Electronic Supplementary Material (ESI) for ChemComm.

General information.

NMR Spectroscopy. ^{1}H NMR spectra were recorded on a high-field spectrometers (^{1}H 600.15 MHz), equipped with a broadband inverse gradient probehead. Spectra were referenced to the residual solvent signal ([D]chloroform, 7.24 ppm). Two dimensional NMR spectra were recorded with 2048 data points in the t_2 domain and up to 1024 points in the t_1 domain, with a 1s recovery delay.

Mass Spectrometry. High resolution and Accurate Mass spectra were recorded on a Bruker apex ultra FTMS and a Bruker microTOF-Q spectrometers using the electrospray technique.

UV-Vis Spectroscopy. Electronic spectra were recorded on a Varian Carry-50 Bio spectrophotometer.

Fluorescence experiments: steady state fluorescence spectra were recorded with a JASCO FP-8600 Spectrofluorometer apparatus. Quantum yields were determined using 5,10,15,20-tetraphenylporphyrin (Φ = 0.11 in toluene[1]) as a reference compound. Time dependent experiments were recorded using the Edinburgh Instrument setup FL-900 using a nitrogen filled nanosecond flash lamp and the excitation wavelength of 450 nm and detected at the maximum emission wavelength and applying time correlated single photon counting (TCSPC technique). The radiative and non-radiative constants were calculated according to equation:

$$\theta_f = \frac{k_r}{k_r + k_{nr}}$$

where ϕ_f = fluorescence quantum yield, k_r – radiative constant, k_{nr} – nonradiative constant, $k_r + k_{nr} = 1/\tau$ where τ = fluorescence life time.

X-Ray Crystallography. X-Ray quality crystals were prepared by slow evaporation of hexane/$CHCl_3$ from saturated solution of **5c**. Data were collected at 100K on an Xcalibur PX-κ geometry diffractometer, with Cu Kα radiation (λ=1.5407). Data were corrected for Lorentz and polarization effect. The structures were solved by direct methods with SHELXS-97 and refined by full matrix least-squares method by using SHELXL-97 with anisotropic thermal parameters for the non-H atoms. Scattering factors were those incorporated in SHELXS-97.

Theoretical calculations. The geometry optimizations were carried out with the Gaussian03 package within unconstrained C1 symmetry, with starting coordinates derived from molecular mechanic calculations[2] or X-ray analysis. Becke's three-parameter exchange functional[3] with the gradient-corrected correlation formula of Lee, Yang and Parr[4] (DFT-RB3LYP). Harmonic vibrational frequencies were calculated using analytical second derivatives. The structure was found to have converged to a minimum on the potential energy surface. Proton chemical shifts were calculated using the GIAO

[1] Ogikubo, J.; Meehan, E.; Engle, J. T.; Ziegler, C. J.; Brückner, C. *J. Org. Chem.* **2013**, *78*, 2840.

[2] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; AlLaham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. **Gaussian 03**, Revision C.01; Pittsburgh, PA, **2004**.

[3] Becke, A. D. Phys. Rev. A 1988, 38, 3098–3100.

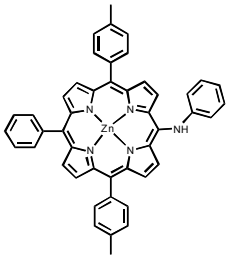
[4] Lee, C.; Yang, W.; Parr, R. G. Phys. Rev. B 1988, 37, 785–789.

method and referenced to the absolute shielding of tetramethylsilane calculated at the same level of theory.[5] NICS values were calculated using GIAO-B3LYP method.

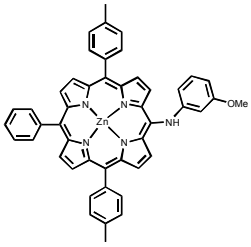
[5] a) P. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. Hommes *J. Am. Chem. Soc.* **1996**, *118*, 6317; b) Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, P. R. Schleyer *Chem. Rev.* **2005**, *105*, 3842.

1. Synthesis.

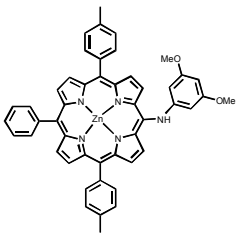
General procedure for meso amino porphyrin. 100 mg (65 mg, 0.092 mmol) of bromoporphyrin was placed in a pear shaped, two necked flask together with a palladium acetate (1.0 mg, 0.0046 mmol), DPEPhos (3.66 mg, 0.007 mmol), and Cs_2CO_3 (41.76 mg, 0.128 mmol) and left or o/n drying joined with a vaccum line. Dry THF (20 mL) and amine (5 eq.) were added and the resulting mixture was degassed with a pump-thaw technique. After degassing flask was placed in a pre-heated oil bath (68°C) and left for 3h in an inert atmosphere. After that time all volatiles were removed and crude mixture was subjected to chromatography with SilicaGel 60 (mesh 70-230).



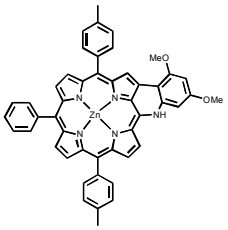
Eluent CH_2Cl_2/Petrol (40-60) (1:1). Yield 75%. **Characteristic of 5a: ^{1}H NMR ($CDCl_3$, 600 MHz, 300 K)** – 9.18 (d, 2H, ^3J = 4.6 Hz), 8.88 (d, 2H, ^3J = 4.6 Hz), 8.85 (d, 2H, ^3J = 4.6 Hz), 8.73 (d, 2H, ^3J = 4.6 Hz), 8.19-8.16 (m, 2H), 8.00 (d, 4H, ^3J = 7.9 Hz), 7.78-7.70 (m, 3H), 7.52 (d, 4H, ^3J = 7.9 Hz), 7.36 (s, 1H), 7.11 (dd, 2H, ^3J = 8.5 Hz, ^3J = 7.6 Hz), 6.8 - 6.74(m, 3H), 2.69 (s, 6H); **^{13}C NMR ($CDCl_3$, 150 MHz, 300 K)** – 162.9, 152.7, 150.4, 150.3, 150.2, 150.0, 142.8, 139.5, 137.1, 134.4 (x2), 132.2, 132.1, 131.8, 129.2, 128.6, 127.5, 127.3 (x2), 126.6, 121.1, 121.0, 118.6, 118.0, 114.5, 21.5; **HRMS:** $[M-H]^-$ 718.1946 (theoretical 718.1949 calc. for $C_{46}H_{32}N_5Zn^-$).



Eluent CH_2Cl_2; Yield 40%. **Characteristic 5b: ^{1}H NMR ($CDCl_3$, 600 MHz, 300 K)** – 9.29 (d, 2H, ^3J = 4.6 Hz), 8.89 (d, 2H, ^3J = 4.6 Hz), 8.85 (d, 2H, ^3J = 4.6 Hz), 8.80 (d, 2H, ^3J = 4.6 Hz), 8.19-8.16 (m, 2H), 8.02 (d, 4H, ^3J = 7.9 Hz), 7.77-7.70 (m, 3H), 7.52 (d, 4H, ^3J = 7.9 Hz), 7.50 (s, 1H), 7.04 (t, 1H, ^3J = 8.5 Hz), 6.45 - 6.42 (m, 1H), 6.36 - 6.33 (m, 2H), 3.55 (s, 3H), 2.69 (s, 6H); **^{13}C NMR ($CDCl_3$, 150 MHz, 300 K)** - 160.8, 154.1, 150.4, 150.3, 150.2, 150.0, 142.8, 139.5, 137.1, 134.4, 134.3, 132.3, 132.0, 131.8, 129.9, 128.7, 128.6, 127.5, 127.3 (x2), 126.6, 121.1, 121.0, 117.6, 107.6, 103.7, 100.9, 55.0, 21.5. **HRMS**: $[M]^+$ 749.2034 (theoretical 749.2133 calc. for $C_{47}H_{35}N_5OZn^+$)



Eluent CH_2Cl_2; Yield 60%. **Characteristic of 5c: ^{1}H NMR ($CDCl_3$, 600 MHz, 300 K)** – 9.04 (d, 2H, ^3J = 4.6 Hz), 8.88 (d, 2H, ^3J = 4.6 Hz), 8.86 (d, 2H, ^3J = 4.6 Hz), 8.65 (d, 2H, ^3J = 4.6 Hz), 8.19-8.16 (m, 2H), 7.98 (d, 4H, ^3J = 7.8 Hz), 7.78-7.71 (m, 3H), 7.52 (d, 4H, ^3J = 7.8 Hz), 7.08 (s, 1H), 5.89 (t, 1H, ^3J = 2.2 Hz), 5.85 (d, 2H, ^3J = 2.2 Hz), 3.49 (s, 6H), 2.70 (s, 6H); **^{13}C NMR ($CDCl_3$, 150 MHz, 300 K)** – 161.6, 154.6, 150.3, 150.2 (x2), 142.9, 139.5, 137.1, 134.4 (x2), 134.3, 132.1, 132.0, 131.8, 128.5 (x2), 127.5, 127.3 (x2), 126.6, 121.1, 121.0, 117.0, 93.8, 90.6, 55.0, 21.5; **HRMS:** $[M+H]^+$ 780.2271 (theoretical 780.2297 calc. for $C_{48}H_{37}N_5O_2Zn$)



Synthesis of 4: 20 mg of **5c** was dissolved in 15 mL of freshly distilled CH_2Cl_2 and DDQ (17 mg, 3 eq.) was added. The colour of the solution has immediately changed from red to green. The resulting mixture was stirred for 1h at room temperature and the crude mixture was passed through a short silica plug (EtOAc). The crude product was collected, evaporated and re-dissolved in dry THF (15 mL) and $SnCl_2$ (100 mg) was added and stirred for 4h. After that time 15 mL of toluene was added and the crude product was passed through a short silica plug. The green product was collected and chromatographed on a silica column (60, mesh 70-230) with a Petrol(40-60):Ethyl Acetate (3:2) mixture used as an eluent. The intensive, green fraction

was collected and precipitated with hexane to give 18 mg (95%) of the fused product. **^{1}H NMR (C_6D_6 (+1% THF), 600 MHz, 300 K)** 10.28 (bs, 1H, *outer NH*), 9.59 (s, 1H, **H(2)**), 8.94 (d, 1H, ^{3}J = 3.6 Hz, **H(18)**), 8.86 (m, 2H, **H(7,8)**), 8.81 (d, 1H, ^{3}J = 4.2 Hz, **H(12)**), 8.73 (d, 1H, ^{3}J = 4.6 Hz, **H(17)**), 8.71 (d, 1H, ^{3}J = 4.6 Hz, **H(13)**), 8.27 (d, 2H, ^{3}J = 7.7 Hz, **H**(**20*o***)), 8.17 (d, 2H, ^{3}J = 7.7 Hz, **H(*10o*)**), 8.12 (d, 2H, ^{3}J = 7.4 Hz, **H(15*o*)**), 7.43-7.38 (m, 5H, **H(*15m,p,* 20*m*)**), 7.29 (d, 2H, ^{3}J = 7.7 Hz, **H(*10m*)**), 6.31 (bs, 1H, **fused aryl**), 6.22 (bs, 1H, **fused aryl**), 3.36 (s, 3H, -O**Me**), 3.22 (s, 3H, -O**Me**) 2.45 (s, 3H, -**Me**), 2.39 (s, 3H, -**Me**); **^{13}C NMR (C_6D_6(+1% THF), 150 MHz, 300 K)** 157.3, 156.6, 151.5, 151.1, 150.1, 148.4, 145.3, 143.9, 142.1, 139.0, 136.4, 134.1, 133.8, 133.2, 133.1, 132.4, 132.0, 130.6, 130.3, 129.1, 128.8, 127.4, 126.3, 126.1, 126.0, 125.8, 125.0, 124.9, 124.4, 124.3, 121.3, 120.5, 116.9, 116.1, 114.1, 111.9, 111.9, 102.2, 90.7, 88.7, 52.9, 52.3, 19.2, 19.0. **HRMS:** $[M]^{\bullet+}H]^{+}$ 777.2076 (theoretical 777.2082 calc. for $C_{48}H_{35}N_5O_2Zn$.

