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Reactions of 2-Aza-21-carbaporphyrin with Aniline Derivatives

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Electronic Supporting Information

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General methods and instrumentation

Commercial reagents were used without further purification. Solvents were freshly distilled from the appropriate drying agents or purified under nitrogen with the mBraun MBSPS-800 before use. The analytical TLCs were performed with silica gel 60 F254 plates. Column chromatography was performed by using silica gel 60 (200-300 mesh ASTM). The NMR spectra were recorded on a Bruker Avance II spectrometer, operating at 500 MHz for ^{1}H and 125 MHz for ^{13}C or a Bruker Avance II spectrometer operating at 600 MHz for ^{1}H and 150 MHz for ^{13}C. TMS was used as an internal reference for ^{1}H and ^{13}C chemical shifts and $CDCl_3$ was used as solvent. Standard pulse programs from the Bruker library were used for homo- and heteronuclear 2D experiments. Mass spectrometry measurements were conducted by using the electrospray ionization technique on a Bruker Daltonics microTOF-Q or Finnigan LCQ Advantage MAX mass spectrometer. Absorption UV/Vis/NIR spectra were recorded by using a Varian Cary 50 Bio and Jasco V-770 spectrophotometers. HPLC separations were carried out by means of Chirex 3010 analytical column (25 cm length, 4.6 mm i.d.) packed with 5 mm silica gel coated with covalently bound (S)-valine and dinitroaniline using Shimadzu chromatographic system or Merck-Hitachi LaChrom series connected to a flow-cell mounted on Jasco J-1500 spectropolarimeter. HPLC-grade hexane was used. The applied dichloromethane was freshly distilled over calcium hydride. Circular dichroism spectra were obtained directly in the flow cell by means of pseudo stopped-flow technique using a Jasco J-1500 spectropolarimeter. Electrochemical measurements were performed by means of Autolab (Metrohm) potentiostat/galvanostat system for dichloromethane solutions with a glassy carbon, a platinum wire, and Ag/AgCl as the working, auxiliary, and reference electrodes, respectively. Tetrabutylammonium hexafluorophosphate was used as a supporting electrolyte. The potentials were referenced with the ferrocene/ferrocenium couple used as an internal standard. Crystal data for **2a** and **3b** were collected at low temperature using Oxford Cryosystem devices on Xcalibur Ruby and Onyx four-circle diffractometers with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and Cu Kα radiation (λ = 1.54184 Å). Data reduction and analysis were carried out with the *CrysAlisPRO* programs[1]. The structures were solved by using the SHELXT program[2] and refined by the full-matrix least-squares method on all F^2 data using the SHELXL program.[3] All hydrogen atoms, including those located in the difference density map, were placed in calculated positions and refined as the riding model. For **2a** the SQUEEZE/PLATON procedure[4] was applied for disordered lattice solvent (methanol) molecules. See Table S1 for detailed data.

Table S1 Crystal data for **2a** and **3b**

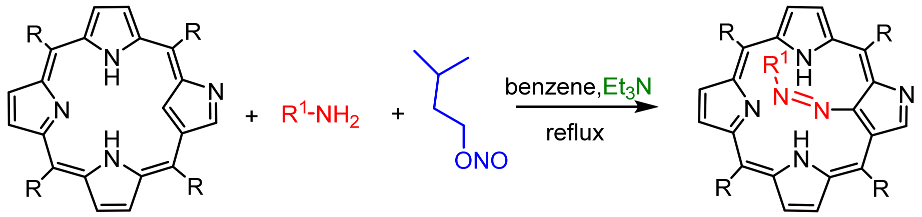
	2a	**3b**
Chemical formula	$C_{63}H_{58}N_6O_{14}\cdot 0.5(CH_3OH)$	$C_{65}H_{56}N_6O_6\cdot 2(C_7H_8)$
M_r	1139.17	1201.43
Crystal system, space group	Monoclinic, *Cc*	Monoclinic, $P2_1/c$
Temperature (K)	90	100
***a*, *b*, *c* (Å)**	36.594 (2), 7.353 (3), 28.802 (3)	33.740 (2), 12.948(3), 14.823(3)
β (°)	123.87 (3)	100.32 (3)
V (Å^3)	6435 (3)	6370.7 (6)
Z	4	4
Radiation type	Mo *K*α	Cu *K*α
μ (mm^{-1})	0.08	0.63
Crystal size (mm)	0.33 × 0.16 × 0.07	0.70 × 0.10 × 0.08
Diffractometer	Xcalibur, Ruby	Xcalibur, Onyx
No. of measured, independent and observed [I > 2σ(I)] reflections	11241, 8011, 5888	41715, 10157, 4894
Rint	0.033	0.137
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.606	0.575
	Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.063, 0.170, 1.04	0.068, 0.171, 0.87
No. of reflections	8011	10157
No. of parameters	771	915
No. of restraints	3	54
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.56, −0.24	0.35, −0.37

Computational methods

Density functional theory (DFT) calculations were performed by using the Gaussian 09.E01 program[5]. DFT geometry optimizations were carried out in the unconstrained C_1 symmetry by using the X-ray structure, molecular mechanics, or semiempirical models as starting geometries. DFT geometries were refined to meet standard convergence criteria, and the existence of a local minimum was verified by a normal mode frequency calculation. DFT calculations were performed by using the hybrid B3LYP functional[6-8] functional combined with the 6-31G(d,p) basis set. The electronic spectra were simulated by means of time-dependent density functional theory (TD-DFT) using the Tamm-Dancoff approximation for 50 states. For TD calculations, the polarizable continuum model of solvation was used (PCM, standard dichloromethane parametrization). The electronic transitions and UV/Vis/NIR as well as CD spectra were analyzed by means of the GaussSum program.[9] The transitions were convoluted by Gaussian curves with 2000 cm^{-1} half line width.

Synthesis and characterization

Synthesis of the precursor. Starting porphyrins **1a** and **1b** were obtained as described previously.[10]



1a-b

2a-c

1a: R=3,4,5-$(OCH_3)_3C_6H_2$
1b: R=4-$CH_3C_6H_4$

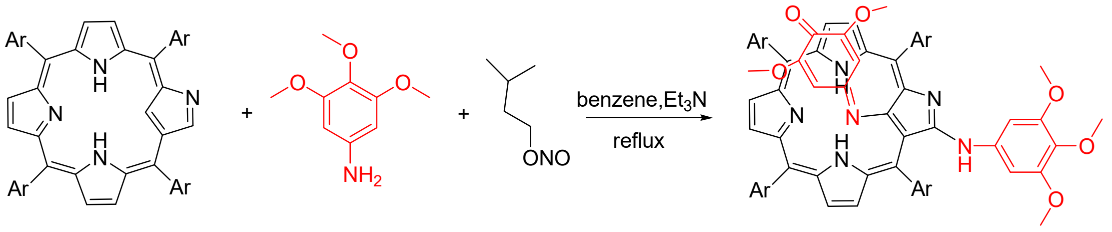
2a: R=3,4,5-$(OCH_3)_3C_6H_2$, R_1=2-$COOHC_6H_4$
2b: R=4-$CH_3C_6H_4$, R^1=2-$COOHC_6H_4$
2c: R =4-$CH_3C_6H_4$, R^1=2-COOH-4-$CH_3C_6H_3$

General method of synthesis of 2. To a solution of NCP **1** (0.1 mmol) and 2-aminobenzoic acid (0.3 mmol) in 5 ml dry benzene was added triethylamine (100 µL, 0.7 mmol) and amyl nitrite (100 µL, 0.7 mmol), the mixture was stirred under nitrogen for 2 hours under reflux and then the solvent was removed under vacuum. The residue was passed down a silica gel column with dichloromethane/ethyl acetate solvent as eluent. The first red colored product fraction was collected, followed by removal of solvent to afford desire NCP derivative **2** that was crystallized from dichloromethane solution by addition of hexane. Yields: 85% for **2a**, 80% for **2b**, 65% for **2c**.

Selected data for **2a:** ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 1.55 (d, J = 8.0 Hz, 1H, ArH), 3.73 (s, 3H, -OCH_3), 3.96 (s, 6H, -OCH_3), 3.97 (s, 3H, -OCH_3), 4.01 (s, 3H, -OCH_3), 4.08-4.09 (m, 9H, -OCH_3), 4.13 (s, 3H, -OCH_3), 4.16 (s, 3H, -OCH_3), 4.17 (s, 3H, -OCH_3), 4.19 (s, 3H, -OCH_3), 5.54 (t, J = 7.5 Hz, 1H, ArH), 6.30 (t, J = 8.0 Hz, 1H, ArH), 6.86 (s, 1H, ArH), 7.10 (s, 1H, ArH), 7.12 (d, J = 8.0 Hz, 1H, ArH), 7.31 (s, 1H, ArH), 7.46 (s, 1H, ArH), 7.61-7.64 (m, 4H), 8.36 (d, J = 4.5 Hz, 1H, pyrrH), 8.44 (d, J = 4.0 Hz, 1H, pyrrH), 8.69 (d, J = 4.0 Hz, 1H, pyrrH), 8.81 (d, J = 4.5 Hz, 1H, pyrrH), 8.92 (s, 1H, pyrrH), 9.17 (d, J = 4.5 Hz, 2H, pyrrH), 9.80 (s, 1H, -COOH); ^{1}H NMR (500 MHz, $CDCl_3$, 248 K): δ = -3.61 (br, 1H, -NH), -2.16 (br, 1H, -NH), 1.40 (d, J = 8.0 Hz, 1H, ArH), 3.94 (s, 3H, -OCH_3), 3.96 (s, 3H, -OCH_3), 4.00-4.04 (m, 12H, -OCH_3), 4.12 (s, 3H, -OCH_3), 4.15-4.20 (m, 12H, -OCH_3), 4.27 (s, 3H, -OCH_3), 5.60 (t, J = 8.0 Hz, 1H, ArH), 6.35 (t, J = 7.5 Hz, 1H, ArH), 6.81 (br, 1H, ArH), 7.11 (d, J = 7.5 Hz, 1H, ArH), 7.27 (s, 2H, ArH), 7.33 (s, 1H, ArH), 7.38 (s, 1H, ArH), 7.50 (s, 1H, ArH), 7.96 (d, J = 12.0 Hz, 1H, ArH), 8.39 (s, 1H, pyrrH), 8.51 (d, J = 4.0 Hz, 1H, pyrrH), 8.69 (s, 1H, pyrrH), 8.86 (s, 1H, pyrrH), 8.93 (s, 1H, pyrrH), 9.23 (s, 1H, pyrrH), 9.26 (s, 1H, pyrrH), 10.27 (s, 1H, COOH); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ = 56.4, 56.47, 56.50, 56.7, 61.2, 61.27, 61.33, 61.37, 110.3, 112.3, 112.7, 112.9, 114.8, 120.9, 122.3, 122.7, 127.2, 127.6, 127.8, 127.9, 129.6, 130.1, 130.2, 130.5, 135.4, 135.6, 135.7, 136.2, 136.4, 136.6, 137.6, 138.1, 138.3, 138.9, 139.6, 140.2, 140.3, 146.7, 151.4, 151.59, 151.64, 151.7, 152.5, 152.7, 157.2, 157.7, 165.6. UV-vis ($CHCl_3$): λ_{max}/nm (log ε) = 403(4.76), 510(4.54), 740(3.94). ESI-HRMS calc. for $[C_{63}H_{59}N_6O_{14}]^+$ (M+H): 1123.4084, Found: 1123.4078.

Selected data for **2b:** ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 2.50 (d, J = 8.0 Hz, 1H, ArH), 2.65 (s, 3H, -CH_3), 2.68 (s, 3H, -CH_3), 2.69 (s, 3H, -CH_3), 2.71 (s, 6H, -CH_3), 5.50 (t, J = 7.5 Hz, 1H, ArH), 6.24 (t, J = 7.5 Hz, 1H, ArH), 7.04 (d, J = 7.5 Hz, 1H, ArH), 7.47 (t, J = 7.5 Hz, 3H, ArH), 7.56 (t, J = 8.0 Hz, 3H, ArH), 7.58 (d, J = 7.5 Hz, H, ArH), 7.68 (t, J = 7.5 Hz, 4H, ArH), 7.76 (d, J = 7.5 Hz, 1H, ArH), 7.90 (d, J = 7.0 Hz, 1H, ArH), 8.12 (d, J = 7.5 Hz, 1H, ArH), 8.28 (d, J = 7.5 Hz, 2H, ArH), 8.31 (d, J = 4.5 Hz, 1H, pyrrH), 8.38 (d, J = 4.5 Hz, 1H, pyrrH), 8.56 (d, J = 5.0 Hz, 1H, pyrrH), 8.72 (d, J = 4.5 Hz, 1H, pyrrH), 8.75 (s, 1H, pyrrH), 9.08 (d, J = 4.5 Hz, 1H, pyrrH), 9.13 (d, J = 4.5 Hz, 1H, pyrrH), 9.92 (s, 1H, -COOH); ^{1}H NMR (500 MHz, CDCl$_3$, 248 K): δ = -3.45 (br, 1H, -NH), -2.35 (br, 1H, -NH), 1.18 (d, J = 8.0 Hz, 1H, ArH), 2.69 (s, 3H, -CH$_3$), 2.73 (s, 3H, -CH$_3$), 2.76 (s, 6H, -CH$_3$), 5.61 (t, J = 7.5 Hz, 1H, ArH), 6.34 (t, J = 7.5 Hz, 1H, ArH), 7.06 (d, J = 7.5 Hz, 1H, ArH), 7.51-7.53 (m, 2H, ArH), 7.76-7.86 (m, 4H, ArH), 7.86 (br, 2H, ArH), 7.94 (br, 1H, ArH), 8.06 (br, 1H, ArH), 8.27 (br, 1H, ArH), 8.39 (br, 1H, ArH), 8.49 (br, 1H, ArH), 8.60 (br, 2H, pyrrH), 8.78 (br, 2H, pyrrH), 8.86 (br, 1H, pyrrH), 9.19 (br, 1H, pyrrH), 9.24 (br, 1H, pyrrH), 10.34 (s, 1H, COOH); ^{13}C NMR (125 MHz, CDCl$_3$, 298 K): δ = 21.45, 21.48, 21.51, 21.7, 110.3, 115.55, 115.62, 120.6, 122.2, 122.5, 124.0, 125.8, 126.0, 127.0, 127.4, 127.7, 127.8, 129.0, 129.8, 130.1, 130.2, 132.4, 133.4, 134.0, 134.2, 134.3, 134.7, 135.3, 135.4, 137.1, 137.2, 137.3, 137.7, 137.99, 138.06, 138.15, 138.18, 138.7, 139.4, 140.2, 140.3, 140.4, 146.9, 151.0, 157.1, 157.4, 165.9. UV-vis (CHCl$_3$): λ_{max}/nm (log ε) = 394(4.75), 501(4.36), 739(3.88). ESI-HRMS calc. for $[C_{55}H_{43}N_6O_2]^+$ (M+H): 819.3442, Found: 819.3455.

Selected data for **2c:** ^{1}H NMR (500 MHz, CDCl$_3$, 298 K): δ = 1.37 (br, 1H, ArH), 1.68 (s, 3H, -CH$_3$), 2.65 (s, 3H, -CH$_3$), 2.68 (s, 3H, -CH$_3$), 2.69 (s, 3H, -CH$_3$), 2.70 (s, 3H, -CH$_3$), 5.34 (d, J = 8.0 Hz, 1H, ArH), 6.90 (br, 1H, ArH), 7.47 (t, J = 6.5 Hz, 3H, ArH), 7.54 (d, J = 7.5 Hz, 1H, ArH), 7.58 (d, J = 7.5 Hz, 2H, ArH), 7.68 (t, J = 6.5 Hz, 1H, ArH), 7.76 (d, J = 7.5 Hz, 1H, ArH), 7.90 (d, J = 7.5 Hz, 1H, ArH), 8.12 (d, J = 7.5 Hz, 1H, ArH), 8.26 (d, J = 7.5 Hz, 2H, ArH), 8.29-8.30(m, 1H, ArH), 8.32 (d, J = 4.5 Hz, 1H, pyrrH), 8.39 (d, J = 4.5 Hz, 1H, pyrrH), 8.53 (d, J = 4.5 Hz, 1H, pyrrH), 8.63 (br, 1H, pyrrH), 8.68 (d, J = 4.5 Hz, 1H, pyrrH), 9.06 (d, J = 5.0 Hz, 1H, pyrrH), 9.10 (d, J = 4.5 Hz, 1H, pyrrH), 9.93 (s, 1H, -COOH); ^{13}C NMR (125 MHz, CDCl$_3$, 298 K): δ = 20.5, 21.50, 21.54, 21.55, 21.60, 110.4, 120.6, 122.0, 122.3, 127.3, 127.5, 127.6, 127.8, 128.7, 129.0, 130.1, 130.5, 130.8, 134.1, 134.2, 134.4, 134.7, 135.3, 135.5, 137.1, 137.27,137.32, 137.6, 137.9, 138.0, 138.1, 138.2, 138.3, 138.7, 139.4, 140.2, 140.4, 145.2, 157.3, 157.5, 166.1. UV-vis (CHCl$_3$): λ_{max}/nm (log ε) = 394(4.76), 498(4.34), 738(3.81). ESI-HRMS calc. for $[C_{56}H_{45}N_6O_2]^+$ (M+H): 833.3599, Found: 833.3604.



1a-b

1a: Ar = 3,4,5-(OCH$_3$)$_3$Ph
1b: Ar = 4-CH$_3$Ph

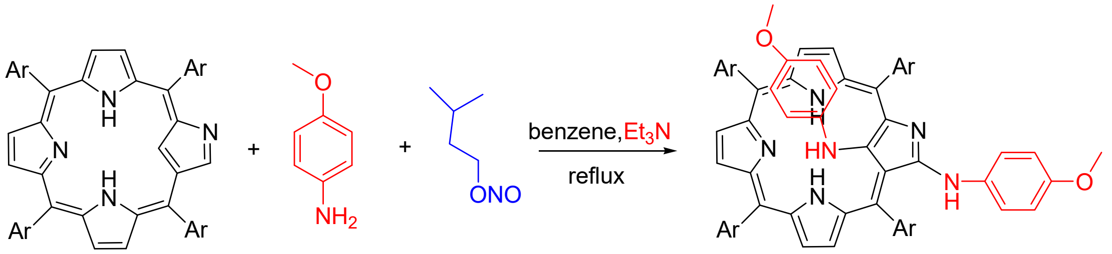
3a-b

3a: Ar = 3,4,5-(OCH$_3$)$_3$Ph
3b: Ar = 4-CH$_3$Ph

General method of synthesis of 3. To a solution of **1a** or **1b** (0.1 mmol) and 3,4,5-trimethoxyaniline (0.33 mmol) in 5 ml of dry benzene was added triethylamine (100 µL, 0.7 mmol) and amyl nitrite (100 µL, 0.7 mmol). The mixture was allowed to react in a sealed tube at 70°Cfor 2 h. The products were separated by column chromatography (silica gel, DCM/ethyl acetate) and precipitated from DCM by addition of hexane, yielding 52 mg of product **3a** (51%) or 45 mg of **3b** (44%).

Selected data for **3a:** ^{1}H NMR (500 MHz, CDCl$_3$, 298 K): δ = -1.35 (br, 1H, -NH), 0.44 (br, 1H, -NH), 0.61 (s, 1H, ArH), 2.01 (s, 3H, -OCH$_3$), 3.05 (s, 3H, -OCH$_3$), 3.68 (s, 6H, -OCH$_3$), 3.77 (s, 3H, -OCH$_3$), 3.91 (s, 3H, -OCH$_3$), 3.95 (s, 3H, -OCH$_3$), 4.02 (s, 6H, -OCH$_3$), 4.04 (s, 10H, -OCH$_3$+ArH), 4.10 (br, 3H, -OCH$_3$), 4.14 (s, 3H, -OCH$_3$), 4.15 (s, 3H, -OCH$_3$), 4.16 (s, 3H, -OCH$_3$), 4.21 (s, 3H, -OCH$_3$), 6.83 (s, 1H), 6.87 (s, 2H), 7.14 (br, 1H), 7.28 (br, 1H), 7.33 (br, 1H), 7.46 (br, 1H), 7.54 (br, 1H), 7.74 (br, 1H), 8.16 (br, 2H), 8.16 (d, J = 3.0 Hz, 1H, pyrrH), 8.46 (br, 1H), 8.49 (br, 2H), 8.66 (d, J = 3.5 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$, 298 K): δ = 53.6, 55.5, 55.8, 56.3, 56.41, 56.44, 56.46, 56.8, 61.0, 61.2, 61.26, 61.31, 61.5, 95.5, 96.4, 108.1, 111.2, 111.6, 112.0, 112.5, 120.5, 120.6, 122.7, 123.2, 124.5, 125.7, 126.7, 127.1, 127.9, 129.8, 133.0, 134.3, 134.5, 135.5, 136.0, 136.7, 136.9, 137.1, 137.3, 137.7, 137.8, 137.9, 138.2, 139.1, 139.5, 145.9, 146.5, 149.8, 151.59, 151.63, 152.1, 152.8, 153.3, 153.4, 155.1, 156.6, 174.4. UV-vis (CHCl$_3$): λ_{max}/nm (log ε) = 406(4.83), 435(4.91), 605(4.10). ESI-HRMS calc. for $[C_{73}H_{73}N_6O_{18}]^+$ (M+H): 1321.4976, Found: 1321.4985.

Selected data for **3b:** ^{1}H NMR (500 MHz, CDCl$_3$, 298 K): δ = -1.16 (br, 1H, -NH), 0.26 (br, 1H, -NH), 0.60 (s, 1H, ArH), 1.96 (s, 3H, -OCH$_3$), 2.59 (s, 3H, -CH$_3$), 2.64 (s, 3H, -CH$_3$), 2.66 (s, 3H, -CH$_3$), 2.74 (s, 3H, -CH$_3$), 3.45 (s, 3H, -OCH$_3$), 3.56 (s, 6H, -OCH$_3$), 3.72 (s, 3H, -OCH$_3$), 4.22 (s, 1H, ArH), 6.66 (s, 2H, ArH), 7.10 (s, 1H, ArH), 7.25(s, 3H), 7.43 (d, J = 7.5 Hz, 1H, ArH), 7.50 (d, J = 7.5 Hz, 5H, ArH), 7.59 (d, J = 7.5 Hz, 1H, ArH), 7.77 (d, J = 7.5 Hz, 2H, ArH), 7.90 (d, J = 8.0 Hz, 2H, ArH), 8.05 (d, J = 7.5 Hz, 1H, ArH), 8.08 (d, J = 5.0 Hz, 1H, pyrrH), 8.32 (d, J = 4.5 Hz, 2H, pyrrH), 8.34 (d, J = 5.0 Hz, 1H, pyrrH), 8.38 (d, J = 4.5 Hz, 1H, pyrrH), 8.54 (d, J = 5.0 Hz, 1H, pyrrH); ^{1}H NMR (500 MHz, CDCl$_3$, 233 K): δ = -1.68 (s, 1H, -NH), 0.41 (s, 1H, -NH), 0.54 (s, 1H, ArH), 1.96 (s, 3H, -OCH$_3$), 2.63 (s, 3H, -CH$_3$), 2.67 (s, 3H, -CH$_3$), 2.69 (s, 3H, -CH$_3$), 2.78 (s, 3H, -CH$_3$), 3.49 (s, 3H, -OCH$_3$), 3.56 (br, 6H, -OCH$_3$), 3.74 (s, 3H, -OCH$_3$), 4.26 (s, 1H, ArH), 7.14 (s, 1H, ArH), 7.45 (d, J = 7.5 Hz, 1H), 7.49 (d, J = 7.5 Hz, 1H), 7.52-7.60 (m, 6H), 7.64 (d, J = 7.5 Hz, 1H), 7.82-7.85 (m, 2H), 7.91 (d, J = 7.5 Hz, 1H), 7.94 (d, J = 7.5 Hz, 1H, ArH), 7.99 (d, J = 7.0 Hz, 1H), 8.09-8.12 (m, 2H), 8.38-8.39 (m, 2H), 8.44 (d, J = 4.5 Hz, 1H), 8.47 (d, J = 4.5 Hz, 1H), 8.51 (d, J = 7.5 Hz, 1H), 8.69 (d, J = 4.5 Hz, 1H), 8.74 (d, J = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$, 298 K): δ = 21.3, 21.5, 53.7, 55.4, 55.7, 60.9, 95.6, 96.3, 107.8, 119.8, 120.0, 123.1, 123.2, 124.5, 125.2, 125.7, 126.8, 127.5, 127.6, 127.7, 127.8, 128.1, 128.5, 132.7, 132.3, 133.7, 134.0, 134.2, 134.4, 135.2, 136.0, 136.8, 137.1, 137.2, 137.3, 137.5, 137.7, 138.0, 138.6, 139.0, 139.1, 139.4, 146.1, 147.6, 150.2, 152.2, 153.1, 153.3, 155.2, 157.0, 174.7. UV-vis (CHCl$_3$): λ_{max}/nm (log ε) = 401(4.89), 431(4.93), 610(4.16). ESI-HRMS calc. for $[C_{65}H_{57}N_6O_6]^+$ (M+H): 1017.4334, Found: 1017.4338.



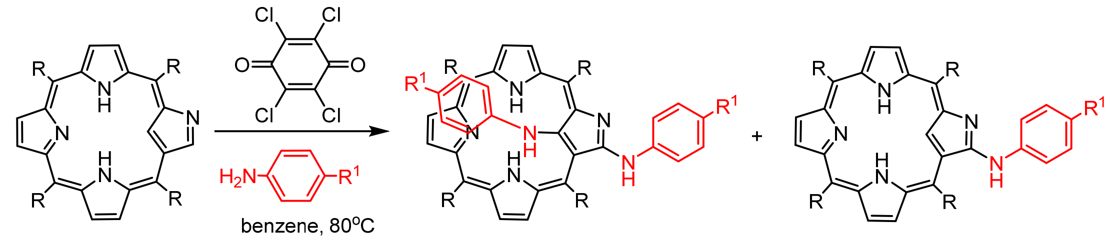
1b: Ar = 4-CH$_3$Ph

4a: Ar = 4-CH$_3$Ph

Synthesis of 4a. To a solution of NCP **1b** (67 mg, 0.1 mmol) and 4-methoxyaniline (37 mg, 0.3 mmol) in 5 ml of dry benzene was added triethylamine (100 μL, 72.6 mg, 0.7 mmol) and amyl nitrite (100 μL, 87 mg, 0.7 mmol). The mixture was stirred under nitrogen for 3 hours at boiling point of the solution under reflux and then the solvent was removed under vacuum. The residue was passed down a silica gel column with dichloromethane/ethyl acetate solvent as eluent. The red colored product fraction was collected, followed by removal of solvent to afford NCP derivative **4a**. Yield 30 mg (33%).

Selected data for **4a:** ^{1}H NMR (500 MHz, CDCl$_3$, 298 K): δ = 2.61 (s, 3H, -CH$_3$), 2.62 (s, 3H, -CH$_3$), 2.64

(s, 3H, -CH_3), 2.66 (s, 3H, -CH_3), 3.23 (s, 3H, -OCH_3), 3.72 (s, 3H, -OCH_3), 4.20 (d, J = 9.0 Hz, 2H, ArH), 5.60 (d, J = 8.5 Hz, 2H, ArH), 6.30 (d, J = 9.0 Hz, 2H, ArH), 7.15 (d, J = 8.0 Hz, 2H, ArH), 7.46 (d, J = 7.5 Hz, 3H, ArH), 7.50 (d, J = 8.0 Hz, 3H, ArH), 7.51-7.53 (m, 1H, ArH), 7.63 (d, J = 7.5 Hz, 2H, ArH), 7.74-7.78 (m, 1H, ArH+pyrrH), 7.80-7.85 (m, 3H, ArH+pyrrH), 7.96 (d, J = 4.5 Hz, 1H, pyrrH), 7.99 (d, J = 3.5 Hz, 1H, pyrrH), 8.08 (d, J = 5.0 Hz, 1H, pyrrH), 8.13 (d, J = 7.5 Hz, 4H, ArH), 8.21 (d, J = 4.5 Hz, 1H, pyrrH); ^{1}H NMR (500 MHz, $CDCl_3$, 230 K): δ = 0.64 (br, 2H, -NH), 2.61 (s, 3H, -CH_3), 2.63 (s, 6H, -CH_3), 2.64 (s, 3H, -CH_3), 3.23 (s, 3H, -OCH_3), 3.73 (s, 3H, -OCH_3), 4.19 (br, 2H, ArH), 5.55 (br, 2H, ArH), 6.64 (d, J = 6.5 Hz, 2H, ArH), 6.74 (s, 1H, ArH), 7.15 (br, 2H, ArH), 7.26 (s, 1H, ArH), 7.46 (br, 3H, ArH), 7.54 (br, 3H, ArH), 7.61 (br, 1H, ArH), 7.67-7.73 (m, 4H, ArH+pyrrH), 7.82-7.98 (m, 5H, ArH+pyrrH), 8.08 (br, 1H, pyrrH), 8.19-8.21 (m, 2H, ArH), 8.36 (br, 1H, pyrrH); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ = 22.9, 23.0, 56.4, 56.9, 113.3, 114.8, 115.4, 118.3, 119.6, 120.5, 121.8, 123.1, 124.3, 124.8, 128.2, 129.3, 131.6, 132.2, 133.0, 134.3, 135.4, 135.5, 136.4, 137.4, 138.4, 138.5, 138.7, 138.9, 139.3, 139.6, 140.0, 140.3, 140.6, 144.1. UV-vis ($CHCl_3$): λ_{max}/nm (log ε) = 439(4.88), 501(4.69), 770(3.90). ESI(–)-HRMS calc. for $[C_{62}H_{51}N_6O_2]^-$ (M–H): 911.4079, Found: 911.4075.



1a: R=3,4,5-$(OCH_3)_3C_6H_2$
1b: R=4-$CH_3C_6H_4$

4a: R^1=OCH_3, R=4-$CH_3C_6H_4$
4b: R^1=CH_3, R=4-$CH_3C_6H_4$
4c: R^1=H, R=4-$CH_3C_6H_4$
4d: R^1=OCH_3, R=3,4,5-$(OCH_3)_3C_6H_2$
4e: R^1=CH_3, R=3,4,5-$(OCH_3)_3C_6H_2$
4f: R^1=H, R=3,4,5-$(OCH_3)_3C_6H_2$

5b: R^1=CH_3, R=4-$CH_3C_6H_4$
5c: R^1=H, R=4-$CH_3C_6H_4$

General method of synthesis of 4: To a solution of **1** (0.05 mmol) and arylamine (0.25 mmol) in benzene (5 ml) *p*-chloranil (61 mg, 0.25 mmol) was added. The mixture was allowed to react in a sealed tube at 80°Cfor 1 h, and then the solvent was removed under vacuum. The residue was passed down a silica gel column with 1% methanol in dichloromethane and first weak red band containing **5** was separated from the fraction consisting of major product **4** that was eluted with a dichloromethane/methanol (*v*/*v* = 100:3) mixture. The solvents were then removed and products were precipitated from DCM solution by addition of hexane and dried *in vacuo.* Yields: 27.5 mg (60%) for **4a**, 29.5 mg (67%) for **4b**, 27.3 mg (64%) for **4c,** 34.7 mg (57%) for **4d,** 30.8 mg (52%) for **4e,** 29.0 mg 50% for **4f**. Product **5** was formed in a minute amount and was characterized only for the reaction products of **1b** with toluidine (**5b**, 3.8 mg, 8%) and aniline (**5c**, 3.8 mg, 10%)

Selected data for **4b:** ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 1.58 (s, 3H), 2.19 (s, 3H), 2.60 (s, 6H), 2.62 (s, 3H), 2.64 (s, 3H), 4.09 (d, J = 7.5 Hz, 2H), 5.80 (d, J = 7.0 Hz, 2H), 6.86 (d, J = 7.5 Hz, 2H), 7.10-7.12 (m, 2H,), 7.44-7.49 (m, 6H), 7.63-7.64 (m, 2H), 7.78-7.83 (m,5H), 8.02-8.03 (m, 2H), 8.10-8.14 (m, 6H), 8.21-8.23 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ = 20.07, 20.70, 21.47, 21.50, 21.55, 113.63, 117.90, 118.07, 118.25, 122.76, 123.56, 123.69, 126.83, 127.15, 127.80, 129.19, 129.25, 130.16, 130.65, 130.83, 132.77, 133.99, 134.12, 135.02, 135.83, 136.05, 136.94, 137.12, 137.23, 137.50, 137.57, 137.97, 138.42, 138.63, 139.16, 142.47, 149.00. UV-vis ($CHCl_3$): λ_{max}/nm (log ε) = 440 (4.65), 497 (4.43), 780(3.55). ESI-HRMS calc. for $[C_{62}H_{53}N_6]^+$ (M+H): 881.4332, Found: 881.4324.

Selected data for **4c:** ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ =2.60 (s, 3H), 2.62 (s, 3H), 2.64 (s, 3H), 2.66 (s, 3H), 4.09 (d, J = 8.0 Hz, 2H), 5.85-5.88 (m, 1H,), 5.95-5.98 (m, 2H), 6.78-6.81 (m, 1H), 7.05-7.08 (m, 2H), 7.21-7.23 (m, 2H), 7.43-7.46 (m, 3H), 7.49-7.52 (m, 3H), 7.65 (d, J = 8.0 Hz, 2H), 7.77-7.80 (m, 3H), 7.85-7.86 (m, 2H), 8.02 (d, J = 5.0 Hz, 1H), 8.07 (d, J = 5.0 Hz, 1H), 8.13-8.14 (m, 2H), 8.16-8.18 (m, 2H), 8.19-8.22 (m, 2H), 8.26 (d, J = 5.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ = 21.49, 21.51, 21.56, 113.94, 117.49, 118.37, 118.51, 118.65, 119.48, 121.32, 122.73, 123.60, 123.80, 124.48, 125.22, 126.55, 126.93, 127.84, 127.89, 128.48, 128.71, 130.22, 130.99, 132.91, 133.95, 134.18, 135.09, 136.21, 136.97, 137.03, 137.43, 137.59, 138.10, 138.16, 138.58, 139.01, 139.04, 140.49, 142.61, 144.46, 148.71, 149.88, 154.92; UV-vis ($CHCl_3$): λ_{max}/nm (log ε) = 439 (4.89), 508 (4.59), 769 (3.61). ESI-HRMS calc. for $[C_{60}H_{49}N_6]^+$ (M+H): 853.4019, Found: 853.4013.

Selected data for **4d:** ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 3.26(s, 3H), 3.72 (s, 3H), 3.92 (s, 6H), 3.98 (s, 3H), 4.03 (s, 9H), 4.05 (s, 6H), 4.08 (s, 3H), 4.10 (s, 3H), 4.12 (s, 6H), 4.25 (d, J = 8.5 Hz, 2H), 5.65(d, J = 8.5Hz, 2H), 6.68 (d, J = 8.5 Hz, 2H), 7.09 (s, 1H), 7.18 (s, 1H), 7.19 (s, 1H), 7.34 (d, J = 8.5 Hz, 2H), 7.37 (s, 2H), 7.46 (s, 2H), 7.48 (s, 1H), 7.89 (d, J = 5.0 Hz, 1H), 7.95 (d, J = 5.0 Hz, 1H), 8.06 (d, J = 5.0 Hz, 1H), 8.12 (d, J = 5.0 Hz, 1H), 8.17 (d, J = 5.0 Hz, 1H) 8.30 (d, J = 5.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ = 55.00, 55.55, 56.32, 56.41, 56.47, 56.52, 56.61, 56.78, 61.17, 61.24, 61.35, 111.76, 111.86, 111.95, 112.01, 113.56, 113.78, 114.12, 118.10, 119.03, 120.68, 122.79, 123.80, 124.11, 126.79, 127.99, 129.90, 130.87, 131.83, 132.88, 135.41, 136.00, 136.77, 137.40, 138.10, 139.15, 142.27, 149.39, 151.80, 151.93, 153.67, 153.90, 154.68; UV-vis ($CHCl_3$): λ_{max}/nm (log ε) = 440 (4.84), 509 (4.64), 780 (3.69). ESI-HRMS calc. for $[C_{70}H_{69}N_6O_{14}]^+$ (M+H): 1217.4872, Found: 1217.4857.

Selected data for **4e:** ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 1.64 (s, 3H), 2.23 (s, 3H), 3.92 (s, 3H), 3.93 (s, 3H), 3.98 (s, 3H), 4.03 (s, 9H), 4.05(s, 6H), 4.10 (s, 3H), 4.11 (s, 3H), 4.12 (s, 3H), 4.13 (s, 3H), 4.14-4.16 (m,2H), 5.86 (d, J = 8.5 Hz, 2H), 6.94 (d, J = 8.0Hz, 2H), 7.11 (s, 1H), 7.18 (s, 1H), 7.19 (s, 1H), 7.32 (d, J = 8.5 Hz, 2H), 7.40 (s, 2H), 7.46 (s, 2H), 7.48 (s, 1H), 7.93 (d, J = 5.0 Hz, 1H), 8.00 (d, J = 5.0 Hz, 1H), 8.12 (d, J = 5.0 Hz, 1H), 8.17 (d, J = 5.0 Hz, 1H), 8.22 (d, J = 5.0 Hz, 1H) 8.34 (d, J = 5.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ = 20.16, 20.72, 56.34, 56.47, 56.54, 56.61, 56.78, 61.19, 61.25, 61.36, 111.91, 112.06, 113.86, 117.92, 118.34, 118.71, 121.46, 122.56, 124.19, 124.48, 126.98, 127.26, 128.12, 129.37, 129.89, 130.61, 131.35, 132.54, 135.43, 136.00, 136.02, 136.77, 137.45, 137.68, 138.02, 138.11, 138.28, 138.68, 139.17, 139.86, 142.52, 144.78, 149.37, 151.88, 151.93, 153.92; UV-vis ($CHCl_3$): λ_{max}/nm (log ε) = 440 (4.71), 506 (4.48), 774 (3.54). ESI-HRMS calc. for $[C_{70}H_{69}N_6O_{12}]^+$ (M+H): 1185.4973, Found: 1185.4956.

Selected data for **4f:** ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 3.93 (s, 3H), 3.94 (s, 3H), 3.98 (s, 3H), 4.04 (s, 9H), 4.07 (s, 6H), 4.09(s, 3H), 4.11 (s, 3H), 4.13 (s, 3H), 4.14 (s, 3H), 4.15-4.17 (m, 2H,), 5.96-5.98(m, 1H), 6.03-6.06 (m, 2H), 6.86-6.89 (m, 1H), 7.12-7.16 (m, 3H), 7.20 (s, 1H), 7.43-7.45 (m, 4H), 7.50 (s, 3H), 7.97 (d, J = 5.0 Hz, 1H), 8.02 (d, J = 5.0 Hz, 1H), 8.14 (d, J = 5.0 Hz, 1H), 8.20 (d, J = 5.0 Hz, 1H), 8.27 (d, J = 5.0 Hz, 1H) 8.38 (d, J = 5.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ =56.33, 56.43, 56.58, 56.62, 56.80, 61.19, 61.26, 61.27, 61.37, 111.80, 111.97, 112.06, 112.12, 114.02, 117.77, 117.95, 118.82, 118.90, 119.96, 120.08, 121.86, 122.46, 124.22, 124.64, 126.68, 127.09, 128.18, 128.90, 130.81, 132.69, 135.34, 135.88, 136.74, 137.25, 137.69, 138.03, 138.23, 138.38, 138.76, 139.23, 142.61, 149.09, 151.84, 151.89, 151.93, 151.97, 153.93. UV-vis ($CHCl_3$): λ_{max}/nm (log ε) = 442(4.95), 506(4.61), 778(3.68). ESI-HRMS calc. for $[C_{68}H_{65}N_6O_{12}]^+$ (M+H): 1157.4655, Found: 1157.4644.

Selected data for **5b:** ^{1}H NMR (500 MHz, CDCl$_3$, 298 K): δ = -4.91(s, 1H, -21-CH), -1.93(br, 2H, 22, 24-NH), 2.29 (s, 3H, -CH$_3$), 2.66 (s, 3H, -CH$_3$), 2.67 (s, 3H, -CH$_3$), 2.68 (s, 3H, -CH$_3$), 3.73 (s, 3H, -CH$_3$), 7.02 (d, J = 8.0 Hz, 2H, ArH), 7.43-7.45 (m, 2H, ArH), 7.51 (d, J = 8.0 Hz, 2H, ArH), 7.52 (d, J = 8.0 Hz, 2H, ArH), 7.60 (d, J = 8.0 Hz, 2H, ArH), 7.70 (d, J = 7.5 Hz, 2H, ArH), 8.00 (d, J = 7.5 Hz, 2H, ArH), 8.05 (d, J = 7.5 Hz, 2H, ArH), 8.16 (d, J = 7.5 Hz, 2H, ArH), 8.32 (d, J = 8.0 Hz, 2H, ArH), 8.41 (d, J = 4.5 Hz, 1H, pyrrH), 8.45 (d, J = 4.5 Hz, 1H, pyrrH), 8.49 (d, J = 4.5 Hz, 1H, pyrrH), 8.51 (d, J = 4.5 Hz, 1H, pyrrH), 8.58 (d, J = 4.5 Hz, 1H, pyrrH), 8.69 (d, J = 4.5 Hz, 1H, pyrrH); ^{13}C NMR (125 MHz, CDCl$_3$, 298 K): δ = 20.8, 21.53, 21.54, 21.57, 21.60, 101.9, 116.8, 117.0, 118.2, 121.2, 124.7, 125.4, 126.6, 126.9, 127.6, 127.7, 127.9, 128.9, 129.4, 130.1, 131.0, 131.2, 132.8, 134.3, 134.4, 134.7, 136.7, 136.9, 137.1, 137.2, 137.5, 138.1, 138.5, 139.09, 139.15, 139.21, 139.4, 154.0, 156.7. UV-vis (CHCl$_3$): λ_{max}/nm (log ε) = 413(4.79), 484(4.93), 652(3.70), 720(3.60). ESI-HRMS calc. for [C$_{55}$H$_{46}$N$_5$]$^+$ (M+H):776.3748, Found: 776.3748.

