

Copper-Catalyzed Synthesis of Aryldiazo Sulfones from Arylhydrazines and Sulfonyl Chlorides under Mild Conditions

Jin-Biao Liu,^{*ac} Fu-Jiao Chen,^a En Liu,^a Jin-Hui Li^a and Guanyinsheng Qiu^{*b}

^a School of Metallurgy and Chemical Engineering, Jiangxi University of Science and Technology, 86 Hongqi Road, Ganzhou 341000, China. E-mail: liujbgood@hotmail.com;

^b College of Biological, Chemical Science and Engineering, Jiaxing University, 118 Jiahang Road, Jiaxing 314001, China. E-mail: 11110220028@fudan.edu.cn;

^c Key Laboratory of Functional Small Organic Molecule, Ministry of Education, Jiangxi Normal University, Nanchang 330022, China.

Supporting Information

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1. General procedures

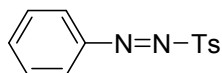
The solvents were distilled from standard drying agents. Unless otherwise stated, commercial reagents purchased from Alfa Aesar, Acros and Aldrich chemical companies were used without further purification. Purification of reaction products was carried out by flash chromatography using Qing Dao Sea Chemical Reagent silica gel (200–300 mesh). ¹H NMR spectra were recorded on a Bruker Avance III 400 (400 MHz) spectrometer and referenced internally to the residual proton resonance in CDCl₃ (δ = 7.26 ppm), or with tetramethylsilane (TMS, δ = 0.00 ppm) as the internal standard. Chemical shifts were reported as parts per million (ppm) in the δ scale downfield from TMS. Multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet), dd (doublet of doublet), bs (broad singlet). Analytical TLC was performed using EM separations percolated silica gel 0.2 mm layer UV 254 fluorescent sheets.

2. Typical procedure for the copper-catalyzed synthesis of aryldiazo sulfones

A mixture of arylhydrazine **1** (0.5 mmol), sulfonyl chloride **2** (0.5 mmol), CuSO₄·5H₂O (10 mol %), and K₂CO₃ (3.0 equiv), was stirred at room temperature in CH₂Cl₂ (3 mL) for 1-4 h. After completion of the reaction (indicated by TLC), the mixture was quenched with saturated NaCl solution, extracted with EtOAc, and dried over Na₂SO₄. The crude product was purified by flash column chromatography to provide the corresponding product **3**.

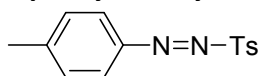
3. Characterization of the products

1-phenyl-2-tosyldiazenes (**3a**)¹



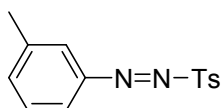
¹H NMR (400 MHz, CDCl₃): δ 7.87 (d, J = 8.0 Hz, 2H), 7.82 (d, J = 8.0 Hz, 2H), 7.60-7.56 (m, 1H), 7.51 (d, J = 8.0 Hz, 2H), 7.47-7.38 (m, 2H), 2.47 (s, 3H).

1-p-tolyl-2-tosyldiazenes (**3b**)¹



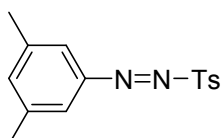
¹H NMR (400 MHz, CDCl₃): δ 7.87 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.29-7.26 (m, 2H), 2.47 (s, 3H), 2.42 (s, 3H).

1-m-tolyl-2-tosyldiazenes (**3c**)¹



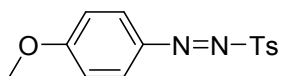
¹H NMR (400 MHz, CDCl₃): δ 7.86 (d, J = 8.0 Hz, 2H), 7.62 (s, 2H), 7.40-7.39 (m, 4H), 2.47 (s, 3H), 2.39 (s, 3H).

1-(3,5-dimethylphenyl)-2-tosyldiazenes (**3d**)¹



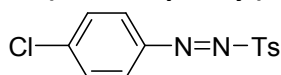
^1H NMR (400 MHz, CDCl_3): δ 7.85 (d, J = 8.0 Hz, 2H), 7.43-7.37 (m, 4H), 7.21 (s, 1H), 2.47 (s, 3H), 2.34 (s, 6H).

1-(4-methoxyphenyl)-2-tosyldiazene (3e)²



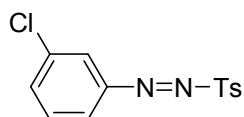
^1H NMR (400 MHz, CDCl_3): δ 7.83 (dd, J = 16.0 Hz, 8.0 Hz, 4H), 7.37 (d, J = 8.0 Hz, 2H), 6.95 (d, J = 8.0 Hz, 2H), 3.88 (s, 3H), 2.45 (s, 3H).

1-(4-chlorophenyl)-2-tosyldiazene (3f)¹



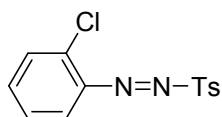
^1H NMR (400 MHz, CDCl_3): δ 7.85 (d, J = 7.2 Hz, 2H), 7.76 (d, J = 7.2 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 7.2 Hz, 2H), 2.48 (s, 3H).

