Electronic Supplementary Material (ESI) for Dalton Transactions

Stable Core-modified Calixsmaragdyrins:

Synthesis, Structure and Specific Sensing of Hydrogen Sulfate Ion

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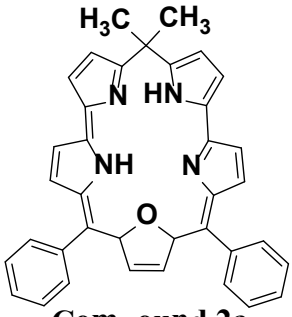


Compound 2a

Mol. Wt. = 544.22

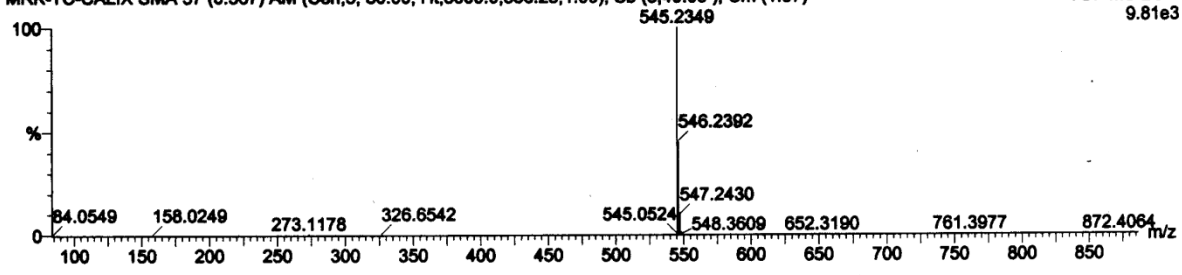
Peak at $[M+1]^+$ = 545.23

Elemental Composition Report

Single Mass Analysis (displaying only valid results)
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 200.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

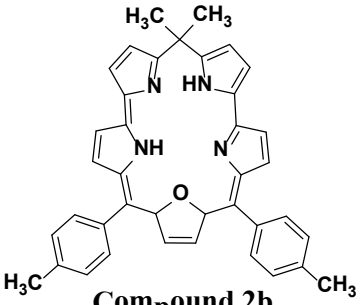
Monoisotopic Mass, Odd and Even Electron Ions
2 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Micromass : Q-Tof micro (YA-105) Dept. Of Chemistry I.I.T.(B) 23-May-201215:16:54
C37H30N4O
MRK-TC-CALIX SMA 57 (0.567) AM (Cen,5, 80.00, Ht,5000.0,556.28,1.00); Sb (5,40.00); Cm (1:57) TOF MS ES+
9.81e3



Minimum:				-1.5		
Maximum:		200.0	10.0	200.0		
Mass	**Calc. Mass**	**mDa**	**PPM**	**DBE**	**Score**	**Formula**
545.2349	545.2341	0.8	1.4	25.5	1	C37 H29 N4 O

Figure S1. HR-MS spectrum of compound **2a**

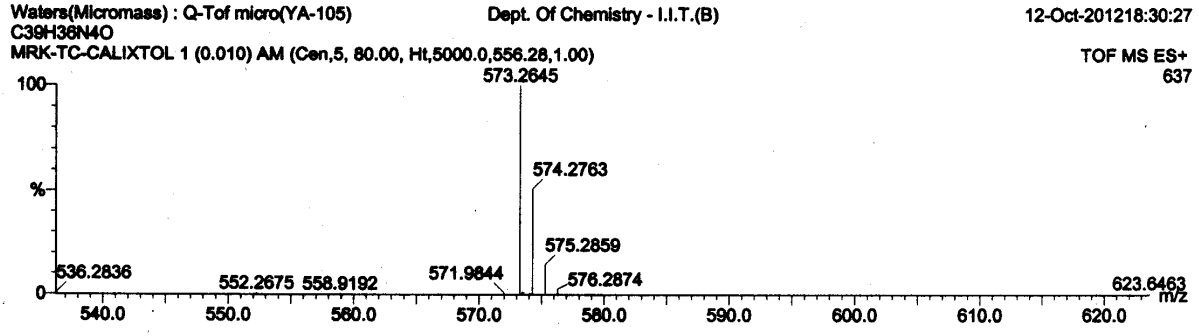


Compound 2b
Mol. Wt. = 572.25
Peak at $[M+1]^+$= 573.26

Elemental Composition Report

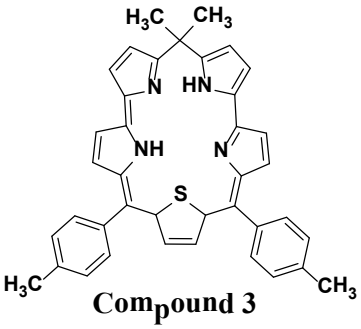
Single Mass Analysis (displaying only valid results)
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 200.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
2 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)



Minimum:				-1.5		
Maximum:		50.0	10.0	200.0		
Mass	**Calc. Mass**	**mDa**	**PPM**	**DBE**	**Score**	**Formula**
573.2645	573.2654	-1.0	-1.7	25.5	1	C39 H33 N4 O

Figure S2. HR-MS spectrum of compound **2b**



Compound 3
Mol. Wt. = 588.23
Peak at $[M+1]^+$= 589.24

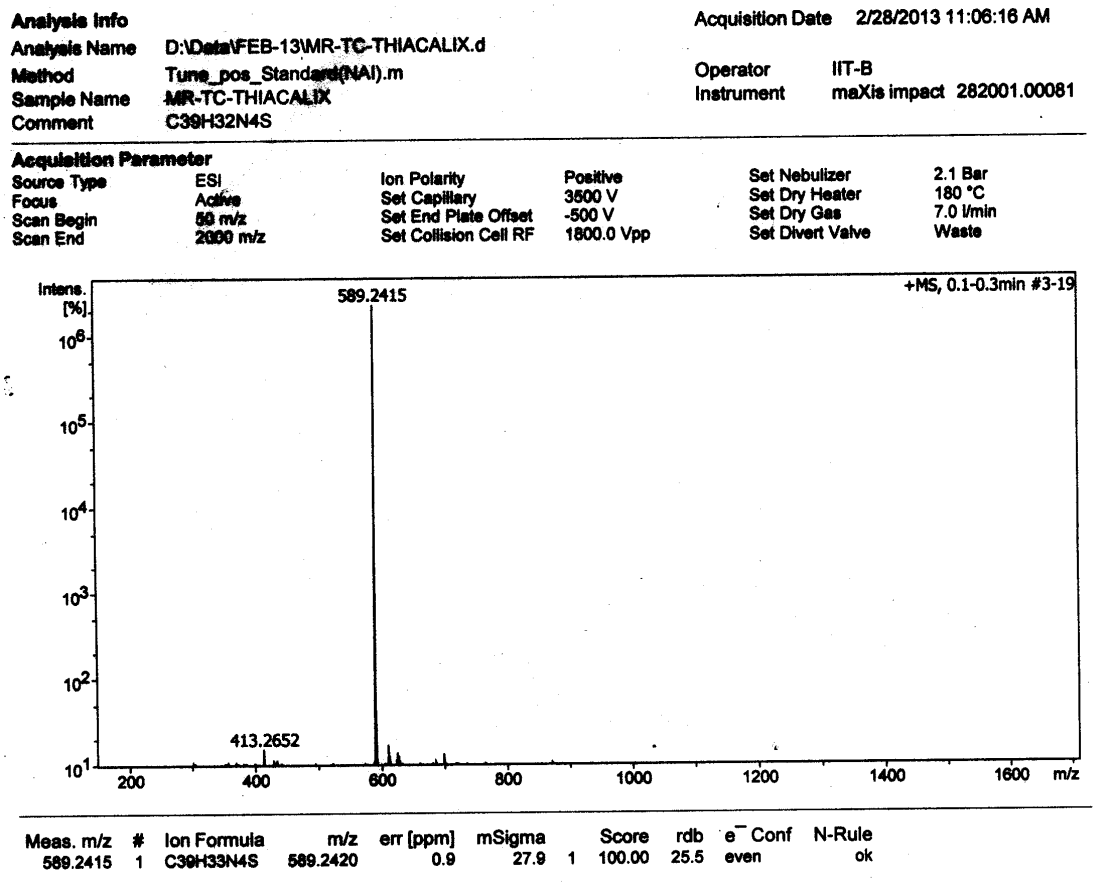
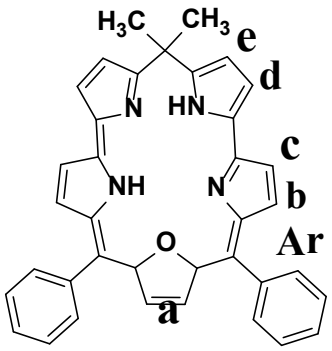


