

CHEMISTRY 
A EUROPEAN JOURNAL

Supporting Information

© Copyright Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, 2009

Step-wise Conversion of Two Pyrrole Moieties of Octaethylporphyrin to
Pyridin-3-ones: Synthesis, Mass Spectral and Photophysical Properties
of Mono- and Bis(oxypyri)porphyrins

*Claudia Ryppa, Dariusz Niedzwiedzki, Nicole L. Morozowich, Rapole Srikanth, Matthias Zeller,
Harry A. Frank, and Christian Brückner**

University of Connecticut, Department of Chemistry, Unit 3060, Storrs, CT 06269-3060, U.S.A.

Contents:

Figure S1. ^1H NMR (CHCl_3 , 400 MHz) of 10	3
Figure S2. ^{13}C NMR (CHCl_3 , 100 MHz) of 10	3
Figure S3. ^1H NMR (CHCl_3 , 400 MHz) of 12	4
Figure S4. ^{13}C NMR (CHCl_3 , 100 MHz) of 12	4
Figure S5. ^1H NMR (CHCl_3 , 400 MHz) of 12Zn	5
Figure S6. ^{13}C NMR (CHCl_3 , 100 MHz) of 12Zn	5
Figure S7. ^1H NMR (CHCl_3 , 400 MHz) of 14	6
Figure S8. ^{13}C NMR (CHCl_3 , 100 MHz) of 14	6
Figure S9. ^1H NMR (CHCl_3 , 500 MHz) of 15	7
Figure S10. ^{13}C NMR (CHCl_3 , 125 MHz) of 15	7
Figure S11. ^1H NMR (CHCl_3 , 500 MHz) of 16a	8
Figure S12. ^{13}C NMR (CHCl_3 , 125 MHz) of 16a	8

Figure S13. ^1H NMR (CHCl_3 , 500 MHz) of 16b .	9
Figure S14. ^{13}C NMR (CHCl_3 , 125 MHz) of 16b .	9
Figure S15. Summary of the HQMC and NOESY correlation data (all CHCl_3 , 500/125 MHz).	10
Figure S16: Normalized absorption and fluorescence emission spectra and triplet life-times of 5 , 12 , 18 , 10 , 15 , 17 , 16a , and 16b , together with their transient triplet-triplet transient spectra and the kinetic traces used for the triplet lifetime determination.	12
Figure S17: UV-vis Spectrophotometric titration of OEP (5) (Q-band region).	14
Figure S18: UV-vis Spectrophotometric titration of oxochlorin 18 (Q-band region).	14
Figure S19: UV-vis Spectrophotometric titration of diol chlorin 10 (Q-band region).	15
Figure S21: UV-vis Spectrophotometric titration of 15 (Q-band region).	15
Figure S20: UV-vis Spectrophotometric titration of oxypyriporphyrin 12 (Q-band region).	16
Figure S22: ^1H NMR of 12 (CDCl_3 + traces TFA, 400 MHz).	16
Figure S22: UV-vis Spectrophotometric titration of 16a (Q-band region).	17
Figure S23: UV-vis Spectrophotometric titration of 16b (Q-band region).	17
Figure S24: FT-IR Spectra (diffuse reflectance, neat sample) of 10 (for comparison).	18
Figure S25: FT-IR Spectra (diffuse reflectance, neat sample) of 12 .	18
Figure S26: FT-IR Spectra (diffuse reflectance, neat sample) of 12Zn .	19
Figure S27: FT-IR Spectra (diffuse reflectance, neat sample) of 15 .	19
Figure S28: FT-IR Spectra (diffuse reflectance, neat sample) of 16a .	20
Figure S29: FT-IR Spectra (diffuse reflectance, neat sample) of 16b .	20
Figure S30: ORTEP (30% occupancy) representation of the structure of 12 .	21
Figure S31: Packing diagram for 12 .	21
Tabel S1. Solvent-dependent UV-vis spectra of 12 .	11
Tabel S2. Solvent-dependent UV-vis spectra of 12Zn .	11
Tabel S3. Solvent-dependent UV-vis spectra of 15 .	11
Table S4. Triplet Relaxation Times (τ) in toluene and 2-MeTHF.	13

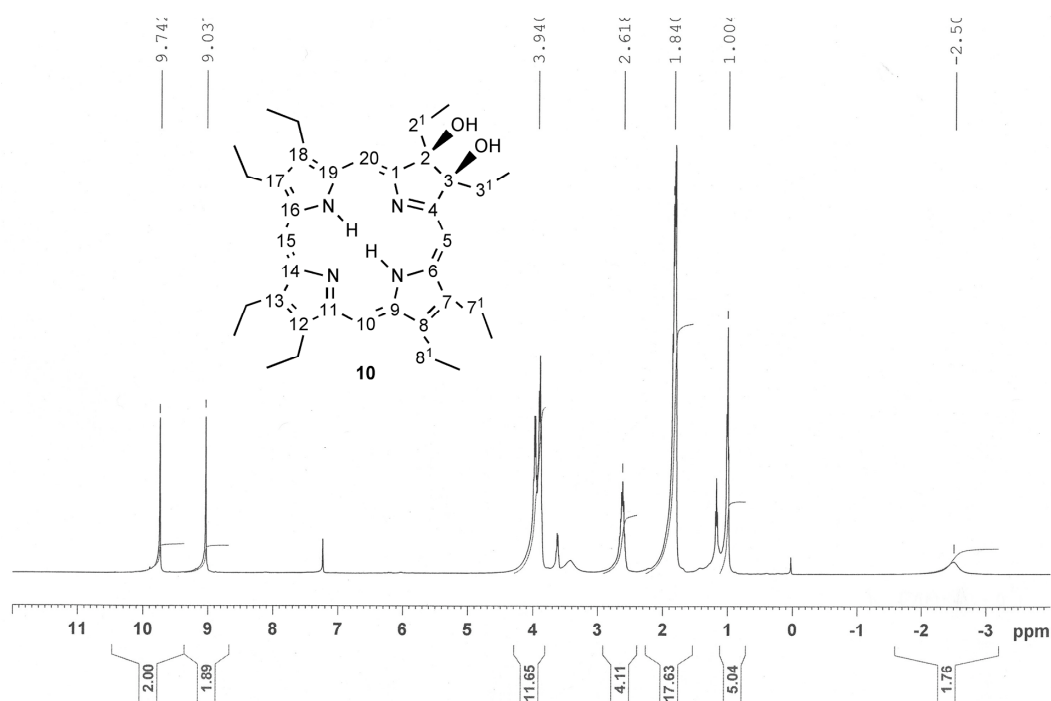


Figure S1. ^1H NMR (CHCl_3 , 400 MHz) of **10**.

Known compound (C. G. Chang, C. Sotiriou, *J. Org. Chem.* **1987**, 52, 926, included for comparison.): $\delta = 9.74$ (s, 2H, 10,15-H), 9.03 (s, 2H, 5,20-H), 4.01-3.98 (m, 12H, 7¹,8¹,12¹,13¹,17¹,18¹-CH₂), 2.62 (m, 4H, 2¹,3¹-CH₂), 1.9-1.8 (m, 18 H, 7¹,8¹,12¹,13¹,17¹,18¹-CH₃), 1.00 (m, 6H, 2¹,3¹-CH₃), -2.5 (br s, 2H, NH; exchangeable with D₂O). The assignments of the proton signals in **10** are commensurate with those made by Tamiaki (H. Tamiaki, S. Kimura, T. Kimura, *Tetrahedron*, **2003**, 59, 7423.).

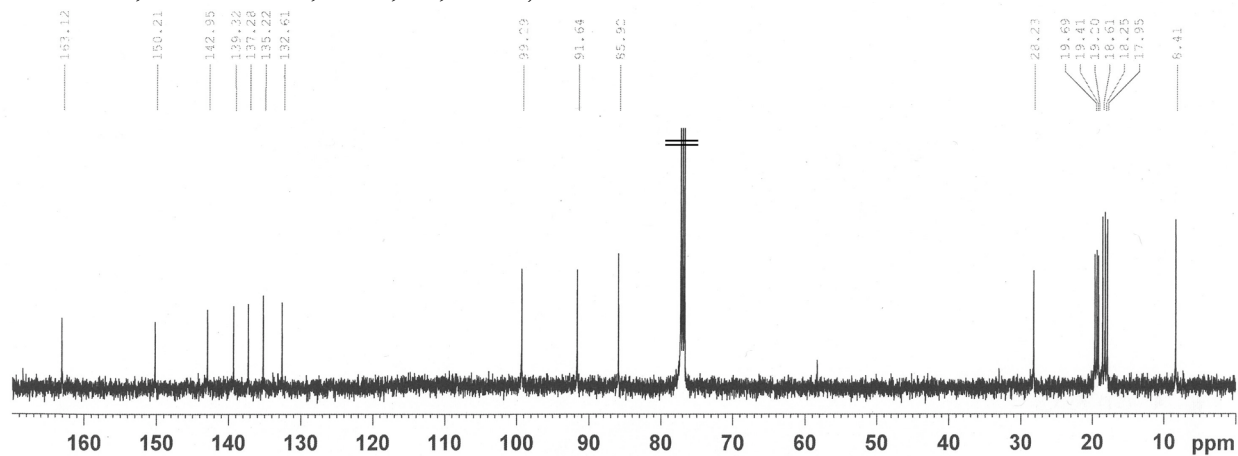


Figure S2. ^{13}C NMR (CHCl_3 , 100 MHz) of **10**.

Known compound (C. G. Chang, C. Sotiriou, *J. Org. Chem.* **1987**, 52, 926, included for comparison.), included for comparison: $\delta = 163.1$ (1,4-C), 150.2 (9,16-C), 143.0 (8,17-C), 139.3 (12,13-C), 137.3 (6,19-C), 135.2 (7,18-C), 132.6 (11,14-C), 99.3 (10,15-CH), 91.6 (5,20-CH), 85.9 (2,3-C), 28.2 (2¹,3¹-CH₂), 19.7, 19.4, 19.2 (7¹,8¹,12¹,13¹,17¹,18¹-CH₂), 18.6, 18.3, 18.0 (7¹,8¹,12¹,13¹,17¹,18¹-CH₃), 8.4 (2¹,3¹-CH₃), (assignments based on HMBC, and HMQC spectra).

