Supporting Information

Meso-Fused Calixbenzipentaphyrins(2.1.1.2.*1*): Synthesis and Studies and Coordination Properties

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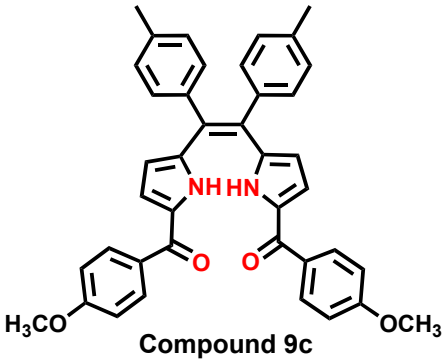
Materials, methods and instrumentation details.

All the chemicals used were reagent grade, unless mentioned otherwise. Synthesis of compounds **6** and **9a-c** 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. Absorption spectra were obtained using Cary series UV−Vis−NIR Spectrophotometer. The solution for absorption studies of compounds **3-5** (9×10^{-5} M) and **3-Pd(II)**–**5-Pd(II)** (3×10^{-6} 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.



Compound 9c

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

Agilent Trusted Answers

Sample Information

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Inj. Vol. (ul)	0.1	**IRM Status**	Success
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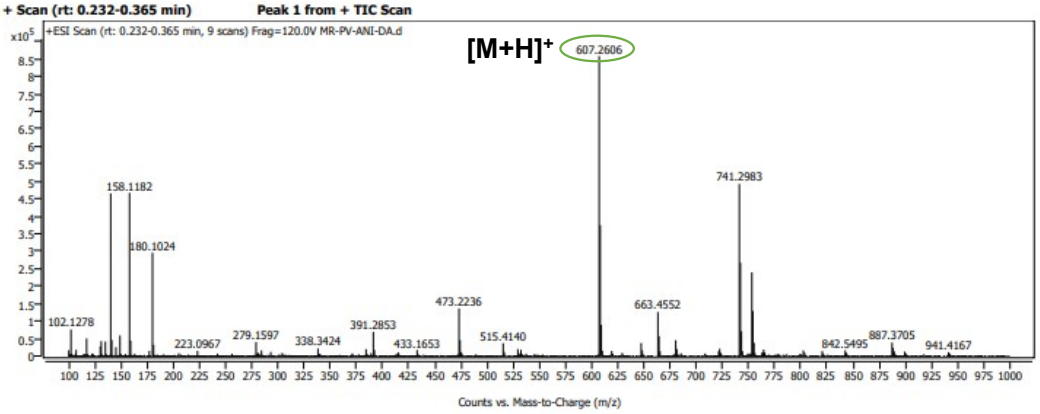

Compound Details

Cpd. 1: C40 H34 N2 O4

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Compound Spectra (Zoomed)

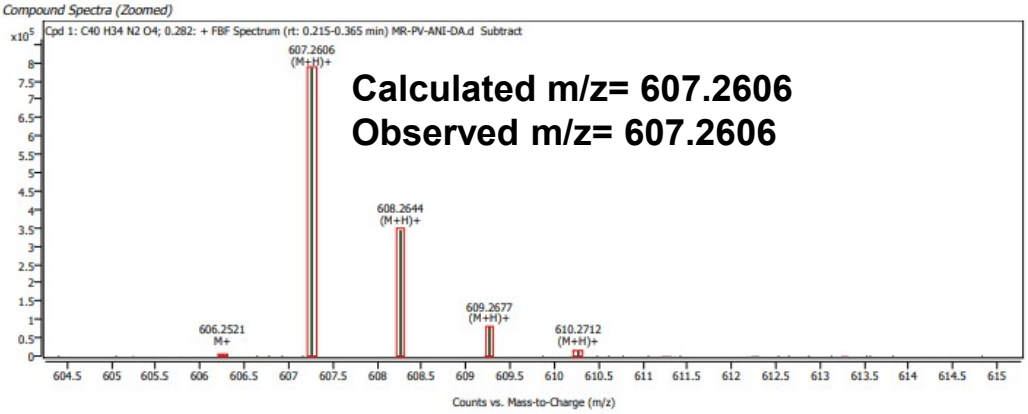


Figure S1. HR-mass spectrum of compound **9c**.

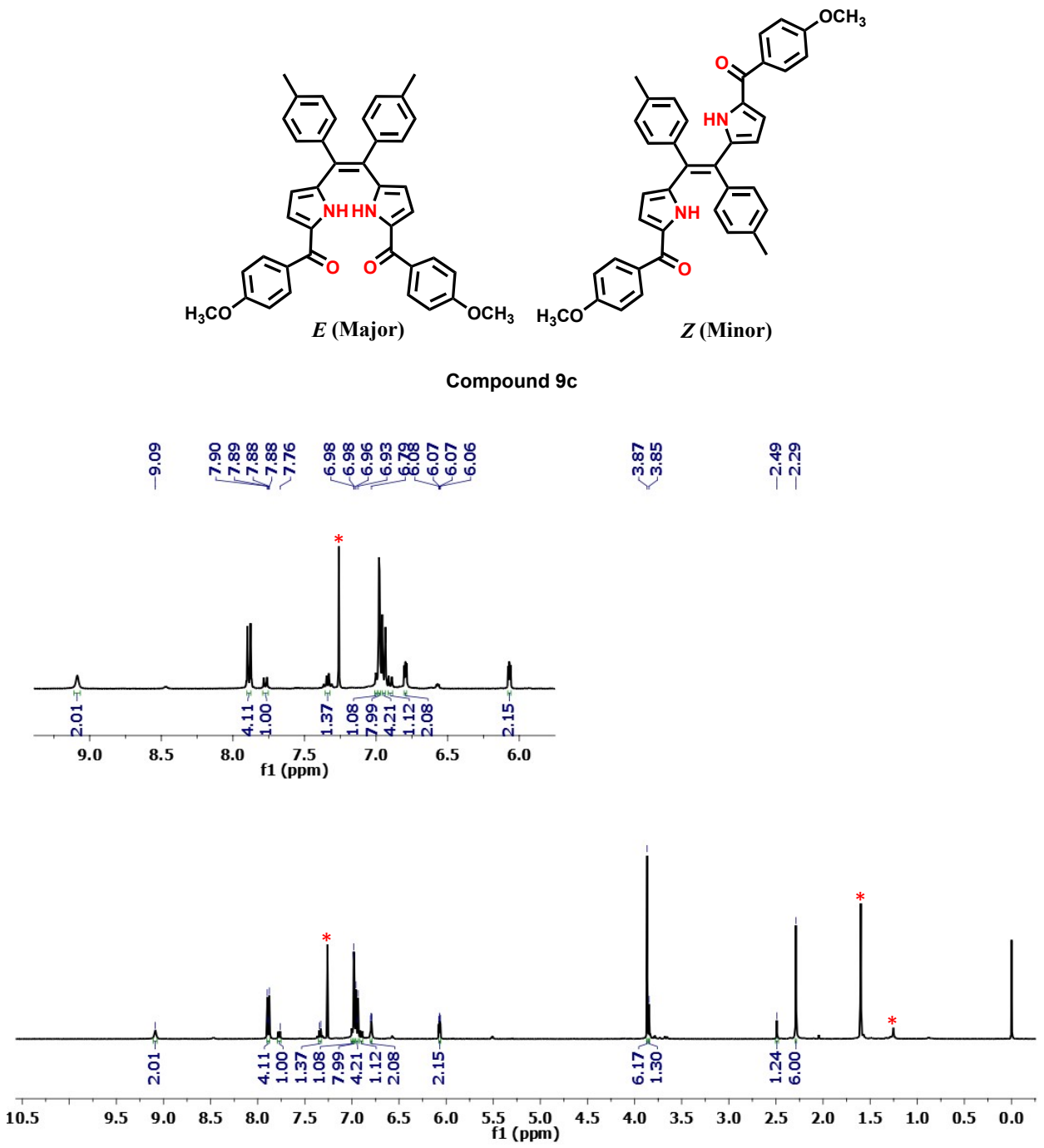


Figure S2. ^{1}H-NMR spectrum of the *E/Z*-**9c** (*E/Z* ratio = 80:20) recorded in $CDCl_3$ on 400 MHz NMR instrument. The *E/Z* ratio is determined by NMR integration method. Note: Peaks marked with asterisk (*) are due to residual solvents.

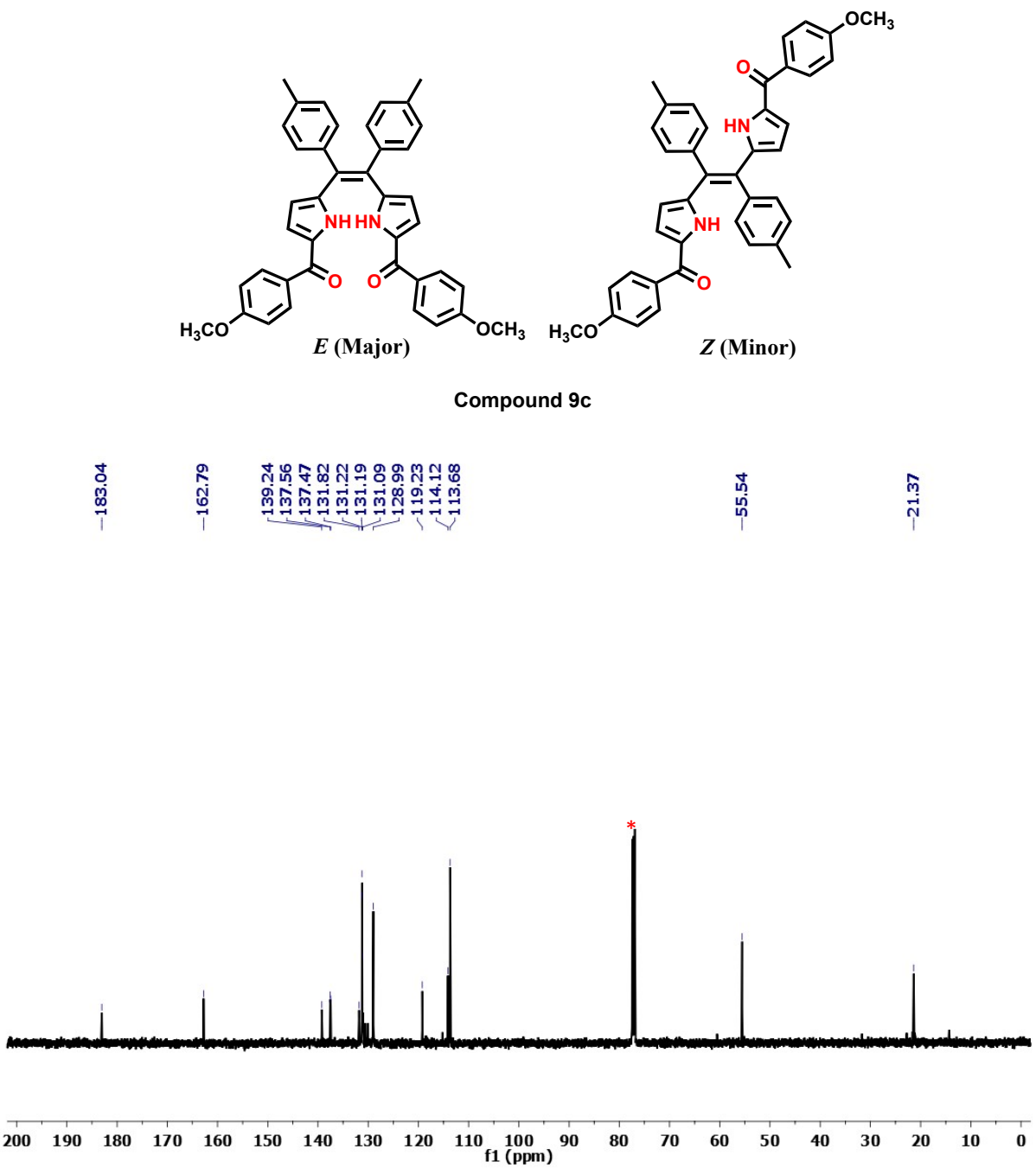
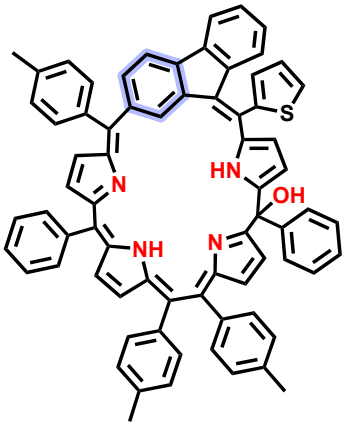


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of the compound **9c** recorded in $CDCl_3$ on 126 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.



Compound 3

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Sample Information

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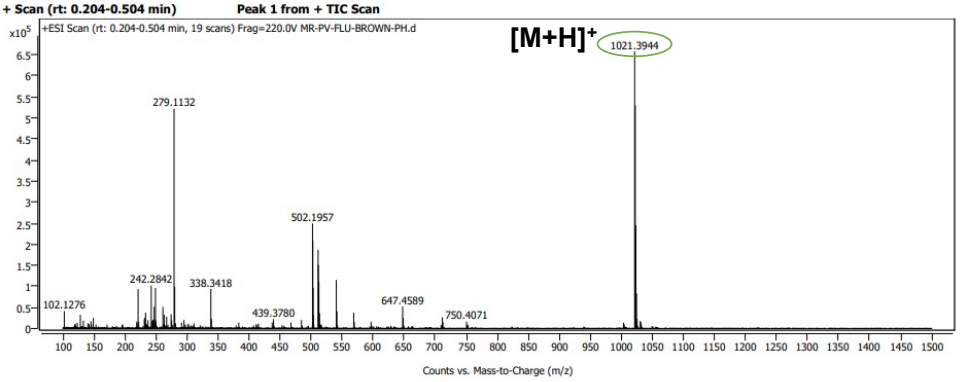

Compound Details

Cpd. 1: C72 H52 N4 O S

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Compound Spectra (Zoomed)

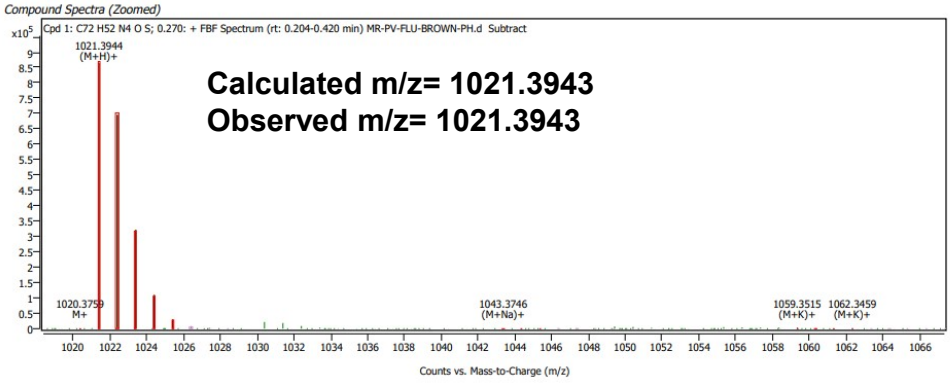
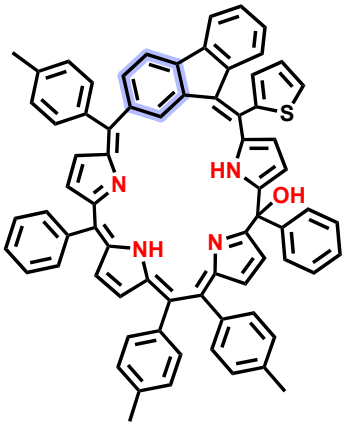


Figure S4. HR-mass spectrum of compound **3.**



Compound 3

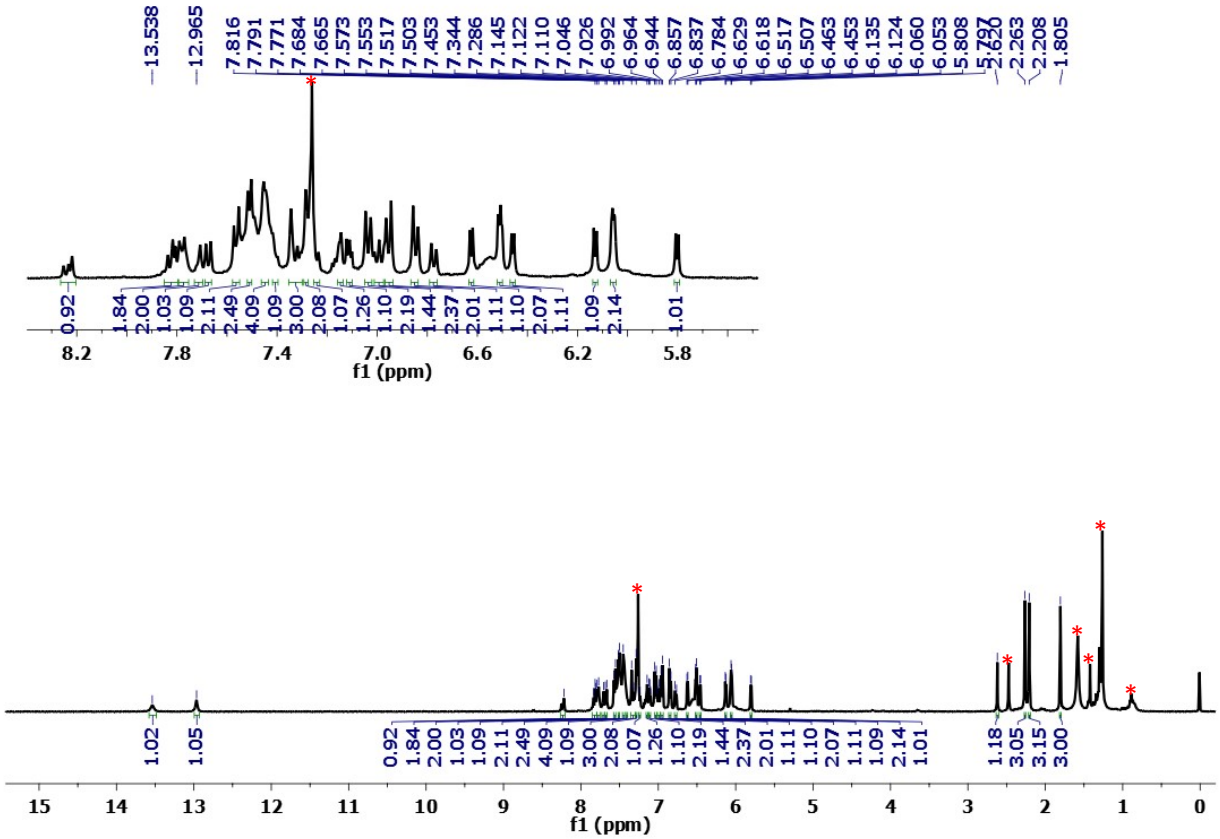
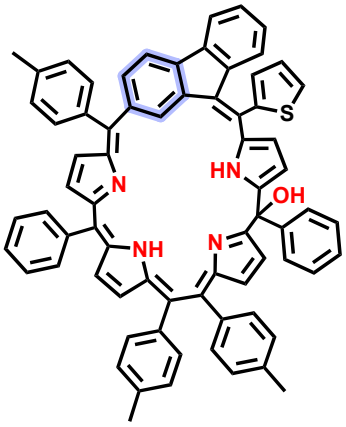


Figure S5. ^{1}H-NMR spectrum of the compound **3** recorded in $CDCl_3$ on 400 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.



Compound 3

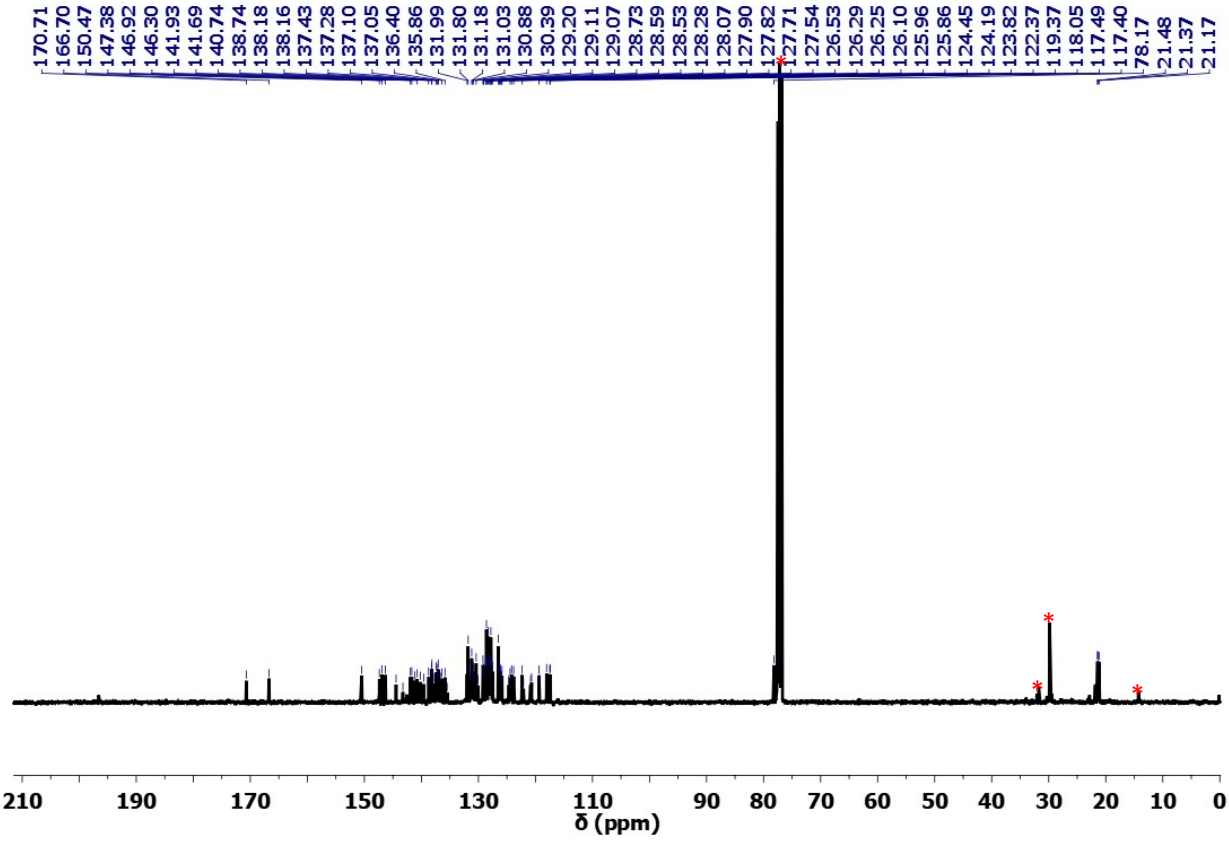
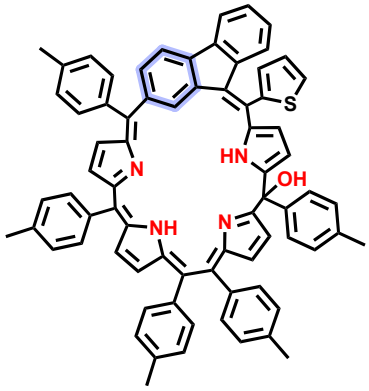


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of the compound **3** recorded in $CDCl_3$ on 101 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.