Figure S3. HR-MS spectrum of compound **3**



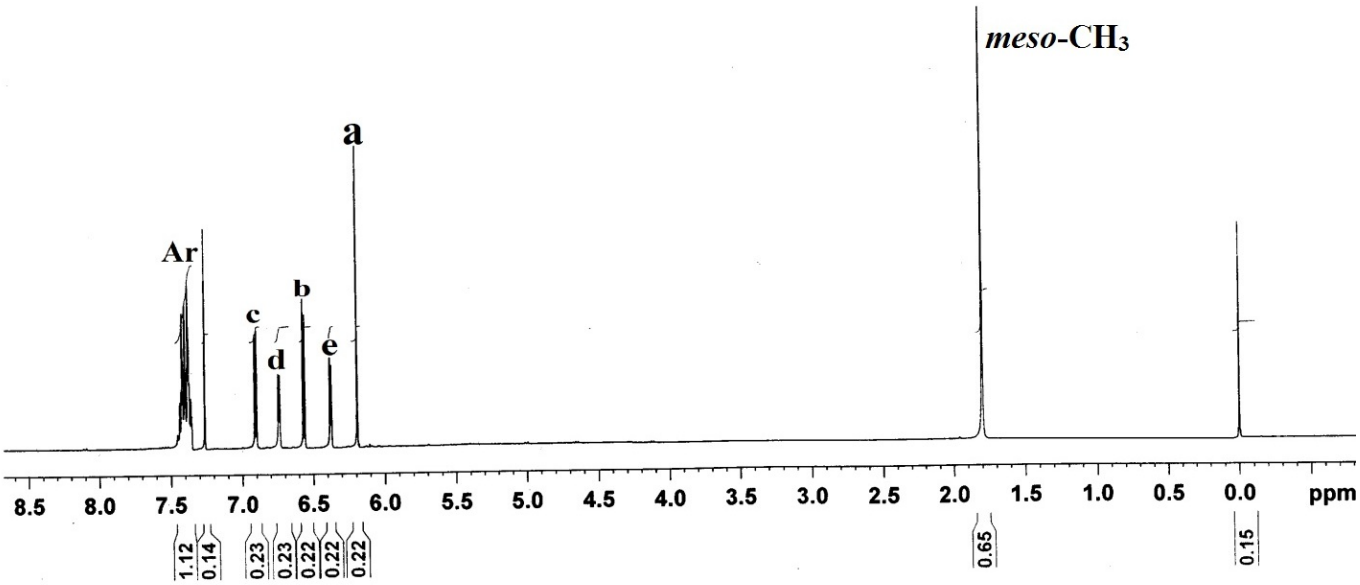


Figure S4. ^{1}H NMR spectrum of compound **2a** recorded in $CDCl_3$ at room temperature.

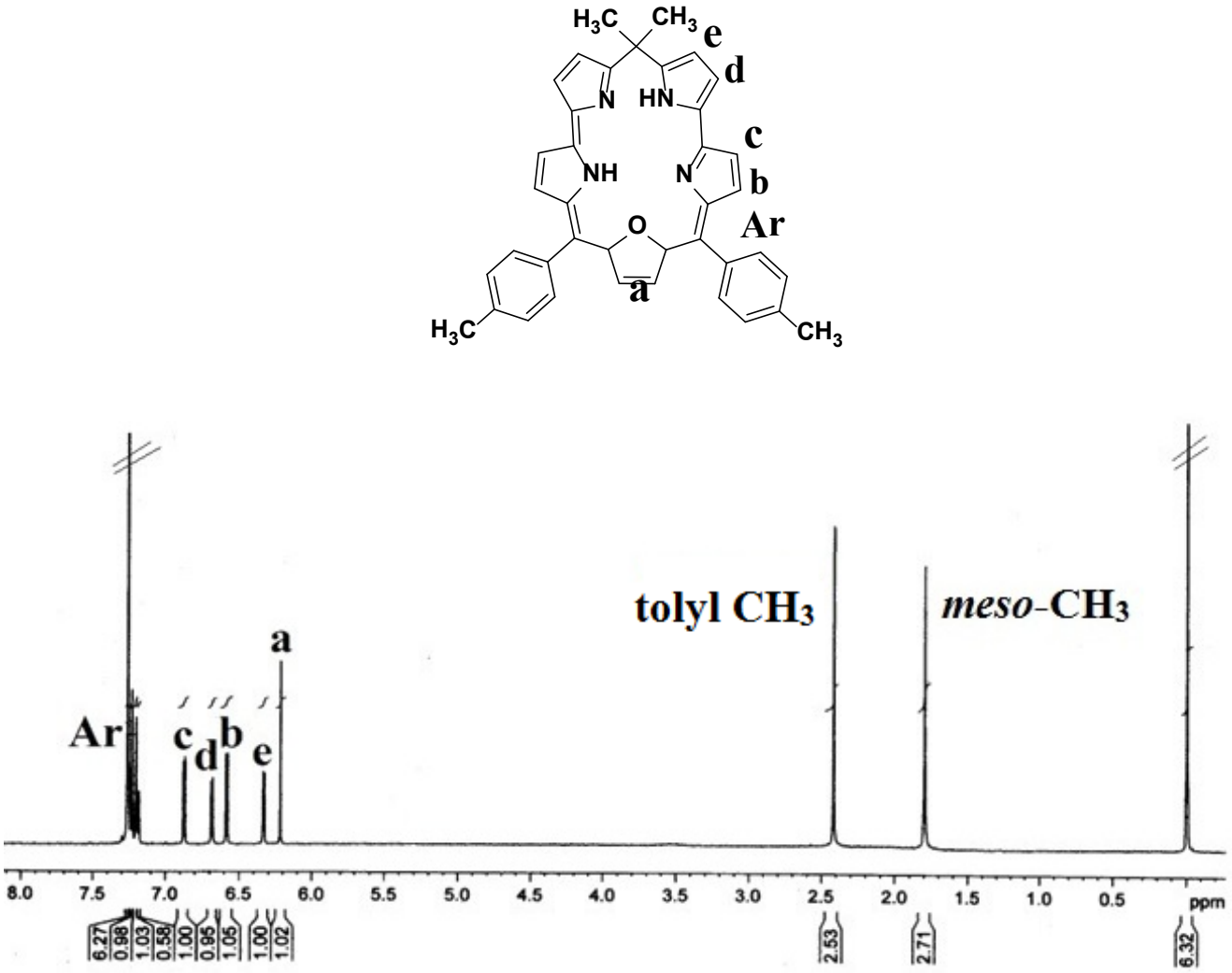


Figure S5. ^{1}H NMR spectrum of compound **2b** recorded in $CDCl_3$ at room temperature.

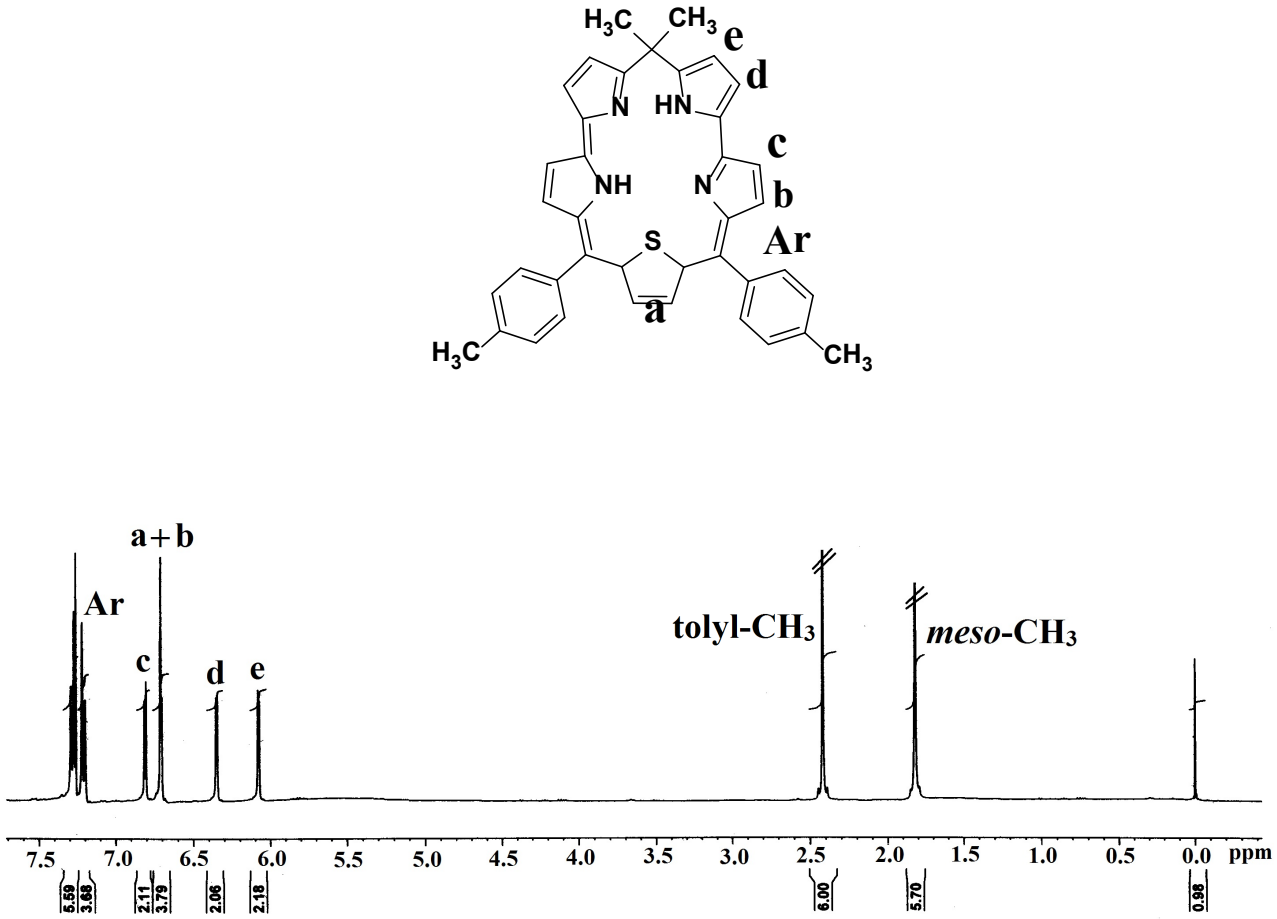


Figure S6. ^{1}H NMR spectrum of compound **3** recorded in $CDCl_3$ at room temperature.