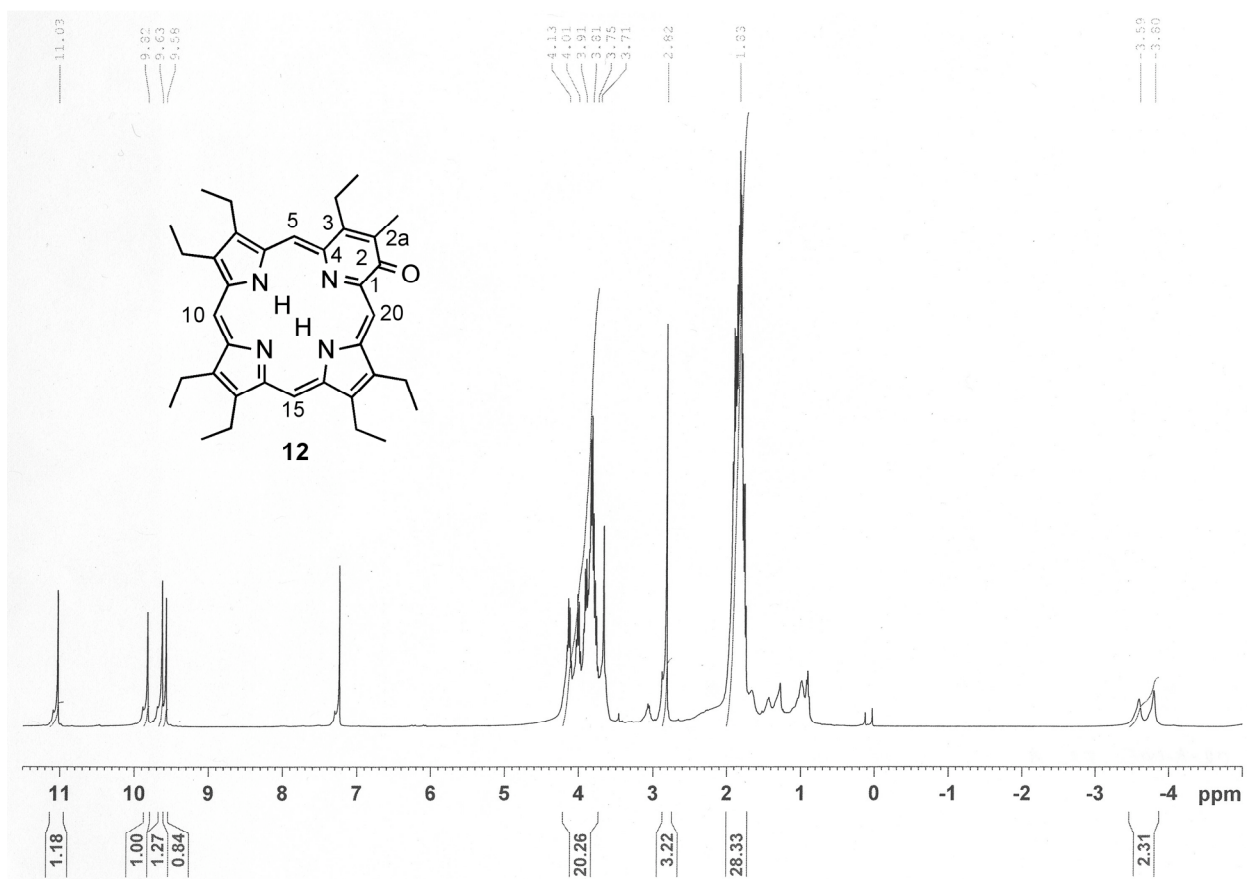


Figure S3. ^1H NMR (CHCl_3 , 400 MHz) of **12.**

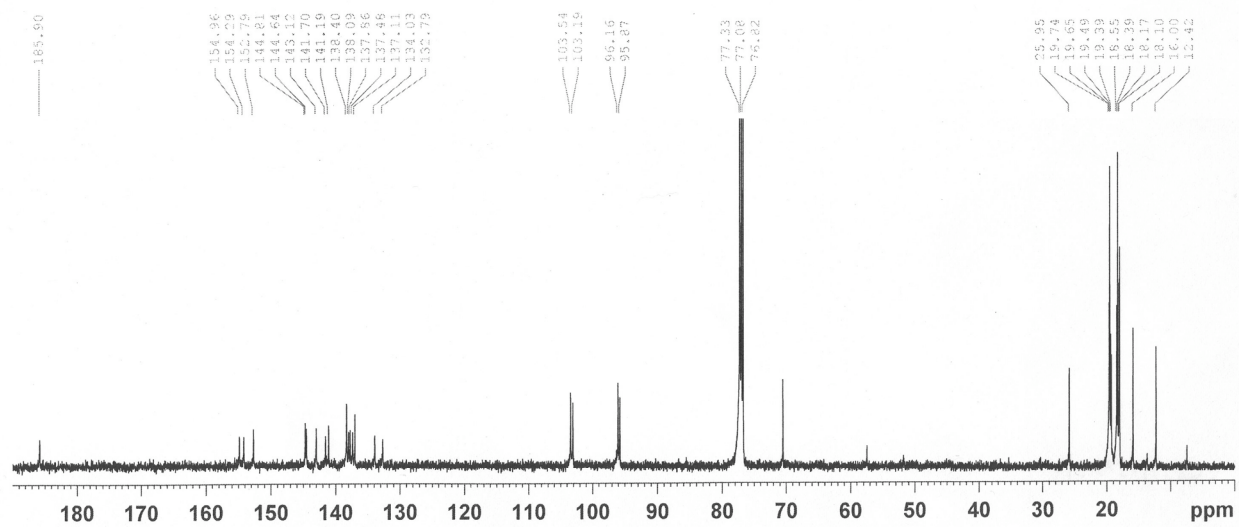


Figure S4. ^{13}C NMR (CHCl_3 , 100 MHz) of **12.**

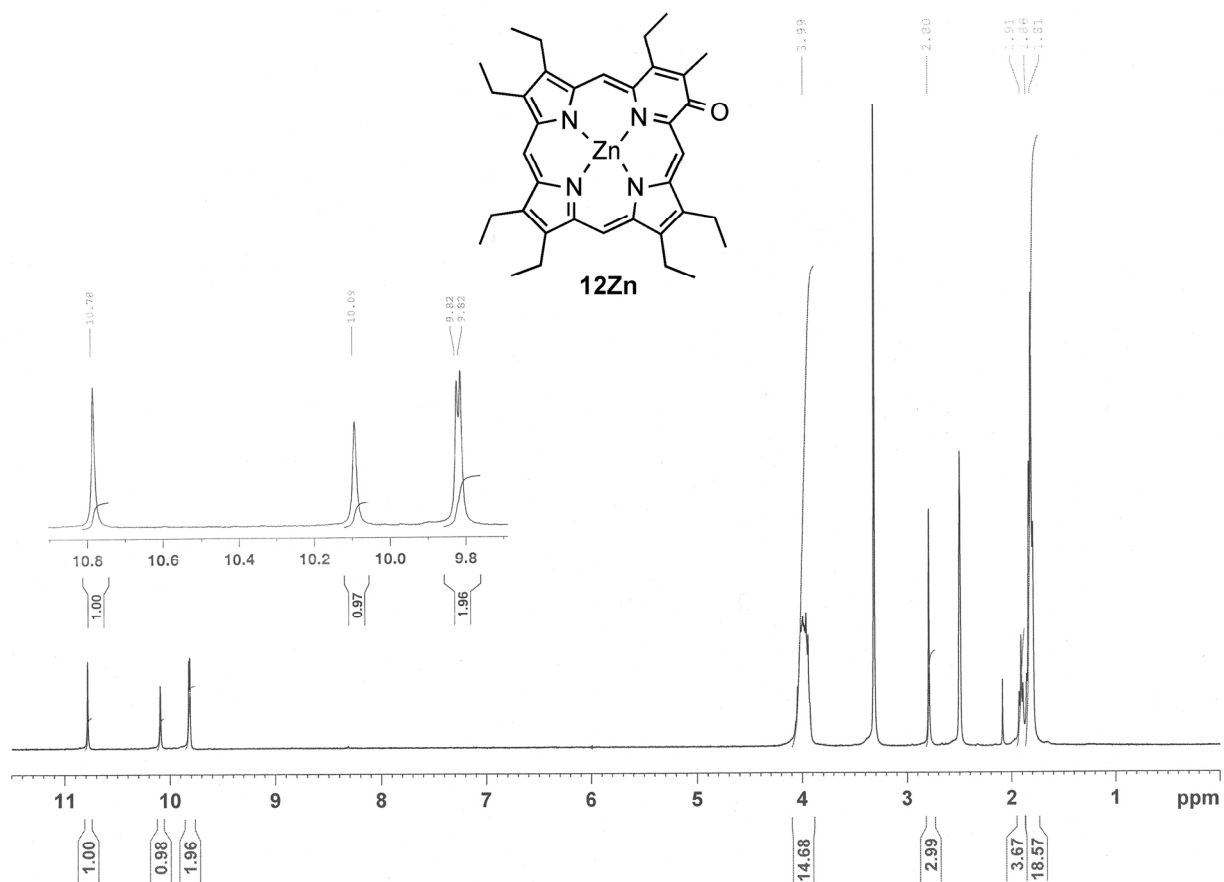


Figure S5. ¹H NMR (CHCl₃, 400 MHz) of **12Zn**.

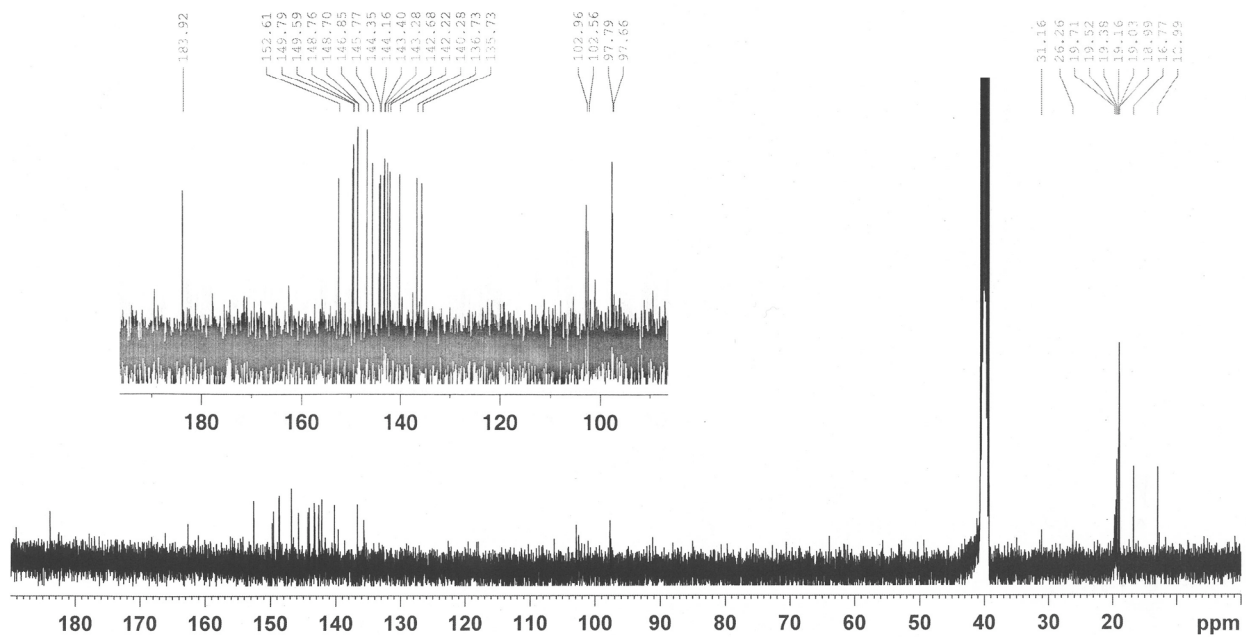
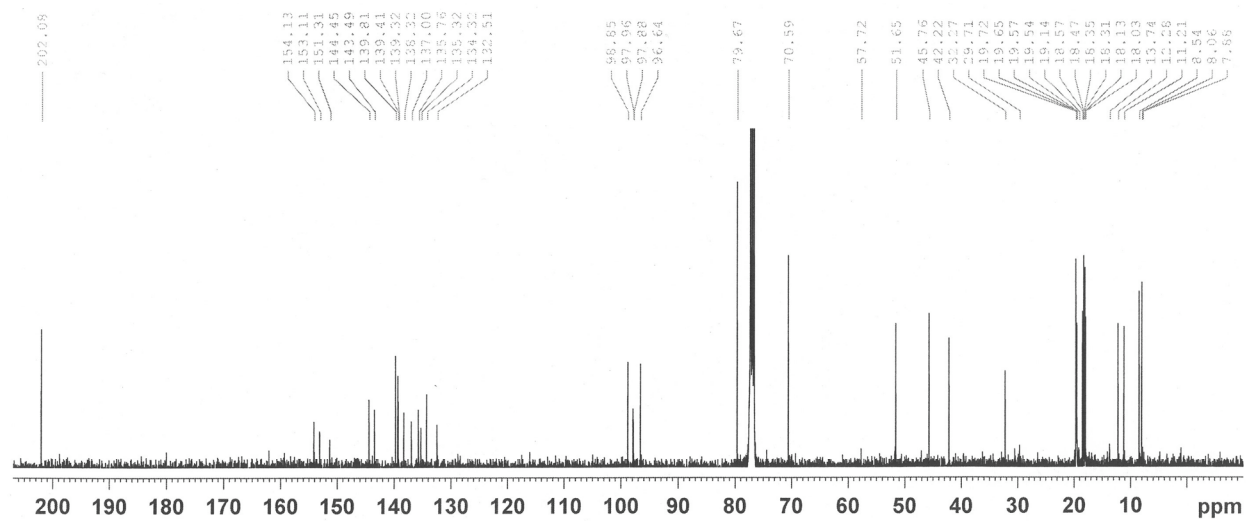
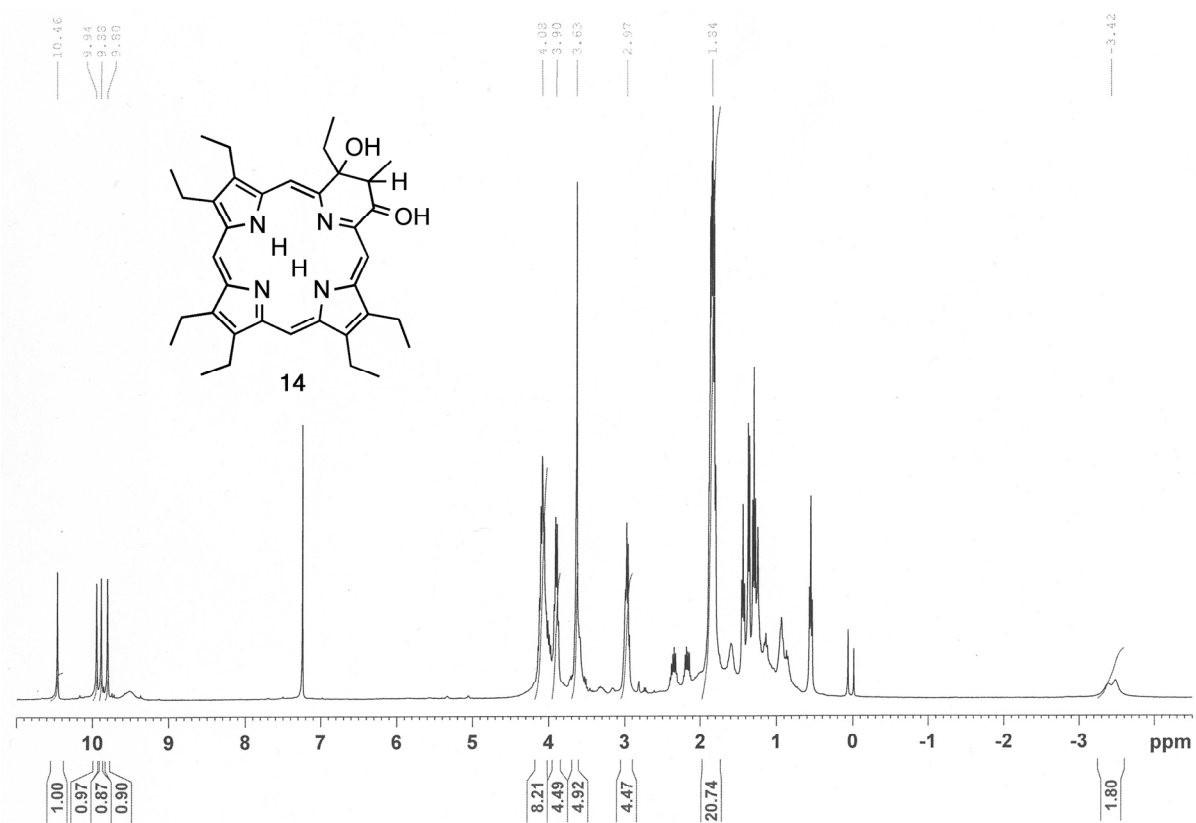


