Pyrrolizinofluorene-embedded Dithiacalixcorrole(1.0.*1.1*)s

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Materials, methods, instrumentation and computational details.

All the chemicals used were reagent grade, unless mentioned otherwise. Synthesis of compounds **8**[1] and **9a-c**[2] were carried out by following reported procedure. Purification of compounds were done using silica gel (60−120 and 100−200 mesh size) and basic alumina column chromatographic methods. The ^{1}H, ^{13}C and 2D NMR spectra were recorded on Bruker 400 MHz and 500 MHz instruments in $CDCl_3$. The frequencies for the ^{13}C nucleus are 100.06 and 125.77 MHz for 400 MHz and 500 MHz instruments, respectively. Tetramethylsilane [Si $(CH_3)_4$] was used as an internal standard for ^{1}H and ^{13}C NMR. Structural assignments were made with additional information from ^{1}H-^{1}H COSY, ^{1}H-^{1}H NOESY, ^{1}H-^{1}H HSQC and ^{1}H-^{1}H HMBC experiments for compound **7a**. Absorption spectra were obtained using Cary series UV−Vis−NIR Spectrophotometer. The solution for absorption studies of compound **7a-c** (4×10^{-5} M) were prepared by using a HPLC grade $CHCl_3$. HRMS were recorded on Bruker maXis Impact and LC-MS Q-TOF micro mass spectrometer using positive mode ESI methods for acetonitrile/methanol solutions. The electrochemical experiments were carried out in dry dichloromethane using 0.1 M tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte. Cyclic voltammetry (CV) studies were performed with BAS electrochemical system employing the three-electrode configuration consisting of a glassy carbon (working electrode), platinum wire (auxiliary electrode) and saturated calomel (reference electrode) electrodes. Half wave potentials were measured using differential pulse voltammetry (DPV) and also calculated manually by taking the average of cathodic and anodic peak potentials.

X-ray Crystal Structure Analysis:

Single crystals for X-ray diffraction were obtained by slow diffusion of CH_3OH solution over the CH_2Cl_2 solution of **7a** for four days. Rigaku Saturn 724 diffractometer was used for performing

Single-crystal X-ray structure analysis which comprised of a low-temperature attachment. Data were collected at 100 K using graphite-monochromated MoK$_\alpha$ radiation (λ_α =0.71073 Å) by the ω-scan technique. The data were reduced using CrysalisPro Red 171.41_64.93a software.[3] The structures were solved using Olex2 1.5[4] with the SHELXT[5] structure solution program using intrinsic phasing and refined the with the SHELXL[6] refinement package using least-squares minimization. All non-hydrogen atoms were refined anisotropically. X-ray data for the compound **7a** was collected on a Bruker Kappa CCD diffractometer equipped with a graphite monochromated MoK$_\alpha$ radiation source at 200 K using the θ−2θ scan mode. An empirical absorption correction by multi scans was applied and all of the non-hydrogen atoms were refined with anisotropic displacement factors. Hydrogen atoms were placed in ideal positions and fixed with relative isotropic displacement parameters. The corresponding loop of the residual electron voids (from PLATON) was appended in the corresponding CIF file. CCDC no. **2365345** contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Computational Details:

All computations were performed using the Gaussian 09 program package. The density functional theory (DFT) method, with hybrid functional B3LYP in conjunction with 6-31G (d,p) basis set was implemented to optimize the geometry of compound **7a** in ground (S_0) state.[7] In order to improve the accuracy of electronic structure calculations and geometry optimization in S_0 state, dispersive interactions in the electron density of the macrocycle **7a** were studied using Grimme's dispersion correction method (GD2) over the B3LYP/6-31G (d,p) level of theory.[8] Oscillator strengths were obtained using identical basis and functional hybrid set B3LYP/6-31G (d,p), whereas the vertical excitation energies were obtained by the help of TD-DFT techniques for

$S_0 \rightarrow S_n$ transitions.[9, 10] All computations were performed in toluene medium using the Polarizable Continuum Model (PCM) and Self-Consistent Reaction Field (SCRF). The electronic absorption spectra, and the oscillator strengths were thoroughly examined using time-dependent DFT with the PCM model based on the optimized structures in the S_0 state.

Experimental Section:

Pyrrolizinofluorene-embedded bithiacalixcorroles 7a-c.

To the well-stirred solution of *meso*-fused fluorene-based tripyrrane (0.21 mmol, 1.0 equiv.) **8** in CH_2Cl_2 (50 mL) in an inert atmosphere at room temperature, a required amount of appropriate bithiophene diol (0.21 mmol, 1.0 equiv.) **9a/9b/9c** was added, and the resultant mixture was stirred until the bithiophene diol dissolved completely. To initiate condensation, a TFA (0.14 mmol, 0.7 equiv.) was added to reaction mixture and stirred under a nitrogen atmosphere at room temperature for 40 min. The oxidant DDQ (0.52 mmol, 2.5 equiv.) was then added to the reaction mixture and stirred in open air at room temperature for another 45 min. After completion of reaction as indicated by TLC analysis, the solvent was removed on a rotary evaporator under vacuum. The obtained crude compounds were subjected to basic alumina column and eluted with dichloromethane followed by further purification on a basic alumina column chromatography using *n*-hexane/ dichloromethane (95:5) as a mobile phase for the macrocycles **7a-c**. The desired **7a-c** were obtained as pink solids in 4-5% yields.

Synthesis of compound 7a

The compound **7a** was synthesized from *meso*-fused fluorene-based tripyrrane (100 mg, 0.21 mmol) **8** and bithiophene diol (90 mg, 0.21 mmol) **9a** by following the general procedure reported above for compounds **7a-c**; pink solid. Yield: 4% (7 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.71 (d, J = 7.3 Hz, 2H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.37 (d, *J* = 3.7

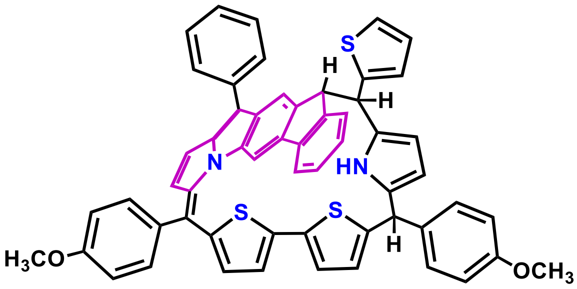
Hz, 1H), 7.35 (d, *J* = 7.4 Hz, 1H), 7.31 (d, *J* = 5.0 Hz, 1H), 7.03 (ddd, *J* = 14.2, 8.8, 3.6 Hz, 8H), 6.96 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 5.8 Hz, 1H), 6.76 (d, *J* = 8.7 Hz, 2H), 6.72 (d, *J* = 3.4 Hz, 1H), 6.60 (s, 1H), 6.58 (d, *J* = 5.7 Hz, 1H), 6.55 (d, *J* = 3.7 Hz, 1H), 5.95 (s, 1H), 5.80 (t, *J* = 2.9 Hz, 1H), 5.28 (d, *J* = 3.8 Hz, 1H), 5.17 (t, *J* = 3.01 Hz, 1H), 5.12 (s, 1H), 4.74 (d, *J* = 3.9 Hz, 1H), 3.89 (s, 3H), 3.74 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 159.9, 158.4, 152.2, 149.4, 145.0, 144.4, 143.6, 142.3, 139.9, 139.6, 138.4, 136.6, 135.1, 134.8, 134.0, 133.2, 131.9, 131.8, 130.6, 129.9, 129.4, 129.0, 128.6, 127.6, 126.9, 126.6, 125.5, 124.6, 124.4, 124.3, 120.7, 120.2, 117.3, 115.2, 113.8, 113.6, 112.7, 108.9, 107.0, 105.5, 55.5, 55.3, 52.9, 44.4, 43.2. HR-MS (ESI-TOF): Calcd. for $C_{57}H_{40}N_2O_2S_3$ $[M]^+$ m/z 880.2246; Found $[M]^+$ m/z 880.2213.

Synthesis of compound 7b

The compound **7b** was synthesized from *meso*-fused fluorene-based tripyrrane (100 mg, 0.21 mmol) **8** and appropriate bithiophene diol (84 mg, 0.21 mmol) **9b** by following the general procedure reported above for compounds **7b-c**; pink solid. Yield: 5% (8 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.73 (d, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.7 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.38 (dd, *J* = 8.4, 5.1 Hz, 2H), 7.34 (d, *J* = 5.1 Hz, 1H), 7.26 (d, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 3.7 Hz, 1H), 7.04 (dt, *J* = 9.1, 4.9 Hz, 8H), 6.99 (dd, *J* = 11.1, 4.8 Hz, 1H), 6.87 (d, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 5.7 Hz, 1H), 6.74 (d, *J* = 3.4 Hz, 1H), 6.63 (s, 1H), 6.61 (d, *J* = 5.7 Hz, 1H), 6.57 (d, *J* = 3.6 Hz, 1H), 5.98 (s, 1H), 5.82 (t, *J* = 2.9 Hz, 1H), 5.30 (d, *J* = 3.7 Hz, 1H), 5.20 (t, *J* = 2.7 Hz, 1H), 5.15 (s, 1H), 4.76 (d, *J* = 3.9 Hz, 1H), 2.46 (s, 3H), 2.30 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 152.1, 149.4, 144.9, 144.4, 143.6, 142.2, 140.4, 139.6, 138.6, 138.4, 138.3, 138.0, 136.7, 136.6, 136.4, 135.2, 134.7, 133.9, 132.0, 131.8, 130.6, 129.8, 129.1, 129.0, 128.9, 128.6, 128.3, 127.6, 126.9, 126.6, 125.7, 125.6, 124.6, 124.4, 124.3, 120.8, 120.7, 120.2, 117.5, 115.2, 112.9, 108.9, 107.0, 105.5, 52.9, 44.8, 43.2, 21.4, 21.1. HR-MS (ESI-TOF): Calcd. for $C_{57}H_{41}N_2S_3$ $[M+H]^+$ m/z 849.2413; Found $[M+H]^+$ m/z 849.2426.

Synthesis of compound 7c

The compound **7c** was synthesized from *meso*-fused tripyrrane (100 mg, 0.21 mmol) **8** and appropriate bithiophene diol (102 mg, 0.21 mmol) **9c** by following the general procedure reported above for compounds **7a-c**; pink solid. Yield: 4% (8 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.71 (d, *J* = 7.6 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.45 (dd, *J* = 21.2, 8.2 Hz, 4H), 7.38 – 7.34 (m, 2H), 7.31 (d, *J* = 5.0 Hz, 1H), 7.24 (s, *J* = 8.2 Hz, 2H), 7.02 (m, 8H), 6.85 (d, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 5.7 Hz, 1H), 6.72 (s, 1H), 6.63 (d, *J* = 5.7 Hz, 1H), 6.60 (s, 1H) 6.55 (d, *J* = 3.3 Hz, 1H), 5.96 (s, 1H), 5.79 (t, *J* = 2.8 Hz, 1H), 5.27 (d, *J* = 3.3 Hz, 1H), 5.20 (s, 1H), 5.12 (s, 1H), 4.74 (d, *J* = 3.4 Hz, 1H), 1.39 (s, 9H), 1.25 (s, 9H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 152.1, 151.4, 149.6, 149.5, 145.0, 144.4, 143.6, 142.1, 140.5, 139.6, 138.5, 137.9, 136.7, 135.3, 134.7, 133.9, 132.1, 131.8, 131.6, 130.7, 129.8, 129.0, 128.6, 128.0, 127.6, 126.9, 126.6, 125.7, 125.5, 125.2, 125.19, 124.6, 124.4, 124.3, 120.7, 120.7, 120.3, 117.5, 115.2, 114.2, 112.9, 108.9, 107.0, 105.6, 52.9, 44.8, 43.3, 31.5. HR-MS (ESI-TOF): Calcd. for $C_{63}H_{53}N_2S_3$ $[M+H]^+$ m/z 955.3355; Found $[M+H]^+$ m/z 933.3355.



Compound **7a**

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Analysis Info

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Comment	C57H40N2O2S3		

Acquisition Parameter

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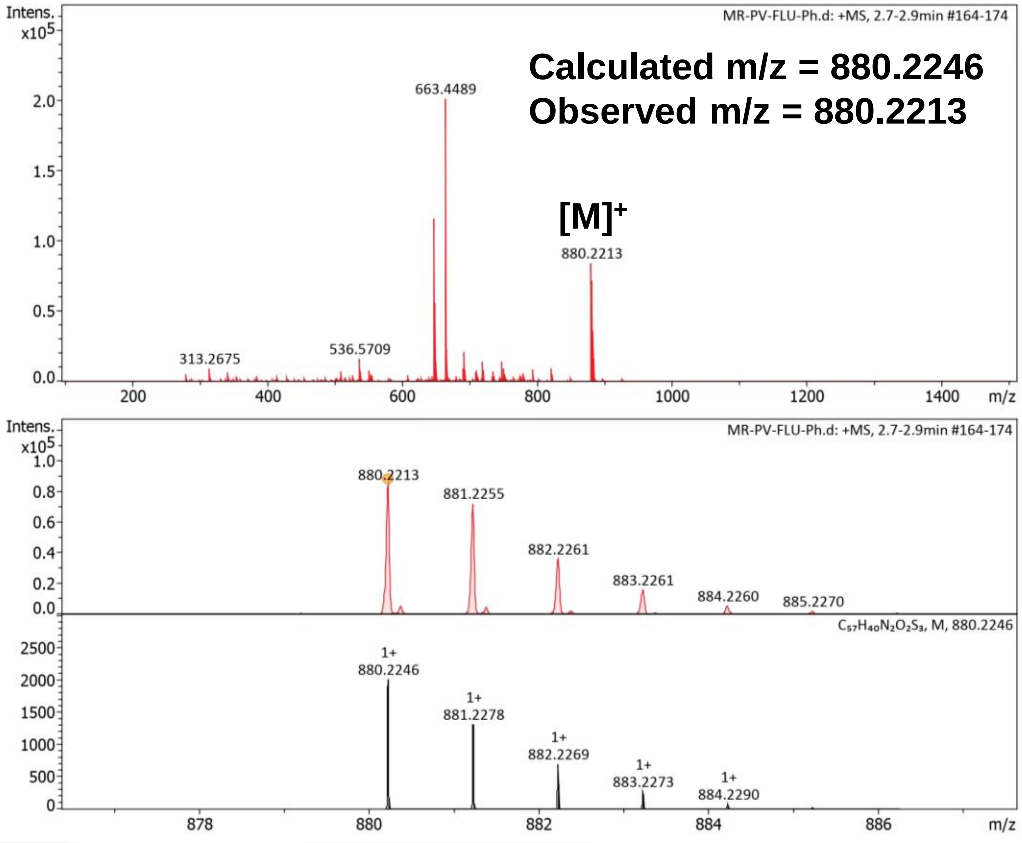
		Set Corona	0 nA	Set APCI Heater	0 °C



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
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Figure S1. HR mass spectrum of the compound **7a**.

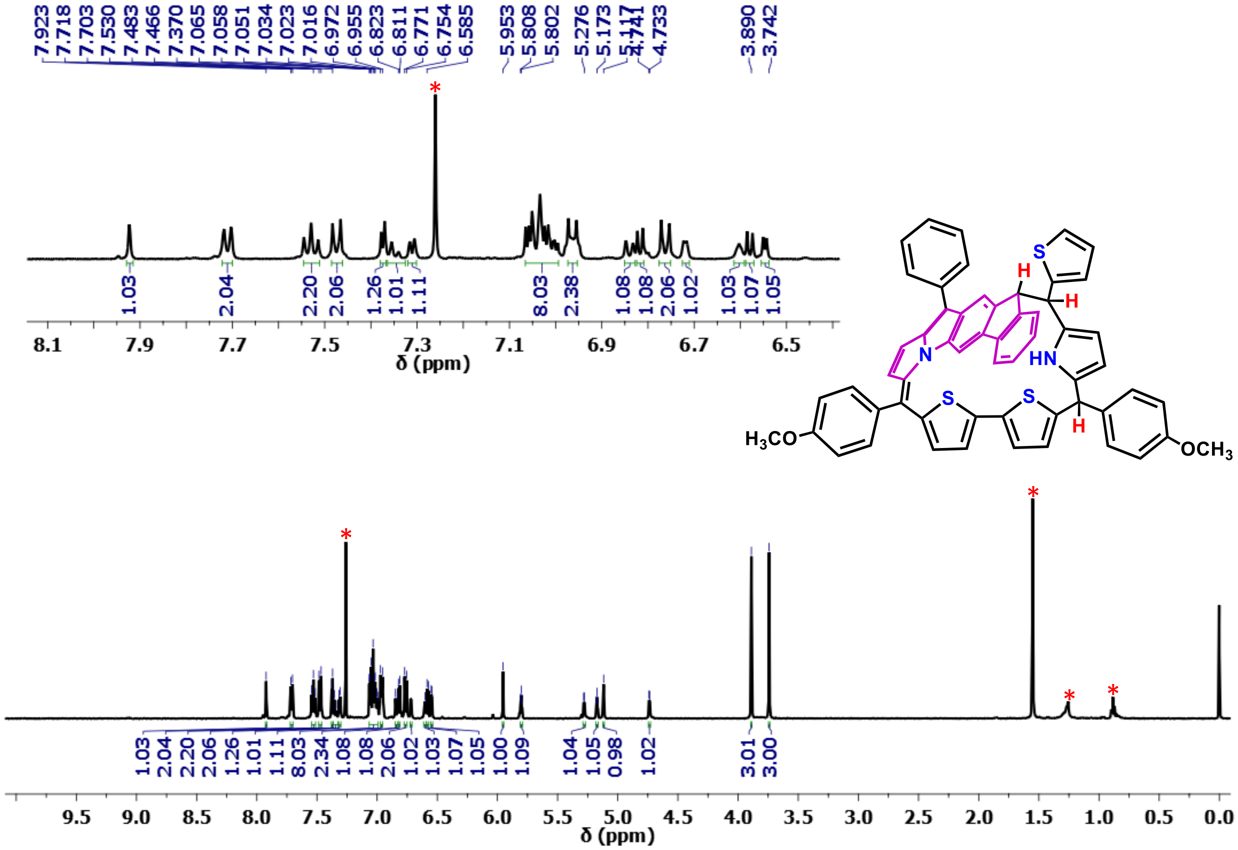


Figure S2. ^{1}H-NMR spectrum of the compound **7a** recorded in $CDCl_3$ on 500 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.

