Supporting Information

Electrocatalytic Water Oxidation by heteroleptic Ruthenium complexes of 2,6-bis(benzimidazolyl) pyridine Scaffold: A mechanistic investigation

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1 Experimental section

1.1 Materials and **Solvents:** All chemicals and reagents like 2,6-Pyridinedicarboxylic acid, o-phenylenediamine, 4,5-dimethyl-1,2- phenylenediamine, 4-fluoro-1,2- phenylenediamine, phosphoric acid(85%), were purchased from Aldrich suppliers and $RuCl_3.3H_2O$ was purchased from AroraMatthey (India) and was used without any further purification. For electrochemical and spectroscopic experiments all the solvents used were of HPLC grade. For water oxidation Milli-Q water was used. For the electrochemical studies, tetra butyl ammonium perchlorate (TBAP) was used as a supporting electrolyte which was prepared by a previously reported procedure.[S1] $Ru^{III}(L^1/L^2/L^3)Cl_3$[S2,S3] precursors were prepared according to the previously reported procedures.

1.2 Synthesis of ligands L^1, L^2, and **L^3:**

2,6-bis(1H-benzo[d]imidazole-2-yl)pyridine(L^1): A mixture of o-phenylenediamine (4.5 g, 41.5 mmol) and pyridine-2,6-dicarboxylic acid (3.34 g, 20 mmol) and polyphosphoric acid (40 ml) was heated at 200°C for 4 h. The deep blue viscous solution that formed was poured into crushed ice water. A blue precipitate thus obtained was filtered, and washed with water, followed by dilute aqueous ammonia and again water. During this process, the residue changed to light pink. This was dissolved in the minimum volume of ethanol; ^{1}H NMR (d6-DMSO) (δ/ppm): 12.989 (2H, s), 8.316-8.297(2H,d), 8.118-8.099(H,t), 7.736-7.714(4H,d), 7.287-7.267(4H,d), ^{13}C NMR (d6-DMSO, (δ/ppm): 163.793(2C,7-C), 158.426(2C,6-C), 152.283(1C,5-C), 148.010(4C,4-C), 139.768(4C,3-C), 122.012(2C,2-C), 111.854(4C,1-C). ESI MS: 310.57 ($M - H^+$), Anal. Calcd. (%) for $C_{19}H_{13}N_5$: C, 73.30; H, 4.21; N, 22.49; found: C 73.35, H 4.26, N 22.55.

2,6-bis(5,6-dimethyl-1H-benzo[d]imidazole-2-yl)pyridine (L^2): Reaction procedure was similar as described for2,6-bis(1H-benzo[d]imidazole-2-yl)pyridine(L^1) except the 4,5-dimethyl-o-phenylenediamine was used in place of o-phenylenediamine;, ^{1}H NMR ($CDCl_3$, δ, ppm): 9.940(2H, s), 9.511-8.785(2H,d), 8.372(1H,t), 7.514-7.275(4H,s), 2.299(12H,s).). ^{13}C NMR ($CDCl_3$, δ, ppm): 161.770(2C,8-C), 147.636(2C,7-C), 144.803(1C,6-C), 142.825(4C,5-C), 135.753(4C,4-C), 127.493(2C,3-C), 126.228(4C,2-C), 19.620(4C,1-C). ESI MS: 366.20 ($M - H^+$), Anal. Calcd. (%) for $C_{23}H_{21}N_5$: C, 75.18; H, 5.76; N, 19.06; found: C 75.25, H 5.79, N 19.11.

2,6-bis(6-fluro-1H-benzo[d]imidazole-2-yl)pyridine (L^3): The reaction procedure was the same as described above for 2,6-bis(1H-benzo[d]imidazole-2-yl)pyridine(L^1) except the 5-fluoro-o-phenylenediamine was used instead of o-phenylenediamine; ^{1}H NMR (d6-DMSO, δ, ppm): 13.079 (2H,s), 8.308-8.276(2H,d), 8.162-8.132(1H,t), 7.720-7.538(4H,d), 7.152(2H,s), ^{13}C NMR (d6-DMSO, δ, ppm): 98.256(1C,1-C), 111.978(2C,2-C), 122.031(2C,3-C), 129.199(2C,4-C), 132.035(2C,-5-C), 132.227(2C,6-C), 139.788(1C,7-C), 148.000(2C,8-C), 152.130(2C,9-C), 167.472(2C,10-C). ESI MS: 346.62 ($M - H^+$), Anal.

Calcd. (%) for $C_{19}H_{11}F_2N_5$: C, 65.70; H, 3.19; F, 10.94; N, 20.16; found: C 65.75, H 3.25, N 20.23.

1.3 Synthesis of complexes:

[Ru^{II}((L)(L^1)(dmso)] [ClO_4](1): $Ru^{III}(L^1)Cl_3$ (518 mg, 1 mmol) was added to a dmso solution (30 ml) of deprotonated Pyrazinecarboxylic acid (HL) (124 mg, 1 mmol). The reaction mixture was refluxed under stirring conditions. With the reaction's progress, the reaction mixture's color changed from deep brown to red. The mixture was refluxed for 20 h and filtered. The volume of the solution was reduced to 5 ml and a 2 ml acetonitrile solution of TBAP was added to give a red-colored solid. The solid was filtered and thoroughly washed with water (3 - 5 ml). The red-colored solid was dried under a vacuum. The pure product was obtained from a silica gel column using DCM: MeOH 20:1; yield: 452 mg, 70% ESI MS: 614.19 ($M + H^+$), ^{1}H NMR (d6-DMSO, δ/ppm): 12.937(2H, s), 8.316(H,s), 8.297(2H,d), 8.137-8.099(3H,d,t), 7.736-7.25(4H,d), 7.287-7.274 (4H,d), 2.460(6H,s).). ^{13}C NMR (d6-DMSO, δ, ppm): 44.775(2C,1-C), 114.738(4C,2-C), 116.406(2C,3-C), 123.056(4C,4-C), 125.778(2C,5-C), 126.448(2C,6-C), 134.642(2C,7-C), 141.714(1C,8-C), 147.042(1C,9-C), 148.929(1C,10-C), 149.533(1C,11-C), 150.951(1C,12-C), 152.245(2C,13-C), 169.398(1C,14-C). IR (cm-1):3059(υ_{N-H}), 1628(υC=O), 1597(υC =N), 1462s(υC-N), 1327m(υC-N). elemental analysis Found C, 50.89; H, 3.61; N, 15.98; found C, 50.97; H, 3.59; N, 15.95.

[Ru^{II}(L)(L^2)(dmso)][PF_6](2): Reaction procedure was similar as described for [$Ru^{II}(L^1)$(L)(dmso)] [ClO_4] except the 2,6-bis(5,6-dimethyl-1H-benzo[d]imidazol-2-yl)pyridine (H_2L^2) was used in place of 2,6-bis(1H-benzo[d]imidazol-2-yl)pyridine(H_2L^1) and here used NH_4PF_6 to get the precipitation. ESI MS: 639 (M – DMSO + EtOH + H^+), ^{1}H NMR ($CDCl_3$, δ, ppm): 10.968(2H,s), 8.602-8.583(1H,s), 8.167-8.144(2H,d), 7.839-7.796(3H,d), 7.399-7.364(4H,s), 2.247(6H,s), 2.109(12H,s). ^{13}C NMR ($CDCl_3$, δ, ppm): 14.493(2C,1-C), 29.797(4C,2-C), 110.033(4C,3-C), 119.012(2C,4-C), 122.491(4C,5-C), 122.692(2C,6-C), 127.129(2C,7-C), 128.902(2C.8-C), 130.013(1C,9-C), 136.079(1C,10-C), 136.481(1C,11-C), 142.538(1C,12-C), 151.632(1C,13-C), 154.114(2C,14-C), 174.343(1C,15-C). IR (KBr; cm^{-1}):3059(υN-H), 1628(υC=O), 1597(υC=N), 1462s(υC-N), 1327m(υC-N). elemental analysis Found: C, 53.80; H, 4.52; N, 14.64; found C, 53.97; H, 4.49; N, 14.68.

[Ru^{II}(L)(L^3)(dmso)][PF_6](3): Reaction procedure was same as described above for [$Ru^{II}(L^1)$(L)(dmso)] [ClO_4] except the 2,6-bis(6-fluoro-1H-benzo[d]imidazol-2-yl)pyridine (L^3) was used instead of 2,6-bis(1H-benzo[d]imidazol-2-yl)pyridine(L^1) and here NH_4PF_6 used for precipitation. ESI MS: 652 ($M + H^+$), ^{1}H NMR (d6-DMSO, δ, ppm): 10.732(2H,s), 9.313-9.292(3H,d), 8.935-8.908(3H,t), 8.770-8.745(2H,d), 7.337-7.312(2H,d), 2.490(6H,s). ^{13}C NMR (d6-DMSO, δ, ppm): 22.974(1C,1-C), 106.689(2C,2-C), 117.115(2C,3-C), 117.450(2C,4-C), 119.089(2C,5-C), 123.669(2C,6-C), 129.524(2C,7-C), 131.173(2C,8-C), 134.201(1C,9-C), 143.726(1C,10-C), 157.736(1C,11-C), 159.739(1C,12-C), 165.393(1C,13-C), 165.632(2C,14-C), 169.005(2C,15-C), 172.915 (1C,16-C). IR (KBr; cm^{-1}): 3059(υN-H),

1628(υC=O), 1597(υC=N), 1462s(υC-N), 1327m(υC-N). elemental analysis Found: C, 48.07; H, 3.10; F, 5.85; N, 15.09; found C, 49.05; H, 5.79; N, 15.12.

2 Physical Measurements:

2.1 Spectroscopic Characterization: FTIR spectra were recorded on a model IR prestige 21, SHIMADZU Corporation (Japan) using samples prepared in flam form. UV-Visible absorption was recorded on a PERKIN-ELMER (LAMBDA-750) UV/VIS/NIR spectrophotometer. ESI-MS measurements were carried out using a JEOL JMS-700 spectrometer and the High-resolution mass spectra were recorded on a Bruker micrOTOFQ II Spectrometer. ^{1}H-NMR and ^{13}C-NMR were recorded on a BRUKER ADVANCE DPX-400 NMR Spectrometer using, $Si(CH_3)_4$ as the internal standard.

2.2 Electrochemistry: All electrochemical experiments were carried out on CHI-730 potentiostat in a typical three-electrode system where the platinum disk was used as working electrodes (WE), and Pt wire was used as a counter electrode (CE). $Ag/AgNO_3$(non-aqueous) and Ag/AgCl (KCl sat. aqueous) are used as reference electrodes (RE) in cyclic voltammetry (CV) and linear sweep voltammetry (LSV) experiments.TBAP was used as a supporting electrolyte. The ferrocene/ferrocenium couple was observed at E^0 (ΔEp) = 0.24 V (50 mV) under pH 1 experimental conditions. The electrolytic solution was prepared by mixing aqueous triflic acid (0.1M pH 1)/MeCN (v: v 9:1) for electrochemical water oxidation. Pourbaix diagrams were drawn from the electrochemical measurements for all complexes (30μM) in 1:9 CH_3CN/H_2O 0.1M aqueous phosphate buffer solution within the range of pH 1 to 10. The required pH solutions of aqueous phosphate buffer were prepared by thermos fisher pH-meter by using 1M H_2SO_4 and 0.2M NaOH.

2.3 Oxygen detection: In the bulk electrolysis experiment, all chambers and the solvent were degassed with N_2 gas and sealed air-tight with septum caps. A Pt dish was used as a working electrode. An Ag/AgCl (KCl sat.) was employed as a reference electrode and a Pt mess cylinder electrode as a counter electrode. The GC monitored the generated amount of oxygen during water oxidation, which was situated in the headspace of the compartment containing the working electrode. The gas chromatograph for O_2 detection using a thermos fisher scientific trace 1110, equipped with a thermal conductivity detector (detector bridge voltage - 5V, detector current - 85 mA, carrier gas - argon) and fitted with an MS-5Å 80/100 2.5m 2.0MMID 1/8INODand calibrated with $H_2/N_2/CH_4/CO/CO_2$ mixtures of known composition. The retention time of O_2 is found to be 1.925 min.

2.4 X-ray crystallographic data collection and refinement of the structure: Single crystals of all complexes were obtained by slow evaporation of methanol. The data were collected with a Rigaku diffractometer and during the data collection of the crystal; the temperature was kept at 298 K. The crystal structure was solved with the Shelxs implemented in the Olex2[S4] software package using Charge Flipping and refined with the SHELXL[S5] using Least Squares minimization.[S6] The glass fiber was used for mounting all Ru single crystals on a Rigaku Oxford Diffraction X-Calibur CCD system, controlled with the user-inspired Crysalis^{Pro} for crystallographic data acquisition. The measurements were made on an Enraf Nonius Kappa CCD diffractometer with Mo-Kα (0.71073 Å).

2.5 Electron Paramagnetic Resonance (EPR) Measurements: The EPR spectrum of all complexes was carried out in JEOL JES-FA200 under non-saturating microwave power conditions. Into the EPR cell (3.0mmi.d.) taking 0.20 μL of complexes **1**, **2**, and **3** ($1.0 * 10^{-3}$ M) of pH 1 0.1M CF_3SO_3H aqueous solution of triflic acid with 1:9, v:v CH_3CN: CF_3SO_3H

after bulk electrolysis. The magnitude of the modulation was chosen to optimize the resolution and the signal-tonoise (S/N) ratio of the observed spectra. The g values were calibrated using the Mn^{2+} marker. The EPR spectrum of the mixture was measured at 298 K. The EPR spectrum of oxidized **2** and **3** was meant similarly to that of **1**.

2.6 Electrochemical cells and bulk electrolysis: A 20 mL glass vial and a Teflon cap with three holes were used for CV and LSV measurements. For CV and LSV experiments, the scan rate was 50 mV/s, amplitude = 50 mV, pulse width = 0.05 s, sampling width = 0.0167 s, and pulse period = 0.2s were used. A three-compartment cell was used with a frit distance for bulk electrolysis experiments. The working electrode was placed in one of the compartments between the reference and counter electrodes.

3 Computational Studies: All density functional theory (DFT) calculations were carried out with the Jaguar 4.0 by Gaussian 16, Revision A.03.[S7] Molecular geometries were optimized at Becke's three-parameter hybrid functional and the LYP correlation functional (B3LYP)[S8] with the LAN2DZ[S9] basis set. And single-point energy corrections were performed with the B3LYP functional using the LAN2DZ basis set augmented with two f functions on the metal. Frequency calculations were performed on the optimized geometries to verify that the geometries correspond to minima on the potential energy surface (PES). The absorption spectra of the ground state were calculated for all Ru complexes. The 50 lowest doublet-doublet transitions were calculated in an acetonitrile solvent using the TDDFT method in combination with the IEFPCM [S10] continuum salvation model. The value of pKa calculated is the following standard schemes as described in e.g. [Jang Y. H. et al. Chem. Res. Toxicol. 2002, 15, 1023-1035]. At 298.15 K and 1 atm, thermal adjustments were performed to the free energies, including zero-point energy (ZPE) adjustments for the zero-point energy (ZPE). The pKa value was calculated using the standard schemes described in e.g. [Jang Y. H. et al. Chem. Res. Toxicol. 2002, 15, 1023-1035]. We computed the free energy according to the following scheme: G = EE(LAN2DZ on Ru) + G_{solv} + ZPE + H_{298} – Sx298 + 1.9 (concentration correction to the free energy of solvation from 1 M(g) → 1 M(aq) to 1 atm(g) → 1 M(aq)). For the proton, the experimental number of Tissandier et al. was used, and the value of 270.3 kcal mol^{-1} was utilized for the proton's free energy in water. We used experimental G_{solv} values for both water and hydroxide. By translating the estimated free energies, which are about the relation to the common hydrogen electrode, the redox potentials (E^0) (SHE). As stated in the literature[s11-12], 4.56 V is assumed to be the SHE's absolute potential for this purpose. To determine redox potentials, the following thermodynamic equations were utilized[S13-14].

$$O_{(sol)} + ne^- + H^+ \xrightarrow{\Delta G_{rxn}} R_{(sol)}$$

$$E^0_{R/O} = -\frac{\Delta G_{rxn}}{nF} - E_{ref}$$

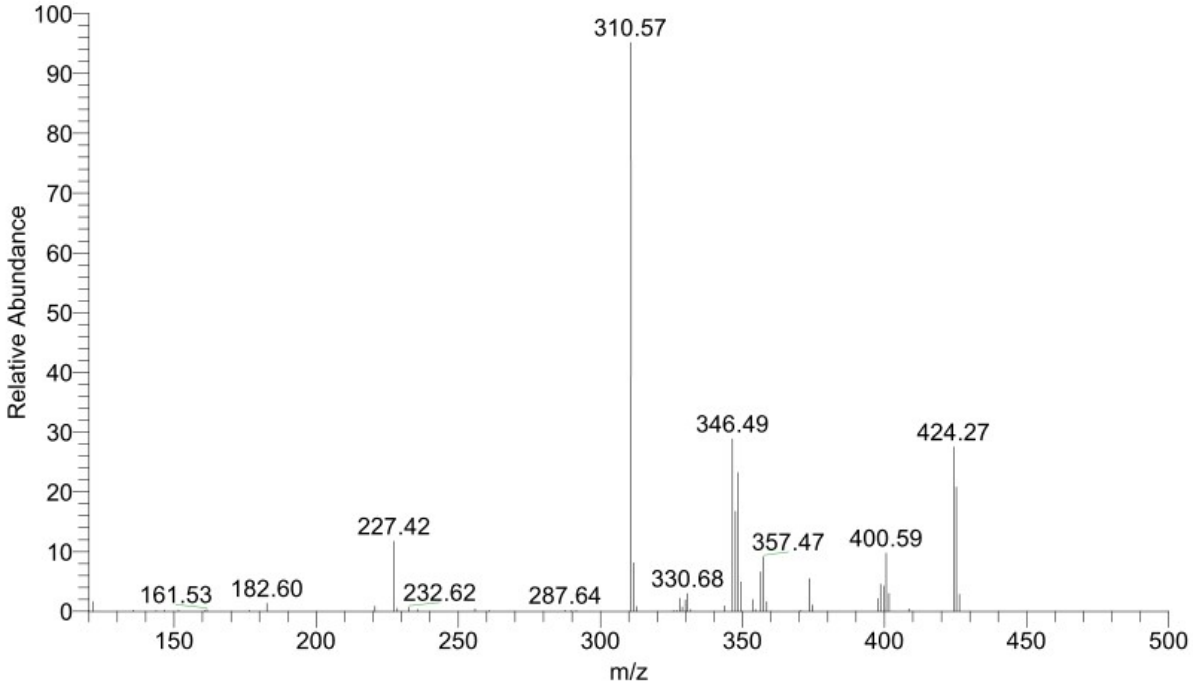


Figure S1: Mass spectra of ligand $\mathbf{L^1}$.

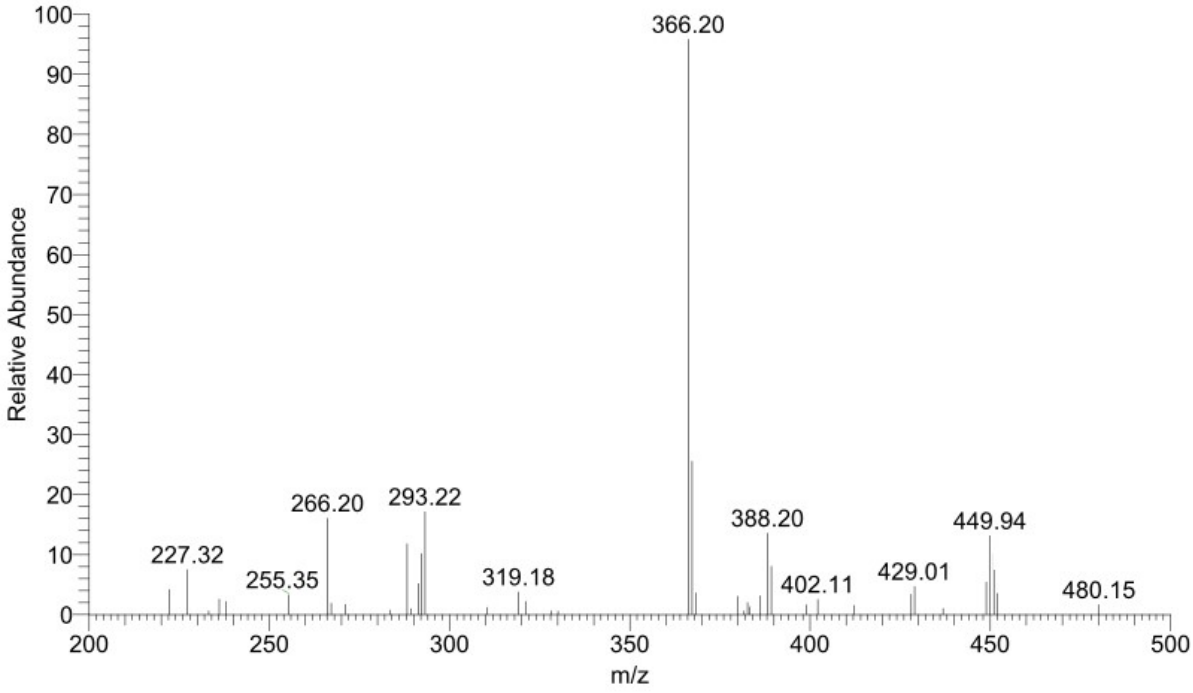


Figure S2: Mass spectra of ligand $\mathbf{L^2}$.

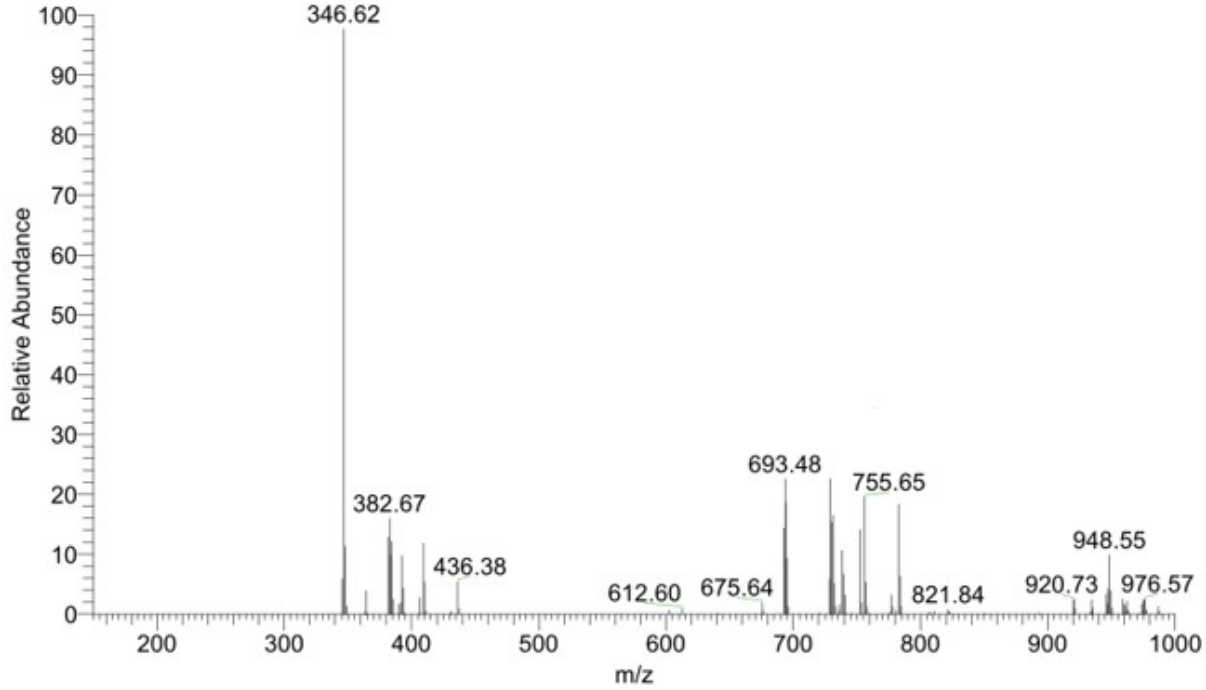


Figure S3: Mass spectra of ligand $\mathbf{L^3}$.

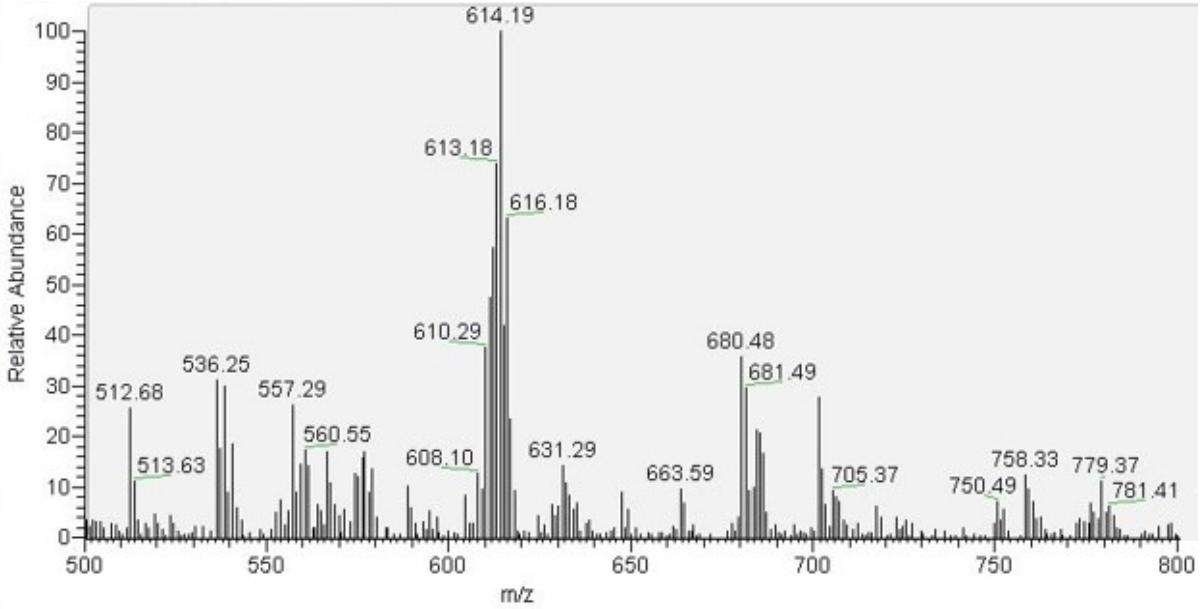


Figure S4: Mass spectra of Complex **1**.

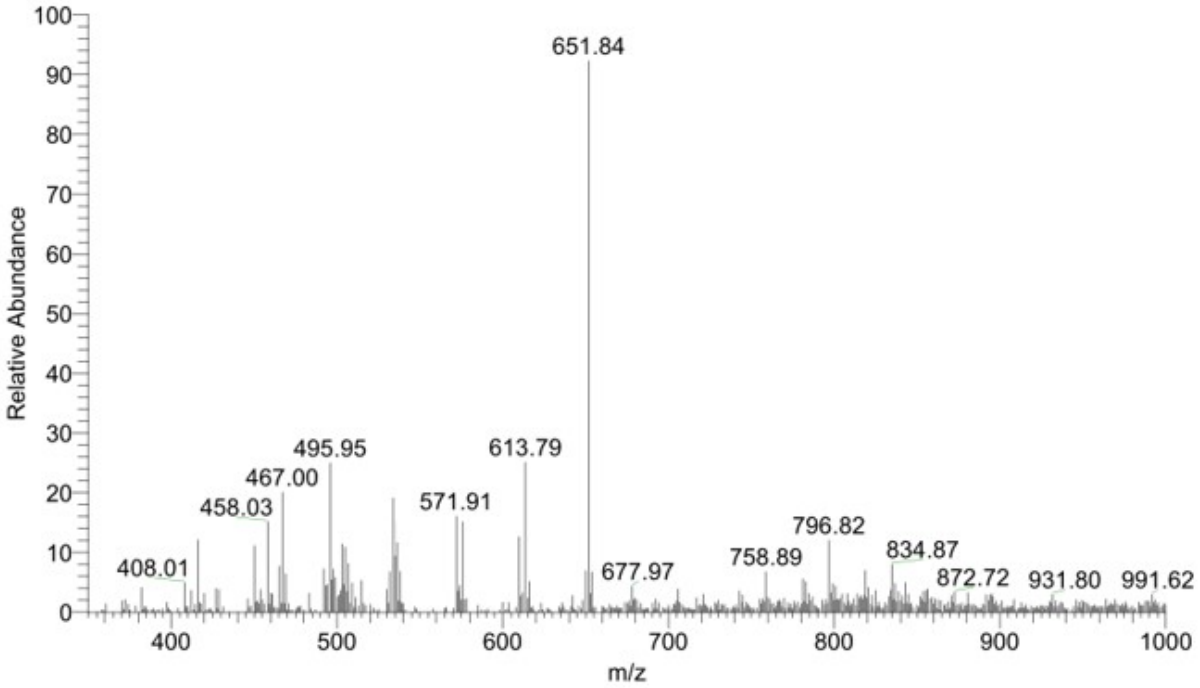


Figure S5: Mass spectra of Complex **2**.

