A New Synthesis of Chlorins

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SUPPORTING INFORMATION

Experimental procedures and spectral data for all new compounds reported. This material is available free of charge via the Internet at http://pubs.acs.org.

Experimental Section

Melting points were determined on a Fisher-Johns microscope melting point apparatus and are not corrected. ^{1}H NMR spectra were recorded at 300 MHz and are expressed as ppm downfield from tetramethylsilane as an internal standard.

***Z*-5-[1-(4,4-Dimethyl-5-oxo-dihydrofuran-2-ylidene)-ethyl]-3,4-dimethyl-1*H*-pyrrole-2-carboxylic acid, *tert*-butyl ester (12a)**. A solution of 21.8 g (68 mmol) of iodopyrrole **11**,[1] 15.2 g (68 mmol) of alkyne acid **10a**,[2] and 15.5 g (68 mmol) of $BnNEt_3Cl$ in 500 mL of CH_3CN and 100 mL of Et_3N was degassed under argon for 10 min, and was then treated with 5.0 g (4.4 mmol) of $Pd(PPh_3)_4$ under an argon atmosphere. The reaction mixture was stirred at reflux temperature for 10 h. At the end of this period the reaction was concentrated to dryness under reduced pressure, and the residue was partitioned between CH_2Cl_2 and H_2O. The organic layer was washed with H_2O, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel, EtOAc:hexanes = 1:15 to 1:4) to afford 21.7 g (96%) of lactone **12a** as a colorless solid, mp 180 °C. R_f (1:4 EtOAc/hexanes) 0.58; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.31 (s, 6H), 1.61 (s, 9H), 1.93 (s, 3H), 2.02 (t, *J* = 1.8, 3H), 2.27 (s, 3H), 2.58 (q, *J* = 1.8, 2H), 8.33 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.1, 11.1, 16.6, 25.0, 28.8, 40.5, 40.54, 80.9, 105.4, 118.2, 120.1, 126.4, 130.8, 146.0, 162.0, 180.2; MS (EI) m/z (%): 333 (29, M^+), 278 (19), 277 (100), 260 (12), 230 (21), 193 (65), 165 (23), 147 (17), 146 (20), 121 (11), 118 (28), 117 (11), 91 (32), 57 (12). HRMS (FAB) Calcd for $C_{19}H_{27}NO_4$: 333.1940; found: 333.1944. Anal. Calcd for $C_{19}H_{27}NO_4$: C, 68.44; H, 8.16; N, 4.20; O, 19.19. Found: C, 68.48; H, 8.09; N, 4.15.

***Z*-5-[1-(4,4-Dimethyl-5-oxo-dihydrofuran-2-ylidene)-methyl]-3,4-dimethyl-1*H*-pyrrole-2-carboxylic acid, *tert*-butyl ester (12b).** This material was prepared in 98% yield from 3.45 g (10.7 mmol) of iodopyrrole **11,** 2.04 g (16.2 mmol) of alkyne acid **10b,** 3.18 g (14.0 mmol) of $BnNEt_3Cl$ and 1.26 g (1.1 mmol) of $Pd(Ph_3P)_4$ in 150 ml of 5:1 acetontrile/Et_3N (17 h) following an identical procedure to that described above for **12a**; mp 205 °C; R_f (1:5 EtOAc/hexanes) 0.47; IR (thin film) 3311, 2967, 1783, 1661 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.34 (s, 6H), 1.57 (s, 9H), 1.96 (s, 3H), 2.23 (s, 3H), 2.94 (d, *J* = 2.5, 2H), 6.20 (t, *J* = 2.5, 1H), 6.44 (bs, 1H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 9.9, 11.3, 25.9, 29.2, 40.9, 41.0, 81.6, 97.8, 120.9, 121.1, 126.9, 127.0, 148.3, 162.3, 178.9; Anal. Calcd. for $C_{18}H_{25}NO_4$: C, 67.69; H, 7.89; N, 4.39. Found: C, 67.69; H, 7.77; N, 4.42.

***Z*-5-[1-(4,4-Dimethyl-5-oxo-dihydrofuran-2-ylidene)-phenyl-methyl]-3,4-dimethyl-1*H*-pyrrole-2-carboxylic acid, *tert*-butyl ester (12c).** This material was prepared in 85% yield from 4.00 g (12.5 mmol) of iodopyrrole **11,** 3.70 g (18.3 mmol) of alkyne acid **10c,** 4.46 g (14.0 mmol) of $BnNEt_3Cl$ and 1.42 g (1.1 mmol) of $Pd(Ph_3P)_4$ in 175 ml of 5:1 acetontrile/Et_3N (17 h) following an identical procedure to that described above for **12a**; mp 129 °C; R_f (1:5 EtOAc/hexanes) 0.60; IR (thin film) 3289, 3056, 1800, 1672 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.38 (s, 6H), 1.60 (s, 9H), 1.91 (s, 3H), 2.33 (s, 3H), 2.72 (s, 2H), 7.31-7.39 (m, 5H), 8.59 (bs, 1H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 9.7, 11.0, 25.0, 28.7, 39.7, 41.8, 80.9, 109.8, 119.9, 120.5, 126.1, 127.3, 128.4 (2C), 128.8 (2C), 128.9, 135.9, 147.2, 161.6, 179.9; Anal. Calcd. for $C_{24}H_{29}NO_4$: C, 72.89; H, 7.39; N, 3.54. Found: C, 72.71; H, 7.43; N, 3.55.

***Z*-5-(3,3-Dimethyl-5-oxo-dihydrofuran-2-ylidenemethyl)-3,4-dimethyl-1*H*-pyrrole-2-carboxylic acid, *tert*-butyl ester (12d).** This material was prepared in 74% yield from 1.0 g (3.1 mmol) of iodopyrrole **11**, 780 mg (6.2 mmol) of alkyne acid **10d**, 706 mg (3.1 mmol) of $BnNEt_3Cl$ and 360 mg (.31 mmol) of $Pd(Ph_3P)_4$ in 24 mL of 5:1 acetonitrile/Et_3N (3 h) following an identical procedure to that described above for **12a**; mp 180 °C; R_f (1:4 EtOAc/hexanes) 0.23; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.33

(s, 6H), 1.63 (s, 9H), 1.92 (s, 3H); 2.28 (s, 3H); 2.62 (s, 2H); 6.09 (s, 1H); 8.50 (br s, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 9.9, 11.0, 27.3, 28.8, 39.9, 44.9; 80.9, 96.9, 120.1, 120.1, 124.6, 126.4, 161.8, 162.1, 172.9; MS (FAB) m/z (%): 321 (15), 320 (29, M^++1), 319 (58, M^+), 266 (11), 265 (23), 264 (100), 263 (87), 262 (23), 248 (14), 246 (24), 179 (18), 152 (10); HRMS (FAB) Calcd for $C_{18}H_{25}NO_4$: 319.1784; found: 319.1784; Anal. Calcd for $C_{18}H_{25}NO_4$: C, 67.69; H, 7.89; N, 4.39; O, 20.04. Found: C, 67.93; H, 7.94; N, 4.38.