Selected data for **5c:** ^{1}H NMR (500 MHz, CDCl$_3$, 300 K): δ = –4.93 (s, 1H, -21-CH), –2.17 (br, 2H, 22, 24-NH), 2.65 (s, 3H, -CH$_3$), 2.66 (s, 3H, -CH$_3$), 2.67 (s, 3H, -CH$_3$), 2.73 (s, 3H, -CH$_3$), 6.91 (tt, ^3J = 7.2 Hz, ^4J = 1.0 Hz 1H, *p*-ArH), 7.21 (m, 2H, ArH), 7.25 (b, 1H, NH), 7.50 (d, J = 8.4 Hz, 2H, ArH), 7.52 (d, J = 8.0 Hz, 2H, ArH), 7.55 (d, J = 7.7 Hz, 2H, ArH), 7.59 (d, J = 7.7 Hz, 2H, ArH), 7.72 (d, J = 7.8 Hz, 2H, ArH), 7.99 (d, J = 7.8 Hz, 2H, ArH), 8.04 (d, J = 7.9 Hz, 2H, ArH), 8.18 (d, J = 7.8 Hz, 2H, ArH), 8.32 (d, J = 7.7 Hz, 2H, ArH), 8.42 (d, J = 4.7 Hz, 1H, pyrrH), 8.45 (d, J = 4.4 Hz, 1H, pyrrH), 8.49 (d, J = 4.9 Hz, 1H, pyrrH), 8.52 (d, J = 4.5 Hz, 1H, pyrrH), 8.58 (d, J = 5.0 Hz, 1H, pyrrH), 8.72 (d, J = 4.8 Hz, 1H, pyrrH); ^{13}C NMR (125 MHz, DCl$_3$, 300 K): δ = 21.5, 21.6, 101.8, 118.2, 121.1, 121.7, 124.7, 125.5, 126.5, 126.9, 127.6, 127.7, 127.9, 128.9, 130.1, 132.9, 134.4, 134.6, 135.2, 136.7, 136.9, 137.2, 137.5, 138.1, 138.4, 139.2, 139.3, 139.4, 154.1, 156.8, 158.1. UV-vis (CHCl$_3$):@ λ_{max}/nm (log ε) = 276 (4.62) 344sh 414 (4.93), 477 (5.07), 553 sh, 652(3.70), 605 sh, 652 (3.96), 718 (3.90). ESI-HRMS calc. for [C$_{54}$H$_{44}$N$_5$]$^+$ (M+H$^+$): 762.3591, Found: 762.3570.

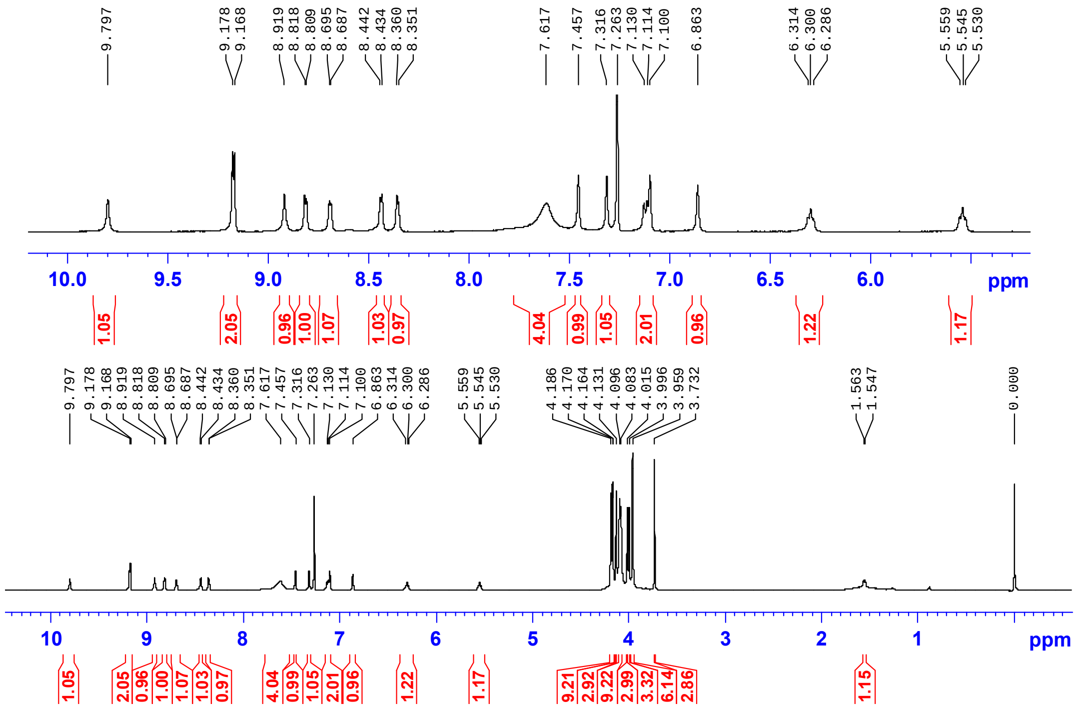


Figure S1. ^{1}H NMR spectrum of **2a**, 298 K, CDCl$_3$.

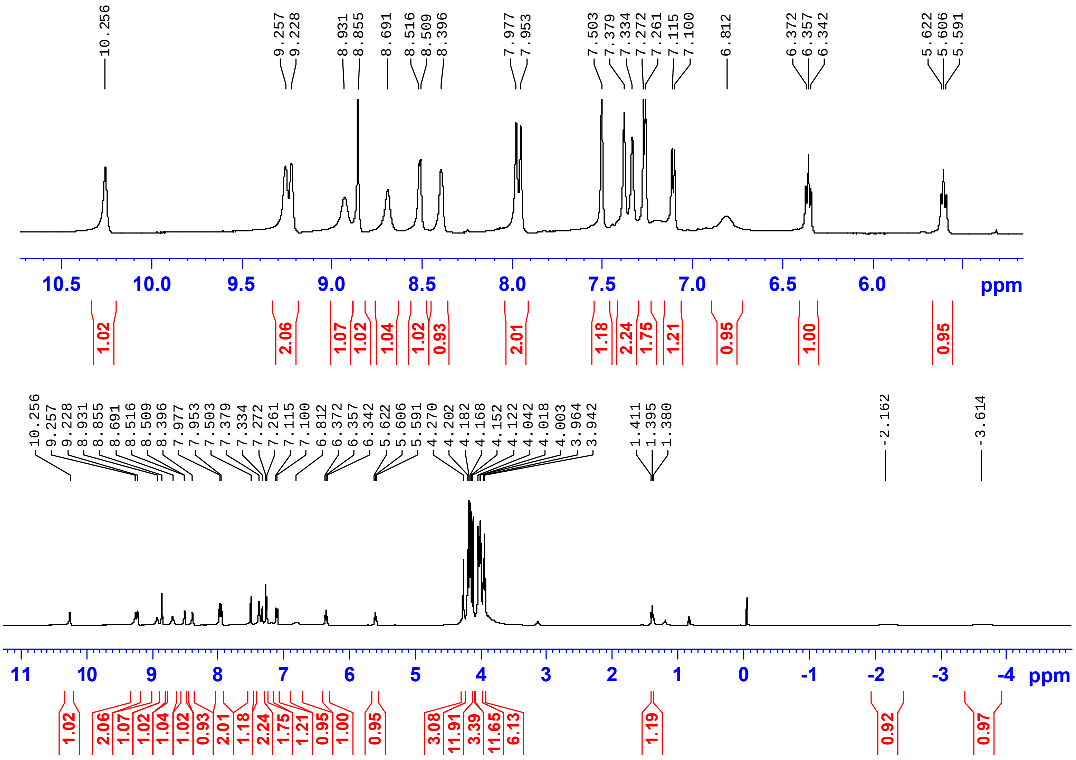


Figure S2. ^{1}H NMR spectrum of **2a**, 248 K, $CDCl_3$.

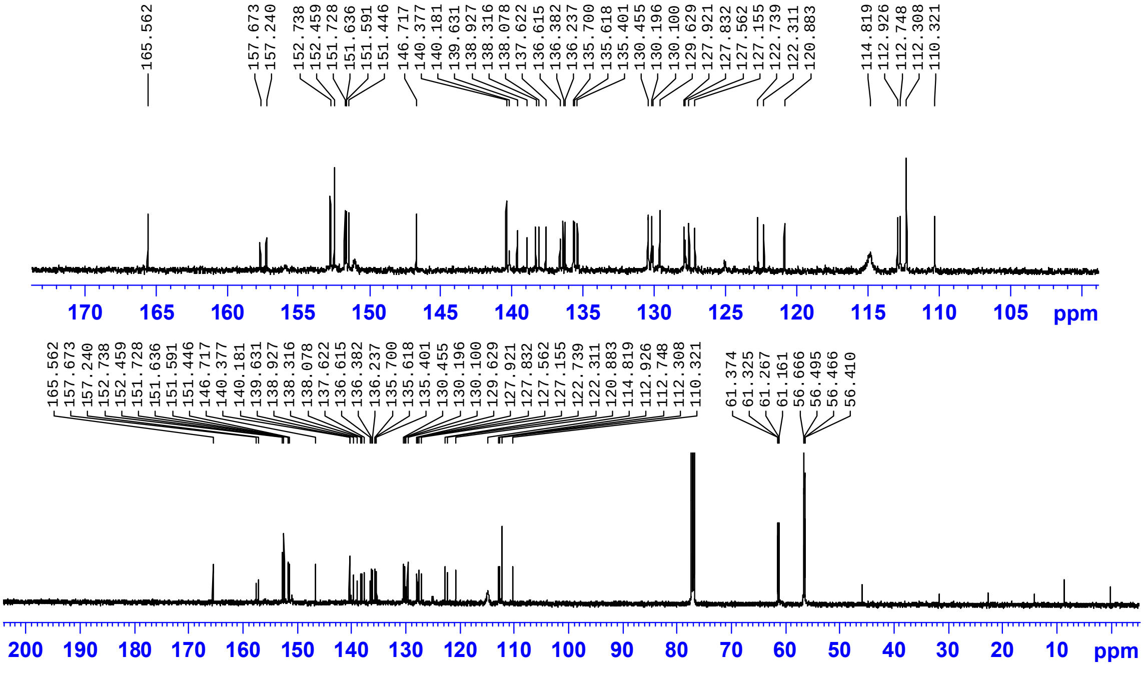


Figure S3. ^{13}C NMR spectrum of **2a**, 298 K, $CDCl_3$.

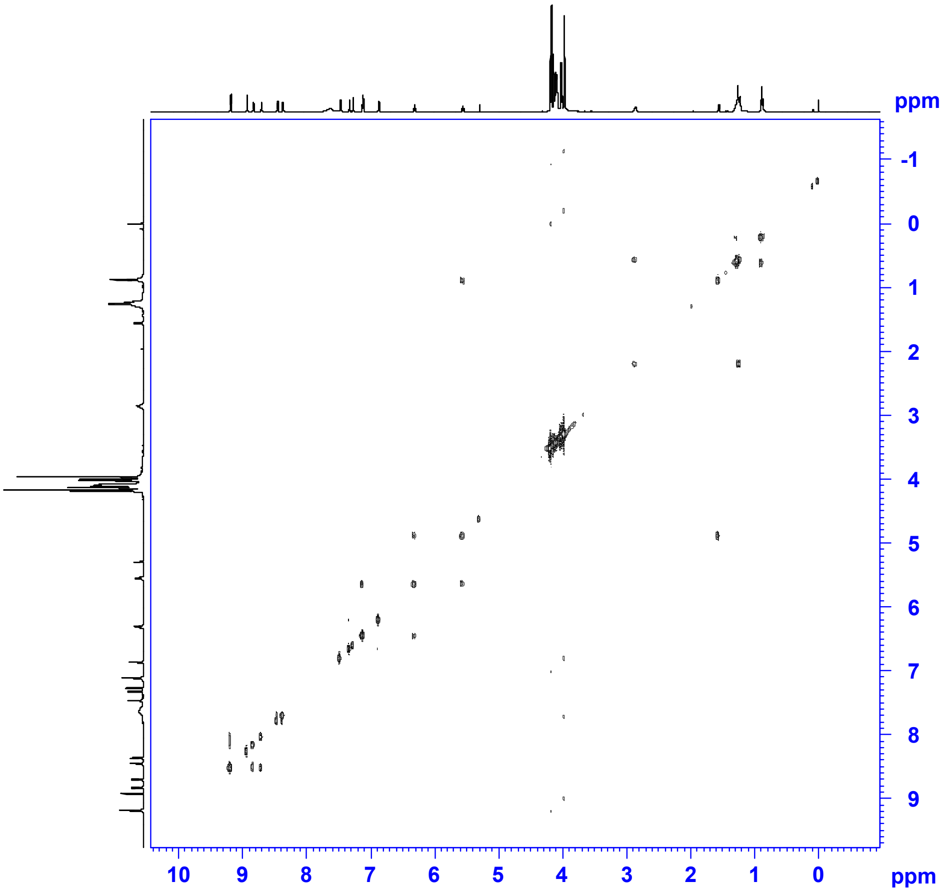


Figure S4. COSY spectrum of **2a** (298K).

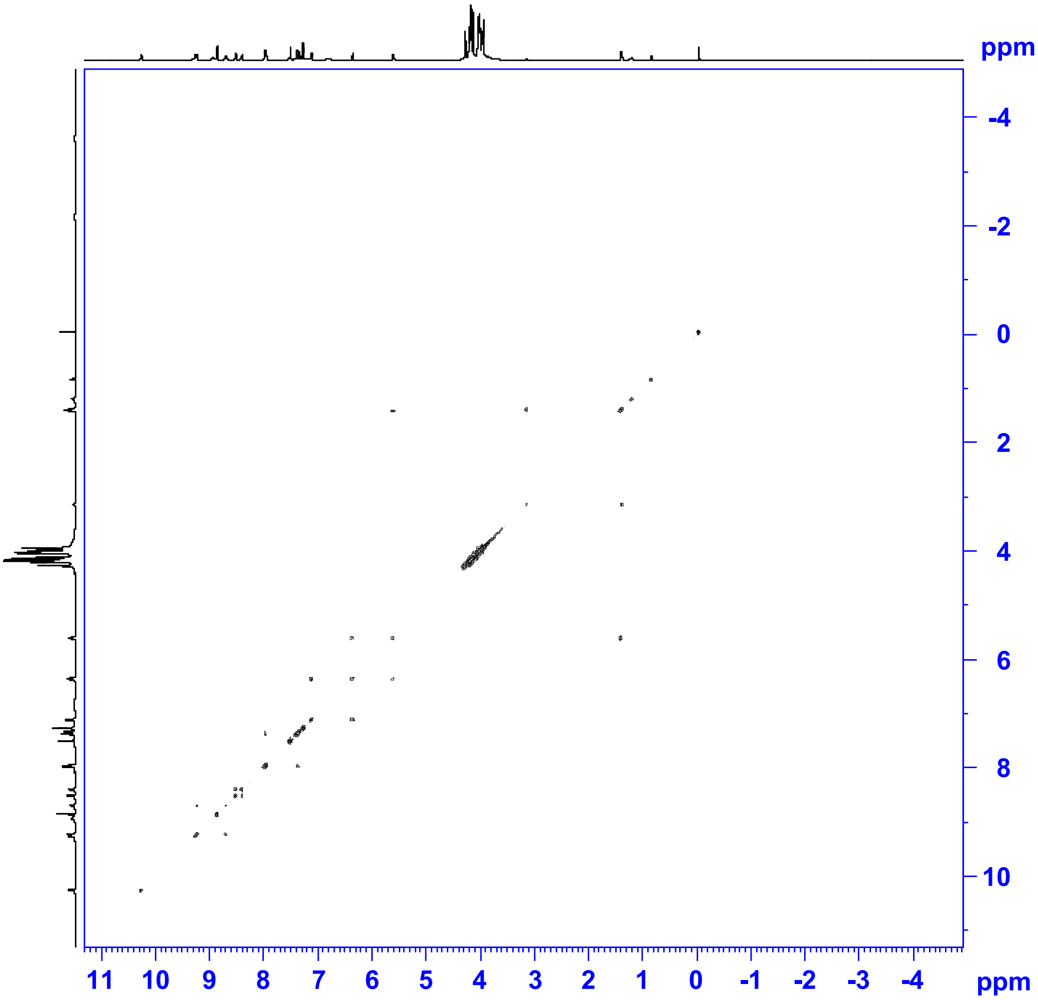


Figure S5. COSY spectrum of **2a** (248K).

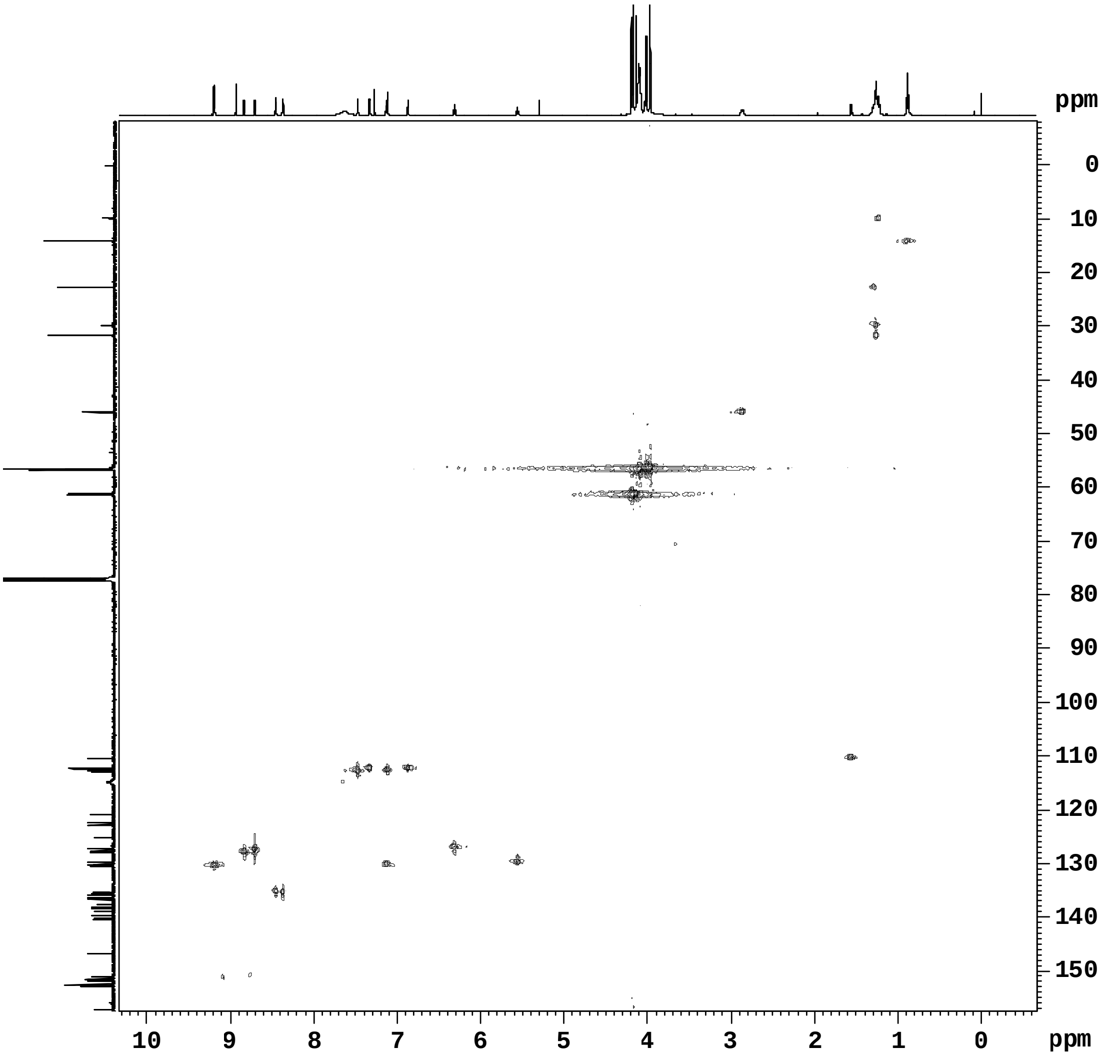


Figure S6. HSQC spectrum of **2a** ($CDCl_3$, 298 K).

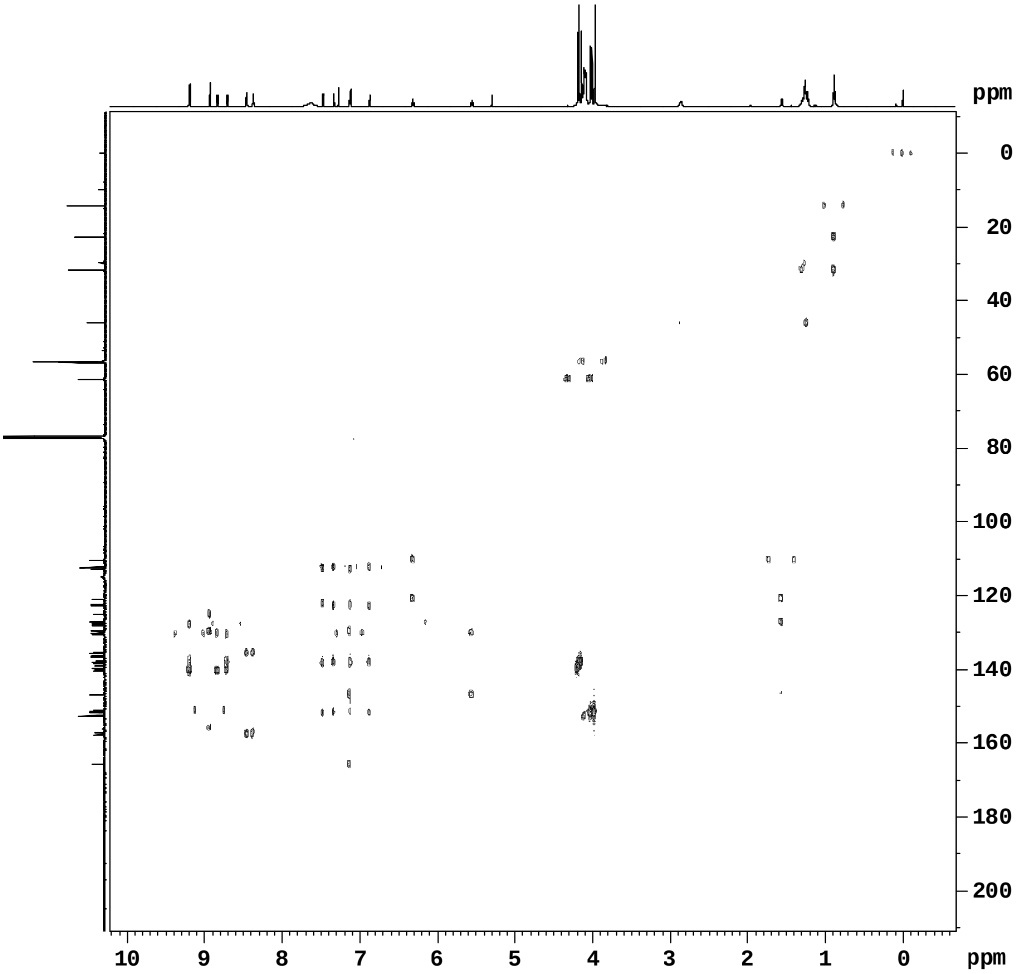


Figure S7. HMBC spectrum of **2a** ($CDCl_3$, 298 K).

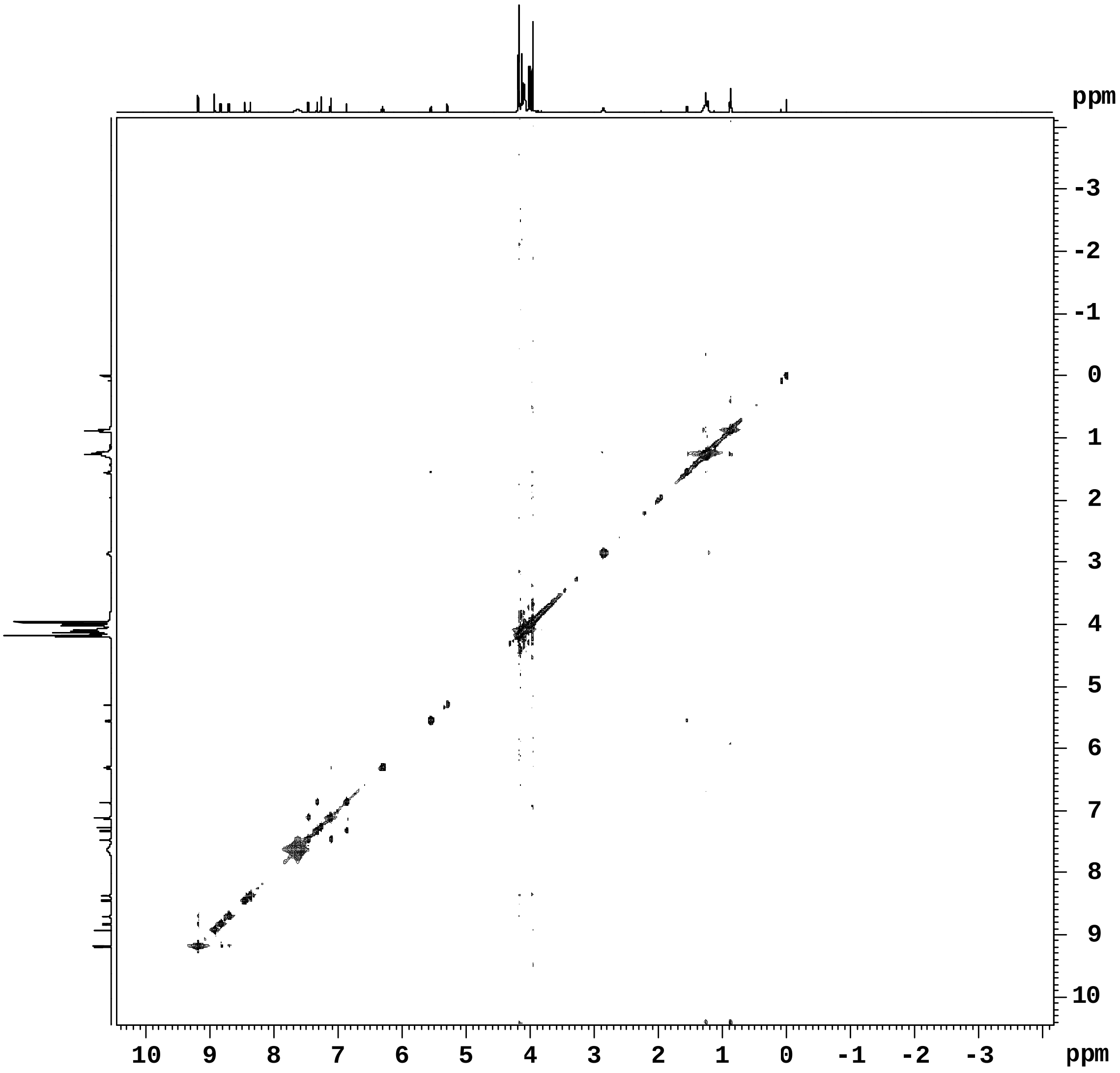


Figure S8. NOESY spectrum of **2a** ($CDCl_3$, 298 K).

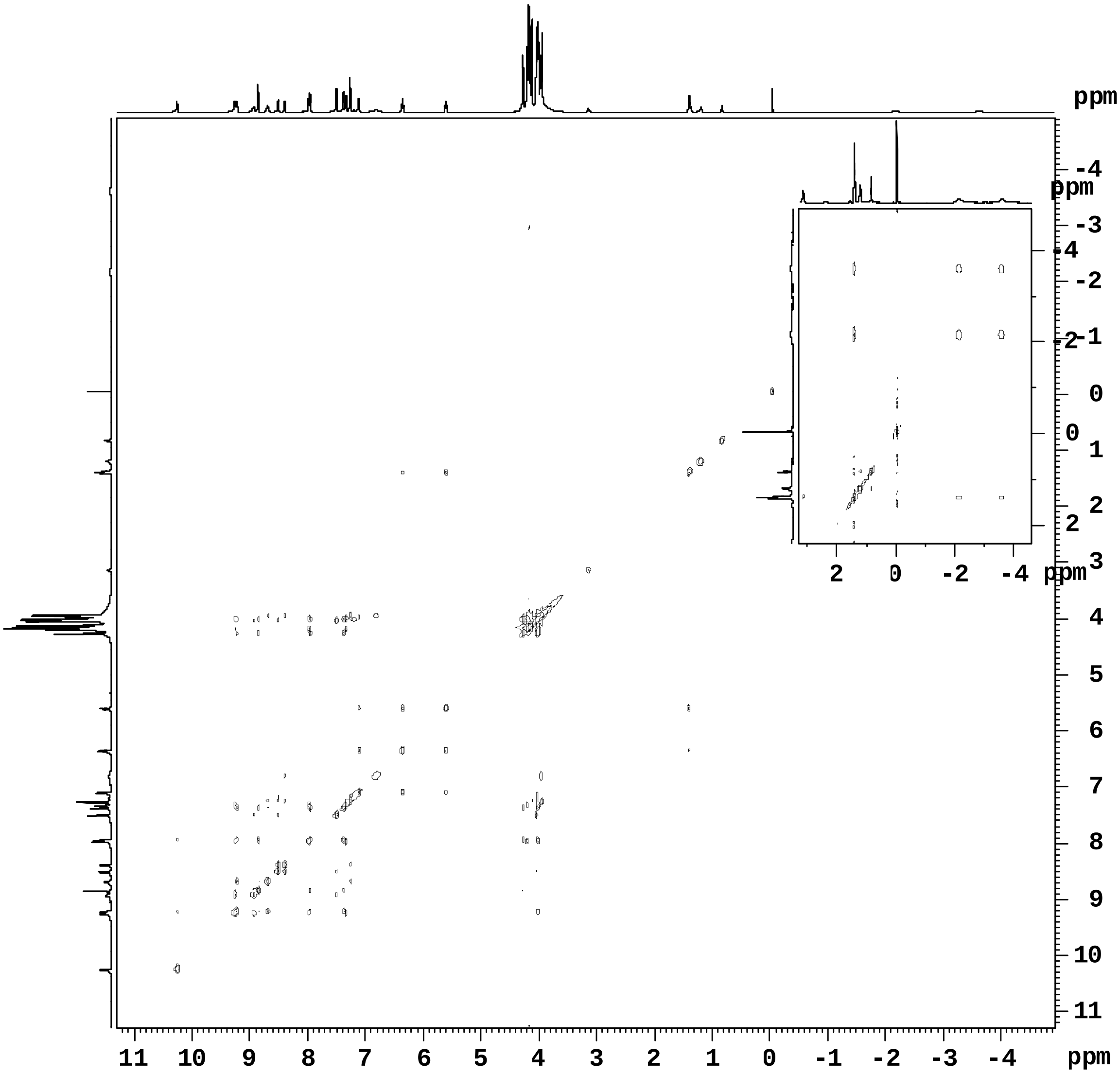


Figure S9. NOESY spectrum of **2a** ($CDCl_3$, 248 K).

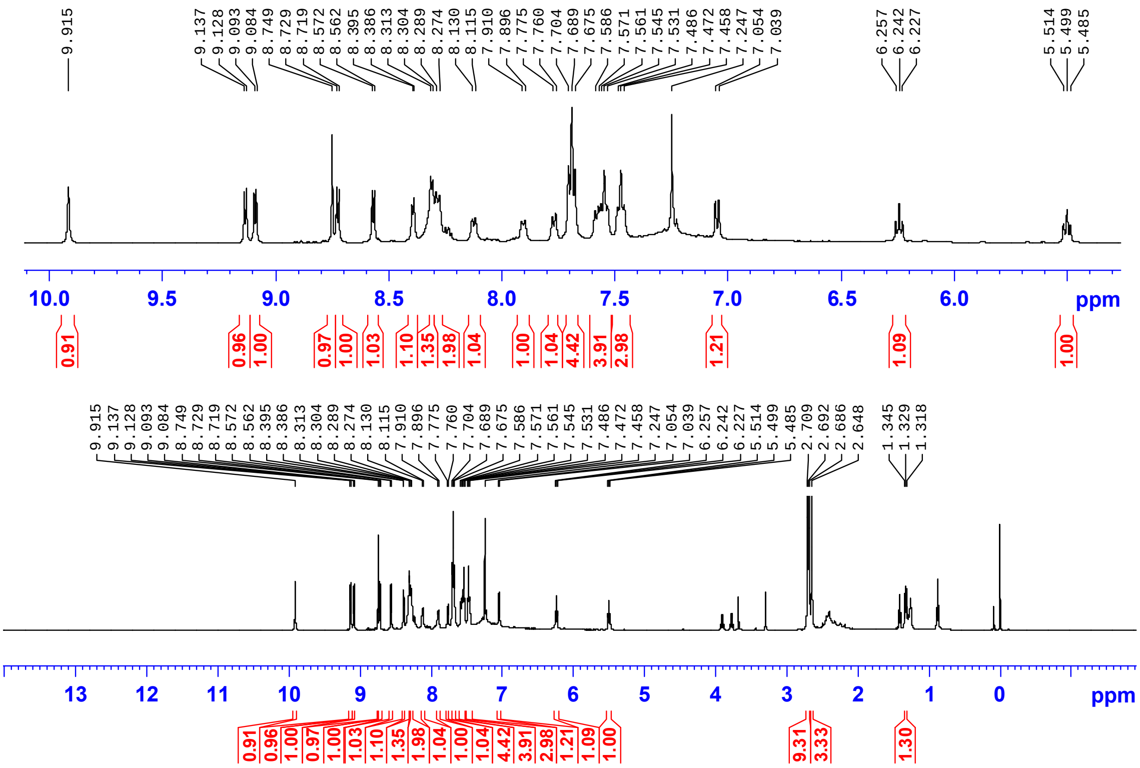


Figure S10. ^{1}H NMR spectrum of **2b**, 298 K, CDCl$_3$.

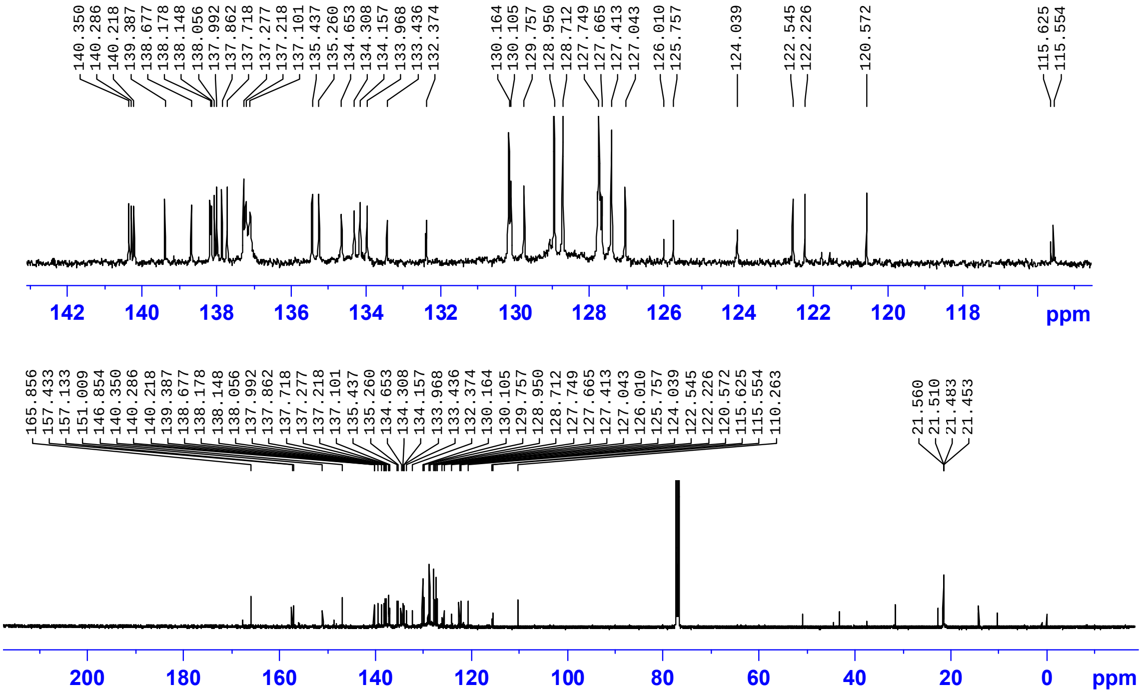


Figure S11. ^{13}C NMR spectrum of **2b**, 298 K, CDCl$_3$.

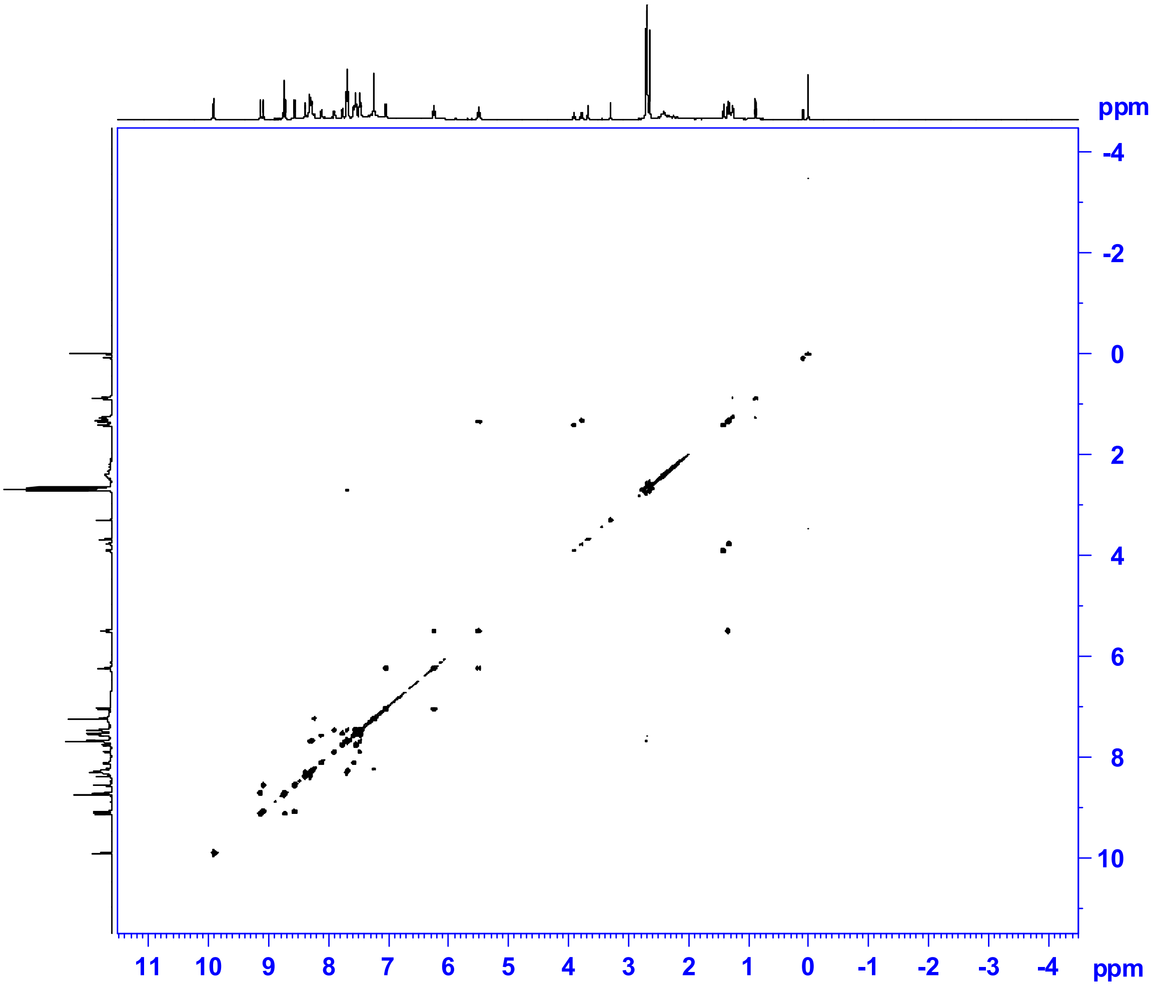


Figure S12. COSY spectrum of **2b** (298K).

