Synthesis of Stable Nonaromatic Phenothiazinophyrins

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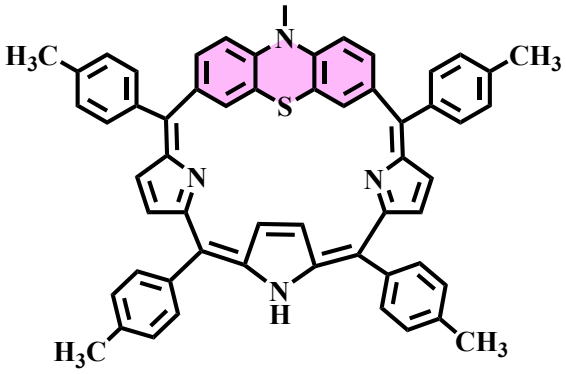
Sr. no	Details	Page no.
1	General Experimental Section	S2
2	**Figures S1-S20.** Characterization (HRMS and NMR) data for compounds **2-4**.	S3-S22
3	**Figure S21-S23.** The absorption spectra and redox data of Compounds **2-4**.	S23-S25
4	**Table S1.** Selected TD-DFT calculated oscillator strengths and compositions of the major electronic transitions of **2**	S26
5	**Table S2.** Cartesian coordinate of the optimized (S_0) geometries of the compound **2**	S27-S28
6	References	S29

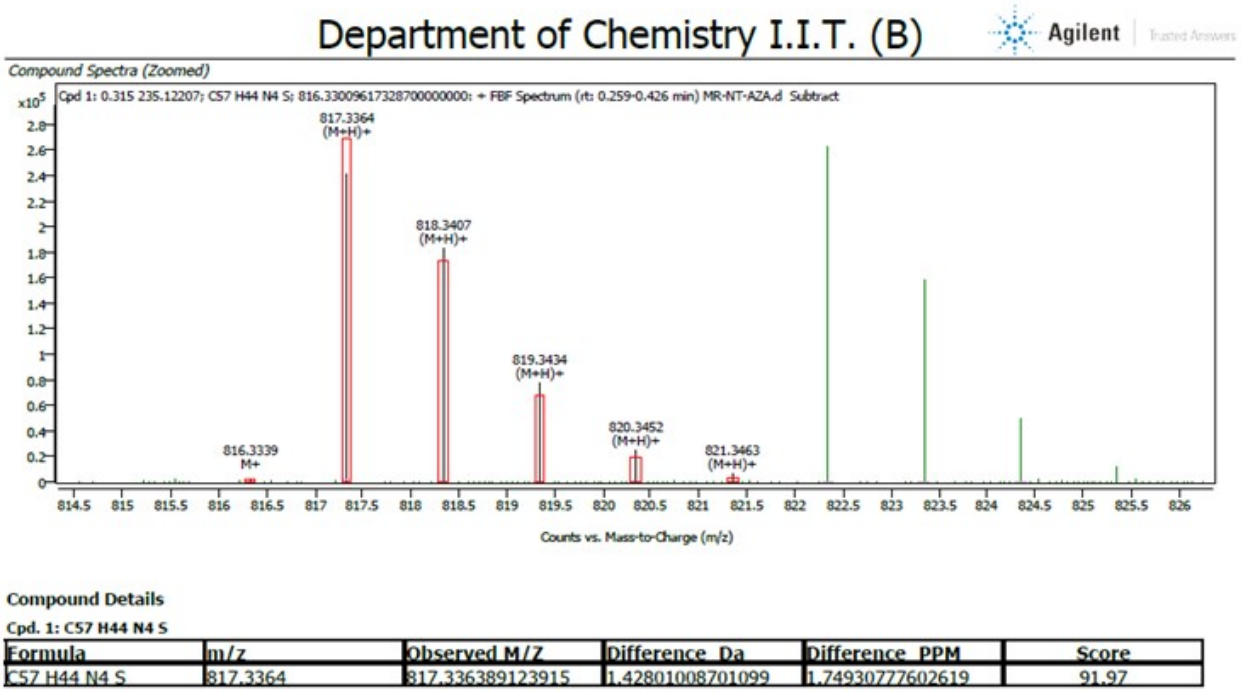
Experimental Section

General Information: All chemicals including Boron trifluoride etherate ($BF_3{\cdot}OEt_2$), 2, 3-dichloro-5, 6-dicyano-1, 4- benzoquinone (DDQ) were procured from Aldrich and used as received. Basic alumina and silica gel (60-120 mesh) column chromatographic methods were used for purification purposes. Reported methods were used for the synthesis of compounds**, 5**, **6,** and **7**.[1-5] The ^1H & ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker 400 and 500 MHz instruments. The ^{13}C NMR frequencies are 125.77 and 100.06 MHz for 500 MHz and 400 MHz instruments respectively. Shimadzu UV-Visible-NIR Spectrophotometer was used for carrying out absorption spectral studies. Cyclic voltammetry (CV) studies were performed with BAS electrochemical system with the three-electrode configuration comprising of a saturated calomel electrode (reference electrode), glassy carbon (working electrode), (auxiliary electrode) and 10^{-3} M of the analyte. Bruker maXis Impact and Q-TOF micro mass spectrometer instrument was used for recording HR mass spectra.

Computational information: For all the calculations Gaussian 09 program package was used. The density functional theory (DFT)[7] method, hybrid functional B3LYP in conjunction with basis set 6-31G(d,p)[8] helped to optimize the structure of compound **2** (S_0) states. To obtain the oscillator strengths, identical basis and functional hybrid set were used whereas the vertical excitation energies were obtained by the help of TD-DFT techniques for $S_0 \rightarrow S_n$ transitions.[9] Under the Polarisable Continuum Model (PCM)[10] in the toluene media all the computations were done using the Self-Consistent Reaction Field (SCRF). The electronic absorption spectra as well as the oscillator strengths were thoroughly examined using TD-DFT with PCM model based on the optimized structures in the S_0 state.



Compound 2



Compound Details

Cpd. 1: C57 H44 N4 S

Formula	m/z	Observed M/Z	Difference_Da	Difference_PPM	Score
C57 H44 N4 S	817.3364	817.336389123915	1.42801008701099	1.74930777602619	91.97

Figure S1. HR mass spectrum of compound **2.**

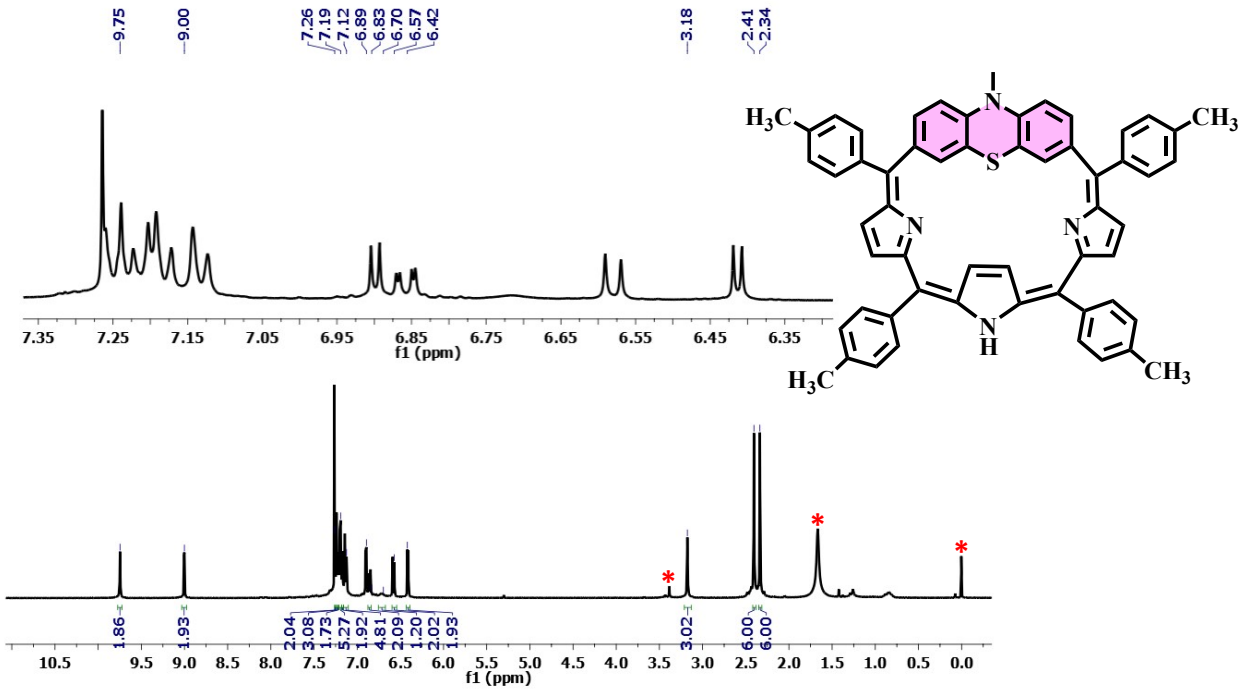


Figure S2. ^{1}H NMR spectrum of the compound **2** recorded in $CDCl_3$ on 400 MHz NMR instrument. Expansion of aromatic region is given as an inset. Note: Peaks marked with asterisk (*) are due to residual solvents.

