

Electronic Supporting Information to:

Porpholactams, Chlorolactams: Replacement of a
 β,β' -double bond in *meso*-tetraphenyl-porphyrin and
-chlorin by a lactam moiety

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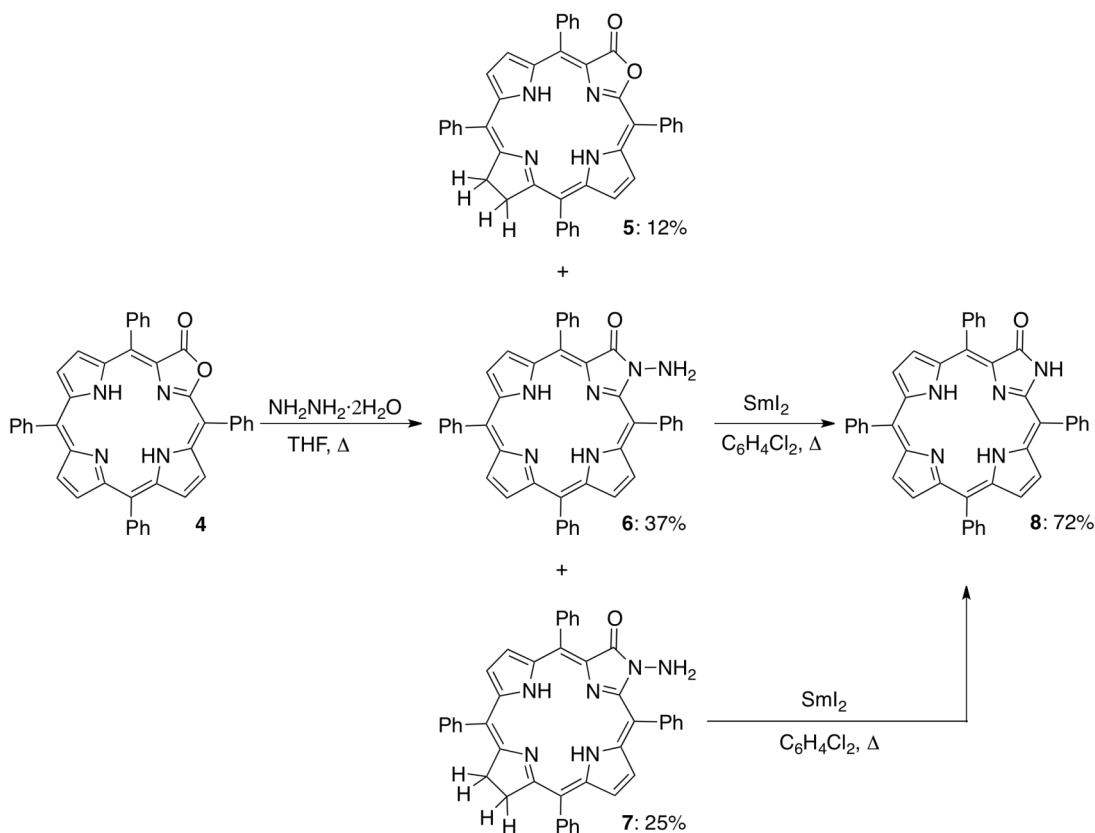
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ESI Table of Contents

Scheme ESI-1. Syntheses of chlorolactone 5 , porpholactams 6 and 8 , and chlorolactam 7 ...	ESI-3
Reaction of <i>meso</i> -tetraphenyl-2-oxa-3-oxo-porphyrin (porpholactone 4) with hydrazine to form <i>meso</i> -tetraphenyl-12-oxa-13-oxo-chlorin (chlorolactone 5), <i>meso</i> -tetraphenyl-2-(<i>N</i> -amino-aza)-3-oxo-porphyrin (<i>N</i> -aminoporpholactam 6), and <i>meso</i> -tetraphenyl-12-(<i>N</i> -amino-aza)-13-oxo-chlorin (chlorolactam 7).....	ESI-4
Figure ESI-1. ¹ H NMR Spectrum (400 MHz, CDCl ₃) of 5	ESI-6
Figure ESI-2. ¹³ C NMR Spectrum (400 MHz, CDCl ₃) of 5	ESI-7
Figure ESI-3. FT-IR Spectrum (neat, diffuse reflectance) of 5	ESI-8
Figure ESI-4. ¹ H NMR Spectrum (400 MHz, CDCl ₃) of 6	ESI-9
Figure ESI-5. ¹³ C NMR Spectrum (400 MHz, CDCl ₃) of 6	ESI-10
Figure ESI-6. FT-IR Spectrum (neat, diffuse reflectance) of 6	ESI-11
Figure ESI-7. ¹ H NMR Spectrum (400 MHz, CDCl ₃) of 7	ESI-12
Figure ESI-8. ¹³ C NMR Spectrum (400 MHz, CDCl ₃) of 7	ESI-13
Figure ESI-9. FT-IR Spectrum (neat, diffuse reflectance) of 7	ESI-14
Reduction of <i>meso</i> -tetraphenyl-2-(<i>N</i> -amino-aza)-3-oxo-porphyrin (<i>N</i> -aminoporpholactam 6) to form <i>meso</i> -tetraphenyl-2-aza-3-oxo-porphyrin (porpholactam 8).....	ESI-15
Figure ESI-10. ¹ H NMR Spectrum (400 MHz, CDCl ₃) of 8	ESI-16
Figure ESI-11. ¹³ C NMR Spectrum (400 MHz, CDCl ₃) of 8	ESI-17
Figure ESI-12. FT-IR Spectrum (neat, diffuse reflectance) of 8	ESI-18
Details to the X-ray structures of <i>N</i> -aminoporpholactam 6 , porpholactam 8 , and <i>N</i> -aminochlorolactam 7	ESI-18
Figure ESI-13. ORTEP representation of crystal structure of 6 ·0.37 H ₂ O.....	ESI-22
Figure ESI-14. ORTEP representation of crystal structure of 7 ·2 C ₂ H ₆ O.....	ESI-23
Figure ESI-15. ORTEP representation of crystal structure of 8	ESI-24

Materials and Instruments

All solvents and reagents (Aldrich, Acros, CIL) were used as received. Analytical (aluminum backed, silica gel 60, 250 μm thickness) and preparative (20 \times 20 cm, glass backed, silica gel 60, 500 or 1000 μm thickness) TLC plates, the flash column silica gel (premium grade, 60 \AA , 32-63 μm), and the basic alumina gel (50-200 μm , PH: 10) used were provided by Sorbent Technologies, Atlanta, GA. ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX400 instrument. High and low resolution mass spectra were provided by the Mass Spectrometry Facilities at the Department of Chemistry, University of Connecticut. UV-vis spectra were recorded on a Cary 50, Varian Inc. IR spectra on a JASCO FT-IR-410 using an ATR unit (ZnSe).



Scheme ESI-1. Syntheses of chlorolactone **5**, porpholactams **6** and **8**, and chlorolactam **7**.

Reaction of *meso*-tetraphenyl-2-oxa-3-oxo-porphyrin (porpholactone **4) with hydrazine to form *meso*-tetraphenyl-12-oxa-13-oxo-chlorin (chlorolactone **5**), *meso*-tetraphenyl-2-(*N*-amino-aza)-3-oxo-porphyrin (*N*-aminoporpholactam **6**), and *meso*-tetraphenyl-12-(*N*-amino-aza)-13-oxo-chlorin (chlorolactam **7**)**

meso-Tetraphenyl-2,3-oxochlorin **4** (56 mg, 8.85×10^{-5} mol) was dissolved in THF (20 mL) and magnetically stirred. Hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot 2\text{H}_2\text{O}$, 11 mL) was added and the mixture was heated to reflux for 5 days. When the starting material was consumed (reaction control by TLC), the reaction mixture was allowed to cool and was evaporated to dryness by rotary evaporation. The residue was taken up in CH_2Cl_2 , washed with H_2O (2×10 mL), and dried over anhyd Na_2SO_4 , and filtered. The filtrate was reduced under vacuum and separated by preparative TLC ($\text{CH}_2\text{Cl}_2/2\%$ MeOH), providing **5** in 12% (7.0 mg), **6** in 37% (21.0 mg), and **7** in 25% (15.0 mg) yields. When the reaction is performed under nitrogen for 5 days, the formation of **5** is almost totally suppressed, and **6** and **7** were isolated in 81-90% and 3-5% yields, respectively.

5: R_f (silica- CH_2Cl_2) 0.50; ^1H NMR (400 MHz, CDCl_3): δ 8.48 (dd, $^3J = 5.0$ Hz, $^4J = 1.6$ Hz, 1H), 8.24 (dd, $^3J = 4.6$ Hz, $^4J = 1.9$ Hz, 1H), 8.15 (dd, $^3J = 5.0$ Hz, $^4J = 1.5$ Hz, 1H), 8.01 and 7.99 (overlapping d and s, 2H), 7.93 (dd, $^3J = 4.6$ Hz, $^4J = 1.8$ Hz, 1H), 7.89 and 7.88 (overlapping s and d, 2H), 7.82 – 7.80 (m, 4H), 7.68 – 7.65 (m, 12H), 4.06 – 3.98 (m, 4H), –0.78 (s, 1H, exchangeable with D_2O), –1.20 (s, 1H, exchangeable with D_2O); ^{13}C NMR (100 MHz, CDCl_3 , neutralized in basic alumina): δ 170.0, 167.6, 164.2, 152.6, 142.8, 142.1, 141.0, 139.1, 139.0, 138.5, 137.5, 134.8, 133.9, 132.3, 132.2, 131.9, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.6, 126.6, 125.9, 125.5, 122.9, 121.7, 116.0, 114.6, 104.9, 36.8, 34.7; UV-vis (CHCl_3) λ_{max} (log ϵ)

412 (5.35), 512 (4.02), 547 (4.02), 625 (3.83), 686 (4.67) nm; HR-MS (ESI⁺, cone voltage = 30 V, 100% CH₃CN) *m/e* calcd for C₄₃H₃₁N₄O₂ 635.2447 ([M]⁺), found 635.2432.

