SUPPORTING INFORMATION

Sequential Amination/ Annulation/ Aromatization Reaction of Carbonyl Compounds and Propargylamine: a New One-Pot Approach to Functionalized Pyridines.

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General considerations: Melting points were uncorrected. ^1H -NMR (200 MHz) and ^{13}C -NMR (50.3 MHz) spectra (CDCl_3 , unless otherwise stated; TMS as internal standard) were recorded. EI (70eV) mass spectra were recorded in machines equipped with an orthogonal ESI source. IR spectra were recorded. Only the most significant IR absorptions are given. Unless otherwise stated, all starting materials, catalysts, and solvents were commercially available and were used as purchased. Reaction products were purified by flash chromatography on silica gel by elution with *n*-hexane/EtOAc mixtures.

6-Phenyl-5,6,7,8-tetrahydroquinoline (4b). ^1H NMR (200 MHz, CDCl_3): 1.99-2.15 (m, 2H), 2.92-3.10 (m, 5H), 7.01 (dd, $J = 7.5$ and 4.8 Hz, 1H), 7.14-7.36 (m, 6H), 8.37 (d, $J = 4.8$ Hz, 1H). ^{13}C NMR (50, 3 MHz, CDCl_3): 30.0, 32.5, 36.7, 40.0, 120.9, 126.3, 126.7, 128.5, 131.5, 136.7, 145.5, 146.8, 156.4. IR (neat): 1540, 750, 690 cm^{-1} . MS (EI) m/z : 210 $[(M+1)^+, 100]$. Anal. Calcd. for $\text{C}_{15}\text{H}_{15}\text{N}$: C, 86.08; H, 7.22; N, 6.69. Found C, 86.05; H, 7.21; N, 6.68.

12-Methyl-6,12-diazatricyclo[7.2.0^{2,7}]dodeca-2(7),3,5-triene (4d). ^1H NMR (200 MHz, CDCl_3): 1.59-2.24 (m, 4H), 2.39 (s, 3H), 3.27-3.60 (m, 2H), 3.82-3.89 (m, 2H), 7.05 (dd, $J = 7.6$ and 4.9 Hz, 1H), 7.28 (dd, $J = 7.6$ and 1.7 Hz, 1H), 8.38 (dd, $J = 4.9$ and 1.7 Hz, 1H). ^{13}C NMR (50, 3 MHz, CDCl_3): 29.2, 34.5, 36.6, 36.8, 58.4, 63.2, 121.3, 127.1, 133.8, 147.7, 153.9. IR (KBr): 1600 cm^{-1} . MS (EI) m/z : 174 (M^+ , 25), 146 (100). Anal. Calcd. for $\text{C}_{11}\text{H}_{14}\text{N}_2$: C, 75.82; H, 8.10; N, 16.08. Found C, 75.80; H, 8.13; N, 16.09.

5-Androsten-3-ol[17,16-*b*]pyridine (4h). ^1H NMR (200 MHz, CDCl_3): 1.00 (s, 3H), 1.19 (s, 3H), 1.55-2.72 (m, 18H), 3.52-3.55 (m, 1H), 5.39 (d, $J = 5.1$ Hz, 1H), 7.02 (dd, $J = 4.7$ and 7.5 Hz, 1H), 7.50 (d, $J = 7.5$ Hz, 1H), 8.32 (d, $J = 4.7$ Hz, 1H). ^{13}C NMR (50, 3 MHz, CDCl_3): 16.8, 19.0, 20.2, 30.0, 30.4, 30.9, 31.2, 33.1, 36.2, 36.8, 41.9, 45.1, 50.2, 55.5, 71.1, 120.5, 120.7, 132.5, 136.1,

141.0, 146.2, 172.3. IR (neat): 3420 cm^{-1} . MS (ESI) m/z : 324 $[(M+1)^+, 100]$. Anal. Calcd. for $\text{C}_{22}\text{H}_{29}\text{NO}$: C, 81.69; H, 9.04; N, 4.33. Found C, 81.41; H, 9.05; N, 4.37.

