SUPPORTING INFORMATION

Silver-Catalyzed Imination of Sulfoxides and Sulfides

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¹H and ¹³C NMR (400 and 100 MHz, respectively) spectra were recorded in CDCl₃ using TMS as internal standard. Chemical shifts are given in ppm and spin-spin coupling constants, *J*, are given in Hz. IR spectra were recorded as KBr pellets. Anhydrous acetonitrile was used and all reagents were purchased from commercial suppliers and used without further purification.

General procedure for the imination of sulfoxides (given in Table 1 and 3): To a suspension of the sulfoxide (0.25 mmol) or sulfide (0.25 mmol), sulfonylamide (0.3 mmol), PhI(OAc)₂ (121 mg, 0.37 mmol), AgNO₃ (3.4 mg, 0.02 mmol) and *t*-Bu₃tpy (8.0 mg, 0.02 mmol) in CH₃CN (2 mL) was added at room temperature and the reaction mixture was stirred for overnight (16 h). The resulting mixture was concentrated under reduced pressure, and then the product purified by column chromatography to afford the corresponding sulfoximines.

***N*-(4-Nitro-benzenesulfonyl)methylphenylsulfoximine (2):**¹ Following the general procedure using methyl phenyl sulfoxide and NsNH₂ gave 71.1 mg (84%) of compound **2** as pale yellow solid. ¹H NMR (CDCl₃): δ 8.32-8.27 (m, 2H), 8.17-8.13 (m, 2H), 8.03-7.99 (m, 2H), 7.77-7.71 (m, 1H), 7.66-7.60 (m, 2H), 3.47 (s, 3H); ¹³C NMR (CDCl₃): δ 149.7, 148.9, 137.7, 134.8, 129.9, 128.1, 127.3, 123.9, 46.8.

***N*-(4-Nitro-benzenesulfonyl)diphenylsulfoximine (3):**¹ Following the general procedure using phenyl sulfoxide and NsNH₂ gave 98 mg (98%) of compound **3** as white solid. ¹H NMR (CDCl₃): δ 8.30-8.27 (m, 2H), 8.18-8.14 (m, 2H), 8.02-7.98 (m, 4H), 7.65-7.61 (m, 2H), 7.58-7.53 (m, 4H); ¹³C NMR (CDCl₃): δ 149.7, 149.1, 139.4, 134.2, 129.7, 128.1, 127.6, 123.9.

***N*-(4-Nitro-benzenesulfonyl)tetramethylenesulfoximine (4):** Following the general procedure using tetramethylenesulfoxide and NsNH₂ gave 63.5 mg (84%) of compound **4** as pale yellow solid. Mp. 222-225 °C; ¹H NMR (DMSO): δ 8.44-8.41 (m, 2H), 8.15-8.12 (m, 2H), 3.80-3.73 (m, 2H), 3.58-3.40 (m, 2H), 2.29-2.16 (m, 4H); ¹³C NMR (DMSO-*d*₆): δ 150.2, 149.7, 128.5, 125.2, 54.7, 23.6; IR (KBr): ν 3110, 2953, 1537, 1301, 1054 cm⁻¹; MS (CI), *m/z* (relative intensity): 305 ([M+1]⁺); Calcd. for C₁₀H₁₂N₂O₅S₂: C, 39.46; H, 3.97; N, 9.20; found C, 39.69; H, 4.37; N, 9.20.

***N*-(4-Nitro-benzenesulfonyl)methylvinylsulfoximine (5):** Following the general procedure using methylvinylsulfoxide and NsNH_2 gave 81.3 mg (92%) of compound **5** as pale yellow solid. Mp. 150-151 °C; ^1H NMR (CDCl_3): δ 8.32-8.30 (m, 2H), 8.16-8.14 (m, 2H), 7.98-7.96 (m, 2H), 7.74-7.70 (m, 1H), 7.64-7.60 (m, 2H), 6.85 (dd, $J = 9.6$, 16.2 Hz, 1H), 6.51 (dd, $J = 1.7$, 16.2 Hz, 1H), 6.26 (dd, $J = 1.7$, 9.6 Hz, 1H); ^{13}C NMR (CDCl_3): δ 150.0, 149.0, 137.2, 136.8, 134.7, 129.9, 129.8, 128.1, 127.9, 124.0; IR (KBr): ν 3114, 1792, 1523, 1158, 1104 cm^{-1} ; MS (CI), m/z (relative intensity): 353 ($[\text{M}+1]^+$); Calcd. for $\text{C}_{15}\text{H}_{15}\text{N}_2\text{O}_5\text{S}_2 + 2\text{H}_2\text{O}$: C, 47.72; H, 3.43; N, 7.95; found C, 47.91; H, 3.80; N, 7.76.

***N*-(*p*-Toluenesulfonyl)methylphenylsulfoximine (6):**² Following the general procedure using methylphenylsulfoxide and TsNH_2 gave 60.9 mg (79%) of compound **6** as white solid. ^1H NMR (CDCl_3): δ 8.02-7.99 (m, 2H), 7.86-7.83 (m, 2H), 7.72-7.67 (m, 1H), 7.62-7.24 (m, 2H), 3.42 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (CDCl_3): δ 142.8, 140.6, 138.4, 134.3, 129.7, 129.3, 127.5, 126.6, 46.6, 21.5.

