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7.0 Hz), 0.51 (s, 9H); ^{13}C NMR (100 MHz, C_6D_6) δ 189.5, 187.7, 157.5, 157.2, 156.5, 144.1, 140.9, 137.2, 131.7, 127.4, 127.1, 124.0, 122.7, 114.7, 113.7, 111.8, 103.6, 101.8, 97.2, 92.2, 89.1, 81.1, 74.2, 66.2, 52.0, 49.4, 44.8, 37.6, 31.1, 16.6, 2.8; FTIR (neat), cm^{-1} : 1746 (m, C=O); HRMS (FAB): m/z calcd for $\text{C}_{33}\text{H}_{31}\text{NO}_9\text{Si}$ (M) $^+$ 613.1768, found: 613.1779.

Methyl (1S, 4R, 4aR, 14S, 14aS, 18Z)-1,4,7,12,13,14-Hexahydro-6,8,11-trihydroxy-3-methoxy-1-methyl-7,12-dioxo-4a,14a-epoxy-4,14-[3]hexene-[1,5]diynonaphtho[2,3-c]phenanthridine-2-carboxylate (112)

A solution of potassium *N,N*-bis(trimethylsilyl)amide in toluene (0.5 M, 216 μL , 108 μmol , 4.18 equiv) was added to a deoxygenated solution of 4,7-bis(trimethylsiloxy)phthalide (**93**, 32.0 mg, 103 μmol , 3.99 equiv, dried by azeotropic distillation with toluene, 1 mL) in tetrahydrofuran (1 mL) at -78 $^\circ\text{C}$, and the resulting bright yellow solution was stirred at -78 $^\circ\text{C}$ for 20 min. A 1:1.6 mixture of chlorotrimethylsilane and triethylamine (82.0 μL , 184 μmol in chlorotrimethylsilane, 7.12 equiv) was added. The reaction mixture was warmed to -20 $^\circ\text{C}$ for 3 min, whereupon the bright yellow solution became colorless. At this point, a solution of methyl (6S, 6aS, 7S, 10R, 10aR, 14Z)-2,6,7,10-tetrahydro-9-methoxy-7-methyl-2-oxo-6a,10a-epoxy-6,10-[3]hexene-[1,5]diynophenanthridine-8-carboxylate (**7**, 10.0 mg, 25.8 μmol , 1 equiv) in tetrahydrofuran (0.75 mL) was transferred to the cold reaction mixture. The resulting solution was heated at 55 $^\circ\text{C}$ for 5 min, then was cooled to 23 $^\circ\text{C}$ and was concentrated to afford methyl (1S, 4R, 4aR, 6aR, 7R, 12R, 12aS, 14S, 14aS, 18Z)-1,4,6,6a,7,12,12a,14-octahydro-3-methoxy-1-methyl-6-oxo-7,8,11-

tris(trimethylsiloxy)-4a,14a:7,12-diepoxy-4,14-[3]hexene[1,5]diynonaphtho[2,3-c]-phenanthridine-2-carboxylate (**109**) as a yellow solid. The yield of product was estimated to be 52% by ^1H NMR analysis of the crude reaction mixture (integration against dichloromethane added as an internal standard). ^1H NMR (400 MHz, C_6D_6 , unobscured protons) δ 6.80 (s, 1H), 5.69 (s, 1H), 5.30 (dd, 1H J = 10.0, 1.5 Hz), 5.25 (dd, 1H, J = 10.0, 1.5 Hz), 4.90 (br s, 1H), 3.86 (br s, 1H), 3.65 (q, 1H, J = 7.3 Hz), 3.46 (s, 3H), 3.46 (s, 3H), 3.21 (d, 1H, J = 7.6 Hz), 2.89 (d, 1H, J = 7.6 Hz), 1.36 (d, 3H, J = 7.3 Hz).

To a solution of the crude product from above in tetrahydrofuran (4 mL) at 23 °C was added sequentially activated manganese dioxide (120 mg, 1.38 mmol) and triethylamine trihydrofluoride (300 μL , 1.84 mmol). The resulting suspension was stirred vigorously at 23 °C for 40 min, then was diluted with ether (25 mL). The resulting suspension was filtered through Celite, eluting with ether (25 mL). The filtrate was concentrated to a volume of ca. 1 mL and the residue was purified by column chromatography on lipophilic Sephadex LH-20 (20% acetonitrile in methanol) to provide methyl (1*S*, 4*R*, 4*aR*, 14*S*, 14*aS*, 18*Z*)-1,4,7,12,13,14-hexahydro-6,8,11-trihydroxy-3-methoxy-1-methyl-7,12-dioxo-4a,14a-epoxy-4,14-[3]hexene[1,5]diynonaphtho[2,3-c]phenanthridine-2-carboxylate (**112**) as a violet solid (4.1 mg, 29% over 2 steps): R_f 0.33, 40% ethyl acetate–hexanes; ^1H NMR (400 MHz, C_6D_6) δ 13.49 (s, 1H), 12.89 (s, 1H), 12.47 (s, 1H), 9.84 (d, 1H, J = 4.2 Hz), 7.38 (s, 1H), 6.96 (d, 1H, J = 9.2 Hz), 6.86 (d, 1H, J = 8.3 Hz), 5.22 (d, 1H, J = 10.0 Hz), 5.19 (dd, 1H, J = 10.0, 1.2 Hz), 3.91 (br s, 1H), 3.81 (br q, 1H, J = 7.3 Hz), 3.63 (br d, 1H, J = 4.0 Hz), 3.51 (s,

3H), 3.50 (s, 3H), 1.44 (d, 3H, $J = 7.3$ Hz); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 190.1, 188.0, 166.9, 157.7, 157.6, 157.0, 154.9, 150.3, 143.3, 135.5, 129.8, 128.0, 126.1, 124.2, 124.1, 115.4, 114.3, 113.4, 112.8, 98.5, 97.3, 90.6, 90.2, 71.1, 63.8, 59.3, 52.1, 45.5, 36.7, 33.5, 19.0; FTIR (neat), cm^{-1} : 1692 (m, C=O); HRMS (FAB) m/z calcd for $\text{C}_{31}\text{H}_{22}\text{NO}_9$ (MH) $^+$ 552.1295, found: 552.1294.