

Supporting Information

1-Methyl-3-[(1-aziridino)(methylthio)methylene]-3-oxindole (2b)

Light yellow Crystals (chloroform-hexane); mp 121-122°C; Yield 69%; IR (KBr): 2929, 1670, 1615, 1583 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 2.55 (s, 3H), 2.65 (brs, 2H), 2.66 (brs, 2H), 3.28 (s, 3H), 6.85 (d, $J = 7.8$ Hz, 1H), 7.07 (t, $J = 7.6$ Hz, 1H), 7.20 (t, $J = 7.8$ Hz, 1H), 7.49 (d, $J = 7.6$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 16.39, 25.67, 34.66, 35.64, 107.12, 121.03, 121.77, 122.05, 122.66, 125.57, 140.21, 164.50, 166.89. MS (m/z , %): 246 (M^+ , 31.2), 173 (100), 158 (48.1).

1-Methyl-1'-methylthio-2-oxospiro(3H-indole-3,3'-pyrroline) (3b)

Light Yellow Crystals (chloroform-hexane); mp 141-142°C; Yield 70%; IR (KBr): 2913, 1700, 1570, 1450 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 2.38 (ddd, $J = 5.1, 7.9, 13.0$ Hz, 1H), 2.39 (s, 3H), 2.71 (ddd, $J = 5.1, 7.9, 13.0$ Hz, 1H), 3.25 (s, 3H), 4.20 (ddd, $J = 5.1, 7.9, 13.0$ Hz, 1H), 4.29 (ddd, $J = 5.1, 7.9, 13.0$ Hz, 1H), 6.88 (d, $J = 7.8$ Hz, 1H), 7.09 (dt, $J = 1.0, 7.6$ Hz, 1H), 7.13 (dd, $J = 1, 7.6$ Hz, 1H), 7.34 (dt, $J = 1.5, 7.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 13.67, 26.57, 37.35, 60.63, 66.27, 108.46, 123.15, 123.33, 129.14, 129.54, 143.88, 171.17, 175.57. MS (m/z , %): 246 (M^+ , 28), 173 (100), 158 (63.3). Anal. Calcd for $\text{C}_{13}\text{H}_{14}\text{N}_2\text{OS}$ (246.18): C, 63.42; H, 5.68; N, 11.37%. Found: C, 63.51; H, 5.51; N, 11.29%.

5-Methoxy-1-methyl-1'-methylthio-2-oxospiro(3H-indole-3,3'-1-pyrroline) (3d)

Light Yellow Crystals (chloroform-hexane); mp 151-152°C; Yield 66%; IR (KBr): 2545, 1830, 1584, 1136 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 2.33-2.36 (m, 1H), 2.39 (s, 3H), 2.68-2.75 (m, 1H), 3.22 (s, 3H), 3.78 (s, 3H), 4.15-4.31 (m, 2H), 6.74 (d, $J = 2.2$ Hz, 1H), 6.79 (d, $J = 8.3$ Hz, 1H), 6.86 (dd, $J = 2.2, 8.3$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 13.72, 26.65, 37.30, 55.77, 60.63, 66.67, 108.73, 110.56, 113.26, 130.79, 137.33, 156.40, 171.17, 175.25; MS (m/z , %): 276 (M^+ , 47.8), 203 (100), 188 (83.1). Anal. Calcd for $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$ (276.18): C, 60.08; H, 5.79; N, 10.13%. Found: C, 60.21; H, 5.56; N, 10.29%.

2'-methyl-2-oxospiro-(3H-indole-3,3'-pyrrolidine) (*dl*-Coerulescine, 4)

Pale yellow Crystals (chloroform-hexane); mp 113-115°C (lit⁹ 112-113°C); Yield 80%; IR (KBr): 2913, 1700, 1570, 1450 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 2.06 (m, 1H), 2.36 (m, 1H), 2.42 (s, 3H), 2.76 (m, 1H), 2.84 (m, 1H), 2.86 (d, $J = 9.3$ Hz, 1H), 3.01 (m, 1H), 6.90 (d, $J = 7.56$ Hz, 1H), 7.02 (t, $J = 9.6$ Hz, 1H), 7.19 (t, 7.5 Hz, 1H), 7.41 (d, $J = 7.6$ Hz, 1H), 8.51 (brs, exchangeable with D_2O , 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 37.92, 41.80, 53.58, 56.72, 66.14, 109.51, 122.87, 123.34, 127.78, 135.85, 140.05, 182.81. MS (m/z , %): 202 (M^+ , 29.9), 159 (17), 130 (18.3) 57 (100). Anal. Calcd for $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}$ (202.11): C, 71.30; H, 6.92; N, 13.85%. Found: C, 71.19; H, 6.85; N, 14.00%.