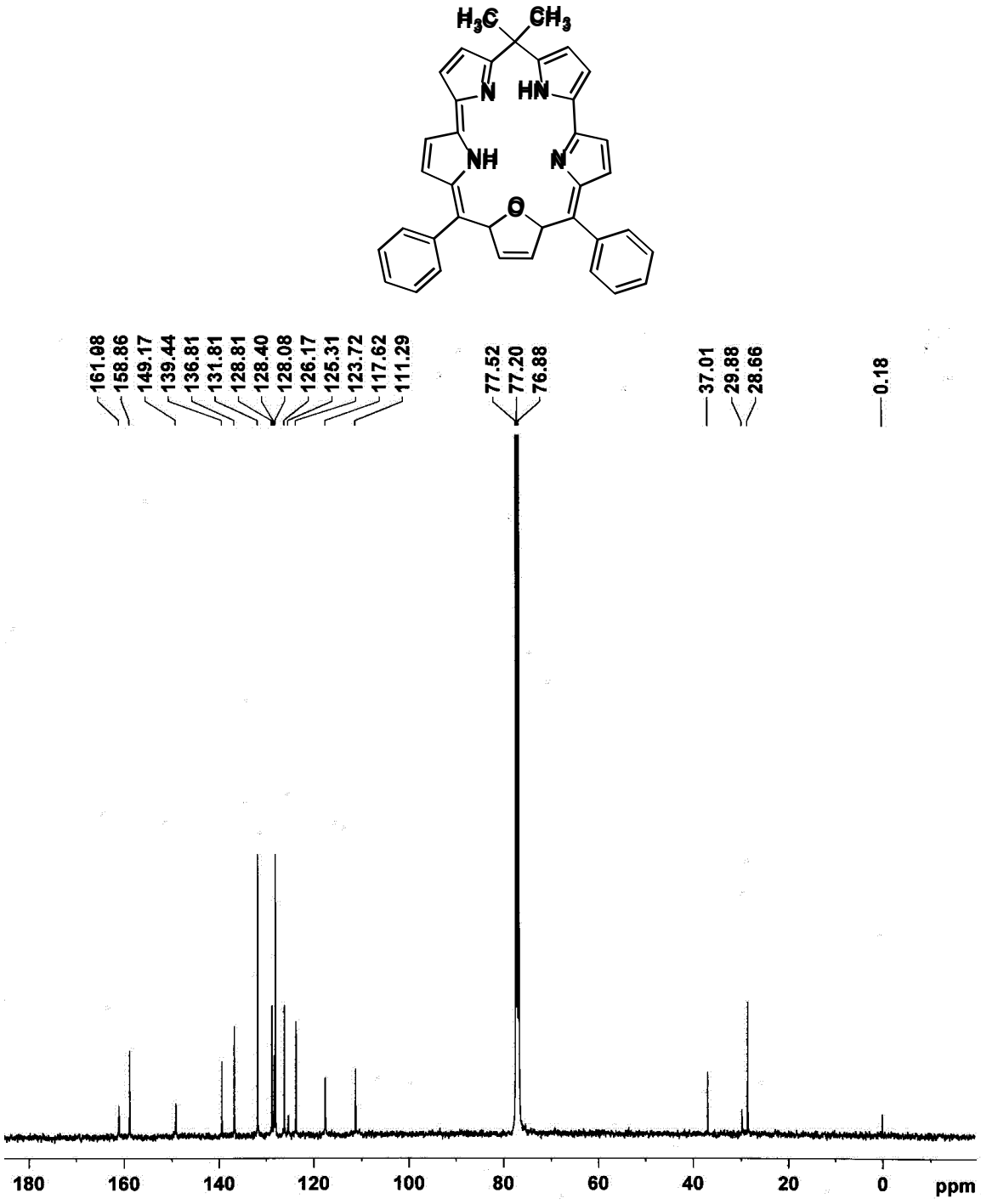


Figure S7. ^{13}C NMR spectrum of compound **2a** recorded in $CDCl_3$ at room temperature.

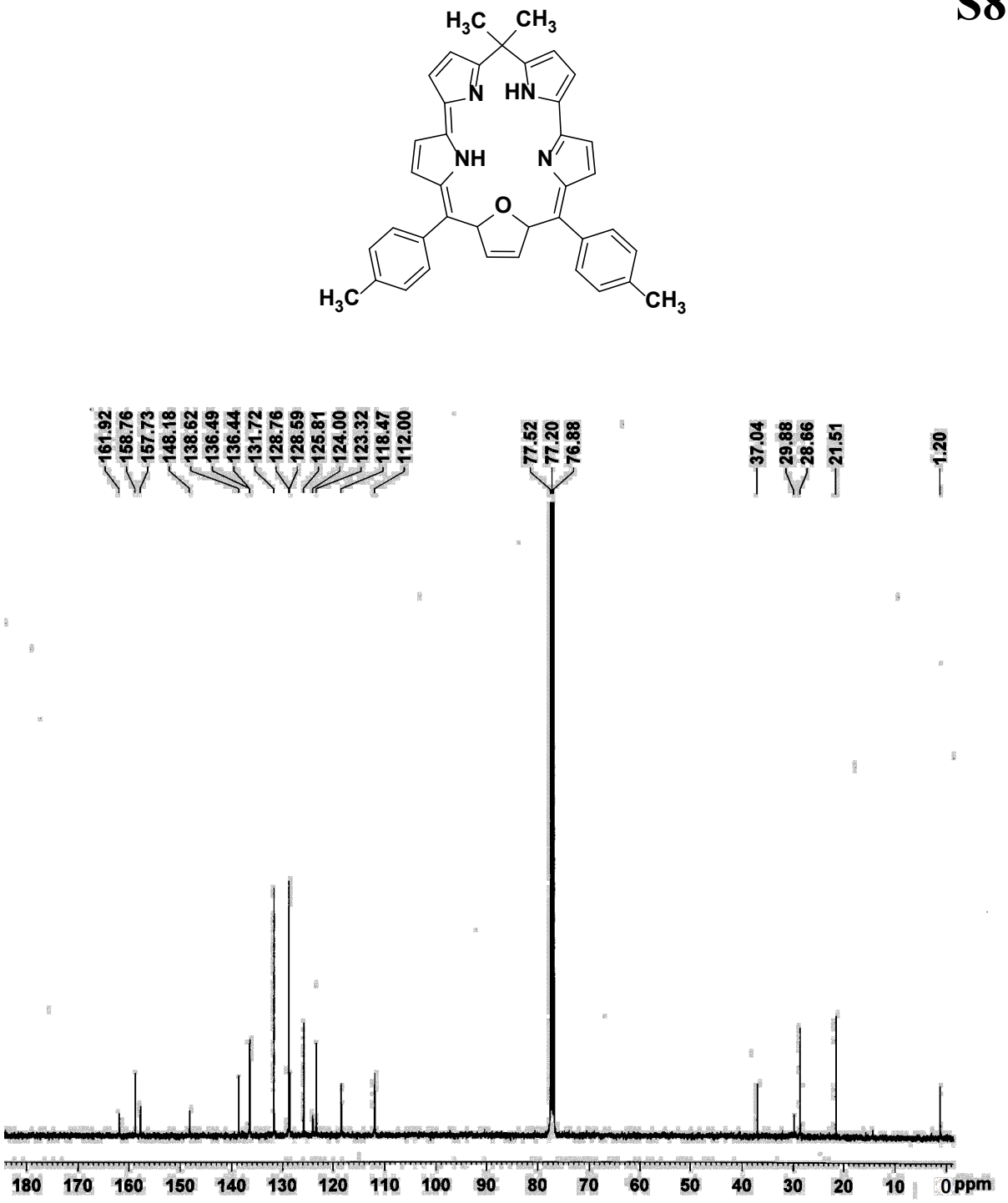


Figure S8. ^{13}C NMR spectrum of compound **2b** recorded in $CDCl_3$ at room temperature.