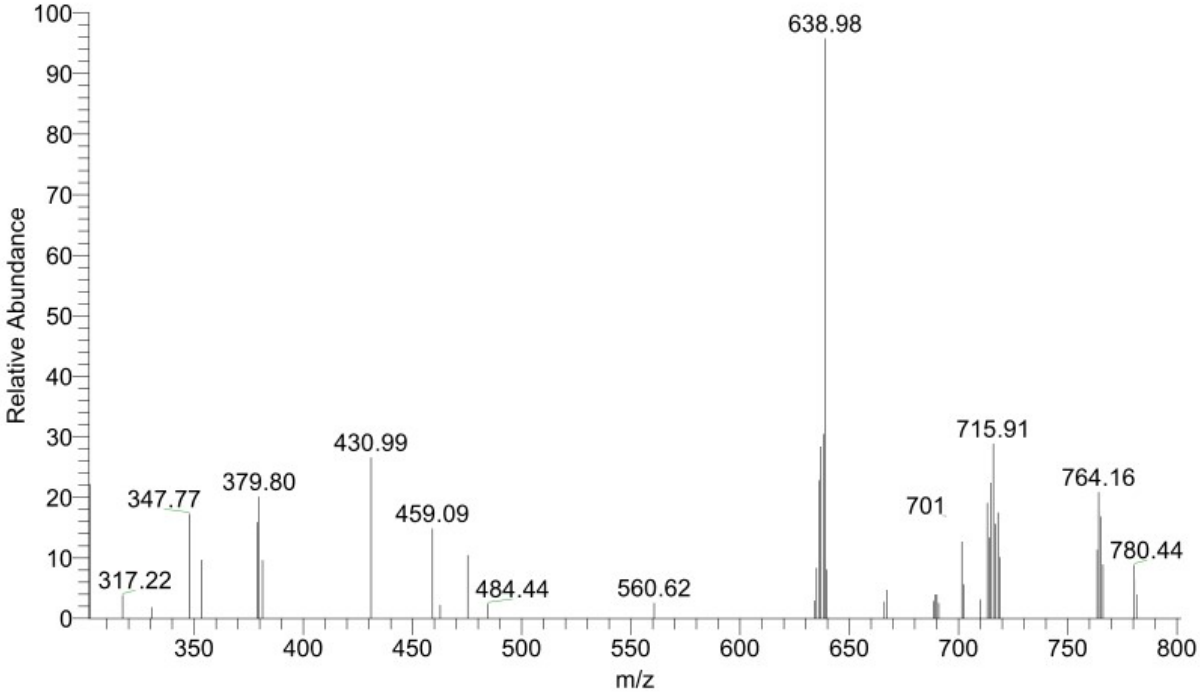


Figure S6: Mass spectra of Complex **3**.

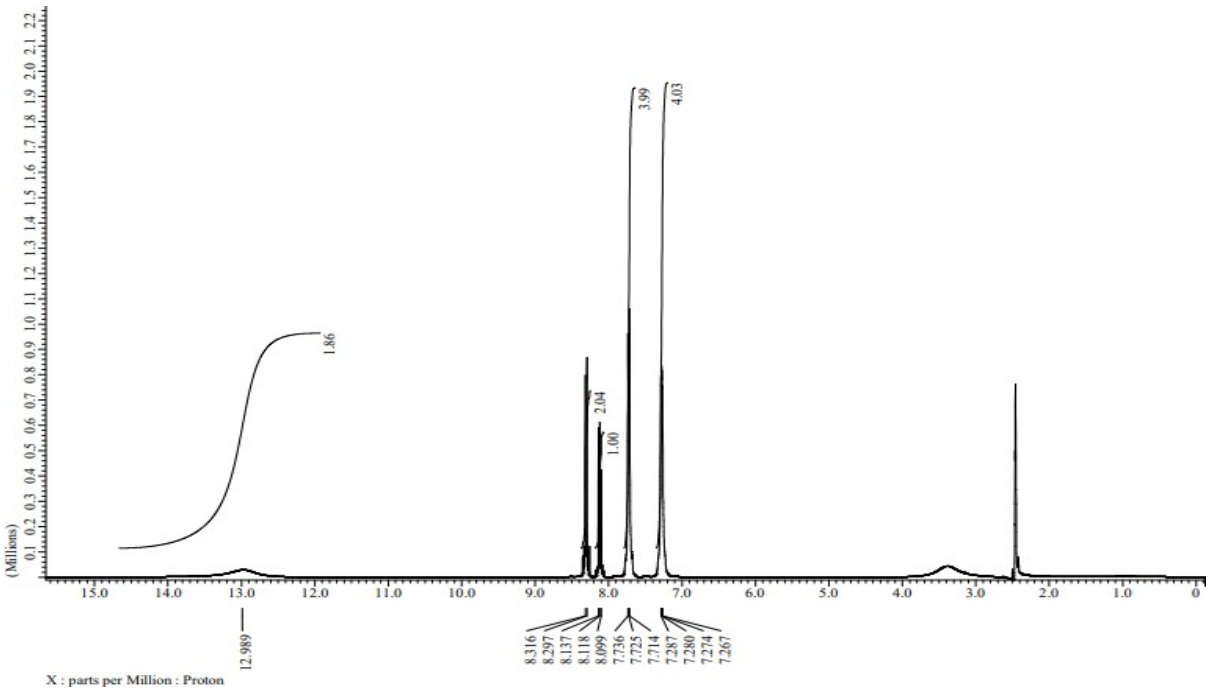


Figure S7: ^{1}H-NMR of ligand **L^{1}**.

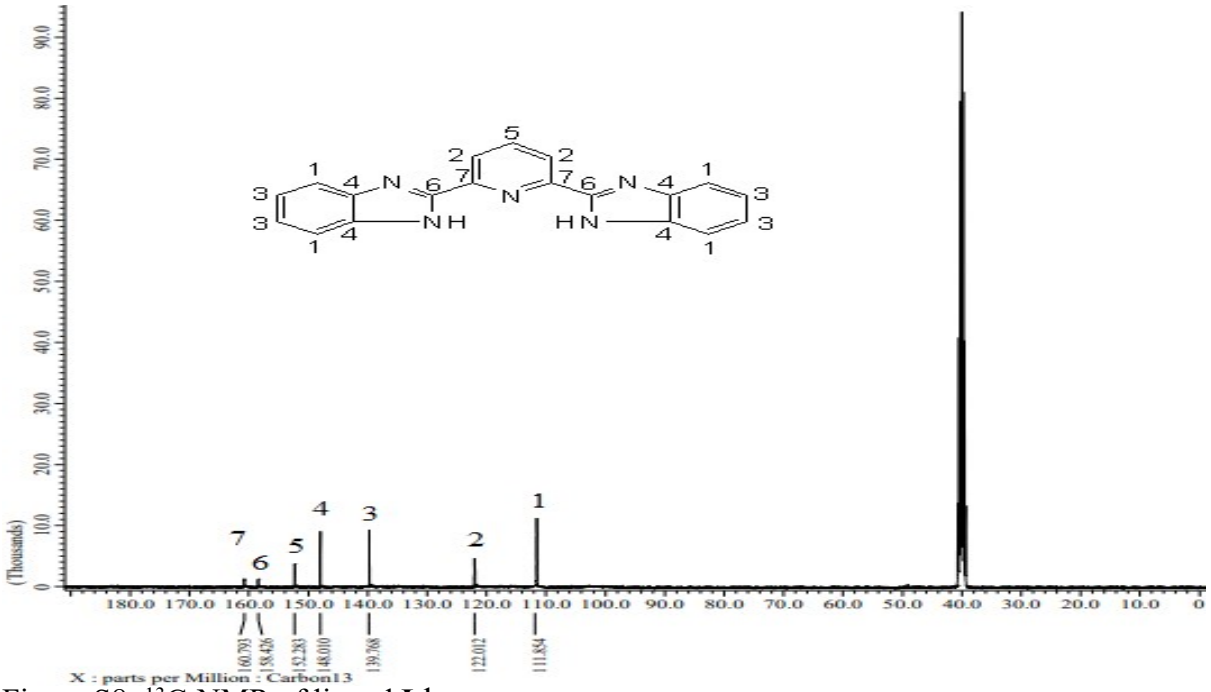


Figure S8: ^{13}C-NMR of ligand **L^{1}**.

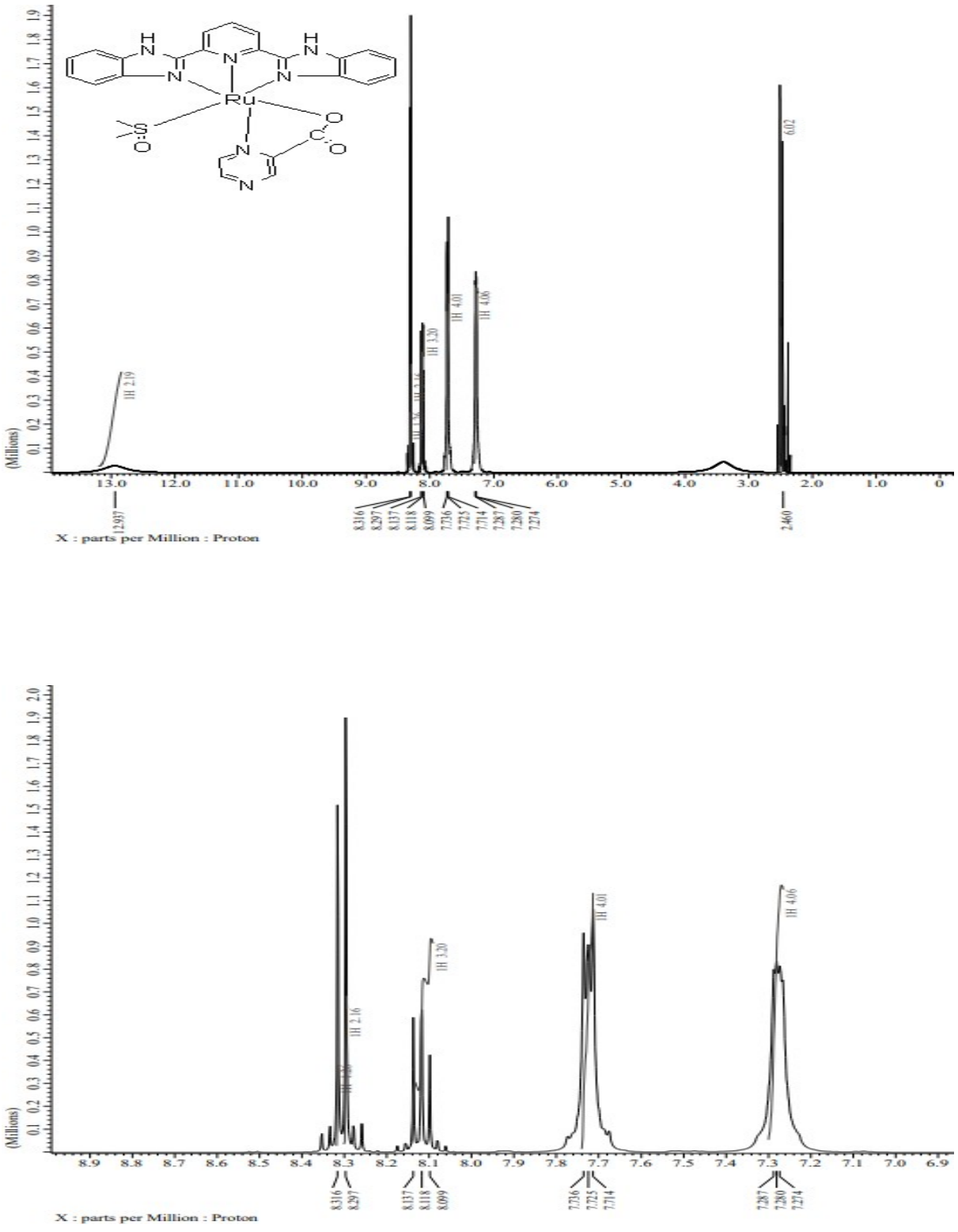


Figure S9: ^{1}H-NMR of complex **1**.

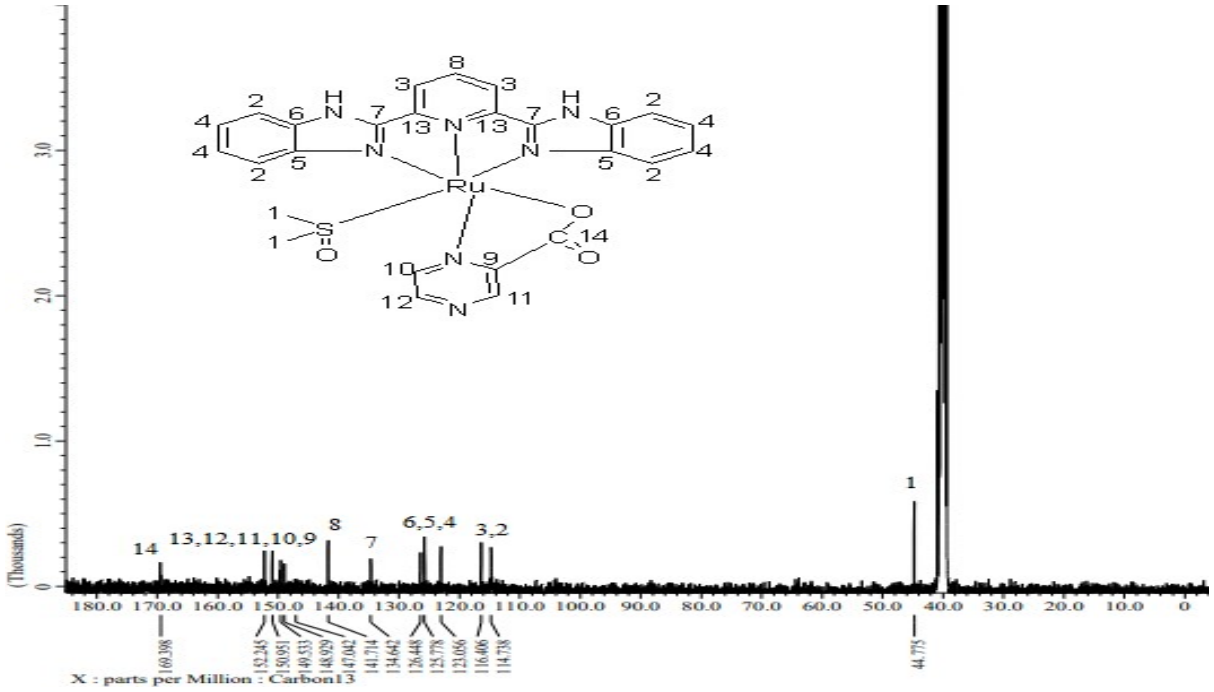


Figure S10: ^{13}C-NMR of complex **1**.

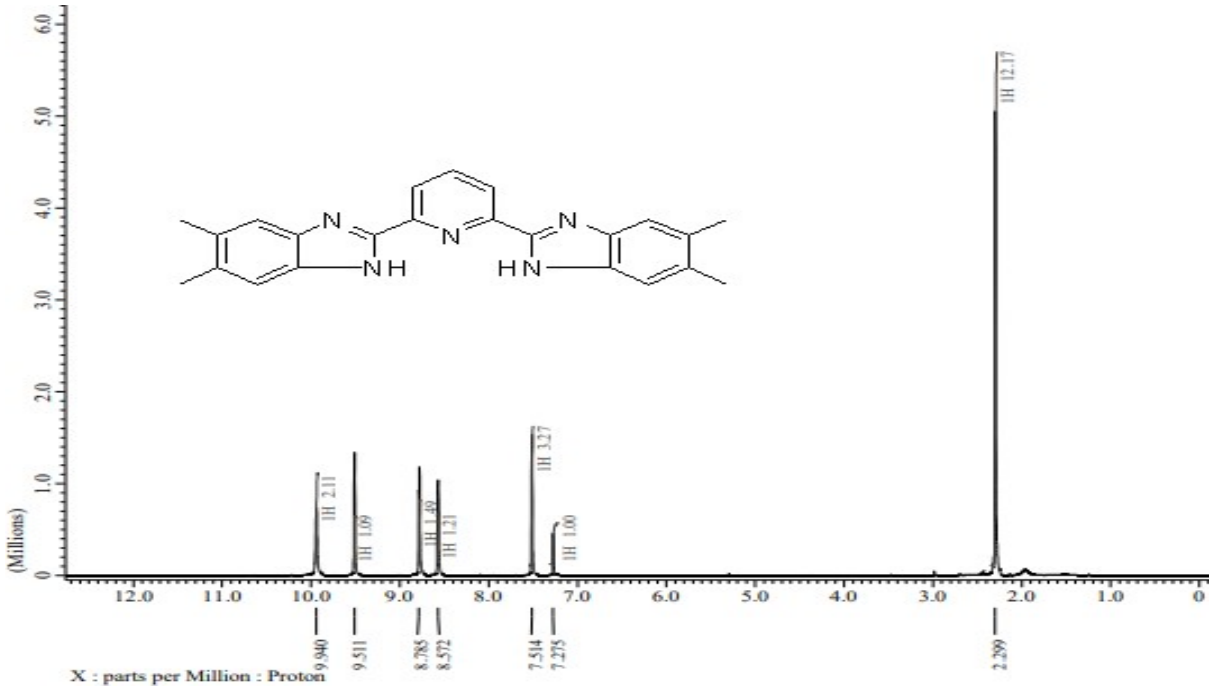


Figure S11: ^{1}H-NMR of ligand **L²**.

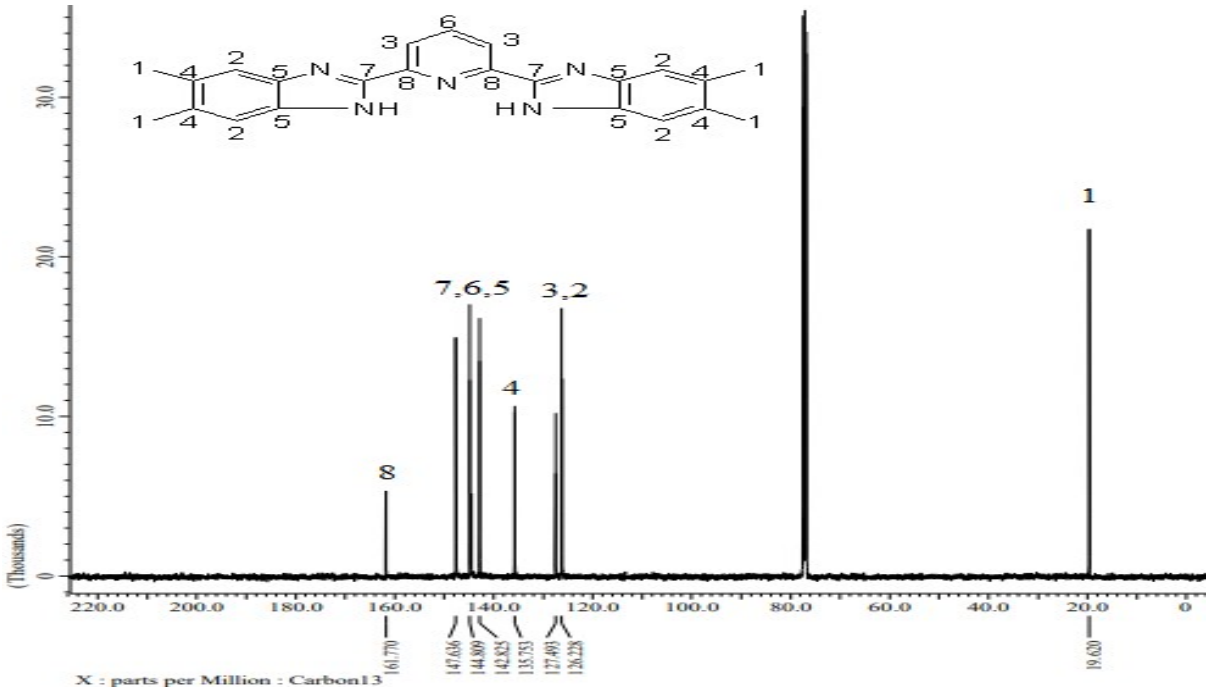
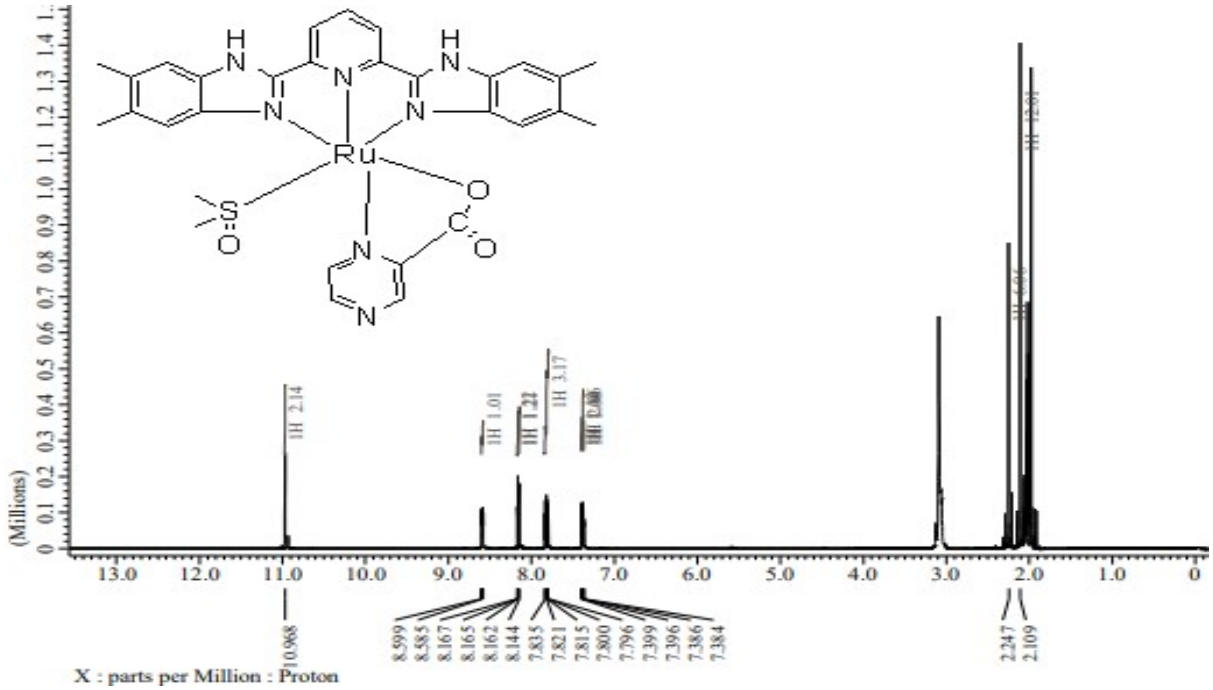


Figure S12: ^{13}C-NMR of ligand **L²**.



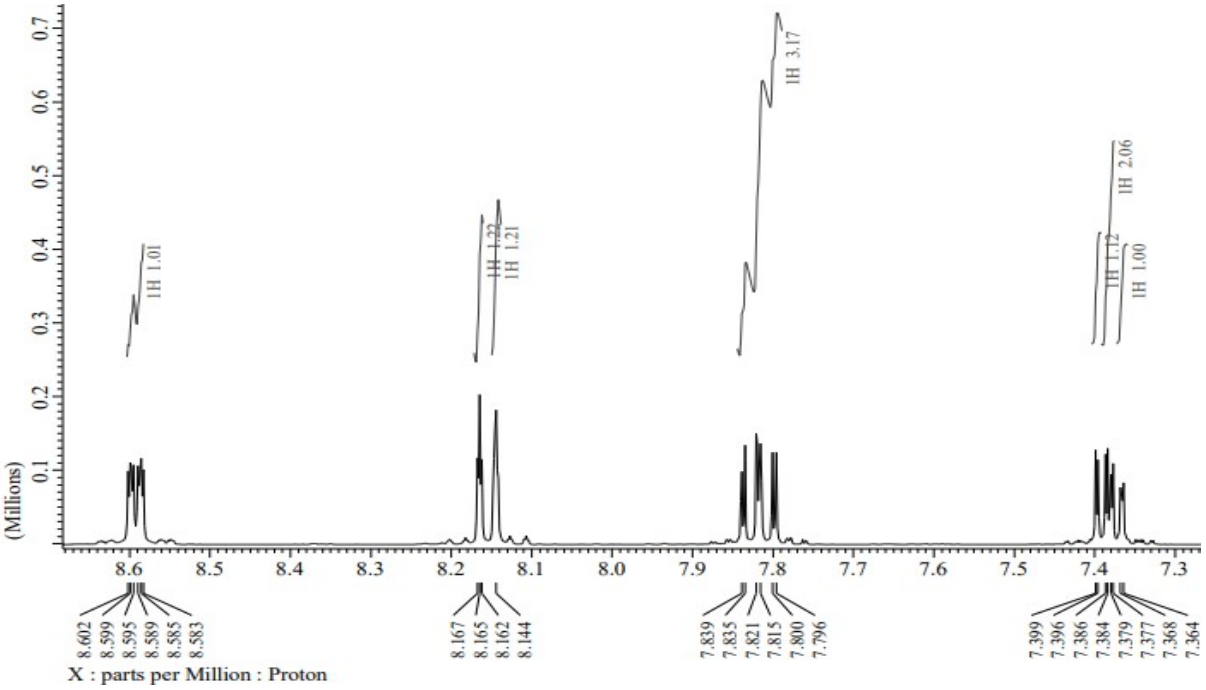


Figure S13: ^{1}H-NMR of complex **2**.

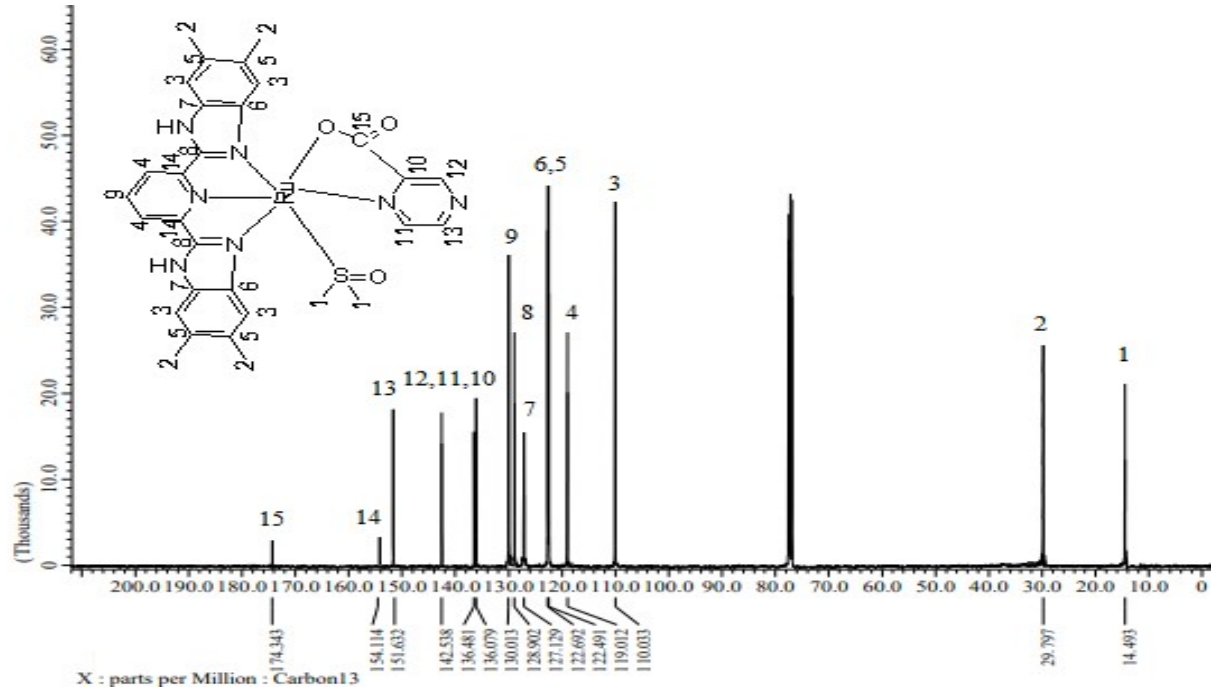


Figure S14: ^{13}C-NMR of complex **2**.

