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Electronic Supporting Information

For

Rod-like nanostructures through amphiphilic OPE-Porphyrin self-organization

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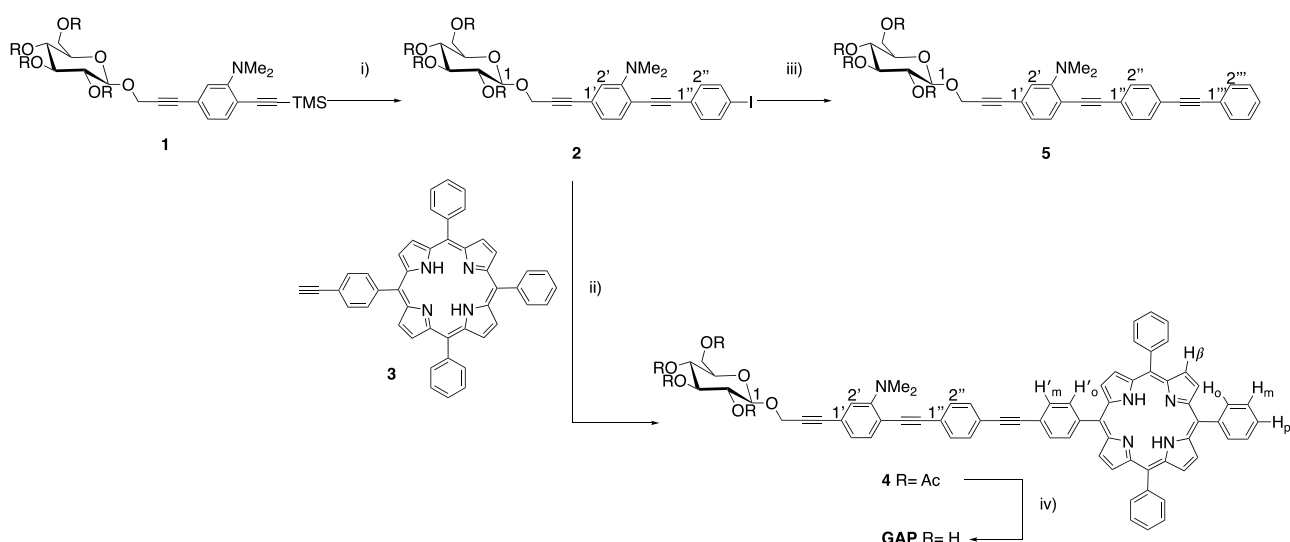
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Chemicals. All Chemicals and solvents were purchased from Merck and, when necessary, purified according to standard procedures. All the syntheses were monitored by TLC on commercially available precoated plates (silica gel 60 F254), and the products were visualized with vanillin [1 g dissolved in MeOH (60 mL) and conc. H₂SO₄ (0.6 mL)] under UV lamp illumination. Silica gel 60 was used for column chromatography.

Instrumentation. Proton (¹H) and carbon (¹³C) NMR spectra were recorded on a Varian 500 spectrometer (at 500 MHz for ¹H; and 125 MHz for ¹³C) using CDCl₃ and, when necessary, MeOD as cosolvents. Chemical shifts are given in parts per million (ppm) (δ) relative to CDCl₃ δ 7.26 ppm for proton and 77.16 ppm for carbon), coupling constants (J) are given in hertz, and the attributions are supported by heteronuclear single-quantum coherence (HSQC) and correlation spectroscopy (COSY) experiments. Mass analysis for final compound (4, 5 and GAP) were performed with a TSQ-Quantum access Triple Quadrupole Mass Spectrometer (Thermo Fisher Scientific, Waltham, MA, USA), equipped with a HESI (Heated ElectroSpray Ionization) source; analyses were run in positive mode. Mass spectrometer parameters were: sheath gas flow rate, 30 (arbitrary units); aux gas flow rate, 15 (arbitrary units); spray voltage, 5.00 kV; capillary temperature, 250° C; tube lens voltage, 55 V; heater temperature, 270° C; scan mode: full scan. UV/vis spectra were obtained on an Agilent model 8453 diode array spectrophotometer using 0.001–1 cm path length quartz cell. When CHCl₃ is used as the solvent, in order to avoid the formation of hydrochloric acid generated at the interface between the light-exposed silica wall and the bulk solvent, a cell with the pure solvent, as neutral filter, was placed on the observation

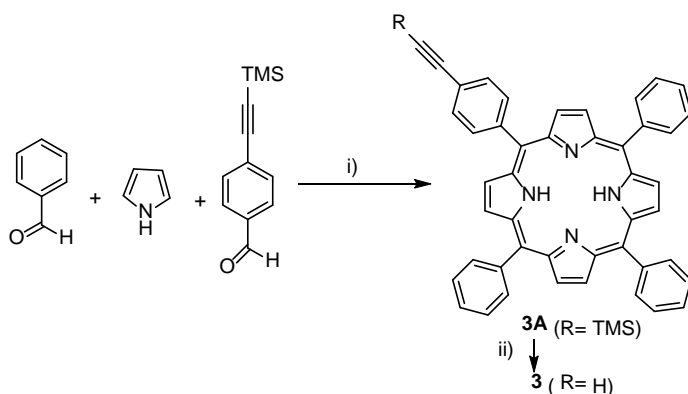
path in the diode array setup between the lamp and the sample cell.¹ A rapid protonation of the porphyrin core and consequent formation of the porphyrin diacid species is clearly evident when filter is absent. Luminescence and resonance light scattering (RLS) spectra were recorded on a Jasco FP-750 spectrofluorimeter adopting a synchronous scan protocol specifically for RLS experiments. The depolarization ratio is defined as $\rho_V(90) = I_{VH}/I_{VV}$, where I_{VH} and I_{VV} are the scattered light intensities with horizontal and vertical polarization, respectively. The different transmission efficiency of polarized light by both excitation and emission monochromators has been accounted for by correcting the I_{VH} value through the equation $\rho_V(90) = G \times I_{VH}/I_{VV}$, where I_{VH} , where $G = I_{HV}/I_{HH}$ is a correction factor. Assuming a parallel arrangement of the transition moments of the exciton-coupled chromophores and applying the model (ref. 45 in the main text) we have calculated the slip angle between adjacent porphyrin planes. The emission spectra were corrected for the absorption of the samples. Time-resolved fluorescence emission measurements were performed on a Jobin Yvon-Spex Fluoromax 4 spectrofluorimeter, using time-correlated single-photon counting technique. The excitation source was a NanoLED at 390, 450 e 590 nm. Dynamic light scattering (DLS) measurements were performed with a Malvern Zetasizer Nano ZS equipped with a 633-nm He-Ne laser and operating at an angle of 173°. The software used to collect and analyze the data was the Dispersion Technology Software from Malvern. For each sample, 15 runs of 10 s were performed, with three repetitions for all the samples. The intensity size distribution, the Z-average diameter (Z-ave), and the polydispersity index (Pdl) were obtained from the autocorrelation function using the “general purpose mode.”



i) 1,4-diiodobenzene, Pd(PPh₃)₄, Ag₂O, THF/DMF (1/1), 60°C, 1h 30 min; *ii)* Pd(PPh₃)₄, Et₃N, DMF, 70°C, 1 h 30 min; *iii)* Ethynylbenzene, Pd(PPh₃)₄, Et₃N, DMF, 70°C, 2 h; *iv)* NH₄OHaq, MeOH/THF (1/1), RT, overnight.

Compound 2. Compound 1² (0.480 g; 0.8 mmol; 1 eq.), 1,4-diiodobenzene (1.18 g; 3.6 mmol; 4.5 eq.), Ag₂O (0.181 g, 0.8 mmol; 1 eq.) and Pd(PPh₃)₄ (0.081 g, 0.08 mmol, 0.1 eq.) were suspended in dry DMF (6 mL) and dry THF (6 mL). The mixture was heated at 60°C and maintained under continuous stirring under Ar atmosphere for 1h 30 min, until the disappearance of 1 by TLC (CH₂Cl₂/Ethyl acetate 95/5). After evaporation of the solvents, the crude product was purified by column chromatography on silica gel with CH₂Cl₂/Ethyl acetate 98/2 as eluant (TLC R_f=0.50 CH₂Cl₂/Ethyl acetate 97/3). Yield 60%. ¹H-NMR (500MHz, CDCl₃) δ 7.69 and 7.25 (4H, d, *J*=7.5 Hz, H-2'', H-3'', H-5'', H-6''), 7.41 (2H, d, *J*=7.5 Hz, H-6'), 7.01-6.92 (3H, m, H-2', H-5'),

5.27 (1H, t, $J_{2,3}=J_{3,4}=9.3$ Hz, H-3), 5.13 (1H, t, $J_{3,4}=J_{4,5}=9.3$ Hz, H-4), 5.04 (1H, dd, $J_{1,2}=8.1$ Hz, $J_{2,3}=9.3$ Hz, H-2), 4.85 (1H, d, $J_{1,2}=8.1$ Hz, H-1), 4.60 (2H, coalescent AB system, $\text{CH}_2\text{C}\equiv$), 4.29 and 4.17 (2H, split AB system, $J_{5,6A}=4.5$ Hz, $J_{5,6B}=2.1$ Hz, $J_{6A,6B}=12.3$ Hz, H₂-6), 3.79-3.74 (1H, m, H-5), 3.01 (6H, s, $\text{N}(\text{CH}_3)_2$), 2.08, 2.06, 2.03 and 2.01 (12H, s, CH_3CO). ^{13}C -NMR (125 MHz, CDCl_3) δ 170.7, 170.3, 169.5, 169.4, 137.9, 137.5, 136.3, 135.5, 134.3, 123.7, 122.9, 115.3, 98.5, 94.1, 89.9, 87.2, 85.6, 72.8, 71.9, 71.2, 68.4, 61.8, 56.9, 43.3, 30.9, 29.7, 20.8, 20.7, 20.6 and 20.5.



i) $\text{CH}_3\text{CH}_2\text{COOH}$, reflux, 1h; ii) K_2CO_3 , EtOH/THF, reflux, 2h.