Compound 4

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Agilent

Sample Information

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Inj. Vol. (ul)		**IRM Status**	Success
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Sample Spectra

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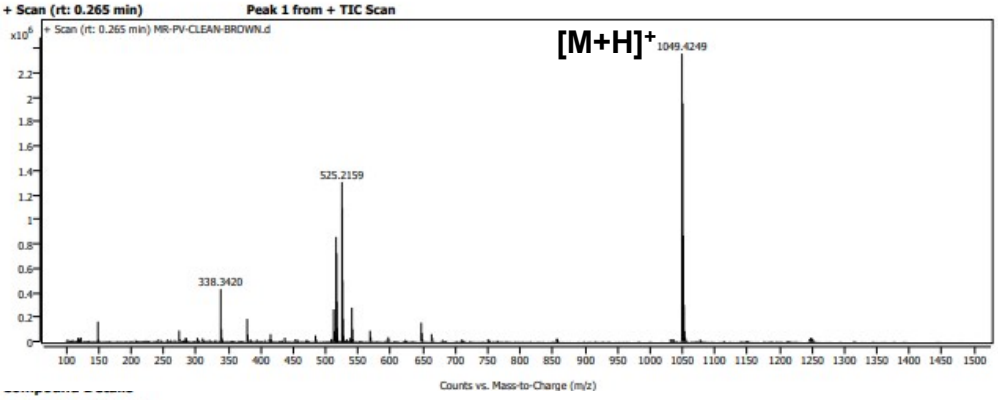

Cpd. 1: C74 H56 N4 O S

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Compound Spectra (Zoomed)

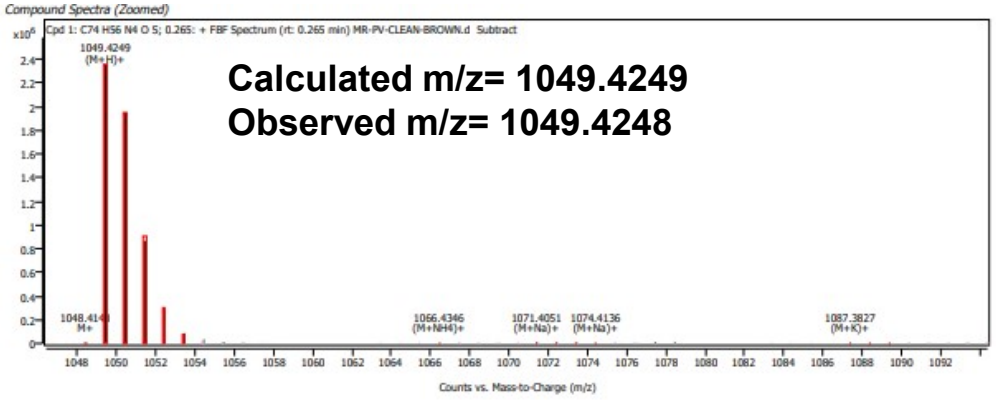


Figure S7. HR-mass spectrum of compound **4.**

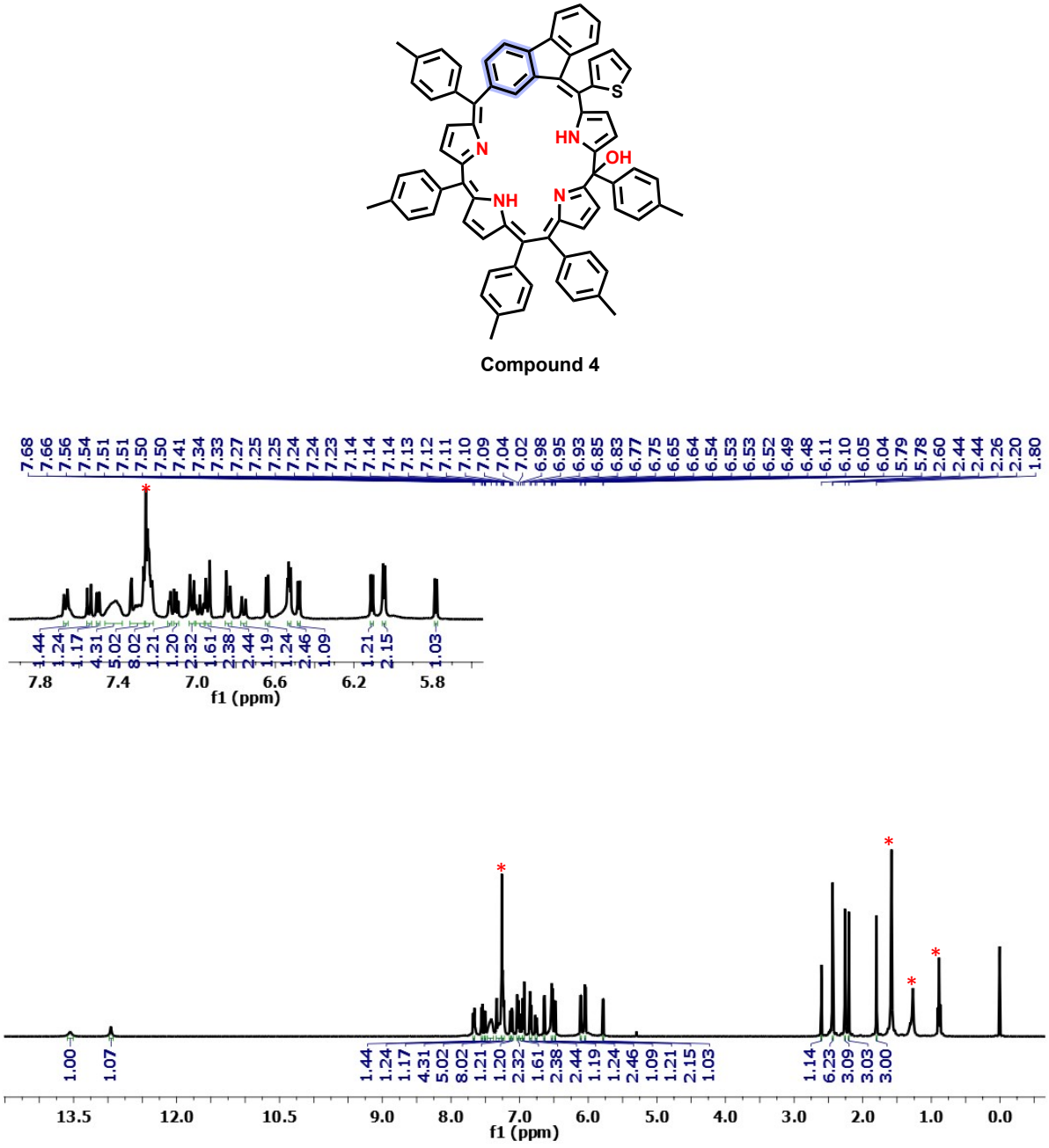
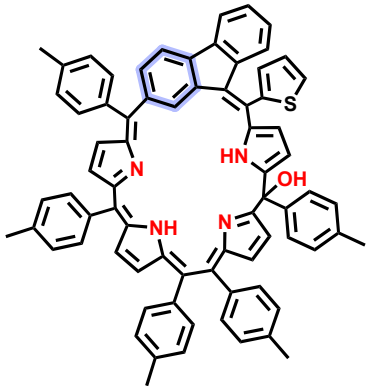
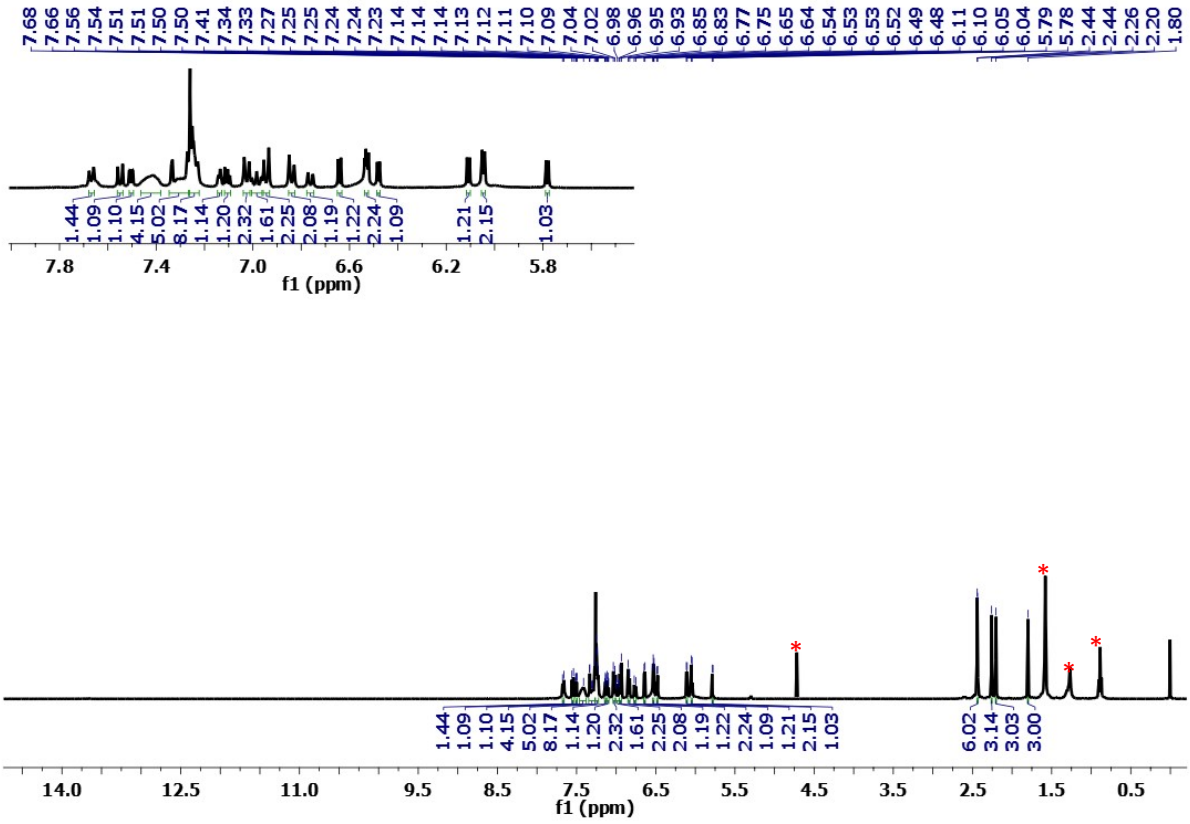


Figure S8. ^{1}H-NMR spectrum of the compound **4** recorded in $CDCl_3$ on 400 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.



Compound 4



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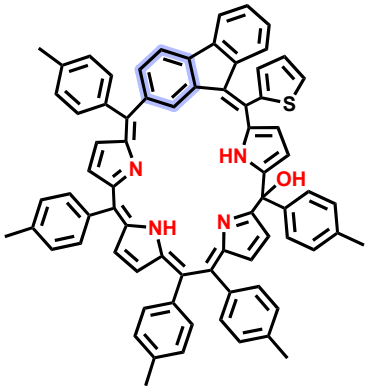
gure S9. ^{1}H-NMR spectra of compound **4** after addition of D_2O to compound **4**. Note: Peaks marked with asterisk (*) are due to residual solvents.



Compound 4

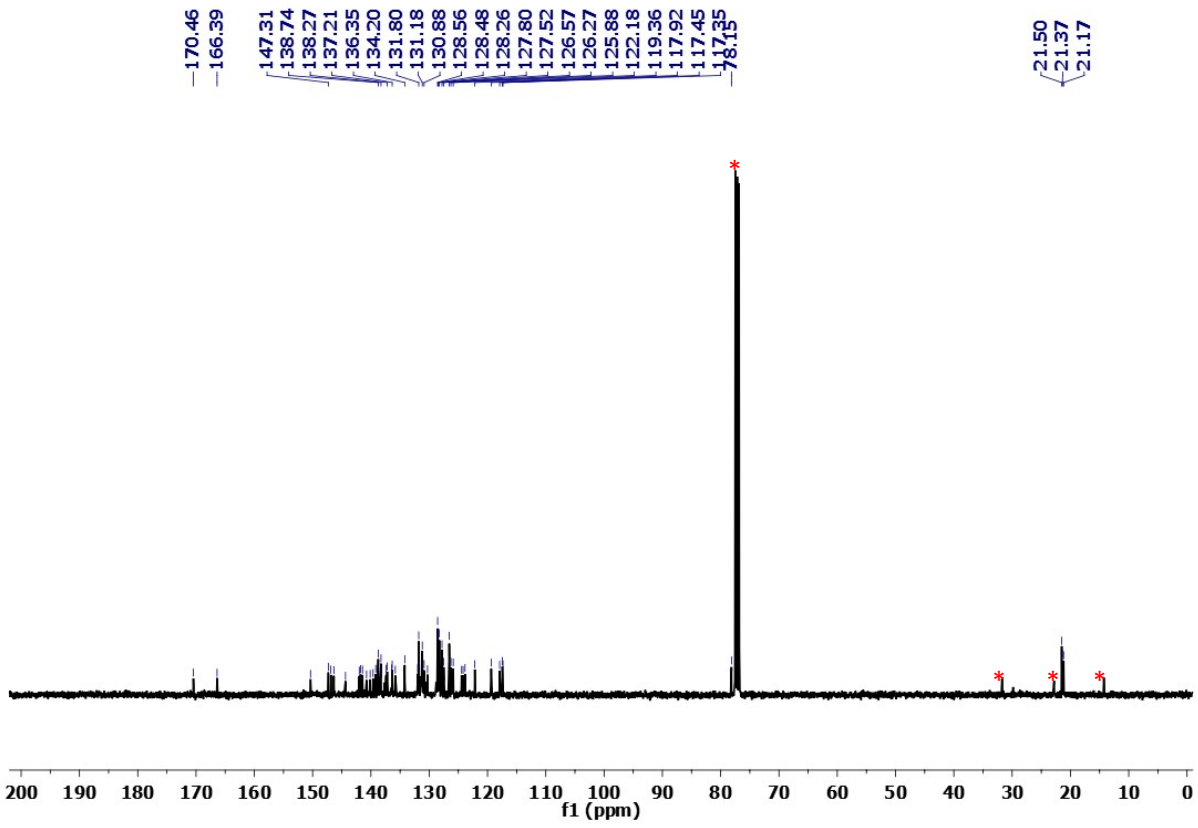


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of the compound **4** recorded in $CDCl_3$ on 101 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.

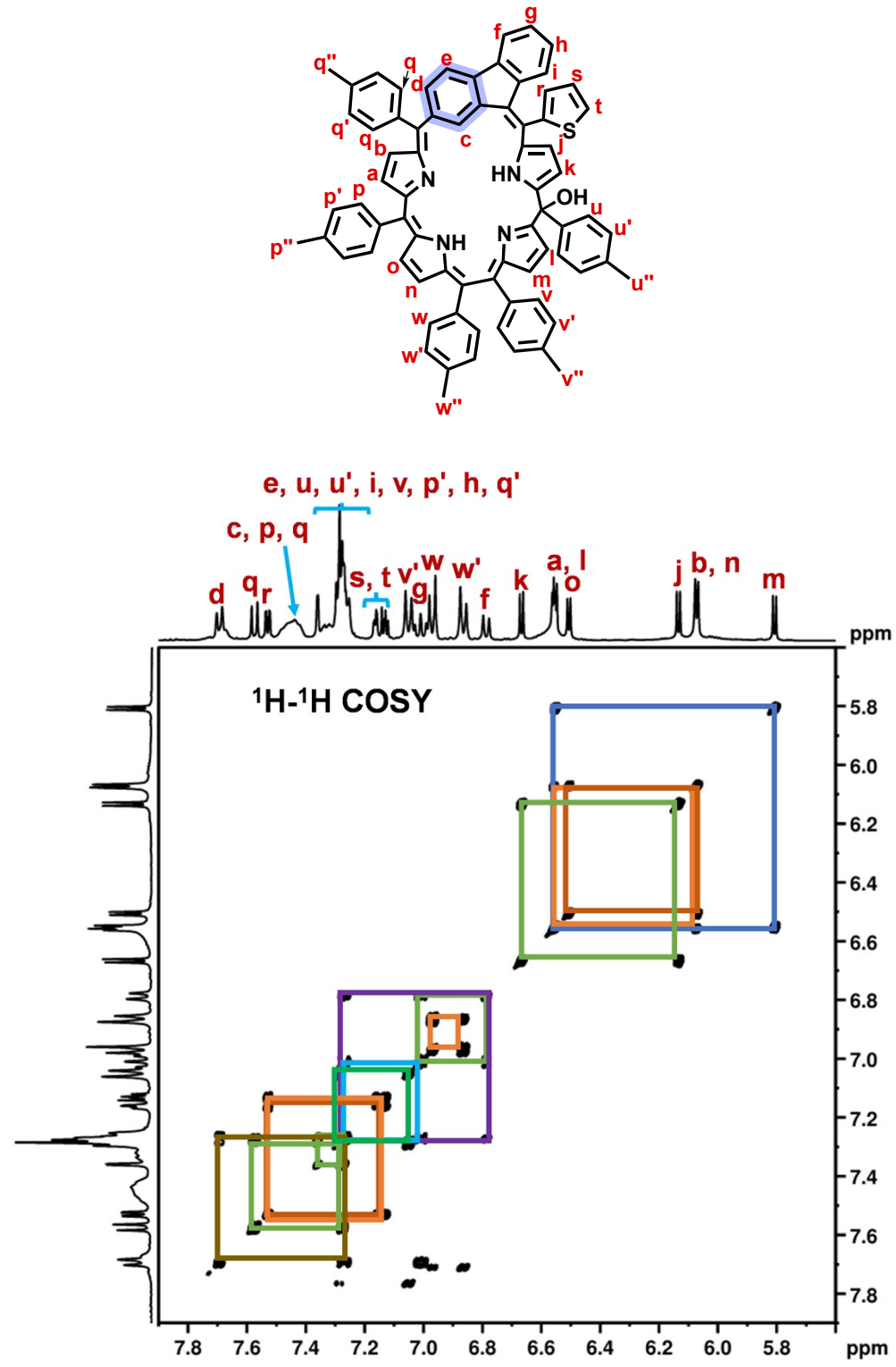
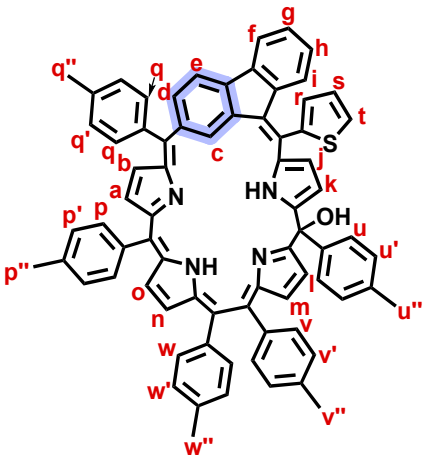


Figure S11. Partial ^{1}H–^{1}H COSY spectrum of **4** recorded in $CDCl_3$ on 400MHz NMR instrument.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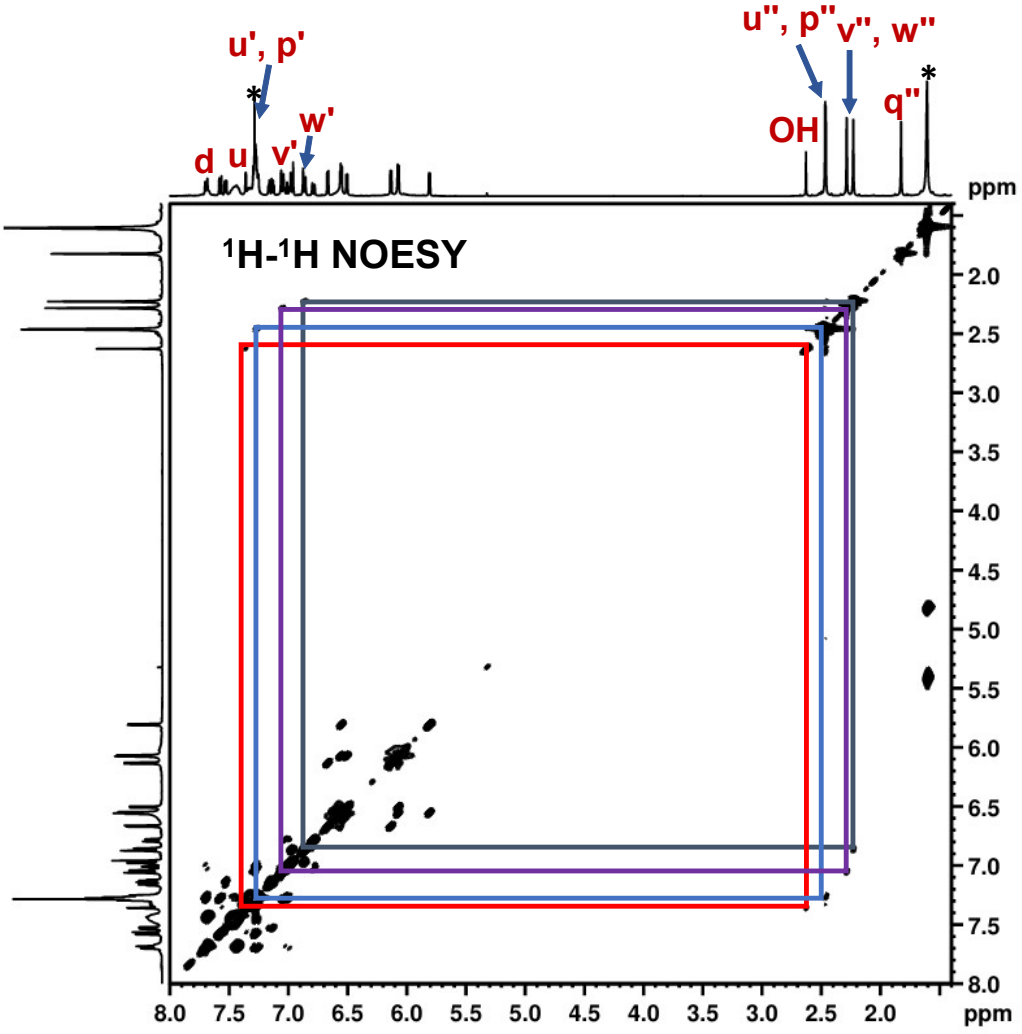
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ppm

Figure S12. $^{1}H–^{1}H$ NOESY spectrum of **4** recorded in $CDCl_3$ on 400MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.

