyl)methyl)furan](image)

2-((Methylsulfinyl)methyl)furan (2l): Known compound. Isolated yield 87% (125 mg). $^1$H NMR ($d^6$-DMSO, 400 MHz): $\delta$ (ppm) 7.69 (s, 1H), 6.49-6.43 (m, 2H), 4.22 (d,
$J = 14.0 \text{ Hz}, 1\text{H}), 4.08 \text{ (d, } J = 14.0 \text{ Hz, } 1\text{H}), 2.52 \text{ (s, } 3\text{H}).$

![Tetramethylene sulfoxide](image)

**Tetramethylene sulfoxide (2m)**: Known compound. Isolated yield 94% (98 mg). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$(ppm) 2.87-2.74 (m, 4H), 2.43-2.34 (m, 2H), 2.02-1.92 (m, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$(ppm) 54.34, 25.32.

![1,3-Dithiane 1-oxide](image)

**1,3-Dithiane 1-oxide (2n)**: Known compound. Isolated yield 95% (129 mg). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$(ppm) 4.00 (d, $J = 12.7 \text{ Hz, } 1\text{H}$), 3.64 (d, $J = 12.7 \text{ Hz, } 1\text{H}$), 3.33-3.31 (m, 1H), 2.68-2.48 (m, 4H), 2.25-2.19 (m, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$(ppm) 52.79, 50.35, 28.22, 27.08.

![2-(Tert-butylsulfinyl)-2-methylpropane](image)

**2-(Tert-butylsulfinyl)-2-methylpropane (2o)**: Known compound. Isolated yield 72% (117 mg). $^1$H NMR (d$_6$-DMSO, 400 MHz): $\delta$(ppm) 1.24 (s, 18H); $^{13}$C NMR (d$_6$-DMSO, 100 MHz): $\delta$(ppm) 56.88, 25.44.

![Ethyl 2-hydroxyethyl sulfoxide](image)

**Ethyl 2-hydroxyethyl sulfoxide (2p)**: Known compound. Isolated yield 99% (120 mg). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$(ppm) 4.16-4.07 (m, 2H), 2.95-2.78 (m, 4H), 1.34 (t, $J = 7.5 \text{ Hz, } 3\text{H}$); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$(ppm) 55.40, 53.51, 45.67, 6.67.
**L-methionine sulfoxide (2q)**: Known compound. Isolated yield 76% (125 mg). \(^1\)H NMR (D\(_2\)O, 400 MHz): \(\delta\) (ppm) 3.87 (td, \(J = 8.0, 7.3, 5.7\) Hz, 1H), 3.06-2.97 (m, 2H), 2.74 (s, 3H), 2.31 (td, \(J = 8.0, 6.4\) Hz, 2H); \(^{13}\)C NMR (D\(_2\)O, 100 MHz): \(\delta\) (ppm) 173.16, 53.29, 48.2, 36.52, 23.73.

**Methyl((methylsulfinyl)methyl)sulfane (2r)**: Known compound. Isolated yield 97% (120 mg). \(^1\)H NMR (d\(^6\)-DMSO, 400 MHz): \(\delta\) (ppm) 3.98 (d, \(J = 13.5\) Hz, 1H), 3.78 (d, \(J = 13.6\) Hz, 1H), 2.59 (s, 3H), 2.26 (s, 3H); \(^{13}\)C NMR (d\(^6\)-DMSO, 100 MHz): \(\delta\) (ppm) 55.21, 37.21, 16.38.

**2-Benzhydrylsulphinylacetic acid (2s)**: Known compound. Isolated yield 71% (195 mg). \(^1\)H NMR (d\(^6\)-DMSO, 400 MHz): \(\delta\) (ppm) 13.20 (s, 1H, COOH), 7.52 (dt, \(J = 6.9, 1.5\) Hz, 4H), 7.45-7.36 (m, 6H), 5.41 (s, 1H), 3.57 (d, \(J = 14.0\) Hz, 1H), 3.32 (d, \(J = 14.0\) Hz, 1H); \(^{13}\)C NMR (d\(^6\)-DMSO, 100 MHz): \(\delta\) (ppm) 167.38, 136.62, 134.88, 129.61, 129.12, 128.58, 128.52, 128.12, 128.06, 69.27, 55.42.

