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Electronic Supplementary Information (ESI)

Isosmaragdyrin with an N_3C_2 core: Stabilization of Rh(I) and Organo-Pt(II) complexes

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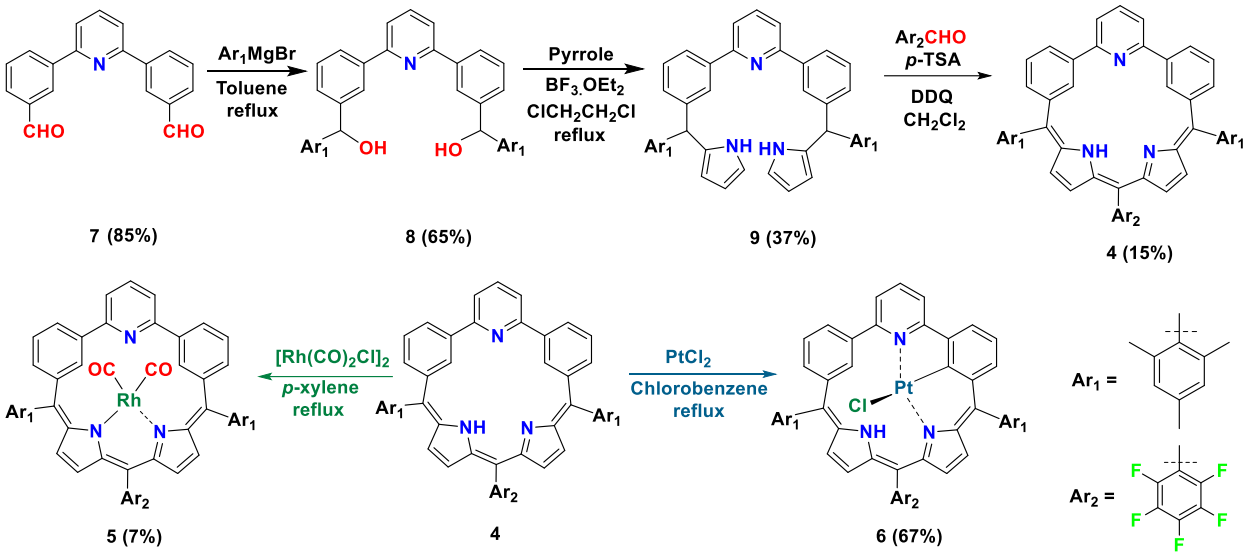
Table of Contents:

1. General Information:

The reagents and materials for the synthesis were used as obtained from Sigma Aldrich chemical suppliers. All solvents were purified and dried by standard methods prior to use. The NMR solvents were used as received and the spectra were recorded in Bruker 300 MHz, 400 MHz and 700 MHz spectrometer with TMS as an internal standard. The HR-ESI mass spectra were recorded in Bruker, micro-TOF-QII mass spectrometer. The Electronic absorption spectra were recorded in Jasco V-730 UV-Visible spectrophotometer. The X-ray quality crystals for the compounds were grown by slow diffusion of *n*-pentane over CH_2Cl_2 solution. Single-crystal X-ray diffraction data of **4**, **5** and **6** were collected in a Rigaku Oxford diffractometer. The crystal has been deposited in the Cambridge Crystallographic Data Centre with reference no. **CCDC 1957037 (4)**, **CCDC 1957039 (5)** and **CCDC 1957046 (6)**. Electrochemical studies of **4**, **5** and **6** were carried out on a CHI1120A instrument in CH_2Cl_2 with 0.1 M nBu$_4$NPF$_6$. Potentials were determined vs ferrocene/ferrocenium ion using a three-electrode system, which consisted of a platinum disk as the working electrode, a platinum wire as the counter electrode, and Ag/AgCl as the reference electrode.

2. Synthesis and Characterization:

2a. Synthetic Schemes



2b. Synthetic procedure and spectral characterization:

Synthesis of 7: 2,6-dibromopyridine (3 gm, 12.6 mmol) and 3-formylphenylboronic acid (4.7 gm, 31.6 mmol) was dissolved in 3:1 (V/V) THF and H_2O solvents mixture under nitrogen atmosphere. K_2CO_3 (8.7 gm, 63 mmol) was immediately added to the reaction mixture and purged with nitrogen gas for about 15 minutes. $Pd(Ph_3P)_4$ (1.16 gm, 1 mmol) was added under nitrogen atmosphere. The reaction was kept for 8 hours and then the work up was performed, dried over sodium sulphate and compound was purified by column chromatography using silica gel (100-200 mesh) in Hexane / EtOAc (70:30) mixture to afford white crystalline solid **7** in 85% Yield. ^{1}H NMR (700 MHz, $CDCl_3$, 298K): δ = 10.15 (s, 2H), 8.62 (s, 2H), 8.48 (d, *J* = 7.7 Hz, 2H), 7.97 (d, *J* = 7.5 Hz, 2H), 7.92 (t, *J* = 7.8 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 2H), 7.70 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (176 MHz, $CDCl_3$): δ = 192.43, 155.80, 140.24, 138.22, 137.01, 133.06, 130.43, 129.69, 128.24, 119.60. HR-MS (ESI-MS): m/z calculated for $C_{19}H_{13}NO_2$ = 287.0946; found = 288.1048 (M+1).

Synthesis of 8: The compound **7** (1.5 gm, 5.2 mmol) was dissolved in toluene under nitrogen atmosphere. Freshly prepared solution of mesitylmagnesium bromide was added dropwise in ice bath condition. Then the reaction was refluxed overnight. The reaction mixture was quenched with 2N HCl and work up was performed, dried over sodium sulphate and purified by column chromatography using silica gel (100-200 mesh) in Hexane / EtOAc (70:30) to afford **8** in 65% yield. ^{1}H NMR (700 MHz, $CDCl_3$, 298K): δ = 8.13 (s, 2H), 8.02 (d, *J* = 7.6 Hz, 2H), 7.76 (t, *J* = 7.7 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 2H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.23 (t, *J* = 6.5 Hz, 2H), 6.88 (s, 4H), 6.41 (s, 2H), 2.38 (s, 2H), 2.29 (s, 18H). ^{13}C NMR (176 MHz, $CDCl_3$): δ = 156.84, 143.63, 139.40, 137.42, 137.36, 137.10, 136.43, 130.10, 128.57, 126.93, 126.19, 125.39, 124.15, 118.77, 71.13, 20.92, 20.71. HR-MS (ESI-MS): m/z calculated for $C_{37}H_{37}NO_2$ = 527.2824; found = 528.2903 (M+1).

Synthesis of 9: The compound **8** (0.500gm, 0.90 mmol) was dissolved in 1,2-dichloroethane under nitrogen atmosphere. Pyrrole (6.2 ml, 90 mmol) was added to the solution and allowed to stir for 10 minutes. Then $BF_3.OEt_2$ (0.702ml, 5.68 mmol) was slowly added and reaction mixture was allowed to reflux for 8 hours. Further workup was performed using CH_2Cl_2 and water, dried over sodium sulphate and purified by column chromatography using silica gel (100-200 mesh) in Hexane / EtOAc (90:10) to afford **9** in 37% yield. ^{1}H NMR (700 MHz, $CDCl_3$, 298K): δ = 8.01 (d, *J* = 7.7 Hz, 2H), 7.98 (s, 2H), 7.86 (s, 2H), 7.73 (t, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 2H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.23 (d, *J* = 7.6 Hz, 2H), 6.89 (s, 4H), 6.69 (s, 2H), 6.17 (d, *J* = 4.6 Hz, 2H), 6.02 (s, 2H), 5.90 (s, 2H), 2.30 (s, 6H), 2.09 (s, 12H). ^{13}C NMR (176 MHz, $CDCl_3$): δ =156.78, 141.67, 139.55, 137.79, 136.41, 135.76, 132.98, 130.39, 129.39, 128.83, 127.44, 125.27, 118.71, 116.46, 108.49, 107.51, 44.88, 21.26, 20.92. HR-MS (ESI-MS): m/z calculated for $C_{45}H_{43}N_3$ = 625.3457; found = 626.3521 (M+1).

Synthesis of 4: The compound **9** (0.150 gm, 0.24 mmol) was mixed in 120 ml CH_2Cl_2 under nitrogen atmosphere covered with aluminum foil. Pentafluorobenzaldehyde (0.061 gm, 0.311 mmol) was added in the reaction mixture and allowed to stir. After 10 minutes, *p*-TSA (0.020 gm, 0.119 mmol) was added under same condition and allowed to stir for about 6 hours. Then DDQ (0.163 gm, 0.718 mmol) was added and reaction was continued for another 2 hours in absence of nitrogen atmosphere. The crude product was passed through basic alumina and purified by using silica gel column (100-200 mesh). The purple color band was eluted with CH_2Cl_2 / Hexane (60:40) and identified as **4** in 15% yield. ^{1}H NMR (400 MHz, CD_2Cl_2, 298K): δ = 9.01 (s, 2H), 7.91 (t, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 7.7 Hz, 2H), 7.74 (d, *J* = 7.8 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 2H), 6.92 (s, 4H), 6.90 (s, 2H), 6.42 (d, *J* = 5.2 Hz, 2H), 6.08 (d, *J* = 5.1 Hz, 2H), 2.32 (s, 6H), 2.03 (s, 12H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 160.64, 157.34, 152.04, 149.93, 142.69, 139.62, 138.84, 138.13, 137.57, 137.45, 137.24, 135.12, 130.12, 129.06, 128.75, 128.37, 128.16, 125.66, 123.88, 123.47, 119.39, 115.79, 31.33, 29.69, 29.66, 29.37, 29.34. UV-Vis (CH_2Cl_2): λ_{max}(nm) (ε[$M^{-1}cm^{-1}$]) = 299 (2.83×10^4), 359 (2.95×10^4), 552 (1.93×10^4); HR-MS (ESI-MS): m/z calculated for $C_{52}H_{38}F_5N_3$ = 799.2986; found = 800.3090 [M+1].

Synthesis of 5: The compound **4** (0.010 gm, 0.001 mmol) was dissolved in 20 ml *p*-xylene under nitrogen atmosphere. The solution was purged with nitrogen for 10 minutes. $[Rh(CO)_2Cl]_2$ (20 mg, 0.028 mmol) was added to it. The reaction was continued to reflux for overnight. The crude product was purified using neutral alumina column in CH_2Cl_2 / CH_3OH (90:10) to obtain green fraction. The green crystals were identified as **5** in 7% yield. ^{1}H NMR (400 MHz, CD_2Cl_2, 298K): δ = 9.76 (s, 2H), 7.92 (t, *J* = 7.7 Hz, 1H), 7.65 (d, *J* = 7.7 Hz, 2H), 7.40 (d, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.7 Hz, 2H), 6.99 (s, 2H), 6.87 (s, 2H), 6.78 (d, *J* = 8.0 Hz, 2H), 6.42 (d, *J* = 5.3 Hz, 2H), 5.97 (d, *J* = 5.3 Hz, 2H), 2.34 (s, 6H), 2.33 (s, 6H), 1.72 (s, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ =141.30, 141.25, 140.22, 138.69, 137.65, 137.48, 137.25, 136.88, 131.45, 129.87, 128.63, 128.21, 128.09, 127.43, 118.27, 20.79, 20.37, 19.56. UV-Vis (CH_2Cl_2): λ_{max}(nm) (ε[$M^{-1}cm^{-1}$]) = 366 (7.02×10^4), 656 (4.49×10^4), 710 (7.45×10^4); HR-MS (ESI-MS): m/z calculated for $C_{54}H_{37}F_5N_3O_2Rh$ = 957.1861; found = 958.1914 [M+1].

Synthesis of 6: The compound **4** (0.010 gm, 0.0126 mmol) was dissolved in 15 ml of dry chlorobenzene in nitrogen atmosphere. $PtCl_2$ (0.017 gm, 0.063 mmol) was added into the reaction

mixture and refluxed for 24 hours under nitrogen atmosphere. The crude reaction mixture was rotary evaporated and subjected to neutral alumina column chromatography. The blue fraction was eluted with CH_2Cl_2 / Hexane (1:9) and recrystallized from CH_2Cl_2 / Hexane to obtain **6** in 67% yield. ^{1}H NMR (400 MHz, CD_2Cl_2, 298K): δ = 11.92 (s, 1H), 8.53 (s, 1H), 7.97 (t, *J* = 7.7 Hz, 1H), 7.87 (d, *J* = 7.0 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 7.1 Hz, 1H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.44 (d, *J* = 6.2 Hz, 1H), 7.14 (d, *J* = 7.7 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 7.03 (s, 1H), 6.98 (s, 1H), 6.93 (s, 1H), 6.88 (s, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.69 (d, *J* = 5.3 Hz, 1H), 6.49 (d, *J* = 4.0 Hz, 1H), 6.19 (d, *J* = 5.2 Hz, 1H), 5.95 (d, *J* = 5.1 Hz, 1H), 2.35 (s, 3H), 2.32 (s, 3H), 2.26 (s, 3H), 2.03 (s, 3H), 2.00 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 167.03, 141.66, 141.24, 138.58,138.27, 137.95, 137.71, 136.46, 135.22, 134.98, 134.15, 132.70, 130.42, 129.98, 129.81, 129.00, 128.46, 128.41, 128.16, 128.01, 127.81, 127.35, 125.34, 124.43, 123.79, 117.92, 20.84, 20.50, 20.40, 19.51, 19.36. UV-Vis (CH_2Cl_2): λ_{max}(nm) (ε[$M^{-1}cm^{-1}$]) = 309 (1.89×10^4), 389 (1.57×10^4), 495 (0.51×10^4), 700 (1.34×10^4); HR-MS (ESI-MS): m/z calculated for $C_{54}H_{37}F_5N_3ClPt$ = 993.2555 (M-Cl); found = 992.2532 [M-Cl].

3. Mass Spectral Analyses:

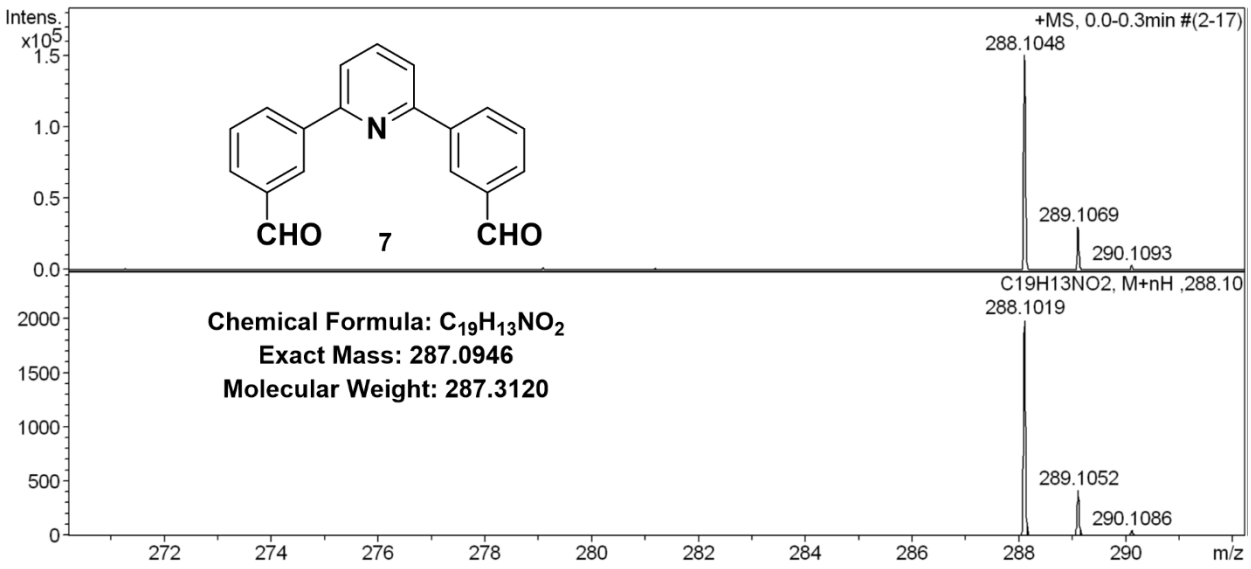


Fig. S1 HR-ESI MS spectrum of **7**.

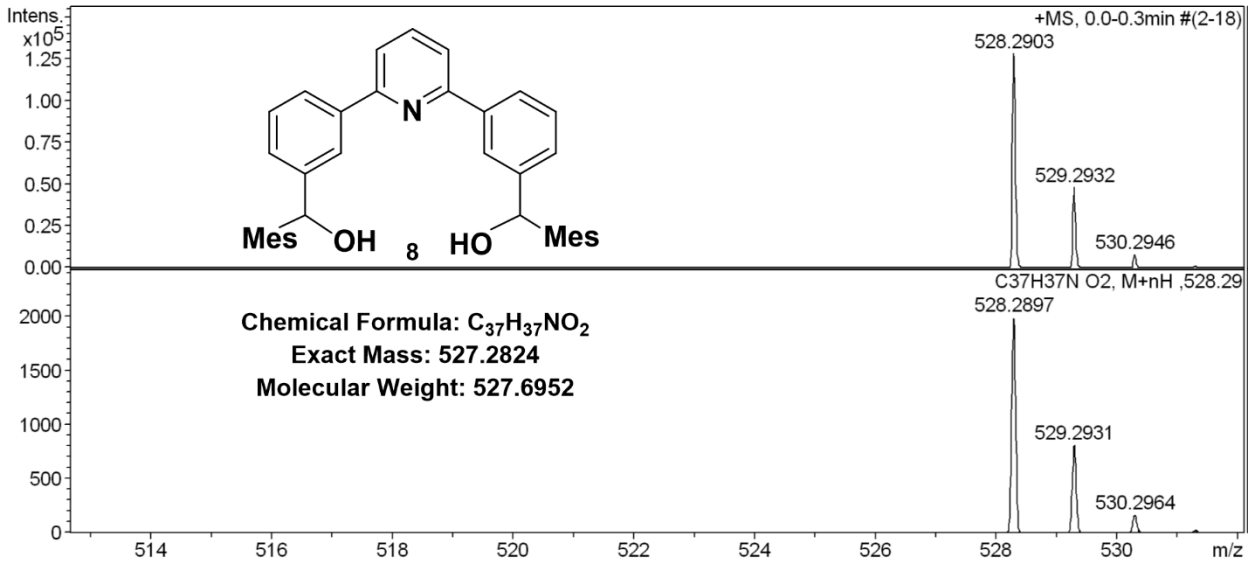


Fig. S2 HR-ESI MS spectrum of **8**.

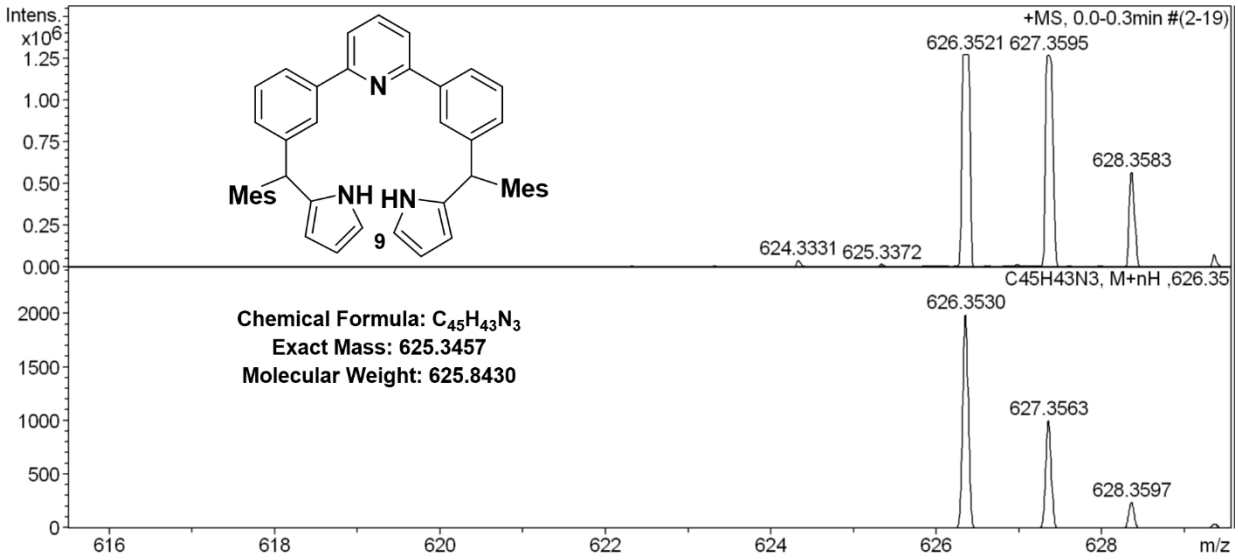


Fig. S3 HR-ESI MS spectrum of **9**.

