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SYNLETT SUPPORTING INFORMATION

For

Synthesis of Chlorin Derivatives by Diels-Alder Cycloadditions of Pheophorbide a and its Derivatives
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S1. General comments

All chemicals were purchased from commercial sources (Sigma Aldrich or Alfa Aesar) and were used as received. Microwave reactions were performed on CEM Discover Microwave Synthesis System with Explorer monomode reactor. High pressure reactions were performed in Teflon cells (V=1.5 mL) using a high-pressure piston cylinder apparatus (Unipress, Polish Academy of Sciences), and pentane as pressure transmitting liquid. ¹H and ¹³C NMR spectra were recorded on a Brucker Avance (300 and 600 MHz) spectrometers with tetramethylsilane as an internal standard. UV spectra were measured on a Varian Cary 100 Bio UV/VIS spectrometer equipped with temperature controller.

S2. Synthesis of target compounds

Dimethyl pheophorbide a 1 was isolated from Spirulina pacifica by modified literature procedure.¹
Conc. H₂SO₄ (15 mL) was added dropwise at 0°C to a mixture of 30 g of Spirulina pacifica and MeOH (90 mL) in a 500 mL round bottomed flask and stirred at room temperature for 3 hours (with stopper), diluted with H₂O (200 mL), and filtered through a pad of Celite (1 cm high, Büchner funnel 8 cm diameter, Büchner flask 250 mL). The content of the filtrating funnel was washed with H₂O up to pH 7 (1 L), ethanol (150 mL), petrol ether (4x90 mL), and methyl pheophorbide
was removed from the filtrating funnel with acetone (360 mL). Solution was concentrated and the residue was washed with CH$_2$Cl$_2$-MeOH (1.5 mL+5 mL), then solvent removed by Pasteur pipette through a cotton wool, then CH$_2$Cl$_2$-MeOH (1.5 mL+10 mL) and finally washed with MeOH (15 mL) to give methyl pheophorbide a (90-140 mg) as a black powder.

$^1$H NMR (CDCl$_3$) $\delta$ -1.61 (1H, brs, NH), 0.56 (1H, br s, NH), 1.71 (t, $J$=7.7 Hz, 3H, 8$_2$-CH$_3$), 1.83 (d, $J$=8.0 Hz, 3H, 18-CH$_3$), 2.23-2.29 (m, 1H, 17$_1$-CH$_2$), 2.30-2.37 (m, 1H, 17$_1$-CH$_2$), 2.50-2.57 (m, 1H, 17$_2$-CH$_2$), 2.63-2.69 (m, 1H, 17$_2$-CH$_2$), 3.23 (s, 3H, 7-CH$_3$), 3.41 (s, 3H, 2-CH$_3$), 3.59 (s, 3H, 12-CH$_3$), 3.68 (q, $J$=7.7 Hz, 2H, 8$_1$-CH$_2$), 3.70 (s, 3H, -OCH$_3$), 3.89 (s, 3H, -OCH$_3$), 4.22 (d, $J$=9.1 Hz, 1H, 17-CH), 4.48 (q, $J$=8.0 Hz, 1H, 18-CH), 6.19 (d, $J$=11.3 Hz, 1H, 3$_2$-=CH), 6.27 (s, 1H, 15$_1$-CH), 6.29 (d, $J$=17.7 Hz, 1H, 3$_2$-=CH), 7.99 (dd, $J$=17.7 Hz, $J$=11.3 Hz, 1H, 3$_1$-=CH), 8.58 (s, 1H, 20-CH), 9.38 (s, 1H, 5-CH), 9.52 (s, 1H, 10-CH).

Comments: If the suspension of *Spirulina* in methanol is too thick and stirring inefficient, an additional amount of methanol could be added (20-40 mL). Mother liquors after CH$_2$Cl$_2$-MeOH washings were collected and kept, since they contain an additional amount of pheophorbide, which could be recovered by column chromatography.

