

ELECTRONIC SUPPLEMENTARY INFORMATION

Two-Photon Absorption in Butadiyne-Linked Porphyrin Dimers: Torsional and Substituent Effects

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1. General Notes

All compounds were used as received unless specified. Solvents were HPLC grade (Sigma). Diisopropylamine (DIPA) was distilled over CaH₂ before use. Dry DMF was commercial anhydrous grade. Dry toluene refers to solvent passed over a column of activated alumina under N₂ atmosphere immediately before use. Petroleum ether refers to boiling point 40–60°C. TLC plates were Merck silica gel 60 F254 indicated, and column chromatography was carried out on Merck silica gel 60 under positive pressure of nitrogen. Size-exclusion chromatography was performed under gravity using BioRad BioBeads grade SX1 (nominal molecular weight range 600–14,000 Da), swollen in the eluent indicated. Standard Schlenk techniques were used for air-sensitive reactions. Solvent ratios and percentages are reported volume/volume. 5,15-Bis[3,4,5-tris(decyloxy)phenyl]porphyrin¹ and 5-bromo-10,20-bis[3,4,5-tris(decyloxy)phenyl]porphyrin² were prepared according to the literature procedure.

NMR data were recorded on either Bruker DPX300, AVII or AVIII 400 spectrometers, and are reported as chemical shifts in parts per million (ppm) referenced to tetramethylsilane, with coupling constants (*J*) in Hz. MALDI TOF MS were acquired using a Waters MALDI Micro MX. Samples were prepared using 1,8,9-anthracenetriol in tetrahydrofuran as the matrix. For centrifugation an MSE Mistral 1000 was used. Absorption spectra were recorded

using a Perkin Elmer Lambda20 UV-vis spectrometer in 10 mm path quartz cuvettes at 25 °C, baseline corrected against a solvent blank. Molar extinction coefficients are reported as $\log \epsilon$. Fluorescence spectra were recorded in a quartz 10 mm cuvette on a Horiba JobinYvon Fluoromax 2, using 5 nm excitation and emission slits.

For the viscous solutions, a stock solution of **R-P2C8(Zn)-R** at 5 μM in CHCl_3 : 1% pyridine was first prepared. Then two BRAND UV micro plastic cuvettes (from Sigma-Aldrich, Z637106, batch # K 175-2, mass 2.90 g) were dissolved in 2.3 mL of the stock solution and sealed in a screw-top vial. After 24 h the solution was then stirred with a spatula and centrifuged (4k rpm, 10 min) to give a homogeneous viscous gel. The final concentration of dye was approximately 2.5 μM due to the volume increase caused by dissolving the plastic cuvette. The gel was transferred to a fluorescence cuvette using a spatula, the lid sealed with parafilm, and centrifuged (1.5k rpm, 45 min).

Electrochemical measurements were carried out using an Autolab Eco-Chemie PGSTAT12 instrument. A glassy carbon working electrode, Ag/AgNO_3 reference electrode (double-frit design, inner solution 0.1 M $\text{Bu}_4\text{NPF}_6/0.002$ M AgNO_3 in acetonitrile, outer solution as the flask) and a Pt counter electrode were used. The flask containing the electrolyte solution (0.1 M Bu_4NPF_6 in THF) was purged with N_2 gas saturated with the solvent. Cyclic voltammetry: scan rate 0.25 V s^{-1} , step potential 10 mV; square wave voltammetry: step potential 2 mV, step amplitude 20 mV, square wave frequency 8 Hz.

2. Supplementary Synthetic Schemes

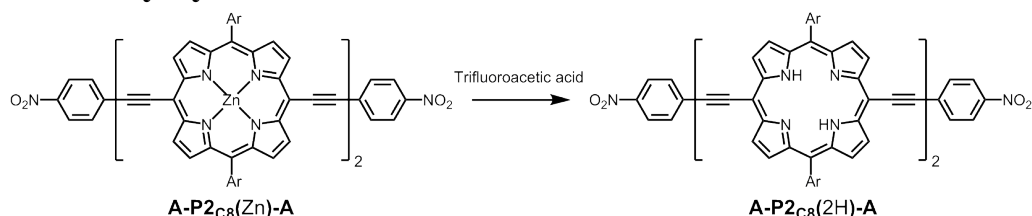


Figure S1 One approach to free-base dimers; demetallation of final Zn dimer **A-P2C8(Zn)-A** (Ar = 3,5-bis-octyloxy-phenyl)

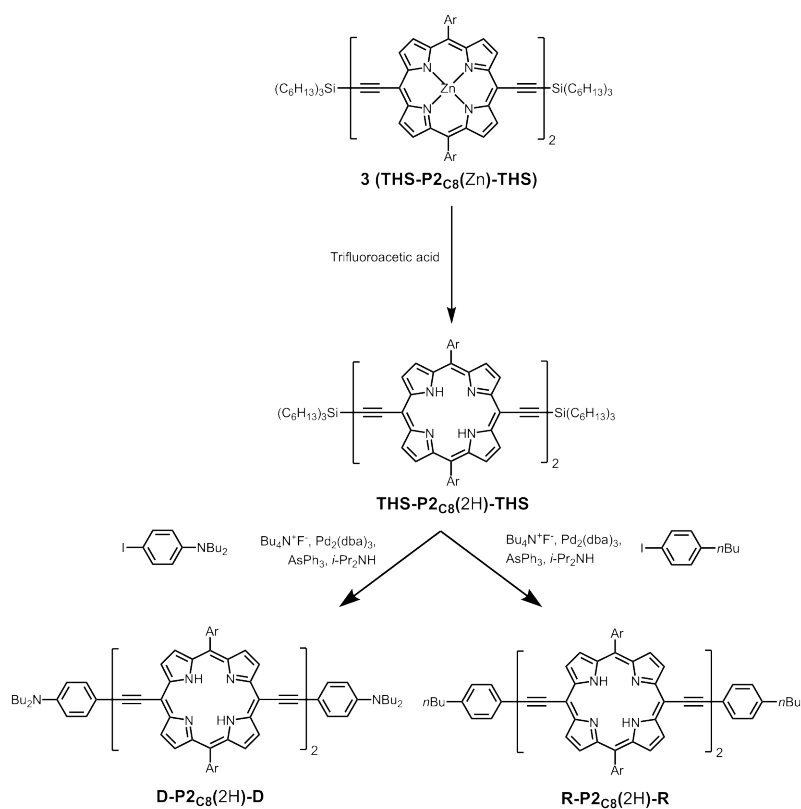


Figure S2 Another approach to free-base dimers; demetallation of intermediate **3** followed by one-pot desilylation and Cu-free Sonogashira coupling (Ar = 3,5-bis-octyloxy-phenyl).

3. One-Photon Spectroscopy

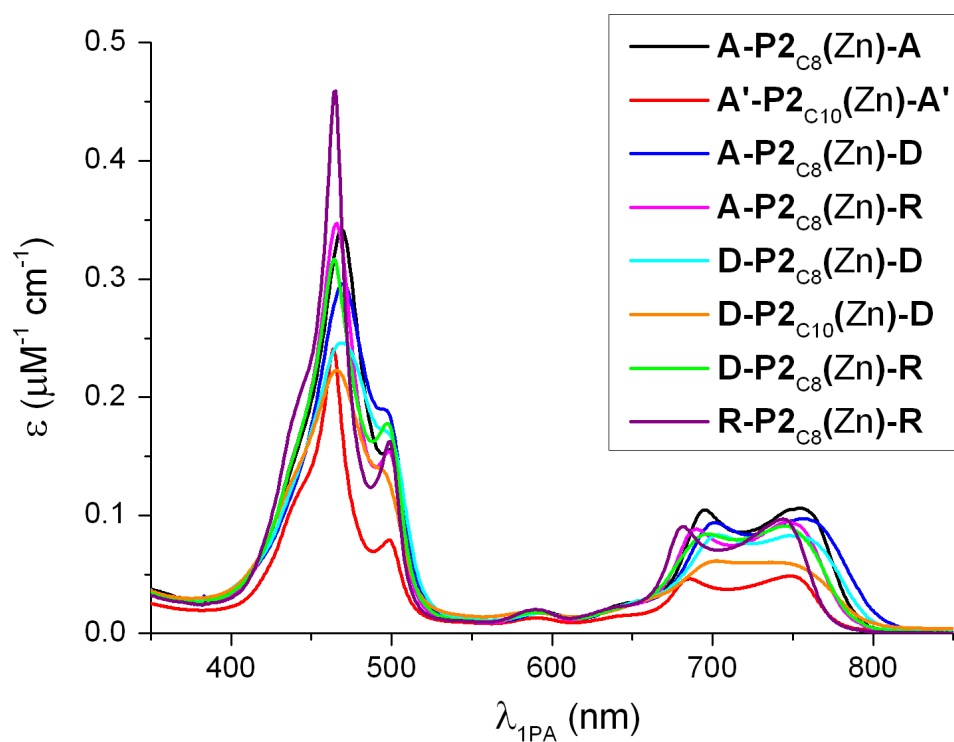


Figure S3 Linear absorption spectra of the set of zinc dimers (in CHCl_3 containing 1% pyridine).

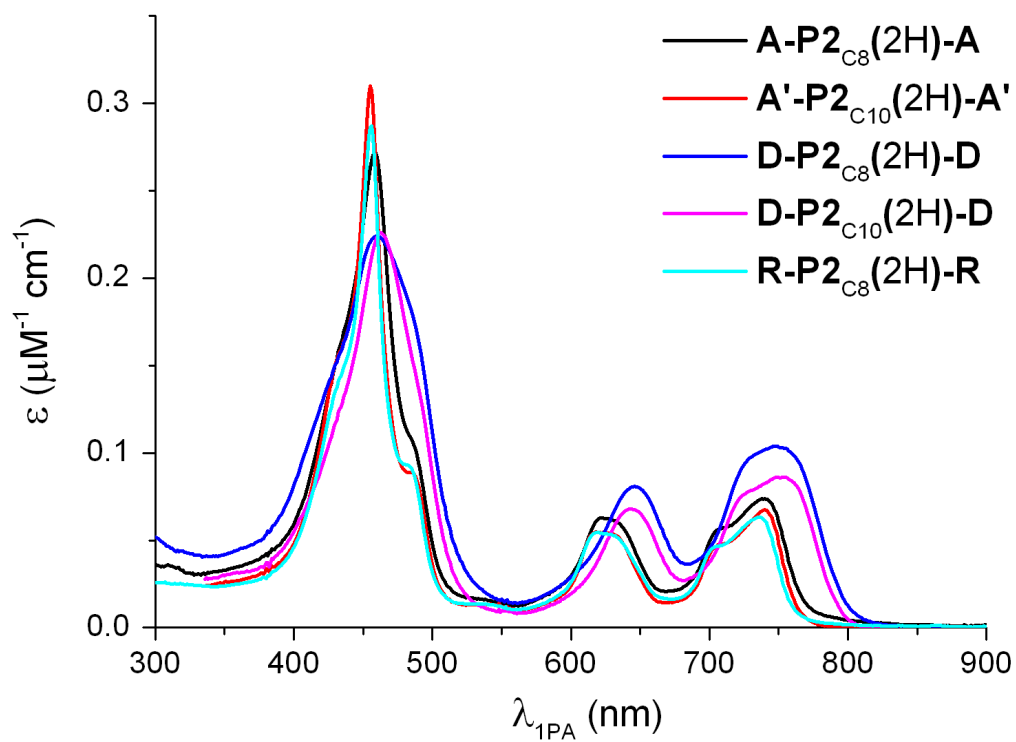


Figure S4 Linear absorption spectra of the set of free-base dimers (in CHCl_3).

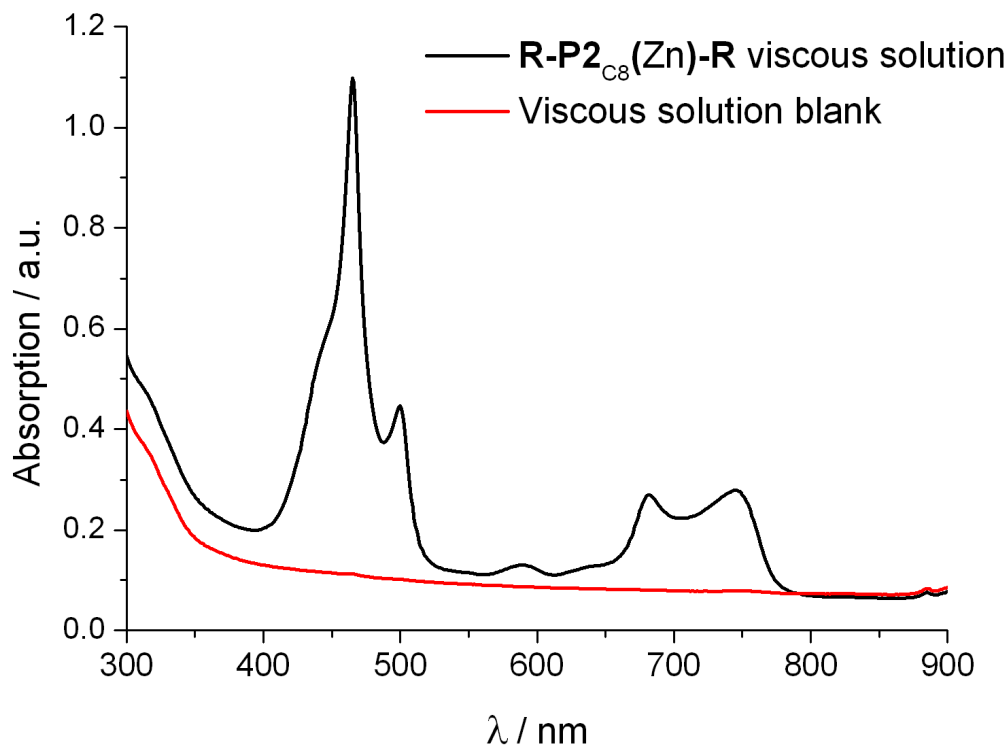


Figure S5 Linear absorption of **R-P2_{C8}(Zn)-R** in viscous solution (in CHCl₃, 1% pyridine and polymer; see above for details).

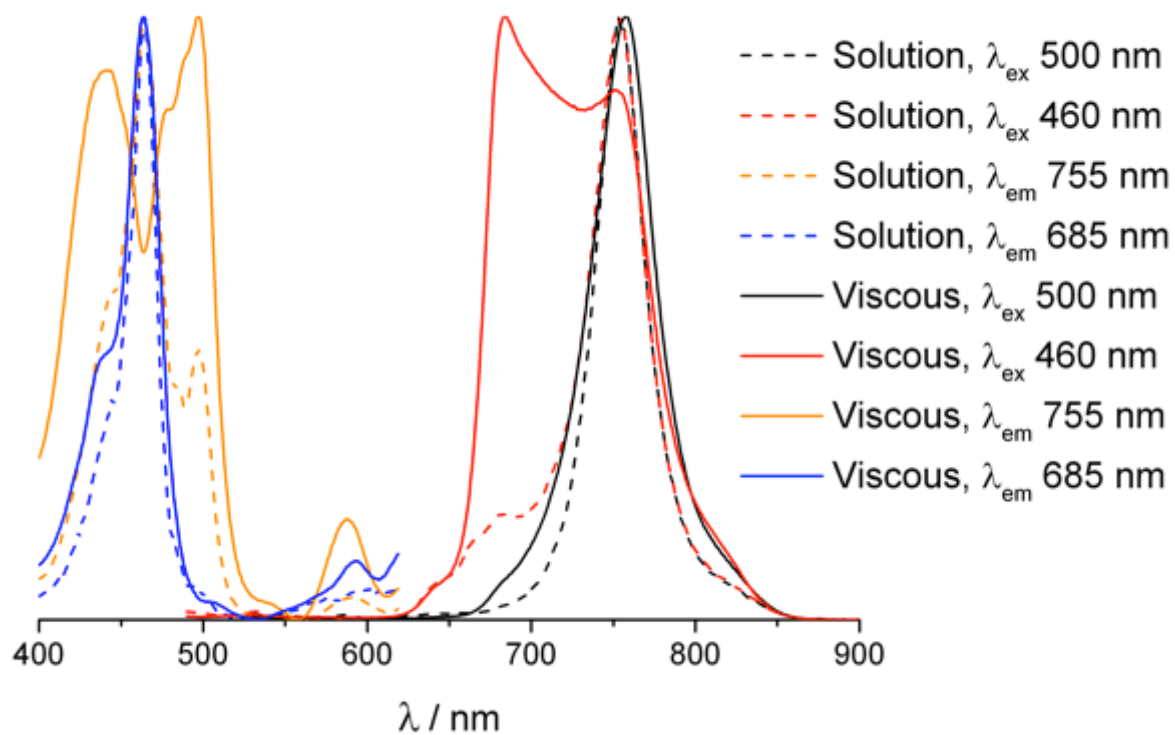


Figure S6 Linear excitation and emission of **R-P2_{C8}(Zn)-R** in fluid (CHCl₃ : 1% pyridine) and viscous solution. (Excitation and emission wavelengths are listed in the key.)

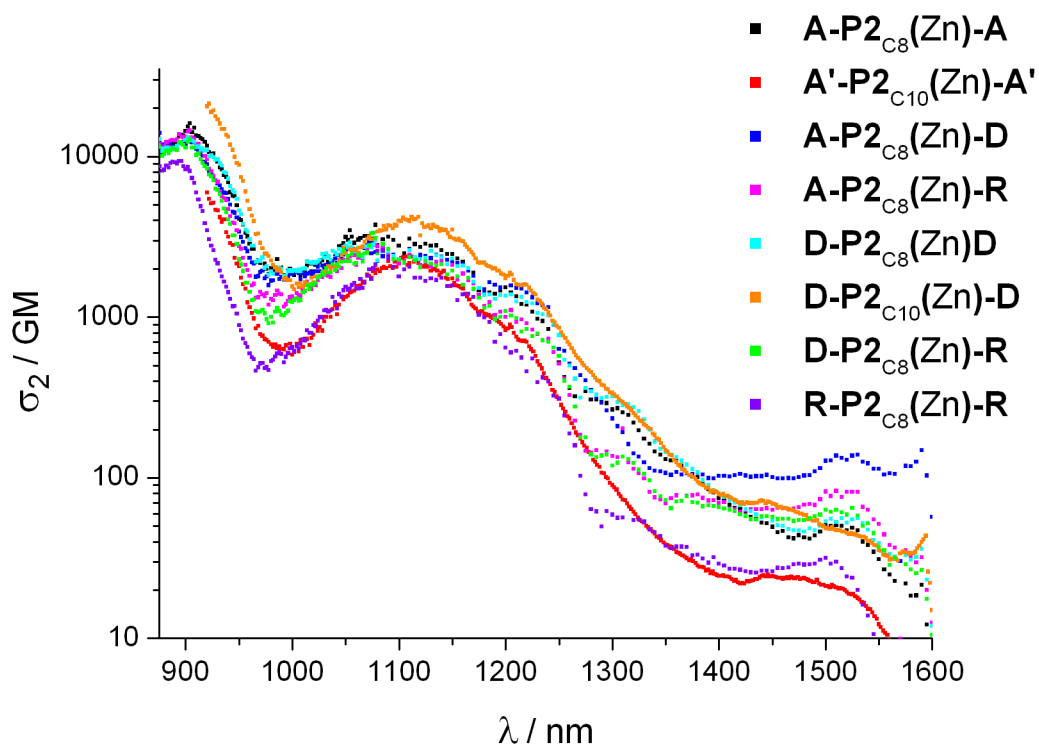


Figure S7 Two-photon absorption of the family of zinc dimers, recorded in CHCl_3 containing 1% pyridine.

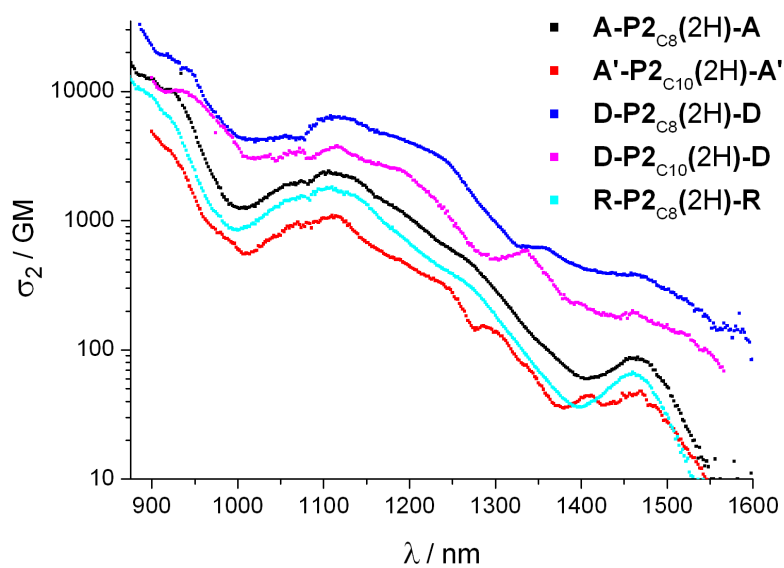


Figure S8 Two-photon absorption of the free-base dimers, recorded in CHCl_3 .

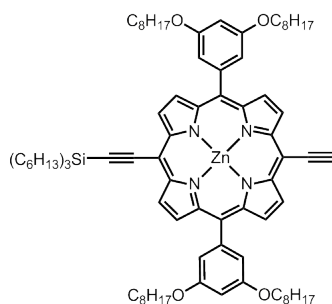
4. Two-Photon Spectroscopy

Two photon absorption (2PA) spectra and cross sections were measured by two photon excited fluorescence (2PEF) method.³ We estimate that the precision of these measurements is $\pm 20\%$. The laser system for the 2PEF measurements comprised a Ti:Sapphire femtosecond oscillator (Lighthouse, Inc.), a 1 kHz pulse repetition rate femtosecond regenerative amplifier (Legend F-HE, Coherent Inc.) and an optical parametric amplifier, OPA (TOPAS-C, Light Conversion). The second harmonic of the idler wave output of the OPA was utilized for excitation in the range 900–1078 nm with the incident pulse energy in the range 10–50 μJ . The average pulse duration was 90–120 fs (FWHM), and the FWHM beam diameter on the sample was 0.5–1 mm. The signal output of the OPA was used in the range 1080–1600 nm, with incident pulse energies in the range 30–200 μJ , 90–120 fs FWHM pulse durations, and FWHM beam diameters from 0.7–1.5 mm. Further details about the laser system are given in ref [3].

Samples were prepared in 1 cm spectroscopic quartz cuvettes (Starna). The linear absorption spectra were measured with PerkinElmer Lambda 950 spectrophotometer and the linear fluorescence emission spectra were measured with PerkinElmer LS 50B fluorescence spectrometer. The 2PEF spectra we collected using diffraction grating spectrometer (Triax 550, Jobin Yvon) equipped with a liquid nitrogen-cooled CCD detector (Spectrum One, Jobin Yvon). As the first step, the relative 2PEF spectra were determined by measuring the fluorescence intensity as a function of the excitation wavelength. The fluorescence signal at each wavelength was normalized to the square of the incident pulse energy (Molelectron P4-35) as well as to the relative fluorescence signal measured under the same conditions for the 2PA reference standard Styryl 9M in chloroform.³ Peak optical density of the samples used for the relative 2PEF spectra was in the range, O.D. = 0.5–1.0. Normalization with respect to the reference standard provided necessary corrections due to possible variations of the incident photon flux density. Quadratic excitation power dependence of the fluorescence signal was measured at 50 nm intervals throughout the entire scan range. The resulting power exponent was in the range, 2.00 ± 0.05 . 2PA cross sections were determined at one selected excitation wavelength by comparing the fluorescence signal from the sample and the reference compound obtained under identical excitation- and detection conditions. The relative fluorescence emission quantum yield of the sample versus the standard was determined by using the fluorescence spectrometer. Samples for the quantum yield measurement were prepared with low optical density, O.D. = 0.05–0.08 to avoid reabsorption.

5. Synthetic Procedures

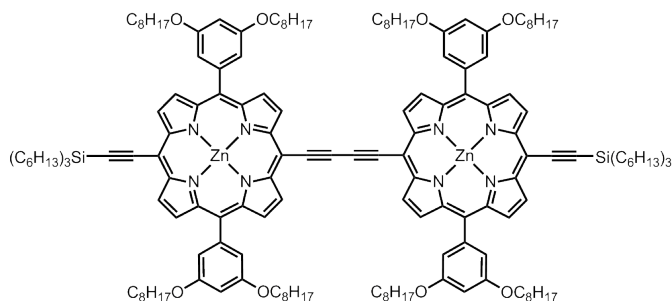
■ Zinc 5,15-bis-(3,5-bis-octyloxy-phenyl)-10-ethynyl-20-trihexylsilanylethynyl-porphyrin THS-P_{C8}(Zn)-H



TBAF (1.0 M solution in THF, 0.41 mL, 0.41 mmol) was added to a solution of zinc 5,15-bis-(3,5-bis-octyloxy-phenyl)-10,20-bis-trihexylsilanylethynyl-porphyrin (0.98 g, 0.59 mmol) in 1:1 CH₂Cl₂ : CHCl₃ (40 mL) and the reaction mixture stirred at room temperature. The progress was monitored carefully by TLC until the starting material and mono-deprotected product (*R_f* 0.90 and 0.70 respectively, 10:1:1 petroleum ether: EtOAc : pyridine) were in roughly equal ratio (26 min.), then CH₃COOH (24 μL, 0.41 mmol) was added. The reaction mixture was passed immediately through a short silica gel plug (CH₂Cl₂). Chromatography on silica gel (10:1:1 petroleum ether : EtOAc : pyridine) gave starting material (0.47 g, 48%), the desired product (0.36 g, 45%) and the doubly-deprotected byproduct.

δ_{H} (400 MHz; CDCl₃ : 1% d₅-pyridine) 9.69 (2 H, d, *J* 4.5, **β -H**), 9.63 (2 H, d, *J* 4.5, **β -H**), 9.00 (2 H, d, *J* 4.5, **β -H**), 8.99 (2 H, d, *J* 4.5, **β -H**), 7.34 (4 H, d, *J* 2.3, **Ar-*o*-H**), 6.90 (2 H, t, *J* 2.3, **Ar-*p*-H**), 4.11 (9 H, t, *J* 6.8, **-O-CH₂-**, **C \equiv C-H**), 1.74–1.90 (15 H, m), 1.17–1.60 (81 H, m), 0.98–1.07 (7 H, m), 0.77–0.95 (29 H, m). δ_{C} (101 MHz; CDCl₃ : 1% d₅-pyridine) 158.2, 152.3, 152.3, 150.0, 149.9, 144.5, 132.6, 132.5, 131.0, 130.7, 122.2, 114.5, 109.5, 101.0, 100.6, 99.4, 99.0, 86.8, 83.3, 68.3, 33.4, 33.4, 31.8, 31.7, 29.4, 29.2, 26.1, 24.4, 22.7, 22.6, 14.2, 14.1, 13.9. *m/z* (MALDI TOF+) Calcd. for C₈₆H₁₂₂N₄O₄SiZn 1368.85, found 1368.60.

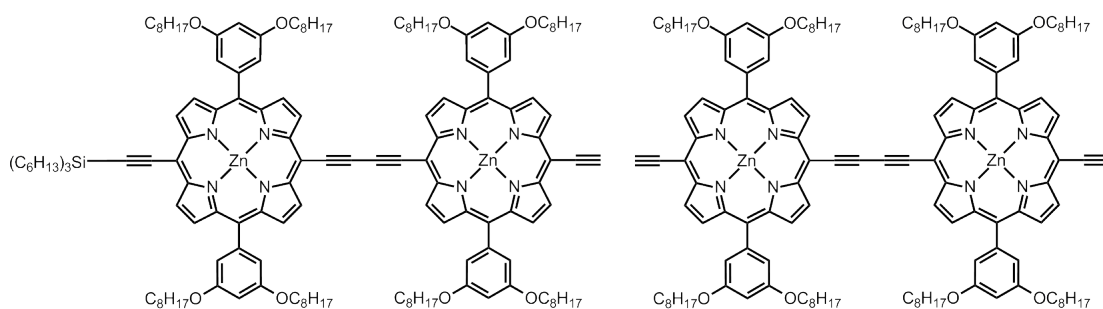
■ Zinc 5,15-bis-(3,5-bis-octyloxy-phenyl)-10,20-bis-trihexylsilanylethynyl-porphyrin dimer THS-P₂C₈(Zn)-THS



To a dried flask were added Pd(PPh₃)₂Cl₂ (13 mg, 19 μmol), CuI (25 mg, 130 μmol) and 1,4-benzoquinone (57 mg, 530 μmol). The reagents were dissolved in dry toluene (18 mL) and dry DIPA (4.5 mL) and added via syringe to a stirring solution of zinc 5,15-bis-(3,5-bis-octyloxy-phenyl)-10-ethynyl-20-trihexylsilanylethynyl-porphyrin (360 mg, 260 μmol) in dry toluene (18 mL) and dry DIPA (4.5 mL). The solution was stirred at room temperature under N₂ and monitored by TLC (25:1:1 petroleum ether: EtOAc : pyridine). Upon completion the solution was concentrated and passed through a short silica plug, eluting with CH₂Cl₂. The crude mixture was purified on silica, eluting with a gradient of 25:1:1 to 10:1:1 petroleum ether: EtOAc : pyridine. The product was isolated as a green oily solid (255 mg, 70%).

δ_{H} (400 MHz; CDCl₃ : 1% d₅-pyridine) 9.85 (4 H, d, *J* 4.5, **β -H**), 9.64 (4 H, d, *J* 4.5, **β -H**), 9.05 (4 H, d, *J* 4.5, **β -H**), 8.95 (4 H, d, *J* 4.5, **β -H**), 7.35 (8 H, d, *J* 2.3, **Ar-*o*-H**), 6.89 (4 H, t, *J* 2.1, **Ar-*p*-H**), 4.13 (16 H, t, *J* 6.6, **-O-CH₂-**), 1.81–1.92 (21 H, m), 1.69–1.81 (19 H, m), 1.44–1.58 (40 H, m), 1.13–1.44 (18 H, m), 0.96–1.04 (16 H, m), 0.79–0.93 (103 H, m), 0.63 (24 H, dt, *J* 9.4 and 6.7). δ_{C} (75 MHz; CDCl₃ : 1% d₅-pyridine) 157.2, 152.0, 151.3, 149.1, 148.7, 143.4, 131.9, 131.5, 130.0, 129.6, 121.8, 113.5, 108.4, 100.7, 99.7, 98.8, 98.3, 87.4, 81.2, 67.3, 32.3, 31.9, 30.8, 30.6, 30.4, 28.4, 28.2, 25.1, 21.7, 21.6, 21.5, 13.0, 12.9. *m/z* (MALDI TOF+) Calcd. for C₁₇₂H₂₄₂N₈O₈Si₂Zn₂ 2736.69, found 2736.81.

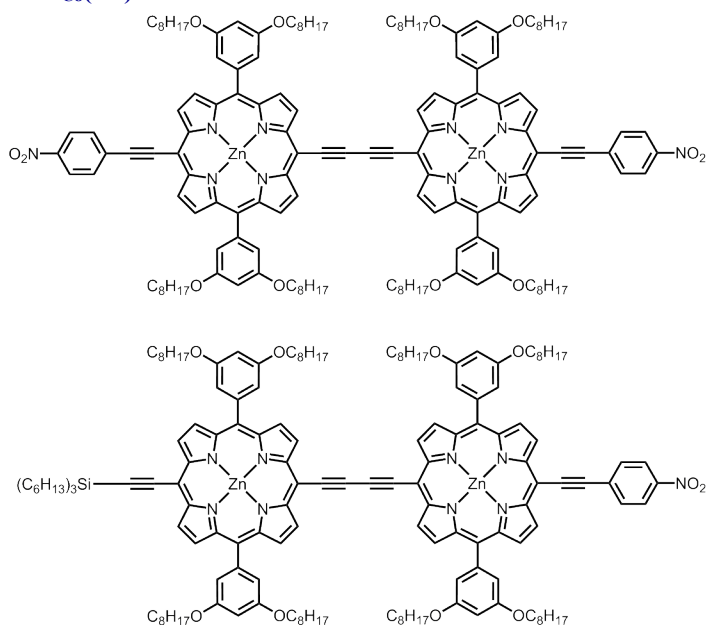
■ Zinc 5,15-bis-(3,5-bis-octyloxy-phenyl)-10-ethynyl-20-trihexylsilanylethynyl-porphyrin dimer and zinc 5,15-bis-(3,5-bis-octyloxy-phenyl)-10,20-bis-ethynyl-porphyrin dimer **THS-P2_{C8}(Zn)-H**, **H-P2_{C8}(Zn)-H**



Zinc 5,15-bis-(3,5-bis-octyloxy-phenyl)-10,20-trihexylsilanylethynyl-porphyrin dimer (260 mg, 93 μmol) was dried under vacuum in a flask then purged with N_2 . CHCl_3 (8 mL) and CH_2Cl_2 (8 mL) were added, followed by TBAF (1.0 M solution in THF, 65 μL , 65 μmol). The solution was stirred at room temperature and monitored carefully by TLC. After 90 min., CH_3COOH (4 μL , 70 μmol) was added and the reaction was immediately passed through a silica gel plug (eluting CH_2Cl_2). The crude mixture was concentrated and the starting material separated by column chromatography on silica gel, eluting with 10:1:1 petroleum ether : EtOAc : pyridine. 105 mg of the crude product mixture and 59 mg (23 %) of starting material were collected.

δ_{H} (400 MHz; CDCl_3 : 1% d_5 -pyridine) 9.76–9.89 (4 H, m, $\beta\text{-H}$), 9.54–9.66 (4 H, m, $\beta\text{-H}$), 8.99–9.08 (4 H, m, $\beta\text{-H}$), 8.86–8.96 (4 H, m, $\beta\text{-H}$), 7.31 (8 H, d, J 2.3, **Ar-*o*-H**), 6.83–6.88 (4 H, m, **Ar-*p*-H**), 4.09 (16 H, t, J 6.7, **-O-CH₂-**), 4.13 (1.5 H, s, **C \equiv C-H**), 1.78–1.88 (15 H, m), 1.66–1.78 (6 H, m), 1.41–1.55 (22 H, m), 1.25–1.38 (44 H, m), 1.15–1.24 (34 H, m), 0.92–1.01 (6 H, m), 0.83–0.89 (10 H, m), 0.80 (22 H, t, J 6.9). m/z (MALDI TOF+) Calcd. for $\text{C}_{136}\text{H}_{166}\text{N}_8\text{O}_8\text{Zn}_2$ 2171.14, found 2171.80. Calcd. for $\text{C}_{154}\text{H}_{204}\text{N}_8\text{O}_8\text{SiZn}_2$ 2453.42, found 2453.81.