6: R_f (silica-CH₂Cl₂/2% MeOH) 0.45; ¹H NMR (400 MHz, CDCl₃ neutralized in basic alumina): δ 8.80 (d, ³J= 4.0 Hz, 1H), 8.77 (d, ³J= 4.0 Hz, 1H), 8.71 (d, ³J= 4.0 Hz, 1H), 8.68 (d, ³J= 4.0 Hz, 1H), 8.64 (d, ³J= 4.0 Hz, 1H), 8.58 (d, ³J= 4.0 Hz, 1H), 8.17 – 8.15 (m, 4H), 8.11 – 8.09 (m, 2H), 8.04 – 8.02 (m, 2H), 7.78 – 7.72 (m, 12H), 4.73 (s, 2H, exchangeable with D₂O), –2.08 (s, 1H, exchangeable with D₂O), –2.35 (s, 1H, exchangeable with D₂O); ¹³C NMR (100 MHz, CDCl₃): δ 168.3, 156.3, 154.3, 147.4, 141.8, 141.7, 141.4, 140.5, 140.1, 139.2, 138.4, 137.3, 135.5, 134.8, 134.6, 134.4, 133.8, 133.6, 132.8, 129.5, 128.3, 128.23, 128.2, 128.1, 127.8, 127.7, 127.1, 127.0, 127.0, 124.3, 121.4, 118.3, 105.8; UV-vis (CHCl₂) λ_{max} (log ε) 424 (5.47), 522 (4.35), 556 (4.04), 597 (3.93), 651 (3.68) nm; HR-MS (ESI⁺, cone voltage = 30 V, 100% CH₃CN) *m/e* calcd for C₄₃H₃₁N₆O 647.2559 ([M]⁺), found 647.2603.

7: R_f (silica-CH₂Cl₂/2% MeOH) 0.17; ¹H NMR (400 MHz, CDCl₃ neutralized in basic alumina): δ 8.43 (dd, ³J = 5.0 Hz, ⁴J = 1.6 Hz, 1H), 8.37 (dd, ³J = 4.7 Hz, ⁴J = 1.8 Hz, 1H), 8.15 (dd, ³J = 4.9 Hz, ⁴J = 1.6 Hz, 1H), 8.02 – 7.98 (m, 3H), 7.95 – 7.93 (m, 2H), 7.84 – 7.82 (m, 4H), 7.72 – 7.66 (m, 12H), 4.62 (s, 2H, exchangeable with D₂O), 4.06 (s, 4H), –1.27 (s, 1H, exchangeable with D₂O), –1.51 (s, 1H, exchangeable with D₂O); ¹³C NMR (100 MHz, CDCl₃): δ 168.8, 167.4, 164.6, 144.8, 142.8, 142.5, 140.8, 140.4, 140.2, 139.3, 138.7, 134.8, 133.2, 132.4, 132.3, 132.1, 131.3, 128.34, 128.33, 128.1, 127.98, 127.93, 127.8, 127.6, 126.7, 125.7, 125.6, 121.9, 121.7, 115.2, 114.0, 107.8, 36.6, 34.9; UV-vis (CHCl₂) λ_{max} (log ε) 414 (5.46), 509 (4.23), 542 (4.17), 634 (3.88), 695 (4.75) nm; HR-MS (ESI⁺, cone voltage = 30 V, 100% CH₃CN) *m/e* calcd for C₄₃H₃₃N₆O 649.2716 ([M]⁺), found 649.2735.

