Supplementary Information (SI) for New Journal of Chemistry.

†Electronic supplementary information (ESI)

Ancillary ligand induced variation in electronic spectral and catalytic properties of heteroleptic ONO-pincer complexes of ruthenium†

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[§] Equal contribution.

Contents:

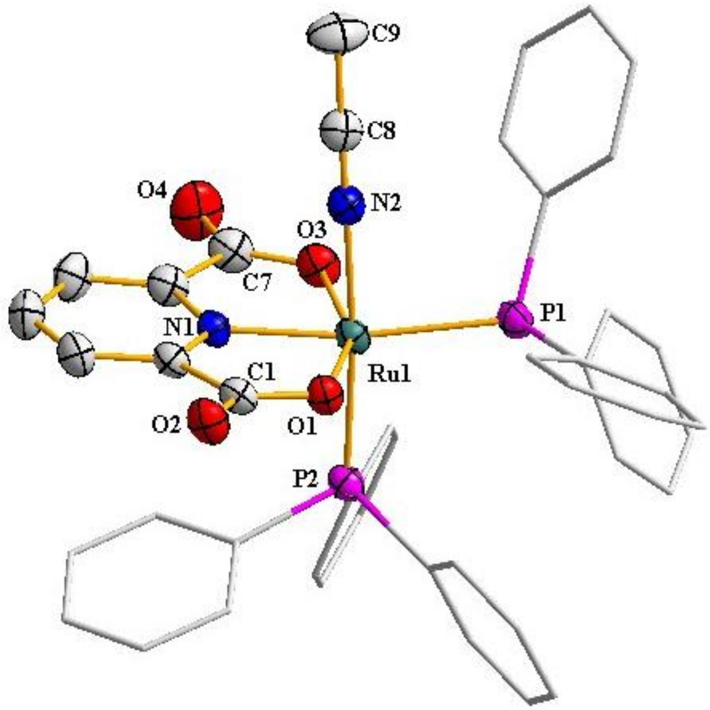


Fig. S1 ORTEP diagram showing the crystal structure of **1** (The ellipsoids are drawn at the 40% probability level).

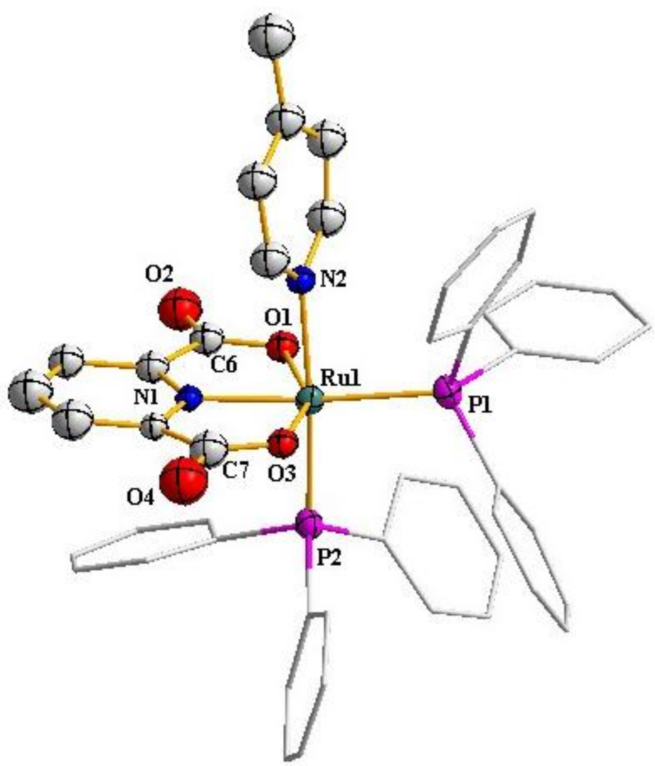


Fig. S2 ORTEP diagram showing the crystal structure of **2** (The ellipsoids are drawn at the 40% probability level).

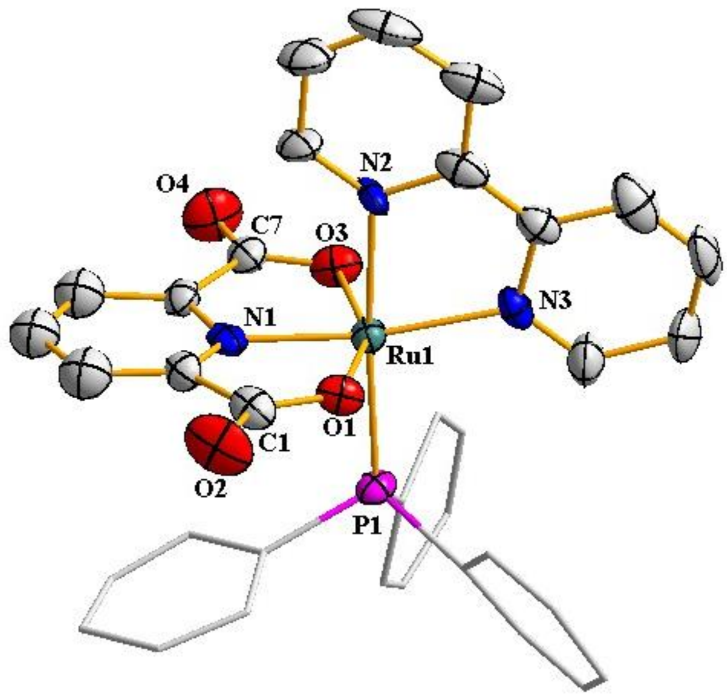


Fig. S3 ORTEP diagram showing the crystal structure of **3** (The ellipsoids are drawn at the 40% probability level).

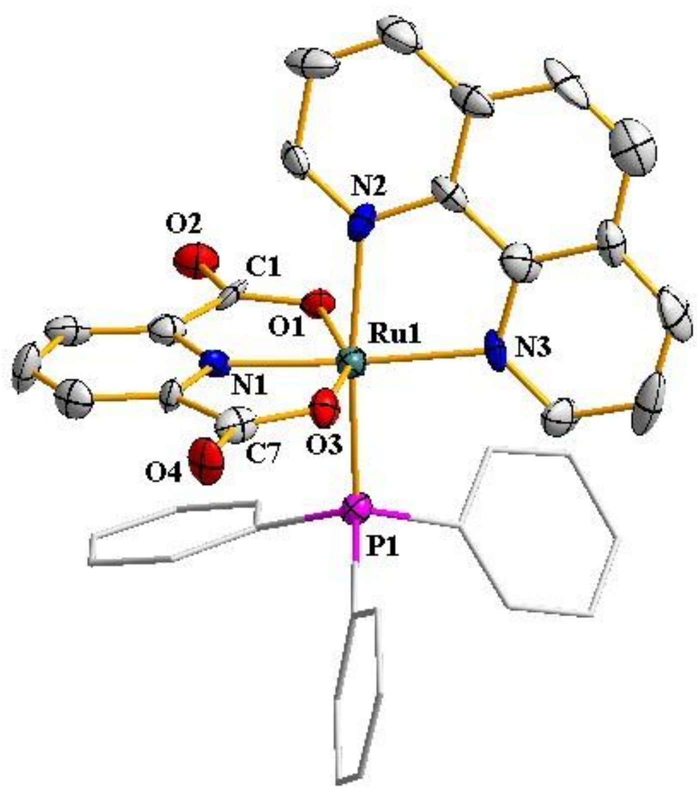


Fig. S4 ORTEP diagram showing the crystal structure of **4** (The ellipsoids are drawn at the 50% probability level).

Table S1 Selected bond distances and bond angles of **1**

Bond distances (Å)			
Ru1-N1	2.0038(15)	C1-O1	1.291(2)
Ru1-N2	2.0949(17)	C1-O2	1.226(2)
Ru1-O1	2.1394(13)	C7-O3	1.294(3)
Ru1-O3	2.1261(13)	C7-O4	1.220(3)
Ru1-P1	2.3462(5)	C8-N2	1.132(3)
Ru1-P2	2.3133(5)	C8-C9	1.452(3)
Bond angles (°)			
N1-Ru1-P1	170.72(5)	N1-Ru1-O1	77.55(5)
N2-Ru1-P2	174.94(5)	N1-Ru1-O3	78.17(6)
O1-Ru1-O3	155.43(5)	Ru1-N2-C8	172.71(16)
N1-Ru1-N2	83.42(6)	N2-C8-C9	177.0(2)

Table S2 Selected bond distances and bond angles for **2**

Bond distances (Å)			
Ru1-N1	2.000(4)	Ru1-P2	2.3255(14)
Ru1-N2	2.160(4)	C6-O1	1.282(6)
Ru1-O1	2.114(3)	C6-O2	1.235(7)
Ru1-O3	2.144(3)	C7-O3	1.300(6)
Ru1-P1	2.3374(15)	C7-O4	1.219(6)
Bond angles (°)			
N1-Ru1-P1	171.59(12)	N1-Ru1-O1	78.20(15)
N2-Ru1-P2	171.61(12)	N1-Ru1-O3	77.68(15)
O1-Ru1-O3	155.61(14)	N1-Ru1-N2	84.29(15)

Table S3 Selected bond distances and bond angles for **3**

Bond distances (Å)			
Ru1-N1	1.98(5)	Ru1-P1	2.35(5)
Ru1-N2	2.11(4)	C1-O1	1.29(3)
Ru1-N3	2.10(5)	C1-O2	1.22(2)
Ru1-O1	2.15(4)	C7-O3	1.29(4)
Ru1-O3	2.13(4)	C7-O4	1.24(2)
Bond angles (°)			
N1-Ru1-N3	170.4(4)	N1-Ru1-O1	78.3(5)
N2-Ru1-P1	172.7(3)	N1-Ru1-O3	78.9(12)
O1-Ru1-O3	156.7(7)	N2-Ru1-N3	78.0(6)

Table S4 Selected bond distances and bond angles for **4**

Bond distances (Å)			
Ru1-N1	1.982(12)	Ru1-P1	2.312(45)
Ru1-N2	2.125(11)	C1-O1	1.287(17)
Ru1-N3	2.111(12)	C1-O2	1.217(16)
Ru1-O1	2.200(10)	C7-O3	1.336(17)
Ru1-O3	2.109(10)	C7-O4	1.179(17)
Bond angles (°)			
N1-Ru1-N3	167.9(5)	N1-Ru1-O1	77.6(4)
N2-Ru1-P1	170.2 (3)	N1-Ru1-O3	78.7(4)
O1-Ru1-O3	155.9 (4)	N2-Ru1-N3	78.1(4)

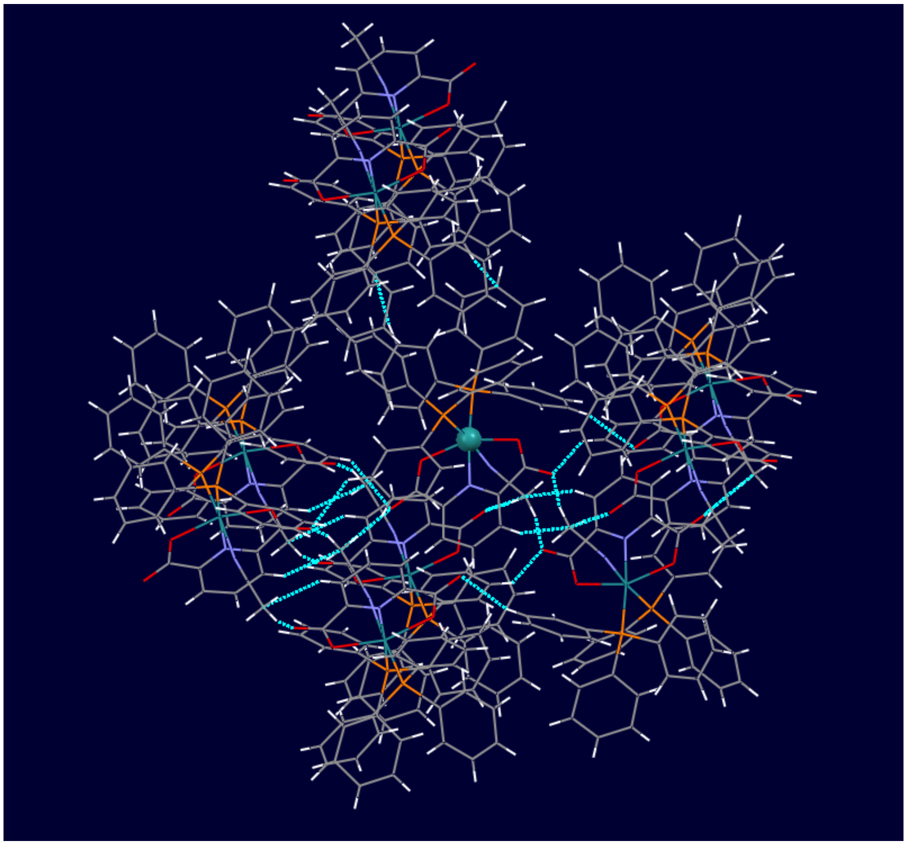


Fig. S5 Intermolecular C-H···O=C, C-H···C and C···O=C interactions in the lattice of complex **1**.

