Supporting Information
for DOI: 10.1055/s-0029-1217338
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A Ring Rearrangement Approach to the Synthesis of Benzo[b]quinolizine and Benzoindolizine Architectures.

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All non-aqueous reactions were carried out under an atmosphere of nitrogen using flame- or oven-dried glassware. Unless otherwise noted, starting materials and reagents were obtained from commercial suppliers and were used without further purification. CH₂Cl₂ was distilled from calcium hydride. Flash column chromatography was carried out on Merck Kieselgel 60 (Merck 9385) under positive pressure by means of an air line or hand pump. TLC was performed on Merck 60F254 (0.25 mm) glass silica plates and visualised by ultraviolet (UV) light and/or KMnO₄ stain. IR spectra were measured on a Biorad FTS-7 or Perkin-Elmer Paragon 1000 FT-IR spectrometer as thin films unless otherwise stated. ¹H and ¹³C NMR spectra were recorded on a Bruker AC250 or Bruker DPX360 instrument. J values are in Hz. Electrospray (ESI) mass spectra were obtained using a Thermo MAT 900 XP mass spectrometer, and fast atom bombardment (FAB) mass spectra were obtained using a Kratos MS50TC mass spectrometer both at The University of Edinburgh. High performance liquid chromatography (HPLC) was carried out using a Gilson instrument fitted with a refractive index detector, using a microsorb 100-5 Si column (length 250 mm, id 21.4 mm, particle size 5 µm). All HPLC samples were filtered through 0.45 µm nylon syringe filters prior to analysis. A standard flow rate of 10.0 ml min⁻¹ was used. All solvents used for HPLC were filtered prior to use.

(2-Bromo-benzyl)-cyclohex-3-enyl-prop-2-ynyl-amine 3 (P = CH=CH)

To a suspension of N-(2-bromobenzyl)-cyclohex-2-enyl-amine hydrochloride d (100 mg, 0.33 mmol) in DMF (5 ml) at r.t. was added K₂CO₃ (137 mg, 1.00 mmol) and the reaction stirred for 10 mins. Propargyl bromide (148 µl, 80 % by w/w, in toluene, 1.66 mmol) was added dropwise and the reaction stirred for 16 h. The reaction was diluted with Et₂O (20 ml) and washed with NaCl (3 x 20 ml, sat. aq.), and the combined organics were dried (MgSO₄) and concentrated under reduced pressure. The resultant oil was purified using flash chromatography (hexane:EtOAc, 100:15) to afford propargyl amine 3 (P = CH₂C=CH) as a colourless oil (103 mg, 99%).

υmax (CHCl₃)/cm⁻¹ 3299(C=CH-H), 2931, 1439, 1025; ¹H NMR δ (250 MHz, CDCl₃) 7.59 (1H, d, J 7.6, ArH), 7.56 (1H, dd, J 7.9, 1.2, ArH), 7.29 (1H, td, J 7.4, 1.2, ArH), 7.10 (1H, td, J 7.8, 1.4, ArH), 5.89-5.76 (2H, m, CH=CH), 3.91 (1H, d, J 15.0, CH₃H₂Ar), 3.82 (1H, d, J 15.0, CH₂H₃Ar), 3.56-3.53 (1H, m, CHN), 3.38 (2H, d, J 2.4, CH₂C=CH), 2.23 (1H, t, J 2.4, =CH), 2.03-1.84 (4H, m, 2xCH₂), 1.69-1.44 (2H, m, CH₂); ¹³C NMR δ (62.9 MHz, CDCl₃) 138.7 (C), 132.5 (CH), 130.6 (CH), 129.7 (CH), 128.1 (C), 127.1 (CH), 124.2 (C), 81.4 (C), 72.2 (CH), 57.6 (CH), 52.9 (CH₃), 39.3 (CH₂), 25.2 (CH₂), 24.8 (CH₂), 21.2 (CH₂); m/z (EI) 305 ([79BrM⁺], 19 %), 303 ([79BrM⁺], 19), 277 (64), 275 (65), 251 (33), 249 (35), 213 (42), 171 (97), 169 (100), 106 (85); HRMS (EI) Found: [79BrM⁺], 303.0618. C₁₀H₁₀N⁺Br requires 303.0617.

