Supporting Information

Copper-catalyzed S-methylation of sulfonyl hydrazides with TBHP for the synthesis of methyl sulfones in water

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**General Remarks**

All substrates were purchased commercially without further purification. The yields were determined based on sulfonyl hydrazides. 

$^1$H and $^{13}$C NMR spectra were recorded on a Bruker AC-300 FT spectrometer at 400 MHz and 100 MHz, respectively, with tetramethylsilane as an internal reference. Chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. High resolution mass spectra (HRMS) were recorded on a LC-TOF spectrometer (Micromass). GC-MS samples were recorded on an Agilent Technologies 7890A-5975C GC-MS system.

**General procedures for the synthesis of Arylsulfonyl Hydrazides**

Arylsulfonyl hydrazides 2b-2s were prepared according to the literature procedure.$^{[1]}$ To a solution of an arylsulfonyl chloride (3.0 mmol) in tetrahydrofuran (15 mL), was added hydrazine monohydrate (375 mg, 7.5 mmol) dropwise under nitrogen at 0 °C. After vigorous stirring for 30 min at 0 °C, the reaction mixture was added ethyl acetate (60 mL), and washed with saturated brine (3 x 10 mL). The organic layer was dried over sodium sulfate, filtered, concentrated and added to hexane (12 mL) over 5 min. The mixture was filtered, and the collected solid was dried in vacuum.
GC-MS analysis for the TEMPO–CH₃ adduct 4
Characterization data of products

1-methyl-4-(methylsulfonyl)benzene (3aa). The title compound was prepared according to the general procedure and purified by column chromatography (Petroleum Ether: EtOAc = 3:1) to give a white solid (88 % yield). $^1$H NMR (400 MHz, CDCl$_3$): 7.84-7.82 (d, 2H, $J = 8.0$ Hz), 7.38-7.36 (d, 2H, $J = 8.0$ Hz), 3.04 (s, 3H), 2.46 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): 144.7, 137.7, 130.0, 127.3, 44.6, 21.6.

1-methyl-2-(methylsulfonyl)benzene (3ba). The title compound was prepared according to the general procedure and purified by column chromatography (Petroleum Ether: EtOAc = 3:1) to give a light yellow oil (83 % yield). $^1$H NMR (400 MHz, CDCl$_3$): 8.04-8.02 (m, 1H), 7.53-7.51 (m, 1H), 7.40-7.28 (m, 2H), 3.08 (s, 3H), 2.72 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): 138.7, 137.5, 133.7, 132.7, 129.2, 126.7, 43.7, 20.3.

methylsulfonylbenzene (3ca). The title compound was prepared according to the general procedure and purified by column chromatography (Petroleum Ether: EtOAc = 3:1) to give a light yellow oil (78 % yield). $^1$H NMR (400 MHz, CDCl$_3$): 7.97-7.94 (m, 2H), 7.69-7.65 (m, 1H), 7.60-7.56 (m, 2H), 3.04 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): 140.6, 133.7, 129.4, 127.3, 44.5.

1-methoxy-4-(methylsulfonyl)benzene (3da). The title compound was prepared according to the general procedure and purified by column chromatography (Petroleum Ether: EtOAc = 3:1) to give a light yellow solid (81 % yield). $^1$H NMR (400 MHz, CDCl$_3$): 7.89-7.85 (m, 2H), 7.05-7.01 (m, 2H), 3.89 (s, 3H), 3.03 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): 163.7, 132.3, 129.5, 114.5, 55.7, 44.8.

1-(methylsulfonyl)-4-(trifluoromethoxy)benzene (3ea). The title compound was prepared according to the general procedure and purified by column chromatography (Petroleum Ether: EtOAc = 3:1) to give a light yellow oil (70% yield). $^1$H NMR (400 MHz, CDCl$_3$): 3.07 (s, 3H),
7.41 (d, $J = 8.1$ Hz, 2H), 8.02 (d, $J = 8.7$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): 43.5, 120.2, 120.5 (q, $J = 258.3$ Hz), 128.8, 137.8, 152.0 (q, $J = 1.5$ Hz).