5-[1-(4,4-Dimethyl-5-oxo-pyrrolidin-2-ylidene)-ethyl]-3,4-dimethyl-1*H*-pyrrole-2-carboxylic acid, *tert*-butyl ester (13a). A solution of 7.26 g (21.8 mmol, 1.0 eq) of lactone **12a** in 20 ml of freshly distilled THF was fitted with a dry ice/acetone condenser, cooled to -78 °C under argon, and treated dropwise with 20 mL of dry liquid NH_3. After addition was complete, the orange reaction solution was maintained at reflux (-33 °C) for 5 h, and then allowed to warm slowly to rt to evaporate excess NH_3. The remaining solution was concentrated to dryness under reduced pressure. The residue was taken up in 200 mL of dry $CHCl_3$ and treated with 0.59g (3.1 mmol, 0.14 eq) of crystallized *p*-TsOH.H_2O to effect dehydration (similar results were obtained with Montmorillonite clay). After stirring 1 h at rt, the reaction was added dropwise to ice cold pH 8 buffer, and the aqueous layer was extracted with $CHCl_3$. The combined organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. Trituration of the residue with CH_2Cl_2 afforded 1.44 g (20%) of the insoluble *E*-**13a** as a pale yellow powder. The CH_2Cl_2 washings were concentrated under reduced pressure and chromatographed (silica gel, 3:7 EtOAc/Pet ether) to afford 3.51 g (48%) of *Z*-**13a** as a pale yellow crystalline solid (total 68%).

E-**13a**: mp 259 °C (d); R_f (1:3 EtOAc/hexanes) 0.29; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.31 (s, 6H); 1.60 (s, 9H), 1.89 (t, J = 1.2, 3H), 1.90 (s, 3H), 2.26 (s, 3H), 2.70 (q, J = 1.2, 2H), 8.47 (br s, 1H); MS (EI) m/z (%): 332 (32, M^+), 277 (20), 276 (100), 259 (15), 258 (24), 243 (22), 230 (17), 215 (17); HRMS (FAB) Calcd for $C_{19}H_{28}N_2O_3$: 332.2100; found: 332.2096. Anal. Calcd for $C_{19}H_{28}N_2O_3$: C, 68.65; H, 8.49; N, 8.43; O, 14.44; found: C, 68.56; H, 8.61; N, 8.32.

Z-**13a**: mp 189-90 °C; R_f (1:3 EtOAc/hexanes) 0.16; ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.51 (br s, 1H), 7.89 (br s, 1H), 2.46 (q, J = 1.5), 2.27 (s, 3H), 1.93 (t, J = 1.5, 3H), 1.92 (s, 3H), 1.61 (s, 9H), 1.23 (s, 6H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 10.2, 11.0, 17.5, 25.4, 28.8, 41.0, 41.2, 80.7, 100.0, 117.9, 119.4, 126.4, 132.5, 134.9, 161.8, 183.1. Anal. Calcd for $C_{19}H_{28}N_2O_3$: C, 68.65; H, 8.49; N, 8.43; O, 14.44; found: C, 68.61; H, 8.54; N, 8.36

5-[1-(4,4-Dimethyl-5-oxo-pyrrolidin-2-ylidene)-methyl]-3,4-dimethyl-1*H*-pyrrole-2-carboxylic acid, *tert*-butyl ester (13b). This material was prepared in 89% (*E*:*Z* = 1:4) yield from 1.26 g (3.94 mmol) of lactone **12b** in 20 mL of THF/20 mL of ammonia (2h) and 1.92 g of Montmorillonite clay in 30 mL of THF (12 h), following an identical procedure to that described above for **13a**.

E-**13b**: mp 206 °C (d); R_f (1:1 EtOAc/hexanes) 0.73; IR (thin film) 3300, 2967, 1722, 1650 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.27 (s, 6H), 1.56 (s, 9H), 1.92 (s, 3H), 2.23 (s, 3H), 2.72 (d, J = 1.5, 2H), 5.31 (br t, 1H), ; ^{13}C NMR (300 MHz, CDCl$_3$, Compound isomerized during acquisition) Anal. Calcd. for $C_{18}H_{26}N_2O_3$: C, 67.90; H, 8.23; N, 8.80. Found: C, 67.72; H, 8.41; N, 8.89.

Z-**13b**: mp 227 °C (d); R_f (1:1 EtOAc/hexanes) 0.40; IR (thin film) 3300, 2956, 1717, 1650 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.29 (s, 6H), 1.58 (s, 9H), 1.96 (s, 3H), 2.23 (s, 3H), 2.86 (d, J = 2.0, 2H), 5.75 (t, J = 2.0, 1H), ; ^{13}C NMR (300 MHz, CDCl$_3$, Compound isomerized during acquisition) Anal. Calcd. for $C_{18}H_{26}N_2O_3$: C, 67.90; H, 8.23; N, 8.80. Found: C, 67.72; H, 8.41; N, 8.89.

5-[1-(4,4-Dimethyl-5-oxo-pyrrolidin-2-ylidene)-phenyl-methyl]-3,4-dimethyl-1*H*-pyrrole-2-carboxylic acid, *tert*-butyl ester (13c) This material was prepared in 75% (*E*:*Z* = 1:1) yield from 1.05 g (2.66 mmol) of lactone **12c** in 15 mL of THF/15 mL of ammonia (2h) and 1.50 g of Montmorillonite clay in 25 mL of THF (12 h), following an identical procedure to that described above for **13a**.

E-**13c**: R_f (1:3 EtOAc/hexanes) 0.23; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.30 (s, 6H), 1.58 (s, 9H), 1.85 (s, 3H), 2.28 (s, 3H), 2.65 (d, 2H), 7.13-7.39 (m, 5H), 8.62 (br s, 1H); Anal. Calcd. for $C_{24}H_{30}N_2O_3$: C, 73.07; H, 7.66; N, 7.10. Found: C, 73.09; H, 7.52; N, 7.19.

Z-**13c**: mp 110 °C; R_f (1:3 EtOAc/hexanes) 0.28; IR (thin film) 3291, 3054, 1781, 1652 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.30 (s, 6H), 1.58 (s, 9H), 1.92 (s, 3H), 2.31 (s, 3H), 2.91 (s, 2H), 7.13-7.39 (m, 5H), 8.46 (br s, 1H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 9.9, 10.9, 25.3, 28.7, 41.4, 41.8, 80.8, 107.0, 119.3, 120.7, 126.3, 126.8, 128.6 (2C), 128.7 (2C), 136.8, 138.4, 161.5, 181.6; Anal. Calcd. for $C_{24}H_{30}N_2O_3$: C, 73.07; H, 7.66; N, 7.10. Found: C, 73.09; H, 7.52; N, 7.19.