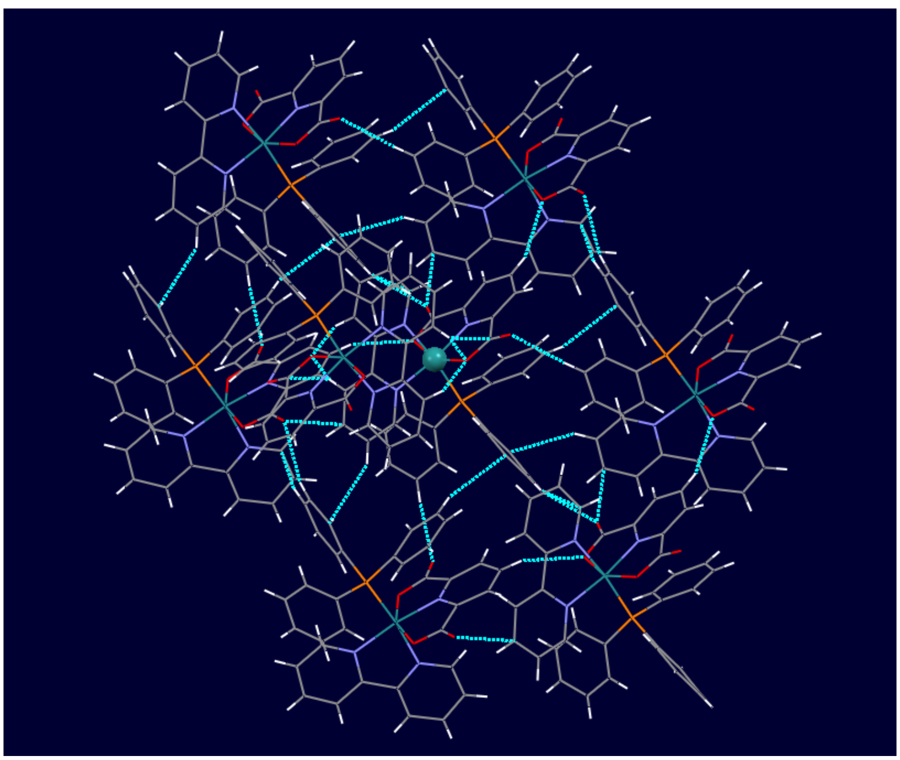


Fig. S6 Intermolecular C-H···O=C, C-H···C, C-H···O-C and C···O=C interactions in the lattice of complex **3**.

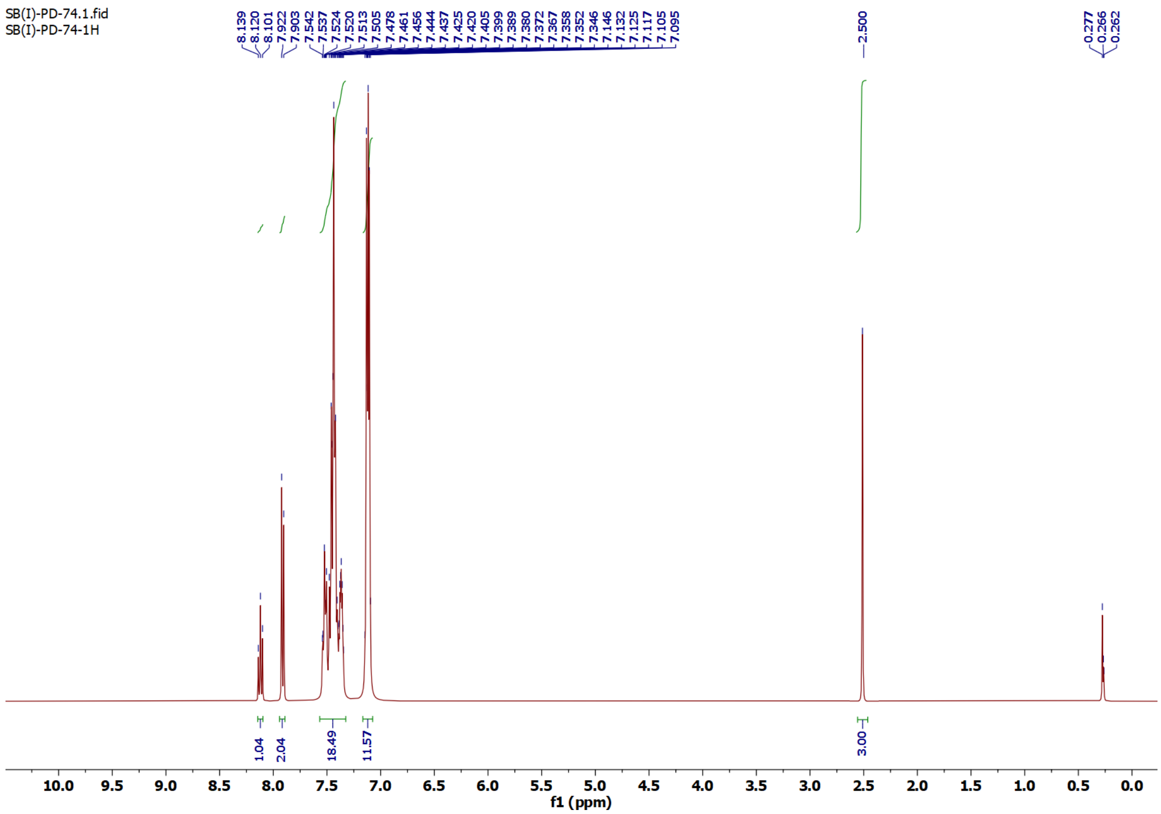


Fig. S7 ^{1}H NMR spectrum of **1** in CD_3OD solution.

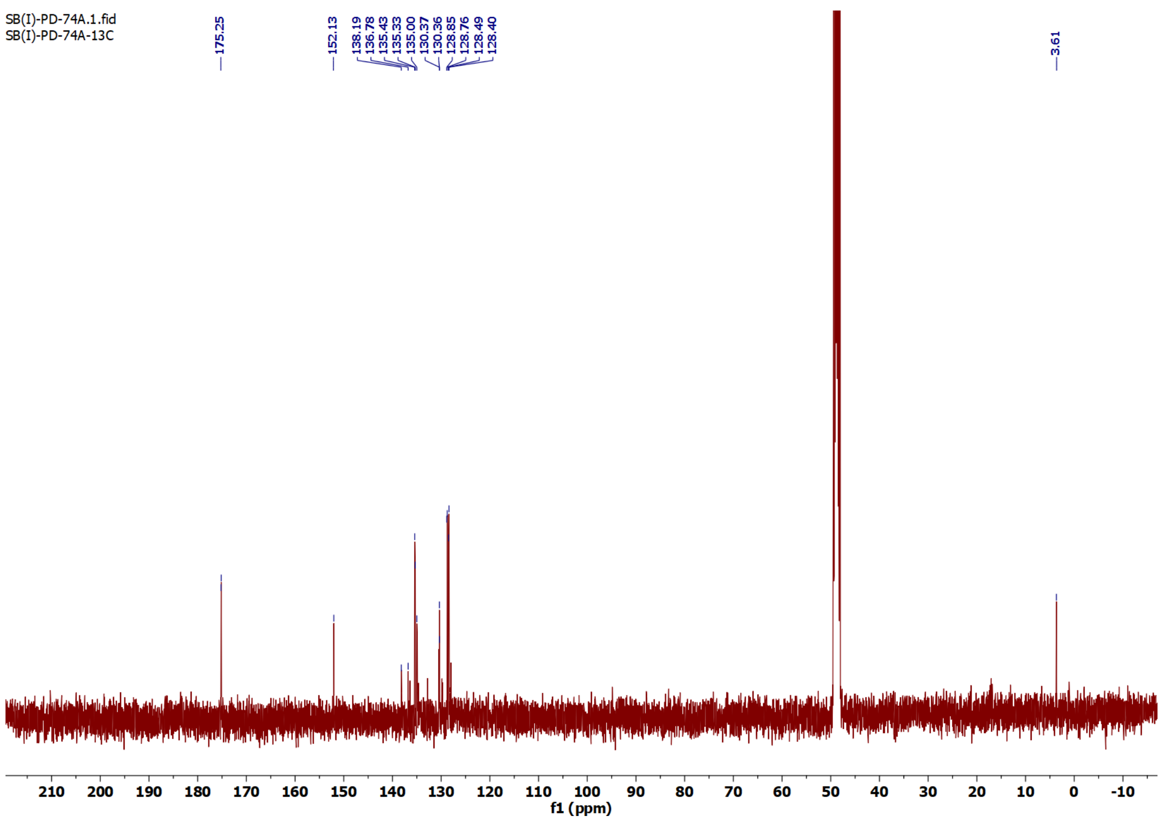


Fig. S8 $^{13}C\{^{1}H\}$ NMR spectrum of **1** in CD_3OD solution.

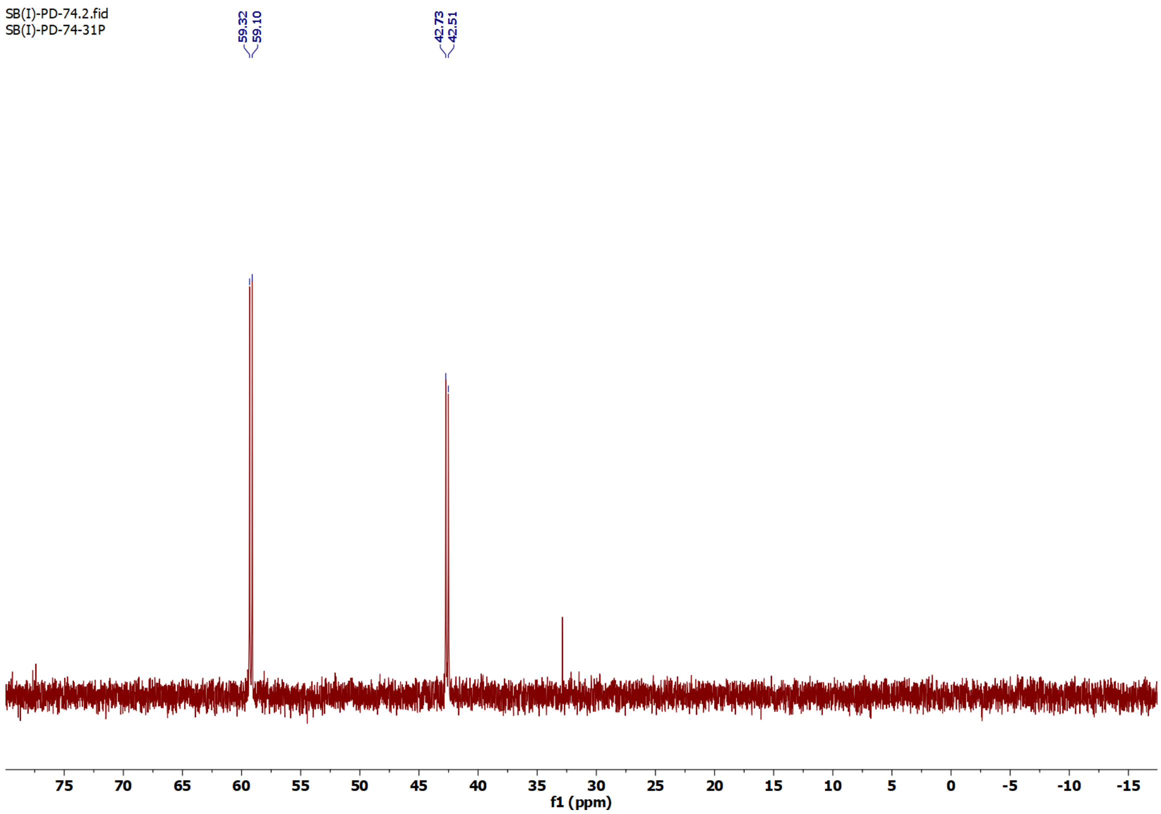


Fig. S9 $^{31}P\{^{1}H\}$ NMR spectrum of **1** in CD_3OD solution.