(4aSR,10bSR)-4,4a,6,10b-Tetrahydro-3H-phenanthridine-5-carboxylic acid tert-butyl ester 4a (Δ1,2 isomer) d

R, [hexane:EtOAc, 92:8] 17 min; υmax (CHCl₃)/cm⁻¹ 3026, 1693 (C=O), 1258, 913, 745; ¹H NMR δ (360 MHz, 323 K, CDCl₃) 7.30 (1H, d, J 7.5, ArH), 7.25-7.17 (2H, m, 2xArH), 7.12 (1H, d, J 7.2, ArH), 6.17-6.13 (1H, m, CHCH=CH), 5.87-5.83 (1H, m, CH=CHCH₂), 4.71 (1H, d, J 16.5, CH₃H₂Ar), 4.41 (1H, br s, NCHCH), 4.39 (1H, d, J 16.5, CH₂H₃Ar), 3.57 (1H, br s, NCHCH), 2.31-2.27 (1H, m, CH₃H₂), 2.15-2.05 (1H, m, CH₃H₂), 1.79-1.69 (1H, m, CH₂H₂), 1.61-1.40 (10H, m, 3 x
CH3+CH2-HO; 13C NMR δ (90.0 MHz, 323 K, CDCl3) 155.0 (C), 137.8 (C), 132.5 (C), 128.3 (CH), 128.1 (C), 127.6 (CH), 127.3 (CH), 126.8 (CH), 126.1 (CH), 125.9 (CH), 79.6 (C), 43.5 (CH2), 37.3 (CH), 28.5 (3xCH3), 25.3 (CH2), 24.2 (CH2); m/z (FAB, THIOG) 284 ([M-H]+, 44%), 228 (66), 184 (49), 130 (25); HRMS (FAB, THIOG) Found: [M-H]+ 284.1643. C13H22NO2 requires 284.1650.

(4aSR,10bSR)-4,4a,6,10b-Tetrahydro-1H-phenanthridine-5-carboxylic acid tert-butyl ester 4b (A3,3 isomer)4
Rf [hexane:EtOAc, 92:8] 16 min; v
max (CHCl3)/cm-1 3352, 1699 (C=O), 1392, 1367, 1167; 1H NMR δ (250 MHz, CDCl3) 7.24-7.16 (4H, m, 4xArH), 5.70-5.66 (1H, m, CH2CH2=), 5.45-5.37 (1H, m, NCHCH2CH=), 4.68-4.66 (3H, m, CH2Ar+NCH2CH2), 3.32-3.18 (1H, m, CHCH2), 2.86 (1H, dd, J 18.0, 4.5, CH2H6), 2.67-2.54 (1H, m, CH3H8), 2.28-2.16 (1H, m, CH2H6), 1.65-1.52 (10H, m, 3xCH3+CH2H2); 13C NMR δ (62.9 MHz, CDCl3) 154.8 (C), 136.4 (C), 133.9 (C), 126.6 (CH), 126.4 (CH), 126.1 (CH), 125.4 (CH), 124.8 (CH), 123.7 (CH), 79.6 (C), 50.3 (CH), 44.6 (CH2), 35.5 (CH), 28.5 (3xCH3), 26.2 (CH2); m/z (EI) 285 ([M]+, 2%), 231 (32), 175 (100), 130 (22); HRMS (EI) Found: [M]+ 285.1726. C13H22NO2 requires 285.1723.

(4aSR,10bSR)-2,4a,6,10b-Tetrahydro-1H-phenanthridine-5-carboxylic acid tert-butyl ester 4c (A3,4 isomer)4
Rf [hexane:EtOAc, 92:8] 16 min; v
max (CHCl3)/cm-1 3359, 1695 (C=O), 1400, 1367; 1H NMR δ (250 MHz, CDCl3) 7.37 (1H, d, J 7.5, ArH), 7.26-7.13 (2H, m, 2xArH), 7.07 (1H, d, J 7.0, ArH), 5.72-5.65 (1H, m, CH2CH=CH), 5.52 (1H, d, J 11.0, CH=CHCH), 5.08 (1H, br s, NCH), 4.86 (1H, d, J 17.0, CH2CH2Ar), 4.24 (1H, d, J 17.0, CH2H2Ar), 3.30 (1H, br s, CH2CH2), 2.45-2.37 (1H, m, CH2CH2), 2.08-1.94 (1H, m, CH2H8), 1.95-1.81 (2H, m, CH2), 1.50 (9H, s, 3xCH3); 13C NMR δ (62.9 MHz, CDCl3) 154.8 (C), 135.1 (C), 133.9 (C), 130.8 (CH), 127.6 (CH), 126.5 (2xCH2), 125.8 (CH), 125.6 (CH), 79.8 (C), 50.0 (CH), 42.6 (CH2), 34.5 (CH), 28.4 (3xCH3), 25.0 (CH2), 20.2 (CH2); m/z (EI) 285 ([M]+, 2%), 229 (77), 228 (100), 184 (32), 175 (48); HRMS (EI) Found: [M]+ 285.1720. C13H22NO2 requires 285.1723.