Figure S6. ¹³C NMR (CHCl₃, 100 MHz) of **12Zn**.



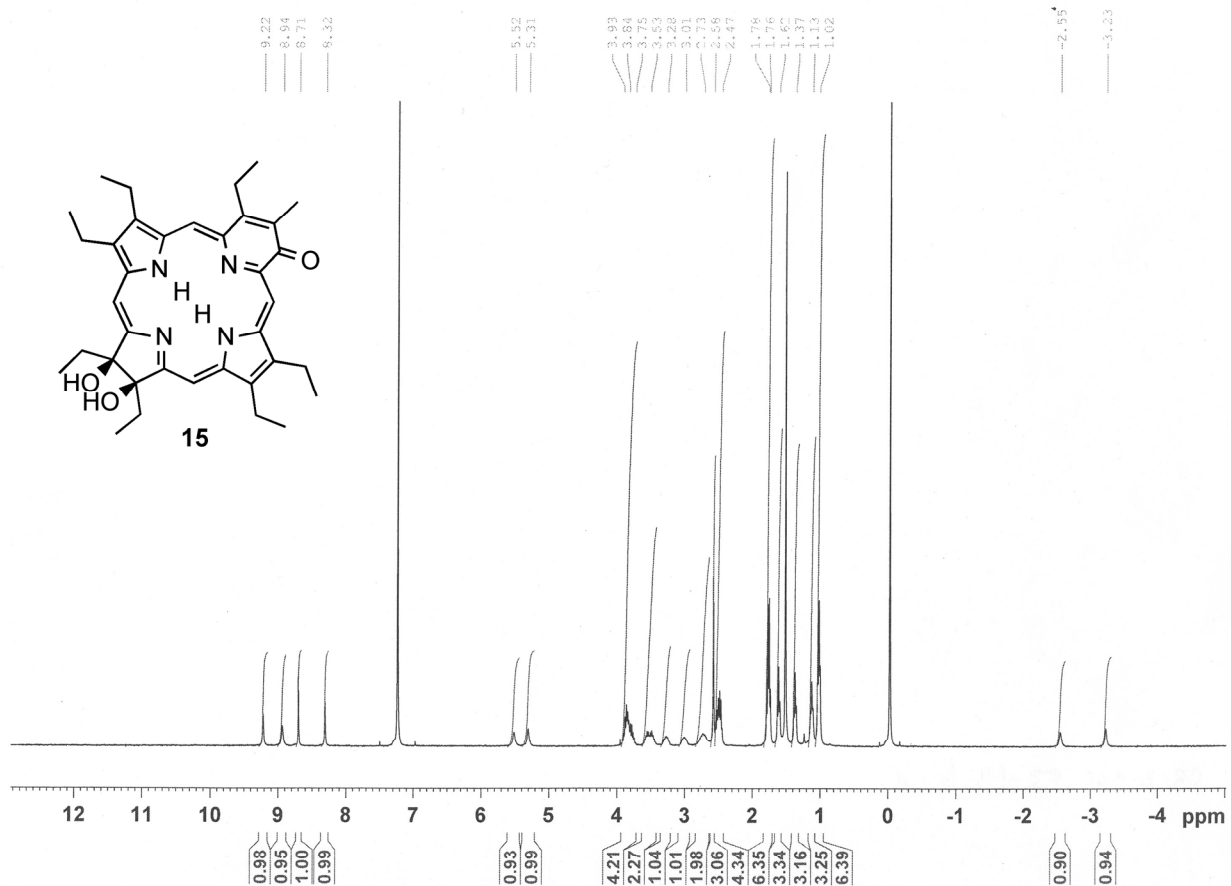


Figure S9. ^1H NMR (CHCl_3 , 500 MHz) of **15**.

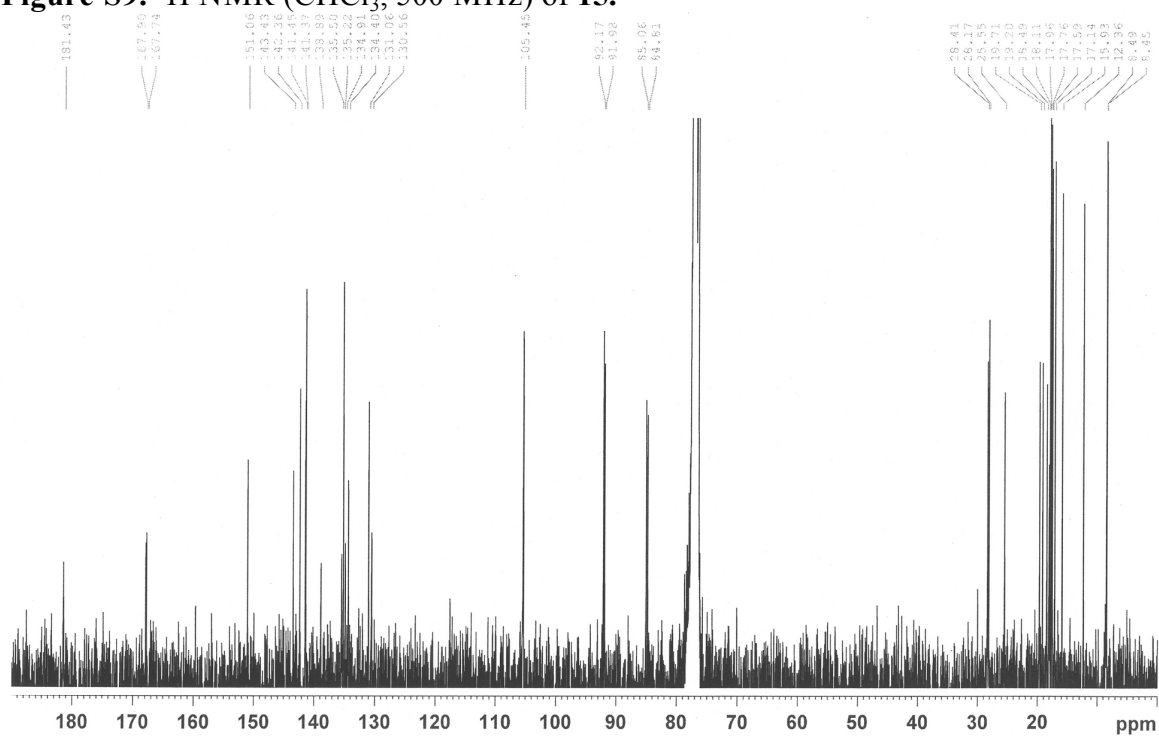
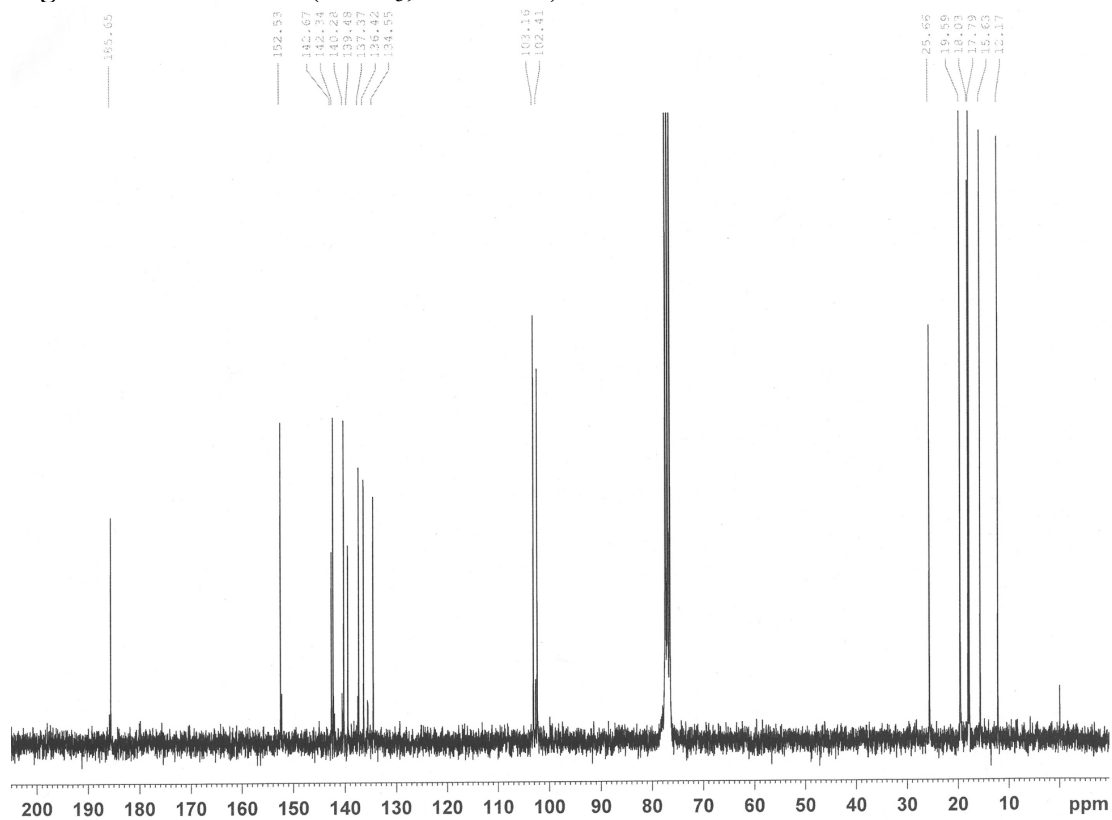
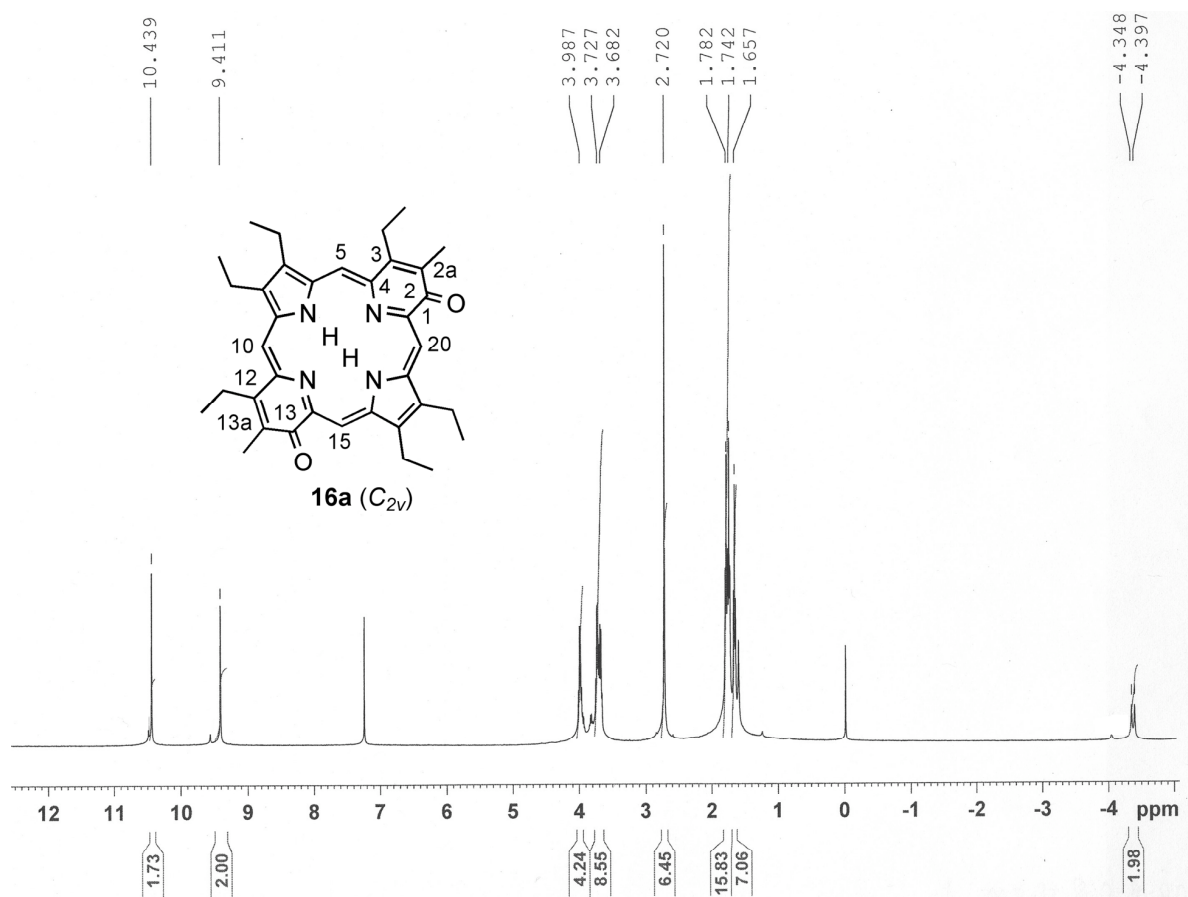


