1β-Azido-2,3,9,9a-tetrahydro-9aα-hydroxy-2α-(methanesulfonyloxy)-7-methoxy-6-methyl-5,8-bis[dimethyl(1,1-dimethylethyl)silyloxy]-9-oxo-1*H*-pyrrolo[1,2-a]indole (7):

To a solution of azido mesylate **1** (160 mg, 0.27 mmol) in 3 mL acetone cooled to -30°C, a pre-cooled (-30°C) solution of DMD (0.061 M, 8.8 mL, 0.54 mmol) was rapidly added, followed by glacial acetic acid (31 μL, 0.54 mmol). The resultant bright-yellow solution was warmed to 0°C. After 1.5 hr, the reaction mixture was diluted with 30 mL Et_2O and the organic layer was washed with saturated $NaHCO_3$ (2 X 15 mL), brine (1 X 15 mL) and dried over Na_2SO_4. The mixture was filtered and the solvent was removed *in vacuo*. Purification of the residue by flash chromatography (10, 20, 40% EtOAc in hexanes, gradient elution) on flash silica afforded 120 mg (71%) of a bright-yellow powder. M.p.: 100°C (decomp.). IR ($CHCl_3$) 3491 (OH), 2932, 2857, 2115 (N_3), 1711 (C=O), 1472, 1287, 1172, 1081, 836 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.07 (s, 3H), 0.20 (s, 3H), 0.22 (s, 3H), 0.30 (s, 3H), 1.05 (s, 18H), 2.18 (s, 3H), 2.95-3.02 (br, 1H), 3.13 (s, 3H), 3.66 (s, 3H), 3.80 (dd, 1H, J = 5.5, 12.8 Hz), 3.88 (dd, 1H, J = 4.0, 12.8 Hz), 4.40 (d, 1H, J = 3.4 Hz), 4.99 (q, 1H, J = 3.9 Hz). ^{13}C NMR ($CDCl_3$): δ -4.9 -4.6, -4.5, 3.3, 12.0, 18.3, 18.5, 25.7, 25.9, 44.4, 45.0, 51.0, 53.5, 60.0, 95.0, 113.2, 134.4, 136.3, 141.5, 144.6, 150.4, 161.3, 195.3. Anal. Calcd. for $C_{26}H_{44}N_4O_8SSi_2$: C, 49.66; H, 7.05; N, 8.91. Found: C, 49.65; H, 7.01; N, 8.62.

1β-Azido-2,3,9,9a-tetrahydro-2α-(methanesulfonyloxy)-7-methoxy-6-methyl-5,8-bis[dimethyl(1,1-dimethylethyl)silyloxy]-1*H*-pyrrolo[1,2-a]indole (8): To a solution of azido mesylate **1** (50 mg, 0.084 mmol) in 600 μL acetone cooled to -78°C, a pre-

cooled (-78°C) solution of DMD (0.061 M, 2.7 mL, 0.17 mmol) was rapidly added. After 10 min, the resultant bright-yellow solution was then warmed to –30°C. After 15 min, the reaction mixture was concentrated *in vacuo*. Purification of the residue by flash chromatography (0, 5, 10, 15, 20% EtOAc:hexanes, gradient elution) on SiO_2 afforded **8** 4.0 mg (8%) as a bright-yellow film: ^{1}H NMR ($CDCl_3$): δ 0.07 (s, 3H), 0.21 (s, 3H), 0.22 (s, 3H), 0.29 (s, 3H), 1.04 (s, 9H), 1.05 (s, 9H), 2.17 (s, 3H), 3.12 (s, 3H), 3.52 (dd, 1H, J = 4.2, 12.8 Hz), 3.66 (s, 3H), 3.86 (d, 1H, J = 12.8 Hz), 4.28 (d, 1H, J = 5.5 Hz), 4.50 (dd, 1H, J = 1.8, 5.5 Hz), 5.19-5.20 (m, 1H,); ^{13}C NMR ($CDCl_3$): δ -4.7 -4.5, -4.4, -3.5, 11.9, 18.4, 18.6, 25.8, 25.9, 38.8, 54.5, 60.0, 64.3, 71.8, 84.0, 117.2, 134.9, 140.8, 144.9, 152.8, 195.8; HPLC/MS *m/z* 613, (M+ H^+).

