Supporting Information

Synthesis of Nonaromatic [16]Thiatriphyrin(2.2.1)s

Shubham Tiwari and Mangalampalli Ravikanth*

Department of Chemistry, IIT Bombay, Powai, Mumbai 400076,

India

Email: ravikanth@chem.iitb.ac.in

General Experimental

All chemicals such as $BF_3{\cdot}OEt_2$, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) were procured and used as received from Aldrich. Neutral alumina and silica gel (60-120 mesh) column chromatographic technique performed for purification purposes. The 1D, 2D & $^{13}C\{1H\}$ 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-Vis-NIR Spectrophotometerwas used for absorption spectral studies of compounds **4-6**. Cyclic voltammetry (CV) studies werecarried out with BASi C3 Cell Stand electrochemical system (Manufacturer: Bioanalytical Systems. Inc.) utilizing the three-electrode configuration consisting of a glassy carbon (working electrode), platinum wire (auxiliary electrode) and saturated calomel as reference electrode (the electrode is composed of Hg/Hg_2Cl_2/Saturated KCl solution). The experiments were done in dry dichloromethane using 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. The initial and final potential was at 0 V, first switching potential at -2.0 V and second switching potential at 2.0 V. Glassy carbon-disk working electrodes (3-mm diameter, part # CHI 104) were purchased from CH Instruments, Inc. Bruker maXis Impact and LC-MS Q-TOF micro mass spectrometer instrument were used for recording HR mass spectra.

Computational Details

Geometry of compound **4** and **4.H**$^+$ were optimized by using Gaussian 09 program package.[1] For both the compounds **4** and **4.H**$^+$, the B3LYP/6-31G(d,p)[2] basis set was used for the density functional theory (DFT)[3] for optimization in S_0 state. To substantiate genuine global minimum energy structures the frequency calculations were performed on S_0 optimized geometries.

The optimized geometries used to obtain frontier molecular orbitals (FMOs) and also subjected to TD-DFT calculations for the first 50 $S_0 \rightarrow S_n$ transitions[4] to understand absorption properties of macrocycle **4** and **4.H**$^+$. The integral equation formalism polarizable continuum model (PCM)[5] within the self-consistent reaction field (SCRF) theory was used in the TD-DFT calculations.

$C_{34}H_{34}N_2O_4S$

Calculated Mass$[M+H]^+$= 567.2323

Observed Mass$[M+H]^+$= 567.2322

Compound Details

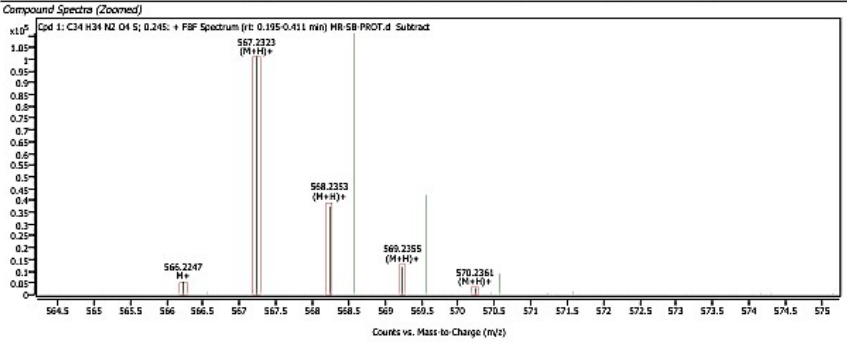
Cpd. 1: C34 H34 N2 O4 S

Formula	m/z	Observed M/Z	Difference_Da	Difference_PPM	Score
C34 H34 N2 O4 S	567.2323	567.232277672044	1.096647688544145	1.936773839811	97.36

Department of Chemistry I.I.T. (B)

Agilent

Compound Spectra (Zoomed)



MassHunter Qual 10.0
(End of Report)

Figure S1. HR mass spectrum of the compound **8**.

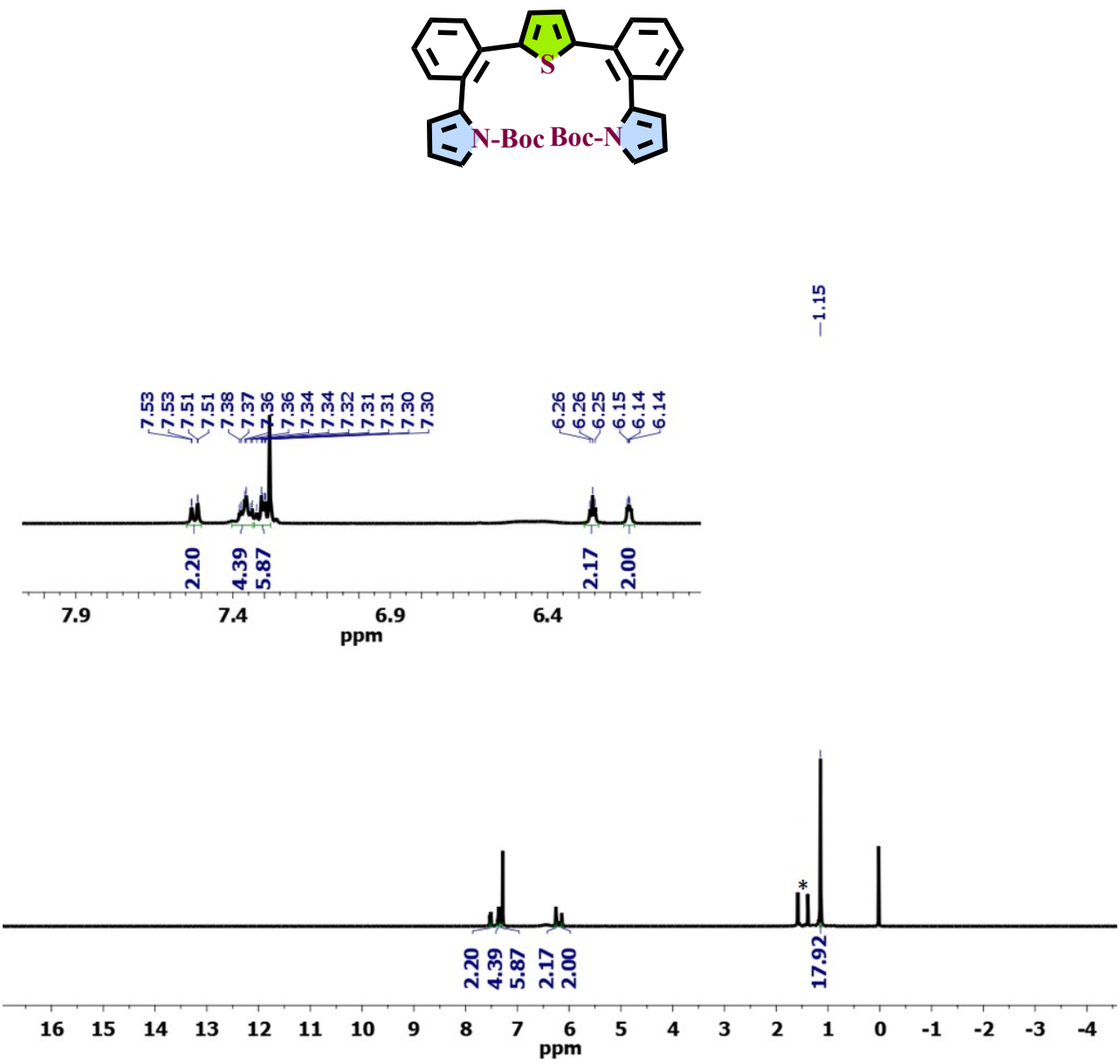


Figure S2. ^{1}H NMR spectrum of the compound **8** recorded in $CDCl_3$ at 25°C at 400 MHz NMR instrument. Asterisk indicates the solvent peaks.

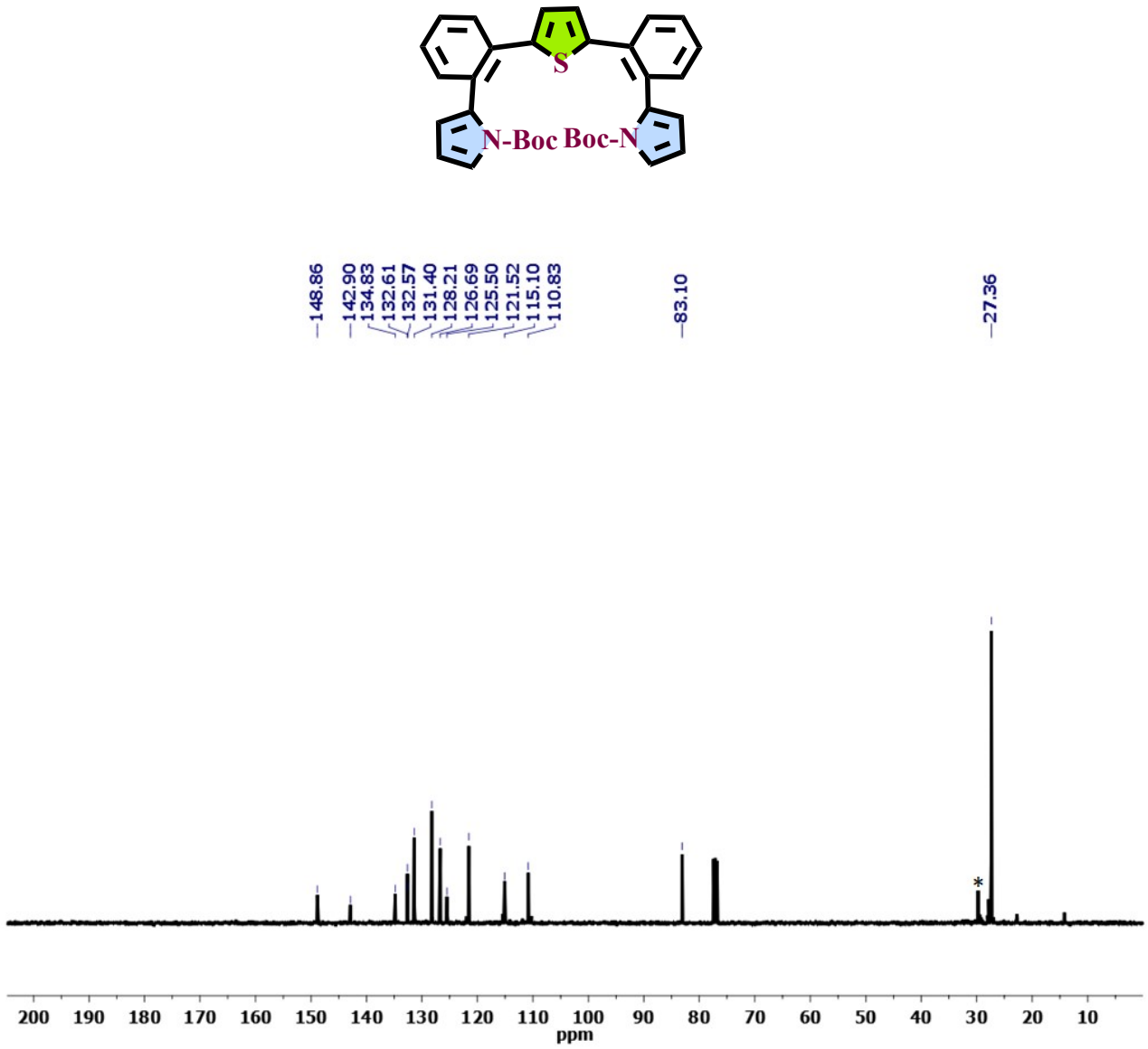
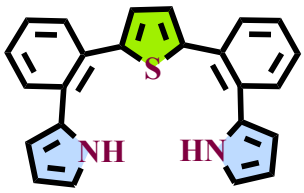