***Z*-5-(3,3-Dimethyl-5-oxo-pyrrolidin-2-ylidenemethyl)-3,4-dimethyl-1*H*-pyrrole-2-carboxylic acid, *tert*-butyl ester (13d).**[7,8]. This material was prepared in 76% yield from 121.6 mg (.38 mmol) of lactone **12d** in 1 mL of THF/1 mL of ammonia (2 h) and 200 mg of Montmorillonite clay in 2 mL of THF (2 h), following an identical procedure to that described above for **13a**; Orange foam; R_f (1:3 EtOAc/hexanes) 0.10; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.38 (s, 6H), 1.57 (s, 9H), 1.95 (s, 3H), 2.24 (s, 3H), 2.43 (s, 2H), 5.30 (s, 1H), 8.48 (br s, 1H), 8.98 (br s, 1H).

***Z*-5-[1-(5-Formyl-4,4-dimethyl-3,4-dihydropyrrol-2-ylidene)-ethyl]-3,4-dimethyl-1*H*-pyrrole-2-carboxylic acid, *tert*-butyl ester (15a).** A solution of 13.1 mg (36 μmol) of **16a** in 1 mL of 1,4-dioxane was treated with 6 mg (54 μmol) of SeO_2 under argon, and the reaction was heated at reflux for 30 min. At the end of this period the reaction was cooled to rt and treated with sat'd. $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2, and the combined organic extracts were dried over $MgSO_4$, filtered, and concentrated to dryness under reduced pressure. The residue was purified by flash chromatography (silica gel, EtOAc:hexanes = 1:15) to afford 4.3 mg (32%) of aldehyde **15a** as an unstable yellow oil. R_f (1:4 EtOAc/hexanes) 0.70; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.40 (s, 6H), 1.62 (s, 9H), 2.25 (s, 6H), 2.31 (s, 3H), 2.76 (s, 2H), 9.93 (s, 1H).

***Z*-3,4-Dimethyl-5-[1-(4,4,5-trimethyl-3,4-dihydropyrrol-2-ylidene)-ethyl]-1*H*-pyrrole-2-carboxylic acid, *tert*-butyl ester (16a).** A solution of 1.1 g (3.5 mmol) of ZnI_2 in 4 mL of THF was treated with 1.1 mL (3.5 mmol) of 3 M MeMgBr in Et_2O under argon. The resultant suspension was then treated dropwise with 127.6 mg (.35 mmol) of sulfide *Z*-**18a** in 10 mL of toluene, followed by 20 mg (35 μmol) of $PdCl_2(PPh_3)_2$. After addition was complete, the reaction was heated at 70 °C for 1 h (vigorous stirring), cooled to rt, and partitioned between CH_2Cl_2 and sat'd. NH_4Cl. The aqueous layer was extracted with CH_2Cl_2, and the combined organic extracts were dried over $MgSO_4$, filtered and concentrated to dryness under reduced pressure. The residue was purified by flash chromatography (silica gel, EtOAc:hexanes = 1:9) to afford 102.7 mg (88%) of **16a** as a colorless crystalline solid, mp 168-69 °C. R_f (1:9 EtOAc/hexanes) 0.36; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.23 (s, 6H), 1.62 (s, 9H), 2.13 (s, 3H), 2.16 (s, 3H), 2.20 (s, 3H), 2.31 (s, 3H), 2.61 (q, J = 1.0, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.5, 11.7, 15.9, 18.4, 26.3, 28.9, 47.9, 79.8, 114.4, 118.4, 128.7, 128.8, 134.0, 149.0, 161.4, 185.4; MS (FAB) m/z (%): 331 (52, M^++1), 330 (63, M^+), 257 (100), 274 (73), 273 (28), 257 (45), 231 (28), 166 (27); HRMS (FAB) Calcd for $C_{20}H_{30}N_2O_7$: 330.2307; found: 330.2307. Anal. Calcd for $C_{20}H_{30}N_2O_2$: C, 72.69; H, 9.15; N, 8.48; O, 9.68; found: C, 72.68; H, 9.18; N, 8.46.

5-[1-(4,4-Dimethyl-5-thioxopyrrolidin-2-ylidene)-ethyl]-3,4-dimethyl-1*H*-pyrrole-2-carboxylic acid, *tert*-butyl ester (17a). A solution of 700 mg (2.1 mmol) of lactam **13a** (*Z/E*= 2:1) and 500 mg (1.2 mmol) of Lawesson's reagent in 60 mL of toluene was stirred for 1 h at 100 °C under argon. An additional 150 mg (370 μmol) of Lawesson's reagent was added, and stirring and heating was continued for 20 min. The reaction was then cooled to rt, diluted with H_2O and the aqueous layer was extracted with EtOAc. The combined organic extracts were dried over $MgSO_4$, filtered and concentrated to dryness under reduced pressure. The residue was purified by flash chromatography (silica gel, EtOAc:hexanes = 1:15 to 1:3) to afford 998 mg (99%) of thiolactam **17a** as a 2:1 mixture of *Z*- and *E*-isomers.

E-**17a**: Yellow solid; mp: 139 °C; R_f (1:4 EtOAc/hexanes) 0.50; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.40 (s, 6H), 1.61 (s, 9H), 1.92 (s, 3H), 1.93 (t, *J* = 1.3, 3H), 2.27 (s, 3H), 2.81 (q, *J* = 1.3, 2H), 8.44 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.0, 11.0, 18.4, 28.7, 28.9, 41.1, 50.4, 80.7, 102.8, 118.0, 120.6, 126.7, 130.9, 137.3, 161.9, 213.3.

Z-**17a**: Yellow crystalline solid; mp 142-43 °C R_f (1:4 EtOAc/hexanes) 0.50; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.38 (s, 6H), 1.61 (s, 9H), 1.92 (s, 3H), 1.99 (t, *J* = 1.7, 3H), 2.27 (s, 3H), 2.59 (q, *J* = 1.7, 2H), 8.53 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.2, 11.1, 18.2, 28.5, 28.8, 42.3, 50.4, 80.8, 103.7, 118.0, 119.8, 126.5, 132.6, 138.3, 162.0, 214.8; MS (EI) m/z (%): 348 (41, M$^+$), 293 (19), 292 (93), 275 (10), 274 (13), 259 (17), 245 (13), 235 (27), 231 (13), 192 (12), 180 (15), 179 (100), 139 (21), 133 (10), 122 (12), 121 (29), 91 (13), 57 (20); HRMS (FAB) Calcd for $C_{19}H_{28}N_2O_3S$: 348.1872; found: 348.1866. Anal. Calcd for $C_{19}H_{28}N_2O_2S$: C, 65.48; H, 8.10; N, 8.04; O, 9.18; S, 9.20; found C, 65.44; H, 8.11; N, 7.99.