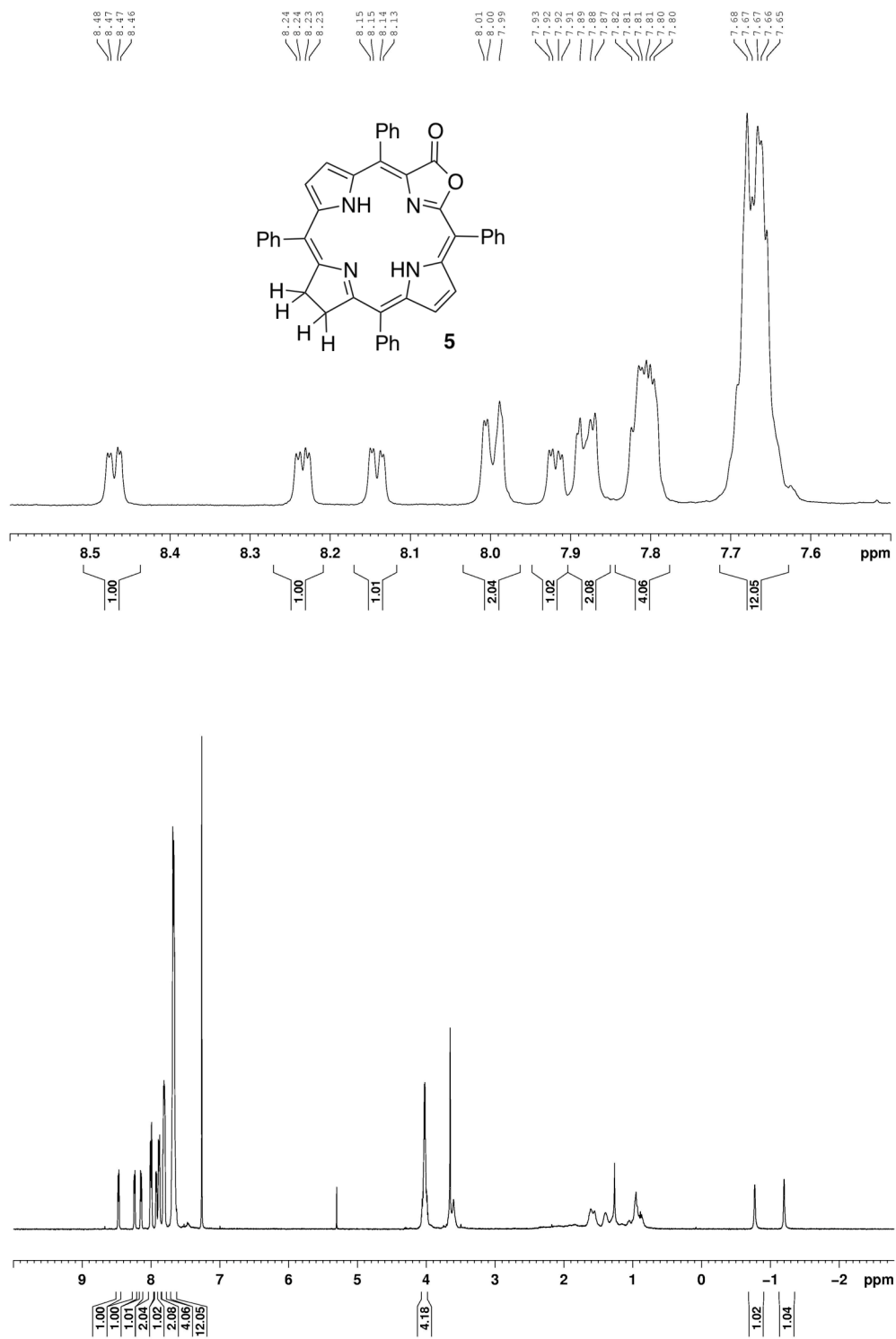


Figure ESI-1. ^1H NMR Spectrum (400 MHz, CDCl_3) of **5**

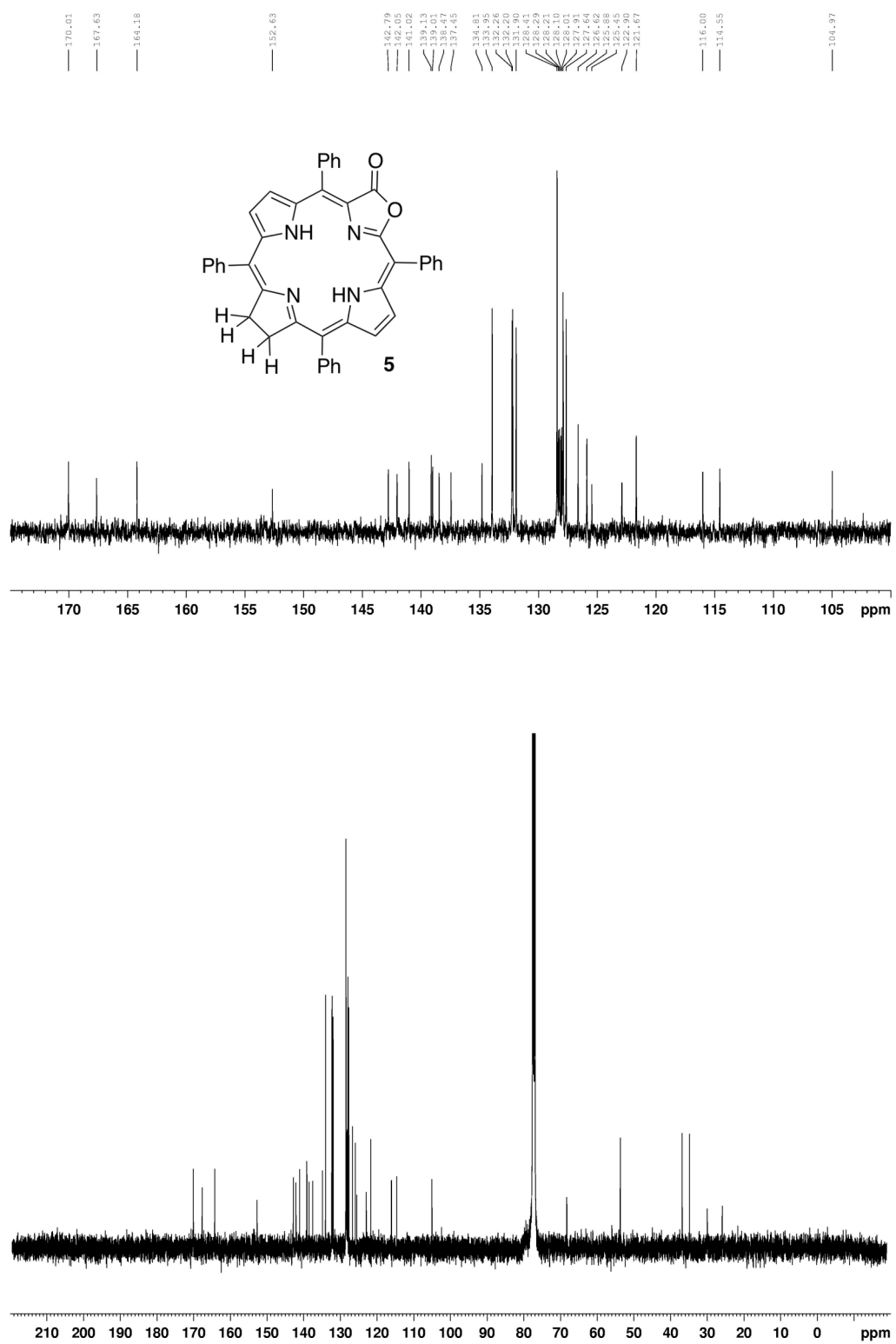


Figure ESI-2. ^{13}C NMR Spectrum (400 MHz, CDCl_3) of 5

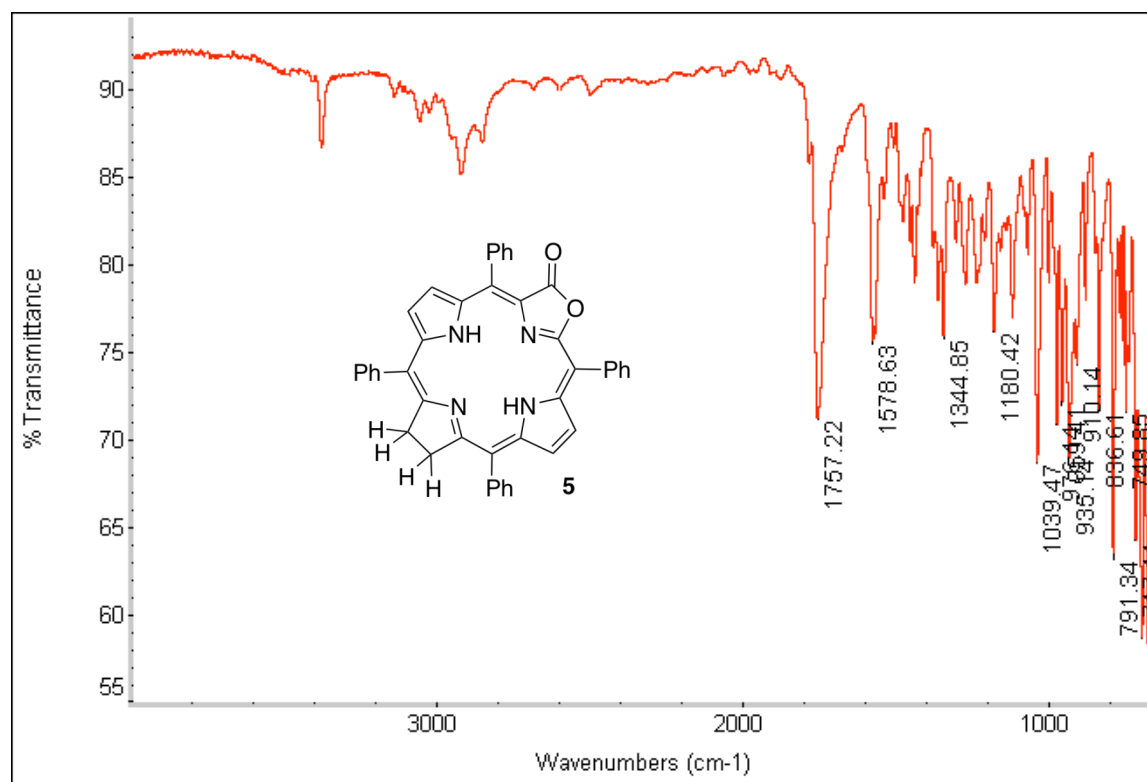


Figure ESI-3. FT-IR Spectrum (neat, diffuse reflectance) of **5**

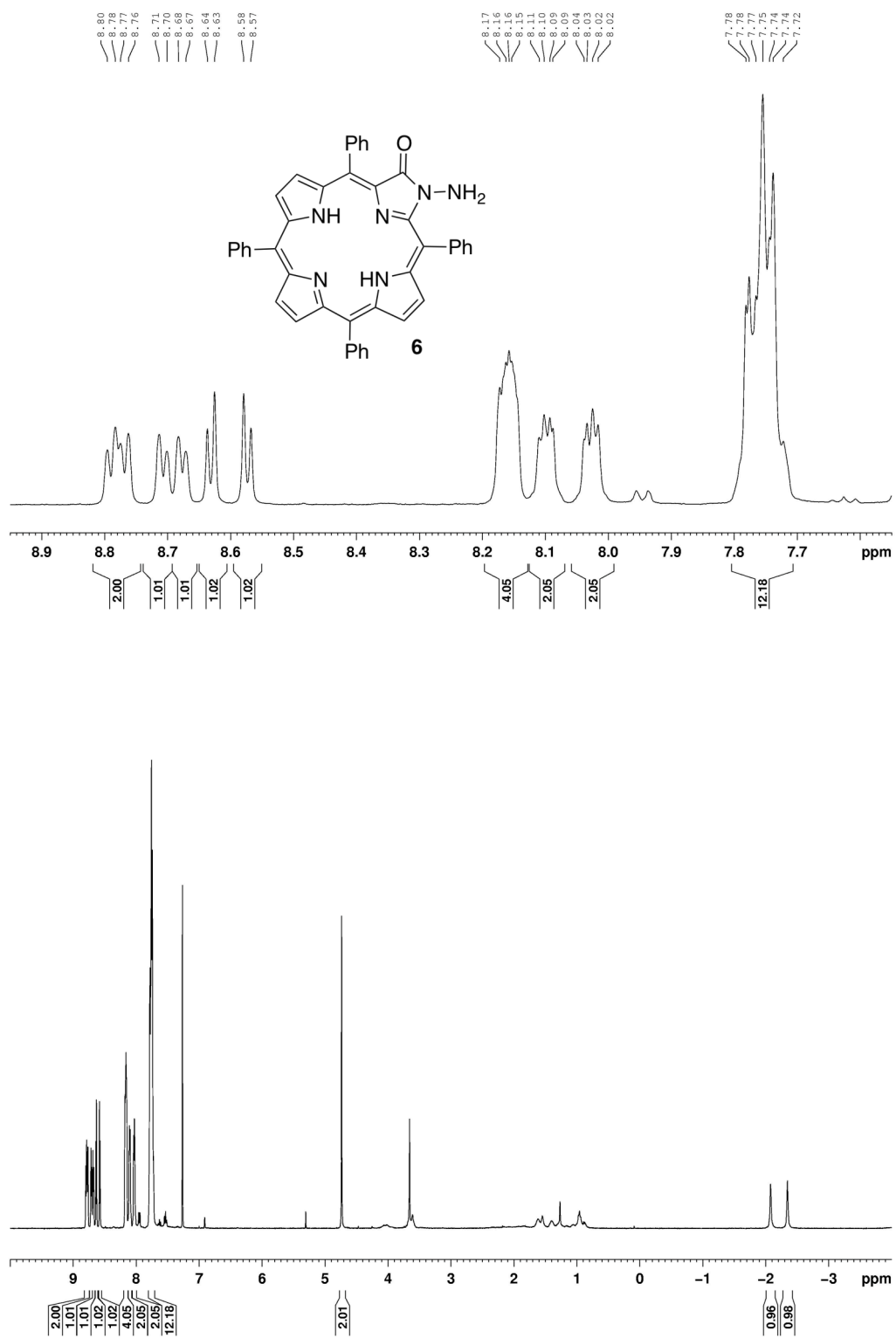