Figure S10. ^{13}C NMR (CHCl_3 , 125 MHz) of **15**.



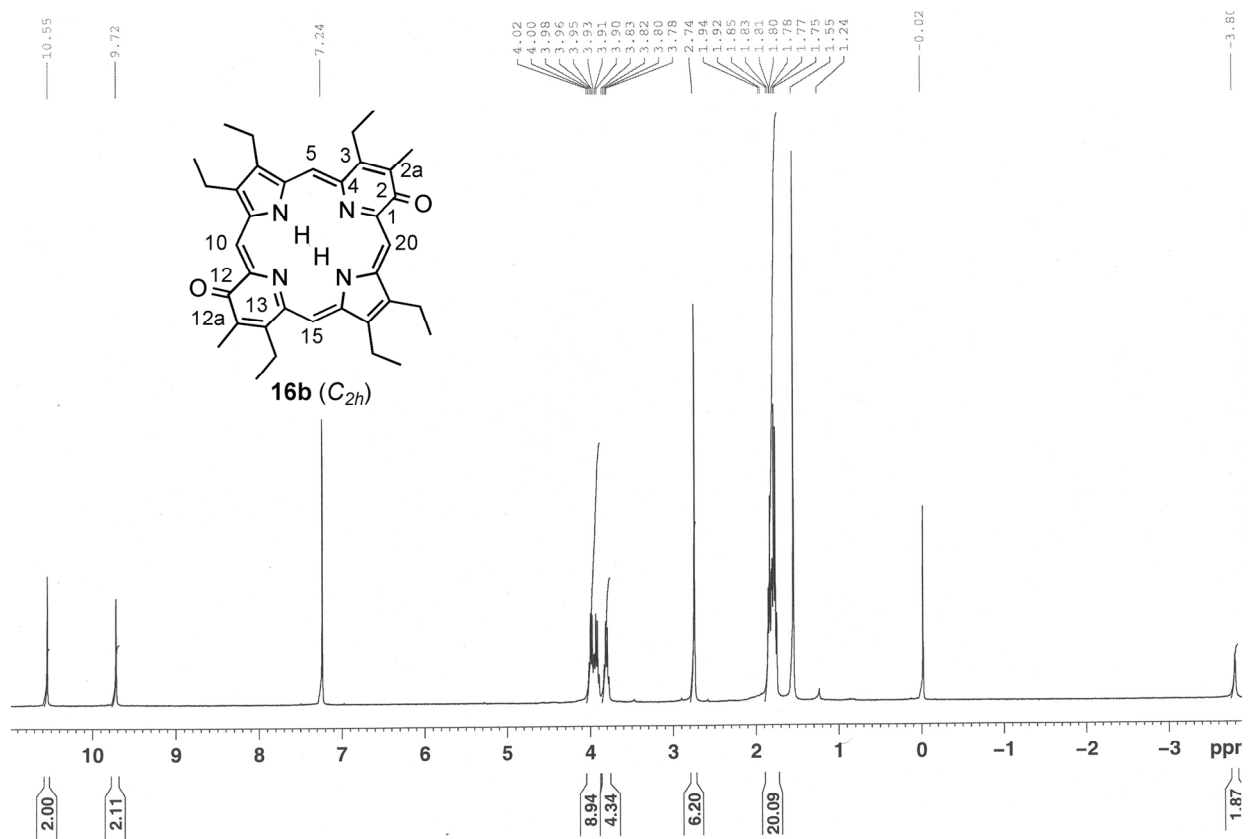


Figure S13. 1H NMR (CHCl₃, 500 MHz) of **16b**.

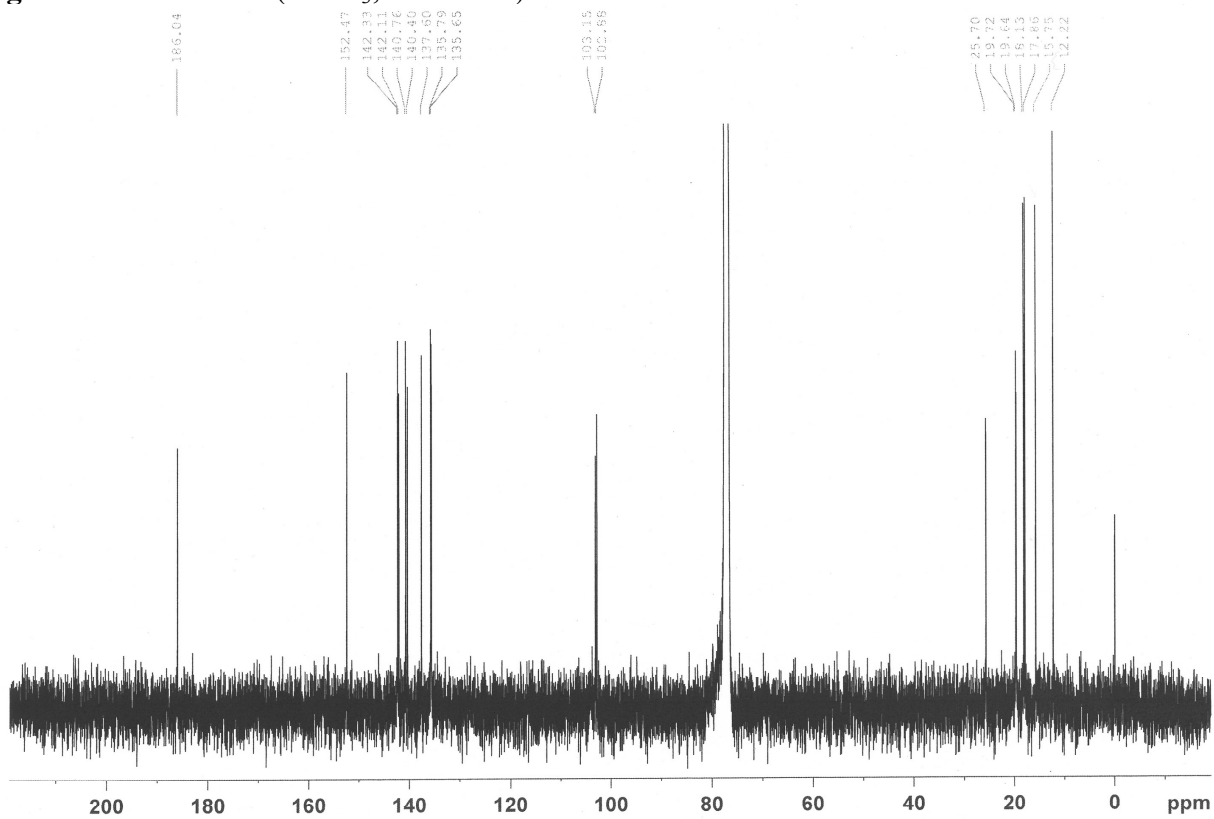


Figure S14. ^{13}C NMR (CHCl₃, 125 MHz) of **16b**.

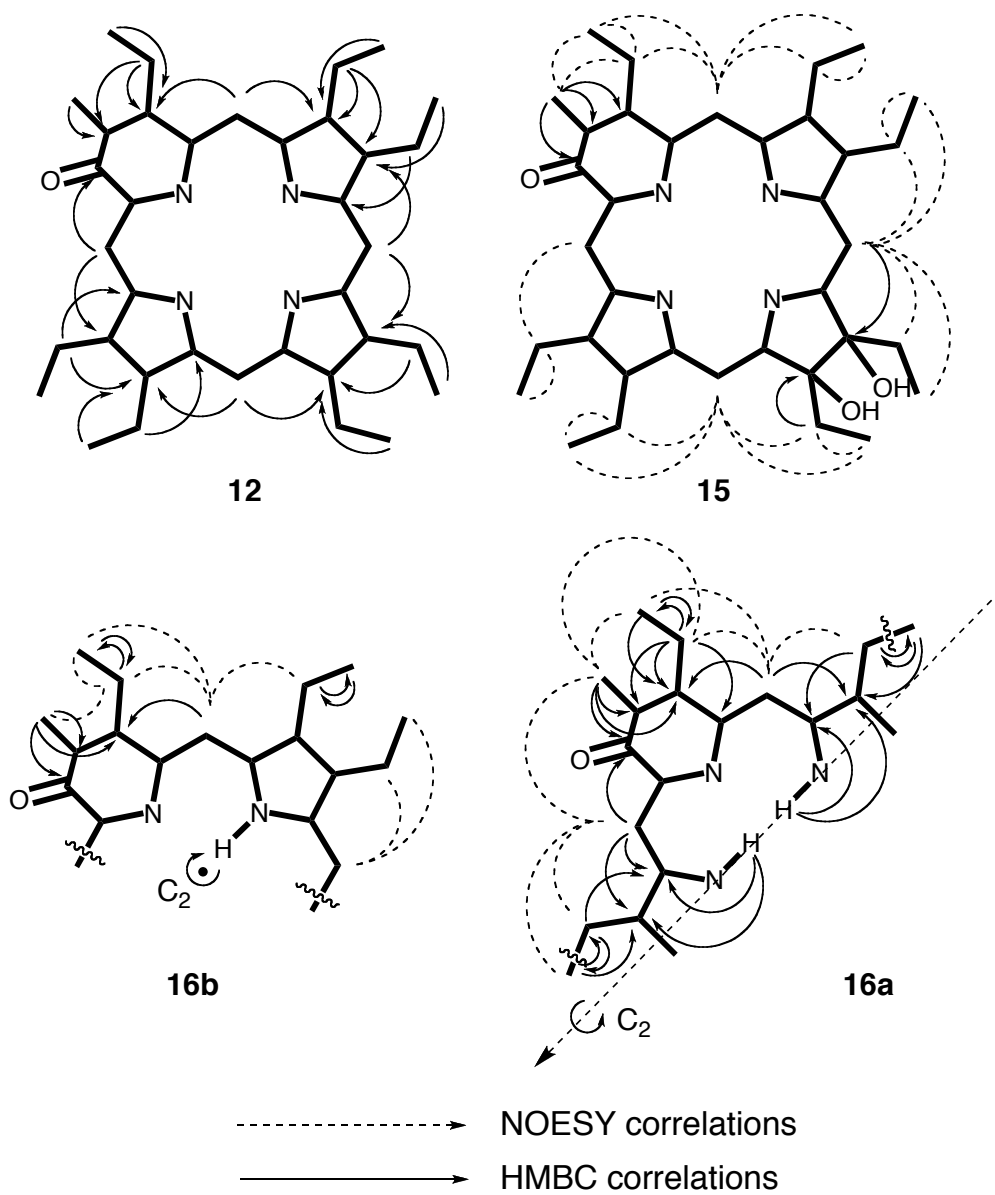


Figure S15. Summary of the HMQC and NOESY correlation data upon which the peak assignments rested. (all CHCl_3 , 500/125 MHz).