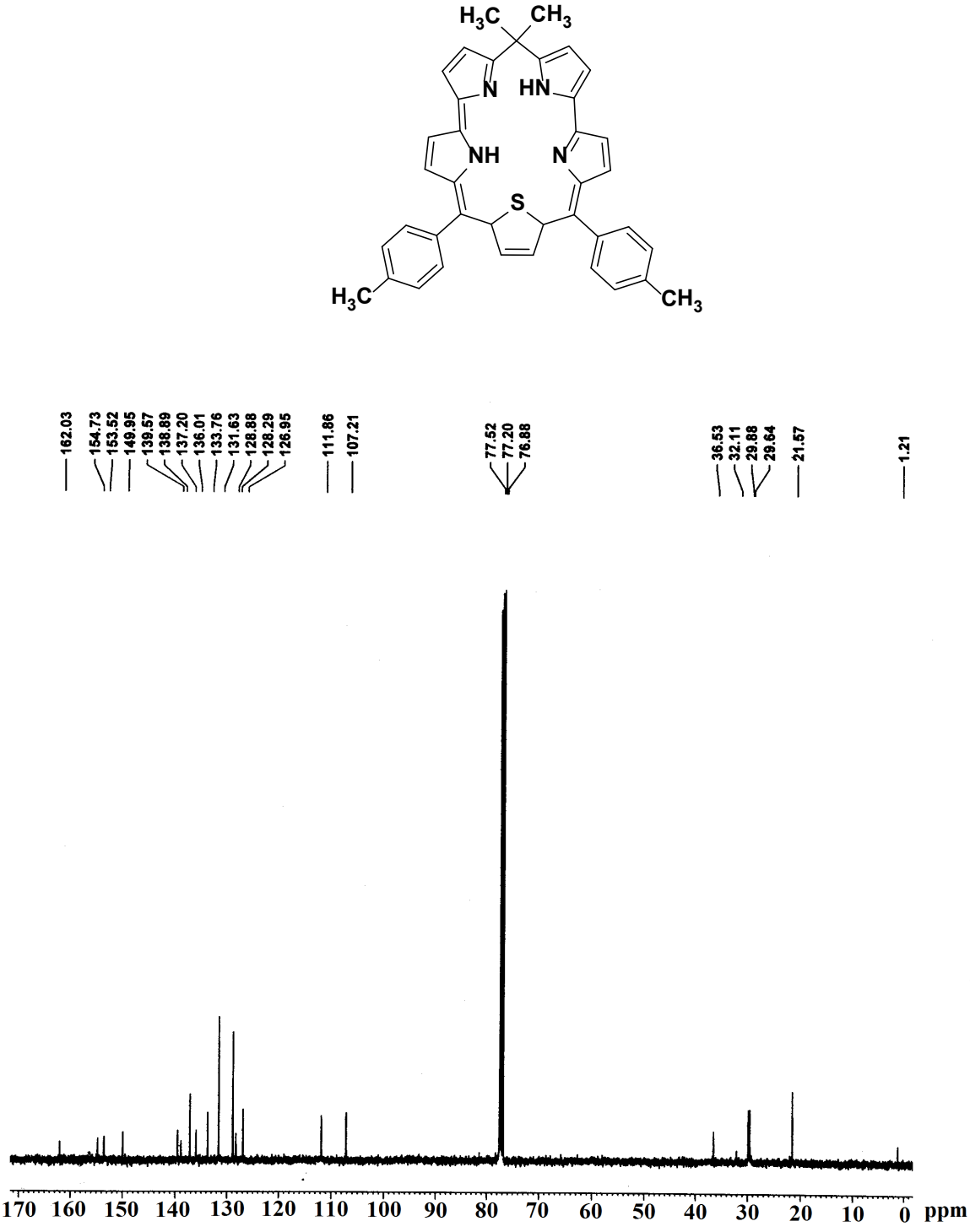


Figure S9. ^{13}C NMR spectrum of compound **3** recorded in $CDCl_3$ at room temperature.

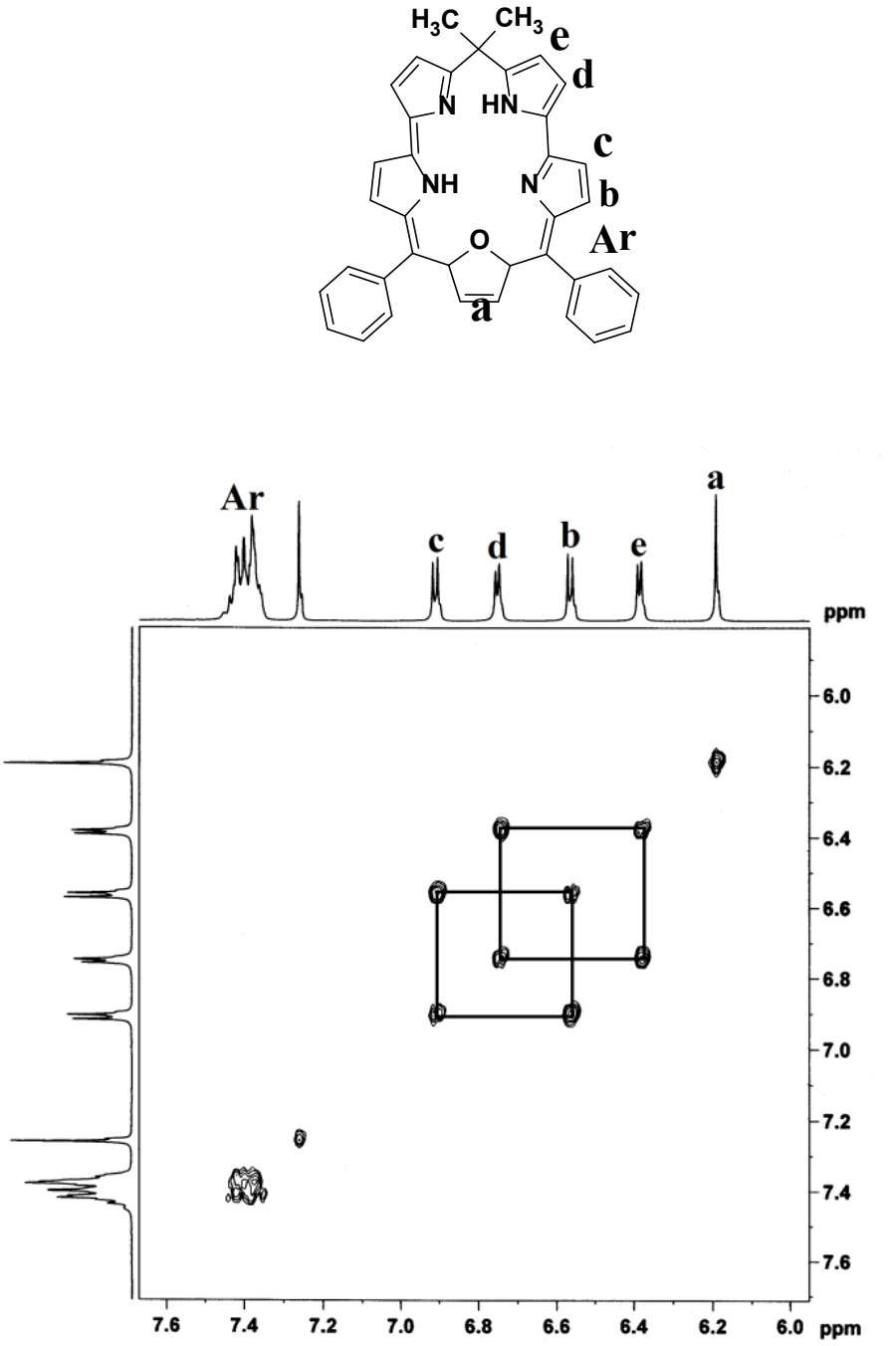


Figure S10. Partial ^{1}H-^{1}H COSY NMR spectrum of compound **2a** recorded in $CDCl_3$ at room temperature.

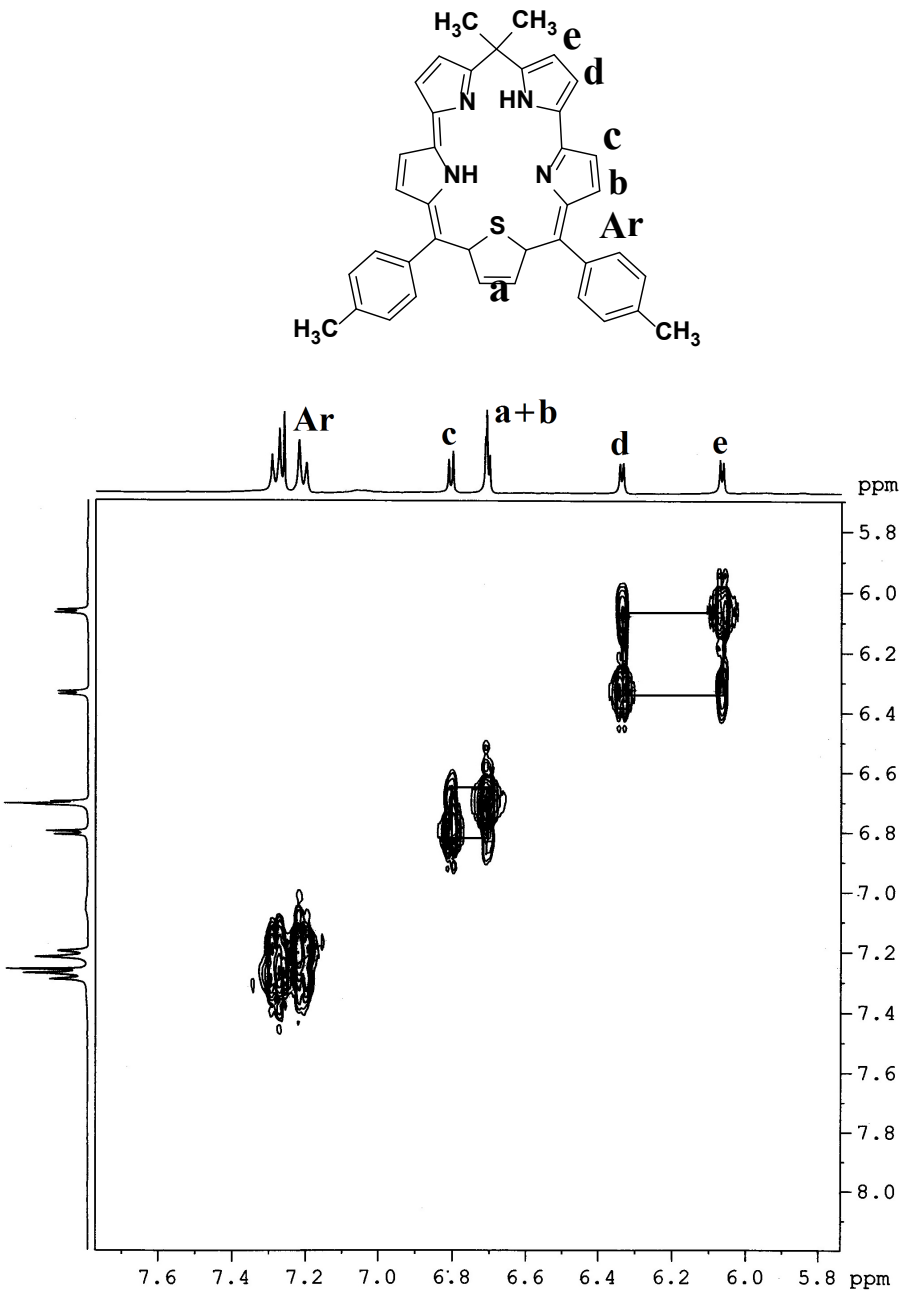


Figure S11. Partial ^{1}H-^{1}H COSY NMR spectrum of compound **3** recorded in $CDCl_3$ at room temperature.