Compound 2 was prepared in analogy to the procedure described by Zhang for chlorin e$_6$.$^2$

To solution of dimethyl pheophorbide a 1 (200 mg, 0.330 mmol) in DCM (30 mL) a solution of DDQ 5 (90 mg, 0.396 mmol) in benzene (15 mL) was added and the resulting solution was stirred at room temperature for 30 min. Solvent was evaporated under reduced pressure and residue purified by flash column chromatography (silica, DCM/diethyl ether 95:5). Combined fractions were washed with 0.1 M HCl (3x 100 mL) and water, then solvent removed under reduced pressure to afford product 2 as black powder (120 mg, 60%), m.p. 157-159 °C. Rf=0.61 (dichloromethane:acetone, 95:5); UV-vis (CH$_2$Cl$_2$): $\lambda_{max}$ = 422 (rel. 1.0), 572 (0.084), 595 nm (0.090); $^1$H NMR (CDCl$_3$) $\delta$ -4.78 (s, 1H, NH), -3.81 (s, 1H, NH), 1.74 (t, $J$=8.3 Hz, 3H, 8$_2$-CH$_3$), 2.69-2.76 (m, 1H, 17$_1$-CH$_2$), 2.85-2.92 (m, 1H, 17$_2$-CH$_2$), 3.29 (s, 3H, 7-CH$_3$), 3.36 (s, 3H, 2-CH$_3$), 3.39 (s, 3H, 12-CH$_3$), 3.74 (s, 3H, 18-CH$_3$), 3.76 (s, 3H, -OCH$_3$), 3.77 (s, 3H, -OCH$_3$), 3.78 (q, $J$=8.3 Hz, 2H, 8$_1$-CH$_2$), 6.09 (d, $J$=11.7 Hz, 1H, 3$_2$-=CH), 6.16 (d, $J$=18.4 Hz, 1H, 3$_1$-=CH), 6.46 (s, 1H, 15$_1$-CH), 7.95 (dd, $J$=18.4 Hz, $J$=11.7 Hz, 1H, 3$_1$-=CH), 9.38 (s, 1H, 20-CH), 9.56 (s, 1H, 5-CH), 9.66 (s, 1H, 10-CH); HRMS (EI) m/z calc for[M+H]$^+$ C$_{36}$H$_{37}$O$_5$N$_4$ 605.2758, found 605.2750.
Compound 3
Solution of dimethyl pheophorphyrin a 2 (8 mg, 0.013 mmol) and TCNE 6 (10 mg, 0.078 mmol) in dry DCM (10 mL) was heated in sealed glass high pressure vessel for 4h at 80 °C. Solvent was removed in vacuo and residue subjected to column chromatography on silica with DCM/acetone 95:5 to afford 1:1 mixture of diastereomeric products 3 as a dark green solid (6 mg, 63%), m.p. 215-218 °C. R=0.61 (dichloromethane:acetone, 95:5); UV-vis (CH₂Cl₂): \( \lambda_{\text{max}} = 425 \) (rel. 1.0), 574 (0.085), 641 nm (0.065); \(^1\)H NMR (CDCl₃) δ -1.81, -1.76 (s, 1H, NH), -0.98, -0.92 (s, 1H, NH), 1.78 (t, J=7.5 Hz, 3H, 8²-CH₃), 2.36, 2.39 (s, 3H, 18¹-CH₃), 2.93-3.01 (m, 1H, 17-CH₂), 3.04-3.11 (m, 1H, 17²-CH₂), 3.41 (s, 3H, 7-CH₃), 3.46, 3.47 (s, 3H, 2-CH₃), 3.70. 3.71 (s, 3H, 12-CH₃), 3.74, 3.75 (s, 3H, -OCH₃), 3.79 (s, 3H, -OCH₃), 3.86 (s, 3H, -OCH₃), 3.91 (q, J=7.5 Hz, 2H, 8¹-CH₂), 3.96 (dd, J=13.9 Hz, J=5.1 Hz, 1H, 17¹-CH₂), 4.05 (dd, J=9.5 Hz, J=3.1 Hz, 1H, 17¹-CH₂), 4.09 (t, J=4.1 Hz, 2H, 3²-CH₂), 4.11-4.15 (m, 1H, 17¹-CH₂), 6.77, 6.79 (s, 1H, 15¹-CH), 7.01 (t, J=4.1 Hz, 1H, 3¹-CH), 7.09 (t, J=4.1 Hz, 1H, 3¹-CH), 9.12, 9.14 (s, 1H, 20-CH), 9.21, 9.24 (s, 1H, 5-CH), 9.78 (s, 1H, 10-CH); \(^13\)C NMR (CDCl₃) δ 10.4, 10.7, 12.4, 16.7, 18.9, 21.5, 21.6, 24.1 24.2, 29.2, 34.4, 34.9. 35.0, 51.4, 52.6, 52.7, 66.0, 66.1, 89.6, 89.7, 89.8, 89.9, 103.0, 103.1, 114.1, 114.2, 108.8, 108.9, 111.2, 111.8, 111.9, 112.5, 113.2, 113.3, 129.9, 130.0, 130.8, 130.9, 134.2, 134.3, 135.3, 135.4, 135.5, 136.5, 136.6, 136.7, 138.6, 138.7, 139.9, 140.0, 140.1, 140.8, 142.4, 142.5, 145.2, 145.3, 153.4, 156.1, 156.2, 160.7, 160.8, 169.2, 169.5, 172.1, 187.8; HRMS (El) m/z calc for [M+H]^+ C₄₂H₃₇O₅N₈ 733.2881, found 733.2849.