Tabel S1. Solvent-dependent UV-vis spectra of **12**

Solvent	λ_{max} (rel. intensity)
C₆H₆	403 (0.30), 425 (1.00), 443 (0.33), 545 (0.04), 581 (0.08), 617 (0.05), 677 (0.14)
DMSO	403 (0.23), 426 (1.00), 446 (0.30), 547 (0.04), 578 (sh), 587 (0.08), 615 (0.07), 672 (0.11)
C₆H₁₁	379 (0.22), 400 (1.00), 418 (0.47), 435 (0.33), 583 (0.08), 615 (0.09), 667 (0.07)

Tabel S2. Solvent-dependent UV-vis spectra of **12Zn**

Solvent	λ_{max} (rel. intensity)
CHCl₃ (EtOH stabilized)	434 (1.00), 454 (0.56), 577 (0.06), 627 (0.16)
CHCl₃ (HPLC)	428 (1.00), 446 (0.96), 633 (0.22)
CHCl₃/Pentane (3:1)	428 (1.00), 446 (0.97), 633 (0.23)
CHCl₃/Pentane (1:1)	427 (0.90), 445 (1.00), 633 (0.24)
CHCl₃/Pentane (1:3)	428 (0.84), 445 (1.00), 633 (0.27)
Pentane	428 (sh), 444 (1.00), 633 (0.26)

Tabel S3. Solvent-dependent UV-vis spectra of **15**

Solvent	λ_{max} (rel. intensity)
CHCl₃	402 (0.27), 426 (1.00), 449 (0.29), 541 (0.04), 575 (sh), 587 (0.08), 613 (0.07), 669 (0.10)
C₆H₆	403 (0.30), 425 (1.00), 443 (0.33), 545 (0.04), 581 (0.08), 617 (0.05), 677 (0.14)
DMSO	403 (0.23), 426 (1.00), 446 (0.30), 547 (0.04), 578 (sh), 587 (0.08), 615 (0.07), 672 (0.11)
C₆H₁₂	379 (0.22), 400 (1.00), 418 (0.47), 4435 (0.33), 583 (0.08), 615 (0.09), 667 (0.07)

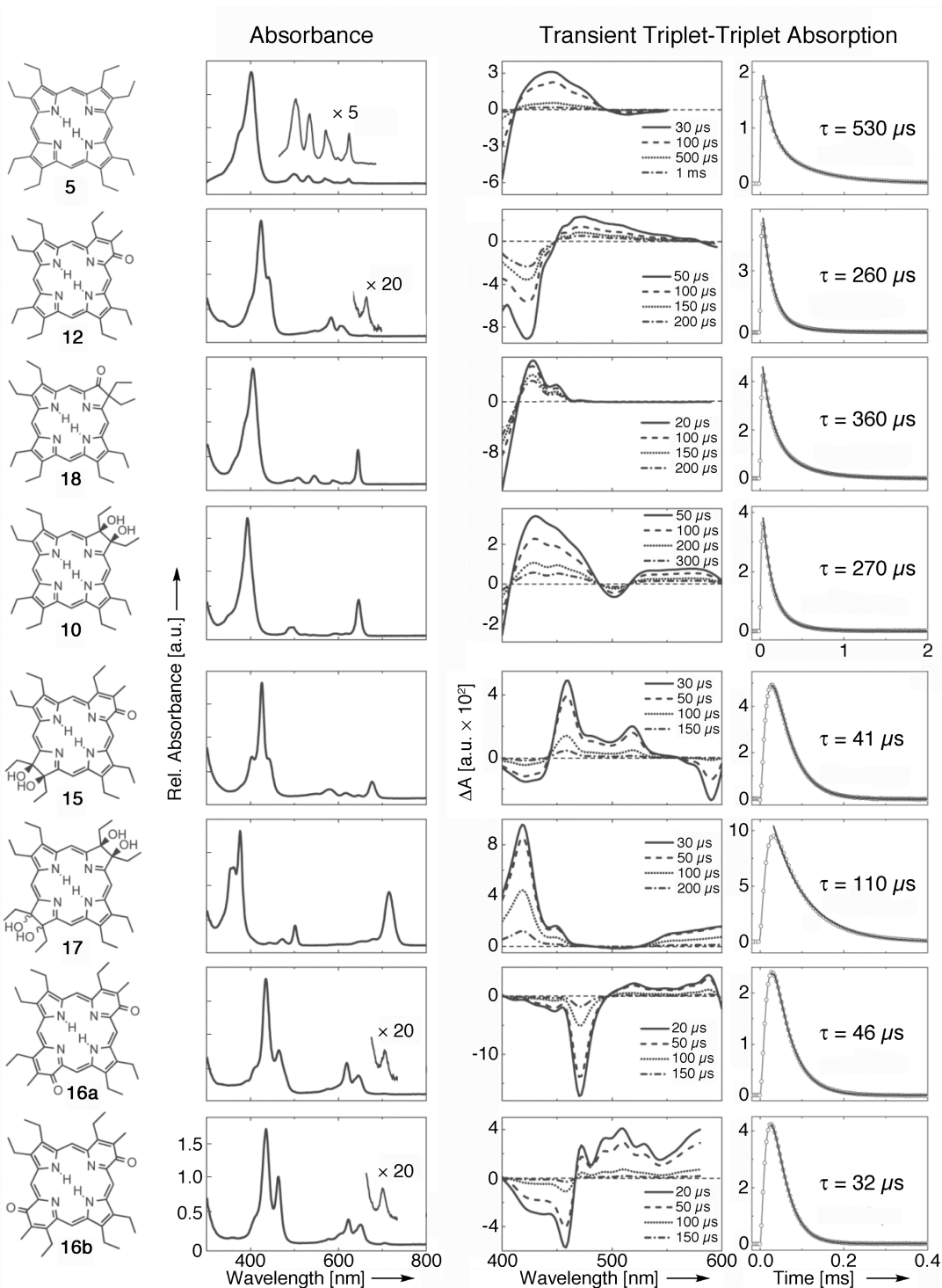


Figure S16: Normalized absorption and fluorescence emission spectra and triplet life-times of **5**, **12**, **18**, **10**, **15**, **17**, **16a**, and **16b** (all at ambient T, degassed toluene), together with their transient triplet-triplet transient spectra and the kinetic traces used for the triplet lifetime determination (solid line represents the fitted trace). The triplet excited state lifetimes were calculated as mean of at least eight decay constants of the decay kinetics taken at different wavelengths (440 nm for **5**, 470 nm for **12**, 470 nm for **18**, 430 nm for **10**, 460 nm for **15**, 420 nm for **17**, 520 nm for **16a** and 510 nm for **16b**). For the lifetimes in different solvent systems, see Table S4.

Table S4. Triplet Relaxation Time (τ) in toluene and 2-MeTHF.

Molecule	Solvent	τ [ms]
5	Toluene	530 ± 25
	2-MeTHF	530 ± 30
12	Toluene	260 ± 40
10	Toluene	270 ± 40
	2-MeTHF	350 ± 10
18	Toluene	360 ± 20
	2-MeTHF	650 ± 20
15	Toluene	41 ± 7
	2-MeTHF	100 ± 5
17	Toluene	110 ± 10
	2-MeTHF	120 ± 10
16a	Toluene	46 ± 4
16b	Toluene	32 ± 2

Spectrophotometric Titrations (Only the Q-band region is shown):

Conditions: Porphyrin indicated in CH_2Cl_2 (spectrograde) at ambient temperature. Aliquots (10-100 μL) of a of TFA solution in CH_2Cl_2 were added until no further significant changes in the spectrum were observed. Concentration of acid (2% to 0.02%) and volume of porphyrin solution (3 to 10 mL) were chosen such that the dilution error at the point of highest [TFA] did not exceed 5%.

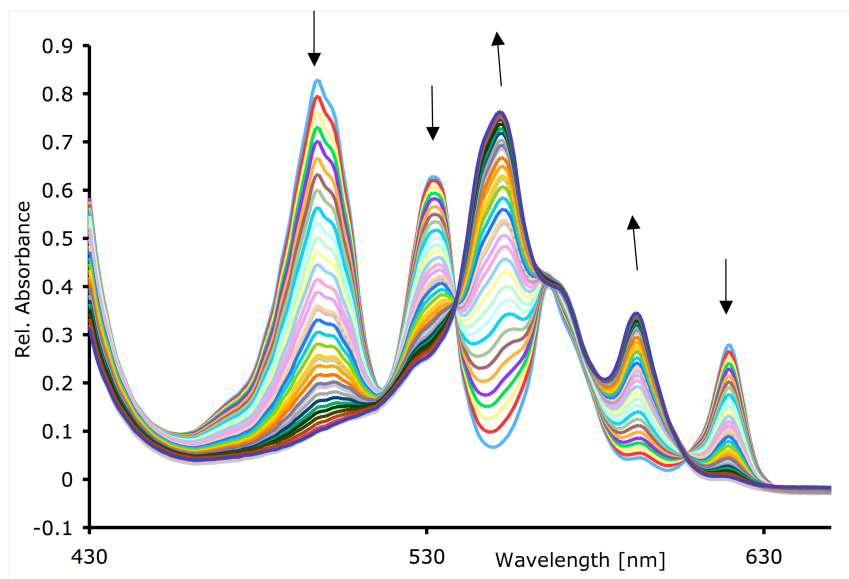


Figure S17: UV-vis Spectrophotometric titration of **OEP (5)** (Q-band region).

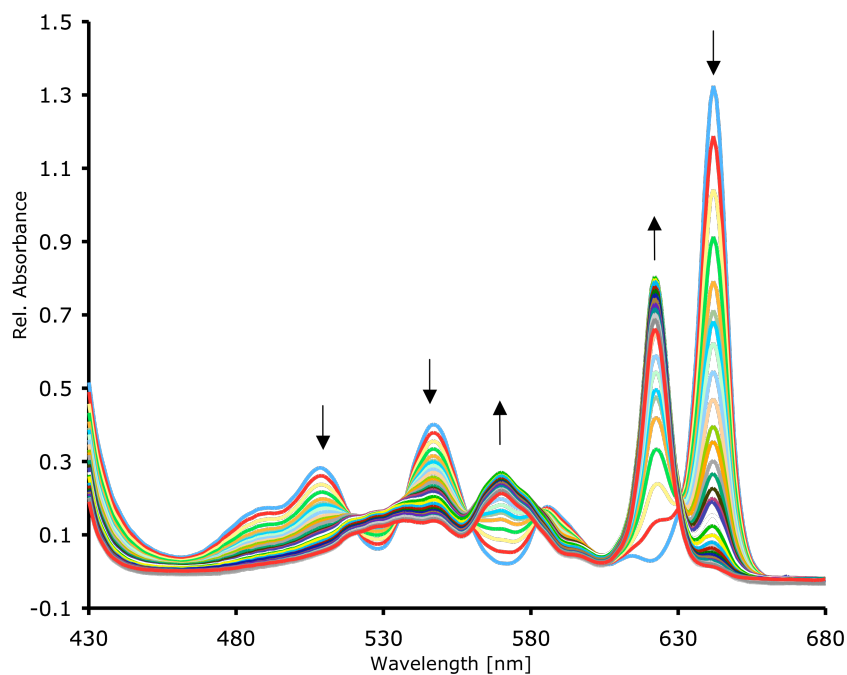


Figure S18: UV-vis Spectrophotometric titration of oxochlorin **18** (Q-band region).

