

Stable Core-modified Calixsmaragdyrins: Synthesis, Structure and Specific Sensing of Hydrogen Sulfate Ion

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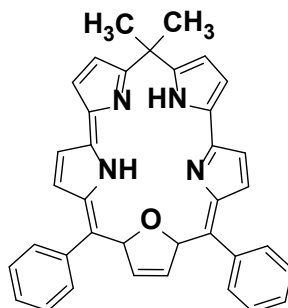
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S1



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)

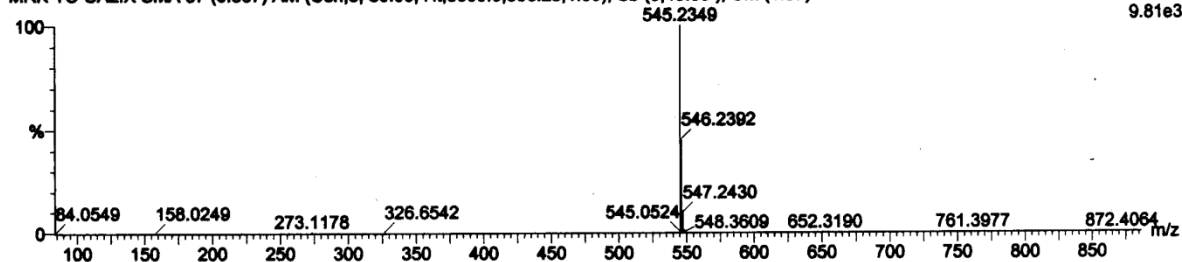
Dept. Of Chemistry I.I.T.(B)

23-May-2012 15:16:54

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

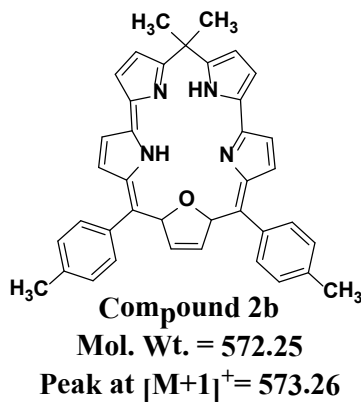


Minimum: -1.5
Maximum: 200.0 10.0 200.0

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

S2



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)

Waters(Micromass) : Q-ToF micro(YA-105)

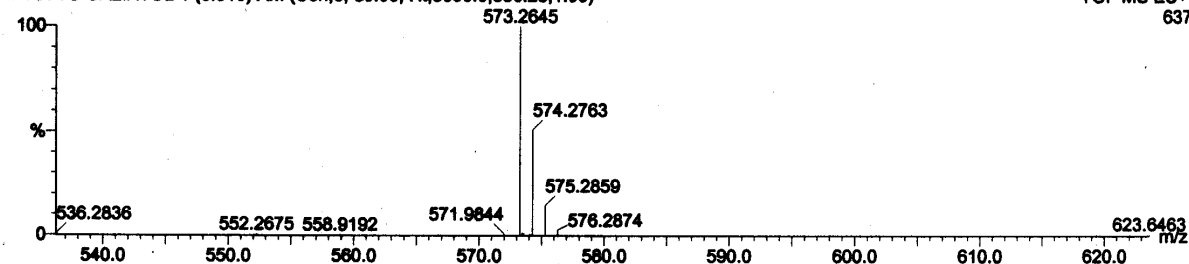
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12-Oct-2012 18:30:27

C39H38N4O

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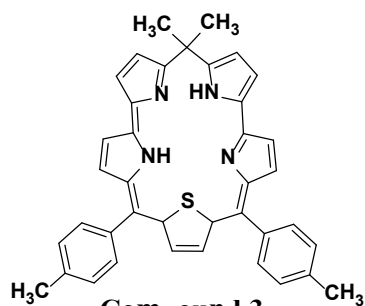
TOF MS ES+
637



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

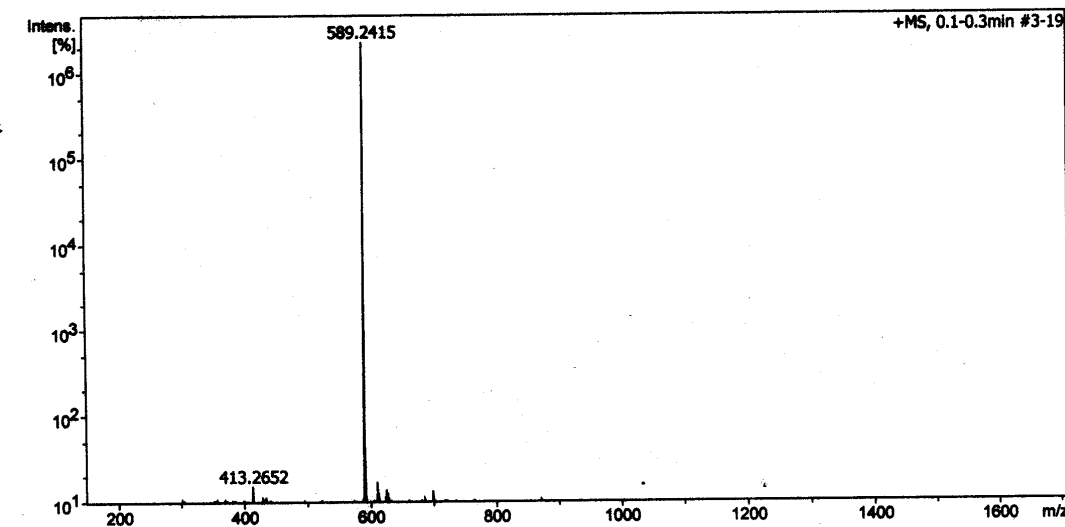
S3



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

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Method	Tune_pos_Standard(NAL).m	Instrument	maXis impact 282001.00081
Sample Name	MR-TC-THIACALIX		
Comment	C39H32N4S		

Acquisition Parameter					
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Scan End	2000 m/z	Set Collision Cell RF	1800.0 Vpp	Set Divert Valve	Waste



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	Score	rdB	e ⁻ Conf	N-Rule
589.2415	1	C39H33N4S	589.2420	0.9	27.9	1	100.00	25.5 even	ok

Figure S3. HR-MS spectrum of compound 3

S4

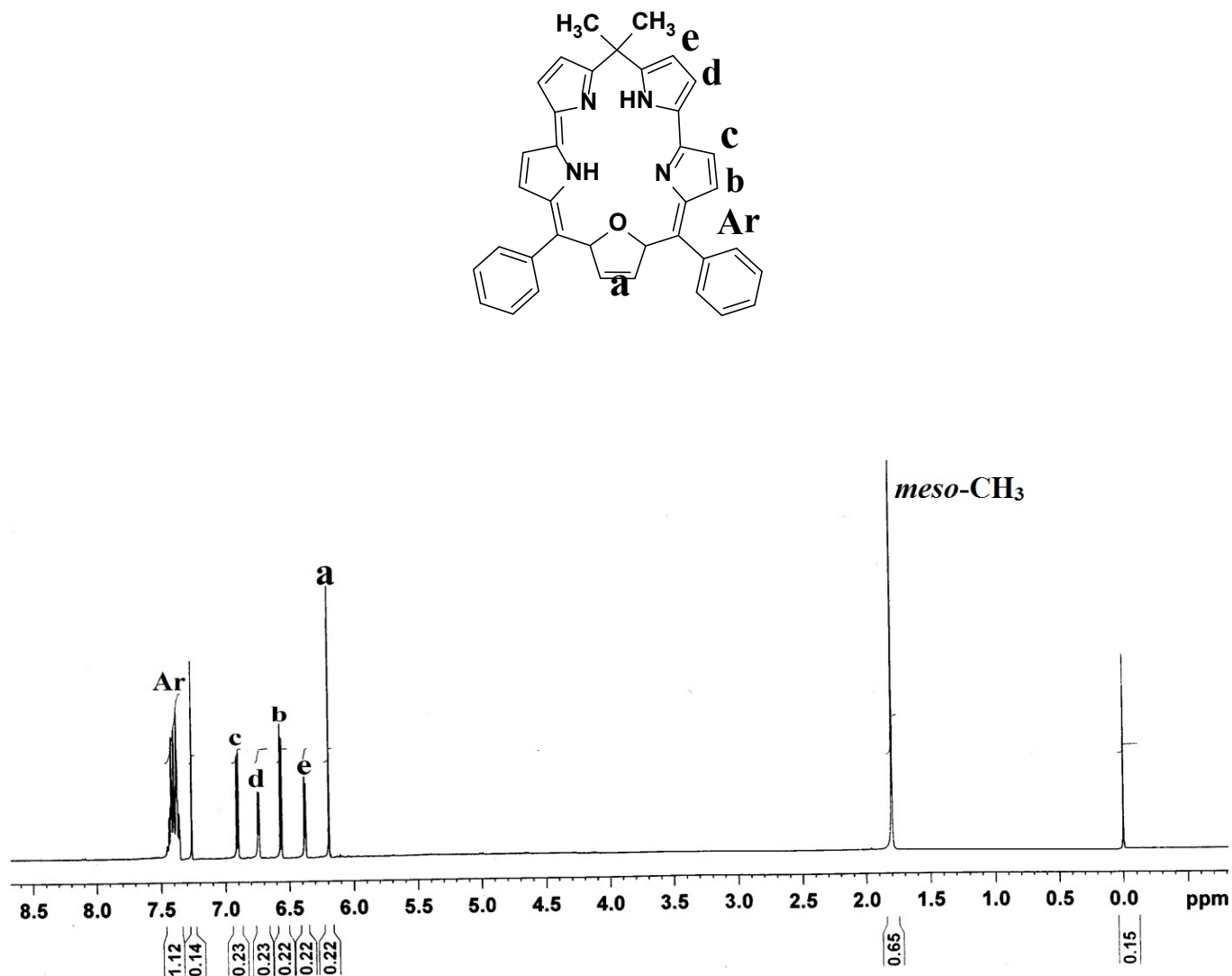


Figure S4. ^1H NMR spectrum of compound **2a** recorded in CDCl_3 at room temperature.