2. NMR spectra

2.1 NMR spectra of 2

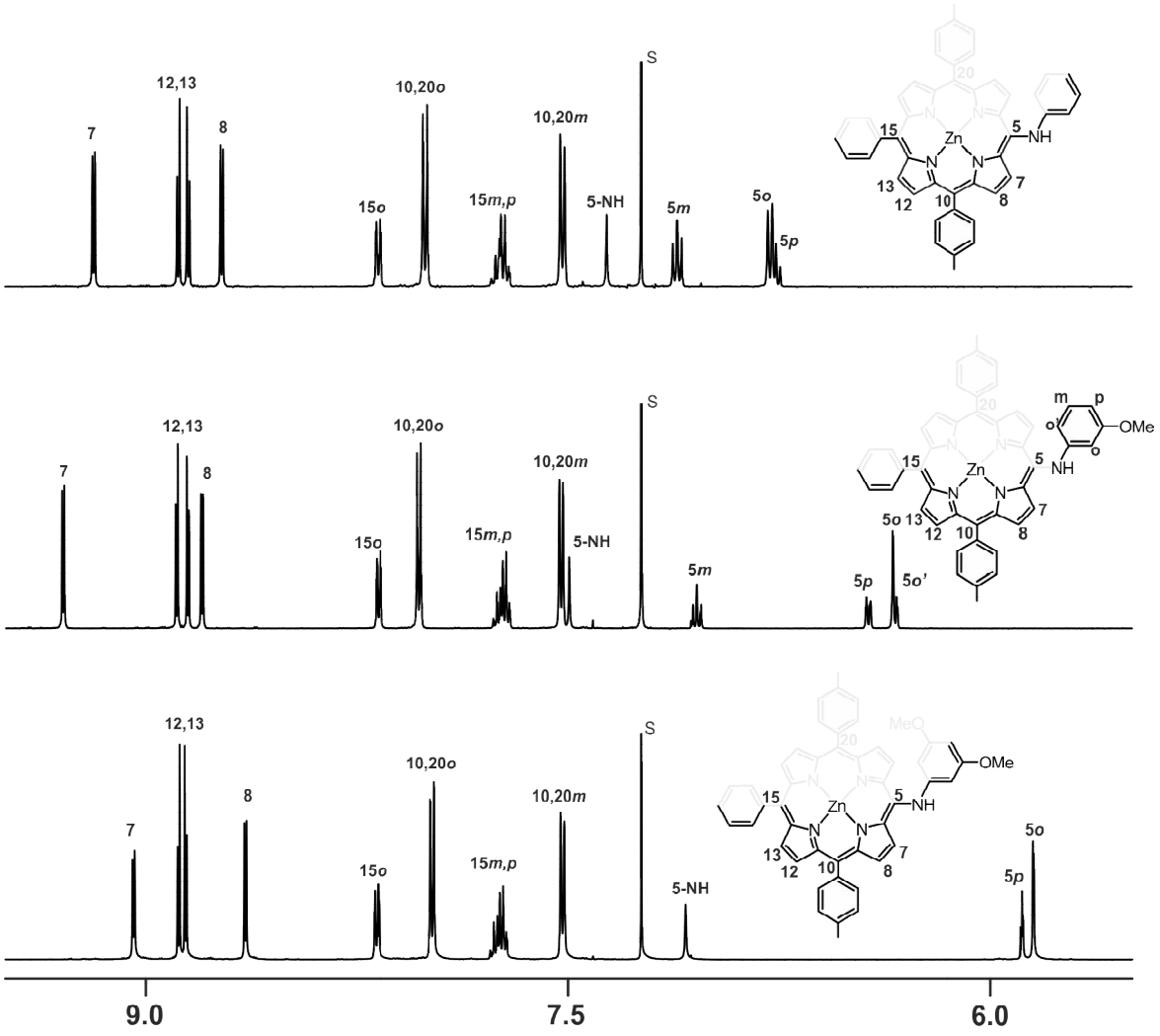


Figure S1. [1]H NMR spectrum of a) **2a** (600 MHz, chloroform - *d*, 300K); b) **2b** (600 MHz, chloroform - *d*, 300K); c) **2c** (600 MHz, chloroform- *d*, 300K).

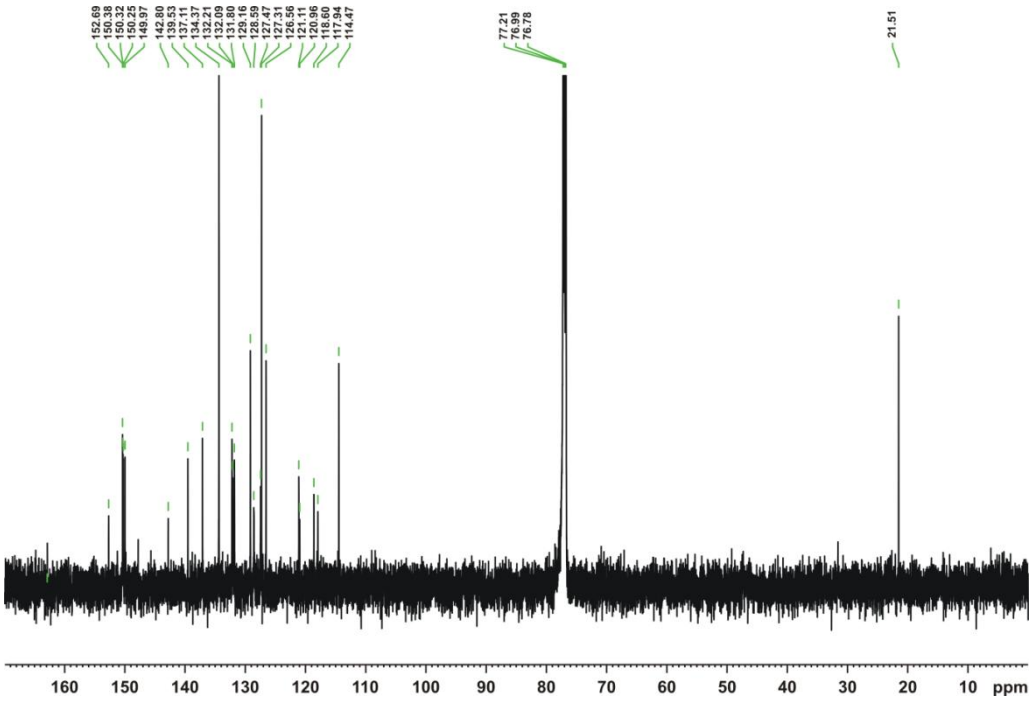


Figure S2. ^{13}C NMR spectrum of **2a** (600 MHz, chloroform-*d*,300K).

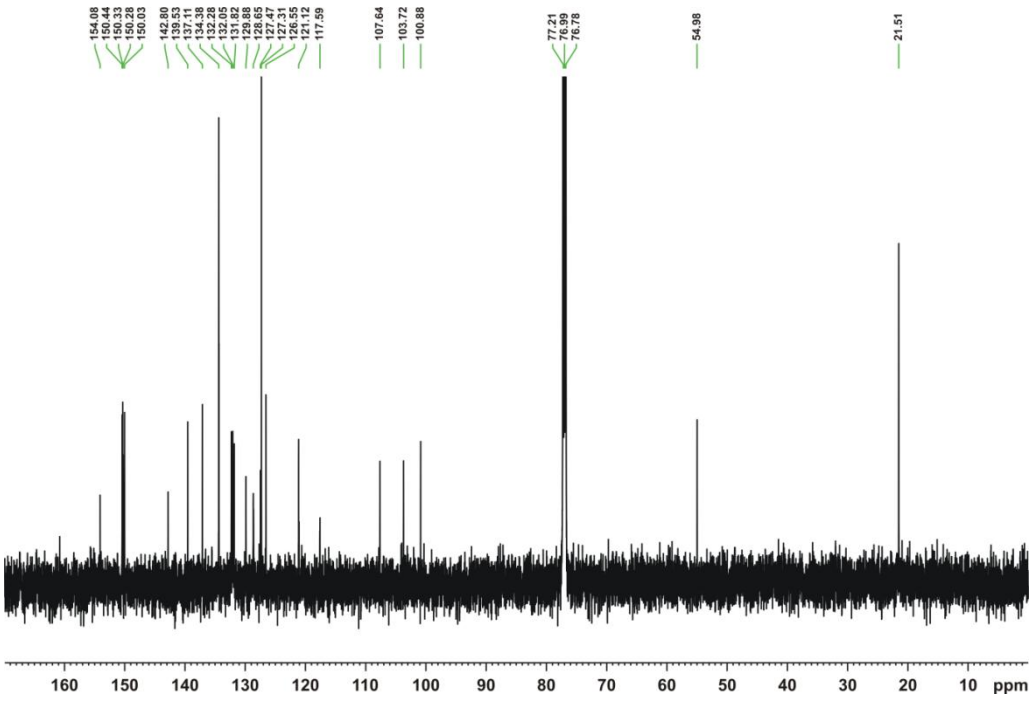


Figure S3. ^{13}C NMR spectrum of **2b** (600 MHz, chloroform-*d*, 300K).

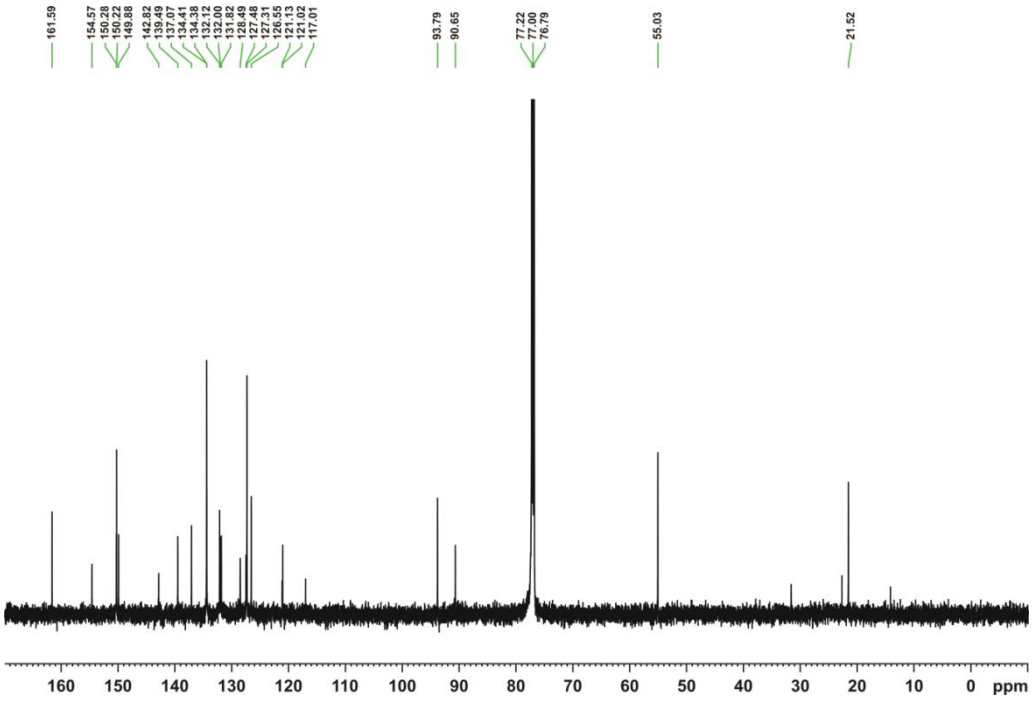


Figure S4. ^{13}C NMR spectrum of **2c** (600 MHz, chloroform-*d*, 300K).

2.2. NMR spectra of 1

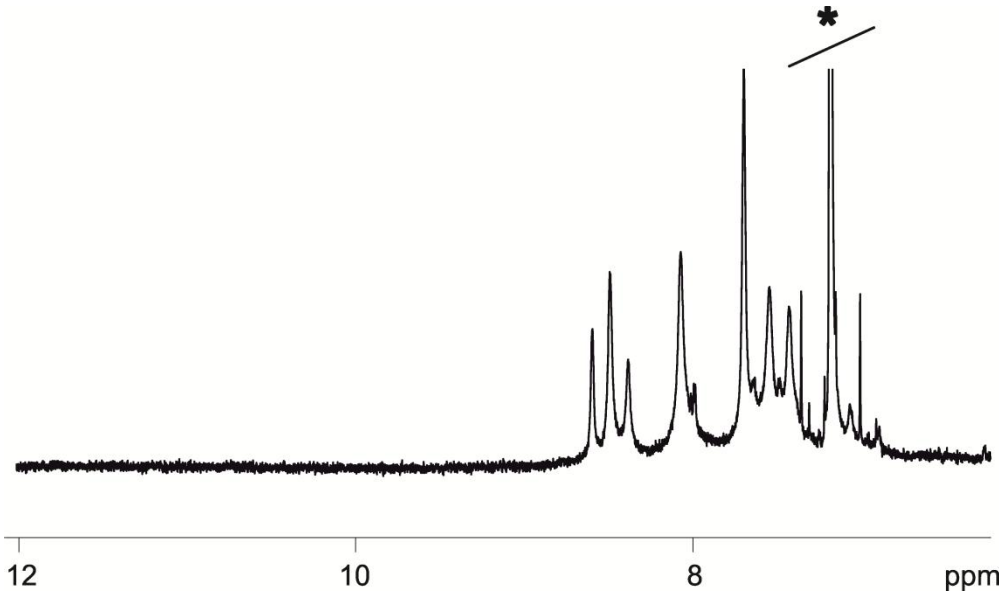


Figure S5. ^{1}H NMR spectrum of **1** (600 MHz, chloroform-*d*, 240K).