**Ricobendazole (2t)**: Known compound. Isolated yield 52% (146 mg). \(^1\)H NMR (d\(^6\)-DMSO, 400 MHz): \(\delta\) (ppm) 11.87 (s, 2H), 7.71 (s, 1H), 7.57 (d, \(J = 8.2\) Hz, 1H), 7.33
(dt, $J = 8.4, 1.4$ Hz, 1H), 3.79 (s, 3H), 2.88-2.74 (m, 2H), 1.61 (dt, $J = 14.7, 7.3$ Hz, 1H), 1.49 (tt, $J = 14.0, 9.1$ Hz, 1H), 0.95 (t, $J = 7.4$ Hz, 3H); $^{13}$C NMR ($d^6$-DMSO, 100 MHz): $\delta$ (ppm) 154.41, 148.64, 136.18, 116.79, 58.22, 52.64, 15.44, 12.98.

Omeprazole (2u)$^6$: Known compound. Isolated yield 46% (159 mg). $^1$H NMR ($d^6$-DMSO, 400 MHz): $\delta$ (ppm) 13.44 (s, 1H), 8.19 (s, 1H), 7.57 (s, 1H), 7.04 (s, 1H), 6.93 (d, $J = 8.9$ Hz, 1H), 4.77 (d, $J = 13.6$ Hz, 1H), 4.69 (d, $J = 13.5$ Hz, 1H), 3.81 (s, 3H), 3.69 (s, 3H), 2.19 (d, $J = 13.2$ Hz, 6H); $^{13}$C NMR ($d^6$-DMSO, 100 MHz): $\delta$ (ppm) 163.98, 157.44, 156.43, 153.03, 150.09, 149.61, 137.96, 135.95, 126.95, 125.98, 120.89, 114.75, 113.35, 101.94, 95.04, 60.55, 60.17, 55.94, 13.36, 11.56.

Diphenyl sulfone (3a)$^2$: Known compound. Isolated yield 93% (203 mg). $^1$H NMR ($d^6$-DMSO, 400 MHz): $\delta$ (ppm) 7.98-7.96 (m, 4H), 7.72-7.61 (m, 6H); $^{13}$C NMR ($d^6$-DMSO, 100 MHz): $\delta$ (ppm) 141.11, 133.67, 129.72, 127.33.

4,4'-Sulfonylbis(methylbenzene) (3b)$^{13}$: Known compound. Isolated yield 96% (236 mg). $^1$H NMR ($d^6$-DMSO, 400 MHz): $\delta$(ppm) 7.81 (d, $J = 8.0$ Hz, 4H), 7.40 (d, $J = 8.0$ Hz, 4H), 2.36 (s, 6H); $^{13}$C NMR ($d^6$-DMSO, 100 MHz): $\delta$(ppm) 144.07, 138.63, 130.09, 127.21, 20.95.
**4,4’-Sulfonyldiphenol (3c)**: Known compound. Isolated yield 92% (230 mg). $^1$H NMR (d$_6$-DMSO, 400 MHz): $\delta$(ppm) 10.53 (s, 2H), 7.70 (d, $J = 8.8$ Hz, 4H), 6.89 (d, $J = 8.8$ Hz, 4H); $^{13}$C NMR (d$_6$-DMSO, 100 MHz): $\delta$(ppm) 161.66, 132.18, 129.42, 116.02.