(4aSR,10bSR)-3,4,4a,5,6,10b-Hexahydro-phenanthridine 9a
Flash vacuum pyrolysis of Boc-protected Δ2,3 isomer phenanthridine 4a [500 mg, T1 600 °C, T2 140 °C, P 3.2 x 10-2 Torr, t 0.5 h], followed by Kugelrohr distillation (70 °C, 0.7 Torr) afforded amine 9a as a yellow oil (193 mg, 60%).

v
max (CHCl3)/cm-1 3274 (NH), 3019, 2920, 1671 (C=C), 1449, 1260 (CN); 1H NMR δ (360 MHz, CDCl3) 7.22-7.21 (2H, m, 2xArH), 7.17-7.14 (1H, m, ArH), 7.03 (1H, d, J 7.5, ArH), 5.74-5.71 (1H, m, CH=CH), 5.66-5.62 (1H, m, CH=CH), 4.12 (1H, d, J 16.3, CH2H2Ar), 4.04 (1H, d, J 16.3, CH3H3Ar), 3.36 (1H, br s, NCHCH), 3.32-3.28 (1H, m, CH2), 2.25-2.03 (2H, m, CH2), 2.03-1.89 (2H, m, CH2); 13C NMR δ (90.6 MHz, CDCl3) 138.4 (C), 135.7 (C), 130.2 (CH), 129.1 (CH), 126.4 (CH), 125.8 (CH), 125.7 (2xCH2), 50.4 (CH), 48.3 (CH2), 38.0 (CH), 27.4 (CH2), 20.0 (CH2); m/z (EI) 185 ([M]+, 77%), 170 (21), 168 (18), 131 (38), 130 (72), 128 (46); HRMS (EI) Found: [M]+ 185.1196. C13H15N requires 185.1199.

(4aSR,10bSR)-1,4,4a,5,6,10b-Hexahydro-phenanthridine 9b
Flash vacuum pyrolysis of Boc-protected Δ2,3 isomer phenanthridine 4b [900 mg, T1 600 °C, T2 140 °C, P 3.2 x 10-2 Torr, t 0.5 h], followed by Kugelrohr distillation (70 °C, 0.7 Torr) afforded amine 9b as a yellow oil (500 mg, 81%).

v
max (CHCl3)/cm-1 3284 (NH), 3021, 2902, 1654 (C=C), 1453, 1260 (CN); 1H NMR δ (360 MHz, CDCl3) 7.17-7.13 (2H, m, 2xArH), 7.09-7.02 (2H, m, ArH), 5.73-5.66 (2H, m, CH=CH), 4.24 (1H, d, J 16.5, CH2H2Ar), 4.15 (1H, d, J 16.5, CH2H2Ar), 3.23 (1H, br d, J 4.0, NCHCH), 2.81 (1H, d, J 10.1, 6.4, 2.7, NCHCH), 2.65-2.59 (1H, m, CH2H8), 2.34-2.28 (1H, m, CH2H8), 2.15-2.10 (2H, m, CH2); 13C NMR δ (90.6 MHz, CDCl3) 141.0 (C), 134.2 (C), 128.2 (CH), 126.0 (CH), 125.9 (CH),
125.8 (CH), 124.7 (CH), 124.1 (CH), 49.9 (CH), 48.5 (CH$_2$), 35.3 (CH), 31.9 (CH$_2$), 30.1 (CH$_2$); $m/z$ (EI) 185 ([M]$^+$, 10 %), 130 (100); HRMS (EI) Found: [M]$^+$, 185.1202. C$_{13}$H$_{12}$N requires 185.1199.

\textbf{(4aSR,10bSR)-1,2,4a,5,6,10b-Hexahydro-phenanthridine 9c}

Flash vacuum pyrolysis of Boc-protected \( \Delta^{3,4} \) isomer phenanthridine 4c [320 mg, T$_f$ 600°C, T$_r$ 140°C, P 3.2 x 10$^{-2}$ Torr, t 0.5 h], followed by Kugelrohr distillation (70°C, 0.7 Torr) gave amine 9c as a yellow oil (190 mg, 71%).