Compound 4
Solution of dimethyl pheophorphyrin a 2 (10 mg, 0.016 mmol) and maleic anhydride 7 (10 mg, 0.102 mmol) in dry toluene (5 mL) under argon was heated in microwave reactor for 2h at 150 °C, (200W). Solvent was removed in vacuo to afford product 4 as a dark green solid (quant.). NMR
chemical shifts identical to literature. \(^3\) Rf=0.36 (dichloromethane:acetone, 95:5); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) -1.78 (s, NH), 1.66 (t, \(J=7.7\) Hz, 3H, 8\(^2\)-CH\(_3\)), 1.82 (d, \(J=7.6\) Hz, 3H, 18\(^1\)-CH\(_3\)), 2.25-2.32 (m, 2H, 17-CH\(_2\)), 2.54-2.61 (m, 1H, 17-CH\(_2\)), 2.66-2.74 (m, 1H, 17-CH\(_2\)), 3.19 (s, 3H, -CH\(_3\)), 3.39 (s, 3H, -CH\(_3\)), 3.61 (s, 3H, -CH\(_3\)), 3.62 (s, 3H, 17-OCH\(_3\)), 3.64 (q, \(J=7.7\) Hz, 2H, 8\(^1\)-CH\(_2\)), 4.29 (d, \(J=9.4\) Hz, 1H, 17-CH), 4.49 (q, \(J=7.2\) Hz, 1H, 18-CH), 5.09 (d, \(J=18.8\) Hz, 1H, 15-CH\(_2\)), 5.23 (d, \(J=18.8\) Hz, 1H, 15-CH\(_2\)), 6.16 (d, \(J=11.6\) Hz, 1H, 3\(^2\)-C=CH\(_2\)), 6.27 (d, \(J=17.4\) Hz, 1H, 3\(^2\)-C=CH\(_2\)), 7.96 (dd, \(J=17.4\) Hz, \(J=11.4\) Hz, 1H, 3\(^1\)-CH=), 8.57 (s, 1H, 20-H), 9.33 (s, 1H, 5-H), 9.44 (s, 1H, 10-H).