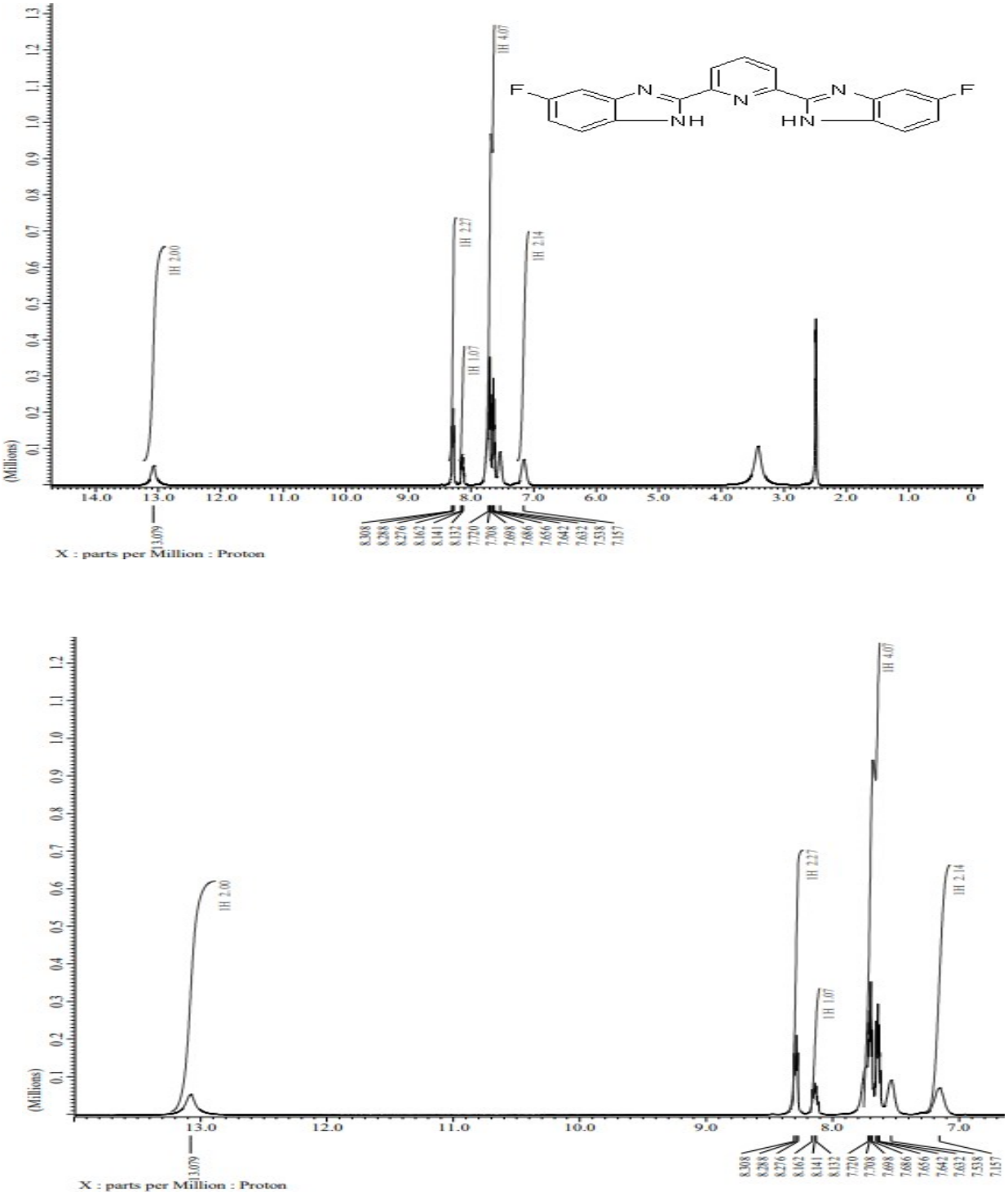


Figure S15: ^{1}H-NMR of ligand **L^{3}**.

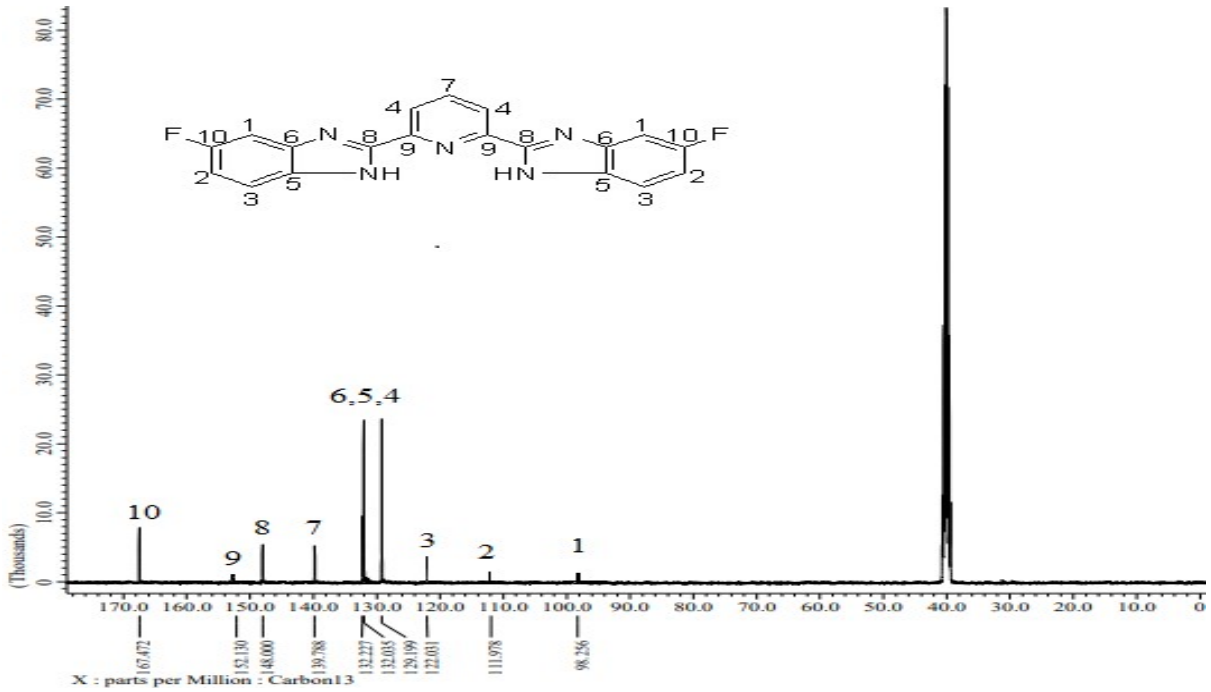
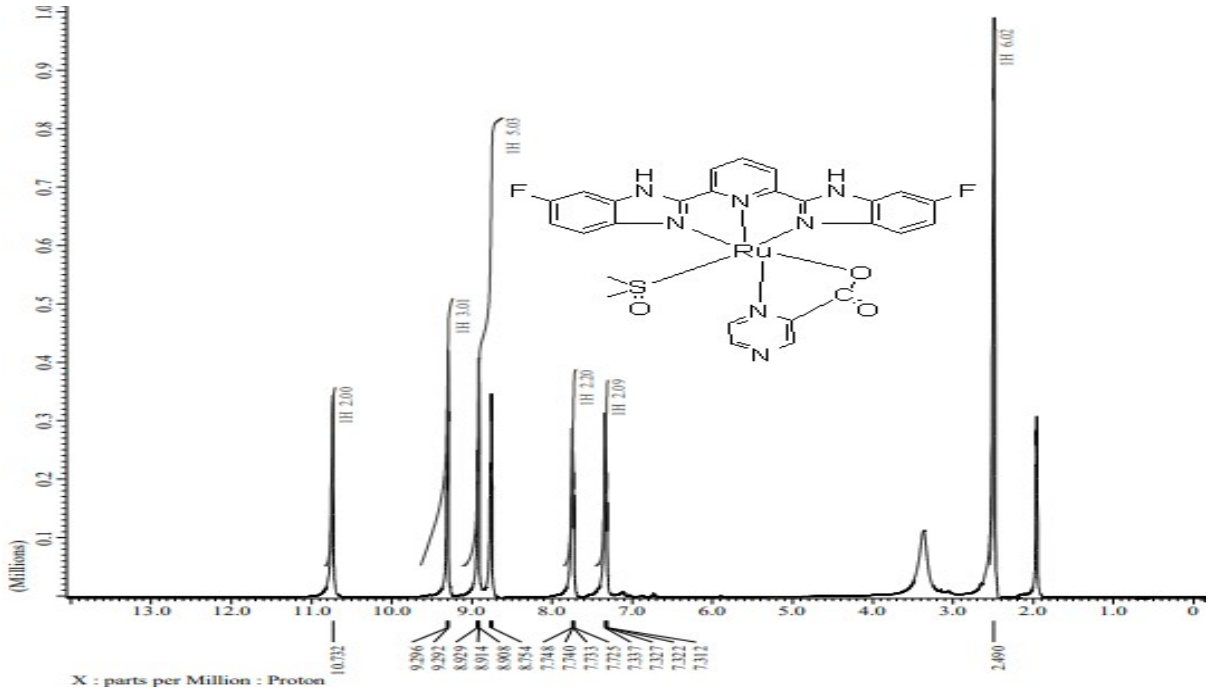


Figure S16: ^{13}C-NMR of ligand **L^3**.



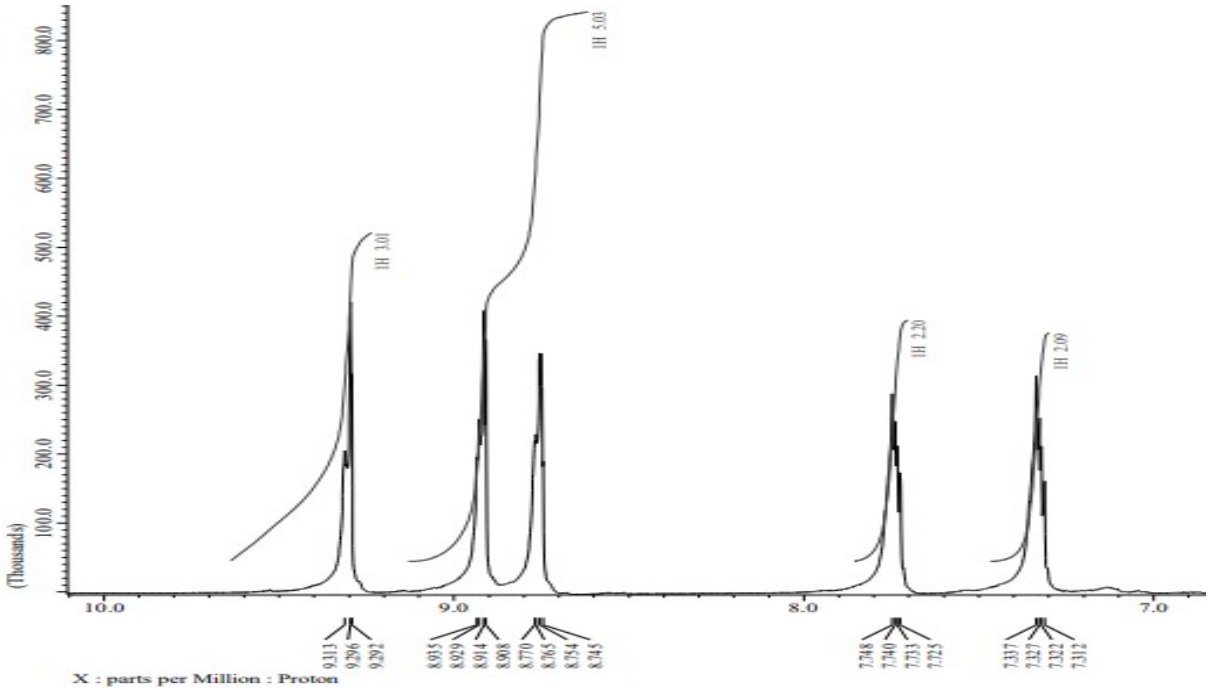


Figure S17: ^{1}H-NMR of complex **3**.

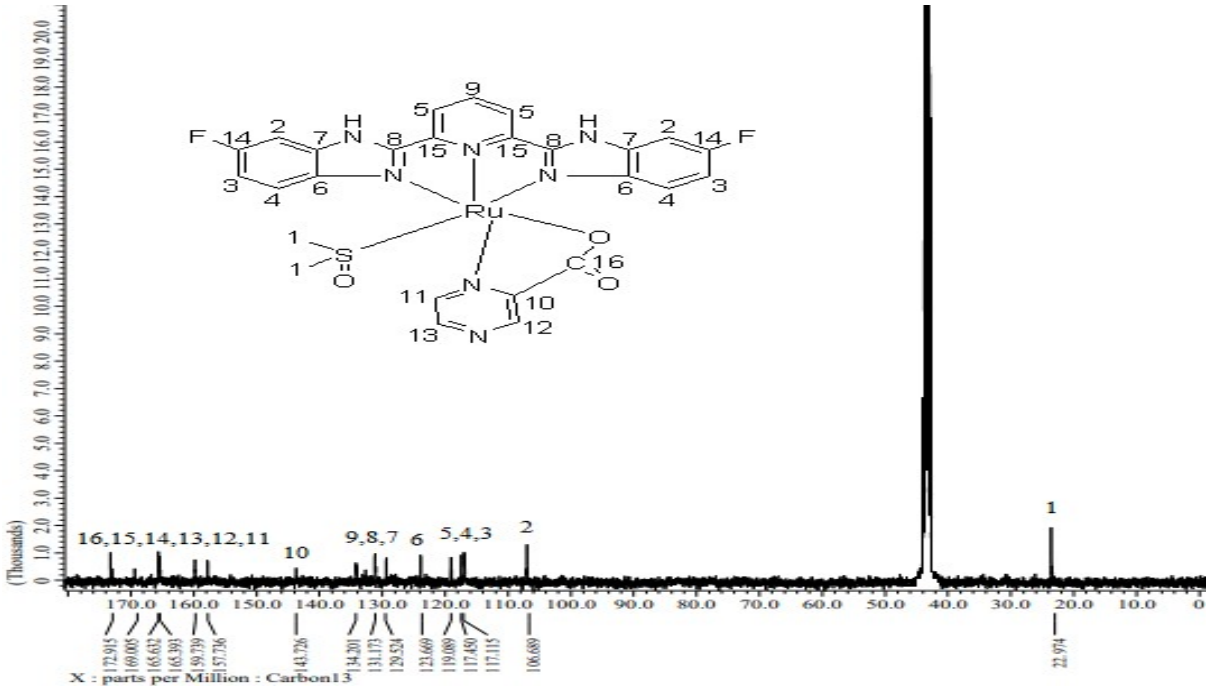


Figure S18: ^{13}C-NMR of complex **3**.

Table S1: Significant bond distances and bond angles of **1, 2,** and **3**.

Complex **1**

Atom	Atom	Length/Å
Ru1	S1	2.2204(8)
Ru1	O1	2.102(2)
Ru1	N4	2.073(2)
Ru1	N2	2.005(2)
Ru1	N3	2.081(2)
Ru1	N1	2.087(2)

Atom	Atom	Atom	Angle/°
O1	Ru1	S1	175.92(6)
N4	Ru1	S1	96.71(7)
N4	Ru1	O1	79.29(9)
N4	Ru1	N3	100.06(9)
N4	Ru1	N1	101.83(10)
N2	Ru1	S1	95.47(7)
N2	Ru1	O1	88.54(9)
N2	Ru1	N4	167.82(10)
N2	Ru1	N3	78.57(10)
N2	Ru1	N1	78.30(10)
N3	Ru1	S1	94.90(7)
N3	Ru1	O1	86.62(9)
N3	Ru1	N1	156.63(10)
N1	Ru1	S1	90.60(7)
N1	Ru1	O1	89.47(9)

Complex **2**

Atom	Atom	Length/Å
Ru1	S1	2.2706(8)
Ru1	O1	2.121(2)
Ru1	N2	1.995(2)
Ru1	N1	2.107(3)
Ru1	N3	2.085(3)
Ru1	N4	2.088(3)

Atom	Atom	Atom	Angle/°
O1	Ru1	S1	93.53(6)
N2	Ru1	S1	94.61(7)
N2	Ru1	O1	171.83(9)
N2	Ru1	N1	78.36(10)
N2	Ru1	N3	78.51(10)
N2	Ru1	N4	93.51(10)
N1	Ru1	S1	93.78(8)
N1	Ru1	O1	101.84(9)
N3	Ru1	S1	89.11(7)
N3	Ru1	O1	100.90(10)
N3	Ru1	N1	156.85(10)
N3	Ru1	N4	91.28(10)
N4	Ru1	S1	171.79(7)
N4	Ru1	O1	78.34(9)
N4	Ru1	N1	89.09(10)

Complex **3**

Atom	Atom	Length/Å
Ru1	S1	2.2552(9)
Ru1	O1	2.110(2)
Ru1	N1	1.987(3)
Ru1	N2	2.086(3)
Ru1	N3	2.101(3)
Ru1	N4	2.074(3)

Atom	Atom	Atom	Angle/°
O1	Ru1	S1	93.75(7)
N1	Ru1	S1	94.60(8)
N1	Ru1	O1	171.64(10)
N1	Ru1	N2	78.58(11)
N1	Ru1	N3	78.46(11)
N1	Ru1	N4	93.59(11)
N2	Ru1	S1	88.78(8)

	N2	Ru1	O1	101.48(11)
	N2	Ru1	N3	157.03(11)
	N3	Ru1	S1	93.61(8)
	N3	Ru1	O1	101.16(10)

Table S2: Crystal data and structure refinement for Complex **1**.

Identification code	SN SK RuLl1
Empirical formula	$C_{28}H_{32}ClN_7O_{12}RuS_2$
Formula weight	859.24
Temperature/K	298.15
Crystal system	triclinic
Space group	P-1
a/Å	10.7530(2)
b/Å	12.5652(4)
c/Å	14.8182(5)
α/°	74.414(3)
β/°	72.884(2)
γ/°	74.855(2)
Volume/Å^3	1806.65(10)
Z	2
ρ_{calc}g/cm^3	1.580
μ/mm^{-1}	0.692
F(000)	876.0
Crystal size/mm^3	0.2 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.86 to 49.99
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 14, -17 ≤ l ≤ 17
Reflections collected	26541
Independent reflections	6316 [R_{int} = 0.0263, R_{sigma} = 0.0188]
Data/restraints/parameters	6316/2/506
Goodness-of-fit on F^2	1.068
Final R indexes [I>=2σ (I)]	R_1 = 0.0366, wR_2 = 0.1053
Final R indexes [all data]	R_1 = 0.0393, wR_2 = 0.1089
Largest diff. peak/hole / e Å^{-3}	0.75/-0.91

Table S3: Crystal data and structure refinement for Complex **2.**

Identification code	Ru_4_4DMeI
Empirical formula	$C_{32}H_{34}F_6N_7O_4PRuS_2$
Formula weight	890.82
Temperature/K	298.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.0563(8)
b/Å	20.5315(13)

c/Å	15.021(2)
α/°	90
β/°	91.989(8)
γ/°	90
Volume/Å^3	3407.8(6)
Z	4
ρ_{calc}g/cm^3	1.736
μ/mm^{-1}	0.714
F(000)	1808.0
Crystal size/mm^3	0.2 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.724 to 49.992
Index ranges	-13 ≤ h ≤ 11, -20 ≤ k ≤ 24, -16 ≤ l ≤ 17
Reflections collected	15683
Independent reflections	5952 [R_{int} = 0.0293, R_{sigma} = 0.0343]
Data/restraints/parameters	5952/28/530
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0369, wR_2 = 0.0891
Final R indexes [all data]	R_1 = 0.0458, wR_2 = 0.0950
Largest diff. peak/hole / e Å^{-3}	0.58/-0.48

Table S4: Crystal data and structure refinement for Complex **3.**

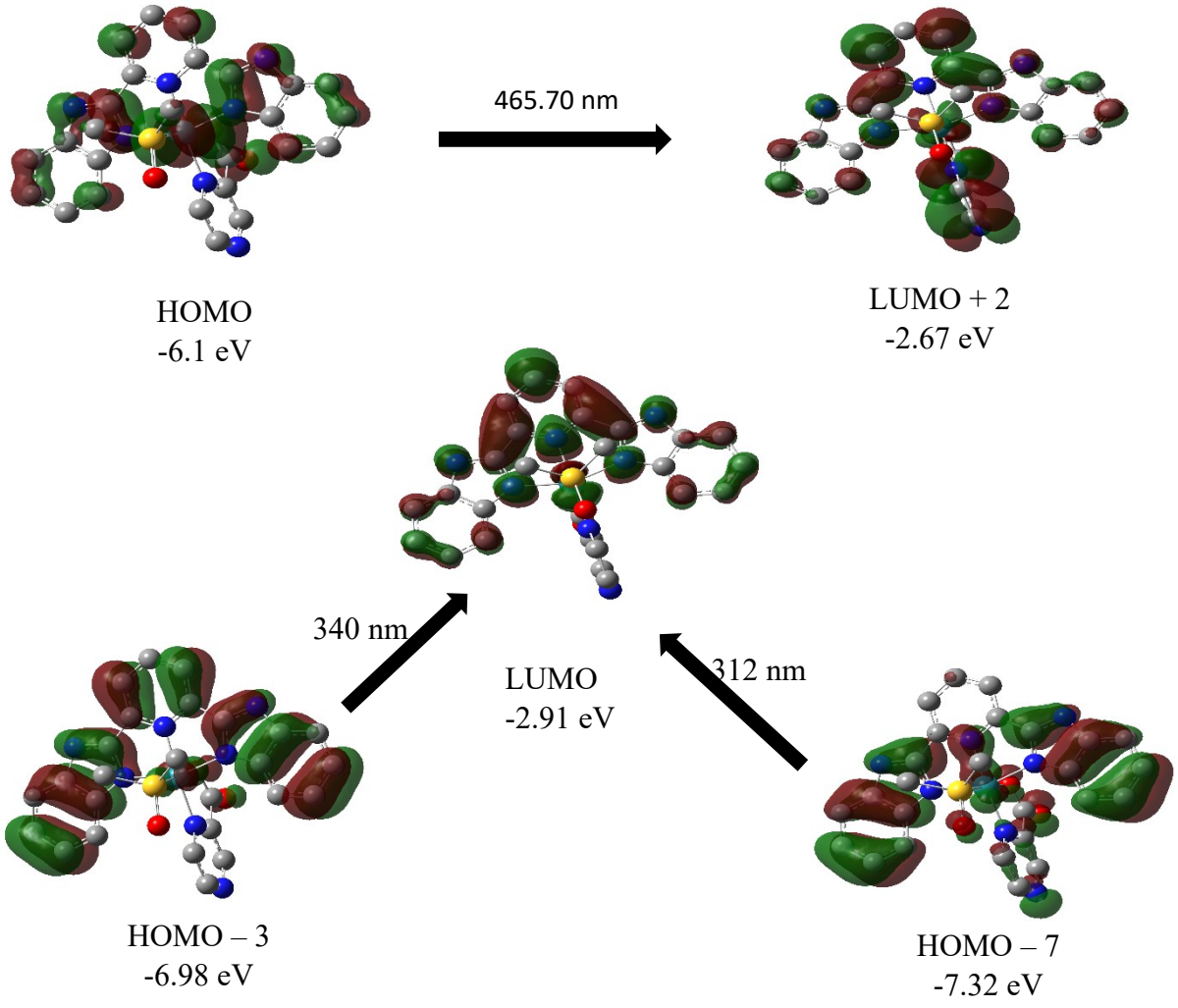
Identification code	Ru 4F
Empirical formula	$C_{28}H_{26}F_{6.5}N_7O_4PRuS_2$
Formula weight	844.22
Temperature/K	298.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.0467(3)
b/Å	20.0220(7)
c/Å	14.8502(4)
α/°	90
β/°	92.084(3)
γ/°	90
Volume/Å^3	3282.35(17)
Z	4
ρ_{calc}g/cm^3	1.708
μ/mm^{-1}	0.738
F(000)	1698.0
Crystal size/mm^3	0.2 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.694 to 50
Index ranges	-11 ≤ h ≤ 13, -16 ≤ k ≤ 23, -17 ≤ l ≤ 17
Reflections collected	15099
Independent reflections	5753 [R_{int} = 0.0188, R_{sigma} = 0.0229]

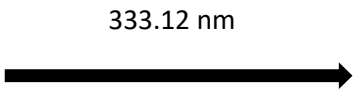
Data/restraints/parameters	5753/2/491
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	$R_1 = 0.0394$, $wR_2 = 0.0979$
Final R indexes [all data]	$R_1 = 0.0453$, $wR_2 = 0.1035$
Largest diff. peak/hole / e $Å^{-3}$	1.18/-1.60

Table S5: Vertical excitations with band position, oscillator strength, and orbital contribution.

