

Supporting Information

5- and 10-Oxocorroles from β -octalkylcorroles

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Experimental part

Reagents and solvents (Aldrich) were of the highest grade available and were used without further purification. Thin-layer chromatography (TLC) was performed on Sigma-Aldrich silica gel plates. Chromatographic purification of the reaction products was accomplished by using silica gel 60 (70–230 mesh, Sigma-Aldrich, St. Louis, MO, USA) as a stationary phase. UV-vis spectra were measured on a Varian Cary 60 Spectrophotometer using CH₂Cl₂ as solvent.

NMR experiments were performed in deuterated chloroform at 20 °C and recorded with a Bruker Advance spectrometer operating at 700 MHz for ¹H, equipped with a 5 mm inverse TXI probe and z-axis gradients.

Electrochemical experiments were performed using PalmSens PS-PSTrace handheld potentiostat (Palm Instruments, Netherlands) using a conventional 3-electrode setup, comprising a glassy carbon working electrode, a platinum counter electrode, and a saturated calomel reference electrode (SCE). The characterization is performed by cyclic voltammetry in the range from -1.5 to -1.5 V at a scan rate of 20 mV/s.

X-ray Crystallography

Intensity data for **3** and **5** were collected at low temperature on a Bruker Kappa Apex-II DUO diffractometer. H atoms were visible in difference maps but were placed in idealized positions for refinement. In **5**, there were two types of disorder: partially occupied ketone O atoms were present at the 5, 10 and 15 positions, and one of the ethyl groups had two disordered conformations.

Crystal Data:

3, C₃₇H₄₄N₄O₆Zn, *M* = 706.13, triclinic, *a* = 11.5986(4), *b* = 12.6596(5), *c* = 13.1983(5) Å, *α* = 78.370(2), *β* = 64.275(2), *γ* = 76.951(3)°, *U* = 1688.92(12) Å³, *T* = 100 K, space group *P*-1 (no.2), *Z* = 2, 45774 reflections measured to *θ*_{max} = 31.6° with MoK α radiation, 11128 unique (*R*_{int} = 0.036), which were used in all calculations. The final *wR* was 0.090 (all data), CCDC 2302278.

5, C₃₇H₄₄N₄O₆Zn, *M* = 706.13, triclinic, *a* = 10.2436(10), *b* = 11.0056(10), *c* = 15.7208(16) Å, *α* = 91.070(8), *β* = 101.638(7), *γ* = 105.968(7)°, *U* = 1663.7(3) Å³, *T* = 90 K, space group *P*-1 (no.2), *Z* = 2, 11312 reflections measured to *θ*_{max} = 68.3° with CuK α radiation, 5877 unique (*R*_{int} = 0.069), which were used in all calculations. The final *wR* was 0.089 (all data), CCDC 2302279.

2,3,17,18-tetraethyl-7,13-dimethyl-8,12-bis-(methyloxycarbonyl)ethylcorrole **1** and 2,3,7,8,12,13,17,18-octaethylcorrole **2** have been prepared according to literature methods.¹

Synthesis of oxocorroles

In methanol

In a 100 mL round-bottomed flask, corrole (40 mg, 0.066 mmol) was dissolved in CHCl₃ and heated to reflux. After that, a saturated solution of zinc acetate (40 mg, 0.182 mmol) in MeOH was added and the reaction was stirred overnight at room temperature. The solvent was then removed under vacuum and the crude mixture purified by chromatography (alumina Brockmann grade III, CH₂Cl₂ eluent), affording two main fractions: the first eluted product always corresponds to the 10-oxo derivative and the second one to the 5-oxo compound.

In pyridine

In a 100 mL round-bottomed flask, corrole (25 mg, 0.048 mmol) and Zn(II) acetate (30 mg; 0.2 mmol) were dissolved in pyridine (40 mL) and the reaction heated to reflux for 1 h. After removing the solvent under vacuum, the crude mixture was purified by chromatographic column using the same procedure utilized for the reaction in MeOH.

From α,c -octaethylbiladiene

α,c -octaethylbiladiene (50 mg, $7.2 \cdot 10^{-5}$ mol), Zn (CH₃COO)₂ (54 mg, $2.9 \cdot 10^{-4}$ mol) were dissolved in methanol (44 mL) and stirred at reflux. The crude mixture was purified by column chromatography (silica gel, elution with CH₂Cl₂), affording two main fractions characterized as **4** and **6**.