■ Zinc 5,15-bis-(3,5-bis-octyloxy-phenyl)-10,20-bis-(4-nitrophenyl)ethynyl-porphyrin dimer **A-P2_{C8}(Zn)-A** and zinc 5,15-bis-(3,5-bis-octyloxy-phenyl)-10-(4-nitrophenyl)ethynyl-20-trihexylsilanylethynyl-porphyrin dimer **A-P2_{C8}(Zn)-THS**



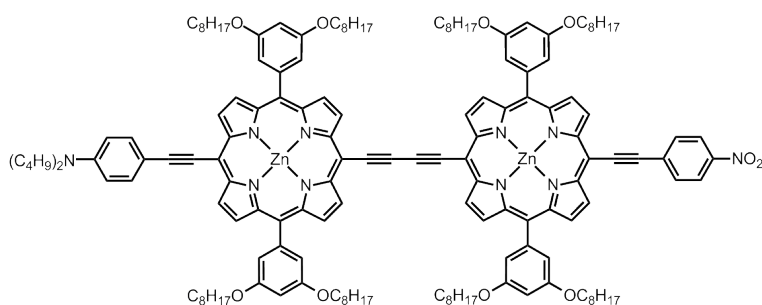
The crude mixture of zinc 5,15-bis-(3,5-bis-octyloxy-phenyl)-10-ethynyl-20-trihexylsilanylethynyl-porphyrin dimer and zinc 5,15-bis-(3,5-bis-octyloxy-phenyl)-10,20-bis-ethynyl-porphyrin dimer (105 mg, 43.0 μmol max. singly-deprotected porphyrin), 4-iodonitrobenzene (107 mg, 430 μmol), tris-(dibenzylideneacetone)-di-palladium(0) (2.0 mg, 2.2 μmol), PPh_3 (2.3 mg, 8.6 μmol) and CuI (0.4 mg, 2 μmol) were dried under vacuum in a pre-dried Schlenk tube before toluene (3.5 mL) and DIPA (3.5 mL) were added. The mixture was deoxygenated by three cycles of freezing under vacuum and saturating with nitrogen, then heated to 50 $^\circ\text{C}$ under N_2 . After 2 h, the mixture was concentrated and purified on silica gel, eluting with 10:1:1 petroleum ether : EtOAc : pyridine. The two collected fractions were

concentrated and passed through a size-exclusion column (eluting with toluene) to remove excess 4-iodonitrobenzene. Zinc 5,15-bis-(3,5-bis-octyloxy-phenyl)-10,20-bis-(4-nitrophenyl)ethynyl-porphyrin dimer was recovered after recrystallization by layered addition of CH₃OH to CH₂Cl₂ (13 mg, 6.0% over two steps), along with zinc 5,15-bis-(3,5-bis-octyloxy-phenyl)-10-(4-nitrophenyl)ethynyl-20-trihexylsilanylethynyl-porphyrin dimer (42 mg, 18% over two steps).

Zinc 5,15-bis-(3,5-bis-octyloxy-phenyl)-10,20-bis-(4-nitrophenyl)ethynyl-porphyrin dimer: δ_{H} (300 MHz; CDCl₃: 1% d₅-pyridine) 9.80 (4 H, d, *J* 4.7, **β -H**), 9.59 (4 H, d, *J* 4.7, **β -H**), 9.00 (4 H, d, *J* 4.7, **β -H**), 8.96 (4 H, d, *J* 4.7, **β -H**), 8.33 (4 H, d, *J* 8.9, **nitro-phenyl-H**), 8.04 (4 H, d, *J* 8.9, **nitro-phenyl-H**), 7.30 (8 H, d, *J* 2.2, **Ar-*o*-H**), 6.85 (4 H, t, *J* 2.3, **Ar-*p*-H**), 4.09 (16 H, t, *J* 6.6, **-O-CH₂-**), 1.75–1.88 (17 H, m), 1.38–1.52 (18 H, m), 1.11–1.36 (78 H, m), 0.74–0.82 (27 H, m). *m/z* (MALDI TOF+) Calcd. for C₁₄₈H₁₇₂N₁₀O₁₂Zn₂ 2414.18, found 2413.81. λ_{max} (CHCl₃) / nm 468 (log ϵ 5.53), 494 (5.21), 591 (4.30), 647 (4.44), 694 (5.01), 748 (5.02).

Zinc 5,15-bis-(3,5-bis-octyloxy-phenyl)-10-(4-nitrophenyl)ethynyl-20-trihexylsilanylethynyl-porphyrin dimer: δ_{H} (400 MHz; CDCl₃: 1% d₅-pyridine) 9.81–9.87 (4 H, m, **β -H**), 9.60–9.65 (4 H, m, **β -H**), 9.03 (4 H, d, *J* 4.5, **β -H**), 9.00 (2 H, d, *J* 4.5, **β -H**), 8.93 (2 H, d, *J* 4.5, **β -H**), 8.34 (2 H, d, *J* 8.6, **nitro-phenyl-H**), 8.05 (2 H, d, *J* 8.8, **nitro-phenyl-H**), 7.34 (8 H, m, **Ar-*o*-H**), 6.88 (4 H, m, **Ar-*p*-H**), 4.07–4.16 (16 H, m, **-O-CH₂-**), 1.79–1.93 (18 H, m), 1.68–1.79 (8 H, m), 1.42–1.57 (27 H, m), 1.27–1.41 (53 H, m), 1.18–1.26 (41 H, m), 0.93–1.03 (8 H, m), 0.84–0.90 (12 H, m), 0.77–0.84 (26 H, m). *m/z* (MALDI TOF+) Calcd. for C₁₆₀H₂₀₇N₉O₁₀SiZn₂ 2575.44, found 2575.63.

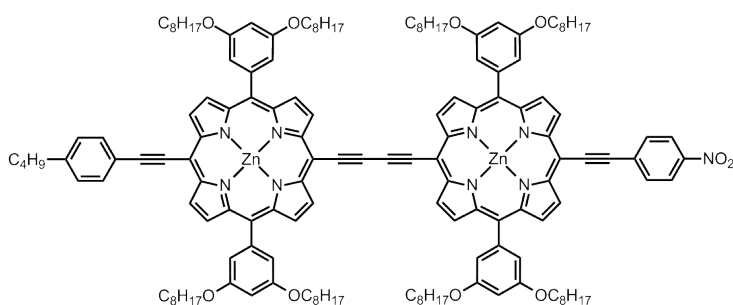
■ **Zinc 5,15-bis-(3,5-bis-octyloxy-phenyl)-10-(4-nitrophenyl)ethynyl-20-(*N,N*-di-*n*-butyl-4-aniline)ethynyl-porphyrin dimer A-P2C₈(Zn)-D**



Zinc 5,15-bis-(3,5-bis-octyloxy-phenyl)-10-(4-nitrophenyl)ethynyl-20-trihexylsilanylethynyl-porphyrin dimer (20 mg, 7.8 μ mol), *N,N*-dibutyl-4-iodo-1-aniline⁴ (13 mg, 39 μ mol), tris-(dibenzylideneacetone)-di-palladium(0) (0.4 mg, 0.4 μ mol), PPh₃ (0.4 mg, 2 μ mol) and CuI (0.1 mg, 0.4 μ mol) were dried under vacuum in a pre-dried Schlenk tube before toluene (0.7 mL) and DIPA (0.7 mL) were added. The mixture was deoxygenated by three cycles of freezing under vacuum and saturating with nitrogen, then TBAF (1.0 M in THF, 78 μ L, 78 μ mol) was added, and the mixture heated to 50 °C under N₂. After 2 h, the mixture was concentrated and purified on silica gel, eluting with 3:1 petrol : CH₂Cl₂, with 1 % pyridine. The desired fractions were concentrated and passed through a size-exclusion column (eluting with toluene) to remove unreacted *N,N*-dibutyl-4-iodo-1-aniline. The title compound was recovered as a green solid by recrystallization by layered addition of pentane to CH₂Cl₂ (12 mg, 62%).

δ_{H} (300 MHz; CDCl₃: 1% d₅-pyridine) 9.80 (2 H, d, *J* 4.7, **β -H**), 9.74 (2 H, d, *J* 4.7, **β -H**), 9.62 (2 H, d, *J* 4.5, **β -H**), 9.59 (2 H, d, *J* 4.7, **β -H**), 8.99 (2 H, d, *J* 4.5, **β -H**), 8.96 (4 H, dd, *J* 4.5 and 1.8, **β -H**), 8.86 (2 H, d, *J* 4.7, **β -H**), 8.34 (2 H, d, *J* 8.9, **nitro-phenyl-H**), 8.05 (2 H, d, *J* 9.1, **nitro-phenyl-H**), 7.78 (2 H, d, *J* 8.9, **aniline-H**), 7.29 (8 H, dd, *J* 2.3, **Ar-*o*-H**), 6.84 (4 H, dt, *J* 5.6 and 2.3, **Ar-*p*-H**), 6.72 (2 H, d, *J* 9.2, **aniline-H**), 4.03–4.12 (16 H, m, **-O-CH₂-**), 3.31 (4 H, t, *J* 7.9, **-N-(CH₂)₂-**), 1.73–1.87 (15 H, m), 1.52–1.65 (4 H, m), 1.37–1.51 (16 H, m), 1.10–1.37 (69 H, m), 0.94 (6 H, t, *J* 7.3, **-N-(CH₂)₂-CH₃**), 0.73–0.84 (23 H, m). *m/z* (MALDI TOF+) Calcd. for C₁₅₆H₁₉₀N₁₀O₁₀Zn₂ 2496.33, found 2496.58. λ_{max} (CHCl₃) / nm 469 (log ϵ 5.47), 495 (5.28), 594 (4.25), 647 (4.38), 702 (4.97), 756 (4.99).

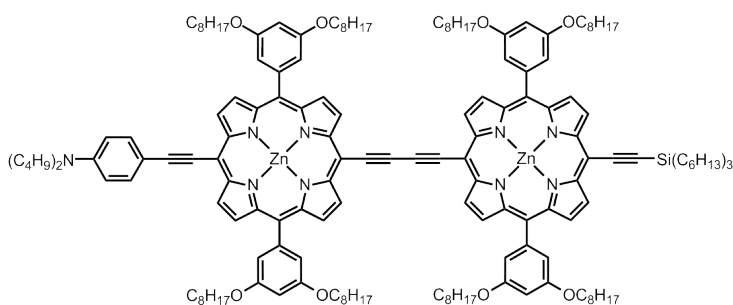
■ **Zinc 5,15-bis-(3,5-bis-octyloxy-phenyl)-10-(4-nitrophenyl)ethynyl-20-(4-*n*-butyl-phenyl)ethynyl-porphyrin dimer A-P2_{C8}(Zn)-R**



Zinc 5,15-bis-(3,5-bis-octyloxy-phenyl)-10-(4-nitrophenyl)ethynyl-20-trihexylsilanylethynyl-porphyrin dimer (40 mg, 16 μmol), tris-(dibenzylideneacetone)-di-palladium(0) (0.7 mg, 0.8 μmol), PPh₃ (0.8 mg, 3 μmol) and CuI (0.2 mg, 0.8 μmol) were dried under vacuum in a pre-dried Schlenk tube before toluene (1.3 mL) and DIPA (1.3 mL) were added. The mixture was deoxygenated by three cycles of freezing under vacuum and saturating with nitrogen, then TBAF (1.0 M in THF, 80 μL , 80 μmol) and 4-iodo-*n*-butylbenzene (14 μL , 80 μmol) added, and the mixture heated to 50 °C under N₂. After 2.5 h the mixture was concentrated and passed through a plug of silica gel, eluting with CH₂Cl₂ : 1% pyridine. The crude mixture was concentrated and passed through a size-exclusion column (eluting with toluene) to remove excess 4-iodo-*n*-butylbenzene. Zinc 5,15-bis-(3,5-bis-octyloxy-phenyl)-10-(4-nitrophenyl)ethynyl-20-(4-*n*-butyl-phenyl)ethynyl-porphyrin dimer was recovered as a green solid by recrystallization by layered addition of pentane to CH₂Cl₂ (28 mg, 72%).

δ_{H} (300 MHz; CDCl₃ : 1% d₅-pyridine) 9.80 (2 H, d, *J* 4.7, β -H), 9.78 (2 H, d, *J* 4.5, β -H), 9.63 (2 H, d, *J* 4.5, β -H), 9.58 (2 H, d, *J* 4.7, β -H), 8.98 (4 H, dd, *J* 4.6 and 1.5, β -H), 8.95 (2 H, d, *J* 4.7, β -H), 8.90 (2 H, d, *J* 4.7, β -H), 8.35 (2 H, d, *J* 8.9, nitro-phenyl-H), 8.05 (2 H, d, *J* 8.9, nitro-phenyl-H), 7.87 (2 H, d, *J* 8.2, *n*Bu-phenyl-H), 7.28–7.33 (10 H, m, Ar-*o*-H, *n*Bu-phenyl-H), 6.84 (4 H, dd, *J* 2.6 and 0.9, Ar-*p*-H), 4.10 (16 H, t, *J* 6.7, -O-CH₂-), 2.68 (2 H, t, *J* 7.7, Ar-CH₂-), 1.75–1.88 (20 H, m), 1.58–1.70 (2 H, m), 1.37–1.53 (15 H, m), 1.17–1.37 (72 H, m), 0.93 (3 H, t, *J* 7.3, Ar-(CH₂)₃-CH₃), 0.74–0.84 (26 H, m). *m/z* (MALDI TOF+) Calcd. for C₁₅₂H₁₈₁N₉O₁₀Zn₂ 2425.26, found 2426.42. λ_{max} (CHCl₃) / nm 466 (log ϵ 5.54), 498 (5.19), 590 (4.27), 648 (4.38), 690 (4.95), 748 (4.98).

■ **Zinc 5,15-bis-(3,5-bis-octyloxy-phenyl)-10-(*N,N*-di-*n*-butyl-4-aniline)ethynyl-20-trihexylsilanylethynyl-porphyrin dimer D-P2_{C8}(Zn)-THS**

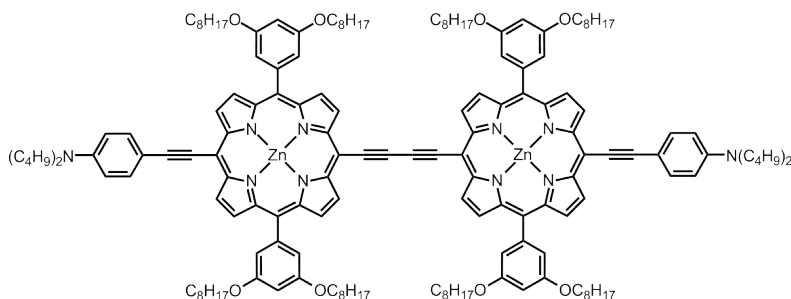


A crude mixture of zinc 5,15-bis-(3,5-bis-octyloxy-phenyl)-10-ethynyl-20-trihexylsilanylethynyl-porphyrin dimer and zinc 5,15-bis-(3,5-bis-octyloxy-phenyl)-10,20-bis-ethynyl-porphyrin dimer (72 mg, 29 μmol max. singly-deprotected porphyrin), tris-(dibenzylideneacetone)-di-palladium(0) (1.4 mg, 1.5 μmol), PPh₃ (1.6 mg, 6.0 μmol) and CuI (0.3 mg, 2 μmol) were dried under vacuum in a pre-dried Schlenk tube before toluene (2.4 mL) and DIPA (2.4 mL) were added. The mixture was deoxygenated by three cycles of freezing under vacuum and saturating with nitrogen, then *N,N*-dibutyl-4-iodo-1-aniline (96 mg, 290 μmol) added and heated to 50 °C. After 2 h, the mixture was concentrated and purified on silica gel, eluting with 15:1:1 petroleum ether : EtOAc : pyridine. The desired fractions were concentrated and passed through a size-exclusion column (eluting with toluene) to remove unreacted aniline. Zinc 5,15-bis-(3,5-bis-octyloxy-phenyl)-10-(*N,N*-di-*n*-butyl-4-aniline)ethynyl-20-trihexylsilanylethynyl-porphyrin dimer was recovered by recrystallization by layered addition of pentane to CH₂Cl₂ (20 mg, 26%), but a clean sample of the symmetrical product was not obtainable.

δ_{H} (400 MHz; CDCl₃ : 1% d₅-pyridine) 9.82 (2 H, d, *J* 4.5, β -H), 9.78 (2 H, d, *J* 4.5, β -H), 9.65 (2 H, d, *J* 4.5, β -H), 9.60 (2 H, d, *J* 4.5, β -H), 9.01 (2 H, d, *J* 4.5, β -H), 8.99 (2 H, d, *J* 4.5, β -H), 8.92 (2 H, d, *J* 4.5, β -H), 8.89 (2 H, d, *J*

4.5, β -H), 7.82 (2 H, d, J 8.8, **aniline-H**), 7.32 (8 H, d, J 1.5, **Ar-*o*-H**), 6.85–6.87 (4 H, m, **Ar-*p*-H**), 6.75 (2 H, d, J 9.1, **aniline-H**), 4.10 (16 H, t, J 6.6, **-O-CH₂-**), 3.34 (4 H, t, J 7.6, **-N-(CH₂)₂-**), 1.79–1.88 (16 H, m), 1.69–1.78 (7 H, m), 1.56–1.67 (5 H, m), 1.41–1.55 (26 H, m), 1.18–1.40 (90 H, m), 0.93–1.02 (13 H, m), 0.83–0.89 (14 H, m), 0.78–0.83 (26 H, m). m/z (MALDI TOF+) Calcd. for C₁₆₈H₂₂₅N₉O₈SiZn₂ 2658.59, found 2657.97

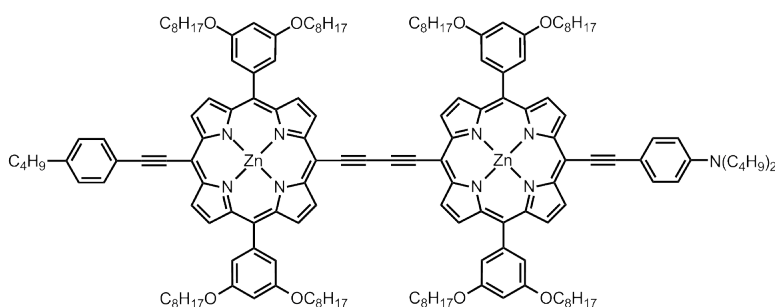
■ **Zinc 5,15-bis-(3,5-bis-octyloxy-phenyl)-10,20-bis-(*N,N*-di-*n*-butyl-4-aniline)ethynyl-porphyrin dimer D-P₂C₈(Zn)-D**



Zinc 5,15-bis-(3,5-bis-octyloxy-phenyl)-10,20-trihexylsilanylethynyl-porphyrin dimer (15 mg, 5.5 μ mol), tris-(dibenzylideneacetone)-di-palladium(0) (0.25 mg, 0.28 μ mol), PPh₃ (0.29 mg, 1.1 μ mol) and CuI (0.05 mg, 0.3 μ mol) were dried under vacuum in a pre-dried Schlenk tube before toluene (0.5 mL) and DIPA (0.5 mL) were added. The mixture was deoxygenated by three cycles of freezing under vacuum and saturating with nitrogen, then TBAF (1.0 M in THF, 55 μ L, 55 μ mol) and *N,N*-dibutyl-4-iodo-1-aniline (36 mg, 110 μ mol) added, and the mixture heated to 50 °C. After 2.5 h, the mixture was concentrated and passed through a plug of silica gel, eluting with CH₂Cl₂ : 1% pyridine. The crude mixture was concentrated and passed through a size-exclusion column (eluting with toluene) to remove unreacted *N,N*-dibutyl-4-iodo-1-aniline. Zinc 5,15-bis-(3,5-bis-octyloxy-phenyl)-10,20-bis-(*N,N*-di-*n*-butyl-4-aniline)ethynyl-porphyrin dimer was recovered as a green solid by recrystallization by layered addition of pentane to CH₂Cl₂ (9.5 mg, 67%).

δ_{H} (400 MHz; CDCl₃ : 1% d₅-pyridine) 9.78 (4 H, d, J 4.5, β -H), 9.65 (4 H, d, J 4.5, β -H), 8.98 (4 H, d, J 4.5, β -H), 8.89 (4 H, d, J 4.5, β -H), 7.82 (4 H, d, J 8.8, **aniline-H**), 7.32 (8 H, d, J 2.3, **Ar-*o*-H**), 6.86 (4 H, t, J 2.3, **Ar-*p*-H**), 6.75 (4 H, d, J 9.1, **aniline-H**), 4.10 (16 H, t, J 6.6, **-O-CH₂-**), 3.34 (8 H, t, J 6.8, **-N-(CH₂)₂-**), 1.77–1.88 (15 H, m), 1.57–1.67 (8 H, m), 1.41–1.52 (18 H, m), 1.15–1.41 (88 H, m), 0.96 (12 H, t, J 7.3, **-N-(CH₂)₂-CH₃**), 0.81 (26 H, t, J 6.8). m/z (MALDI TOF+) Calcd. for C₁₆₄H₂₀₈N₁₀O₈Zn₂ 2578.49, found 2577.52. λ_{max} (CHCl₃) / nm 468 (log ϵ 5.39), 496 (5.24), 592 (4.24), 658 (4.47), 704 (4.92), 752 (4.92).

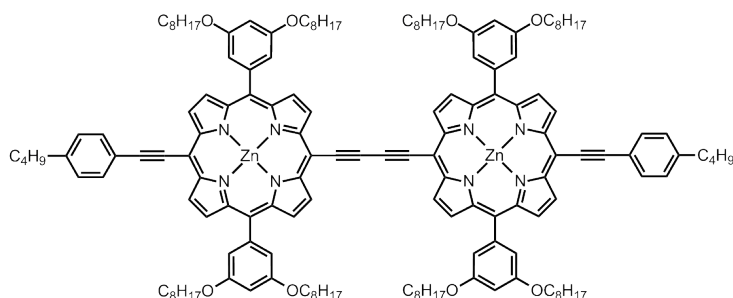
■ **Zinc 5,15-bis-(3,5-bis-octyloxy-phenyl)-10-(*N,N*-di-*n*-butyl-4-aniline)ethynyl-20-(4-*n*-butyl-phenyl)ethynyl-porphyrin dimer D-P₂C₈(Zn)-R**



Zinc 5,15-bis-(3,5-bis-octyloxy-phenyl)-10-(*N,N*-di-*n*-butyl-4-aniline)ethynyl-20-trihexylsilanylethynyl-porphyrin dimer (20 mg, 7.5 μ mol), tris-(dibenzylideneacetone)-di-palladium(0) (0.4 mg, 0.4 μ mol), PPh₃ (0.4 mg, 2 μ mol) and CuI (0.1 mg, 0.4 μ mol) were dried under vacuum in a pre-dried Schlenk tube before toluene (0.7 mL) and DIPA (0.7 mL) were added. The mixture was deoxygenated by three cycles of freezing under vacuum and saturating with nitrogen, then TBAF (1.0 M in THF, 37 μ L, 37 μ mol) and 4-iodo-*n*-butylbenzene (7 μ L, 40 μ mol) added, and heated to 50 °C. After 2 h, the mixture was concentrated and passed through a plug of silica gel, eluting with CH₂Cl₂ : 1% pyridine. The crude mixture was concentrated and passed through a size-exclusion column (eluting with toluene) to remove unreacted 4-iodo-*n*-butylbenzene. The title compound was recovered as a green solid by recrystallization by layered addition of pentane to CH₂Cl₂ (11 mg, 58%).

δ_{H} (300 MHz; CDCl_3 : 1% d_5 -pyridine) 9.78 (2 H, d, J 4.5, $\beta\text{-H}$), 9.75 (2 H, d, J 4.5, $\beta\text{-H}$), 9.63 (4 H, t, J 4.5, $\beta\text{-H}$), 8.97 (4 H, dd, J 7.2 and 4.5, $\beta\text{-H}$), 8.90 (2 H, d, J 4.7, $\beta\text{-H}$), 8.86 (2 H, d, J 4.5, $\beta\text{-H}$), 7.86 (2 H, d, J 8.2), 7.78 (2 H, d, J 8.9, **aniline-H**), 7.26–7.32 (10 H, m, **Ar-*o*-H**, ***n*Bu-phenyl-H**), 6.80–6.85 (4 H, m, **Ar-*p*-H**), 6.72 (2 H, d, J 8.9, **aniline-H**), 4.07 (16 H, t, J 6.7, **-O-CH₂-**), 3.31 (4 H, t, J 7.8, **-N-(CH₂)₂-**), 2.66 (2 H, t, J 7.8, **Ar-CH₂-**), 1.74–1.86 (23 H, m), 1.52–1.68 (8 H, m), 1.38–1.50 (23 H, m), 1.10–1.37 (94 H, m), 0.87–0.97 (11 H, m), 0.78 (32 H, t, J 7.2). m/z (MALDI TOF+) Calcd. for $\text{C}_{160}\text{H}_{199}\text{N}_9\text{O}_8\text{Zn}_2$ 2507.41, found 2507.57. λ_{max} (CHCl_3) / nm 464 (log ϵ 5.5), 497 (5.25), 592 (4.26), 647 (4.38), 697 (4.93), 745 (4.96).

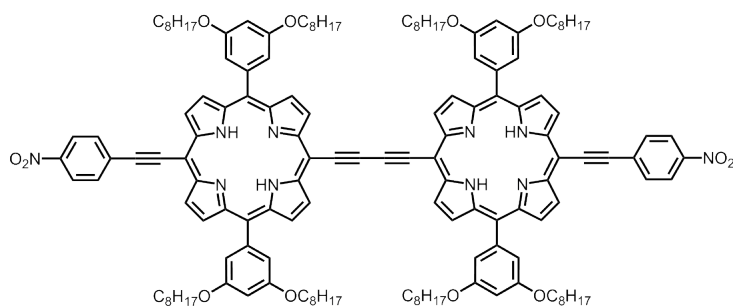
■ **Zinc 5,15-bis-(3,5-bis-octyloxy-phenyl)-10,20-bis-(4-*n*-butyl-phenyl)ethynyl-porphyrin dimer R-P2_{C8}(Zn)-R**



Zinc 5,15-bis-(3,5-bis-octyloxy-phenyl)-10,20-trihexylsilanylethynyl-porphyrin dimer (15 mg, 5.5 μmol), tris-(dibenzylideneacetone)-di-palladium(0) (0.3 mg, 0.3 μmol), PPh_3 (0.3 mg, 1 μmol) and CuI (0.05 mg, 0.3 μmol) were dried under vacuum in a pre-dried Schlenk tube before toluene (0.5 mL) and DIPA (0.5 mL) were added. The mixture was deoxygenated by three cycles of freezing under vacuum and saturating with nitrogen, then TBAF (1.0 M in THF, 55 μL , 55 μmol) and 4-iodo-*n*-butylbenzene (10 μL , 55 μmol) added, and the mixture heated to 50 $^\circ\text{C}$. After 2 h, the mixture was concentrated and passed through a plug of silica gel, eluting with CH_2Cl_2 : 1% pyridine. The crude mixture was concentrated and passed through a size-exclusion column (eluting with toluene) to remove unreacted 4-iodo-*n*-butylbenzene. The desired product was recovered as a green solid by recrystallization by layered addition of pentane to CH_2Cl_2 (10 mg, 75%).

δ_{H} (300 MHz; CDCl_3 : 1% d_5 -pyridine) 9.79 (4 H, d, J 4.7, $\beta\text{-H}$), 9.64 (4 H, d, J 4.5, $\beta\text{-H}$), 8.98 (4 H, d, J 4.5, $\beta\text{-H}$), 8.90 (4 H, d, J 4.5, $\beta\text{-H}$), 7.86 (4 H, d, J 8.2, ***n*Bu-phenyl-H**), 7.30 (8 H, d, J 2.2, **Ar-*o*-H**), 7.30 (4 H, d, J 7.7, ***n*Bu-phenyl-H**), 6.83 (4 H, t, J 2.3, **Ar-*p*-H**), 4.08 (16 H, t, J 6.6, **-O-CH₂-**), 2.66 (4 H, t, J 7.7, **Ar-CH₂-**), 1.74–1.86 (18 H, m), 1.57–1.69 (5 H, m), 1.36–1.52 (22 H, m), 1.10–1.35 (81 H, m), 0.91 (6 H, t, J 7.3, **Ar-(CH₂)₃-CH₃**), 0.71–0.84 (30 H, m). m/z (MALDI TOF+) Calcd. for $\text{C}_{156}\text{H}_{190}\text{N}_8\text{O}_8\text{Zn}_2$ 2436.34, found 2436.34. λ_{max} (CHCl_3) / nm 465 (log ϵ 5.66), 499 (5.21), 590 (4.31), 646 (4.37), 681 (4.96), 744 (4.99).

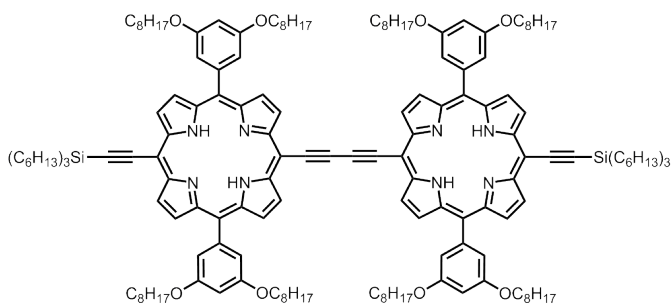
■ **5,15-Bis-(3,5-bis-octyloxy-phenyl)-10,20-bis-(4-nitrophenyl)ethynyl-porphyrin dimer A-P2_{C8}(2H)-A**



Porphyrin dimer **A-P2_{C8}(Zn)-A** (5 mg, 2.1 μmol) was dissolved in CHCl_3 (1.6 mL), and trifluoroacetic acid (32 μL , 420 μmol) was added dropwise with stirring. The reaction was judged complete by UV-vis after 10 min and quenched after 17 min by addition of pyridine (135 μL). The solution was immediately poured onto a short plug of silica, the product eluted with CHCl_3 , and the solvent concentrated. The compound was precipitated from $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$, giving 4.5 mg of a dark green powder (94%).

δ_{H} (400 MHz; CDCl_3 : 1% d -TFA) 9.52 (4 H, d, J 4.9, $\beta\text{-H}$), 9.33 (4 H, d, J 4.7, $\beta\text{-H}$), 8.86 (4 H, d, J 4.9, $\beta\text{-H}$), 8.76 (4 H, d, J 4.6, $\beta\text{-H}$), 8.47 (4 H, d, J 8.7, **nitro-phenyl-H**), 8.19 (4 H, d, J 8.5, **nitro-phenyl-H**), 7.57 (8 H, s, **Ar-*o*-H**), 7.03 (4 H, s, **Ar-*p*-H**), 4.20 (16 H, t, J 6.6, **-O-CH₂-**), 1.82–1.95 (16 H, m), 1.46–1.58 (16 H, m), 1.15–1.43 (94 H, m), 0.81 (32 H, t, J 6.7), free-base NH not seen due to exchange. m/z (MALDI TOF+) Calcd. for $\text{C}_{148}\text{H}_{176}\text{N}_{10}\text{O}_{12}$ 2286.35, found 2286.58. λ_{max} (CHCl_3) / nm 458 (log ϵ 5.43), 484 (5.04), 622 (4.80), 708 (4.75), 738 (4.87).

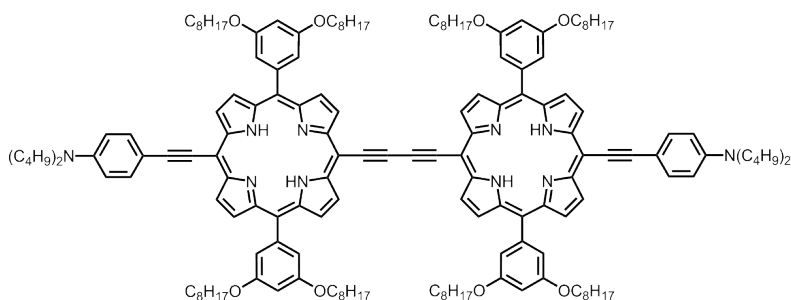
■ **5,15-Bis-(3,5-bis-octyloxy-phenyl)-10,20-trihexylsilylethynyl-porphyrin dimer THS-P2_{C8}(2H)-THS**



Porphyrin dimer **THS-P2_{C8}(Zn)-THS** (60 mg, 22 μmol) was dissolved in CHCl₃ (16 mL), and trifluoroacetic acid (340 μL, 4.4 mmol) was added dropwise with stirring. The reaction was quenched after 3 min by addition of pyridine (1.5 mL). The solution was immediately poured onto a short plug of silica, the product eluted with \ CHCl₃, and the solvent concentrated to yield the product (55 mg, 95%).

δ_{H} (400 MHz; CDCl₃) 9.78 (4 H, d, *J* 4.7, **β -H**), 9.53 (4 H, d, *J* 4.7, **β -H**), 8.98 (4 H, d, *J* 4.7, **β -H**), 8.87 (4 H, d, *J* 4.7, **β -H**), 7.31 (8 H, d, *J* 2.3, **Ar-*o*-H**), 6.85 (4 H, t, *J* 2.3, **Ar-*p*-H**), 4.09 (16 H, t, *J* 6.6, **-O-CH₂-**), 1.82 (16 H, quin, *J* 7.2), 1.64–1.74 (12 H, m), 1.40–1.54 (34 H, m), 1.13–1.39 (100 H, m), 0.92–1.01 (12 H, m), 0.84 (18 H, t, *J* 7.1), 0.79 (32 H, t, *J* 7.0), –2.00 (4 H, s, **N-H**). δ_{C} (126 MHz; CDCl₃) 157.5, 141.9, 131.0 (broad), 129.5 (broad), 121.2, 113.3, 106.7, 100.9, 100.8, 100.3, 98.1, 86.4, 81.8, 67.4, 32.3, 30.8, 30.6, 28.4, 28.2, 25.1, 23.3, 21.7, 21.6, 13.2, 13.1, 12.7 (peaks broadened due to exchange). *m/z* (MALDI TOF+) Calcd. for C₁₇₂H₂₄₆N₈O₈Si₂ 2609.87, found 2609.44.

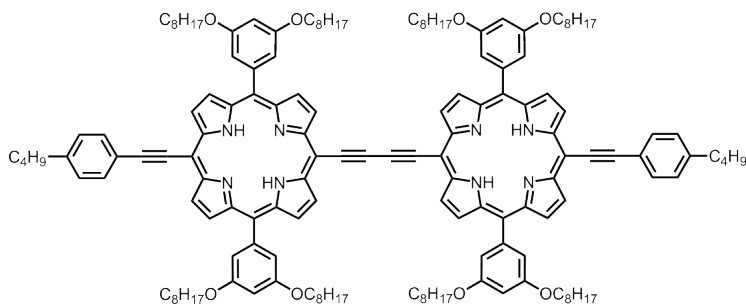
■ **5,15-Bis-(3,5-bis-octyloxy-phenyl)-10,20-bis-(*N,N*-di-*n*-butyl-4-aniline)ethynyl-porphyrin dimer D-P2_{C8}(2H)-D**



Porphyrin dimer **THS-P2_{C8}(2H)-THS** (10 mg, 3.8 μmol) was dissolved in THF (1 mL), and TBAF (1.0 M in THF, 38 μL, μmol) was added. The reaction was stirred and monitored by TLC (25 : 1 petrol : ethyl acetate, *R_f* change from 0.6 to 0.5). Upon completion (25 minutes), acetic acid was added (20 μL) and the mixture passed through a short plug of silica, eluting with CHCl₃. The solution was concentrated in a 2-neck flask and MALDI+TOF confirmed the identity of the intermediate as the doubly-deprotected bis free alkyne. The intermediate was dried under vacuum, and *N,N*-dibutyl-4-iodo-1-aniline (13 mg, 38 μmol), Pd₂(dba)₃ (0.5 mg, 0.6 μmol) and AsPh₃ (0.7 mg, 2 μmol) were added under N₂. THF (0.5 mL) and DIPA (0.5 mL) were added, the mixture was deoxygenated by three cycles of freezing under vacuum and saturating with nitrogen, then heated to 50 °C. After 2 h, the reaction was passed through a plug of silica, eluting with CHCl₃. The crude residue was purified by column chromatography on silica, eluting the excess aniline with petrol and the product with 25 : 1 petrol : ethyl acetate. After precipitating the product from CH₂Cl₂/MeOH, 4.7 mg (51%) of clean product was obtained.