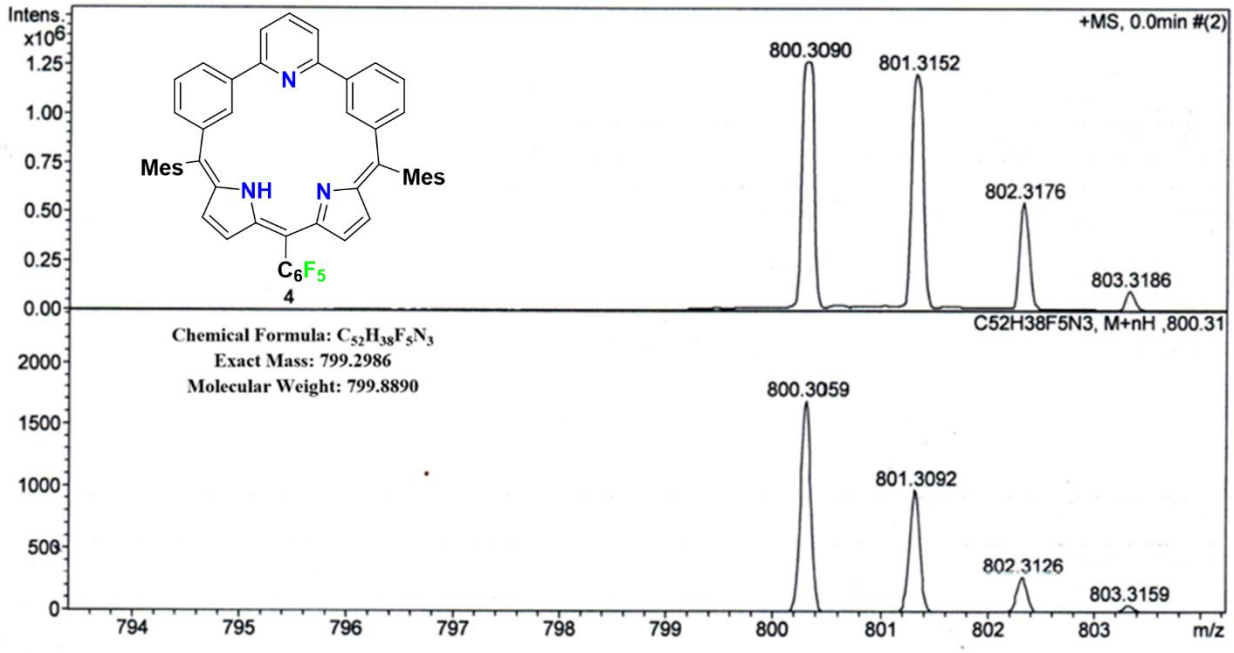


Fig. S4 HR-ESI MS spectrum of **4**.

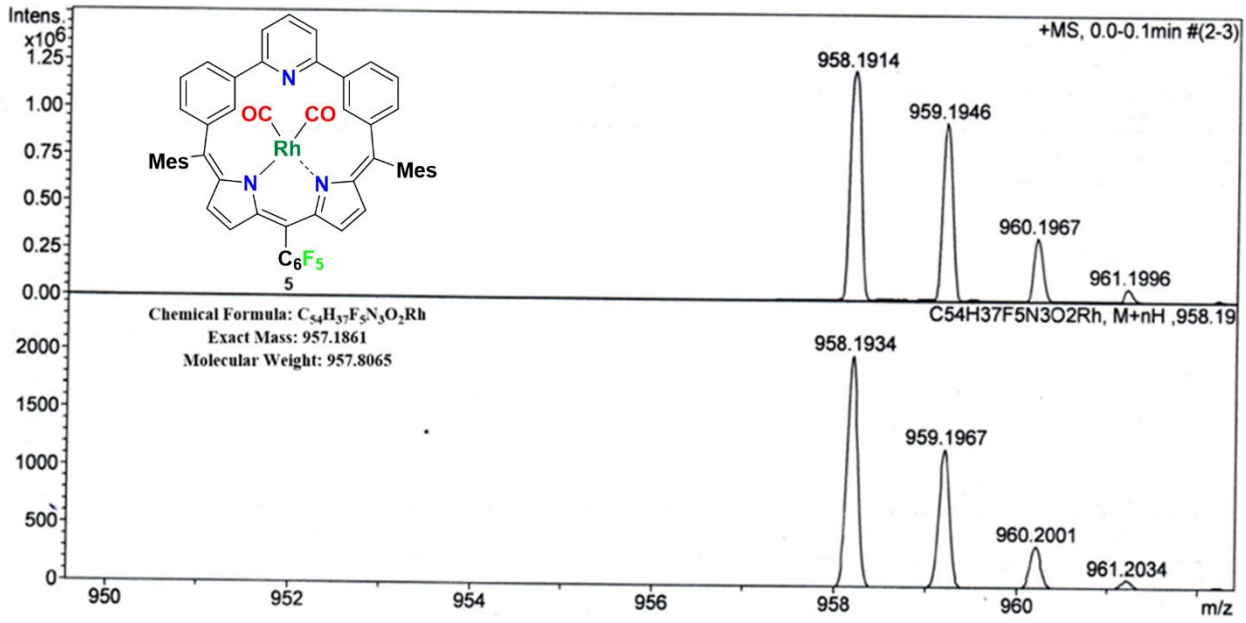


Fig. S5 HR-ESI MS spectrum of **5**.

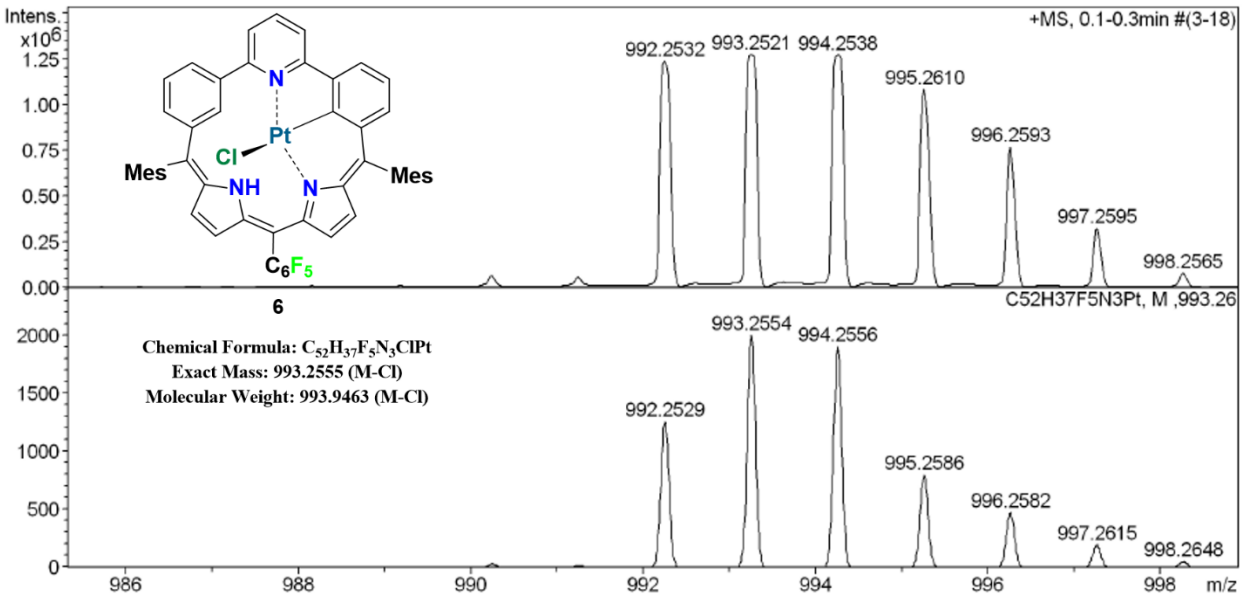


Fig. S6 HR-ESI MS spectrum of **6**.

4. NMR Spectral analysis:

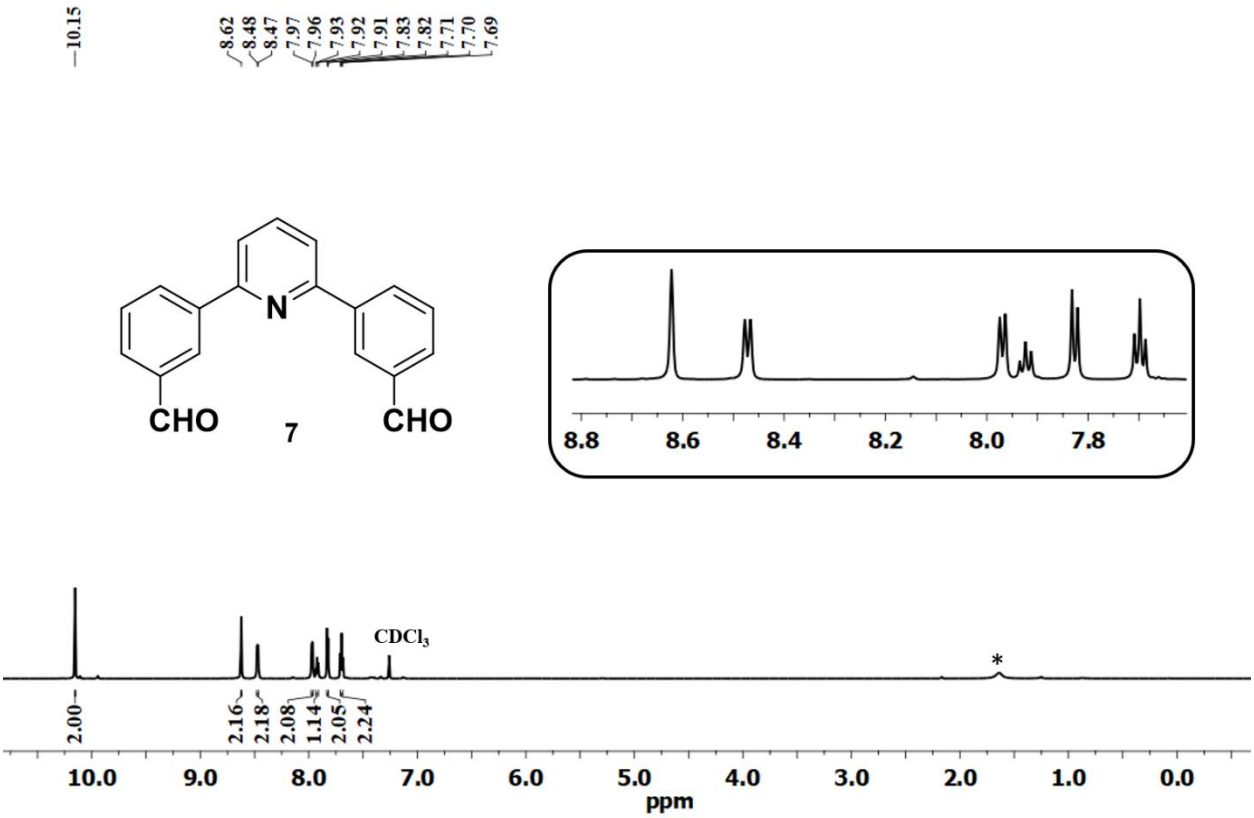


Fig. S7 ^{1}H-NMR spectrum of **7** in $CDCl_3$. (*Residual solvents and impurity grease).

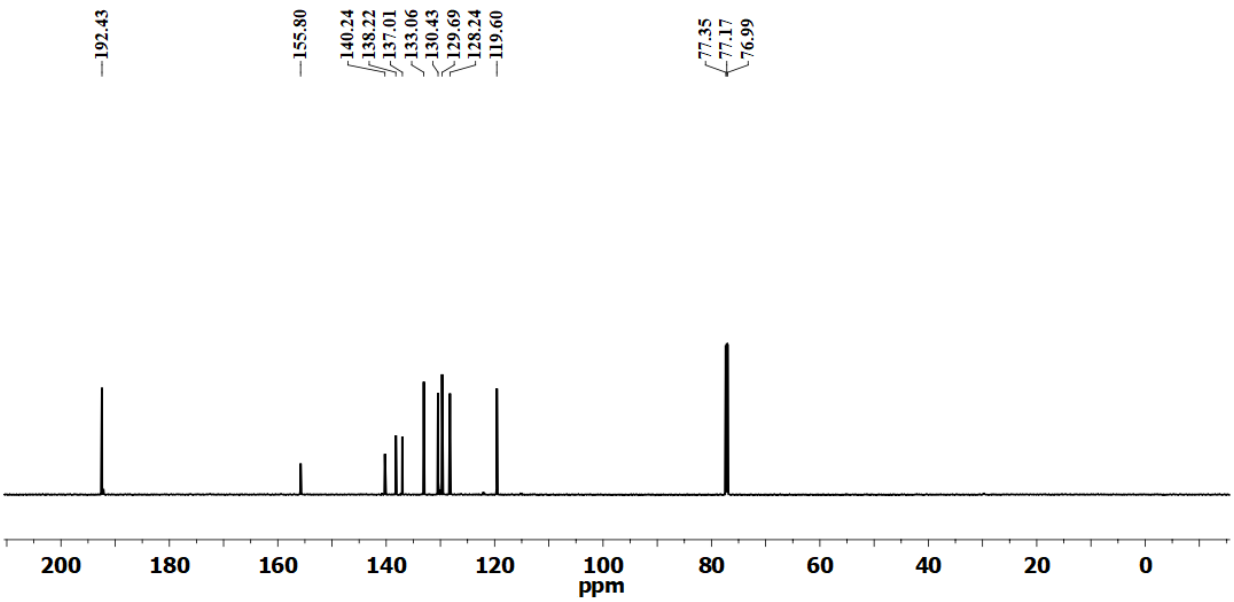


Fig. S8 ^{13}C-NMR spectrum of **7** in $CDCl_3$.

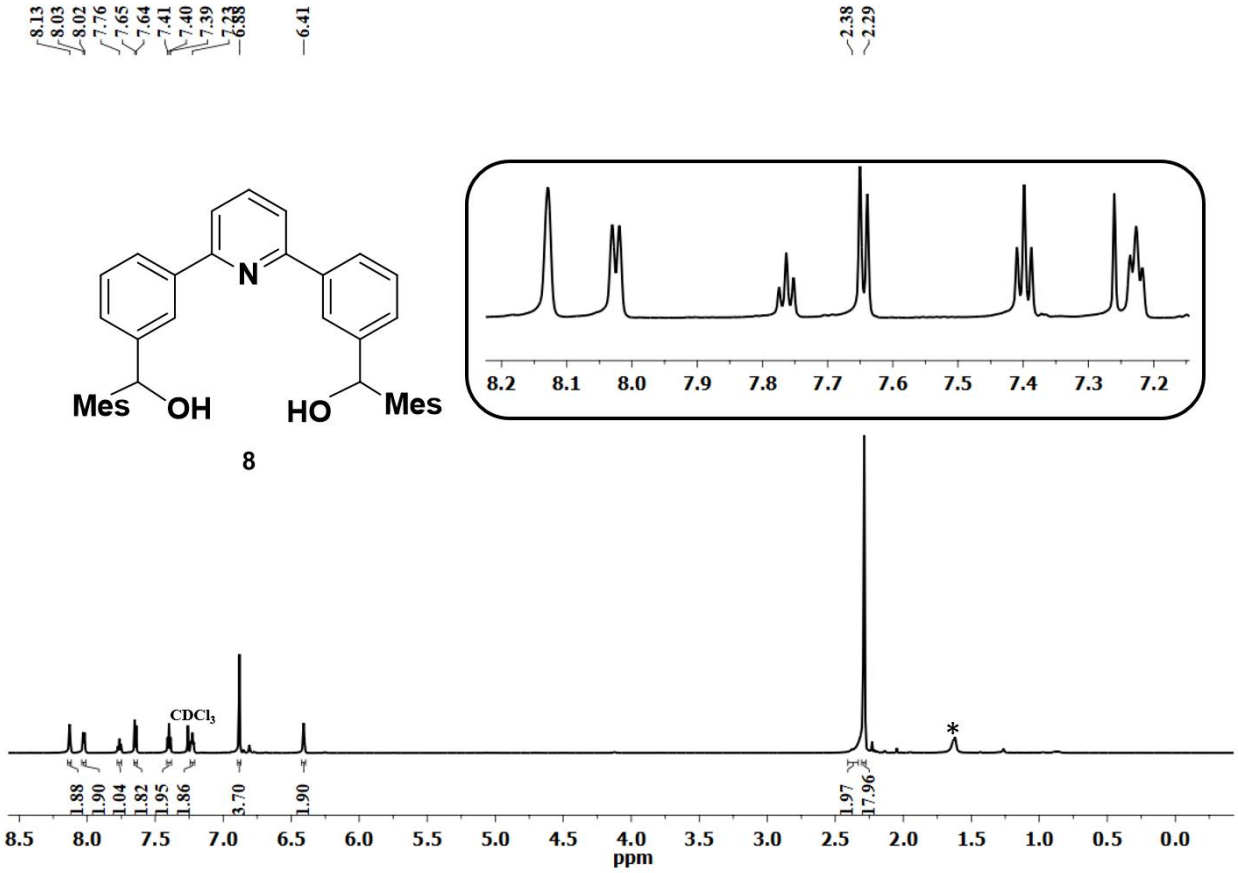


Fig. S9 ^{1}H-NMR spectrum of **8** in $CDCl_3$. (*Residual solvents and impurity grease).

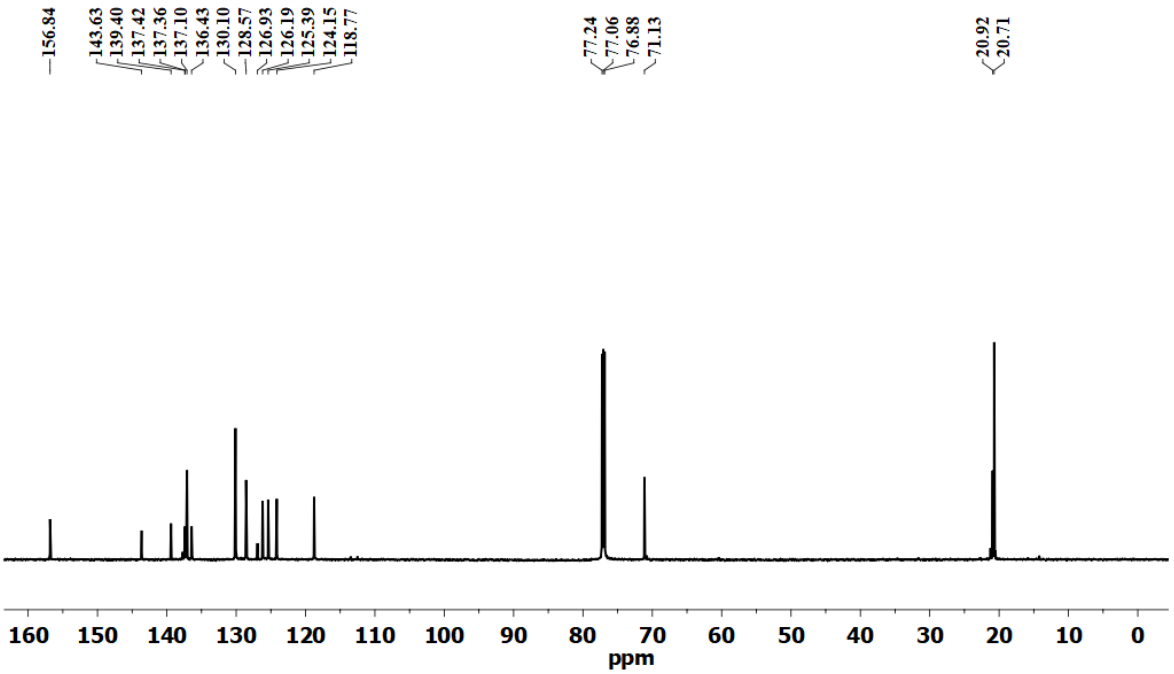


Fig. S10 ^{13}C-NMR spectrum of **8** in $CDCl_3$.

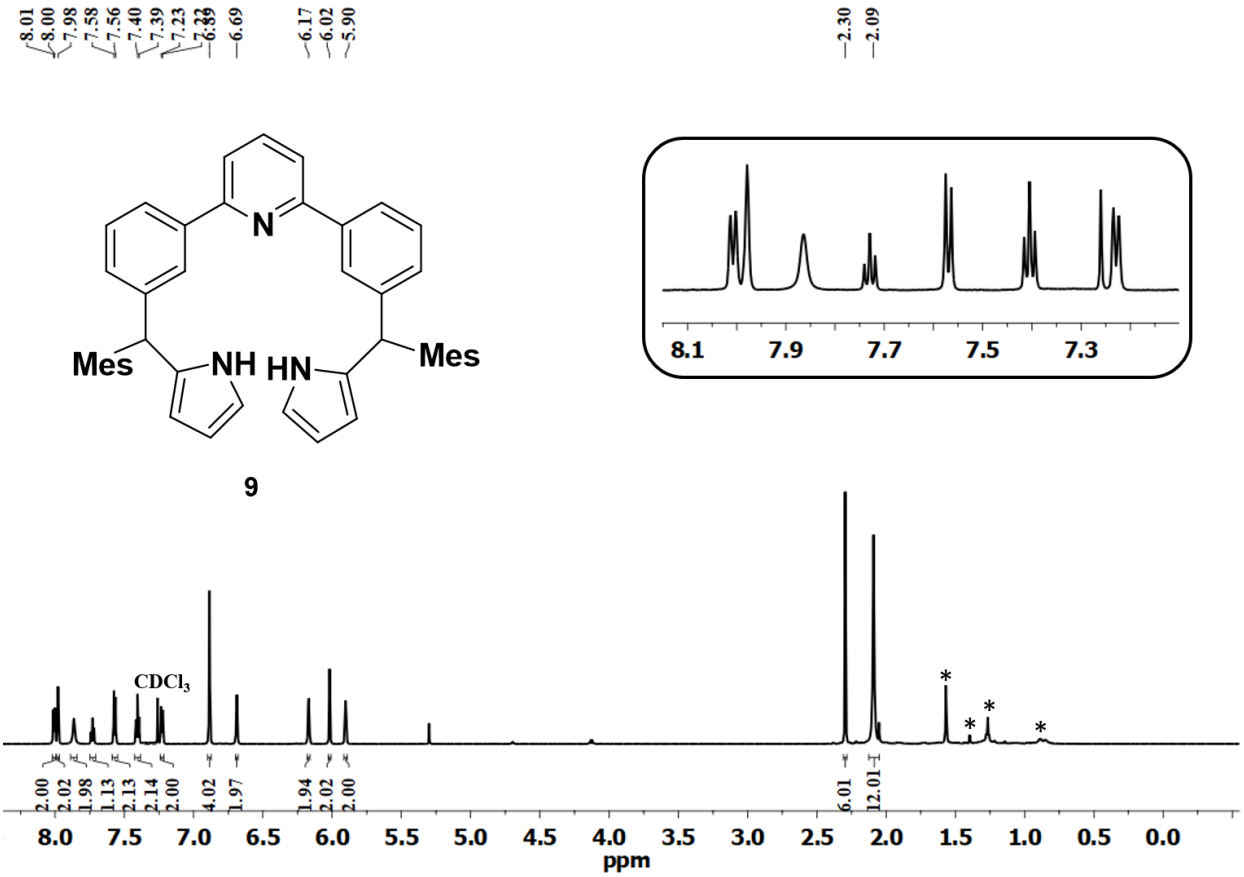


Fig. S11 ^{1}H-NMR spectrum of **9** in $CDCl_3$. (*Residual solvents and impurity grease).