Cholesta-3,5-dien[3,4-*b*]pyridine (4j). ^1H NMR (200 MHz, CDCl_3): 0.68 (s, 3 H), 0.72 (s, 3H), 0.85 (s, 3H), 0.88 (s, 3H), 0.95 (s, 3H), 1.11-2.10 (m, 24H), 2.98-3.01 (m, 2H), 6.15 (m, 1H), 7.08 (dd, $J = 7.8$ and 3.9 Hz, 1H), 7.79 (d, $J = 7.8$ Hz, 1H), 8.35 (d, $J = 3.9$ Hz, 1H) ^{13}C NMR (50, 3 MHz, CDCl_3): 11.9, 18.4, 18.7, 21.2, 21.5, 22.5, 22.8, 24.2, 27.9, 28.2, 28.4, 28.6, 29.6, 31.3, 31.4, 33.9, 34.3, 39.4, 39.7, 49.0, 56.3, 56.6, 121.4, 122.5, 132.8, 139.2, 146.7, 154.4, 174.4. IR (KBr): 1590 cm^{-1} . MS (ESI) m/z : 420 $[(M+1)^+, 100]$. Anal. Calcd. for $\text{C}_{30}\text{H}_{45}\text{N}$: C, 85.86; H, 10.81; N, 3.34; Found C, 85.84; H, 10.79; N, 3.37.

5-Pregnen-20-oxo[3,4-*b*]pyridine (4k). ^1H NMR (200 MHz, CDCl_3): 0.67 (s, 3H), 0.97 (s, 3H), 1.24-2.04 (m, 13H), 2.13 (s, 3H), 2.20-2.61 (m, 4H), 2.97-3.04 (m, 1H), 6.13-6.17 (m, 1H), 7.08 (dd, $J = 7.9$ and 4.7 Hz, 1H), 7.78 (dd, $J = 7.9$ and 1.4 Hz, 1H), 8.37 (d, $J = 4.7$ Hz, 1H). ^{13}C NMR (50, 3 MHz, CDCl_3): 13.2, 18.4, 21.2, 22.7, 23.0, 23.6, 28.8, 31.4, 32.4, 34.0, 35.5, 38.7, 43.9, 48.8, 56.5, 63.5, 121.3, 121.9, 132.4, 139.4, 145.9, 147.4, 154.6, 209.3. IR (neat): 1710 cm^{-1} . MS (ESI) m/z : 350 $[(M+1)^+, 100]$. Anal. Calcd. for $\text{C}_{24}\text{H}_{31}\text{NO}$: C, 82.47; H, 8.94; N, 4.01. Found C, 82.40; H, 8.91; N, 4.07.

6a-Methyl-5,6a,8,9-tetrahydro-5H-benzo[*f*]quinolin-7-one (4l). ^1H NMR (200 MHz, CDCl_3): 1.24 (s, 3H), 2.10-2.44 (m, 2H), 2.63-2.78 (m, 4H), 3.04-3.11 (m, 2H), 6.32 (t, $J = 4.3$ Hz, 1H), 7.13 (dd, $J = 4.8$ and 8.0 Hz, 1H), 7.84 (dd, $J = 1.6$ and 8.0 Hz, 1H), 8.42 (dd, $J = 1.5$ and 4.8 Hz, 1H). ^{13}C NMR (50, 3 MHz, CDCl_3): 21.6, 21.8, 25.3, 28.3, 29.2, 34.9, 37.6, 121.6, 123.5, 132.5, 137.2, 148.3, 154.5, 213.9. IR (neat): 1720 cm^{-1} . MS (EI) m/z : 213 (M^+ , 100), 156 (51). Anal. Calcd. for $\text{C}_{14}\text{H}_{15}\text{NO}$: C, 78.84; H, 7.09; N, 6.57. Found C, 78.86; H, 7.05; N, 6.54.

10-Fluoro-6,7-dihydro-5H-benzo[6,7]cyclohepta[1,2-*b*]pyridine (4m). ¹HNMR (200 MHz, CDCl₃): 2.21 (q, J = 6.4 Hz, 2H), 2.49 (t, J = 6.4 Hz, 4H), 6.98-7.07 (m, 1H), 7.15-7.27 (m, 2H), 7.45 (dd, J = 9.5 and 2.7 Hz, 1H), 7.55 (dd, J = 7.6 and 1.7 Hz, 1H), 8.59 (dd, J = 4.8 and 1.7 Hz, 1H). ¹³C NMR (50, 3 MHz, CDCl₃): 30.1, 30.2, 32.9, 115.2 (d, J_{C-F} = 21.0 Hz), 116.4 (d, J_{C-F} = 26.8 Hz), 122.4, 129.8 (d, J = 7.9 Hz), 135.1 147.7, 161.9 (d, J_{C-F} = 243.9 Hz). IR (neat): 1610, 1590, 680 cm⁻¹. MS (EI) *m/z*: 213 (M⁺, 100). Anal. Calcd. for C₁₄H₁₂FN: C, 78.85; H, 5.67; F, 8.91; N, 6.57. Found C, 78.80; H, 5.64; N, 6.59.

4b

P81/F2

4k

P83 F2