***Z*-5-[1-(4,4-Dimethyl-5-thioxopyrrolidin-2-ylidene)-methyl]-3,4-dimethyl-1*H*-pyrrole-2-carboxylic acid, *tert*-butyl ester (17b).** This material was prepared in 91% (trace amounts of *E*-isomer) yield from 550 mg (1.73 mmol) of lactam **13b** and 432 mg (1.07 mmol) of Lawesson's reagent in 40 mL of toluene (30 min at reflux) following an identical procedure to that described for **17a.** Yellow solid; mp: 215 °C R_f (1:9 EtOAc/hexanes) 0.16; IR (thin film) 3289, 2967, 1656 cm^{-1}; 1H NMR (300 MHz, $CDCl_3$) δ 1.35 (s, 6H), 1.59 (s, 9H), 1.97 (s, 3H), 2.23 (s, 3H), 2.96(d, J = 2.0, 2H), 6.00 (t, J = 2.0, 1H), 8.54, (br s, 1H), 10.37 (br s, 1H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 9.9, 11.3, 29.3, 29.5, 42.3, 51.6, 81.6, 96.6, 121.0, 121.1, 127.0, 129.0, 139.0, 162.5, 215.0; Anal. Calcd. for $C_{18}H_{26}N_2O_2S$: C, 64.64; H, 7.84; N, 8.38; Found C, 64.43; H, 7.97; N, 8.24.

5-[1-(4,4-Dimethyl-5-thioxopyrrolidin-2-ylidene)-phenyl-methyl]-3,4-dimethyl-1*H*-pyrrole-2-carboxylic acid, *tert*-butyl ester (17c). This material was prepared in 85% (*E:Z* = 1:2) yield from 520 mg (1.32 mmol) of lactam **13c** and 380 mg (0.94 mmol) of Lawesson's reagent in 30 mL of toluene (30 min at reflux) following an identical procedure to that described for **17a**. The reaction gave an inseparable mixture of *E*- and *Z*- isomers. R_f (1:3 EtOAc/hexanes) 0.71; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.35 (s, 6H), 1.36 (s, 6H), 1.55 (s, 9H), 1.56 (s, 9H), 1.80 (s, 3H), 1.91 (s, 3H), 2.24 (s, 3H), 2.29 (s, 3H), 2.77 (s, 2H), 3.01 (s, 2H), 7.12-7.40 (m, 10H), 8.32 (br s, 1H), 8.35 (br s, 1H), 8.62 (br s, 1H), 8.92 (br s, 1H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 10.0, 10.3, 11.0, 11.0, 28.5, 28.7, 28.7 (2C), 43.0, 43.2, 50.7, 51.1, 81.0, 81.1, 109.4, 109.6, 120.0, 120.1, 121.4, 126.3, 126.4, 127.4, 128.2, 128.8 (2C), 128.8 (2C), 128.9, 128.9, 129.7, 130.3, 137.5, 138.1, 138.8, 139.6, 161.4, 161.6, 213.8, 214.8; Anal. Calcd. for $C_{24}H_{30}N_2O_2S$: C, 70.21; H, 7.36; N, 6.82; Found: C, 70.43; H, 7.37; N, 6.74.

***Z*-5-(3,3-Dimethyl-5-thioxopyrrolidin-2-ylidenemethyl)-3,4-dimethyl-1*H*-pyrrole-2-carboxylic acid, *tert*-butyl ester (17d).** This material was prepared in 49% yield from 92.3 mg (.29 mmol) of lactam **13d** and 65 mg (161 μmol) of Lawesson's reagent in 1 mL of toluene (4 h at 100 °C) following an identical procedure to that described above for **17a**. Yellow solid; mp 199 °C; R_f (1:4 EtOAc/hexanes) 0.35; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.39 (s, 6H), 1.60 (s, 9H), 1.98 (s, 3H); 2.27 (s, 3H), 2.94 (s, 2H), 5.40 (s, 1H), 9.00 (br s, 1H), 9.45 (br s, 1H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 9.8, 10.9, 28.7, 28.7, 41.8, 57.4, 81.0, 91.9, 119.2, 120.9, 125.8, 127.1, 152.6, 161.7, 204.1; MS (EI) m/z (%): 334 (41, M$^+$), 279 (23), 278 (100), 263 (15), 261 (15), 260 (22), 245 (38), 232 (13), 205 (19), 77 (11), 57 (24); HRMS (FAB) Calcd for $C_{18}H_{26}N_2O_2S$: 334.1715; found: 334.1724

5-[1-(4,4-Dimethyl-5-methylsulfanyl-3,4-dihydropyrrol-2-ylidene)-ethyl]-3,4-dimethyl-1*H*-pyrrole-2-carboxylic acid, *tert*-butyl ester (18a). A solution of 235.5 mg (.68 mmol) of thiolactam **17a**

(*Z/E* 2:1) in 1 mL of THF was treated with 0.1 mL of MeI under argon. After heating at reflux for 1 h, an additional 0.1 mL of MeI was added, and heating was continued for 1 h. If necessary, this process was repeated once again before cooling to rt and diluting with CH_2Cl_2 and sat'd. $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2, and the combined organic extracts were dried over $MgSO_4$, filtered and concentrated to dryness under reduced pressure. The residue was purified by flash chromatography (silica gel, EtOAc:hexanes = 1:5) to afford 162.6 mg (66%) of *Z*-**18a** and 15.5 mg (6%) of *E*-**18a** as yellow solids.

E-**18a**: mp: 130 °C; R_f (1:9 EtOAc/hexanes) 0.59; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.31 (s, 6H), 1.61 (s, 9H), 2.14 (t, *J* = 1.0, 3H), 2.22 (s, 3H), 2.31 (s, 3H), 2.66 (s, 3H), 2.73 (q, *J* = 1.0, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.8, 11.8, 14.8, 18.3, 27.7, 29.0, 45.7, 49.1, 79.9, 112.0, 118.2, 119.2, 126.6, 132.5, 148.4, 161.7, 187.3; MS (EI) m/z (%): 362 (28, M^+), 307 (21), 306 (100), 291 (13), 273 (14), 181 (10), 57 (17), 56 (19); HRMS (FAB) Calcd for $C_{20}H_{30}N_2O_2S$: 362.2028; found: 362.2022.

