Electronic supplementary information

Synthesis, Structure, and Properties of Palladium(II) Complex of α-Formyl Pyrrolyl Dipyrromethene

Sabari Panchavarnam, Rima Sengupta, and Mangalampalli Ravikanth*

Indian Institute of Technology, Powai, Mumbai, 400076, India, Fax:91-22-5723480;

Tel: 91-22-5767176; E-mail: ravikanth@chem.iitb.ac.in

Table of contents

General experimental section

Materials, methods, instrumentation and computational details:

The general chemicals such as 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), $BF_3.OEt_2$, $PdCl_2$, benzene-1,2-diamine and Silica (60− 120 mesh) were obtained from Aldrich. Acetonitrile, dichloromethane (HPLC grade) and all other solvents from Merck India, was used for spectroscopic, electrochemical measurements without further purification. The electrochemical measurements were carried out on a Bio-analytical systems epsilon potentiostat connected to C-3 cell stand. Cyclic voltammetric (CV) and Differential pulse voltammetric (DPV) studies were carried out with an electrochemical system utilizing a three-electrode configuration consisting of a glassy-carbon working electrode, platinum-wire auxiliary electrode, and a saturated calomel reference electrode. The experiments were performed in dry CH_2Cl_2 using 0.1 M TBAP as the supporting electrolyte. The $CDCl_3$ used for NMR studies was purchased from Sigma-Aldrich, USA. The ^1H and ^{13}C NMR spectra were recorded on Bruker 400 and 500 MHz instruments. Absorption spectra were recorded with Shimadzu Uv−Vis-NIR spectrophotometer. The HR mass spectra were recorded with a Q-TOF micro mass spectrometer. The Single-crystal X-ray structure analyses were carried out on a Rigaku Saturn724 diffractometer conjugated with a low-temperature attachment. Data were collected at 100 K through graphite monochromated Mo Kα radiation (λα= 0.71073 Å) by the ω-scan method. The structure was solved by direct method and refined by least-squares against F2 employing the software packages SHELXL-97,18 SIR-92,19 and WINGX.20. All non-hydrogen atoms were refined anisotropically. CCDC no. 2128295 and 2128296 for compound **6** and **10** contains the supplementary crystallographic data of these compounds. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

All DFT calculations were carried out using Gaussian 09 program package. The ground state optimized structures of compounds **10** were generated using the density functional theory (DFT) technique, hybrid functional B3LYP with basis set 6-31G(d,p), and LANL2DZ.[1,2] Functional hybrid set

and identical basis sets were used to obtain the oscillator strengths, and vertical excitation energies were obtained for $S_0 \rightarrow Sn$ transitions with the help of TD-DFT techniques.[3-7] By making use of the self-consistent reaction field (SCRF), several computations were performed in toluene under the polarizable continuum model PCM.[8-9]