**Compound 8**

Solution of dimethyl pheophorphide a \(1\) (360 mg, 0.593 mmol) and furfurylamine \(12\) (700 mg, 7.209 mmol) in dry THF (50 mL) was heated at reflux for 1h at 60-70 °C. Solvent was removed in vacuo and excess of amine by high vacuo pump. Residue was subjected to flash column chromatography on silica with DCM/acetone 95 : 5 to afford product \(8\) as a dark green solid (119 mg, 29%), m.p. 155-157 °C. Rf=0.48 (dichloromethane:acetone, 95:5); UV-vis (CH\(_2\)Cl\(_2\)): \(\lambda_{max}\) = 402 (rel. 1.0), 506 (0.934), 666 nm (0.305); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) -1.79 (s, 1H, NH), -1.59 (brs, 1H, NH), 1.69 (t, \(J=6.6\) Hz, 3H, 8\(^2\)-CH\(_3\)), 1.71 (d, \(J=7.3\) Hz, 3H, 18\(^1\)-CH\(_3\)), 1.76-1.84 (m, 1H, 17-CH\(_2\)), 2.11-2.17 (m, 1H, 17-CH\(_2\)), 2.18-2.25 (m, 1H, 17-CH\(_2\)), 2.46-2.55 (m, 1H, 17-CH\(_2\)), 3.31 (s, 3H, 7-CH\(_3\)), 3.48 (s, 3H, 12-CH\(_3\)), 3.53 (s, 3H, 2-CH\(_3\)), 3.59 (s, 3H, 15-OCH\(_3\)), 3.73 (s, 3H, 17-OCH\(_3\)), 3.81 (q, \(J=6.6\) Hz, 2H, 8\(^1\)-CH\(_2\)), 4.37 (dd, \(J=10.4\) Hz, \(J=2.3\) Hz, 1H, 17-CH), 4.45 (q, \(J=7.3\) Hz, 1H, 18-CH), 4.85 (dd, \(J=15.3\) Hz, \(J=4.9\) Hz, 1H, 13\(^2\)-CH\(_2\)), 5.04 (dd, \(J=15.3\) Hz, \(J=4.9\) Hz, 1H, 13\(^1\)-CH\(_2\)), 5.26 (d, \(J=18.8\) Hz, 1H, 15\(^1\)-CH\(_2\)), 5.52 (d, \(J=18.8\) Hz, 1H, 15\(^1\)-CH\(_2\)), 6.14 (dd, \(J=11.6\) Hz, \(J=1.1\) Hz, 1H, 3\(^2\)-C=CH\(_2\)), 6.35 (dd, \(J=11.6\) Hz, \(J=1.1\) Hz, 1H, 3\(^2\)-C=CH\(_2\)), 6.42 (dd, \(J=3.3\) Hz, \(J=1.8\) Hz, 1H, 13\(^2\)-ArH), 6.49 (d, \(J=2.9\) Hz, 1H, 13\(^2\)-ArH), 6.75 (t, \(J=5.3\) Hz, 1H, 13\(^2\)-NH), 7.49 (dd, \(J=1.8\) Hz, \(J=0.8\) Hz, 1H, 13\(^8\)-ArH), 8.08 (dd, \(J=18.1\) Hz, \(J=11.5\) Hz, 1H, 3\(^1\)-CH=), 8.79 (s, 1H, 20-H), 9.62 (s, 1H, 5-H), 9.68 (s, 1H, 10-H); HRMS (El) \(m/z\) calc for [M+H]\(^+\) C\(_{41}\)H\(_{46}\)O\(_6\)N\(_5\) 704.3442, found 704.3469.
Compound 9

Solution of 13-furfurylamide chlorin 8 (40 mg, 0.057 mmol) and DMAD 13 (250 mg, 1.759 mmol) in dry toluene (10 mL) was heated in sealed glass high pressure vessel for 1.5h at 100 °C. Solvent and excess of DMAD were removed in high vacuo and residue subjected to column chromatography on silica with DCM/diethylether 1:1 to afford 1:1 mixture of diastereomeric products 9 as a dark green solid (18 mg, 38%), m.p. 115-117 °C. Rr=0.54 (dichloromethane: acetone, 95:5); UV-vis (CH2Cl2): λ\text{max} = 405 (rel. 1.0), 506 (0.080), 665 nm (0.332); ¹H NMR (CDCl3) δ -1.72 (s, 1H, NH), -1.51 (brs, 1H, NH), 1.73-1.76 (m, 6H, 8²-CH₃, 18¹-CH₃), 1.81-1.88 (m, 1H, 17-CH₂), 2.14-2.20 (m, 1H, 17-CH₂), 2.22-2.28 (m, 1H, 17-CH₂), 2.53-2.59 (m, 1H, 17-CH₂), 3.33 (s, 3H, 7-CH₃), 3.50 (s, 3H, 12-CH₃), 3.57 (s, 3H, 2-CH₃), 3.64 (s, 3H, 17-OCH₃), 3.77, 3.79 (s, 3H, 15-OCH₃), 3.81 (q, J= 7.8 Hz, 2H, 8¹-CH₂), 3.84, 3.86 (s, 3H, 13⁵-OCH₃), 3.97, 4.01 (s, 3H, 13⁶-OCH₃), 4.42 (dt, J= 9.8 Hz, J= 3.1 Hz, 1H, 17-CH₂), 4.39-4.43 (m, 1H, 17-CH₂), 4.49 (q, J= 7.8 Hz, 1H, 18-CH), 4.59 (dd, J= 15.0 Hz, J= 5.5 Hz, 1H, 13³-NCH₂), 4.71 dd, J= 15.0 Hz, J= 5.7 Hz, 1H, 13³-NCH₂), 4.98 (dd, J= 15.0 Hz, J= 7.3 Hz, 1H, 13³-NCH₂), 5.27 (d, J=19.2 Hz, 1H, 15¹-CH₂), 5.31 (d, J=19.2 Hz, 1H, 15¹-CH₂), 5.53 (d, J=19.2 Hz, 1H, 15¹-CH₂), 5.56 (d, J=19.2 Hz, 1H, 15¹-CH₂), 5.71 (d, J= 1.8 Hz, 1H, 13⁷-OCH oxa bridgehead), 5.72 (t, J= 1.1 Hz, 1H, 13⁷-OCH oxa bridgehead), 6.15 (dd, J= 17.9 Hz, J= 1.1 Hz, 1H, 3²-C=CH₂), 6.38 (dd, J= 17.9 Hz, J= 1.1 Hz, 1H, 3²-C=CH₂), 6.77 (t, J=4.9 Hz, 1H, 13²-NH), 6.79 (t, J=4.9 Hz, 1H, 13²-NH), 7.35-7.36 (m, 1H, 13⁸ =CH), 7.42 (d, 1H, J= 5.5 Hz, 13⁹ =CH), 8.09 (dd, J= 18.1 Hz, J= 11.5 Hz, 1H, 3¹=CH), 8.81 (s, 1H, 20-H), 9.64 (s, 1H, 5-H), 9.71 (s, 1H, 10-H); HRMS (El) m/z calc for [M+H]+ C₄₇H₅₂O₁₀N₅ 846.3708, found 846.3735.
Compound 10
Solution of 13-furfurylamide chlorin 8 (20 mg, 0.028 mmol) and maleic anhydride 7 (35 mg, 0.357 mmol) in dry DCM (1.5 mL) was subjected to high pressure at 6 kbar for 16h at room temperature. Solvent was removed in vacuo at room temperature and residue subjected to flash column chromatography on silica with DCM/acetone 95:5 to afford impure 1:1 mixture of diastereomeric products 10 as a dark green solid (12 mg, 34%).