Compound **3**³ In a 100mL flask 4-((trimethylsilyl)ethynyl)-benzaldehyde (0.296g, 1.34 mmol, 1 eq.) and benzaldehyde (0.8 mL, 7.8 mmol, 5.8 eq.) in propionic acid (40mL); the reaction mixture was heated to reflux temperature (140°C) and pyrrole was added (0.7 mL, 9.10 mmol, 6.8 eq.). The reaction was left under stirring for 1h. The solvent was removed under vacuum and the crude taken up with CHCl_3 . The organic solution was washed three times (x2 100 mL $\text{NaHCO}_{3\text{sat}}$; x1 with 100 mL Brine). The organic phase was dried over Na_2SO_4 , filtered and the solvent removed under reduced pressure. The crude product was then solubilized in hexane/dichloromethane 1/1 and filtered on alumina. The crude was purified via chromatography (Silica Gel; hexane/toluene 1:1) to give **3A**⁴ in 15.4% yield. **3A** (0.125 g, 0.19 mmol) and 0.056 mg of K_2CO_3 (0.41 mmol) were suspended in 20 mL of EtOH/THF 1/3. The mixture was kept under continuous stirring at reflux temperature for 2h, until disappearance of the starting product by TLC (hexane/ CH_2Cl_2 1/1). The reaction crude was filtered and the solid was washed on the filter with CH_2Cl_2 and CHCl_3 . After drying of the mother liquors on anhydrous Na_2SO_4 , evaporation under vacuum gave **3** in 42.2% yield.

Compound **4**. Porphyrin derivative **3** (0.100 g, 0.15 mmol, 2.5 eq.), compound **2** (0.040 g, 0.06 mmol, 1 eq.), $\text{Pd}(\text{PPh}_3)_4$ (8 mg, 6.8×10^{-6} mol, 0.12 eq.) and dry Et_3N (1 mL) were dissolved in dry DMF (1 mL). The mixture was heated at 70°C and maintained under continuous stirring under Ar atmosphere for 1h 30 min, until the disappearance of **2** by TLC (CH_2Cl_2 /Ethyl acetate 95/5). After evaporation of the solvent, the crude product was purified by column chromatography on silica gel with CH_2Cl_2 /Ethyl acetate 98/2 as eluant (TLC $R_f=0.70$ CH_2Cl_2 /Ethyl acetate 97/3). Yield 58%. ^1H -NMR (500 MHz, CDCl_3) δ 8.89-8.87 (8H, m, H_β pyr), 8.24 (8H, m, H_o , H'_o), 7.94 (2H, d, $J=8.0$ Hz, H'_m); 7.79 (9H, m, H_m , H_p), 7.67 and 7.60 (4H, AA'XX' system, $J=8.0$ Hz, H-2", H-3", H-5", H-6"), 7.47 (1H, d, $J=7.5$, H-6'), 7.08 (1H, s, H-2'), 7.01 (1H, d, $J=7.5$ Hz, H-5'), 5.30 (1H, t, $J_{2,3}=J_{3,4}=9.3$ Hz, H-3), 5.16 (1H, t, $J_{3,4}=J_{4,5}=9.3$ Hz, H-4), 5.08 (1H, dd, $J_{1,2}=8.1$ Hz, $J_{2,3}=9.3$ Hz, H-2), 4.87 (1H, d, $J_{1,2}=8.1$ Hz, H-1), 4.63 (2H, coalescent AB system, $\text{CH}_2\equiv\text{C}$), 4.31 and 4.17 (2H, split AB system, $J_{5,6A}=4.5$ Hz, $J_{5,6B}=2.1$ Hz, $J_{6A,6B}=12.3$ Hz, H₂-6), 3.80- 3.77 (1H, m, H-5), 3.06 (6H, s, $\text{N}(\text{CH}_3)_2$), 2.12, 2.10, 2.06 and 2.04 (12H, s, CH_3CO), -2.76 (2H, s, NH pyr). ^{13}C -NMR (125MHz CDCl_3) δ 170.6, 170.3, 169.5, 169.4, 154.5, 142.6, 142.2, 134.6, 134.5, 134.3, 131.8, 131.7, 131.5, 131.3, 130.0, 127.7, 126.6, 123.6, 123.5, 123.1, 122.9, 122.5, 120.4, 120.3, 120.1, 119.0, 115.3, 98.4, 96.2, 91.3, 90.5, 90.3, 87.2, 84.6, 72.8, 71.9, 71.1, 68.3, 61.8, 56.9, 43.3, 20.8, 20.7, 20.6 and 20.5. ESI (m/z) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{79}\text{H}_{64}\text{N}_5\text{O}_{10}^+$ 1242.46, found: 1242.42. UV-vis (CHCl_3): $\lambda_{\text{max}} = 278$ nm, 327 nm, 370 nm, 421 nm, 517 nm, 552 nm, 592 nm, 647 nm. Fluorescence Emission (CHCl_3): 654 nm, 718 nm.

Compound **5**. Ethynylbenzene (0.060 g, 0,6 mmol, 5 eq.), compound **2** (0,090 g, 0,12 mmol, 1 eq.), Pd(PPh₃)₄ (0.004 g, 0,012 mmol, 0.1 eq.) and dry Et₃N (1 mL) were dissolved in dry DMF (1 mL).⁵ The mixture was heated at 70 °C and maintained under continuous stirring under Ar atmosphere for 2 hours, until the disappearance of **2** by TLC (CH₂Cl₂/Ethyl acetate 95/5). After evaporation of the solvent, the crude product was purified by column chromatography on silica gel with CH₂Cl₂/Ethyl acetate 98/2 as eluant (TLC R_f=0.50 CH₂Cl₂/Ethyl acetate 99/1). Yield 67%. ¹H-NMR (500 MHz, CDCl₃) δ 7.60-7.47 (6H, m, H-2'', H-3'', H-5'', H-6'', H-2''', H-6'''), 7.42 (1H, d, *J*=7.5 Hz, H-6'), 7.40-7.30 (3H, m, H-3''', H-4''', H-5'''), 7.03-6.88 (2H, m, H-5', H-2') 5.27 (1H, t, *J*_{2,3}=*J*_{3,4}= 9.3 Hz, H-3), 5.13 (1H, t, *J*_{3,4}=*J*_{4,5}= 9.3 Hz, H-4), 5.04 (1H, dd, *J*_{1,2}=8.1 Hz, *J*_{2,3}= 9.3 Hz, H-2), 4.85 (1H, d, *J*_{1,2}=8.1 Hz, H-1), 4.60 (2H, coalescent AB system, CH₂C≡), 4.29 and 4.17 (2H, split AB system, *J*_{5,6A}= 4.5 Hz, *J*_{5,6B}= 2.1 Hz, *J*_{6A,6B}= 12.3 Hz, H₂-6), 3.79-3.74 (1H, m, H-5), 3.01 (6H, s, N(CH₃)₂), 2.08, 2.06, 2.03 and 2.01 (12H, s, CH₃CO). ¹³C-NMR (125 MHz, CDCl₃) δ 170.8, 170.3, 169.5, 169.4, 154.5, 134.3, 131.6, 131.5, 131.2, 128.5, 128.4, 123.6, 123.3, 123.1, 123.0, 122.8, 120.3, 115.4, 98.4, 96.2, 91.3, 90.4, 89.1, 87.2, 84.5, 72.8, 71.9, 71.2, 68.4, 61.8, 57.1, 43.3, 20.8, 20.7, 20.6, 20.5. ESI (m/z) [M+H]⁺ calcd for C₄₁H₄₀NO₁₀⁺ 706.26, found: 706.33.

GAP. Compound **4** (0.05 g, 0.02 mmol, 1eq.) was dissolved in MeOH (2 mL) and THF (2 mL), then a large excess of aqueous ammonia (28% w/v, 1 mL) was slowly added. The reaction was maintained under continuous stirring at room temperature overnight, until the disappearance of compound **4** by TLC (CH₂Cl₂/Ethyl acetate 99/1). The solvents were removed under reduced pressure. The recovered solid underwent washings with Et₂O (3 mL x 3) to eliminate undesired acetamide. **GAP** was obtained in quantitative yield. ¹H NMR (500 MHz, CDCl₃/CD₃OD 13/1) δ 8.8-8.6 (8H, br s, H_β-pyr), 8.2-8.16 (8H, m, H_o, H'_o), 7.77 (2H, d, *J*=8.0 Hz, H'_m), 7.74-7.64 (9H, m, H_m, H_p), 7.64 and 7.53 (4H, d, *J*= 8.0 Hz, H-2'', H-3'', H-5'', H-6''), 7.40 (1H, d, *J*= 7.5 Hz, H-6'), 6.97 (1H, s, H-2'), 6.94 (1H, d, *J*= 7.5 Hz, H-5'), 4.63 and 4.59 (2H, AB system, *J*=12.3 Hz, CH₂C≡C), 4.50 (1H, d, *J*=8.0 Hz, H-1), 3.90-3.40 (2H, m, H₂-6), 3.52- 3.12 (4H, m, H-2, H-3, H-4, H-5), 2.97 (6H, s, N(CH₃)₂). ¹³C NMR (125 MHz, CDCl₃/CD₃OD 13/1) δ 154.3, 142.3, 141.9, 134.5, 134.4, 134.1, 131.6, 131.3, 131.1, 129.8, 129.6, 127.6, 126.6, 123.7, 123.4, 123.0, 122.9, 122.4, 120.2, 118.9, 115.3, 101.0, 96.0, 91.1, 90.3, 90.2, 86.7, 85.1, 76.2, 75.8, 73.3, 69.8, 61.6, 57.0, 43.2. ESI (m/z) [M+H]⁺ calcd for C₇₁H₅₆N₅O₆⁺ 1074.42, found: 1074.42. UV-vis (CHCl₃): λ_{max} = 288 nm, 327 nm, 370 nm, 421 nm, 517 nm, 552 nm, 592 nm, 647 nm. Fluorescence Emission (CHCl₃): 654 nm, 718 nm.

