Supporting Information

Structural and electronic forms of doubly oxido/Pz and triply oxido/$(Pz)_2$ bridged mixed valent and isovalent diruthenium complexes (Pz=Pyrazolate)

Sudip Kumar Bera and Goutam Kumar Lahiri*

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai-400076, India, E-mail: lahiri@chem.iitb.ac.in

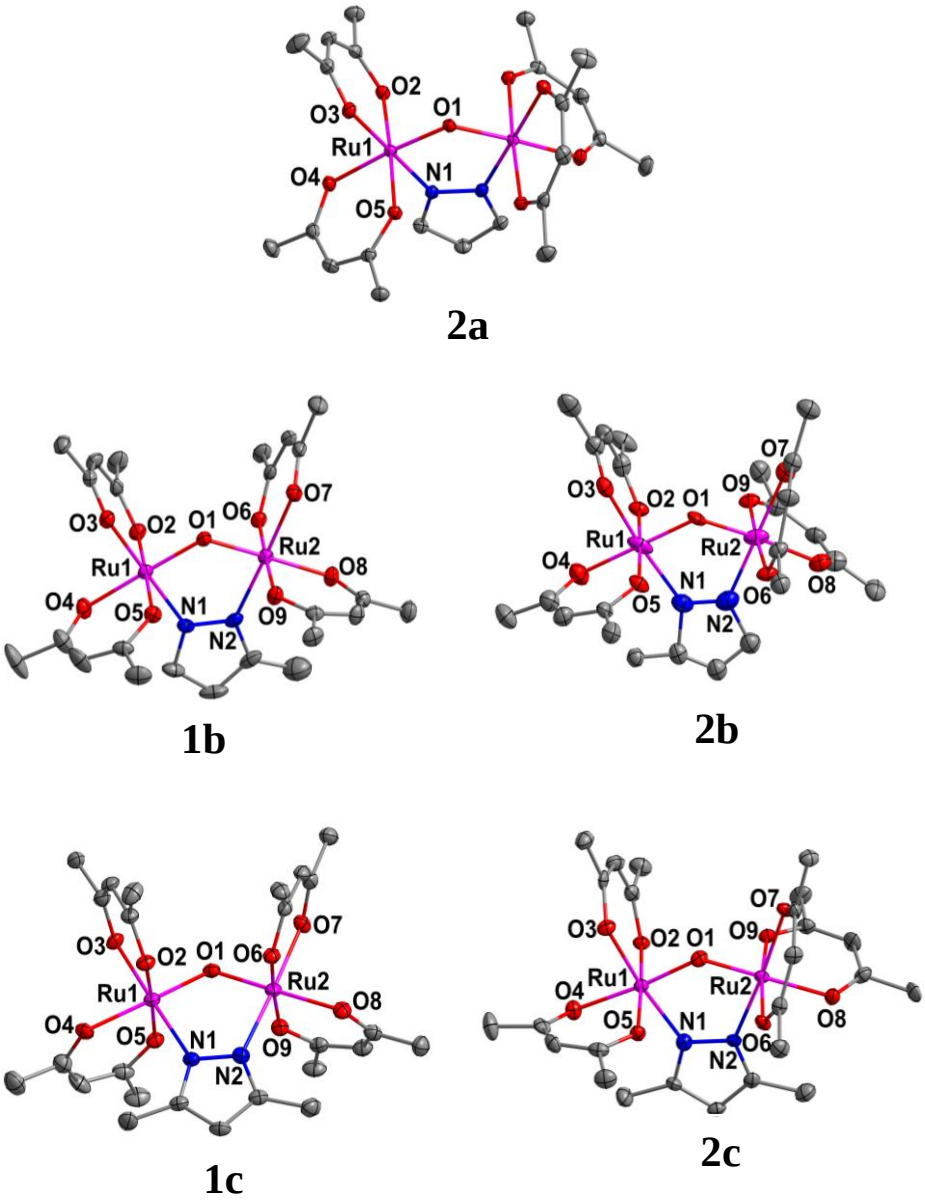


Fig. S1 Perspective views of the complexes. Ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for clarity.

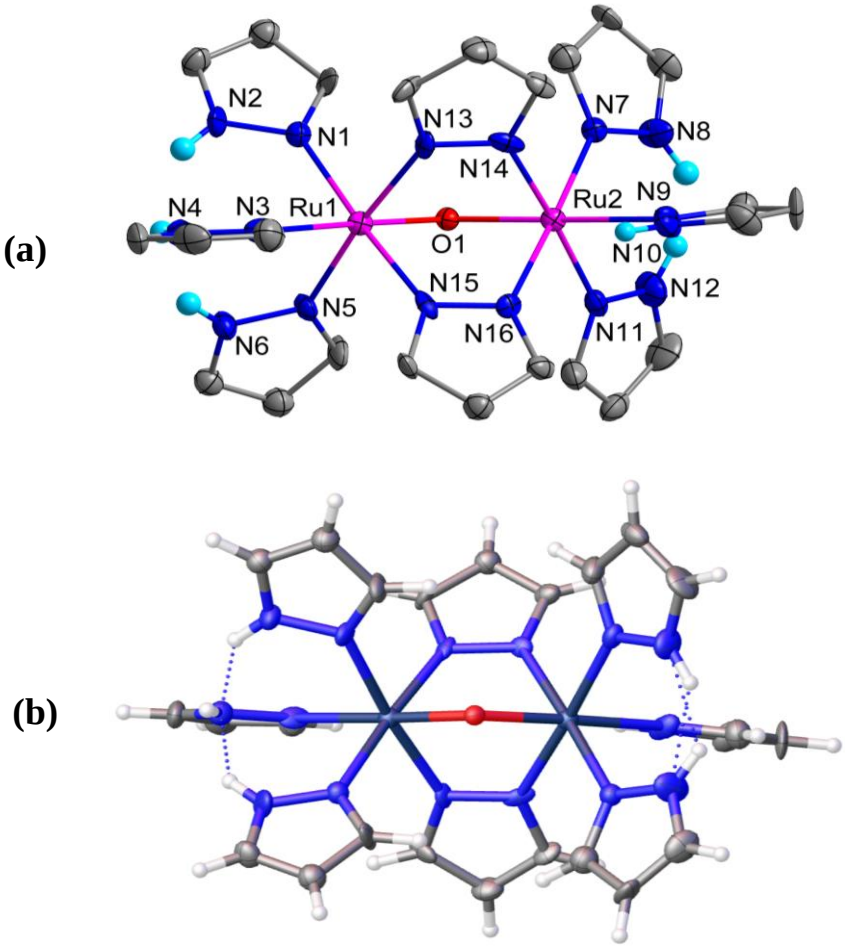


Fig. S2 (a) Perspective view of **3a**. Ellipsoids are drawn at 30% probability level. Except N-H other hydrogen atoms are omitted for clarity. (b) Olex graphic of complex **3a** showing hydrogen bonding interactions.

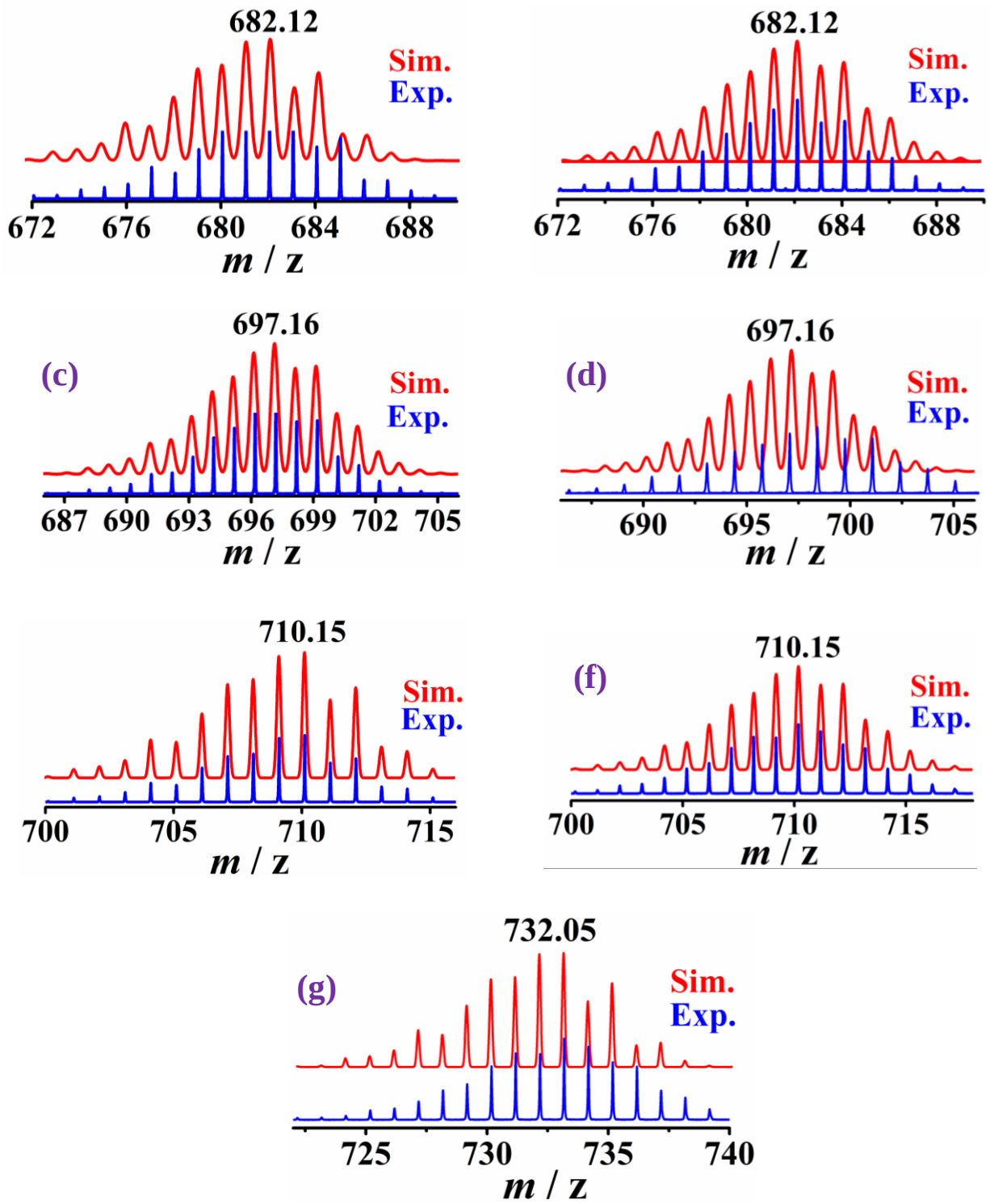


Fig. S3a ESI (+) mass spectra of (a) {**1a**+H}$^+$, (b) {**2a**+H}$^+$, (c) {**1b**+H}$^+$, (d) {**2b**+H}$^+$, (e) {**1c**+H}$^+$, (f) {**2c**+H}$^+$ and (g) {**2d**+H}$^+$ in CH_3CN.

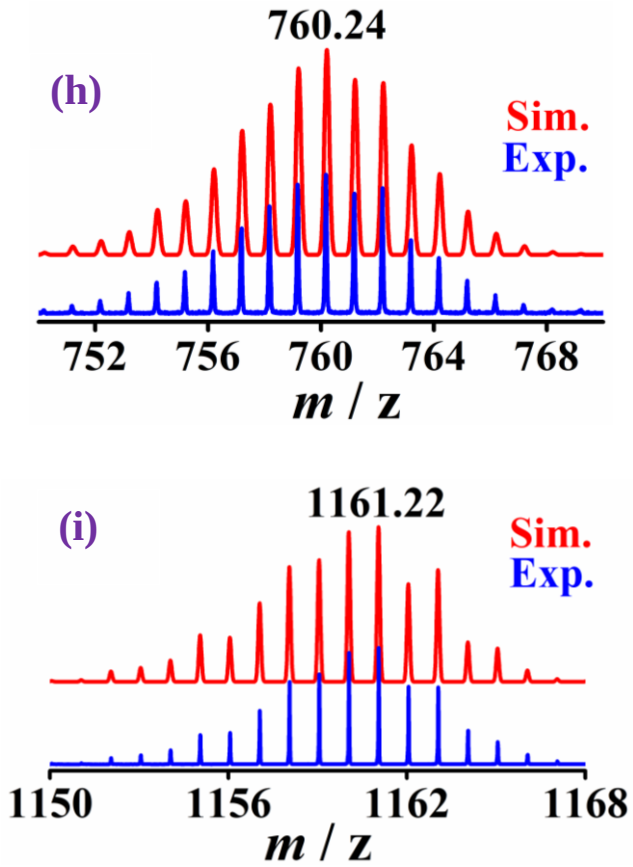


Fig. S3b ESI (+) mass spectra of (h) {**3a**+H}$^+$ and (i) {**3d**+H}$^+$ in CH_3CN.

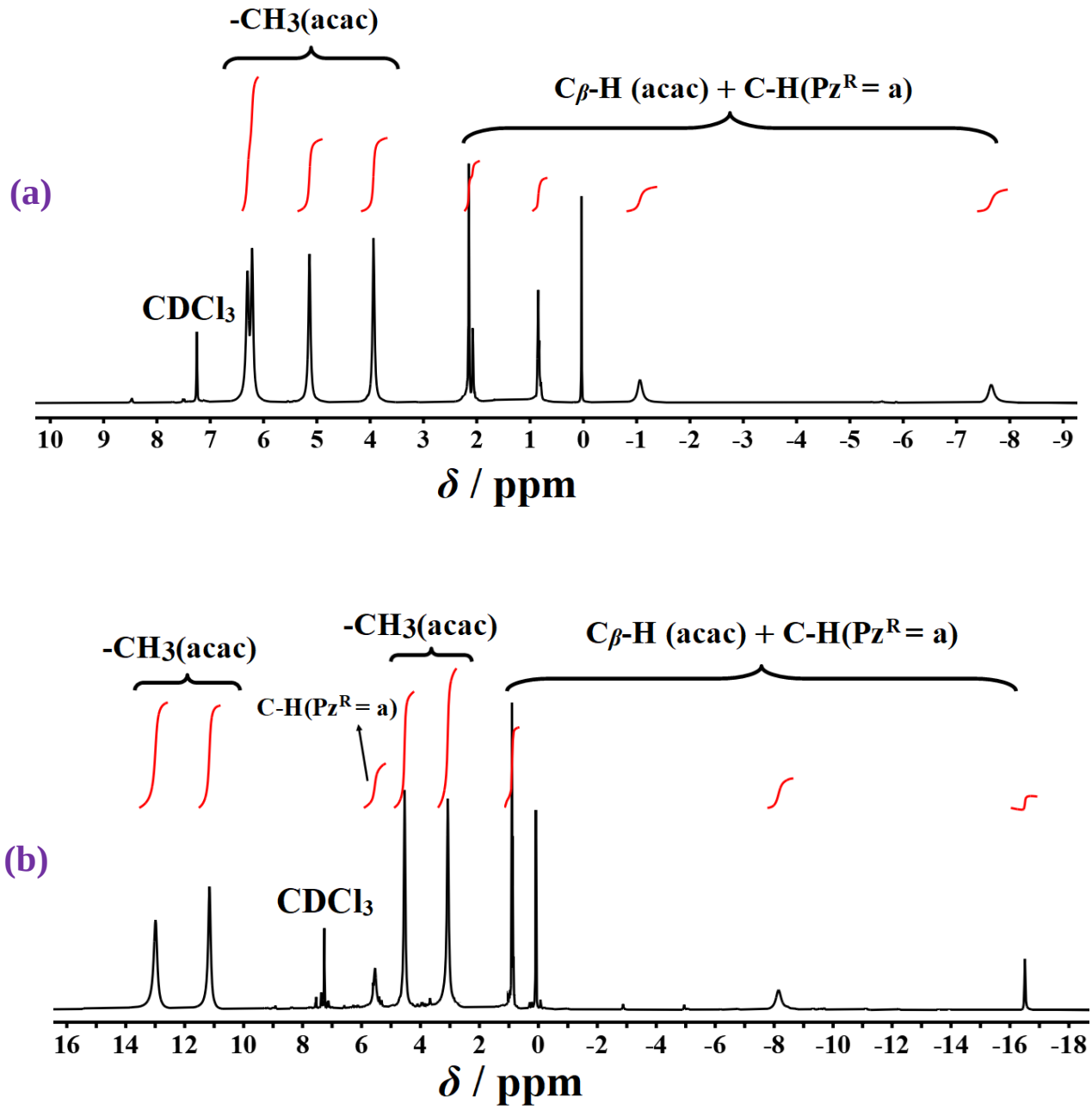


Fig. S4a ^{1}H NMR spectra of (a) **1a** and (b) **2a** in $CDCl_3$.

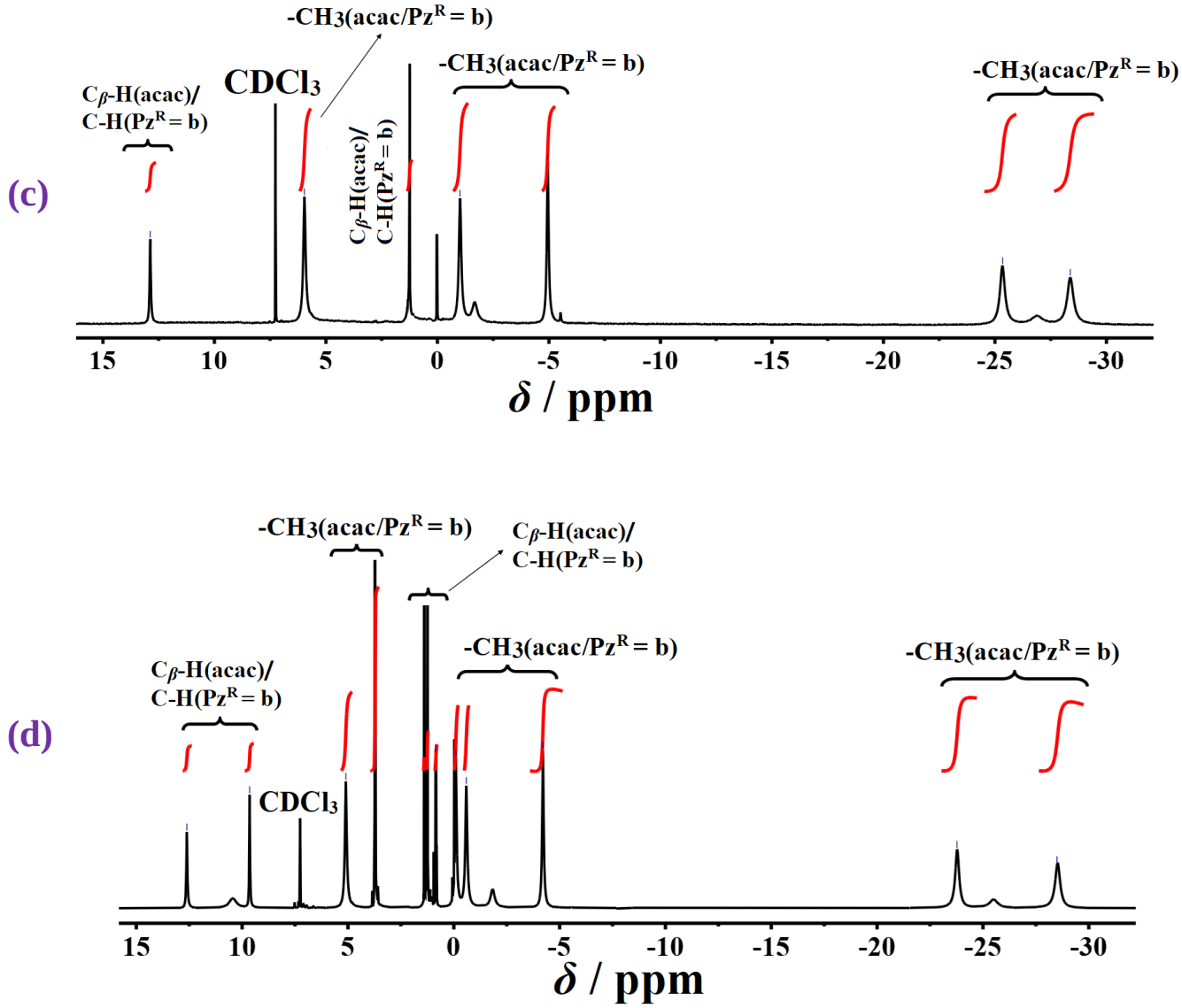


Fig. S4b ^{1}H NMR spectra of (c) **1b** and (d) **2b** in $CDCl_3$.

