Synthesis of *N,N*-Dialkyl-*N'*-arylhydrazines via Palladium-Catalyzed *N*-Arylation by Using *N,N*-Dialkylhydrazines/2LiCl Adducts

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Melting points were determined with a Büchi B-545 apparatus and are uncorrected. All of the reagents and the catalysts are commercially available and were used as purchased, without further purification. Reaction products were purified on axially compressed columns, packed with SiO₂ 25-40 µm (Macherey Nagel), connected to a Gilson solvent delivery system and to a Gilson refractive index detector, and eluting with *n*-hexane/ethyl acetate mixtures. ¹H NMR (200 MHz) and ¹³C NMR (50.3 MHz) spectra were recorded with a Bruker Avance 200 spectrometer. IR spectra were recorded with a Jasco FT/IR 430 spectrometer.

Typical procedure for the synthesis of *N,N*-dialkyl-*N'*-arylhydrazines (**3**) - Preparation of (**3r**):

In a Carousel Tube Reaction (Radley Discovery), to a suspension of LiCl (0.0955 g, 2.267 mmol) in 3 mL of anhydrous THF, 1-aminomorpholine (0.108 mL, 1.126 mmol) was added. The mixture was stirred under argon at room temperature for 1 h. Then, the solvent was evaporated under reduced pressure. To the resultant white solid, 2 mL of toluene, 3-bromoanisole (0.105 mL, 0.563 mmol), Pd₂(dba)₃ (0.0129 g, 0.014 mmol), recrystallized Xantphos (0.0163 mg, 0.037 mmol) and sodium *tert*-butoxide (0.0757 g, 0.788 mmol) were added; The reaction mixture was stirred at 80 °C under argon for 3 h. After cooling, the reaction mixture was diluted with ethyl acetate, washed with NaHCO₃, dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by chromatography (silica gel, 35 g; *n*-hexane/ethylacetate 80/20 v/v) to give 0.083 g (71%) of **3r**; oil; IR (neat) 3249, 2959, 2855 cm⁻¹; ¹H NMR (CDCl₃) δ 7.11 (t, *J* = 8.1 Hz), 6.53-6.58 (m, 1 H), 6.48 (dd, *J*₁ = 7.7 Hz, *J*₂ = 1.4 Hz, 1 H), 6.37 (dd, *J*₁ = 7.8 Hz, *J*₂ = 2.4 Hz, 1 H), 4.48 (bs, 1 H), 3.77-3.90 (m, 7 H), 2.70-2.77 (m, 4 H); ¹³C NMR (CDCl₃) δ 160.9, 148.7, 130.0, 106.9, 104.8, 99.6, 67.1, 56.4, 55.2. Anal calcd for C₁₁H₁₆N₂O₂, C, 63.44; H, 7.74; N, 13.45; found C, 63.31; H, 7.75; N, 13.43.

3a: oil; IR (neat) 3242, 2948, 1610 cm⁻¹; ¹H NMR (CDCl₃) δ 7.66, 7.44 (m, 7 H), 7.01 (d, *J* = 8.7 Hz, 2 H), 4.36 (bs, 1 H), 2.62 (s, 6 H); ¹³C NMR (CDCl₃) δ 147.2, 141.3, 132.3, 128.7, 127.9, 126.5, 126.3, 113.9, 47.8. Anal calcd for C₁₄H₁₆N₂, C, 79.21; H, 7.60; N, 13.20; found C, 79.08; H, 7.58; N, 13.17.

3b: mp: 124-125 °C; IR (KBr) 3255, 2951, 2211 cm⁻¹; ¹H NMR (CDCl₃) δ 7.46 (d, *J* = 8.8 Hz, 1 H), 6.88 (d, *J* = 8.8 Hz, 1 H), 4.77 (bs, 1 H), 2.57 (s, 3 H); ¹³C NMR (CDCl₃) δ 146.4, 133.6, 122.0, 112.4, 106.5, 47.6; Anal calcd for C₉H₁₁N₃, C, 67.06; H, 6.88; N, 26.07; found C, 66.91; H, 6.86; N, 26.06.

3c: oil; IR (neat) 3218, 2978 cm^{-1} ; ^1H NMR (CDCl_3) δ 6.89-6.80 (m, 4 H), 3.78 (s, 1 H), 2.53 (s, 6 H); ^{13}C NMR (CDCl_3) δ 153.5, 141.6, 115.4, 114.6, 55.7, 47.8. Anal calcd for $\text{C}_9\text{H}_{14}\text{N}_2\text{O}$, C, 65.03; H, 8.49; N, 16.85; found C, 64.89; H, 8.47; N, 16.88.