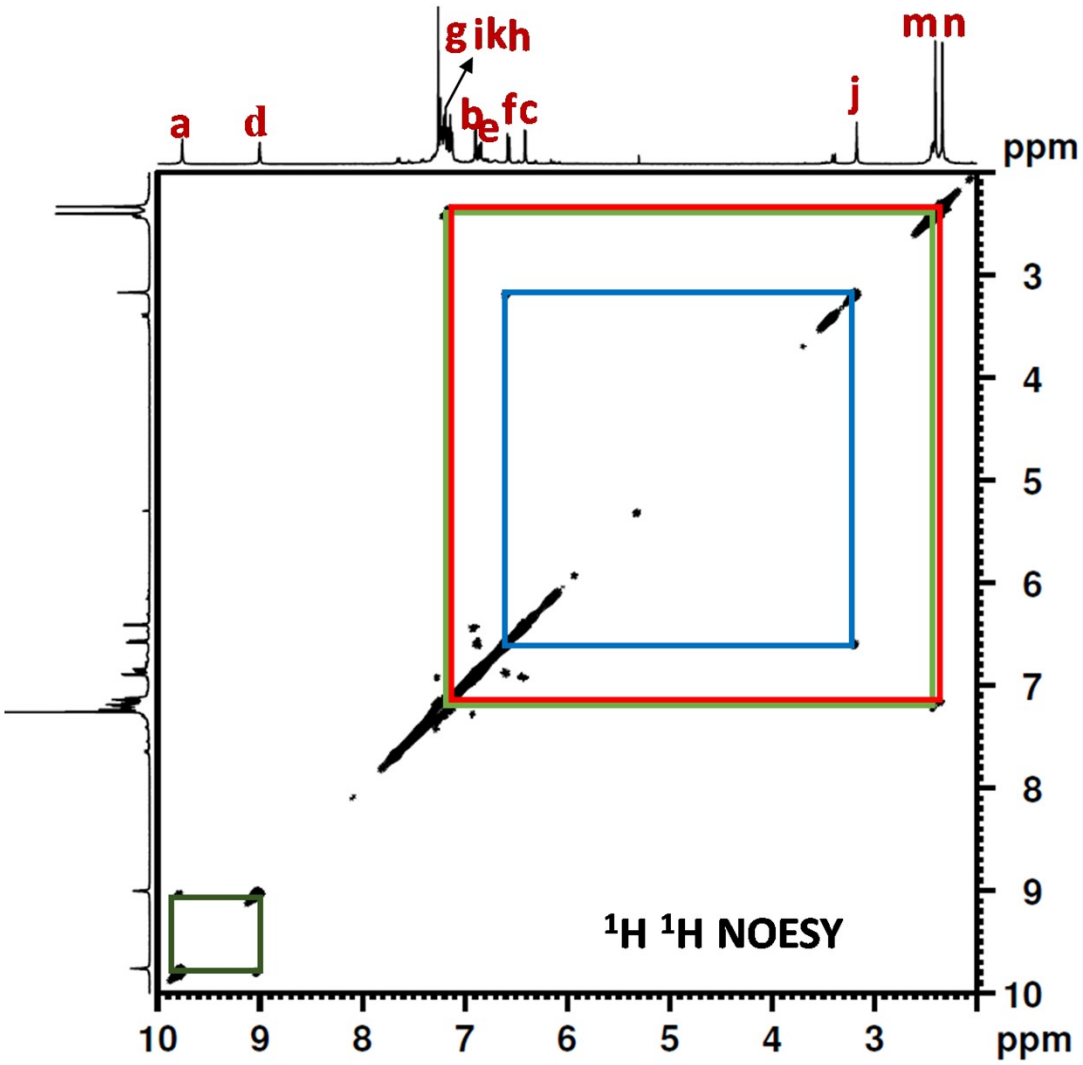


Figure S3. ^{1}H-^{1}H NOESY of compound **2** recorded in $CDCl_3$ at 25 °C.

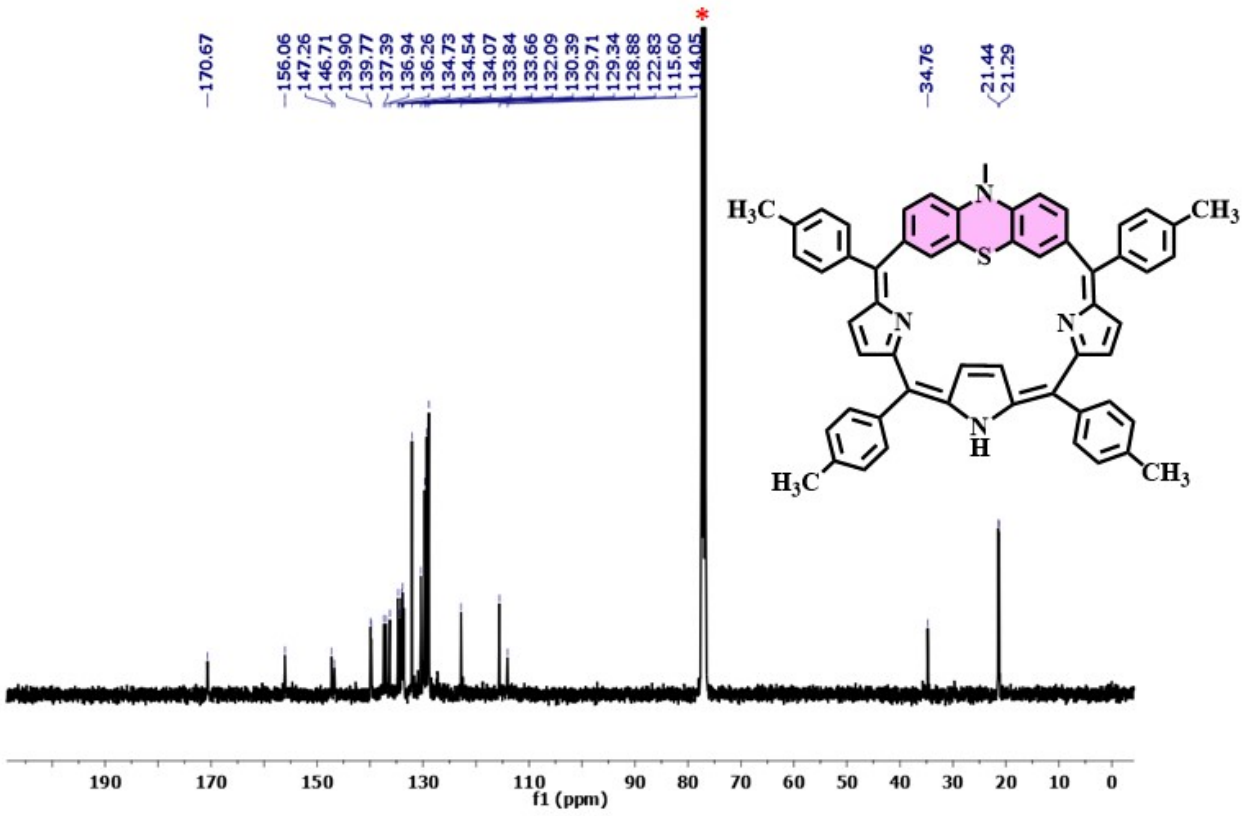
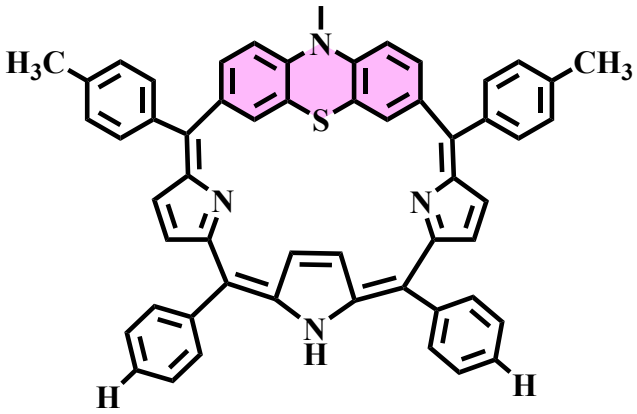


Figure S4. $^{13}C\{1H\}$ NMR spectrum of the compound **2** recorded in $CDCl_3$ on 100.06 MHz NMR instrument; Note: Peaks marked with asterisk (*) are due to residual solvents.



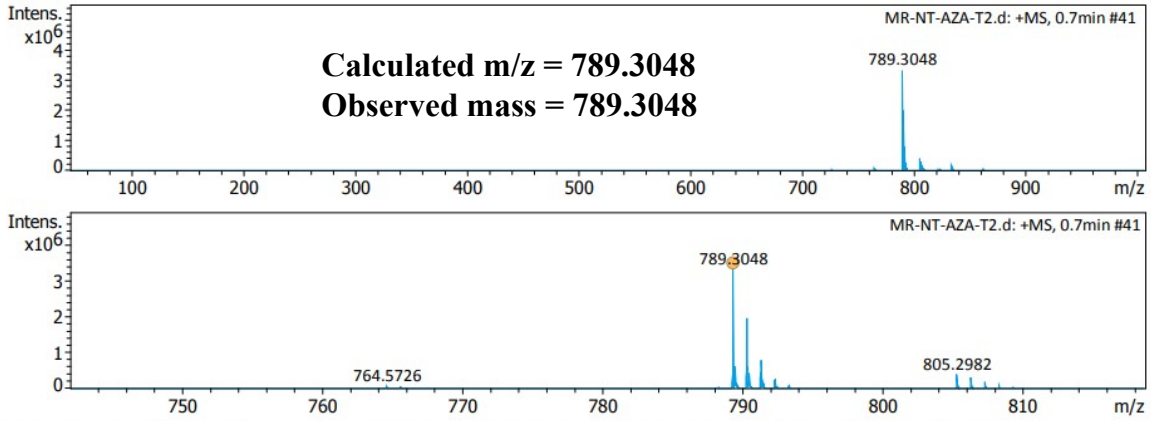
Compound 3

Analysis Info

Analysis Name	D:\Data\MAR-2023\MR-NT-AZA-T2.d	Acquisition Date	3/6/2023 12:18:25 PM
Method	Naformat_pos_1000a.m	Operator	PG SRD OUT
Sample Name	MR-NT-AZA-T2	Instrument	maXis impact 282001.00081
Comment	C55H40N4S		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	3700 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
789.3048	1	C55H41N4S	789.3046	-0.2	13.9	1	100.00	40.0	even	ok

Figure S5. HR mass spectrum of compound **3**.

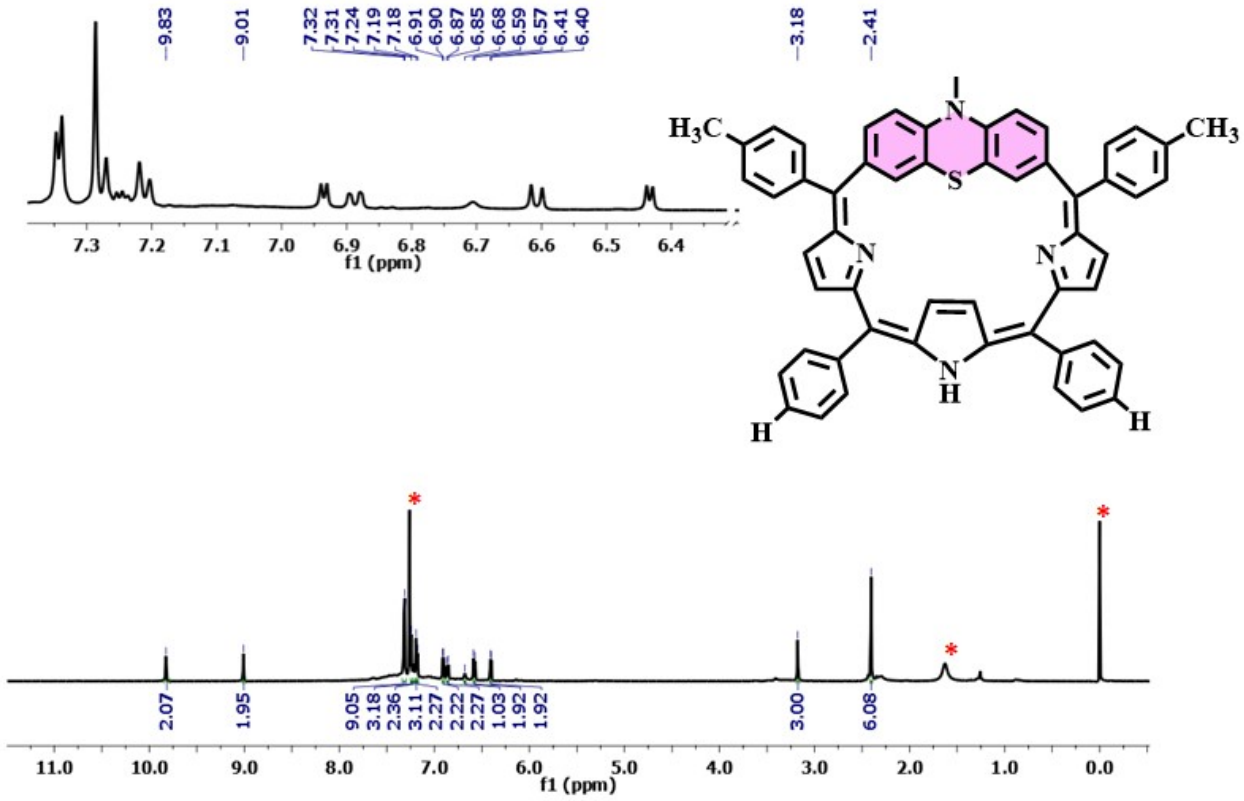


Figure S6. ^{1}H NMR spectrum of the compound **3** recorded in $CDCl_3$ on 500 MHz NMR instrument. Expansion of aromatic region is given as an inset. Note: Peaks marked with asterisk (*) are due to residual solvents.