S5

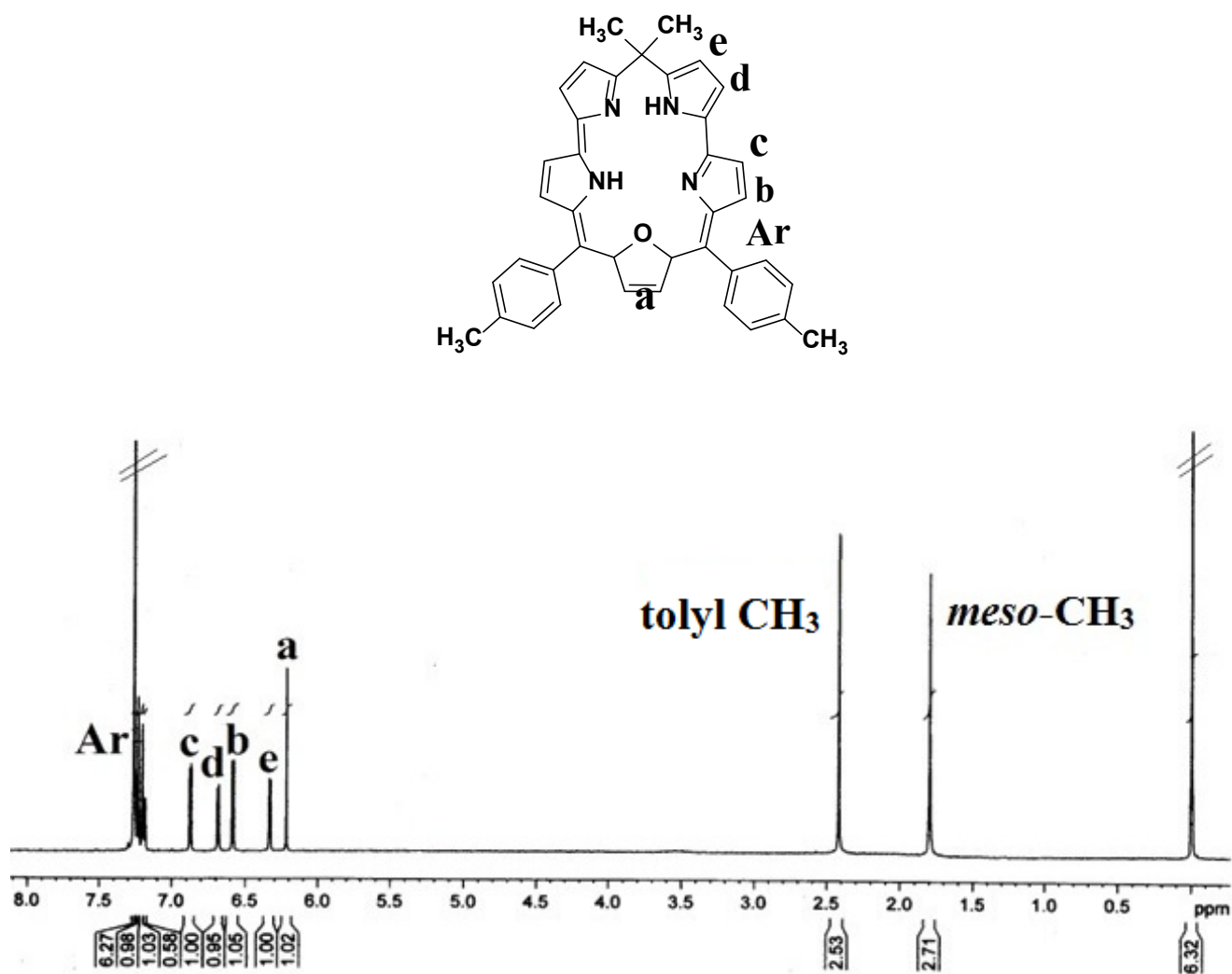


Figure S5. ¹H NMR spectrum of compound **2b** recorded in CDCl₃ at room temperature.

S6

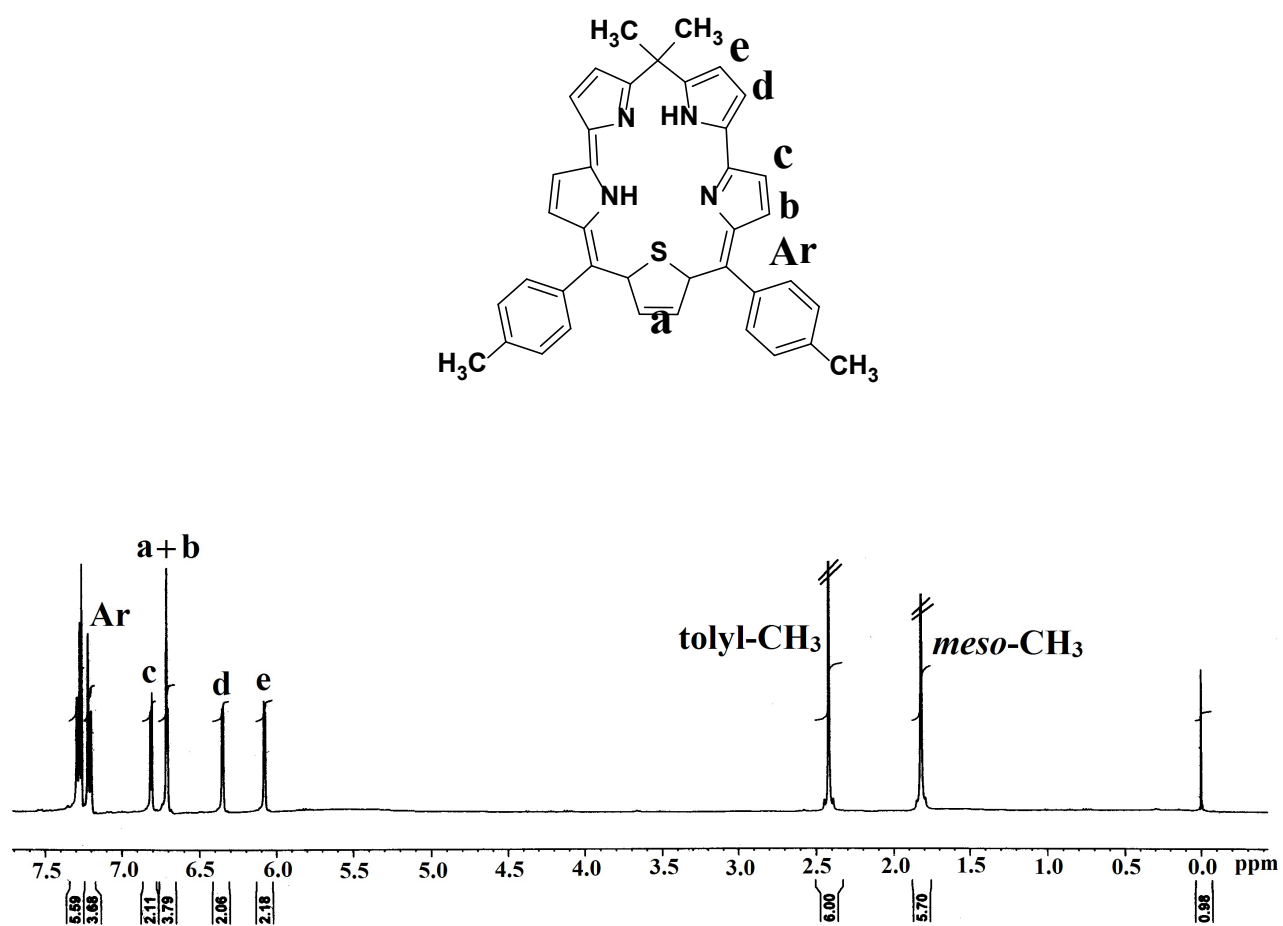


Figure S6. ¹H NMR spectrum of compound **3** recorded in CDCl₃ at room temperature.