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of the compound **8** recorded in $CDCl_3$ at 25°C at 400 MHz NMR instrument.



$C_{24}H_{18}N_2S$

Calculated Mass$[M+Na]^+$= 367.1261

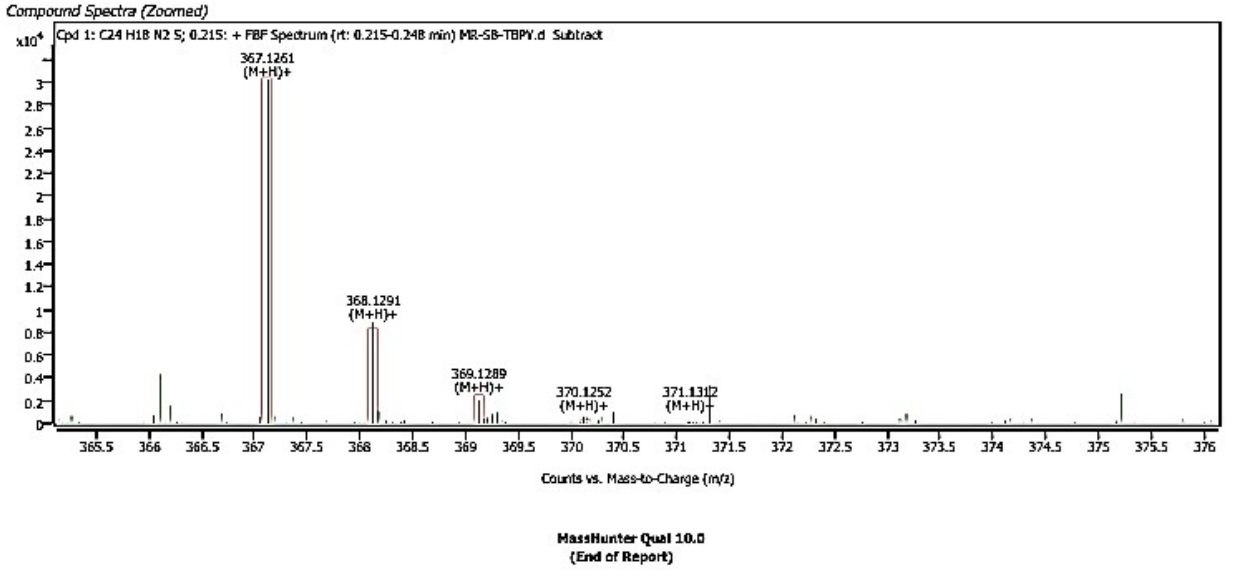
Observed Mass$[M+Na]^+$= 367.1260

Compound Details

Cpd. 1: C24 H18 N2 S

Formula	m/z	Observed M/Z	Difference_Da	Difference_PPM	Score
C24 H18 N2 S	367.1261	367.126092074437	-0.174094458827767	-0.475513223475608	97.48

Compound Spectra (Zoomed)



MassHunter Qual 10.0
(End of Report)

Figure S4. HR mass spectrum of the compound **9**.

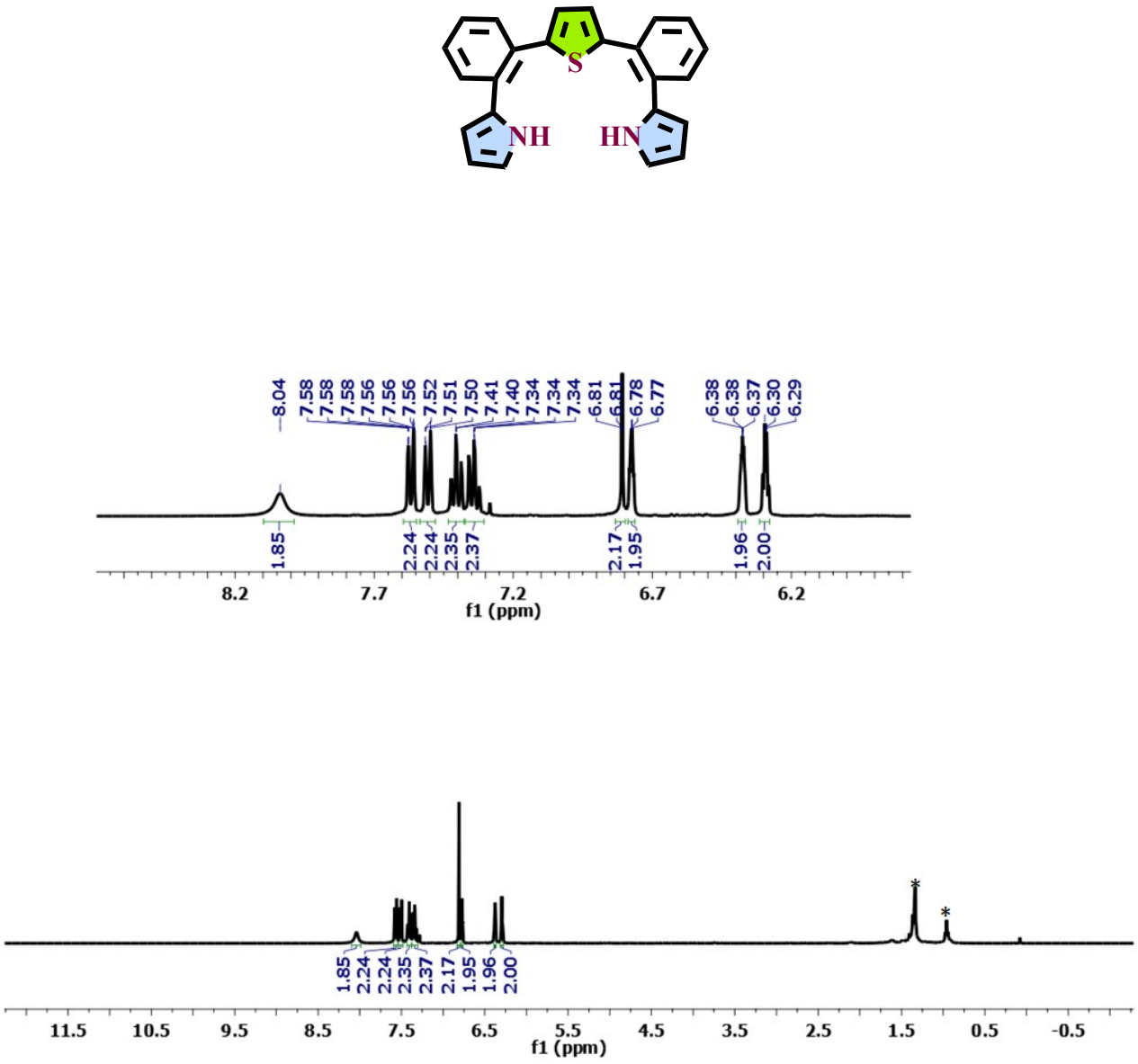


Figure S5. ^{1}H NMR spectrum of the compound **9** recorded in $CDCl_3$ at 25°C at 400 MHz NMR instrument. Asterisk indicates the residual solvent peaks.