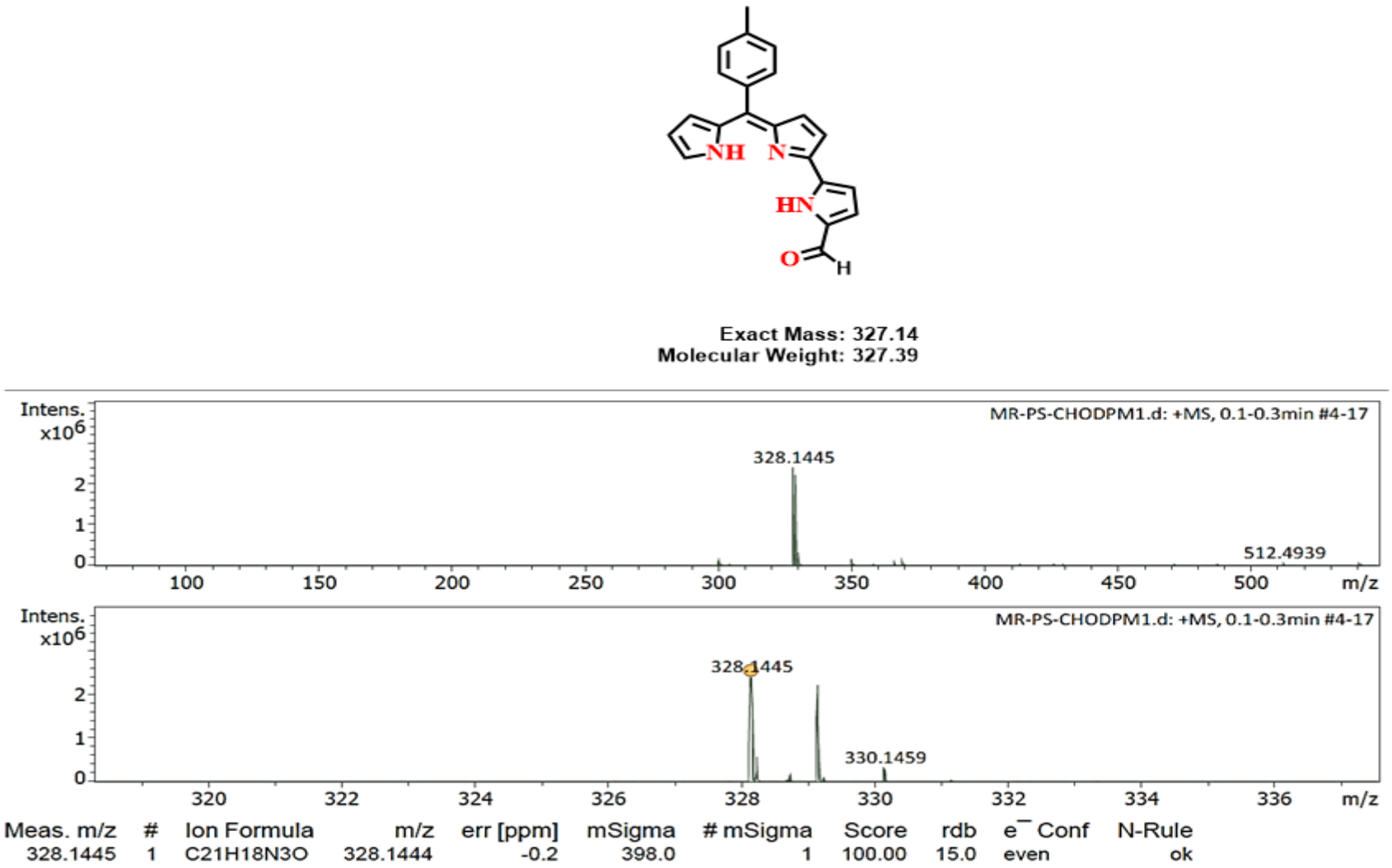

Figure S1: HR mass spectrum of compound **6.**

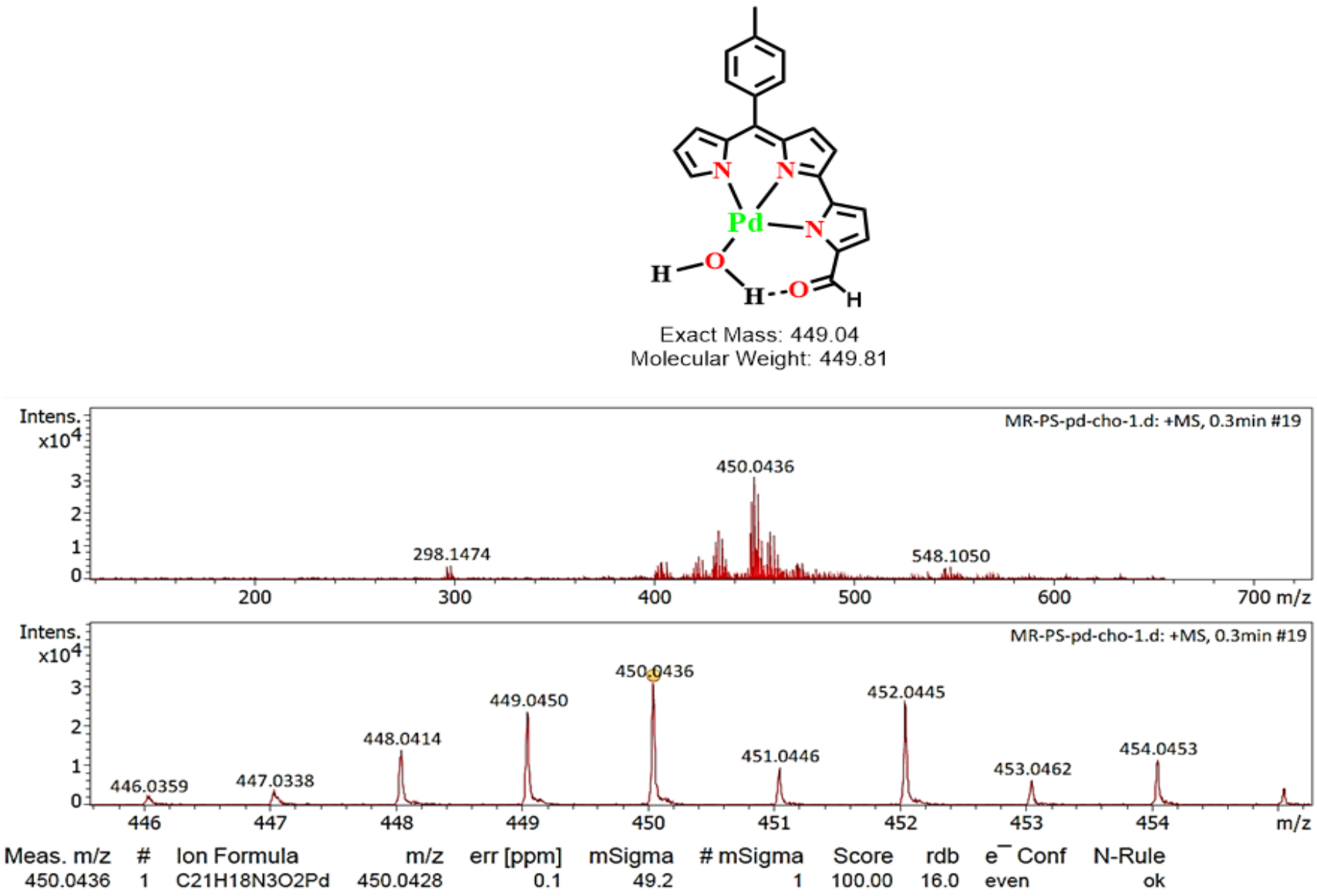

Figure S2: HR Mass spectrum of Compound **10.**