δ_{H} (400 MHz; CDCl₃) 9.72 (4 H, d, *J* 4.7, **β -H**), 9.58 (4 H, d, *J* 4.7, **β -H**), 8.94 (4 H, d, *J* 4.7, **β -H**), 8.83 (4 H, d, *J* 4.4, **β -H**), 7.80 (4 H, d, *J* 8.9, **aniline-H**), 7.31 (8 H, d, *J* 2.0, **Ar-*o*-H**), 6.85 (4 H, t, *J* 2.3, **Ar-*p*-H**), 6.74 (4 H, d, *J* 9.2, **aniline-H**), 4.09 (16 H, t, *J* 6.6, **-O-CH₂-**), 3.34 (8 H, t, *J* 7.9, **N-CH₂-**), 1.78–1.87 (16 H, m), 1.57–1.66 (8 H, m), 1.09–1.47 (96 H, m), 0.96 (12 H, t, *J* 7.3), 0.79 (24 H, t, *J* 6.9), –1.69 (4 H, s, **N-H**). *m/z* (MALDI TOF+) Calcd. for C₁₆₄H₂₁₂N₁₀O₈ 2450.65, found 2450.19. λ_{max} (CHCl₃) / nm 460 (log ϵ 5.35), 646 (4.91), 747 (5.02).

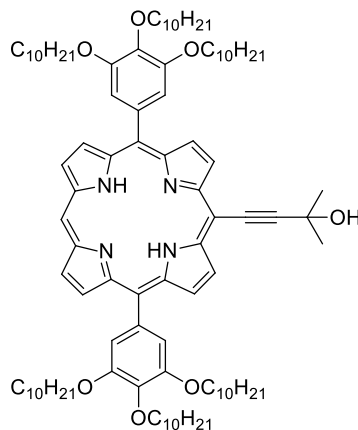
■ **5,15-Bis-(3,5-bis-octyloxy-phenyl)-10,20-bis-(4-*n*-butyl-phenyl)ethynyl-porphyrin dimer R-P_{2C₈(2H)-R}**



Porphyrin dimer **THS-P_{2C₈(2H)-THS}** (20 mg, 7.7 μmol) was dissolved in THF (2 mL), and TBAF (1.0 M in THF, 77 μL , 77 μmol) was added. The reaction was stirred and monitored by TLC. Upon completion (25 minutes), acetic acid was added (40 μL) and the mixture passed through a short plug of silica, eluting with CHCl_3 . The solution was concentrated in a 2-neck flask and the intermediate was then dried under vacuum, and 4-iodo-*n*-butylbenzene (14 μL , 77 μmol), $\text{Pd}_2(\text{dba})_3$ (1.0 mg, 1.1 μmol) and AsPh_3 (1.4 mg, 4.6 μmol) were added under N_2 . THF (1.0 mL) and DIPA (1.0 mL) were added, the mixture was deoxygenated by three cycles of freezing under vacuum and saturating with nitrogen, then heated to 50 $^\circ\text{C}$. After 90 min, the reaction was passed through a plug of silica, eluting with CHCl_3 . The crude residue was purified by size exclusion chromatography, eluting with CHCl_3 : 1% pyridine. After precipitating the product from $\text{CH}_2\text{Cl}_2/\text{MeOH}$, 9.2 mg (52%) of a green powder was obtained.

δ_{H} (200 MHz; CDCl_3) 9.84 (4 H, d, J 4.6, $\beta\text{-H}$), 9.69 (4 H, d, J 4.7, $\beta\text{-H}$), 9.06 (4 H, d, J 4.8, $\beta\text{-H}$), 8.97 (4 H, d, J 4.8, $\beta\text{-H}$), 7.96 (4 H, d, J 8.1, *n*Bu-phenyl-H), 7.37–7.46 (12 H, m, Ar-*o*-H, *n*Bu-phenyl-H), 6.94 (4 H, t, J 2.3, Ar-*p*-H), 4.18 (16 H, t, J 6.6, -O-CH₂-), 2.78 (4 H, t, J 7.7, Ph-CH₂-), 1.82–2.00 (16 H, m), 1.63–1.82 (8 H, m), 1.19–1.62 (100 H, m), 1.02 (6 H, t, J 7.2), 0.88 (24 H, t, J 6.3), -1.80 (4 H, br. s, N-H). Calcd. for $\text{C}_{156}\text{H}_{194}\text{N}_8\text{O}_8$ 2308.51, found 2308.14. λ_{max} (CHCl_3) / nm 456 (log ϵ 5.46), 481 (4.97), 623 (4.73), 706 (4.67), 736 (4.80).

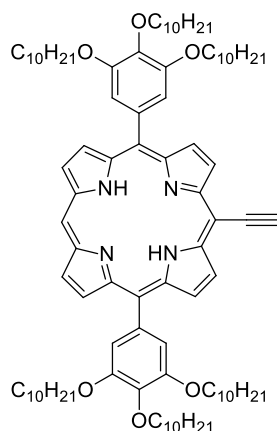
■ **5,15-Bis[3,4,5-tris(decyloxy)phenyl]-10-(3-hydroxy-3-methyl-1-butynyl)porphyrin 7**



Porphyrin **6** (165 mg, 0.11 mmol) was placed in a dried Schlenk tube, purged with argon, and dissolved in anhydrous toluene (15.8 mL). Then, anhydrous THF (5 mL), and Et_3N (3.6 mL) were added. The vessel was evacuated and backfilled with argon (this process was repeated 3 times). Subsequently, 2-methyl-3-butyn-2-ol (56 μl , 0.58 mmol) was added, followed by AsPh_3 (47 mg, 0.15 mmol), and $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (49 mg, 0.047 mmol). The reaction mixture was stirred at RT for 19 h. Afterwards, the reaction mixture was filtered through a short pad of Celite and evaporated to dryness. The crude product was purified by column chromatography (silica, hexanes/ EtOAc 19:1) and SEC (toluene) to obtain pure porphyrin **7** (105 mg, 64%) as an claret-colored oil. R_f = 0.29 (silica gel, hexanes/ CH_2Cl_2 2:3); UV/vis (CH_2Cl_2) λ (ϵ) = 426 (274 000), 520 (13 400), 558 (9 000), 595 (4 700), 653 nm (3 800); ^1H NMR (500 MHz, CDCl_3): δ -2.70 (br s, 2H, NH); 0.81–0.88 (m, 12H, CH₃), 0.89–0.96 (m, 6H, CH₃), 1.17–1.56 (m, 80H, CH₂), 1.68 (m, 4H, OCH₂CH₂CH₂), 1.90 (m, 8H, OCH₂CH₂), 1.96–2.04 (m, 4H, OCH₂CH₂), 2.09 (s, 6H, CH₃), 4.12 (t, J = 6.5 Hz, 8H, OCH₂), 4.32 (t, J = 6.6 Hz, 4H, OCH₂), 7.43 (s, 4H, ArH), 9.05 (2 overlapping d, J = 4.7 and 4.5 Hz, 4H, $\beta\text{-H}$), 9.27 (d, J = 4.6 Hz, 2H, $\beta\text{-H}$), 9.68 (d, J = 4.7 Hz, 2H, $\beta\text{-H}$), 10.15 (s, 1H, *meso*-H), OH proton was not observed; ^{13}C NMR (125 MHz, CDCl_3): δ 14.07, 14.10, 14.2, 22.6, 22.7, 22.8, 26.2, 26.3, 28.9, 29.2, 29.32, 29.35, 29.45, 29.48, 29.50, 29.52, 29.56, 29.63, 29.64, 29.68, 29.76, 29.78, 29.9, 30.2, 30.6, 31.4, 31.87, 31.91, 32.0, 33.8, 66.6, 69.4, 73.8, 84.7,

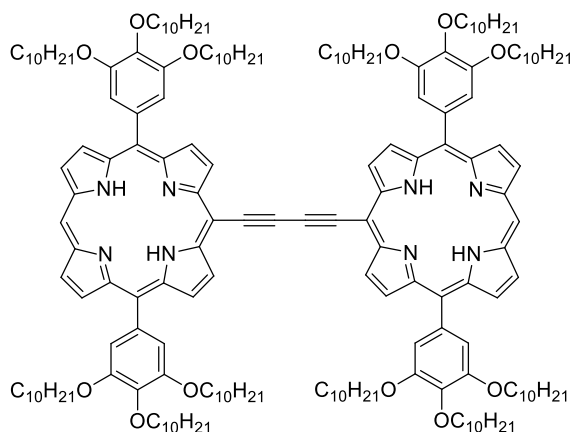
98.9, 100.6, 106.4, 114.0, 114.4, 120.5, 130.4, 131.4, 131.6, 136.2, 138.1, 139.3, 151.4. HR MS (FD) calcd for $C_{97}H_{148}N_4O_7$ 1481.1348, found 1481.1284, isotope profiles match. Elemental analysis calcd (%) for $C_{97}H_{148}N_4O_7$: C, 78.60; H, 10.06; N, 3.78, found: C, 78.72; H, 9.90; N, 3.51.

■ **5,15-Bis[3,4,5-tris(decyloxy)phenyl]-10-ethynylporphyrin 8**



Porphyrin **7** (85 mg, 0.057 mmol) was placed in a round-bottomed flask purged with argon. Then, toluene (9.5 mL) was added, followed by ground NaOH (240 mg, 6 mmol). The reaction mixture was refluxed under an argon atmosphere for 20.5 h. After cooling the solvent was evaporated and the crude product was chromatographed (silica, hexanes/ CH_2Cl_2 1:1) to obtain porphyrin **8** (65 mg, 79%). R_f = 0.51 (silica, hexanes/ CH_2Cl_2 1:1); UV/vis (CH_2Cl_2) λ (ϵ) = 421 (102 000), 513 (12 000), 586 (6 000), 646 nm (4 100); 1H NMR (500 MHz, $CDCl_3$): δ -2.72 (br s, 2H, NH), 0.81–0.87 (m, 12H, CH_3), 0.90–0.95 (m, 6H, CH_3), 1.24–1.54 (m, 80H, CH_2), 1.68 (m, 4H, $OCH_2CH_2CH_2$), 1.89 (m, 8H, OCH_2CH_2), 1.96–2.02 (m, 4H, OCH_2CH_2), 4.12 (m, 8H, OCH_2), 4.20 (s, 1H, CH_{alkyne}), 4.32 (m, 4H, OCH_2), 7.43 (s, 4H, ArH), 9.05 (d, J = 4.6 Hz, 2H, β -H); 9.07 (d, J = 4.9 Hz, 2H, β -H), 9.27 (d, J = 4.6 Hz, 2H, β -H), 9.75 (d, J = 4.9 Hz, 2H, β -H), 10.17 (s, 1H, *meso*-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.07, 14.10, 14.2, 22.6, 22.7, 22.8, 26.2, 26.3, 28.9, 29.2, 29.3, 29.35, 29.45, 29.48, 29.50, 29.52, 29.56, 29.63, 29.64, 29.68, 29.76, 29.78, 29.9, 30.2, 30.6, 31.4, 31.87, 31.91, 32.0, 33.8, 66.6, 69.4, 73.8, 84.7, 98.9, 100.6, 106.4, 114.0, 114.4, 130.4, 131.4, 131.6, 136.2, 138.1, 139.3, 151.4. LR MS (FD) calcd for $C_{94}H_{142}N_4O_6$ 1423.1, found 1425.1, isotope profiles match.

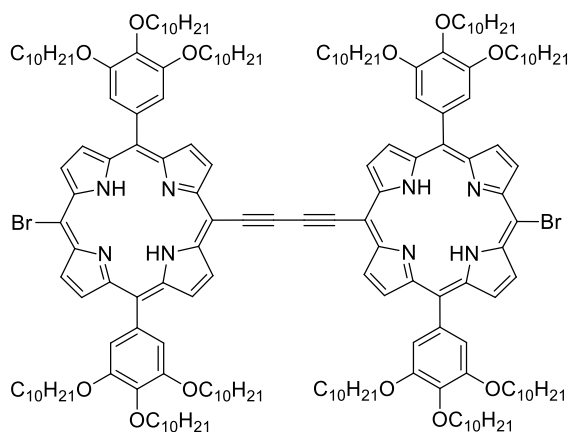
■ **Bis[5,5'-10,20-bis[3,4,5-tris(decyloxy)phenyl]porphyrin]butadiyne 9**



A dried Schlenk tube, purged with argon, was charged with porphyrin **8** (350 mg, 0.25 mmol). Then, porphyrin was dissolved in anhydrous toluene (11 mL), and anhydrous THF (3.6 mL) was added, followed by Et_3N (3 mL). The vessel was evacuated and backfilled with argon (this process was repeated 3 times). Next, $AsPh_3$ (109 mg, 0.36 mmol), and $Pd_2(dba)_3 \cdot CHCl_3$ (73 mg, 0.071 mmol) were added. The reaction mixture was stirred at RT for 26 h. Afterwards, the reaction mixture was filtered through a pad of Celite and evaporated to dryness. The crude product was chromatographed (silica, hexanes/ CH_2Cl_2 4:1 to 3:2) to obtain pure green-colored product **9** (273 mg, 78%). R_f = 0.36 (silica, CH_2Cl_2 /hexanes 1:1); UV/vis (CH_2Cl_2) λ (ϵ) = 443 (275 000), 472 (195 000), 695 (49 600), 603 (46 700), 307

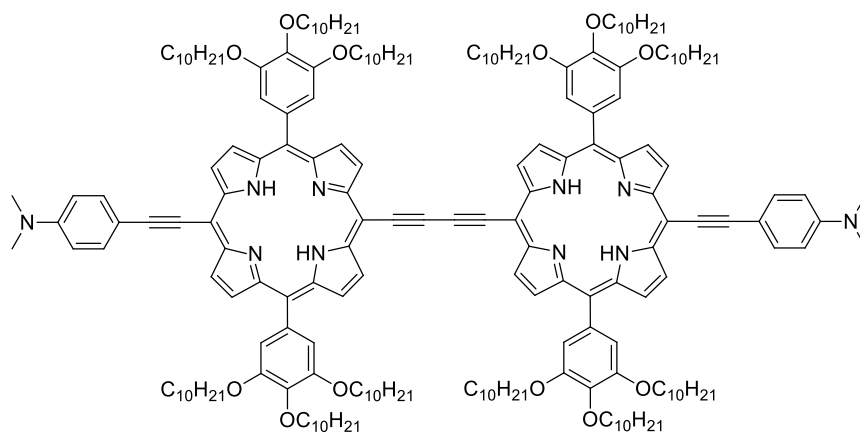
(30 900), 519 nm (30 400); ^1H NMR (500 MHz, CDCl_3): δ -2.35 (br s, 4H, NH), 0.82 (m, 24H, CH_3), 0.91 (m, 12H, CH_3), 1.22–1.44 (m, 136H, CH_2), 1.48–1.53 (m, 24H, CH_2), 1.69 (m, 8H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.91 (m, 16H, OCH_2CH_2), 2.00 (m, 8H, OCH_2CH_2), 4.16 (m, 16H, OCH_2), 4.33 (m, 8H, OCH_2), 7.49 (s, 8H, ArH), 9.06 (d, $J = 4.7$ Hz, 4H, β -H); 9.18 (d, $J = 4.7$ Hz, 4H, β -H), 9.29 (d, $J = 4.4$ Hz, 4H, β -H), 10.00 (d, $J = 4.7$ Hz, 4H, β -H), 10.19 (s, 2H, *meso*-H); ^{13}C NMR (125 MHz, CDCl_3): δ 1.02, 1.07, 1.09, 1.11, 1.13, 14.02, 14.05, 14.13, 22.6, 22.7, 26.2, 26.3, 29.3, 29.46, 29.47, 29.53, 29.55, 29.62, 29.68, 29.76, 29.78, 29.87, 30.6, 30.9, 31.9, 32.0; 69.4, 73.8, 82.4, 87.4, 98.1, 107.3, 114.4, 121.2, 130.5, 131.6, 132.2, 136.1, 138.2, 151.5. LR MS (FD) calcd for $\text{C}_{188}\text{H}_{282}\text{N}_8\text{O}_{12}$ 2844.2, found 2944.2, isotope profiles match. Elemental analysis calcd (%) $\text{C}_{188}\text{H}_{282}\text{N}_8\text{O}_{12}$: C, 79.33; H, 9.99; N, 3.94, found: C, 79.43; H, 10.17; N, 4.03.

■ **Bis[5,5'-15-bromo-10,20-bis[3,4,5-tris(decyloxy)phenyl]porphyrin]butadiyne **10****



To the solution of porphyrin **9** (237 mg, 0.083 mmol) in CHCl_3 (7.3 mL) NBS (100 mg, 0.56 mmol) was added and the reaction was stirred at RT for 3 h. Then, the second portion of NBS (100 mg, 0.56 mmol) was added and after 19 h the third portion of NBS (206 mg, 1.16 mmol) was added. After 5 h the reaction was quenched by acetone (10 mL). The crude product was chromatographed twice (silica, hexanes/ CH_2Cl_2 7:3 to 3:2) to obtain pure product **10** (58 mg, 23%). $R_f = 0.51$ (silica gel, CH_2Cl_2 /hexanes 1:1); UV/vis (CH_2Cl_2) λ (ϵ) = 446 (168 000), 477 (94 100), 714 (34 900), 614 (27 800), 527 nm (15 000); ^1H NMR (500 MHz, CDCl_3): δ -2.10 (br s, 4H, NH), 0.83 (t, $J = 7.0$ Hz, 24H, CH_3), 0.88–0.94 (m, 12H, CH_3), 1.17–1.59 (m, 160H, CH_2), 1.69 (m, 8H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.91 (m, 16H, OCH_2CH_2), 2.00 (m, 8H, OCH_2CH_2), 4.14 (t, $J = 6.5$ Hz, 16H, OCH_2), 4.33 (t, $J = 6.6$ Hz, 8H, OCH_2), 7.43 (s, 8H, ArH), 8.93 (d, $J = 4.5$ Hz, 4H, β -H), 9.06 (d, $J = 4.3$ Hz, 4H, β -H), 9.61 (d, $J = 4.7$ Hz, 4H, β -H), 9.85 (d, $J = 4.6$ Hz, 4H, β -H); ^{13}C NMR (125 MHz, CDCl_3): δ 14.06, 14.11, 14.14, 22.63, 22.68, 22.74, 26.2, 26.3, 29.3, 29.45, 29.47, 29.51, 29.56, 29.62, 29.69, 29.75, 29.78, 29.9, 30.2, 30.6, 31.4, 31.87, 31.91, 32.0, 69.4, 73.8, 82.7, 87.1, 98.4, 105.9, 114.4, 122.4, 136.1, 138.3, 151.4. LR MS (FD) calcd for $\text{C}_{188}\text{H}_{280}\text{Br}_2\text{N}_8\text{O}_{12}$ 3000.0, found 3001.3.

■ **Bis[5,5'-10,20-bis[3,4,5-tris(decyloxy)phenyl]-15-[4-(*N,N*-dimethylamino)phenyl]porphyrin]butadiyne **D-P2**_{C10}(2H)-**D****

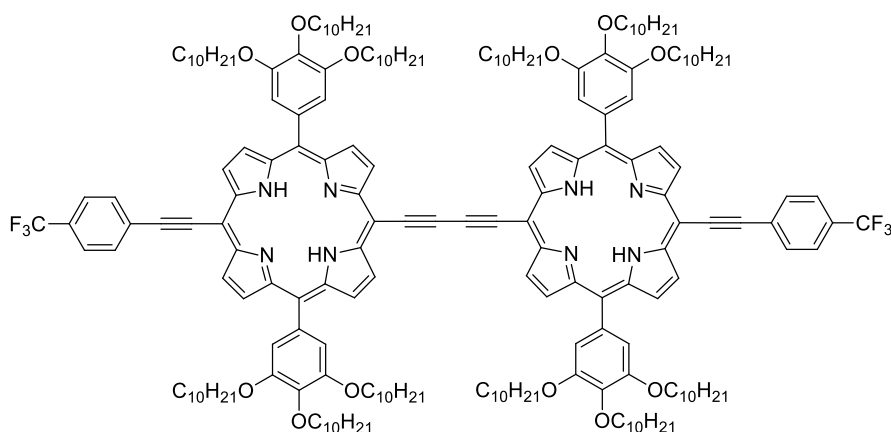


A dried Schlenk tube, purged with argon, was charged with dimer **10** (25 mg, 8.3 μmol) and alkyne **11** (35 mg, 0.23 mmol). The substrates were dissolved in anhydrous toluene (1.2 mL), and anhydrous THF (0.5 mL). Then, Et_3N (0.46

mL, 3.3 mmol) was added. The vessel was evacuated and backfilled with argon (this process was repeated 3 times). To the oxygen-free mixture, AsPh₃ (32 mg, 0.10 mmol), and Pd₂(dba)₃·CHCl₃ (18 mg, 0.017 mmol) were added. The reaction mixture was stirred at RT for 20.5 h. After the given time, the temperature was raised to 50 °C and the mixture was stirred for the next 1.5 h. Then, the reaction mixture was filtered through a short pad of Celite, and evaporated. The crude product was chromatographed (silica, hexanes/CH₂Cl₂ 3:2 to 1:1). The consecutive chromatography (silica, hexanes/CH₂Cl₂ 7:3 to 1:1) afforded pure green-colored product **D-P-P-D** (7 mg, 27%). *R_f* = 0.67 (silica, hexanes/CH₂Cl₂ 2:3); UV/vis (CCl₄) λ (ε) = 463 (252 000), 752 (79 500), 636 (75 000), 720 (70 500), 353 nm (36 300); ¹H NMR (500 MHz, CDCl₃): δ -1.60 (br s, 4H, NH), 0.79–0.85 (m, 24H, CH₃), 0.89–0.94 (m, 12H, CH₃), 1.17–1.59 (m, 160H, CH₂), 1.69 (m, 8H, OCH₂CH₂CH₂), 1.91 (m, 16H, OCH₂CH₂), 2.00 (m, 8H, OCH₂CH₂), 3.13 (s, 12H, NCH₃), 4.15 (t, *J* = 6.5 Hz, 16H, OCH₂), 4.33 (t, *J* = 6.5 Hz, 8H, OCH₂), 6.89 (AA'BB', *J* = 8.9 Hz, 4H, ArH), 7.44 (s, 8H, ArH), 7.91 (AA'BB', *J* = 8.8 Hz, 4H, ArH), 8.90 (d, *J* = 4.6 Hz, 4H, β-H), 9.01 (d, *J* = 4.6 Hz, 4H, β-H), 9.68 (d, *J* = 4.7 Hz, 4H, β-H), 9.80 (d, *J* = 4.7 Hz, 4H, β-H). ¹³C NMR (125 MHz, CDCl₃): δ 14.06, 14.11, 14.14, 22.63, 22.68, 22.74, 26.2, 26.3, 29.3, 29.46, 29.48, 29.52, 29.56, 29.63, 29.69, 29.76, 29.78, 29.9, 30.2, 30.6, 31.4, 31.87, 31.92, 32.0, 34.5, 34.9, 40.3, 69.4, 73.8, 82.7, 87.4, 90.5, 98.4, 100.2, 104.4, 110.3, 112.1, 114.3, 122.4, 124.0, 124.4, 133.0, 136.2, 138.2, 151.4, 150.6. LR MS (FD) calcd for C₂₀₈H₃₀₀N₁₀O₁₂ 3130.3, found 3130.5.

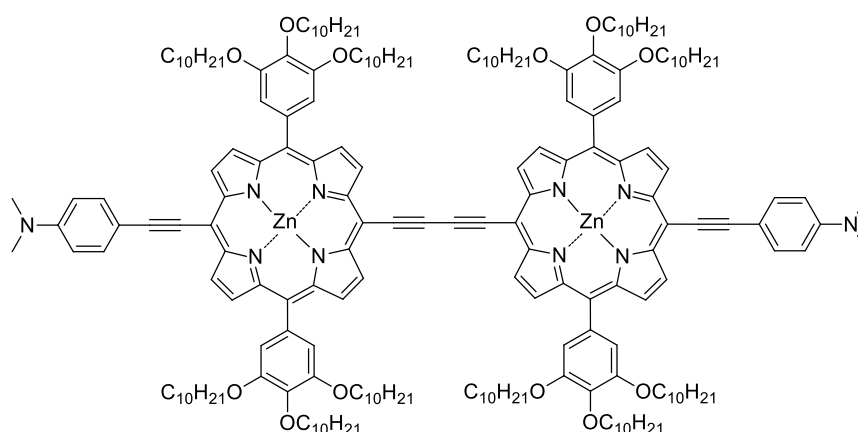
■ Bis[5,5'-10,20-bis[3,4,5-tris(decyloxy)phenyl]-15-[4-(trifluoromethyl)phenyl]-porphyrin]butadiyne

A'-P₂C₁₀(2H)-A'



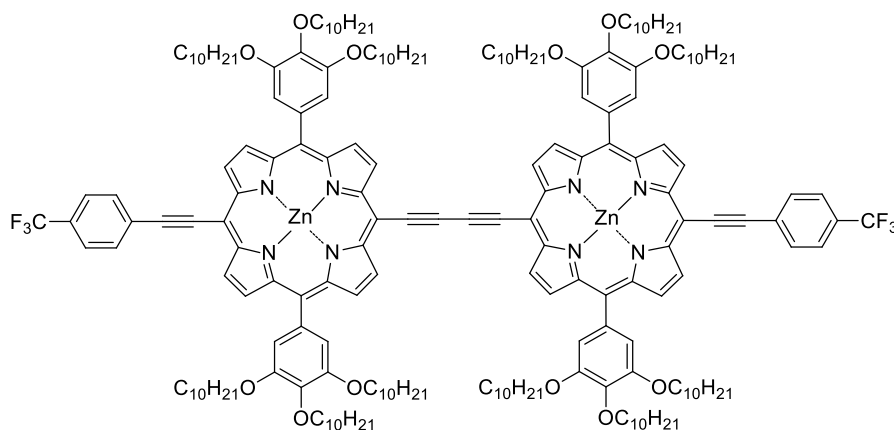
A dried Schlenk tube, purged with argon, was charged with dimer **10** (28 mg, 9.3 μmol) and alkyne **12** (43 μL, 0.26 mmol). The substrates were dissolved in anhydrous toluene (1.4 mL), and anhydrous THF (0.4 mL). Then, Et₃N (0.52 mL, 3.7 mmol) was added. The vessel was evacuated and backfilled with argon (this process was repeated 3 times). To the oxygen-free mixture AsPh₃ (32 mg, 0.10 mmol), and Pd₂(dba)₃·CHCl₃ (18 mg, 0.017 mmol) were added. The reaction mixture was stirred at RT for 22.5 h. After this time the temperature was raised to 50 °C and the stirring was continued for the next 1.5 h. Then, the reaction mixture was filtered through a short pad of Celite, and evaporated. The crude product was chromatographed (silica, hexanes/CH₂Cl₂ 7:3 to 1:1). The impurities were removed by SEC (toluene) and column chromatography (silica, hexanes/0.2% EtOAc to hexanes/0.9% EtOAc) to obtain pure green-colored product **A-P-P-A** (23 mg, 77%). *R_f* = 0.52 (silica, hexanes/CH₂Cl₂ 3:2); UV/vis (CCl₄) λ (ε) = 455 (320 000), 486 (93 300), 744 (73 000), 617 (58 000), 279 nm (37 400); ¹H NMR (500 MHz, CDCl₃): δ -1.81 (br s, 4H, NH), 0.82 (m, 24H, CH₃), 0.91 (m, 12H, CH₃), 1.22–1.53 (m, 160H, CH₂), 1.69 (m, 8H, OCH₂CH₂CH₂), 1.91 (m, 16H, OCH₂CH₂), 2.00 (m, 8H, OCH₂CH₂), 4.16 (d, *J* = 6.5 Hz, 16H, OCH₂), 4.33 (d, *J* = 6.5 Hz, 8H, OCH₂), 7.45 (s, 8H, ArH), 7.85 (AA'BB', *J* = 8.0 Hz, 4H, ArH), 8.14 (AA'BB', *J* = 7.9 Hz, 4H, ArH), 8.99 (d, *J* = 4.8 Hz, 4H, β-H), 9.06 (d, *J* = 4.6 Hz, 4H, β-H), 9.67 (d, *J* = 4.7 Hz, 4H, β-H), 9.86 (d, *J* = 4.6 Hz, 4H, β-H); ¹³C NMR (125 MHz, CDCl₃): δ 14.05, 14.14, 22.6, 22.7, 26.2, 26.3, 29.3, 29.46, 29.48, 29.52, 29.56, 29.63, 29.69, 29.76, 29.78, 29.9, 30.6, 31.9, 32.0, 69.5, 73.8, 83.0, 87.4, 94.2, 96.0, 99.6, 100.8, 114.4, 122.8, 125.1, 125.71, 125.74, 127.5, 130.3, 130.5, 131.9, 135.9, 138.3, 151.5. LR MS (FD) calcd for C₂₀₆H₂₈₈F₆N₈O₁₂ 3180.2, found 3180.6.

■ [Bis[5,5'-10,20-bis[3,4,5-tris(decyloxy)phenyl]-15-[4-(*N,N*-dimethylamino)phenyl]-porphyrin]butadiyne] zinc(II)
D-P2_{C10}(Zn)-D



To the solution of porphyrin **D-P-P-D** (40 mg, 0.013 mmol) in CHCl₃ (2 mL), MeOH (0.18 mL) and Et₃N (0.26 mL), zinc(II) acetate dihydrate (31 mg, 0.14 mmol) was added and the reaction mixture was stirred under reflux for 23 h. Then, the reaction mixture was evaporated to dryness and the residue was chromatographed (silica, hexane/DCM 4:6). A solid was crystallized (acetone) to afford **D-P2_{C10}(Zn)-D** (15 mg, 42%) in form of green-brown crystals: $R_f = 0,7$ (DCM/hexane 8:2). UV/vis (CHCl₃ 99% / pyridine 1%) λ (ϵ) = 470 (210 000), 496 (117 000), 703 (65 000), 758 (66 000). ¹H NMR (500 MHz, CDCl₃ 99% / pyridine 1%): δ 0.79–0.85 (m, 24H, CH₃), 0.93–0.99 (m, 12H, CH₃), 1.14–1.36 (m, 160H, CH₂), 1.53 (m, 8H, OCH₂CH₂CH₂), 1.92 (m, 16H, OCH₂CH₂), 2.23 (m, 8H, OCH₂CH₂), 2.78 (s, 12H, NCH₃), 3.56 (t, $J = 6.5$ Hz, 16H, OCH₂), 3.98 (t, $J = 6.5$ Hz, 8H, OCH₂), 7.04 (AA'BB', $J = 8.5$ Hz, 4H, ArH), 7.44 (s, 8H, ArH), 8.00 (AA'BB', $J = 8.4$ Hz, 4H, ArH), 8.86 (d, $J = 4.6$ Hz, 4H, β -H), 8.96 (d, $J = 4.6$ Hz, 4H, β -H), 9.64 (d, $J = 4.8$ Hz, 4H, β -H), 9.77 (d, $J = 4.8$ Hz, 4H, β -H). LR MS (FD) calcd for C₂₁₂H₃₀₈N₁₀O₁₂Zn₂ 3314.2, found 3314.4.

■ [Bis[5,5'-10,20-bis[3,4,5-tris(decyloxy)phenyl]-15-[4-(trifluoromethyl)phenyl]- porphyrin]butadiyne] zinc(II)
A'-P2_{C10}(Zn)-A'



To the solution of porphyrin **A-P-P-A** (43 mg, 0.013 mmol) in CHCl₃ (2 mL), MeOH (0.18 mL) and Et₃N (0.26 mL), zinc(II) acetate dihydrate (31 mg, 0.14 mmol) was added and the reaction mixture was stirred under reflux for 22 h. Then, the reaction mixture was evaporated to dryness and the residue was chromatographed (silica, hexane/DCM 1:1). A solid was crystallized (acetone) to afford **A'-P2_{C10}(Zn)-A'** (22 mg, 38%) in form of green-brown crystals: $R_f = 0,32$ (DCM/hexane 1:1). UV/vis (CHCl₃ 99% / pyridine 1%) λ (ϵ) = 464 (240 000), 499 (77 000), 686 (46 000), 749 (50 000); ¹H NMR (500 MHz, CDCl₃): δ 0.83 (m, 24H, CH₃), 0.91 (m, 12H, CH₃), 1.24–1.37 (m, 160H, CH₂), 1.70 (m, 8H, OCH₂CH₂CH₂), 1.90 (m, 16H, OCH₂CH₂), 2.00 (m, 8H, OCH₂CH₂), 4.15 (d, $J = 6.4$ Hz, 16H, OCH₂), 4.34 (d, $J = 6.6$ Hz, 8H, OCH₂), 7.42 (s, 8H, ArH), 7.89 (AA'BB', $J = 8.0$ Hz, 4H, ArH), 8.24 (AA'BB', $J = 7.8$ Hz, 4H, ArH), 8.03 (d, $J = 4.5$ Hz, 4H, β -H), 9.07 (d, $J = 4.4$ Hz, 4H, β -H), 9.78 (d, $J = 4.5$ Hz, 4H, β -H), 9.90 (d, $J = 4.5$ Hz, 4H, β -H). LR MS (FD) calcd for C₂₁₂H₃₀₂F₆N₈O₁₂Zn₂ 3330.2, found 3330.2.3.