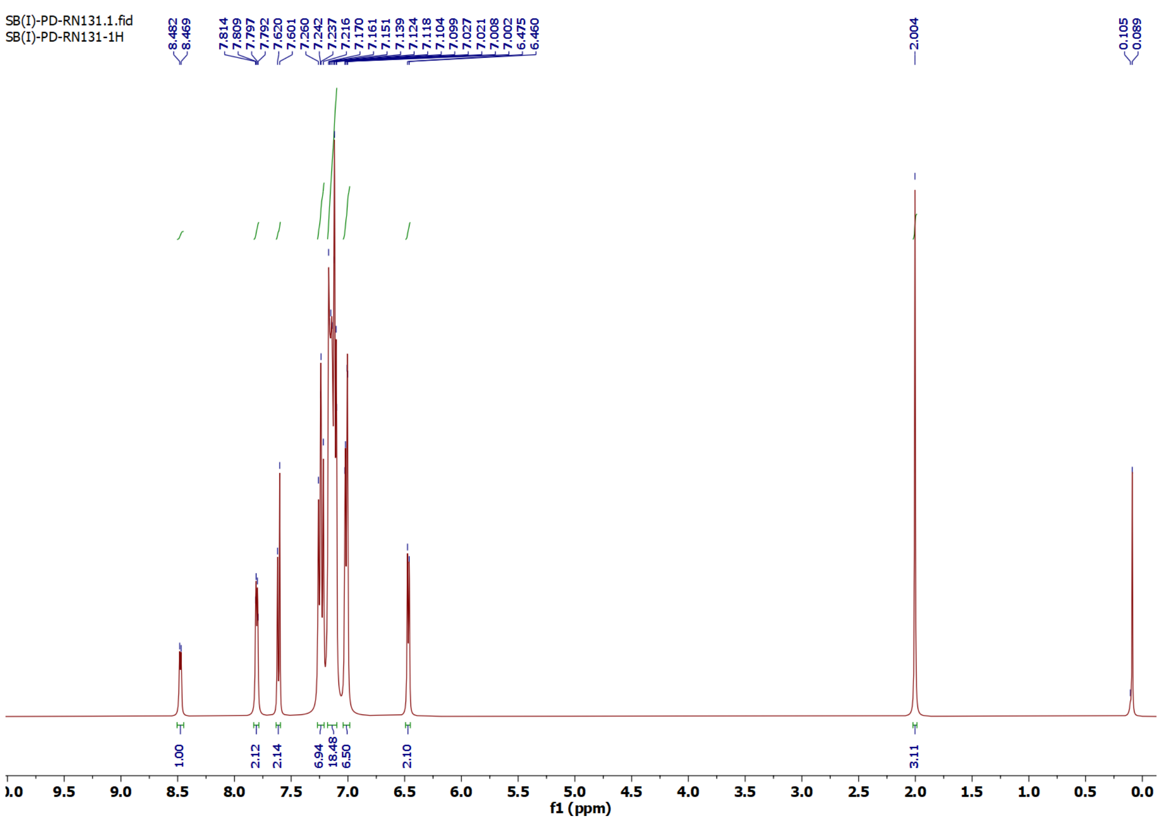


Fig. S10 ^{1}H NMR spectrum of **2** in $CDCl_3$ solution.

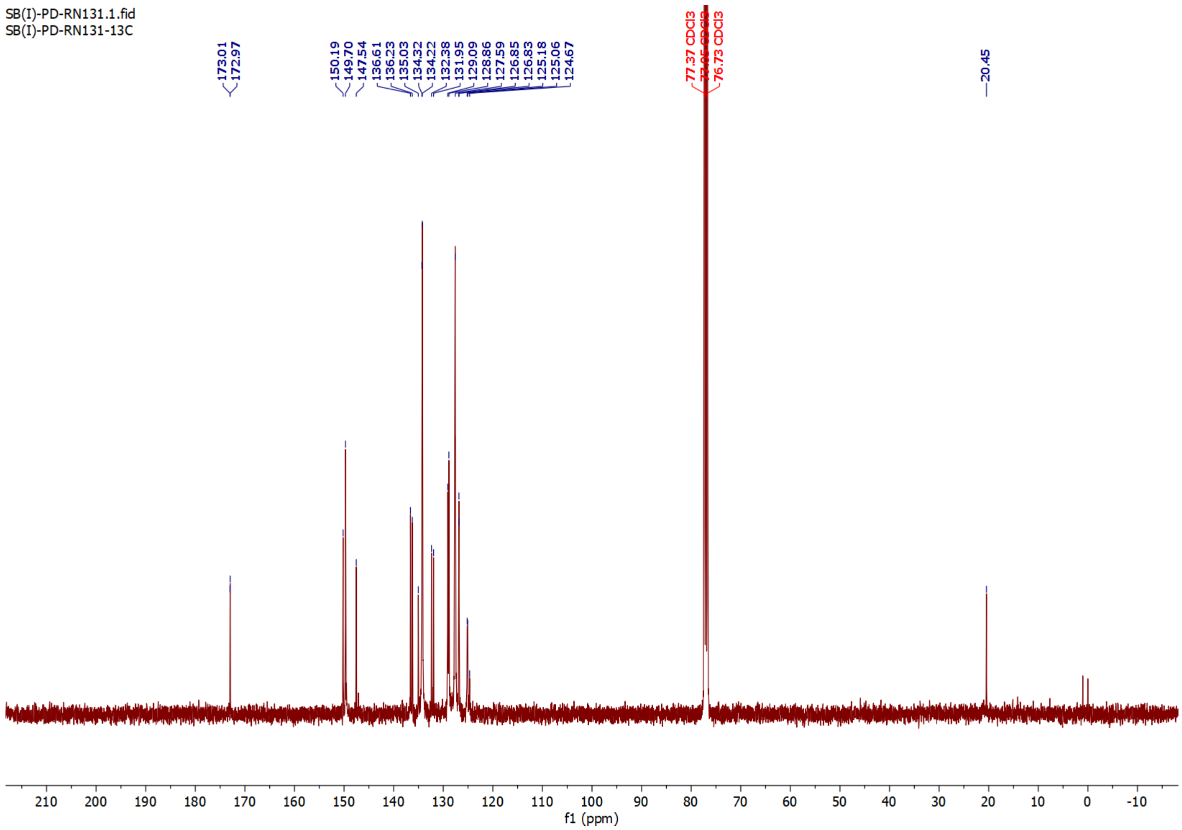


Fig. S11 $^{13}C\{^{1}H\}$ NMR spectrum of **2** in $CDCl_3$ solution.

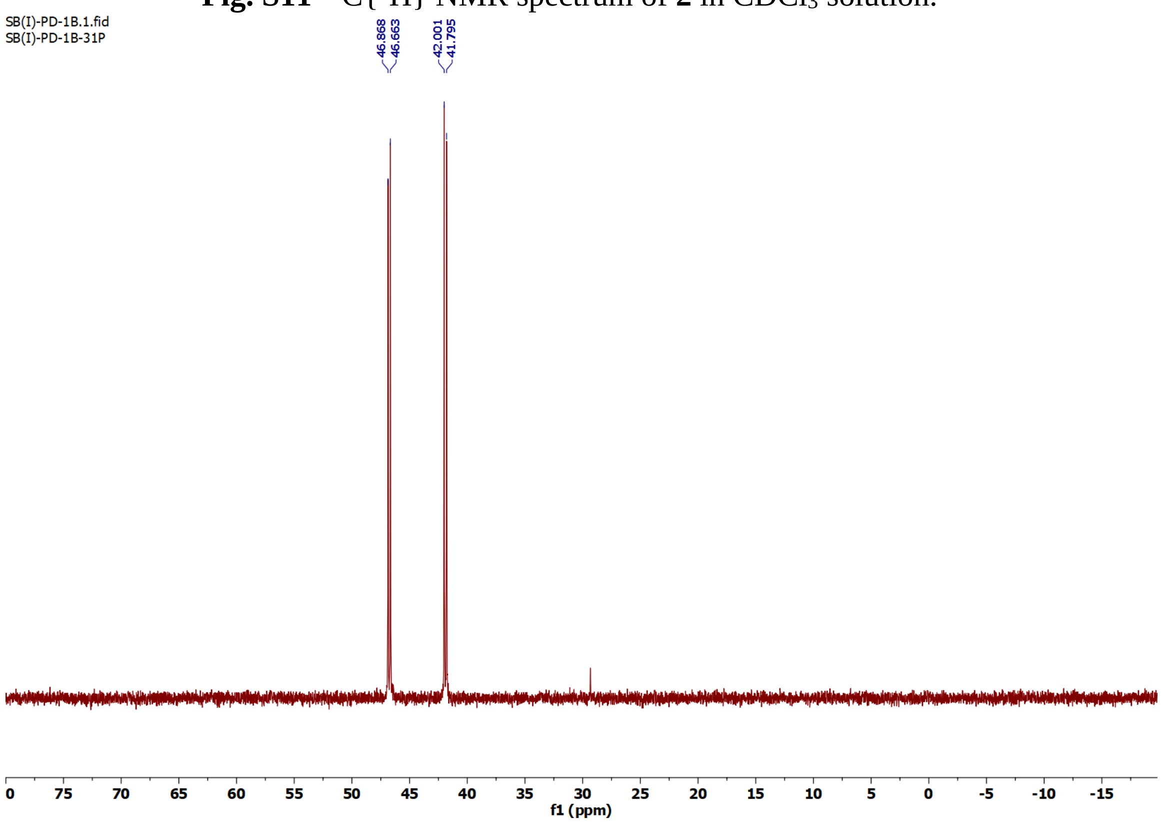


Fig. S12 $^{31}P\{^{1}H\}$ NMR spectrum of **2** in $CDCl_3$ solution.

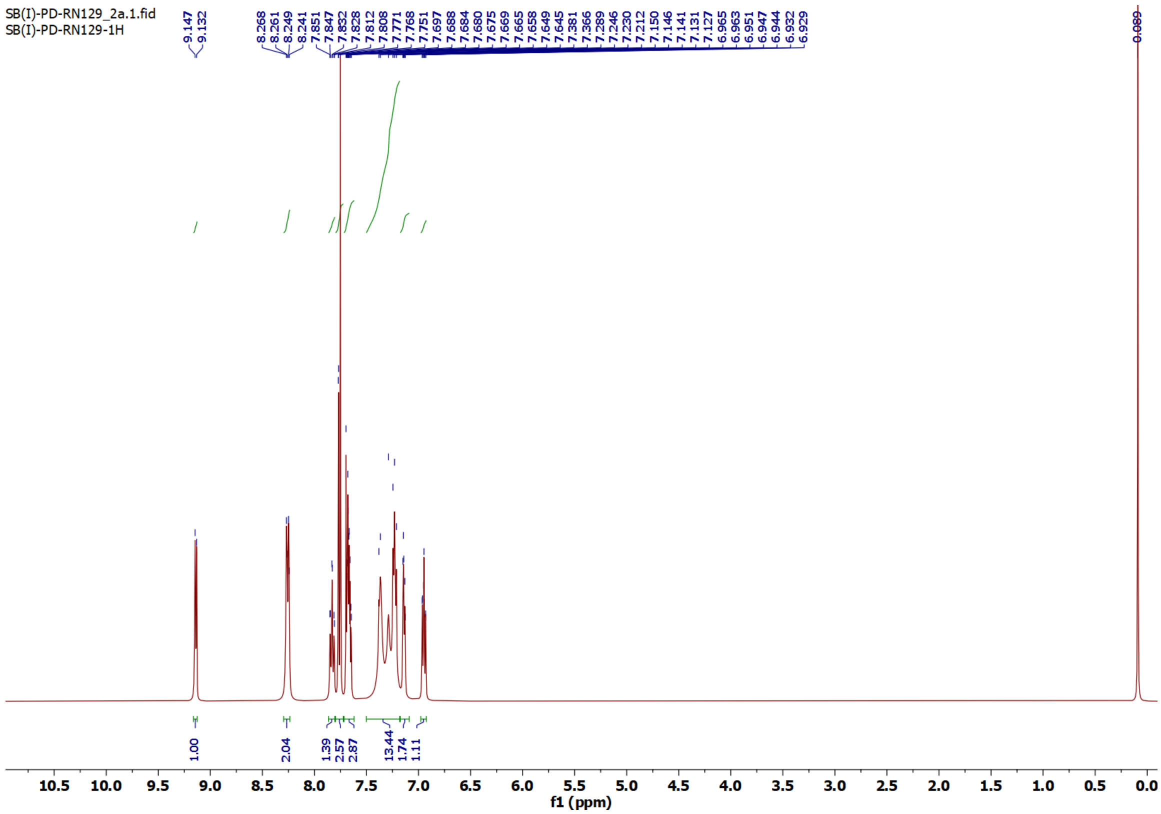


Fig. S13 [1]H NMR spectrum of **3** in $CDCl_3$ solution.