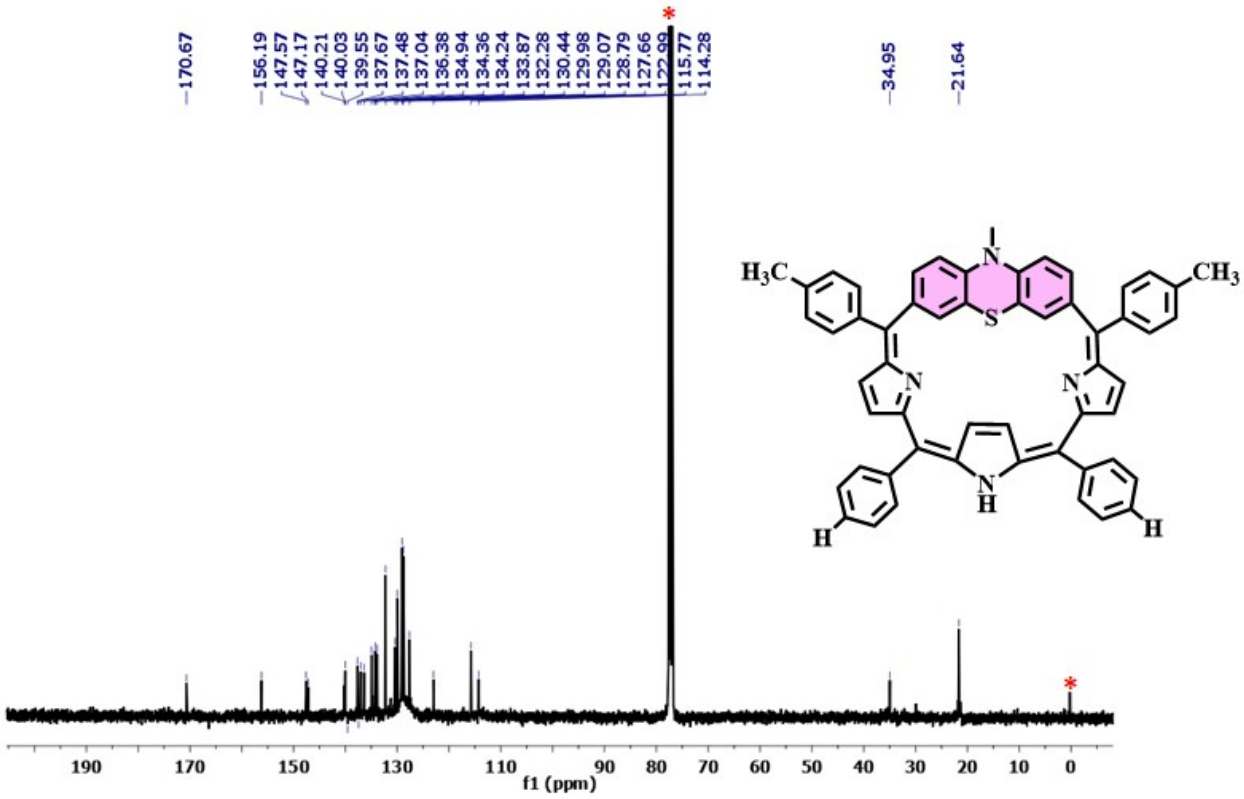
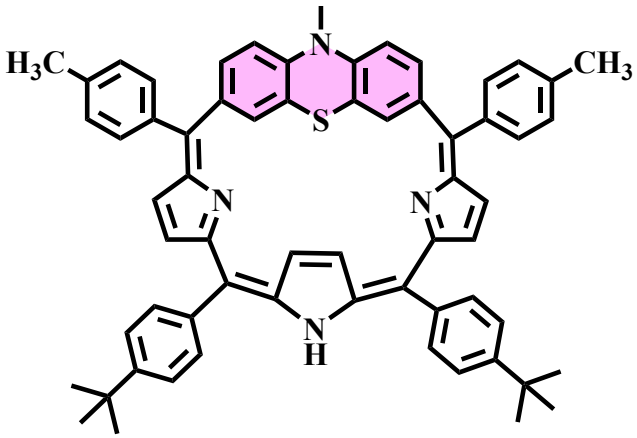


Figure S7. $^{13}C\{1H\}$ NMR spectrum of the compound **3** recorded in $CDCl_3$ on 100.06 MHz NMR instrument; Note: Peaks marked with asterisk (*) are due to residual solvents.



Compound 4

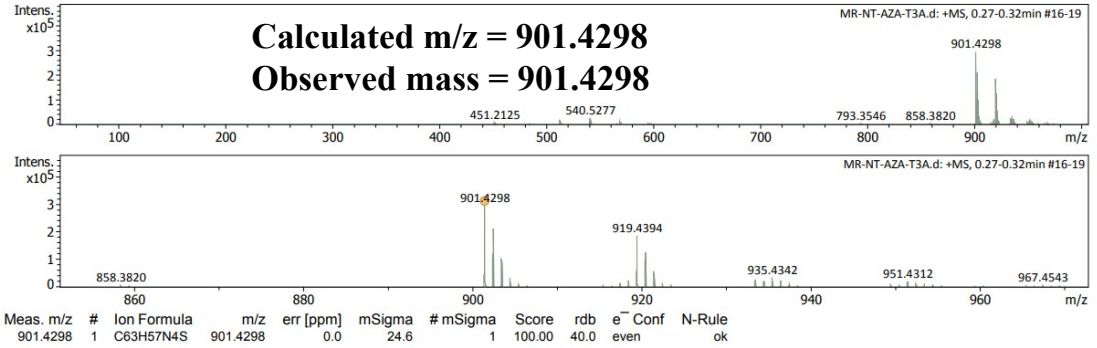
DEPARTMENT OF CHEMISTRY, I.I.T.(B)

Analysis Info

Analysis Name	D:\Data\Oct-2022\MR-NT-AZA-T3A.d	Acquisition Date	10/13/2022 3:13:07 PM
Method	Naformat_pos_50-600.m	Operator	PPI out
Sample Name	MR-NT-AZA-T3A	Instrument	maXis impact 282001.00081
Comment	C63H56N4S		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	3700 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
901.4298	1	C63H57N4S	901.4298	0.0	24.6	1	100.00	40.0	even	ok

Figure S8. HR mass spectrum of compound **4**.

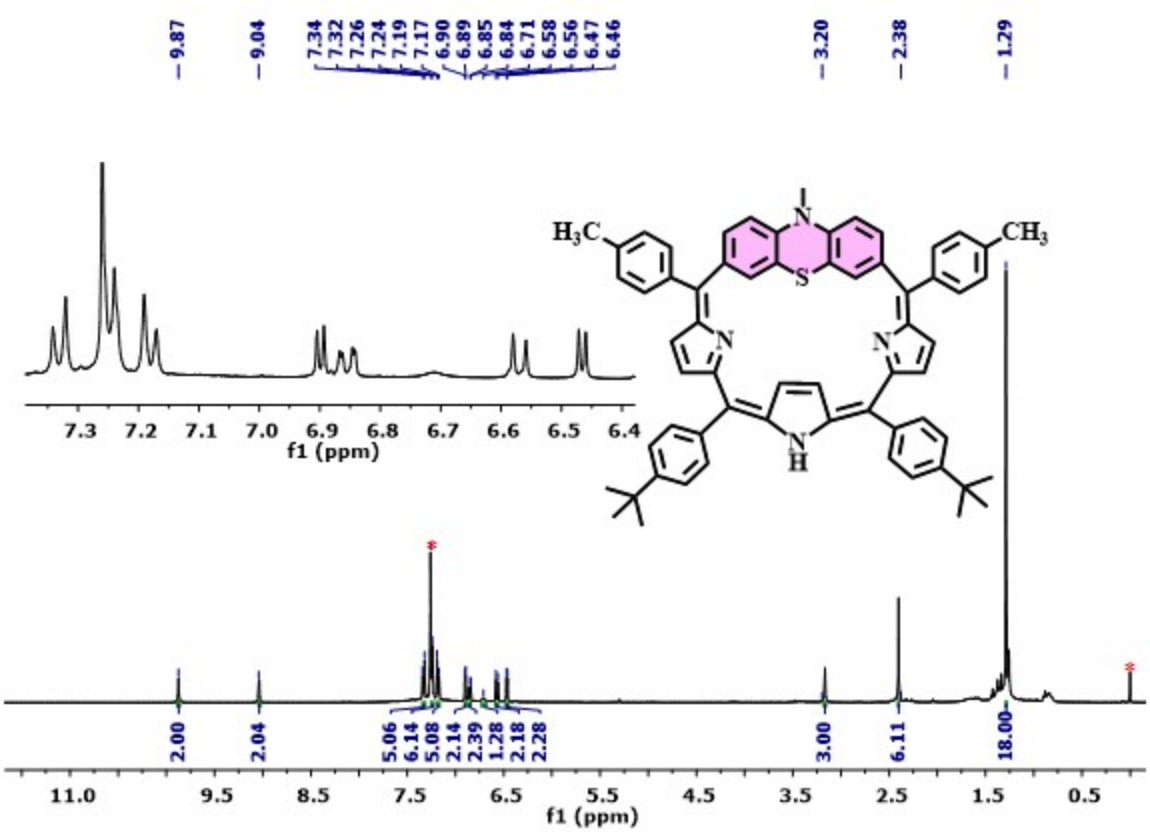


Figure S9. ^{1}H NMR spectrum of the compound **4** recorded in $CDCl_3$ on 500 MHz NMR instrument. Expansion of aromatic region is given as an inset. Note: Peaks marked with asterisk (*) are due to residual solvents.