***N*-(Trimethylsilylethylsulfonyl)methylphenylsulfoximine (7):** To a suspension of methylphenylsulfoxide (70 mg, 0.5 mmol), SES-NH_2 ³ (108 mg, 0.6 mmol), $\text{PhI}(\text{OAc})_2$ (242 mg, 0.8 mmol), AgNO_3 (3.4 mg, 0.02 mmol) and *t*- Bu_3py (8 mg, 0.02 mmol) in acetonitrile (4 mL) was added and the reaction mixture was heated to reflux for 90 min. The resulting mixture was concentrated under reduced pressure and purified by chromatography on silica gel to afford 119.5 mg (75%) of the desired compound **7** as white solid. Mp. 106-108 °C; ^1H NMR (CDCl_3): δ 8.07-8.03 (m, 2H), 7.74-7.68 (m, 1H), 7.65-7.59 (m, 2H), 3.43 (s, 3H), 3.16-3.10 (m, 3H), 3.16-3.10 (m, 2H), 1.18-1.10 (m, 2H), 0.00 (s, 9H); ^{13}C NMR (CDCl_3): δ 138.4, 134.4, 129.7, 127.4, 53.6, 46.5, 10.3, 1.9; MS (CI), m/z (relative intensity): 320 ($[\text{M}+1]^+$); Calcd. for $\text{C}_{12}\text{H}_{21}\text{NO}_3\text{S}_2\text{Si}$: C, 45.11; H, 6.62; N, 4.38; found C, 45.21; H, 6.40; N, 4.29.

***N*-(*p*-Methyl-2-pyridinylsulfonyl)methylphenylsulfoximine (8):** Following the general procedure using methylphenyl sulfoxide and *p*-methyl-2-pyridinyl sulfonyl amide⁴ gave 56.9 mg (73%) of compound **8** as colorless oil. ^1H NMR (CDCl_3): δ 8.49-8.48 (m, 1H), 8.00-7.98 (m, 2H), 7.90 (d, $J = 8.6$ Hz, 1H), 7.69-7.62 (m, 2H), 7.62-7.55 (m, 2H), 3.55 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (CDCl_3): δ 156.7, 149.9, 138.1, 137.8, 136.8, 134.2, 129.5, 127.3, 121.1, 46.3, 18.5; IR (KBr): ν 3015, 2924, 1453, 1326, 1166, 1059 cm^{-1} ; MS (CI), m/z (relative intensity): 311 ($[\text{M}+1]^+$); Calcd. for $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}_3\text{S}_2$: C, 50.30; H, 4.55; N, 9.03; found C, 50.33; H, 4.79; N, 9.10.

***N*-(4-Nitro-benzenesulfonyl)methylphenylsulfilimine (10):**¹ Following the general procedure using methylphenylsulfide and NsNH_2 gave 67.2 mg (83%) of compound **10** as white solid. ^1H NMR (CDCl_3): δ 8.22-8.18 (m, 2H), 8.01-7.98 (m, 2H), 7.71-7.68 (m, 2H), 7.60-7.55 (m, 1H), 7.53-7.49 (m, 2H), 2.92 (s, 3H); ^{13}C NMR (CDCl_3): δ 149.7, 149.1, 135.0, 133.0, 130.2, 127.4, 125.9, 123.9, 39.1.

***N*-(4-Nitro-benzenesulfonyl)-*tert*-butylmethylsulfilimine (11):**¹ Following the general procedure using *tert*-butylmethylsulfoxide and NsNH_2 gave 58.8 mg (77%) of

compound **11** as white solid. ^1H NMR (CDCl_3): δ 8.31-8.26 (m, 2H), 8.09-8.05 (m, 2H), 2.49 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (CDCl_3): δ 150.1, 149.1, 127.5, 124.0, 55.7, 28.0, 23.4.

Deprotection of *N*-(4-nitro-benzenesulfonyl)methylphenylsulfoximine to give *NH*-methylphenylsulfoximine (9**):**⁴ To a solution of compound **2** (170mg, 0.5 mmol) in acetonitrile (4 mL) was added Cs_2CO_3 (293 mg, 0.9 mmol) and thiophenol (83 mg, 0.8 mmol) at room temperature and the reaction mixture was stirred overnight. Water was added to the reaction mixture and the product was extracted with dichloromethane. The combined organic layers were dried over MgSO_4 and concentrated. Purification by silica column chromatography gave 58.8 mg (76%) of compound **9** as colorless oil. ^1H NMR (CDCl_3): δ 8.05-8.01 (m, 2H), 7.68-7.55 (m, 3H), 3.12 (s, 3H), 2.78 (brs, 1H); ^{13}C NMR (CDCl_3): δ 143.3, 132.8, 129.0, 127.5, 46.1.

References

1. Okamura, H.; Bolm, C. *Org. Lett.* **2004**, *6*, 1305.
2. (a) Johnson, C. R.; Stark, C. J. *J. Org. Chem.* **1982**, *47*, 1196. (b) Johnson, C. R.; Haake, M.; Schroek, C. W. *J. Am. Chem. Soc.* **1973**, *95*, 7418. (c) Johnson, C. R.; Schroek, C. W.; Shanklin, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 7424.
3. Declerck, V.; Ribière, P.; Martinez, J.; Lamaty, F. *J. Org. Chem.* **2004**, *69*, 8372.
4. Cren, S.; Kinahan, T. C.; Skinner, C. L.; Tye, H. *Tetrahedron Lett.* **2002**, *43*, 2749.