[2,3,17,18-tetraethyl-7,13-dimethyl-8,12-bis-(methyloxycarbonylethyl)-10-oxocorrolate]Zn (**3**)

Crystallized from CH₂Cl₂/Petroleum ether; brown powder yield 13%, mp > 300°C.

¹H NMR (400 MHz; CDCl₃) δ , ppm: 5.12 (2H, s, 5,15-meso), 3.63 (6H, s, CO₂CH₃), 2.49 (4H, t, J = 7.6 Hz, -CH₂CH₂CO₂CH₃), 2.21 (4H, t, J = 7.6 Hz, -CH₂CH₂CO₂CH₃), 1.92 (8H, q, J = 7.6 Hz, -CH₂CH₃), 1.42 (6H, s, -CH₃), 0.90-0.82 (12H, m, -CH₂CH₃) Elemental analysis found: C, 64.49; H 6.09; N, 8.19%; calculated for C₃₇H₄₂N₄O₅Zn: C, 64.58; H 6.15; N, 8.14%; MS (MALDI-TOF m/z): 686.116; UV-vis (CH₂Cl₂): λ_{\max} nm (ϵ) 429 (4.3×10^4) and 332 (3.2×10^4).

[2,3,17,18-tetraethyl-7,13-dimethyl-8,12-bis-(methyloxycarbonylethyl)-5-oxocorrolate]Zn (**5**)

Crystallized from CH₂Cl₂/Petroleum ether; brown powder yield 28%, mp > 300°C.

¹H NMR (400 MHz; CDCl₃) δ , ppm: 5.02 (1H, s, 15-meso), 4.51 (1H, s, 10-meso), 3.67 (6H, s, CO₂CH₃), 2.28 (4H, m, -CH₂CH₂CO₂CH₃), 2.21-2.04 (4H, m, -CH₂CH₂CO₂CH₃ + 4H, m -CH₂CH₃), 1.83 (4H, m, -CH₂CH₃), 1.70 (3H, s, -CH₃), 1.59 (3H, s, -CH₃), 1.00-0.86 (12H, m, -CH₂CH₃). UV-vis (CH₂Cl₂): λ_{\max} nm 422 and 338.

2,3,7,8,12,13,17,18-octaethyl-10-oxocorrole (**4**)

Crystallized from CH₂Cl₂/Petroleum ether; brown-orange powder yield 15%, mp > 300°C.

¹H NMR (700 MHz, CDCl₃) δ , ppm: 20.73 (s, 2H, NH), 5.46 (s, 2H, 5,15-meso), 2.45 (q, 4H, J=7, -CH₂CH₃), 2.16 (m, 12H, -CH₂CH₃), 1.04-0.96 (overlapping t, 21 H, -CH₂CH₃), 0.91 (t, J=7, 3 H, -CH₂CH₃). Elemental analysis found: C, 78.28; H 8.27; N, 10.41%; calculated for C₃₅H₄₄N₄O: C, 78.32; H 8.26; N, 10.44%. MALDI-TOF (m/z) calcd. for C₃₅H₄₄N₄O 536.75, found 536.739. UV-vis (CH₂Cl₂), λ_{\max} [nm] (ϵ): 412 (2×10^4).

2,3,7,8,12,13,17,18-octaethyl-5-oxocorrole (**6**)

Crystallized from CH₂Cl₂/Petroleum ether; orange powder yield 32%, mp > 300°C.

¹H NMR (700 MHz, CDCl₃) δ , ppm: 22.10 (s, 1H, -NH), 21.33 (s, 1H, -NH), 5.44 (s, 1H, 15-meso), 5.07 (s, 1H, 10-meso), 2.45 (q, 4H, J=7, -CH₂CH₃), 2.12-2.22 (overlapping q, 12H, J=7, -CH₂CH₃), 1.04 (t, 3H, J=7, -CH₂CH₃), 1.01-0.89 (m, 21H, -CH₂CH₃).

Elemental analysis found: C, 78.30; H 8.24; N, 10.46%; calculated for C₃₅H₄₄N₄O: C, 78.32; H 8.26; N, 10.44% (MALDI-TOF) m/z calcd. for C₃₅H₄₄N₄O 536.75, found 536.739.