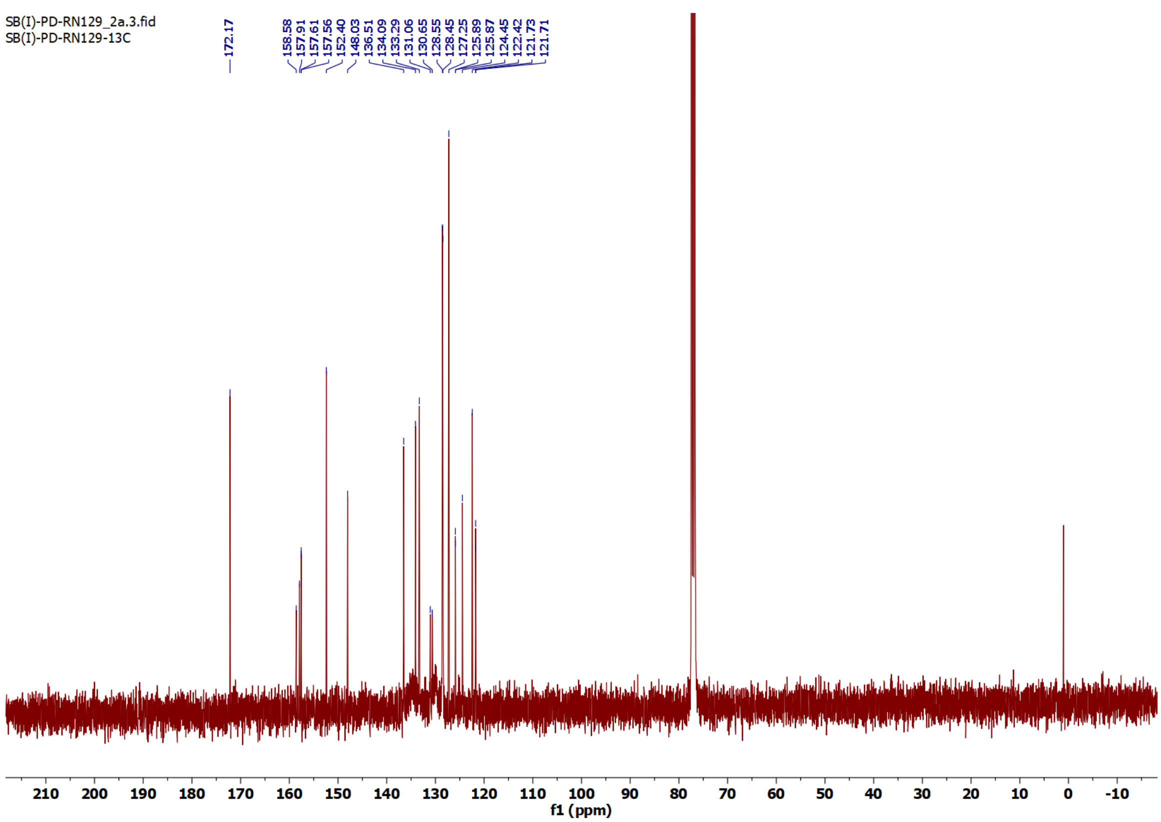


Fig. S14 $^{13}C\{^1H\}$ NMR spectrum of **3** in $CDCl_3$ solution.

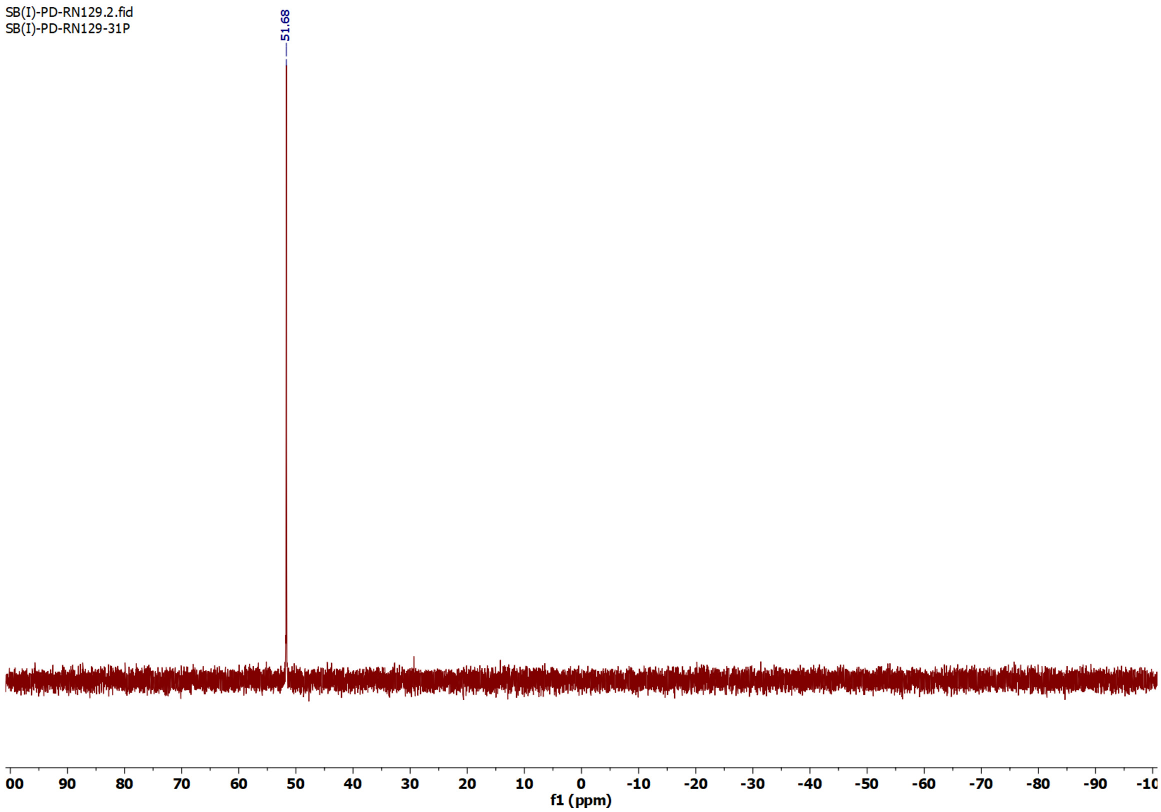


Fig. S15 $^{31}P\{^{1}H\}$ NMR spectrum of **3** in $CDCl_3$ solution.

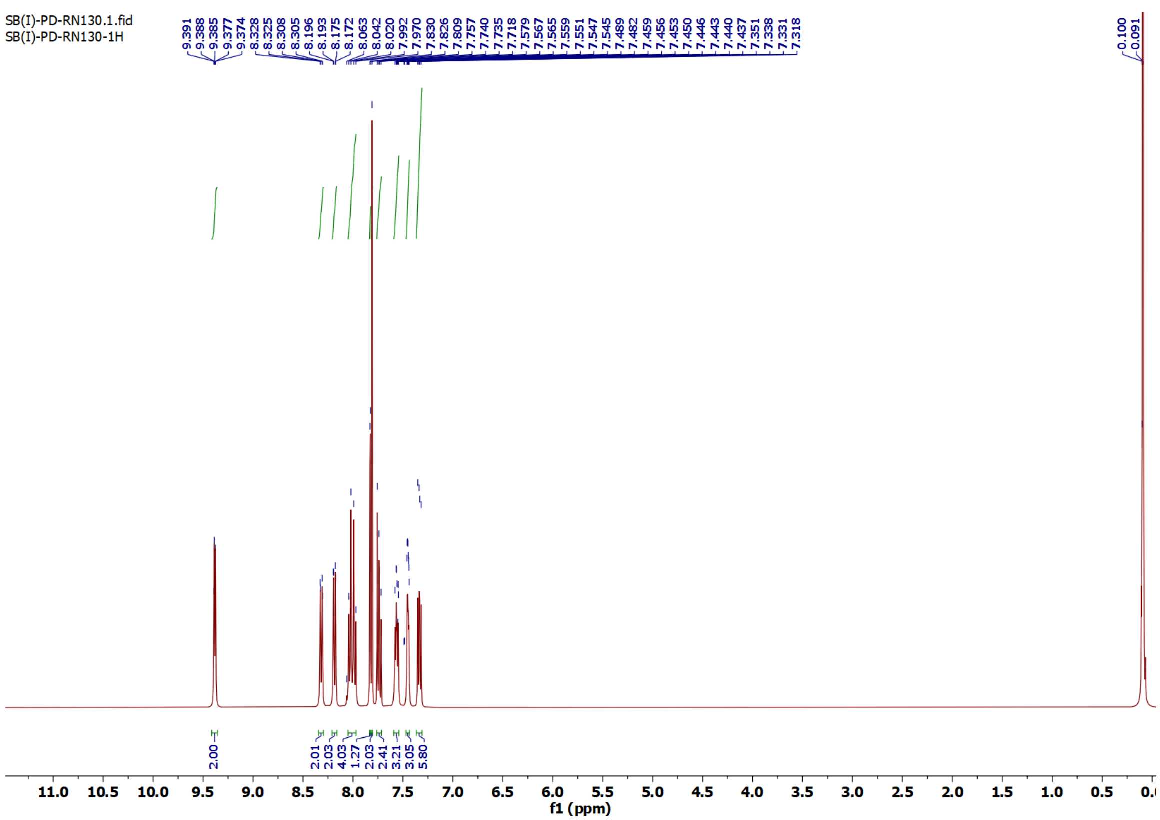


Fig. S16 ^{1}H NMR spectrum of **4** in $CDCl_3$ solution.