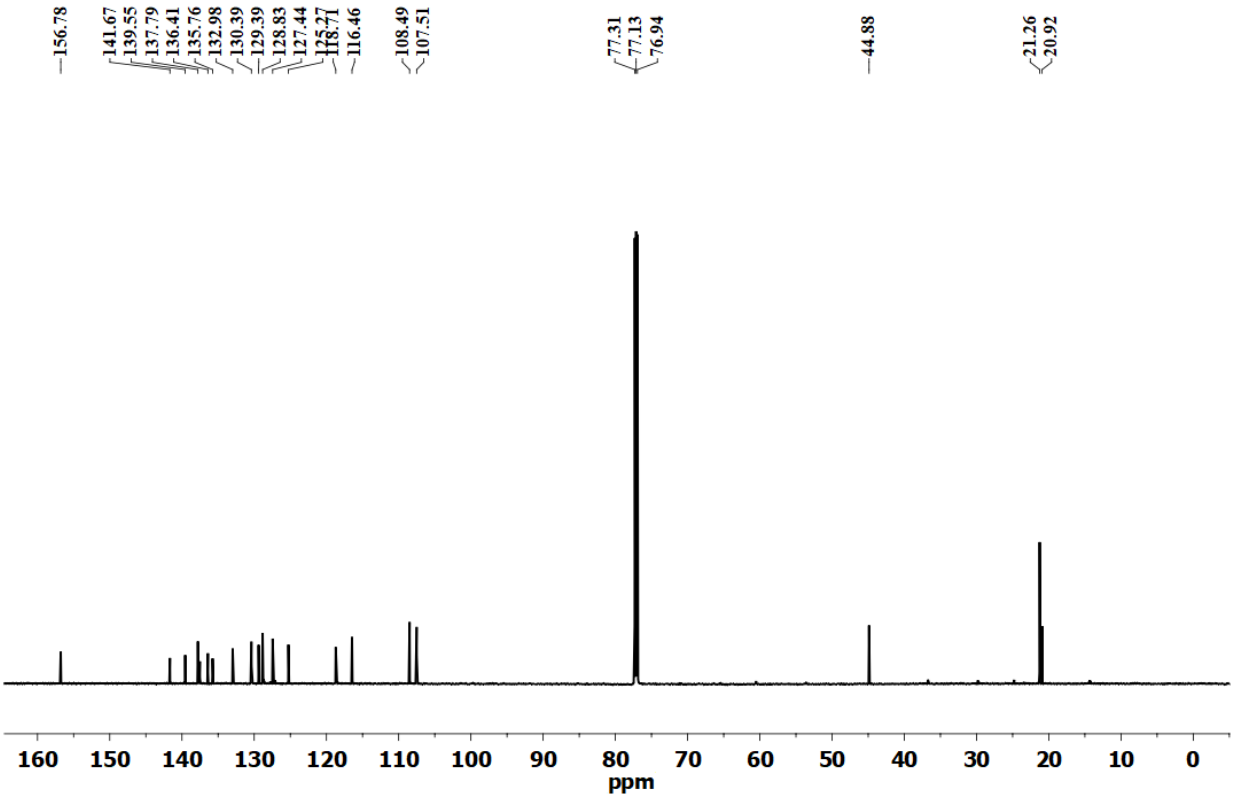


Fig. S12 ^{13}C-NMR spectrum of **9** in $CDCl_3$.

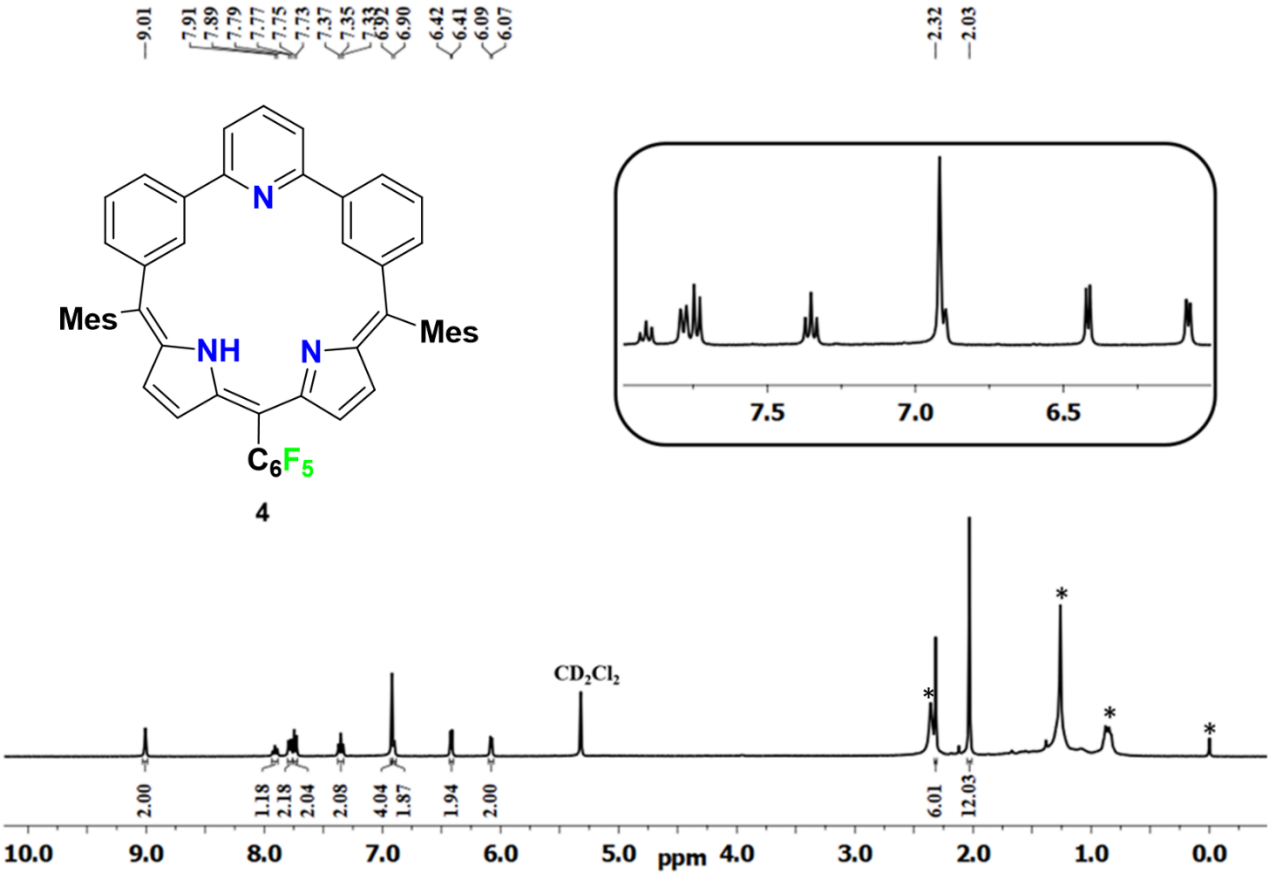


Fig. S13 ^{1}H-NMR spectrum of **4** in CD_2Cl_2. (*Residual solvents and impurity grease).

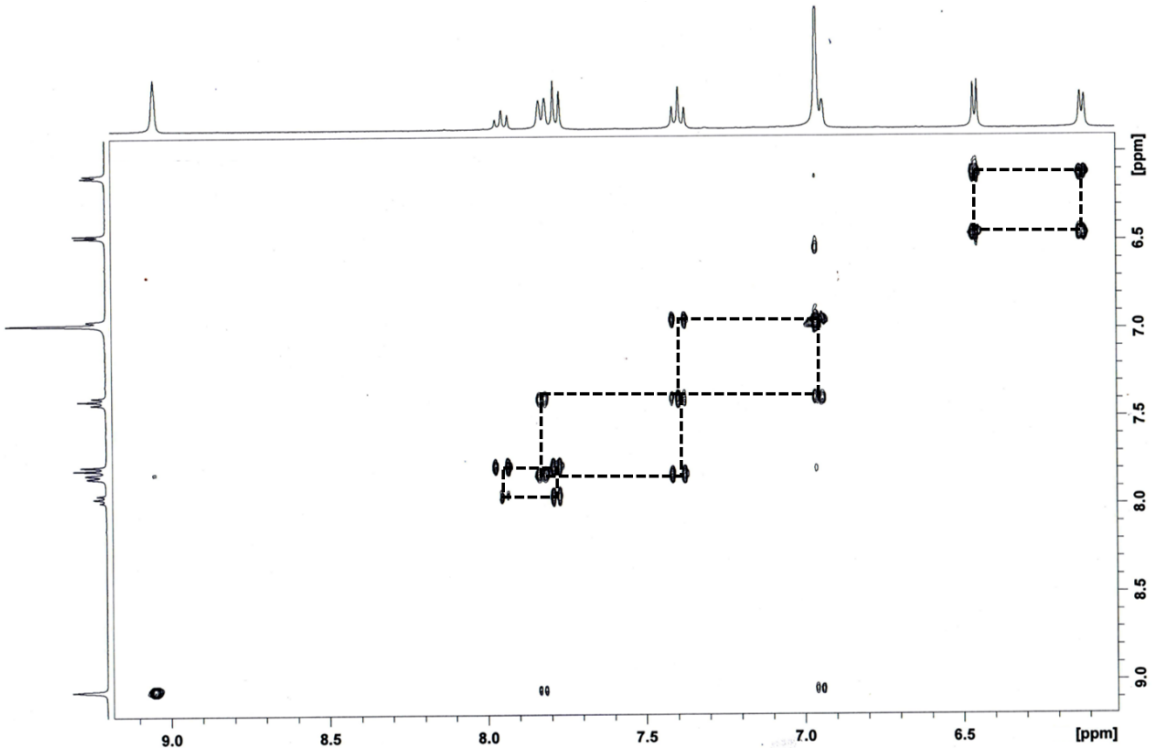


Fig. S14 ^{1}H-^{1}H COSY spectrum of **4** in CD_2Cl_2.

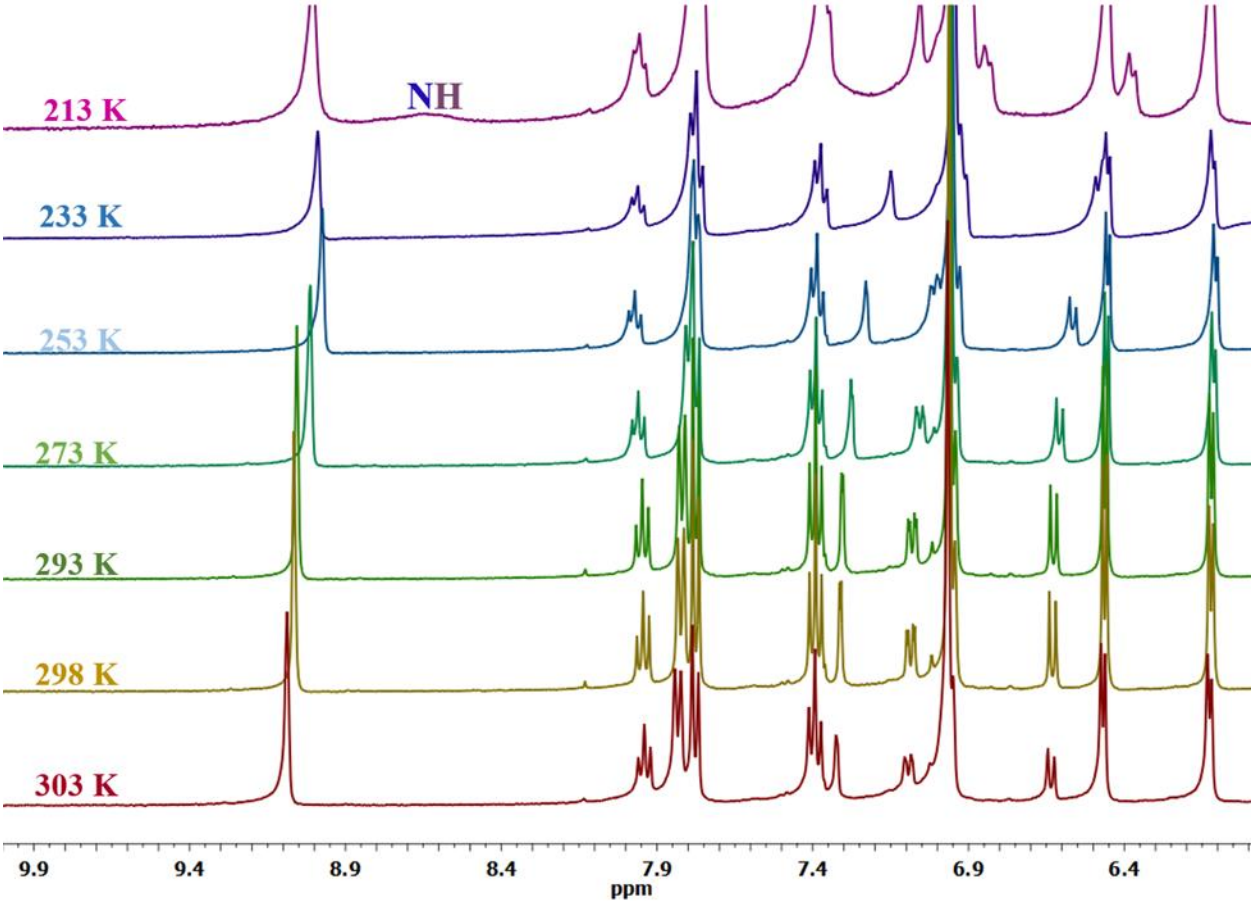


Fig. S15 Variable temperature ^{1}H-NMR Spectra of **4** in CD_2Cl_2.

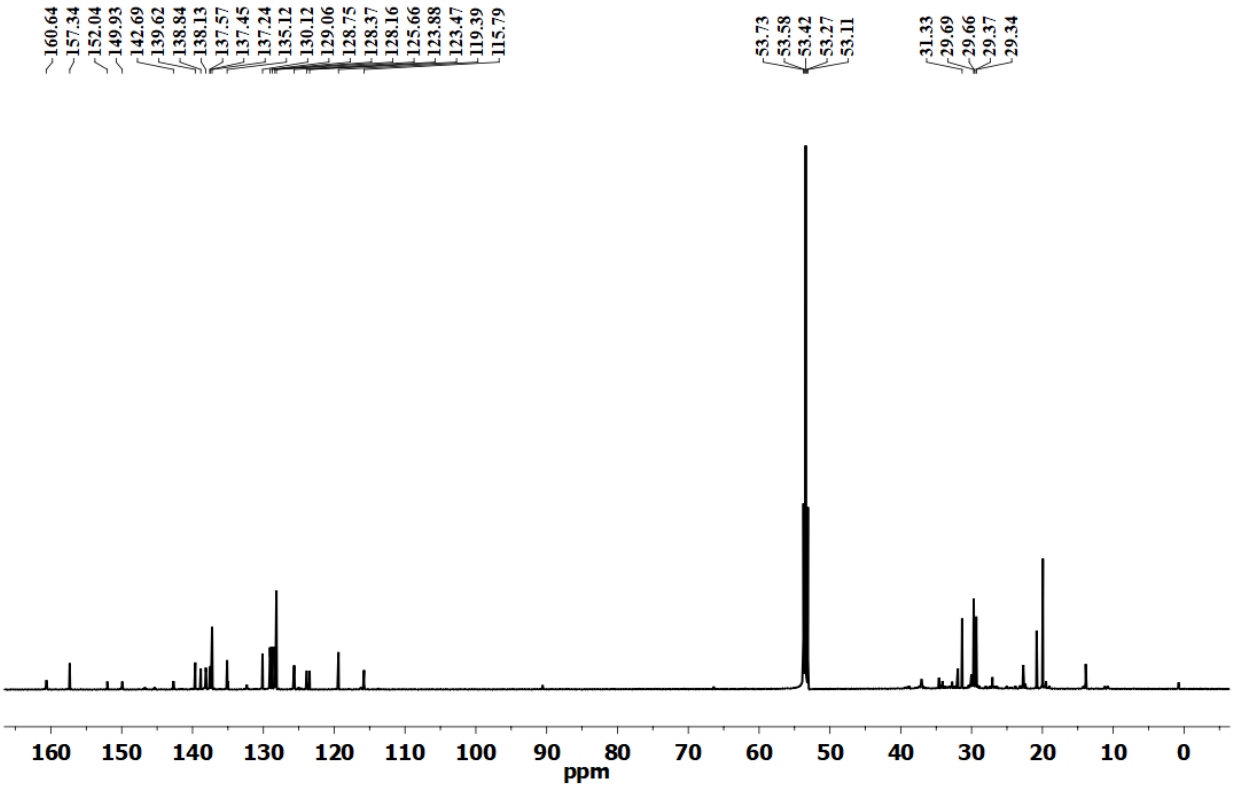


Fig. S16 ^{13}C-NMR spectrum of **4** in CD_2Cl_2.

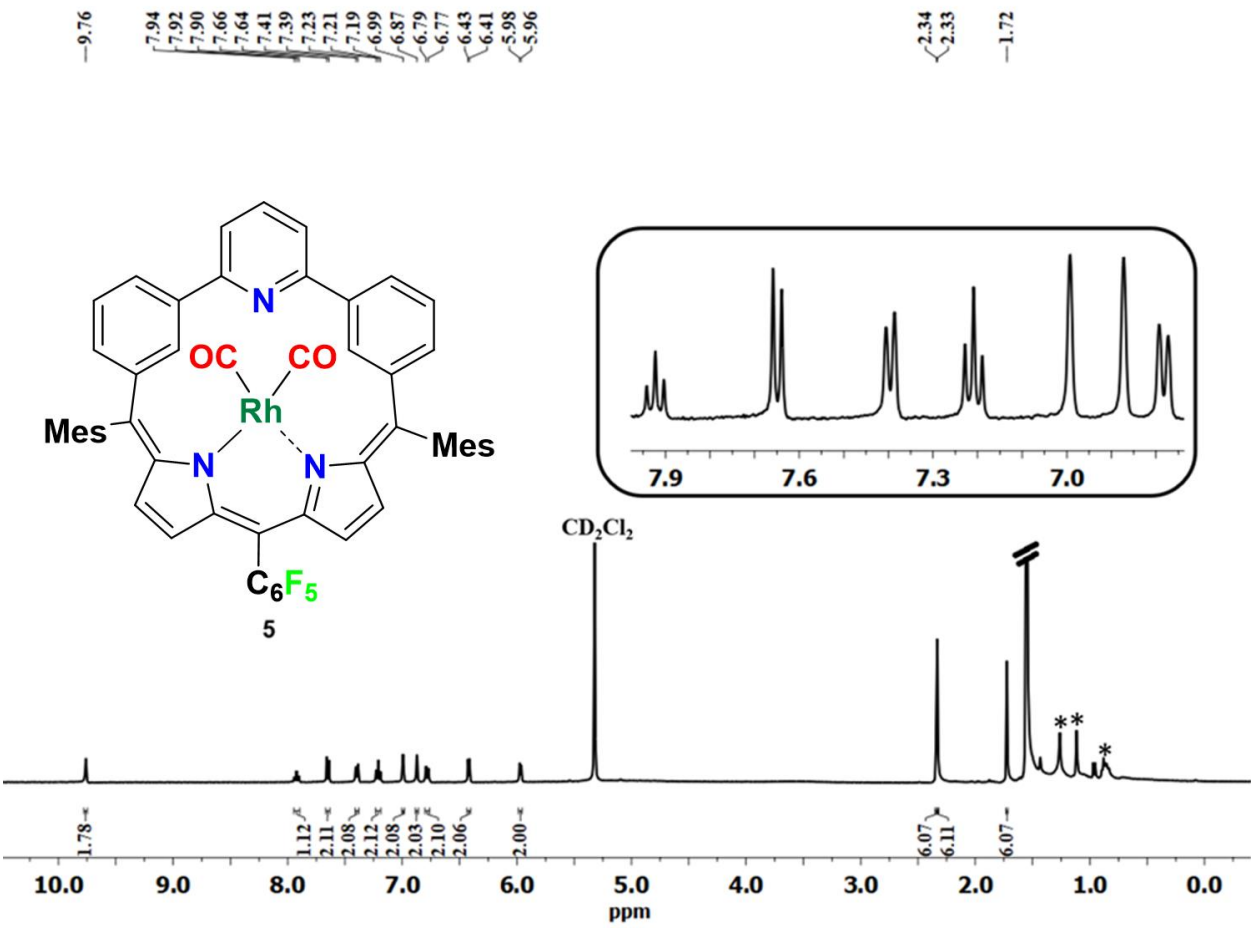


Fig. S17 ^{1}H-NMR spectrum of **5** in CD_2Cl_2. (*Residual solvents and impurity grease).