1-fluoro-4-(methylsulfonyl)benzene (3fa)\cite{1}. The title compound was prepared according to the general procedure and purified by column chromatography (Petroleum Ether: EtOAc = 3:1) to give a light yellow oil (90 % yield). $^1$H NMR (400 MHz, CDCl$_3$): 8.00-7.96 (m, 2H), 7.28-7.24 (m, 2H), 3.07 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): 165.8 (d, $J = 254$ Hz), 136.7 (d, $J = 3$ Hz), 130.3 (d, $J = 10$ Hz), 116.7 (d, $J = 23$ Hz), 44.7.

1-chloro-4-(methylsulfonyl)benzene (3ga)\cite{1}. The title compound was prepared according to the general procedure and purified by column chromatography (Petroleum Ether: EtOAc = 3:1) to give a white solid (84 % yield). $^1$H NMR (400 MHz, CDCl$_3$): 7.91-7.88 (m, 2H), 7.57-7.54 (m, 2H), 3.06 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): 140.5, 139.1, 129.7, 128.9, 44.5.

1-iodo-4-(methylsulfonyl)benzene (3ha)\cite{3}. The title compound was prepared according to the general procedure and purified by column chromatography (Petroleum Ether: EtOAc = 3:1) to give a white solid (58 % yield). $^1$H NMR (400 MHz, CDCl$_3$): 7.96-7.94 (d, 2H, $J = 8.0$ Hz), 7.67-7.65 (d, 2H, $J = 8.0$ Hz), 3.05 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): 140.2, 138.7, 128.8, 101.6, 44.5.

1-(methylsulfonyl)-4-(trifluoromethyl)benzene (3ia)\cite{4}. The title compound was prepared according to the general procedure and purified by column chromatography (Petroleum Ether: EtOAc = 3:1) to give a white solid (73 % yield). $^1$H NMR (400 MHz, CDCl$_3$): 8.12-8.10 (d, 2H, $J = 8.0$ Hz), 7.87-7.85 (d, 2H, $J = 8$ Hz), 3.09 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): 144.0, 135.6 (q, $J = 33$ Hz), 128.1, 126.6 (q, $J = 7$ Hz), 123.1 (q, $J = 272$ Hz), 44.3.

4-(methylsulfonyl)benzonitrile (3ja). \cite{5} The title compound was prepared according to the general procedure and purified by column chromatography (Petroleum Ether: EtOAc = 3:1) to give a white solid (56 % yield). $^1$H NMR (400 MHz, CDCl$_3$): 8.03-8.01 (d, 2H, $J = 8.0$ Hz), 7.84-7.82 (d, 2H, $J = 8.0$ Hz), 3.03 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): 143.5, 132.2, 127.2, 116.6, 116.0, 43.2.
1-(methylsulfonyl)-4-nitrobenzene (3ka). The title compound was prepared according to the general procedure and purified by column chromatography (Petroleum Ether: EtOAc = 3:1) to give a white solid (73 % yield). $^1$H NMR (400 MHz, CDCl$_3$): 8.45-8.43 (d, 2H, $J$ = 8.0 Hz), 8.18-8.16 (d, 2H, $J$ = 8.0 Hz), 3.13 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): 150.9, 146.0, 129.0, 124.6, 44.3.

1-(methylsulfonyl)-3-nitrobenzene (3la). The title compound was prepared according to the general procedure and purified by column chromatography (Petroleum Ether: EtOAc = 3:1) to give a light yellow solid (65 % yield). $^1$H NMR (400 MHz, CDCl$_3$): 8.91 (s, 1H), 8.55-8.52 (m, 1H), 8.32-8.29 (m, 1H), 7.86-7.82 (m, 1H), 3.15 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): 148.5, 142.6, 133.0, 130.9, 128.3, 122.9, 44.4.