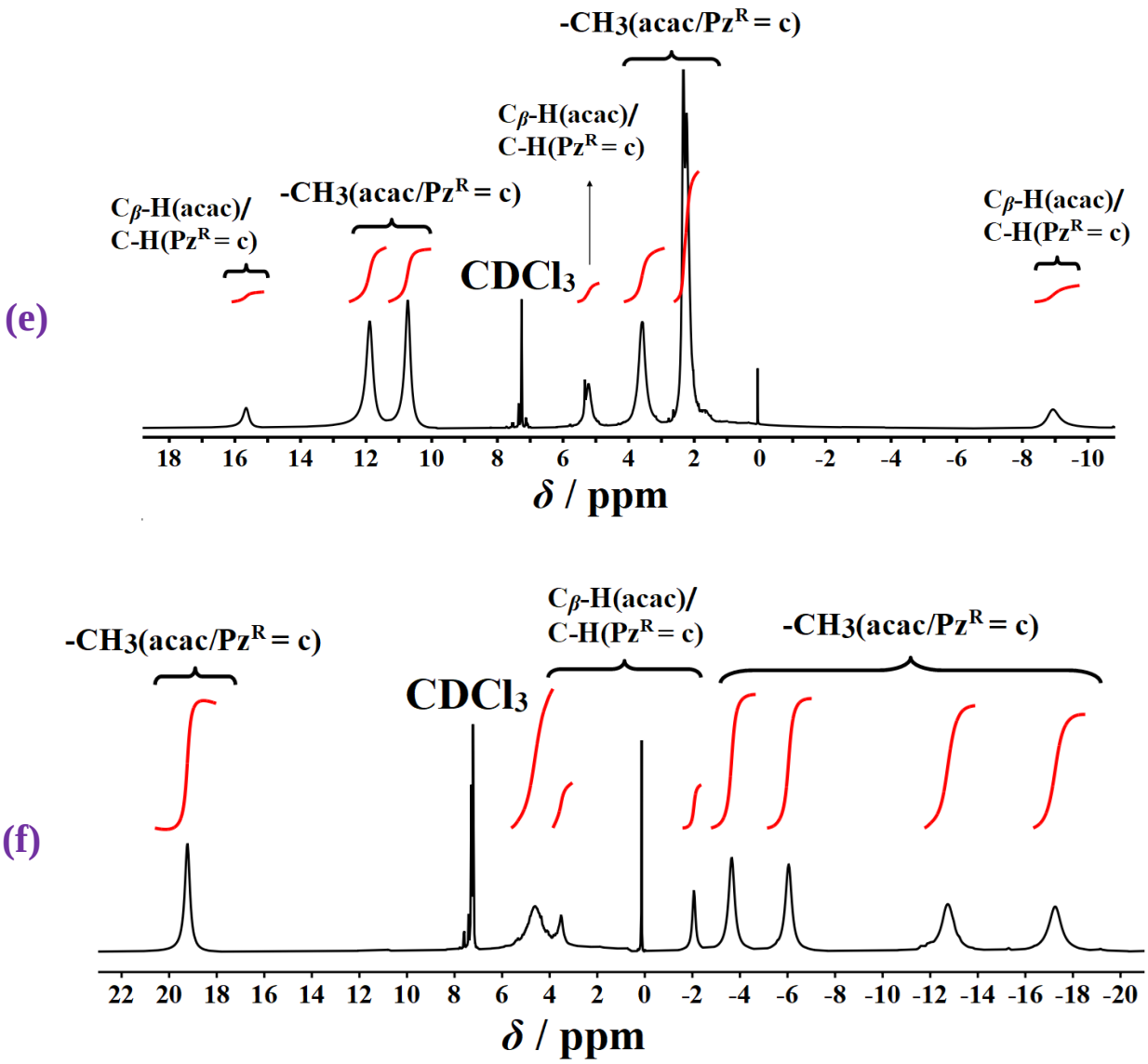


Fig. S4c ^{1}H NMR spectra of (e) **1c** and (f) **2c** in $CDCl_3$.

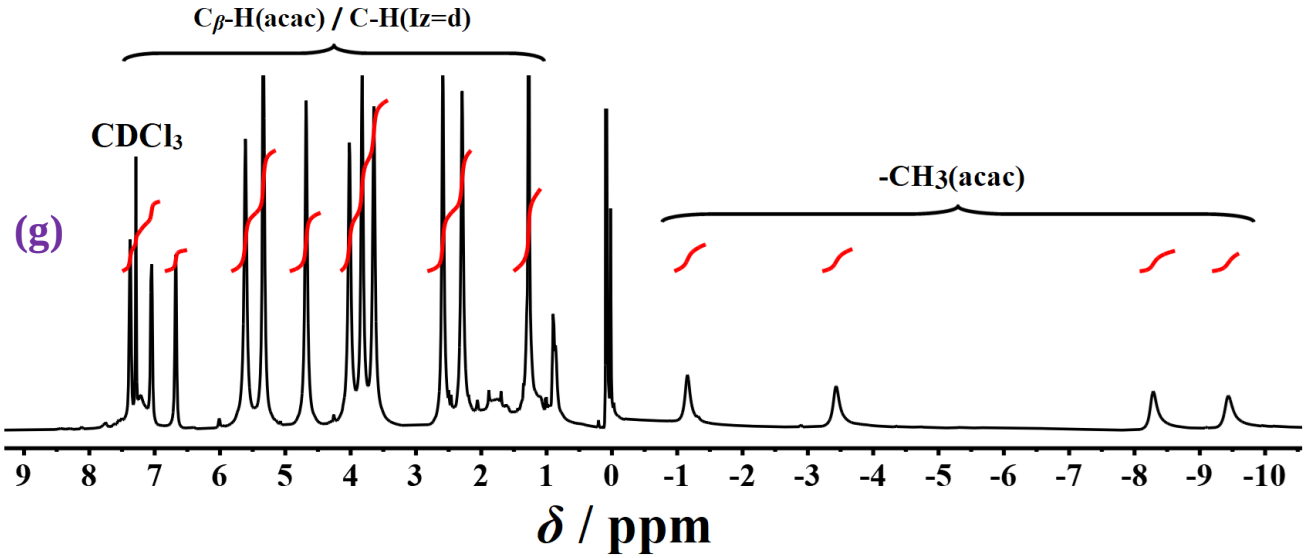


Fig. S4d ^{1}H NMR spectra of (g) **2d** in $CDCl_3$.

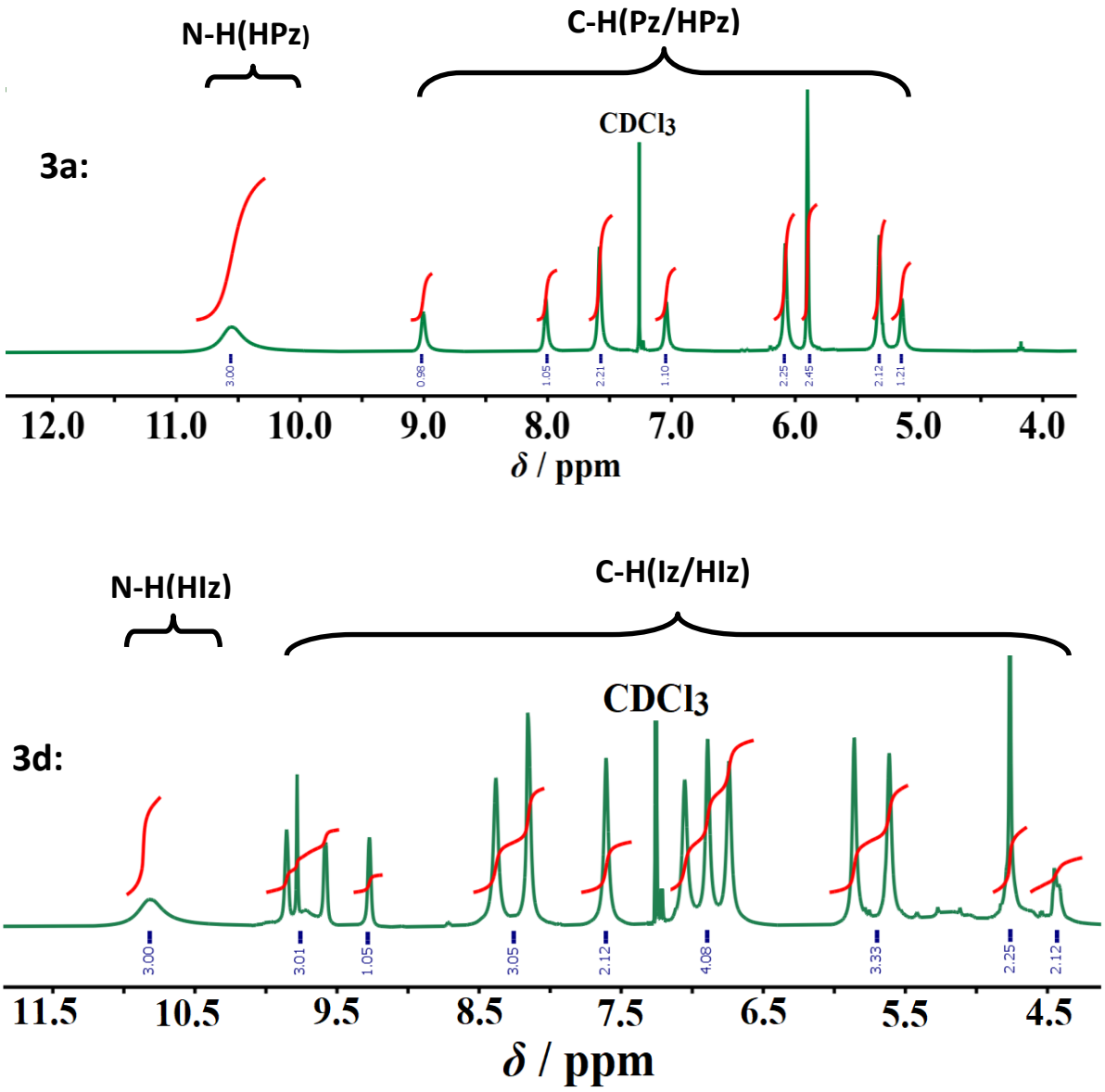


Fig. S5 500 MHz ^{1}H NMR spectra of **3a** and **3d** in $CDCl_3$ with TMS (δ = 0 ppm) as an internal standard.

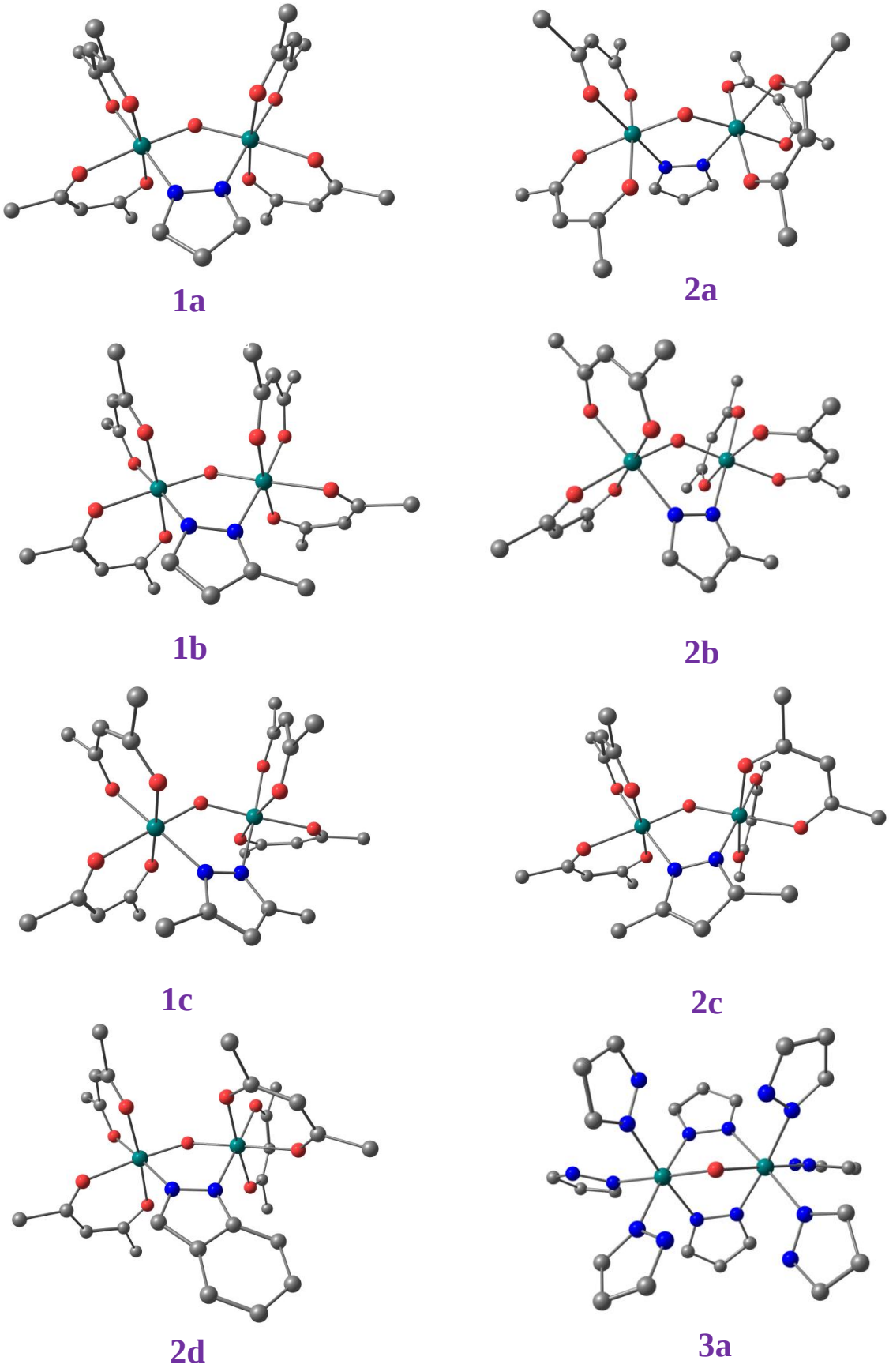


Fig. S6 DFT (M06L/LanL2DZ/6-31G*) optimised structures.

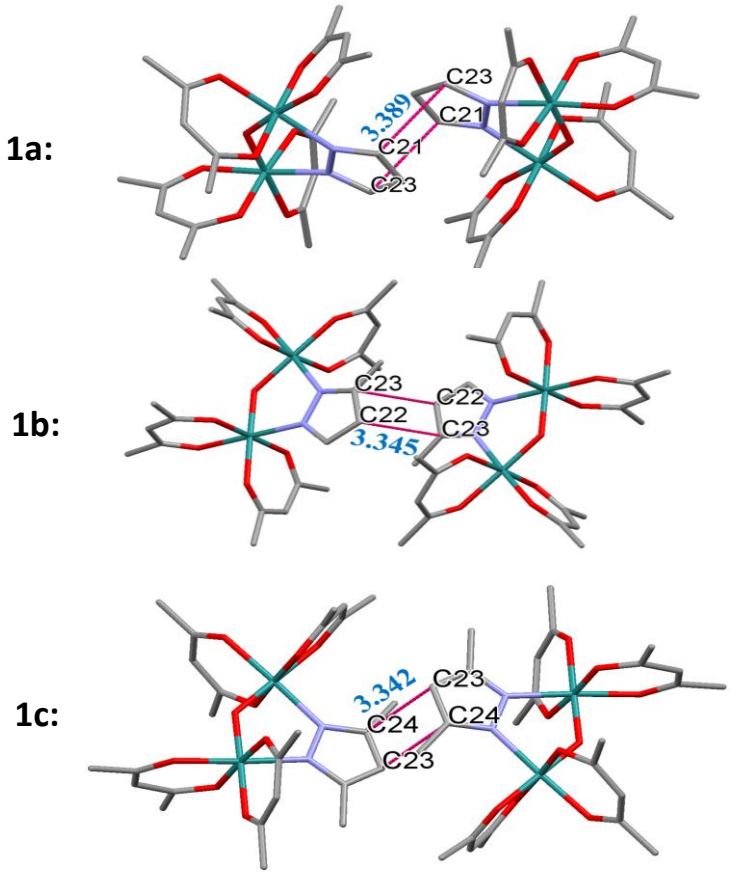


Fig. S7 Intermolecular π---π interaction in terms of distance in Å.

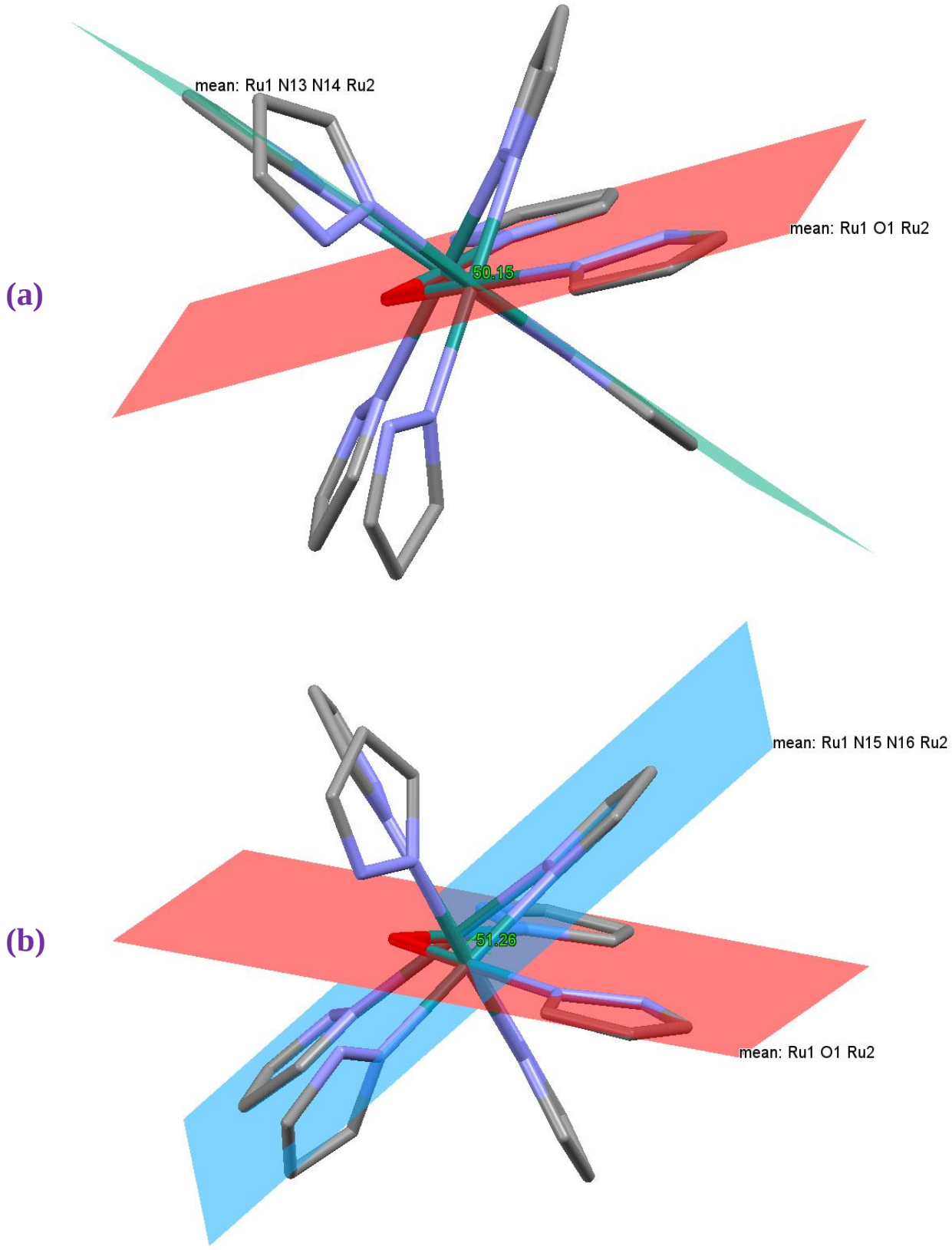


Fig. S8 Angle between the planes (a) Ru1N13N14Ru2/Ru1O1Ru2 and (b) Ru1N15N16Ru2/Ru1O1Ru2 for **3a**.

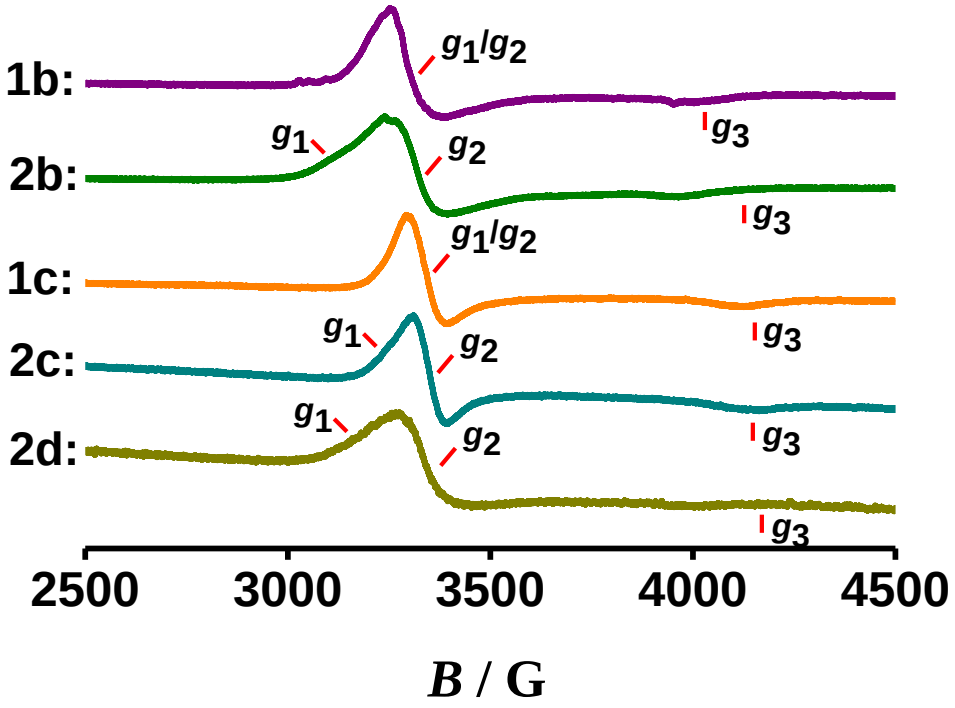


Fig. S9 X-band EPR spectra of Ru complexes in glassy frozen CH_2Cl_2 matrix at 100 K.