S7

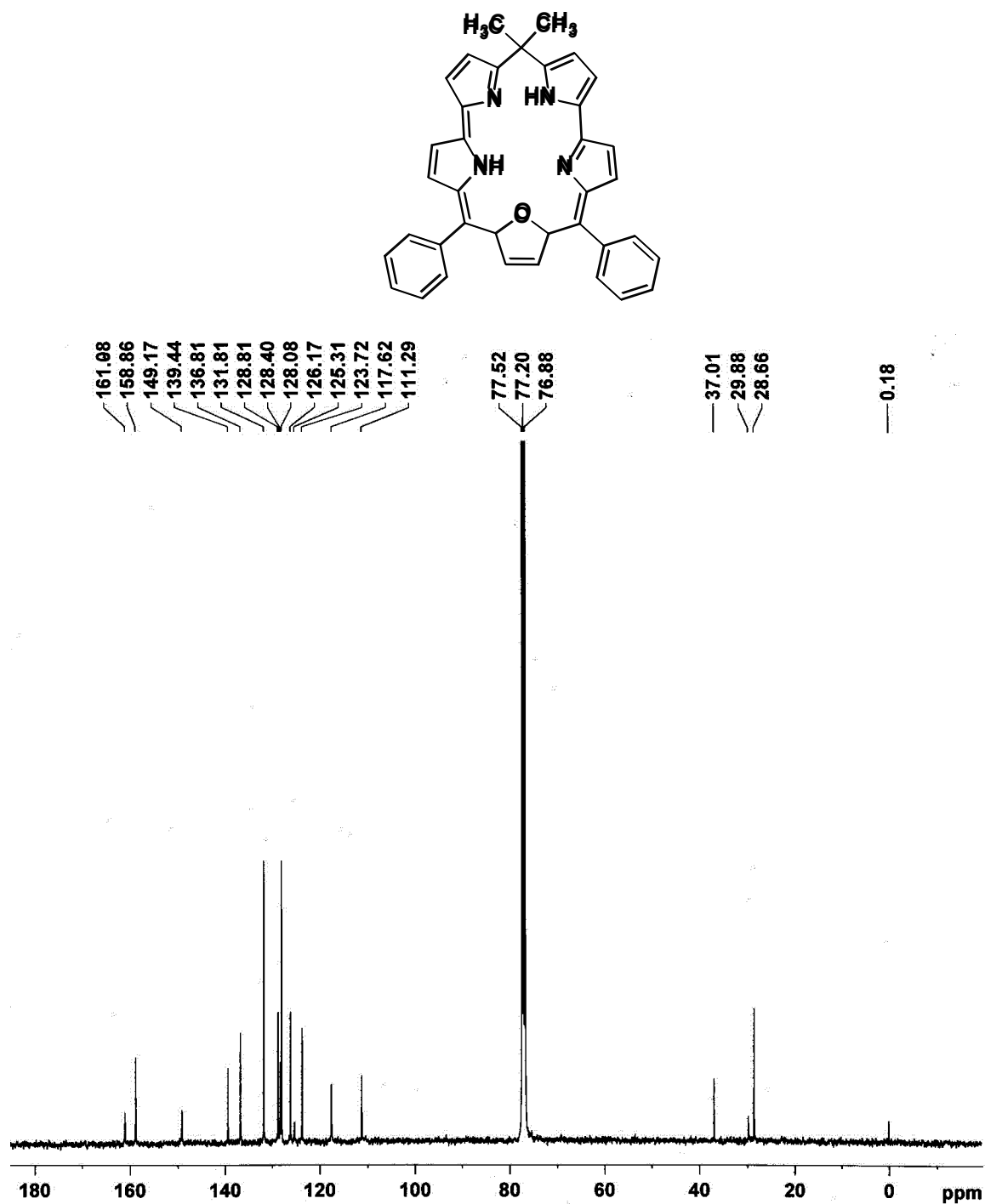


Figure S7. ^{13}C NMR spectrum of compound **2a** recorded in CDCl_3 at room temperature.

S8

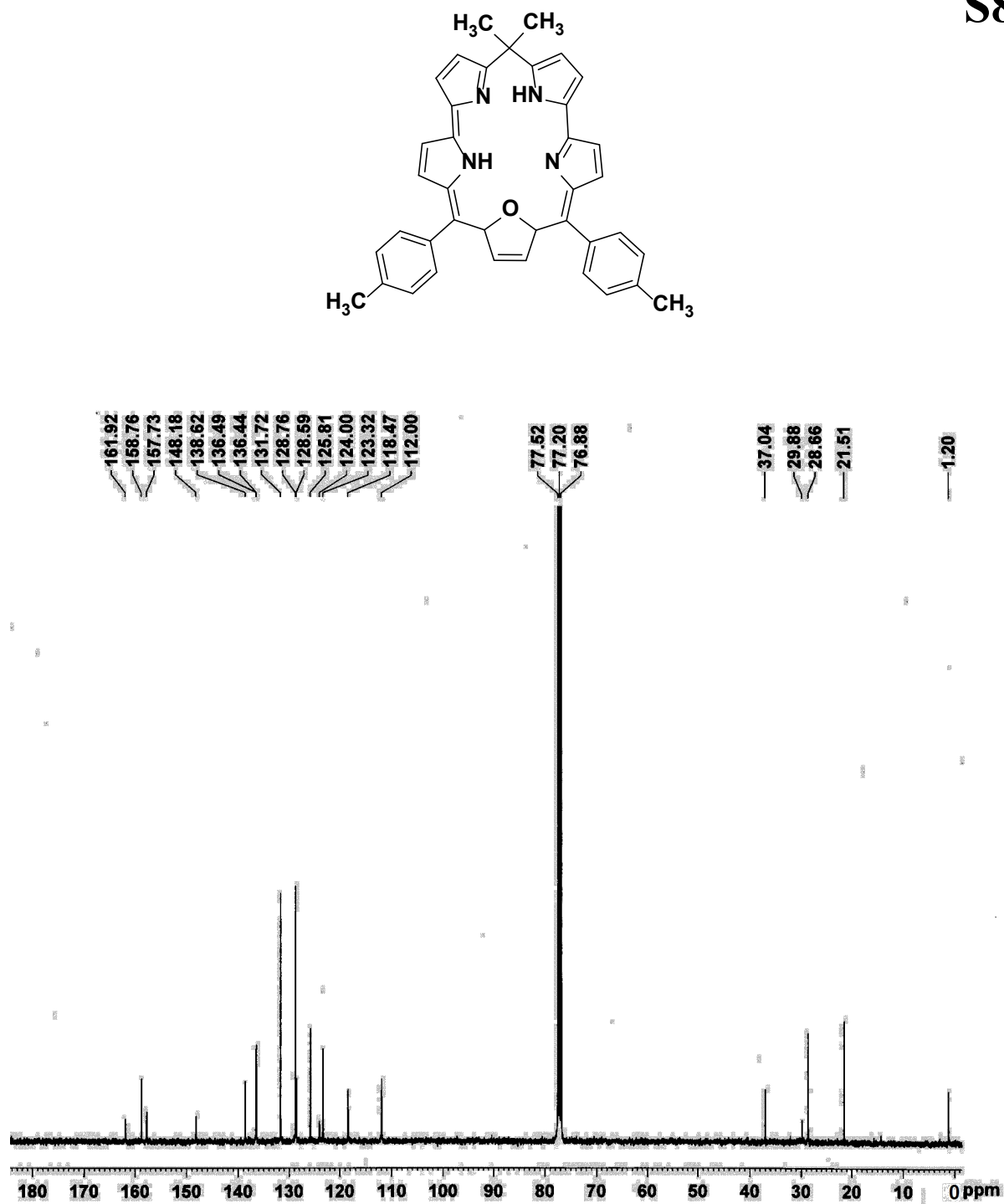


Figure S8. ^{13}C NMR spectrum of compound **2b** recorded in CDCl_3 at room temperature.