2-fluoro-1-methyl-4-(methylsulfonyl)benzene (3na). The title compound was prepared according to the general procedure and purified by column chromatography (Petroleum Ether: EtOAc = 3:1) to give a colorless oil (77 % yield). $^1$H NMR (400 MHz, CDCl$_3$): 7.65-7.57 (m, 2H), 7.43-7.39 (m, 1H), 3.05 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): 160.9 (d, $J$ = 249 Hz), 139.72, 132.5 (d, $J$ = 6 Hz), 131.9 (d, $J$ = 18 Hz), 122.9 (d, $J$ = 4 Hz), 114.3 (d, $J$ = 26 Hz), 44.5, 14.8 (d, $J$ = 4 Hz). HRMS [M+H]$^+$ calcd. for C$_8$H$_{10}$FO$_2$S: 189.0386, found : 189.0388.

1-bromo-3-(methylsulfonyl)-5-(trifluoromethyl)benzene (3oa). The title compound was prepared according to the general procedure and purified by column chromatography (Petroleum Ether: EtOAc = 3:1) to give a white solid (68 % yield). $^1$H NMR (400 MHz, CDCl$_3$): 8.29 (s, 1H), 8.15 (s, 1H), 8.05 (s, 1H), 3.13 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): 143.4, 133.8, 133.7 (q, $J$ = 68 Hz), 133.6 (q, $J$ = 3 Hz), 124.1, 123.2 (q, $J$ = 3 Hz), 122.2 (q, $J$ = 271 Hz), 44.4.

2-(methylsulfonyl)naphthalene (3pa). The title compound was prepared according to the general procedure and purified by column chromatography (Petroleum Ether: EtOAc = 3:1) to give a white solid (81 % yield). $^1$H NMR (400 MHz, CDCl$_3$): 8.53 (s, 1H), 8.03-8.00 (m, 2H), 7.95-7.80 (m, 2H), 7.71-7.62 (m, 2H), 3.13 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): 137.5, 135.3, 132.2, 129.7, 129.42, 129.3, 129.1, 128.0, 127.8, 122.1, 44.6.
1-(methylsulfonyl)naphthalene (3qa). The title compound was prepared according to the general procedure and purified by column chromatography (Petroleum Ether: EtOAc = 3:1) to give a light blue oil (59 % yield). 1H NMR (400 MHz, CDCl3): 8.74-8.72 (m, 1H), 8.35-8.33 (m, 1H), 8.14-8.12 (m, 1H), 7.99-7.97 (m, 1H), 7.74-7.70 (m, 1H), 7.65-7.58 (m, 2H), 3.22 (s, 2H); 13C NMR (100 MHz, CDCl3): 135.6, 135.2, 134.2, 129.7, 129.3, 128.8, 128.7, 127.1, 124.5, 123.9, 44.3.

2-(methylsulfonyl)thiophene (3ra). The title compound was prepared according to the general procedure and purified by column chromatography (Petroleum Ether: EtOAc = 3:1) to give a light yellow oil (69 % yield). 1H NMR (400 MHz, CDCl3): 7.73-7.71 (m, 2H), 7.17-7.15 (m, 1H), 3.19 (s, 3H); 13C NMR (100 MHz, CDCl3): 141.8, 133.7, 133.5, 127.9, 46.1.

(methylsulfonylmethyl)benzene (3sa). The title compound was prepared according to the general procedure and purified by column chromatography (Petroleum Ether: EtOAc = 3:1) to give a light yellow solid (71 % yield). 1H NMR (400 MHz, CDCl3): 7.40 (m, 5H), 4.25 (s, 2H), 2.75 (s, 3H); 13C NMR (100 MHz, CDCl3): 130.9, 130.5, 129.2, 129.0, 61.3, 39.0.

1-(methylsulfonyl)octane (3ta). The title compound was prepared according to the general procedure and purified by column chromatography (Petroleum Ether: EtOAc = 3:1) to give a white solid (62 % yield). 1H NMR (400 MHz, CDCl3): 3.02-2.98 (m, 2H), 2.89 (s, 3H), 1.89-1.81 (m, 2H), 1.46-1.41 (m, 2H), 1.32-1.28 (m, 8H), 0.90-0.87 (m, 3H); 13C NMR (100 MHz, CDCl3): 54.9, 40.4, 31.7, 29.0, 28.9, 28.4, 22.6, 22.5, 14.1.

Reference
NMR Spectra of products