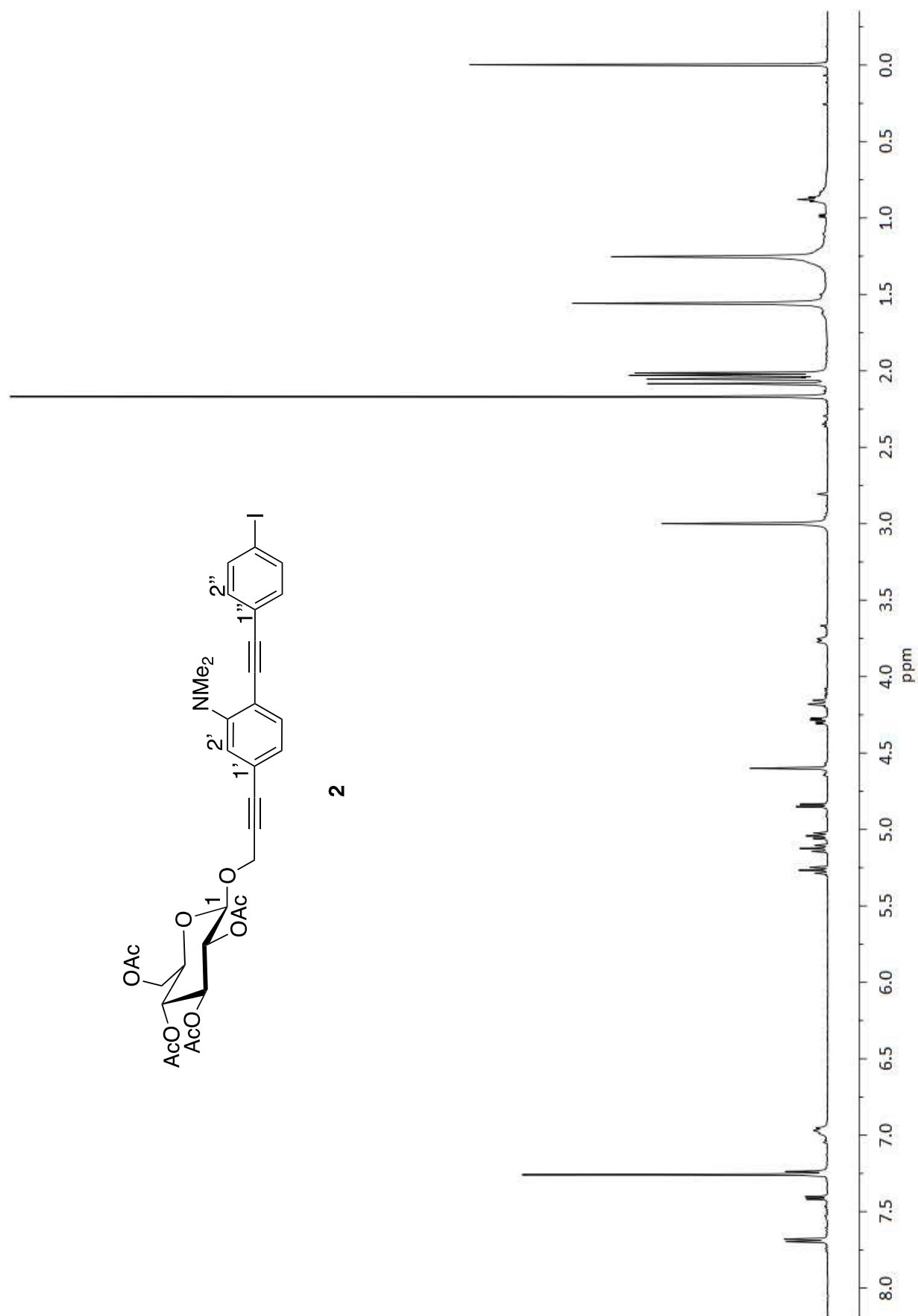


Figure S1 ¹H NMR of compound **2** in CDCl₃

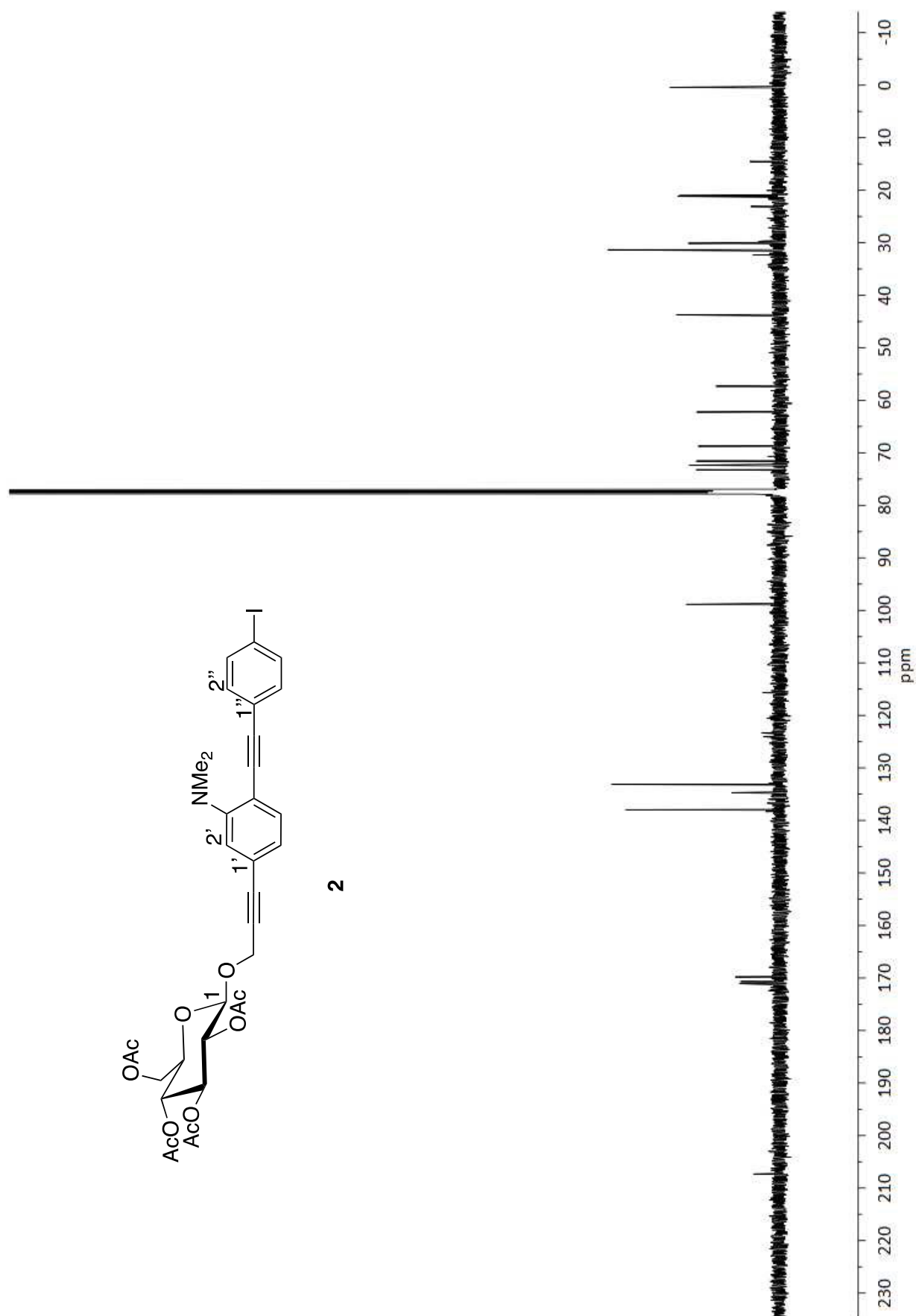


Figure S2. ^{13}C NMR of compound **2** in CDCl₃

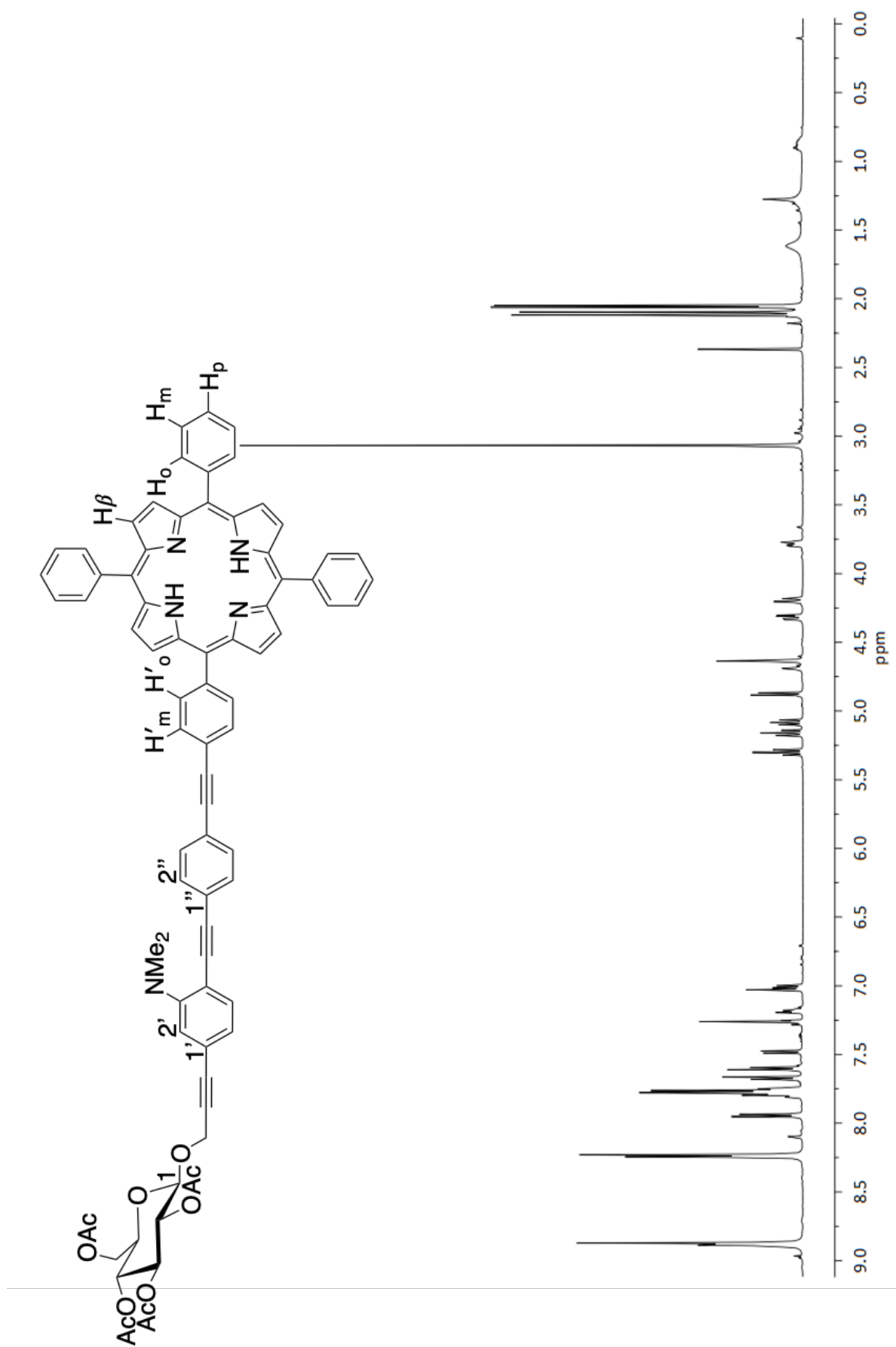


Figure S3. ¹H NMR of compound 4 in CDCl₃