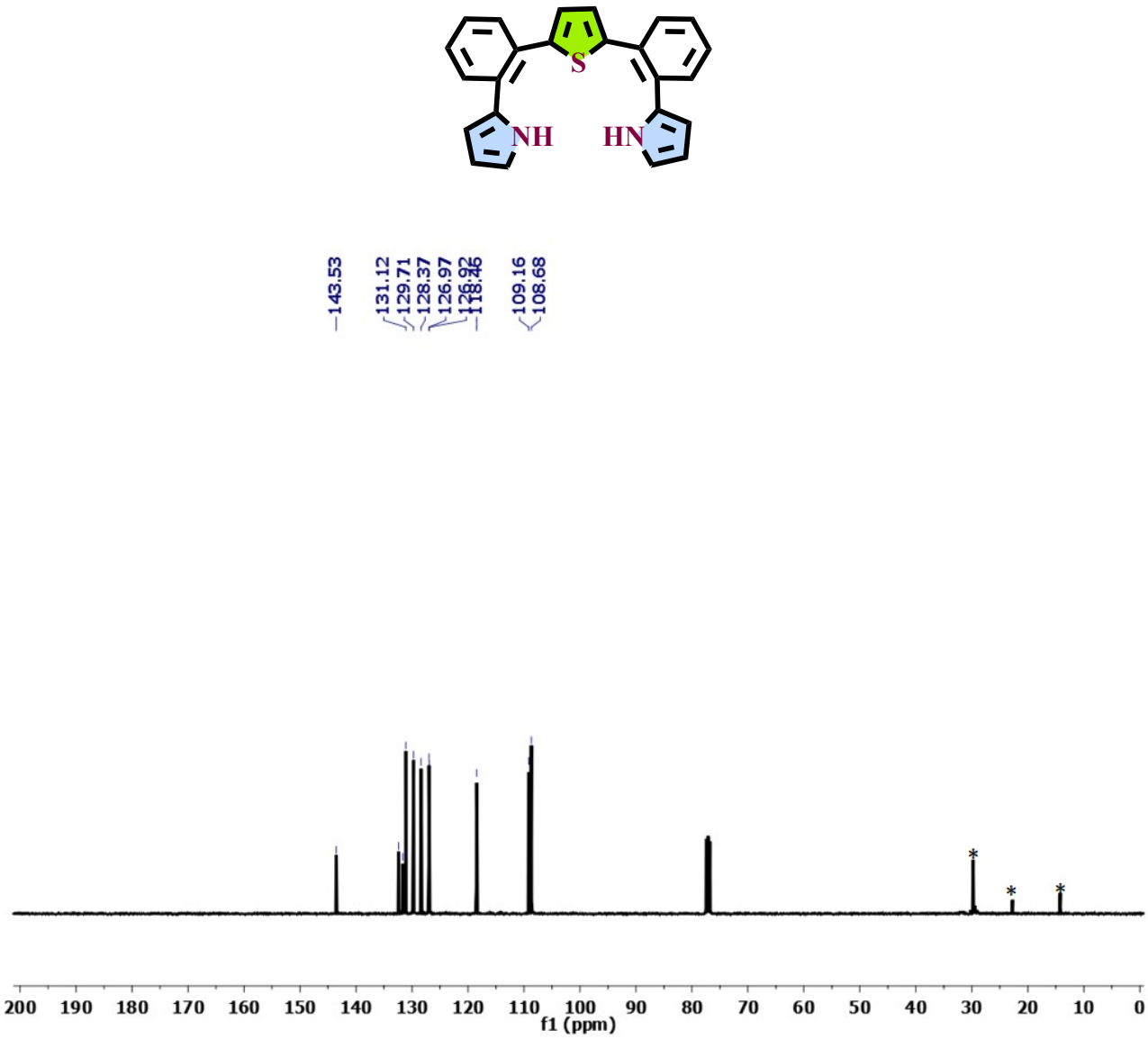
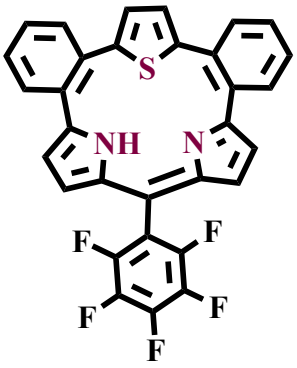


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of the compound **9** recorded in $CDCl_3$ at 25°C at 400 MHz NMR instrument. Asterisk indicates the residual solvent peaks.



$C_{31}H_{16}F_5N_2S$

Calculated Mass$[M+H]^+$= 543.0949

Observed Mass$[M+H]^+$= 543.0944

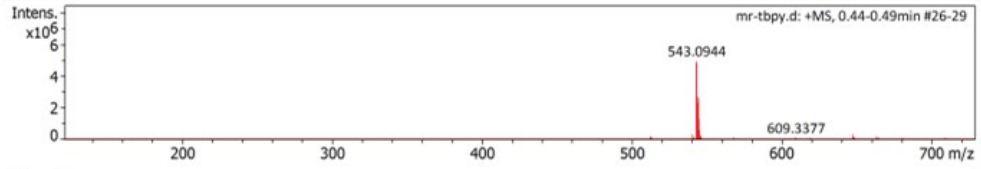
DEPARTMENT OF CHEMISTRY, I.I.T.(B)

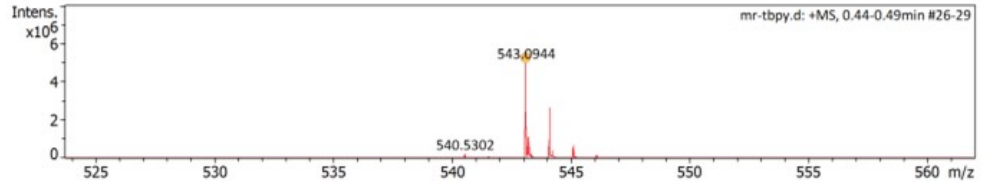
Analysis Info

Analysis Name	D:\Data\AUG-2023\mr-tbpy.d	Acquisition Date	8/31/2023 3:37:58 PM
Method	NaICsI_pos_1000-a.m	Operator	PG SRD IN
Sample Name	mr-tbpy	Instrument	maXis impact 282001.00081
Comment	C31H15F5N2S		

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	4.5 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
543.0944	1	C31H16F5N2S	543.0949	0.8	93.6	1	100.00	25.0	even	ok

Figure S7. HR mass spectrum of the compound **4**.

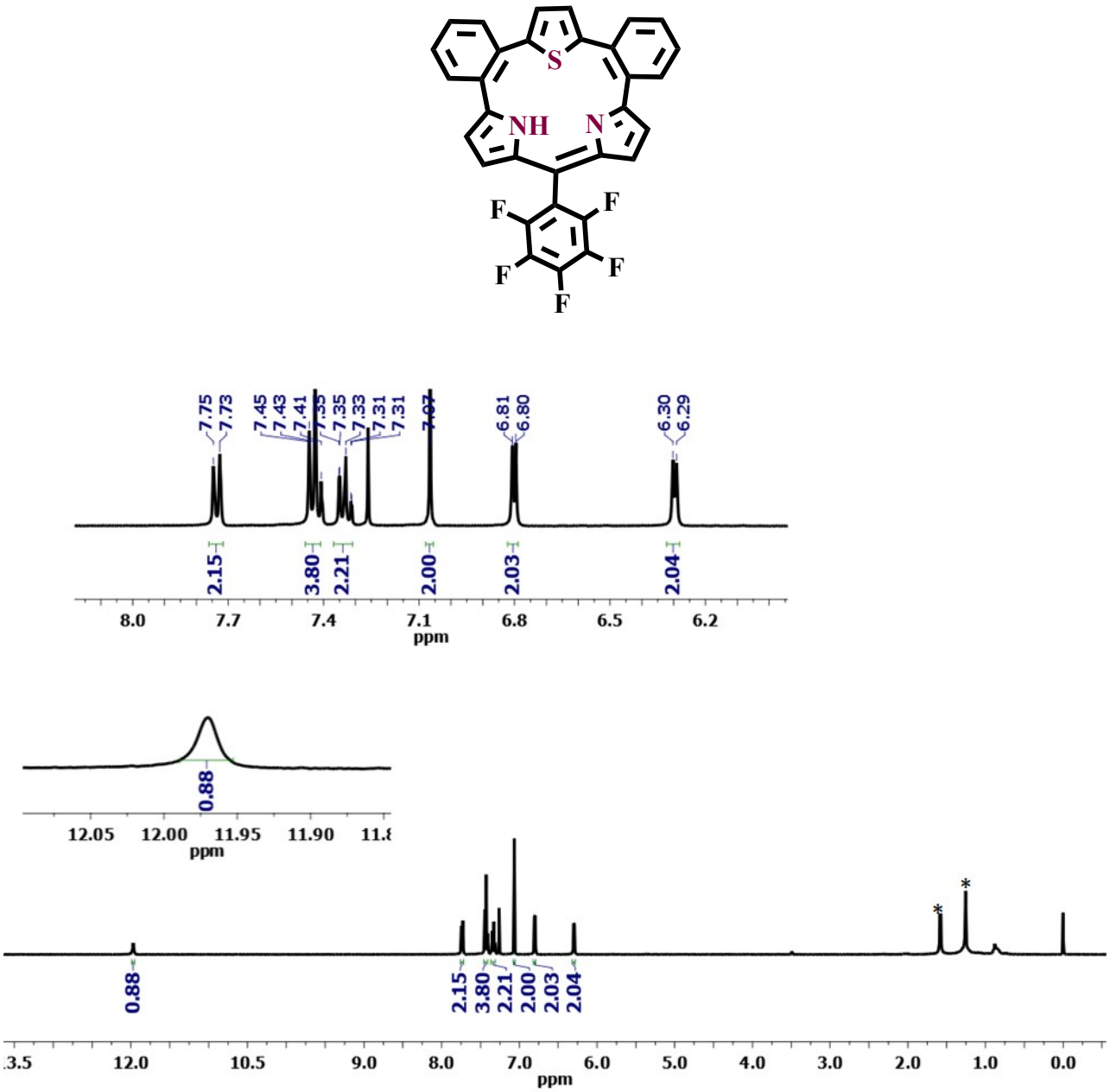


Figure S8. ^{1}H NMR spectrum of the compound **4** recorded in $CDCl_3$ at 25°C at 500 MHz NMR instrument. Asterisk indicates the residual solvent peaks.