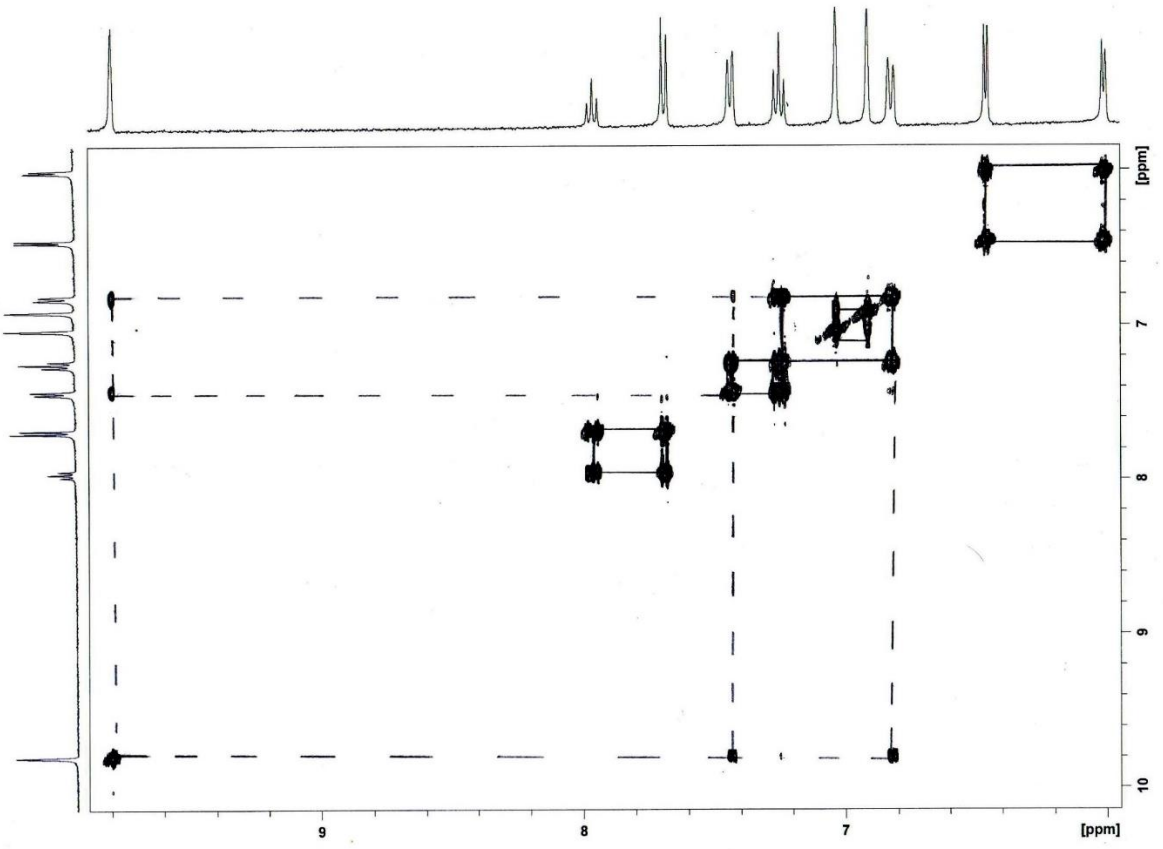


Fig. S18 ^{1}H-^{1}H COSY spectrum of **5** in CD_2Cl_2.

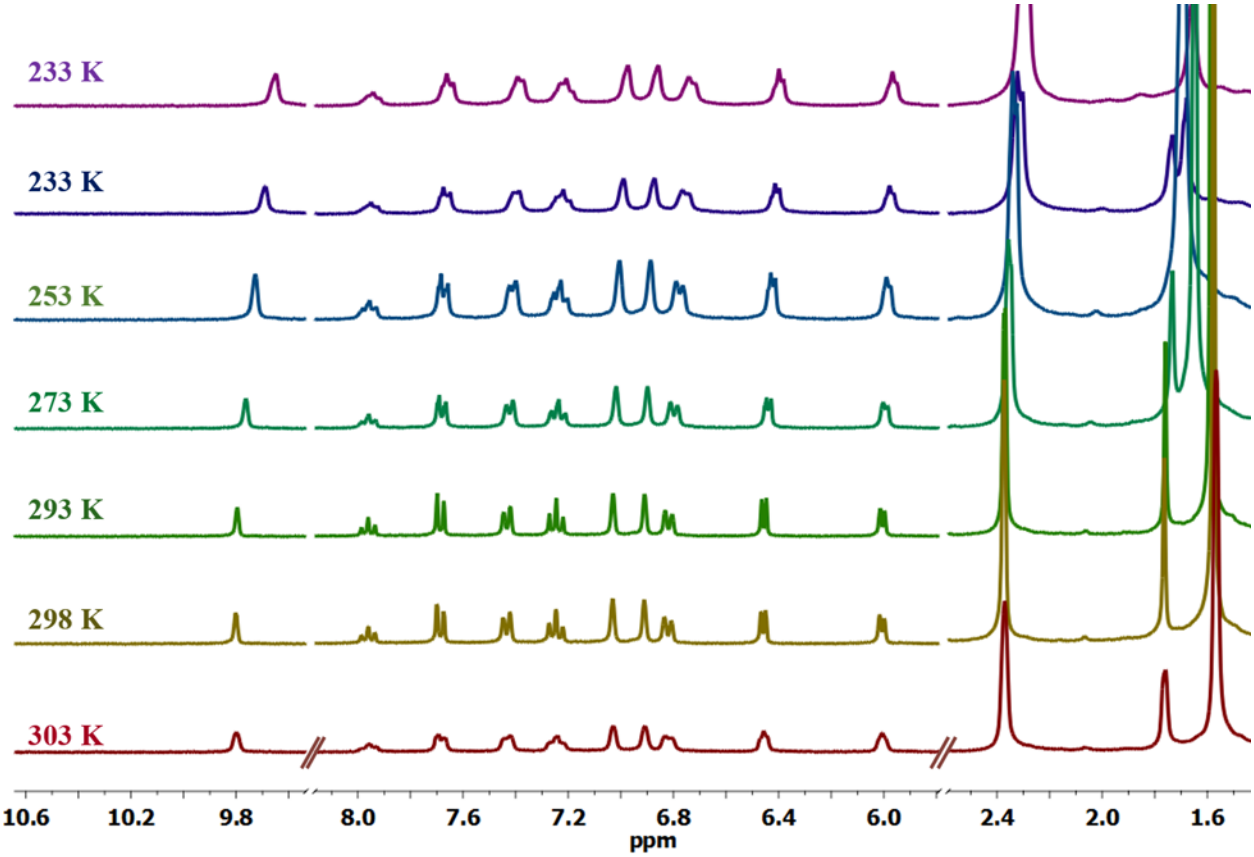


Fig. S19 Variable temperature ^{1}H-NMR Spectra of **5** in CD_2Cl_2.

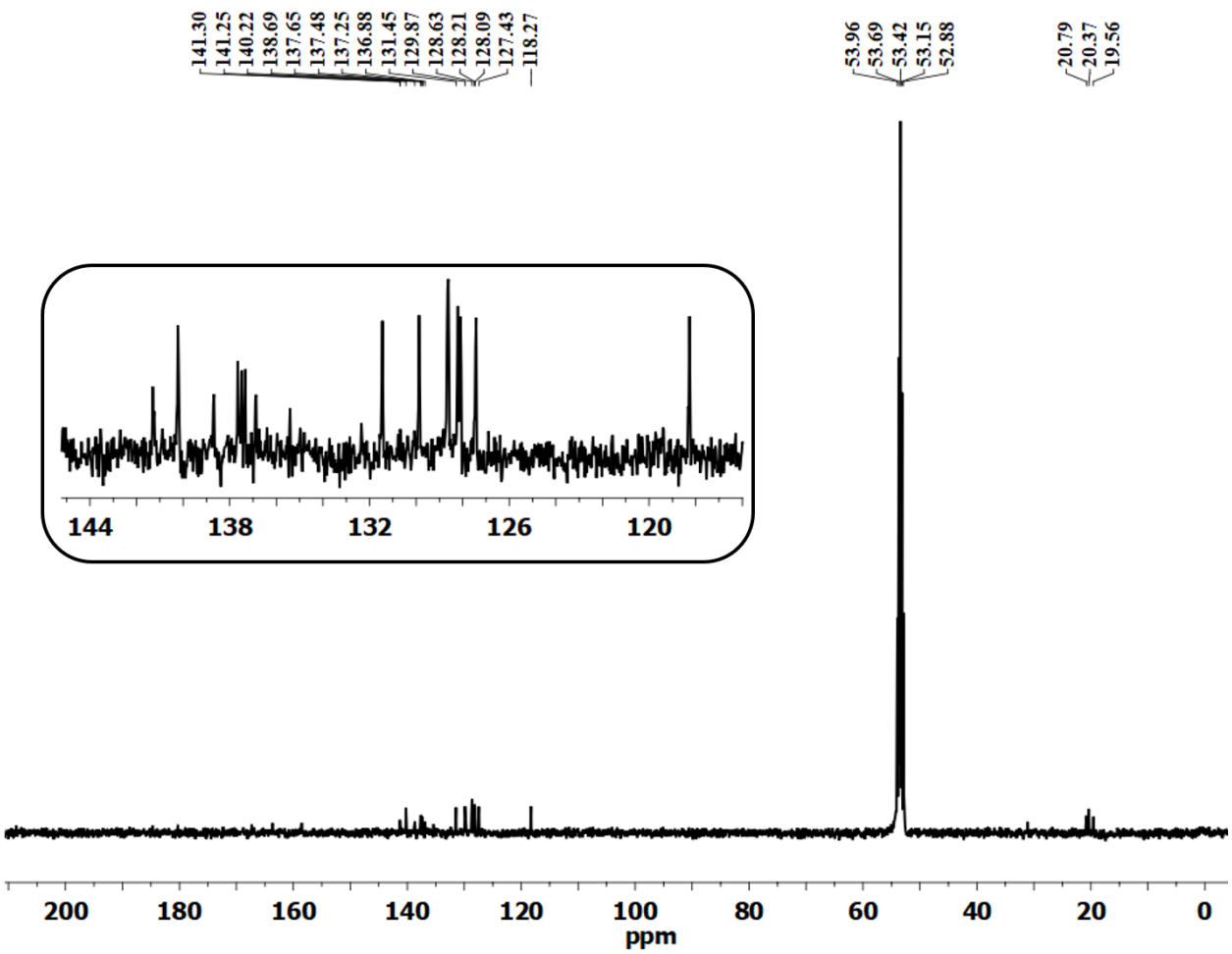


Fig. S20 ^{13}C-NMR spectrum of **5** in CD_2Cl_2.

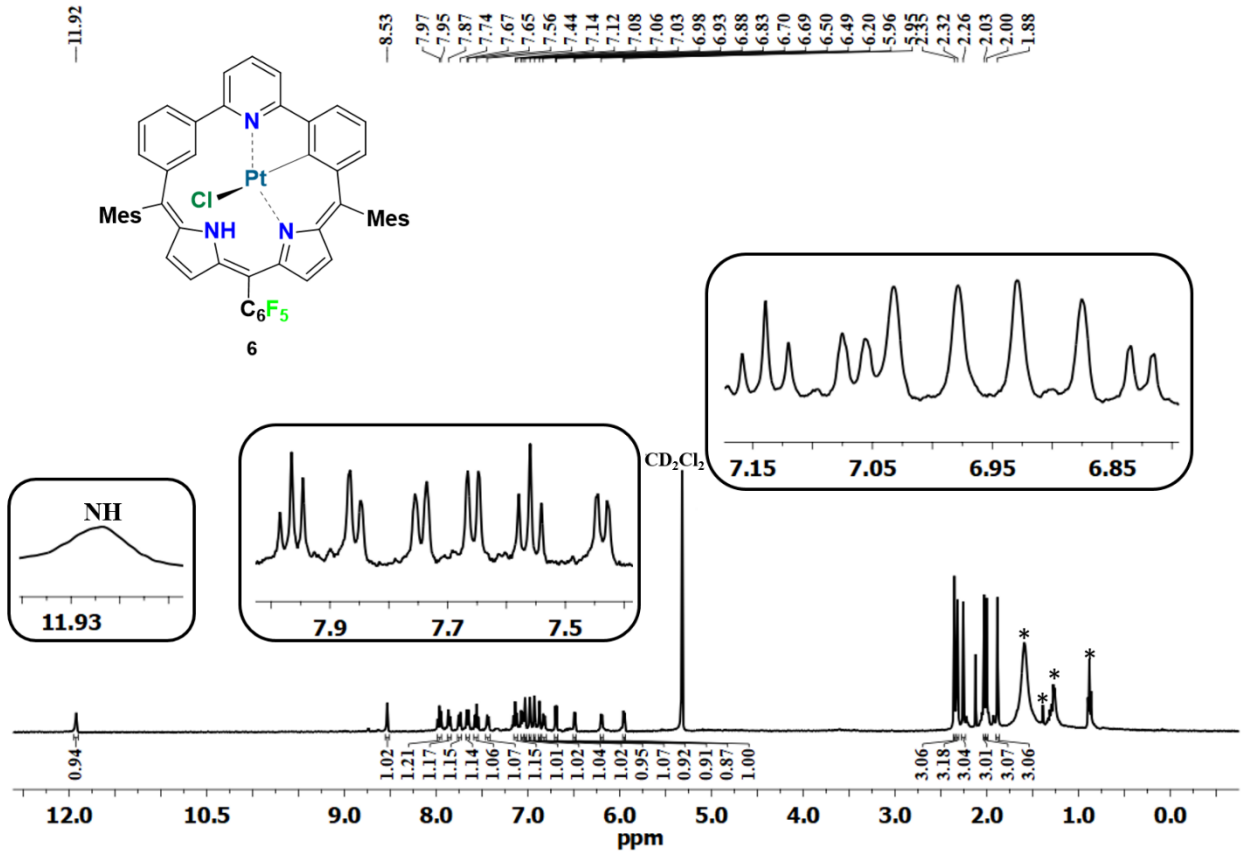


Fig. S21 ^{1}H-NMR spectrum of **6** in CD_2Cl_2. (*Residual solvents and impurity grease).

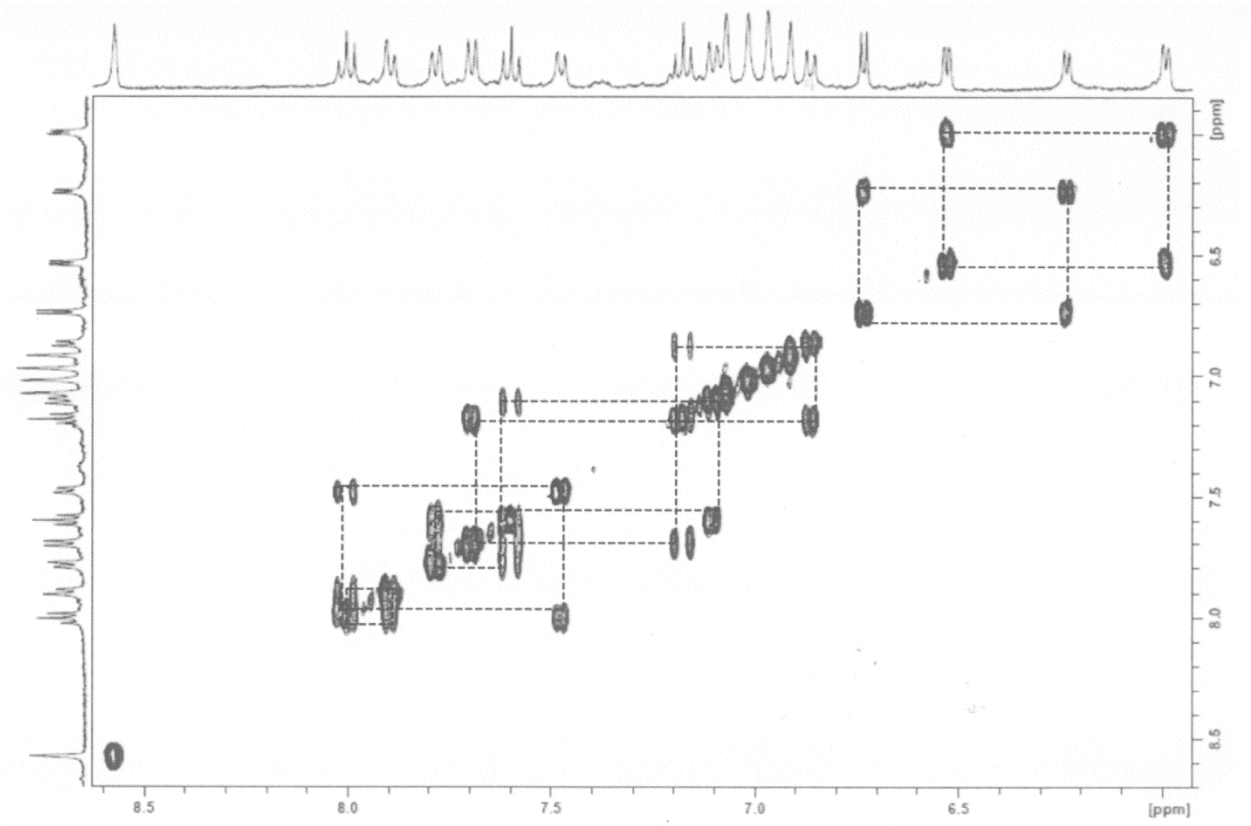


Fig. S22 ^{1}H-^{1}H COSY spectrum of **6** in CD_2Cl_2.

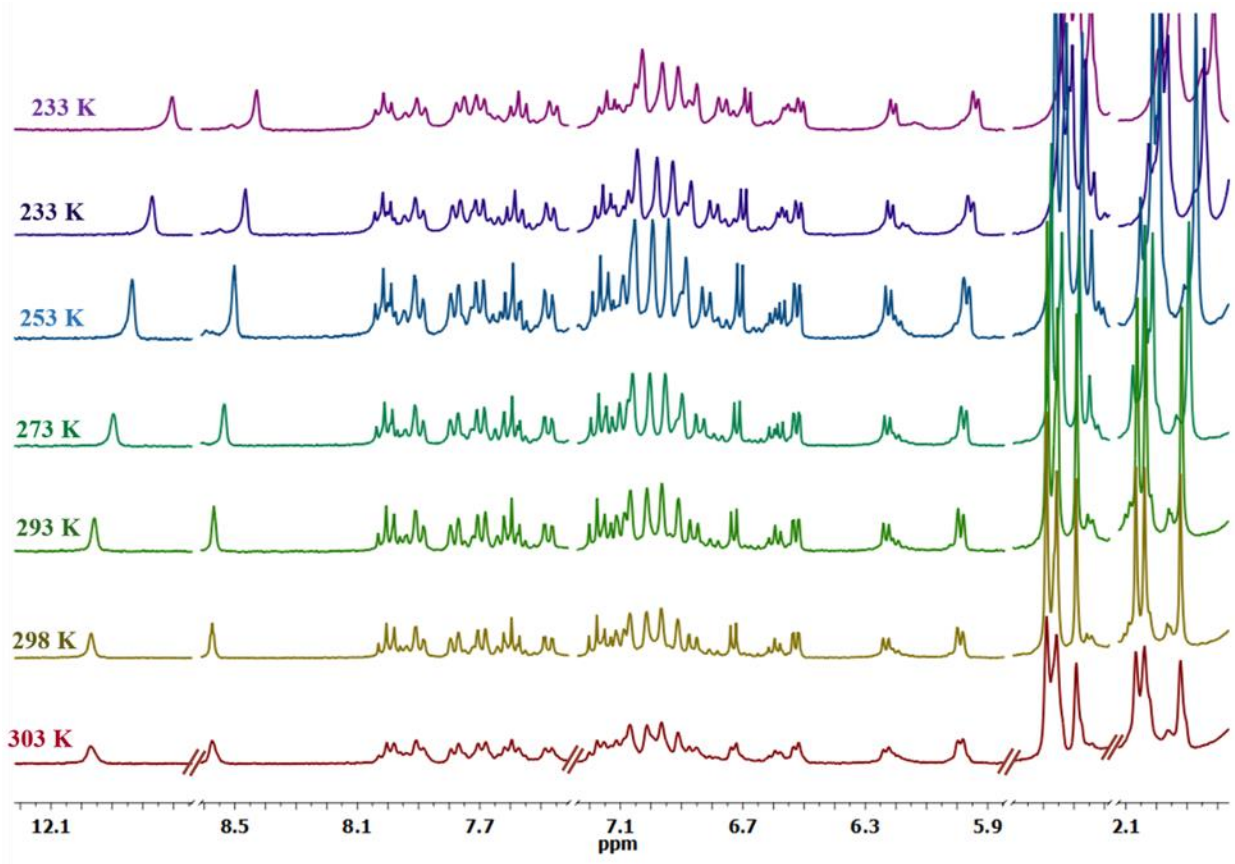


Fig. S23 Variable temperature ^{1}H-NMR Spectrum of **6** in CD_2Cl_2.

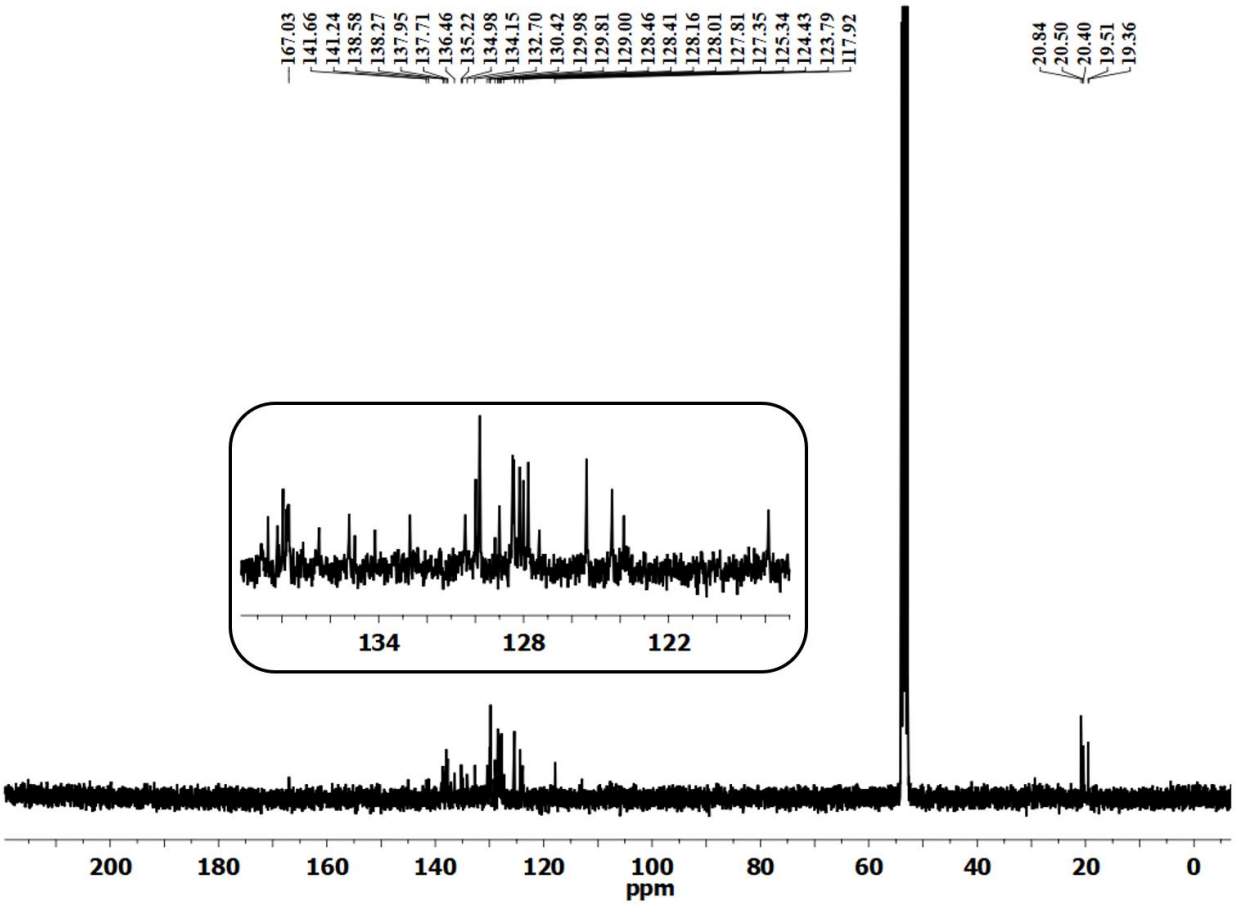


Fig. S24 ^{13}C-NMR spectrum of **6** in CD_2Cl_2.