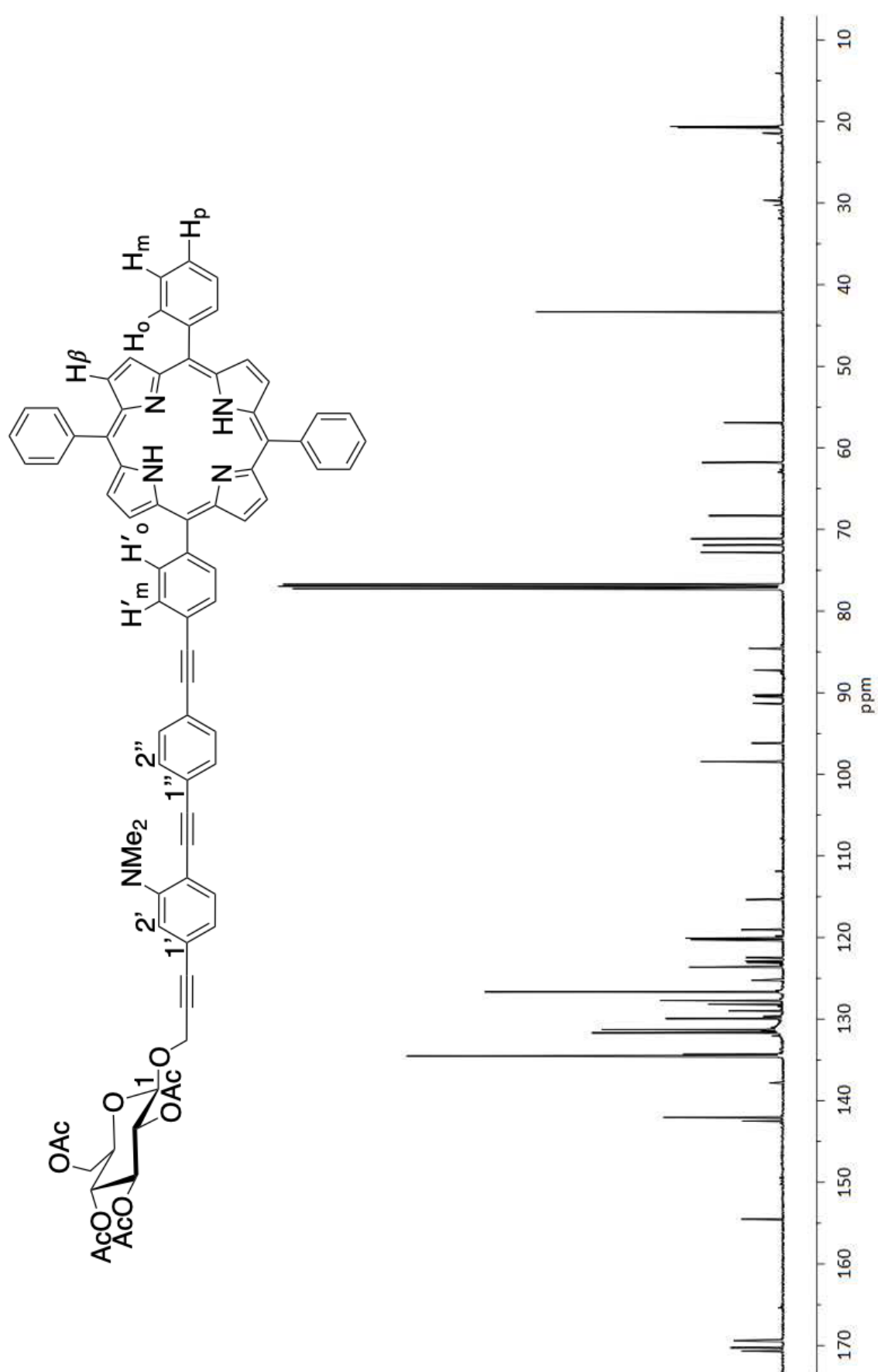


Figure S4. ^{13}C NMR of compound 4 in CDCl_3

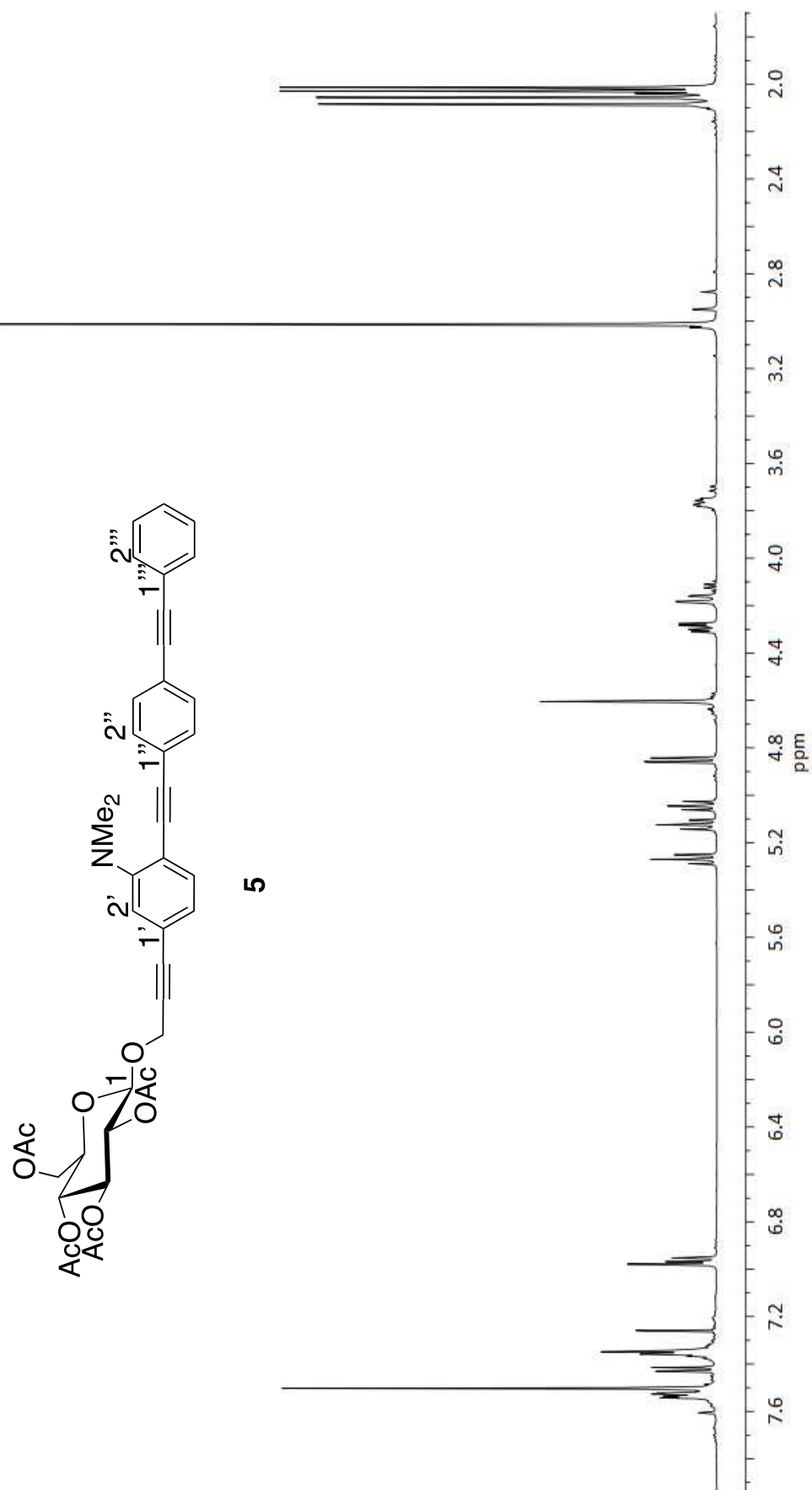


Figure S5. ¹H NMR of compound **5** in CDCl₃

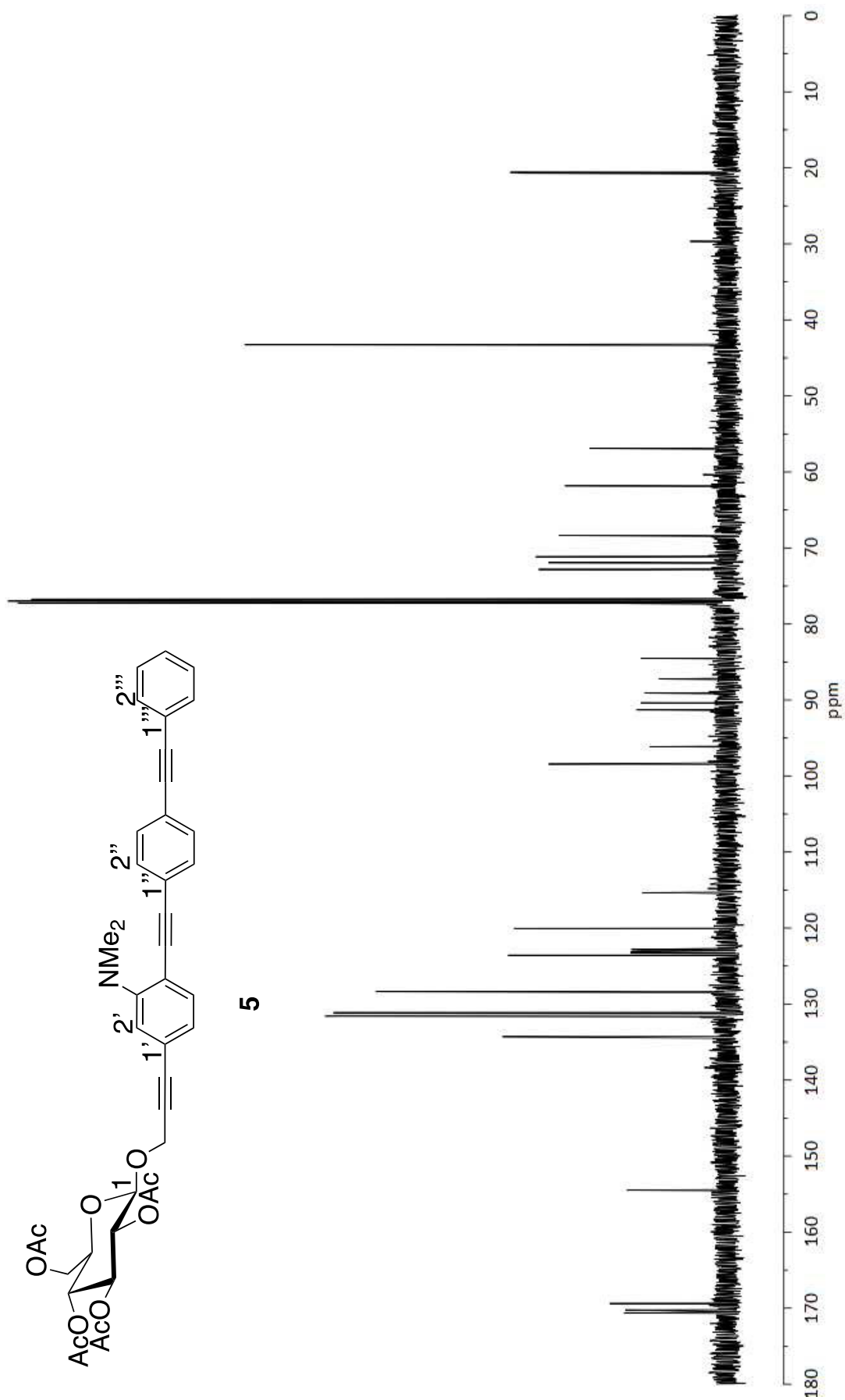


Figure S6. ¹³C NMR of compound **5** in CDCl₃