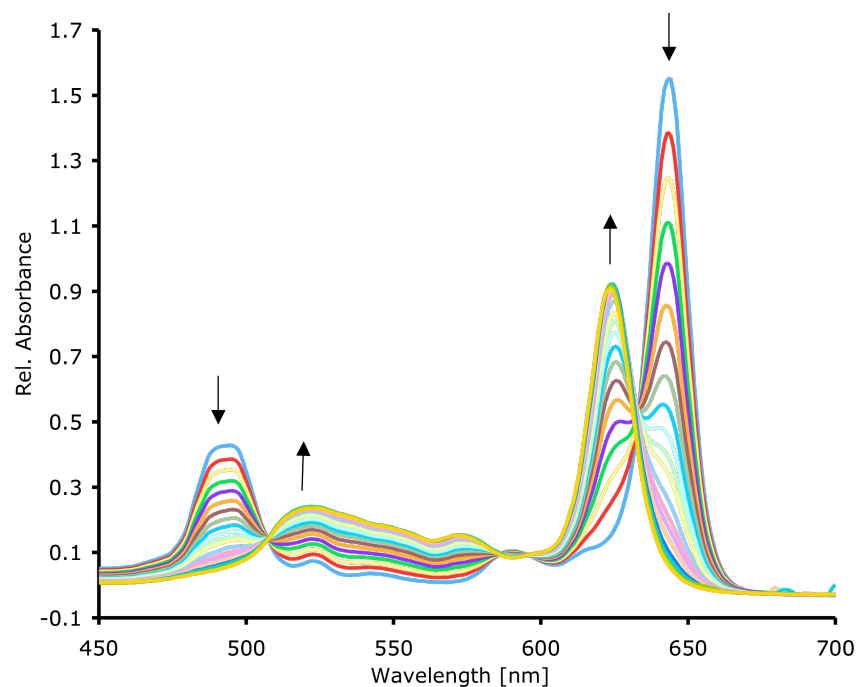


Figure S19: UV-vis Spectrophotometric titration of diol chlorin **10** (Q-band region).

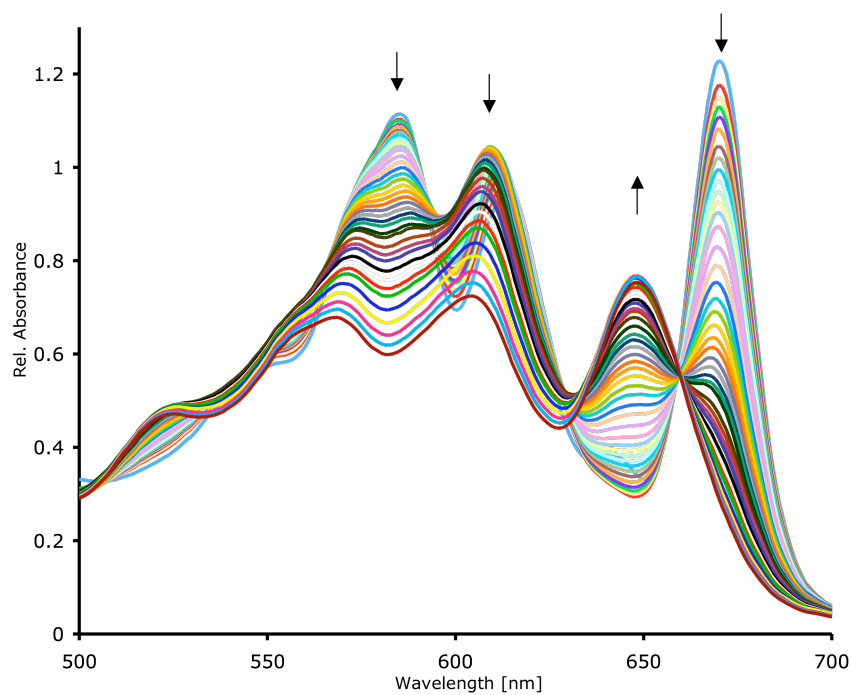


Figure S20: UV-vis Spectrophotometric titration of 12,13-dihydro,dihydroxyoxypyriporphyrin **15** (Q-band region).

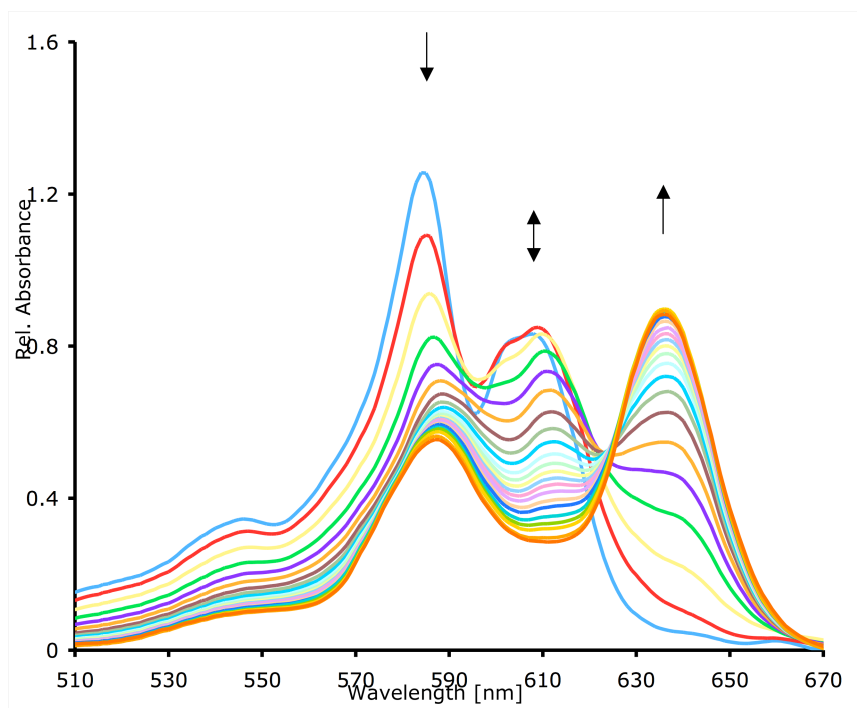


Figure S21: UV-vis Spectrophotometric titration of oxypyriporphyrin **12** (Q-band region).

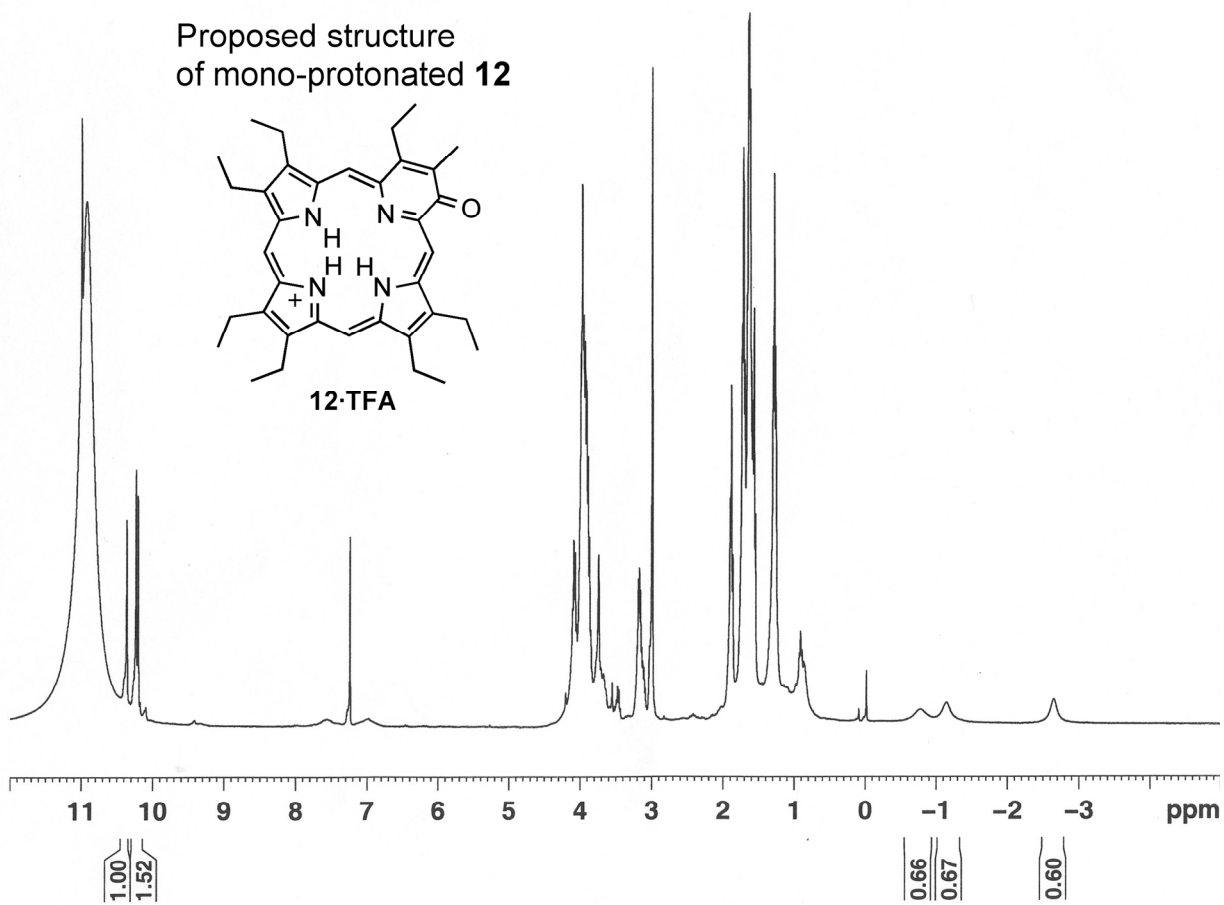


Figure S22: ^1H NMR of **12** (CDCl_3 + traces TFA, 400 MHz).

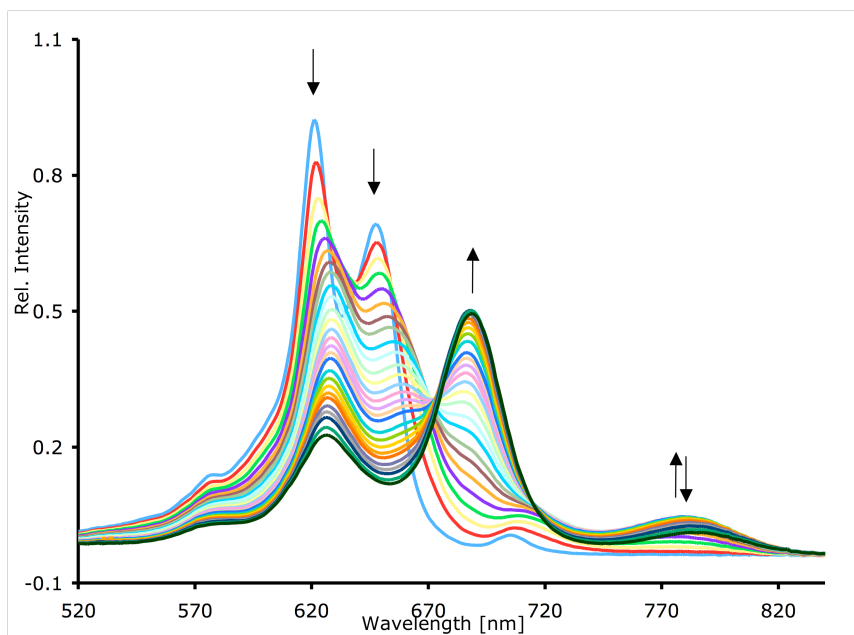


Figure S23: UV-vis Spectrophotometric titration of bis(oxypyri) porphyrin **16a** (Q-band region).