$^1$H NMR (CDCl$_3$) estimated from crude reaction mixture: δ -3.59 (s, 1H, NH), -3.04 (s, 1H, NH), 1.61 (q, $J = 7.9$ Hz, 3H, 8$^2$-CH$_3$), 1.77, 1.78 (t, $J = 8.7$ Hz, 3H, 18$^1$-CH$_3$), 1.94-2.09 (m, 1H, 17-CH$_2$), 2.11-2.21 (m, 1H, 17-CH$_2$), 2.27-2.37 (m, 1H, 17-CH$_2$), 2.58-2.68 (m, 1H, 17-CH$_2$), 3.43 (s, 3H, 7-CH$_3$), 3.53 (s, 3H, 2-CH$_3$), 3.54, 3.55 (s, 3H, 12-CH$_3$), 3.61 (d, $J = 9.6$ Hz, 1H, endo-13$^8$-CH), 3.65, 3.68 (s, 3H, 3H, 15-OCH$_3$), 3.79 (d, $J = 7.0$ Hz, 1H, endo-13$^8$-CH), 3.83, 3.84 (s, 3H, 3H, 17-OCH$_3$), 4.74-4.80 (m, 1H, 13$^3$-NCH$_2$), 4.49 (dd, 1H, $J = 23.6$ Hz, $J = 10.5$ Hz, 17-CH), 4.59 (q, $J = 7.0$ Hz, 1H, 18-CH), 4.11-4.29 (m, 1H, 13$^3$-NCH$_2$), 5.25 (d, $J = 18.8$ Hz, 1H, 15$^1$-CH$_2$), 5.45, 5.49 (s, 1H, oxa bridgehead), 5.49 (d, $J = 18.8$ Hz, 1H, 15$^1$-CH$_2$), 6.34 (d, $J = 11.7$ Hz, 1H, 3$^2$-C=CH$_2$), 6.41 (d, $J = 17.9$ Hz, 1H, 3$^2$-C=CH$_2$), 6.67 (d, $J = 5.0$ Hz, 1H, 13$^{11}$-CH), 6.72 (d, $J = 5.4$ Hz, 1H, 13$^{12}$-CH), 6.85 (d, $J = 5.4$ Hz, 1H, 13$^{12}$-CH), 7.01 (d, $J = 5.4$ Hz, 1H, 13$^{12}$-CH), 8.08 (dd, $J = 17.5$ Hz, $J = 12.1$ Hz, 1H, 3$^1$-CH=), 8.21 (t, $J = 5.8$ Hz, 1H, 13$^2$-NH), 9.17, 9.18 (s, 1H, 20-H), 10.03, 10.04 (s, 1H, 5-H), 10.06, 10.07 (s, 1H, 10-H).