Figure ESI-4. ¹H NMR Spectrum (400 MHz, CDCl₃) of **6**

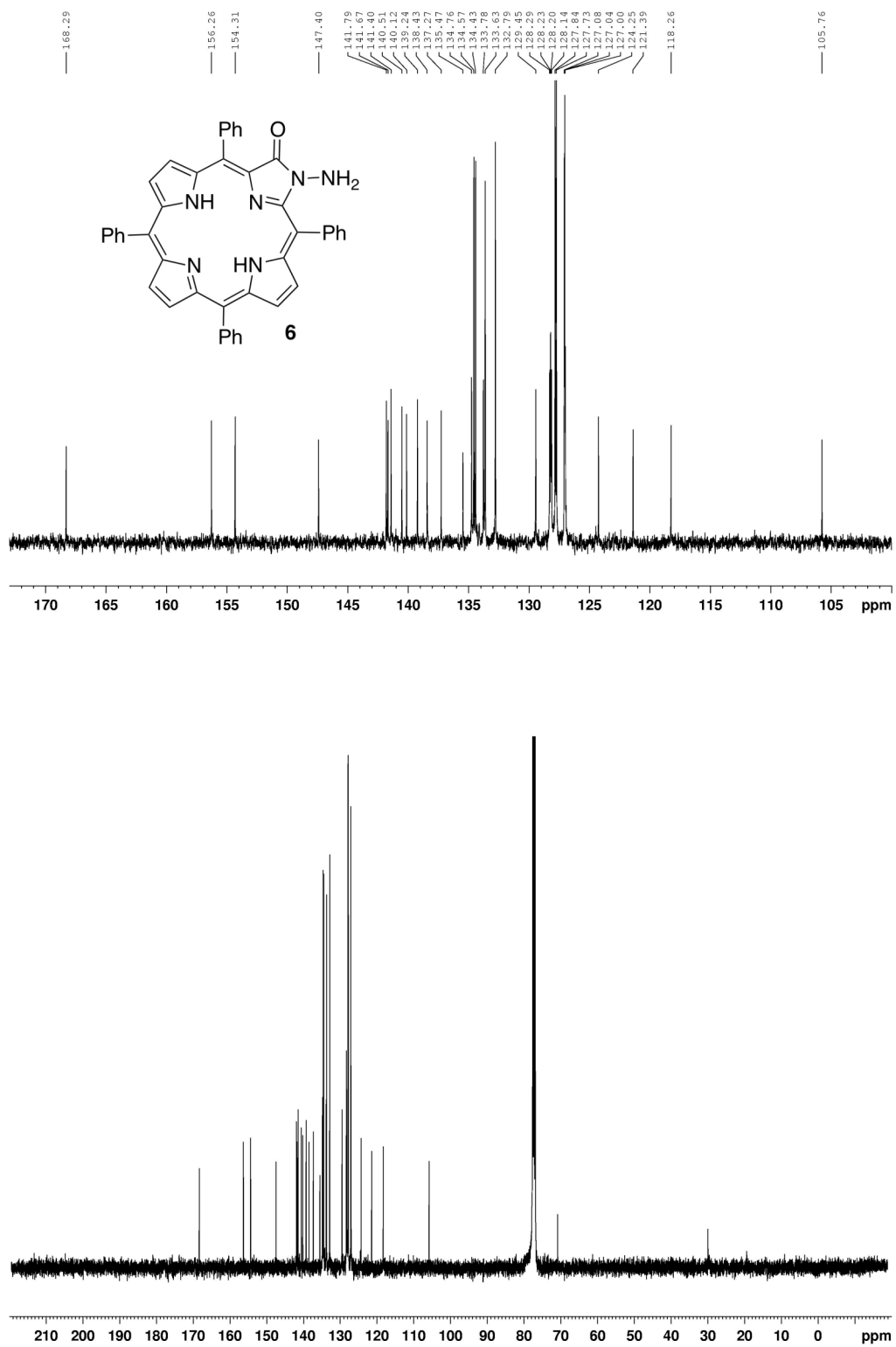


Figure ESI-5. ¹³C NMR Spectrum (400 MHz, CDCl₃) of 6

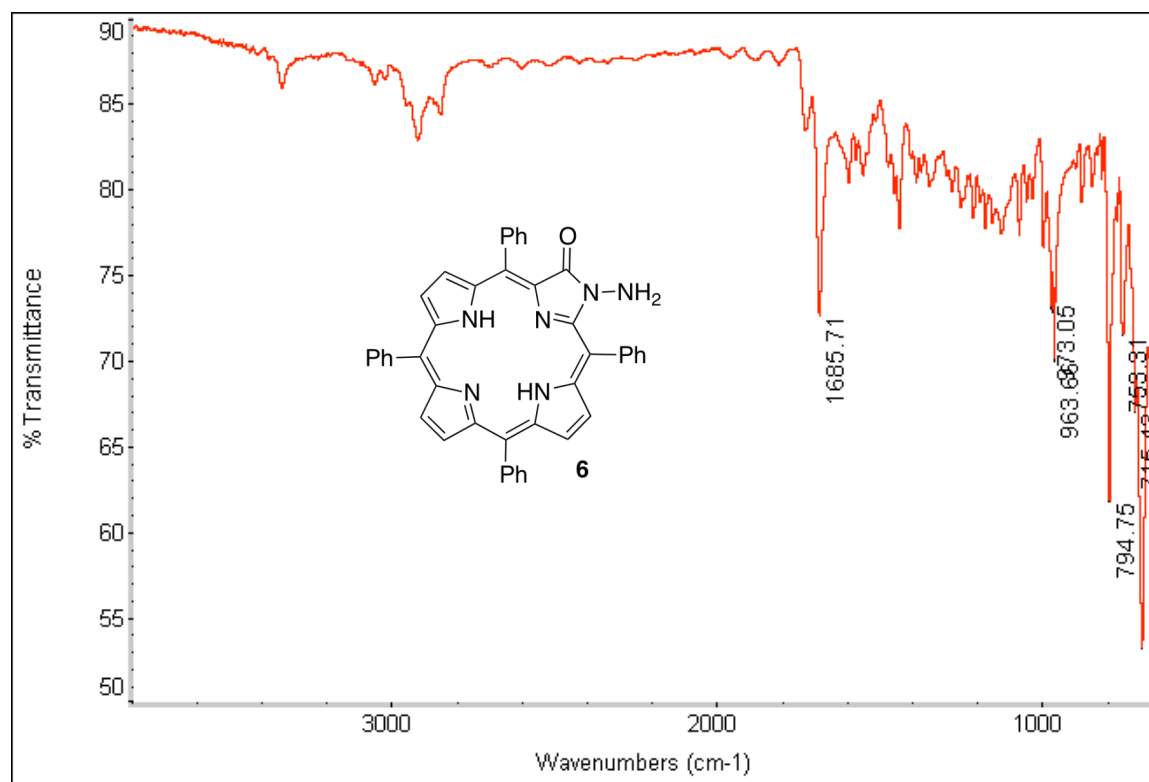


Figure ESI-6. FT-IR Spectrum (neat, diffuse reflectance) of **6**

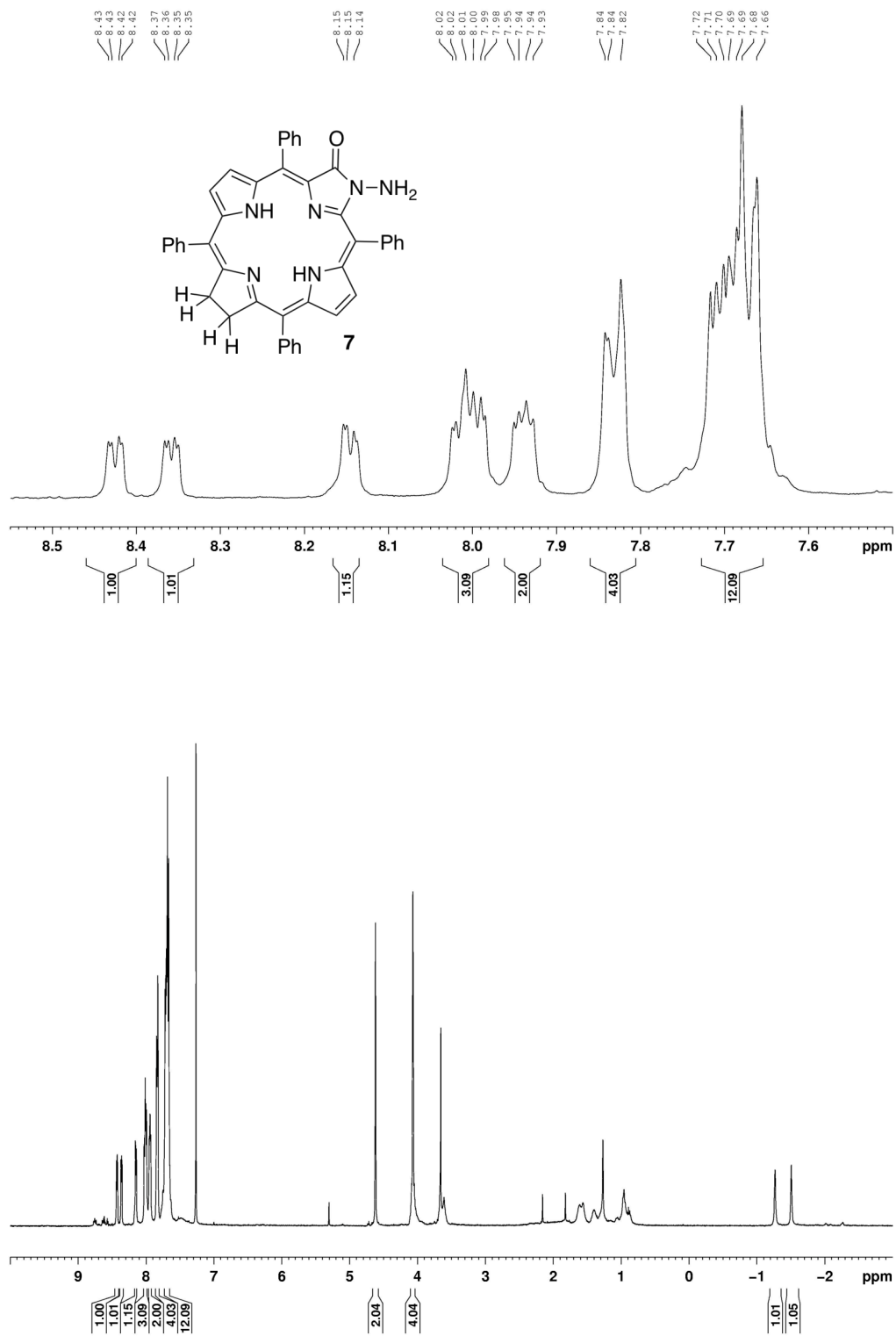


Figure ESI-7. ^1H NMR Spectrum (400 MHz, CDCl_3) of 7