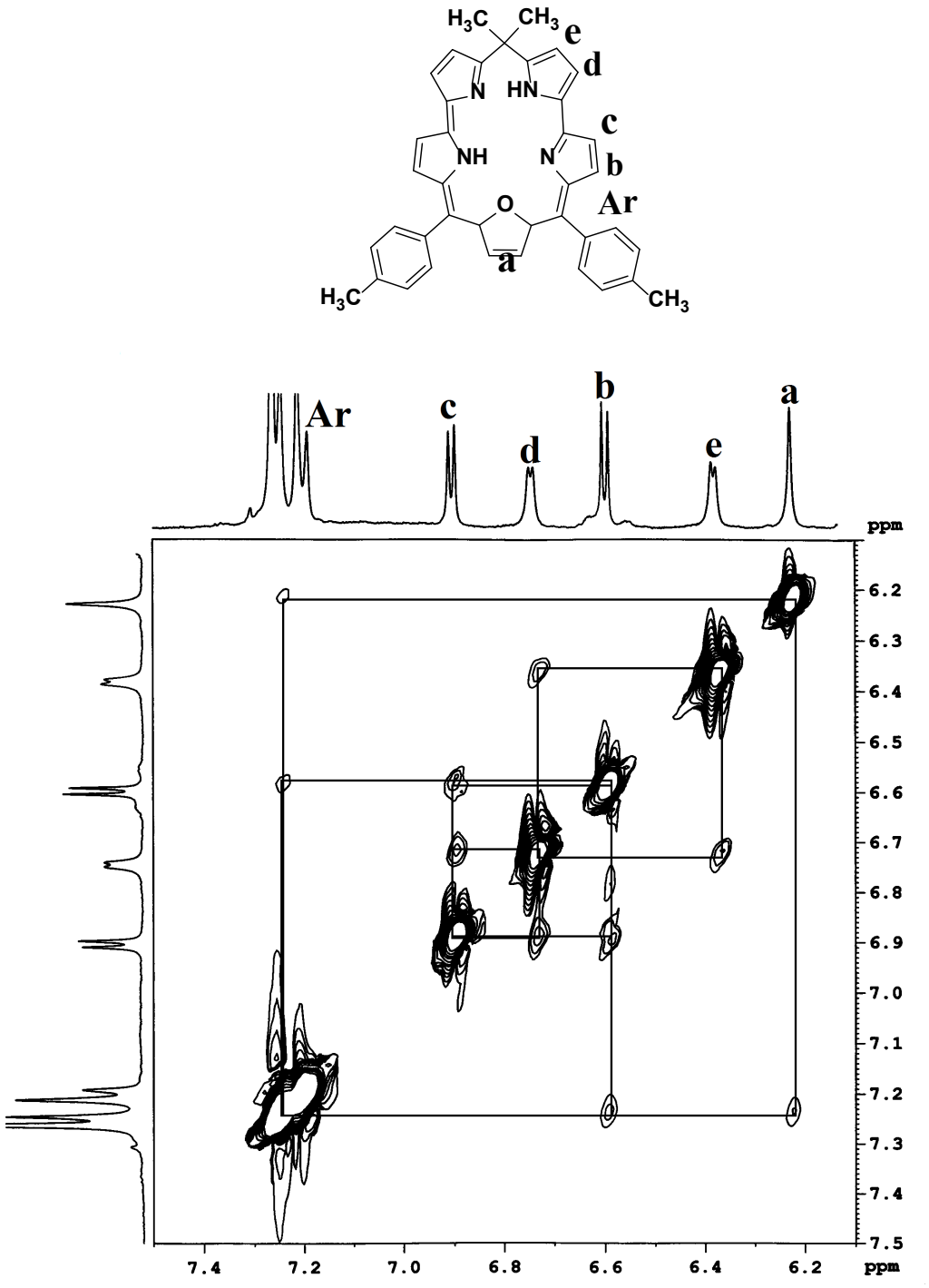


Figure S12. Partial ^{1}H-^{1}H NOESY NMR spectrum of compound **2b** recorded in $CDCl_3$ at room temperature.

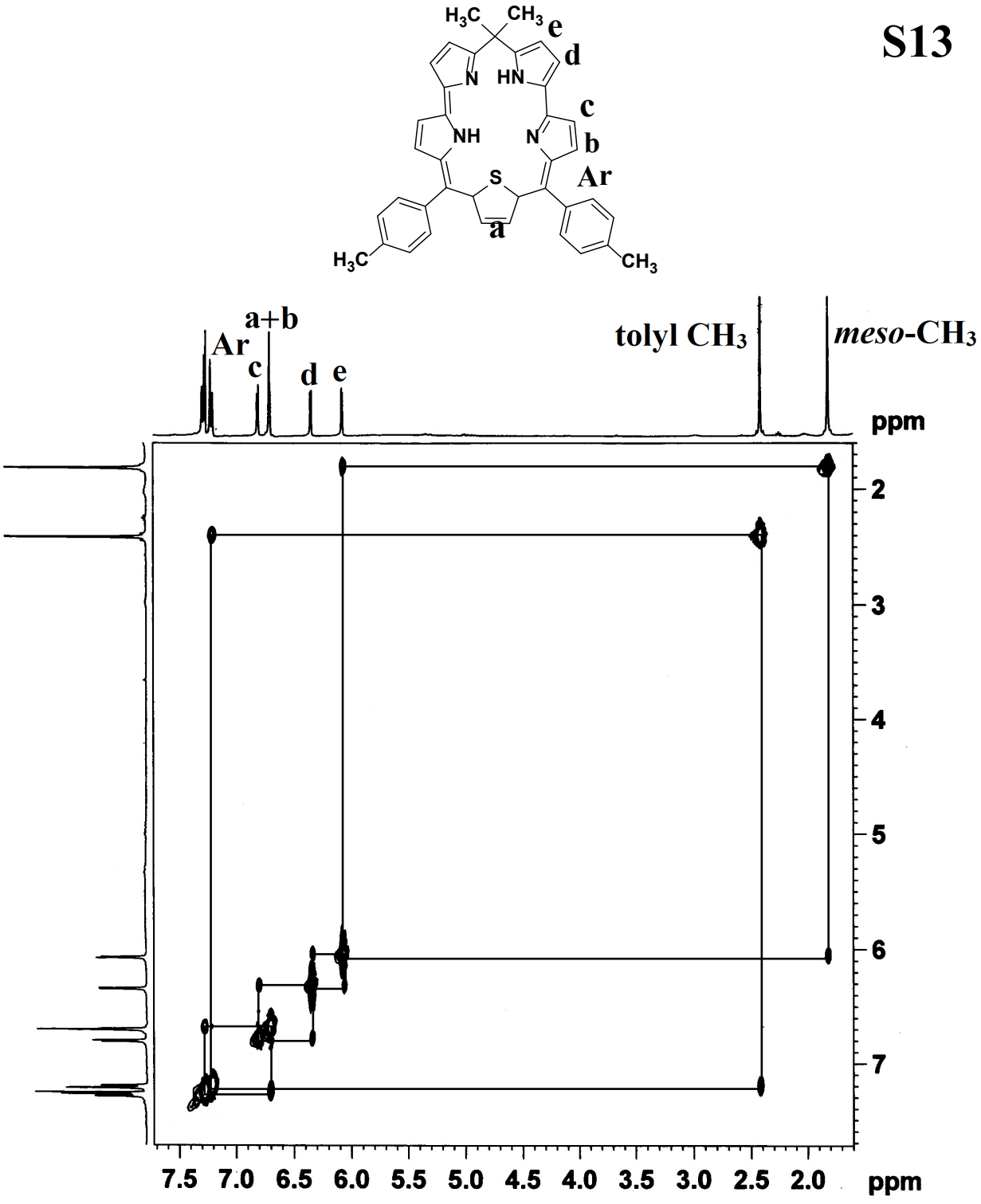


Figure S13. ^{1}H-^{1}H NOESY NMR spectrum of compound **3** recorded in $CDCl_3$ at room temperature.