Compound 11
Solution of 13-furfurylamide chlorin 8 (20 mg, 0.028 mmol) and N-methylmaleimide 14 (35 mg, 0.315 mmol) in dry DCM (1.5 mL) was subjected to high pressure at 6 kbar for 16h at room temperature. Solvent was removed in vacuo at room temperature and residue subjected to flash column chromatography on silica with DCM/acetone 95:5 to afford 1:1 mixture of diastereomeric products 11 as a dark green solid (12 mg, 34%), m.p. 120-122 °C. Rf=0.24 (dichloromethane:acetone, 95:5); UV-vis (CH2Cl2): \( \lambda_{\text{max}} = 404 \text{ (rel. 1.0)}, 504 \text{ (0.16)}, 668 \text{ nm (0.49)}; \\
1H NMR (CDCl3) \delta -1.75, -1.74, -1.70 (s, 1H, NH), -1.54 (brs, 1H, NH), 1.70-1.72 (m, 6H, \text{82-CH3, 181-CH3}), 1.78-1.86 (m, 1H, 17-CH2), 2.11-2.17 (m, 1H, 17-CH2), 2.18-2.25 (m, 1H, 17-CH2), 2.49-2.58 (m, 1H, 17-CH2), 2.96, 2.97 (s, 3H, N-CH3), 3.29 (s, 3H, 7-CH3), 3.37, 3.41 (d, \( J = 7.5 \text{ Hz, 1H, endo-138-CH} \)), 3.48 (s, 3H, 2-CH3), 3.52, 3.53 (s, 3H, 12-CH3), 3.60, 3.62 (s, 3H, 15-OCH3), 3.65-3.69 (m, 2H, endo-138-CH), 3.77 (s, 3H, 17-OCH3), 3.78 (q, \( J = 7.6 \text{ Hz, 2H, 81-CH2} \)), 4.05 (m, 1H, 13 3-NCH2), 4.26-4.76 (m, 3H, 13 3-NCH2, 17-CH, 18-CH), 5.16-5.59 (m, 3H, 15 1-CH2, 139-CH), 6.13 (d, \( J = 17.9 \text{ Hz, 1H, 32-C=CH2} \)), 6.34 (d, \( J = 17.9 \text{ Hz,1H, 32-C=CH2} \)), 6.52 (brs, 1H, 13 11=-CH), 6.59 (dd, \( J = 14.9 \text{ Hz, J= 5.0 Hz, 1H, 1311=-CH} \)), 6.65 (dd, \( J = 14.9 \text{ Hz, J= 5.0 Hz, 1H, 1312=-CH} \)), 6.89 (t, \( J = 5.5 \text{ Hz, 1H, 132-NH} \)), 6.93 (dd, \( J = 11.4 \text{ Hz, J= 5.5 Hz, 1H, 1312=-CH} \)), 6.97, 7.12 (t, \( J = 6.5 \text{ Hz, 1H, 132-NH} \)), 8.07 (dd, \( J = 18.9 \text{ Hz, J= 11.4 Hz, 1H, 31-CH=} \)), 8.79 (s, 1H, 20-H), 9.61 (s, 1H, 5-H), 9.67 (s, 1H, 10-H); HRMS (El) \( m/z \) calc for [M+H]+ C46H51O8N6 815.3762, found 815.3779.

![Diagram A](https://via.placeholder.com/150)

**Compound A**, N-Boc protected furfuryl amine was prepared by literature procedure.\(^4\)

To the solution of furfuryl amine (1.11 g, 11.5 mmol), dichloromethane (40 mL) and triethylamine (2.33 g, 22.9 mmol), di-tert-butyl dicarbonate (3.76 g, 17.2 mmol) was added and the solution was stirred at room temperature for 4 h. The reaction mixture was washed with brine (40 mL, 3 times). The dichloromethane layer was separated and dried with magnesium sulfate, filtered and evaporated under vacuum to obtain product (2.19 g, 96%).

\(1H \text{ NMR (CDCl3)} \delta 1.45 (s, 9H, Boc), 4.28 (s, 2H, -NCH2), 4.86 (brs, 1H, NH), 6-18-6.19 (m, 1H, Fur), 6.29 (t, \( J=2.2 \text{ Hz, 1H, Fur} \)), 7.32-7.33 (m, 1H, Fur).