6. Characterization Data and Spectra

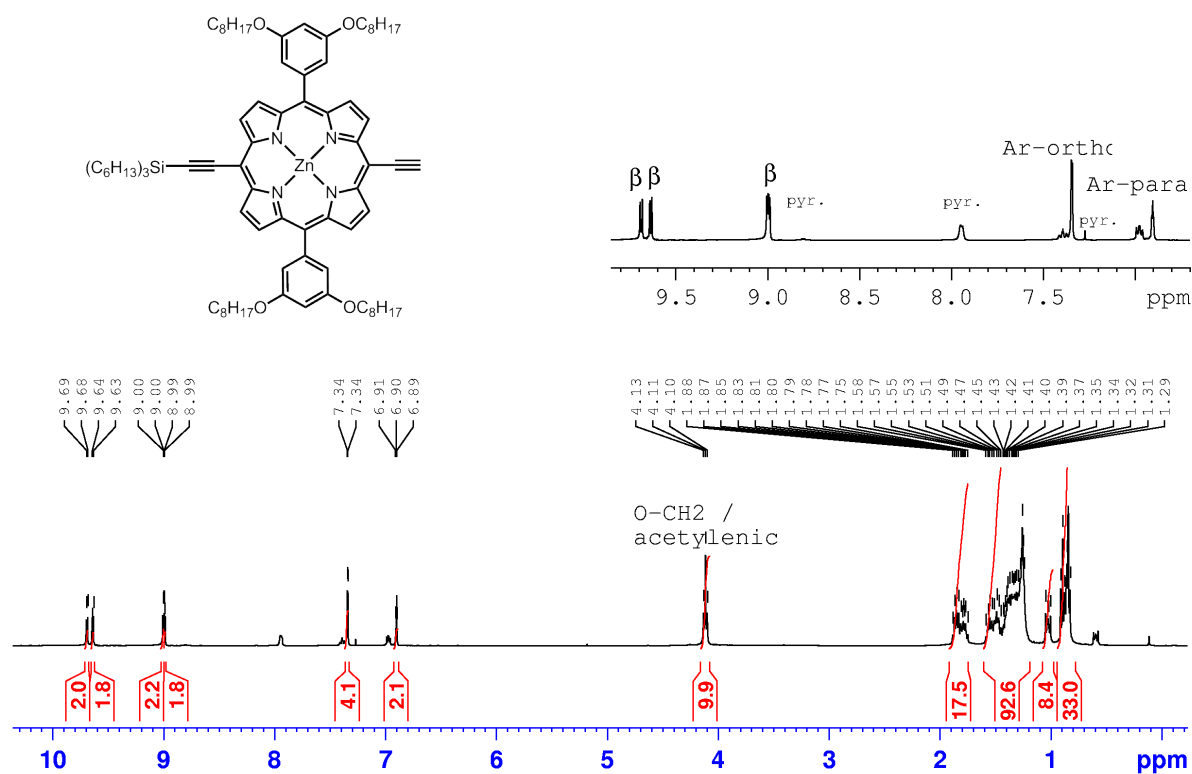


Figure S9 ¹H NMR of THS-P(Zn)-H (400 MHz, CDCl₃ : 1% d₅-pyridine)

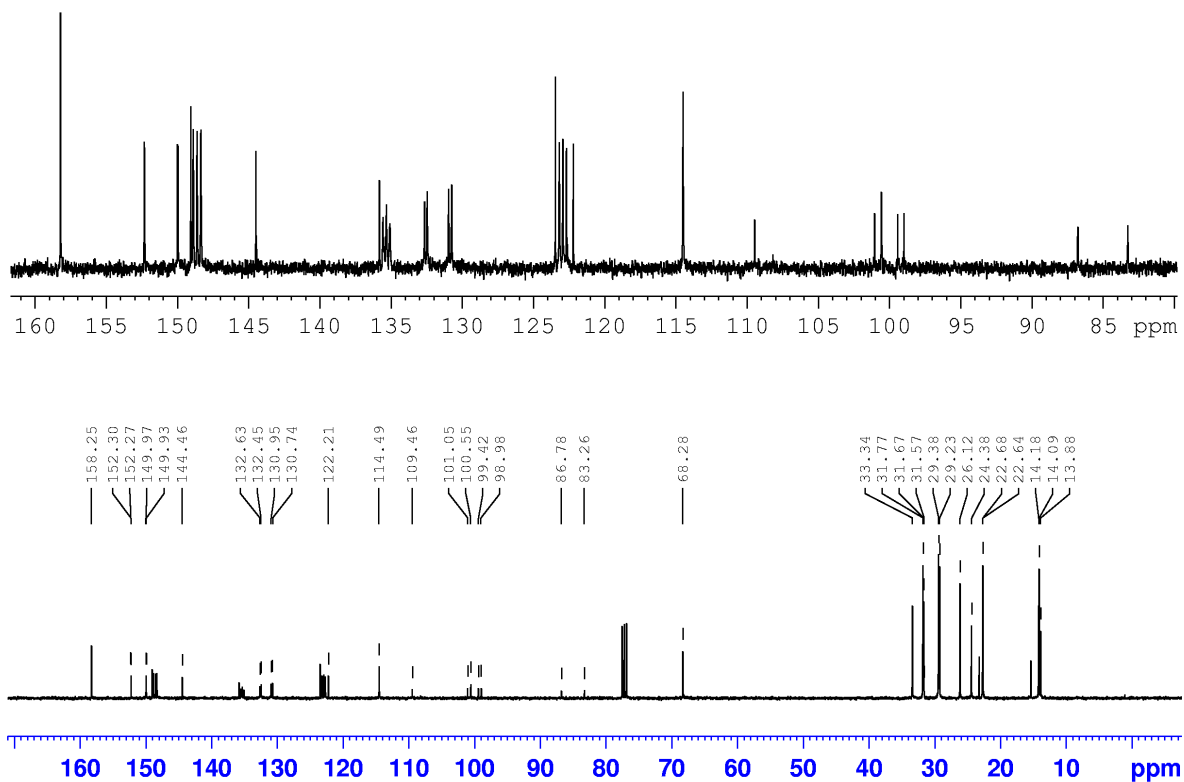
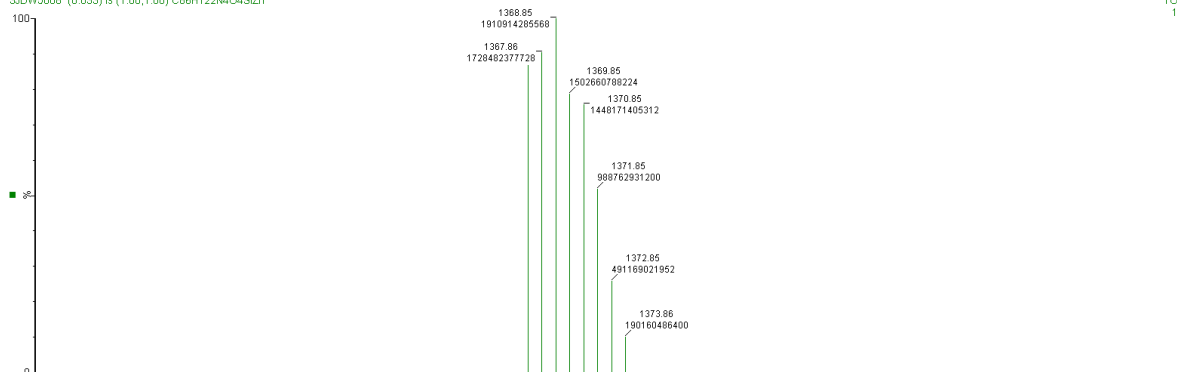


Figure S10 ¹³C NMR of THS-P(Zn)-H (101 MHz, CDCl₃ : 1% d₅-pyridine)

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MALDI

28-Nov-2013 10:16:02
TOF LD+
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3J0W5008 2 (0.066) Cm (1:3)

TOF LD+
3.31e3

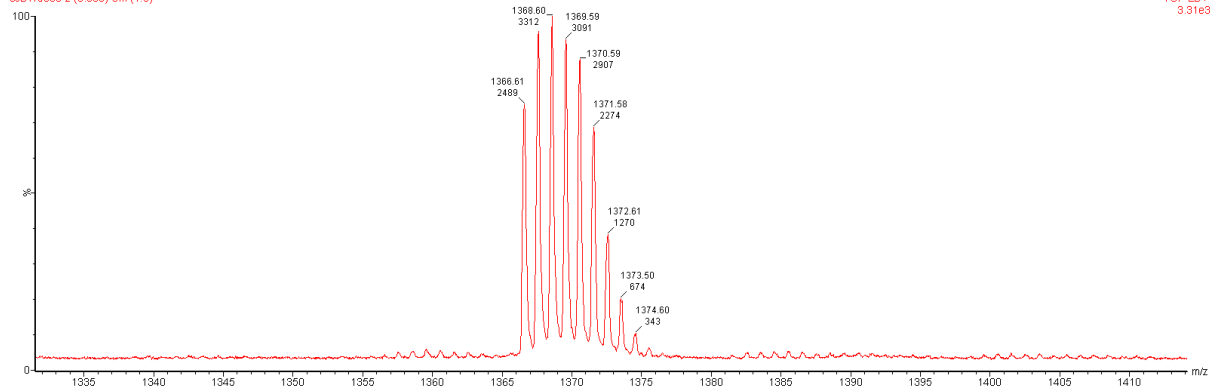


Figure S11 MALDI-TOF MS of THS-PC₈(Zn)-H

3J0W5008
3J0W5008 2 (0.066) Cm (1:3)

MALDI

28-Nov-2013 10:16:02
TOF LD+
3.31e3

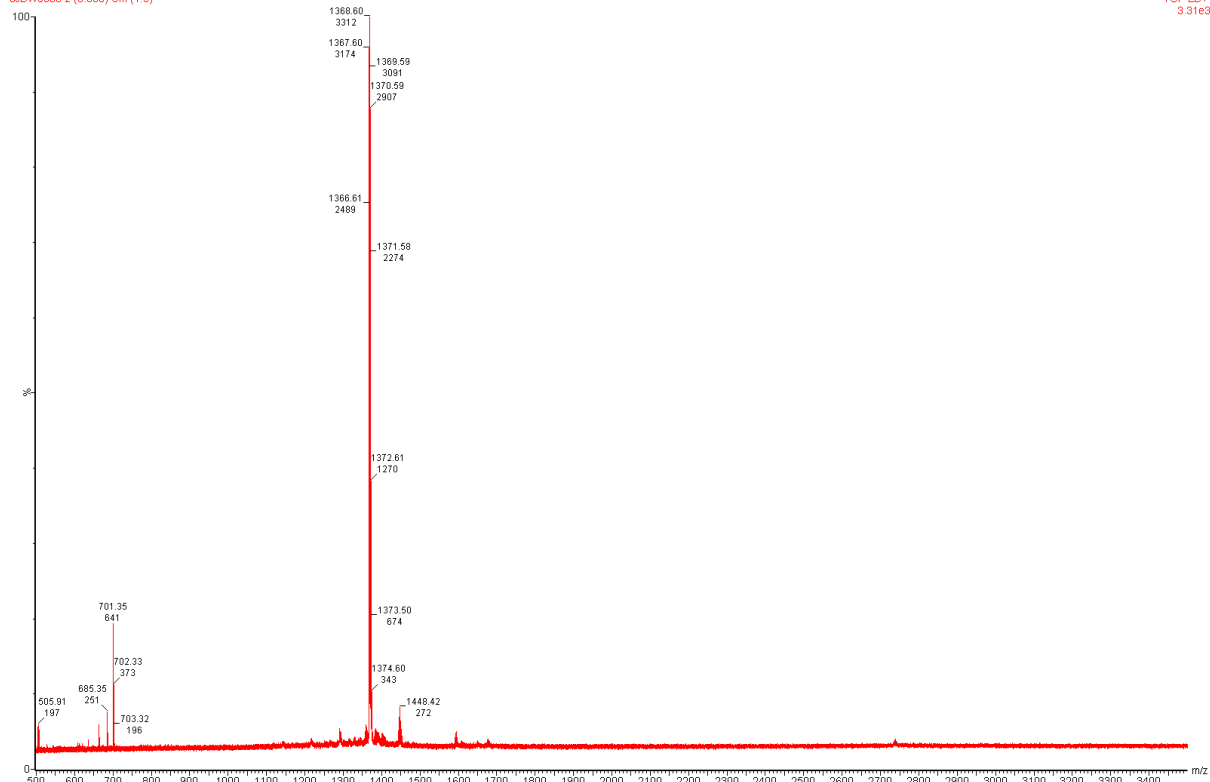


Figure S12 MALDI-TOF MS of THS-PC₈(Zn)-H

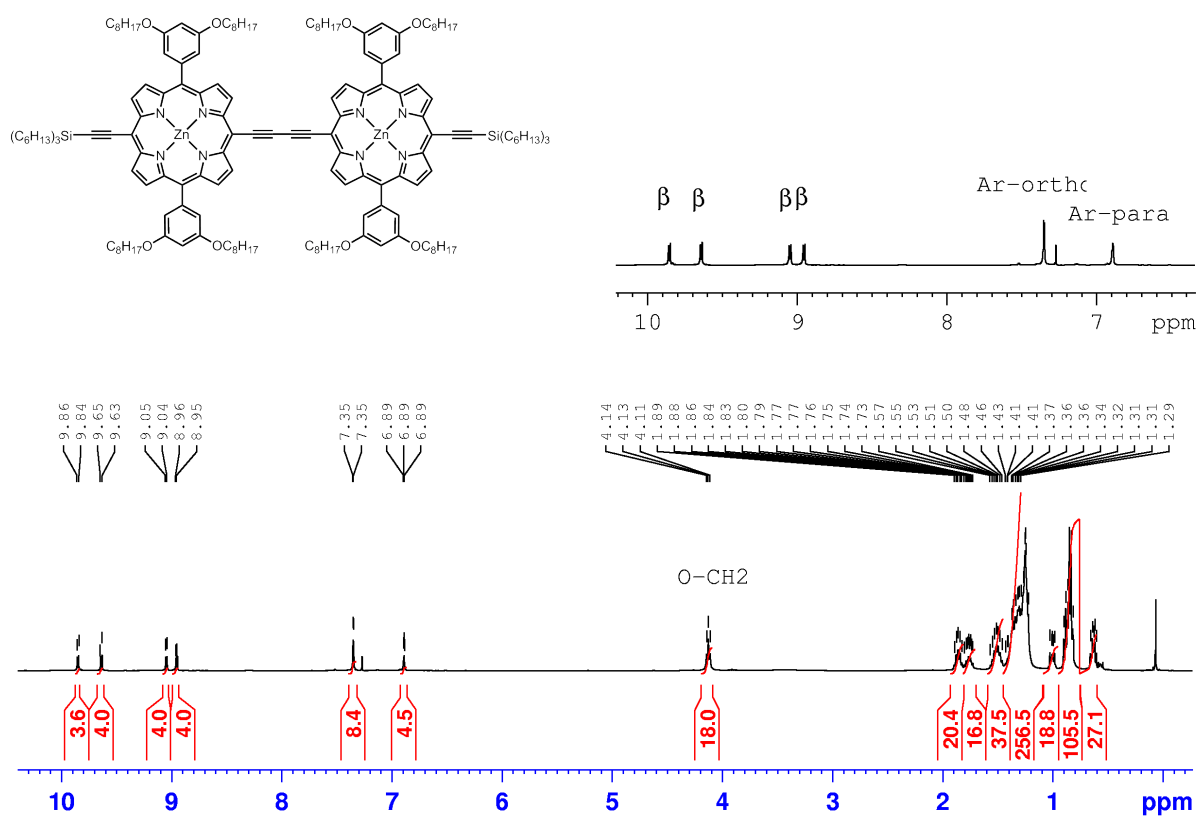


Figure S13 ^1H NMR of THS-P 2C_8 (Zn)-THS (400 MHz, CDCl_3 : 1% d_5 -pyridine)

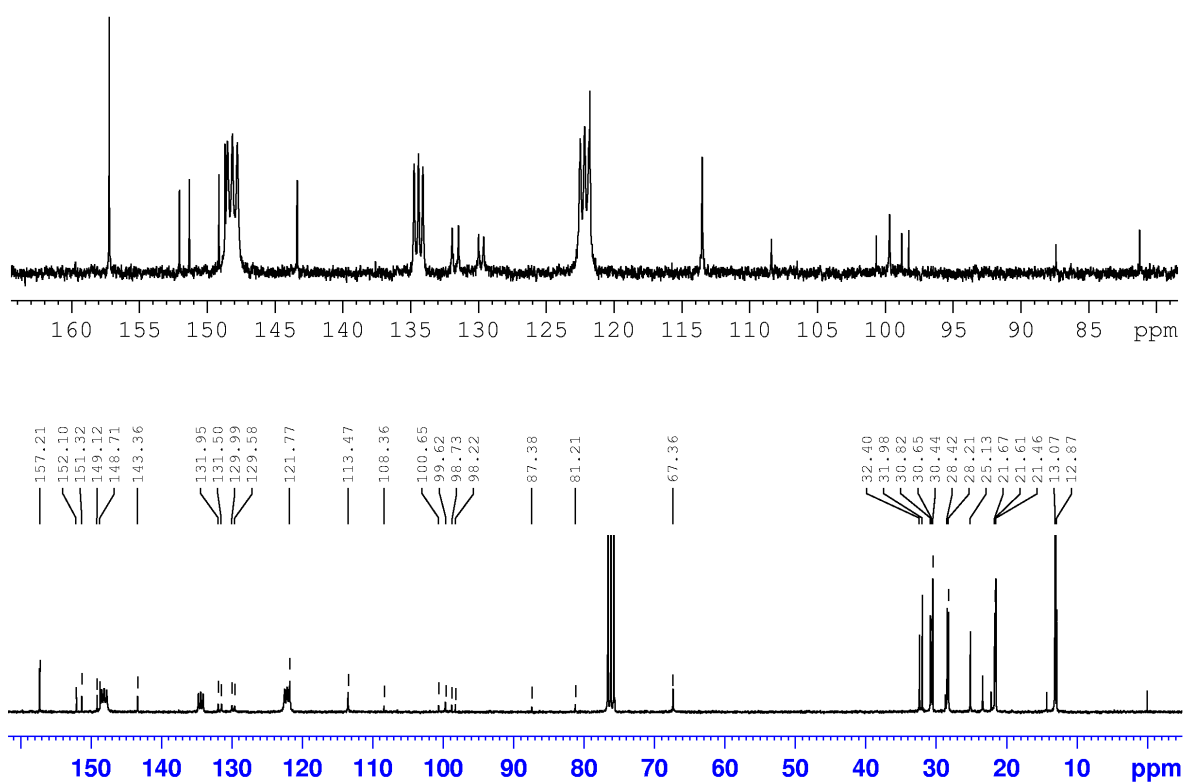


Figure S14 ^{13}C NMR of THS-P 2C_8 (Zn)-THS (75 MHz, CDCl_3 : 1% d_5 -pyridine)

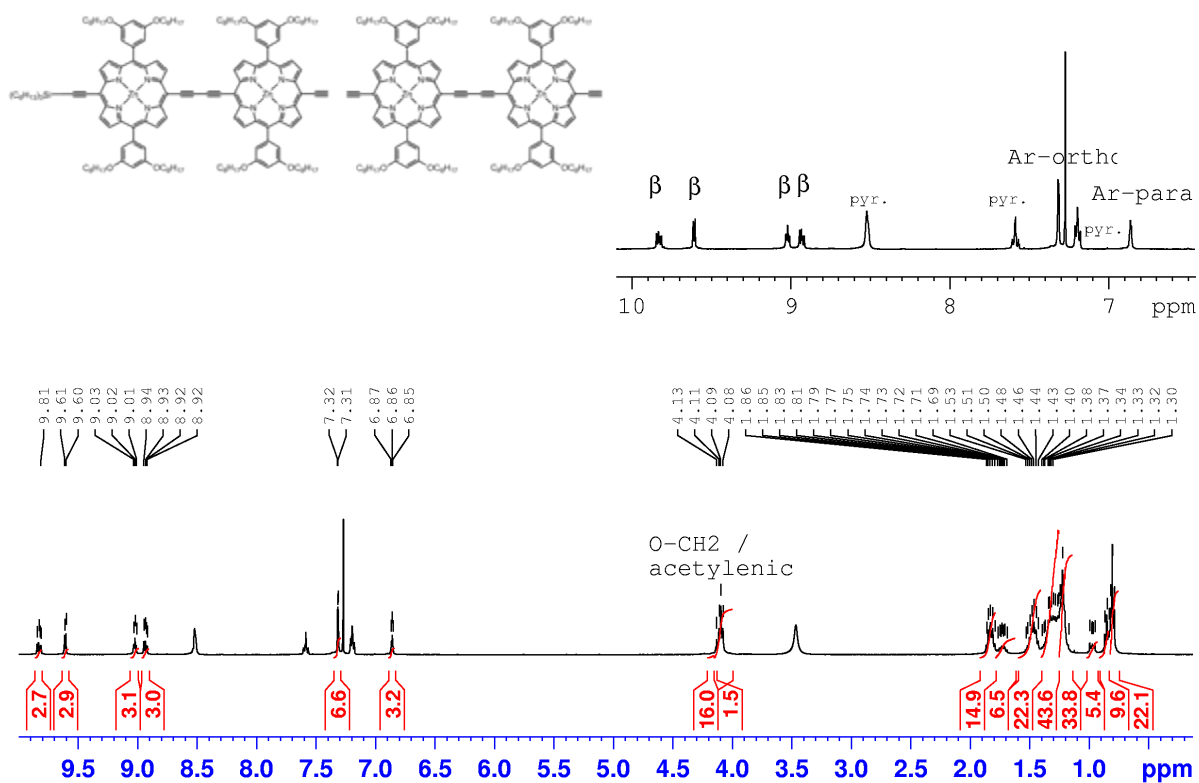


Figure S17 ^1H NMR of THS- $\text{P}2\text{C}_8(\text{Zn})\text{-H}$ & H- $\text{P}2\text{C}_8(\text{Zn})\text{-H}$ (400 MHz, CDCl_3 : 1% $\text{d}_5\text{-pyridine}$)

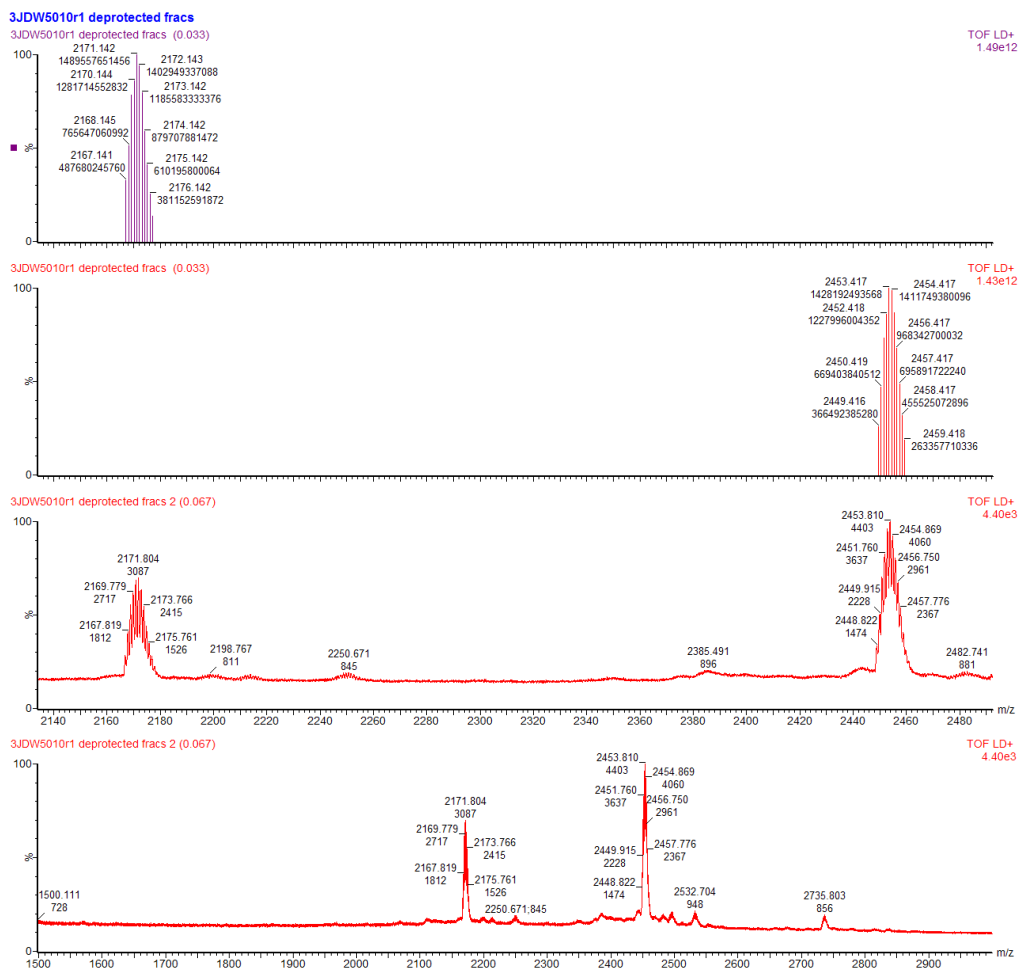


Figure S18 MALDI-TOF MS of the crude mixture of THS- $\text{P}2\text{C}_8(\text{Zn})\text{-H}$ and H- $\text{P}2\text{C}_8(\text{Zn})\text{-H}$

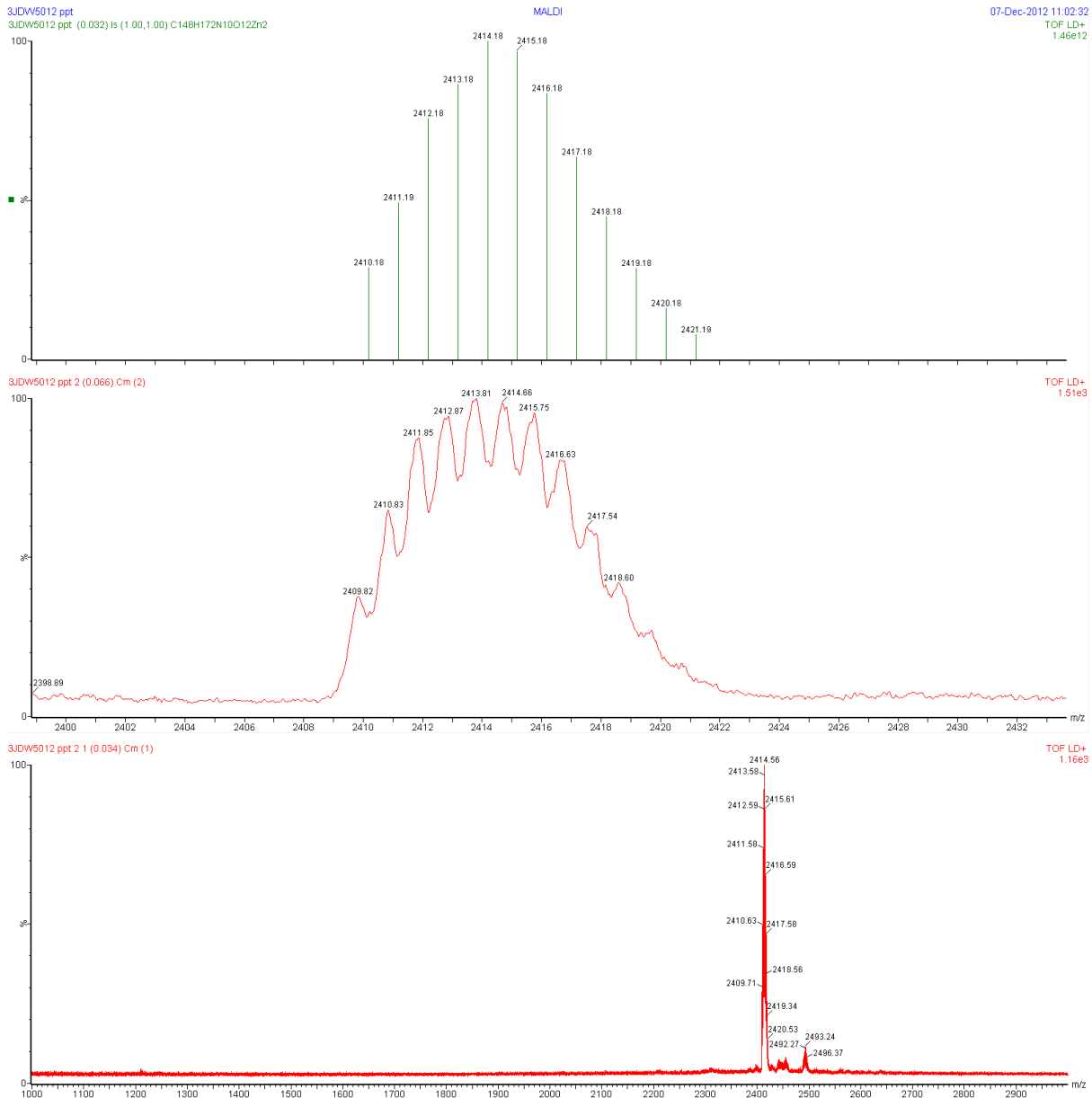


Figure S20 MALDI-TOF MS of A-P2_{C8}(Zn)-A

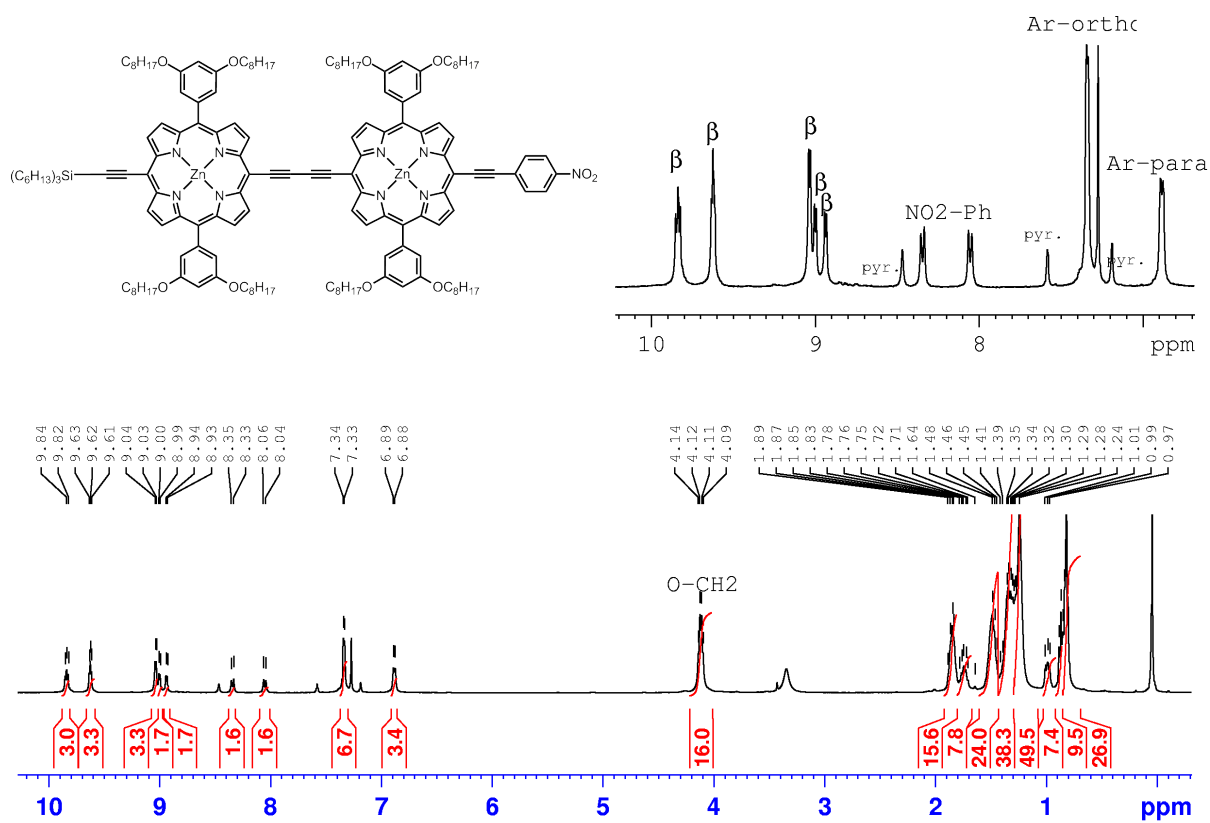


Figure S21 ¹H NMR of **A-P2C₈(Zn)-THS** (400 MHz, CDCl₃ : 1% d₅-pyridine)

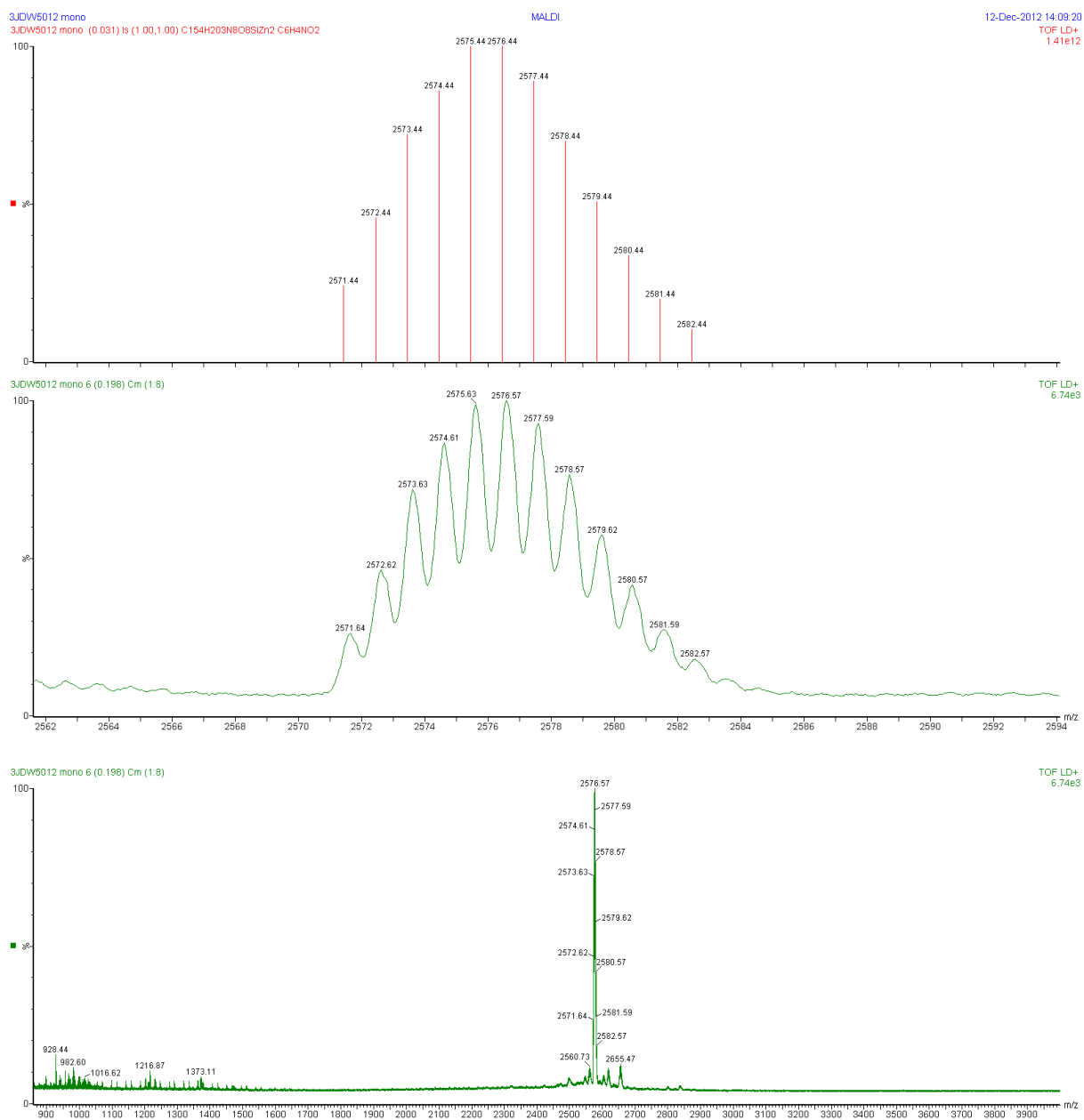


Figure S22 MALDI-TOF MS of A-P2C₈(Zn)-THS

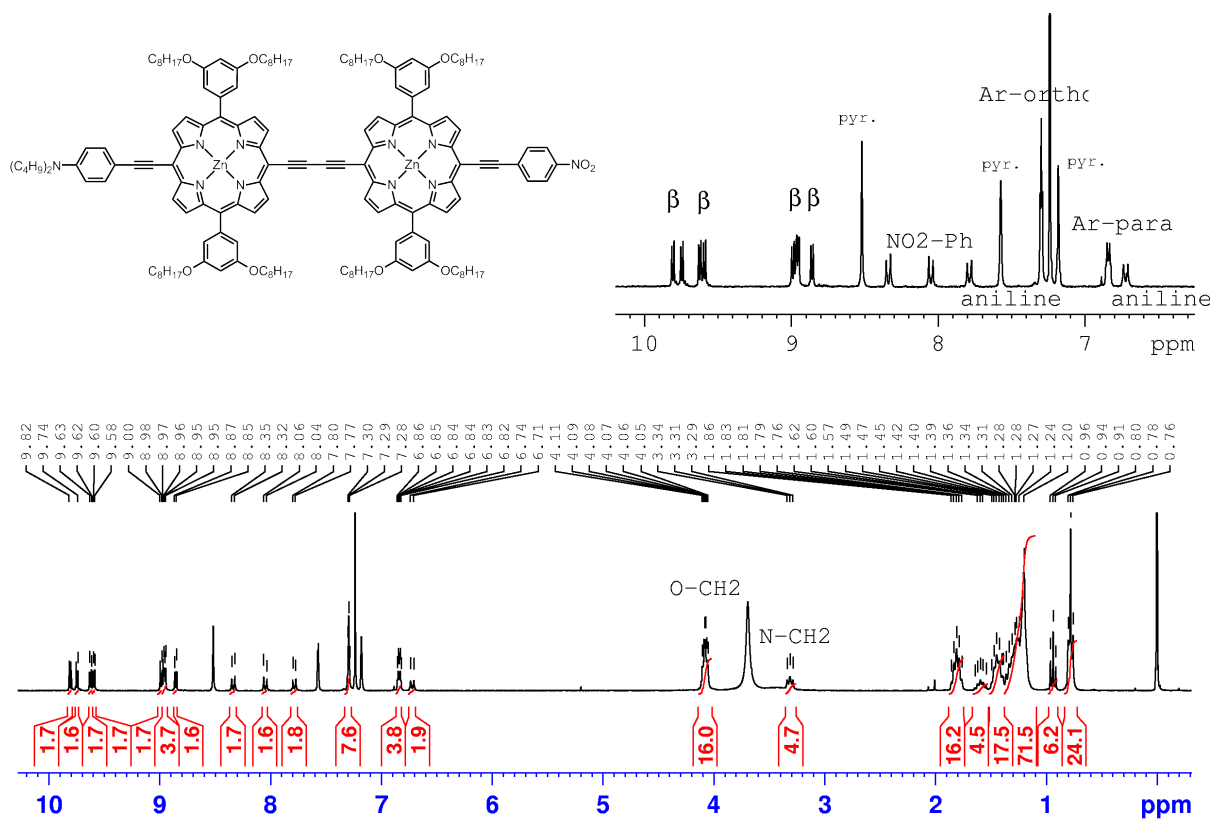


Figure S23 ^1H NMR of A-P2C8(Zn)-D (300 MHz, CDCl_3 : 1% d_5 -pyridine)

