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Supplementary Information

General procedure for dihydroxylation: (a) Et_4NOAc/*t*-BuOOH route; tetraethylammonium acetate solution is added to *t*-BuOOH (70% in H_2O, 2 ml). The resulting solution was cooled to 0 °C before being treated with the OsO_4 catalyst solution (14 μmol OsO_4). The olefin **5** (815 mg, 2.1 mmol) in acetone (15 ml) was then added dropwise over 3h, maintaining the stirring solution at 0 °C throughout the addition. (b) NMO route; the olefin **5** (2 g, mmol) was dissolved in dioxane (50 mL) and water (2 mL) then NMO (2 g, mmol) was added. The mixture was stirred for 10 min then the OsO_4 catalyst solution (28 μmol OsO_4) was added and the mixture was continued to stir for 12 h.

OsO_4 catalyst solution: Prepared by dissolving OsO_4 (0.1 g) in *t*-BuOH (19 ml) and adding *t*-BuOOH (0.5 ml).

Workup: Ether (10 ml) was added to the yellow solution and the solution cooled to 0 °C before the sodium metabisulfite (2.0 g). The resulting mixture was stirred for 30 min, then more ether (20 ml) was added and the aqueous phase was saturated with NaCl. The organic phase was washed with brine (2 x 50 ml), dried (Na_2SO_4), and the solvent removed. The crude residue was purified by column chromatography (EtOAc:light petroleum; 3:7) and recrystallised from light petroleum to yield the desired diol.

10: m.p. 189-191 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.86 (6H, s), 1.45-1.60 (2H, m), 1.65-1.80 (2H, m), 1.81 (2H, s), 1.96 (2H, s), 2.04 (2H, s), 2.49 (2H, bs), 3.48 (2H, s), 3.55 (2H, s), 3.78 (6H, s), 6.59 (2H, s); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 9.4, 28.6, 40.1, 42.8, 43.4, 43.5, 46.8, 49.7, 56.0, 74.0, 109.0, 136.5, 147.7. MS (EI): *m/z* 382 (M^+).

11: m.p. 205-207 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.93 (6H, s), 1.52 (1H, d, *J* 10.7 Hz), 1.69 (1H, d, *J* 9.7 Hz), 1.83 (1H, d, *J* 10.7 Hz), 1.86 (2H, s), 1.92 (1H, d, *J* 9.7 Hz), 2.11 (2H, s), 2.18 (2H, s), 2.53 (2H, bs), 3.58 (2H, s), 3.65 (2H, s), 3.78 (6H, s), 7.40-7.48 (2H, m), 8.03-8.10 (2H, m); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 9.7, 28.7, 40.5, 42.7, 43.5, 43.7, 47.0, 50.7, 61.9, 74.3, 122.0, 125.0, 127.9, 135.1, 144.3. MS (EI): *m/z* 432 (M^+).

General procedure for oxidation: To a solution of diol **11** (1.20 g, 2.8 mmol) and *p*-TsOH (2.64 g, 14 mmol) in dichloromethane (45 mL) maintained at 0 °C was added a solution of 4-acetamido TEMPO (2.96 g, 14 mmol) in dichloromethane (78 mL) over 45 min. The reaction mixture is stirred at 0 °C for 1 h then warmed to room temperature and stirred for a further 95 h in the dark. Ethanol (5 mL) was added and the mixture

stirred for 30 min. Water (40 mL) and dichloromethane (30 mL) were added, the organics were separated, and the aqueous layer reextracted with dichloromethane (30 mL). The combined organic layers were washed with water (50 mL), dried ($MgSO_4$), and the solvent removed to afford an orange oil. Chromatgraphy (dichloromethane) yields the dione **16** as a yellow solid.

15: m.p. 208-211 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.97 (6H, s), 1.60 (1H, m), 1.71-1.75 (2H, m), 2.05-2.10 (1H, m), 2.10 (2H, s), 2.37 (2H, s), 2.99 (2H, s), 3.54 (2H, s), 3.78 (6H, s), 6.61 (2H, s); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 9.4, 27.8, 40.2, 43.4, 44.0, 45.2, 48.9, 49.8, 55.9, 109.2, 135.9, 147.8, 200.4. HRMS: *m/z* (M^+) calcd for $C_{24}H_{26}O_4$ 378.1831, found 378.1824.

16: m.p. 130-133 °C; Found C: 78.2; H: 6.9. $C_{28}H_{28}O_4$ requires C: 78.5; H: 6.6; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.03 (6H, s), 1.76 (1H, d, *J* 9.7 Hz), 1.94 (1H, d, *J* 9.7 Hz), 2.10 (1H, d, *J* 12.3 Hz), 2.33 (2H, s), 2.38 (1H, d, *J* 12.3 Hz), 2.43 (2H, s), 3.02 (2H, s), 3.72 (2H, bs), 3.97 (6H, s), 7.42-7.48 (2H, m), 8.03-8.10 (2H, m); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 9.6, 27.8, 40.5, 42.8, 44.2, 45.7, 48.8, 50.8, 62.0, 122.1, 125.2, 128.0, 127.9, 134.3, 144.5, 200.2. HRMS: *m/z* (M^+) calcd for $C_{28}H_{28}O_4$ 428.1987, found 428.1983.