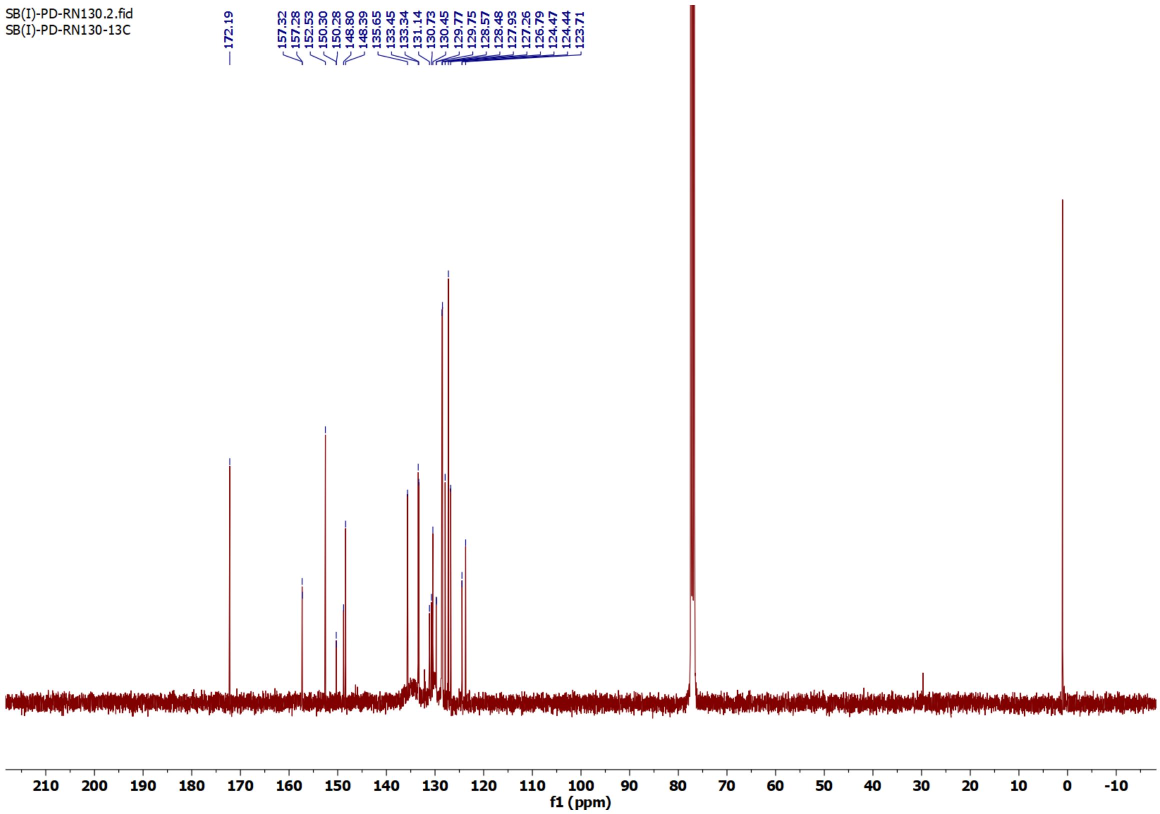


Fig. S17 $^{13}C\{^{1}H\}$ NMR spectrum of **4** in $CDCl_3$ solution.

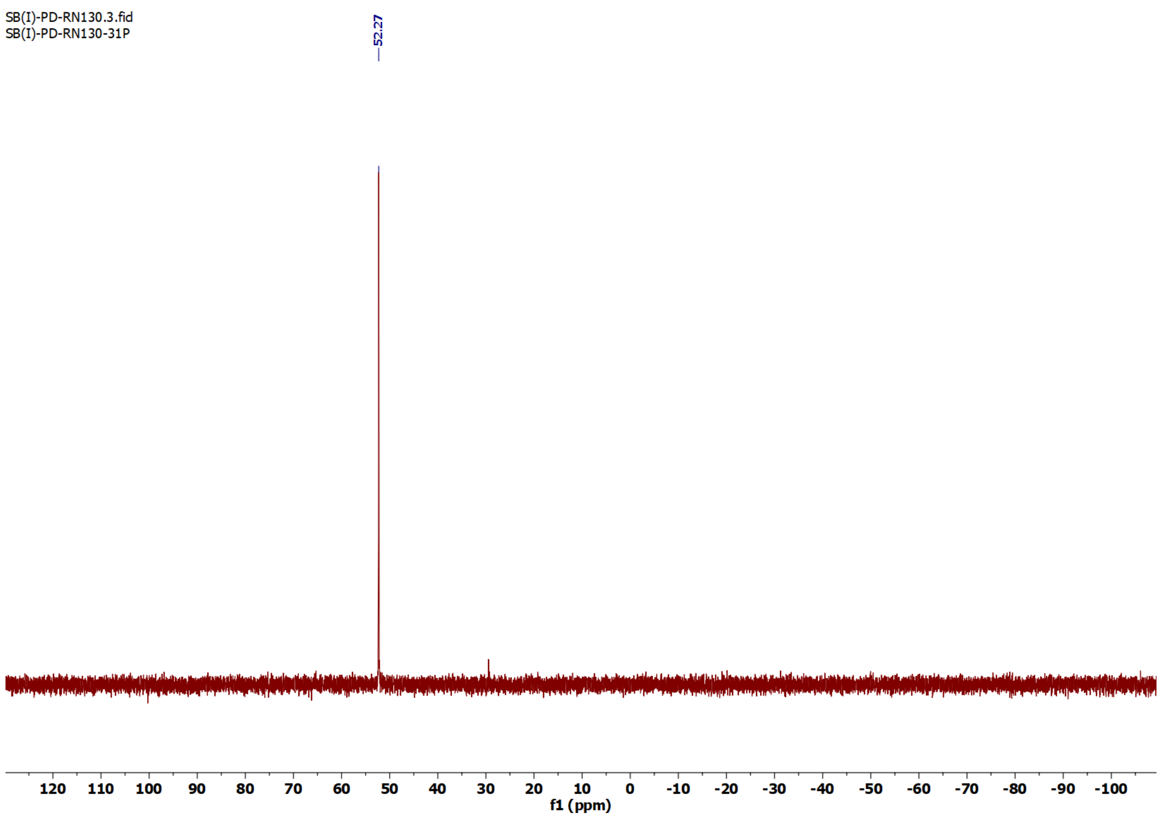


Fig. S18 $^{31}P\{^{1}H\}$ NMR spectrum of **4** in $CDCl_3$ solution.

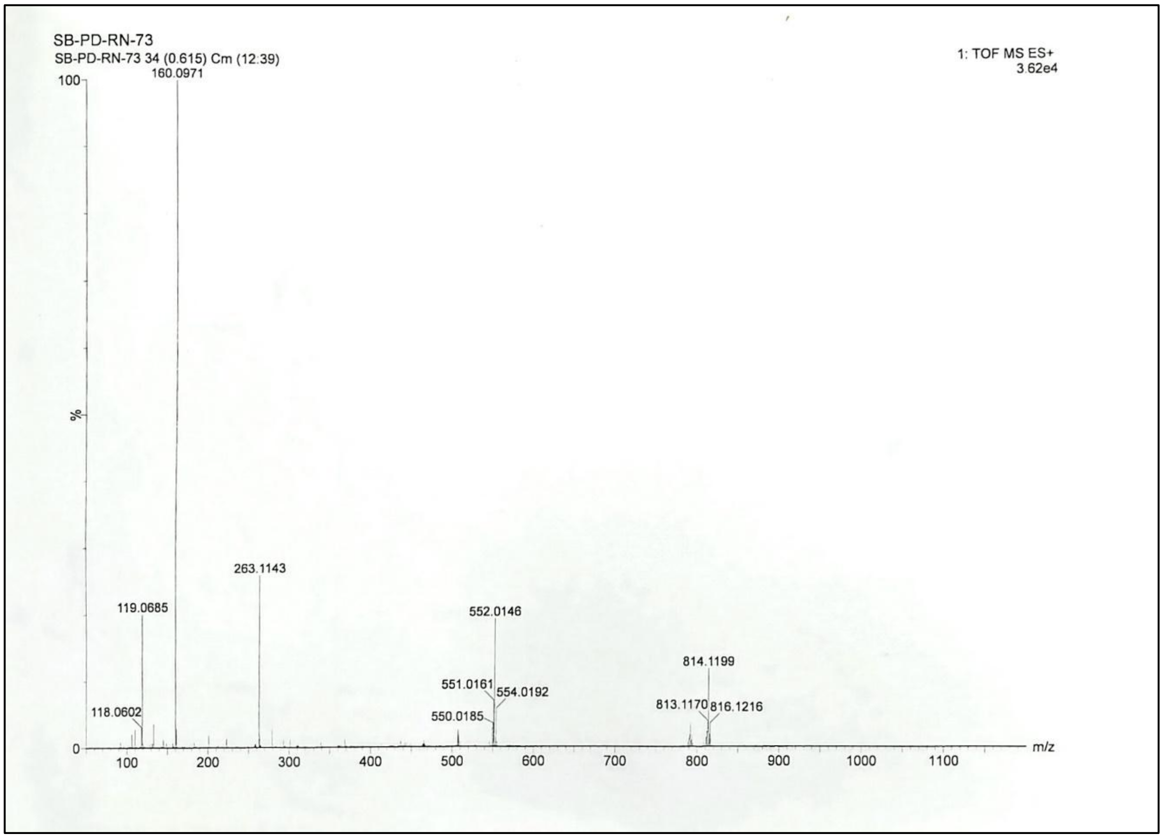


Fig. S19 ESI-MS spectrum of **1**.

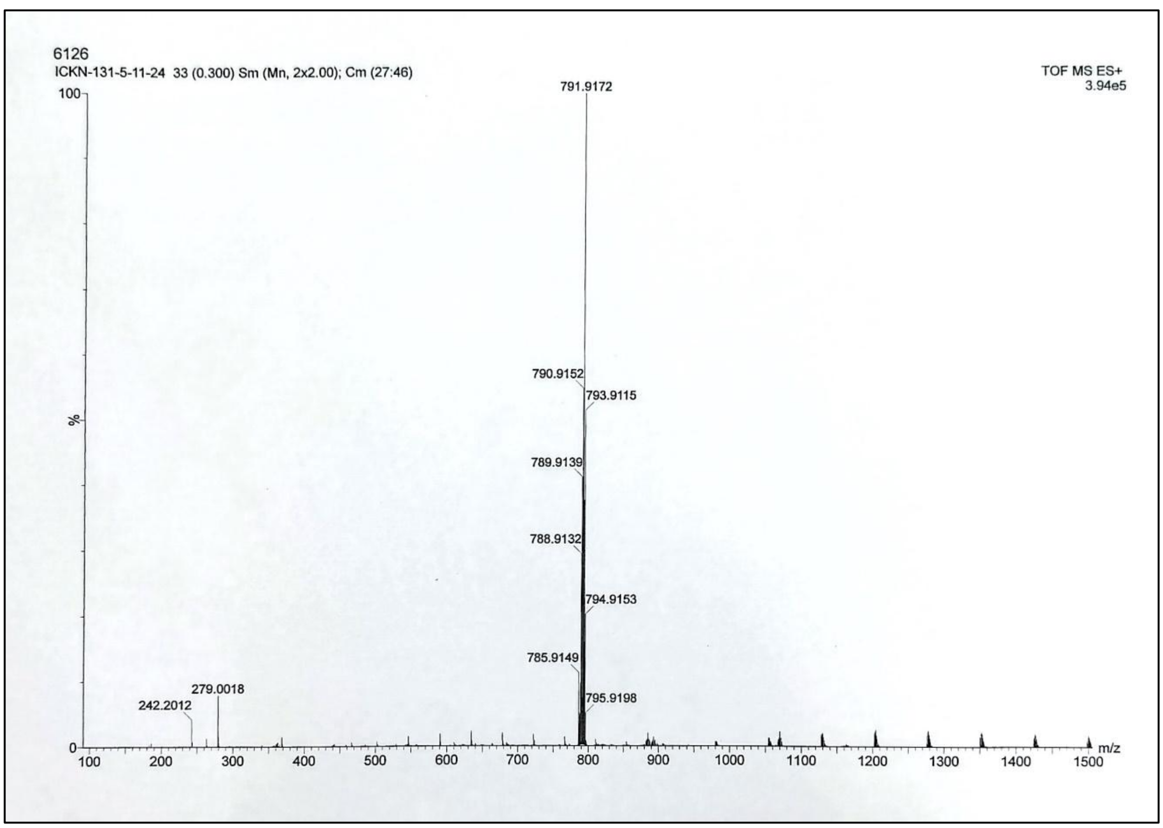


Fig. S20 ESI-MS spectrum of **2**.

