Supporting Information

Gold(I)-Catalyzed Intramolecular Acetylenic Schmidt Reaction

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General Information. Unless otherwise noted, all reagents were obtained commercially and used without further purification. ACS grade dichloromethane (CH_2Cl_2) was obtained from EMD. All substrate azides were prepared by the method of Knouzi *et al.* via tosylation of the corresponding homopropargyl alcohol followed by displacement with sodium azide.¹ TLC analysis of reaction mixtures was performed on Merck silica gel 60 F254 TLC plates using potassium permanganate stain to visualize the reaction components. Chromatography was carried out on activated, neutral, aluminum oxide (Brockmann I, standard grade, ~150 mesh, 58 Å) purchased from Aldrich Chemical Company. ^1H and ^{13}C NMR spectra were recorded with Bruker AM-300, AMX-400, and DRX-500 spectrometers referenced to benzene, unless otherwise noted. Mass spectral and CHN data were obtained via the Micro-Mass/Analytical Facility operated by the College of Chemistry, University of California, Berkeley.

General procedure for the synthesis of pyrroles from homopropargyl azides.

To a 20 mL vial with a threaded cap containing a magnetic stir bar was added AgSbF_6 (0.05 equiv.). A solution of the appropriate azide (0.3 mmol, 1 equiv.) in CH_2Cl_2 (0.05 M) was added to the vial. The resulting suspension was heated to 35 °C, followed by addition of $(\text{dppm})(\text{AuCl})_2$ (0.025 equiv.).² Subsequently, evolution of gas was observed from the reaction mixture. After TLC indicated full consumption of starting material (20-40 min.), the reaction mixture was cooled to room temperature and filtered through neutral alumina with excess CH_2Cl_2 . The filtrate was then concentrated and chromatographed on neutral alumina to afford analytically pure pyrroles.³

Pyrrole **2** was obtained as a clear oil (58.9 mg, 82% yield).

^1H NMR (C_6D_6 , 400 MHz) δ 6.70 (bs, 1 H), 5.99 (s, 2 H), 2.36 (t, 4 H, $J = 7.6$ Hz), 1.44 (m, 4 H), 1.28 (m, 4 H), 0.86 (t, 6 H, $J = 8$ Hz); ^{13}C NMR (C_6D_6 , 100 MHz) δ 130.2, 105.1, 32.1, 27.6, 22.4, 13.8; Anal. Calcd for $\text{C}_{12}\text{H}_{21}\text{N}$: C, 80.38; H, 11.81; N, 7.81. Found: C, 80.50; H, 12.02; N, 7.87.

Pyrrole **4** was obtained as a clear oil (38.9 mg, 76% yield).

^1H NMR (C_6D_6 , 400 MHz) δ 6.75 (bs, 1 H), 6.68 (d, 1 H, $J = 1.2$ Hz), 6.30 (d, 1 H, $J = 1.2$ Hz), 6.06 (s, 1 H), 2.32 (t, 2 H, $J = 7.6$ Hz), 1.42 (m, 2 H), 1.25 (m, 6 H), 0.87 (t, 3 H, $J = 6.4$ Hz); ^{13}C NMR (C_6D_6 , 100 MHz) δ 131.8, 115.7, 108.3, 105.2, 31.7, 29.9, 29.0, 27.6, 22.6, 14.0; Anal. Calcd for $\text{C}_{10}\text{H}_{17}\text{N}$: C, 79.41; H, 11.33; N, 9.26. Found: C, 79.78; H, 11.64; N, 9.14.

Pyrrole **6** was obtained as a clear oil (17.7 mg, 78% yield).

^1H NMR (C_6D_6 , 400 MHz) δ 6.85 (s, 1 H), 5.93 (s, 2 H), 2.31 (t, 2 H, $J = 7.6$ Hz), 1.51 (m, 2 H), 1.40 (m, 2 H), 1.25 (sextet, 1 H, $J = 7.6$ Hz), 0.85 (t, 3 H, $J = 7.6$ Hz), 0.53 (m, 4 H); ^{13}C NMR (C_6D_6 , 100 MHz) δ 131.9, 130.5, 105.0, 104.3, 32.1, 27.5, 22.4, 13.8, 8.3, 6.2; HRMS (EI) Calcd. For $[\text{C}_{11}\text{H}_{17}\text{N}]$ 163.1361, Found 163.1358.

Pyrrole **8** was isolated as a white solid (32.2 mg, 73% yield).