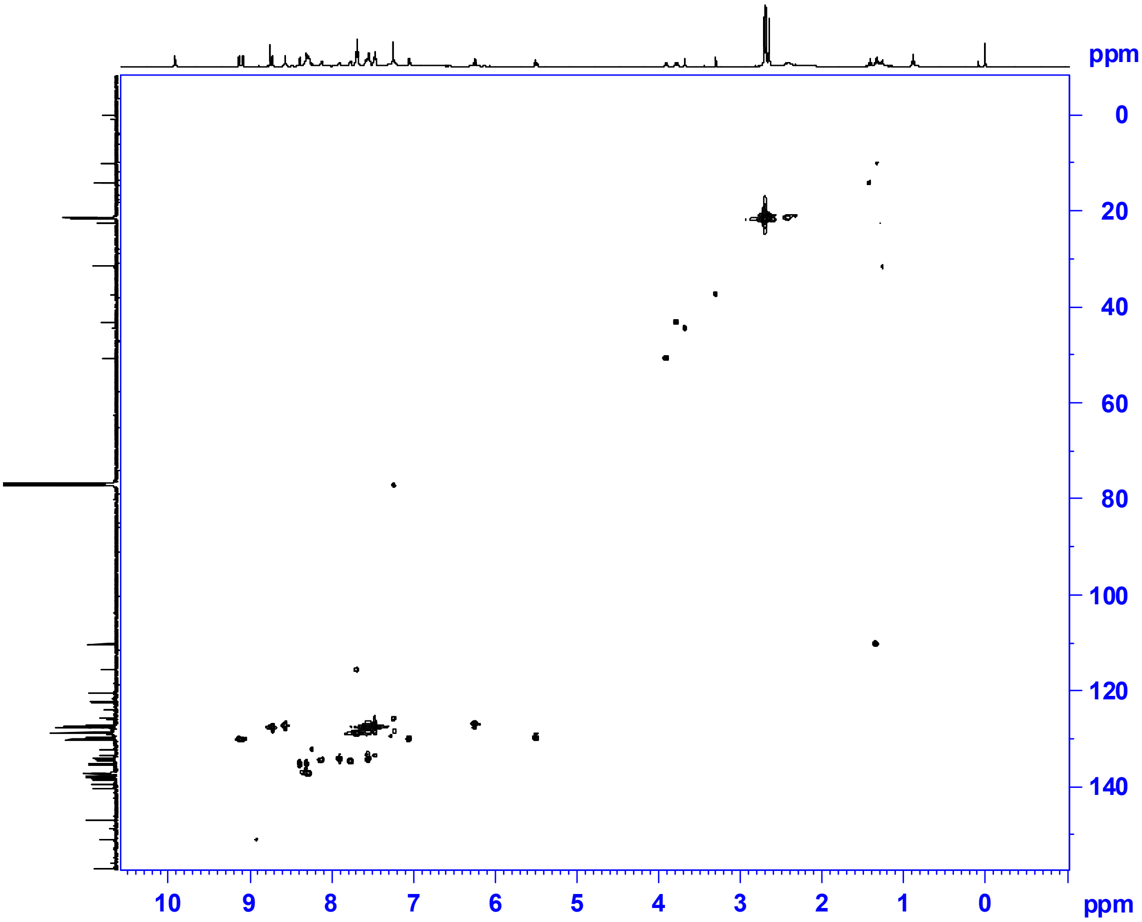


Figure S13. HSQC spectrum of **2b** ($CDCl_3$, 298 K).

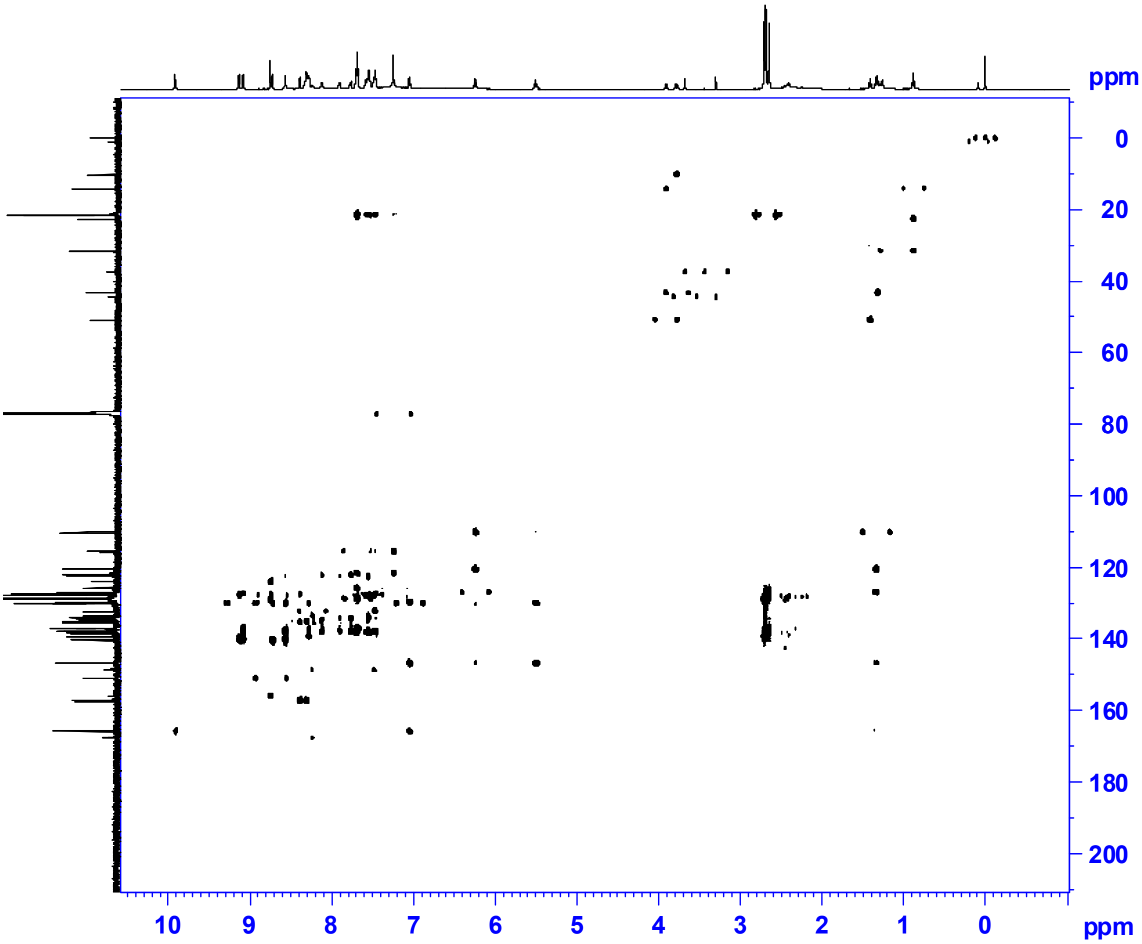


Figure S14. HMBC spectrum of **2b**(CDCl$_3$, 298 K).

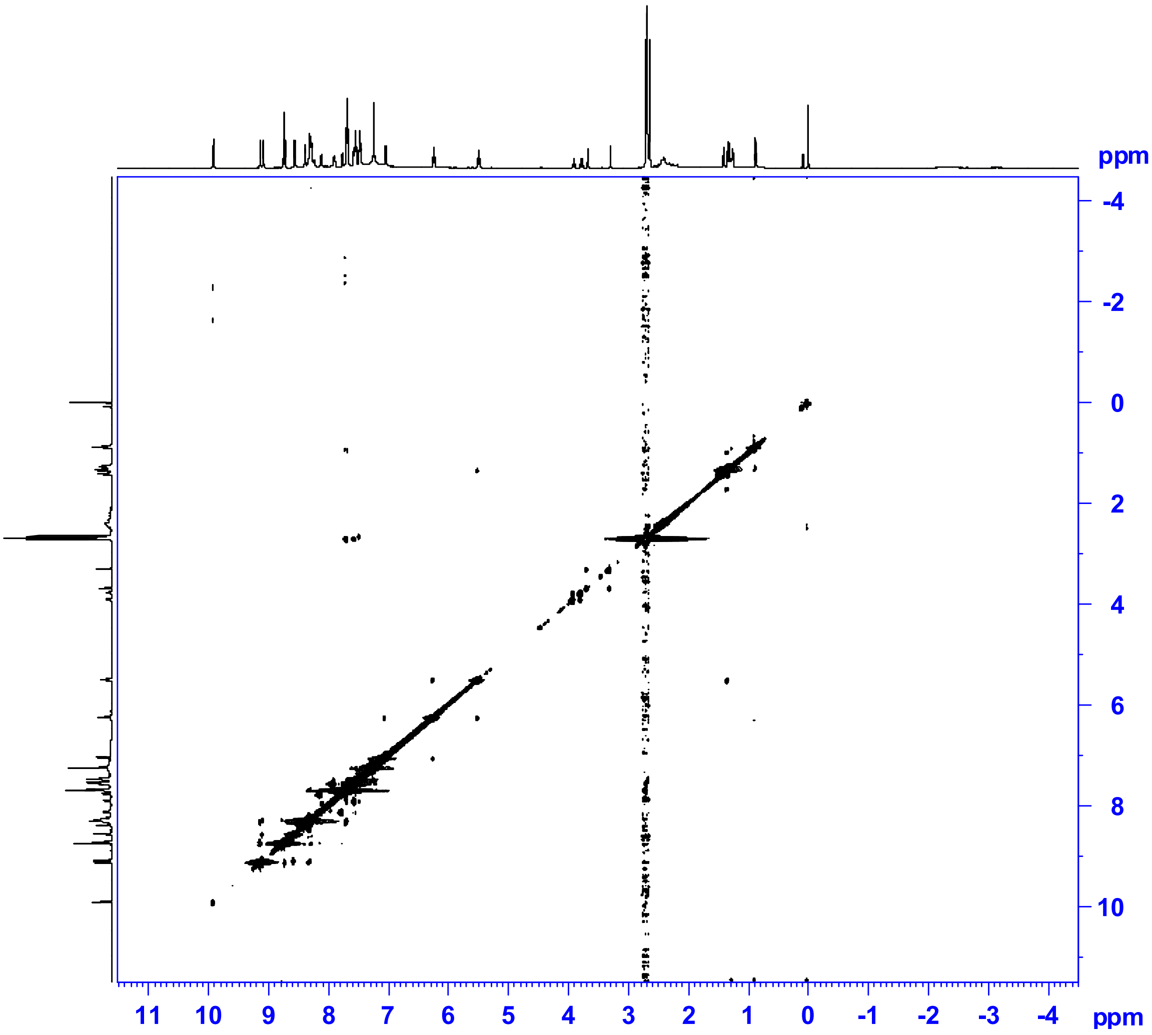


Figure S15. NOESY spectrum of **2b** ($CDCl_3$, 298 K).

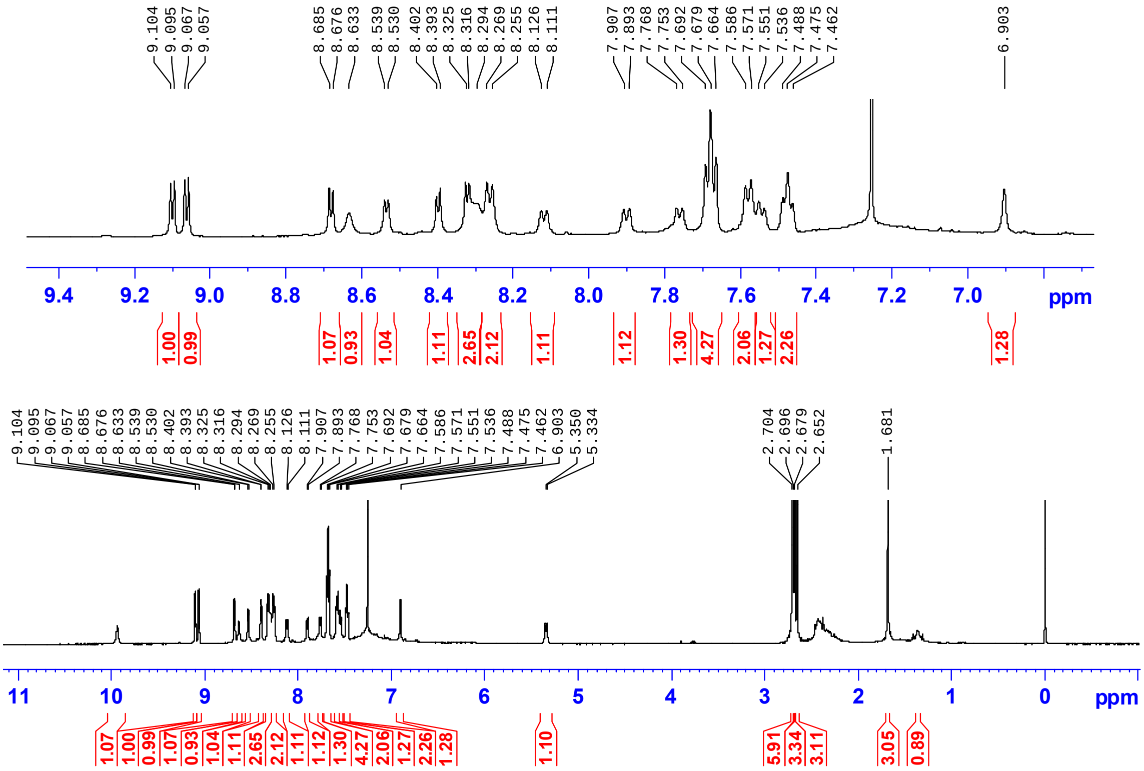


Figure S16. ^{1}H NMR spectrum of **2c**, 298 K, CDCl$_3$.

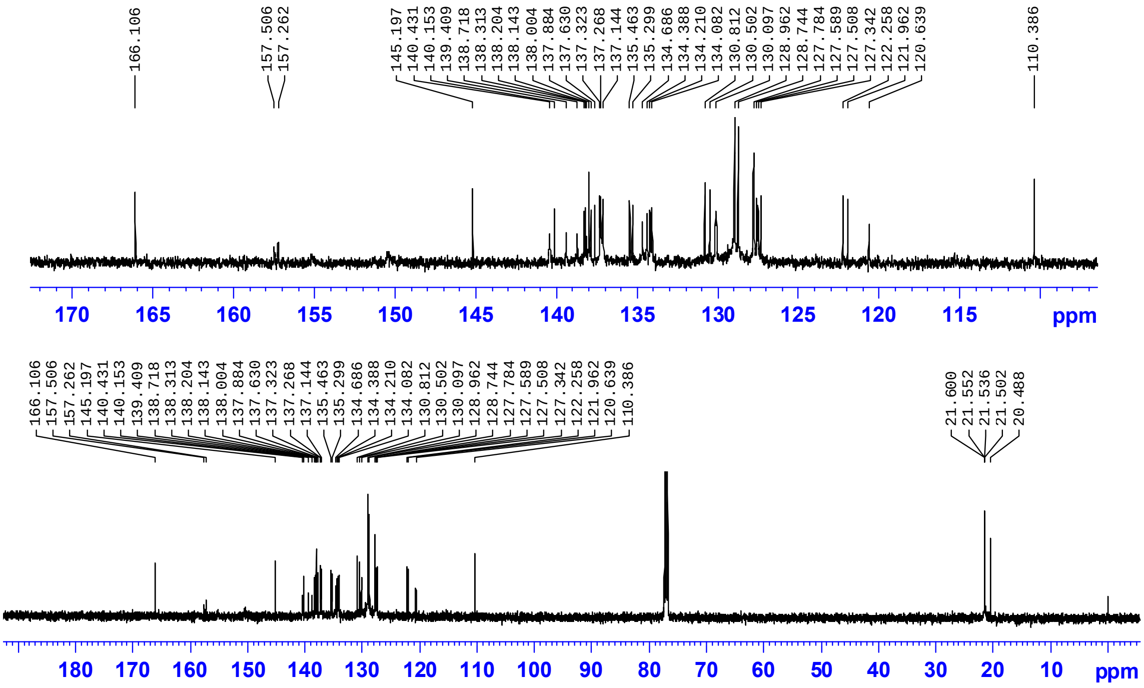


Figure S17. ^{13}C NMR spectrum of **2c**, 298 K, CDCl$_3$.

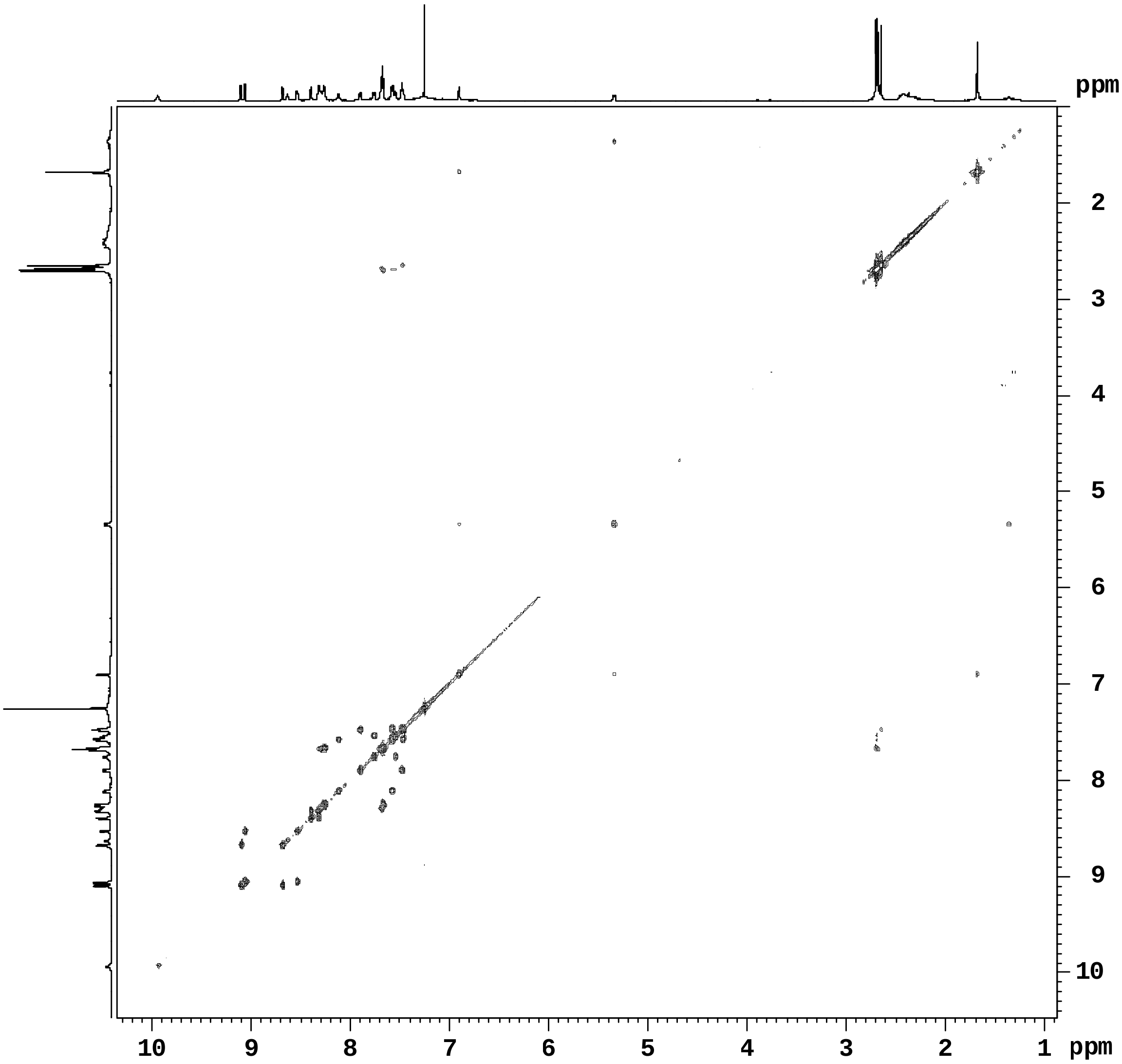


Figure S18. COSY spectrum of **2c** (298K).

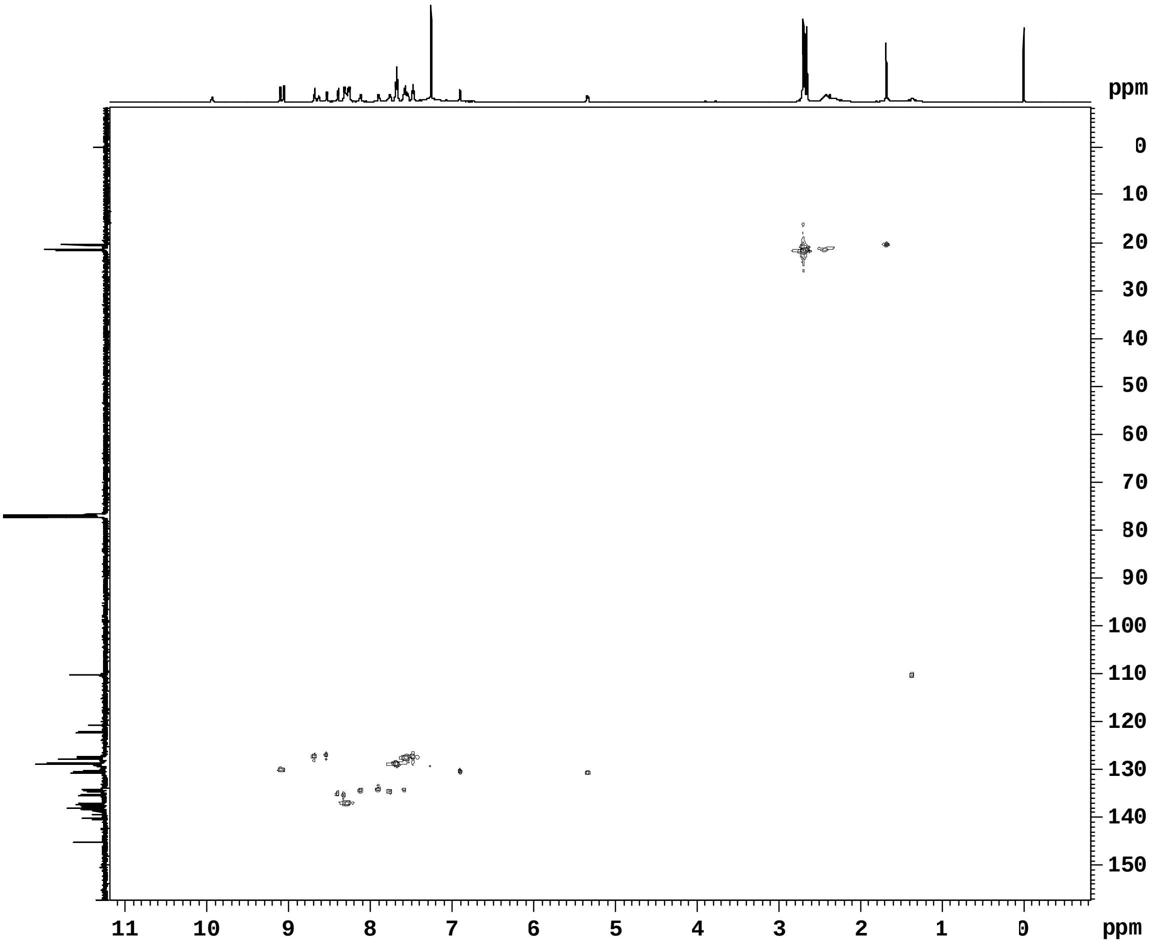


Figure S20. HSQC spectrum of **2c** ($CDCl_3$, 298 K).

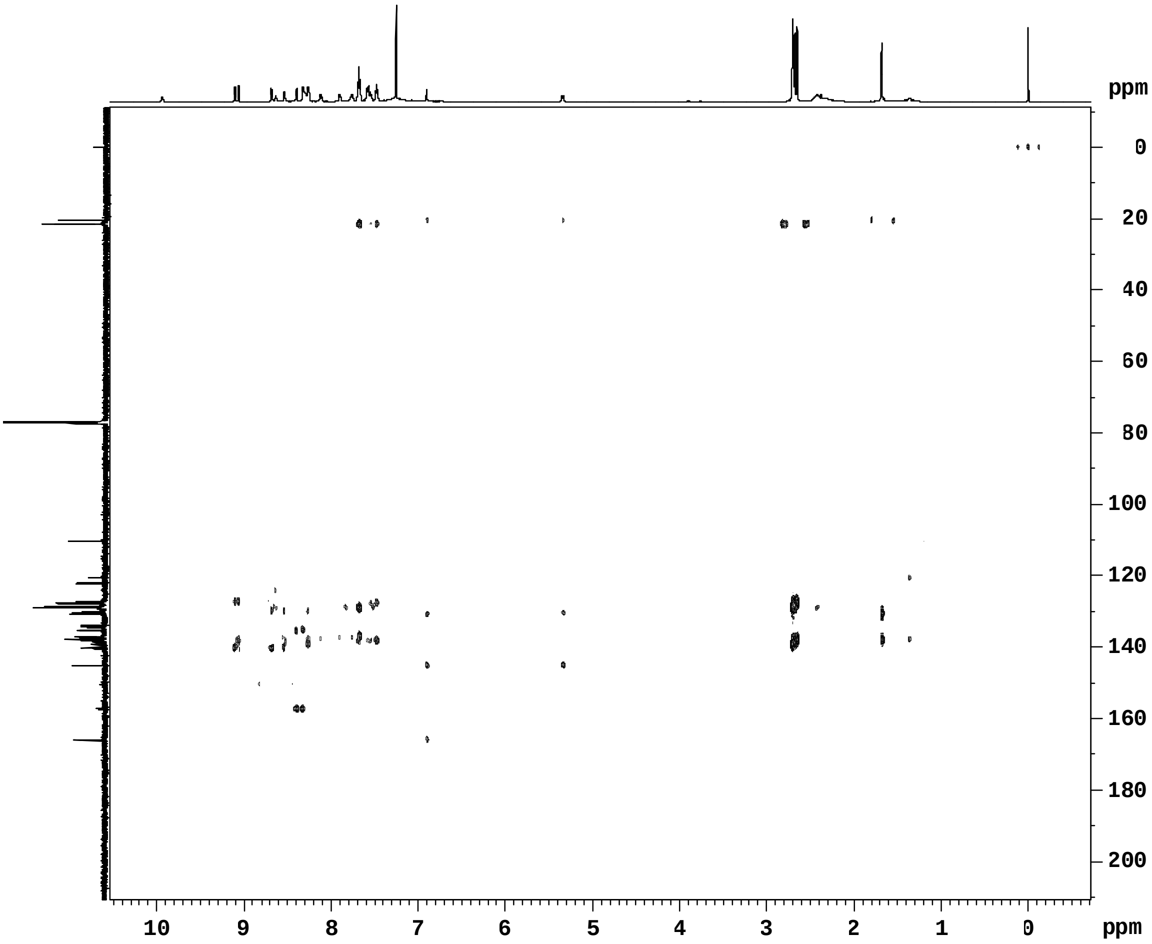


Figure S21. HMBC spectrum of **2c**($CDCl_3$, 298 K).

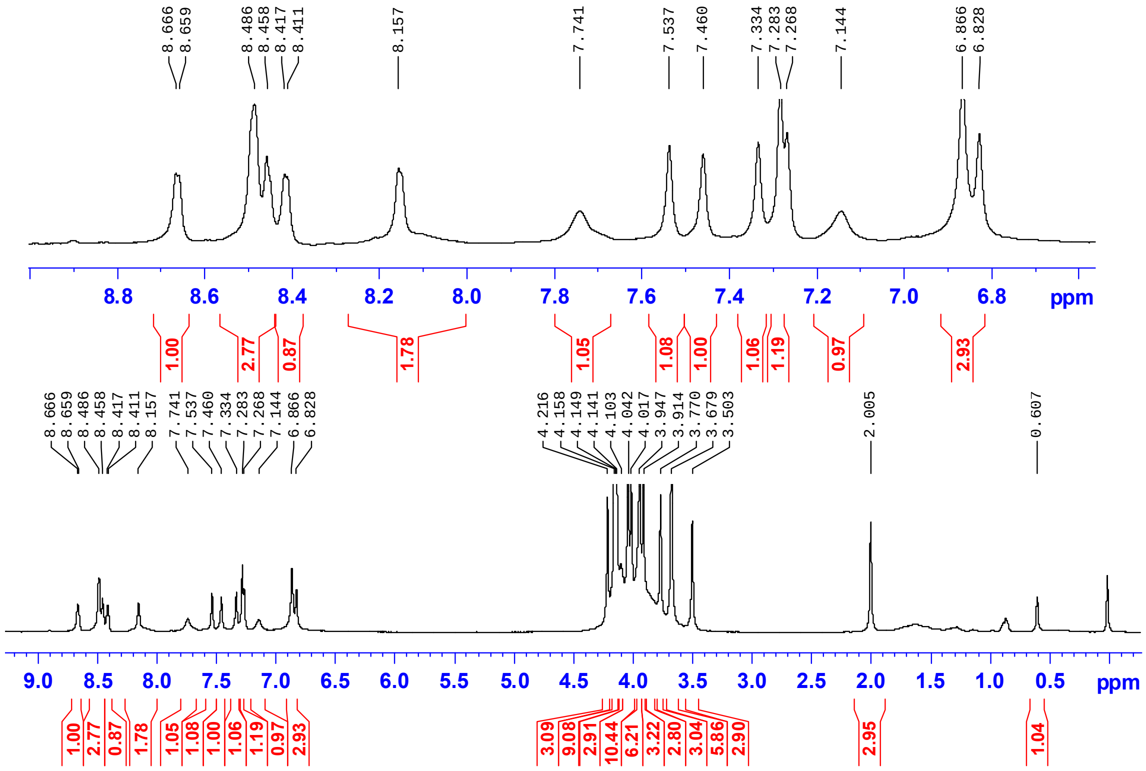


Figure S22. ^{1}H NMR spectrum of **3a**, 298 K, $CDCl_3$.

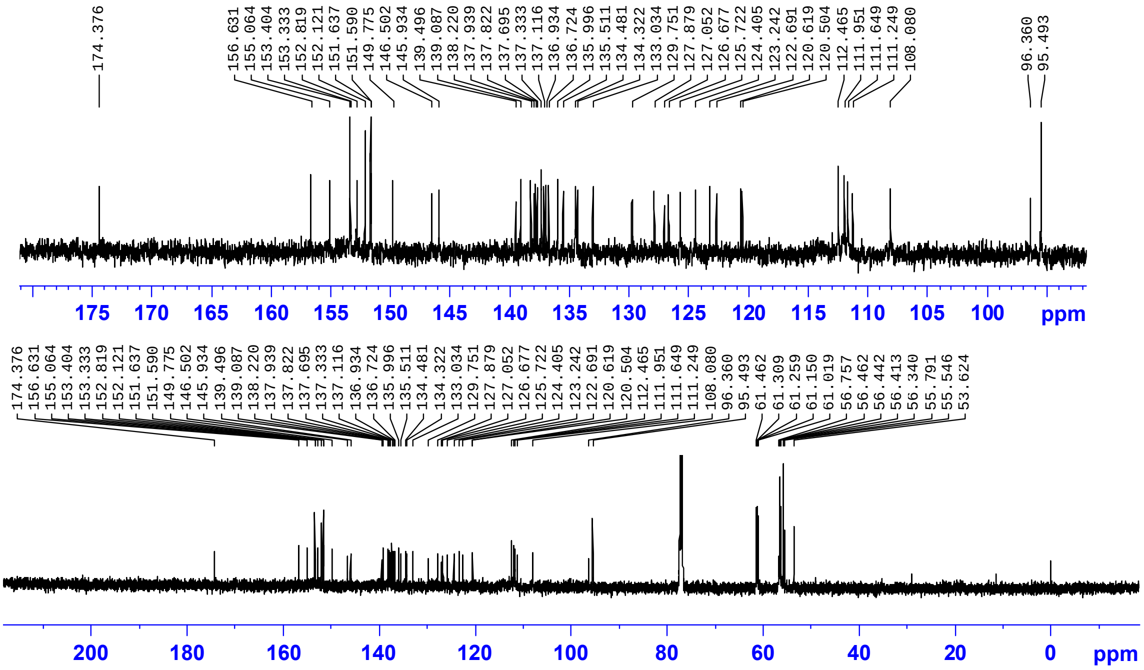


Figure S23. ^{13}C NMR spectrum of **3a**, 298 K, $CDCl_3$.

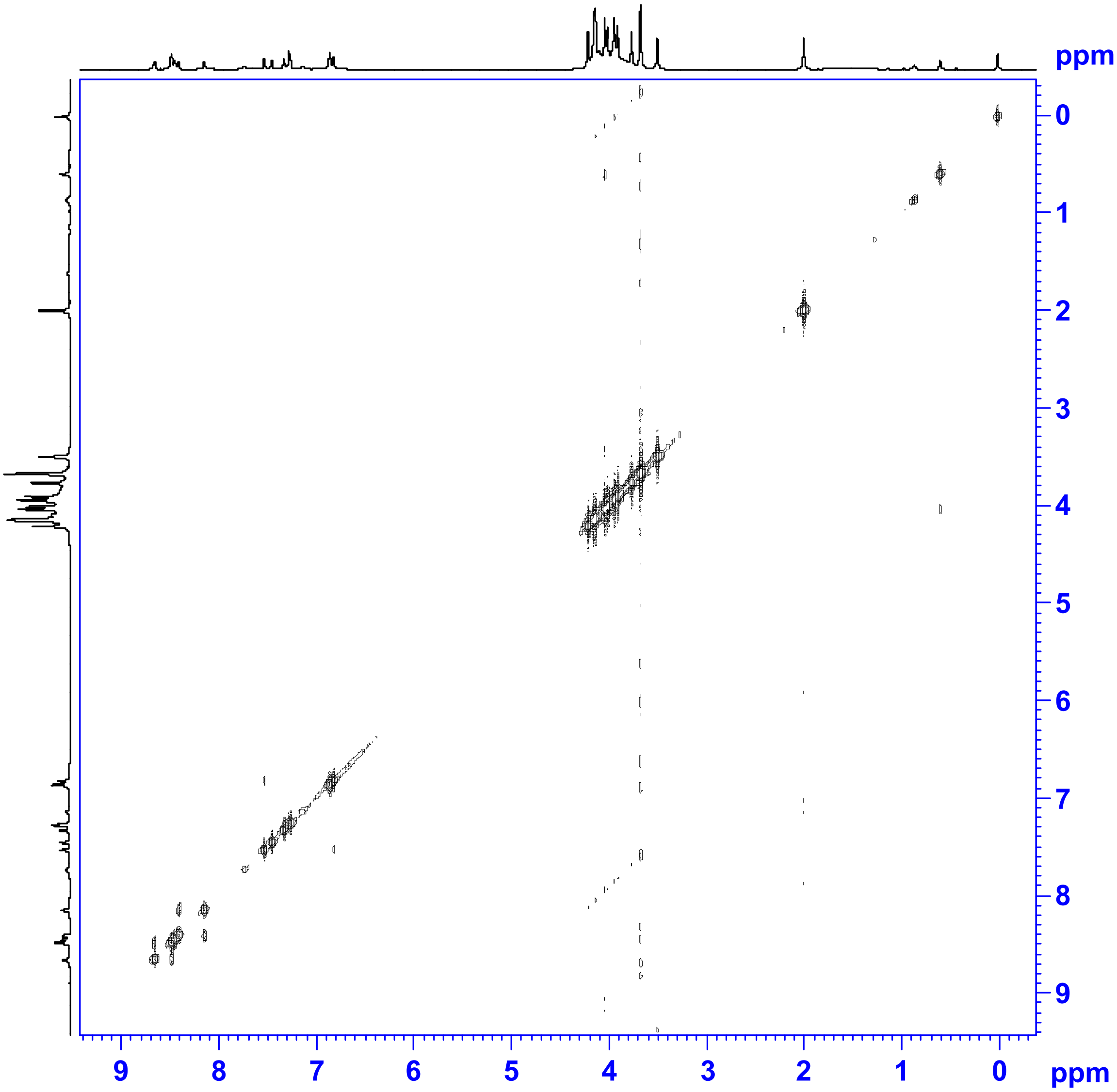


Figure S24. COSY spectrum of **3a** (298K).

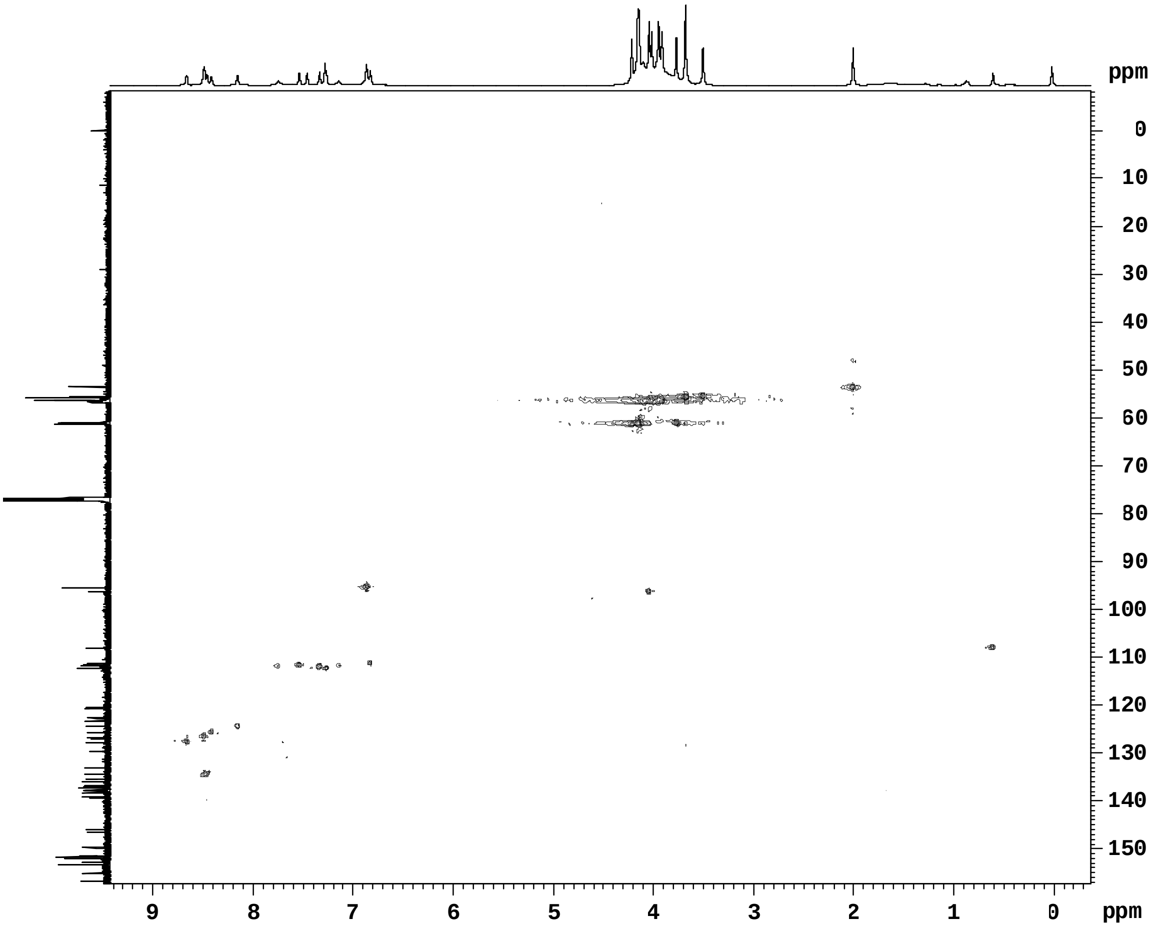


Figure S25. HSQC spectrum of **3a** ($CDCl_3$, 298 K).

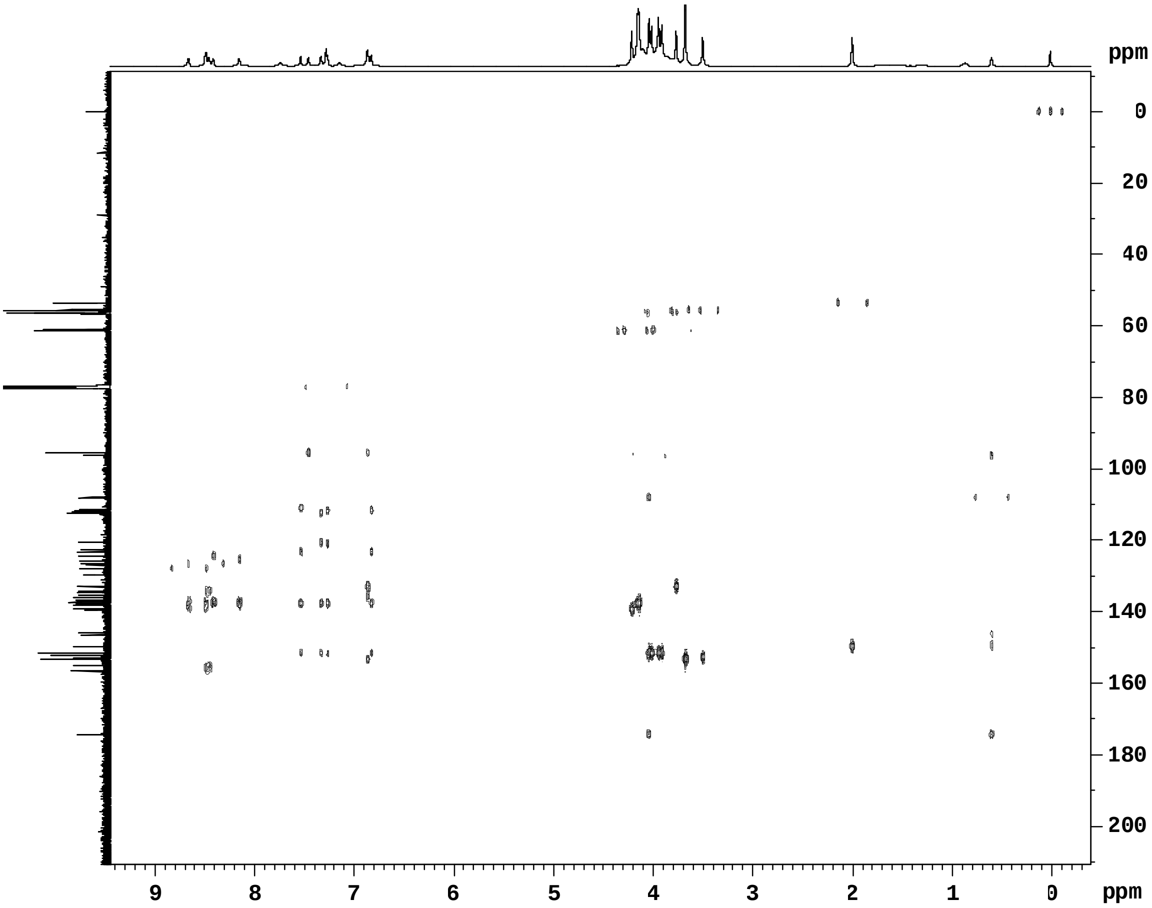


Figure S26. HMBC spectrum of **3a** ($CDCl_3$, 298 K).