S9

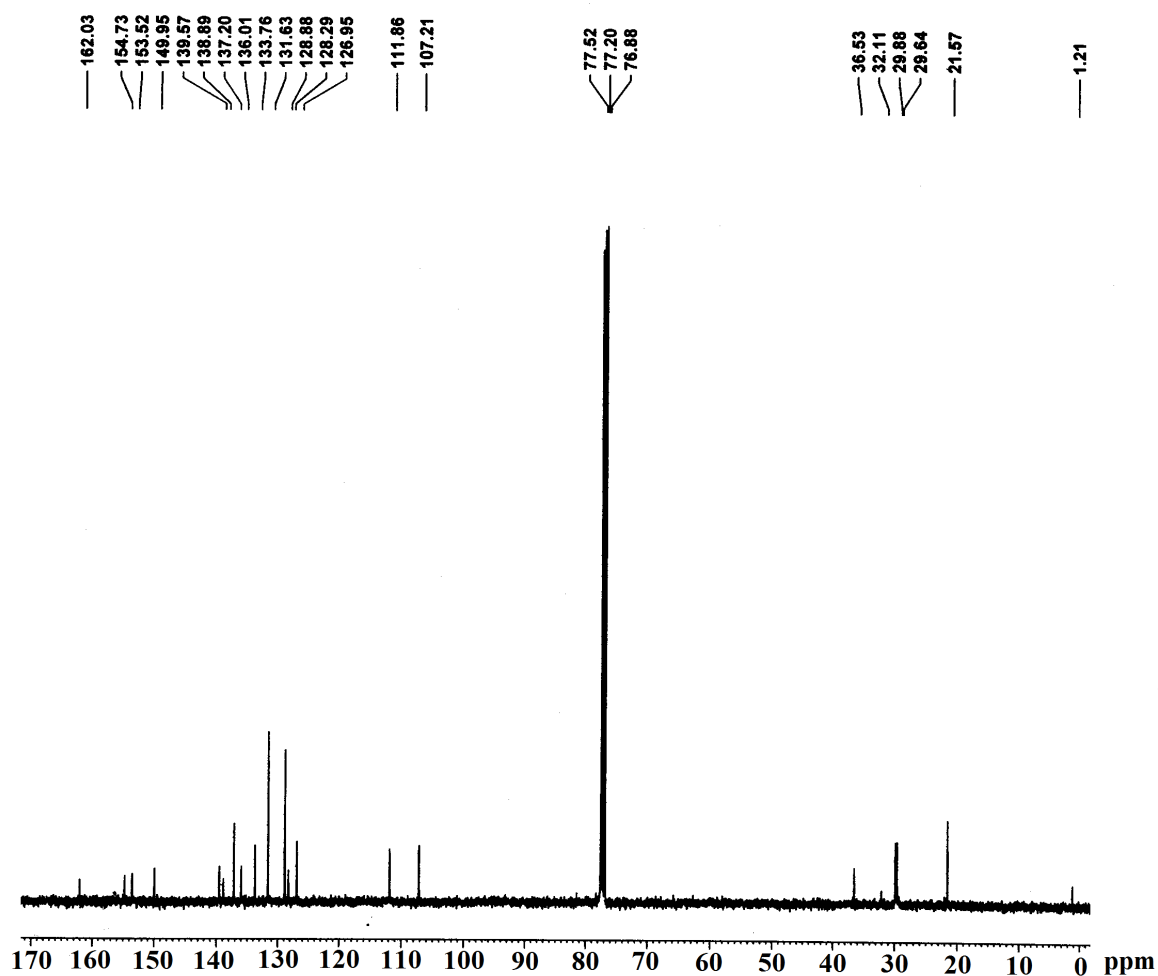
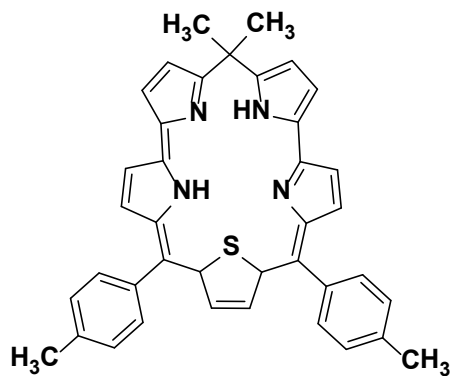


Figure S9. ¹³C NMR spectrum of compound 3 recorded in CDCl₃ at room temperature.

S10

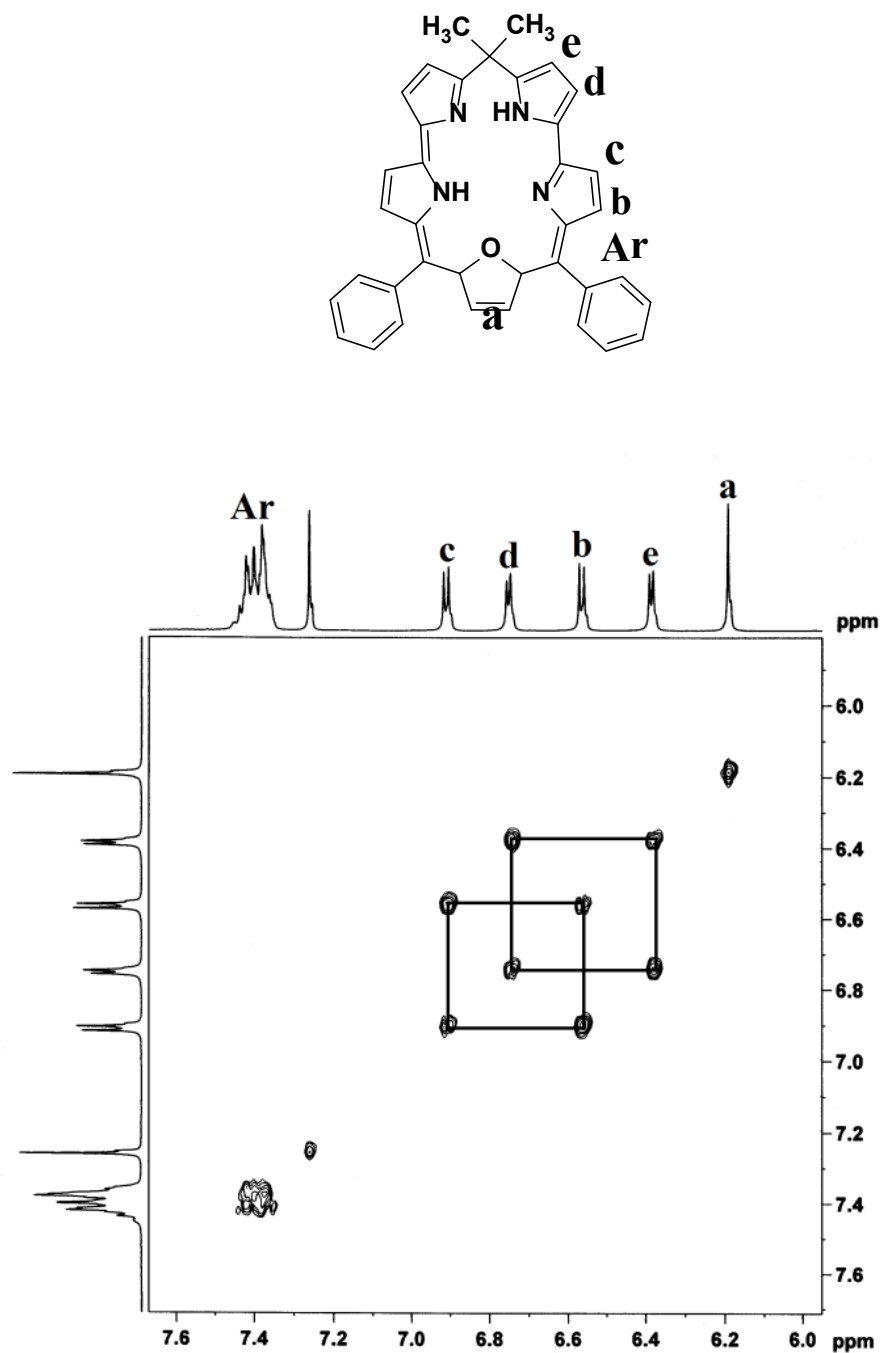


Figure S10. Partial ^1H - ^1H COSY NMR spectrum of compound **2a** recorded in CDCl_3 at room temperature.