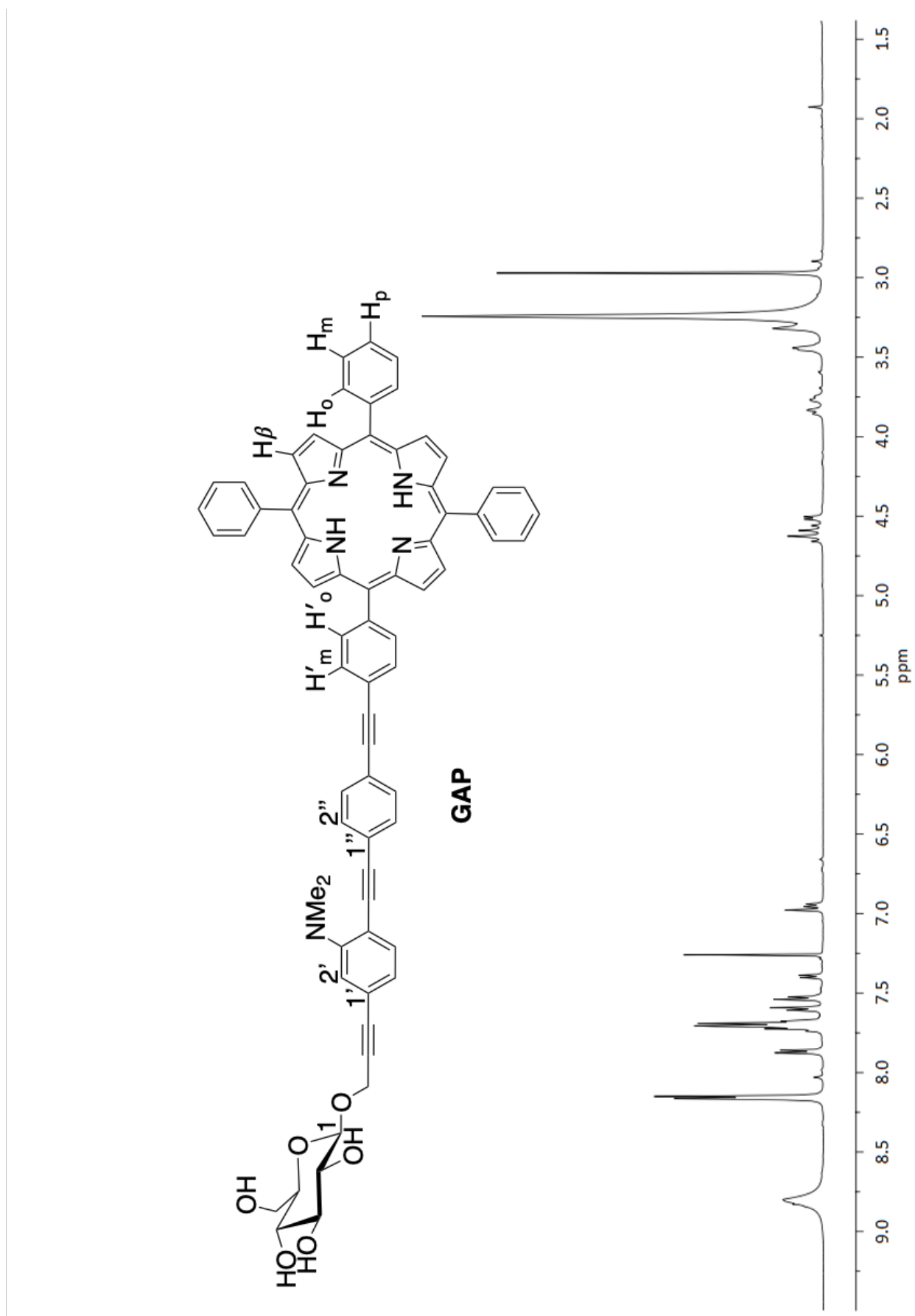


Figure S7. ¹H NMR of GAP in CDCl₃/MeOD

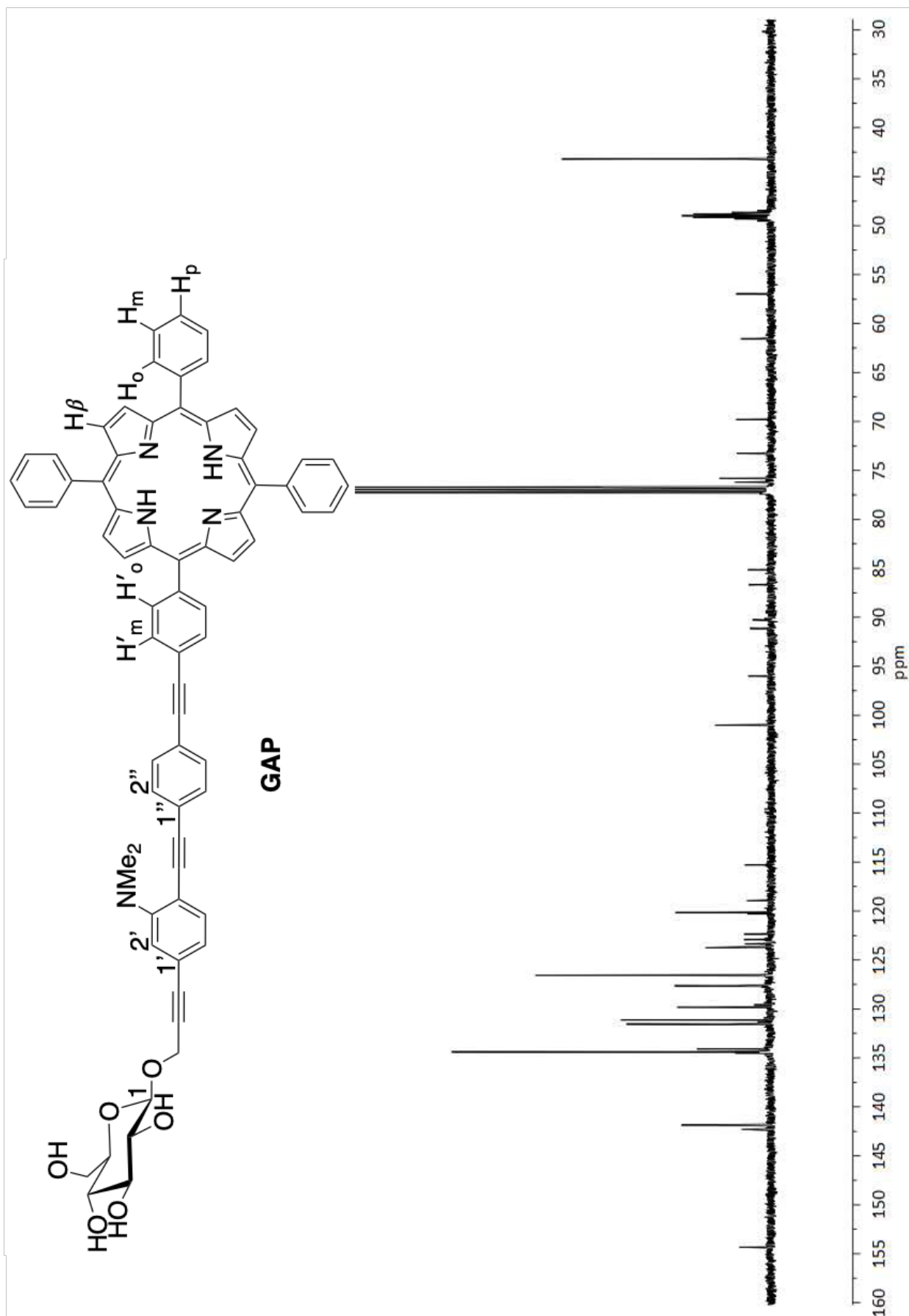


Figure S8. ^{13}C NMR of GAP in $\text{CDCl}_3/\text{MeOD}$

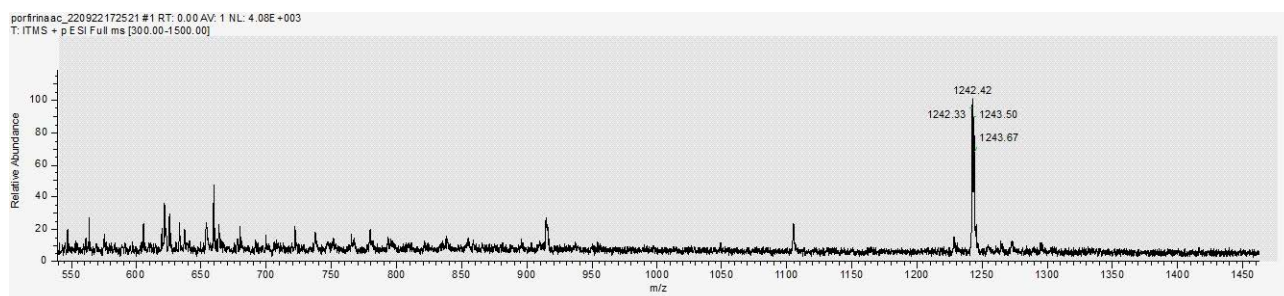


Figure S99. ESI/MS of compound 4