UV-vis (CH₂Cl₂), λ_{\max} [nm] (ϵ): 365 (1.2×10^4)

Reaction with Tl acetate

2,3,7,8,12,13,17,18-octaethylcorrole **2** (29 mg, $5.5 \cdot 10^{-5}$ mol), thallium acetate (62 mg, $1.65 \cdot 10^{-4}$ mol) were dissolved in DMF (10 mL) and stirred at room temperature overnight. The mixture was then purified by preparative thin layer chromatography (silica gel, elution with CH_2Cl_2), allowing, together with the isolation of compounds **4** and **6**, the collection of the intermediate **7**.

5,5'-dimethoxy-2,3,7,8,12,13,17,18-octaethyl-isocorrole **7**:

Crystallized from CH_2Cl_2 /Petroleum ether; green powder yield 10%, mp > 300°C.

^1H NMR (700 MHz, CDCl_3) δ , ppm: 16.77 (s, 1H, -NH), 16.54 (s, 1H, -NH), 6.29 (s, 1H, 15-meso), 6.01 (s, 1H, 10-meso), 2.61 (q, 4H, J=7, $-\text{CH}_2\text{CH}_3$), 2.56-2.53 (m, 4H, $-\text{CH}_2\text{CH}_3$), 2.48-2.43 (m, 8H, $-\text{CH}_2\text{CH}_3$), 1.59 (s, 6H, $-\text{OCH}_3$), 1.19-1.12 (m, 21H, $-\text{CH}_2\text{CH}_3$), 1.09 (t, 3H, J=7, $-\text{CH}_2\text{CH}_3$).

UV-vis (CH_2Cl_2), λ_{max} [nm] (ϵ): 361 (1×10^4).