^1H NMR (C_6D_6 , 400 MHz) δ 7.2-7.5 (m, 4 H), 7.19 (bs, 1 H), 7.12 (t, 1 H, $J = 7.2$ Hz), 6.65 (s, 1 H), 2.64 (s, 2 H), 2.35 (s, 2 H), 1.73 (m, 4 H); ^{13}C NMR (C_6D_6 , 100 MHz) δ 133.8, 130.0, 128.7, 125.1, 123.4, 118.7, 105.6, 24.0, 23.6, 23.2, 22.9; Anal. Calcd for $\text{C}_{14}\text{H}_{15}\text{N}$: C, 85.24; H, 7.66; N, 7.10. Found: C, 84.96; H, 7.56; N, 6.86.

Pyrrole **10a** was isolated as a white solid (37.3 mg, 68% yield). The spectral data were consistent with reported values.⁴

^1H NMR (C_6D_6 , 400 MHz) δ 7.33 (bs, 1 H), 7.14 (m, 4 H), 7.03 (t, 1 H, $J = 7.2$ Hz), 6.57 (t, 1 H, $J = 1.6$ Hz), 6.38 (q, 1 H, $J = 1.6$ Hz), 6.32 (q, $J = 2.4$ Hz); ^{13}C NMR (C_6D_6 , 100 MHz) δ 133.1, 131.7, 128.7, 125.7, 123.7, 118.7, 110.0, 106.2.

Pyrrole **10b** was isolated as a white solid (89.4 mg, 88% yield).

^1H NMR (C_6D_6 , 400 MHz) δ 7.64 (dd, 1 H, $J = 8, 2$ Hz), 6.94 (dt, 1 H, $J = 8.0, 1.6$ Hz), 6.85 (dt, 1 H, $J = 7.6, 1$ Hz), 6.78 (m, 1 H), 6.58 (q, 1 H, $J = 2.4$ Hz), 6.51 (d, 1 H, $J = 7.6$ Hz), 6.42 (q, 1 H, $J = 2.8$ Hz) 3.13 (s, 3 H); ^{13}C NMR (C_6D_6 , 100 MHz) δ 154.7, 129.7, 126.5, 126.2, 121.6, 121.4, 117.7, 111.6, 109.0, 106.7, 54.7; Anal. Calcd for $\text{C}_{11}\text{H}_{11}\text{NO}$: C, 76.28; H, 6.40; N, 8.09. Found: C, 76.06; H, 6.67; N, 8.38.

Pyrrole **10c** was isolated as a white solid (100.4 mg, 93% yield). ^1H NMR (C_6D_6 , 400 MHz) δ 7.50 (s, 1 H), 7.25 (d, 1 H, $J = 8$ Hz), 7.19 (d, 1 H, $J = 8$ Hz), 7.121 (bs, 1 H), 6.96 (t, 1 H, $J = 8$ Hz), 6.50 (t, 1 H, $J = 3.6$ Hz), 6.40 (q, 1 H, $J = 2.8$ Hz), 6.32 (q, 1 H, $J = 2.8$ Hz); ^{13}C NMR (C_6D_6 , 100 MHz) δ 133.8, 130.8 (q, $J = 32$ Hz), 130.0, 128.8, 127.0, 126.1, 123.4, 122.1 (q, $J = 4$ Hz), 119.8 (t, $J = 4$ Hz), 110.2, 107.4; Anal. Calcd for $\text{C}_{11}\text{H}_8\text{F}_3\text{N}$: C, 62.56; H, 3.82; N, 6.63. Found: C, 62.44; H, 3.94; N, 6.71.

Pyrrole **10d** was isolated as a white solid (38.3 mg, 87% yield). ^1H NMR (C_6D_6 , 400 MHz) δ 7.46 (d, 2 H, $J = 8.4$ Hz), 7.10 (bs, 1 H), 6.68 (d, 2 H, $J = 8.4$ Hz), 6.45 (m, 1 H), 6.37 (m, 1 H), 6.30 (q, 1 H, $J = 2.8$ Hz); ^{13}C NMR (C_6D_6 , 100 MHz) δ 137.6, 132.4, 130.4, 125.3, 110.1, 106.7, 106.6, 90.2; HRMS (EI) Calcd. For $[\text{C}_{10}\text{H}_8\text{NI}]$ 268.9702, Found 268.9701.