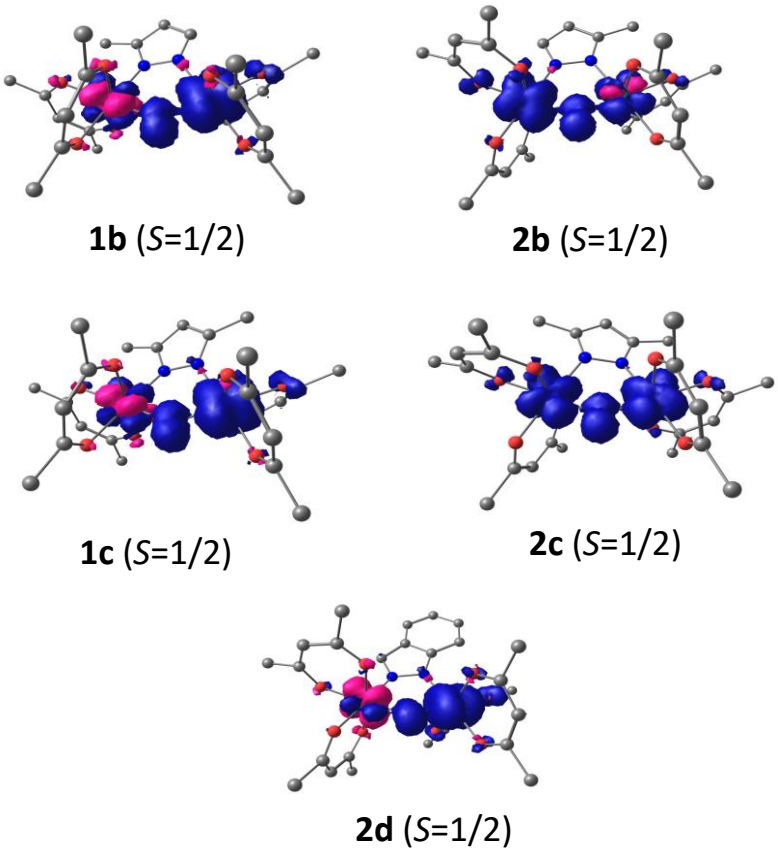


Fig. S10 Mulliken spin density plots.

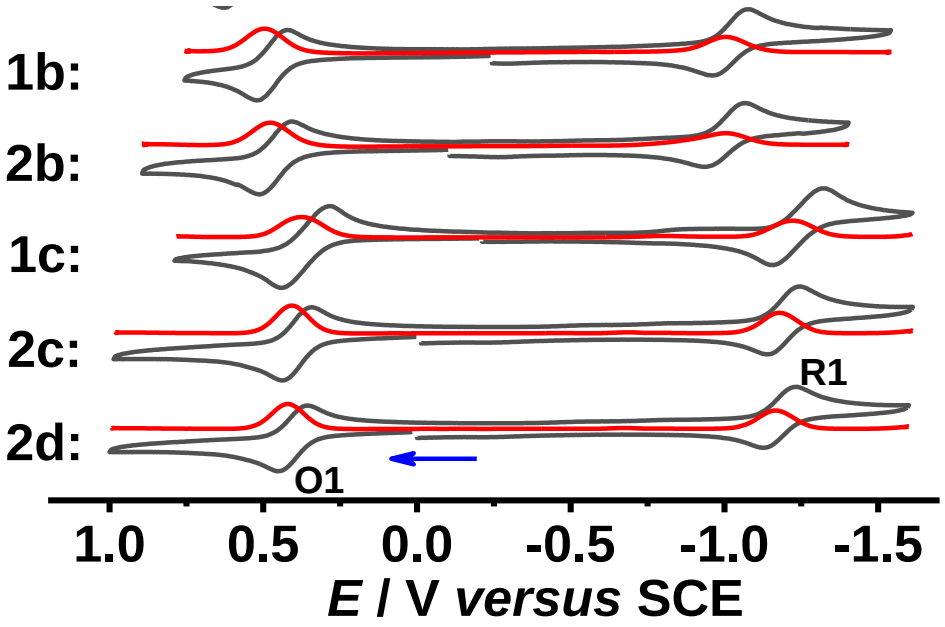


Fig. S11 Cyclic (black) and differential pulse (red) voltammograms in CH_3CN/0.1M Et_4NClO_4.

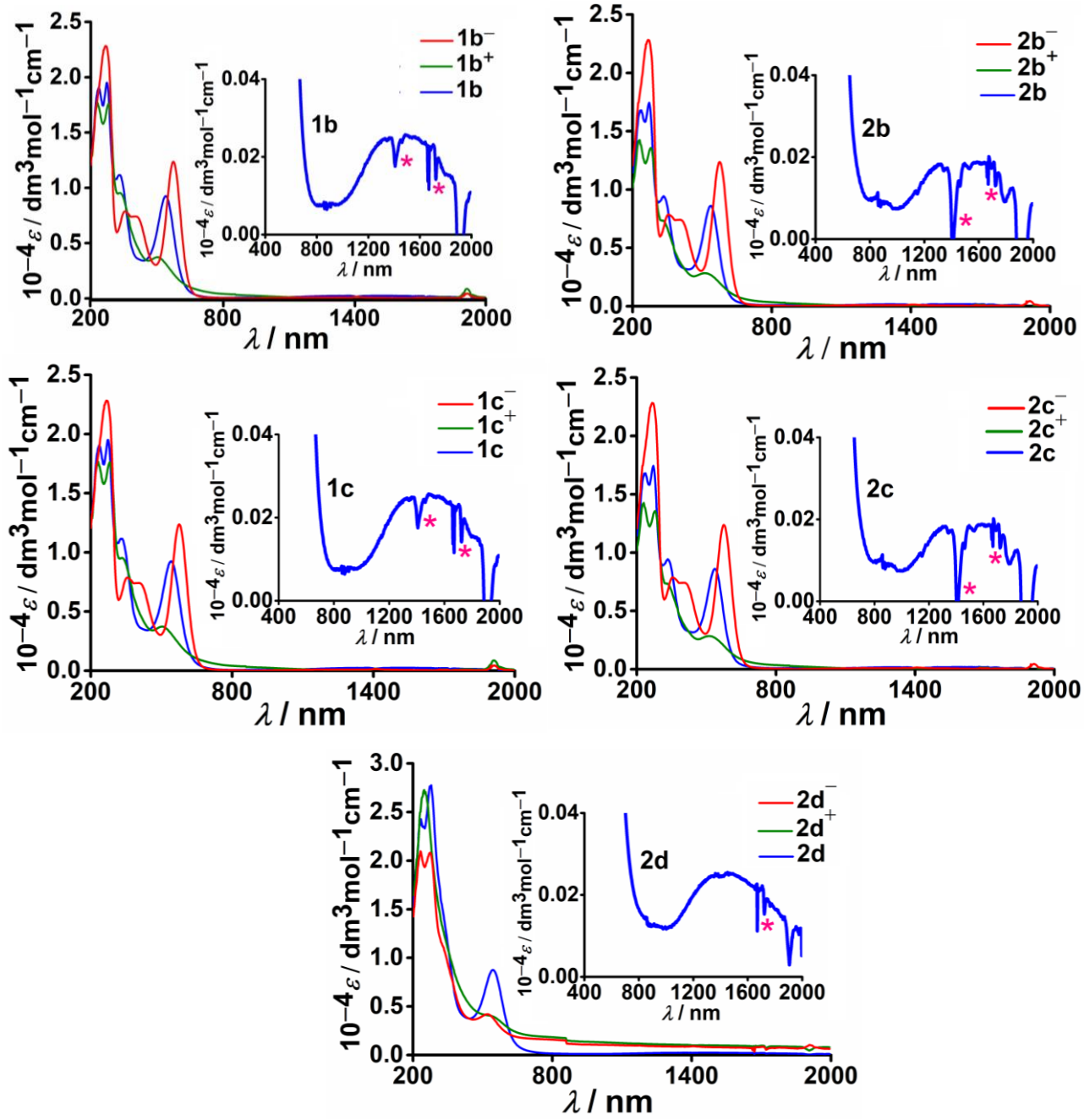


Fig. S12 Electronic spectra in CH_3CN. *Instrumental.

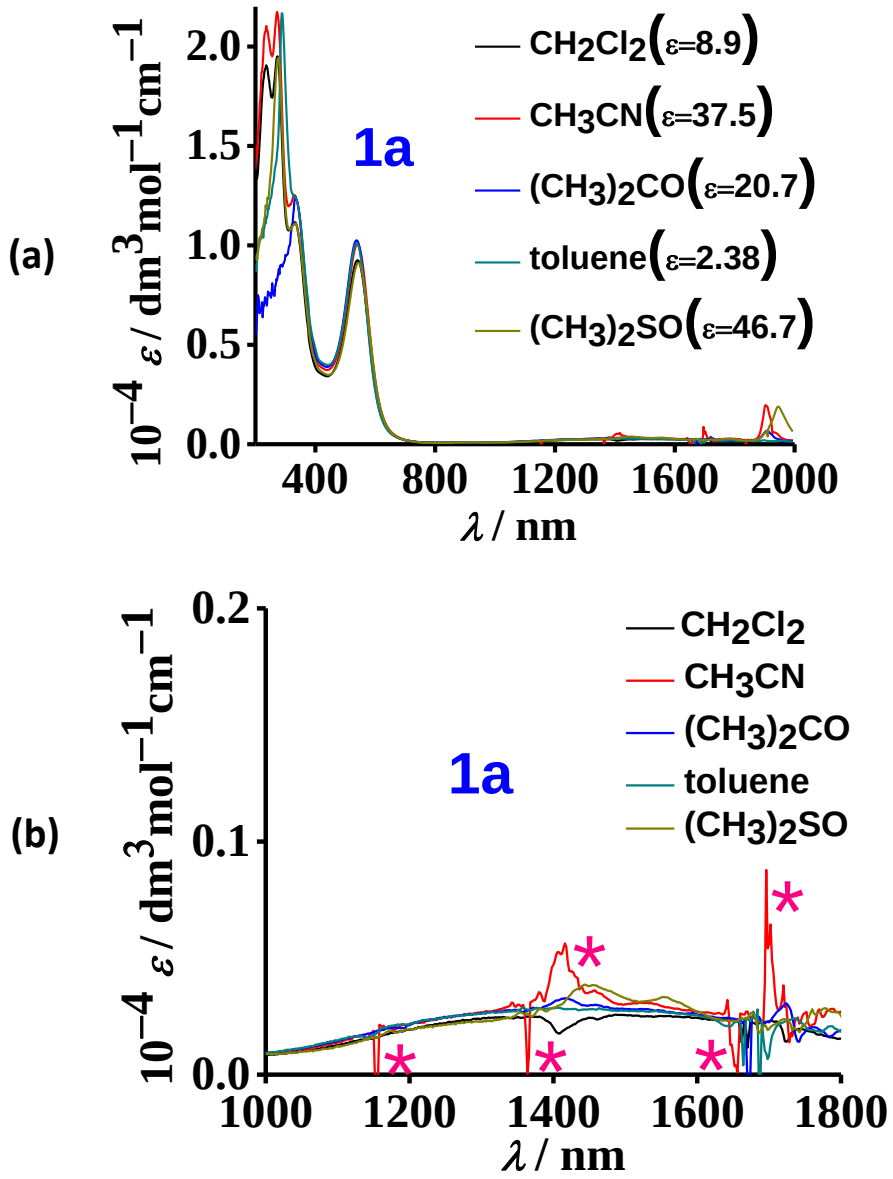


Fig. S13 Electronic spectral data in different solvents with varying polarity for representative **1a**. (a) 2000-200 nm region and (b) expanded IVCT region. *Instrumental.

Table S1 Selected crystallographic parameters

Complex	**1a**	**2a**	**1b**	**2b**
empirical formula	$C_{23}H_{31}N_2O_9Ru_2$	$C_{11.5}H_{15.5}NO_{4.5}Ru$	$C_{24}H_{33}N_2O_9Ru_2$	$C_{24}H_{33}N_2O_9Ru_2$
formula weight	681.64	340.82	695.66	695.66
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	*C12/C1*	*I12/a1*	*C12/C1*	*C 2/C*
a (Å)	30.4609(5)	11.5517(3)	31.0077(16)	16.1406(8)
b (Å)	8.14030(10)	16.3753(4)	8.1608(3)	17.1433(5)
c (Å)	23.6002(4)	14.4599(5)	23.5756(12)	21.2754(10)
α (deg)	90	90	90	90
β (deg)	109.249(2)	97.099(3)	105.161(5)	97.538(14)
γ (deg)	90	90	90	90
V (Å^3)	5524.77(16)	2714.32(13)	5758.1(5)	5836.1(4)
Z	8	8	8	8
μ (mm^{-1})	9.292	1.164	1.099	1.084
T (K)	150(2)	150(2)	150(2)	300(2)
D_{calcd} (g cm^{-3})	1.639	1.668	1.605	1.583
F (000)	2744	1372	2808	2808
θ range (deg)	3.073 to 64.997	2.488 to 25.000	3.201 to 24.999	1.741 to 24.994
data/restraints/ parameters	4702 / 0 / 333	2334 / 0 / 168	5024 / 0 / 343	5113 / 38 / 397
R1, *w*R2 [$I > 2\sigma(I)$]	0.0572, 0.1478	0.0200, 0.0492	0.0318, 0.0808	0.1104, 0.2494
R1, *w*R2(all data)	0.0692, 0.1622	0.0242, 0.0502	0.0366, 0.0836	0.1395, 0.2736
GOF	1.092	1.090	1.055	
largest diff. peak/hole, (e Å^{-3})	1.859 / -0.965	0.382 / -0.318	1.416 / -0.420	2.400 / -1.753

Table S2 Selected crystallographic parameters

complex	**1c**	**2c**	**2d**	**3a**
empirical formula	$C_{25}H_{35}N_2O_9Ru_2$	$C_{25}H_{35}N_2O_9Ru_2$	$C_{27}H_{33}N_2O_9Ru_2$	$C_{24}H_{30}N_{16}ORu_2$
formula weight	709.69	709.69	731.69	760.78
crystal system	monoclinic	triclinic	triclinic	tetragonal
space group	*C12/C1*	*P-1*	*P-1*	*I41cd*
a (Å)	30.8051(7)	10.7709(4)	10.8202(8)	29.6769(4)
b (Å)	8.1833(2)	11.4776(4)	11.3874(8)	29.6769(4)
c (Å)	24.0310(6)	13.8804(7)	14.8695(10)	15.2915(4)
α (deg)	90	99.002(4)	110.833(6)	90
β (deg)	104.800(2)	105.311(4)	96.149(6)	90
γ (deg)	90	107.152(3)	111.215(7)	90
V (Å^3)	5856.9(2)	1529.46(12)	1536.7(2)	13467.5(5)
Z	8	2	2	16
μ (mm^{-1})	8.790	8.415	1.034	0.941
T (K)	150(2)	150(2)	150(2)	150(2)
D_{calcd} (g cm^{-3})	1.610	1.541	1.581	1.501
F (000)	2872	718	738	6112
θ range (deg)	2.967 to 72.931	3.413 to 64.982	2.016 to 24.997	2.170 to 24.999
data/restraints/ parameters	4962 / 0 / 353	5128 / 0 / 353	5405 / 0 / 369	5912 / 0 / 388
R1, *w*R2 [$I > 2\sigma(I)$]	0.0582, 0.1395	0.0672, 0.1075	0.0685, 0.1660	0.0637, 0.1603
R1, *w*R2(all data)	0.0677, 0.1535	0.0747, 0.1188	0.1148, 0.1911	0.0752, 0.1745
GOF	1.050	1.066	1.036	
largest diff. peak/hole, (e Å^{-3})	1.317 / -0.881	1.431 / -0.677	1.435 / -0.840	1.259 / -1.391

Table S3 Selected experimental and DFT calculated bond lengths (Å)

	1a		**2a**		**1b**		**2b**	
Bond	X-ray	DFT (*S*=1/2)	X-ray	DFT (*S*=1/2)	X-ray	DFT (*S*=1/2)	X-ray	DFT (*S*=1/2)
Ru1-O1	1.848(4)	1.852	1.8430(8)	1.850	1.880(2)	1.892	1.825(9)	1.846
Ru1-O2	2.018(4)	2.021	2.0197(15)	2.032	2.009(2)	2.023	2.003(9)	2.043
Ru1-O3	2.057(4)	2.076	2.0127(14)	2.030	2.036(2)	2.050	2.058(11)	2.002
Ru1-O4	2.024(4)	2.034	2.0488(14)	2.056	2.017(3)	2.009	2.009(11)	2.054
Ru1-O5	2.025(4)	2.012	2.0137(15)	2.022	2.006(2)	2.019	2.031(9)	2.041
Ru1-N1	2.047(5)	2.074	2.0288(16)	2.041	2.044(3)	2.065	2.21(3)	2.330
Ru2-O1	1.842(4)	1.855	–	–	1.885(2)	1.870	1.834(9)	1.843
Ru2-O6	2.012(4)	2.030	–	–	2.006(2)	2.013	2.007(8)	2.011
Ru2-O7	2.046(4)	2.078	–	–	2.042(2)	2.051	2.040(10)	2.074
Ru2-O8	2.039(5)	2.029	–	–	2.015(2)	2.026	2.036(11)	2.029
Ru2-O9	2.015(4)	2.011	–	–	2.020(2)	2.020	2.010(9)	2.013
Ru2-N2	2.044(5)	2.058	–	–	2.059(3)	2.055	1.88(2)	2.018
N1-N2	1.359(7)	1.355	1.369(3)	1.353	1.373(4)	1.360	1.43(3)	1.361
Ru1---Ru2	3.369	3.371	3.359	3.362	3.409	3.359	3.351	3.387

Table S4 Selected experimental and DFT calculated bond lengths (Å)

	1c		**2c**		**2d**	
Bond	X-ray	DFT (*S*=1/2)	X-ray	DFT (*S*=1/2)	X-ray	DFT (*S*=1/2)
Ru1-O1	1.832(4)	1.830	1.826(4)	1.846	1.897(5)	1.870
Ru1-O2	2.018(4)	2.031	2.019(4)	2.032	1.998(5)	2.003
Ru1-O3	2.052(4)	2.049	2.057(3)	2.068	2.050(6)	2.036
Ru1-O4	2.054(4)	2.051	2.047(4)	2.066	2.033(6)	2.029
Ru1-O5	2.016(4)	2.025	2.028(4)	2.040	2.032(5)	2.043
Ru1-N1	2.070(5)	2.085	2.082(4)	2.077	2.024(7)	2.019
Ru2-O1	1.823(4)	1.835	1.811(4)	1.835	1.885(5)	1.870
Ru2-O6	2.024(4)	2.022	2.033(4)	2.049	2.021(5)	1.025
Ru2-O7	2.057(4)	2.065	2.024(4)	2.032	2.004(6)	2.012
Ru2-O8	2.029(5)	2.045	2.061(4)	2.055	2.044(6)	2.040
Ru2-O9	2.038(4)	2.056	2.003(4)	2.016	2.013(6)	2.031
Ru2-N2	2.074(5)	2.080	2.074(5)	2.061	2.098(7)	2.071
N1-N2	1.380(8)	1.370	1.387(7)	1.375	1.356(9)	1.366
Ru1---Ru2	3.373	3.382	3.371	3.379	3.404	3.359

Table S5 Selected experimental and DFT calculated bond angles (deg**)**

	1a		**2a**		**1b**		**2b**	
Bond	X-ray	DFT (*S*=1/2)	X-ray	DFT (*S*=1/2)	X-ray	DFT (*S*=1/2)	X-ray	DFT (*S*=1/2)
Ru1-O1-Ru2	131.9(2)	135.45	131.36(11)	133.29	129.78(13)	132.03	132.6(5)	133.51
O1-Ru1-N1	84.24(19)	83.02	84.89(7)	85.98	85.02(11)	87.15	80.4(8)	88.35
O1-Ru1-O2	93.84(18)	90.65	92.09(4)	95.32	91.82(10)	92.65	92.0(4)	95.36
O1-Ru1-O3	95.21(18)	98.32	90.79(6)	89.11	93.88(10)	91.61	93.5(4)	90.47
O1-Ru1-O4	174.98(19)	176.21	175.40(6)	177.82	178.75(10)	179.01	177.4(4)	179.21
O1-Ru1-O5	89.91(18)	88.78	89.09(4)	92.41	89.86(10)	90.44	91.9(4)	88.71
O2-Ru1-N1	86.69(18)	89.14	90.69(6)	90.11	89.45(11)	88.23	88.0(7)	89.64
O2-Ru1-O3	93.60(18)	96.36	89.39(6)	88.02	93.11(10)	92.29	93.5(4)	97.19
O2-Ru1-O4	85.86(16)	84.11	88.23(6)	89.68	87.32(10)	88.32	85.7(4)	82.32
O2-Ru1-O5	176.18(16)	176.95	175.80(5)	176.16	177.75(10)	176.95	175.9(4)	178.59
O3-Ru1-N1	179.40(19)	178.22	178.89(6)	177.83	177.26(10)	178.10	173.8(8)	178.67
O3-Ru1-O4	89.81(18)	90.55	89.44(6)	90.22	87.69(11)	87.31	87.9(5)	90.43
O3-Ru1-O5	86.81(18)	88.18	86.61(6)	87.23	88.27(10)	89.39	87.7(4)	87.11
O4-Ru1-N1	90.73(18)	93.63	90.79(6)	93.09	93.42(11)	96.28	98.3(8)	98.56
O4-Ru1-O5	90.34(17)	92.74	93.03(6)	91.03	90.96(10)	89.67	90.4(4)	93.82
O6-Ru2-N2	89.47(18)	88.61	–	–	86.89(10)	87.52	88.8(9)	90.22
O6-Ru2-O7	93.33(17)	95.11	–	–	93.73(10)	94.61	92.7(4)	91.64
O6-Ru2-O8	86.94(18)	88.23	–	–	86.80(10)	87.39	87.9(4)	88.44
O6-Ru2-O9	176.24(17)	177.72	–	–	177.35(10)	178.55	177.0(5)	178.02
O7-Ru2-N2	176.98(18)	178.05	–	–	177.48(11)	177.63	175.0(9)	179.27
O7-Ru2-O8	87.59(19)	87.21	–	–	88.68(10)	89.06	90.6(4)	93.09
O7-Ru2-O9	88.78(17)	90.22	–	–	86.88(10)	87.13	86.3(4)	89.21
O8-Ru2-N2	93.70(19)	96.88	–	–	93.79(11)	95.36	84.7(10)	95.38
O8-Ru2-O9	90.04(18)	92.63	–	–	90.64(10)	93.44	89.2(4)	90.15
Ru1-N1-N2	120.0(4)	119.27	119.27(5)	122.39	121.1(2)	122.52	118.6(19)	123.32
Ru2-N2-N1	118.8(4)	121.36	–	–	118.4(2)	117.20	117(2)	122.07