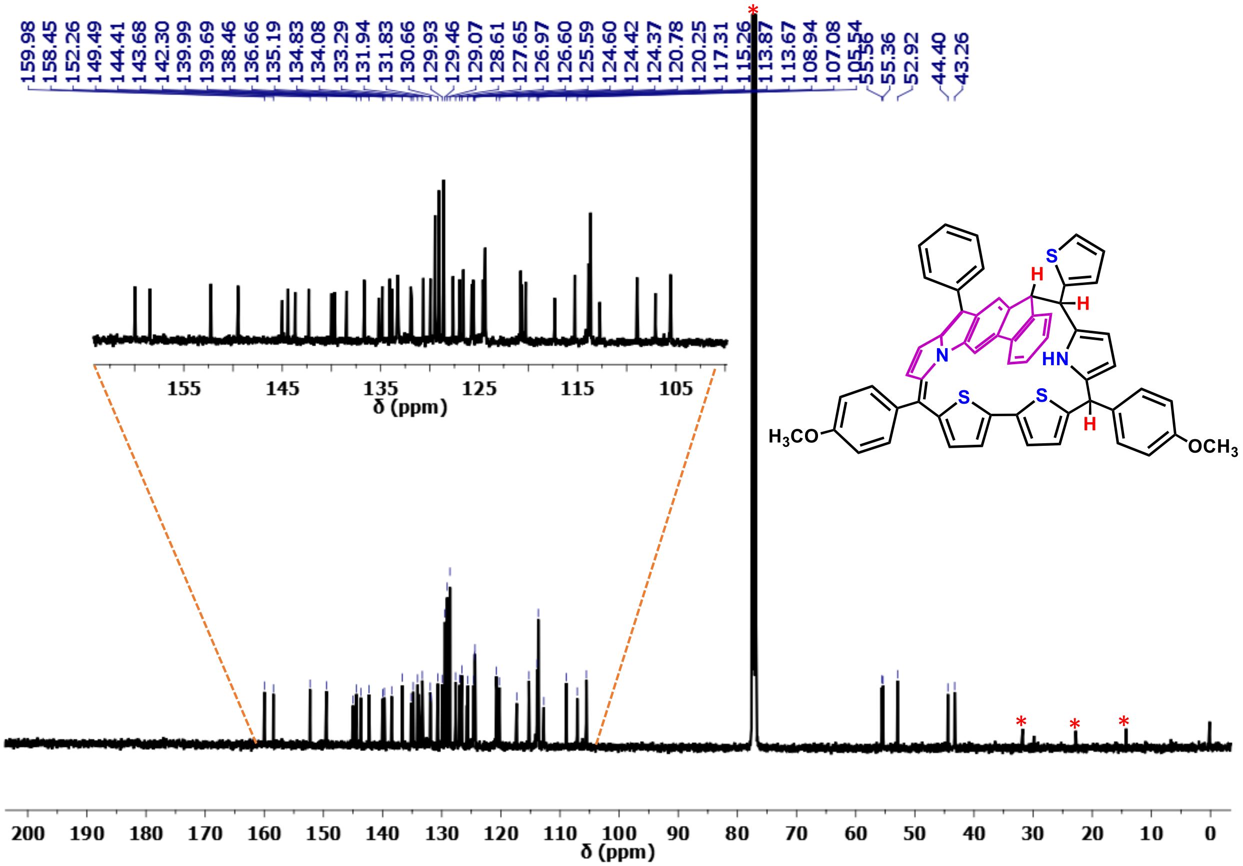


Figure S3. ^{13}C NMR spectrum of the compound **7a** recorded in $CDCl_3$ on 126 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.

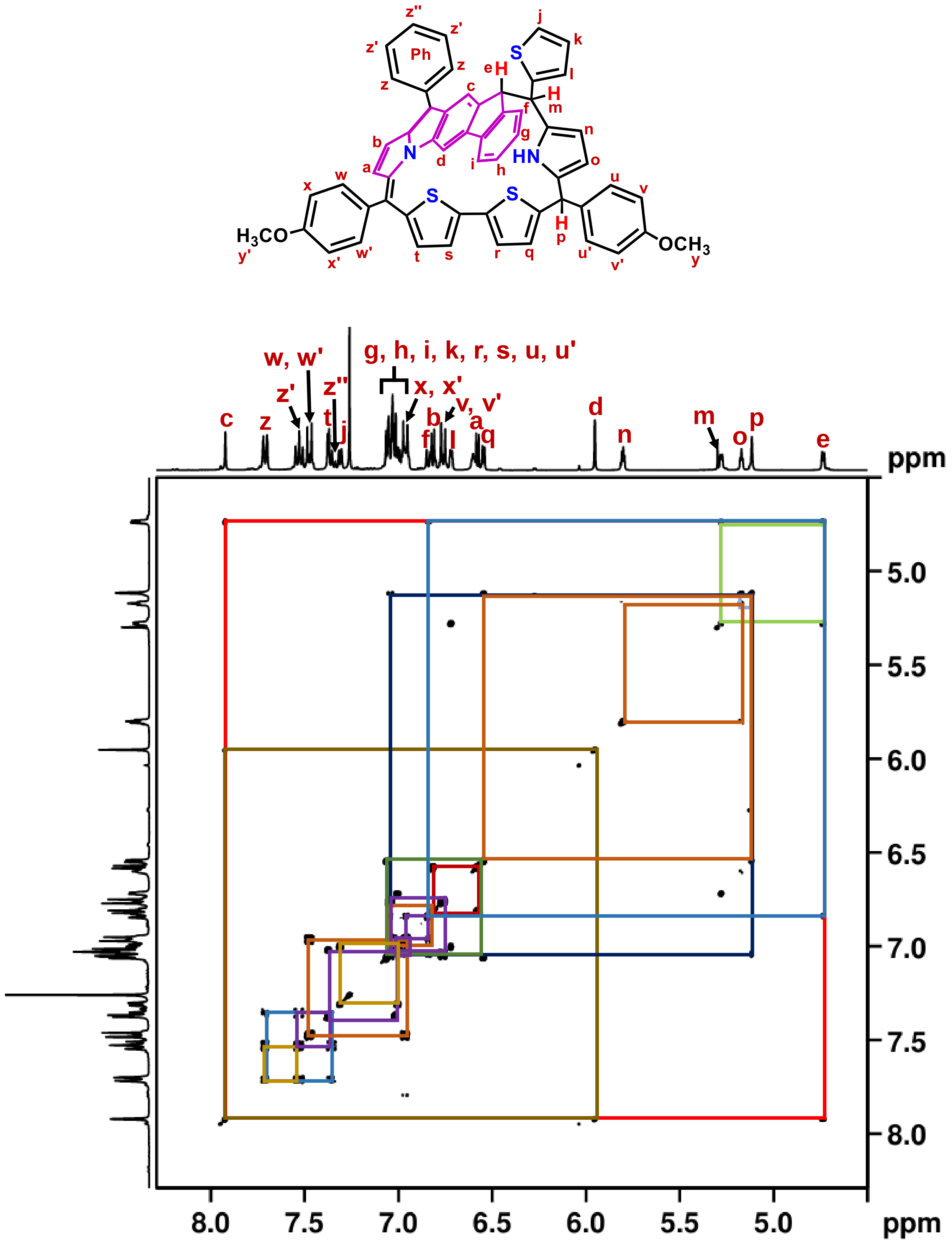


Figure S4. Partial ^{1}H–^{1}H COSY of compound **7a** recorded in $CDCl_3$ at 25 °C.

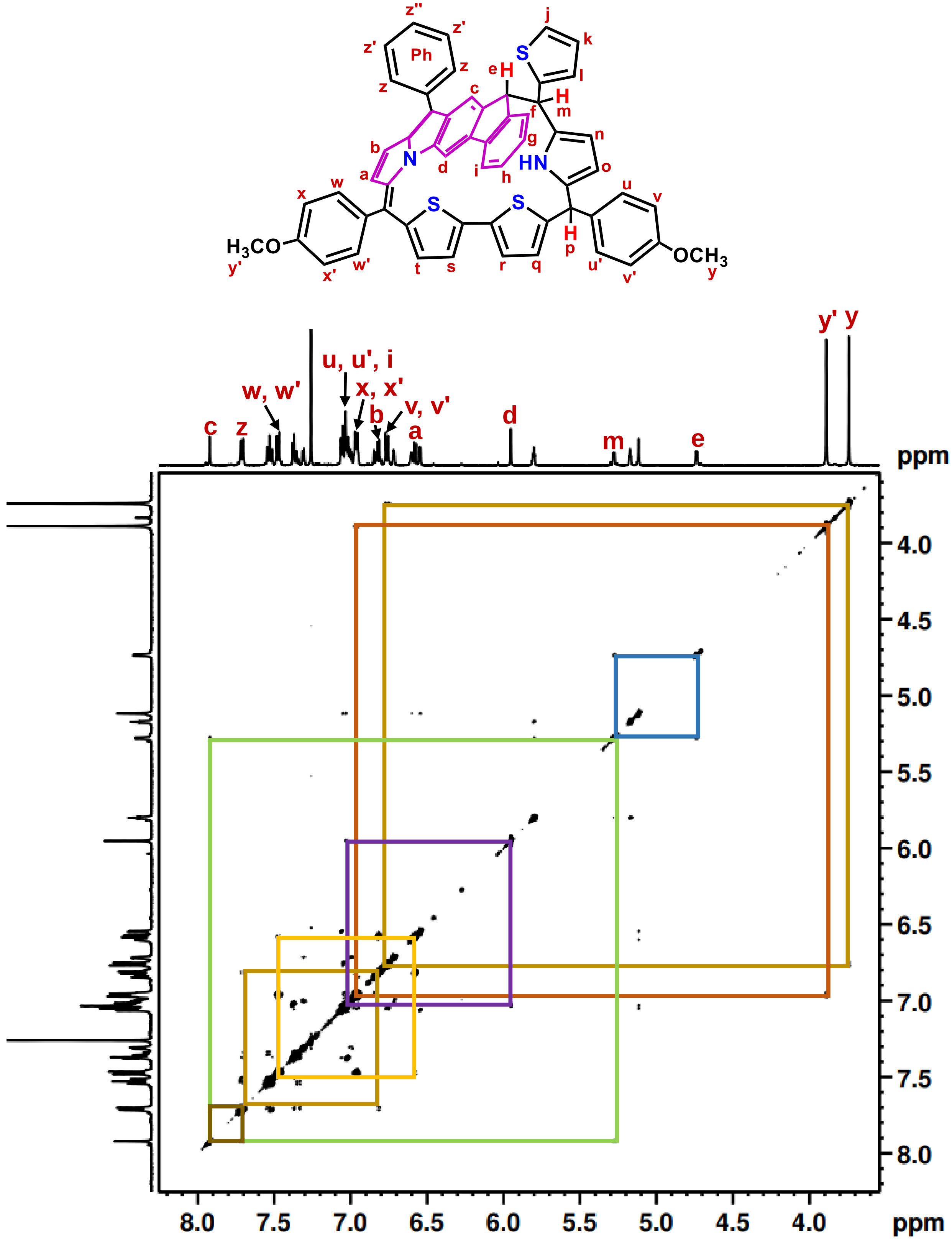
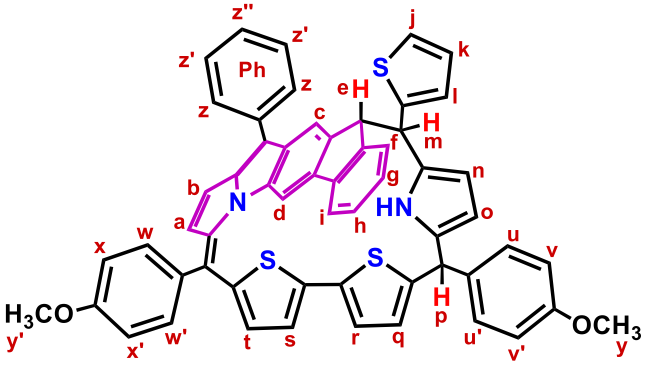


Figure S5. ^{1}H–^{1}H NOESY of compound **7a** recorded in CDCl$_3$ at 25 °C.



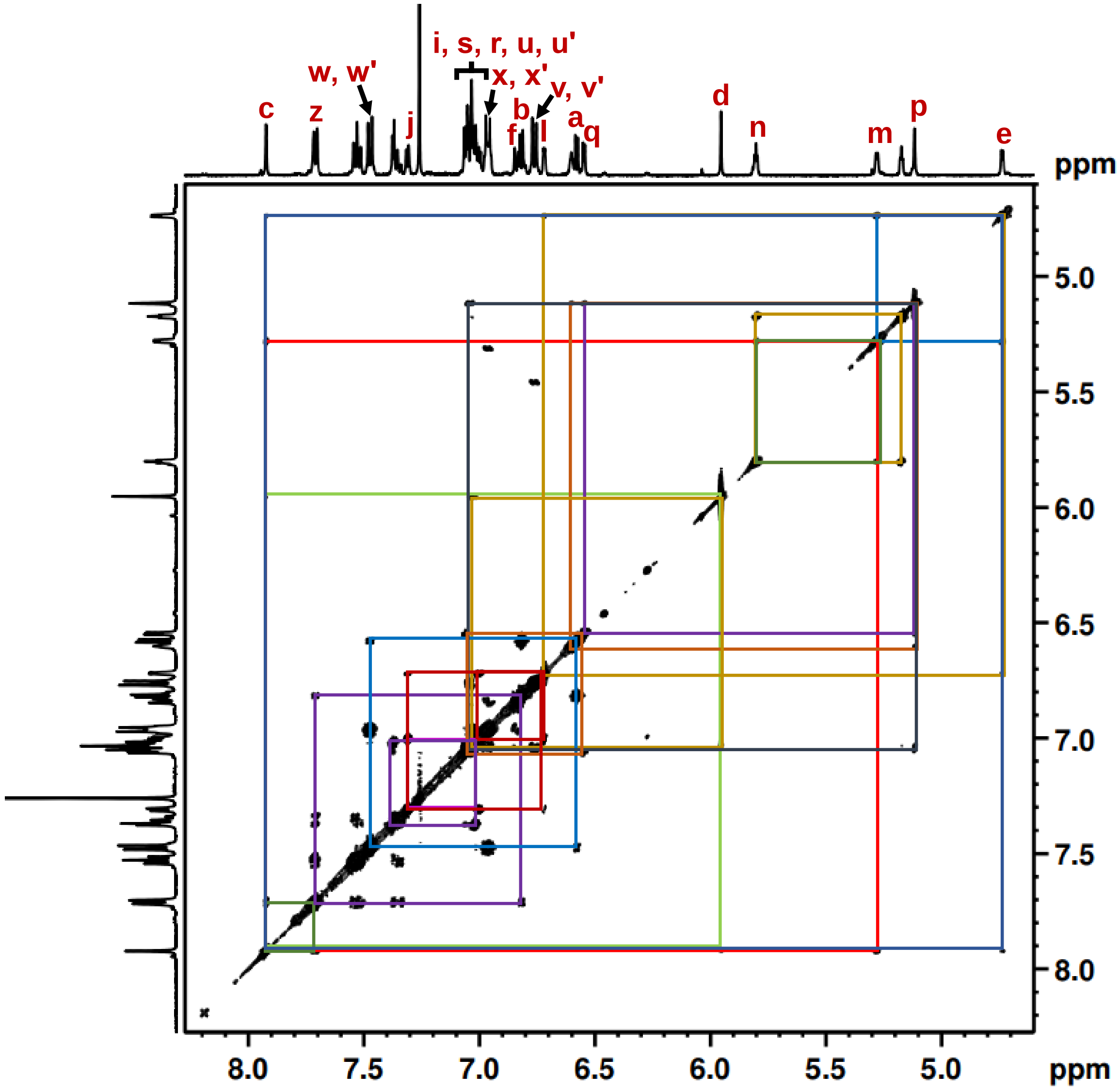


Figure S6. Expanded ^{1}H–^{1}H NOESY of compound **7a** recorded in CDCl$_3$ at 25 °C.

