Supplementary Information for:

Synthesis and photophysical properties of chlorins bearing 0–4 distinct meso-substituents

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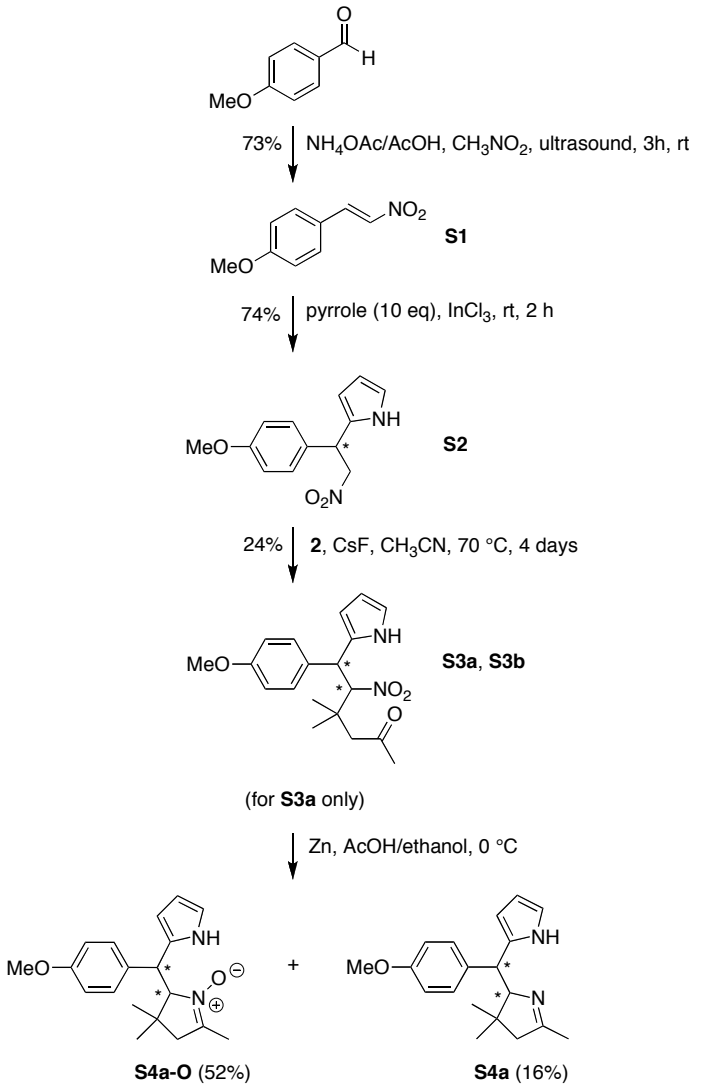
1. Synthesis of a second meso-substituted Western half



Scheme S1. Exploratory synthesis of a 5-aryltetrahydrodipyrrin (Western half).

The Henry reaction of *p*-anisaldehyde and nitromethane under ultrasound conditions[59] afforded the nitrovinyl arene **S1** in 73% yield (Scheme S1). Compound **S1** has been reported

and characterized by mp only;[50,61] full characterization is presented here. The reaction of **S1** and pyrrole in dichloromethane containing $InCl_3$ at room temperature afforded 2-(2-nitro-1-(4-methoxyphenyl)ethyl)pyrrole **S2** in 74% yield. Compound **S2** was reported and fully characterized by Zhan *et al*. during the course of this work,[60] and has since been prepared by a number of other methods.[52-56] Treatment of **S2** with mesityl oxide (**2**) in the presence of CsF in anhydrous CH_3CN at 70 °C provided the nitrohexanone adduct in 24% overall yield; two isomers were isolated in 22% (**S3a**) and 2% yield (**S3b**) without stereochemical identification. The reductive cyclization of **S3a** in the presence of excess zinc and acetic acid in ethanol at 0 °C gave *N*-oxide **S4a-O** (52% yield) and the corresponding Western half **S4a** (16% yield).