S11

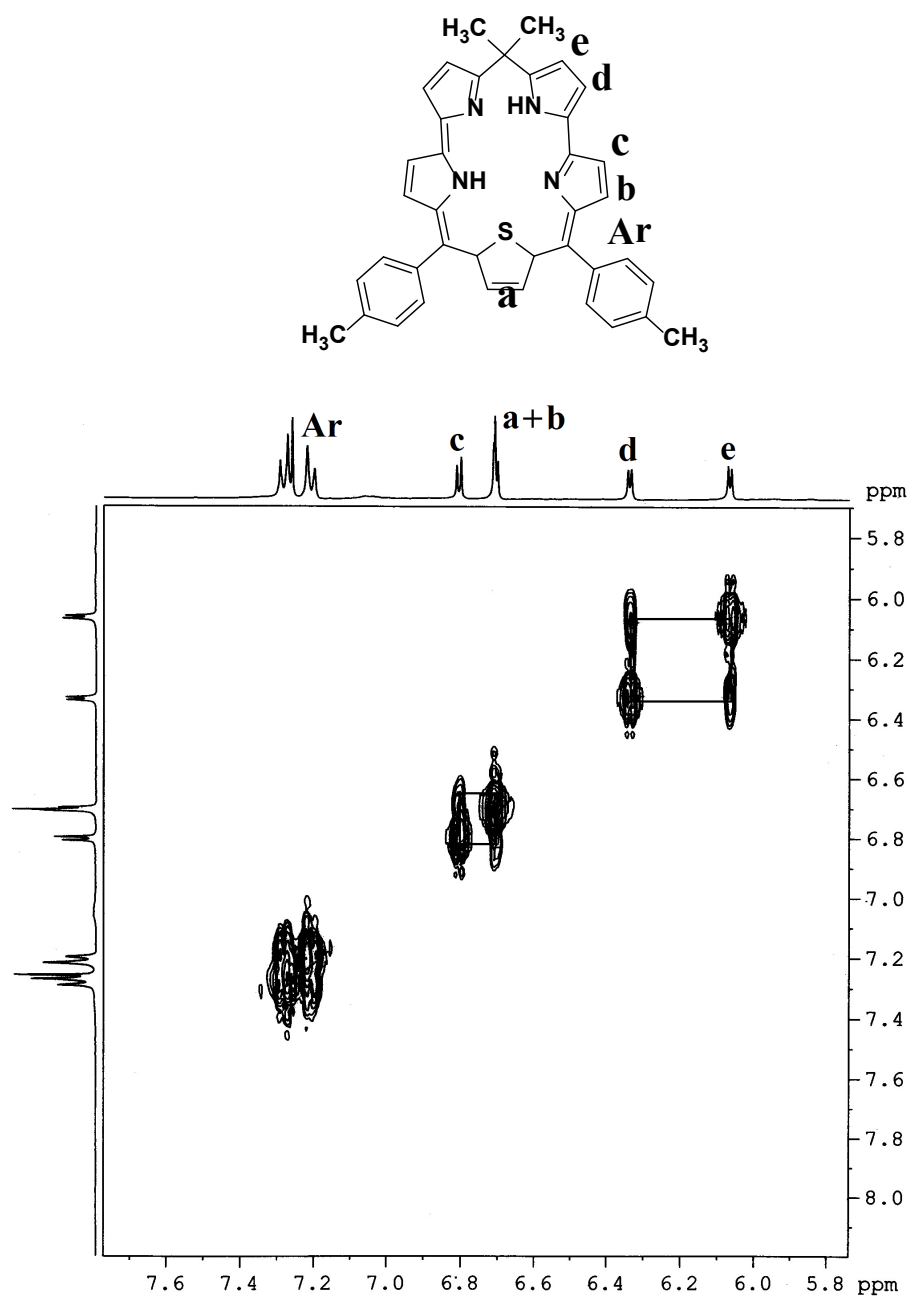


Figure S11. Partial ^1H - ^1H COSY NMR spectrum of compound **3** recorded in CDCl_3 at room temperature.

S12

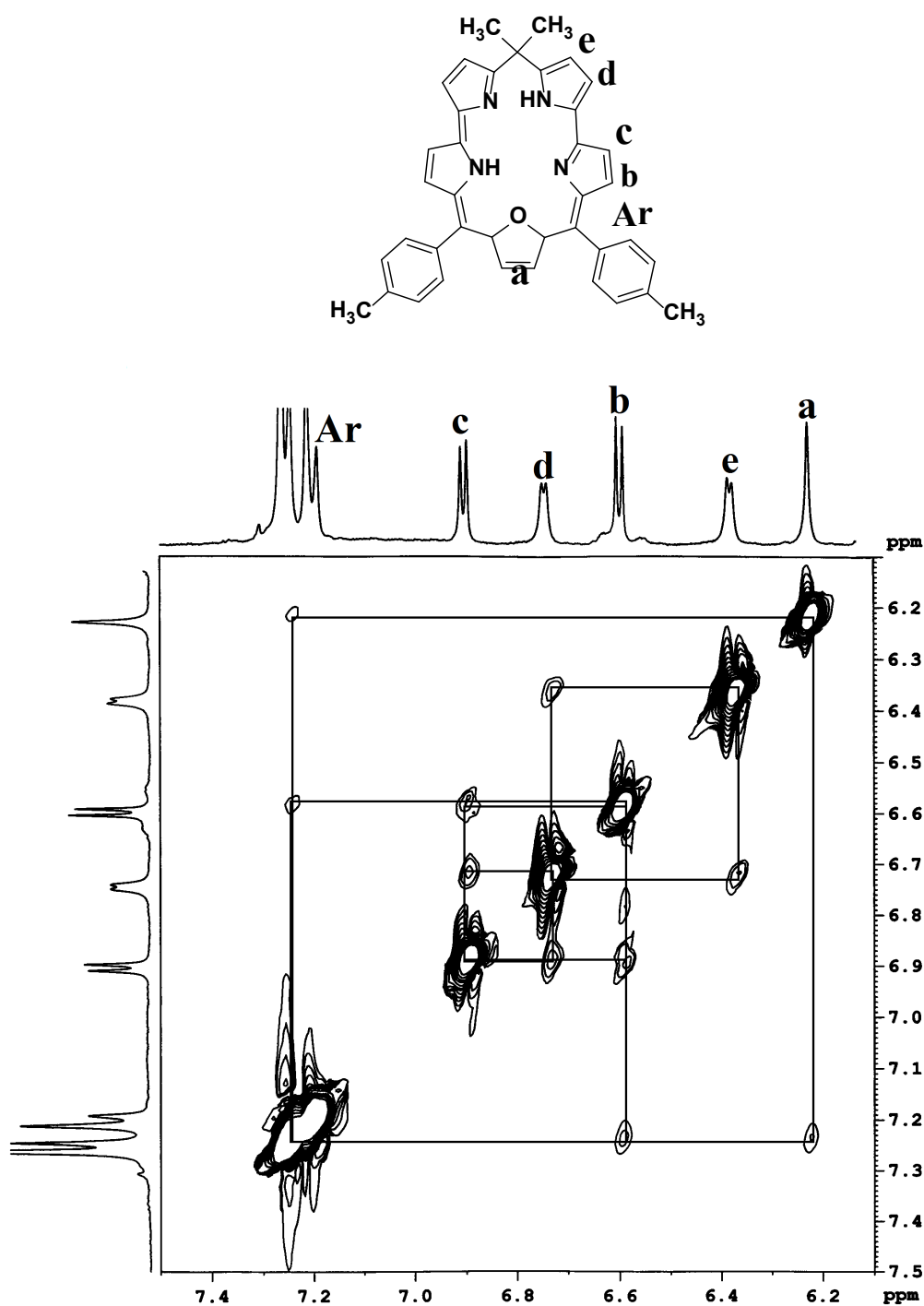


Figure S12. Partial ^1H - ^1H NOESY NMR spectrum of compound **2b** recorded in CDCl_3 at room temperature.

S13

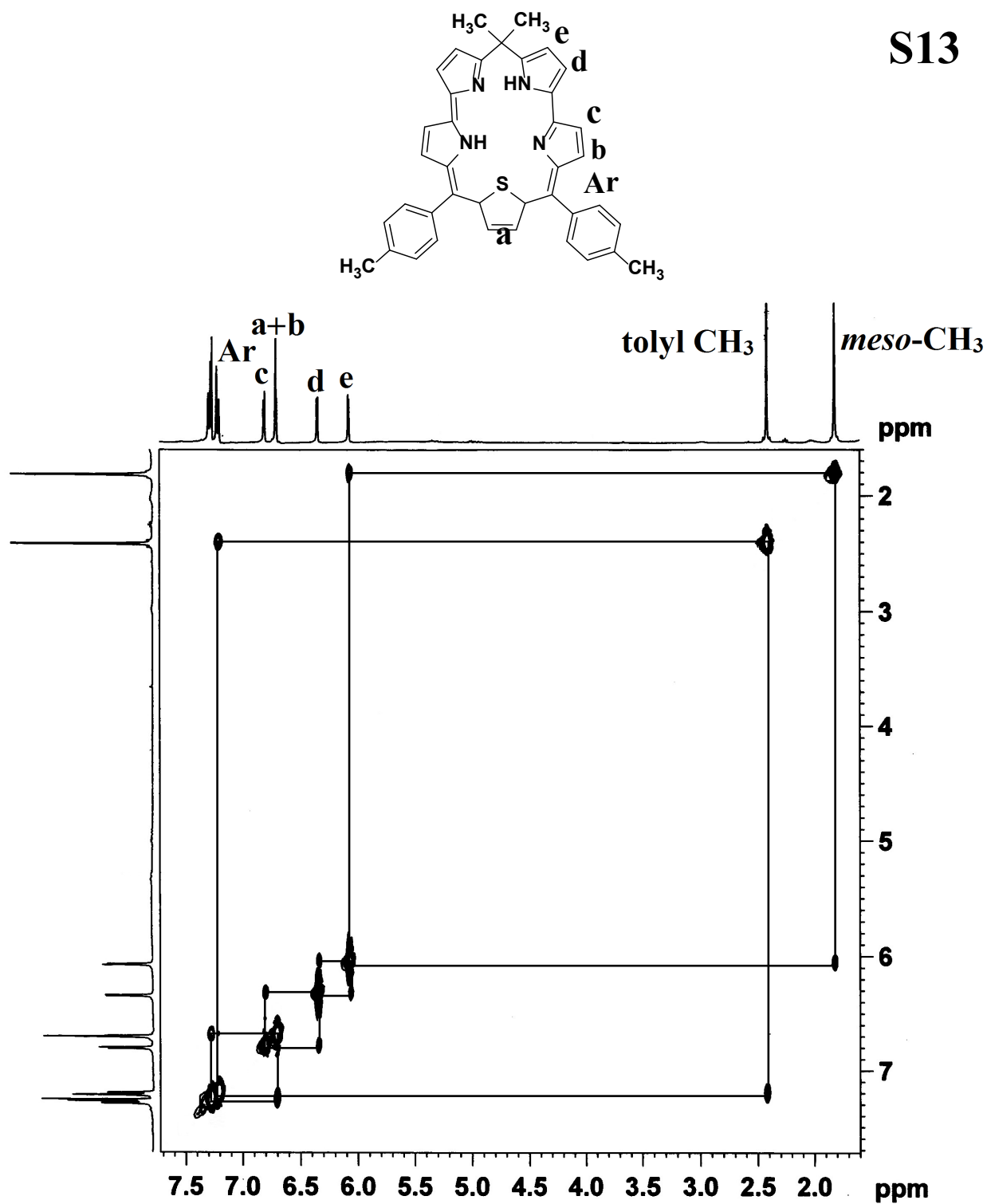


Figure S13. ^1H - ^1H NOESY NMR spectrum of compound 3 recorded in CDCl_3 at room temperature.