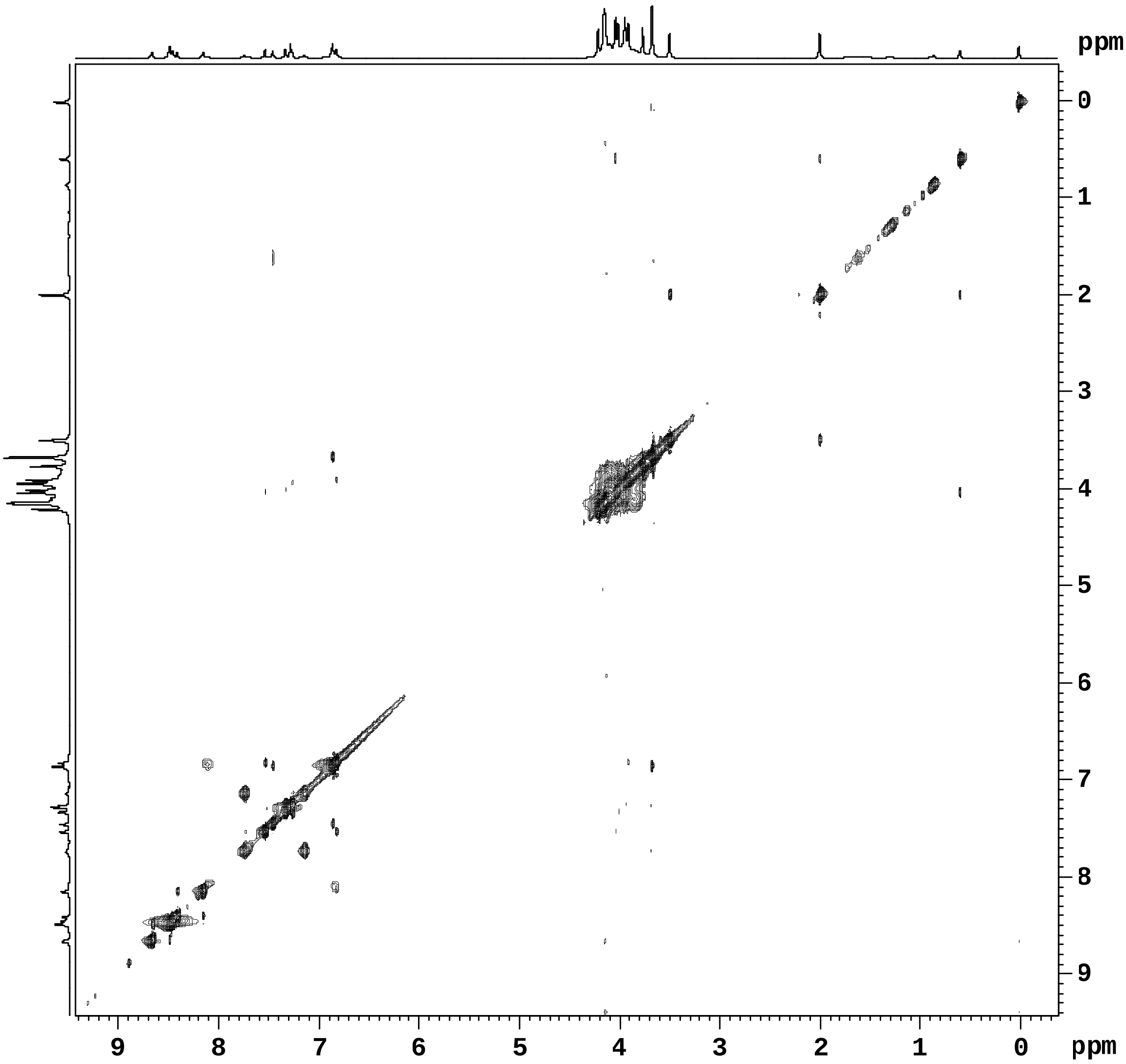


Figure S27. NOESY spectrum of **3a** ($CDCl_3$, 298 K).

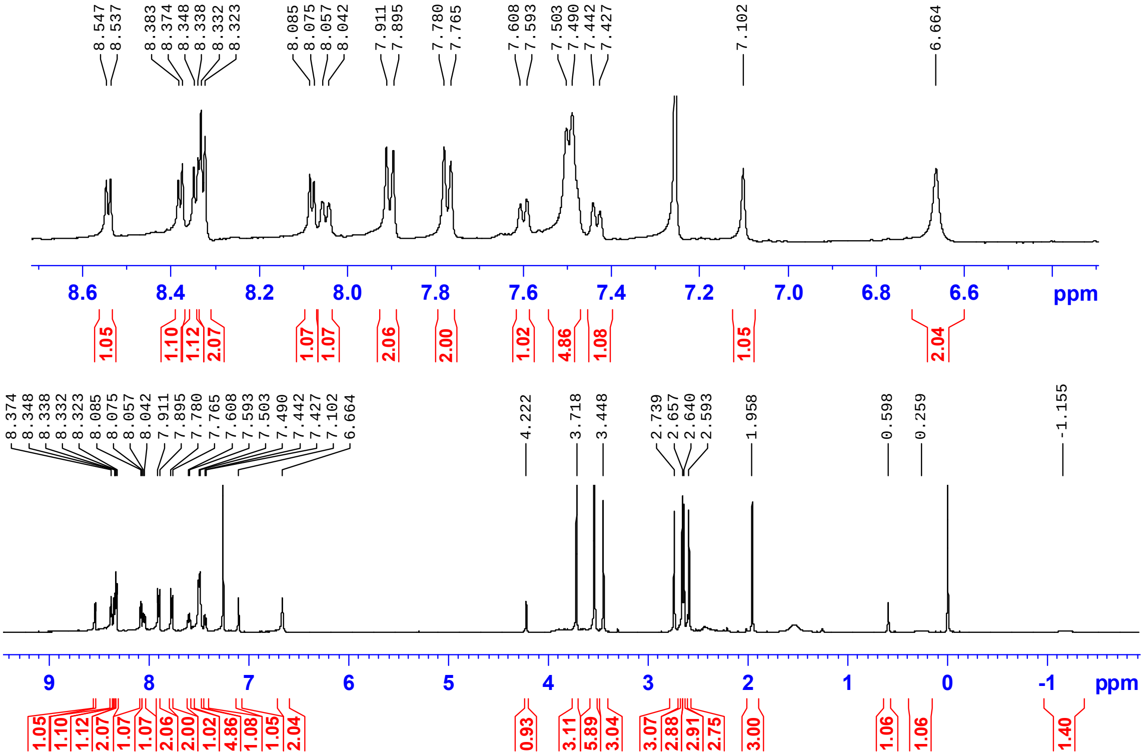


Figure S28. ^{1}H NMR spectrum of **3b**, 298 K, CDCl$_3$.

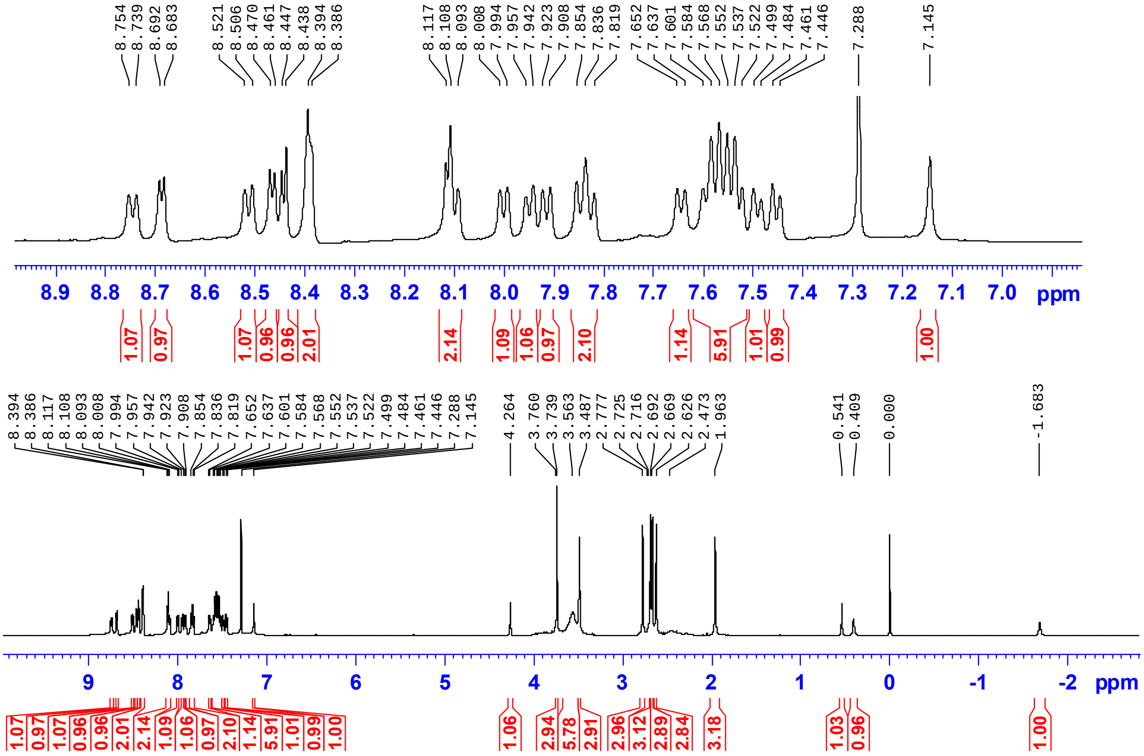


Figure S29. ^{1}H NMR spectrum of **3b**, 233 K, CDCl$_3$.

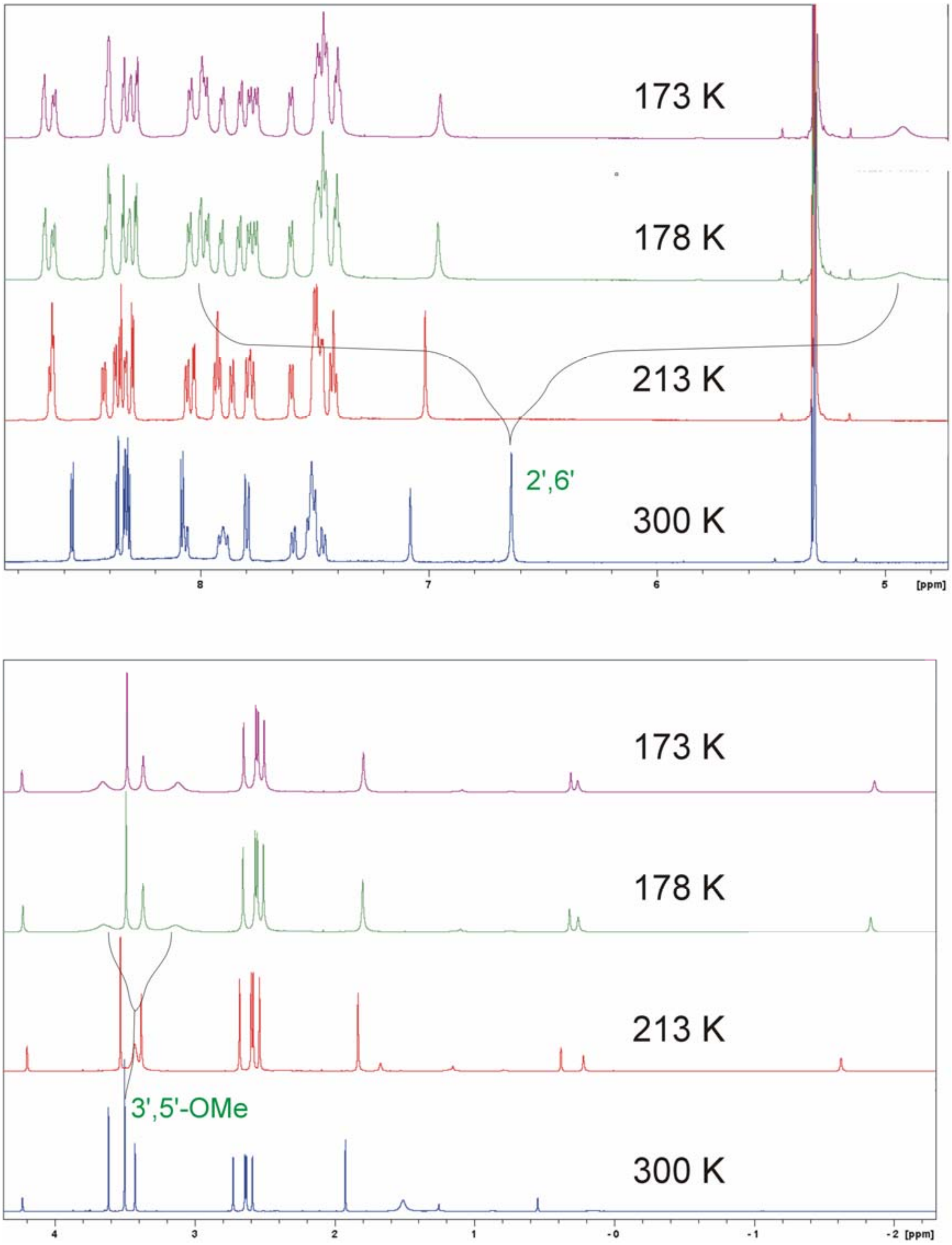


Figure S29a. Variable temperature ^{1}H NMR spectrum of **3b** (600 MHz, CD_2Cl_2).

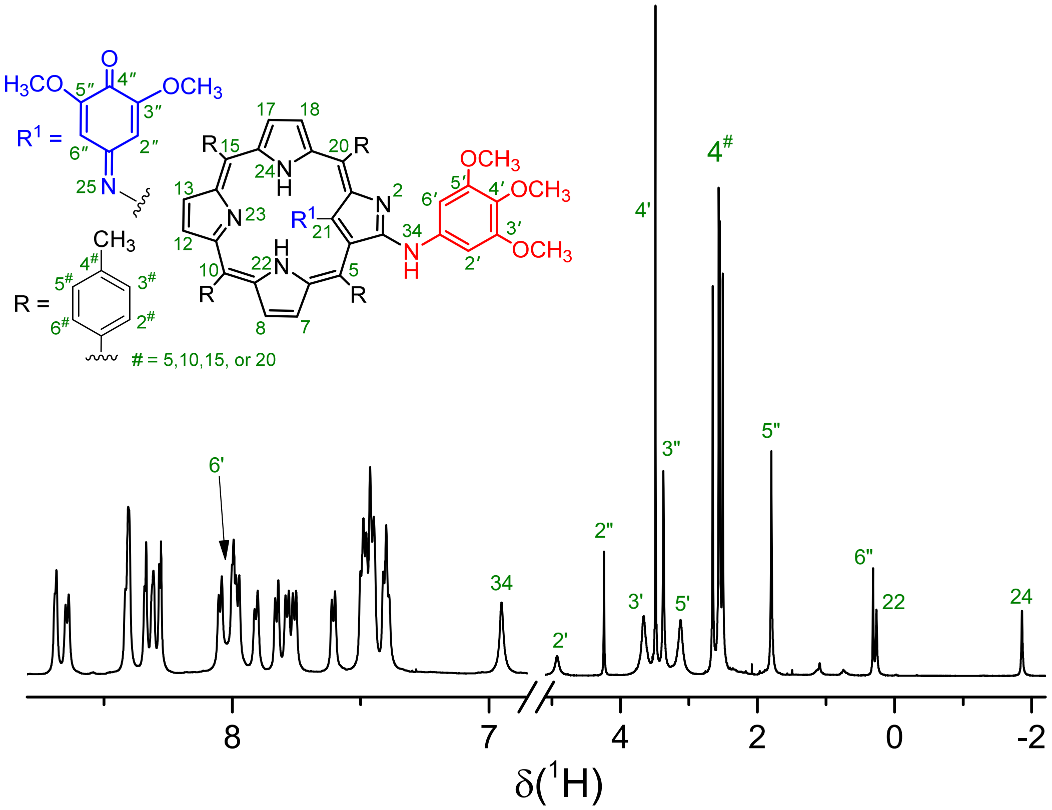


Figure S29b. ^{1}H NMR spectrum (600 MHz, CD_2Cl_2, 173 K) of **3b** with a partial assignment of signals.

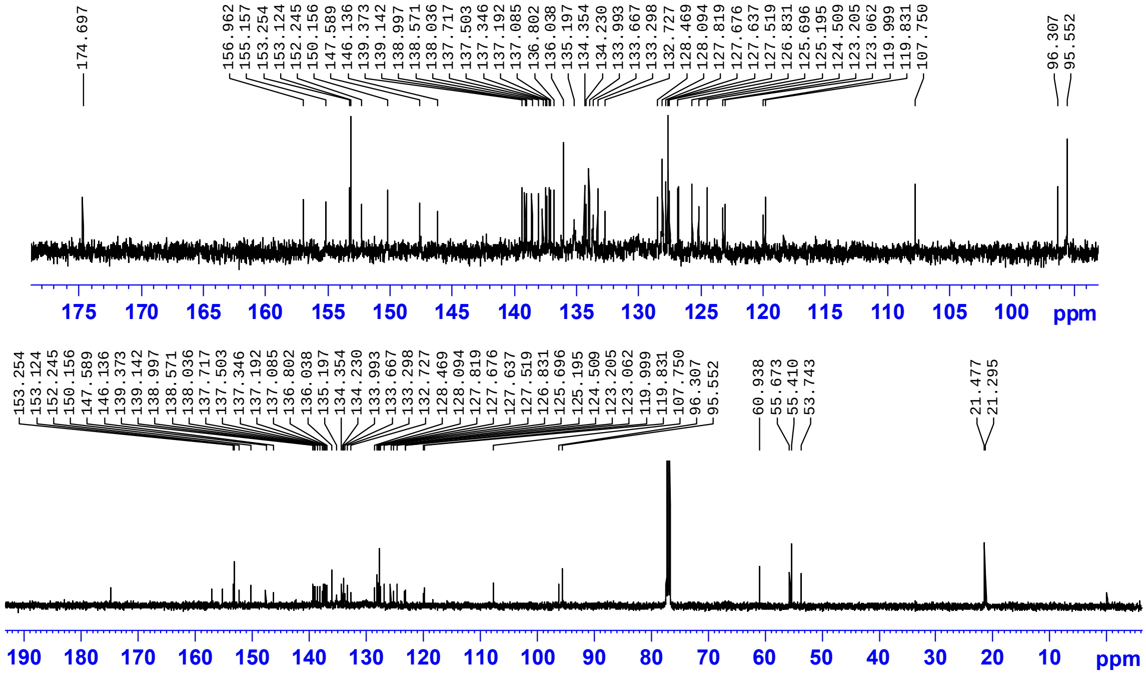


Figure S30. ^{13}C NMR spectrum of **3b**, 298 K, $CDCl_3$.

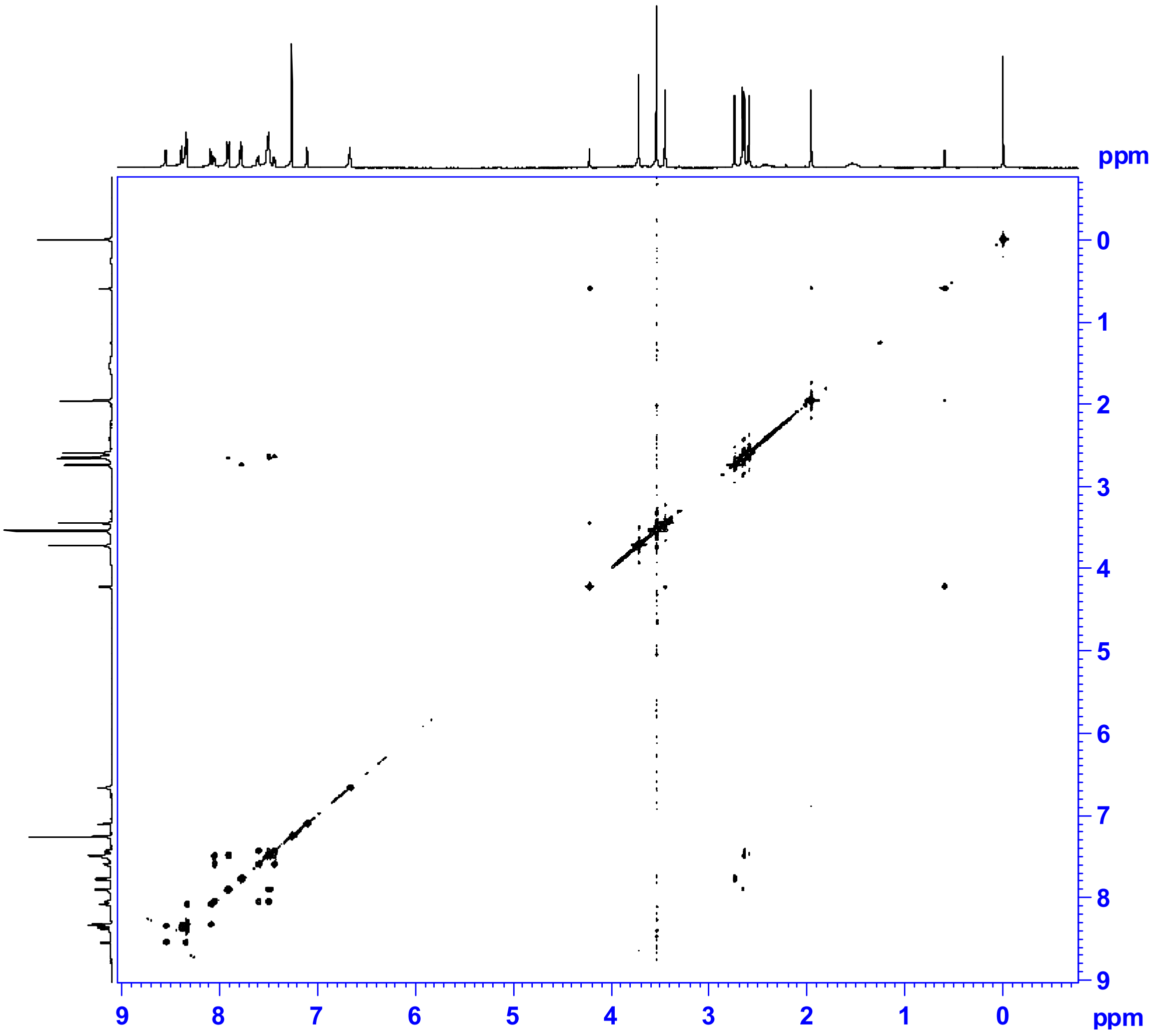


Figure S31. COSY spectrum of **3b** (298K).

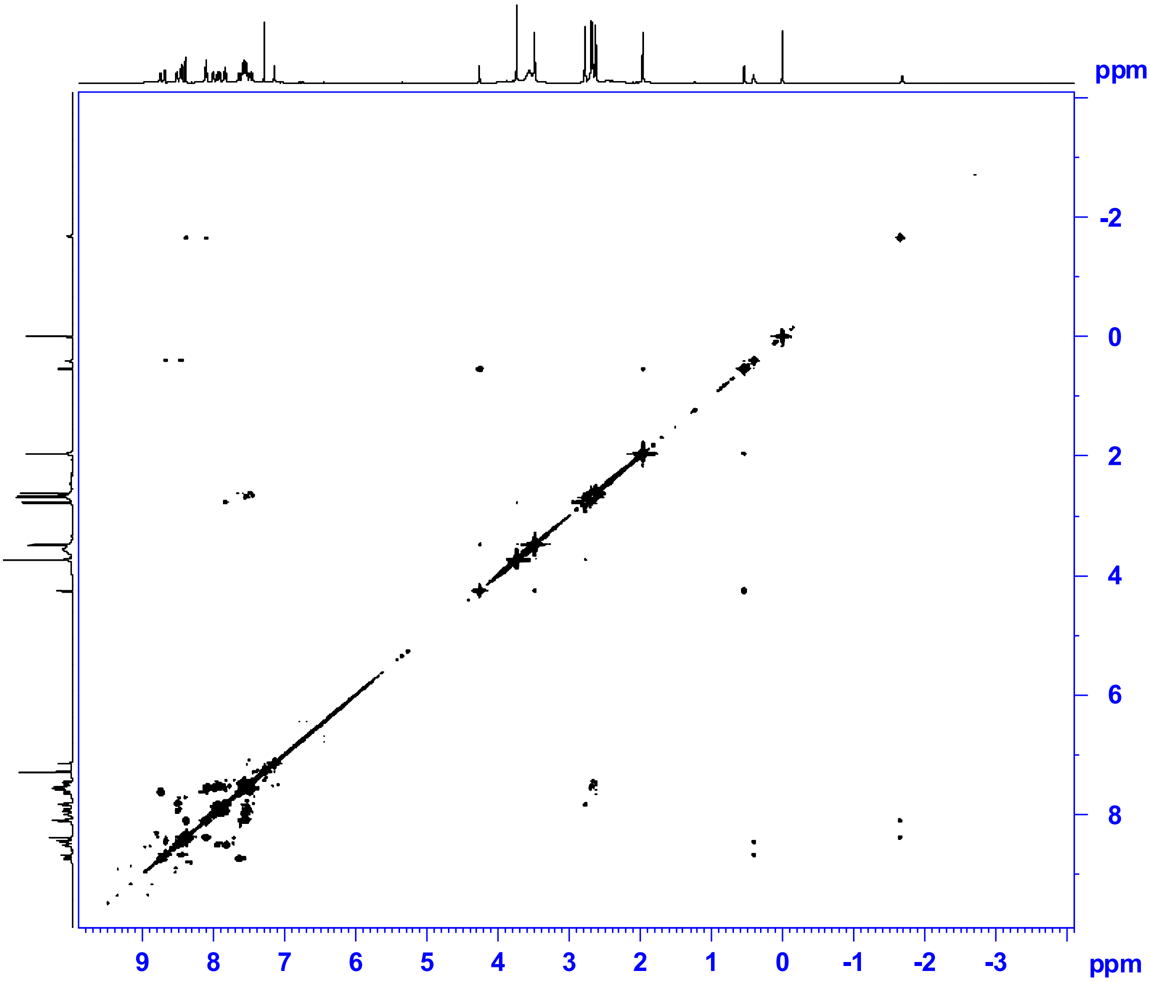


Figure S32. COSY spectrum of **3b** (233K).

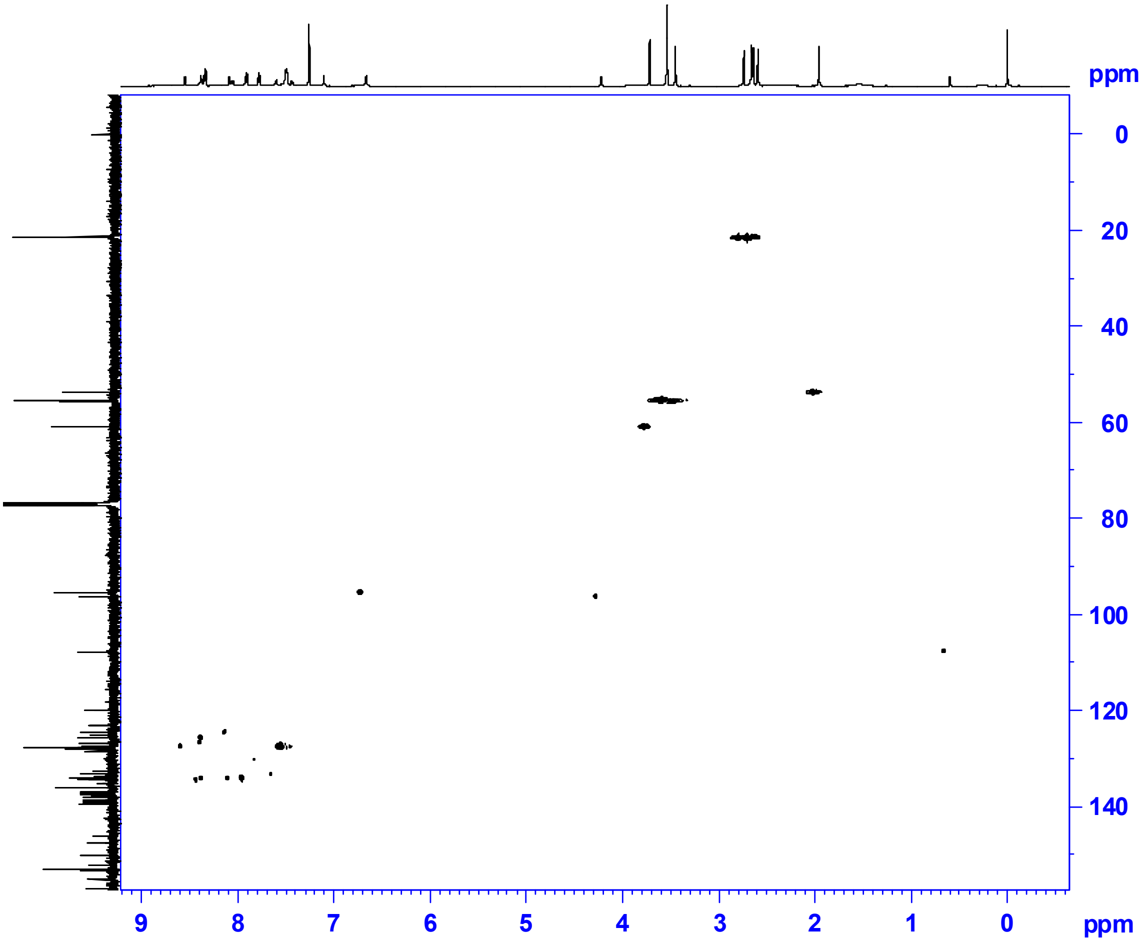


Figure S33. HSQC spectrum of **3b** ($CDCl_3$, 298 K).

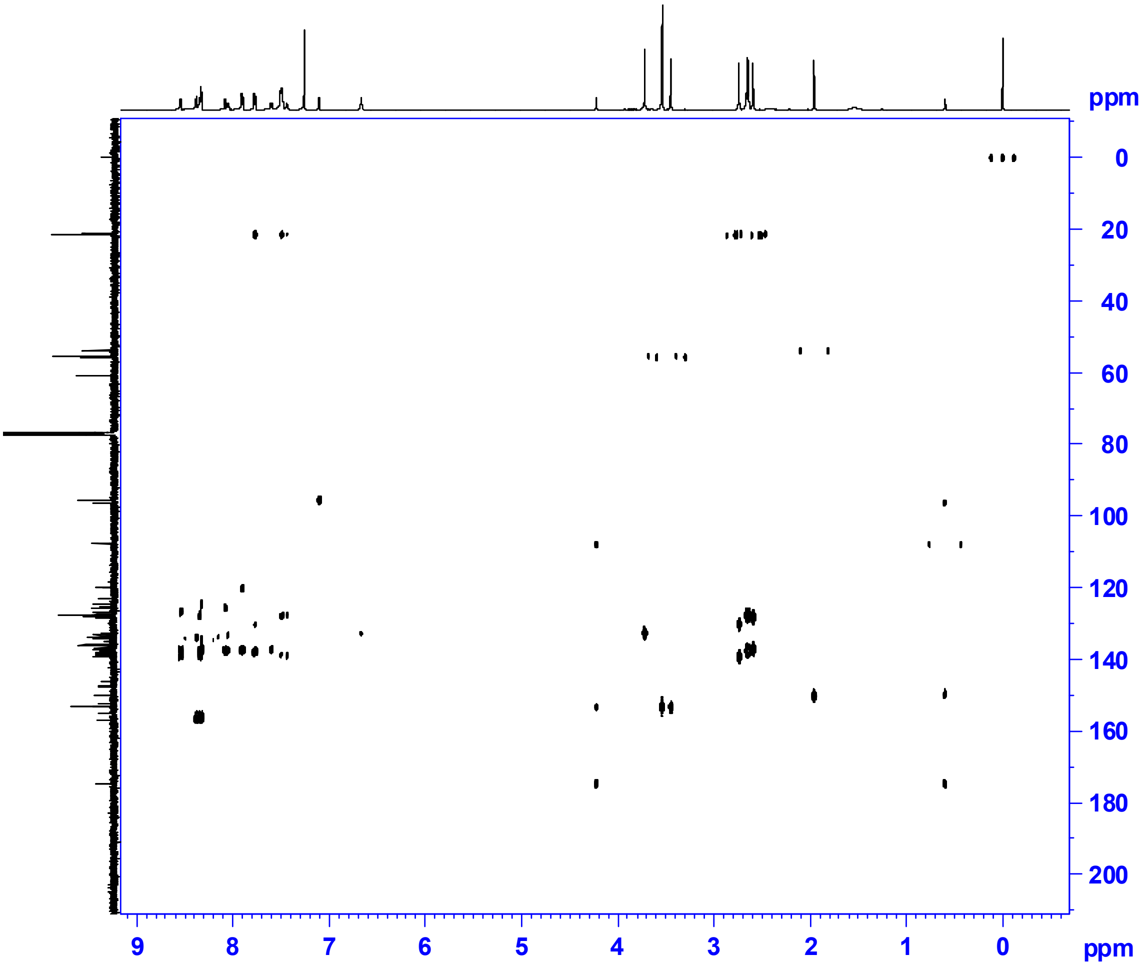


Figure S34. HMBC spectrum of **3b** ($CDCl_3$, 298 K).

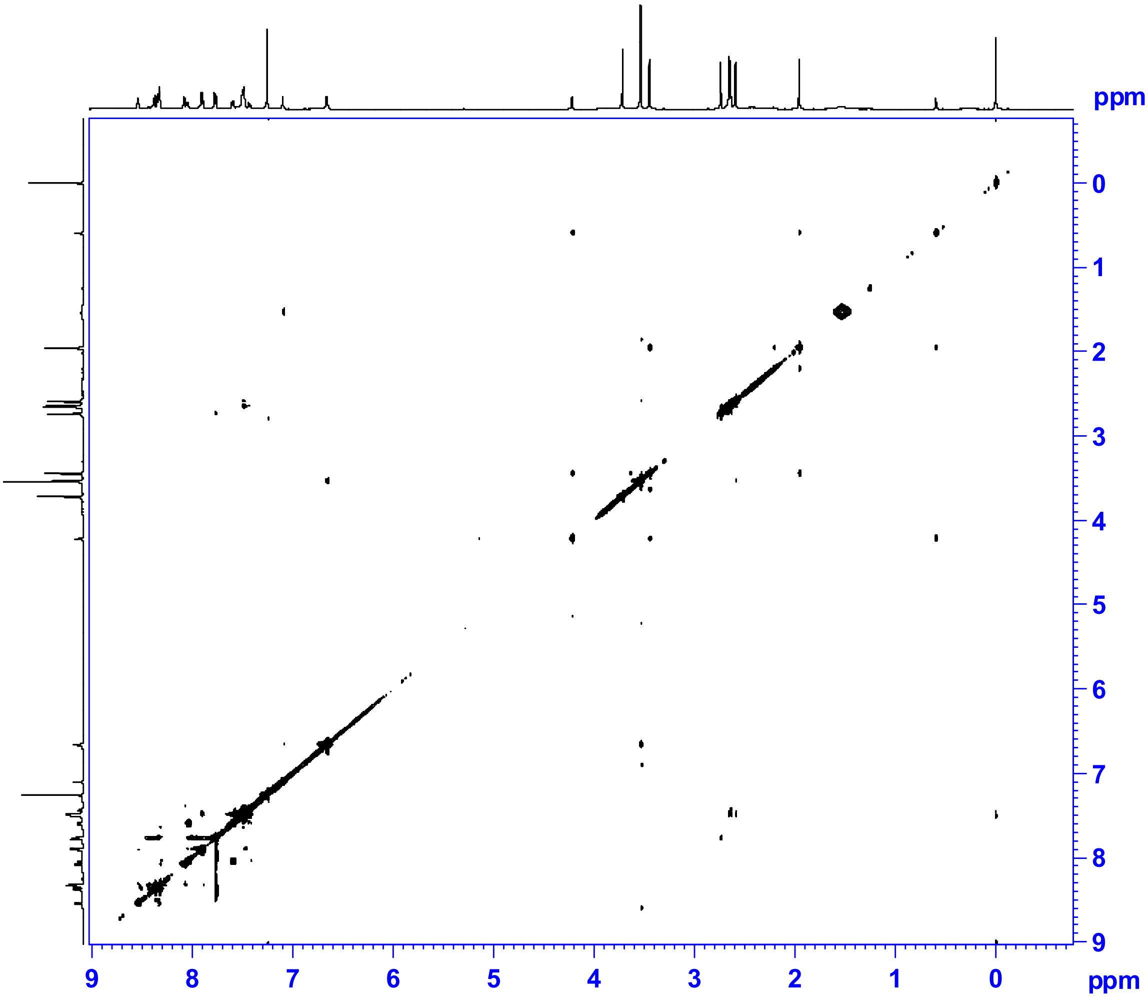


Figure S35. NOESY spectrum of **3b** ($CDCl_3$, 298 K).

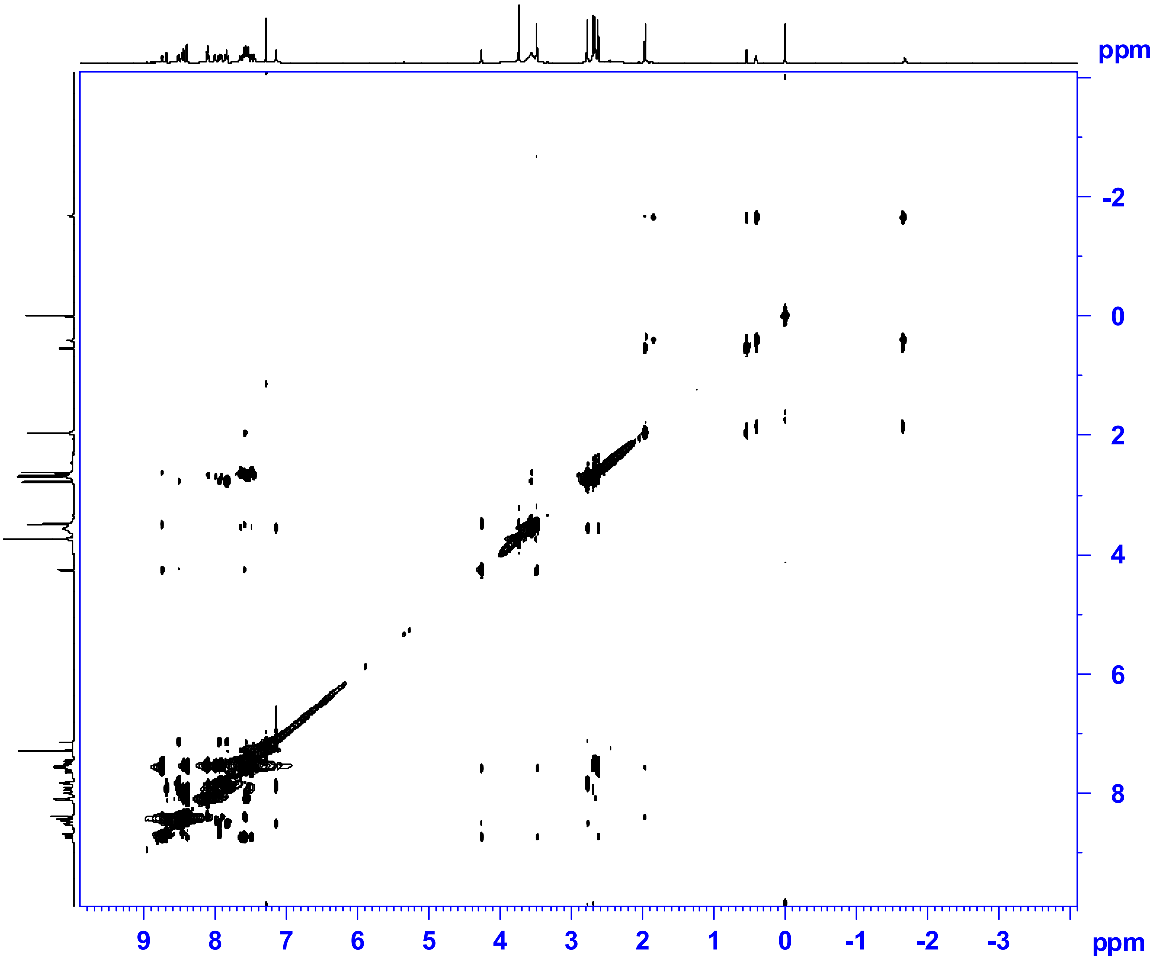


Figure S36. NOESY spectrum of **3b** ($CDCl_3$, 233 K).