Table S6 Selected experimental and DFT calculated bond angles (deg**)**

	1c		**2c**		**2d**	
Bond	X-ray	DFT (*S*=1/2)	X-ray	DFT (*S*=1/2)	X-ray	DFT (*S*=1/2)
Ru1-O1-Ru2	134.7(2)	131.20	136.0(2)	133.71	128.4(3)	128.4(3)
O1-Ru1-N1	83.77(19)	85.61	82.92(17)	84.68	85.3(3)	85.1(3)
O1-Ru1-O2	92.45(18)	96.33	91.97(18)	90.84	92.7(2)	92.9(2)
O1-Ru1-O3	94.57(18)	92.52	90.29(16)	93.70	91.2(2)	91.2(2)
O1-Ru1-O4	179.02(18)	178.55	174.75(15)	175.10	176.6(2)	176.6(2)
O1-Ru1-O5	90.87(18)	93.65	92.20(17)	93.12	93.5(2)	93.4(2)
O2-Ru1-N1	88.99(18)	88.17	88.80(16)	90.30	87.4(2)	87.5(3)
O2-Ru1-O3	93.59(18)	95.35	93.54(15)	95.05	94.1(2)	94.0(3)
O2-Ru1-O4	87.26(18)	90.11	87.29(17)	88.67	84.0(2)	83.8(2)
O2-Ru1-O5	176.32(17)	179.41	175.33(16)	177.34	172.6(2)	172.7(2)
O3-Ru1-N1	176.99(19)	177.28	172.90(17)	175.51	176.3(2)	176.1(2)
O3-Ru1-O4	84.51(18)	85.38	84.57(16)	86.27	88.2(2)	88.1(2)
O3-Ru1-O5	87.75(18)	84.58	88.54(16)	87.69	89.9(2)	89.7(2)
O4-Ru1-N1	97.16(19)	94.64	102.25(17)	105.13	95.3(3)	95.6(3)
O4-Ru1-O5	89.45(18)	90.36	88.84(17)	90.21	89.9(2)	90.0(2)
O6-Ru2-N2	86.69(18)	88.29	88.74(17)	89.82	91.7(2)	91.7(2)
O6-Ru2-O7	94.30(17)	96.21	89.99(16)	93.19	89.4(2)	89.3(2)
O6-Ru2-O8	84.30(17)	90.89	88.70(15)	87.04	85.4(2)	85.4(2)
O6-Ru2-O9	175.20(17)	176.12	172.83(15)	175.80	173.2(2)	173.1(2)
O7-Ru2-N2	177.1(2)	176.06	176.04(17)	177.10	97.3(3)	97.2(3)
O7-Ru2-O8	86.64(18)	89.36	85.98(16)	88.00	88.0(2)	87.8(2)
O7-Ru2-O9	86.66(17)	88.49	83.75(16)	84.41	83.8(2)	83.8(2)
O8-Ru2-N2	96.13(19)	94.93	176.10(15)	177.32	174.0(3)	174.2(2)
O8-Ru2-O9	90.06(17)	92.66	94.32(15)	93.62	93.4(2)	93.4(2)
Ru1-N1-N2	119.1(4)	119.37	119.2(3)	122.40	120.8(5)	121.0(5)
Ru2-N2-N1	118.4(4)	120.27	117.7(3)	119.08	119.4(5)	119.2(5)

Table S7 Selected experimental and DFT calculated bond lengths (Å)

	3a	
Bond	X-ray	DFT (*S*=0)
Ru1-O1	1.900(8)	1.915
Ru1-N1	2.129(9)	2.118
Ru1-N3	2.123(10)	2.117
Ru1-N5	2.094(9)	2.099
Ru1-N13	2.048(9)	2.120
Ru1-N15	2.013(9)	2.075
Ru2-O1	1.893(8)	1.912
Ru2-N7	2.077(9)	2.096
Ru2-N9	2.126(10)	2.113
Ru2-N11	2.094(10)	2.109
Ru2-N14	2.047(10)	2.126
Ru2-N16	2.057(10)	2.082
N1-N2	1.351(13)	1.359
N3-N4	1.405(15)	1.350
N5-N6	1.365(13)	1.357
N7-N8	1.358(14)	1.360
N9-N10	1.353(14)	1.354
N11-N12	1.346(13)	1.351
N13-N14	1.349(14)	1.353
N15-N16	1.352(14)	1.360
Ru1---Ru2	3.185	3.210

Table S8 Selected experimental and DFT calculated bond angles (deg)

	3a	
Bond	X-ray	DFT (*S*=0)
Ru1-O1-Ru2	114.2(4)	106.86
N1-Ru1-N3	91.1(4)	95.45
N1-Ru1-N5	91.4(4)	93.11
N1-Ru1-N13	91.4(4)	92.65
N1-Ru1-N15	175.5(3)	177.21
N3-Ru1-N5	91.1(4)	89.68
N3-Ru1-N13	94.2(4)	90.05
N3-Ru1-N15	93.0(4)	96.39
N13-Ru1-N15	87.1(4)	88.25
N7-Ru2-N9	89.6(4)	88.31
N7-Ru2-N11	92.6(4)	92.93
N7-Ru2-N14	90.4(4)	89.49
N7-Ru2-N16	177.7(3)	178.22
N9-Ru2-N11	91.0(4)	89.69
N9-Ru2-N14	90.6(4)	93.03
N9-Ru2-N16	92.1(4)	90.27
N14-Ru2-N16	88.0(4)	89.57
Ru1-N13-N14	115.5(6)	119.31
Ru1-N15-N16	118.0(7)	120.04
Ru2-N14-N13	117.7(7)	121.55
Ru2-N16-N15	115.5(6)	118.85

Table S9 Hydrogen bonding distances in Å

N-H···N (Å)	**3a**
N2-H2···N4	2.20
N6-H6···N4	2.37
N12-H12···N10	2.02
N8-H8···N10	2.11

Table S10 Angle (deg) between the planes for **3a**

Complex	Planes	Angle (deg) between the planes
3a	Ru1N13N14Ru2/Ru1O1Ru2	50.15
3a	Ru1N15N16Ru2/Ru1O1Ru2	51.26

Table S11 Energies of DFT (M06L/LanL2DZ/6-31G*) optimised structures

Complex	*E* (Hartrees)					Δ*E*
	S = 0	*S* = 1	*S* = 2	*S* = 3/2	*S* = 1/2	
1a	–	–		-1869.4355	-1869.44395	0.00837 Hartrees 1837.0027 cm^{-1}
1a^{+}	-1869.2239	-1869.2201	-1869.2199	–	–	0.00373 Hartrees 818.64037 cm^{-1}
1a^{-}	-1869.5271	-1869.5089		–	–	0.01818 Hartrees 3990.0488 cm^{-1}
2a	–	–		-1869.4294	-1869.43764	0.00819 Hartrees 1797.4972 cm^{-1}
2a^{+}	-1869.2249	-1869.2212	-1869.2206	–	–	0.00368 Hartrees 807.6666 cm^{-1}
2a^{-}	-1869.52912	-1869.5107	–	–	–	0.01834 Hartrees 4025.1647 cm^{-1}
1b	–	–	–	-1908.8037	-1908.81187	0.00814 Hartrees 1786.5235 cm^{-1}
1b^{+}	-1908.5972	-1908.5936	-1908.5929	–	–	0.00353 Hartrees 774.74544 cm^{-1}
1b^{-}	-1908.8885	-1908.8705	–	–	–	0.018056 Hartrees 3962.83392 cm^{-1}
2b	–	–	–	-1908.8039	-1908.81211	0.00820 Hartrees 1799.6200 cm^{-1}
2b^{+}	-1908.6005	-1908.5968	-1908.5961	–	–	0.00365 Hartrees 801.0824 cm^{-1}
2b^{-}	-1908.8886	-1908.8704	–	–	–	0.018111 Hartrees 3974.90502 cm^{-1}
1c	–	–	–	-1948.0546	-1948.06295	0.00828 Hartrees 1817.2499 cm^{-1}
1c^{+}	-1947.9136	-1947.9099	-1947.9069	–	–	0.00378 Hartrees 829.6141 cm^{-1}
1c^{-}	-1948.1408	-1948.1225	–	–	–	0.018310 Hartrees 4018.58048 cm^{-1}
2c	–	–	–	-1948.0547	-1948.06277	0.00801 Hartrees 1759.30863 cm^{-1}
2c^{+}	-1947.91514	-1947.91155	-1947.91125	–	–	0.00359 Hartrees 787.91392 cm^{-1}
2c^{-}	-1948.20606	-1948.18773	–	–	–	0.018321 Hartrees 4020.9947 cm^{-1}
2d	–	–	–	-2023.0535	-2023.0619	0.00841 Hartrees 1845.7816 cm^{-1}
2d^{+}	-2022.91288	-2022.90949	-2022.90921	–	–	0.00339 Hartrees 744.0190 cm^{-1}
2d^{-}	-2023.14589	-2023.12766	–	–	–	0.018222 Hartrees 3999.26671 cm^{-1}

Table S12 DFT calculated selected MO compositions (M06L/LanL2DZ/6-31G*)

Complex	MO	Fragments	% Contribution
1a^{+} (*S*=0)	LUMO	Ru/acac/μ-O	63/21/15
1a (*S*=1/2)	SOMO β-LUMO	Ru/acac/μ-O Ru/μ-O/acac	65/19/14 66/17/16
1a^{-} (*S*=0)	HOMO	Ru/μ-O/acac	63/18/18
2a^{+} (*S*=0)	LUMO	Ru/acac/μ-O	65/20/13
2a (*S*=1/2)	SOMO β-LUMO	Ru/acac/μ-O Ru/μ-O/acac	62/20/16 65/18/16
2a^{-} (*S*=0)	HOMO	Ru/μ-O/acac	66/20/17
1b^{+} (*S*=0)	LUMO	Ru/acac/μ-O	68/18/14
1b (*S*=1/2)	SOMO β-LUMO	Ru/acac/μ-O Ru/μ-O/acac	66/21/12 61/19/17
1b^{-} (*S*=0)	HOMO	Ru/μ-O/acac	69/19/12
2b^{+} (*S*=0)	LUMO	Ru/acac/μ-O	64/24/14
2b (*S*=1/2)	SOMO β-LUMO	Ru/acac/μ-O Ru/μ-O/acac	65/18/13 67/17/16
2b^{-} (*S*=0)	HOMO	Ru/μ-O/acac	69/18/15
1c^{+} (*S*=0)	LUMO	Ru/acac/μ-O	63/21/15
1c (*S*=1/2)	SOMO β-LUMO	Ru/acac/μ-O Ru/μ-O/acac	65/19/14 66/18/15
1c^{-} (*S*=0)	HOMO	Ru/μ-O/acac	63/19/18
2c^{+} (*S*=0)	LUMO	Ru/acac/μ-O	68/21/15
2c (*S*=1/2)	SOMO β-LUMO	Ru/acac/μ-O Ru/μ-O/acac	65/17/14 68/19/16
2c^{-} (*S*=0)	HOMO	Ru/μ-O/acac	62/21/14
2d^{+} (*S*=0)	LUMO	Ru/acac/μ-O	62/20/14
2d (*S*=1/2)	SOMO β-LUMO	Ru/acac/μ-O Ru/μ-O/acac	62/21/16 66/19/13
2d^{-} (*S*=0)	HOMO	Ru/μ-O/acac	61/21/119
3a^{+} (*S*=1/2)	β-LUMO	Ru/μ-O/Pz-H	68/14/14
3a (*S*=0)	HOMO LUMO	Ru/μ-O/Pz-H Pz-H/Ru/μ-O	69/26/05 89/08/02
3a^{-} (*S*=1/2)	SOMO	Pz-H/Ru/μ-Pz	80/19/01

Table S13 DFT calculated selected MO compositions for **1a** in *S* = 1/2 state

MO	Energy (eV)	% Composition			
		Ru	acac	μ-O	Pz
		α-MO			
LUMO+5	-0.888	55	39	04	01
LUMO+4	-1.138	06	94	00	00
LUMO+3	-1.196	03	96	00	01
LUMO+2	-1.229	08	91	00	01
LUMO+1	-1.256	12	85	02	01
LUMO	-3.442	65	15	20	00
SOMO	-4.063	65	19	14	02
HOMO-1	-4.166	66	17	02	14
HOMO-2	-4.245	63	21	00	16
HOMO-3	-4.556	58	41	00	01
HOMO-4	-4.945	66	30	00	04
HOMO-5	-5.313	02	67	00	31
		β-MO			
LUMO+5	-1.096	07	92	00	00
LUMO+4	-1.165	08	90	00	01
LUMO+3	-1.178	05	94	00	01
LUMO+2	-1.223	06	92	01	01
LUMO+1	-3.192	65	14	21	00
LUMO	-3.393	66	16	17	01
HOMO	-4.032	68	17	01	15
HOMO-1	-4.063	66	22	00	12
HOMO-2	-4.399	64	34	00	02
HOMO-3	-4.560	77	19	00	03
HOMO-4	-5.295	01	65	00	33
HOMO-5	-5.412	07	85	01	07

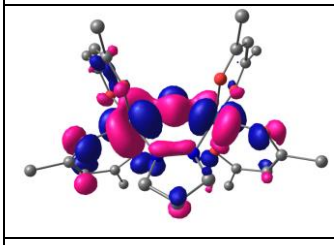
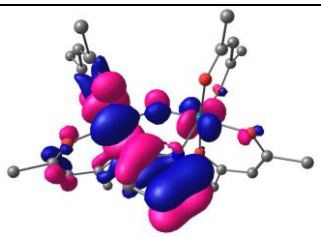
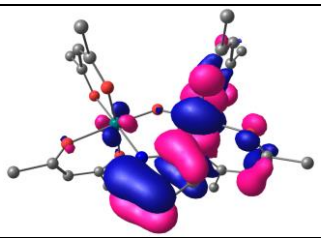
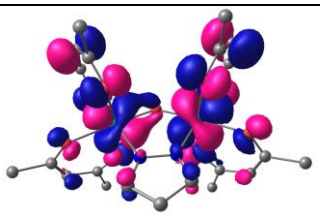
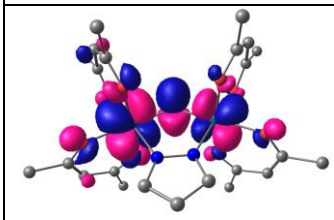
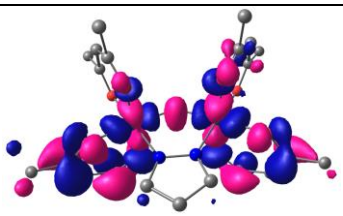
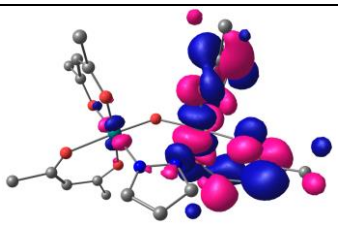
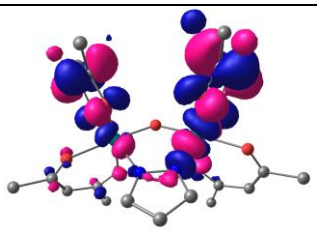
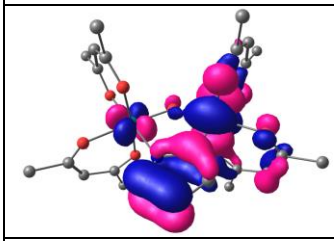
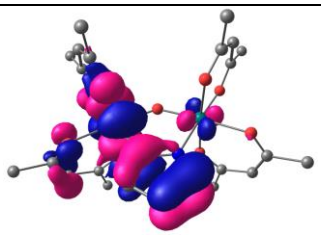
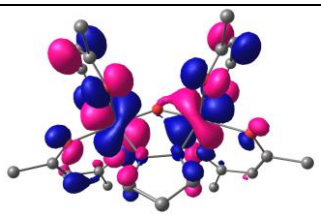
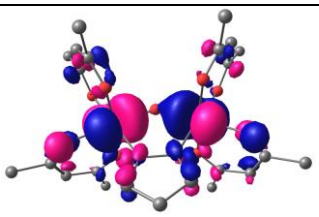
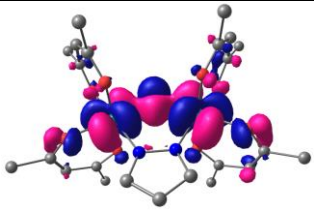
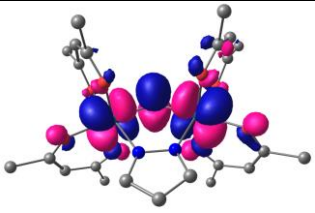
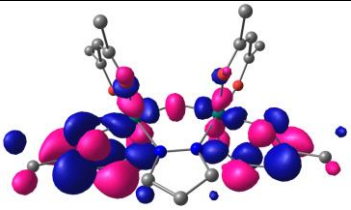
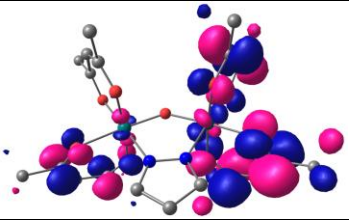
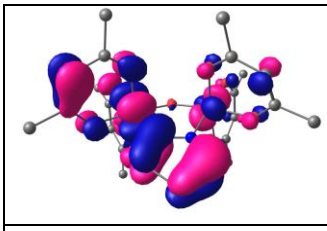
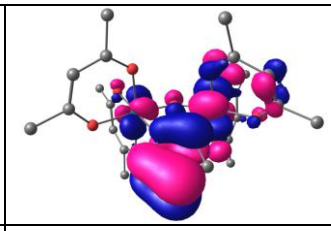
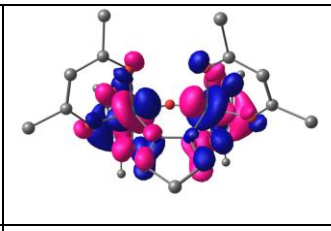
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

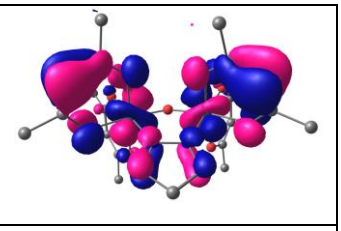
Table S14 DFT calculated selected MO compositions for **1a**$^{+}$ in *S* = 0 state

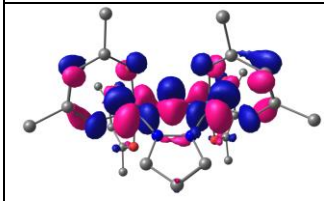
MO	Energy (eV)	% Composition			
		Ru	acac	μ-O	Pz
LUMO+5	-4.430	17	79	01	02
LUMO+4	-4.515	10	87	00	02
LUMO+3	-4.552	10	87	00	02
LUMO+2	-4.754	52	35	10	03
LUMO+1	-7.191	64	17	19	00
LUMO	-7.677	63	21	15	02
HOMO	-7.755	59	16	02	23
HOMO-1	-7.825	57	23	00	19
HOMO-2	-8.059	41	57	00	01
HOMO-3	-8.519	44	46	00	10
HOMO-4	-8.578	05	76	01	18
HOMO-5	-8.733	16	63	06	14

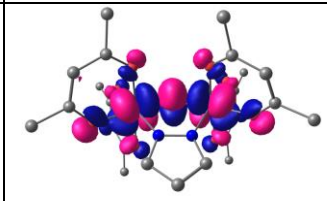

HOMO

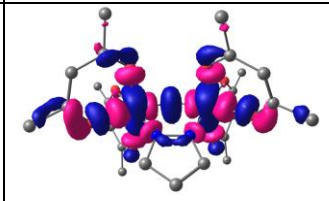

HOMO-1


HOMO-2


HOMO-3


LUMO


LUMO+1


LUMO+2

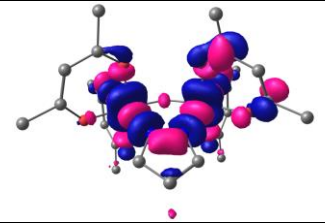

LUMO+3

Table S15 DFT calculated selected MO compositions for **1a**$^{-}$ in *S* = 0 state

MO	Energy (eV)	% Composition			
		Ru	acac	μ-O	Pz
LUMO+5	3.035	56	38	01	04
LUMO+4	2.169	10	89	00	01
LUMO+3	2.114	11	88	00	01
LUMO+2	2.074	05	94	00	01
LUMO+1	2.007	06	93	00	01
LUMO	0.707	63	15	15	00
HOMO	0.335	63	18	18	01
HOMO-1	-0.352	72	18	00	10
HOMO-2	-0.409	71	20	00	09
HOMO-3	-0.684	73	26	00	02
HOMO-4	-0.813	79	18	00	03
HOMO-5	-2.086	01	68	00	30

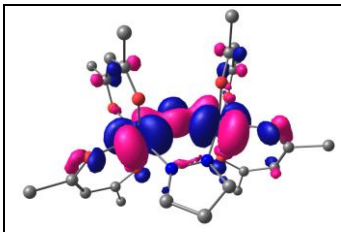
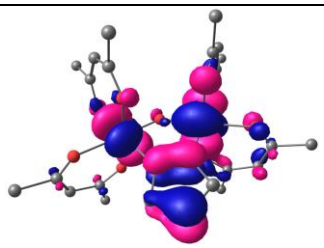
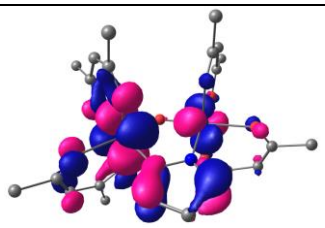
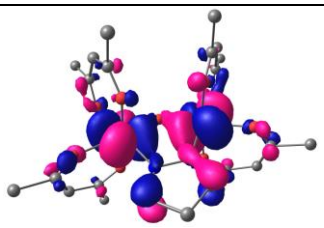
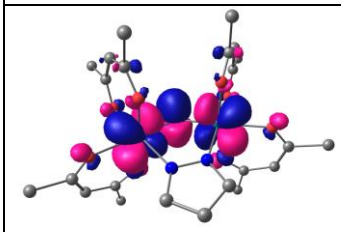
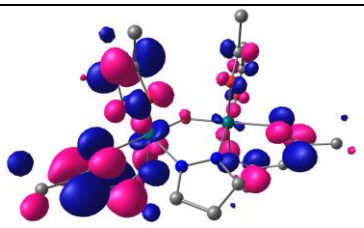
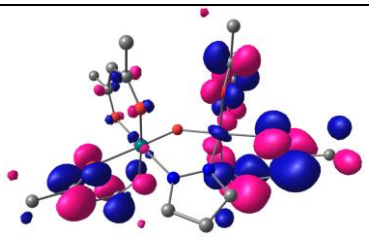
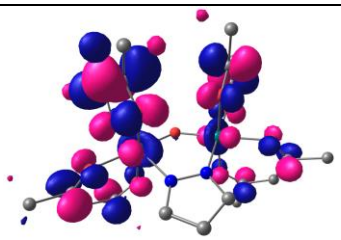
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S16. DFT calculated selected MO compositions for **2a** in *S* = 1/2 state