**4,4’-Sulfonyldianiline (3d)**: Known compound. Isolated yield 86% (213 mg). $^1$H NMR (d$_6$-DMSO, 400 MHz): $\delta$(ppm) 7.44 (d, $J = 8.4$ Hz, 4H), 6.57 (d, $J = 8.5$ Hz, 4H), 5.99 (s, 4H); $^{13}$C NMR (d$_6$-DMSO, 100 MHz): $\delta$(ppm) 152.75, 128.60, 128.18, 112.90.

**1-Nitro-2-(phenylsulfonyl)benzene (3e)**: Known compound. Isolated yield 82% (216 mg). $^1$H NMR (d$_6$-DMSO, 400 MHz): $\delta$(ppm) 8.41-8.39 (m, 1H), 8.05-7.97 (m, 5H), 7.78-7.68 (m, 3H); $^{13}$C NMR (d$_6$-DMSO, 100 MHz): $\delta$(ppm) 147.80, 139.97, 135.96, 134.34, 133.29, 132.43, 131.50, 129.63, 127.69, 124.92.

**4,4’-Sulfonylbis(fluorobenzene) (3f)**: Known compound. Isolated yield 80% (203 mg). $^1$H NMR (d$_6$-DMSO, 400 MHz): $\delta$(ppm) 8.07 (dd, $J = 8.6$, 5.2 Hz, 4H), 7.47 (t, $J = 8.6$ Hz, 4H); $^{13}$C NMR (d$_6$-DMSO, 100 MHz): $\delta$(ppm) 164.93 (d, $J = 252.36$ Hz), 137.34 (d, $J = 3.11$ Hz), 130.62 (d, $J = 9.34$ Hz), 116.99 (d, $J = 23.24$ Hz).
4,4'-Dichlorodiphenyl sulfone (3g): Known compound. Isolated yield 78% (223 mg).

$^1$H NMR (d$_6$-DMSO, 400 MHz): $\delta$(ppm) 8.00 (d, $J = 8.4$ Hz, 4H), 7.71 (d, $J = 8.4$ Hz, 4H); $^{13}$C NMR (d$_6$-DMSO, 100 MHz): $\delta$(ppm) 139.45, 139.07, 129.95, 129.40.

2-Nitro-4-methylsulfonyltoluene (3h): Known compound. Isolated yield 77% (166 mg).

$^1$H NMR (d$_6$-DMSO, 400 MHz): $\delta$(ppm) 8.47 (d, $J = 1.7$ Hz, 1H), 8.16 (dt, $J = 8.2$, 1.6 Hz, 1H), 7.82 (d, $J = 8.1$ Hz, 1H), 3.33 (s, 3H), 2.63 (s, 3H); $^{13}$C NMR (d$_6$-DMSO, 100 MHz): $\delta$(ppm) 148.82, 139.74, 138.78, 134.22, 131.14, 123.35, 43.23, 19.61.

Dibenzo[b,d]thiophene 5,5-dioxide (3i): Known compound. Isolated yield 65% (140 mg).

$^1$H NMR (d$_6$-DMSO, 400 MHz): $\delta$(ppm) 8.21 (d, $J = 7.7$ Hz, 2H), 7.99 (d, $J = 7.7$ Hz, 2H), 7.82 (t, $J = 7.6$ Hz, 2H), 7.67 (t, $J = 7.6$ Hz, 2H); $^{13}$C NMR (d$_6$-DMSO, 100 MHz): $\delta$(ppm) 136.95, 134.52, 130.92, 130.83, 122.67, 121.97.

Methyl phenyl sulfone (3j): Known compound. Isolated yield 94% (147 mg).

$^1$H NMR (d$_6$-DMSO, 400 MHz): $\delta$(ppm) 7.96-7.94 (m, 2H), 7.77-7.65 (m, 3H), 3.37 (s, 0H), 3.23 (s, 3H); $^{13}$C NMR (d$_6$-DMSO, 100 MHz): $\delta$(ppm) 140.84, 133.60, 129.41, 126.90, 43.51.
4-Methylsulphonyl benzaldehyde (3k): Known compound. Isolated yield 75% (138 mg). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ (ppm) 10.13 (s, 1H), 8.14-8.07 (m, 4H), 3.10 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ (ppm) 190.67, 145.31, 139.62, 130.35, 128.16, 44.24.