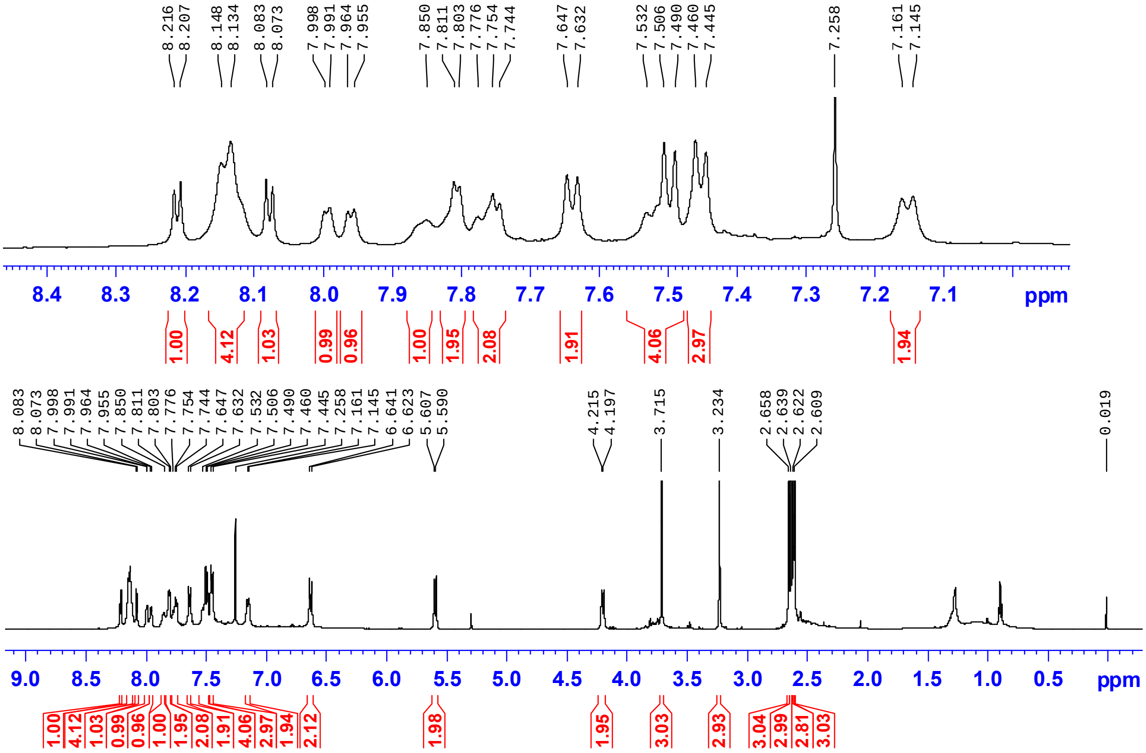


Figure S37. ^{1}H NMR spectrum of **4a**, 298 K, CDCl$_3$.

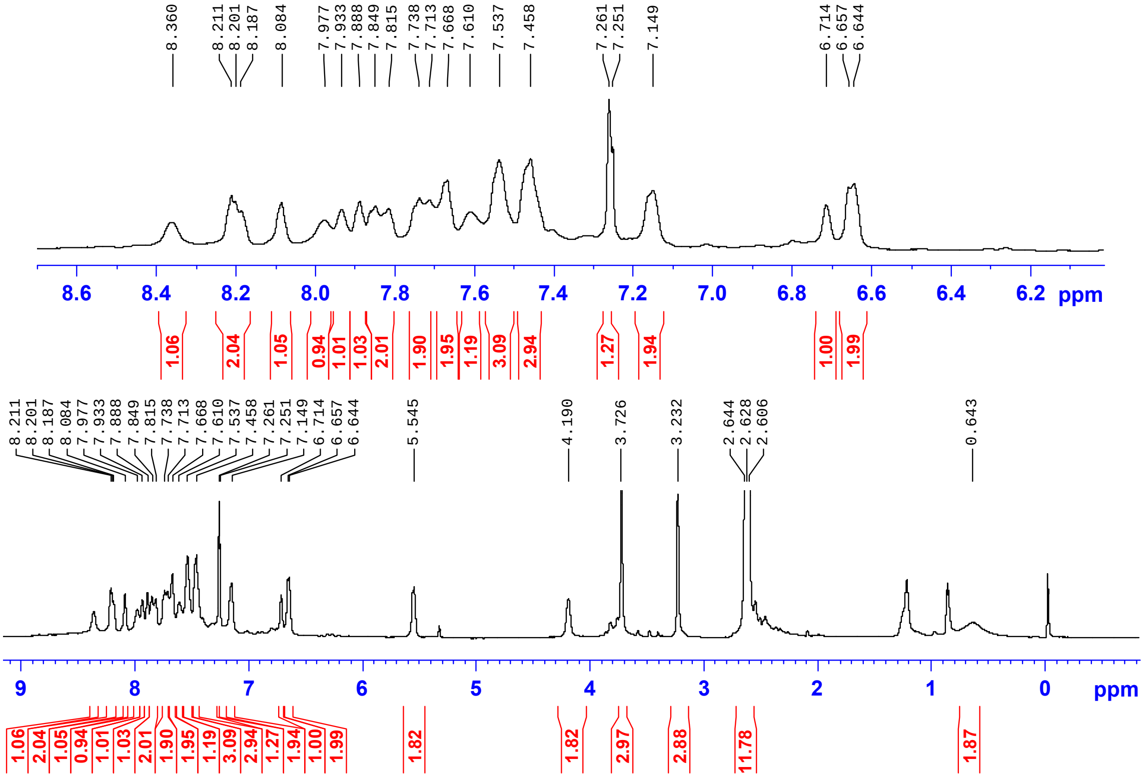


Figure S38. ^{1}H NMR spectrum of **4a**, 230 K, CDCl$_3$.

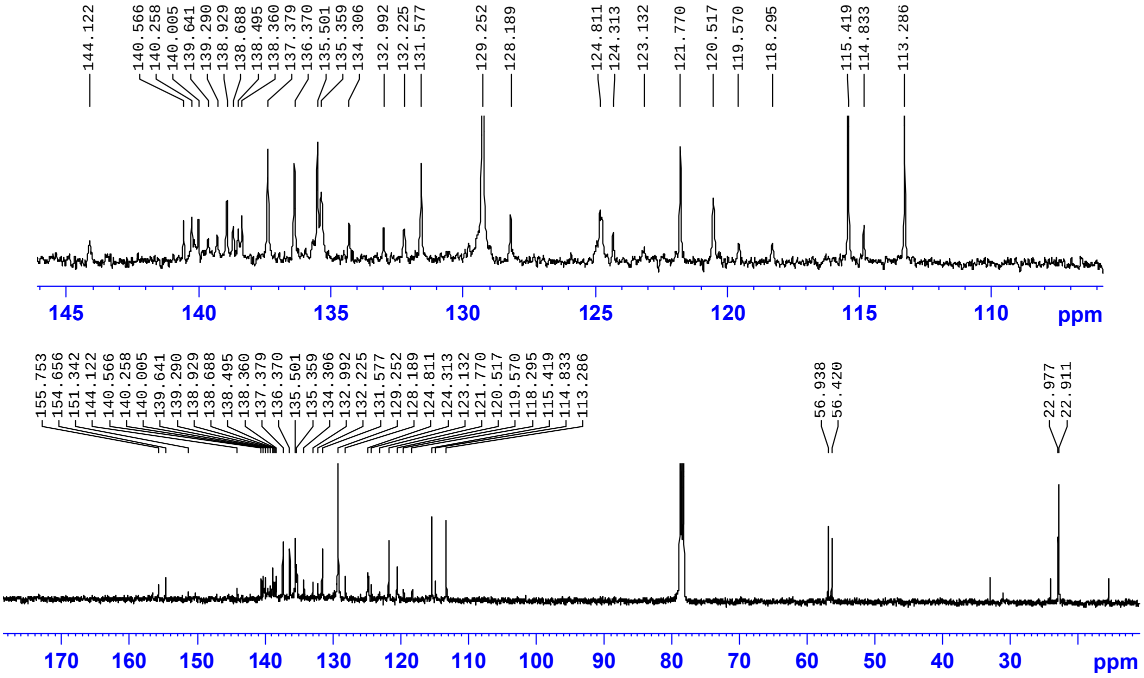
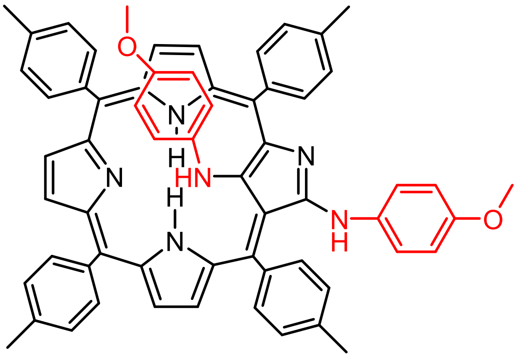


Figure S39. ^{13}C NMR spectrum of **4a**, 298 K, $CDCl_3$.



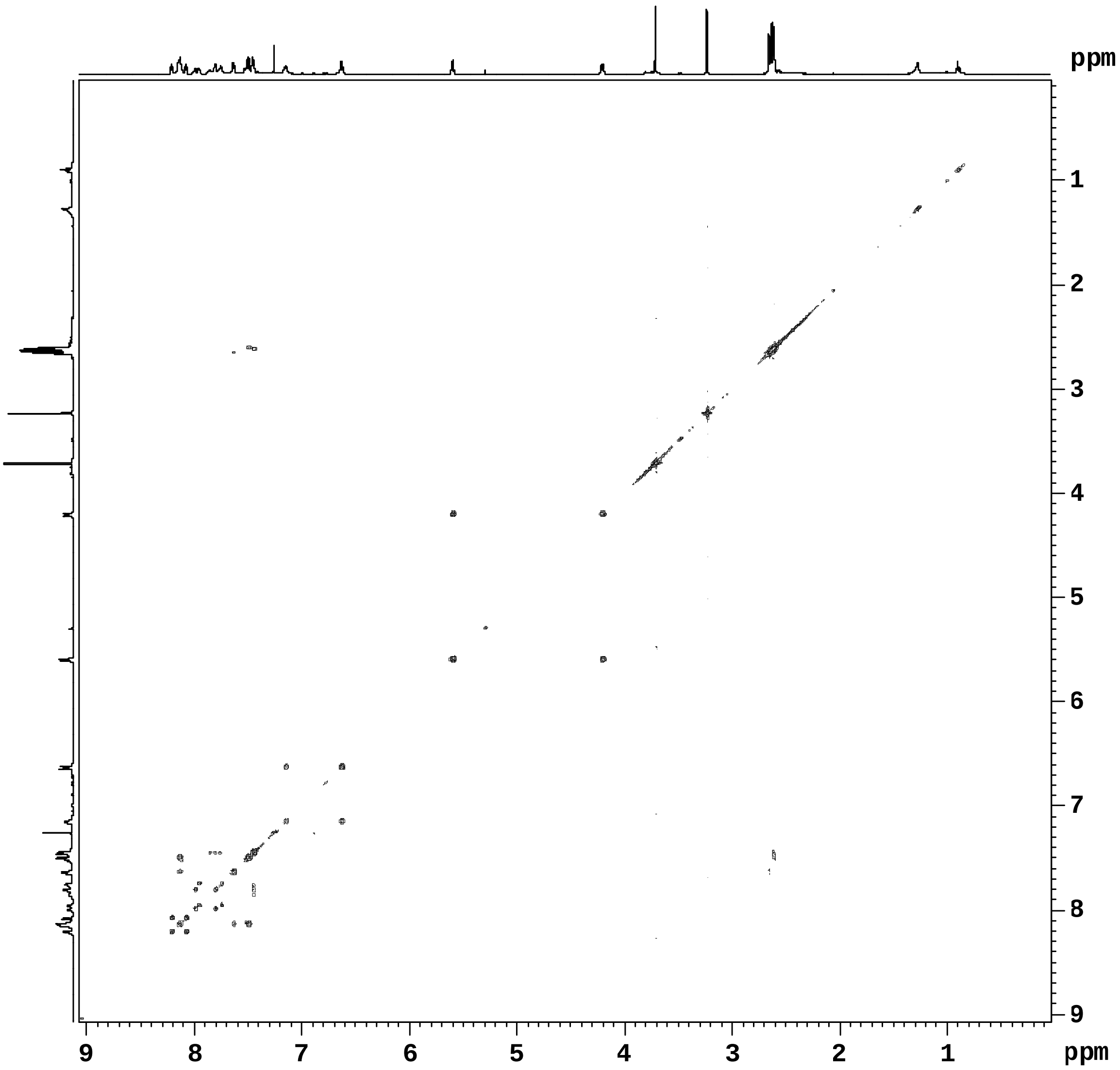
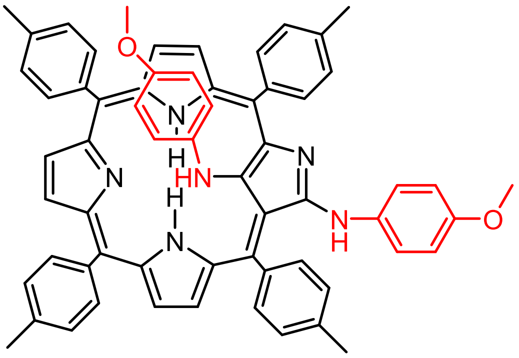


Figure S40. COSY spectrum of **4a** (298K).



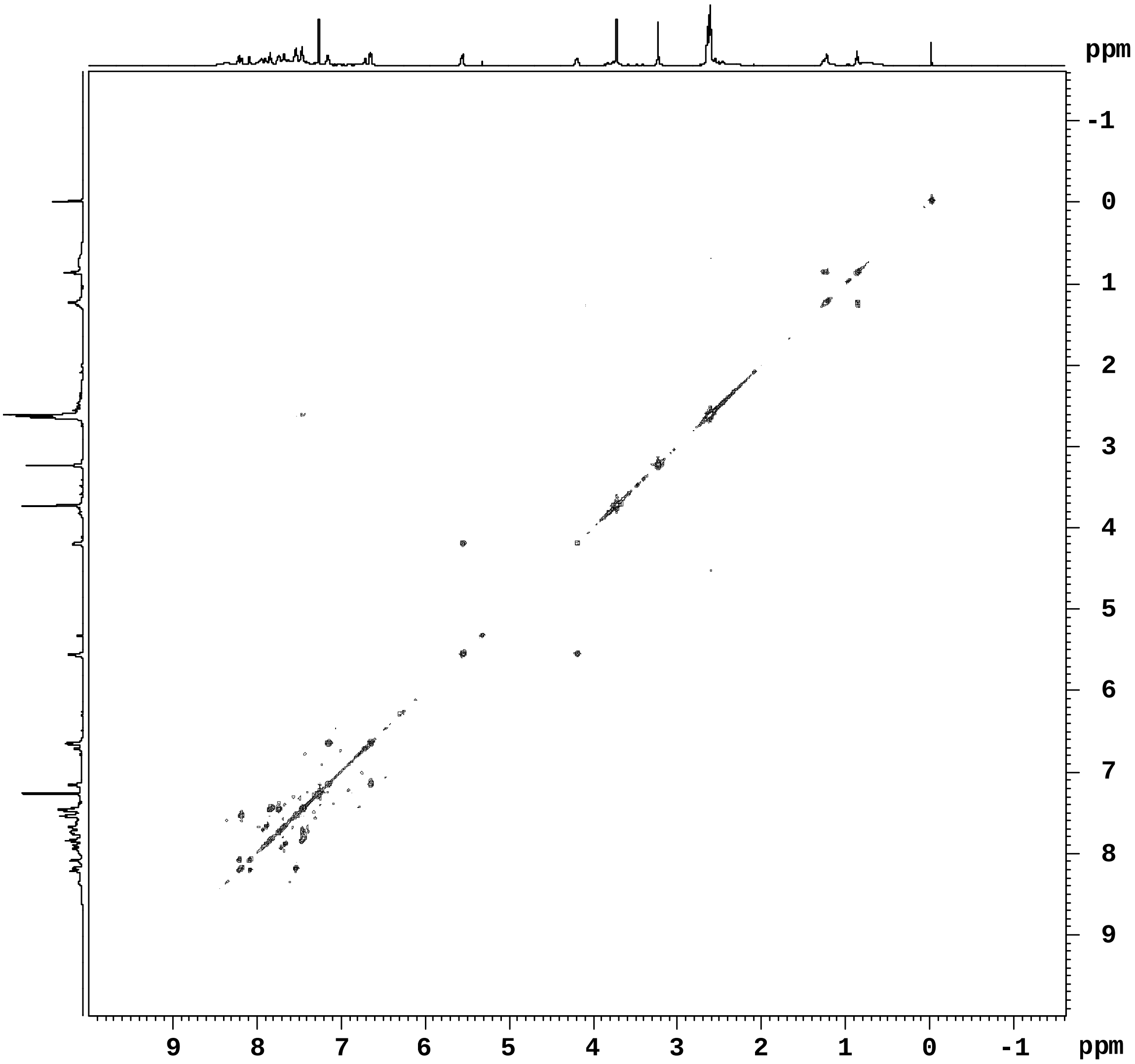
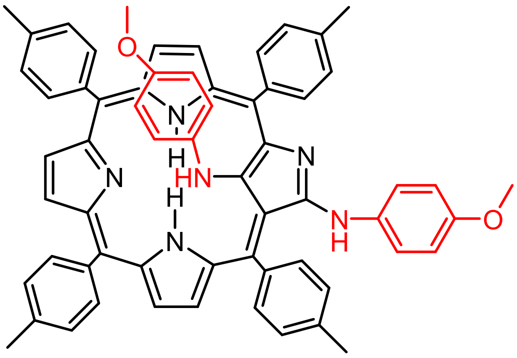


Figure S41. COSY spectrum of **4a** (230K).



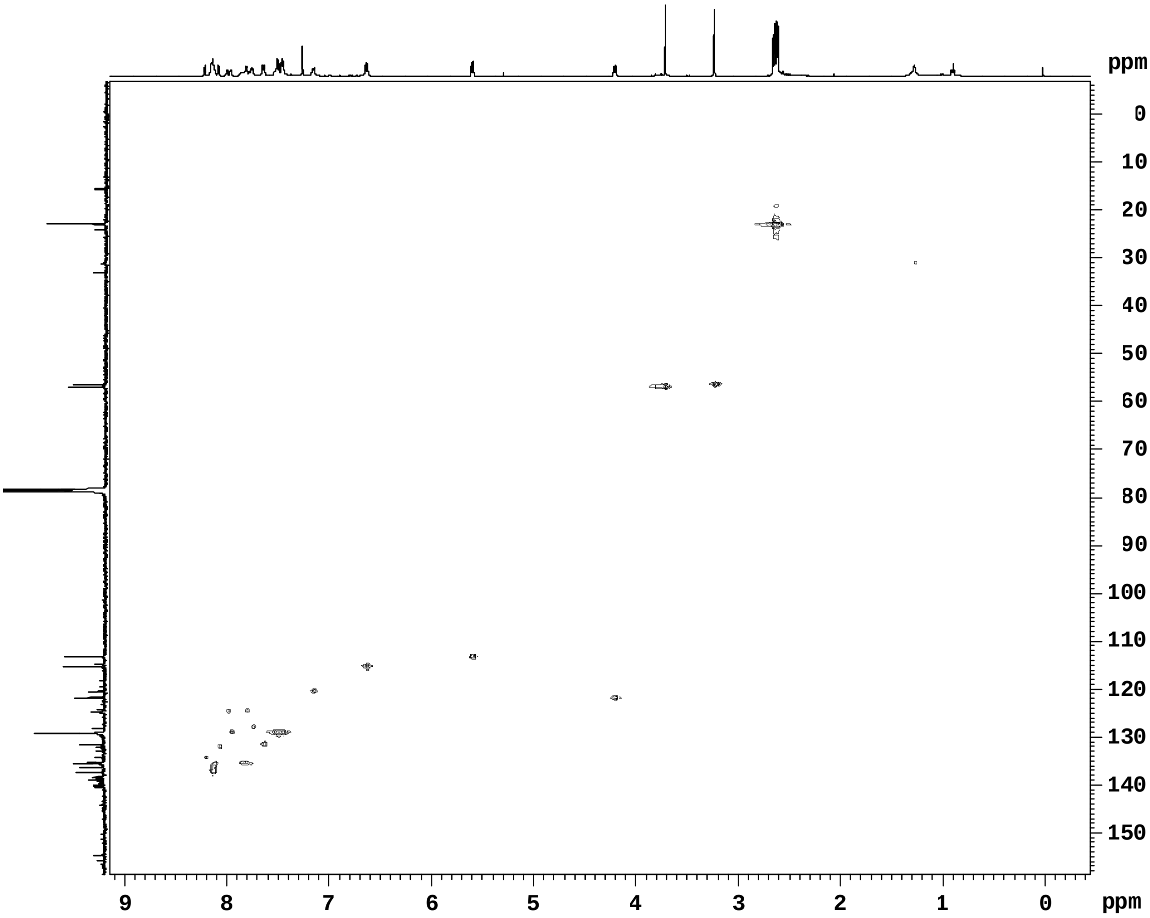
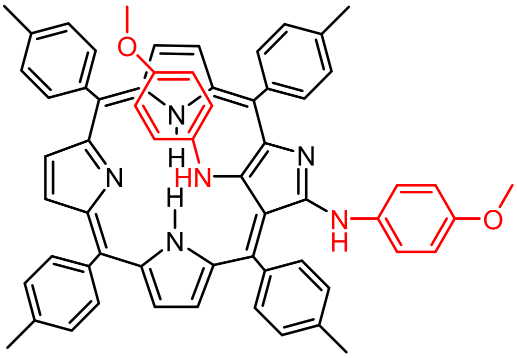


Figure S42. HSQC spectrum of **4a** ($CDCl_3$, 298 K).



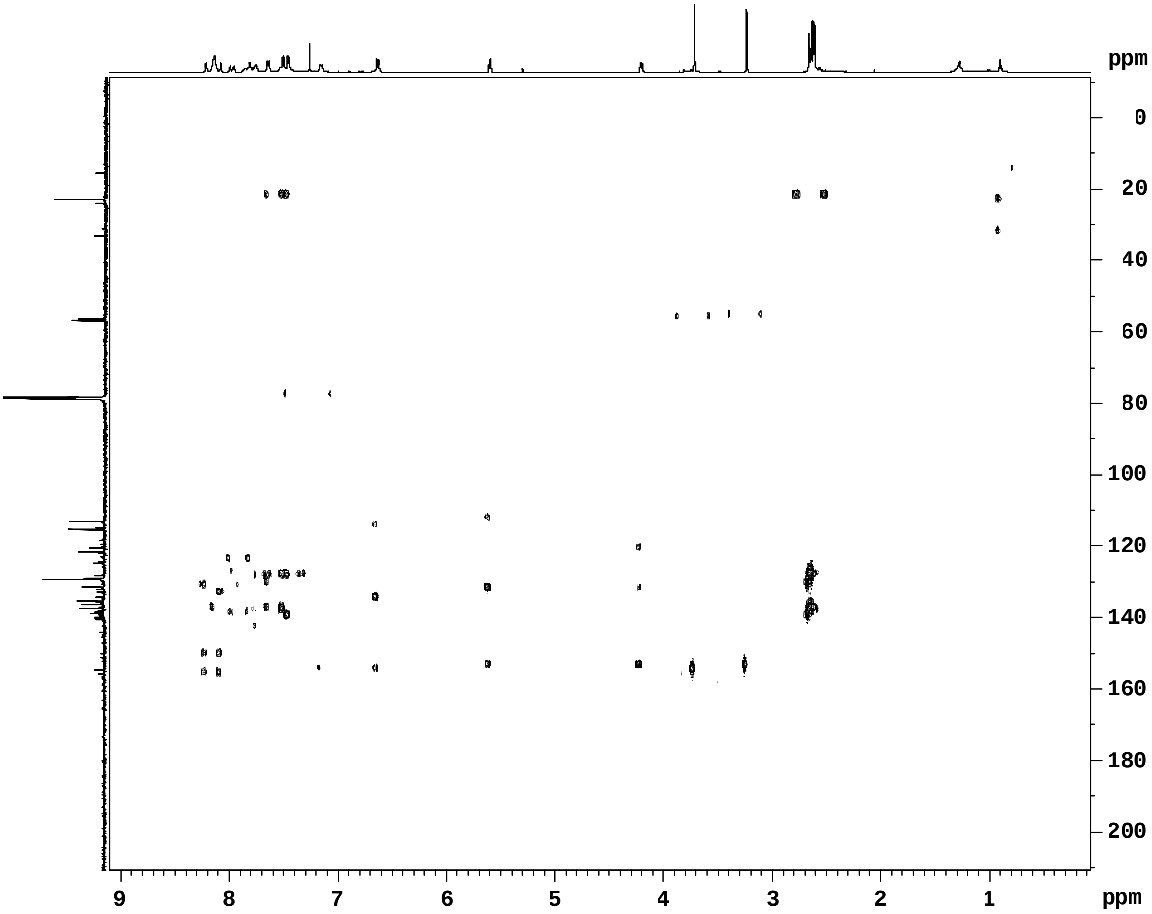
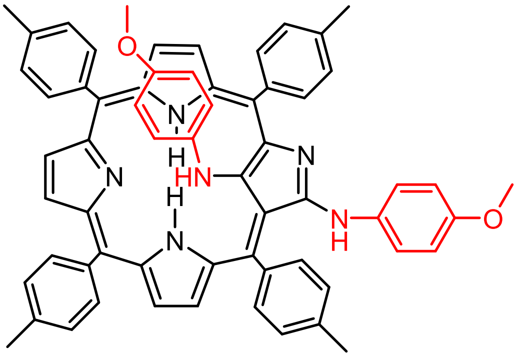


Figure S43. HMBC spectrum of **4a** ($CDCl_3$, 298 K).



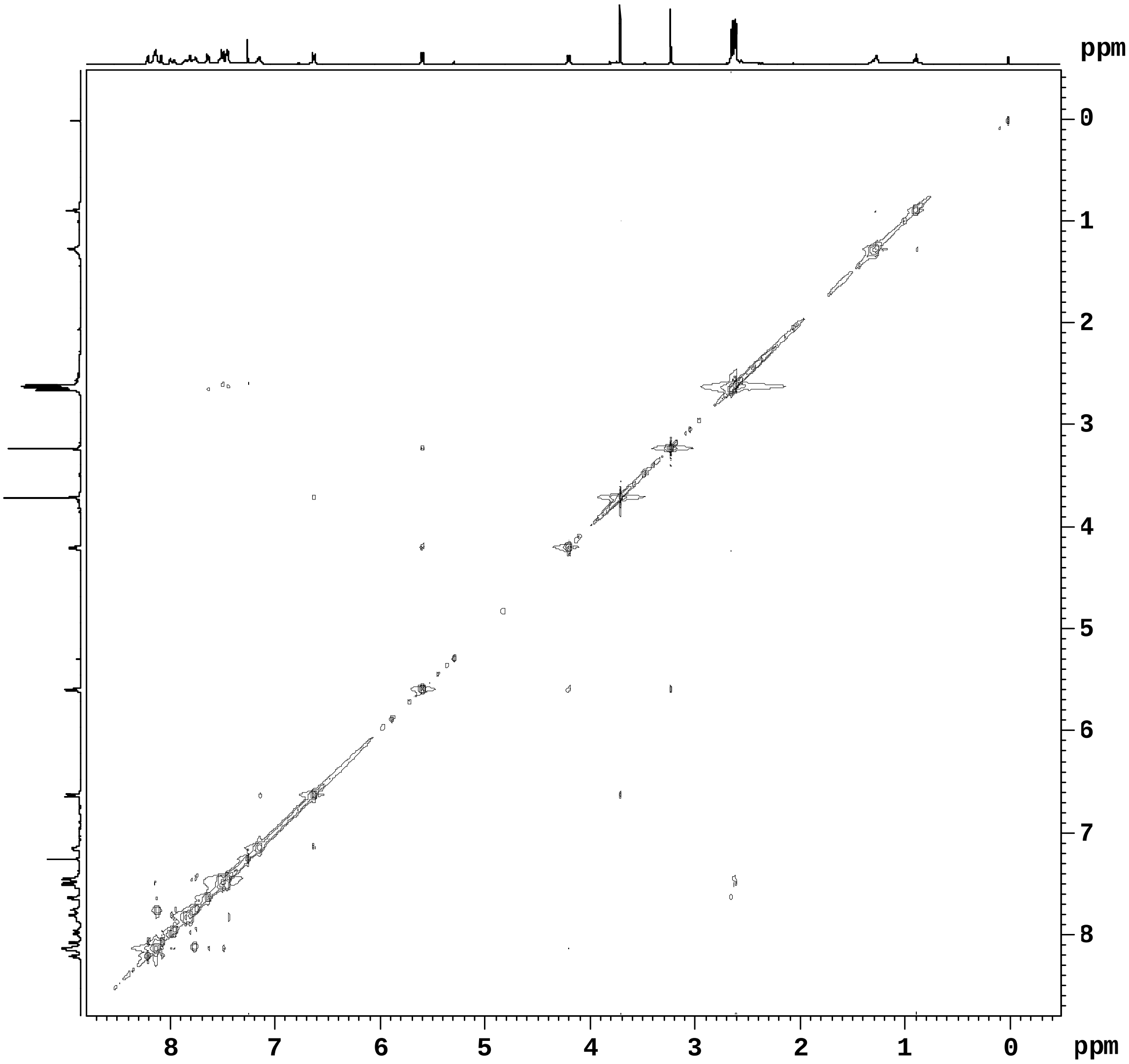
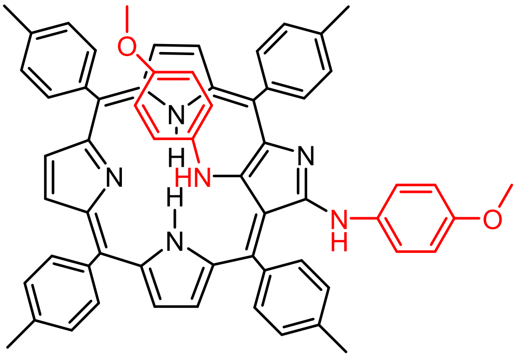


Figure S44. NOESY spectrum of **4a** ($CDCl_3$, 298 K).



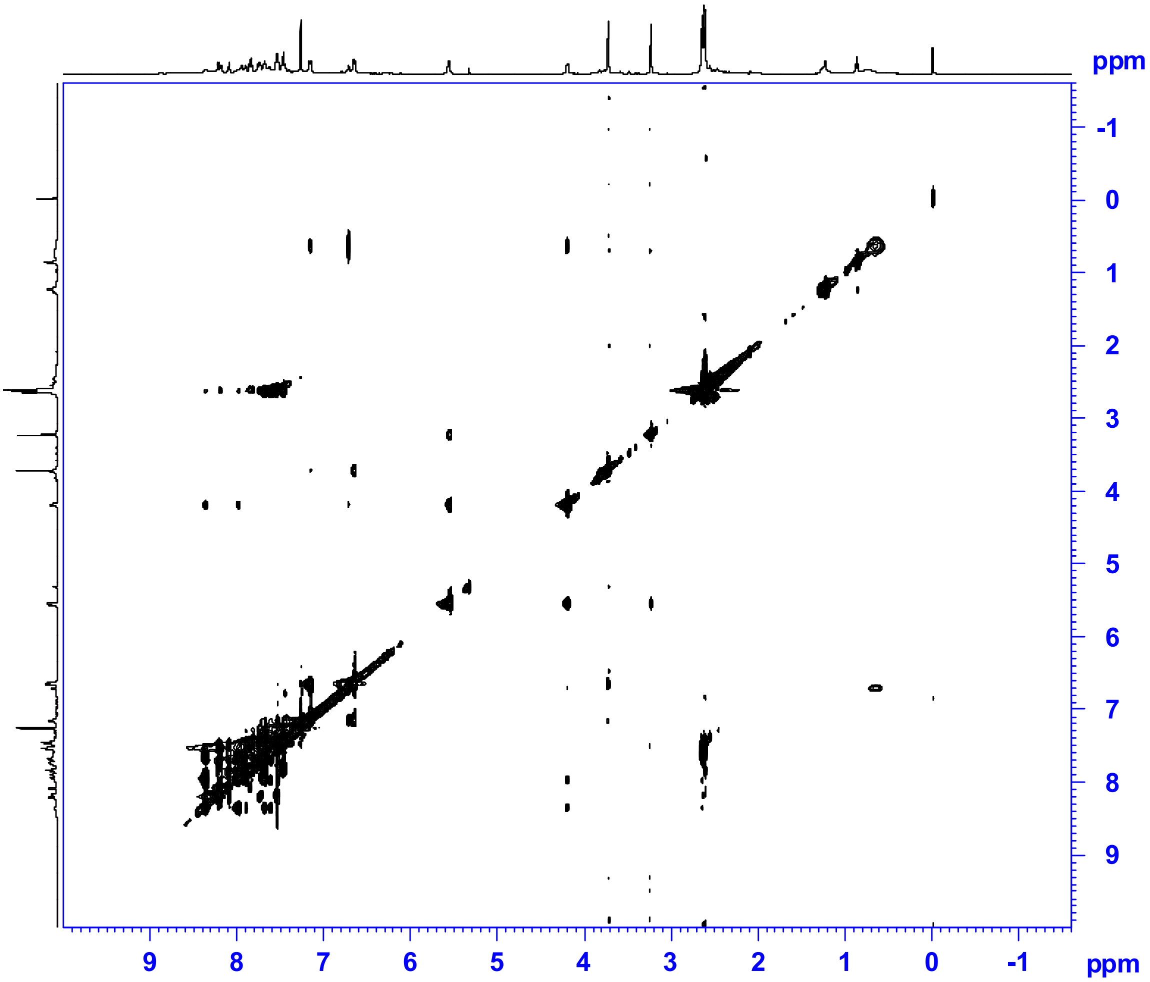
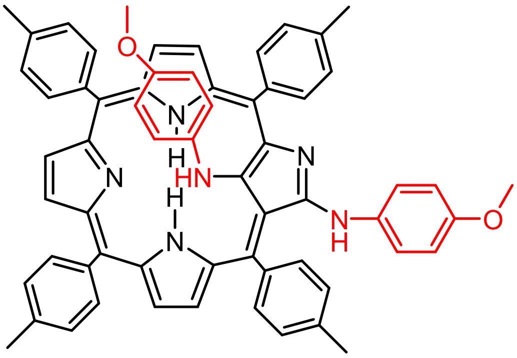


Figure S45. NOESY spectrum of **4a** ($CDCl_3$, 230 K).



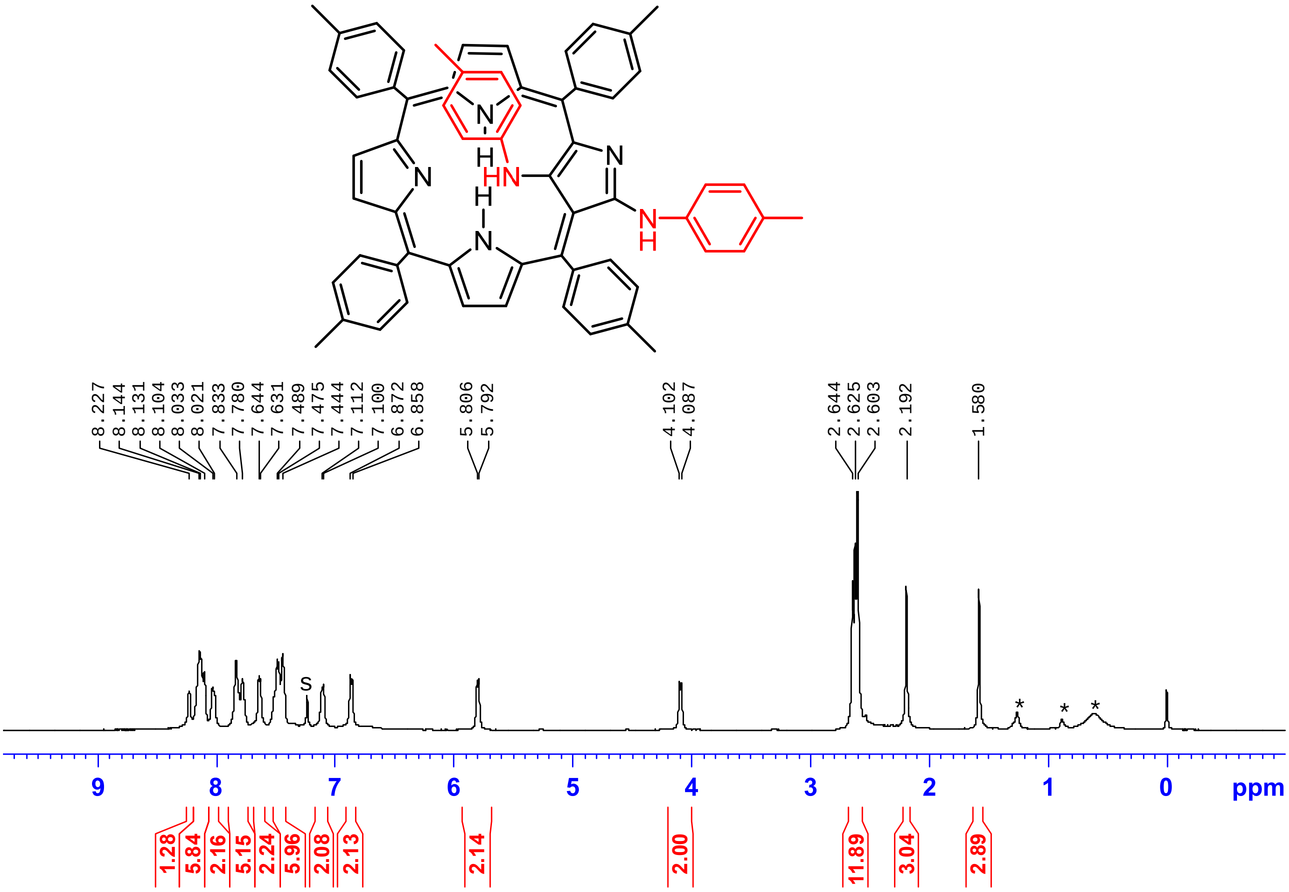


Figure S46. ^{1}H NMR spectrum of **4b**, 298 K, $CDCl_3$.

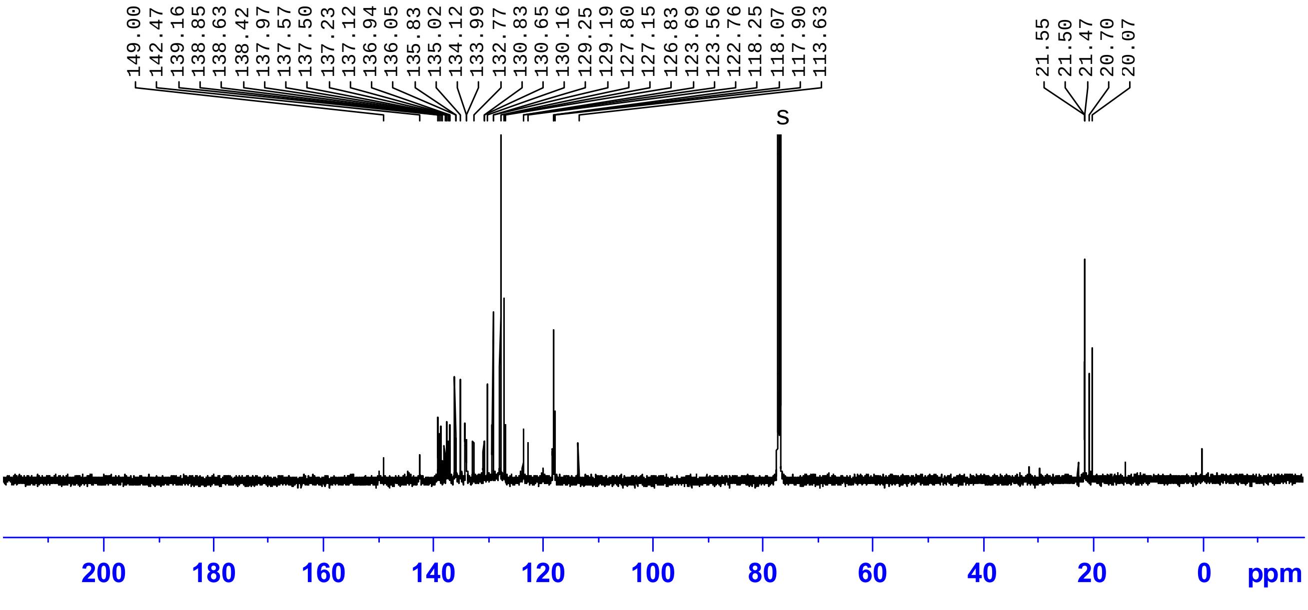
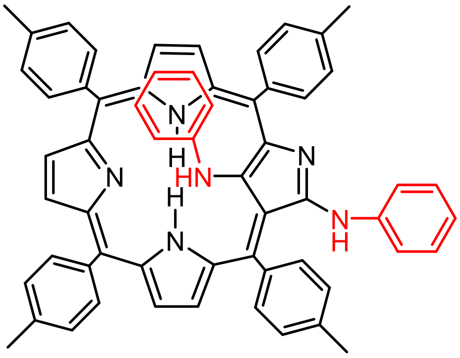


Figure S47. ^{13}C NMR spectrum of **4b**, 298 K, $CDCl_3$.



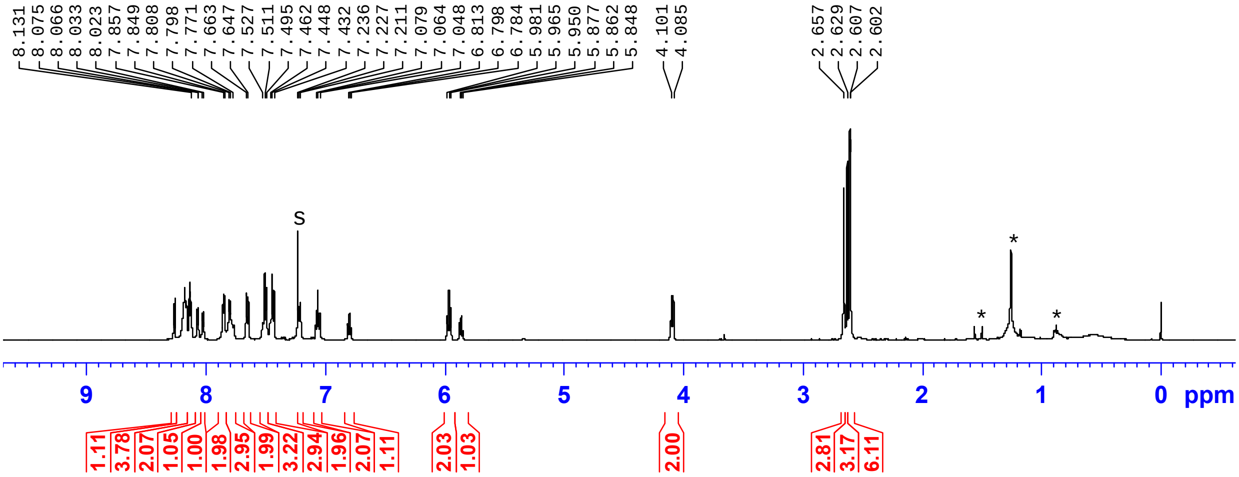


Figure S48. ^{1}H NMR spectrum of **4c**, 298 K, $CDCl_3$.