5. Single crystal X-ray structural analyses of 4, 5 and 6

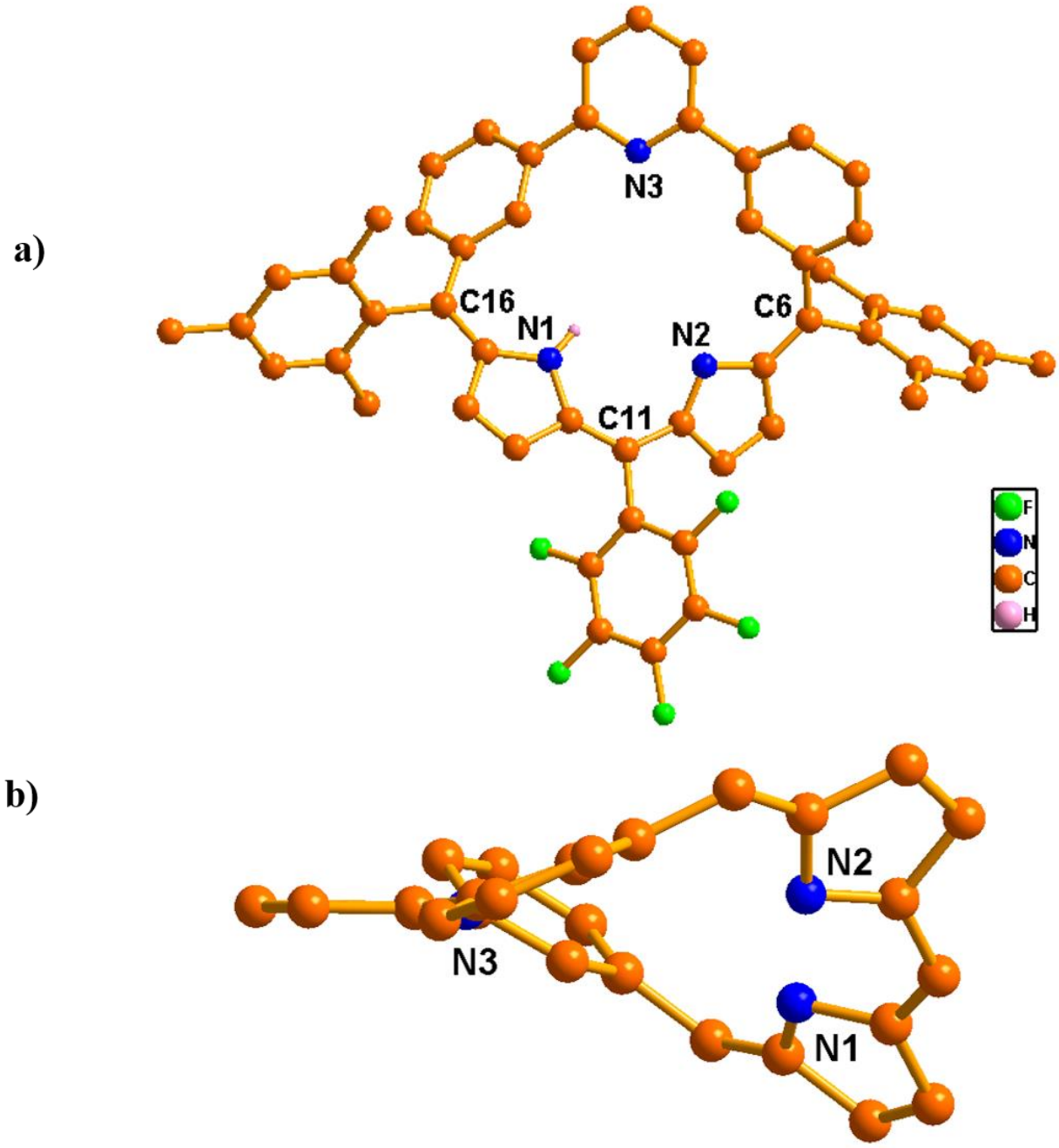


Fig. S25 Single crystal X-ray structure of **4**. a) Top view and b) side view. Peripheral H-atoms in a) & b) and *meso*-aryl groups in b) are omitted for clarity.

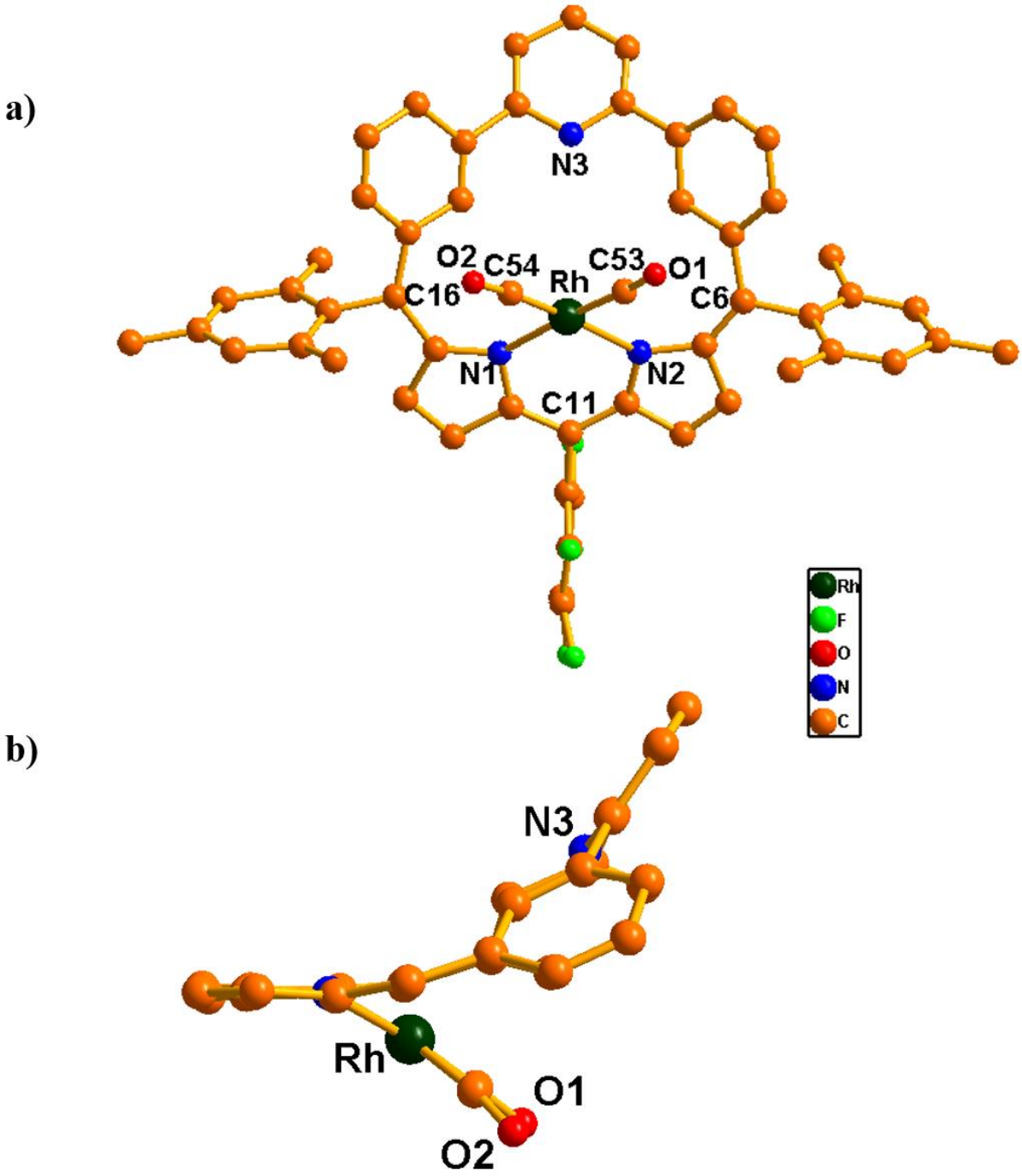


Fig. S26 Single crystal X-ray structure of **5**. a) Top view and b) side view. Peripheral H-atoms in a) & b) and *meso*-aryl groups in b) are omitted for clarity.

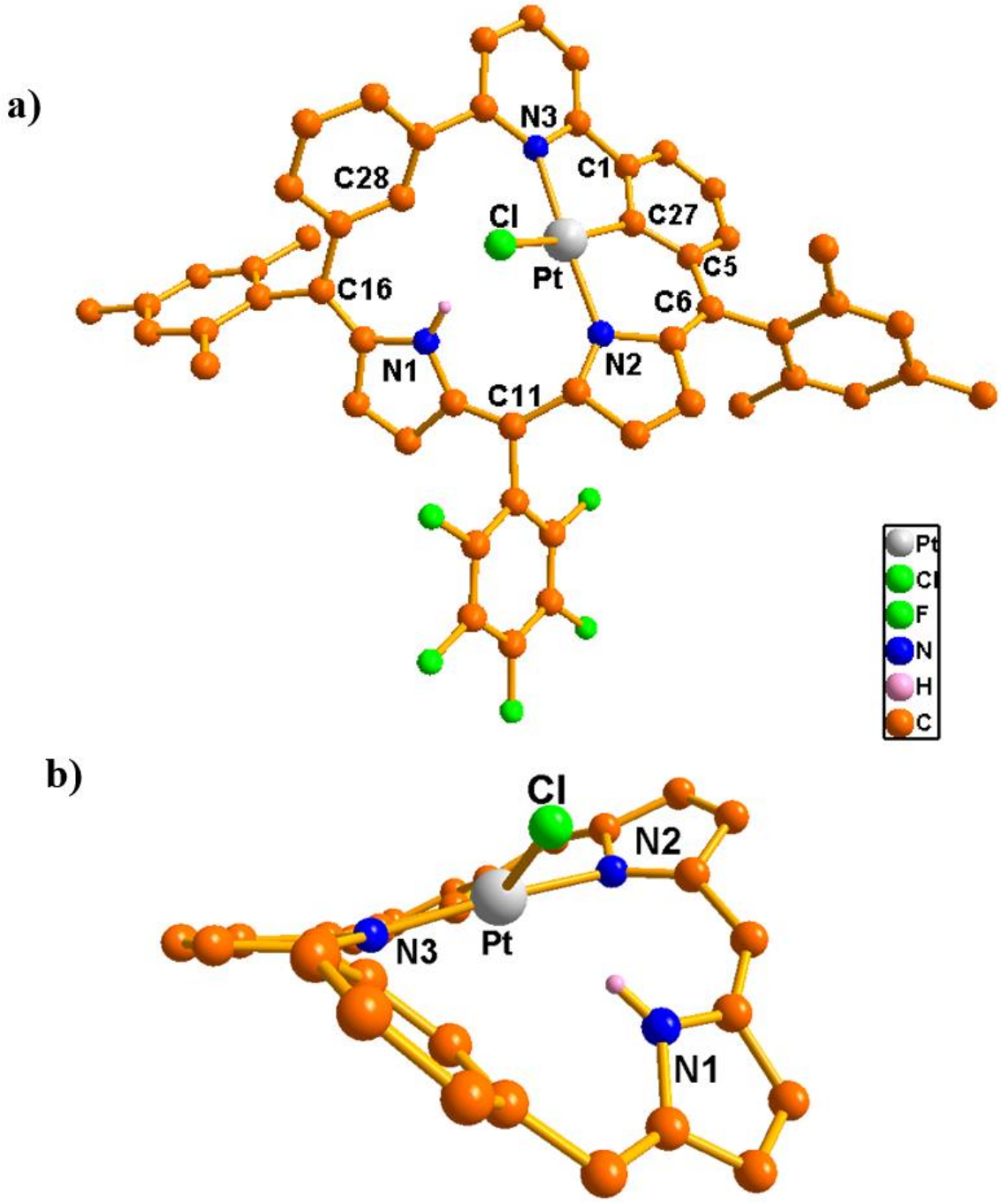


Fig. S27 Single crystal X-ray structure of **6**. a) Top view and b) side view. Peripheral H-atoms in a) & b) and *meso*-aryl groups in b) are omitted for clarity.

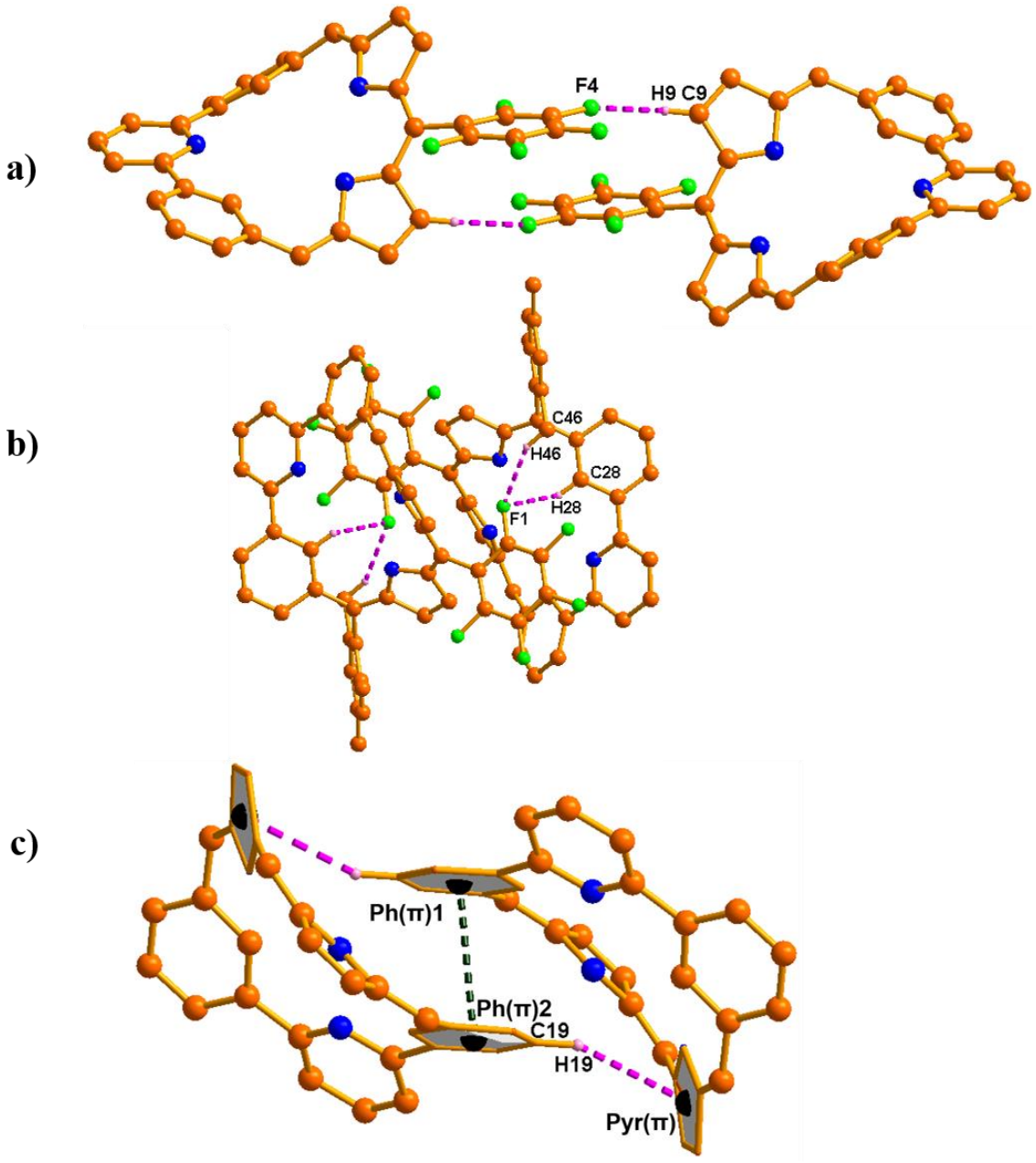


Fig. S28 Single crystal X-ray analysis of **4**. a), b) and c) are Self-assembled dimers. The bond distances and angles are: a) C9-H9…F4: 2.628(3) Å & 144.42(3)°; b) C28-H28…F1: 2.527(2) Å & 127.72(3)° and C46-H46…F1: 2.546(2) Å & 151.91(2)°; c) C19-H19…Pyr(π): 3.010(1) Å and 152.24(3)°; Ph(π)1- Ph(π)2: 3.634(3) respectively. The hydrogen atoms and the *meso*-aryl groups are omitted for clarity.

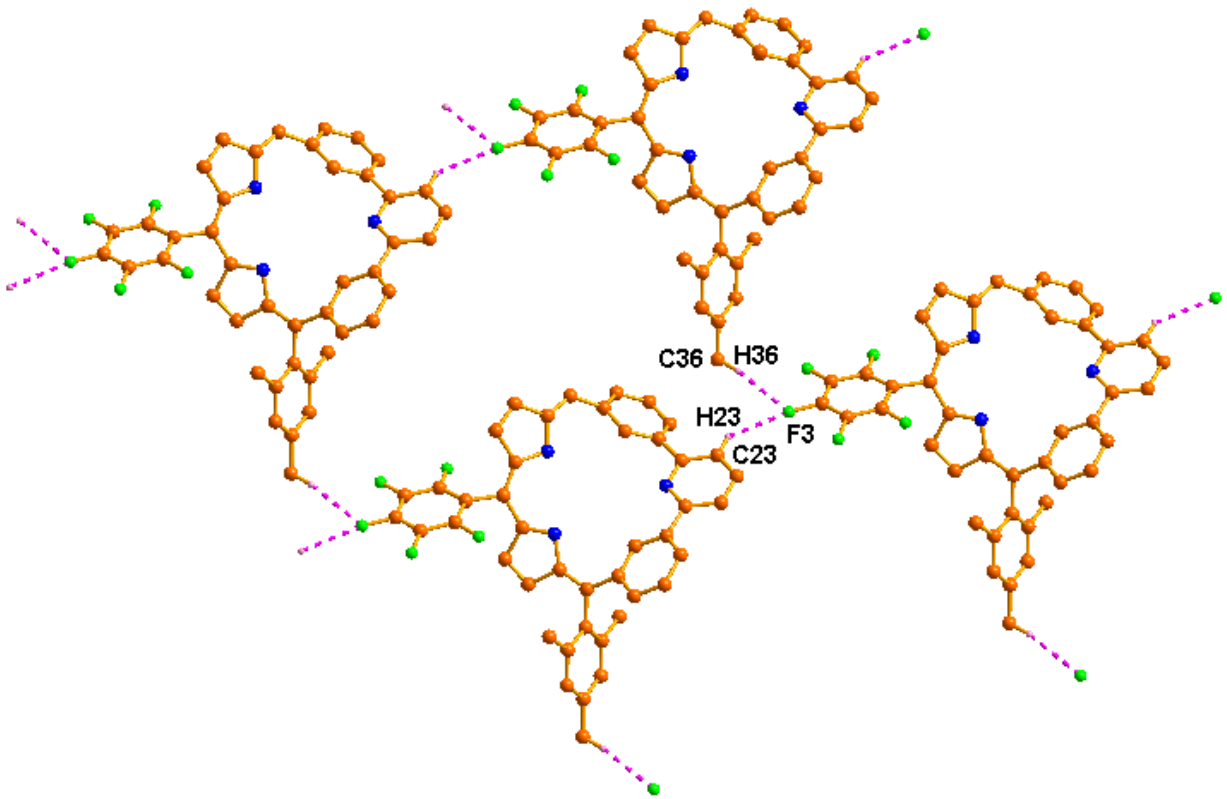


Fig. S29 Single crystal X-ray analysis of **4** in 2-D array. The bond distances and angles are C23-H23…F3: 2.548(2) Å and 133.91(3)°; C36-H36…F3: 2.541(3) Å and 150.59(3)° respectively. The hydrogen atoms and the *meso*-aryl groups are omitted for clarity.