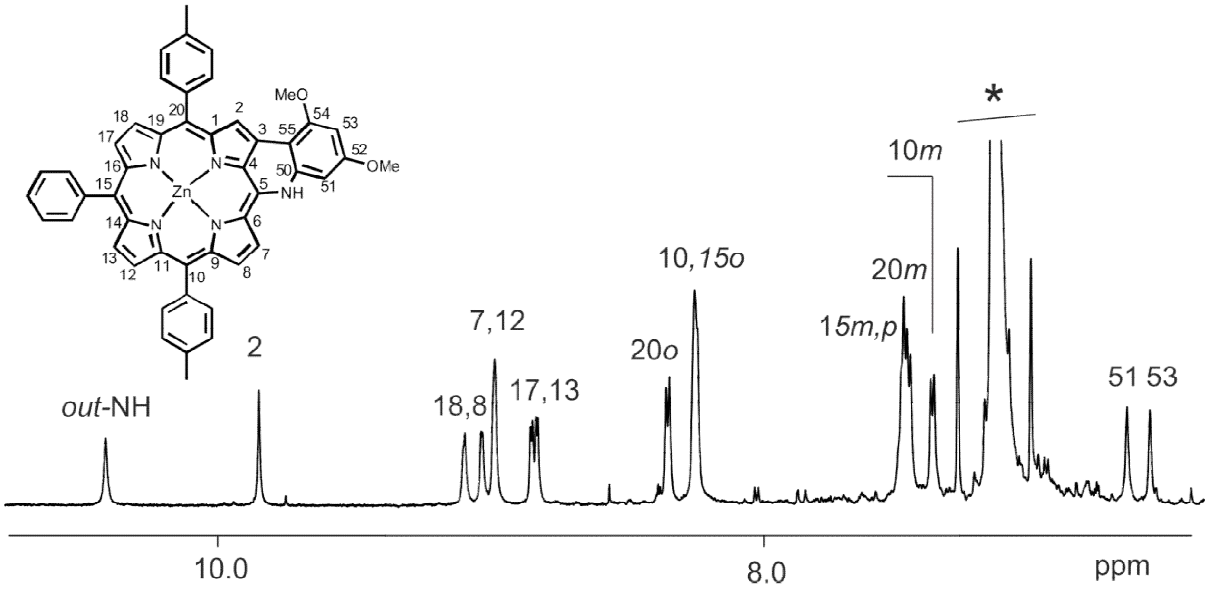


Figure S6. ^{1}H NMR spectrum of **1 (+1%THF)** (600 MHz, benzene-*d*, 300K).

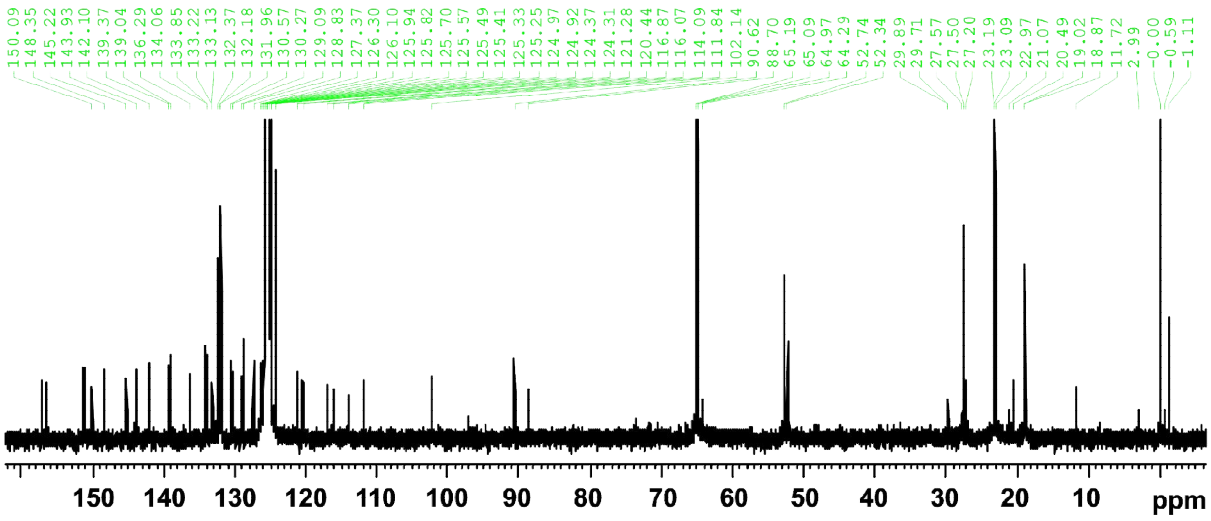


Figure S7. ^{13}C NMR spectrum of **1** (600 MHz, benzene-*d*, 300K).

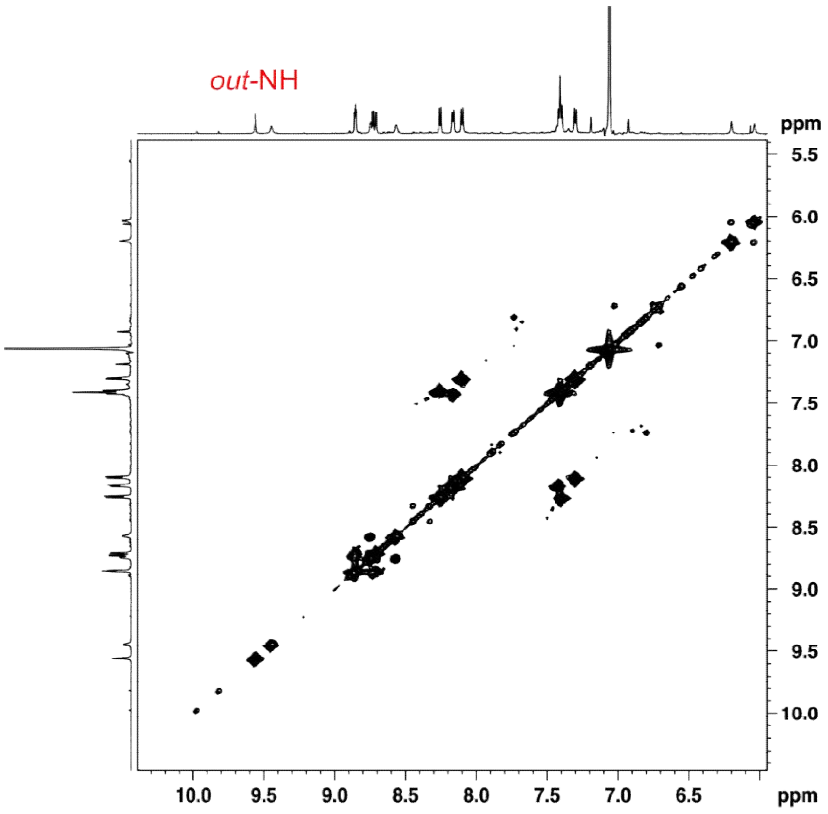


Figure S8. COSY spectrum of **1 (+1%THF)** (600 MHz, benzene-*d*, 300K).

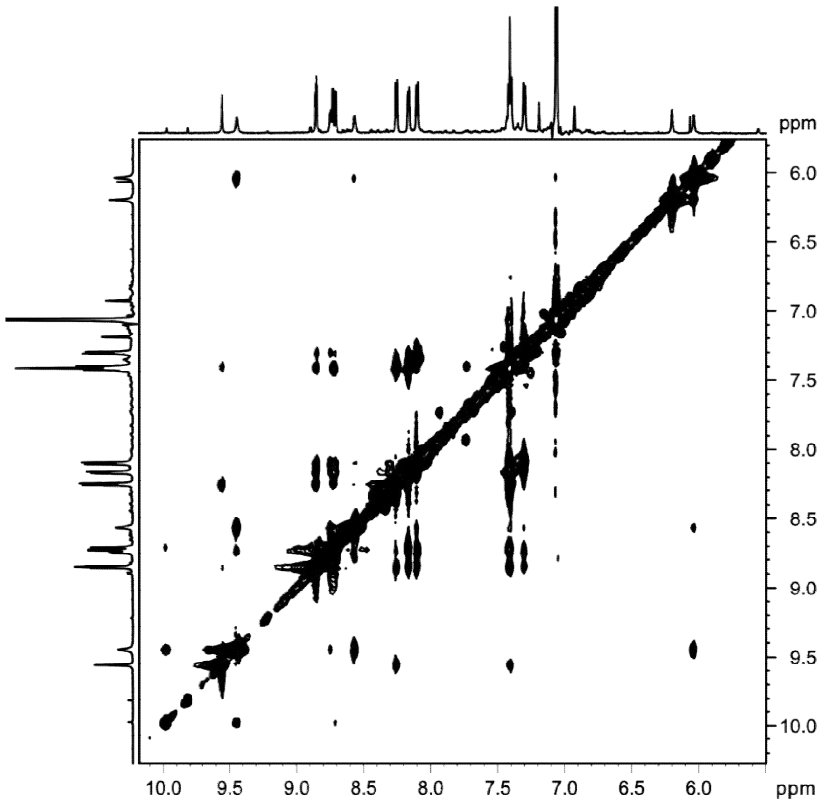


Figure S9. NOESY spectrum of **1 (+1%THF)** (600 MHz, benzene-*d*, 300K).

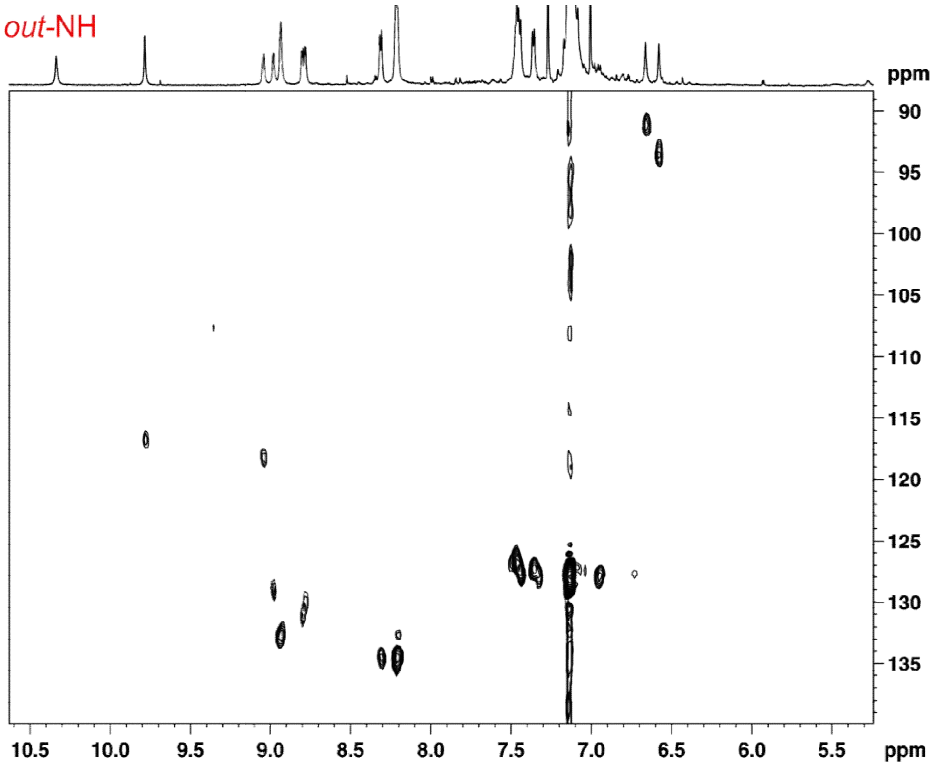


Figure S10. HSQC spectrum of **1 (+1%THF)** (600 MHz, benzene-*d*, 300K).

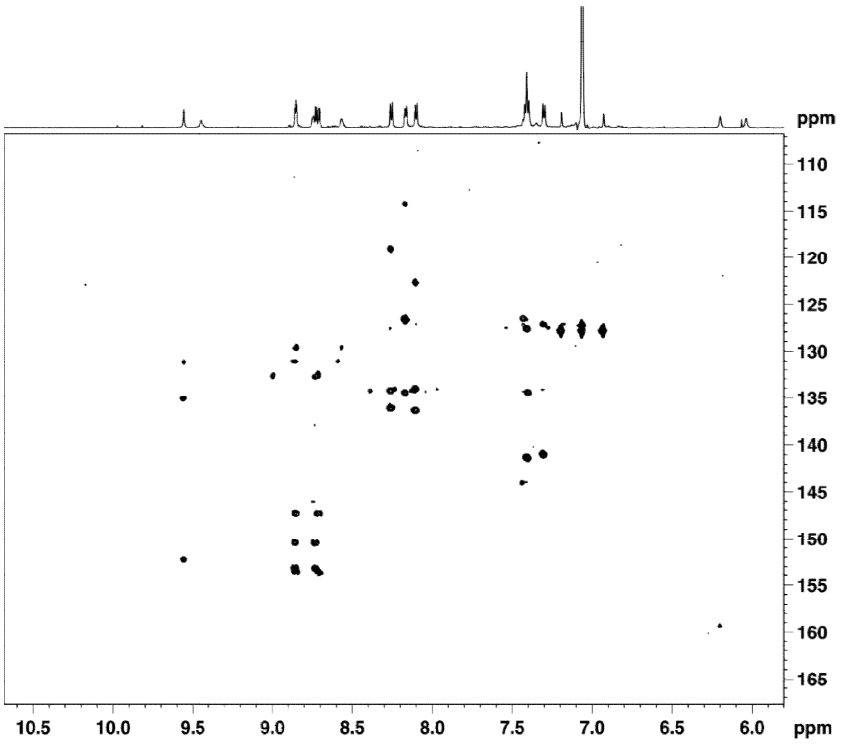


Figure S11. HMBC spectrum of **1 (+1%THF)** (600 MHz, benzene-*d*, 300K).