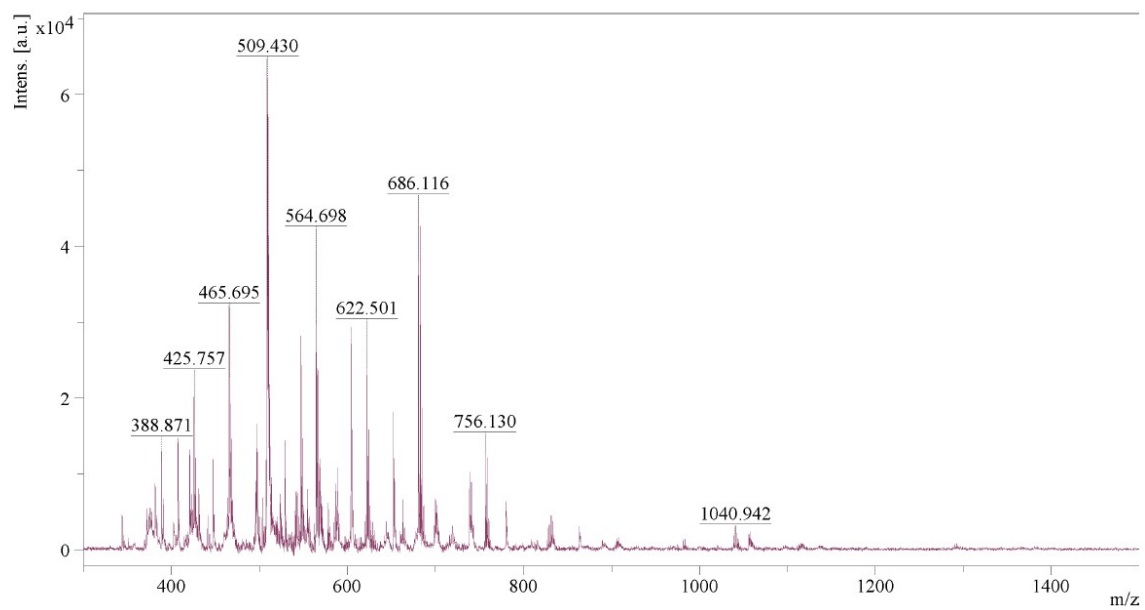


Figure S1. Mass spectrum of **3**

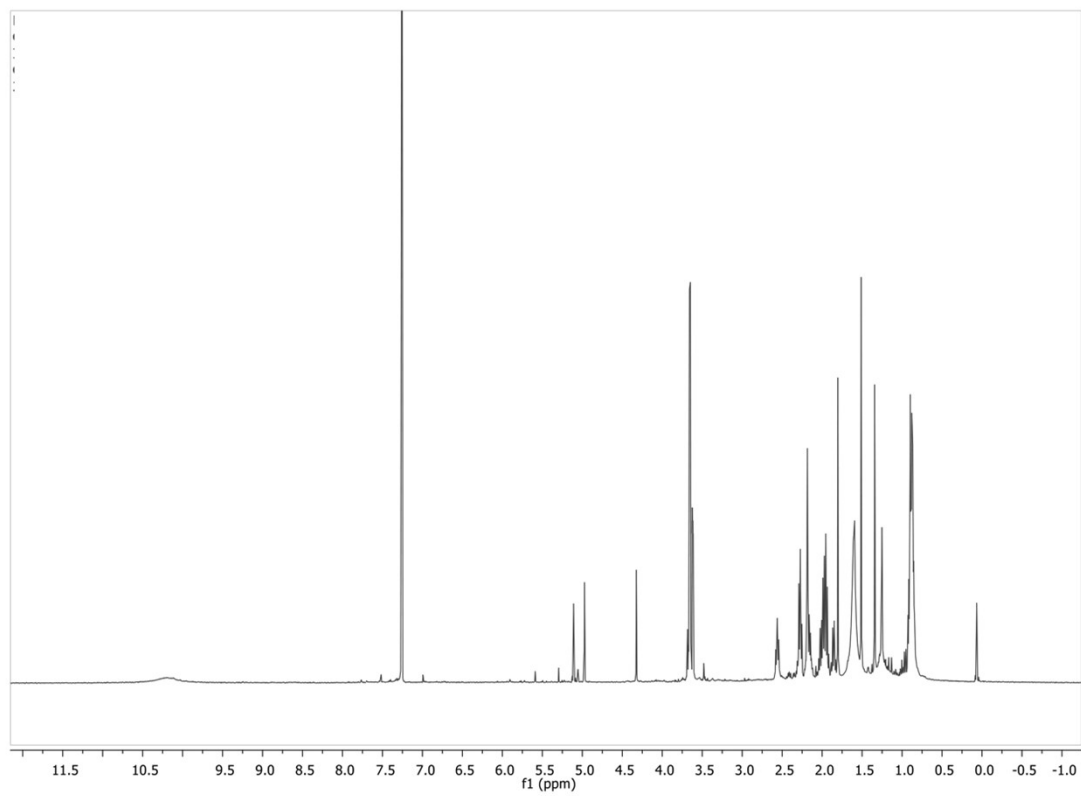


Figure S2. ¹H NMR spectrum of **5** in CDCl₃.

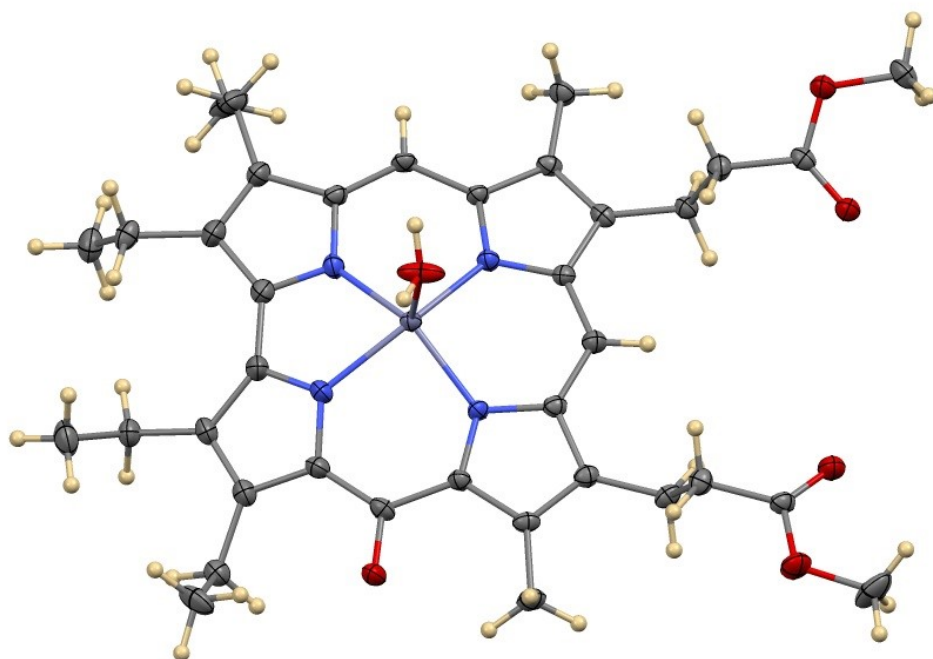


Figure S3. Crystal structure of **5**, showing only one of the partially occupied ketone O atoms and one orientation of the disordered ethyl group.