λ_{ex} (nm)	λ_{theo} (nm)	f	Contributing orbital	Percentage (%)
Complex - **1**				
467	465.70	0.097	H – 2 → L H → L + 2	24 57
340	452.53	0.441	H – 3 → L H – 1 → L + 4	89 3
334	333.27	0.002	H – 9 → L + 1 H – 9 → L + 2	39 21
313	312	0.121	H – 7 → L H – 6 → L + 2 H – 3 → L + 2	32 31 21
Complex - **2**				
402	404.62	0.0274	H – 3 → L H – 2 → L + 1 H – 2 → L + 2	5 6 84
346	349.13	0.0176	H – 4 → L	80
332	330.36	0.1292	H – 7 → L H – 5 → L H – 4 → L H – 3 → L + 2	58 10 7 17
312	314	0.1033	H – 6 → L + 1 H – 6 → L + 2 H – 5 → L	2 88 3
Complex - **3**				

410	411.35	0.0380	H – 2 → L + 1	62
347	351.30	0.3863	H – 3 → L H – 1 → L + 4	93 2
333	332.43	0.0020	H – 7 → L + 2 H – 9 → L + 2 H – 7 → L + 1 H – 9 → L + 1	38 11 7 5
316	315.47	0.0265	H – 6 → L H – 5 → L + 1 H – 8 → L	40 7 2

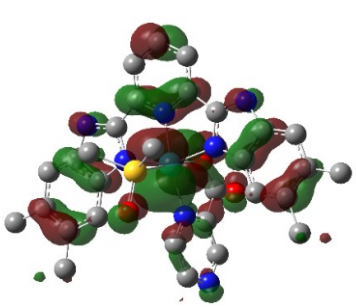




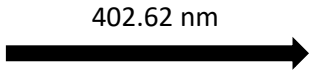
HOMO - 9
-7.56 eV

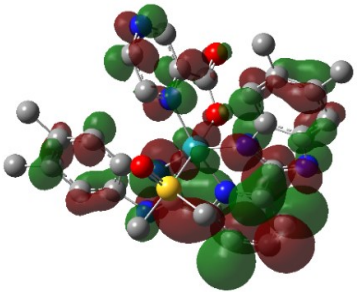
LUMO + 1
-2.75 eV

Figure S19: The major electronic transition of complex **1.**

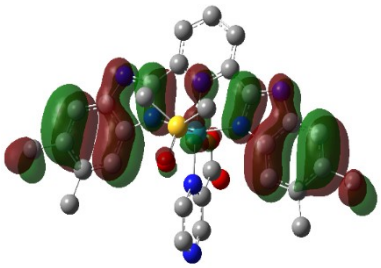


HOMO – 2
-6.43 eV

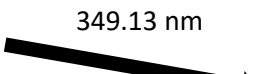


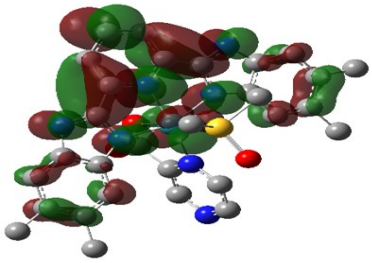


LUMO + 2
-2.59 eV

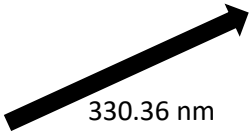


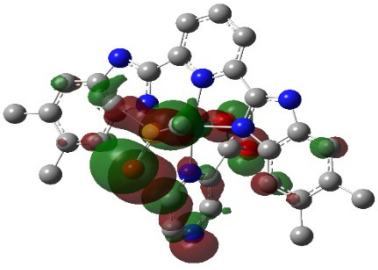
HOMO – 4
-6.84 eV



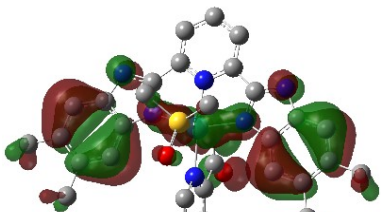


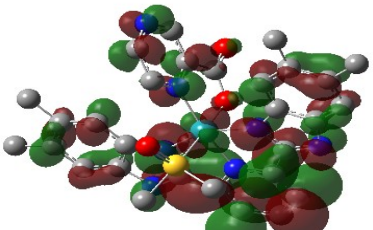
LUMO
-2.82 eV





HOMO – 7
-7.16 eV





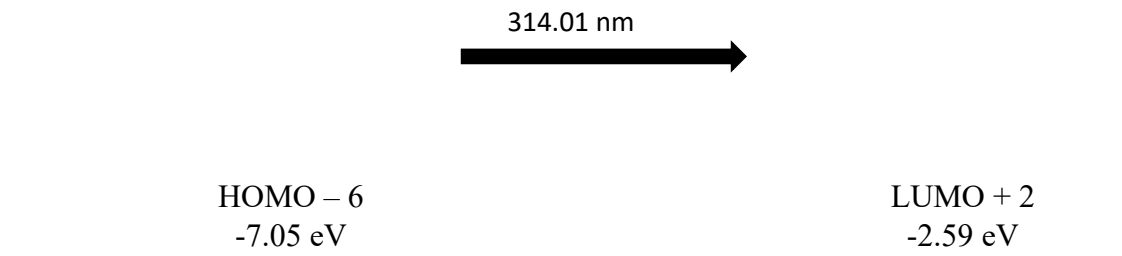
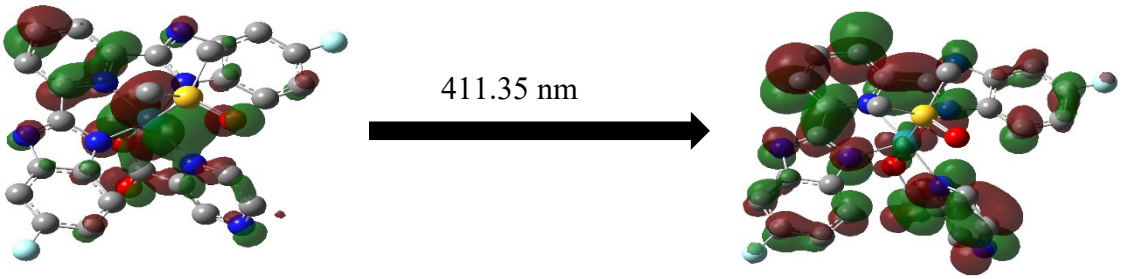
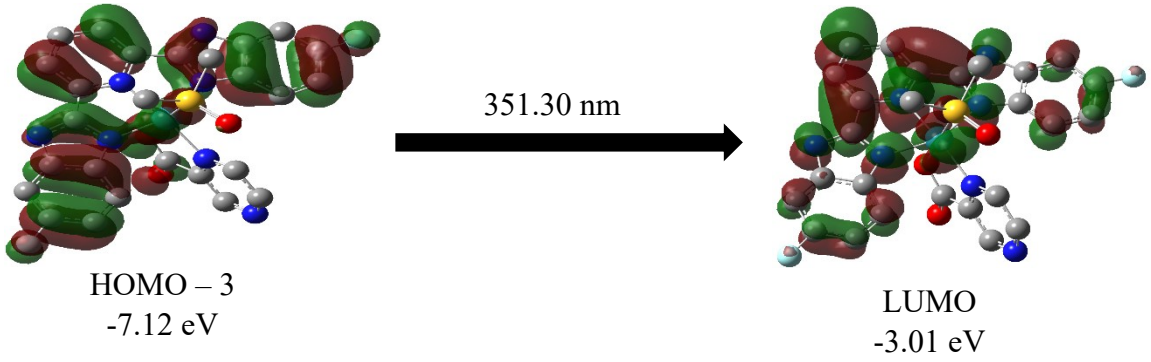
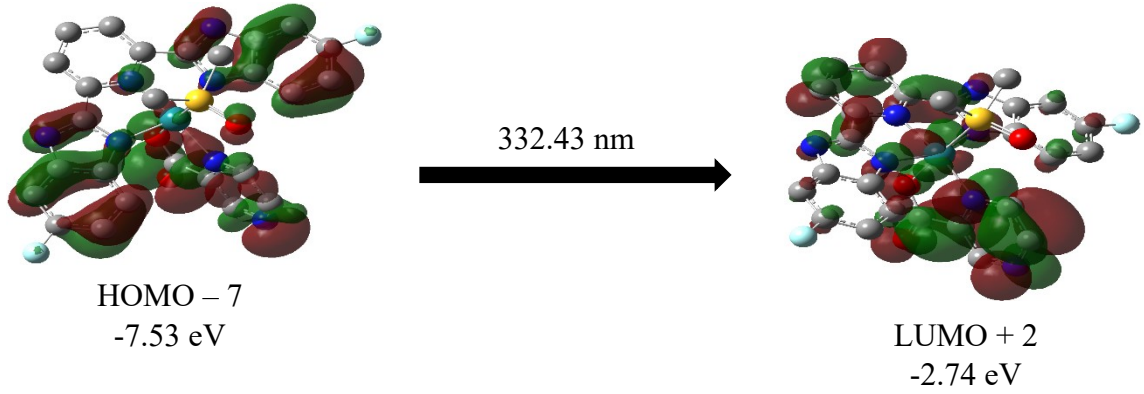
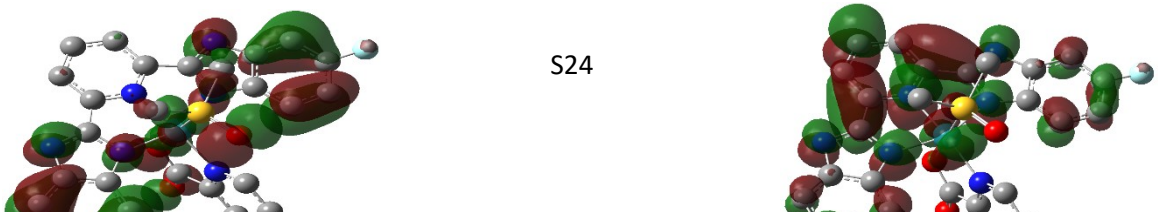


Figure S20: The major electronic transition of complex **2**.









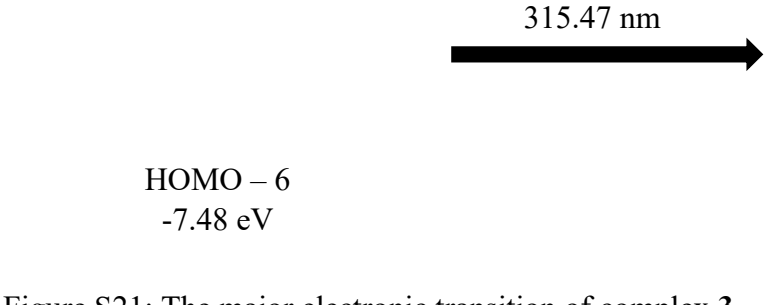


Figure S21: The major electronic transition of complex **3.**

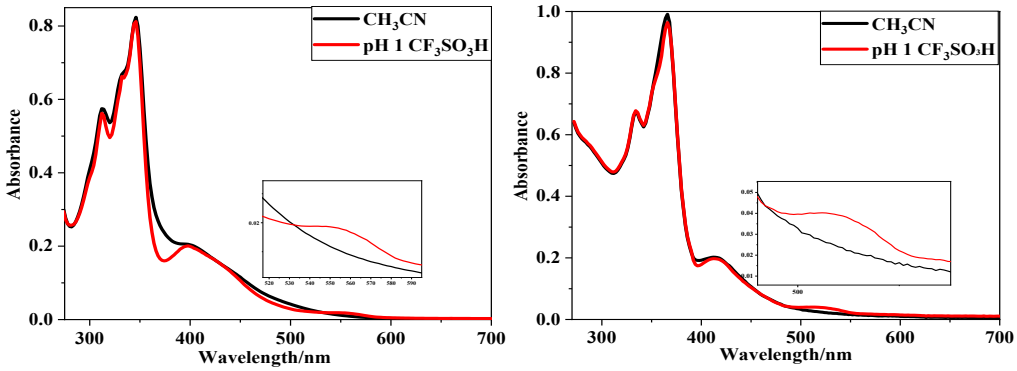


Figure S22: UV/Vis spectrum of Complex **2** (left) and **3** (right) with concentration 50 µM in CH_3CN and pH 1 CF_3SO_3H.

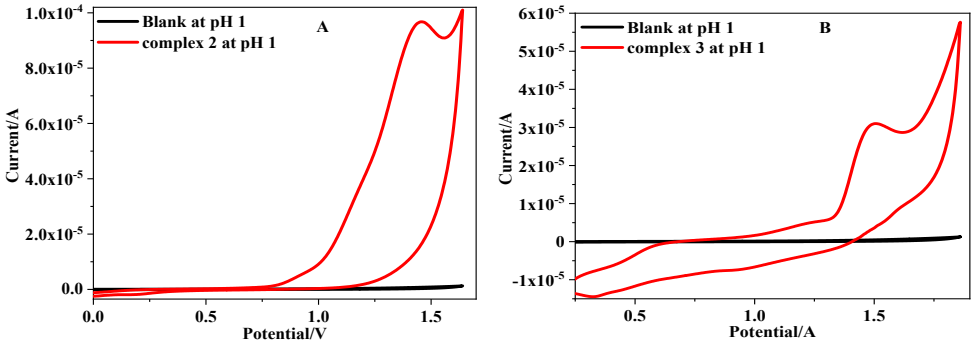


Figure S23: The black line and red line are the CVs of without-complex and with-complex **2** (A) and complex **3** (B) (20µM) at pH-1 (1:9,v:v, CH_3CN:CF_3SO_3H).

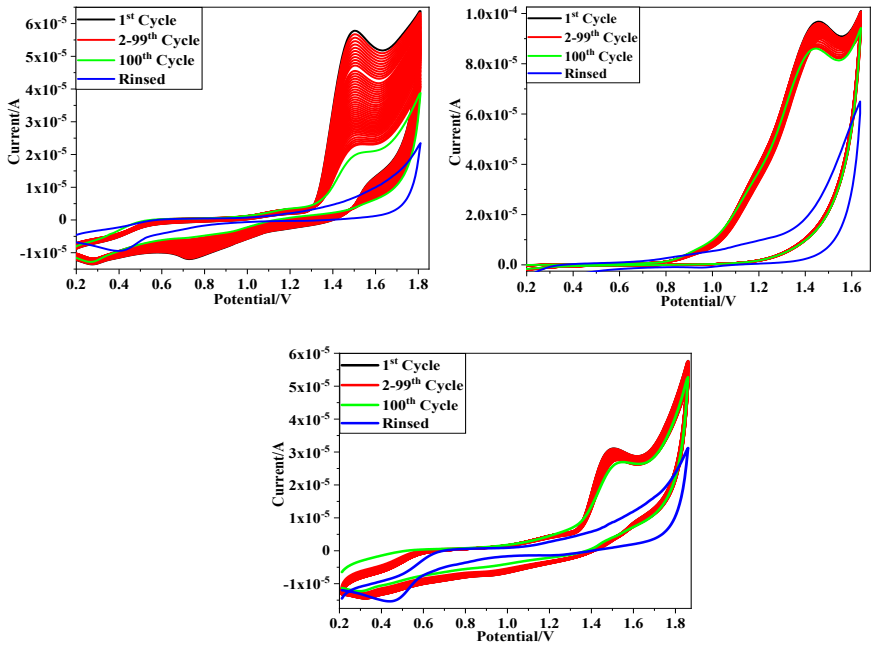


Figure S24: A consecutive CV scan and rinse test experiment of complex **1** (top left), **2** (top right), and **3** (bottom) (20 µM) in SF_3SO_3H solution at pH 1 (Pt disk working electrode, Pt wire counter electrode and Ag/AgCl in saturated KCl were used as reference electrode, 50 mV/s scan rate).

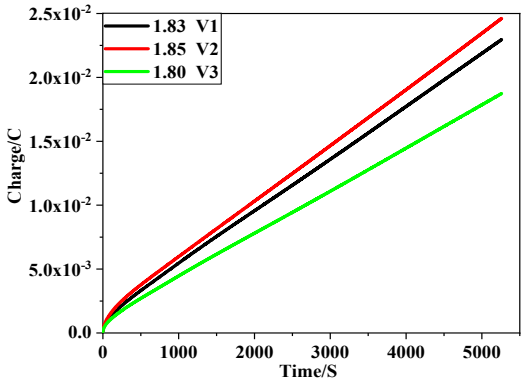


Figure S25: controlled-potential coulometry plot of complex **1**(black line), **2**(red line), and **3** (green line) 1 mM in CF_3SO_3H:CH_3CN(1:1, v:v) at pH 1.

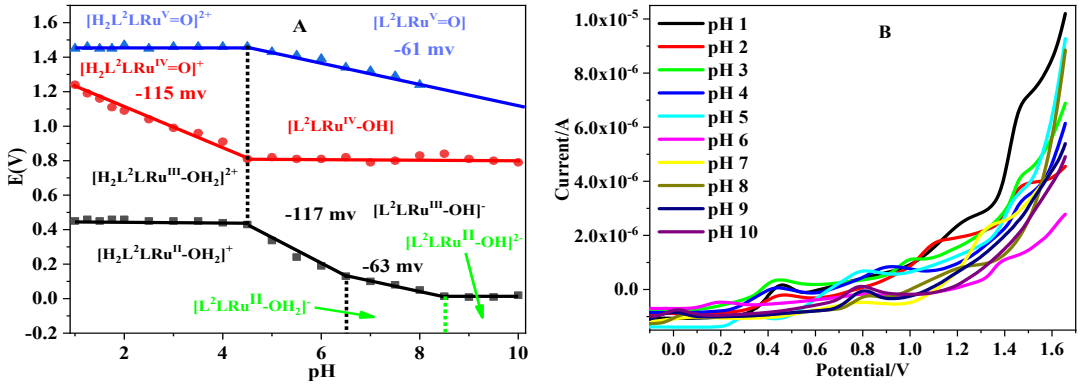


Figure S26: (A) Pourbaix diagram (E vs pH) of complex **2** at 30µM in phosphate buffer solution. (B) the LSV plot at pH 1-10.

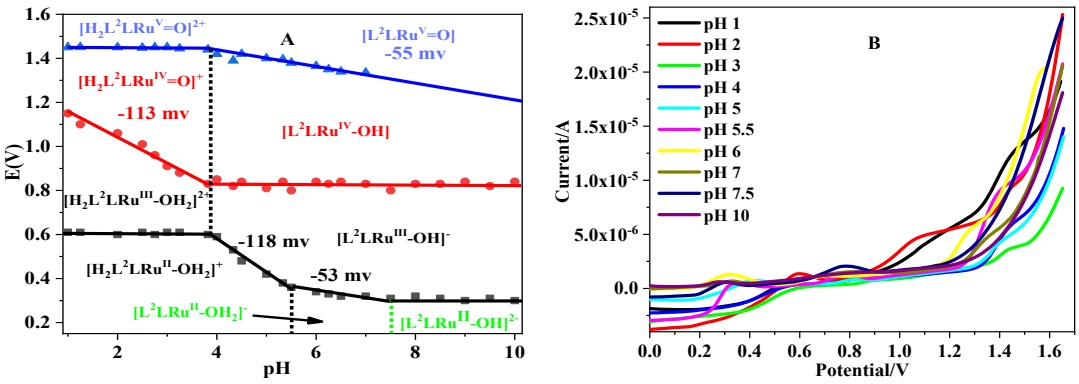


Figure S27: (A) Pourbaix diagram (E vs pH) of complex **3** at 30µM in phosphate buffer solution. (B) the LSV plot of at pH 1-10.

Table S6: Key equations obtained for the WNA and I2M mechanisms including TOF–η relationships and TOF_{MAX} formulas.

WNA	I2M
$\frac{i}{i_P} = \frac{4 \times 2.24 \sqrt{\frac{RT}{Fv} K_{WNA}}}{1 + e^{\frac{F(E^\circ - E)}{RT}}}$ S1	$\frac{i}{i_P} = \frac{4 \times 2.24 \sqrt{\frac{RT}{3Fv} K_D C_{cat}^\circ}}{[1 + e^{\frac{F(E^\circ - E)}{RT}}]^{3/2}}$ S2
$TOF = \frac{4 \times 2.24 \sqrt{\frac{RT}{Fv} K_{WNA}}}{1 + e^{\frac{F(E^\circ - E_{H_2O/O_2} - \eta)}{RT}}}$ S3	$TOF = \frac{4 \times 2.24 \sqrt{\frac{RT}{3Fv} K_D C_{cat}^\circ}}{[1 + e^{\frac{F\left(E^\circ - E_{H_2O/O_2} - \eta\right)}{RT}}]^{3/2}}$ S4
$TOF_{MAX} = K_{WNA}$ S5	$TOF_{MAX} = \frac{1}{3} K_D C_{cat}^\circ$ S6

where R is the gas constant, T is temperature, F is the Faraday constant, v is the scan rate, and $E°$ is the apparent standard potential for the redox couple which onsets water oxidation $E(Ru^{V/IV})$. η is overpotential, and $E_{H2O/O2}$ is the standard potential of water oxidation at the working pH. i is the current intensity from the CV and i_p is the peak current intensity of the one-electron redox process of the catalyst.

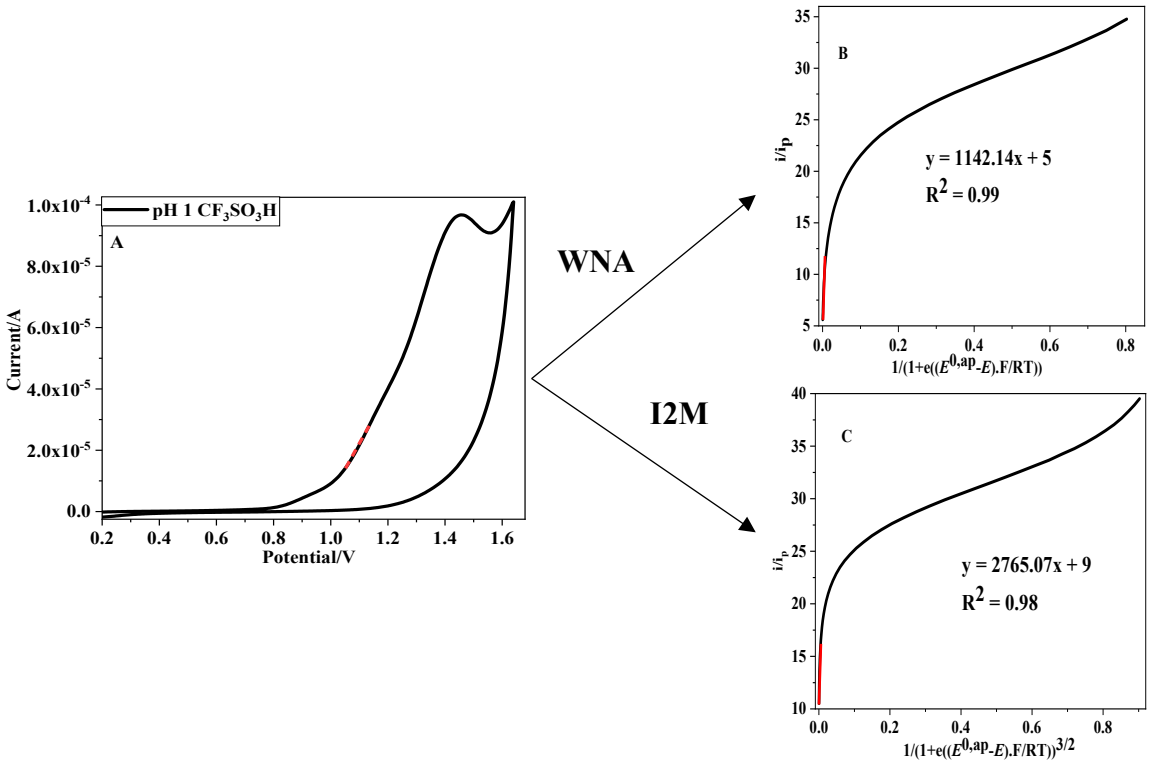
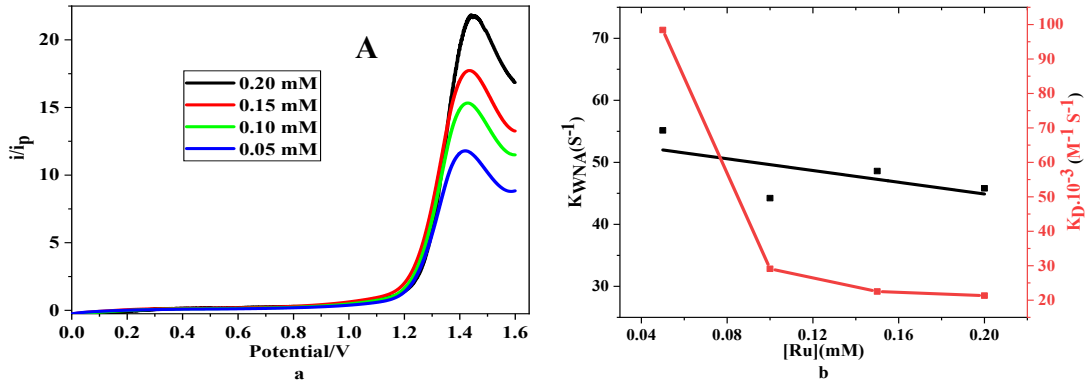


Figure S28: (A) black solid line shows a CV of complex **2** (20 µM) at pH 1. The black dashed line indicates the data points used for the FOWA. (B) i/i_p vs. $1/\{1+e\,[(E^{0,ap} - E)(F/RT)]\}$ plot assuming a WNA (equation S1). (C) i/i_p vs. $1/\{1+e[(E^{0,ap} - E)(F/RT)]\}^{3/2}$ plot assuming a I2M (equation S 2). The two graphs represent the fitting points for the extraction of rate constants at the foot of the wave as a red solid line.



B

Figure S29: (A) i_p normalized LSV plot of complex **2** at different Ru concentrations at pH 1 and (B) Plot of calculated K_D and K_{WNA} vs. [**2**].

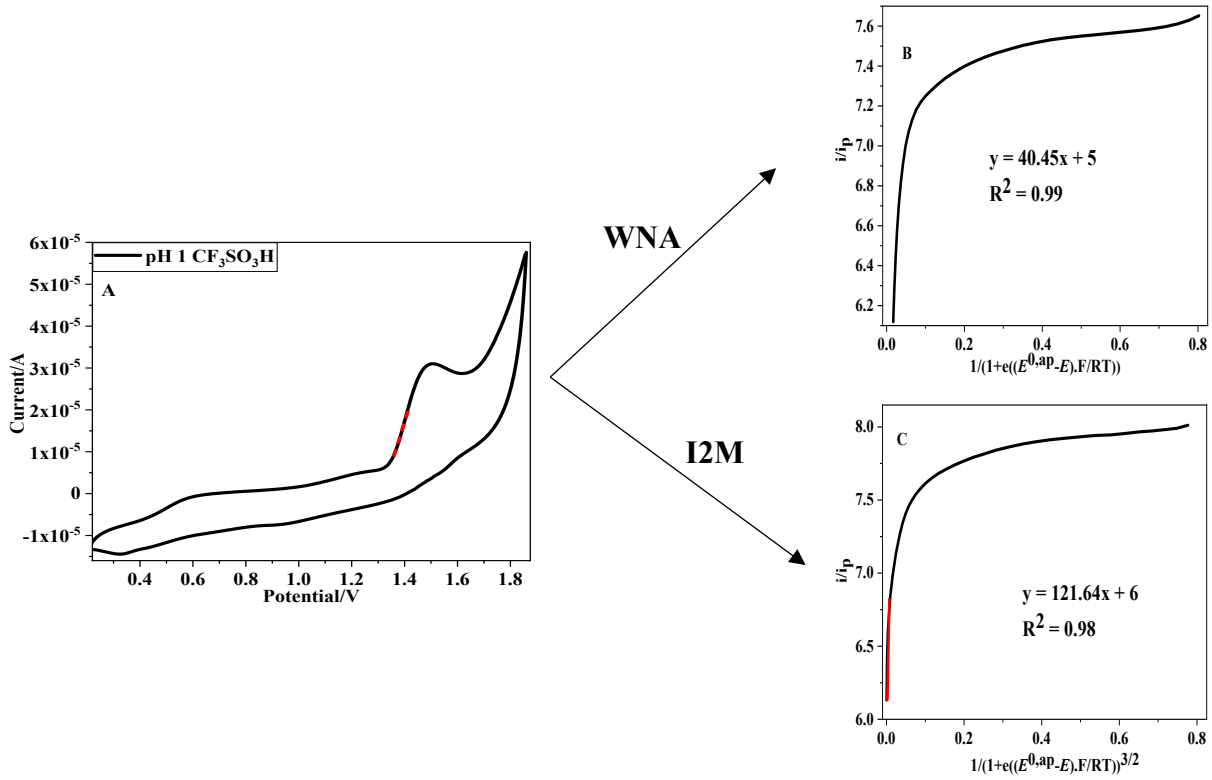


Figure S30: (A) black solid line shows a CV of complex **3** (20 µM) at pH 1. The black dashed line indicates the data points used for the FOWA. (B) i/i_p vs. $1/\{1+e\,[(E^{0,ap} - E)(F/RT)]\}$ Plot assuming a WNA (equation S1). (C) i/i_p vs. $1/\{1+e[(E^{0,ap} - E)(F/RT)]\}^{3/2}$ plot assuming a I2M (equation S2). The two graphs represent the fitting points for the extraction of rate constants at the foot of the wave as a red solid line.

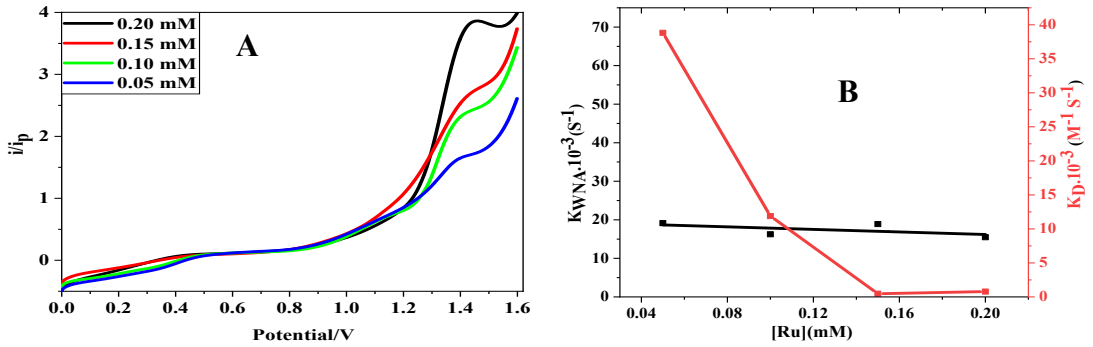


Figure S31: (A) i_p normalized LSV plot of complex **3** at different Ru concentrations at pH 1 and (B) Plot of calculated K_D and K_{WNA} vs. [**3**].

The calculation of K_{cat} values[S15]:

For all complexes the peak currents (i_p) of the redox couple Ru^{III}/Ru^{II} show constant redox currents[S16] (Figure S33A,S34A,S35A) and a linear relationship with the square root of scan rates, $\nu^{1/2}$ (Figure S33B,S34B,S35B) confirmed. Therefore, these redox currents of Ru^{III}/Ru^{II} can be used to calculate the diffusion coefficient.[S17,18] A diffusion coefficient of 1.085 x 10^{-6} cm^2s^{-1}, 3.341 x 10^{-6} cm^2s^{-1}, and 1.975 x 10^{-5} cm^2s^{-1} were measured for **1**, **2,** and **3** respectively from the dependence of the i_p on $\nu^{1/2}$ by using the Randles-Sevcik relation in Equation S7[S19] given below:

$$i_p = 0.446nFA[Ru]\left(\frac{\upsilon nFD_{Ru}}{RT}\right)^{1/2} \qquad \text{(S7)}$$

whereas n (=1e^-) is the number of electron transferred in the corresponding process, F is the Faraday constant (96500 C), A is the surface area of the working electrode (0.07 cm^2), [Ru] is the concentration of complexes, R is the universal gas constant (8.314 J/mol.K), T is the absolute temperature (298 k) and υ is the scan rate (50 mV/s).