2.3. NMR spectra of 1(-).

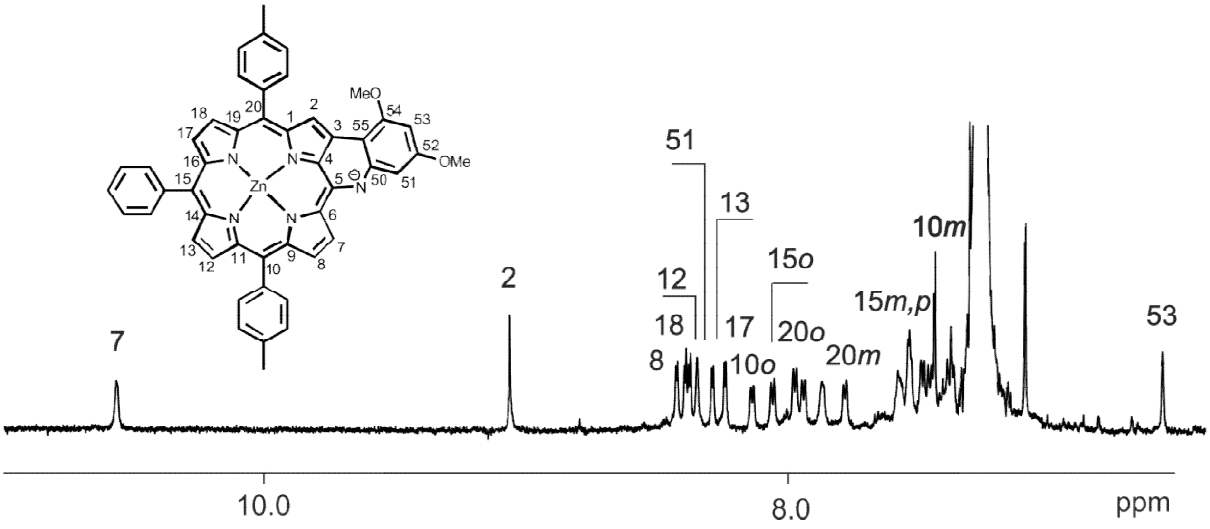


Figure S12. ^{1}H NMR spectrum of **1(-)**(600 MHz, chloroform-*d*, 230K).

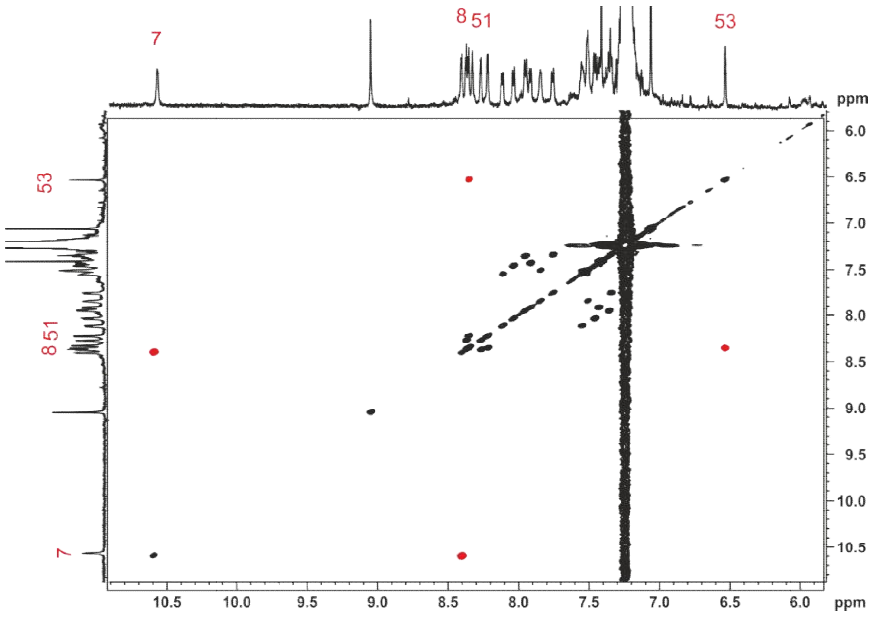


Figure S13. COSY spectrum of **1(-)**(600 MHz, chloroform-*d*, 230K).

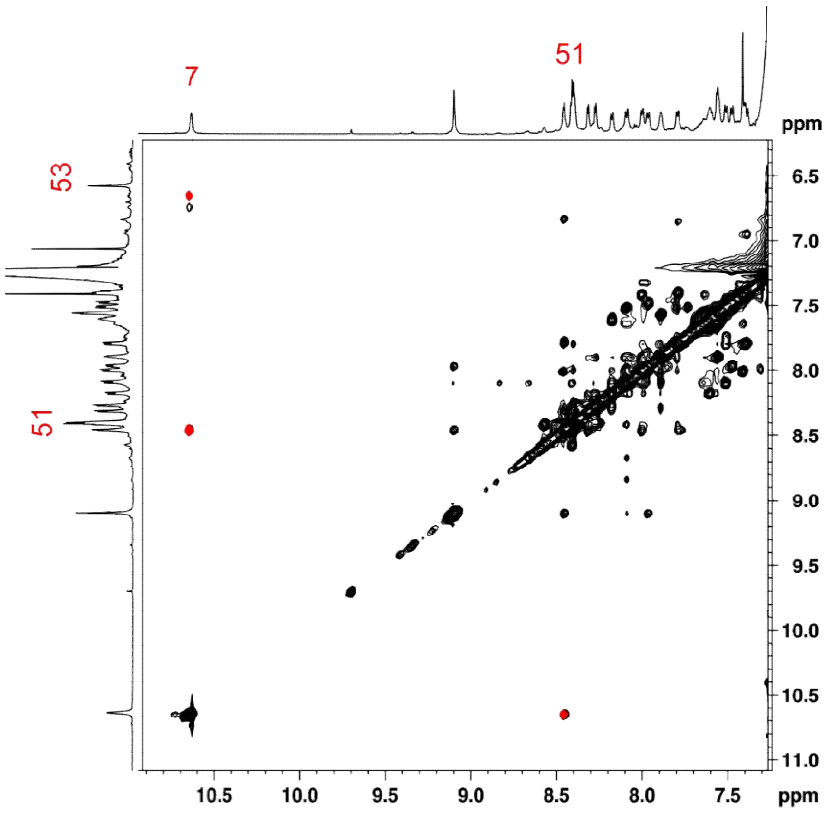


Figure S14. NOESY spectrum of **1(-)**(600 MHz, chloroform-*d*, 220K).

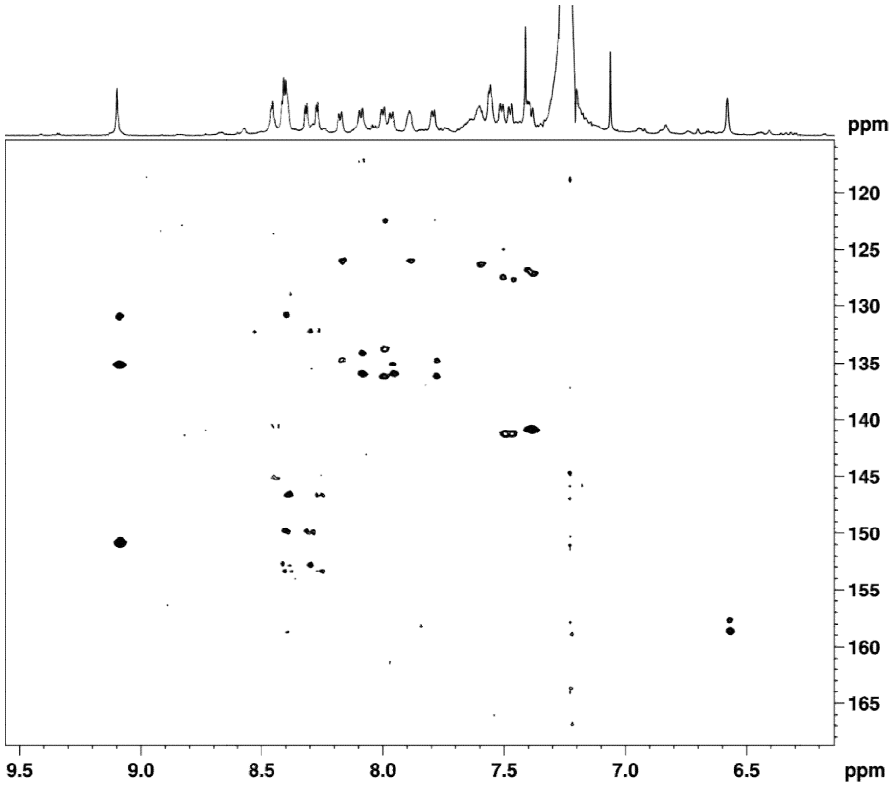


Figure S15. HMBC spectrum of **1(-)**(600 MHz, chloroform-*d*, 220K).

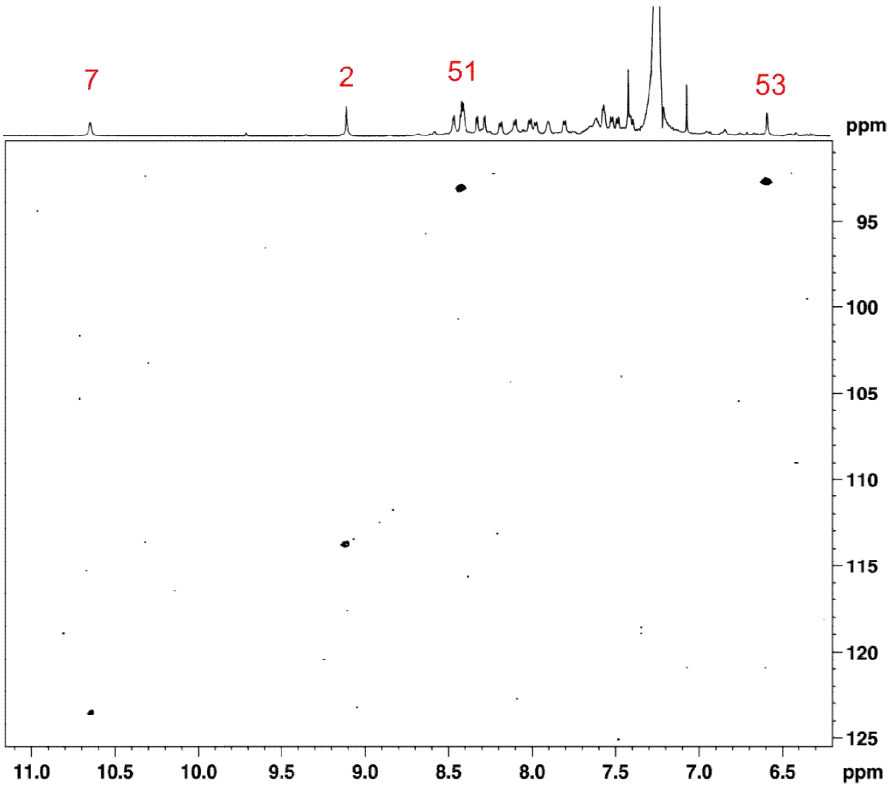


Figure S16. Part of HSQC spectrum of **1(-)**(600 MHz, chloroform-*d*, 220K).

2.4. NMR spectra of 1(+)

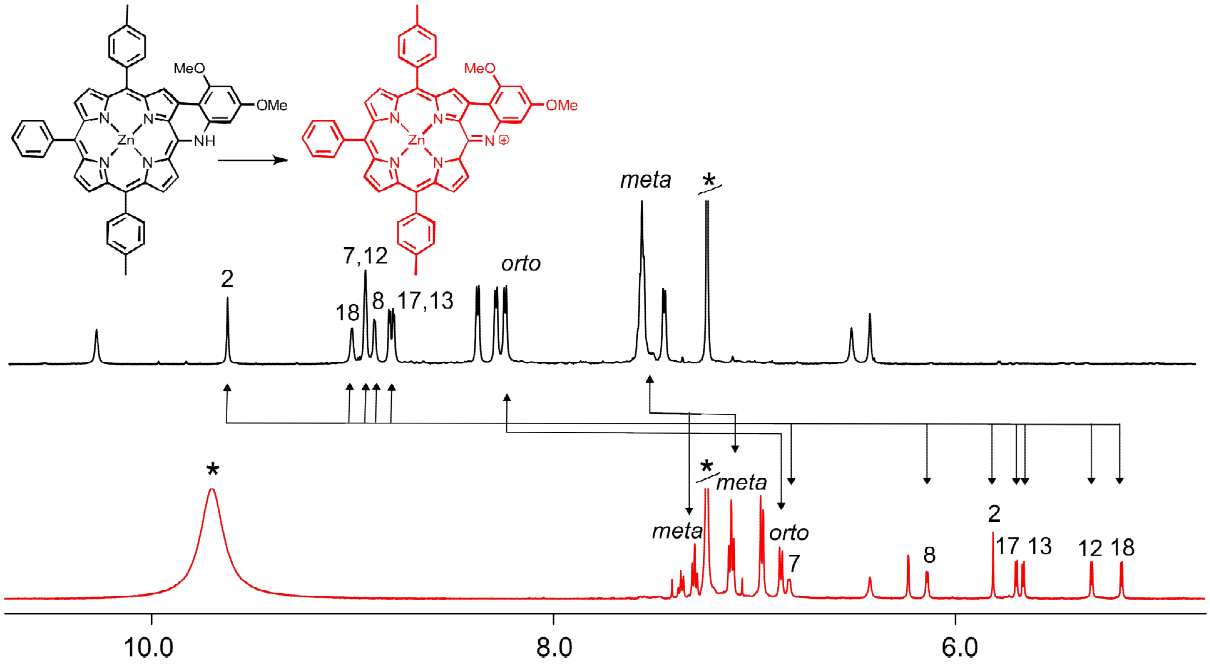


Figure S17. 1H NMR spectra for **1** (black) and **1*(+)*** (red) showing a difference in chemical shifts ($CDCl_3$, VT, 600 MHz).