3d: oil; IR (neat) 3409, 2950, 1508 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.11 (t, $J = 8.1$ Hz, 1 H), 6.54 (t, $J = 2.2$ Hz, 1 H), 6.49-6.33 (m, 2 H), 4.24 (s, 1 H), 3.80 (s, 3 H), 2.54 (s, 6 H); ^{13}C NMR (CDCl_3) δ 160.8, 149.3, 129.9, 106.2, 104.9, 99.3, 55.1, 47.8. Anal calcd for $\text{C}_9\text{H}_{14}\text{N}_2\text{O}$, C, 65.03; H, 8.49; N, 16.85; found C, 64.85; H, 8.52; N, 16.81.

3e: wax; IR (neat) 3398, 2972 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.86-7.81 (m, 2 H), 7.49-7.25 (m, 5 H), 4.86 (s, 1 H), 2.67 (s, 6 H); ^{13}C NMR (CDCl_3) δ 142.2, 134.3, 130.8, 128.7, 126.7, 125.6, 124.8, 123.0, 120.1, 119.5, 108.1, 87.9, 47.9. Anal calcd for $\text{C}_{12}\text{H}_{14}\text{N}_2$, C, 77.38; H, 7.58; N, 15.04; found C, 77.25; H, 7.56; N, 15.02.

3f: oil; IR (neat) 3481, 2971 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.75-7.66 (m, 3 H), 7.45-7.36 (m, 1 H), 7.31-7.23 (m, 2 H), 7.07 (dd, $J_1 = 8.8$ Hz, $J_2 = 2.1$ Hz, 1 H), 4.38 (s, 1 H), 2.61 (s, 6 H); ^{13}C NMR (CDCl_3) δ 145.4, 135.1, 129.0, 128.8, 127.8, 126.5, 126.3, 122.7, 116.9, 107.5, 47.8. Anal calcd for $\text{C}_{12}\text{H}_{14}\text{N}_2$, C, 77.38; H, 7.58; N, 15.04; found C, 77.52; H, 7.57; N, 15.07.

3g: mp: 82-83 $^\circ\text{C}$; IR 3244, 2935, 2852 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.66-7.34 (m, 7 H), 7.06-7.02 (m, 2 H), 4.52 (bs, 1 H), 2.85-2.70 (m, 4 H), 1.81-1.75 (m, 4 H), 1.52-1.35 (m, 2 H); ^{13}C NMR (CDCl_3) δ 147.3, 141.3, 132.0, 128.6, 127.8, 126.4, 126.2, 113.8, 57.4, 26.1, 23.7. Anal calcd for $\text{C}_{17}\text{H}_{20}\text{N}_2$, C, 80.91; H, 7.99; N, 11.10; found C, 80.78; H, 7.98; N, 11.11.

3h: mp: 85-86 $^\circ\text{C}$; IR (KBr) 3444, 2848, 2806 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.68-7.33 (m, 7 H), 7.09-7.03 (m, 2 H), 4.59 (bs, 1 H), 3.90 (t, $J = 4.4$ Hz, 2 H), 2.84 (t, $J = 4.4$ Hz, 2 H); ^{13}C NMR (CDCl_3) δ 146.7, 141.3, 132.8, 128.8, 128.1, 126.6, 126.5, 114.1, 67.2, 56.6. Anal calcd for $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}$, C, 75.56; H, 7.13; N, 11.01; found C, 75.47; H, 7.11; N, 11.03.

3i: wax; IR (neat) 3265, 2946, 2853, 2210 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.41 (d, $J = 8.8$ Hz, 2 H), 6.84 (d, $J = 8.8$ Hz, 2 H), 4.91 (bs, 1 H), 2.70-2.60 (m, 4 H), 1.75-1.62 (m, 4 H), 1.45-1.33 (m, 2 H); ^{13}C NMR (CDCl_3) δ 151.1, 133.6, 120.4, 112.3, 100.1, 57.2, 25.9, 23.4. Anal calcd for $\text{C}_{12}\text{H}_{15}\text{N}_3$, C, 71.61; H, 7.51; N, 20.88; found C, 71.48; H, 7.53; N, 20.86.

3j: oil; IR (neat) 3335, 2935, 2853 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.88-7.80 (m, 2 H), 7.48-7.29 (m, 5 H), 5.04 (bs, 1 H), 2.88-2.60 (m, 4 H), 1.85-1.72 (m, 4 H), 1.58-1.50 (m, 2 H); ^{13}C NMR (CDCl_3) δ 142.3, 134.4, 128.7, 126.8, 125.5, 124.7, 120.1, 119.0, 107.7, 57.4, 26.2, 23.9. Anal calcd for $\text{C}_{15}\text{H}_{18}\text{N}_2$, C, 79.61; H, 8.02; N, 12.38; found C, 79.74; H, 8.00; N, 12.35.

3k: oil; IR (neat) 3389, 2935, 2853, 1035 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.69-6.75 (m, 4 H), 4.14 (bs, 1 H), 3.76 (s, 3 H), 2.76-2.52 (m, 4 H), 1.75-1.62 (m, 4 H), 1.49-1.42 (m, 2 H); ^{13}C NMR (CDCl_3) δ 153.4, 141.7, 115.2, 114.6, 57.4, 55.7, 26.1, 23.8. Anal calcd for $\text{C}_{12}\text{H}_{18}\text{N}_2\text{O}$, C, 69.87; H, 8.80; N, 13.58; found C, 69.77; H, 8.82; N, 13.56.