MO	Energy (eV)	% Composition			
		Ru	acac	μ-O	Pz
		α-MO			
LUMO+5	-0.863	58	36	06	00
LUMO+4	-1.119	06	93	00	00
LUMO+3	-1.134	05	94	00	01
LUMO+2	-1.265	05	94	00	01
LUMO+1	-1.289	04	95	00	00
LUMO	-3.393	64	15	21	00
SOMO	-3.385	63	21	14	02
HOMO-1	-4.092	66	20	00	14
HOMO-2	-4.216	65	19	01	15
HOMO-3	-4.607	63	36	01	00
HOMO-4	-4.773	58	37	00	05
HOMO-5	-5.361	02	84	02	13
		β-MO			
LUMO+5	-1.096	07	92	00	01
LUMO+4	-1.108	06	93	00	01
LUMO+3	-1.225	05	94	00	01
LUMO+2	-1.262	04	95	00	00
LUMO+1	-3.148	65	21	14	00
LUMO	-3.260	64	18	16	01
HOMO	-3.903	68	21	00	11
HOMO-1	-4.080	66	19	01	14
HOMO-2	-4.440	67	32	01	00
HOMO-3	-4.448	71	23	00	06
HOMO-4	-5.329	02	86	02	11
HOMO-5	-5.475	16	83	01	00

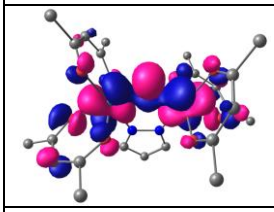
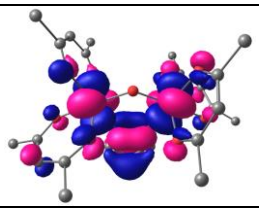
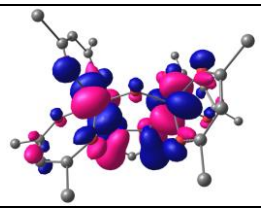
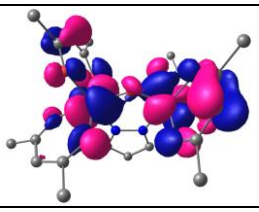
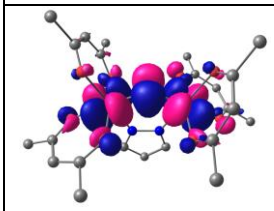
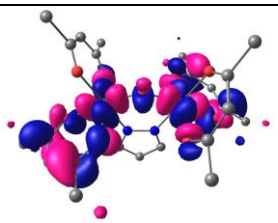
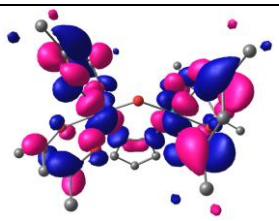
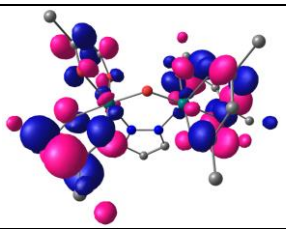
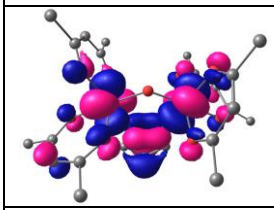
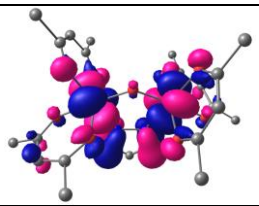
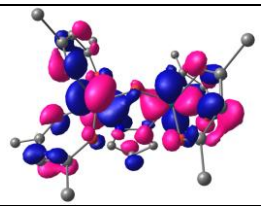
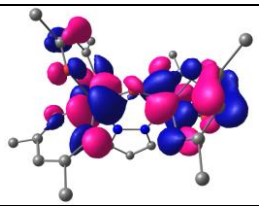
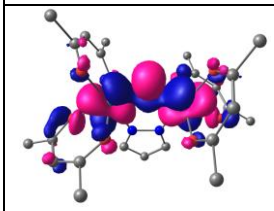
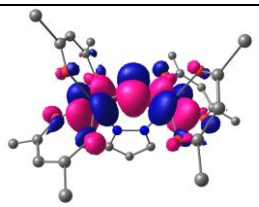
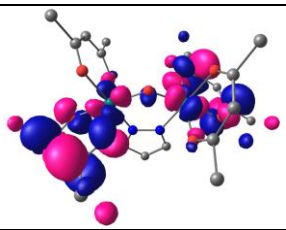
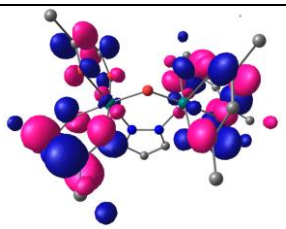
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S17 DFT calculated selected MO compositions for **2a**$^{+}$ in *S* = 0 state

MO	Energy (eV)	% Composition			
		Ru	acac	μ-O	Pz
LUMO+5	-4.388	56	29	02	13
LUMO+4	-4.532	14	82	02	02
LUMO+3	-4.562	05	94	00	01
LUMO+2	-4.590	54	37	09	01
LUMO+1	-7.121	64	16	20	00
LUMO	-7.469	60	25	14	02
HOMO	-7.670	59	21	00	20
HOMO-1	-7.784	60	21	02	18
HOMO-2	-8.613	49	49	02	00
HOMO-3	-8.252	41	50	01	09
HOMO-4	-8.627	04	82	02	13
HOMO-5	-8.882	30	68	00	02

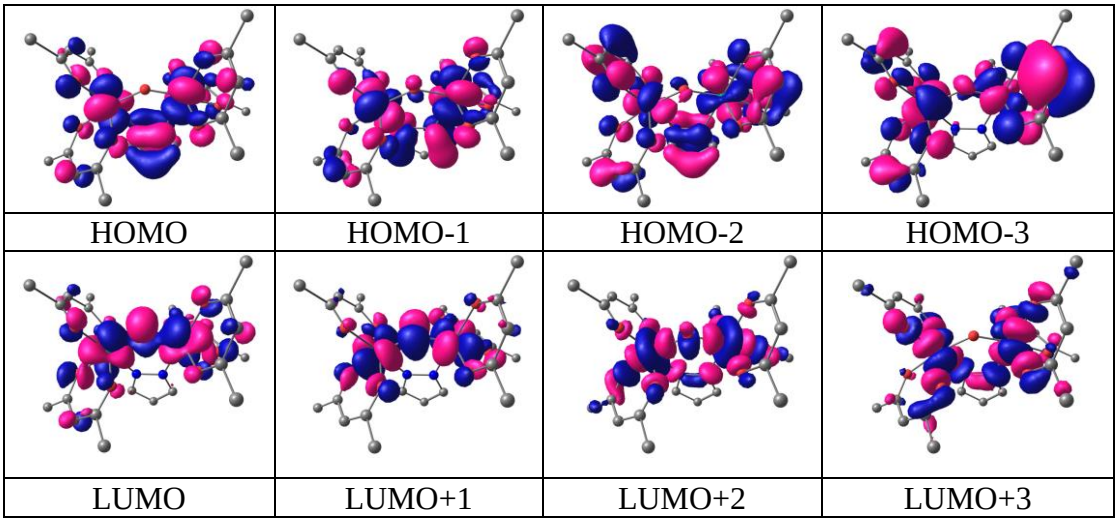


Table S18 DFT calculated selected MO compositions for **2a**$^{-}$ in *S* = 0 state

MO	Energy (eV)	% Composition			
		Ru	acac	μ-O	Pz
LUMO+5	3.055	55	39	02	04
LUMO+4	2.125	12	86	01	00
LUMO+3	2.123	12	86	01	01
LUMO+2	2.030	03	95	00	01
LUMO+1	2.005	04	95	00	00
LUMO	0.719	61	16	23	00
HOMO	0.442	62	20	17	01
HOMO-1	-0.217	73	19	00	09
HOMO-2	-0.429	69	19	01	12
HOMO-3	-0.713	74	26	00	00
HOMO-4	-0.759	76	19	00	04
HOMO-5	-2.100	01	81	01	16

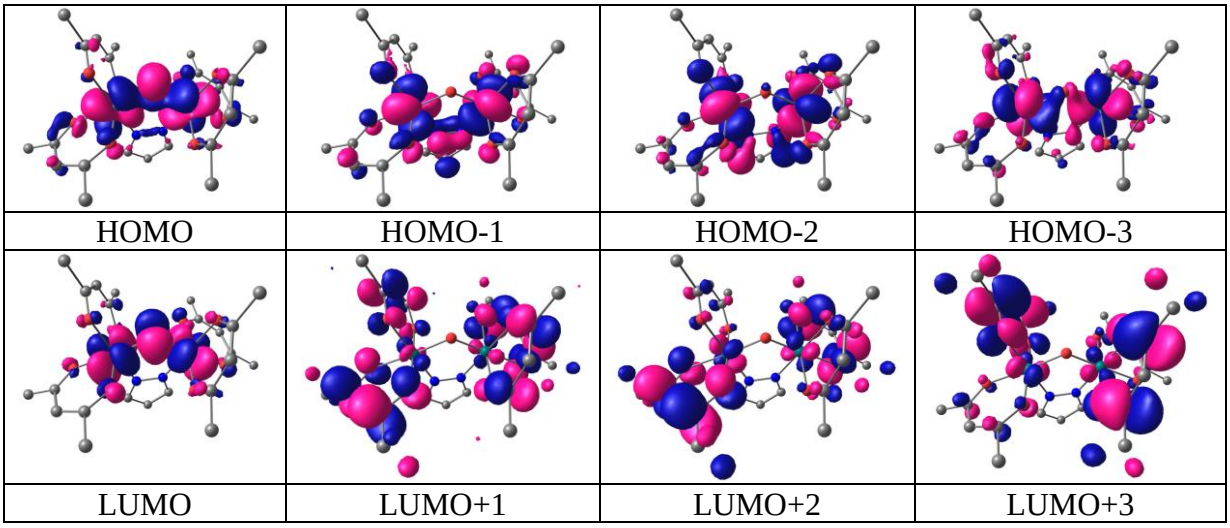


Table S19 DFT calculated selected MO compositions for **1b** in *S* = 1/2 state

MO	Energy (eV)	% Composition			
		Ru	acac	μ-O	Pz
		α-MO			
LUMO+5	-1.435	20	77	00	04
LUMO+4	-1.475	04	96	00	00
LUMO+3	-1.501	17	78	02	04
LUMO+2	-1.582	26	66	03	06
LUMO+1	-1.645	47	48	01	04
LUMO	-3.608	66	14	20	00
SOMO	-4.295	65	18	12	04
HOMO-1	-4.385	67	17	01	15
HOMO-2	-4.595	60	17	01	17
HOMO-3	-4.844	56	42	01	02
HOMO-4	-5.136	59	34	01	06
HOMO-5	-5.413	09	64	00	27
		β-MO			
LUMO+5	-1.431	06	94	00	00
LUMO+4	-1.454	11	86	01	02
LUMO+3	-1.485	13	83	00	03
LUMO+2	-1.569	20	77	01	02
LUMO+1	-3.392	65	22	13	00
LUMO	-3.650	68	15	14	03
HOMO	-4.298	67	16	02	15
HOMO-1	-4.378	66	20	00	14
HOMO-2	-4.623	65	32	00	03
HOMO-3	-4.806	75	22	00	03
HOMO-4	-5.356	07	54	00	39
HOMO-5	-5.497	05	78	01	15

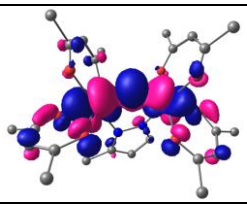
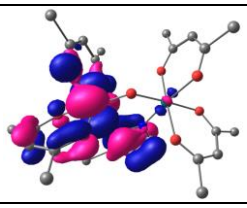
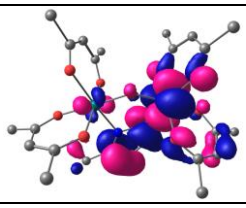
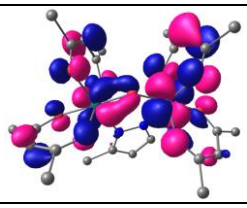
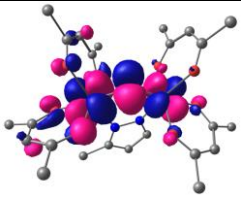
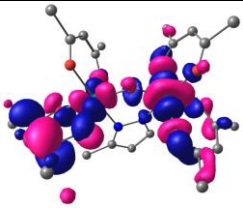
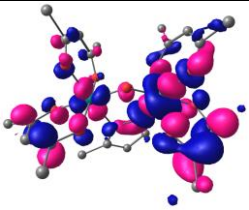
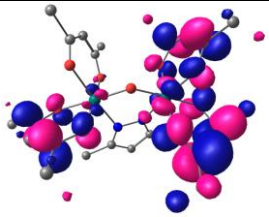
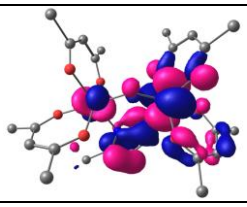
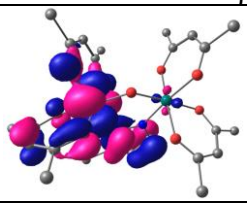
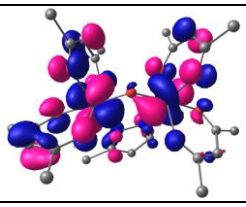
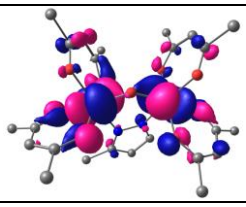
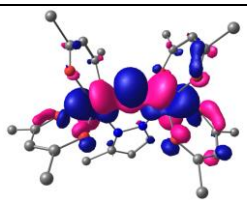
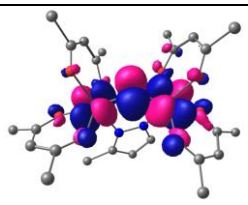
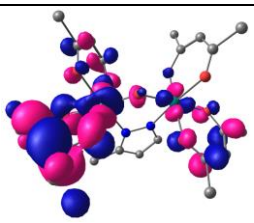
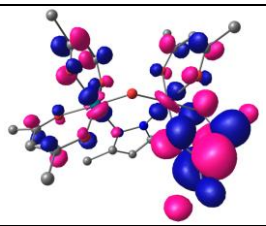
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S20 DFT calculated selected MO compositions for **1b**$^{+}$ in *S* = 0 state

MO	Energy (eV)	% Composition			
		Ru	acac	μ-O	Pz
LUMO+5	-4.634	08	90	00	02
LUMO+4	-4.877	53	35	00	12
LUMO+3	-5.043	58	36	06	00
LUMO+2	-5.057	58	21	05	15
LUMO+1	-7.214	64	16	20	00
LUMO	-7.721	61	21	12	06
HOMO	-7.895	59	22	01	18
HOMO-1	-7.896	58	18	03	20
HOMO-2	-8.130	41	58	00	01
HOMO-3	-8.511	39	47	00	13
HOMO-4	-8.570	03	85	02	11
HOMO-5	-8.708	14	69	05	12

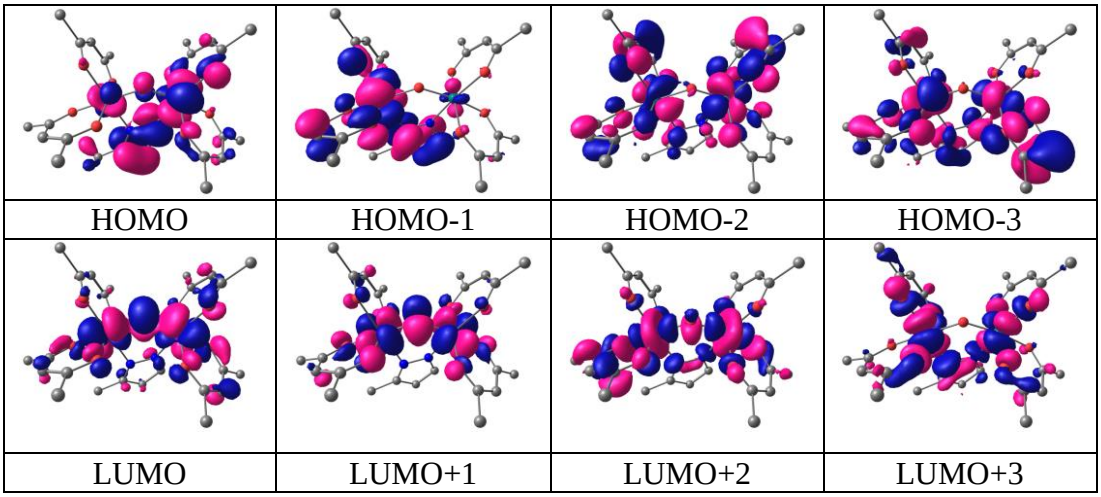
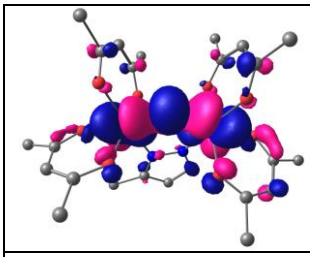
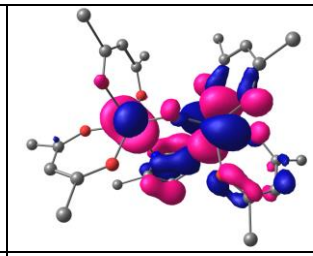


Table S21 DFT calculated selected MO compositions for **1b**$^{-}$ in *S* = 0 state

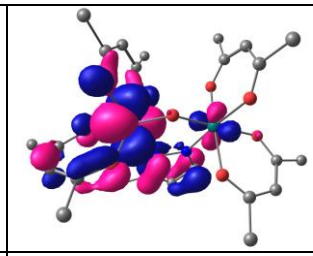
MO	Energy (eV)	% Composition			
		Ru	acac	μ-O	Pz
LUMO+5	2.273	55	33	00	12
LUMO+4	1.739	10	88	01	01
LUMO+3	1.676	05	94	00	00
LUMO+2	1.664	08	91	00	01
LUMO+1	1.545	06	93	00	01
LUMO	0.376	63	14	23	00
HOMO	-0.025	66	17	16	02
HOMO-1	-0.680	73	16	01	10
HOMO-2	-0.796	73	17	00	10
HOMO-3	-1.000	76	22	00	02
HOMO-4	-1.110	80	19	00	01
HOMO-5	-2.176	03	48	00	48



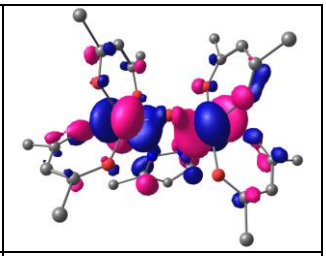
HOMO



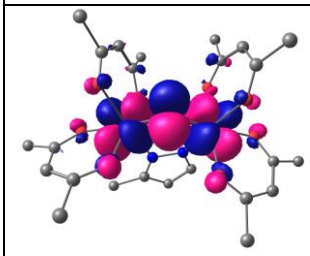
HOMO-1



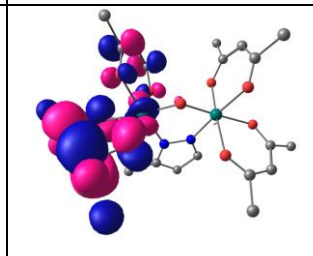
HOMO-2



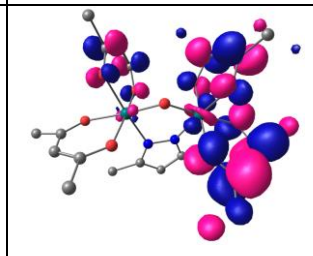
HOMO-3



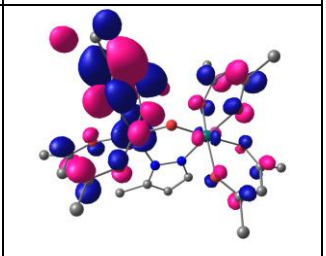
LUMO



LUMO+1



LUMO+2



LUMO+3

Table S22 DFT calculated selected MO compositions for **2b** in *S* = 1/2 State

MO	Energy (eV)	% Composition			
		Ru	acac	μ-O	Pz
		α-MO			
LUMO+5	-1.394	27	67	00	05
LUMO+4	-1.448	06	93	00	01
LUMO+3	-1.560	24	70	01	05
LUMO+2	-1.581	26	68	01	06
LUMO+1	-1.694	32	64	04	00
LUMO	-3.704	65	13	21	00
SOMO	-4.356	64	19	14	03
HOMO-1	-4.413	61	16	00	23
HOMO-2	-4.501	62	16	01	21
HOMO-3	-4.928	62	36	01	00
HOMO-4	-5.035	52	41	01	06
HOMO-5	-5.396	09	60	01	31
		β-MO			
LUMO+5	-1.419	06	93	00	00
LUMO+4	-1.477	14	82	00	03
LUMO+3	-1.534	08	90	00	01
LUMO+2	-1.608	18	80	02	01
LUMO+1	-3.448	66	13	21	00
LUMO	-3.694	68	16	15	01
HOMO	-4.275	64	17	00	19
HOMO-1	-4.375	65	16	00	19
HOMO-2	-4.669	71	24	01	04
HOMO-3	-4.749	67	32	01	00
HOMO-4	-5.365	07	54	01	38
HOMO-5	-5.456	02	79	01	18