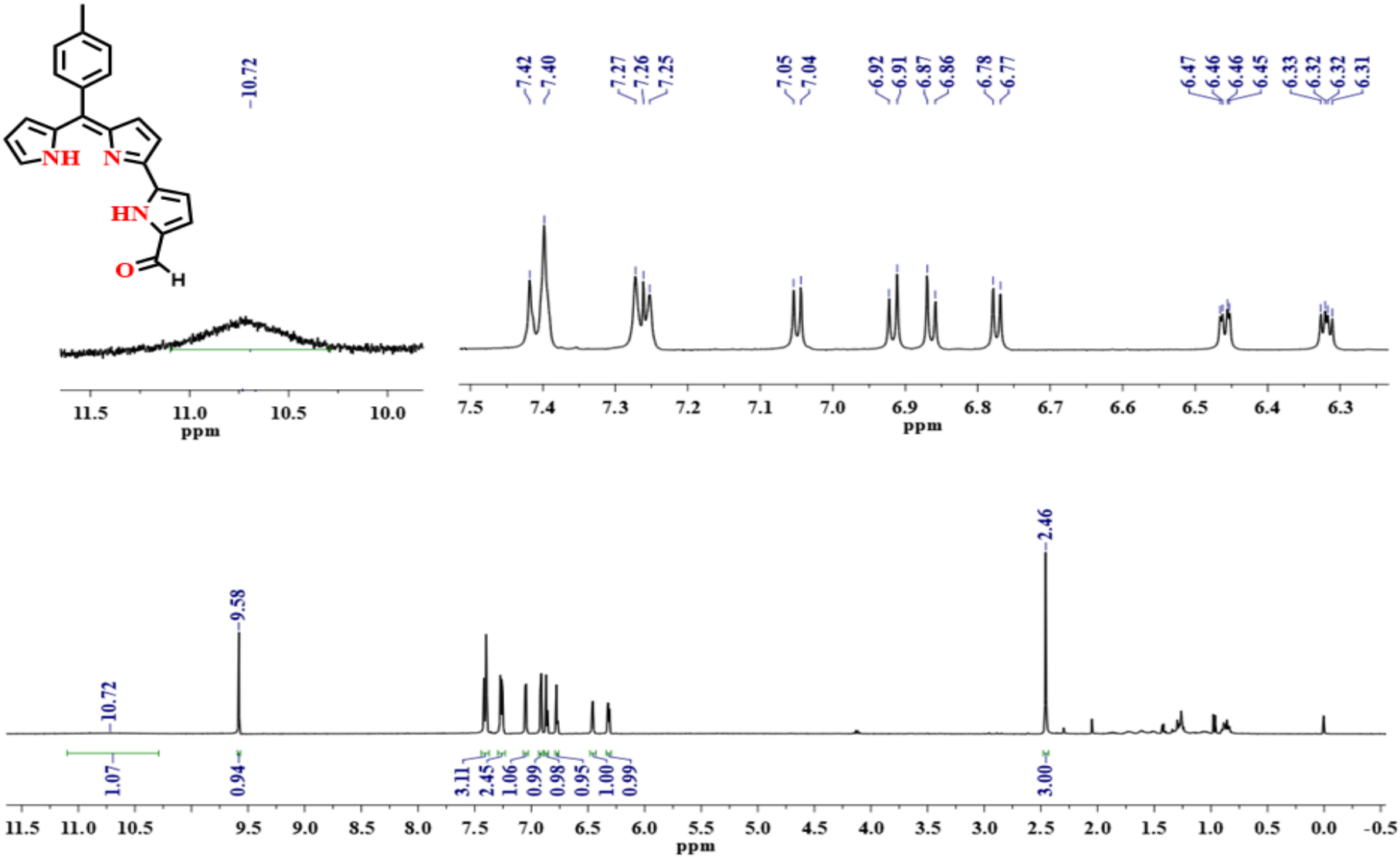

Figure S3: ^{1}H NMR spectrum of compound **9** in $CDCl_3$ at 25 °C. The inset shows the expansion.