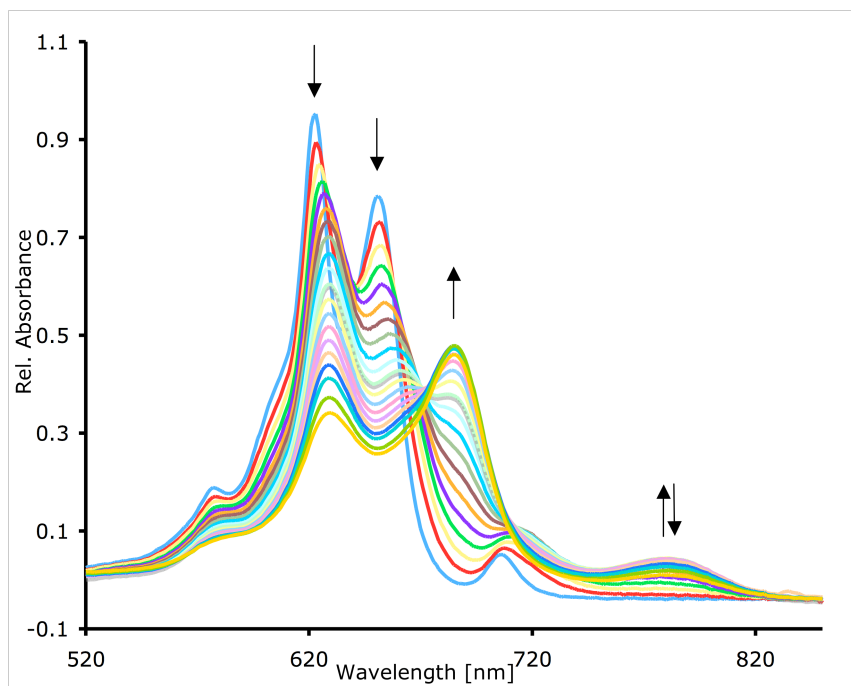


Figure S24: UV-vis Spectrophotometric titration of bis(oxypyri) porphyrin **16b** (Q-band region).

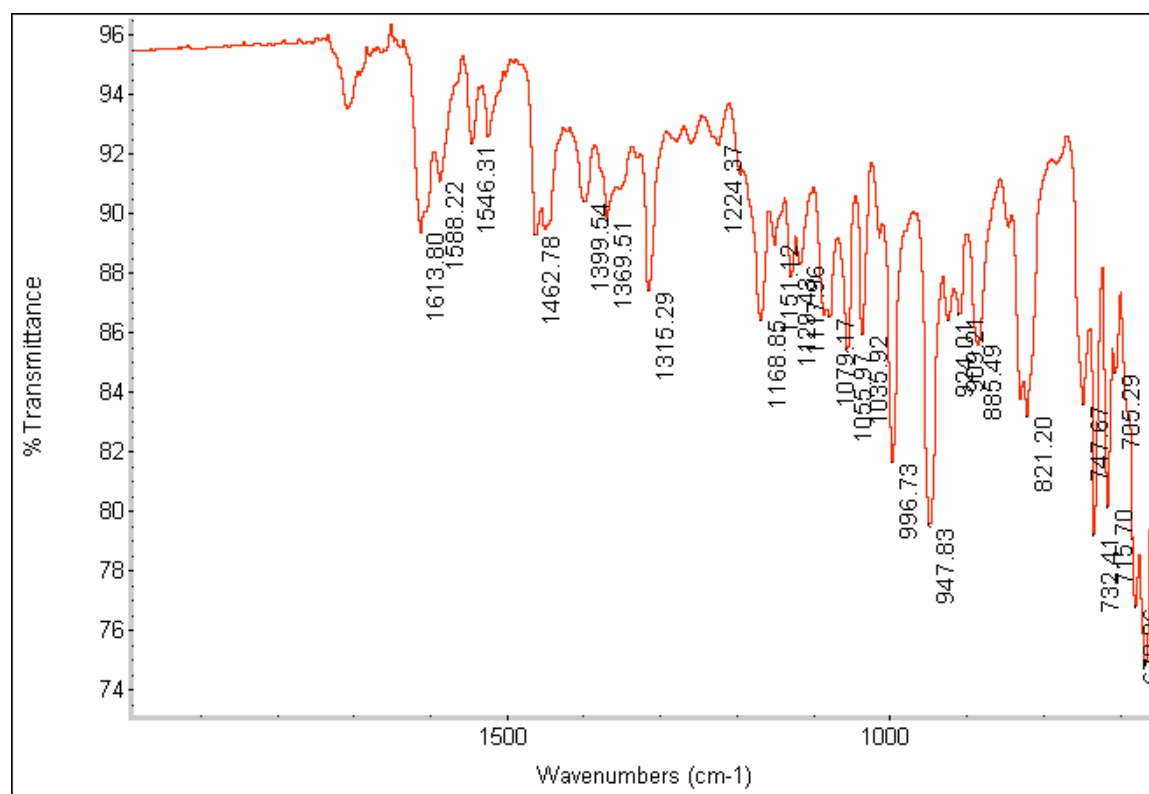


Figure S25: FT-IR Spectra (diffuse reflectance, neat sample) of **10** (for comparison)