Porphyrin products: To a solution of the porphyrin 2,3-dione (165 mg, 0.15 mmol) in deoxygenated dry pyridine (2 ml) under argon was added benzenetetramine tetrahydrochloride (41 mg, 0.15 mmol). The mixture was allowed to stir in the dark for 48 h, then the norbornane dione **15** or **16** (1.2 equiv.) was added. The mixture was then heated to 80 °C for 3-5 days. Demethylation (BBr_3, CH_2Cl_2) of the aromatic methoxy groups, followed by oxidation (PbO_2, $CHCl_3$) gave the porphyrin-bridge-quinone systems **1a** or **1b** in high (>90%) yield. At each stage the reaction mixtures are purified by aqueous acid workup, dried (Na_2SO_4), the solvent removed, and the crude product chromatographed on silica (dichloromethane/light petroleum mixtures).

1a: m.p. > 300 °C; $\upsilon_{max}(CCl_4)$: 1598, 1660 (C=O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ -2.42 (2H, bs), 1.08 (6H, s), 1.47 (18H, s), 1.50 (18H, s), 1.53 (36H, s), 1.46-1.70 (1H, underlying), 1.71 (1H, d, *J* 10.2 Hz), 2.02 (2H, s), 2.11 (1H, d, *J* 10.2 Hz), 2.30 (1H, d, *J* 10.2 Hz), 2.37 (2H, s), 3.51 (2H, s), 3.66 (2H, s), 6.56 (2H, s), 7.79 (2H, t, *J* 1.5 Hz), 7.95-8.04 (6H, m), 8.09 (4H, d, *J* 2.0 Hz), 8.53 (2H, s), 8.77 (2H, s), 8.98 and 9.02 (4H, ABq, *J* 4.6 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 9.4, 31.7, 31.9, 32.0, 35.0, 35.1, 41.2, 41.8, 43.8, 44.4, 48.1, 48.5, 118.0, 120.7, 121.2, 123.0, 128.1, 128.4, 128.5, 128.6, 129.2, 129.5, 134.2, 136.2, 138.1, 139.4, 139.8, 140.1, 140.7, 141.0, 145.6, 148.8, 149.1, 149.2, 151.6, 153.7, 154.9, 163.7, 183.9. Mass Spectrum (MALDI): *m/z* 1505 $[M+Na]^+$.

1b: m.p. > 300 °C; $\upsilon_{max}(CCl_4)$: 1600, 1665 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ -2.42 (2H, bs), 1.12 (6H, s), 1.46 (18H, s), 1.50 (18H, s), 1.52 (36H, s), 1.46-1.70 (1H, underlying), 1.77 (1H, d, *J* 9.7 Hz), 2.11 (2H, s), 2.12 (1H, d, *J* 10.2 Hz), 2.30 (1H, d, *J* 10.2 Hz), 2.38 (2H, s), 3.66 (4H, s), 7.62-7.70 (2H, m), 7.79 (2H, t, *J* 1.5 Hz), 7.93 (2H, t, *J* 1.5 Hz), 7.96-8.05 (6H, m), 8.09 (4H, d, *J* 1.5 Hz), 8.53 (2H, s), 8.79 (2H, s), 9.00 and 9.04 (4H, ABq, *J* 5.1 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 9.1, 31.3, 31.4, 31.5, 34.6, 34.7, 41.1, 41.2, 43.6, 44.0, 47.7, 48.1, 117.5, 120.3, 120.8, 122.6, 125.8, 127.7, 127.9, 128.1, 128.2, 128.8, 129.1, 132.5, 132.9, 133.8, 137.7, 138.9, 139.4, 139.7, 140.3, 140.6, 145.1, 148.4, 148.6, 148.7, 153.3, 153.7, 154.5, 163.2, 181.2. Mass Spectrum (MALDI): *m/z* 1555 $[M+1]^+$.

Phenanthroline condensation products: Formed by taking the appropriate dione, **18** or **19** (0.60 mmol), and phenanthroline-5,6-diamine (0.66 mmol) and heating them in a mixture of absolute ethanol and chloroform (10:1, 22 ml), in the case of **3**, at reflux overnight, or absolute ethanol and dichloroethane (1:1, 1 ml), for **4**, at reflux for 5 days.

3: m.p. > 300 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 1.26 (6H, s), 2.14 and 2.31 (2H, ABq, *J* 10.7 Hz), 2.34 (2H, s), 3.77 (2H, s), 7.75 (4H, dd, *J* 8.2 Hz, *J* 4.6 Hz), 9.22 (4H, dd, *J* 4.6 Hz, *J* 1.5 Hz), 9.48 (4H, dd, *J* 8.2 Hz, *J* 1.5 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 9.7, 41.0, 43.8, 44.4, 48.5, 123.6, 127.4, 132.7, 137.5, 146.5, 151.4, 162.5. Mass Spectrum (MALDI): *m/z* 647 $[M+1]^+$.

4: m.p. 264-267 °C; ^1H NMR (300 MHz, $CDCl_3$) δ -1.45 (1H, d, *J* 11.8 Hz), 0.26 (1H, d, *J* 11.8 Hz), 1.06-1.18 (2H, m), 1.34-1.42 (2H, m), 1.98 (1H, dt, *J* 9.2 Hz, *J* 1.3 Hz), 2.09 (2H, s), 2.11 (1H, dt, *J* 9.2 Hz, *J* 1.3 Hz), 2.53 (2H, s), 3.66 (2H, s), 7.76 (2H, dd, *J* 8.2 Hz, *J* 4.1 Hz), 9.22 (4H, dd, *J* 4.4 Hz, *J* 1.5 Hz), 9.48 (4H, dd, *J* 8.2 Hz, *J* 1.5 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 30.1, 33.4, 36.6, 47.7, 48.5, 49.5, 123.2, 127.2, 132.6, 136.8, 145.7, 150.7, 162.9. Mass Spectrum (EI): *m/z* 364 $[M]^+$.