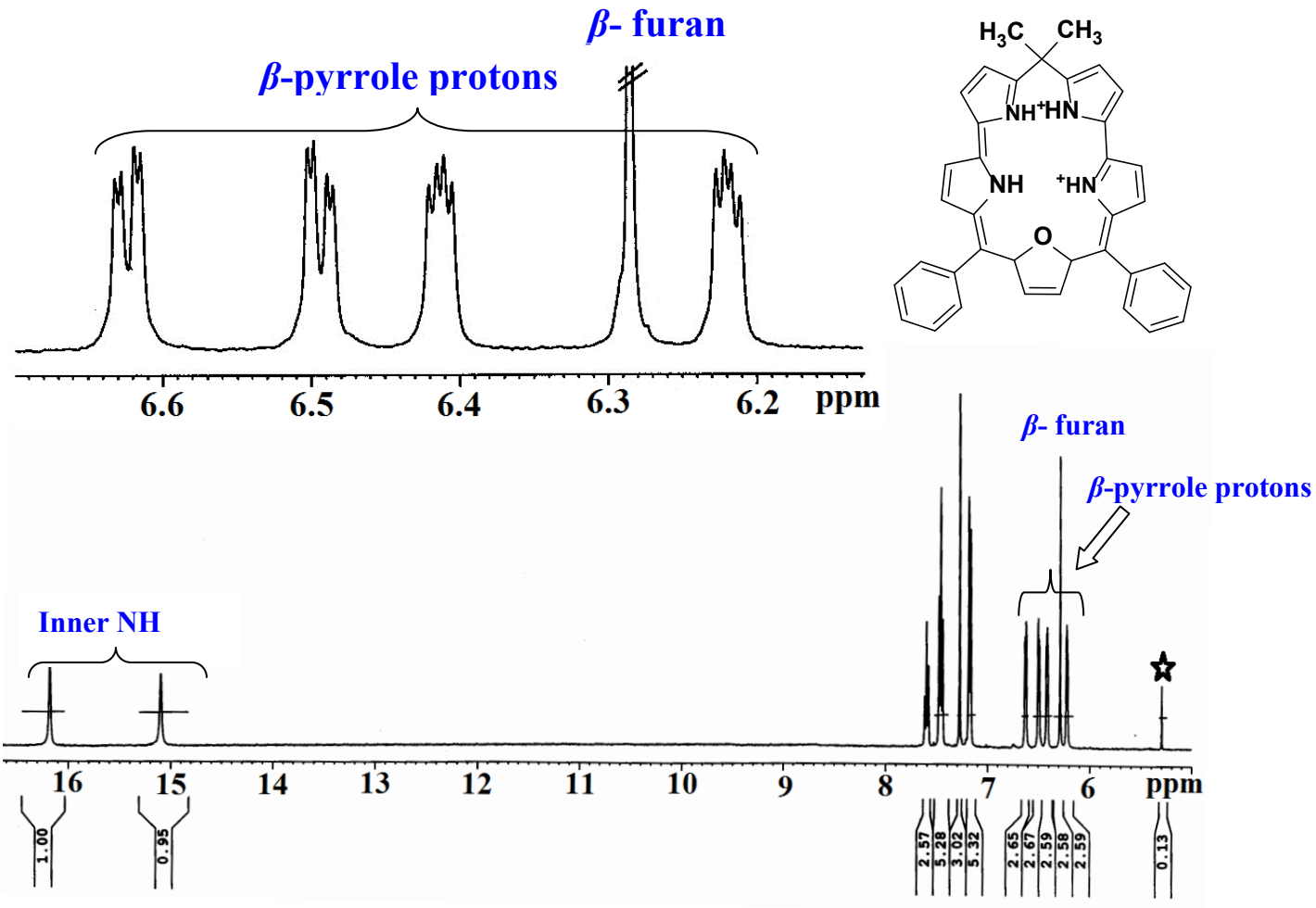


Figure S14. Partial ^{1}H NMR spectrum of compound **2a.2H**$^{2+}$ recorded in $CDCl_3$ (✯ residual solvent peak) at room temperature.

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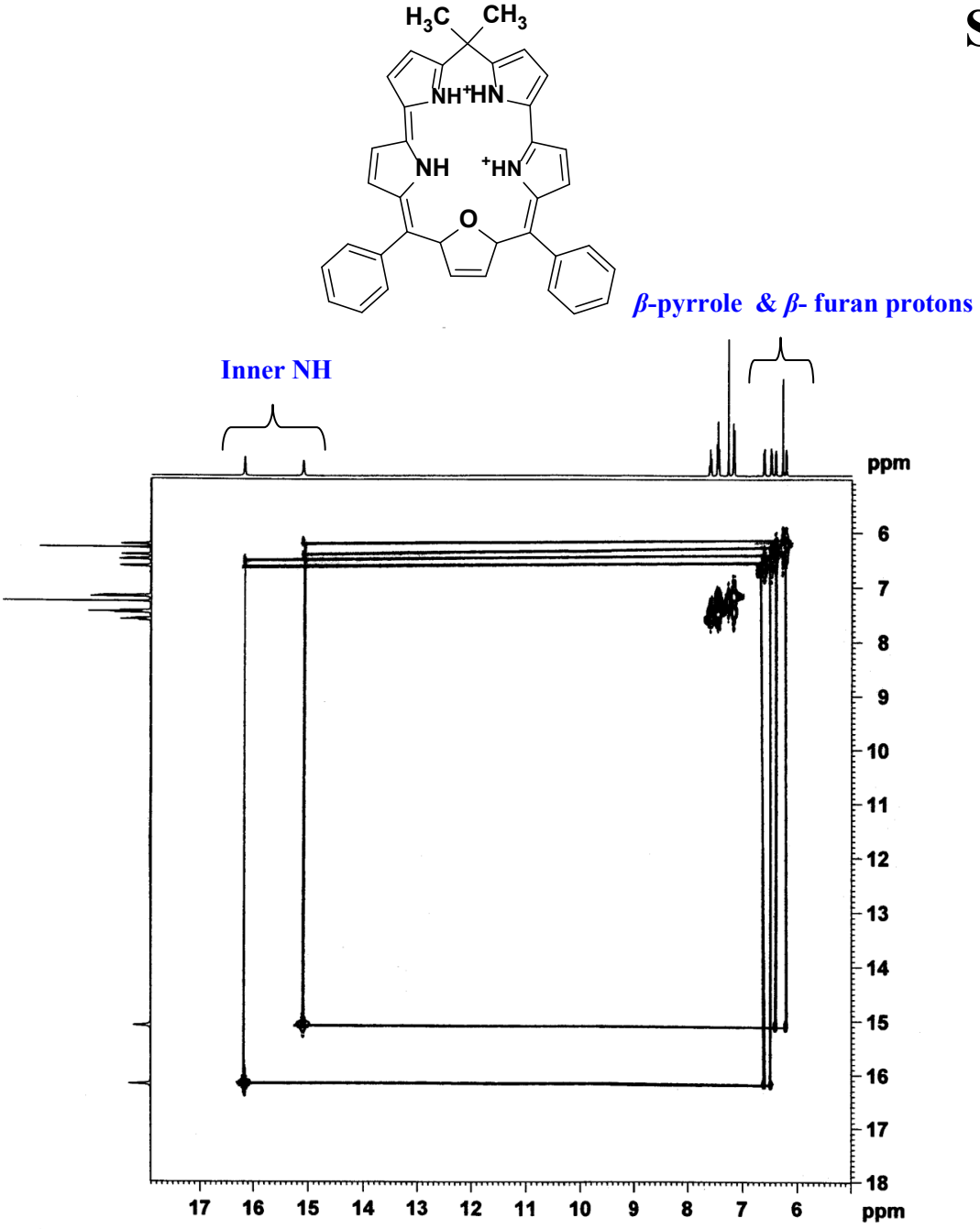


Figure S15. Partial ^{1}H-^{1}H COSY NMR spectrum of compound **2a.2H**$^{2+}$ showing the cross-peak connectivities between inner NH protons and β-pyrrole and β-furan protons recorded in $CDCl_3$ at room temperature.

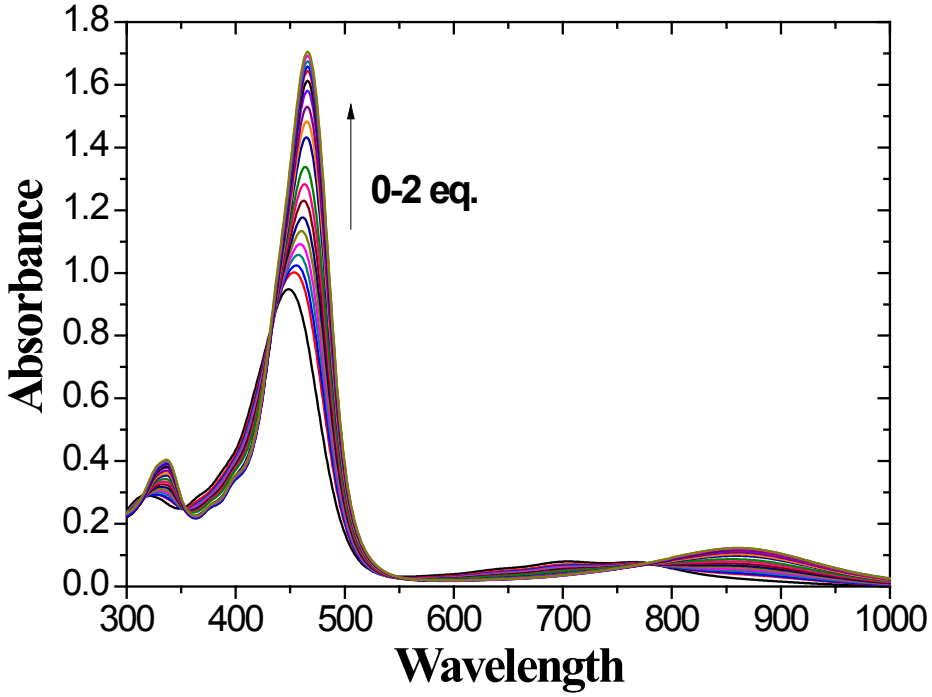


Figure S16. Change in absorption spectra of compound **2b** ($1x10^{-5}$ M) upon systematic addition of TFA solution (0-2 equiv.) in $CHCl_3$ solution.