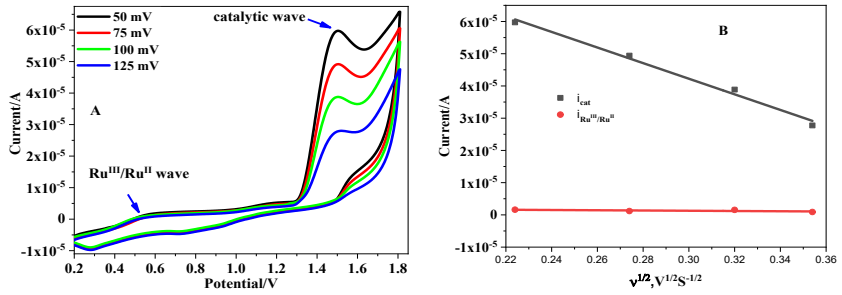
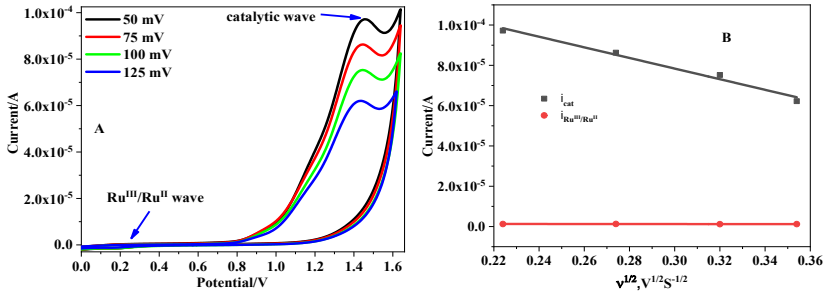
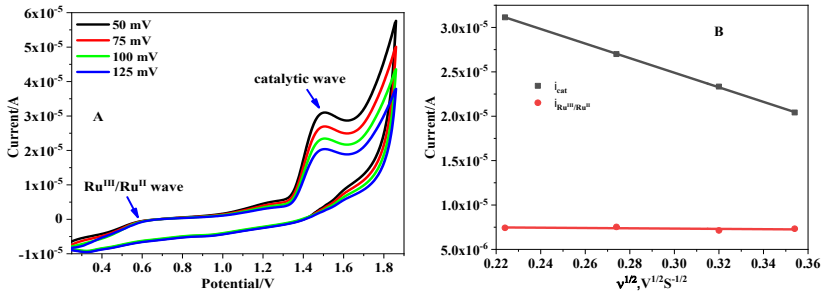


Figure S32: (A) CV of the complex **1** at pH 1 (1:9,v:v, $CH_3CN:CF_3SO_3H$) with the scan rate 50-125 mV and (B) the plot of i_{cat} and $i_{Ru}{}^{III}/Ru^{II}$ vs the square root of the scan rate.



FigS33: (A) CV of the complex **2** at pH 1 (1:9,v:v, $CH_3CN:CF_3SO_3H$) with the scan rate 50-125 mV and (B) the plot of i_{cat} and $i_{Ru}{}^{III}/Ru^{II}$ vs the square root of the scan rate.



FigS34: (A) CV of the complex **2** at pH 1 (1:9,v:v, $CH_3CN:CF_3SO_3H$) with the scan rate 50-125 mV and (B) the plot of i_{cat} and $i_{Ru^{III}/Ru^{II}}$ vs the square root of the scan rate.

The dependence of the catalytic current (i_{cat}) on complex concentration could be illustrated by Equation S8[S19] where n_{cat} is the number of electrons involved in WOR (= 4) and k_{cat} is the rate constant for water oxidation. Therefore, the catalytic process follows equation S8 given below:

$$i_{cat} = n_{cat}FA[Ru](k_{cat}D_{Ru})^{1/2} \qquad \text{(S8)}$$

k_{cat} can be calculated by comparing the catalytic current to the diffusive current for a reversible process (Eq. S7). Taking the ratio of equations S8 and S7, substituting in the appropriate constants, and setting n_{cat} = 4, results in equation S9, which gives a simple relationship between $\frac{i_{cat}}{i_p}$ and the TOF. The k_{cat} could be measured by the linear slope of $\frac{i_{cat}}{i_p}$ and $v^{-1/2}$ (Figure S36)

$$\frac{i_{cat}}{i_p} = 1.554 k_{cat}^{1/2} v^{-1/2} \qquad \text{(S9)}$$

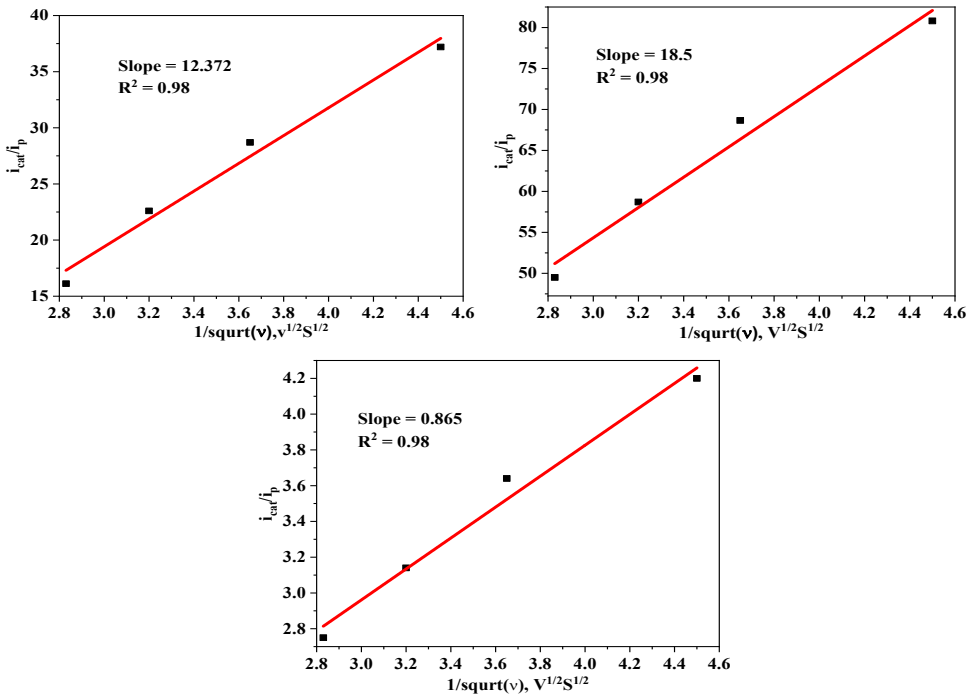


Figure S35: The plot of i_{cat} /i_p as a function of the inverse of the square root of the scan rate experiment of complex **1** (top left), **2** (top right), and **3** (bottom).

From the above equations, the slope value (Figure S36) was calculated to be 12.372, 18.49565, and 0.86503 with the R^2 being 0.98, and k_{cat} was calculated to be 63.384 s^{-1}, 141.66 s^{-1}, and 0.31 s^{-1} for **1**, **2** and **3** respectively.

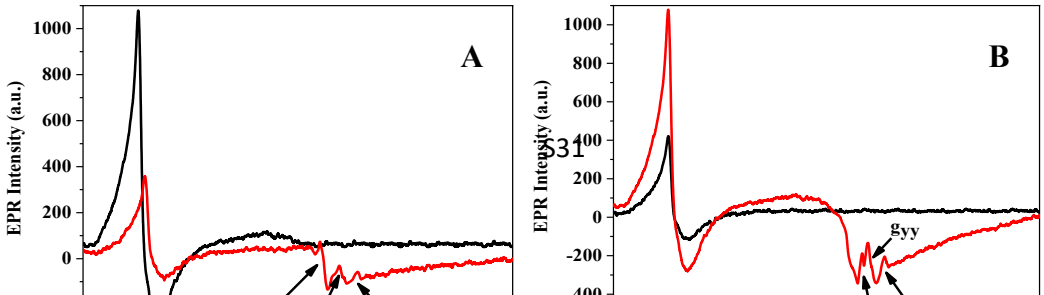


Figure S36: (A) and (B) are the X-band EPR spectrum of Ru(II) of complex **2** and **3** before electrolysis (black line) and after bulk electrolysis (red line) of Ru^{V}=O species at pH 1, 0.10 M CF_3SO_3H solution of triflic acid with 1:9, v:v CH_3CN: CF_3SO_3H measured at 298 K.

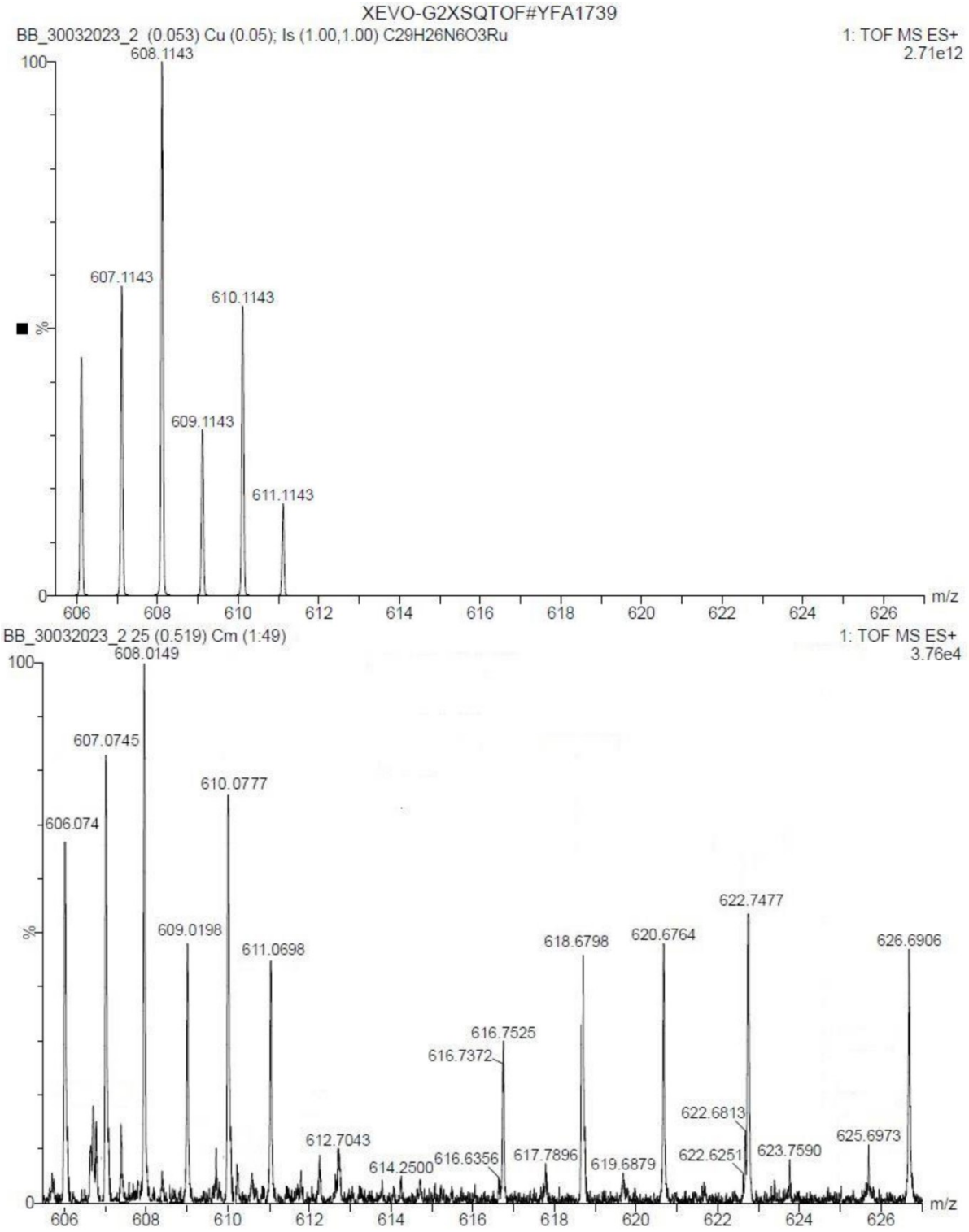


Figure S37: High resolution mass spectrum of the corresponding RuV=O of complex **2** bulk electrolysis, simulation (Top) and experimental (bottom).

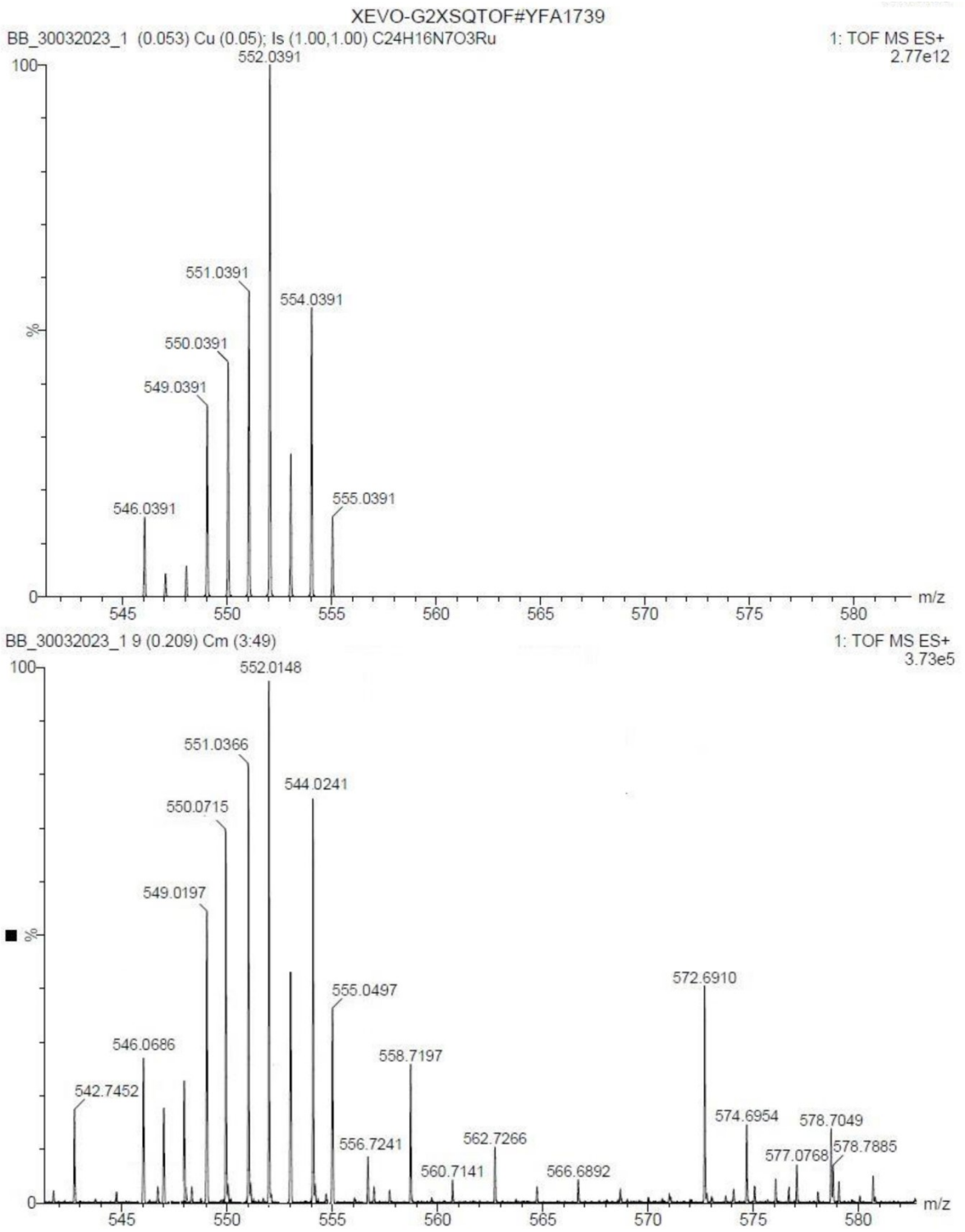


Figure S38: High-resolution mass spectrum of the corresponding RuV=O of complex **3** bulk electrolysis, simulation (Top) and experimental (bottom).

I2M path

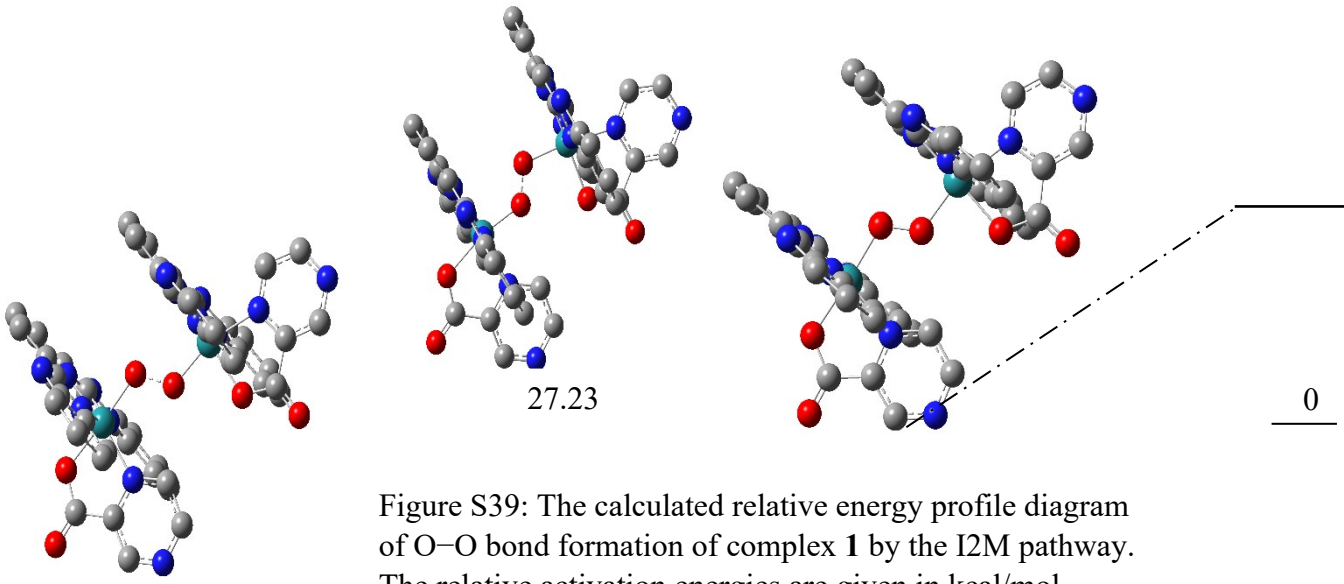
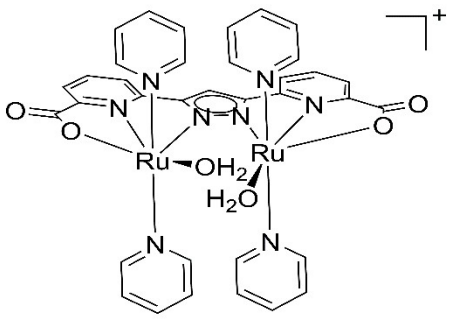


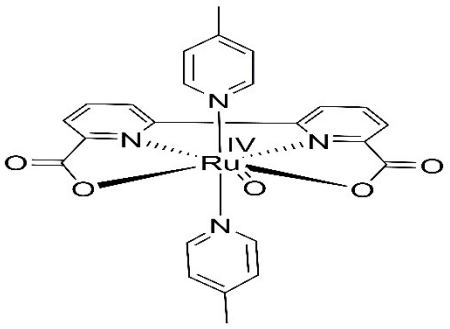
Figure S39: The calculated relative energy profile diagram of O−O bond formation of complex **1** by the I2M pathway. The relative activation energies are given in kcal/mol.

According to the harmonic frequencies analysis of the transition state, the single negative Eigenvalue is ca. 14.51 cm^{-1}.

Table S7: Energy values of reactant(R), transition state(TS), and product(P) for **I2M**		
	E [water] (hartree)	$\Delta E^{\ddagger}$ [water] (kcal/mol)
Complex **1**		
R	-3253.12492	0
TS	-3253.081509	27.22954975
P	-3253.081916	26.974259
Complex **2**		
R	-3567.600571	0
TS	-3567.586393	8.8931505
P	-3567.586415	8.879351
Complex **3**		
R	-3650.075275	0
TS	-3649.997162	34.867573
P	-3650.021224	33.90348975



4



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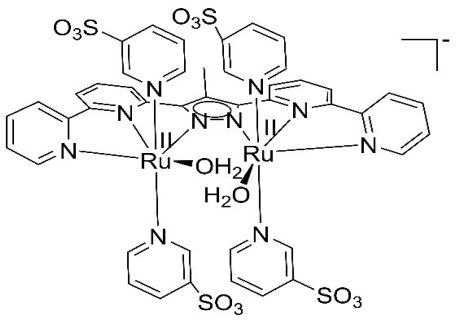

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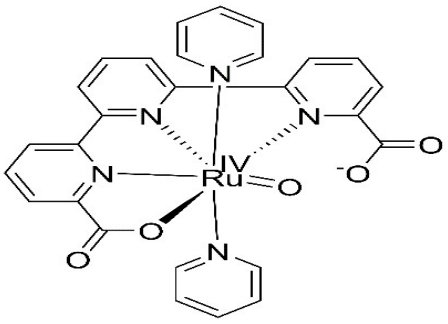

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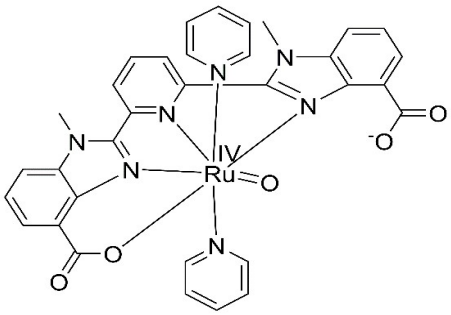

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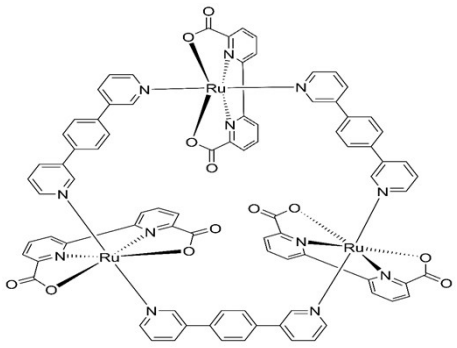

9

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Cartesian coordinates of computed structures
for complex 1 of Fig. Ru (II)-DMSO
E(UB3LYP) =-1716.6583 Hartree
ZPE (kcal mol^{-1}) = 286.04795375

C	**-0.0514**	**0.75385**	**-0.79818**
C	**1.07577**	**1.08478**	**-0.02599**
C	**0.28127**	**3.31492**	**0.2695**
C	**-0.8651**	**3.04075**	**-0.49632**
C	**-1.01605**	**1.75091**	**-1.04107**
H	**-0.18716**	**-0.24681**	**-1.19265**
H	**-1.62381**	**3.79806**	**-0.65902**
H	**-1.89166**	**1.51773**	**-1.63707**
C	**2.16904**	**0.21715**	**0.40522**
C	**3.56826**	**-1.49311**	**0.78485**
C	**4.25285**	**-2.7197**	**0.84007**
C	**4.03228**	**-0.33046**	**1.47316**
C	**5.42535**	**-2.7508**	**1.60931**
H	**3.89416**	**-3.5985**	**0.31418**
C	**5.21394**	**-0.37536**	**2.24011**
C	**5.89893**	**-1.59607**	**2.29763**
H	**5.98886**	**-3.67657**	**1.68277**
H	**5.57961**	**0.5018**	**2.76214**
H	**6.81335**	**-1.66789**	**2.87941**
N	**3.13777**	**0.71824**	**1.21604**
N	**2.39628**	**-1.10703**	**0.12621**
C	**0.6243**	**4.54304**	**0.98125**
C	**0.67796**	**6.60478**	**1.86061**
C	**1.81702**	**5.86395**	**2.30226**
C	**0.45137**	**7.93532**	**2.25451**
C	**2.76893**	**6.45391**	**3.15781**
C	**1.40523**	**8.50888**	**3.10809**
H	**-0.41604**	**8.49227**	**1.9156**
C	**2.54668**	**7.77955**	**3.55191**
H	**3.63947**	**5.90304**	**3.4955**
H	**1.27354**	**9.53491**	**3.43972**
H	**3.2594**	**8.267**	**4.21087**
N	**1.75316**	**4.58242**	**1.73676**
N	**-0.04545**	**5.73954**	**1.03283**
N	**1.23593**	**2.35383**	**0.45689**
Ru	**2.7751**	**2.73428**	**1.73244**
C	**5.33067**	**3.47281**	**3.39534**
C	**3.50275**	**2.56922**	**4.5514**

C	**6.03422**	**3.53537**	**4.61147**
H	**5.7497**	**3.82114**	**2.45289**
C	**4.22961**	**2.64585**	**5.74825**
N	**5.50045**	**3.12375**	**5.7918**
H	**7.04623**	**3.92464**	**4.63441**
H	**3.77611**	**2.31721**	**6.67614**
N	**4.06007**	**2.97894**	**3.36409**
C	**2.089**	**2.05367**	**4.49061**
O	**1.55587**	**2.06959**	**3.27425**
O	**1.49417**	**1.65629**	**5.53129**
H	**1.82221**	**-1.70392**	**-0.45694**
H	**-0.90902**	**5.96267**	**0.55263**
O	**5.68486**	**4.38352**	**0.52207**
C	**3.53082**	**4.7286**	**-1.27105**
H	**4.32182**	**5.01511**	**-1.96551**
H	**3.17728**	**5.58556**	**-0.69856**
H	**2.71308**	**4.21341**	**-1.77652**
C	**5.02426**	**2.22662**	**-1.16656**
H	**5.55732**	**1.52572**	**-0.52474**
H	**5.70447**	**2.74305**	**-1.84559**
H	**4.20688**	**1.74052**	**-1.69964**
S	**4.31414**	**3.54931**	**-0.02068**

Cartesian coordinates of computed
Structure for complex 2 of Fig. Ru (II)-DMSO
E(UB3LYP) = -1873.9052 Hartree
ZPE (kcal mol^{-1}) = 355.95496625

C	**0.11618**	**0.88116**	**-0.87615**
C	**1.26943**	**1.19688**	**-0.13591**
C	**0.47549**	**3.41567**	**0.24835**
C	**-0.69769**	**3.15468**	**-0.48148**
C	**-0.86167**	**1.87897**	**-1.05504**
H	**-0.02675**	**-0.10796**	**-1.2965**
H	**-1.46493**	**3.91216**	**-0.59662**
H	**-1.75715**	**1.65704**	**-1.62544**
C	**2.38188**	**0.32611**	**0.23111**
C	**3.80264**	**-1.38337**	**0.52214**
C	**4.49977**	**-2.60247**	**0.53346**
C	**4.28925**	**-0.23568**	**1.21048**
C	**5.70684**	**-2.66838**	**1.2474**
H	**4.11961**	**-3.47191**	**0.00616**
C	**5.50202**	**-0.30007**	**1.92421**
C	**6.21151**	**-1.50937**	**1.94614**
H	**5.88234**	**0.57126**	**2.44656**
N	**3.38234**	**0.81445**	**1.01229**
N	**2.60295**	**-0.99231**	**-0.08181**

C	**0.84183**	**4.62701**	**0.97467**
C	**0.92171**	**6.66408**	**1.90656**
C	**2.08338**	**5.92571**	**2.27216**
C	**0.71255**	**7.9798**	**2.35112**
C	**3.06379**	**6.51139**	**3.09687**
C	**1.68834**	**8.56342**	**3.17466**
H	**-0.17683**	**8.53391**	**2.0679**
C	**2.87185**	**7.82478**	**3.54877**
H	**3.95348**	**5.95716**	**3.37622**
N	**2.00565**	**4.65872**	**1.67735**
N	**0.16509**	**5.81575**	**1.09091**
N	**1.43993**	**2.45437**	**0.37427**
Ru	**3.03738**	**2.81774**	**1.58245**
C	**5.6881**	**3.51204**	**3.10246**
C	**3.91377**	**2.63341**	**4.3573**
C	**6.4554**	**3.57098**	**4.27932**
H	**6.06584**	**3.83754**	**2.13439**
C	**4.70416**	**2.7047**	**5.51346**
N	**5.97979**	**3.17125**	**5.48859**
H	**7.4721**	**3.94721**	**4.24696**
H	**4.29774**	**2.38093**	**6.46461**
N	**4.41009**	**3.03794**	**3.14141**
C	**2.49745**	**2.12189**	**4.37012**
O	**1.90547**	**2.12991**	**3.18189**
O	**1.95513**	**1.72984**	**5.44186**
H	**2.00547**	**-1.58198**	**-0.64827**
H	**-0.72291**	**6.04282**	**0.66001**
O	**5.98829**	**4.25219**	**0.17892**
C	**3.70334**	**5.04296**	**-1.27334**
H	**4.42867**	**5.28951**	**-2.04999**
H	**3.55827**	**5.87593**	**-0.58588**
H	**2.75848**	**4.69689**	**-1.69408**
C	**4.84889**	**2.38032**	**-1.59497**
H	**5.3872**	**1.57224**	**-1.10044**
H	**5.47615**	**2.88773**	**-2.32927**
H	**3.91295**	**2.03069**	**-2.03161**
S	**4.46483**	**3.64988**	**-0.25047**
C	**7.51865**	**-1.59819**	**2.71102**
H	**7.47032**	**-2.35855**	**3.50236**
H	**7.76698**	**-0.64054**	**3.17937**
H	**8.35196**	**-1.87846**	**2.05257**
C	**6.48407**	**-3.96994**	**1.2814**
H	**5.97577**	**-4.74992**	**0.70584**
H	**6.60866**	**-4.33512**	**2.30983**
H	**7.49297**	**-3.84542**	**0.86529**
C	**3.91704**	**8.473**	**4.437**

