Supporting data I for

Novel Synthesis of 2-Chloroquinolines from 2-Vinylanilines in Nitrile Solvent

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General Procedure for the Preparation of Vinylanilines 1a-e and 1h. Under N₂ atmosphere, to a suspension of **5a-f** (0.79 mmol) and tetrakis(triphenylphosphine)palladium (18 mg, 0.016 mmol) in 6 mL of sodium-dried dioxane in a pressure tube was added tributyl(vinyl)tin (0.28 mL, 0.95 mmol) at rt. The pressure tube was tightly capped, heated at 130 °C for 5 h, and then cooled to rt. After 10% aqueous KF solution (10 mL) was added to the mixture, the reaction mixture was allowed to stand for 2 h and then filtered with celite, washed with water and EtOAc. The filtrate was transferred to separatory funnel and organic phase was separated. Organic compounds were extracted with EtOAc (50 mL x 2) from aqueous phase. The collected EtOAc solution was dried over Na₂SO₄, concentrated by rotary evaporator and then dissolved in 7 mL of THF and 3 mL of 10% aqueous K₂CO₃. The two phases solution was refluxed for 12 h and cooled to rt, and then transferred to separatory funnel. Organic compounds were extracted with EtOAc (50 mL x 3) from aqueous phase. Flash column chromatography (5% EtOAc/hexane) gave **1a-e** and **1h**.

2-Vinylaniline (1a). 26% as a brown liquid: ¹H NMR (200 MHz, CDCl₃) δ 7.28 (dd, 1H, *J* = 7.7, 1.6 Hz), 7.09 (td, 1H, *J* = 7.8, 1.4 Hz), 6.66-6.84 (m, 3H), 5.62 (dd, 1H, *J* = 17.6, 1.4 Hz), 5.31 (dd, 1H, *J* = 10.9, 1.5 Hz), 3.75 (br s, 2H); ¹³C NMR (50 MHz, CDCl₃) δ 132.8, 128.7, 127.7, 127.3, 118.9, 118.5, 116.0, 115.6; MS (ESI) *m/z* (relative intensity) 221 (MH⁺, 100), 205, 176. The experiment data is agreement with those reported in the literature (King, F. D.; Walton, R. M. *J. Chem. Soc., Chem. Commun.* **1974**, 256).

4-Chloro-2-vinylaniline (1b). 68% as a brown liquid: ¹H NMR (200 MHz, CDCl₃) δ 7.24 (d, 1H, *J* = 2.6 Hz), 7.03 (dd, 1H, *J* = 8.5, 2.3 Hz), 6.68 (dd, 1H, *J* = 17.2, 11.0 Hz), 6.60 (d, 1H, *J* = 8.8 Hz), 5.63 (dd, 1H, *J* = 17.4, 1.2 Hz), 5.35 (dd, 1H, *J* = 10.9, 1.1 Hz), 3.73 (br s, 2H); ¹³C NMR (50 MHz, CDCl₃) δ 142.2, 131.7, 128.4, 126.9, 125.4, 123.6, 117.1, 116.8; MS (ESI) *m/z* (relative intensity)

156 (MH⁺), 154 (MH⁺, 100), 119. HRMS (CI) m/z C₈H₉ClN (MH⁺) calcd: 154.0401; found: 154.0428.

4-Methyl-2-vinylaniline (1c). 77% as a brown liquid: ¹H NMR (200 MHz, CDCl₃) δ 7.10 (s, 1H), 6.90 (dd, 1H, *J* = 8.3, 1.9 Hz), 6.76 (dd, 1H, *J* = 17.4, 11.0 Hz), 6.60 (d, 1H, *J* = 8.0 Hz), 5.61 (dd, 1H, *J* = 17.5, 1.5 Hz), 5.29 (dd, 1H, *J* = 11.0, 1.6 Hz), 3.61 (br s, 2H), 2.24 (s, 3H); ¹³C NMR (50 MHz, CDCl₃) δ 141.2, 132.9, 129.3, 128.1, 127.7, 124.1, 116.3, 115.3, 20.4; MS (ESI) m/z (relative intensity) 134 (MH⁺, 100), 119. HRMS (CI) m/z C₉H₁₂N (MH⁺) calcd: 134.0945; found: 134.0974.