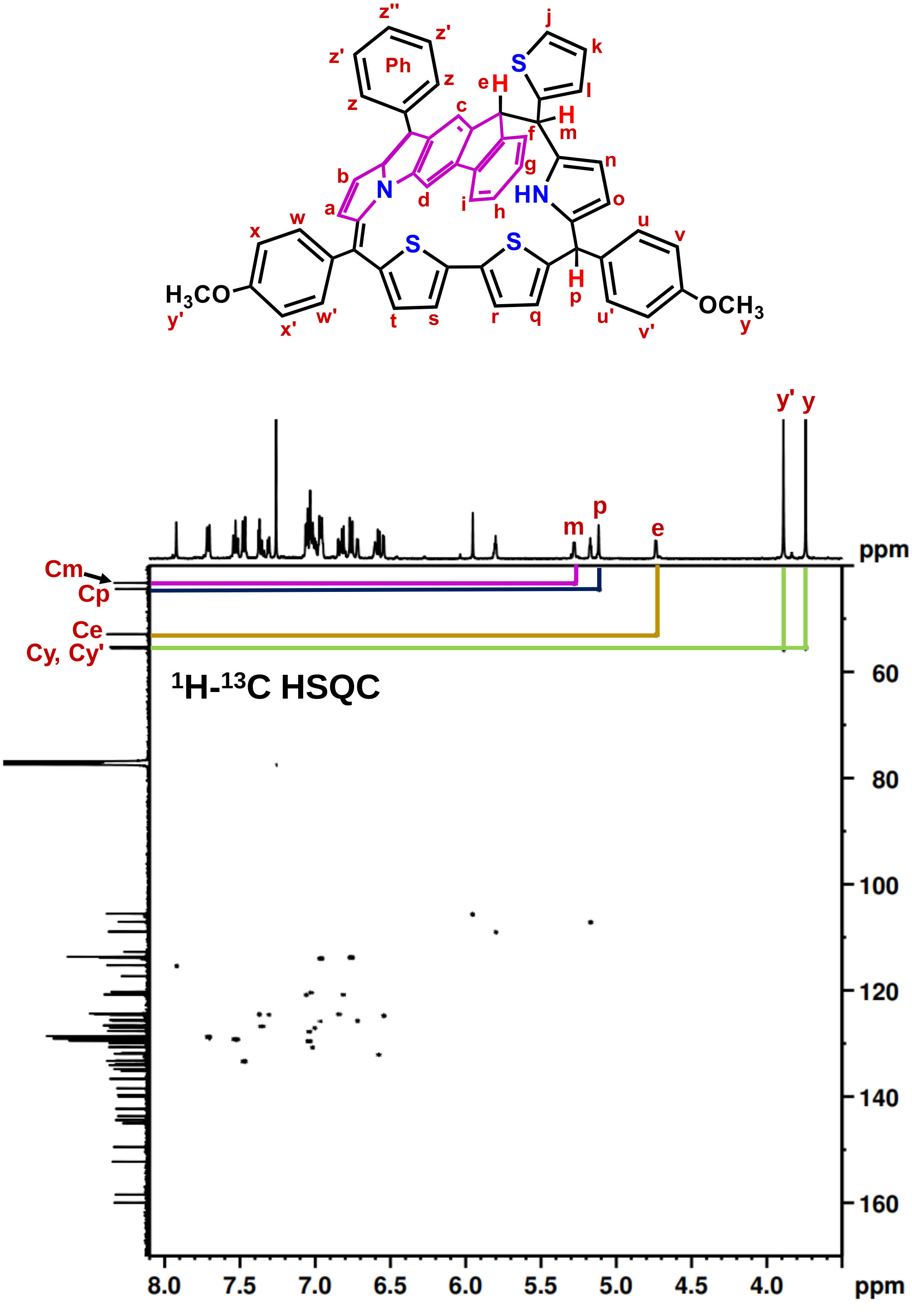


Figure S7. ^{1}H–^{13}C HSQC of compound **7a** recorded in CDCl$_3$ at 25 °C.

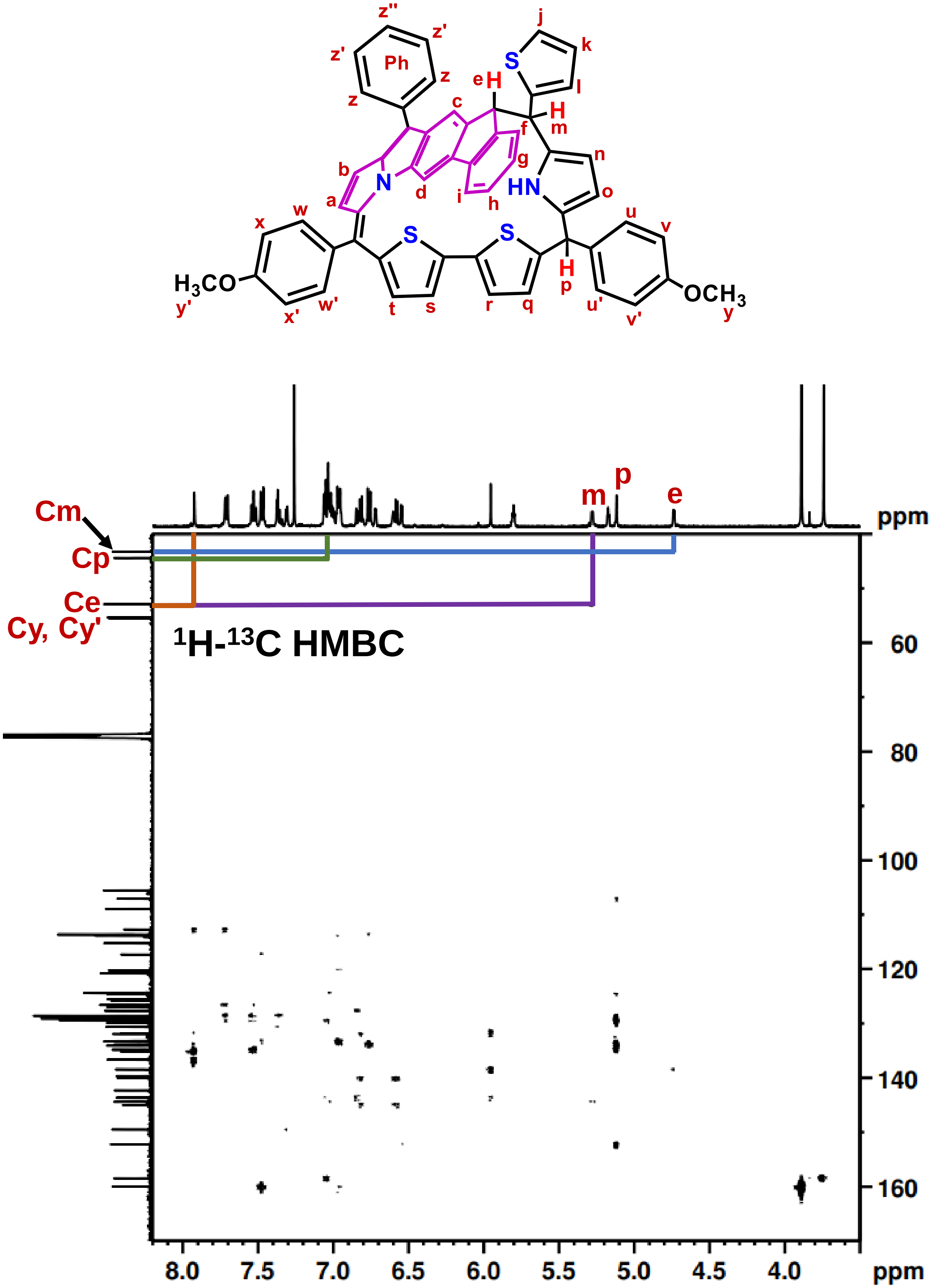
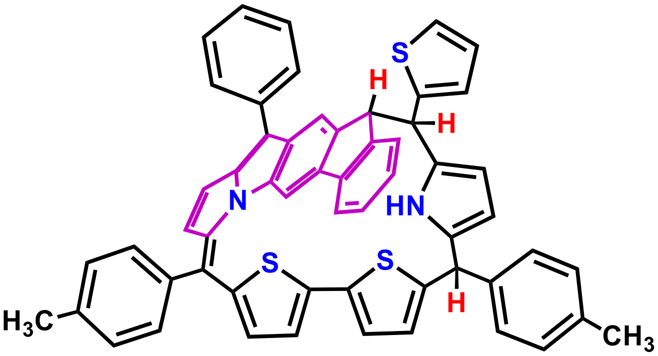
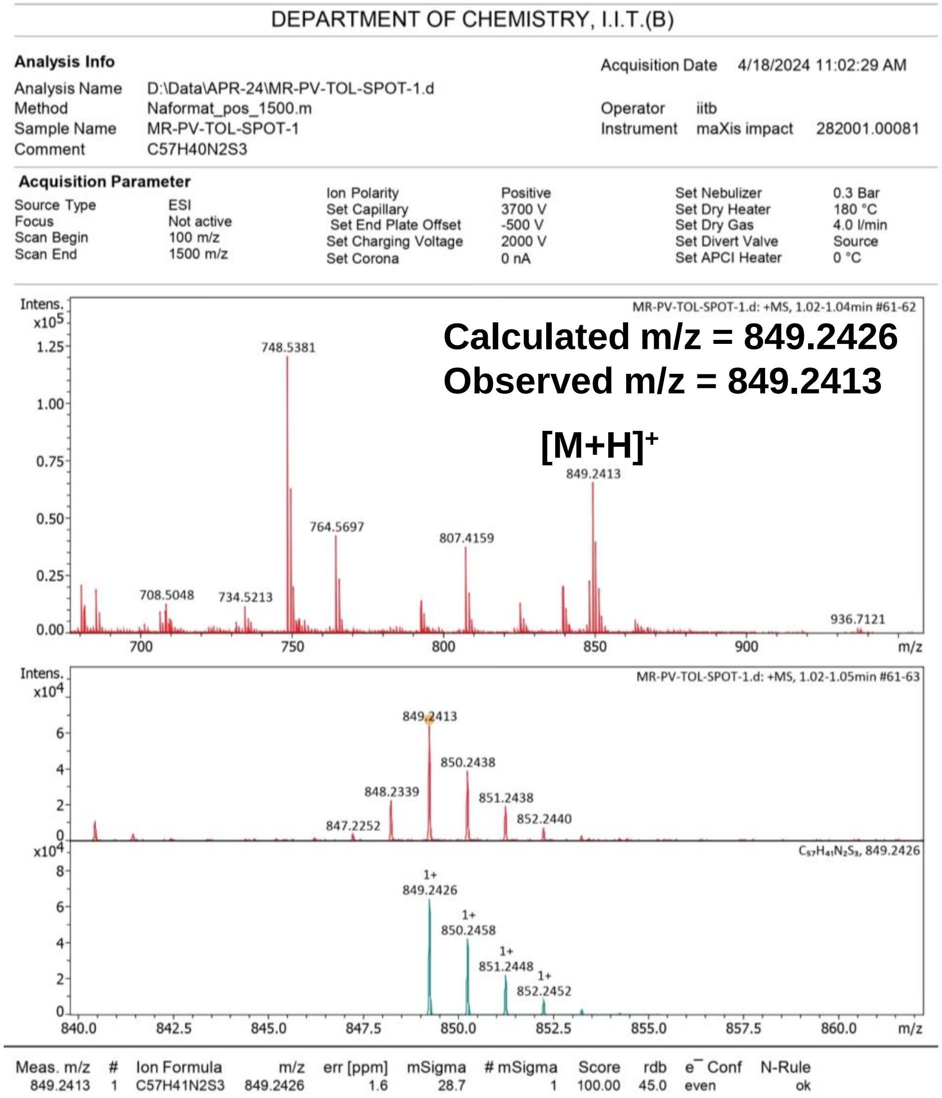


Figure S8. ^{1}H–^{13}C HMBC of compound **7a** recorded in $CDCl_3$ at 25 °C.



Compound **7b**



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Analysis Info

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Comment	C57H40N2S3		

Acquisition Parameter

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Scan End	1500 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
849.2413	1	C57H41N2S3	849.2426	1.6	28.7	1	100.00	45.0	even	ok

Figure S9. HR mass spectrum of the compound **7b**.

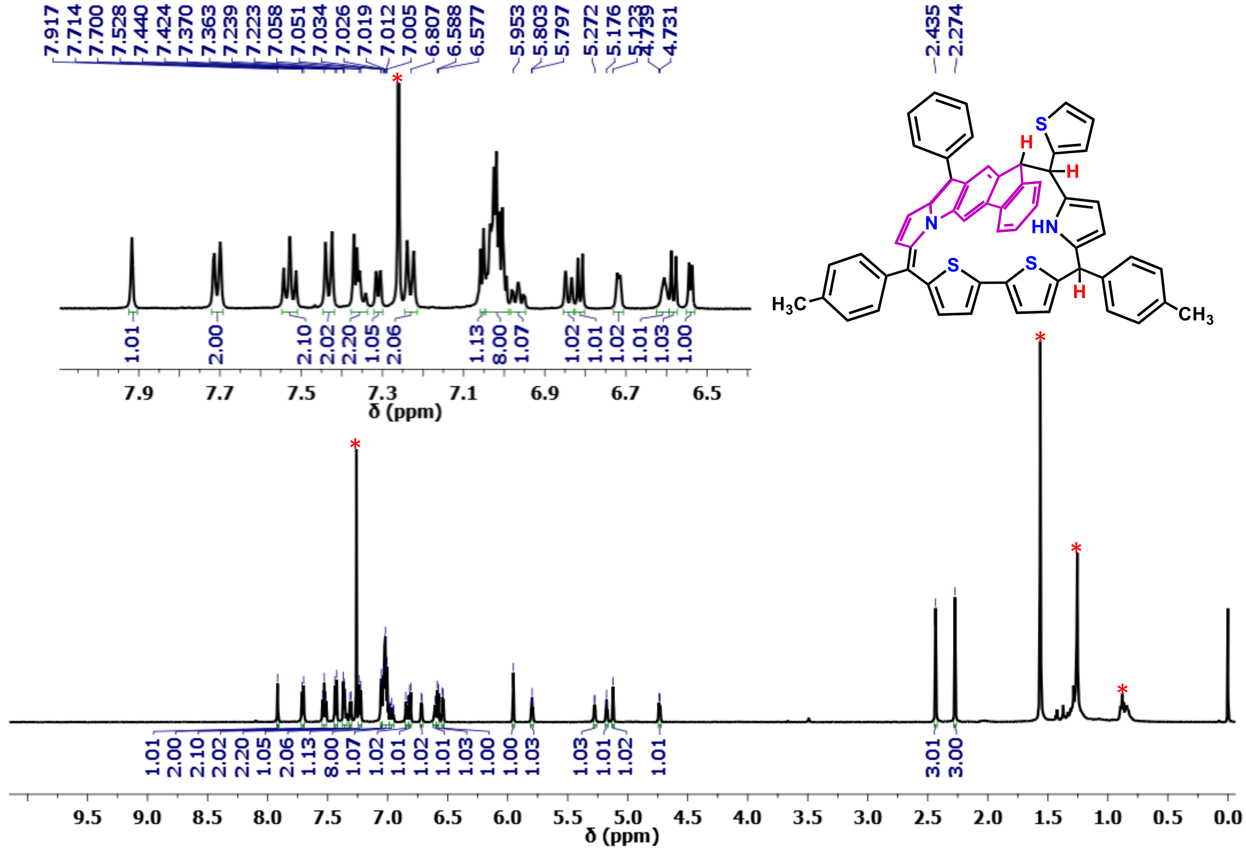


Figure S10. ^{1}H-NMR spectrum of the compound **7b** recorded in $CDCl_3$ on 400 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.