H	**4.3255**	**9.38368**	**3.97823**
H	**4.75034**	**7.78955**	**4.62847**
H	**3.49327**	**8.76899**	**5.40624**
C	**1.49383**	**9.9825**	**3.67239**
H	**0.55482**	**10.4066**	**3.30307**
H	**2.31286**	**10.6375**	**3.34571**
H	**1.47496**	**10.02285**	**4.76992**

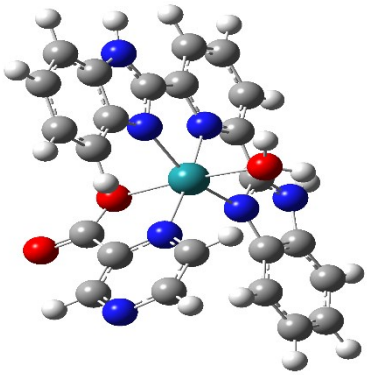
Cartesian coordinates of computed
Structure for complex 3 of Fig. Ru (II)-DMSO
E(UB3LYP) = -1915.1436 Hartree
ZPE (kcal mol^{-1}) = 275.3791

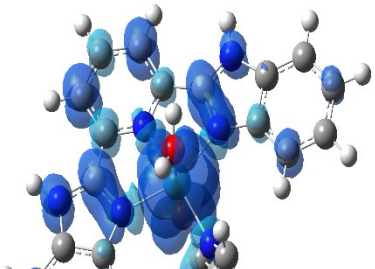
C	**-0.0171**	**0.71317**	**-0.79952**
C	**1.10613**	**1.0536**	**-0.02614**
C	**0.30916**	**3.28462**	**0.24189**
C	**-0.83302**	**3.00217**	**-0.52678**
C	**-0.98114**	**1.70665**	**-1.05851**
H	**-0.15165**	**-0.29265**	**-1.18104**
H	**-1.59214**	**3.75667**	**-0.70058**
H	**-1.85412**	**1.46629**	**-1.65529**
C	**2.19626**	**0.18952**	**0.42021**
C	**3.59467**	**-1.51436**	**0.81931**
C	**4.28099**	**-2.7394**	**0.88669**
C	**4.05211**	**-0.34487**	**1.50148**
C	**5.44915**	**-2.7732**	**1.65882**
H	**3.92863**	**-3.62286**	**0.36618**
C	**5.22876**	**-0.37405**	**2.27557**
C	**5.88127**	**-1.60086**	**2.32082**
H	**6.02998**	**-3.68417**	**1.75719**
H	**5.61059**	**0.49277**	**2.80016**
N	**3.15974**	**0.69907**	**1.23411**
N	**2.42657**	**-1.13471**	**0.15205**
C	**0.6446**	**4.51921**	**0.94673**
C	**0.67864**	**6.58131**	**1.8207**
C	**1.81995**	**5.84766**	**2.27008**
C	**0.44003**	**7.91097**	**2.21018**
C	**2.76751**	**6.44002**	**3.12797**
C	**1.37806**	**8.50168**	**3.06644**
H	**-0.42837**	**8.46197**	**1.86657**
C	**2.50074**	**7.75495**	**3.49223**
H	**3.6482**	**5.91933**	**3.48258**
H	**1.25911**	**9.52429**	**3.40853**
N	**1.76987**	**4.56686**	**1.70919**
N	**-0.03254**	**5.70985**	**0.99073**
N	**1.26406**	**2.32753**	**0.44477**
Ru	**2.79351**	**2.7193**	**1.72782**

C	5.3497	3.42875	3.40398
C	3.48096	2.61121	4.56034
C	6.03447	3.5186	4.62957
H	5.79987	3.71017	2.45295
C	4.19029	2.71245	5.76592
N	5.47012	3.16533	5.81432
H	7.056	3.88181	4.65605
H	3.71582	2.42386	6.69659
N	4.06565	2.97175	3.37041
C	2.06148	2.11181	4.49112
O	1.55324	2.08569	3.26386
O	1.44281	1.75857	5.53304
H	1.85573	-1.73774	-0.42836
H	-0.89614	5.92582	0.50707
O	5.89236	3.97497	0.47636
C	3.73196	4.95852	-1.04945
H	4.50406	5.16857	-1.7908
H	3.61901	5.7858	-0.34938
H	2.78287	4.69114	-1.5153
C	4.69869	2.22938	-1.39229
H	5.17138	1.3797	-0.90073
H	5.38012	2.71087	-2.09515
H	3.75705	1.94903	-1.86598
S	4.35141	3.4929	-0.03168
F	7.0635	-1.69195	3.07997
F	3.41264	8.40051	4.34899

Cartesian coordinates of computed Structure for complex 1 of Ru (II)-H_2O
E(UB3LYP) =-1628.0336 Hartree
ZPE (kcal mol^{-1}) = 250.445871

C	-0.05025	0.7558	-0.80057
C	1.07557	1.08577	-0.02603
C	0.28137	3.31596	0.26955
C	-0.86361	3.04285	-0.49863
C	-1.0141	1.75338	-1.04439
H	-0.18535	-0.24436	-1.19646
H	-1.62138	3.80077	-0.66269
H	-1.88859	1.52104	-1.64234
C	2.16853	0.21774	0.40533
C	3.56808	-1.49237	0.78339
C	4.25315	-2.71877	0.83702
C	4.03123	-0.3306	1.47381
C	5.42523	-2.75067	1.60689
H	3.89507	-3.59671	0.3093
C	5.21251	-0.37626	2.24129
C	5.89795	-1.59683	2.29731
H	5.98912	-3.67632	1.67908

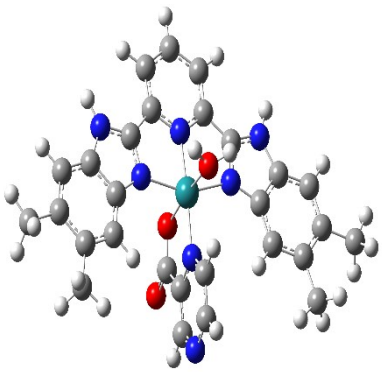




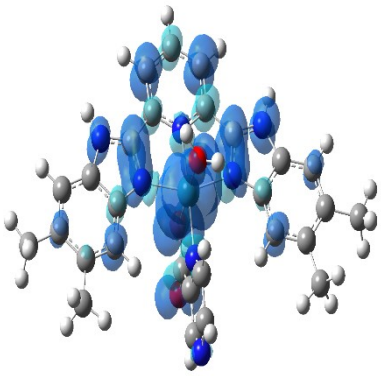
H	5.57778	0.50028	2.76463
H	6.81218	-1.66912	2.87934
N	3.13646	0.7181	1.21762
N	2.39645	-1.10579	0.12461
C	0.6242	4.54387	0.98183
C	0.67857	6.60582	1.86022
C	1.81622	5.86412	2.30409
C	0.45268	7.93683	2.25298
C	2.76729	6.45365	3.16089
C	1.4057	8.50999	3.10778
H	-0.4136	8.49433	1.91212
C	2.54571	7.77976	3.5539
H	3.63673	5.90212	3.50034
H	1.27452	9.53637	3.43849
H	3.25786	8.26689	4.21373
N	1.75201	4.58239	1.73912
N	-0.04434	5.74093	1.03181
N	1.23498	2.35418	0.45854
Ru	2.77381	2.73401	1.73496
C	5.3306	3.47339	3.39475
C	3.50476	2.56892	4.55329
C	6.03602	3.53581	4.60977
H	5.74793	3.8225	2.45185
C	4.23338	2.64544	5.74903
N	5.50419	3.12362	5.79083
H	7.04793	3.92538	4.63117
H	3.78143	2.3165	6.67756
N	4.06018	2.979	3.36516
C	2.09111	2.0533	4.49432
O	1.55621	2.06925	3.27906
O	1.49752	1.65577	5.53608
H	1.8235	-1.70182	-0.46059
H	-0.90654	5.9649	0.54947
O	4.31061	3.54895	-0.01965
H	5.27061	3.54895	-0.01965
H	3.99015	4.45388	-0.01965

Cartesian coordinates of computed Structure for complex 2 of Ru (II)-H_2O
E(UB3LYP) -1785.28 Hartree
ZPE (kcal mol^{-1}) = 320.1891712

C	0.11618	0.88116	-0.87615
C	1.26943	1.19688	-0.13591
C	0.47549	3.41567	0.24835
C	-0.69769	3.15468	-0.48148
C	-0.86167	1.87897	-1.05504
H	-0.02675	-0.10796	-1.2965
H	-1.46493	3.91216	-0.59662
H	-1.75715	1.65704	-1.62544

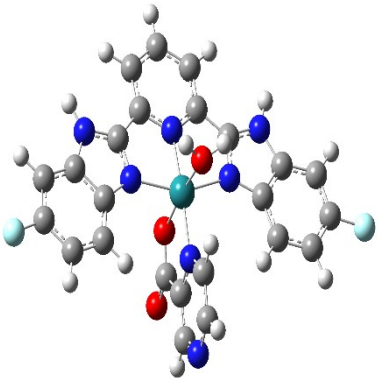


C	2.38188	0.32611	0.23111
C	3.80264	-1.38337	0.52214
C	4.49977	-2.60247	0.53346
C	4.28925	-0.23568	1.21048
C	5.70684	-2.66838	1.2474
H	4.11961	-3.47191	0.00616
C	5.50202	-0.30007	1.92421
C	6.21151	-1.50937	1.94614
H	5.88234	0.57126	2.44656
N	3.38234	0.81445	1.01229
N	2.60295	-0.99231	-0.08181
C	0.84183	4.62701	0.97467
C	0.92171	6.66408	1.90656
C	2.08338	5.92571	2.27216
C	0.71255	7.9798	2.35112
C	3.06379	6.51139	3.09687
C	1.68834	8.56342	3.17466
H	-0.17683	8.53391	2.0679
C	2.87185	7.82478	3.54877
H	3.95348	5.95716	3.37622
N	2.00565	4.65872	1.67735
N	0.16509	5.81575	1.09091
N	1.43993	2.45437	0.37427
Ru	3.03738	2.81774	1.58245
C	5.6881	3.51204	3.10246
C	3.91377	2.63341	4.3573
C	6.4554	3.57098	4.27932
H	6.06584	3.83754	2.13439
C	4.70416	2.7047	5.51346
N	5.97979	3.17125	5.48859
H	7.4721	3.94721	4.24696
H	4.29774	2.38093	6.46461
N	4.41009	3.03794	3.14141
C	2.49745	2.12189	4.37012
O	1.90547	2.12991	3.18189
O	1.95513	1.72984	5.44186
H	2.00547	-1.58198	-0.64827
H	-0.72291	6.04282	0.66001
C	7.51865	-1.59819	2.71102
H	7.47032	-2.35855	3.50236
H	7.76698	-0.64054	3.17937
H	8.35196	-1.87846	2.05257
C	6.48407	-3.96994	1.2814
H	5.97577	-4.74992	0.70584
H	6.60866	-4.33512	2.30983
H	7.49297	-3.84542	0.86529

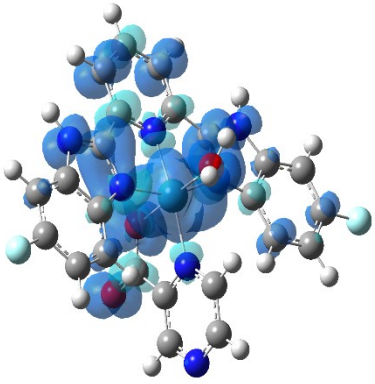


C	3.91704	8.473	4.437
H	4.3255	9.38368	3.97823
H	4.75034	7.78955	4.62847
H	3.49327	8.76899	5.40624
C	1.49383	9.9825	3.67239
H	0.55482	10.4066	3.30307
H	2.31286	10.6375	3.34571
H	1.47496	10.02285	4.76992
O	4.13643	3.45844	0.17122
H	3.65519	3.40799	-0.65792
H	5.73887	3.393	0.05882

Cartesian coordinates of computed
Structure for complex 3 of Fig. Ru (II)-H_2O
E(UB3LYP) =-1826.5193 Hartree
ZPE (kcal mol^{-1}) = 239.5229395



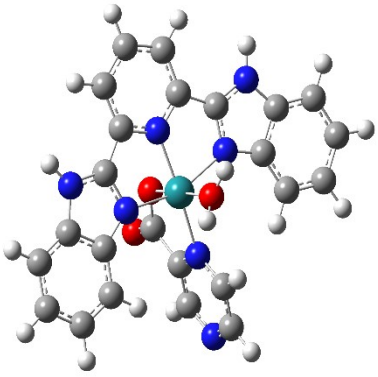
C	-0.0171	0.71317	-0.79952
C	1.10613	1.0536	-0.02614
C	0.30916	3.28462	0.24189
C	-0.83302	3.00217	-0.52678
C	-0.98114	1.70665	-1.05851
H	-0.15165	-0.29265	-1.18104
H	-1.59214	3.75667	-0.70058
H	-1.85412	1.46629	-1.65529
C	2.19626	0.18952	0.42021
C	3.59467	-1.51436	0.81931
C	4.28099	-2.7394	0.88669
C	4.05211	-0.34487	1.50148
C	5.44915	-2.7732	1.65882
H	3.92863	-3.62286	0.36618
C	5.22876	-0.37405	2.27557
C	5.88127	-1.60086	2.32082
H	6.02998	-3.68417	1.75719
H	5.61059	0.49277	2.80016
N	3.15974	0.69907	1.23411
N	2.42657	-1.13471	0.15205
C	0.6446	4.51921	0.94673
C	0.67864	6.58131	1.8207
C	1.81995	5.84766	2.27008
C	0.44003	7.91097	2.21018
C	2.76751	6.44002	3.12797
C	1.37806	8.50168	3.06644
H	-0.42837	8.46197	1.86657
C	2.50074	7.75495	3.49223
H	3.6482	5.91933	3.48258
H	1.25911	9.52429	3.40853

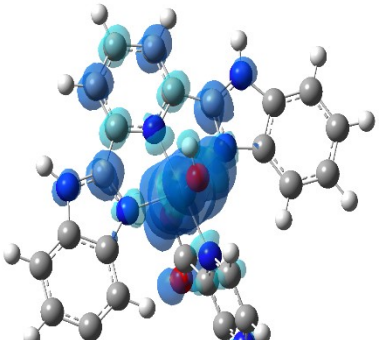


N	1.76987	4.56686	1.70919
N	-0.03254	5.70985	0.99073
N	1.26406	2.32753	0.44477
Ru	2.79351	2.7193	1.72782
C	5.3497	3.42875	3.40398
C	3.48096	2.61121	4.56034
C	6.03447	3.5186	4.62957
H	5.79987	3.71017	2.45295
C	4.19029	2.71245	5.76592
N	5.47012	3.16533	5.81432
H	7.056	3.88181	4.65605
H	3.71582	2.42386	6.69659
N	4.06565	2.97175	3.37041
C	2.06148	2.11181	4.49112
O	1.55324	2.08569	3.26386
O	1.44281	1.75857	5.53304
H	1.85573	-1.73774	-0.42836
H	-0.89614	5.92582	0.50707
F	7.0635	-1.69195	3.07997
F	3.41264	8.40051	4.34899
O	4.35141	3.4929	-0.03168
H	5.31141	3.4929	-0.03168
H	4.03096	4.39783	-0.03168

Cartesian coordinates of computed structure for complex 1 of Ru (III)-H_2O
E(UB3LYP) = -1627.8418 Hartree
ZPE (kcal mol^{-1}) = 251.547322

C	0.04738	0.81743	-0.93087
C	1.1012	1.10749	-0.04724
C	0.29936	3.3342	0.25729
C	-0.77418	3.09926	-0.61926
C	-0.89216	1.828	-1.21424
H	-0.04797	-0.1624	-1.38533
H	-1.50086	3.87514	-0.83398
H	-1.71354	1.62488	-1.89275
C	2.17822	0.23222	0.40143
C	3.59247	-1.47113	0.75759
C	4.29844	-2.68655	0.78087
C	3.99382	-0.3417	1.53519
C	5.42717	-2.74314	1.61236
H	3.98723	-3.5393	0.1862
C	5.1303	-0.41318	2.36547
C	5.83655	-1.6233	2.39254
H	6.00468	-3.66184	1.66391
H	5.44722	0.4362	2.95992

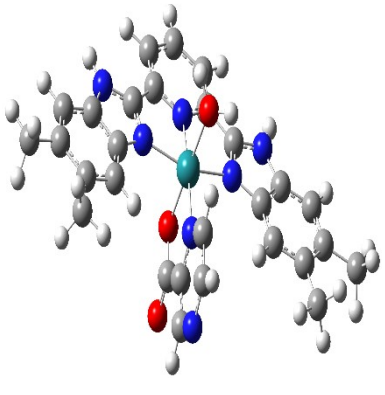




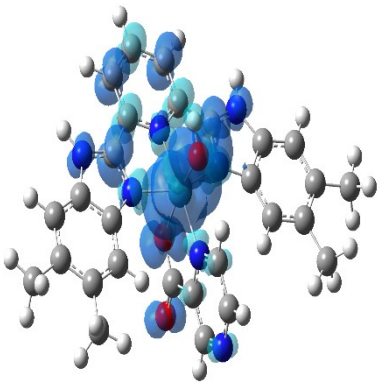
H	6.71723	-1.71313	3.02207
N	3.09198	0.7056	1.28975
N	2.4482	-1.07019	0.06021
C	0.62168	4.55119	0.9936
C	0.67464	6.61473	1.86957
C	1.76134	5.84439	2.38635
C	0.45754	7.95181	2.24561
C	2.66644	6.41249	3.30514
C	1.36605	8.50355	3.16146
H	-0.3704	8.52989	1.84815
C	2.45397	7.74525	3.68266
H	3.49679	5.84069	3.70374
H	1.23913	9.53374	3.48209
H	3.13272	8.21431	4.38924
N	1.70126	4.56147	1.81975
N	-0.01686	5.76675	0.99836
N	1.21028	2.34701	0.52528
Ru	2.69773	2.70121	1.85179
C	5.33206	3.46348	3.27583
C	3.59389	2.64085	4.61956
C	6.1297	3.59446	4.42363
H	5.68736	3.73086	2.28913
C	4.41385	2.78146	5.74874
N	5.68429	3.2572	5.66516
H	7.14195	3.97565	4.34631
H	4.03718	2.50667	6.72724
N	4.05966	2.98502	3.37274
C	2.18024	2.12019	4.67625
O	1.57271	2.06592	3.49754
O	1.65829	1.77683	5.77675
H	1.9193	-1.64109	-0.58794
H	-0.83991	6.01154	0.46148
O	4.05882	3.39828	0.3229
H	4.4376	2.75714	-0.30837
H	3.9073	4.26538	-0.09926

Cartesian coordinates of computed structure for complex 2 of Ru (III)-H_2O
E(UB3LYP) = -1785.091 Hartree
ZPE (kcal mol^{-1}) = 321.281

C	0.17238	0.89737	-0.96086
C	1.26969	1.17902	-0.12803
C	0.47724	3.40006	0.24736
C	-0.63972	3.17217	-0.57557
C	-0.78341	1.90849	-1.18107
H	0.05825	-0.07567	-1.42572



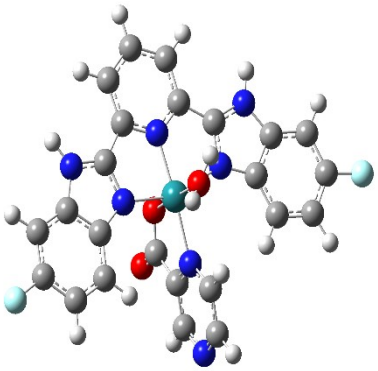
H	-1.3784	3.94846	-0.7425
H	-1.63761	1.71151	-1.81994
C	2.37095	0.30327	0.25307
C	3.80545	-1.39875	0.52415
C	4.51897	-2.6083	0.51055
C	4.24996	-0.27451	1.27643
C	5.70007	-2.69016	1.26588
H	4.1705	-3.45951	-0.0663
C	5.43487	-0.35638	2.03365
C	6.16084	-1.55661	2.03184
H	5.78268	0.49495	2.60889
N	3.33582	0.7736	1.08873
N	2.62155	-0.99926	-0.10547
C	0.8338	4.60771	0.98139
C	0.92447	6.65502	1.89119
C	2.04476	5.88964	2.32337
C	0.72857	7.98079	2.31115
C	2.99527	6.45921	3.19301
C	1.67502	8.548	3.17988
H	-0.12989	8.55505	1.97679
C	2.816	7.78244	3.62262
H	3.85397	5.88532	3.52485
N	1.9626	4.61588	1.74017
N	0.18546	5.81717	1.04871
N	1.4041	2.41251	0.45246
Ru	2.968	2.76196	1.6911
C	5.68324	3.52596	2.95107
C	4.03778	2.68352	4.39534
C	6.55163	3.65097	4.04668
H	5.97386	3.8035	1.94613
C	4.92734	2.81904	5.47115
N	6.18793	3.30149	5.31142
H	7.55542	4.03744	3.90841
H	4.61515	2.5343	6.4693
N	4.42129	3.04032	3.12394
C	2.63358	2.15404	4.5377
O	1.95295	2.10606	3.39984
O	2.18479	1.79813	5.66662
H	2.05366	-1.57127	-0.71821
H	-0.67295	6.06227	0.57098
C	7.43927	-1.66111	2.8425
H	7.37519	-2.45996	3.5938
H	7.65161	-0.72345	3.36596
H	8.30259	-1.89458	2.20457
C	6.49367	-3.98259	1.27418
H	6.02064	-4.74175	0.64322

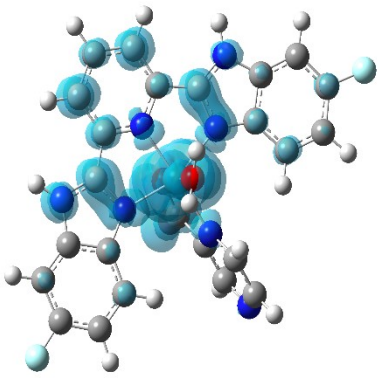


H	6.58046	-4.39299	2.28948
H	7.51728	-3.82749	0.90706
C	3.82986	8.41079	4.56055
H	4.28895	9.30476	4.11688
H	4.63157	7.70616	4.8036
H	3.36305	8.72879	5.50272
C	1.49183	9.97689	3.65416
H	0.58539	10.42136	3.23106
H	2.34394	10.60761	3.36655
H	1.41488	10.02901	4.74872
O	4.22047	3.48177	0.08014
H	4.02183	4.34364	-0.33343
H	4.56192	2.84414	-0.57567

Cartesian coordinates of computed structure for complex 3 of Ru (III)-H_2O
E(UB3LYP) =-1826.3248 Hartree
ZPE (kcal mol^{-1}) = 240.65888925

C	0.07503	0.77164	-0.92443
C	1.1274	1.07344	-0.04348
C	0.32191	3.3007	0.23572
C	-0.74951	3.05506	-0.64008
C	-0.86534	1.77738	-1.22123
H	-0.01956	-0.21393	-1.36637
H	-1.47725	3.82725	-0.86434
H	-1.68564	1.56542	-1.89814
C	2.20347	0.20293	0.41693
C	3.61674	-1.49418	0.79388
C	4.32391	-2.70842	0.83075
C	4.01099	-0.35661	1.56436
C	5.44795	-2.76729	1.66547
H	4.01916	-3.56654	0.24212
C	5.14083	-0.41264	2.40395
C	5.81569	-1.62851	2.41735
H	6.04114	-3.67217	1.74464
H	5.47269	0.42624	3.00242
N	3.11249	0.68613	1.30681
N	2.47668	-1.10019	0.08757
C	0.6378	4.5258	0.96151
C	0.68039	6.59538	1.81843
C	1.76686	5.83116	2.34646
C	0.4572	7.93492	2.18131
C	2.6695	6.4034	3.26439
C	1.35315	8.50645	3.09465
H	-0.36956	8.50782	1.77626
C	2.41964	7.72946	3.60076

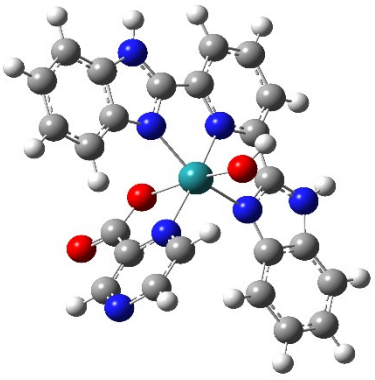




H	3.50569	5.8601	3.686
H	1.24249	9.53541	3.42015
N	1.71468	4.54569	1.79317
N	-0.00358	5.73796	0.95212
N	1.23505	2.31901	0.5161
Ru	2.71325	2.68678	1.84725
C	5.33509	3.46143	3.29391
C	3.58195	2.64923	4.62507
C	6.12004	3.60174	4.44984
H	5.7013	3.7208	2.30903
C	4.38927	2.79906	5.7623
N	5.66043	3.27435	5.68851
H	7.13303	3.98245	4.38097
H	4.00183	2.53228	6.73877
N	4.06198	2.9836	3.38127
C	2.16729	2.12891	4.6704
O	1.57265	2.06518	3.48527
O	1.63363	1.79472	5.76741
H	1.95251	-1.67772	-0.55888
H	-0.8256	5.97587	0.41023
F	6.95405	-1.74222	3.24042
F	3.29157	8.35363	4.51532
O	4.08899	3.37235	0.32623
H	4.4785	2.72892	-0.29603
H	3.94833	4.23894	-0.10056

Cartesian coordinates of computed structure for complex 1 of Ru (III)-OH
E(UB3LYP) = -1627.4127 Hartree
ZPE (kcal mol^{-1}) = 243.30337525

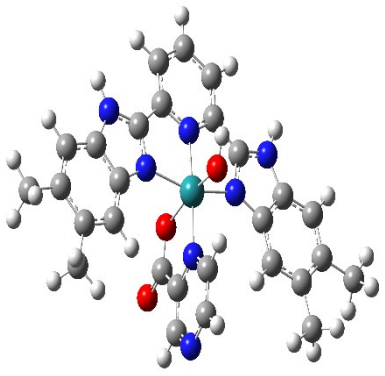
C	0.04738	0.81743	-0.93087
C	1.1012	1.10749	-0.04724
C	0.29936	3.3342	0.25729
C	-0.77418	3.09926	-0.61926
C	-0.89216	1.828	-1.21424
H	-0.04797	-0.1624	-1.38533
H	-1.50086	3.87514	-0.83398
H	-1.71354	1.62488	-1.89275
C	2.17822	0.23222	0.40143
C	3.59247	-1.47113	0.75759
C	4.29844	-2.68655	0.78087
C	3.99382	-0.3417	1.53519
C	5.42717	-2.74314	1.61236
H	3.98723	-3.5393	0.1862
C	5.1303	-0.41318	2.36547
C	5.83655	-1.6233	2.39254



H	6.00468	-3.66184	1.66391
H	5.44722	0.4362	2.95992
H	6.71723	-1.71313	3.02207
N	3.09198	0.7056	1.28975
N	2.4482	-1.07019	0.06021
C	0.62168	4.55119	0.9936
C	0.67464	6.61473	1.86957
C	1.76134	5.84439	2.38635
C	0.45754	7.95181	2.24561
C	2.66644	6.41249	3.30514
C	1.36605	8.50355	3.16146
H	-0.3704	8.52989	1.84815
C	2.45397	7.74525	3.68266
H	3.49679	5.84069	3.70374
H	1.23913	9.53374	3.48209
H	3.13272	8.21431	4.38924
N	1.70126	4.56147	1.81975
N	-0.01686	5.76675	0.99836
N	1.21028	2.34701	0.52528
Ru	2.69773	2.70121	1.85179
C	5.33206	3.46348	3.27583
C	3.59389	2.64085	4.61956
C	6.1297	3.59446	4.42363
H	5.68736	3.73086	2.28913
C	4.41385	2.78146	5.74874
N	5.68429	3.2572	5.66516
H	7.14195	3.97565	4.34631
H	4.03718	2.50667	6.72724
N	4.05966	2.98502	3.37274
C	2.18024	2.12019	4.67625
O	1.57271	2.06592	3.49754
O	1.65829	1.77683	5.77675
H	1.9193	-1.64109	-0.58794
H	-0.83991	6.01154	0.46148
O	4.05882	3.39828	0.3229
H	4.4376	2.75714	-0.30837