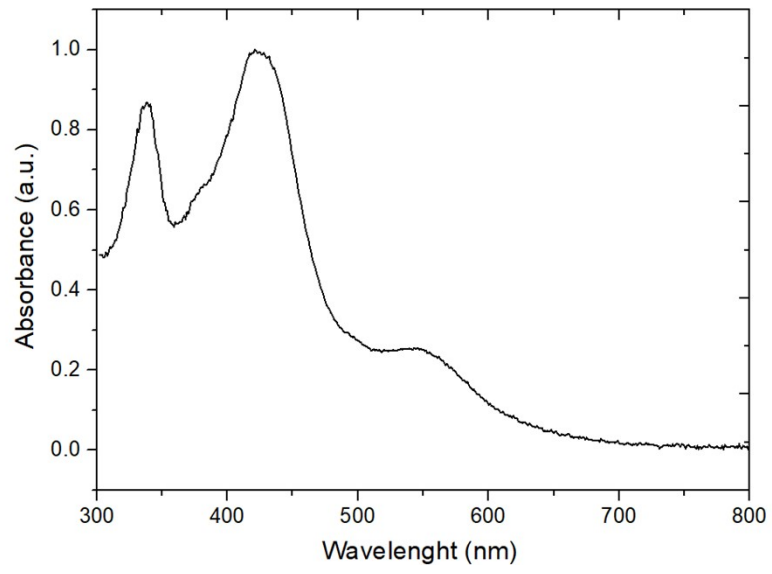


Figure S4. UV-visible spectrum of **5** in CH_2Cl_2 .