3l: oil; IR (neat) 3255, 2936, 1038 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.11 (t, $J = 8.0$ Hz, 1 H), 6.58 (t, $J = 2.0$ Hz, 1 H), 6.46 (dt, $J_1 = 8.0$ Hz, $J_2 = 0.9$ Hz, 1 H), 6.35 (ddd, $J_1 = 8.0$ Hz, $J_2 = 2.0$ Hz, $J_3 = 0.9$ Hz, 1 H), 4.42 (bs, 1 H), 3.80 (s, 3 H), 2.75-2.52 (m, 4 H), 1.77-1.64 (m, 4 H), 1.52-1.42 (m, 2 H); ^{13}C NMR (CDCl_3) δ 160.9, 149.4, 129.9, 106.3, 104.4, 99.4, 57.4, 55.1, 26.1, 23.7. Anal calcd for $\text{C}_{12}\text{H}_{18}\text{N}_2\text{O}$, C, 69.87; H, 8.80; N, 13.58; found C, 69.74; H, 8.78; N, 13.55.

3m: mp: 56-57 $^\circ\text{C}$; IR 3477, 2936, 2853 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.75-7.66 (m, 3 H), 7.40 (dt, $J_1 = 6.8$ Hz, $J_2 = 1.1$ Hz, 1 H), 7.30-7.20 (m, 2 H), 7.09 (dd, $J_1 = 8.8$ Hz, $J_2 = 2.1$ Hz, 1 H), 4.54 (bs, 1 H), 2.85-2.63 (m, 4 H), 1.83-1.69 (m, 4 H), 1.54-1.47 (m, 2 H); ^{13}C NMR (CDCl_3) δ 145.4, 135.0, 128.9, 128.7, 127.7, 126.4, 126.2, 122.5, 116.9, 107.2, 57.4, 26.1, 23.8. Anal calcd for $\text{C}_{15}\text{H}_{18}\text{N}_2$, C, 79.61; H, 8.02; N, 12.38; found C, 79.49; H, 8.01; N, 12.36.

3n: mp: 167-168 $^\circ\text{C}$; IR (KBr); ^1H NMR (CDCl_3) δ 7.44 (d, $J = 8.8$ Hz, 2 H), 6.89 (d, $J = 8.8$ Hz, 2 H), 5.06 (bs, 1 H), 3.85-3.74 (m, 4 H), 2.80-2.71 (m, 4 H); ^{13}C NMR (CDCl_3) δ 150.7, 133.7, 120.2, 112.6, 100.8, 66.9, 56.2. Anal calcd for $\text{C}_{11}\text{H}_{13}\text{N}_3\text{O}$, C, 65.01; H, 6.45; N, 20.68; found C, 64.92; H, 6.44; N, 20.69.

3o: mp: 121-123 °C; IR (KBr) 3497, 2859 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.88-7.77 M, 2 H), 7.51-7.24 (m, 5 H), 5.07 (bs, 1 H), 3.93-3.83 (m, 4 H), 2.89-2.83 (m, 4 H); ^{13}C NMR (CDCl_3) δ 141.6, 134.4, 128.7, 126.6, 125.7, 124.9, 122.9, 120.0, 119.7, 107.9, 67.2, 56.5. Anal calcd for $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}$, C, 73.66; H, 7.06; N, 12.27; found C, 73.57; H, 7.05; N, 12.25.

3p: oil; IR (neat) 3207, 2969, 2874 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.79-7.70 (m, 3 H), 7.46-7.43 (m, 1 H), 7.35-7.28 (m, 2 H), 7.14 (dd, $J_1 = 8.8$ Hz, $J_2 = 2.2$ Hz, 1 H), 4.63 (bs, 1 H), 3.95-3.87 (m, 4 H), 2.89-2.81 (m, 4 H); ^{13}C NMR (CDCl_3) δ 144.7, 134.9, 129.1, 128.9, 127.7, 126.4, 126.3, 122.8, 116.8, 107.5, 67.1, 56.5. Anal calcd for $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}$, C, 73.66; H, 7.06; N, 12.27; found C, 73.51; H, 7.09; N, 12.24.

3q: mp: 83-84 °C; IR (KBr) 3240, 2940, 2854 cm^{-1} ; ^1H NMR (CDCl_3) δ 6.92-6.74 (m, 4 H), 4.25 (bs, 1 H), 3.82-3.76 (m, 4 H), 2.76-2.69 (m, 4 H); ^{13}C NMR (CDCl_3) δ 153.8, 140.8, 115.4, 114.7, 67.1, 56.5, 55.7. Anal calcd for $\text{C}_{11}\text{H}_{16}\text{N}_2\text{O}_2$, C, 63.44; H, 7.74; N, 13.45; found C, 63.32; H, 7.73; N, 13.43.