ELECTRONIC SUPPORTING INFORMATION (ESI)

to:

Supersizing pyrrole-modified porphyrins by reversal of the 'breaking and mending' strategy

Michael Luciano[a], Weston Tardie[a], Matthias Zeller[b], and Christian Brückner[a]*

Department of Chemistry, University of Connecticut, Storrs, CT, 06269-3060, USA
and
Department of Chemistry, Purdue University, West Lafayette, IN 47907-2084, USA

[a] University of Connecticut

[b] Purdue University

* Author to whom correspondence should be addressed: Fax: (+1) 860-486-2981; Tel: (+1) 860-486-2743; e-mail: c.bruckner@uconn.edu

TABLE OF CONTENTS

Materials and Instruments

All solvents and reagents (Aldrich, Acros, CIL) were used as received. Tetraphenyl-2,3-dioxochlorin was prepared as described previously.[1]

Analytical (aluminum backed, silica gel 60, 250 μm thickness) and preparative (20 × 20 cm, glass backed, silica gel 60, 500 or 1000 μm thickness) TLC plates and the flash column silica gel (premium grade, 60 Å, 32-63 μm) were provided by Sorbent Technologies, Atlanta, GA.

^{1}H 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 Bruker Alpha FT-IR with ATR (diamond) cell.

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(1) Daniell, H. W.; Williams, S. C.; Jenkins, H. A.; Brückner, C. *Tetrahedron Lett.* **2003**, *44*, 4045-4049.

meso-Tetraphenyl imidazolidinone-annulated dihydroxychlorin 8.

Porphyrin Dione **7** (118.0 mg, 1.83×10^{-4} mol) was dissolved in pyridine (25.0 mL) in a RBF equipped with a magnetic stir bar. Urea (245 mg, 4.1×10^{-3} mol, 22 equiv) was added and the mixture was heated to reflux for 30 min under a N_2 atmosphere. Subsequently, the solvent was evaporated _in vacuo_. The remaining residue was taken up in $CHCl_3$ and filtered through a glass frit. The filtrate was washed with water (5 × 25 mL) and dried over Na_2SO_4. The dried residue was separated by column chromate-graphy (CH_2Cl_2-5% MeOH), recovering dione **7** in 8% yield (9 mg), followed by the magenta product **8** in 85% yield (110.5 mg): R_f (silica-CH_2Cl_2/5% MeOH) = 0.36; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (d, ^3J = 4.7 Hz, 1H), 8.49 (s, 1H), 8.21 (s, 1H), 8.14 (d, ^3J = 5.8 Hz, 3H), 7.86 (d, ^3J = 6.8 Hz, 1H), 7.72 (m, 6H), 5.34 (br s, 1H, exchangeable with D_2O), 4.26 (br s, 1H, exchangeable with D_2O), -2.03 (br s, 1H, exchangeable with D_2O) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 159.5, 158.5, 152.8, 141.4, 141.1, 140.0, 135.4, 135.2, 134.12, 134.10, 134.08, 134.06, 133.18, 133.13, 128.55, 128.44, 127.50, 127.33, 127.26, 125.7, 123.1, 112.9, 93.5 ppm; UV-vis (CH_2Cl_2) λ_{max} (log ε) 406 (5.41), 512 (4.30), 541 (4.30), 591 (3.96), 642 (4.53) nm; FT-IR (neat, diamond ATR): $\nu_{C=O}$ = 1715.7 cm^{-1}; MS (ESI$^+$, 100% CH_3CN, TOF) _m/z_ cald for $C_{45}H_{33}N_6O_3$ ([M·H]$^+$) 705.2609, found 705.2605.
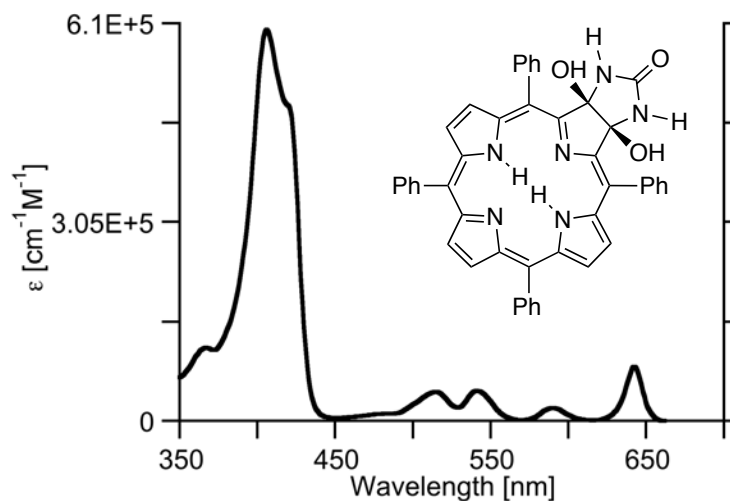

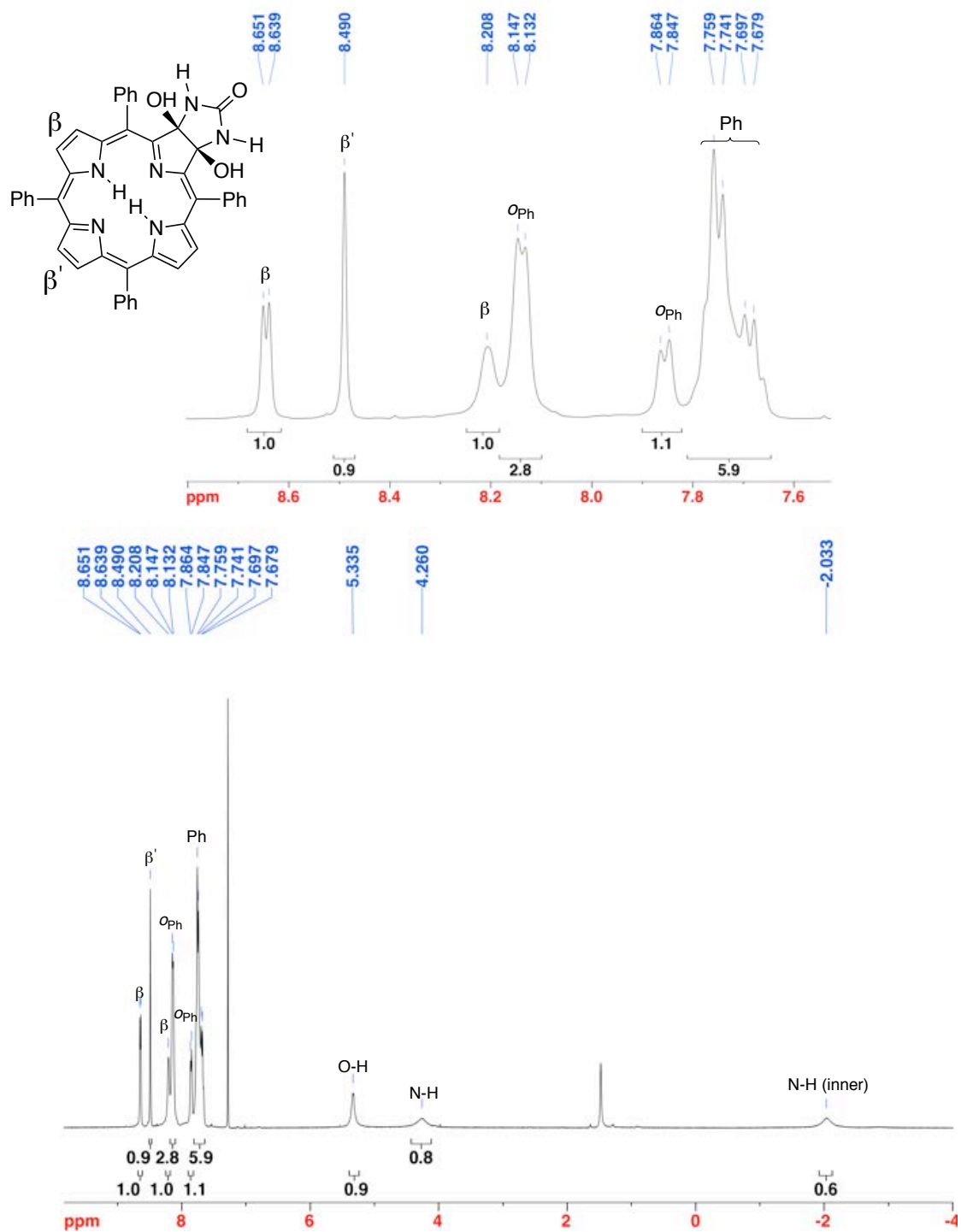**Figure S1.** UV-vis spectrum (CH_2Cl_2) of **8**.