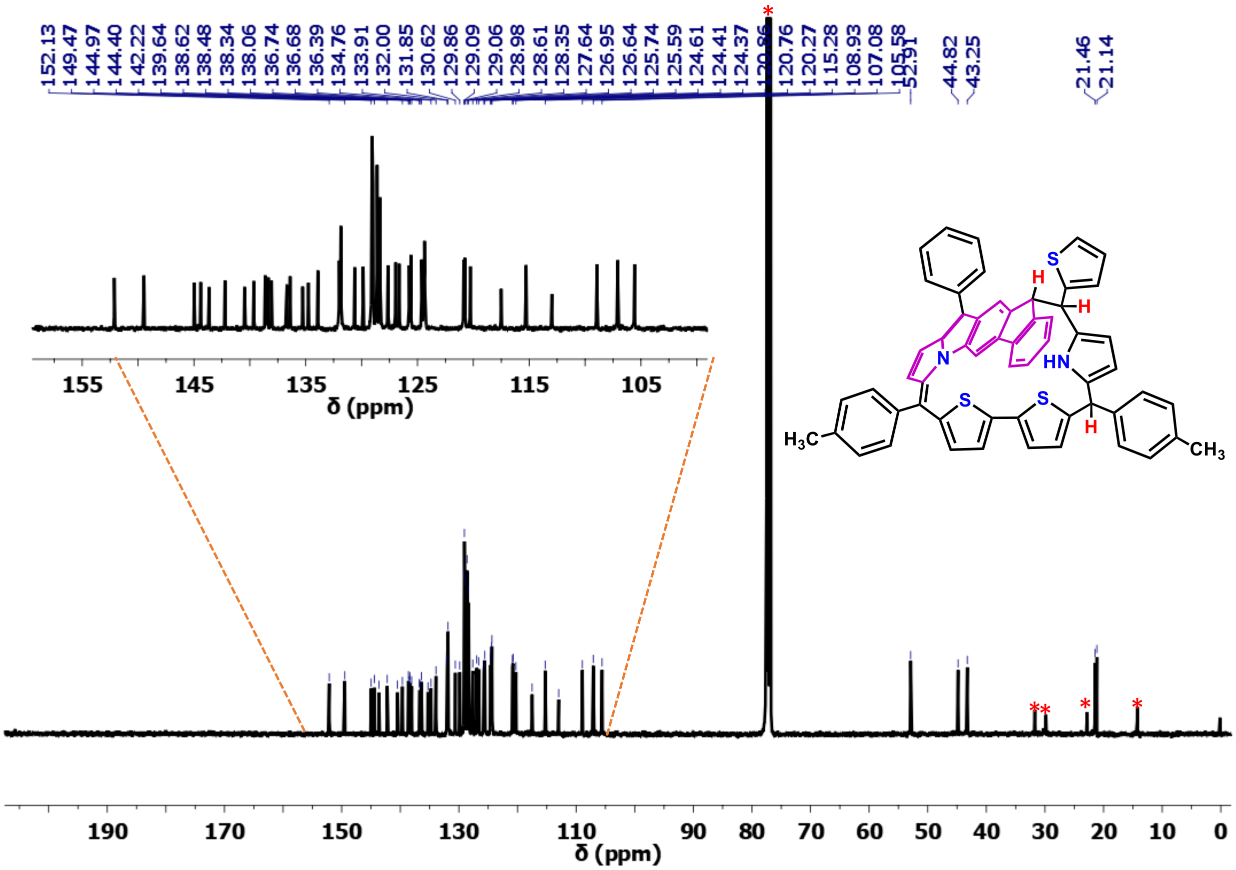


Figure S11. ^{13}C NMR spectrum of the compound **7b** recorded in $CDCl_3$ on 101 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.

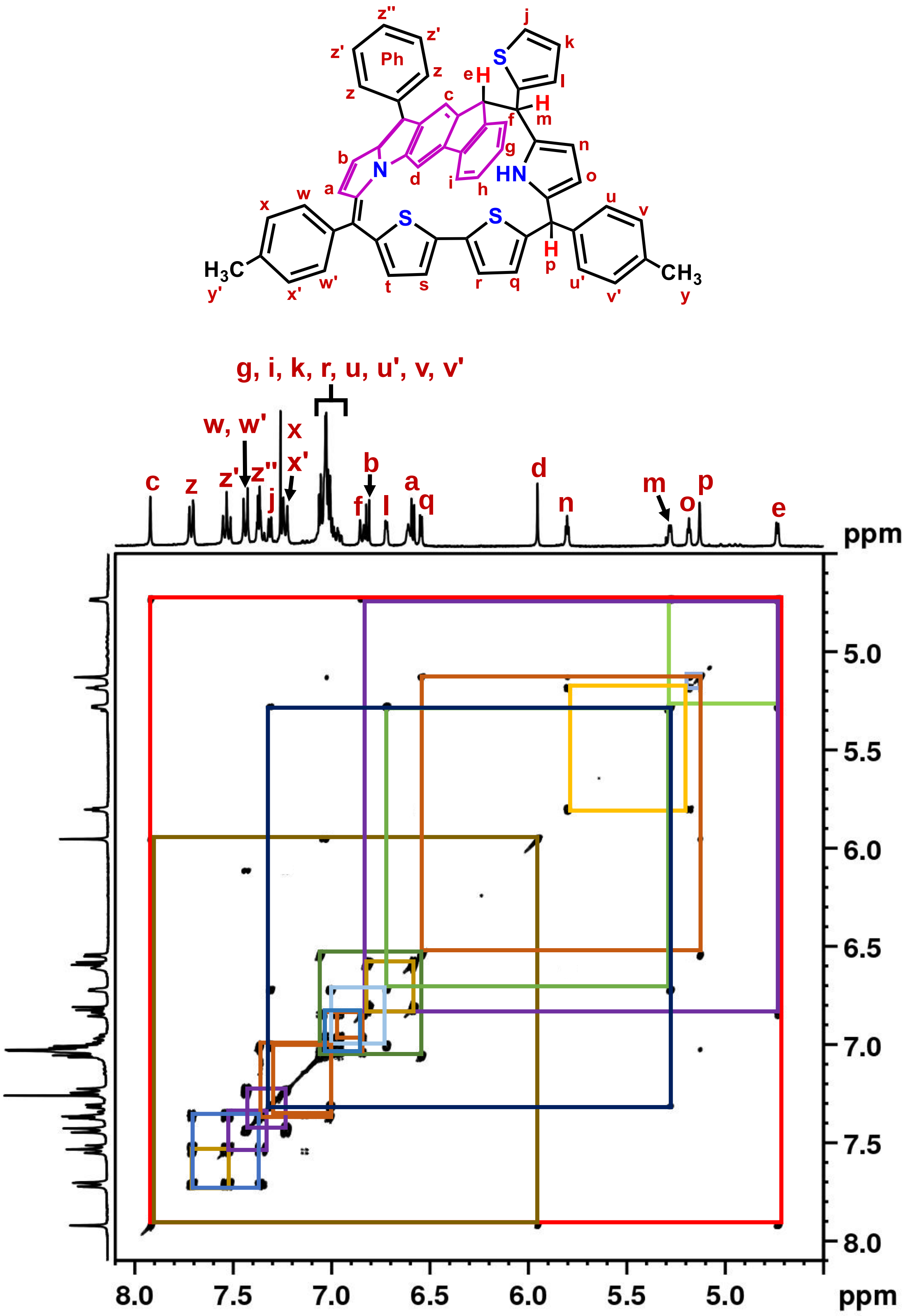


Figure S12. Partial ^1H–^1H COSY of compound **7b** recorded in $CDCl_3$ at 25 °C.

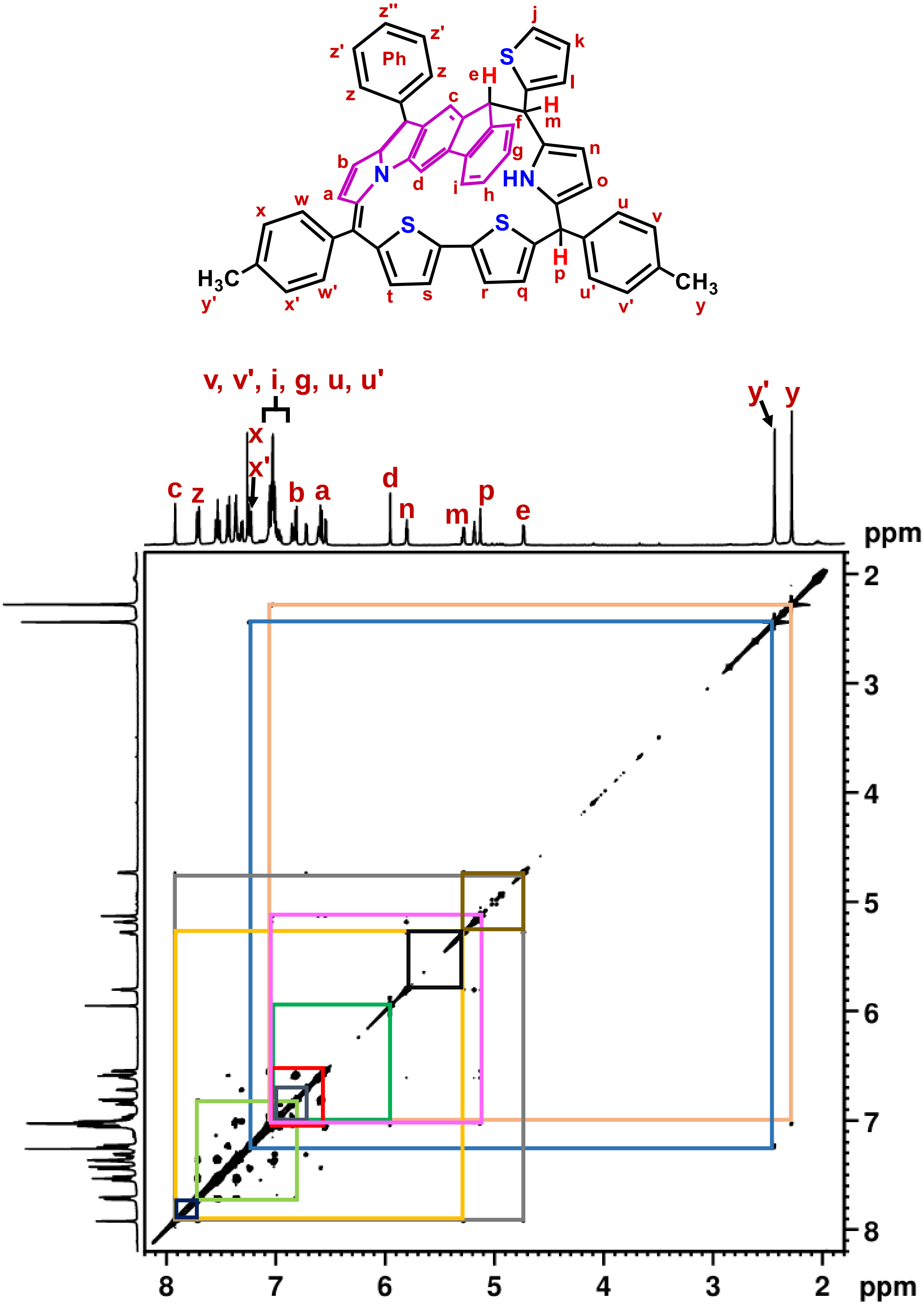


Figure S13. ^{1}H–^{1}H NOESY of compound **7b** recorded in $CDCl_3$ at 25 °C.

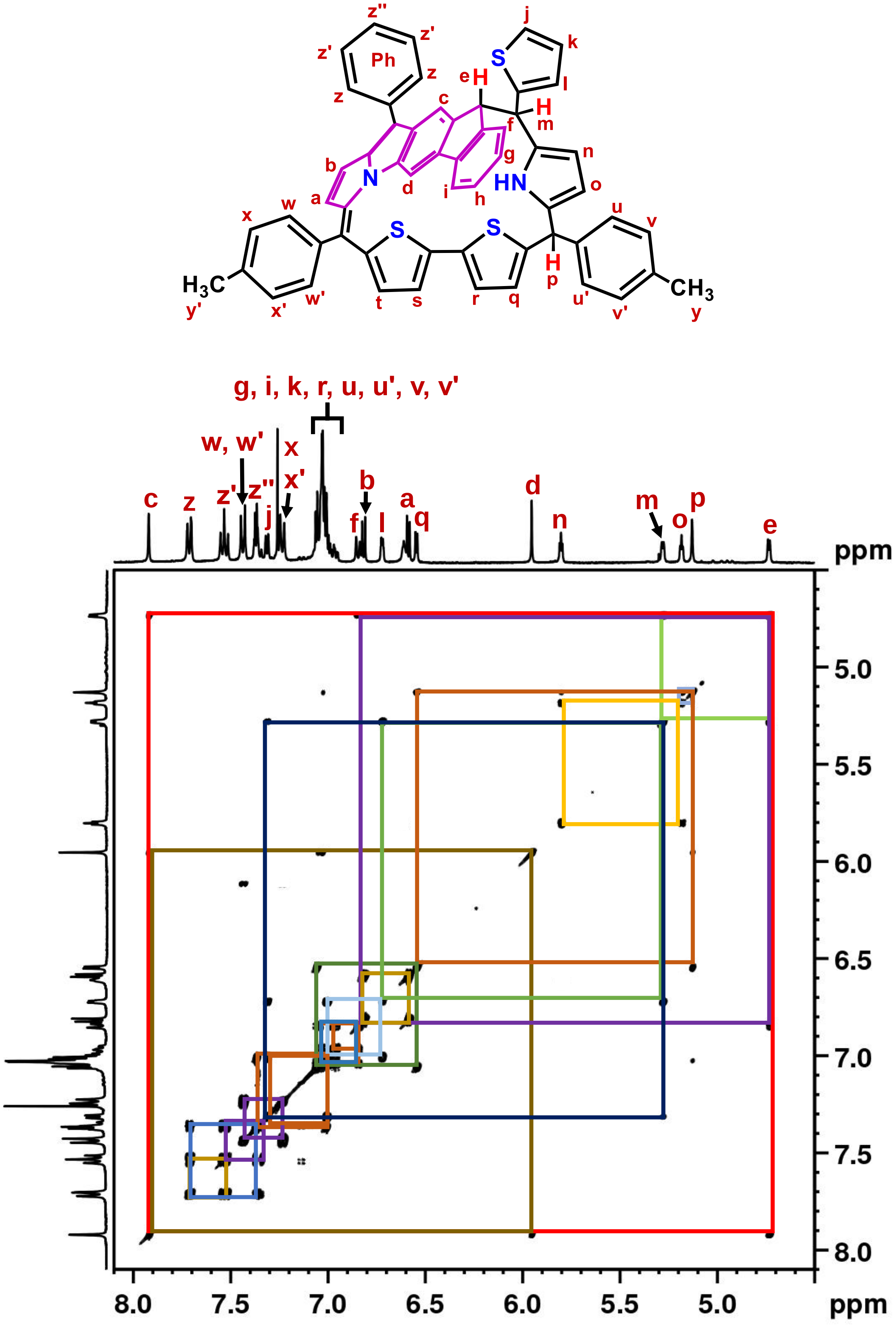


Figure S14. Expanded ^{1}H–^{1}H NOESY of compound **7b** recorded in $CDCl_3$ at 25 °C.

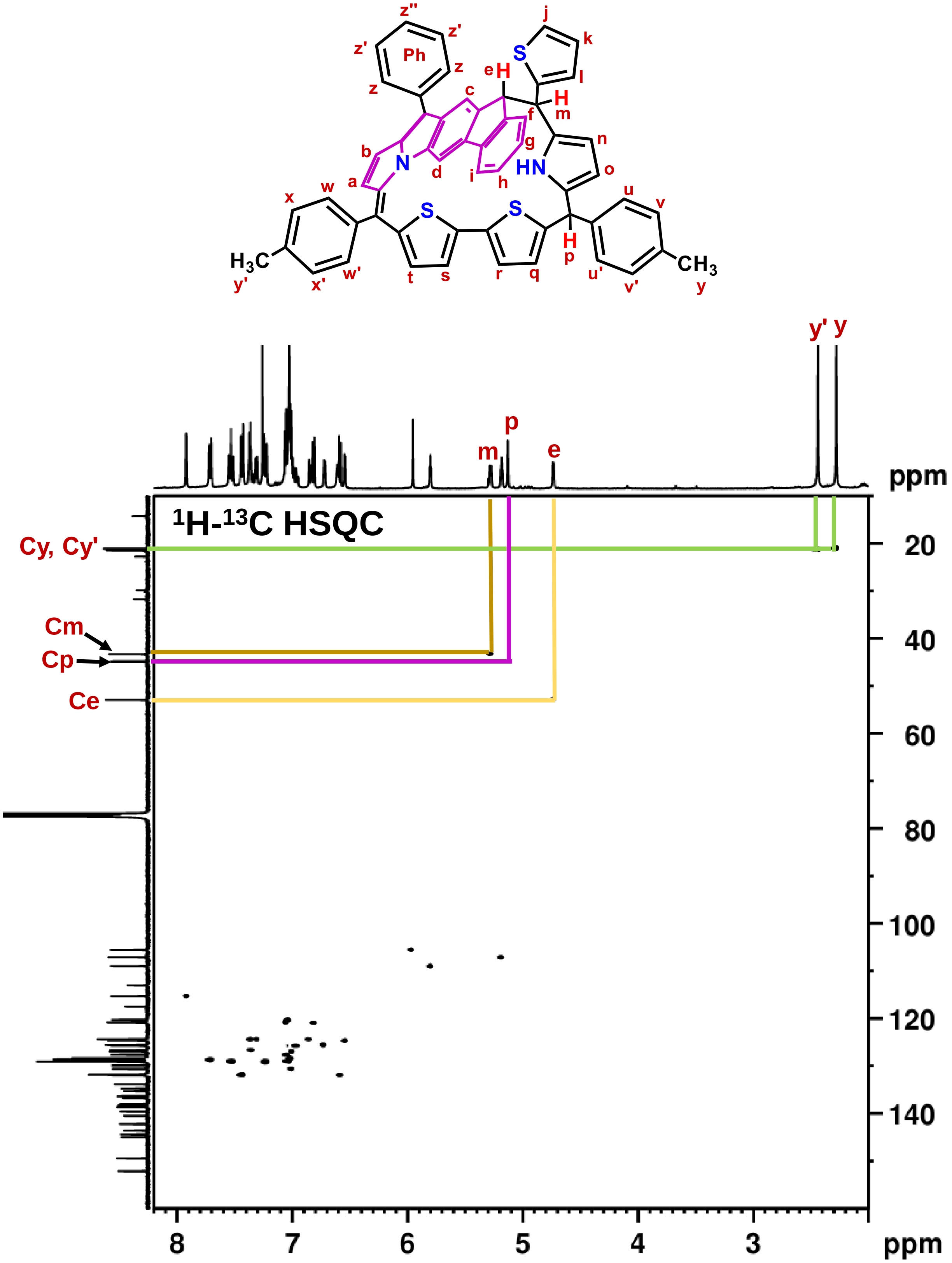


Figure S15. ^{1}H–^{13}C HSQC of compound **7b** recorded in $CDCl_3$ at 25 °C.