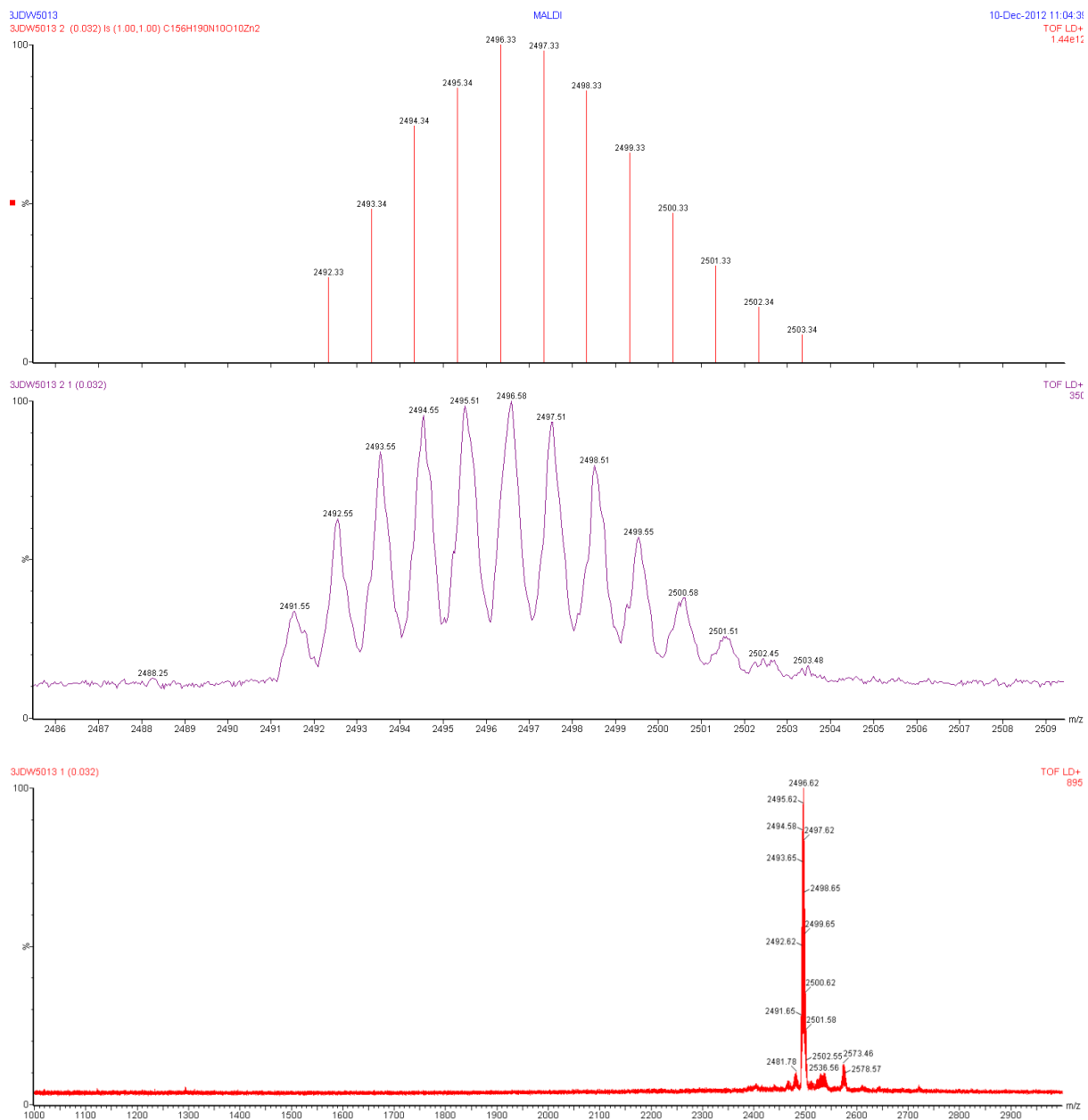


Figure S24 MALDI-TOF MS of A-P2C₈(Zn)-D

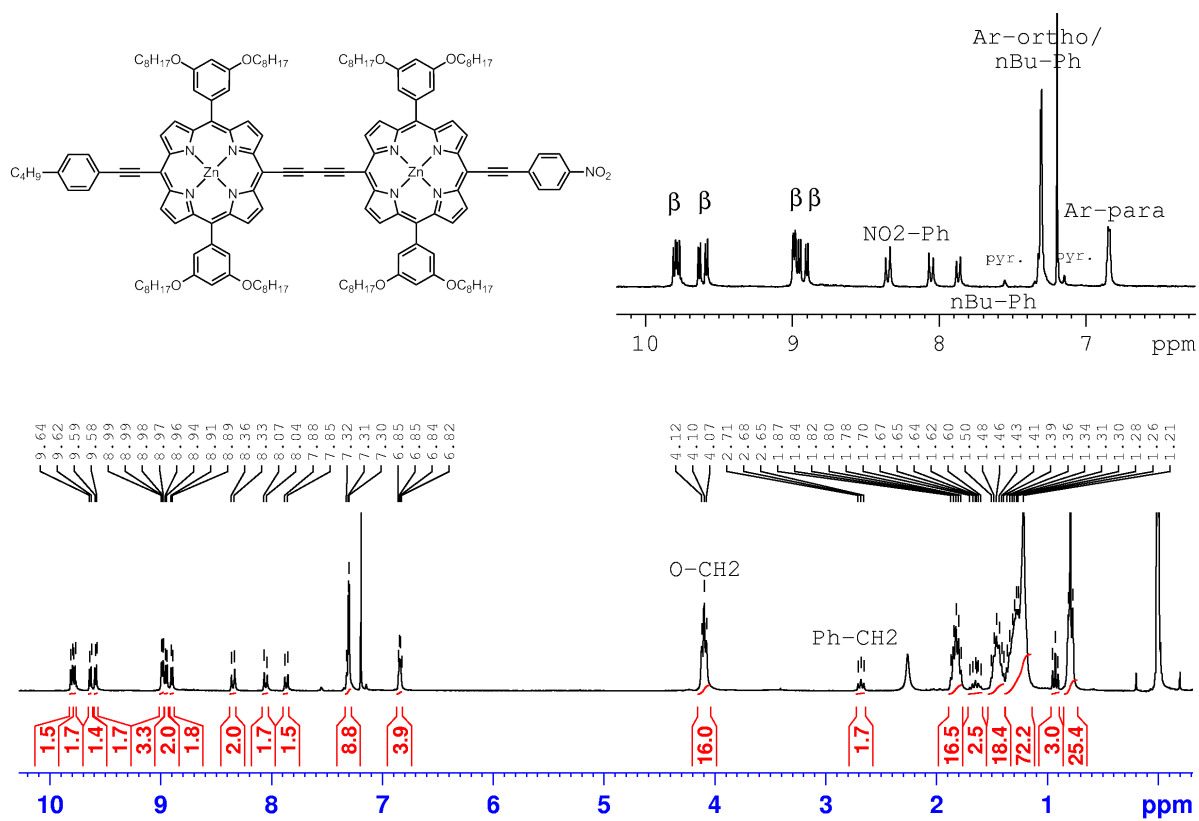


Figure S25 ¹H NMR of A-P2C₈(Zn)-R (300 MHz, CDCl₃ : 1% d₅-pyridine)

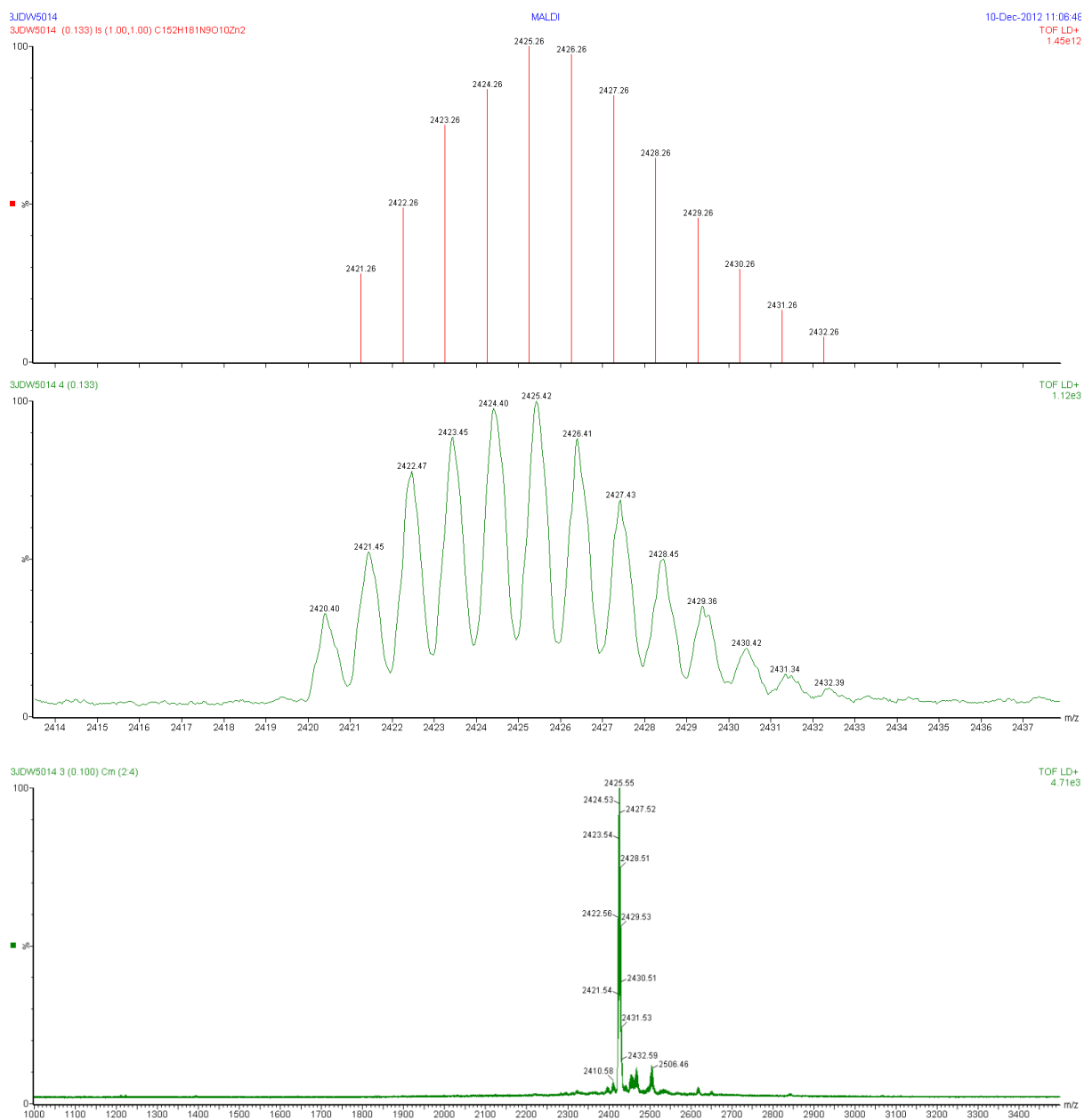


Figure S26 MALDI-TOF MS of A-P2C8(Zn)-R

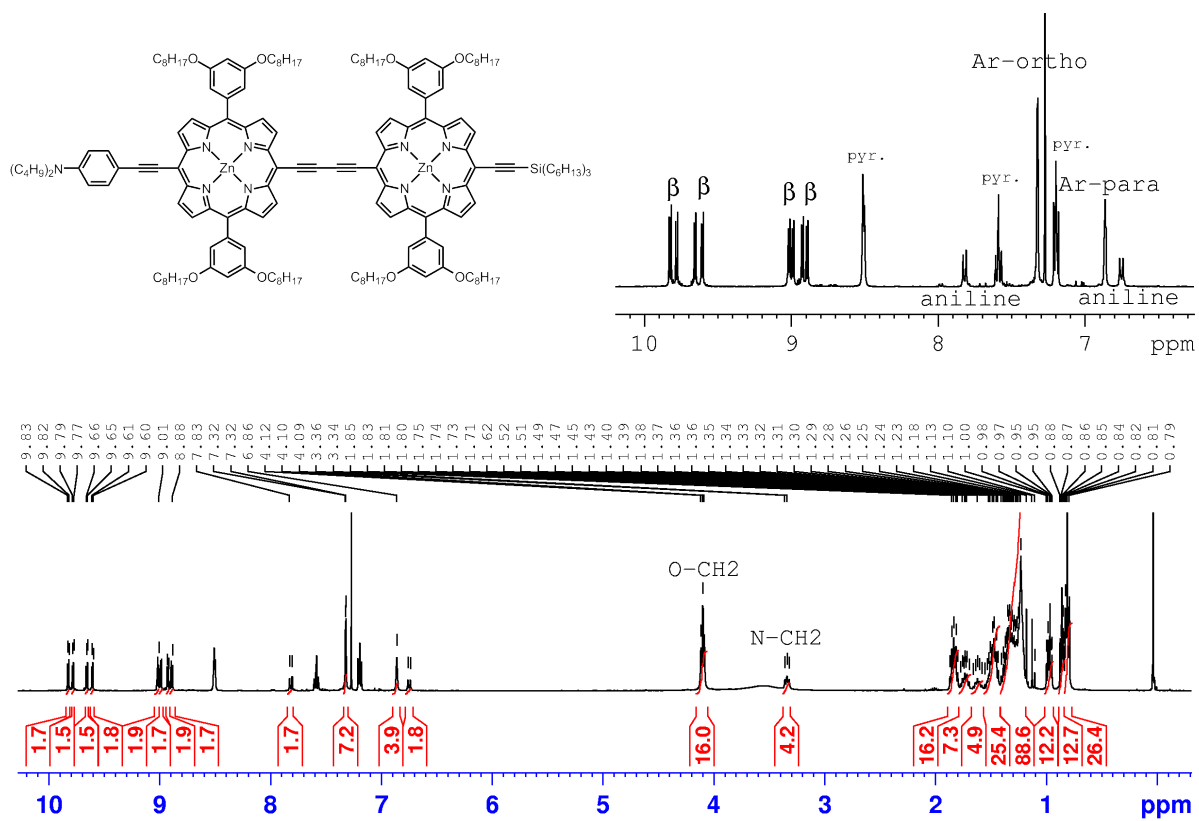


Figure S27 ¹H NMR of **D-P2C₈(Zn)-THS** (400 MHz, CDCl₃ : 1% d₅-pyridine)

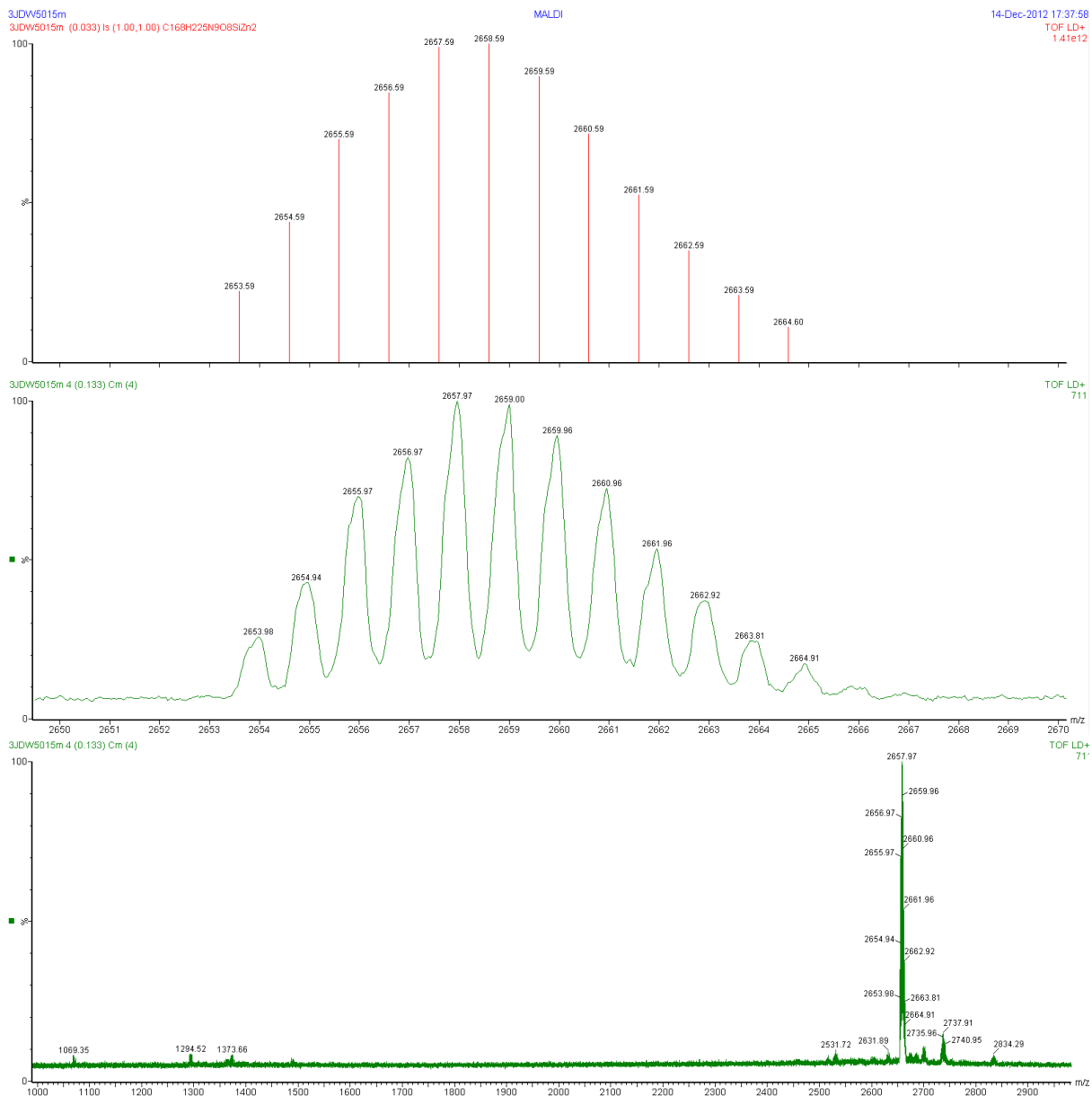


Figure S28 ^1H NMR of **D-P2C₈(Zn)-THS** (400 MHz, CDCl_3 : 1% d_5 -pyridine)

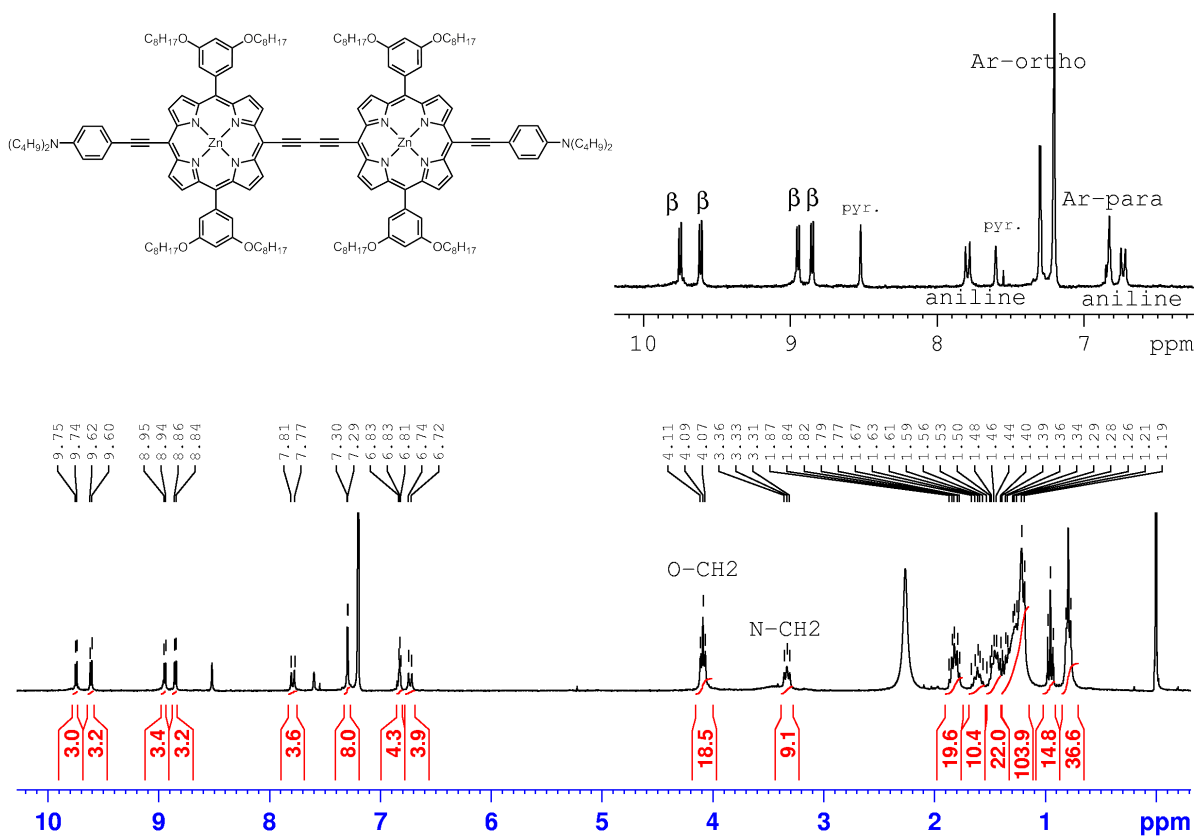


Figure S29 ¹H NMR of **D-P2C₈(Zn)-D** (400 MHz, CDCl₃ : 1% d₅-pyridine)

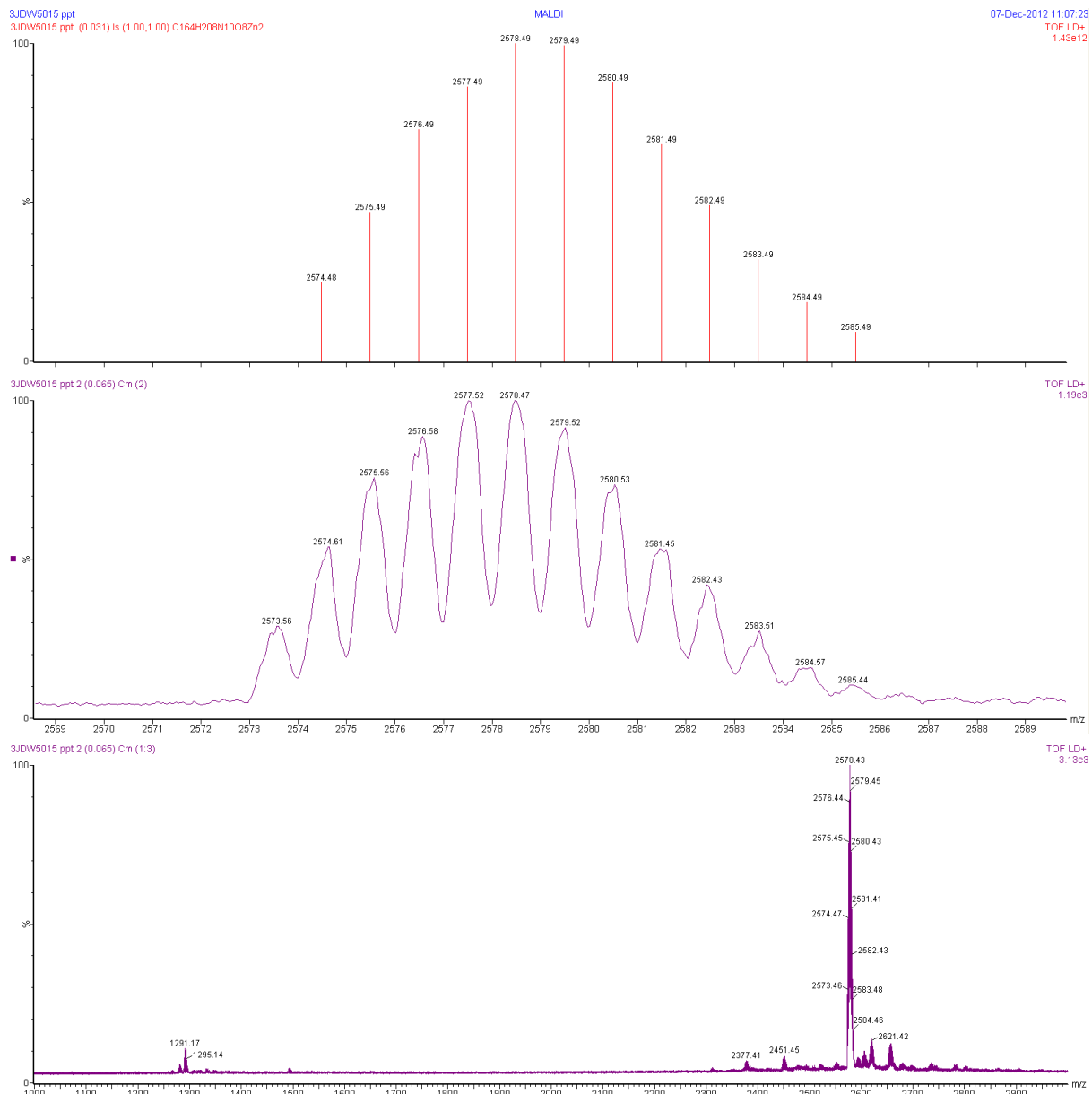


Figure S30 MALDI-TOF MS of THS-P2_{C8}(Zn)-THS

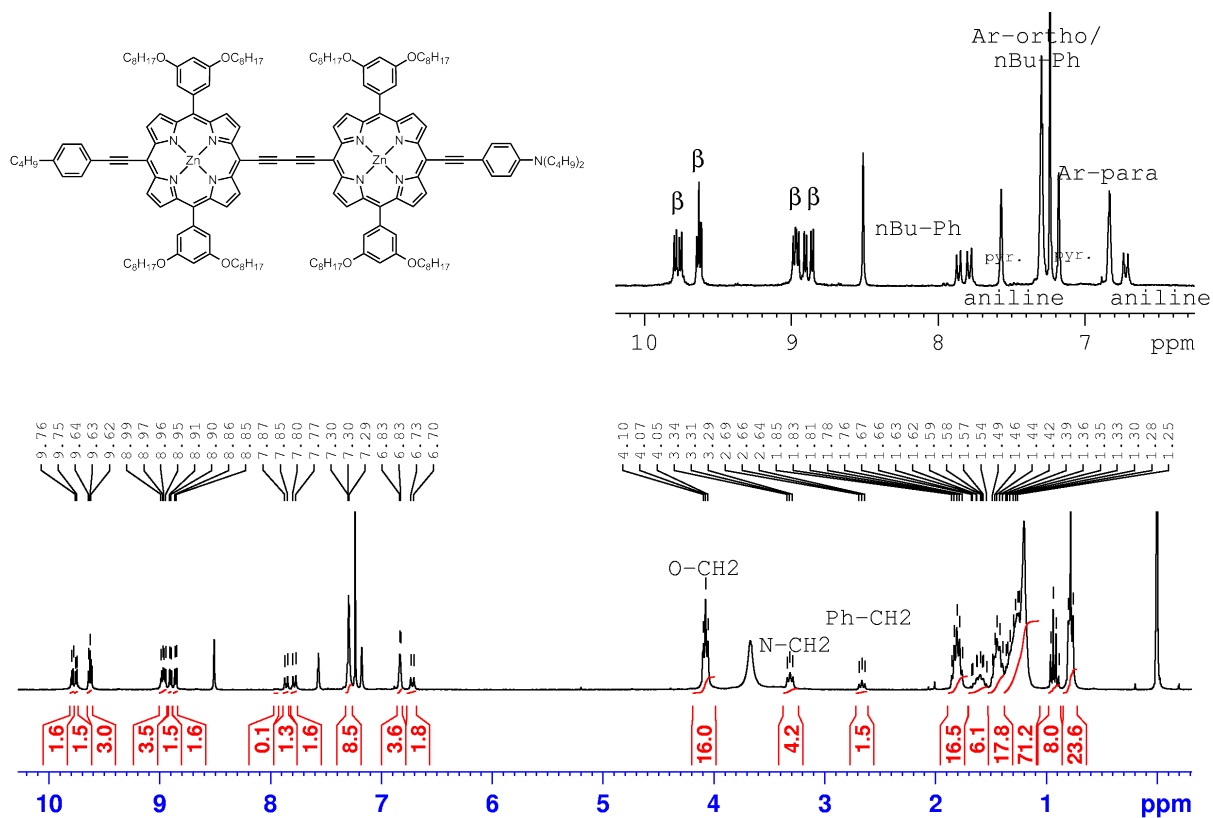


Figure S31 ¹H NMR of **D-P2C₈(Zn)-R** (300 MHz, CDCl₃ : 1% d₅-pyridine)

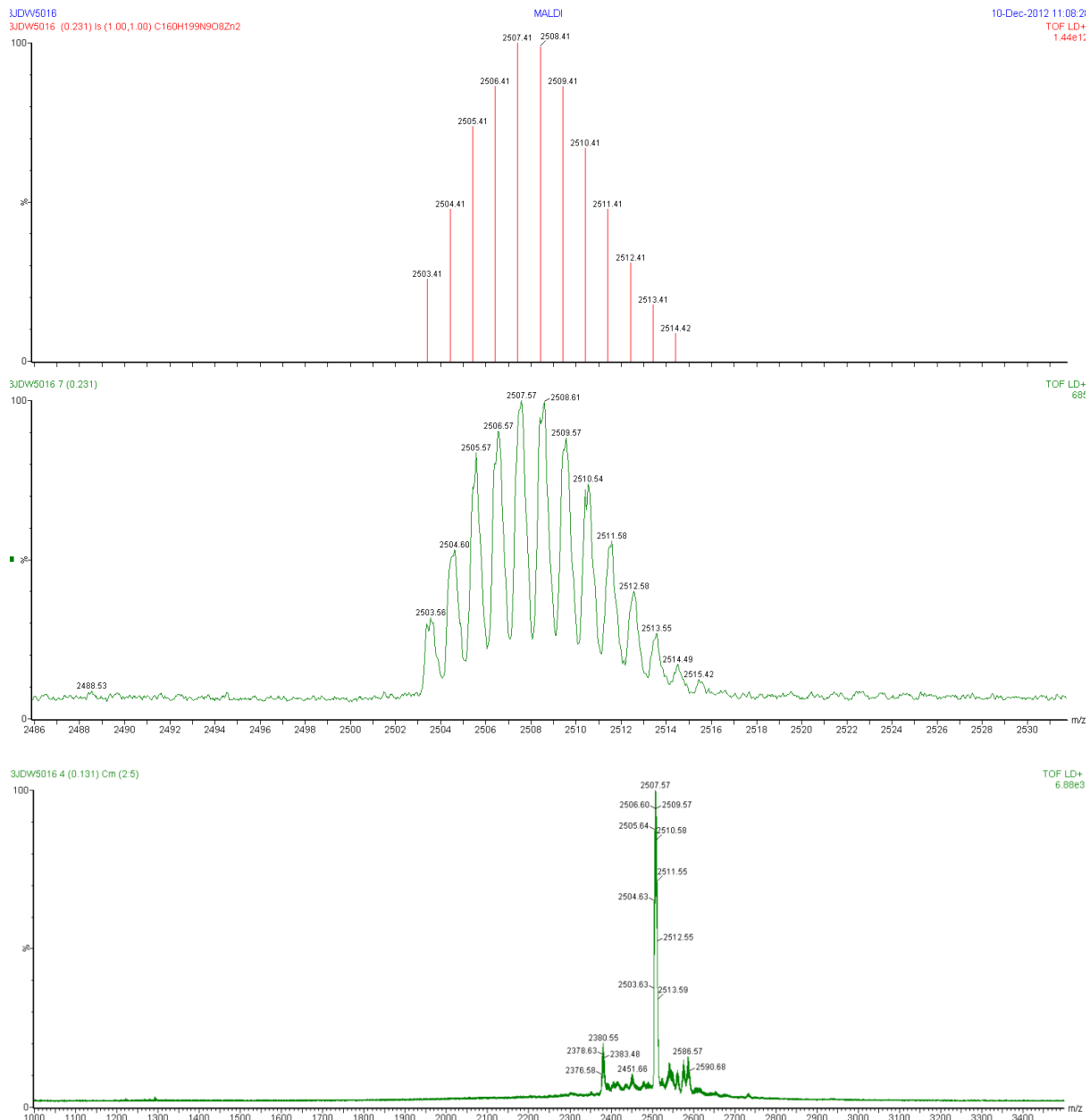


Figure S32 MALDI-TOF MS of D-P2C₈(Zn)-R

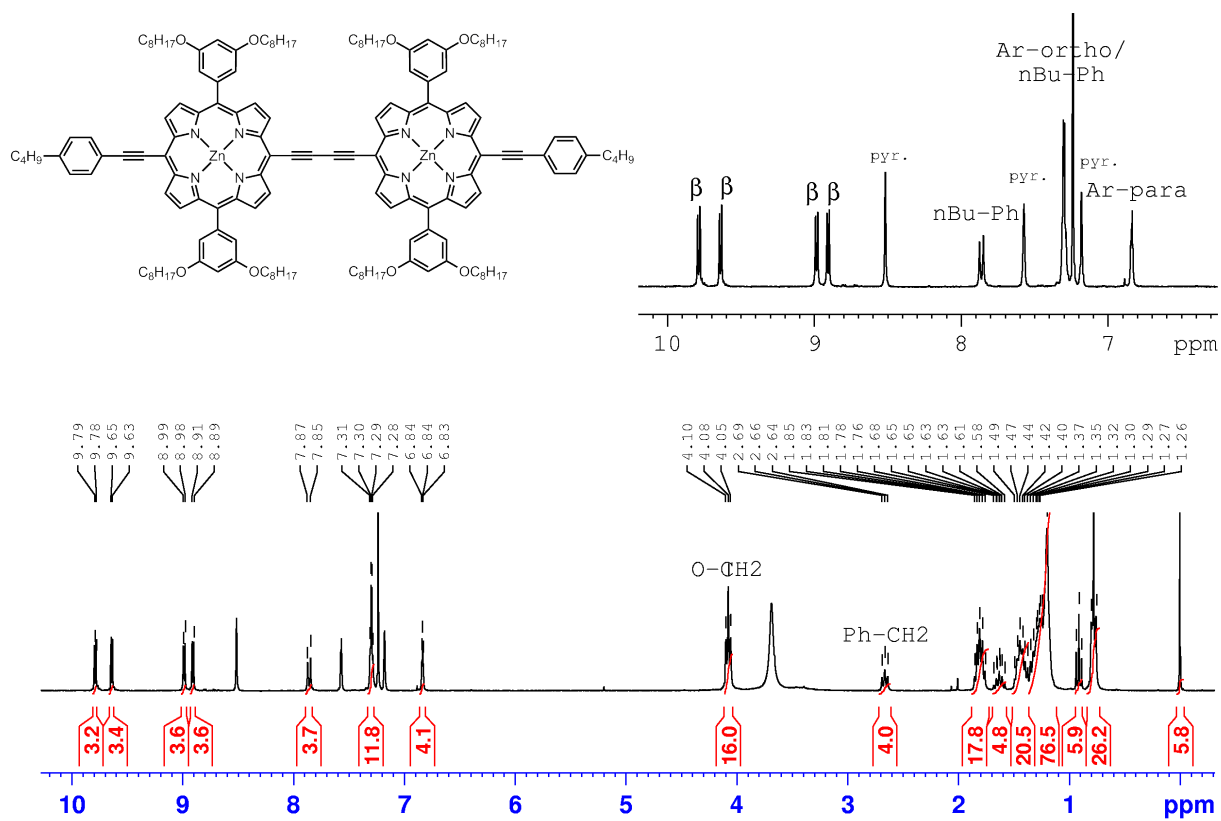


Figure S33 ¹H NMR of **R-P2C₈(Zn)-R** (300 MHz, CDCl₃ : 1% d₅-pyridine)