![Diagram B](https://via.placeholder.com/150)

**Compound B** furan / DMAD cycloadduct

The solution of furan A (1.00 g, 5.07 mmol) and DMAD (0.70 g, 4.93 mmol) in chloroform (10 mL) was heated at 80°C overnight in sealed glass high pressure vessel. Solvent was removed in vacuo
to afford product B as colorless solid (1.47 g, 92 %), m.p. 85-87 °C. $^1$H NMR (CDCl$_3$) δ 1.38 (s, 9H, Boc), 3.72 (s, 3H, CH$_3$), 3.76 (s, 3H, CH$_3$), 4.95 (brs, 1H, NH), 5.58 (d, $J$=1.8 Hz, 1H, oxa-bridgehead), 6.97 (d, $J$=5.3 Hz, 1H, C=CH), 7.15 (dd, $J$=5.3 Hz, $J$=1.8 Hz, 1H, C=CH); $^{13}$C NMR (CDCl$_3$) δ 27.8, 38.5, 51.7, 51.8, 84.5, 96.8, 142.4, 144.7, 152.2, 153.2, 155.1, 162.1, 163.4.

Compound C furan / N-methyl maleimide cycloadduct

The solution of furan A (0.50 g, 2.53 mmol) and N-methyl maleimide (0.28 g, 2.50 mmol) in chloroform (10 mL) was heated at 70°C overnight in sealed glass high pressure vessel. Solvent was removed in vacuo at room temperature and residue recrystallized from diethyl ether to afford product C as colorless solid (1.47 g, 92 %), m.p. 128-130 °C. $^1$H NMR (CDCl$_3$) δ 1.47 (s, 9H, Boc), 2.91 (d, $J$=6.5 Hz, 1H, endo-CH), 2.98 (s, 3H, NMe), 2.99 (d, $J$=6.5 Hz, 1H, endo-CH), 3.72 (dd, $J$=14.5 Hz, $J$=6.1, 1H, -NCH$_2$), 3.83 (dd, $J$=14.5 Hz, $J$=6.1, 1H, -NCH$_2$), 5.23 (s, 2H, oxa-bridgehead + NH), 6.52 (d, $J$=5.5 Hz, 1H, C=CH), 6.56 (d, $J$=5.5 Hz, 1H, C=CH); $^{13}$C NMR (CDCl$_3$) δ 28.1, 39.4, 47.7, 47.9, 49.9, 80.2, 90.3, 90.4, 136.4, 138.1, 155.5, 174.7, 175.4. Spectra compared to cycloadduct with unsubstituted furan.$^5$
S3. NMR spectra of novel chlorins

$^1$H-NMR spectrum of pheophorbide a 1 (300 MHz, CDCl$_3$)

$^1$H-NMR spectrum of 2 (300 MHz, CDCl$_3$)
$^1$H-NMR spectrum of 3 (300 MHz, CDCl$_3$)

$^{13}$C-NMR spectrum of 3 (75 MHz, CDCl$_3$)
$^1$H-$^1$H COSY spectrum of 3 (CDCl$_3$)

$^1$H-$^1$H NOESY spectrum of 3 (CDCl$_3$)
\( ^1 \text{H-NMR spectrum of 8 (300 MHz, CDCl}_3) \)

\( ^1 \text{H-NMR spectrum of 9 (300 MHz, CDCl}_3) \)
$^1$H-$^1$H COSY spectrum of 9 (CDCl$_3$)

$^1$H-$^1$H NOESY spectrum of 9 (CDCl$_3$)
$^1$H-NMR spectrum of 10 (300 MHz, CDCl$_3$)

$^1$H-$^1$H COSY spectrum of 10 (CDCl$_3$)
$^1$H-$^1$H NOESY spectrum of 10 (CDCl$_3$)
S4. UV spectra of novel chlorins

UV-vis spectra were taken in dichloromethane at 25 °C in visible region from 350-750 nm.

UV of compound 2 (CH$_2$Cl$_2$, 25°C)

UV of compound 3 (CH$_2$Cl$_2$, 25°C)
UV of compound 8 (CH$_2$Cl$_2$, 25°C)

UV of compound 9 (CH$_2$Cl$_2$, 25°C)
UV of compound **10** (CH$_2$Cl$_2$, 25°C)

References and notes