Supporting information

Formation of Aromatic Rings Through Enamine Annulation

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Experimental Section

^{1}H and ^{13}C NMR spectra were recorded on a General Electric QE-300 spectrometer or as indicated. Mass spectral (MS) data were obtained by Dr. Mehdi Moini at the University of Texas at Austin. The low-resolution MS studies were run on a Finnegan TSQ-70 triple quadrupole mass spectrometer, and the high-resolution MS studies were conducted on a Micromass ZAB-E mass spectrometer. FT-IR spectra were run on a Mattson Galaxy Series FT-IR 5000 spectrometer.

General procedure for the reaction of enamines with 8.

To dry benzene (20 mL) under N_2 were added the ketone (1~ 2 mmol), pyrrolidine (2 equiv), and *p*-toluenesulfonic acid (PTSA, 5 mg). The solution was heated at reflux (6 h) using a modified Dean-Stark apparatus containing 3Å molecule sieves. For ketones in entries 7 and 8 (Table 1), 10 mmol of pyrrolidine was used and the reaction time was 30 h. After evaporation of benzene and excess pyrrolidine *in vacuo*, the crude enamines were dissolved in an anhydrous benzene solution (2 mL) containing **8** (1.5 equiv) and the reaction was stirred at room temperature (18 h). Final products were isolated by preparative TLC.

6-(1-Pyrrolidino)-1,2,3,4-tetrahydronaphthalene (7), 1-acetoxy-4,4a,5,6,7,8-hexahydro-2(3*H*)-naphthalenone (9), and 1-acetoxy-1,4,5,6,7,8-hexahydro-2(3*H*)-naphthalenone (10). Using the general procedure with cyclohexanone (210 μL, 2 mmol), pyrrolidine (330 μL, 4 mmol), PTSA (5

mg), and **8** (564 mg, 3 mmol), compound **7** (165 mg, 41%) and the binary mixture of **9** and **10** (30 mg, ~7%) were obtained, respectively.

Compound **7**: R_f 0.90 (hexanes/EtOAc = 10/1); IR (neat) 2960, 2833, 1615, 1515, 1370, 817, 792 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.77-1.82 (m, 4 H), 1.97-2.02 (m, 4 H), 2.68-2.72 (m, 2 H), 2.75-2.78 (m, 2 H), 3.25-3.29 (m, 4 H), 6.31 (d, J = 2.4 Hz, 1 H), 6.41 (dd, J = 2.4, 8.1 Hz, 1 H), 6.95 (d, J = 8.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$) 23.6, 23.8, 25.4 (2), 28.5, 29.9, 47.8 (2), 110.0, 111.9, 124.2, 129.7, 137.6, 146.3 ppm; MS (EI) m/z (rel intensity) 201 (M^+, 100), 172 (13), 158 (5), 145 (20), 131 (6), 115 (5), 91 (6), 77 (5); M_r (EI) 201.151 83 $[M]^+$ (calcd for $C_{14}H_{19}N$ 201.151 75).

Compound **9** (major isomer): R_f 0.20 (hexanes/EtOAc = 10/1); ^1H NMR ($CDCl_3$) δ 1.20-2.80 (m, 13 H), 2.24 (s, 3 H); ^{13}C NMR ($CDCl_3$) 20.3, 25.1, 25.8, 27.4, 28.5, 34.3, 36.1, 37.8, 139.7, 151.8, 168.7, 191.4 ppm; MS (EI) m/z (rel intensity) 209 $[(M+1)^+, 64]$, 184 (20), 166 (100), 137 (23), 124 (42), 95 (14); M_r (EI) m/z (rel intensity) 209.117 31 $[M+1]^+$ (calcd for $C_{12}H_{17}O_3$ 209.117 77). Compound **10** was isolated along with **9**. Only the following signals could be assigned for **10** from the spectra of the binary mixture of **9** and **10**: ^1H NMR ($CDCl_3$) δ 2.09 (s, 3 H), 4.55 (s, 1 H); ^{13}C NMR ($CDCl_3$) 20.1, 80.5, 206.4 ppm.

3-Ethyl-4-methyl-(1-pyrrolidino)benzene (16). Using the general procedure with 3-pentanone (110 μL, 1 mmol), pyrrolidine (165 μL, 2 mmol), PTSA (5 mg), and **8** (282 mg, 1.5 mmol), compound **16** (65 mg, 34%) was obtained as a clear oil: R_f 0.82 (hexanes/EtOAc = 10/1); IR (neat) 2966, 2812, 1616, 1511, 1366 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.21 (t, J = 7.5 Hz, 3 H), 1.96-2.00 (m, 4 H), 2.21 (s, 3 H), 2.59 (q, J = 7.5 Hz, 2 H), 3.24-3.29 (m, 4 H), 6.36 (dd, J = 1.5, 8.4 Hz, 1 H), 6.42 (d, J = 1.5 Hz, 1 H), 6.99 (d, J = 8.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) 14.7,

18.1, 25.4 (2), 26.9, 47.8 (2), 109.4, 111.8, 122.5, 130.7, 143.0, 146.8 ppm; MS (EI) m/z (rel intensity) 189 (M^+, 100), 133 (25); M_r (EI) 189.151 90 $[M]^+$ (calcd for $C_{13}H_{19}N$ 189.151 75).