Pyrrole **12** was isolated as a white solid in 61 % yield
 ^1H NMR: (C_6D_6 , 300 MHz) δ 7.49 (bs, 1H), 7.02 (d, 1H, $J = 1.5$ Hz), 6.54 (t, 1H, $J = 3.6$ Hz), 6.24 (m, 2H), 6.14, (dd, 1H, $J = 3.3, 1.8$ Hz), 6.07 (d, 1H, $J = 3.3$ Hz); ^{13}C NMR: (CDCl_3 , 75 MHz) 148.30, 140.30, 124.01, 118.09, 111.42, 109.73, 105.29, 102.20. HRMS (EI) Calcd. For $[\text{C}_8\text{H}_7\text{NO}]$ 133.0528, Found 133.0528.

Pyrrole **14** was isolated as a white solid (20.1 mg, 41% yield) and decomposed within hours in solution. Azide **13** was recovered in 27% yield (15.2 mg).

^1H NMR (C_6D_6 , 400 MHz) δ 7.18 (m, 2 H), 7.10 (m, 3 H), 6.85 (s, 1 H), 6.35 (t, 2 H, $J = 2.4$ Hz), 6.24 (m, 1 H), 5.77 (m, 1 H), 5.00 (m, 2 H), 3.77 (t, 1 H, $J = 7.6$ Hz), 2.77 (quintet, 1 H, $J = 6.8$ Hz), 2.60 (quintet, 1 H, $J = 6.8$ Hz); ^{13}C NMR (C_6D_6 , 100 MHz) δ 143.8, 136.7, 133.8, 128.4, 128.2, 126.4, 116.8, 116.1, 108.0, 105.7, 44.8, 40.1.

Pyrrole **17a** was isolated as a white solid (21.5 mg, 80% yield).

^1H NMR (C_6D_6 , 500 MHz) δ 7.20 (m, 5 H), 6.97 (m, 1 H), 6.10 (s, 1 H), 2.72 (t, 2 H, $J = 7$ Hz), 2.62 (t, 2 H, $J = 7$ Hz), 2.21 (m, 4 H); ^{13}C NMR (C_6D_6 , 125 MHz) δ 133.8, 131.6, 128.61, 128.58, 124.7, 123.3, 122.5, 31.6, 26.3, 24.8; HRMS (EI) Calcd. For $[\text{C}_{13}\text{H}_{13}\text{N}]$ 183.1048, Found 183.1048.

Pyrrole **17b** was isolated as a white solid (13.7 mg, 84% yield).

^1H NMR (C_6D_6 , 400 MHz) δ 7.73 (s, 1 H), 7.25 (m, 8 H), 7.06 (m, 2 H), 2.73 (m, 4 H), 1.63 (m, 4 H); ^{13}C NMR (C_6D_6 , 100 MHz) δ 133.8, 128.6, 126.7, 125.4, 119.6, 24.0, 23.8; HRMS (EI) Calcd. For $[\text{C}_{20}\text{H}_{19}\text{N}]$ 273.1518, Found 273.1519.

To a 20 mL vial with a threaded cap containing a magnetic stir bar was added AgSbF_6 (9.4 mg, 0.1 equiv.). A solution of azide **18** (103 mg, 0.27 mmol, 1 equiv.) in nitromethane (5.5 mL, 0.05 M) was added to the vial. The resulting suspension was stirred at room temperature, and $(\text{dppm})(\text{AuCl})_2$ (11.6 mg, 0.05 equiv.) was added. Subsequently, evolution of gas was observed from the reaction mixture. After 30 minutes, TLC indicated full consumption of starting material. The reaction mixture was then cooled to room temperature and filtered through neutral alumina with excess CH_2Cl_2 . The filtrate was then concentrated and chromatographed on neutral alumina to afford **19** (55 mg, 58% yield) as an impure pink solid which decomposed within minutes in solution at both room temperature and at 0 °C in the dark. ^1H NMR (C_6D_6 , 400 MHz) δ 7.76 (dd, 2 H, $J = 8, 1.2$ Hz), 7.55 (dd, 2 H, $J = 8.8, 1.2$ Hz), 7.0-7.35 (m, 7 H), 6.39 (d, 1 H, $J = 3.6$ Hz), 1.03 (s, 9 H), -0.32 (s, 6 H); ^{13}C NMR (C_6D_6 , 100 MHz) δ 137.0, 136.0, 133.4, 130.0, 129.0, 128.7, 126.7, 125.9, 119.9, 119.6, 114.5, 26.2, 18.2, -4.6.

References:

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