S14

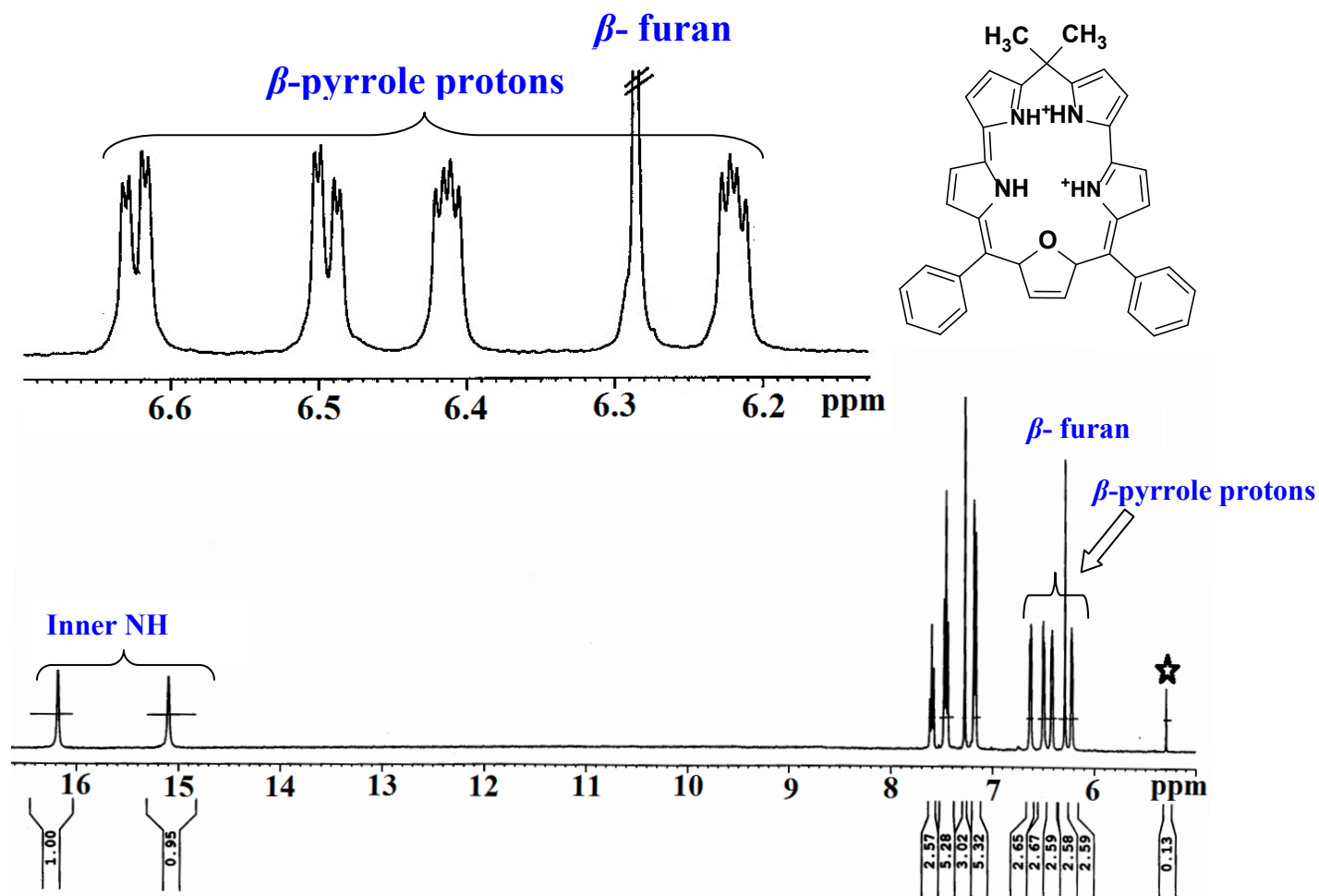


Figure S14. Partial ^1H NMR spectrum of compound **2a.2H²⁺** recorded in CDCl_3 (★ residual solvent peak) at room temperature.

S15

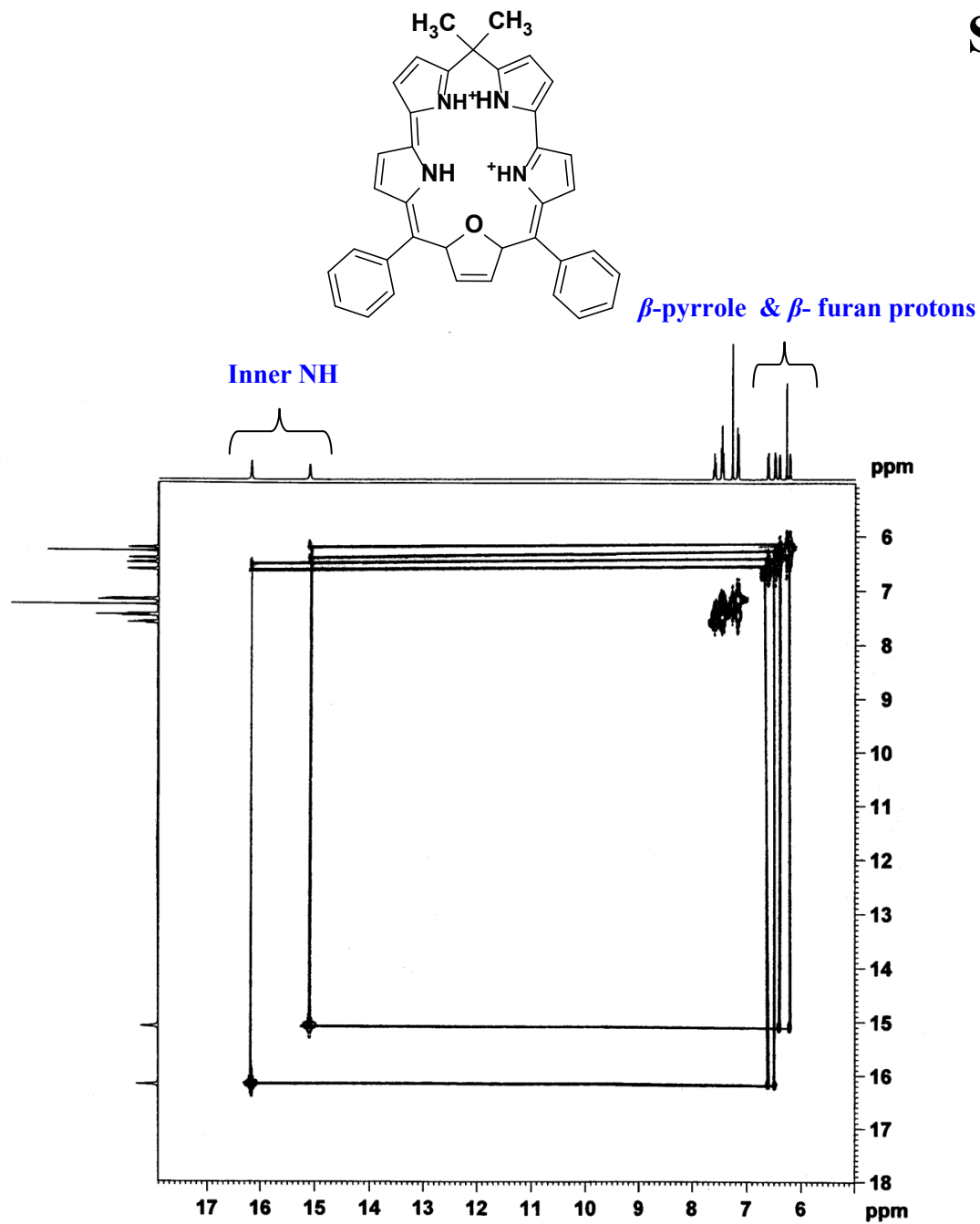


Figure S15. Partial ¹H-¹H COSY NMR spectrum of compound **2a.2H²⁺** showing the cross-peak connectivities between inner NH protons and β-pyrrole and β-furan protons recorded in CDCl₃ at room temperature.