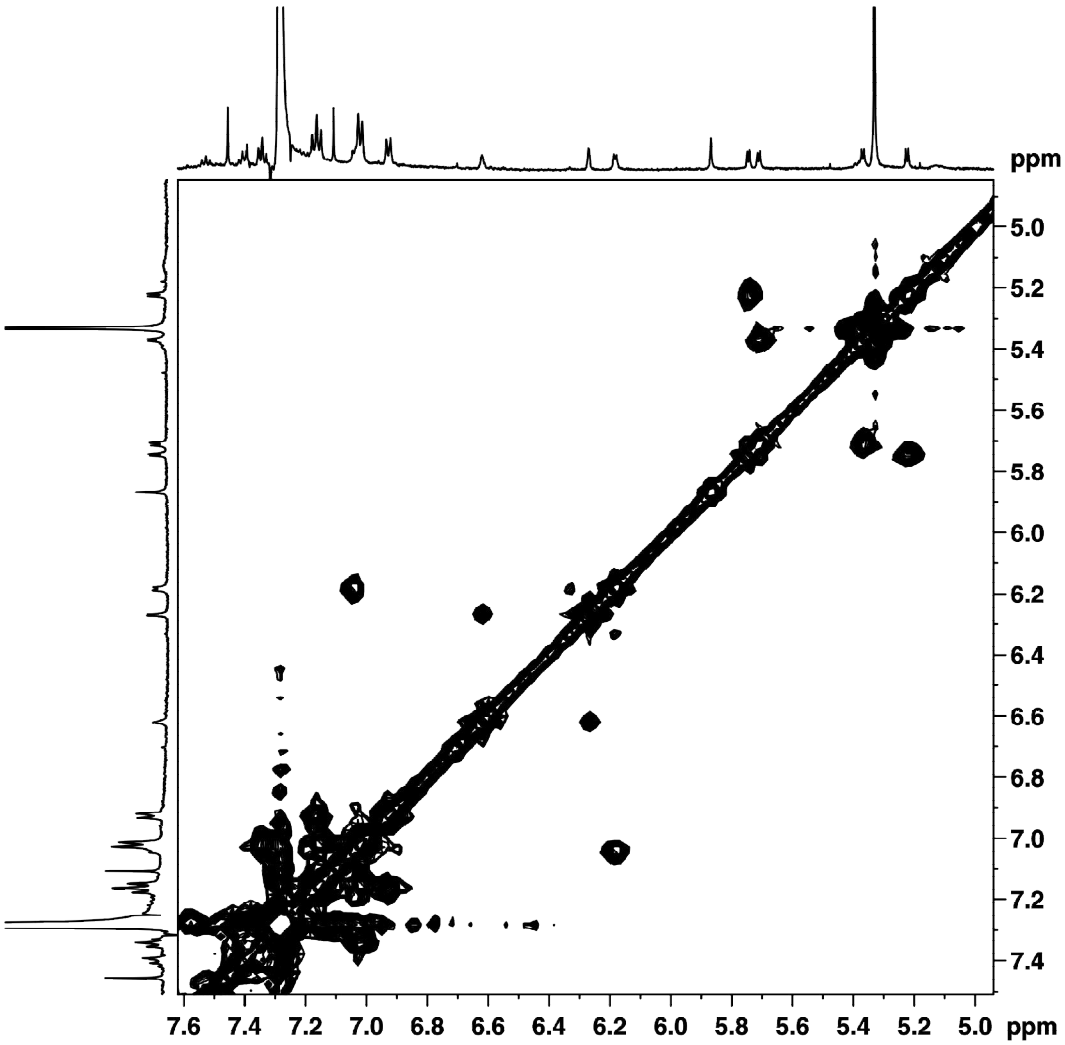


Figure S18. COSY experiment for **1(+)** ($CDCl_3$, 270 K, 600 MHz).

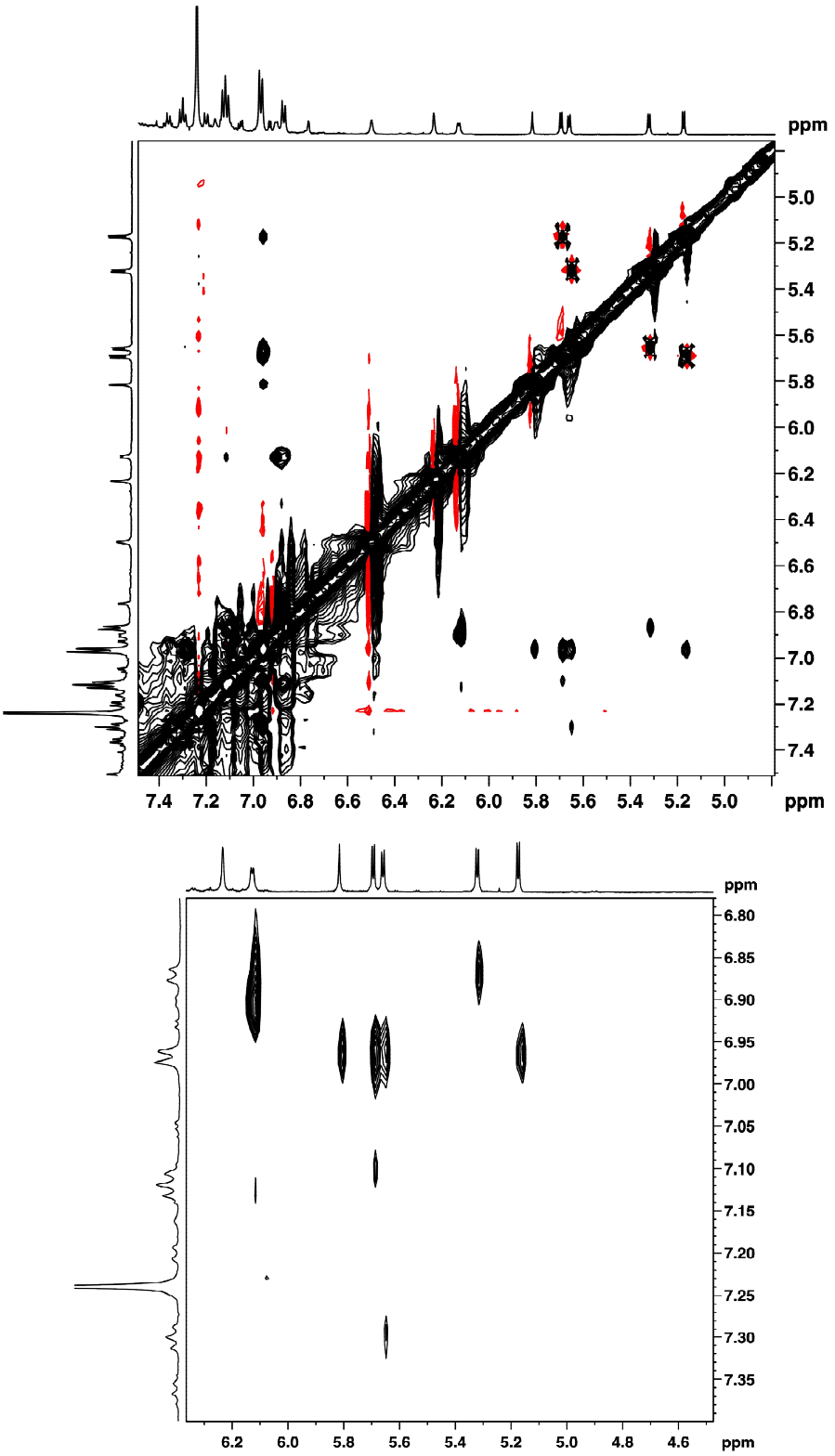


Figure S19. COSY experiment for **1(+)** ($CDCl_3$, 270 K, 600 MHz).

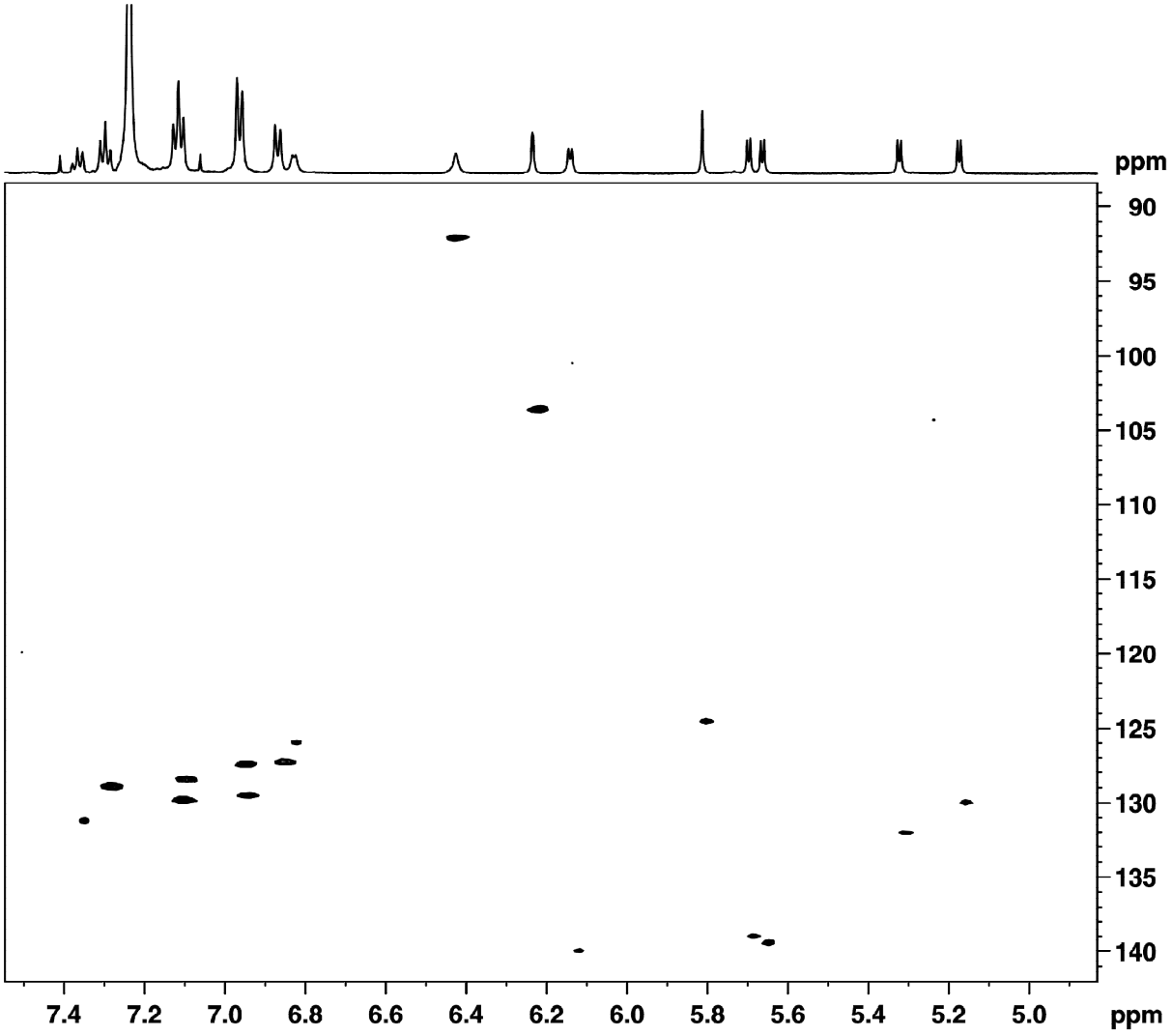


Figure S20. HSQC experiment for **1(+)** ($CDCl_3$, 270 K, 600 MHz).