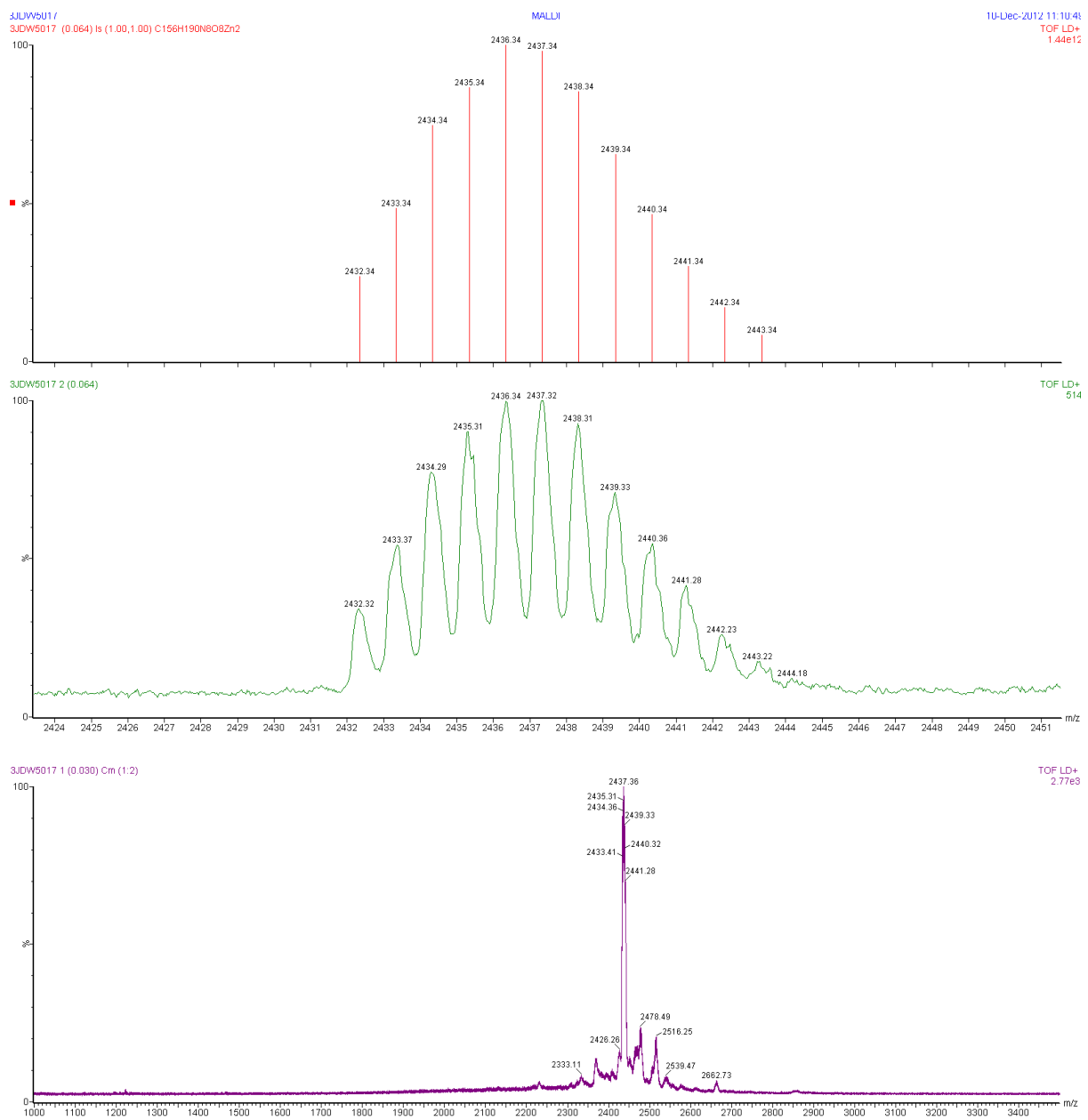


Figure S34 MALDI-TOF MS of R-P2C8(Zn)-R

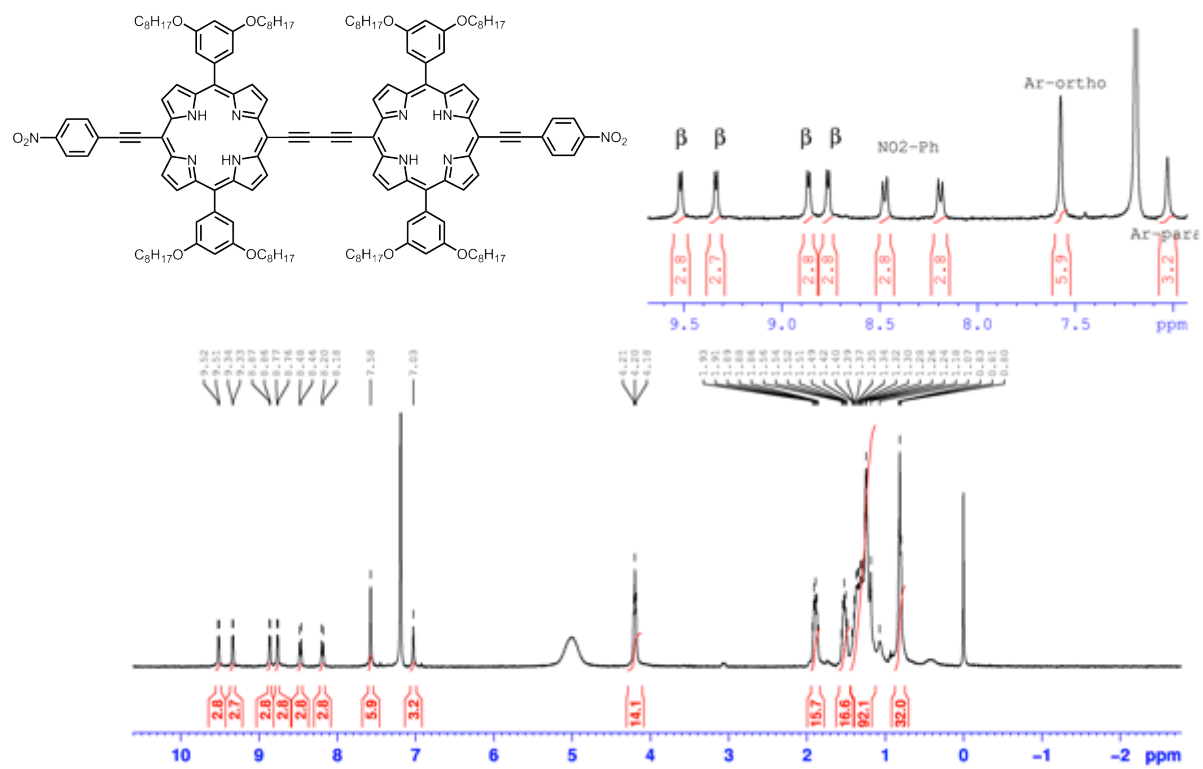


Figure S35 ¹H NMR of **A-P2C₈(2H)-A** (400 MHz; CDCl₃; 1% d-TFA).

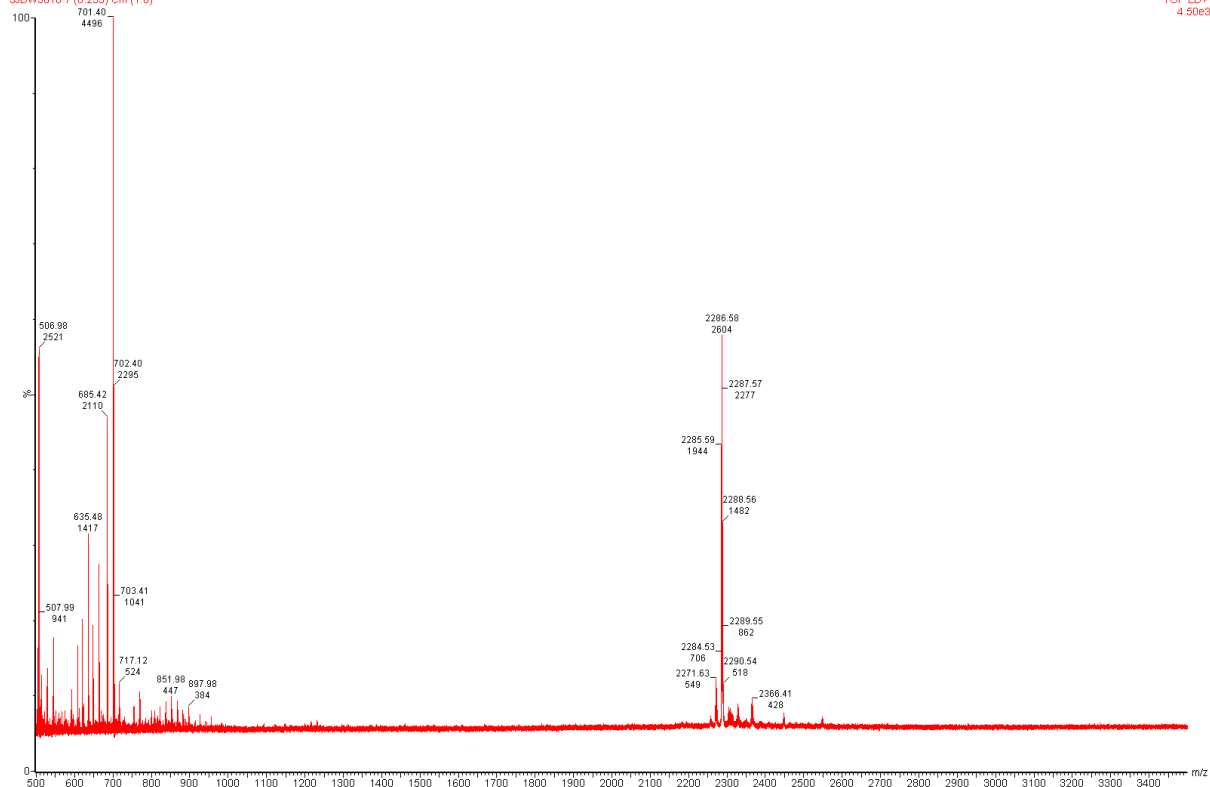
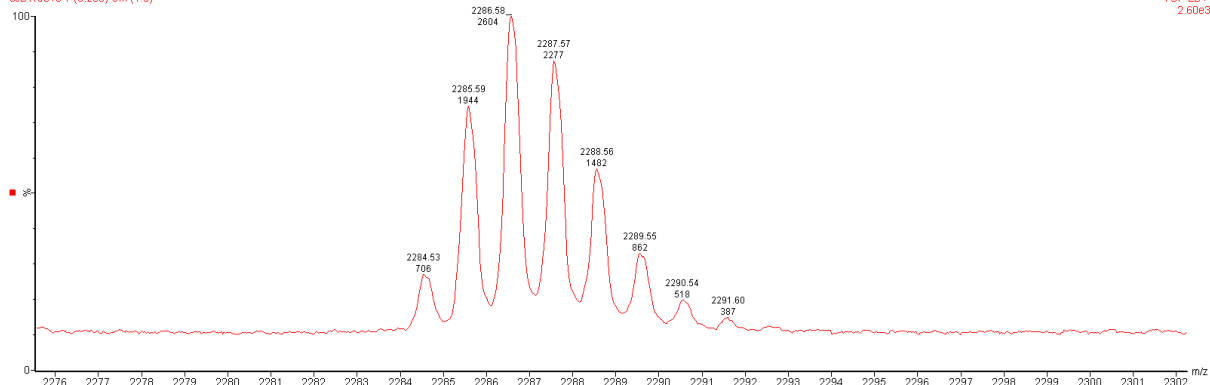
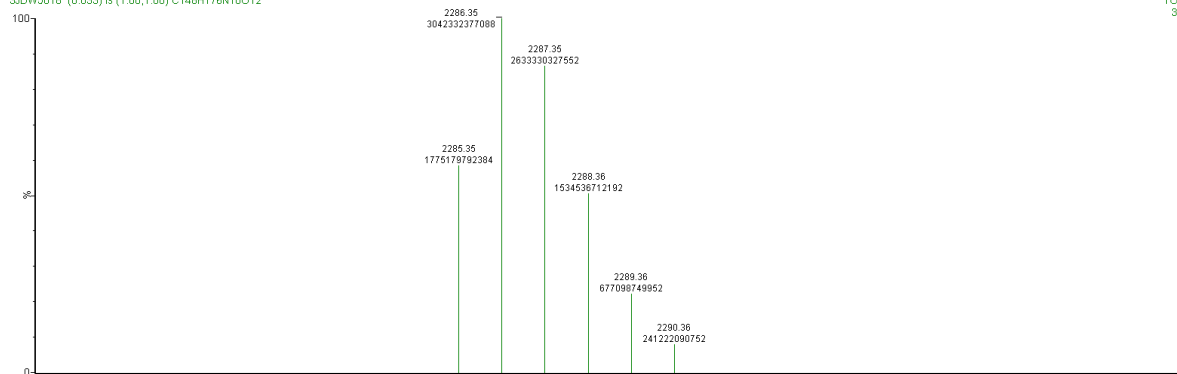


Figure S36 MALDI-TOF MS of A-P₂C₈(2H)-A

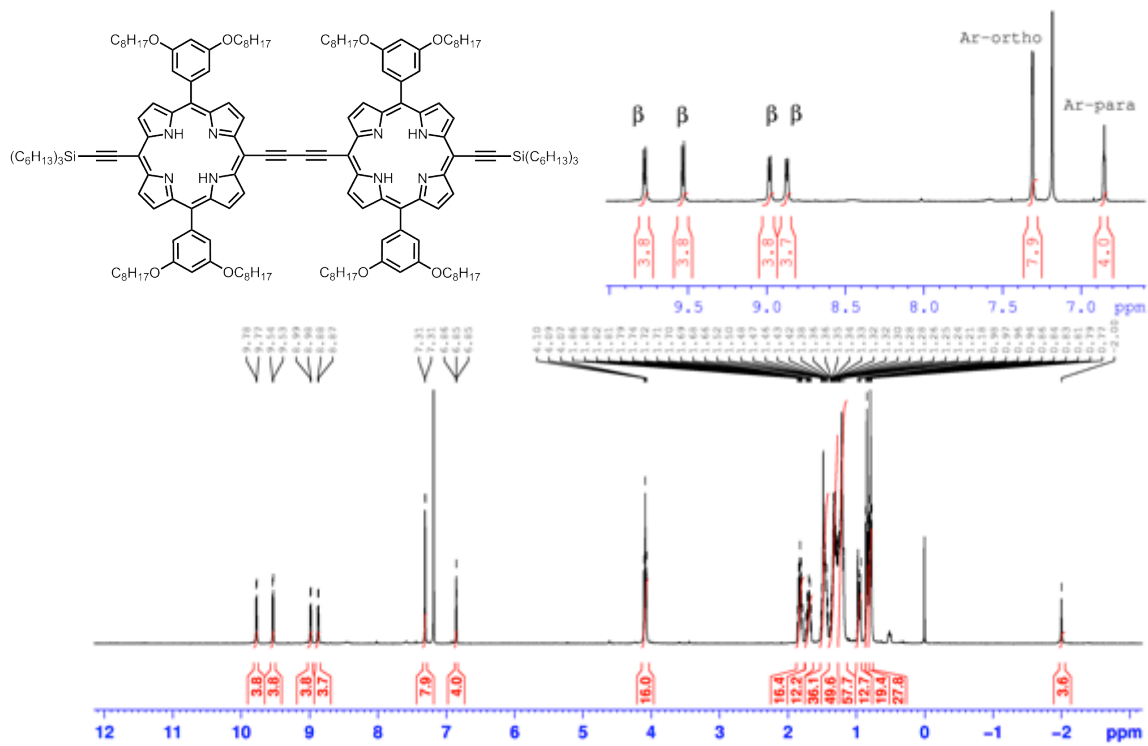


Figure S37 ¹H NMR of THS-P2C₈(2H)-THS (400 MHz; CDCl₃)

■ 5,15-Bis-(3,5-bis-octyloxy-phenyl)-10,20-trihexylsilylethynyl-porphyrin dimer THS-P2C8(2H)-THS

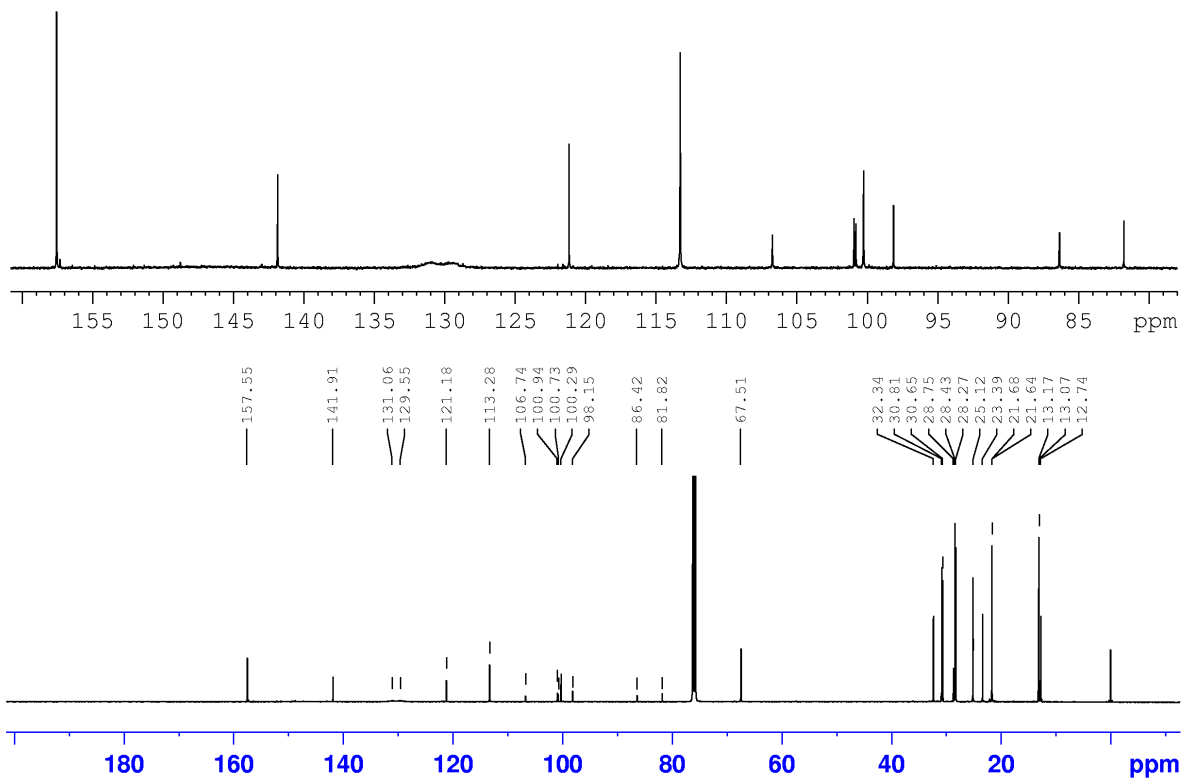
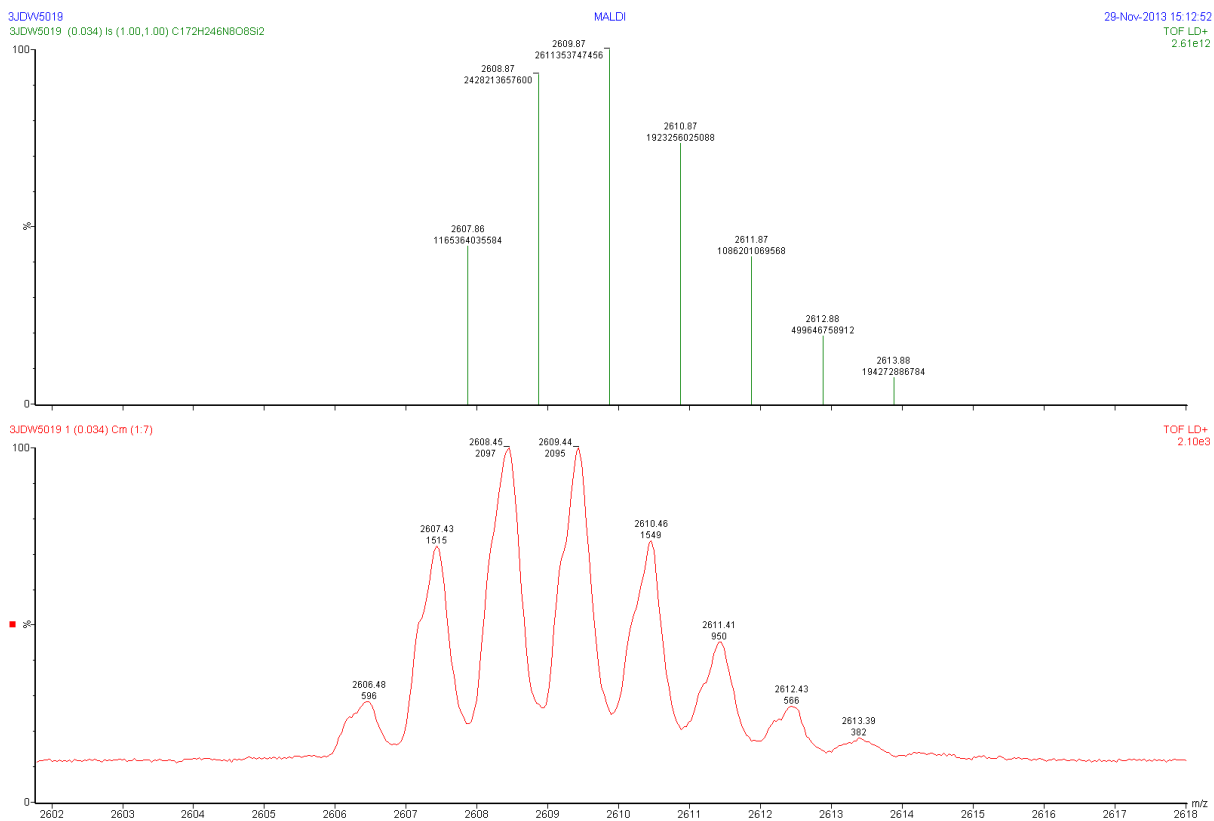


Figure S38 ^{13}C NMR of THS-P2C₈(2H)-THS (126 MHz; CDCl₃)



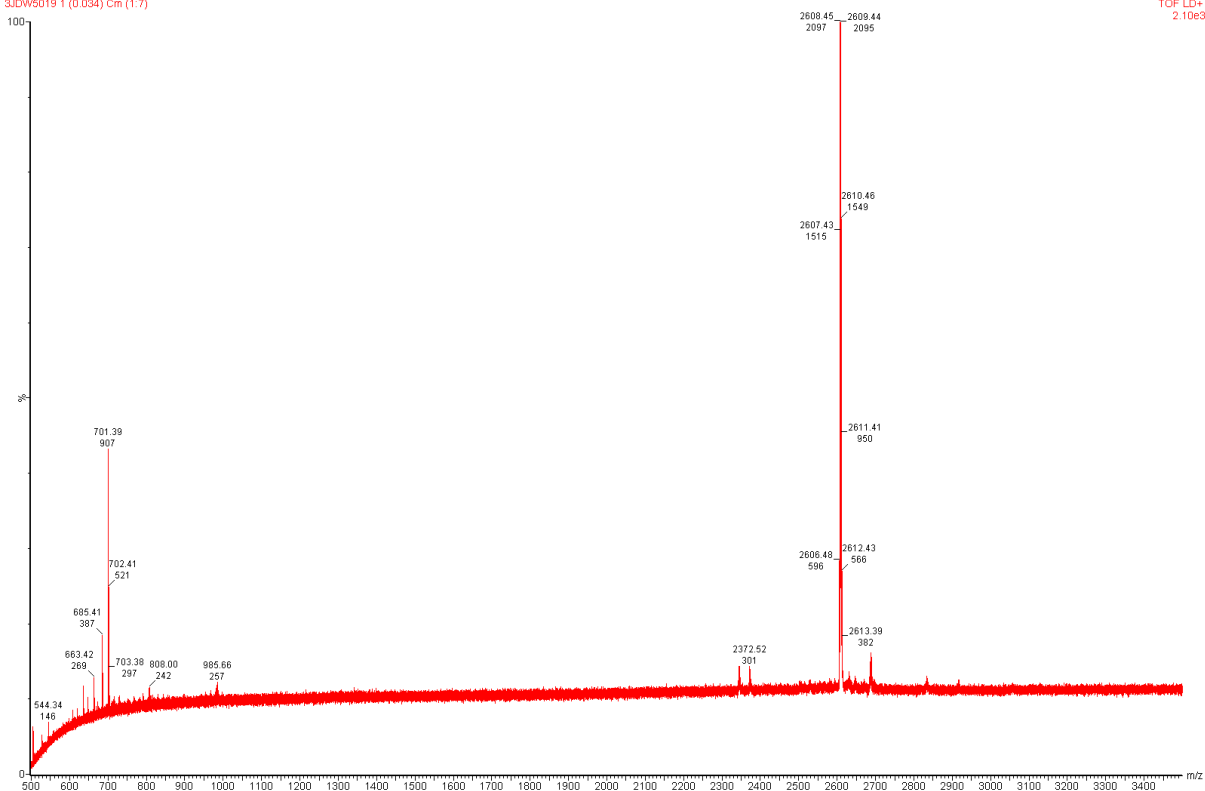


Figure S39 MALDI-TOF MS of THS-P2C₈(2H)-THS

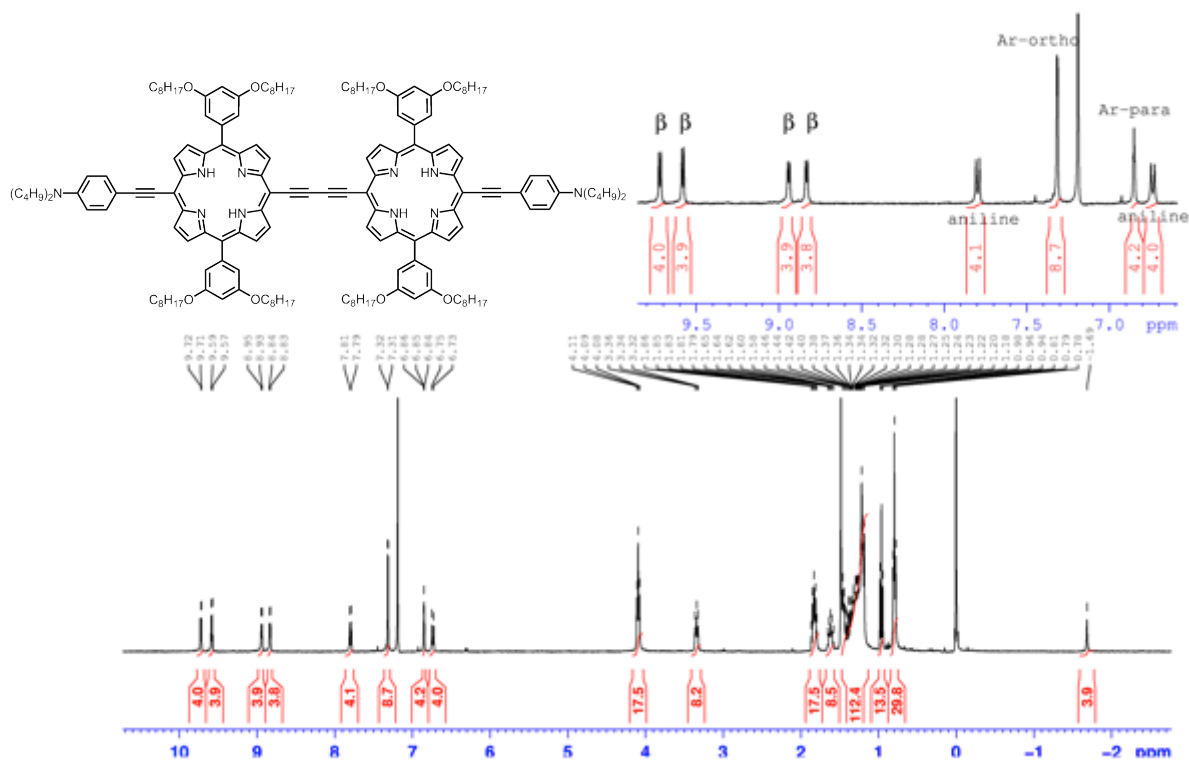


Figure S40 ¹H NMR of D-P2C₈(2H)-D (400 MHz; CDCl₃)

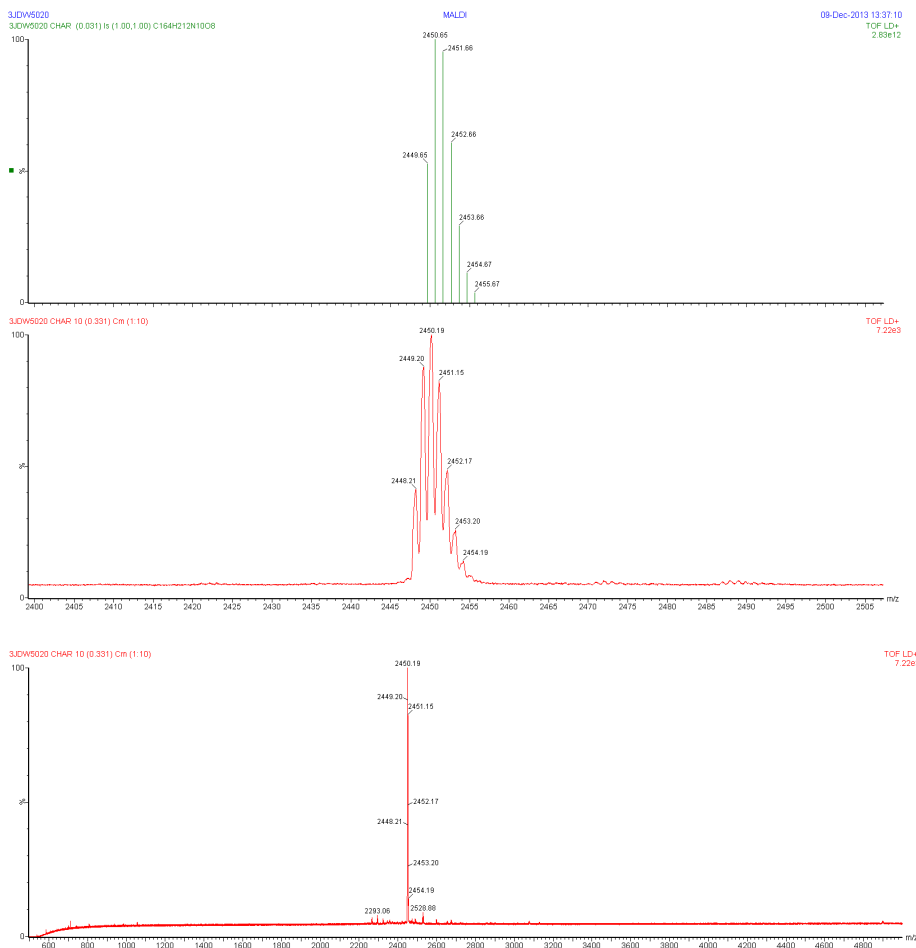


Figure S41 MALDI-TOF MS of **D-P2C₈(2H)-D**

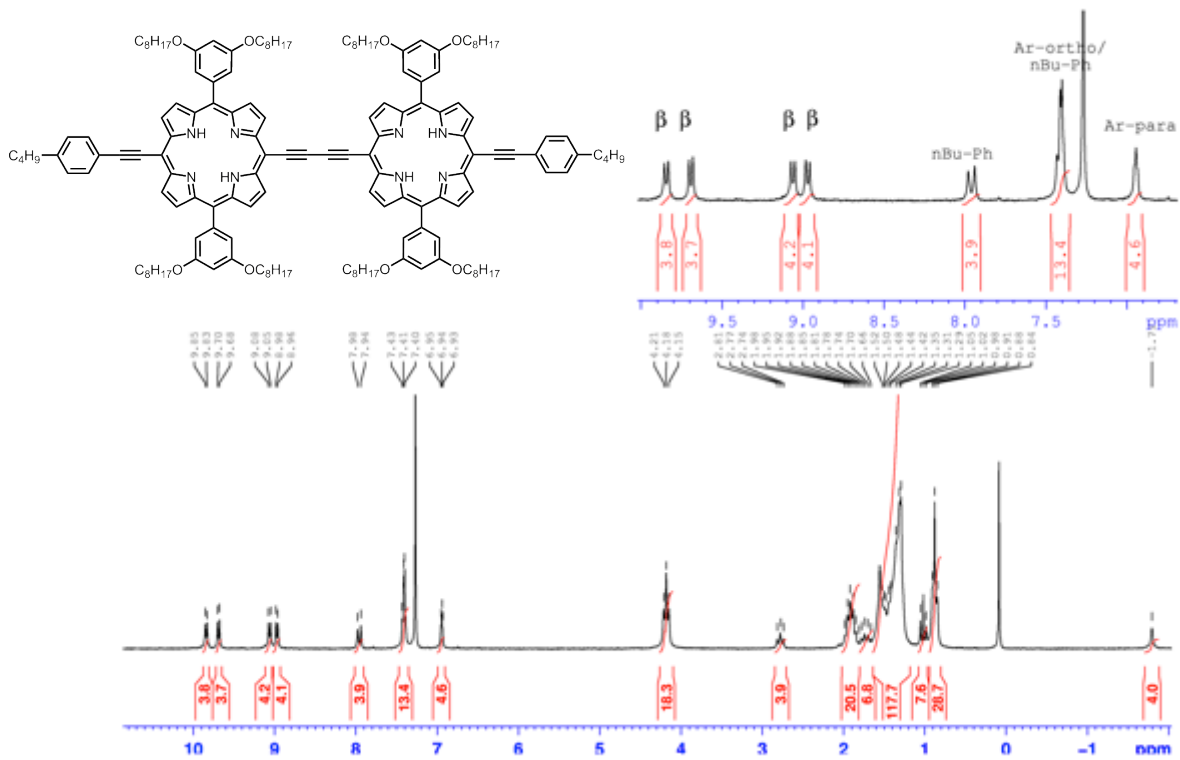
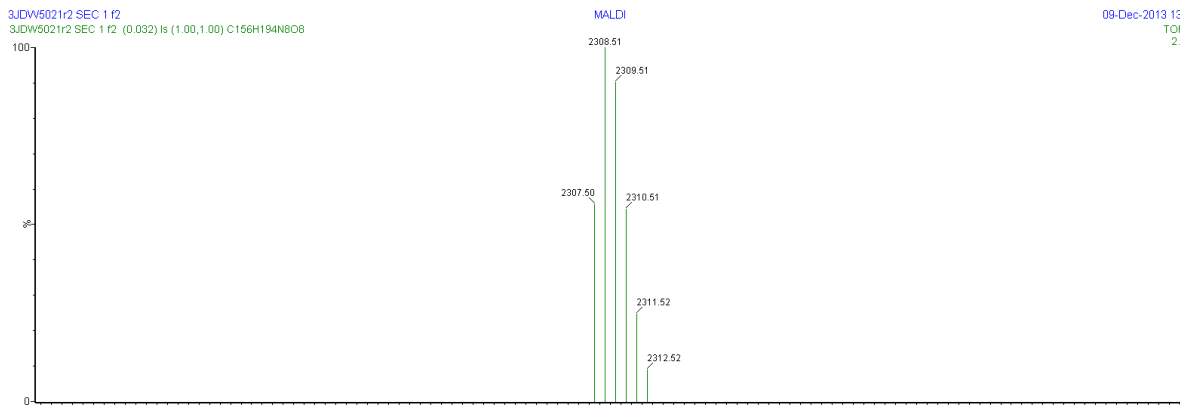