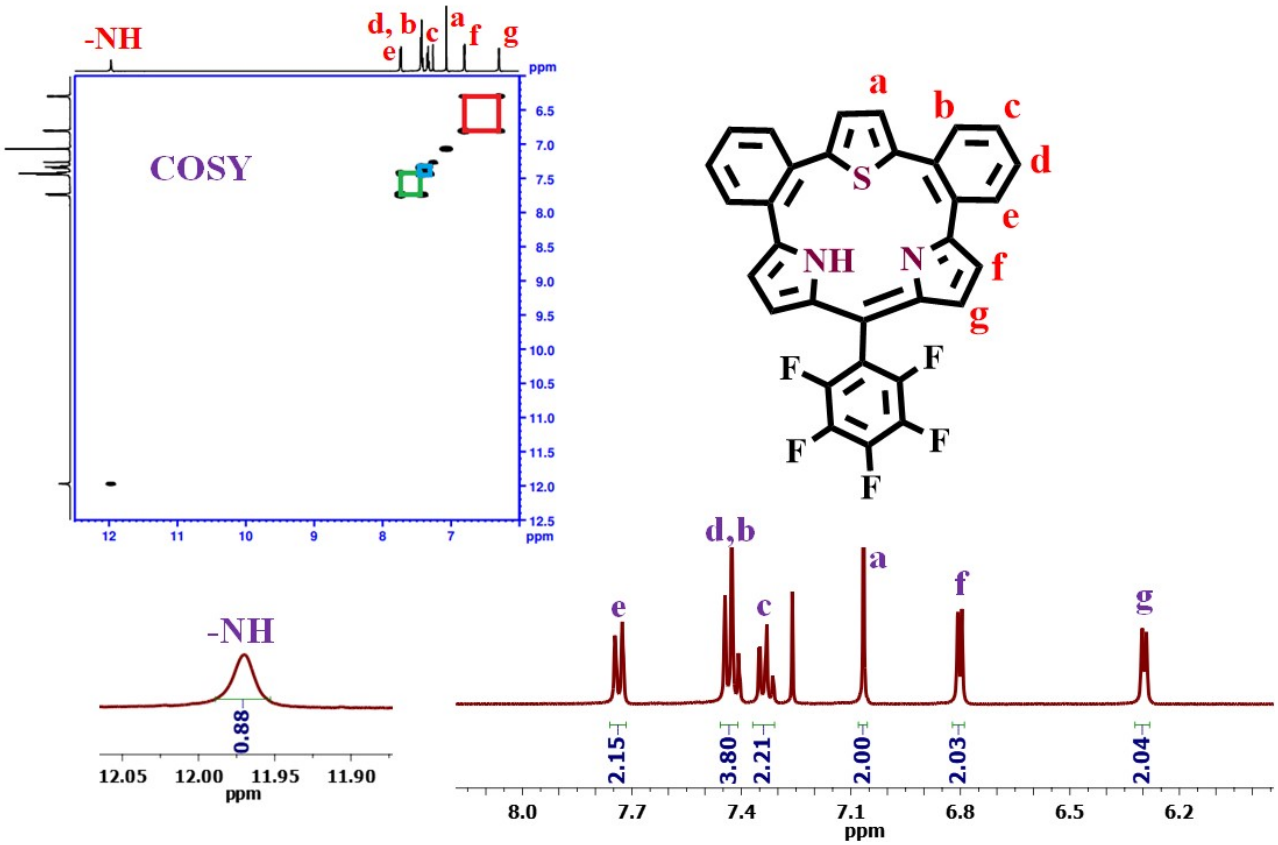


Figure S9. Partial ^{1}H and ^{1}H-^{1}H COSY NMR spectrum of the compound **4** recorded in $CDCl_3$ at 25°C at 400 MHz NMR instrument.

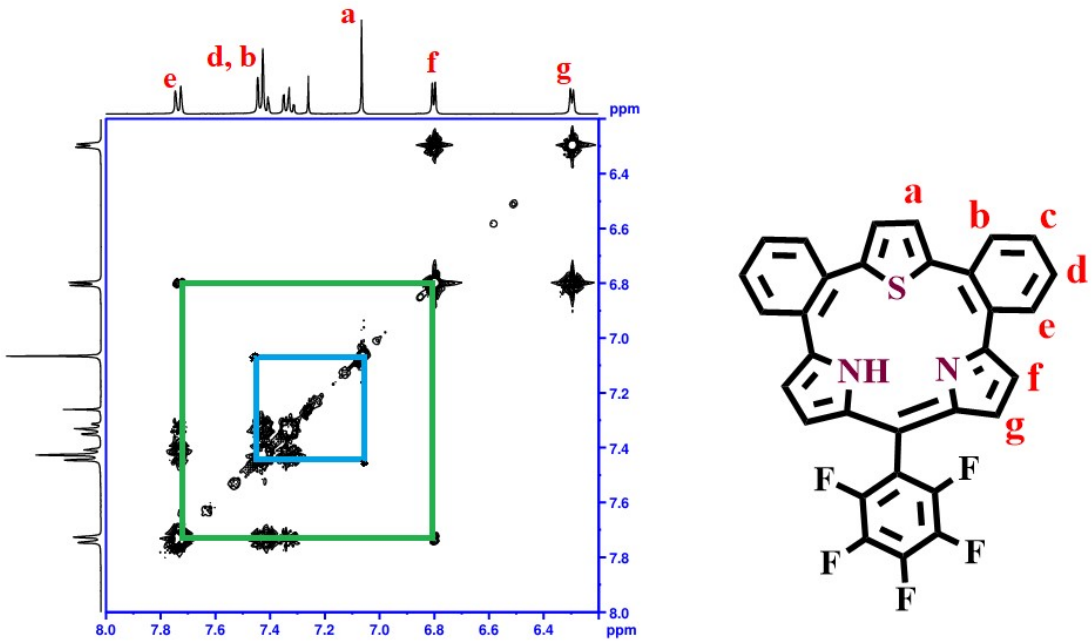


Figure S10. ^{1}H-^{1}H NOSY NMR spectrum of the compound **4** recorded in $CDCl_3$ at 25°C at 400 MHz NMR instrument.

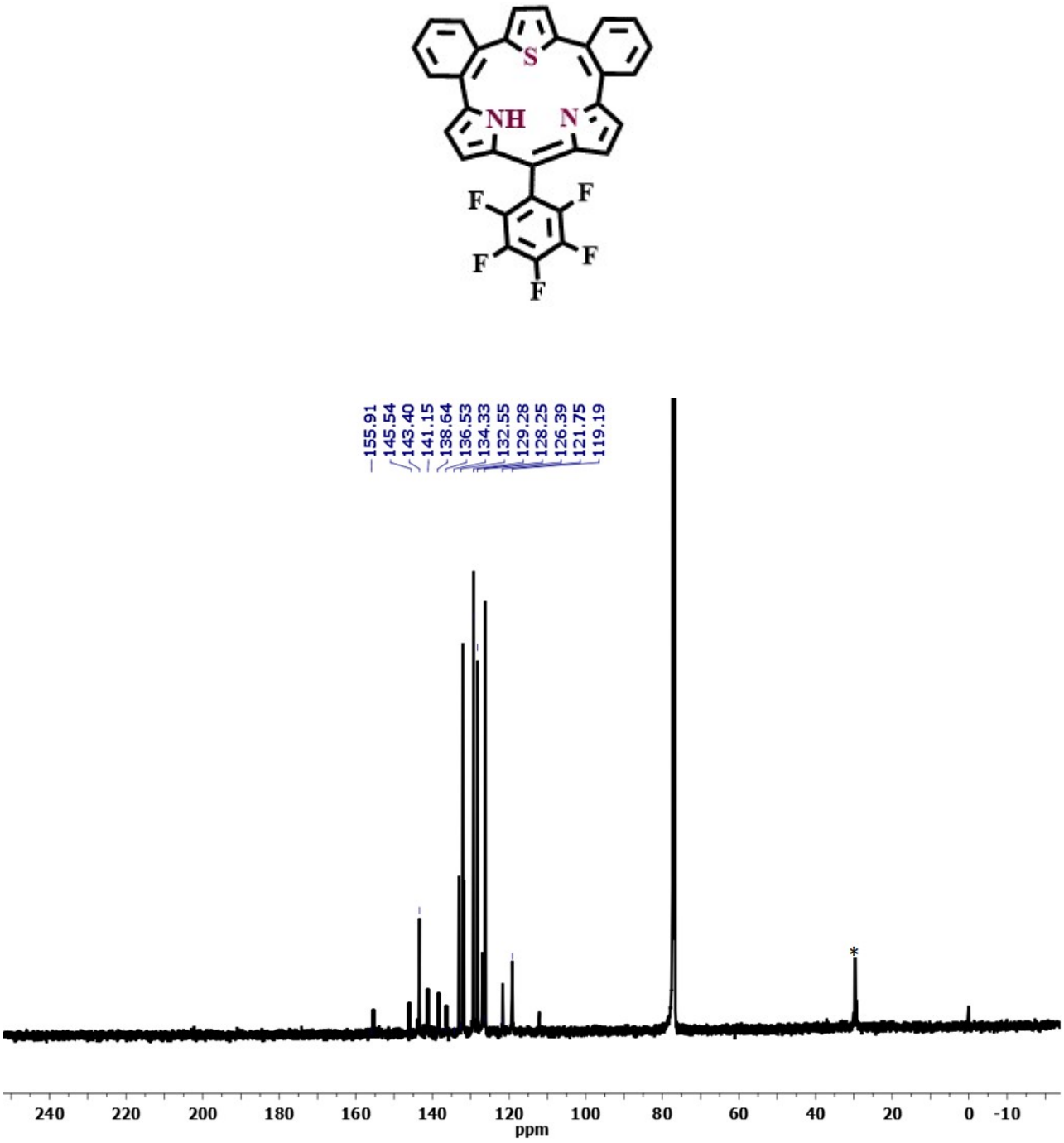
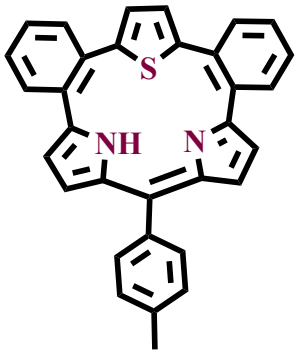


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of the compound **4** recorded in $CDCl_3$ at 25°C at 400 MHz NMR instrument. The asterisk indicates the residual solvent peaks.