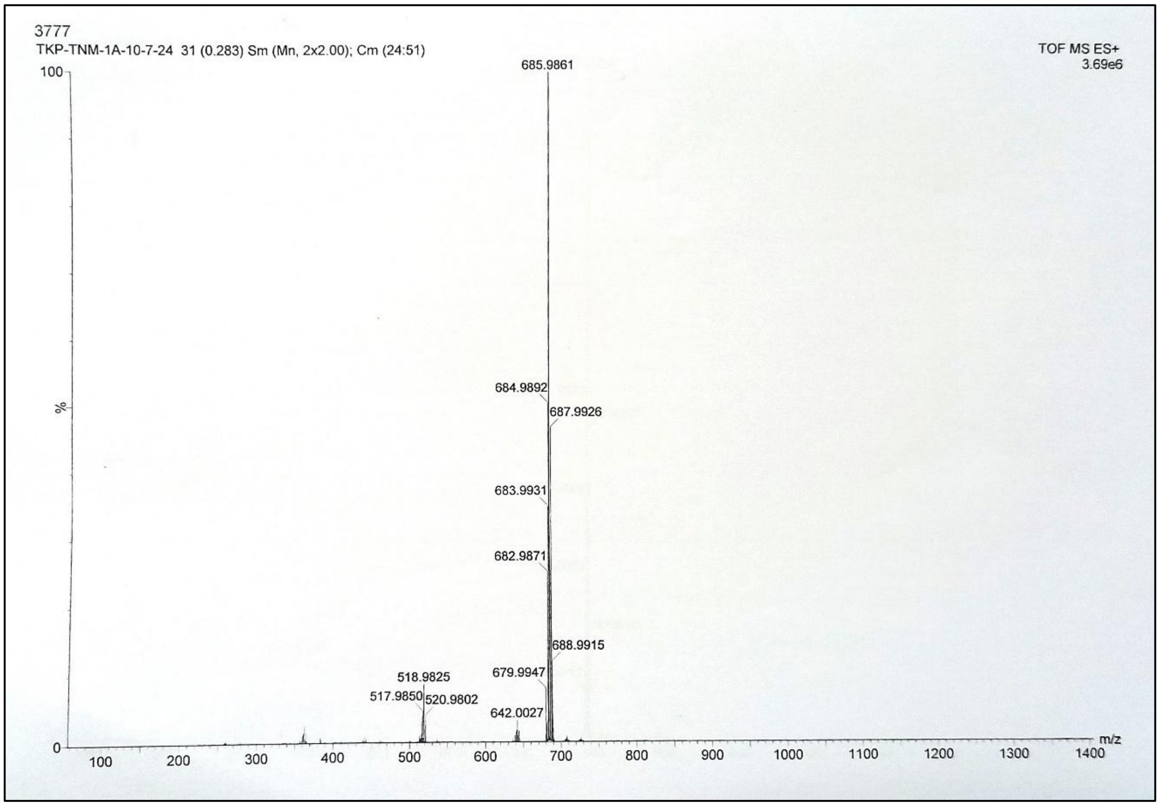


Fig. S21 ESI-MS spectrum of **3**.

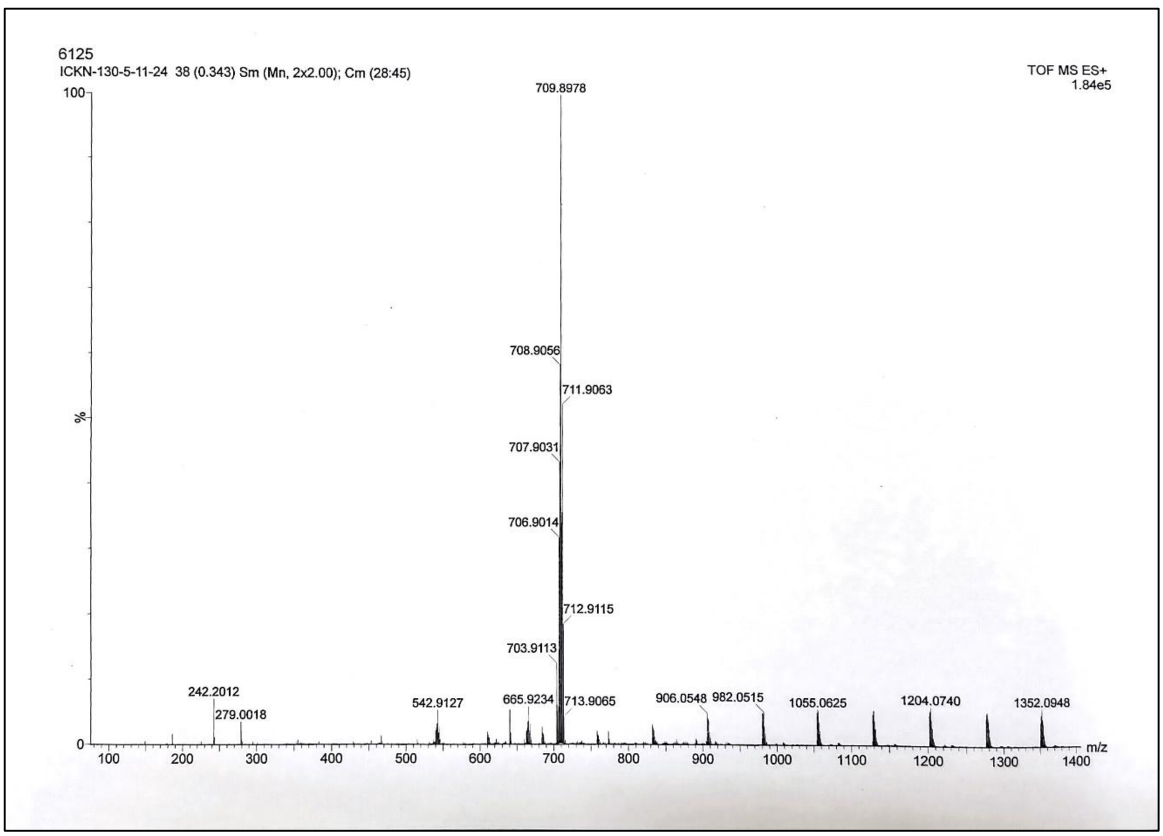


Fig. S22 ESI-MS spectrum of **4**.

Table S5 Computed parameters from TDDFT calculations on complex **1** for electronic spectral properties in methanol solution

Excited State	Composition	CI value	*E* (eV)	Oscillator strength (*f*)	λ_{theo} (nm)	Assignment	λ_{exp} (nm)
3	H-2 → L	0.10167	3.3138	0.0602	374.15	MLCT/LLCT	459
	H-1 → L+1	0.69043				MLCT/LLCT	
8	H-2 → L	0.66426	3.7094	0.1472	334.24	MLCT/LLCT	361
	H-2 → L+2	0.11316				MLCT/LLCT	
	H-2 → L+4	0.10065				MLCT/LLCT	
79	H-6 → L+2	0.11626	5.3017	0.0730	233.86	LLCT/LMCT	268
	H-4 → L+4	0.19772				LLCT/LMCT	
	H-3 → L+2	0.20626				LLCT/LMCT	
	H-3 → L+4	0.37762				LLCT/LMCT	
	H-3→ L+5	0.17837				LLCT/LMCT	
	H-3 → L+7	0.14843				LLCT/LMCT	
	H-2→ L+10	0.16199				MLCT/LLCT	

Table S6 Compositions of selected molecular orbitals of complex **1** associated with the electronic spectral transitions

% Contribution of fragments to	Fragments				
	Ru	MeCN	PPh_3(1)	PPh_3(2)	DPA
H-1	64	2	1	2	31
H-2	68	3	8	5	16
H-3	1	0	0	0	99
H-4	4	0	9	1	86
H-6	6	0	76	3	15
LUMO (L)	3	0	3	1	93
L+1	0	0	0	3	97
L+2	9	3	60	26	2
L+4	5	0	62	30	3
L+5	10	4	41	43	2
L+7	3	1	43	51	2
L+10	2	0	88	10	0

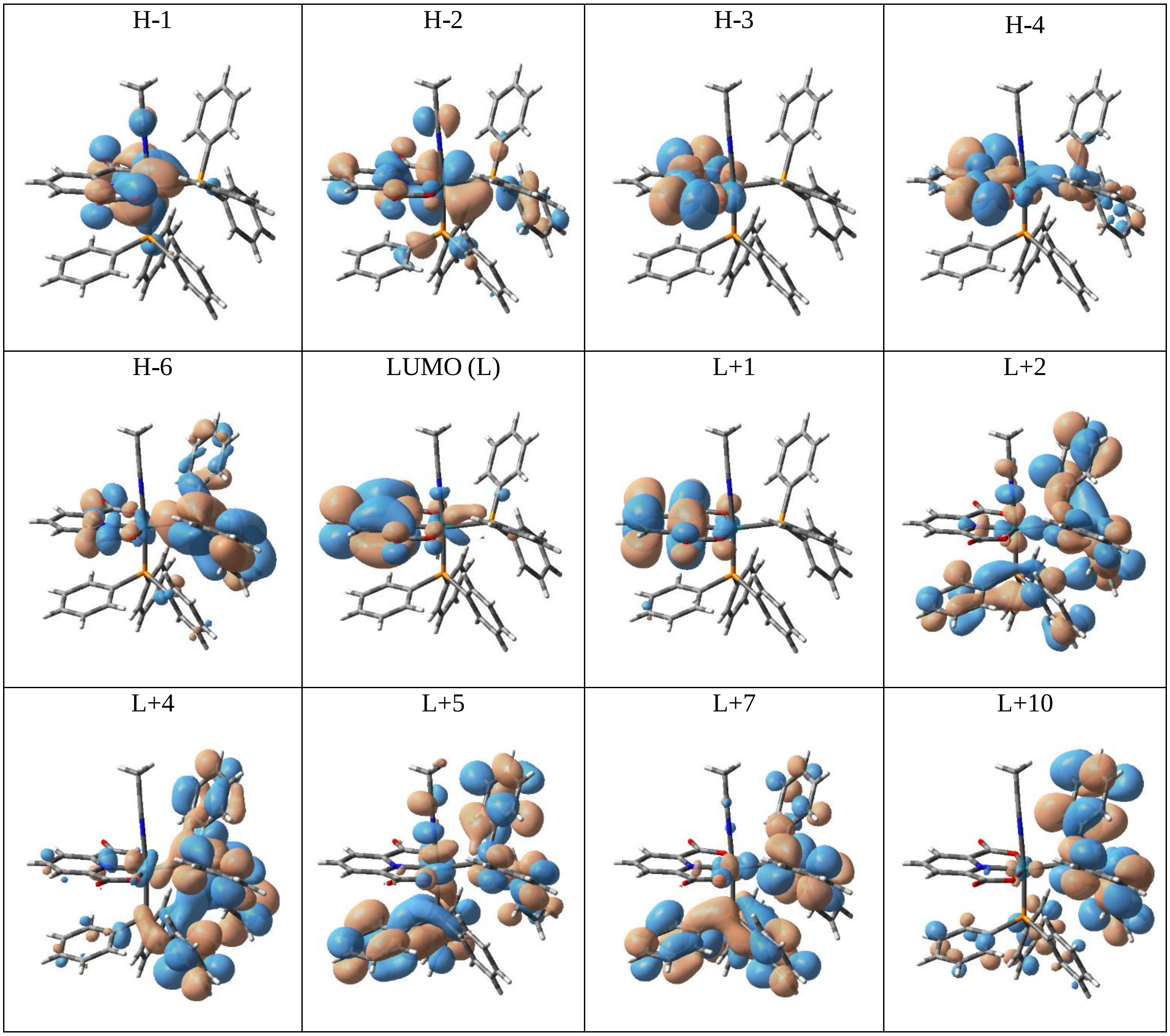


Fig. S23 Contour plots of the molecular orbitals of complex **1**, which are associated with the electronic spectral transitions (See **Table S5**).