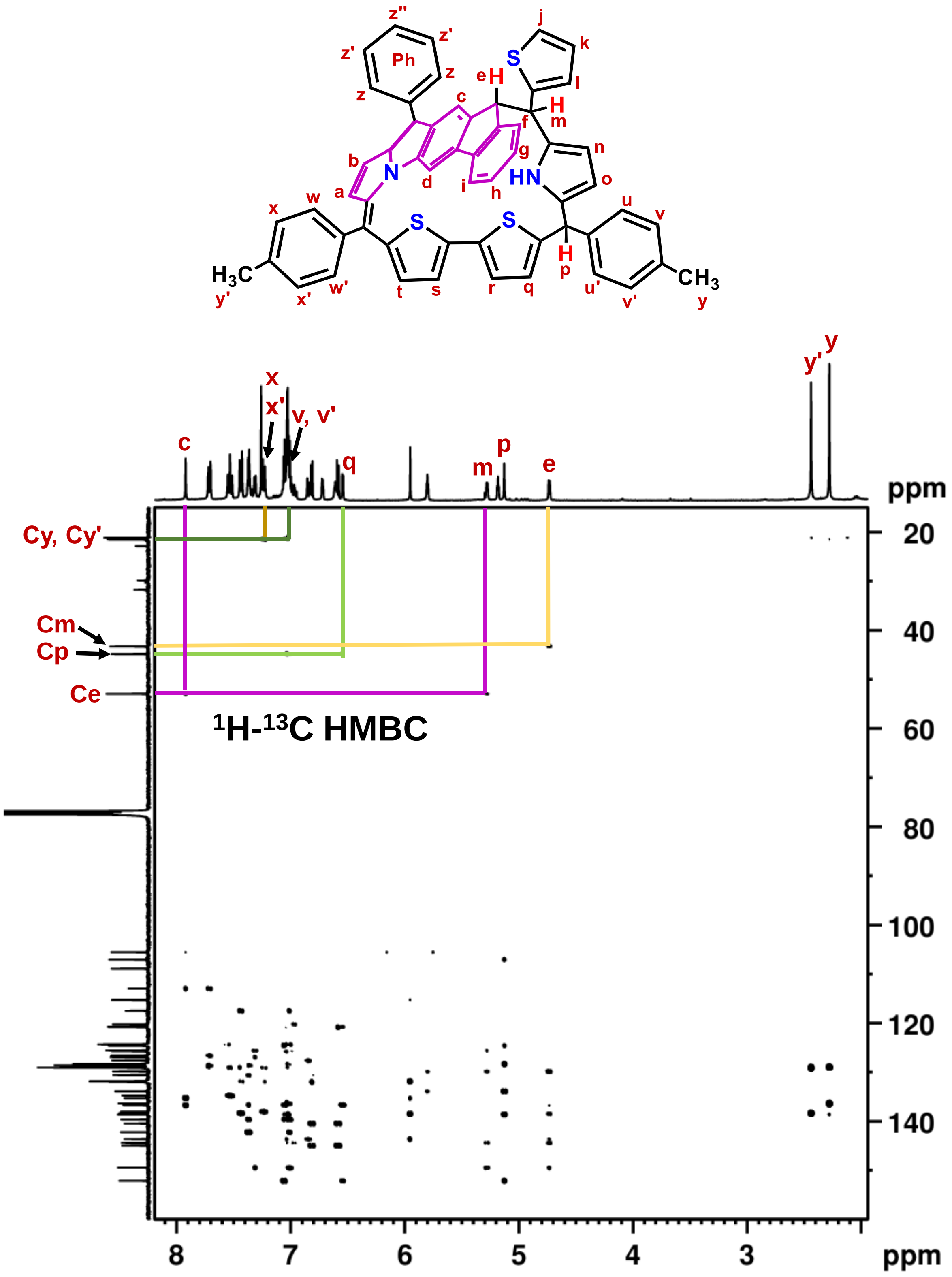
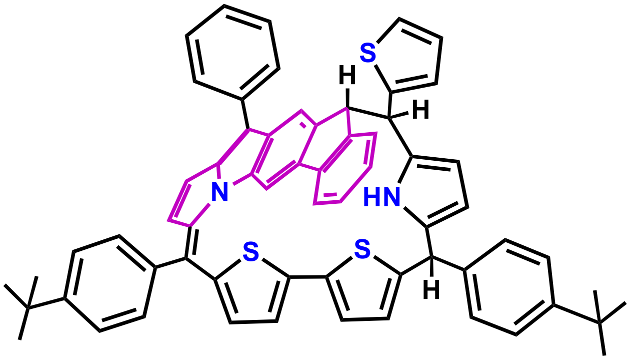
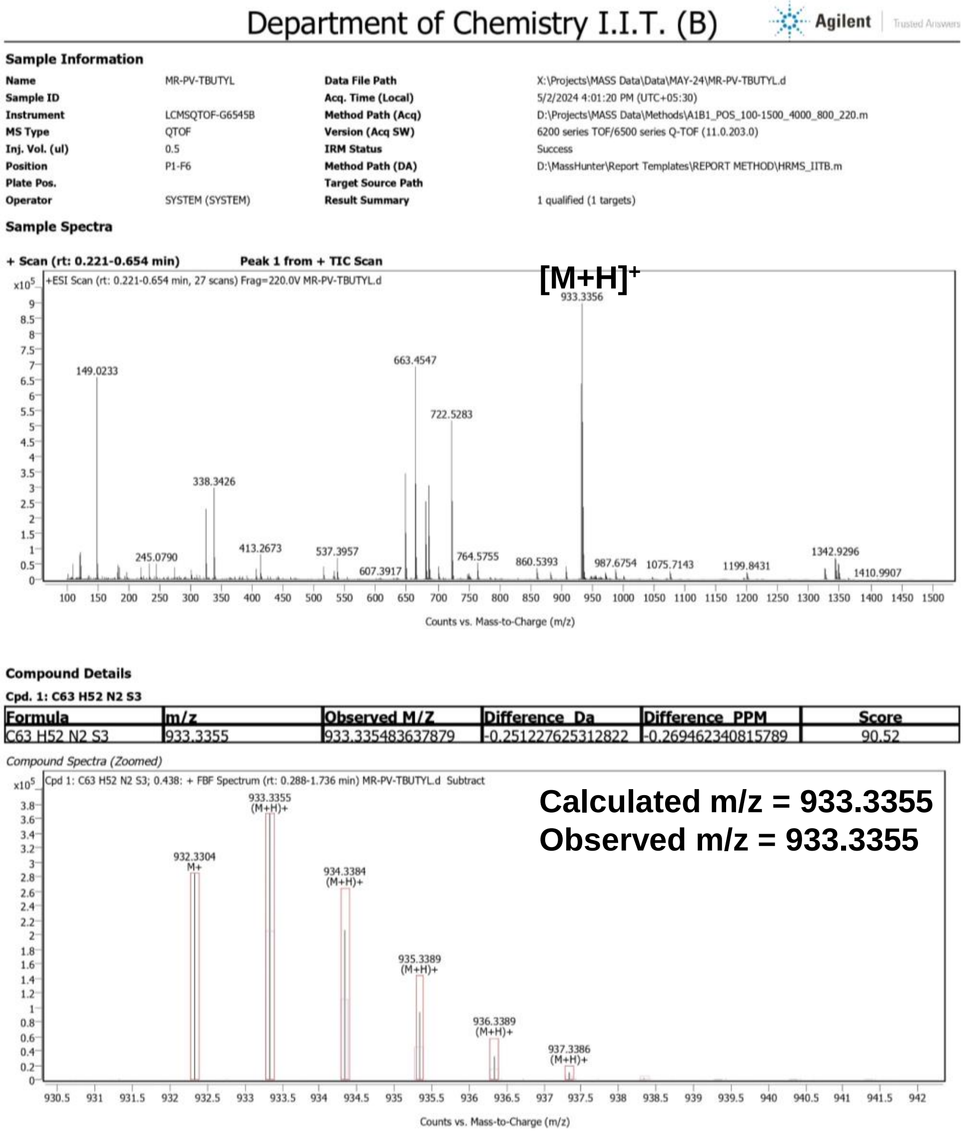


Figure S16. ^1H–^{13}C HMBC of compound **7b** recorded in $CDCl_3$ at 25 °C.



Compound **7c**



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

Sample Information

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MS Type	QTOF	**Version (Acq SW)**	6200 series TOF/6500 series Q-TOF (11.0.203.0)
Inj. Vol. (ul)	0.5	**IRM Status**	Success
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Plate Pos.		**Target Source Path**	
Operator	SYSTEM (SYSTEM)	**Result Summary**	1 qualified (1 targets)

Sample Spectra

+ Scan (rt: 0.221-0.654 min) **Peak 1 from + TIC Scan**

Compound Details

Cpd. 1: C63 H52 N2 S3

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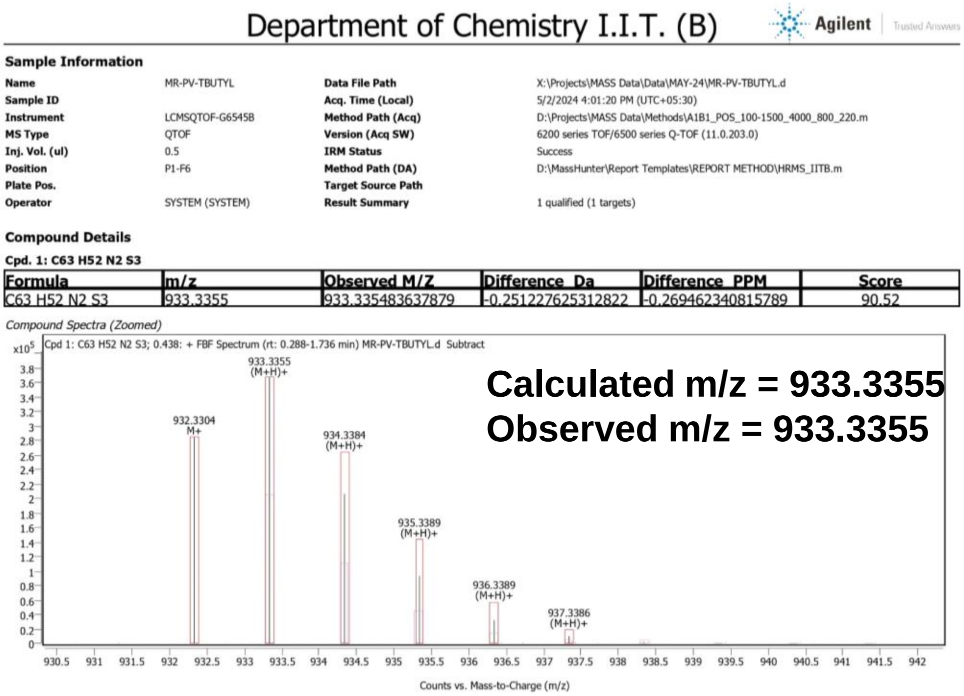
Compound Spectra (Zoomed)

Calculated m/z = 933.3355
Observed m/z = 933.3355

Figure S17(a). HR mass spectrum of the compound **7c**.



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

Sample Information

Name	MR-PV-TBUTYL	**Data File Path**	X:\Projects\MASS Data\Data\MAY-24\MR-PV-TBUTYL.d
Sample ID		**Acq. Time (Local)**	5/2/2024 4:01:20 PM (UTC+05:30)
Instrument	LCMSQTOF-G6545B	**Method Path (Acq)**	D:\Projects\MASS Data\Methods\A1B1_POS_100-1500_4000_800_220.m
MS Type	QTOF	**Version (Acq SW)**	6200 series TOF/6500 series Q-TOF (11.0.203.0)
Inj. Vol. (ul)	0.5	**IRM Status**	Success
Position	P1-F6	**Method Path (DA)**	D:\MassHunter\Report Templates\REPORT METHOD\HRMS_IITB.m
Plate Pos.		**Target Source Path**	
Operator	SYSTEM (SYSTEM)	**Result Summary**	1 qualified (1 targets)

Compound Details

Cpd. 1: C63 H52 N2 S3

Formula	m/z	Observed M/Z	Difference Da	Difference PPM	Score
C63 H52 N2 S3	933.3355	933.335483637879	-0.251227625312822	-0.269462340815789	90.52

Compound Spectra (Zoomed)

Cpd 1: C63 H52 N2 S3; 0.438: + FBF Spectrum (rt: 0.288-1.736 min) MR-PV-TBUTYL.d Subtract

Calculated m/z = 933.3355
Observed m/z = 933.3355

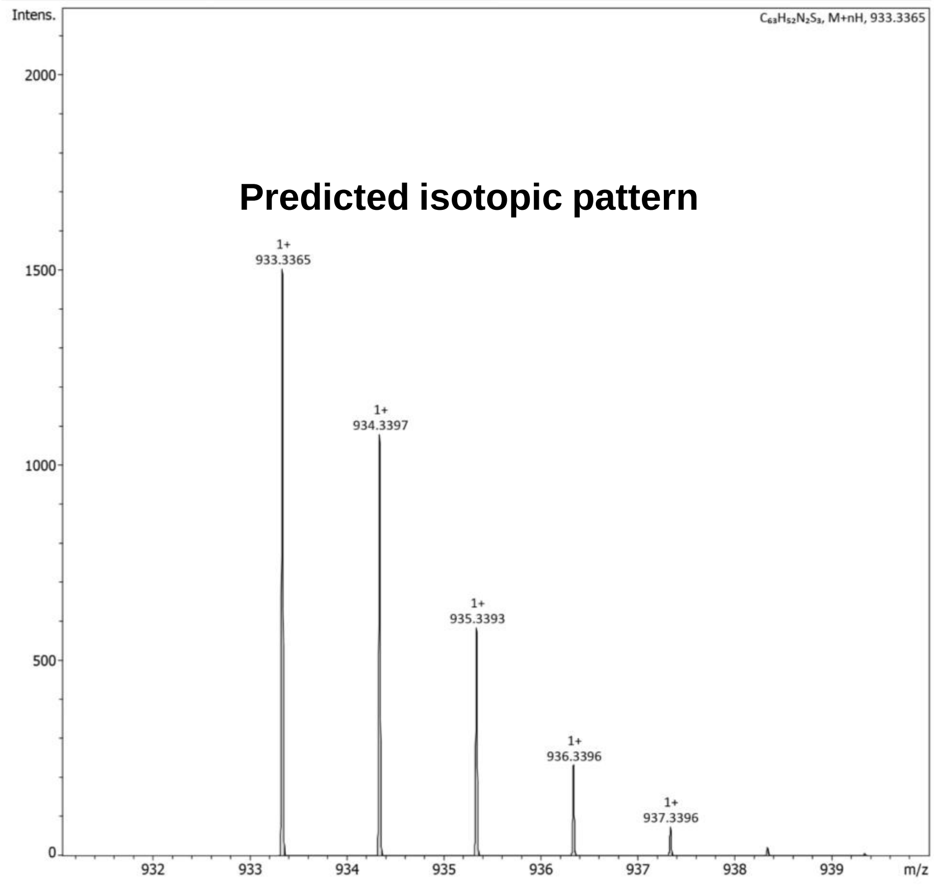


Figure S17(b). HR mass spectrum of the compound **7c**.