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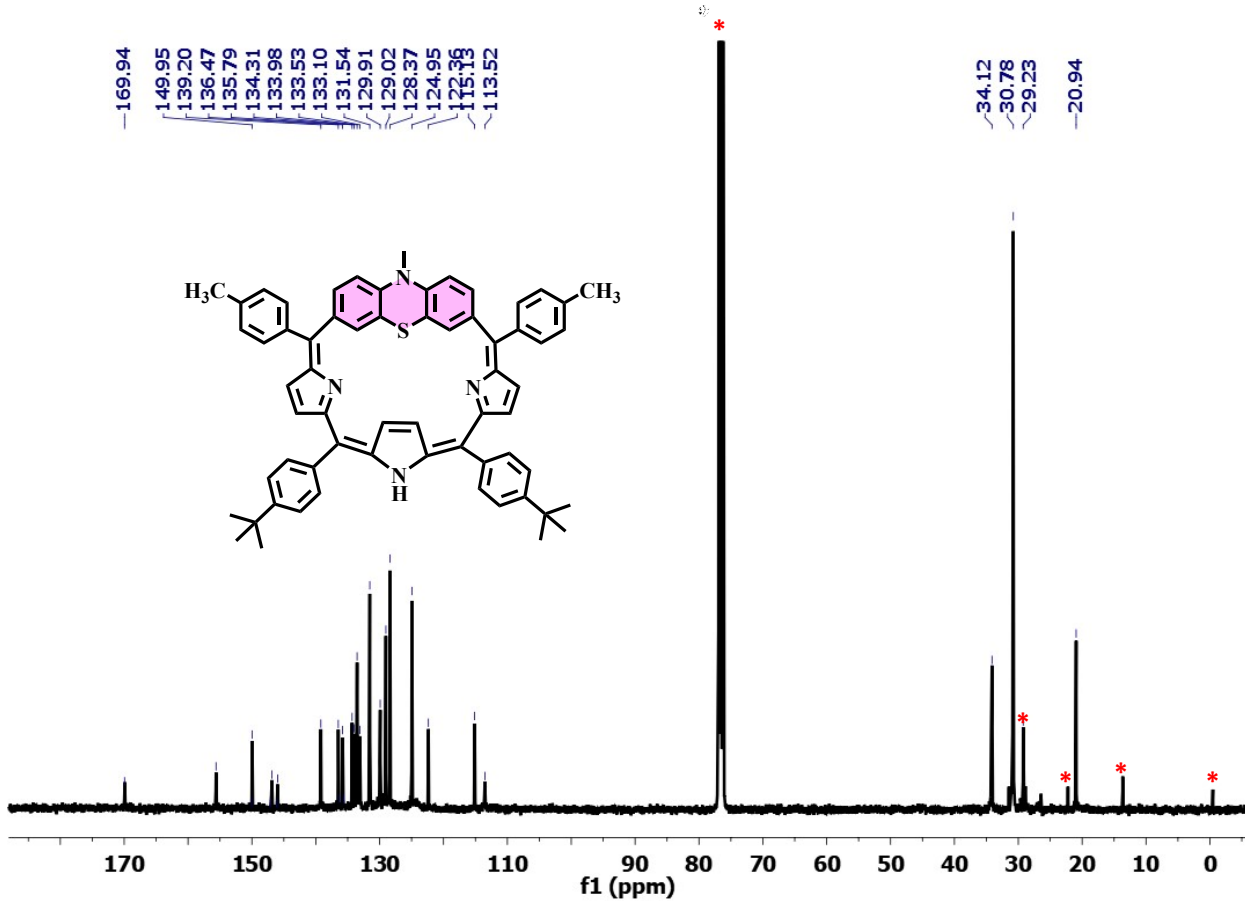


Figure S10. $^{13}C\{1H\}$ NMR spectrum of the compound **4** recorded in $CDCl_3$ on 125.77 MHz NMR instrument; Note: Peaks marked with asterisk (*) are due to residual solvents.

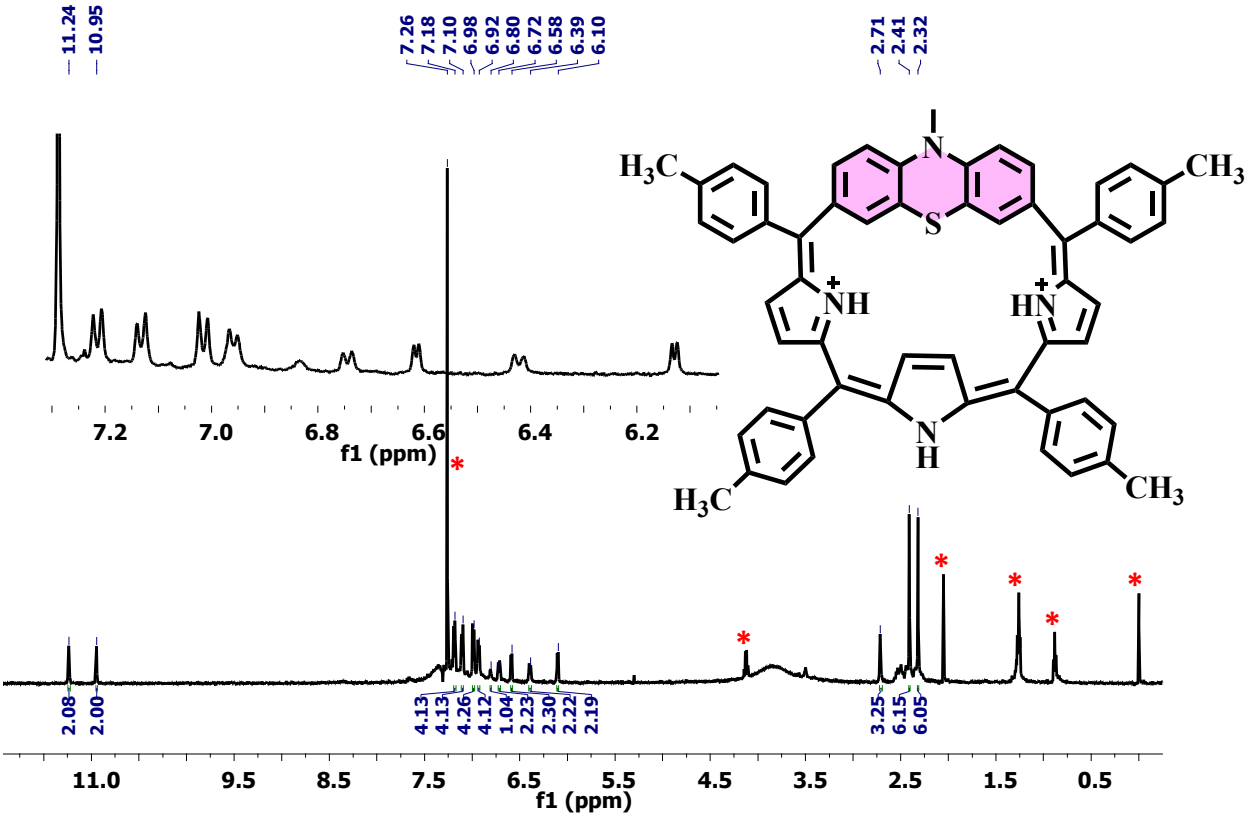


Figure S11. ^{1}H NMR spectrum of the compound **2.2H**$^{+}$ recorded in $CDCl_3$ on 400 MHz NMR instrument. Expansion of aromatic region is given as an inset. Note: Peaks marked with asterisk (*) are due to residual solvents

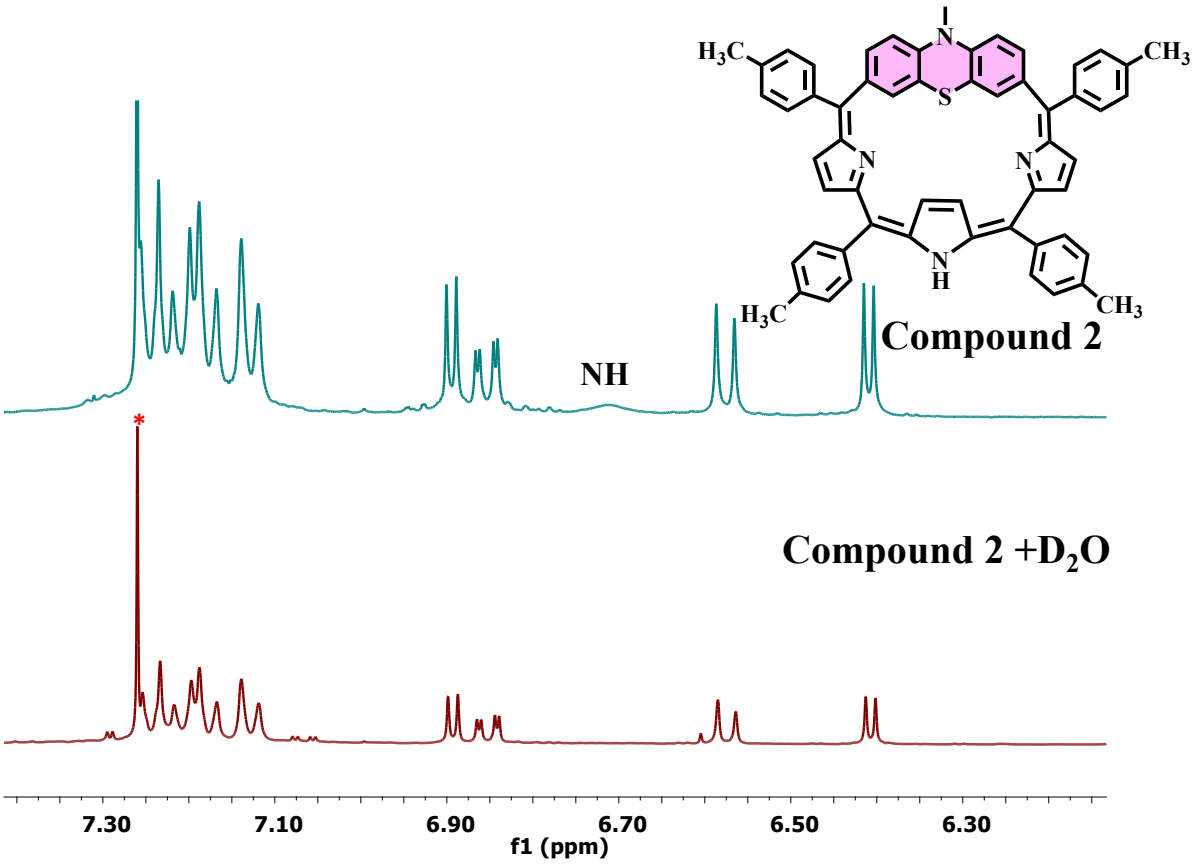
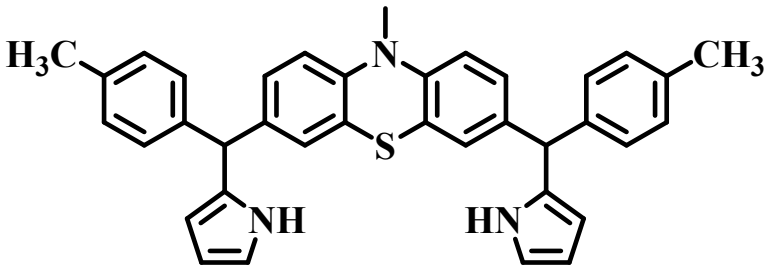