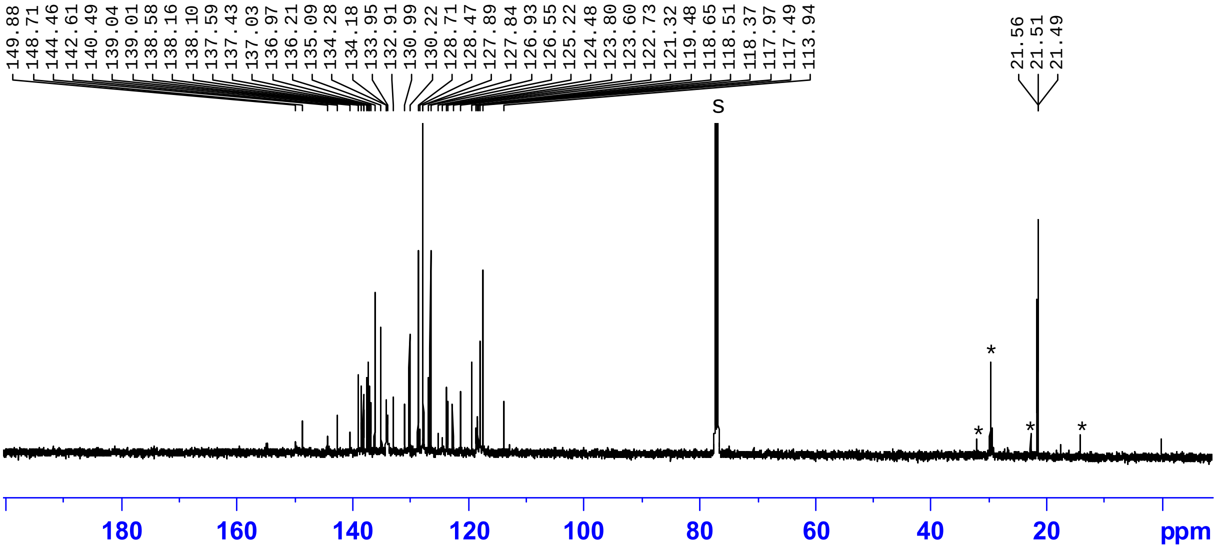


Figure S49. ^{13}C NMR spectrum of **4c**, 298 K, $CDCl_3$.

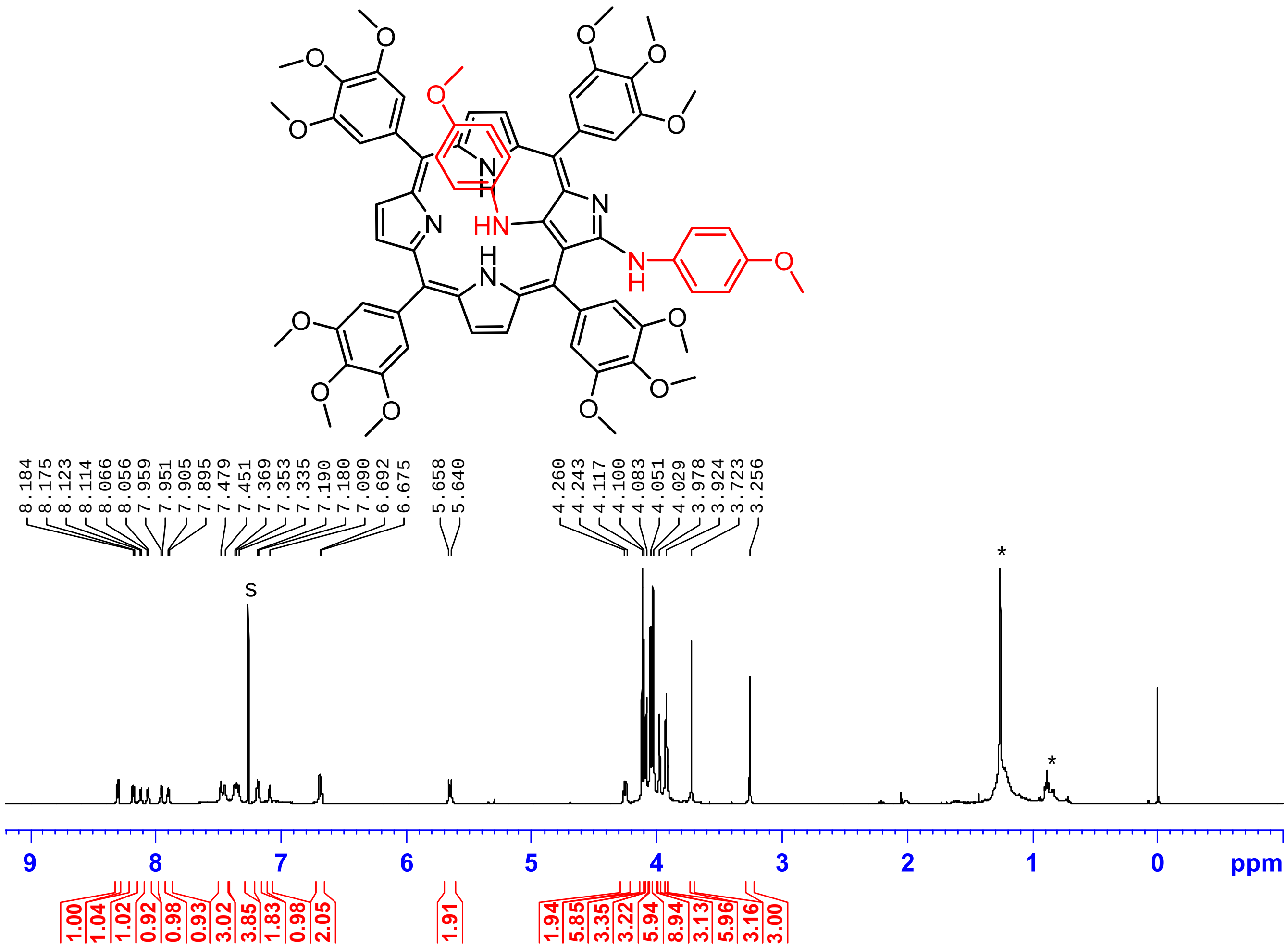


Figure S50. ^{1}H NMR spectrum of **4d**, 298 K, $CDCl_3$.

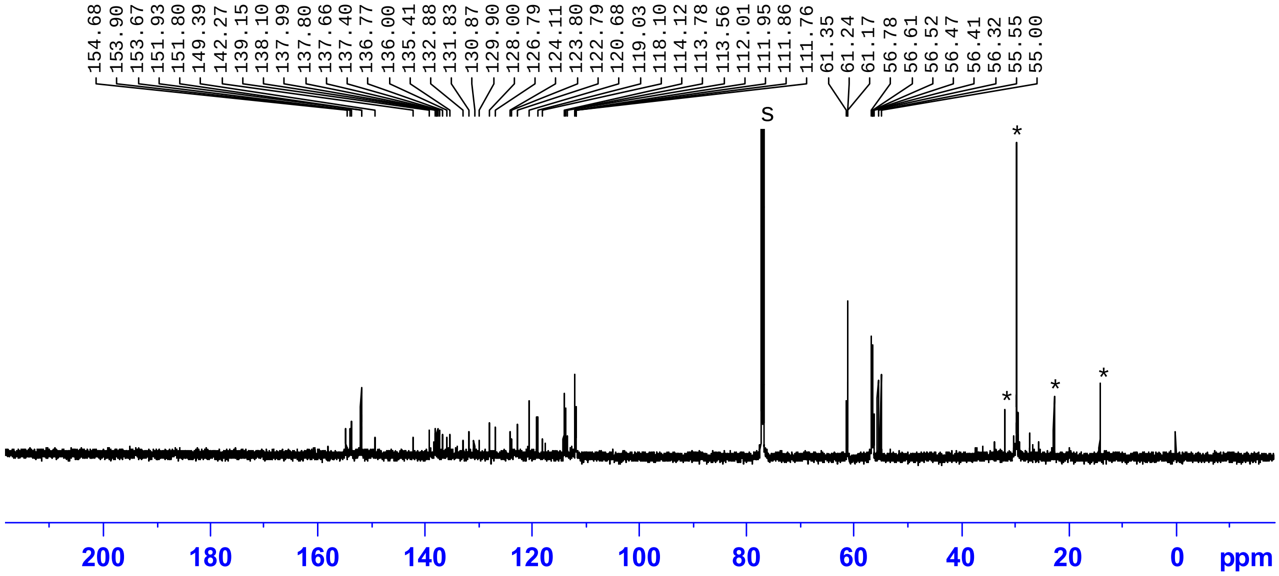


Figure S51. ^{13}C NMR spectrum of **4d**, 298 K, $CDCl_3$.

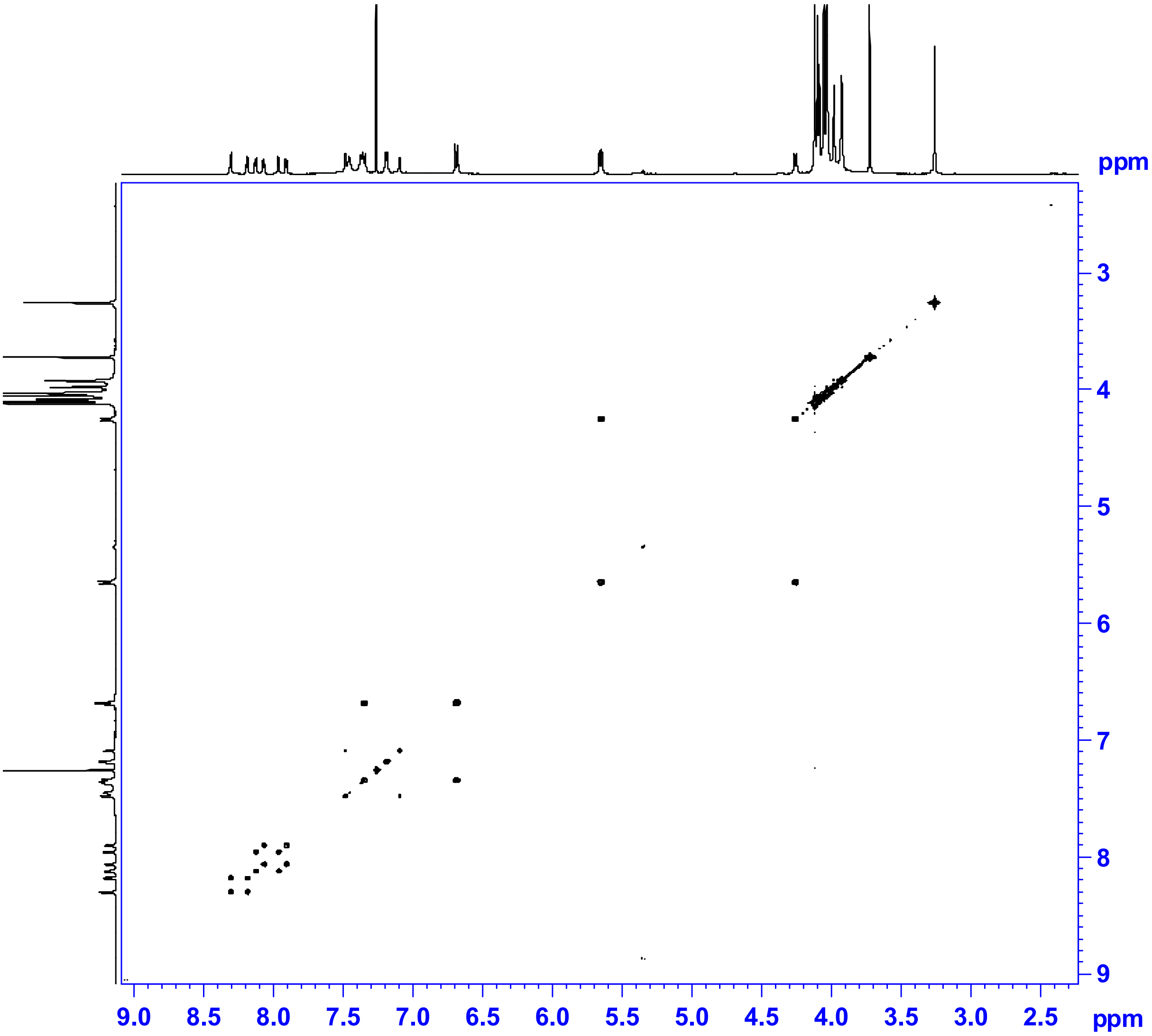
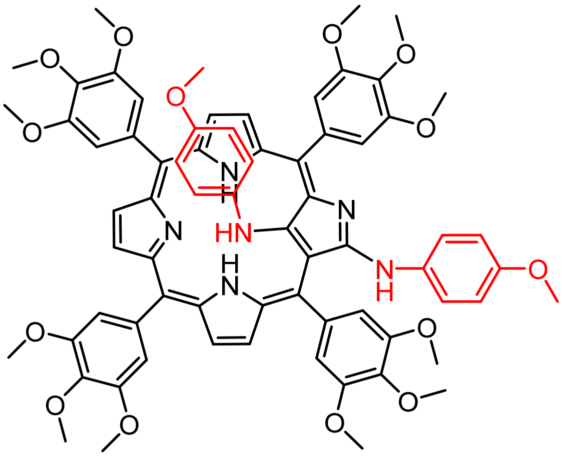


Figure S52. COSY spectrum of **4d** ($CDCl_3$, 298 K).



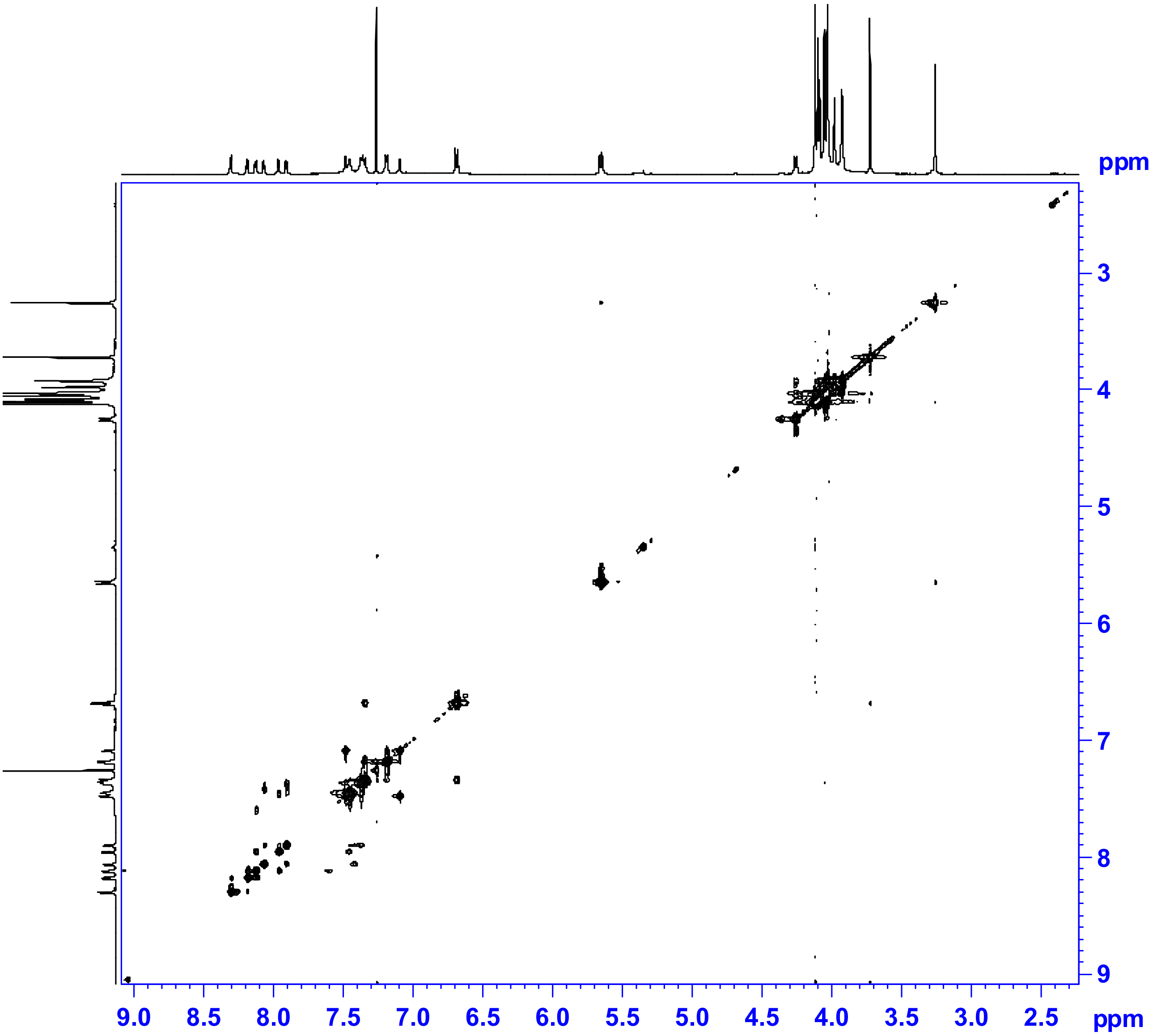
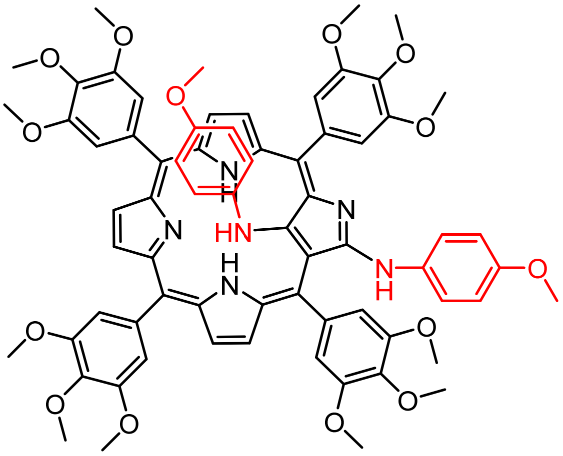


Figure S53. NOESY spectrum of **4d** ($CDCl_3$, 298 K).



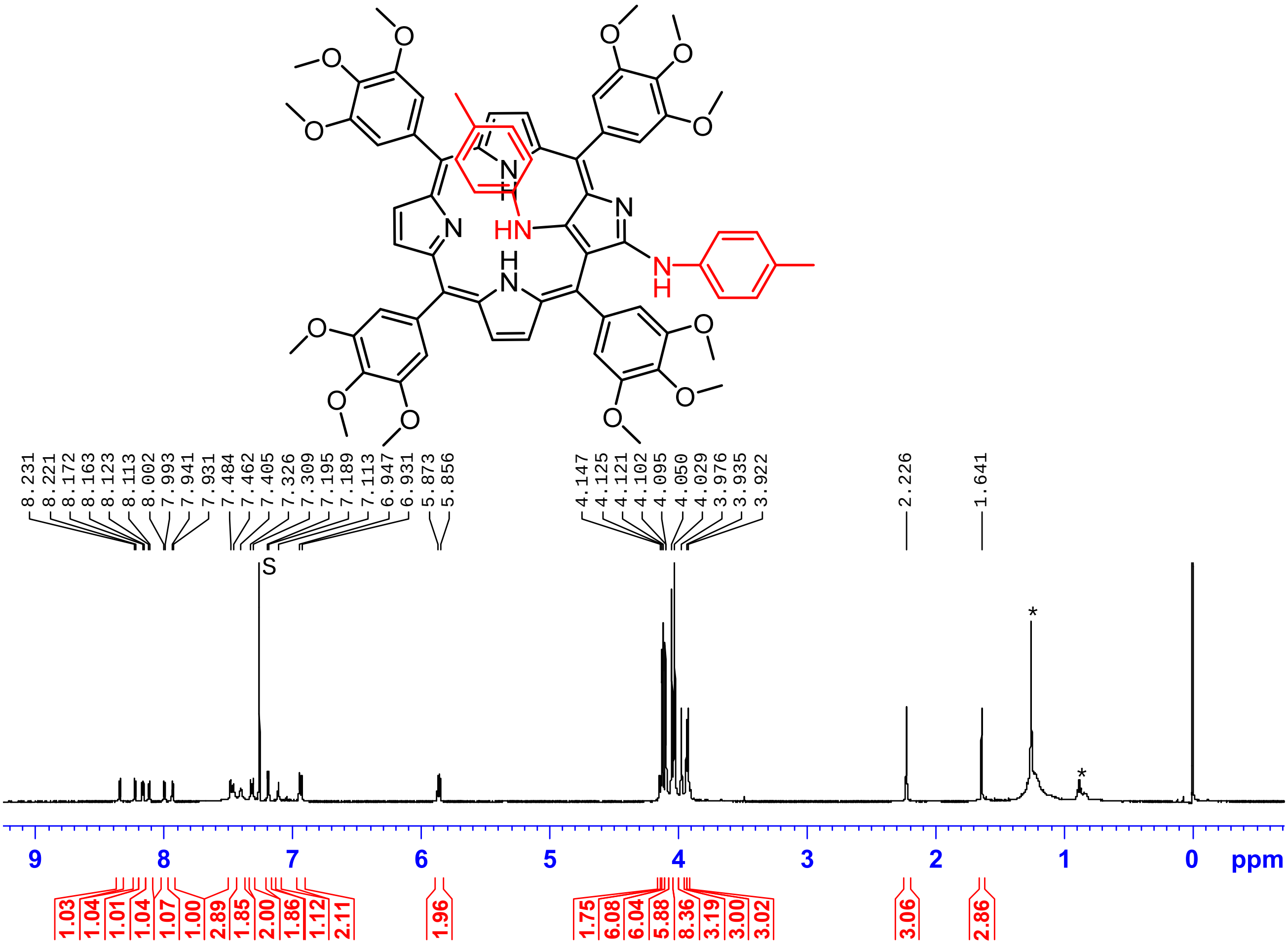


Figure S54. ^{1}H NMR spectrum of **4e**, 298 K, $CDCl_3$.

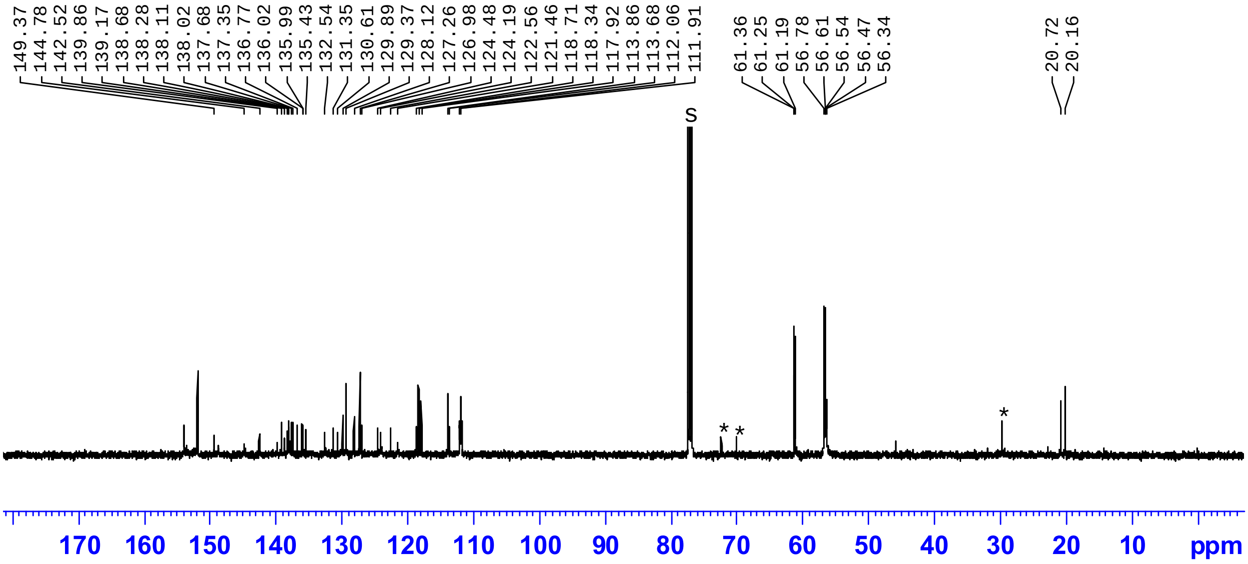
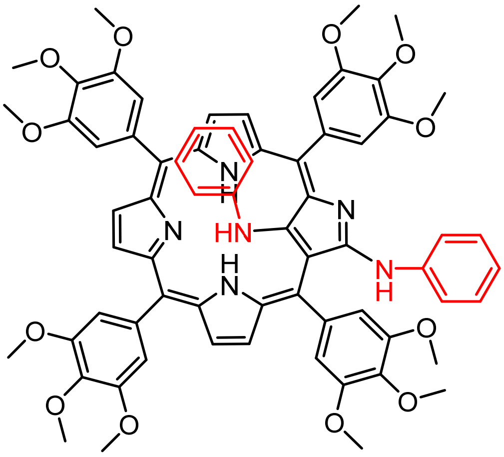


Figure S55. ^{13}C NMR spectrum of **4e**, 298 K, $CDCl_3$.



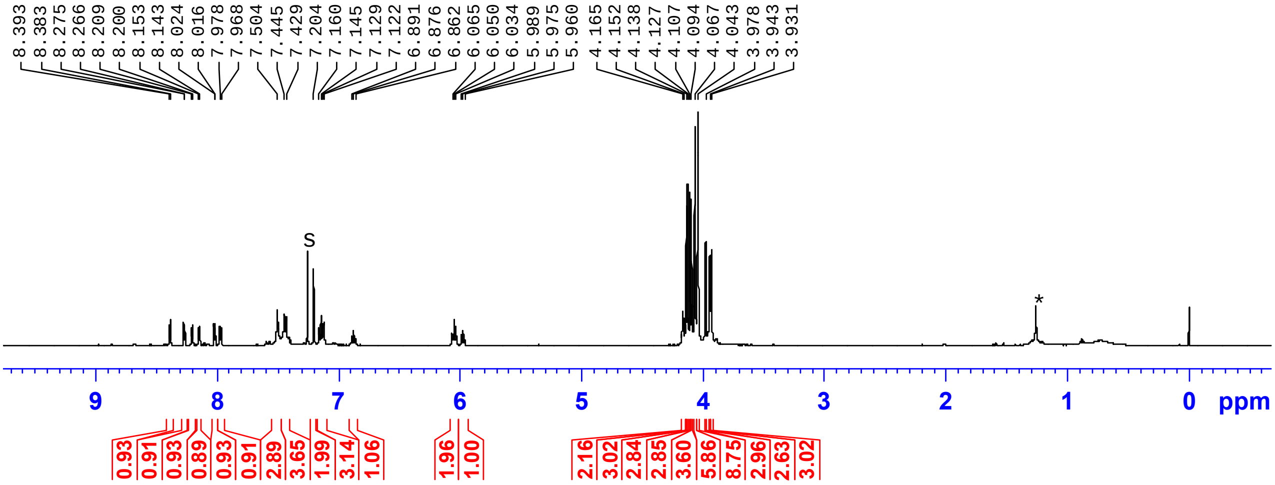


Figure S56. ^{1}H NMR spectrum of **4f**, 298 K, $CDCl_3$.

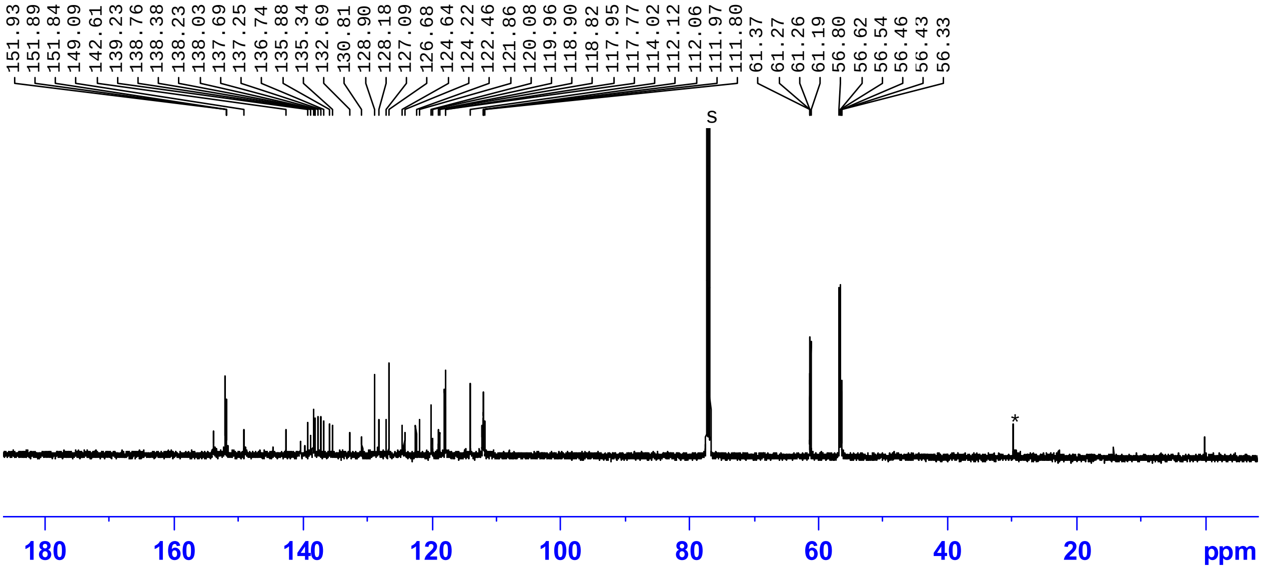


Figure S57. ^{13}C NMR spectrum of **4f**, 298 K, $CDCl_3$.

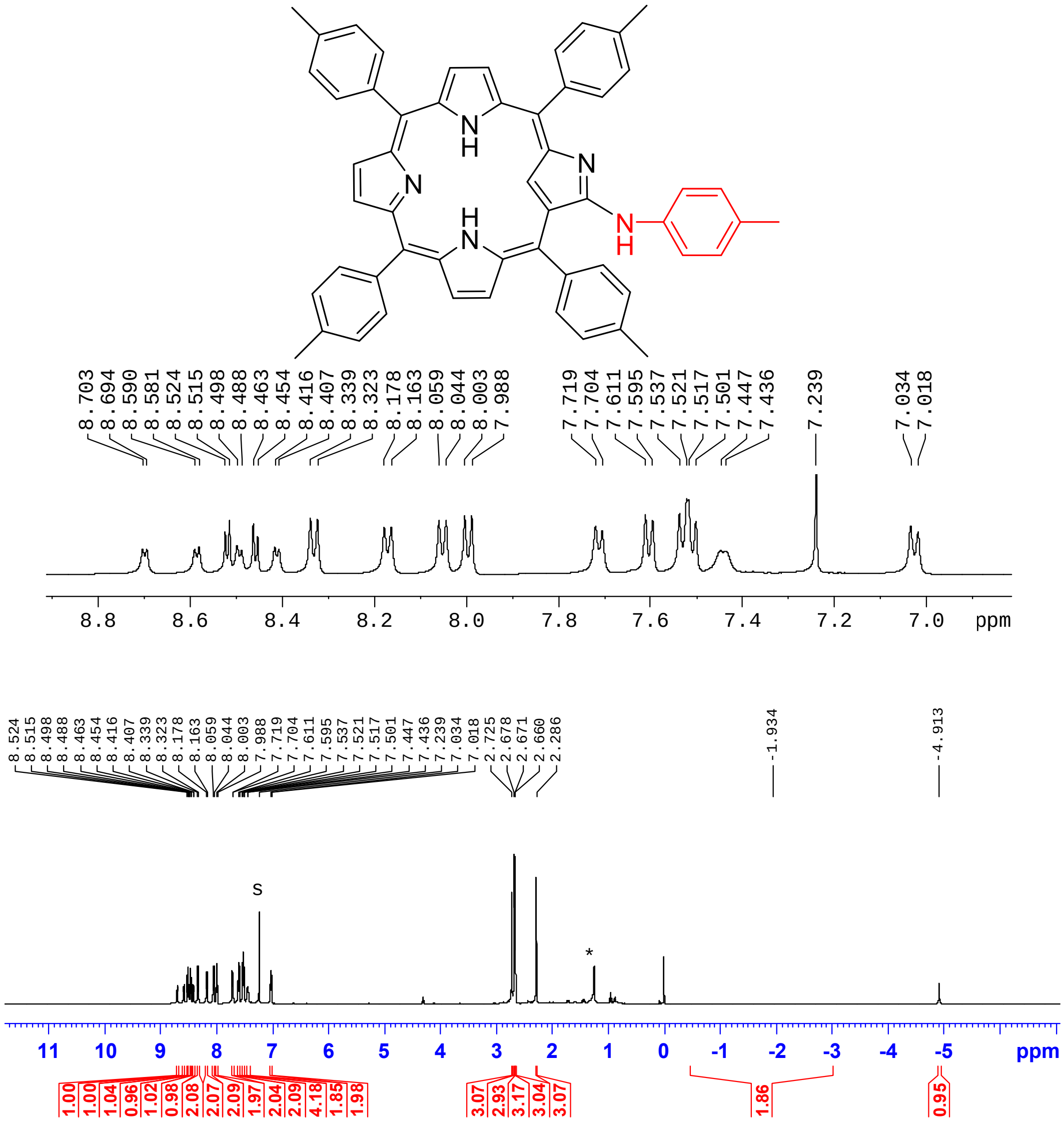


Figure S58. ^{1}H NMR spectrum of **5b**, 298 K, $CDCl_3$.

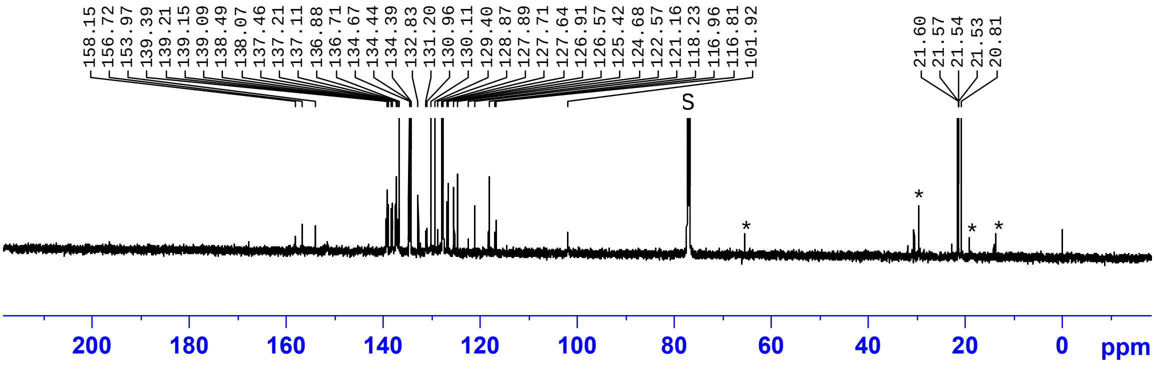


Figure S59. ^{13}C NMR spectrum of **5b**, 298 K, $CDCl_3$.

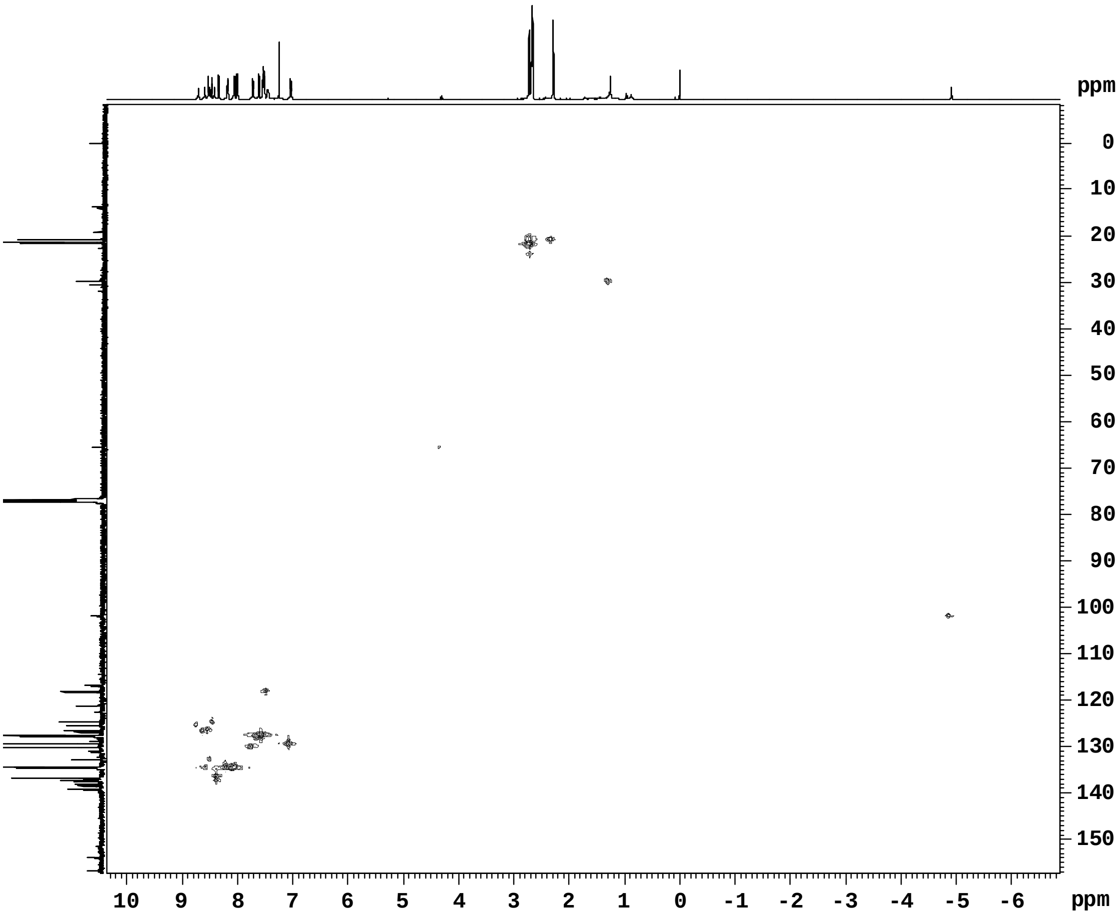
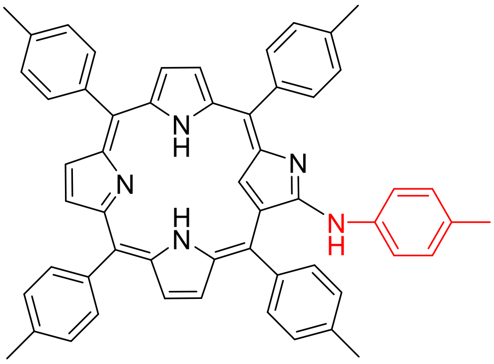


Figure S60. HSQC spectrum of **5b** ($CDCl_3$, 298 K).



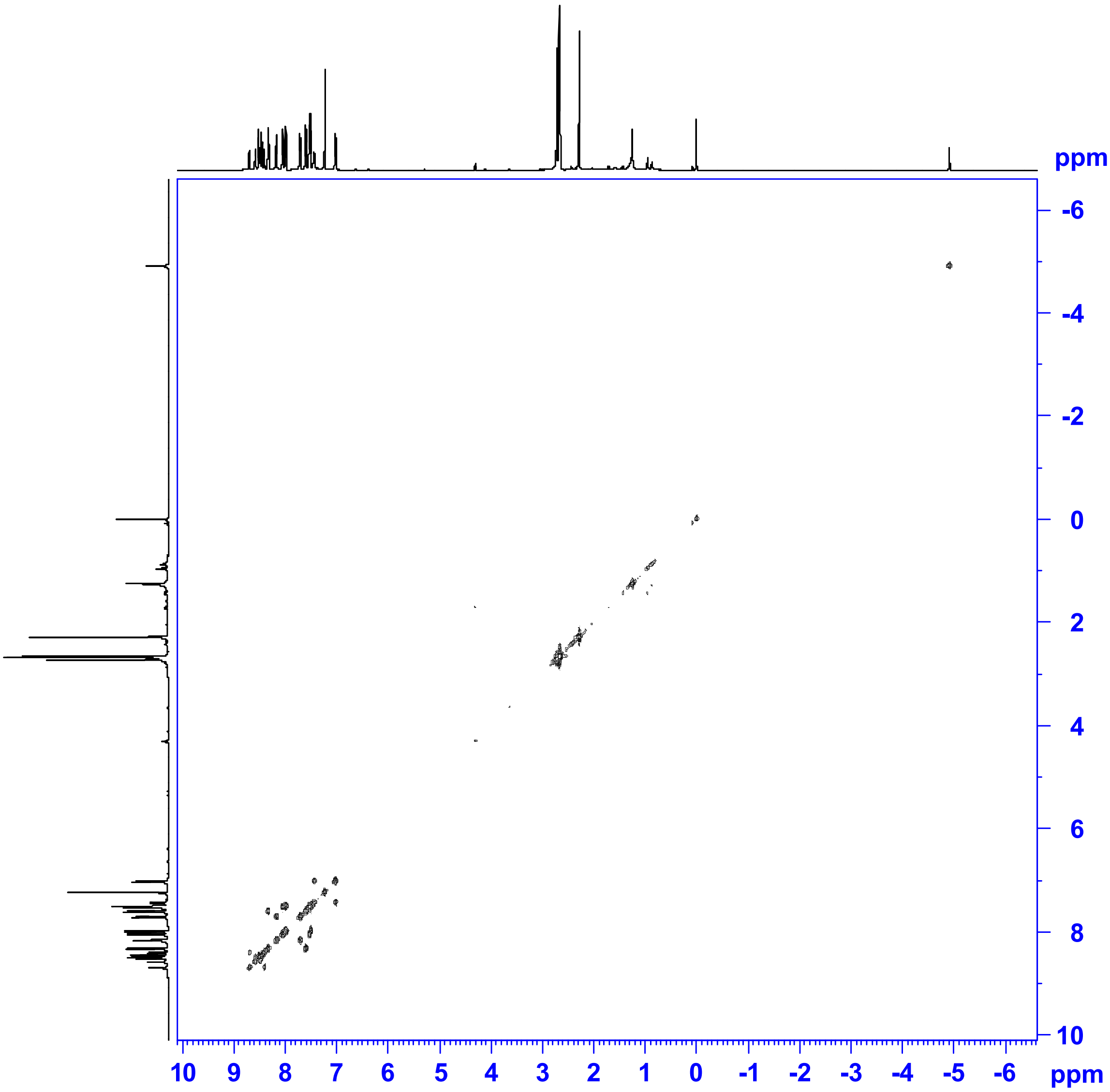
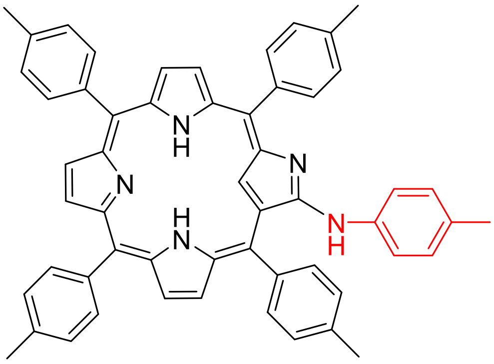


Figure S61. COSY spectrum of **5b** (CDCl3, 298 K).