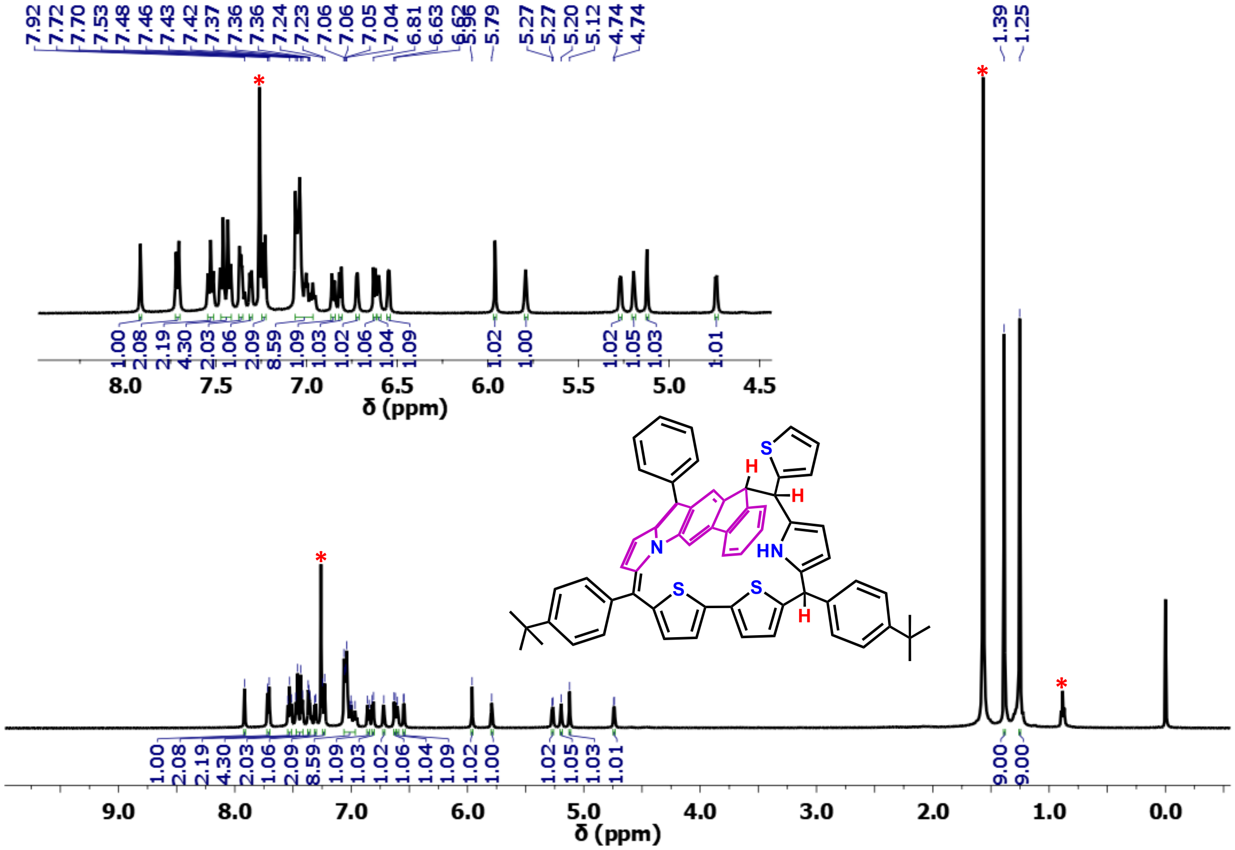


Figure S18. ^{1}H-NMR spectrum of the compound **7c** recorded in $CDCl_3$ on 500 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.

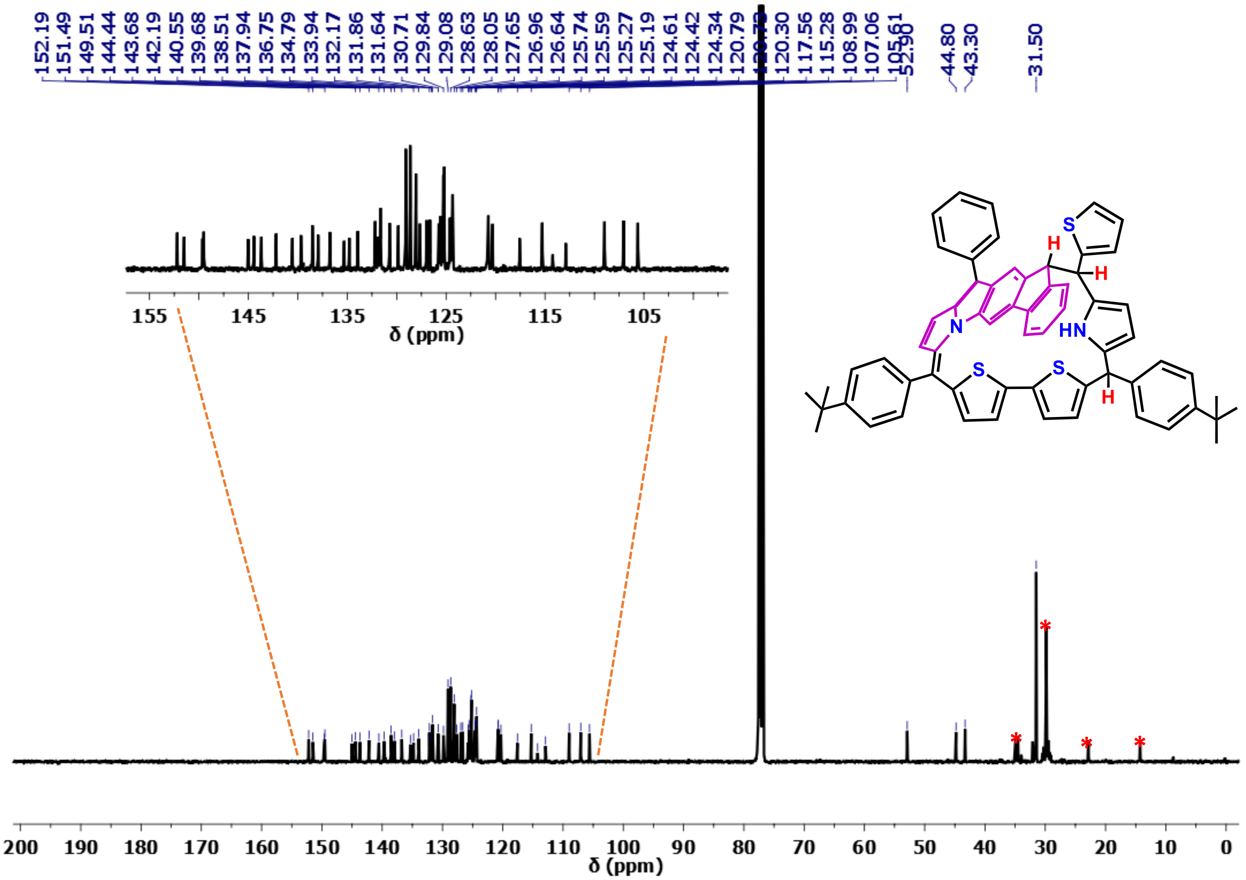


Figure S19. ^{13}C NMR spectrum of the compound **7c** recorded in $CDCl_3$ on 101 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.

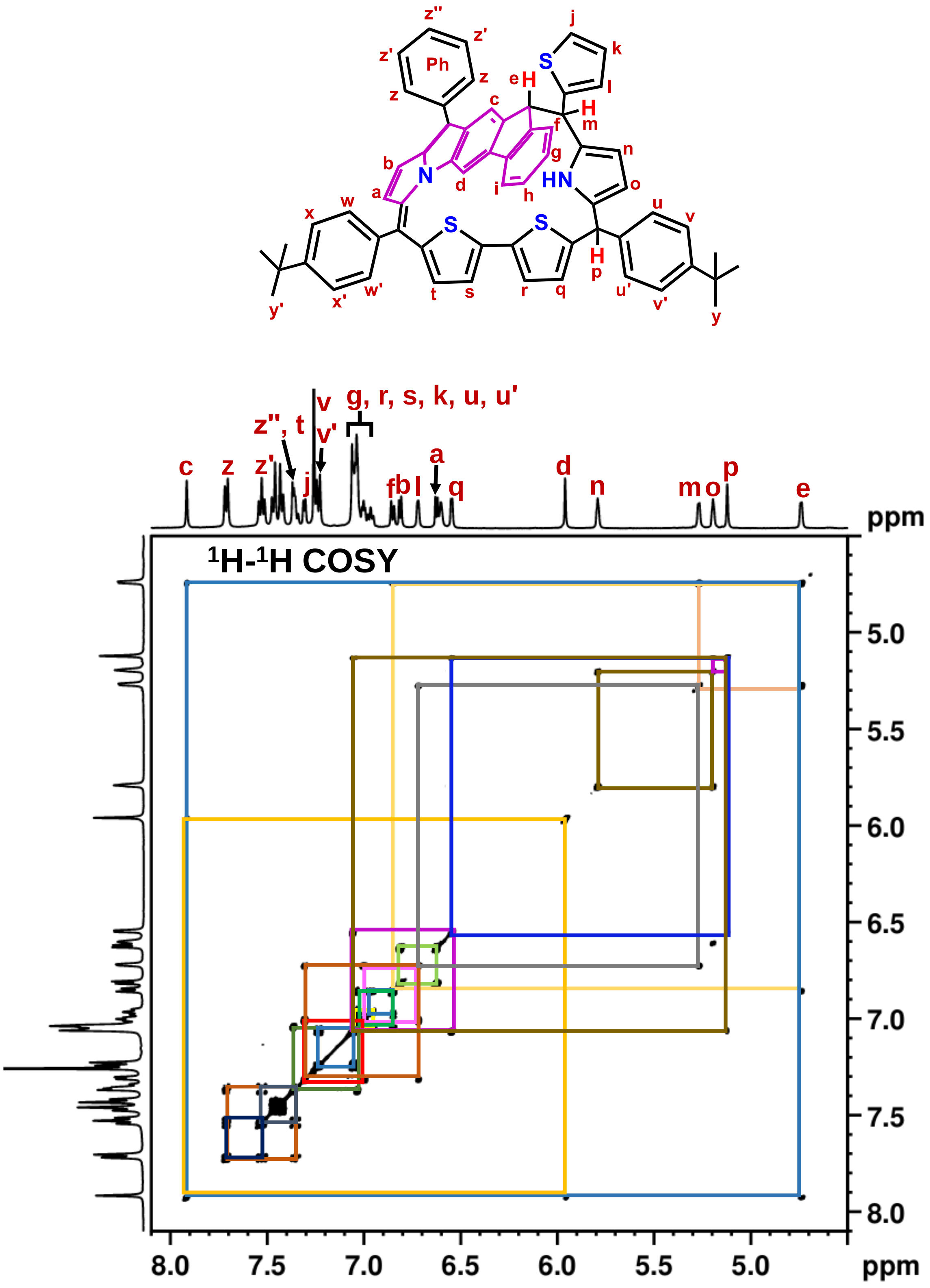


Figure S20. Partial ^{1}H–^{1}H COSY of compound **7c** recorded in $CDCl_3$ at 25 °C.

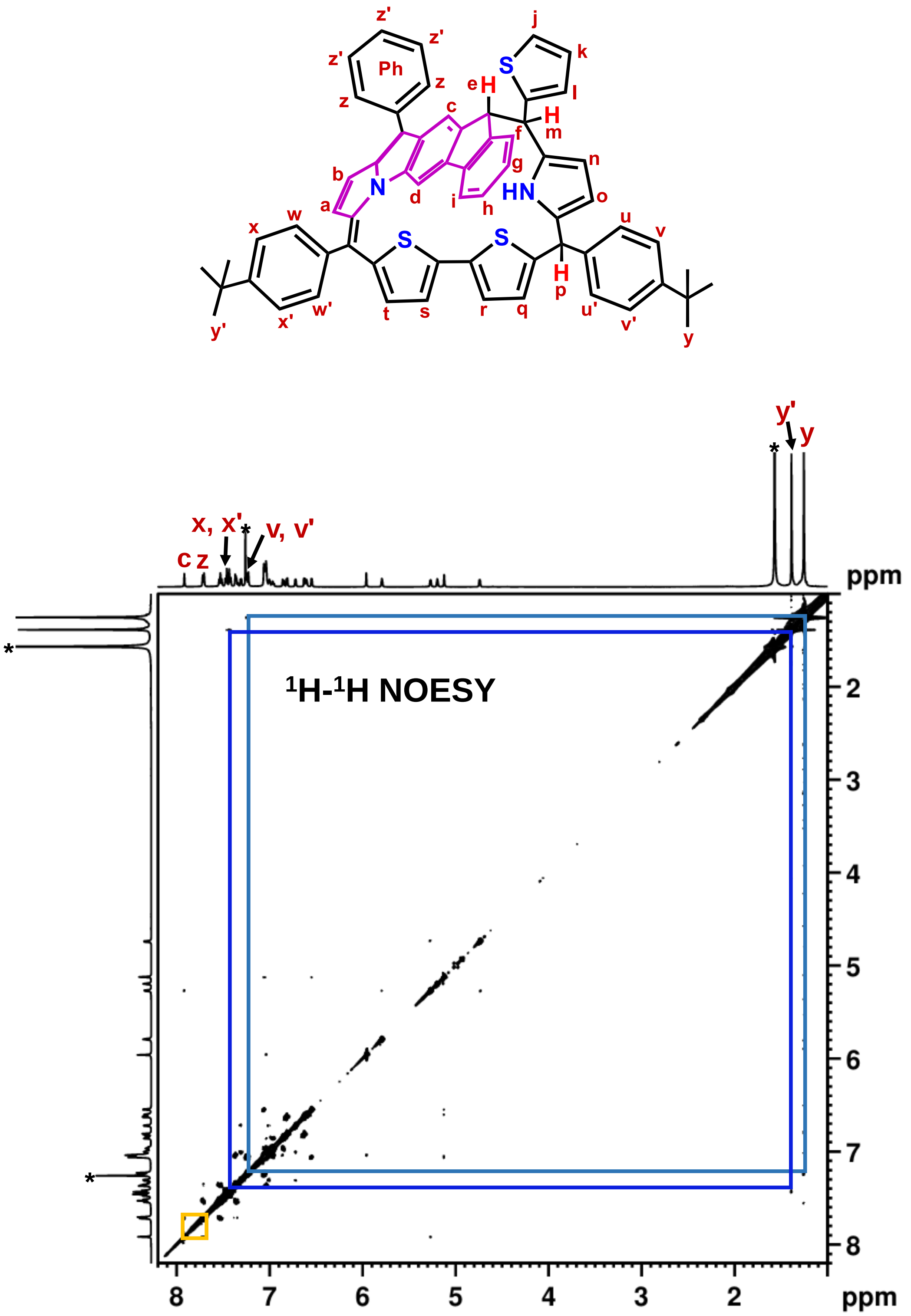


Figure S21. ^{1}H–^{1}H NOESY of compound **7c** recorded in $CDCl_3$ at 25 °C. Note: Peaks marked with asterisk (*) are due to residual solvents.