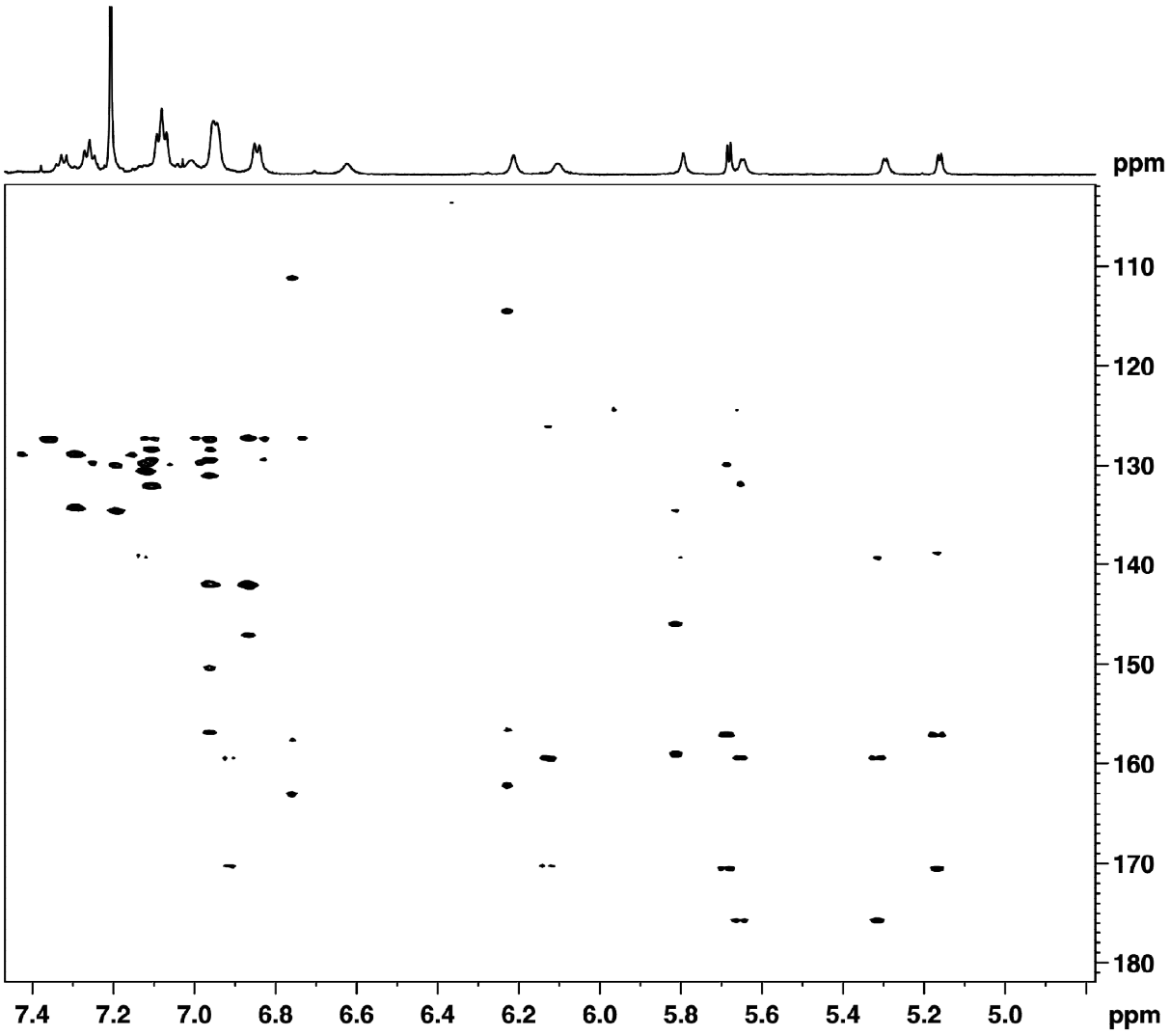


Figure S21. HMBC experiment for **1(+)** ($CDCl_3$, 270 K, 600 MHz).

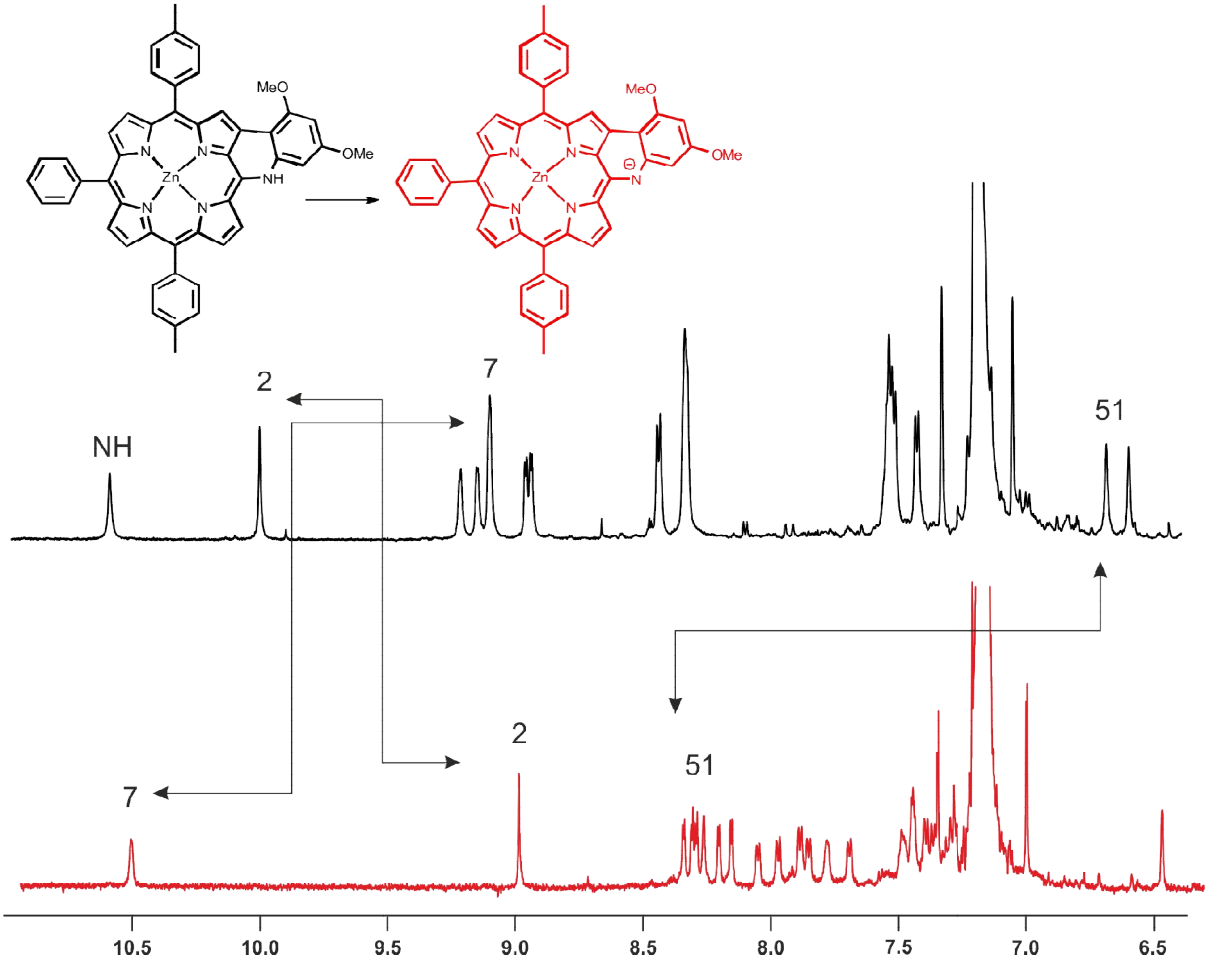


Figure S22. ^{1}H NMR spectrum of titration **1** (600 MHz, chloroform-*d*, 230K, TBAF) with formation of **1*(-)***.

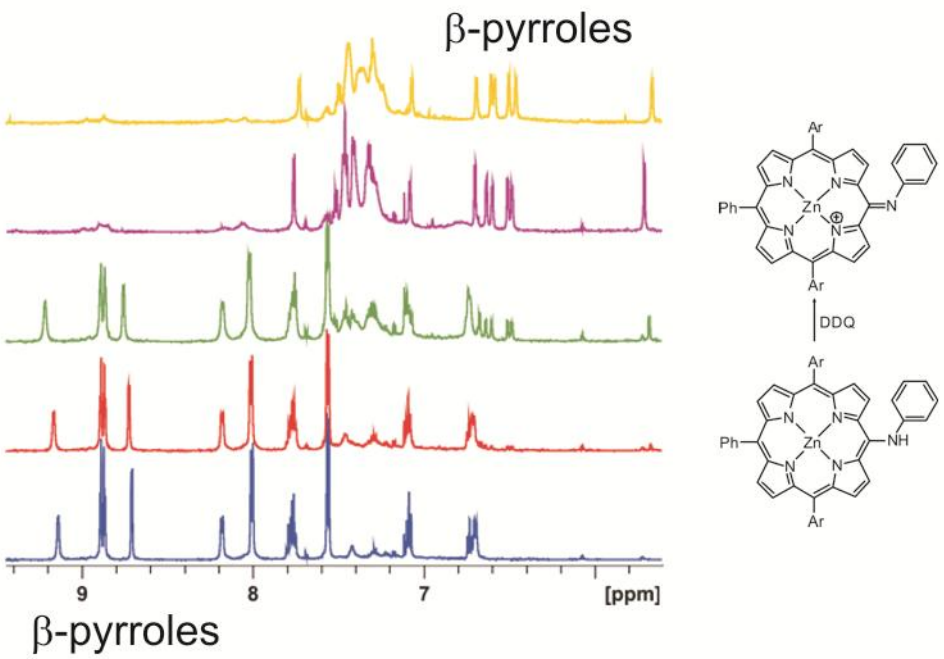


Figure S23. ^{1}H NMR titration of **2a** with DDQ with quantitative formation of **2a*(+)*** (600 MHz, dichloromethane-*d*, 300K).

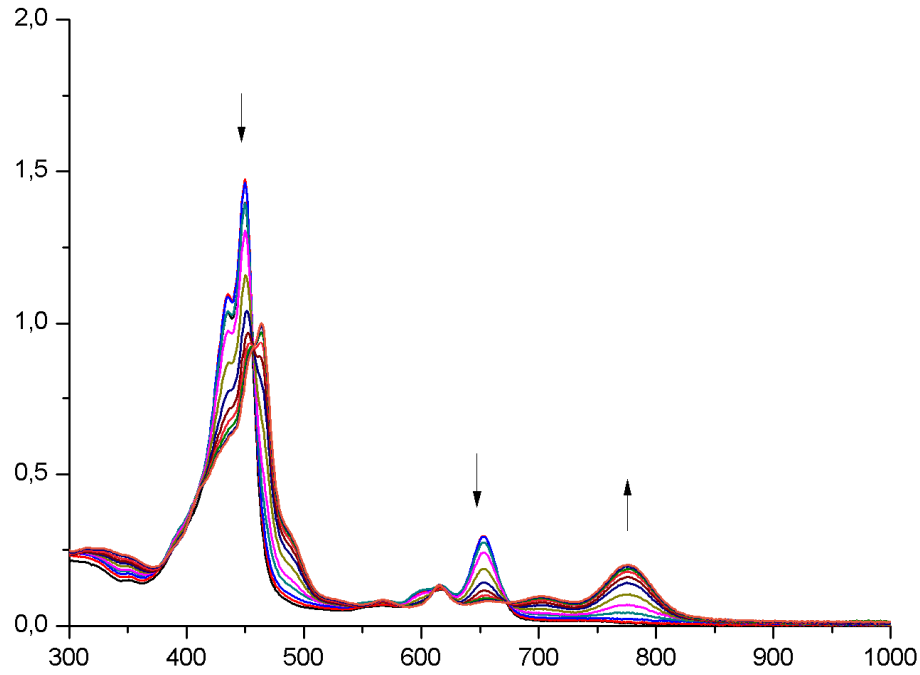


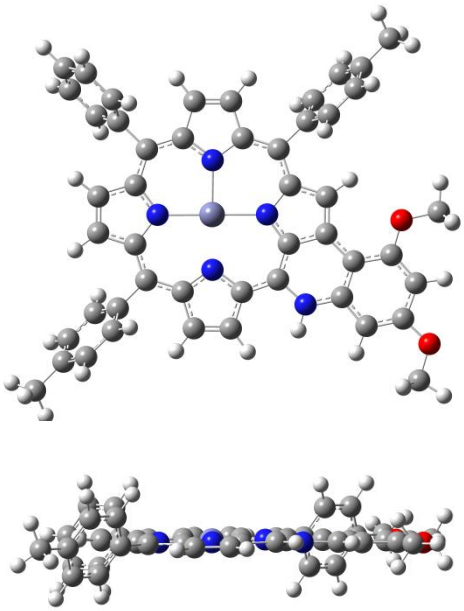
Figure S24. Titration of **1** (TBAF, THF, 300K) with formation of **1*(-)***.