Figure S2. ^{1}H NMR (400 MHz, CDCl$_3$) of **8**.
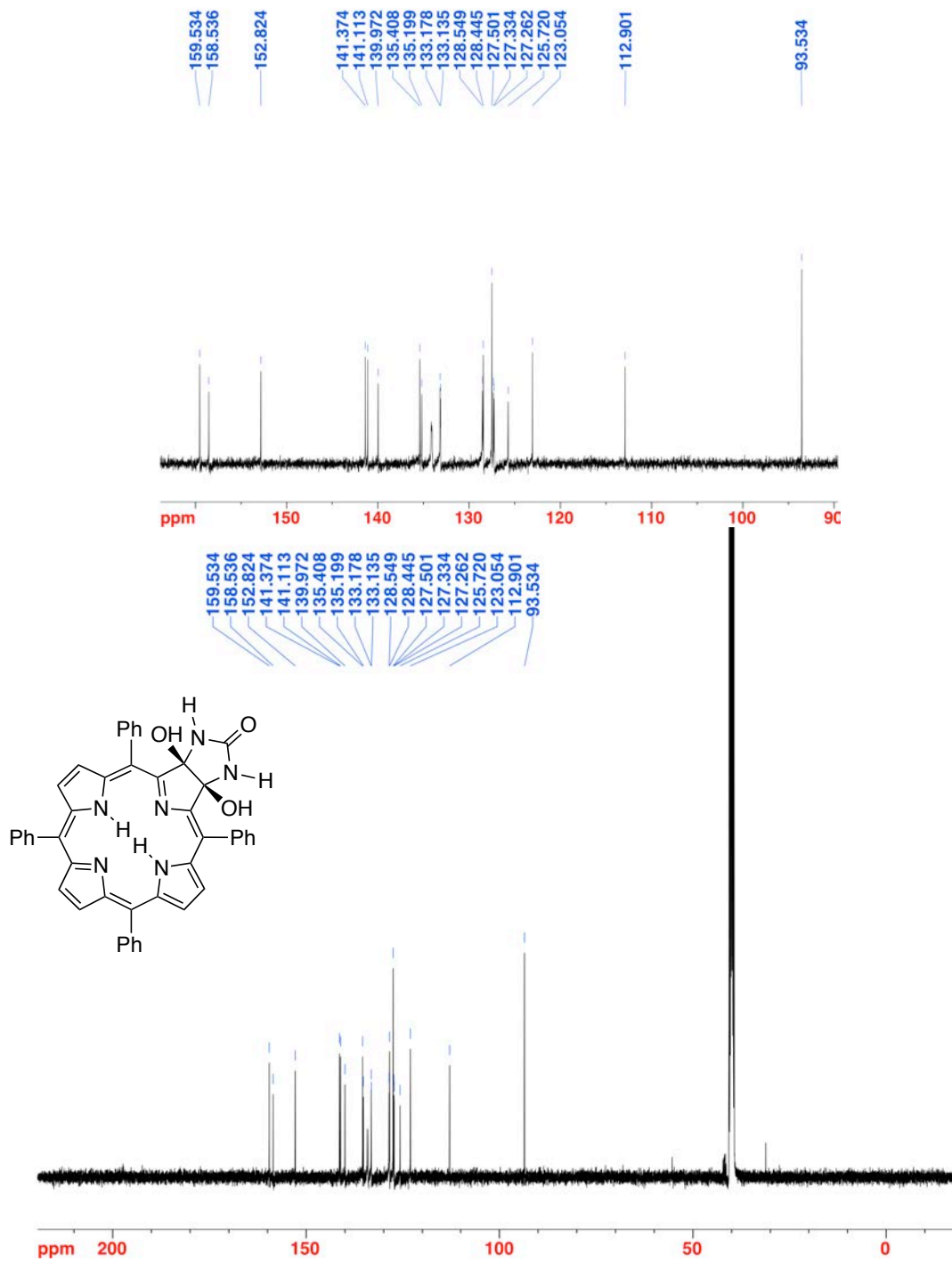
Figure S3. ^{13}C NMR (100 MHz, DMSO-d$_6$) of **8**.
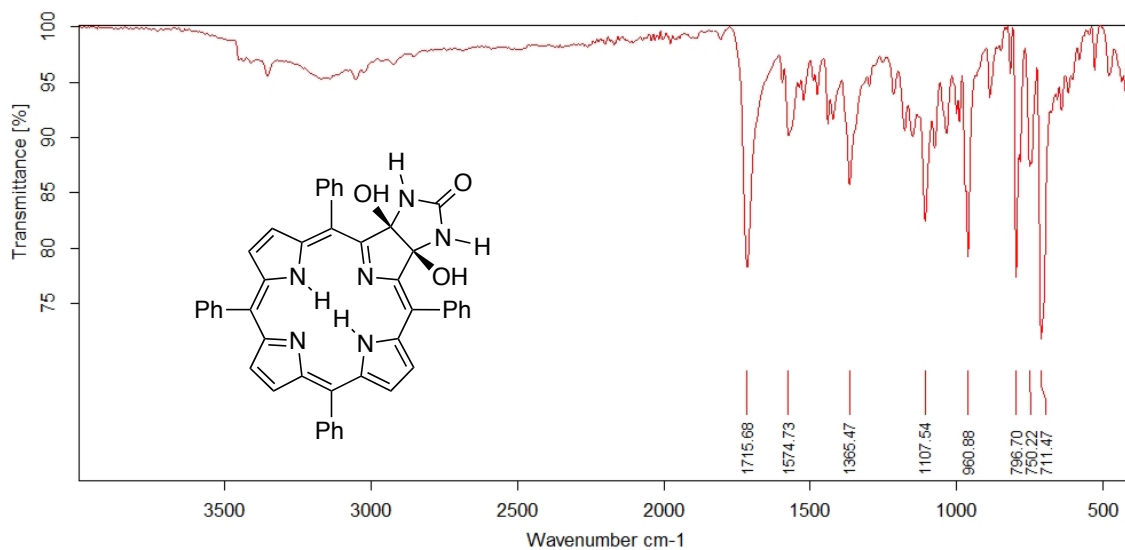
Figure S4. FT-IR (neat, diamond ATR) of **8**.

Chemical Formula: $C_{45}H_{33}N_6O_3^+$
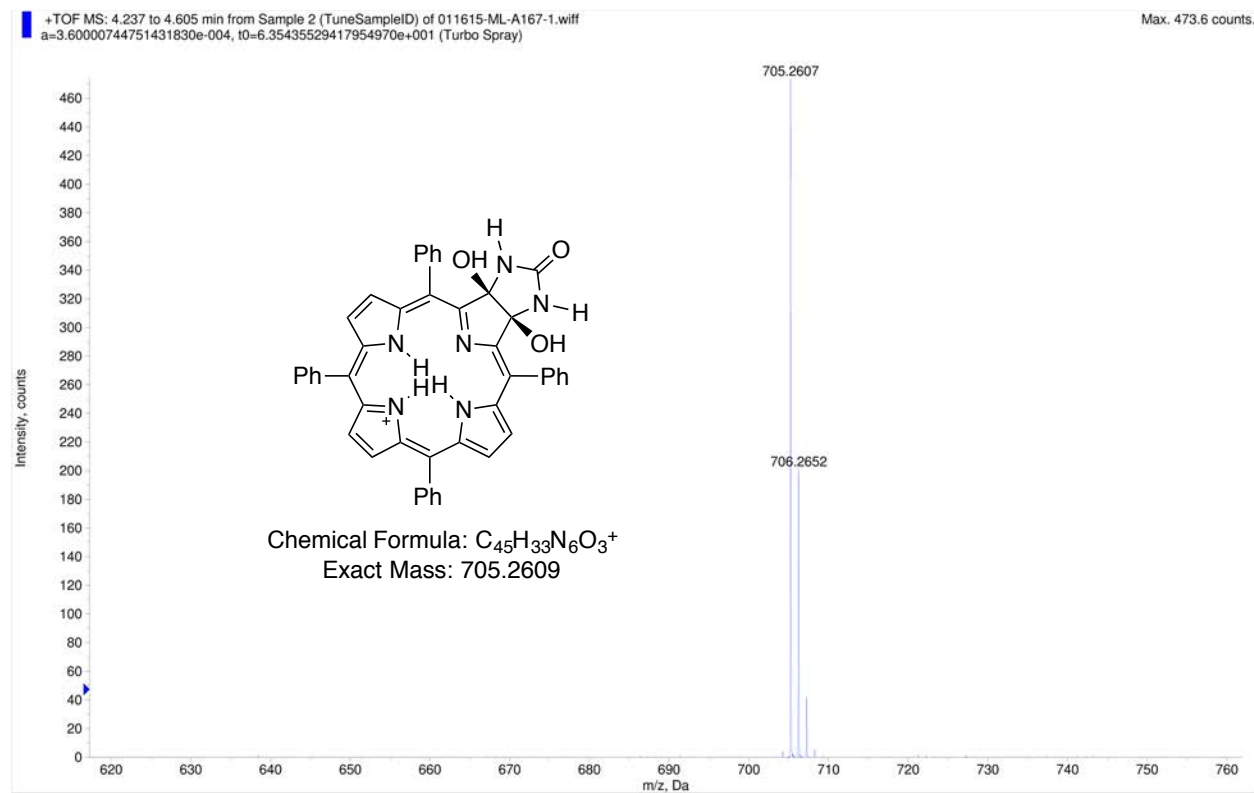Exact Mass: 705.2609