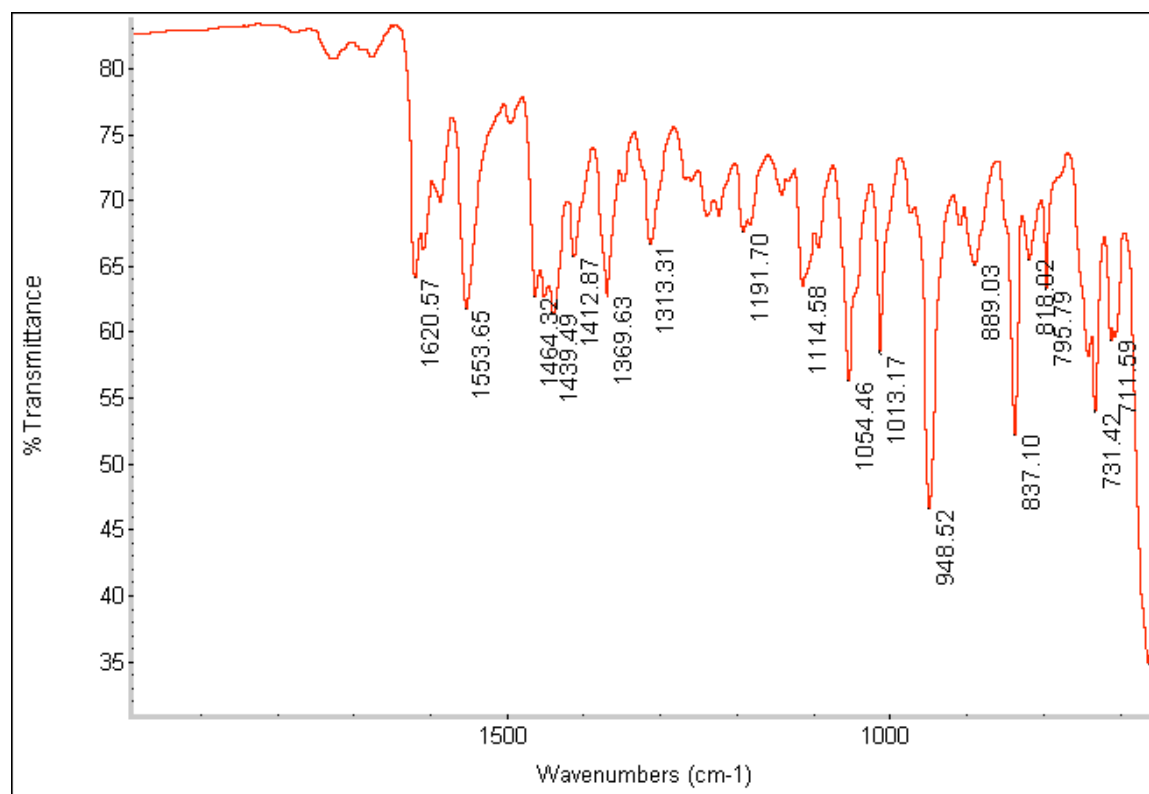


Figure S26: FT-IR Spectra (diffuse reflectance, neat sample) of **12**

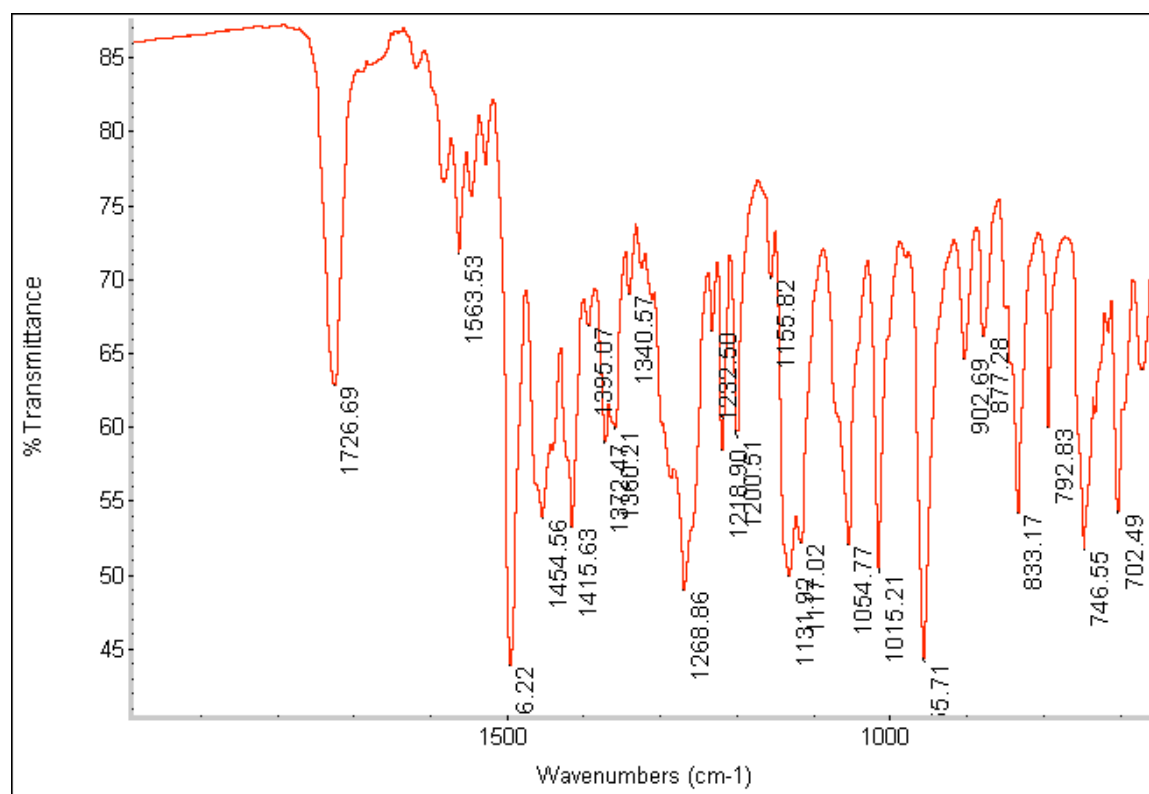


Figure S27: FT-IR Spectra (diffuse reflectance, neat sample) of **12Zn**

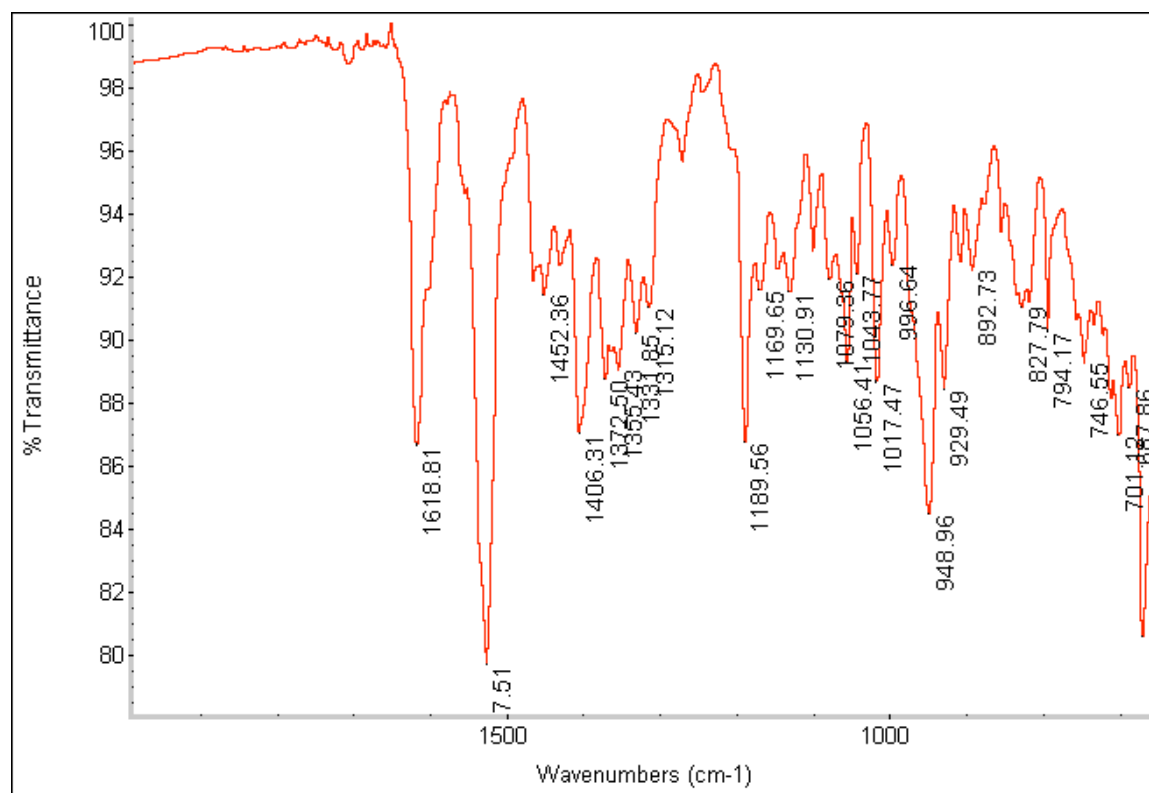


Figure S28: FT-IR Spectra (diffuse reflectance, neat sample) of **15**

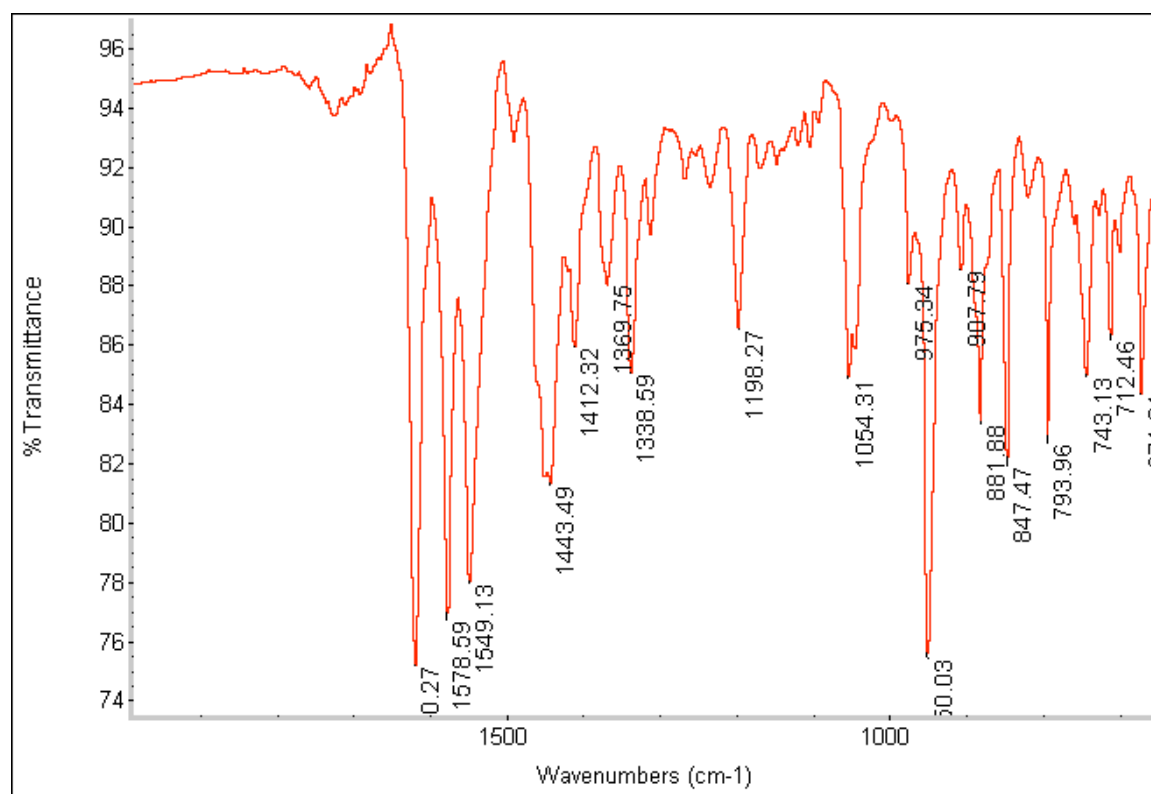


Figure S29: FT-IR Spectra (diffuse reflectance, neat sample) of **16a**

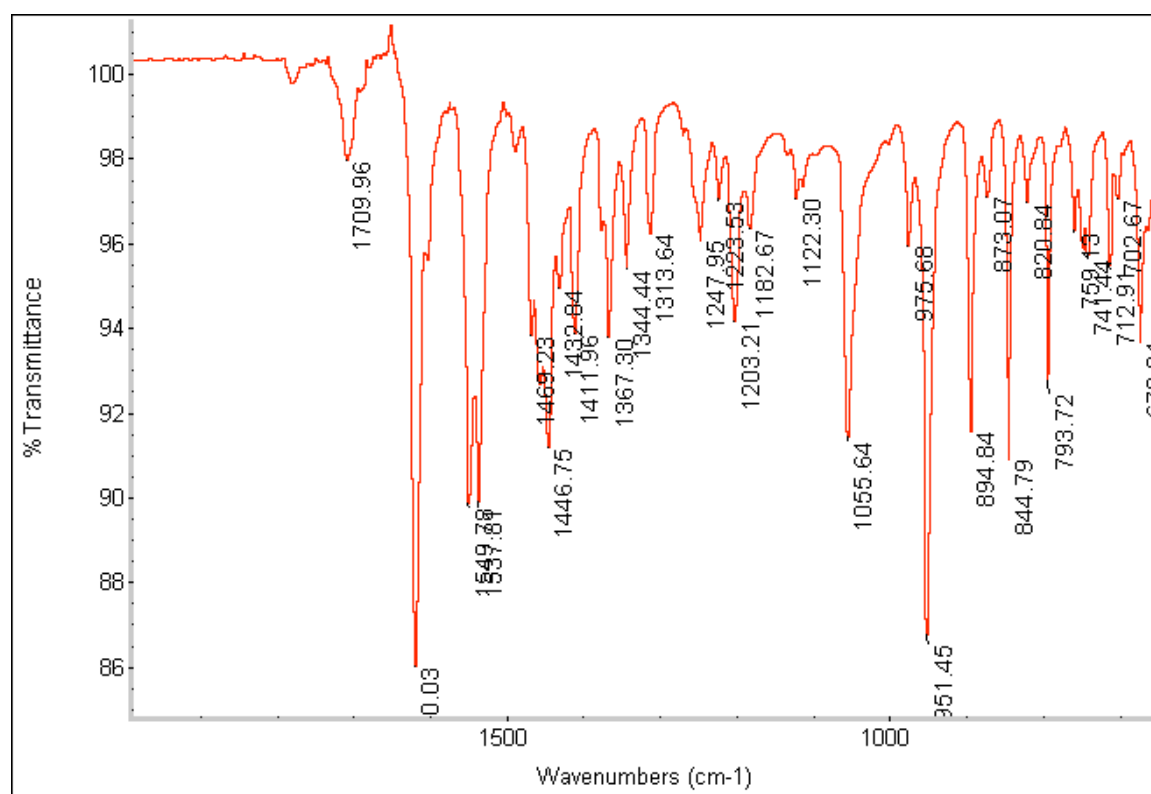


Figure S30: FT-IR Spectra (diffuse reflectance, neat sample) of **16b**

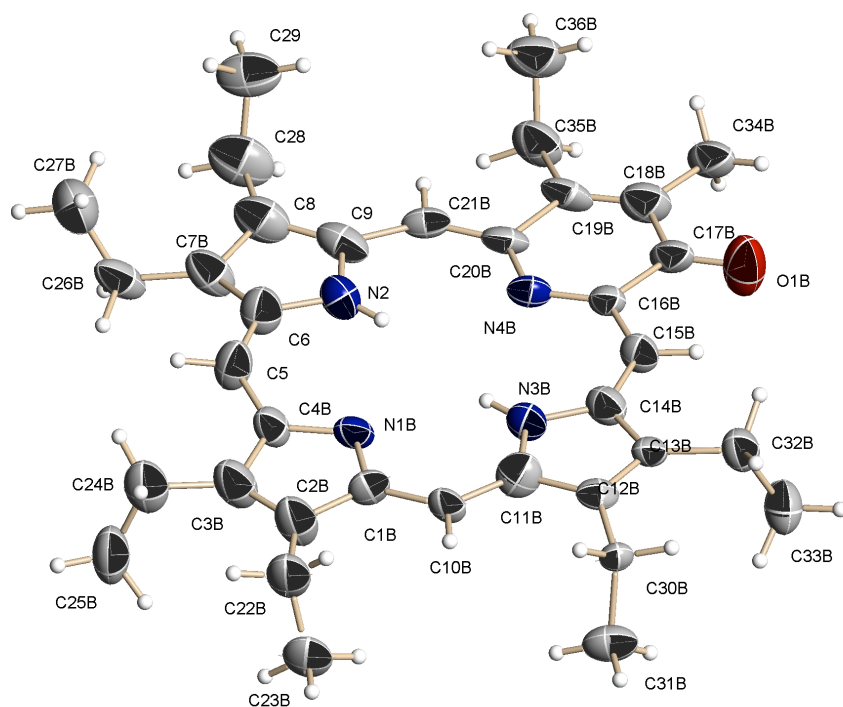


Figure S31: ORTEP (30% occupancy) representation of the structure of **12** with numbering system used in the structural analysis (note that this numbering differs from the numbering used in the NMR analyses).

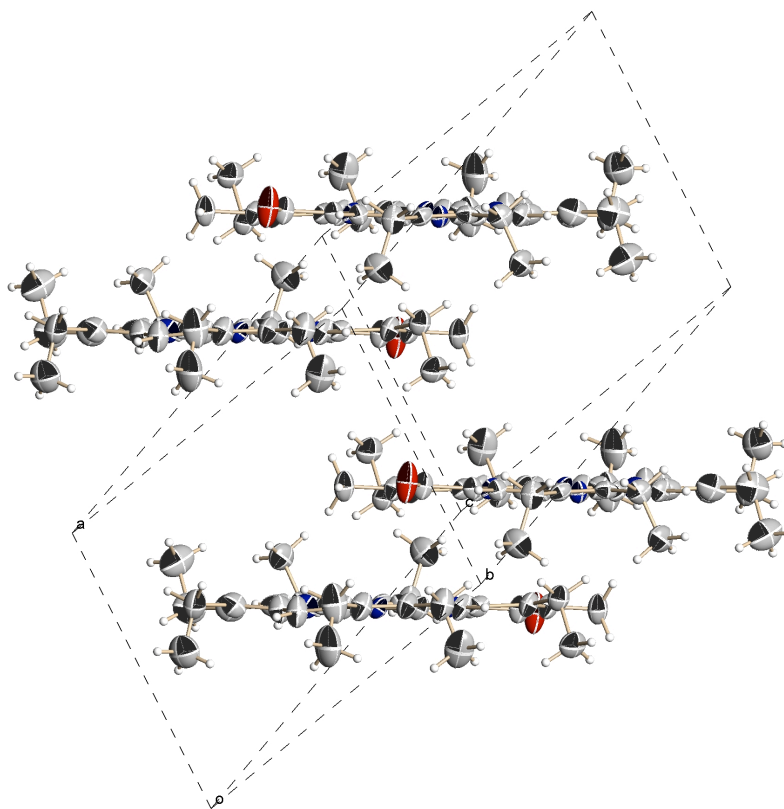


Figure S32: Packing diagram for **12**.