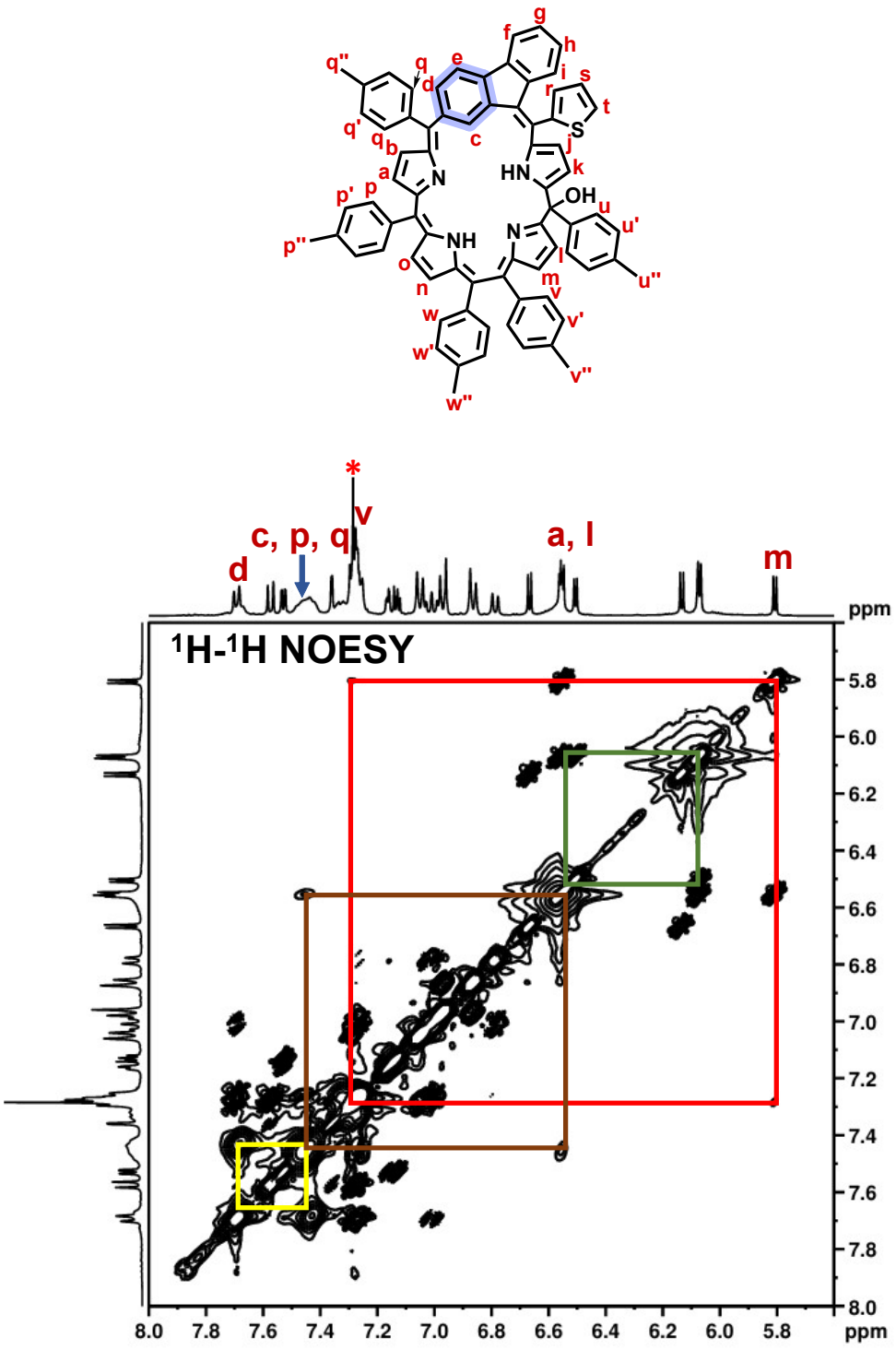
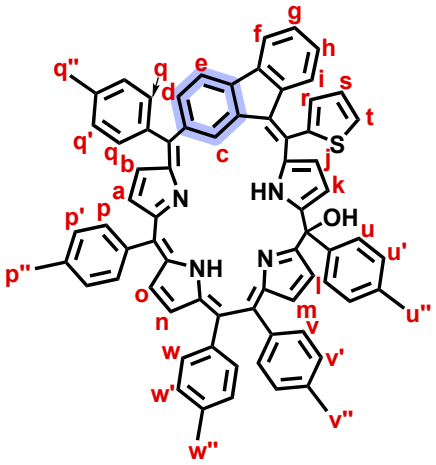


Figure S13. Expanded ^{1}H–^{1}H NOESY spectrum of **4** recorded in $CDCl_3$ on 400MHz NMR instrument.



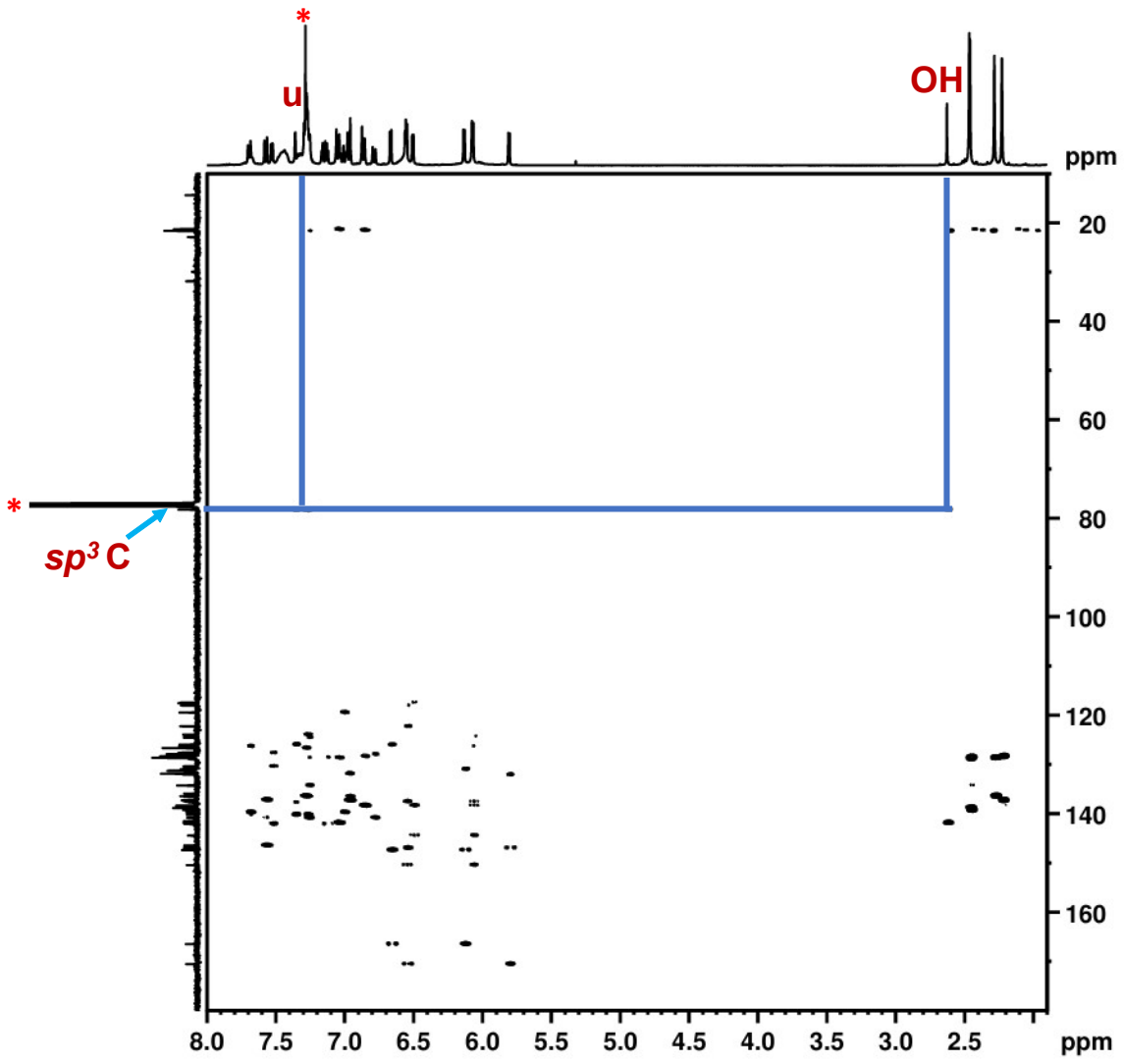
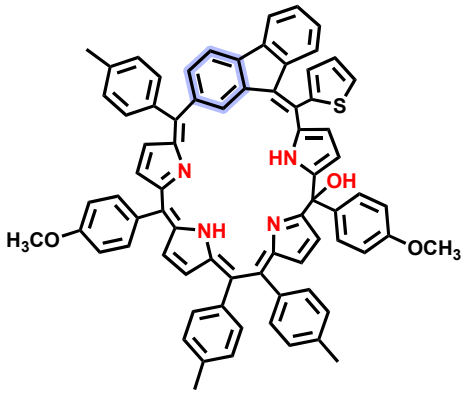


Figure S14. $^{1}H–^{13}C$ HMBC spectrum of **4** recorded in $CDCl_3$ on 400MHz NMR instrument.



Compound 5

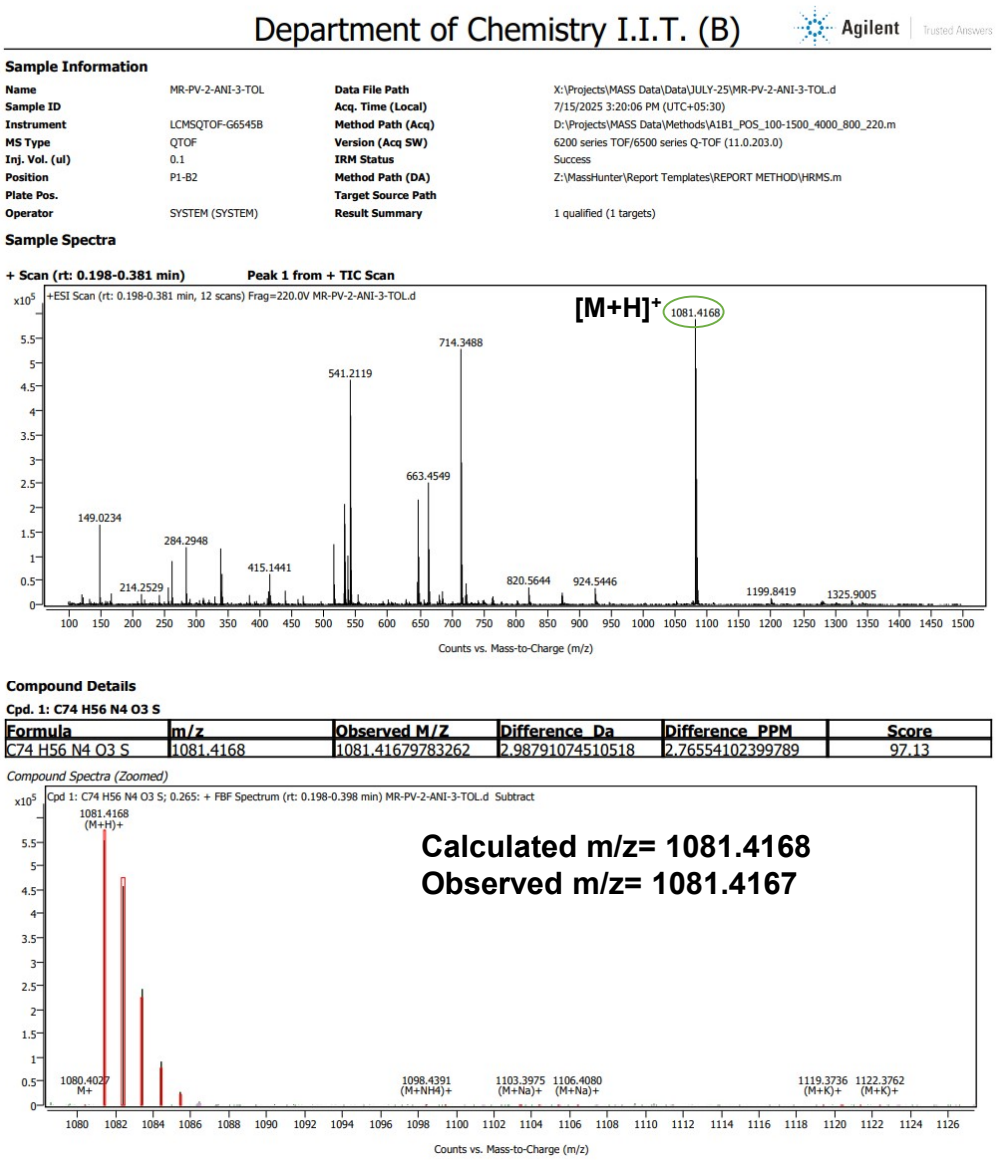
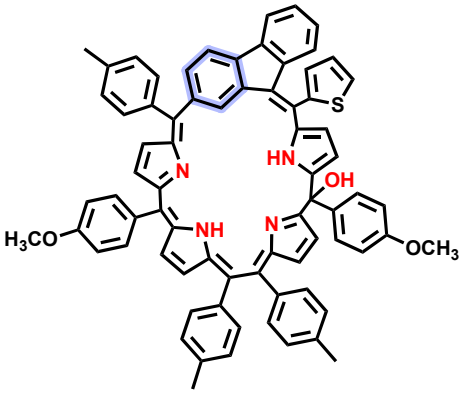


Figure S15. HR-mass spectrum of compound **5**.



Compound 5

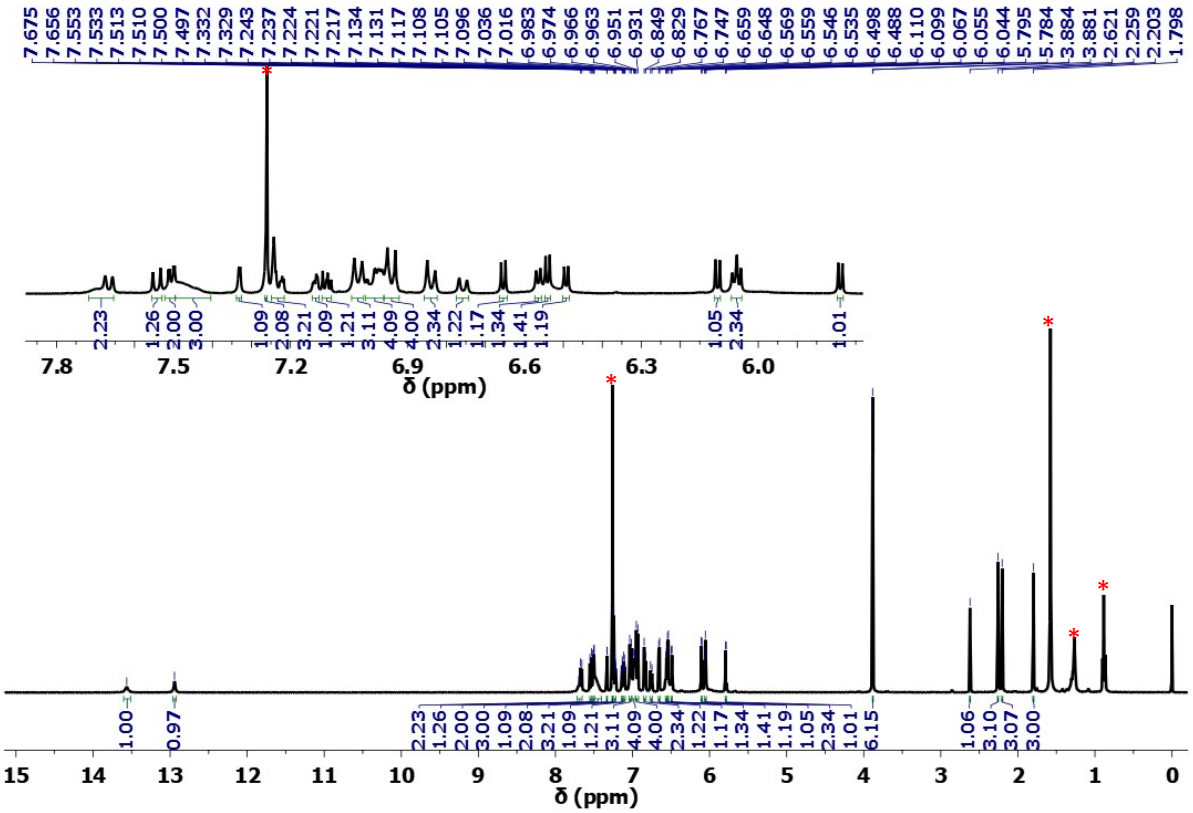
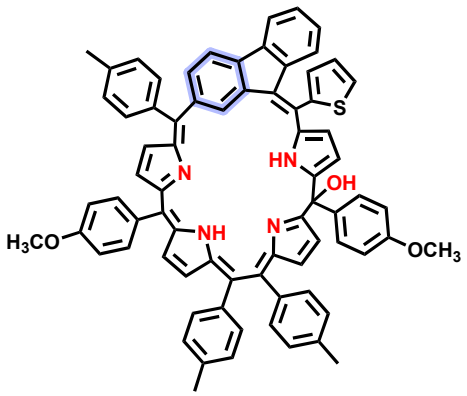


Figure S16. ^{1}H-NMR spectrum of the compound **5** recorded in $CDCl_3$ on 400 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.



Compound 5

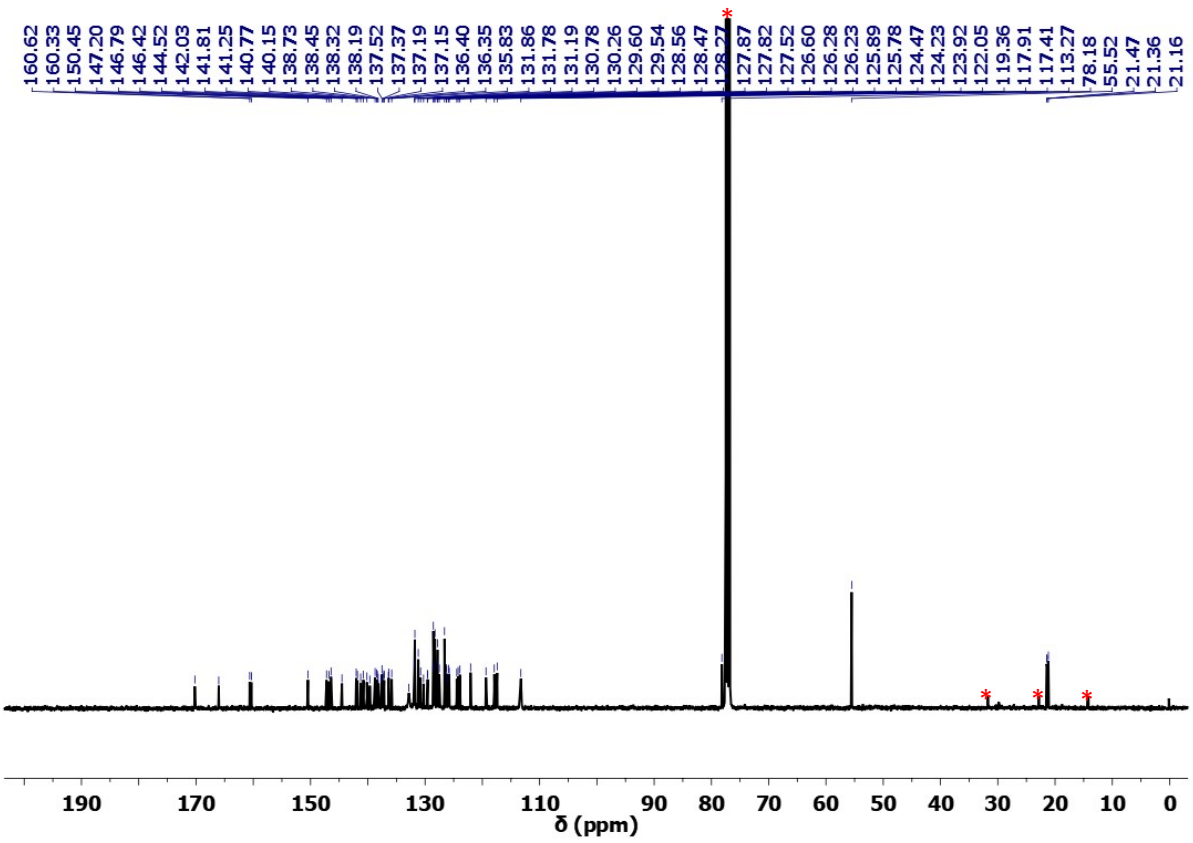
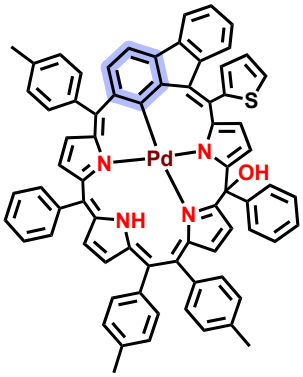


Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of the compound **5** recorded in $CDCl_3$ on 101 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.