Figure S5. HR-MS (ESI$^+$, 100% CH$_3$CN, TOF) of **8**.

meso-Tetraphenyl-*N,N'*-dimethylimidazolidinone-annulated dihydroxychlorin 9.

Prepared from 2,3-dioxochlorin **7** (30.0 mg, 4.65×10^{-5} mol) in pyridine (8.0 mL) as described for **8** using *N,N'*-dimethylurea (82 mg, 9.31×10^{-4} mol, 20 equiv.) to afford the red dihydroxychlorin **9** in 54% yield (18.5 mg): R_f (silica-CH_2Cl_2/3% MeOH) = 0.56; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (d, ^3J = 4.9 Hz, 1H), 8.45 (s, 1H), 8.16 (d, ^3J = 6.7 Hz, 1H), 8.07 (d, ^3J = 5.2 Hz, 4H), 7.78-7.67 (m, 6H), 4.55 (s, 1H, exchangeable with D_2O), 2.28 (s, 3H), -1.75 (s, 1H, exchangeable with D_2O) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.4, 154.2, 153.5, 141.4, 139.8, 136.0, 135.4, 134.1, 132.9, 128.7, 127.97, 127.88, 127.6, 127.3, 126.81, 126.73, 125.3, 123.7, 112.8, 97.1, 26.4 ppm; UV-vis (CH_2Cl_2) λ_{max} (log ε) 410 (4.99), 520 (3.84), 549 (3.88), 596 (3.53), 649 (4.08) nm; FT-IR (neat, diamond ATR): $\nu_{C=O}$ = 1680.4 cm^{-1}; HR-MS (ESI⁻, 100% CH_3CN, TOF) *m/z* cald for $C_{47}H_{37}N_6O_3$ ([M·H]$^+$) 733.2922, found 733.2941.
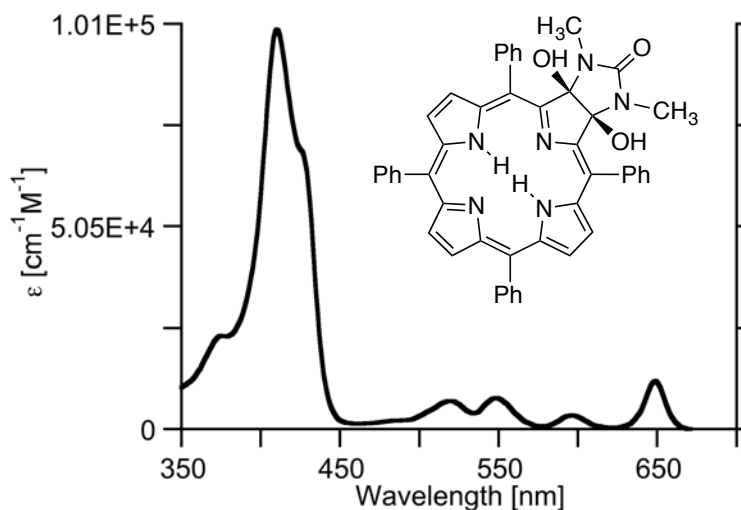