2. Experimental procedures

1-Methoxy-4-(2-nitrovinyl)benzene (S1). Following a literature procedure,[59] a mixture of *p*-anisaldehyde (2.43 mL, 20.0 mmol), nitromethane (13.0 mL, 241 mmol), glacial acetic acid (3.30 mL, 57.2 mmol) and ammonium acetate (3.32 g, 43.1 mmol) was sonicated at room temperature for 3 h, causing an increase in reaction temperature to ~55 °C. The nitromethane and glacial acetic acid were removed under reduced pressure. The residue was treated with water (30 mL) and extracted with CH_2Cl_2. The combined organic extract was evaporated under reduced pressure to leave ~10 mL of solvent, whereupon aqueous ethanol was added. The resulting yellow solid was filtered (2.61 g, 73%): mp 86–88 °C (lit mp 84–86 °C;[50] 86–87 °C[61]); ^{1}H NMR δ 3.88 (s, 3H), 6.96 (d, J = 9.0 Hz, 2H), 7.51 (d, J = 9.0 Hz, 2H), 7.53 (d, J = 13.6 Hz, 1H), 7.98 (d, J = 13.6 Hz, 1H); ^{13}C NMR δ 55.7, 115.1, 122.7, 131.4, 135.2, 139.3, 163.1; Anal. Calcd. for $C_9H_9NO_3$: C, 60.33; H, 5.06; N, 7.82. Found C, 60.39; H, 5.04; N, 7.80.

2-[(4-Methoxyphenyl)-2-nitroethyl]pyrrole (S2). A stirred solution of **S1** (6.89 g, 38.5 mmol) in CH_2Cl_2 (77.0 mL) containing $InCl_3$ (852 mg, 3.85 mmol) at 0 °C was treated with pyrrole (26.9 mL, 385 mmol). The mixture was stirred at room temperature for 2 h. After complete conversion as indicated by TLC, the reaction was quenched by the addition of water (80.0 mL). The mixture was extracted with CH_2Cl_2 (3 x 70.0 mL). The combined organic extract was dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by column chromatography (silica, CH_2Cl_2) to give a pale yellow oil (6.98 g, 74%): ^{1}H NMR δ 3.78 (s, 3H), 4.76 (ABX, ^3J = 8.0 Hz, ^2J = 12.0 Hz, 1H), 4.84 (ABX, ^3J = 6.8 Hz, ^3J = 8.0 Hz, 1H), 4.95 (ABX, ^3J = 6.8 Hz, ^2J = 12.0 Hz, 1H), 6.04–6.07 (m, 1H), 6.14–6.18 (m, 1H), 6.66–6.69 (m, 1H), 6.87 (d, J = 8.6 Hz, 2H), 7.14 (d, J = 8.6 Hz, 2H), 7.75–7.92 (br, 1H); ^{13}C NMR δ 42.4, 55.5, 79.6, 105.7, 108.8, 114.7, 118.3, 129.2, 129.5, 130.0, 159.5; FAB-MS obsd 246.1008, calcd 246.1004 ($C_{13}H_{14}N_2O_3$); Anal. Calcd. for $C_{13}H_{14}N_2O_3$: C, 63.40; H, 5.73; N, 11.38. Found C, 63.42; H, 5.70; N, 11.30.

6-(4-Methoxyphenyl)-4,4-dimethyl-5-nitro-6-(2-pyrrolyl)-2-hexanone (S3a, S3b). Cesium fluoride (731 mg, 4.81 mmol, freshly dried by heating to 100 °C under vacuum for 1 h and then cooling to room temperature under argon) was placed in a flask under argon. A mixture of **S2** (236 mg, 0.962 mmol) and mesityl oxide (**2**, 11.0 mL, 96.0 mmol) was transferred by cannula to the flask containing CsF. The mixture was heated and stirred at 70 °C for 4 days. The reaction mixture was filtered and the filtrate was concentrated under reduced pressure. TLC analysis [silica, ethyl acetate/hexanes (1:3)] showed two components with R_f = 0.32 (**S3a**, major) and R_f = 0.27 (**S3b**, minor). Column chromatography [silica, ethyl acetate/hexanes (1:3)] afforded each component as a light yellow oil (**S3a**, 72 mg, 22%; **S3b**, 6.1 mg, 2%); the two were found to be isomers.