Compound 3-Pd(II)

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Agilent

Sample Information

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Inj. Vol. (ul)		**IRM Status**	Success
Position		**Method Path (DA)**	C:\Users\LCMS QTOF G6545\Desktop\Report Templates\REPORT METHOD\HRMS_1.m
Plate Pos.		**Target Source Path**	
Operator		**Result Summary**	1 qualified (1 targets)

Sample Spectra

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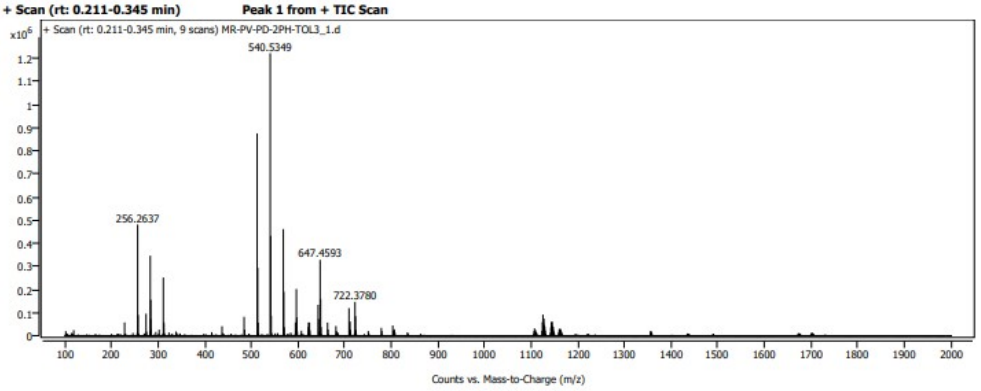


Compound Details

Cpd. 1: C72 H50 N4 O Pd S

Formula	m/z	Observed M/Z	Difference_Da	Difference_PPM	Score
C72 H50 N4 O Pd S	1125.2832	1125.28319800626	-0.781024755951876	-0.697171641956045	98.04

Compound Spectra (Zoomed)

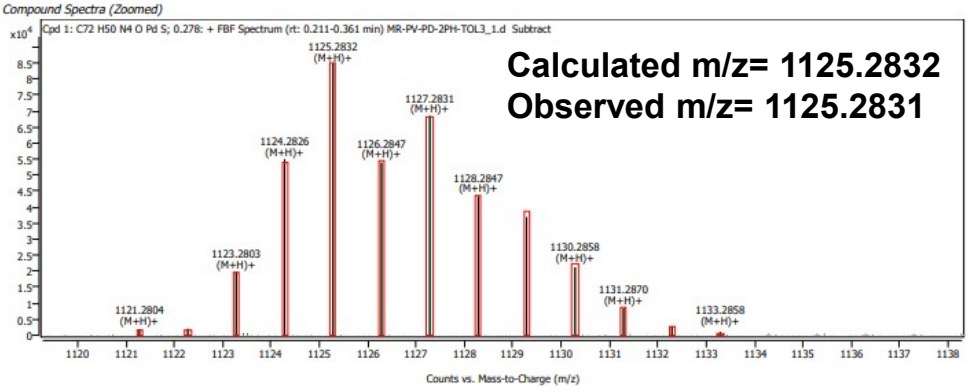


Figure S18. HR-mass spectrum of compound **3-Pd(II)**.

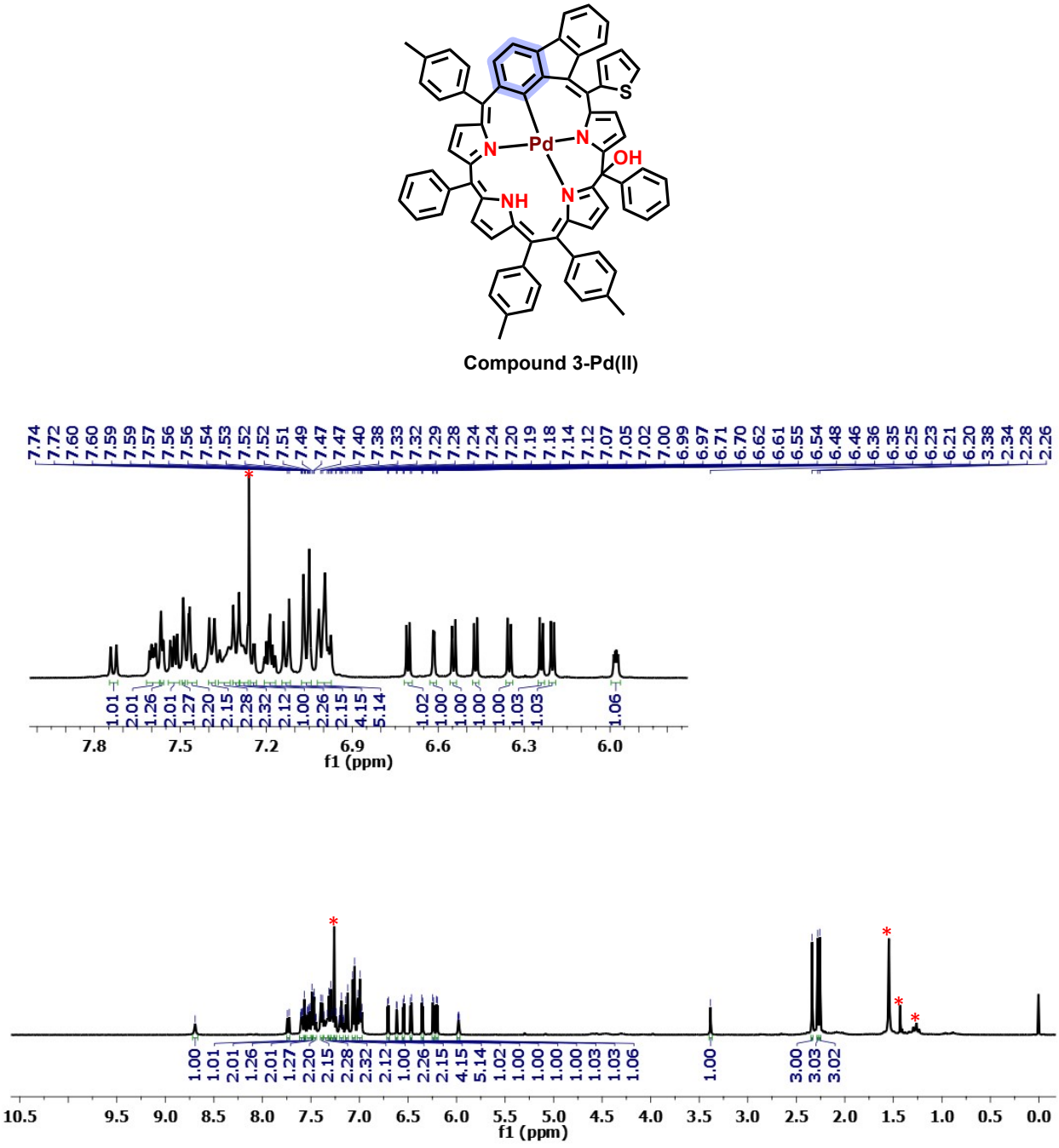


Figure S19. ^{1}H-NMR spectrum of the compound **3-Pd(II)** recorded in $CDCl_3$ on 400 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.

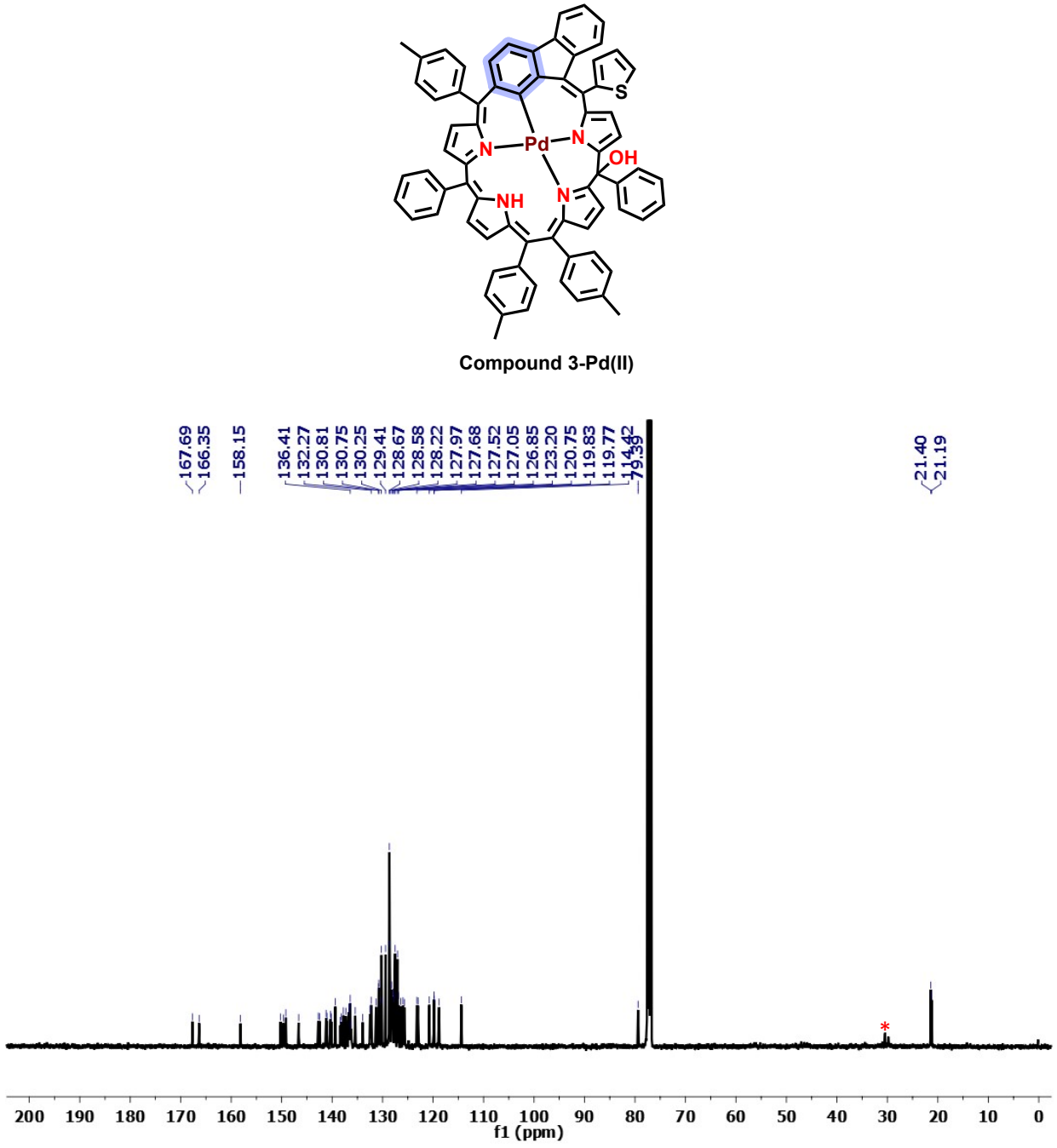
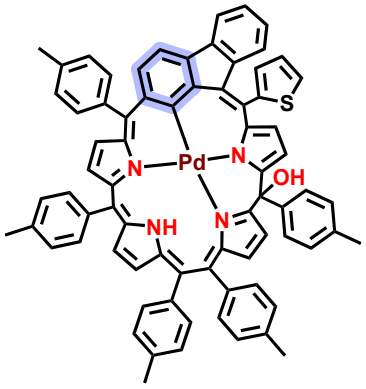


Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum of the compound **3-Pd(II)** recorded in $CDCl_3$ on 101 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.



Compound 4-Pd(II)

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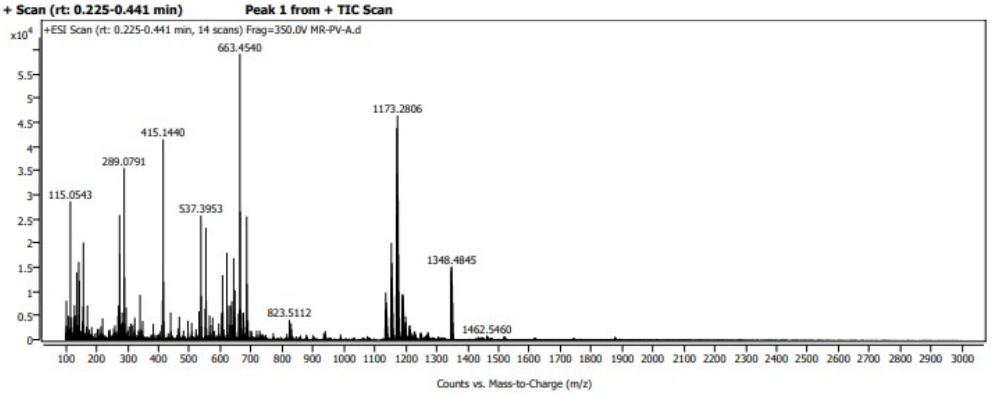
Sample Information

Name	MR-PV-A	**Data File Path**	X:\Projects\MASS Data\Data\JULY-25\MR-PV-A.d
Sample ID		**Acq. Time (Local)**	7/17/2025 1:04:43 PM (UTC+05:30)
Instrument	LCMSQTOF-G6545B	**Method Path (Acq)**	D:\Projects\MASS Data\Methods\A1B1_POS_100-3000_4000_2000_350_HIGH MASS.m
MS Type	QTOF	**Version (Acq SW)**	6200 series TOF/6500 series Q-TOF (11.0.203.0)
Inj. Vol. (ul)	0.2	**IRM Status**	Success
Position	P2-C9	**Method Path (DA)**	Z:\MassHunter\Report Templates\REPORT METHOD\HRMS_IITB_1.m
Plate Pos.		**Target Source Path**	
Operator	SYSTEM (SYSTEM)	**Result Summary**	1 qualified (1 targets)

Sample Spectra

+ Scan (rt: 0.225-0.441 min) **Peak 1 from + TIC Scan**



Compound Details

Cpd. 1: C74 H54 N4 O Pd S

Formula	m/z	Observed M/Z	Difference_Da	Difference_PPM	Score
C74 H54 N4 O Pd S	1153.3145	1153.31447232672	-0.71686193723508	-0.624277011711989	99.75

Compound Spectra (Zoomed)

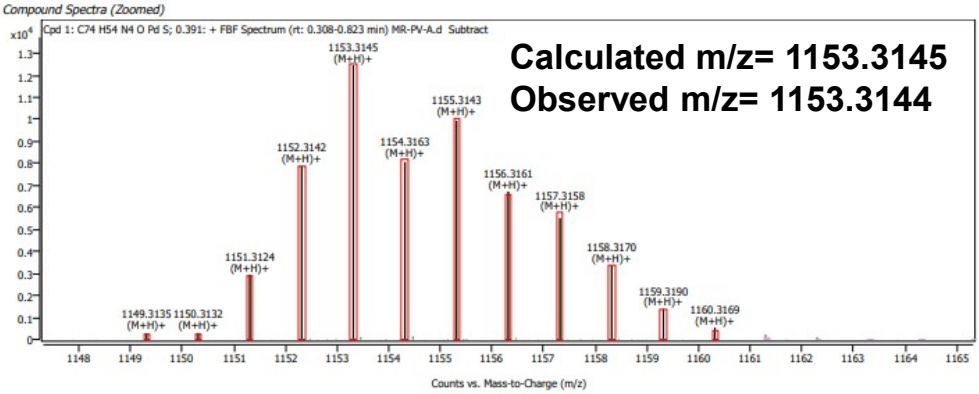


Figure S21. HR-mass spectrum of compound **4-Pd(II)**.

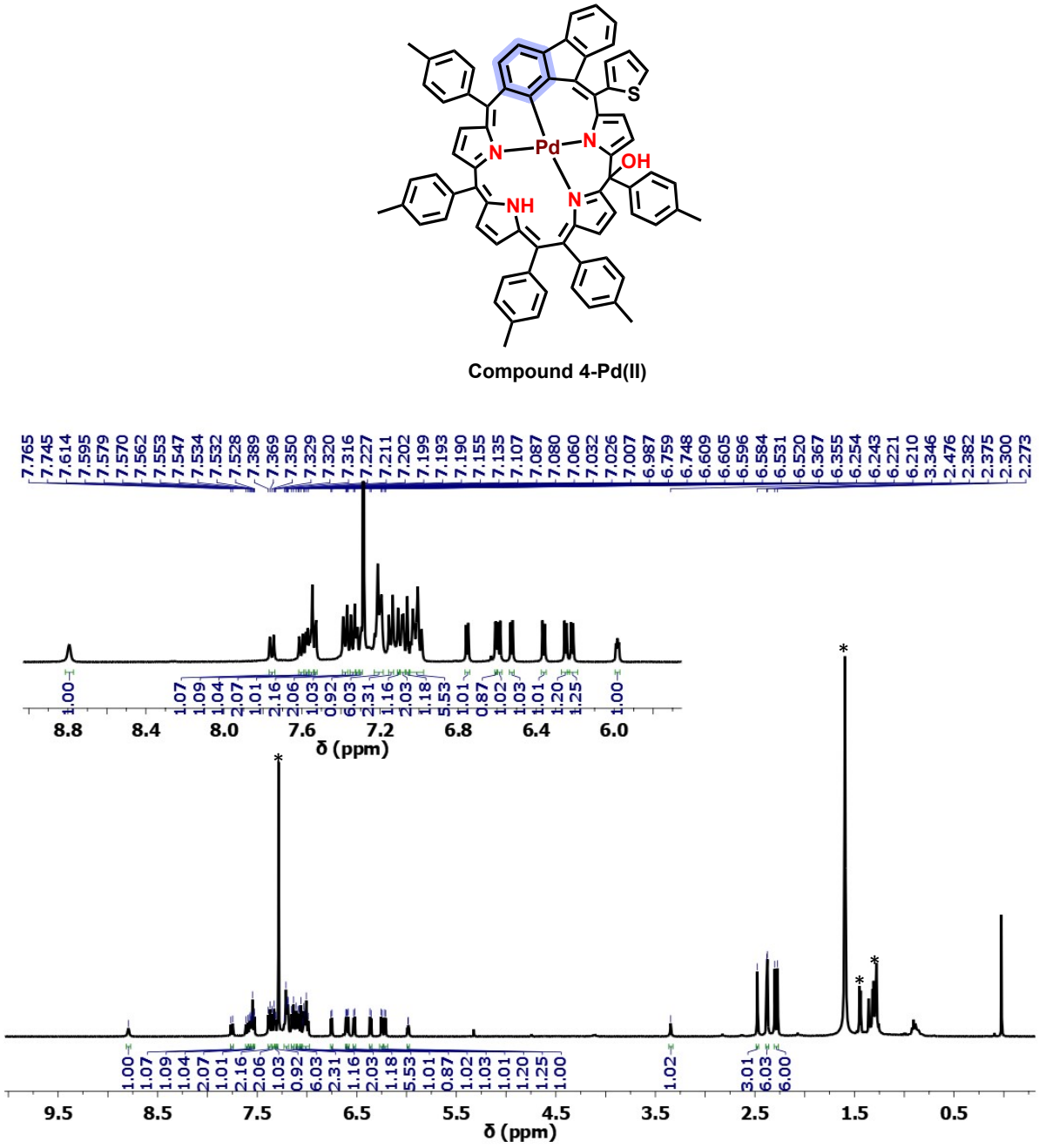
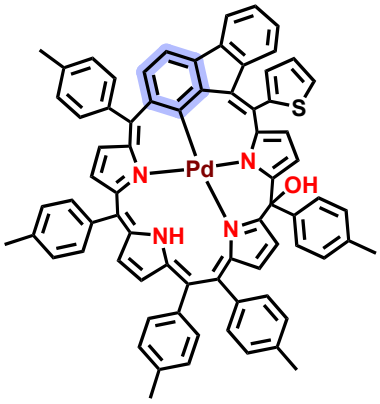


Figure S22. ^{1}H-NMR spectrum of the compound **4-Pd(II)** recorded in $CDCl_3$ on 400 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.



Compound 4-Pd(II)

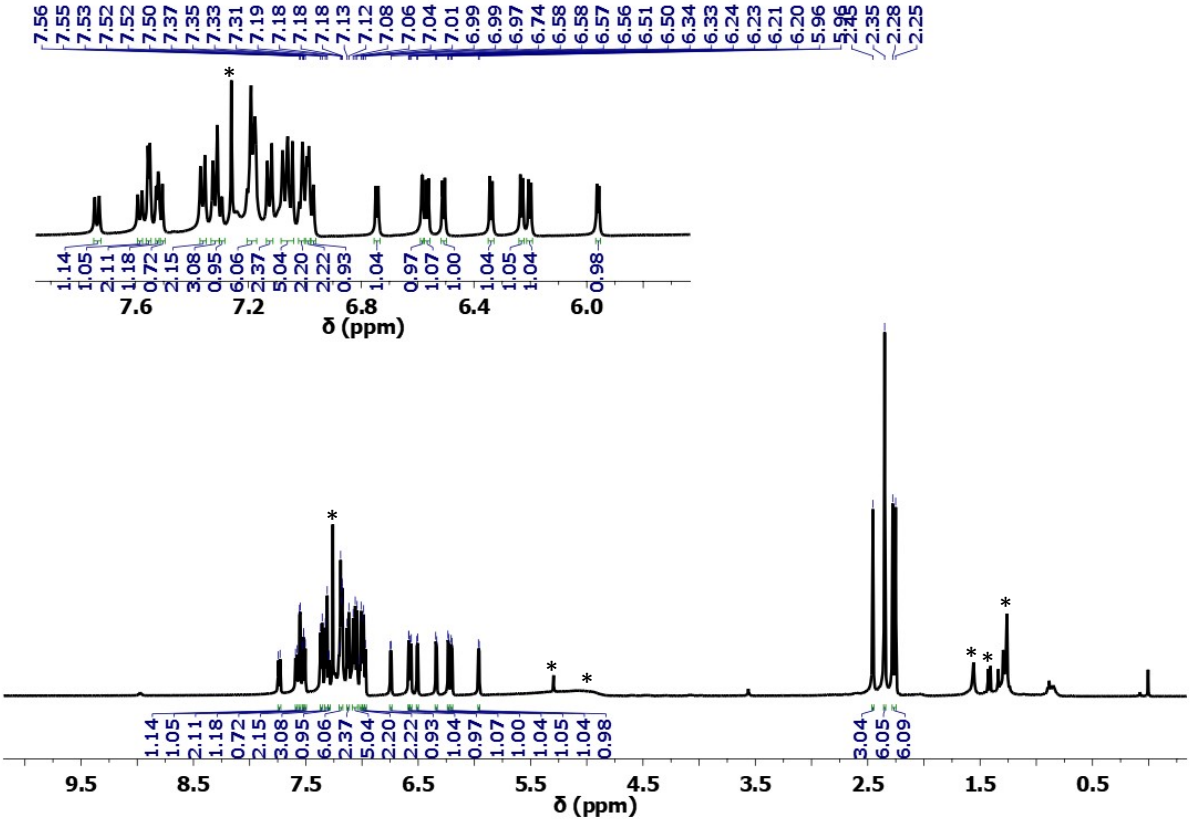
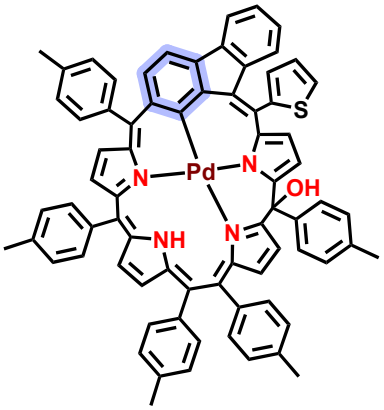


Figure S23. ^{1}H-NMR spectrum of the compound **4-Pd(II)** recorded in $CDCl_3$ on 500 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.