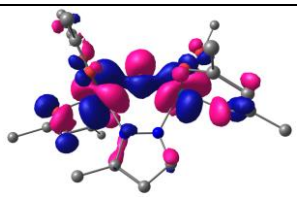
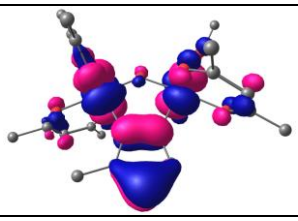
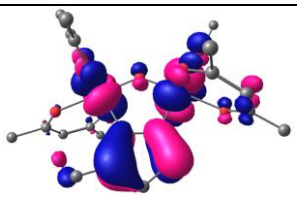
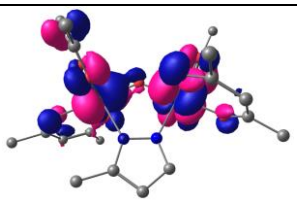
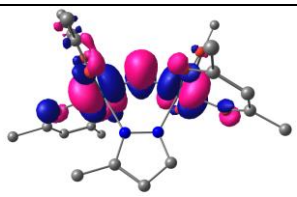
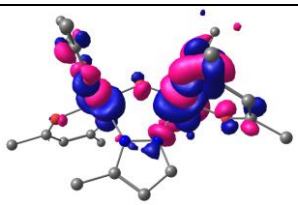
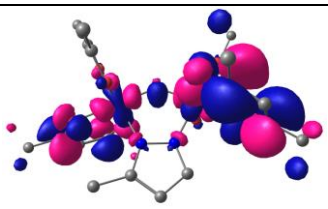
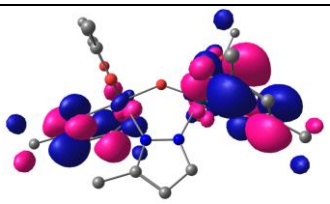
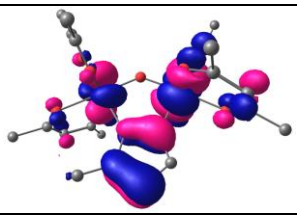
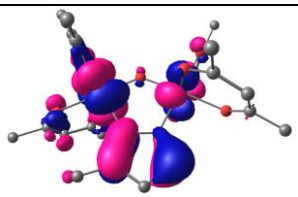
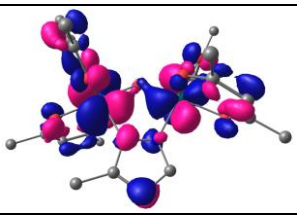
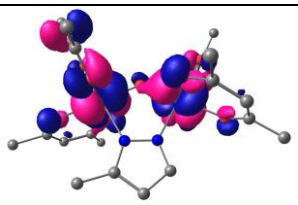
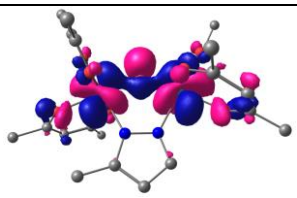
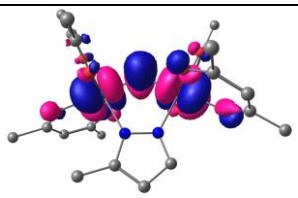
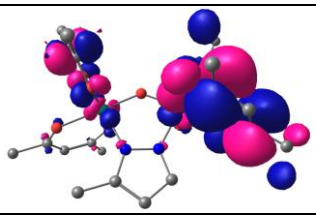
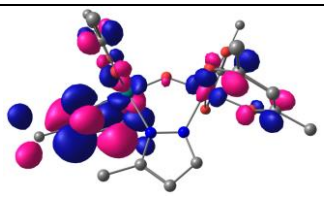
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S23 DFT calculated selected MO compositions for **2b**$^{+}$ in *S* = 0 state

MO	Energy (eV)	% Composition			
		Ru	acac	μ-O	Pz
LUMO+5	-4.658	05	94	00	01
LUMO+4	-4.862	55	33	00	11
LUMO+3	-5.021	58	27	02	13
LUMO+2	-5.106	61	28	10	01
LUMO+1	-7.331	65	15	15	00
LUMO	-7.727	61	24	13	03
HOMO	-7.822	51	15	01	33
HOMO-1	-7.930	57	19	01	24
HOMO-2	-8.346	35	57	01	07
HOMO-3	-8.371	40	53	02	05
HOMO-4	-8.593	06	75	01	19
HOMO-5	-8.691	18	58	02	22

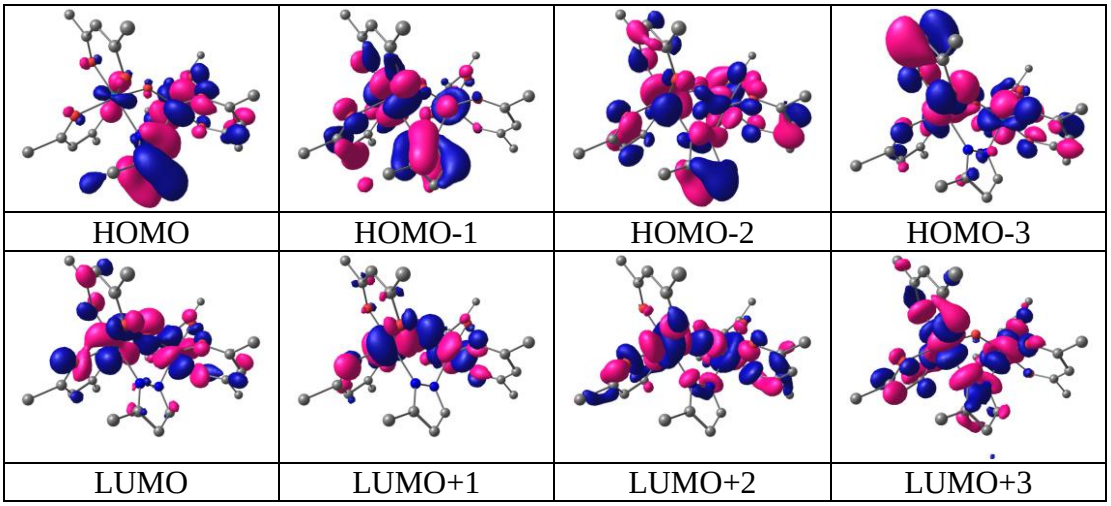


Table S24 DFT calculated selected MO compositions for **2b**$^{-}$ in *S* = 0 state

MO	Energy (eV)	% Composition			
		Ru	acac	μ-O	Pz
LUMO+5	2.297	58	37	01	04
LUMO+4	1.699	10	89	00	01
LUMO+3	1.665	09	89	00	01
LUMO+2	1.644	06	93	01	01
LUMO+1	1.605	04	95	00	01
LUMO	0.333	63	14	23	00
HOMO	0.029	65	17	16	01
HOMO-1	-0.639	74	16	00	10
HOMO-2	-0.799	71	16	00	13
HOMO-3	-1.068	78	18	00	04
HOMO-4	-1.131	77	23	00	00
HOMO-5	-2.220	03	48	00	48

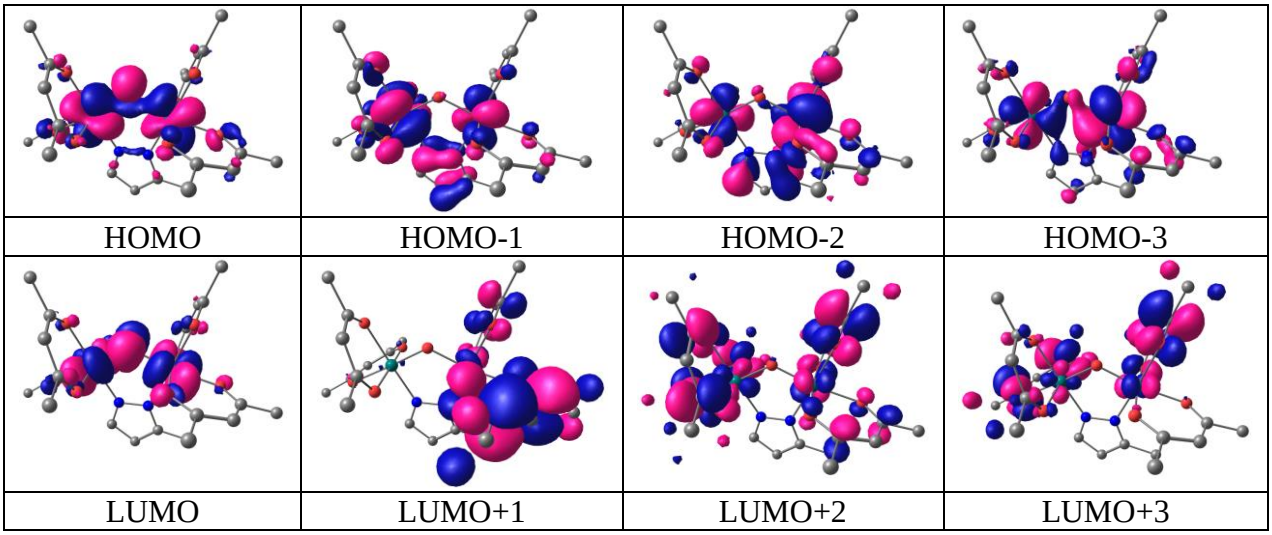


Table S25 DFT calculated selected MO compositions for **1c** in *S* = 1/2 state

MO	Energy (eV)	% Composition			
		Ru	acac	μ-O	Pz
		α-MO			
LUMO+5	-0.914	56	39	04	01
LUMO+4	-1.165	05	93	00	02
LUMO+3	-1.173	06	93	01	00
LUMO+2	-1.240	08	90	01	00
LUMO+1	-1.262	06	93	01	00
LUMO	-3.396	65	14	21	00
SOMO	-4.046	64	19	10	05
HOMO-1	-4.132	64	19	10	05
HOMO-2	-4.149	60	15	07	16
HOMO-3	-4.579	58	41	01	00
HOMO-4	-4.890	57	34	02	06
HOMO-5	-5.213	10	40	07	42
		β-MO			
LUMO+5	-1.134	07	92	01	00
LUMO+4	-1.138	06	92	00	01
LUMO+3	-1.190	07	92	00	01
LUMO+2	-1.237	05	94	00	02
LUMO+1	-3.149	65	14	21	00
LUMO	-3.403	66	16	16	01
HOMO	-3.960	64	17	00	19
HOMO-1	-4.005	63	16	08	12
HOMO-2	-4.386	64	32	01	02
HOMO-3	-4.562	72	23	01	03
HOMO-4	-5.181	08	38	06	47
HOMO-5	-5.220	14	48	12	26

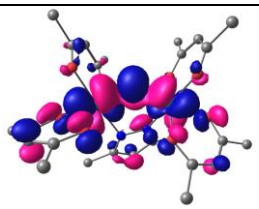
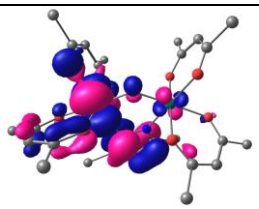
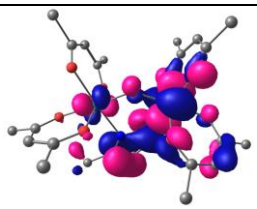
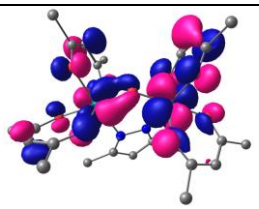
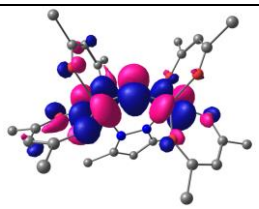
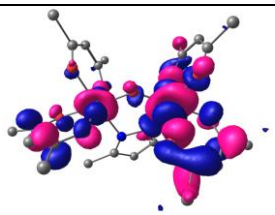
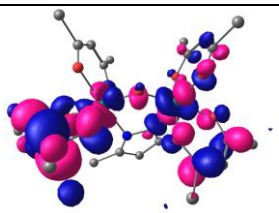
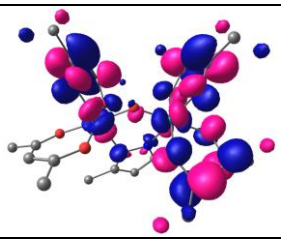
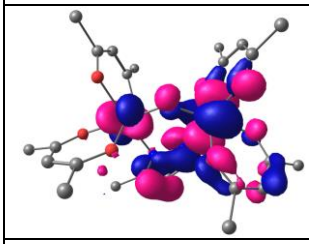
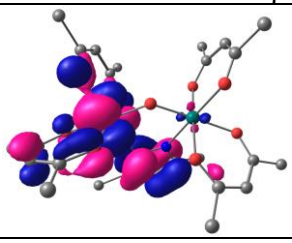
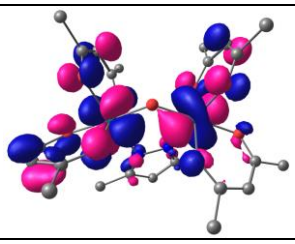
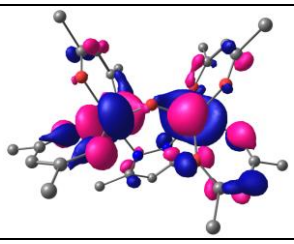
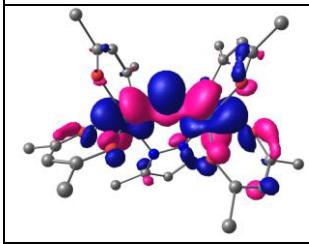
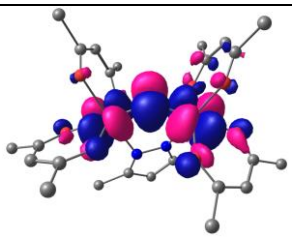
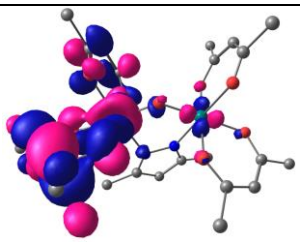
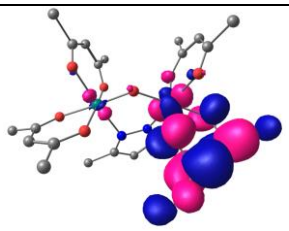
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S26 DFT calculated selected MO compositions for **1c**$^{+}$ in *S* = 0 state

MO	Energy (eV)	% Composition			
		Ru	acac	μ-O	Pz
LUMO+5	-4.634	09	88	01	02
LUMO+4	-4.838	52	36	05	07
LUMO+3	-5.008	58	20	07	11
LUMO+2	-5.013	58	37	04	01
LUMO+1	-7.184	64	16	20	00
LUMO	-7.685	61	20	12	00
HOMO	-7.786	55	19	15	10
HOMO-1	-7.953	58	16	03	22
HOMO-2	-8.104	41	57	00	02
HOMO-3	-8.455	31	53	04	11
HOMO-4	-8.538	06	77	02	14
HOMO-5	-8.655	16	67	05	08

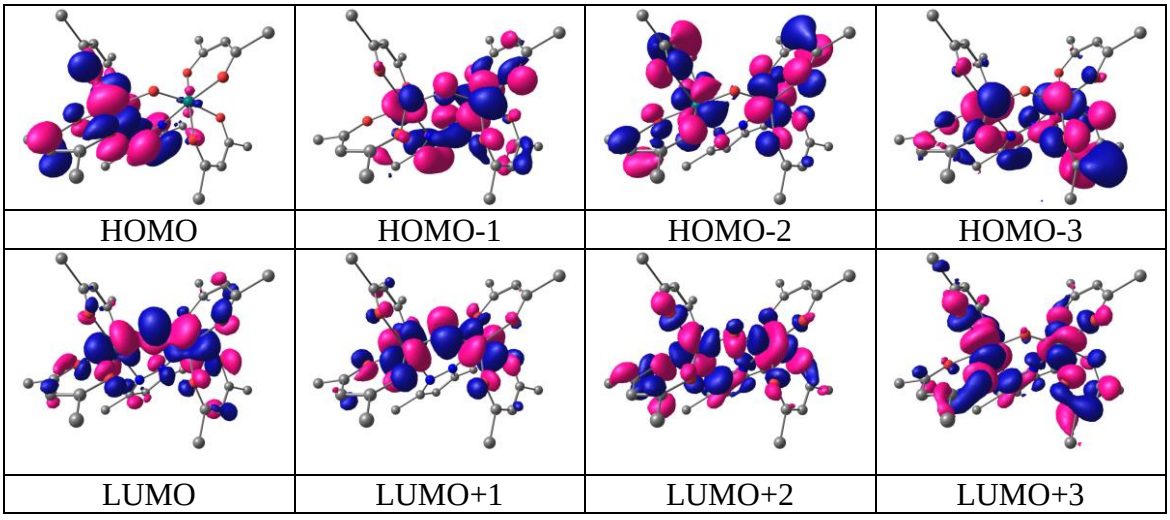


Table S27 DFT calculated selected MO compositions for **1c**$^{-}$ in *S* = 0 state

MO	Energy (eV)	% Composition			
		Ru	acac	μ-O	Pz
LUMO+5	2.281	55	34	04	07
LUMO+4	1.704	11	87	01	02
LUMO+3	1.666	09	90	00	01
LUMO+2	1.645	05	94	00	01
LUMO+1	1.548	06	93	01	00
LUMO	0.370	63	14	23	00
HOMO	-0.028	66	16	15	02
HOMO-1	-0.688	73	15	02	09
HOMO-2	-0.762	71	16	03	10
HOMO-3	-1.005	75	22	02	01
HOMO-4	-1.120	79	19	02	01
HOMO-5	-2.156	05	41	02	51

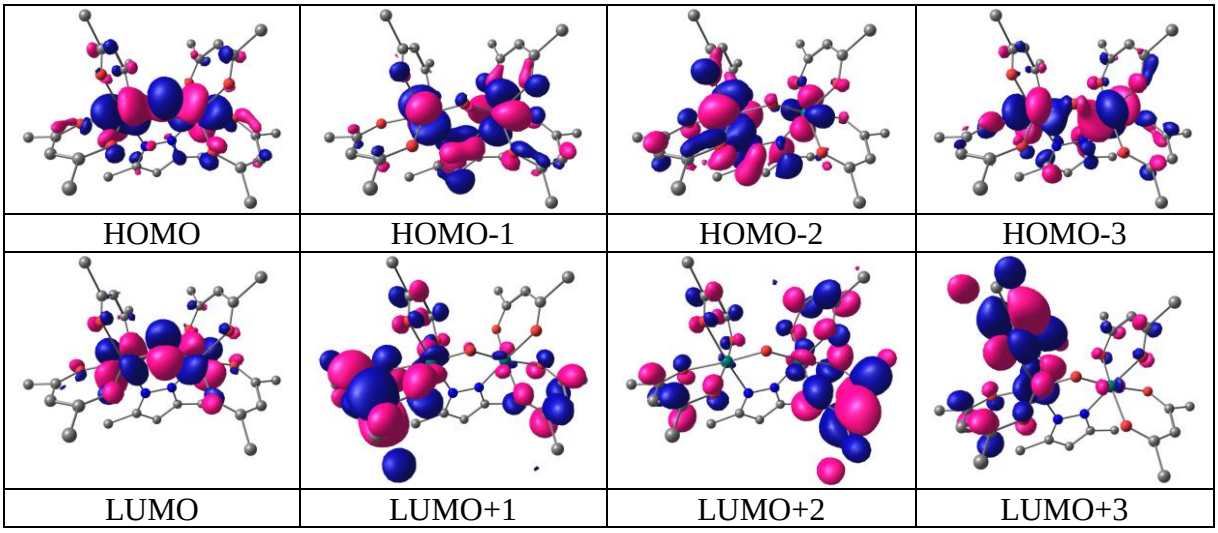


Table S28 DFT calculated selected MO compositions for **2c** in *S* = 1/2 state

MO	Energy (eV)	% Composition			
		Ru	acac	μ-O	Pz
		α-MO			
LUMO+5	-0.823	55	37	00	08
LUMO+4	-1.169	07	93	00	01
LUMO+3	-1.222	05	94	00	01
LUMO+2	-1.268	10	88	01	02
LUMO+1	-1.410	13	85	01	01
LUMO	-3.296	64	14	21	00
SOMO	-3.984	65	20	13	02
HOMO-1	-4.013	60	15	00	25
HOMO-2	-4.140	60	15	01	24
HOMO-3	-4.636	61	35	01	02
HOMO-4	-4.682	58	35	01	05
HOMO-5	-5.096	19	38	00	43
		β-MO			
LUMO+5	-1.143	07	92	01	00
LUMO+4	-1.199	06	92	00	01
LUMO+3	-1.231	07	92	00	01
LUMO+2	-1.371	09	89	01	01
LUMO+1	-3.043	65	14	21	00
LUMO	-3.316	68	16	15	01
HOMO	-3.859	64	19	00	17
HOMO-1	-4.003	63	16	00	20
HOMO-2	-4.317	67	24	01	08
HOMO-3	-4.467	69	29	01	00
HOMO-4	-5.055	16	33	00	51
HOMO-5	-5.191	08	49	01	42