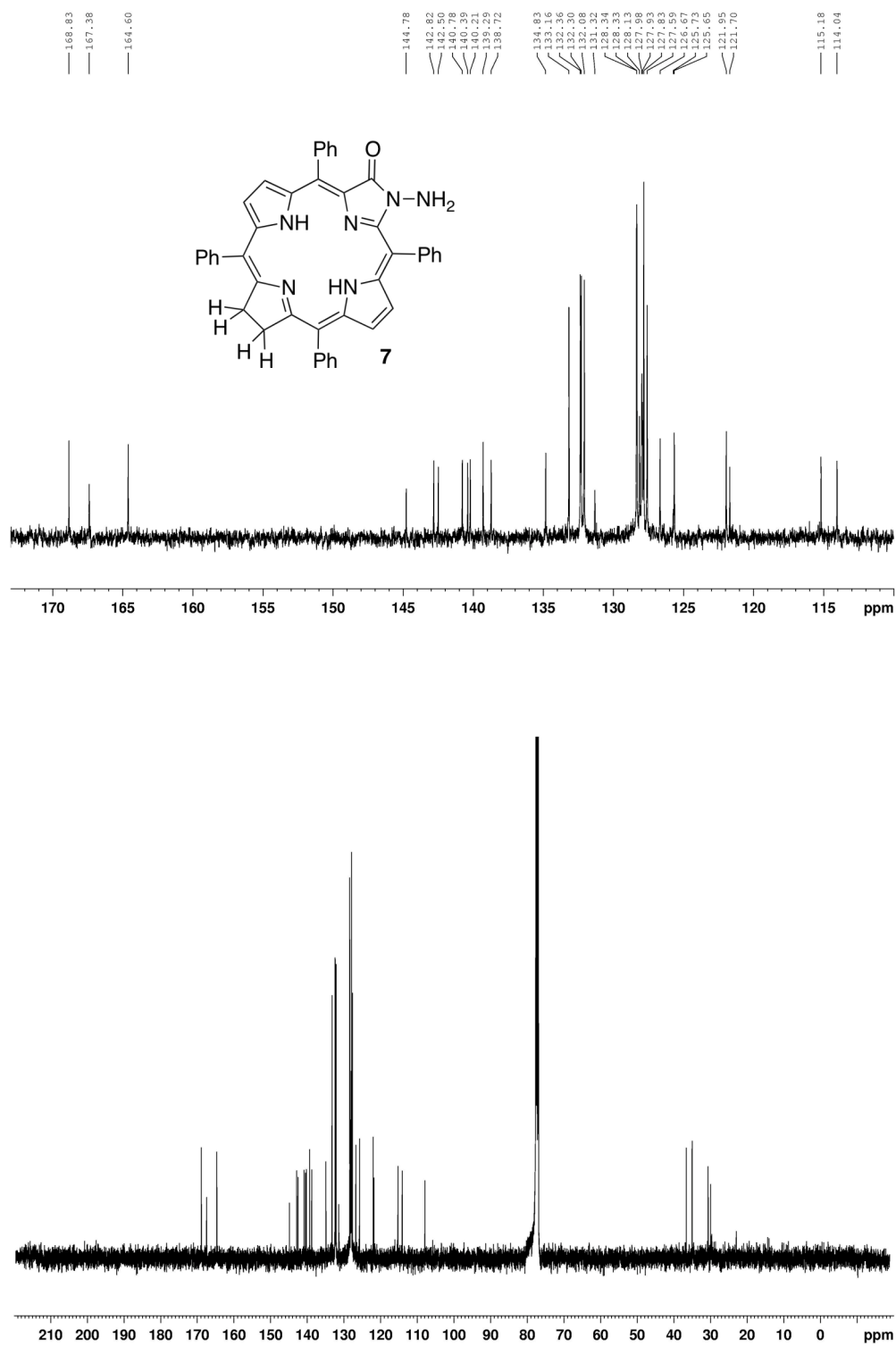


Figure ESI-8. ¹³C NMR Spectrum (400 MHz, CDCl₃) of 7

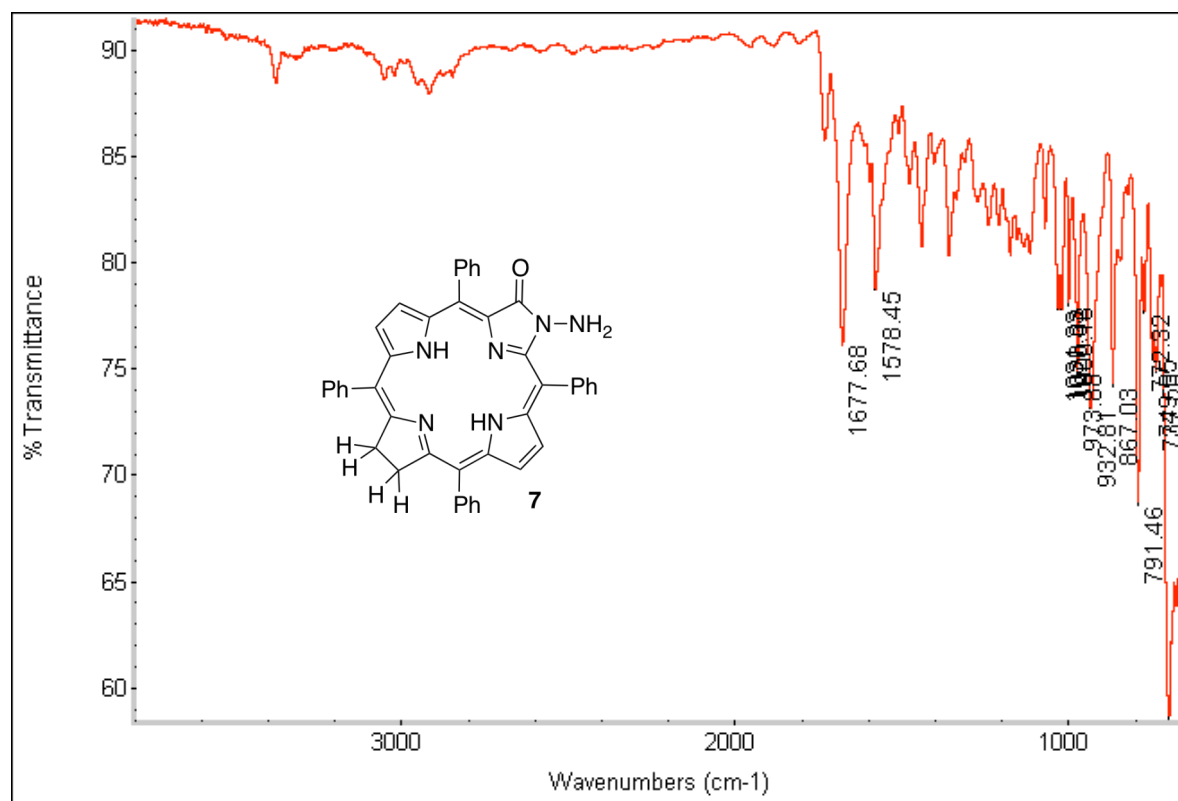


Figure ESI-9. FT-IR Spectrum (neat, diffuse reflectance) of 7

Reduction of *meso*-tetraphenyl-2-(*N*-amino-aza)-3-oxo-porphyrin (*N*-aminoporpholactam **6**) to form *meso*-tetraphenyl-2-aza-3-oxo-porphyrin (porpholactam **8**)