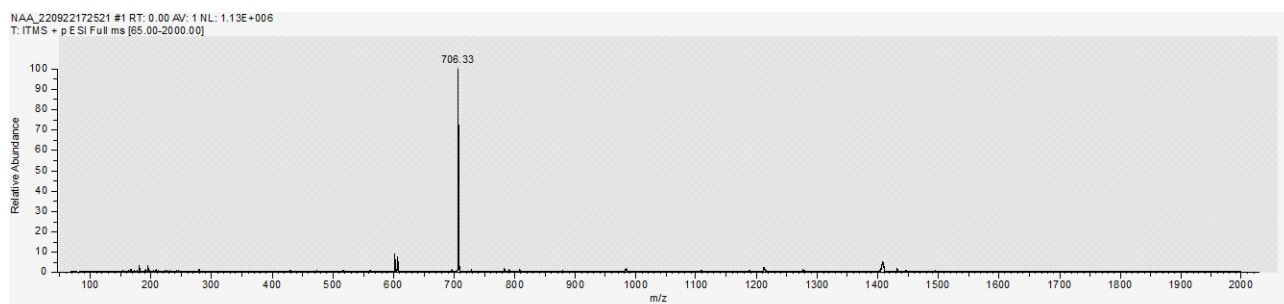


Figure S10. ESI/MS of compound 5

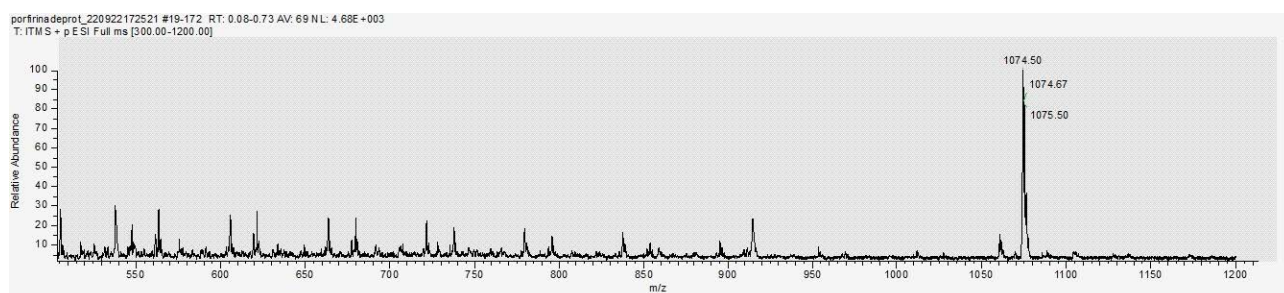


Figure S10. ESI/MS of GAP

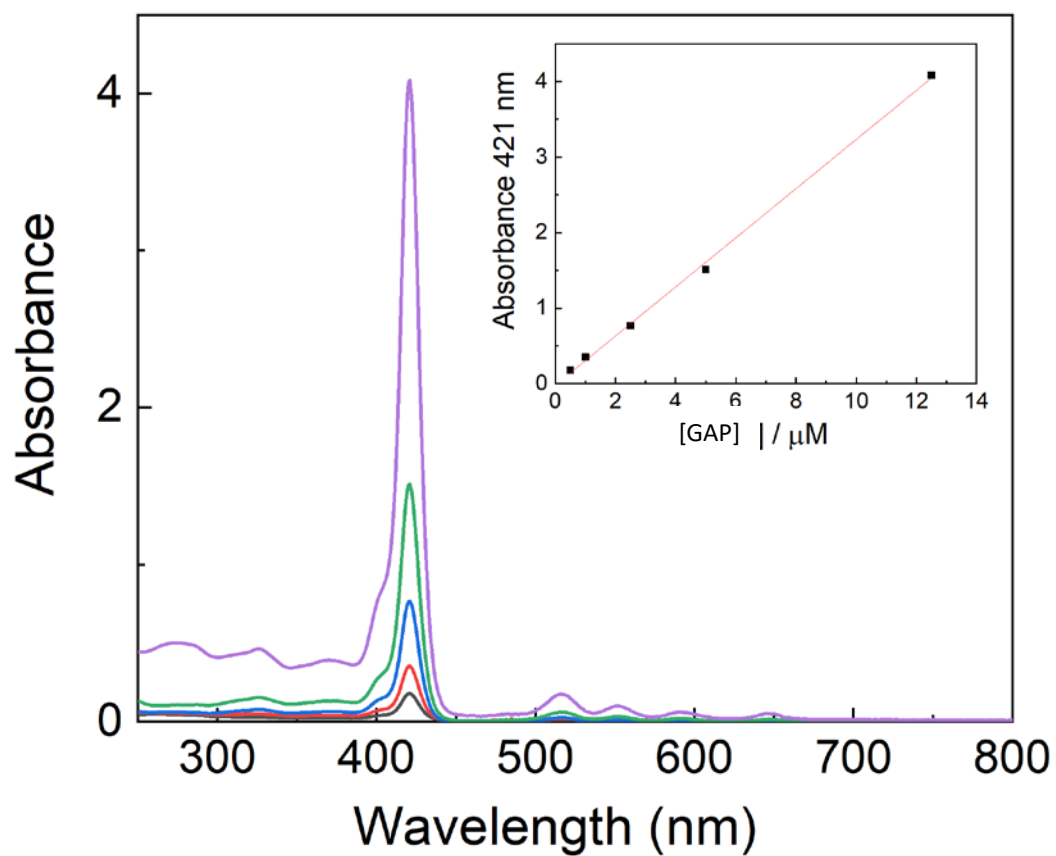


Figure S12. Absorption spectrum of GAP in chloroform, $T = 298$ K. In the inset: Beer's plot.