4-Methylsulphonylbenzoic acid (3l): Known compound. Isolated yield 79% (158 mg). $^1$H NMR (d$_6$-DMSO, 400 MHz): $\delta$ (ppm) 13.56 (s, 1H), 8.18 (d, $J = 8.1$ Hz, 2H), 8.06 (d, $J = 8.1$ Hz, 2H), 3.29 (s, 3H); $^{13}$C NMR (d$_6$-DMSO, 100 MHz): $\delta$ (ppm) 166.21, 144.35, 135.29, 130.26, 127.37, 43.30.

Tetrahydrothiophene 1,1-dioxide (3m): Known compound. Isolated yield 95% (114 mg). $^1$H NMR (d$_6$-DMSO, 400 MHz): $\delta$ (ppm) 3.02-2.98 (m, 4H), 2.10-2.06 (m, 4H); $^{13}$C NMR (d$_6$-DMSO, 100 MHz): $\delta$ (ppm) 50.58, 22.16.

4-Bromophenyl methyl sulfone (3n): Known compound. Isolated yield 94% (220 mg). $^1$H NMR (d$_6$-DMSO, 400 MHz): $\delta$ (ppm) 7.89-7.87 (m, 4H), 3.25 (s, 3H); $^{13}$C NMR (d$_6$-DMSO, 100 MHz): $\delta$ (ppm) 140.04, 132.45, 129.05, 127.68, 43.39.
1-Methyl-4-(methylsulfonyl)-benzene (3o): Known compound. Isolated yield 97% (165 mg). $^1$H NMR (d$_6$-DMSO, 400 MHz): $\delta$ (ppm) 7.82 (d, $J = 8.0$ Hz, 2H), 7.47 (d, $J = 8.0$ Hz, 2H), 3.18 (s, 3H), 2.42 (s, 3H); $^{13}$C NMR (d$_6$-DMSO, 100 MHz): $\delta$ (ppm) 144.07, 138.07, 129.81, 126.94, 43.68, 21.01.

![1-Methyl-4-(methylsulfonyl)-benzene](image)

(E)-[2-(Phenylsulfonyl)vinyl]benzene (3p): Known compound. Isolated yield 95% (232 mg). $^1$H NMR (d$_6$-DMSO, 400 MHz): $\delta$ (ppm) 7.95 (d, $J = 7.6$ Hz, 2H), 7.77-7.61 (m, 7H), 7.44 (d, $J = 6.6$ Hz, 3H); $^{13}$C NMR (d$_6$-DMSO, 100 MHz): $\delta$ (ppm) 142.04, 140.72, 133.58, 132.37, 131.17, 129.62, 129.01, 128.98, 128.06, 127.13.

![E-(2-(Phenylsulfonyl)vinyl)benzene](image)

(Vinylsulfonyl)benzene (3q): Known compound. Isolated yield 83% (139 mg). $^1$H NMR (d$_6$-DMSO, 400 MHz): $\delta$ (ppm) 7.90-7.87 (m, 2H), 7.78-7.65 (m, 3H), 7.14 (dd, $J = 16.4$, 9.8 Hz, 1H), 6.36 (d, $J = 16.4$ Hz, 1H), 6.22 (d, $J = 9.9$ Hz, 1H); $^{13}$C NMR (d$_6$-DMSO, 100 MHz): $\delta$ (ppm) 139.50, 138.52, 133.83, 129.61, 128.71, 127.38.