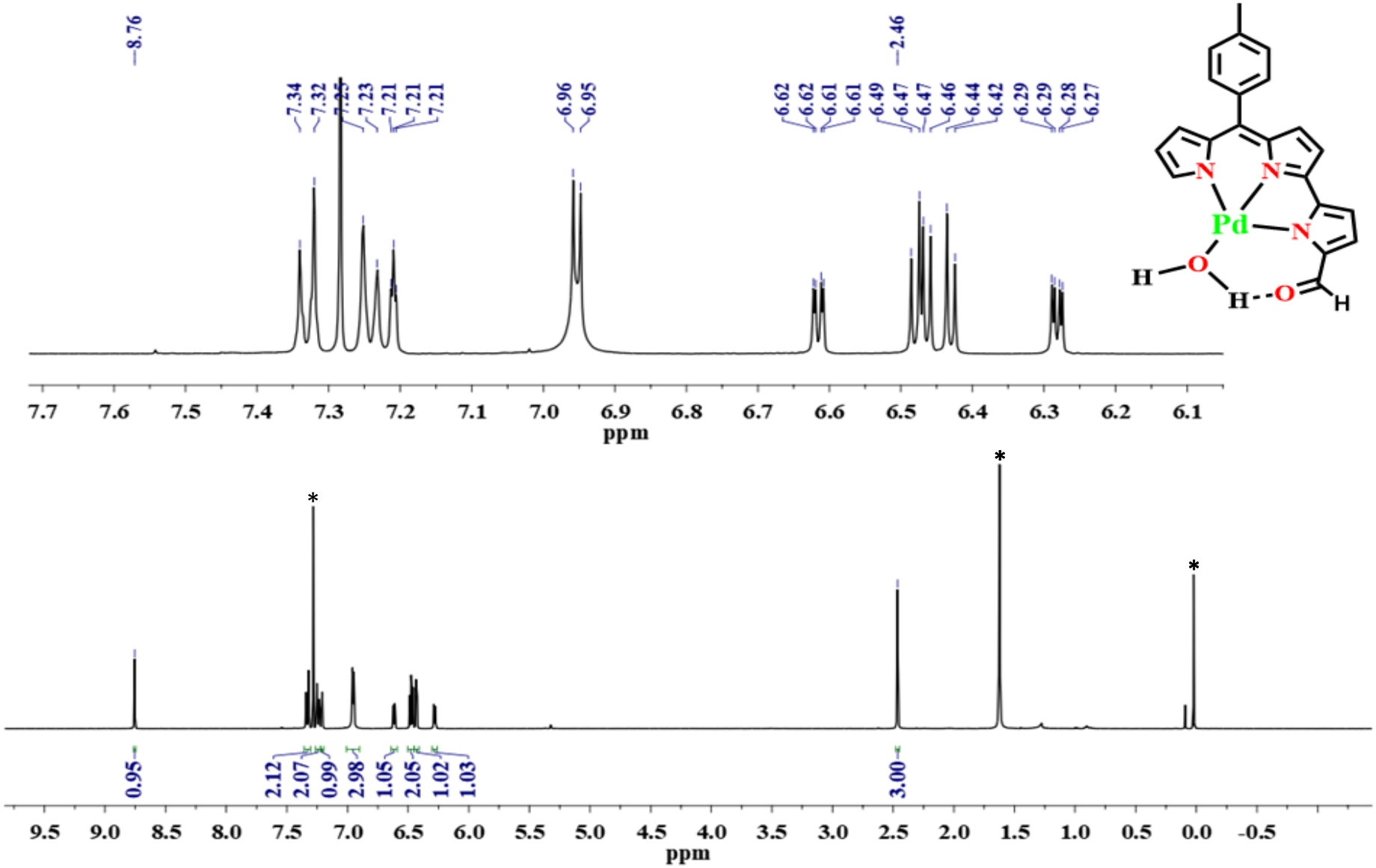

Figure S4: ^{1}H NMR spectrum of compound **10** in $CDCl_3$ at 25 °C. The inset shows the expansion. *indicates residual solvent peaks.

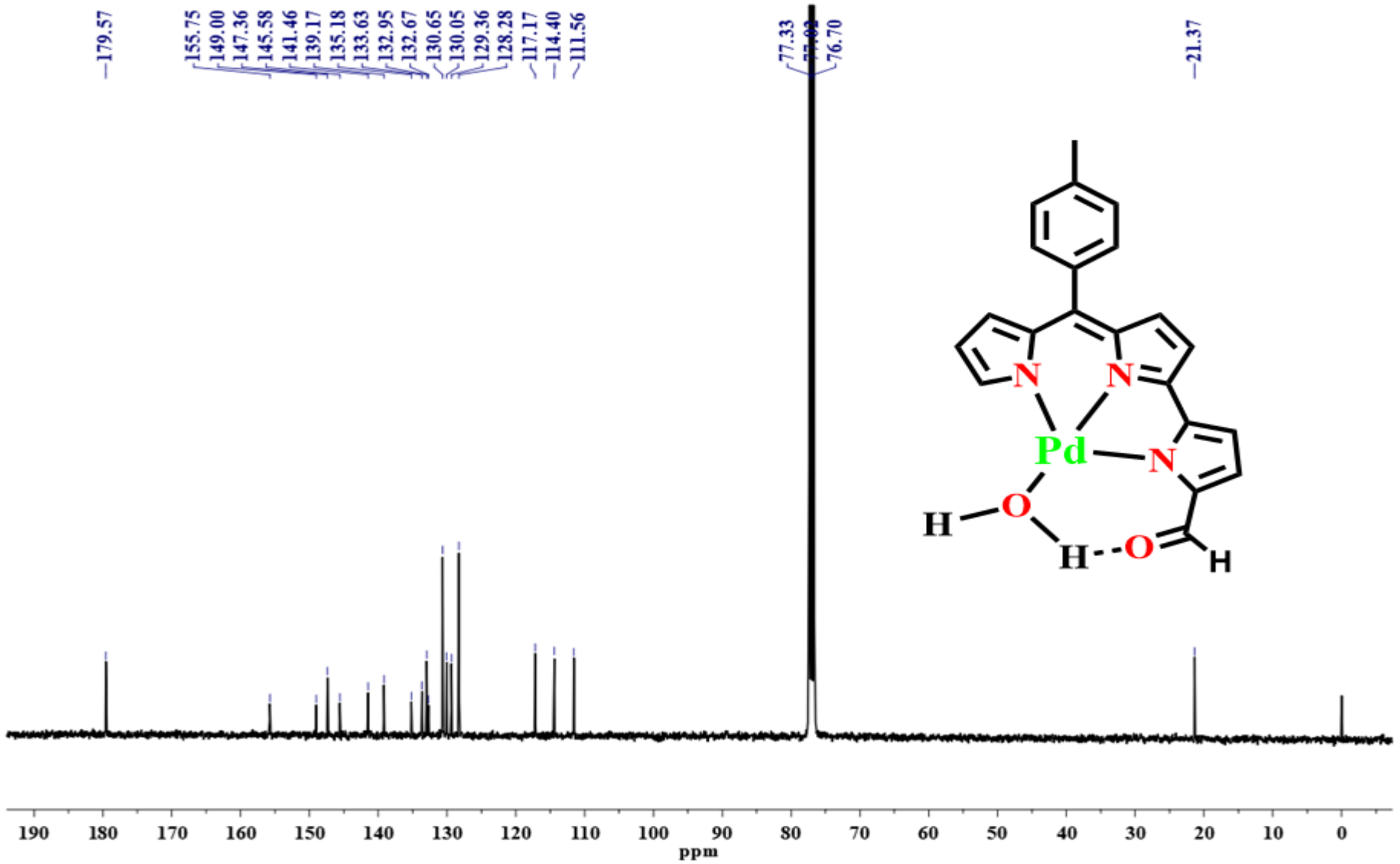

Figure S5: ^{13}C NMR spectrum of compound **10** in $CDCl_3$ at 25 °C.

