**Palladium-Catalyzed Rearrangement/Arylation of 2-Allyloxypyridine
Leading to the Synthesis of N-Substituted 2-Pyridones**

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General. ^1H and ^{13}C NMR spectra were recorded on Varian GEMINI-2000 (^1H 300 MHz, ^{13}C 75 MHz) spectrometer in CDCl_3 with chemical shifts referenced to internal standards (7.26 ppm ^1H , 77.0 ppm ^{13}C). EI mass spectra were recorded on JMS-SX102A spectrometer. Unless otherwise noted, all materials, anhydrous tetrahydrofuran (THF), and anhydrous diethyl ether (Et_2O) were obtained from commercial suppliers and used without further purification. Xylene was dried over CaH_2 under argon. 2-Allyloxypyridine (**1**) was prepared according to the literature.¹

Typical Procedure for One-Pot Rearrangement/Arylation of **1 with Aryl Iodide (Table 4, entry 4).** A solution of **1** (53.8 mg, 0.40 mmol) and $\text{Pd}[\text{P}(t\text{-Bu})_3]_2$ (10.3 mg, 5 mol%) in dry xylenes (1.5 mL) was stirred at 80 °C for 2 h under argon to give **2** in situ. To this solution were added 4-iodoanisole (132.2 mg, 0.56 mmol), Ag_2CO_3 (154.3 mg, 0.56 mmol), and dry xylenes (0.5 mL). After stirring the resultant mixture at 100 °C for 22 h, the catalyst and inorganic salts were removed by filtration through a short silica gel pad (EtOAc). The filtrate was evaporated, and the residue was chromatographed on silica gel (hexane/ EtOAc = 1/1) to afford **6d** (90.8 mg, 95%) as pale yellow oil.

Compound 6a:² ^1H -NMR: δ 4.73 (dd, J = 6.3, 1.2 Hz, 2H), 6.18 (dd, J = 6.6, 5.1 Hz, 1H), 6.32 (dt, J = 15.9, 6.3 Hz, 1H), 6.59 (d, J = 15.9 Hz, 1H), 6.61 (dd, J = 9.6, 1.2 Hz, 1H), 7.20–7.40 (m, 7H). ^{13}C NMR: δ 50.4, 106.0, 120.8, 123.4, 126.3, 127.9, 128.4, 133.8, 135.8, 136.8, 139.3, 162.2.

Compound 6b: ^1H -NMR: δ 2.34 (s, 3H), 4.74 (dd, J = 6.6, 1.5 Hz, 2H), 6.14–6.24 (m, 2H), 6.61 (dd, J = 10.2, 1.5 Hz, 1H), 6.81 (d, J = 15.6 Hz, 1H), 7.13–7.18 (m, 3H), 7.30–7.35 (m, 2H), 7.40–7.45 (m, 1H). ^{13}C NMR: δ 19.6, 50.7, 106.1, 120.9, 124.8, 125.6, 126.0, 130.2, 131.8, 135.0, 135.4, 136.8, 139.4, 162.4. HRMS (EI) m/z calcd for $\text{C}_{15}\text{H}_{15}\text{NO}$: 225.1154, found 225.1157.

Compound 6c: ^1H -NMR: δ 2.33 (s, 3H), 4.71 (d, J = 6.6 Hz, 2H), 6.17–6.31 (m, 2H), 6.53–6.62 (m, 2H), 7.12 (d, J = 8.1 Hz, 2H), 7.25–7.35 (m, 4H). ^{13}C NMR: δ 21.0, 50.5, 106.0, 120.8, 122.3, 126.3, 129.2, 133.0,

(1) Dinan, F. J.; Tieckelmann, H. *J. Org. Chem.* **1964**, 29, 892.

(2) Bowman, W. R.; Bridge, C. F. *Synth. Commun.* **1999**, 29, 4051.

133.8, 136.8, 137.8, 139.3, 162.3. HRMS (EI) m/z calcd for $C_{15}H_{15}NO$: 225.1154, found 225.1155.

Compound 6d: 1H -NMR: δ 3.80 (s, 3H), 4.70 (dd, J = 6.6, 1.2 Hz, 2H), 6.15–6.20 (m, 2H), 6.54 (d, J = 15.6 Hz, 1H), 6.60 (dd, J = 9.6, 1.5 Hz, 1H), 6.84 (d, J = 8.7 Hz, 2H), 7.30–7.35 (m, 4H). ^{13}C NMR: δ 50.6, 55.1, 106.0, 113.9, 120.8, 121.2, 127.7, 128.6, 133.5, 136.9, 139.3, 159.4, 162.4. HRMS (EI) m/z calcd for $C_{15}H_{15}NO_2$: 241.1103, found 241.1109.

Compound 6e: 1H -NMR: δ 4.72 (dd, J = 6.6, 1.5 Hz, 2H), 6.19 (td, J = 6.6, 1.5 Hz, 1H), 6.30 (dt, J = 15.9, 6.3 Hz, 1H), 6.52 (d, J = 15.9 Hz, 1H), 6.61 (dm, J = 8.4 Hz, 1H), 7.27–7.37 (m, 6H). ^{13}C NMR: δ 50.6, 106.2, 121.0, 124.2, 127.6, 128.6, 132.4, 133.5, 134.4, 136.9, 139.5, 162.3. HRMS (EI) m/z calcd for $C_{14}H_{12}NOCl$: 245.0607, found 245.0607.

Compound 6f: 1H -NMR: δ 4.75 (dd, J = 6.0, 1.2 Hz, 2H), 6.21 (td, J = 6.6, 1.5 Hz, 1H), 6.42 (td, J = 15.9, 6.0 Hz, 1H), 6.55–6.64 (m, 2H), 7.29–7.38 (m, 2H), 7.45 (d, J = 8.7 Hz, 2H), 7.56 (d, J = 8.7 Hz, 2H). ^{13}C NMR: δ 50.6, 106.3, 121.0, 122.2, 125.4 (q, J_{C-F} = 3.5 Hz), 126.4, 126.6, 129.6 (q, J_{C-F} = 31.9 Hz), 132.1, 137.0, 139.4, 139.6, 162.3. HRMS (EI) m/z calcd for $C_{15}H_{12}F_3NO$: 279.0871, found 279.0872.

Compound 6g: 1H -NMR: δ 2.58 (s, 3H), 4.75 (d, J = 5.7 Hz, 2H), 6.20 (td, J = 6.6, 1.5 Hz, 1H), 6.44 (td, J = 16.2, 6.0 Hz, 1H), 6.58 (d, J = 16.2 Hz, 1H), 6.62 (d, J = 9.0 Hz, 1H), 7.30–7.40 (m, 2H), 7.44 (d, J = 8.7 Hz, 2H), 7.89 (d, J = 8.7 Hz, 2H). ^{13}C NMR: δ 26.4, 50.6, 106.2, 120.9, 126.47, 126.53, 128.55, 132.3, 136.1, 137.0, 139.5, 140.4, 162.2, 197.3. HRMS (EI) m/z calcd for $C_{16}H_{15}NO_2$: 253.1103, found 253.1104.