Cartesian coordinates of computed structure for complex 2 of Ru (III)-OH
E(UB3LYP) = -1784.6605 Hartree
ZPE (kcal mol^{-1}) = 313.226069

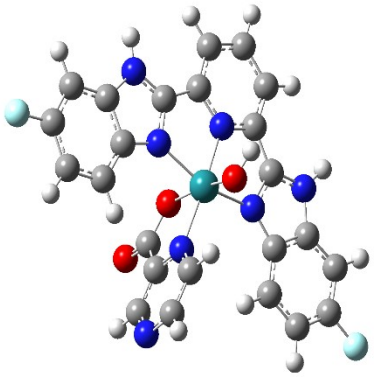
C	0.17238	0.89737	-0.96086
C	1.2697	1.17902	-0.12803
C	0.47724	3.40006	0.24736
C	-0.63972	3.17217	-0.57557
C	-0.78341	1.90849	-1.18107



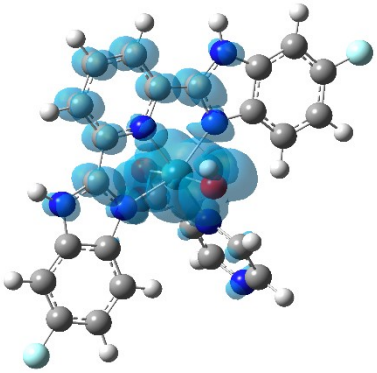
H	**0.05825**	**-0.07567**	**-1.42572**
H	**-1.3784**	**3.94846**	**-0.7425**
H	**-1.63761**	**1.71151**	**-1.81994**
C	**2.37095**	**0.30327**	**0.25307**
C	**3.80545**	**-1.39875**	**0.52415**
C	**4.51897**	**-2.6083**	**0.51055**
C	**4.24996**	**-0.27451**	**1.27643**
C	**5.70007**	**-2.69016**	**1.26589**
H	**4.17049**	**-3.45951**	**-0.0663**
C	**5.43487**	**-0.35638**	**2.03365**
C	**6.16084**	**-1.55661**	**2.03184**
H	**5.78268**	**0.49495**	**2.60889**
N	**3.33582**	**0.7736**	**1.08873**
N	**2.62155**	**-0.99926**	**-0.10547**
C	**0.8338**	**4.60771**	**0.98139**
C	**0.92447**	**6.65502**	**1.89119**
C	**2.04476**	**5.88964**	**2.32337**
C	**0.72857**	**7.98079**	**2.31115**
C	**2.99527**	**6.4592**	**3.19301**
C	**1.67503**	**8.54799**	**3.17988**
H	**-0.12989**	**8.55505**	**1.97679**
C	**2.816**	**7.78244**	**3.62262**
H	**3.85397**	**5.88532**	**3.52485**
N	**1.9626**	**4.61588**	**1.74017**
N	**0.18546**	**5.81717**	**1.04871**
N	**1.4041**	**2.41251**	**0.45246**
Ru	**2.968**	**2.76196**	**1.6911**
C	**5.68324**	**3.52596**	**2.95107**
C	**4.03778**	**2.68352**	**4.39534**
C	**6.55163**	**3.65097**	**4.04668**
H	**5.97386**	**3.8035**	**1.94613**
C	**4.92734**	**2.81904**	**5.47115**
N	**6.18793**	**3.30149**	**5.31142**
H	**7.55542**	**4.03744**	**3.90841**
H	**4.61515**	**2.5343**	**6.4693**
N	**4.42129**	**3.04032**	**3.12394**
C	**2.63358**	**2.15404**	**4.5377**
O	**1.95295**	**2.10606**	**3.39984**
O	**2.18479**	**1.79813**	**5.66662**
H	**2.05366**	**-1.57127**	**-0.71821**
H	**-0.67295**	**6.06227**	**0.57098**
C	**7.43927**	**-1.66111**	**2.8425**
H	**7.37519**	**-2.45996**	**3.5938**
H	**7.65161**	**-0.72345**	**3.36596**
H	**8.30259**	**-1.89458**	**2.20457**
C	**6.49367**	**-3.98259**	**1.27418**

H	6.02064	-4.74175	0.64322
H	6.58046	-4.39299	2.28948
H	7.51728	-3.82749	0.90706
C	3.82986	8.41079	4.56055
H	4.28895	9.30476	4.11688
H	4.63157	7.70616	4.8036
H	3.36305	8.72879	5.50272
C	1.49183	9.97689	3.65416
H	0.58539	10.42136	3.23106
H	2.34394	10.60761	3.36655
H	1.41488	10.02901	4.74872
O	4.22047	3.48177	0.08014
H	4.56192	2.84414	-0.57567

Cartesian coordinates of computed structures for complex 3 of Ru (III)-OH
E(UB3LYP) = -1825.8972 Hartree
ZPE (kcal mol^{-1}) = 232.4651225



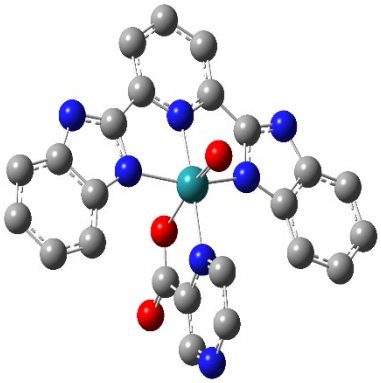
C	0.07504	0.77164	-0.92443
C	1.1274	1.07344	-0.04348
C	0.32191	3.3007	0.23572
C	-0.74951	3.05506	-0.64008
C	-0.86534	1.77738	-1.22123
H	-0.01957	-0.21393	-1.36638
H	-1.47725	3.82725	-0.86434
H	-1.68564	1.56542	-1.89814
C	2.20347	0.20293	0.41694
C	3.61674	-1.49418	0.79388
C	4.32391	-2.70842	0.83075
C	4.01099	-0.35661	1.56436
C	5.44795	-2.76729	1.66547
H	4.01916	-3.56654	0.24212
C	5.14083	-0.41264	2.40395
C	5.81569	-1.62851	2.41735
H	6.04114	-3.67217	1.74464
H	5.47269	0.42624	3.00242
N	3.11249	0.68613	1.30681
N	2.47668	-1.10019	0.08757
C	0.6378	4.5258	0.96151
C	0.68039	6.59538	1.81843
C	1.76686	5.83116	2.34646
C	0.4572	7.93492	2.18131
C	2.6695	6.4034	3.26439
C	1.35315	8.50645	3.09465
H	-0.36956	8.50782	1.77626
C	2.41964	7.72946	3.60076



H	3.50569	5.8601	3.686
H	1.24249	9.53541	3.42015
N	1.71468	4.54569	1.79317
N	-0.00358	5.73796	0.95212
N	1.23505	2.31901	0.5161
Ru	2.71325	2.68678	1.84725
C	5.33509	3.46143	3.29391
C	3.58195	2.64923	4.62507
C	6.12004	3.60174	4.44984
H	5.7013	3.7208	2.30904
C	4.38927	2.79906	5.76229
N	5.66043	3.27435	5.68851
H	7.13303	3.98245	4.38097
H	4.00183	2.53228	6.73877
N	4.06198	2.9836	3.38127
C	2.16729	2.12891	4.6704
O	1.57265	2.06518	3.48527
O	1.63364	1.79472	5.76741
H	1.95251	-1.67772	-0.55888
H	-0.8256	5.97587	0.41023
F	6.95405	-1.74222	3.24042
F	3.29157	8.35363	4.51532
O	4.08899	3.37235	0.32623
H	4.4785	2.72892	-0.29603

Cartesian coordinates of computed structures for complex 1 of Ru (IV) =O
E(UB3LYP) = -1626.7468 Hartree
ZPE (kcal mol^{-1}) = 236.49520375

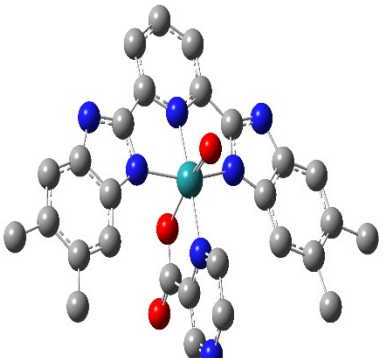
C	0.1934	0.87672	-1.14966
C	1.20319	1.14742	-0.21064
C	0.39828	3.37306	0.09201
C	-0.63588	3.15795	-0.8342
C	-0.719	1.90188	-1.46662
H	0.10841	-0.09691	-1.61829
H	-1.36107	3.93184	-1.05741
H	-1.50448	1.7168	-2.19066
C	2.21029	0.24656	0.33958
C	3.50081	-1.49605	0.90521
C	4.13402	-2.743	1.03402
C	3.89172	-0.35696	1.67108
C	5.1851	-2.82022	1.9594
H	3.82742	-3.60155	0.44596
C	4.9531	-0.44673	2.59145
C	5.58848	-1.68873	2.72385
H	5.70663	-3.76296	2.09562



H	5.27249	0.40757	3.1754
H	6.41041	-1.79267	3.42588
N	3.06502	0.71328	1.29474
N	2.44574	-1.07098	0.08586
C	0.66	4.5454	0.91994
C	0.62163	6.51911	1.98109
C	1.69568	5.73277	2.49565
C	0.34766	7.81517	2.44759
C	2.53678	6.2439	3.50203
C	1.18926	8.30996	3.45473
H	-0.47043	8.40501	2.04795
C	2.26707	7.53637	3.97168
H	3.36268	5.66731	3.89959
H	1.01856	9.30734	3.84892
H	2.89587	7.96121	4.74844
N	1.69126	4.5071	1.81201
N	0.0019	5.73541	0.99738
N	1.29812	2.38314	0.35858
Ru	2.79329	2.74501	1.67516
C	5.48801	3.55281	2.97692
C	3.83495	2.7417	4.43672
C	6.35262	3.7118	4.07693
H	5.76808	3.79882	1.96042
C	4.7178	2.90972	5.51642
N	5.97552	3.39301	5.34199
H	7.35559	4.09831	3.93741
H	4.40489	2.65255	6.52125
N	4.23891	3.06743	3.17195
C	2.42426	2.20758	4.58615
O	1.74536	2.11854	3.44685
O	1.98551	1.89049	5.7238
H	1.94294	-1.65203	-0.57566
H	-0.79836	6.01469	0.44108
O	3.90393	3.32234	0.37632

Cartesian coordinates of computed structure for complex 2 of Ru (IV) =O
E(UB3LYP) = -1783.9952 Hartree
ZPE (kcal mol^{-1}) = 306.54146575

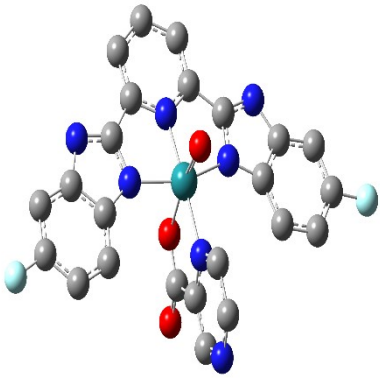
C	0.2428	0.92912	-1.11576
C	1.34451	1.21704	-0.29276
C	0.55997	3.44228	0.06796
C	-0.56159	3.21149	-0.74707
C	-0.70296	1.94656	-1.35021
H	0.11122	-0.0533	-1.55422



H	**-1.30946**	**3.98052**	**-0.90297**
H	**-1.55894**	**1.74726**	**-1.98528**
C	**2.40722**	**0.32848**	**0.15916**
C	**3.76936**	**-1.39617**	**0.59513**
C	**4.43638**	**-2.62849**	**0.66403**
C	**4.21007**	**-0.25938**	**1.32863**
C	**5.56936**	**-2.72193**	**1.48789**
H	**4.09011**	**-3.4862**	**0.09641**
C	**5.34983**	**-0.34952**	**2.1482**
C	**6.02885**	**-1.57446**	**2.23291**
H	**5.70484**	**0.50881**	**2.70561**
N	**3.34023**	**0.80258**	**1.03582**
N	**2.63814**	**-0.98427**	**-0.12343**
C	**0.8885**	**4.61837**	**0.86295**
C	**0.92801**	**6.59211**	**1.9226**
C	**2.04096**	**5.81442**	**2.34806**
C	**0.69189**	**7.88372**	**2.4169**
C	**2.94732**	**6.3389**	**3.28768**
C	**1.59249**	**8.40597**	**3.35861**
H	**-0.16127**	**8.4648**	**2.08184**
C	**2.72744**	**7.62849**	**3.79494**
H	**3.80302**	**5.76297**	**3.61909**
N	**1.99089**	**4.58797**	**1.66758**
N	**0.23369**	**5.80641**	**0.99226**
N	**1.48806**	**2.4595**	**0.25203**
Ru	**3.08763**	**2.83137**	**1.43723**
C	**5.87491**	**3.64922**	**2.52466**
C	**4.34155**	**2.83763**	**4.10877**
C	**6.81873**	**3.81993**	**3.55566**
H	**6.07616**	**3.89186**	**1.48888**
C	**5.30155**	**3.01832**	**5.11832**
N	**6.53946**	**3.50822**	**4.84758**
H	**7.80615**	**4.21089**	**3.33866**
H	**5.06611**	**2.76606**	**6.1453**
N	**4.64637**	**3.15914**	**2.81553**
C	**2.95068**	**2.29396**	**4.36906**
O	**2.18257**	**2.20294**	**3.28909**
O	**2.60779**	**1.97163**	**5.53838**
H	**2.08991**	**-1.56692**	**-0.74611**
H	**-0.61053**	**6.0792**	**0.50196**
C	**7.2567**	**-1.68873**	**3.11533**
H	**7.12167**	**-2.45345**	**3.892**
H	**7.47627**	**-0.73882**	**3.61252**
H	**8.14233**	**-1.97924**	**2.53439**
C	**6.31314**	**-4.03862**	**1.58991**
H	**5.84558**	**-4.80746**	**0.96714**

H	6.33325	-4.40683	2.62446
H	7.35867	-3.93332	1.27053
C	3.69362	8.20719	4.81023
H	4.15442	9.13364	4.44193
H	4.49623	7.49971	5.04039
H	3.18402	8.45814	5.75019
C	1.36731	9.79686	3.91705
H	0.47148	10.256	3.48784
H	2.22024	10.45572	3.70595
H	1.24666	9.77433	5.00849
O	4.08406	3.42604	0.05569

Cartesian coordinates of computed structure for complex 3 of Ru (IV) =O
E(UB3LYP) = -1825.2305 Hartree
ZPE (kcal mol^{-1}) = 225.64503325

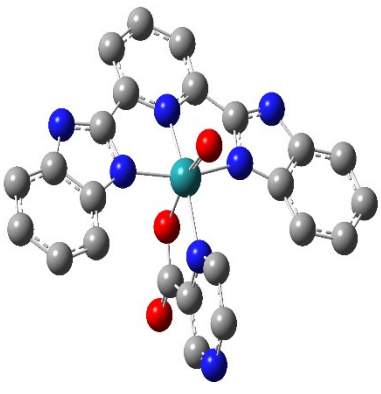


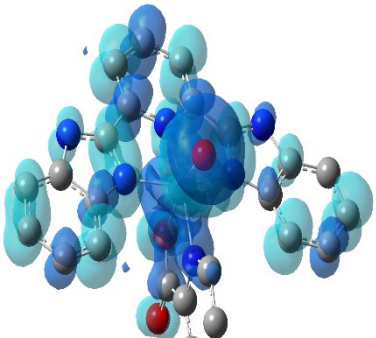
C	0.11809	0.77208	-0.97613
C	1.16296	1.07188	-0.08634
C	0.36262	3.30209	0.18438
C	-0.70123	3.0612	-0.70118
C	-0.81081	1.78442	-1.28553
H	0.01645	-0.21538	-1.41123
H	-1.43016	3.83128	-0.92708
H	-1.62478	1.5754	-1.97061
C	2.21846	0.1925	0.41109
C	3.61175	-1.50797	0.83447
C	4.31039	-2.72629	0.88393
C	3.98714	-0.37726	1.62263
C	5.40915	-2.79448	1.74966
H	4.01865	-3.57865	0.28098
C	5.09368	-0.44112	2.4908
C	5.76158	-1.66072	2.5165
H	5.99609	-3.70215	1.84087
H	5.41873	0.39201	3.09997
N	3.09885	0.66532	1.33658
N	2.49706	-1.10457	0.09051
C	0.66304	4.51563	0.94087
C	0.6927	6.5675	1.83576
C	1.76085	5.79361	2.38391
C	0.46096	7.90267	2.20763
C	2.64218	6.35272	3.3288
C	1.33312	8.46032	3.15087
H	-0.35329	8.48137	1.78643
C	2.38542	7.67522	3.67423
H	3.46975	5.80748	3.76313
H	1.21642	9.48543	3.48588

N	1.71371	4.5192	1.80767
N	0.03145	5.72513	0.93512
N	1.26829	2.31859	0.45873
Ru	2.74179	2.68433	1.80429
C	5.37969	3.46554	3.21485
C	3.64219	2.67505	4.58521
C	6.184	3.61703	4.36018
H	5.7171	3.70711	2.21457
C	4.46531	2.8366	5.71069
N	5.73603	3.30636	5.6048
H	7.19747	3.99199	4.27486
H	4.0953	2.58539	6.6977
N	4.11476	2.99431	3.3411
C	2.22357	2.15505	4.64972
O	1.61371	2.07528	3.46642
O	1.70463	1.83669	5.75134
H	1.99368	-1.67936	-0.57589
H	-0.77445	5.9779	0.37463
F	6.87546	-1.78263	3.36737
F	3.23471	8.28583	4.61513
O	4.03684	3.30802	0.4715

Cartesian coordinates of computed structure for complex 1 of Ru (V) =O
E(UB3LYP) = -1626.5429 Hartree
ZPE (kcal mol^{-1}) = 237.1393895

C	0.0446	0.79486	-0.94712
C	1.13555	1.10419	-0.11391
C	0.33511	3.3407	0.1817
C	-0.7702	3.08909	-0.64535
C	-0.89705	1.80507	-1.21715
H	-0.08217	-0.19754	-1.36273
H	-1.51682	3.85093	-0.83618
H	-1.74372	1.5885	-1.85855
C	2.20176	0.23417	0.36415
C	3.5893	-1.45953	0.8228
C	4.27296	-2.68221	0.88815
C	4.00155	-0.30838	1.56492
C	5.39371	-2.7273	1.73209
H	3.95522	-3.54606	0.31473
C	5.13285	-0.36822	2.40563
C	5.81502	-1.58825	2.47693
H	5.95652	-3.65157	1.81894
H	5.4675	0.48903	2.97592
H	6.68918	-1.67085	3.11511
N	3.1204	0.73043	1.254

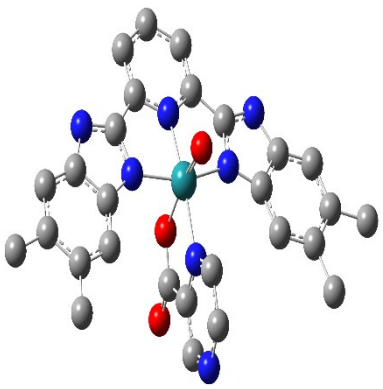




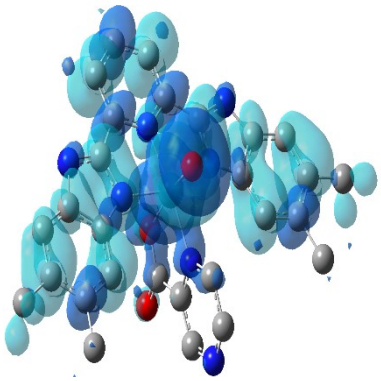
N	2.46176	-1.06837	0.08926
C	0.66464	4.54171	0.94274
C	0.72483	6.55311	1.9245
C	1.83942	5.7884	2.38317
C	0.48538	7.86774	2.34481
C	2.76625	6.35055	3.28241
C	1.41008	8.41125	3.25433
H	-0.36325	8.4389	1.98487
C	2.53123	7.66597	3.70961
H	3.63175	5.80331	3.63185
H	1.26877	9.42605	3.61266
H	3.22505	8.12815	4.40457
N	1.7792	4.53529	1.75641
N	0.02656	5.72838	1.02791
N	1.25567	2.36002	0.39535
Ru	2.79136	2.75054	1.66989
C	5.36212	3.53828	3.26784
C	3.58676	2.64558	4.52016
C	6.10747	3.66	4.45929
H	5.757	3.83528	2.30497
C	4.35057	2.77542	5.6903
N	5.61001	3.28235	5.66253
H	7.11212	4.06508	4.43541
H	3.94197	2.47002	6.64626
N	4.10766	3.0311	3.31792
C	2.18348	2.0944	4.49148
O	1.66558	2.0504	3.25096
O	1.59035	1.72608	5.52543
H	1.93836	-1.66413	-0.54431
H	-0.81795	5.99046	0.52815
O	4.02794	3.22988	0.50707

Cartesian coordinates of computed structure for complex 2 of Ru (V) =O
E(UB3LYP) = -1783.7955 Hartree
ZPE (kcal mol^{-1}) = 306.28805675

C	0.24282	0.92945	-1.11614
C	1.34462	1.21718	-0.29297
C	0.55999	3.44237	0.06791
C	-0.56137	3.21185	-0.74721
C	-0.70277	1.94688	-1.35055
H	0.11122	-0.05292	-1.55469
H	-1.30914	3.98096	-0.90321
H	-1.55871	1.74775	-1.98574
C	2.40705	0.32849	0.15897
C	3.76875	-1.3964	0.59528



C	4.43564	-2.6288	0.66458
C	4.20975	-0.25943	1.3284
C	5.5687	-2.72211	1.48831
H	4.08915	-3.48667	0.09735
C	5.34967	-0.34946	2.14783
C	6.02851	-1.57443	2.23287
H	5.70491	0.50904	2.70487
N	3.3401	0.80249	1.03542
N	2.63764	-0.98454	-0.12335
C	0.88875	4.61849	0.86298
C	0.92848	6.5923	1.92253
C	2.04108	5.81443	2.34845
C	0.69234	7.88396	2.41663
C	2.947	6.33867	3.28853
C	1.5926	8.40607	3.35876
H	-0.16054	8.46519	2.08112
C	2.72712	7.62834	3.79569
H	3.80232	5.76251	3.62048
N	1.99109	4.58787	1.66791
N	0.23429	5.8066	0.99201
N	1.48809	2.45952	0.25199
Ru	3.08762	2.83149	1.43716
C	5.87407	3.65237	2.52428
C	4.34248	2.83726	4.1083
C	6.81808	3.82345	3.55504
H	6.07464	3.89597	1.48859
C	5.30258	3.01856	5.11764
N	6.53973	3.51033	4.84682
H	7.8049	4.21589	3.33797
H	5.06785	2.76522	6.14453
N	4.64636	3.16023	2.81521
C	2.95247	2.2914	4.36863
O	2.18507	2.1976	3.28842
O	2.6097	1.96974	5.53817
H	2.08922	-1.56724	-0.74581
H	-0.60973	6.07955	0.50142
C	7.2565	-1.68861	3.11512
H	7.12143	-2.45294	3.89217
H	7.47637	-0.73852	3.61184
H	8.14197	-1.97959	2.53417
C	6.31228	-4.03888	1.59072
H	5.84444	-4.80791	0.96837
H	6.33256	-4.40667	2.62541
H	7.35775	-3.9339	1.27105
C	3.69287	8.20679	4.81152
H	4.15406	9.13315	4.44349



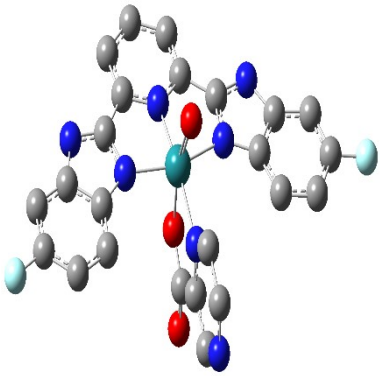
H	4.49519	7.49913	5.04212
H	3.18279	8.45784	5.7512
C	1.36745	9.79703	3.91704
H	0.47195	10.25636	3.48736
H	2.22065	10.45568	3.70632
H	1.24627	9.77457	5.00841
O	4.08693	3.41762	0.05388

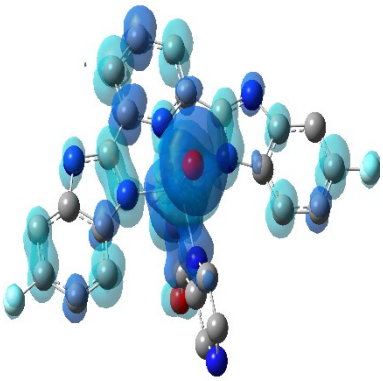
Cartesian coordinates of computed structure for complex 3 of Ru (V) =O

E(UB3LYP) = -1825.0237 Hartree

ZPE (kcal mol^{-1}) = 226.492448

C	0.21869	0.82847	-1.13722
C	1.22367	1.11002	-0.19566
C	0.40927	3.33326	0.08702
C	-0.62046	3.10773	-0.84056
C	-0.69683	1.84656	-1.46451
H	0.1405	-0.14846	-1.60011
H	-1.34761	3.877	-1.07305
H	-1.4789	1.65353	-2.19003
C	2.23182	0.2154	0.3619
C	3.52812	-1.51797	0.93394
C	4.16837	-2.76121	1.06729
C	3.91232	-0.37262	1.69492
C	5.22063	-2.83966	1.98786
H	3.86673	-3.62403	0.48439
C	4.97333	-0.44592	2.61611
C	5.58612	-1.69026	2.72366
H	5.76172	-3.76665	2.1441
H	5.30678	0.39616	3.20759
N	3.08291	0.69036	1.31668
N	2.47245	-1.10164	0.11359
C	0.66715	4.51749	0.90045
C	0.62887	6.50913	1.92337
C	1.70265	5.73119	2.45184
C	0.35512	7.8143	2.36444
C	2.54861	6.25527	3.44592
C	1.19034	8.33714	3.35972
H	-0.4623	8.3969	1.95509
C	2.24995	7.54916	3.86168
H	3.38138	5.70916	3.86761
H	1.03998	9.33798	3.74984
N	1.69896	4.49406	1.7946
N	0.00983	5.70719	0.95552
N	1.31208	2.34928	0.36598
Ru	2.79915	2.726	1.68835

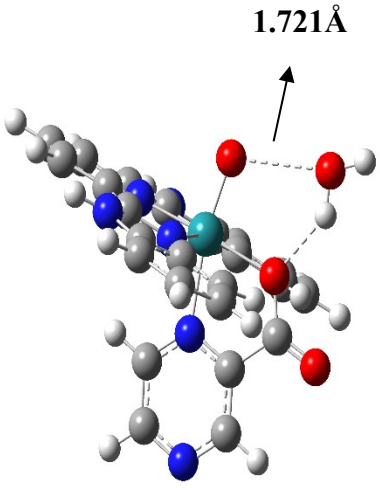




C	5.47834	3.55623	3.01344
C	3.81689	2.73508	4.4589
C	6.33217	3.71977	4.12143
H	5.767	3.80312	1.99957
C	4.68934	2.9073	5.54632
N	5.94579	3.3978	5.38275
H	7.33404	4.1122	3.99102
H	4.36932	2.64786	6.54832
N	4.2304	3.06331	3.19749
C	2.40735	2.19419	4.59445
O	1.74572	2.08916	3.44489
O	1.95337	1.88536	5.72734
H	1.97309	-1.68837	-0.54573
H	-0.79019	5.9776	0.39397
F	6.65232	-1.82013	3.63043
F	3.06238	8.12247	4.85487
O	3.93235	3.25767	0.38997

Cartesian coordinates of computed structure for complex 1 of TS$^{\#}$
E(UB3LYP) = -1702.6876 Hartree
ZPE (kcal mol^{-1}) = 252.21157975

C	0.25435	0.3117	-0.11338
C	1.49939	0.79039	0.33166
C	0.60889	3.0053	0.59754
C	-0.6619	2.57403	0.15935
C	-0.81982	1.22459	-0.20465
H	0.10906	-0.72836	-0.37941
H	-1.50109	3.25741	0.1053
H	-1.78575	0.87434	-0.54945
C	2.75027	0.07594	0.56112
C	4.42712	-1.3879	0.83172
C	5.24371	-2.51801	0.85688
C	4.89718	-0.09511	1.21272
C	6.57537	-2.31855	1.29386
C	6.23093	0.09657	1.63381
C	7.05682	-1.03855	1.66994
H	6.60122	1.07542	1.91355
N	3.85301	0.80803	1.03496
N	3.08359	-1.21727	0.43575
C	1.03637	4.32067	1.05148
C	1.22969	6.44794	1.72203
C	2.50758	5.81203	1.83974
C	1.03204	7.79342	2.04125
C	3.64004	6.53886	2.27712
C	2.16515	8.50101	2.49344