Table S7 Computed parameters from TDDFT calculations on complex **2** for electronic spectral properties in acetonitrile solution

Excited State	Composition	CI value	*E* (eV)	Oscillator strength (*f*)	λ_{theo} (nm)	Assignment	λ_{exp} (nm)
7	H-2 → L	0.67454	3.2923	0.1004	376.59	MLCT/LLCT	454
27	H-10 → L	0.12360	4.2813	0.0761	289.59	LLCT/LMCT	362
	H-2 → L+2	0.64551				MLCT/LLCT	
98	H-8 → L+3	0.19343	5.3289	0.0376	232.66	LLCT/MLCT	262
	H-8 → L+4	0.18742				LLCT/MLCT	
	H-7 → L+2	0.16610				LLCT	
	H-5 → L+3	0.25100				LLCT/MLCT	
	H-5→ L+4	0.30057				LLCT/MLCT	
	H-4 → L+3	0.21253				LLCT/LMCT	
	H-4→ L+4	0.31488				LLCT/LMCT	
	H-4→ L+5	0.12434				LLCT/LMCT	
	H-3→ L+5	0.10354				LLCT	

Table S8 Compositions of selected molecular orbitals of complex **2** associated with the electronic spectral transitions

% Contribution of fragments to	Fragments				
	Ru	4-picoline	PPh_3(1)	PPh_3(2)	DPA
H-2	72	3	6	5	14
H-3	2	0	0	0	98
H-4	0	0	35	64	1
H-5	3	3	23	60	11
H-7	2	3	19	54	22
H-8	1	3	41	53	2
H-10	1	5	63	16	15
LUMO (L)	3	1	1	1	94
L+2	2	78	16	2	2
L+3	2	61	31	1	5
L+4	2	0	6	90	2
L+5	2	8	67	22	1

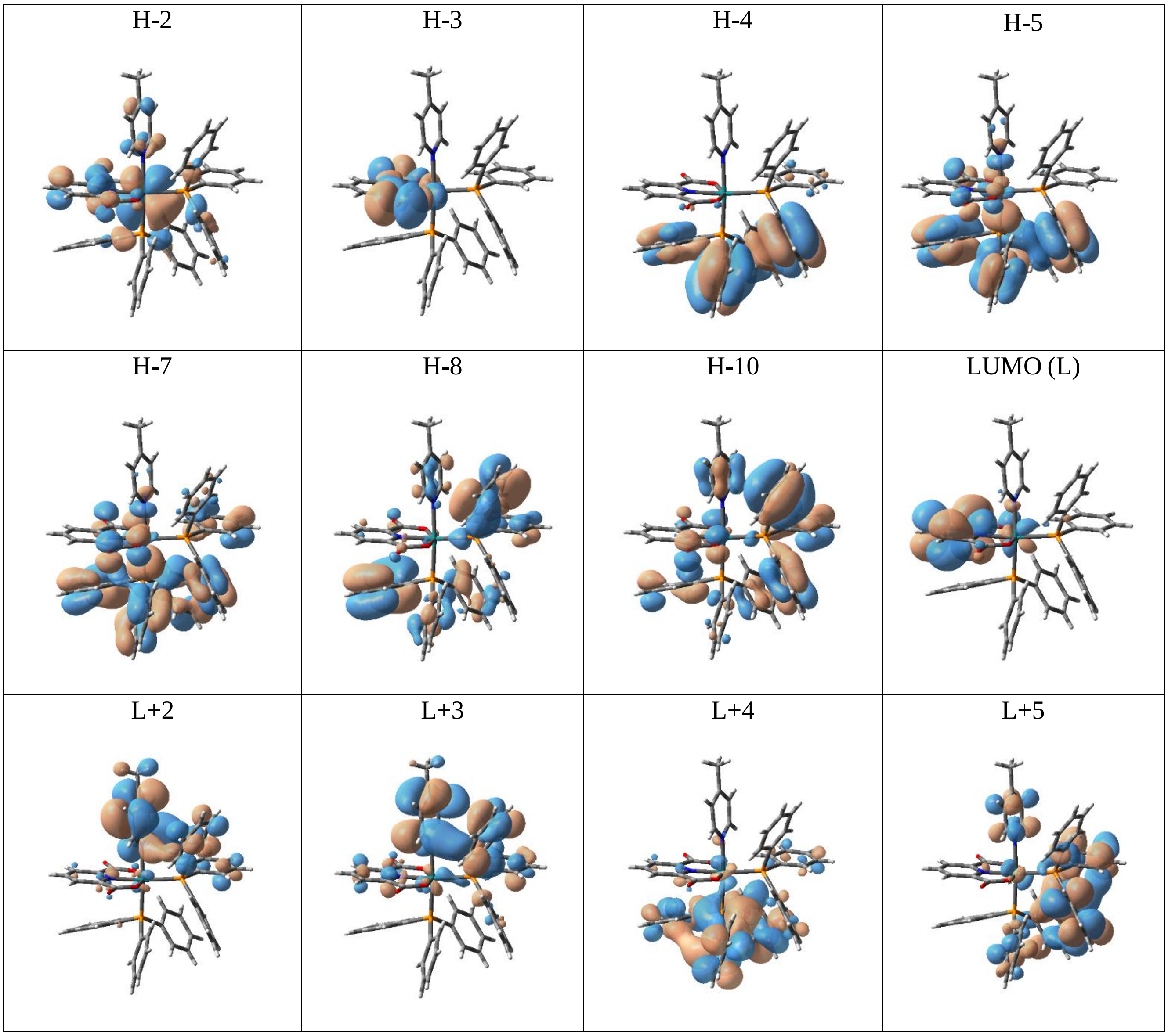


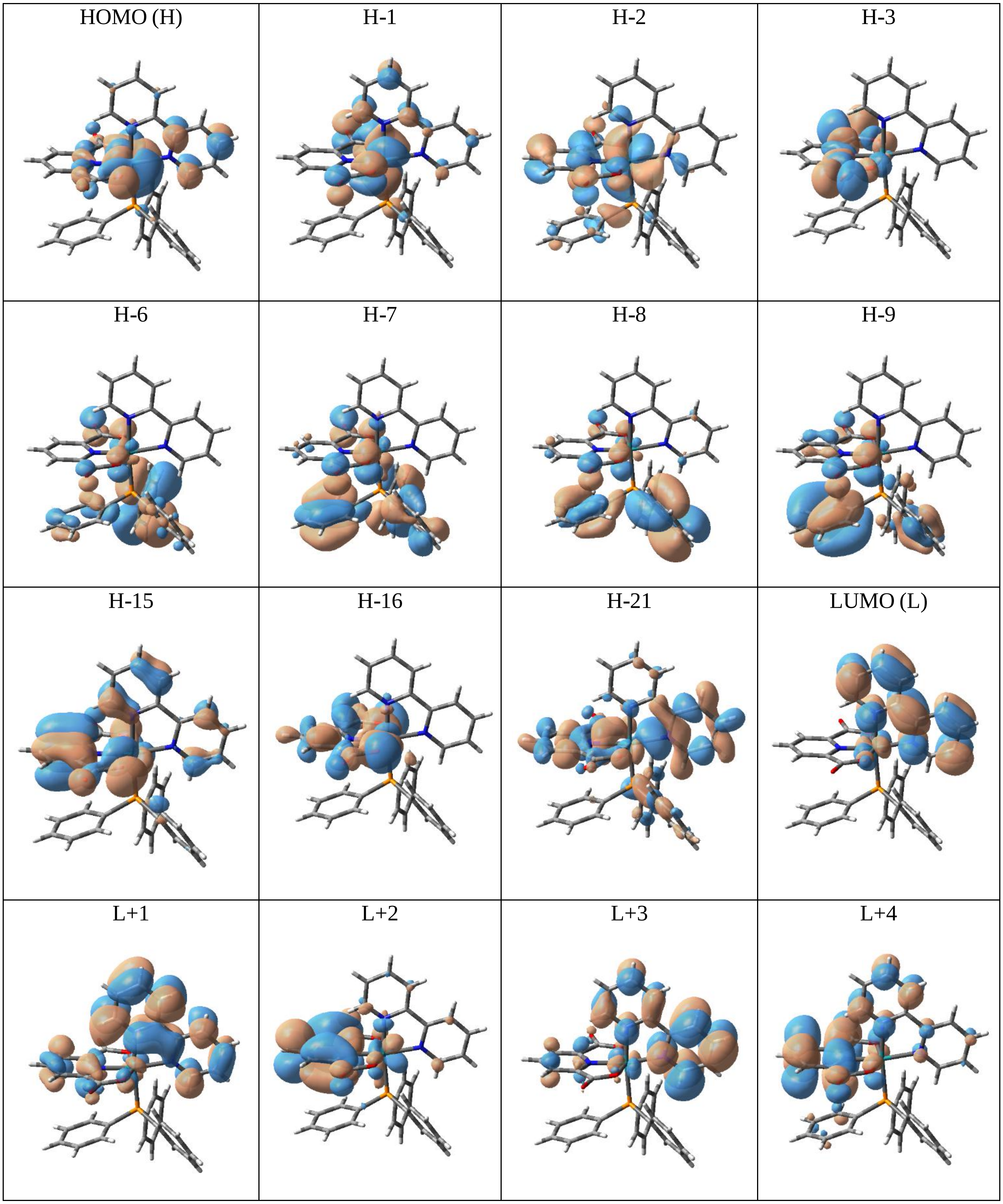
Fig. S24 Contour plots of the molecular orbitals of complex **2**, which are associated with the electronic spectral transitions (See **Table S7**).

Table S9 Computed parameters from TDDFT calculations on complex **3** for electronic spectral properties in acetonitrile solution

Excited State	Composition	CI value	*E* (eV)	Oscillator strength (*f*)	λ_{theo} (nm)	Assignment	λ_{exp} (nm)
3	H-1 → L	0.63806	2.6069	0.0932	475.60	MLCT/LLCT	513
	H → L	0.23872				MLCT/LLCT	
	H → L+1	0.11771				MLCT/LLCT	
12	H-2 → L+1	0.43887	3.5036	0.1171	353.88	MLCT/LLCT	387
	H-1 → L+2	0.10027				MLCT/LLCT	
	H-1 → L+3	0.50622				MLCT/LLCT	
36	H-9 → L	0.16716	4.4913	0.2624	276.05	LLCT/LMCT	299
	H-7 → L	0.62354				LLCT/LMCT	
90	H-21 → L	0.10230	5.4056	0.1327	229.36	LLCT/LMCT	263
	H-16 → L	0.10434				LLCT/MLCT	
	H-15 → L	0.18178				LLCT/MLCT	
	H-8 → L+4	0.22810				LLCT/MLCT	
	H-7→ L+4	0.24834				LLCT/MLCT	
	H-6 → L+5	0.15602				LMCT/LLCT	
	H-3→ L+6	0.40871				LLCT/LMCT	

Table S10 Compositions of selected molecular orbitals of complex **3** associated with the electronic spectral transitions

% Contribution of fragments to	Fragments			
	Ru	bpy	PPh_3	DPA
HOMO (H)	66	10	1	23
H-1	61	7	2	30
H-2	69	3	7	21
H-3	1	0	0	99
H-6	2	0	83	15
H-7	2	1	65	32
H-8	1	1	86	12
H-9	1	0	80	19
H-15	11	11	3	75
H-16	10	1	2	87
H-21	3	53	7	37
LUMO (L)	6	92	1	1
L+1	3	85	1	11
L+2	5	3	2	90
L+3	2	92	1	5
L+4	0	14	3	83
L+5	7	3	87	3
L+6	8	1	89	2


HOMO (H)
H-1
H-2
H-3
H-6
H-7
H-8
H-9
H-15
H-16
H-21
LUMO (L)
L+1
L+2
L+3
L+4

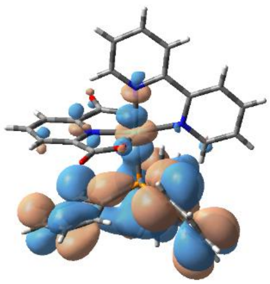
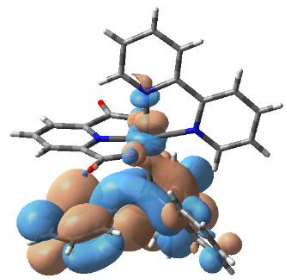
L+5 	L+6 		