Figure S6. UV-vis spectrum (CH_2Cl_2) of **9**.
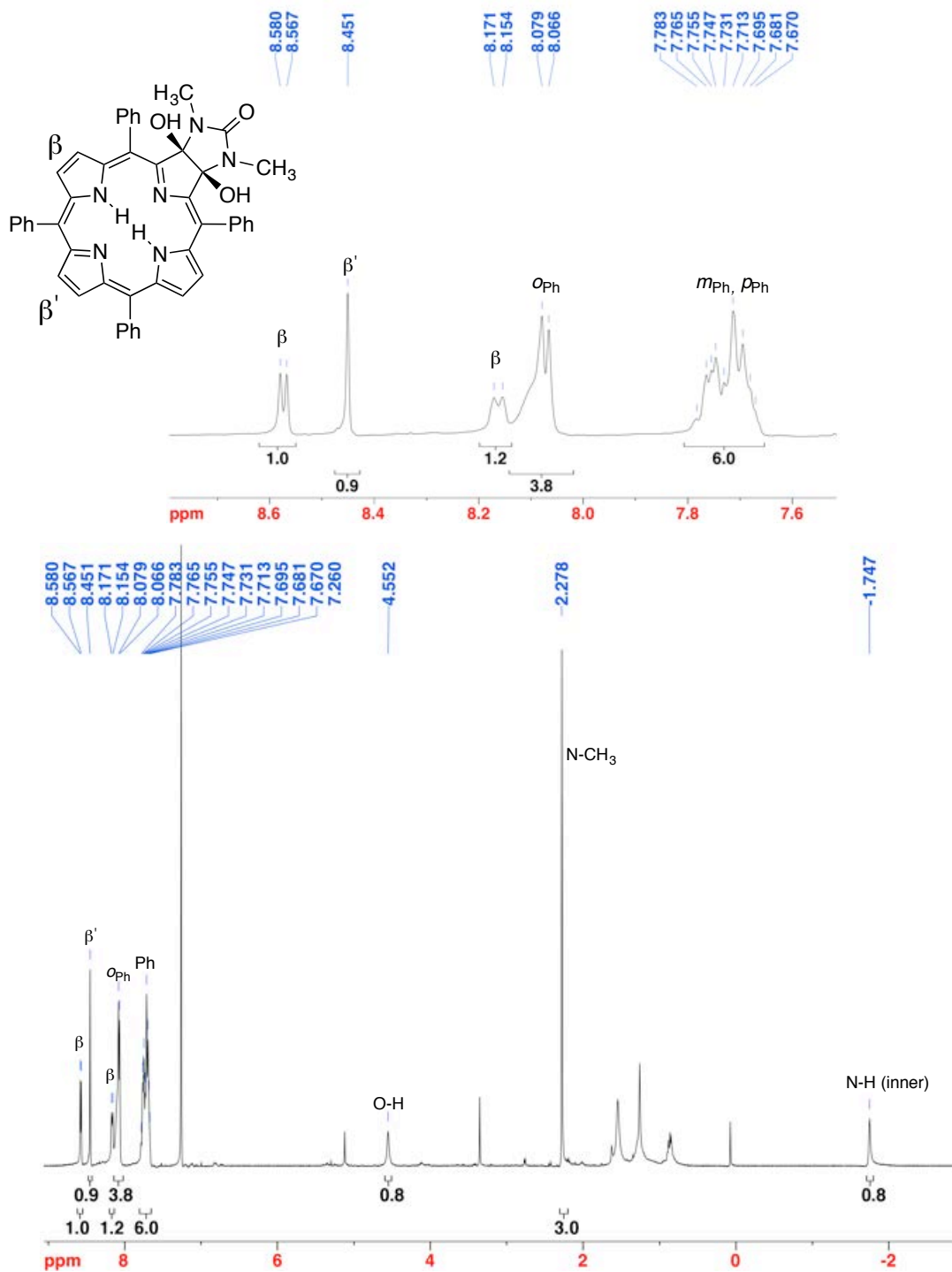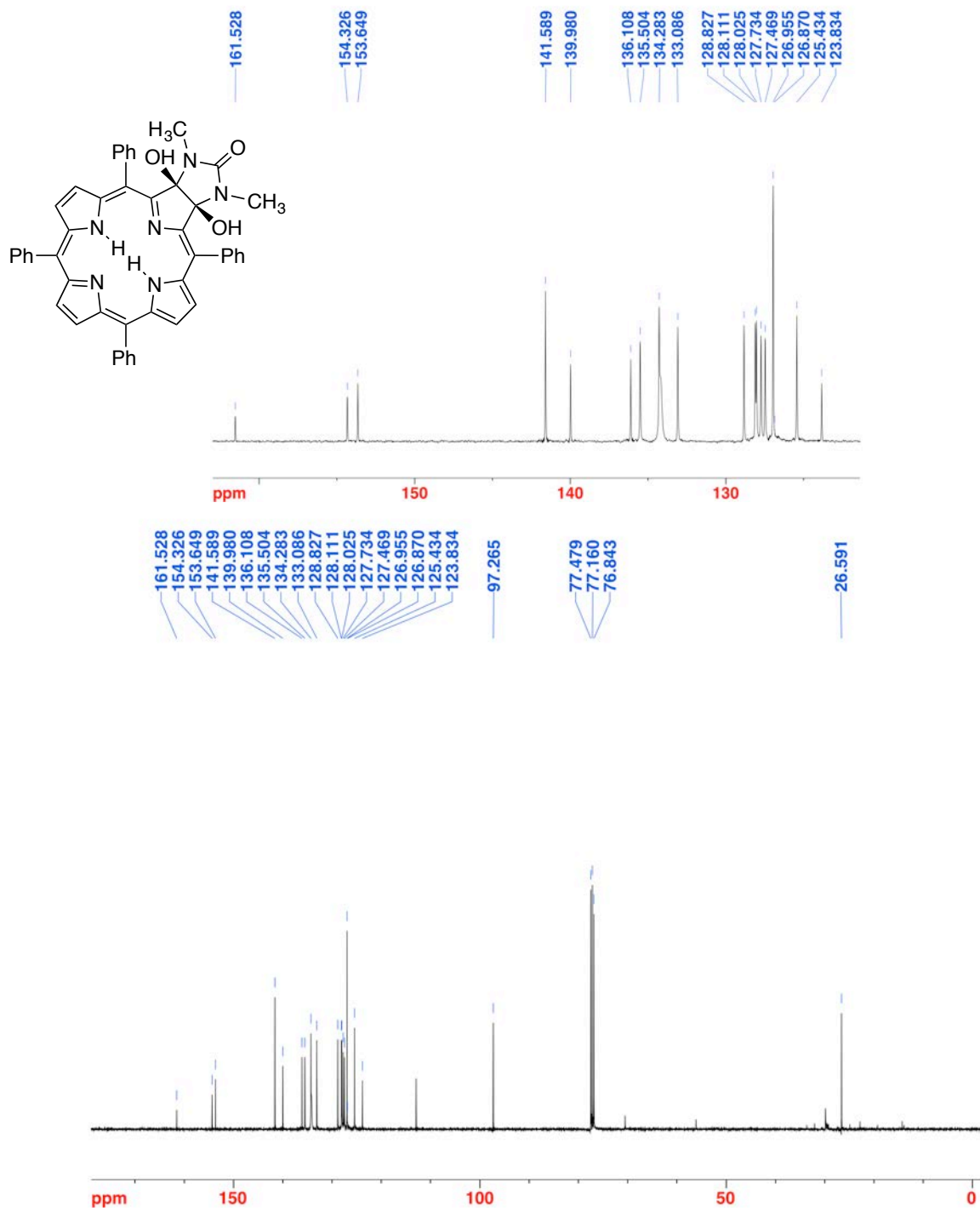
Figure S7. ^{1}H NMR (400 MHz, CDCl$_3$) of **9**.

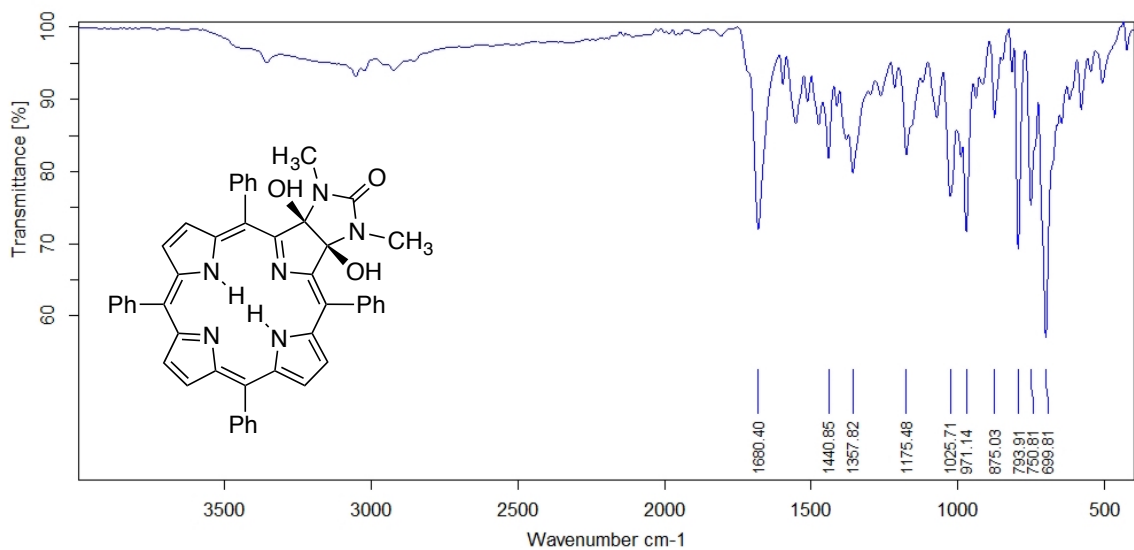**Figure S8.** ^{13}C NMR (100 MHz, CDCl$_3$) of **9**.

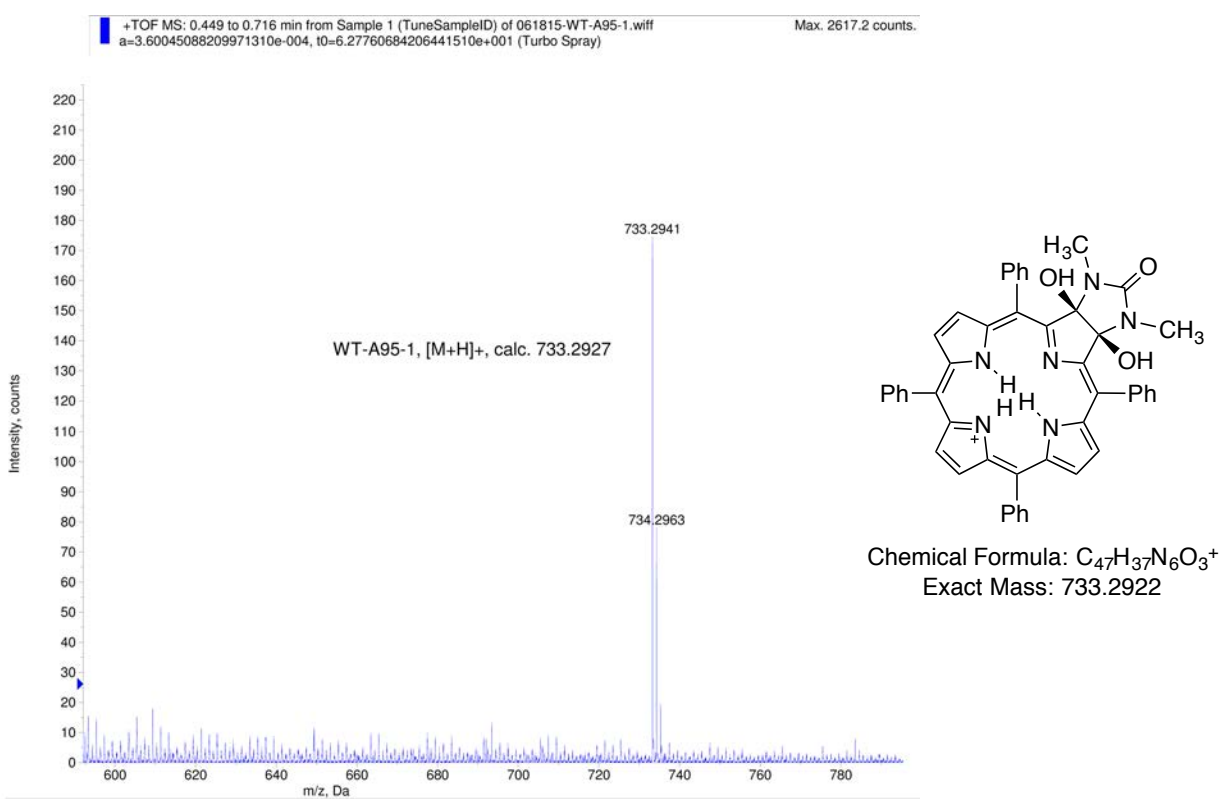**Figure S9.** FT-IR (neat, diamond ATR) of **9**.