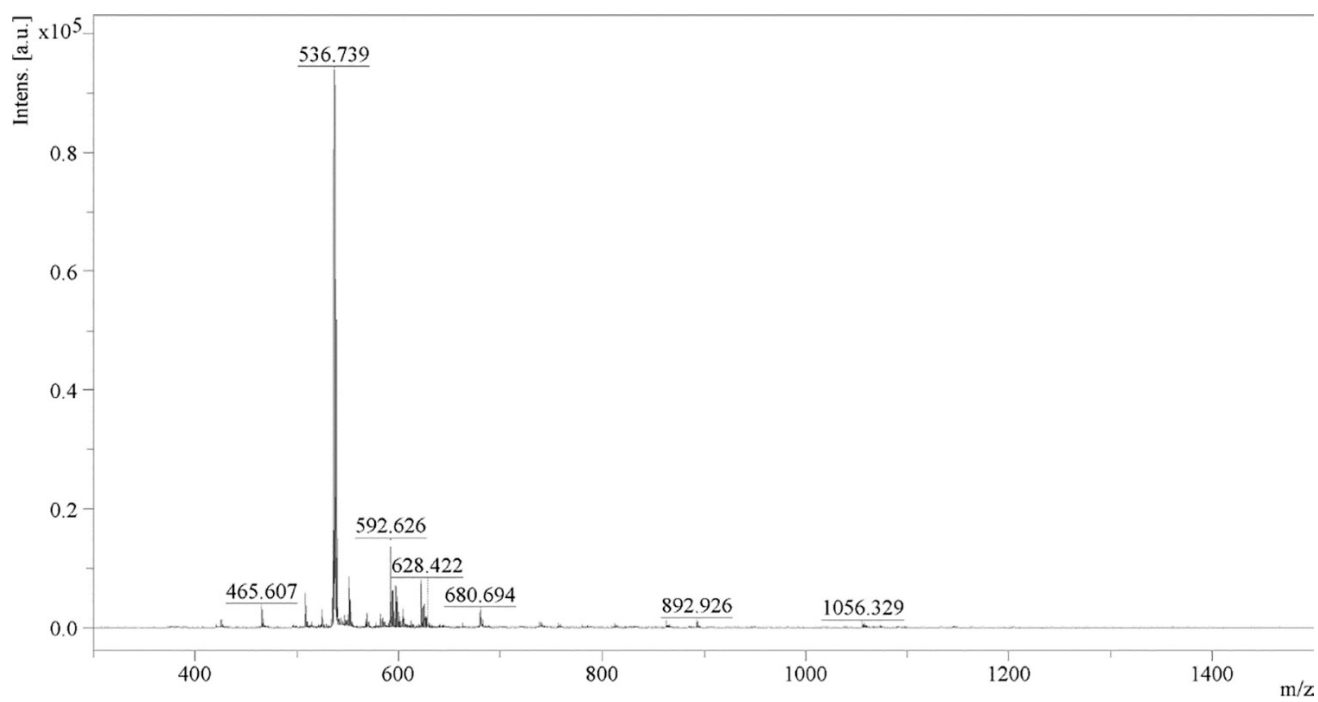


Figure S5. Mass spectrum of **4**

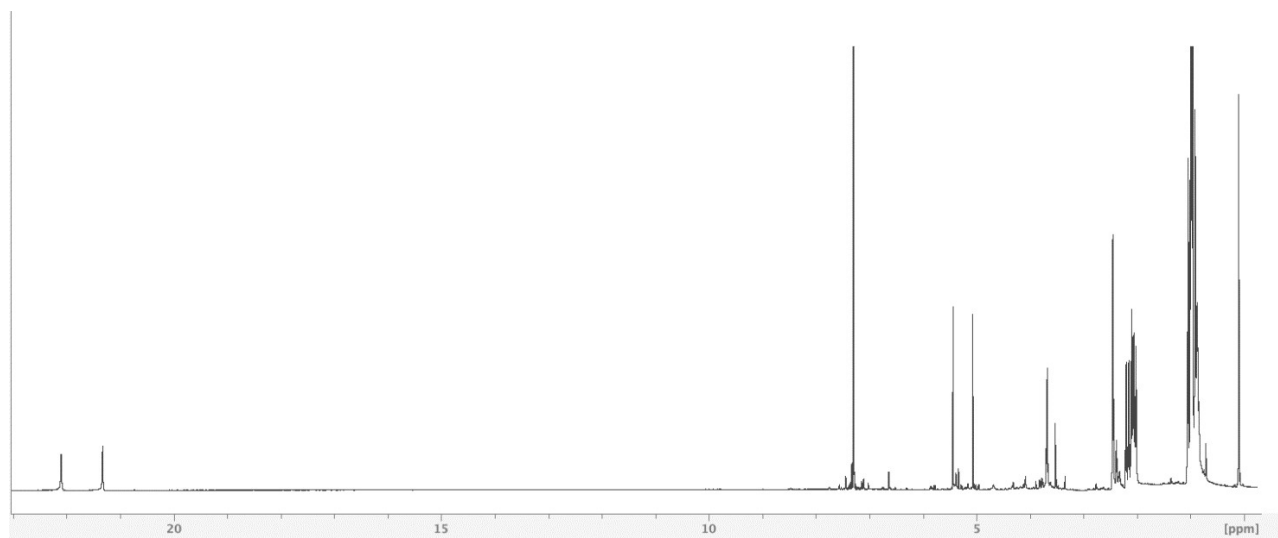


Figure S6. ^1H NMR spectrum of **6** in CDCl_3

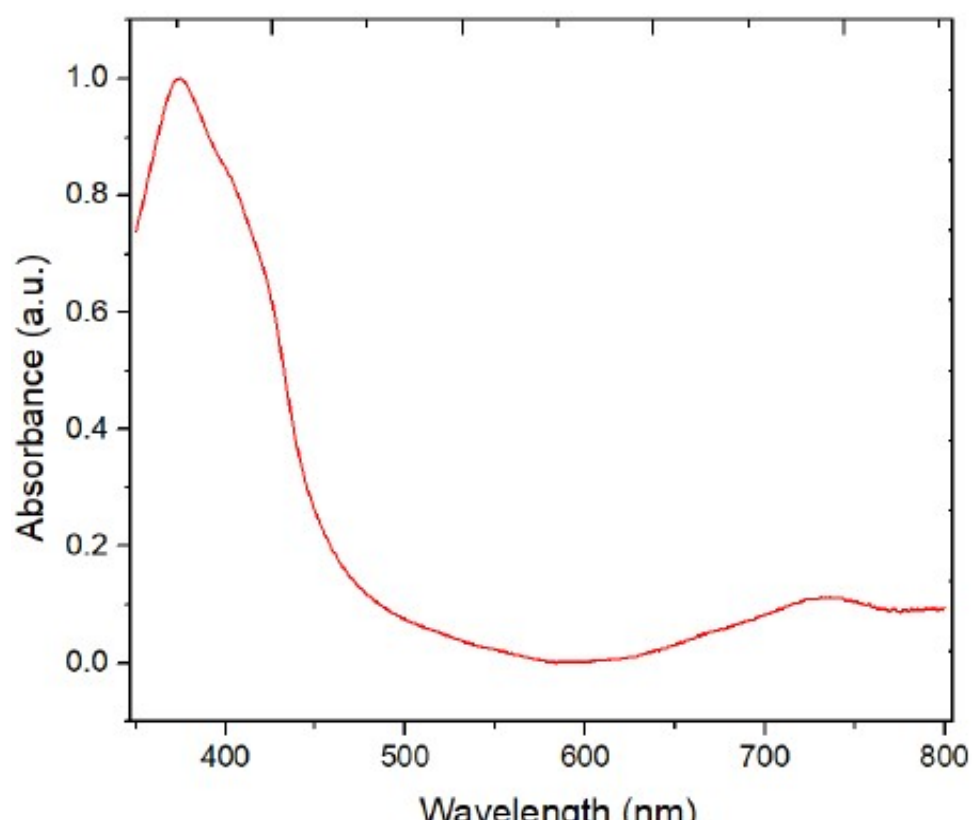


Figure S7. UV-visible spectrum of 7 in CH₂Cl₂

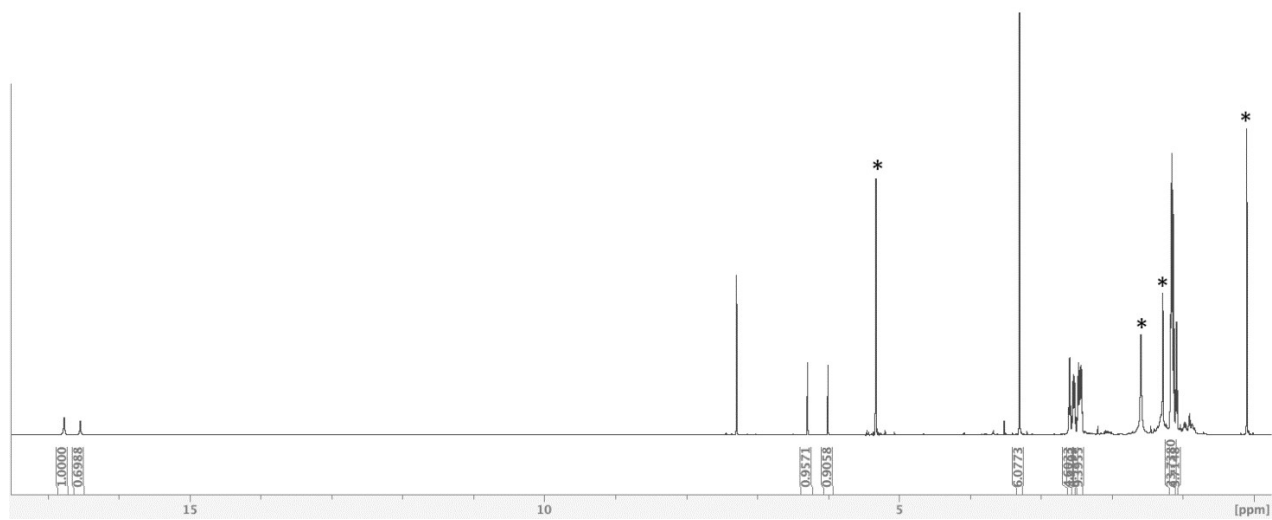


Figure S8. ^1H NMR spectrum of **7** in CDCl_3

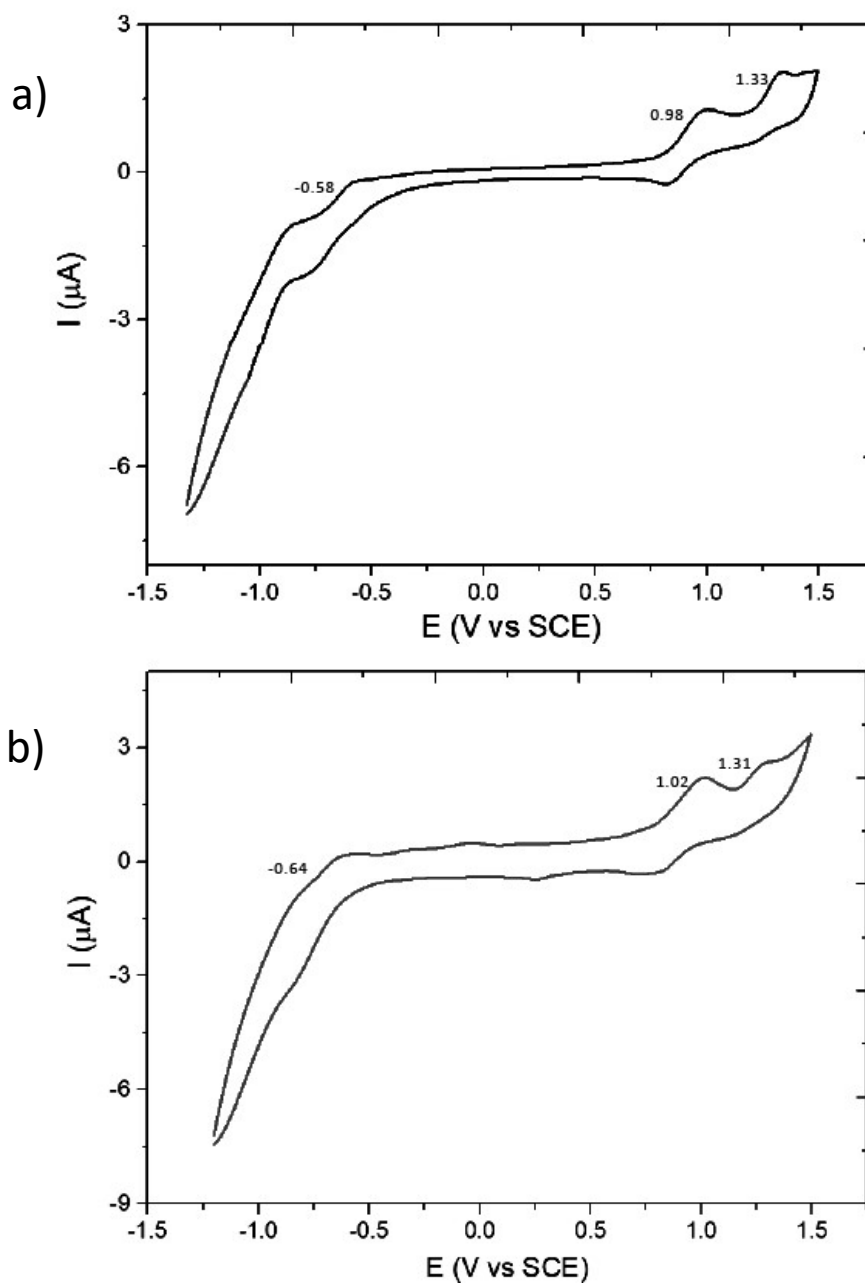