Figure S12. Comparison of partial ^{1}H NMR spectrum of the compound **2** recorded in $CDCl_3$ and D_2O exchange experiment of compound **2** on 400 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents



Compound 5

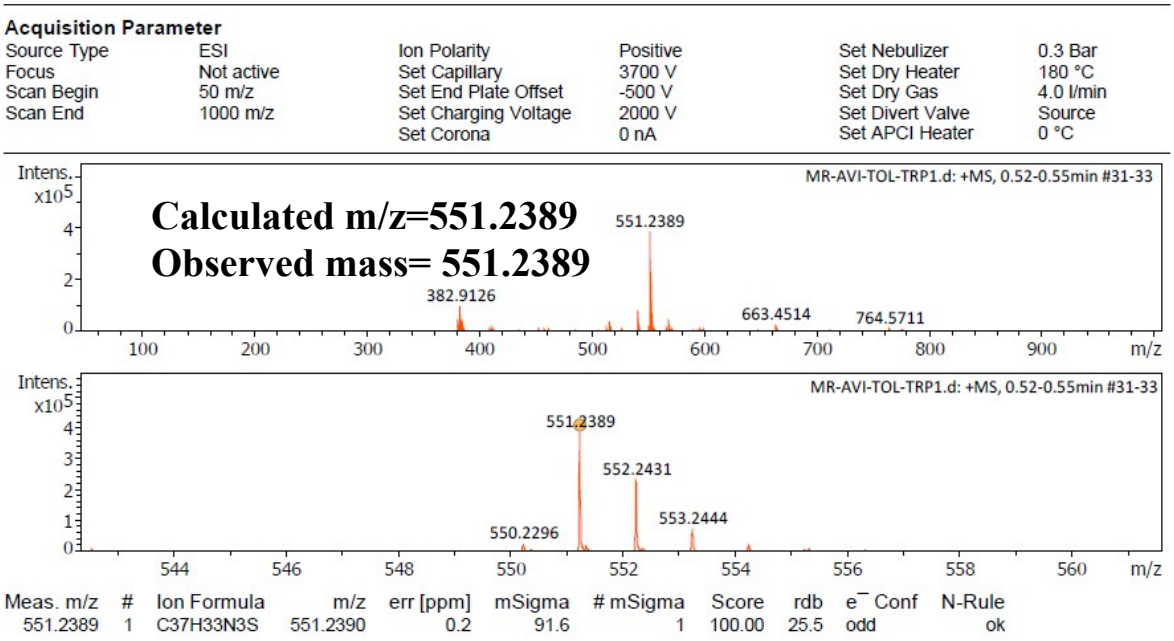


Figure S13. HR mass spectrum of compound **5**.

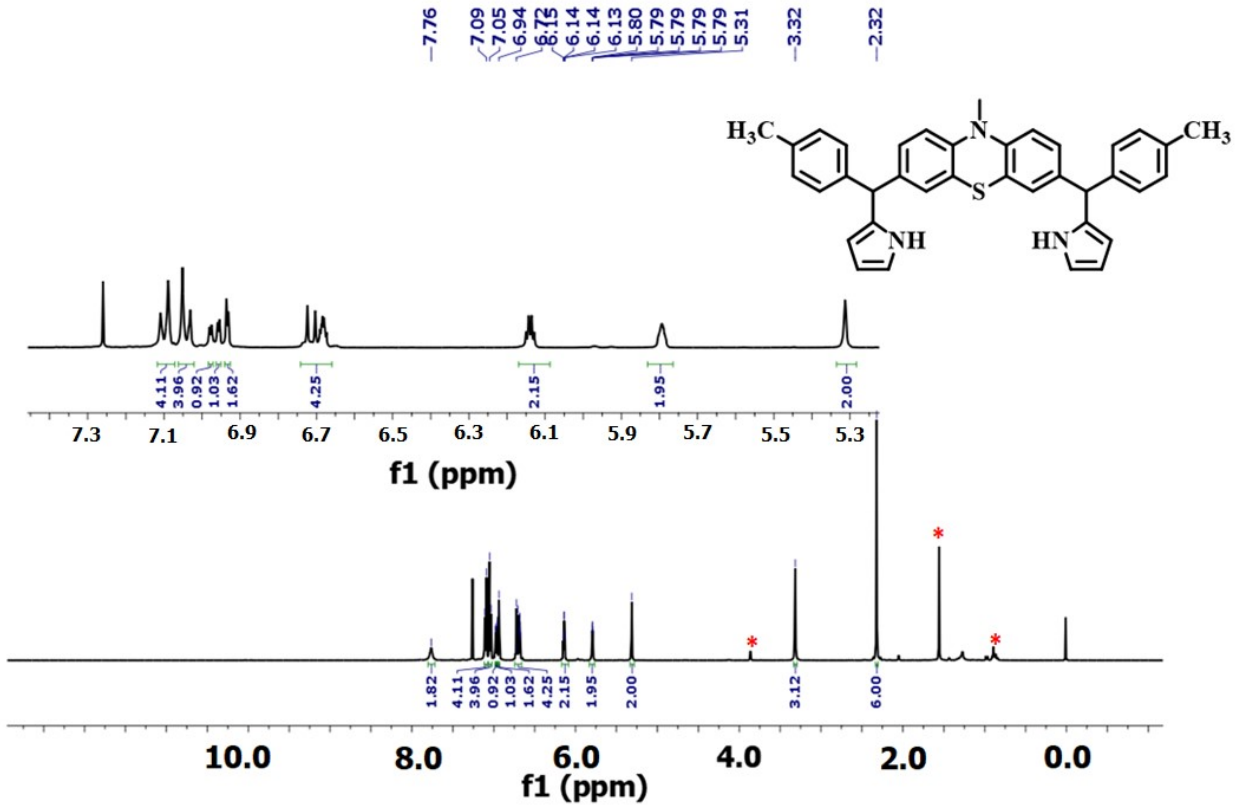


Figure S14. ^{1}H NMR spectrum of the compound **5** recorded in $CDCl_3$ on 400 MHz NMR instrument. Expansion of aromatic region is given as an inset. Note: Peaks marked with asterisk (*) are due to residual solvents.[1]

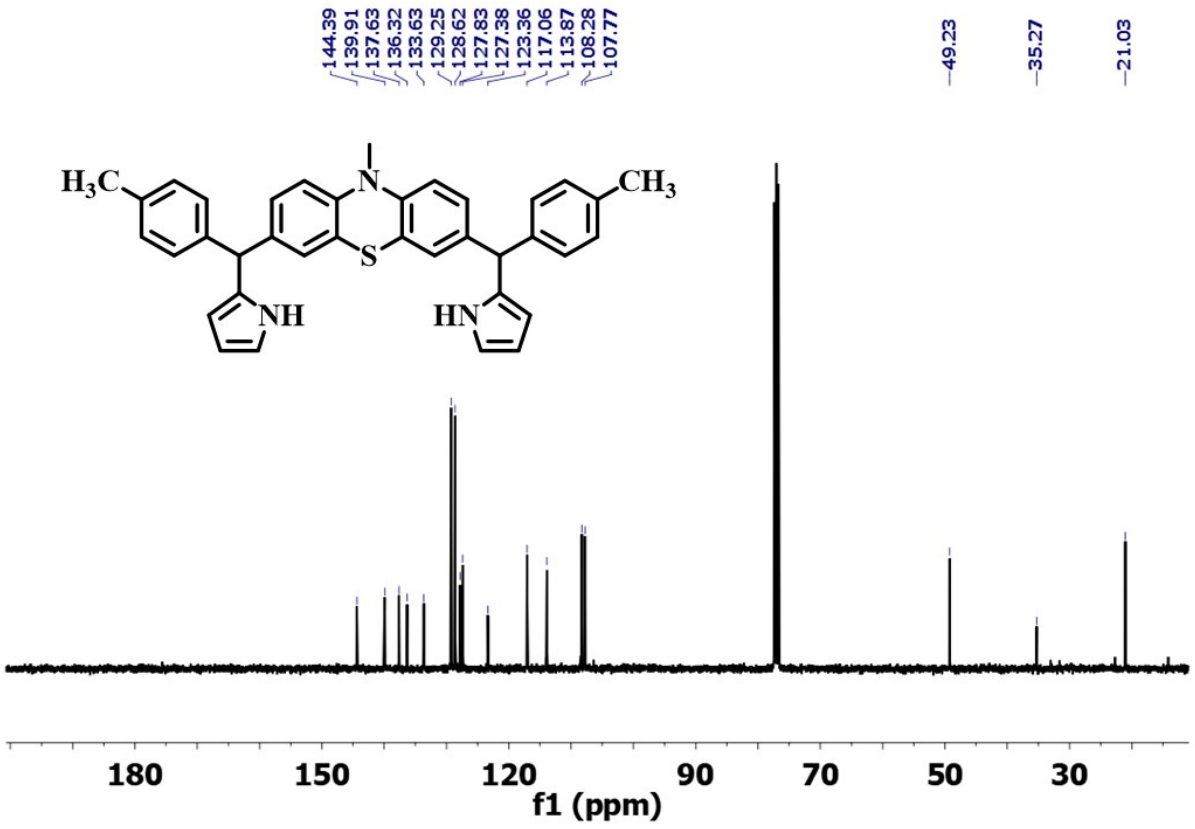
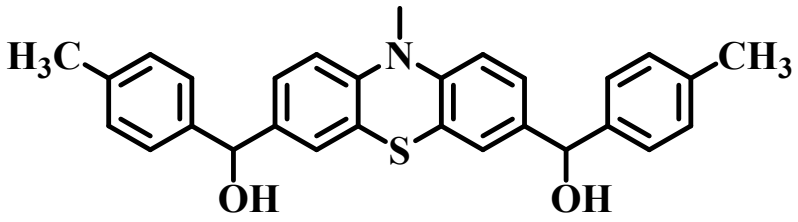