5-Methoxy-2'-methyl-2-oxospiro-(3H-indole-3,3'-pyrrolidine) (*dl*-Horsfiline, 5)

Light Yellow Crystals (chloroform-hexane); mp 151-152°C (lit.⁷ 151-152°C); Yield 75%; IR (KBr): 2937, 1700, 1586, 1383 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 2.14 (ddd, *J* = 7.0, 7.4, 12.8 Hz, 1H), 2.40 (ddd, *J* = 5.0, 7.5, 12.8 Hz, 1H), 2.52 (s, 3H), 2.85 (ddd, *J* = 7.3, 7.4, 8.8 Hz, 1H), 2.92 (d, *J* = 9.5 Hz, 1H), 2.98 (d, *J* = 9.5 Hz, 1H), 3.10 (ddd, *J* = 5.0, 7.4, 8.8 Hz, 1H), 3.79 (s, 3H), 6.72 (dd, *J* = 2.7, 8.3 Hz, 1H), 6.81 (d, *J* = 8.6 Hz, 1H), 7.05 (d, *J* = 2.7 Hz, 1H), 8.80 (brs, exchangeable with D₂O, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 38.03, 41.77, 54.13, 55.90, 56.65, 65.87, 110.00, 110.28, 112.77, 133.56, 136.86, 156.30, 183.32. MS (*m/z*, %): 232 (M⁺, 23.5), 175 (47), 160 (16.2), 57 (100). Anal. Calcd for C₁₃H₁₆N₂O₂ (232.12): C, 67.26; H, 6.89; N, 12.06%. Found: 67.32; H, 6.78; N, 12.10%.

1-Methyl-2-oxospiro-(N'-ethyl-indole-3,3'-pyrrolidine) (6b)

Viscous Liquid; Yield 65%; IR (Nujol): 2968, 2800, 1708, 1612 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 1.07 (t, *J* = 7.3 Hz, 3H), 1.99 (ddd, *J* = 4.2, 8.0, 12.5 Hz, 1H), 2.27 (ddd, *J* = 4.2, 8.0, 12.5 Hz, 1H), 2.58 (q, *J* = 7.3 Hz, 2H), 2.68 (ddd, *J* = 4.2, 8.0, 12.5 Hz, 1H), 2.74 (d, *J* = 9.3 Hz, 1H), 2.58 (d, *J* = 9.3 Hz, 1H), 3.06 (ddd, *J* = 4.2, 8.0, 12.5 Hz, 1H), 3.13 (s, 3H), 6.73 (d, *J* = 7.8 Hz, 1H), 6.99 (dt, *J* = 1, 7.6 Hz, 1H), 7.18 (dt, *J* = 1.2, 7.8 Hz, 1H), 7.38 (d, *J* = 7.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 13.86, 26.78, 37.17, 49.66, 52.59, 54.19, 63.75, 107.60, 122.81, 123.01, 127.63, 135.92, 142.79, 180.25; MS (*m/z*, %): 230 (M⁺, 25.0), 159 (41.0), 71 (100.0). Anal. Calcd for C₁₄H₁₈N₂O (230.13): C, 73.06; H, 7.82; N, 12.16%. Found: C, 73.17; H, 7.76; N, 12.29%.

1-Methyl-3-[(methylthio)methylene]-2-oxindole (7a)

Light Yellow Crystals (chloroform-hexane); mp 100-101°C; Yield 38%; IR (KBr): 2925, 2401, 1676, 1406, 1217, 1099 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 2.61 (s, 3H), 3.21 (s, 3H), 6.76 (d, *J* = 7.6 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.76 (s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 18.91, 25.97, 107.61, 121.50, 121.92, 122.21, 123.30, 127.98, 142.35, 147.53, 165.97; MS (*m/z*, %): 205 (100), 190 (82), 172 (77.1). Anal. Calcd for C₁₁H₁₁NOS (205.16): C, 64.39; H, 5.36; N, 6.82%. Found: C, 64.21; H, 5.45; N, 6.89%.