Z-**18a**: mp 151 °C; R_f (1:9 EtOAc/hexanes) 0.47; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.22 (s, 6H), 1.60 (s, 9H), 1.96 (s, 3H), 2.27 (t, *J* = 1.7, 3H), 2.28 (s, 3H), 2.27 (q, *J* = 1.7, 2H), 2.58 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.4, 11.1, 13.7, 18.3, 27.2, 28.8, 45.2, 50.6, 80.5, 113.5, 117.7, 119.3, 126.4, 134.5, 152.2, 162.0, 187.1; MS (EI) m/z (%): 362 (30, M^+), 307 (22), 306 (100), 291 (13), 273 (15); HRMS (FAB) Calcd for $C_{20}H_{30}N_2O_2S$: 362.2028; found: 362.2028.

5-[1-(4,4-Dimethyl-5-methylsulfanyl-3,4-dihydropyrrol-2-ylidene)-ethyl]-3,4-dimethyl-1*H*-pyrrole-2-carbaldehyde (19a). A solution of 101.9 mg (.29 mmol) of thiolactam **17a** (Z/E 2:1) in 1 mL of TFA was degassed with argon, and after stirring 20 min at rt was treated with 0.3 mL of TMOF. After stirring an additional 20 min at rt, the reaction was concentrated and partitioned between CH_2Cl_2 and sat'd. $NaHCO_3$. The organic extracts were dried over $MgSO_4$, filtered and concentrated to dryness under reduced pressure. The residue was purified by flash chromatography (silica gel, EtOAc:hexanes = 1:5) to afford 29.2 mg (34%) of *Z*-**19a** and 29.2 mg (34%) of *E*-**19a** (total 68%).

E-**19a**: Yellow Solid; mp 128 °C; R_f (1:3 EtOAc/hexanes) 0.34; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.31 (s, 6H), 2.15 (s, 3H), 2.15 (t, *J* = 1.2, 3H), 2.23 (s, 3H), 2.29 (s, 3H), 2.70 (s, 3H), 2.76 (q, *J* = 1.2, 2H), 9.60 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.5, 14.8, 17.7, 27.7, 45.8, 49.2, 111.2, 128.5, 137.1, 150.6, 176.1, 189.4; MS (EI) m/z (%): 320 (28), 292 (20), 291 (24, M^++1), 290 (100, M^+), 276 (21), 275 (73), 273 (19), 247 (12), 243 (18), 215 (10), 196 (11), 148 (17), 120 (12), 91 (12); HRMS (FAB) Calcd for $C_{16}H_{22}N_2OS$: 290.1453; found: 290.1443.

Z-**19a**: Yellow solid; mp 162 °C; R_f (1:3 EtOAc/hexanes) 0.28; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.23 (s, 6H), 1.97 (s, 3H), 2.28 (t, *J* = 1.7, 3H), 2.30 (s, 3H), 2.48 (q, *J* = 1.7, 2H), 2.58 (s, 3H), 9.57 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.0, 13.8, 17.7, 27.2, 45.2, 50.8, 112.7, 119.0, 128.6, 132.6, 139.6, 153.1, 176.5, 188.4; MS (EI) m/z (%): 291 (22, M^++1), 290 (100, M^+), 276 (15), 275 (73), 247 (12), 243 (15), 148 (11), 120 (10); HRMS (FAB) Calcd for $C_{16}H_{22}N_2OS$: 290.1453; found: 290.1454.

***Z*-5-[1-(4,4-Dimethyl-5-methylsulfanyl-3,4-dihydropyrrol-2-ylidene)-methyl]-3,4-dimethyl-1*H*-pyrrole-2-carbaldehyde (19b).** This material was prepared in 68% (trace amounts of *E*-isomer) yield from 170 mg (0.51 mmol) of thiolactam **17b** and 5.9 mL of TFA (1 h) and 0.95 mL of TMOF (1 h) following an identical procedure to that described above for **19a**; Yellow solid; mp 188 °C; R_f (1:4 EtOAc/hexanes) 0.15; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.36 (s, 6H), 2.15 (s, 3H), 2.36 (s, 3H), 2.56 (s, 3H), 2.89 (d, *J* = 2.0, 2H), 6.52 (t, *J* = 2.0, 1H), 8.61 (br s, 1H), 9.56 (s, 1H); ^{13}C NMR (300 MHz, $CDCl_3$, Compound isomerized during acquisition) δ 8.6, 8.8, 8.9, 8.9, 13.9, 14.7, 27.2, 27.7, 45.3, 46.4, 50.0, 52.0, 100.5 (2C), 104.7 (2C), 121.7 (2C), 129.0, 129.3, 132.0 (2C), 135.2, 135.8, 175.9 (2C), 189.6, 192.4; Anal. Calcd. for $C_{15}H_{20}N_2OS$: C, 65.18; H, 7.29; N, 10.14; Found: C, 65.37; H, 7.11; N, 10.19.

***Z*-5-[1-(4,4-Dimethyl-5-methylsulfanyl-3,4-dihydropyrrol-2-ylidene)-phenyl-methyl]-3,4-dimethyl-1*H*-pyrrole-2-carbaldehyde (19c).** This material was prepared in 71% (*E/Z* = 1:4) yield from 150 mg (0.36 mmol) of thiolactam **17c** and 4.2 mL of TFA (1 h) and 0.80 mL of TMOF (1 h) following an identical procedure to that described above for **19a**; Yellow solid; mp 163 °C; R_f (1:4 EtOAc/hexanes) 0.38; IR (thin film) 3267, 3056, 1722, 1622 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.22 (s, 3H); 1.23 (s, 6H); 2.19 (s, 3H), 2.50 (s, 2H), 2.73 (s, 3H), 7.24-7.42 (m, 5H), 9.61 (s, 1H); 11.98 (br s, 1H); ^{13}C NMR (300 MHz, $CDCl_3$,) δ 8.9, 10.00, 14.9, 27.4, 46.4, 49.7, 117.9, 120.2, 127.5, 128.8, 128.9 (2C), 130.2 (2C), 131.6, 135.9, 139.4, 152.2, 176.3, 192.0; Anal. Calcd. for $C_{21}H_{24}N_2OS$: C, 71.55; H, 6.86; N, 7.95; Found: C, 71.61; H, 7.01; N, 7.81.

***Z*-5-(3,3-Dimethyl-5-methylsulfanyl-3,4-dihydropyrrol-2-ylidenemethyl)-3,4-dimethyl-1*H*-pyrrole-2-carbaldehyde (19d).** This material was prepared in 41% yield from 15.8 mg (47 μmol) of thiolactam **17d** and 0.1 mL of TFA (5 min) and 0.1 mL of TMOF (20 min) following an identical procedure to that described above for **19a**; Yellow solid; mp 158 °C; R_f (1:3 EtOAc/hexanes) 0.30; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.31 (s, 6H), 2.08 (s, 3H), 2.30 (s, 3H), 2.74 (s, 2H), 2.76 (s, 3H), 5.67 (s, 1H), 9.56 (s, 1H), 11.30 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.7, 14.9, 29.1, 43.3, 52.7, 89.0, 98.4, 119.0, 129.1, 130.9, 135.8, 164.9, 175.8, 180.4; MS (FAB) m/z (%): 279 (11), 278 (27), 277 (100, M^++1), 276 (55, M^+), 275 (23), 261 (21), 249 (20); HRMS (FAB): Calcd for $C_{15}H_{20}N_2O_4S$: 276.1296; found: 276.1295.