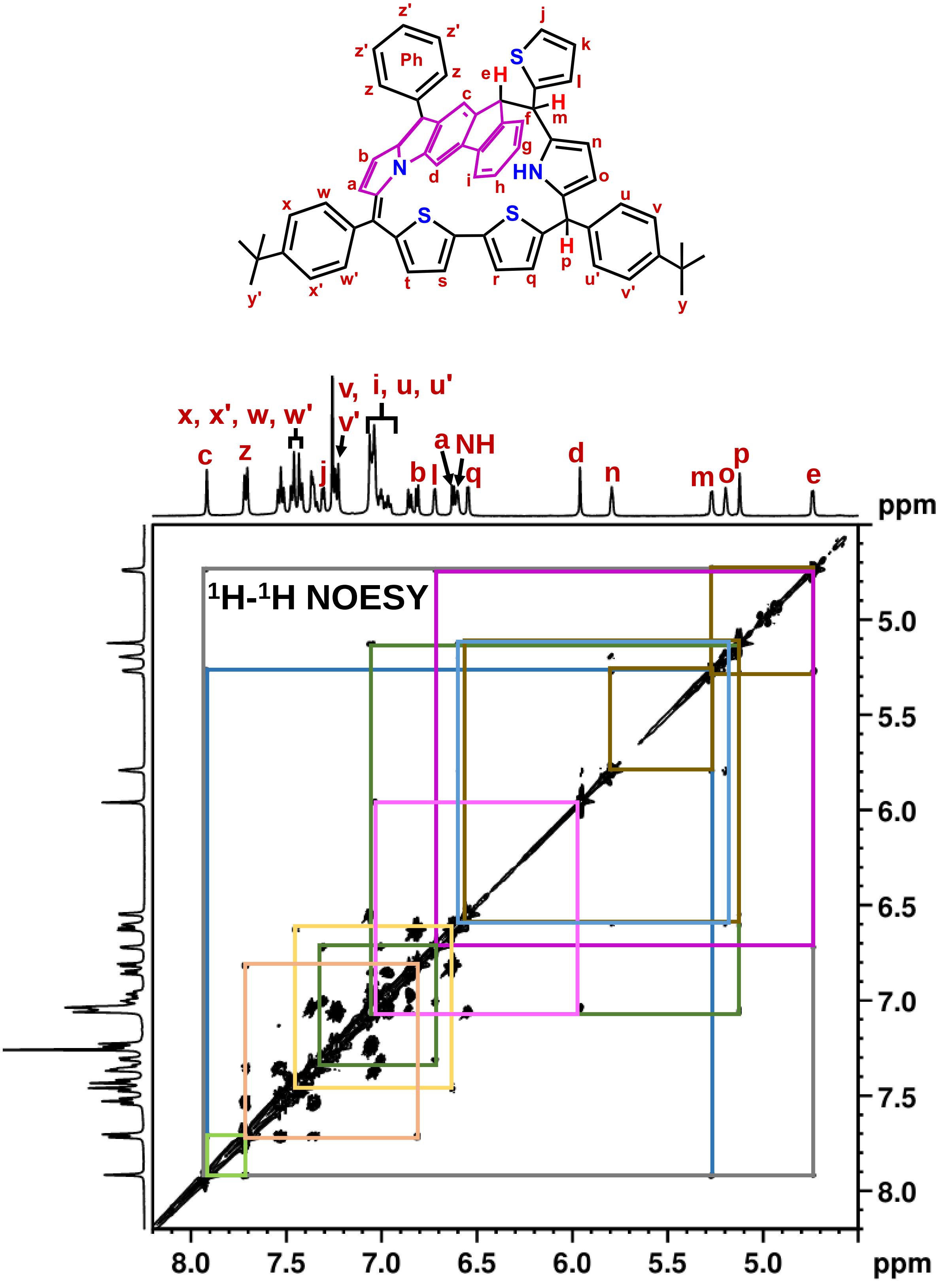


Figure S22. Expanded ^{1}H–^{1}H NOESY of compound **7c** recorded in $CDCl_3$ at 25 °C.

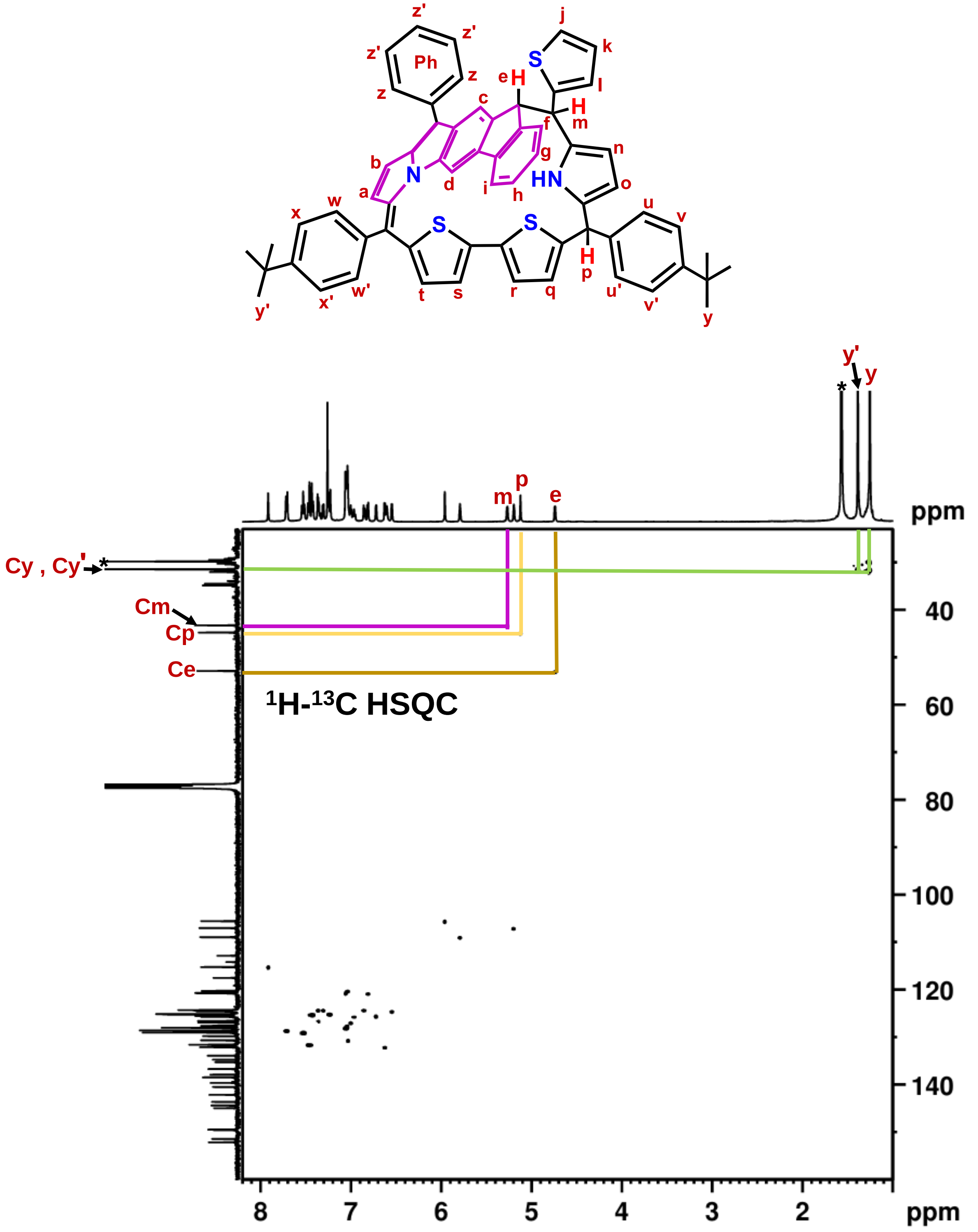


Figure S23. ^{1}H–^{13}C HSQC of compound **7c** recorded in $CDCl_3$ at 25 °C. Note: Peaks marked with asterisk (*) are due to residual solvents.

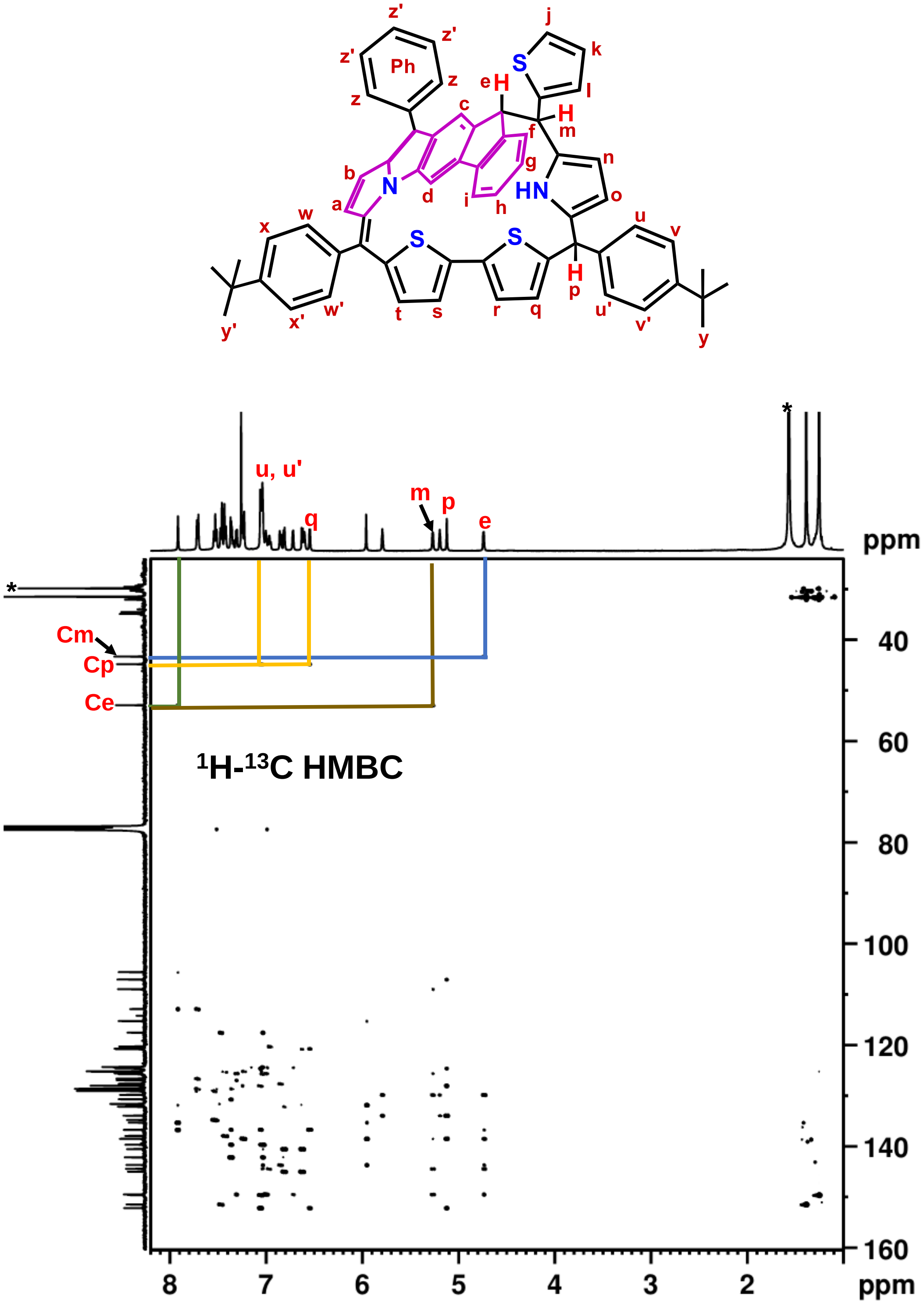


Figure S24. ^{1}H–^{13}C HMBC of compound **7c** recorded in $CDCl_3$ at 25 °C. Note: Peaks marked with asterisk (*) are due to residual solvents.

Table S1. Crystal data and structure refinement for Compound **7a**.

Compound	**7a**
Empirical Formula	$C_{57}H_{40}N_2O_2S_3$
Crystal System	Triclinic
Space Group	P-1
R_1 ($I > 2.00\ \sigma(I)$)	0.0816
wR_2 (All reflections)	0.2464
Goodness-of-fit on F^2	1.032
a [Å]	11.9857(9)
b [Å]	13.2787(8)
c [Å]	13.8288(10)
α [º]	100.139(5)
β [º]	90.991(6)
γ [º]	94.836(5)
V [Å^3]	2157.7(3)
Z	2
T [K]	150.15
δ_{calc} [g/cm^3]	1.356
F_{000}	920.0
2 θ_{max} [°]	50
Reflections collected	61621
Independent reflections	7602
no. params.	579
CCDC no.	**2365345**

Table S2. Bond Lengths for compound **7a.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C23	1.723(5)	C5	C17	1.435(6)	C14	C9	1.396(7)
S1	C20	1.734(5)	C5	C4	1.447(6)	C14	C13	1.395(7)
S2	C24	1.732(5)	C4	C38	1.472(6)	C9	C10	1.393(7)
S2	C27	1.726(5)	C7	C15	1.402(7)	C35	C34	1.407(7)
S3	C34	1.720(5)	C7	C8	1.517(6)	C35	C36	1.439(8)
S3	C37	1.697(6)	C44	C45	1.411(6)	C22	C21	1.411(7)
O1	C47	1.361(5)	C44	C19	1.480(6)	C28	C29	1.504(7)
O1	C48	1.425(6)	C44	C50	1.385(7)	C28	C27	1.535(6)
N1	C3	1.395(6)	C45	C46	1.383(7)	C29	C30	1.366(7)
N1	C18	1.429(6)	C38	C43	1.399(7)	C13	C12	1.389(7)
N1	C17	1.393(6)	C38	C39	1.374(7)	C27	C26	1.333(7)
N2	C32	1.385(6)	C19	C20	1.465(6)	C31	C30	1.429(7)
N2	C29	1.367(6)	C33	C32	1.504(6)	C10	C11	1.397(7)
O2	C54	1.390(6)	C33	C8	1.568(6)	C41	C42	1.385(8)
O2	C55	1.458(9)	C33	C34	1.516(6)	C41	C40	1.370(8)
C6	C5	1.411(6)	C51	C28	1.521(6)	C12	C11	1.381(8)
C6	C7	1.380(6)	C51	C57	1.414(7)	C25	C26	1.409(7)
C3	C2	1.442(6)	C51	C52	1.358(7)	C57	C56	1.377(7)
C3	C4	1.378(7)	C23	C24	1.453(6)	C43	C42	1.368(8)
C1	C2	1.352(6)	C23	C22	1.380(7)	C56	C54	1.391(8)

C1	C18	1.456(6)	C50	C49	1.392(6)	C54	C53	1.369(8)
C18	C19	1.366(6)	C20	C21	1.376(7)	C52	C53	1.396(7)
C16	C17	1.382(6)	C15	C14	1.453(6)	C39	C40	1.389(8)
C16	C15	1.398(6)	C32	C31	1.339(7)	C36	C37	1.330(9)
C47	C49	1.389(6)	C8	C9	1.513(7)			
C47	C46	1.388(7)	C24	C25	1.352(7)			

Table S3. Bond Angles for compound **7a**.

Atom	**Atom**	**Atom**	**Angle/º**	**Atom**	**Atom**	**Atom**	**Angle/º**
C23	S1	C20	92.7(2)	C21	C20	C19	128.3(4)
C27	S2	C24	91.9(2)	C16	C15	C7	121.8(4)
C37	S3	C34	92.1(3)	C16	C15	C14	129.1(4)
C47	O1	C48	117.5(4)	C7	C15	C14	108.9(4)
C3	N1	C18	109.7(4)	N2	C32	C33	121.4(4)
C17	N1	C3	109.2(4)	C31	C32	N2	106.9(4)
C17	N1	C18	140.9(4)	C31	C32	C33	131.5(5)
C29	N2	C32	110.9(4)	C7	C8	C33	115.8(4)
C54	O2	C55	117.1(5)	C9	C8	C7	102.5(4)
C7	C6	C5	118.3(4)	C9	C8	C33	114.8(4)
N1	C3	C2	107.2(4)	C23	C24	S2	119.4(3)
C4	C3	N1	110.5(4)	C25	C24	S2	109.7(4)
C4	C3	C2	142.3(4)	C25	C24	C23	129.9(4)
C2	C1	C18	110.2(4)	C9	C14	C15	109.0(4)

C1	C2	C3	108.3(4)
N1	C18	C1	104.5(4)
C19	C18	N1	129.7(4)
C19	C18	C1	125.1(4)
C17	C16	C15	116.8(4)
O1	C47	C49	124.2(5)
O1	C47	C46	116.2(4)
C46	C47	C49	119.6(4)
C6	C5	C17	119.0(4)
C6	C5	C4	132.4(4)
C17	C5	C4	108.4(4)
N1	C17	C5	106.1(4)
C16	C17	N1	131.4(4)
C16	C17	C5	122.5(4)
C3	C4	C5	105.7(4)
C3	C4	C38	125.8(4)
C5	C4	C38	128.5(4)
C6	C7	C15	121.6(4)
C6	C7	C8	128.5(4)
C15	C7	C8	109.5(4)
C45	C44	C19	122.4(4)
C50	C44	C45	116.8(4)
C50	C44	C19	120.7(4)
C13	C14	C15	130.4(5)
C13	C14	C9	120.6(4)
C14	C9	C8	109.9(4)
C10	C9	C8	129.7(5)
C10	C9	C14	120.3(5)
C45	C46	C47	120.3(4)
C34	C35	C36	108.1(5)
C33	C34	S3	120.6(4)
C35	C34	S3	112.1(4)
C35	C34	C33	127.2(4)
C23	C22	C21	112.8(4)
C51	C28	C27	112.8(4)
C29	C28	C51	113.1(4)
C29	C28	C27	110.8(4)
N2	C29	C28	118.9(4)
C30	C29	N2	106.0(4)
C30	C29	C28	135.0(4)
C12	C13	C14	118.8(5)
C28	C27	S2	121.2(4)
C26	C27	S2	111.2(4)
C26	C27	C28	127.3(4)
C20	C21	C22	113.8(4)
C32	C31	C30	107.9(5)