Figure S42 ¹H NMR of **R-P2C₈(2H)-R** (200 MHz; CDCl₃)

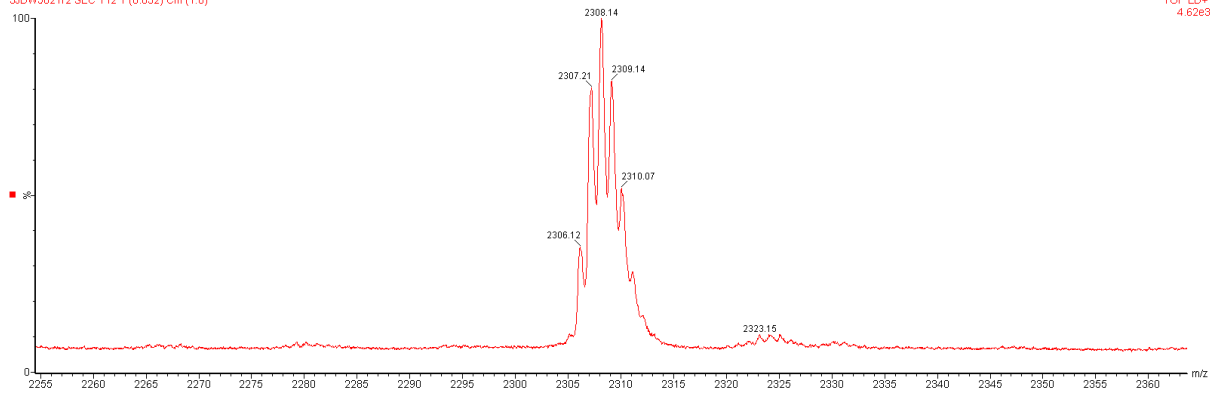
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09-Dec-2013 13:31:16
TOF LD+
2.96e12



3J0W5021r2 SEC 1 f2 1 (0.032) Cm (1.8)

TOF LD+
4.62e3



3J0W5021r2 SEC 1 f2 1 (0.032) Cm (1.8)

TOF LD+
4.62e3

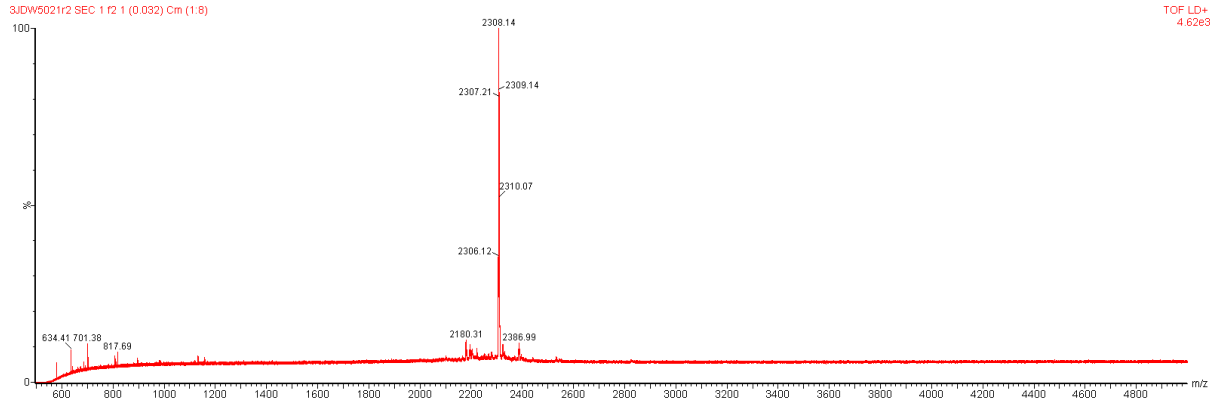
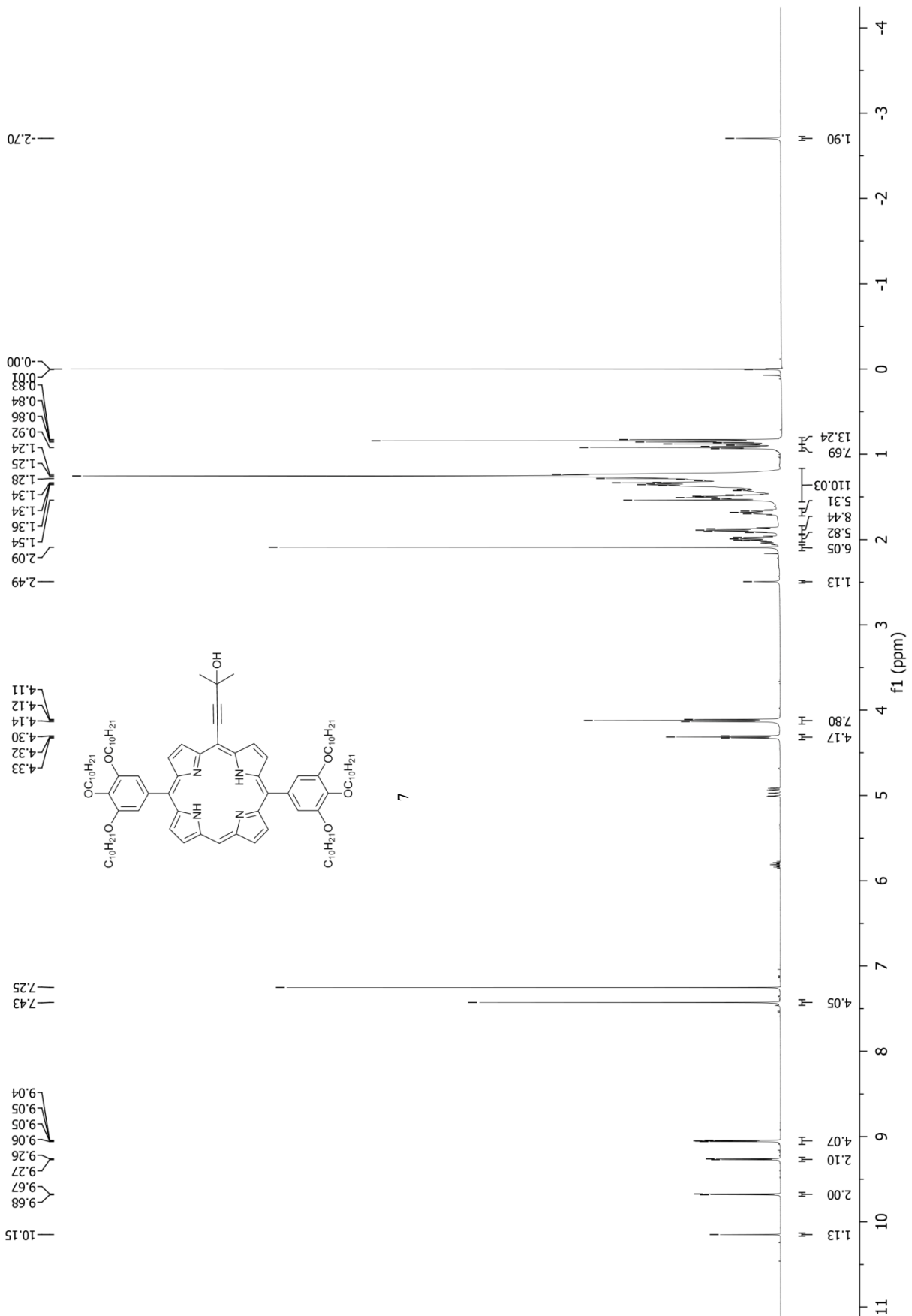
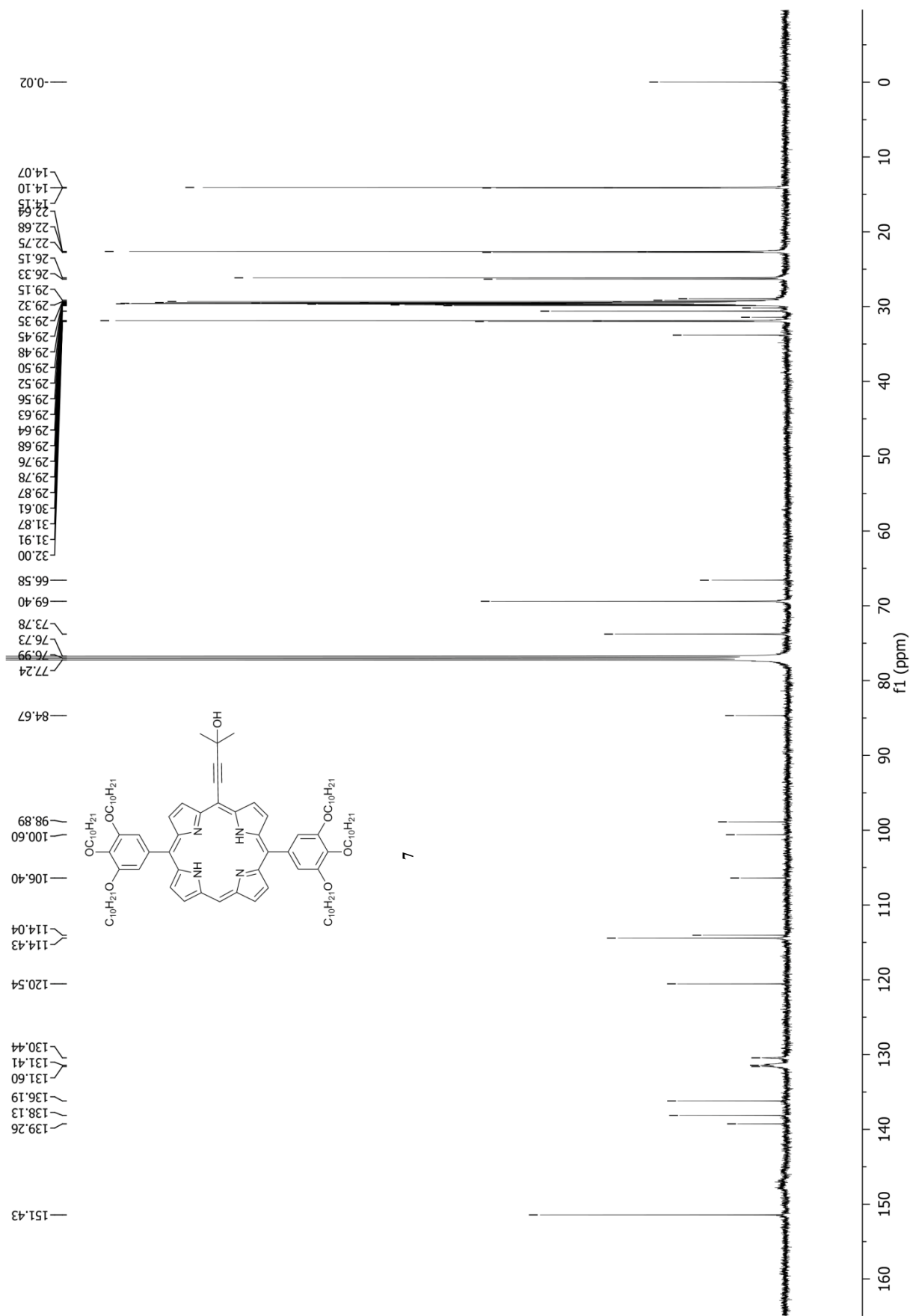
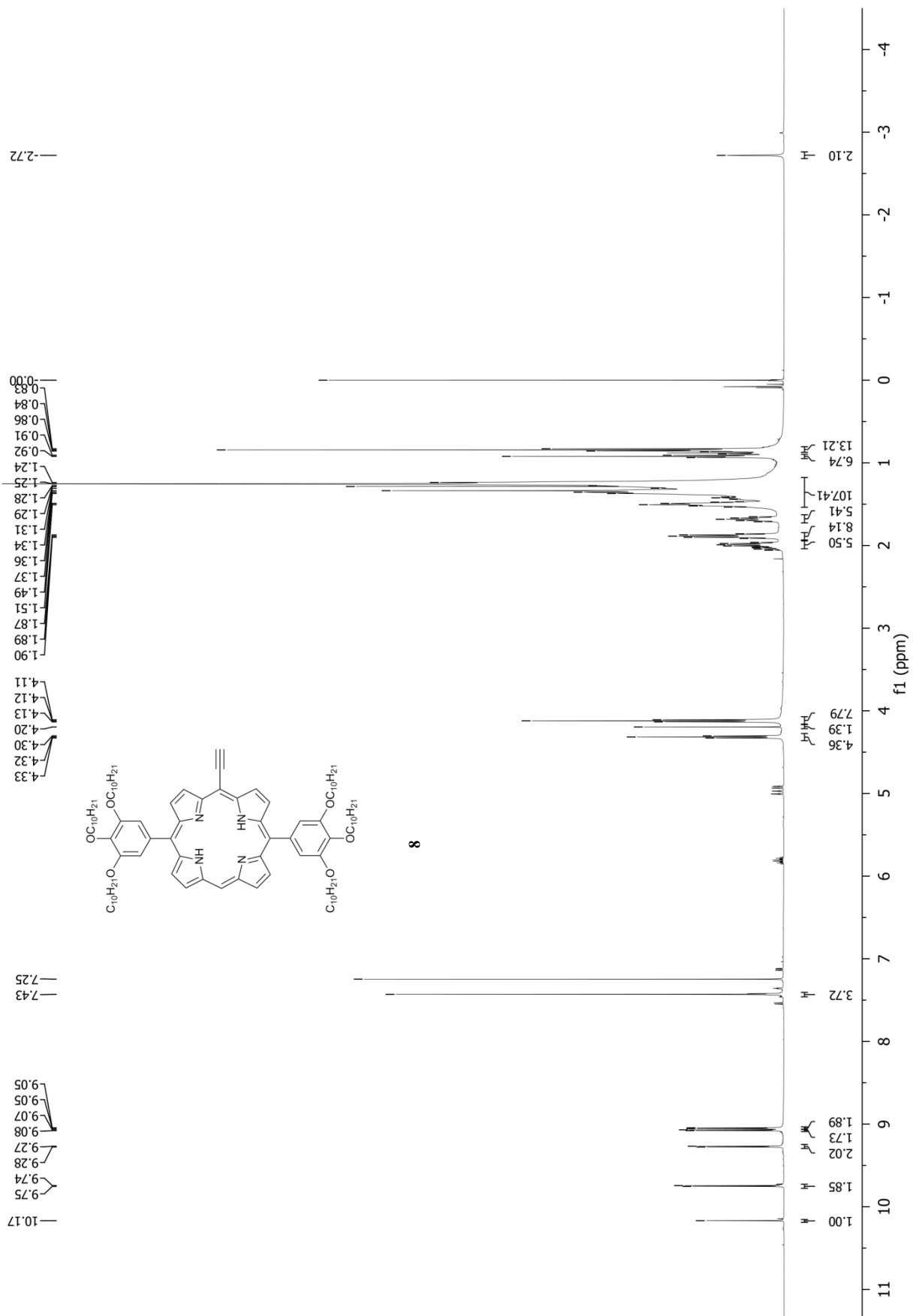
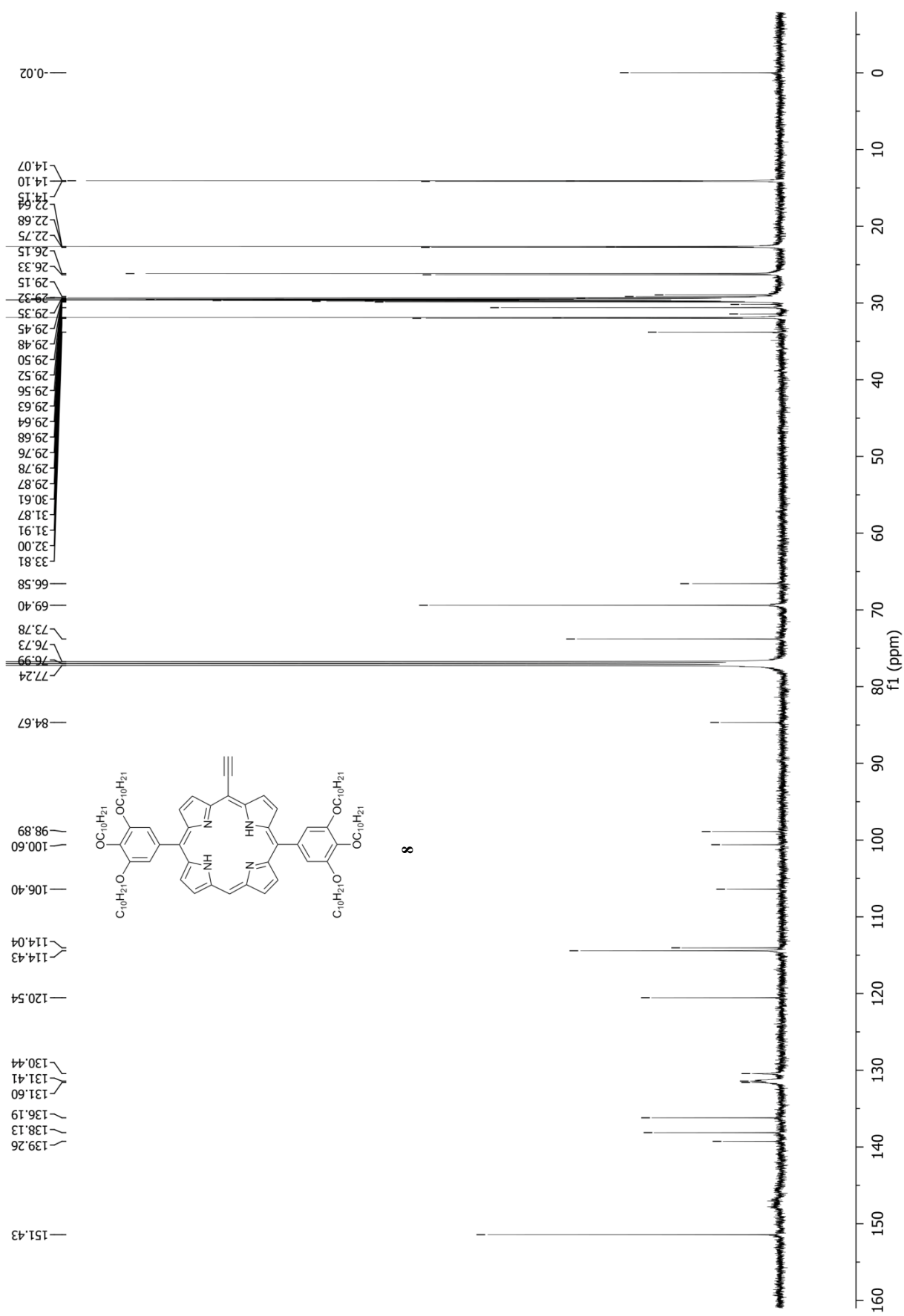