Compound 4-Pd(II)

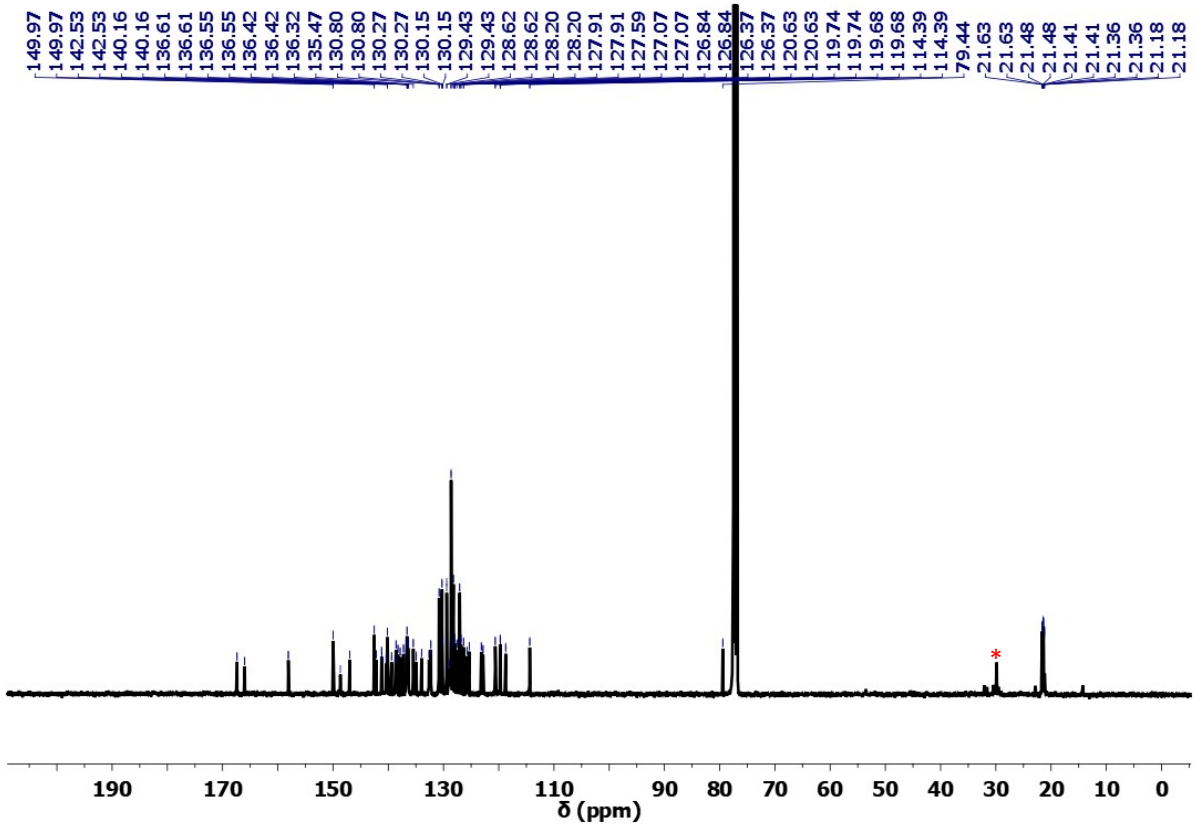
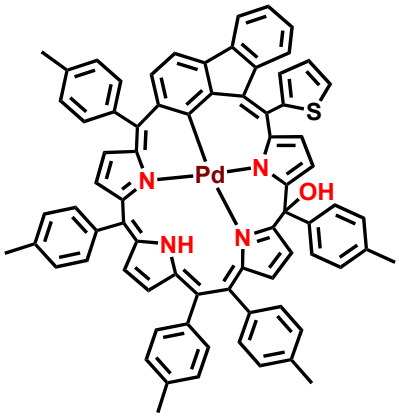


Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum of the compound **4-Pd(II)** recorded in $CDCl_3$ on 101 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.



Compound 4-Pd(II)

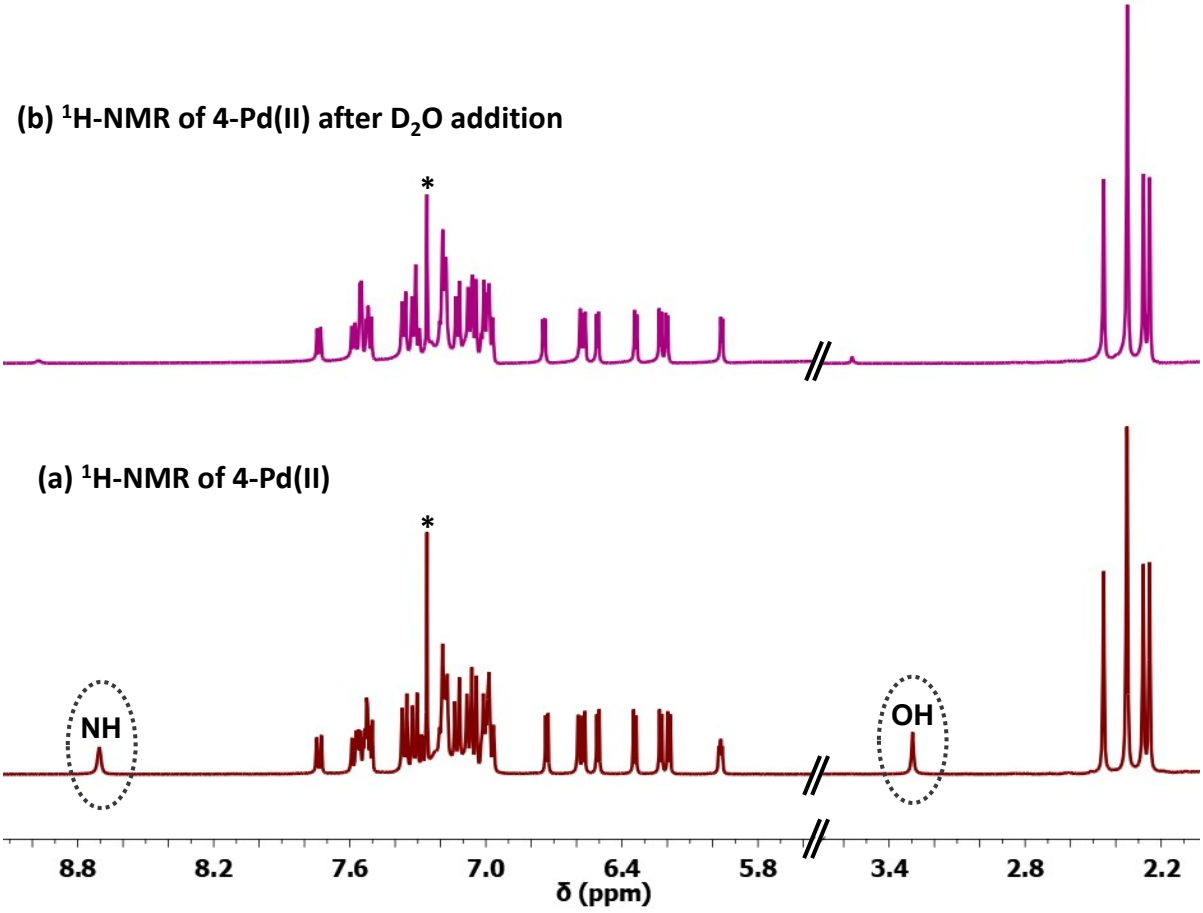


Figure S25. Comparison of partial ^{1}H-NMR spectra of (a) compound **4-Pd(II)** and (b) after addition of D_2O to compound **4-Pd(II)**. Note: Peaks marked with asterisk (*) are due to residual solvents.

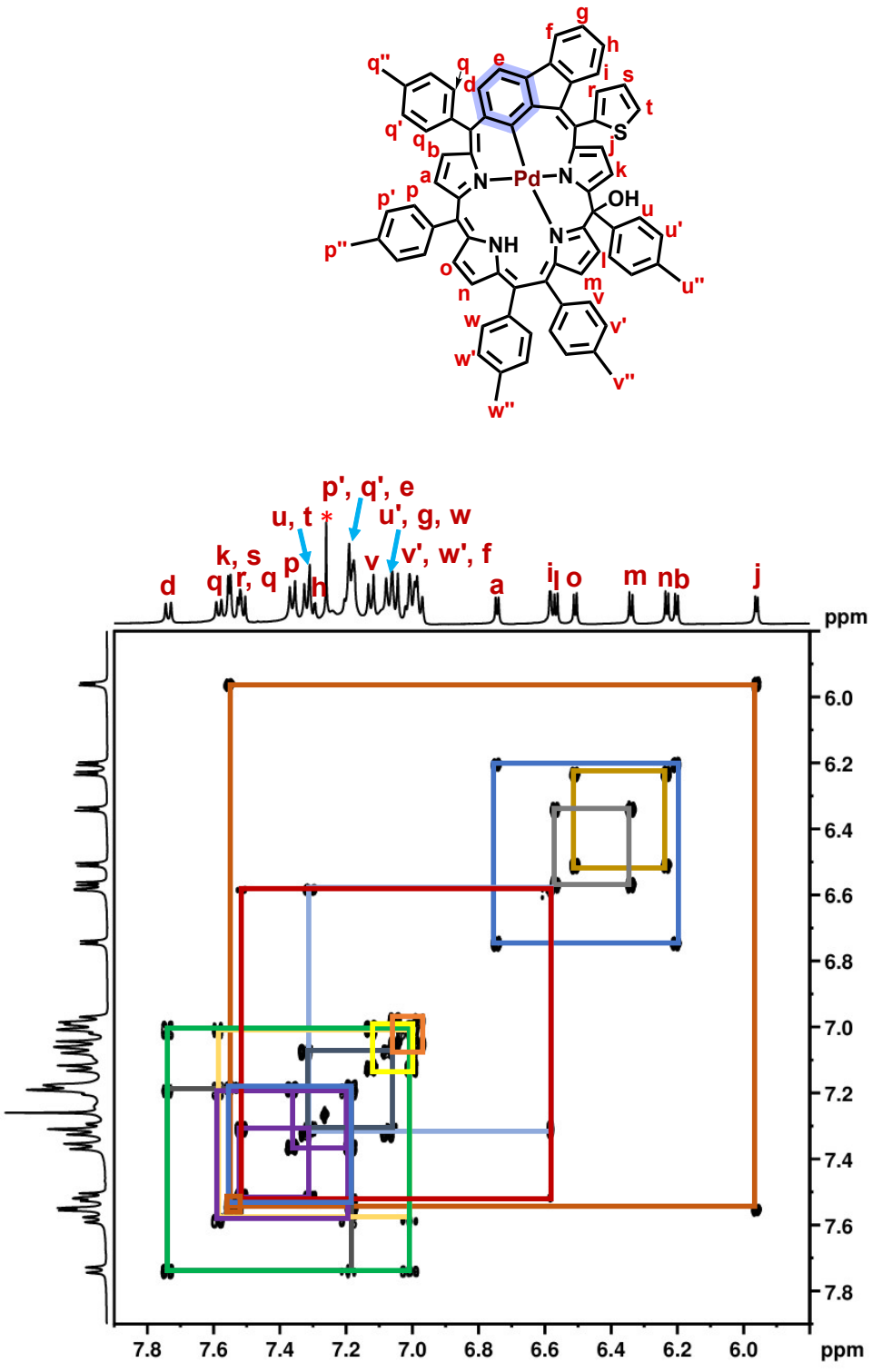


Figure S26. ^{1}H-^{1}H COSY spectrum of the compound **4-Pd(II)** recorded in $CDCl_3$ on 400 MHz NMR instrument.

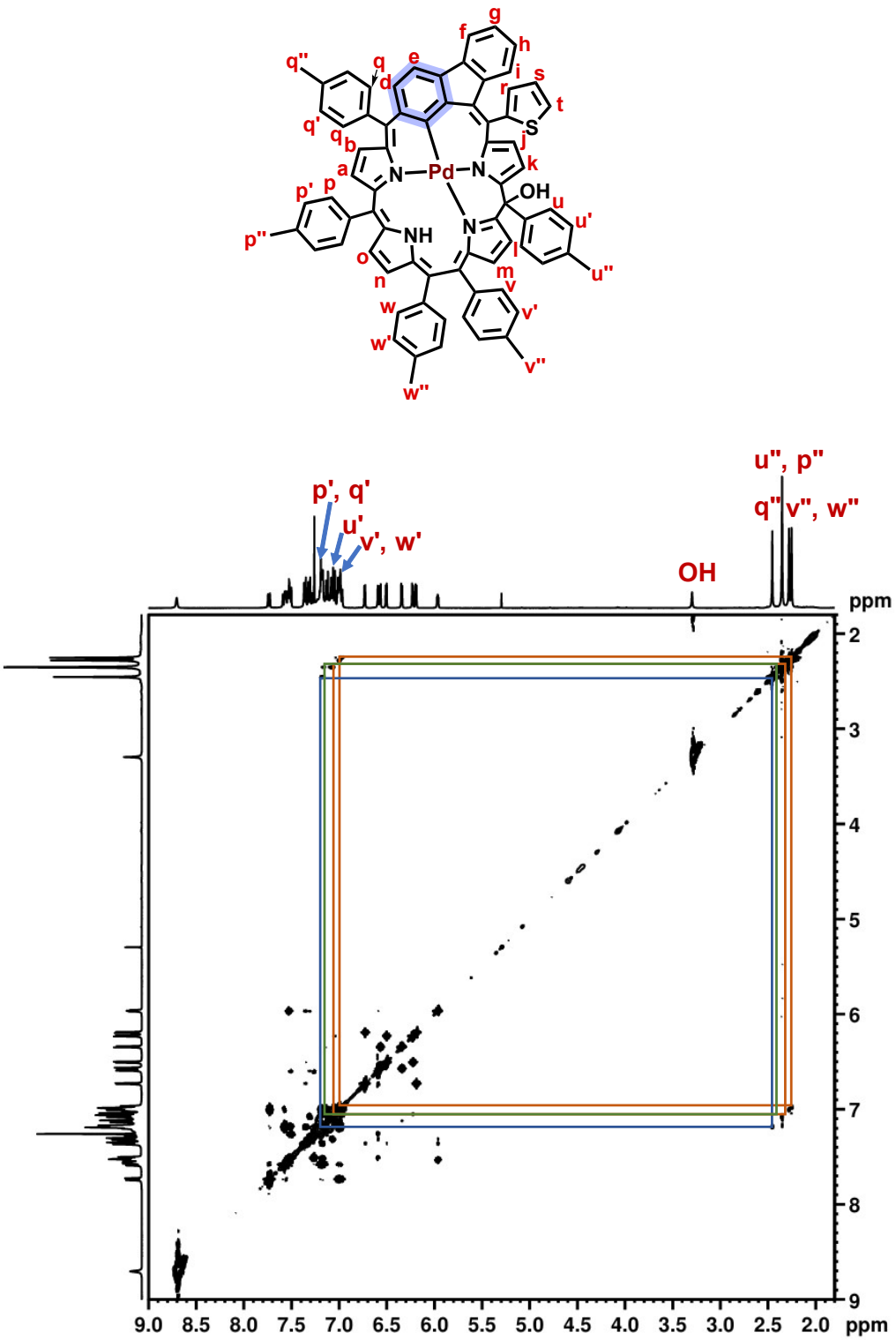


Figure S27. Expanded ^{1}H-^{1}H NOESY spectrum of the compound **4-Pd(II)** recorded in $CDCl_3$ on 400 MHz NMR instrument.

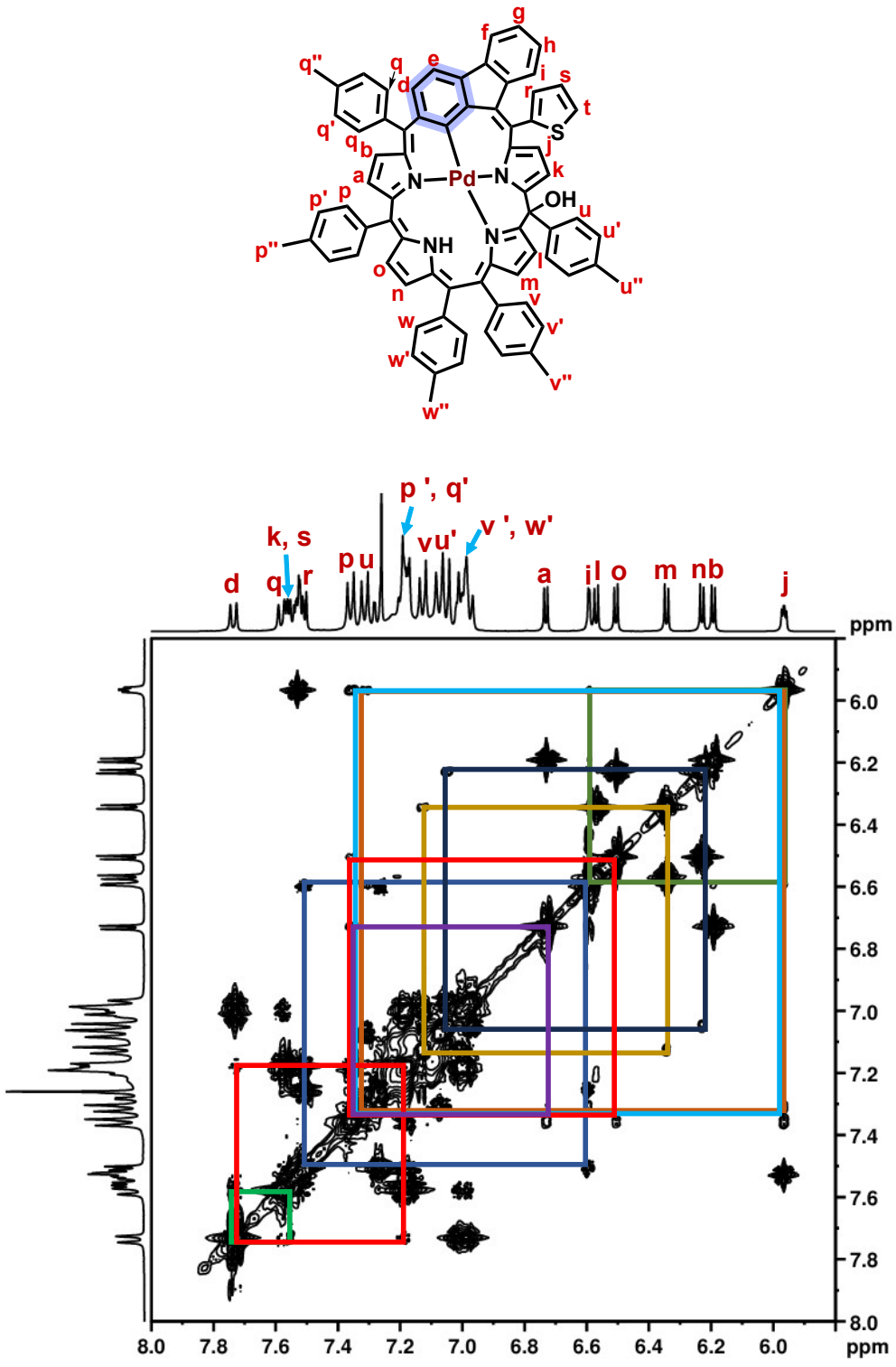


Figure S28. Expanded ^{1}H-^{1}H NOESY spectrum of the compound **4-Pd(II)** recorded in $CDCl_3$ on 400 MHz NMR instrument.

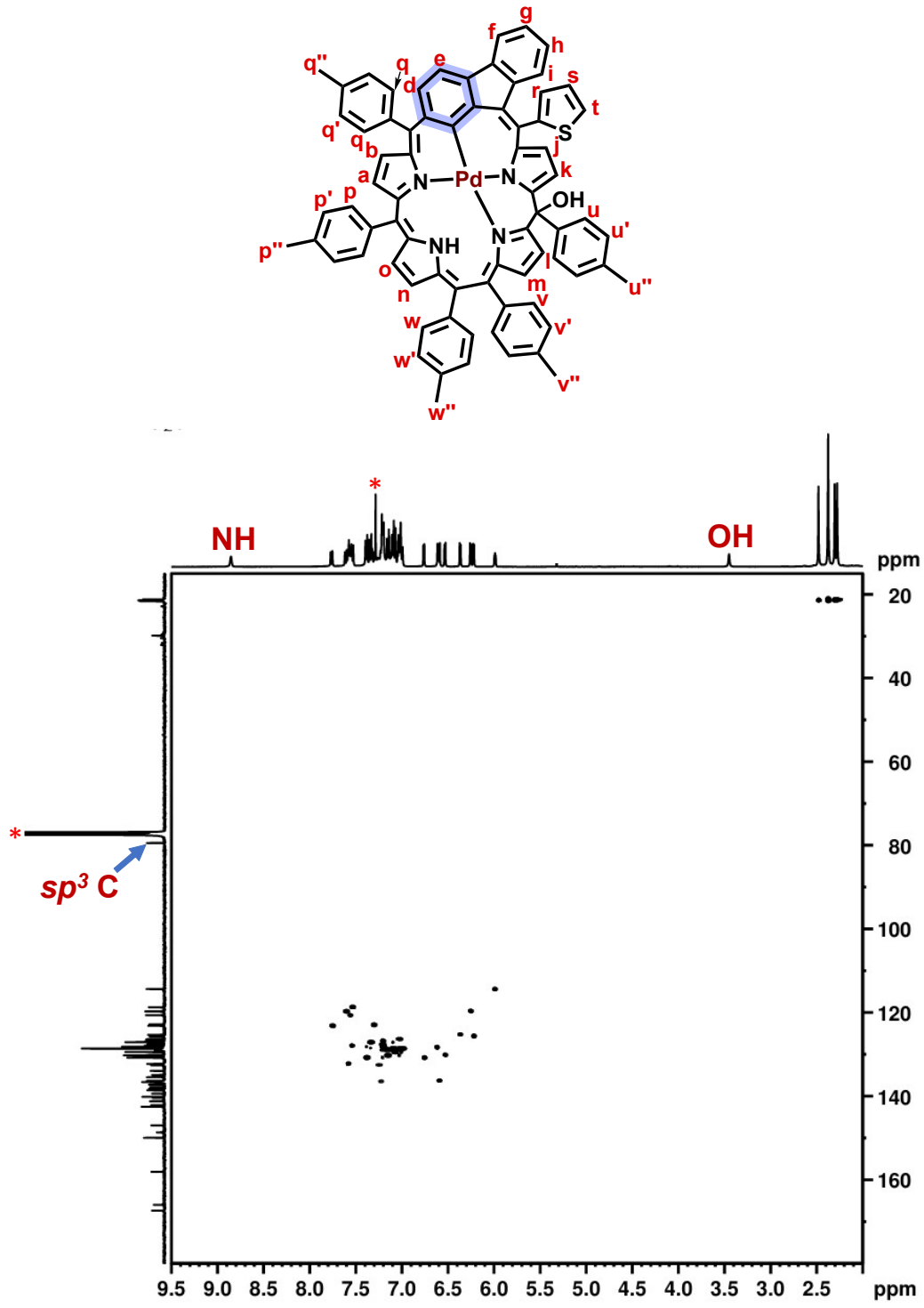


Figure S29. ^{1}H-^{13}C HSQC spectrum of the compound **4-Pd(II)** recorded in $CDCl_3$ on 400 MHz NMR instrument.