Figure S10. HR-MS (ESI$^+$, 100% CH$_3$CN, TOF) of **9**.

***meso*-Tetraphenyl-2-aza-3-oxoporphyrin 10.**

Dihydroxychlorin **8** (28.8 mg, 4.6 × 10^{-5} mol) was dissolved in dry THF (11.0 mL) and Et$_3$N (5-6 drops) in a RBF equipped with a magnetic stir bar. Pb(OAc)$_4$ (31.4 mg, 7.1 × 10^{-5} mol, 1.7 equiv.) was added in portions and the reaction mixture was stirred at ambient temperature. When the starting material was consumed (reaction control by UV-vis and TLC), the solvent was removed by rotary evaporation and the remaining residue was purified by preparative TLC (silica-CH$_2$Cl$_2$/1% MeOH) to afford known.[2] porpholactam **10** in 69% yield (17.8 mg): (data included for comparison) ^{1}H NMR (400 MHz, CDCl$_3$): δ 9.65 (s, 1H, exchangeable with D$_2$O), 8.79 (d, [3]*J* = 5.0 Hz, 1H), 8.71 (d, [3]*J* = 4.7 Hz, 1H), 8.64 (d, [3]*J* = 5.0 Hz, 1H), 8.61-8.54 (m, 3H), 8.16-8.12 (m, 4H), 8.10-8.07 (m, 2H), 7.99 (m, 2H), 7.81 (m, 3H), 7.77-7.69 (m, 9H), -1.87 (s, 1H, exchangeable with D$_2$O), -2.14 (s, 1H, exchangeable with D$_2$O) ppm.
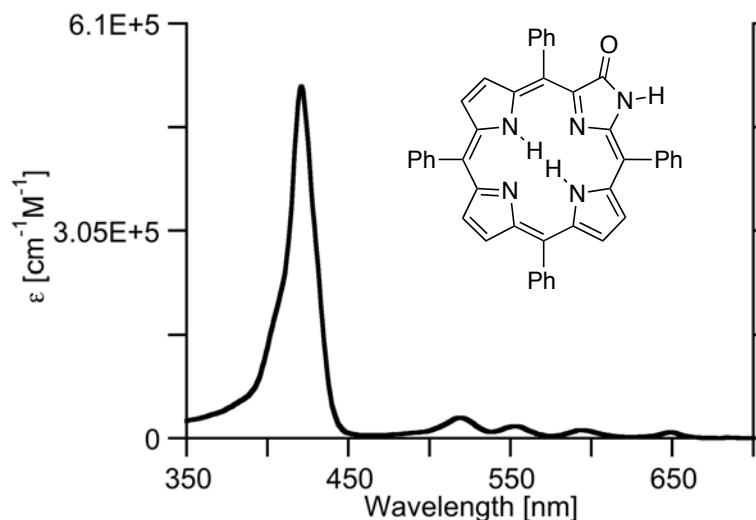

Figure S11. UV-vis spectrum (CH$_2$Cl$_2$) of **10**

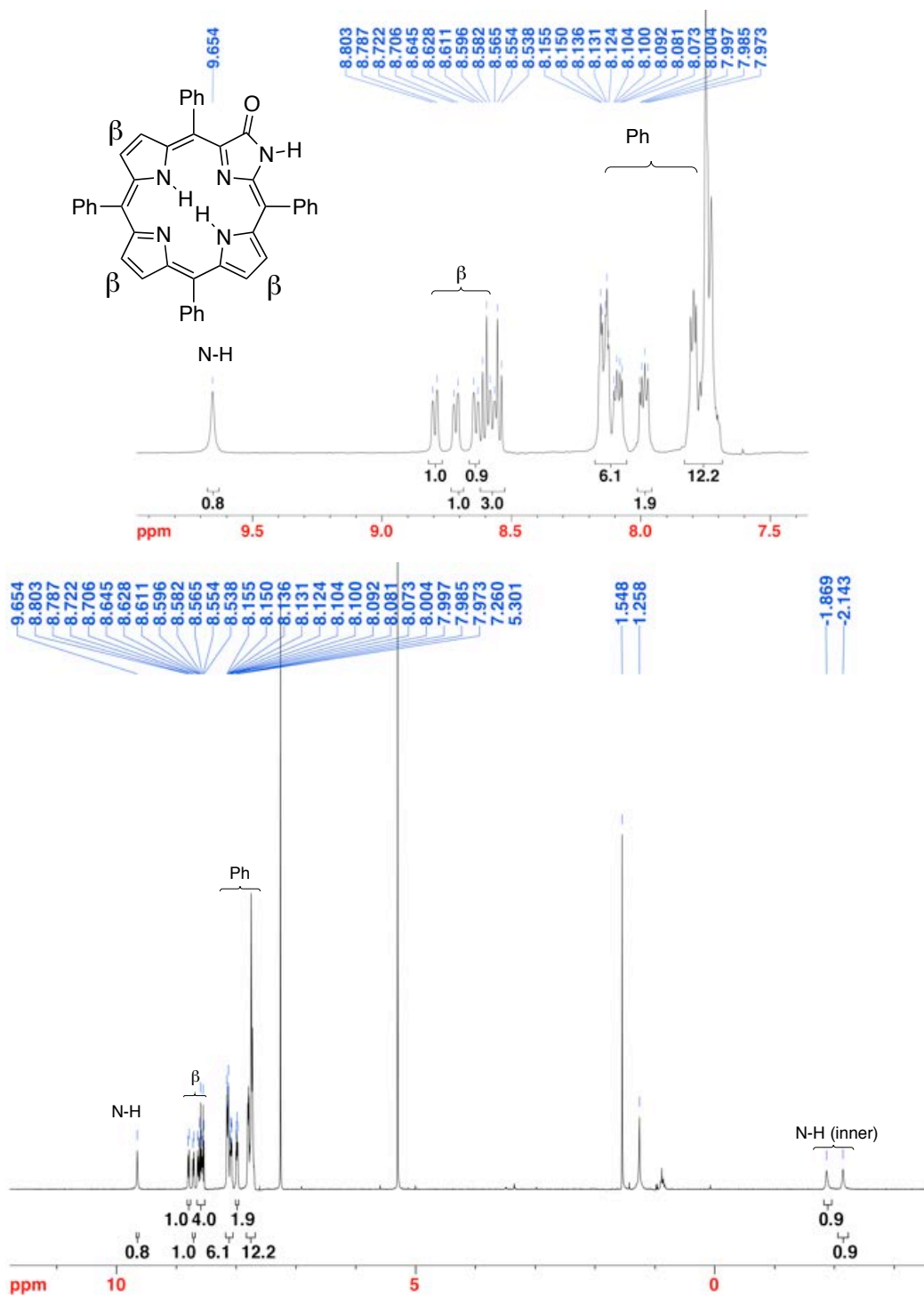(2) J. Akhigbe, J. P. Haskoor, J. A. Krause, M. Zeller and C. Brückner, *Org. Biomol. Chem.*, 2013, **11**, 3616–3628.
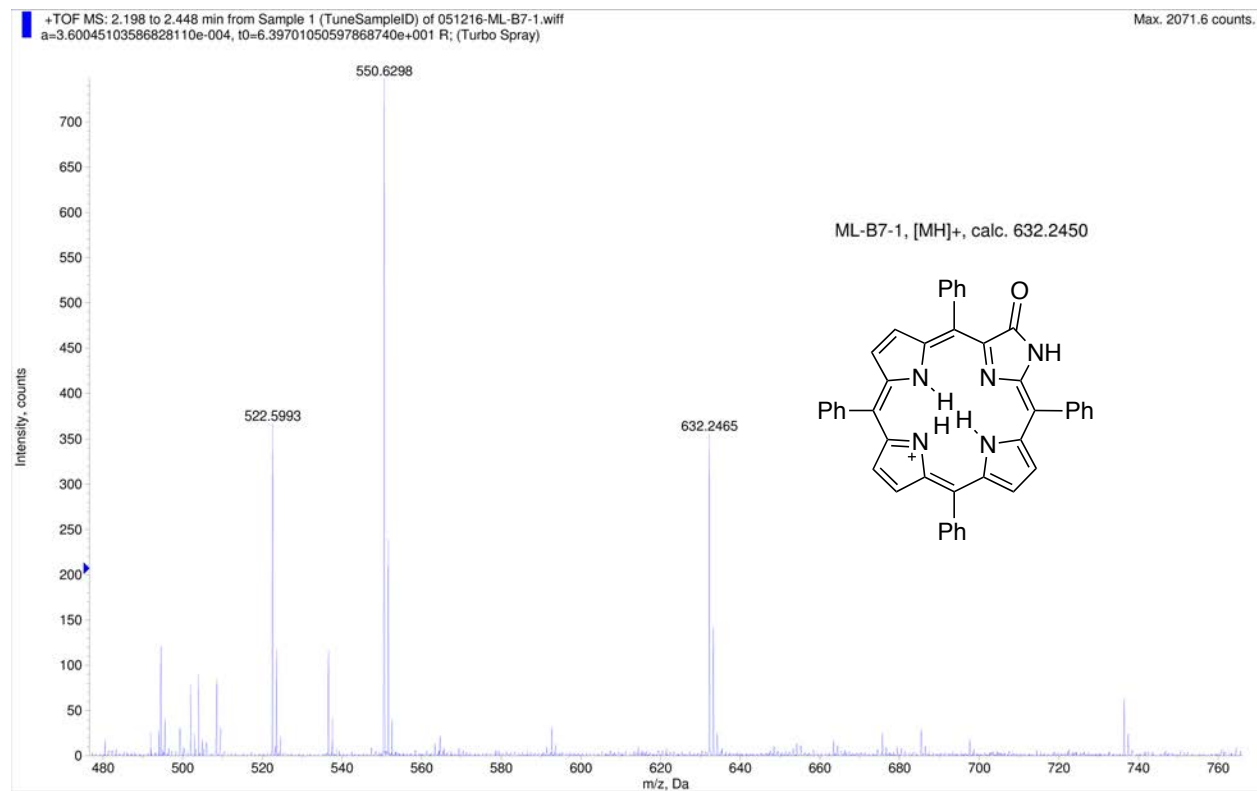
Figure S12. ^{1}H NMR (400 MHz, CDCl$_3$) of **10**.