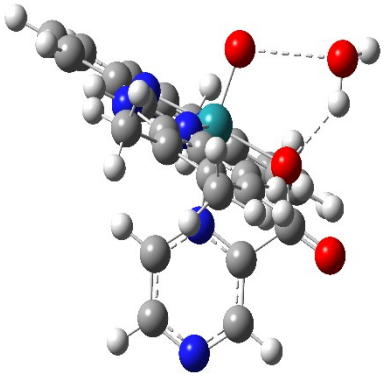


C	**3.44449**	**7.88473**	**2.60333**
H	**4.61845**	**6.07922**	**2.34779**
N	**2.36774**	**4.49712**	**1.41992**
N	**0.35189**	**5.47054**	**1.22388**
N	**1.63358**	**2.10974**	**0.64931**
Ru	**3.46213**	**2.76403**	**1.22196**
C	**4.2123**	**2.93092**	**4.09688**
C	**2.04995**	**2.03254**	**4.01527**
C	**4.18693**	**2.85149**	**5.49794**
C	**2.05029**	**1.96176**	**5.42417**
N	**3.10847**	**2.36768**	**6.16452**
H	**5.04087**	**3.18211**	**6.07717**
H	**1.18609**	**1.57301**	**5.9496**
N	**3.13277**	**2.51255**	**3.36138**
H	**2.47573**	**-1.96539**	**0.10896**
H	**-0.63479**	**5.61733**	**1.02864**
C	**5.41047**	**3.46553**	**3.35495**
O	**6.41**	**3.93**	**3.92905**
O	**5.28279**	**3.36197**	**2.01606**
H	**1.1903**	**1.70522**	**3.44736**
H	**0.06558**	**8.27378**	**1.94021**
H	**4.88861**	**-3.49544**	**0.55046**
O	**3.9964**	**3.25296**	**-0.43714**
H	**4.28637**	**8.47774**	**2.94461**
H	**2.06142**	**9.54875**	**2.75722**
H	**8.088**	**-0.93502**	**1.99006**
H	**7.24731**	**-3.16972**	**1.3342**
O	**5.80167**	**3.64978**	**-0.42992**
H	**5.77762**	**4.50213**	**-0.92427**
H	**5.94847**	**3.74654**	**0.57884**

Cartesian coordinates of computed structure for complex 2 of TS$^{\#}$
E(UB3LYP) = -1859.9449 Hartree
ZPE (kcal mol^{-1}) = 329.2623425

C	**0.27849**	**0.32927**	**-0.07126**
C	**1.52161**	**0.81881**	**0.37139**
C	**0.61937**	**3.02947**	**0.61864**
C	**-0.64837**	**2.58832**	**0.18552**
C	**-0.8001**	**1.23343**	**-0.1662**
H	**0.14014**	**-0.71312**	**-0.3328**
H	**-1.49233**	**3.26491**	**0.12504**
H	**-1.76515**	**0.87577**	**-0.50591**
C	**2.77691**	**0.11091**	**0.59338**
C	**4.45889**	**-1.35885**	**0.81977**

1.726Å



C	5.26435	-2.50232	0.81698
C	4.9201	-0.0656	1.21451
C	6.61922	-2.30315	1.25525
C	6.25681	0.12156	1.6302
C	7.0772	-1.01126	1.64216
H	6.63086	1.09542	1.92203
N	3.87583	0.83412	1.06977
N	3.11052	-1.18252	0.44017
C	1.04592	4.3533	1.05366
C	1.25653	6.50932	1.64339
C	2.51579	5.85394	1.81801
C	1.04913	7.86906	1.89966
C	3.64563	6.57795	2.26308
C	2.20007	8.59099	2.36377
C	3.45687	7.93601	2.52786
H	4.61147	6.10343	2.3871
N	2.37156	4.52692	1.45423
N	0.37691	5.51812	1.161
N	1.64816	2.13885	0.683
Ru	3.45565	2.80128	1.30285
C	4.18936	2.82663	4.17956
C	2.0268	1.93672	4.03908
C	4.15451	2.67398	5.5745
C	2.01761	1.79158	5.44154
N	3.07148	2.15819	6.20939
H	5.00637	2.97021	6.17499
H	1.15058	1.37608	5.9413
N	3.11164	2.45433	3.4173
H	2.49313	-1.91691	0.10629
H	-0.59982	5.66545	0.92524
C	5.39642	3.39372	3.47539
O	6.41647	3.76428	4.08379
O	5.24461	3.44994	2.13541
H	1.1733	1.63767	3.44662
O	4.0376	3.25169	-0.38408
H	4.30066	8.52505	2.87203
H	8.10995	-0.9058	1.9579
O	5.80208	3.71793	-0.30056
H	5.77535	4.57926	-0.77764
H	5.91699	3.79771	0.71481
C	-0.28547	8.54469	1.70088
H	-0.19785	9.3856	1.00195
H	-0.65701	8.95419	2.64907
H	-1.05047	7.86783	1.31107
C	2.09011	10.06244	2.67355
H	3.03876	10.46486	3.03713

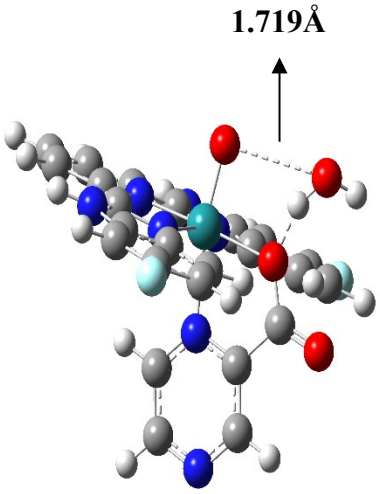
H	1.32081	10.25369	3.43405
H	1.7946	10.63398	1.78242
C	7.57134	-3.47113	1.3046
H	7.2248	-4.23305	2.01713
H	8.57317	-3.1554	1.60549
H	7.64507	-3.9691	0.32846
C	4.76385	-3.85382	0.37206
H	5.30184	-4.1912	-0.52341
H	3.69604	-3.85493	0.13781
H	4.93424	-4.60778	1.15024

Cartesian coordinates of computed structure for complex 3 of TS#

E(UB3LYP) = -1901.1667 Hartree

ZPE (kcal mol^{-1}) = 241.451106

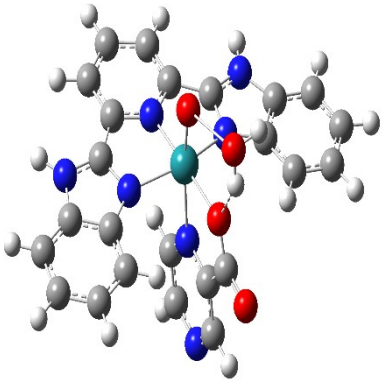
C	0.24948	0.31293	-0.05791
C	1.49623	0.80437	0.37023
C	0.59486	3.01593	0.62369
C	-0.67797	2.57187	0.20555
C	-0.83107	1.21725	-0.14427
H	0.10903	-0.73018	-0.31477
H	-1.5238	3.24679	0.15624
H	-1.79907	0.85784	-0.47343
C	2.75322	0.09885	0.58967
C	4.43648	-1.36086	0.83316
C	5.25724	-2.48837	0.84442
C	4.90653	-0.06656	1.21135
C	6.59369	-2.28569	1.26303
C	6.24644	0.12734	1.61364
C	7.07616	-1.00448	1.63558
H	6.62034	1.106	1.88906
N	3.85684	0.83313	1.05245
N	3.08842	-1.19381	0.45515
C	1.02327	4.33816	1.05953
C	1.23856	6.48468	1.66204
C	2.50445	5.83726	1.82163
C	1.05556	7.84298	1.9277
C	3.63948	6.56161	2.25612
C	2.19236	8.5516	2.37387
C	3.45877	7.92222	2.53025
H	4.60682	6.08611	2.36536
N	2.35426	4.51066	1.44455
N	0.3542	5.50155	1.18382
N	1.62519	2.12621	0.6739
Ru	3.44608	2.79358	1.25447
C	4.20311	2.84708	4.133



C	2.03185	1.97357	4.02179
C	4.18083	2.71071	5.52972
C	2.03546	1.84408	5.42641
N	3.09935	2.21066	6.17953
H	5.04008	3.00794	6.11913
H	1.16976	1.44114	5.93848
N	3.11605	2.47353	3.38538
H	2.47805	-1.94181	0.13379
H	-0.62682	5.6589	0.96837
C	5.40317	3.40173	3.40989
O	6.4299	3.78226	3.99654
O	5.2381	3.43518	2.06683
H	1.16932	1.6754	3.44241
H	0.09876	8.33382	1.79114
H	4.90069	-3.46637	0.54152
O	3.99565	3.26788	-0.41126
H	4.30305	8.51438	2.86688
H	8.11152	-0.89823	1.94098
O	5.78709	3.69123	-0.37687
H	5.76729	4.54307	-0.87232
H	5.92279	3.78723	0.6325
F	2.07603	9.86765	2.65135
F	7.43405	-3.34163	1.29889

Cartesian coordinates of computed structure for complex 1 of Ru(III)-OOH
E(UB3LYP) = -1703.1776 Hartree
ZPE (kcal mol^{-1}) = 251.6865715

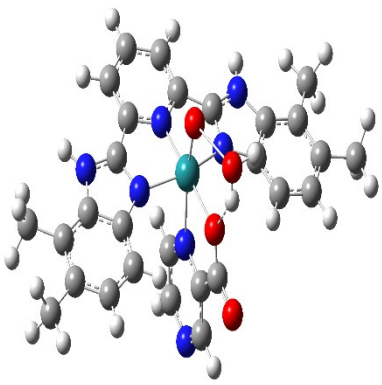
C	0.25166	0.35732	-0.25741
C	1.48134	0.83553	0.22537
C	0.58917	3.04234	0.45168
C	-0.66166	2.61792	-0.02667
C	-0.81443	1.26782	-0.39727
H	0.11567	-0.68714	-0.512
H	-1.4956	3.30589	-0.1048
H	-1.76922	0.92022	-0.77548
C	2.7059	0.10157	0.53384
C	4.31866	-1.41328	0.90281
C	5.11441	-2.56633	1.00344
C	4.79142	-0.12704	1.29881
C	6.40938	-2.39061	1.51334
C	6.09736	0.04102	1.79512
C	6.89341	-1.10777	1.89878
H	6.47542	1.0181	2.07192
N	3.76034	0.7929	1.06042
N	3.01004	-1.22117	0.43137



C	0.98474	4.34661	0.97243
C	1.11748	6.45713	1.71805
C	2.37649	5.81526	1.91485
C	0.89571	7.79646	2.0783
C	3.46468	6.51596	2.46747
C	1.98273	8.48154	2.6412
C	3.24676	7.85247	2.82833
H	4.43367	6.04797	2.59431
N	2.25687	4.49909	1.44555
N	0.27868	5.49993	1.12608
N	1.62616	2.15786	0.53549
Ru	3.43257	2.82917	1.13186
C	4.40866	2.94795	3.98941
C	2.25526	2.0376	4.04154
C	4.48002	2.84328	5.39001
C	2.34622	1.93952	5.44357
N	3.45208	2.34133	6.12
H	5.37037	3.16597	5.91582
H	1.5235	1.53592	6.02231
N	3.28708	2.54334	3.32695
H	2.4009	-1.95065	0.07619
H	-0.68872	5.64865	0.86069
C	5.54844	3.49634	3.16021
O	6.61041	3.88525	3.71529
O	5.32007	3.51922	1.8517
H	1.369	1.71378	3.51194
H	-0.06404	8.27838	1.92576
H	4.74974	-3.54136	0.69845
O	3.88133	3.20774	-0.57675
H	4.0624	8.42674	3.2574
H	1.86155	9.51968	2.93594
H	7.90721	-1.01968	2.27774
H	7.06316	-3.2522	1.6108
O	6.52577	4.12523	-0.5918
H	5.62172	3.82927	-0.86324
H	6.51322	4.0595	0.39161

Cartesian coordinates of computed structure for complex 2 of Ru(III)-OOH
E(UB3LYP) = -1860.4246 Hartree
ZPE (kcal mol^{-1}) = 321.1858715

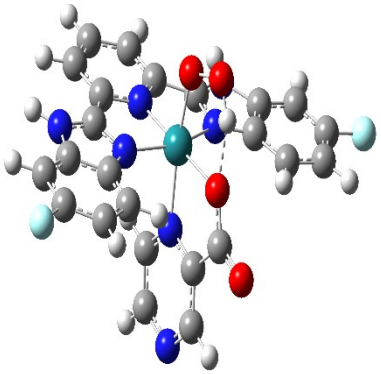
C	0.27757	0.36577	-0.21951
C	1.51526	0.83949	0.25658
C	0.62377	3.04914	0.49302
C	-0.62703	2.62944	0.02137
C	-0.78599	1.27574	-0.34603



H	**0.14048**	**-0.67725**	**-0.47968**
H	**-1.45888**	**3.32001**	**-0.05688**
H	**-1.74509**	**0.93118**	**-0.71646**
C	**2.74003**	**0.10287**	**0.53354**
C	**4.36414**	**-1.42217**	**0.83187**
C	**5.15183**	**-2.58957**	**0.89181**
C	**4.83979**	**-0.13621**	**1.23079**
C	**6.47305**	**-2.41854**	**1.37106**
C	**6.15739**	**0.02592**	**1.69244**
C	**6.94797**	**-1.12664**	**1.75352**
H	**6.5446**	**0.99758**	**1.97657**
N	**3.80282**	**0.78266**	**1.04298**
N	**3.04206**	**-1.22317**	**0.3993**
C	**1.03221**	**4.3649**	**0.97944**
C	**1.18129**	**6.50826**	**1.63892**
C	**2.43696**	**5.86274**	**1.84532**
C	**0.94562**	**7.86301**	**1.94422**
C	**3.52841**	**6.5786**	**2.3617**
C	**2.05012**	**8.57532**	**2.4729**
C	**3.30719**	**7.9275**	**2.66636**
H	**4.49556**	**6.11336**	**2.50977**
N	**2.30883**	**4.52916**	**1.43053**
N	**0.3329**	**5.52547**	**1.09467**
N	**1.66047**	**2.15933**	**0.57958**
Ru	**3.46433**	**2.82696**	**1.18738**
C	**4.42276**	**2.87767**	**4.05304**
C	**2.29175**	**1.9191**	**4.04395**
C	**4.4743**	**2.73689**	**5.45087**
C	**2.36008**	**1.7897**	**5.44487**
N	**3.44583**	**2.19449**	**6.15054**
H	**5.34941**	**3.06355**	**5.99946**
H	**1.53547**	**1.35538**	**5.99814**
N	**3.32391**	**2.46617**	**3.35957**
H	**2.4182**	**-1.9389**	**0.04692**
H	**-0.63545**	**5.65996**	**0.82769**
C	**5.55556**	**3.47975**	**3.25786**
O	**6.59971**	**3.88526**	**3.83158**
O	**5.33609**	**3.52836**	**1.94796**
H	**1.42186**	**1.58675**	**3.49304**
O	**4.08101**	**3.04127**	**-0.49364**
H	**4.12927**	**8.51399**	**3.06742**
H	**7.97243**	**-1.04081**	**2.10537**
O	**6.67279**	**4.66965**	**-0.20028**
H	**6.00033**	**4.53791**	**-0.89768**
H	**6.27034**	**4.35071**	**0.64406**
C	**-0.40354**	**8.51632**	**1.72615**

H	-0.31043	9.41567	1.10509
H	-0.84541	8.83005	2.68113
H	-1.12069	7.85094	1.23541
C	1.90956	10.04152	2.83393
H	2.83836	10.43379	3.25901
H	1.10739	10.20048	3.56695
H	1.65849	10.64909	1.95356
C	7.40511	-3.61007	1.47921
H	7.00865	-4.36848	2.16833
H	8.39142	-3.30741	1.8437
H	7.54025	-4.10536	0.50818
C	4.62013	-3.94242	0.46444
H	5.1865	-4.33643	-0.38948
H	3.5659	-3.90713	0.17234
H	4.71199	-4.67532	1.27582

Cartesian coordinates of computed structure for complex 3 of Ru(III)-OOH
E(UB3LYP) = -1901.6588 Hartree
ZPE (kcal mol^{-1}) = 240.226714

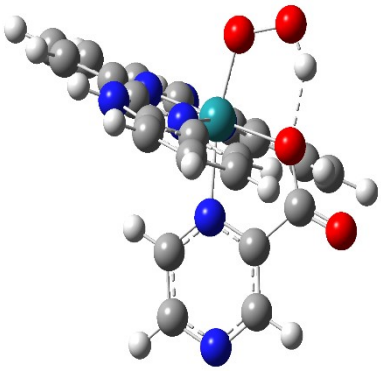


C	0.23273	0.35876	-0.24088
C	1.46534	0.82692	0.25521
C	0.58694	3.03866	0.46717
C	-0.65809	2.62862	-0.02595
C	-0.82057	1.2754	-0.3934
H	0.09096	-0.68532	-0.49324
H	-1.48103	3.32737	-0.12258
H	-1.7745	0.9368	-0.78157
C	2.67818	0.08529	0.56541
C	4.2833	-1.43913	0.89738
C	5.07597	-2.59544	0.96981
C	4.76624	-0.15547	1.29548
C	6.36579	-2.38442	1.45039
C	6.08624	0.00949	1.75876
C	6.89171	-1.13083	1.83808
H	6.47232	0.98317	2.03428
N	3.73333	0.76469	1.08857
N	2.97347	-1.24318	0.44973
C	0.99159	4.34899	0.97132
C	1.1276	6.47164	1.6679
C	2.38246	5.82951	1.8885
C	0.9008	7.81687	1.99339
C	3.46996	6.53664	2.43322
C	2.00155	8.47142	2.54223
C	3.26527	7.88059	2.76611
H	4.43344	6.06686	2.58463

N	2.25957	4.50343	1.44683
N	0.28956	5.50577	1.09466
N	1.61709	2.14524	0.56828
Ru	3.42483	2.81525	1.1856
C	4.42245	2.92324	4.03661
C	2.27033	1.99567	4.1004
C	4.51057	2.80196	5.43377
C	2.3786	1.88895	5.50118
N	3.49215	2.2854	6.16891
H	5.40563	3.12169	5.95341
H	1.56267	1.47928	6.08524
N	3.29383	2.5111	3.38064
H	2.35755	-1.96716	0.09573
H	-0.67857	5.64902	0.82604
C	5.54873	3.48993	3.19428
O	6.62434	3.87252	3.72157
O	5.29234	3.49839	1.8866
H	1.37698	1.67589	3.58047
H	-0.04507	8.32044	1.83273
H	4.72853	-3.57815	0.67355
O	4.01234	3.05627	-0.46867
H	4.06359	8.47997	3.19027
H	7.91717	-1.06998	2.18612
O	6.45313	4.44926	-0.47253
H	7.26362	4.96204	-0.68018
H	6.44618	4.20016	0.53486
F	1.85112	9.82108	2.89382
F	7.21663	-3.49594	1.54996

Cartesian coordinates of computed structure for complex 1 of Ru(IV)-OOH
E(UB3LYP) = -1702.3166 Hartree
ZPE (kcal mol^{-1}) = 246.03065825

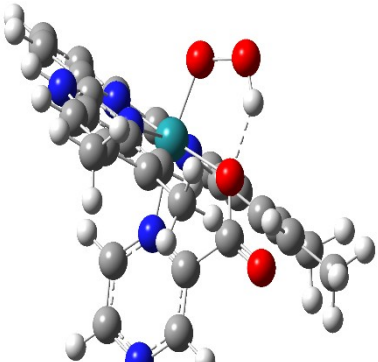
C	0.37449	0.45586	2.32181
C	1.18485	1.02229	1.32542
C	0.09289	3.14192	1.57339
C	-0.74348	2.62556	2.57791
C	-0.59464	1.27292	2.94013
H	0.48651	-0.58038	2.61718
H	-1.48512	3.24696	3.0658
H	-1.23152	0.85426	3.71126
C	2.26879	0.41358	0.5522
C	3.82524	-0.93344	-0.33473
C	4.66817	-1.9984	-0.69243
C	3.93389	0.3582	-0.93139
C	5.63071	-1.73001	-1.67649



H	4.57914	-2.97736	-0.23411
C	4.89897	0.61407	-1.92388
C	5.74218	-0.4457	-2.28307
H	6.30698	-2.52051	-1.98774
H	4.98215	1.58687	-2.39484
H	6.49996	-0.28782	-3.04456
N	2.95068	1.17637	-0.35696
N	2.77062	-0.84974	0.58637
C	0.1494	4.49454	1.0224
C	-0.14531	6.65691	0.51435
C	0.90308	6.12482	-0.29603
C	-0.56275	7.99473	0.41458
C	1.55898	6.9298	-1.24795
C	0.10319	8.78849	-0.53022
H	-1.35943	8.39325	1.03331
C	1.14481	8.26356	-1.34959
H	2.34441	6.53194	-1.88026
H	-0.18284	9.82974	-0.64512
H	1.62568	8.9167	-2.07157
N	1.06409	4.77768	0.04793
N	-0.58609	5.60033	1.32323
N	1.01552	2.33101	0.98106
Ru	2.18899	3.10297	-0.48474
H	2.44369	-1.60879	1.17529
H	-1.32901	5.65516	2.01183
C	5.88022	5.02906	0.60891
C	4.7567	4.47083	-0.02031
N	3.78276	3.85999	0.72864
C	3.93191	3.80798	2.07195
C	5.0716	4.37438	2.67886
N	6.04197	4.98344	1.95633
H	6.64929	5.5131	0.01884
H	3.16427	3.32567	2.66191
H	5.19571	4.33343	3.75456
O	0.95021	2.66986	-1.83589
O	1.75383	2.8649	-3.35313
H	2.58319	3.439	-3.07326
C	4.58314	4.52168	-1.52006
O	5.41791	5.06145	-2.27085
O	3.44834	3.92713	-1.93243

Cartesian coordinates of computed structure for complex 2 of Ru(IV)-OOH
E(UB3LYP) = -1859.5682 Hartree
ZPE (kcal mol^{-1}) = 315.647254

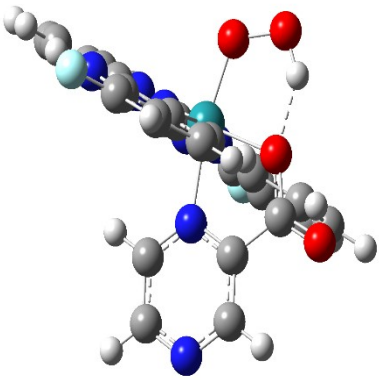
C	0.3393	0.39544	-0.20179



C	**1.55623**	**0.87971**	**0.30868**
C	**0.6312**	**3.0738**	**0.56182**
C	**-0.60619**	**2.64129**	**0.05503**
C	**-0.73957**	**1.29243**	**-0.32823**
H	**0.22533**	**-0.64215**	**-0.49396**
H	**-1.44244**	**3.32438**	**-0.04044**
H	**-1.6859**	**0.93886**	**-0.72268**
C	**2.8057**	**0.16109**	**0.54787**
C	**4.45502**	**-1.34708**	**0.73068**
C	**5.28348**	**-2.48066**	**0.72748**
C	**4.92119**	**-0.08181**	**1.18591**
C	**6.60243**	**-2.33634**	**1.18662**
C	**6.24541**	**0.06793**	**1.63952**
C	**7.08675**	**-1.05395**	**1.64271**
H	**6.60828**	**1.03497**	**1.97145**
N	**3.87121**	**0.83592**	**1.06407**
N	**3.12362**	**-1.15295**	**0.33859**
C	**1.01811**	**4.40084**	**1.03373**
C	**1.12267**	**6.56089**	**1.62624**
C	**2.38516**	**5.94646**	**1.85963**
C	**0.90194**	**7.92013**	**1.90061**
C	**3.4606**	**6.69989**	**2.36706**
C	**1.97087**	**8.67249**	**2.41341**
C	**3.2583**	**8.05933**	**2.64506**
H	**4.42866**	**6.23812**	**2.53021**
N	**2.28756**	**4.60073**	**1.48648**
N	**0.29179**	**5.5576**	**1.10938**
N	**1.67117**	**2.19328**	**0.66961**
Ru	**3.4507**	**2.86605**	**1.34765**
C	**4.34133**	**2.94267**	**4.14155**
C	**2.18457**	**2.0271**	**4.09666**
C	**4.35904**	**2.80467**	**5.53897**
C	**2.22776**	**1.89833**	**5.49792**
N	**3.3075**	**2.28444**	**6.22269**
H	**5.22972**	**3.1173**	**6.10282**
H	**1.38489**	**1.48151**	**6.03703**
N	**3.2401**	**2.5486**	**3.42674**
H	**2.5073**	**-1.8658**	**-0.03404**
H	**-0.67838**	**5.67244**	**0.84042**
C	**5.51141**	**3.51949**	**3.37357**
O	**6.55039**	**3.89892**	**3.97255**
O	**5.31544**	**3.57118**	**2.05971**
H	**1.3174**	**1.71632**	**3.52939**
H	**-0.06389**	**8.38123**	**1.72014**
H	**4.91984**	**-3.44218**	**0.3793**
O	**3.95204**	**3.28446**	**-0.50669**

O	5.31457	3.86868	-0.63412
H	5.65569	3.90863	0.30955
C	1.76876	10.14321	2.72084
H	0.74591	10.45905	2.49325
H	1.96267	10.36071	3.77985
H	2.45512	10.77189	2.13766
C	4.40407	8.89098	3.18902
H	4.6445	9.72881	2.52059
H	4.15593	9.32626	4.16646
H	5.30799	8.28573	3.30919
C	7.52432	-3.53985	1.19773
H	7.88818	-3.75564	2.21136
H	7.01414	-4.43344	0.82488
H	8.41122	-3.37036	0.57236
C	8.51755	-0.91606	2.12635
H	8.71736	-1.57532	2.98188
H	9.23477	-1.18972	1.34076
H	8.73202	0.11168	2.43548

Cartesian coordinates of computed structure for complex 3 of Ru(IV)-OOH
E(UB3LYP) = -1900.7868 Hartree
ZPE (kcal mol^{-1}) = 235.26955725



C	0.33903	0.39503	-0.19138
C	1.55524	0.87959	0.31907
C	0.63179	3.07178	0.57112
C	-0.60547	2.64052	0.06443
C	-0.74012	1.29166	-0.31807
H	0.22451	-0.64227	-0.48423
H	-1.44136	3.3239	-0.03186
H	-1.68639	0.93826	-0.71234
C	2.8072	0.16043	0.55518
C	4.45568	-1.34727	0.72038
C	5.27449	-2.4885	0.69929
C	4.92391	-0.07953	1.18256
C	6.57173	-2.27828	1.15952
C	6.24927	0.08351	1.63095
C	7.08094	-1.04119	1.61724
H	6.61507	1.0472	1.96533
N	3.87035	0.83397	1.07066
N	3.1257	-1.153	0.33671
C	1.01999	4.40146	1.03981
C	1.12146	6.56368	1.61533
C	2.38776	5.94812	1.85648
C	0.88583	7.92431	1.87328
C	3.47158	6.69465	2.35883

C	**1.98489**	**8.61649**	**2.37523**
C	**3.25763**	**8.05188**	**2.62122**
H	**4.43931**	**6.23686**	**2.52679**
N	**2.28644**	**4.60084**	**1.49293**
N	**0.2933**	**5.55969**	**1.10583**
N	**1.67194**	**2.19236**	**0.68137**
Ru	**3.45004**	**2.86371**	**1.36449**
C	**4.33423**	**2.93545**	**4.15955**
C	**2.17518**	**2.02539**	**4.11004**
C	**4.34913**	**2.79673**	**5.55678**
C	**2.21569**	**1.89592**	**5.51149**
N	**3.29494**	**2.27885**	**6.23822**
H	**5.21958**	**3.10687**	**6.12238**
H	**1.37066**	**1.48107**	**6.04866**
N	**3.2332**	**2.54456**	**3.44215**
H	**2.50866**	**-1.86471**	**-0.03787**
H	**-0.67636**	**5.67344**	**0.83319**
C	**5.5072**	**3.51035**	**3.39493**
O	**6.54622**	**3.8863**	**3.99394**
O	**5.31229**	**3.56436**	**2.07946**
H	**1.30792**	**1.71678**	**3.54179**
O	**3.96235**	**3.28627**	**-0.48597**
O	**5.32386**	**3.86055**	**-0.60912**
H	**5.66455**	**3.90039**	**0.33563**
H	**8.11199**	**-0.9819**	**1.94911**
H	**4.05197**	**8.68159**	**3.00755**
F	**-0.30005**	**8.53128**	**1.65469**
F	**4.85762**	**-3.69809**	**0.26846**
H	**1.86267**	**9.65776**	**2.58903**
H	**7.23976**	**-3.1141**	**1.16565**