\( v_{\text{max}} \) (CHCl$_3$)/cm$^{-1}$ 3283 (NH), 3020, 2902, 1654 (C=C), 1453, 1260 (CN); $^1$H NMR $\delta$ (360 MHz, CDCl$_3$) 7.23-7.13 (3H, m, 3xArH), 7.03 (1H, d, J 7.2, ArH), 5.96-5.85 (2H, m, CH=CH), 4.05 (1H, d, J 16.6, CH$_3$H$_2$Ar), 4.00 (1H, d, J 16.9, CH$_3$H$_2$Ar), 3.46 (1H, br s, NCHCH), 2.74 (1H, dt, J 12.6, 3.6, NCHCH), 2.22-1.62 (4H, m, 2xCH$_2$); $^{13}$C NMR $\delta$ (90.6 MHz, CDCl$_3$) 139.3 (C), 135.8 (C), 130.0 (CH), 129.2 (CH), 128.3 (C), 126.1 (CH), 125.7 (CH), 125.5 (CH), 50.7 (CH), 48.2 (CH$_2$), 36.5 (CH), 27.5 (CH$_2$), 25.8 (CH$_2$); $m/z$ (EI) 185 ([M]$^+$, 10 %), 130 (100); HRMS (EI) Found: [M]$^+$, 185.1202. C$_{13}$H$_{12}$N requires 185.1199.

\textbf{(4aSR,10bSR)-5-(Prop-2'-ynyl)-3,4,4a,5,6,10b-hexahydro-phenanthridine 5a}

To a solution of amine 9a (150 mg, 0.81 mmol) in acetonitrile (5 ml) was added K$_2$CO$_3$ (368 mg, 2.67 mmol), and propargyl bromide (100 µl, 80 % w/w in toluene, 0.89 mmol). The reaction was heated at 60°C for 2 h and then concentrated under reduced pressure. Flash chromatography (CH$_2$Cl$_2$) afforded propargyl amine 5a as a yellow oil (103 mg, 57%).

\( v_{\text{max}} \) (CHCl$_3$)/cm$^{-1}$ 3290 (C=C-H), 2925, 1696; $^1$H NMR $\delta$ (250 MHz, CDCl$_3$) 7.27-7.10 (3H, m, 3xArH), 7.10 (1H, d, J 7.2, ArH), 5.79 (2H, s, CH=CH), 4.01 (1H, d, J 15.0, CH$_2$H$_2$Ar), 3.83 (1H, dd, J 17.4, 2.4, CH$_3$H$_2$C=C=CH), 3.81 (1H, d, J 15.0, CH$_2$H$_2$Ar), 3.56 (1H, dd, J 17.4, 2.4, CH$_3$H$_2$C=C=CH), 3.56 (1H, br s, NCHCH), 3.16 (1H, br s, NCHCH), 2.28 (1H, t, J 2.4, =CH), 2.14-2.00 (3H, m, CH$_2$+CH$_2$H$_2$), 1.87-1.75 (1H, m, CH$_3$H$_2$); $^{13}$C NMR $\delta$ (62.9 MHz, CDCl$_3$) 137.3 (C), 133.8 (C), 129.8 (CH), 128.0 (CH), 126.5 (CH), 126.1 (CH), 125.6 (CH), 78.3 (C), 73.4 (CH), 53.8 (CH), 53.4 (CH$_2$), 42.3 (CH$_2$), 39.2 (CH$_2$), 23.2 (CH$_2$), 21.9 (CH$_2$); $m/z$ (EI) 223 ([M]$^+$, 59 %), 222 (100), 208 (16), 184 (17), 168 (36), 140 (34); HRMS (EI) Found: [M]$^+$, 223.1354. C$_{13}$H$_{12}N$ requires 223.1356.

\textbf{(4aSR,10bSR)-5-(Prop-2'-ynyl)-1,4,4a,5,6,10b-hexahydro-phenanthridine 5b}

To a solution of amine 9b (50 mg, 0.27 mmol) in acetonitrile (2 ml) was added K$_2$CO$_3$ (112 mg, 0.81 mmol) and propargyl bromide (33 µl, 80 % w/w in toluene, 0.30 mmol). The reaction was heated at 60°C for 2 h and then concentrated under reduced pressure. Flash chromatography (CH$_2$Cl$_2$) afforded propargyl amine 5b as a colourless oil (45 mg, 75%).