Data for **S3a**: ^{1}H NMR δ 1.12 (s, 3H), 1.17 (s, 3H), 1.72, 2.22 (AB, ^{2}J = 18.4 Hz, 2H), 1.98 (s, 3H), 3.72 (s, 3H), 4.67 (d, J = 12.2 Hz, 1H), 6.04–6.07 (m, 1H), 6.10–6.12 (m, 1H), 6.21 (d, J = 12.2 Hz, 1H), 6.59–6.62 (m, 1H), 6.79 (d, J = 8.8 Hz, 2H), 7.29 (d, J = 8.8 Hz, 2H), 8.31–8.39 (br, 1H); ^{13}C NMR δ 23.0, 26.2, 31.8 36.6, 44.9, 51.7, 55.4, 93.6, 107.7, 109.0, 114.5, 118.5, 128.4, 129.5, 132.0, 158.9, 209.2; FAB-MS obsd 344.1732, calcd 344.1736 ($C_{19}H_{24}N_2O_4$).

Data for **S3b**: ^{1}H NMR δ 1.03 (s, 3H), 1.05 (s, 3H), 1.94 (s, 3H), 2.05, 2.31 (AB, ^{2}J = 18.8 Hz, 2H), 3.77 (s, 3H), 4.61 (d, J = 10.2 Hz, 1H), 5.93 (d, J = 10.2 Hz, 1H), 6.07–6.11 (m, 2H), 6.64-6.66 (m, 1H), 6.83 (d, J = 8.8 Hz, 2H), 7.21 (d, J = 8.8 Hz, 2H), 8.28–8.40 (br, 1H); ^{13}C NMR δ 24.3, 25.8, 31.4, 37.0, 44.9, 52.6, 55.5, 95.8, 107.3, 108.8, 114.6, 117.9, 129.4, 129.9, 131.3, 159.1, 207.1; FAB-MS obsd 345.1802, calcd 345.1814 [$(M + H)^+$, M = $C_{19}H_{24}N_2O_4$].

5-(4-Methoxyphenyl)-2,3,4,5-tetrahydro-1,3,3-trimethyldipyrrin N^{10}-oxide (S4a-O). Following a literature procedure,[32] a vigorously stirred solution of **S3a** (64 mg, 0.19 mmol) in acetic acid (0.93 mL) and ethanol (0.93 mL) at 0 °C was treated portionwise with zinc dust (300 mg, 4.7 mmol) for 5 min. The reaction mixture was stirred at 0 °C for 15 min and then filtered through Celite. The filtrate was concentrated under high vacuum. The resulting oil was chromatographed (silica, ethyl acetate) to afford a pale yellow oil (**S4a**, 9 mg, 16%) and the title compound as a yellow oil (30 mg, 52%).

Data for **S4a-O**: ^{1}H NMR δ 1.16 (s, 3H), 1.36 (s, 3H), 1.70–1.77 (m, 1H), 1.91 (s, 3H), 1.97–2.04 (m, 1H), 4.14–4.16 (m, 1H), 4.47–4.50 (m, 1H), 5.88–5.91 (m, 1H), 6.02–6.05 (m, 1H), 6.72–6.75 (m, 1H), 6.75 (d, J = 8.8 Hz, 2H), 7.29 (d, J = 8.8 Hz, 2H), 12.11–12.20 (br, 1H); ^{13}C NMR δ 13.4, 23.0, 31.5, 37.6, 44.9, 46.4, 55.4, 85.6, 105.2, 107.6, 114.0, 117.4, 130.0, 131.8, 134.1, 149.7, 158.7; FAB-MS obsd 313.1916, calcd 313.1916 [$(M + H)^+$, M = $C_{19}H_{24}N_2O_2$].

Data for **S4a**: ^{1}H NMR δ 0.97 (s, 3H), 1.05 (s, 3H), 1.60–1.72 (m, 1H), 2.01–2.02 (m, 3H), 2.06–2.08 (m, 1H), 3.74 (s, 3H), 4.17–4.21 (m, 1H), 4.20–4.23 (m, 1H), 5.93–5.96 (m, 1H), 6.05–6.08 (m, 1H), 6.65–6.68 (m, 1H), 6.73 (d, J = 8.6 Hz, 2H), 7.21 (d, J = 8.6 Hz, 2H), 9.59–9.66 (br, 1H); FAB-MS obsd 297.1971, calcd 297.1967 [$(M + H)^+$, M = $C_{19}H_{24}N_2O$].