$C_{32}H_{22}N_2S$

Calculated Mass$[M+H]^+$= 467.1576

Observed Mass$[M+H]^+$= 467.1585

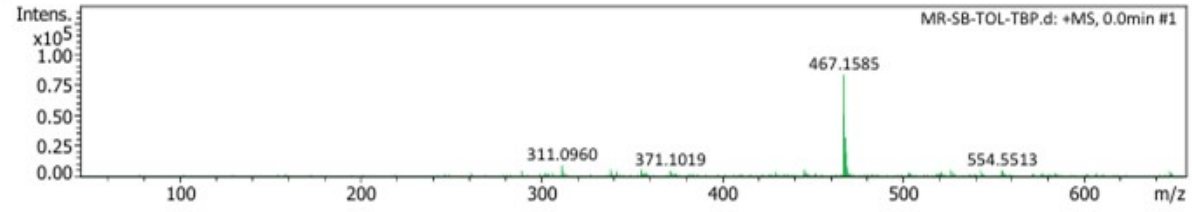
DEPARTMENT OF CHEMISTRY, I.I.T.(B)

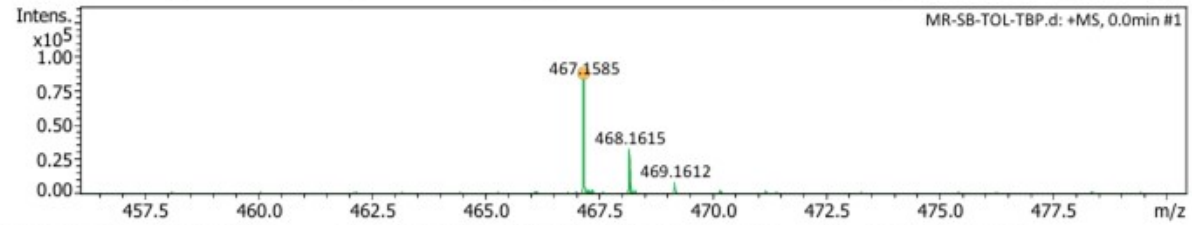
Analysis Info

Analysis Name	D:\Data\OCT-2023\MR-SB-TOL-TBP.d	Acquisition Date	11/2/2023 3:44:26 PM
Method	Naformat_pos_50-600.m	Operator	PG-JS-OUT
Sample Name	MR-SB-TOL-TBP	Instrument	maXis impact 282001.00081
Comment	C32H22N2S		

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	650 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
467.1585	1	C32H23N2S	467.1576	-1.9	14.4	1	100.00	25.0	even	ok

Figure S12. HR mass spectrum of the compound **5**.

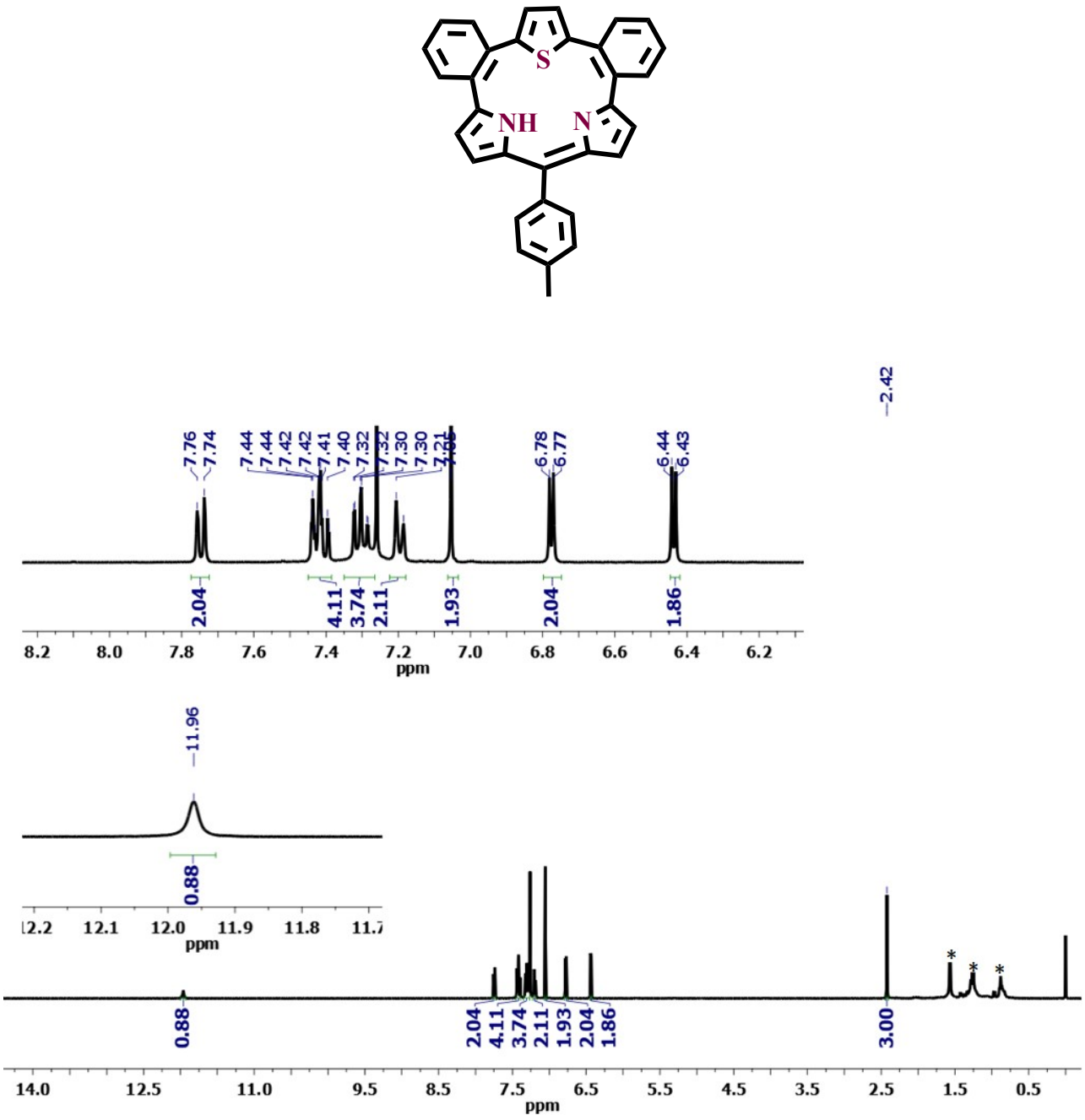


Figure S13. ^{1}H NMR spectrum of the compound **5** recorded in $CDCl_3$ at 25°C at 400 MHz NMR instrument. The asterisk indicates the residual solvent peaks.

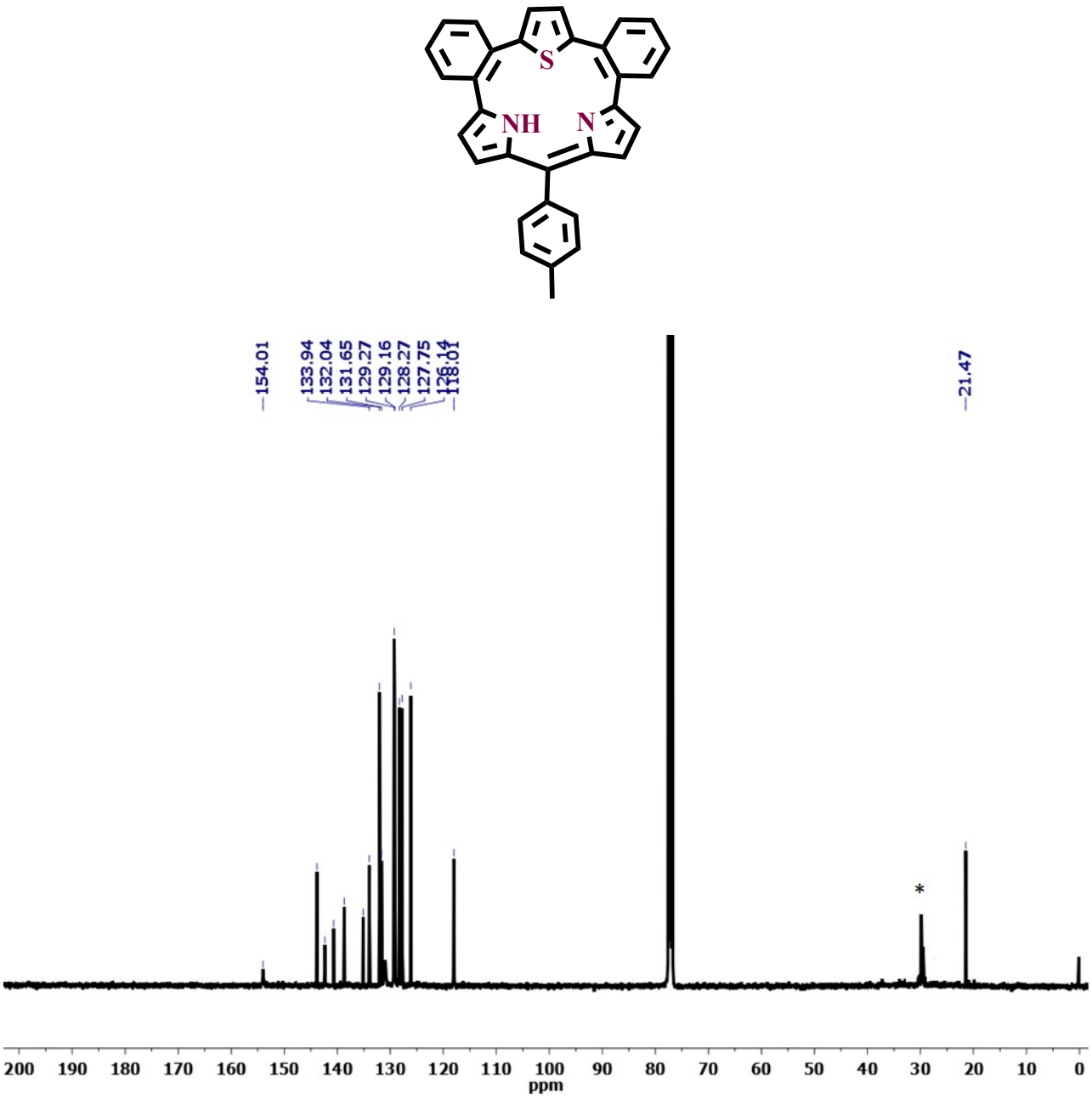
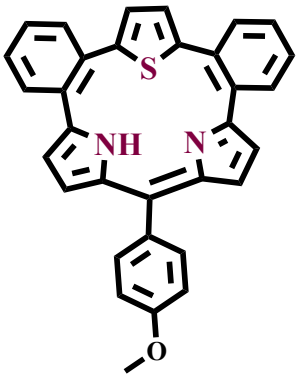


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of the compound **5** recorded in $CDCl_3$ at 25°C at 400 MHz NMR instrument. The asterisk indicates the residual solvent peaks.