S16

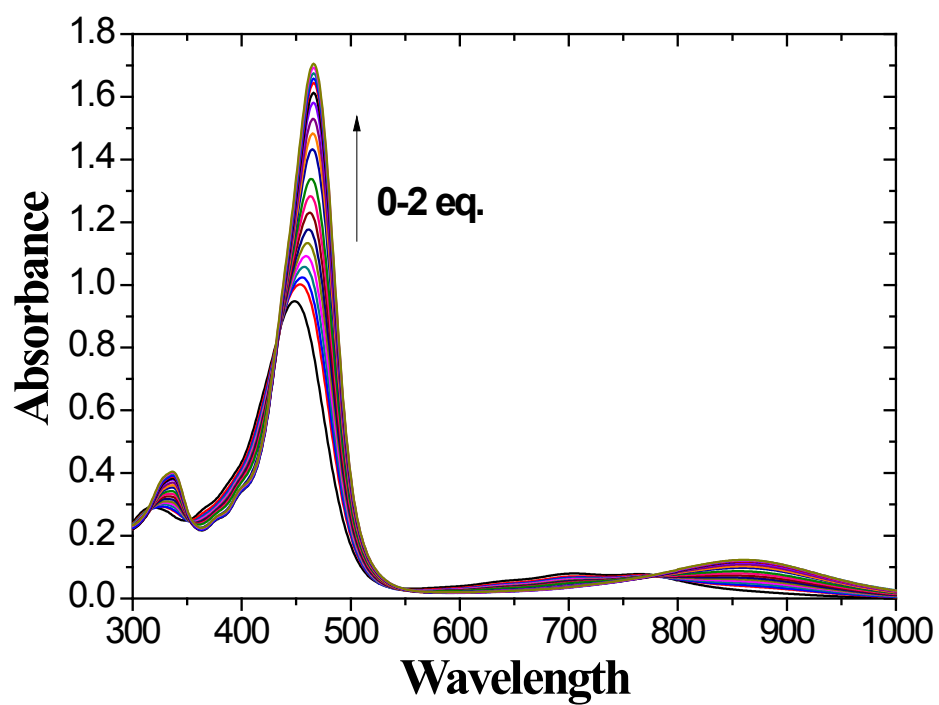


Figure S16. Change in absorption spectra of compound **2b** (1x10⁻⁵ M) upon systematic addition of TFA solution (0-2 equiv.) in CHCl₃ solution.

S17

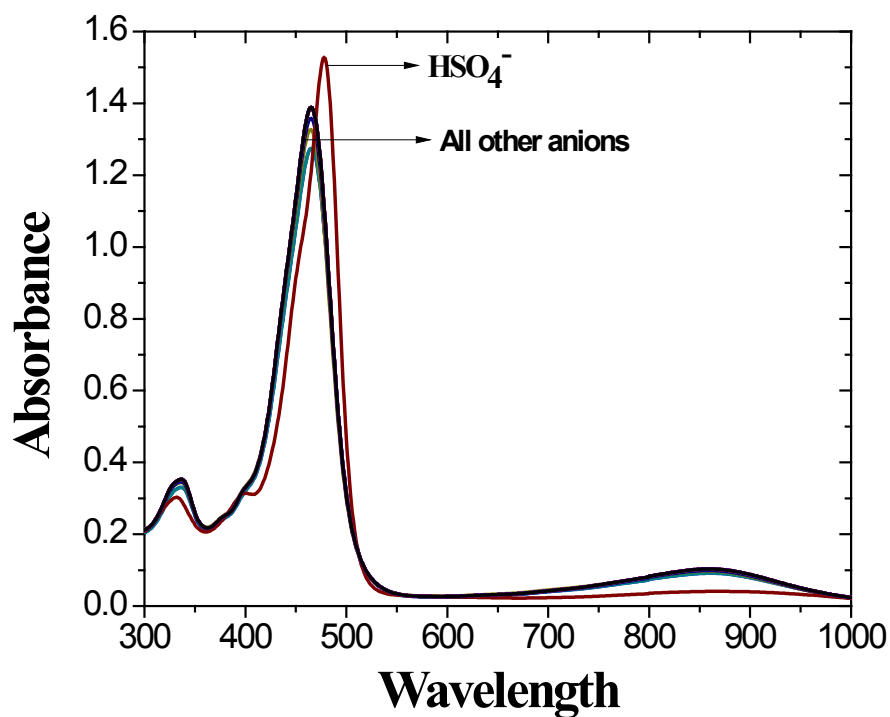


Figure S17. Absorption spectra of compound **2b.2H**²⁺ (1 × 10⁻⁵ M) in the presence of various anions such as F⁻, Cl⁻, Br⁻, I⁻, ClO₄⁻, CH₃COO⁻, H₂PO₄⁻, HPO₄⁻², HSO₄⁻, SO₄⁻, SCN⁻, S₂O₃⁻, NO₃⁻ and N₃⁻ (excess of equivalents) recorded in CHCl₃ solution.

S18

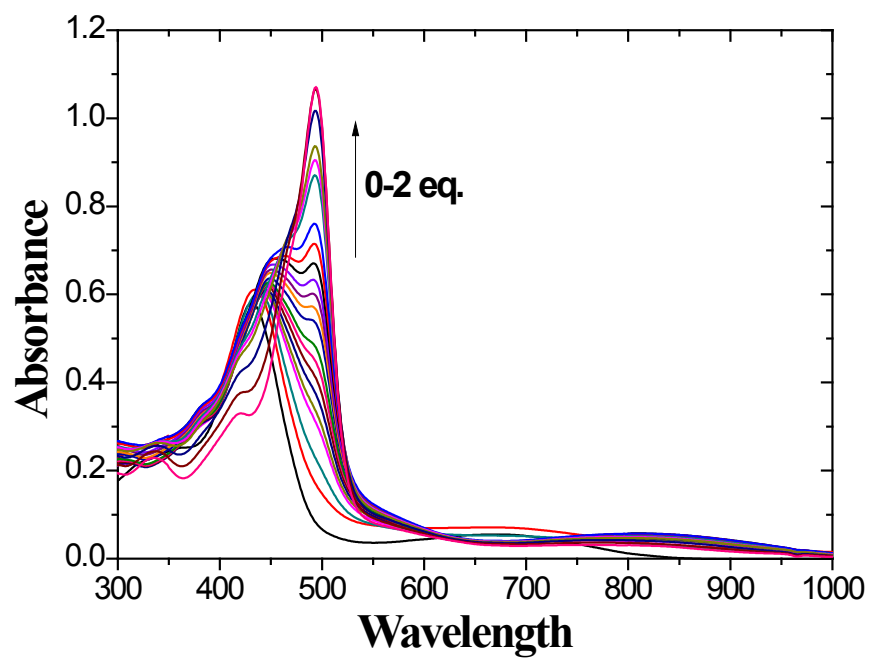


Figure S18. Change in absorption spectra of compound **3** (1x10⁻⁵ M) upon systematic addition of TFA solution (0-2 equiv.) in CHCl₃ solution.

S19

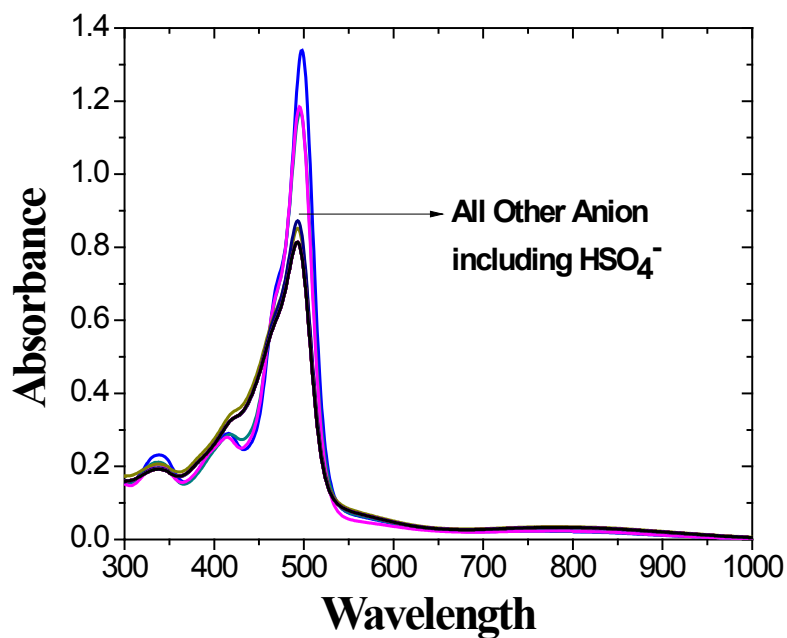


Figure **S19**. Absorption spectra of compound $3.2H^{+2}$ (1×10^{-5} M) in the presence of various anions F^- , Cl^- , Br^- , I^- , ClO_4^- , CH_3COO^- , $H_2PO_4^-$, HPO_4^{2-} , HSO_4^- , SO_4^{2-} , SCN^- , $S_2O_3^{2-}$, NO_3^- and N_3^- (excess of equivalents) recorded in $CHCl_3$ solution.