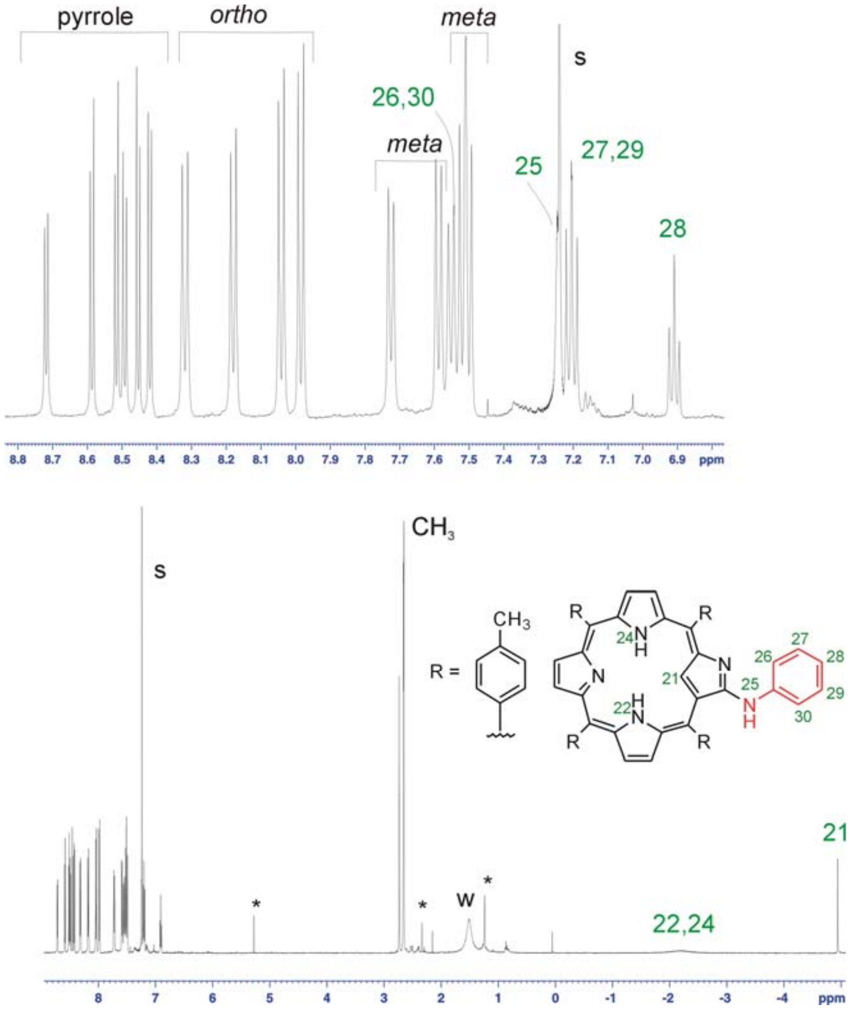


Figure S62. ^{1}H NMR spectrum (500 MHz, CDCl$_3$, 300 K) of **5c**.

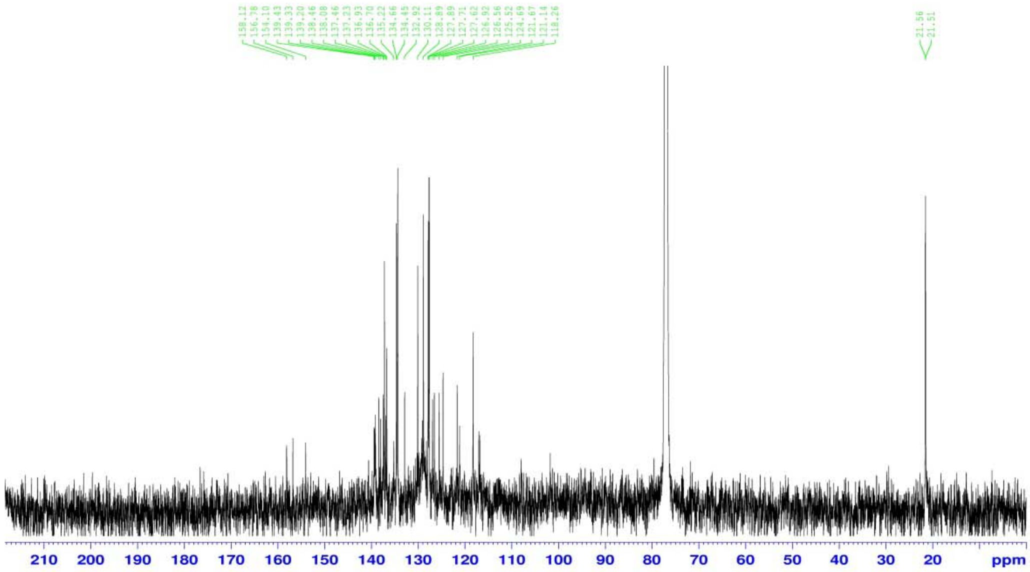


Figure S63. ^{13}C NMR (126 MHz, 300 K, CDCl$_3$) for **5c**.

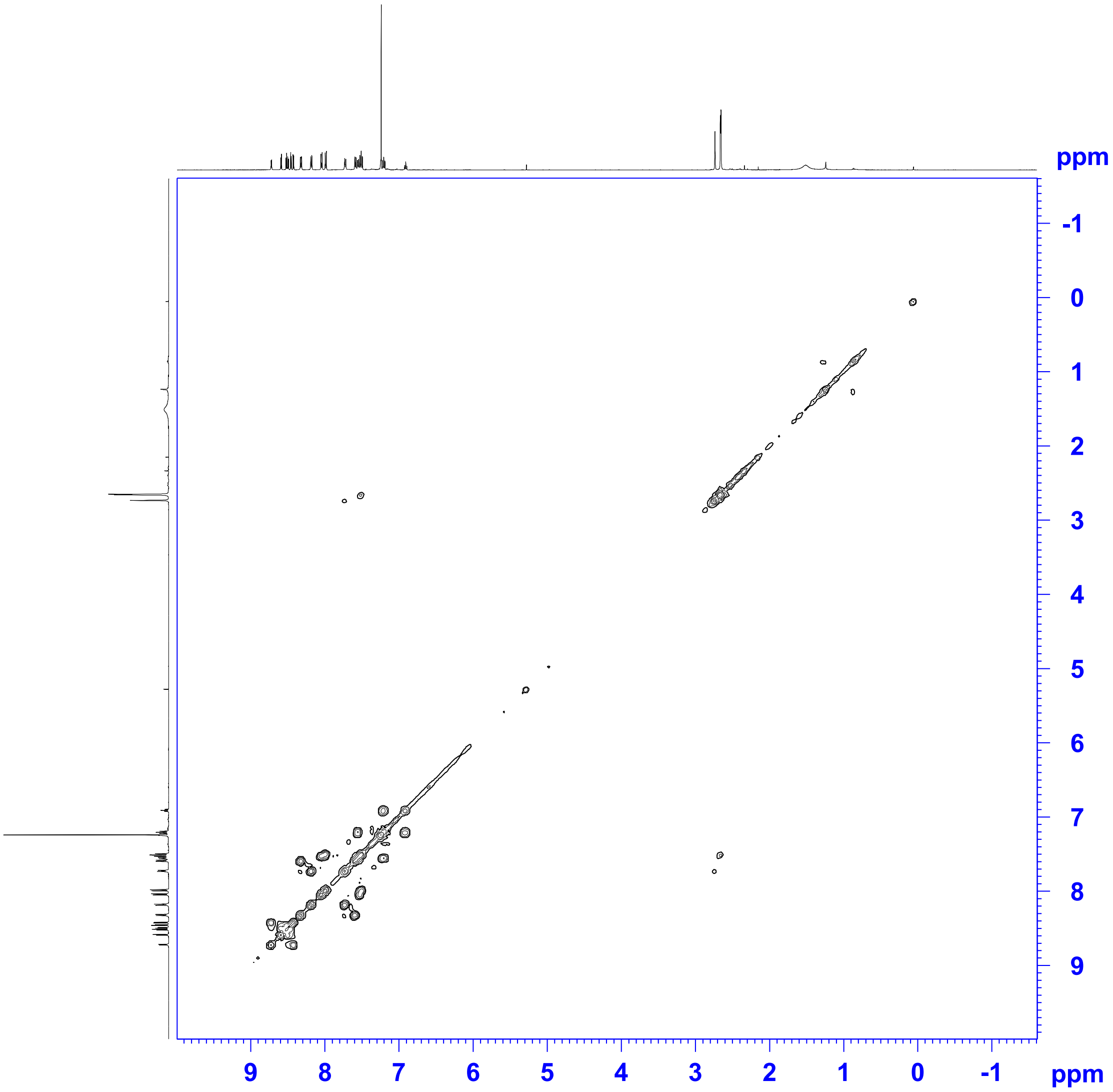
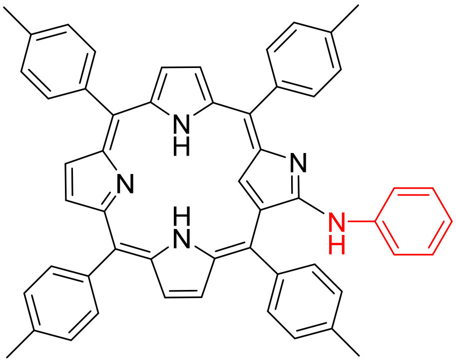


Figure S64. COSY spectrum (600 MHz, 300 K $CDCl_3$) of **5c**.



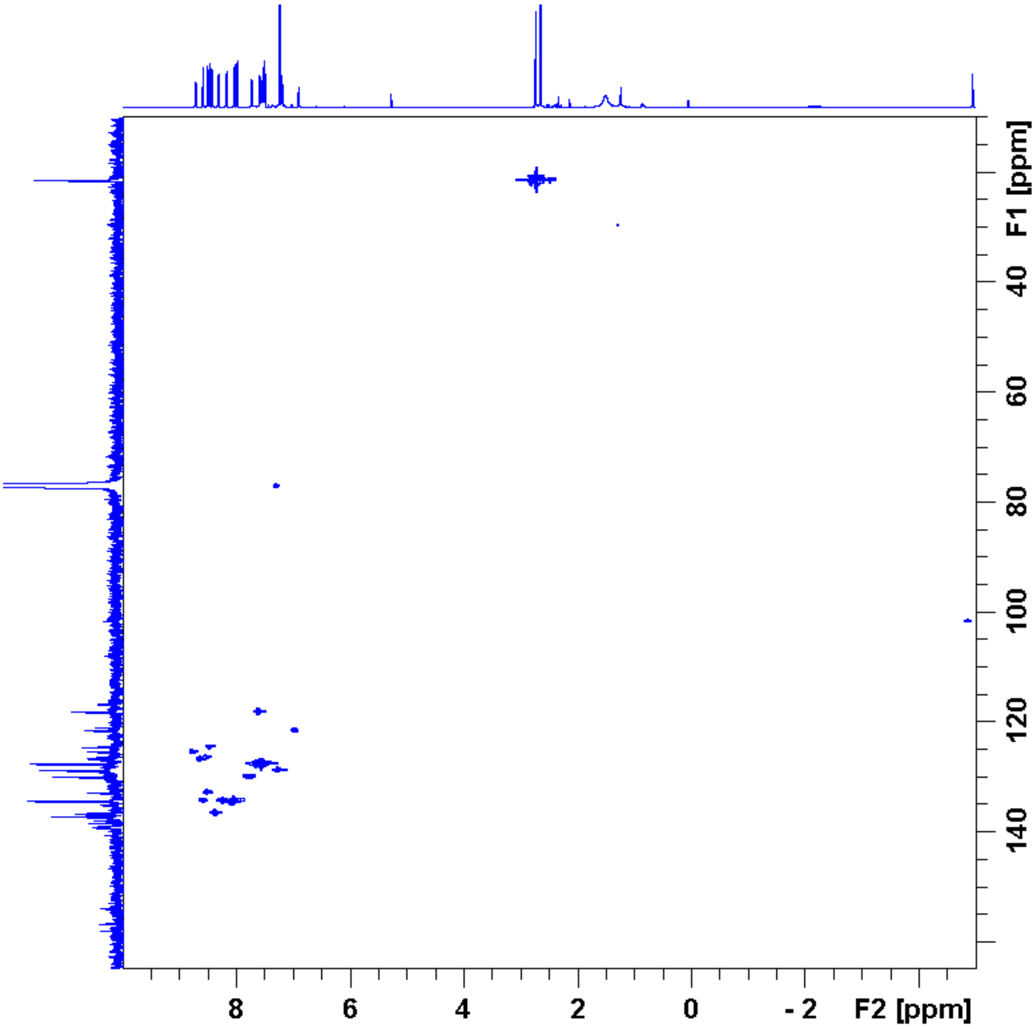
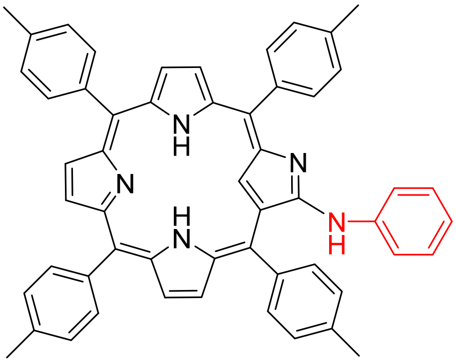
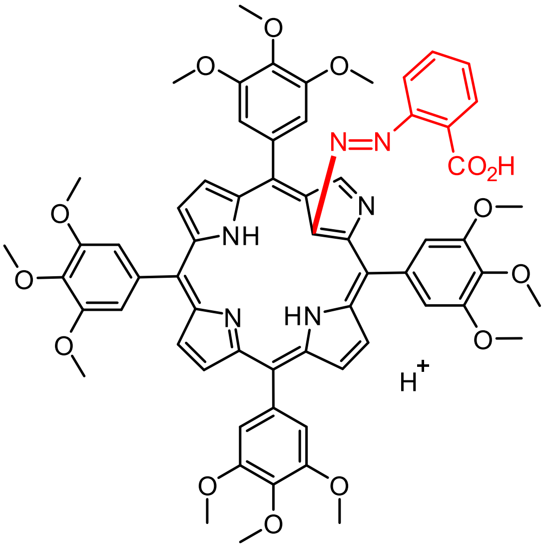


Figure S65. HSQC spectrum (300 K $CDCl_3$) of **5c**.





Chemical Formula: $C_{63}H_{59}N_6O_{14}^+$
Exact Mass: 1123.4084

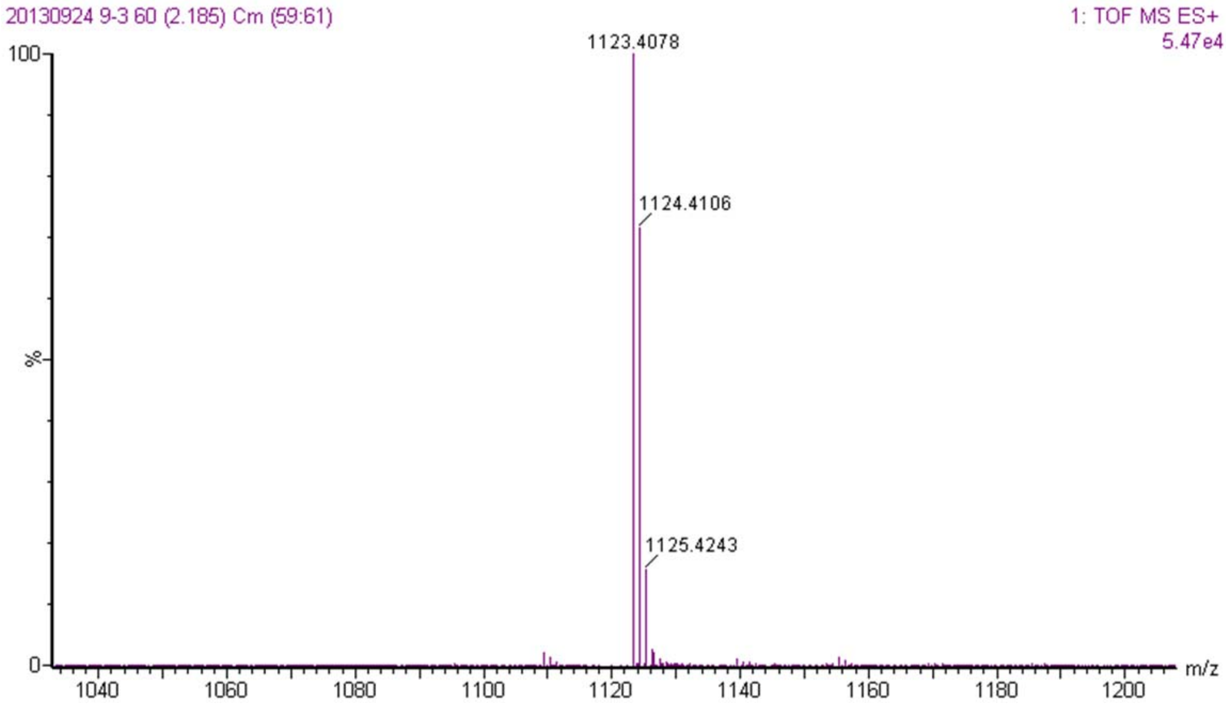
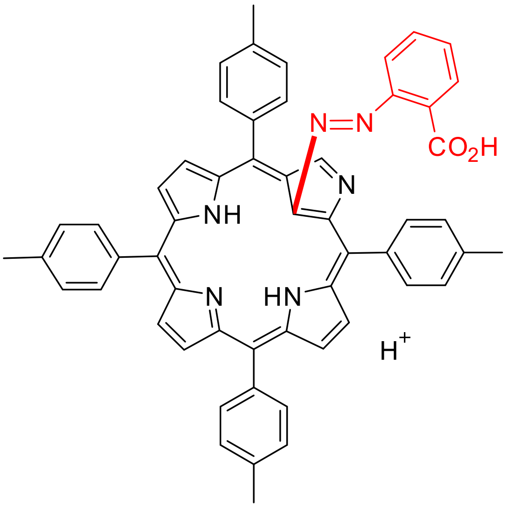


Figure S66. HRMS spectrum of **2a**.



Chemical Formula: $C_{55}H_{43}N_6O_2^+$
Exact Mass: 819.3442

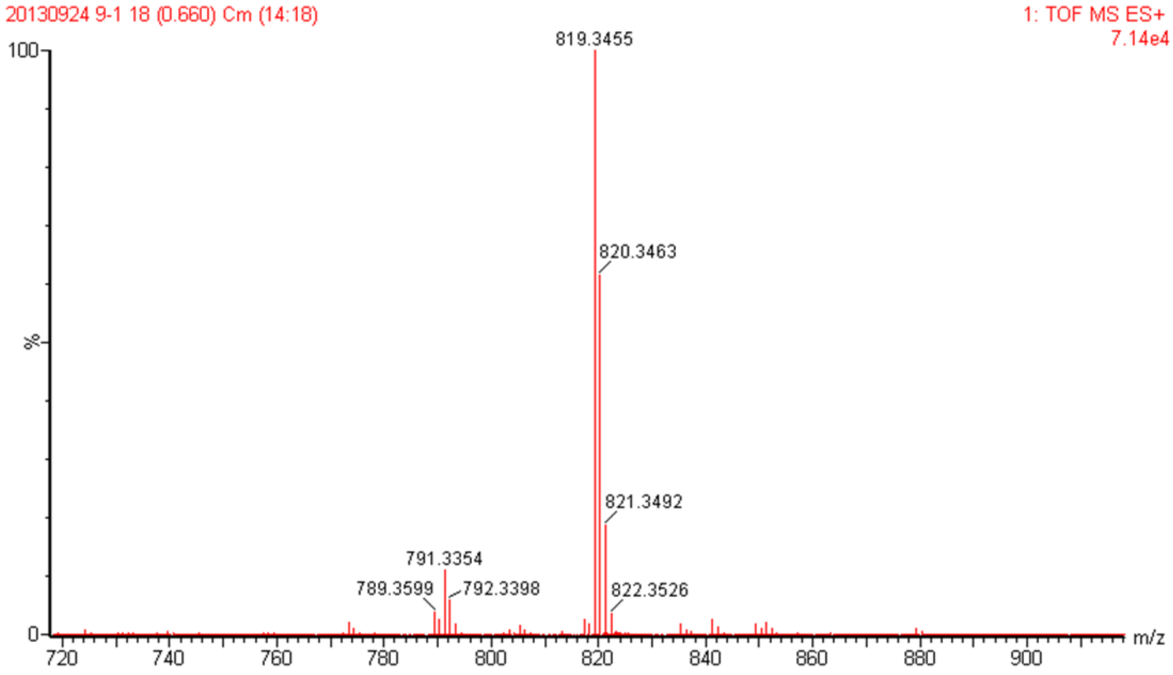
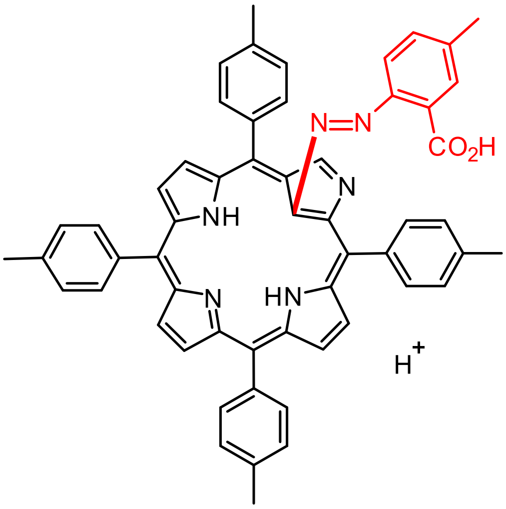


Figure S67. HRMS spectrum of **2b**.



Chemical Formula: $C_{56}H_{45}N_6O_2^+$
Exact Mass: 833.3599

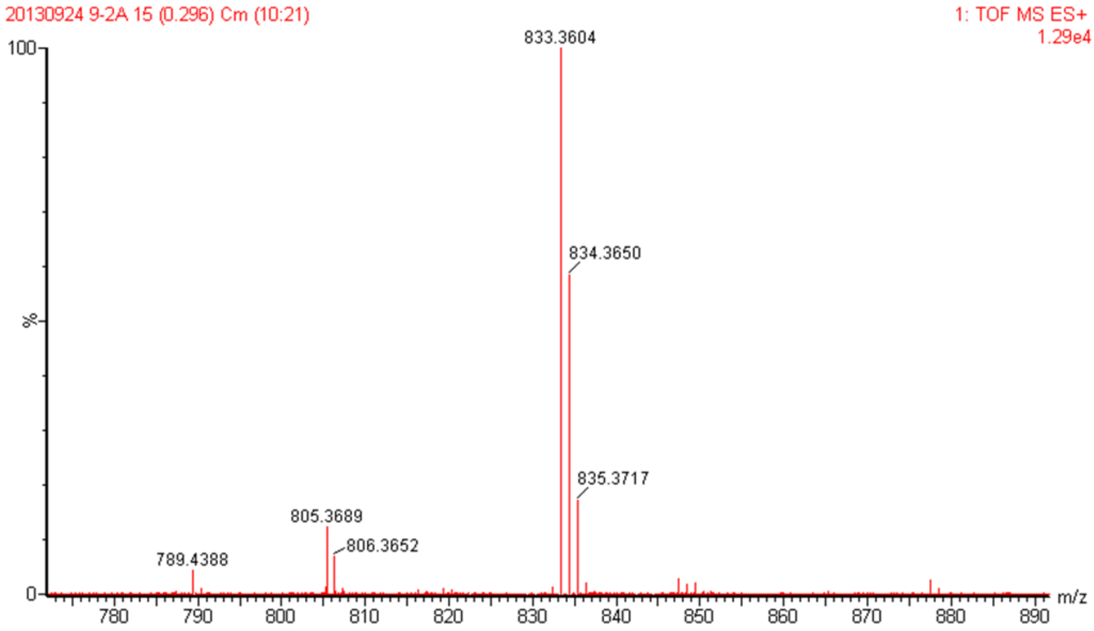
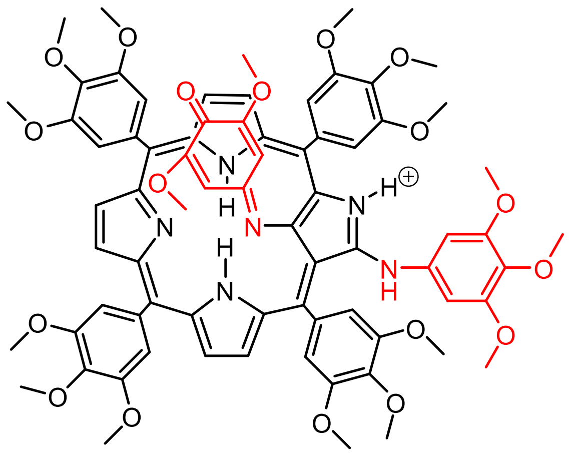


Figure S68. HRMS spectrum of **2c**.



Chemical Formula: $C_{73}H_{73}N_6O_{18}^+$
Exact Mass: 1321.4976

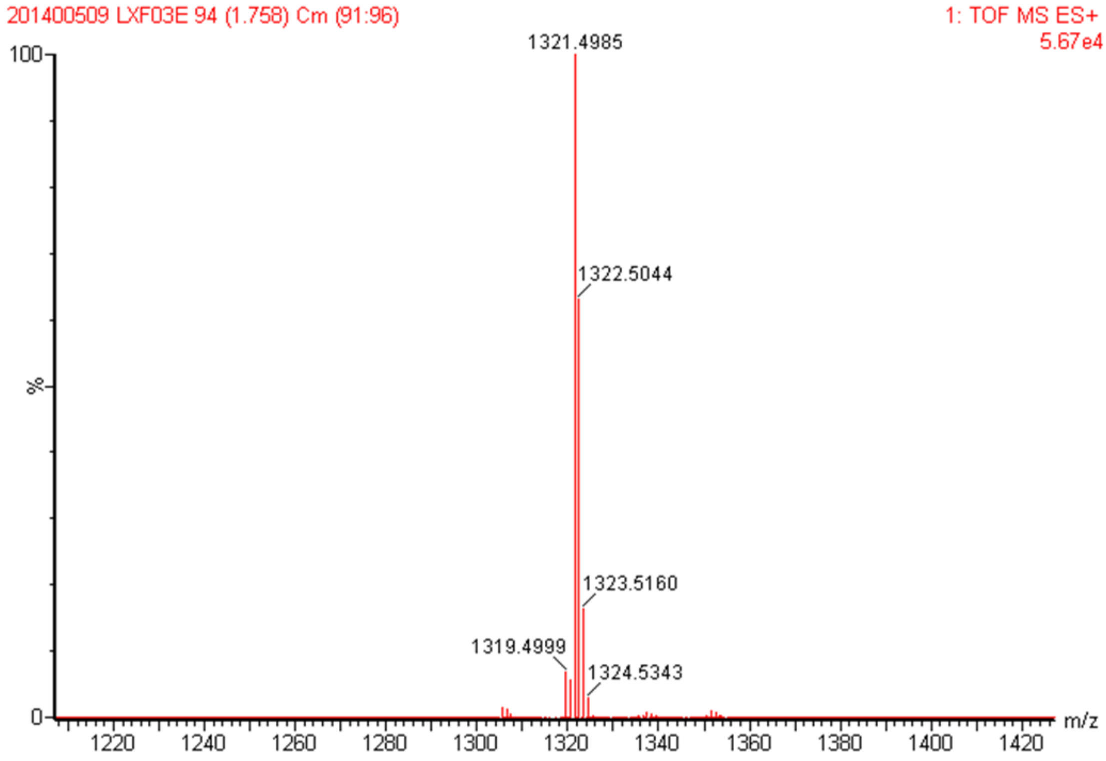
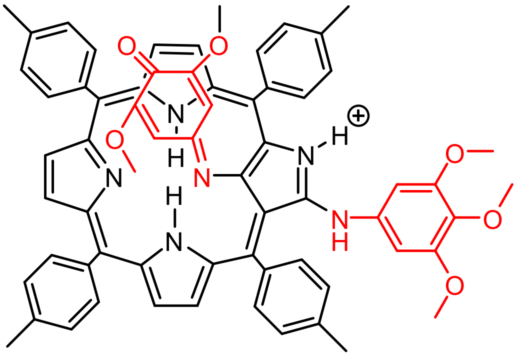


Figure S69. HRMS spectrum of **3a**.



Chemical Formula: $C_{65}H_{57}N_{6}O_{6}^{+}$

Exact Mass: 1017.4334

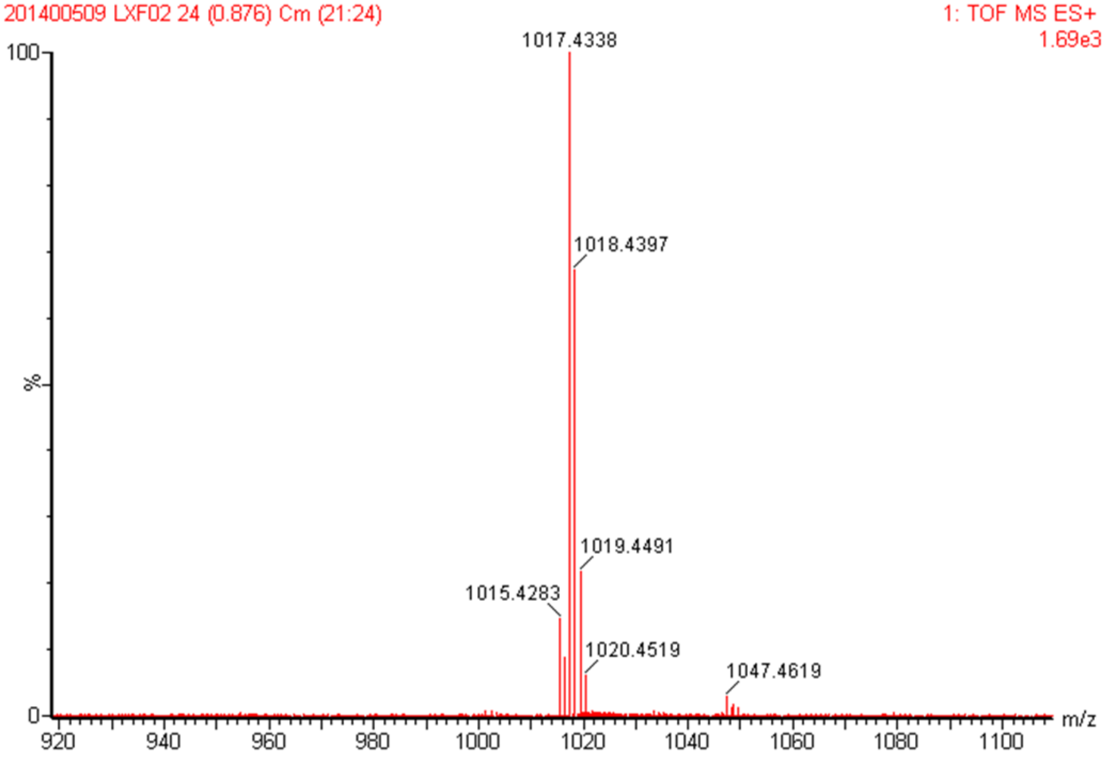
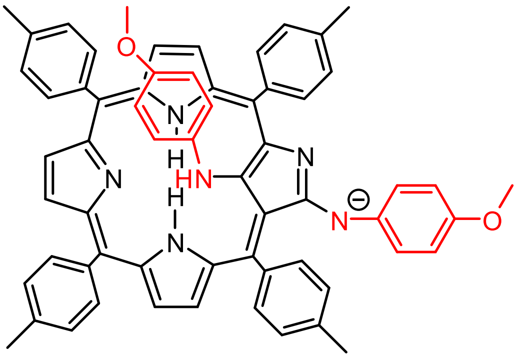


Figure S70. HRMS spectrum of **3b**.



Chemical Formula: $C_{62}H_{51}N_6O_2^-$
Exact Mass: 911.4079

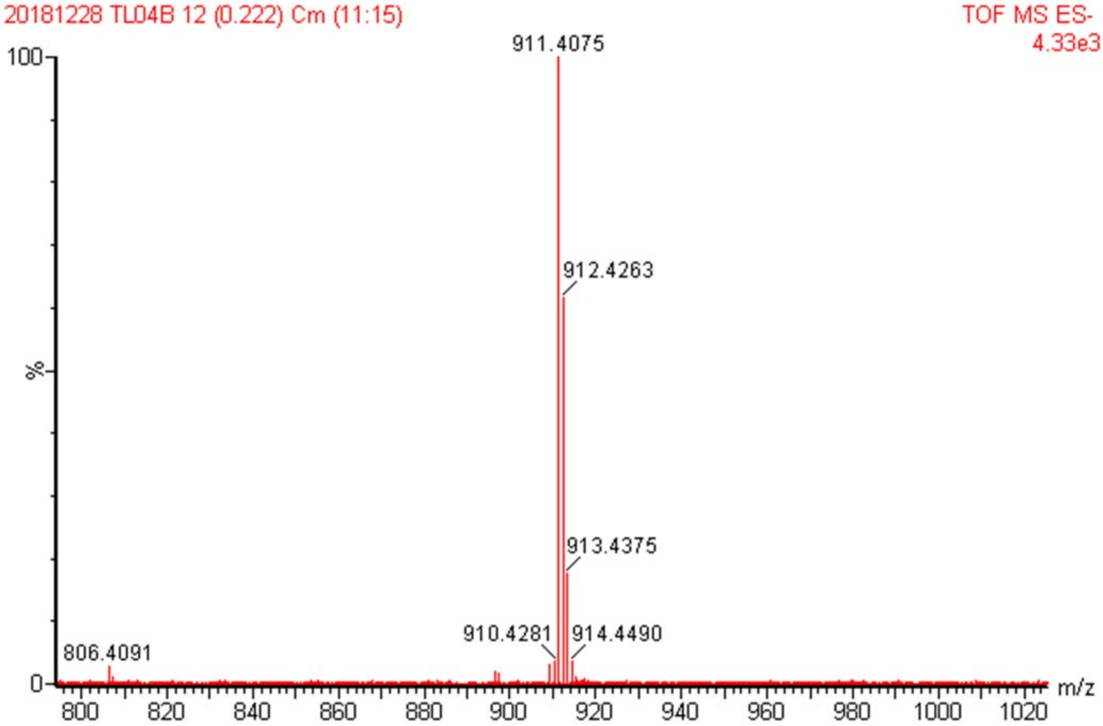
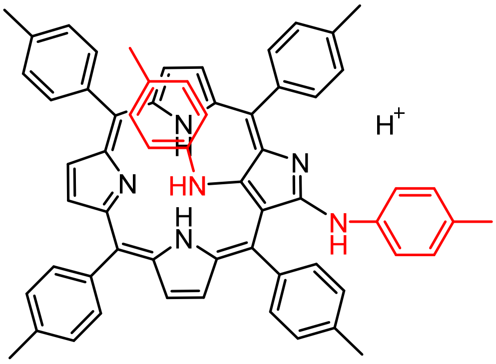


Figure S71. HRMS spectrum of **4a**.



$C_{62}H_{53}N_6$
Exact Mass: 881.4332

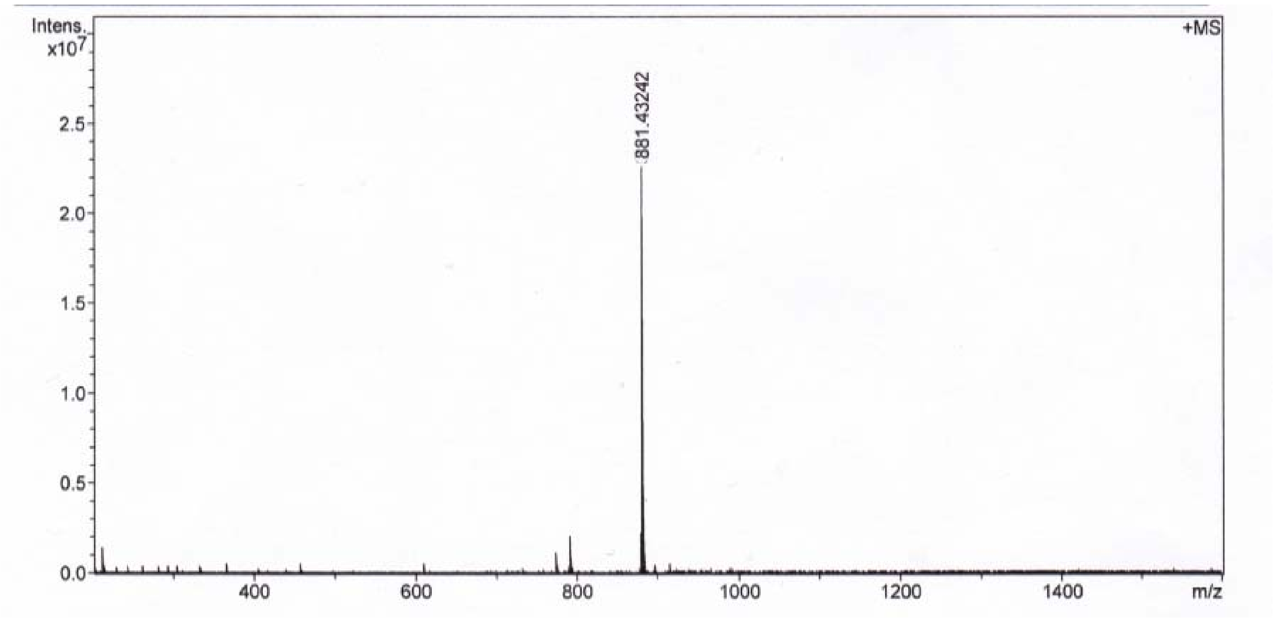
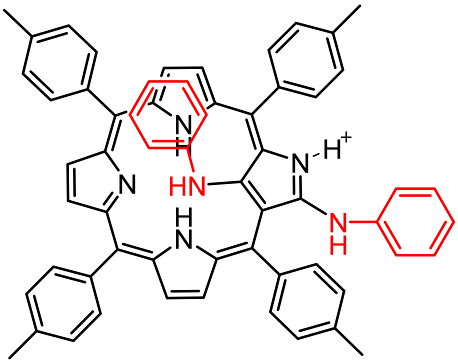


Figure S72. HRMS spectrum of **4b**.