$C_{32}H_{22}N_2OS$

Calculated Mass$[M+H]^+$= 483.1532

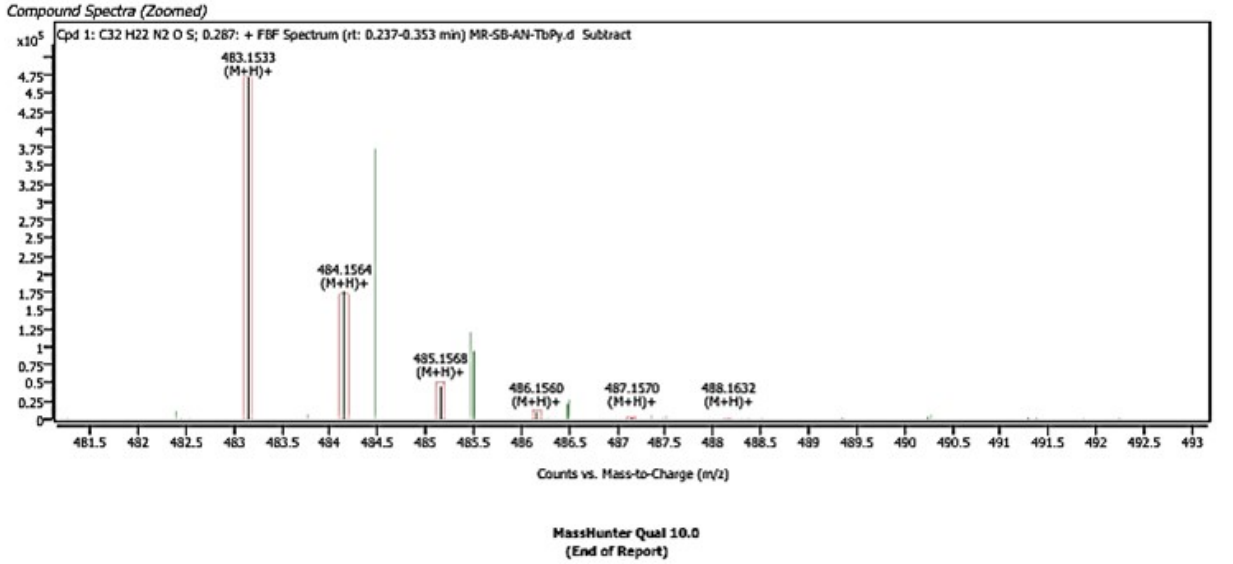
Observed Mass$[M+H]^+$= 483.1533

Compound Details

Cpd. 1: C32 H22 N2 O S

Formula	m/z	Observed M/Z	Difference Da	Difference PPM	Score
C32 H22 N2 O S	483.1533	483.15327261588	0.811306387845434	1.68270107507574	97.00

Compound Spectra (Zoomed)



MassHunter Qual 10.0
(End of Report)

Figure S15. HR mass spectrum of the compound **6**.

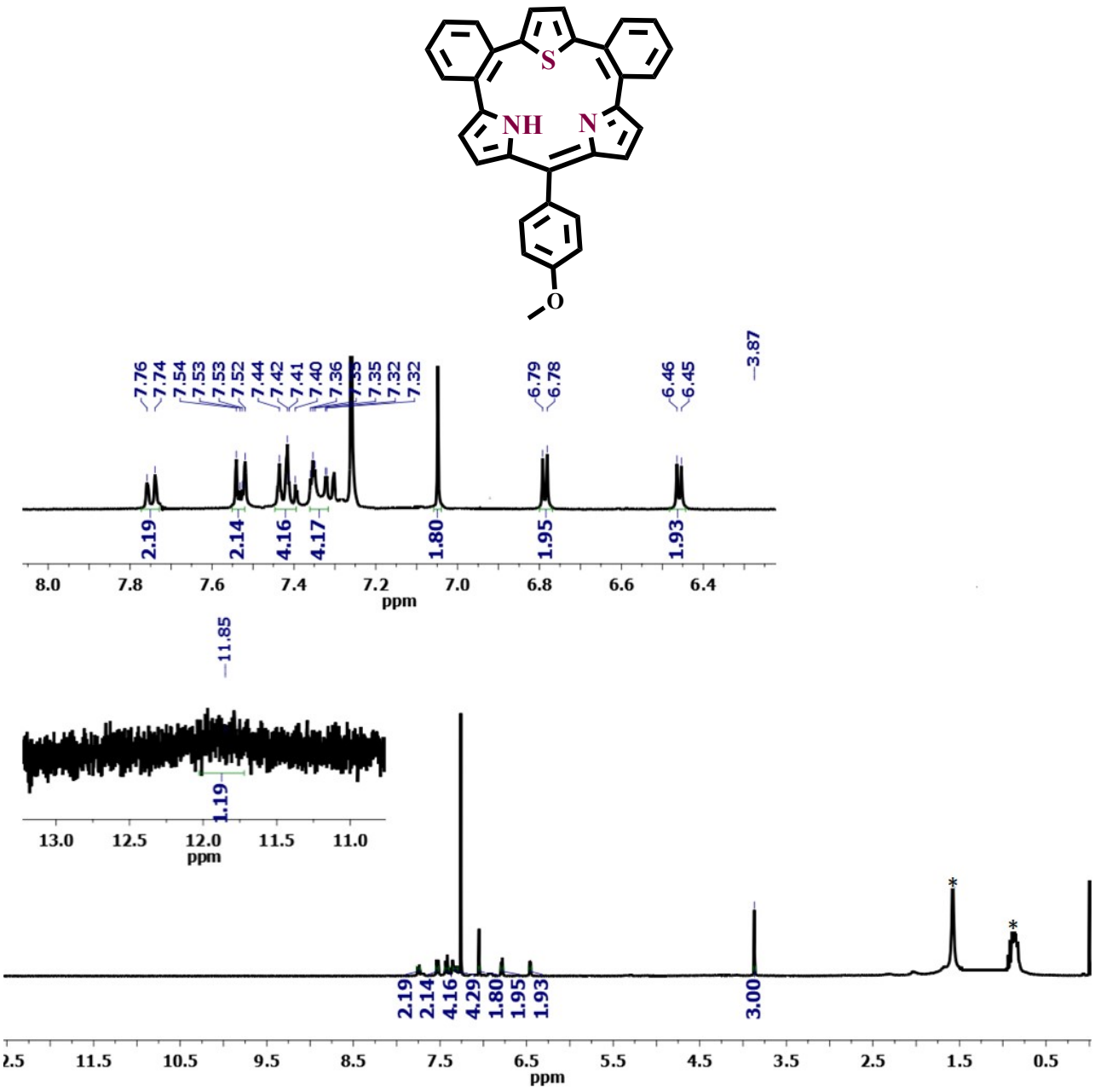


Figure S16. ^{1}H NMR spectrum of the compound **6** recorded in $CDCl_3$ at 25°C at 400 MHz NMR instrument. The asterisk indicates the residual solvent peaks.