2,3-Dihydro-5-(1-pyrrolidino)indene (19). Using the general procedure with cyclopentanone (177 μL, 2 mmol), pyrrolidine (330 μL, 4 mmol), PTSA (5 mg), and **8** (564 mg, 3 mmol), compound **19** (105 mg, 28%) was obtained as a clear oil: R_f 0.95 (hexanes/EtOAc = 10/1); IR (neat) 2951, 2886, 2843, 1615, 1505, 1367, 828, 794 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.10-2.14 (m, 4 H), 2.21-2.25 (m, 2 H), 2.95-3.05 (m, 4 H), 3.38-3.41 (m, 4 H), 6.54 (dd, J = 2.1, 8.1 Hz, 1 H), 6.65 (d, J = 2.1 Hz, 1 H), 7.24 (d, J = 8.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$) 25.5, 25.6 (2), 32.1, 32.5, 48.2 (2), 108.0, 110.2, 124.8, 131.1, 145.4, 147.4 ppm; MS (EI) m/z (rel intensity) 187 (M^+, 100), 170 (3), 158 (6), 144 (10), 131 (25), 115 (15), 91 (5), 77 (4); M_r (EI) 187.135 73 $[M]^+$ (calcd for $C_{13}H_{17}N$ 187.136 10).

2-Methyl-6-(1-pyrrolidino)-1,2,3,4-tetrahydronaphthalene (22). Using the general procedure with 4-methylcyclohexanone (124 μL, 1 mmol), pyrrolidine (165 μL, 2 mmol), PTSA (5 mg), and **8** (282 mg, 1.5 mmol), compound **22** (130 mg, 60%) was obtained as a clear oil: R_f 0.90 (hexanes/EtOAc = 10/1); IR (neat) 2948, 2906, 2832, 1614, 1514, 1368 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.12 (d, J = 6.3 Hz, 3 H), 1.41-1.47 (m, 1 H), 1.85-1.95 (m, 2 H), 2.02-2.07 (m, 4 H), 2.38 (dd, J = 10.5, 15.9 Hz, 1 H), 2.88 (dd, J = 5.1, 15.9 Hz, 1 H), 2.82-2.87 (m, 2 H), 3.29-3.34 (m, 4 H), 6.39 (d, J = 2.4 Hz, 1 H), 6.47 (dd, J = 2.4, 8.4 Hz, 1 H), 7.00 (d, J = 8.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) 22.2, 25.5 (2), 29.9 (2, overlap), 31.9, 37.4, 47.9 (2), 110.1, 111.7, 124.1, 129.7, 137.2, 146.4 ppm; MS (EI) m/z (rel intensity) 215 (M^+, 100), 173 (42), 159 (8), 115 (10), 84 (14); M_r (EI) 215.166 94 $[M]^+$ (calcd for $C_{15}H_{21}N$ 215.167 40).

1-Methyl-7-(1-pyrrolidino)-1,2,3,4-tetrahydronaphthalene (25). Using the general procedure with 2-methylcyclohexanone (124 μL, 1 mmol), pyrrolidine (165 μL, 2 mmol), PTSA (5 mg), and **8** (282 mg, 1.5 mmol), compound **25** (100 mg, 47%) was obtained as a clear oil: R_f 0.90 (hexanes/EtOAc = 10/1); IR (neat) 2948, 2906, 2832, 1614, 1514, 1368 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.12 (d, J = 6.3 Hz, 3 H), 1.50-1.61 (m, 1 H), 1.64-1.75 (m, 2 H), 1.88-1.95 (m, 1 H), 1.98-2.08 (m, 4 H), 2.68-2.72 (m, 2 H), 2.88-2.95 (m, 1 H), 3.21-3.32 (m, 4 H), 6.41-6.45 (m, 2 H), 6.96 (d, J = 8.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) 20.8, 23.1, 25.4 (2), 29.1, 31.8, 32.9, 47.9 (2), 110.1, 111.1, 124.0, 129.6, 142.7, 146.4 ppm; MS (EI) m/z (rel intensity) 215 (M^+, 100), 186 (10), 159 (7), 115 (8), 84 (16); M_r (EI) 215.166 94 $[M]^+$ (calcd for $C_{15}H_{21}N$ 215.167 40).