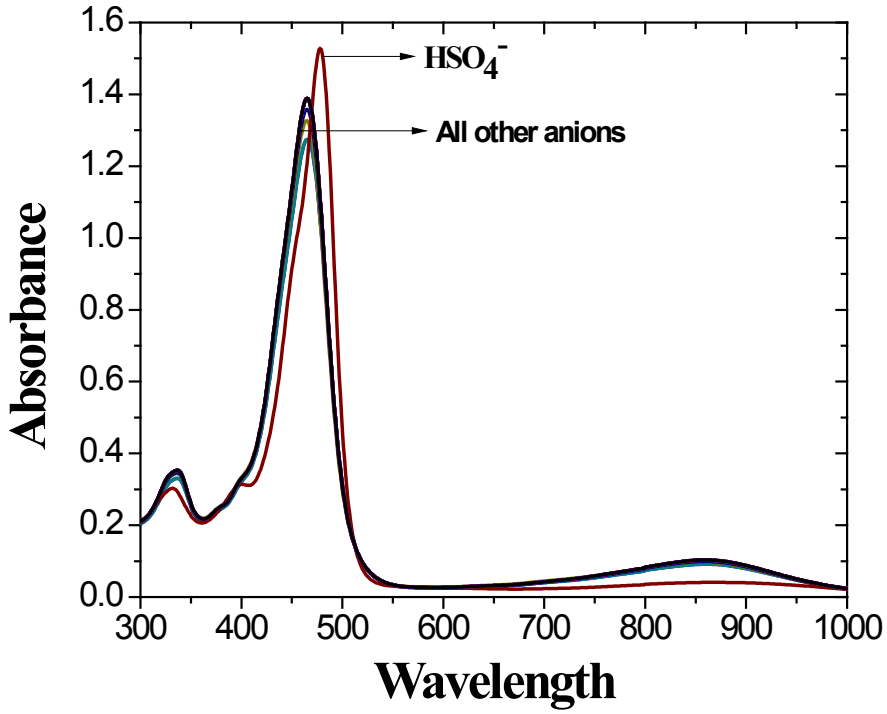


Figure S17. Absorption spectra of compound **2b.2H^{+2}** ($1x10^{-5}$ M) in the presence of various anions such as F^-, Cl^-, Br^-, I^-, ClO_4^-, CH_3COO^-, $H_2PO_4^-$, HPO_4^{-2}, HSO_4^-, SO_4^-, SCN^-, $S_2O_3^-$, NO_3^- and N_3^- (excess of equivalents) recorded in $CHCl_3$ solution.

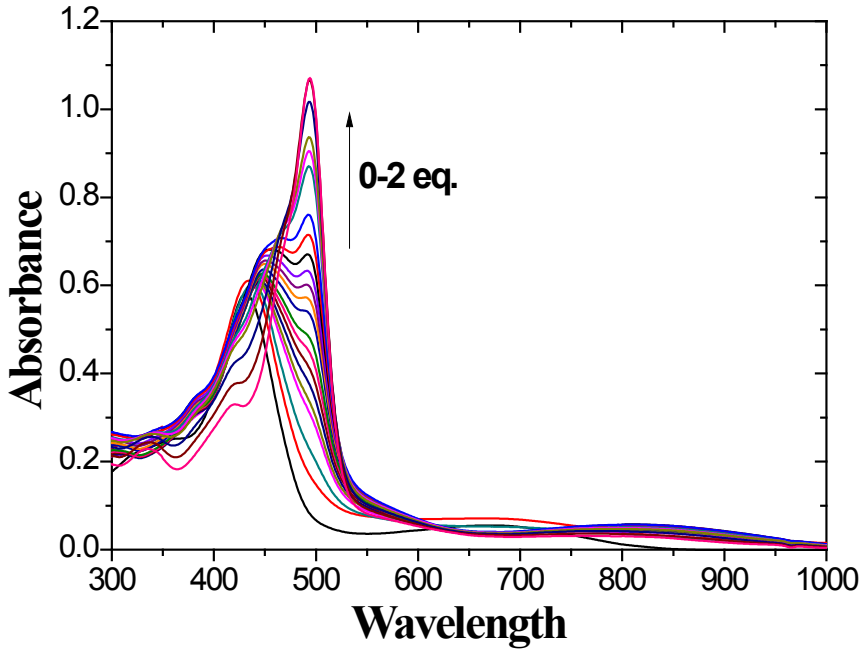


Figure S18. Change in absorption spectra of compound **3** ($1x10^{-5}$ M) upon systematic addition of TFA solution (0-2 equiv.) in $CHCl_3$ solution.

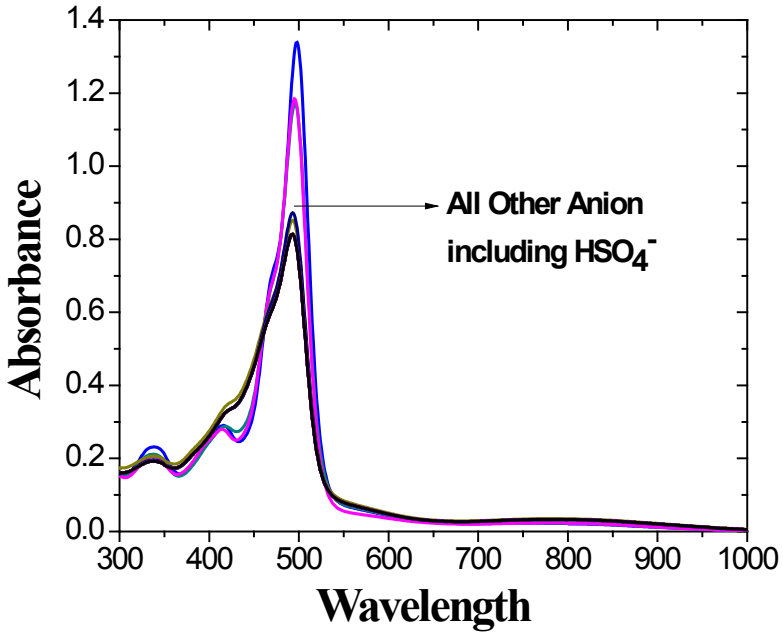


Figure **S19**. Absorption spectra of compound **3.2H^{+2}** ($1x10^{-5}$ M) in the presence of various anions F^-, Cl^-, Br^-, I^-, ClO_4^-, CH_3COO^-, $H_2PO_4^-$, HPO_4^{-2}, HSO_4^-, SO_4^-, SCN^-, $S_2O_3^-$, NO_3^- and N_3^- (excess of equivalents) recorded in $CHCl_3$ solution.

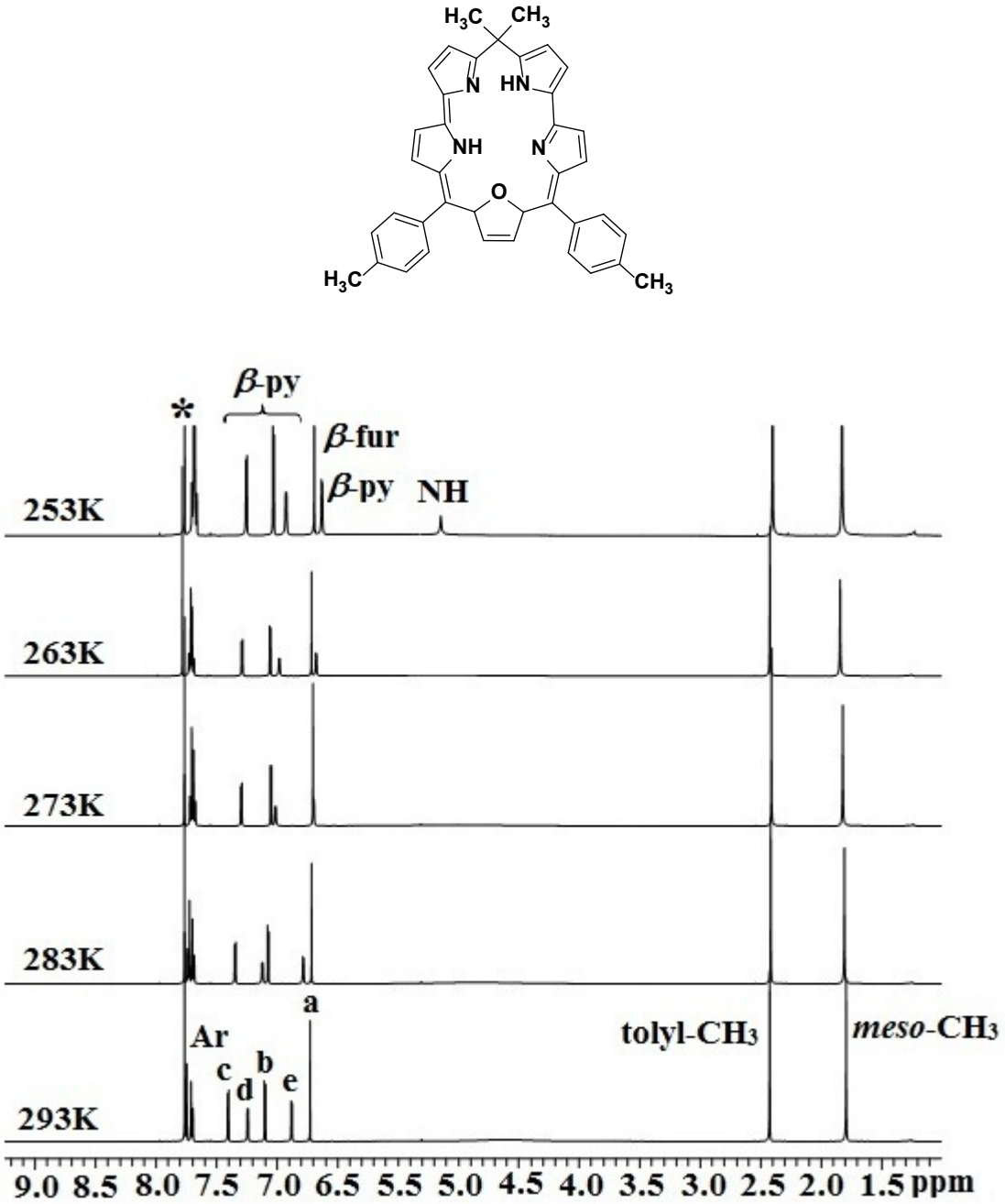


Figure S20. Variable temperature ^{1}H NMR spectra of compound **2b** recorded in the temperature range 20˚C to -20˚C in $CDCl_3$ (* $CDCl_3$ peak).