S20

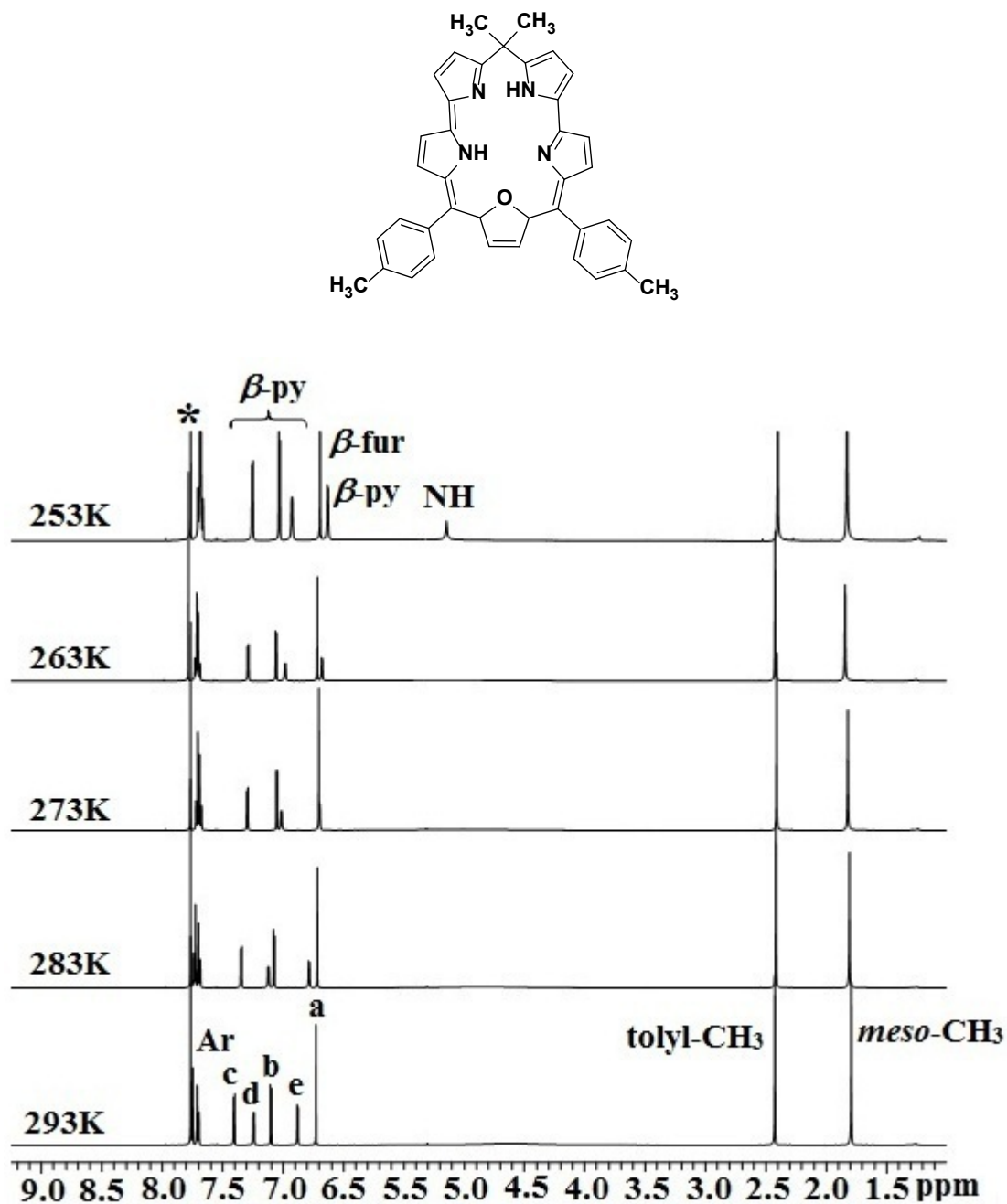


Figure S20. Variable temperature ¹H NMR spectra of compound **2b** recorded in the temperature range 20°C to -20°C in CDCl₃ (* CDCl₃ peak).

S21

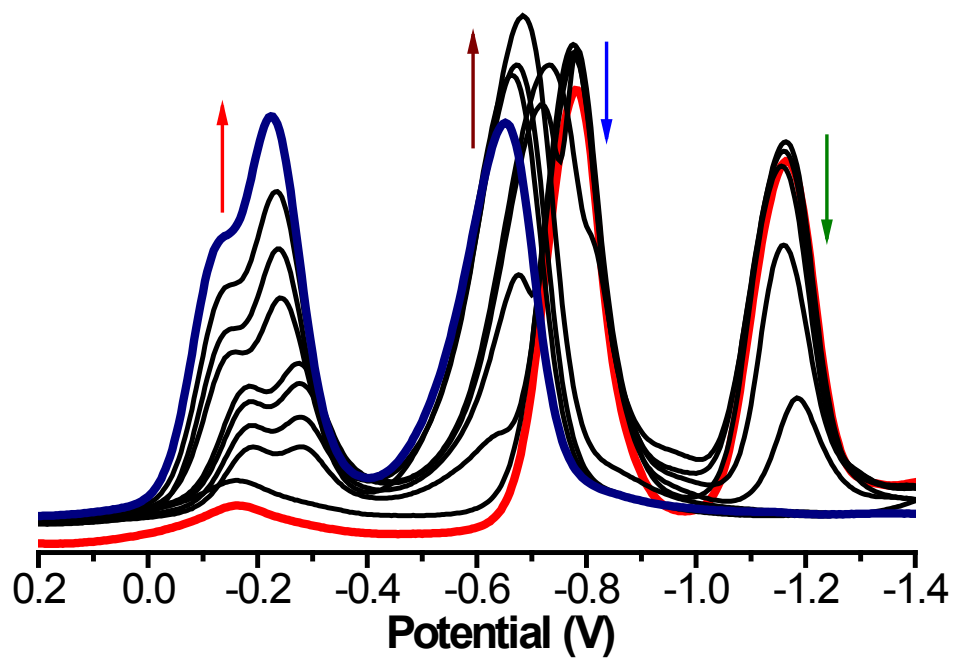


Figure S21. Square Wave Voltamogram of compound **2b** (1.2×10⁻² M) upon titration with HSO₄⁻ ion (0-20 equiv.) recorded in CH₂Cl₂ containing 0.1 M TBAP as supporting electrolyte at scan rates of 50 mVs⁻¹.

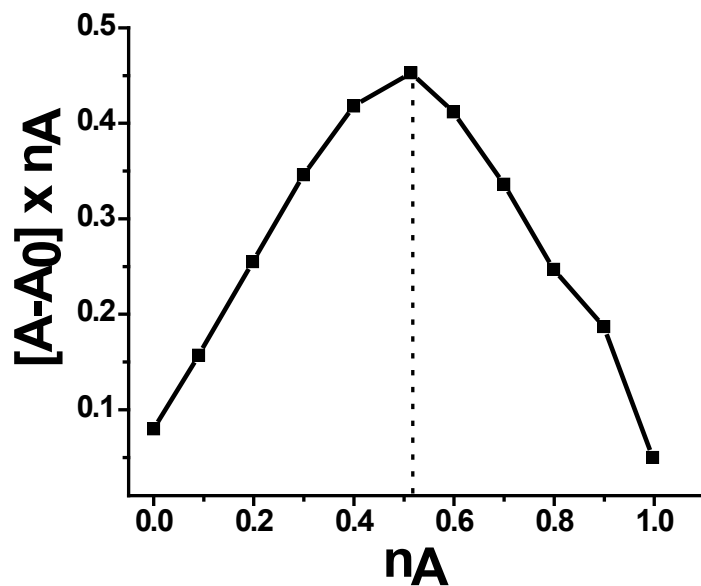
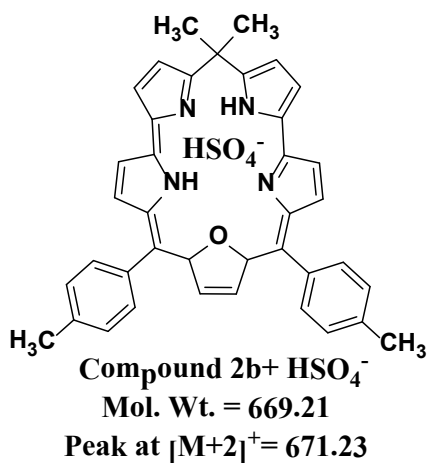


Figure S22. Job's plot for evolution of binding stoichiometry between Compound **2b** and HSO_4^- in CHCl_3 solution. Where n_A is mole fraction of the anion added and A is absorbance of compound **2b** in the presence of anion and A_0 is the absorbance of compound **2b** in the absence of anion which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



Indian Institute of Technology (B)

Analysis Info

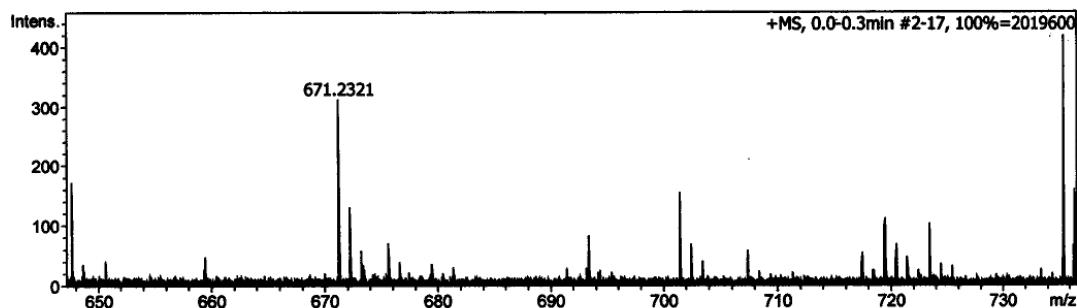
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Method Tune_pos_Standard_NAI-1000.m
Sample Name MR-TC-TITRA-2
Comment C39H33N4O5S

Acquisition Date 8/26/2013 6:39:53 PM

Operator mrk
Instrument maXis impact 282001.00081

Acquisition Parameter

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Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdB	e ⁻ Conf	N-Rule
671.2321	1	C39H35N4O5S	671.2323	0.2	765.2	1	-1.#J	24.5	even	ok

Figure S23. HR-MS spectrum of compound 2b+ HSO₄⁻ 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)