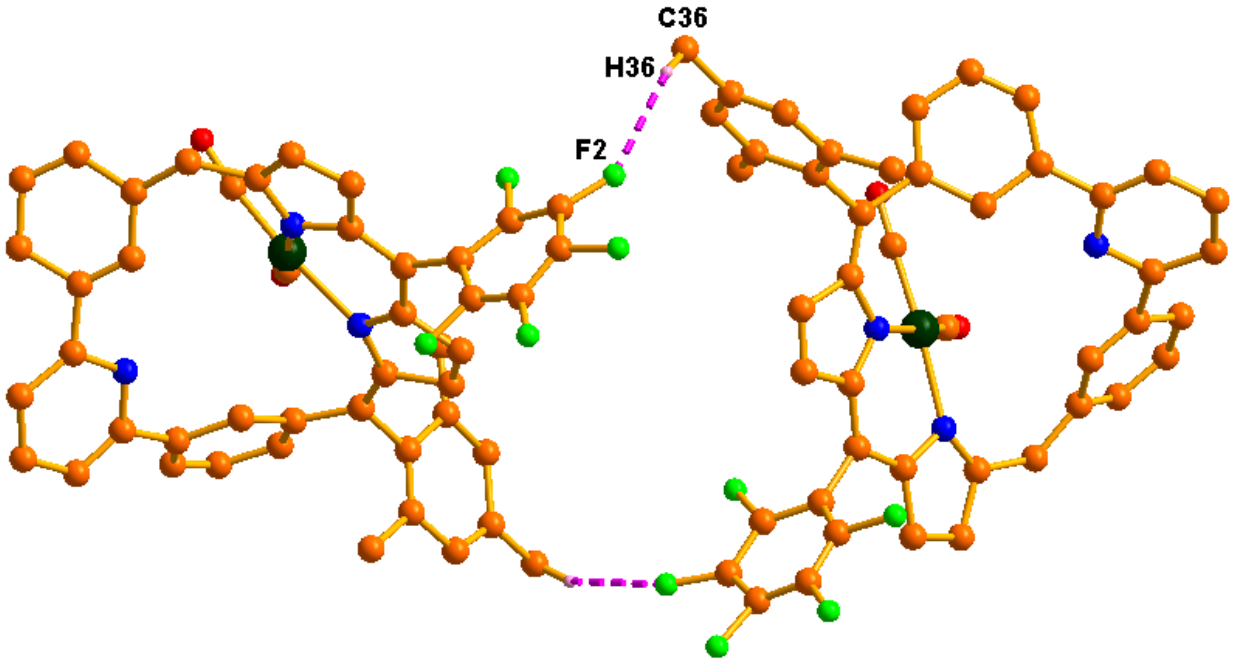


Fig. S30 Self-assembled dimer in **5**. The bond distances and angles are: C36-H36…F2: 2.774(1) Å & 157.66(1)° respectively. The hydrogen atoms and the *meso*-aryl groups are omitted for clarity.

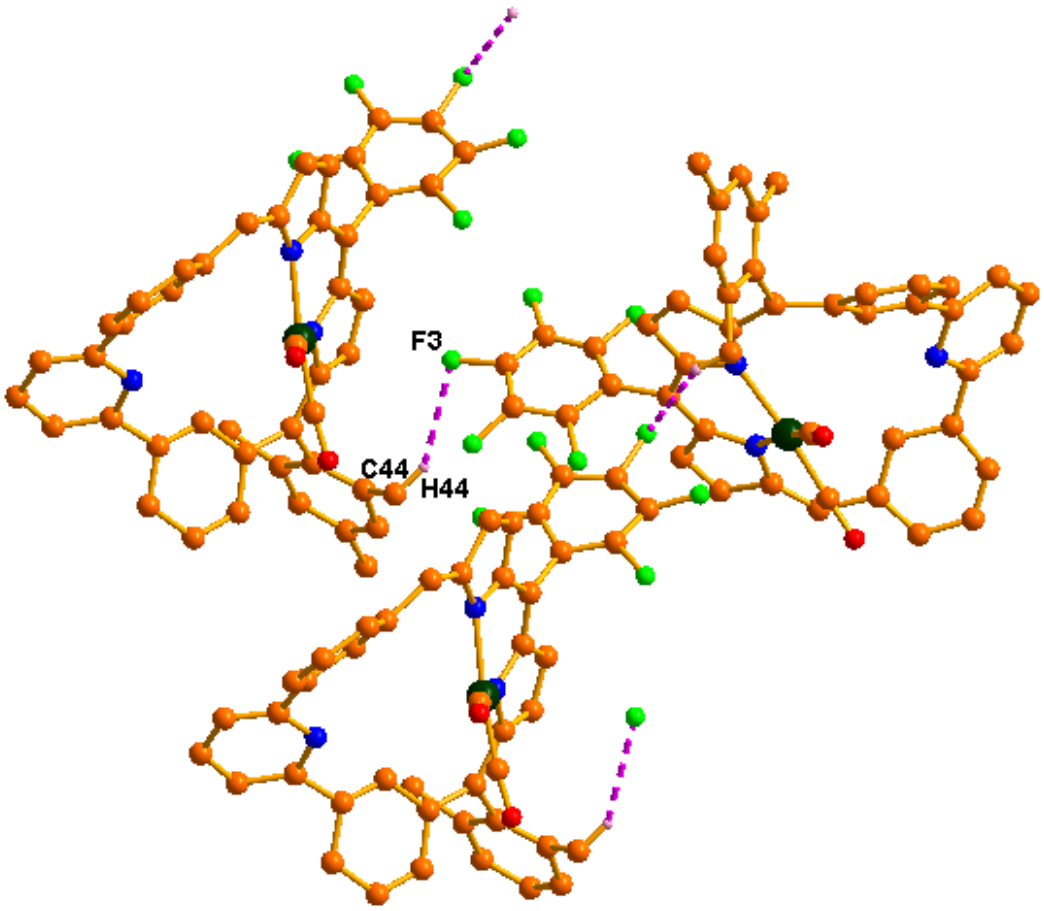


Fig. S31 Single crystal X-ray analysis of **5** in 1-D array. The bond distances and angles are C44-H44…F3: 2.877(1) Å and 142.23(1)°; respectively. The hydrogen atoms and the *meso*-aryl groups are omitted for clarity.

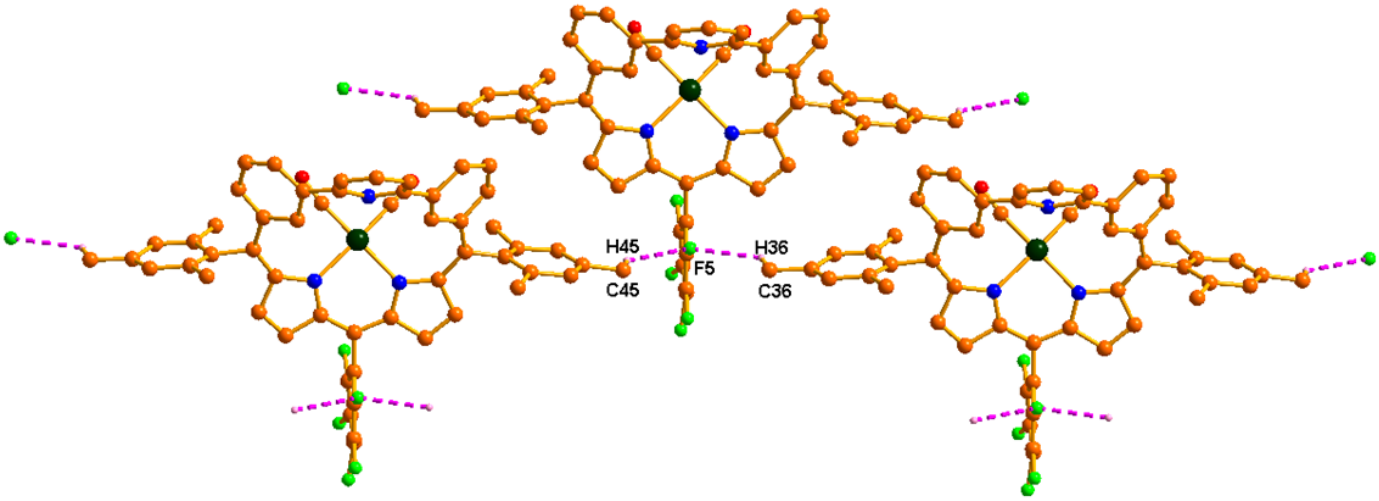


Fig. S32 Single crystal X-ray analysis of **5** in 2-D array. The bond distances and angles are C45-H45…F5: 2.759(1) Å and 133.87(1)°; C36-H36…F5: 2.702(1) Å and 127.16(9)° respectively. The hydrogen atoms and the *meso*-aryl groups are omitted for clarity.

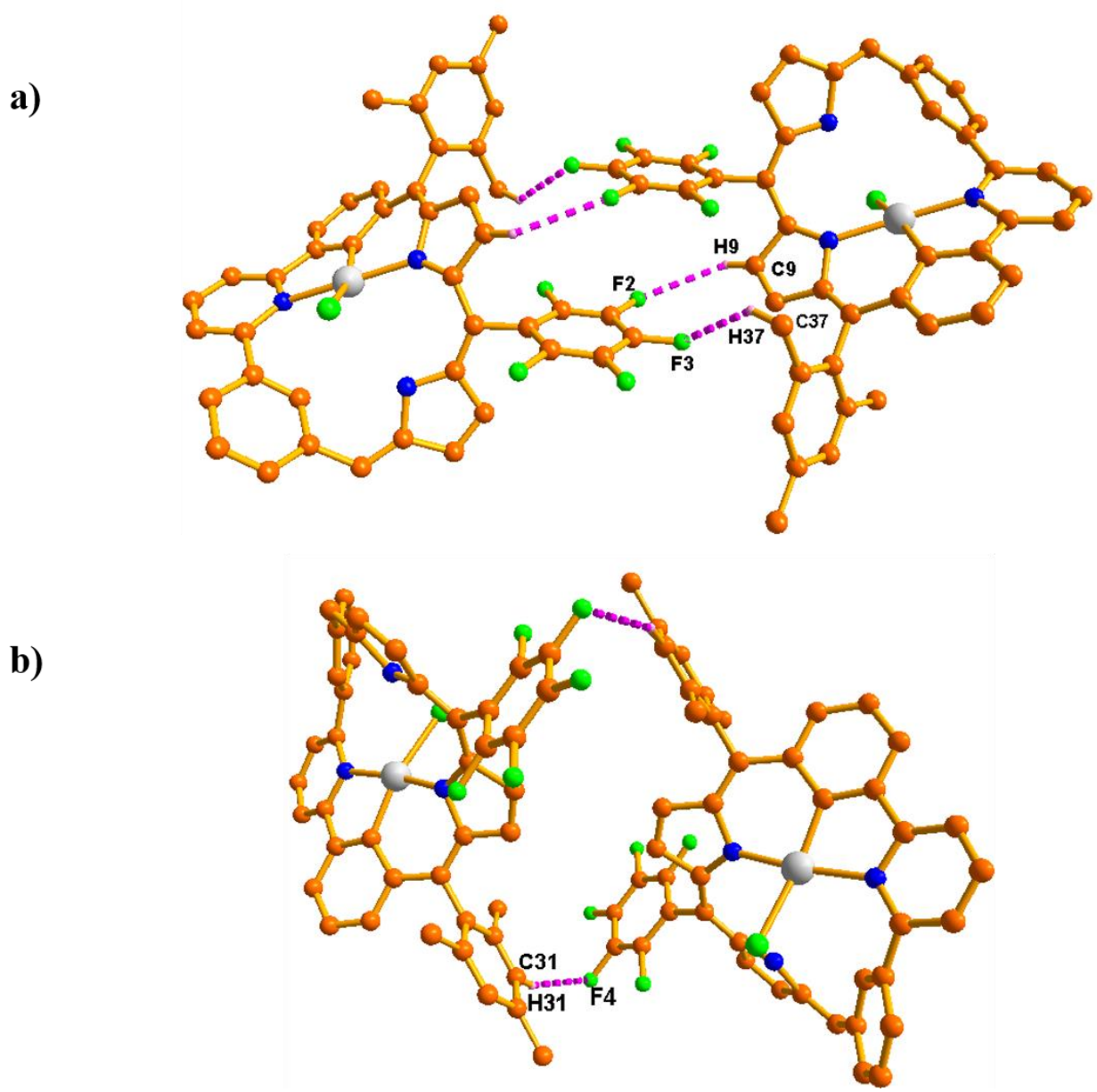


Fig. S33 Single crystal X-ray analysis of **6**. a) and b) are Self-assembled dimers. The bond distances and angles are: a) C9-H9…F2: 2.821(8) Å & 133.99(7)° and C37-H37…F3: 2.477(9) Å & 135.89(9)°; b) C31-H31…F4: 2.604(8) Å & 155.95(8)° respectively. The hydrogen atoms and the *meso*-aryl groups are omitted for clarity.

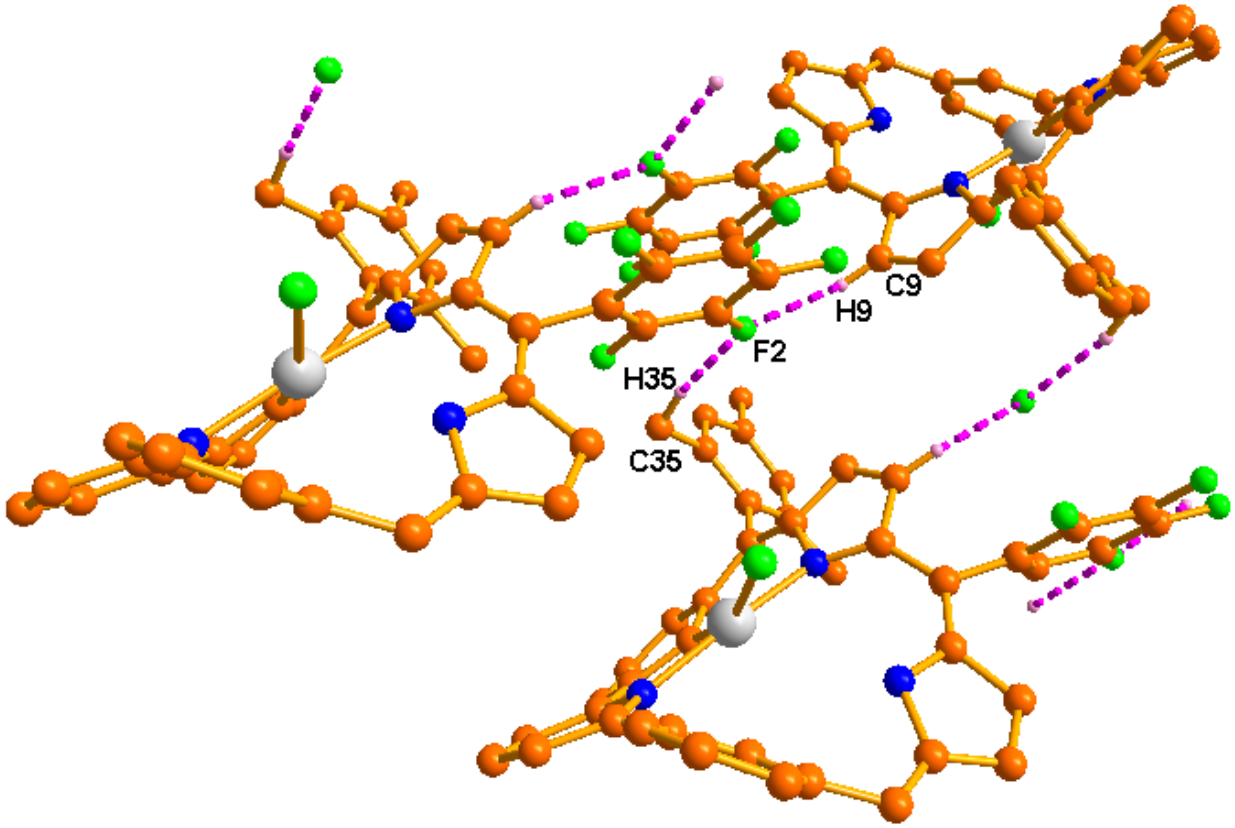


Fig. S34 Single crystal X-ray analysis of **6** in 2-D array. The bond distances and angles are C35-H35…F2: 2.579(9) Å and 159.43(7)°; C9-H9…F2: 2.821(8) Å and 133.99(7)° respectively. The hydrogen atoms and the *meso*-aryl groups are omitted for clarity.

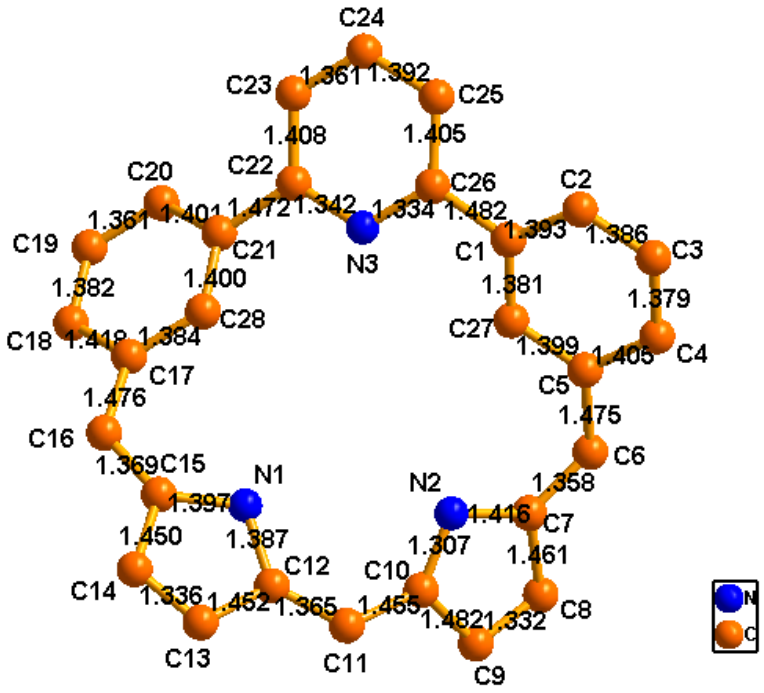


Fig. S35 Bond lengths in **4** (Å).

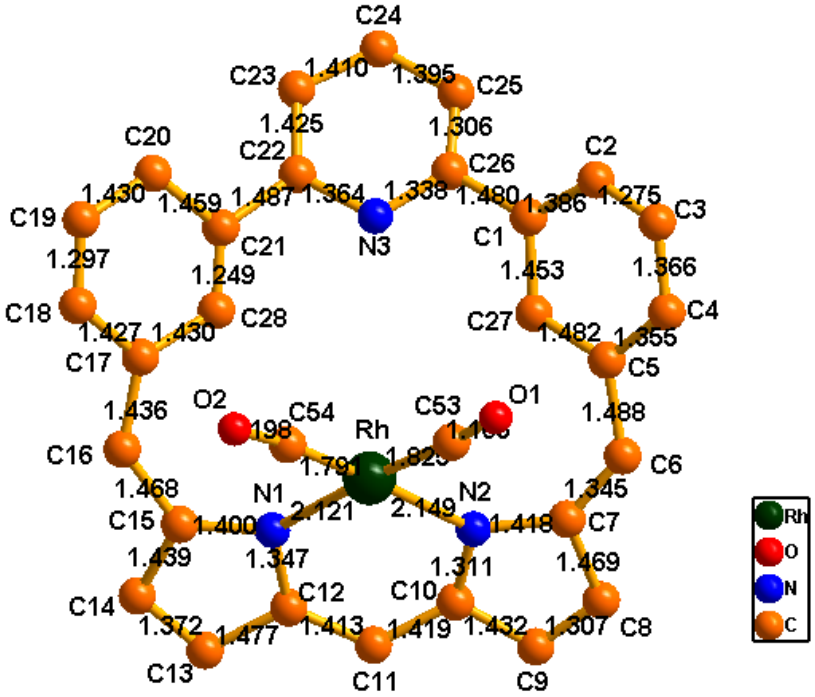


Fig. S36 Bond lengths in **5** (Å).

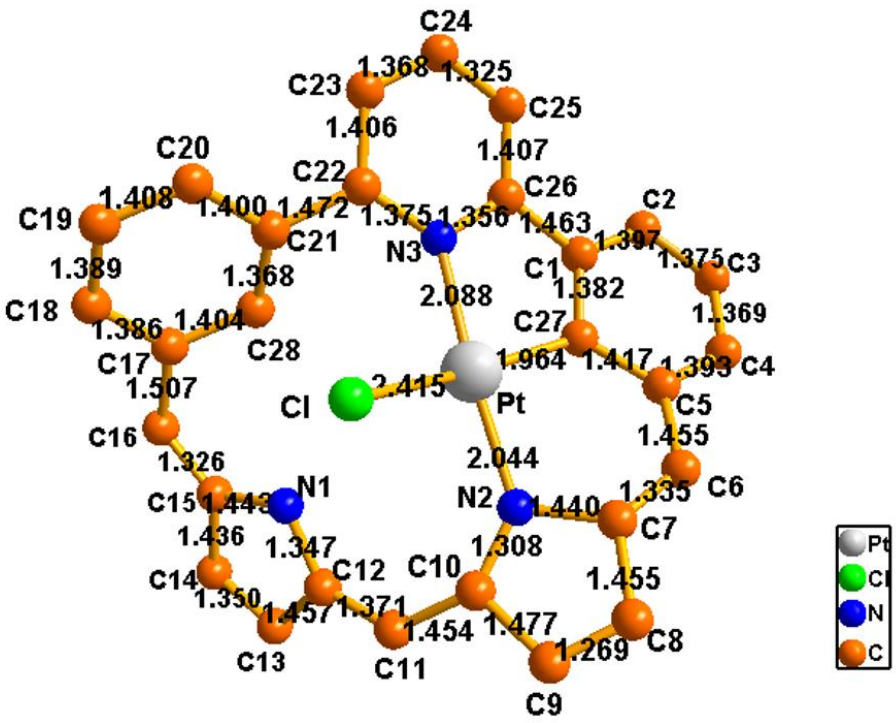


Fig. S37 Bond lengths in **6** (Å).

