Supporting Information

Palladium(0)-Catalyzed Hydrogen-Transfer of Alcohols with 2-nitroanilines for the Synthesis of Benzimidazoles

Qianqian Guan, Qi Sun, Lixian Wen, Zhenggen Zha, Yu Yang* and Zhiyong Wang*

Hefei National Laboratory for Physical Sciences at Microscale, Center for Excellence in Molecular Synthesis of Chinese Academy of Sciences, Collaborative Innovation Center of Suzhou Nano Science and Technology & Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China

Fax: (+86)551-6360-3185; E-mail: zwang3@ustc.edu.cn

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(A) General Procedures for the preparations of 1

To a solution of pyridin-2-amine (940 mg, 10 mmol, 1 equiv.) and triethylamine (1214 mg, 12 mmol, 1.2 equiv.) in dichloromethane (15 mL) in ice bath was added dropwise a solution of 2-nitrobenzenesulfonyl chloride (2651 mg, 12 mmol, 1.2 equiv.) in dichloromethane (10 mL). The mixture was allowed to warm to room temperature and stirred for 2 hours or until TLC showed no starting material left. Dichloromethane was removed in vacuum and the crude residue was redissolved in EtOAc, then washed with water (2 x 30 mL), saturated NaHCO₃ (2 x 15 mL), 1 M HCl (2 x 15 mL) and brine (2 x 30 mL). The crude was further purified by column chromatography (petroleum ether / ethyl acetate = 15:1) to give the product as a yellow solid (1538 mg, 72%). 1b, 1d were synthesized with the same procedures.

To a solution of 2-nitroaniline (553 mg, 4 mmol, 1 equiv.), DMAP (5 mg, 1 %) and triethylamine (81 mg, 0.8 mmol, 0.2 equiv.) in dichloromethane (10 mL) at room temperature was added dropwise a solution of acetyl chloride (628 mg, 8 mmol, 2 equiv.) in dichloromethane (5 mL). The mixture was stirred until TLC showed no starting material left. Then saturated NaHCO₃ 10 mL added. The mixture was extracted with CH₂Cl₂ (50mL x 2). The crude was further purified by column chromatography (petroleum ether / ethyl acetate = 5:1) to give the product 1h as a yellow solid (715 mg, 99%).

Other 2-nitroanilines were synthesized according to previously reported procedures.¹

(2-nitro-phenyl)-pyridin-2-yl-amine (1a)
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 15:1) to give the product as a yellow solid: mp = 74 - 76 °C; ¹H NMR (400 MHz, CDCl₃, ppm): δ = 10.16 (s, 1H), 8.71 (dd, J = 8.7 Hz 0.9 Hz, 1H), 8.33 (dd, J = 5.6 Hz 1.7 Hz, 1H), 8.21 (dd, J = 8.5 Hz 1.5 Hz, 1H), 7.67 – 7.62 (m, 1H), 7.58 – 7.54 (m, 1H), 6.98 – 6.94 (m, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 153.4, 147.5, 138.6, 138.2, 135.6, 135.0, 126.1, 119.9, 119.8, 117.7, 113.7. HRMS (ESI) m/z calcd for. C₁₁H₁₀N₃O₂ [M+H]+ 216.0773, found 216.0770.

(2-nitro-4-trifluoromethyl-phenyl)-pyridin-2-yl-amine (1b)
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 15:1) to give the product as a yellow solid: mp = 116 - 118 °C; ¹H NMR (400 MHz, CDCl₃, ppm): δ = 10.41 (s, 1H), 9.01 (d, J = 9.1 Hz, 1H), 8.52 (d, J = 1.2 Hz, 1H), 8.39 (dd, J = 4.9 Hz 1.2 Hz, 1H), 7.76 – 7.69 (m, 2H), 7.05 (ddd, J = 7.3 Hz 5.0 Hz 0.8 Hz, 1H), 7.00 (d, J = 8.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 152.8, 147.9, 141.3, 138.4, 133.4, 131.8 (q, J = 3.2 Hz), 124.0 (q, J = 4.3 Hz), 123.2 (q, J = 269.6), 121.4 (q, 34.2 Hz), 120.2, 118.9, 114.5. HRMS (ESI) m/z calcd for. C₁₂H₉F₃N₃O₂ [M+H]+ 284.0647, found 284.0648.

(N-(4-methyl-2-nitrophenyl)pyridin-2-amine (1c)
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 15:1) to the product as a yellow solid; ¹H NMR (400 MHz, CDCl₃, ppm): δ = 10.01 (s, 1H), 8.61 (d, J = 8.8 Hz, 1H), 8.33 – 8.32 (m, 1H), 8.03 – 8.02 (m, 1H), 7.64 – 7.60 (m, 1H), 7.40 – 7.37 (m, 1H), 6.94 – 6.91 (m, 2H), 2.35 (s, 3H).