1-(3-chlorophenyl)-2-tosyldiazene (3g)³



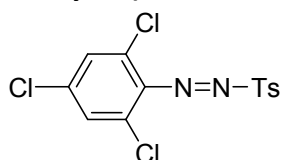
^1H NMR (400 MHz, CDCl_3): δ 7.86 (d, J = 8.0 Hz, 2H), 7.78 (s, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.47 (dd, J = 8.0 Hz, 4.8, 1H), 7.41 (t, J = 7.4 Hz, 2H), 2.49 (s, 3H).

1-(2-chlorophenyl)-2-tosyldiazene (3h)¹



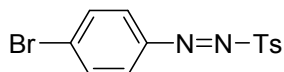
^1H NMR (400 MHz, CDCl_3): δ 7.84 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 8.0 Hz, 1H), 7.50 (d, J = 4.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 4.0 Hz, 1H), 2.48 (s, 3H).

1-tosyl-2-(2,4,6-trichlorophenyl)diazene (3i)³



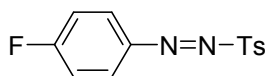
^1H NMR (400 MHz, CDCl_3): δ 7.84 (d, J = 8.0 Hz, 2H), 7.40-7.38 (m, 4H), 2.47 (s, 3H).

1-(4-bromophenyl)-2-tosyldiazene (3j)¹



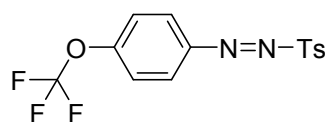
^1H NMR (400 MHz, CDCl_3): δ 7.86 (d, J = 8.0 Hz, 2H), 7.66 (dd, J = 20.0 Hz, 8.0 Hz, 4H), 7.40 (d, J = 8.0 Hz, 2H), 2.48 (s, 3H).

1-(4-fluorophenyl)-2-tosyldiazene (3k)⁴



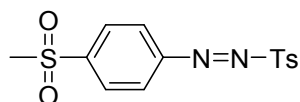
^1H NMR (400 MHz, CDCl_3): δ 7.86 (d, J = 4.0 Hz, 4H), 7.39 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 2.46 (s, 3H).

1-tosyl-2-(4-(trifluoromethoxy)phenyl)diazene (3l)⁴



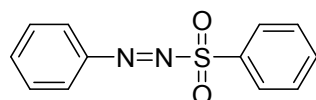
¹H NMR (400 MHz, CDCl₃): δ 7.87 (t, *J* = 8.8 Hz, 4H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.8 Hz, 2H), 2.48 (s, 3H).

1-(4-(methylsulfonyl)phenyl)-2-tosyldiazene (3m)



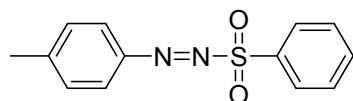
¹H NMR (400 MHz, CDCl₃): δ 8.09 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 3.08 (s, 3H), 2.49 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 151.9, 146.8, 145.3, 130.7, 130.3, 129.3, 129.0, 125.1, 44.5, 21.90. HRMS (ESI): *m/z*: calcd. for C₁₄H₁₄N₂O₄S₂Na [M+Na]⁺: 361.0297; found 361.0286.

1-phenyl-2-(phenylsulfonyl)diazene (3n)¹

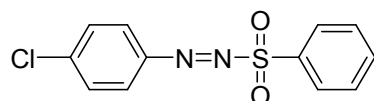


¹H NMR (400 MHz, CDCl₃): δ 8.0 (d, *J* = 8.0 Hz, 2H), 7.82-7.70 (m, 2H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.58-7.51 (m, 3H), 7.49 (d, *J* = 8.0 Hz, 2H).

1-(phenylsulfonyl)-2-p-tolyldiazene (3o)¹

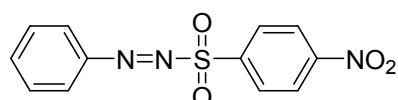


¹H NMR (400 MHz, CDCl₃): δ 7.98 (dt, *J* = 8.4 Hz, 1.6 Hz, 2H), 7.70 (ddd, *J* = 10.8 Hz, 8.0 Hz, 6.0 Hz, 3H), 7.59-7.57 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.39 (s, 3H). **1-(4-chlorophenyl)-2-(phenylsulfonyl)diazene (3p)¹**



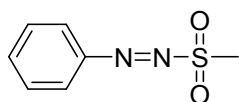
¹H NMR (400 MHz, CDCl₃): δ 7.98 (d, *J* = 7.6 Hz, 2H), 7.75 (dd, *J* = 16.0 Hz, 8.0 Hz, 3H), 7.61 (t, *J* = 7.6 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H).

1-(4-nitrophenylsulfonyl)-2-phenyldiazene (3q)²



¹H NMR (400 MHz, CDCl₃): δ 8.34 (d, *J* = 8.4 Hz, 2H), 8.13 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 7.2 Hz, 2H), 7.63 (d, *J* = 7.2 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 2H).

1-(methylsulfonyl)-2-phenyldiazene(3r)³



¹H NMR (400 MHz, CDCl₃): δ 7.95 (d, *J* = 7.2 Hz, 2H), 7.66 (d, *J* = 7.2 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 2H), 3.22 (s, 3H).

References

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4. NMR spectra of the products