![Vinylsulfonyl)benzene](image)

(4-(Methylsulfonyl)phenyl)methanol (3r): Known compound. Isolated yield 87% (162 mg). $^1$H NMR (d$_6$-DMSO, 400 MHz): $\delta$ (ppm) 7.88 (d, $J = 8.0$ Hz, 2H), 7.58 (d, $J = 8.0$ Hz, 2H), 5.46 (td, $J = 5.8$, 1.0 Hz, 1H), 4.62 (d, $J = 5.7$ Hz, 2H), 3.20 (d, $J = 1.0$ Hz, 3H); $^{13}$C NMR (d$_6$-DMSO, 100 MHz): $\delta$ (ppm) 148.77, 139.09, 126.89, 126.87, 62.21, 43.69.
**Benzylsulfonyl-benzene (3s)**: Known compound. Isolated yield 92% (213 mg). $^1$H NMR (d$_6$-DMSO, 400 MHz): $\delta$(ppm) 7.71 (d, $J$ = 7.4 Hz, 3H), 7.59 (t, $J$ = 7.7 Hz, 2H), 7.30 (t, $J$ = 7.4 Hz, 3H), 7.14 (dd, $J$ = 7.6, 1.8 Hz, 2H), 4.68 (s, 2H); $^{13}$C NMR (d$_6$-DMSO, 100 MHz): $\delta$(ppm) 138.33, 133.79, 130.96, 129.09, 128.65, 128.32, 128.20, 128.02, 60.69.

**Bis(phenylsulfonyl)methane (3t)**: Known compound. Isolated yield 72% (213 mg). $^1$H NMR (d$_6$-DMSO, 400 MHz): $\delta$(ppm) 7.90-7.88 (m, 4H), 7.76 (t, $J$ = 7.5 Hz, 2H), 7.63 (t, $J$ = 7.7 Hz, 4H), 5.94 (s, 2H); $^{13}$C NMR (d$_6$-DMSO, 100 MHz): $\delta$(ppm) 138.85, 134.40, 129.15, 128.33, 71.83.

**3-(Methylsulfonyl)propan-1-ol (3u)**: Known compound. Isolated yield 98% (135 mg). $^1$H NMR (d$_6$-DMSO, 400 MHz): $\delta$(ppm) 4.71-4.68 (t, $J$ = 4.8 Hz, 1H), 3.49 (q, $J$ = 5.8 Hz, 2H), 3.14-3.10 (dd, $J$ = 10.4, 5.8 Hz, 2H), 2.97 (s, 3H), 1.86-1.79 (m, 2H); $^{13}$C NMR (d$_6$-DMSO, 100 MHz): $\delta$(ppm) 59.12, 51.07, 40.23, 25.42.
4. References


5. NMR Spectra

$^1$H NMR (400 MHz, $d^6$-DMSO)

$^{13}$C NMR (100 MHz, $d^6$-DMSO)
$^{1}H$ NMR (400 MHz, $d^6$-DMSO)

$^{13}C$ NMR (100 MHz, $d^6$-DMSO)
$^{1}H$ NMR (400 MHz, $d^6$-DMSO)

$^{13}C$ NMR (100 MHz, $d^6$-DMSO)
$^{1}H$ NMR (400 MHz, $d^6$-DMSO)

$^{13}C$ NMR (100 MHz, $d^6$-DMSO)
$\textbf{2f}$

$^1\text{H NMR (400 MHz, CDCl}_3)$

$\textbf{2f}$

$^{13}\text{C NMR (100 MHz, CDCl}_3)$
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$ NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
**1H NMR (400 MHz, d$_6$-DMSO)**

![1H NMR Spectrum](image)

**13C NMR (100 MHz, d$_6$-DMSO)**

![13C NMR Spectrum](image)
\[ \text{\textsuperscript{1}H NMR (400 MHz, d}\textsuperscript{6}-\text{DMSO)} \]

\[ \text{\textsuperscript{13}C NMR (100 MHz, d}\textsuperscript{6}-\text{DMSO)} \]
2m

$^1$H NMR (400 MHz, CDCl$_3$)

2m

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{1}$H NMR (400 MHz, $d^6$-DMSO)

$^{13}$C NMR (100 MHz, $d^6$-DMSO)
$^1$H NMR (400 MHz, CDCl$_3$)