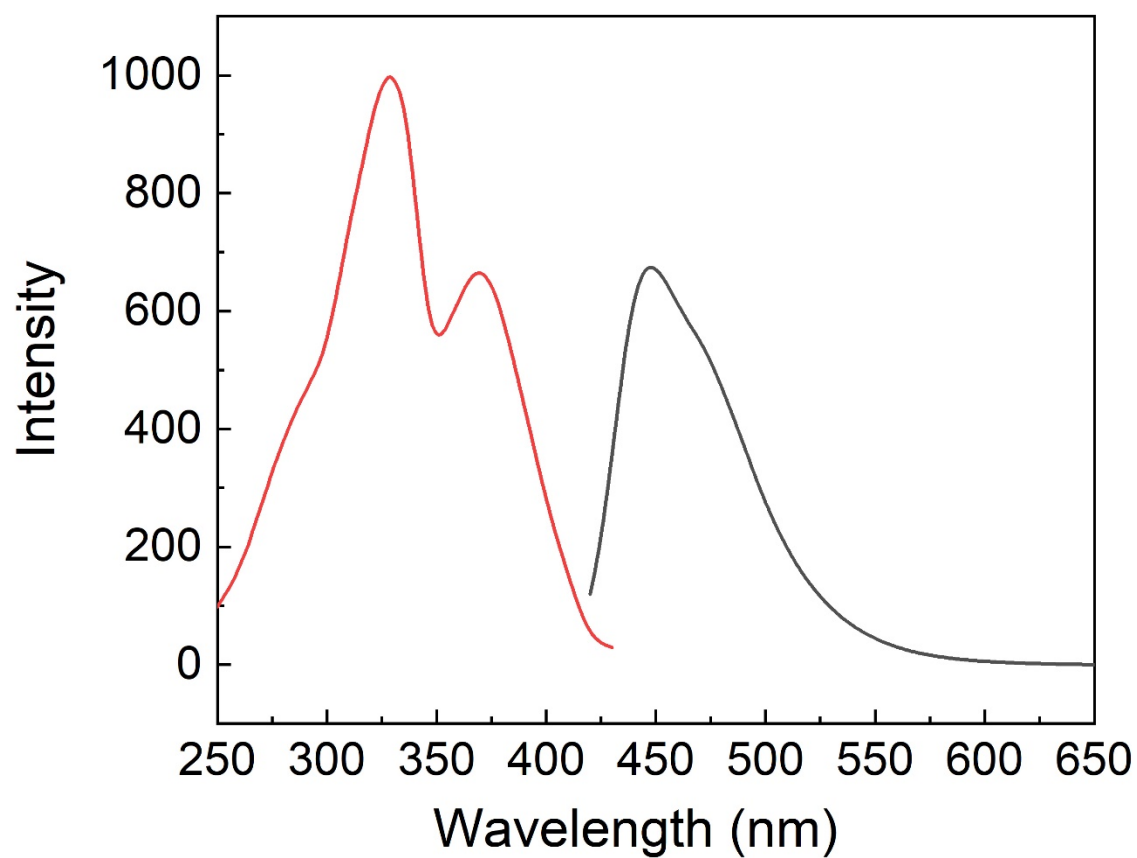


Figure S13. Excitation (red line) and emission (black line) spectra of OPE 5 in chloroform, $\lambda_{\text{ex}} = 390\text{nm}$; $\lambda_{\text{em}} = 450\text{ nm}$; $T = 298\text{ K}$.

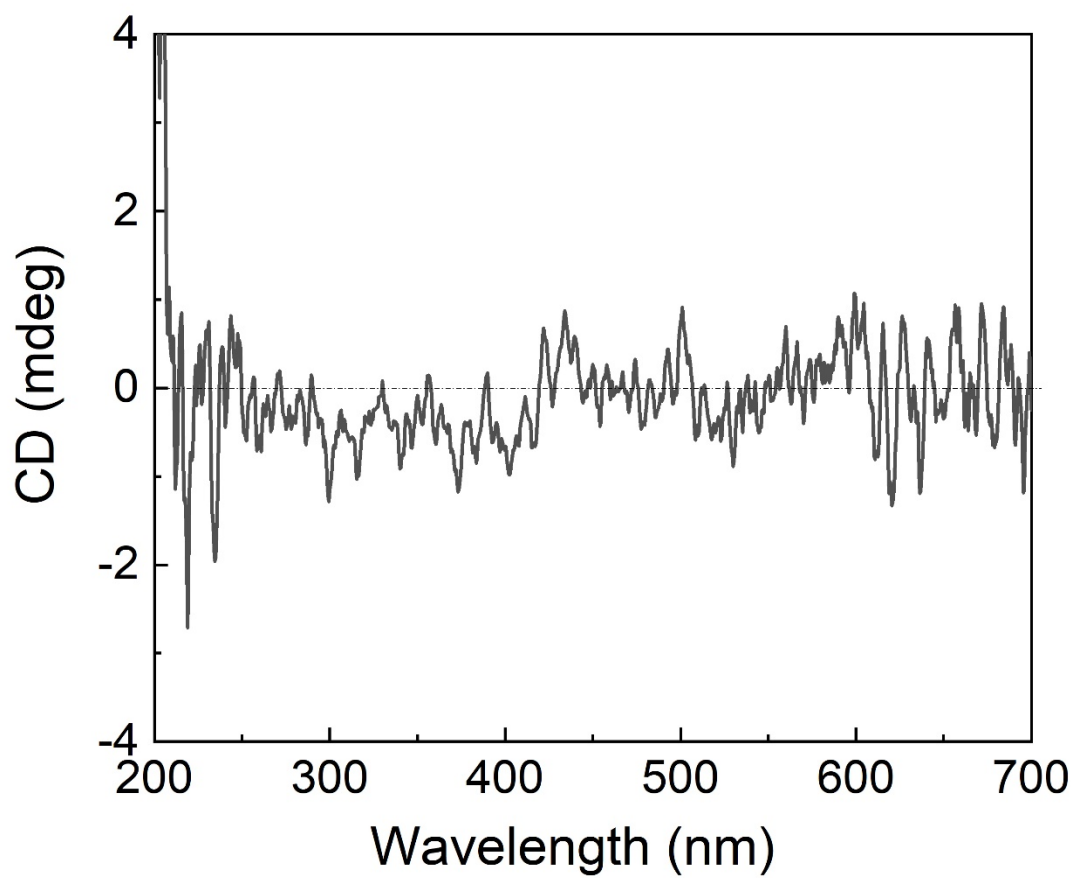


Figure S14. CD spectrum of GAP in chloroform, T = 298 K.

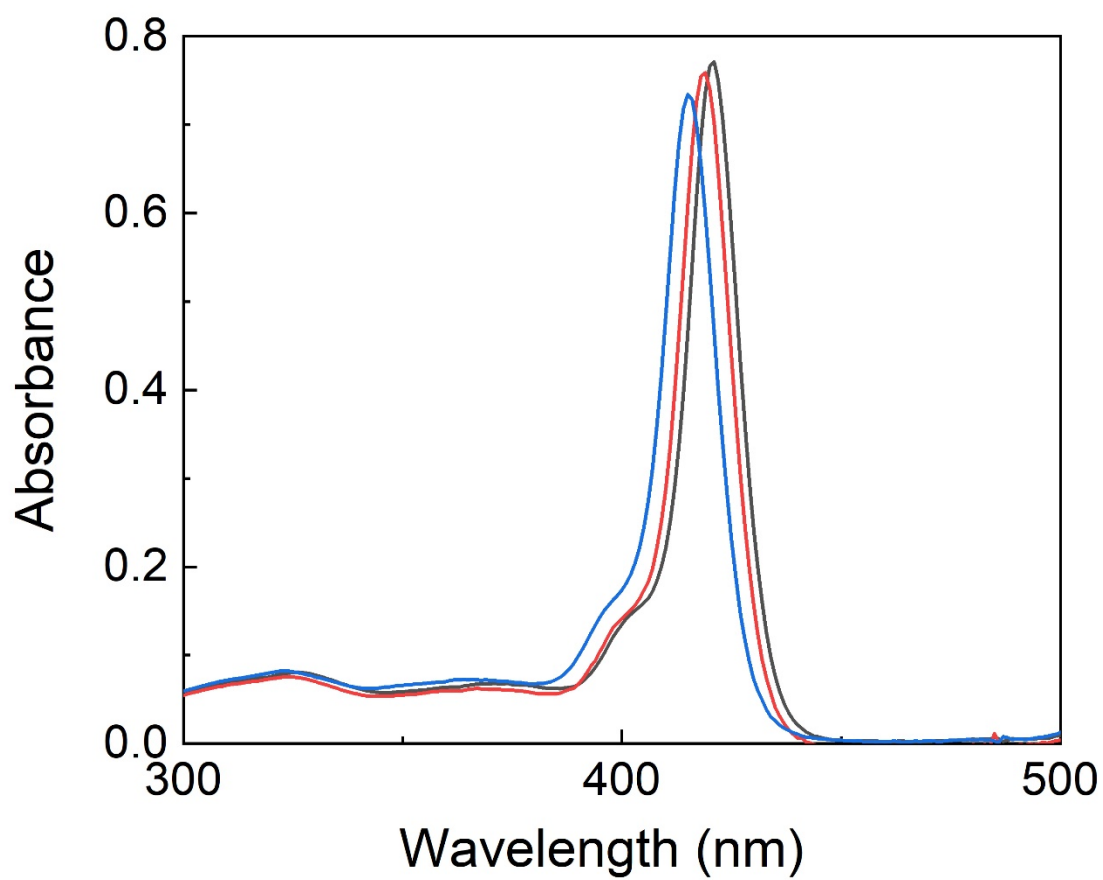


Figure S15. Absorption spectra of GAP in chloroform (black line), chloroform/methanol 50/50 v/v (red line); methanol (blue line). [GAP] = 2.5 μ M, T = 298 K.