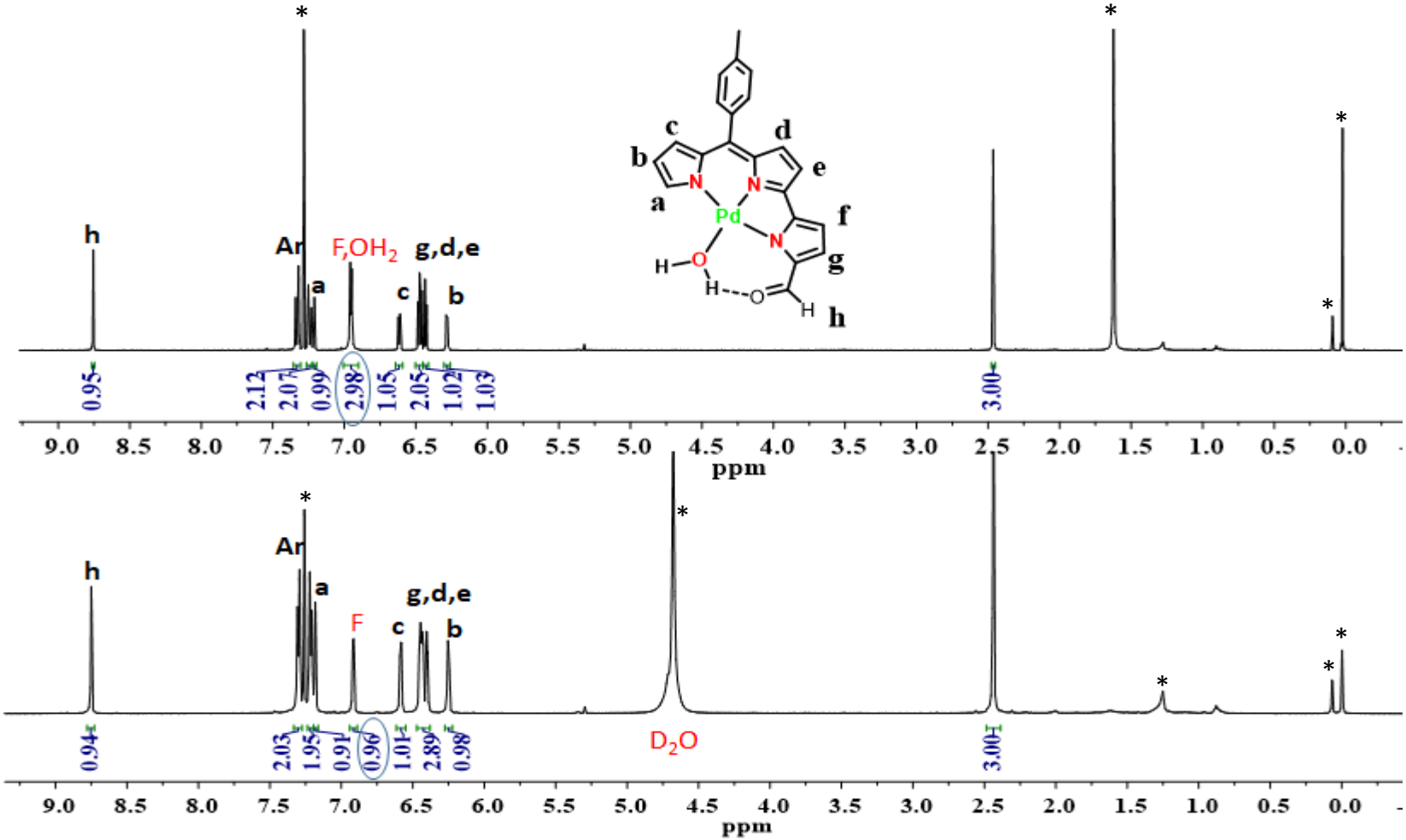

Figure S6: Comparison of ^{1}H NMR spectrum of compound **10** in $CDCl_3$ at 25 °C and D_2O experiment of compound **10**. *indicates residual solvent peaks.

Table S1 Crystal data and structure refinement for compound 6.