$^1$C NMR (100 MHz, CDCl$_3$)
2q

$^1$H NMR (400 MHz, D$_2$O)

2q

$^{13}$C NMR (100 MHz, D$_2$O)
$\text{SO}_2\text{S}$

$2r$

$^1$H NMR (400 MHz, d$_6$-DMSO)

$\text{OS=}$

$2r$

$^{13}$C NMR (100 MHz, d$_6$-DMSO)
$^{1}$H NMR (400 MHz, d$_6$-DMSO)

$^{13}$C NMR (100 MHz, d$_6$-DMSO)
$^{1}H$ NMR (400 MHz, d$_6$-DMSO)

$^{13}$C NMR (100 MHz, d$_6$-DMSO)
$^1$H NMR (400 MHz, $d^6$-DMSO)

$^{13}$C NMR (100 MHz, $d^6$-DMSO)
$^1$H NMR (400 MHz, $d^6$-DMSO)

$^{13}$C NMR (100 MHz, $d^6$-DMSO)
$^1$H NMR (400 MHz, d$_6$-DMSO)

$^{13}$C NMR (100 MHz, d$_6$-DMSO)
$^1$H NMR (400 MHz, d$_6$-DMSO)

$^1$C NMR (100 MHz, d$_6$-DMSO)
**3d**

$^1$H NMR (400 MHz, d$_6$-DMSO)

$^{13}$C NMR (100 MHz, d$_6$-DMSO)
$^1$H NMR (400 MHz, d$_6$-DMSO)

$^{13}$C NMR (100 MHz, d$_6$-DMSO)
$^1$H NMR (400 MHz, d$_6$-DMSO)

$^{13}$C NMR (100 MHz, d$_6$-DMSO)
$^{1}H$ NMR (400 MHz, $d^6$-DMSO)

$^{13}C$ NMR (100 MHz, $d^6$-DMSO)
$^{1}H$ NMR (400 MHz, $d^6$-DMSO)

$^{13}C$ NMR (100 MHz, $d^6$-DMSO)
$^1$H NMR (400 MHz, $d^6$-DMSO)

$^{13}$C NMR (100 MHz, $d^6$-DMSO)
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$ NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, $d^6$-DMSO)

$^{13}$C NMR (100 MHz, $d^6$-DMSO)
$^1$H NMR (400 MHz, $d^6$-DMSO)

$^{13}$C NMR (100 MHz, $d^6$-DMSO)
$^1$H NMR (400 MHz, d$_6$-DMSO)

$^{13}$C NMR (100 MHz, d$_6$-DMSO)
$^{1}H$ NMR ($400$ MHz, $d^6$-DMSO)

$^{13}C$ NMR ($100$ MHz, $d^6$-DMSO)
$^1$H NMR (400 MHz, d$_6$-DMSO)

$^{13}$C NMR (100 MHz, d$_6$-DMSO)
$^{1}\text{H} \text{NMR (400 MHz, d}^{6}\text{-DMSO)}$

$^{13}\text{C} \text{NMR (100 MHz, d}^{6}\text{-DMSO)}$
$^{1}$$H$ NMR (400 MHz, $d^6$-DMSO)

$^{13}$C NMR (100 MHz, $d^6$-DMSO)
$^1$H NMR (400 MHz, $d_6$-DMSO)

$^{13}$C NMR (100 MHz, $d_6$-DMSO)
1H NMR (400 MHz, d6-DMSO)

3t

13C NMR (100 MHz, d6-DMSO)
$\text{HO-} \begin{array}{c} \text{S} \\ \text{O} \end{array}$

$3u$

$^1\text{H NMR (400 MHz, d}$-$\text{DMSO)}$

$\text{HO-} \begin{array}{c} \text{S} \\ \text{O} \end{array}$

$3u$

$^{13}\text{C NMR (100 MHz, d}$-$\text{DMSO)}$