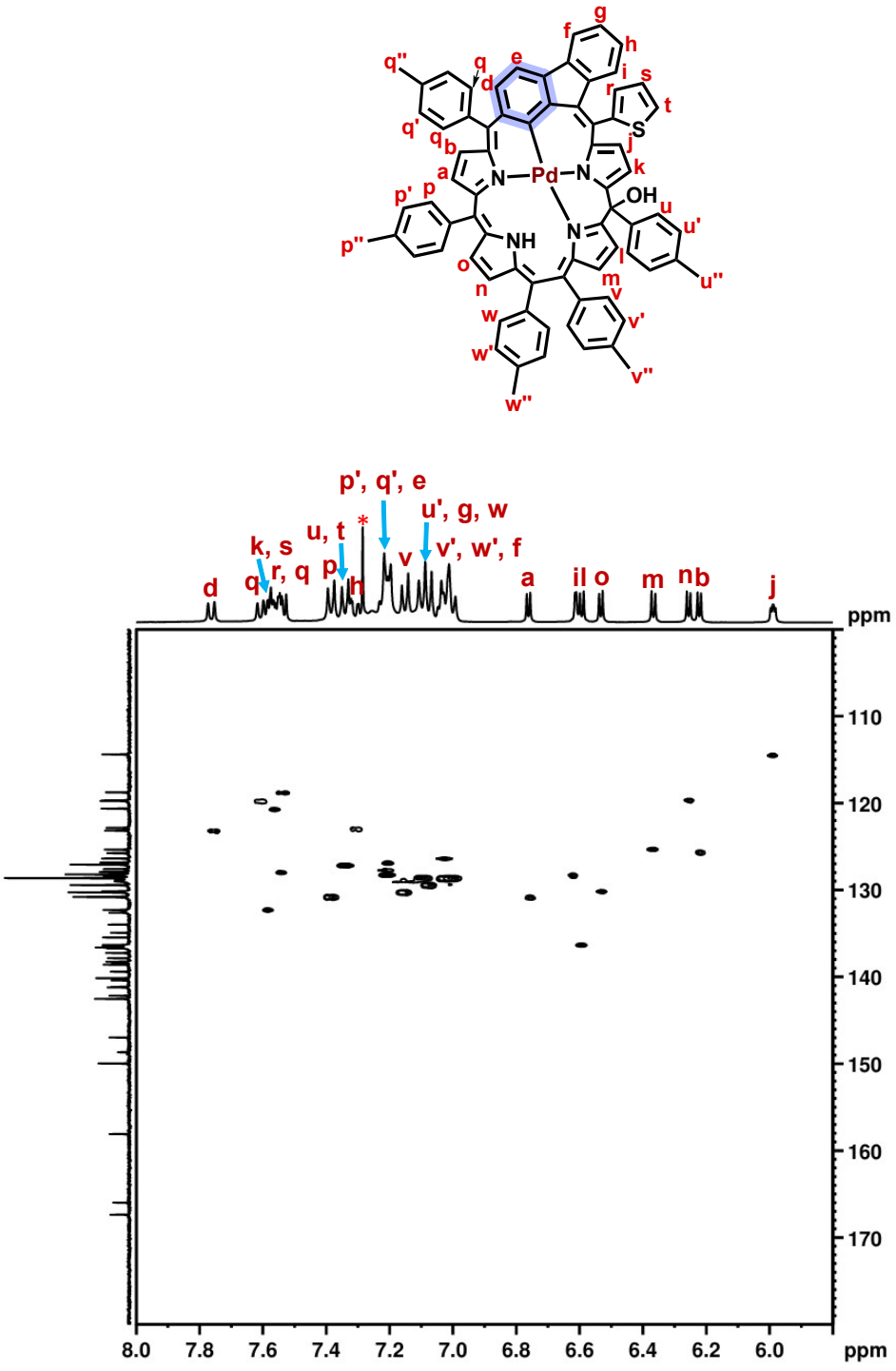
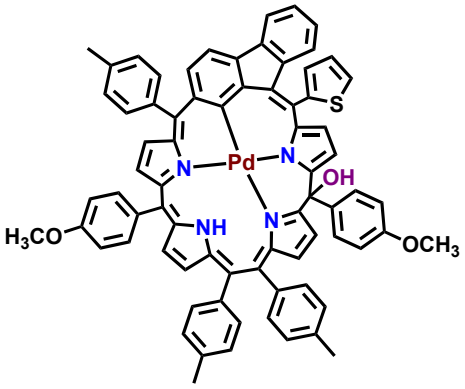


Figure S30. Expanded ^{1}H-^{13}C HSQC spectrum of the compound **4-Pd(II)** recorded in $CDCl_3$ on 400 MHz NMR instrument.



Compound 5-Pd(II)

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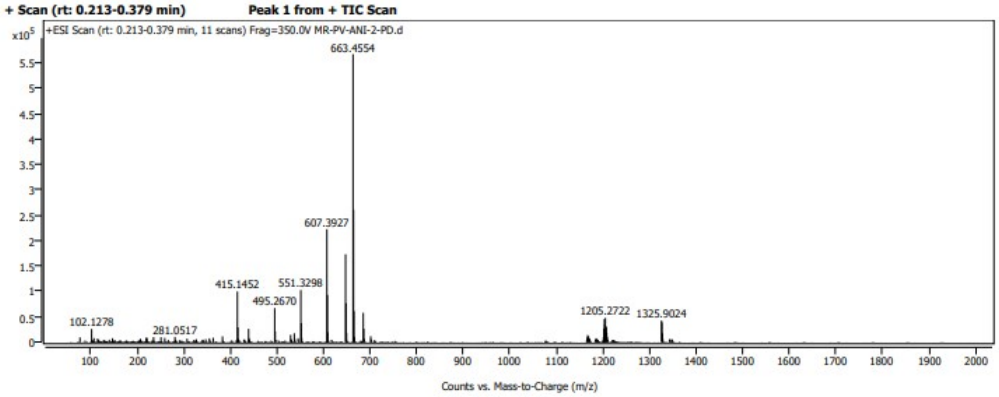
Sample Information

Name	MR-PV-ANI-2-PD	**Data File Path**	X:\Projects\MASS Data\Data\JULY-25\MR-PV-ANI-2-PD.d
Sample ID		**Acq. Time (Local)**	7/31/2025 3:00:10 PM (UTC+05:30)
Instrument	LCMSQTOF-G6545B	**Method Path (Acq)**	D:\Projects\MASS Data\Methods\A1B1_POS_100-2000_4000_2000_350_HIGH MASS.m
MS Type	QTOF	**Version (Acq SW)**	6200 series TOF/6500 series Q-TOF (11.0.203.0)
Inj. Vol. (ul)	0.1	**IRM Status**	Success
Position	P2-C4	**Method Path (DA)**	Z:\MassHunter\Report Templates\REPORT METHOD\HRMS.m
Plate Pos.		**Target Source Path**	
Operator	SYSTEM (SYSTEM)	**Result Summary**	1 qualified (1 targets)

Sample Spectra

+ Scan (rt: 0.213-0.379 min) **Peak 1 from + TIC Scan**



Compound Details

Cpd. 1: C74 H54 N4 O3 Pd S

Formula	m/z	Observed M/Z	Difference_Da	Difference_PPM	Score
C74 H54 N4 O3 Pd S	1185.3060	1185.30597652031	0.787509320161917	0.667212693456628	99.06

Compound Spectra (Zoomed)

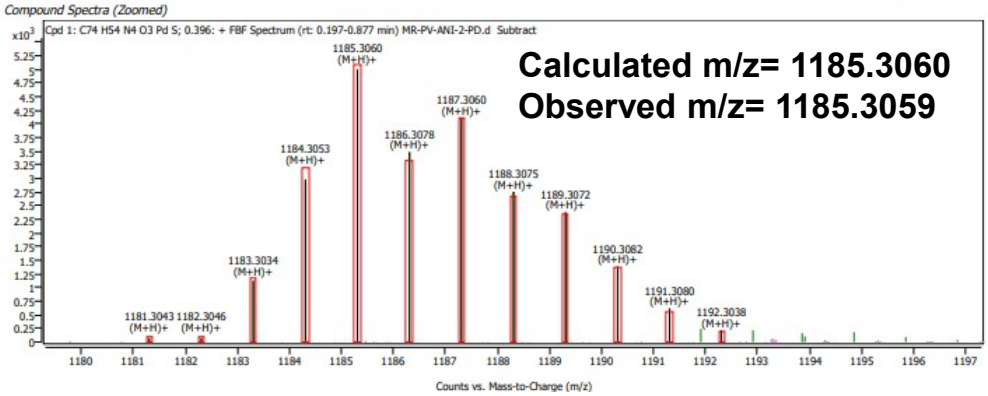
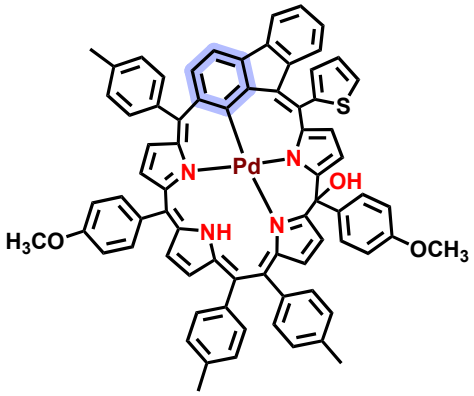


Figure S31. HR-mass spectrum of compound **5-Pd(II)**.



Compound 5-Pd(II)

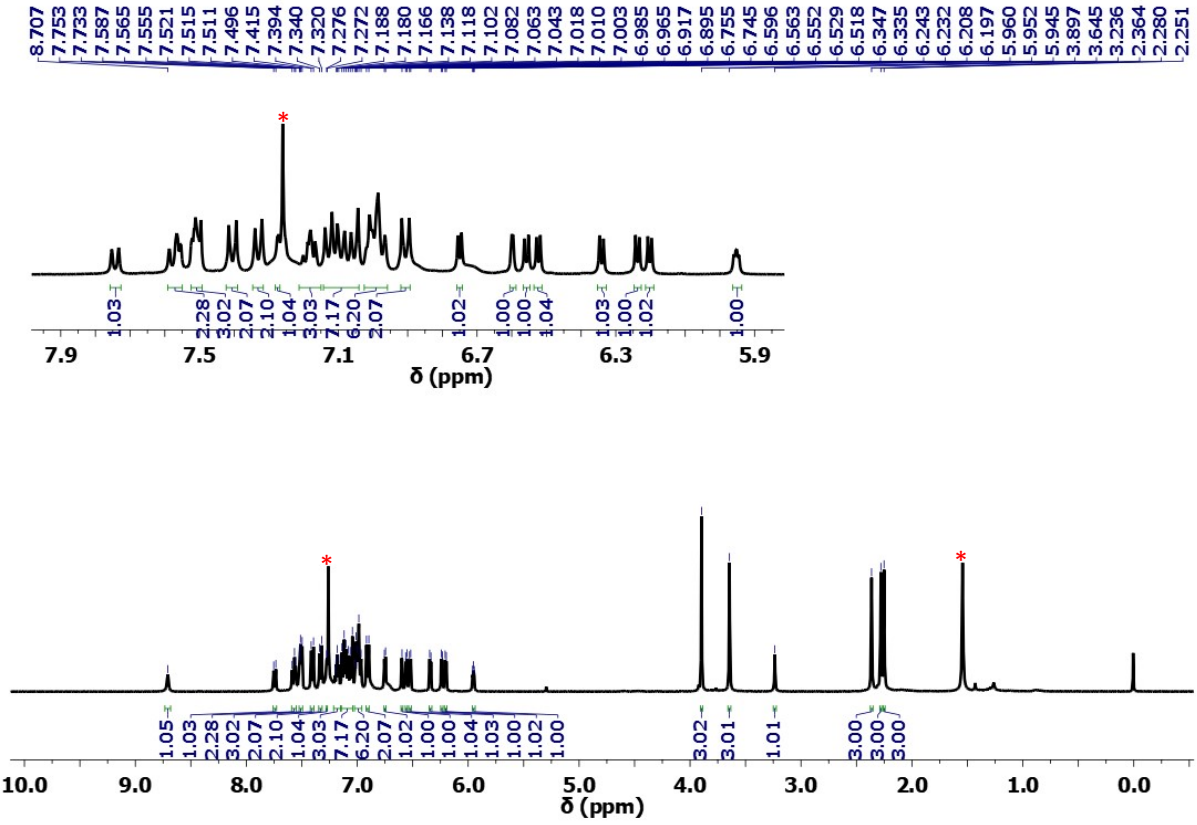


Figure S32. ^{1}H-NMR spectrum of the compound **5-Pd(II)** recorded in $CDCl_3$ on 400 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.

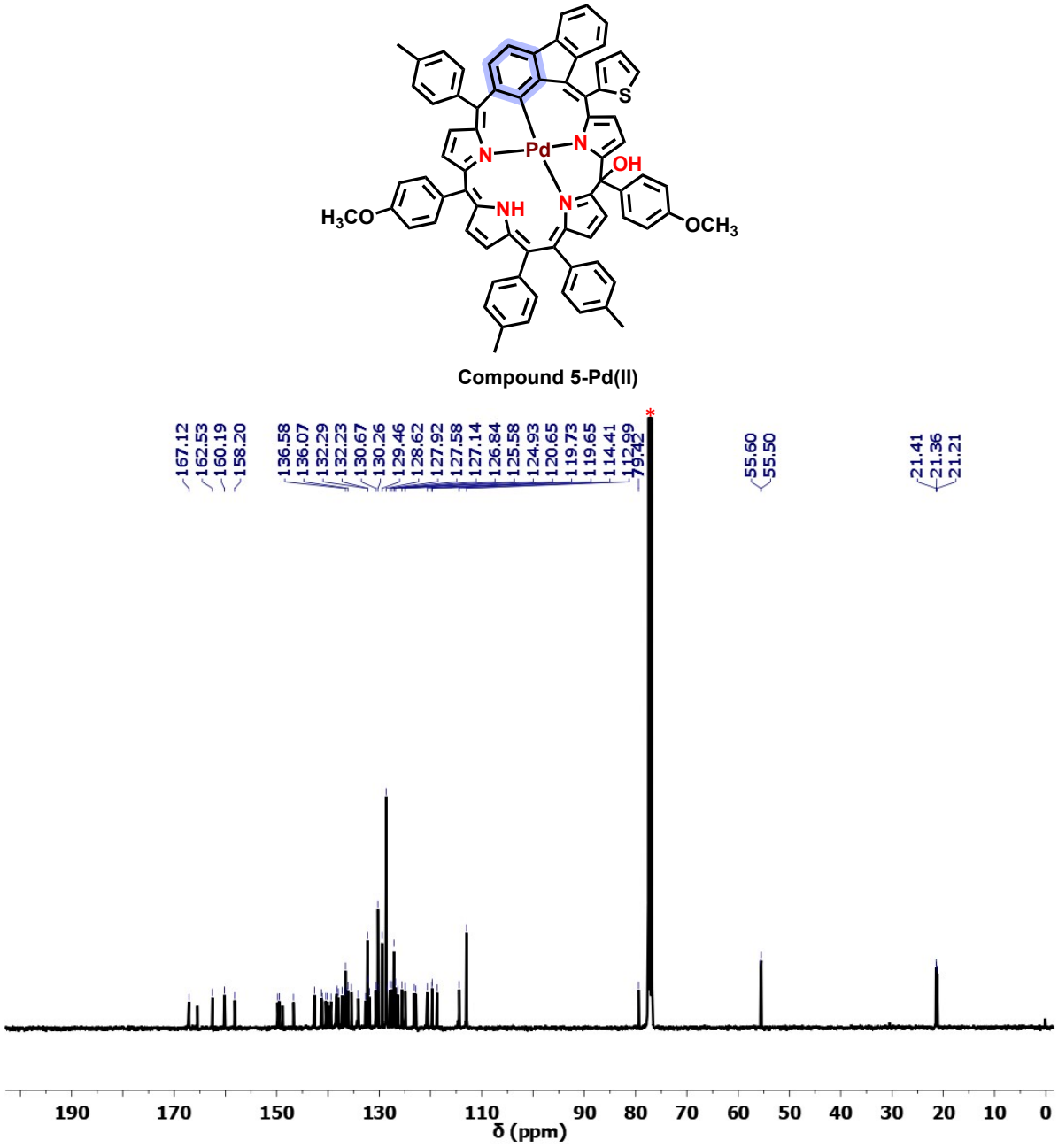


Figure S33. $^{13}C\{^{1}H\}$ NMR spectrum of the compound **5-Pd(II)** recorded in $CDCl_3$ on 101 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvent.

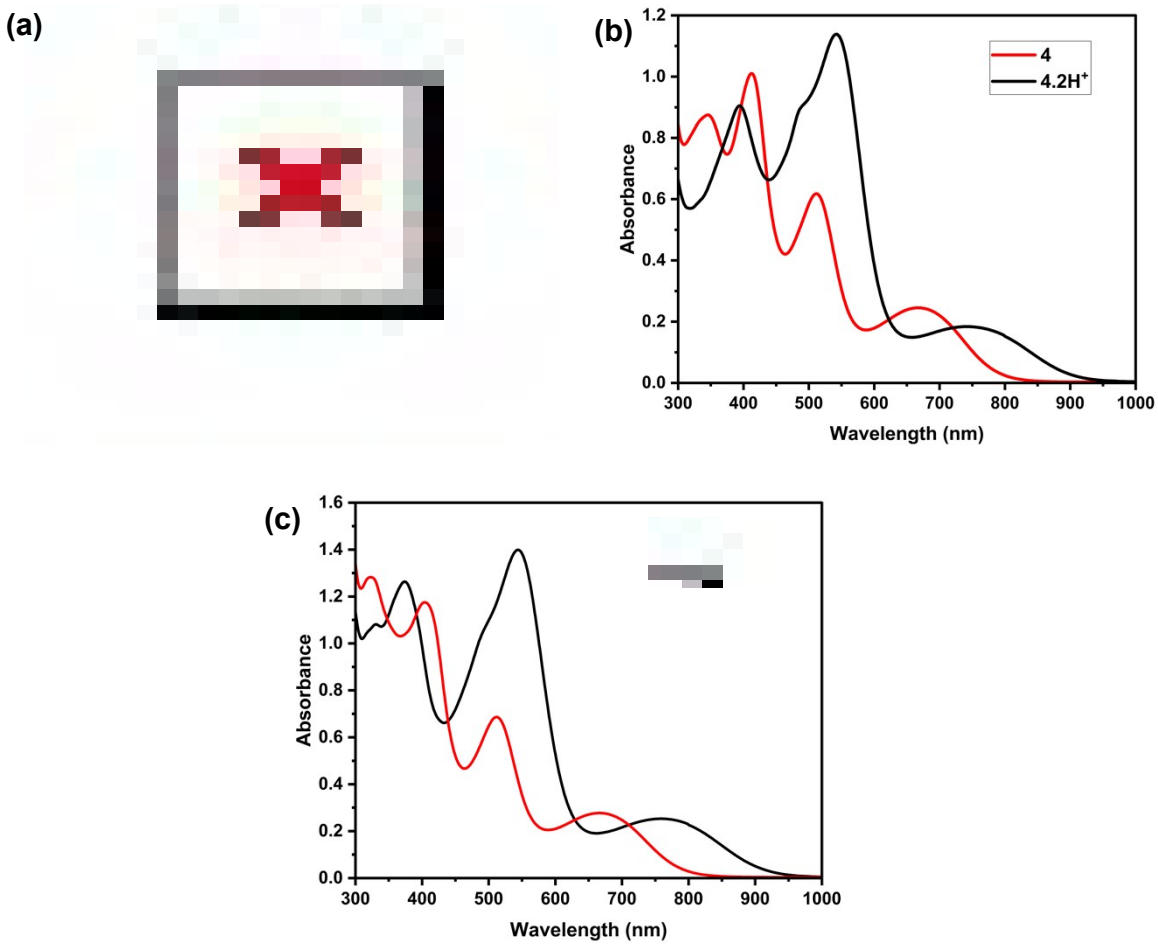


Figure S34. Comparison of absorption spectra of compounds **3-5** (9×10^{-5} M) free base (red line) and in presence of TFA (excess) (black line) recorded in chloroform at room temperature.