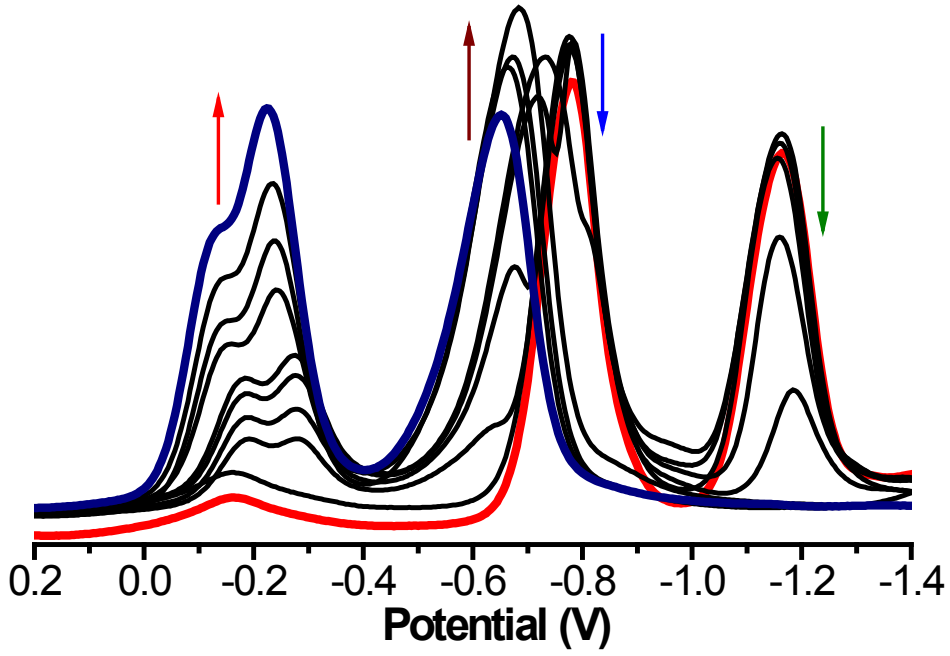


Figure S21. Square Wave Voltamogram of compound **2b** ($1.2x10^{-2}$ M) upon titration with HSO_4^- ion (0-20 equiv.) recorded in CH_2Cl_2 containing 0.1 M TBAP as supporting electrolyte at scan rates of 50 mVs^{-1}.

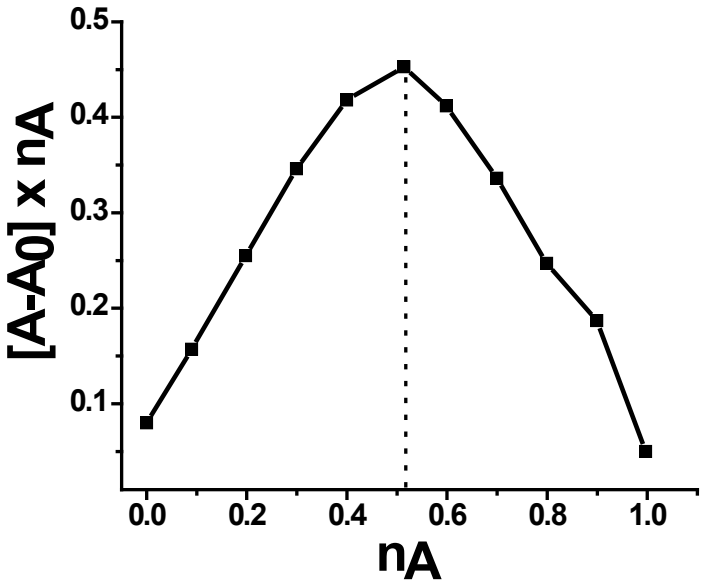
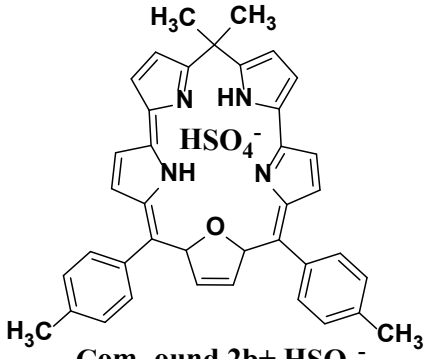


Figure S22. Job's plot for evolution of binding stoichiometry between Compound **2b** and HSO_4^- in $CHCl_3$ solution. Where n_A is mole fraction of the anion added and A is absorbance of compound **2b** in the presence of anion and A_0 is the absorbance of compound **2b** in the absence of anion which forms 1:1 complex.



Compound 2b+ HSO_4^-
Mol. Wt. = 669.21
Peak at $[M+2]^+$= 671.23

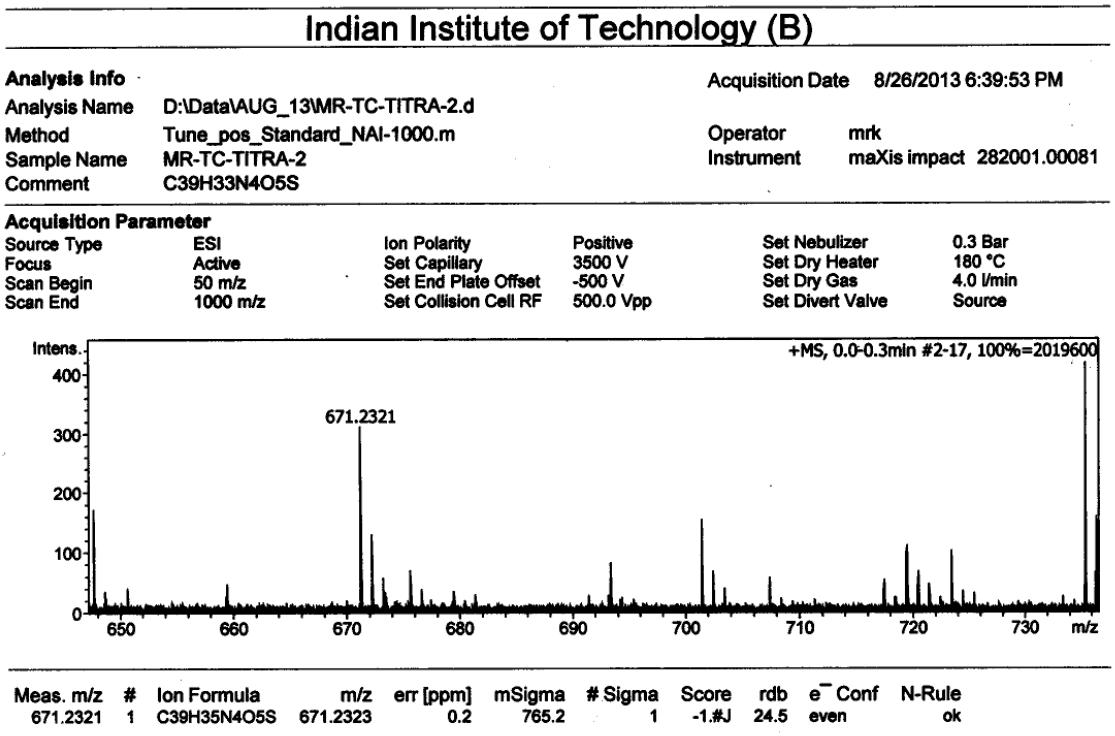


Figure S23. HR-MS spectrum of compound **2b+ HSO_4^-** ion complex

Table S1. Selected bond lengths [Å] and angles [˚] for compound **2a**.

Parameters	Bond length[Å]	Parameters	Bond angle[˚]
N(1)-C(1)	1.3617(17)	C(22)-C(23)-C(1)	111.64(11)
N(1)-C(4)	1.3744(17)	C(24)-C(23)-C(25)	109.09(13)
N(2)-C(5)	1.3327(17)	C(8)-C(9)-C(10)	128.57(12)
N(2)-C(8)	1.3968(16)	C(8)-C(9)-C(26)	117.62(11)
N(3)-C(15)	1.3929(17)	C(10)-C(9)-C(26)	113.78(11)
N(3)-C(18)	1.3677(17)	C(13)-C(14)-C(15)	127.82(12)
N(4)-C(19)	1.3834(18)	C(13)-C(14)-C(32)	114.40(11)
N(4)-C(22)	1.3327(18)	C(15)-C(14)-C(32)	117.72(12)
O(1)-C(10)	1.3834(15)		
O(1)-C(13)	1.3791(16)		
C(1)-C(23)	1.5186(19)		
C(22)-C(23)	1.5180(2)		
C(4)-C(5)	1.4322(18)		
C(18)-C(19)	1.3920(2)		

Table S2. Hydrogen bonding parameter for compound **2a** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(3)-H(3N)...O(2)	0.89(2)	2.00(2)	2.8710(16)	165(2)
N(1)-H(1N)...N(4)	0.87(2)	1.99(2)	2.6235(16)	128.7(18)
N(1)-H(1N)...O(2)	0.87(2)	2.40(2)	3.0684(16)	134.7(17)
O(2)-H(1O)...N(2)	0.823(2)	1.910(5)	2.7147(16)	165.6(19)