1β-Azido-9-formyl-2,3-dihydro-2α-(methanesulfonyloxy)-1*H*-pyrrolo[1,2-a]indole:

A total of 0.335 mL (3.77 mmol) of phosphorus oxychloride was dissolved in 2 mL of dimethylformamide (DMF) under nitrogen at 0°C and stirred vigorously. After 40 min., a total of 0.524 g (1.79 mmol) of **12** dissolved in 4 mL of THF was added to the reaction flask. It was stirred for 1 h at 0°C, warmed to rt and stirred for another 8 h. A total of 2 mL of deionized water was added to the reaction mixture and stirred at rt for 10 h. After completion of the reaction, the reaction mixture was extracted with ethyl acetate (2x20 mL) and the combined organic layer was dried over anhydrous sodium sulfate. The solvent was evaporated *in vacuo*. The product was purified by flash chromatography with 1:1 hexane/ethyl acetate as the eluent. A total of 0.500 g (87%) of the aldehyde was obtained as a pale yellow oil. IR: 2921.3, 2101.4, 1705.2, 1365.4, 1295.8, 1265.7, 1196.7, 1185.4 784.2, 739.1 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.15 (s, 3H), 4.40 (dd, 1H, J = 4

Hz, 10 Hz), 4.59-4.68 (m, 2H, J = 2 Hz, 5 Hz), 5.55 (d, 1H, J = 8 Hz), 7.35 (d, 1H), 7.90-8.11 (m, 3H), 10.21 (s, 1H). MS (EI): m/z 320 (M^+). Anal. Calcd. for $C_{13}H_{12}N_4O_4S$: C, 48.75; H, 3.75; N, 17.50. Found: C, 48.64; H, 3.82; N, 17.16.

1β-Azido-9-methyl-2,3-dihydro-2α-(methanesulfonyloxy)-1*H*-pyrrolo[1,2-a]indole (13): A total of 0.219 g (0.684 mmol) of the aldehyde was dissolved in 10 mL of dry methanol. A total of 0.108 g (1.71 mmol) of sodium cyanoborohydride was added to the reaction flask under nitrogen and stirred at rt for 4 h. A trace of 2N hydrochloric acid in methanol and orange-G indicator were added to maintain and indicate the acidic pH respectively. The reaction progress was monitored by TLC (3:1 hexane/ethyl acetate). The solvent was evaporated *in vacuo* and the product was purified by flash chromatography using 3:1 hexane/ethyl acetate as the eluent. A total of 0.170 g (81%) of **13** was obtained as a yellow oil. IR: 2984.6, 2125.3, 1321.8, 1266.8, 1261.8, 1161.4, 784.5, 754.3, 737.8 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.42 (s, 3H), 3.11 (s, 3H), 4.27 (dd, 1H, J = 4.5 Hz, 11.7 Hz), 4.54 (m, 1H, J = 5.1 Hz, 12 Hz), 5.21 (dd, 1H, J = 5.1 Hz), 5.50 (dd, 1H, J = 5.1 Hz), 7.17 (d, 1H, J = 7.8 Hz), 7.24-7.26 (m, 2H), 7.60 (d, 1H, J = 8.1 Hz). ^{13}C NMR ($CDCl_3$): δ 39.04, 49.50, 61.68, 62.82, 84.89, 109.69, 110.16, 119.65, 119.79, 119.97, 120.47, 123.14, 123.22. MS (EI): m/z 306 (M^+). Anal. Calcd. for $C_{13}H_{14}N_4O_3S$: C, 50.98; H, 4.58; N, 18.30; S, 10.46. Found: C, 50.94; H, 4.58; N, 18.26; S, 10.48.

3β-Azido-3,4,5,6-tetrahydro-5α,6α-dihydroxy-4α-(methanesulfonyloxy)-6β-methyl-2*H*-1,5-epoxy-1-benzazocine (14): A total of 0.015 g (0.049 mmol) of **13** was dissolved in 2 mL of dry acetone at 0°C under nitrogen. A total of 0.02 mL (excess) of

deionized water, followed by 1.27 mL of 0.085 M dimethyldioxirane (DMDO, freshly distilled) in acetone were added to the reaction mixture. It was stirred at rt for 4 h under nitrogen. The reaction was monitored by TLC (100% dichloromethane). The product was purified by flash chromatography using 98:2 dichloromethane/methanol as the eluent. A total of 0.0102 g (59%) of **14** was obtained as a pale yellow oil. IR: 3541.6, 3054.1, 2118.0, 1421.9, 1364.8, 1265.3, 1179.1, 896.1, 737.5 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.78 (s, 3H), 3.02 (s, 3H), 3.72-4.32 (m, 4H), 5.50 (bs, 1H), 6.92 (d, 1H, J = 8.1 Hz), 7.23-7.35 (m, 2H), 7.59 (d, 1H, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$): δ 21.24, 38.80, 59.62, 66.53, 71.17, 72.63, 100.38, 120.27, 126.44, 127.17, 129.61, 130.50, 143.26 MS (EI): m/z 356 (M^+). Anal. Calcd. for $C_{13}H_{16}N_4O_6S$: C, 43.82; H, 4.49; N, 15.73; S, 8.99. Found: C, 43.81; H, 4.45; N, 15.78; S, 8.97.