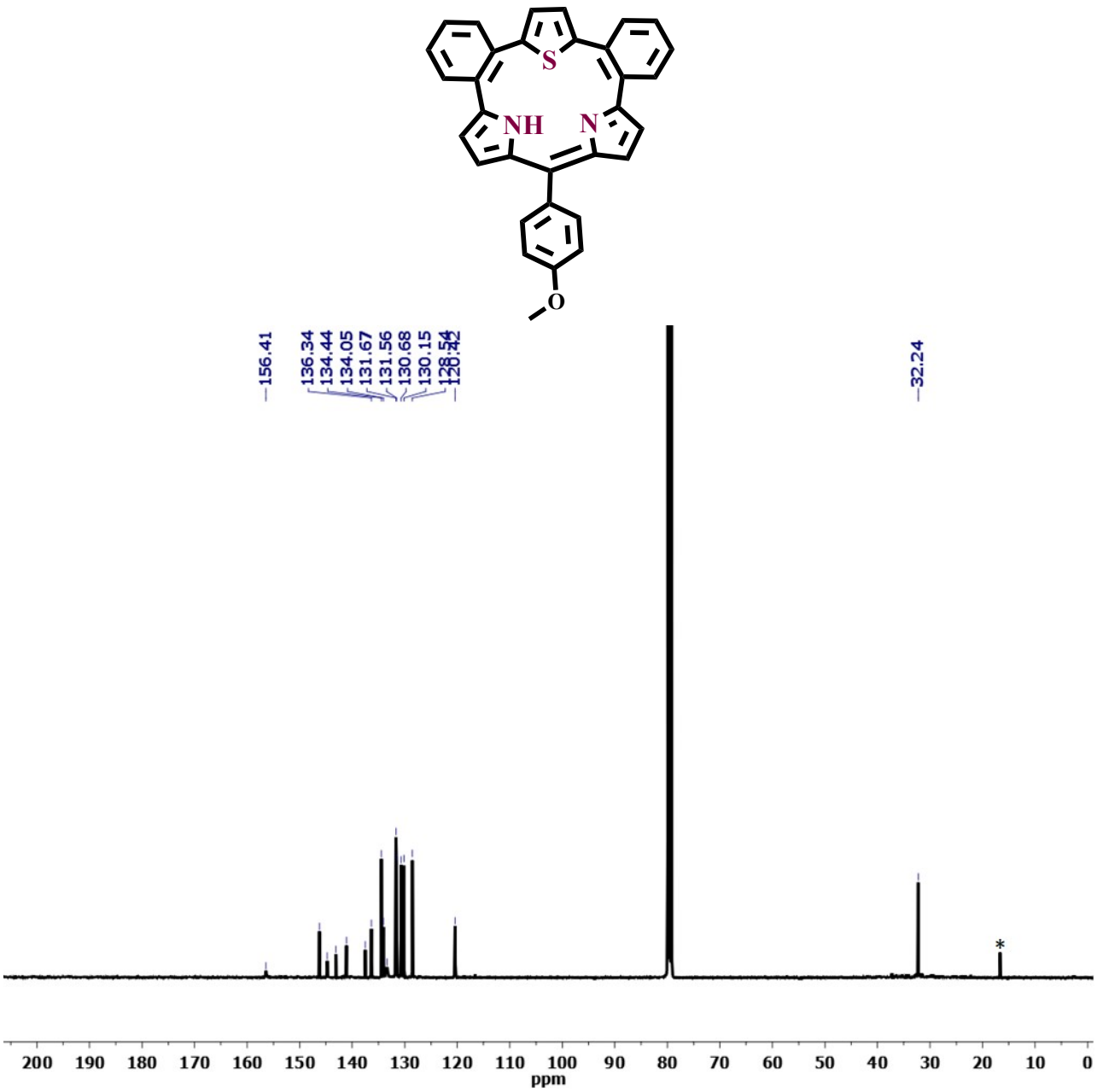


Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of the compound **6** recorded in $CDCl_3$ at 25°C at 400 MHz NMR instrument. The asterisk indicates the residual solvent peaks.

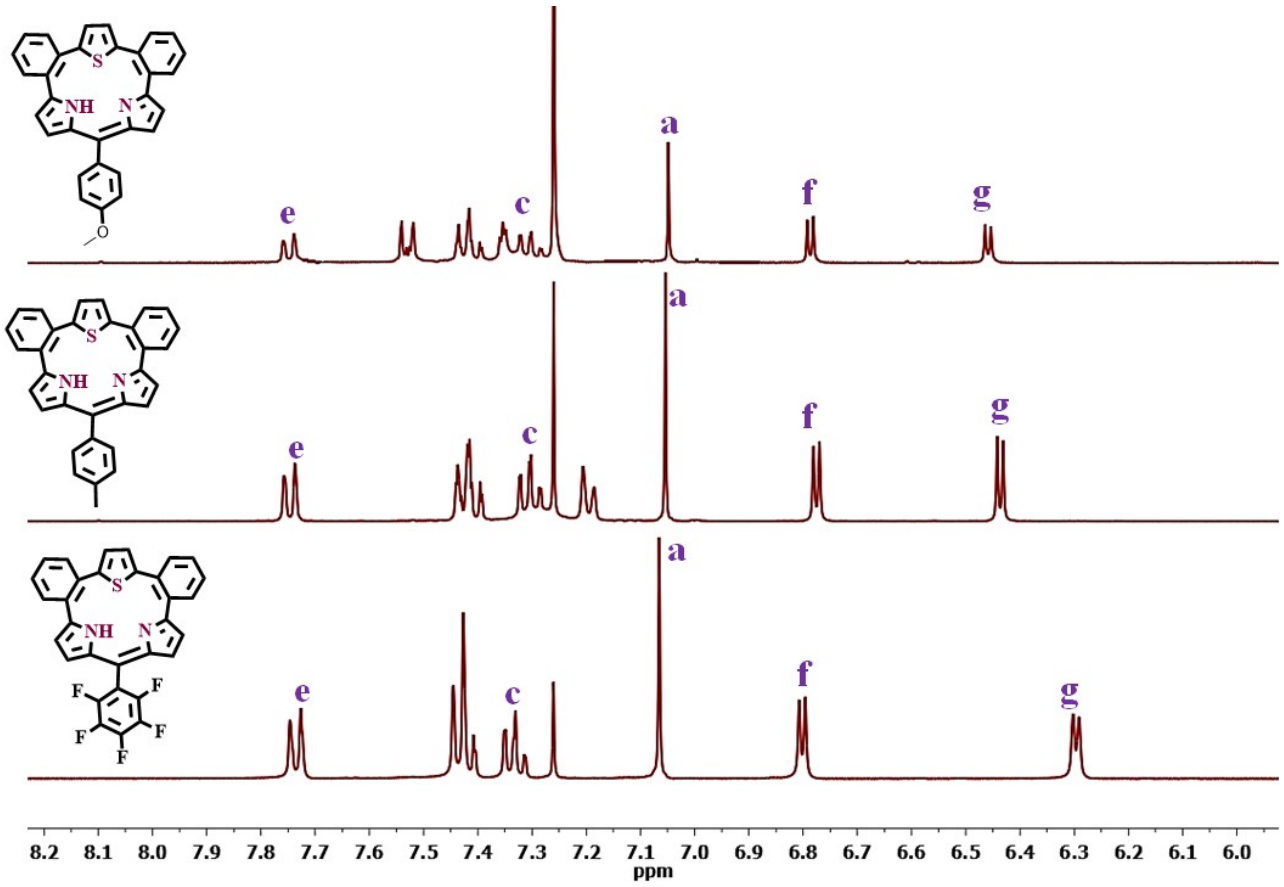


Figure S18. Comparison of ^{1}H NMR spectrum of macrocycles **4-6**.

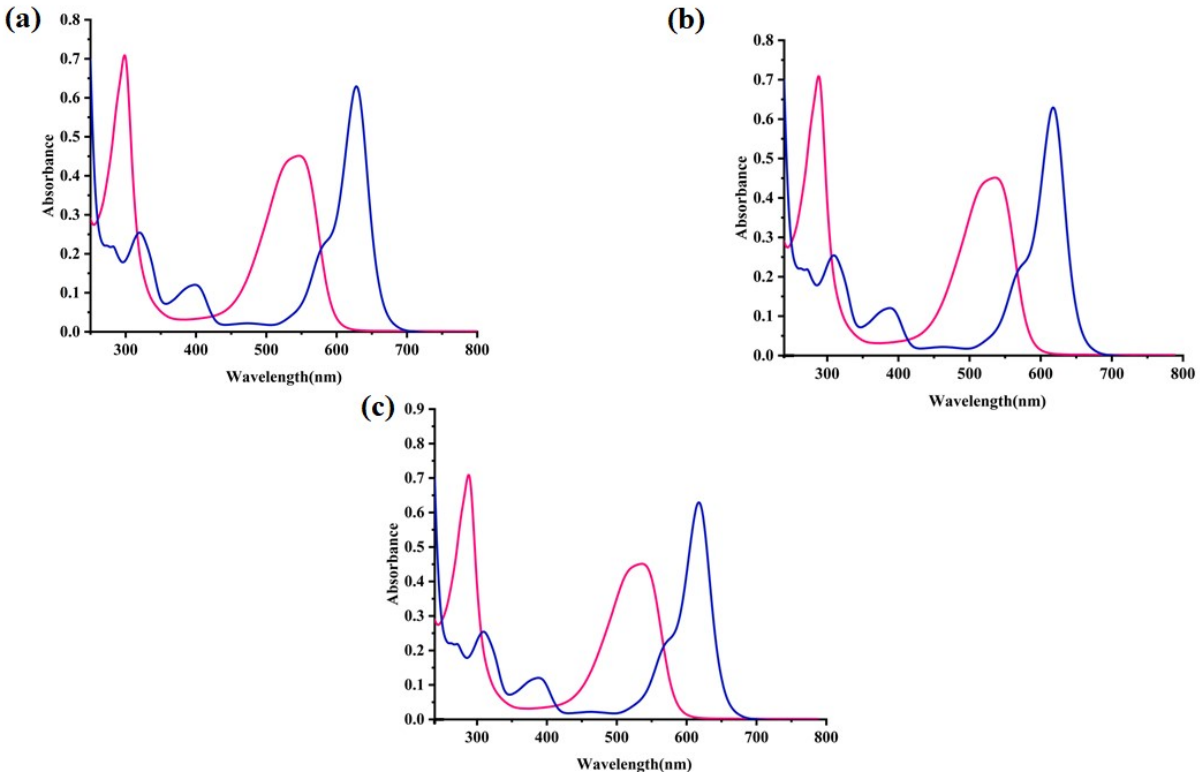


Figure S19. Comparison of UV-Vis absorption spectra of Macrocycles **4-6** free base (pink line) and in the presence of excess TFA (blue line) recorded in chloroform at 25°C.

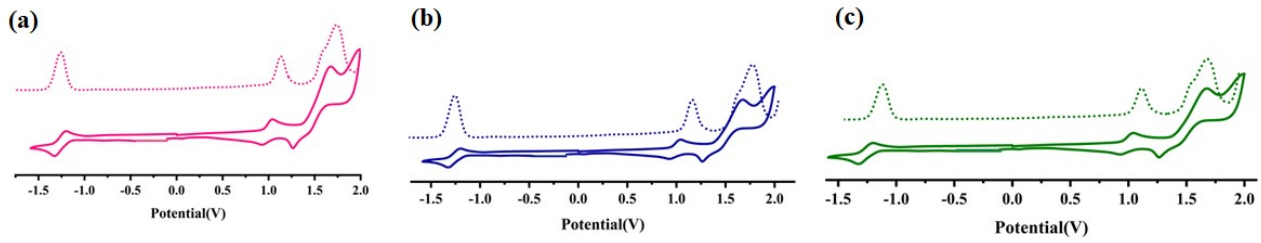


Figure S20. Cyclic voltammograms (colored lines) along with differential pulse voltammograms (dotted lines) of macrocycles **4-6** recorded in CH_2Cl_2 containing 0.1 M TBAP as the supporting electrolyte and a saturated calomel electrode (SCE) as the reference electrode at scan rates of 50 mVs^{-1}.