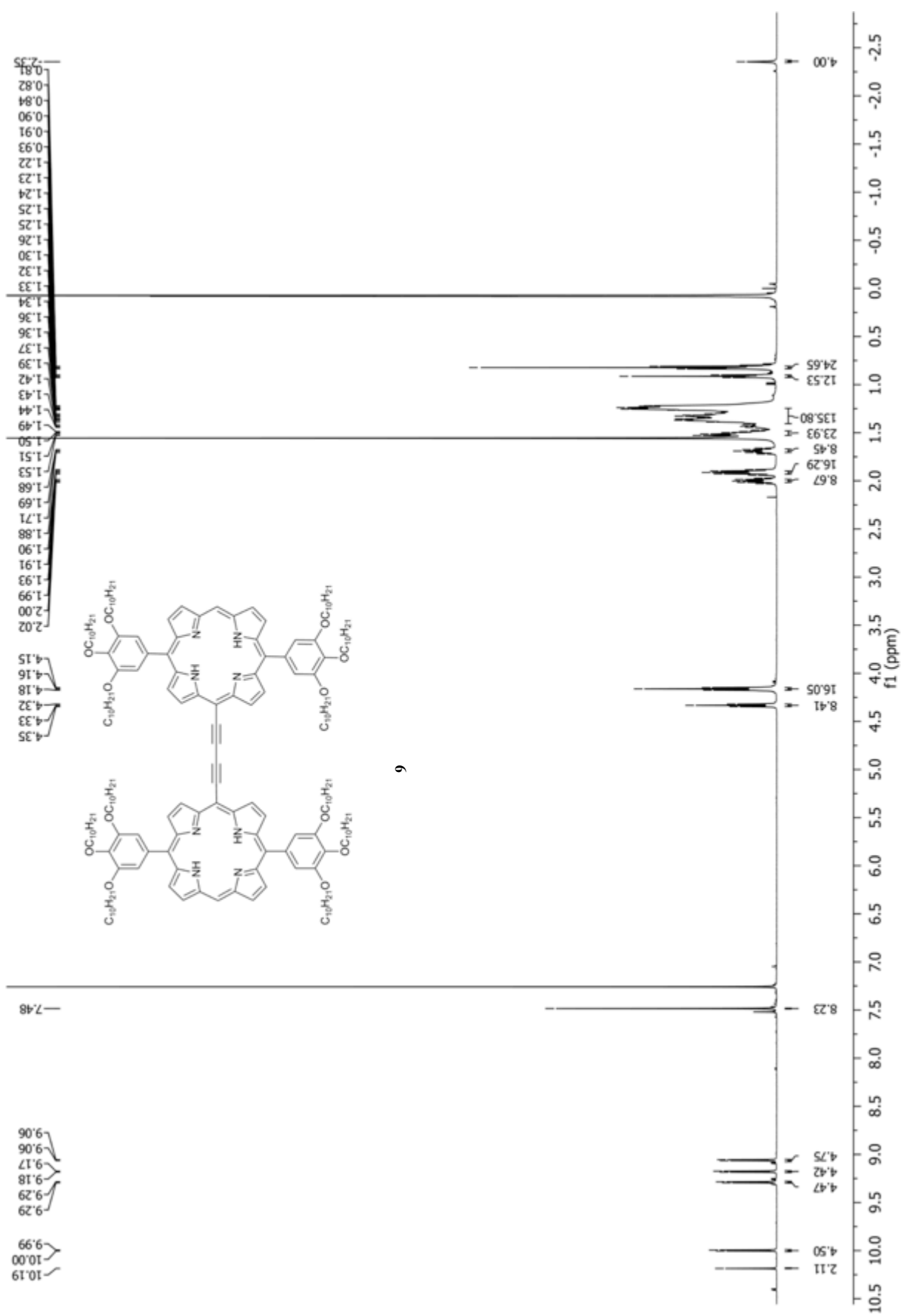
Figure S43 MALDI-TOF MS of R-P2C₈(2H)-R

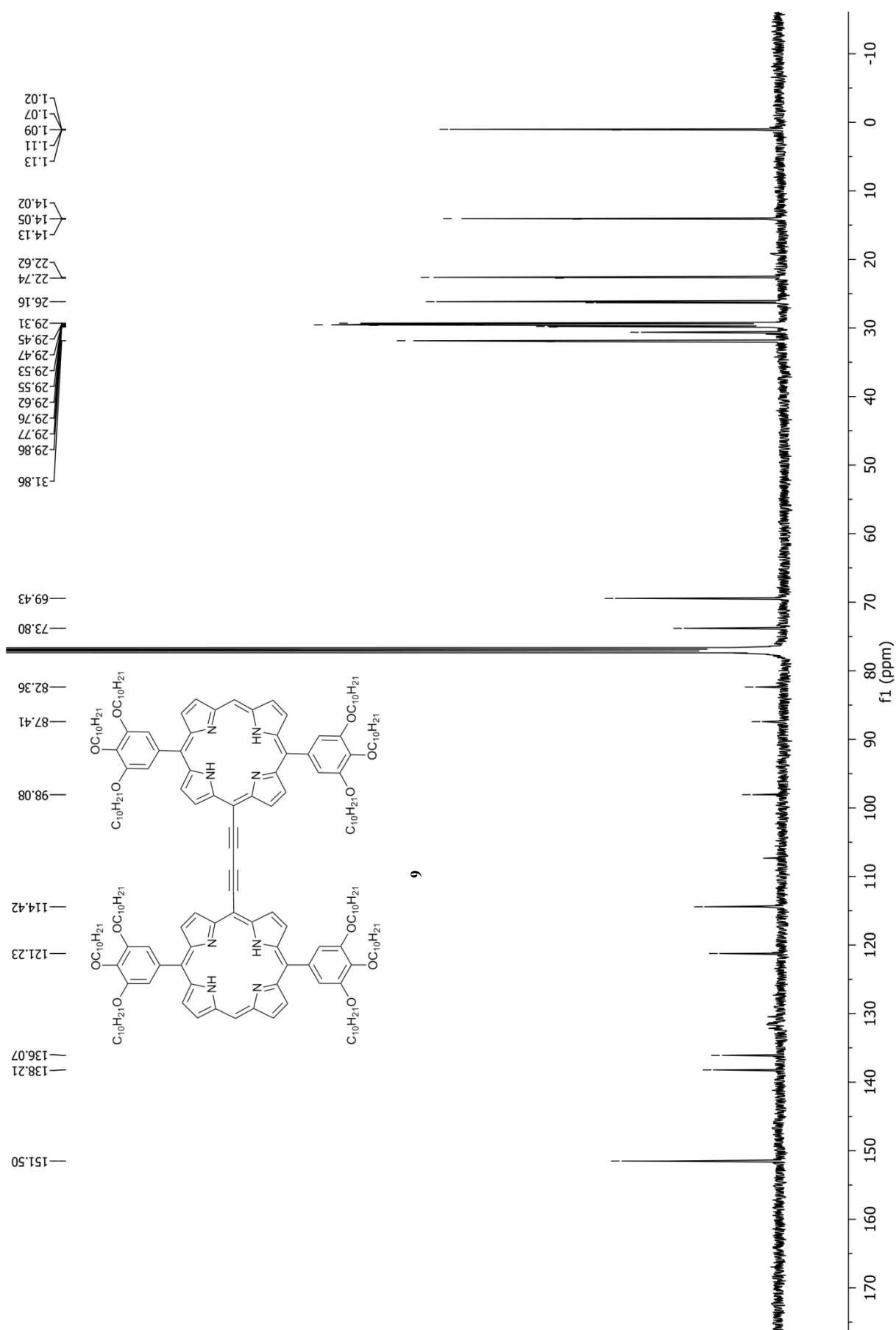


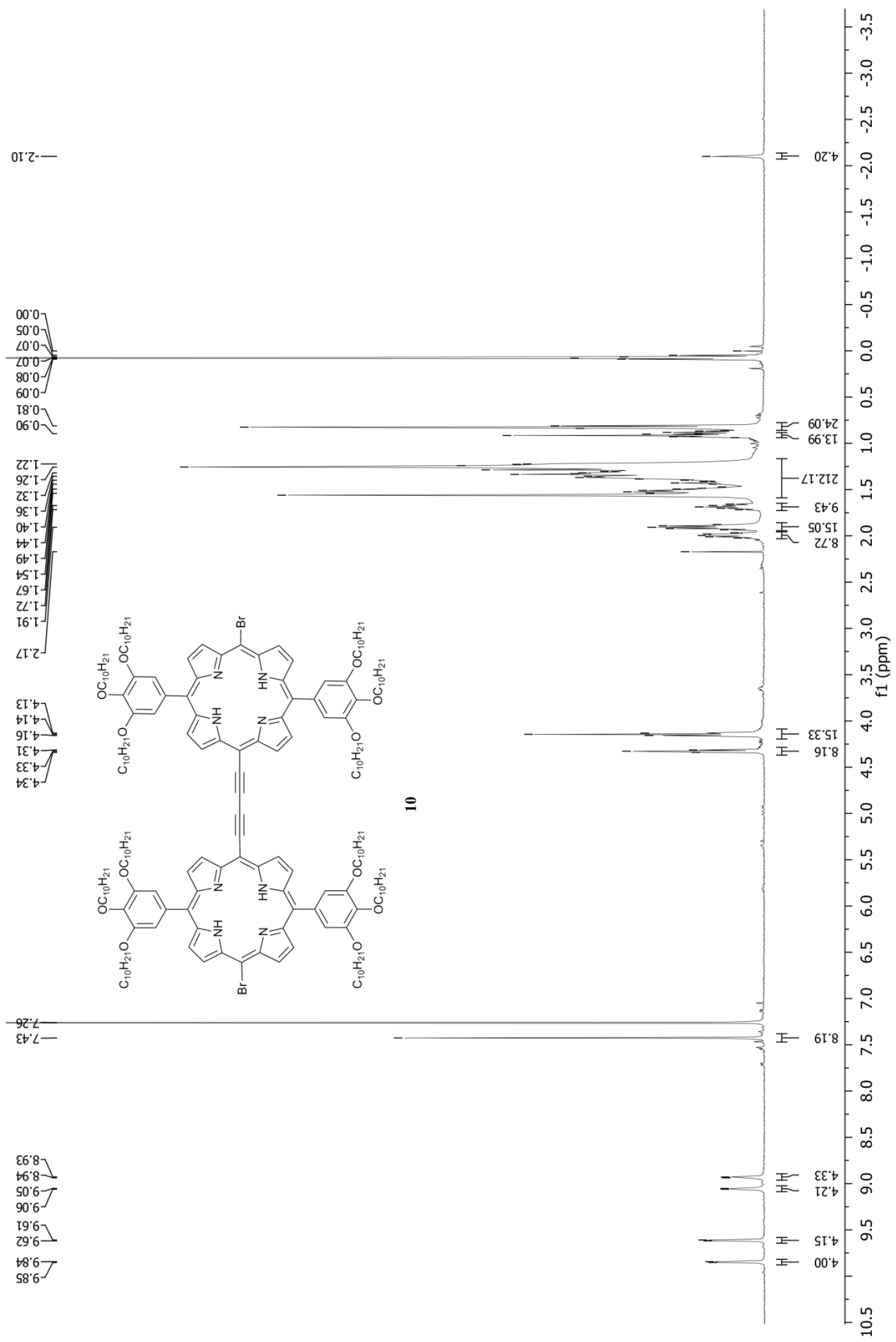


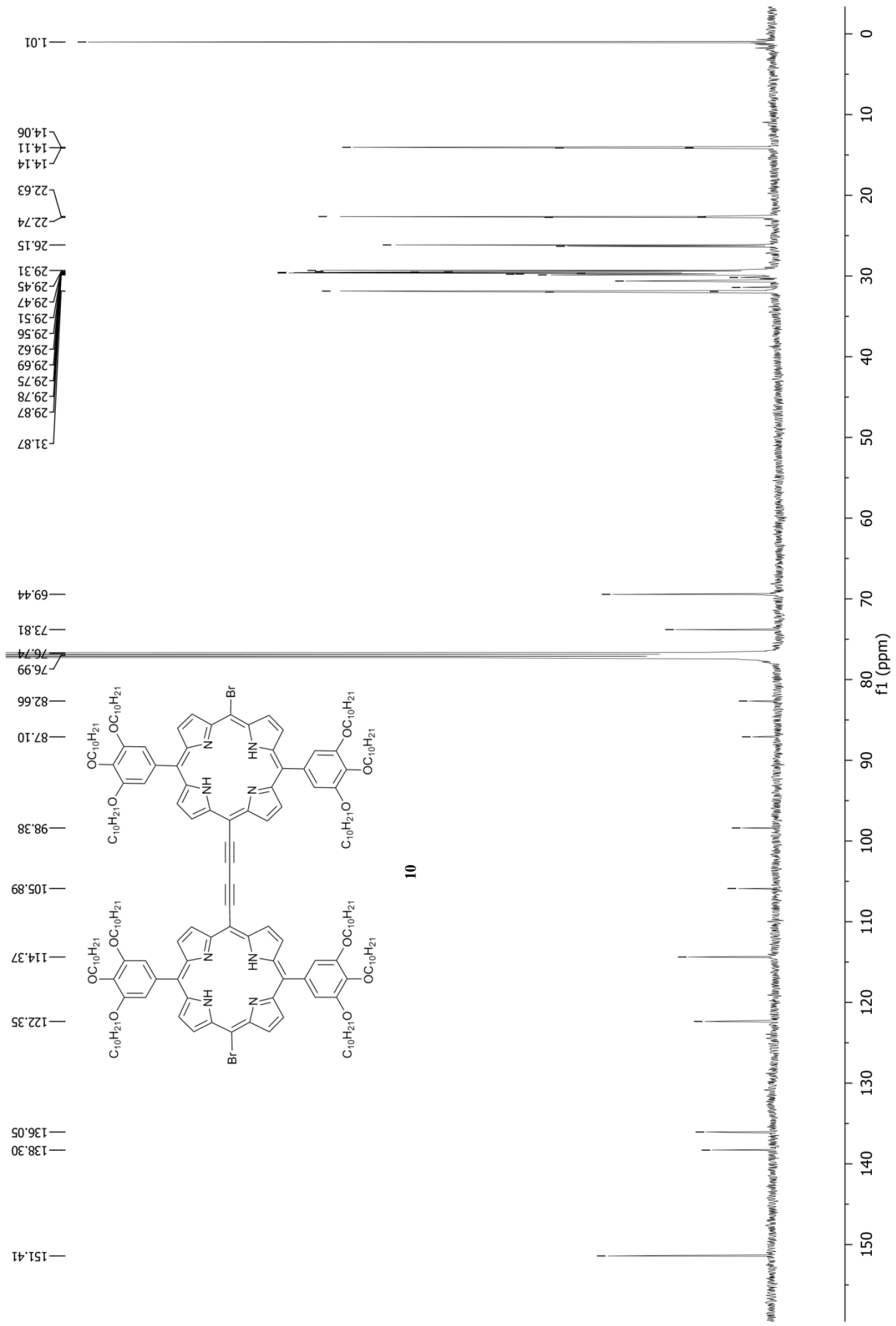


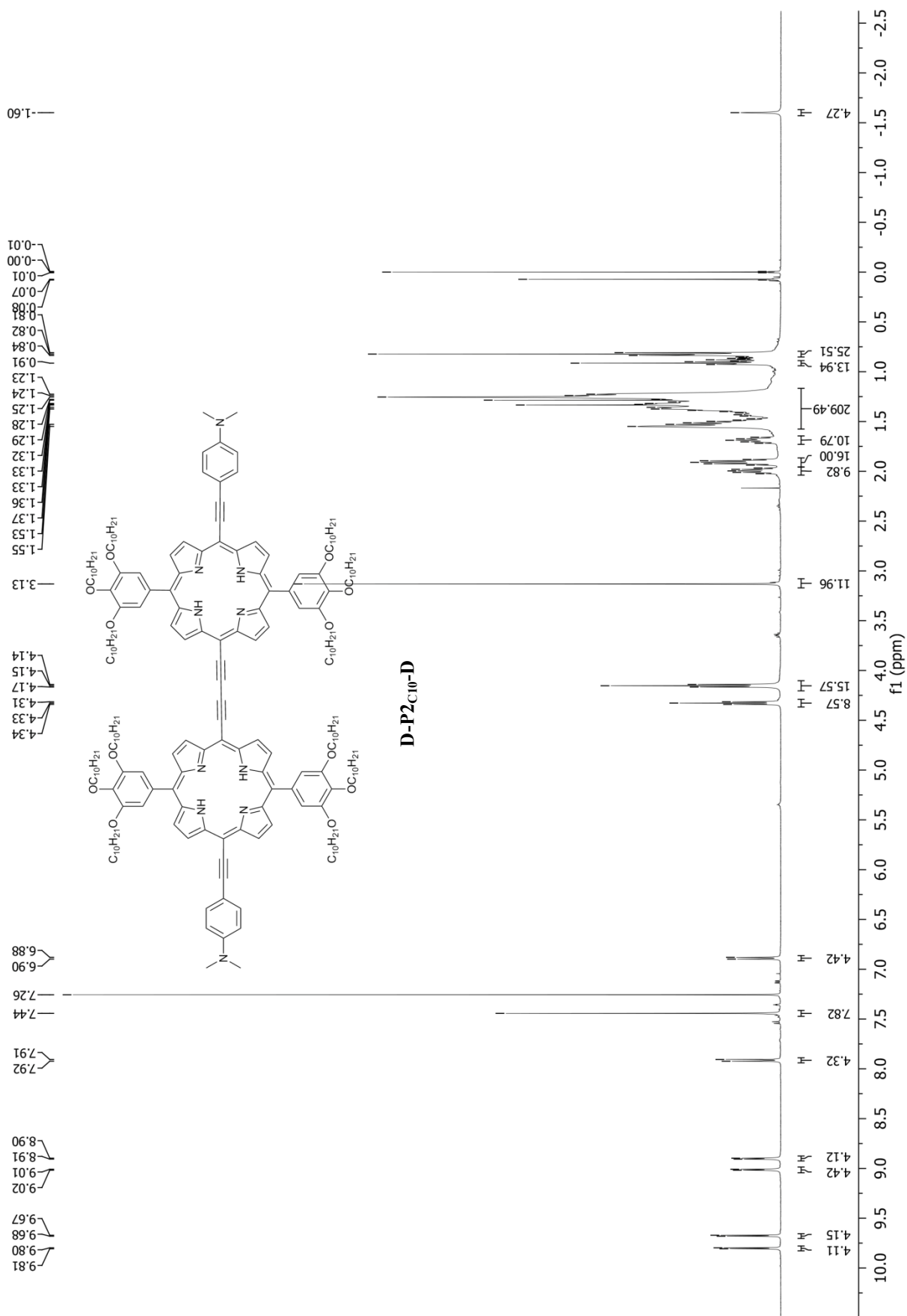


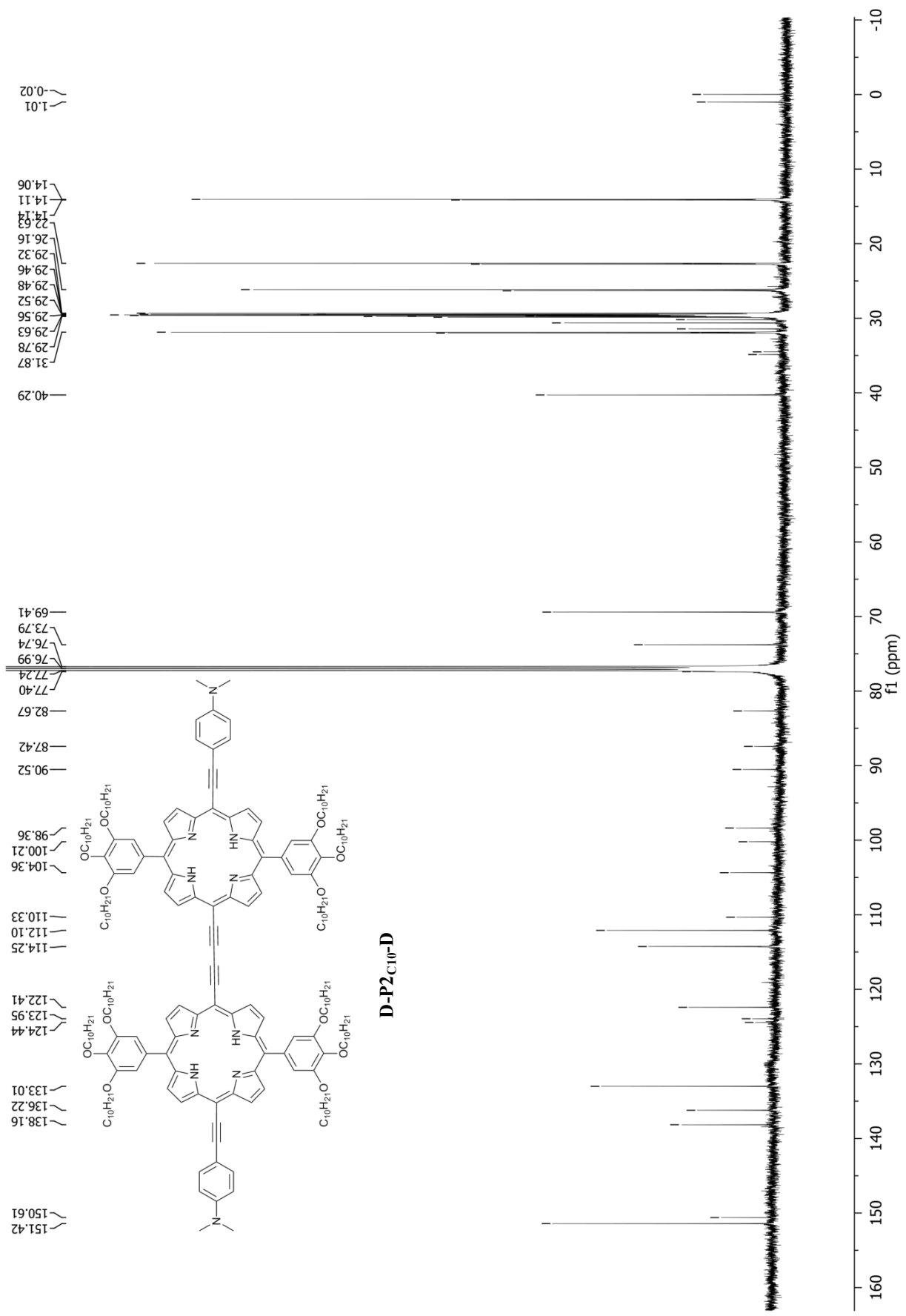


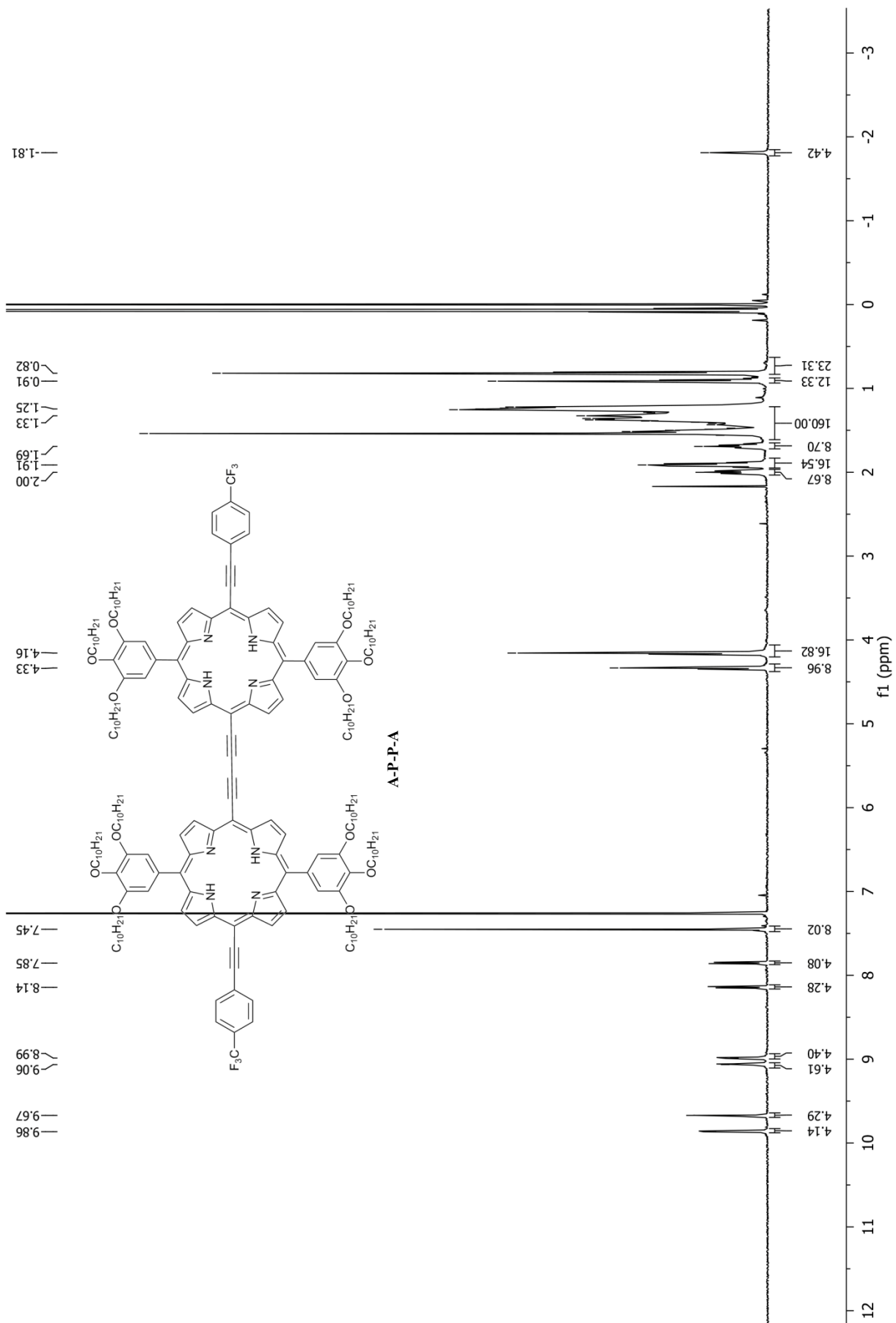


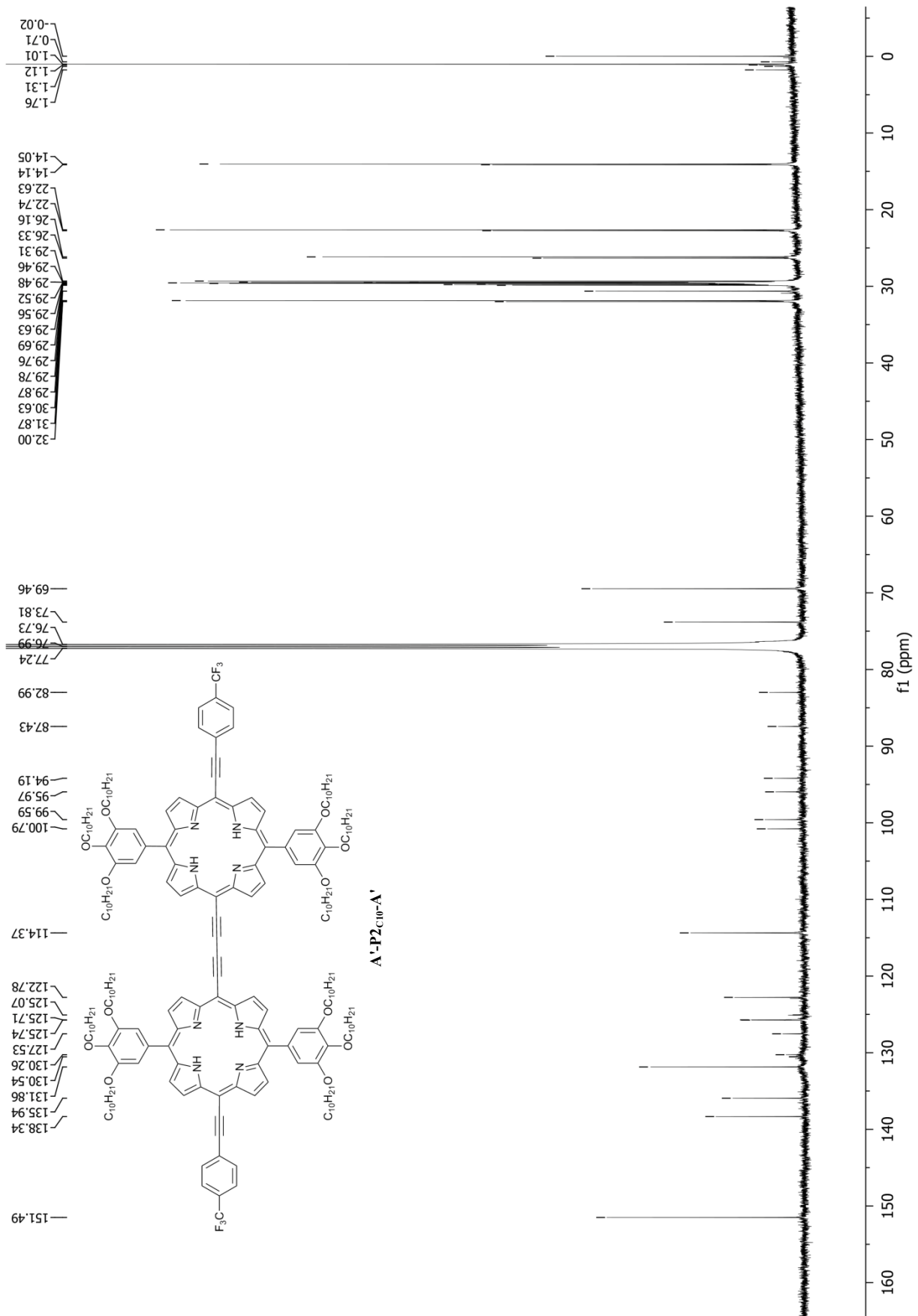


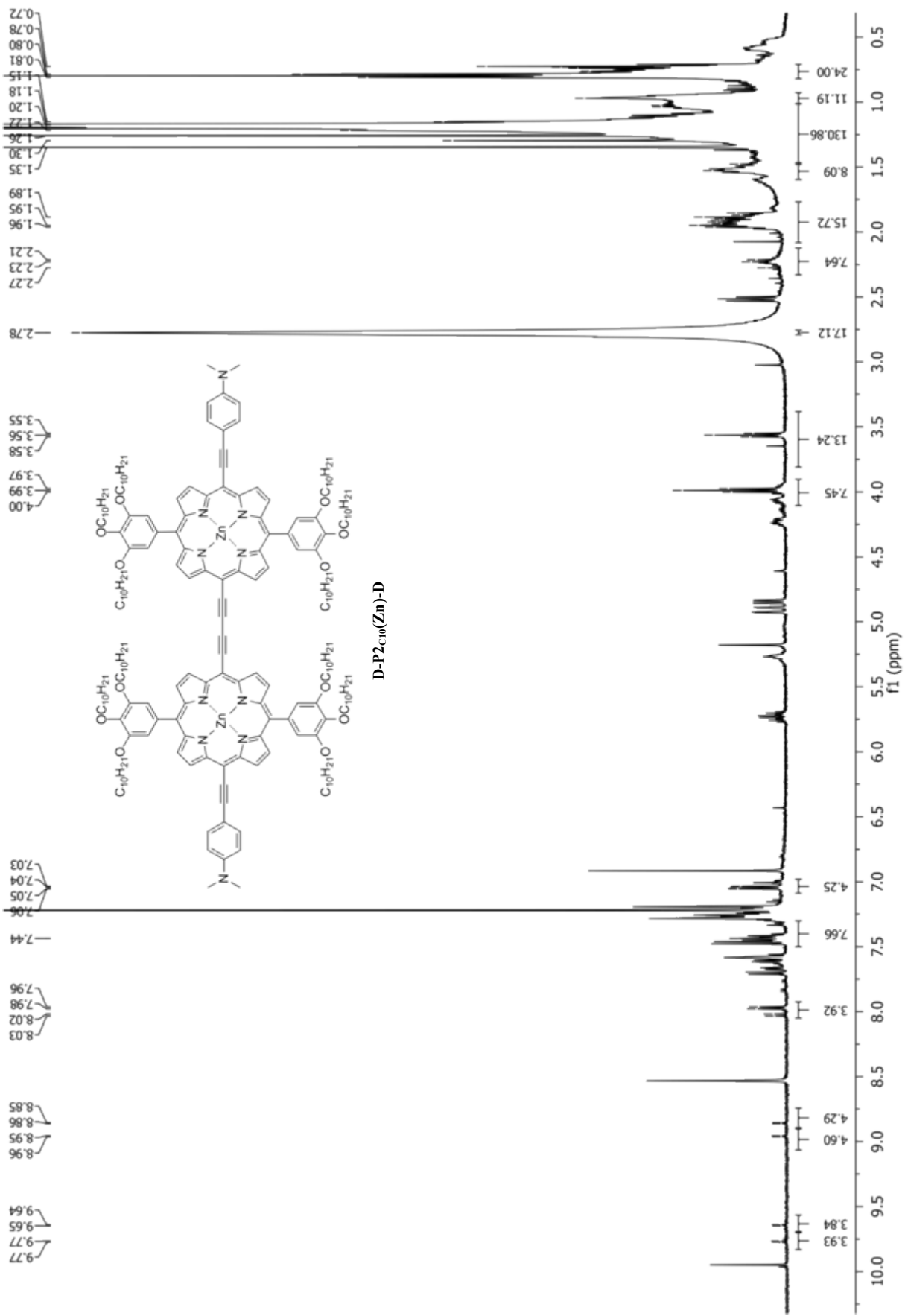


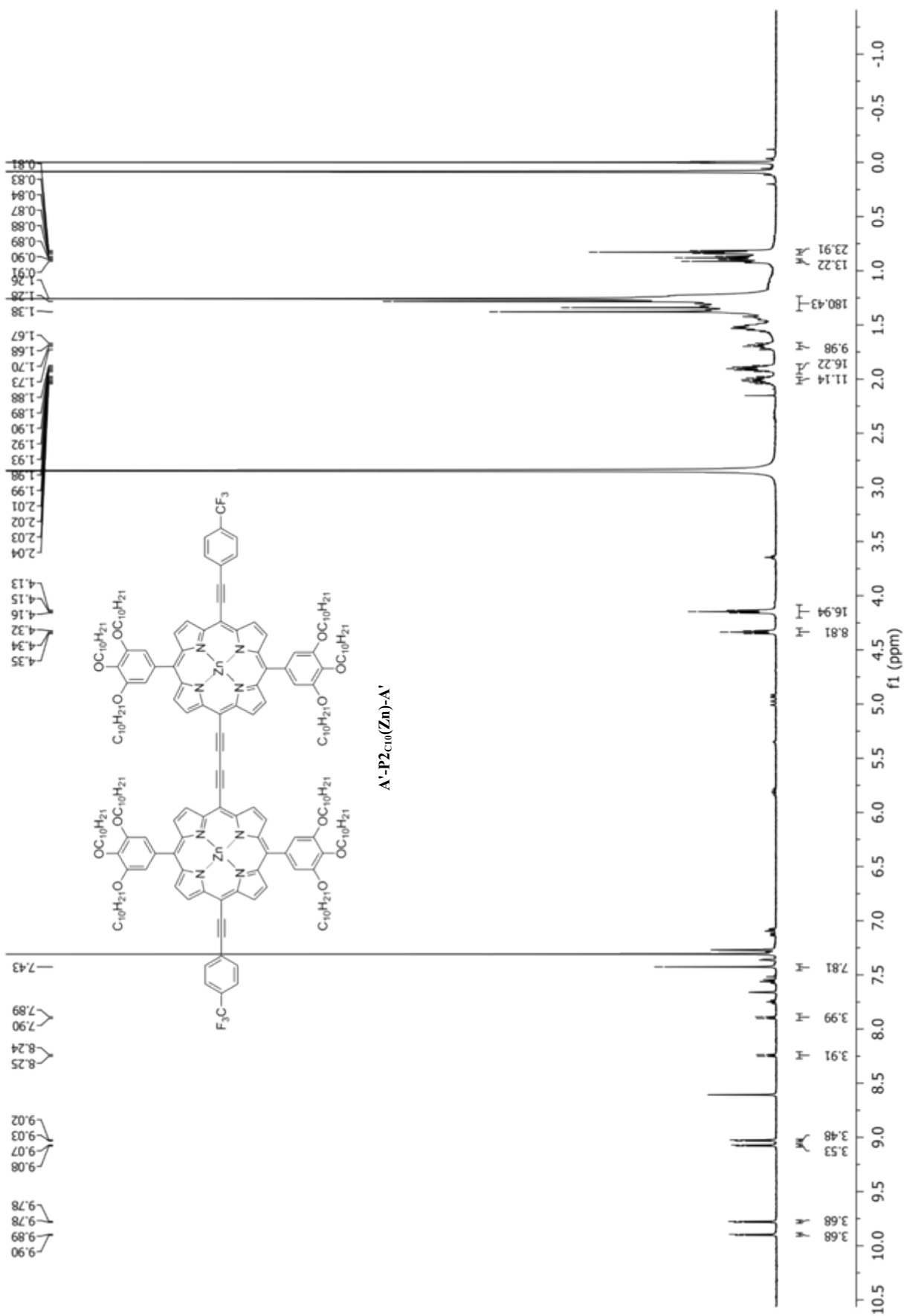






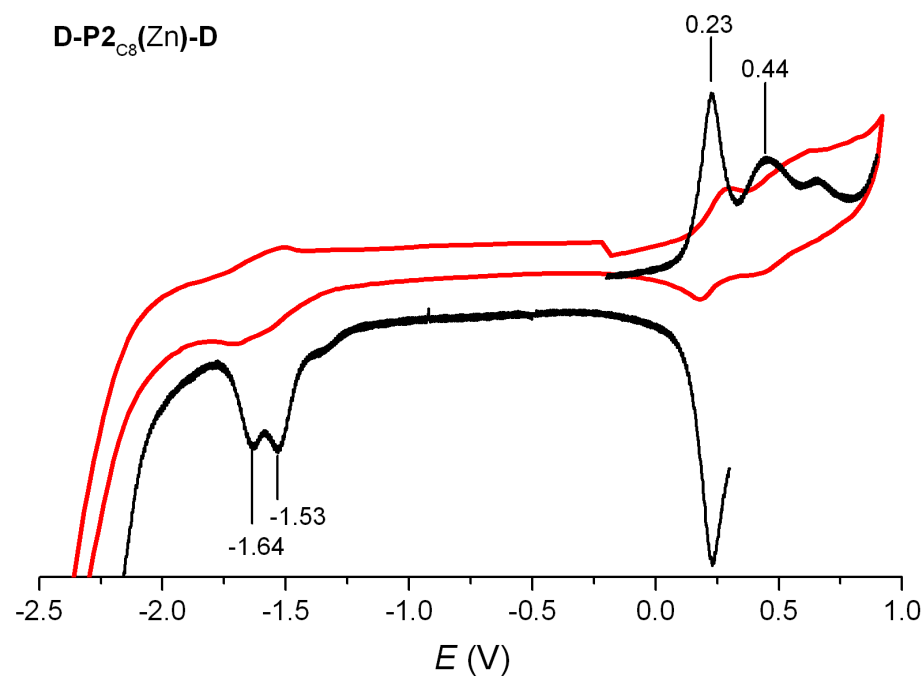
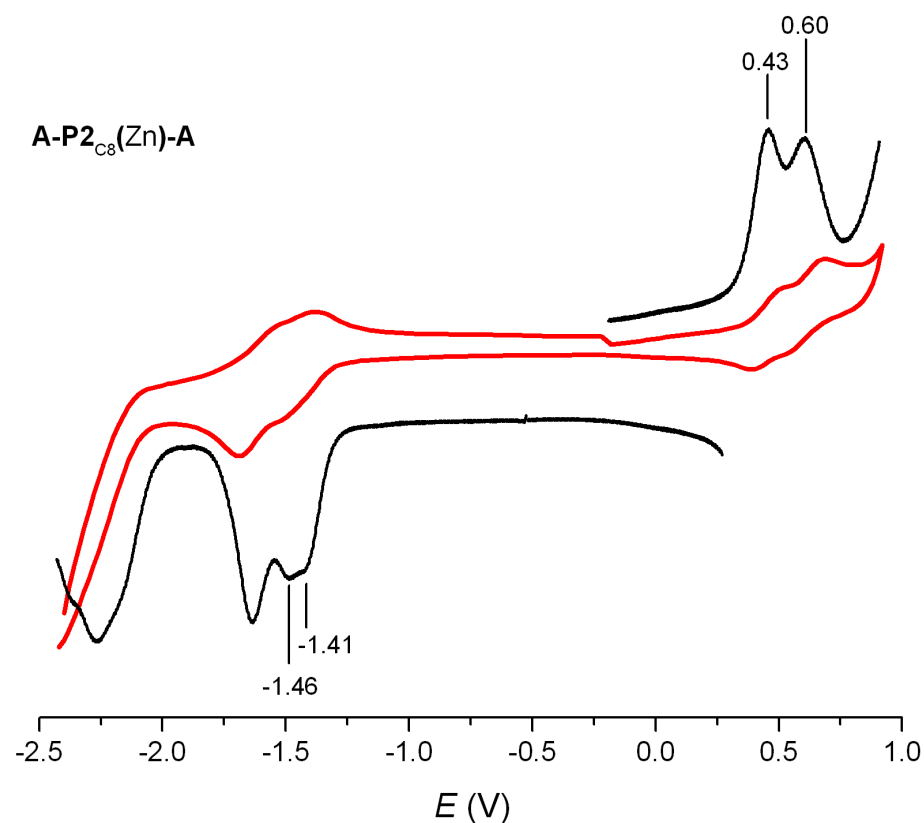






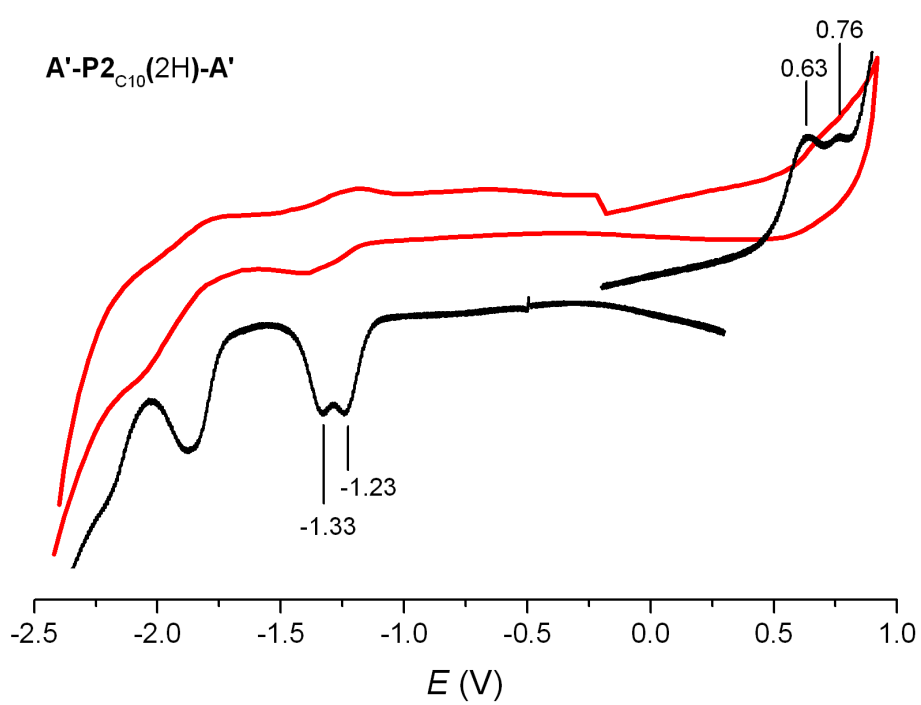
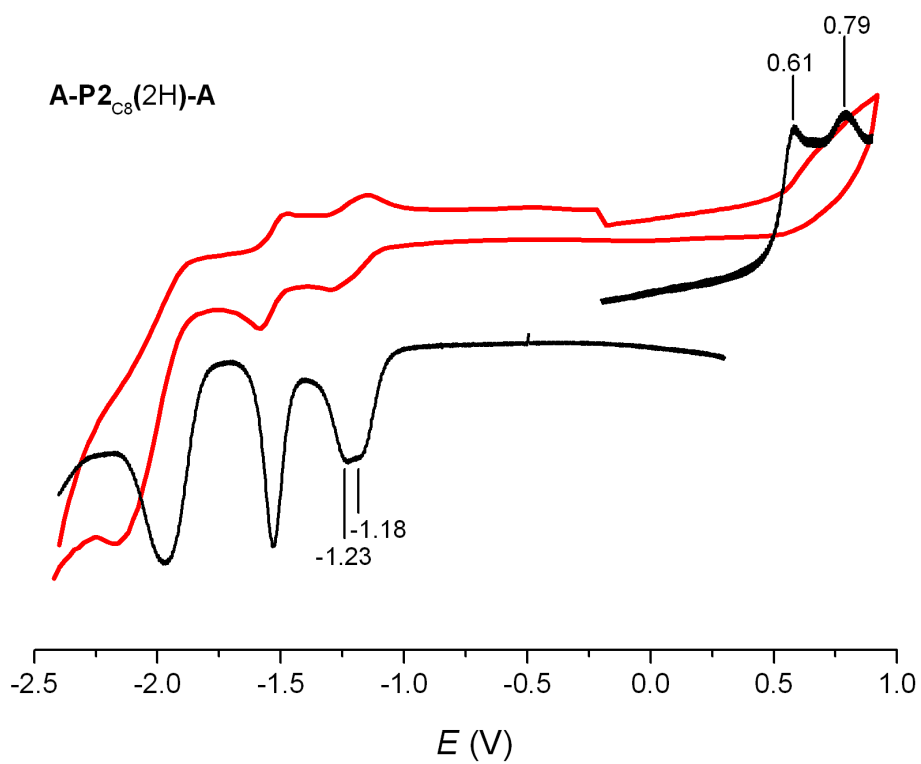
7. Electrochemical Data

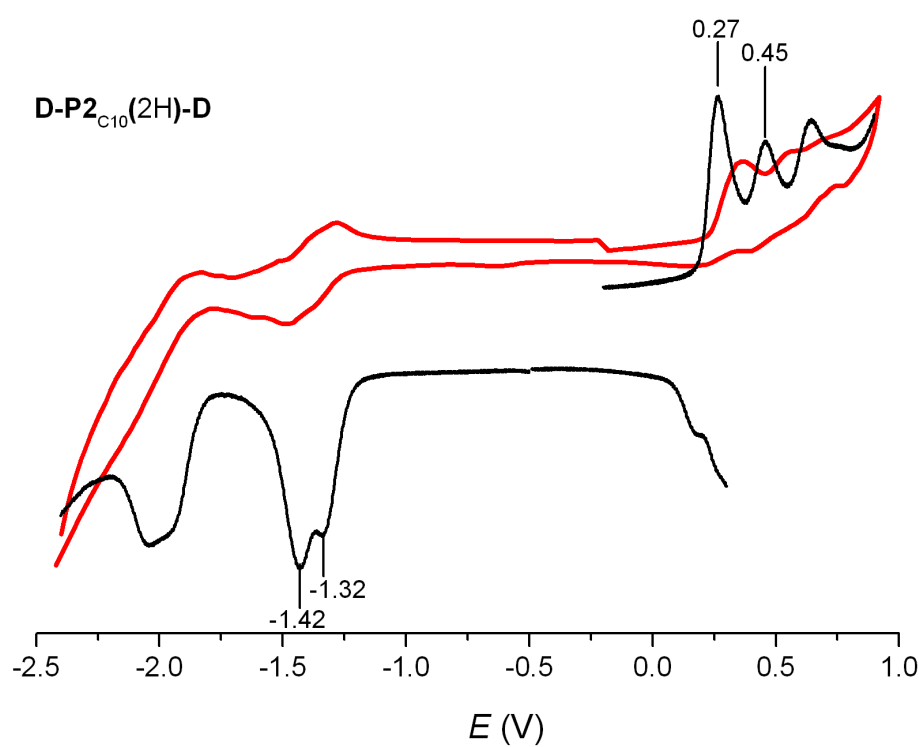
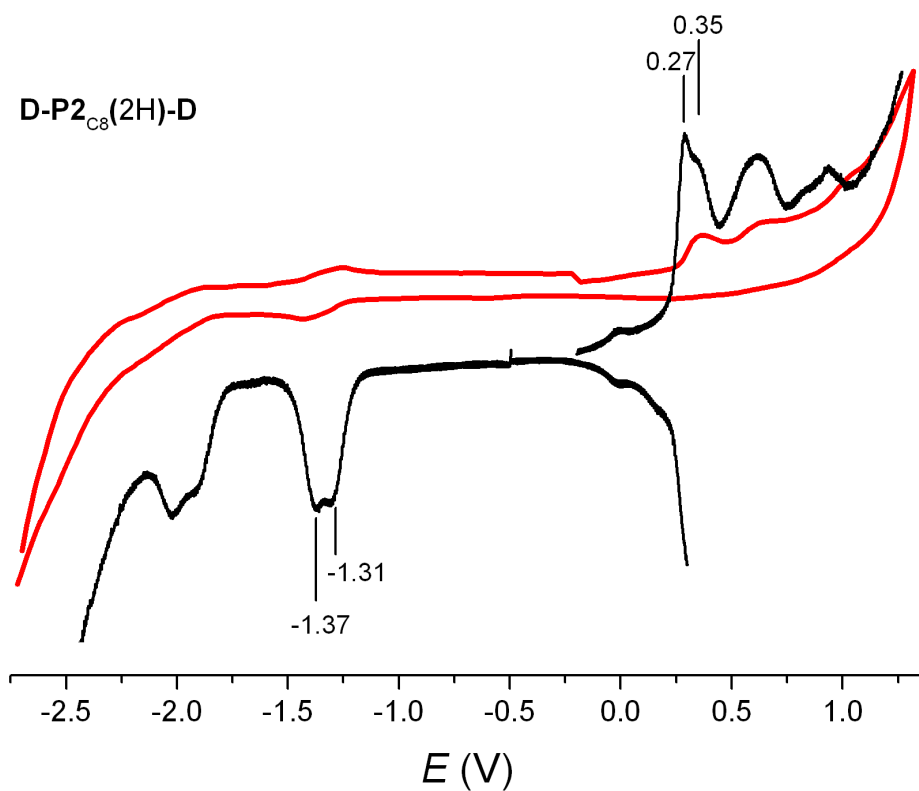
Zn-dimers



Cyclic (red) and square wave (black) voltammograms vs. Fc/Fc^+ with the 1st and 2nd oxidation and reduction potentials labeled. CVs measured in the positive direction first. SW measured from 0.5 towards -ve potential and 0.0 towards +ve potential (relative to the reference electrode).⁵

2H-dimers





Cyclic (red) and square wave (black) voltammograms vs. Fc/Fc^+ with the 1st and 2nd oxidation and reduction potentials labeled. CVs measured in the positive direction first. SW measured from 0.5 towards -ve potential and 0.0 towards +ve potential (relative to the reference electrode).

8. Bibliography

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4. F. Mitzel, C. Boudon, J.-P. Gisselbrecht, P. Seiler, M. Gross and F. Diederich, *Helv. Chim. Acta*, 2004, **87**, 1130–1157.
5. M. U. Winters, E. Dahlstedt, H. E. Blades, C. J. Wilson, M. J. Frampton, H. L. Anderson and B. Albinsson, *J. Am. Chem. Soc.*, 2007, **129**, 4291–4297.