Table S1: Crystal data for 4, 5 and 6

Crystal parameters	**4**	**5**	**6**
Formula	$C_{52}H_{38}F_5N_3$	$C_{54}H_{37}F_5N_3O_2Rh$	$C_{52}H_{37}F_5N_3ClPt$
M/g mol^{-1}	799.85	957.79	1029.39
T/K	100	293(2)	293(2)
Crystal dimensions/mm^3	0.729 × 0.452 ×0.192	0.22 × 0.15 × 0.12	0.362 × 0.25 × 0.212
Crystal system	triclinic	orthorhombic	monoclinic
Space group	P-1	$C222_1$	$C2/c$
a/Å	12.1765(4)	12.7471(2)	31.6392(15)
b/Å	13.0482(6)	24.2024(4)	8.7956(4)
c/Å	15.2310(5)	35.7587(13)	37.084(2)
α/°	111.513(4)	90	90
β/°	112.548(4)	90	93.548(5)
γ/°	93.946(3)	90	90
V/Å^3	2016.53(15)	11031.9(5)	10300.1(9)
Z	2	8	1
ρcalcd/mg m^{-3}	1.317	1.156	1.489
μ/mm^{-1}	0.765	2.958	5.819
F(000)	832.0	3920.0	4593.0
Reflns. collected	28909	22736	39416
Indep.reflns.[R(int)]	7384 [0.2074]	11555 [0.0730]	9420 [0.1227]
Max/min transmission	0.863, 0.693	0.701, 0.617	0.291, 0.218
Data/restraints/parameters	7384/0/535	11555/582/592	9420/0/565
GOF on F^2	0.952	1.120	0.994
Final R indices[I > 2σ(I)]	R_1 = 0.0804, wR_2 = 0.2193	R_1 = 0.1014, wR_2 = 0.2736	R_1 = 0.0907, wR_2 = 0.2424
R indices (all data)	R_1 = 0.1331, wR_2 = 0.2602	R_1 = 0.1123, wR_2 = 0.2901	R_1 = 0.1237, wR_2 = 0.2739
Largest diff peak and hole [e Å^{-3}]	0.41 and -0.41	1.89 and -2.49	4.56 and -1.81

The crystals have been deposited in the Cambridge Crystallographic Data Centre with reference no. **CCDC 1957037 (4)**, **CCDC 1957039 (5)** and **CCDC 1957046 (6)**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The residual density is around the heavy metal atom (Pt) for **6** which might be caused by the improper absorption correction or the highly polarized electron densities.

6. Electronic absorption spectral analysis and DFT studies

Table S2. Electronic absorption spectral data for **4**, **5** and **6** (concentration ≈ 10^{-6} M)

Compd.	λ_{max}/nm (ε[$M^{-1}cm^{-1}$]x10^4)
4	299 (2.83), 359 (2.95), 552 (1.93)
5	366 (7.02), 656 (4.49), 710 (7.45)
6	309 (1.89), 389 (1.57), 495 (0.51), 700 (1.34)

The geometry optimization of **4**, **5** and **6** have been done with the solvation effect included M06-2X/SMD/6-31G(d,p) level of density functional theory (DFT)[1] using Gaussian16 suite of programs.[2] Here SMD stands for the self-consistent reaction field method used for incorporating the solvation effect due to CH_2Cl_2.[3] All the optimized geometries were confirmed as energy minima by vibrational frequency calculation (all show zero imaginary frequency).

The optimized M062X/6-31G(d,p) level geometries of **4**, **5** and **6** are presented in Fig. S38. The geometry parameters of all the structures agreed very well with the X-ray crystal data as the mean and maximum deviations observed for the bond distance parameters of the macrocycle are (0.0001 Å, 0.0008 Å) for **4**, (0.0037 Å, 0.0228 Å) for **5**, and (0.0013 Å, 0.0269 Å) for **6**. The theoretical results (Table S3 and Fig. S39 – S45) are in good agreement with the experimental values (Table S2). The preliminary results concluded that the higher molar extinction coefficient observed in **5** at 710 nm may be due to aggregate formation.

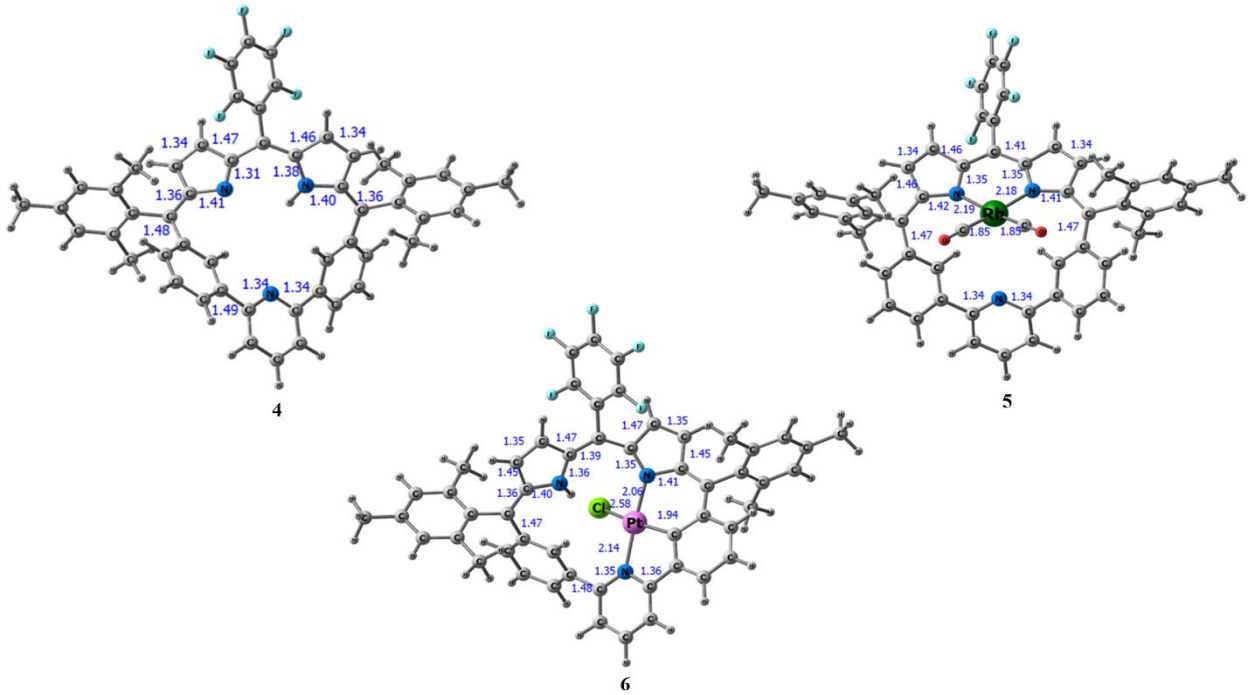


Fig. S38 Optimized geometries of **4**, **5** and **6** at M06-2X/SMD/6-31G(d,p) level DFT. All distances are in Å.

Table S3. λ_{max} (nm), oscillator strength **f**, and orbital contribution (%) of HOMO - LUMO transition in ligand **4**, **5** and **6** at various DFT/SMD/6-31G(d,p) levels.

Sl No.	Method	4			5			6		
		λ_{max}	**f**	MO Contribution	λ_{max}	**f**	MO Contribution	λ_{max}	**f**	MO Contribution
1	PBE0	556	0.6561	H-L (98.6)	646	0.5669	H-L (98.5)	633	0.5085	H-L (97.2)
2	mPW1PW91	555	0.6575	H-L (98.6)	645	0.5683	H-L (98.5)	632	0.51	H-L (97.2)
3	B1LYP	554	0.6541	H-L (98.6)	646	0.5673	H-L (98.5)	632	0.5119	H-L (97.1)
4	X3LYP	567	0.6295	H-L (98.6)	657	0.5508	H-L (98.6)	645	0.4863	H-L (97.3)
5	B971	571	0.627	H-L (98.6)	660	0.5495	H-L (98.7)	649	0.4807	H-L (97.1)
6	B972	567	0.6334	H-L (98.6)	655	0.5536	H-L (98.6)	643	0.4891	H-L (97.0)
7	B3PW91	574	0.6202	H-L (98.6)	662	0.5422	H-L (98.6)	652	0.4713	H-L (97.1)

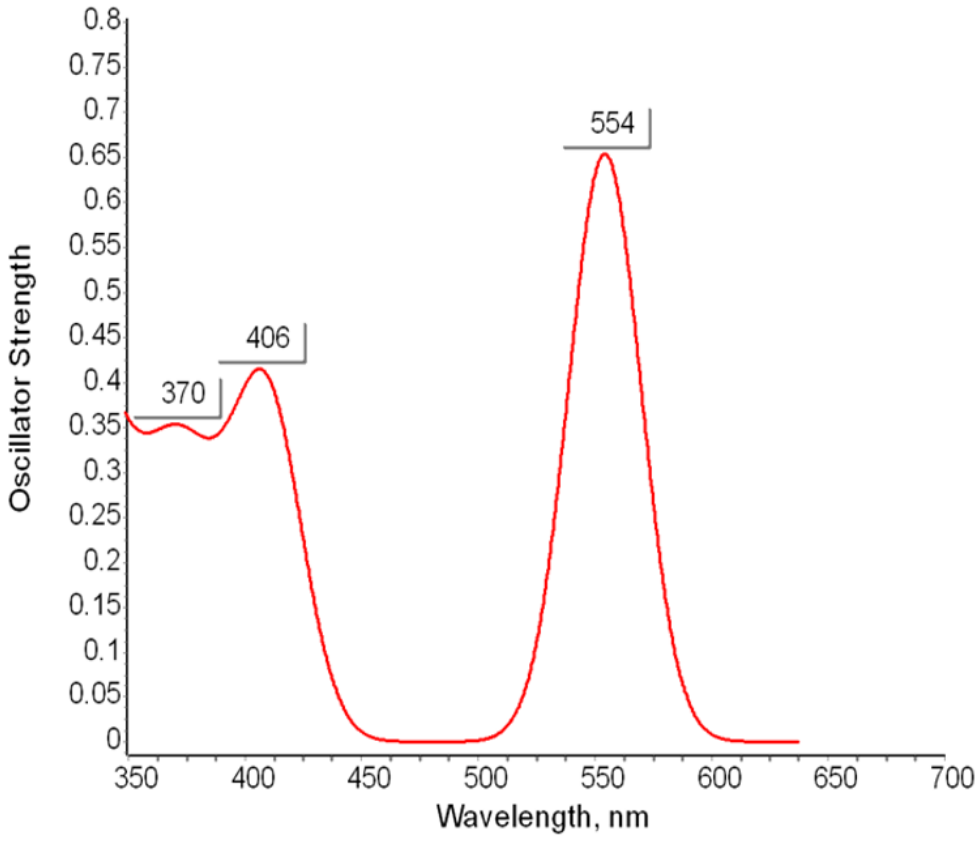


Fig. S39 TD-DFT absorption spectrum of **4**.

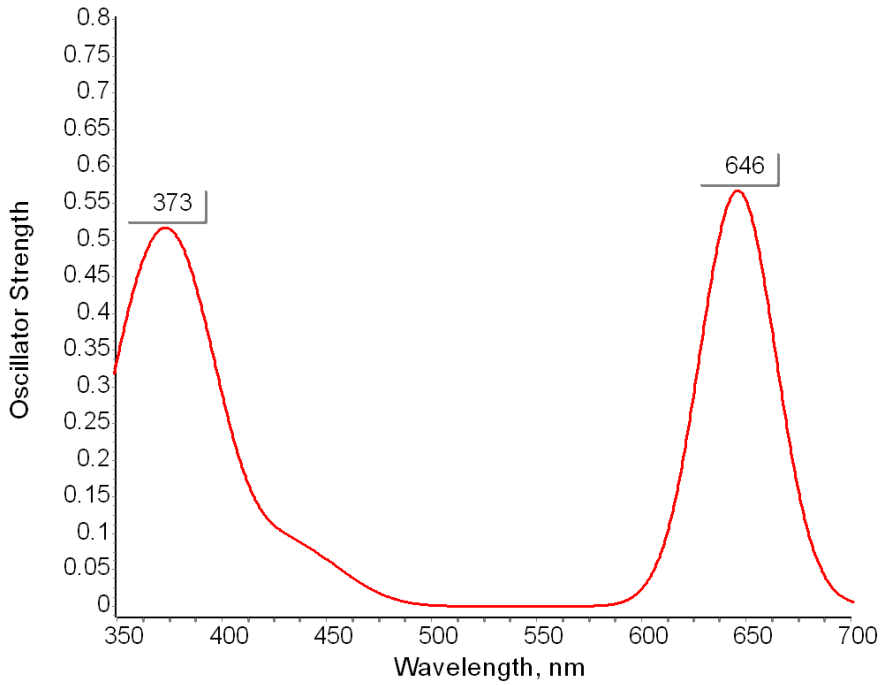


Fig. S40 TD-DFT absorption spectrum of **5**.

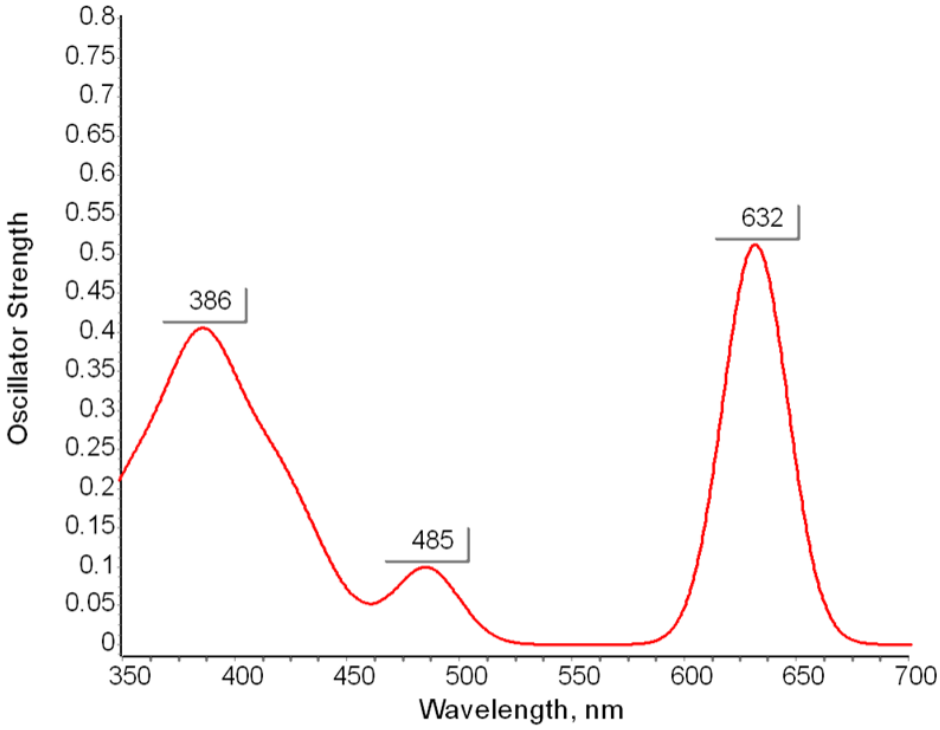
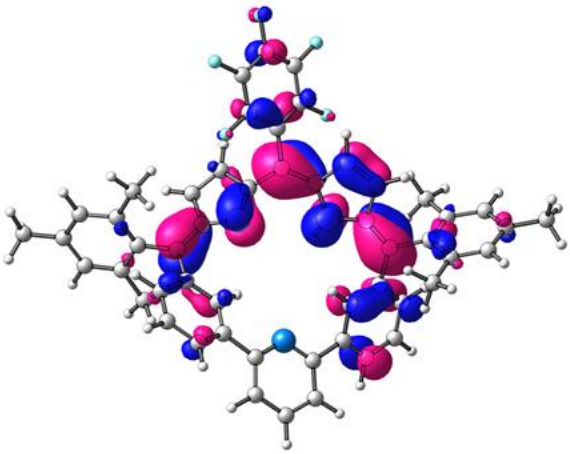
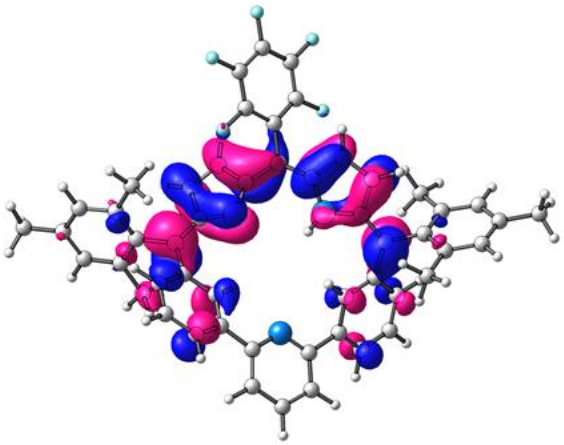


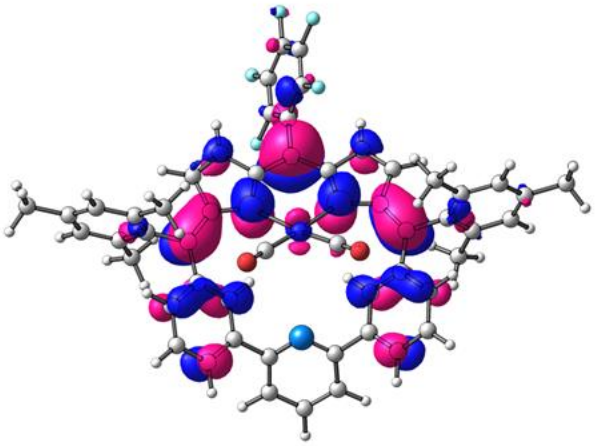
Fig. S41 TD-DFT absorption spectrum of **6**.



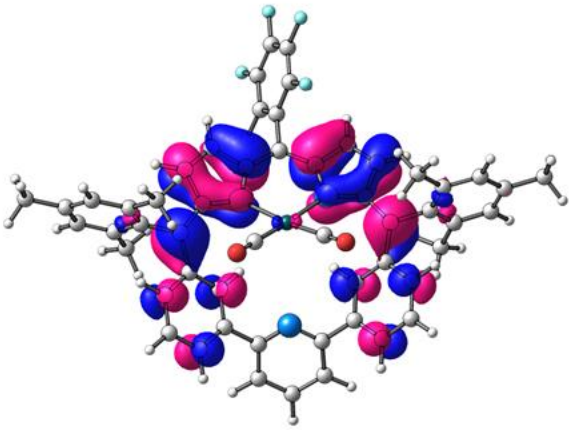
HOMO of **4** (-5.08 eV)



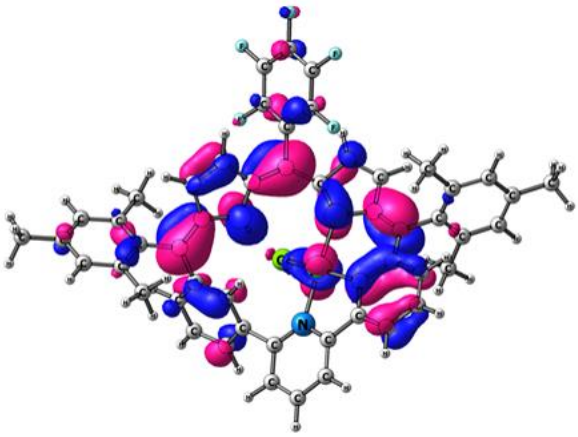
LUMO of **4** (-2.30 eV)



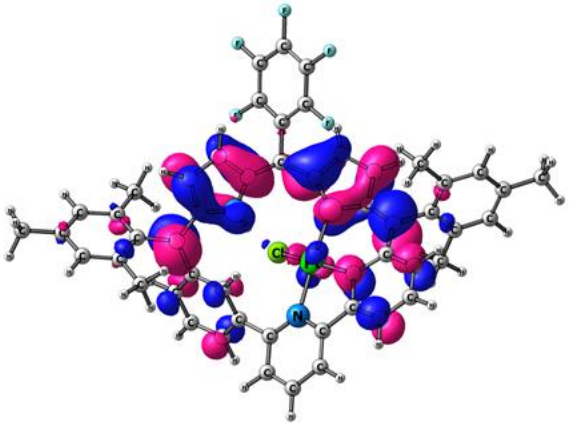
HOMO of **5** (-5.01 eV)



LUMO of **5** (-2.56 eV)



HOMO of **6** (-4.84 eV)



LUMO of **6** (-2.31 eV)

Fig. S42 HOMO and LUMO distributions for **4**, **5** and **6**.

Optimized structure of molecules at M06-2X/SMD/6-31G(d,p) level. All the X, Y, Z coordinates are given in Å.

Atoms and their X, Y, Z Coordinates of 4:

Structure 4

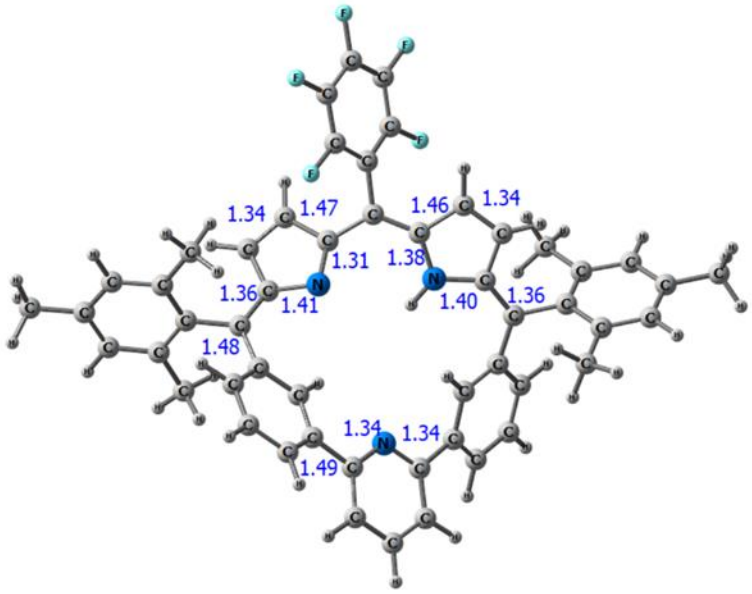


Fig. S43 Optimized structure of **4** at M06-2X/SMD/6-31G(d,p) level.

All the X, Y, Z coordinates are given in Å.