Figure S9. Cyclic voltammograms of a) **6** and b) **4** in CH_2Cl_2 containing 0.1 M TBAP at a scan rate of 0.10 V s^{-1} .

Table S1. Calculated energies for 5- and 10-oxocorrole MO orbitals

Compound	ΔE (eV)	ΔE (nm)	Configuration
10-Oxo1	1.826	679	H \rightarrow L
	2.816	440	H-1 \rightarrow L
	2.987	415	H \rightarrow L+1
	3.977	312	H-1 \rightarrow L+1
10-Oxo2	1.904	651	H \rightarrow L
	2.769	448	H-1 \rightarrow L
	3.140	395	H \rightarrow L+1
	4.005	310	H-1 \rightarrow L+1
5-Oxo1	1.667	744	H \rightarrow L
	2.692	461	H-1 \rightarrow L
	3.304	375	H \rightarrow L+1
	4.329	286	H-1 \rightarrow L+1
5-Oxo2	1.817	682	H \rightarrow L
	2.716	456	H-1 \rightarrow L
	3.329	372	H \rightarrow L+1
	4.228	293	H-1 \rightarrow L+1

References

1. R. Paolesse, A. Froiio, S. Nardis, M. Mastroianni, M. Russo, D. J. Nurco, K. M. Smith, *J. Porphyrins Phthalocyanines* 2003, **7**, 585.