***Z*-3,4-Dimethyl-5-[1-(4,4,5-trimethyl-3,4-dihydropyrrol-2-ylidene)-ethyl]-1*H*-pyrrole-2-carbaldehyde (20a).** *Method A.* A solution of 37.3 mg (.11 mmol) of ester **16a** in 0.3 mL of TFA was stirred for 5 min under argon, and was then treated with 0.1 mL of TMOF. After stirring an additional 20 min at rt, the reaction was diluted with CH_2Cl_2 and sat'd. $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2, and the combined organic extracts were dried over $MgSO_4$, filtered and concentrated to dryness under reduced pressure. The residue was purified by flash chromatography (silica gel, EtOAc:hexanes = 1:4 to 1:3) to afford 19.0 mg (65%) of aldehyde **20a**, identical to the material prepared following *Method B* below.

Method B. A solution of 25.0 mg (0.086 mmol) of **19a** and 5 mg (7.1 μmol) of $PdCl_2(Ph_3P)_2$ in 1 mL of toluene was treated with 1.0 mL of MeZnI in THF under argon. After stirring for 30 min at 80°C (oilbath temperature), the mixture was cooled to rt and concentrated *in vacuo*. The residue was taken up in 5 mL of Et_2O and to it was added 5 mL of sat'd NH_4Cl. The mixture was stirred for 10 min at rt. The aqueous layer was extracted with Et_2O. The combined organic layers was washed with sat'd $NaHCO_3$, dried over $MgSO_4$, filtered and concentrated to dryness under reduced pressure. The residue was purified by flash chromatography (silica gel, EtOAc:hexanes = 1:4 to 1:3) to give 13.0 mg (62%) of the aldehyde **20a**. Off-white solid; R_f (1:2 EtOAc/hexanes) 0.27; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.23 (s, 6H), 2.13 (s, 3H), 2.19 (s, 3H), 2.20 (s, 3H), 2.29 (s, 3H), 2.61 (s, 2H), 9.61 (s, 1H); MS (FAB) m/z (%): 413 (26), 261 (16), 260 (27), 259 (100, M^++1), 258 (M^+), 257 (22), 243 (17), 231 (17), 150 (13), 122 (11); HRMS (FAB) Calcd for $C_{16}H_{22}N_2O$: 258.1732; found: 259.1811 (M+H).

***Z*-3,4-Dimethyl-5-[1-(4,4,5-trimethyl-3,4-dihydropyrrol-2-ylidene)-methyl]-1*H*-pyrrole-2-carbaldehyde (20b).** This material was prepared in 71% yield from 80 mg (0.29 mmol) of **19b** (*Z*-isomer only), 20 mg (0.03 mmol) of $PdCl_2(PPh_3)_2$ and 2.0 mL of freshly prepared MeZnI in THF in 2 mL of toluene (45 min, 75 °C) following an identical procedure to that described above for **20a**; white solid; mp 181 °C; R_f (40% EtOAc/hexanes) 0.10; ^{1}H NMR 1.21 (s, 6H); 2.03 (s, 3H); 2.19 (s, 3H); 2.26 (s, 3H); 2.61 (d, *J* = 2.0, 2H); 5.85 (t, *J* = 2.0 Hz, 1H), 9.57 (s, 1H); Anal. Calcd. for $C_{15}H_{20}N_2O$: C, 73.74; H, 8.25; N, 11.47; Found: C, 73.57; H, 8.41; N, 11.21.

***Z*-3,4-Dimethyl-5-[phenyl-(4,4,5-trimethyl-3,4-dihydropyrrol-2-ylidene)-phenyl-methyl]-1*H*-pyrrole-2-carbaldehyde (20c).** This material was prepared in 73% yield from 100 mg (0.25 mmol) of **19c** (*Z*-isomer only), 17.9 mg (0.025 mmol) of $PdCl_2(PPh_3)_2$ and 1.7 mL of freshly prepared MeZnI in THF in 2 mL of toluene (30 min, 75 °C) following an identical procedure to that described above for **20a**; off-white solid; mp 167 °C; R_f (1:4 EtOAc/hexanes) 0.29; IR (thin film) 3221, 2923, 1727, 1623 cm^{-1}; ^1H NMR 1.14 (s, 6H); 1.23 (s, 3H); 2.19 (s, 3H); 2.22 (s, 3H); 2.40 (s, 2H); 7.22-7.39 (m, 5H); 9.61(s, 1H); 11.47 (br s, 1H); ^{13}C NMR (300 MHz, $CDCl_3$,) δ 8.9, 9.9, 16.2, 25.8, 44.7, 48.4, 120.2, 120.5, 127.4, 128.8 (2C), 128.8, 129.9 (2C), 131.8, 135.8, 139.6, 153.4, 176.6, 189.8; Anal. Calcd. for $C_{21}H_{24}N_2O$: C, 78.71; H, 7.55; N, 8.74; Found: C, 78.89; H, 7.56; N, 8.69.

***Z*-3,4-Dimethyl-5-(3,3,5-trimethyl-3,4-dihydropyrrol-2-ylidenemethyl)-1*H*-pyrrole-2-carbaldehyde (20d).** This material was prepared in 57% yield from 100 mg (.36 mmol) of **19d**, 10 mg (14 µmol) of $PdCl_2(Ph_3)_2$ and 2.0 mL of MeZnI in THF in 2 mL of toluene (30 min, 75 °C) following an identical procedure to that described above for **20a**; orange solid, mp 161 °C; R_f (1:2 EtOAc/hexanes) 0.21.; ^1H NMR (300 MHz, $CDCl_3$) δ 1.26 (s, 6H), 2.07 (s, 3H), 2.29 (s, 3H), 2.37 (d, *J* = 0.5, 3H), 2.58 (s, 2H), 5.72 (s, 1H), 9.60 (s, 1H), 11.2 (br s, 1H); MS (EI) m/z (%): 245 (17, M^++1), 244 (100, M^+), 229 (61), 202 (14), 201 (80); HRMS (FAB) Calcd for $C_{15}H_{20}N_2O$: 244.1576; found: 244.1579.