6-(1-Pyrrolidino)-2-oxa-1,2,3,4-tetrahydronaphthalene (28). Using the general procedure with tetrahydro-4(4*H*)-pyranone (92 μL, 1 mmol), pyrrolidine (165 μL,1 mmol), PTSA (5 mg), and **8** (282 mg, 1.5 mmol), compound **28** (86 mg, 42%) was obtained as a clear oil: R_f 0.50 (hexanes/EtOAc = 10/1); IR (neat) 2958, 2921, 2843, 1618, 1516, 1374, 1101 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.99-2.03 (m, 4 H), 2.85 (t, J = 5.7 Hz, 2 H), 3.26-3.31 (m, 4 H), 3.98 (t, J = 5.7 Hz, 2 H), 4.74 (s, 2 H), 6.34 (br s, 1 H), 6.46 (br d, J = 8.4 Hz, 1 H), 6.87 (d, J = 8.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) 25.4 (2), 28.9, 47.8 (2), 65.6, 67.9, 110.3, 111.4, 121.9, 125.1, 133.8, 146.7 ppm; MS (EI) m/z (rel intensity) 203 (M^+, 100), 173 (24); M_r (EI) 203.126 81 $[M]^+$ (calcd for $C_{13}H_{17}NO$ 203.126 54).

6-(1-Pyrrolidino)-1,2,3,4-tetrahydro-2-thianaphthalene (31). Using the general procedure with tetrahydrothiopyran-4-one (116 mg, 1 mmol), pyrrolidine (165 μL, 2 mmol), PTSA (5 mg), and **8** (282 mg, 1.5 mmol), compound **31** (90 mg, 41%) was obtained as a clear oil: R_f 0.55 (hexanes/EtOAc = 10/1); IR (neat) 2954, 2832, 1612, 1511, 1375, 1187 cm^{-1}; ^1H

NMR ($CDCl_3$) δ 1.99-2.03 (m, 4 H), 2.09 (t, J = 5.7 Hz, 2 H), 3.00 (t, J = 5.7 Hz, 2 H), 3.27-3.31 (m, 4 H), 3.73 (s, 2 H), 6.38 (d, J = 2.4 Hz, 1 H), 6.42 (dd, J = 2.4, 8.4 Hz, 1 H), 6.99 (d, J = 8.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) 25.5 (2), 26.6, 28.6, 31.2, 47.7 (2), 109.9, 112.1, 122.0, 128.4, 137.5, 147.1 ppm; MS (EI) m/z (rel intensity) 219 (M^+, 100), 191 (15), 184 (18), 173 (32), 115 (16); M_r (EI) 219.108 22 $[M]^+$ (calcd for $C_{13}H_{17}NS$ 219.108 19).

9,10-Dihydro-3-(1-pyrrolidino)phenanthrene (34). Using the general procedure with α-tetralone (140 μL, 1 mmol), pyrrolidine (0.83 mL, 10 mmol), PTSA (5 mg), and **8** (282 mg, 1.5 mmol), compound **34** (162 mg, 65%) was obtained as a clear oil: R_f 0.70 (hexanes/EtOAc = 5/1); IR (neat) 2966, 2930, 2831, 1615, 1508, 1371, 764 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.04-2.09 (m, 4 H), 2.81-2.85 (m, 2 H), 2.90-2.92 (m, 2 H), 3.37-3.42 (m, 4 H), 6.55 (dd, J = 2.4, 8.1 Hz, 1 H), 7.03 (d, J = 2.1, Hz, 1 H), 7.16 (d, J = 8.1 Hz, 1 H), 7.23-7.28 (m, 3 H), 7.81 (d, J = 7.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) 25.5 (2), 28.1, 29.8, 47.9 (2), 107.0, 111.2, 123.7, 124.8, 126.7, 127.1, 128.1, 128.7, 134.9, 135.3, 138.0, 147.4 ppm; MS (EI) m/z (rel intensity) 249 (M^+, 100), 78 (30); M_r (EI) 249.151 03 $[M]^+$ (calcd for $C_{18}H_{19}N$ 249.151 75).

***trans*-1,2,3,4,4a,9,10,10a-Octahydro-6-(1-pyrrolidino)phenanthrene (37).** Using the general procedure with *trans*-1-decalone (154 μL, 1 mmol), pyrrolidine (0.83 mL, 10 mmol), PTSA (5 mg), and **8** (282 mg, 1.5 mmol), compound **37** (90 mg, 35%) was obtained as a clear oil: R_f 0.75 (hexanes/EtOAc = 10/1); IR (neat) 2921, 2853, 1614, 1510, 1367 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.25-1.80 (m, 11 H), 1.95-2.01 (m, 4 H), 2.66-2.75 (m, 3 H), 3.23-3.28 (m, 4 H), 6.33 (d, J = 2.1 Hz, 1 H), 6.41 (d, J = 2.1, 8.4 Hz, 1 H), 6.94 (d, J = 8.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) 21.5, 24.2, 25.4 (2), 26.5, 28.8, 31.7, 32.0, 34.1, 40.9 (2, overlap), 47.9 (2), 91.9, 110.2, 111.6,

123.2, 129.5 ppm; MS (EI) m/z (rel intensity) 255 (M^+, 100), 227 (2), 173 (4), 128 (2), 84 (7); M_r (EI) 255.199 12 $[M]^+$ (calcd for $C_{18}H_{25}N$ 255.198 70).