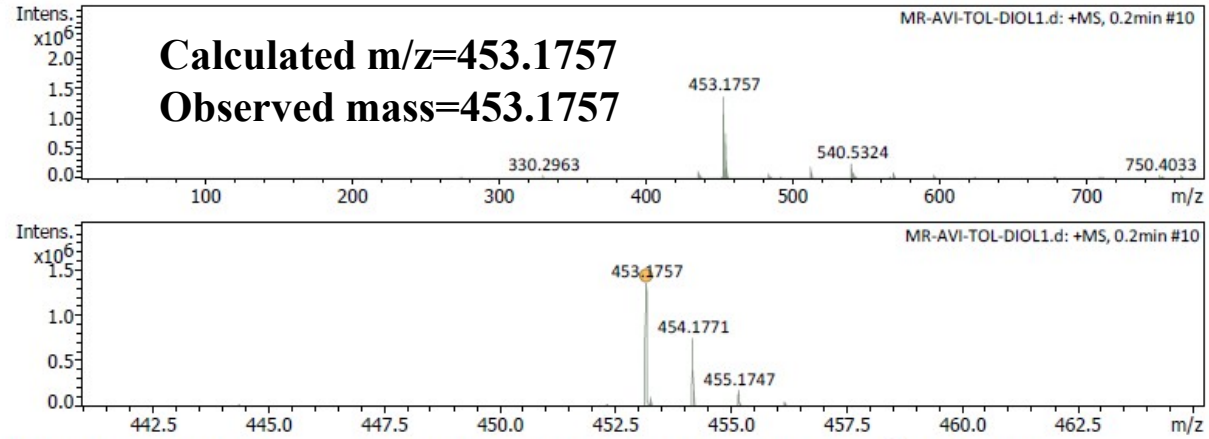
Figure S15. $^{13}C\{1H\}$ NMR spectrum of the compound **5** recorded in $CDCl_3$ on 100.06 MHz NMR instrument.[1]



Compound 6

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	3700 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
453.1757	1	C29H27NO2S	453.1757	0.1	113.7	1	100.00	19.5	odd	ok

Figure S16. HR mass spectrum of compound **6**.

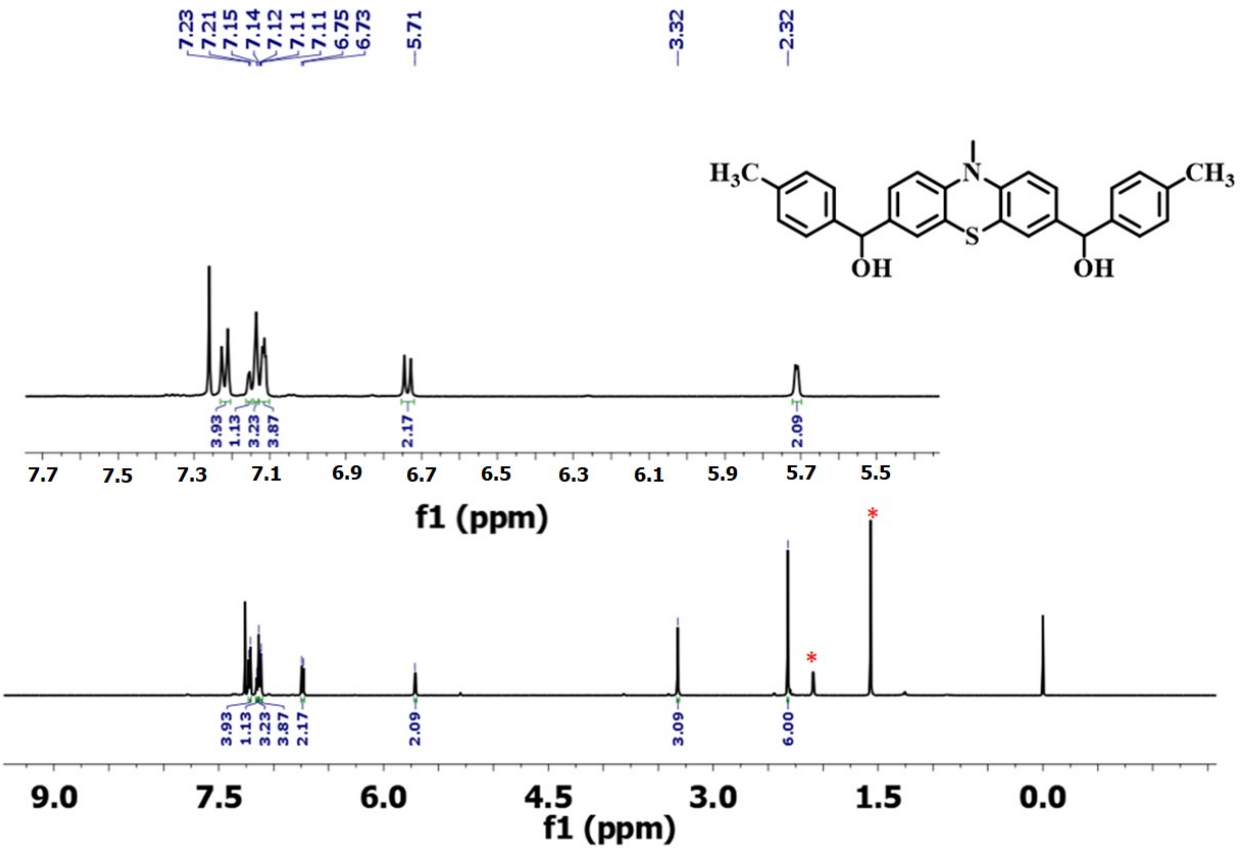


Figure S17. ^{1}H NMR spectrum of the compound **6** recorded in $CDCl_3$ on 500 MHz NMR instrument. Expansion of aromatic region is given as an inset. Note: Peaks marked with asterisk (*) are due to residual solvents. [1]

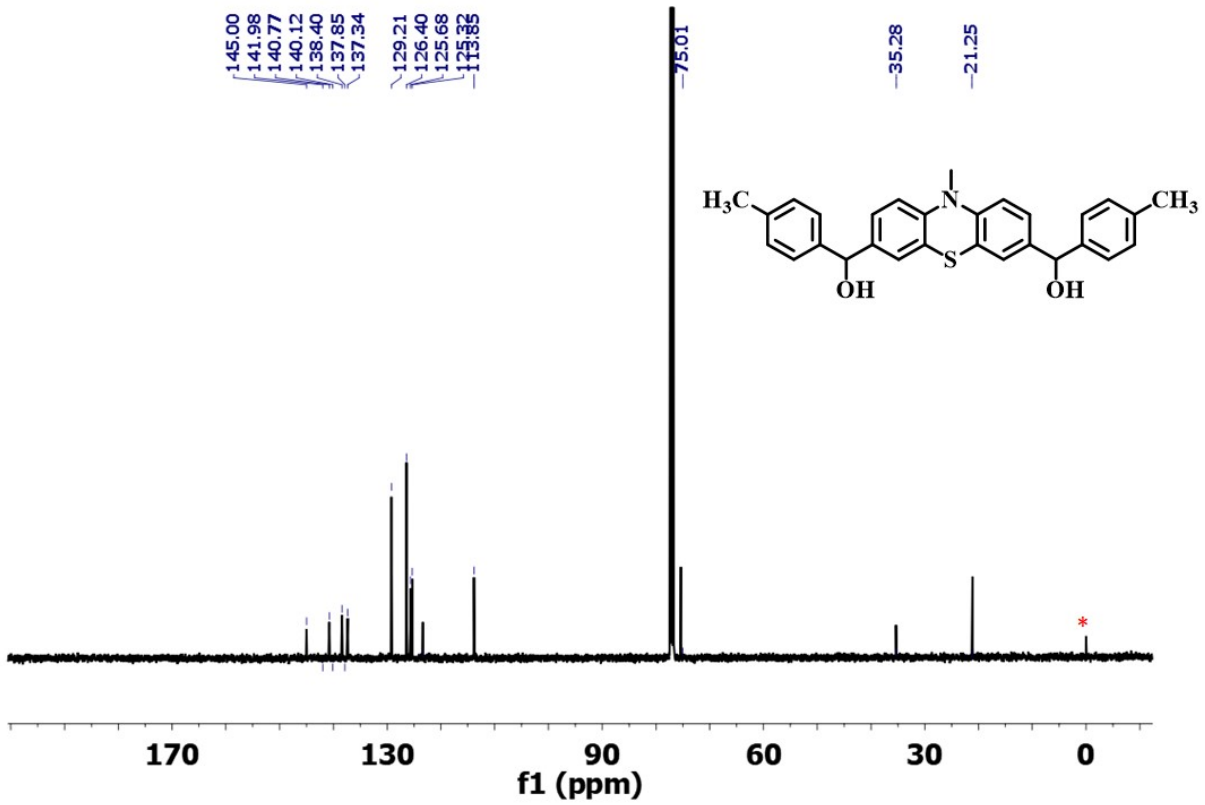


Figure S18. $^{13}C\{1H\}$ NMR spectrum of the compound **6** recorded in $CDCl_3$ on 125.77 MHz NMR instrument; Note: Peaks marked with asterisk (*) are due to residual solvents. [1]

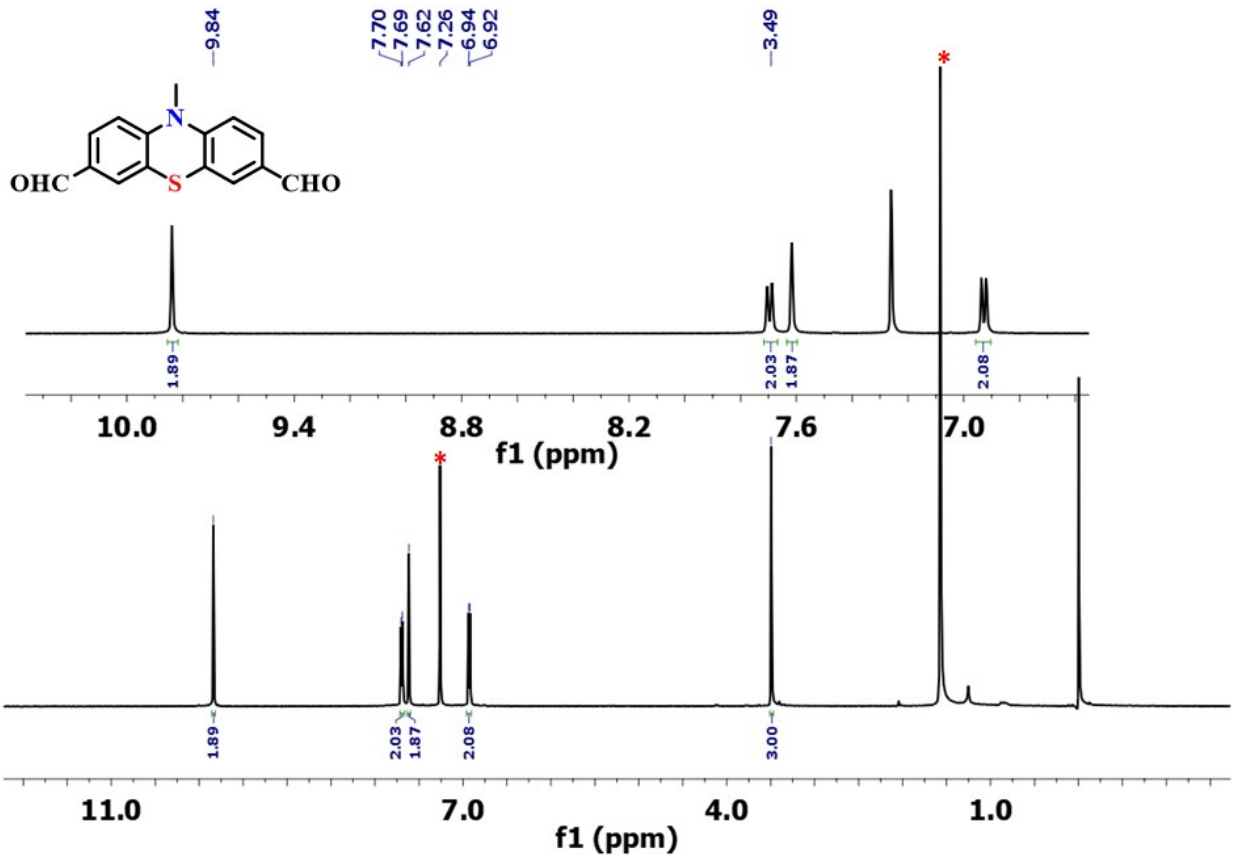


Figure S19. ^{1}H NMR spectrum of the compound **7** recorded in $CDCl_3$ on 500 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.[2]