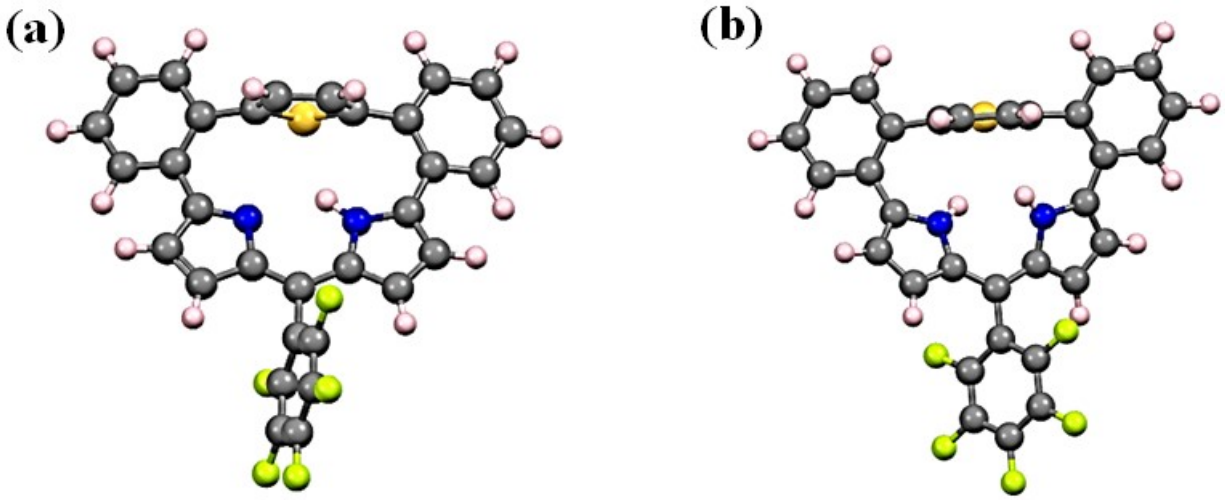


Figure S21. Ground state optimized structures of macrocycles **4** and **4.H**$^+$.

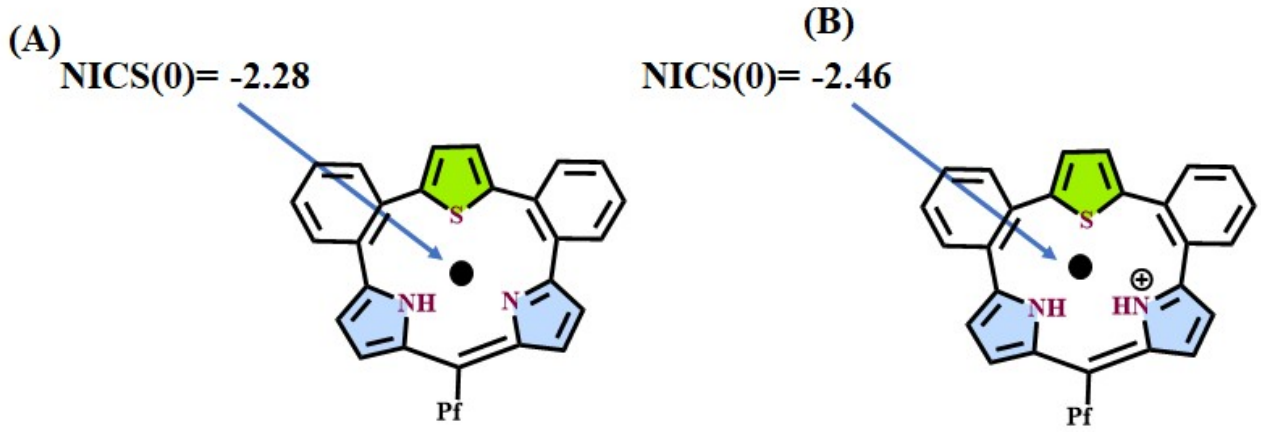


Figure S22. NICS values of compound **4** (A) and its protonated derivative **4.H**$^{+}$ (B) on the optimized structures (B3LYP/6-31g(d,p))(Black dots represent Bq atoms.)

Table S1. S_0 optimized geometry of the compound **4** at B3LYP/6-31g (d,p) level of theory

Sum of imaginary frequencies= 0

Atom	X	Y	Z	Atom	X	Y	Z
C	3.364572	-1.24609	0.546149	C	-0.38843	-3.45579	-0.26677
C	3.072969	-0.75672	1.79236	C	-1.51448	0.019821	-0.08169
C	3.057081	0.669362	1.853526	C	-3.00871	-0.01038	-0.02587
C	3.327936	1.26773	0.653134	C	-3.78668	0.424642	-1.10356
S	3.67243	0.068691	-0.57025	C	-5.17907	0.400521	-1.06426
C	3.279819	2.700773	0.283472	C	-5.82719	-0.07021	0.074726
C	3.372729	-2.64589	0.060922	C	-5.08019	-0.5119	1.16419
C	4.482296	3.416951	0.232386	C	-3.68933	-0.47747	1.103229
C	4.51634	4.765115	-0.11934	F	-7.16135	-0.0976	0.123016
C	3.324954	5.416676	-0.43262	F	-3.0033	-0.9019	2.172448

C	2.121817	4.719962	-0.38353
C	2.059293	3.35753	-0.03036
C	2.181776	-3.31256	-0.33567
C	2.297947	-4.6353	-0.81088
C	3.523237	-5.28634	-0.88524
C	4.687001	-4.62759	-0.48907
C	4.599984	-3.31693	-0.02702
C	0.827201	-2.74009	-0.27047
C	0.728658	2.715268	-0.00064
C	-0.51962	3.462576	0.148837
C	-1.52363	2.546297	0.125091
C	-0.88427	1.25357	-0.03631
N	0.500403	1.412792	-0.10676
N	0.50243	-1.41473	-0.20903
C	-0.86694	-1.24866	-0.16942
C	-1.43357	-2.53754	-0.20752

F	-5.7007	-0.95934	2.261701
F	-5.89442	0.821908	-2.11313
F	-3.19946	0.875889	-2.21857
H	2.84156	-1.40074	2.633408
H	2.804942	1.23274	2.74455
H	5.40239	2.896278	0.47985
H	5.462704	5.296365	-0.15059
H	3.329316	6.464044	-0.7193
H	1.206828	5.235927	-0.6518
H	1.407915	-5.15164	-1.15196
H	3.568126	-6.30369	-1.26209
H	5.650876	-5.12384	-0.54509
H	5.495954	-2.78733	0.281847
H	-0.61738	4.529439	0.292468
H	-2.58362	2.727433	0.234499
H	1.117381	-0.60365	-0.20649
H	-2.4898	-2.76056	-0.18737
H	-0.48382	-4.53097	-0.27317

Table S2. S_0 optimized geometry of the compound **4.H**$^+$ at B3LYP/6-31g (d,p) level of theory

Sum of imaginary frequencies= 0

Atom	X	Y	Z	Atom	X	Y	Z
C	3.344101	-1.25624	0.468126	C	-0.27851	-3.20783	-1.24126
C	3.241094	-0.70038	1.719074	C	-1.54037	0.008865	0.001532
C	3.253926	0.727671	1.717773	C	-3.01611	-0.013	0.010318
C	3.381882	1.274475	0.468863	C	-3.78604	0.917454	-0.71098
S	3.523618	0.006819	-0.73869	C	-5.17743	0.90467	-0.69813
C	3.315821	2.706354	0.09223	C	-5.85439	-0.0659	0.035941
C	3.317103	-2.69317	0.102989	C	-5.12883	-1.01131	0.756563
C	4.498154	3.387575	-0.2273	C	-3.73824	-0.97322	0.74215
C	4.498385	4.753575	-0.4996	F	-7.19088	-0.09008	0.048736
C	3.294876	5.459823	-0.45357	F	-3.08977	-1.88274	1.483198
C	2.108594	4.795955	-0.16339	F	-5.77406	-1.93654	1.478961
C	2.081846	3.412863	0.106229	F	-5.8694	1.804721	-1.40906
C	2.140372	-3.34944	-0.35811	F	-3.18702	1.847648	-1.46748
C	2.240796	-4.7289	-0.64795	H	3.135157	-1.30389	2.613994
C	3.431932	-5.42786	-0.51406	H	3.139659	1.334105	2.608861
C	4.581754	-4.77489	-0.06482	H	5.430711	2.831145	-0.23433
C	4.509379	-3.41959	0.240622	H	5.427713	5.260996	-0.73874
C	0.834791	-2.71462	-0.54654	H	3.2769	6.525218	-0.66321
C	0.78295	2.790771	0.377129	H	1.170192	5.340667	-0.17459
C	-0.34369	3.338633	0.998542	H	1.352032	-5.26303	-0.9639
C	-1.36863	2.383049	0.973039	H	3.459366	-6.48784	-0.74884
C	-0.88075	1.23311	0.322578	H	5.517161	-5.31311	0.050603
N	0.438879	1.509864	-0.00389	H	5.391398	-2.89294	0.592299

N	0.459552	-1.48115	-0.04361	H	-0.38545	4.316065	1.457885
C	-0.85908	-1.19353	-0.36481	H	-2.35463	2.479343	1.403308
C	-1.32087	-2.28291	-1.12616	H	0.99482	0.93563	-0.62042
				H	0.996169	-0.97604	0.646332
				H	-2.29843	-2.34949	-1.58072
				H	-0.30842	-4.12646	-1.80834

References:

1 O. Treutler and R. Ahlrichs, *J. Chem. Phys.*, 1995, **102**, 346–354.

2 C. Xiii, F. Component, L. Radom, W. J. Hehre and J. A. Pople, 1971, **4064**, 2371–2381.

3 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372–1377.

4 J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.*, 2005, **105**, 2999–3093.

5 R. Bauernschmitt and R. Ahlrichs, *Chem. Phys. Lett.*, 1996, **256**, 454–464.