4-Trifluoromethyl-2-vinylaniline (1d). 41% as a brown liquid: ¹H NMR (200 MHz, CDCl₃) δ 7.52 (s, 1H), 7.32 (dd, 1H, *J* = 8.2, 2.0 Hz), 6.71 (dd, 1H, *J* = 17.2, 11.0 Hz), 6.69 (d, 1H, *J* = 8.2 Hz), 5.71 (dd, 1H, *J* = 17.2, 1.2 Hz), 5.41 (dd, 1H, *J* = 11.0, 1.0 Hz), 4.04 (br s, 2H); ¹³C NMR (50 MHz, CDCl₃) δ 146.5, 131.6, 125.6 (q, *J* = 3.8 Hz), 124.8 (q, *J* = 269.3 Hz), 123.4, 122.3 (q, *J* = 3.8 Hz), 120.5 (q, *J* = 32.6 Hz), 117.4, 115.3; MS (CI) m/z (relative intensity) 188 (MH⁺), 168 (100). HRMS (CI) m/z C₉H₉F₃N (MH⁺) calcd: 188.0701; found: 188.0684.

4-Nitro-2-vinylaniline (1e). 84% as a yellow solid: mp 93-94 °C; ¹H NMR (200 MHz, CDCl₃) δ 8.18 (d, 1H, *J* = 2.6 Hz), 7.99 (d, 1H, *J* = 8.8, 2.6 Hz), 6.66 (dd, 1H, *J* = 17.2, 11.0 Hz), 6.64 (d, 1H, *J* = 8.8 Hz), 5.75 (dd, 1H, *J* = 17.4, 1.0 Hz), 5.49 (dd, 1H, *J* = 10.9, 1.1 Hz), 4.44 (br s, 2H); ¹³C NMR (50 MHz, CDCl₃) δ 149.7, 130.8, 125.0, 125.0, 124.0, 122.9, 118.8, 114.4; MS (ESI) m/z (relative intensity) 165 (MH⁺, 100), 148. HRMS (CI) m/z C₈H₉N₂O₂ (MH⁺) calcd: 165.0656; found: 165.0665.

2-(Furan-2-yl)-4-nitroaniline (1h). 65% as a yellow solid: mp 128-129 °C; ¹H NMR (200 MHz, CDCl₃) δ 8.37 (d, 1H, *J* = 2.6 Hz), 7.99 (dd, 1H, *J* = 8.8, 2.6 Hz), 7.54 (d, 1H, *J* = 1.0 Hz), 6.70 (m, 2H), 6.56 (dd, 1H, *J* = 3.8, 1.8 Hz), 5.19 (br s, 2H); ¹³C NMR (50 MHz, CDCl₃) δ 151.4, 148.9, 142.1, 138.8, 124.8, 124.1, 115.4, 114.6, 111.7, 107.8; MS (ESI) m/z (relative intensity) 205 (MH⁺, 100), 176, 165. Anal. calcd for C₁₀H₈N₂O₃: C, 58.82; H, 3.95; N, 13.72. found: C, 58.73; H, 3.98; N, 14.10.

General Procedure for the Preparation of Vinylanilines 1f,g and 1i,j. Under N₂ atmosphere, to a

suspension of *N*-(4-nitro-2-tri-*n*-butylstannanylphenyl)acetamide (300 mg, 0.64 mmol) and tetrakis(triphenylphosphine)palladium (8 mg, 6.39 μ mol) in 5 mL of sodium-dried dioxane in a pressure tube was added vinyl bromide or triflate (0.11 mL, 1.28 mmol) at rt. The pressure tube was tightly capped and heated at 130 °C for 12 h and cooled to rt. After 10% aqueous KF solution (10 mL) was added to the mixture, the reaction mixture was allowed to stand for 2 h and then filtered with celite, washed with water and EtOAc. The filtrate was transferred to separatory funnel and organic phase was separated. Organic compounds were extracted with EtOAc (50 mL x 2) from aqueous phase. The combined organic solution was dried over Na₂SO₄, concentrated by rotary evaporator and then dissolved in 7 mL of THF and 3 mL of 10% aqueous K₂CO₃. The two phases solution was refluxed for 12 h and cooled to rt, and then transferred to separatory funnel. Organic compounds were extracted with EtOAc (50 mL x 3) from aqueous phase. Flash column chromatography (5% EtOAc/hexane) gave **1f,g** and **1i,j**.