Empirical formula	$C_{21}H_{16}BF_2N_3O$
Formula weight	375.20
Temperature/K	105.15
Crystal system	orthorhombic
Space group	Pbca
a/Å	10.1997(8)
b/Å	15.3185(11)
c/Å	22.490(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3513.9(5)
Z	8
ρ_{calc}g/cm^3	1.4183
μ/mm^{-1}	0.103
F(000)	1552.8
Crystal size/mm^3	0.154 × 0.121 × 0.091
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.32 to 50
Index ranges	$-15 \le h \le 13$, $-21 \le k \le 23$, $-30 \le l \le 31$
Reflections collected	33811
Independent reflections	3093 [R_{int} = 0.2034, R_{sigma} = 0.2269]
Data/restraints/parameters	3093/0/254
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0560, wR_2 = 0.1210
Final R indexes [all data]	R_1 = 0.0986, wR_2 = 0.1457
Largest diff. peak/hole / e Å^{-3}	0.41/-0.47

Table S2 Bond Lengths for Compound 6.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F1	B1	1.403(4)	C6	C7	1.404(4)
F2	B1	1.388(4)	C7	C8	1.369(4)
O1	C1	1.216(4)	C8	C9	1.408(4)
N1	C2	1.382(4)	C9	C10	1.411(4)
N1	C5	1.358(4)	C10	C11	1.409(4)
N2	C6	1.363(4)	C10	C15	1.466(4)
N2	C9	1.400(4)	C11	C12	1.401(4)
N2	B1	1.551(4)	C12	C13	1.377(4)
N3	C11	1.390(4)	C13	C14	1.398(4)
N3	C14	1.353(4)	C15	C16	1.404(4)
N3	B1	1.533(4)	C15	C20	1.405(4)
C1	C2	1.427(4)	C16	C17	1.384(4)
C2	C3	1.389(4)	C17	C18	1.395(4)
C3	C4	1.381(4)	C18	C19	1.388(4)
C4	C5	1.398(4)	C18	C21	1.503(5)
C5	C6	1.447(4)	C19	C20	1.385(4)

Table S3 Bond Angles for Compound 6.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C5	N1	C2	109.8(2)	C15	C10	C9	121.1(3)
C9	N2	C6	107.3(2)	C15	C10	C11	119.7(3)
B1	N2	C6	128.4(3)	C10	C11	N3	120.7(3)
B1	N2	C9	124.2(2)	C12	C11	N3	108.1(3)
C14	N3	C11	107.9(2)	C12	C11	C10	131.2(3)
B1	N3	C11	126.5(2)	C13	C12	C11	107.3(3)
B1	N3	C14	125.5(3)	C14	C13	C12	107.6(3)
C2	C1	O1	125.5(3)	C13	C14	N3	109.2(3)
C1	C2	N1	122.3(3)	C16	C15	C10	121.8(3)
C3	C2	N1	107.2(3)	C20	C15	C10	120.6(3)
C3	C2	C1	130.4(3)	C20	C15	C16	117.6(3)
C4	C3	C2	107.6(3)	C17	C16	C15	121.1(3)
C5	C4	C3	108.4(3)	C18	C17	C16	120.9(3)
C4	C5	N1	107.0(3)	C19	C18	C17	118.3(3)
C6	C5	N1	126.9(3)	C21	C18	C17	120.3(3)
C6	C5	C4	126.2(3)	C21	C18	C19	121.4(3)
C5	C6	N2	126.6(3)	C20	C19	C18	121.3(3)
C7	C6	N2	109.2(3)	C19	C20	C15	120.8(3)
C7	C6	C5	124.2(3)	F2	B1	F1	108.4(3)
C8	C7	C6	107.8(3)	N2	B1	F1	110.3(2)
C9	C8	C7	107.7(3)	N2	B1	F2	110.5(2)
C8	C9	N2	108.0(2)	N3	B1	F1	109.5(2)
C10	C9	N2	122.0(3)	N3	B1	F2	111.0(2)
C10	C9	C8	130.0(3)	N3	B1	N2	107.1(3)
C11	C10	C9	119.3(3)				

Table S4 Crystal data and structure refinement for Compound 10.

Empirical formula	$C_{21}H_{17}N_3O_2Pd$
Formula weight	449.77
Temperature/K	100(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.2123(4)
b/Å	8.5123(5)
c/Å	29.3664(14)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1802.90(17)
Z	4
ρ_{calc}g/cm^3	1.657
μ/mm^{-1}	1.051
F(000)	904.0
Crystal size/mm^3	0.11 × 0.09 × 0.07
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.982 to 50.048
Index ranges	$-8 \le h \le 8$, $-9 \le k \le 10$, $-34 \le l \le 34$
Reflections collected	10282
Independent reflections	3171 [R_{int} = 0.0698, R_{sigma} = 0.0722]
Data/restraints/parameters	3171/303/236
Goodness-of-fit on F^2	1.129
Final R indexes [I>=2σ (I)]	R_1 = 0.0910, wR_2 = 0.2385
Final R indexes [all data]	R_1 = 0.0972, wR_2 = 0.2450
Largest diff. peak/hole / e Å^{-3}	2.00/-1.13
Flack parameter	0.01(4)

Table S5 Bond Lengths for Compound 10.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd1	O2	2.058(15)	C7	C6	1.43(3)
Pd1	N1	2.047(14)	C7	C8	1.41(3)
Pd1	N2	1.924(19)	C8	C9	1.41(4)
Pd1	N3	1.998(18)	C9	C10	1.37(3)
O1	C1	1.23(2)	C11	C10	1.34(4)
N1	C2	1.37(2)	C11	C12	1.49(4)
N1	C5	1.35(2)	C12	C13	1.32(4)
N2	C6	1.36(3)	C14	C13	1.33(4)
N2	C9	1.38(3)	C15	C10	1.55(3)
N3	C11	1.44(3)	C15	C16	1.3900
N3	C14	1.37(3)	C15	C20	1.3900
C2	C1	1.42(3)	C17	C16	1.3900
C2	C3	1.40(3)	C18	C17	1.3900
C3	C4	1.39(3)	C18	C21	1.61(4)
C5	C4	1.37(3)	C19	C18	1.3900
C5	C6	1.45(3)	C20	C19	1.3900