5-[1-(5-Formyl-4,4-dimethyl-3,4-dihydropyrrol-2-ylidene)-ethyl]-3,4-dimethyl-1*H*-pyrrole-2-carbaldehyde (7a). A solution of 583 mg (2.7 mmol) of aldehyde **20a** in 30 mL of 1,4-dioxane was treated with 400 mg (3.6 mmol) of SeO_2 under argon, and stirred for 2 h at rt. The reaction was then partitioned between CH_2Cl_2 and sat'd. $NaHCO_3$, and the aqueous layer was extracted with CH_2Cl_2. The combined organic extracts were dried over $MgSO_4$, filtered and concentrated to dryness under reduced pressure. The residue was purified by flash chromatography (silica gel, EtOAc:hexanes = 1:4 to 1:3) to afford 670 mg (99%) of dialdehyde **7a** as an unstable yellow oil (E/Z =1:5, inseparable mixture). R_f (1:2 EtOAc/hexanes) 0.34; ^1H NMR (300 MHz, $CDCl_3$) δ (*Z-isomer*): 1.31 (s, 6H), 2.16 (t, *J* = 1.4, 3H), 2.14 (s, 3H), 2.22 (s, 3H), 2.66 (q, *J* = 1.4, 2H), 9.60 (s, 1H), 9.89 (s, 1H); (*E-isomer*): 1.34 (s, 6H), 1.47 (s, 3H), 2.03 (s, 3H), 2.44 (t, *J* = 1.9, 3H), 2.56 (q, *J* = 1.9, 2H), 9.65 (s, 1H), 9.94 (s, 1H).

***Z*-5-[1-(5-Formyl-4,4-dimethyl-3,4-dihydropyrrol-2-ylidene)-methyl]-3,4-dimethyl-1*H*-pyrrole-2-carbaldehyde (7b).** This material was prepared in 68% yield from 20 mg (0.08 mmol) of **20b** and 14 mg (0.13 mmol) of SeO_2 in 1 mL of dioxane following an identical procedure to that described above for **7a**; Unstable brown solid; R_f (40% EtOAc/hexanes) 0.36 ^1H NMR (300 MHz, $CDCl_3$) δ 1.38 (s, 6H); 2.07 (s, 3H); 2.28 (s, 3H); 2.75 (d, J = 2.0, 2H);. 6.27 (t, J = 2.0, 1H); 9.66 (s, 1H), 10.02 (s, 1H), 10.8 (br s, 1H).

***Z*-5-[1-(5-Formyl-4,4-dimethyl-3,4-dihydropyrrol-2-ylidene)-phenyl-methyl]-3,4-dimethyl-1*H*-pyrrole-2-carbaldehyde (7c).** This material was prepared in 62% yield from 40 mg (0.12 mmol) of **20c** and 21 mg (0.19 mmol) of SeO_2 in 1 mL of dioxane following an identical procedure to that described above for **7a**; Unstable brown solid; R_f (20% EtOAc/hexanes) 0.36 ^1H NMR (300 MHz, $CDCl_3$) δ 1.28 (s, 3H); 1.31 (s, 6H); 2.22 (s, 3H); 2.54 (2H);. 7.25-7.48 (m, 5H); 9.70(s, 1H), 10.03 (s, 1H), 11.05 (br s, 1H).

5-(5-Formyl-3,3-dimethyl-3,4-dihydropyrrol-2-ylidenemethyl)-3,4-dimethyl-1*H*-pyrrole-2-carbaldehyde (7d). This material was prepared in 99% yield from 55.8 mg (229 µmol) of **20d**, and 38 mg (342 µmol) of SeO_2 in 2 mL of dioxane (2 h) following an identical procedure to that described above for **7a**; Unstable yellow solid; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.31 (s, 6H), 2.13 (s, 3H), 2.31 (s, 3H), 2.77 (s, 2H), 6.17 (s, 1H), 9.70 (s, 1H), 10.10 (s, 1H), 10.8 (br s, 1H).

2,2,5,7,8,12,13,17,18-Nonamethyl-2,3-dihydroporphyrin (9ae). A mixture of 42.8 mg (147 μmol) of diacid **8e**[3,4] and 63.9 mg (234 μmol) of freshly prepared dialdehyde **7a** was taken up in 1 ml of TFA, and the resultant solution was stirred for 2 h at rt under argon. The reaction mixture was then concentrated under reduced pressure and partitioned between sat'd. NaHCO$_3$ and CH$_2$Cl$_2$. The aqueous layer was extracted with CH$_2$Cl$_2$, and the combined organic extracts were dried over MgSO$_4$, filtered and concentrated to dryness under reduced pressure. The residue was purified by flash chromatography (silica gel, EtOAc:hexanes = 1:4) to yield 28.4 mg (44%) of chlorin **9ae** as green solid, mp >300 °C. R$_f$ (1:2 EtOAc/hexanes) 0.55; ^{1}H NMR (300 MHz, CDCl$_3$) δ -2.39 (s, 2H), 2.10 (s, 6H), 3.43 (s, 3H), 3.45 (s, 3H), 3.49 (s, 3H), 3.52 (s, 6H), 3.56 (s, 3H), 3.89 (s, 3H), 4.49 (s, 2H), 8.82 (s, 1H), 9.59 (s, 1H), 9.76 (s, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 11.6, 11.6, 11.9, 12.0, 12.1, 16.6, 21.5, 32.1, 46.1, 52.4, 90.7, 97.5, 99.1, 105.1, 128.1, 129.4, 131.1, 132.9, 133.0, 134.8, 135.0, 136.1, 137.2, 138.0, 149.6, 152.1, 161.5, 172.0; UV(CHCl$_3$): λ_{max} (ε, lmol^{-1}cm^{-1}) = 376 (26,393), 382 (27,121), 386 (26,882), 394 (25,600), 400 (25,277), 406 (23,392), 502 (7,362), 596 (2,632), 648 (15,357) nm; MS (EI) m/z (%): 440 (36), 439 (100, M$^+$+1), 438 (27, M$^+$), 307 (19), 289 (10); HRMS (FAB) Calcd for C$_{29}$H$_{34}$N$_4$: 438.2783; found: 439.2863 (M+H).