N-Aminoporpholactam **6** (27 mg, 4.18×10^{-5} mol) (or the corresponding chlorolactam **7**) was dissolved in anhydrous 1,2-dichlorobenzene (10 mL) and magnetically stirred. To this was added SmI₂ (6 equiv; 2.5 mL of a 0.1 M solution in THF) and heated to reflux for 14 h. When the starting material was consumed (reaction control by TLC), the reaction mixture was allowed to cool and was evaporated to dryness by rotary evaporation. The residue was taken up in CH₂Cl₂, filtered and washed with water (2 × 10 mL), dried over anhydrous Na₂SO₄, and filtered. The filtrate was reduced and separated by preparative TLC (CH₂Cl₂/1% MeOH). Isolated yields for **8** were 72% (19.0 mg): R_f (silica-CH₂Cl₂) 0.20; ¹H NMR (400 MHz, CDCl₃): δ 9.64 (s, 1H, exchangeable with D₂O), 8.80 (d, ³J = 4.0 Hz, 1H), 8.72 (d, ³J = 4.0 Hz, 1H), 8.64 (d, ³J = 4.0 Hz, 1H), 8.61 (d, ³J = 4.0 Hz, 1H), 8.58 (d, ³J = 4.0 Hz, 1H), 8.55 (d, ³J = 4.0 Hz, 1H), 8.15 – 8.13 (m, 4H), 8.10 – 8.07 (m, 2H), 8.00 – 7.97 (m, 2H), 7.81 – 7.79 (m, 3H), 7.78 – 7.71 (m, 9H), –1.86 (s, 1H, exchangeable with D₂O), –2.13 (s, 1H, exchangeable with D₂O); ¹³C NMR (100 MHz, CDCl₃): δ 169.5, 156.4, 153.9, 147.4, 141.9, 141.7, 140.2, 139.9, 139.6, 138.6, 138.3, 136.8, 134.9, 134.5, 134.3, 133.7, 133.4, 132.7, 129.6, 129.2, 128.8, 128.2, 128.1, 127.9, 127.7, 127.1, 126.9, 126.8, 126.4, 124.8, 121.2, 118.0, 103.9; UV-vis (CHCl₂) λ_{max} (log e) 421 (5.49), 519 (4.28), 554 (4.08), 595 (3.87), 649 (3.84) nm; HR-MS (ESI⁺, cone voltage = 30 V, 100% CH₃CN) *m/e* calcd for C₄₃H₃₀N₅O 632.2450 ([M]⁺), found 632.2398.