Table S6 Bond Angles for Compound 10.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	Pd1	O2	97.5(6)	C7	C6	C5	135(2)
N2	Pd1	O2	177.7(6)	C8	C7	C6	105(2)
N2	Pd1	N1	80.8(7)	C7	C8	C9	109(2)
N2	Pd1	N3	88.3(8)	N2	C9	C8	107(2)
N3	Pd1	O2	93.4(7)	C10	C9	N2	122(2)
N3	Pd1	N1	169.1(8)	C10	C9	C8	131(2)
C2	N1	Pd1	140.9(12)	C9	C10	C15	108(2)
C5	N1	Pd1	114.1(11)	C11	C10	C9	122(2)
C5	N1	C2	105.1(15)	C11	C10	C15	130(2)
C6	N2	Pd1	115.8(13)	N3	C11	C12	100(3)
C6	N2	C9	110.1(19)	C10	C11	N3	130(2)
C9	N2	Pd1	134.0(17)	C10	C11	C12	130(2)
C11	N3	Pd1	122.9(17)	C13	C12	C11	112(3)
C14	N3	Pd1	129.9(18)	C12	C13	C14	107(3)
C14	N3	C11	107(2)	C13	C14	N3	113(3)
O1	C1	C2	130.5(17)	C16	C15	C10	127.0(15)
N1	C2	C1	126.9(16)	C20	C15	C10	112.4(16)
N1	C2	C3	110.0(16)	C20	C15	C16	120.0
C3	C2	C1	123.1(17)	C17	C16	C15	120.0
C4	C3	C2	106.4(18)	C18	C17	C16	120.0
C5	C4	C3	105.6(18)	C17	C18	C19	120.0
N1	C5	C4	112.7(17)	C17	C18	C21	123.4(19)
N1	C5	C6	113.0(17)	C19	C18	C21	114(2)
C4	C5	C6	134.2(18)	C18	C19	C20	120.0
N2	C6	C5	116.2(18)	C15	C20	C19	120.0
N2	C6	C7	108.8(19)				

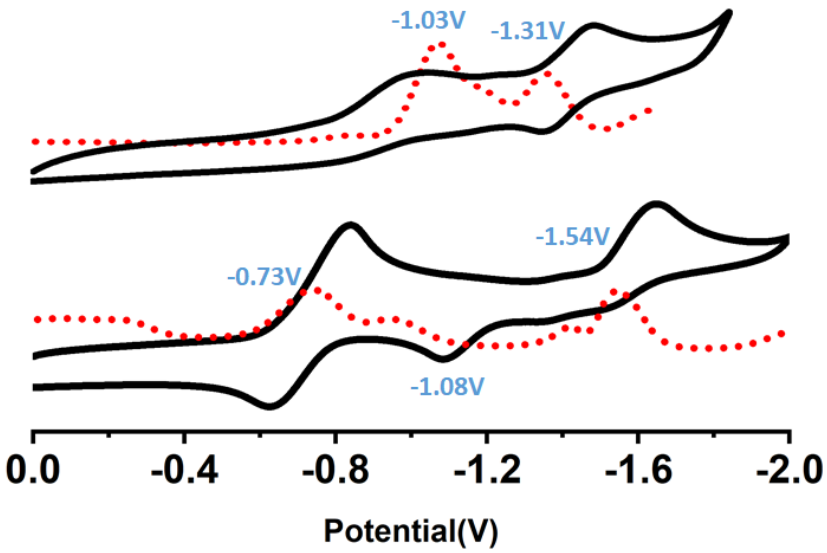

Figure S7. Comparison of cyclic voltammograms (CV) and differential pulse voltammograms (DPV) of the compounds **6** and **10** recorded in CH_2Cl_2 containing 0.1 M TBAP as supporting electrolyte recorded at 50 mV/s scan speed.