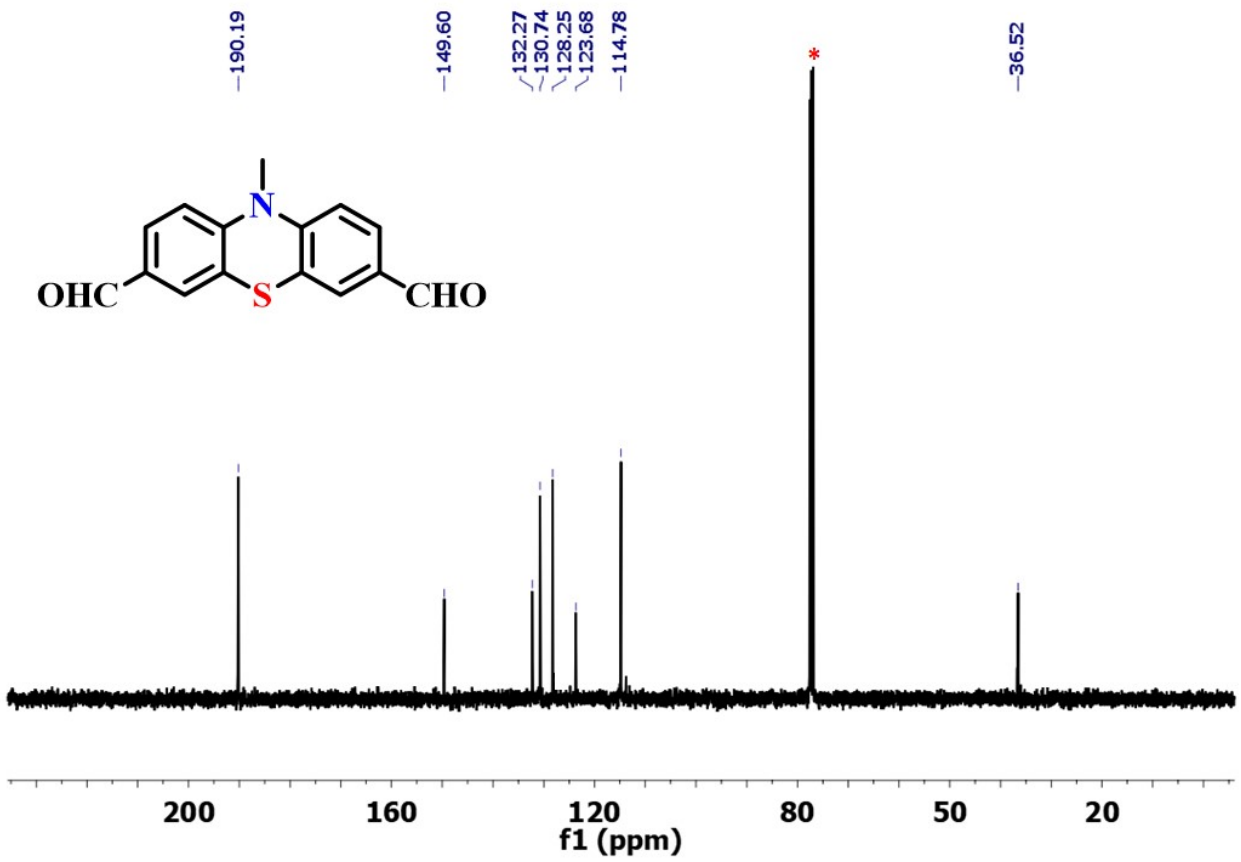


Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum of the compound **7** recorded in $CDCl_3$ on 125.77 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.[2]

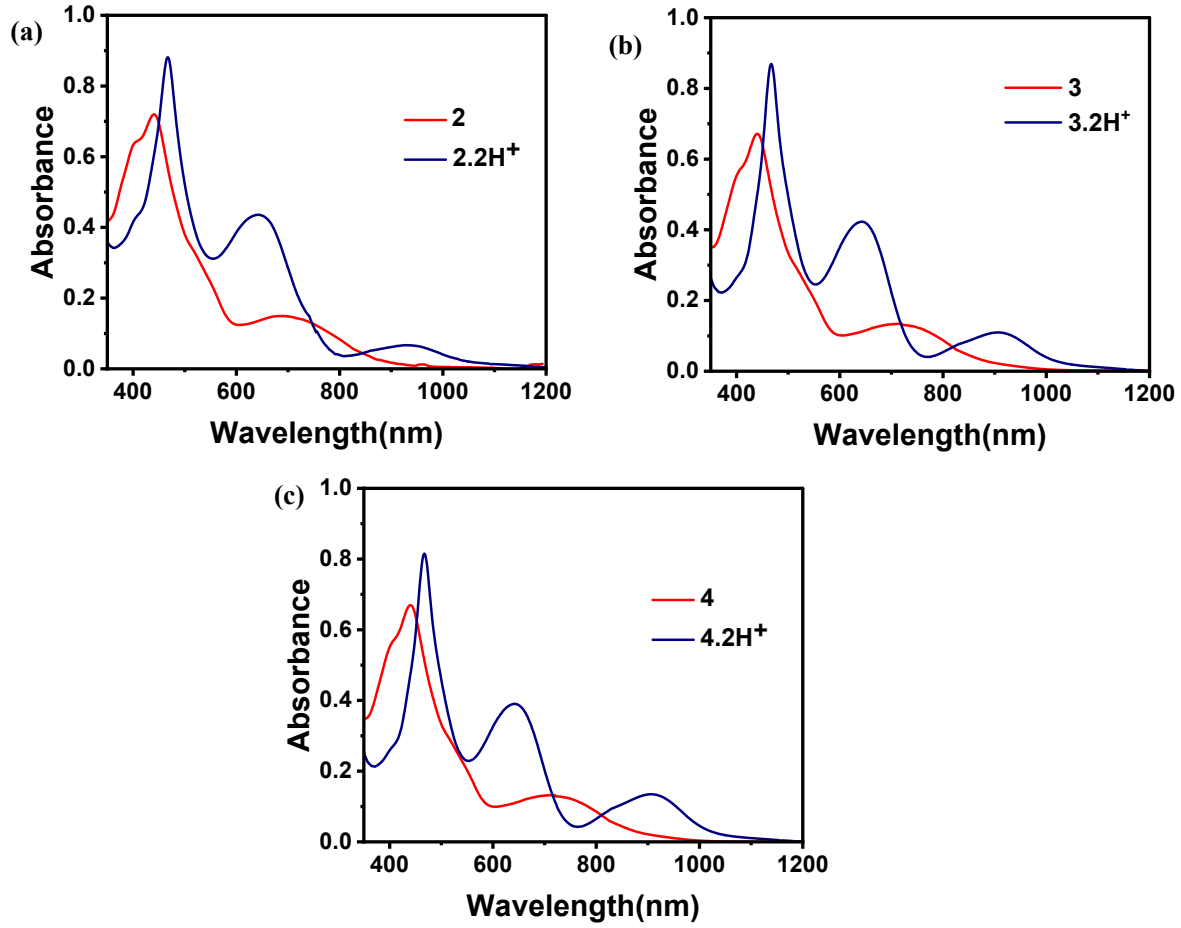


Figure S21. Comparison of absorption spectra of the compounds **2-4** (10^{-5} M) free base and in presence of TFA (excess) recorded in toluene at room temperature.

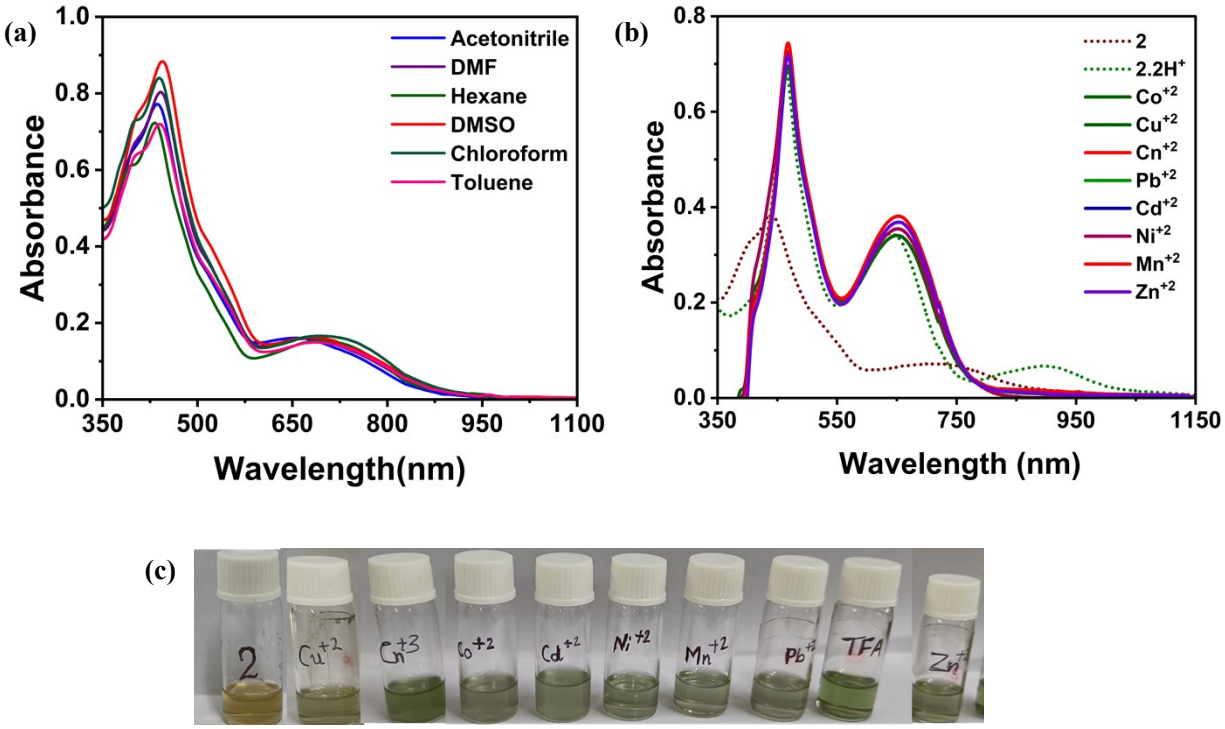


Figure S22. (a) Absorption spectra of macrocycle **2** (10^{-5}) in various solvents. **(b)** Absorption spectra of macrocycle **2** in presence of various metal perchlorate salts (excess of equivalents) recorded in toluene solution. **(c)** Image of change in colour of solutions of macrocycle **2** in toluene after addition of various metal perchlorate salts.