ML-B7-1, [MH]+, calc. 632.2450

Figure S13. HR-MS (ESI$^+$, 100% CH$_3$CN, TOF) of **10**.

1,3,6-Triazocine-2,4-8-trione-based Pyrrole-modified Porphyrin 11.

Dihydroxychlorin-dimethylurea adduct **9** was dissolved in dry THF (5.0 mL) in a RBF equipped with a magnetic stir bar. Pb(OAc)$_4$ (13.3 mg, 3.00 × 10^{-5} mol) was added and the reaction mixture was stirred at ambient temperature. When the starting material was consumed (reaction control by UV-vis and TLC), the solvent was evaporated and the residue separated by preparative TLC (silica-CH$_2$Cl$_2$/3% MeOH) to afford **11** as a bright green solid in 71% yield (14.1 mg): R_f (silica-CH$_2$Cl$_2$/2% MeOH) = 0.66; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.35 (d, ^3J = 4.9 Hz, 1H), 8.28 (br s, 1H), 8.16 (s, 1H), 8.04 (d, ^3J = 4.9 Hz, 1H), 7.99 (br s, 2H), 7.70 (m, 4H), 7.56 (t, ^3J = 7.5 Hz, 1H), 7.43 (br s, 1H), 7.10 (br s, 1H), 3.28-3.15 (s, 3H), 1.88 (s, 1H, exchangeable with D$_2$O) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ 173.1, 155.5, 155.1, 147.3, 140.9, 140.21, 140.08, 136.5, 135.5, 133.6, 131.9, 129.2, 128.41, 128.32, 128.13, 127.4, 126.3, 125.5, 119.5, 32.9 ppm; UV-vis (CH$_2$Cl$_2$) λ_{max} (log ε) 365 (3.98) 454 (4.76), 578 (3.54), 625 (3.55), 670 (3.40), 741 (3.59) nm; FT-IR (neat, diamond ATR): $\nu_{C=O}$ = 1709.6, 1614.8 cm^{-1}; HR-MS (ESI$^+$, 100% CH$_3$CN, TOF) *m/z* cald for C$_{47}$H$_{34}$O$_6$N$_3$ ([M·H]$^+$), 731.2771 found 731.2775.
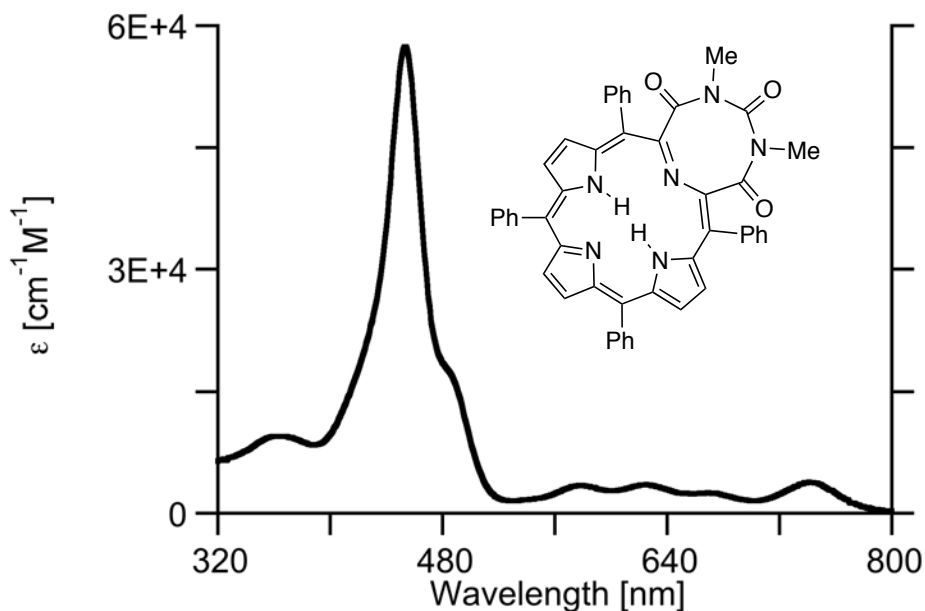
Figure S14. UV-vis spectrum (CH$_2$Cl$_2$) of **11**.
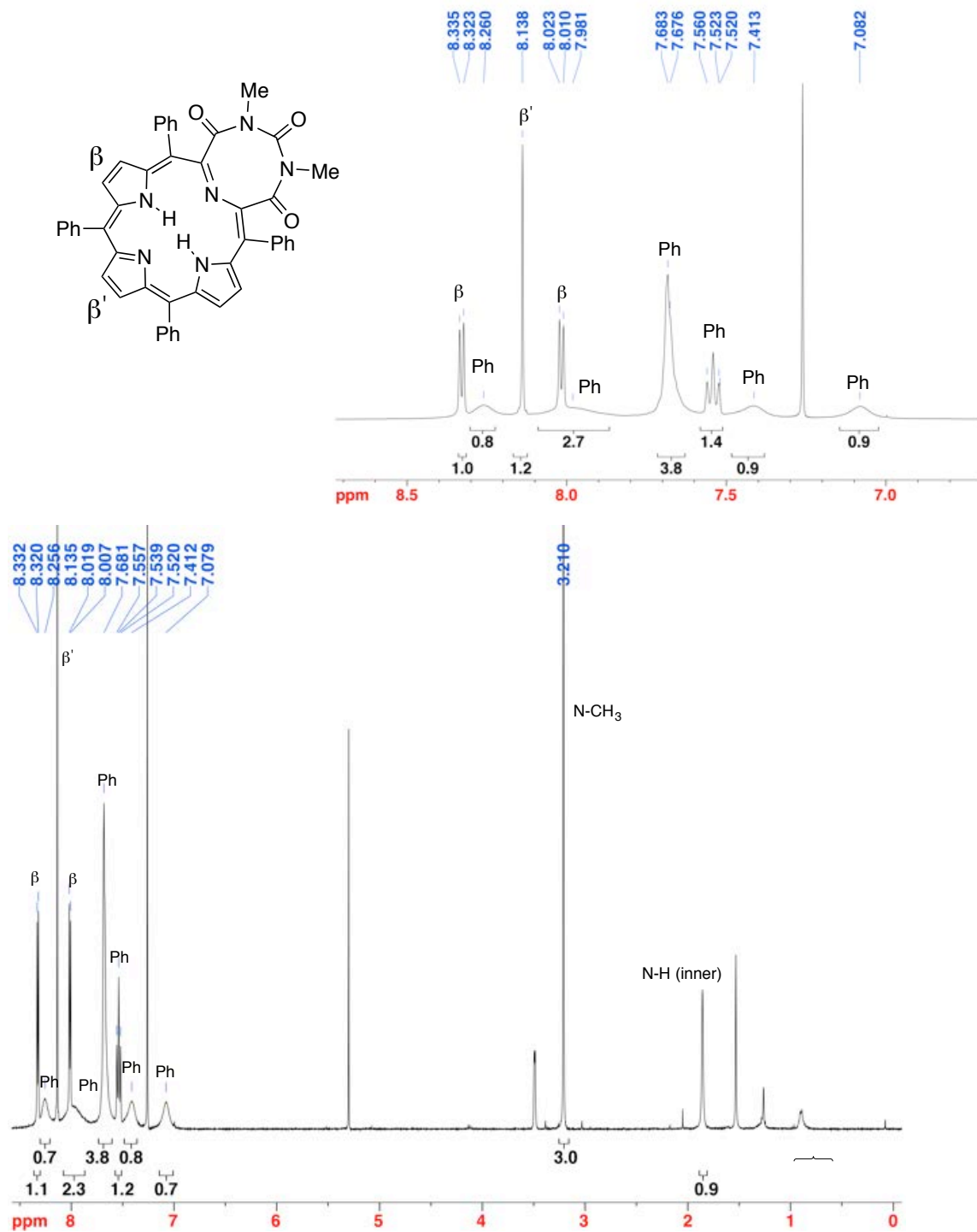
Figure S15. ^{1}H NMR (400 MHz, CDCl$_3$) of **11**.
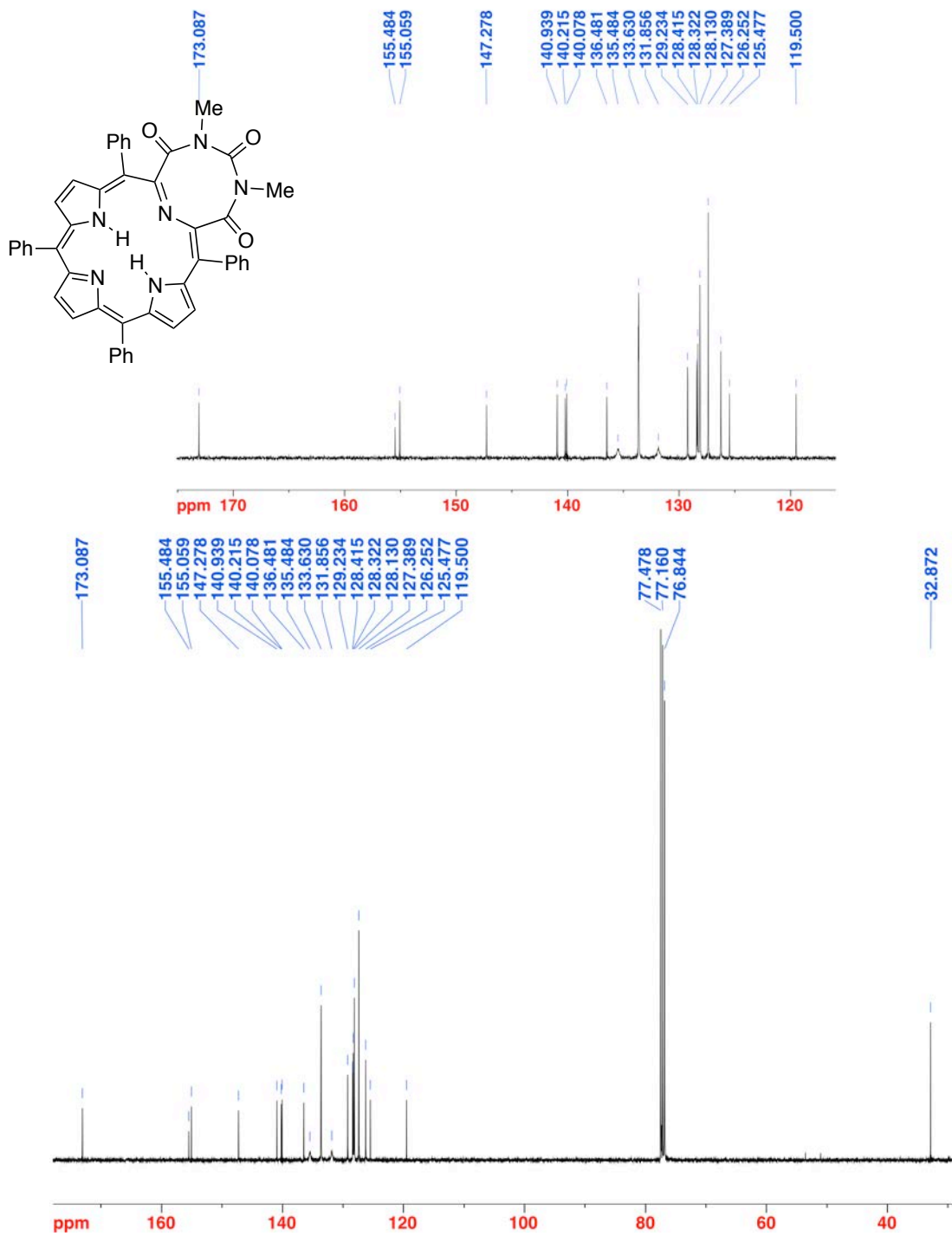
Figure S16. ^{13}C NMR (100 MHz, CDCl$_3$) of **11**.
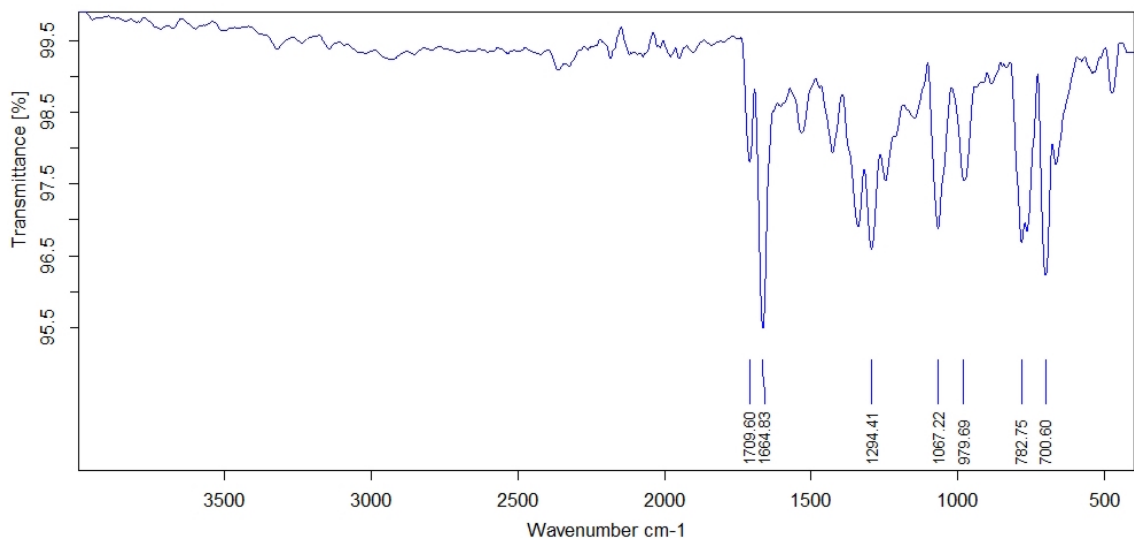
Figure S17. FT-IR (neat, diamond ATR) of **11**.