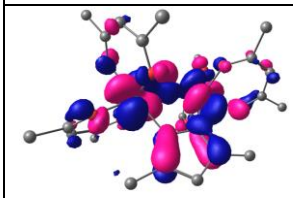
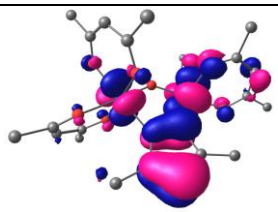
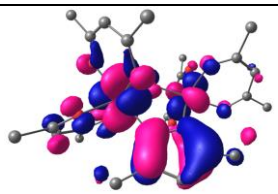
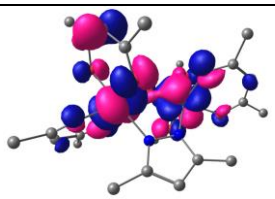
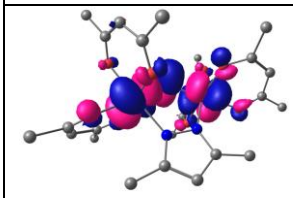
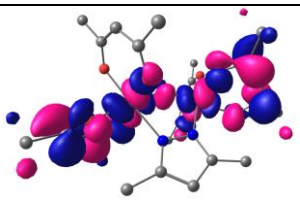
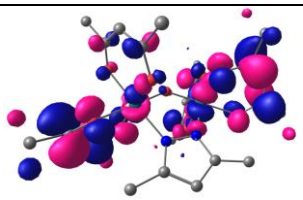
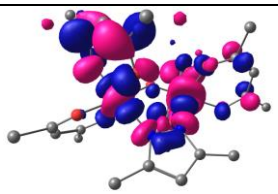
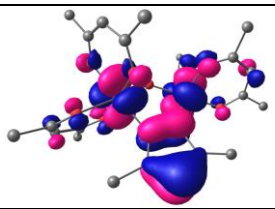
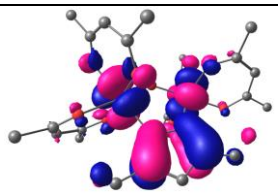
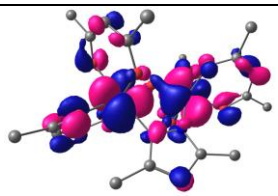
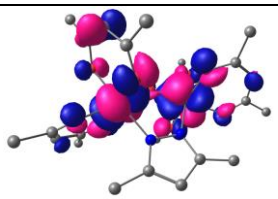
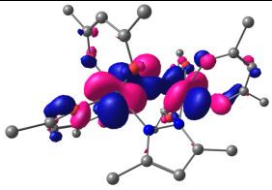
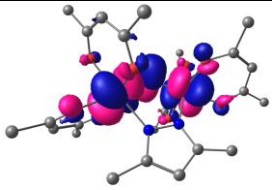
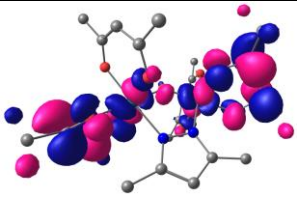
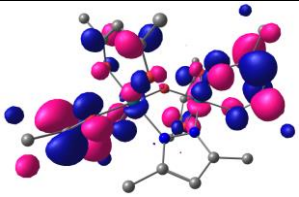
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S29 DFT calculated selected MO compositions for **2c**$^{+}$ in *S* = 0 state

MO	Energy (eV)	% Composition			
		Ru	acac	μ-O	Pz
LUMO+5	-4.579	11	85	00	03
LUMO+4	-4.820	51	39	00	10
LUMO+3	-4.973	58	29	01	12
LUMO+2	-5.060	54	33	10	03
LUMO+1	-7.214	65	15	20	00
LUMO	-7.705	60	23	10	06
HOMO	-7.745	51	17	00	32
HOMO-1	-7.782	54	15	01	34
HOMO-2	-8.278	49	48	02	00
HOMO-3	-8.319	37	50	02	11
HOMO-4	-8.544	07	76	01	17
HOMO-5	-8.560	09	70	02	19

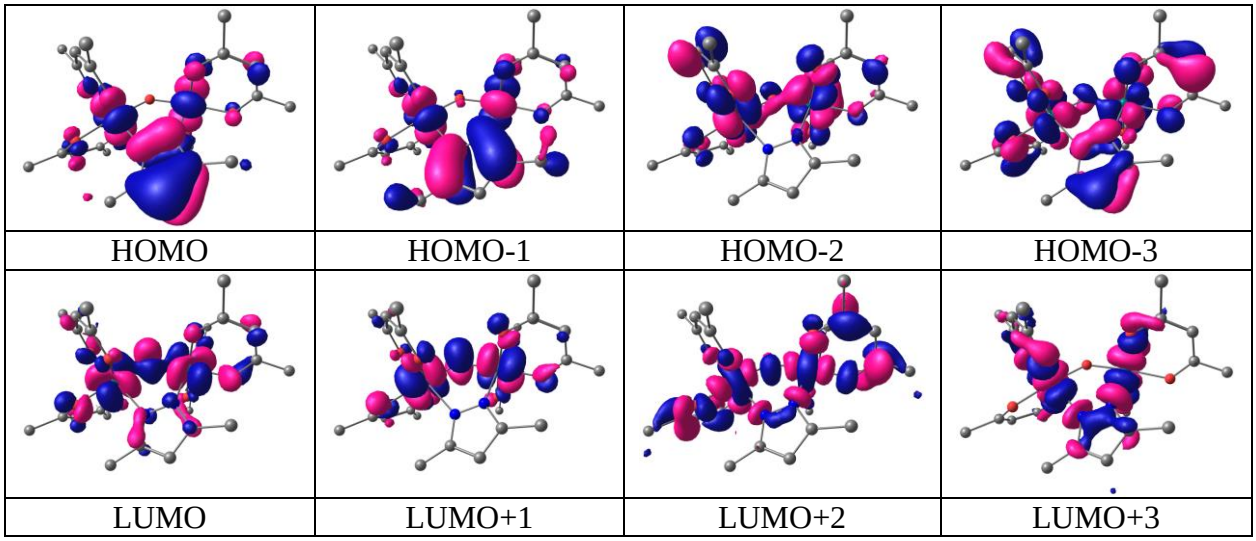


Table S30 DFT calculated selected MO compositions for **2c**$^{-}$ in *S* = 0 state

MO	Energy (eV)	% Composition			
		Ru	acac	μ-O	Pz
LUMO+5	3.054	56	37	00	07
LUMO+4	2.120	11	88	00	01
LUMO+3	2.039	11	88	01	00
LUMO+2	2.012	05	94	00	01
LUMO+1	1.868	06	92	00	01
LUMO	0.859	61	17	22	00
HOMO	0.438	66	17	16	01
HOMO-1	-0.203	72	17	00	11
HOMO-2	-0.370	69	17	00	13
HOMO-3	-0.626	73	20	01	05
HOMO-4	-0.701	76	24	01	00
HOMO-5	-1.856	07	27	00	65

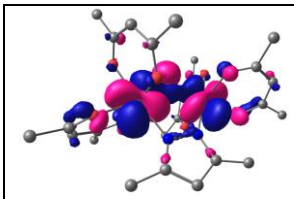
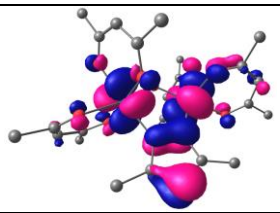
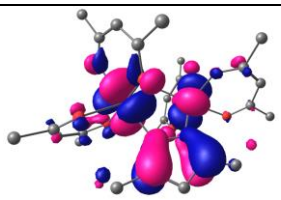
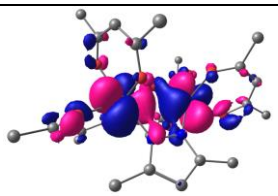
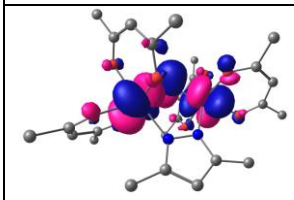
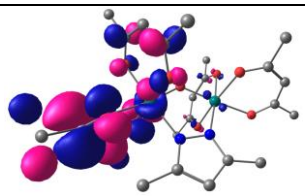
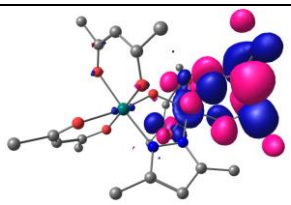
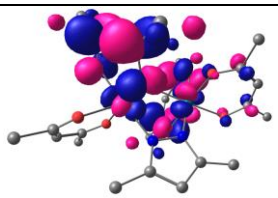
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S31 DFT calculated selected MO compositions for **2d** in *S* = 1/2 state

MO	Energy (eV)	% Composition			
		Ru	acac	μ-O	Iz
		α-MO			
LUMO+5	-1.085	24	71	00	04
LUMO+4	-1.142	30	63	00	08
LUMO+3	-1.375	07	90	01	03
LUMO+2	-1.396	17	79	00	04
LUMO+1	-1.607	13	85	01	02
LUMO	-3.414	65	16	19	01
SOMO	-3.897	49	12	00	38
HOMO-1	-4.078	65	19	12	04
HOMO-2	-4.258	54	18	01	27
HOMO-3	-4.658	64	34	02	01
HOMO-4	-4.845	57	33	06	04
HOMO-5	-4.948	41	32	01	27
		β-MO			
LUMO+5	-1.115	06	92	00	02
LUMO+4	-1.301	09	89	00	02
LUMO+3	-1.362	06	91	01	03
LUMO+2	-1.549	08	90	00	02
LUMO+1	-3.223	63	15	21	01
LUMO	-3.498	65	17	13	04
HOMO	-3.882	43	10	02	44
HOMO-1	-4.034	69	21	01	09
HOMO-2	-4.432	73	20	20	05
HOMO-3	-4.534	65	32	01	02
HOMO-4	-4.816	35	27	01	37
HOMO-5	-5.382	07	81	01	11

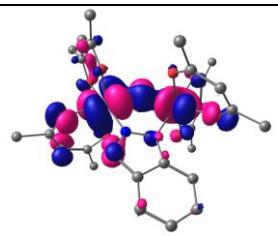
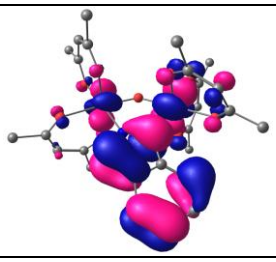
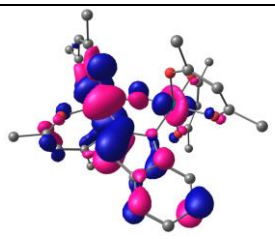
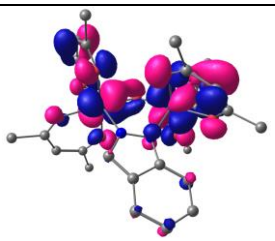
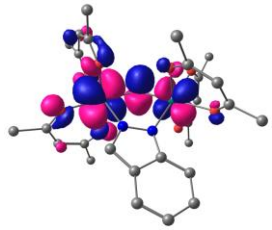
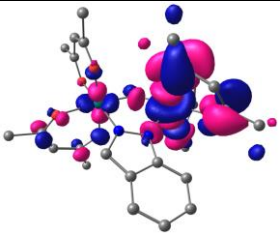
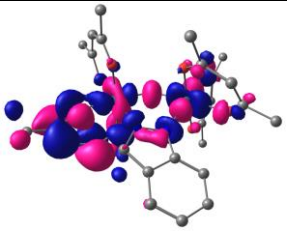
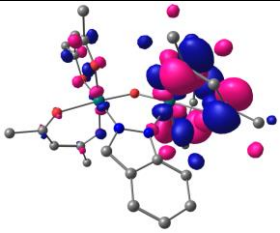
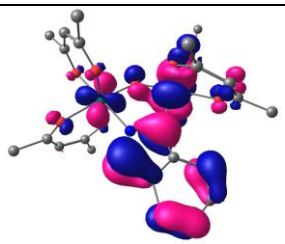
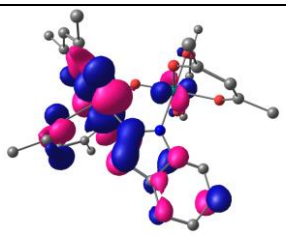
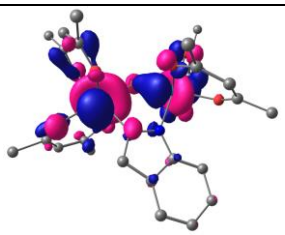
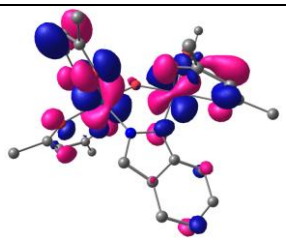
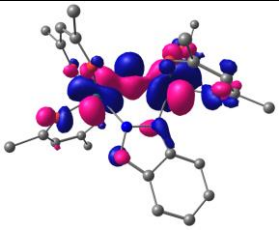
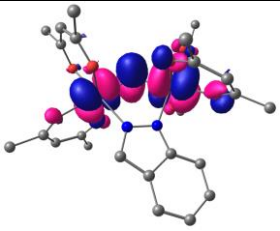
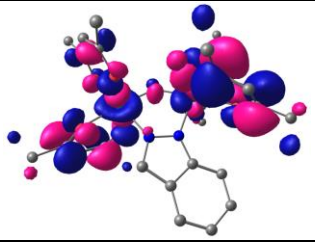
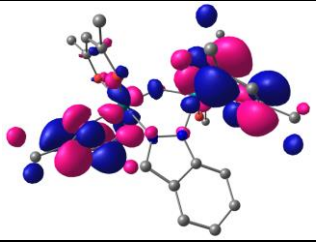
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S32 DFT calculated selected MO compositions for **2d**$^{+}$ in *S* = 0 state

MO	Energy (eV)	% Composition			
		Ru	acac	μ-O	Iz
LUMO+5	-4.561	11	82	00	06
LUMO+4	-4.743	54	34	00	12
LUMO+3	-4.938	55	23	04	18
LUMO+2	-4.989	56	35	07	02
LUMO+1	-7.150	0.63	16	20	02
LUMO	-7.567	58	21	12	10
HOMO	-7.694	44	17	03	37
HOMO-1	-7.859	61	26	01	12
HOMO-2	-8.163	34	53	02	11
HOMO-3	-8.285	50	44	01	04
HOMO-4	-8.401	32	47	01	20
HOMO-5	-8.538	12	70	01	18

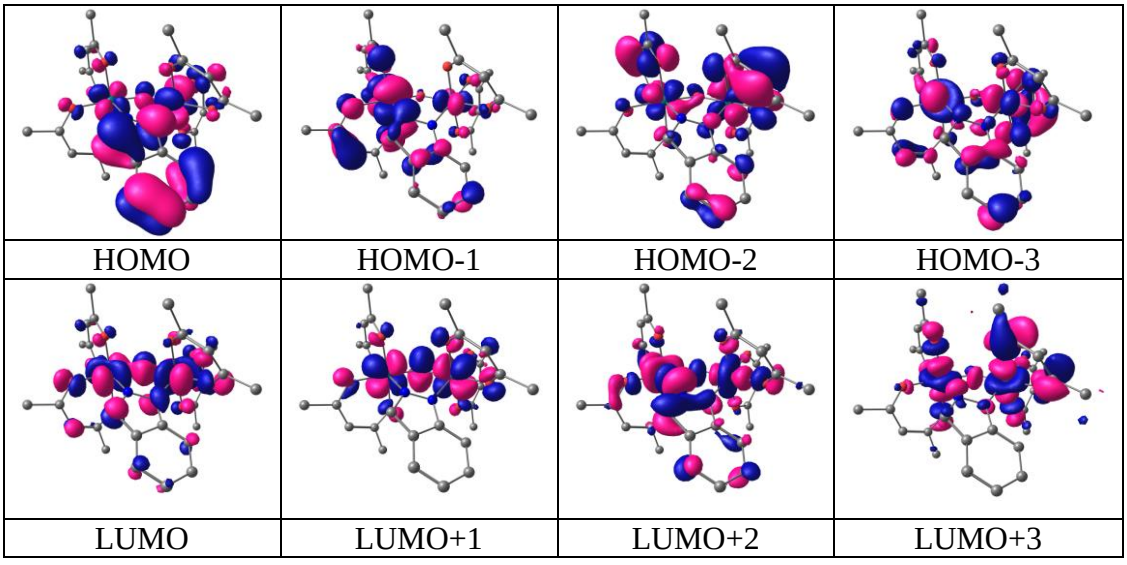


Table S33 DFT calculated selected MO compositions for **2d**$^{-}$ in *S* = 0 state

MO	Energy (eV)	% Composition			
		Ru	acac	μ-O	Iz
LUMO+5	-4.561	11	82	00	06
LUMO+4	-4.743	54	34	00	12
LUMO+3	-4.938	55	23	04	18
LUMO+2	-4.989	56	35	07	02
LUMO+1	-7.150	0.63	16	20	02
LUMO	-7.567	58	21	12	10
HOMO	-7.694	44	17	03	37
HOMO-1	-7.859	61	26	01	12
HOMO-2	-8.163	34	53	02	11
HOMO-3	-8.285	50	44	01	04
HOMO-4	-8.401	32	47	01	20
HOMO-5	-8.538	12	70	01	18

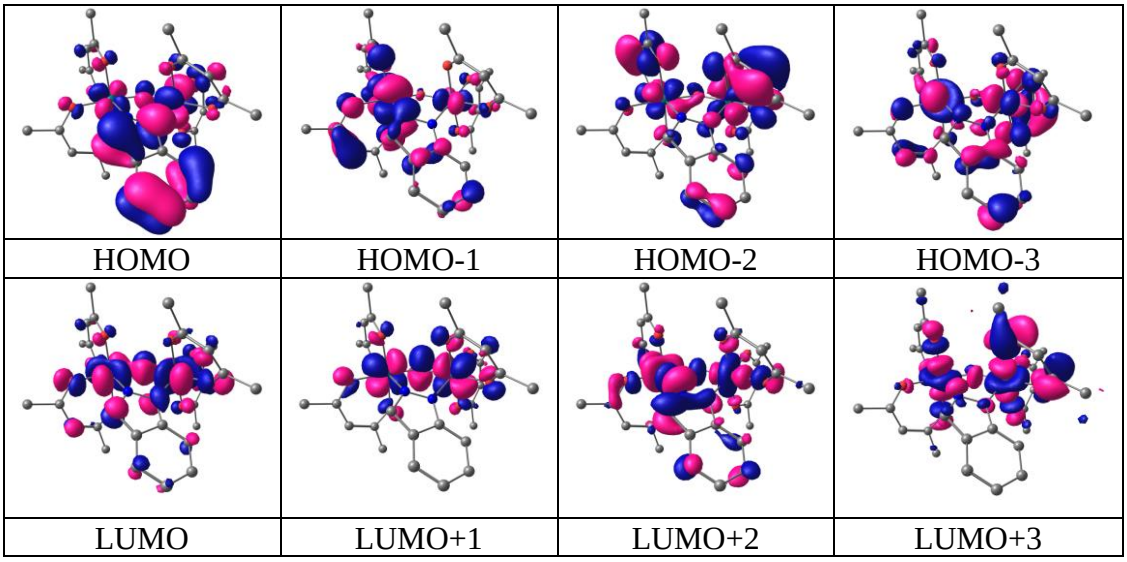


Table S34 Experimental and TD-DFT (M06L/CPCM/CH_3CN) calculated electronic transitions

λ_{max}/nm (expt.)[a] (ε/dm^3mol^{-1} cm^{-1})[b]	λ/nm (DFT) (f)[c]	Transitions	Character
		1a$^+$ (S=0)	
520(1700)	558(0.03)	HOMO-10→LUMO+1 (0.58)	acac(π)/Ru(dπ)→ Ru(dπ)/μ-O(π*)
		HOMO-9→LUMO+1 (0.35)	acac(π)→ Ru(dπ)/μ-O(π*)
335(7120)	330(0.01)	HOMO-6→LUMO+2 (0.41)	acac(π)/Ru(dπ)→ Ru(dπ)/acac(π*)
		HOMO-2→LUMO+7 (0.39)	acac(π)/Ru(dπ)→ acac(π*)/Ru(dπ)
272(12600)	290(0.21)	HOMO-3→LUMO+9 (0.29)	acac(π)/Ru(dπ)→ acac(π*)
		HOMO-3→LUMO+10 (0.25)	acac(π)/Ru(dπ)→ acac(π*)
		1a (S=1/2)	
1440 (250)	1380(0.004)	HOMO−1(β)→LUMO(β)(0.90)	Ru(dπ)/μ-O(π)→Ru(dπ)/acac(π*)
540 (7840)	530(0.02)	HOMO−4(β)→LUMO(β)(0.72)	acac(π)/Pz(π)→Ru(dπ)/acac(π*)
325 (8000)	350(0.02)	HOMO-2(α)→LUMO+2(α) (0.54)	Ru(dπ)/acac(π)→acac(π*)
270(9330)	260(0.09)	HOMO−4(β)→LUMO+5(β)(0.38)	acac(π)/Pz(π)→acac(π*)
		HOMO−5(β)→LUMO+5(β)(0.22)	acac(π)→acac(π*)
		1a$^-$ (S=0)	
582 (5400)	617(0.03)	HOMO-2→LUMO(0.68)	Ru(dπ)→Ru(dπ)/μ-O(π*)
350 (7000)	336(0.02)	HOMO-4→LUMO+5(0.47)	Ru(dπ)/acac(π)→ Ru(dπ)/acac(π*)
		HOMO-2→LUMO+7(0.33)	Ru(dπ)→ Ru(dπ)/acac(π*)
270(19500)	303(0.15)	HOMO-5→LUMO+9(0.45)	acac(π)→ Ru(dπ)/acac(π*)
		2a$^+$ (S=0)	
530(1950)	532(0.01)	HOMO-8→LUMO (0.68)	acac(π)→Ru(dπ)/acac(π*)
330(7000)	338(0.01)	HOMO-5→LUMO+2 (0.67)	acac(π)/Ru(dπ)→ Ru(dπ)/acac(π*)
276(12300)	265(0.04)	HOMO-6→LUMO+6 (0.46)	acac(π)/Pz(π)→acac(π*)
		2a (S=1/2)	
1450(250)	1340(0.004)	HOMO−2(β)→LUMO+1(β)(0.98)	Ru(dπ)/acac(π)→Ru(dπ)/μ-O(π*)
540(8000)	544(0.02)	HOMO−8(β)→LUMO(β)(0.94)	acac(π)/pz(π)→Ru(dπ)
332(8600)	339(0.02)	HOMO-4(α)→LUMO+5(α) (0.54)	Ru(dπ)/acac(π)→Ru(dπ)/acac(π*)
		HOMO-3(α)→LUMO+4(α) (0.54)	Ru(dπ)/acac(π)→acac(π*)
270(16100)	300(0.17)	HOMO−3(β)→LUMO+8(β)(0.38)	acac(π) →acac(π*)/Pz(π*)
		HOMO−4(β)→LUMO+7(β)(0.21)	acac(π) →Pz(π*)/acac(π*)
		2a$^-$ (S=0)	
584(5050)	560(0.24)	HOMO-4→LUMO(0.63)	Ru(dπ)→Ru(dπ)/μ-O(π*)
350(6700)	346(0.06)	HOMO-1→LUMO+7(0.62)	Ru(dπ)/acac(π)→Ru(dπ)/acac(π*)
266(18400)	290(0.09)	HOMO-5→LUMO+10(0.45)	acac(π)→acac(π*)
		1b$^+$ (S=0)	
515(3800)	532(0.10)	HOMO-5→LUMO+1 (0.68)	acac(π)/Pz(π)→Ru(dπ)/acac(π*)