Chemical Formula: $C_{60}H_{49}N_6^+$
Exact Mass: 853.4013

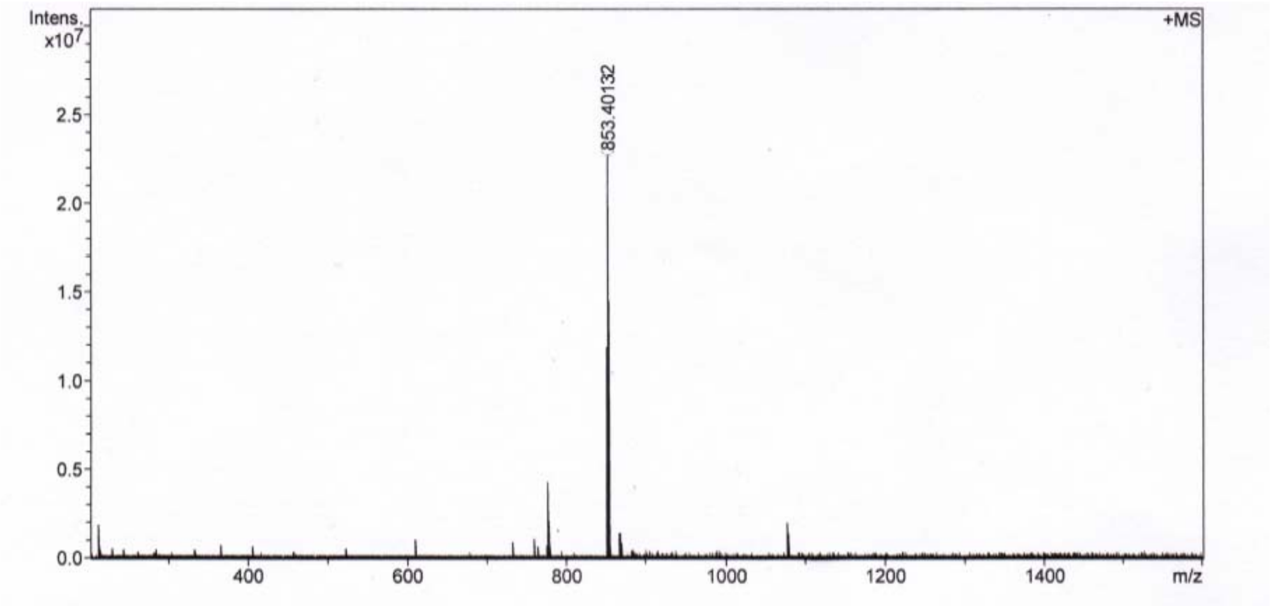
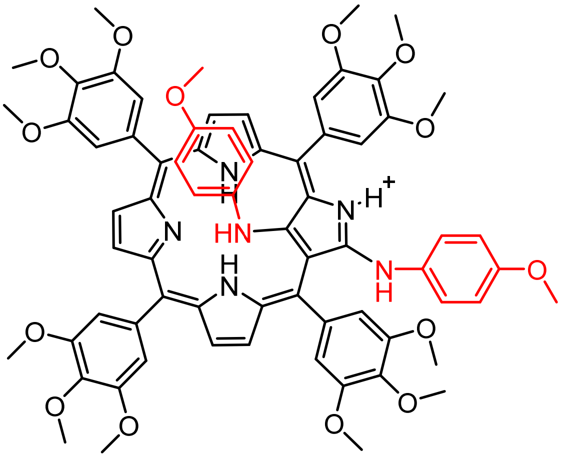


Figure S73. HRMS spectrum of **4c**.



Chemical Formula: $C_{70}H_{69}N_6O_{14}^+$
Exact Mass: 1217.4866

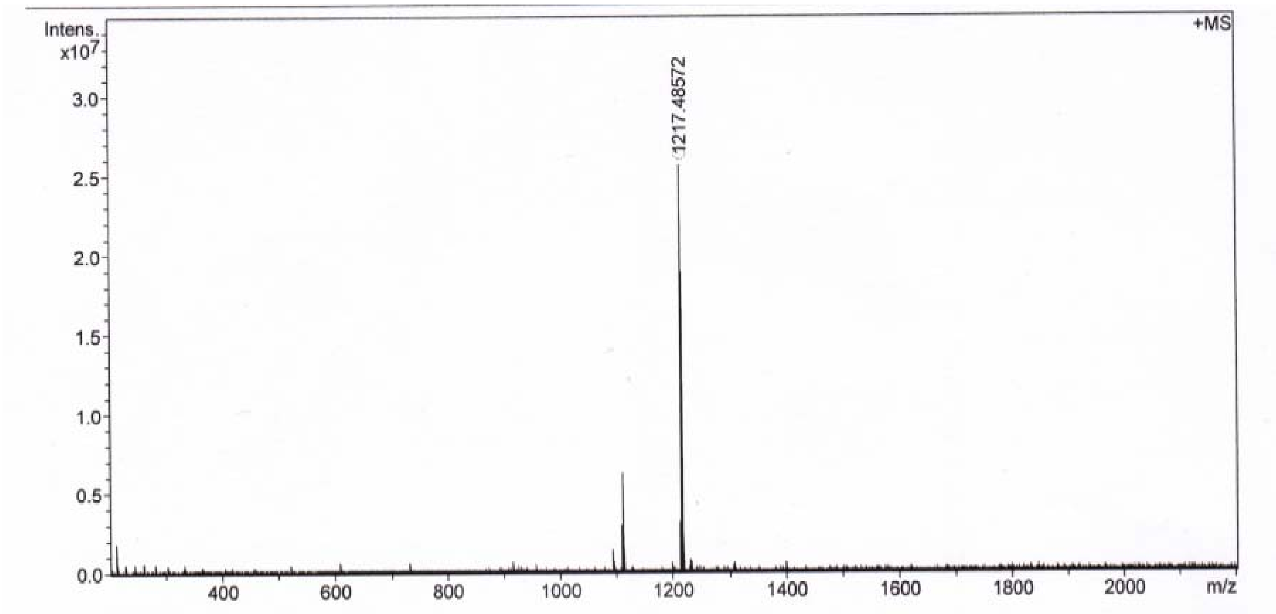
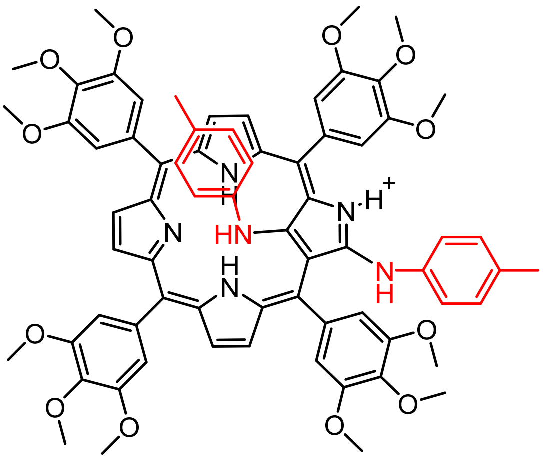


Figure S74. HRMS spectrum of **4d**.



Chemical Formula: $C_{70}H_{69}N_6O_{12}^+$
Exact Mass: 1185.4968

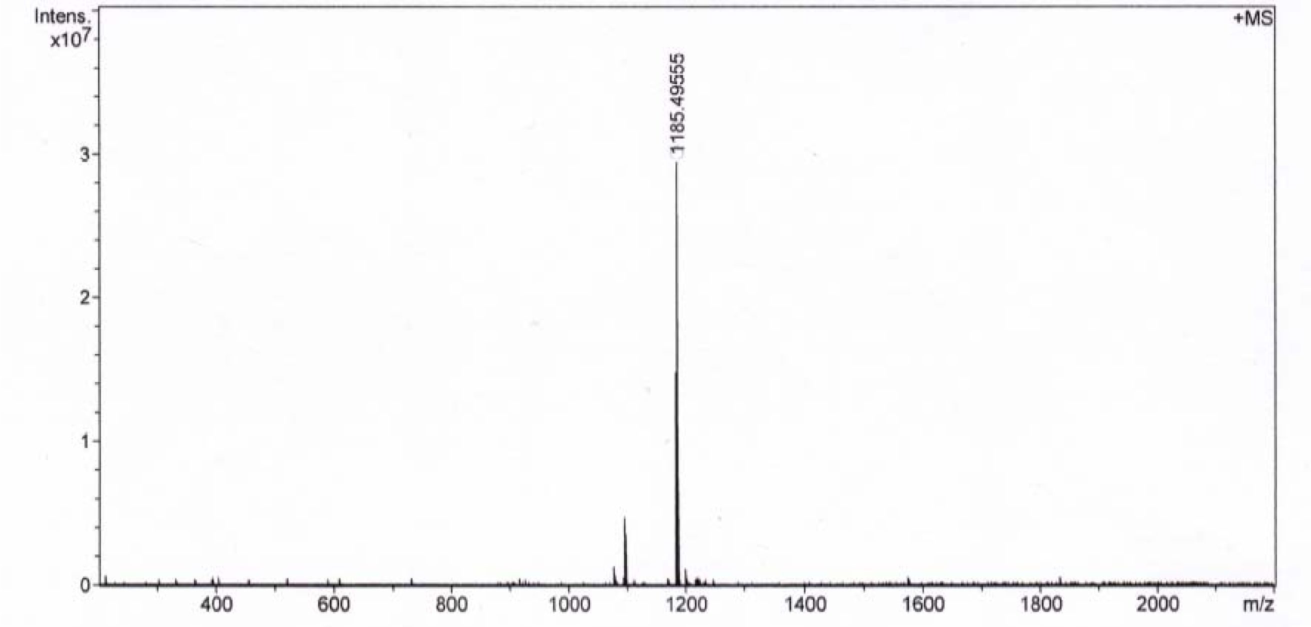
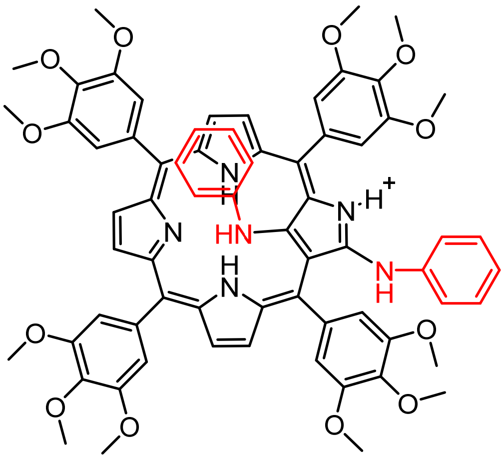


Figure S75. HRMS spectrum of **4e**.



Chemical Formula: $C_{68}H_{65}N_6O_{12}^+$
Exact Mass: 1157.4655

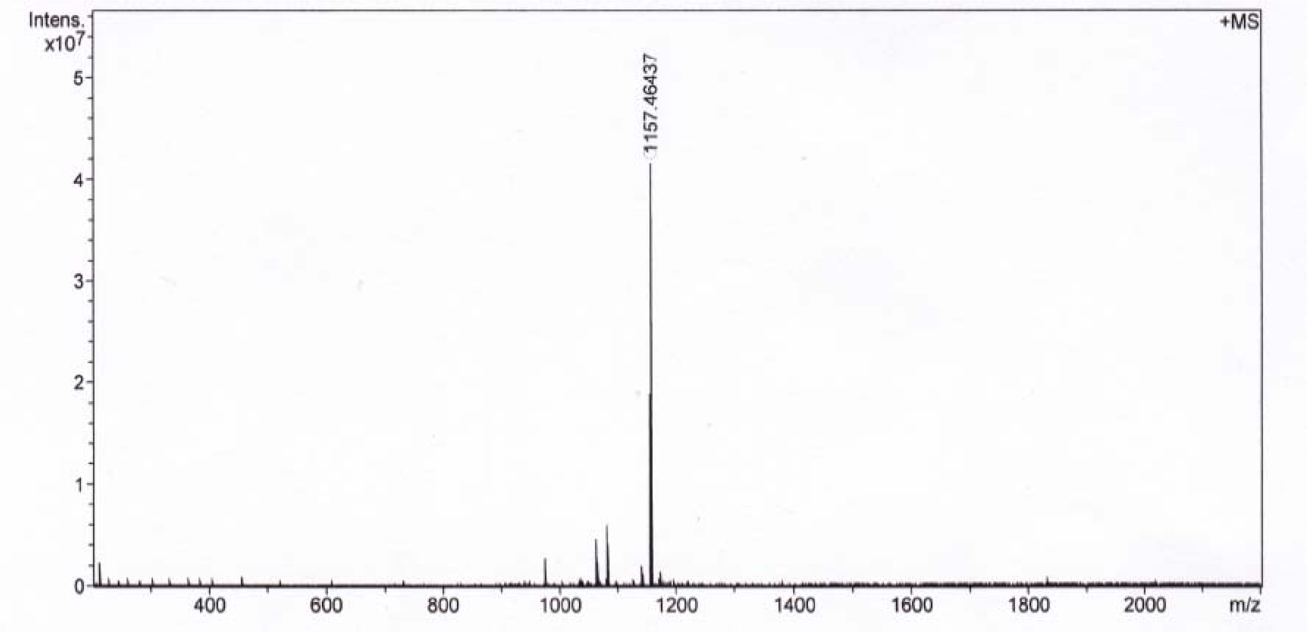
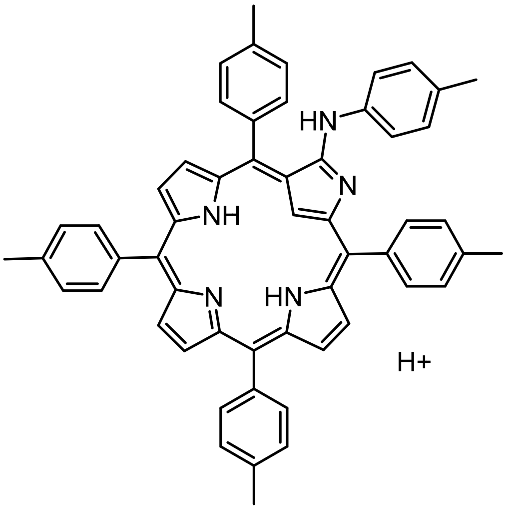


Figure S76. HRMS spectrum of **4f**.



Chemical Formula: $C_{55}H_{46}N_5^+$
Exact Mass: 776.3748

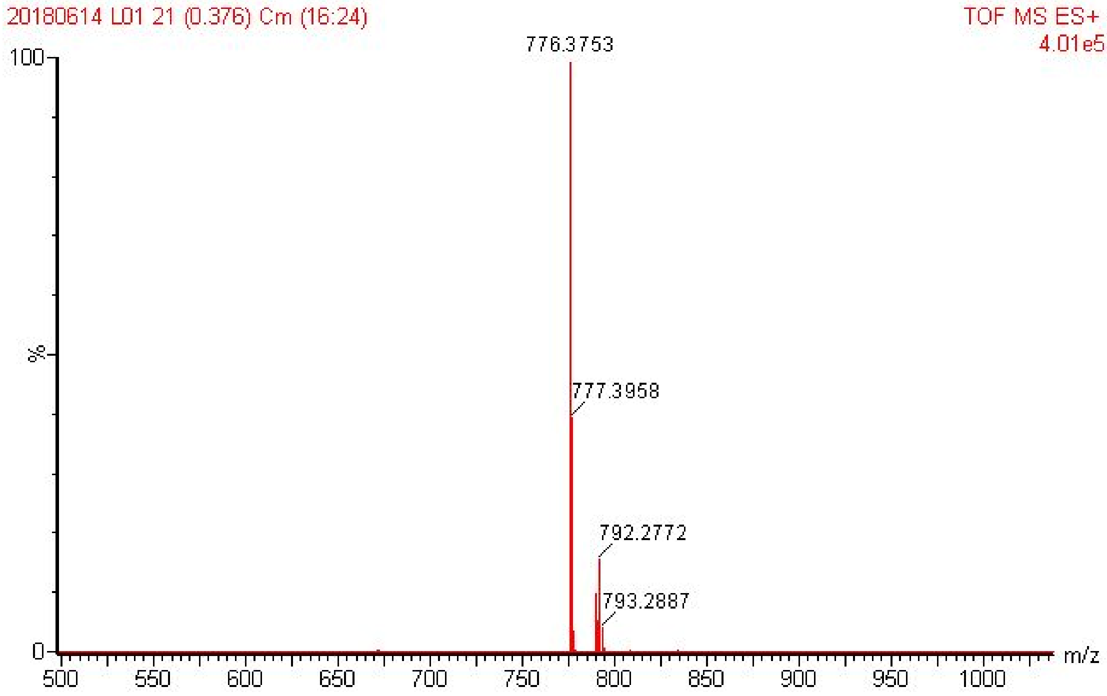
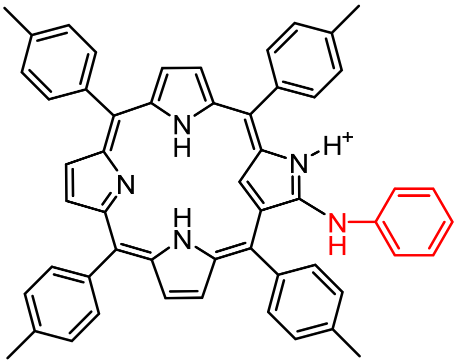


Figure S77. HRMS spectrum of **5b**.



Chemical Formula: $C_{54}H_{44}N_5^+$
Exact Mass: 762.3591

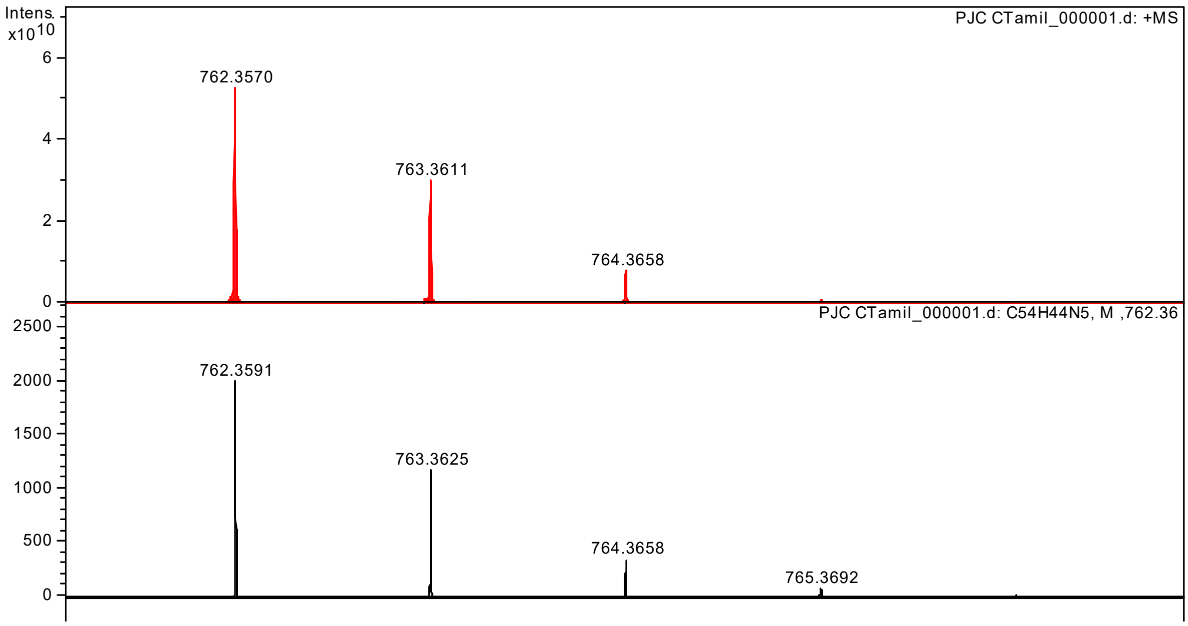


Figure S78. HRMS spectrum of **5c**. Top, experimental; bottom, simulated isotope pattern.

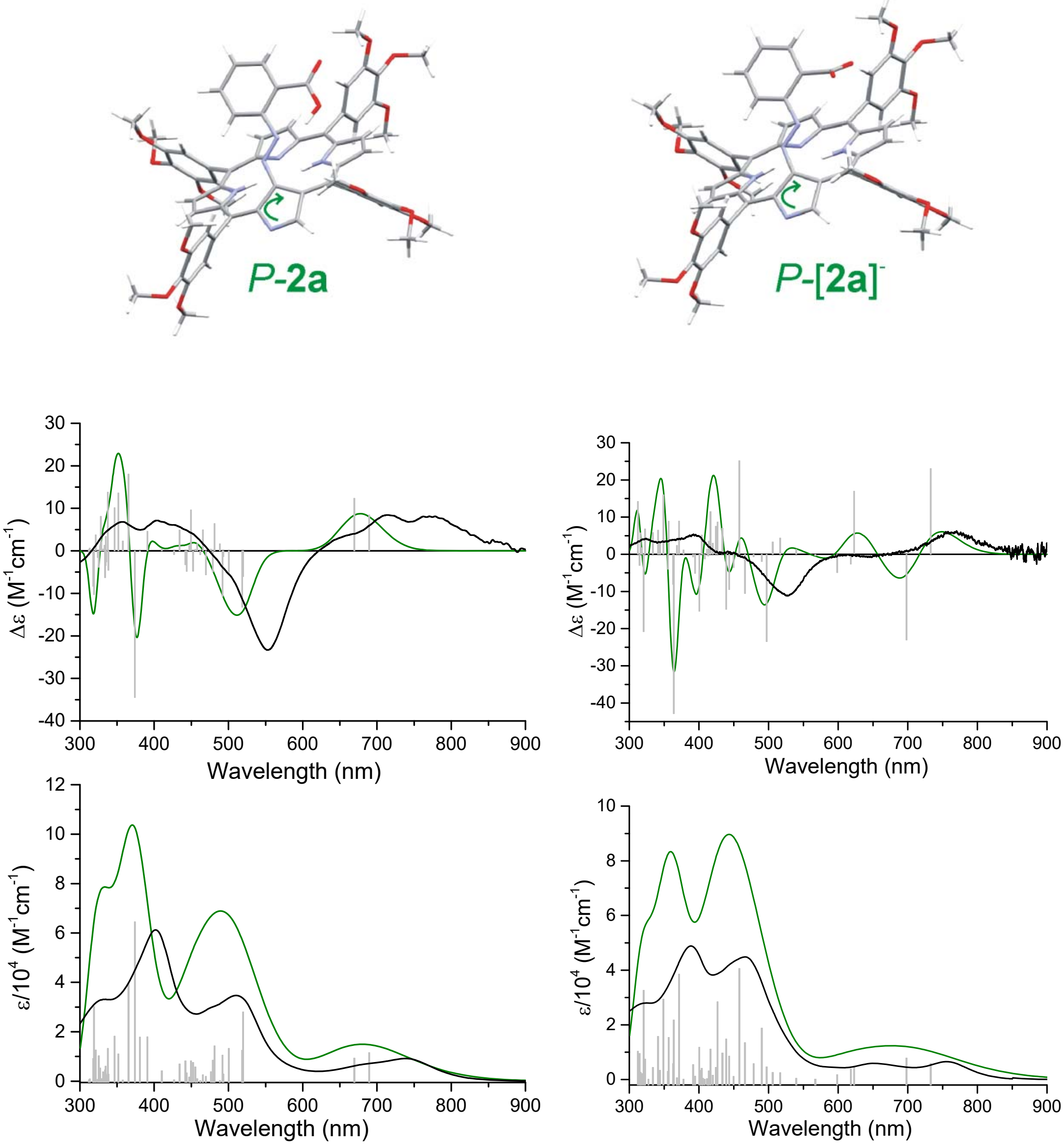
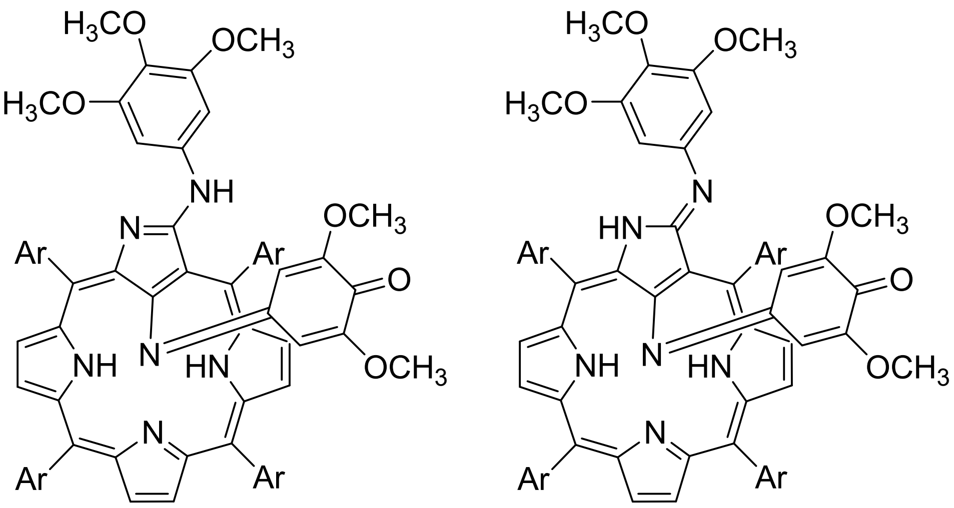


Figure S79. Experimental (black line) and calculated (green line) CD (top) and UV-vis-NIR (bottom) spectra of *P*-**2a** (left column) and *P*-[**2a**]$^{-}$ (right column). The gray sticks represent oscillator strengths or rotational strengths of the calculated transitions. The column headings are the DFT-optimized structures of the molecules for which spectra were simulated with definitions of their absolute configurations marked with curved arrows.



0 kcal/mol

Ar = *p*Tol

4.14 kcal/mol

3b amine

3b imine

Figure S80. Tautomers of **3b**.

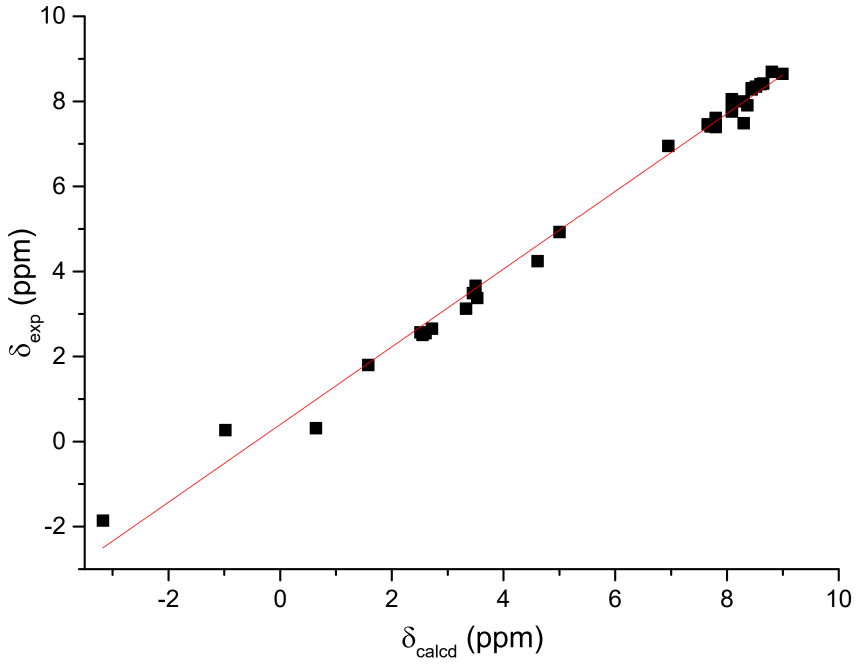


Figure S81. Correlation of experimental (600 MHz, CD_2Cl_2, 173 K) and GIAO-calculated chemical shifts for the amine tautomer of **3b**.

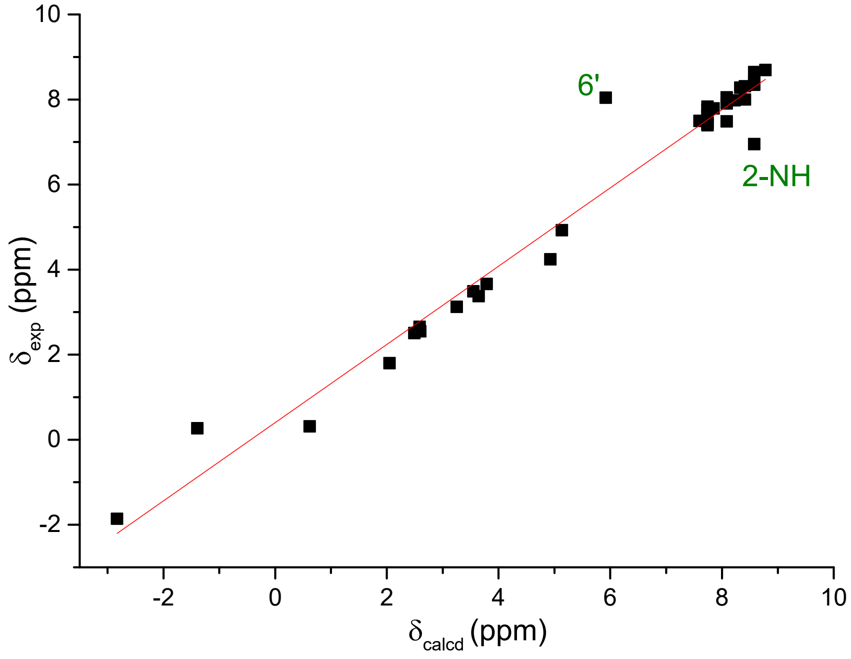


Figure S82. Correlation of experimental (600 MHz, CD_2Cl_2, 173 K) and GIAO-calculated chemical shifts for the imine tautomer of **3b**.

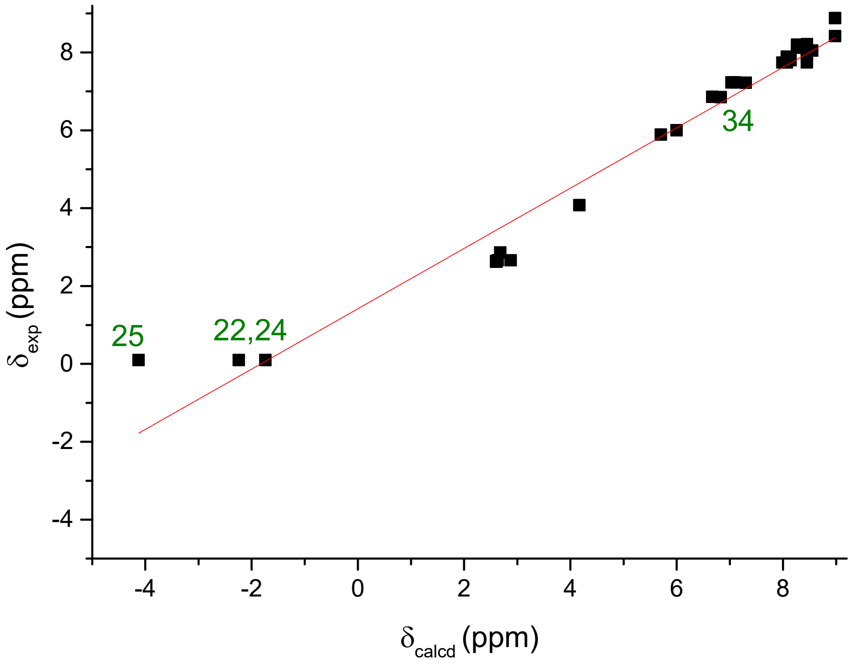


Figure S83. Correlation of experimental (600 MHz, CD_2Cl_2, 240 K) and GIAO-calculated chemical shifts for the amine tautomer of **4c**.

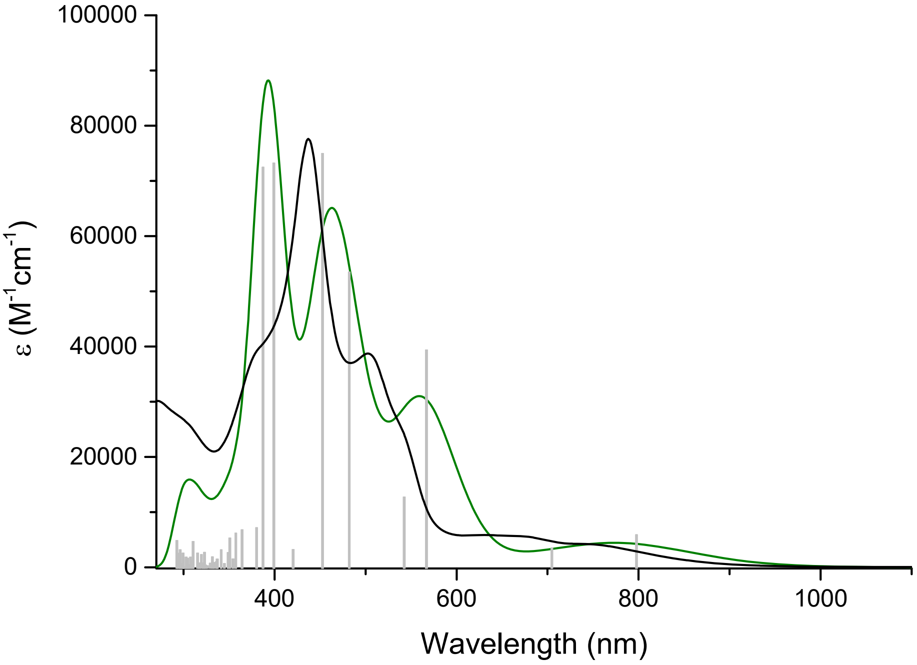


Figure S84. Experimental (black line, DCM) and TD DFT simulated (green line) optical spectra of **4c**. The gray sticks represent a histogram consisting of calculated transitions with oscillator strengths multiplied by 10^5 for scaling.

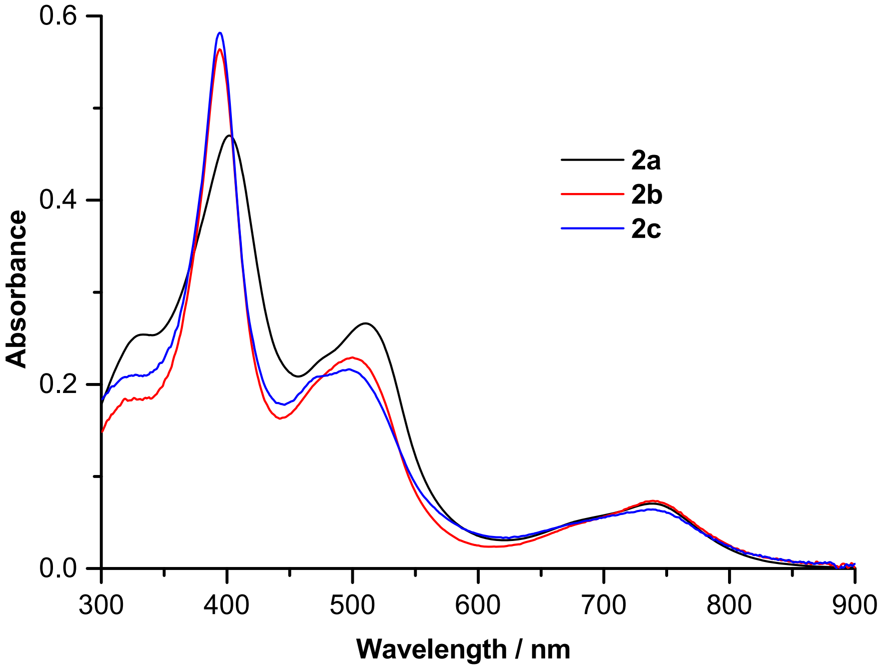


Figure S85. UV-vis-NIR absorption spectra ($CHCl_3$, 298 K) of 21-arylazo-NCP derivatives **2a-c**.

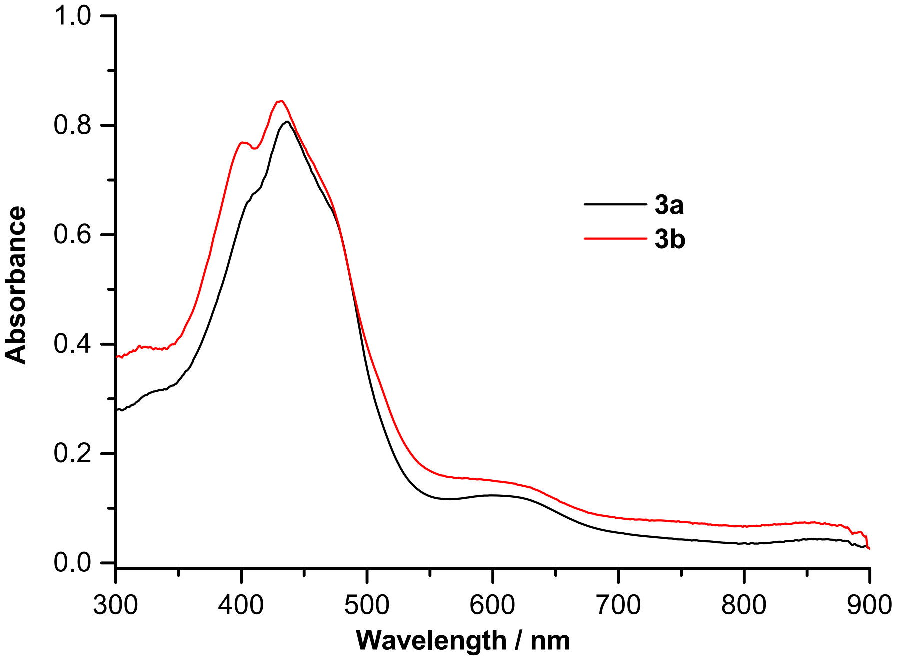


Figure S86. UV-vis-NIR absorption spectra ($CHCl_3$, 298 K) of 3-arylamino-21-quinoneimino-NCP derivatives **3a-b**.

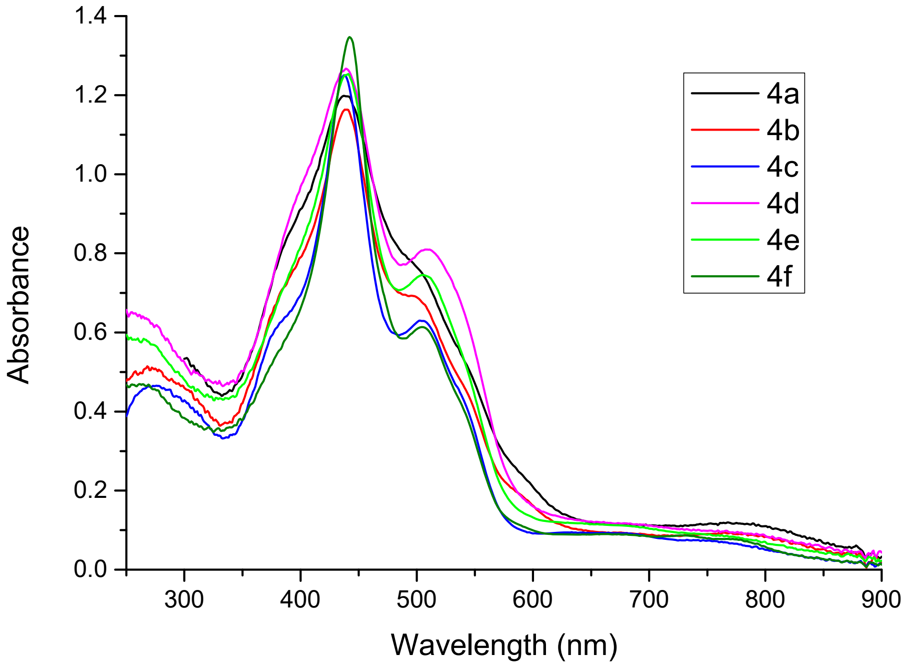
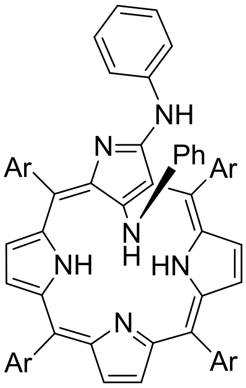


Figure S87. UV-vis-NIR absorption spectra ($CHCl_3$, 298 K) of 3,21-bis(arylamine)NCP derivatives **4a-f**.

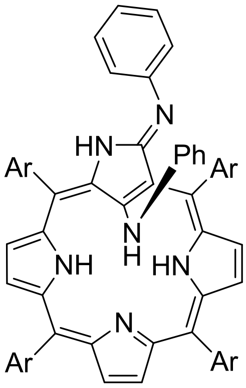
Table S2. Computational details for structures discussed in the paper. Optimizations were performed at the PCM(CH_2Cl_2)/B3LYP/6-31G(d,p) level of theory.

Structure	**Code**[a]	**SCF *E***[b]	**ZPV**[c]	**lowest freq.** [d]	***G***[e]	**HOMO**	**LUMO**	**HLG**
		a.u.	a.u.	cm^{-1}	a.u.	eV	eV	eV
2a	PJC_2a	-3817.16252546	1.110974	6.70	-3816.051551	-5.24	-3.06	2.18
[**2a**]$^-$	PJC_2a_neg	-3816.65615019	1.097942	9.27	-3815.558208	-4.61	-2.43	2.18
3b amine	PJC_3b_a	-3290.52006418	1.064930	9.53	-3289.455135	-4.72	-2.91	1.81
3b imine	PJC_3b_i	-3290.51346583	1.064070	7.69	-3289.449396	-4.74	-3.03	1.71
4c a/a[f]	PJC_4c_a_a	-2643.91054305	0.922494	11.67	-2642.988049	-4.59	-2.52	2.07
4c i/a[f]	PJC_4c_i_a	-2643.89123836	0.922388	11.15	-2642.968850	-4.18	-2.48	1.70
4c a/i[f]	PJC_4c_a_i	-2643.90758534	0.922029	11.04	-2642.985556	-4.60	-2.42	2.18
4c i/i[f]	PJC_4c_i_i	-2643.88970233	0.921707	11.26	-2642.967996	-4.33	-2.51	1.82

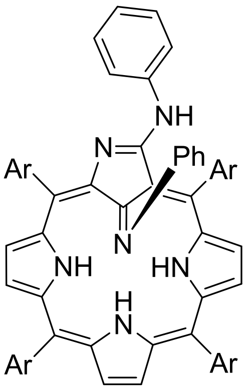
[a] Optimized geometry available as <code>.pdb file. [b] Electronic energy. [c] Zero-point vibrational energy. [d] Lowest vibrational frequency. [e] Gibbs free energy. [f] Tautomers: a/a, 3,21-amine; i/a, 3-imine-21-amine; a/i, 3-amine-21-imine; i/i, 3,21-imine.



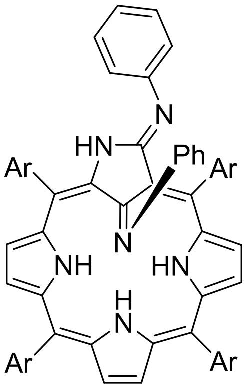
PJC_4c_a_a
-2643.91054305
0 kcal/mol



PJC_4c_i_a
-2643.90758534
+1.85 kcal/mol



PJC_4c_a_i
-2643.89123836
+12.11 kcal/mol



PJC_4c_i_i
-2643.88970233
+13.08 kcal/mol

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