Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Palladium-catalyzed reductive homocoupling of *N*'-tosyl arylhydrazines

Jin-Biao Liu,[a] Lin Nie,[a] Hui Yan,[a] Li-Hua Jiang,[c] Jiang Weng[a] and Gui Lu[a,b,*]

[a] *Institute of Drug Synthesis and Pharmaceutical Process, School of Pharmaceutical Sciences, Sun Yat-sen University, Guangzhou, 510006 (P. R. China)*

[b] *Institute of Human Virology, Sun Yat-sen University, Guangzhou, 510080 (P. R. China)*

[c] *School of Pharmacy, Guangxi University of Chinese Medicine, Nanning, 530001 (P. R. China)*

Fax: (+86)-20-39943048

E-mail: lugui@mail.sysu.edu.cn

Supporting Information

1. General procedures

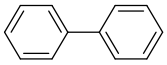
The solvents were distilled from standard drying agents. Unless otherwise stated, commercial reagents purchased from Alfa Aesar, Acros and Aldrich chemical companies were used without further purification. Purification of reaction products was carried out by flash chromatography using Qing Dao Sea Chemical Reagent silica gel (200–300 mesh). ^{1}H NMR spectra were recorded on a Bruker Avance III 400 (400 MHz) spectrometer and referenced internally to the residual proton resonance in $CDCl_3$ (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). ^{13}C NMR spectra were recorded on Bruker spectrometer with complete proton decoupling, and chemical shifts were reported in ppm from TMS with the solvent as the internal reference ($CDCl_3$, δ = 77.0 ppm). High resolution mass spectra were recorded on an ESI-ion trap mass spectrometer (Shimadzu, LCMS-IT-TOF). Analytical TLC was performed using EM separations percolated silica gel 0.2 mm layer UV 254 fluorescent sheets.

2. Typical procedure for the Pd-catalyzed homocoupling of *N*'-tosyl arylhydrazines

A mixture of *N*'-tosyl arylhydrazine **1** (0.3 mmol), $PdCl_2$ (0.0075 mmol, 2.5 mol %), and K_2CO_3 (0.3 mmol, 1 equiv.) in DMSO (1 mL) was stirred at room temperature or 60 °C for 2-12 h. After completion of the reaction (indicated by TLC), the mixture was quenched with saturated NaCl solution, extracted by EtOAc and dried over Na_2SO_4. The crude product was purified by flash column chromatography to provide the corresponding product **2**.

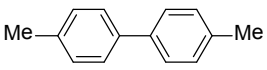
3. Characterization of the products

Biphenyl (2a)[1]



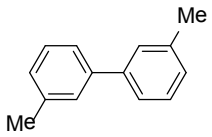
White solid; mp: 68-69 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, J = 7.4 Hz, 4H), 7.47 (t, J = 7.7 Hz, 4H), 7.37 (t, J = 7.3 Hz, 2H).

4,4'-Dimethylbiphenyl (2b)[1]



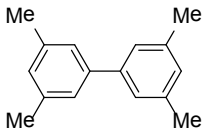
White solid; mp: 119-120 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, J = 8.0 Hz, 4H), 7.27 (d, J = 7.8 Hz, 4H), 2.42 (s, 6H).

3,3'-Dimethylbiphenyl (2c)[1]



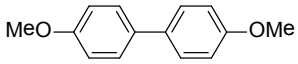
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.33 (m, 4H), 7.32-7.25 (m, 2H), 7.16 (d, J = 7.2 Hz, 2H), 2.42 (s, 6H).

3,3',5,5'-Tetramethylbiphenyl (2d)[5]



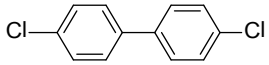
White solid; mp: 44-45 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (s, 4H), 6.98 (s, 2H), 2.37 (t, J = 4.1 Hz, 12H).

4,4'-Dimethoxybiphenyl (2f)[1]



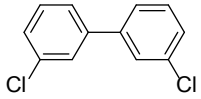
White solid; mp: 169-170 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, J = 8.6 Hz, 4H), 6.95 (d, J = 8.6 Hz, 4H), 3.84 (s, 6H).

4,4'-Dichlorobiphenyl (2g)[1]



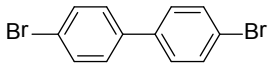
White solid; mp: 144-146 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, J = 8.4 Hz, 4H), 7.40 (d, J = 8.4 Hz, 4H).

3,3'-Dichlorobiphenyl (2h)[1]



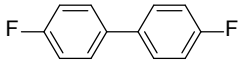
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 0.6 Hz, 2H), 7.45 (dd, J = 7.0, 0.9 Hz, 2H), 7.41-7.35 (m, 4H).

4,4'-Dibromobiphenyl (2i)[1]



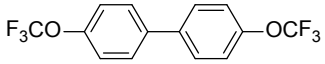
White solid; mp: 168-170 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, J = 8.4 Hz, 4H), 7.42 (d, J = 8.4 Hz, 4H).

4,4'-Difluorobiphenyl (2j)[6]



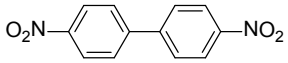
White solid; mp: 88-89 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (m, 4H), 7.12 (m, 4H).

4,4'-Bis(trifluoromethoxy)biphenyl (2k)[2]



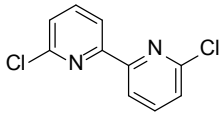
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, J = 8.4 Hz, 4H), 7.30 (d, J = 8.8 Hz, 4H).

4,4'-Dinitrobiphenyl (2l)[3]



Yellow solid; mp: 201-203 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (d, J = 8.5 Hz, 4H), 7.80 (d, J = 8.5 Hz, 4H).

6,6'-Dichloro-2,2'-bipyridine (2m)[4]



White solid; mp: 202-203 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (dd, J = 7.5, 4.5 Hz, 2H), 7.78 (td, J = 7.8, 4.9 Hz, 2H), 7.38 (dd, J = 7.7, 4.6 Hz, 2H).

4. References

[1] N. Kirai and Y. Yamamoto. *Eur. J. Org. Chem.* 2009, 1864.

[2] A. S. Demir, O. Reis and M. Emrullahoglu. *J. Org. Chem.* 2003, **68**, 10130.

[3] D. D. Hennings, T. Iwama and V. H. Rawal. *Org. Lett.* 1999, **1**, 1205.

[4] S. Wakabayashi, T. Tanaka, Y. Kubo, J. Uenishi and S. Oae. *Bull. Chem. Soc. Jpn.* 1989, **62**, 3848.

[5] C. E. Castro. *J. Am. Chem. Soc.* 1958, **80**, 2322.

[6] Y. Tamura. *Synthesis* 1978, **11**, 822.