340(9600)	351(0.08)	HOMO-7→LUMO+2 (0.67)	acac(π)/Ru(dπ)→ Ru(dπ)/acac(π*)
280(17600)	271(0.15)	HOMO-9→LUMO+8 (0.46)	acac(π)/Pz(π)→acac(π*)/Pz(π*)
1b (*S*=1/2)			
1480(260)	1405(0.004)	HOMO−1(β)→LUMO+1(β)(0.88)	Ru(dπ)→Ru(dπ)/μ-O(π*)
540(9300)	584(0.20)	HOMO−4(β)→LUMO(β)(0.68)	acac(π)/pz(π)→Ru(dπ)
330(11300)	362(0.19)	HOMO-2(β)→LUMO+5(β) (0.62)	Ru(dπ)/acac(π)→Ru(dπ)/acac(π*)
272(19600)	280(0.25)	HOMO−3(α)→LUMO+8(α)(0.32)	acac(π) →acac(π*)
		HOMO−4(α)→LUMO+7(α)(0.25)	acac(π) →Ru(dπ)/Pz(π*)
1b^{-} (*S*=0)			
580(12380)	595(0.11)	HOMO-3→LUMO+1(0.71)	Ru(dπ)→Ru(dπ)/μ-O(π*)
410(7400)	440(0.06)	HOMO→LUMO+5(0.55)	Ru(dπ)/acac(π)→Ru(dπ)
350(7900)	320(0.07)	HOMO-6→LUMO+5(0.47)	acac(π)/pz(π)→acac(π*)
2b^{+} (*S*=0)			
520(2900)	505(0.05)	HOMO-3→LUMO+1 (0.59)	acac(π)/Pz(π)→Ru(dπ)
340(7300)	332(0.06)	HOMO-6→LUMO+2 (0.48)	acac(π)/Ru(dπ)→ Ru(dπ)/acac(π*)
		HOMO-6→LUMO+3 (0.41)	acac(π)/Ru(dπ)→ Ru(dπ)/acac(π*)
280(13700)	291(0.19)	HOMO-8→LUMO+8 (0.36)	acac(π)/Pz(π)→acac(π*)
		HOMO-8→LUMO+10 (0.32)	acac(π)/Pz(π)→acac(π*)/Pz(π*)
2b (*S*=1/2)			
1480(250)	1410(0.001)	HOMO−2(β)→LUMO+1(β)(0.80)	Ru(dπ)→Ru(dπ)/μ-O(π*)
540(8600)	555(0.21)	HOMO−3(β)→LUMO(β)(0.62)	acac(π)/pz(π)→Ru(dπ)
330(9500)	310(0.16)	HOMO−2(α)→LUMO+5(α) (0.56)	Ru(dπ)→Ru(dπ)/acac(π*)
270(17400)	265(0.13)	HOMO−4(α)→LUMO+9(α)(0.43)	acac(π)→acac(π*)
2b^{-} (*S*=0)			
575(12400)	610(0.03)	HOMO→LUMO+2(0.56)	Ru(dπ)→Ru(dπ)/μ-O(π*)
415(7500)	421(0.09)	HOMO→LUMO+5(0.50)	Ru(dπ)→Ru(dπ)/acac(π*)
350(7900)	329(0.11)	HOMO-3→LUMO+5(0.31)	Ru(dπ)/acac(π)→acac(π*)
		HOMO-4→LUMO+5(0.27)	acac(π)/Ru(dπ)→acac(π*)
1c^{+} (*S*=0)			
505(3800)	545(0.07)	HOMO-3→LUMO+1 (0.62)	acac(π)/Pz(π)→Ru(dπ)/acac(π*)
340(9500)	315(0.14)	HOMO→LUMO+2 (0.53)	Ru(dπ)→ Ru(dπ)/acac(π*)
280(17700)	285(0.23)	HOMO-5→LUMO+8 (0.41)	acac(π)/Pz(π)→acac(π*)
1c (*S*=1/2)			
1485(250)	1408(0.001)	HOMO(*β*)→LUMO+1(*β*)(0.85)	Ru(dπ)→Ru(dπ)/μ-O(π*)
330(11200)	380(0.20)	HOMO−4(*β*)→LUMO(*β*)(0.52)	acac(π)/pz(π)→ Ru(dπ)/acac(π*)
270(19500)	290(0.16)	HOMO−8(*α*)→LUMO+9(*α*) (0.32)	acac(π)→acac(π*)
1c^{-} (*S*=0)			
575(12400)	559(0.05)	HOMO→LUMO+2(0.50)	Ru(dπ)→Ru(dπ)/μ-O(π*)
415(7500)	430(0.13)	HOMO−3→LUMO+4(0.62)	Ru(dπ)/acac(π)→Ru(dπ)/acac(π*)
350(7960)	315(0.17)	HOMO-3→LUMO+5(0.30)	Ru(dπ)/acac(π)→acac(π*)
2c^{+} (*S*=0)			
515(2900)	550(0.11)	HOMO-3→LUMO+1 (0.59)	acac(π)/Pz(π)→Ru(dπ)/acac(π*)
335(7300)	310(0.03)	HOMO→LUMO+2 (0.60)	Ru(dπ)→ Ru(dπ)/acac(π*)
278(13500)	295(0.08)	HOMO-3→LUMO+9 (0.39)	acac(π)/Pz(π)→acac(π*)
2c (*S*=1/2)			

1485(240)	1393(0.001)	HOMO(β)→LUMO+1(β)(0.88)	Ru(dπ)→Ru(dπ)/μ-O(π^*)
540(8700)	569(0.12)	HOMO−2(β)→LUMO(β)(0.46)	acac(π)/pz(π)→ Ru(dπ)/acac(π^*)
330(9500)	310(0.21)	HOMO−6(α)→LUMO+13(α) (0.37)	acac(π)→acac(π^*)/Pz(π*)
2c$^-$ (*S*=0)			
570(12400)	564(0.24)	HOMO→LUMO+2(0.62)	Ru(dπ)→Ru(dπ)/μ-O(π^*)
450(7500)	421(0.09)	HOMO−4→LUMO+4(0.60)	Ru(dπ)/μ-O(π)→Ru(dπ)/acac(π^*)
350(7800)	312(0.13)	HOMO−3→LUMO+7(0.29)	Ru(dπ)/acac(π)→acac(π^*)
2d$^+$ (*S*=0)			
550(4000)	563(0.22)	HOMO−2→LUMO+3 (0.65)	acac(π)/Iz(π)→Ru(dπ)/acac(π^*)
246(27200)	271(0.15)	HOMO−4→LUMO+5 (0.41)	Iz(π)/acac(π)→acac(π^*)
2d (*S*=1/2)			
1480(400)	1415(0.002)	HOMO−1(β)→LUMO+1(β)(0.79)	Ru(dπ)→Ru(dπ)/μ-O(π^*)
545(8900)	532(0.12)	HOMO−2(β)→LUMO(β)(0.55)	acac(π)/Iz(π)→ Ru(dπ)/acac(π^*)
280(27800)	318(0.19)	HOMO−6(α)→LUMO+13(α) (0.33)	acac(π)→acac(π^*)/Iz(π*)
		HOMO−5(α)→LUMO+13(α) (0.29)	acac(π)→acac(π^*)/Iz(π*)
2d$^-$ (*S*=0)			
525(4200)	545(0.03)	HOMO−2→LUMO+2(0.68)	Ru(dπ)→Ru(dπ)/μ-O(π^*)
270(20800)	285(0.11)	HOMO−8→LUMO+7(0.30)	acac(π)→acac(π^*)
3a$^+$ (*S*=1/2)			
1580(450)	1386(0.004)	HOMO−1(β)→LUMO(β)(0.99)	Ru(dπ)→Ru(dπ)/PzH(π^*)
890(800)	847(0.11)	HOMO−2(β)→LUMO(β)(0.96)	Ru(dπ)/PzH(π)→Ru(dπ)/PzH(π^*)
531(3000)	452(0.02)	HOMO−5(β)→LUMO(β)(0.97)	Pz(π)→Ru(dπ)/PzH(π^*)
350(2600)	352(0.02)	HOMO−2(β)→LUMO+4(β)(0.57)	Ru(dπ)/PzH(π)→PzH(π^*)
		HOMO−2(α)→LUMO+2(α) (0.34)	Ru(dπ)/Pz(π)→PzH(π^*)
290(8000)	297(0.019)	HOMO(α)→LUMO+11(α) (0.45)	Ru(dπ)/μ-O(π)→Pz(π^*)/PzH(π^*)
		HOMO(α)→LUMO+12(α) (0.38)	Ru(dπ)/μ-O(π)→Pz(π^*)/Ru(dπ)
3a (*S*=0)			
810(520)	740(0.012)	HOMO−1→LUMO(0.78)	PzH(π)→Ru(dπ)/PzH(π^*)/μ-O(π^*)
575(3300)	562(0.04)	HOMO−6→LUMO(0.65)	Ru(dπ)→ Ru(dπ)/PzH(π^*)/μ-O(π^*)
460(1500)	435(0.19)	HOMO−7→LUMO+6(0.46)	Ru(dπ)/PzH(π)→Pz(π^*)/μ-O(π^*)
345(2700)	310(0.13)	HOMO−4→LUMO+6(0.45)	PzH(π)→Pz(π^*)/μ-O(π^*)
3a$^-$ (*S*=1/2)			
595(850)	563(0.02)	HOMO(α)→LUMO+11(α) (0.86)	PzH(π)→Ru(dπ)/PzH(π^*)
341(6050)	384(0.04)	HOMO-1(α)→LUMO+15(α) (0.86)	Ru(dπ)/μ-O(π)→Pz(π^*)/PzH(π^*)

[a]Experimental absorption maxima from spectroelectrochemistry in CH_3CN/ 0.1M Et_4NClO_4.

[b]Molar extinction coefficients in $dm^3mol^{-1}cm^{-1}$. [c]Calculated oscillator strengths.

Table S35 DFT calculated selected MO compositions for **3a** in *S* = 0 state

MO	Energy (eV)	% Composition			
		Ru	PzH	μ-O	Pz
LUMO+5	0.415	11	82	02	01
LUMO+4	0.210	06	92	00	01
LUMO+3	0.142	07	92	00	02
LUMO+2	0.101	06	92	00	02
LUMO+1	-0.094	06	92	00	02
LUMO	-0.191	08	89	20	01
HOMO	-1.203	39	36	23	02
HOMO-1	-1.943	63	17	18	02
HOMO-2	-2.554	75	11	03	11
HOMO-3	-2.634	75	11	03	11
HOMO-4	-2.835	78	17	00	05
HOMO-5	-2.898	74	09	00	17

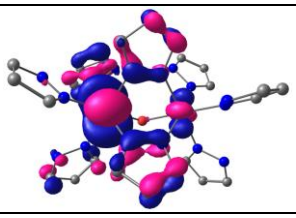
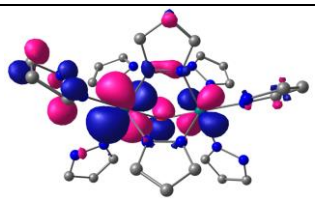
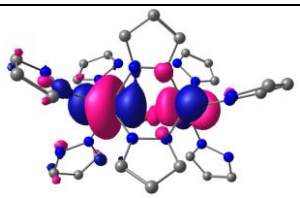
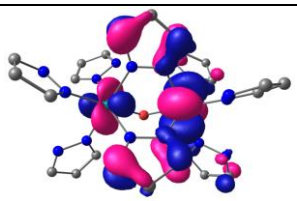
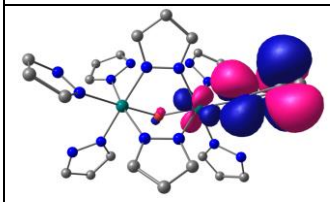
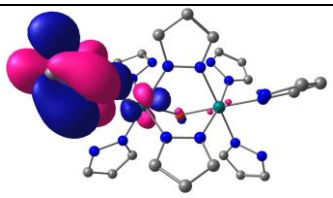
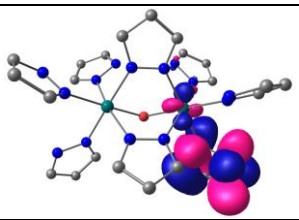
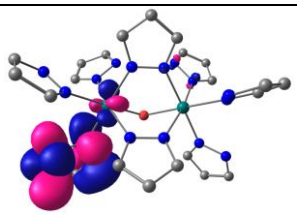
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S36 DFT calculated selected MO compositions for **3a**$^{+}$ in *S* = 1/2 state

MO	energy (eV)	% composition			
		Ru	PzH	μ-O	Pz
		α-MO			
LUMO+5	-2.610	04	94	00	02
LUMO+4	-2.698	08	91	01	01
LUMO+3	-2.738	05	93	00	02
LUMO+2	-2.812	04	94	00	02
LUMO+1	-3.038	05	94	01	00
LUMO	-3.657	06	92	01	01
SOMO	-5.261	59	18	21	03
HOMO-1	-5.581	69	14	11	06
HOMO-2	-5.953	69	10	04	17
HOMO-3	-6.102	73	09	09	14
HOMO-4	-6.317	81	07	01	11
HOMO-5	-6.523	78	16	00	06
		β-MO			
LUMO+5	-2.628	08	89	00	02
LUMO+4	-2.731	05	93	00	02
LUMO+3	-2.794	03	95	00	02
LUMO+2	-3.022	05	93	00	02
LUMO+1	3.509	10	86	03	01
LUMO	-4.434	41	34	23	02
HOMO	-5.401	68	14	14	04
HOMO-1	-5.826	70	11	03	16
HOMO-2	-5.964	73	09	04	14
HOMO-3	-6.094	16	32	00	05
HOMO-4	-6.188	81	07	01	11
HOMO-5	-7.346	05	03	10	83

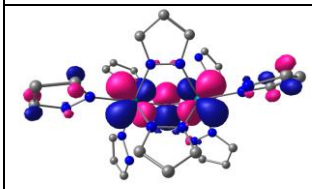
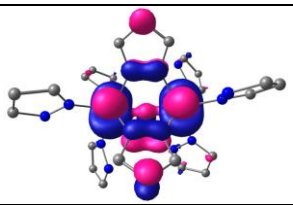
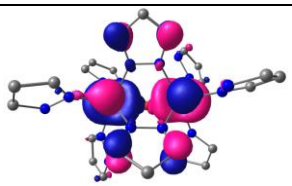
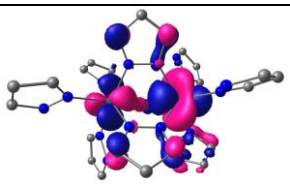
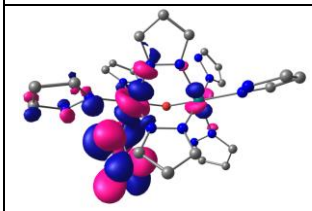
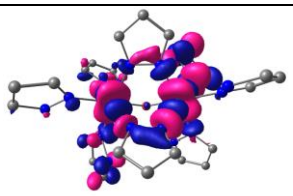
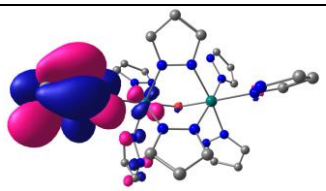
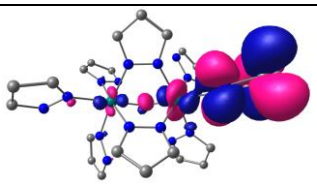
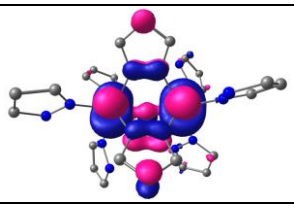
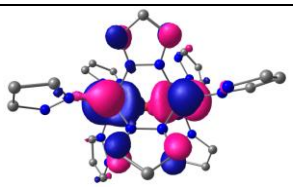
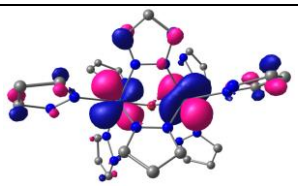
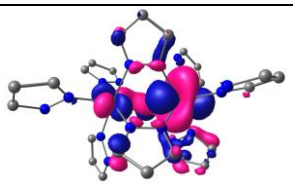
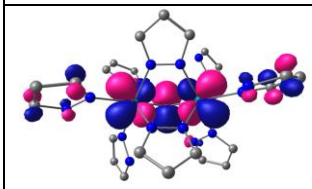
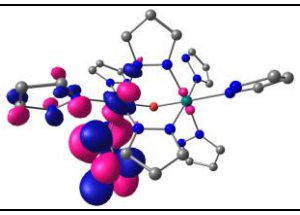
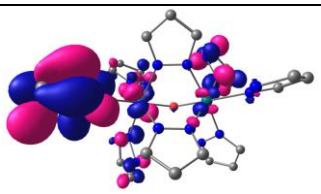
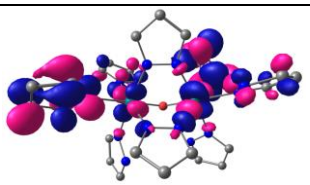
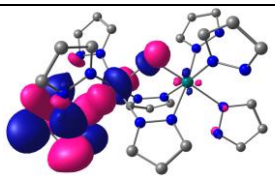
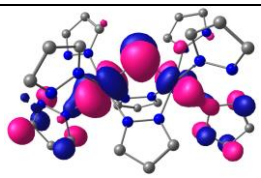
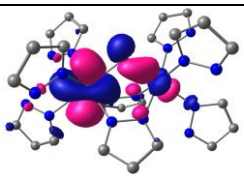
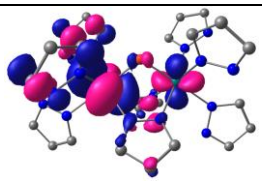
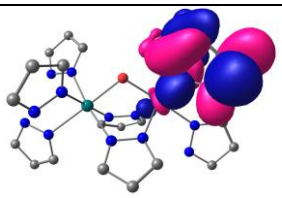
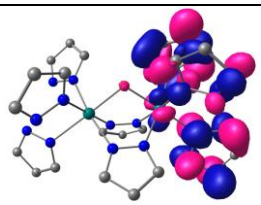
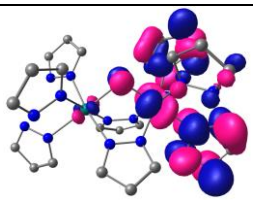
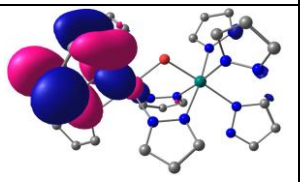
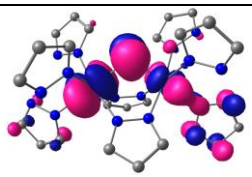
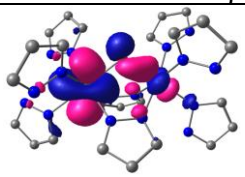
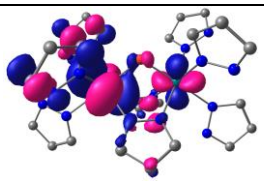
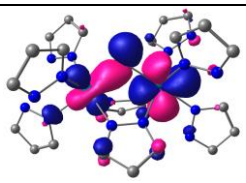
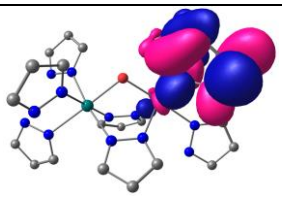
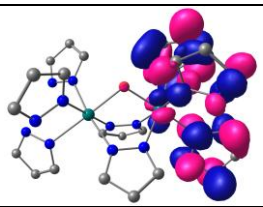
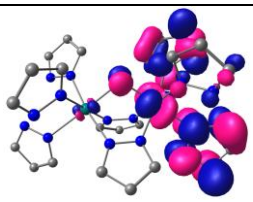
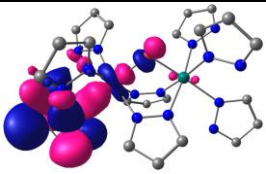
α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3

Table S37 DFT calculated selected MO compositions for **3a**$^{-}$ in *S* = 1/2 state

MO	Energy (eV)	% Composition			
		Ru	PzH	μ-O	Pz
		α-MO			
LUMO+5	2.899	10	87	01	02
LUMO+4	2.859	22	77	00	01
LUMO+3	2.696	04	94	01	01
LUMO+2	2.571	12	86	00	02
LUMO+1	2.454	01	98	00	01
LUMO	2.411	15	84	00	01
SOMO	2.397	19	80	00	01
HOMO-1	1.220	45	26	27	02
HOMO-2	0.451	70	15	12	04
HOMO-3	2.218	80	09	03	07
HOMO-4	-0.015	73	14	04	09
HOMO-5	-0.092	81	15	00	04
		β-MO			
LUMO+5	2.885	33	66	00	01
LUMO+4	2.866	36	63	00	01
LUMO+3	2.711	54	45	00	01
LUMO+2	2.697	58	41	00	01
LUMO+1	2.565	37	61	00	02
LUMO	2.493	03	96	00	01
HOMO	1.239	47	23	27	02
HOMO-1	0.453	70	14	12	07
HOMO-2	0.225	81	09	03	07
HOMO-3	-0.003	74	13	09	04
HOMO-4	-0.077	81	15	00	04
HOMO-5	-0.184	76	11	00	13

α-MO			
			
SOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3
β-MO			
			
HOMO	HOMO-1	HOMO-2	HOMO-3
			
LUMO	LUMO+1	LUMO+2	LUMO+3