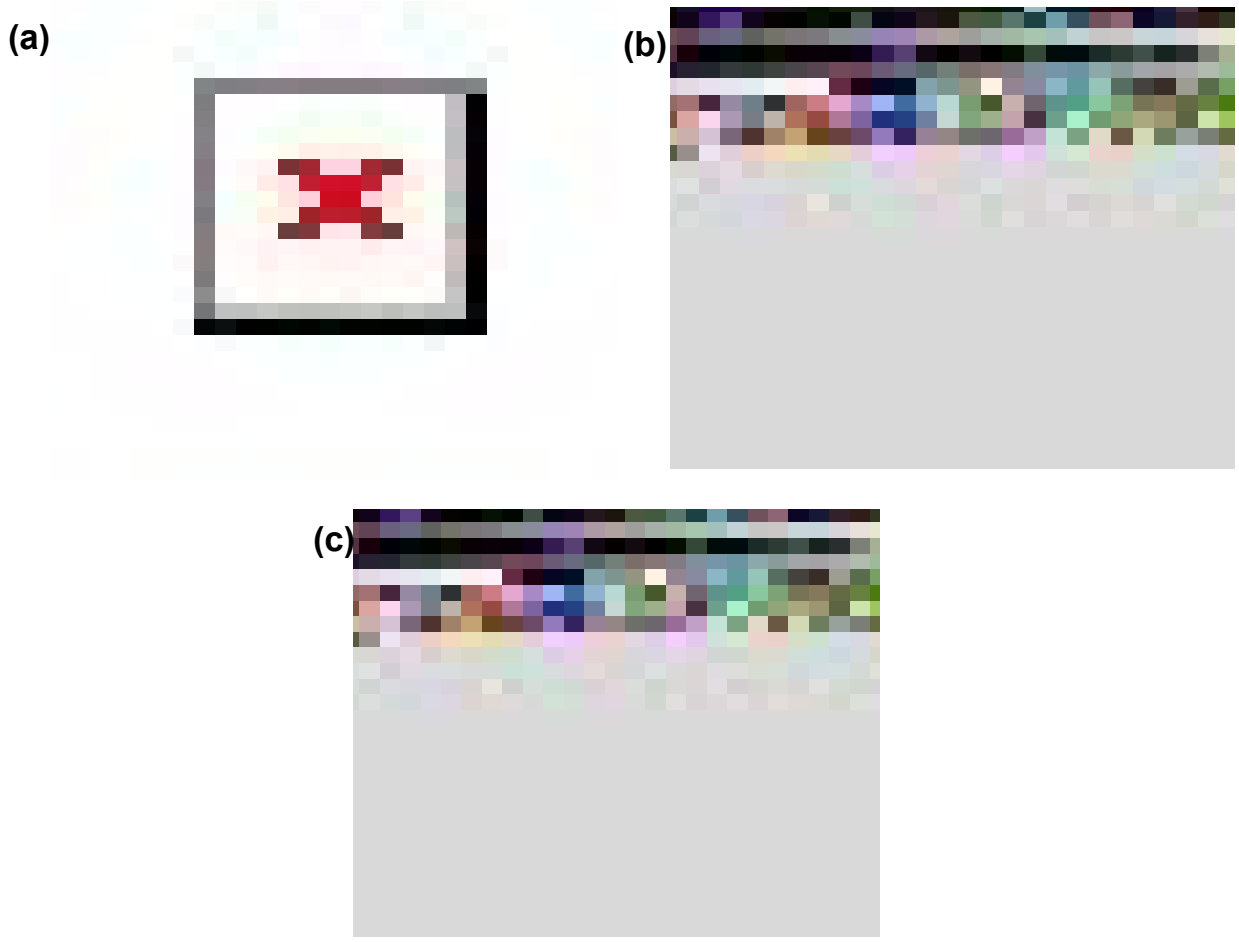


Figure S35. Absorption spectra of organopalladium complexes **3-Pd(II)**, **4-Pd(II)** and **5-Pd(II)** (3×10^{-6} M) organopalladium complex (blue line) recorded in chloroform at room temperature.

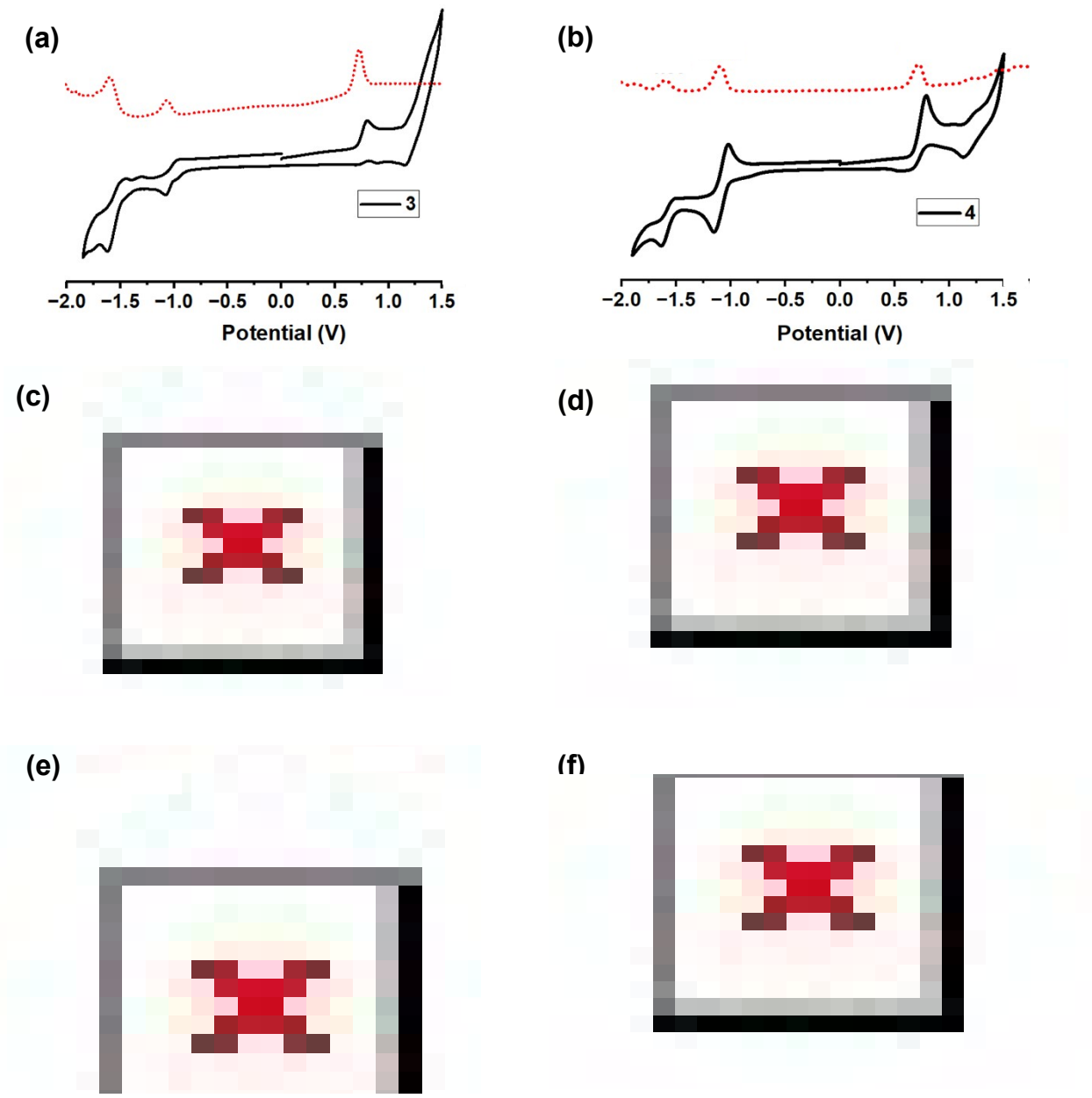


Figure S36. Cyclic voltammograms (black solid lines) and differential pulse voltammograms (red dotted lines) of free-base compounds **3–5** and their corresponding Pd(II) complexes **3-Pd(II)**, **4-Pd(II)** and **5-Pd(II)**, recorded in dry dichloromethane containing 0.1 M TBAP as the supporting electrolyte and a saturated calomel electrode (SCE) as the reference electrode at scan rates of 50 mV s^{-1}.

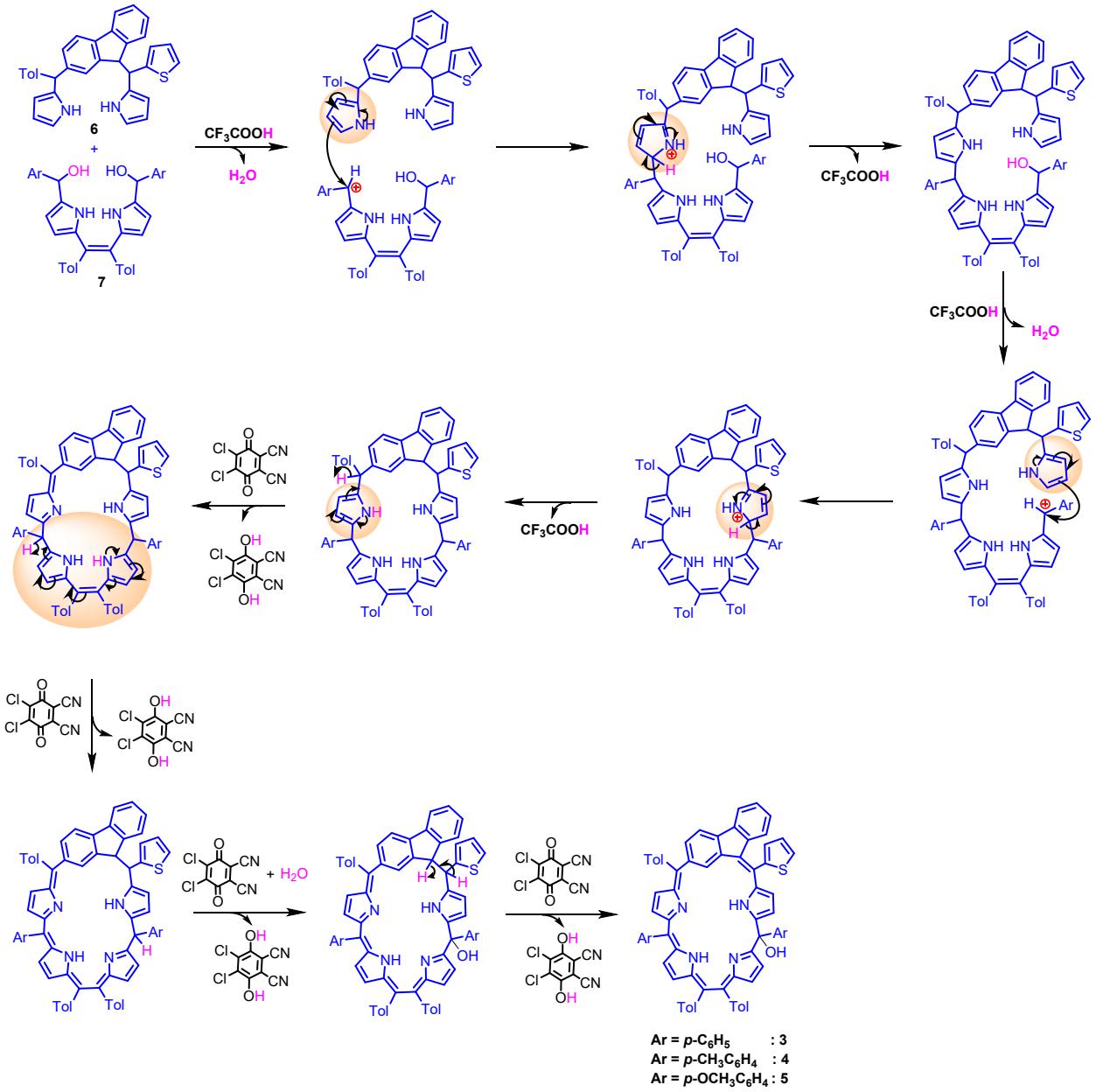


Figure S37. Probable mechanism for the formation of *meso*-fused calixbenzipentaphyrins **3-5**.

Note: All the different aryl groups are denoted as Ar in the molecular structures for simplicity.

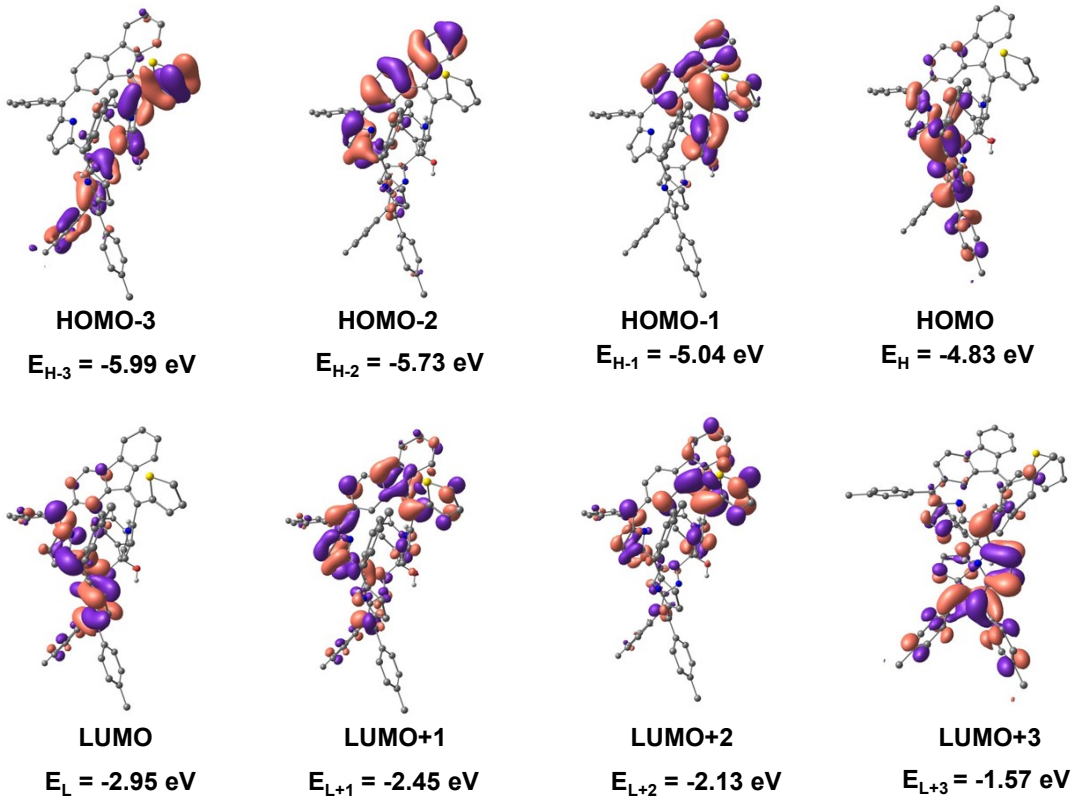


Figure S38. Selected Frontier Molecular Orbitals of macrocycle **4**.

Table S1. Selected TD-DFT calculated oscillator strengths and compositions of the major electronic transitions of **4**.

Wavelength (nm)	Oscillator Strength	Major contributions
811.3	0.3013	HOMO->LUMO (95%)
761.7	0.0819	H-1->LUMO (96%)
629.5	0.0964	HOMO->L+1 (93%)
578.1	0.1655	H-1->L+1 (91%)
542.4	0.0452	HOMO->L+2 (95%)
520.0	0.1015	H-2->LUMO (63%), H-1->L+2 (28%)
482.3	0.4429	H-2->LUMO (17%), H-1->L+2 (63%)
478.7	0.1552	H-3->LUMO (77%)
452.1	0.0284	H-5->LUMO (63%), H-4->LUMO (19%)
441.4	0.0387	H-5->LUMO (17%), H-4->LUMO (43%), HOMO->L+3 (30%)
438.0	0.2521	H-4->LUMO (11%), H-2->L+1 (69%)
423.0	0.1722	H-6->LUMO (22%), H-4->LUMO (12%), H-2->L+2 (12%), HOMO->L+3 (36%)

417.6	0.1351	H-7->LUMO (27%), H-6->LUMO (44%)
410.5	0.1499	H-8->LUMO (12%), H-7->LUMO (45%), H-6->LUMO (18%)
407.2	0.0312	H-9->LUMO (73%)
402.9	0.0166	H-1->L+3 (87%)
400.9	0.0641	H-8->LUMO (75%)
399.0	0.2808	H-3->L+1 (77%)
393.7	0.1459	H-10->LUMO (28%), H-2->L+2 (46%)
391.1	0.0786	H-11->LUMO (25%), H-10->LUMO (16%), H-2->L+2 (18%)
387.7	0.068	H-11->LUMO (19%), H-10->LUMO (31%)
374.5	0.0212	H-5->L+1 (59%), H-4->L+1 (22%)
370.9	0.0385	H-12->LUMO (40%), H-4->L+1 (37%)
368.7	0.0775	H-12->LUMO (37%), H-5->L+1 (17%), H-4->L+1 (27%)
363.3	0.0654	H-16->LUMO (13%), H-13->LUMO (15%), H-11->LUMO (18%), H-3->L+2 (24%)
362.8	0.0154	H-18->LUMO (21%), H-17->LUMO (10%), H-6->L+1 (13%), H-3->L+2 (16%)
360.6	0.0448	H-3->L+2 (41%)
356.5	0.0106	H-14->LUMO (58%)
355.5	0.0741	H-14->LUMO (19%), H-7->L+1 (31%), H-6->L+1 (35%)
353.3	0.0276	H-7->L+1 (39%), H-6->L+1 (25%)
350.6	0.0021	H-13->LUMO (49%)
348.4	0.0358	H-16->LUMO (19%), H-9->L+1 (52%)
345.9	0.01	H-16->LUMO (18%), H-15->LUMO (51%), H-9->L+1 (12%)
345.3	0.0029	H-8->L+1 (91%)
338.2	0.0249	H-10->L+1 (60%)
336.9	0.0054	H-18->LUMO (21%), H-17->LUMO (34%)
336.4	0.0028	H-17->LUMO (10%), H-11->L+1 (45%), HOMO->L+4 (20%)
335.3	0.0112	H-11->L+1 (12%), H-4->L+2 (38%), H-1->L+4 (12%)
333.1	0.0853	H-5->L+2 (20%), H-4->L+2 (37%), H-1->L+4 (18%)
332.5	0.0815	H-20->LUMO (16%), H-19->LUMO (29%), H-5->L+2 (19%), HOMO->L+4 (14%)
331.1	0.0234	H-19->LUMO (24%), H-5->L+2 (28%), HOMO->L+4 (13%)
329.4	0.0409	H-1->L+4 (24%), HOMO->L+4 (20%)
328.4	0.0192	H-21->LUMO (17%), H-20->LUMO (21%), H-1->L+4 (18%), HOMO->L+4 (12%)
325.9	0.0658	H-12->L+1 (17%), H-2->L+3 (52%)
323.8	0.0806	H-7->L+2 (38%), H-6->L+2 (15%), H-2->L+3 (27%)

323.5	0.0748	H-12->L+1 (47%), H-2->L+3 (11%)
321.3	0.0213	H-7->L+2 (11%), H-6->L+2 (56%)
320.3	0.0077	H-22->LUMO (12%), H-21->LUMO (28%), H-20->LUMO (19%), H-19->LUMO (18%)
318.4	0.0157	H-22->LUMO (19%), H-9->L+2 (21%), H-8->L+2 (13%)
316.4	0.0039	H-9->L+2 (43%), H-8->L+2 (11%)

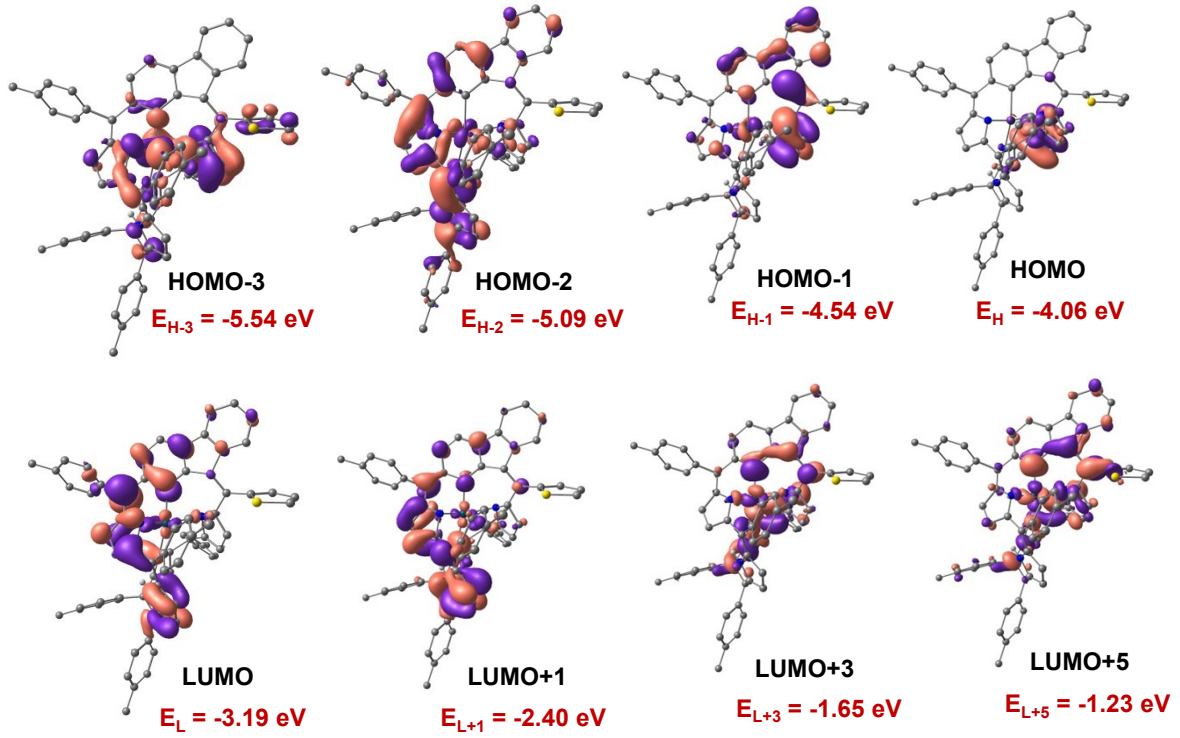


Figure S39. Selected Frontier molecular orbitals of complex **4-Pd(II)**.

Table S2. Selected TD-DFT calculated oscillator strengths and compositions of the major electronic transitions of **4-Pd(II)**.