C46	C45	C44	121.3(5)	C9	C10	C11	118.5(5)
C43	C38	C4	120.7(4)	C40	C41	C42	118.5(5)
C39	C38	C4	122.2(4)	C11	C12	C13	120.7(5)
C39	C38	C43	117.0(5)	C24	C25	C26	114.0(5)
C18	C19	C44	120.1(4)	C29	C30	C31	108.1(4)
C18	C19	C20	123.8(4)	C27	C26	C25	113.2(5)
C20	C19	C44	115.9(4)	C56	C57	C51	121.4(5)
C32	C33	C8	114.6(4)	C12	C11	C10	121.0(5)
C32	C33	C34	112.2(4)	C42	C43	C38	121.6(5)
C34	C33	C8	109.7(4)	C57	C56	C54	118.5(5)
C57	C51	C28	118.7(5)	O2	C54	C56	115.1(5)
C52	C51	C28	123.1(4)	C53	C54	O2	123.7(6)
C52	C51	C57	118.0(5)	C53	C54	C56	121.2(5)
C24	C23	S1	121.5(3)	C51	C52	C53	121.8(5)
C22	C23	S1	110.6(3)	C54	C53	C52	119.1(5)
C22	C23	C24	127.0(4)	C38	C39	C40	121.5(5)
C44	C50	C49	122.5(4)	C43	C42	C41	120.6(5)
C47	C49	C50	119.3(5)	C37	C36	C35	115.9(6)
C19	C20	S1	121.9(3)	C36	C37	S3	111.7(5)
C21	C20	S1	109.8(3)	C41	C40	C39	120.7(6)

Electronic absorption spectral analysis:

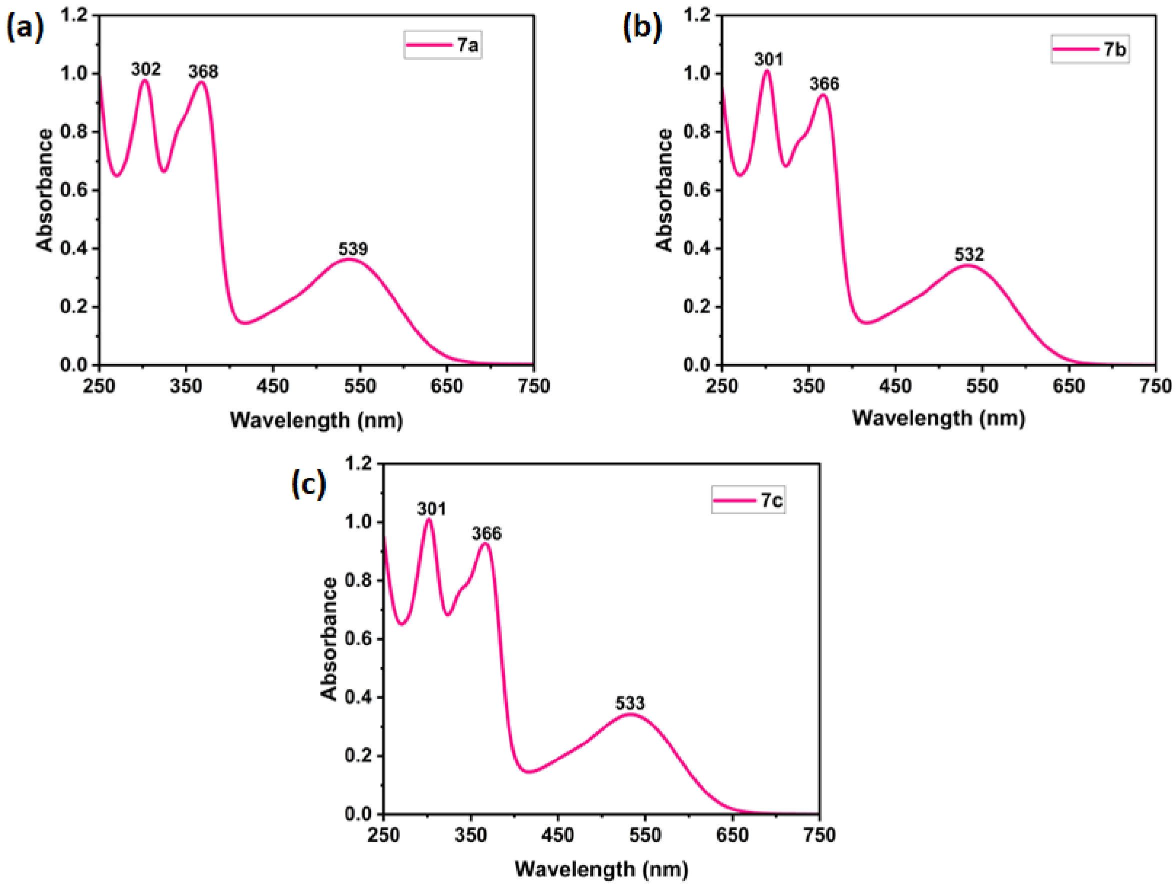


Figure S25. Absorption spectra of the compounds **7a-c** (4×10^{-5} M) free base (pink line) recorded in $CHCl_3$ at room temperature.

Electrochemical properties:

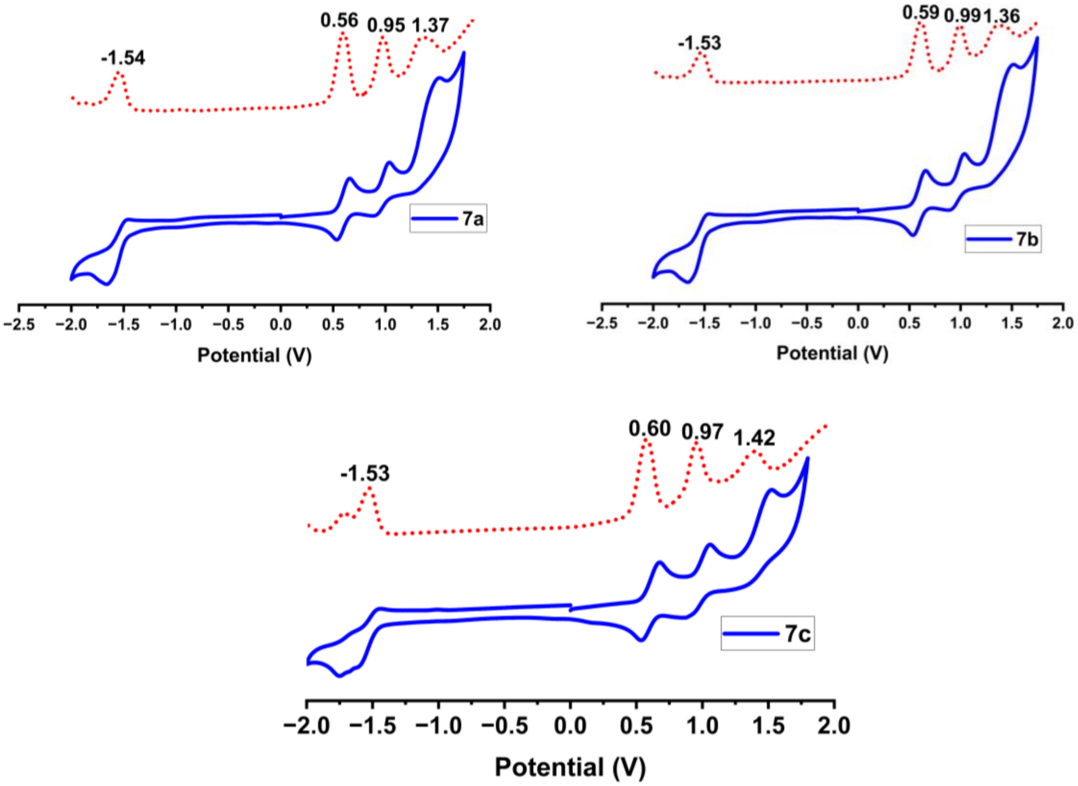


Figure S26. Comparison of cyclic voltammograms (blue solid lines) along with differential pulse voltammograms (red dotted lines) of the compounds **7a-c** recorded in CH_2Cl_2.

Table S4. Selected TD-DFT calculated oscillator strengths and compositions of the major electronic transitions of **7a**.

Wavelength (nm)	**Oscillator Strength**	**Major contributions**
581.239	0.4053	HOMO->LUMO (98%)
444.962	0.1317	H-2->LUMO (33%), H-1->LUMO (58%)
424.052	0.0624	H-2->LUMO (56%), H-1->LUMO (34%)
406.519	0.0028	H-3->LUMO (55%), HOMO->L+1 (31%)
383.804	0.7462	H-3->LUMO (35%), HOMO->L+1 (55%)

364.177	0.0314	H-6->LUMO (23%), H-5->LUMO (37%), HOMO->L+2 (26%)
351.838	0.0382	H-4->LUMO (92%)
349.094	0.28	H-5->LUMO (15%), HOMO->L+2 (69%)
343.971	0.029	H-7->LUMO (86%)
340.916	0.0114	H-6->LUMO (59%), H-5->LUMO (38%)
330.695	0.1703	HOMO->L+3 (86%)
319.275	0.0043	H-8->LUMO (92%)
317.623	0.0151	HOMO->L+4 (90%)
316.230	0.0923	H-1->L+1 (86%)
313.060	0.0466	H-2->L+1 (93%)
303.630	0.0706	H-9->LUMO (13%), HOMO->L+5 (14%), HOMO->L+6 (44%)
302.703	0.004	H-10->LUMO (69%), HOMO->L+8 (18%)
301.269	0.0159	H-9->LUMO (68%), HOMO->L+6 (16%)
297.239	0.0192	H-11->LUMO (84%), H-3->L+1 (10%)
295.123	0.0875	H-11->LUMO (11%), H-3->L+1 (77%)
294.920	0.021	HOMO->L+5 (64%), HOMO->L+6 (24%)
292.533	0.0587	H-1->L+2 (13%), HOMO->L+7 (34%), HOMO->L+8 (11%), HOMO->L+9 (10%)
291.831	0.3195	H-1->L+2 (43%)
290.811	0.0089	H-10->LUMO (14%), HOMO->L+8 (42%), HOMO->L+9 (24%)
290.545	0.0096	H-15->LUMO (41%), HOMO->L+9 (25%)
289.974	0.0204	H-15->LUMO (26%), HOMO->L+7 (30%), HOMO->L+8 (14%)
287.893	0.0305	H-2->L+2 (55%), H-1->L+2 (19%)
286.907	0.0553	H-16->LUMO (57%), H-15->LUMO (11%), H-2->L+2 (15%)
285.533	0.0448	H-14->LUMO (34%), H-13->LUMO (11%), HOMO->L+10 (19%)

283.263	0.0143	H-12->LUMO (78%)
280.717	0.0138	H-2->L+3 (25%), H-1->L+3 (61%)
279.741	0.0034	H-13->LUMO (71%), HOMO->L+10 (12%)
278.835	0.0064	H-14->LUMO (26%), HOMO->L+10 (21%), HOMO->L+11 (12%)
274.569	0.073	H-3->L+2 (30%), H-2->L+3 (44%)
273.105	0.0143	H-3->L+2 (41%), H-2->L+3 (14%), H-1->L+3 (13%)
272.679	0.019	H-4->L+1 (69%), H-3->L+2 (10%)
270.525	0.0277	H-17->LUMO (10%), H-6->L+1 (15%), H-5->L+1 (33%), HOMO->L+11 (13%)
268.783	0.0329	H-17->LUMO (18%), H-14->LUMO (10%), H-5->L+1 (20%), HOMO->L+11 (15%)
266.243	0.0027	H-17->LUMO (48%), HOMO->L+11 (27%)
263.965	0.0062	H-6->L+1 (56%), H-5->L+1 (31%)
260.855	0.0209	H-7->L+1 (30%), HOMO->L+12 (36%), HOMO->L+13 (12%)
260.416	0.0283	H-2->L+5 (28%), H-1->L+5 (55%)
259.604	0.0284	H-7->L+1 (23%), H-3->L+3 (18%), HOMO->L+12 (42%)
259.186	0.0012	H-7->L+1 (30%), H-3->L+3 (38%)
258.327	0.021	H-2->L+4 (23%), H-1->L+4 (62%)
257.828	0.0478	H-18->LUMO (23%), H-3->L+3 (12%), HOMO->L+13 (37%)
255.627	0.0043	H-2->L+6 (16%), H-2->L+7 (14%), H-1->L+6 (23%), H-1->L+7 (22%)
253.500	0.0774	H-2->L+5 (11%), H-1->L+5 (10%), H-1->L+6 (19%), H-1->L+7 (16%), H-1->L+9 (11%)
252.231	0.006	H-8->L+1 (53%), H-5->L+2 (22%)

Table S5. S_0 optimized geometry of the compound **7a** at B3LYP/6-31G (d,p) level of theory and Empirical Dispersion GD2.

Charge = 0

Sum of imaginary frequencies= 0

Total Energy (hartree) = -3650.687583

Atom	X	Y	Z	Atom	X	Y	Z
S	2.13042	-1.90302	0.34434	H	4.58658	-2.27875	-1.10334
S	1.13497	-1.94182	-0.00152	C	3.87084	-0.78687	0.24444
S	4.29623	4.76021	-2.23588	C	0.52151	-0.27610	-3.43327
O	-9.95894	-2.23034	-0.95732	H	-0.34210	-0.92531	-3.32750
N	-3.14057	1.24877	0.75322	C	2.55870	-2.66829	-0.68855
N	3.57354	0.22279	-0.64208	C	-3.43716	-2.01005	-1.87554
H	3.39185	0.09207	-1.62646	H	-4.21171	-1.87099	-2.62090
O	6.40161	-5.44115	3.78165	C	3.59281	1.15224	1.37255
C	-0.01184	2.97602	0.27684	H	3.54287	1.89123	2.16103
H	0.47773	3.82041	0.75071	C	2.79165	1.39974	-3.66027
C	-3.25175	2.21570	1.75815	H	3.66899	2.03184	-3.74465
C	-5.20709	1.08513	1.68904	C	-1.36165	6.19991	4.55664
H	-6.18837	0.69254	1.91093	H	-1.17310	7.01307	5.25136
C	-4.54923	2.07772	2.35303	C	1.49727	-0.52743	-4.40139
H	-4.91036	2.65258	3.19413	H	1.38750	-1.37834	-5.06767
C	-4.33272	0.48979	0.68747	C	0.82075	-3.73265	-1.83600
C	-1.38872	0.83873	-1.05291	H	0.36624	-4.40507	-2.55545
H	-1.91083	0.07260	-1.60814	C	3.89744	-0.23281	1.50927
C	-8.65168	-1.92499	-0.73465	H	4.10351	-0.77753	2.41922
C	-1.25157	2.51287	0.75679	C	2.22431	-3.59206	-1.64841
C	-1.92891	1.44672	0.07788	H	2.96860	-4.14974	-2.20728
C	-2.10709	2.99217	1.81882	C	5.91199	-3.39995	0.82209
C	0.53822	2.35110	-0.82818	H	6.52083	-2.99966	0.01516

C	-5.99171	-1.07900	-0.28005	C	2.61733	0.30520	-4.52080
C	-7.03294	-0.14537	-0.47768	H	3.36178	0.10006	-5.28464
H	-6.79769	0.91356	-0.47961	C	-2.90005	4.91521	3.19765
C	-1.85027	4.09173	2.74557	H	-3.90236	4.74896	2.81546
C	-4.60071	-0.64962	-0.04916	C	6.50817	-4.17568	1.80913
C	3.09728	2.70843	-0.66241	H	7.57036	-4.39737	1.78846
H	2.87656	3.43015	0.13408	C	5.73221	-4.69006	2.85888
C	4.53856	-3.12076	0.84830	C	3.77732	-3.63874	1.89691
C	-1.33389	-2.61119	-1.04329	H	2.71120	-3.43982	1.93413
C	-6.32317	-2.44378	-0.34430	C	-10.3141	-3.60797	-1.02441
H	-5.53963	-3.18198	-0.20869	H	-9.78398	-4.11423	-1.84170
C	-7.63087	-2.87189	-0.56386	H	-11.3890	-3.63444	-1.21097
H	-7.84573	-3.93317	-0.59483	H	-10.0899	-4.12147	-0.08034
C	-3.54162	-1.47809	-0.60408	C	4.35876	-4.41889	2.90093
C	-0.13214	1.28105	-1.46610	H	3.73873	-4.80795	3.69951
C	3.38246	1.40820	0.03252	C	-0.55018	4.34770	3.22283
C	1.82023	2.68164	-1.57059	H	0.26388	3.70081	2.91385
H	1.73231	3.68460	-2.01052	C	-2.65853	5.95313	4.09554
C	0.08171	-2.90478	-1.01690	H	-3.48212	6.57945	4.42703
C	0.69503	0.81193	-2.57511	C	6.42013	3.32444	-2.44109
C	1.83538	1.63742	-2.67542	H	7.41394	2.98075	-2.70658
C	-8.33941	-0.55621	-0.69340	C	5.90944	4.52603	-2.84247
H	-9.13509	0.16390	-0.85465	H	6.37752	5.29046	-3.44809
C	5.50745	2.57279	-1.63565	C	-0.31018	5.39183	4.11526
H	5.72287	1.59488	-1.22315	H	0.69963	5.56850	4.47502
C	4.30867	3.20247	-1.42917	C	5.64813	-5.97494	4.86386
C	-2.18739	-2.62829	-2.13149	H	6.35590	-6.52987	5.48244
H	-1.88014	-2.99753	-3.10344	H	4.86130	-6.65219	4.50535
C	3.93145	-2.22154	-0.22242	H	5.18529	-5.17618	5.45869

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