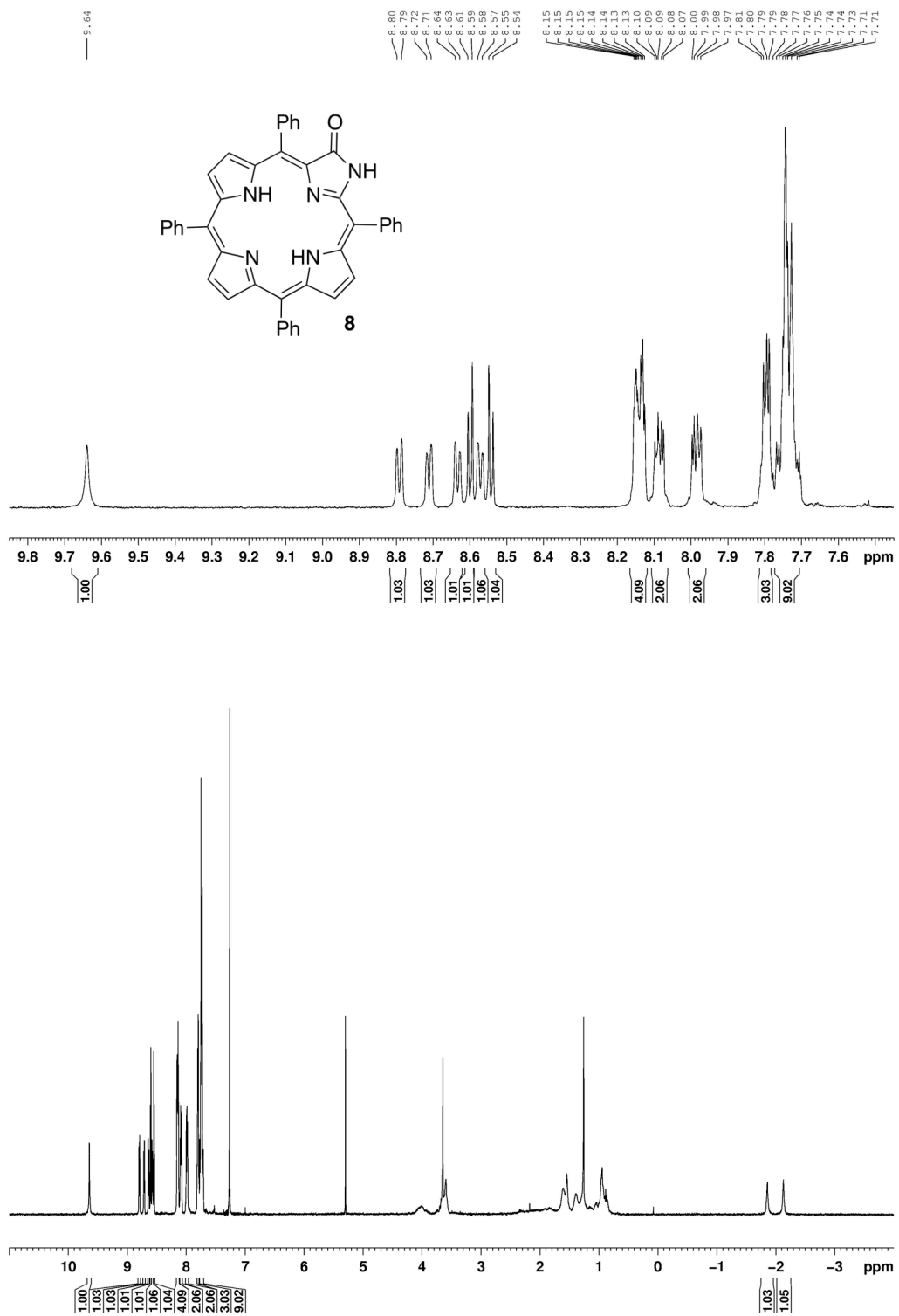


Figure ESI-10. ^1H NMR Spectrum (400 MHz, CDCl_3) of **8**

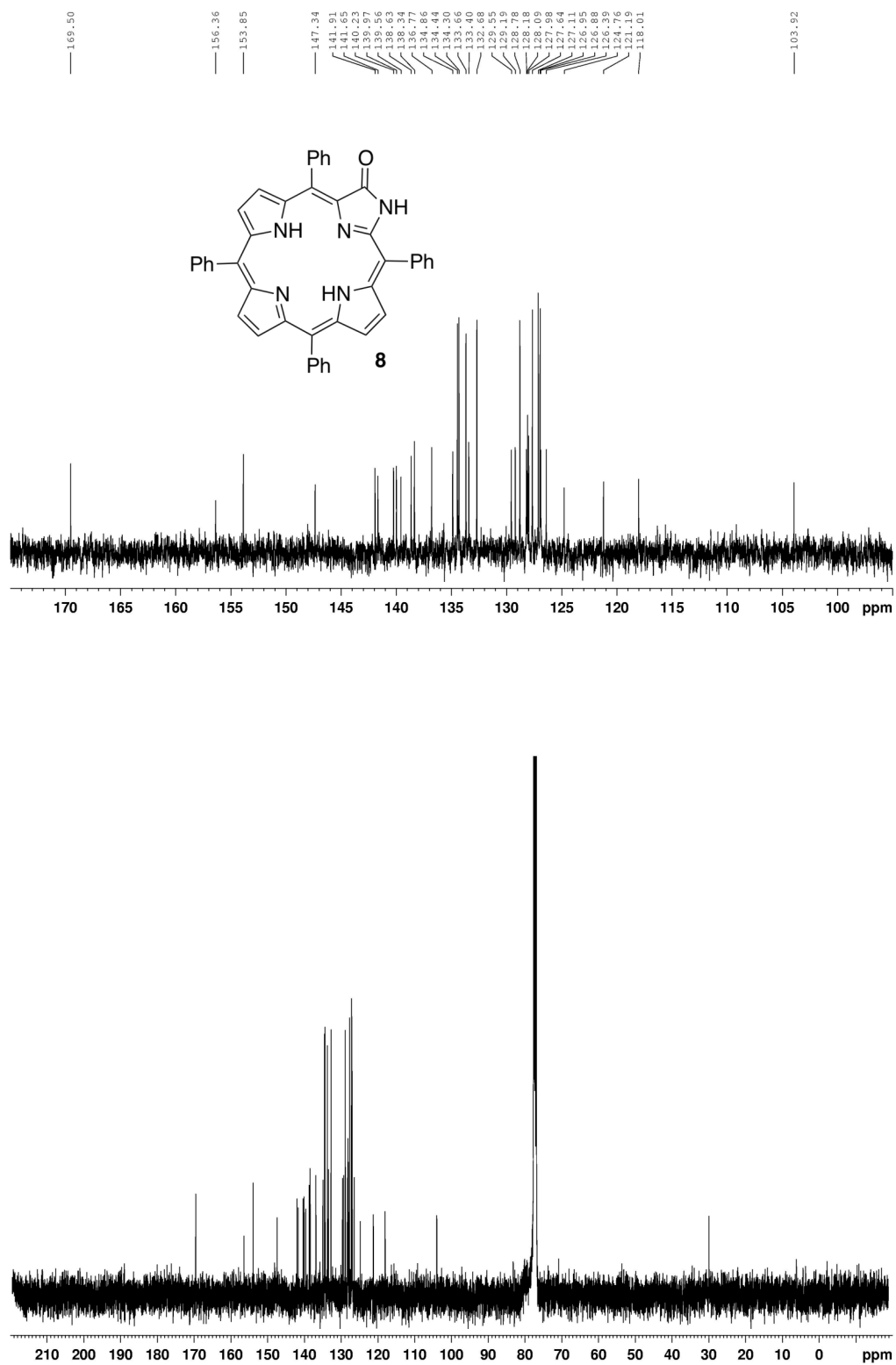


Figure ESI-11. ¹³C NMR Spectrum (400 MHz, CDCl₃) of **8**

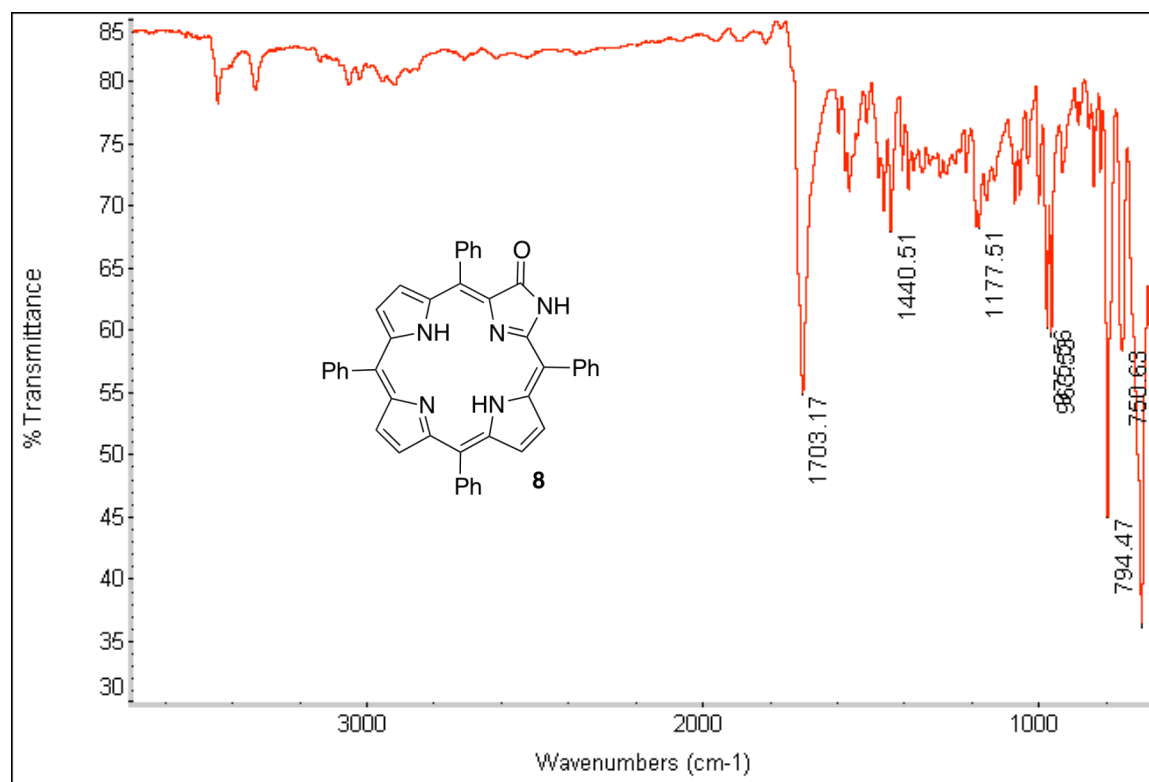


Figure ESI-12. FT-IR Spectrum (neat, diffuse reflectance) of **8**

Table 1. Experimental details

For all structures: triclinic, $P\bar{1}$. Experiments were carried out at 100 K with Mo $K\alpha$ radiation using a Bruker AXS SMART APEX CCD diffractometer. Crystals were mounted on MITEGEN micromesh mounts with the help of a trace of mineral oil. Data collection used ω scans. Absorption was corrected for by multi-scan methods, Apex2 v2009.7-0 (Bruker, 2009).

	8	6	7
<i>Crystal data</i>			
Chemical formula	C ₄₃ H ₂₉ N ₅ O	C ₄₃ H ₃₀ N ₆ O·0.37(H ₂ O)	C ₄₃ H ₃₂ N ₆ O·2(C ₂ H ₆ O)
M_r	631.71	653.34	740.88
a, b, c (Å)	6.3503 (15), 10.384 (3), 12.353 (3)	11.737 (4), 12.257 (4), 13.154 (4)	11.805 (2), 12.627 (2), 13.460 (2)
α, β, γ (°)	94.720 (4), 99.884 (4), 100.532 (4)	76.707 (4), 78.360 (4), 65.649 (4)	107.192 (2), 95.593 (2), 90.383 (3)
V (Å ³)	783.5 (3)	1665.6 (9)	1906.2 (6)
Z	1	2	2
$F(000)$	330	683.1	784
D_x (Mg m ⁻³)	1.339	1.303	1.291
No. of reflections for cell measurement	940	2668	7477
μ (mm ⁻¹)	0.08	0.08	0.08
Crystal shape	Block	Block	Plate
Colour	Black	Black	Black
Crystal size (mm)	0.21 × 0.11 × 0.06	0.15 × 0.12 × 0.09	0.55 × 0.35 × 0.11
<i>Data collection</i>			
Radiation source	fine-focus sealed tube	fine-focus sealed tube	fine-focus sealed tube
Monochromator	graphite	graphite	graphite
T_{\min}, T_{\max}	0.637, 0.746	0.569, 0.746	0.597, 0.746
No. of measured, independent and observed [$I > 2s(I)$] reflections	8429, 3844, 2446	12566, 5846, 3393	25313, 9008, 7105
R_{int}	0.037	0.047	0.035

θ values ($^{\circ}$)	$\theta_{\max} = 28.3, \theta_{\min} = 2.0$	$\theta_{\max} = 25.0, \theta_{\min} = 1.6$	$\theta_{\max} = 27.9, \theta_{\min} = 1.7$
Range of h, k, l	$h = -8 \rightarrow 8, k = -13 \rightarrow 13, l = -16 \rightarrow 16$	$h = -13 \rightarrow 13, k = -14 \rightarrow 14, l = -15 \rightarrow 15$	$h = -15 \rightarrow 15, k = -16 \rightarrow 16, l = -17 \rightarrow 17$
Refinement			
$R[F^2 > 2s(F^2)], wR(F^2), S$	0.056, 0.159, 1.06	0.086, 0.261, 1.05	0.059, 0.164, 1.06
No. of reflections	3844	5846	9008
No. of parameters	247	516	569
No. of restraints	21	85	15
H-atom treatment	H-atom parameters constrained	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$(\Delta/\sigma)_{\max}$	0.002	0.004	0.001
$\Delta\rho_{\max}, \Delta\rho_{\min}$ ($\epsilon \text{ \AA}^{-3}$)	0.83, -0.22	0.83, -0.40	0.41, -0.50

Computer programs: Apex2 v2009.7-0 (Bruker, 2009), Apex2 v2009.7-0, *SHELXTL* 6.14 (Bruker, 2000-2003; Sheldrick, 2008), *SHELXTL* 6.14.

Special Details:

Compound 8: Reflection 0 0 1 was obstructed by the beam stop and was omitted from the refinement. The lactame moiety is disordered over four mutually exclusive positions with both of the pyrrole moieties, and across the crystallographic inversion centers. Occupancies for the four sites are 0.2353(15) for the A moiety, 0.118(2) for the B moiety, 0.108(2) for the C moiety, and 0.039(3) for the D moiety, thus summing up to 50% occupancy. The second half of the lactame moiety is created by the crystallographic inversion center. The remainder of each site is occupied by the three pyrrole units. Moieties A and B, and C and D each occupy the same sites but are flip disordered with each other. Overlapping atoms in the disordered sites were constrained to have identical ADPs and identical positions (exceptions: atoms C7B and C3D whose positions were allowed to refine but which were restrained to be in plane with their three next neighbour atoms and to have covalent bond lengths similar to those of the atoms of the other moieties they are disordered with). The ADPs of the oxygen atoms were constrained to be identical to those of the

carbon atoms they are bonded to. The oxygen atoms of the four moieties were restrained to have similar C-O bond lengths and N...O distances. The largest residual electron density is located at the center of inversion in the middle of the molecule. The reduction of the hydrazine amide to the amide was accomplished using Raney Ni/SmI₃, so some Ni might have been incorporated into the porphyrine like structure. Inclusion of a partially occupied Ni atom resulted in marginally lower R values and an occupancy of 1.3% Ni at the center of the molecule.

Compound 6: The structure exhibits disorder of one of the two pyrrole rings with the lactam ring in a ratio of 0.633(5) to 0.367(5). The disorder extends to one of the phenyl rings, and the minor moiety is accompanied with an interstitial water molecule. The two pyrrole ring that were refined as not disordered shows signs of additional minor disorder as the largest residual electron density peaks are located where oxygen or nitrogen atoms of the lactam would be found if additional disorder were present (Q1 and Q2 with 0.76 and 0.60 electrons each). No attempts were made to refine this additional disorder. All pyrrole rings (including the disordered ones) were restrained to have similar geometries. The lactam rings were restrained to be flat. ADPs of overlapping atoms were constrained to be identical. The ADPs of the two oxygen atoms and of the two amino groups were also constrained to be identical. Amino and water H atoms were placed in meaningful positions and were restrained. The water H atoms were constrained to ride on the carrying O atom in the final refinement cycles.