Wavelength (nm)	Oscillator Strength	Major Contributions
892.7	0.0086	HOMO->L+2 (81%)
845.6	0.0879	H-2->LUMO (44%), H-1->L+1 (34%)
819.6	0.066	HOMO->L+2 (10%), HOMO->L+4 (73%)
778.6	0.1421	H-3->LUMO (30%), H-2->LUMO (15%), H-1->L+1 (40%)
722.4	0.2024	H-3->LUMO (56%), H-2->LUMO (20%), H-1->L+1 (13%)
698.7	0.0052	H-1->L+2 (24%), HOMO->L+3 (68%)
692.9	0.0022	H-1->L+2 (52%), HOMO->L+3 (29%)

610.7	0.0158	H-5->LUMO (10%), H-4->LUMO (54%), H-2->L+1 (16%)
604.4	0.0118	H-5->LUMO (67%), H-2->L+1 (10%)
583.7	0.071	H-2->L+1 (20%), HOMO->L+5 (47%)
571.8	0.03	H-4->LUMO (15%), H-2->L+1 (33%), HOMO->L+5 (24%)
555.0	0.0519	H-1->L+4 (77%)
537.5	0.0067	H-7->LUMO (25%), H-6->LUMO (48%)
533.5	0.0133	H-9->LUMO (10%), H-7->LUMO (10%), H-6->LUMO (13%), H-1->L+3 (42%)
528.4	0.0032	H-7->LUMO (30%), H-6->LUMO (12%), H-1->L+3 (20%)
513.7	0.0314	H-10->LUMO (10%), H-9->LUMO (15%), H-8->LUMO (32%)
509.0	0.1123	H-2->L+2 (51%)
502.9	0.0274	H-9->LUMO (22%), H-8->LUMO (38%), H-6->LUMO (10%), H-2->L+2 (11%)
499.2	0.0186	H-3->L+1 (50%), H-1->L+3 (16%)
480.6	0.0156	H-10->LUMO (51%), H-9->LUMO (17%)
474.3	0.0251	H-9->LUMO (11%), H-3->L+1 (16%), H-3->L+2 (11%), H-1->L+5 (26%)
462.2	0.015	H-11->LUMO (41%), HOMO->L+6 (26%)
460.9	0.0442	H-11->LUMO (22%), HOMO->L+6 (52%)
450.6	0.1522	H-3->L+2 (12%), H-2->L+3 (16%), H-1->L+5 (42%)
448.0	0.0328	H-5->L+1 (14%), H-3->L+2 (17%)
447.1	0.0046	HOMO->L+6 (12%), HOMO->L+7 (76%)
444.0	0.0077	H-12->LUMO (61%)
433.6	0.1287	H-4->L+1 (37%)
430.3	0.0426	H-5->L+1 (12%), H-4->L+1 (10%), H-2->L+3 (47%)
427.1	0.0185	H-14->LUMO (14%), H-2->L+4 (58%)
423.8	0.0518	H-14->LUMO (35%), H-2->L+4 (22%)
418.1	0.0351	H-13->LUMO (63%)
416.0	0.0054	H-6->L+1 (17%)
412.2	0.0114	HOMO->L+8 (30%), HOMO->L+9 (60%)
410.4	0.0055	HOMO->L+8 (50%), HOMO->L+9 (36%)
407.6	0.0045	H-7->L+1 (11%), HOMO->L+8 (16%), HOMO->L+10 (47%)
406.2	0.0507	H-7->L+1 (21%), HOMO->L+10 (31%)
402.6	0.0666	H-5->L+1 (21%), H-5->L+2 (34%)
400.1	0.0749	H-15->LUMO (21%), H-6->L+1 (32%)
398.8	0.0184	H-15->LUMO (59%), H-6->L+1 (11%)
393.6	0.049	H-4->L+2 (27%), H-3->L+4 (36%)
390.2	0.0259	H-18->LUMO (14%), H-17->LUMO (12%), H-16->LUMO (54%)
387.0	0.0073	H-8->L+1 (25%), H-6->L+1 (13%), H-3->L+4 (22%)
385.9	0.032	H-9->L+1 (16%), H-7->L+1 (12%), H-4->L+2 (20%), H-3->L+4 (17%)
385.4	0.036	H-18->LUMO (52%)
381.9	0.0029	HOMO->L+11 (22%), HOMO->L+12 (47%)

380.1	0.0077	H-3->L+3 (36%), H-2->L+5 (17%)
378.5	0.0042	HOMO->L+11 (63%), HOMO->L+12 (14%)
378.3	0.0048	H-8->L+1 (13%), H-7->L+1 (11%), H-3->L+3 (23%)
377.8	0.0008	H-20->LUMO (11%), H-19->LUMO (57%)
377.5	0.0094	H-1->L+6 (49%)
376.3	0.0098	H-17->LUMO (55%), H-16->LUMO (19%)
371.3	0.0061	H-3->L+3 (20%), H-2->L+5 (43%)
370.3	0.0069	H-1->L+7 (14%), H-1->L+9 (59%), H-1->L+10 (11%)
369.7	0.007	H-1->L+6 (17%), H-1->L+7 (64%), H-1->L+9 (13%)
368.7	0.0088	H-9->L+1 (20%), H-8->L+1 (10%), H-7->L+2 (12%)
367.7	0.0029	HOMO->L+12 (20%), HOMO->L+13 (13%), HOMO->L+14 (30%), HOMO->L+15 (17%), HOMO->L+16 (11%)
367.3	0.0014	HOMO->L+13 (81%)
365.6	0.016	H-22->LUMO (47%)
363.9	0.015	H-10->L+1 (13%), H-7->L+2 (14%)
361.7	0.0172	H-20->LUMO (35%), H-19->LUMO (14%)
360.3	0.0293	H-10->L+1 (10%), H-6->L+2 (13%), H-1->L+10 (45%)
360.1	0.0227	H-6->L+2 (38%), H-1->L+10 (25%)
357.4	0.011	H-11->L+1 (39%), H-8->L+2 (14%)
356.0	0.0031	HOMO->L+14 (51%), HOMO->L+15 (31%), HOMO->L+16 (10%)
352.3	0.0073	H-21->LUMO (73%), H-20->LUMO (19%)
351.3	0.0058	H-10->L+1 (15%), H-8->L+2 (13%), H-3->L+5 (13%)
349.4	0.0174	H-5->L+4 (16%), H-4->L+3 (32%)
347.9	0.0179	H-6->L+4 (21%), H-5->L+4 (14%), H-4->L+4 (18%)
346.0	0.0058	H-23->LUMO (16%), H-11->L+1 (12%), H-3->L+5 (14%)
345.5	0.0264	H-6->L+4 (11%), H-5->L+4 (10%), H-4->L+4 (10%)
344.7	0.0068	H-1->L+8 (78%)
343.8	0.0075	H-23->LUMO (33%), H-5->L+4 (10%), H-4->L+4 (16%)
342.9	0.0504	H-10->L+2 (10%), H-4->L+4 (25%)
342.1	0.0595	H-6->L+4 (13%), H-4->L+3 (14%), H-3->L+5 (26%)
340.5	0.0163	HOMO->L+15 (24%), HOMO->L+16 (52%)
338.8	0.0067	H-12->L+1 (51%)
337.1	0.0154	H-6->L+3 (12%), H-5->L+3 (18%), H-4->L+3 (10%)
335.2	0.0125	H-11->L+1 (13%), H-11->L+2 (18%), H-9->L+2 (13%)
333.3	0.0004	H-13->L+1 (56%), H-5->L+3 (10%)
331.5	0.0363	H-2->L+6 (29%), H-2->L+7 (15%)
331.1	0.0375	H-7->L+4 (17%), H-5->L+3 (10%), H-2->L+6 (15%), H-2->L+7 (15%)
330.0	0.0102	H-1->L+11 (90%)
328.1	0.0043	H-2->L+6 (29%), H-2->L+7 (32%)
327.4	0.003	H-6->L+3 (16%), H-5->L+3 (15%), H-2->L+7 (10%)
326.7	0.0105	H-24->LUMO (37%), H-1->L+12 (20%), H-1->L+14 (10%)
326.6	0.0108	H-24->LUMO (17%), H-14->L+1 (25%)
326.0	0.004	H-24->LUMO (22%), H-1->L+12 (30%), H-1->L+14 (15%)

325.6	0.0277	H-26->LUMO (10%), H-25->LUMO (18%), H-14->L+1 (35%)
324.2	0.0322	H-25->LUMO (12%), H-9->L+4 (11%), H-8->L+4 (11%), H-7->L+4 (10%)
322.0	0.008	H-1->L+13 (11%), HOMO->L+17 (67%)
321.6	0.0019	H-15->L+1 (17%), H-1->L+13 (68%)
321.2	0.0324	H-15->L+1 (53%), H-1->L+13 (14%), HOMO->L+17 (10%)
319.0	0.0014	H-27->LUMO (56%), H-26->LUMO (10%), H-16->L+1 (11%)
318.1	0.0068	H-16->L+1 (29%), H-6->L+3 (16%), H-1->L+14 (12%)
317.7	0.0155	H-1->L+12 (18%), H-1->L+14 (42%), H-1->L+15 (11%)
317.0	0.0133	H-7->L+3 (16%), H-6->L+3 (10%)

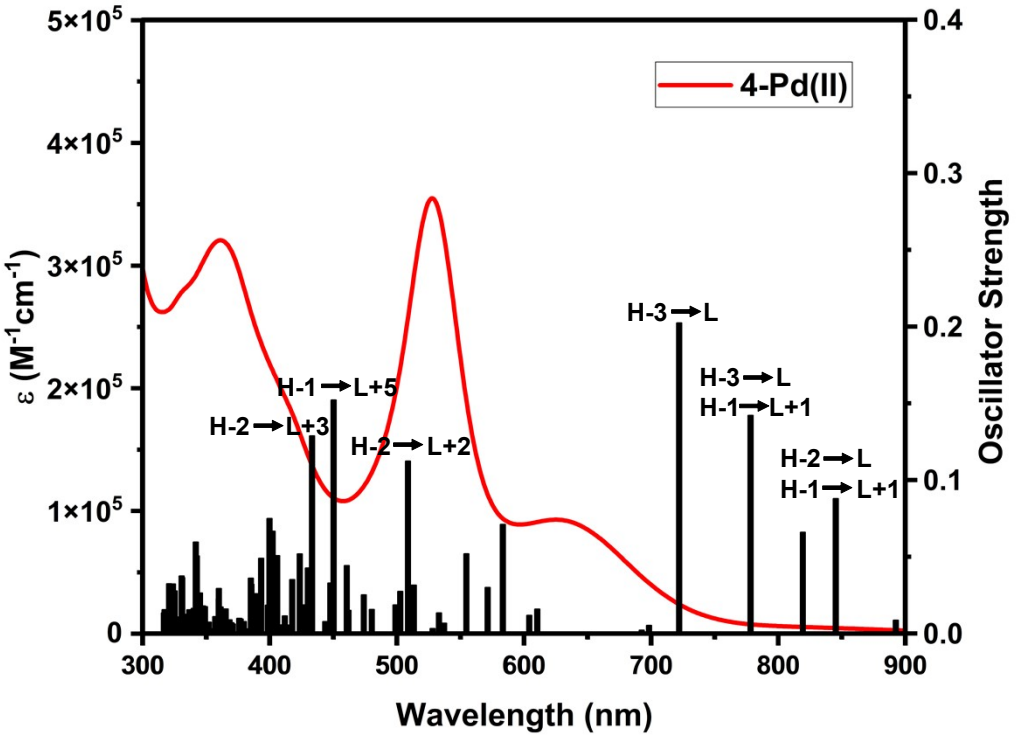


Figure S40. Calculated excitations (black vertical lines) and experimental absorption spectra (red line) for macrocycle **4-Pd(II)** (ε in M^{-1} cm^{-1}).

Table S3. S_0 optimized geometry of the compound **4** at B3LYP/def2TZVP level of theory.

Charge = 0

Sum of imaginary frequencies = 0

Total Energy (hartree) = -3547.161559

Atom	X	Y	Z	Atom	X	Y	Z
C	4.2466	2.8391	1.2623	H	0.8785	5.8518	4.9802
C	3.0678	2.0463	1.2267	H	1.1901	3.4725	4.3609
C	3.0851	0.8462	0.4812	H	1.2116	8.2123	4.4584
C	4.24	0.4316	-0.1689	H	0.1056	8.3838	3.088
C	5.4234	1.2143	-0.0744	H	1.8281	8.7057	2.8653
C	5.4126	2.4254	0.6264	H	-0.8773	2.9491	2.8549
C	5.981	-0.7599	-1.1819	H	-2.2734	0.6575	2.9674
C	6.4935	0.4949	-0.7416	H	-1.8056	-4.3005	1.499
C	6.8052	-1.6115	-1.931	H	-4.0713	-3.9857	0.122
C	8.1229	-1.2344	-2.1848	H	-2.5086	-0.1808	0.9809
C	8.633	-0.011	-1.7149	H	-3.6975	3.0151	-0.1228
C	7.8172	0.8635	-0.9992	H	-1.1807	3.2108	-1.103
C	1.8602	2.4596	1.9475	H	2.0945	-1.7957	1.8279
C	1.6925	3.8852	2.3106	H	3.6434	-3.6114	2.4449
C	0.8413	1.5794	2.2974	H	0.4133	-5.7555	4.2847
C	1.8887	4.9088	1.3663	H	-1.137	-3.9335	3.6723
C	1.7019	6.2431	1.713	H	2.5718	-6.8038	4.1634
C	1.3305	6.6079	3.0158	H	3.6844	-6.2485	2.8937
C	1.1502	5.59	3.9609	H	3.8185	-5.5974	4.5285
C	1.3225	4.2507	3.6166	H	-6.0599	-3.1566	1.134
C	1.1122	8.0555	3.3796	H	-8.0675	-4.4062	0.4275
C	-0.5177	1.9453	2.6811	H	-8.2685	-2.0595	-3.1598
C	-1.2305	0.7857	2.7091	H	-6.2346	-0.8351	-2.4719
C	-0.2853	-0.2806	2.3699	H	-6.6544	-0.1388	1.3869
N	0.9305	0.1991	2.1703	H	-8.6604	1.2373	1.8257
C	-0.6048	-1.7027	2.2338	H	-7.548	3.8786	-1.3707
C	-1.7892	-2.0639	1.6185	H	-5.5418	2.4945	-1.8137
C	0.3526	-2.7453	2.6646	H	-9.6248	-4.1794	-2.9132
C	-1.5445	1.0624	-1.6929	H	-9.631	-5.0426	-1.3597
C	-2.2983	-3.3711	1.2578	H	-10.471	-3.4943	-1.5221
C	-3.4552	-3.2116	0.5541	H	-9.6849	4.177	-0.2897
C	-3.7147	-1.795	0.4032	H	-10.338	2.8883	0.7468
N	-2.7023	-1.164	1.0845	H	-9.3005	4.1385	1.4383
N	-2.537	0.2008	-1.5418	C	0.4454	-0.4475	-1.8076
C	-3.5508	0.8999	-0.8904	C	-0.0061	-1.5989	-1.1604
C	-3.1243	2.2618	-0.6459	C	1.123	-2.3624	-0.8143

C	-1.8413	2.3557	-1.1247	C	2.2607	-1.6552	-1.2249
C	-4.7763	-1.1505	-0.2414	N	1.8048	-0.5124	-1.8487
C	-4.7328	0.2777	-0.4693	H	2.4077	0.2045	-2.2239
C	1.7268	-2.6611	2.3602	H	-1.0443	-1.827	-0.9786
C	2.5943	-3.688	2.7169	H	1.144	-3.2884	-0.2603
C	2.1422	-4.8269	3.3997	C	-0.3448	0.6347	-2.5324
C	0.7855	-4.8949	3.7344	O	-0.8456	0.0681	-3.7558
C	-0.0935	-3.8711	3.3802	H	-1.6417	-0.4196	-3.4881
C	3.1018	-5.9317	3.7672	C	0.5579	1.8148	-2.8805
C	-5.9806	-1.9141	-0.6265	C	1.3176	2.43	-1.8737
C	-5.938	1.0913	-0.2304	C	0.698	2.2654	-4.1945
C	-6.5253	-2.9296	0.1801	C	2.2308	3.434	-2.1859
C	-7.6659	-3.6261	-0.215	H	1.2206	2.0923	-0.8486
C	-8.3181	-3.326	-1.4177	C	1.591	3.2975	-4.4956
C	-7.7835	-2.3059	-2.2184	H	0.1184	1.7927	-4.9779
C	-6.6397	-1.6143	-1.8336	C	2.3793	3.8901	-3.5035
C	-6.8478	0.7446	0.7879	H	2.8639	3.843	-1.4036
C	-7.9738	1.52	1.0316	H	1.6928	3.633	-5.5248
C	-8.2427	2.667	0.2666	C	3.3566	4.9927	-3.8309
C	-7.3462	3.0064	-0.7544	H	3.5892	5.0114	-4.9004
C	-6.2132	2.2344	-1.0025	H	2.9472	5.9755	-3.5622
C	-9.5756	-4.0535	-1.8261	H	4.2926	4.8675	-3.2749
C	-9.4588	3.5125	0.5501	C	5.0289	-5.545	-0.503
H	4.2465	3.7619	1.8306	C	4.0279	-5.6122	-1.4382
H	2.1871	0.2534	0.4471	C	3.4811	-4.3368	-1.7455
H	6.3156	3.0246	0.7041	C	4.0796	-3.2963	-1.0615
H	6.4239	-2.5514	-2.3136	S	5.3247	-3.9186	0.0105
H	8.7652	-1.8955	-2.7596	H	5.6144	-6.3576	-0.0934
H	9.6641	0.258	-1.9247	H	3.6951	-6.5392	-1.8914
H	8.1975	1.8224	-0.6575	H	2.674	-4.1668	-2.4473
H	2.16	4.6467	0.3509	C	3.6744	-1.8949	-1.0482
H	1.8446	7.0172	0.9632	C	4.5555	-0.8388	-0.8458

Table S4. S_0 optimized geometry of the compound **4-Pd(II)** at B3LYP/def2TZVP + SDD level of theory.

Charge = 0

Sum of imaginary frequencies = 0

Total Energy (hartree) = -3673.085665

Atom	X	Y	Z	Atom	X	Y	Z
C	-3.4816	3.75541	0.35225	H	-2.3341	5.19829	-2.174

C	-2.4404	2.85417	0.00151	H	-0.7088	9.59469	-1.4626
C	-2.7211	1.46942	-0.0039	H	0.99311	9.14214	-1.6327
C	-3.996	1.00303	0.28847	H	0.33484	9.47627	-0.028
C	-5.0357	1.92705	0.58384	H	1.76694	3.71259	-0.7673
C	-4.7655	3.29917	0.63259	H	2.82919	1.5941	-2.031
C	-6.0018	-0.1908	0.4567	H	1.4849	-3.2213	-3.4315
C	-6.2723	1.18117	0.73184	H	3.57902	-4.0915	-2.0222
C	-7.0262	-1.1354	0.61221	H	2.6898	-0.1755	-0.7846
C	-8.2991	-0.705	0.98315	H	2.50432	-1.1111	3.7633
C	-8.5679	0.65543	1.21659	H	4.16836	-1.3199	1.63702
C	-7.5528	1.60348	1.10129	H	-1.9497	-0.2295	-2.5125
C	-1.105	3.34624	-0.3497	H	-3.6481	-1.1401	-4.0497
C	-0.9118	4.82061	-0.6053	H	-0.5451	-2.5865	-6.6372
C	-0.1842	2.60063	-1.0787	H	1.156	-1.6685	-5.1005
C	0.06337	5.4103	0.21888	H	-2.8275	-3.1226	-7.1625
C	0.38533	6.7575	0.08946	H	-4.0028	-3.1057	-5.8295
C	-0.2636	7.5702	-0.8523	H	-3.8352	-1.6929	-6.8738
C	-1.246	6.98712	-1.6628	H	5.55559	-1.5326	-2.4563
C	-1.5637	5.63518	-1.5474	H	7.85316	-2.2033	-3.0585
C	0.10358	9.0259	-0.9993	H	8.53957	-3.4857	0.97874
C	1.25037	2.85082	-1.1644	H	6.22558	-2.8516	1.57278
C	1.79042	1.76269	-1.779	H	5.00489	0.55738	2.25755
C	0.6691	0.87268	-2.0887	H	6.85131	2.20072	2.2818
N	-0.4824	1.39764	-1.7059	H	6.37321	2.80079	-1.9422
C	0.76516	-0.4462	-2.7167	H	4.51842	1.15881	-1.9635
C	1.79914	-1.2867	-2.3474	H	10.1243	-4.1364	-0.8811
C	-0.2671	-0.9169	-3.6666	H	9.89092	-3.464	-2.5096
C	2.44682	-0.3444	0.55039	H	10.4774	-2.4345	-1.1963
C	2.069	-2.6607	-2.7179	H	7.89849	4.21598	-0.7196
C	3.13807	-3.1064	-1.9984	H	7.83054	4.26062	1.05653
C	3.57325	-2.0482	-1.1108	H	8.86018	3.08106	0.24079
N	2.75466	-0.9802	-1.3873	C	-1.0042	-1.677	1.68913
N	1.23062	0.05608	0.88308	C	-1.008	-2.8999	1.01623
C	1.10787	-0.1959	2.24773	C	-2.102	-2.8954	0.13259
C	2.33438	-0.7809	2.74759	C	-2.7417	-1.6544	0.24888
C	3.1707	-0.9052	1.66625	N	-2.0613	-0.9555	1.22451
C	4.33651	-1.7804	-0.0036	H	-0.2845	-3.6837	1.1749
C	3.75262	-0.4704	0.18424	H	-2.3752	-3.6615	-0.5769
C	-1.643	-0.7471	-3.4099	C	-0.1986	-0.8382	2.67658
C	-2.5942	-1.2597	-4.2857	O	-1.2984	-1.0632	3.70899
C	-2.2241	-1.944	-5.4529	H	-1.7826	-1.1411	4.54731

C	-0.8592	-2.0814	-5.7271	C	0.29482	-1.1922	4.0772
C	0.10318	-1.5723	-4.8547	C	0.3123	-0.0145	4.84011
C	-3.2753	-2.4989	-6.3821	C	0.4847	-2.4133	4.7267
C	5.70753	-2.1615	-0.3994	C	0.46382	-0.0663	6.22347
C	4.64238	0.71973	0.13994	C	0.67118	-2.4552	6.1112
C	6.19714	-1.9838	-1.706	H	0.46808	-3.3271	4.1455
C	7.49875	-2.3521	-2.0414	C	0.65224	-1.289	6.88345
C	8.36775	-2.8935	-1.0855	H	0.39729	0.85001	6.80331
C	7.88555	-3.0611	0.22093	H	0.81187	-3.4147	6.60282
C	6.58422	-2.7043	0.55871	C	0.83605	-1.3352	8.38079
C	5.30964	1.04459	1.33756	H	0.64971	-2.3404	8.77212
C	6.34645	1.96833	1.34753	H	1.8595	-1.0533	8.66164
C	6.7553	2.61079	0.16717	H	0.15722	-0.6367	8.88292
C	6.08508	2.29874	-1.0222	C	-5.5313	-4.9651	-1.3495
C	5.04578	1.37095	-1.0398	C	-5.8154	-4.989	-0.0079
C	9.78932	-3.2554	-1.4395	C	-5.3775	-3.8156	0.66399
C	7.89383	3.5996	0.18487	C	-4.78	-2.8889	-0.1685
H	-3.2793	4.82015	0.3601	S	-4.7309	-3.5022	-1.8142
H	-5.5578	4.00876	0.85431	H	-5.7544	-5.7201	-2.0919
H	-6.8328	-2.1898	0.45074	H	-6.3203	-5.8144	0.48111
H	-9.0958	-1.4344	1.09806	H	-5.4912	-3.6366	1.72605
H	-9.569	0.96458	1.50247	C	-4.1119	-1.6509	0.21792
H	-7.7478	2.65249	1.3075	C	-4.5707	-0.3494	0.17777
H	0.58708	4.79605	0.94119	Pd	-0.8469	0.47813	0.0787
H	1.15285	7.18925	0.72684	H	0.20814	0.933	4.35394
H	-1.7725	7.60263	-2.3876				