2-Isopropenyl-4-nitro-phenylamine (1f). 48% as a brown liquid: ¹H NMR (200 MHz, CDCl₃) δ 7.94 (m, 2H), 6.64 (d, 1H, *J* = 9.8 Hz), 5.39 (m, 1H), 5.10 (m, 1H), 4.63 (br s, 2H), 2.07 (s, 3H); ¹³C NMR (50 MHz, CDCl₃) δ 149.3, 141.3, 127.8, 124.7, 124.6, 121.8, 117.1, 113.9, 21.0; MS (EI) *m/z* (relative intensity) 178 (*M*⁺, 100), 162, 148, 117, 105, 91, 77. HRMS (CI) *m/z* C₉H₁₁N₂O₂ (*MH*⁺) calcd: 179.0798; found: 179.0825.

2-(Cyclohex-1-enyl)-4-nitroaniline (1g). 43% as a yellow solid: mp 101-102 °C; ¹H NMR (200 MHz, CDCl₃) 7.89-7.96 (m, 2H), 6.62 (d, 1H, *J* = 8.8 Hz), 5.82 (q, 1H, *J* = 1.8 Hz), 4.51 (s, 2H), 2.20 (t, 4H, *J* = 3.2 Hz), 1.82-1.60 (m, 4H); ¹³C NMR (50 MHz, CDCl₃) δ 149.7, 138.9, 134.5, 128.9, 128.8, 125.1, 124.3, 113.6, 29.1, 25.3, 22.9, 21.9; MS (ESI) *m/z* (relative intensity) 219 (*MH*⁺, 100), 193, 165. HRMS (CI) *m/z* C₁₂H₁₅N₂O₂ (*MH*⁺) calcd: 219.1139; found: 219.1132.

4-Nitro-2-(thiophen-2-yl)aniline (1i). 94% as a yellow solid: mp 101-102 °C; ¹H NMR (200 MHz, CDCl₃) δ 8.19 (d, 1H, *J* = 2.6 Hz), 8.06 (dd, 1H, *J* = 9.0, 2.8 Hz), 7.44 (dd, 1H, *J* = 4.9, 1.3 Hz), 7.23-7.14 (m, 2H), 6.73 (d, 1H, *J* = 9.0 Hz), 4.75 (br s, 2H); ¹³C NMR (50 MHz, CDCl₃) δ 150.4, 138.6, 137.9, 127.8, 127.3, 126.8, 126.4, 125.4, 118.6, 114.2; MS (ESI) *m/z* (relative intensity) 221

(MH⁺, 100), 205, 176. Anal. calcd for C₁₀H₈N₂O₂S: C, 54.53; H, 3.66; N, 12.72. found: C, 54.68; H, 3.65; N, 13.04.

4-Nitro-2-(thiophen-3-yl)phenylamine (1j). 42% as a yellow solid: mp 110 °C; ¹H NMR (200 MHz, CDCl₃) δ 8.12 (d, 1H, *J* = 2.6 Hz), 8.05 (dt, 1H, *J* = 8.8, 1.3 Hz), 7.52-7.41 (m, 2H), 7.24 (dt, 1H, *J* = 6.07, 1.7 Hz), 6.71 (d, 1H, *J* = 8.8 Hz), 4.56 (br s, 2H); ¹³C NMR (50 MHz, CDCl₃) δ 147.7, 134.8, 126.9, 125.3, 124.7, 124.1, 122.6, 121.3, 118.9, 111.6; MS (ESI) *m/z* (relative intensity) 221 (MH⁺, 100), 205, 176. HRMS (CI) *m/z* C₁₀H₉N₂O₂S (MH⁺) calcd: 221.0371; found: 221.0388.

Figure 1. Time courses of percentage of conversions of 4-nitro-2-vinylaniline (**1e**) depended on the equiv of diphosgene in a typical reaction of formation of 2-chloroquinoline. Each percentage of conversion was obtained by reverse phase HPLC column (Mightysil, C18, 250 mm x 4.6 mm) at the flow-rate of 1mL/min with the eluent of 70% CH₃CN:30% water (*t_R*=9.2 min of **2e**). The area of each peak was calculated with the calibration curve of product (**2e**) to give each concentration.