13,17-Bis(2-methoxycarbonylethyl)-2,2,5,7,8,12,18-heptamethyl-2,3-dihydroporphyrin (9af). This material was prepared in 42% yield form 669.6 mg (2.46 mmol) of dialdehyde **7a** and 467.6 mg (1.08 mmol) of diacid **8f**[5,6] in 10 mL of TFA (1.5 h) following an identical procedure to that described above for **9ae**; mp 198 °C; R$_f$ (1:1 EtOAc/hexanes) 0.57; ^{1}H NMR (300 MHz, CDCl$_3$) δ -2.46 (br s, 2H), 2.07 (s, 6H), 3.20 (t, J = 7.9, 2H), 3.24 (t, J = 7.9, 2H), 3.48 (s, 3H), 3.51 (s, 3H), 3.52 (s, 3H), 3.56 (s, 3H), 3.72 (s, 3H), 3.73 (s, 3H), 3.91 (s, 3H), 4.23 (t, J = 7.9, 2H), 4.35 (t, J = 7.9, 2H), 4.51 (s, 2H), 8.86 (s, 1H), 9.65 (s, 1H), 9.80 (s, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 11.6, 11.9, 12.0, 16.5, 21.3, 21.9, 22.3, 32.1, 37.1, 37.5, 46.1, 52.0, 52.1, 52.4, 91.2, 97.6, 99.0, 105.4, 128.6, 131.5, 129.7, 133.6, 135.5, 135.5, 137.8, 137.9, 138.5, 138.9, 149.3, 150.3, 162.3, 172.1, 173.9, 174.3; UV(CHCl3): λ_{max} (ε, lmol^{-1}cm^{-1}) = 396 (62,408), 504 (11,162), 648 (30,397) nm; MS (EI) m/z (%): 583 (22, M$^+$+1), 582 (56, M$^+$), 446 (35), 436 (21), 434 (26), 423 (36), 407 (46), 406 (66), 405 (100), 391 (52), 390 (20), 363 (26), 362 (48), 261 (53), 258 (31), 243 (32), 229 (25), 215 (28), 166 (22), 150 (46), 148 (26), 120 (21), 57 (28), 55 (21); HRMS (FAB) Calcd for C$_{35}$H$_{42}$N$_4$O$_4$: 582.3206; found: 582.3212.

2,2,7,8,12,13,17,18-Octamethyl-2,3-dihydroporphyrin (9be) This material was prepared in 38% yield from 5.42 mg (0.021mmol) of dialdehyde **7b** and 6.10 mg (0.021 mmol) of diacid **8e**[5,6] in 0.5 mL of TFA (1.5 h) following an identical procedure to that described above for **9ae**; R$_f$ (30% EtOAc/hexanes) 0.65; ^{I}H NMR (500 MHz, CDCl$_3$) δ -2.58 (br s, 1H); 2.06 (s, 6H); 3.40 (s, 6H); 3.44 (s,3H); 3.51 (s, 3H); 3.52 (s, 3H); 4.64 (s, 2H), 8.79 (s, 1H), 8.92 (s, 1H), 9.69 (s, 1H), 9.71 (s, 1H); UV (CHCl$_3$):λ_{max}(ε) = 394 (72,233), 502 (6,245), 648 (21,162); HRMS (FAB) Calcd for C$_{28}$H$_{32}$N$_4$: 424.2627; found: 425.2629 (M+H).

13,17-Bis(2-methoxycarbonylethyl)-2,2,7,8,12,18-hexamethyl-2,3-dihydroporphyrin (9bf). This material was prepared in 39% yield from 6.20 mg (0.024mmol) of dialdehyde **7b** and 10.6 mg (0.024 mmol) of diacid **8f**[5,6] in 0.5 mL of TFA (1.5 h) following an identical procedure to that described above for **9ae**; R$_f$ (30% EtOAc/hexanes) 0.35; ^{I}H NMR (500 MHz, CDCl$_3$) δ -2.58 (br s, 1H); 2.06 (s, 6H); 3.17 (t, J = 7.5, 2H); 3.22 (t, J = 8.0, 2H), 3.41 (s, 3H), 3.45 (s, 3H); 3.49 (s, 3H); 3.67 (s, 3H), 3.68 (s, 3H); 4.22 (t, J = 8.0, 2H), 4.35 (t, J = 7.5, 2H), 4.66 (s, 2H), 8.83 (s, 1H), 8.95 (s, 1H); 9.73 (s, 1H); 9.79 (s, 1H); UV (CHCl$_3$):λ_{max}(ε) = 394 (82,200), 504 (7,900), 648 (27,300); HRMS (FAB) Calcd for C$_{34}$H$_{40}$N$_4$O$_4$: 568.7060; found: 568.7064.

2,2,7,8,12,13,17,18-Octamethyl-5-phenyl-2,3-dihydroporphyrin (9ce). This material was prepared in 40% yield from 20.0 mg (0.06mmol) of dialdehyde **7c** and 17.4 mg (0.06 mmol) of diacid **8e**[5,6] in 1.0 mL of TFA (1.5 h) following an identical procedure to that described above for **9ae**; R*f* (30% EtOAc/hexanes) 0.71; ^{I}H NMR (500 MHz, $CDCl_3$) δ -2.40 (br s, 1H);-2.08 (br s, 1H), 1.96 (s, 6H), 2.41(s, 3H); 3.41 (s, 3H); 3.42 (s, 3H); 3.45 (s, 3H); 3.51 (s, 3H); 4.10 (s, 2H); 7.70-7.72 (m, 2H); 7.84-7.86 (m, 3H); 8.79 (s, 1H); 9.63 (s, 1H); 9.77 (s, 1H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 11.6, 11.6, 12.0 (2C), 12.0, 14.0, 31.8, 46.1, 52.8, 92.0, 98.3, 99.4, 111.7, 127.7, 128. 5 (2C), 129.4, 129.4, 131.8, 132.5 (2C), 133.4, 134.5, 135.0, 136.3, 136.8, 137.1, 138.6, 144.1, 149.8, 159.1, 161.9, 173.2; UV ($CHCl_3$):λ_{max}(ε) = 395 (79,100), 495 (6,900), 648 (22,200); HRMS (FAB) Calcd for $C_{34}H_{36}N_4$: 500.2940; found: 501.2948

13,17-Bis(2-methoxycarbonylethyl)-2,2,7,8,12,18-hexamethyl-5-phenyl-2,3-dihydroporphyrin (9cf). This material was prepared in 39% yield from 10.0 mg (0.03mmol) of dialdehyde **7c** and 12.0 mg (0.03 mmol) of diacid **8f**[5,6] in 0.5 mL of TFA (1.5 h) following an identical procedure to that described above for **9ae**; R*f* (30% EtOAc/hexanes) 0.45; ^{I}H NMR (500 MHz, $CDCl_3$) δ -2.42 (s, 1H); -1.97 (br s, 1H); 1.95 (s, 6H); 2.41 (s, 3H); 3.18-3.25 (m, *J* = 7.5, 8.0, 4H); 4.21 t, J = 8.0, 2H); 4.34 (t, J = 7.5, 2H); 7.70-7.73 (m, 2H); 7.83-7.85 (m, 3H); 8.82 (s, 1H); 9.66 (s, 1H); 9.79 (s, 1H), UV ($CHCl_3$):λ_{max}(ε) = 399 (117,000), 498 (9,833), 648 (32,333); HRMS (FAB) Calcd for $C_{34}H_{36}N_4$: 644.3363; found: 644.3364.

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