F	2.165775000	3.274153000	-1.581171000
F	-1.513128000	4.271890000	1.221945000
F	2.670894000	5.893443000	-1.828886000
F	1.078423000	7.719766000	-0.592363000
F	-1.017558000	6.880506000	0.923413000
N	1.572407000	0.246823000	0.016093000
N	-0.257847000	-4.104998000	-0.332186000
C	2.882229000	0.057899000	0.504353000
C	-3.422479000	1.718988000	-0.756361000
H	-4.420529000	1.983447000	-1.077368000
C	-2.618166000	-2.634300000	0.226642000
H	-1.968026000	-2.240785000	-0.550036000

C	-3.987734000	-0.523306000	0.182712000
C	-3.081296000	0.423347000	-0.176753000
C	0.286363000	3.659964000	-0.195666000
C	-2.314510000	2.475866000	-0.816421000
H	-2.226156000	3.478926000	-1.208947000
C	1.238502000	1.458454000	0.399539000
C	-1.352922000	-4.769551000	0.047259000
C	-1.193474000	1.705700000	-0.279438000
C	5.191583000	-0.793943000	0.485934000
C	-3.672977000	-1.860866000	0.723208000
C	2.213651000	-2.800317000	-0.517112000
H	1.509180000	-2.474806000	0.240136000
C	5.736180000	-1.667329000	1.447165000
C	3.282046000	1.211686000	1.315092000
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C	3.748262000	-0.917143000	0.111552000
C	3.394138000	-2.081431000	-0.724583000
C	1.359953000	4.135910000	-0.954637000
C	7.909323000	-0.598526000	1.171956000
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C	-5.442239000	-0.190566000	0.051154000
C	-4.318953000	-3.719128000	2.147211000
H	-4.973642000	-4.134026000	2.906974000
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C	4.030754000	-3.669287000	-2.441814000
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C	6.003689000	0.161820000	-0.148481000

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C	0.060651000	2.203293000	-0.030063000
C	0.701771000	-6.157194000	-1.107580000
H	1.545638000	-6.684858000	-1.536613000
C	2.866105000	-4.394438000	-2.210153000
H	2.662022000	-5.284436000	-2.797159000
C	2.270184000	2.093985000	1.237803000
H	2.192529000	3.072315000	1.694089000
C	1.638857000	5.486437000	-1.090394000
C	4.310301000	-2.537625000	-1.685925000
H	5.238930000	-1.996584000	-1.840735000
C	-4.524568000	-2.424427000	1.689584000
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C	-1.492810000	-6.148973000	-0.140051000
H	-2.406628000	-6.655610000	0.148839000
C	7.353902000	0.239328000	0.207292000
H	7.985634000	0.973456000	-0.287904000
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C	0.827454000	6.420074000	-0.462755000
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H	-8.162035000	-1.027445000	-1.810414000
C	-5.591014000	-1.841459000	-1.869184000
H	-4.662643000	-1.458585000	-2.304095000
H	-6.277309000	-2.091209000	-2.681398000
H	-5.339598000	-2.768326000	-1.341438000
C	5.457230000	1.077267000	-1.217628000

H	4.839900000	0.527858000	-1.935480000
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H	4.825362000	1.865776000	-0.795002000
C	-7.413176000	0.993688000	0.796095000
H	-7.880748000	1.696399000	1.482631000
C	-0.443636000	-6.844903000	-0.726662000
H	-0.516034000	-7.916514000	-0.883448000
C	-6.214753000	-0.836782000	-0.934412000
C	-8.189384000	0.381195000	-0.185922000
C	7.083189000	-1.547080000	1.781187000
H	7.500817000	-2.211543000	2.535158000
C	-0.245057000	5.989206000	0.302345000
C	4.876995000	-2.710274000	2.115424000
H	3.952913000	-2.273986000	2.507551000
H	5.413329000	-3.181832000	2.941696000
H	4.587201000	-3.494774000	1.407690000
C	-5.261760000	1.403826000	2.026085000
H	-4.600429000	0.698425000	2.538331000
H	-5.937392000	1.842710000	2.763875000
H	-4.629262000	2.207728000	1.632991000
C	9.362564000	-0.494524000	1.555493000
H	9.870764000	-1.456037000	1.433452000
H	9.469534000	-0.202942000	2.605365000
H	9.881566000	0.246620000	0.943437000
C	-9.652652000	0.705979000	-0.338092000
H	-9.812772000	1.398113000	-1.171999000
H	-10.050202000	1.175765000	0.564736000
H	-10.237884000	-0.194107000	-0.545909000

N	-1.689740000	0.450576000	-0.005657000
H	-1.153422000	-0.261788000	0.473074000

Atoms and their X, Y, Z Coordinates of 5:

Structure 5:

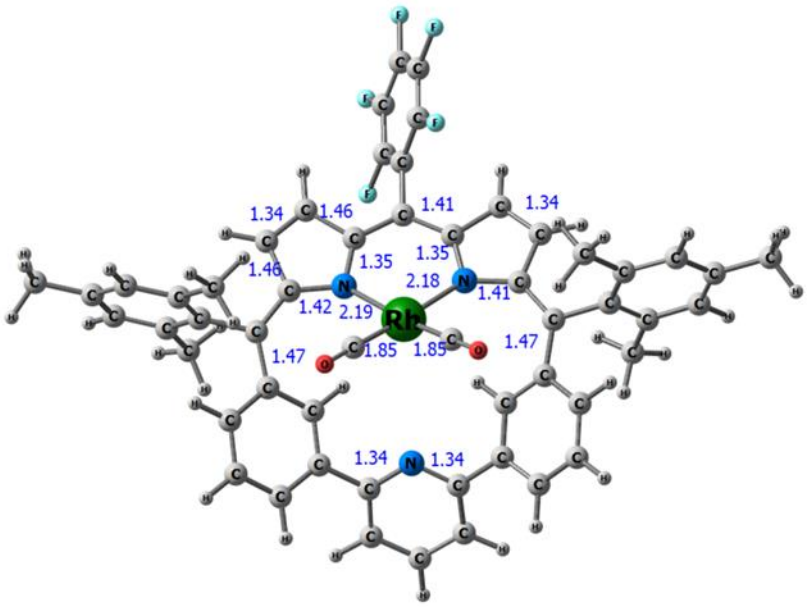

Fig. S44 Optimized structure of **5** at M06-2X/SMD/6-31G(d,p) level.

All the X, Y, Z coordinates are given in Å.

Rh	-0.018526000	-0.665953000	-0.992837000
F	1.040835000	3.613844000	2.732614000
F	-1.006070000	4.380586000	-1.449699000
F	1.037843000	6.258762000	3.212090000
F	-1.005349000	7.023150000	-0.958781000
F	0.016031000	7.978388000	1.372365000
O	-2.013552000	-2.008214000	-2.763330000
O	1.944004000	-2.176648000	-2.665331000
N	1.548374000	0.517754000	-0.023049000
N	-1.552257000	0.536158000	-0.008865000

N	0.010279000	-3.922459000	1.238175000
C	-2.481976000	2.585888000	0.526277000
H	-2.526245000	3.616291000	0.847207000
C	1.265996000	1.824027000	0.192809000
C	0.007857000	2.432379000	0.360659000
C	-2.962872000	0.437758000	-0.011187000
C	-3.511101000	1.760641000	0.288174000
H	-4.565404000	1.977466000	0.381833000
C	-1.258830000	1.819100000	0.297499000
C	5.696857000	-0.038449000	-1.790310000
C	-3.543560000	-2.065860000	-0.040845000
C	2.484022000	-2.551280000	0.746954000
H	1.713095000	-1.865809000	1.086679000
C	4.555444000	-2.995064000	-0.405904000
H	5.404045000	-2.649729000	-0.985665000
C	2.378927000	-3.908732000	1.058037000
C	0.014030000	3.898767000	0.625264000
C	4.456058000	-4.341625000	-0.086809000
H	5.218387000	-5.034632000	-0.427763000
C	3.582207000	-2.069537000	0.021958000
C	-2.343502000	-3.935566000	0.935198000
C	-1.147148000	-4.457268000	1.637767000
C	-3.821003000	-0.623416000	-0.148977000
C	-2.473341000	-2.564408000	0.710521000
H	-1.750232000	-1.880207000	1.145600000
C	-6.177532000	-0.500925000	0.733583000
C	5.262955000	-0.287024000	-0.479612000
C	1.182936000	-5.458641000	2.655558000

H	2.130552000	-5.831543000	3.028784000
C	-4.457342000	-2.980985000	-0.597457000
H	-5.280499000	-2.612967000	-1.200730000
C	3.821839000	-0.634338000	-0.215031000
C	2.956905000	0.428079000	-0.137805000
C	1.152795000	-4.433214000	1.705670000
C	0.522905000	4.427988000	1.809940000
C	7.043273000	0.267620000	-2.012652000
H	7.378470000	0.456483000	-3.030152000
C	-3.284755000	-4.825818000	0.411999000
H	-3.172185000	-5.892228000	0.583967000
C	-1.214508000	-5.489096000	2.577836000
H	-2.175529000	-5.885845000	2.886971000
C	1.237446000	-1.594605000	-1.981731000
C	-5.274875000	-0.288765000	-0.328025000
C	-0.025062000	-5.978612000	3.106094000
H	-0.039048000	-6.765985000	3.853150000
C	-4.330681000	-4.344206000	-0.370112000
H	-5.045935000	-5.033875000	-0.806529000
C	4.737849000	-0.118952000	-2.950962000
H	5.260575000	0.040587000	-3.896656000
H	3.942209000	0.629310000	-2.869525000
H	4.253402000	-1.100247000	-2.989150000
C	3.375929000	-4.802552000	0.658052000
H	3.280113000	-5.858617000	0.892017000
C	2.490755000	2.622072000	0.197931000
H	2.545131000	3.690250000	0.348054000
C	6.175037000	-0.232297000	0.591373000

C	-1.294348000	-1.504379000	-2.031699000
C	7.507024000	0.083645000	0.329990000
H	8.208989000	0.136314000	1.160065000
C	-7.524815000	-0.199328000	0.546109000
H	-8.218235000	-0.350371000	1.371241000
C	3.505989000	1.782798000	-0.046264000
H	4.557388000	2.024122000	-0.100347000
C	0.537102000	5.790388000	2.069188000
C	-0.492498000	4.813881000	-0.295702000
C	-5.702381000	-1.026244000	2.064635000
H	-5.449094000	-2.090649000	2.004254000
H	-6.478055000	-0.907075000	2.824443000
H	-4.803813000	-0.500054000	2.401992000
C	-8.006886000	0.292242000	-0.670221000
C	5.715567000	-0.481177000	2.004623000
H	4.909015000	0.205604000	2.282929000
H	6.539070000	-0.347581000	2.709392000
H	5.325801000	-1.497971000	2.122984000
C	-7.098585000	0.486964000	-1.708218000
H	-7.455094000	0.864594000	-2.664053000
C	-0.505551000	6.179989000	-0.055568000
C	9.409312000	0.671808000	-1.216435000
H	9.601138000	0.834786000	-2.279463000
H	10.064315000	-0.134591000	-0.871634000
H	9.700041000	1.577930000	-0.675350000
C	-4.794325000	0.442800000	-2.712810000
H	-4.145792000	1.307285000	-2.532726000
H	-5.354133000	0.629120000	-3.632167000

H	-4.141715000	-0.420333000	-2.875816000
C	7.961897000	0.335772000	-0.967326000
C	0.015664000	6.670066000	1.132368000
C	-5.736094000	0.209753000	-1.557315000
C	-9.470278000	0.607231000	-0.839631000
H	-10.090054000	-0.260761000	-0.594447000
H	-9.694689000	0.908561000	-1.865364000
H	-9.774731000	1.420668000	-0.172960000

Atoms and their X, Y, Z Coordinates of 6:

Structure 6:

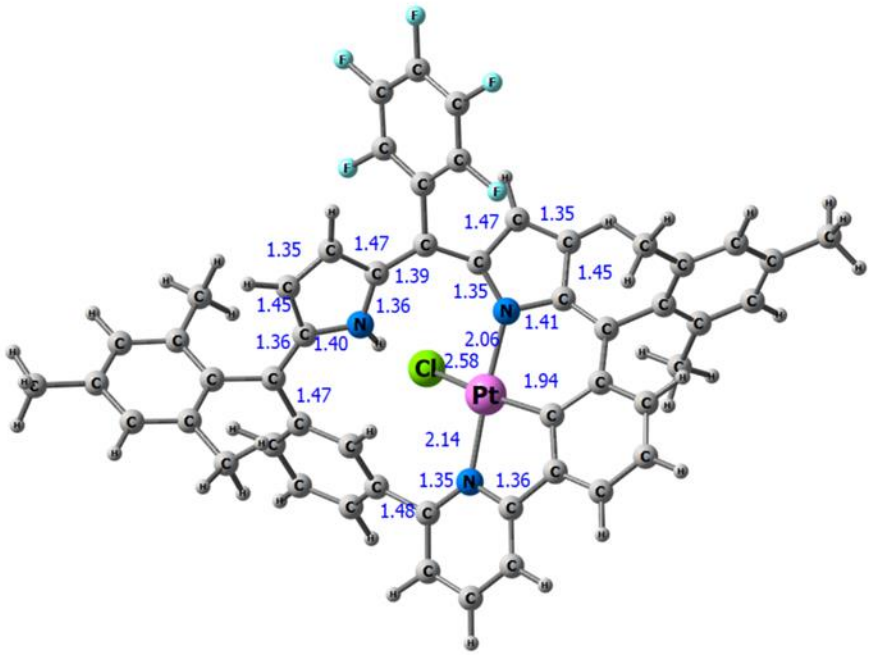

Fig. S45 Optimized structure of **6** at M06-2X/SMD/6-31G(d,p) level.

All the X, Y, Z coordinates are given in Å.

Pt	-0.671836000	-1.585037000	0.223969000
Cl	0.650734000	-0.953484000	2.346640000
F	-1.857558000	3.376428000	-1.581310000

F	1.631038000	4.248646000	1.483005000
F	1.255350000	6.882639000	1.147834000
N	-1.520768000	0.287408000	0.353394000
F	-2.223298000	6.017157000	-1.901801000
N	0.072634000	-3.541196000	-0.220145000
N	1.986225000	0.634414000	0.033102000
H	1.645874000	0.012199000	0.774225000
F	-0.671816000	7.786045000	-0.541839000
C	-2.913870000	0.313904000	0.565971000
C	-0.102674000	3.709228000	-0.032219000
C	-5.267999000	-0.214982000	0.158975000
C	-3.814150000	-0.521196000	-0.026198000
C	-1.077019000	4.214547000	-0.894980000
C	-2.167683000	-2.249958000	-0.821044000
C	-3.268183000	1.569110000	1.193725000
H	-4.260242000	1.836207000	1.530236000
C	-0.796431000	-4.248915000	-0.994852000
C	2.348181000	2.629432000	-0.968860000
H	2.131096000	3.596487000	-1.399392000
C	-3.455909000	-1.670658000	-0.857968000
C	3.511547000	1.950802000	-1.033929000
H	4.430075000	2.253332000	-1.519030000
C	-1.075196000	1.539061000	0.581892000
C	0.106004000	2.241148000	0.139542000
C	1.214350000	-4.147627000	0.181690000
C	2.320239000	-3.368245000	0.779624000
C	-6.002093000	-0.918050000	1.129820000
C	6.411413000	-0.765179000	-1.252516000

C	3.334790000	0.680535000	-0.354669000
C	3.034712000	-3.856072000	1.877878000
H	2.699679000	-4.757196000	2.382877000
C	-2.012550000	-3.530678000	-1.387275000
C	5.714982000	0.013439000	-0.303964000
C	-1.282362000	5.573969000	-1.068902000
C	6.389831000	1.007088000	0.428481000
C	-4.459646000	-2.270212000	-1.644174000
H	-5.436792000	-1.801333000	-1.699995000
C	1.372856000	1.811997000	-0.241824000
C	7.763214000	-0.515603000	-1.471314000
H	8.295168000	-1.106471000	-2.214365000
C	-7.358605000	-0.631986000	1.284543000
H	-7.927907000	-1.171965000	2.038373000
C	-5.892296000	0.746777000	-0.652153000
C	0.671183000	4.649605000	0.647468000
C	-2.155883000	2.326435000	1.182854000
H	-2.046760000	3.342975000	1.532184000
C	5.705915000	-1.843559000	-2.034515000
H	5.453138000	-2.695599000	-1.394265000
H	6.339147000	-2.207758000	-2.846551000
H	4.769074000	-1.475718000	-2.464866000
C	0.493507000	6.015771000	0.482056000
C	4.271722000	-0.255336000	-0.058431000
C	2.746028000	-2.211585000	0.136581000
H	2.208974000	-1.856492000	-0.740060000
C	-0.490072000	6.479365000	-0.377684000
C	1.454200000	-5.498614000	-0.073358000

H	2.380092000	-5.938505000	0.277157000
C	7.750939000	1.217329000	0.182934000
H	8.274883000	1.980248000	0.754428000
C	4.596475000	-2.026679000	1.675088000
H	5.484606000	-1.502583000	2.017115000
C	-5.334902000	-1.958170000	1.992525000
H	-4.908428000	-2.762480000	1.383134000
H	-6.049228000	-2.400338000	2.690225000
H	-4.512707000	-1.524427000	2.571021000
C	-7.253826000	0.999123000	-0.469447000
H	-7.741386000	1.738765000	-1.100875000
C	-4.228782000	-3.451531000	-2.333327000
H	-5.007552000	-3.884691000	-2.951423000
C	8.452107000	0.473475000	-0.762604000
C	-8.001484000	0.324626000	0.496181000
C	3.871368000	-1.518069000	0.590272000
C	-3.017715000	-4.112148000	-2.164743000
H	-2.872209000	-5.082150000	-2.628247000
C	4.167972000	-3.181848000	2.322165000
H	4.719698000	-3.558719000	3.177148000
C	-0.576598000	-5.588749000	-1.310887000
H	-1.293091000	-6.124710000	-1.918995000
C	0.545435000	-6.232011000	-0.818955000
H	0.723350000	-7.279786000	-1.036494000
C	-5.115395000	1.482952000	-1.714418000
H	-4.369658000	2.154720000	-1.275586000
H	-5.784465000	2.080171000	-2.337759000
H	-4.573543000	0.785043000	-2.361741000

C	5.695814000	1.829081000	1.487832000
H	5.108066000	2.643816000	1.051193000
H	6.431113000	2.276020000	2.160881000
H	5.007584000	1.220993000	2.081880000
C	-9.461716000	0.633398000	0.701081000
H	-10.026407000	-0.269785000	0.947353000
H	-9.900694000	1.083279000	-0.192781000
H	-9.596958000	1.339069000	1.528045000
C	9.917651000	0.711063000	-1.016460000
H	10.504506000	-0.183677000	-0.785229000
H	10.297536000	1.533675000	-0.406423000
H	10.098619000	0.953271000	-2.068379000

7. Electrochemical analysis

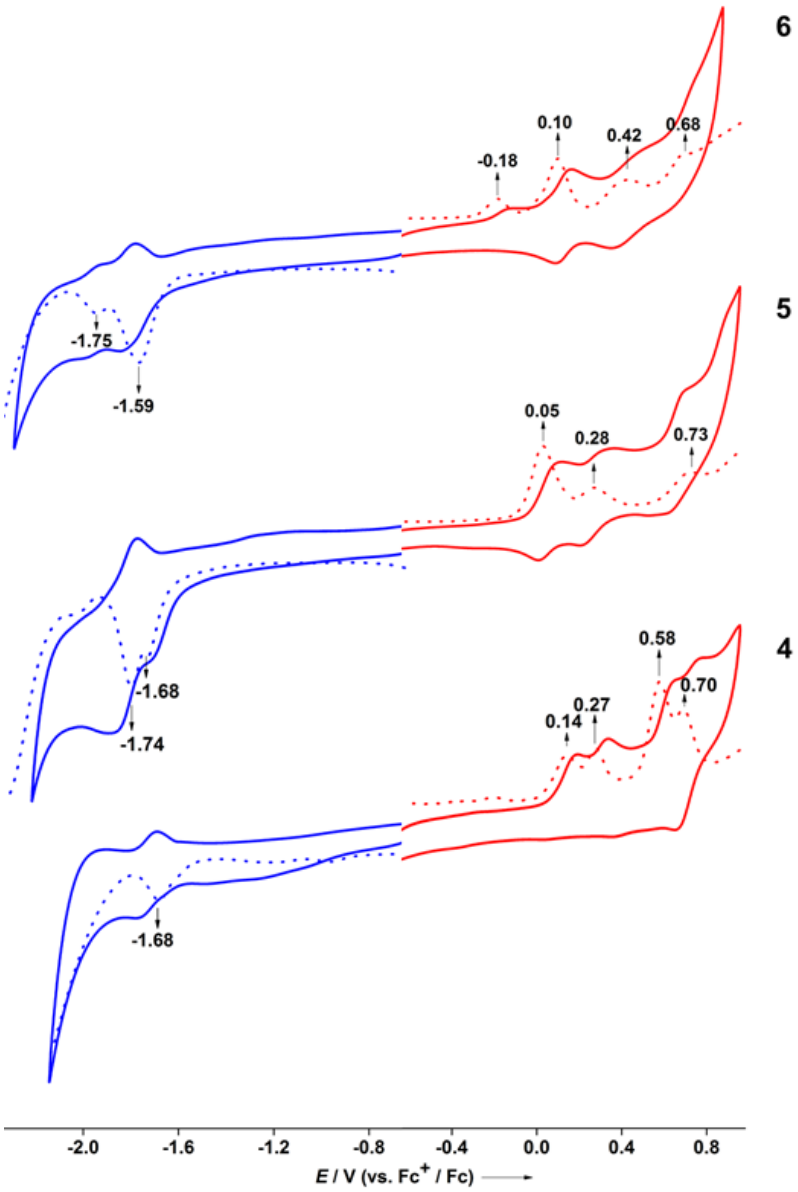

Fig. S46 Cyclic (__) and differential pulse (....) voltammograms of **4**, **5** and **6**.

Table S4. Electrochemical potentials (V vs. Fc^{+}/Fc) of **4**, **5** and **6**

Compound	E_{ox4}	E_{ox3}	E_{ox2}	E_{ox1}	E_{red1}	E_{red2}
6	0.68	0.42	0.10	-0.18	-1.59	-1.75
5	---	0.73	0.28	0.05	-1.68	-1.74
4	0.70	0.58	0.27	0.14	-1.68	---

References

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3. A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378.