3. Theoretical calculation

3.1 Cartesian coordinates for 1

C	3.44238	0.59867	-0.01530	C	4.16323	5.18706	-1.16647	H	-1.88438	5.32407	-0.00723
C	3.35645	-0.78234	-0.00228	C	4.98917	5.36472	-0.04979	H	0.79009	5.18148	0.00155
C	1.94359	-1.07814	0.01902	C	4.73996	4.57394	1.07957	H	2.12857	-4.33852	0.03211
C	1.47300	-2.39623	0.01206	C	3.70083	3.64520	1.09595	H	7.65078	-2.70457	-0.04064
C	0.11002	-2.78914	-0.01189	C	6.09536	6.39334	-0.05265	H	4.23113	-5.30002	0.01020
C	-0.37778	-4.13001	-0.09033	C	-4.52632	-3.15602	-0.00620	H	2.50018	4.13367	-2.03570
C	-1.74612	-4.05130	-0.09746	C	-5.39478	-3.26841	-1.10237	H	4.33957	5.77906	-2.06146
C	-2.08750	-2.66115	-0.01621	C	-6.43611	-4.19523	-1.10034	H	5.36612	4.68898	1.96131
C	-3.41182	-2.15630	-0.00378	C	-6.64945	-5.04447	-0.00721	H	3.52669	3.04496	1.98400
C	-3.75312	-0.80061	0.01072	C	-5.78343	-4.92984	1.08788	H	5.73978	7.36104	0.32326
C	-5.10339	-0.29464	0.10161	C	-4.73950	-4.00615	1.08975	H	6.93007	6.08643	0.58503
C	-5.02418	1.06265	0.10778	C	-7.76103	-6.06695	-0.01946	H	6.48395	6.56122	-1.06165
C	-3.62261	1.40838	0.02227	C	-4.13539	3.84340	0.04832	H	-5.24799	-2.62198	-1.96240
C	-3.13120	2.73061	0.02350	C	-4.94568	4.10451	-1.06794	H	-7.09358	-4.26024	-1.96403
C	-1.77020	3.07614	0.01142	C	-5.88166	5.13903	-1.04698	H	-5.93255	-5.56764	1.95590
C	-1.26999	4.43637	-0.00141	C	-6.02422	5.93360	0.09177	H	-4.08748	-3.92957	1.95477
C	0.08530	4.36365	-0.00195	C	-5.22527	5.68534	1.20900	H	-7.42208	-7.01792	-0.44960
C	0.44008	2.95815	-0.00754	C	-4.29074	4.64933	1.18709	H	-8.12141	-6.27905	0.99162
C	1.75161	2.47585	-0.00461	O	6.96064	-5.10397	-0.01648	H	-8.61164	-5.72647	-0.61756
C	2.10669	1.10145	0.00908	C	6.50130	-6.44664	-0.00240	H	-4.83234	3.49184	-1.95742
N	1.19644	0.06069	0.02603	O	6.16987	-0.41822	-0.04014	H	-6.49618	5.32700	-1.92295
N	-0.93852	-1.90244	0.02776	C	7.57002	-0.18023	-0.05788	H	-6.75221	6.73954	0.10840
N	-2.86593	0.26297	-0.02716	H	4.33761	1.19406	-0.04625	H	-5.33193	6.29536	2.10162
N	-0.71407	2.19565	0.00289	H	0.20417	-5.04092	-0.15445	H	-3.67523	4.45389	2.06019
N	2.44482	-3.38202	0.01244	H	-2.44877	-4.86773	-0.16550	H	7.39553	-7.07118	-0.00624
C	3.81116	-3.18021	0.00067	H	-5.99201	-0.90374	0.17096	H	5.91359	-6.66253	0.89892
C	4.31302	-1.85988	-0.01157	H	-5.83578	1.77076	0.18017	H	5.89686	-6.67560	-0.88931
C	5.72795	-1.70450	-0.02777					H	7.68764	0.90387	-0.06651
C	6.57413	-2.80280	-0.02895					H	8.05843	-0.59275	0.83336
C	6.03343	-4.10430	-0.01413					H	8.03775	-0.60432	-0.95468
C	4.66137	-4.30595	0.00069					Zn	-0.84320	0.16429	0.00872
C	2.86930	3.47274	-0.02094								
C	3.12214	4.25938	-1.15438								

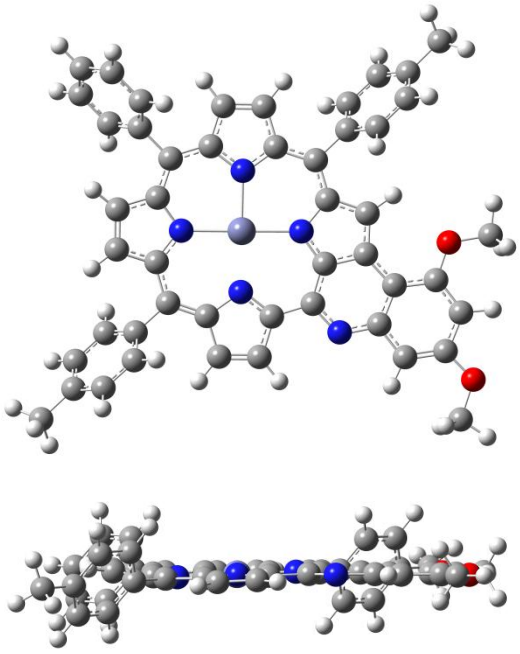
3.2. Optimized geometry of 1



3.3Cartesian coordinates for 1(+)

C	-3.46668	0.58595	0.03414	C	-4.52466	-4.36493	-0.03219	H	5.78117	1.78753	-0.36988
C	-3.35410	-0.79999	-0.00837	C	-2.91877	3.46180	0.05908	H	1.83926	5.34253	0.09151
C	-1.94760	-1.06573	-0.05071	C	-3.08042	4.34642	1.13980	H	-0.83572	5.19626	0.07803
C	-1.49331	-2.41443	-0.05507	C	-4.13354	5.25549	1.15906	H	-7.55995	-2.86784	0.04287
C	-0.09043	-2.78565	-0.03643	C	-5.04759	5.33446	0.09756	H	-4.03475	-5.32845	-0.05287
C	0.37794	-4.14704	0.05687	C	-4.87883	4.45430	-0.97969	H	-2.39407	4.29901	1.97947
C	1.73401	-4.07902	0.09505	C	-3.84028	3.52673	-0.99965	H	-4.25095	5.91398	2.01535
C	2.09585	-2.67618	0.00451	C	-6.16038	6.35251	0.10690	H	-5.56922	4.49667	-1.81765
C	3.38284	-2.17196	0.01004	C	4.52198	-3.13254	0.03301	H	-3.72611	2.86184	-1.84982
C	3.71309	-0.76613	-0.02815	C	5.44921	-3.12132	1.08889	H	-5.80560	7.32173	-0.26422
C	5.05228	-0.27670	-0.20848	C	6.50534	-4.02711	1.11426	H	-6.99220	6.04371	-0.53163
C	4.97539	1.08520	-0.22418	C	6.68657	-4.96352	0.08549	H	-6.54590	6.51500	1.11749
C	3.58879	1.42991	-0.04966	C	5.76767	-4.96126	-0.97225	H	5.33081	-2.41038	1.90103
C	3.09553	2.74206	-0.04062	C	4.69860	-4.06832	-0.99898	H	7.20206	-4.00821	1.94786
C	1.71790	3.10367	0.00537	C	7.82285	-5.95464	0.12904	H	5.89289	-5.66439	-1.79104
C	1.23052	4.45269	0.06110	C	4.08987	3.85250	-0.08860	H	4.00933	-4.07689	-1.83776
C	-0.13445	4.37693	0.06771	C	5.02857	4.01333	0.94472	H	7.52954	-6.86054	0.67352
C	-0.47493	2.98198	0.04953	C	5.95369	5.05550	0.90225	H	8.12546	-6.26203	-0.87553
C	-1.80451	2.47642	0.03512	C	5.96598	5.93924	-0.17815	H	8.69718	-5.53943	0.63789
C	-2.13559	1.10838	-0.00877	C	5.04296	5.78251	-1.21438	H	5.01588	3.33187	1.78952
N	-1.21134	0.07093	-0.05353	C	4.10471	4.75323	-1.16759	H	6.66347	5.17694	1.71452
N	0.92397	-1.90790	-0.06806	O	-6.79906	-5.22990	-0.00861	H	6.69103	6.74629	-0.21284
N	2.83229	0.26842	0.05591	C	-6.30766	-6.56815	-0.03793	H	5.05420	6.46093	-2.06169
N	0.67078	2.22025	0.00661	O	-6.17764	-0.51993	0.05463	H	3.39360	4.63012	-1.97837
N	-2.35523	-3.42470	-0.04543	C	-7.59251	-0.33391	0.08255	H	-7.18939	-7.20842	-0.03443
C	-3.70319	-3.20846	-0.02935	H	-4.37260	1.16178	0.10830	H	-5.72255	-6.75651	-0.94555
C	-4.27293	-1.89778	-0.00212	H	-0.26529	-5.01144	0.10355	H	-5.69450	-6.78548	0.84435
C	-5.68657	-1.78499	0.02622	H	2.43434	-4.89423	0.19209	H	-7.74877	0.74445	0.10183
C	-6.47941	-2.92468	0.02229	H	5.93103	-0.88895	-0.33463	H	-8.06606	-0.75546	-0.81108
C	-5.90102	-4.21656	-0.00791					H	-8.03434	-0.78207	0.97939
								Zn	0.79901	0.16395	-0.00447

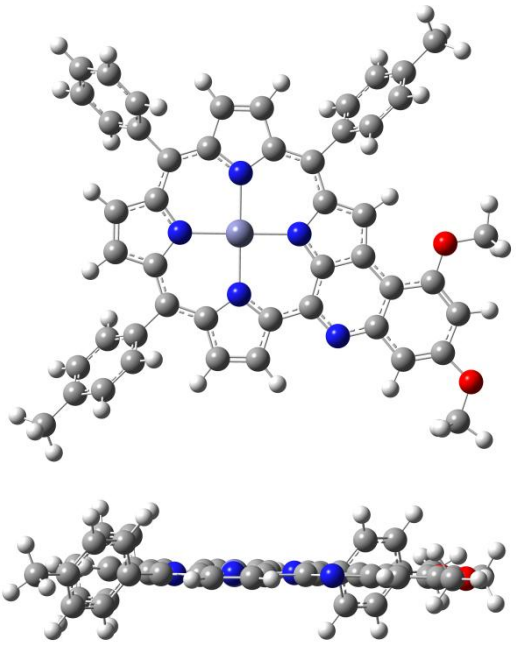
3.4. Optimized geometry of 1(+)



3.5 Cartesian coordinates for 1(-)

C	3.46178	0.60244	-0.02120	C	5.96623	-4.16123	-0.02363	H	-5.82554	1.76246	0.19783
C	3.37069	-0.79201	-0.00835	C	4.60096	-4.33393	-0.00985	H	-1.86120	5.33193	-0.02191
C	1.96693	-1.08480	0.01452	C	2.88249	3.47544	-0.02075	H	0.80719	5.18483	-0.00836
C	1.52371	-2.43580	0.01002	C	3.11360	4.30307	-1.12976	H	7.62000	-2.79167	-0.04605
C	0.12346	-2.79090	-0.00513	C	4.15172	5.23545	-1.13195	H	4.12744	-5.30696	-0.00199
C	-0.35225	-4.13058	-0.06957	C	5.00154	5.37592	-0.02920	H	2.47330	4.20430	-2.00115
C	-1.72393	-4.06091	-0.08151	C	4.77875	4.54342	1.07584	H	4.30802	5.85870	-2.01015
C	-2.07416	-2.67289	-0.01389	C	3.74234	3.61227	1.08115	H	5.42624	4.62630	1.94653
C	-3.39044	-2.16010	-0.00733	C	6.10774	6.40555	-0.01838	H	3.59202	2.97390	1.94616
C	-3.73983	-0.80317	0.00122	C	-4.50840	-3.15597	-0.00264	H	5.78744	7.33659	0.46782
C	-5.08457	-0.30167	0.10480	C	-5.39880	-3.25509	-1.08266	H	6.98638	6.04485	0.52687
C	-5.00957	1.06032	0.11184	C	-6.44486	-4.17745	-1.07312	H	6.42465	6.66327	-1.03395
C	-3.61313	1.41046	0.01181	C	-6.64151	-5.03910	0.01253	H	-5.26410	-2.59736	-1.93583
C	-3.11995	2.73785	0.01465	C	-5.75444	-4.94074	1.09223	H	-7.11833	-4.23009	-1.92615
C	-1.75736	3.08104	0.00583	C	-4.70750	-4.02050	1.08540	H	-5.88859	-5.59032	1.95478
C	-1.25205	4.44018	-0.01118	C	-7.75550	-6.06021	0.00825	H	-4.03455	-3.95865	1.93497
C	0.10409	4.36489	-0.01168	C	-4.12262	3.84764	0.04138	H	-7.41787	-7.02217	-0.39939
C	0.45991	2.96097	-0.01740	C	-5.00693	4.05364	-1.03210	H	-8.12739	-6.25227	1.02003
C	1.76728	2.47721	-0.01074	C	-5.94463	5.08636	-1.00950	H	-8.60042	-5.72875	-0.60387
C	2.13620	1.09980	0.00577	C	-6.01860	5.94614	0.08822	H	-4.94708	3.39285	-1.89172
N	1.21958	0.05483	0.02422	C	-5.14795	5.75814	1.16308	H	-6.61354	5.22457	-1.85537
N	-0.91808	-1.90701	0.02480	C	-4.21616	4.71972	1.14004	H	-6.74677	6.75281	0.10579
N	-2.85404	0.26710	-0.04436	O	6.89023	-5.18566	-0.02775	H	-5.19898	6.41636	2.02689
N	-0.70212	2.19960	-0.00481	C	6.38799	-6.50615	-0.01676	H	-3.54791	4.57069	1.98282
N	2.39991	-3.45166	0.00296	O	6.19247	-0.46971	-0.04154	H	7.25890	-7.16626	-0.02140
C	3.73506	-3.19932	-0.00671	C	7.59068	-0.27690	-0.05797	H	5.78672	-6.70741	0.88036
C	4.29697	-1.88221	-0.01661	H	4.36074	1.19283	-0.05860	H	5.77063	-6.71619	-0.90085
C	5.71431	-1.75707	-0.03205	H	0.28855	-4.99809	-0.10907	H	7.74827	0.80369	-0.06448
C	6.54082	-2.86723	-0.03518	H	-2.42365	-4.88168	-0.14341	H	8.07342	-0.70694	0.83061
				H	-5.97330	-0.91024	0.18548	H	8.05349	-0.71438	-0.95341
								Zn	-0.81410	0.15498	0.00081