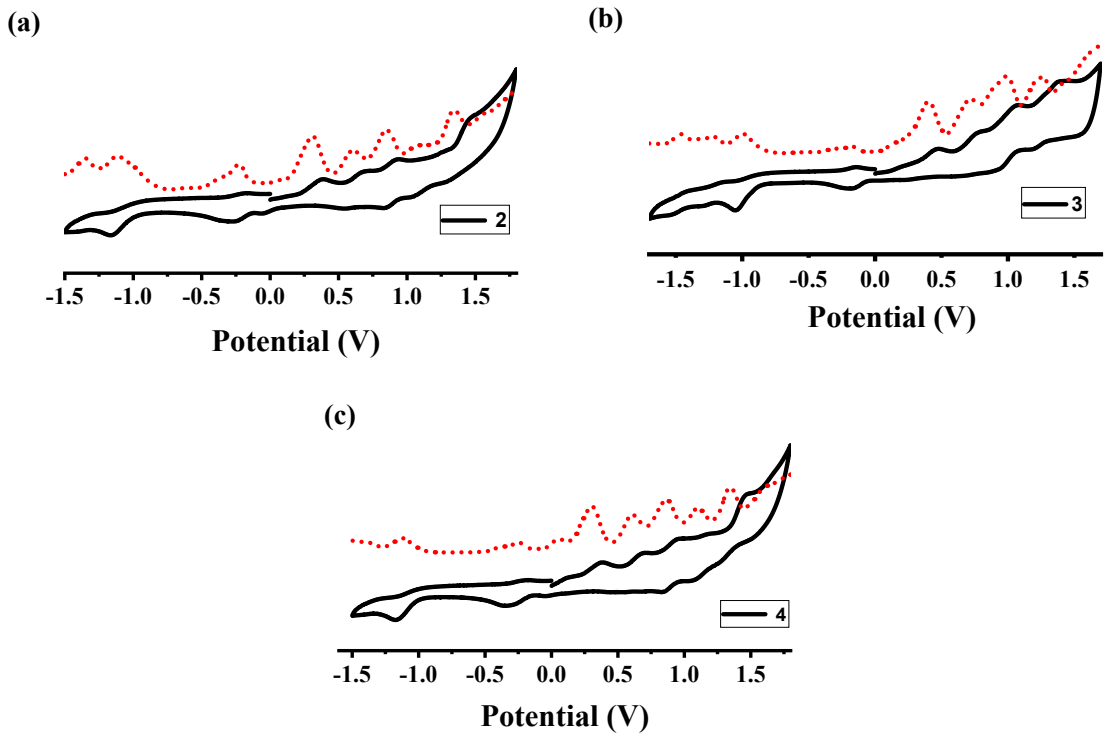


Figure S23. Cyclic voltammogram (black line) and differential pulse voltammogram (red dotted line) of compounds **2-4** (IUPAC convention has been followed for plotting Cyclic Voltammogram), recorded in CH_2Cl_2 containing 0.1 M TBAP as the supporting electrolyte and 10^{-3} M of the analyte at scan rates of 50 mVs^{-1} at 25 °C. Saturated calomel electrode (SCE) was used as the reference electrode, glassy carbon as the working electrode and platinum wire as the auxiliary electrode.

Table S1. Selected TD-DFT calculated oscillator strengths and compositions of the major electronic transitions of **2**.

Wavelength (nm)	Osc. Strength	Major contributions	Minor contributions
997.9341	0.3467	H->L (98%)	H-1->L (2%)
606.8393	0.3391	H->L+1 (93%)	H-2->L (6%)
588.24	0.2465	H-1->L (95%)	H->L+2 (2%)
483.9696	0.1576	H-3->L (16%), H->L+2 (80%)	
460.8018	0.6619	H-2->L (88%)	H-8->L (3%), H->L+1 (6%)
450.8977	0.3599	H-3->L (77%), H->L+2 (14%)	H-5->L (3%)
429.1714	0.0093	H-1->L+1 (96%)	
404.9097	0.0276	H-8->L (19%), H-7->L (10%), H-4->L (62%)	H-3->L+1 (3%)
398.1098	0.0855	H-9->L (11%), H-6->L (42%), H-5->L (37%)	H-4->L+1 (3%), H-2->L+1 (3%)
395.7968	0.2499	H-8->L (51%), H-4->L (28%)	H-7->L (2%), H-3->L+1 (3%), H-2->L (5%)
388.6259	0.0004	H-9->L (27%), H-6->L (47%), H-5->L (11%)	H-3->L (3%), H-2->L+1 (5%)

Table S2. S_0 optimized geometry of compound **2** at B3LYP/6-31g (d,p) level of theory
Sum of imaginary frequencies= 0
Total Energy (Hartree) = -2817.047663.

Atom	X	Y	Z	Atom	X	Y	Z
C	3.485225	-3.72008	-0.70719	C	-3.52998	4.766209	0.933601
C	3.596611	-2.60723	0.150311	C	2.133999	4.690874	-1.02629
C	2.499994	-2.3571	1.005435	C	2.333757	6.058702	-1.2194
C	1.341984	-3.12646	0.958593	C	3.141399	6.800318	-0.34974
C	1.214369	-4.1887	0.040263	C	3.738663	6.128769	0.726643
C	2.323606	-4.48261	-0.77233	C	3.529551	4.766562	0.933158
S	0.00009	-2.81318	2.098707	C	-3.38345	8.273696	-0.5708
C	-1.34176	-3.12656	0.958573	C	3.382784	8.273752	-0.57202
C	-1.21406	-4.18881	0.040251	H	4.310579	-3.95812	-1.36936
N	0.000189	-4.90095	-0.05256	H	2.568632	-1.55957	1.736268
C	-2.49982	-2.35728	1.005388	H	2.267871	-5.28992	-1.49304
C	-3.59639	-2.60746	0.150215	H	-2.56854	-1.55978	1.736237
C	-3.4849	-3.72027	-0.70731	H	-4.3102	-3.95836	-1.36953
C	-2.32324	-4.48276	-0.77239	H	-2.26743	-5.29004	-1.49312
C	0.000252	-6.15657	-0.7915	H	0.887281	-6.7297	-0.51353
C	4.774983	-1.72101	0.086824	H	-0.88672	-6.72979	-0.51353
C	-4.77482	-1.72132	0.086724	H	0.000244	-6.01071	-1.88223
C	-6.09291	-2.32177	-0.19348	H	6.686229	0.551811	0.21564
C	-4.63315	-0.34773	0.187158	H	5.423088	2.902742	0.245802
C	6.093123	-2.32139	-0.1933	H	2.541362	-0.14437	0.020896
C	4.633208	-0.34743	0.187186	H	-2.54133	-0.1445	0.020869
C	5.619067	0.716062	0.206839	H	-5.42329	2.902371	0.245893
C	4.973098	1.920604	0.224209	H	-6.68624	0.55133	0.215603
N	3.409214	0.305028	0.269922	H	-6.72499	-0.84825	-1.63304
N	-3.40921	0.304813	0.269967	H	-8.93722	-1.86547	-2.03611
C	-4.97322	1.920267	0.224279	H	-7.97322	-5.04067	0.68376
C	-5.6191	0.715675	0.206841	H	-5.77281	-4.00654	1.111641
C	-7.00894	-1.74611	-1.09447	H	6.725145	-0.84791	-1.63293
C	-8.25336	-2.32926	-1.3291	H	8.937453	-1.86502	-2.03589
C	-8.63064	-3.51744	-0.69155	H	7.973563	-5.04012	0.684141
C	-7.70927	-4.11122	0.18446	H	5.773092	-4.00609	1.111923
C	-6.469	-3.5302	0.428178	H	-9.92824	-5.23013	-0.93666
C	7.00914	-1.74572	-1.0943	H	-10.6931	-3.8546	-0.13551
C	8.253606	-2.32881	-1.32886	H	-10.4124	-3.80475	-1.88124
C	8.630921	-3.51694	-0.69126	H	9.928534	-5.22959	-0.93663
C	7.709574	-4.11072	0.184769	H	10.41283	-3.80396	-1.88074
C	6.469266	-3.52976	0.428431	H	10.69328	-3.8543	-0.13498
C	-9.98662	-4.136	-0.92822	H	1.319618	0.189452	1.639217
C	9.986933	-4.13546	-0.92788	H	-1.31959	0.189373	1.639272

C	1.142554	2.096039	0.518633	H	-0.00013	3.721275	-0.22635
C	0.697999	0.919758	1.14901	H	-1.53533	4.129892	-1.73836
C	-0.69804	0.919723	1.149044	H	-1.86506	6.556383	-2.06387
C	-1.14268	2.095985	0.518702	H	-4.36364	6.685695	1.421641
N	-9.2E-05	2.795684	0.173362	H	-3.97868	4.269008	1.788066
C	-2.48361	2.570137	0.28503	H	1.534997	4.129619	-1.73871
C	-2.72199	4.019664	0.059435	H	1.864451	6.556072	-2.06461
C	-3.54883	1.685053	0.262837	H	4.362928	6.686257	1.42094
C	2.483436	2.570274	0.284887	H	3.978265	4.269561	1.787732
C	2.721684	4.019795	0.059102	H	-3.36279	8.825061	0.375897
C	3.54873	1.685276	0.262744	H	-2.62805	8.702837	-1.23691
C	-2.13438	4.69097	-1.02583	H	-4.36693	8.447951	-1.02695
C	-2.33431	6.05882	-1.21874	H	3.366938	8.824706	0.374983
C	-3.14204	6.800194	-0.34899	H	4.364216	8.447504	-1.03278
C	-3.73926	6.1284	0.727288	H	2.624613	8.703704	-1.23446

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