\( v_{\text{max}} \) (CHCl$_3$)/cm$^{-1}$ 3292 (C=C-H), 2925, 1663, 1604, 1430; $^1$H NMR $\delta$ (360 MHz, CDCl$_3$) 7.17-7.14 (2H, m, 2xArH), 7.12-7.08 (2H, m, 2xArH), 5.76-5.72 (1H, m, CH=CH), 5.67-5.63 (1H, m, CH=CH), 4.10 (1H, d, J 15.2, CH$_3$H$_2$Ar), 3.88 (1H, d, J 15.2, CH$_2$H$_2$Ar), 3.75 (1H, dd, J 15.3, 2.3, CH$_3$H$_2$C=C=CH), 3.49 (1H, dd, J 15.3, 2.3, CH$_2$H$_2$C=C=CH), 3.08-3.05 (1H, m, NCHCH), 2.99 (1H, dd, J 7.9, 2.4, NCHCH), 2.53-2.43 (1H, m, CH$_2$H$_2$), 2.38-2.13 (3H, m, CH$_2$+CH$_2$H$_2$), 2.26 (1H, t, J 2.3, =CH); $^{13}$C NMR $\delta$ (90.6 MHz, CDCl$_3$) 140.2 (C), 134.0 (C), 127.0 (CH), 126.5 (CH), 126.3 (CH), 125.8 (CH), 125.7 (CH), 122.9 (CH), 78.3 (C), 73.4 (CH), 54.4 (CH$_2$), 53.3 (CH), 42.2 (CH$_2$), 37.6 (CH), 31.4 (CH$_2$), 26.4 (CH$_2$); $m/z$ (EI) 223 ([M]$^+$, 6 %), 222 (6), 168 (100), 129 (25); HRMS (EI) Found: [M]$^+$, 223.1350. C$_{13}$H$_{12}$N requires 223.1356.

\textbf{(4aSR,10bSR)-5-(Prop-2'-ynyl)-1,2,4a,5,6,10b-hexahydro-phenanthridine 5c}

To a solution of amine 9c (52 mg, 0.28 mmol) in acetonitrile (5 ml) was added K$_2$CO$_3$ (116 mg, 0.84 mmol) and propargyl bromide (35 µl, 80 % w/w in toluene, 0.31 mmol). The reaction was heated at 60°C for 2 h and then concentrated under reduced pressure. Flash chromatography (CH$_2$Cl$_2$) afforded propargyl amine 5c as a yellow oil (37 mg, 60%).
$\nu_{\text{max}}$ (CHCl$_3$/cm$^{-1}$) 3291 (C≡C-H), 3027, 2925, 1663; $^1$H NMR $\delta$ (360 MHz, CDCl$_3$) 7.20-7.04 (3H, m, 3xArH), 7.05 (1H, d, $J$ 7.3, 2xArH), 6.02-5.93 (2H, m, CH=CH), 3.98 (1H, d, $J$ 15.1, CH$_3$Ar), 3.82 (1H, dd, $J$ 17.2, 2.3, CH$_3$H=CHH), 3.78 (1H, d, $J$ 15.1, CH$_3$H=CH), 3.51 (1H, dd, $J$ 17.2, 2.3, CH$_3$H=CHH), 3.26 (1H, br s, NCH=CH), 3.84 (1H, dt, $J$ 11.2, 3.5, NCH=CHH), 3.27 (1H, t, $J$ 2.3, CH), 2.16-2.04 (3H, m, CH$_2$+CH$_3$H$_B$), 1.85-1.76 (1H, m, CH$_3$H$_B$); $^{13}$C NMR $\delta$ (90.6 MHz, CDCl$_3$) 138.8 (C), 134.5 (C), 132.1 (CH), 128.2 (CH), 126.2 (CH), 126.0 (CH), 125.6 (CH), 125.5 (CH), 78.5 (C), 73.1 (CH), 54.0 (CH$_2$), 54.0 (CH), 42.3 (CH$_2$), 38.0 (CH), 27.7 (CH$_2$), 25.7 (CH$_2$); $m/z$ (EI) 223 ([M]$^+$, 30 %), 222 (47), 194 (10), 169 (100), 129 (15).