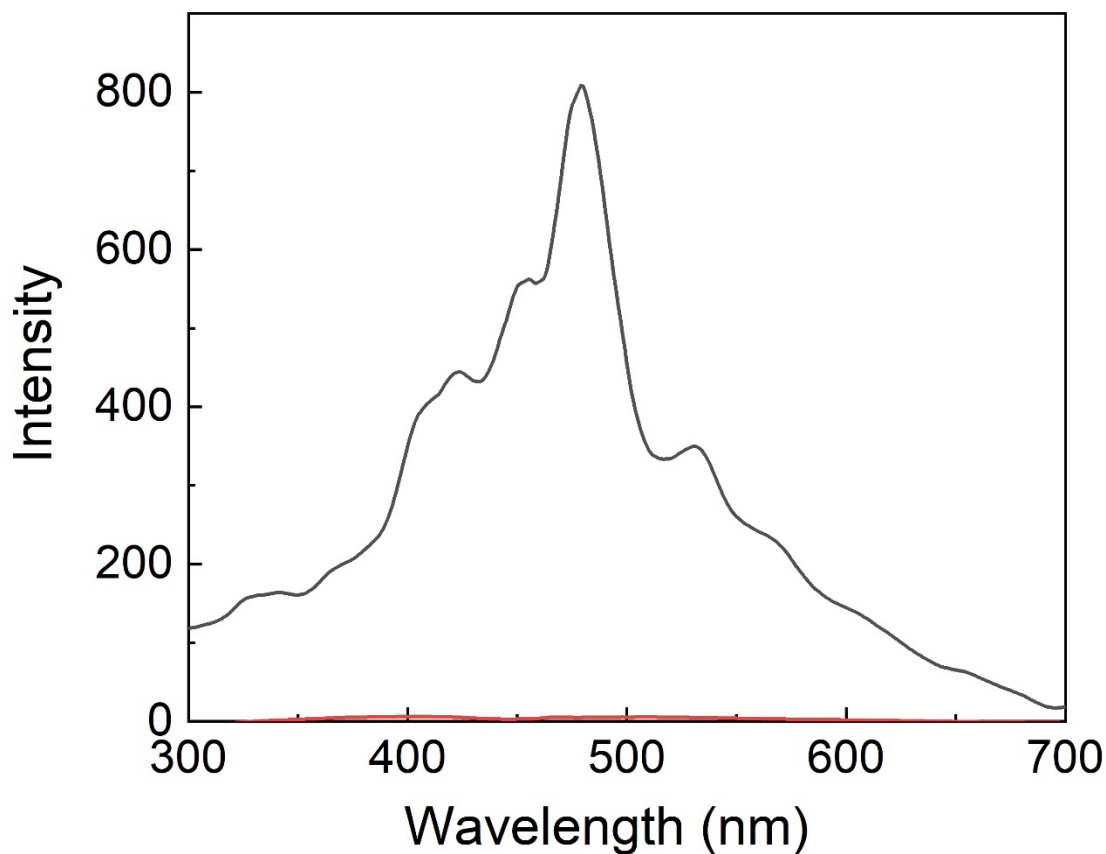


Figure S16. RLS spectra of GAP in methanol (red line), water/methanol/ 40/60 v/v (black line). [GAP] = 2.5 μ M, T = 298 K.

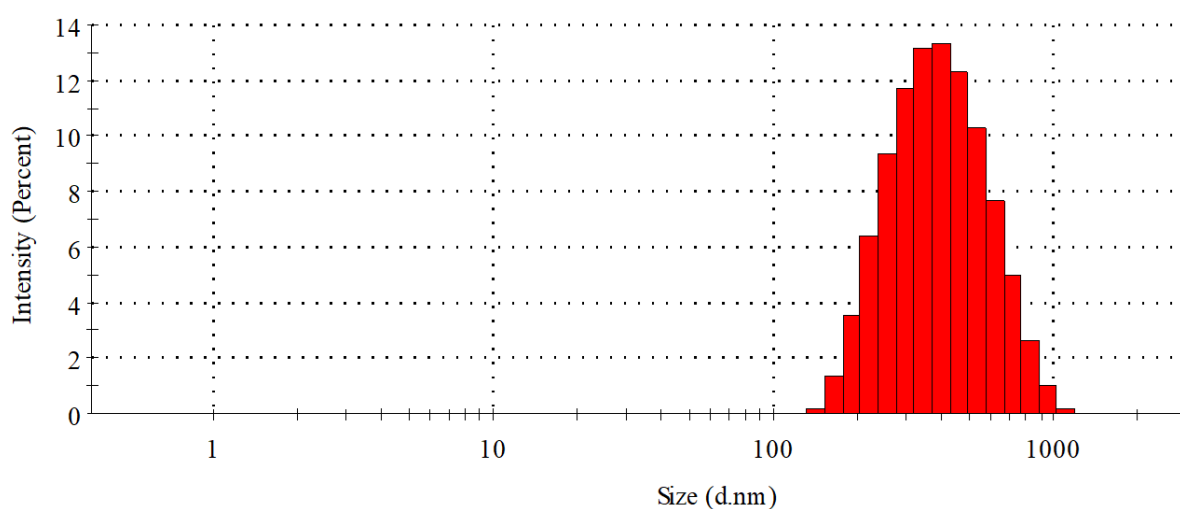


Figure S17. DLS intensity distribution of GAP in water/methanol/ 40/60 v/v. [GAP] = 2.5 μ M, T = 298 K.

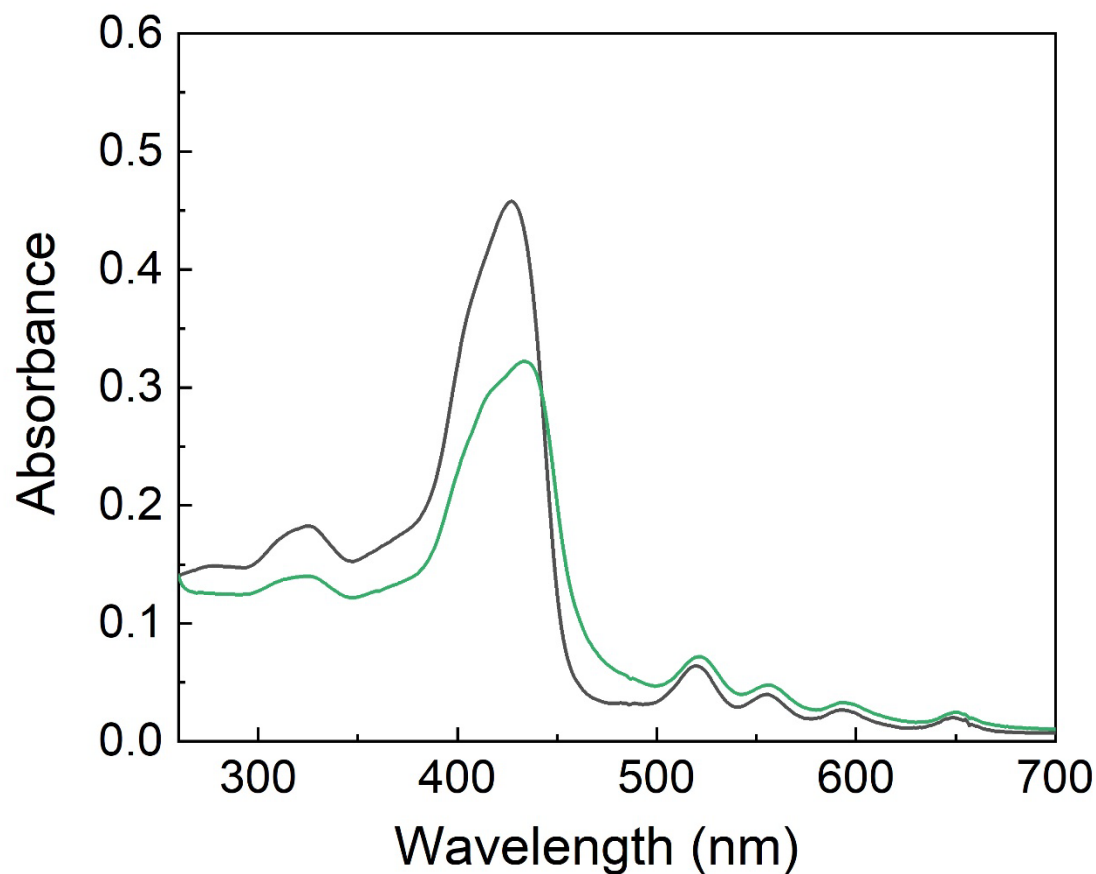


Figure S18. Absorption spectrum of GAP in water/methanol/ 40/60 v/v (black line) and in presence of KI (green line). [GAP] = 2.5 μ M, [KI] =5mM, T = 298 K.

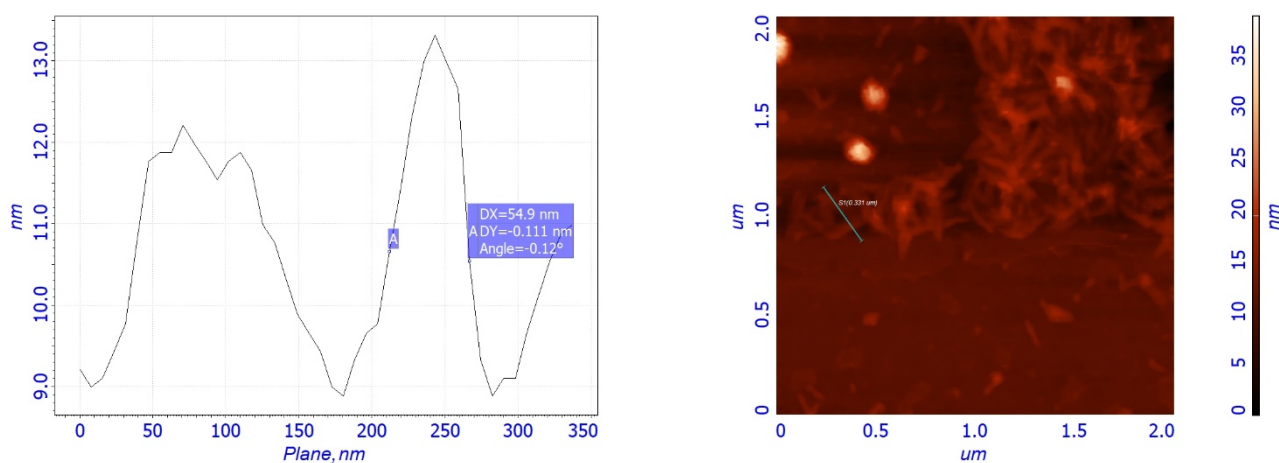


Figure S19 AFM image and relative profile of GAP aggregates on silicon surface. GAP 1 μ M in 60/40 v/v methanol/water dropped and evaporated at room temperature on silicon surface.

References

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