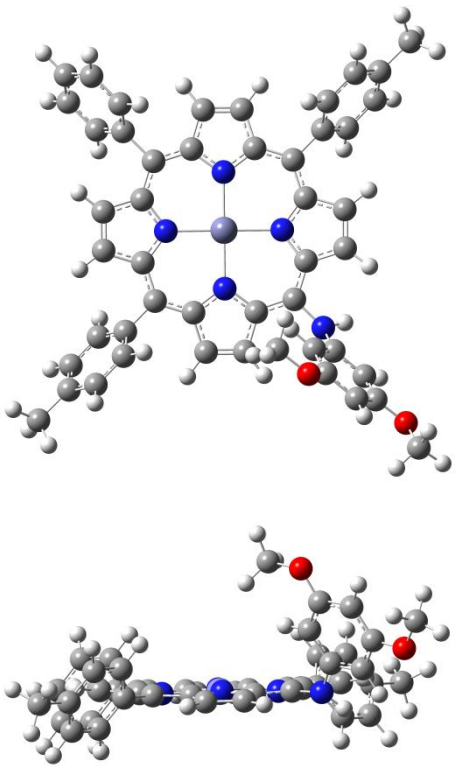
3.6. Optimized geometry of 1(-)



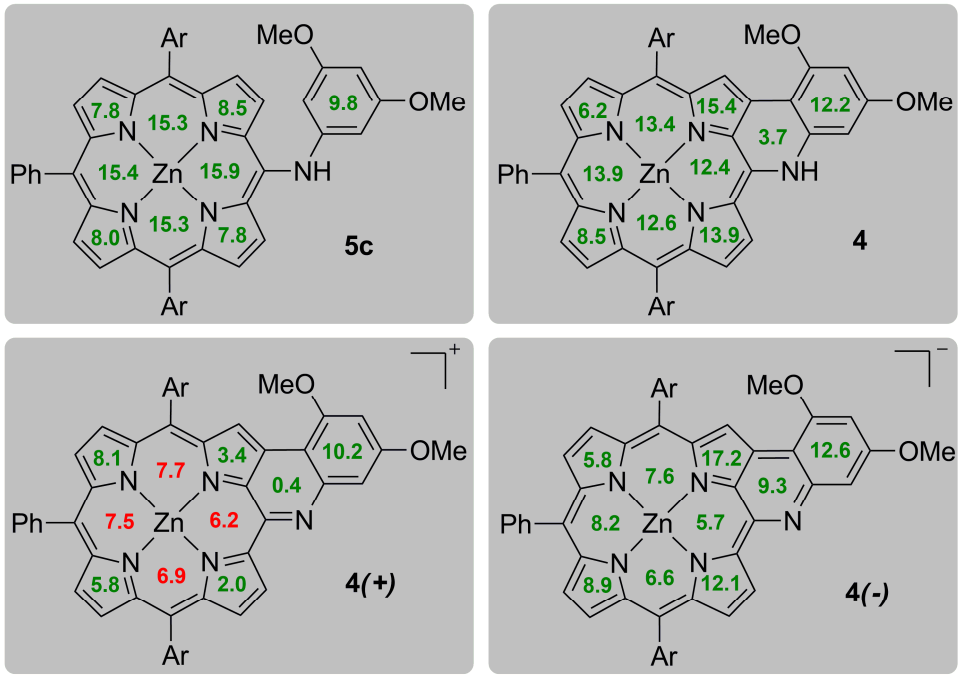
3.7 Cartesian coordinates for 2c

C	-2.90262	2.23445	-1.06452	C	-1.34288	4.63837	-0.45598	H	-3.47310	-2.68159	-1.86853
C	-3.33812	0.95384	-1.22120	C	-0.95996	5.58560	-1.41820	H	-7.76139	-2.17204	1.95189
C	-2.22881	0.09638	-0.89488	C	-1.56309	6.84125	-1.46778	H	-0.19218	5.32660	-2.14100
C	-2.27846	-1.30880	-0.91795	C	-2.56639	7.20104	-0.55915	H	-1.25391	7.55137	-2.23092
C	-1.17584	-2.16233	-0.73103	C	-2.95073	6.25387	0.39890	H	-3.72848	6.50451	1.11626
C	-1.25870	-3.59878	-0.67723	C	-2.35200	4.99663	0.45148	H	-2.66402	4.28093	1.20610
C	0.01377	-4.06163	-0.52069	C	-3.19609	8.57315	-0.59437	H	-4.24119	8.54297	-0.27169
C	0.88059	-2.90886	-0.46946	C	2.91572	-4.31983	-0.25365	H	-2.67080	9.26794	0.07303
C	2.27549	-2.96756	-0.27566	C	2.92116	-5.13567	-1.39570	H	-3.16396	9.00257	-1.60004
C	3.10173	-1.84521	-0.09267	C	3.52167	-6.39321	-1.37502	H	2.46135	-4.77160	-2.30962
C	4.54052	-1.90037	0.02653	C	4.13367	-6.88652	-0.21543	H	3.52033	-6.99924	-2.27779
C	4.97692	-0.62294	0.19249	C	4.12862	-6.07115	0.92347	H	4.59614	-6.42759	1.83814
C	3.81013	0.22924	0.17502	C	3.53147	-4.81178	0.90735	H	3.53620	-4.20033	1.80466
C	3.84653	1.62956	0.30916	C	4.75511	-8.26266	-0.18740	H	5.57016	-8.31960	0.54017
C	2.72661	2.47476	0.19995	C	5.17396	2.26722	0.58221	H	4.01740	-9.02583	0.09093
C	2.75603	3.90191	0.42198	C	5.85037	2.03281	1.78997	H	5.15494	-8.54145	-1.16698
C	1.49144	4.36254	0.22388	C	7.08651	2.62781	2.04336	H	5.39565	1.38560	2.53385
C	0.67387	3.22299	-0.12168	C	7.66972	3.46733	1.09288	H	7.59156	2.43859	2.98630
C	-0.70286	3.28725	-0.40404	C	7.00831	3.70840	-0.11242	H	8.63229	3.93011	1.29010
C	-1.52066	2.16640	-0.64688	C	5.77164	3.11426	-0.36466	H	7.45672	4.35619	-0.86025
N	-1.12779	0.84939	-0.55714	O	-5.86558	-0.86808	2.94346	H	5.26195	3.29801	-1.30563
N	0.13298	-1.75996	-0.59391	C	-4.75790	-0.13068	3.43658	H	-5.06034	0.24770	4.41433
N	2.68017	-0.53481	-0.01226	O	-7.93874	-3.46625	-0.47666	H	-3.86939	-0.76389	3.55408
N	1.44544	2.08081	-0.11571	C	-9.11646	-3.58422	0.30503	H	-4.50955	0.71368	2.78147
N	-3.52539	-1.91201	-1.21726	H	-3.45591	3.14477	-1.23879	H	-9.81243	-4.18052	-0.28718
C	-4.63598	-1.97244	-0.35851	H	-2.16819	-4.18151	-0.71088	H	-8.92210	-4.09509	1.25664
C	-5.76538	-2.67198	-0.79031	H	0.33446	-5.08730	-0.41926	H	-9.56558	-2.60455	0.51192
C	-6.89172	-2.75500	0.03871	H	5.13553	-2.79928	-0.02858	H	-4.31137	0.61303	-1.54024
C	-6.90879	-2.13680	1.28789	H	5.99563	-0.28226	0.29886	H	-3.74221	-0.82832	1.23690
C	-5.76578	-1.43604	1.70464	H	3.62814	4.46996	0.70815	H	-5.79545	-3.14858	-1.76466
C	-4.62744	-1.35009	0.90421	H	1.13615	5.37724	0.31975	Zn	0.78680	0.16114	-0.32424

3.8. Optimized geometry of 2c

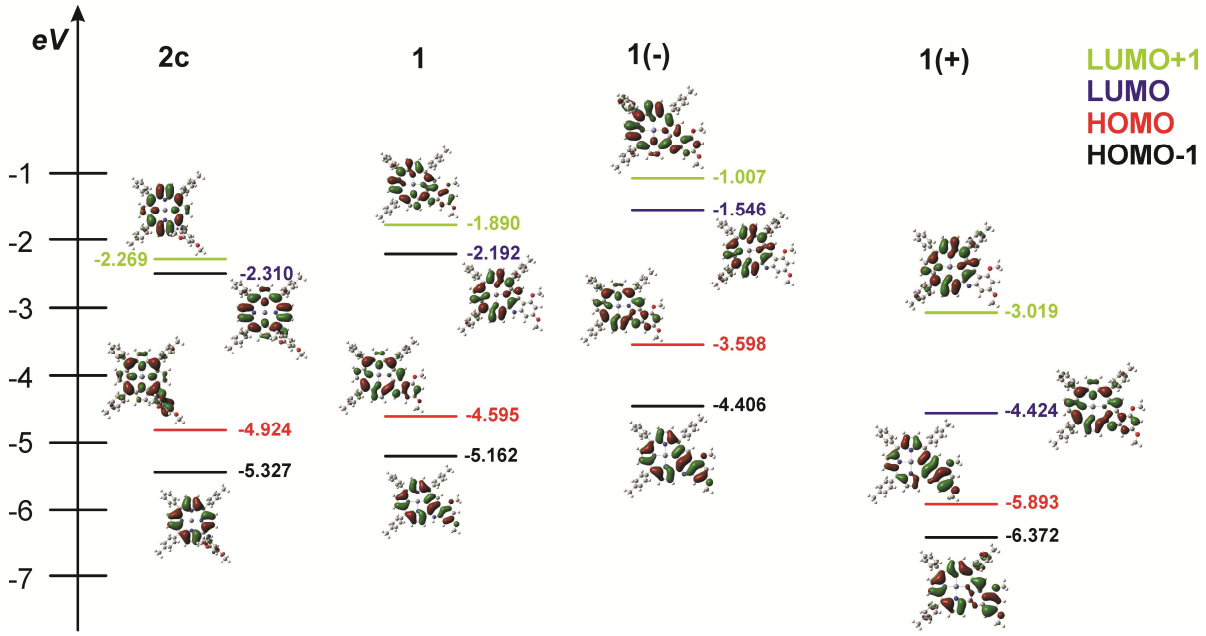


3.9. NICS values observed for 2c, 1, 1(-) and 1(+)



positive
negative

3.10. Frontier orbitals 2c, 1, 1(-) and 1(+)



3.11. Decay profiles for 2c, 1 and 1(-)

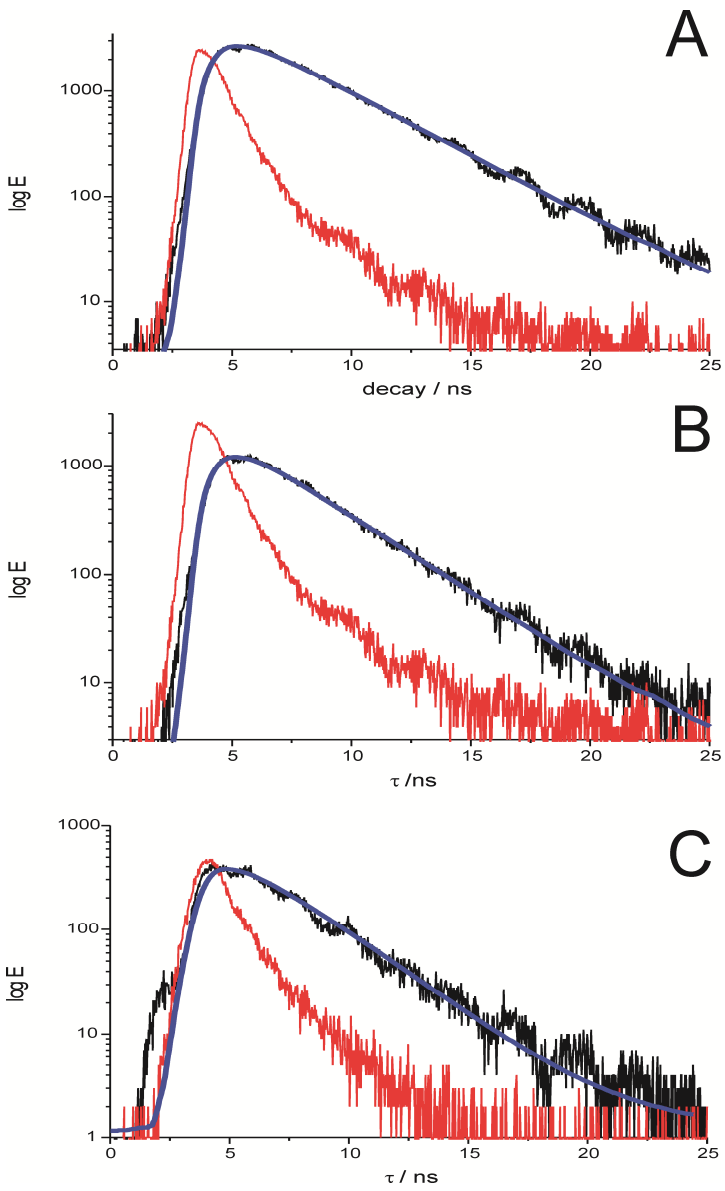


Figure S25. Decay profiles for **2c** (A), **1** (B) and **1*(-)*** (C) in chloroform solutions. Red – IRF, black – decay, blue – fitting curve.