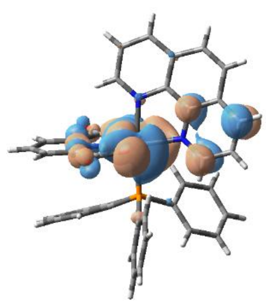
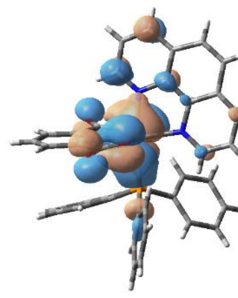
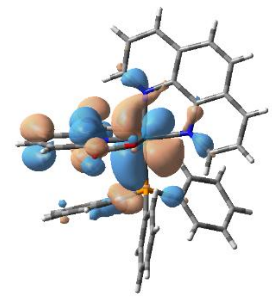
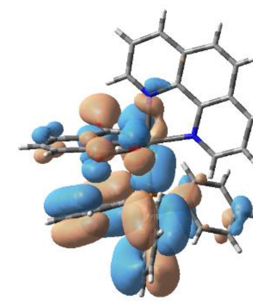
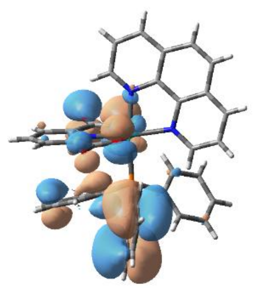
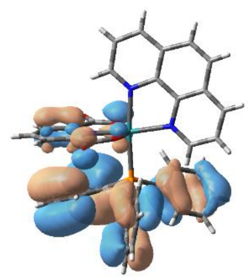
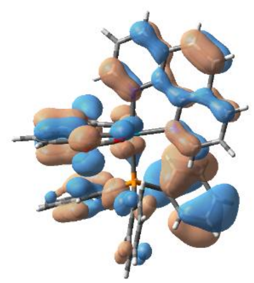
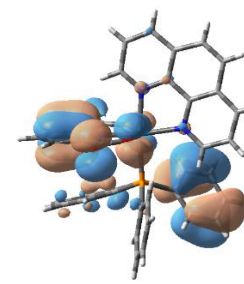
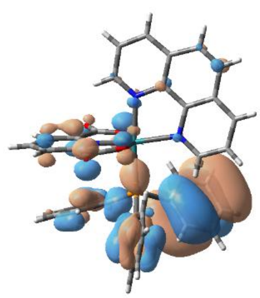
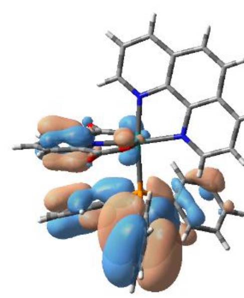
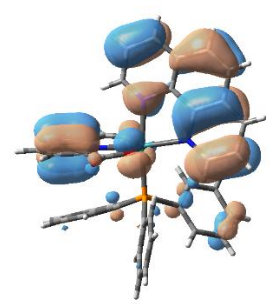
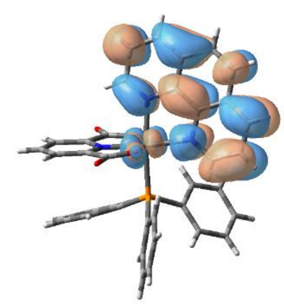
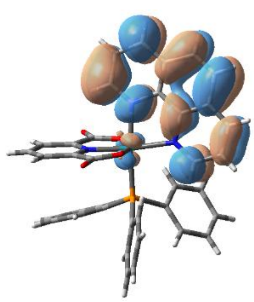
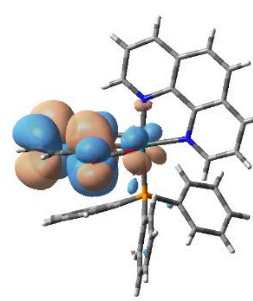
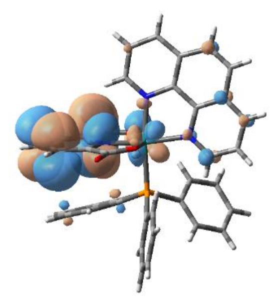
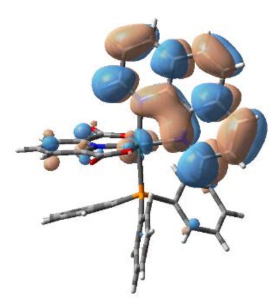
Fig. S25 Contour plots of the molecular orbitals of complex **3**, which are associated with the electronic spectral transitions (See **Table S9**).

Table S11 Computed parameters from TDDFT calculations on complex **4** for electronic spectral properties in acetonitrile solution

Excited State	Composition	CI value	*E* (eV)	Oscillator strength (*f*)	λ_{theo} (nm)	Assignment	λ_{exp} (nm)
4	H-1 → L	0.51756	2.6570	0.0786	466.62	MLCT/LLCT	476
	H → L	0.24878				MLCT/LLCT	
	H → L+1	0.20871				MLCT/LLCT	
	H → L+2	0.32094				MLCT/LLCT	
15	H-2 → L+3	0.56820	3.6675	0.0899	338.06	MLCT/LLCT	386
	H-2 → L+4	0.16805				MLCT/LLCT	
	H-2 → L+6	0.10052				MLCT/LLCT	
	H → L+4	0.11333				MLCT/LLCT	
	H → L+5	0.27218				MLCT/LLCT	
69	H-14 → L	0.11245	4.8637	0.2272	254.92	LLCT/LMCT	269
	H-13 → L+1	0.15110				LLCT/LMCT	
	H-11 → L	0.22491				LLCT/LMCT	
	H-11 → L+1	0.13565				LLCT/LMCT	
	H-10→ L+3	0.10540				LLCT/MLCT	
	H-9→ L+1	0.15723				LLCT/MLCT	
	H-8→ L+1	0.19173				LLCT/LMCT	
	H-7 → L+1	0.14266				LLCT	
	H-7 → L+3	0.10250				LLCT/LMCT	
	H-6 → L+1	0.12431				LLCT/MLCT	
	H-6 → L+3	0.18111				LLCT/MLCT	
	H-1 → L+12	0.38372				LLCT/MLCT	
	H-1 → L+13	0.12879				LLCT/MLCT	

Table S12 Compositions of selected molecular orbitals of complex **4** associated with the electronic spectral transitions

% Contribution of fragments to	Fragments			
	Ru	phen	PPh_3	DPA
HOMO (H)	66	10	1	23
H-1	61	7	3	29
H-2	70	3	6	21
H-6	4	2	59	35
H-7	2	1	56	41
H-8	0	0	88	12
H-9	3	18	55	24
H-10	6	2	43	49
H-11	1	3	88	8
H-13	1	0	90	9
H-14	1	69	6	24
LUMO (L)	6	93	0	1
L+1	2	97	0	1
L+2	3	1	3	93
L+3	3	3	2	92
L+4	3	91	3	3
L+5	7	2	88	3
L+6	13	2	82	3
L+12	53	7	22	18
L+13	55	12	25	8

HOMO (H)	H-1	H-2	H-6
			
H-7	H-8	H-9	H-10
			
H-11	H-13	H-14	LUMO (L)
			
L+1	L+2	L+3	L+4
			

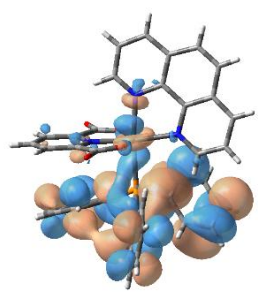
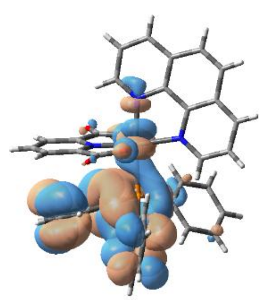
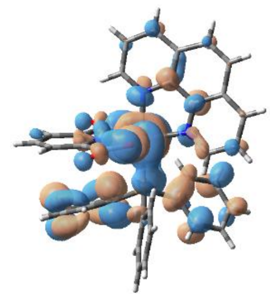
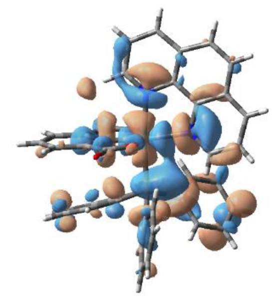
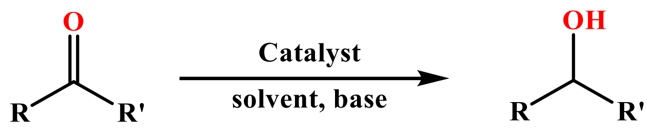
L+5	L+6	L+12	L+13
			

Fig. S26 Contour plots of the molecular orbitals of complex **4**, which are associated with the electronic spectral transitions (See **Table S11**).

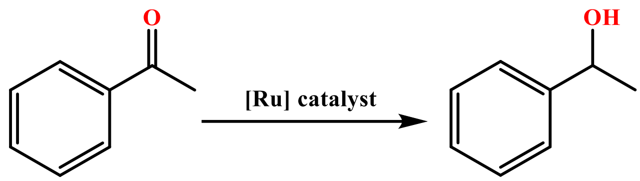
Table S13 Optimization of the reaction conditions for the catalysis[a]



Entry	Catalyst	Mole % of catalyst	Solvent	Base	Amount of base, equiv.	Temp, ºC	Time, h	Yield, %
1	**1**	1	2-propanol	KOH	1	100	12	NO
2	**3**	1	2-propanol	KOH	1	100	12	>99
3	**3**	1	2-propanol	KOH	1	100	6	>99
4	**3**	1	2-propanol	KOH	1	80	6	48
5	**3**	0.5	2-propanol	KOH	1	100	6	>99
6	**3**	0.5	2-propanol	KOH	1	100	3	87
7	**3**	0.5	2-propanol	KOH	1	100	4	97
8	**3**	0.5	2-propanol	KOH	1	100	5	>99
9	**3**	0.5	1-propanol	KOH	1	100	4	68
10	**3**	0.5	2-propanol	Na_2CO_3	1	100	4	54
11	**3**	0.5	2-propanol	KO^tBu	1	100	4	41
12	**3**	0.5	2-propanol	KOH	0.1	100	6	39
13	**2**	0.5	2-propanol	KOH	1	100	4	NO
14	**4**	0.5	2-propanol	KOH	1	100	4	76
15	**-**	-	2-propanol	KOH	1	100	4	NO
16	**3**	0.5	2-propanol	-	-	100	4	NO

[a] Reaction conditions: Substrate, Acetophenone (1 mmol); solvent (5.0 mL).

Table S14 Comparison of efficiency of different Ru-catalysts for the transfer hydrogenation



Entry	Cat. loading (mol%)	Time (h)	Yield (%)	TON	TOF (h^{-1})	Reference
1	1	24	99	99	4.125	**14a**
2	2	24	94	47	1.96	**14b**
3	1	24	99	99	4.125	**14c**
4	1	24	88.5	88.5	3.68	**14d**
5	0.7	3	89	127	42	**14e**
6	1	24	99	99	4.125	**14f**
7	0.5	1.5	94	188	125	**14g**
8	1.5	4	99	66	16.5	**14h**
9	0.1	2	97	970	485	**14i**
10	0.5	4	97	194	48.5	**This work**

Table S15 Crystallographic data for complex **1, 2, 3** and **4**

Complex	**1**	**2**	**3**	**4**
Empirical formula	$C_{45}H_{36}N_2O_4P_2Ru$	$C_{49}H_{40}N_2O_4P_2Ru$, 2[H_2O]	$C_{35}H_{26}N_3O_4PRu$, 2[H_2O]	2($C_{37}H_{26}N_3O_4PRu$), 1[CH_2CL_2], 0.9[H_2O]
Formula mass	831.81	919.87	720.66	1518.50
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_12_12_1$
a (Å)	17.9919(6)	11.009(3)	11.4(3)	11.011 (9)
b (Å)	11.6497(4)	33.411(11)	15.1(4)	16.07(2)
c (Å)	18.6138(6)	11.823(4)	19.2(5)	37.32(4)
α (deg)	90	90	90	90
β (deg)	98.072(2)	90.06	101.3(3)	90
γ (deg)	90	90	90	90
V (Å ^{3})	3862.8(2)	4349(2)	3262(15)	6605(13)
Z	4	4	4	4
D_{calcd} (g/cm^{-3})	1.430	1.405	1.467	1.593
F(000)	1701	1896	1472	3208
crystal size (mm^3)	0.08 × 0.11 × 0.16	0.13 × 0.17 × 0.23	0.12 × 0.19 × 0.24	0.14 × 0.16 × 0.32
T (K)	296	252	293	293
μ (mm^{-1})	0.535	0.486	0.579	0.702
$R1^a$	0.0276	0.0592	0.0703	0.0847
$wR2^b$	0.0780	0.1627	0.1618	0.2243
GOF^c	1.099	1.026	1.164	1.014

$^a R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$

$^b wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$

^{c}GOF = $[\Sigma[w(F_o^2-F_c^2)^2]/(M-N)]^{1/2}$, where M is the number of reflections and N is the number of parameters refined.