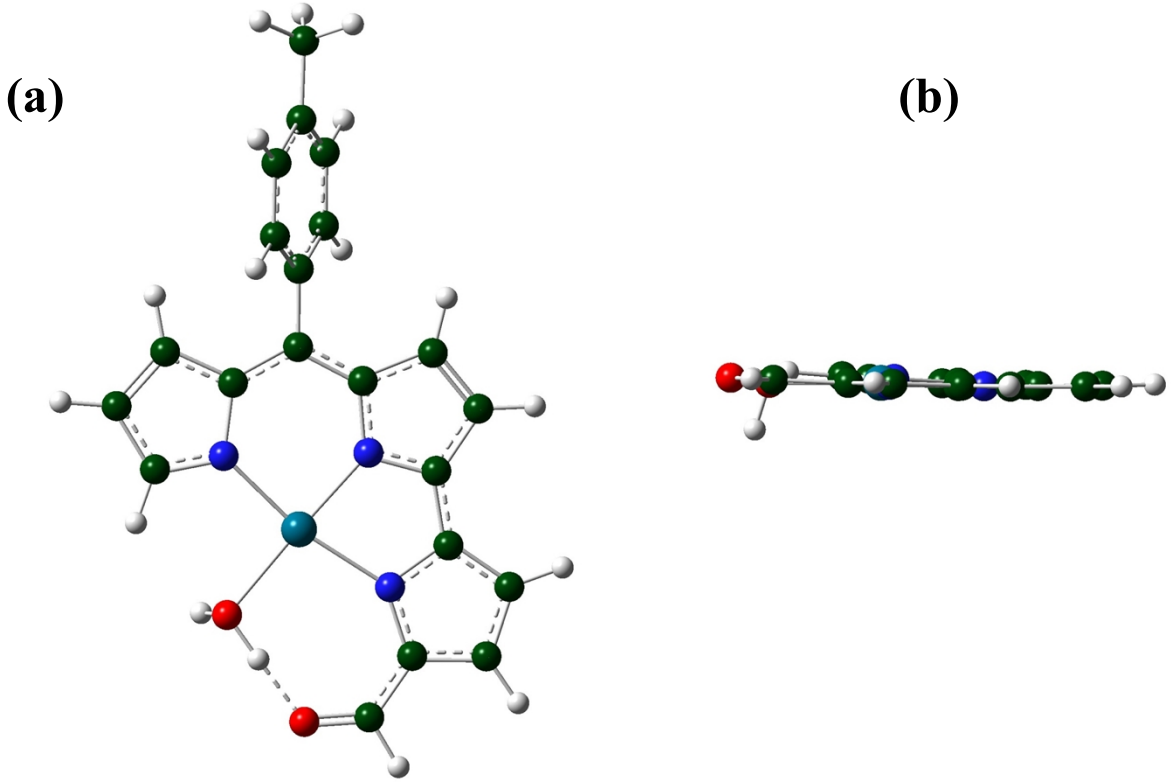

Figure S8. DFT optimized structure of compound **10**. (a) top view, (b) side view.

Table S7. S_0 optimized geometry of the compound **10** at B3LYP/6-31g (d,p) level of theory

Sum of imaginary frequencies= 0

Atom	X	Y	Z	Atom	X	Y	Z
Pd	1.624029	0.678673	0.027492	C	-1.80227	0.12141	0.017804
O	2.989788	2.300946	0.118011	C	-1.3565	1.462885	0.047916
H	3.919895	1.86523	0.014852	C	-2.16939	2.637664	0.120684
H	2.972366	2.643712	1.022484	H	-3.24714	2.643766	0.186692
O	5.249906	1.200046	-0.02604	C	-1.32441	3.733765	0.099522
N	3.026547	-0.85471	-0.01433	H	-1.59628	4.779612	0.133816
N	0.429137	-0.87489	0.000117	C	-0.01046	3.217714	0.027878
N	-0.02232	1.877929	0.008328	H	0.926013	3.757305	-0.02047
C	5.392443	-0.04146	-0.05218	C	-3.26904	-0.14029	0.009405
H	6.423361	-0.4341	-0.08307	C	-3.86615	-0.91406	1.017219
C	4.390494	-1.05021	-0.05193	H	-3.25239	-1.30395	1.823241
C	4.653399	-2.44505	-0.111	C	-5.23796	-1.16088	1.006888
H	5.637927	-2.89319	-0.14854	H	-5.67848	-1.74941	1.807879
C	3.428664	-3.09914	-0.11561	C	-6.05875	-0.65977	-0.01171
H	3.247858	-4.16428	-0.15883	C	-5.4584	0.109463	-1.01813
C	2.443367	-2.08657	-0.05804	H	-6.07074	0.509565	-1.82261
C	1.001753	-2.09398	-0.05419	C	-4.09007	0.369707	-1.00982
C	-0.02495	-3.07807	-0.11398	H	-3.64632	0.960946	-1.80455
H	0.121594	-4.14756	-0.17164	C	-7.53856	-0.95884	-0.04093
C	-1.2301	-2.3955	-0.09898	H	-7.75176	-1.83535	-0.66566
H	-2.22034	-2.82411	-0.14723	H	-8.1084	-0.12114	-0.45459
C	-0.9413	-0.99235	-0.01606	H	-7.92441	-1.17091	0.960375

References

(1) Treutler, O.; Ahlrichs, R. Efficient molecular numerical integration schemes. *J. Chem. Phys.* **1995**, *102,* 346–354.

(2) Becke, A. D. A new mixing of Hartree–Fock and local density-functional theories. *J. Chem. Phys.* **1993**, *98* 1372–1377.

(3) Hehre, W. J. Ab initio molecular orbital theory. *Acc. Chem. Res*. **1976**, *9*, 399–406.

(4) Bauernschmitt, R.; Ahlrichs, R. Treatment of electronic excitations within the adiabatic approximation of time dependent density functional theory. Chem. *Phys. Lett.* **1996**, *256*, 454–464.

(5) Gabe, Y.; Ueno, T.; Urano, Y.; Kojima, H.; Nagano, T. Tunable design strategy for fluorescence probes based on 4-substituted BODIPY chromophore: improvement of highly sensitive fluorescence probe for nitric oxide. *Anal. Bioanal. Chem*. **2006,** *386*, 621–626.

(6) Furche, F.; Ahlrichs, R. Adiabatic time-dependent density functional methods for excited state properties. *J. Chem. Phys*. **2002**, *117,* 7433–7447.

(7) Scalmani, G.; Frisch, M. J.; Mennucci, B.; Tomasi, J.; Cammi, R.; Barone, V. Geometries and properties of excited states in the gas phase and in solution: Theory and application of a time-dependent density functional theory polarizable continuum model. *J. Chem. Phys.* **2006**, *124,* 94107–94115.

(8) Cossi, M.; Barone, V.; Cammi, R.; Tomasi, Ab initio study of solvated molecules: a new implementation of the polarizable continuum model. *J. Chem. Phys. Lett.* **1996**, *255*, 327–335.

(9) Tomasi, J.; Mennucci, B.; Cammi, R. Quantum Mechanical Continuum Solvation Models. *Chem. Rev.* **2005**, *105*, 2999–3094.