Compound 7: The two ethanol solvent molecules are disordered over each two mutually exclusive positions. The occupancy ratios of the two neighboring sites are unrelated and are 0.753(7) to 0.247(7) and 0.637(8) to 0.363(8), respectively. The geometries of the four ethanol molecules were restrained to be similar. The positions of acidic H atoms were restrained based on hydrogen bonding considerations.

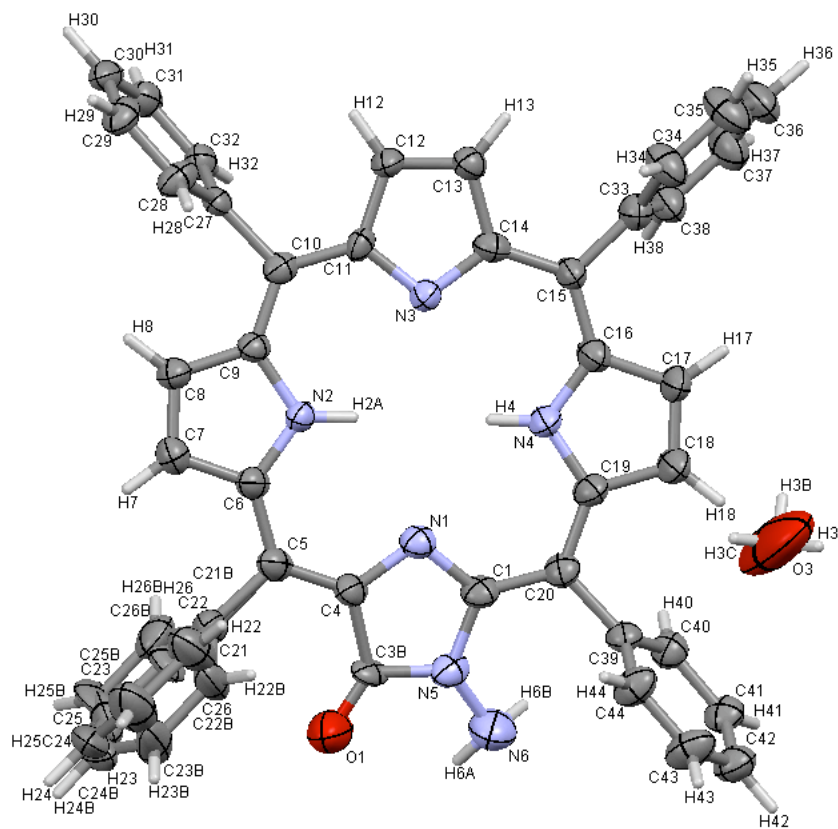


Figure ESI-13. ORTEP representation of crystal structure of **6·0.37 H₂O**

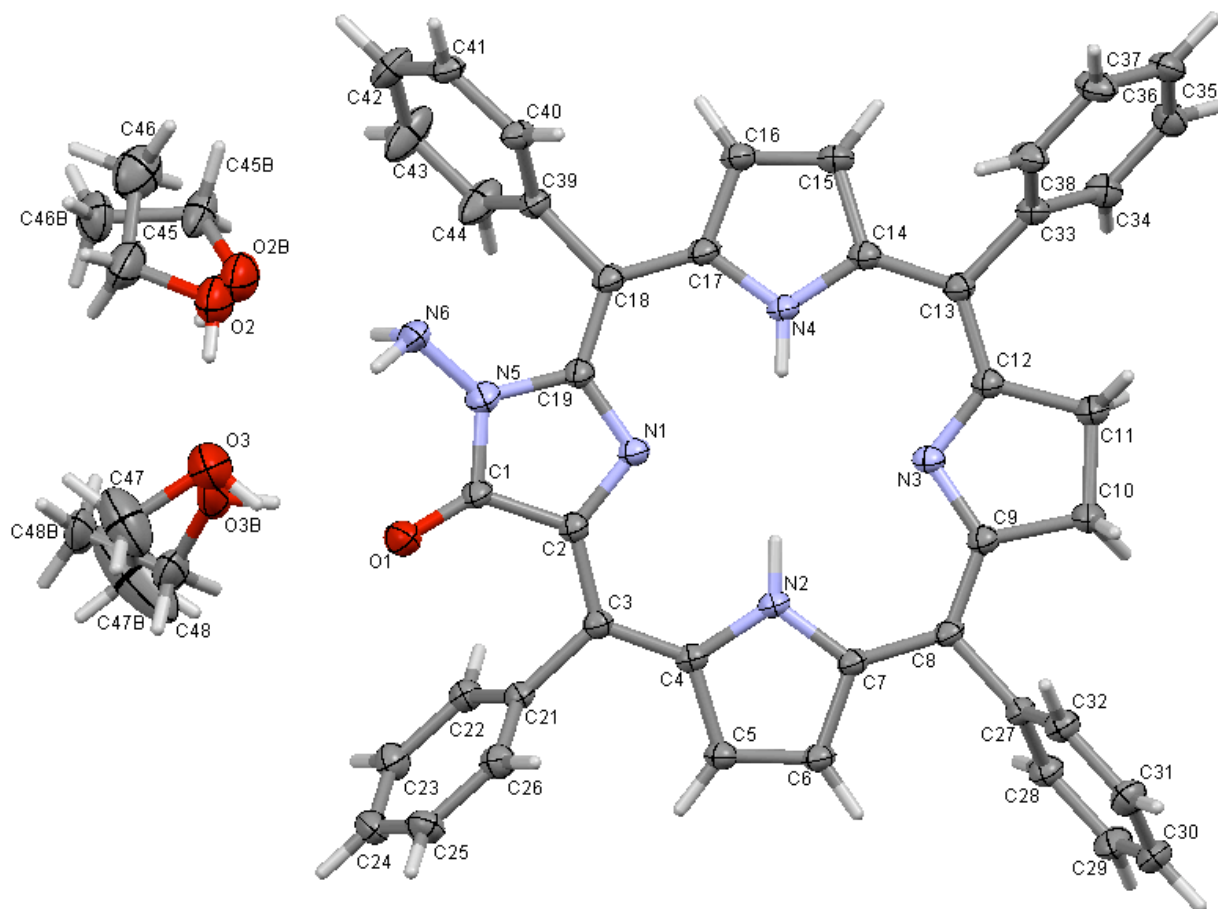


Figure ESI-14. ORTEP representation of crystal structure of 7·2 C₂H₆O

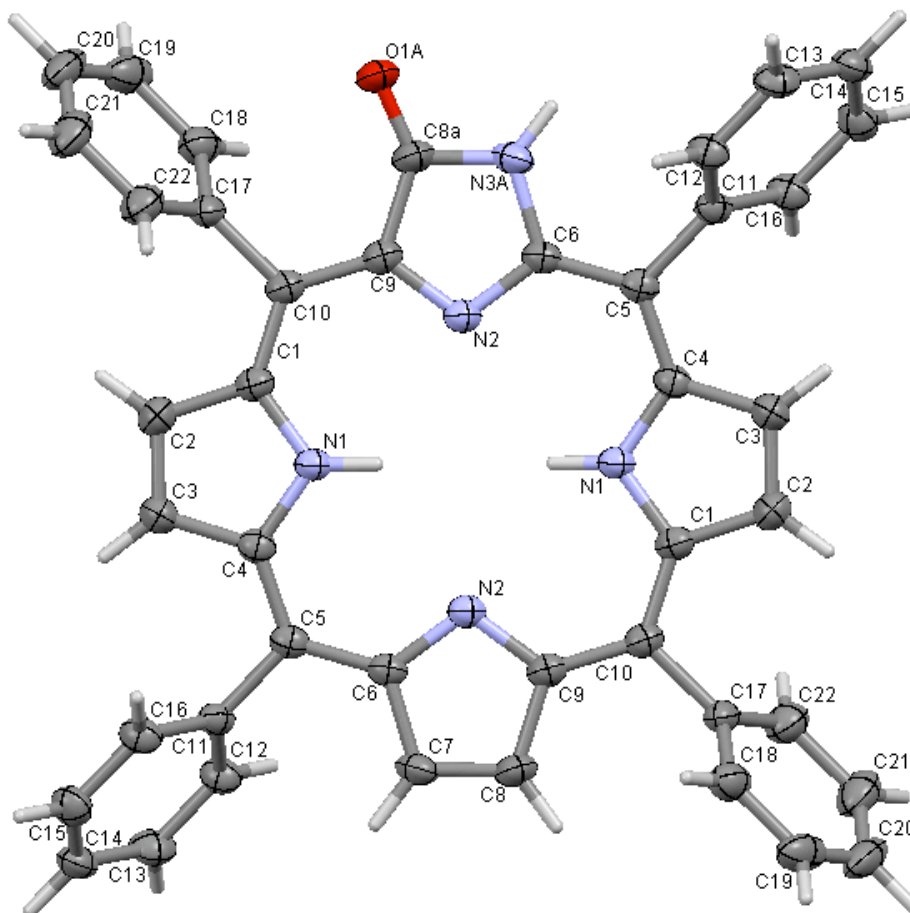


Figure ESI-15. ORTEP representation of crystal structure of **8**