Chemical Formula: $C_{47}H_{35}N_6O_3^+$
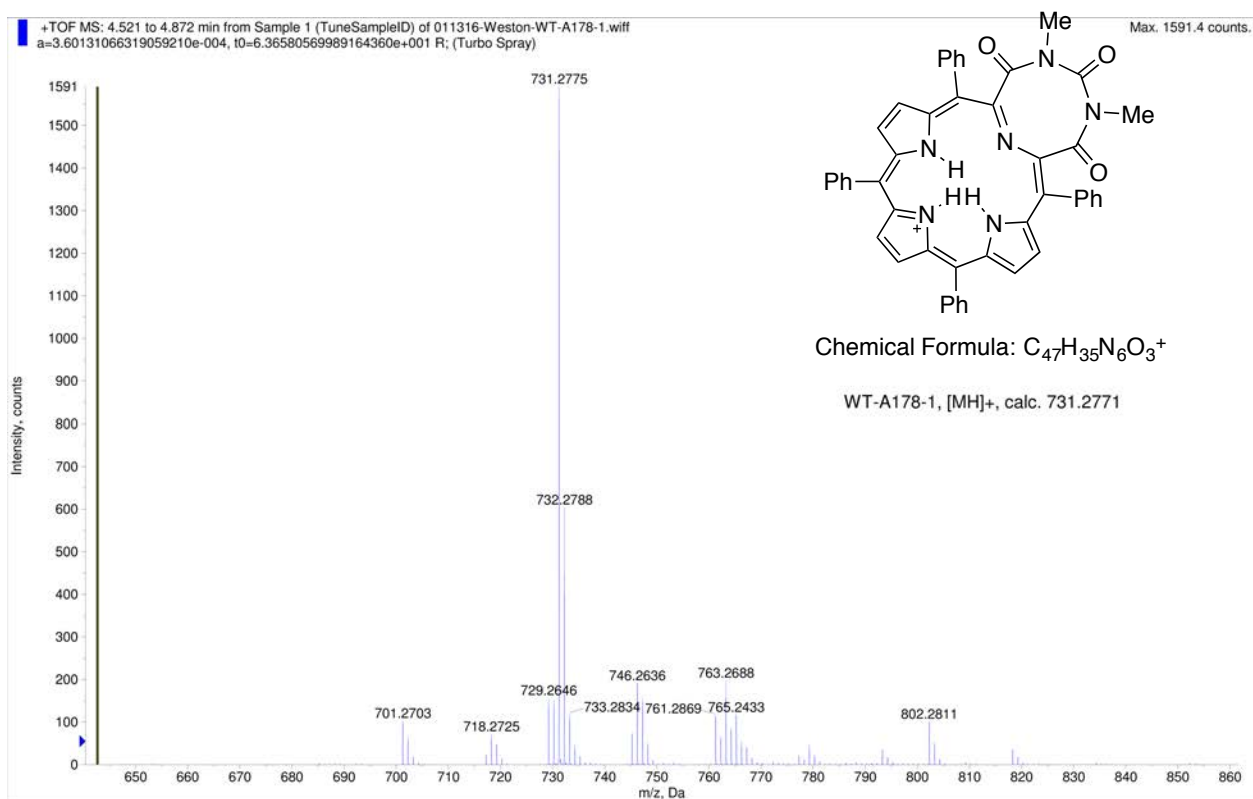
WT-A178-1, [MH]+, calc. 731.2771

Figure S18. HR-MS (ESI⁺, 100% CH₃CN, TOF) of **11**.

Crystallographic Details for 1,3,6-Triazocine-2,4-8-trione-based Pyrrole-modified Porphyrin 11:

X-ray diffraction data for **11** were collected using a Rigaku Rapid II curved image plate diffractometer with Cu-Kα (λ = 1.54178 Å). The instrument is equipped with an X-ray microsources with a laterally graded multilayers (Goebel) mirror for monochromatization. Single crystals were mounted on a Mitegen microloop mount using a trace of mineral oil and cooled *in situ* to 100(2) K for data collection. Data were collected using the dtrek option of CrystalClear.[3] and processed using HKL3000 [B] and data were corrected for absorption and scaled using Scalepack.[4] The space group was assigned and the structure solved by direct methods using XPREP and XM within the SHELXTL suite of programs,[5] and refined by full matrix least squares against F^2 with all reflections using Shelxl2014[6] using the graphical interface Shelxle.[7] H atoms attached to carbon and nitrogen atoms and hydroxyl hydrogens were positioned geometrically and constrained to ride on their parent atoms, with N-H distances of 0.88 Å, carbon hydrogen bond distances of 0.95 Å for and aromatic C-H, 1.00, and 0.98 Å for aliphatic C-H and CH_3 moieties, respectively. Methyl H atoms were allowed to rotate but not to tip to best fit the experimental electron density. $U_{iso}(H)$ values were set to a multiple of $U_{eq}(C)$ with 1.5 for CH_3, and 1.2 for C-H and N-H units, respectively.

(3) Rigaku (2014). CrystalClear-SM Expert 2.1 b32, Rigaku Corp., The Woodlands, Texas, USA.
(4) Otwinowski Z. & Minor, W. (1997). *Methods Enzymol.* 276, 307-327.
(5) a) SHELXTL (Version 6.14) (2000-2003) Bruker Advanced X-ray Solutions, Bruker AXS Inc., Madison, Wisconsin: USA. b) Sheldrick, G. M. (2008). *Acta Cryst.* A64, 112-122.
(6) a) Sheldrick, G. M. (2015). *Acta Cryst.* C71, 3-8. b) Sheldrick, G. M. (2013).

University of Göttingen, Germany.

(7) SHELXLE Rev656, Rev714, SHELXLE. Hübschle, C. B., Sheldrick, G. M. and Dittrich, B. (2011). *J. Appl. Cryst.* 44, 1281-1284.

Table 1. Experimental Details for X-Ray Analysis of 11

Crystal data

Chemical formula	$C_{47}H_{34}N_6O_3$
M_r	730.80
Crystal system, space group	Orthorhombic, $Pca2_1$
Temperature (K)	100
a, b, c (Å)	26.853 (2), 10.1988 (10), 27.005 (3)
V (Å^3)	7395.8 (13)
Z	8
$F(000)$	3056
D_x (Mg m^{-3})	1.312
Radiation type	Cu $K\alpha$
No. of reflections for cell measurement	68142
θ range (°) for cell measurement	3.3–63.5
μ (mm^{-1})	0.67
Crystal shape	Plate
Colour	Purple
Crystal size (mm)	0.34 × 0.27 × 0.01

Data collection

Diffractometer	Rigaku Rapid II curved image plate diffractometer
Radiation source	microfocus X-ray tube
Monochromator	Laterally graded multilayer (Goebel) mirror
Scan method	ω scans
Absorption correction	Multi-scan, *SCALEPACK* (Otwinowski & Minor, 1997)
T_{min}, T_{max}	0.472, 0.993
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	68142, 11219, 5550
R_{int}	0.140
θ values (°)	θ_{max} = 63.5, θ_{min} = 3.3
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.580
Range of h, k, l	h = -31→30, k = -11→11, l = -31→31

Refinement

$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.157, 0.414, 1.05
No. of reflections	11219
No. of parameters	1014
No. of restraints	1
H-atom treatment	H-atom parameters constrained $w = 1/[\sigma^2(F_o^2) + (0.150P)^2 + 50.P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.96, -0.41
Absolute structure	Refined as an inversion twin
Absolute structure parameter	0.1 (15)