(3-methyl-pyridin-2-yl)-(2-nitro-phenyl)-amine (1d)
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 15:1) to give the product as a yellow solid; mp = 112 – 114 °C; ¹H NMR (400 MHz, CDCl₃, ppm): δ = 10.28 (s, 1H), 9.00 (dd, J = 8.8 Hz 1.2 Hz, 1H), 8.24 (dd, J = 8.6 Hz 1.6 Hz, 1H), 8.21 (dd, J = 4.9 Hz 1.4 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.51 – 7.48 (m, 1H), 6.97 – 6.93 (m, 1H), 6.90 (dd, J = 7.3 Hz
5.0 Hz, 1H), 2.38 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta$ = 152.3, 145.0, 139.1, 138.6, 135.7, 134.5, 126.1, 121.5, 120.0, 119.5, 117.7, 17.4. HRMS (ESI) m/z calcd for C$_{12}$H$_8$N$_3$O$_2$ [M+H]$^+$ 230.0930, found 230.0925.

**N-methyl-2-nitroaniline (1f)**

The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 10:1) to give the product as a yellow solid; $^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta$ = 8.18 – 8.15 (m, 1H), 8.05 (s, 1H), 7.49 – 7.44 (m, 1H), 6.85 – 6.83 (m, 1H), 6.67 – 6.63 (m, 1H), 3.02 (s, 3H).

**2-nitro-$N$-phenylaniline (1g)**

The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 10:1) to give the product as a brown solid; $^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta$ = 9.50 (s, 1H), 8.20 (dd, $J$ = 8.6 Hz 1.6 Hz, 1H), 7.44 – 7.34 (m, 3H), 7.29 – 7.21 (m, 4H), 6.79 – 6.75 (m, 1H).

**$N$-[2-nitrophenyl]acetamide (1h)**

The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 10:1) to give the product as a yellow solid; $^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta$ = 10.34 (s, 1H), 8.78 – 8.76 (m, 1H), 8.22 – 8.20 (m, 1H), 7.68 – 7.63 (m, 1H), 7.21 – 7.16 (m, 1H), 2.30 (s, 3H).

**$N$-Pyridin-2-yl-benzene-1,2-diamine (1a’)**

The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether / ethyl acetate = 15:1) to give the product as a yellow oil; $^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta$ = 8.14 – 8.13 (m, 1H), 7.44 – 7.39 (m, 1H), 7.18 (dd, $J$ = 7.18 Hz 1.4 Hz, 1H), 7.10 – 7.06 (m, 1H), 6.83 – 6.75 (m, 3H), 6.68 – 6.64 (m, 1H), 6.41 (d, $J$ = 8.4 Hz, 1H), 3.83 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta$ = 157.7, 148.1, 143.0, 137.9, 127.1, 127.0, 125.7, 118.9, 116.1, 114.2, 107.2. HRMS (ESI) m/z calcd for C$_{12}$H$_{12}$N$_3$ [M+H]$^+$ 186.1031, found 186.1030.
(B) NMR spectra

3aa

3aa
(C) Crystal structure data
A single crystal for X-ray analysis of 3aa was obtained by recrystallation from acetone/petroleum ether. CCDC-1551540 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

CCDC 1551540

Table 1 Crystal data and structure refinement for 3aa.

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\( \alpha /^\circ \) 90
\( \beta /^\circ \) 108.488(2)
\( \gamma /^\circ \) 90
Volume/Å\(^3\) 1402.24(5)

\( Z \) 4
\( \rho_{\text{calc}} \) g/cm\(^3\) 1.285
\( \mu /\text{mm}^{-1} \) 0.612
\( F(000) \) 568.0
Crystal size/\( \text{mm}^3 \) 0.25 \( \times \) 0.21 \( \times \) 0.2
Radiation CuK\( \alpha \) (\( \lambda = 1.54184 \))
2\( \Theta \) range for data collection/\(^\circ \) 10.088 to 142.44
Index ranges \(-9 \leq h \leq 10, -21 \leq k \leq 19, -11 \leq l \leq 9\)
Reflections collected 4882
Independent reflections 2630 [\( R_{\text{int}} = 0.0134, R_{\text{sigma}} = 0.0165 \)]
Data/restraints/parameters 2630/0/191
Goodness-of-fit on \( F^2 \) 1.036
Final R indexes [\( I \geq 2 \sigma (I) \)] \( R_1 = 0.0360, \ wR_2 = 0.0983 \)
Final R indexes [all data] \( R_1 = 0.0403, \ wR_2 = 0.1028 \)
Largest diff. peak/hole / e Å\(^{-3} \) 0.16/–0.14